Supporting information

Designing a Cr-catalyst Bearing Redox Non-innocent Phenalenyl-Based Ligand towards Hydrosilylative CO_2 Functionalization

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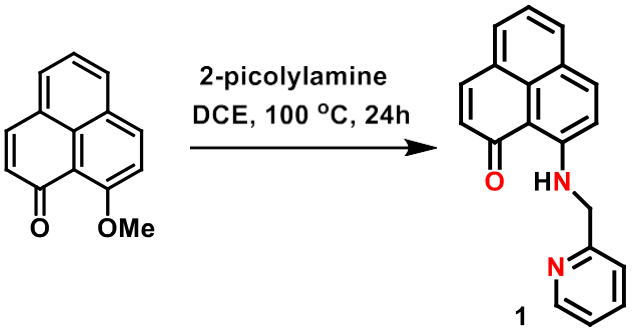
Contents:

I. General considerations and instrumentations.

All catalytic and controlled reactions were performed under oxygen free atmosphere (Argon or nitrogen) using standard Schlenk techniques or inside a glovebox. All solvents used in the experiments were dried over a sodium/benzophenone mixture or CaH_2 and distilled prior to use. All chemicals were purchased from Sigma-Aldrich or Merck or Spectrochem or Alfa Aesar and used as received. Analytical thin layer chromatography (TLC) was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness). Column chromatography was performed on Merck 60 silica gel (100-200 mesh). The ^{1}H and ^{13}C NMR spectra were recorded on JEOL ECS 400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with residual undeuterated solvent (eg. $CDCl_3$, 7.26/77.0) as an internal standard. Chemical shifts (δ) are given in ppm, and *J* values are given in Hz. All chemical shifts were reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Evaporation of solvents was performed under reduced pressure using a rotary evaporator. High-resolution mass spectra (HRMS) were obtained on a Bruker maXis impact. EPR spectroscopic measurements were performed in Bruker (X-band) spectrometer. All the glassware and NMR tubes used for experiments were kept in oven at 120 °C for overnight (12h). X-ray crystallographic measurements were performed in Agilent X-ray diffractometer. Cyclic voltammetry was performed with glassy carbon and platinum wire electrodes, Ag/AgCl reference electrode, tetrabutylammonium perchlorate electrolyte, under N_2 atmosphere. Carbon dioxide was purchased from Praxair in a 5.5 purity gas cylinder with 99.995% purity. The ligands 9-methoxy-1H-phenalen-1-one and 9-methoxy-1H-phenalen-1-one were synthesized following reported literature.[1-2]

II. Experimental Procedures.

*a) Synthetic Procedure of 9-((pyridin-2-ylmethyl)amino)-1H-phenalen-1-one (**1**).*



The synthesis of **1** was accomplished by the treatment of 1 equiv. of 9-methoxy-1H-phenalen-1-one (1.1g) with 1.5 equiv. of 2-picolylamine (0.9 mL) in 1,2-dichloroethane under a reflux condition for 24 h. After completion of reaction, the solvent was evaporated under a vacuum and reaction mixture was purified by column chromatography with neutral alumina by 50% DCM in hexane. Analytically pure orange colored crystals of **1** were obtained in 60% isolated yield (0.87g) from a concentrated THF-hexane solution at room temperature. Also, it was characterized by NMR spectroscopy and HRMS technique. ^{1}H-NMR ($CDCl_3$, 400MHz, rt): 12.68 (1H, s), 8.62-8.64 (1H, d, J=8Hz), 7.92-7.94 (1H, d, J=8Hz), 7.84-7.87 (3H, m), 7.60-7.64 (1H, m), 7.40-7.44 (1H, t), 7.34-7.36 (1H, d, J=8.0Hz), 7.20-7.21 (1H, m), 7.15-7.17 (1H, m), 7.00-7.02 (1H, m), 4.91-4.92 (2H, d, J=4Hz) ppm; ^{13}C-NMR ($CDCl_3$, 125 MHz, rt): 184.74, 157.33, 155.90, 149.52, 138.44, 136.99, 131.83, 131.46, 128.90, 128.16, 125.15, 124.41, 122.43, 121.92, 121.05, 114.63, 108.55, 48.47 ppm. HRMS calculated for $C_{19}H_{14}N_2ONa$ [M + Na]+ 309.1004, found 309.1079 (Fig. S1).

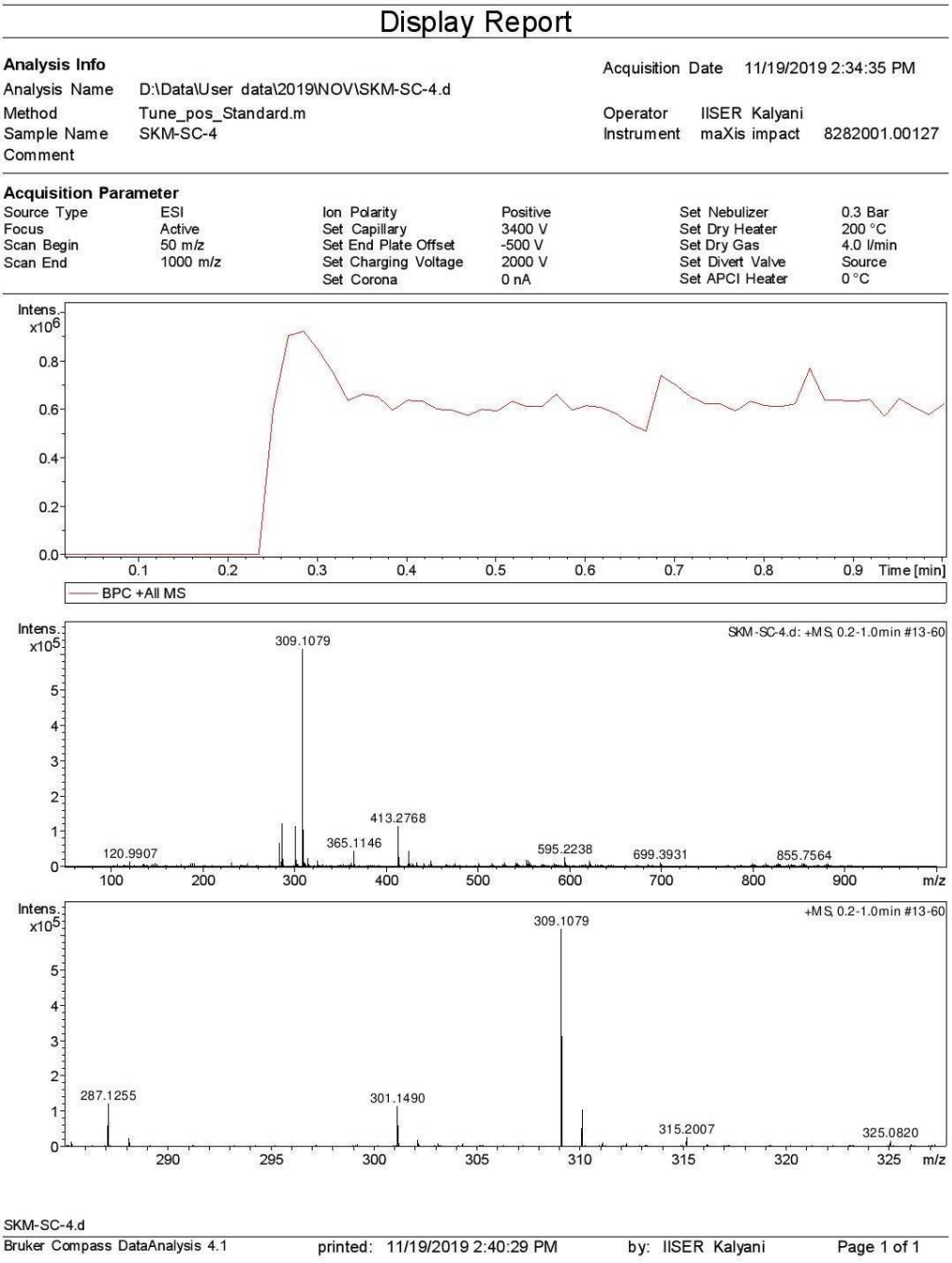
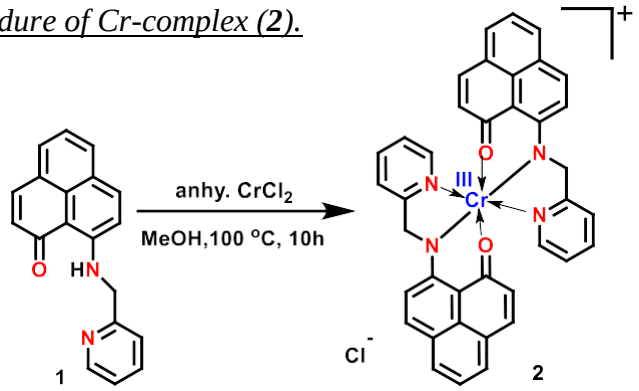


Fig. S1 HRMS spectrum for N,N,O-PLY ligand (**1**).

b) *Synthetic Procedure of Cr-complex (**2**).*



In open atmosphere, a 100 mL round bottom flask, **1** (0.3 g, 1.04 mmol) was dissolved in 20 mL MeOH upon heating at 60 ^{o}C. Separately, a 50 mL conical flask was taken and anhydrous $CrCl_2$ (0.064 g) was dissolved in 10 mL MeOH. To the hot methanolic solution of **1**, the solution of $CrCl_2$ dissolved in methanol was added dropwise. The orange solution was changed to reddish and finally turned to a dark red solution. The reaction mixture was stirred with heating at 100 ^{o}C for another 10 h, and filtered in hot condition through a Whatman-1 filter paper. The filtrate was kept for 8-10 h to form crystalline dark red compound. The mother liquor was transferred, red crystals were washed with MeOH and dried. Crystals suitable for SCXRD were grown from concentrated methanolic solution layer with DCM of the crystalline material at room temperature for one week. The complex was characterized by UV-vis, EPR, IR spectroscopy, cyclic voltammetry and X-ray diffraction study. IR (400-2000 cm^{-1}): 1624, 1576, 1498, 1414, 1348, 1284, 1240, 1186, 1164, 1134, 1052, 974, 950, 872, 844, 814, 760, 678, 684, 520. Anal. calculated for $C_{38}H_{26}ClCrN_4O_2.(C_2H_{10}O_2)$: C, 66.34; H, 5.01; N 7.74. Found: C, 65.96; H, 4.53; N, 7.43. The calculated molecular formula was determined from crystallographically determined unit which contains lattice held methanol and water molecules. HRMS calculated for $[C_{38}H_{26}ClCrN_4O_2]$ $[M - Cl]^+$: m/z 622.1455. Found: 622.1440 (data recorded in positive ion polarity mode). (Fig. S2).

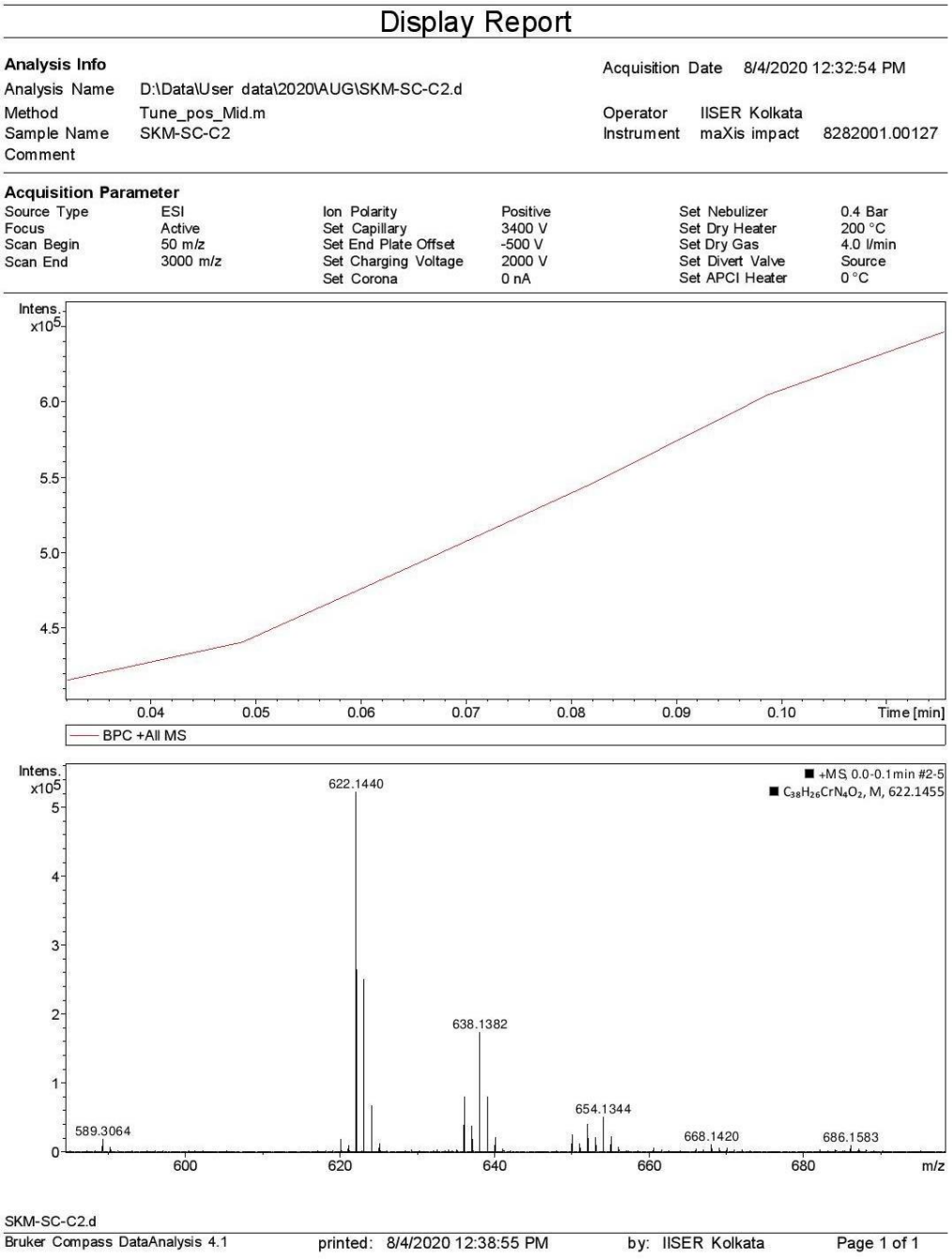
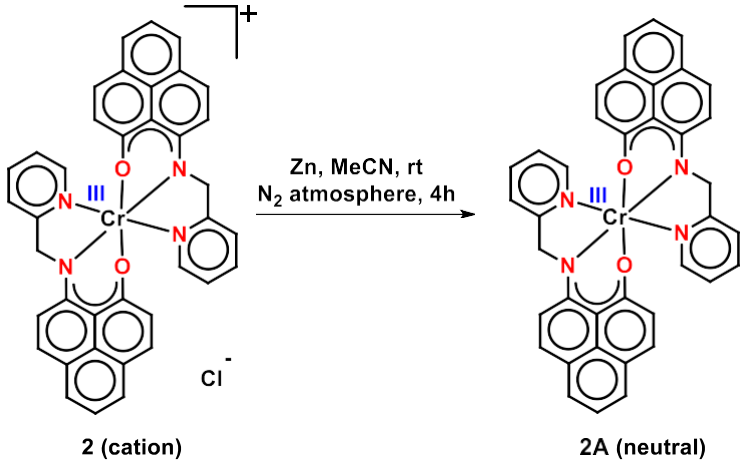


Fig. S2 HRMS spectrum (recorded in positive ion polarity mode) for Cr(III)-complex (**2**).

c) *Procedure for isolation of first reduced species of Cr-complex **2** (**2A**).*



In nitrogen filled glove-box, **2** (30 mg, 0.04 mmol) and Zn powder (2.6 mg, 0.04 mmol) were mixed with 10 mL acetonitrile in a 30 mL vial equipped with a stir bar and stirred for 4 hours at room temperature. Thereafter the solution was filtered through a small celite plug. The red colored filtrate was layered with THF and diethyl ether and kept at room temperature for crystallization. Red colored block shaped single crystals were obtained on overnight standing. A suitable crystal was coated with inert oil and was analyzed by single crystal X-ray diffraction. IR (400-2000 cm^{-1}): 1628, 1580, 1492, 1460, 1404, 1344, 1282, 1240, 1184, 1158, 1136, 1102, 1050, 976, 944, 846, 806, 766, 678, 660, 520. HRMS calculated for $C_{38}H_{26}CrN_4O_2$ $[M]^+$: m/z 622.1455. Found: 622.1449 (Fig. S3). Due to moisture sensitivity of the compound, elemental analysis experiment of **2A** was unsuccessful.

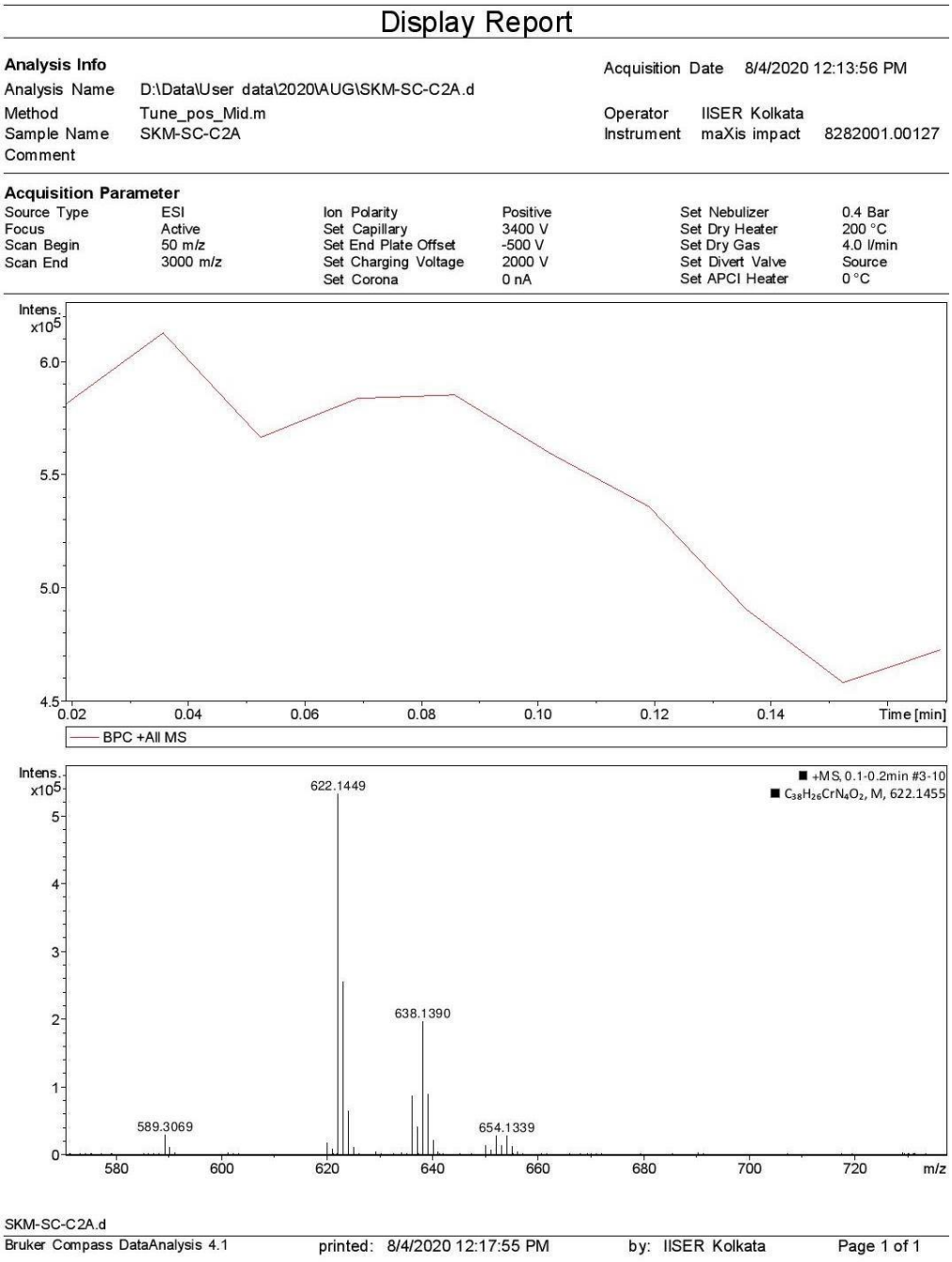
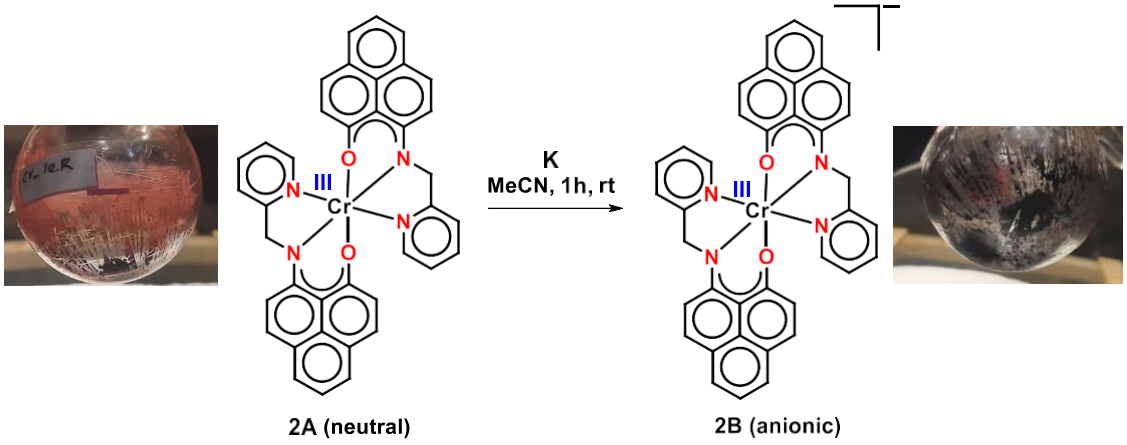


Fig. S3 HRMS spectrum for neutral Cr-complex (2A).

d) *Procedure for isolation of second reduced species of Cr-complex **2** (**2B**).*



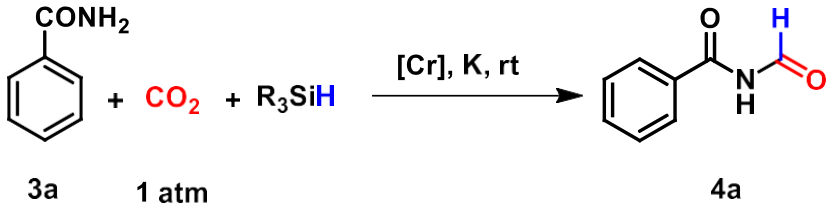
In a nitrogen filled glovebox, 1 equiv. of both **2** (50 mg, 0.07 mmol) and Zn powder (5 mg, 0.07 mmol) were mixed in acetonitrile. After 4 hours stirring at room temperature, the reaction mixture was filtered. Filtrate was collected in a 50 mL Schlenk flask equipped with a stir bar and treated with 1 equiv. of potassium (3 mg, 0.07 mmol). Colour of the reaction mixture turned deep green immediately. It was stirred at room temperature for 2-4 hours and finally dried over vacuum to obtain a dark green solid. This green solid was highly air and moisture sensitive and stored inside glovebox at room temperature. Alternatively, synthesis of **2B** was done by treating **2** and potassium in 1:2 ratio in dry and distilled acetonitrile inside a nitrogen filled glovebox by stirring at room temperature for 4 hours. After that, reaction mixture was dried over high vacuum to obtain **2B**.

e) *General Procedure for optimization of CO_2 functionalization.*

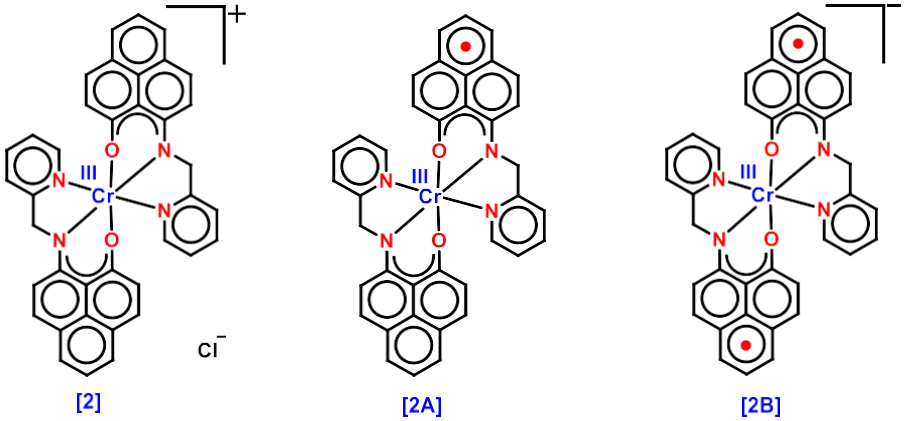
In a nitrogen filled glovebox, **2** (5 mol%) and a suitable reductant (10 mol%) were taken in a 15mL high pressure J-Young tube with teflon cap equipped with a stir bar. 800µL acetonitrile was added to that and kept for stirring for 20min. at room temperature. Silane (2 equiv.) was added to it followed by benzamide (1 equiv.) The tube was closed properly and took out from glovebox. In Schlenk line freeze-pump thaw was done twice to evacuate any gasses present.

Then CO_2 was charged at 1 atm pressure. Tube was closed properly and kept for stirring at room temperature for 12 hours. After completion, the reaction mixture was dried completely and exposed to air. Product was isolated through silica column with 10% EtOAc-hexane mixture and characterized by ^{1}H and ^{13}C NMR spectroscopy. Yield was calculated with respect to benzamide. By varying different silane and reductant, the reaction condition was optimized.

Table S1. Optimization of formylation reaction condition using catalytic amount of **2**.



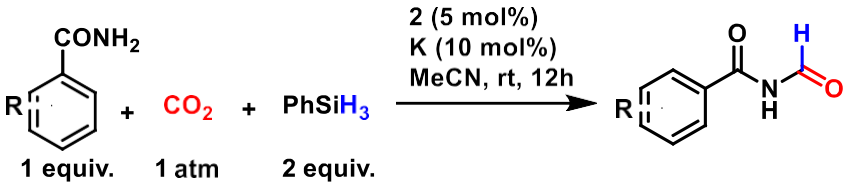
[Cr]-catalyst used:



Entry	Silane (equiv.)	[Cr] (mol%)	K (mol%)	Isolated Yield (%)
1	$PhSiH_3$ (2)	**2** (5)	K (10)	80
2	$PhSiH_3$ (2)	**2** (5)	-	-
3	$PhSiH_3$ (2)	-	K (10)	25
4	$PhSiH_3$ (2)	**2A** (5)	-	-
5	$PhSiH_3$ (2)	**2A** (5)	K (5)	75
6	$PhSiH_3$ (2)	**2B** (5)	-	76
7	$PhSiH_3$ (2)	**2** (5)	K (10)	65 (in THF)

8	Ph_2SiH_2 (2)	**2** (5)	K (10)	-
9	PMHS (2)	**2** (5)	K (10)	-
10	Et_3SiH (2)	**2** (5)	K (10)	-
11	$Me_2HSiOSiHMe_2$	**2** (5)	K (10)	-
12	$PhSiH_3$ (2)	**2** (5)	K (10)	78 (in dark)

f) *General Procedure for catalytic CO_2 functionalization.*



In a nitrogen filled glovebox, **2** (5 mol%) and potassium (10 mol%) were taken in a 15mL high pressure J-Young tube with teflon cap equipped with a stir bar. 800 µL acetonitrile was added to the reaction mixture and kept for stirring for 20 min. at room temperature. Phenylsilane (2 equiv.) was added to it followed by addition of arylbenzamide (1 equiv.). The tube was closed properly and was taken out from glovebox. In the Schlenk line, freeze-pump-thaw cycle was applied twice to evacuate any inert gas present. Next CO_2 was purged to the reaction mixture. Reaction tube was closed properly and was kept for stirring at room temperature for 12 hours. After completion, the reaction mixture was dried completely and exposed to air. Product was isolated through silica column with EtOAc-hexane mixture and characterized by ^{1}H and ^{13}C NMR spectroscopy.

g) *Procedure for catalytic CO_2 functionalization in presence of radical scavengers.*

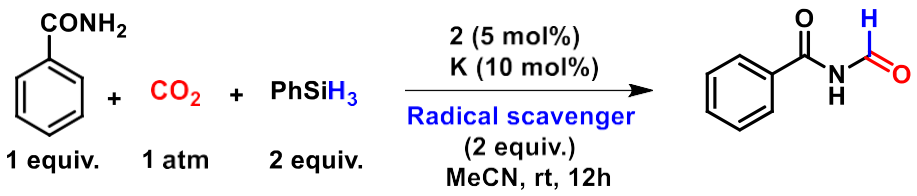


Table S2. Controlled reaction in presence of radical scavenger.

Entry	Radical scavenger	Yield
1	TEMPO	<10 %
2	Galvinoxyl free radical	-

In a nitrogen filled glovebox, catalyst **2** (5 mol%) and potassium (10 mol%) were taken in a 15mL high pressure J-Young tube with teflon cap equipped with a stir bar. 800µL acetonitrile was added to that and kept for stirring for 20 min. at room temperature. Phenylsilane (2 equiv.) was added to it followed by addition of benzamide (1 equiv.) and a radical scavenger (2 equiv.). The tube was closed properly and was taken out from glovebox. In Schlenk line, freeze-pump thaw was done twice to evacuate the tube. Then CO_2 was charged at 1 atm pressure. Tube was closed properly and kept for stirring at room temperature for 12 hours. After completion, the reaction mixture was dried completely and exposed to air. Product was isolated through silica column with 10% EtOAc-hexane mixture isolated yield was determined.

h) Procedure for characterization of siloxane as a side product.

in a nitrogen filled glovebox, Cr-catalyst (**2**, 5 mol%) and potassium (10 mol%) were taken in acetonitrile within a 15mL high pressure J-Young tube with teflon cap equipped with a stir bar. 4-Methylbenzamide (0.3 mmol) and triphenylsilane (0.3 mmol) was added to it. The tube was closed properly and taken out from the glovebox. In Schlenk line, freeze-pump thaw was done

twice to evacuate the inside gas. CO_2 was charged at 1 atm pressure. Tube was closed properly and kept for stirring at room temperature for 24 hours. After completion the reaction mixture was dried and ^{1}H NMR spectroscopy of the reaction mixture was recorded in CDCl3. No peak at 5.1 indicates no unreacted silane present, however unreacted amide and relevant silyl ether peaks can be identified from the aromatic region.

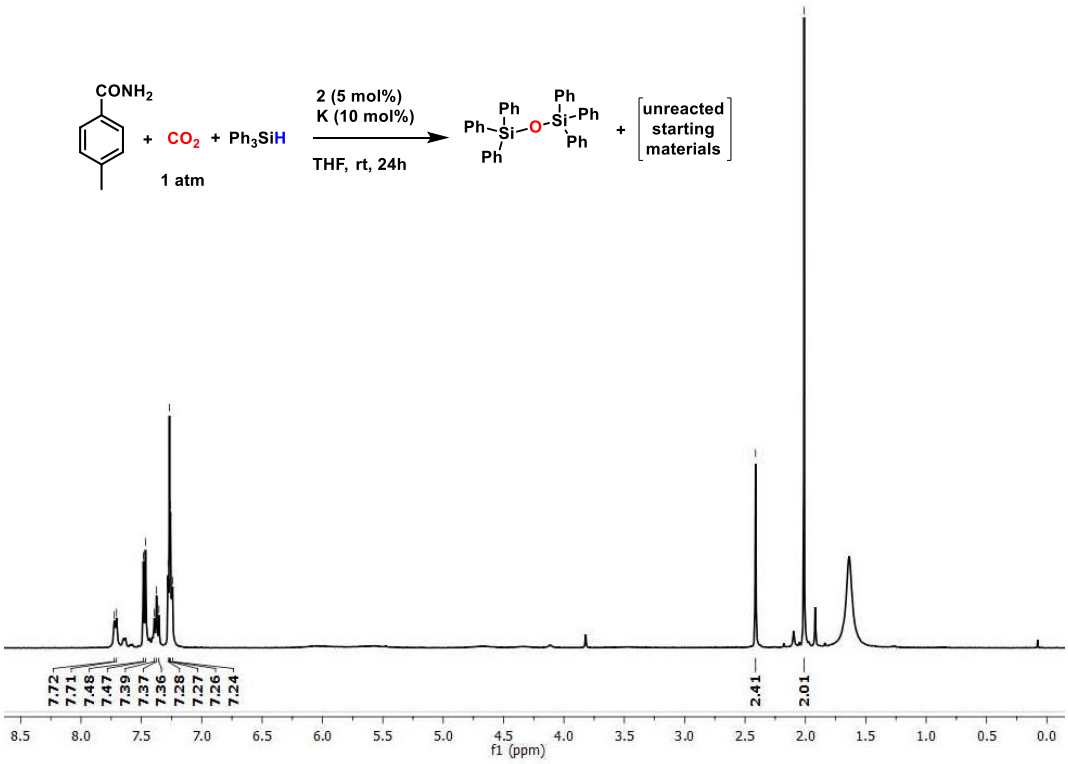


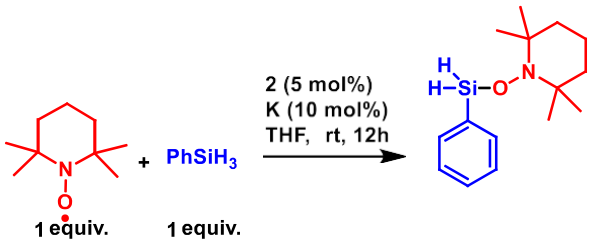
Fig. S4 ^{1}H NMR spectrum indication formation of siloxane.

Further, to characterize silyl ether, in a nitrogen filled glovebox, Cr-catalyst (**2**, 5 mol%) and potassium (10 mol%) were taken in a 15mL high pressure J-Young tube with teflon cap equipped with a stir bar. 800 µL THF was added to that and kept for stirring for 4h at room temperature. Triphenylsilane (10 equiv. wrt **2**) was added to it. The tube was closed properly and taken out from the glovebox. In Schlenk line, freeze-pump thaw was done twice to evacuate the inside

gases. Then CO_2 was charged at 1 atm pressure. Tube was closed properly and kept for stirring at room temperature for 24 hours. After completion the reaction mixture was dried and taken back to glovebox. It was next dissolved in THF and was kept at room temperature. On standing overnight, colorless crystals were observed and characterized by NMR spectroscopy to determine the siloxane (1,1,1,3,3,3- hexaphenyldisiloxane) side product. ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 7.46-7.44 (m, 2H), 7.37-7.33 (m, 1H). 7.24-7.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 135.4, 135.1, 129.7, 127.6. ^{29}Si-NMR[5] (100 MHz, $CDCl_3$, 298 K) δ (ppm) -18.6.

Procedures to trap reaction intermediates by mass spectroscopy.

i) *Procedure for characterization of TEMPO-trapped silyl radical intermediate (**5**).*



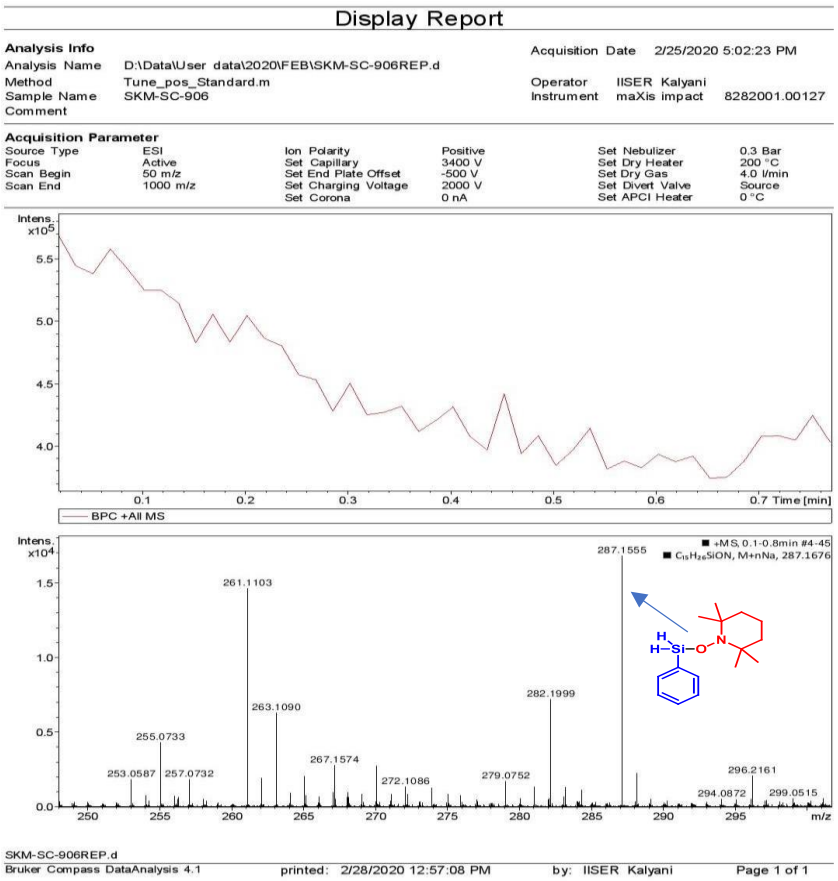
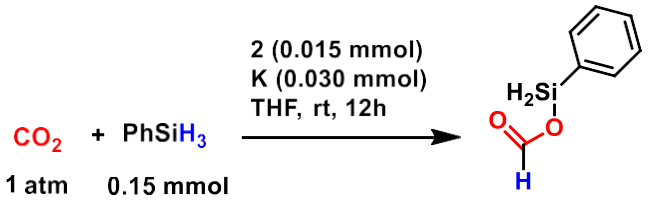


Fig. S5. HRMS data recorded for detecting TEMPO-trapped silyl radical.

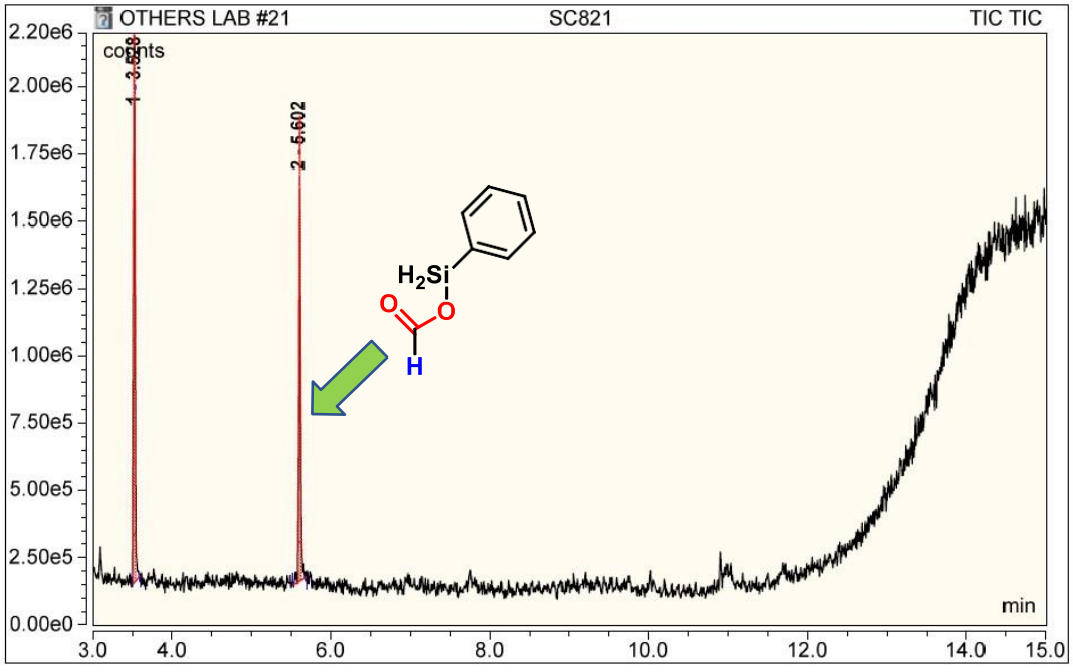
In a nitrogen filled glovebox, **2** (5 mol%) and potassium (10 mol%) were taken in a 15mL high pressure J-Young tube with teflon cap equipped with a stir bar. 800 µL THF was added to that and kept for stirring for 4 hours at room temperature. Phenylsilane (1 equiv.) and TEMPO (1 equiv.) were added to it and continued to stir for 12 hours. After completion, the reaction mixture was dried completely and analysed by HRMS technique to detect the TEMPO-trapped silyl radical species.

j) *Procedure for trapping silyl-formate intermediate (**6**).*



(a) **Peak Analysis Report**

Sample Name:	**SC821**	*Injection Volume:*	**1.00**
Injection Type:	**Unknown**	*Dilution Factor:*	**1.0000**
Instrument Method:	**Others Lab Method**	*Operator:*	**ISQ7000**
Inj. Date / Time:	**04-Dec-2019 / 20:30**	*Run Time:*	**15.00**



No.	Time min	Peak Name	Width min	Height counts	Resol. (USP)	Resol. (EP)	Plates (USP)	Plates (EP)	Asymmetry
1	3.528		0.029	1801224.847	71.326	71.182	232750	227582	1.158
2	5.602		0.029	1457524.682	n.a.	n.a.	600153	602546	1.274
		AVERAGE:	0.029	1,629,374.764	71.326	71.182	416,452.	415,064.	1.216

(b)

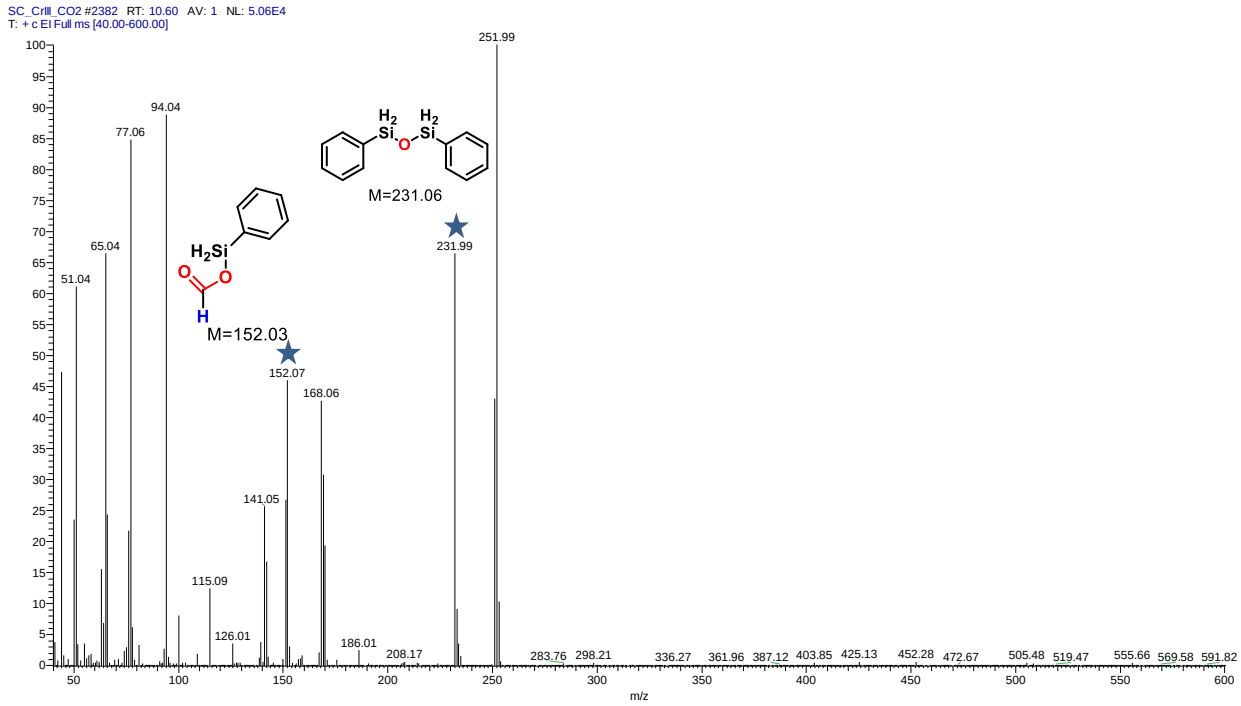


Fig. S6. (a) Retention time graph and (b) corresponding mass spectroscopic plot in GC supporting formation of silyl formate.

In a nitrogen filled glovebox, **2** (5 mol%) and potassium (10 mol%) were taken in a 15mL high pressure J-Young tube with teflon cap equipped with a stir bar. 800µL THF was added to that and kept for stirring for 4 hours at room temperature. Phenylsilane (10 equiv. wrt to catalyst) was added to it. The tube was closed properly and took out from glovebox. In Schlenk line, freeze-pump thaw was done twice to evacuate the inside gasses. Then CO_2 was charged at 1 atm pressure. Tube was closed properly and kept for stirring at room temperature for 12 hours. After completion the reaction mixture was dried completely and taken back to glove box. The reaction mixture was analysed by GC technique (in acetonitrile) to find the mass for silyl formate. Along with formate, formation of siloxane ($PhH_2SiOSiH_2Ph$) as co-product has been noted.

k) Procedure for trapping silyl-formate intermediate with DMMS:

In a nitrogen filled glovebox, **2** (0.015 mmol) and potassium (0.03 mmol) were taken in a vial in MeCN (0.8 mL) and stirred for 2-3 minutes. It was then allowed to settle down and the upper clear solution portion was transferred to a 15 mL J-Young tube with teflon cap followed by addition of dimethoxy(methyl)silane (DMMS) (0.15 mmol). Tube was closed and freeze-pump-thaw was done twice. CO_2 was charged and the reaction was allowed to stir at room temperature for 4h. Reaction mixture was dried over vacuum and NMR spectroscopy was recorded in $CDCl_3$. Characteristic peaks of silyl formate was observed in ^1H (8.10 ppm)[3] and ^{13}C (160.4 ppm) spectra.

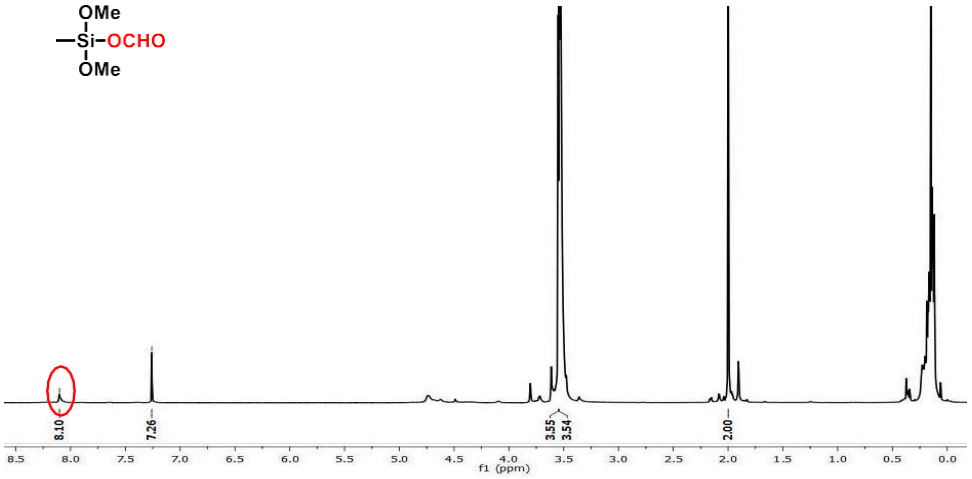


Fig. S7. ^1H NMR spectrum for silyl-formate (in $CDCl_3$ at room temperature)

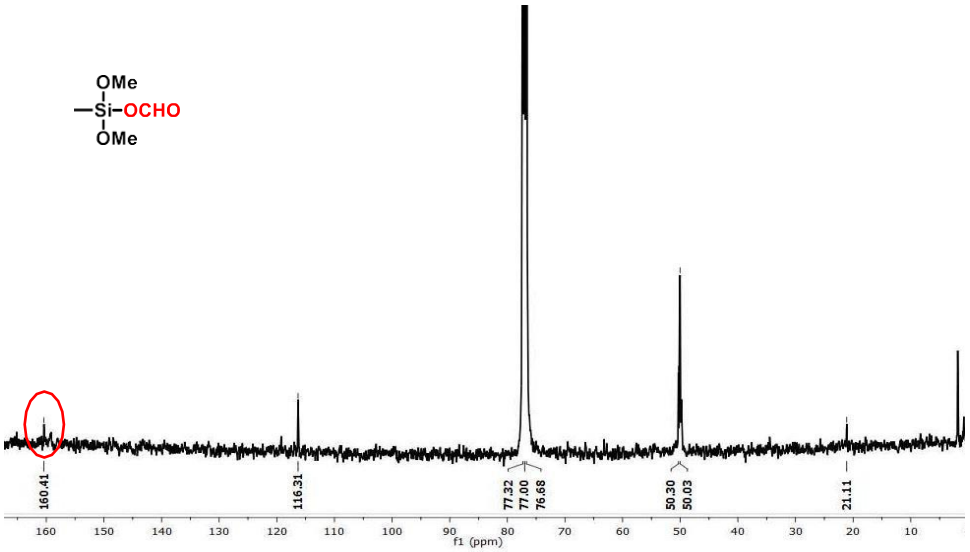


Fig. S8. ^{13}C NMR spectrum for silyl-formate (in $CDCl_3$ at room temperature)

l) *H_2 evolution experiment:*

In a nitrogen filled glovebox, 2 (0.015 mmol) and potassium (0.03 mmol) were taken in a vial in CD_3CN (0.6 mL) and stirred for 2-3 minutes. It was then allowed to settle down (as the catalyst is sparingly soluble in acetonitrile) and the upper clear solution portion was transferred to a screw capped NMR tube. Phenylsilane (0.45 mmol) and benzamide (0.45 mmol) were added to it and immediately the tube was closed tightly. ^{1}H NMR spectrum of the reaction mixture was recorded. Gas bubbling was observed in the reaction medium. A peak at 4.57 ppm[4] indicates formation of H_2 in the reaction.

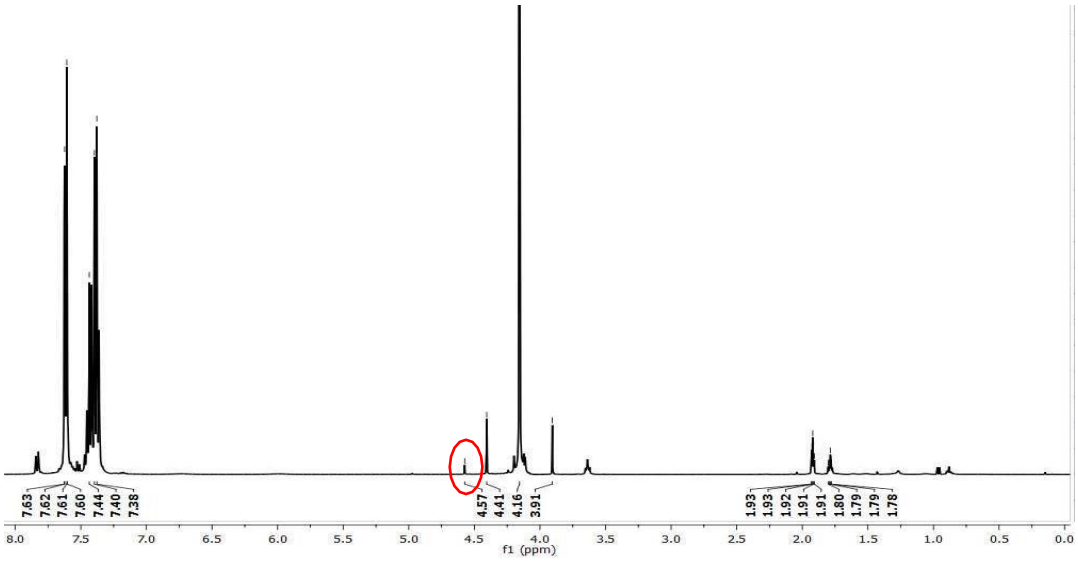
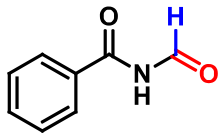


Fig. S9. ^{1}H NMR spectrum for H_2 evolution (in CD_3CN at room temperature)

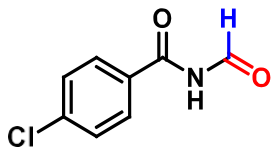
III. Characterization of N-formylamide compounds



N-formylbenzamide (**4a**)[5]: White crystalline solid. Yield 80%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 10.02 (br s, 1H), 9.39 (d, J = 8Hz, 1H), 7.99 (d, J = 8Hz, 2H), 7.65 (t, 1H, J_1= 2.5Hz, J_2= 1.25Hz), 7.52-7.55 (m, 2H).

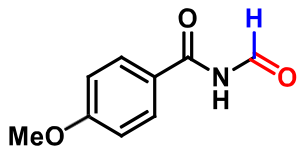
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 166.6, 164.6, 133.9, 131.0, 129.0, 128.0.



4-chloro-N-formylbenzamide (**4b**)[5]: White crystalline solid. Yield 55%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane.

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm) 11.80 (br s, 1H), 9.25 (m, 1H), 8.03 (d, J = 8Hz, 2H), 7.62 (d, J = 8Hz, 2H).

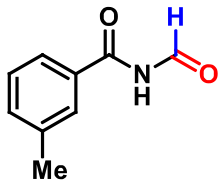
^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm) 167.1, 164.8, 138.9, 130.8, 130.8, 129.



N-formyl-4-methoxybenzamide (**4c**)[6]: White crystalline solid. Yield 75%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$ + DMSO-d_6, 298 K) δ (ppm) 10.95 (br s, 1H), 8.92 (d, J = 8Hz, 1H), 7.63 (d, J = 8Hz, 2H), 6.55 (d, J = 8Hz, 2H), 3.45 (s, 3H).

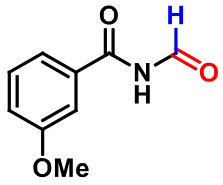
^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6, 298 K) δ (ppm) 166.0, 163.6, 162.7, 129.8, 122.8, 112.9, 54.5.



N-formyl-3-methylbenzamide (**4d**)[7]: White crystalline solid. Yield 60%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 9.97 (br s, 1H), 9.38 (d, J = 8Hz, 1H), 7.80 (s, 1H), 7.76 (d, J = 8Hz, 1H), 7.35-7.46 (m, 2H), 2.43 (s, 3H).

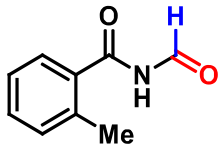
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 166.7, 164.5, 139.0, 134.7, 131.0, 128.9, 128.7, 125.0, 21.2.



N-formyl-3-methoxybenzamide (**4e**)[7]: White crystalline solid. Yield 66%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm) 10.87 (br s, 1H), 8.40 (s, 1H), 6.74-6.76 (m, 1H), 6.70-6.71 (m, 1H), 6.57-6.61 (m, 1H), 6.35-6.38 (m, 1H), 2.96 (s, 3H).

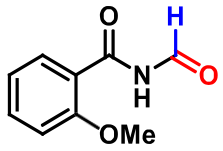
^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm) 167.3, 164.5, 159.3, 132.8, 129.9, 120.7, 119.7, 113.0, 55.4.



N-formyl-2-methylbenzamide (**4f**)[7]: White crystalline solid. Yield 40%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 9.23 (d, J = 12Hz, 1H), 9.07 (br s, 1H), 7.47-7.51 (m, 1H), 7.43-7.47 (m, 1H), 7.28-7.32 (m, 2H), 2.53 (s, 3H).

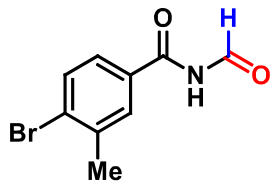
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 168.6, 163.4, 138.4, 132.2, 132.0, 131.9, 127.3, 126.2, 20.2.



N-formyl-2-methoxybenzamide (**4g**)[8]: White crystalline solid. Yield 70%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 10.18 (br s, 1H), 9.41 (d, J = 8Hz, 1H), 8.20-8.22 (m, 1H), 7.57-7.58 (m, 1H), 7.12-7.15 (m, 1H), 7.03-7.05 (m, 1H), 4.02 (s, 3H).

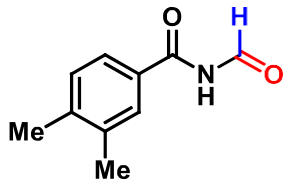
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 165.2, 163.2, 158.4, 135.5, 132.7, 121.7, 118.8, 111.7, 56.1.



4-bromo-N-formyl-3-methylbenzamide (**4h**)[7]: White crystalline solid. Yield 35%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$ + DMSO-d_6, 298 K) δ (ppm) 11.11 (br s, 1H), 9.25 (d, J = 8Hz, 1H), 7.84 (s, 1H), 7.61 (m, 1H), 7.51-7.53 (m, 1H), 2.44 (s, 3H).

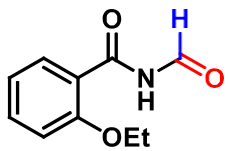
^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6, 298 K) δ (ppm) 166.8, 164.1, 138.3, 132.4, 130.6, 130.5, 130.4, 126.9, 22.5.



N-formyl-3,4-dimethylbenzamide (**4i**)[7]: White solid. Yield 60%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 9.82 (br s, 1H), 9.37 (d, J =8Hz, 1H), 7.75 (s, 1H), 7.68 (d, J =8Hz, 1H), 7.26-7.28 (m, 1H), 2.34 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 166.6, 164.5, 143.7, 137.6, 130.2, 129.2, 128.5, 125.4, 19.7, 20.0.

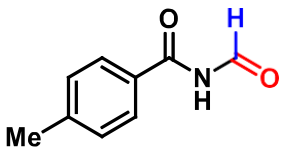


2-ethoxy-N-formylbenzamide (**4j**): Pale white solid. Yield 58%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 10.35 (br s, 1H), 9.38 (d, J = 12Hz, 1H), 8.18-8.20 (dd, J_1 = 8Hz, J_2 = 4Hz, 1H), 7.52-7.57 (m, 1H), 7.08-7.13 (t, J_1 = 8Hz, J_2 = 8Hz, 1H), 7.0 (d, J = 8Hz, 1H), 4.23-4.28 (q, 3H), 1.54-1.58 (t, J_1 = 8Hz, J_2 = 8Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 165.2, 163.0, 157.9, 135.3, 132.6, 121.6, 118.8, 112.7, 65.3, 14.5.

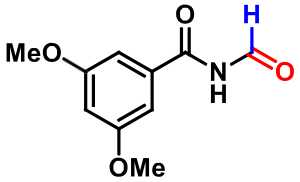
HRMS calculated for $C_{10}H_{11}NO_3Na$ [M + Na]+ 216.0637, found 216.0631.



N-formyl-4-methylbenzamide (**4k**)[5]: White solid. Yield 72%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 10.11 (br s, 1H), 9.38 (d, J = 8Hz, 1H), 7.89 (d, J = 8Hz, 2H), 7.32 (d, J = 8Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 166.5, 164.8, 144.9, 129.7, 128.1, 127.9, 21.6.

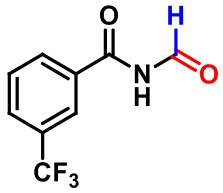


N-formyl-3,5-dimethoxybenzamide (**4l**): Off-white solid. Yield 71%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, DMSO-$d_{6,}$ 298 K) δ (ppm) 11.0 (br s, 1H), 8.77 (d, J = 8Hz, 1H), 6.67 (s, 2H), 6.1 (s, 1H), 3.27 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm) 167.5, 165.0, 161.0, 133.9, 106.5, 106.2, 55.1.

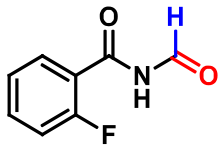
HRMS calculated for $C_{10}H_{11}NO_4Na$ [M + Na]+ 232.0586, found 232.0590.



N-formyl-3-(trifluoromethyl)benzamide (**4m**)[7]: Off-white solid. Yield 30%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_{3,}$ 298 K) δ (ppm) 10.3 (br s, 1H), 9.41 (d, J = 9Hz, 1H), 8.31 (s, 1H), 8.19-8.20 (m, 1H), 7.90-7.92 (m, 1H), 7.68-7.72 (m, 1H).

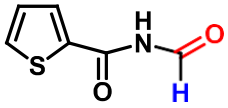
^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) 165.4, 164.6, 131.9, 131.9 (q, $^{2}J_{C\text{-}F}$ = 33.8 Hz), 131.1, 130.4 (q, $^{3}J_{C\text{-}F}$ = 3.8Hz), 129.8, 125.3 (q, $^{3}J_{C\text{-}F}$ = 3.7Hz), 123.4 (q, $^{1}J_{C\text{-}F}$ = 270Hz).



N-formyl-2-fluorobenzamide (**4n**)[7]: Off-white solid. Yield 30%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 15% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_{3,}$ 298 K) δ (ppm) 9.39 (d, J = 12Hz, 1H), 9.07 (br s, 1H), 8.13 (d, J = 4Hz, 1H), 7.62-7.64 (m, 1H), 7.35-7.37 (m, 1H), 7.18-7.24 (m, 1H).

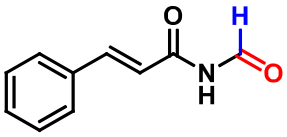
^{13}C NMR (125 MHz, $CDCl_3$, 298 K) δ (ppm) 163.06 (d, $^3J_{C\text{-}F}$ = 2.5Hz), 162.42, 161.2 (d, $^1J_{C\text{-}F}$ = 248Hz), 135.9 (d, $^3J_{C\text{-}F}$ = 8.8Hz), 132.31, 125.4 ($^3J_{C\text{-}F}$ = 3.8Hz), 118.6 (d, $^2J_{C\text{-}F}$ = 10Hz), 116.6 (d, $^2J_{C\text{-}F}$ = 23.75Hz).



N-formylthiophene-2-carboxamide (**4o**)[8]: Off-white solid. Yield 40%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 10.14 (br s, 1H), 9.35, (d, J = 8Hz, 1H), 7.93-7.94 (m, 1H), 7.73-7.75 (m, 1H), 7.19-7.22 (m, 1H).

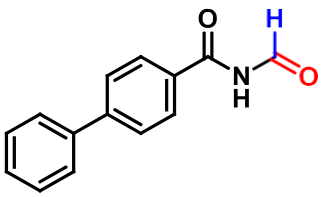
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 164.3, 160.9, 136.0, 134.6, 131.7, 128.6.



N-formylcinnamamide (**4p**)[8]: White solid. Yield 40%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 10% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 9.70 (br s, 1H), 9.28 (d, J =8Hz, 1H), 7.89 (d, J = 16Hz, 1H), 7.56-7.58 (m, 2H), 7.39-7.44 (m, 3H), 6.54 (d, J = 16Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 165.4, 164.4, 146.6, 133.6, 131.2, 129.0, 128.6, 117.9.

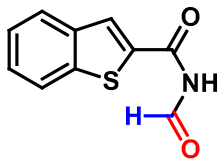


N-formyl-[1,1'-biphenyl]-4-carboxamide (**4q**): Off-white solid. Yield 35%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 20% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm) 9.41 (d, J = 8Hz, 1H), 8.01 (d, J =8Hz, 2H), 7.76 (d, J = 12Hz, 2H), 7.63-7.65 (m, 2H), 7.48-7.51 (m, 2H), 7.41-7.45 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm) 166.0, 163.6, 146.8, 139.3, 129.6, 129.0, 128.6, 128.5, 127.7, 127.3.

HRMS calculated for $C_{14}H_{11}NO_2Na$ [M + Na]+ 248.0687, found 248.0683.



N-formylbenzo[b]thiophene-2-carboxamide (**4r**): Off-white solid. Yield 70%. The crude product was purified by column chromatography using silica gel (100-200 mesh) with 20% of EtOAc in hexane.

^{1}H-NMR (400 MHz, $CDCl_3$ + DMSO-d_6, 298 K) δ (ppm) 11.45 (br s, 1H), 8.91-8.95 (m, 1H), 8.04 (d, J = 8Hz, 1H), 7.48-7.52 (m, 2H), 7.02-7.08 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6, 298 K) δ (ppm) 162.9, 162.2, 141.2, 138.2, 135.8, 128.7, 126.4, 125.2, 124.1, 121.7.

HRMS calculated for $C_{10}H_7NO_2SNa$ [M + Na]+ 228.0095, found 228.0094.

IV. Spectroscopic characterization data of Cr-complex.

a) <u>EPR spectroscopy for characterization of different Cr-PLY redox species.</u>

All EPR spectra were recorded in solid state at 100K, packed under N_2 atmosphere.

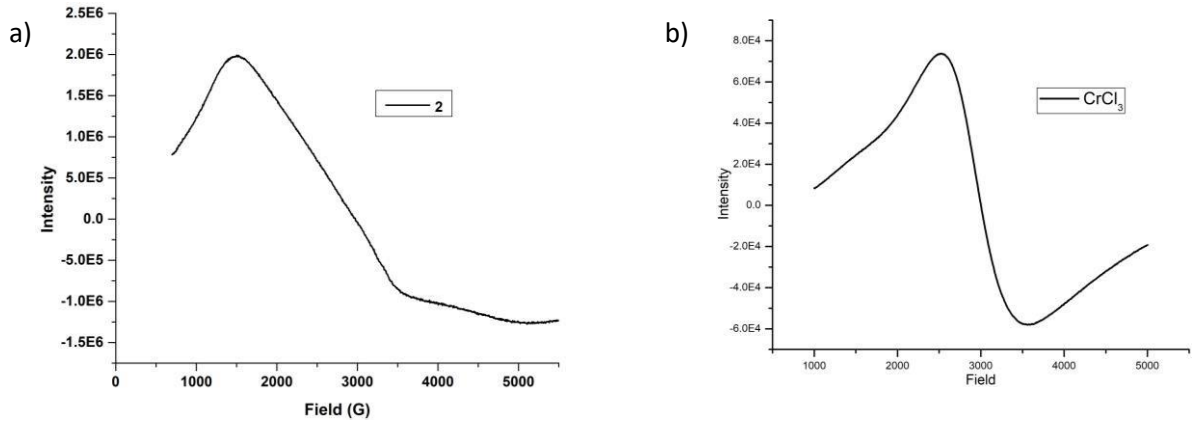


Fig. S10. EPR spectra of (a) Cr(III) complex **2** and (b) standard Cr(III) complex ($CrCl_3$).

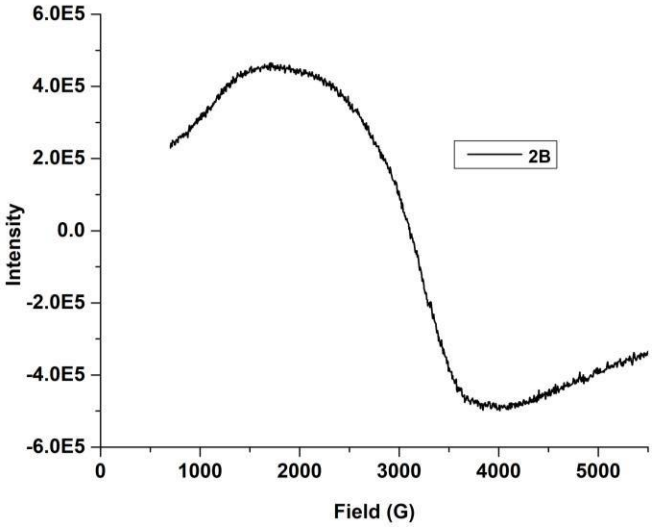


Fig. S11. EPR spectrum of doubly reduced anionic Cr-PLY complex (**2B**).

*b) UV-Vis spectroscopy for **1**, **2** and **2A**.*

All UV-vis spectra were recorded in dry acetonitrile solution at room temperature.

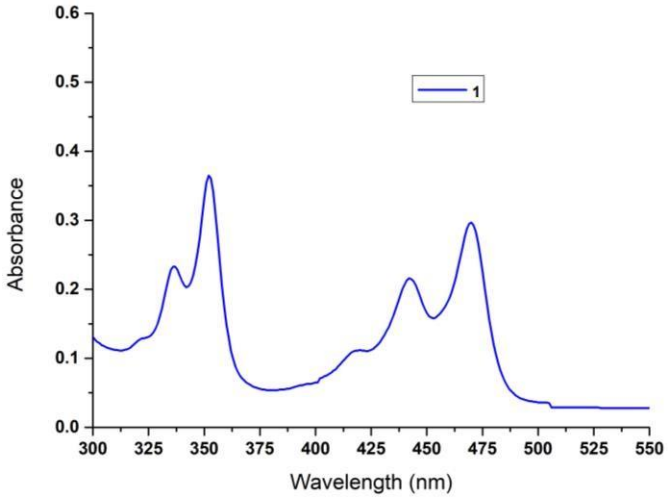


Fig. S12. UV-Vis spectrum of ligand **1**.

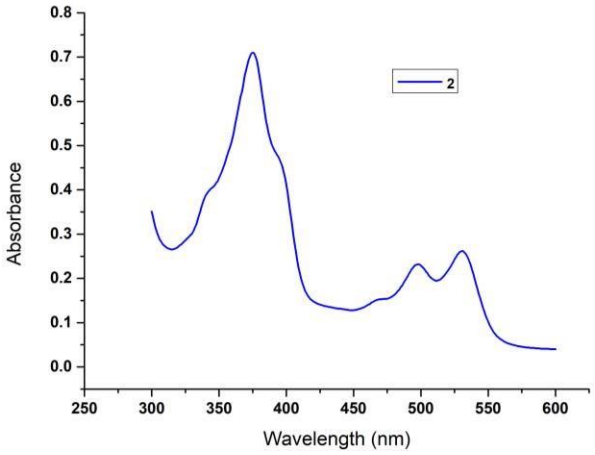


Fig. S13. UV-Vis spectrum of Cr(III)-complex **2**.

V. X-ray crystallographic details.

Suitable single crystals of **1**, **2** and **2A** were selected and mounted under nitrogen atmosphere using the X-TEMP2 and intensity data were collected on a Super Nova, Dual, Cu at zero, Eos diffractometer. All the crystals were kept at 100 K during data collection. Using Olex2,[9] the structure was solved with the ShelXT[10] structure solution program using Intrinsic Phasing and refined with the ShelXL[11] refinement package using Least Squares minimisation. All

nonhydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data (including structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* 2011059, 2015086 and 2011060 contain the supplementary crystallographic data of compounds **1**, **2** and **2A** respectively for this paper.

Crystallographic and data collection parameters for 2, 3 and 4.

	1	**2**	**2A**
CCDC	2011059	2015086	2011060
Identification code	Lig_NNO	Cr_NNO	soumi_191019
Empirical formula	$C_{19}H_{14}N_2O$	$C_{80}H_{72}Cl_2Cr_2N_8O_{10}$	$C_{38}H_{26}CrN_4O_2$
Formula weight	286.32	1480.35	622.63
Temperature/K	100.00(10)	100.0(2)	100.00(10)
Crystal system	Triclinic	triclinic	orthorhombic
Space group	P-1	P-1	Pbca
a/Å	6.1633(9)	9.8879(7)	8.78070(10)
b/Å	10.2878(14)	16.9397(10)	25.3182(3)
c/Å	11.0233(16)	20.5976(14)	29.7149(3)
α/°	88.901(11)	83.383(5)	90
β/°	81.769(12)	76.246(6)	90
γ/°	81.501(12)	89.429(5)	90
Volume/$Å^3$	684.16(17)	3328.3(4)	6605.96(13)
Z	2	2	8
$\rho_{calc}g/cm^3$	1.390	1.477	1.252

μ/mm^{-1}	0.087	0.478	3.153
F(000)	300.0	1540.0	2576.0
Crystal size/mm^3	0.3 × 0.2 × 0.15	0.25 × 0.15 × 0.1	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	3.734 to 52.638	3.348 to 50.044	5.948 to 132.418
Index ranges	$-6 \leq h \leq 7$, $-12 \leq k \leq 11$, $-13 \leq l \leq 13$	$-4 \leq h \leq 11$, $-20 \leq k \leq 20$, $-24 \leq l \leq 24$	$-10 \leq h \leq 9$, $-30 \leq k \leq 29$, $-26 \leq l \leq 35$
Reflections collected	3749	10387	37306
Independent reflections	2679 [R_{int} = 0.0293, R_{sigma} = 0.0526]	8861 [R_{int} = 0.0665, R_{sigma} = 0.0743]	5789 [R_{int} = 0.0489, R_{sigma} = 0.0240]
Data/restraints/parameters	2679/0/199	8861/0/911	5789/0/406
Goodness-of-fit on F^2	1.033	1.168	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0742, wR_2 = 0.1928	R_1 = 0.1025, wR_2 = 0.2616	R_1 = 0.0403, wR_2 = 0.1172
Final R indexes [all data]	R_1 = 0.0925, wR_2 = 0.2178	R_1 = 0.1123, wR_2 = 0.2673	R_1 = 0.0455, wR_2 = 0.1229
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.46	0.84/-0.77	0.20/-0.38

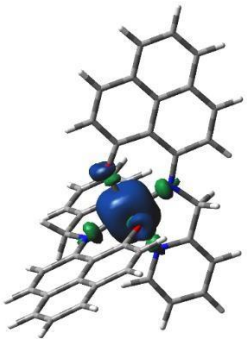
VI. Computational details.

Geometry optimization and frequency calculations have been carried out in Gaussian 16[12] with B3LYP[13] method 6-31+g(d) for C, H, N, O and lanl2dz[14] for Cr metal.

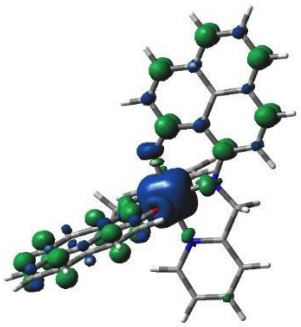
Table S3. Energy value (in H) for different spin states of 2, 2A and 2B.

Cr-PLY species	Spin state	Energy (H)
2	Doublet (S = ½)	1918. 961813
	Quartet (S = 3/2)	1918.997801 H
2A	Singlet (S = 0)	1919.083804 H
	Triplet (S = 1)	1919.144978 H
	Quintet (S = 2)	1919.129894 H
2B	Doublet (S = ½)	1919.186523 H
	Quartet (S = 3/2)	1919.182342 H
	Sextet (S = 5/2)	1919.175738 H

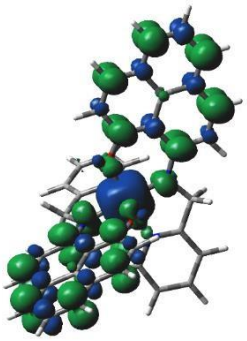
Spin Density Plots for 2, 2A and 2B:



Cationic Cr-PLY **2**



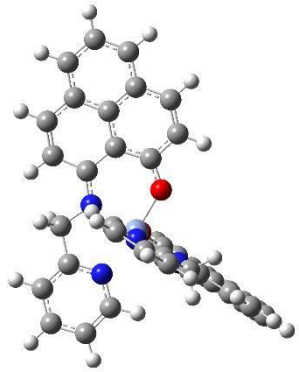
Neutral Cr-PLY **2A**



Anionic Cr-PLY **2B**

Optimized geometry for 2, 2A and 2B.

CrPLY1gen2m062x



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N	0.70864900	2.04664200	1.30029100
C	3.03919100	-0.93932600	-0.05245900
C	6.51435000	-2.06092600	-0.97782600
C	5.27652700	-1.41111600	-1.02942900
C	2.10562300	-1.21930200	0.99093600
C	0.20178800	3.23478600	3.29921300
C	-3.75061400	0.09580700	2.18065300
C	4.64290200	-2.49249100	1.04952500
C	1.88408800	2.68812100	1.21903500
C	-5.27645100	-1.41138900	1.02940900
C	4.30894300	-1.60615500	-0.00974300

C	2.27604600	3.62724100	2.15757300
C	3.68003000	-2.73112200	2.07800000
C	6.83093800	-2.91539700	0.07189800
C	-4.30904800	-1.60600100	0.00947600
C	-0.12312700	2.29972500	2.31658700
C	5.89377300	-3.12596700	1.07383200
C	2.46758100	-2.12752900	2.04603000
C	1.41346700	3.90496900	3.21778100
C	-4.94126100	-0.54831000	2.11598100
O	0.92313600	-0.71894700	1.08025500
N	1.61287800	0.66945700	-1.21552300
C	2.74278200	-0.03449900	-1.14659000
N	-0.70848900	2.04700000	-1.29995700
C	4.94146300	-0.54769000	-2.11577500
C	3.75077800	0.09634500	-2.18045400
C	0.12330500	2.30023400	-2.31619300
C	1.41880100	1.52904700	-2.37717800
C	-1.88381800	2.68866400	-1.21847300
C	-2.27562600	3.62813400	-2.15671900

C	-0.20148000	3.23562500	-3.29855100
C	-1.41303100	3.90600500	-3.21688000
C	-2.10586400	-1.21878900	-0.99138200
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C	-3.03929600	-0.93917200	0.05224600
C	-6.51426200	-2.06124200	0.97779100
C	-3.68053600	-2.73002400	-2.07890300
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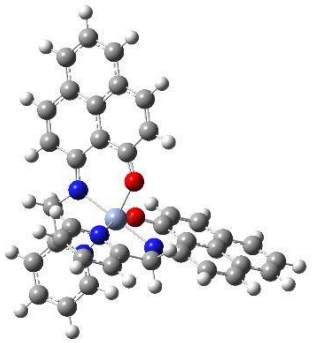
C	-2.46808900	-2.12644200	-2.04689200
C	-5.89403300	-3.12541900	-1.07441800
O	-0.92333700	-0.71854900	-1.08062400
N	-1.61291400	0.66939500	1.21552900
C	-1.41872500	1.52869600	2.37737900
H	1.41198700	0.93899500	-3.30602100
H	2.23598900	2.25900100	-2.47719400
H	1.71521000	-2.30058200	2.80713800
H	3.93544200	-3.41280000	2.88490900
H	7.22903600	-1.88899200	-1.77816500
H	7.79272900	-3.41424800	0.10448700

H	6.11951900	-3.79639600	1.89874500
H	3.55679100	0.72578600	-3.03720900
H	5.66829400	-0.41256400	-2.91295300
H	0.49115200	3.42440900	-4.11239300
H	-1.68622900	4.63611400	-3.97161400
H	-3.23296100	4.12622900	-2.06125600
H	-2.50983300	2.41711600	-0.37426000
H	2.51007700	2.41674100	0.37474700
H	3.23348100	4.12517600	2.06228200
H	1.68676900	4.63481000	3.97273700
H	-0.49083800	3.42346600	4.11308500
H	-5.66797300	-0.41347400	2.91331600
H	-3.55656700	0.72505000	3.03753700
H	-1.71586900	-2.29913100	-2.80823300
H	-3.93611300	-3.41131700	-2.88608500
H	-6.11992700	-3.79550600	-1.89956900
H	-7.79278400	-3.41419300	-0.10481000
H	-7.22879900	-1.88964300	1.77833500
H	-1.41195000	0.93844500	3.30609600

H	-2.23584000	2.25871100	2.47757400

CrPLY2gen1m062x



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N	0.39584600	2.35246400	1.36026400
C	2.92901100	-1.02263700	0.10975100
C	6.21986900	-2.64915400	-0.76712700
C	5.10258000	-1.81338000	-0.82523000
C	1.96280200	-1.13089800	1.16708900
C	-0.44311500	3.57865100	3.22081600
C	-3.88358600	-0.04351200	1.95958000
C	4.27741900	-2.80457100	1.22896400
C	1.50614200	3.09909100	1.38118700
C	-5.10245500	-1.81365900	0.82530800
C	4.08672500	-1.86943100	0.17023100
C	1.70803500	4.11142400	2.30741100

C	3.29496100	-2.87692800	2.26778500
C	6.38082400	-3.56254900	0.26866900
C	-4.08633500	-1.87002900	-0.16986100
C	-0.56364500	2.57116600	2.26163100
C	5.40936500	-3.62855900	1.25747900
C	2.20963500	-2.07438600	2.24179600
C	0.70580200	4.35617300	3.24437000
C	-4.95072600	-0.86650800	1.88760000
O	0.88612000	-0.46071800	1.27096900
N	1.76842100	0.75455000	-1.10233900
C	2.79748700	-0.06720900	-0.98316100
N	-0.39635000	2.35166300	-1.36074800
C	4.95061500	-0.86649200	-1.88774300
C	3.88345000	-0.04353300	-1.95972200
C	0.56297200	2.57021400	-2.26233500
C	1.77827500	1.67456000	-2.22747300
C	-1.50687400	3.09795300	-1.38189800
C	-1.70917300	4.10977600	-2.30858700
C	0.44203300	3.57721100	-3.22198300

C	-0.70711600	4.35437900	-3.24577500
C	-1.96206100	-1.13195900	-1.16634300
C	-4.27674800	-2.80554100	-1.22832200
C	-2.92863300	-1.02320200	-0.10935500
C	-6.21975000	-2.64943600	0.76717100
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C	-6.38044700	-3.56314500	-0.26837600
C	-2.20859900	-2.07586700	-2.24076300
C	-5.40870300	-3.62950200	-1.25689100
O	-0.88521900	-0.46204900	-1.27006400
N	-1.76848500	0.75463200	1.10229200
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H	3.44331600	-3.58897900	3.07619700
H	6.96867200	-2.57156600	-1.55167300
H	7.25113200	-4.20886000	0.30513900
H	5.51535500	-4.33013400	2.08135400

H	3.82937900	0.64638600	-2.79062500
H	5.72467200	-0.81914300	-2.65068400
H	1.24176900	3.73548900	-3.93908400
H	-0.82356900	5.13934200	-3.98637000
H	-2.62541400	4.68850200	-2.29470000
H	-2.24616800	2.85059200	-0.62429300
H	2.24560200	2.85158100	0.62379100
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H	0.82194000	5.14152100	3.98460600
H	-1.24297800	3.73703400	3.93775100
H	-5.72492200	-0.81900100	2.65039000
H	-3.82968500	0.64654900	2.79036600
H	-1.44679200	-2.10862400	-3.01253000
H	-3.44211500	-3.59066900	-3.07501300
H	-5.51447200	-4.33135300	-2.08055900
H	-7.25075800	-4.20945100	-0.30488000
H	-6.96875200	-2.57159400	1.55150200
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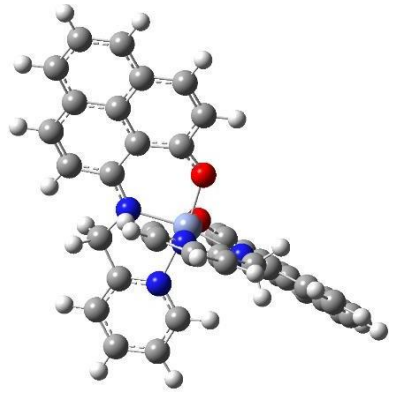
CrPLY3gen2m062x



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C	3.21693200	0.23424100	-0.83963200
C	6.84119800	1.24083200	-1.27456100
C	5.47924800	1.29435300	-0.90530500
C	2.38205600	-0.86019900	-1.24567400
C	0.81327900	-3.45171200	2.59368000
C	-3.61220700	-2.44107500	0.14343900
C	5.15572300	-0.91013300	-1.92559800
C	2.14938600	-1.10546500	2.20005300
C	-5.48029400	-1.28831900	-0.90971300
C	4.60287000	0.20383400	-1.21700900
C	2.75226100	-2.09187900	2.96698500

C	4.29686300	-1.98148800	-2.27330800
C	7.35614600	0.13970500	-1.94674400
C	-4.60309000	-0.19761200	-1.21841900
C	0.27256800	-2.41379100	1.83159200
C	6.52732000	-0.92334400	-2.27161400
C	2.96652000	-1.94474000	-1.94969100
C	2.06548100	-3.28744800	3.16740600
C	-4.93360700	-2.40842700	-0.24579200
O	1.09451400	-0.94691100	-1.03306400
N	1.44208700	1.38107700	0.41605000
C	2.71052700	1.36943400	-0.08457600
N	-0.93538600	1.25894700	1.66544700
C	4.93157900	2.41250200	-0.23887300
C	3.61019200	2.44305600	0.15057400
C	-0.27256100	2.40482000	1.84351900
C	1.07698900	2.54083500	1.18634200
C	-2.14811400	1.09353900	2.20787000
C	-2.75025400	2.07542800	2.98115700
C	-0.81253600	3.43824200	2.61223600

C	-2.06372800	3.27020000	3.18708000
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C	-3.21725000	-0.22984900	-0.84072900
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C	-4.29559000	1.99036700	-2.26879400
C	-7.35615600	-0.12993400	-1.94886600
C	-2.96549700	1.95228500	-1.94437600
C	-6.52656200	0.93340700	-2.27076900
O	-1.09463400	0.95197100	-1.02837200
N	-1.44257400	-1.38263400	0.40999300
C	-1.07836500	-2.54527100	1.17635800
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H	1.80585400	2.74752300	1.99365000
H	2.29099600	-2.74746400	-2.22977800
H	4.71062000	-2.83021500	-2.81367400
H	7.47914500	2.08497700	-1.02349800
H	8.40740400	0.11433200	-2.22297100
H	6.91650800	-1.78626200	-2.80660400

H	3.25601100	3.33528100	0.65172500
H	5.57575300	3.26379400	-0.02938100
H	-0.25066100	4.35853900	2.73985700
H	-2.50469800	4.06397700	3.78287400
H	-3.73707300	1.90859100	3.39700100
H	-2.63116100	0.14538300	1.99154600
H	2.63250600	-0.15636200	1.98813600
H	3.73983800	-1.92782400	3.38213000
H	2.50705500	-4.08473000	3.75804900
H	0.25118600	-4.37245200	2.71707700
H	-5.57852100	-3.25962800	-0.03820300
H	-3.25886100	-3.33483900	0.64242000
H	-2.28951500	2.75557400	-2.22171500
H	-4.70869500	2.84065100	-2.80720400
H	-6.91502600	1.79793400	-2.80368200
H	-8.40730600	-0.10322500	-2.22538000
H	-7.48064500	-2.07739600	-1.03044200
H	-1.05947000	-3.46373100	0.56069100
H	-1.80621400	-2.75279900	1.9844

VI. ^{1}H and ^{13}C NMR spectra.

Fig. S14. ^{1}H NMR spectrum ($CDCl_3$) of 9-((pyridin-2-ylmethyl)amino)-1H-phenalen-1-one (**1**):

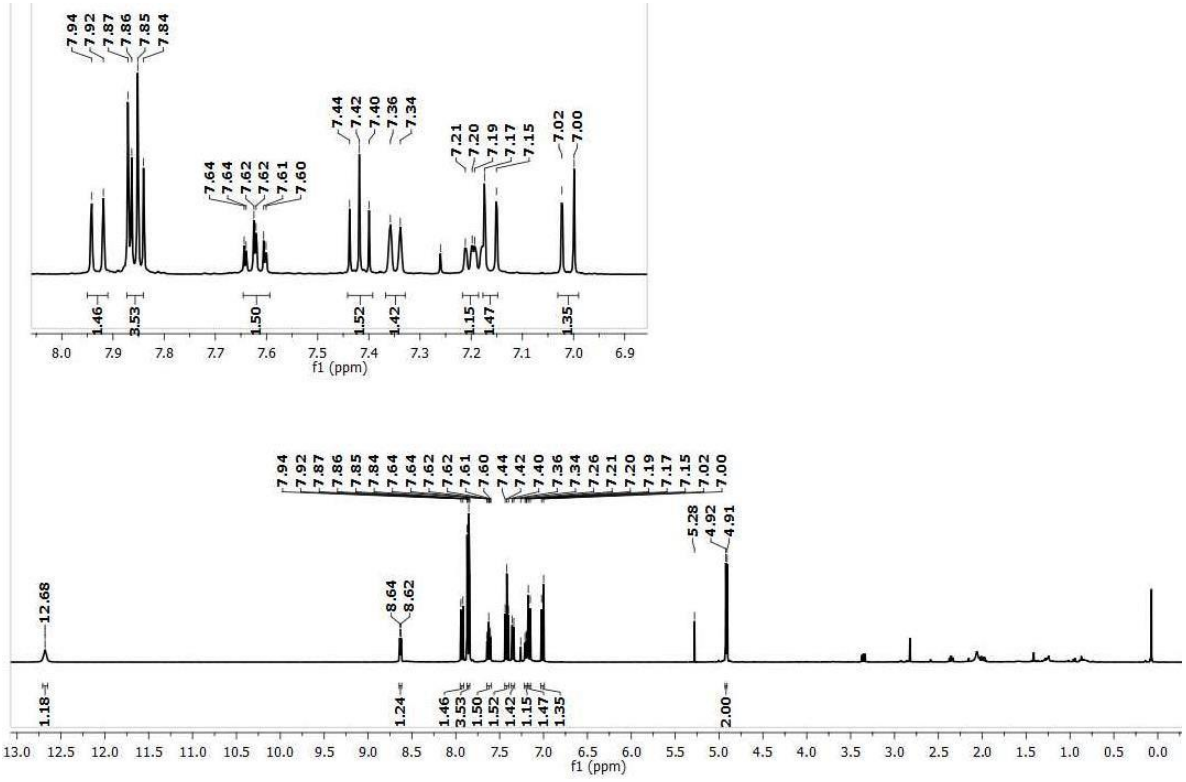


Fig. S15. ^{13}C NMR spectrum ($CDCl_3$) of 9-((pyridin-2-ylmethyl)amino)-1H-phenalen-1-one (**1**):

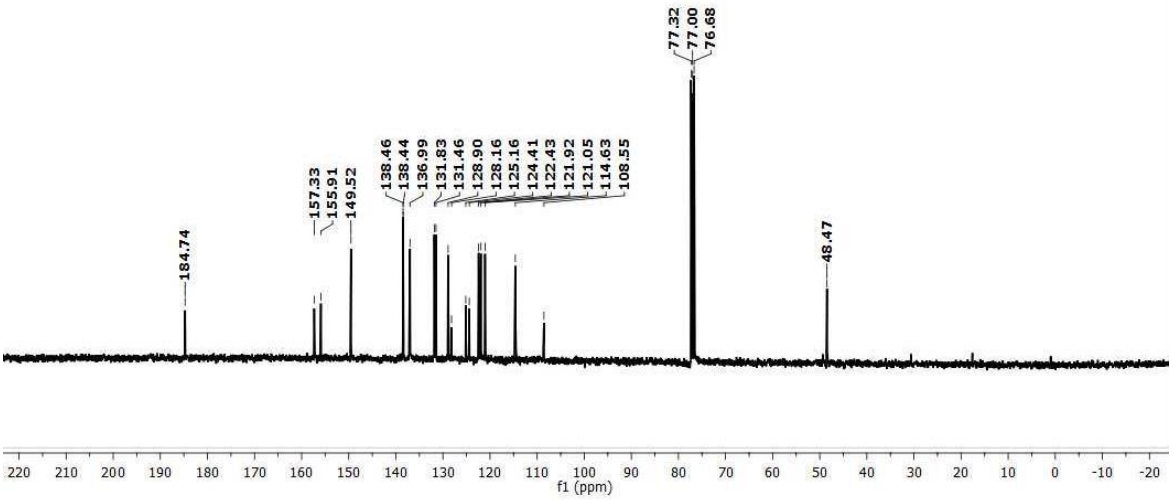


Fig. S16. ^{1}H NMR spectrum ($CDCl_3$) of N-formylbenzamide (**4a**):

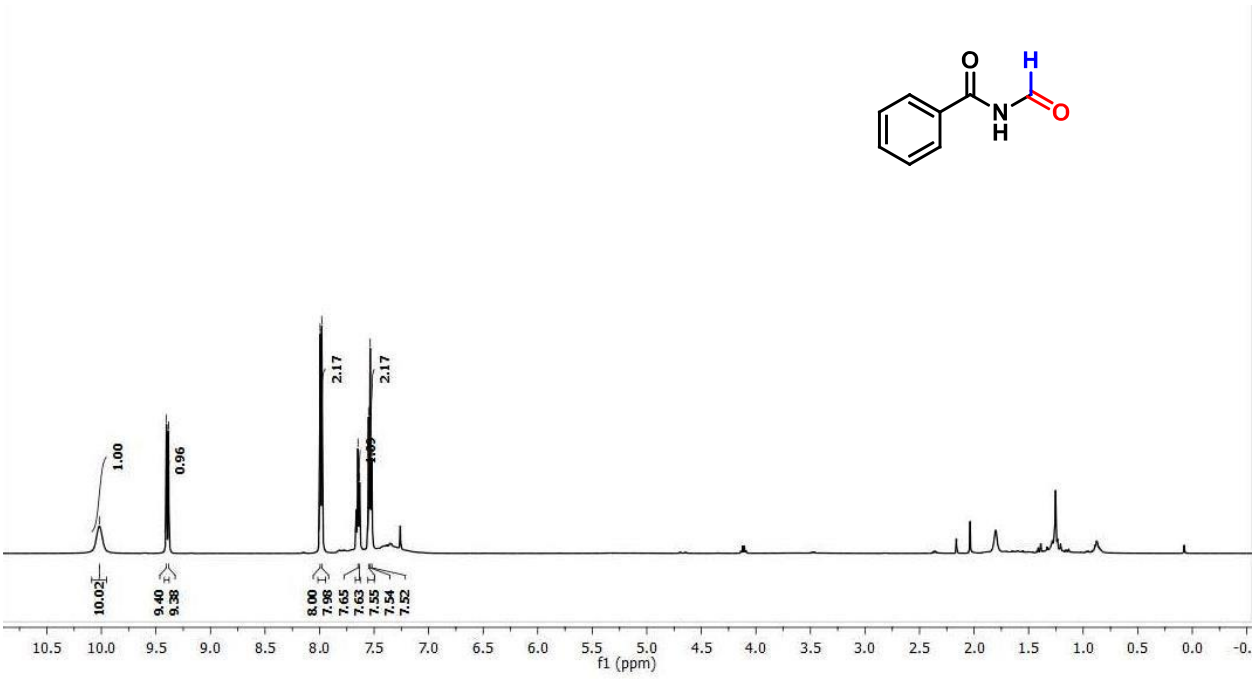


Fig. S17. ^{13}C NMR spectrum ($CDCl_3$) of N-formylbenzamide (**4a**):

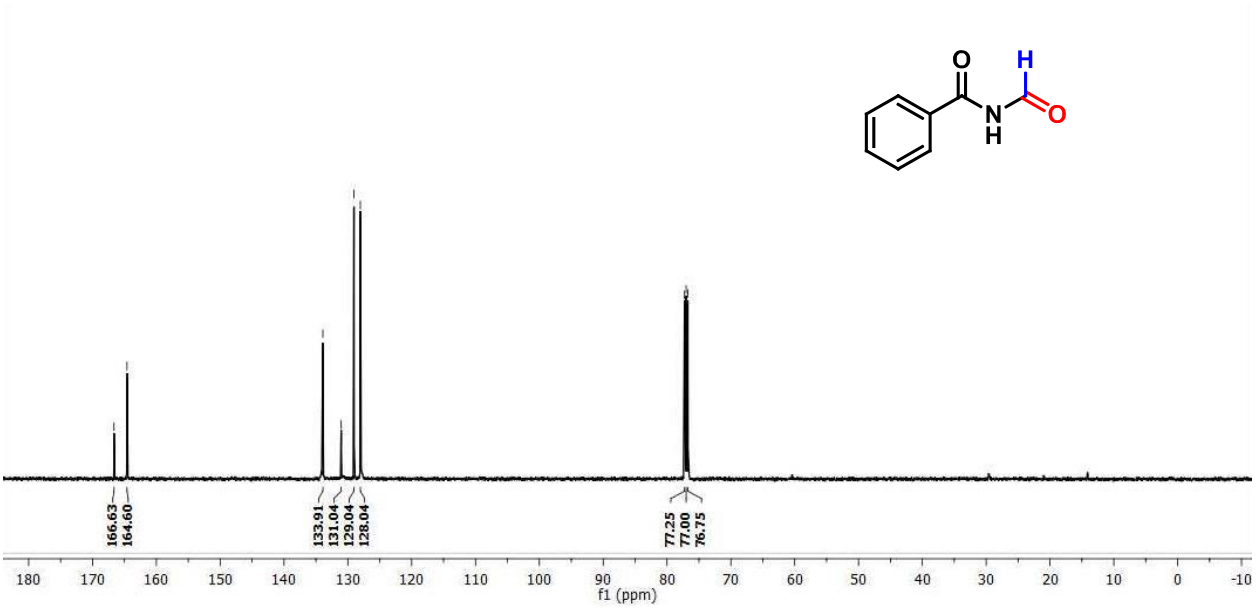


Fig. S18. ^{1}H NMR spectrum (DMSO-d_6) of 4-chloro-N-formylbenzamide (**4b**):

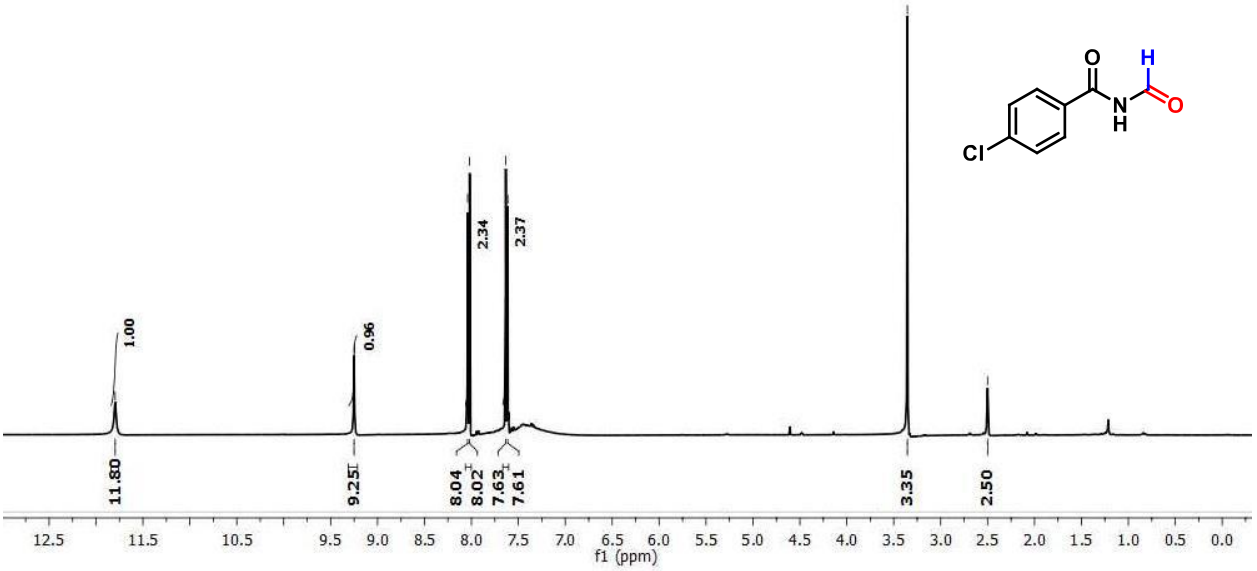


Fig. S19. ^{13}C NMR spectrum (DMSO-d_6) of 4-chloro-N-formylbenzamide (**4b**):

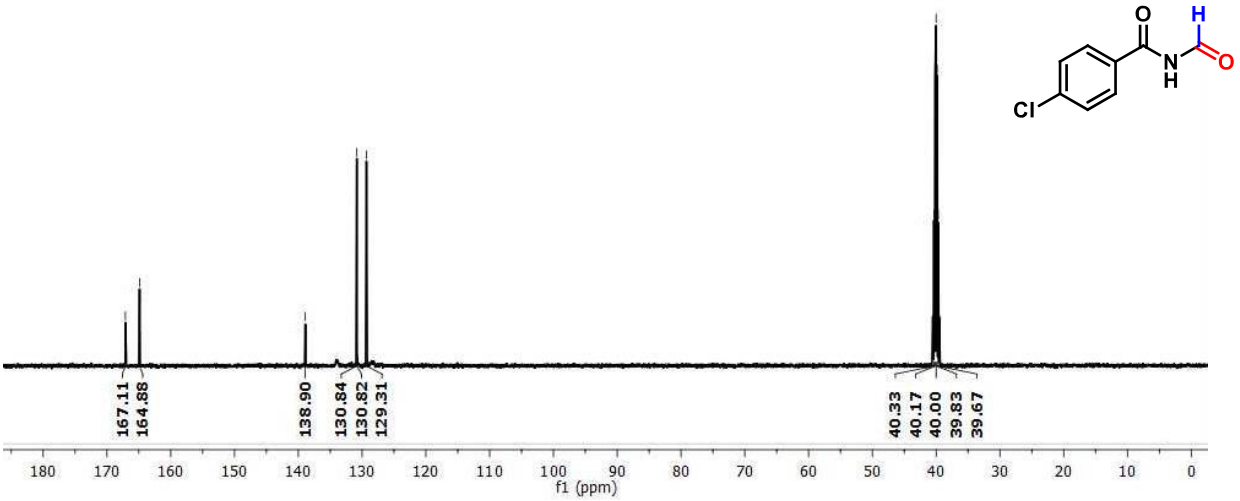


Fig. S20. ^{1}H NMR spectrum ($CDCl_3$ + DMSO-d_6) of N-formyl-4-methoxybenzamide (**4c**):

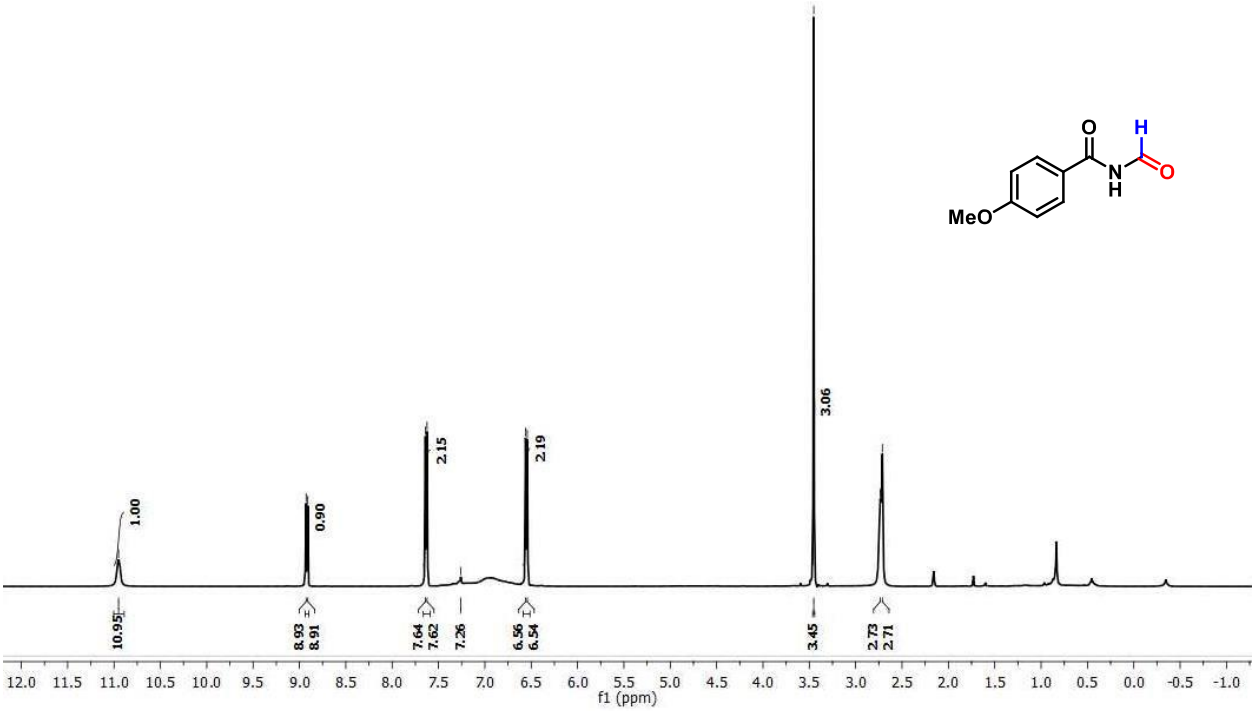


Fig. S21. ^{13}C NMR spectrum ($CDCl_3$ + DMSO-d_6) of N-formyl-4-methoxybenzamide (**4c**):

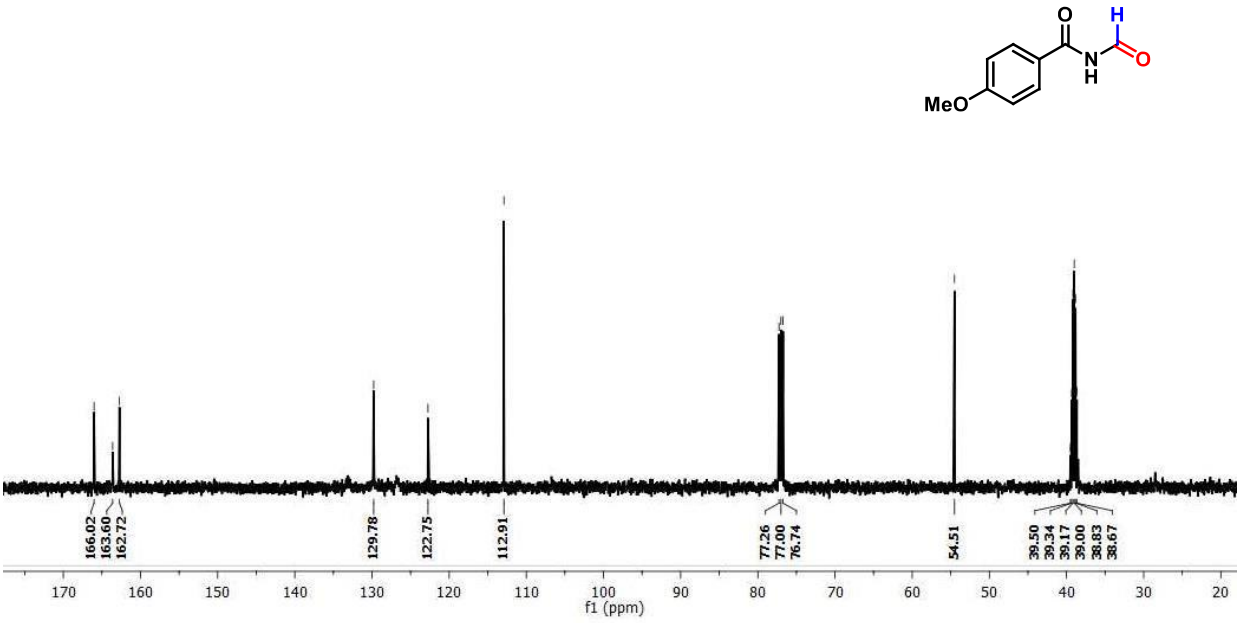


Fig. S22. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-3-methylbenzamide (**4d**):

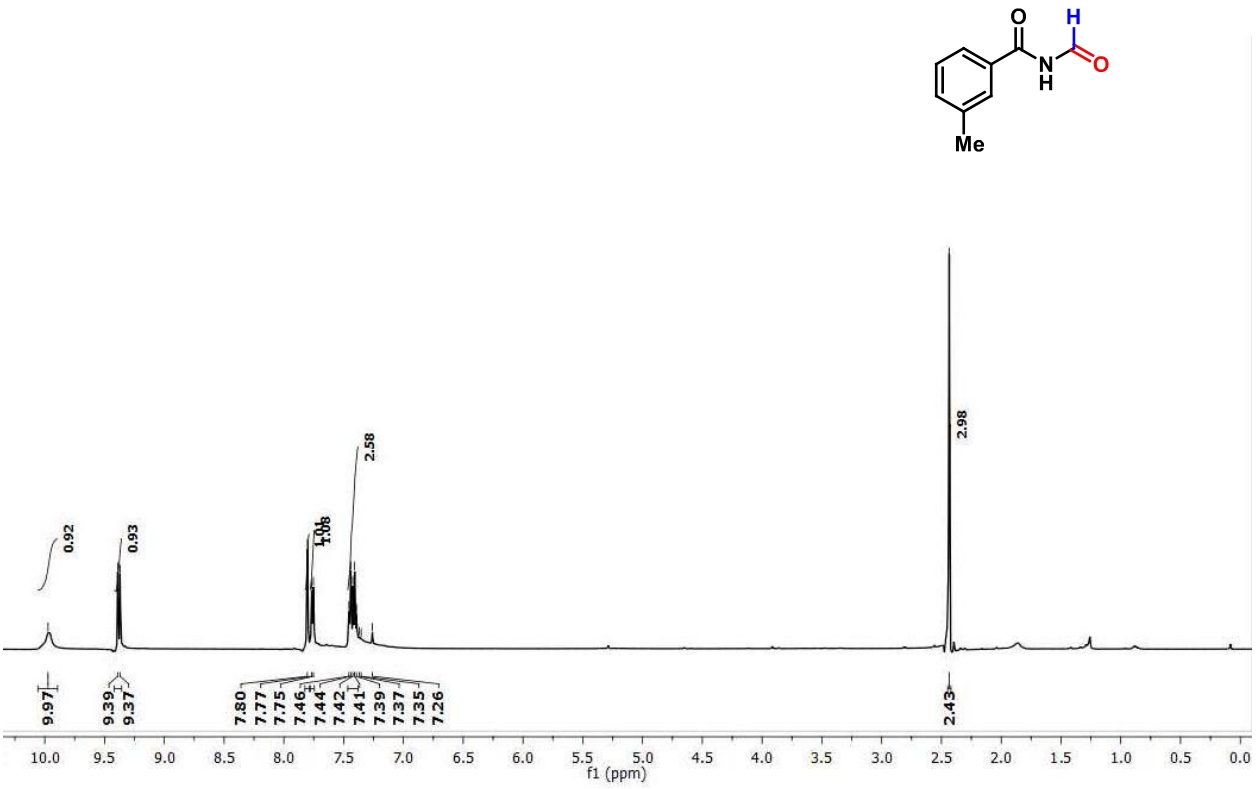


Fig. S23. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-3-methylbenzamide (**4d**):

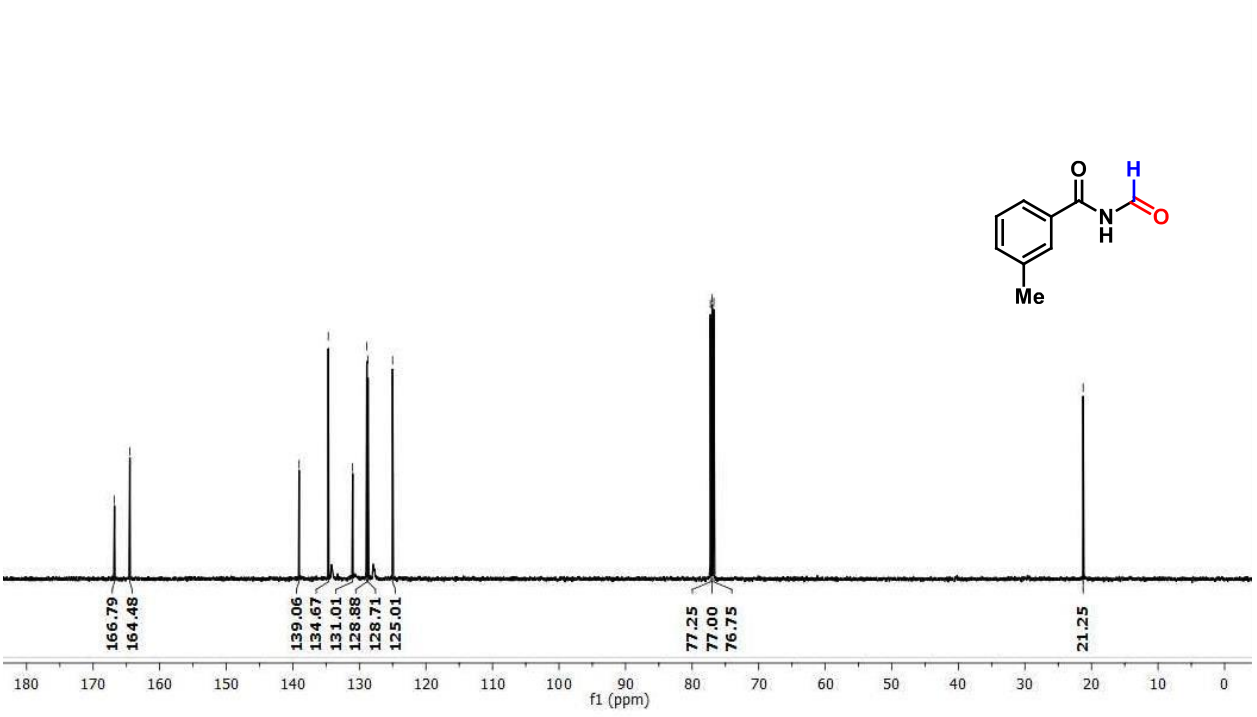


Fig. S24. ^{1}H NMR spectrum (DMSO-d_6) of N-formyl-3-methoxybenzamide (**4e**):

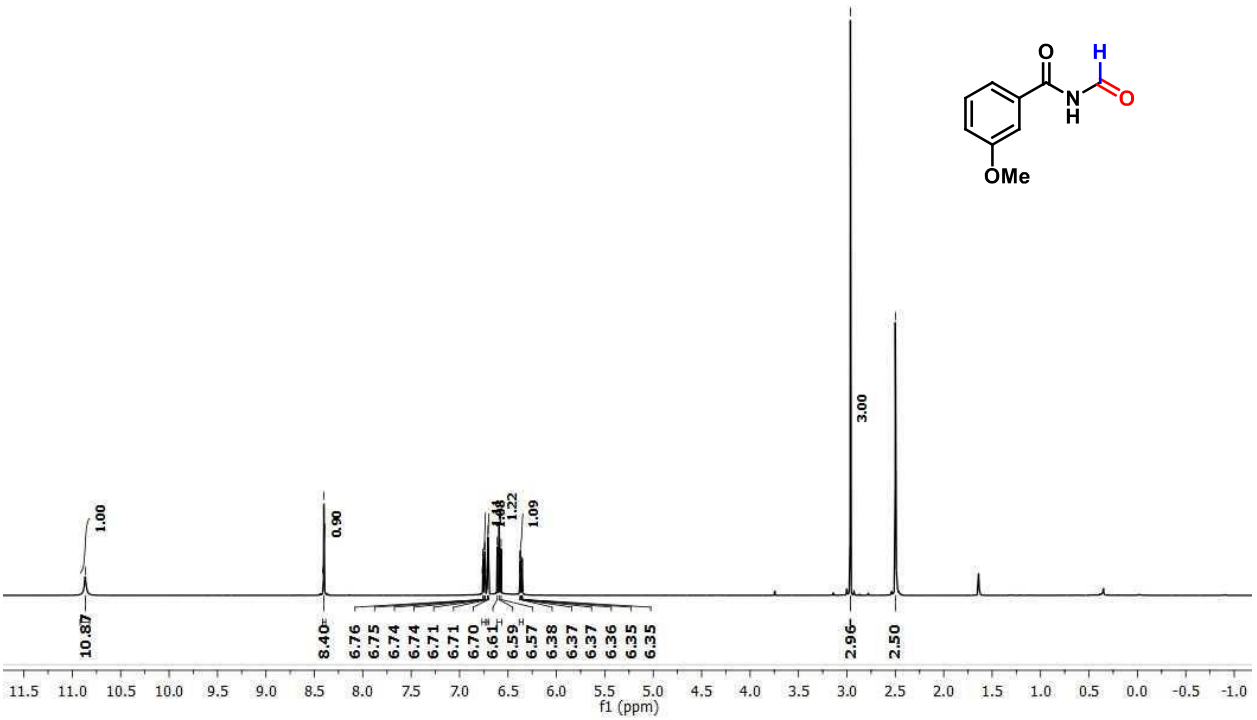


Fig. S25. ^{13}C NMR spectrum (DMSO-d_6) of N-formyl-3-methoxybenzamide (**4e**):

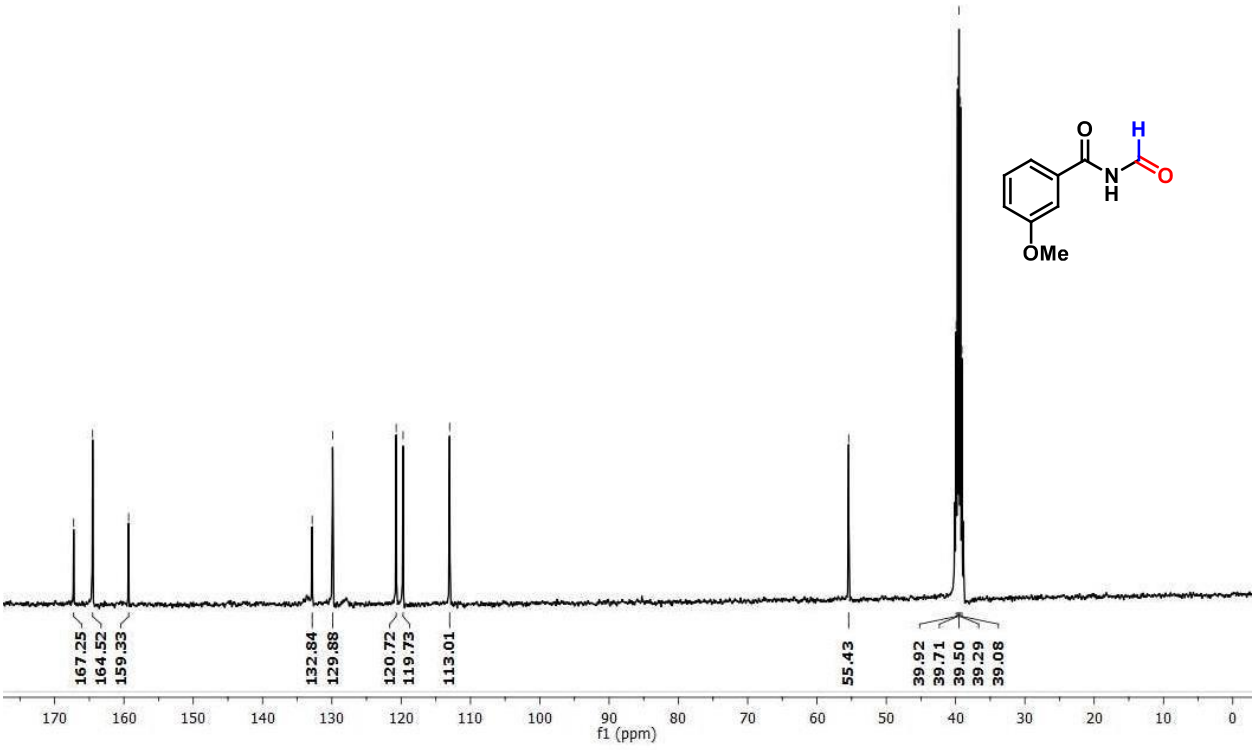


Fig. S26. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-2-methylbenzamide (**4f**):

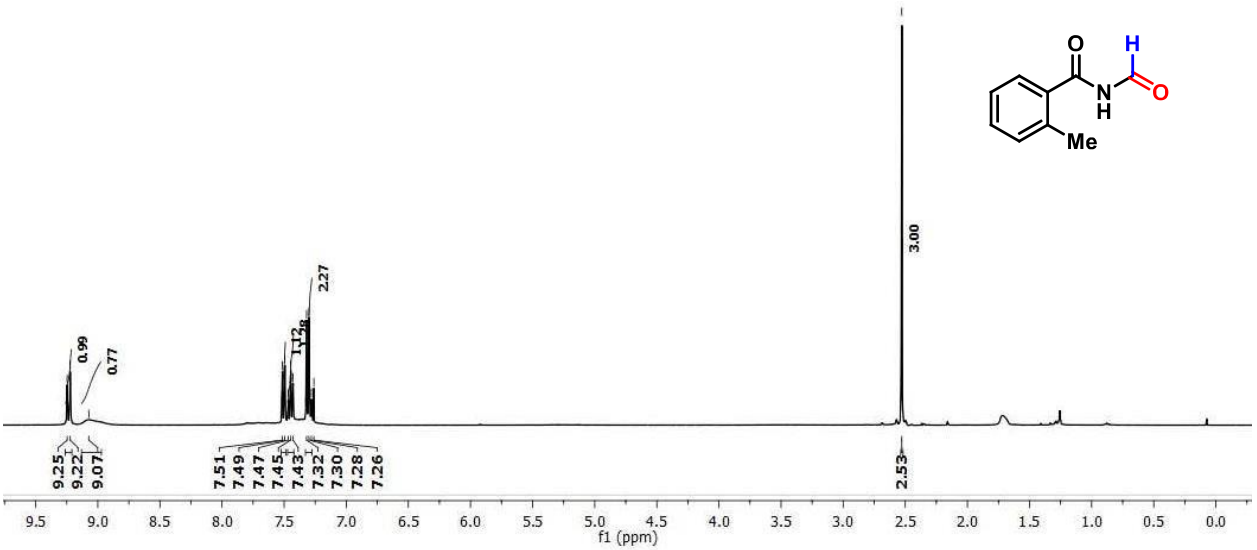


Fig. S27. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-2-methylbenzamide (**4f**):

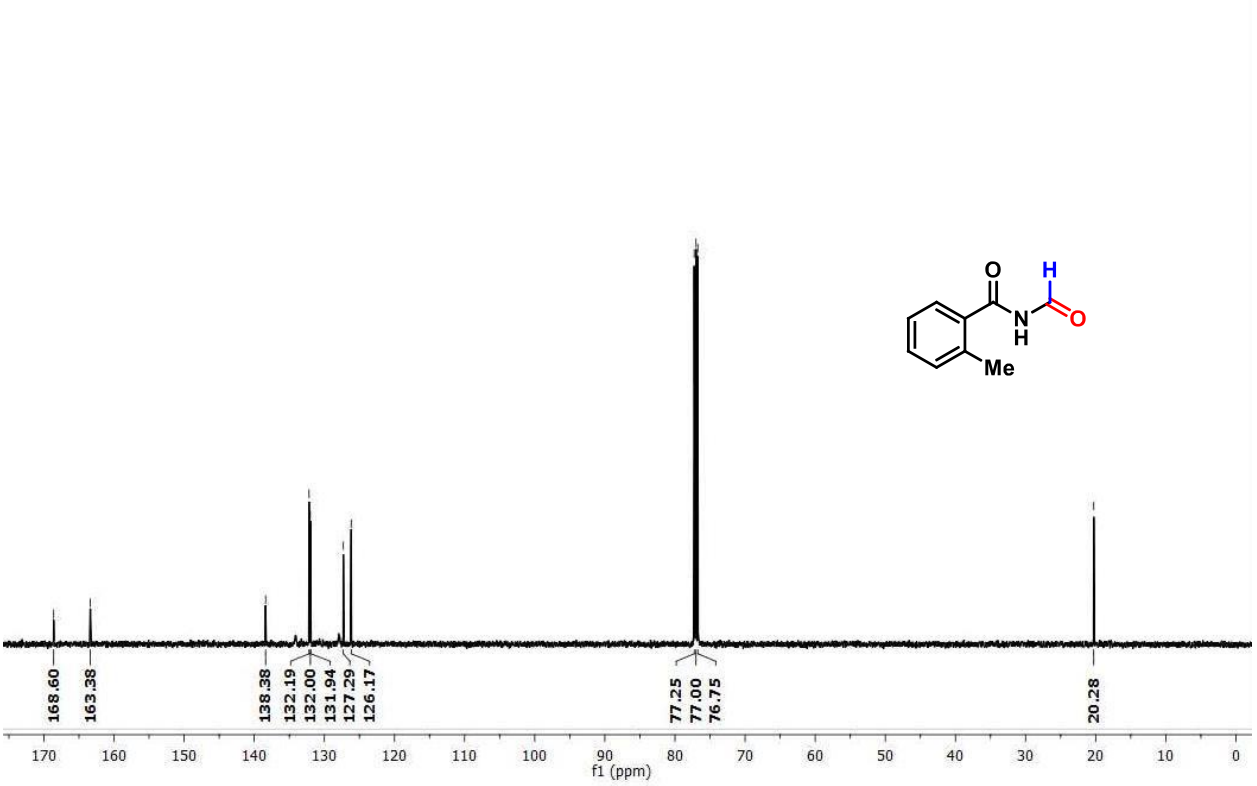


Fig. S28. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-2-methoxybenzamide (**4g**):

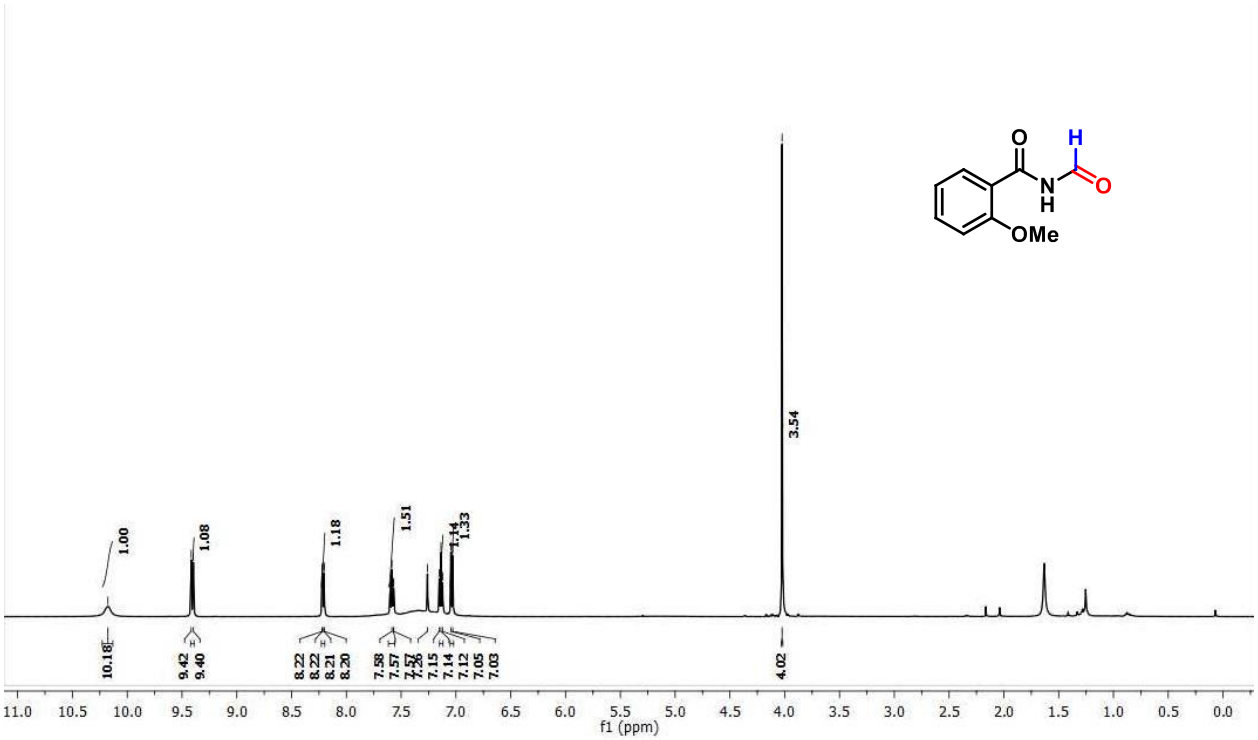


Fig. S29. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-2-methoxybenzamide (**4g**):

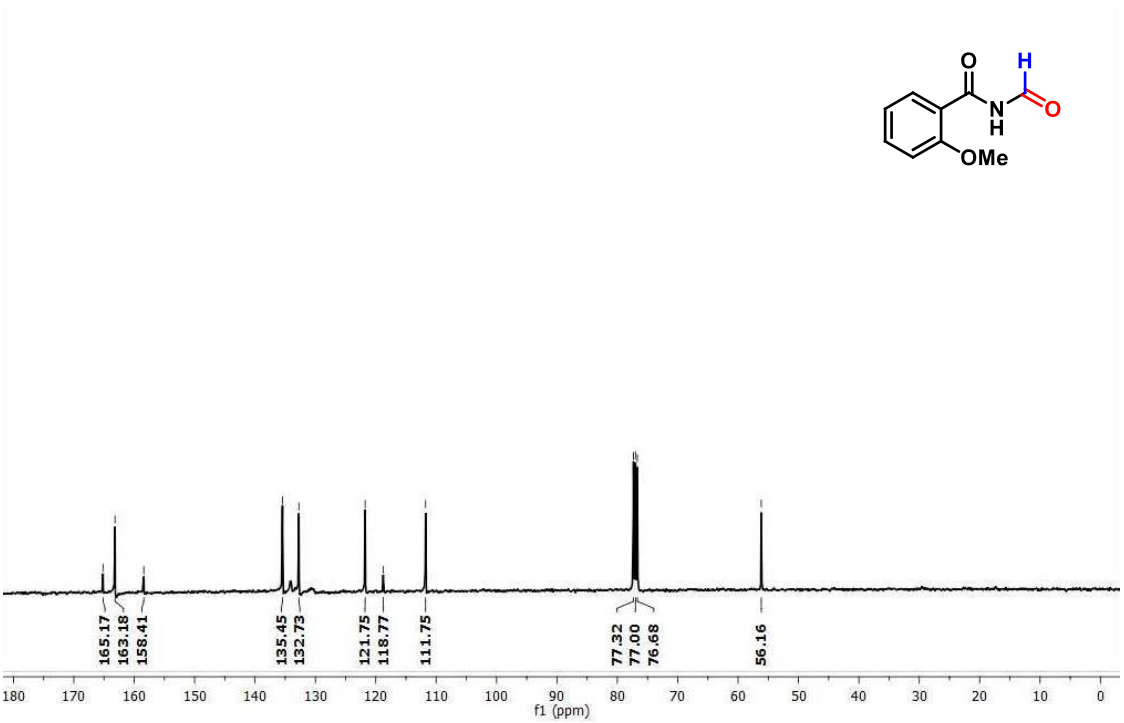


Fig. S30. ^{1}H NMR spectrum ($CDCl_3$ + DMSO-d_6) of 4-bromo-N-formyl-3-methylbenzamide (**4h**):

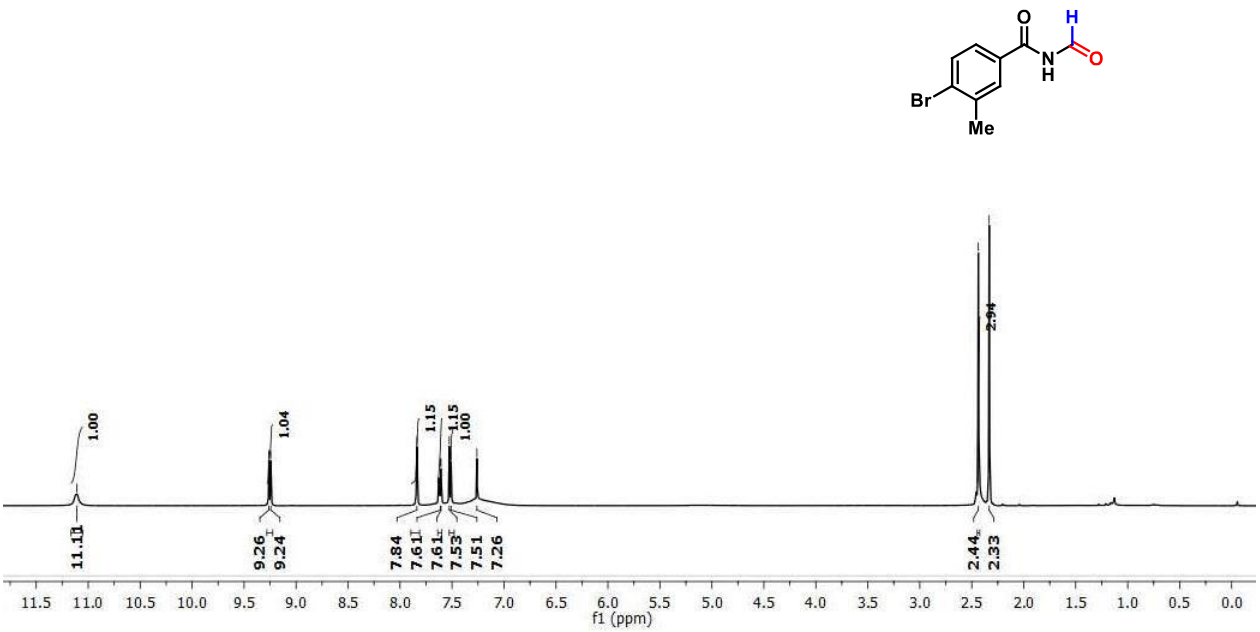


Fig. S31. ^{13}C NMR spectrum ($CDCl_3$ + DMSO-d_6) of 4-bromo-N-formyl-3-methylbenzamide (**4h**):

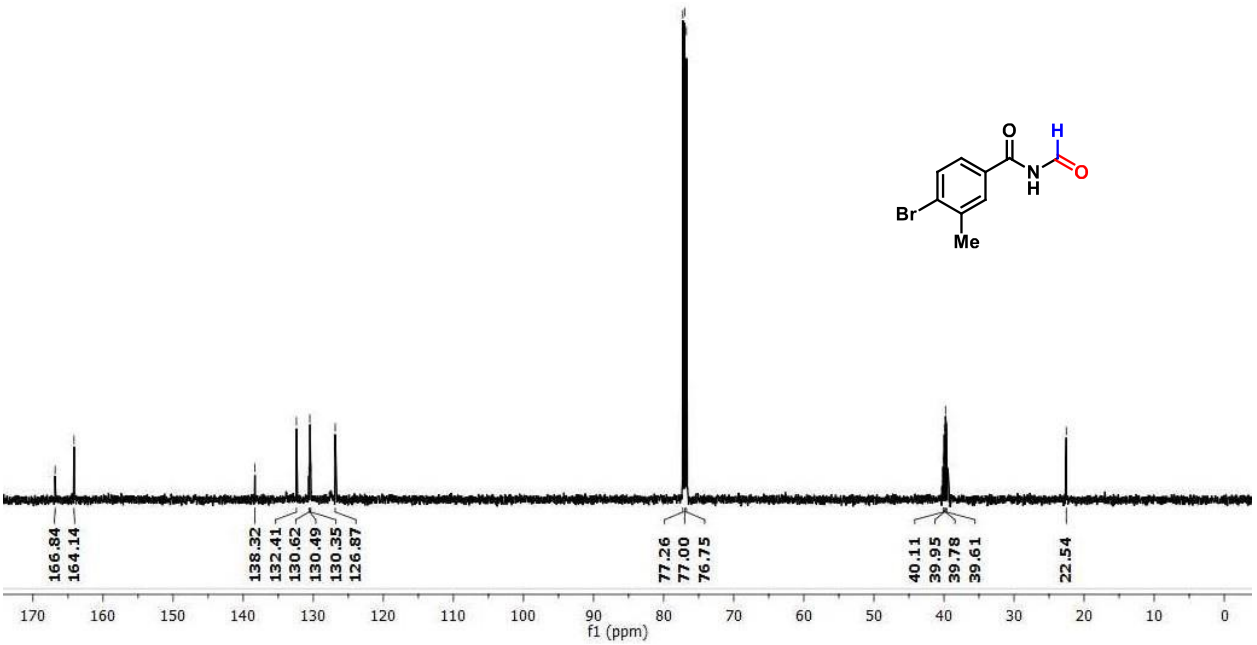


Fig. S32. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-3,4-dimethylbenzamide (**4i**):

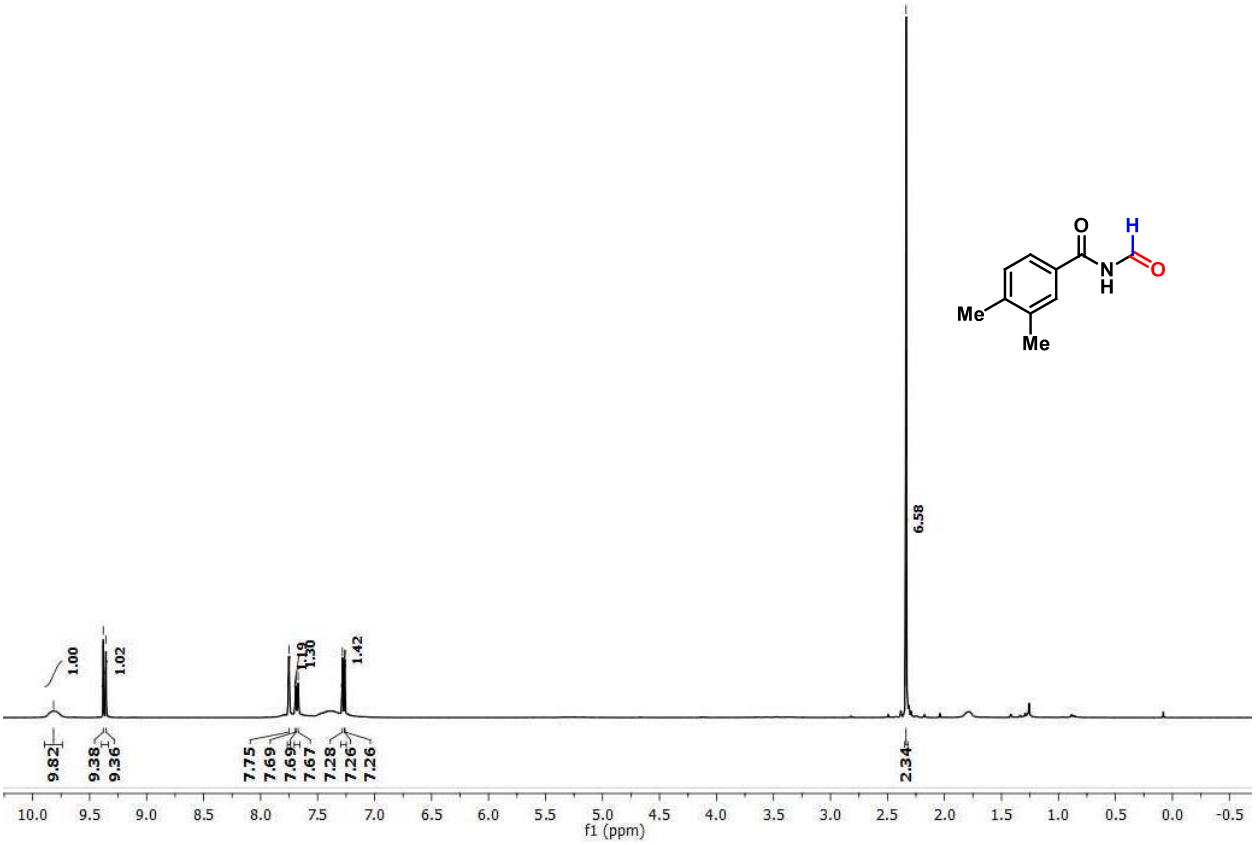


Fig. S33. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-3,4-dimethylbenzamide (**4i**):

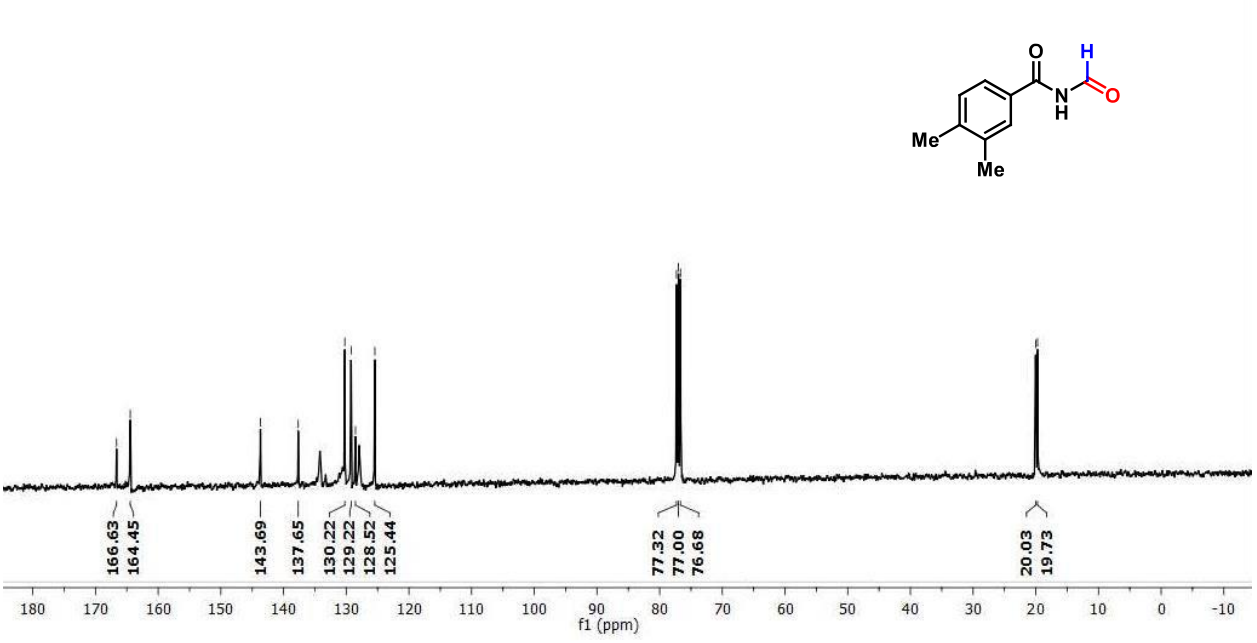


Fig. S34. ^{1}H NMR spectrum ($CDCl_3$) of 2-ethoxy-N-formylbenzamide (**4j**):

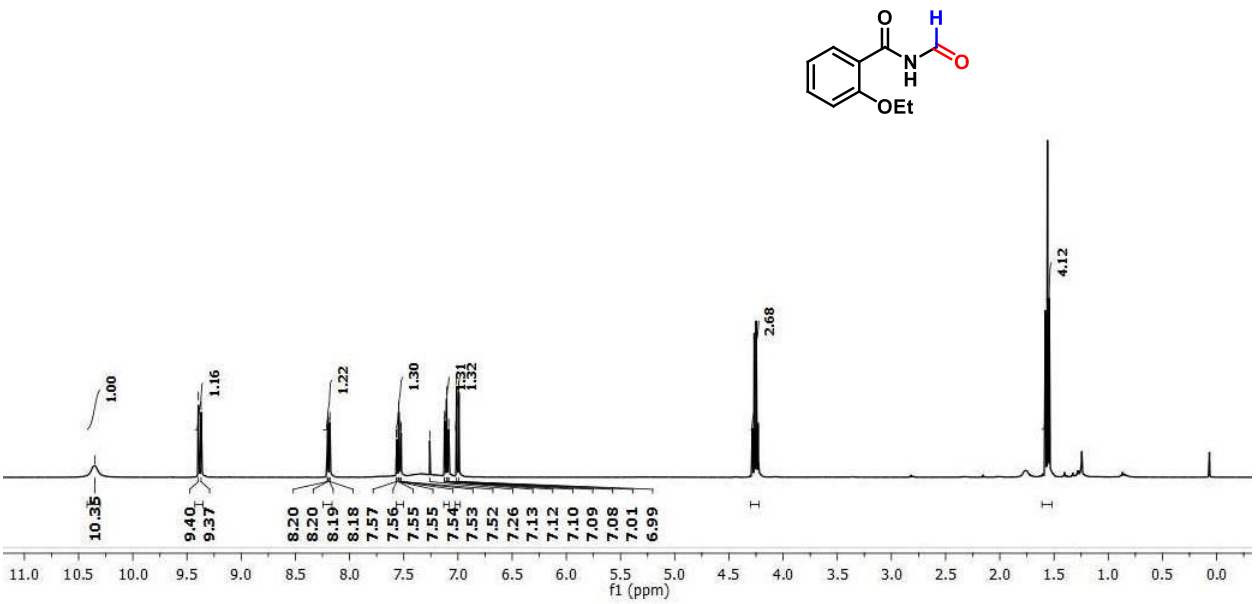


Fig. S35. ^{13}C NMR spectrum ($CDCl_3$) of 2-ethoxy-N-formylbenzamide (**4j**):

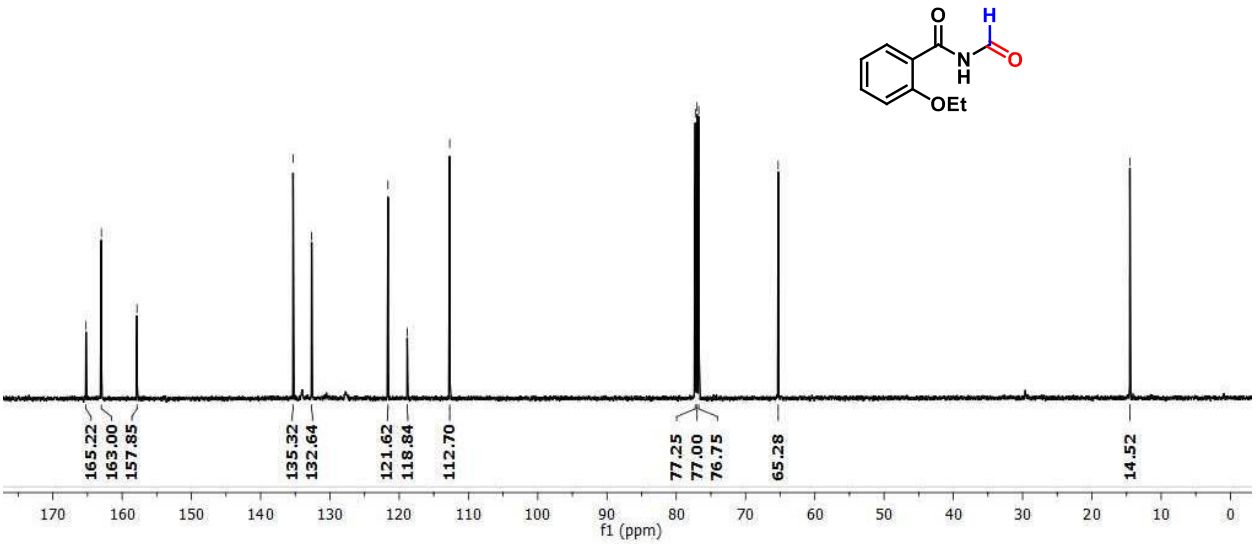


Fig. S36. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-4-methylbenzamide (**4k**):

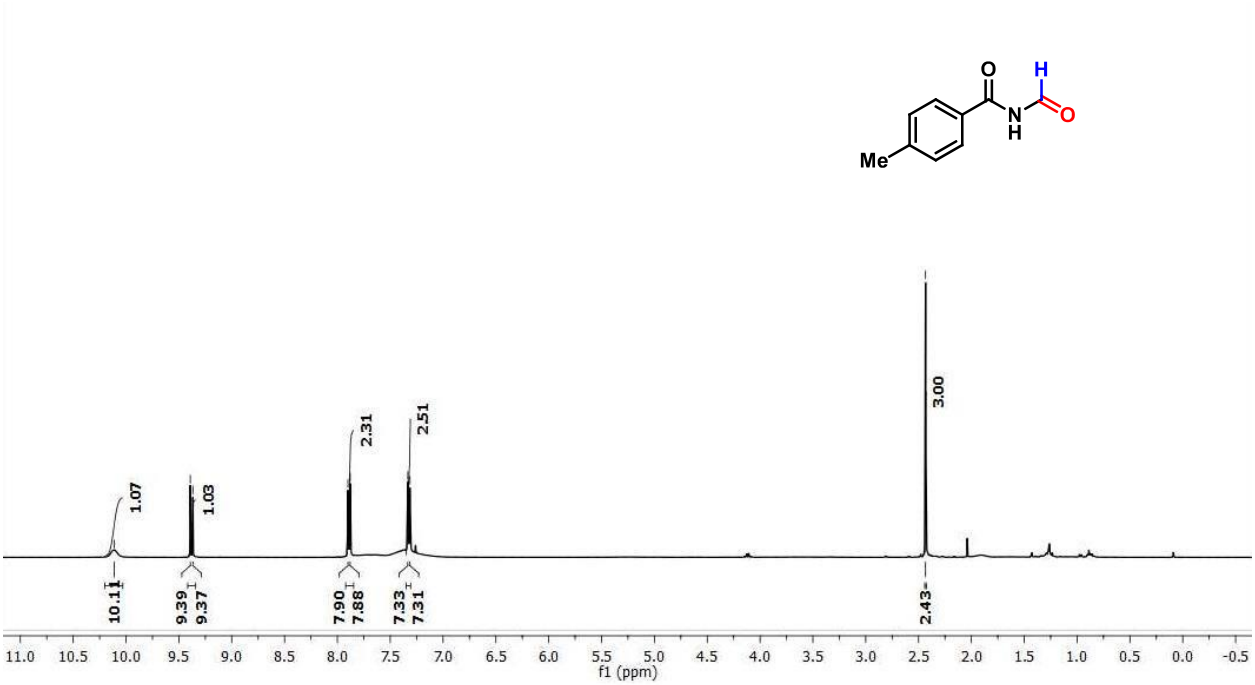


Fig. S37. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-4-methylbenzamide (**4k**):

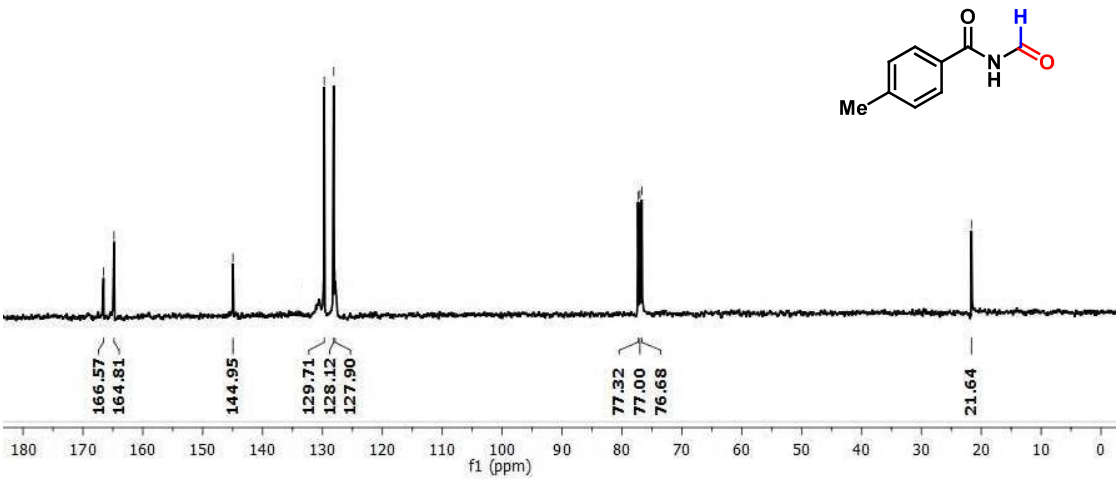


Fig. S38. ^{1}H NMR spectrum (DMSO-d_6) of N-formyl-3,5-dimethoxybenzamide (**4l**):

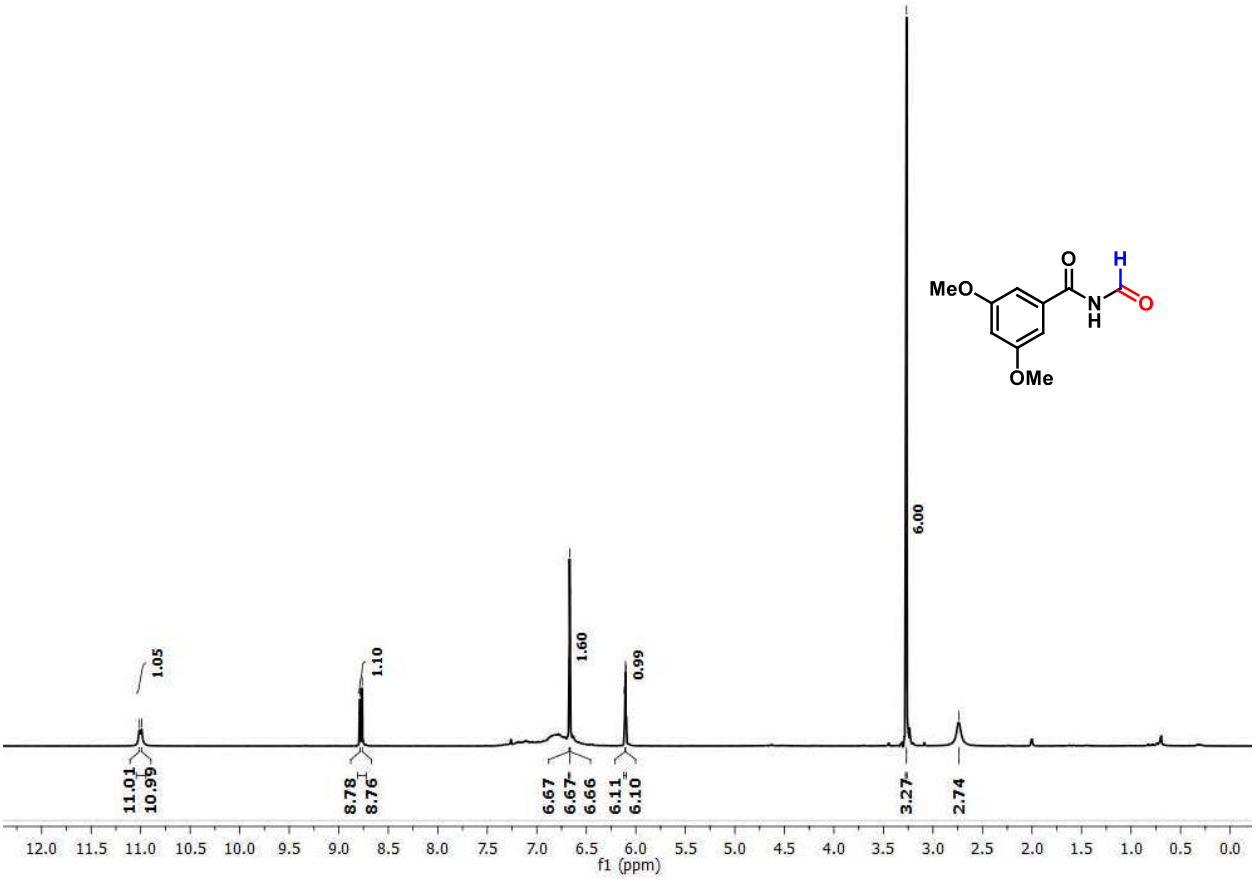


Fig. S39. ^{13}C NMR spectrum (DMSO-d_6) of N-formyl-3,5-dimethoxybenzamide (**4l**):

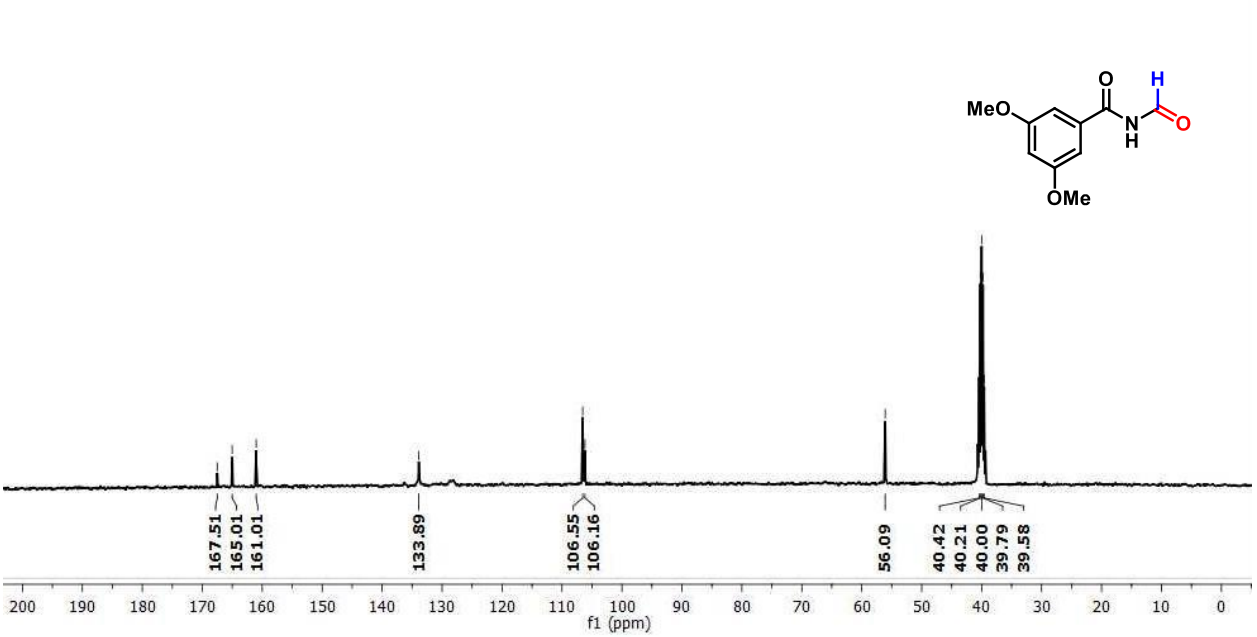


Fig. S40. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-3-(trifluoromethyl)benzamide (**4m**):

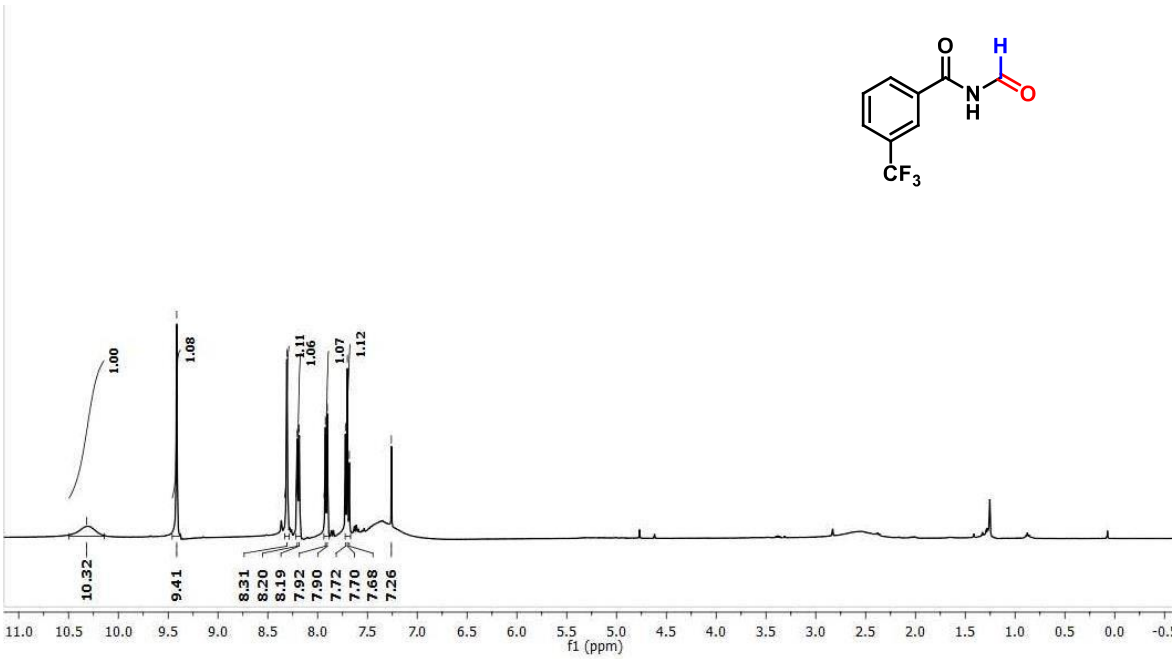


Fig. S41. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-3-(trifluoromethyl)benzamide (**4m**):

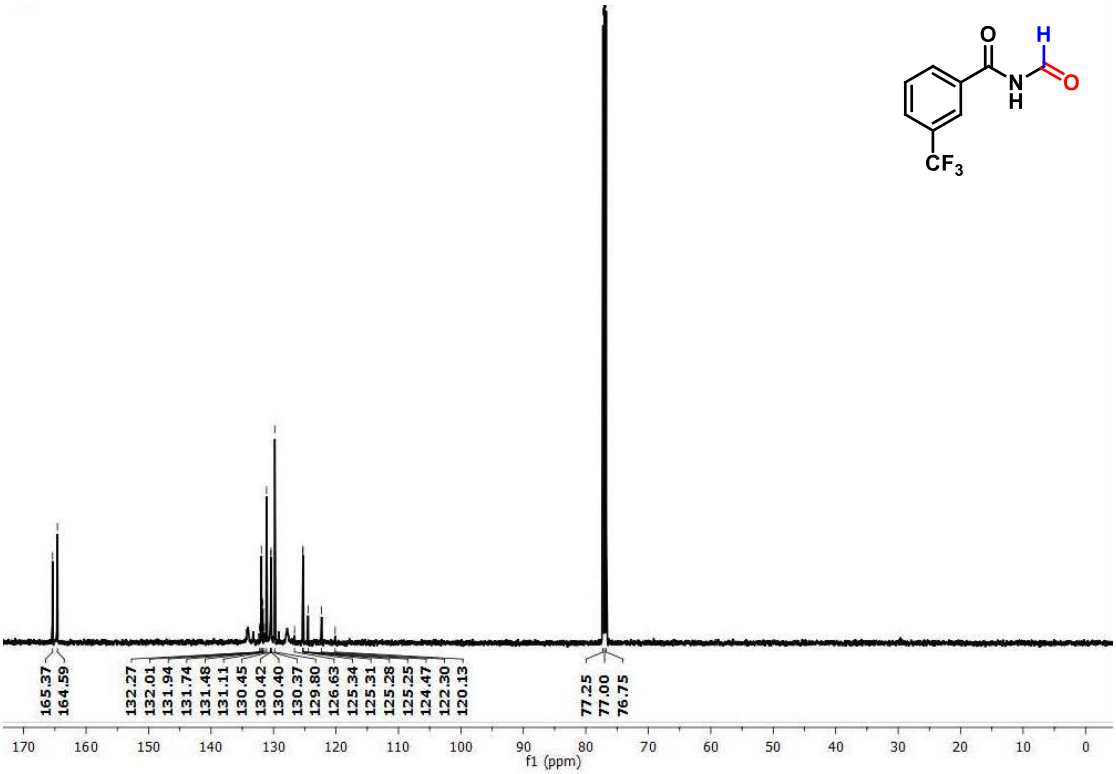


Fig. S42. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-2-fluorobenzamide (**4n**):

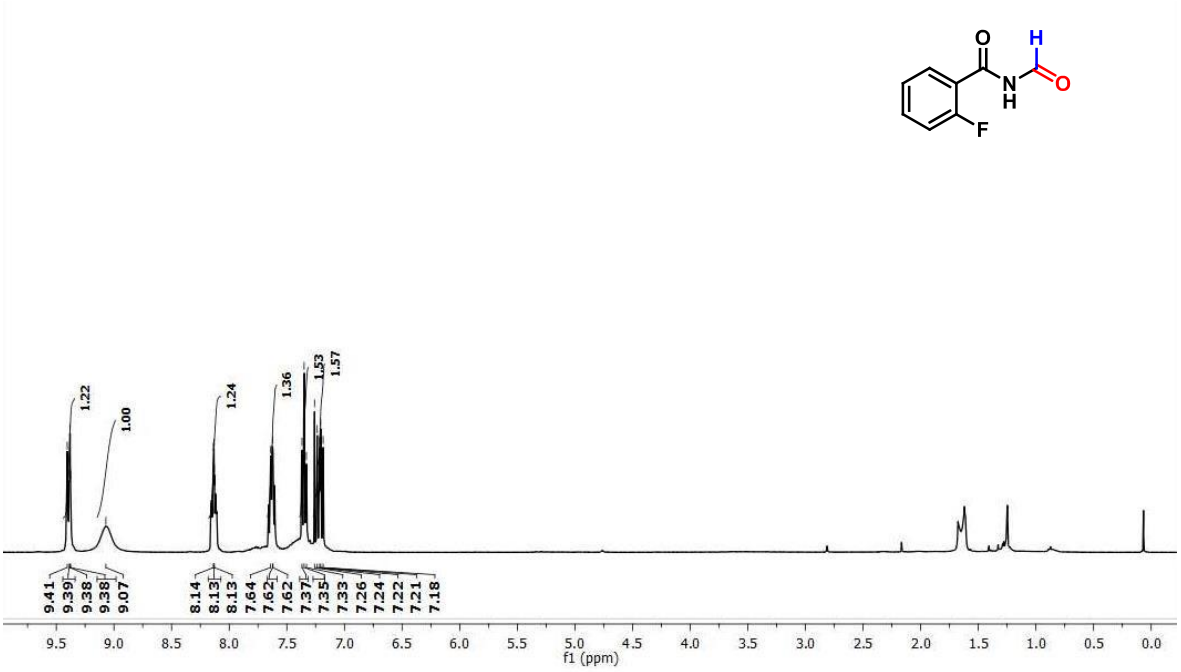


Fig. S43. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-2-fluorobenzamide (**4n**):

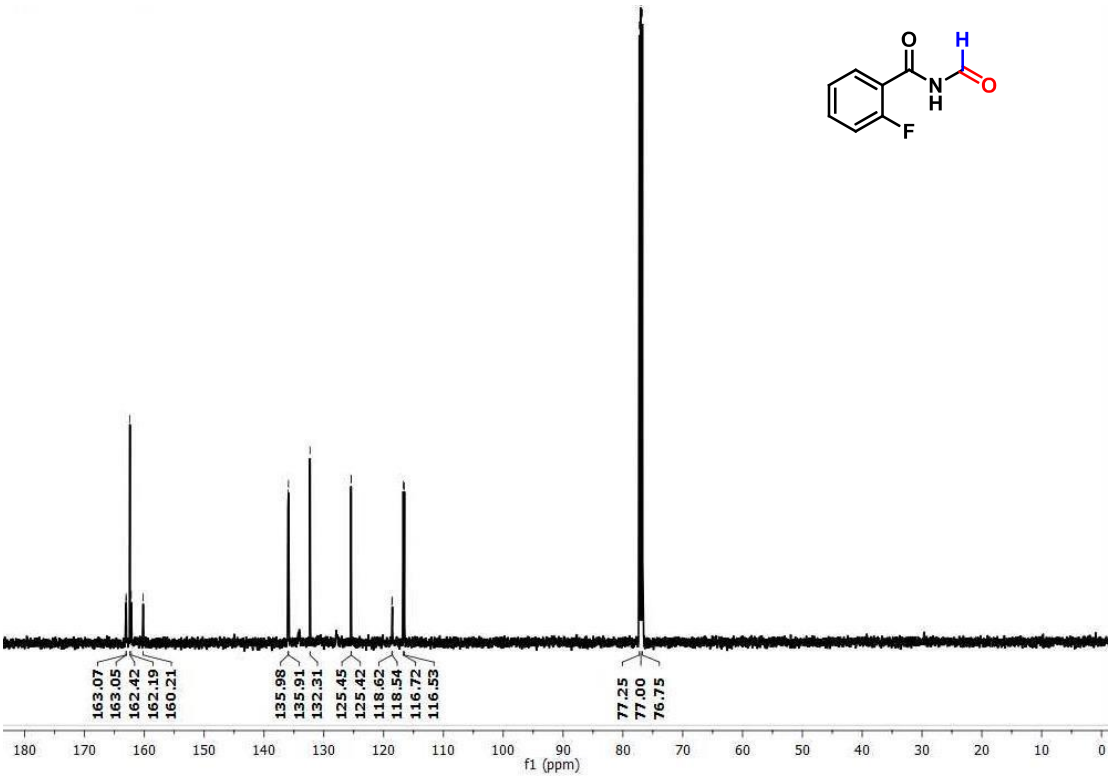


Fig. S44. ^{1}H NMR spectrum ($CDCl_3$) of N-formylthiophene-2-carboxamide (**4o**):

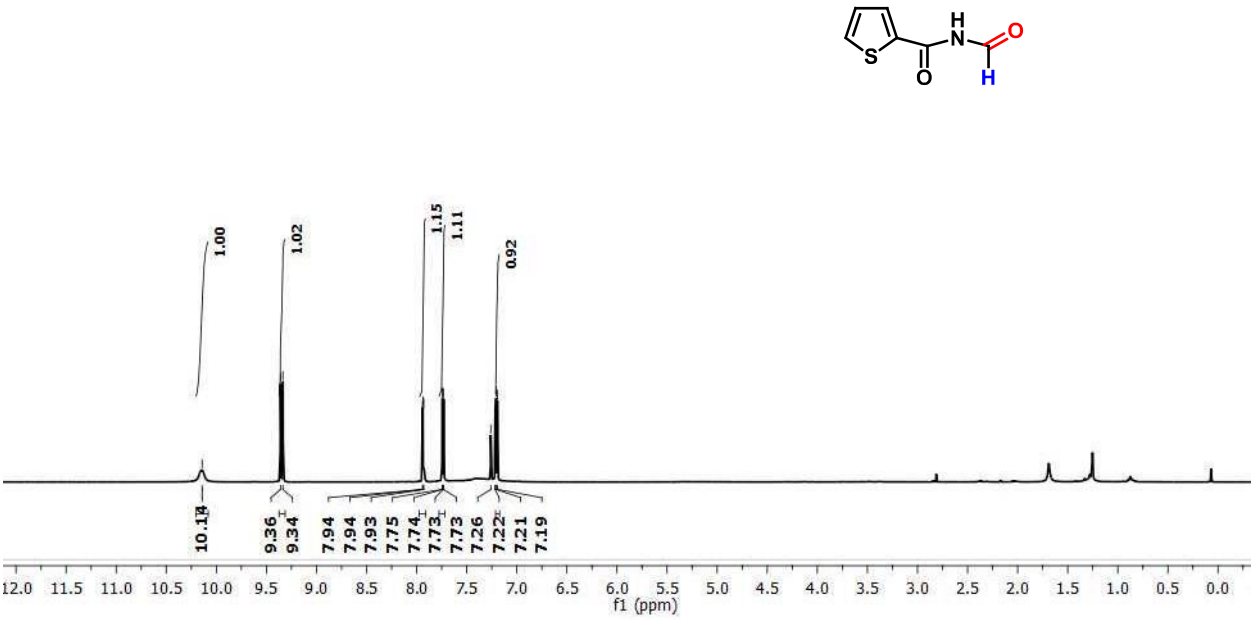


Fig. S45. ^{13}C NMR spectrum ($CDCl_3$) of N-formylthiophene-2-carboxamide (**4o**):

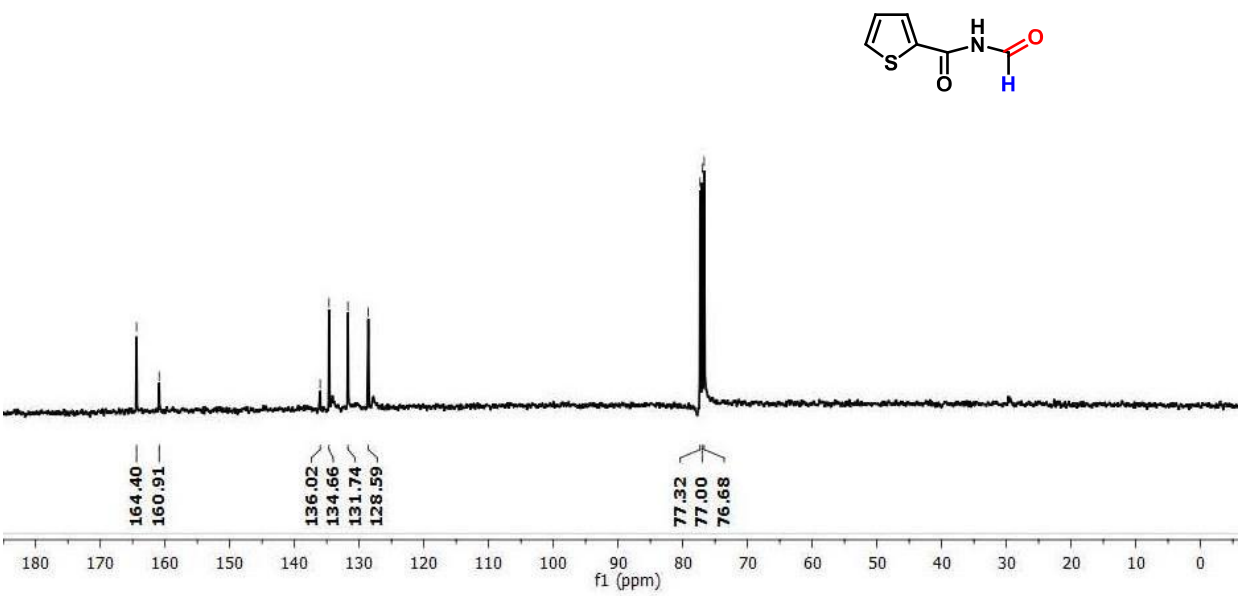


Fig. S46. ^{1}H NMR spectrum ($CDCl_3$) of N-formylcinnamamide (**4p**):

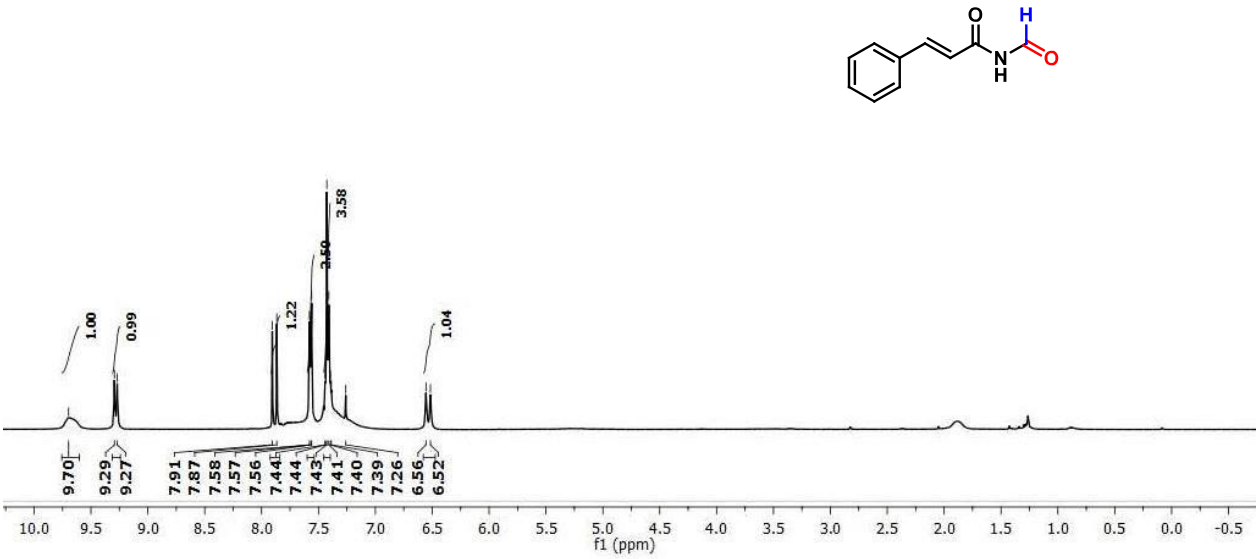


Fig. S47. ^{13}C NMR spectrum ($CDCl_3$) of N-formylcinnamamide (**4p**):

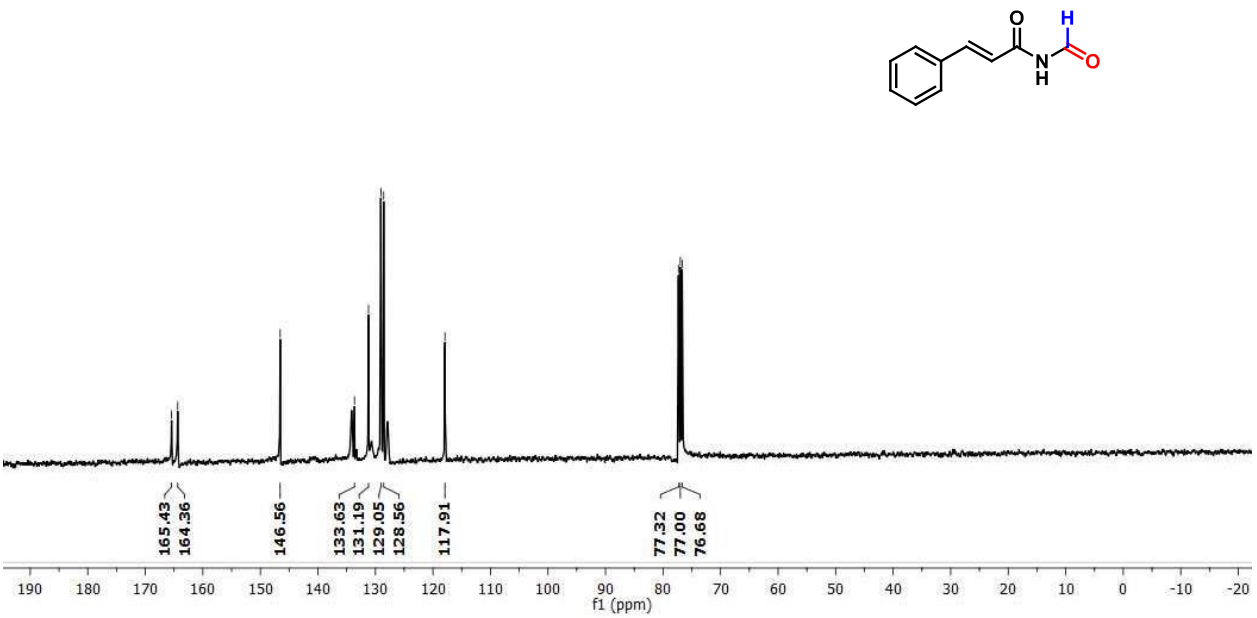


Fig. S48. ^{1}H NMR spectrum ($CDCl_3$) of N-formyl-[1,1'-biphenyl]-4-carboxamide (**4q**):

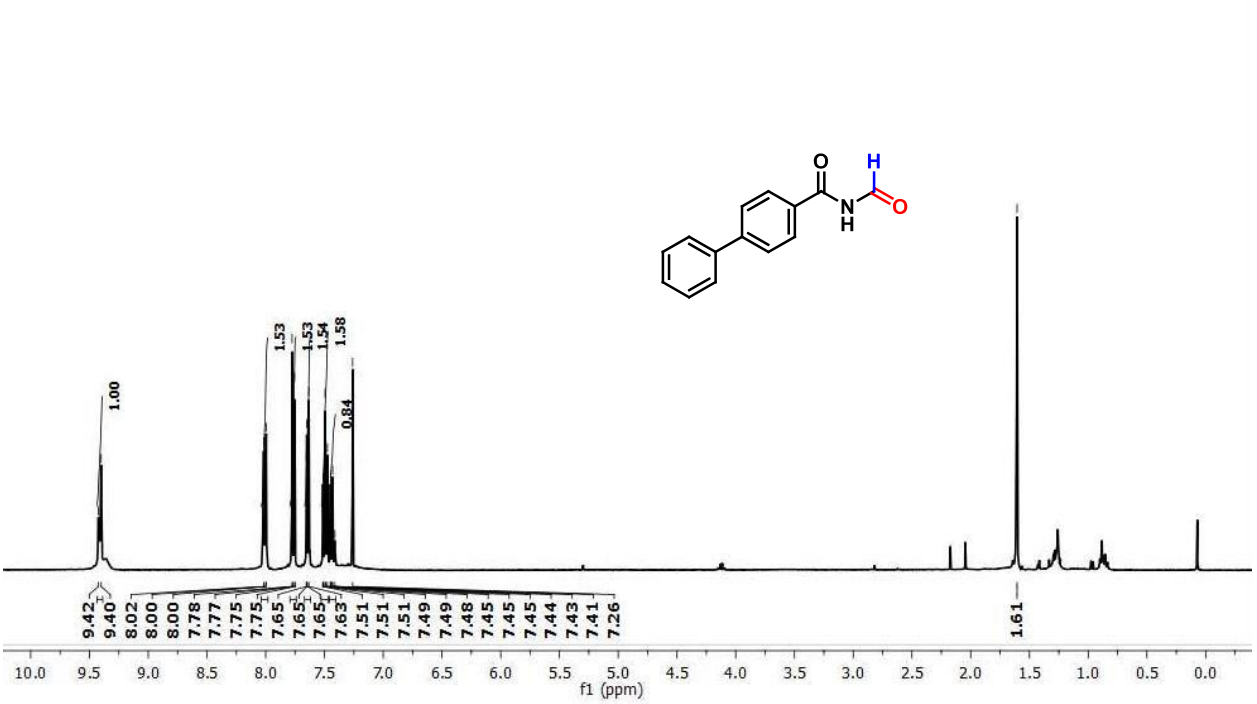


Fig. S49. ^{13}C NMR spectrum ($CDCl_3$) of N-formyl-[1,1'-biphenyl]-4-carboxamide (**4q**):

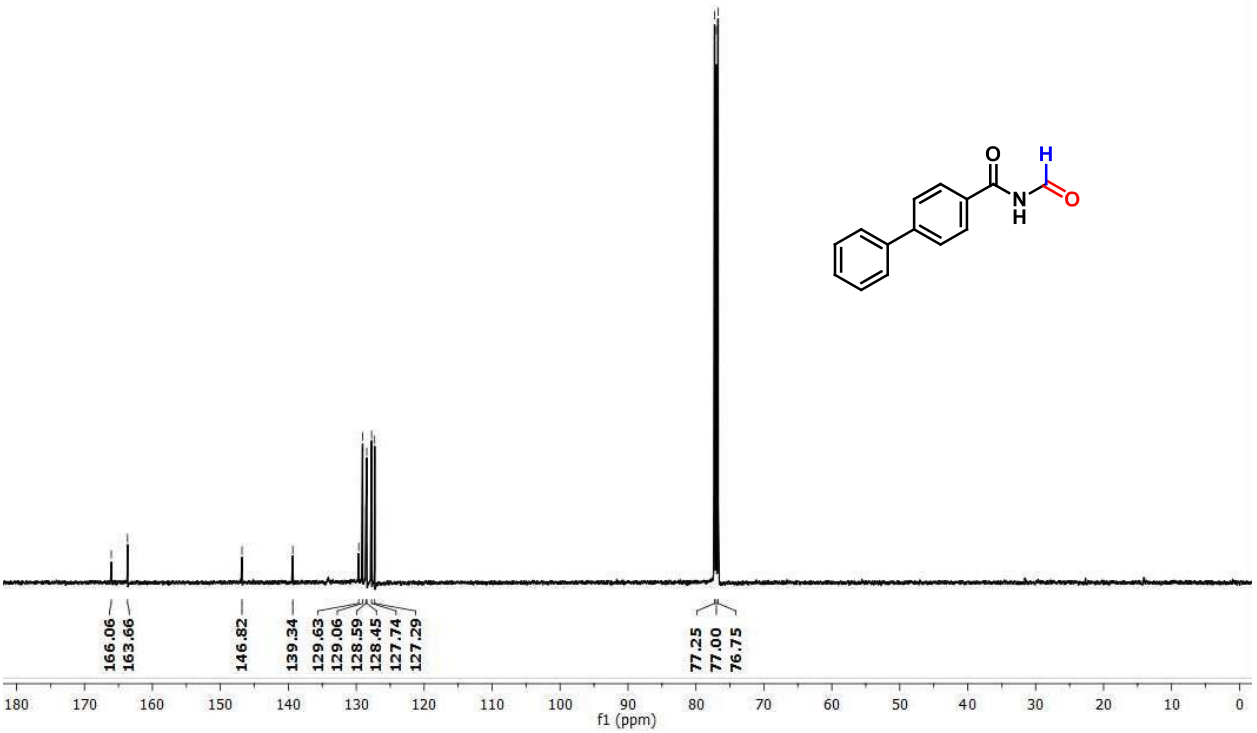


Fig. S50. ^{1}H NMR spectrum ($CDCl_3$ + DMSO-d_6) of N-formylbenzo[b]thiophene-2-carboxamide (**4r**):

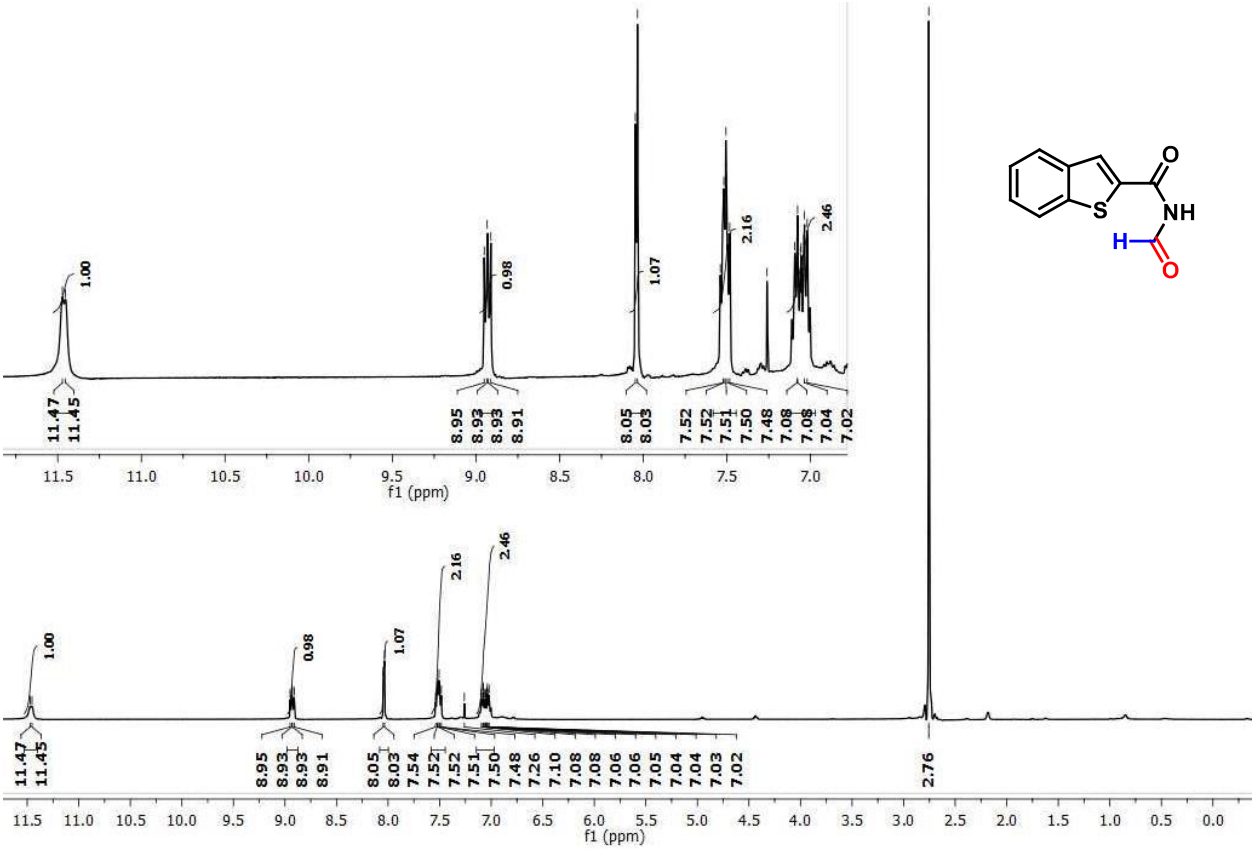


Fig. S51. ^{13}C NMR spectrum ($CDCl_3$ + DMSO-d_6) of N-formylbenzo[b]thiophene-2-carboxamide (**4r**):

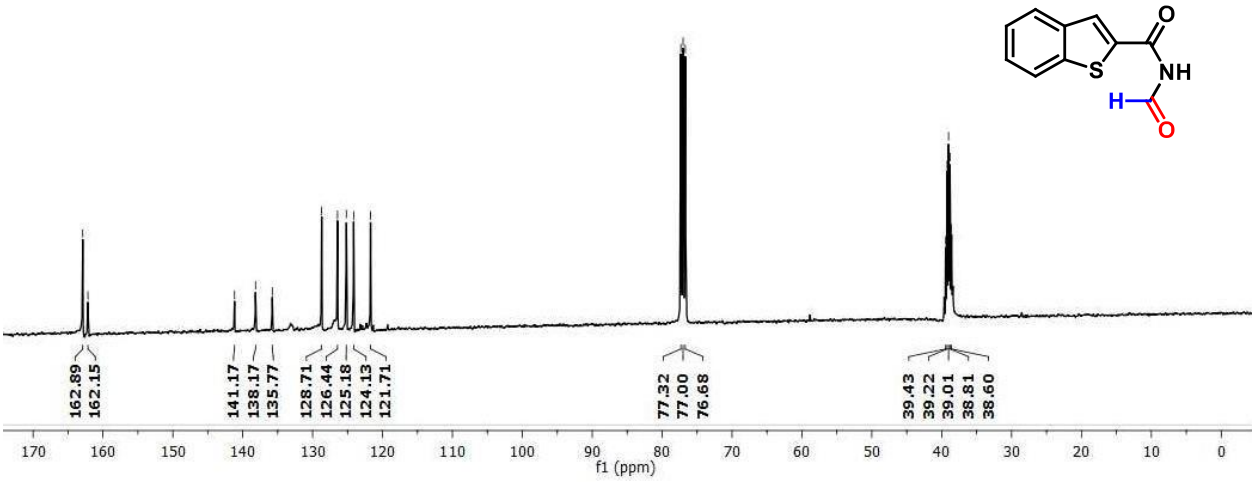


Fig. S52. ^{1}H NMR spectrum ($CDCl_3$) of 1,1,1,3,3,3-hexaphenyldisiloxane (**7**):

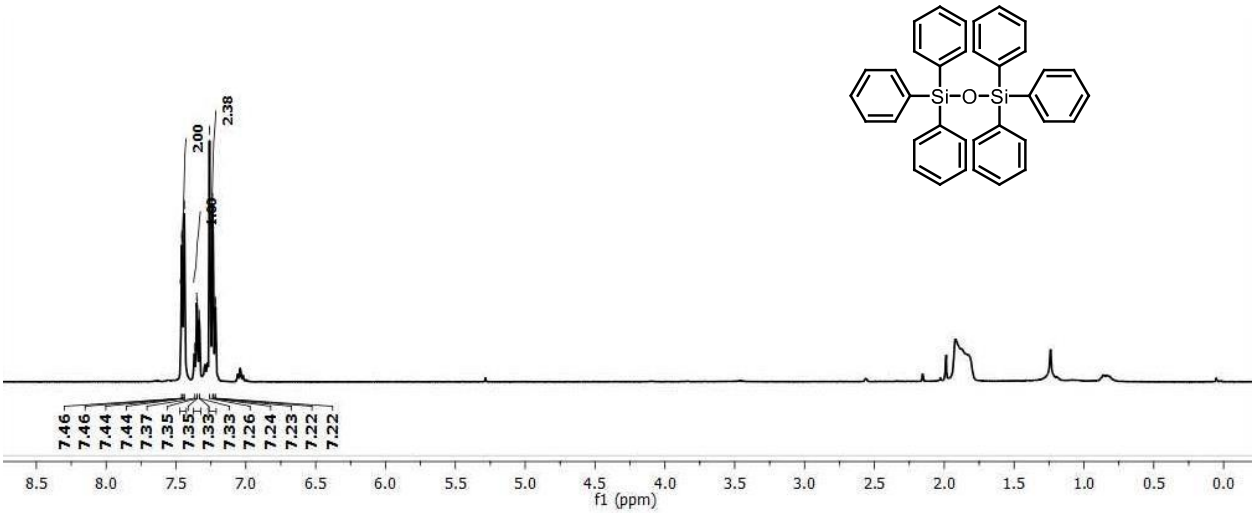


Fig. S53. ^{13}C NMR spectrum ($CDCl_3$) of 1,1,1,3,3,3-hexaphenyldisiloxane (**7**):

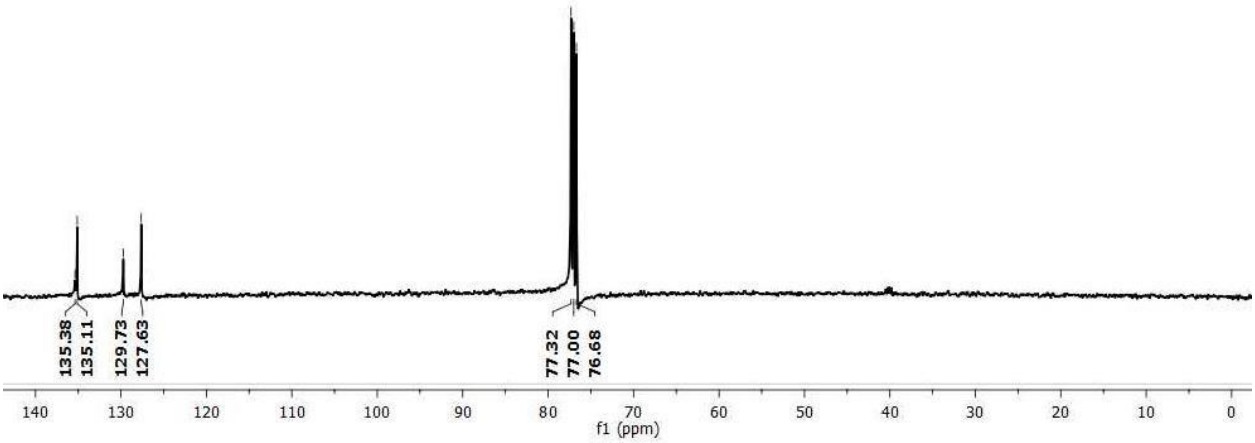
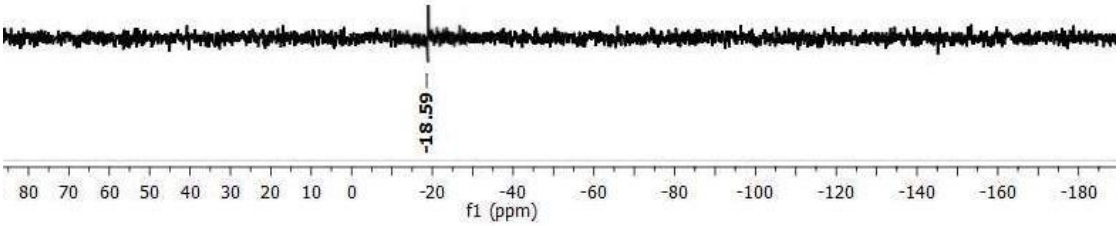


Fig. S54. ^{29}Si spectrum ($CDCl_3$) of 1,1,1,3,3,3-hexaphenyldisiloxane (**7**):



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