

## Supporting Information

# N-heterocyclic carbene supported zinc catalysed N-formylation of diverse N-H functionalities with carbon dioxide under ambient conditions

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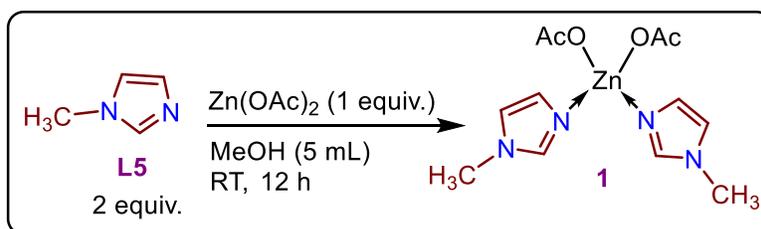
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### General experimental description:

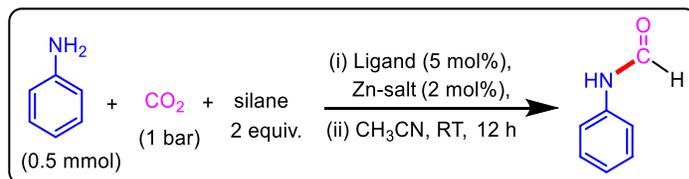
All the reactions were performed under an argon atmosphere using a glove box and/or standard Schlenk techniques unless stated otherwise. All non-deuterated solvents used for the synthesis were distilled, and degassed by standard methods and kept under an inert atmosphere over 4 Å molecular sieves, whereas the deuterated solvents were used as received from the commercial sources. NMR spectra were recorded using the Bruker 400 and 500 MHz FT-NMR spectrometers at ambient temperature. All the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced internally to the residual solvent signals.  $^{19}\text{F}$  NMR spectra were referenced externally to  $\alpha,\alpha,\alpha$ -trifluorotoluene (0.05% in  $\text{CDCl}_3$ ,  $\delta = -63.73$  ppm). Phenylsilane and zinc salts were purchased from TCI and all other chemicals were purchased from the other commercial sources and used directly without further purification. Ligands were synthesized according to the literature procedures.<sup>1</sup>

### Scheme S1: Synthesis and characterization of the complex 1



To a 25 mL Schlenk tube, equipped with a magnetic stirring bar,  $\text{Zn}(\text{OAc})_2$  (100.0 mg, 0.545 mmol, 1 equiv.), **L5** (89.5 mg, 1.09 mmol, 2 equiv.) and methanol (5 mL) were added with constant stirring at ambient temperature for 12 h. After that, all the volatiles were removed in high vacuum and the residue was then dissolved in dichloromethane followed by filtration through a small pad of celite. The obtained solution was concentrated and precipitated with diethyl ether. The precipitate was then collected and dried to yield a white solid (Figure S2 and S3). Suitable crystals of **1** for single-crystal X-ray diffraction study were obtained by slow diffusion of diethyl ether into a saturated solution of the complex in DCM. Yield: 62 mg (0.756 mmol, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (s, 2H), 7.29 (s, 2H), 6.88 (s, 2H), 3.71 (s, 6H), 2.01 (s, 6H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  179.1, 139.8, 128.6, 120.6, 34.4, 23.2 ppm.

**Table S1: Optimization of the reaction conditions for the N-formylation reactions<sup>a</sup>**



Entry	Ligand	Zn Salt	Silane	Yield
1	<b>L1</b>	ZnBr <sub>2</sub>	PhSiH <sub>3</sub>	15%
2	<b>L1</b>	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	40%
3 <sup>b</sup>	[ <b>L3-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	56%
4 <sup>b</sup>	[ <b>L4-H<sub>2</sub></b> ]Br <sub>2</sub>	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	73%
5 <sup>b</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	89%
6	<b>L5</b>	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	63%
7 <sup>b,c</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	59%
8 <sup>b,d</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	77%
9 <sup>b</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	Et <sub>3</sub> SiH	49%
10 <sup>b</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PMHS	ND
11 <sup>b</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	HBpin	27%
12 <sup>b</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	Ph <sub>2</sub> SiH <sub>2</sub>	38%
13 <sup>b,e</sup>	[ <b>L2-H</b> ]Br	ZnX <sub>2</sub>	PhSiH <sub>3</sub>	trace
14	-	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	trace
15 <sup>f</sup>	-	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	28%
16 <sup>b,g</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	34%
17 <sup>b,h</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	47%
18 <sup>b,i</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	79%
19 <sup>b,j</sup>	[ <b>L2-H</b> ]Br	Zn(OAc) <sub>2</sub>	PhSiH <sub>3</sub>	61%
20 <sup>f</sup>	[ <b>L2-H</b> ]Br	-	PhSiH <sub>3</sub>	27%
21	-	-	PhSiH <sub>3</sub>	ND
22	<b>1</b>	-	PhSiH <sub>3</sub>	68%
23 <sup>f</sup>	-	-	PhSiH <sub>3</sub>	-

<sup>a</sup>**Reaction condition:** aniline (0.5 mmol), PhSiH<sub>3</sub> (1 mmol), ligand (0.025 mmol), Zn-salt (0.01 mmol), CO<sub>2</sub> (1 bar), CH<sub>3</sub>CN (2 mL), room temperature, 12 h. <sup>b</sup>for the generation of Zn-(**L2-L4**) complex, KO<sup>t</sup>Bu (0.0375 mmol) was used. <sup>c</sup>6 h. <sup>d</sup>[**L2-H**]Br (0.015 mmol). <sup>e</sup>ZnX<sub>2</sub> (X = Cl, Br, OTf). ND: not detected. <sup>f</sup>KO<sup>t</sup>Bu (0.0375 mmol) was used. <sup>g</sup>1,4 dioxane was used instead of CH<sub>3</sub>CN. <sup>h</sup>DMSO was used instead of CH<sub>3</sub>CN. <sup>i</sup>NaOAc was used instead of KO<sup>t</sup>Bu. <sup>j</sup>K<sub>2</sub>CO<sub>3</sub> was used instead of KO<sup>t</sup>Bu

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

An oven-dried 25 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol, 2 mol%), [L2-H]Br (9.1 mg, 0.025 mmol, 5 mol%), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 7.5 mol%), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad to obtain a clear filtrate, which was dried in high vacuum to get the expected *in situ* generated Zn-L2 complex. To this, amine (0.5 mmol), phenylsilane (123 μL, 1.0 mmol), and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 12 h at ambient temperature. After completion of the reaction, the desired products were isolated by column chromatography over silica gel using hexane/ethyl acetate as eluent.

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

An oven-dried 25 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol, 2 mol%), [L2-H]Br (9.1 mg, 0.025 mmol, 5 mol%), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 7.5 mol%), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad to obtain a clear filtrate, which was dried in high vacuum to get the expected *in situ* generated Zn-L2 complex. To this, amine (0.5 mmol), phenylsilane (123 μL, 1.0 mmol), and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 24 h at ambient temperature. After completion of the reaction, the desired products were isolated by column chromatography over silica gel using hexane/ethyl acetate as eluent.

**General procedure for the N-formylation of hydrazines, hydrazides and amides:**

An oven-dried 25 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (4.5 mg, 0.025 mmol, 5 mol%), [L2-H]Br (9.1 mg, 0.025 mmol, 5 mol%), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 7.5 mol%), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad to obtain a clear filtrate, which was dried in high vacuum to get the expected *in situ* generated Zn-L2 complex. To this, hydrazine/hydrazide/amide (0.5 mmol), phenylsilane (123 μL, 1.0 mmol), and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three

freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 24 h at ambient temperature. After completion of the reaction, the desired products were isolated by column chromatography over silica gel using dichloromethane/methanol as eluent.

**General synthetic method for the N-formylation of aniline in gram scale:**

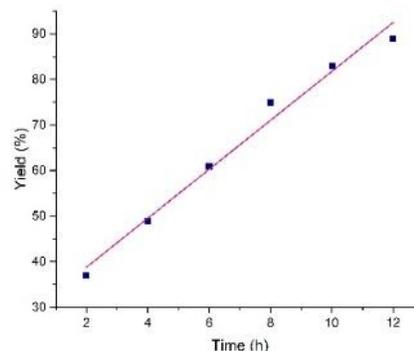
An oven-dried 50 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (39.4 mg, 0.215 mmol, 2 mol%), [L2-H]Br (194 mg, 0.536 mmol, 5 mol%), and KO<sup>t</sup>Bu (90.3 mg, 0.805 mmol, 7.5 mol%), followed by the addition of THF (10 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad to obtain a clear filtrate and the filtrate was dried in the high vacuum to get the expected *in situ* generated Zn-L2 complex. To this, aniline (1g, 10.7 mmol), phenylsilane (2.7 mL, 21.5 mmol) and acetonitrile (10 mL) were added under inert condition. The reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar) and the pressure tube was sealed and stirred for 12 h at ambient temperature. The desired product (**3a**) was isolated by column chromatography over silica gel using hexane/ethyl acetate as eluent.

**General procedure for the time profile diagram:**

An oven-dried pressure tube was charged with Zn(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol), [L2-H]Br (9.1 mg, 0.025 mmol), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad to obtain a clear filtrate, which was dried in high vacuum to get the expected *in situ* generated Zn-L2 complex. To this, amine (0.5 mmol), phenylsilane (123 μL, 1.0 mmol), and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 2 h at ambient temperature. The same reaction procedure was repeated for different reaction duration of 4 h, 6 h, 8 h, 10 h and 12 h. After completion of each individual reactions, the desired product (**3a**) were isolated by column chromatography over silica gel using hexane/ethyl acetate as eluent.

### Time profile for the reaction progress of aniline formylation:

Time (h)	Yield (%)
2	37
4	49
6	61
8	75
10	83
12	89

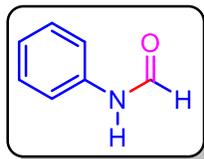


**Table S2:** Variation of N-formylated product (**3a**) yield with reaction time

**Figure S1:** Time profile diagram

### Analytical data for the N-formylated products:

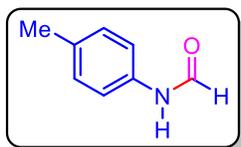
*N*-phenylformamide (Compound-**3a**):<sup>2</sup> Compound **3a** was synthesized following the general



procedure by reacting aniline (46.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 54 mg, 0.445 mmol, 89%).

Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) major rotamer (51%)  $\delta$  8.27 (s, 1H), 8.24 (s, 1H), 7.49 (d,  $J$  = 8.1 Hz, 1H), 7.13-7.03 (m, 4H) ppm; minor rotamer (49%)  $\delta$  8.98 (s, 1H), 8.63 (d,  $J$  = 11.4 Hz, 1H), 7.49 (d,  $J$  = 8.1 Hz, 1H), 7.30-7.22 (m, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) major rotamer  $\delta$  163.3, 137.1, 130.0, 124.9, 119.0 ppm; minor rotamer  $\delta$  159.8, 136.9, 129.2, 125.4, 120.4 ppm. HRMS (ESI)  $m/z$ : [M]<sup>+</sup>: Calcd. for C<sub>7</sub>H<sub>8</sub>NO 122.0606; Found 122.0604.

*N*-*p*-tolylformamide (Compound-**3b**):<sup>2</sup> Compound **3b** was synthesized following the general

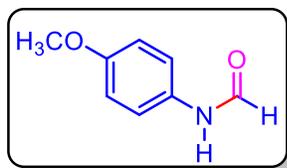


procedure by reacting *p*-toluidine (53.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 56.7 mg, 0.419 mmol, 84%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>) major rotamer (53%)  $\delta$  8.58-8.61 (d,  $J$  = 11.4 Hz, 1H), 7.94 (s, 1H), 7.40-7.42 (d,  $J$  = 8.3 Hz, 2H), 6.96-6.98 (d,  $J$  = 8.3 Hz, 2H), 2.32 (s, 3H) ppm; minor rotamer (47%)  $\delta$  8.73 (s, 1H), 8.27 (s, 1H), 7.09-7.14 (m, 4H), 2.30 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) major rotamer  $\delta$  163.2, 135.2, 134.5, 130.3, 119.2, 20.9 ppm; minor rotamer  $\delta$  159.5,

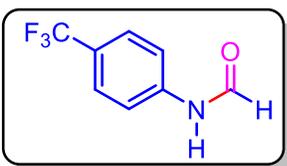
135.2, 134.2, 129.6, 120.2, 20.9 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_8H_{10}NO$  136.0762; Found 136.0757.

*N*-(4-methoxyphenyl)formamide (Compound-3c):<sup>2</sup> Compound **3c** was synthesized following the



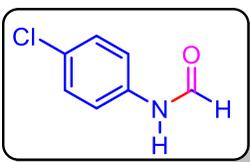
general procedure by reacting 4-methoxyaniline (61.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 61.9 mg, 0.409 mmol, 82%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (400 MHz,  $CDCl_3$ ) rotamer 1 (50%)  $\delta$  8.26 (s, 1H), 7.64 (s, 1H), 7.42 (d,  $J$  = 8.9 Hz, 2H), 7.00-7.02 (d,  $J$  = 8.8 Hz, 2H), 3.77 (s, 3H) ppm; rotamer 2 (50%)  $\delta$  8.47 (d,  $J$  = 11.5 Hz, 1H), 8.31-8.34 (br, 1H), 6.82-6.88 (m, 4H), 3.79 (s, 3H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ ) rotamer 1  $\delta$  159.3, 156.8, 130.1, 122.0, 114.3, 55.6 ppm; rotamer 2  $\delta$  163.4, 157.7, 129.7, 121.6, 115.0, 55.6 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_8H_{10}NO_2$  152.0712; Found 152.0712.

*N*-(4-(trifluoromethyl)phenyl)formamide (Compound-3d):<sup>2</sup> Compound **3d** was synthesized



following the general procedure by reacting 4-(trifluoromethyl)aniline (80.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 69.0 mg, 0.364 mmol, 73%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (400 MHz,  $CDCl_3$ ) major rotamer (61%)  $\delta$  8.43 (s, 1H), 7.67-7.69 (d,  $J$  = 8.4 Hz, 2H), 7.58-7.64 (m, 2H, merged with minor rotamer), 7.52 (s, 1H) ppm; minor rotamer (39%)  $\delta$  8.78 (d,  $J$  = 11.1 Hz, 1H), 8.36 (s, 1H), 7.58-7.64 (m, 2H, merged with major rotamer), 7.19 (d,  $J$  = 8.3 Hz, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ ) major rotamer  $\delta$  159.2, 140.0, 127.3, 126.6, 119.7 ppm; minor rotamer  $\delta$  162.1, 147.0, 127.3, 126.5, 118.1 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_8H_7F_3NO$  190.0480; Found 190.0473.  $^{19}F$  NMR (471 MHz,  $CDCl_3$ )  $\delta$  = -62.12 ppm.

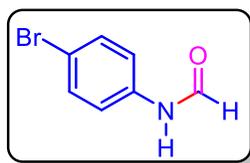
*N*-(4-chlorophenyl)formamide (Compound-3e):<sup>2</sup> Compound **3e** was synthesized following the



general procedure by reacting 4-chloroaniline (63.7 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 61.4 mg, 0.394 mmol, 79%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (400 MHz,  $CDCl_3$ ) major rotamer (59%)  $\delta$  8.28 (s, 1H), 8.26 (s, 1H), 7.43-7.45 (d,  $J$  = 8.7 Hz, 2H), 7.19-7.24 (m, 2H, merged with minor rotamer) ppm; minor rotamer (41%)  $\delta$  8.95-

8.97 (s, 1H), 8.58-8.61 (d,  $J = 11.2$  Hz, 1H), 7.19-7.24 (m, 2H, merged with major rotamer), 6.98 (d,  $J = 8.6$  Hz, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) major rotamer  $\delta$  159.6, 135.6, 130.7, 129.1, 121.4 ppm; minor rotamer  $\delta$  162.9, 135.5, 130.7, 129.9, 120.1 ppm. HRMS (ESI):  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_7\text{H}_7\text{ClNO}$  156.0216; Found 156.0215.

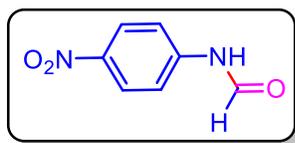
*N*-(4-bromophenyl)formamide (Compound-3f):<sup>3</sup> Compound **3f** was synthesized following the



general procedure by reacting 4-bromoaniline (86.0 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 12 h at room temperature (yield: 78.0 mg, 0.389 mmol, 78%). Formation of a mixture of rotamers is observed;

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) major rotamer (78%)  $\delta$  10.31 (s, 1H), 8.29 (d,  $J = 1.9$  Hz, 1H), 7.54-7.56 (d,  $J = 8.9$  Hz, 2H), 7.49 (d,  $J = 8.9$  Hz, 2H, merged with minor rotamer) ppm; minor rotamer (22%)  $\delta$  10.20-10.22 (d,  $J = 10.9$  Hz, 1H), 8.77-8.80 (d,  $J = 10.9$  Hz, 1H), 7.49 (d,  $J = 8.8$  Hz, 1H, merged with major rotamer), 7.16 (d,  $J = 8.6$  Hz, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  159.8, 137.6, 131.7, 121.1, 115.2 ppm; minor rotamer  $\delta$  162.5, 137.6, 132.1, 119.3, 115.2 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_7\text{H}_7\text{BrNONa}$  199.9711; Found 199.9708.

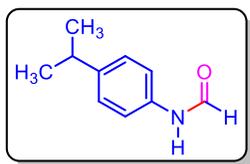
*N*-(4-nitrophenyl)formamide (Compound-3g):<sup>3</sup> Compound **3g** was synthesized following the



general procedure by reacting 4-nitroaniline (69.0 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 12 h at room temperature (yield: 49.8 mg, 0.299 mmol, 60%). Formation of a mixture of rotamers is

observed;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) major rotamer (78%)  $\delta$  10.80 (s, 1H), 8.40 (s, 1H), 8.18-8.23 (d,  $J = 9.0$  Hz, 2H), 7.80-7.83 (d,  $J = 8.8$  Hz, 2H) ppm; minor rotamer (22%)  $\delta$  10.70 (s, 1H), 9.03-9.06 (d,  $J = 9.6$  Hz, 1H), 8.18 (s, 1H, merged with major rotamer), 7.42 (d,  $J = 8.7$  Hz, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  160.6, 144.2, 142.5, 125.1, 119.0 ppm; minor rotamer  $\delta$  162.8, 145.0, 142.5, 125.5, 116.6 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_7\text{H}_6\text{N}_2\text{O}_3\text{Na}$  189.0276; Found: 189.0274.

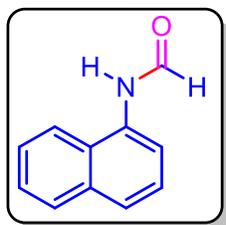
*N*-(4-isopropylphenyl)formamide (Compound-3h): Compound **3h** was synthesized following the



general procedure by reacting 4-isopropylaniline (67.6 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 12 h at room temperature (yield: 61.9 mg, 0.409 mmol, 82%). Formation of a mixture of rotamers is observed;

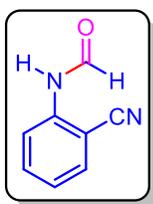
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major rotamer (53%)  $\delta$  8.54 (s, 1H), 8.30 (d,  $J = 2.1$  Hz, 1H), 7.49 (d,  $J = 8.6$  Hz, 2H), 7.18 (m, 1H, merged with major rotamer), 7.04 (d,  $J = 8.6$  Hz, 1H), 2.84-2.93 (m, 1H, merged with minor rotamer), 1.24 (t,  $J = 7.4$  Hz, 6H, merged with minor rotamer) ppm; minor rotamer (43%)  $\delta$  9.14-9.17 (s, 1H), 8.64-8.67 (d,  $J = 2.1$  Hz, 1H), 7.18 (m, 2H, merged with major rotamer), 2.84-2.93 (m, 1H, merged with major rotamer), 1.24 (t,  $J = 7.4$  Hz, 6H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) major rotamer  $\delta$  163.4, 145.4, 134.8, 126.9, 120.4, 33.6, 24.0 ppm; minor rotamer  $\delta$  159.8, 146.1, 134.5, 127.6, 119.1, 33.5, 24.0 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_{10}\text{H}_{14}\text{NO}$  164.1075; Found 164.1074.

*N*-(naphthalen-1-yl)formamide (Compound-3i):<sup>2</sup> Compound **3i** was synthesized following the



general procedure by reacting naphthalen-1-amine (71.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 12 h at room temperature (yield: 66.7 mg, 0.389 mmol, 78%) ppm. Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) major rotamer (78%)  $\delta$  8.61-8.64 (d,  $J = 11.0$  Hz, 1H), 7.98-8.00 (d,  $J = 7.9$  Hz, 1H), 7.86-7.91 (m, 1H, merged with minor rotamer), 7.79-7.81 (d,  $J = 8.5$  Hz, 1H), 7.45-7.62 (m, 4H, merged with minor rotamer), 7.33 (d,  $J = 7.3$  Hz, 1H) ppm; minor rotamer (22%)  $\delta$  8.32 (s, 1H), 8.02-8.03 (d,  $J = 7.6$  Hz, 1H), 7.86-7.91 (m, 1H, merged with major rotamer), 7.73 (d,  $J = 8.2$  Hz, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ) major rotamer  $\delta$  164.1, 134.4, 132.2, 128.7, 127.2, 127.0, 126.7, 125.7, 121.4, 119.3 ppm; minor rotamer  $\delta$  159.7, 134.1, 129.0, 128.9, 127.9, 126.4, 126.3, 126.2, 125.8, 121.0, 120.5 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_{11}\text{H}_{10}\text{NO}$  172.0762; Found 172.0758.

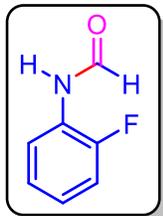
*N*-(2-cyanophenyl)formamide (Compound-3j):<sup>3</sup> Compound **3j** was synthesized following the



general procedure by reacting 2-aminobenzonitrile (59.0 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 48.9 mg, 0.334 mmol, 67%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) major rotamer (79%)  $\delta$  10.35 (s, 1H), 8.36 (s, 1H), 7.92 (d,  $J = 8.4$  Hz, 1H), 7.84 (d,  $J = 7.8$  Hz, 1H, merged with minor rotamer), 7.68-7.71 (m, 1H, merged with minor rotamer), 7.31-7.34 (t,  $J = 7.7$  Hz, 1H, merged with minor rotamer) ppm; minor rotamer (21%)  $\delta$  10.44 (s, 1H), 8.59 (d,  $J = 10.1$  Hz, 1H), 7.81-7.86 (m, 1H, merged with major rotamer), 7.68-7.71 (m, 1H, merged with major rotamer), 7.46-7.47 (d,  $J = 8.2$  Hz, 1H), 7.31-7.37 (m, 1H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) major

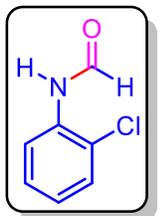
rotamer  $\delta$  160.5, 139.4, 134.1, 133.3, 125.3, 123.5, 116.5, 104.5 ppm. HRMS (ESI)  $m/z$ :  $[M + Na]^+$ : Calcd. for  $C_8H_6N_2ONa$  169.0377; Found 169.0376.

*N*-(2-fluorophenyl)formamide (Compound-**3k**):<sup>5</sup> Compound **3k** was synthesized following the



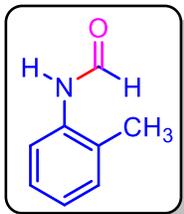
general procedure by reacting 2-fluoroaniline (55.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 45.9 mg, 0.329 mmol, 66%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ) major rotamer (82%)  $\delta$  10.11 (s, 1H, merged with minor rotamer), 8.36 (s, 1H), 8.12-8.16 (m, 1H), 7.20-7.25 (m, 1H, merged with minor rotamer), 7.07-7.16 (m, 2H, merged with minor rotamer) ppm; minor rotamer (18%)  $\delta$  10.06 (s, 1H, merged with major rotamer), 8.57-8.60 (d,  $J = 10.8$  Hz, 1H, merged with major rotamer), 7.34-7.38 (m, 1H), 7.20-7.25 (m, 1H, merged with major rotamer), 7.07-7.16 (m, 2H, merged with major rotamer) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz,  $DMSO-d_6$ ) major rotamer  $\delta$  163.5, 160.2, 153.9, 151.5, 125.8, 125.9, 124.6, 122.8, 115.3 ppm; minor rotamer  $\delta$  163.2, 155.0, 152.6, 125.7, 124.9, 122.4, 116.4 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_7H_7FNO$  140.0512; Found 140.0510.

*N*-(2-chlorophenyl)formamide (Compound-**3l**):<sup>2</sup> Compound **3l** was synthesized following the



general procedure by reacting 2-chloroaniline (63.7 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 50.5 mg, 0.325 mmol, 65%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ) major rotamer (84%)  $\delta$  9.86 (s, 1H), 8.09 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.49 (dd,  $J = 8.0, 1.4$  Hz, 2H), 7.30-7.35 (m, 2H) ppm; minor rotamer (16%)  $\delta$  9.90-9.91 (s, 1H), 8.47 (d,  $J = 10.95$  Hz, 1H), 8.09 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.16-7.12 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz,  $DMSO-d_6$ ) major rotamer  $\delta$  160.4, 134.3, 129.5, 127.6, 125.5, 123.3 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_7H_7ClNO$  156.0216; Found 156.0215.

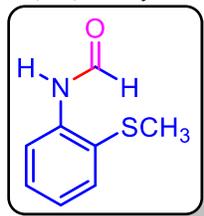
*N*-*o*-tolylformamide (Compound-**3m**):<sup>6</sup> Compound **3m** was synthesized following the general



procedure by reacting *o*-toluidine (53.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 46.6 mg, 0.344 mmol, 69%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ) major rotamer (72%)  $\delta$  9.54 (s, 1H), 8.30 (s, 1H), 7.74 (d,  $J = 8.3$ , 1H), 7.16-7.21 (m, 3H), 2.22 (s, 3H) ppm; minor rotamer (28%)  $\delta$  9.71 (d,  $J = 10.9$  Hz, 1H), 8.41 (d,  $J = 10.9$ , 1H), 7.03-7.06 (m, 1H), 2.24 (s, 1H) ppm.  $^{13}C\{^1H\}$  NMR (126 MHz,  $DMSO-d_6$ )

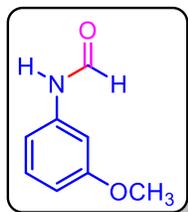
major rotamer  $\delta$  159.8, 135.6, 130.4, 129.3, 126.1, 124.6, 122.8, 17.8 ppm; minor rotamer  $\delta$  163.6, 136.2, 130.8, 130.3, 126.7, 125.3, 121.9, 17.7 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_8H_{10}NO$  136.0762; Found 136.0757.

*N*-(2-(methylthio)phenyl)formamide (Compound-**3n**):<sup>7</sup> Compound **3n** was synthesized following



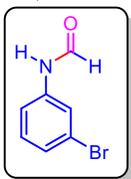
the general procedure by reacting 2-(methylthio)aniline (69.6 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 59.3 mg, 0.355 mmol, 71%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ ) major rotamer (76%)  $\delta$  10.17 (s, 1H), 8.25 (s, 1H), 7.54 (d,  $J = 8.8$  Hz, 2H), 7.25-7.21 (m,  $J = 8.3$  Hz, 2H, merged with minor rotamer), 2.44 (s, 3H) ppm; minor rotamer (24%)  $\delta$  10.09 (d,  $J = 13$  Hz, 1H), 8.73 (d,  $J = 10.5$  Hz, 1H), 8.65 (s, 1H), 7.41 (d,  $J = 8.8$  Hz, 1H), 7.25-7.21 (m,  $J = 8.3$  Hz, 2H, merged with major rotamer), 7.15 (d,  $J = 8.6$  Hz, 1H), 2.51 (s, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz,  $DMSO-d_6$ ) major rotamer  $\delta$  159.6, 135.7, 132.4, 128.0, 127.8, 127.2, 120.0, 119.1, 118.5, 15.5 ppm. minor rotamer  $\delta$  162.5, 135.9, 132.4, 127.8, 127.2, 120.0, 119.1, 16.0 ppm.

*N*-(3-methoxyphenyl)formamide (Compound-**3o**):<sup>3</sup> Compound **3o** was synthesized following the



general procedure by reacting 3-methoxyaniline (61.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 55.1 mg, 0.365 mmol, 73%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (500 MHz,  $DMSO-d_6$ ) major rotamer (73%)  $\delta$  10.15 (s, 1H), 8.25 (m, 1H), 7.27-7.28 (t,  $J = 2.3$  Hz, 1H), 7.19-7.23 (t,  $J = 8.1$  Hz, 1H), 7.08-7.11 (m, 1H), 6.64-6.67 (m, 1H, merged with minor rotamer), 3.72 (s, 3H) ppm; minor rotamer (27%)  $\delta$  10.06-10.09 (d,  $J = 10.2$  Hz, 1H), 8.81 (d,  $J = 10.9$  Hz, 1H), 7.19-7.23 (t,  $J = 8.1$  Hz, 1H), 6.74-6.78 (m, 1H), 6.64-6.67 (m, 1H, merged with major rotamer), 3.74 (s, 1H) ppm.  $^{13}C\{^1H\}$  NMR (126 MHz,  $DMSO-d_6$ ) major rotamer  $\delta$  162.6, 159.6, 139.4, 129.7, 111.4, 109.0, 105.0, 55.0 ppm; minor rotamer  $\delta$  160.1, 159.6, 139.6, 130.3, 111.4, 109.6, 103.3, 55.1 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_8H_{10}NO_2$  152.0712; Found 152.0712.

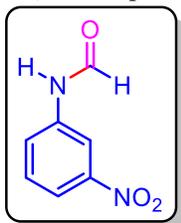
*N*-(3-bromophenyl)formamide (Compound-**3p**):<sup>3</sup> Compound **3p** was synthesized following the



general procedure by reacting 3-bromoaniline (85.4 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 67.4 mg, 0.335 mmol,

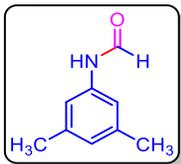
67%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) major rotamer (60%)  $\delta$  8.51 (d,  $J = 11.2$  Hz, 1H), 8.16 (d,  $J = 2.0$  Hz, 1H), 7.63 (t,  $J = 2.0$  Hz, 1H), 6.95-7.06 (m, 2H), 6.85-6.87 (m, 1H) ppm; minor rotamer (40%)  $\delta$  9.03 (d,  $J = 13.0$  Hz, 1H), 8.48 (s, merged with major rotamer, 1H), 7.26-7.27 (m, 1H), 7.09-7.12 (m, 2H), 6.85-6.87 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ) major rotamer  $\delta$  159.9, 138.2, 130.4, 127.8, 123.1, 121.6, 118.7 ppm; minor rotamer  $\delta$  162.9, 138.2, 131.1, 128.2, 123.3, 122.6, 117.2 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_7\text{H}_7\text{NOBr}$  199.9711; Found 199.9708.

*N*-(3-nitrophenyl)formamide (Compound-3q):<sup>6</sup> Compound **3q** was synthesized following the



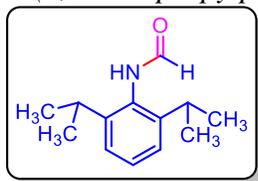
general procedure by reacting 3-nitroaniline (69.0 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 53.9 mg, 0.325 mmol, 65%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) major rotamer (83%)  $\delta$  10.68 (s, 1H), 8.61-8.62 (t,  $J = 2.2$  Hz, 1H), 8.39 (d,  $J = 1.7$  Hz, 1H), 7.88-7.95 (m, 2H, merged with minor rotamer), 7.60-7.64 (m, 1H, merged with minor rotamer) ppm; minor rotamer (17%)  $\delta$  10.48 (d,  $J = 10.6$  Hz, 1H), 8.95 (d,  $J = 10.6$  Hz, 1H), 8.02-8.03 (m, 1H), 7.88-7.95 (m, 1H, merged with major rotamer), 7.68-7.70 (m, 1H), 7.60-7.65 (m, 1H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  160.4, 148.0, 139.2, 130.4, 125.2, 118.2, 113.3 ppm; minor rotamer  $\delta$  162.8, 148.0, 139.2, 130.8, 123.1, 117.9, 111.6 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{K}]^+$ : Calcd. for  $\text{C}_7\text{H}_6\text{N}_2\text{O}_3\text{K}$  205.0010; Found 205.0008.

*N*-(3,5-dimethylphenyl)formamide (Compound-3r):<sup>8</sup> Compound **3r** was synthesized following



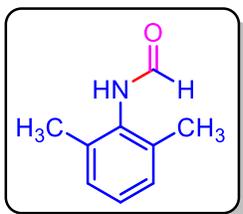
the general procedure by reacting 3,5-dimethylaniline (60.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 12 h at room temperature (yield: 61.9 mg, 0.415 mmol, 83%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) major isomer (57%)  $\delta$  8.86-8.89 (m, 1H), 8.66-8.69 (d,  $J = 11.4$  Hz, 1H), 7.18 (s, 1H), 6.72 (s, 2H), 2.30 (s, 6H) ppm; minor rotamer (43%)  $\delta$  8.30 (s, 1H), 7.90 (s, 1H), 6.82 (s, 1H), 6.77 (s, 1H), 2.28 (s, 4H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ) major rotamer  $\delta$  163.2, 139.6, 136.7, 127.0, 116.5, 21.3 ppm; minor rotamer  $\delta$  159.5, 138.8, 136.9, 126.5, 117.9, 21.4 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}]^+$ : Calcd. for  $\text{C}_9\text{H}_{12}\text{NO}$  150.0919; Found 150.0916.

*N*-(2,6-diisopropylphenyl)formamide (Compound-3s):<sup>9</sup> Compound **3s** was synthesized following



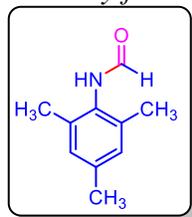
the general procedure by reacting 2,6-diisopropylaniline (88.6 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 80.0 mg, 0.390 mmol, 78%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) major rotamer (66%)  $\delta$  8.01-8.04 (d,  $J$  = 11.9 Hz, 1H), 7.19-7.21 (m, 3H), 3.18-3.24 (sept,  $J$  = 6.9 Hz, 2H), 1.21-1.22 (d,  $J$  = 7.0 Hz, 12H, merged with minor rotamer) ppm; minor rotamer (34%)  $\delta$  8.48-8.48 (m, 1H), 7.30-7.35 (q,  $J$  = 7.6 Hz, 2H), 3.08-3.14 (sept,  $J$  = 6.7 Hz, 1H), 1.21-1.22 (d,  $J$  = 7.0 Hz, 12H, merged with major rotamer) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) major rotamer  $\delta$  165.3, 146.9, 129.1, 124.0, 28.6, 23.8 ppm; minor rotamer  $\delta$  160.7, 146.3, 129.1, 123.7, 29.0, 23.8 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>, Calcd. for C<sub>13</sub>H<sub>20</sub>NO 206.1545; Found 206.1541.

*N*-(2,6-dimethylphenyl)formamide (Compound-3t):<sup>10</sup> Compound **3t** was synthesized following



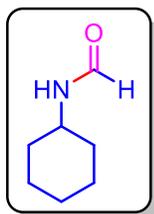
the general procedure by reacting 2,6-dimethylaniline (60.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 58.9 mg, 0.395 mmol, 79%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) rotamer 1 (50%)  $\delta$  8.36-8.38 (m, 1H), 7.07-7.14 (m, 3H, merged with rotamer 2), 2.25 (s, 6H) ppm; rotamer 2 (50%)  $\delta$  8.09 (d,  $J$  = 11.9 Hz, 1H), 7.07-7.14 (m, 3H, merged with rotamer 1), 2.30 (s, 6H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) rotamer 1/2  $\delta$  165.1, 159.5, 135.4, 128.8, 128.4, 127.9, 18.8, 18.7 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>; Calcd. for C<sub>9</sub>H<sub>12</sub>NO 150.0919; Found 150.0916.

*N*-mesitylformamide (Compound-3u):<sup>6</sup> Compound **3u** was synthesized following the general



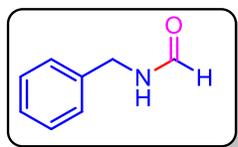
procedure by reacting 2,4,6-trimethylaniline (67.6 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 66.0 mg, 0.404 mmol, 81%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) rotamer 1 (50%)  $\delta$  8.39 (s, 1H), 6.93 (s, 2H), 6.78 (s, 1H), 2.27 (s, 3H), 2.21 (s, 6H) ppm; rotamer 2 (50%)  $\delta$  8.05 (d,  $J$  = 12.0 Hz, 1H), 6.91 (s, 2H), 6.87 (s, 1H), 2.29 (s, 3H), 2.26 (s, 6H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) rotamer 1  $\delta$  165.1, 137.8, 135.3, 129.5, 21.0, 18.8 ppm; rotamer 2  $\delta$  159.7, 135.1, 129.2, 21.1, 18.6 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>; Calcd. for C<sub>10</sub>H<sub>14</sub>NO 164.1075; Found 164.1070.

*N*-cyclohexylformamide (Compound-**3v**):<sup>2</sup> Compound **3v** was synthesized following the general



procedure by reacting cyclohexanamine (49.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 40.0 mg, 0.315 mmol, 63%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.47 (s, 1H), 2.97-3.03 (m, 1H), 2.01-2.04 (dd,  $J$  = 12.7, 3.5 Hz, 2H), 1.75-1.79 (m, 2H), 1.61-1.65 (m, 1H), 1.34-1.42 (m, 2H), 1.22-1.31 (m, 2H), 1.12-1.20 (m, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  169.3, 50.4, 31.2, 24.9, 24.5 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>, Calcd. for C<sub>7</sub>H<sub>14</sub>NO 128.1075; Found 128.1072.

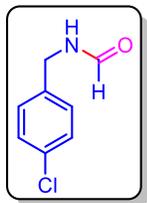
*N*-benzylformamide (Compound-**3w**):<sup>2</sup> Compound **3w** was synthesized following the general



procedure by reacting phenylmethanamine (53.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 57.4 mg, 0.425 mmol, 85%). Formation of a mixture of rotamers is observed; <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>) major rotamer (85%)  $\delta$  8.22 (s, 1H), 7.21-7.32 (m, 5H), 4.45-4.46 (d,  $J$  = 6.0 Hz, 2H) ppm; minor rotamer (15%)  $\delta$  8.14 (d,  $J$  = 11.9 Hz, 1H), 7.34-7.40 (m, 5H), 4.37-4.39 (d,  $J$  = 6.5 Hz, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) major rotamer  $\delta$  161.2, 137.8, 128.9, 127.9, 127.8, 42.3 ppm; minor rotamer  $\delta$  161.2, 131.8, 130.0, 129.2, 127.1, 50.3 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>; Calcd. for C<sub>8</sub>H<sub>10</sub>NO 136.0762; Found 136.0760.

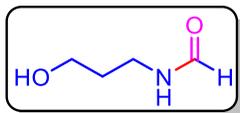
*N*-(4-chlorobenzyl)formamide (Compound-**3x**):<sup>11</sup> Compound **3x** was synthesized following the



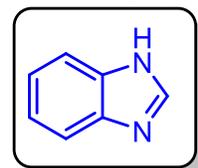
general procedure by reacting 4-chlorophenylmethanamine (70.8 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 67.8 mg, 0.400 mmol, 80%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500

MHz, CDCl<sub>3</sub>) major rotamer (87%)  $\delta$  8.25 (s, 1H), 7.28-7.31 (d,  $J$  = 8.4 Hz, 2H), 7.21 (d,  $J$  = 8.4 Hz, 2H), 4.43 (d,  $J$  = 6.0 Hz, 2H) ppm; minor rotamer (83%)  $\delta$  8.14-8.16 (d,  $J$  = 11.8 Hz, 1H), 7.32-7.34 (d,  $J$  = 8.4 Hz, 2H), 7.17-7.19 (d,  $J$  = 8.4 Hz, 2H), 4.37-4.38 (d,  $J$  = 6.5 Hz, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) major rotamer  $\delta$  161.2, 136.2, 129.2, 129.0, 128.4, 41.6 ppm; minor rotamer  $\delta$  164.8, 133.6, 129.2, 129.0, 128.4, 45.2 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>; Calcd. for C<sub>8</sub>H<sub>9</sub>NOCl 170.0373; Found 170.0373.

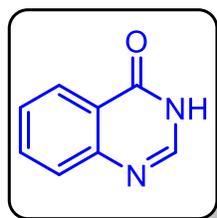
*N*-(3-hydroxypropyl)formamide (**3y**):<sup>12</sup> Compound **3y** was synthesized following the general procedure by reacting 3-aminopropan-1-ol (37.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 12 h at room temperature (yield: 35.5 mg, 0.346 mmol, 69%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.39-8.40 (m, 1H), 3.45-3.47 (t, *J* = 6.1 Hz, 2H), 2.81-2.84 (t, *J* = 6.1 Hz, 2H), 1.66-1.71 (m, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  167.2, 58.1, 36.6, 30.4 ppm; HRMS (ESI) *m/z*: [M + Na]<sup>+</sup>: Calcd. for C<sub>4</sub>H<sub>9</sub>NO<sub>2</sub>Na 126.0530; Found 126.0526.



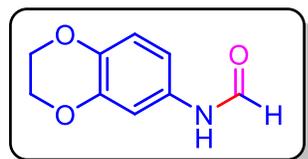
*1H*-benzo[d]imidazole (Compound-**3z**): Compound **3z** was synthesized following the general procedure by reacting benzene-1,2-diamine (54.0 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 24.2 mg, 0.205 mmol, 41 %). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  12.42 (s, 1H), 8.20 (m, 1H), 7.57-7.60 (m, 2H), 7.17-7.20 (m, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  141.7, 121.6, 79.1 ppm. HRMS (ESI) *m/z*: [M + H]<sup>+</sup>: Calcd. for C<sub>7</sub>H<sub>7</sub>N<sub>2</sub> 119.0609; Found 119.0605.



*Quinazolin-4(1H)-one* (Compound-**3a'**): Compound **3a'** was synthesized following the general procedure by reacting 2-aminobenzamide (73.0 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 62.1 mg, 0.425 mmol, 85%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  12.23 (s, 1H), 8.12 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.08 (s, 1H), 7.79-7.82 (m, 1H), 7.66 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.50-7.53 (m, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  160.8, 148.7, 145.4, 134.4, 127.2, 126.8, 125.9, 122.6 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup>: Calcd. for C<sub>8</sub>H<sub>6</sub>N<sub>2</sub>ONa 169.0378; Found 169.0371.

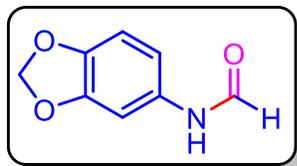


*N*-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)formamide(Compound-**3b'**):<sup>13</sup> Compound **3b'** was synthesized following the general procedure by reacting 2,3-dihydrobenzo[*b*][1,4]dioxin-6-amine (89.0 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 64.4 mg, 0.360 mmol, 72%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) major rotamer (76%)  $\delta$  9.95 (s, 1H), 8.18 (d, *J* = 2.0 Hz, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 6.95-6.97 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.78-6.81 (m, 1H, merged with minor rotamer), 4.18-4.23 (m, 4H, merged with minor rotamer) ppm; minor rotamer (24%)  $\delta$  9.86-9.88 (d, *J* =



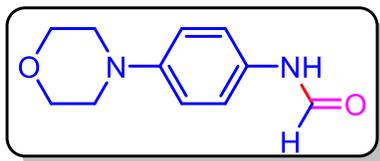
11.0 Hz, 1H), 8.58-8.60 (d,  $J = 11.1$  Hz, 1H), 6.78-6.81 (m, 1H, merged with major rotamer), 6.73 (d,  $J = 2.6$  Hz, 1H), 6.63-6.65 (dd,  $J = 8.7, 2.6$  Hz, 1H), 4.18-4.23 (m, 4H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  159.1, 143.0, 139.6, 131.9, 116.9, 112.3, 108.3, 64.2 ppm; minor rotamer  $\delta$  162.5, 143.7, 140.0, 117.5, 111.2, 107.0, 63.9 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_9\text{H}_9\text{NO}_3\text{Na}$  202.0475; Found 202.0478.

*N*-(benzo[*d*][1,3]dioxol-5-yl)formamide (Compound-**3c'**):<sup>14</sup> Compound **3c'** was synthesized



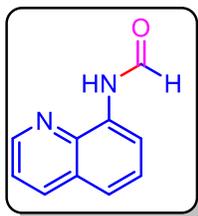
following the general procedure by reacting benzo[*d*][1,3]dioxol-5-amine (68.1 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 64.4 mg, 0.390 mmol, 78%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) Major rotamer (53%)  $\delta$  8.30 (s, 1H), 7.71 (s, 1H), 7.23-7.24 (m, 1H) 6.83-6.85 (m, 1H), 6.74-7.78 (m, 1H), 5.95 (s, 2H) ppm; Minor rotamer (47%)  $\delta$  8.47-8.50 (d,  $J = 11.4$  Hz, 1H), 7.23 (s, 1H) 6.74-7.78 (m, 1H), 6.61-6.62 (d,  $J = 2.2$  Hz, 1H), 6.53-6.55 (dd,  $J = 8.2, 2.2$  Hz, 1H), 5.98 (s, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ ) Major rotamer  $\delta$  158.9, 113.2, 108.3, 103.0, 101.5 ppm; Minor rotamer  $\delta$  162.9, 113.5, 108.8, 102.4, 101.8 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_8\text{H}_8\text{NO}_3$  166.0504; Found 166.0504.

*N*-(4-morpholinophenyl)formamide (Compound-**3d'**): Compound **3d'** was synthesized following



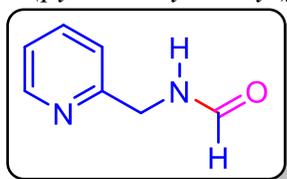
the general procedure by reacting *N*-(4-morpholinophenyl)formamide (89.1 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 81.4 mg, 0.394 mmol, 79%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major isomer (53%)  $\delta$  8.31 (s, 1H), 7.82 (d,  $J = 10.3$  Hz, 1H), 7.43 (d,  $J = 9.0$  Hz, 2H), 7.02 (d,  $J = 8.9$  Hz, 2H), 3.84-3.87 (m, 8H) ppm; minor isomer (47%)  $\delta$  8.50 (d,  $J = 11.6$  Hz, 1H), 7.32 (s, 1H), 6.88 (t,  $J = 8.1$  Hz, 4H), 3.10-3.13 (m, 8H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) major isomer  $\delta$  158.9, 149.6, 129.0, 121.5, 116.4, 67.0, 49.6 ppm; minor isomer  $\delta$  163.0, 148.7, 129.6, 121.5, 116.9, 66.9, 49.8 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_{11}\text{H}_{15}\text{N}_2\text{O}_2$  207.1134; Found 207.1136.

*N*-(quinolin-8-yl)formamide (Compound-3e'):<sup>3</sup> Compound 3e' was synthesized following the



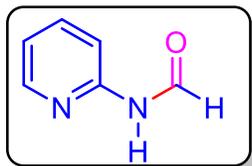
general procedure by reacting quinolin-5-amine (72.0 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 65.4 mg, 0.380 mmol, 76%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) major rotamer (85%)  $\delta$  9.85 (s, 1H), 8.82-8.83 (dd,  $J$  = 4.3, 1.7 Hz, 1H), 8.75-8.77 (m, 1H), 8.70 (d,  $J$  = 1.8 Hz, 1H), 8.19-8.21 (dd,  $J$  = 8.3, 1.7 Hz, 1H), 7.53-7.57 (m, 2H, merged with minor rotamer), 7.47-7.50 (m, 1H, merged with minor rotamer) ppm; minor rotamer (15%)  $\delta$  9.46 (s, 1H), 9.12 (d,  $J$  = 11.7 Hz, 1H), 8.84-8.85 (m, 1H), 8.15-8.17 (dd,  $J$  = 8.3, 1.7 Hz, 1H), 7.53-7.57 (m, 2H, merged with major rotamer), 7.47-7.50 (m, 2H, merged with major rotamer) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) major rotamer  $\delta$  159.4, 148.4, 136.9, 128.2, 127.6, 122.4, 121.9, 118.0 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>: Calcd. for C<sub>10</sub>H<sub>9</sub>N<sub>2</sub>O 173.0715; Found 173.0709.

*N*-(pyridin-2-ylmethyl)formamide (Compound-3f'): Compound 3f' was synthesized following the



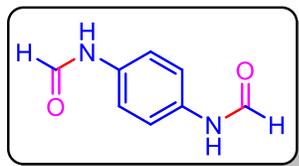
general procedure by reacting pyridin-2-ylmethanamine (54.1 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 44.2 mg, 0.325 mmol, 65%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) major rotamer (90%)  $\delta$  8.41-8.43 (m, 1H), 8.22 (s, 1H), 7.57-7.63 (m, 1H), 7.50 (s, 1H), 7.21 (s, 1H), 7.10-7.13 (m, 1H), 4.49-4.51 (d,  $J$  = 5.7 Hz, 2H) ppm; minor rotamer (10%)  $\delta$  8.46-8.47 (m, 1H), 8.16-8.13 (1H), 7.19 (s, 1H), 4.45-4.46 (d,  $J$  = 5.7 Hz, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>) major rotamer  $\delta$  161.5, 156.1, 148.9, 136.9, 122.5, 122.0, 43.0 ppm; minor rotamer  $\delta$  165.4, 149.5, 137.1, 122.7, 121.2, 47.1 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>: Calcd. for C<sub>7</sub>H<sub>9</sub>N<sub>2</sub>O 137.0715; Found 137.0708.

*N*-(pyridin-2-yl)formamide (Compound-3g'):<sup>2</sup> Compound 3g' was synthesized following the



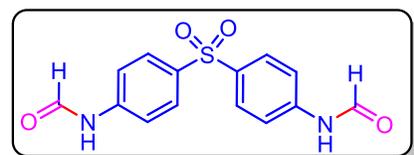
general procedure by reacting pyridin-2-amine (47.0 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 41.5 mg, 0.340 mmol, 68 %). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.18 (s, 1H), 7.87-7.88 (m, 1H), 7.38-7.42 (m, 1H), 6.48-6.51 (m, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>) major rotamer  $\delta$  163.8, 159.2, 146.4, 137.7, 111.7, 108.5 ppm; minor rotamer  $\delta$  163.6, 159.2, 146.1, 137.9, 112.0, 108.9 ppm. HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup>: Calcd. for C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O 123.0558; Found 123.0552.

*N,N'*-(1,4-phenylene)diformamide (Compound-**3h'**):<sup>6</sup> Compound **3h'** was synthesized following



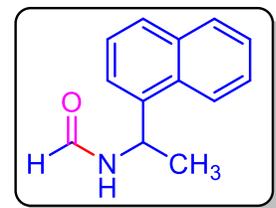
the general procedure by reacting benzene-1,4-diamine (54.0 mg, 0.5 mmol) and phenylsilane (246  $\mu$ L, 2.0 mmol) for 24 h at room temperature (yield: 63.2 mg, 0.385 mmol, 77%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) major rotamer (78%)  $\delta$  10.11 (s, 2H), 8.22 (s, 2H), 7.52-7.53 (m, 4H) ppm; minor rotamer (22%)  $\delta$  10.04 (d, *J* = 10.9 Hz, 2H), 8.67-8.69 (d, *J* = 11.0 Hz, 2H), 7.13-7.14 (d, *J* = 7.9 Hz, 4H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>) major rotamer  $\delta$  159.2, 134.0, 120.2, 119.6, 118.3 ppm. HRMS (ESI) *m/z*: [M + H]<sup>+</sup>: Calcd. for C<sub>8</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub> 165.0664; Found 165.0663.

*N,N'*-(sulfonylbis(4,1-phenylene))diformamide (Compound-**3i'**):<sup>15</sup> Compound **3i'** was synthesized



following the general procedure by reacting 4,4'-sulfonyldianiline (124 mg, 0.5 mmol) and phenylsilane (246  $\mu$ L, 2.0 mmol) for 24 h at room temperature (yield: 100.4 mg, 0.330 mmol, 66%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) major rotamer (79%)  $\delta$  10.61 (s, 2H), 8.94 (d, *J* = 10.4 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 4H), 7.77 (d, *J* = 8.8 Hz, 5H) ppm; minor rotamer (21%)  $\delta$  10.49 (d, *J* = 10.6 Hz, 2H), 8.94 (d, *J* = 10.4 Hz, 1H), 8.31-8.34 (m, 4H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.36-7.39 (m, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, DMSO-*d*<sub>6</sub>) major rotamer  $\delta$  160.3, 142.5, 128.6, 119.3, 117.1 ppm; minor rotamer  $\delta$  162.6, 135.6, 128.9, 117.1 ppm. HRMS (ESI) *m/z*: [M + Na]<sup>+</sup>: Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>SNa 372.0409; Found 372.0403.

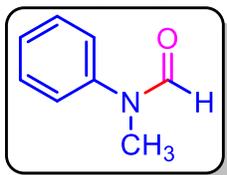
*N*-(1-(naphthalen-1-yl)ethyl)formamide (Compound-**3j'**): Compound **3j'** was synthesized



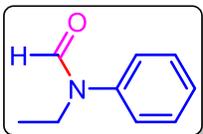
following the general procedure by reacting *N*-(1-(naphthalen-1-yl)ethyl)formamide (70.7 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 70.7 mg, 0.355 mmol, 71%). Formation of a mixture of rotamers is observed; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) major rotamer (88%)  $\delta$  8.05 (d, *J* = 8.4 Hz, 1H), 7.99 (s, 1H), 7.84 (d, *J* = 6.0 Hz, 1H), 7.46-7.52 (m, 3H), 6.45 (s, 1H), 5.90-5.94 (q, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 6.9 Hz, 3H) ppm; minor rotamer (12%)  $\delta$  8.07 (s, 1H), 7.94-7.95 (d, *J* = 8.4 Hz, 1H), 7.78-7.89 (d, *J* = 5.8 Hz, 1H), 7.78-7.89 (d, *J* = 5.8 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.39-7.43 (m, 1H), 6.65 (s, 1H), 5.35-5.39 (q, *J* = 7.2 Hz, 1H), 1.62-1.63 (d, *J* = 6.7 Hz, 1H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>)

major rotamer  $\delta$  160.3, 137.9, 133.9, 130.9, 130.0, 129.2, 128.8, 128.4, 128.3, 126.5, 125.9, 125.9, 125.2, 123.2, 122.6, 48.0, 43.4, 20.9 ppm; minor rotamer  $\delta$  164.4, 138.5, 133.9, 130.0, 129.2, 128.4, 126.6, 125.5, 122.8, 122.3, 48.0, 23.3 ppm. HRMS (ESI)  $m/z$ :  $[M + Na]^+$ : Calcd. for  $C_{13}H_{13}NONa$  222.0895; Found 222.0908.

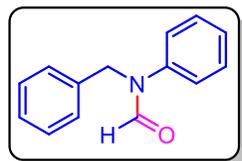
*N*-methyl-*N*-phenylformamide (**3k'**):<sup>13</sup> Compound **3k'** was synthesized following the general procedure by reacting *N*-methylaniline (53.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 55.4 mg, 0.410 mmol, 82%). <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.42 (s, 1H), 7.35-7.38 (t,  $J = 7.4$  Hz, 2H), 7.22-7.24 (m, 1H), 7.11-7.13 (m, 2H), 3.27 (s, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz,  $CDCl_3$ )  $\delta$  162.3, 142.1, 129.6, 126.4, 122.3, 32.0 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_8H_{10}NO$  136.0757; Found 136.0761.



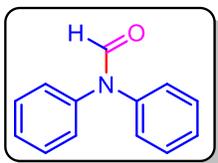
*N*-ethyl-*N*-phenylformamide (Compound-**3l'**):<sup>6</sup> Compound **3l'** was synthesized following the general procedure by reacting *N*-ethyl aniline (60.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 59.6 mg, 0.400 mmol, 80%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.32 (s, 1H), 7.40 (t,  $J = 7.7$  Hz, 2H), 7.30 (d,  $J = 7.5$  Hz, 1H), 7.16-7.13 (m, 2H), 3.84 (q,  $J = 7.2$  Hz, 2H), 1.14 (t,  $J = 7.2$  Hz, 3H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz,  $CDCl_3$ )  $\delta$  162.2, 140.9, 129.7, 127.0, 124.2, 40.2, 13.2 ppm.



*N*-benzyl-*N*-phenylformamide (Compound-**3m'**): Compound **3m'** was synthesized following the general procedure by reacting *N*-benzylaniline (91.6 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 82.3 mg, 0.390 mmol, 78%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.56 (s, 1H), 7.28-7.36 (m, 4H), 7.22-7.25 (m, 4H), 7.10 (d,  $J = 7.7$  Hz, 2H), 5.00 (s, 2H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz,  $CDCl_3$ )  $\delta$  162.6, 141.1, 136.8, 129.7, 128.7, 128.0, 127.6, 127.1, 124.3, 49.0 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_{14}H_{14}NO$  212.1075; Found 212.1068.

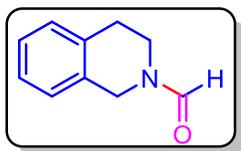


*N,N*-diphenylformamide (Compound-**3n'**):<sup>6</sup> Compound **3n'** was synthesized following the general procedure by reacting diphenylamine (84.6 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 79.8



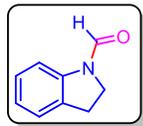
mg, 0.405 mmol, 81%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.63 (s, 1H), 7.34-7.38 (m, 4H), 7.22-7.29 (m, 4H), 7.12-7.14 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.8, 141.9, 139.7, 129.8, 129.3, 127.2, 127.0, 126.2, 125.2 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_{13}\text{H}_{12}\text{NO}$  198.0919; Found 198.0920.

*3,4-dihydroisoquinoline-2(1H)-carbaldehyde (Compound-3o')*:<sup>6</sup> Compound **3o'** was synthesized



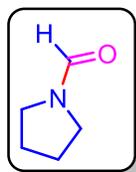
following the general procedure by reacting 1,2,3,4-tetrahydroisoquinoline (66.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 56.4 mg, 0.350 mmol, 70%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major rotamer (62%)  $\delta$  8.18 (s, 1H), 7.08-7.15 (m, 5H), 4.68 (s, 2H), 3.64 (t,  $J = 5.9$  Hz, 2H), 2.86-2.91 (m, 2H, merged with minor rotamer) ppm; minor rotamer (38%)  $\delta$  8.24 (s, 1H), 7.16-7.22 (m, 4H), 4.53 (s, 2H), 3.78 (t,  $J = 3.1$  Hz, 2H), 2.86-2.91 (m, 2H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) major rotamer  $\delta$  161.8, 133.6, 131.8, 129.0, 126.8, 126.7, 43.3, 42.4, 29.8 ppm; minor rotamer  $\delta$  161.3, 134.5, 132.3, 129.3, 127.2, 126.6, 126.0, 47.4, 38.1, 28.0 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_{10}\text{H}_{12}\text{NO}$  162.0919; Found 162.0915.

*Indoline-1-carbaldehyde (Compound-3p')*:<sup>6</sup> Compound **3p'** was synthesized following the



general procedure by reacting indoline (59.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 54.4 mg, 0.370 mmol, 74%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major rotamer (94%)  $\delta$   $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (s, 1H), 7.01-7.13 (m, 3H), 6.91-6.95 (m, 1H), 3.89-3.97 (m, 2H), 2.98-3.06 (m, 2H) ppm; minor rotamer (16%)  $\delta$  8.37 (s, 1H), 7.95 (d,  $J = 9.8$  Hz, 1H), 7.18 (s, 1H), 7.01-7.13 (m, 0.20H, merged with major rotamer), 3.89-3.97 (m, 0.12H, merged with major rotamer), 2.98-3.06 (m, 0.13H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) major rotamer  $\delta$  157.5, 140.9, 148.2, 131.8, 127.5, 126.0, 124.2, 109.3, 44.6, 27.1 ppm; minor rotamer  $\delta$  159.3, 141.1, 132.0, 124.8, 124.5, 116.5, 46.9, 27.6 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_9\text{H}_9\text{NONa}$  170.0582; Found 170.0577.

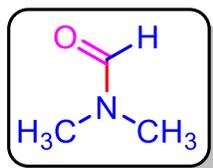
*Pyrrolidine-1-carbaldehyde (Compound-3q')*:<sup>16</sup> Compound **3q'** was synthesized following the



general procedure by reacting pyrrolidine (35.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 32.7 mg, 0.330 mmol,

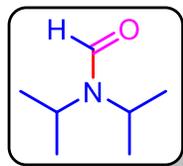
66%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (s, 1H), 3.50 (t,  $J = 6.6$  Hz, 2H), 3.42 (d,  $J = 7.0$  Hz, 2H), 1.94-1.88 (m, 4H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 46.3, 43.4, 25.0, 24.3 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_5\text{H}_{10}\text{NO}$  100.0762; Found 100.0759.

*N,N*-dimethylformamide (Compound-**3r'**):<sup>17</sup> Compound **3r'** was synthesized following the



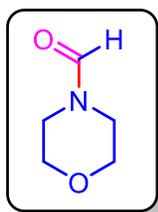
general procedure by reacting dimethylamine (22.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 26.6 mg, 0.365 mmol, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.96 (s, 1H), 2.90 (s, 3H), 2.74 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  162.3, 35.7, 30.7 ppm.

*N,N*-diisopropylformamide (**3s'**):<sup>11</sup> Compound **3s'** was synthesized following the general



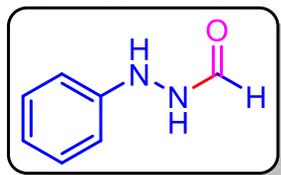
procedure by reacting diisopropylamine (50.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 45.8 mg, 0.355 mmol, 71%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.34 (s, 1H), 3.27-3.33 (m, 2H), 1.20 (d,  $J = 4.9$  Hz, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO}-d_6$ )  $\delta$  165.6, 46.1, 18.9 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_7\text{H}_{16}\text{NO}$  130.1231; Found 130.1230.

*Morpholine-4-carbaldehyde* (Compound-**3t'**):<sup>16</sup> Compound **3t'** was synthesized following the



general procedure by reacting morpholine (43.5 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (NMR yield: 63.3 mg 0.285 mmol, 57%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (s, 1H), 3.37-3.43 (m, 8H), 3.22-3.28 (m, 2H), 3.14-3.16 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.3, 66.6, 66.1, 44.9, 39.8 ppm.

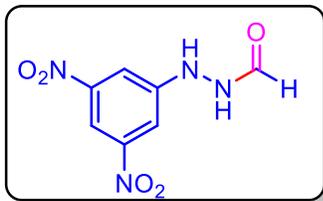
*N'*-phenylformohydrazide (Compound-**5a**): Compound **5a** was synthesized following the general



procedure by reacting phenylhydrazine (54 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 50.3 mg, 0.370 mmol, 74%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ) major rotamer  $\delta$  9.70 (s, 1H), 8.11 (s, 1H), 7.77 (s, 1H), 7.12-7.16 (t,  $J = 7.8$  Hz, 2H), 6.70-6.75 (m, 3H, merged with minor rotamer) ppm; minor rotamer  $\delta$  9.40-9.43 (d,  $J = 10.7$  Hz, 1H), 8.07 (d,  $J = 10.7$  Hz, 1H), 7.99 (s, 1H), 7.18-7.21 (t,  $J = 7.7$  Hz, 2H), 6.77-6.79 (t,  $J = 7.3$  Hz, 1H), 6.75-6.80 (m, 2H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO}-d_6$ ) major rotamer  $\delta$  160.5, 148.8, 128.8, 118.6, 112.1 ppm;

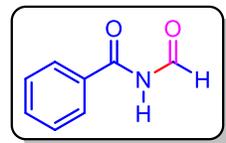
minor rotamer  $\delta$  167.6, 149.4, 129.0, 119.4, 112.3 ppm. HRMS (ESI)  $m/z$ :  $[M + Na]^+$ : Calcd. for  $C_7H_8N_2NaO$  159.0534; Found 159.0530.

*N'-(3,5-dinitrophenyl)formohydrazine (Compound-5b)*: Compound **5b** was synthesized following



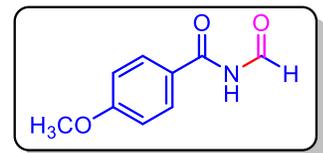
the general procedure by reacting 3,5-dinitrophenylhydrazine (54 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 50.3 mg, 0.265 mmol, 53%). Formation of a mixture of rotamers is observed;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  10.60 (s, 1H), 10.15 (s, 1H), 8.92 (s, 1H), 8.38-8.42 (d,  $J = 12.5$  Hz, 1H), 8.31 (s, 1H), 7.30 (d,  $J = 9.5$  Hz, 1H) ppm.  $^{13}C\{^1H\}$  NMR (126 MHz,  $DMSO-d_6$ ) major rotamer  $\delta$  160.7, 137.0, 130.3, 123.3, 115.6 ppm; minor rotamer  $\delta$  163.3, 148.2, 129.8, 123.7, 116.1 ppm. HRMS (ESI)  $m/z$ :  $[M + Na]^+$ : Calcd. for  $C_7H_6N_4NaO_5$  249.0236; Found 249.0204.

*N-formylbenzamide (Compound-5c)*: Compound **5c** was synthesized following the general



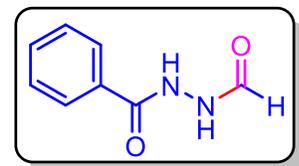
procedure by reacting benzamide (60.5 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 52.5 mg, 0.355 mmol, 71%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.63 (s, 1H), 9.38-9.40 (d,  $J = 9.6$  Hz, 1H), 7.94-7.97 (m, 2H), 7.64-7.68 (m, 1H), 7.53-7.56 (m, 2H) ppm.  $^{13}C\{^1H\}$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  166.6, 164.2, 134.1, 131.2, 129.3, 128.1 ppm. HRMS (ESI)  $m/z$ :  $[M + H]^+$ : Calcd. for  $C_8H_8NO_2$  150.0550; Found: 150.0549.

*N-formyl-4-methoxybenzamide (5d)*:<sup>18</sup> Compound **5d** was synthesized following the general



procedure by reacting 4-methoxybenzamide (75.6 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 52.5 mg, 0.365 mmol, 73%).  $^1H$  NMR (500 MHz,  $DMSO-d_6$ )  $\delta$  11.62 (m, 1H), 9.26-9.28 (d,  $J = 6.4$  Hz, 1H), 8.04-8.06 (d,  $J = 8.9$  Hz, 2H), 7.06-7.08 (d,  $J = 8.9$  Hz, 2H), 3.84 (s, 3H) ppm;  $^{13}C\{^1H\}$  NMR (126 MHz,  $DMSO-d_6$ ) major rotamer  $\delta$  163.3, 159.2, 129.1, 121.7, 115.0, 55.6 ppm; minor rotamer  $\delta$  157.7, 156.8, 130.1, 129.6, 117.5, 55.7 ppm.

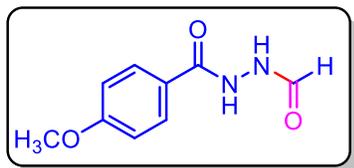
*N'-formylbenzohydrazide (Compound-5e)*:<sup>19</sup> Compound **5e** was synthesized following the



general procedure by reacting benzohydrazide (68.0 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield:

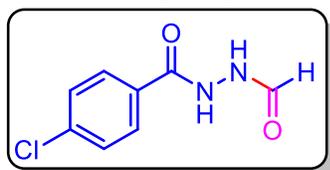
55.8 mg, 0.340 mmol, 68%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) major rotamer (91%)  $\delta$  10.03-10.39 (d,  $J = 10.0\text{ Hz}$ , 2H), 8.13 (d,  $J = 2.4\text{ Hz}$ , 1H), 7.88-7.87 (m, 2H), 7.56-7.60 (t,  $J = 7.4\text{ Hz}$ , 1H), 7.48-7.53 (q,  $J = 7.6\text{ Hz}$ , 2H) ppm; minor rotamer (9%)  $\delta$  9.55-9.57 (d,  $J = 10.7\text{ Hz}$ , 2H), 8.04 (d,  $J = 9.7\text{ Hz}$ , 1H), 7.81 (d,  $J = 7.3\text{ Hz}$ , 1H), 7.43-7.46 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  165.2, 159.8, 131.8, 128.4, 127.4 ppm; minor rotamer (9%)  $\delta$  167.2, 159.8, 132.3, 128.5, 127.4 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_8\text{H}_9\text{N}_2\text{O}_2$  165.0664; Found 165.0721.

*N'*-formyl-4-methoxybenzohydrazide (Compound-5f):<sup>20</sup> Compound **5f** was synthesized following



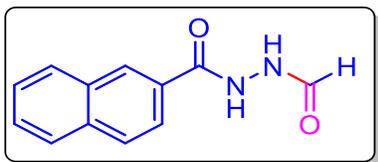
the general procedure by reacting 4-methoxybenzohydrazide (83.0 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 70.0 mg, 0.360 mmol, 72%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) major rotamer (87%)  $\delta$  10.26-9.98 (d, 2H), 8.12 (s, 1H), 7.85-7.87 (d,  $J = 8.8\text{ Hz}$ , 2H), 7.01-7.04 (m, 2H, merged with minor rotamer), 3.82 (s, 3H, merged with minor rotamer) ppm; minor rotamer (9%)  $\delta$  9.53 (d,  $J = 10.6\text{ Hz}$ , 2H), 8.02 (d,  $J = 10.4\text{ Hz}$ , 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  167.5, 164.8, 162.1, 160.0, 129.4, 124.4, 113.7, 55.4 ppm; minor rotamer  $\delta$  166.7, 164.8, 162.3, 160.0, 124.1, 129.4, 113.9, 55.5 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_3\text{Na}$  217.0589; Found 217.0581.

4-chloro-*N'*-formylbenzohydrazide (Compound-5g): Compound **5g** was synthesized following



the general procedure by reacting 4-chlorobenzohydrazide (85.3 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 55.6 mg, 0.280 mmol, 56%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) major rotamer (90%)  $\delta$  10.15-10.51 (s, 2H), 8.13 (s, 1H), 8.03-8.05 (d,  $J = 9.4\text{ Hz}$ , 1H), 7.88-7.90 (m, 2H, merged with major rotamer), 7.56-7.60 (m, 2H, merged with major rotamer) ppm; minor rotamer (9%)  $\delta$  9.62 (s, 1H), 8.04 (d,  $J = 9.4\text{ Hz}$ , 1H), 7.89 (d,  $J = 8.6\text{ Hz}$ , 0.33H, merged with major rotamer), 7.56-7.60 (m, 0.33H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  167.4, 164.5, 160.2, 136.9, 131.1, 129.6, 128.8 ppm; minor rotamer  $\delta$  166.4, 164.5, 160.2, 137.2, 130.9, 129.7, 128.8 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{H}]^+$ : Calcd. for  $\text{C}_8\text{H}_7\text{N}_2\text{O}_2\text{ClNa}$  221.0094; Found 221.0082.

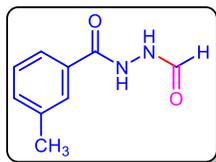
*N'*-formyl-1-naphthohydrazide (Compound-5h): Compound **5h** was synthesized following the



general procedure by reacting 2-naphthohydrazide (93.1 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 65.3 mg, 0.305 mmol, 61%). Formation of a

mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) major rotamer (89%)  $\delta$  10.32 (s, 2H), 8.31-8.32 (m, 1H), 8.20-8.23 (m, 1H, merged with minor rotamer), 8.19 (s, 1H), 8.05-8.10 (m, 2H), 7.99-8.01 (m, 1H), 7.56-7.60 (m, 2H, merged with minor rotamer) ppm; minor rotamer (11%)  $\delta$  9.73 (s, 1H), 8.20-8.23 (m, 0.61H, merged with major rotamer), 7.73 (d,  $J = 5.7$  Hz, 1H), 7.67 (d,  $J = 7.0$  Hz, 1H), 7.56-7.60 (m, 2H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  167.5, 160.1, 133.2, 132.4, 130.9, 129.9, 128.3, 127.0, 126.5, 125.8, 125.4, 125.1 ppm; minor rotamer  $\delta$  169.3, 160.1, 133.2, 132.4, 130.9, 129.9, 128.5, 127.2, 126.6, 126.1, 125.4, 125.1 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2\text{Na}$  237.0640; Found 237.0623.

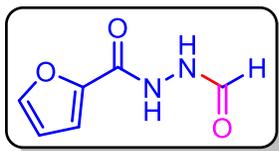
*N'*-formyl-3-methylbenzohydrazide (Compound-5i): Compound **5i** was synthesized following the



general procedure by reacting 3-methylbenzohydrazide (75 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 62.3 mg, 0.350 mmol, 70%). Formation of a mixture of rotamers is observed;

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) major rotamer (79%)  $\delta$  10.37 (s, 2H) 10.08 (s, 1H), 8.12 (s, 1H), 7.65-7.69 (m, 2H, merged with minor rotamer), 7.35-7.40 (m, 2H, merged with minor rotamer), 2.35 (s, 3H, merged with minor rotamer) ppm; minor rotamer (21%)  $\delta$  9.61 (d,  $J = 10.8$  Hz, 1H), 8.03 (d,  $J = 9.5$  Hz, 1H), 7.65-7.69 (m, 0.54H, merged with major rotamer), 7.35-7.40 (m, 0.58H, merged with major rotamer), 2.35 (s, 0.57H, merged with major rotamer) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{DMSO-}d_6$ ) major rotamer  $\delta$  165.7, 160.2, 138.0, 132.7, 132.4, 128.6, 124.7, 21.1 ppm; minor rotamer  $\delta$  167.6, 160.2, 138.2, 132.9, 132.1, 128.7, 128.2, 124.7, 21.1 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2\text{Na}$  201.0640; Found 201.0635.

*N'*-formylfuran-2-carbohydrazide (Compound-5j): Compound **5j** was synthesized following the

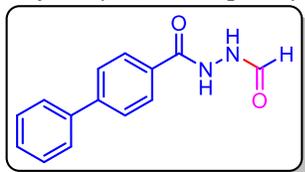


general procedure by reacting furan-2-carbohydrazide (63.6 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 48.5 mg, 0.315 mmol, 63%). Formation of a mixture

of rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ ) major rotamer (83%)  $\delta$  10.23 (s, 2H),

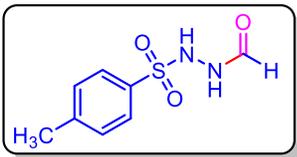
8.09 (s, 1H), 7.84 (s, 1H), 7.20-7.21 (d,  $J = 3.5$  Hz, 1H), 6.63-6.64 (m, 1H) ppm; minor rotamer  $\delta$  9.61 (s, 1H), 7.99 (s, 1H), 7.87 (s, 1H), 7.23-7.24 (d,  $J = 3.7$  Hz, 1H), 6.65-6.66 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, DMSO- $d_6$ ) major rotamer  $\delta$  160.6, 157.3, 146.5, 146.2, 115.3, 112.3 ppm; minor rotamer  $\delta$  167.7, 159.0, 146.2, 145.9, 115.8, 112.5 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_6\text{H}_6\text{N}_2\text{O}_3\text{Na}$  177.0276; Found 177.0271.

*N'*-formyl-[1,1'-biphenyl]-4-carbohydrazide (Compound **5k**): Compound **5k** was synthesized



following the general procedure by reacting [1,1'-biphenyl]-4-carbohydrazide (106.1 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 80.4 mg, 0.335 mmol, 67%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) major rotamer (74%)  $\delta$  10.45-10.14 (s, 2H), 8.15 (s, 1H), 7.99 (d,  $J = 8.2$  Hz, 3H), 7.73-7.75 (d,  $J = 7.7$  Hz, 3H), 7.48-7.52 (m, 3H) ppm; minor rotamer (26%)  $\delta$  9.65 (s, 1H), 8.06-8.08 (d,  $J = 8.4$  Hz, 1H), 7.80-7.83 (m, 3H), 7.39-7.43 (m, 2H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, DMSO- $d_6$ ) major rotamer  $\delta$  167.4, 165.0, 160.0, 143.4, 139.0, 131.1, 129.1, 128.2, 126.9, 126.7 ppm; minor rotamer  $\delta$  166.9, 143.7, 139.0, 130.8, 126.8 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2\text{Na}$  263.0796; Found 263.0787.

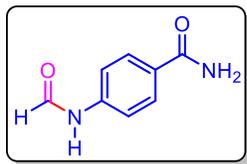
*N'*-formyl-4-methylbenzenesulfonylhydrazide (Compound **5l**): Compound **5l** was synthesized



following the general procedure by reacting 4-methylbenzenesulfonylhydrazide (93.1 mg, 0.5 mmol) and phenylsilane (123  $\mu\text{L}$ , 1.0 mmol) for 24 h at room temperature (yield: 70.6 mg, 0.330 mmol, 66%). Formation of a mixture of rotamers is observed;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ) major rotamer (54%)  $\delta$   $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  10.00 (s, 1H), 9.79 (d,  $J = 10.2$  Hz, 1H), 7.89 (d,  $J = 10.2$  Hz, 1H), 7.69 (t,  $J = 7.9$  Hz, 4H), 2.41 (s, 3H) ppm; minor rotamer (46%)  $\delta$  10.03-10.04 (s, 1H), 9.89-9.88 (d,  $J = 3.4$  Hz, 1H), 7.80 (s, 1H), 7.44 (d,  $J = 8.2$  Hz, 2H), 7.37 (d,  $J = 8.1$  Hz, 2H), 2.38 (s, 3H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz, DMSO- $d_6$ ) major rotamer  $\delta$  166.7, 144.0, 134.6, 129.9, 127.8, 21.1 ppm; minor rotamer  $\delta$  159.2, 143.4, 135.9, 129.4, 127.7, 21.0 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_3\text{SNa}$  237.0309; Found 237.0289.

### Intramolecular chemoselectivity:

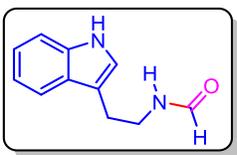
*4-formamidobenzamide (Compound-7a)*: Compound **7a** was synthesized following the general



procedure by reacting 4-aminobenzamide (68.0 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 67.3 mg, 0.410 mmol, 82%). Formation of a mixture of rotamers is observed;

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ) major rotamer (73%)  $\delta$  10.42 (s, 1H), 8.31 (d,  $J = 2.1$  Hz, 1H), 7.82-7.85 (m, 3H, merged with minor rotamer), 7.62-7.65 (m, 2H), 7.24-7.26 (d,  $J = 8.5$  Hz, 1H) ppm; minor rotamer (27%)  $\delta$  10.32 (d,  $J = 10.8$  Hz, 1H), 8.91 (d,  $J = 10.8$  Hz, 1H), 7.85-7.87 (m, 1H, merged with major rotamer), 7.24-7.26 (d,  $J = 8.5$  Hz, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz, DMSO- $d_6$ ) major rotamer  $\delta$  167.3, 160.0, 140.8, 129.0, 128.5, 118.3 ppm; minor rotamer  $\delta$  167.3, 162.6, 140.8, 129.2, 128.5, 116.3 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_8\text{H}_8\text{N}_2\text{O}_2\text{Na}$  187.0483; Found 187.0481.

*N-(2-(1H-indol-3-yl)ethyl)formamide (Compound-7b)*: Compound **7b** was synthesized following

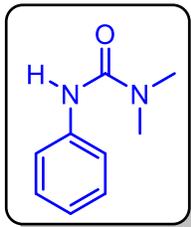


the general procedure by reacting 2-(1H-indol-3-yl)ethan-1-amine (80.1 mg, 0.5 mmol) and phenylsilane (123  $\mu$ L, 1.0 mmol) for 24 h at room temperature (yield: 48.9 mg, 0.260 mmol, 52%). Formation of a mixture of

rotamers is observed;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major rotamer (71%)  $\delta$  8.37 (m, 1H, merged with minor rotamer), 8.06 (s, 1H), 7.59 (d,  $J = 7.8$  Hz, 1H), 7.36 (d,  $J = 8.2$  Hz, 1H, merged with minor rotamer), 7.20 (d,  $J = 7.7$  Hz, 1H, merged with minor rotamer), 7.13 (d,  $J = 7.8$  Hz, 1H, merged with minor rotamer), 7.01 (s, 1H), 5.74 (s, 1H, merged with minor rotamer), 3.60-3.65 (m, 2H), 2.96-3.00 (m, 2H) ppm; minor rotamer (29%)  $\delta$  8.37 (m, 0.14H, merged with major rotamer), 7.84 (d,  $J = 12.8$  Hz, 1H), 7.54 (d,  $J = 7.8$  Hz, 1H), 7.36 (d,  $J = 8.2$  Hz, 0.20H, merged with major rotamer), 7.20 (d,  $J = 7.7$  Hz, 0.54H, merged with major rotamer), 7.13 (d,  $J = 7.8$  Hz, 0.55H, merged with major rotamer), 6.97 (s, 1H), 5.74 (s, 1H, merged with major rotamer), 3.45-3.50 (m, 1H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ) major isomer  $\delta$  161.5, 127.3, 122.4, 119.6, 118.7, 112.5, 111.5, 38.5, 25.3 ppm; minor isomer  $\delta$  136.6, 126.7, 127.0, 122.9, 122.3, 119.7, 118.4, 112.5, 111.6, 42.1, 27.4 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{ONa}$  211.0847; Found 211.0839.

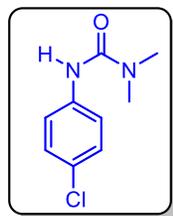
## Biologically relevant N-formylated compounds

*N*-phenylisobutyramide (Compound-**8a**):<sup>21</sup> Compound **8a** was synthesized following the general



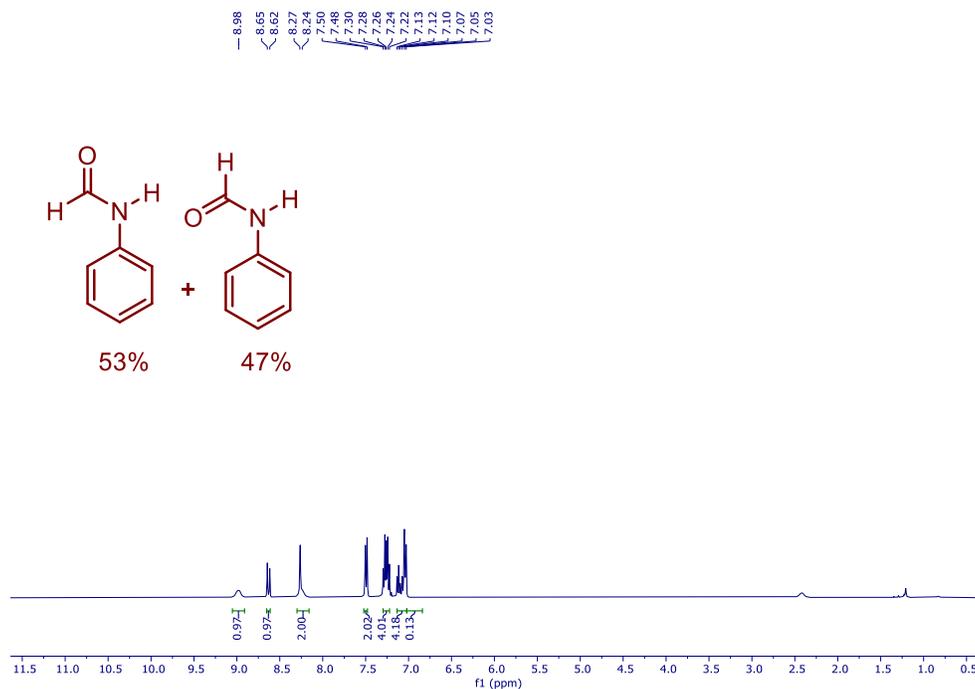
procedure by reacting *N*-phenylformamide (60.6 mg, 0.5 mmol), amine (45  $\mu$ L, 1.0 mmol) and [bis(trifluoroacetoxy)iodo]benzene (215 mg, 0.5 mmol) for 2 h at room temperature (yield: 64.4 mg, 0.395 mmol, 79%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (s, 1H), 7.27 (s, 1H), 3.02 (s, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 139.3, 128.9, 123.1, 120.0, 36.6 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{ONa}$  165.1028; Found 165.1026.

*N*-(4-chlorophenyl)isobutyramide (compound-**8b**):<sup>21</sup> Compound **8b** was synthesized following

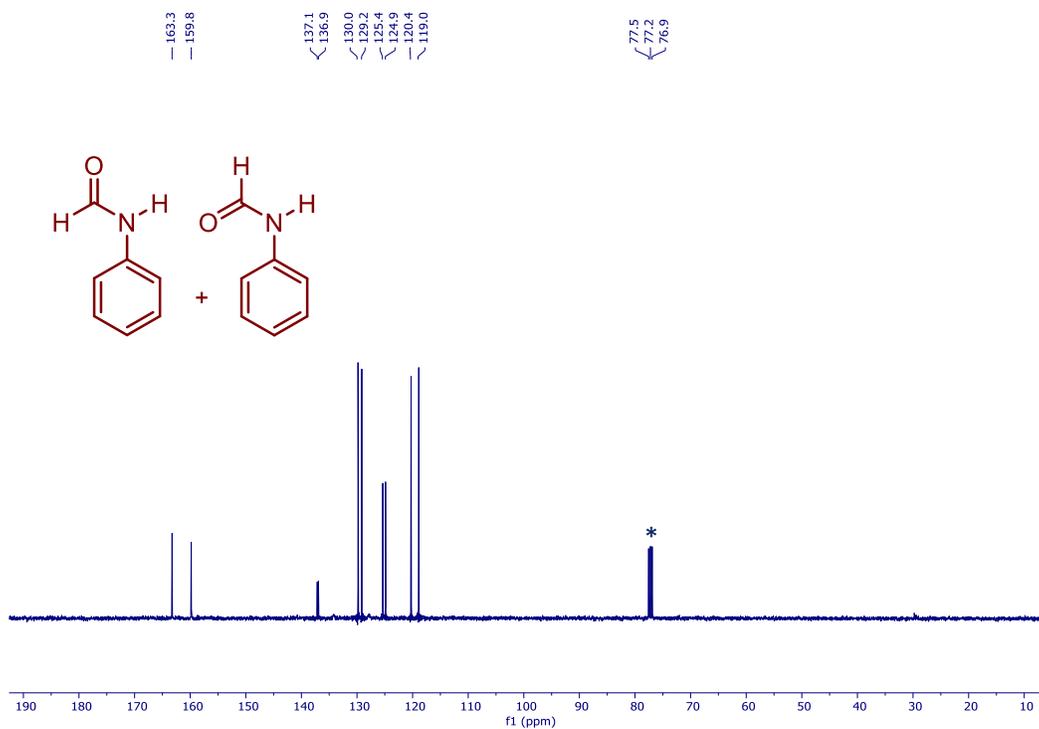


the general procedure by reacting *N*-(4-chlorophenyl)formamide (77.7 mg, 0.5 mmol), amine (45  $\mu$ L, 1.0 mmol) and [bis(trifluoroacetoxy)iodo]benzene (215 mg, 0.5 mmol) for 2 h at room temperature (yield: 66.2 mg, 0.335 mmol, 67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (s, 1H), 7.27 (s, 1H), 3.02 (s, 12H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.2, 139.3, 128.9, 123.1, 120.0, 36.6 ppm. HRMS (ESI)  $m/z$ :  $[\text{M} + \text{Na}]^+$ : Calcd. for  $\text{C}_{11}\text{H}_{12}\text{N}_2\text{ONa}$  211.0847; Found 211.0839.

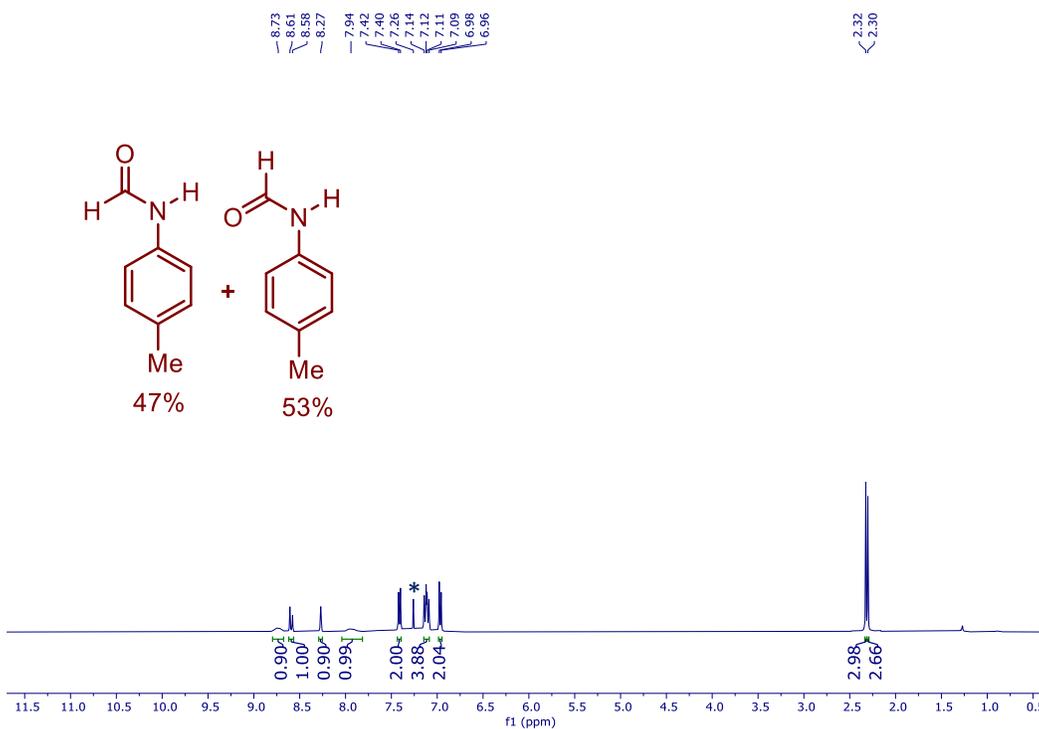
## $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the isolated N-formylated products



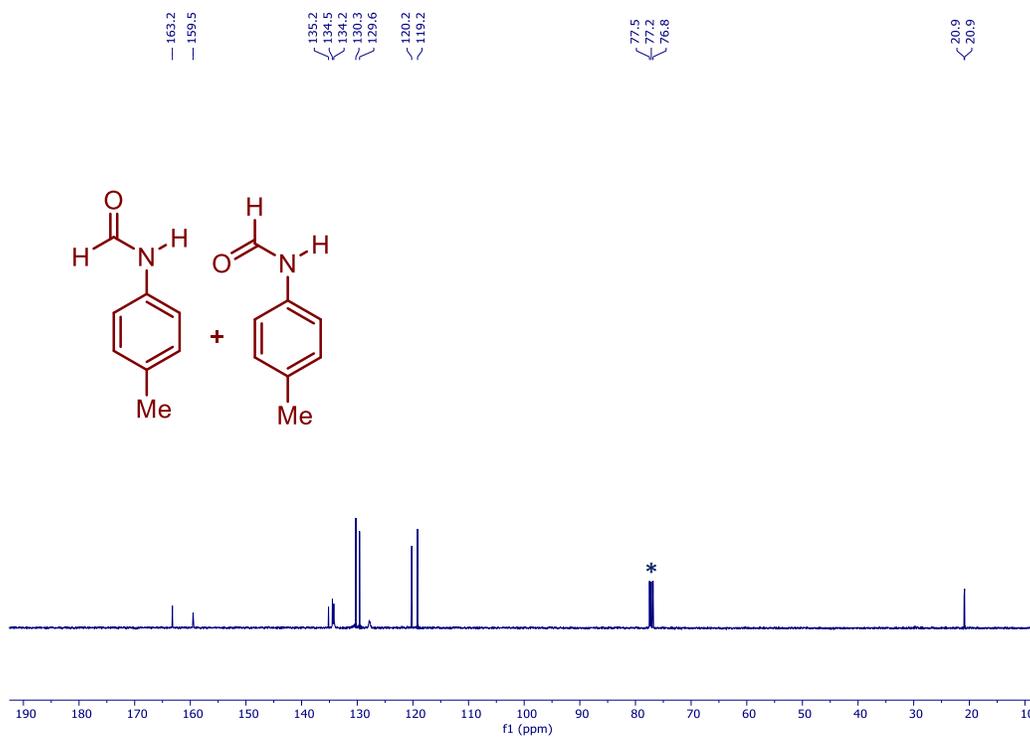
$^1\text{H}$  NMR of *N*-phenylformamide (compound-**3a**) in  $\text{CDCl}_3$



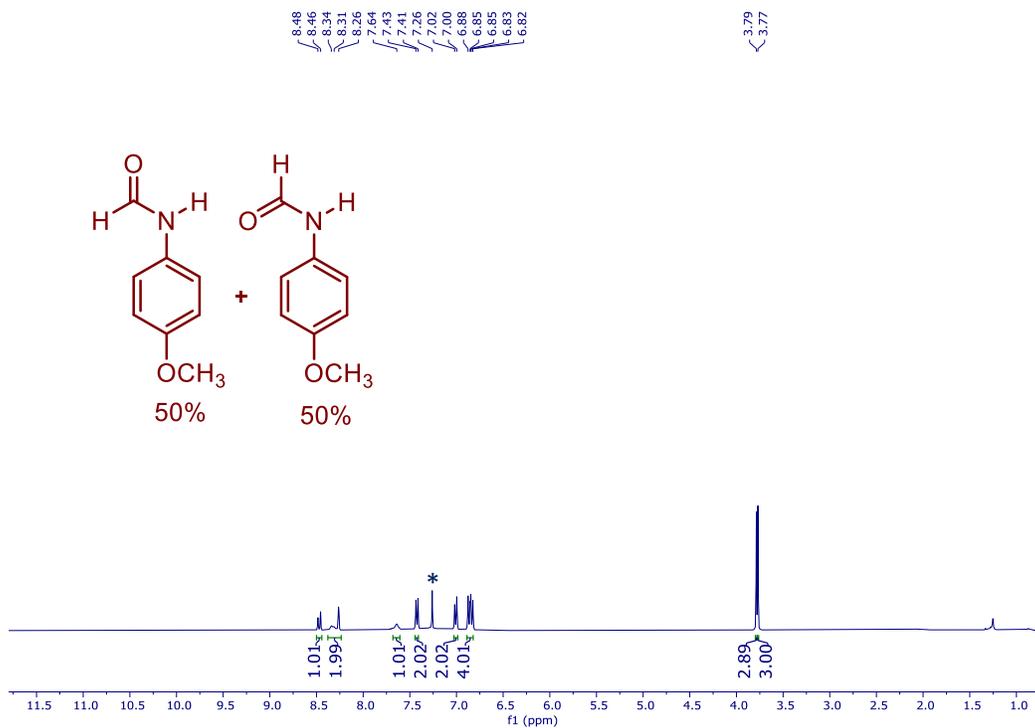
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-phenylformamide (compound-**3a**) in  $\text{CDCl}_3$  (\*)



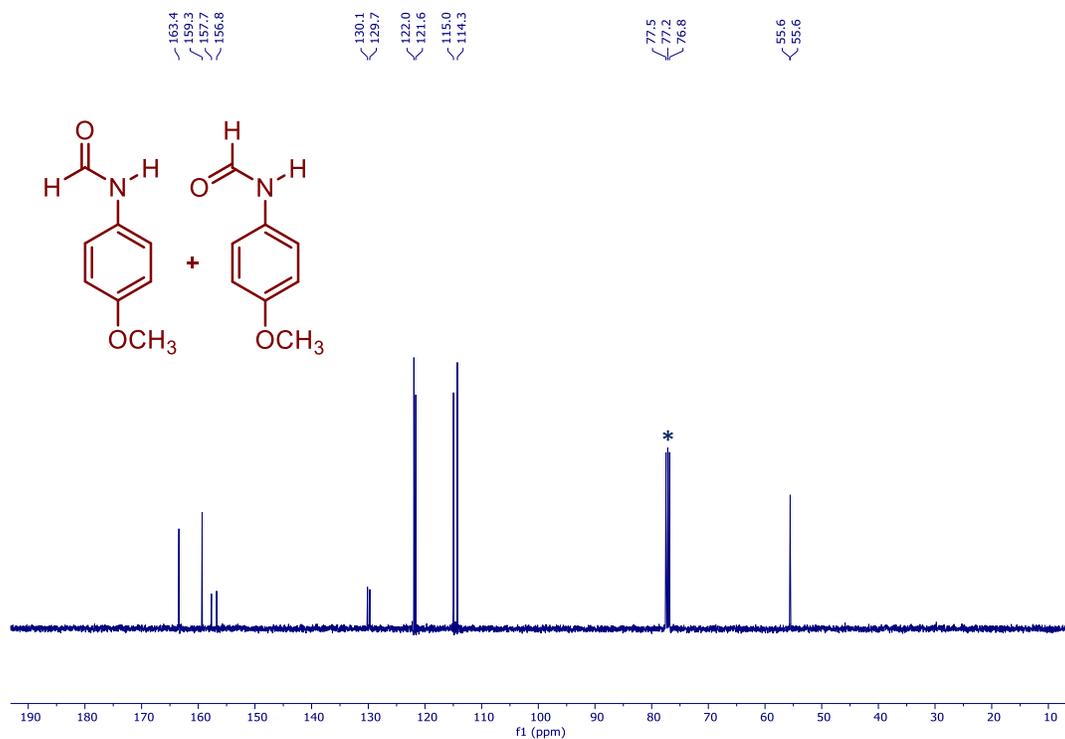
$^1\text{H}$  NMR of *N*-*p*-tolylformamide (compound-**3b**) in  $\text{CDCl}_3$  (\*)



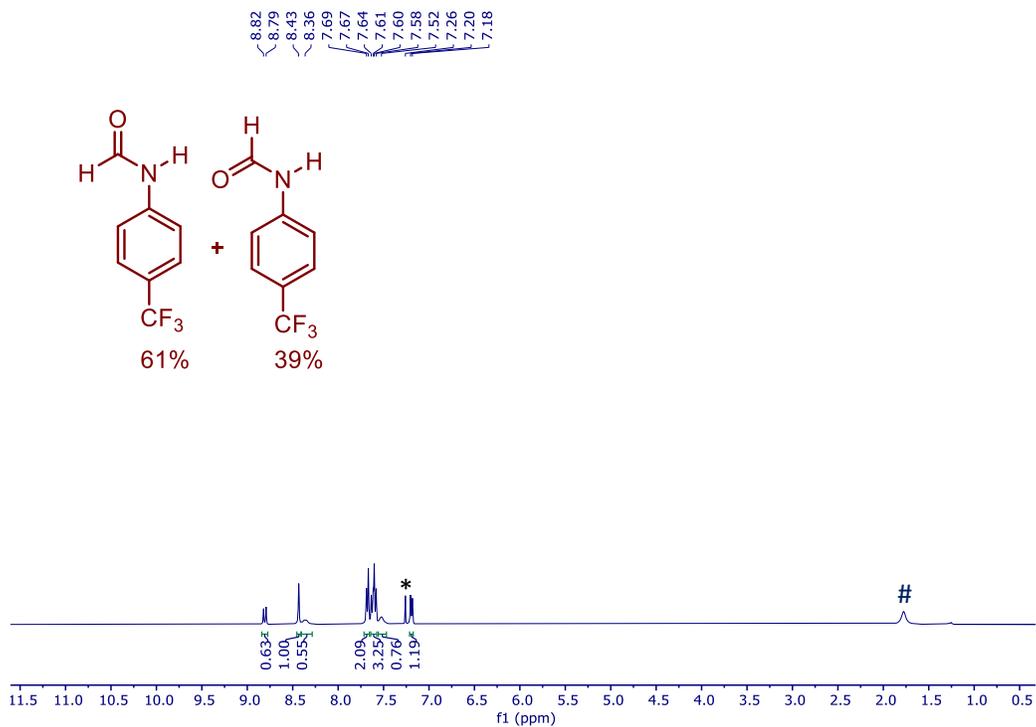
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-*p*-tolylformamide (compound-3b) in  $\text{CDCl}_3$  (\*)



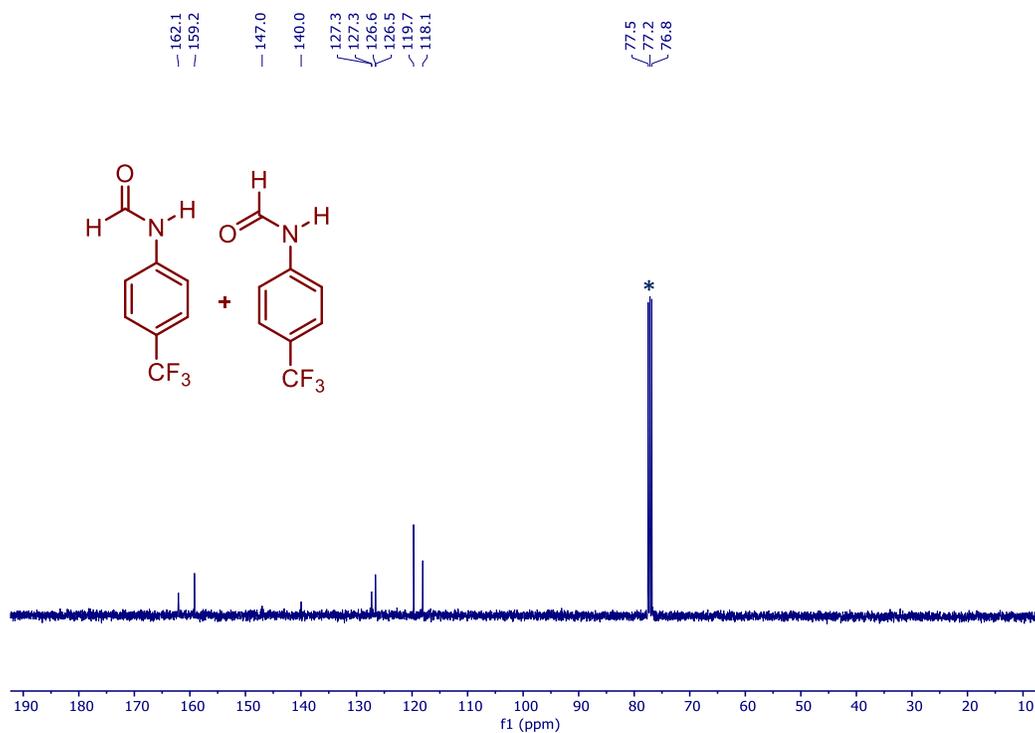
$^1\text{H}$  NMR of *N*-(4-methoxyphenyl)formamide (compound-3c) in  $\text{CDCl}_3$  (\*)



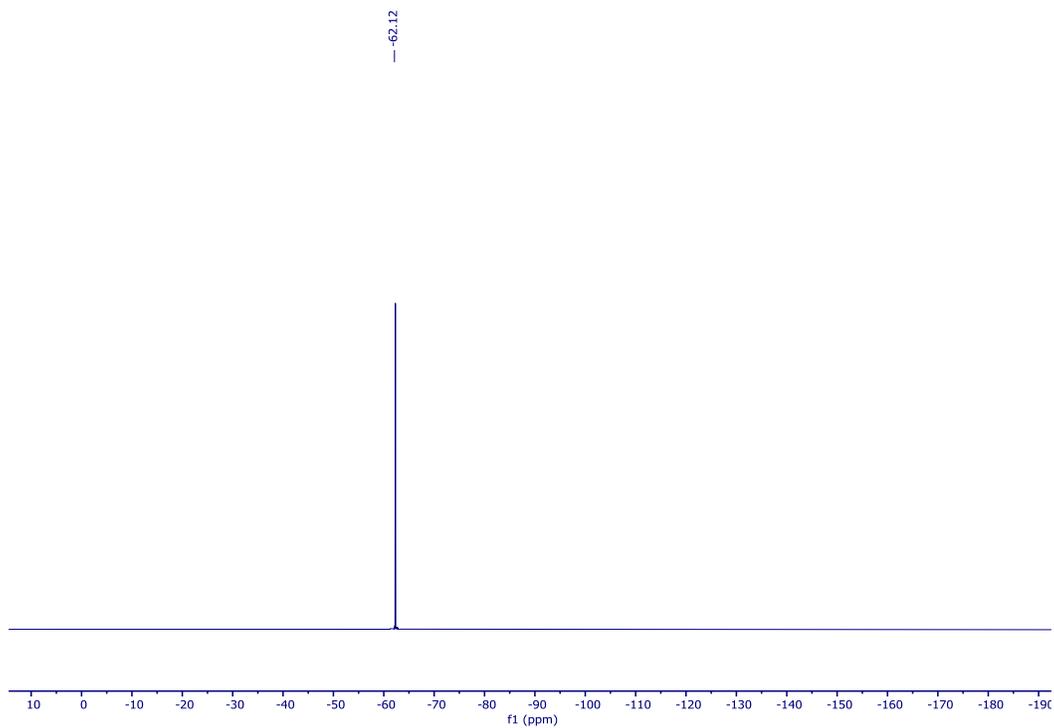
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-methoxyphenyl)formamide (compound-3c) in  $\text{CDCl}_3$  (\*)



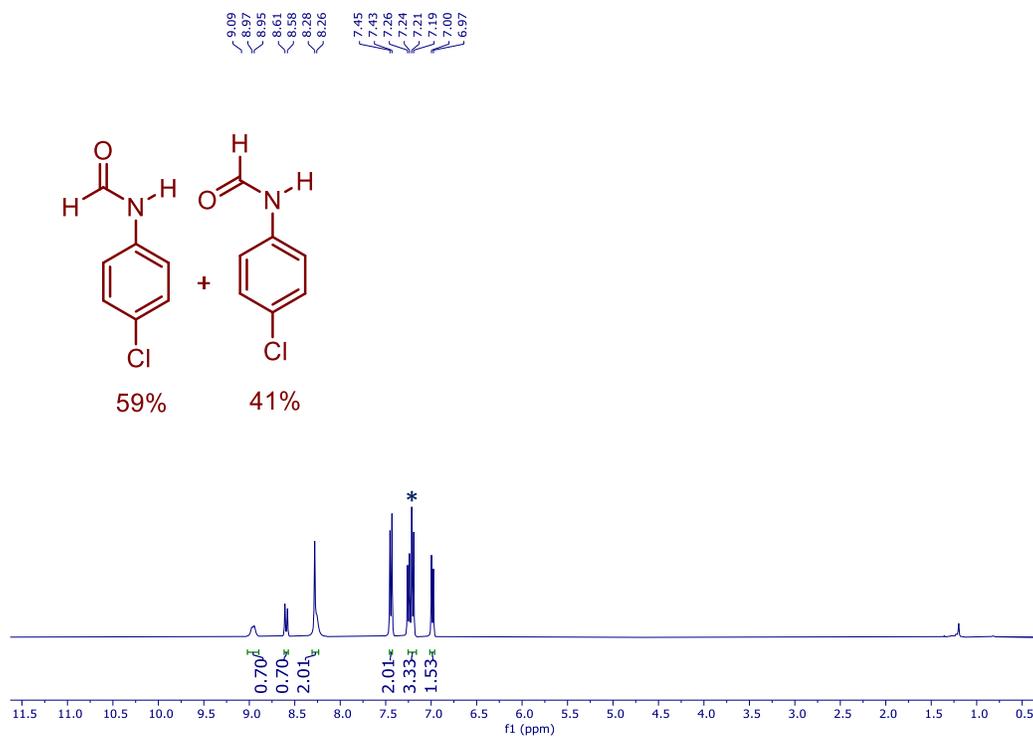
$^1\text{H}$  NMR of *N*-(4-trifluoromethyl)phenyl)formamide (compound-3d) in  $\text{CDCl}_3$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{CDCl}_3$



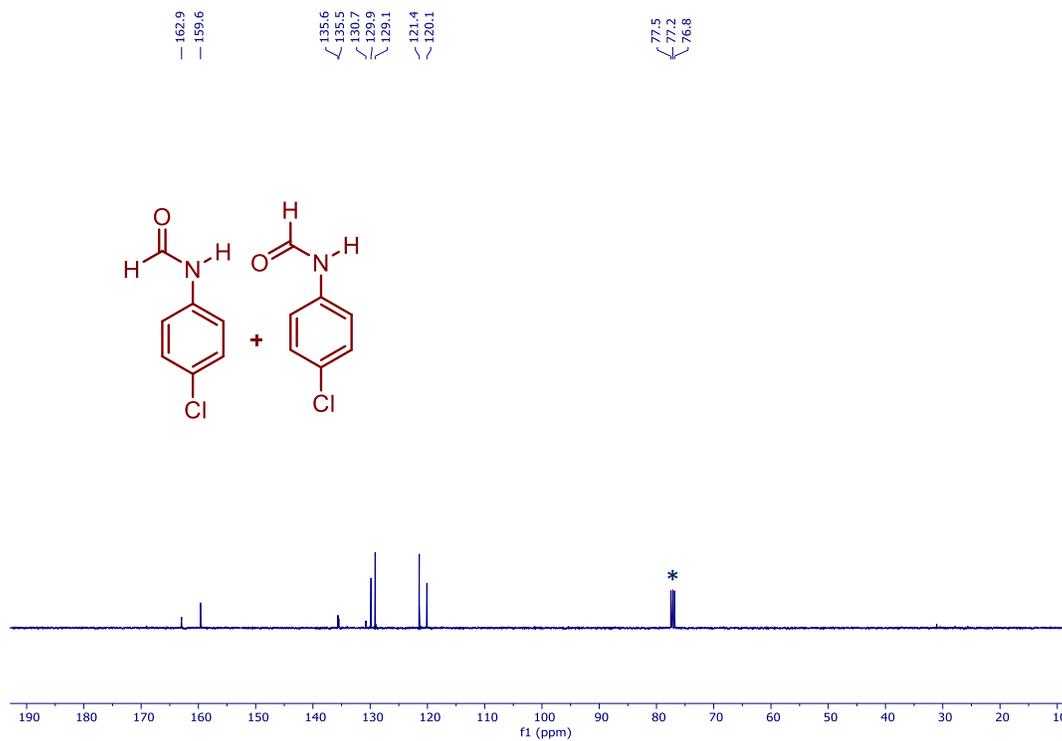
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-trifluoromethyl)phenyl)formamide (compound-3d) in  $\text{CDCl}_3$  (\*)



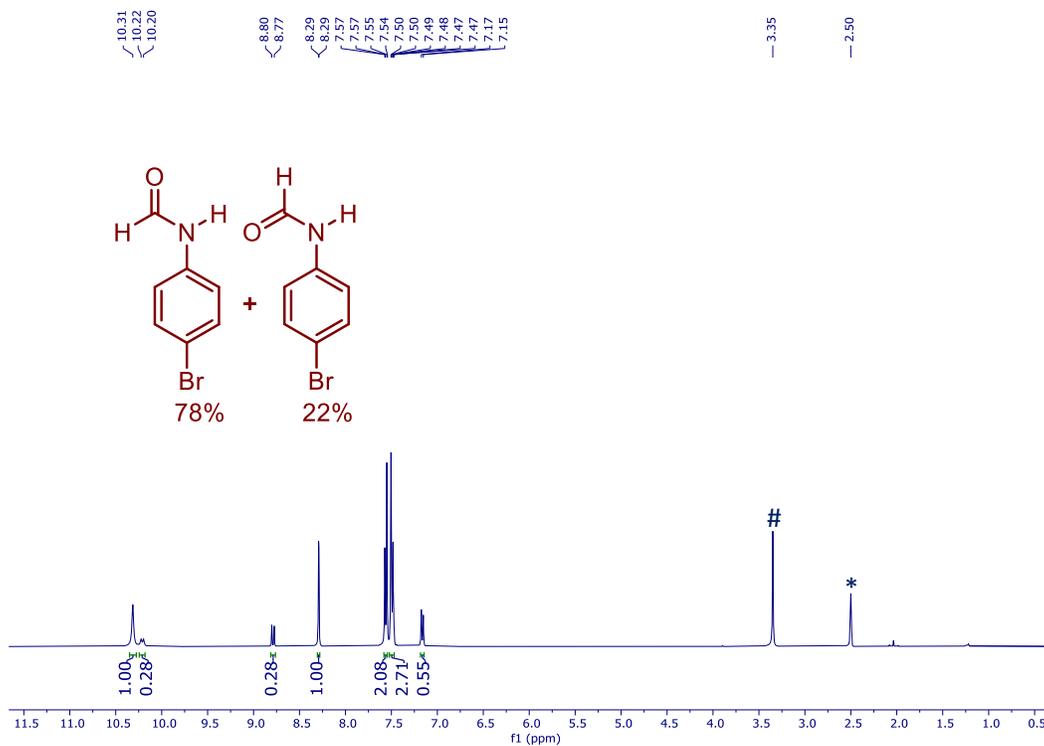
$^{19}\text{F}$  NMR of *N*-(4-trifluoromethyl)phenyl)formamide (compound-3d) in  $\text{CDCl}_3$



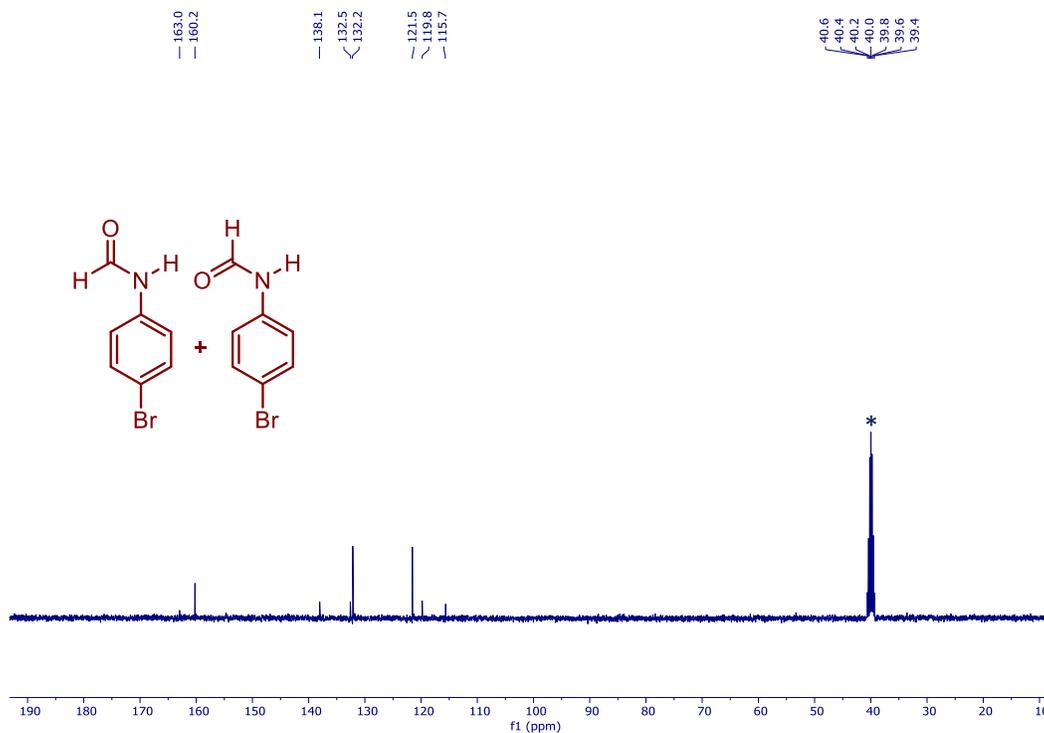
$^1\text{H}$  NMR of *N*-(4-chlorophenyl)formamide (compound-3e) in  $\text{CDCl}_3$  (\*)



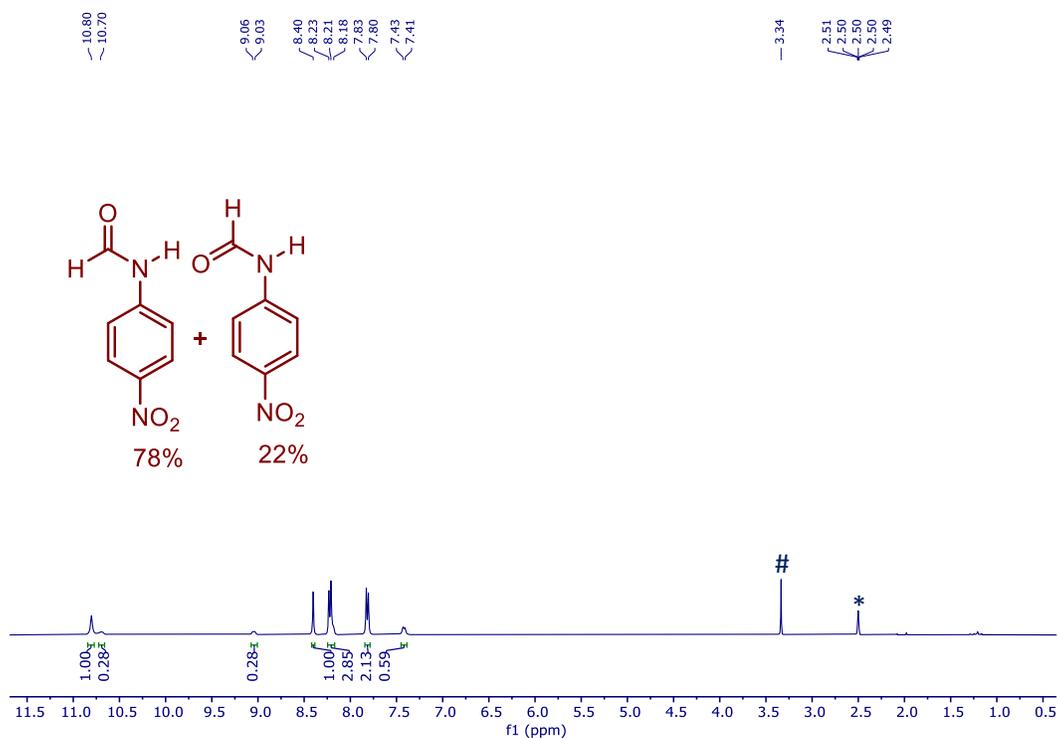
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-chlorophenyl)formamide (compound-3e) in  $\text{CDCl}_3$  (\*)



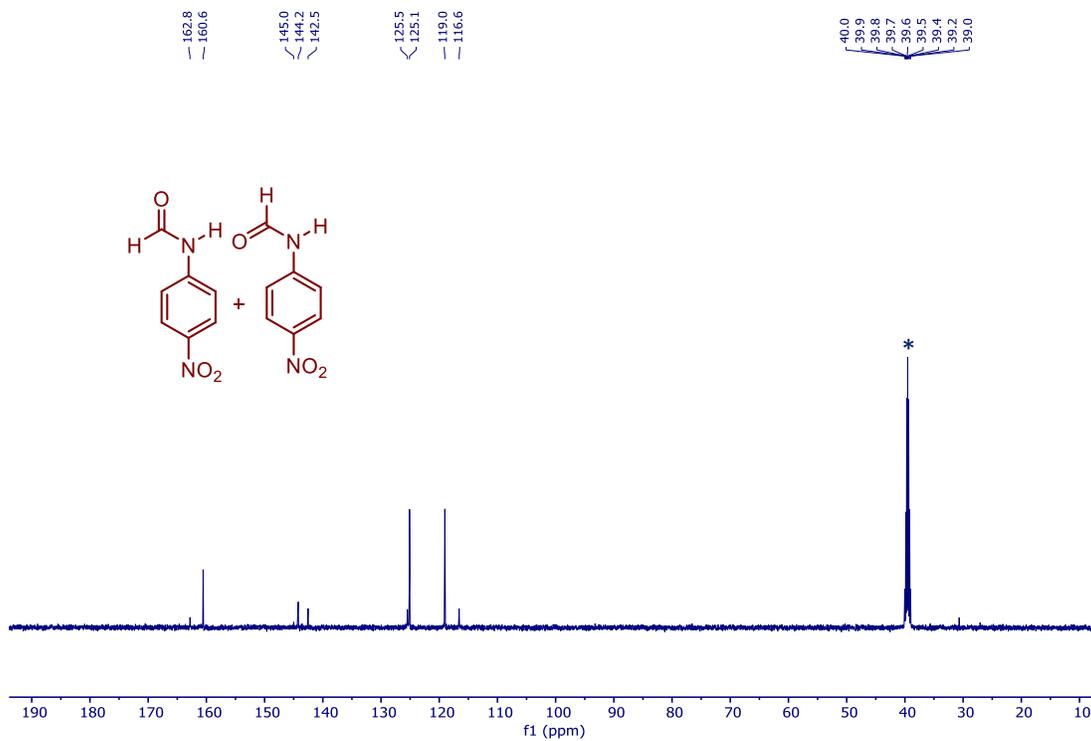
$^1\text{H}$  NMR of *N*-(4-bromophenyl)formamide (compound-3f) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



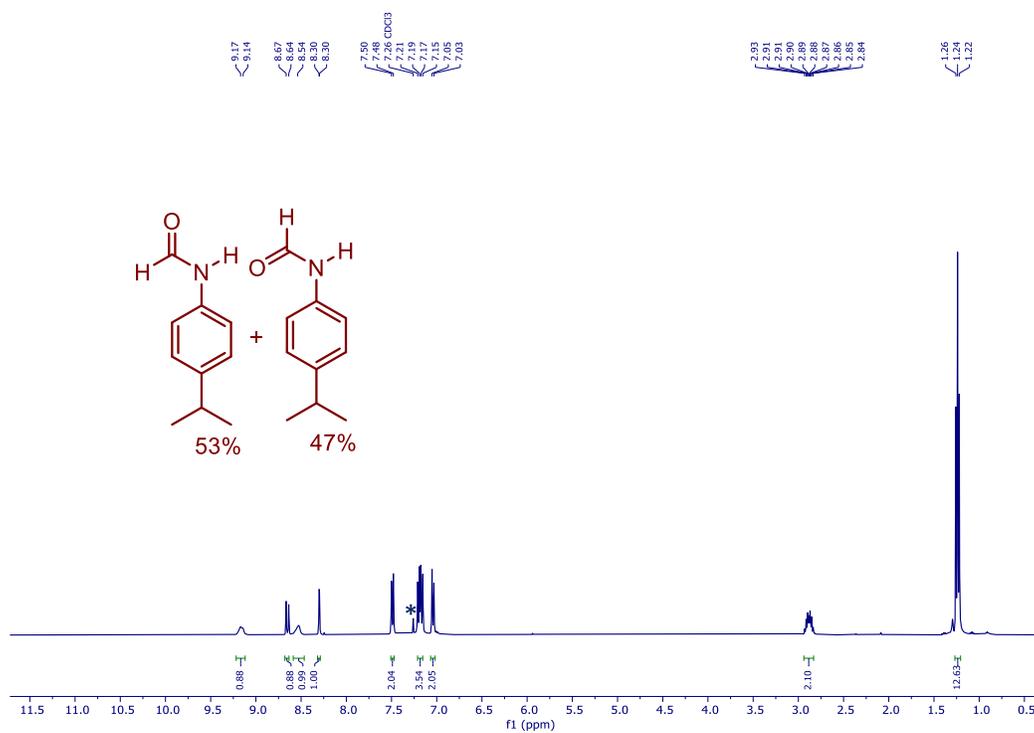
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-bromophenyl)formamide (compound-3f) in  $\text{DMSO-}d_6$  (\*)



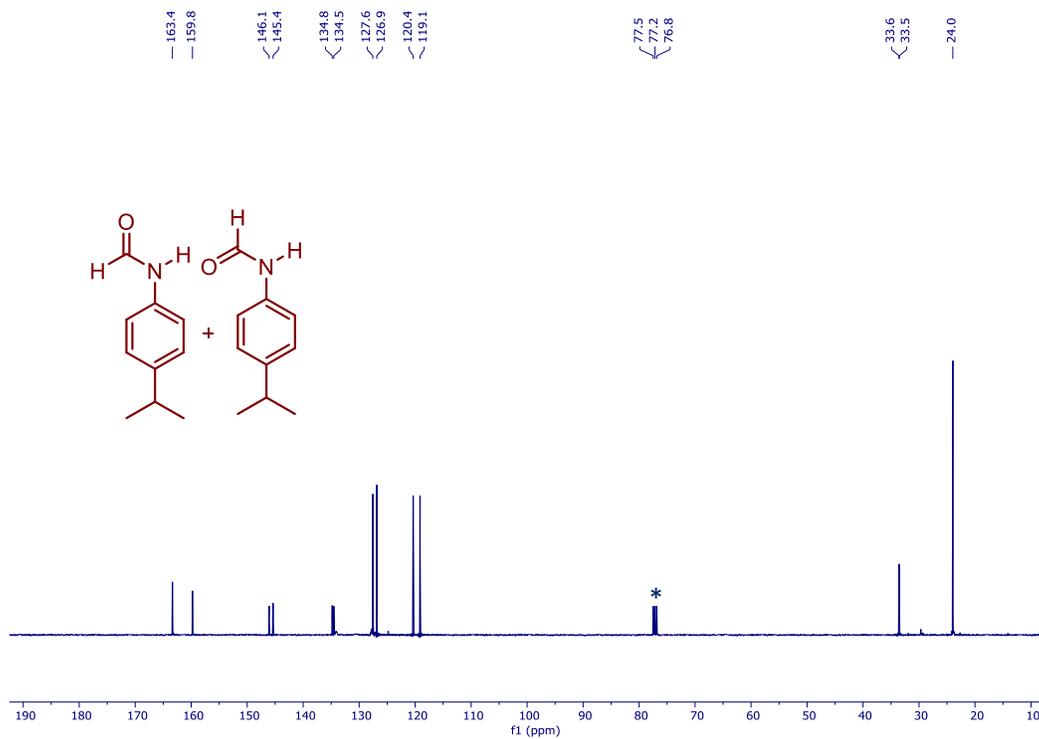
$^1\text{H}$  NMR of *N*-(4-nitrophenyl)formamide (compound-3g) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



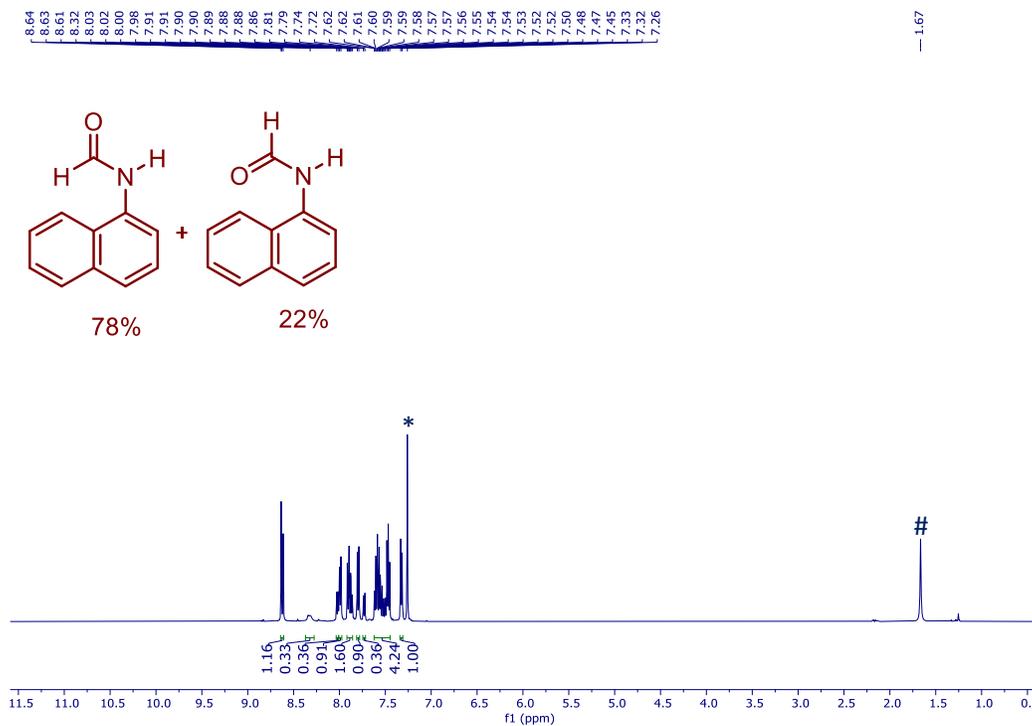
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-nitrophenyl)formamide (compound-3g) in  $\text{DMSO-}d_6$  (\*)



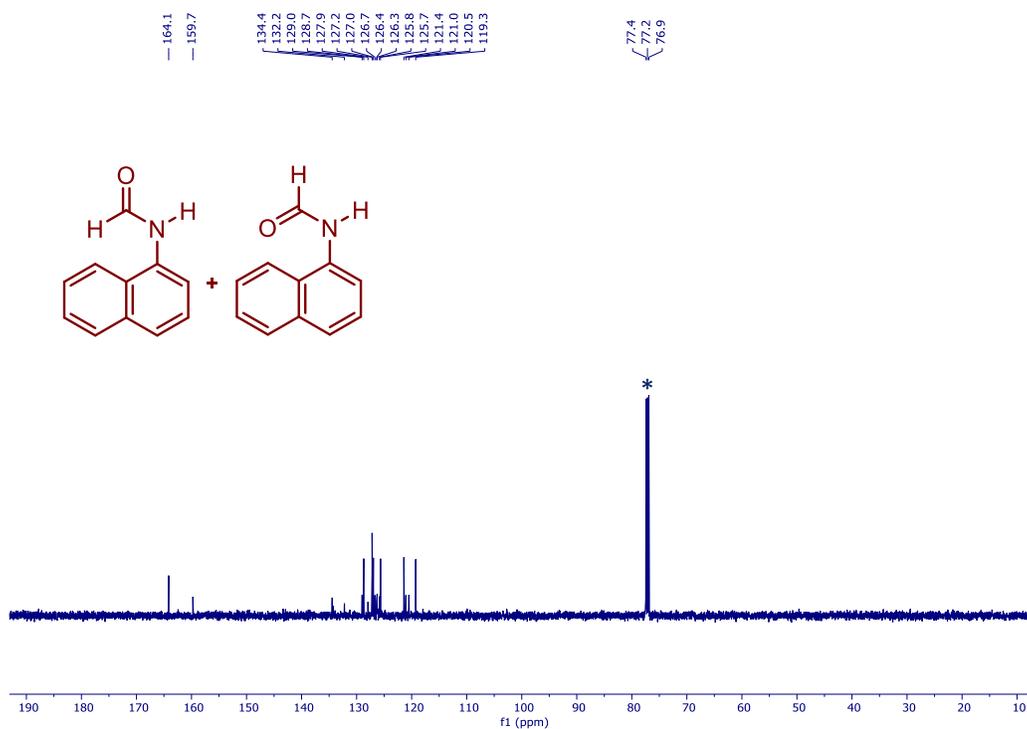
$^1\text{H}$  NMR of *N*-(4-isopropylphenyl)formamide (compound-3h) in  $\text{CDCl}_3$  (\*)



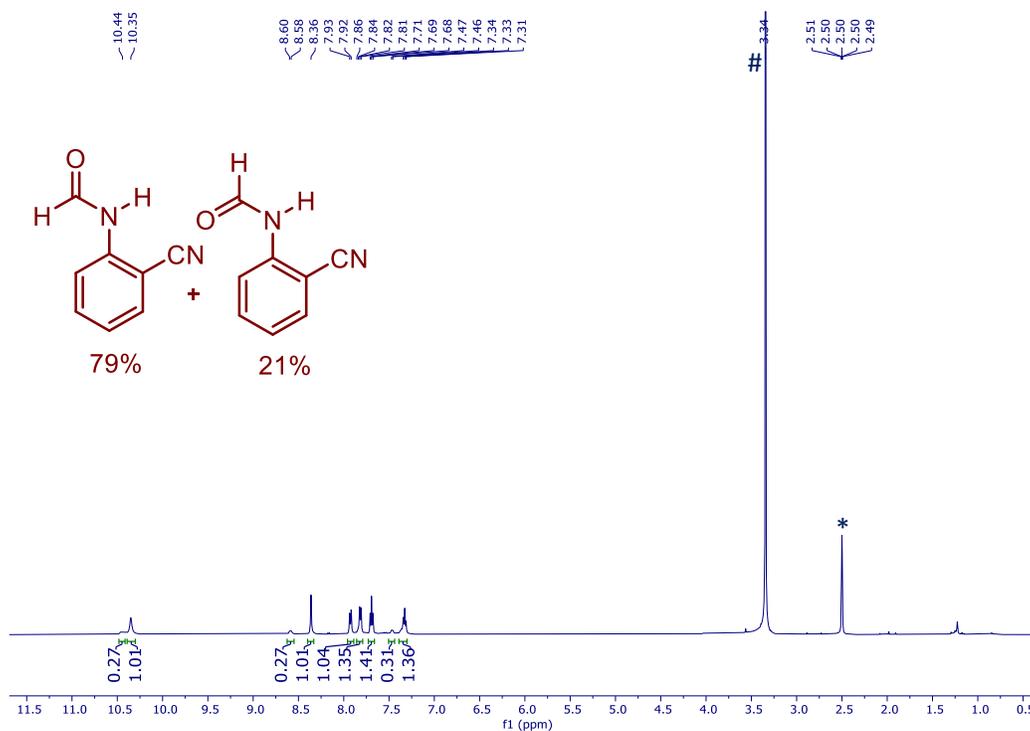
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-isopropylphenyl)formamide (compound-3h) in  $\text{CDCl}_3$  (\*)



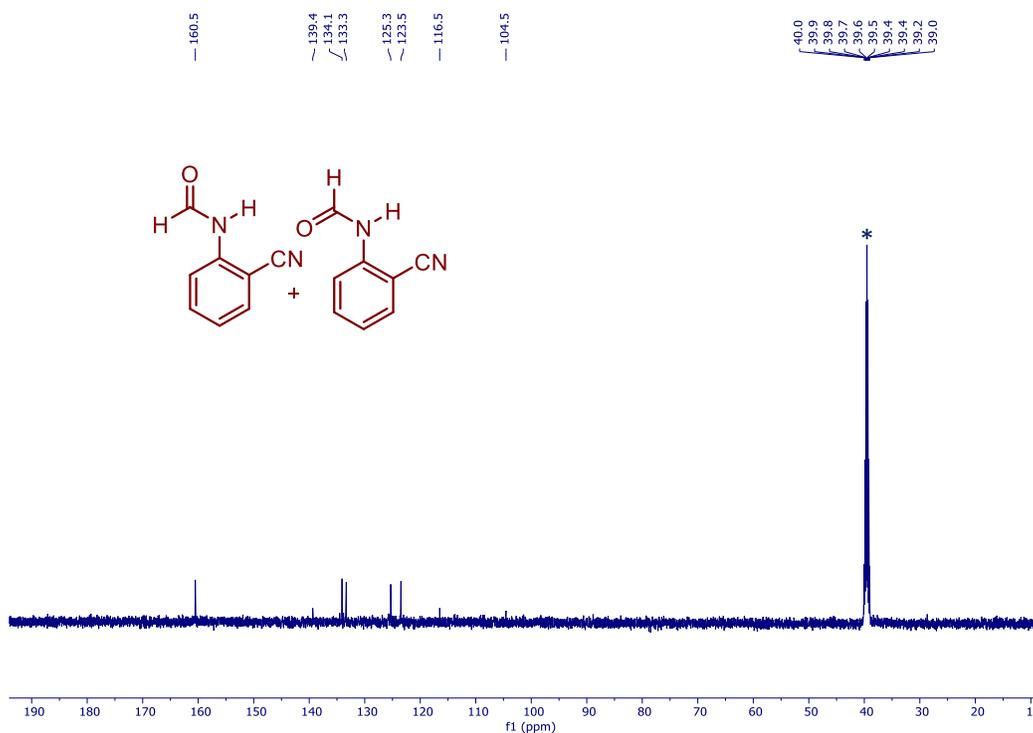
$^1\text{H}$  NMR of *N*-(naphthalen-1-yl)formamide (compound-3i) in  $\text{CDCl}_3$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{CDCl}_3$



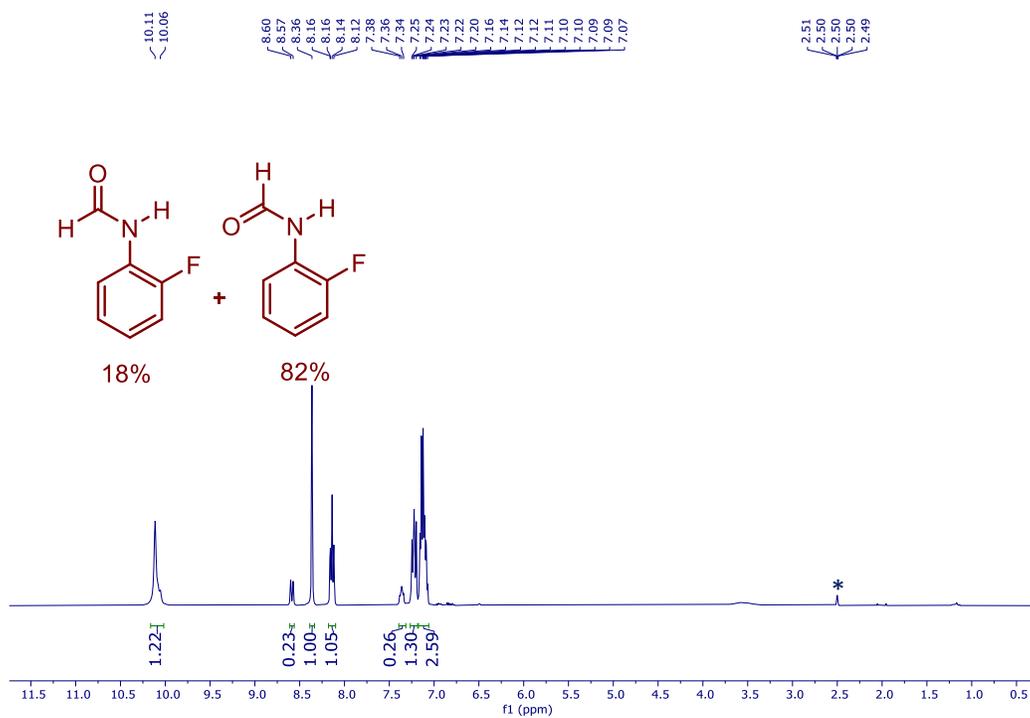
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(naphthalen-1-yl)formamide (compound-3i) in  $\text{CDCl}_3$  (\*)



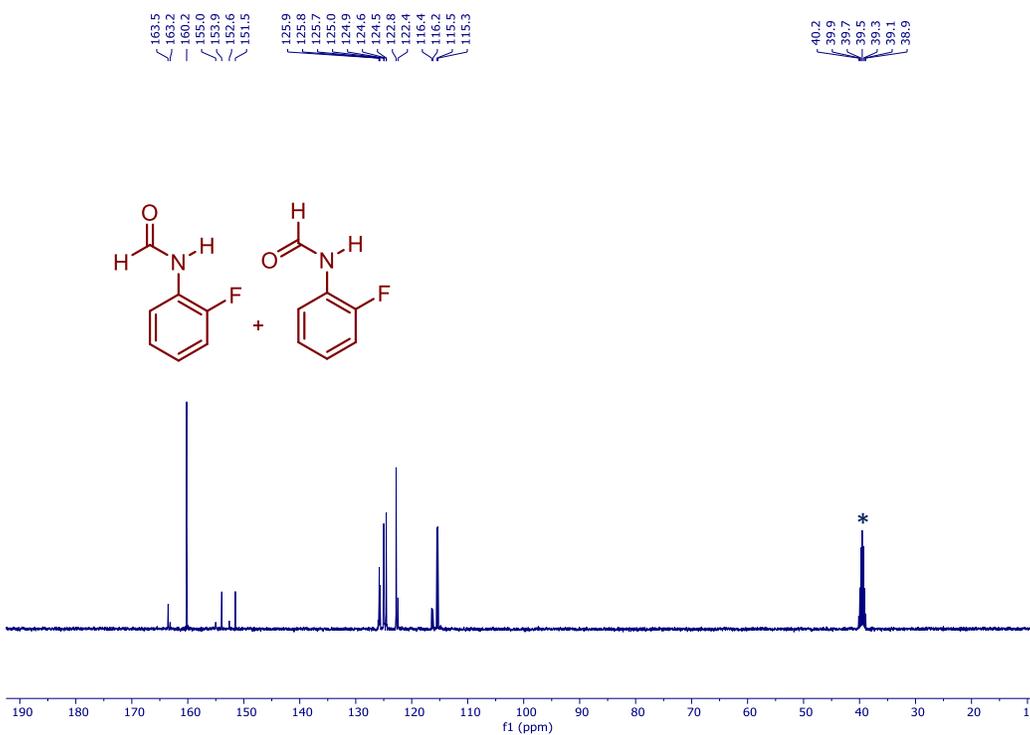
$^1\text{H}$  NMR of *N*-(2-cyanophenyl)formamide (compound-3j) in  $\text{DMSO-d}_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-d}_6$



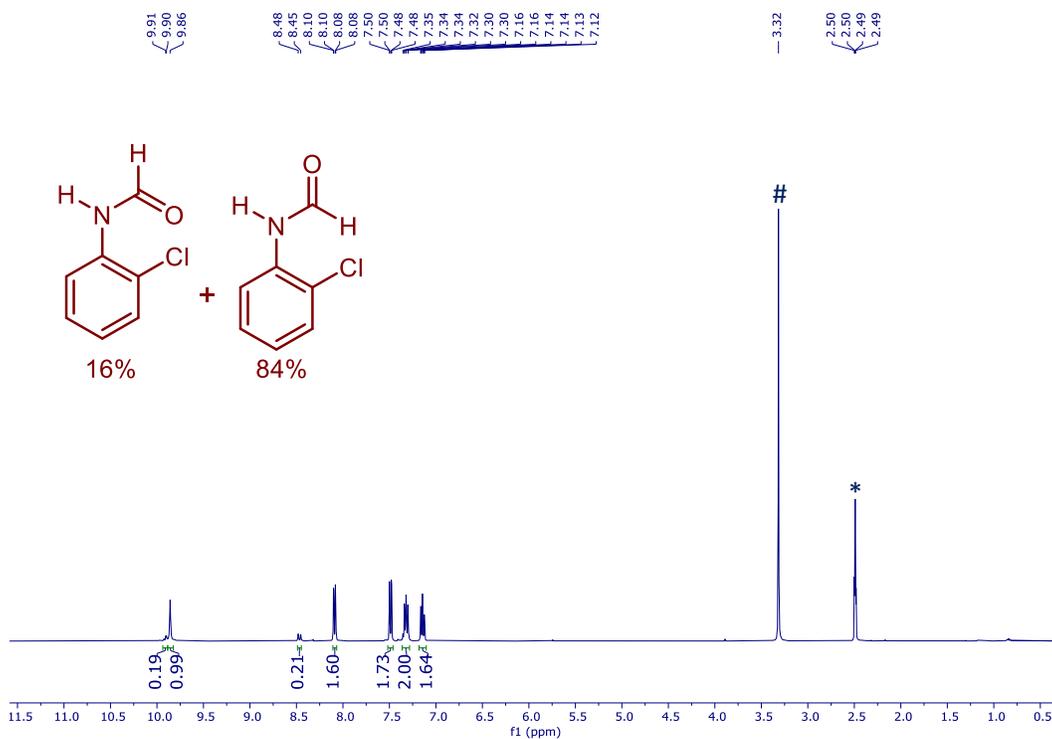
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(2-cyanophenyl)formamide (compound-3j) in  $\text{DMSO-d}_6$  (\*)



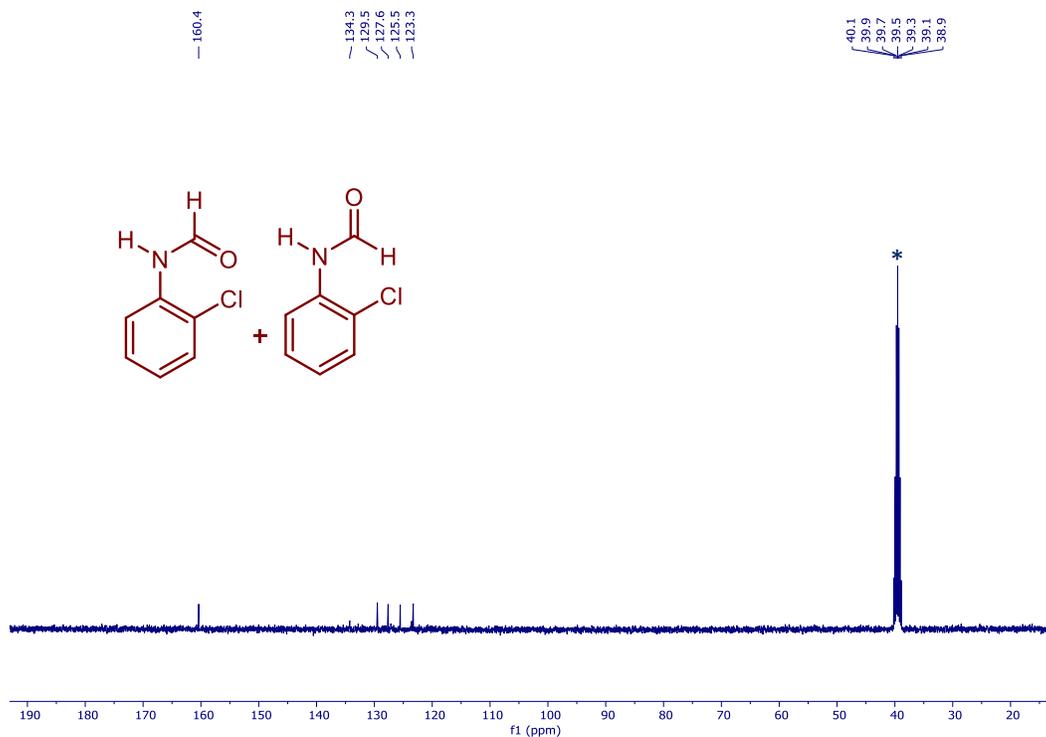
$^1\text{H}$  NMR of *N*-(2-fluorophenyl)formamide (compound-3k) in  $\text{DMSO-d}_6$  (\*)



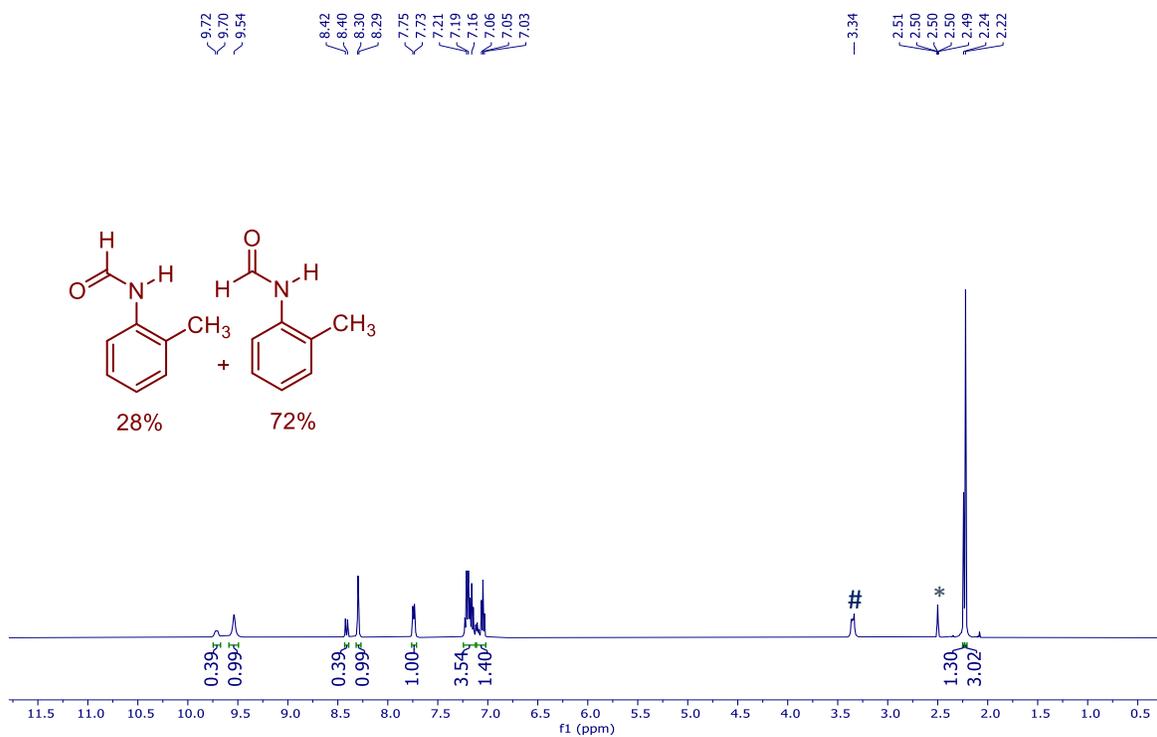
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(2-fluorophenyl)formamide (compound-3k) in  $\text{DMSO-d}_6$  (\*)



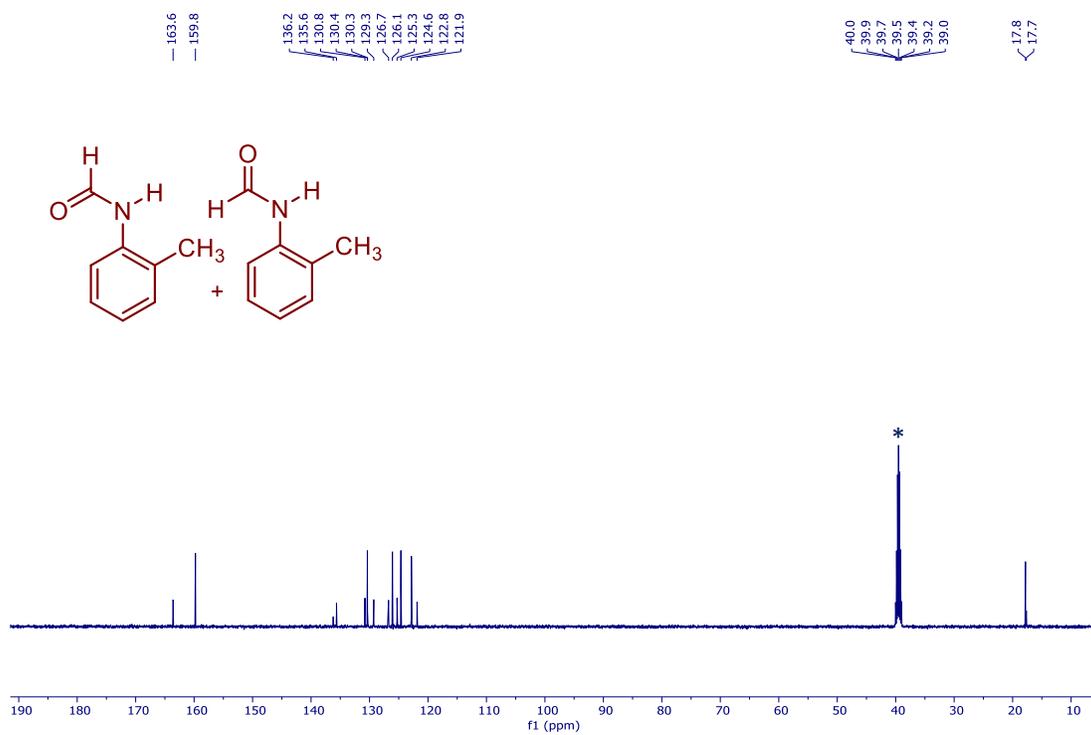
$^1\text{H}$  NMR of *N*-(2-chlorophenyl)formamide (compound-3I) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



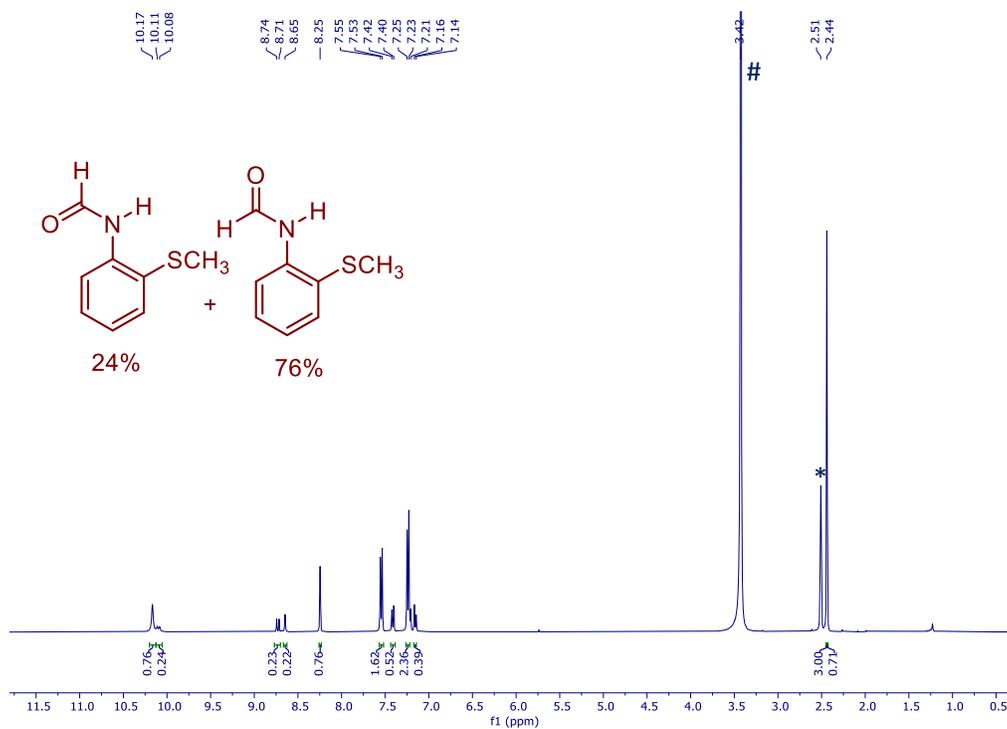
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(2-chlorophenyl)formamide (compound-3I) in  $\text{DMSO-}d_6$  (\*)



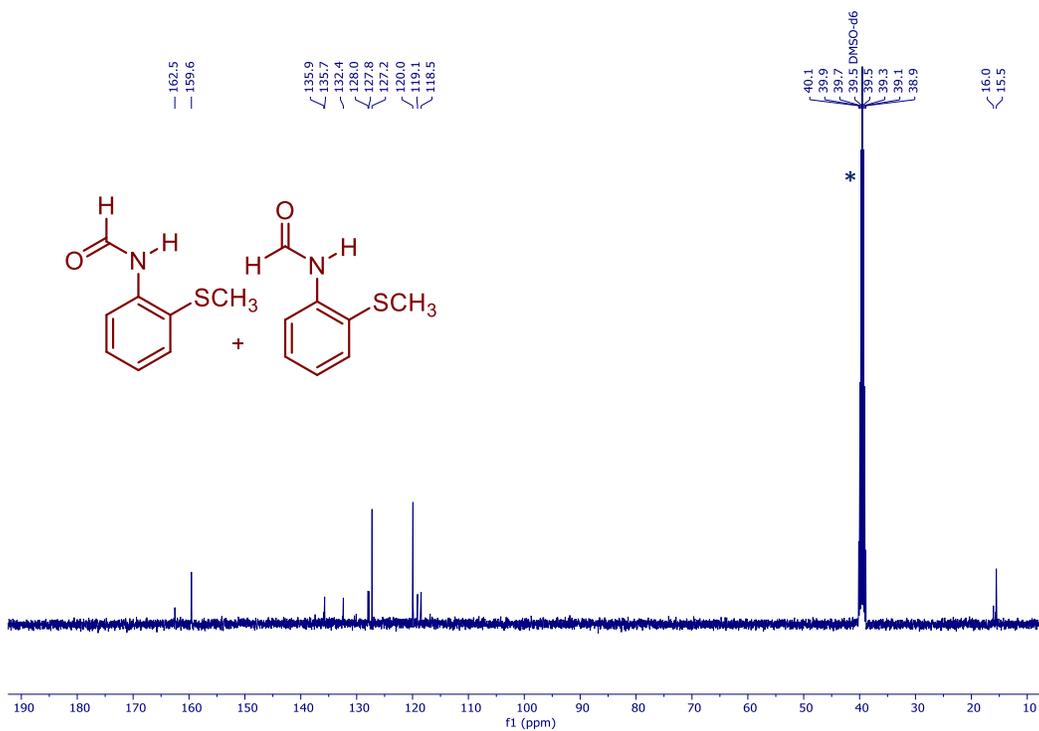
$^1\text{H}$  NMR of *N*-*o*-tolylformamide (compound-3m) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



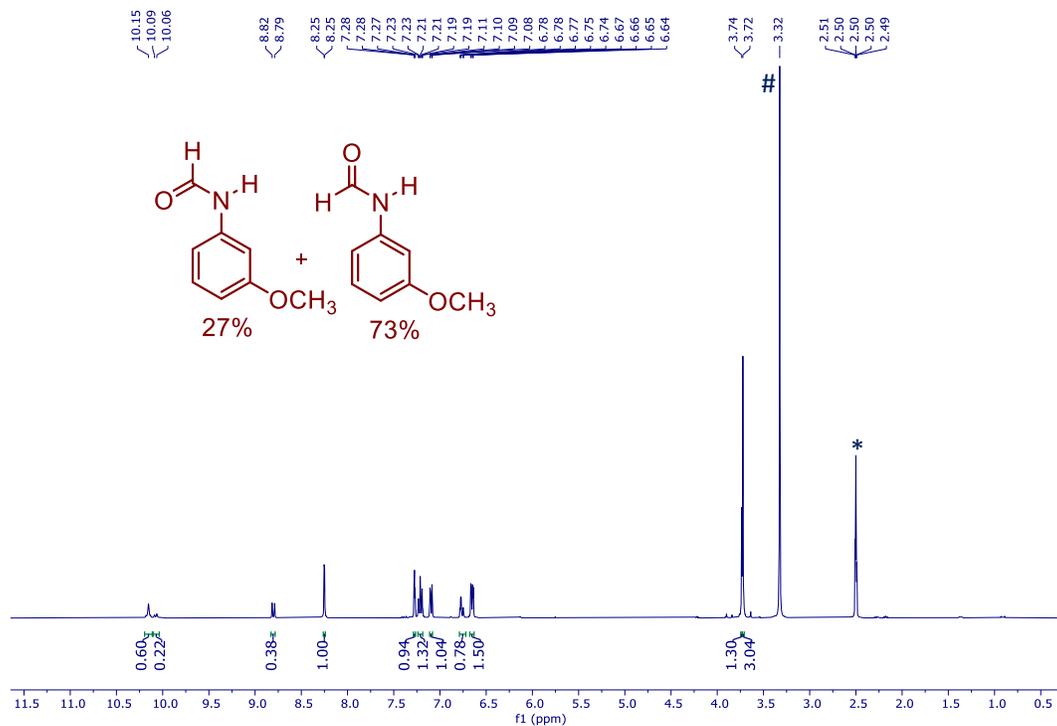
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-*o*-tolylformamide (compound-3m) in  $\text{DMSO-}d_6$  (\*)



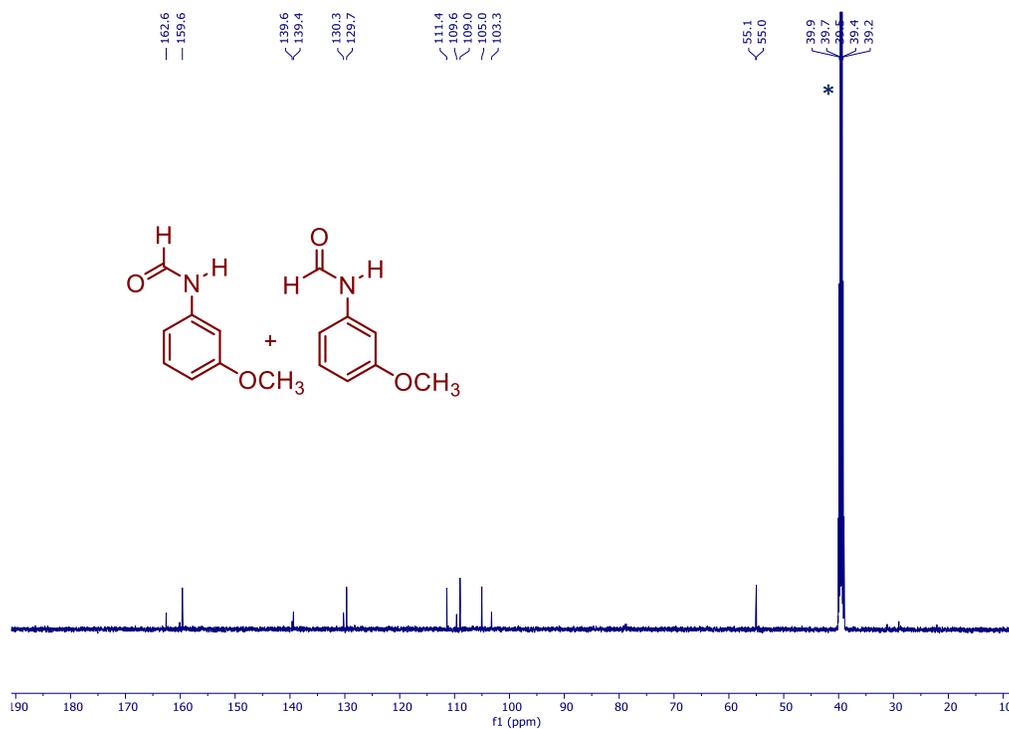
<sup>1</sup>H NMR of *N*-(2-(methylthio)phenyl)formamide (compound-3n) in DMSO-d<sub>6</sub> (\*). # indicates the solvent impurity of H<sub>2</sub>O in DMSO-d<sub>6</sub>



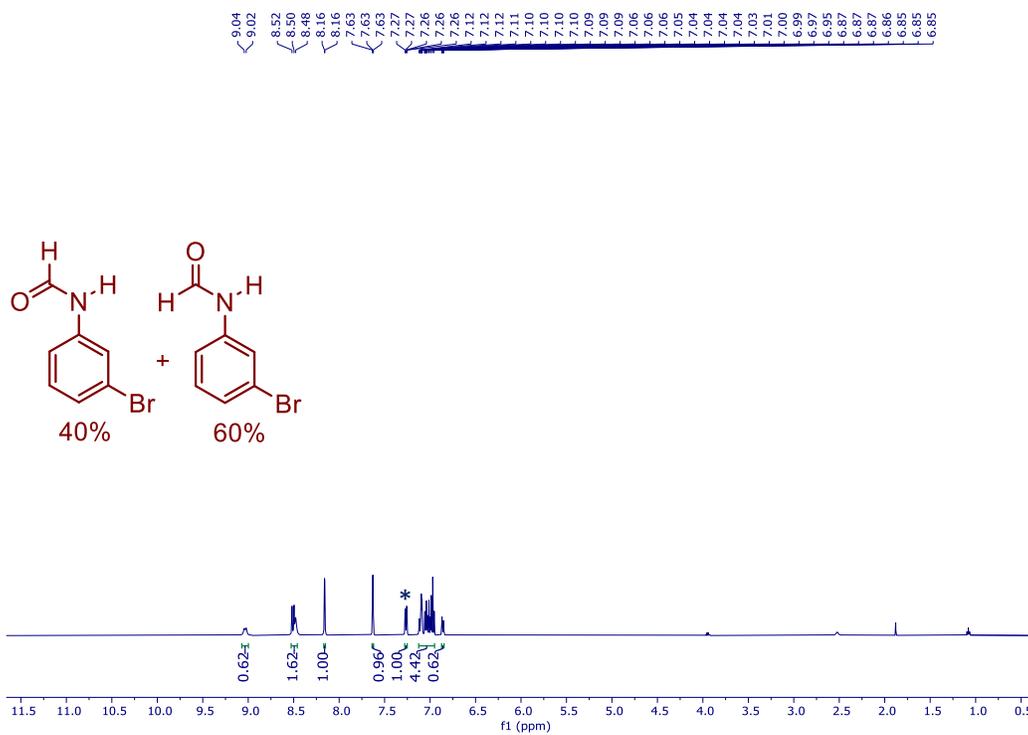
<sup>13</sup>C{<sup>1</sup>H} NMR of *N*-(2-(methylthio)phenyl)formamide (compound-3n) in DMSO-d<sub>6</sub> (\*)



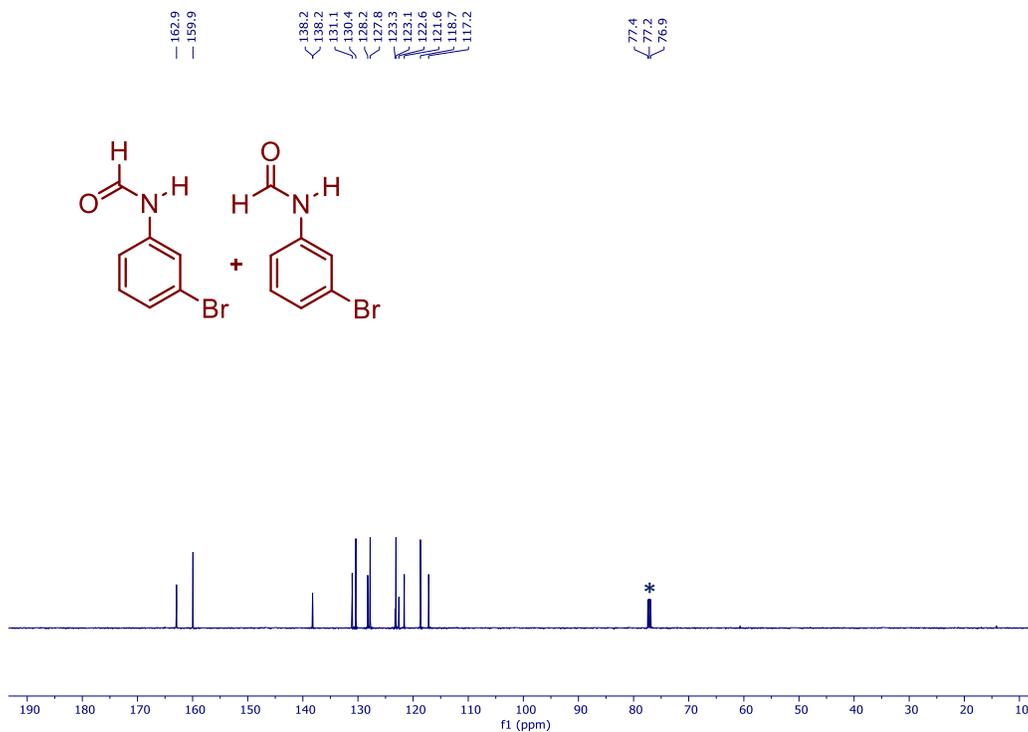
$^1\text{H}$  NMR of *N*-(3-methoxyphenyl)formamide (compound-3o) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



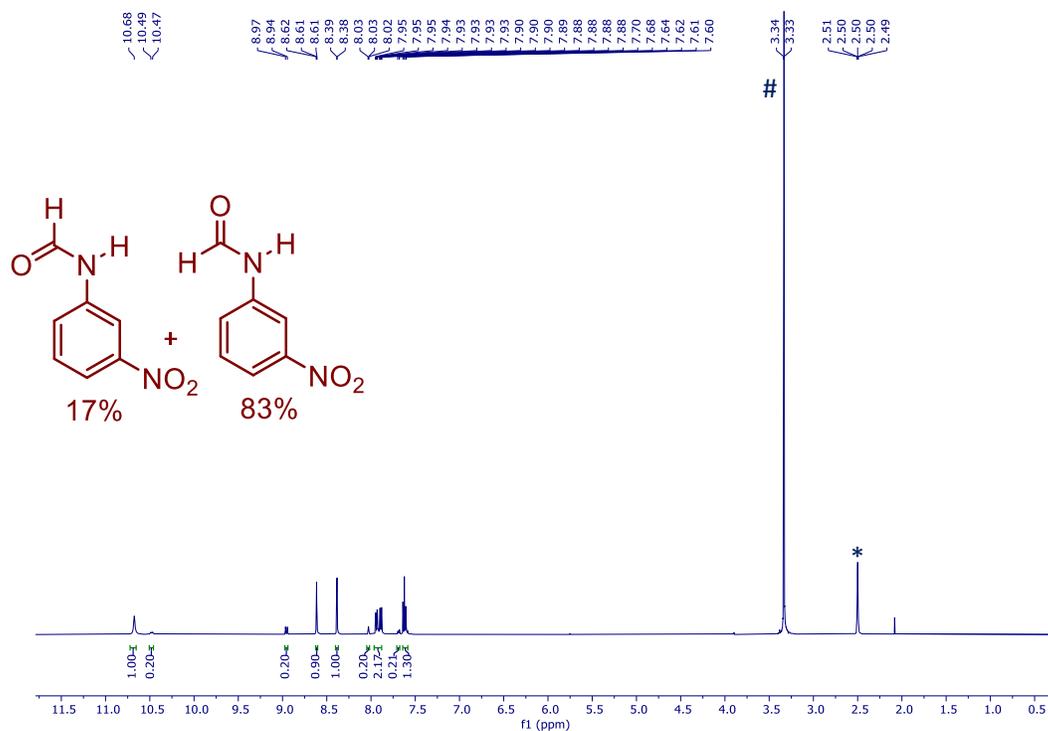
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(3-methoxyphenyl)formamide (compound-3o) in  $\text{DMSO-}d_6$  (\*)



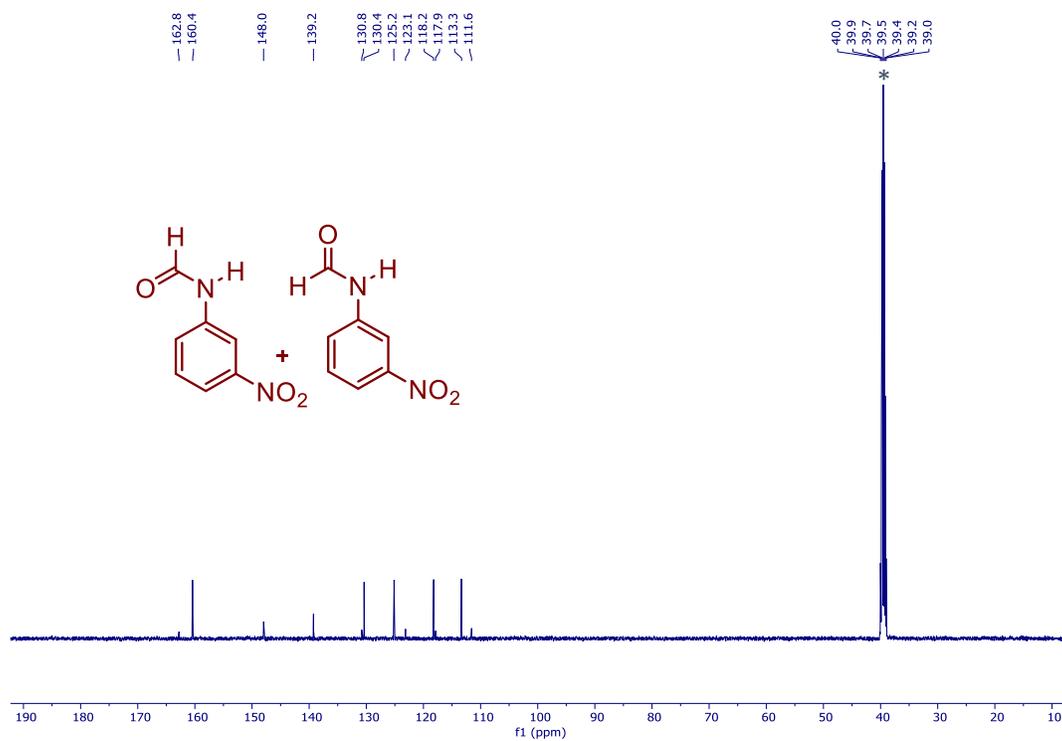
<sup>1</sup>H NMR of *N*-(3-bromophenyl)formamide (compound-3p) in CDCl<sub>3</sub> (\*)



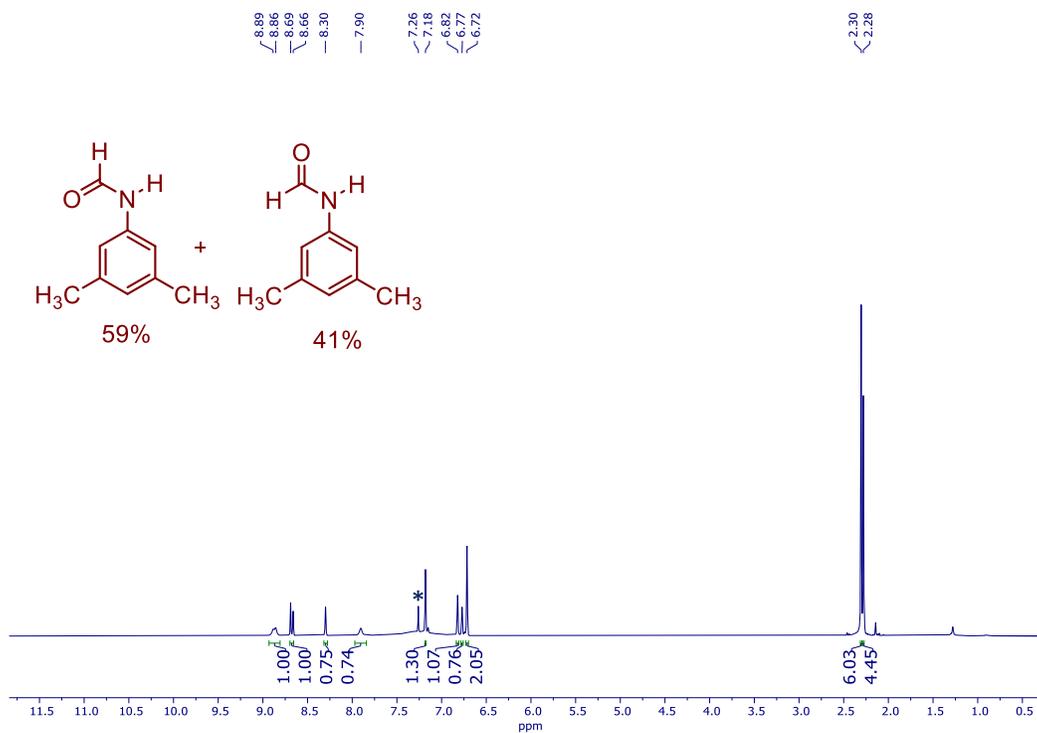
<sup>13</sup>C{<sup>1</sup>H} NMR of *N*-(3-bromophenyl)formamide (compound-3p) in CDCl<sub>3</sub> (\*)



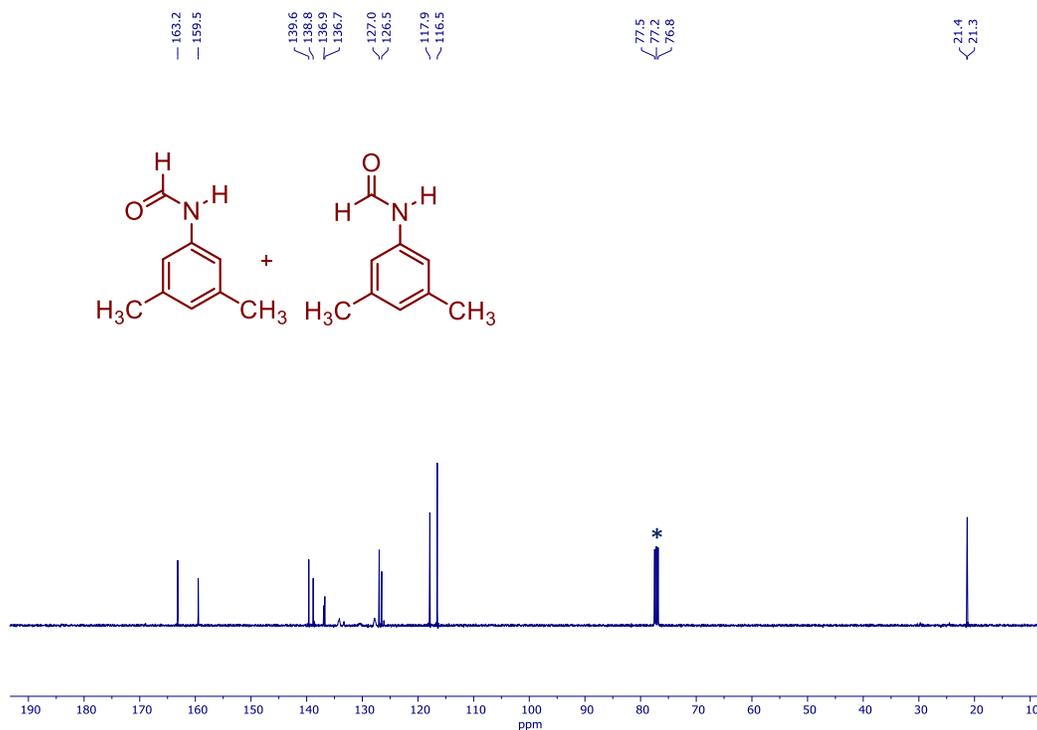
$^1\text{H}$  NMR of *N*-(3-nitrophenyl)formamide (compound-**3q**) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



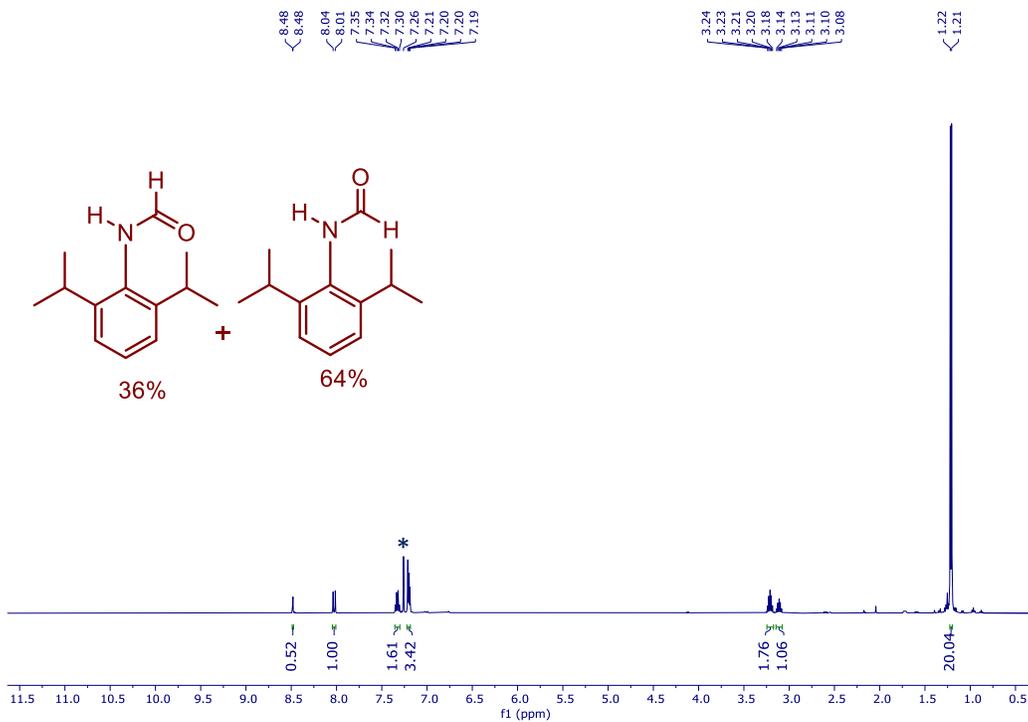
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(3-nitrophenyl)formamide (compound-**3q**) in  $\text{DMSO-}d_6$  (\*)



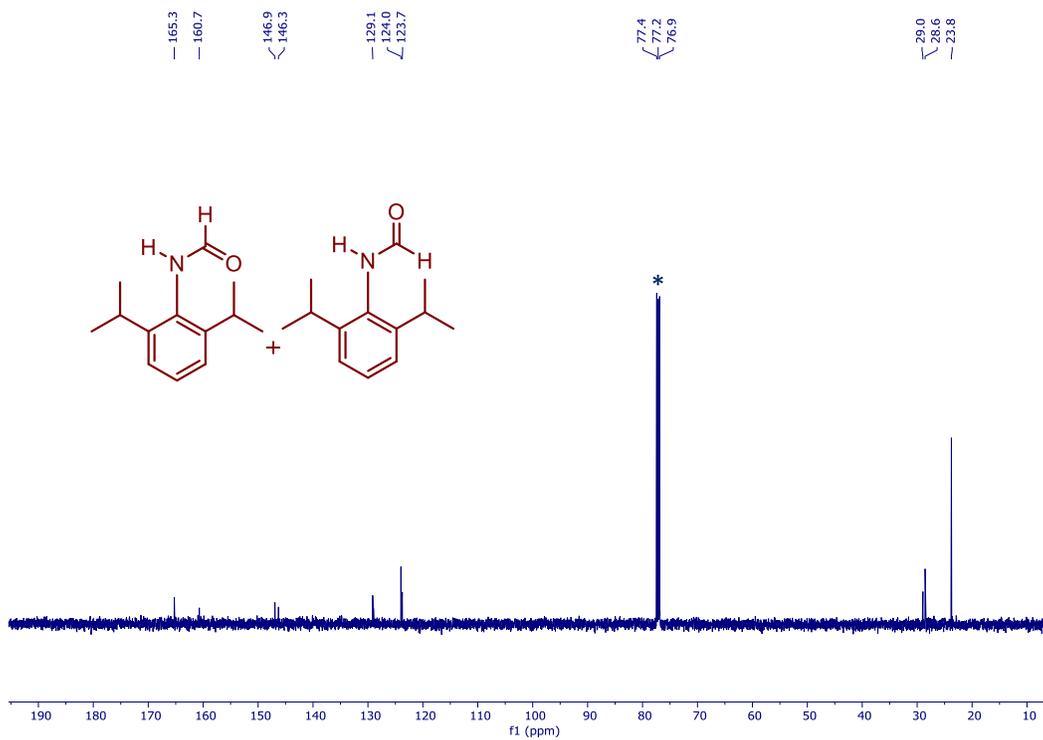
$^1\text{H}$  NMR of *N*-(3,5-dimethylphenyl)formamide (compound-**3r**) in  $\text{CDCl}_3$  (\*)



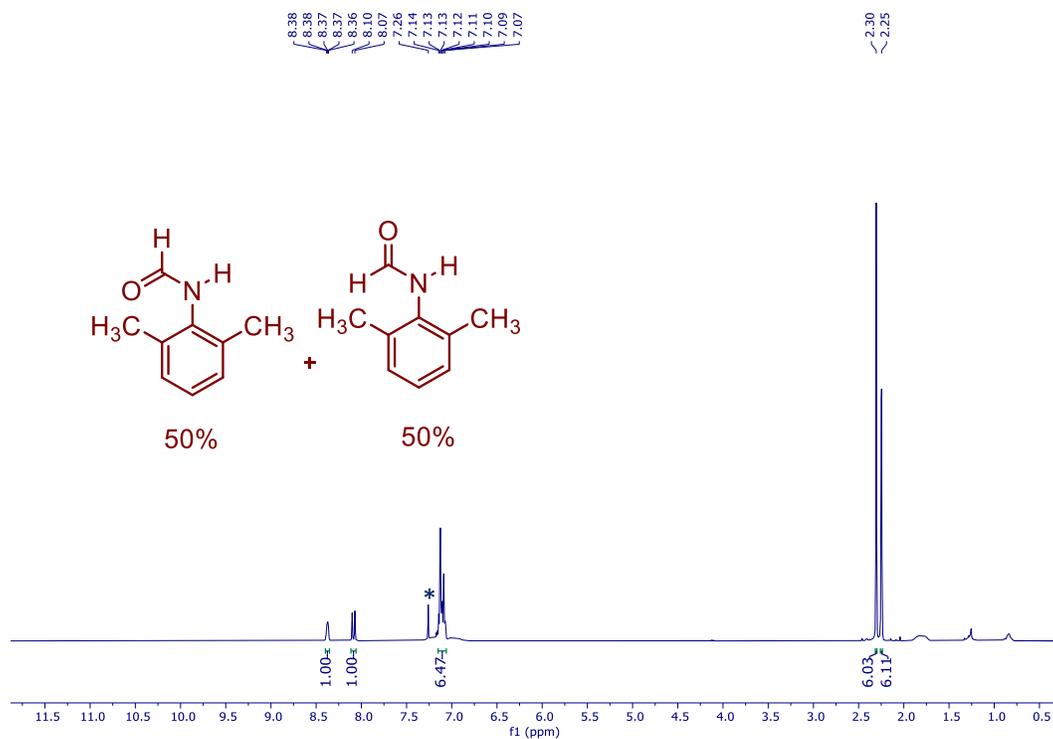
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(3,5-dimethylphenyl)formamide (compound-**3r**) in  $\text{CDCl}_3$  (\*)



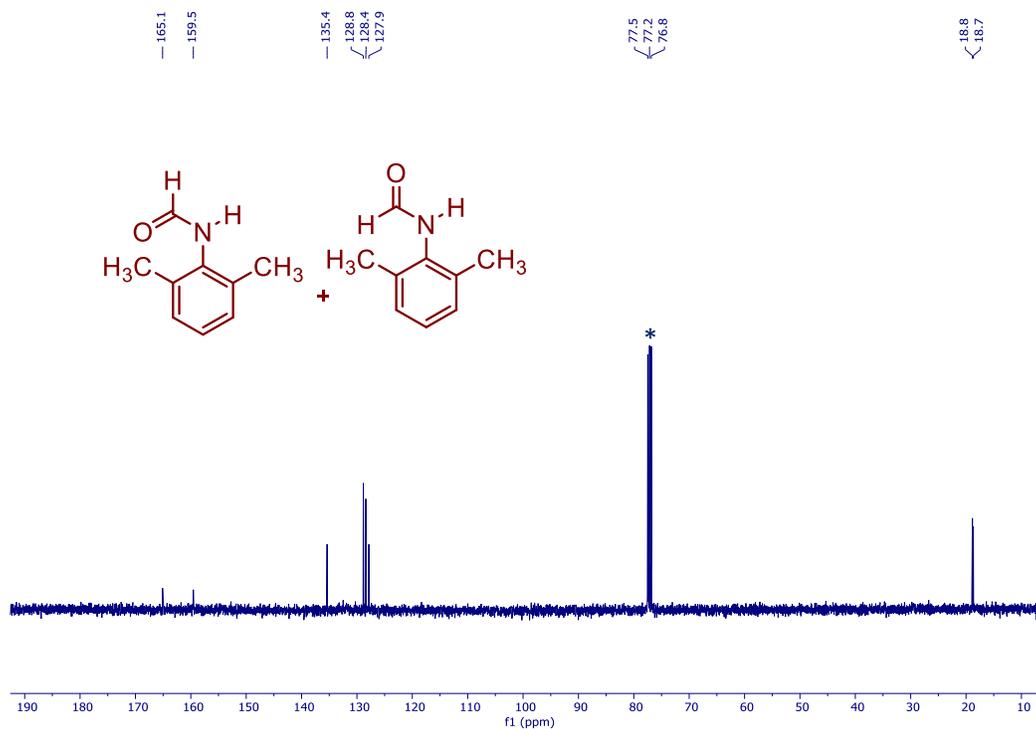
$^1\text{H}$  NMR of *N*-(2,6-diisopropylphenyl)formamide (compound-3s) in  $\text{CDCl}_3$  (\*)



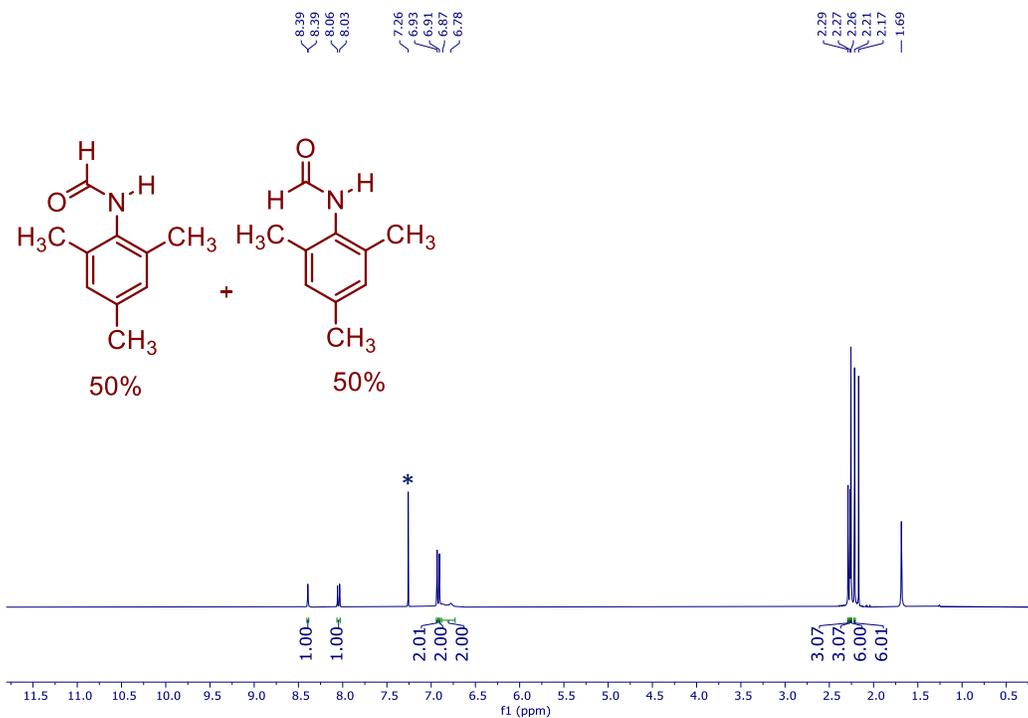
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(2,6-diisopropylphenyl)formamide (compound-3s) in  $\text{CDCl}_3$  (\*)



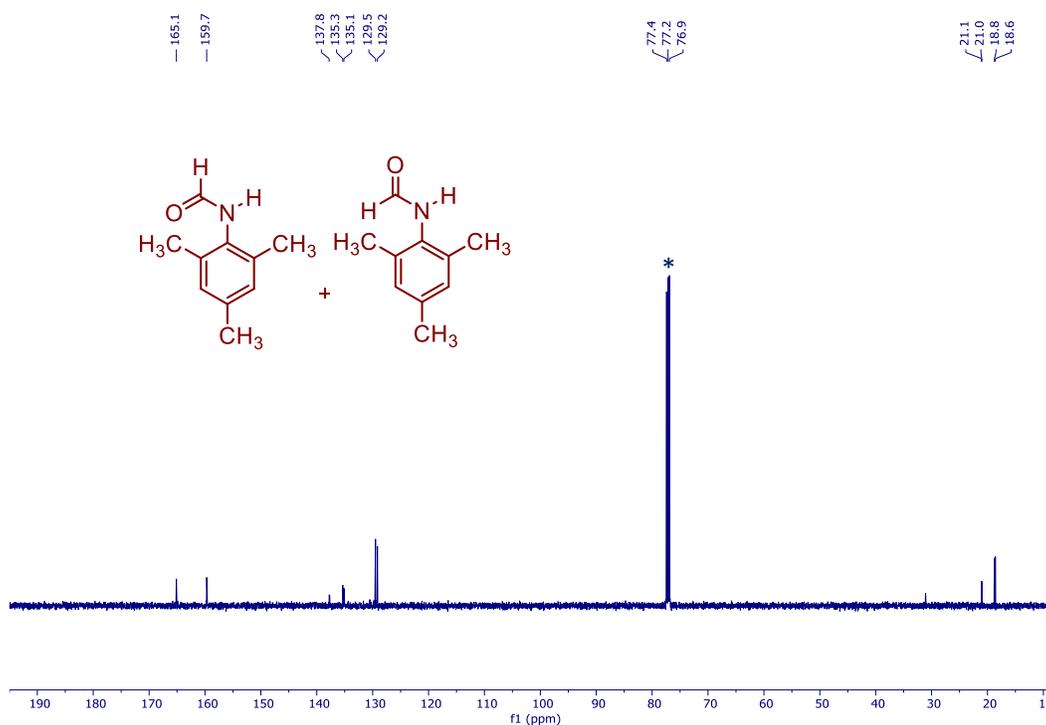
$^1\text{H}$  NMR of *N*-(2,6-dimethylphenyl)formamide (compound-3t) in  $\text{CDCl}_3$  (\*)



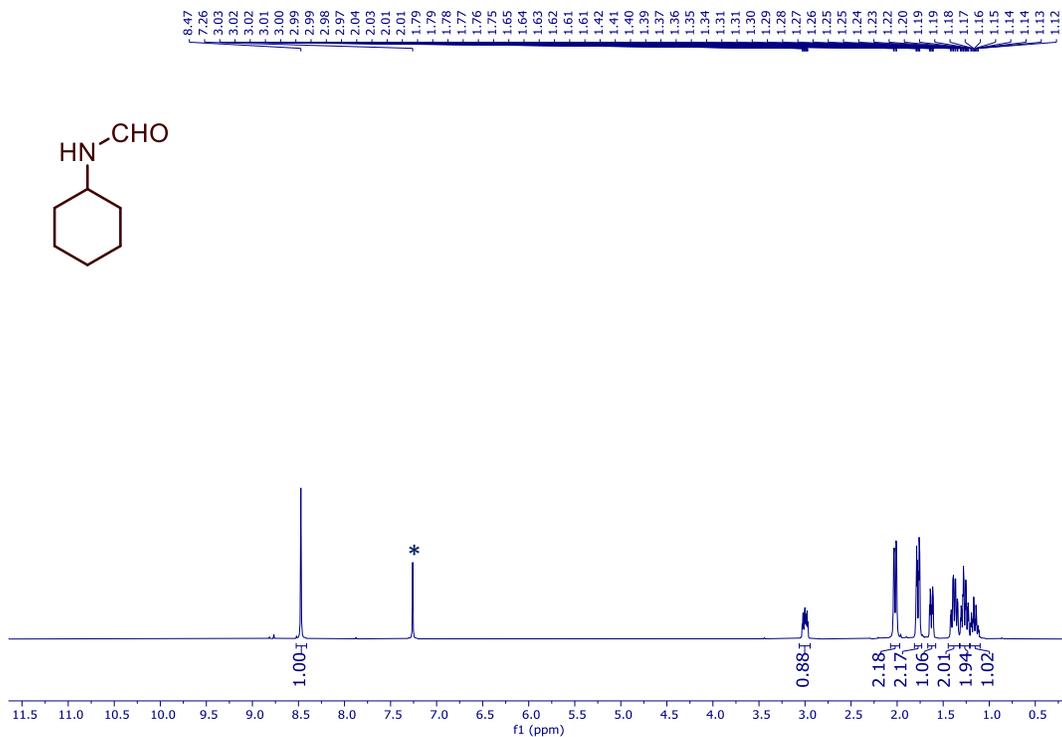
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(2,6-dimethylphenyl)formamide (compound-3t) in  $\text{CDCl}_3$  (\*)



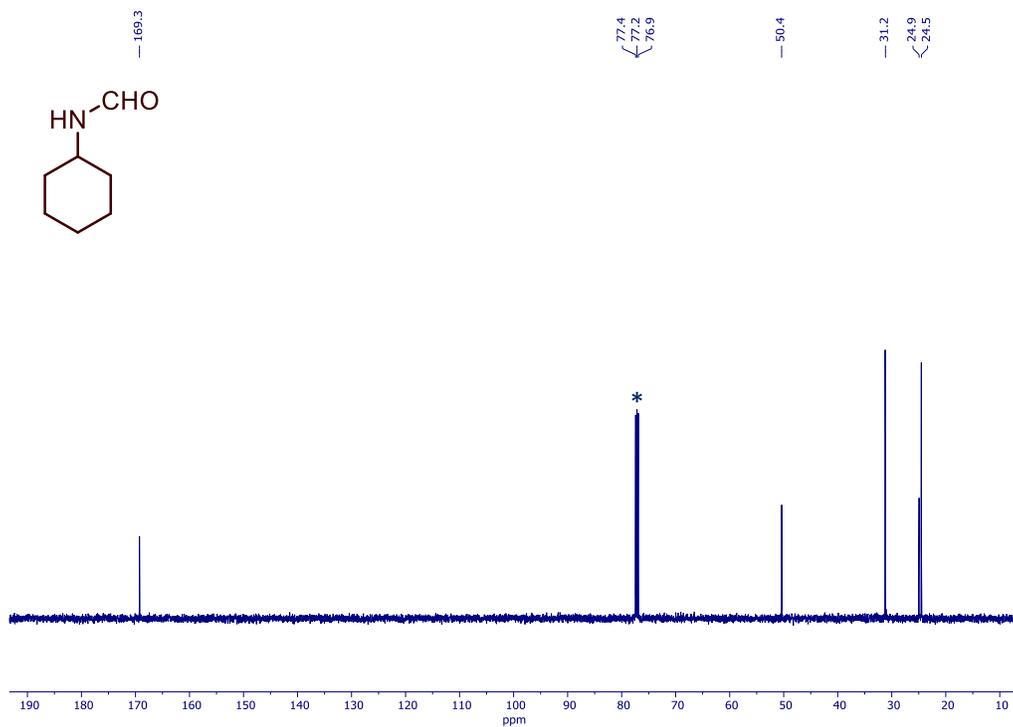
$^1\text{H}$  NMR of *N*-mesitylformamide (compound-**3u**) in  $\text{CDCl}_3$  (\*)



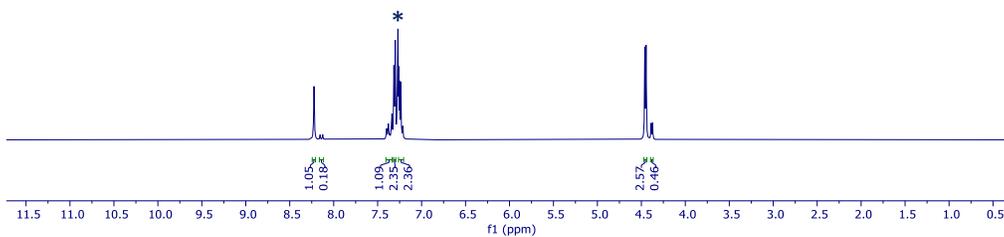
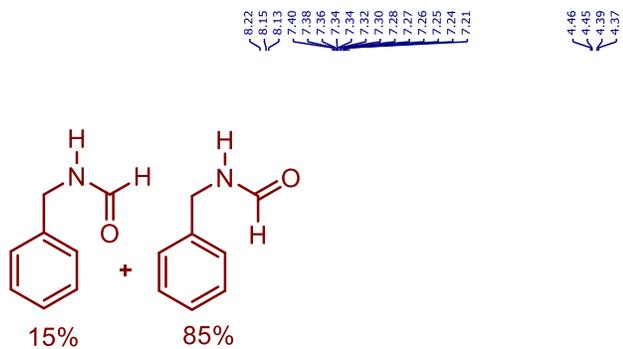
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-mesitylformamide (compound-**3u**) in  $\text{CDCl}_3$  (\*)



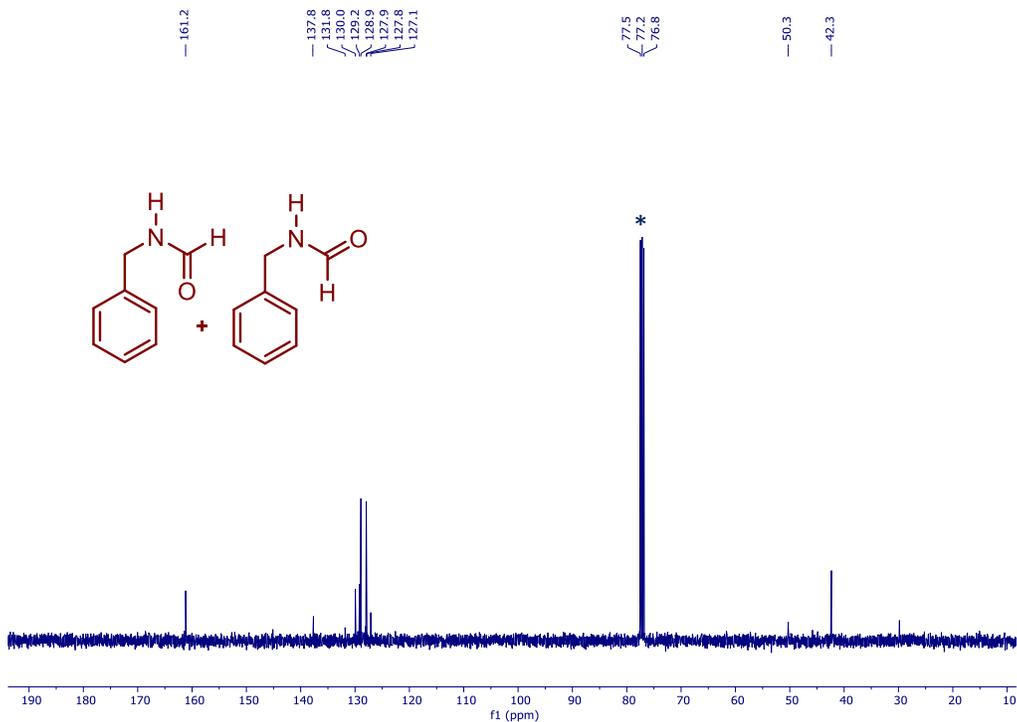
$^1\text{H}$  NMR of *N*-cyclohexylformamide (compound-3v) in  $\text{CDCl}_3$  (\*)



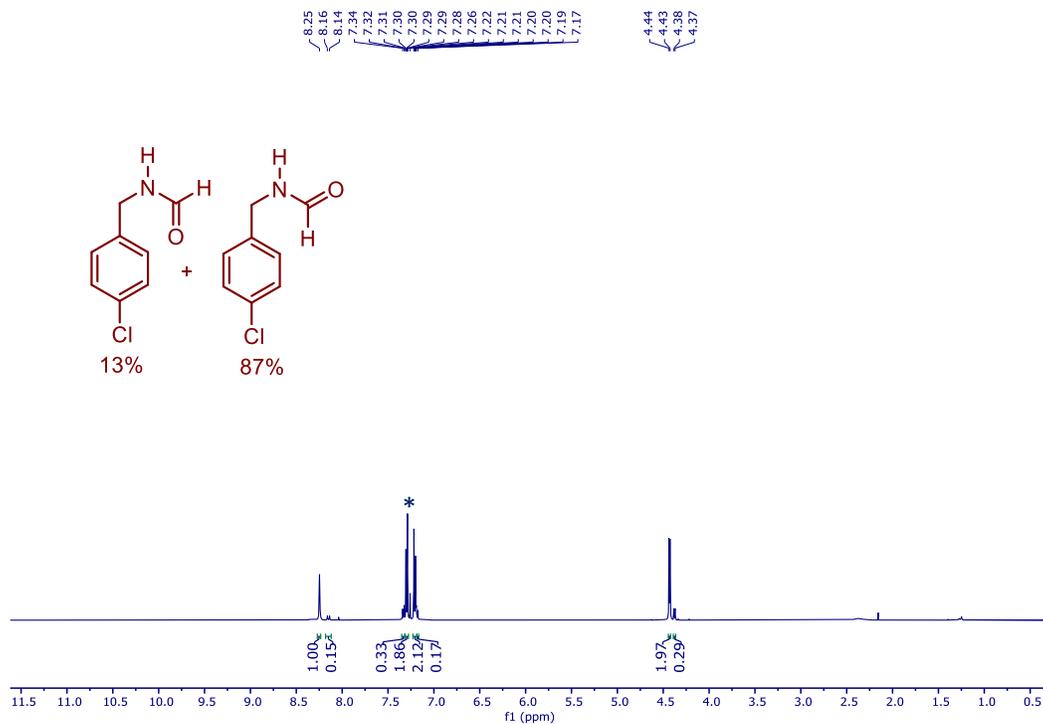
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-cyclohexylformamide (compound-3v) in  $\text{CDCl}_3$  (\*)



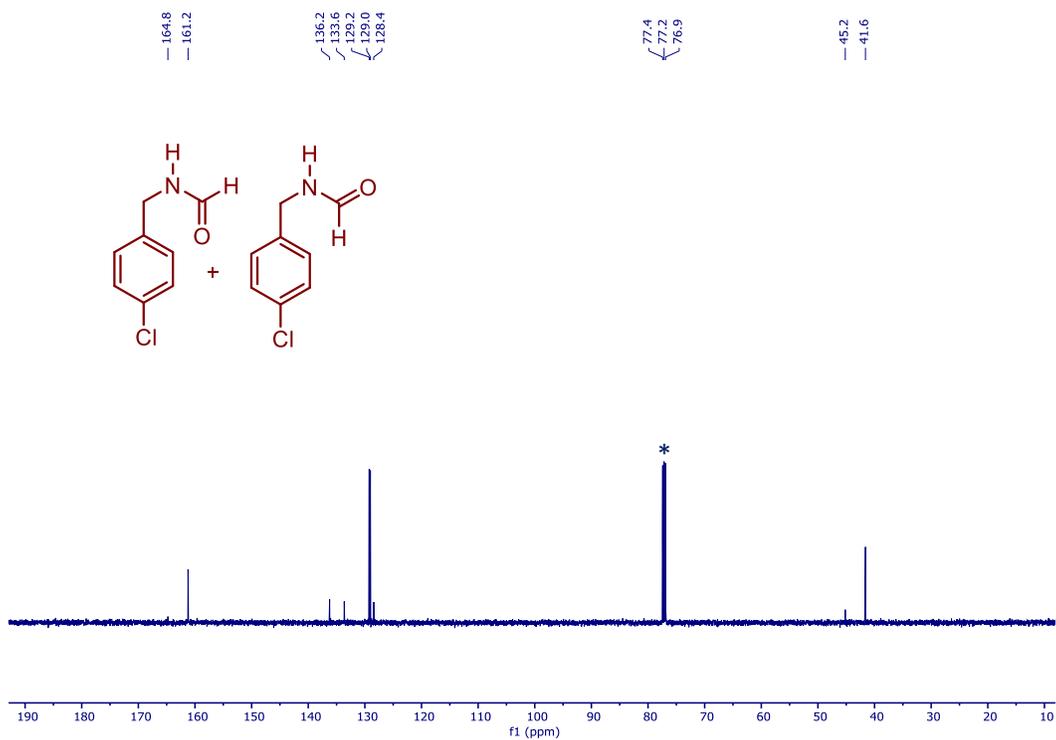
$^1\text{H}$  NMR of *N*-benzylformamide (compound-**3w**) in  $\text{CDCl}_3$  (\*)



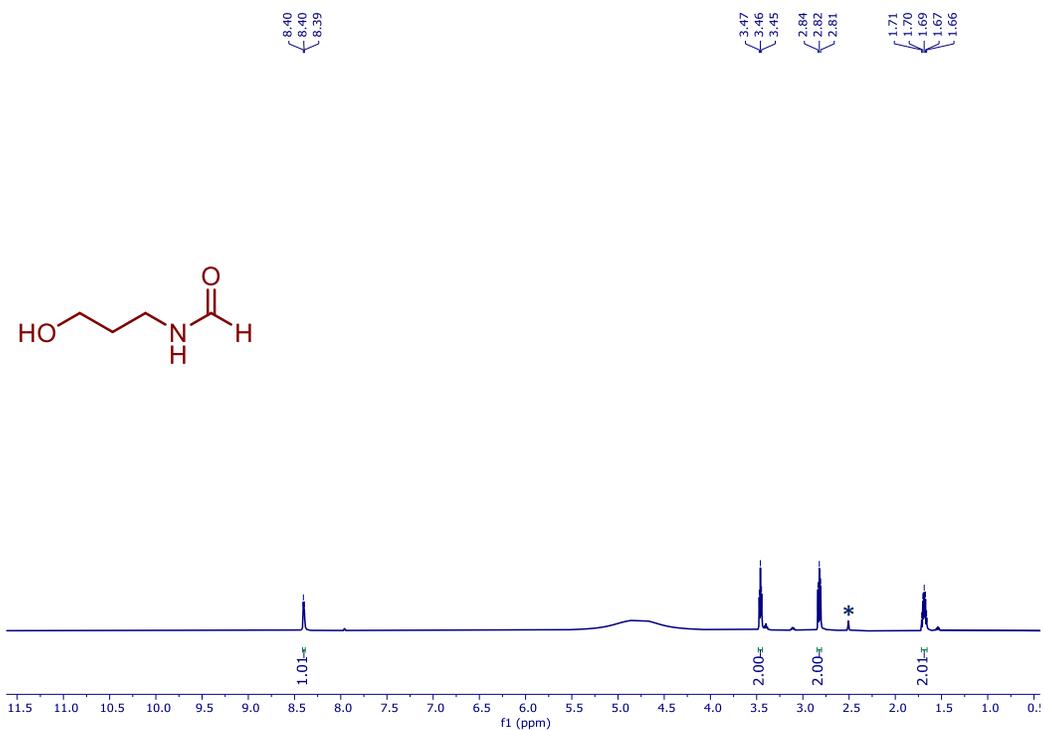
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-benzylformamide (compound-**3w**) in  $\text{CDCl}_3$  (\*)



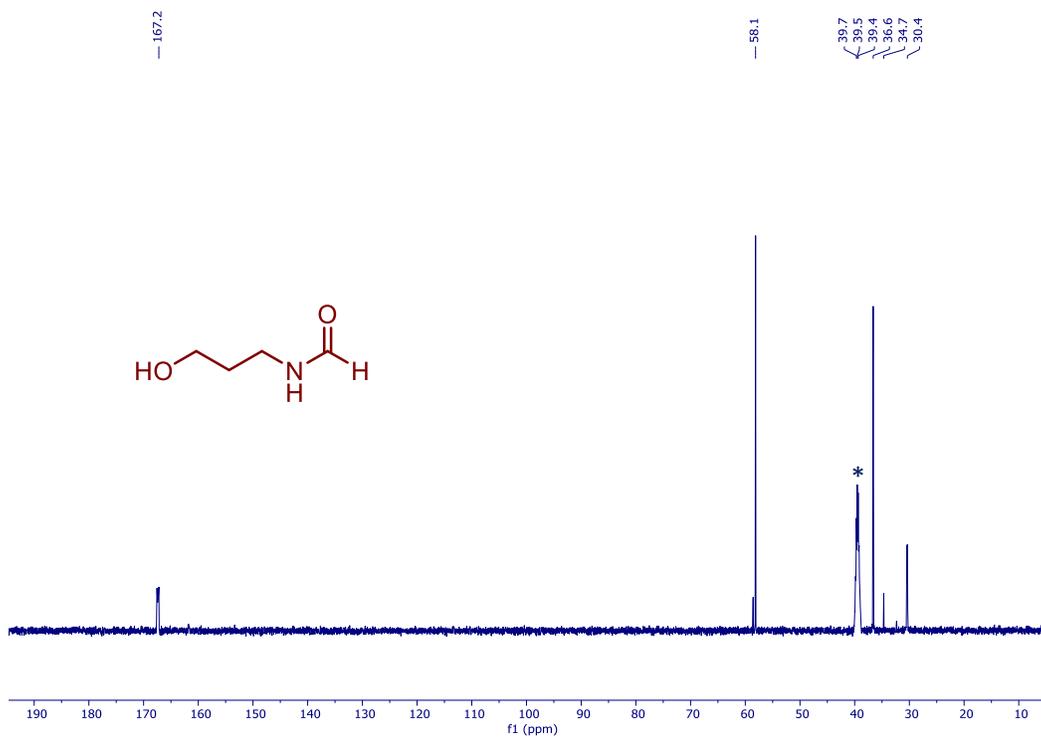
$^1\text{H}$  NMR of *N*-(4-chlorobenzyl)formamide (compound-3x) in  $\text{CDCl}_3$  (\*)



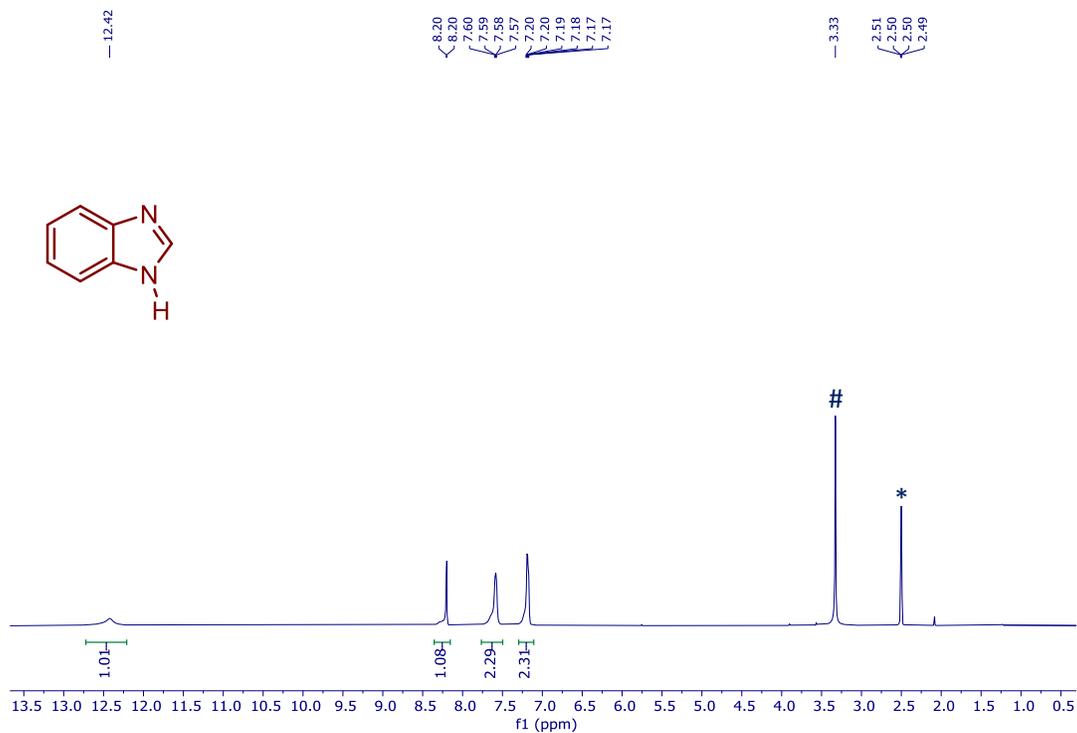
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-chlorobenzyl)formamide (compound-3x) in  $\text{CDCl}_3$  (\*)



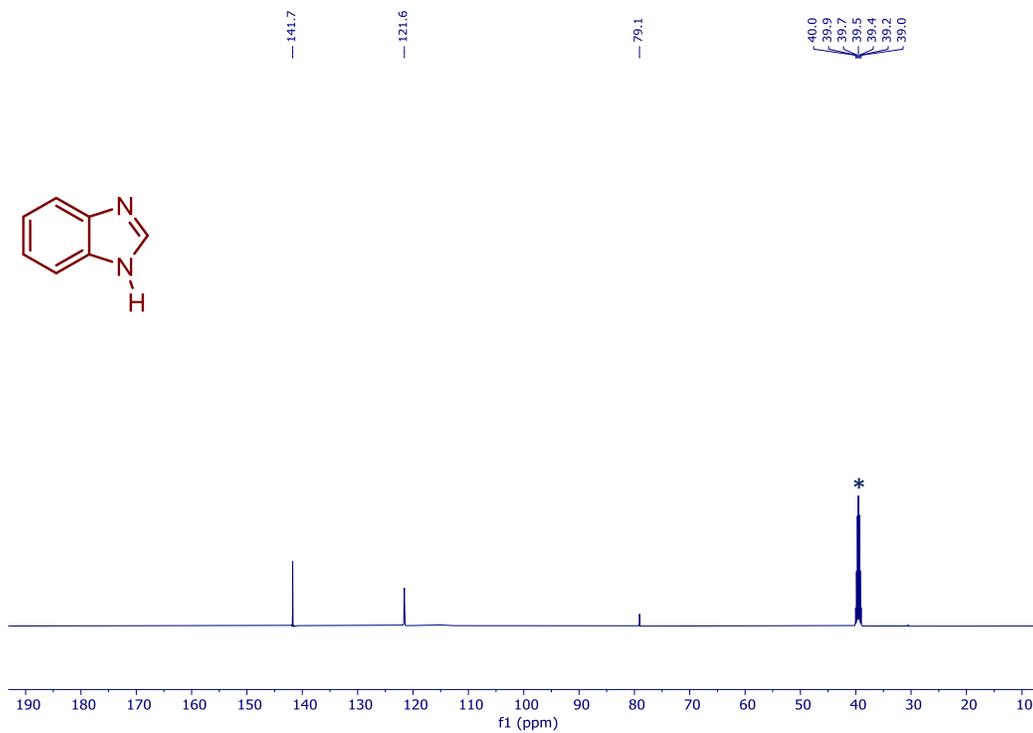
$^1\text{H}$  NMR spectrum of *N*-(3-hydroxypropyl)formamide (compound-3y) in  $\text{DMSO-}d_6$  (\*)



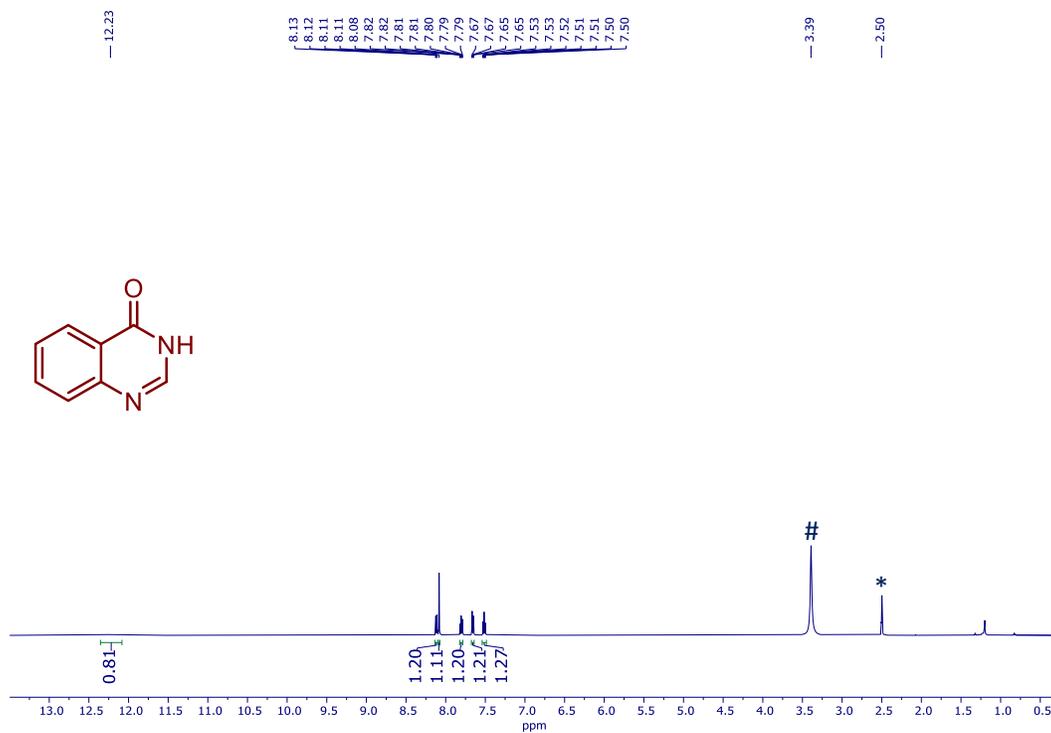
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of *N*-(3-hydroxypropyl)formamide (compound-3y) in  $\text{DMSO-}d_6$  (\*)



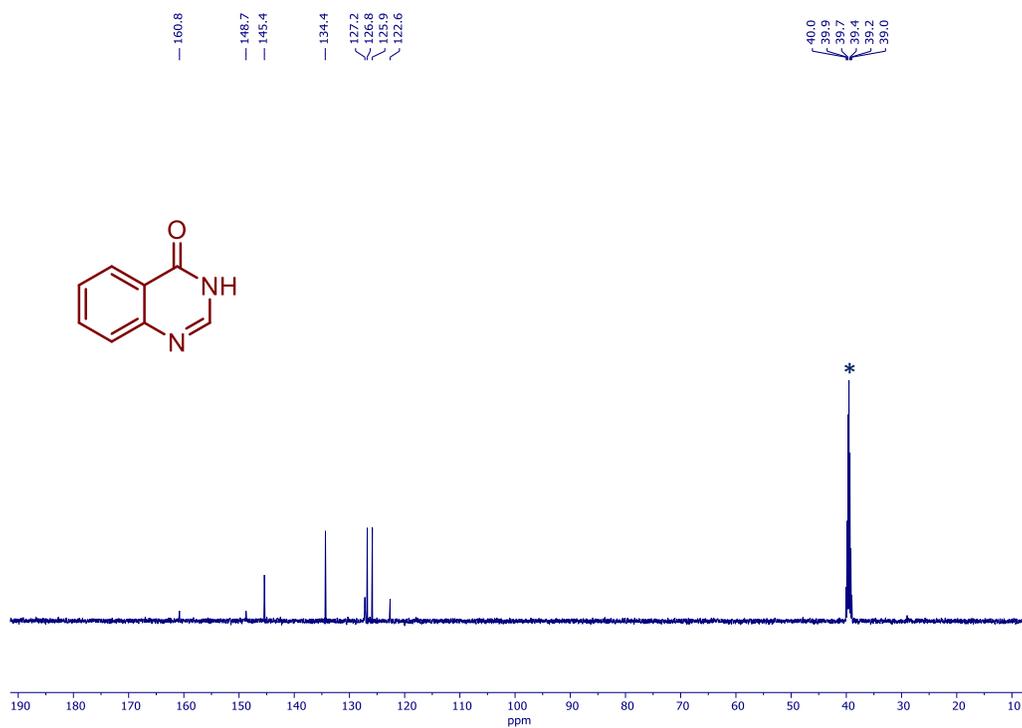
$^1\text{H}$  NMR of spectrum of 1H-benzo[d]imidazole (compound-3z) in DMSO- $d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in DMSO- $d_6$



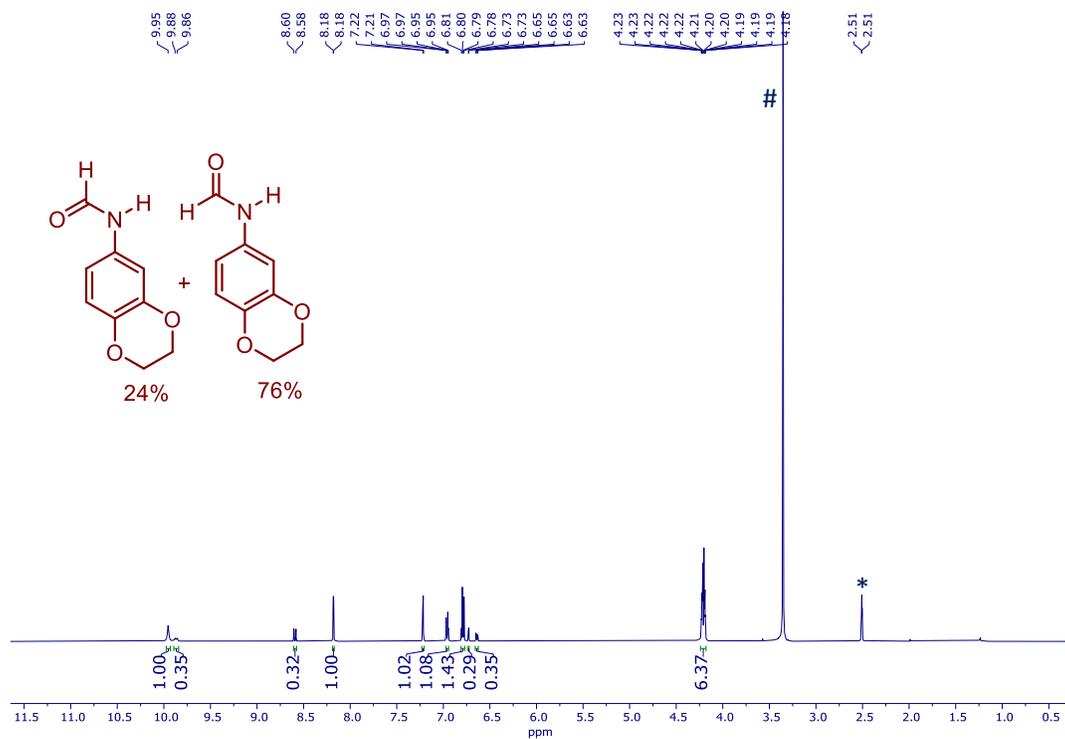
$^{13}\text{C}\{^1\text{H}\}$  NMR of spectrum of 1H-benzo[d]imidazole (compound-3z) in DMSO- $d_6$  (\*)



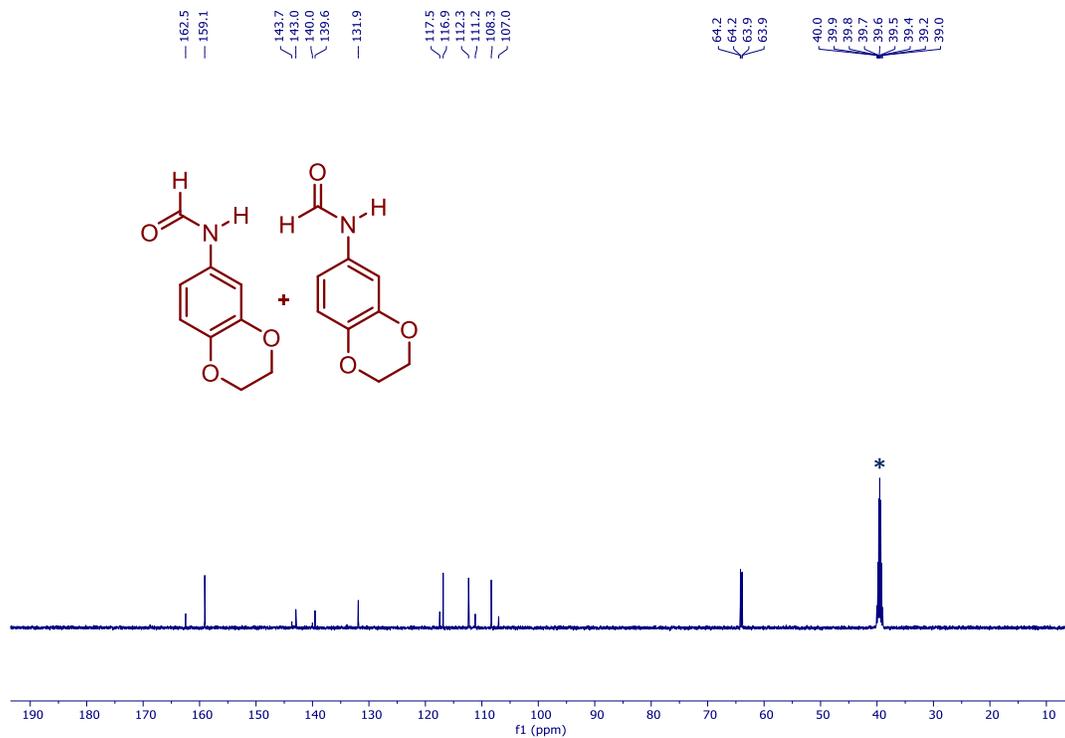
$^1\text{H}$  NMR of quinazolin-4(1H)-one (compound-3a') in DMSO- $d_6$  (\*). # indicates the solvent impurity of H<sub>2</sub>O in DMSO- $d_6$



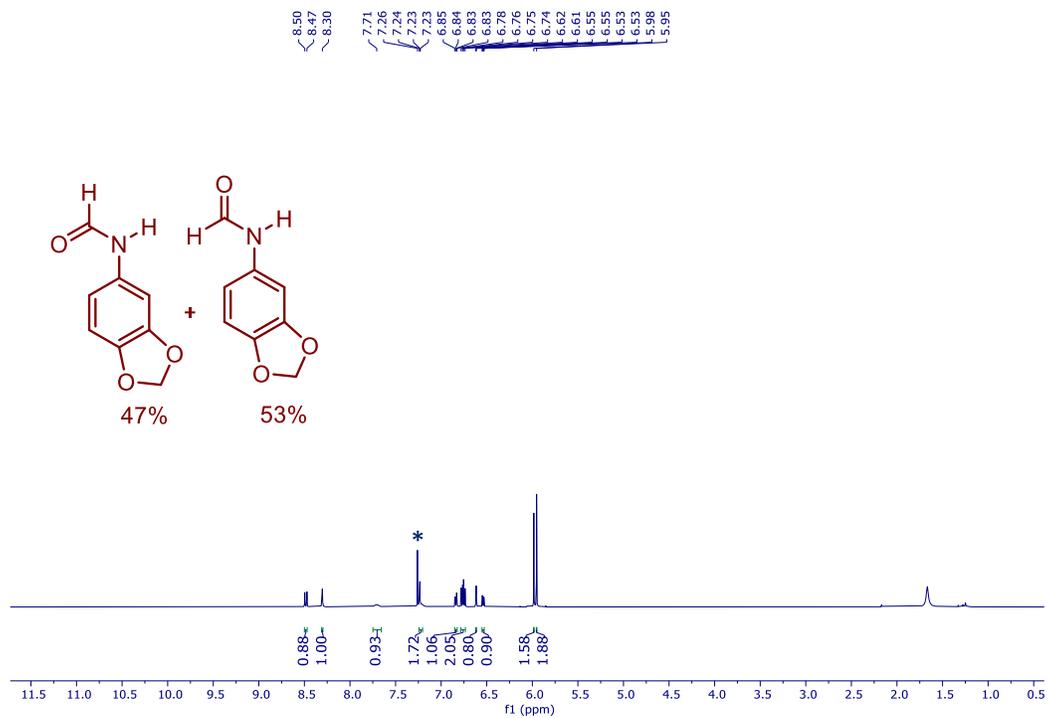
$^{13}\text{C}\{^1\text{H}\}$  NMR of quinazolin-4(1H)-one (compound-3a') in DMSO- $d_6$  (\*)



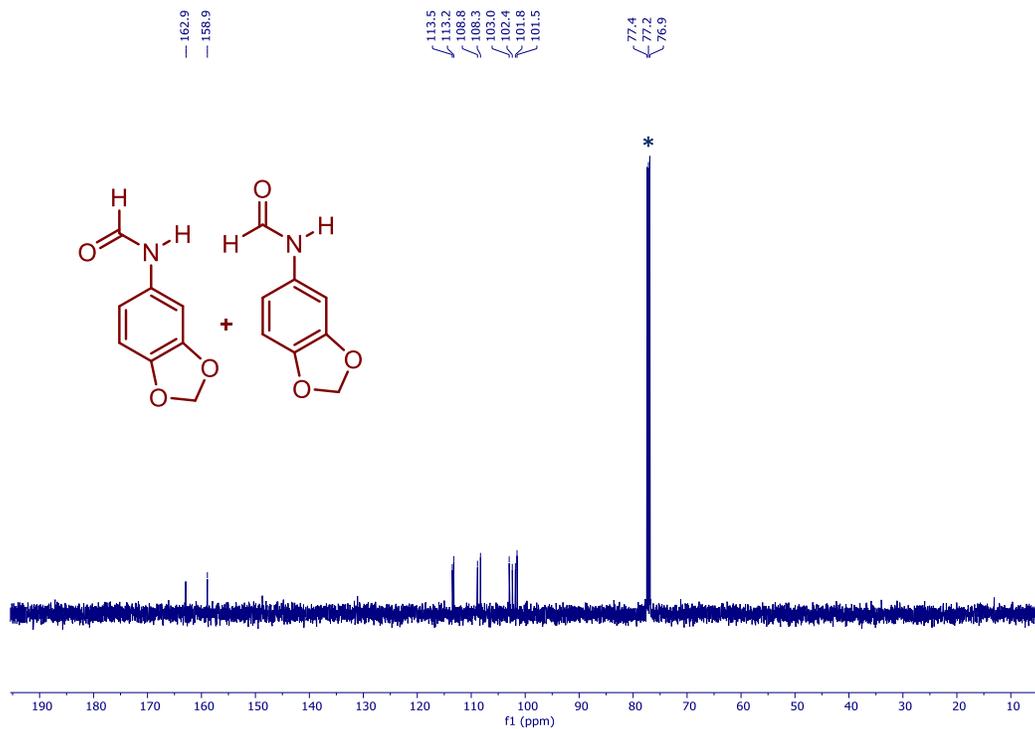
$^1\text{H}$  NMR of *N*-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)formamide (compound-**3b'**) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



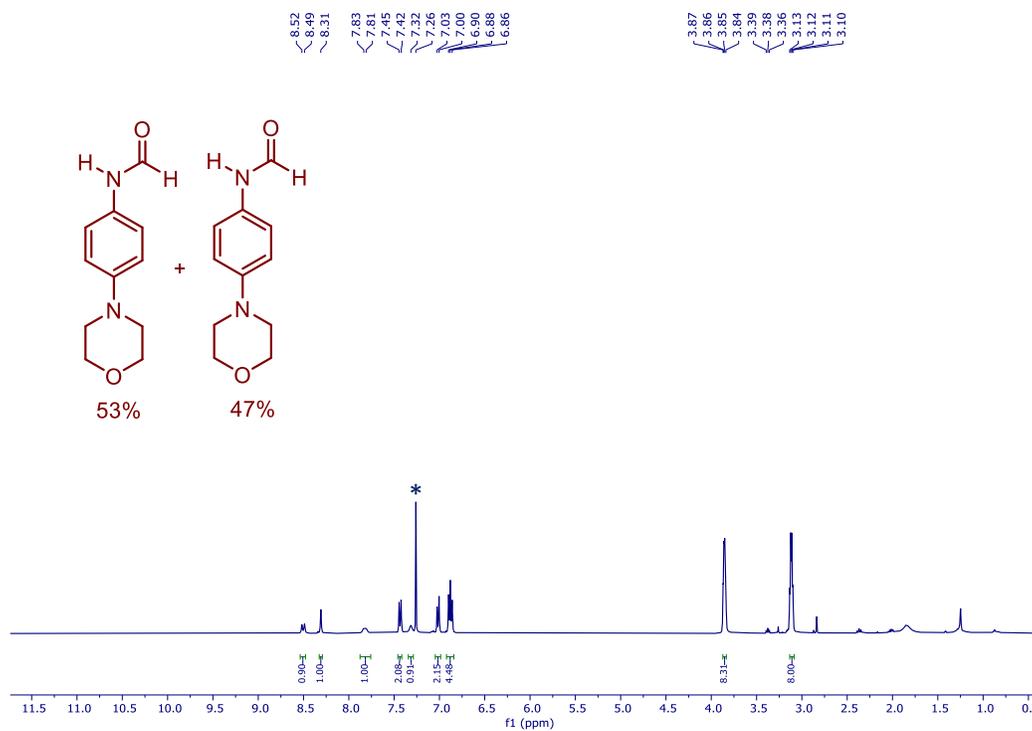
$^{13}\text{C}\{^1\text{H}\}$  of *N*-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)formamide (compound-**3b'**) in  $\text{DMSO-}d_6$  (\*)



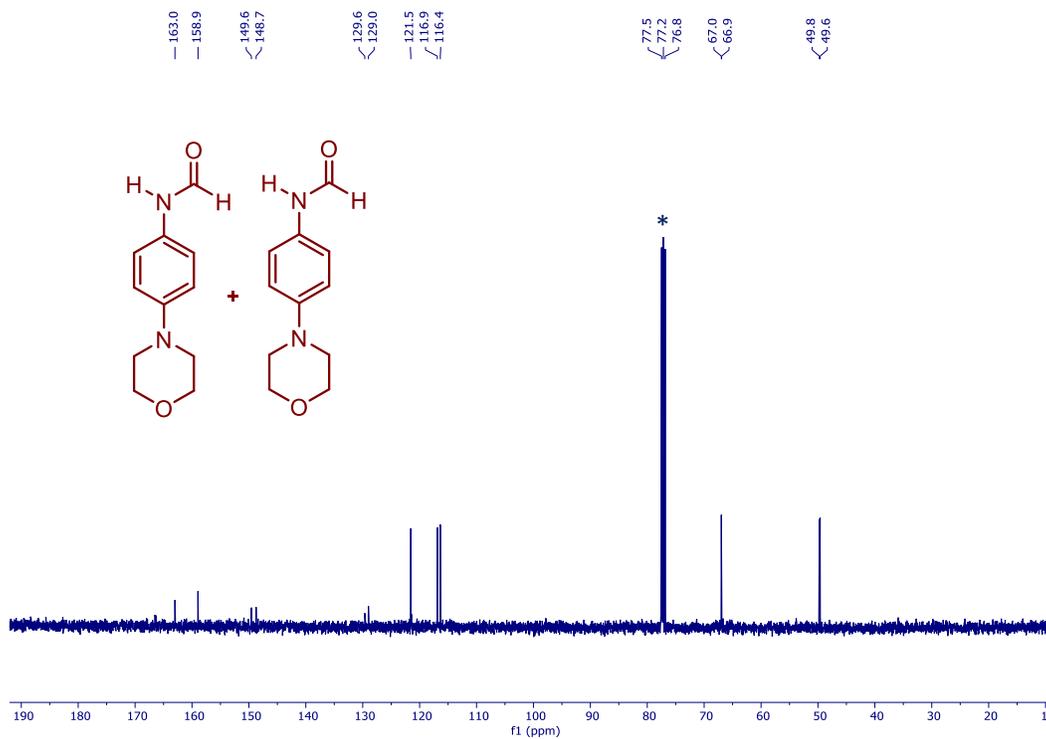
$^1\text{H}$  NMR of *N*-(benzo[d][1,3]dioxol-5-yl)formamide (compound-3c') in  $\text{CDCl}_3$  (\*)



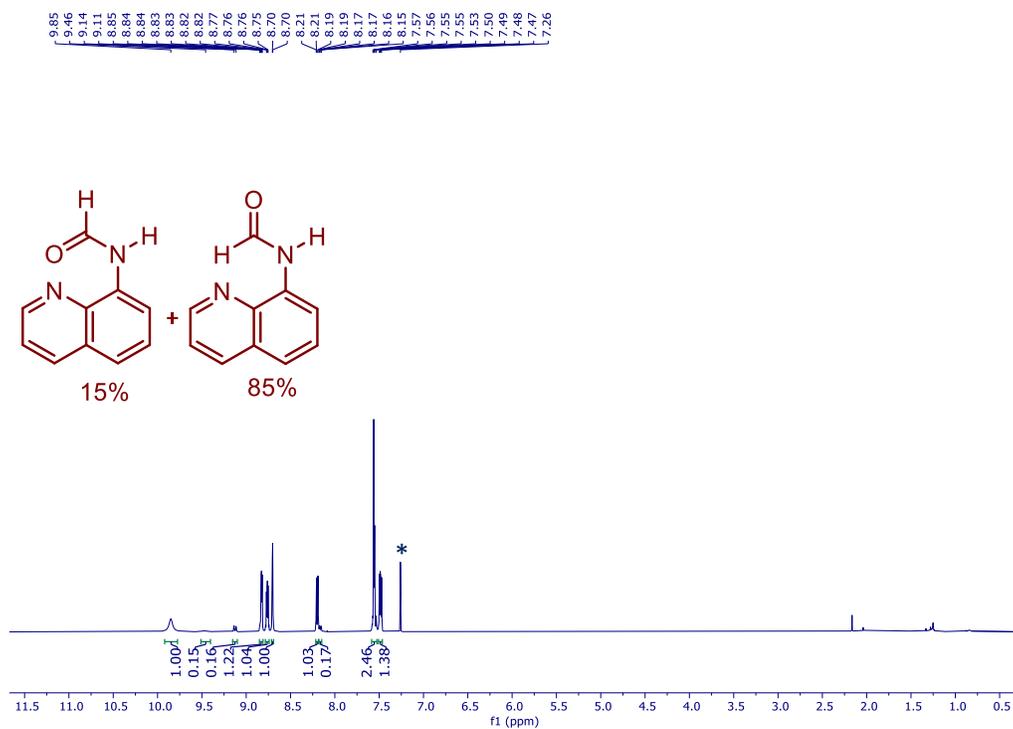
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(benzo[d][1,3]dioxol-5-yl)formamide (compound-3c') in  $\text{CDCl}_3$  (\*)



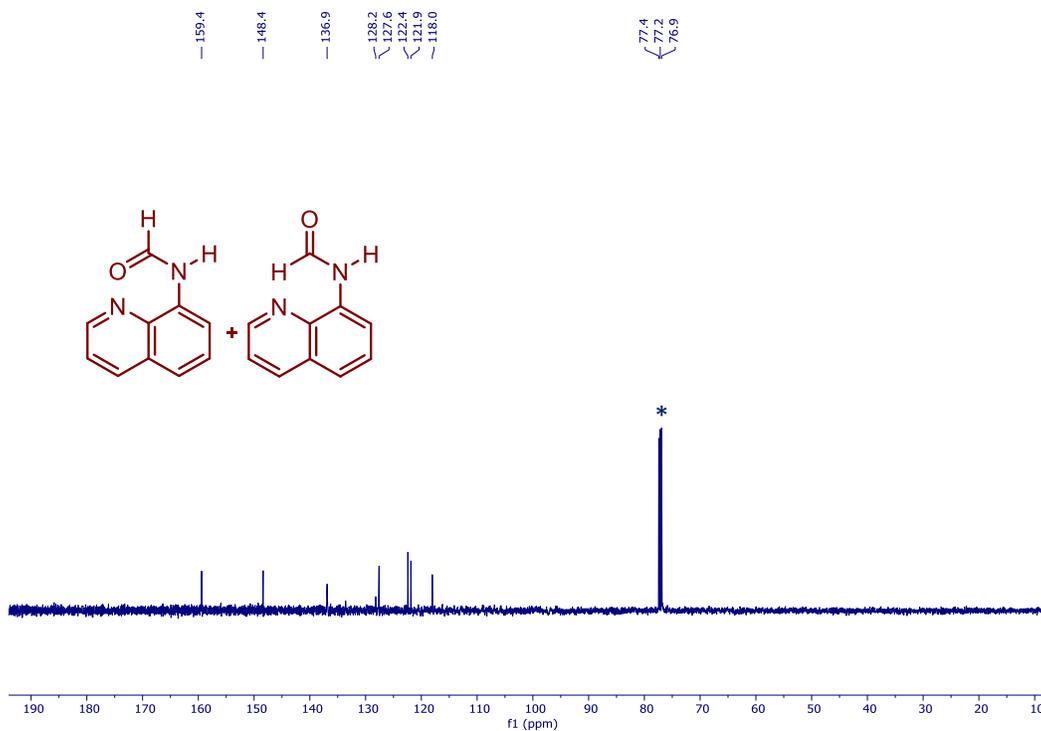
$^1\text{H}$  NMR of spectrum of *N*-(4-morpholinophenyl)formamide (compound-3d') in  $\text{CDCl}_3$  (\*)



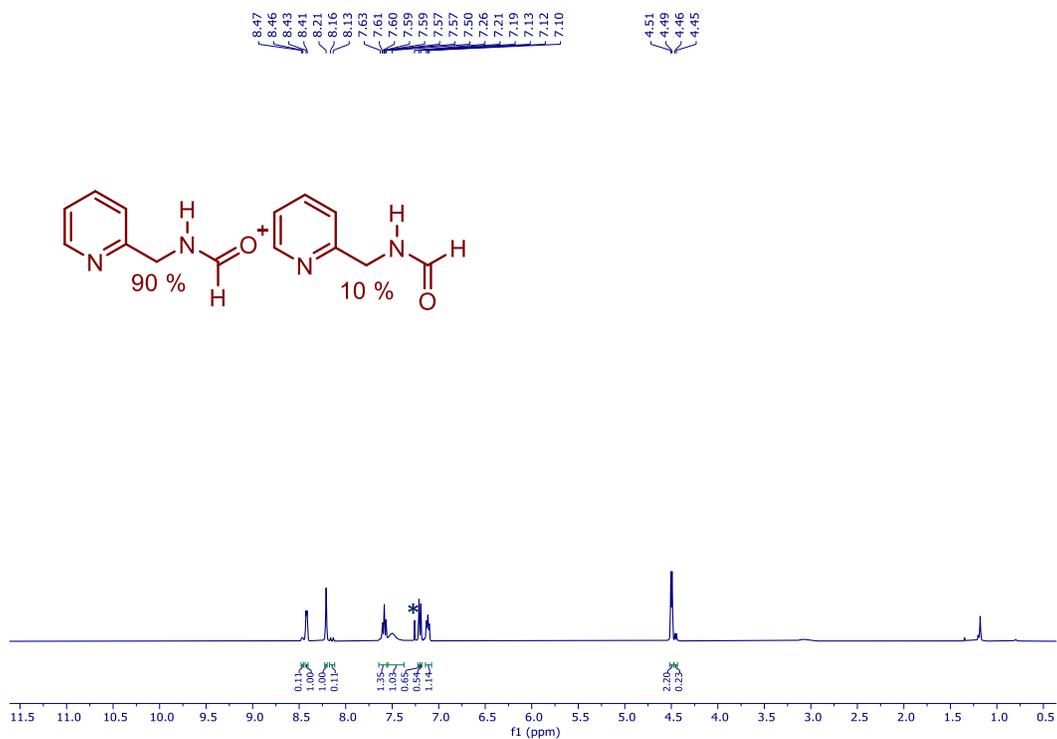
$^{13}\text{C}\{^1\text{H}\}$  NMR of spectrum of *N*-(4-morpholinophenyl)formamide (compound-3d') in  $\text{CDCl}_3$  (\*)



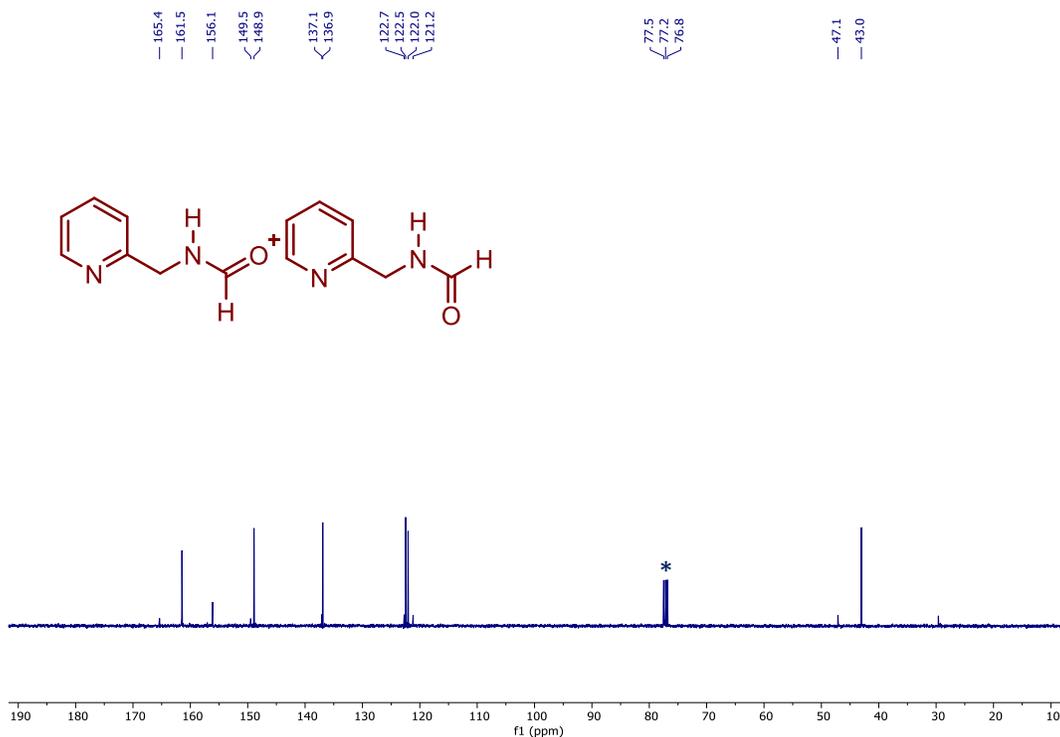
<sup>1</sup>H NMR of *N*-(quinolin-5-yl)formamide (compound-3e') in CDCl<sub>3</sub> (\*)



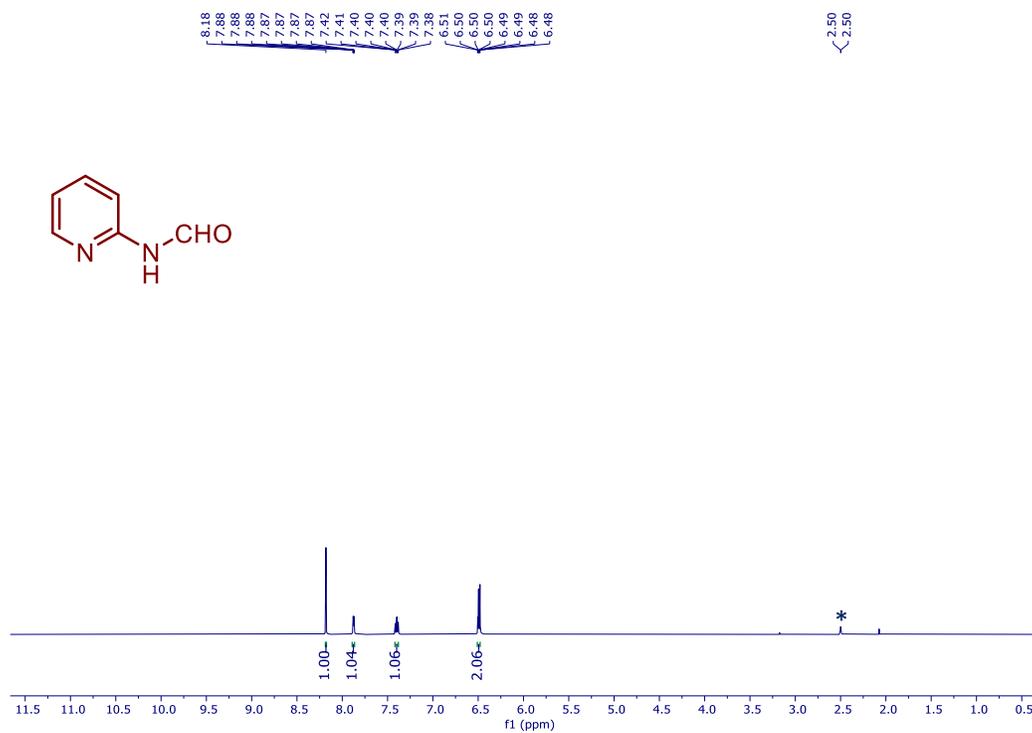
<sup>13</sup>C{<sup>1</sup>H} NMR of *N*-(quinolin-5-yl)formamide (compound-3e') in CDCl<sub>3</sub> (\*)



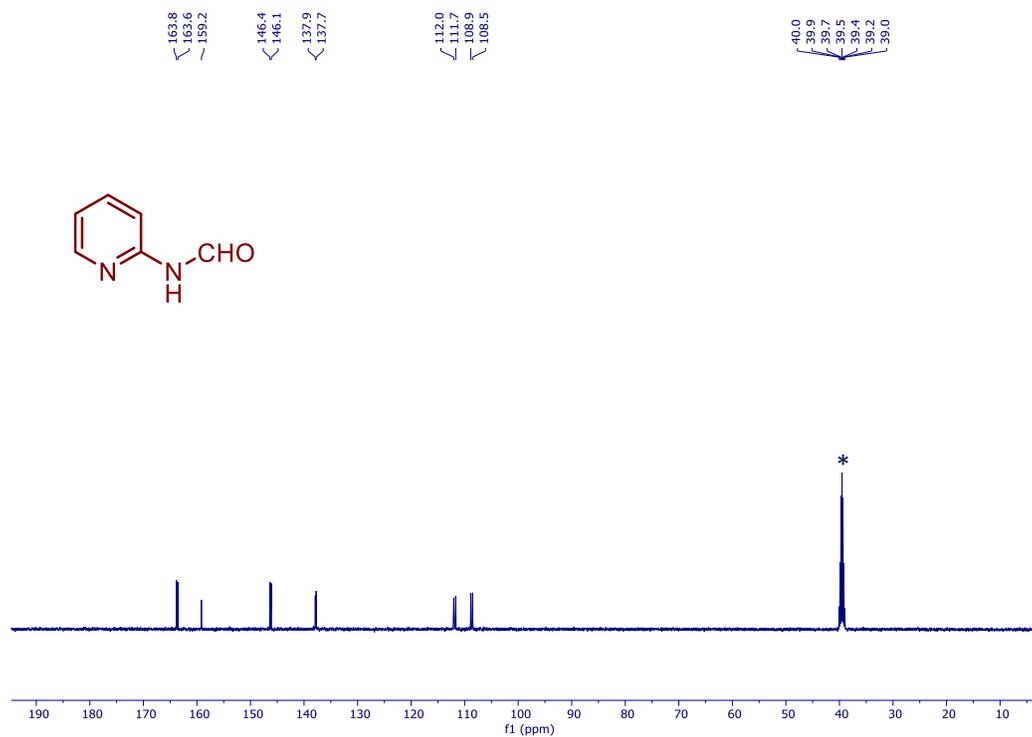
$^1\text{H}$  NMR of spectrum of *N*-(pyridin-2-ylmethyl)formamide (compound-3f') in  $\text{CDCl}_3$  (\*)



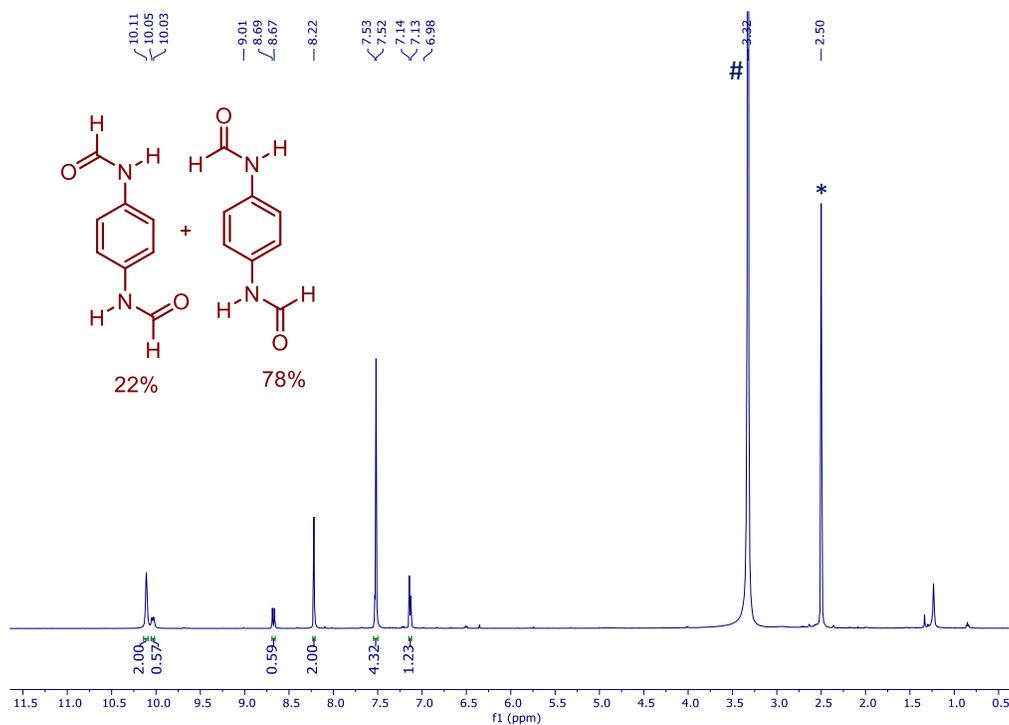
$^{13}\text{C}\{^1\text{H}\}$  NMR of spectrum of *N*-(pyridin-2-ylmethyl)formamide (compound-3f') in  $\text{CDCl}_3$  (\*)



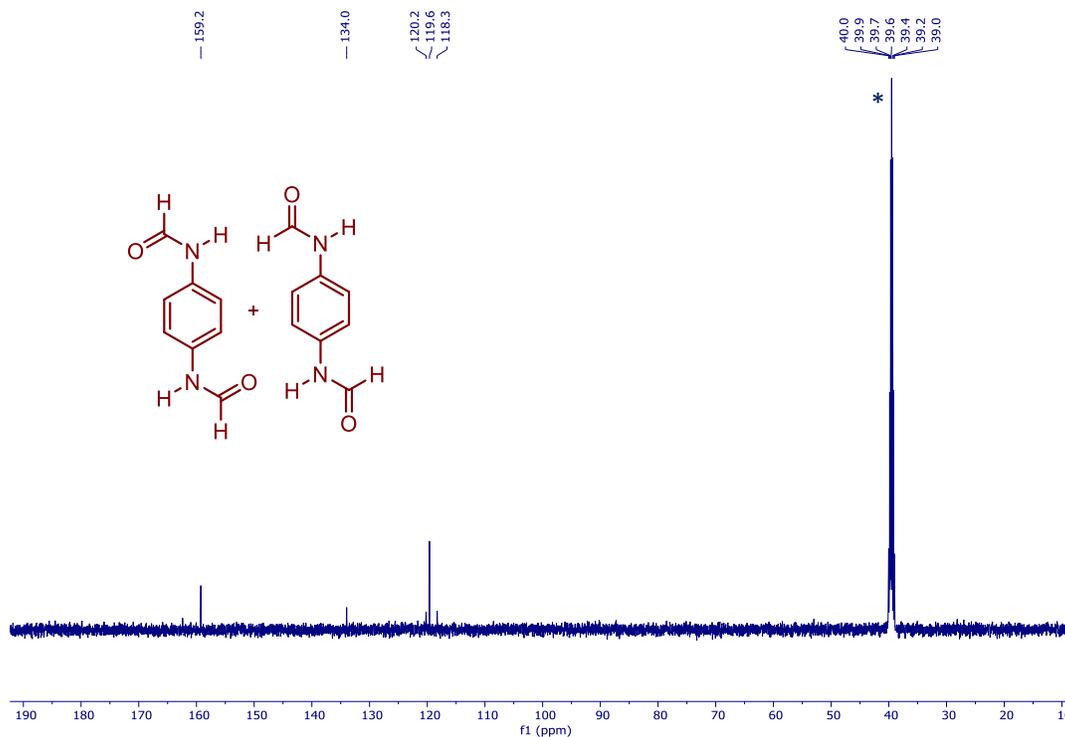
$^1\text{H}$  NMR of spectrum of *N*-(pyridin-2-yl)formamide (compound-3g') in  $\text{DMSO-}d_6$  (\*)



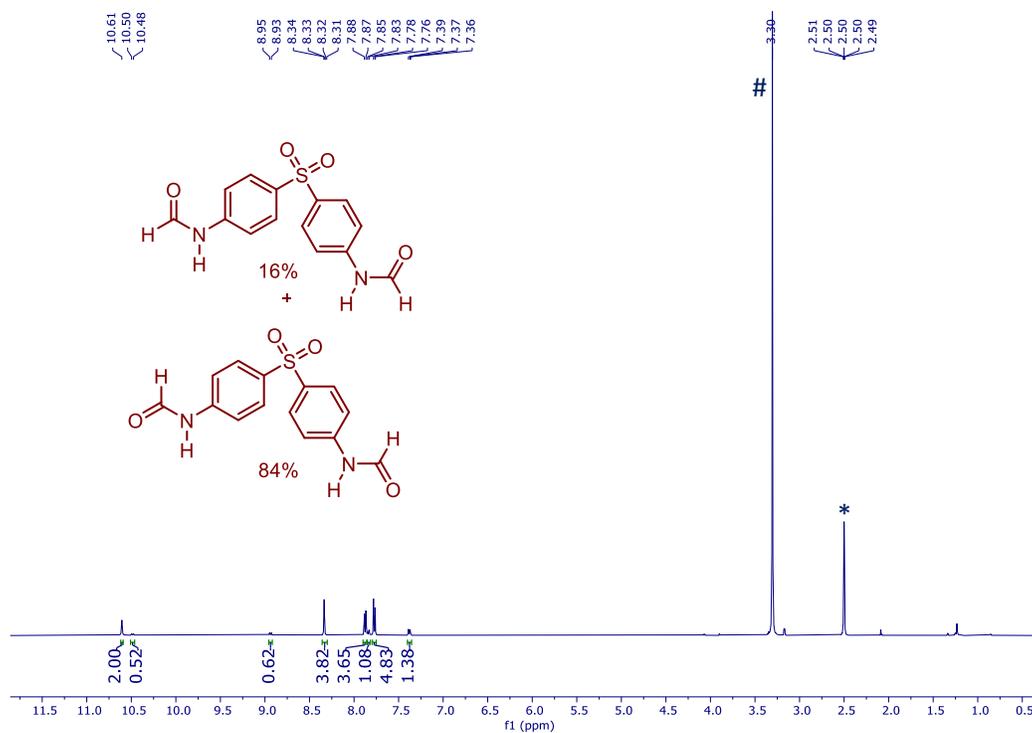
$^{13}\text{C}\{^1\text{H}\}$  NMR of spectrum of *N*-(pyridin-2-yl)formamide (compound-3g') in  $\text{DMSO-}d_6$  (\*)



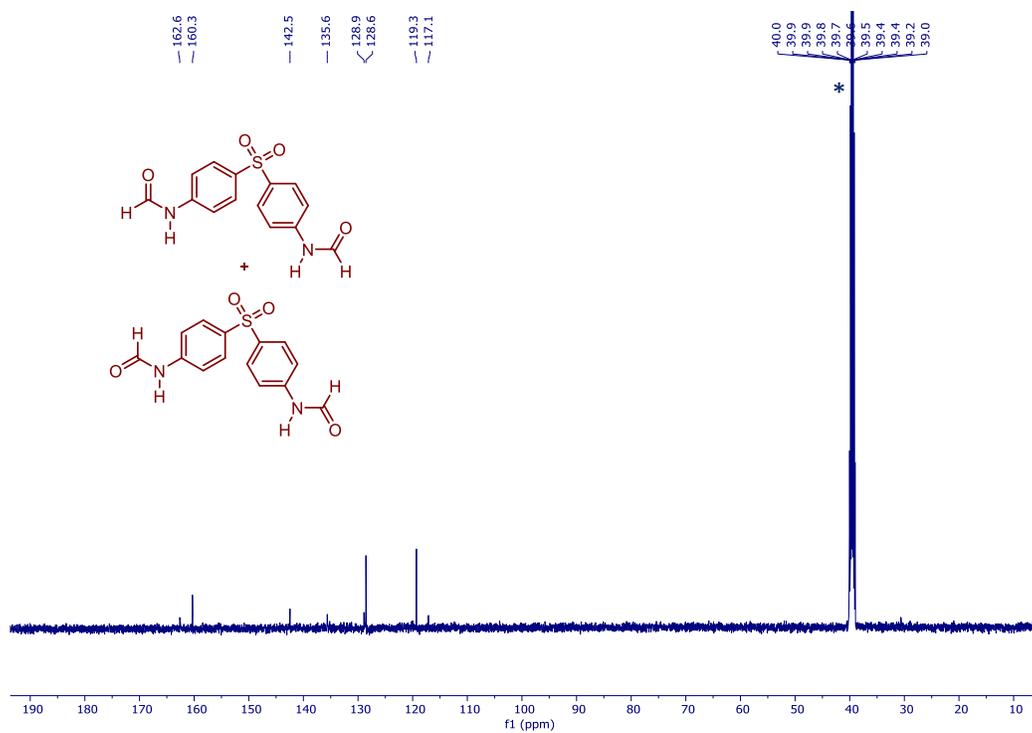
$^1\text{H}$  NMR of *N,N'*-(1,4-phenylene)diformamide (compound-3h') in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



$^{13}\text{C}\{^1\text{H}\}$  NMR of *N,N'*-(1,4-phenylene)diformamide (compound-3h') in  $\text{DMSO-}d_6$  (\*)



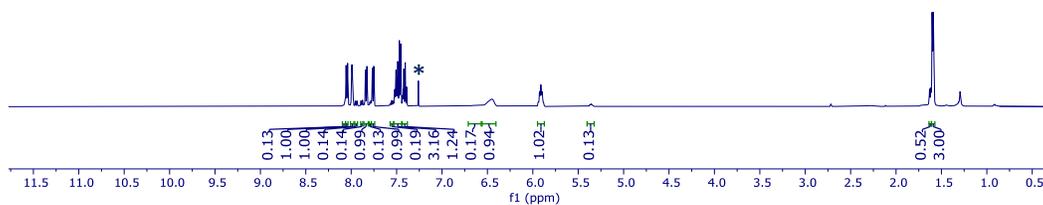
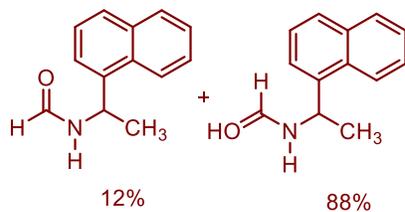
$^1\text{H}$  NMR of *N,N'*-(sulfonylbis(4,1-phenylene))diformamide (compound-3i') in  $\text{DMSO-d}_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-d}_6$



$^{13}\text{C}\{^1\text{H}\}$  NMR of *N,N'*-(sulfonylbis(1,4-phenylene))diformamide (compound-3i') in  $\text{DMSO-d}_6$  (\*)

8.07  
8.06  
8.04  
7.99  
7.95  
7.94  
7.89  
7.88  
7.84  
7.83  
7.79  
7.78  
7.77  
7.75  
7.72  
7.65  
7.52  
7.51  
7.49  
7.47  
7.46  
7.43  
7.42  
7.40  
7.39  
7.26  
6.65  
6.45  
5.94  
5.93  
5.91  
5.90  
5.39  
5.37  
5.36  
5.35

1.63  
1.62  
1.60  
1.59



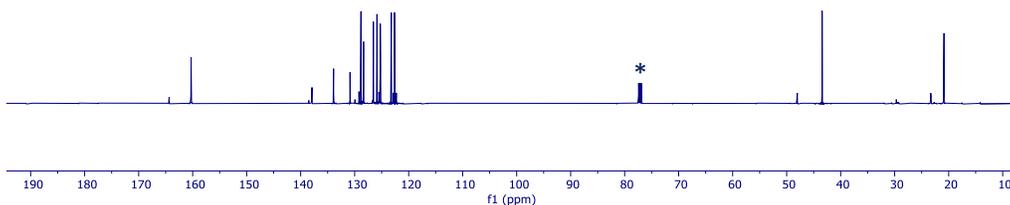
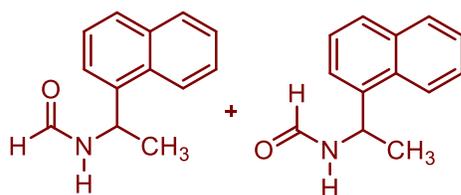
$^1\text{H}$  NMR of spectrum of *N*-(1-(naphthalen-1-yl)ethyl)formamide (compound-3j') in  $\text{CDCl}_3$  (\*)

164.4  
160.3  
138.5  
137.9  
133.9  
133.9  
130.9  
130.0  
129.2  
128.8  
128.4  
128.3  
126.5  
126.5  
125.9  
125.5  
123.2  
122.8  
122.6  
122.3

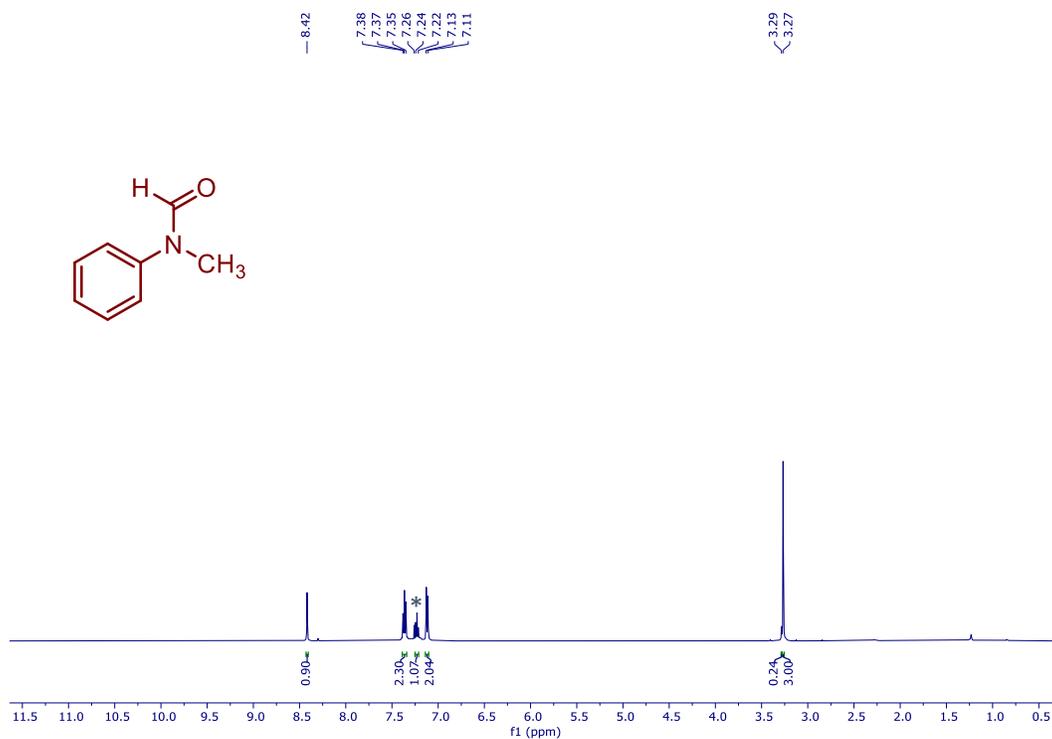
77.4  
77.2  
76.9

48.0  
43.4

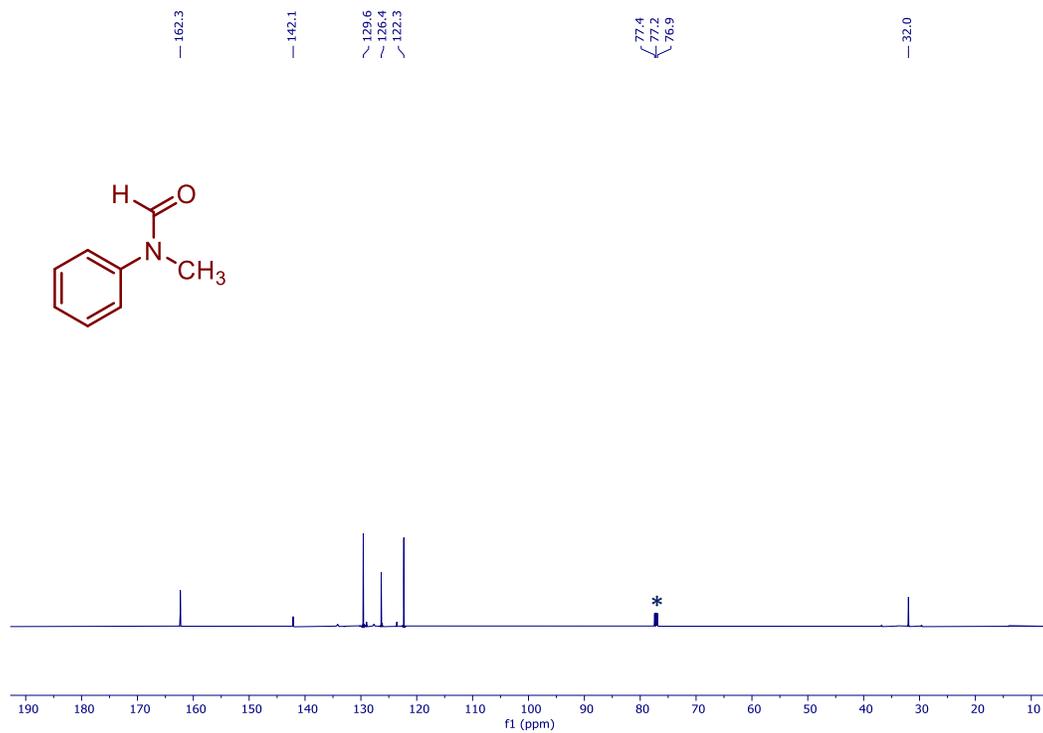
23.3  
20.9



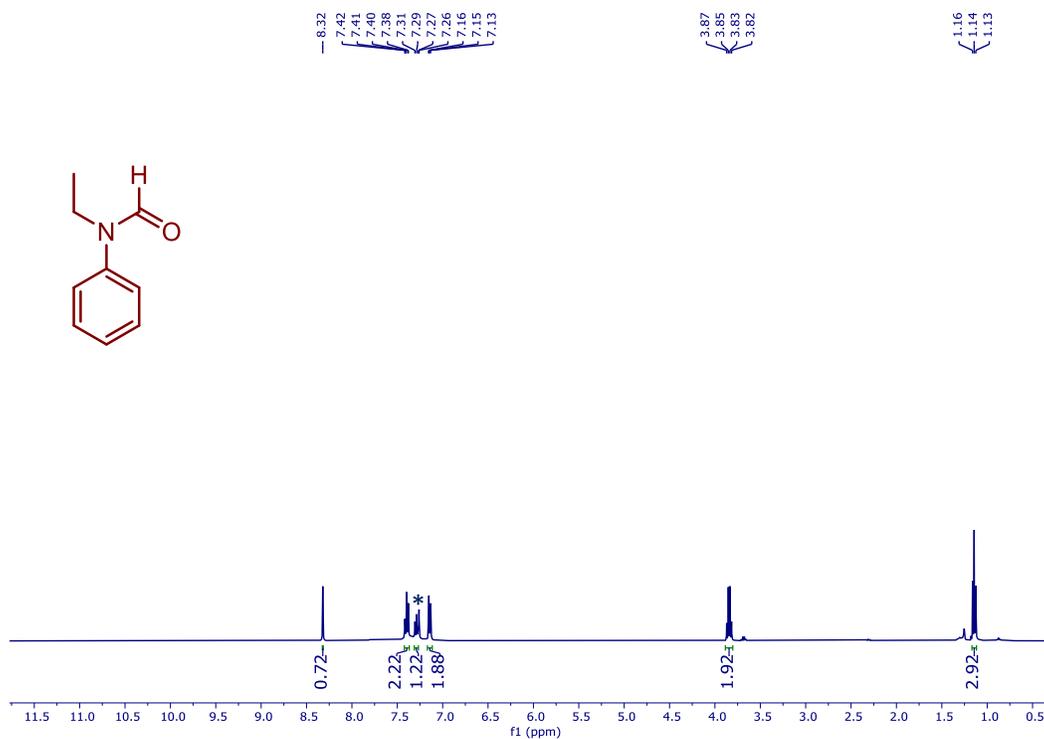
$^{13}\text{C}\{^1\text{H}\}$  NMR of spectrum of *N*-(1-(naphthalen-1-yl)ethyl)formamide (compound-3j') in  $\text{CDCl}_3$  (\*)



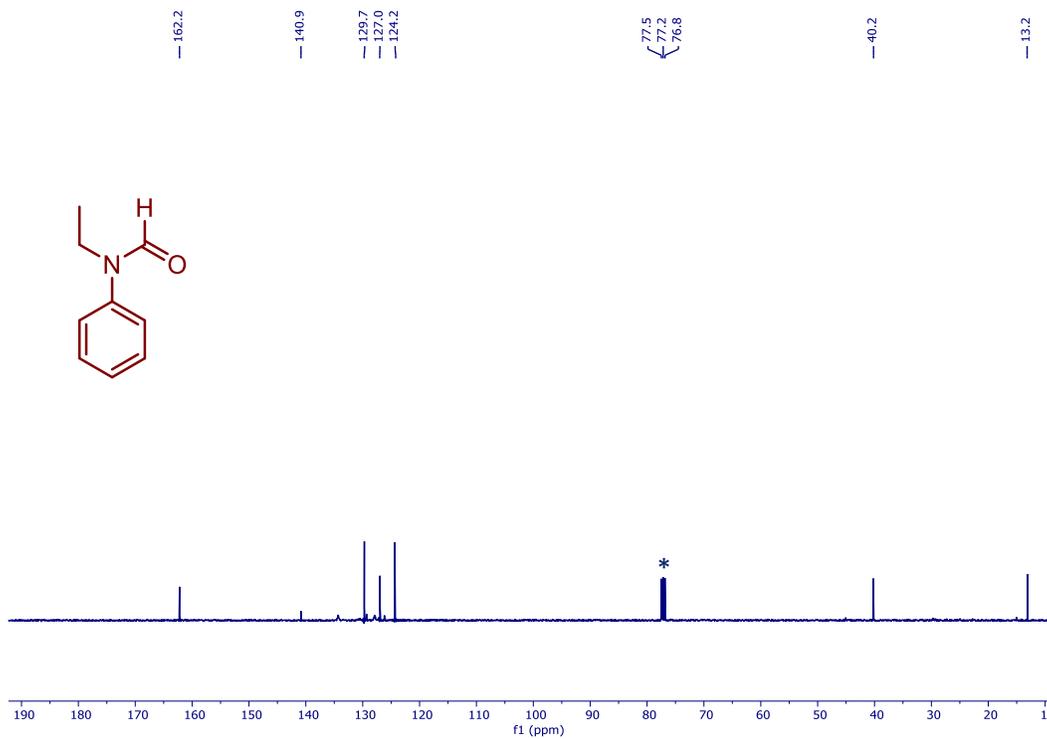
$^1\text{H}$  NMR of *N*-methyl-*N*-phenylformamide (compound-**3k'**) in  $\text{CDCl}_3$  (\*)



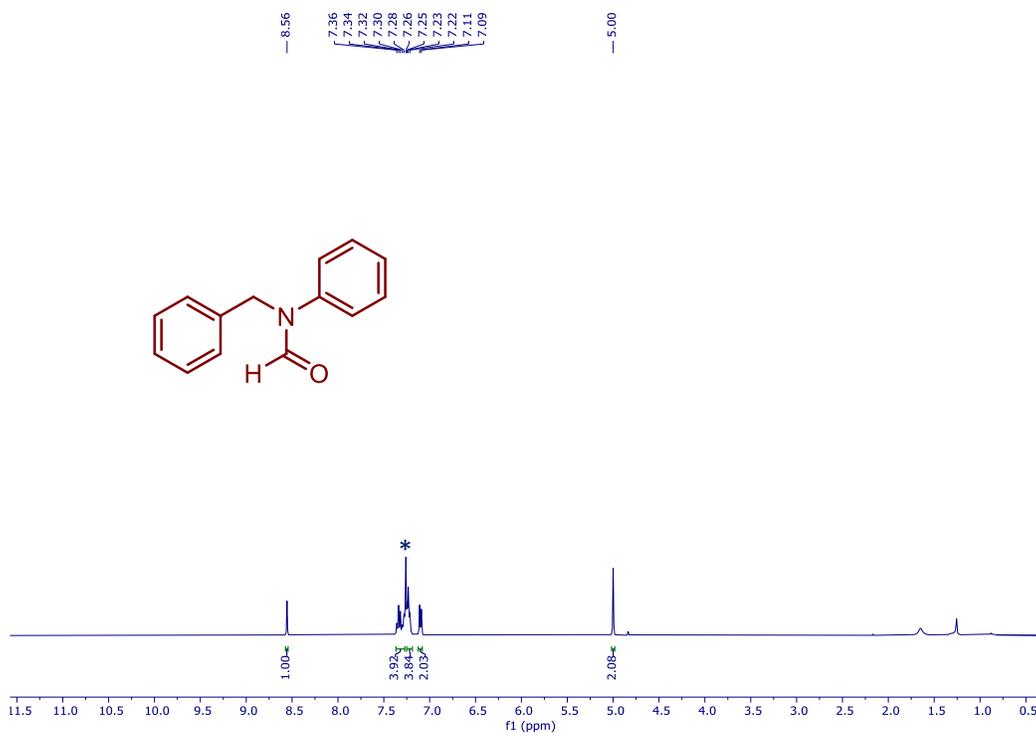
$^{13}\text{C}\{^1\text{H}\}$  of *N*-methyl-*N*-phenylformamide (compound-**3k'**) in  $\text{CDCl}_3$  (\*)



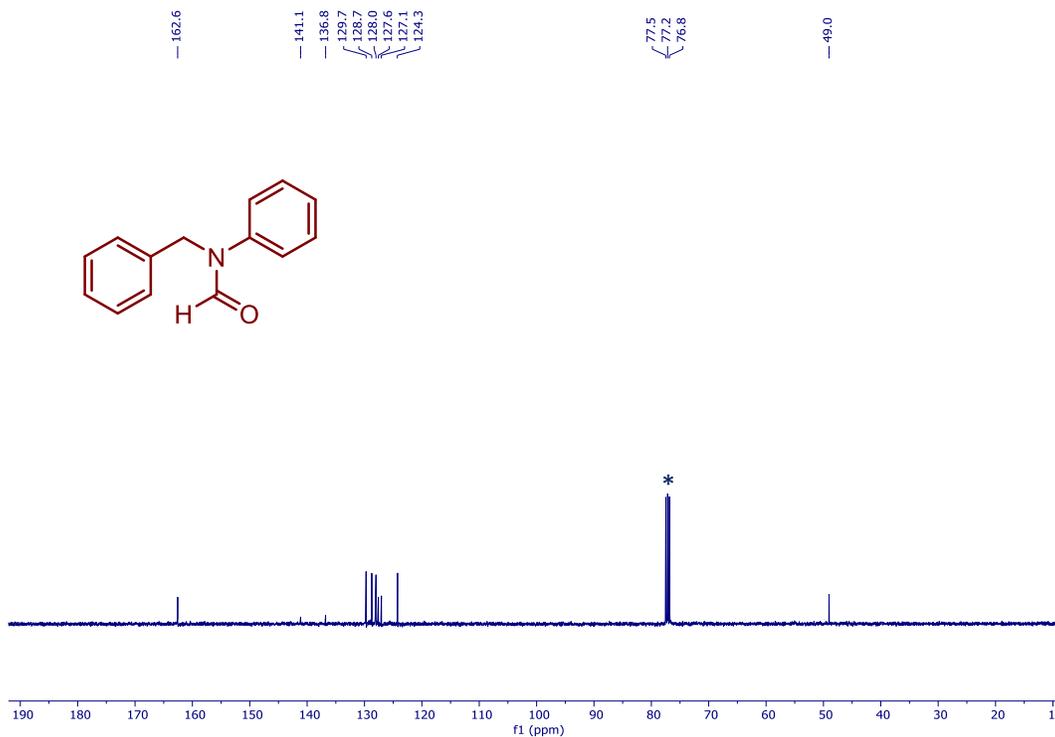
*<sup>1</sup>H NMR of *N*-ethyl-*N*-phenylformamide (compound-3I') in CDCl<sub>3</sub> (\*)*



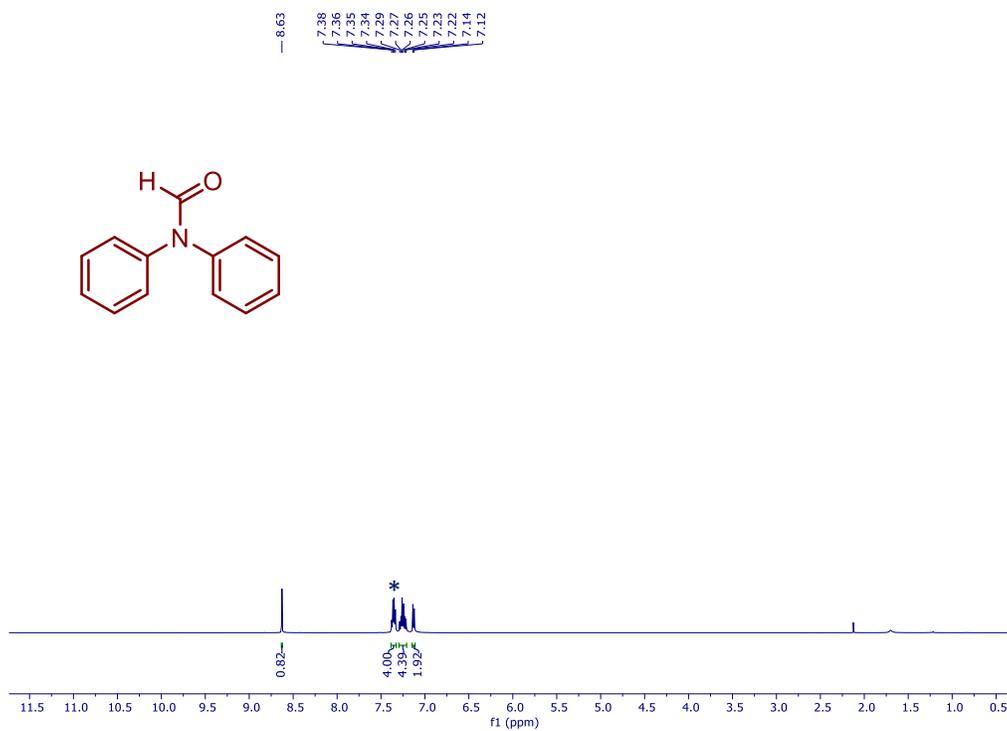
*<sup>13</sup>C{<sup>1</sup>H} NMR of *N*-ethyl-*N*-phenylformamide (compound-3I') in CDCl<sub>3</sub> (\*)*



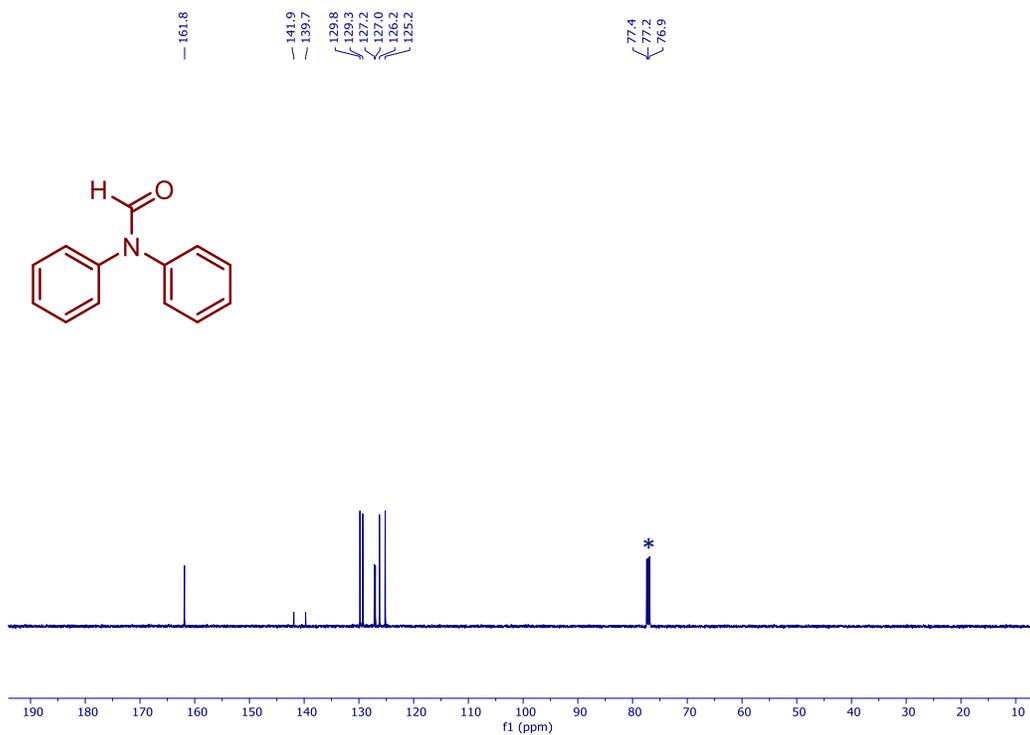
$^1\text{H}$  NMR of *N*-benzyl-*N*-phenylformamide (compound-**3m'**) in  $\text{CDCl}_3$  (\*)



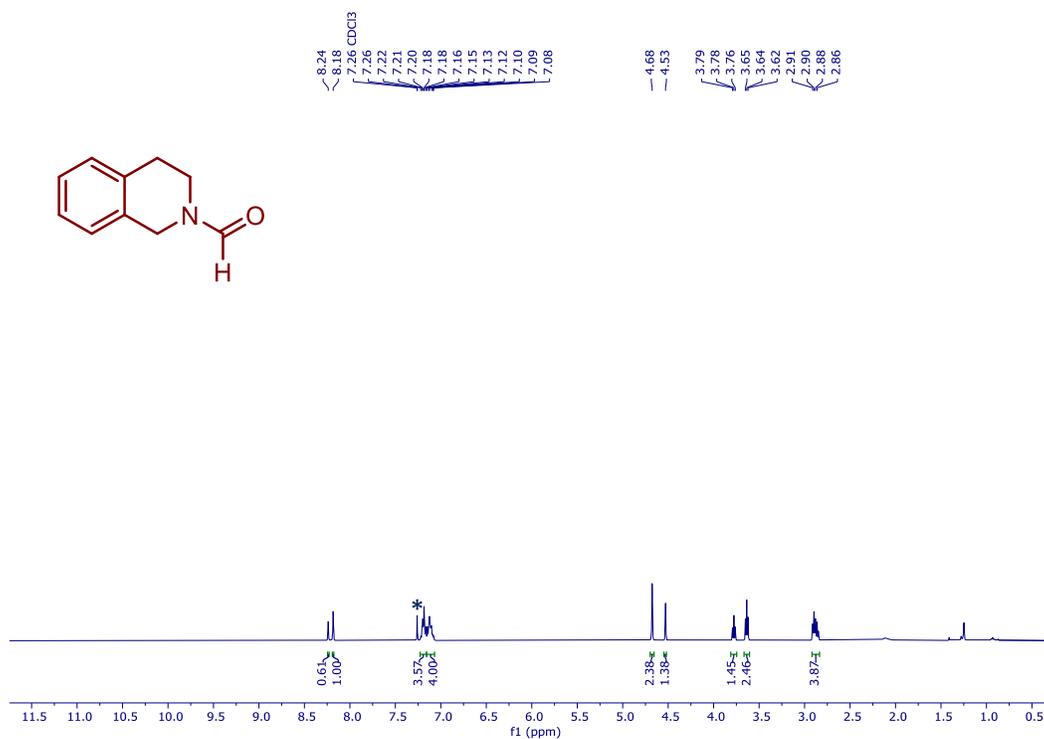
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-benzyl-*N*-phenylformamide (compound-**3m'**) in  $\text{CDCl}_3$  (\*)



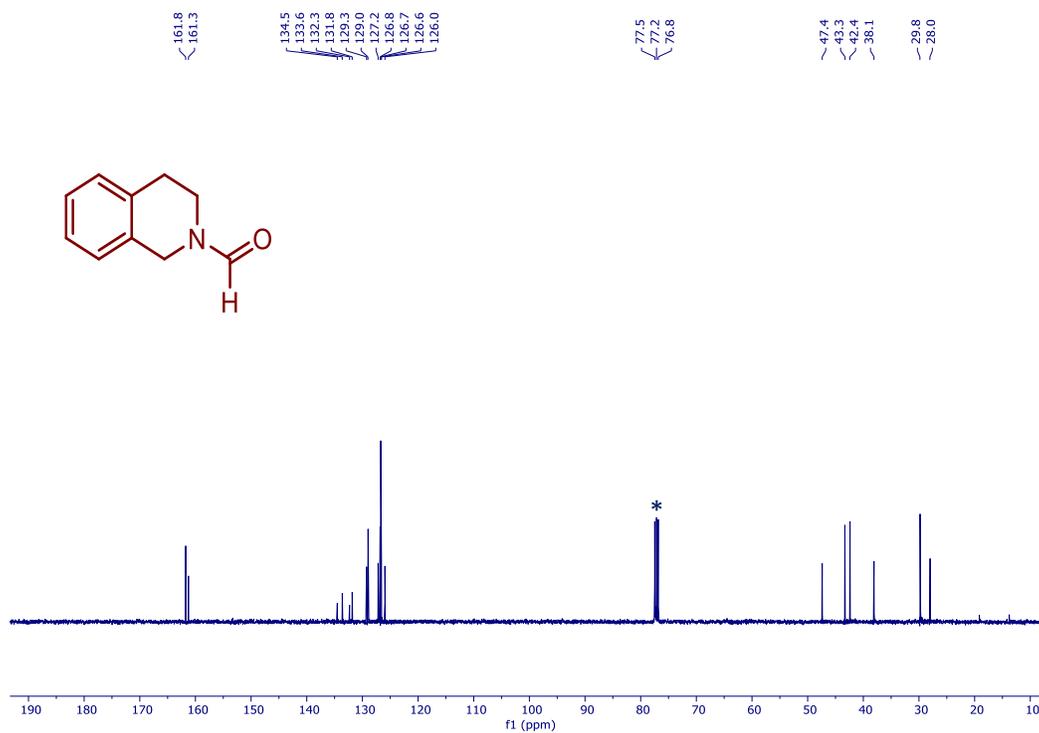
$^1\text{H NMR}$  of *N,N*-diphenylformamide (compound-**3n'**) in  $\text{CDCl}_3$  (\*)



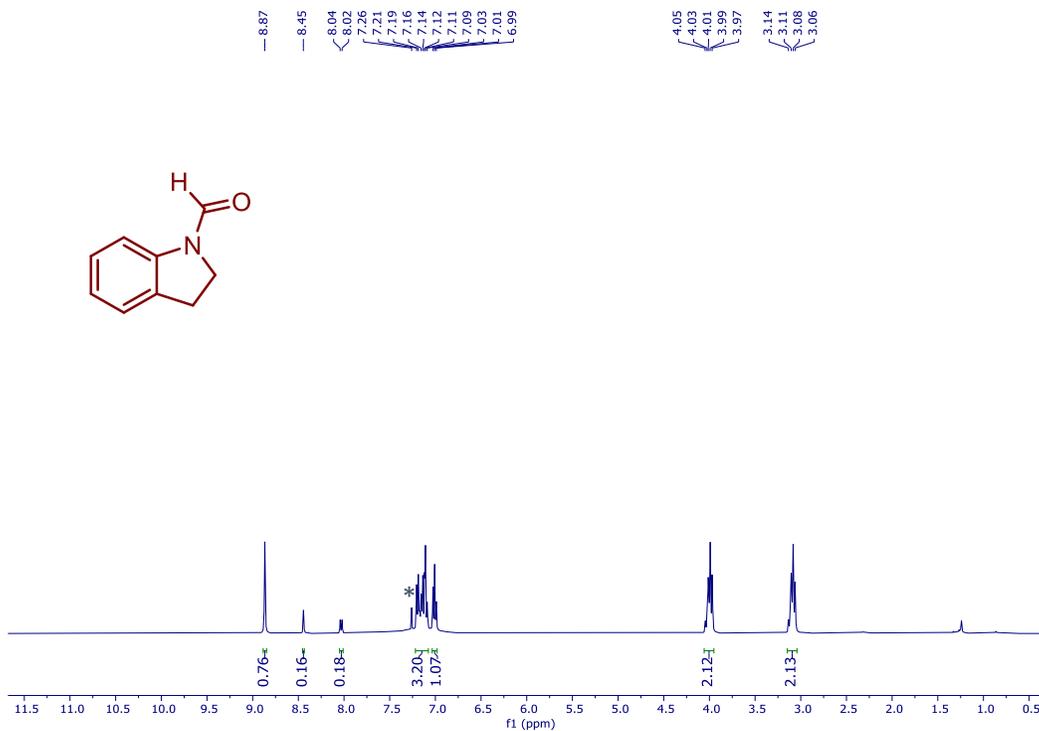
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N,N*-diphenylformamide (compound-**3n'**) in  $\text{CDCl}_3$  (\*)



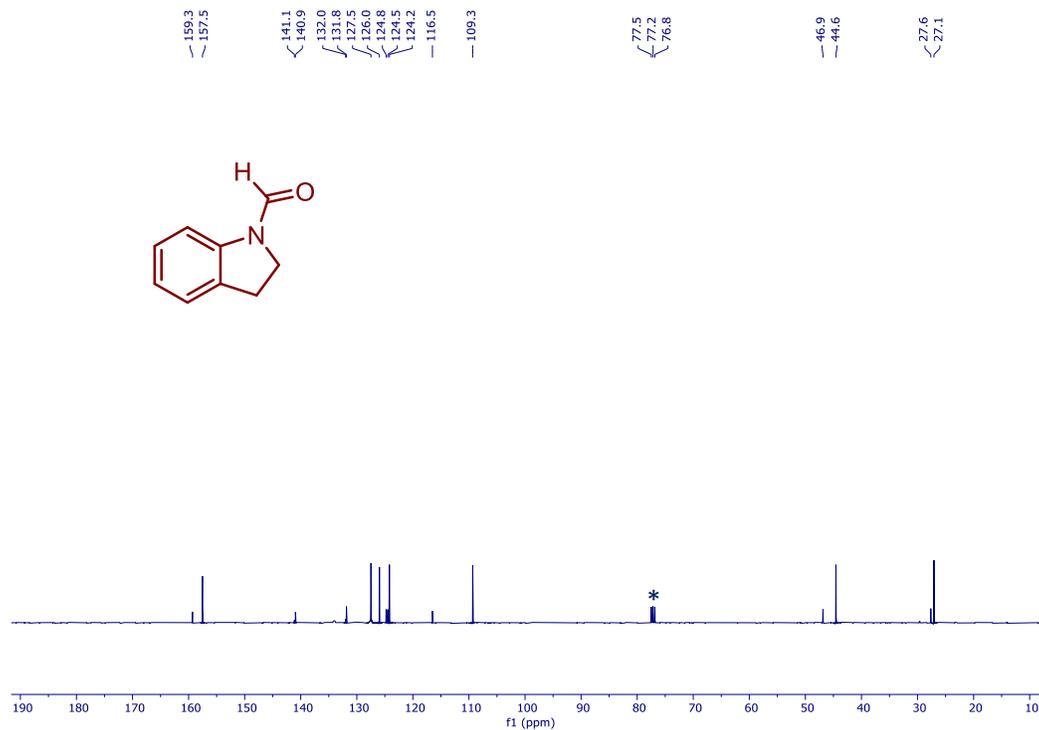
*<sup>1</sup>H NMR of 3,4-dihydroisoquinoline-2(1H)-carbaldehyde (compound-3o') in CDCl<sub>3</sub> (\*)*



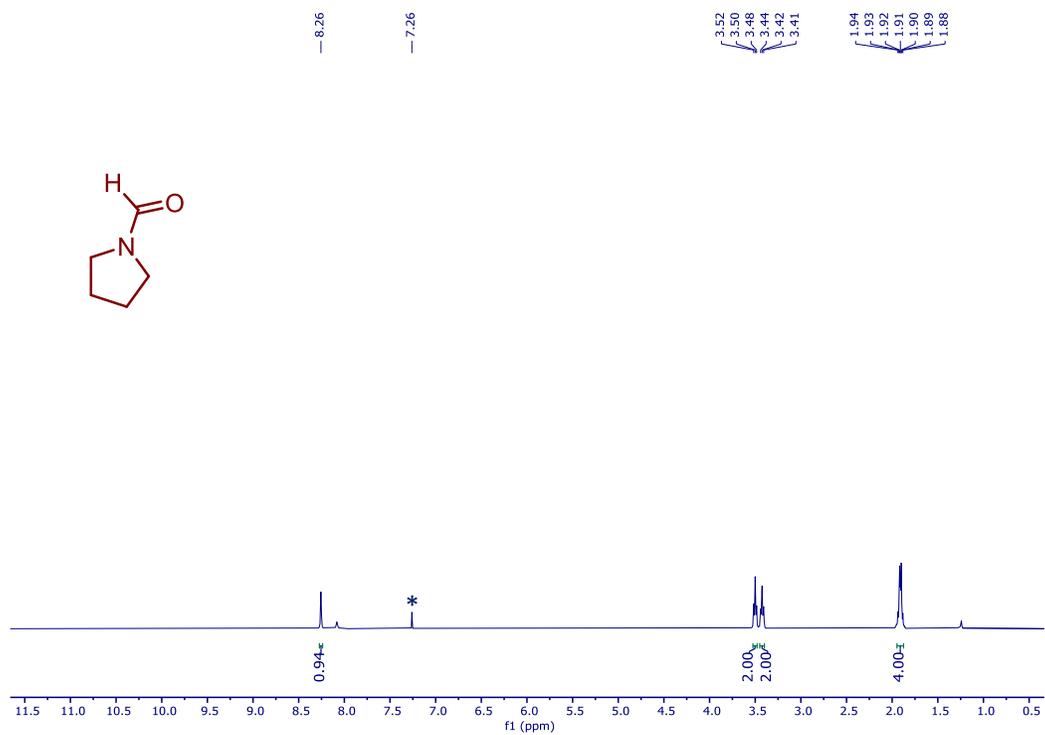
*<sup>13</sup>C{<sup>1</sup>H} NMR of 3,4-dihydroisoquinoline-2(1H)-carbaldehyde (compound-3o') in CDCl<sub>3</sub> (\*)*



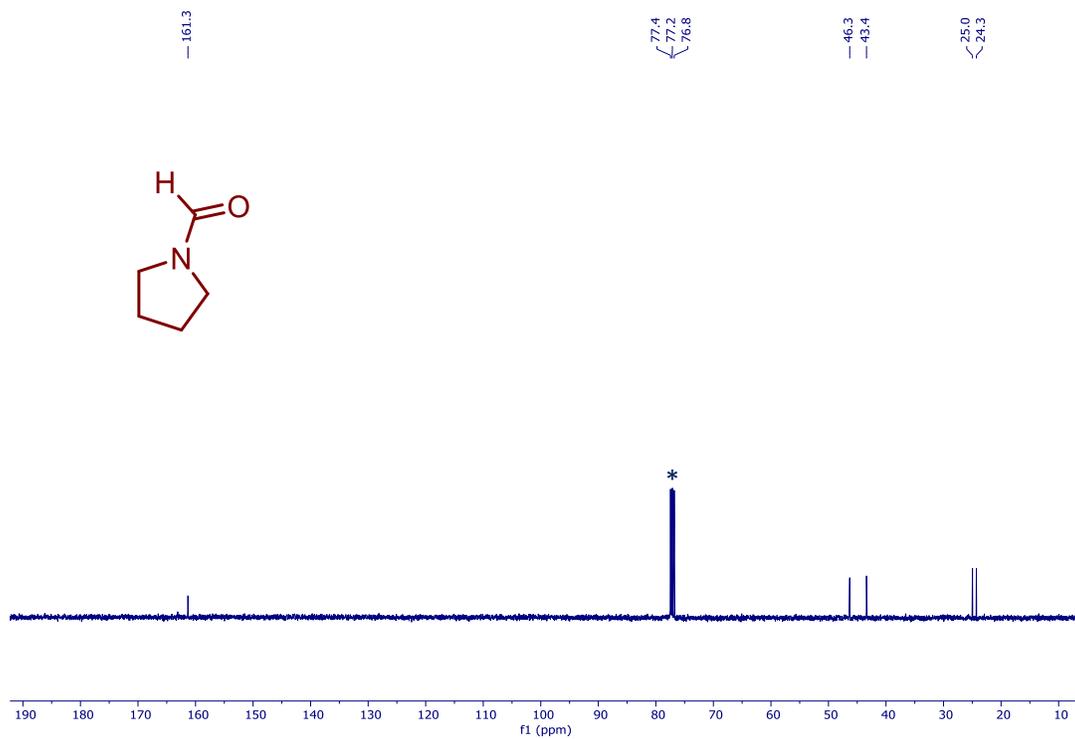
$^1\text{H}$  NMR of indoline-1-carbaldehyde (compound-3p') in  $\text{CDCl}_3$  (\*)



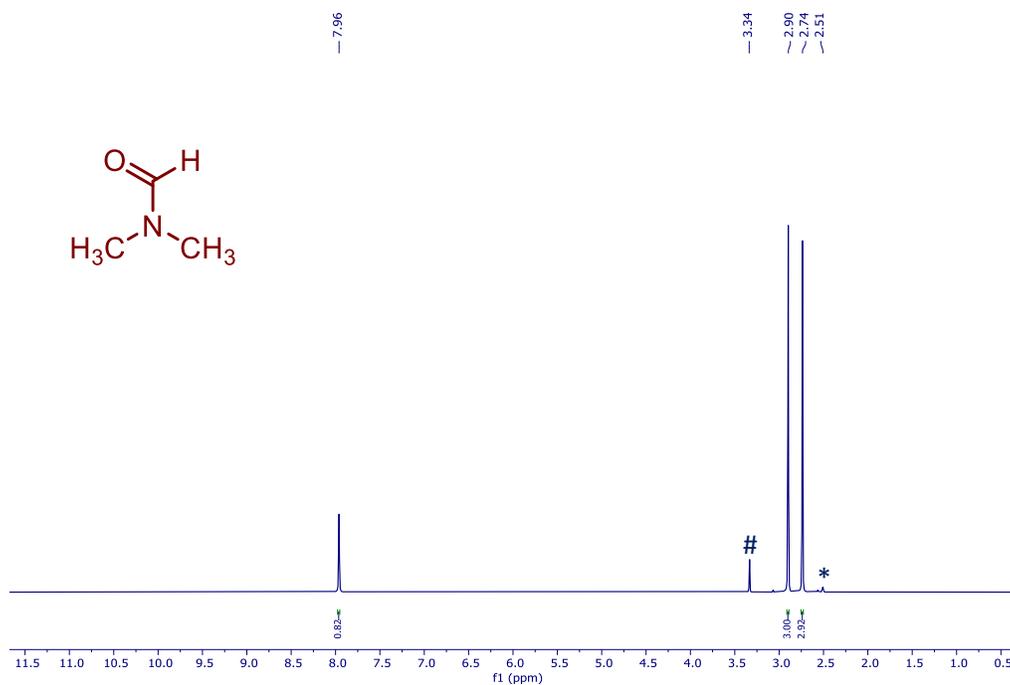
$^{13}\text{C}\{^1\text{H}\}$  NMR of indoline-1-carbaldehyde (compound-3p') in  $\text{CDCl}_3$  (\*)



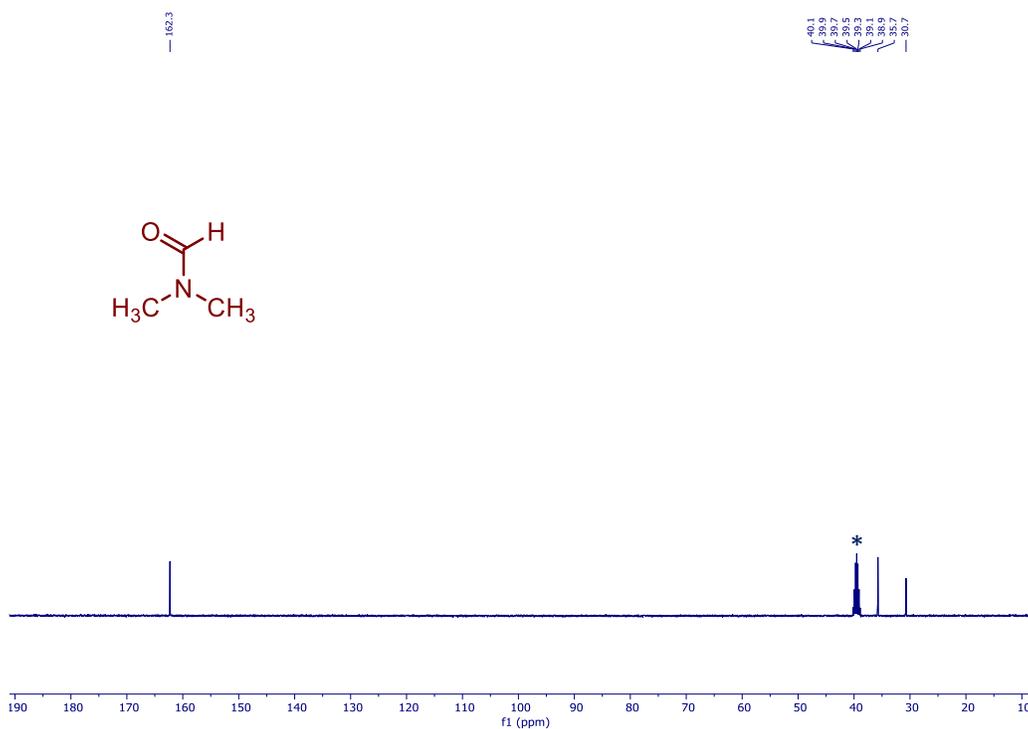
$^1\text{H}$  NMR of pyrrolidine-1-carbaldehyde (compound-3q') in  $\text{CDCl}_3$  (\*)



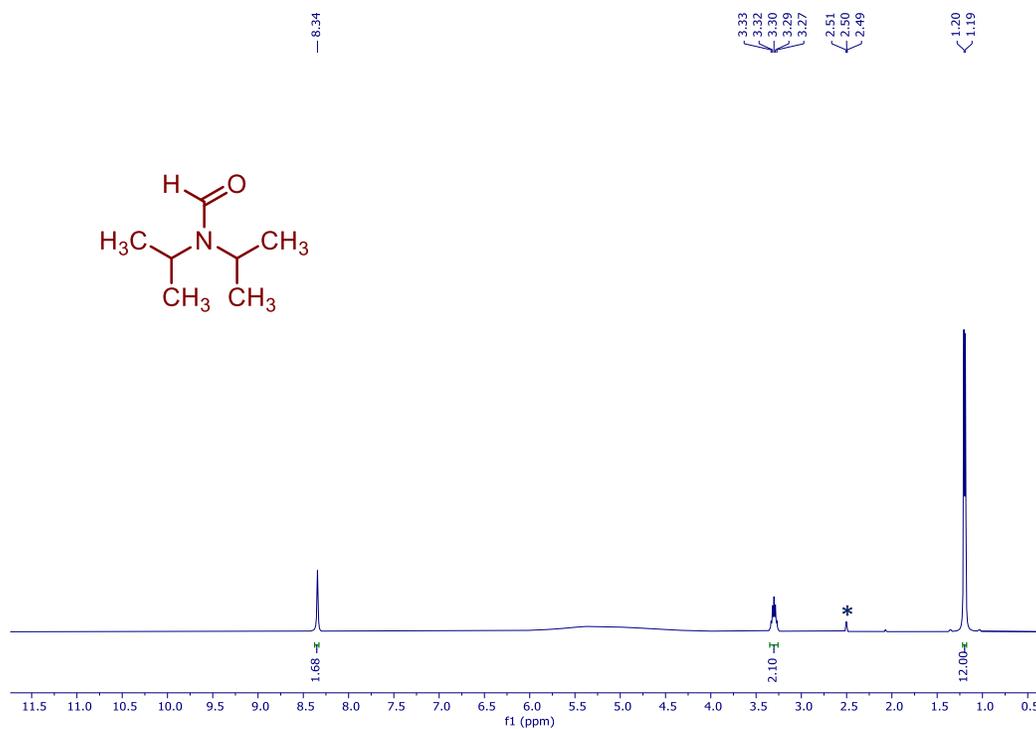
$^{13}\text{C}\{^1\text{H}\}$  NMR of pyrrolidine-1-carbaldehyde (compound-3q') in  $\text{CDCl}_3$  (\*)



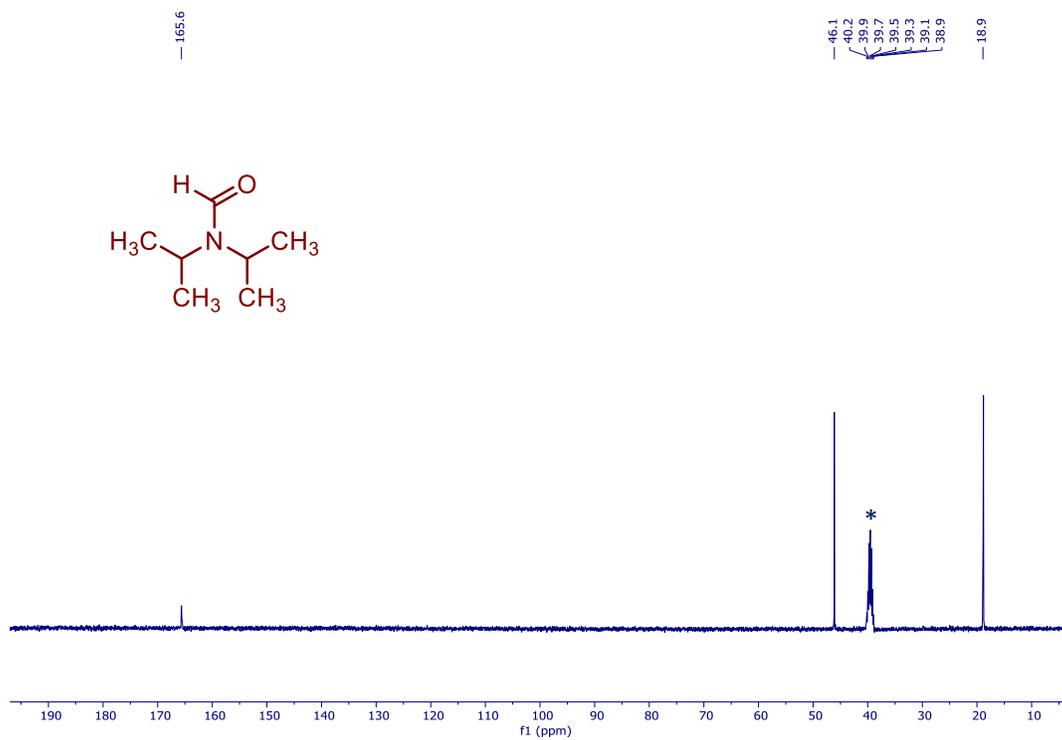
$^1\text{H}$  NMR of 2-(methyl(phenyl)amino)-2-phenylacetonitrile (compound-**3r'**) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



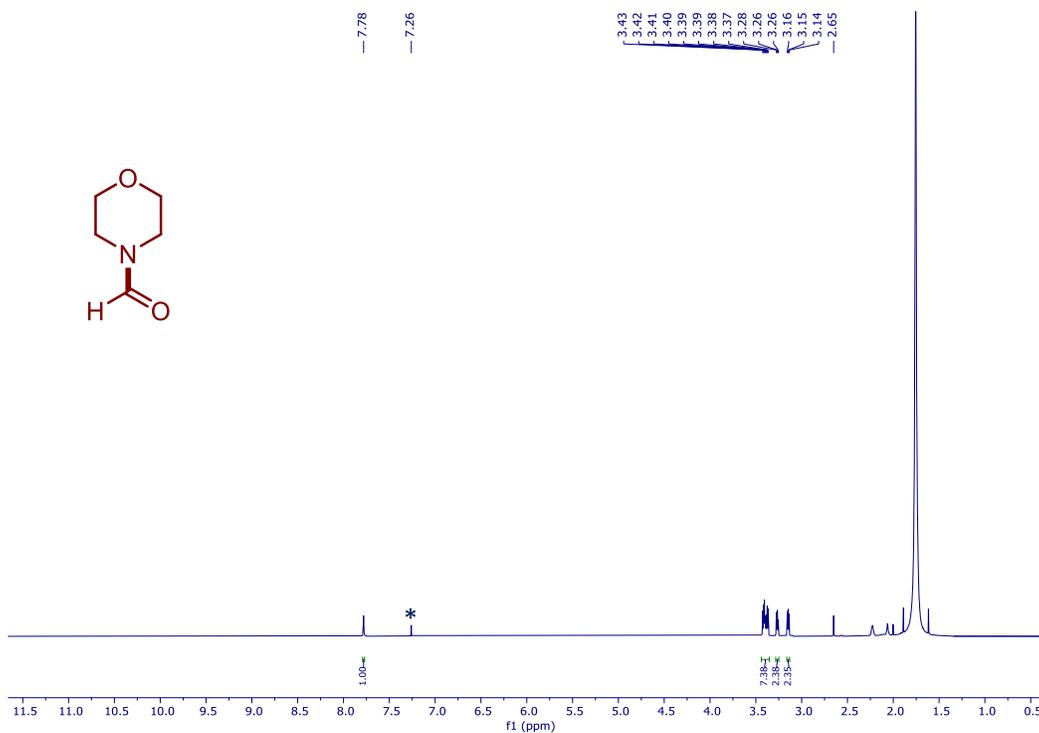
$^{13}\text{C}$  NMR of 2-(methyl(phenyl)amino)-2-phenylacetonitrile (compound-**3r'**) in  $\text{DMSO-}d_6$  (\*)



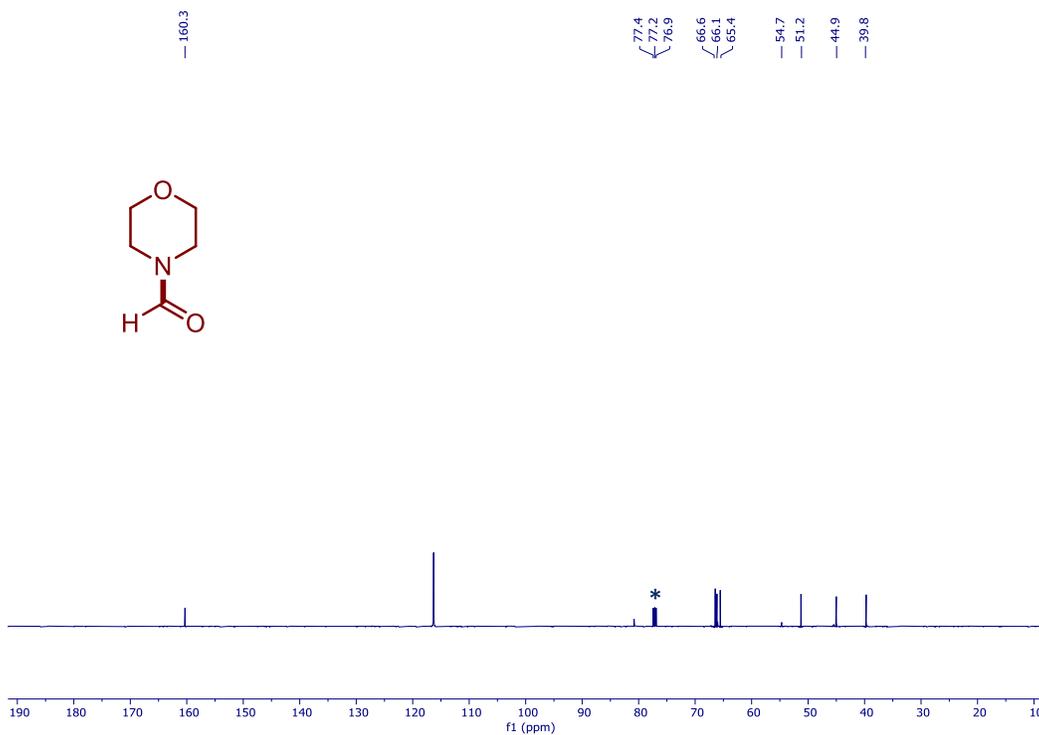
$^1\text{H}$  NMR of *N,N*-diisopropylformamide (compound-3s') in  $\text{DMSO-}d_6$  (\*)



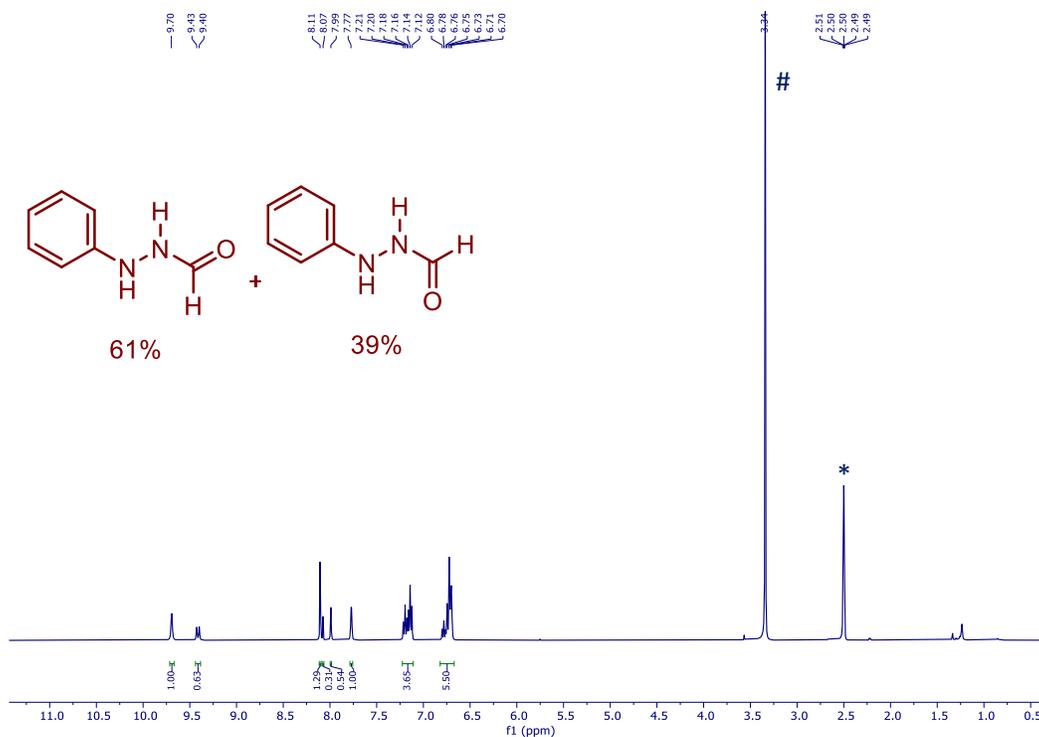
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N,N*-diisopropylformamide (compound-3s') in  $\text{DMSO-}d_6$  (\*)



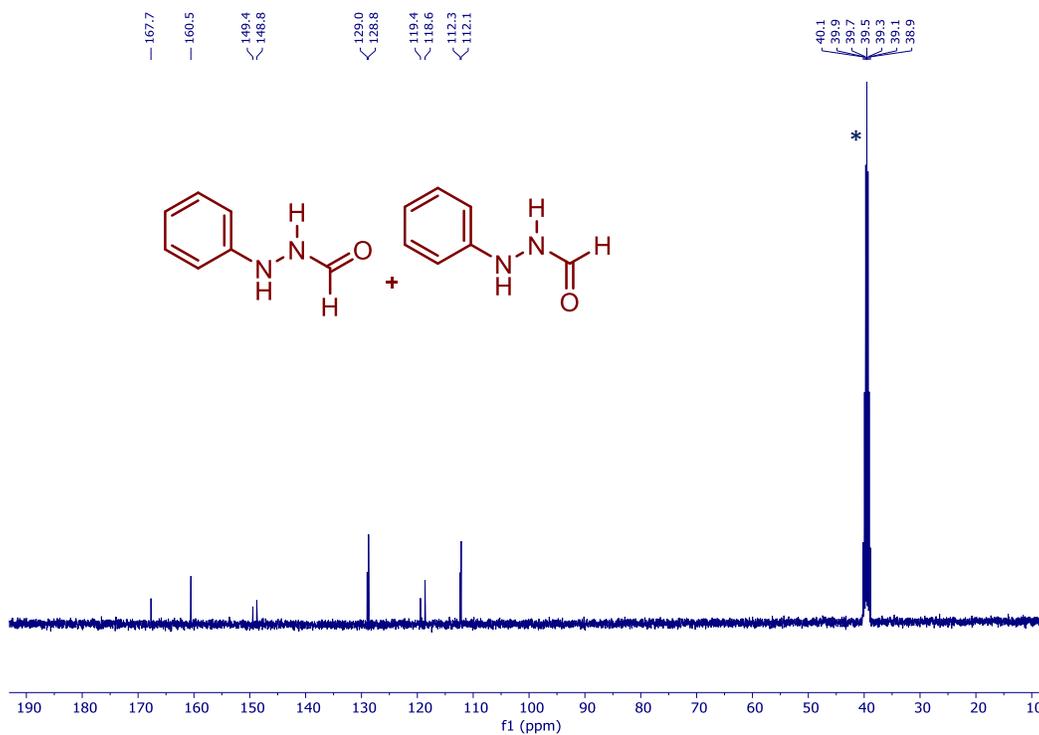
$^1\text{H}$  NMR of morpholine-4-carbaldehyde (compound-3t') in  $\text{CDCl}_3$  (\*)



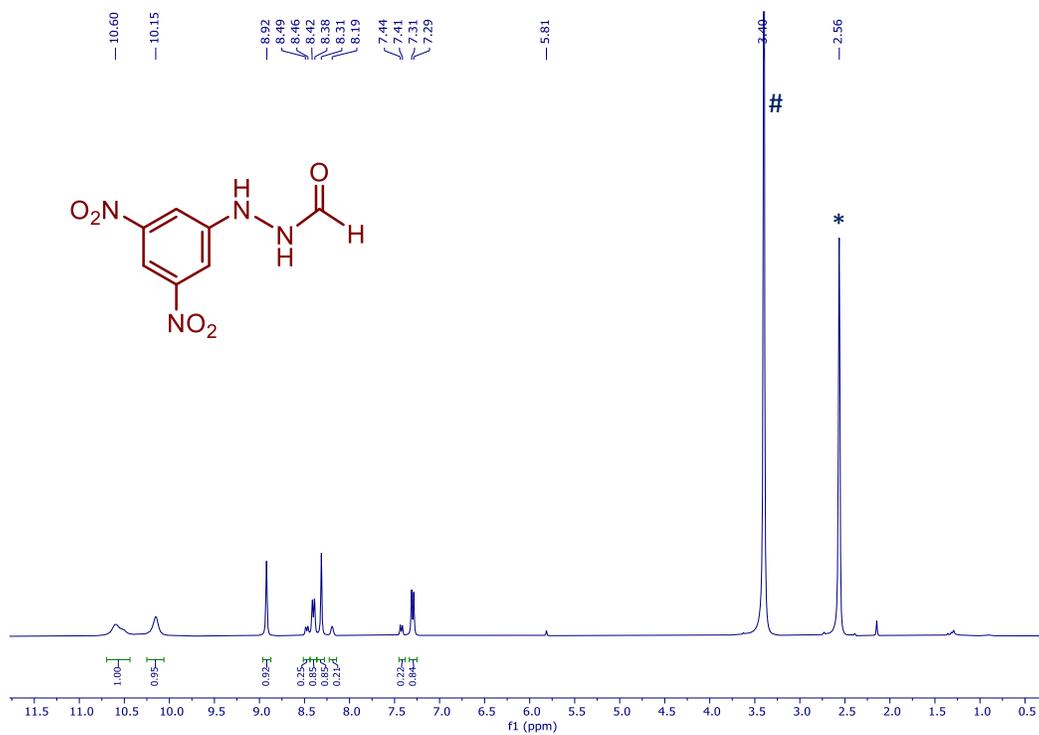
$^{13}\text{C}\{^1\text{H}\}$  NMR of morpholine-4-carbaldehyde (compound-3t') in  $\text{CDCl}_3$  (\*)



<sup>1</sup>H NMR of *N'*-phenylformohydrazide (compound-5a) in DMSO-d<sub>6</sub> (\*). # indicates the solvent impurity of H<sub>2</sub>O in DMSO-d<sub>6</sub>



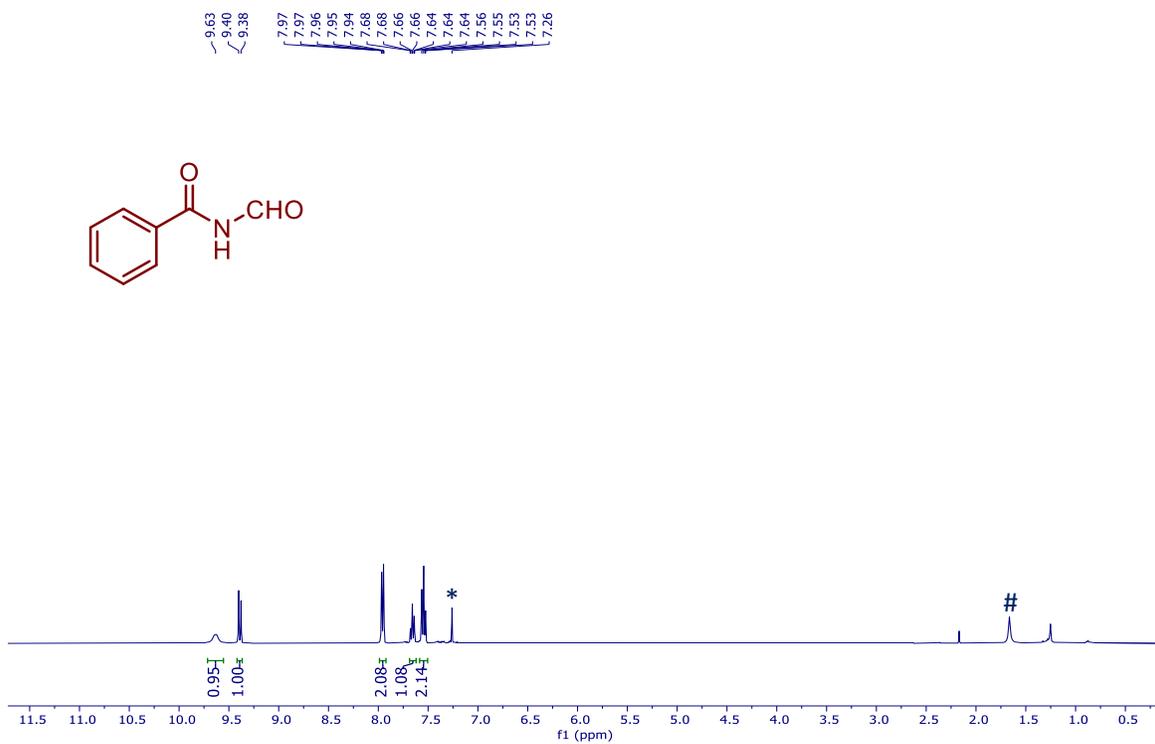
<sup>13</sup>C{<sup>1</sup>H} NMR of *N'*-phenylformohydrazide (compound-5a) in DMSO-d<sub>6</sub> (\*)



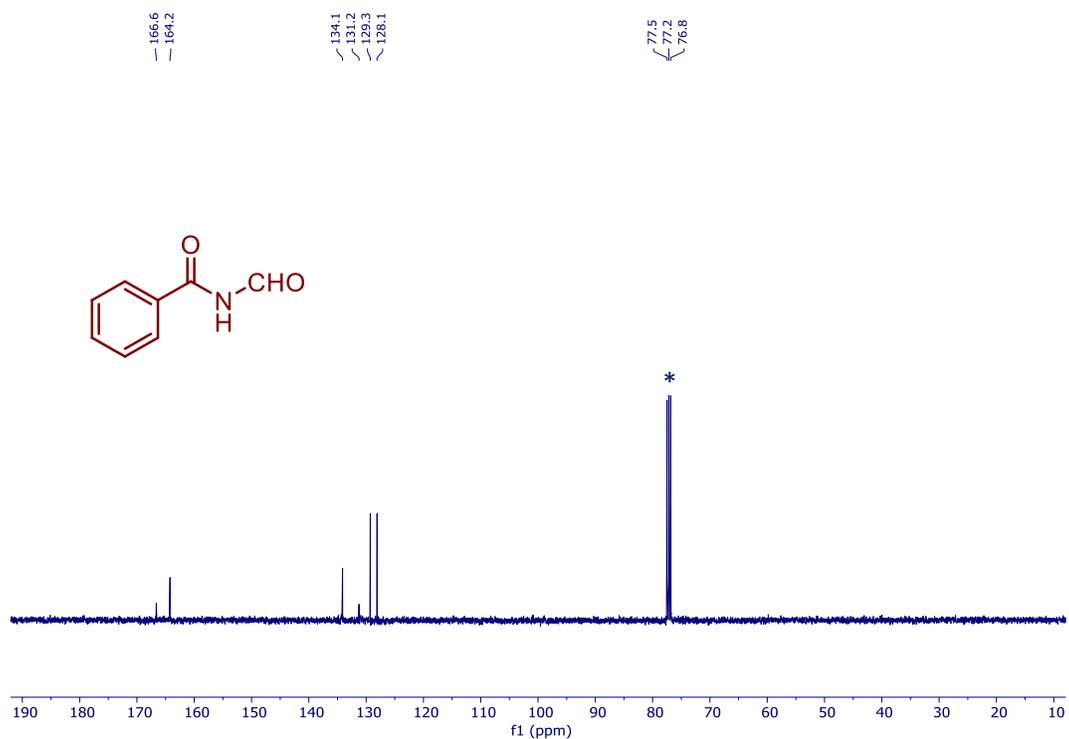
<sup>1</sup>H NMR of *N'*-(3,5-dinitrophenyl)formohydrazide (compound-5b) in DMSO-*d*<sub>6</sub> (\*). # indicates the solvent impurity of H<sub>2</sub>O in DMSO-*d*<sub>6</sub>



<sup>13</sup>C{<sup>1</sup>H} NMR of *N'*-(3,5-dinitrophenyl)formohydrazide (compound-5b) in DMSO-*d*<sub>6</sub> (\*)

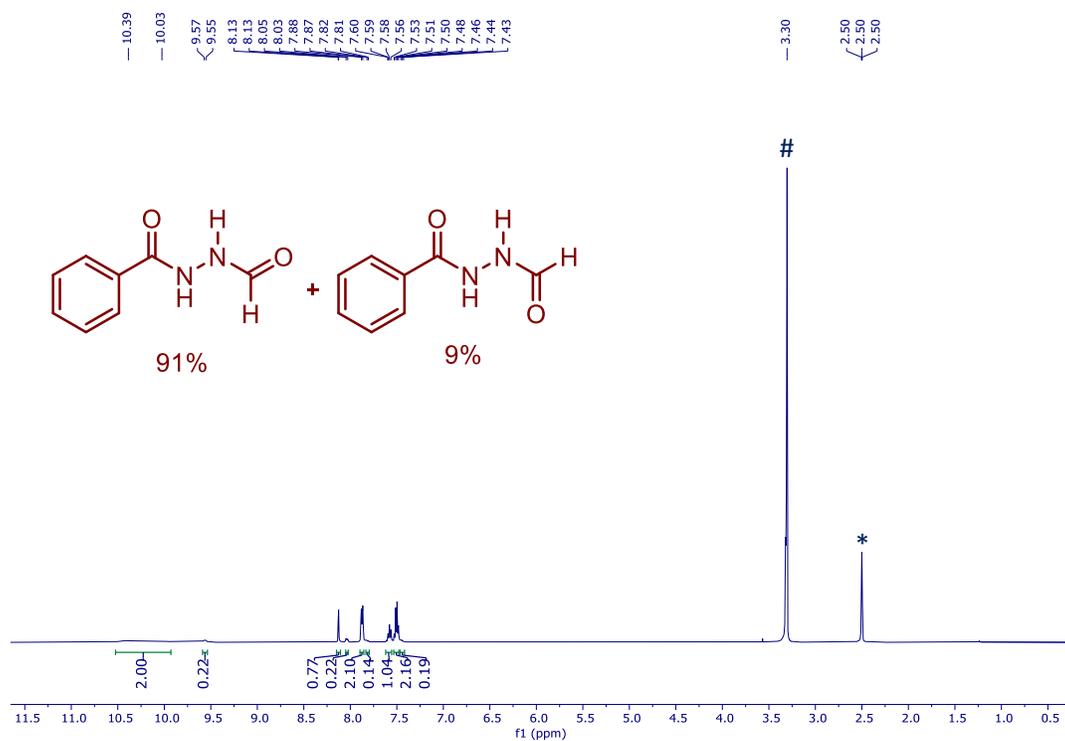


$^1\text{H}$  NMR of *N*-formylbenzamide (compound-5c) in  $\text{CDCl}_3$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{CDCl}_3$

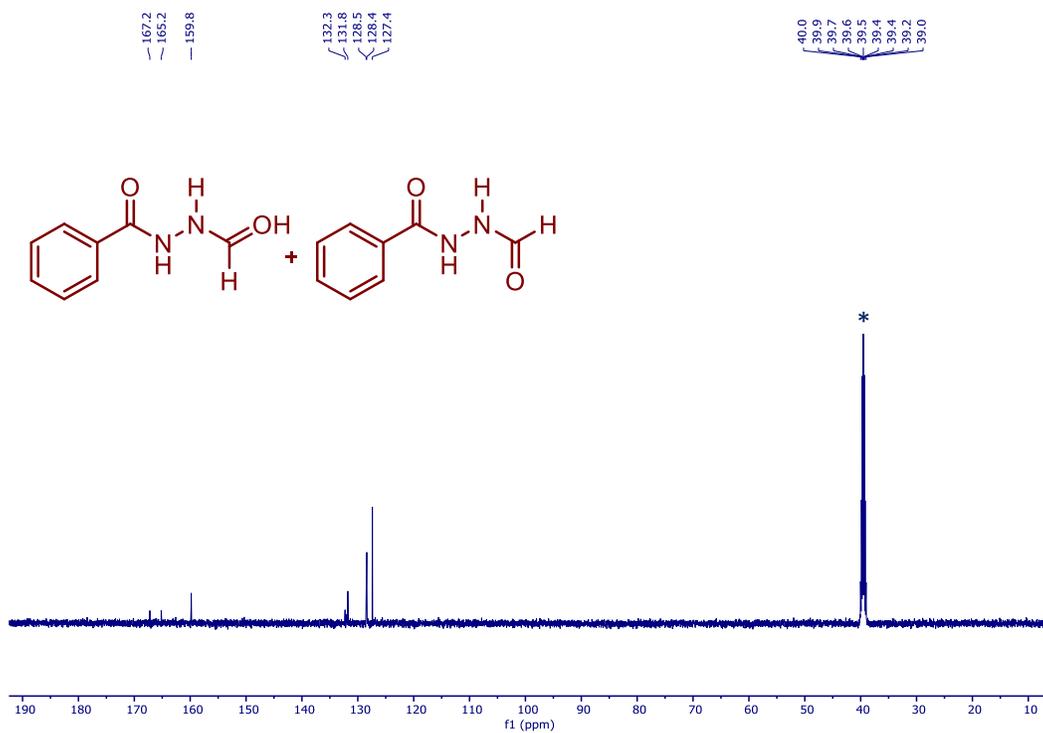


$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-formylbenzamide (compound-5c) in  $\text{CDCl}_3$  (\*)

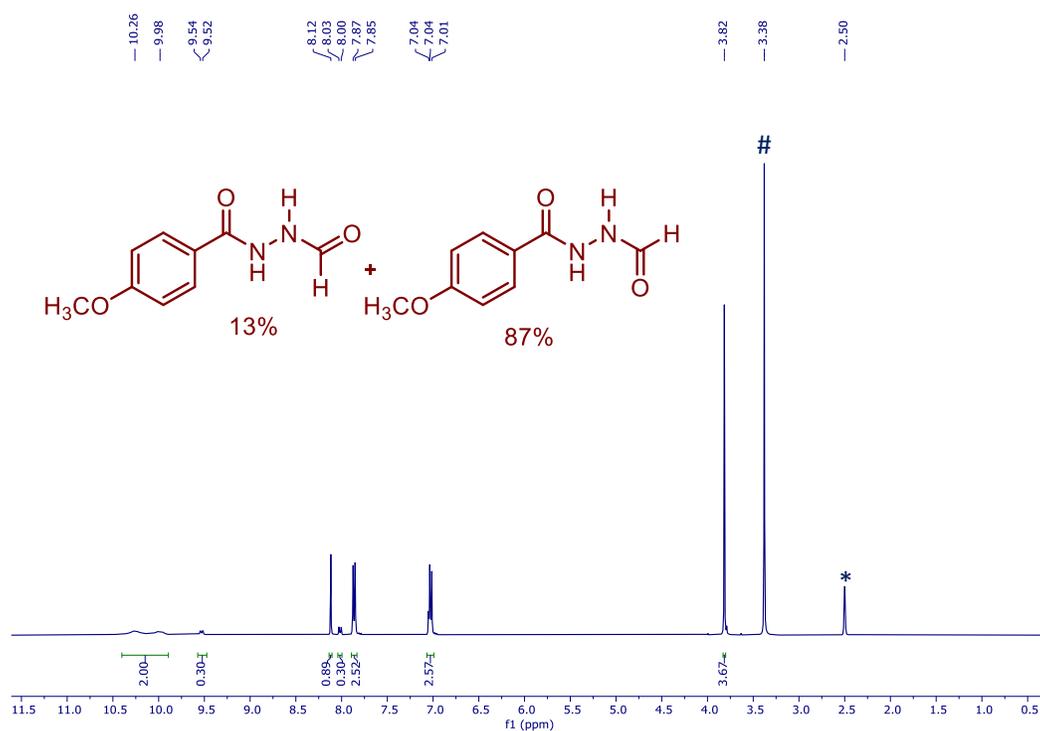




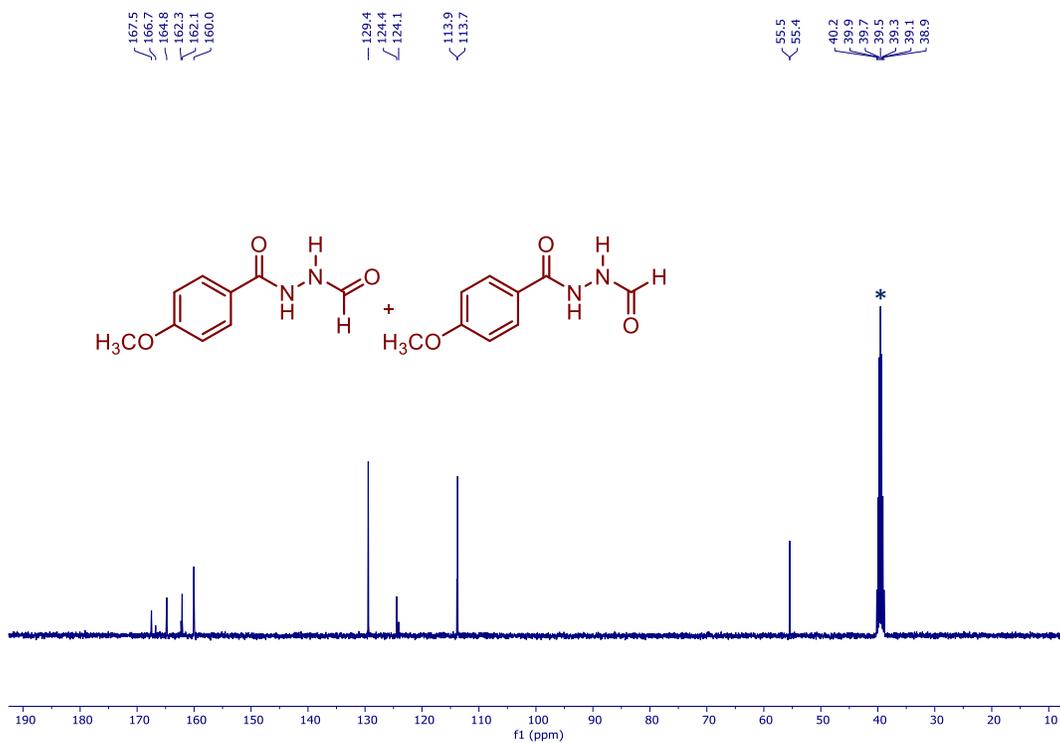
$^1\text{H}$  NMR of *N'*-formylbenzohydrazide (compound-5e) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



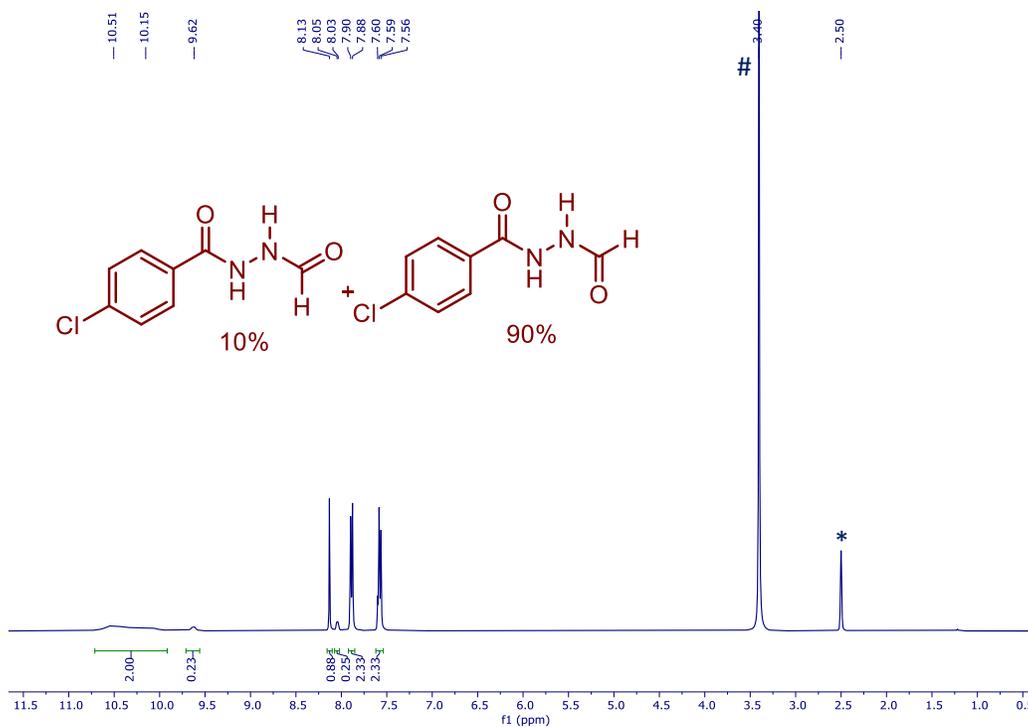
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N'*-formylbenzohydrazide (compound-5e) in  $\text{DMSO-}d_6$  (\*)



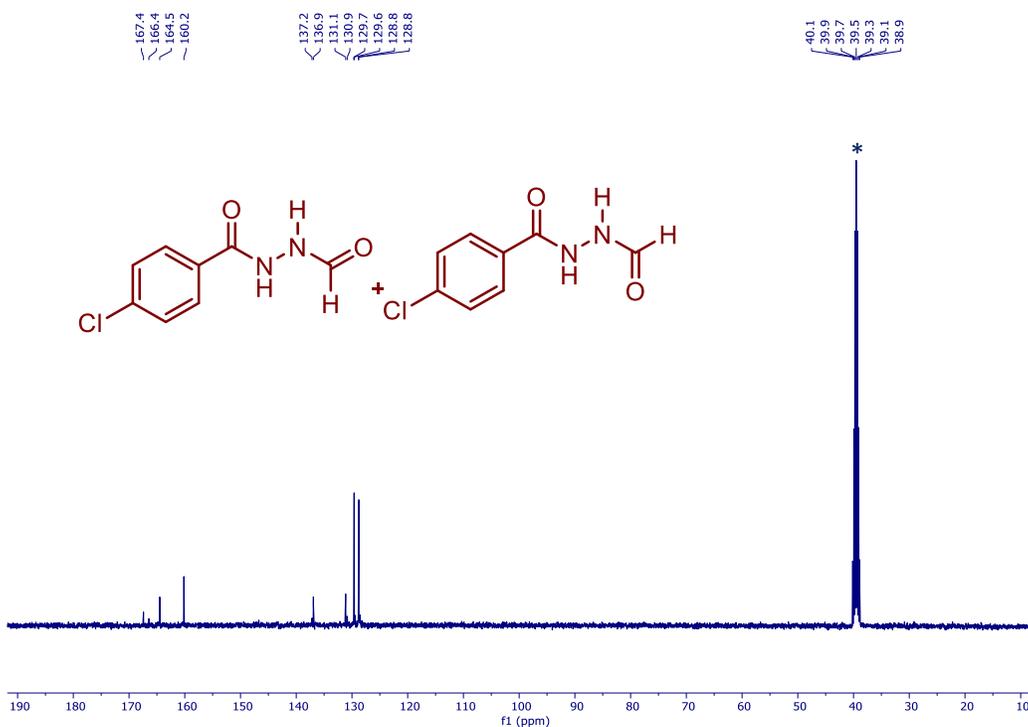
$^1\text{H}$  NMR of *N'*-formyl-4-methoxybenzohydrazide (compound-5f) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



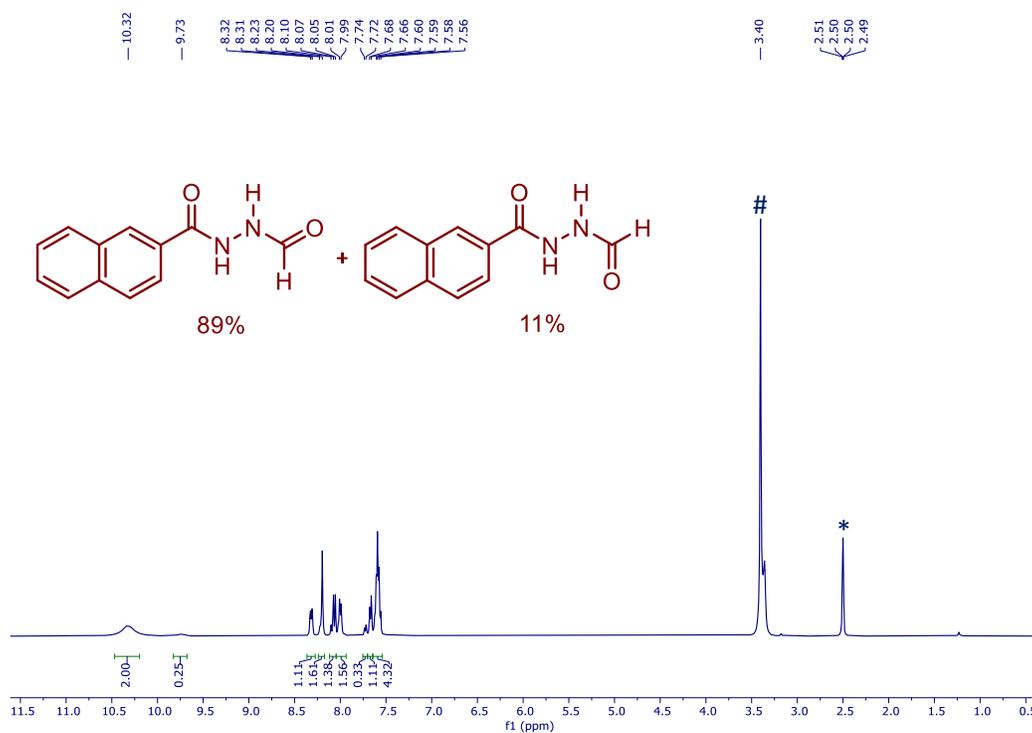
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N'*-formyl-4-methoxybenzohydrazide (compound-5f) in  $\text{DMSO-}d_6$  (\*)



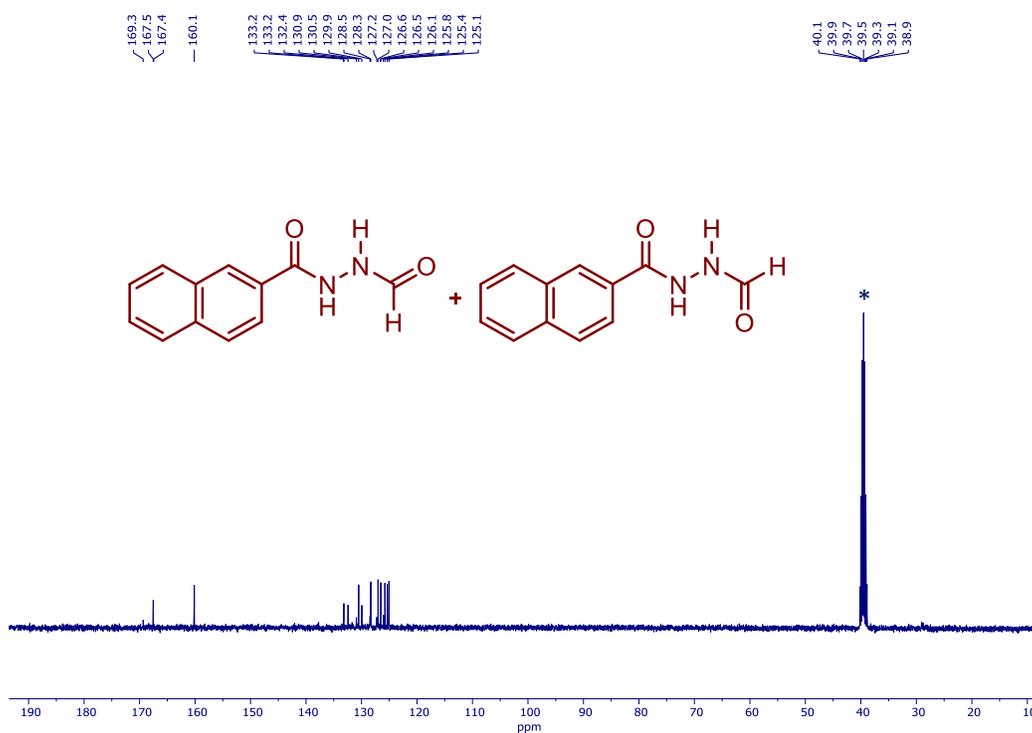
$^1\text{H}$  NMR of 4-chloro-N'-formylbenzohydrazide (compound-5g) in  $\text{DMSO-d}_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-d}_6$



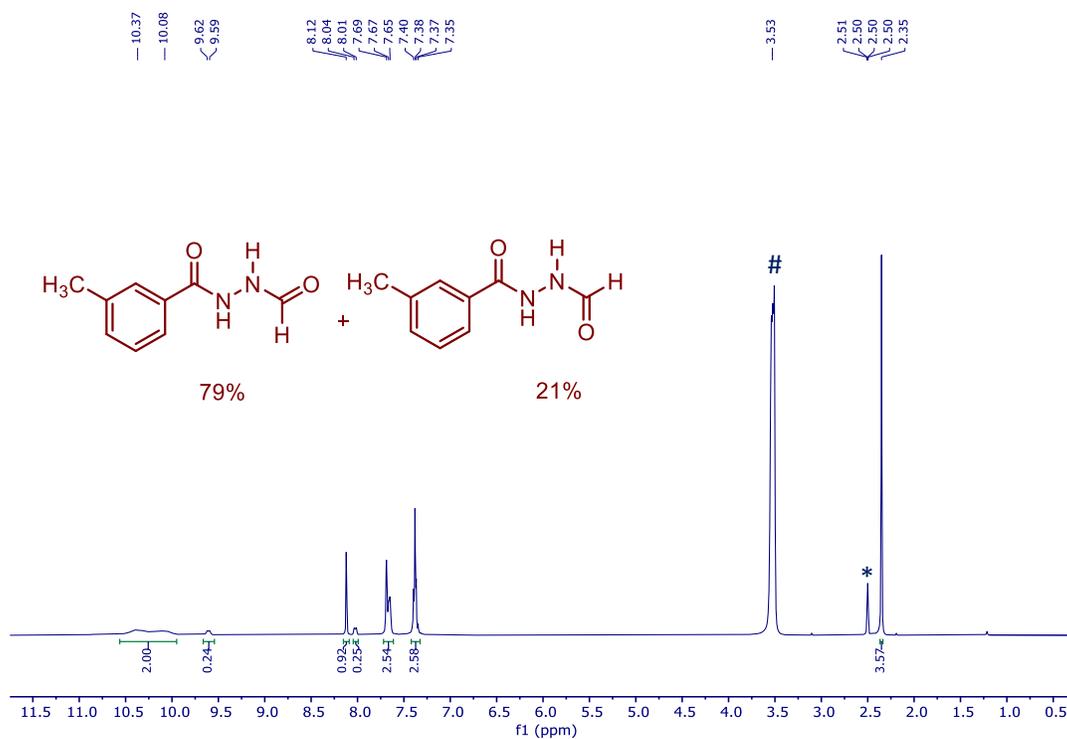
$^{13}\text{C}\{^1\text{H}\}$  NMR of 4-chloro-N'-formylbenzohydrazide (compound-5g) in  $\text{DMSO-d}_6$  (\*)



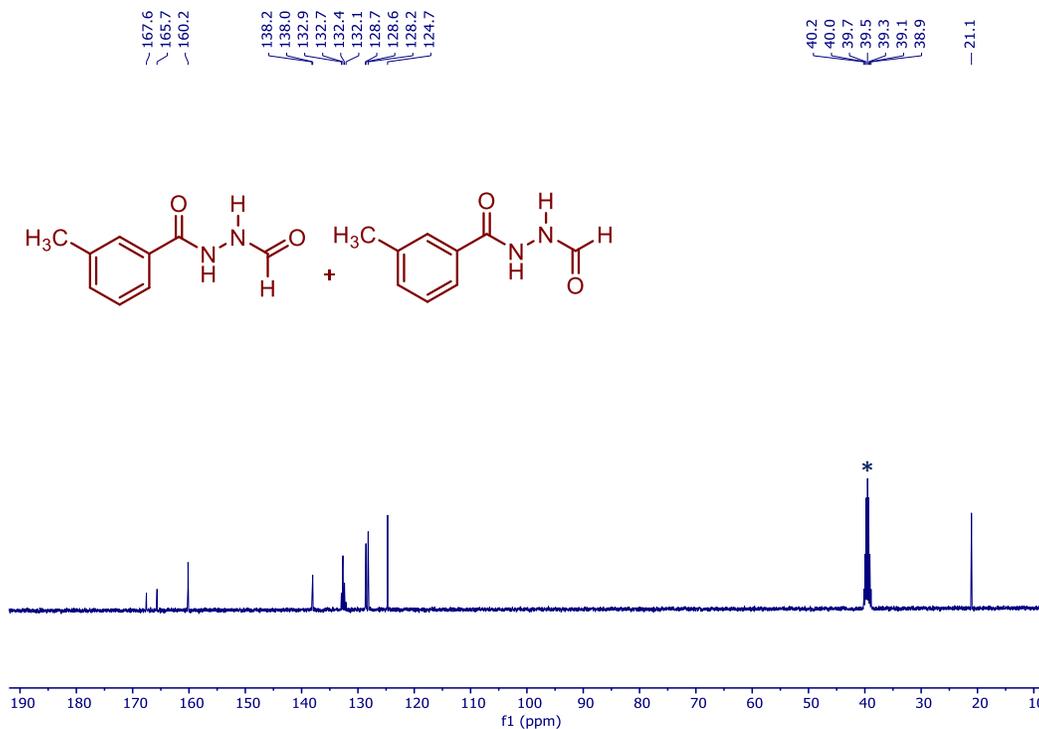
$^1\text{H}$  NMR of *N'*-formyl-1-naphthohydrazide (compound-5h) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



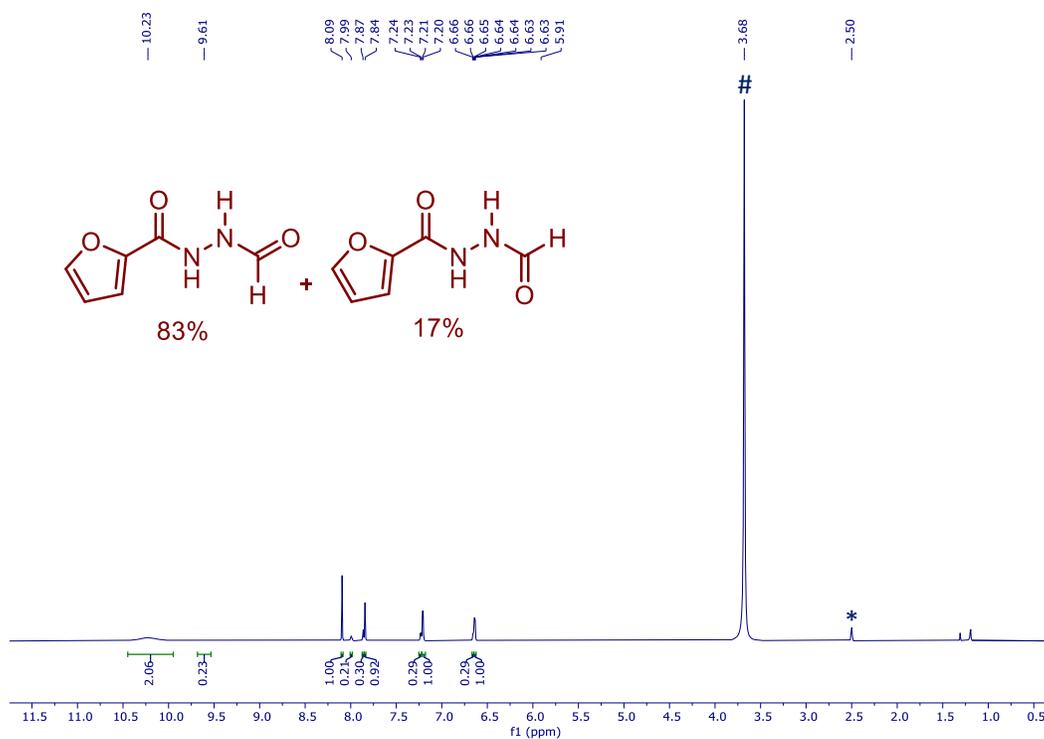
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N'*-formyl-1-naphthohydrazide (compound-5h) in  $\text{DMSO-}d_6$  (\*)



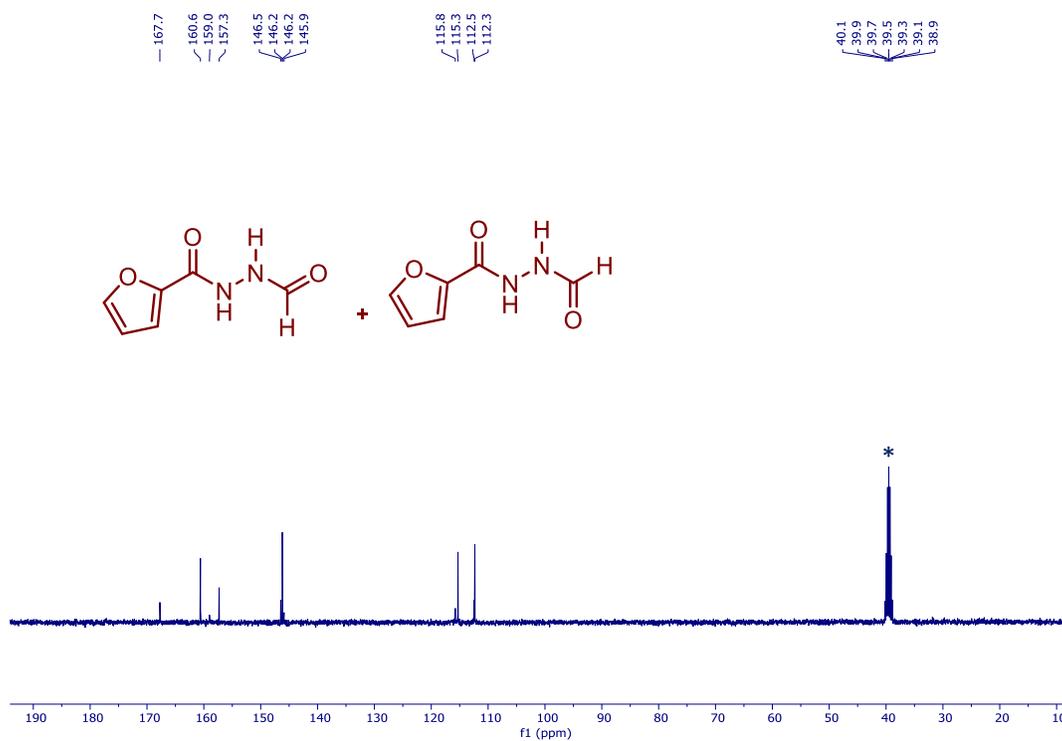
$^1\text{H}$  NMR of *N'*-formyl-3-methylbenzohydrazide (compound-5i) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



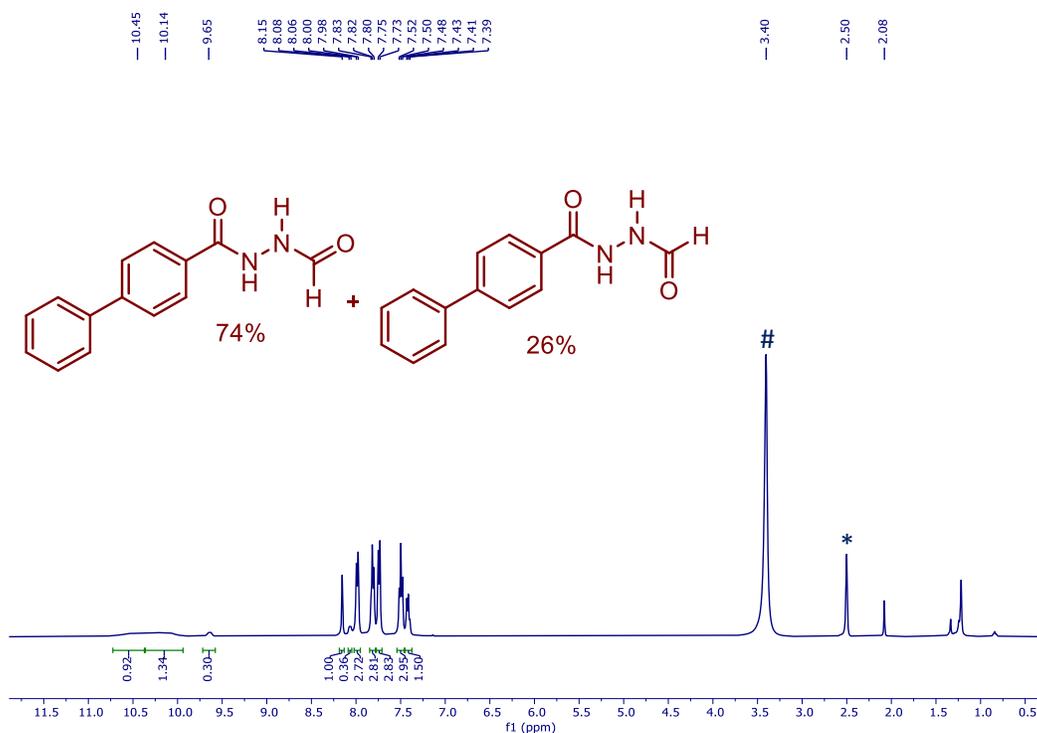
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N'*-formyl-3-methylbenzohydrazide (compound-5i) in  $\text{DMSO-}d_6$  (\*)



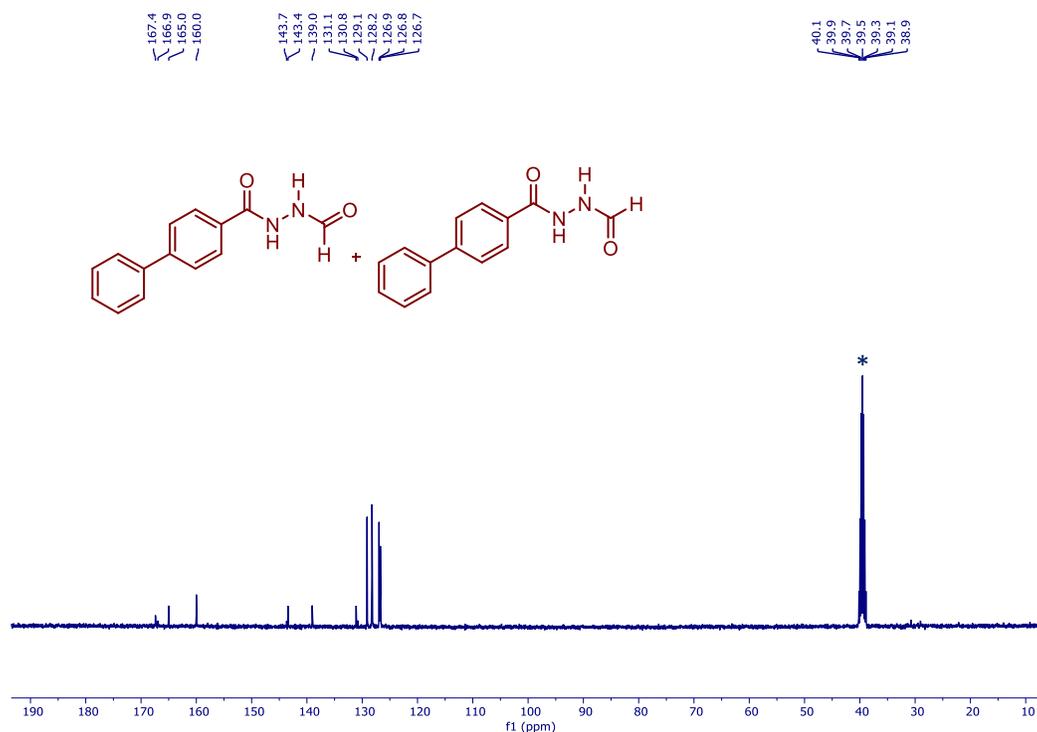
$^1\text{H}$  NMR of *N'*-formylfuran-2-carbohydrazide (compound-5j) in  $\text{DMSO-d}_6$  (\*)



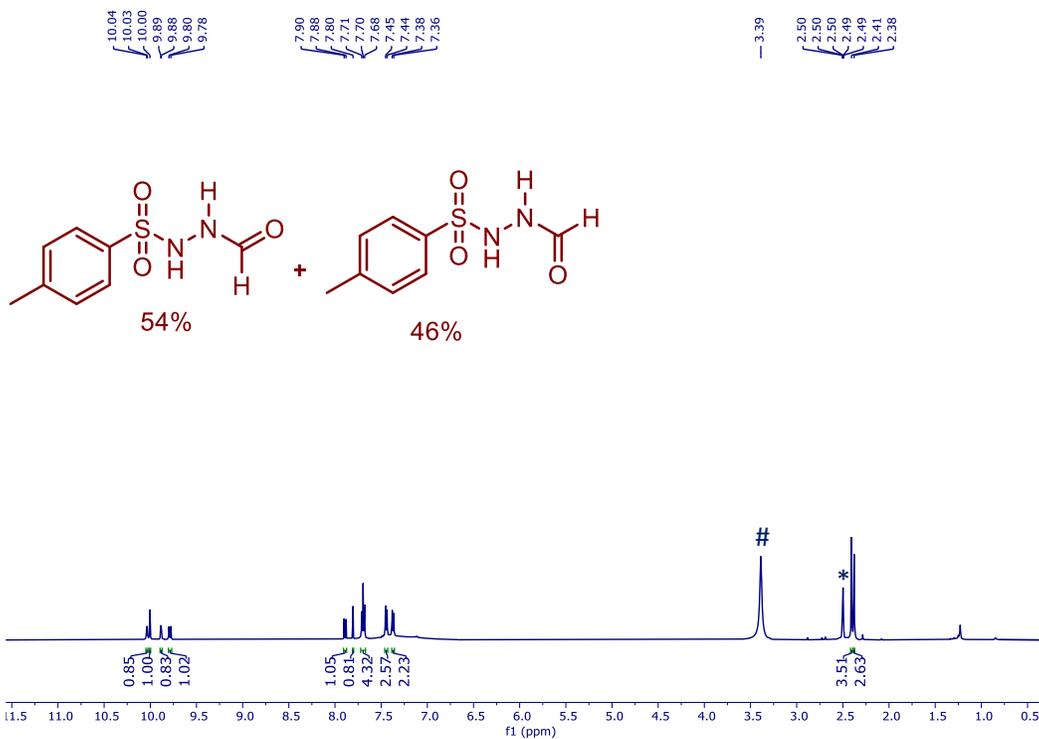
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N'*-formylfuran-2-carbohydrazide (compound-5j) in  $\text{DMSO-d}_6$  (\*)



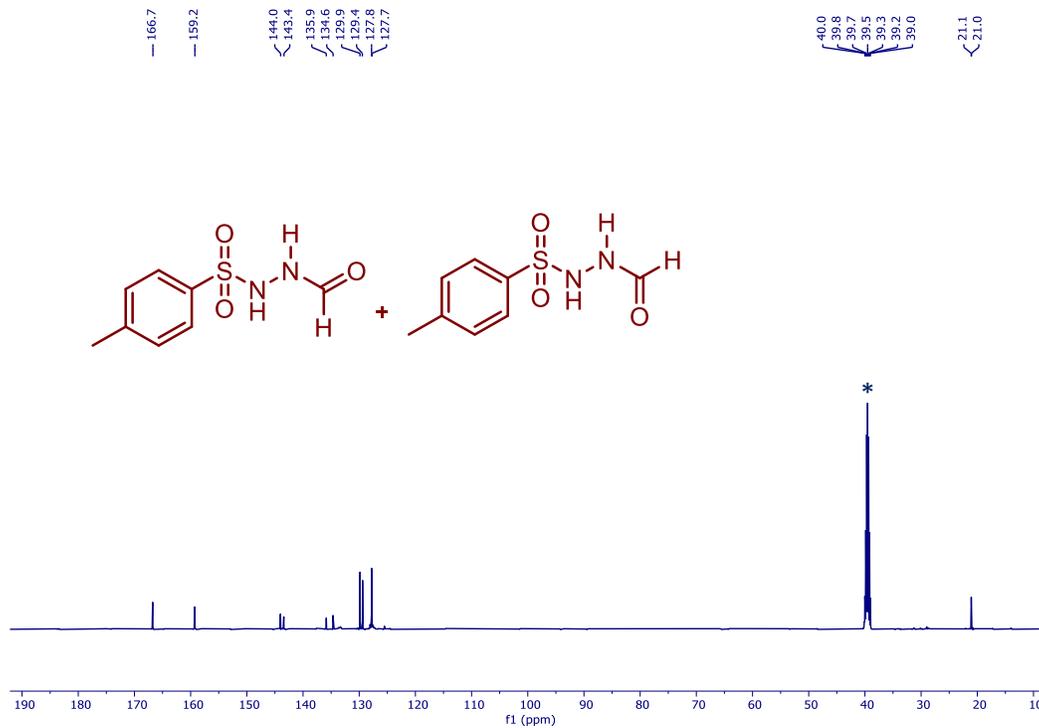
$^1\text{H}$  NMR of *N'*-formyl-[1,1'-biphenyl]-4-carbohydrazide (compound-5k) in  $\text{DMSO-d}_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-d}_6$



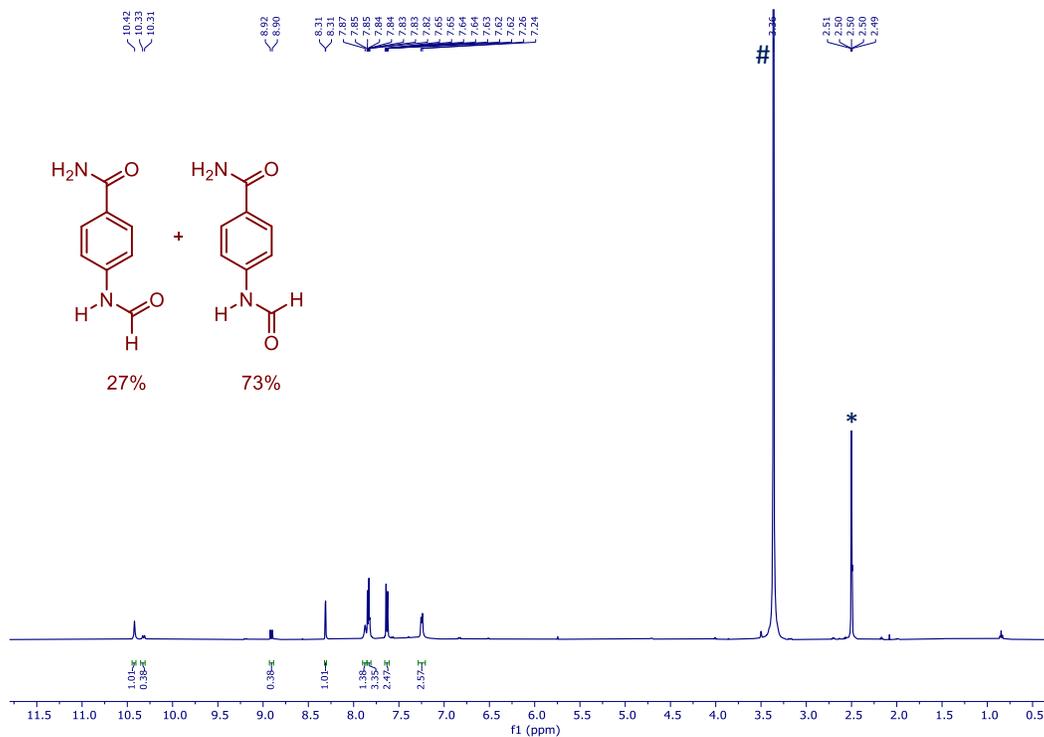
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N'*-formyl-[1,1'-biphenyl]-4-carbohydrazide (compound-5k) in  $\text{DMSO-d}_6$  (\*)



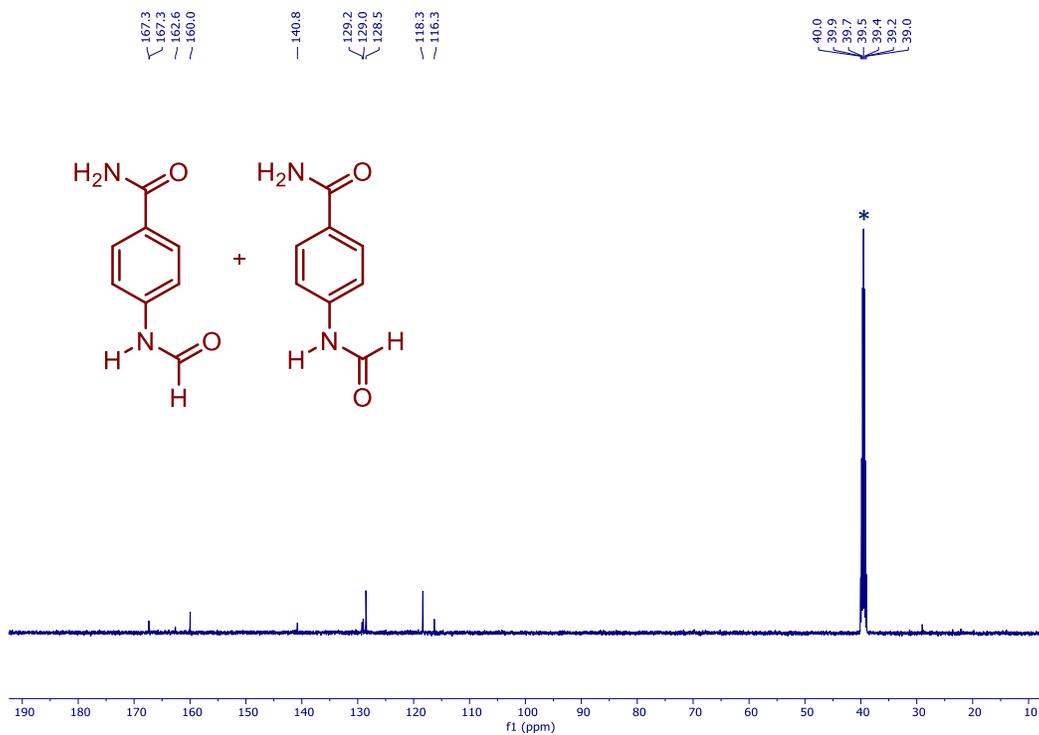
$^1\text{H}$  NMR of *N'*-formyl-4-methylbenzenesulfonylhydrazide (compound-5I) in  $\text{DMSO-}d_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-}d_6$



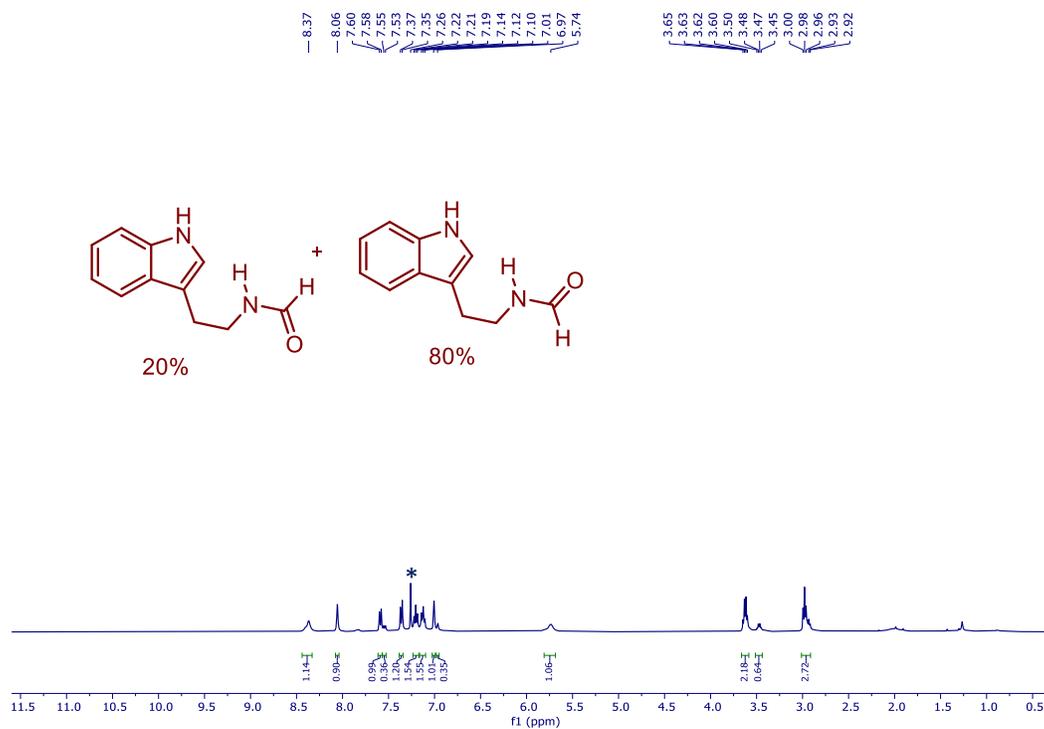
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N'*-formyl-4-methylbenzenesulfonylhydrazide (compound-5I) in  $\text{DMSO-}d_6$  (\*)



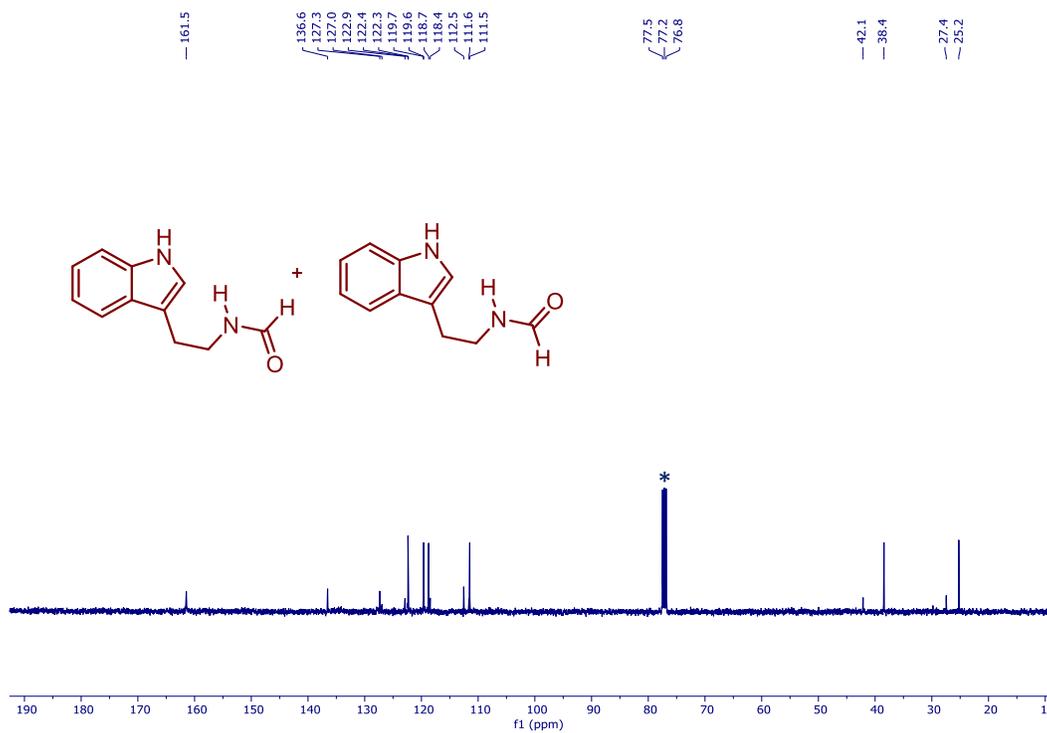
$^1\text{H}$  NMR of 4-formamidobenzamide (compound-7a) in  $\text{DMSO-d}_6$  (\*). # indicates the solvent impurity of  $\text{H}_2\text{O}$  in  $\text{DMSO-d}_6$



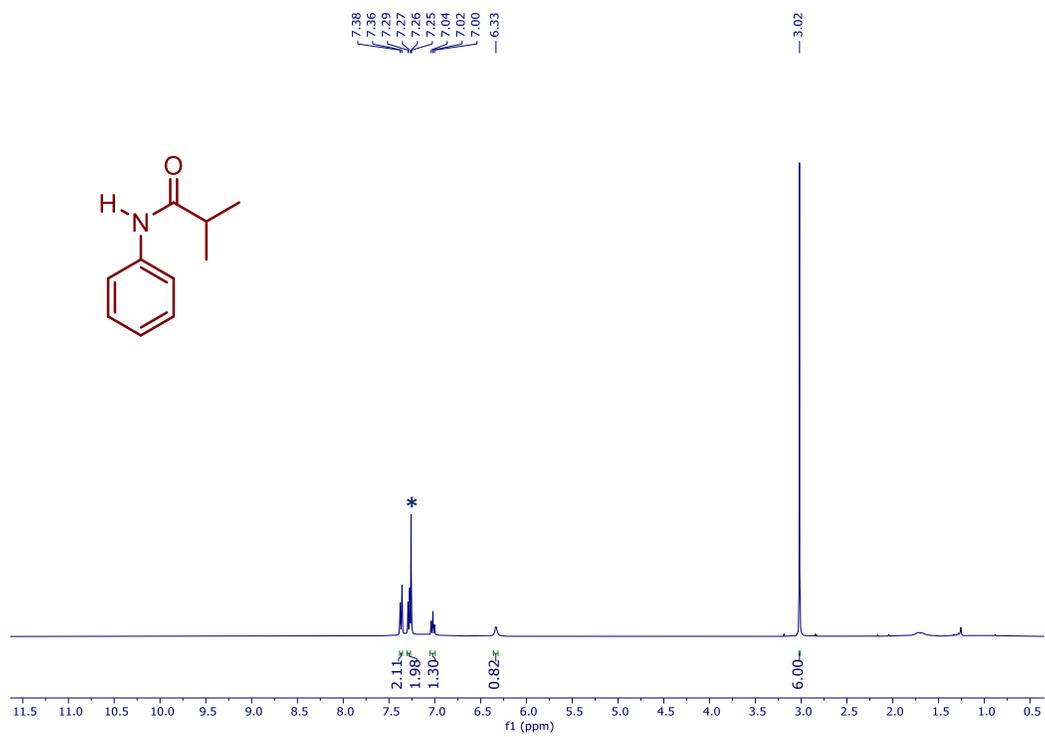
$^{13}\text{C}\{^1\text{H}\}$  NMR of 4-formamidobenzamide (compound-7a) in  $\text{DMSO-d}_6$  (\*)



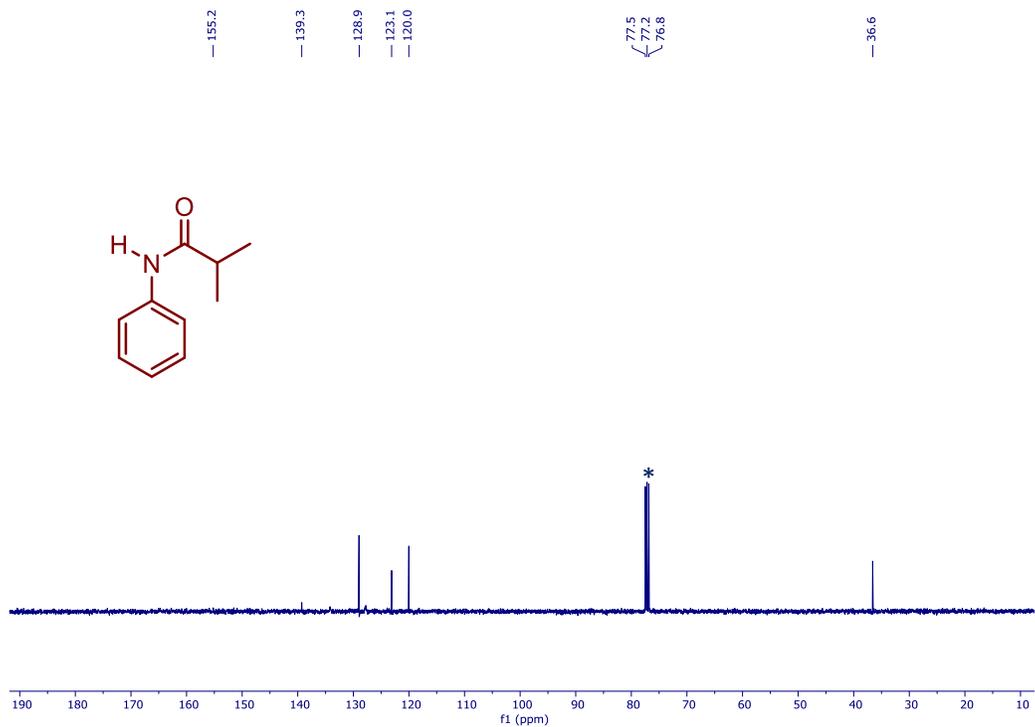
$^1\text{H}$  NMR of *N*-(2-(1*H*-indol-3-yl)ethyl)formamide (compound-**7b**) in  $\text{CDCl}_3$



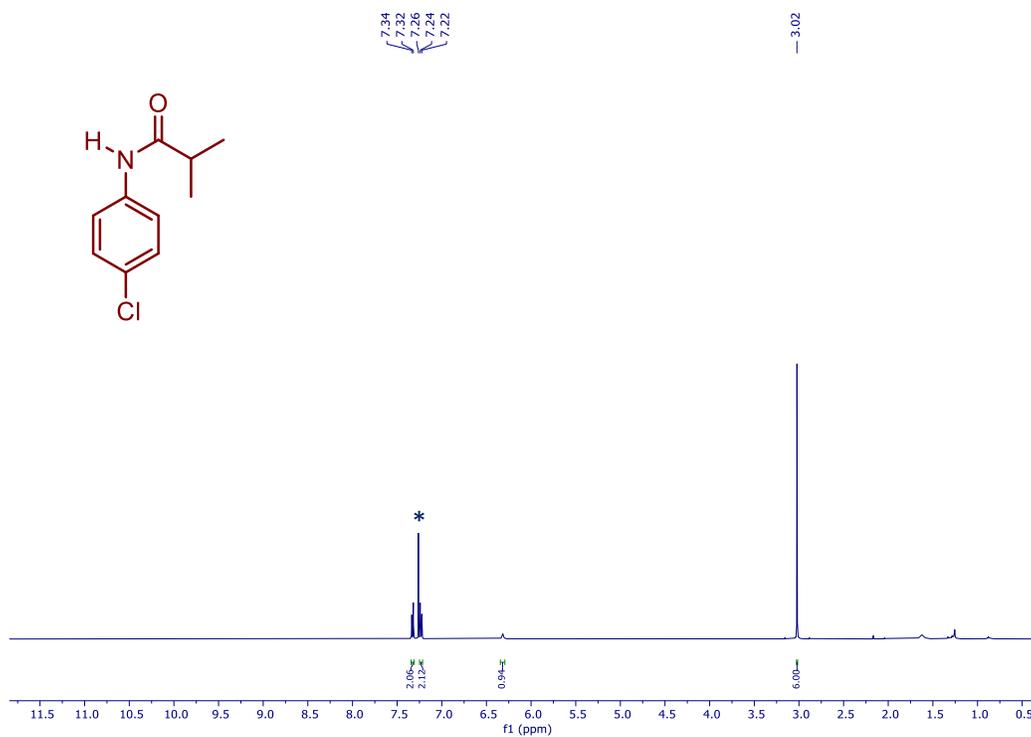
$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(2-(1*H*-indol-3-yl)ethyl)formamide (compound-**7b**) in  $\text{CDCl}_3$  (\*)



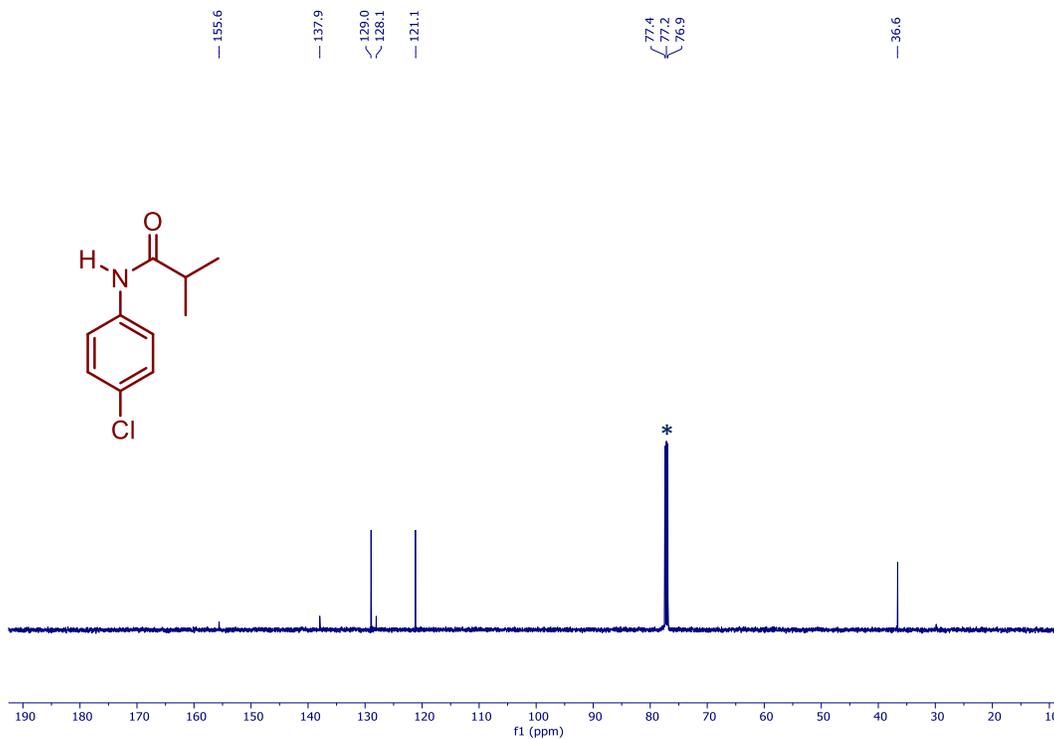
$^1\text{H}$  NMR of *N*-phenylisobutyramide (compound-**8a**) in  $\text{CDCl}_3$  (\*)



$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-phenylisobutyramide (compound-**8a**) in  $\text{CDCl}_3$  (\*)



$^1\text{H NMR}$  of *N*-(4-chlorophenyl)isobutyramide (compound-**8b**) in  $\text{CDCl}_3$  (\*)



$^{13}\text{C}\{^1\text{H}\}$  NMR of *N*-(4-chlorophenyl)isobutyramide (compound-**8b**) in  $\text{CDCl}_3$  (\*)

**Procedure for the intermolecular chemoselective formylation of amine:**

**Aniline and N-methyl aniline/benzamide/benzohydrazide:** An oven-dried 25 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol, 2 mol%), [L2-H]Br (9.1 mg, 0.025 mmol, 5 mol%), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 7.5 mol%), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad and the obtained clear filtrate was dried in the high vacuum to get the expected in situ generated Zn-L2 complex. To this, aniline (46.5 mg, 0.5 mmol), N-methyl aniline (53.6 mg, 0.5 mmol)/benzamide (60.5 mg, 0.5 mmol)/benzohydrazide (68.0 mg, 0.5 mmol), phenylsilane (123 μL, 1.0 mmol), and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 12 h at ambient temperature. After completion of the reaction, the desired product (**3a**) was isolated by column chromatography over silica gel using hexane/ethyl acetate as eluent in 78-82% (47.2-49.6 mg) yield and N-methyl aniline/benzamide/benzohydrazide was recovered in >99% yield.

**N-methyl aniline and benzohydrazide/phenylhydrazine:** An oven-dried 25 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol, 2 mol%), [L2-H]Br (9.1 mg, 0.025 mmol, 5 mol%), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 7.5 mol%), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad and the obtained clear filtrate was dried in the high vacuum to get the expected in situ generated Zn-L2 complex. To this, N-methyl aniline (53.6 mg, 0.5 mmol), benzohydrazide (68.0 mg, 0.5 mmol)/benzohydrazine (54.0 mg, 0.5 mmol), phenylsilane (123 μL, 1.0 mmol), and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 12 h at ambient temperature. After completion of the reaction, the desired product (**3k'**) was isolated by column chromatography over silica gel using hexane/ethyl acetate as eluent in 80-82% (54.0-55.4 mg) yield and benzohydrazide/phenylhydrazine was recovered in >99% yield.

## Control experiments for the formylation of amines using carbon dioxide and phenylsilane

**Radical scavenger experiments:** An oven-dried 25 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol, 2 mol%), [L2-H]Br (9.1 mg, 0.025 mmol, 5 mol%), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 7.5 mol%), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad and the obtained clear filtrate was dried in the high vacuum to get the expected in situ generated Zn-L2 complex. To this, aniline (46.5 mg, 0.5 mmol), phenylsilane (123 μL, 1.0 mmol), radical scavengers (0.25-0.5 mmol) and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 12 h at ambient temperature. After completion of the reaction, the desired product **3a** was isolated by column chromatography over silica gel using hexane/ethyl acetate as eluent in 80-85% yields.

**Procedure for mercury dropping test:** An oven-dried 25 mL pressure tube was charged with Zn(OAc)<sub>2</sub> (1.8 mg, 0.01 mmol, 2 mol%), [L2-H]Br (9.1 mg, 0.025 mmol, 5 mol%), and KO<sup>t</sup>Bu (4.2 mg, 0.0375 mmol, 7.5 mol%), followed by the addition of THF (2 mL). Then, the tube was kept in oil bath at 80 °C and heated for 12 h. After that, the reaction mixture was cooled, filtered through a celite pad and the obtained clear filtrate was dried in high vacuum to get the expected in situ generated Zn-L2 complex. To this, aniline (46.5 mg, 0.5 mmol), phenylsilane (123 μL, 1.0 mmol), mercury (40 mg, 2 mmol, 4 equiv. w.r.t. substrate) and acetonitrile (2 mL) were added and the resulted reaction mixture was then degassed by three freeze-pump-thaw cycle, and exposed to carbon dioxide (1 bar). The closed pressure tube was then stirred for 12 h at ambient temperature. After completion of the reaction, the desired product **3a** was isolated in 80% by column chromatography over silica gel using hexane/ethyl acetate as eluent.

## In situ NMR monitoring experiment

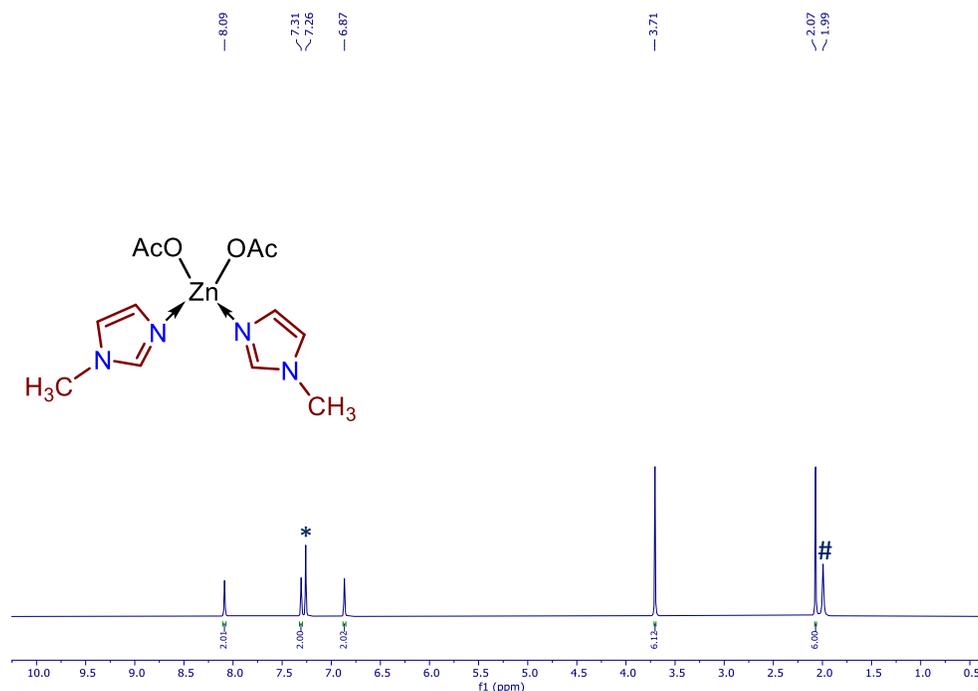
### Procedure for stepwise formylation of aniline with CO<sub>2</sub> using complex **1**

Isolated catalyst **1** (10 mg, 0.029 mmol) and phenylsilane (356 μL, 2.889 mmol) were taken in a Young NMR tube inside the glove box. Subsequently, CD<sub>3</sub>CN (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 multinuclear NMR analysis (Figure S4). Further, the reaction mixture was

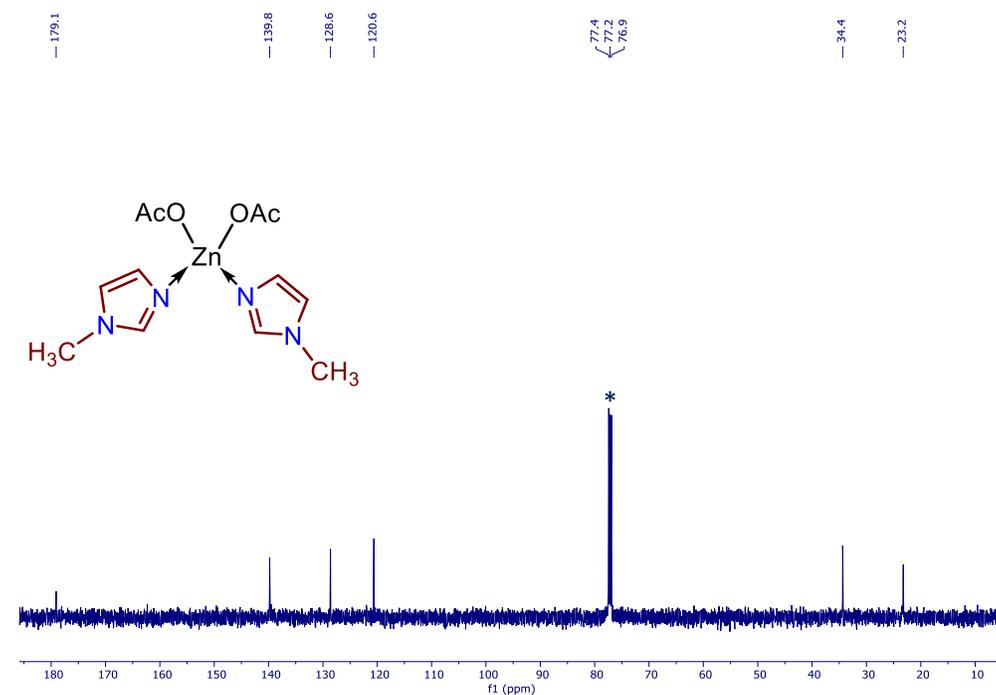
degassed followed by the exposure to carbon dioxide (1 bar pressure) and stirred for 1-2 h at ambient temperature (the reaction mixture was analyzed by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy, Figure S5-S8). After subsequent addition of aniline (134.1 mg, 1.44 mmol) into the same Young NMR tube, the reaction mixture was stirred at room temperature for 2 h and the outcome was monitored by  $^1\text{H}$  NMR spectroscopy (Figure S9-S10).

### Procedure for stepwise formylation of aniline with $\text{CO}_2$ using in-situ generated Zn-NHC catalyst

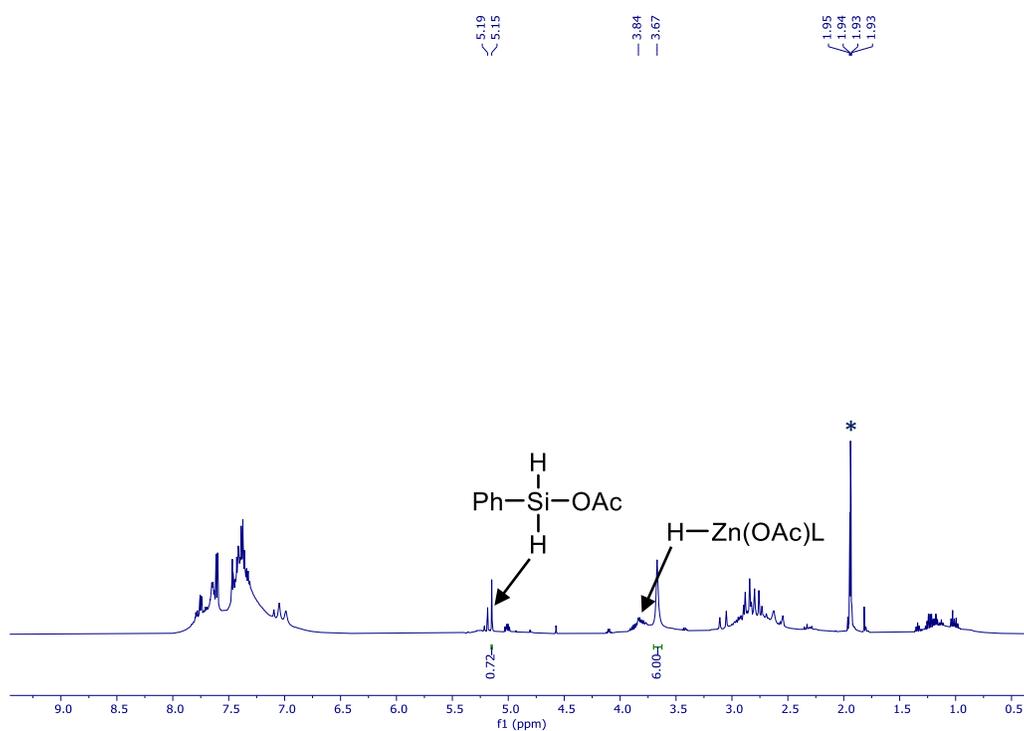
*In-situ* generated catalyst (10 mg,  $\sim 0.018$  mmol) and phenylsilane (226  $\mu\text{L}$ , 1.833 mmol) were taken in a Young NMR tube inside the glove box. Subsequently,  $\text{CD}_3\text{CN}$  (0.5 mL) was added and the tube was closed with a PTFE stopper and allowed to stir at room temperature for 3 h. The mixture was monitored using multinuclear NMR analysis (Figure S13). Further, the reaction mixture was degassed followed by the exposure to  $\text{CO}_2$  (1 bar) and stirred for 1-2 h at ambient temperature (the reaction mixture was analyzed by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy, Figure S14-S15). After subsequent addition of aniline/phenylhydrazine/phenylhydrazide/benzamide (0.916 mmol) into the same Young NMR tube, the reaction mixture was stirred at room temperature for 2 h and the outcome was monitored by  $^1\text{H}$  NMR spectroscopy (Figure S16-S23).



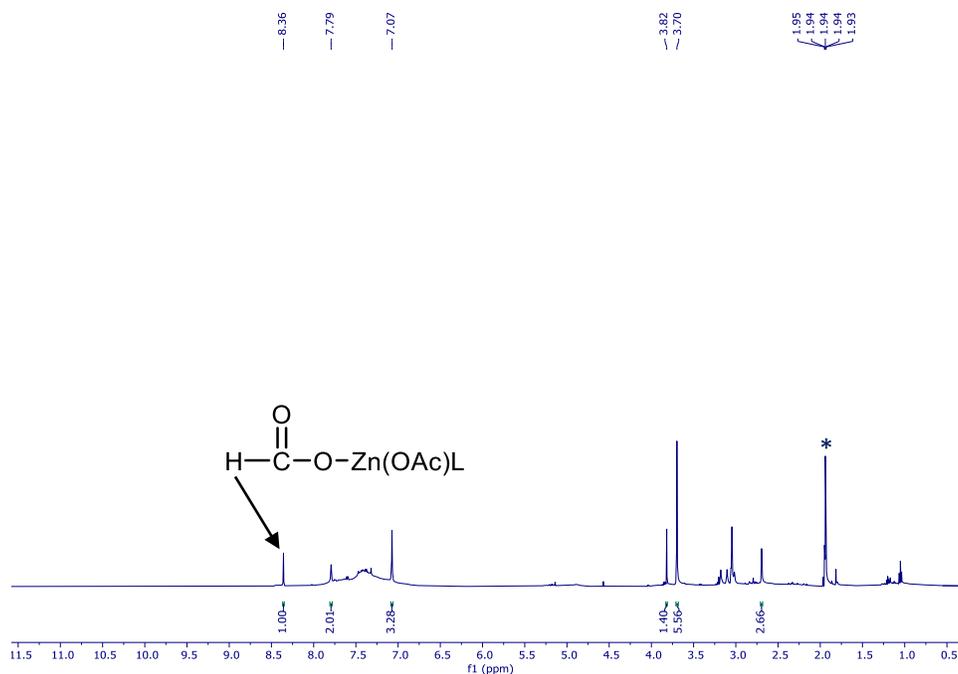
**Figure S2.**  $^1\text{H}$  NMR spectrum of the complex **1** in  $\text{CDCl}_3$  (\*). # indicates the solvent impurity of acetone



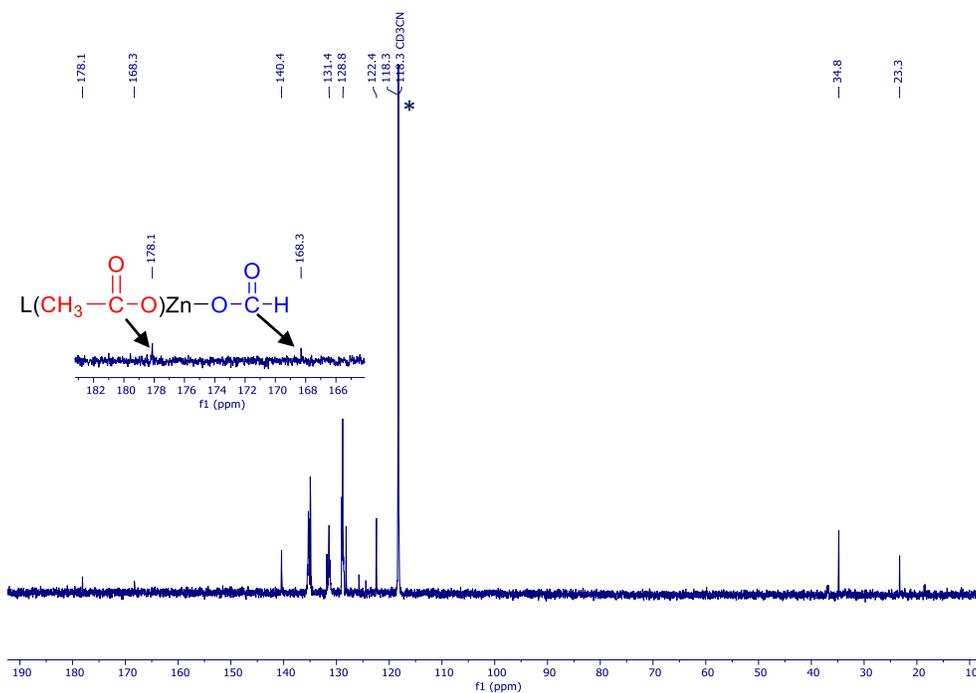
**Figure S3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the complex **1** in  $\text{CDCl}_3$  (\*)



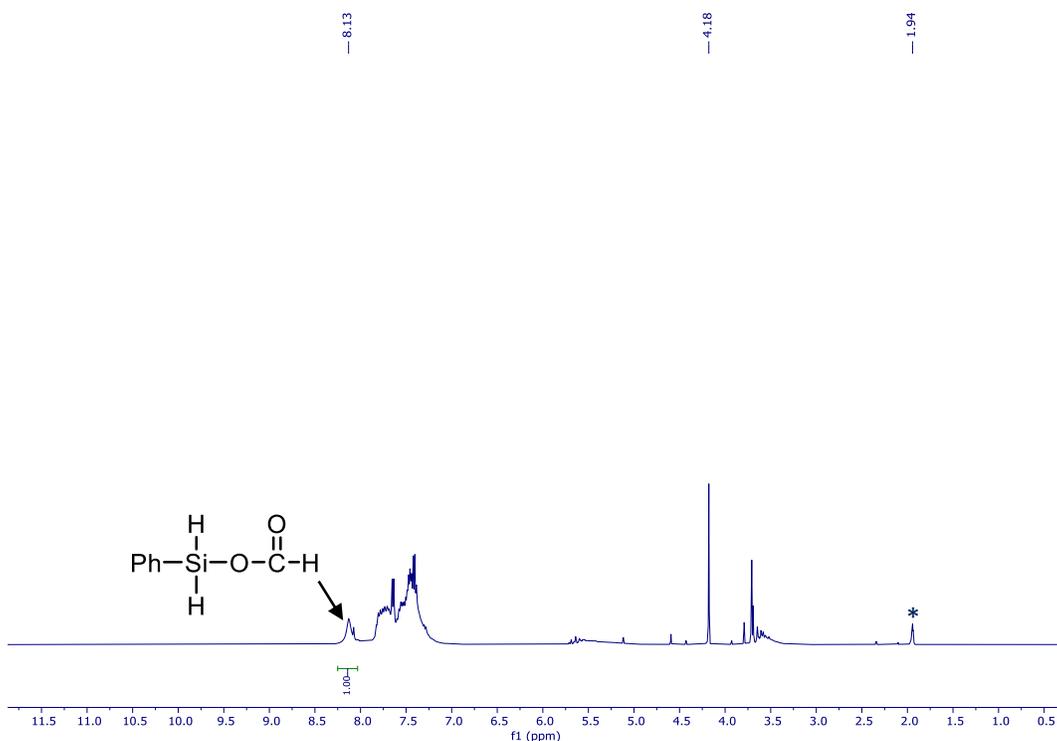
**Figure S4.**  $^1\text{H}$  NMR spectrum of the reaction mixture for the reaction between complex **1** and phenylsilane in  $\text{CD}_3\text{CN}$  (\*) showing the formation of a Zn-H complex



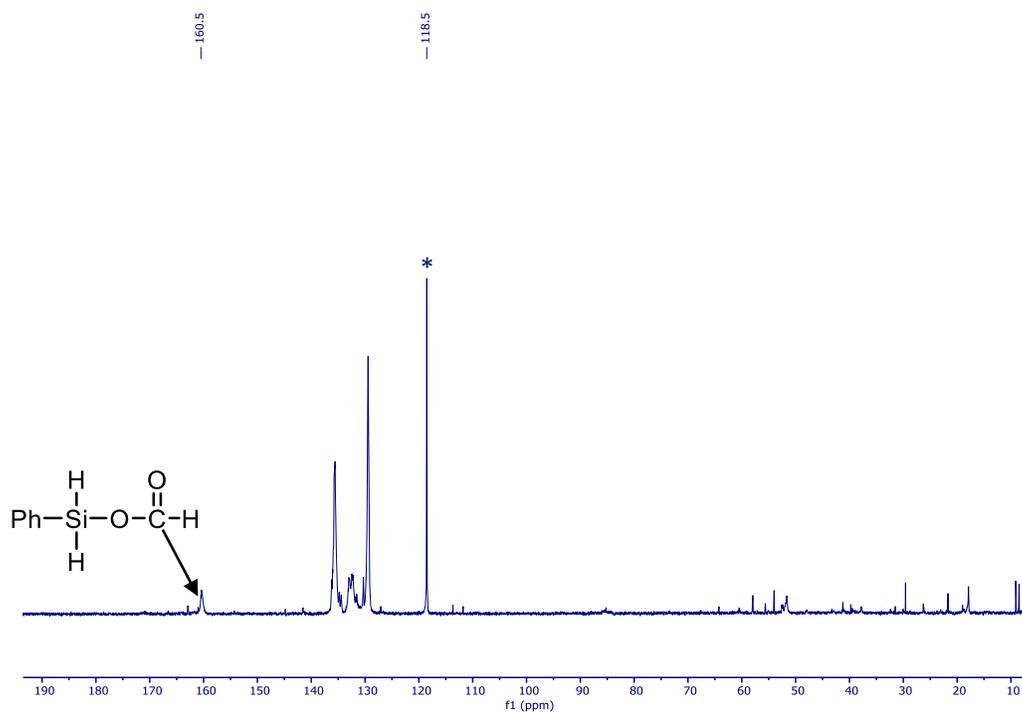
**Figure S5.**  $^1\text{H}$  NMR spectrum of the reaction mixture for a reaction between complex **1** and phenylsilane in  $\text{CD}_3\text{CN}$  (\*) after passing  $\text{CO}_2$  showing the formation of a Zn-formate complex after 1 h



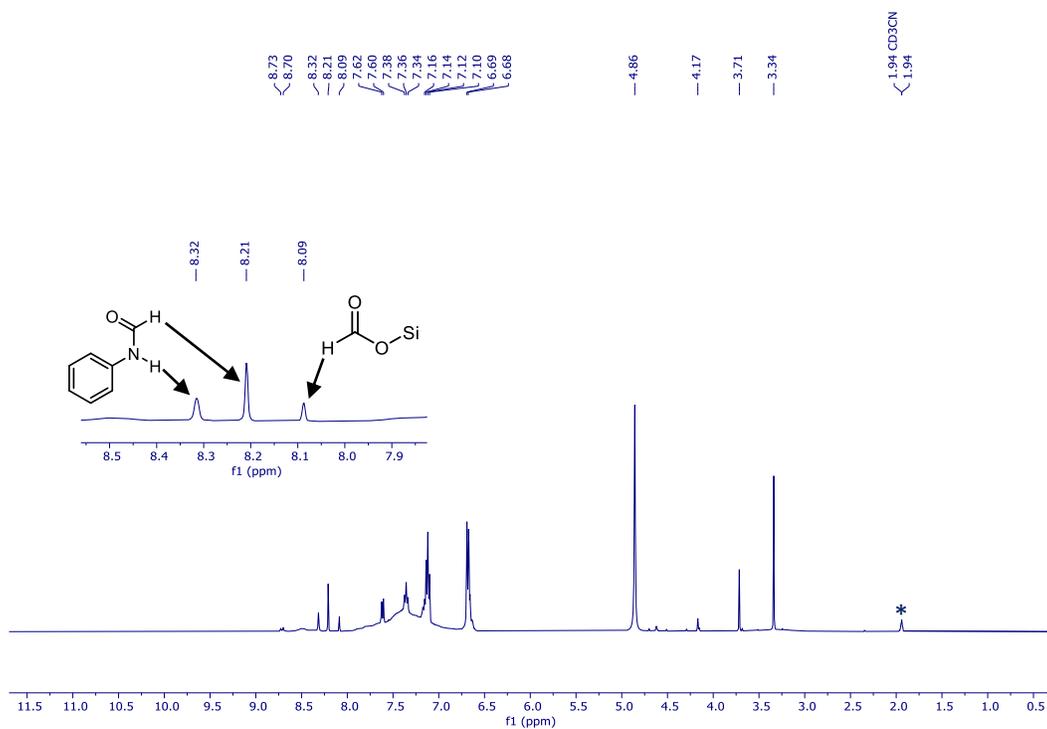
**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the reaction mixture for the reaction between complex **1** and phenylsilane in  $\text{CD}_3\text{CN}$  (\*) after passing  $\text{CO}_2$  showing the formation of a Zn-formate complex after 1 h



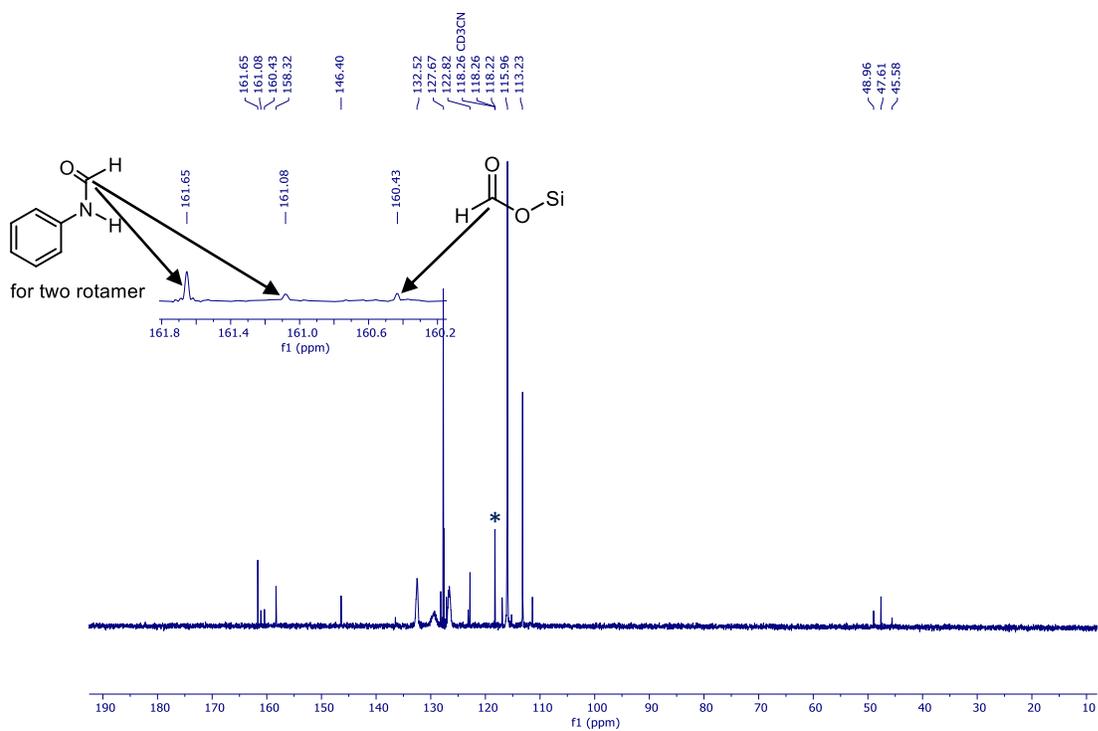
**Figure S7.**  $^1\text{H}$  NMR spectrum of the above reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after 3 h showing the formation of a formoxysilane intermediate



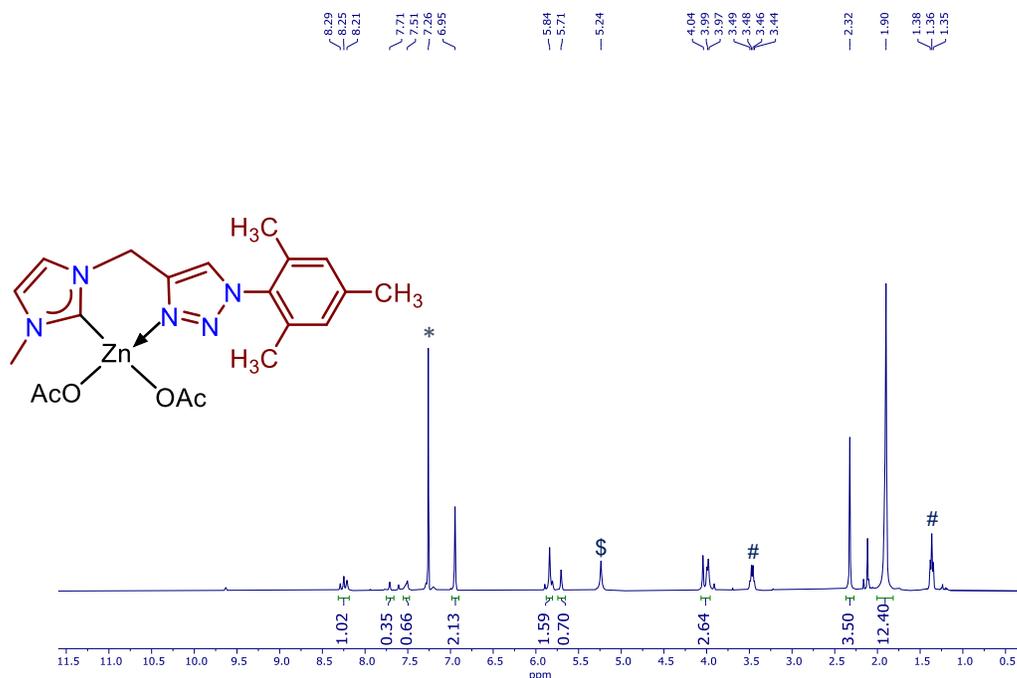
**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the above reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after 3 h showing the formation of a formoxysilane intermediate



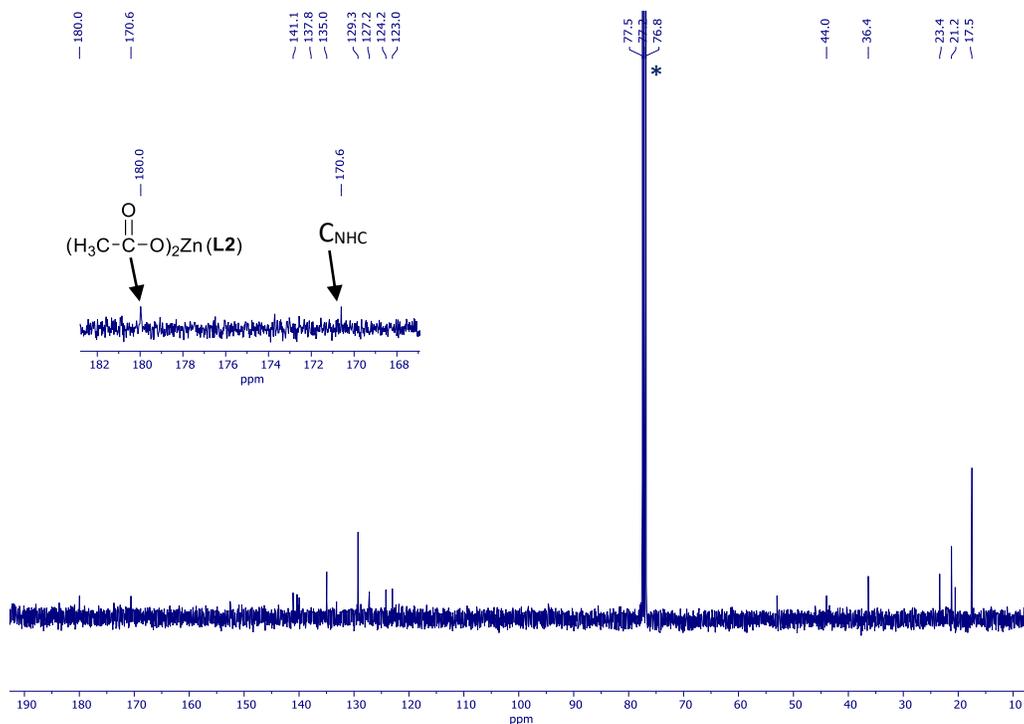
**Figure S9.**  $^1\text{H}$  NMR spectrum of the same reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after the addition of 1 equiv. aniline indicating the formation of the *N*-formylated species **3a**



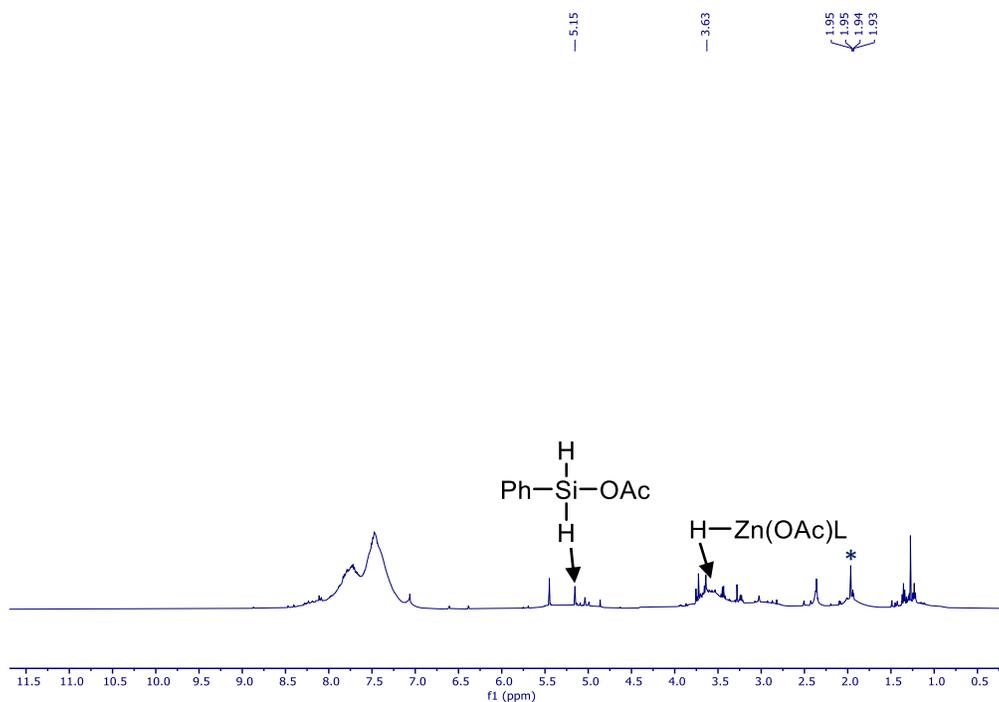
**Figure S10.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after the addition of 1 equiv. aniline indicating the formation of the *N*-formylated species **3a**



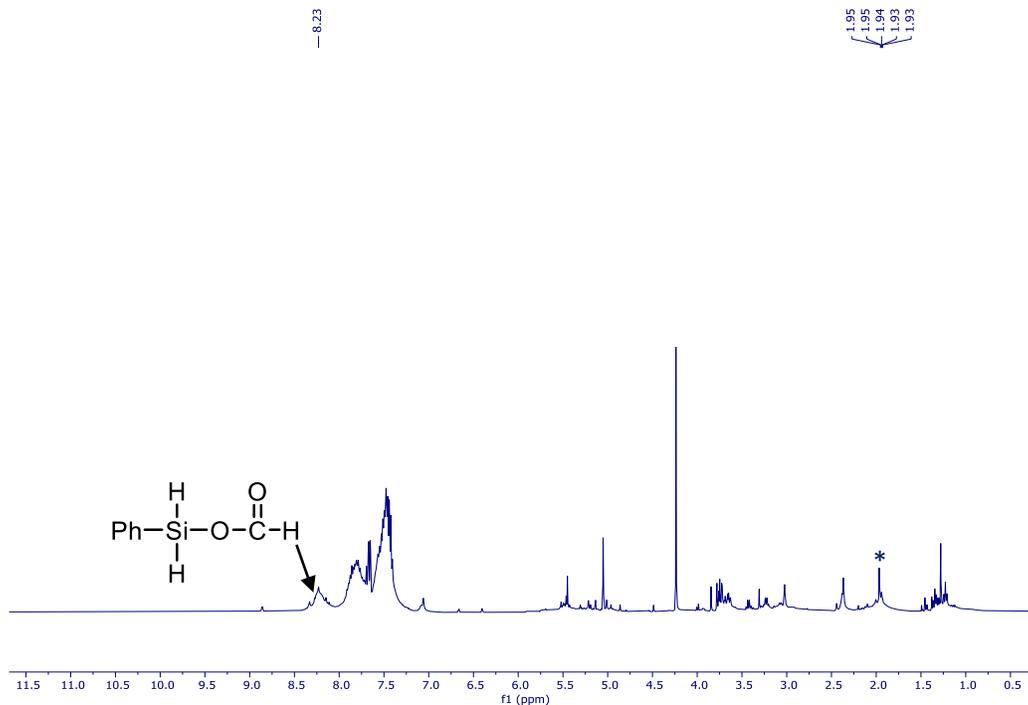
**Figure S11.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  (\*) of an attempted synthesis of Zn-L2 Complex from the reaction of  $\text{Zn}(\text{OAc})_2$  and  $[\text{L2-H}]\text{Br}$  using base  $\text{KO}^t\text{Bu}$ . \$ and # indicate the solvent impurity of  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{O}$ , respectively.



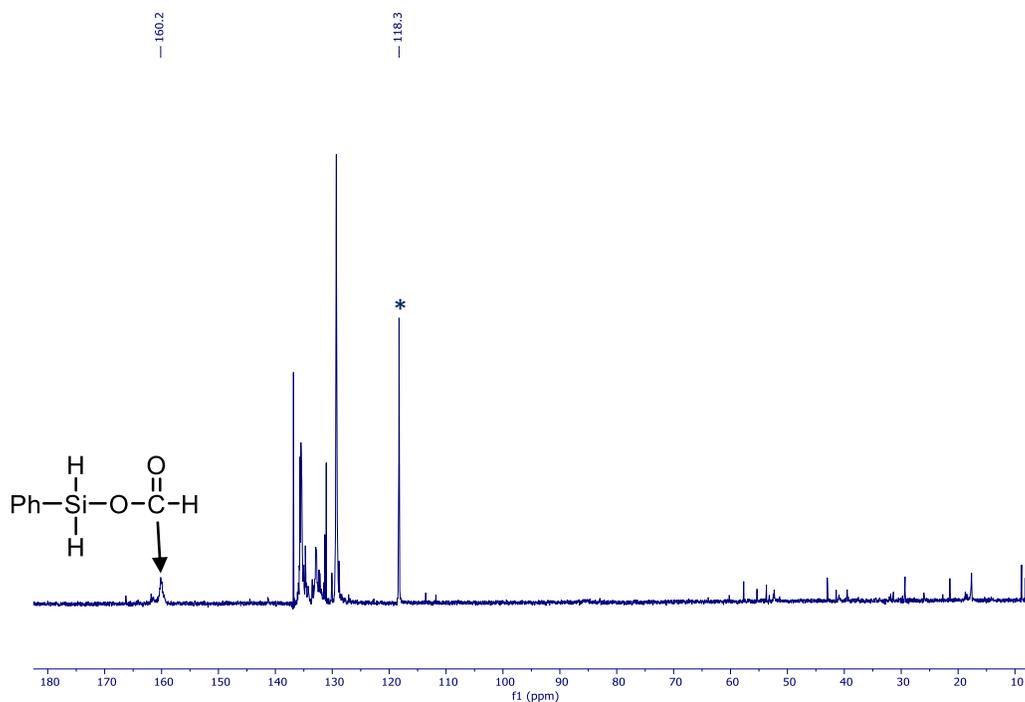
**Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of an attempted synthesis of Zn-L2 Complex in  $\text{CDCl}_3$  (\*) from the reaction of  $\text{Zn}(\text{OAc})_2$  and  $[\text{L2-H}]\text{Br}$  using base  $\text{KO}^t\text{Bu}$ .



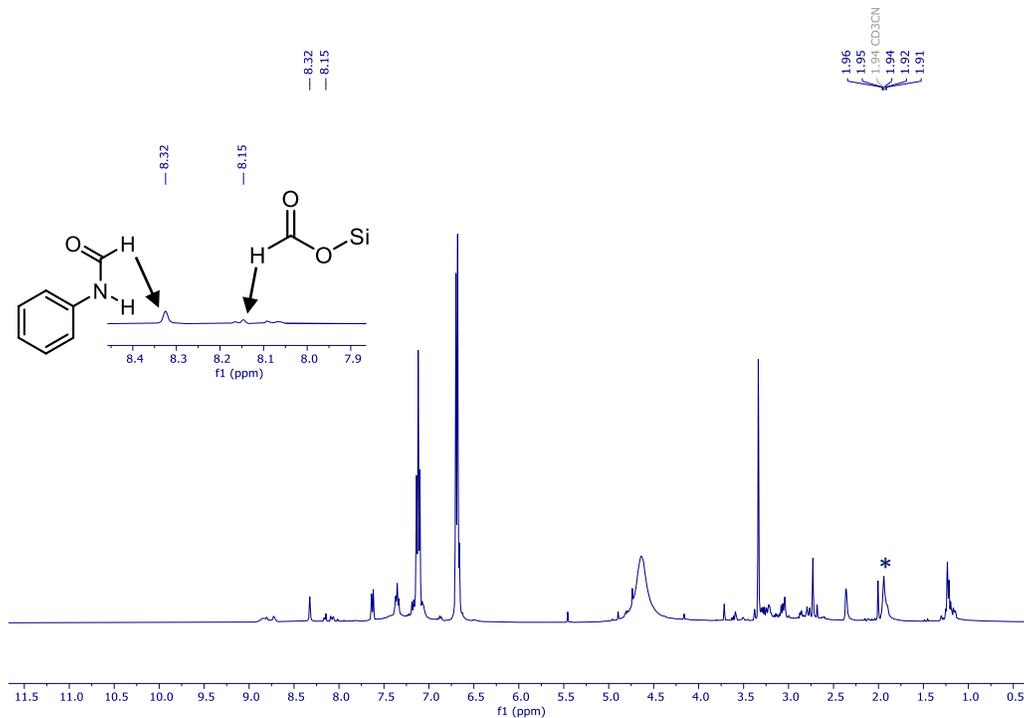
**Figure S13.**  $^1\text{H}$  NMR spectrum of the reaction mixture for the reaction between in-situ generated Zn-L2 complex and phenylsilane in  $\text{CD}_3\text{CN}$  (\*) showing the formation of a Zn-H complex



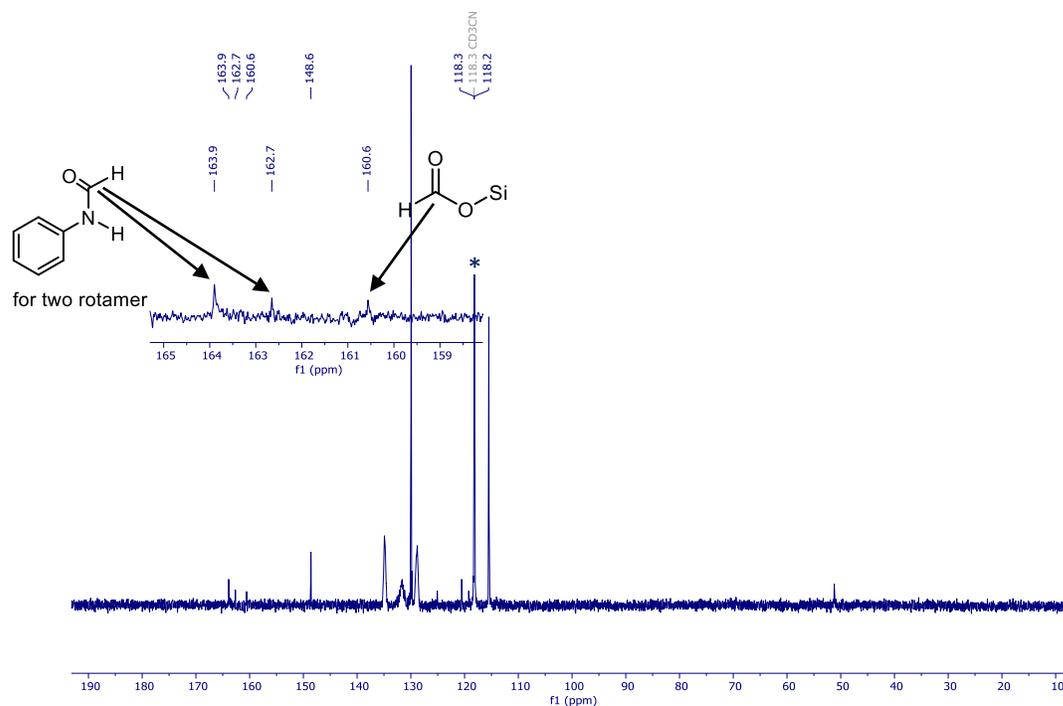
**Figure S14.**  $^1\text{H}$  NMR spectrum of the reaction mixture for a reaction between in-situ generated Zn-L2 complex and phenylsilane in  $\text{CD}_3\text{CN}$  (\*) after passing  $\text{CO}_2$  showing the formation of formoxysilane intermediate.



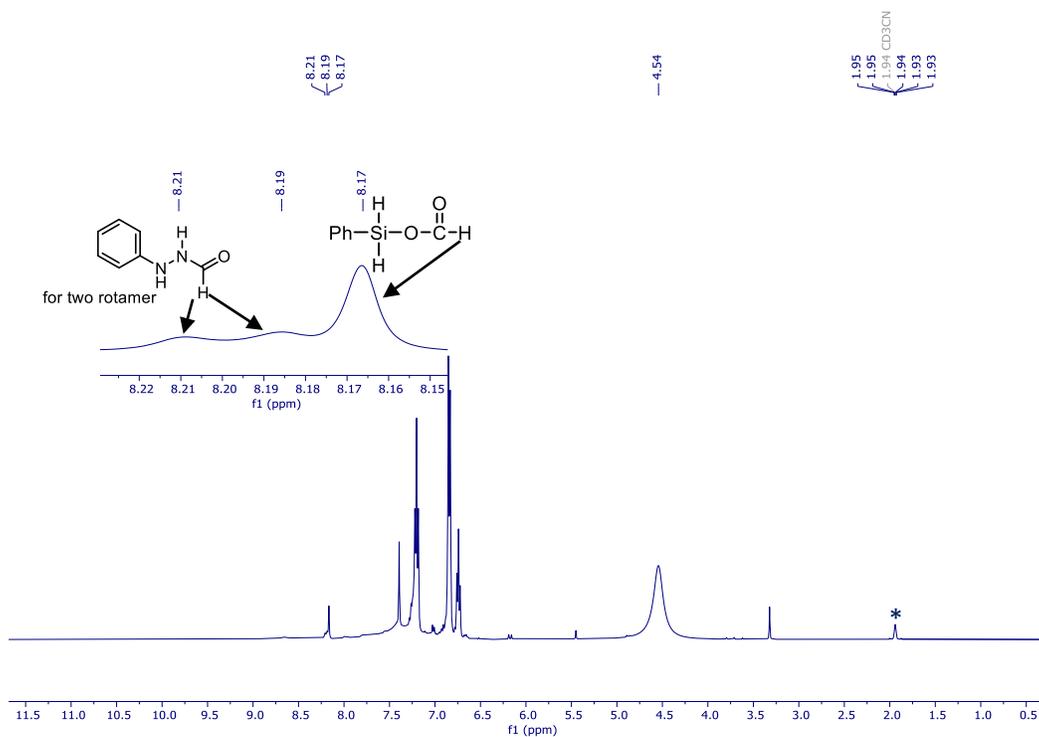
**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the reaction mixture for a reaction between in-situ generated Zn-L2 complex and phenylsilane in  $\text{CD}_3\text{CN}$  (\*) after passing  $\text{CO}_2$  showing the formation of formoxysilane intermediate.



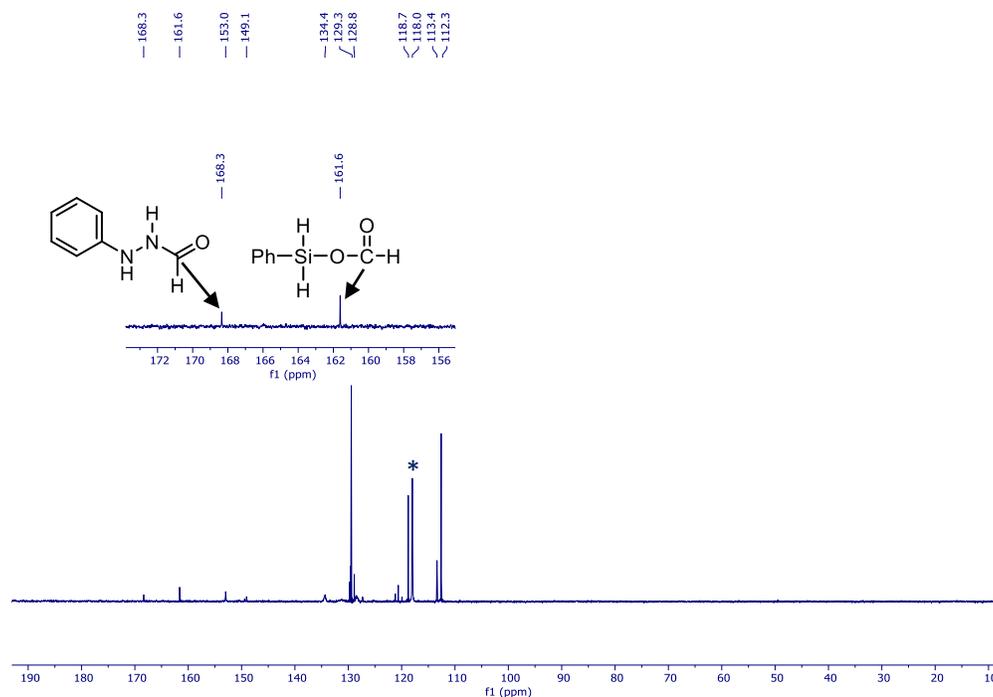
**Figure S16.**  $^1\text{H}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of aniline to the reaction mixture (Figure S14) showing formation of the N-formylated species **3a**



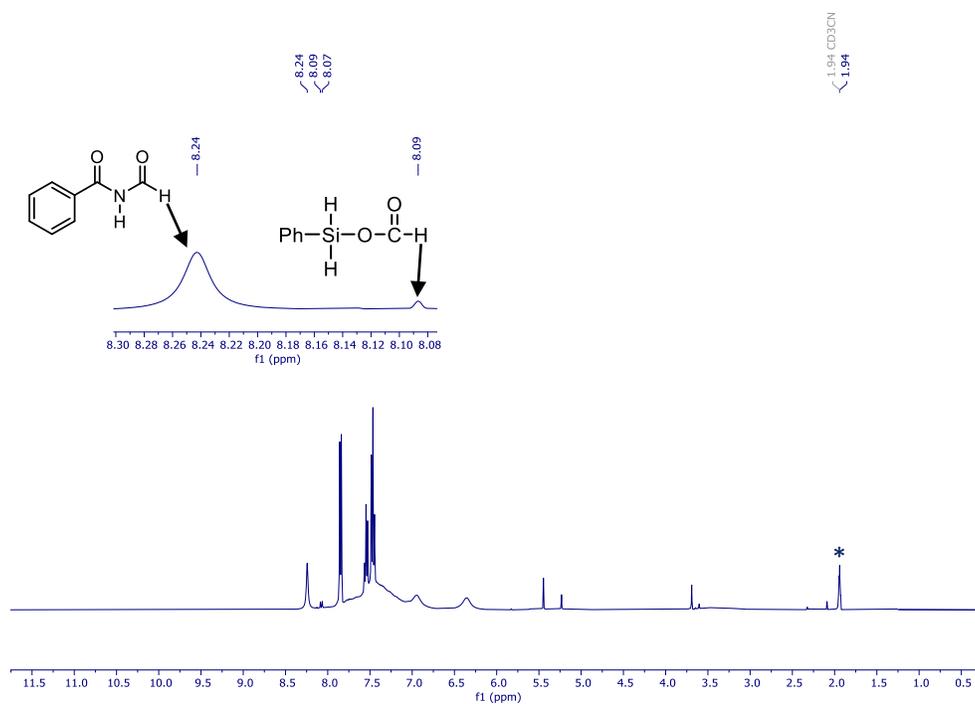
**Figure S17.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of aniline to the reaction mixture (Figure S14) showing the formation of the N-formylated species **3a**



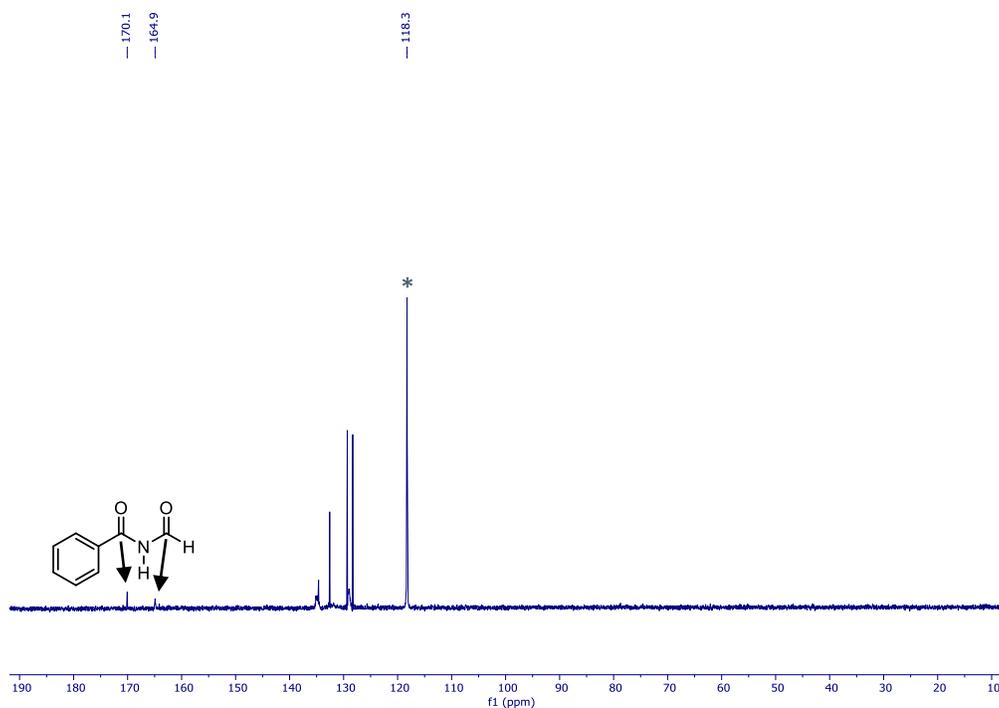
**Figure S18.**  $^1\text{H}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of hydrazine to the reaction mixture (Figure S14) showing formation of the N-formylated species **5a**



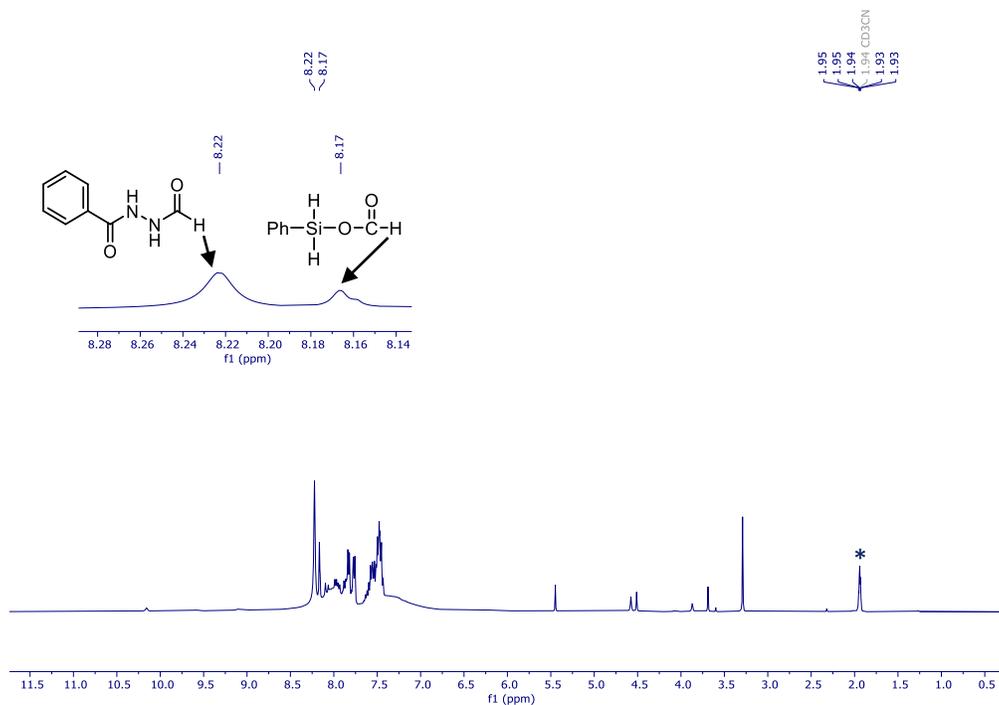
**Figure S19.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of hydrazine to the reaction mixture (Figure S14) showing formation of the N-formylated species **5a**



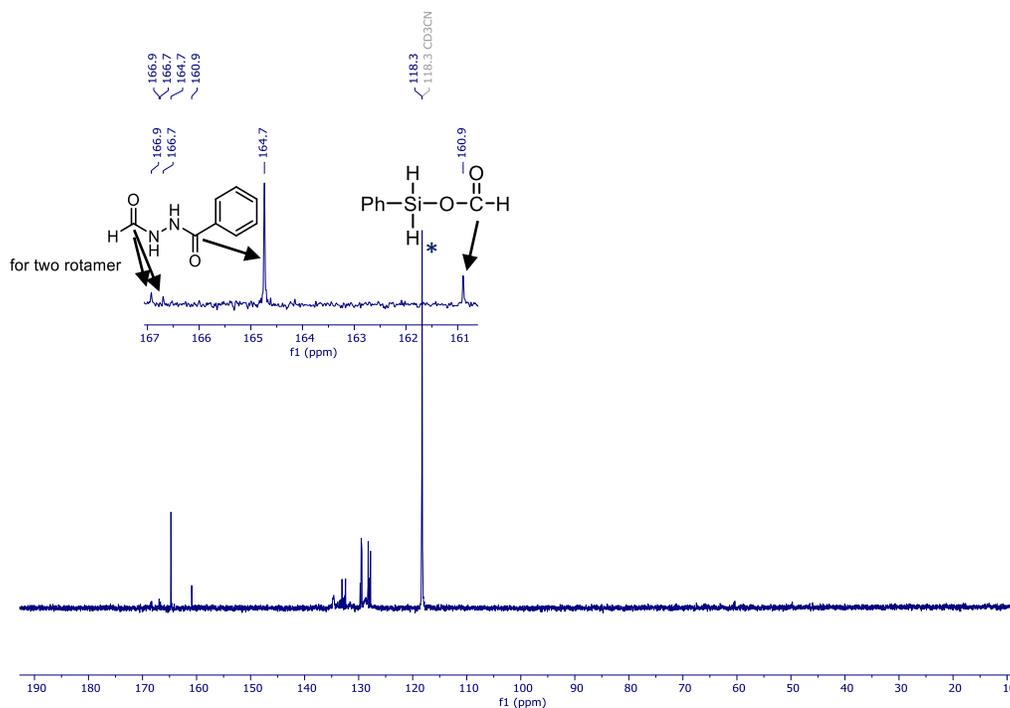
**Figure S20.**  $^1\text{H}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of benzamide to the reaction mixture (Figure S14) showing formation of the N-formylated species **5c**



**Figure S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of benzamide to the reaction mixture (Figure S14) showing formation of the N-formylated species **5c**



**Figure S22.**  $^1\text{H}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of phenylhydrazide to the reaction mixture (Figure S14) showing formation of the N-formylated species **5e**



**Figure S23.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of reaction mixture in  $\text{CD}_3\text{CN}$  (\*) after addition of 1 equiv. of phenylhydrazide to the reaction mixture (Figure S14) showing formation of the N-formylated species **5e**

**Table S2.** Crystallographic data for the complex **1**

Compound	<b>1</b>
CCDC No	2238980
Empirical formula	$\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_4\text{Zn}$
Formula weight	347.67
Crystal system	Monoclinic
Space group	$\text{P } 2_1$
a (Å)	9.374(2)
b (Å)	8.2061(18)
c (Å)	10.172(2)
$\alpha$ (°)	90
$\beta$ (°)	90.621(10)
$\gamma$ (°)	90

V (Å <sup>3</sup> )	782.5(3)
Z	2
D calc (Mg/m <sup>3</sup> )	1.476
F (000)	360
μ (mm <sup>-1</sup> )	2.374
θ Range (°)	4.347 to 68.232
Crystal size (mm)	0.196 x 0.150 x 0.110
No. of total reflns collected	1514
No. of unique reflns [I > 2σ(I)]	1514
Data/restraints/ parameters	1514/ 1 / 195
Goodness-of-fit on F <sup>2</sup>	1.238
Final R indices [I > 2σ(I)]	0.0346, 0.0951
R indices (all data)	0.0362, 0.1005

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