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Electronic Supplementary Information

An ionic porous organic polymer with hydroxide anions as efficient catalyst for *N*-formylation of amines and amides with carbon dioxide

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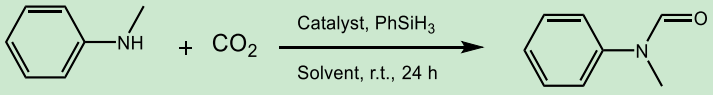
Optimization of reaction conditions

Table S1. Optimization of the *N*-formylation reaction conditions of *N*-methylaniline with CO_2.[a]



1a **2a**

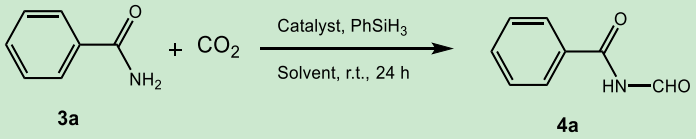
Entry	*N*-methylaniline/mmol	$PhSiH_3$/mmol	Yield/%[b]
1	1.0	3.0	75
2	1.5	3.0	99
3	2.0	3.0	87
4	2.5	3.0	98
5	3.0	3.0	83
6	3.5	3.0	61
7	2.5	2.0	70
8	2.5	2.5	84
9	2.5	3.5	93
10	2.5	4.0	89
11	3.0	4.0	86
12	3.0	5.0	77

[a] Reaction conditions: PT-OH catalyst (0.1 mmol), DMF solvent (2 mL), CO_2 (1 atm), room temperature, 24 h.

[b] Determined by ^1H NMR by using 1,3,5-trimethoxybenzene as internal standard.

The most proper ratio of *N*-methylaniline to $PhSiH_3$ to PT-OH was determined to be 2.5:3.0:0.1 (entry 4), considering more substrate and higher product yield, and less consumption of $PhSiH_3$. Based on the reactions with the *N*-methylaniline variation (entries 1-6), the proper ratio of *N*-methylaniline to $PhSiH_3$ to PT-OH was 2.5:3.0:0.1. Based on the reactions with the $PhSiH_3$ variation (entries 4, 5, 7-12), the proper ratio of *N*-methylaniline to $PhSiH_3$ to PT-OH was 2.5:3.0:0.1, too.

Table S2. Optimization of the *N*-formylation reaction conditions of benzamide CO_2.[a]



3a 4a

Entry	benzamide/mmol	$PhSiH_3$/mmol	Yield/%[b]
1	0.75	3.0	67
2	1.0	3.0	81
3	1.5	3.0	69
4	2.0	3.0	44
5	1.0	2.5	72
6	1.0	3.5	77

[a] Reaction conditions: PT-OH catalyst (0.1 mmol), MeCN solvent (2 mL), CO_2 (1 atm), room temperature, 24 h.

[b] Determined by ^1H NMR by using 1,3,5-trimethoxybenzene as internal standard.

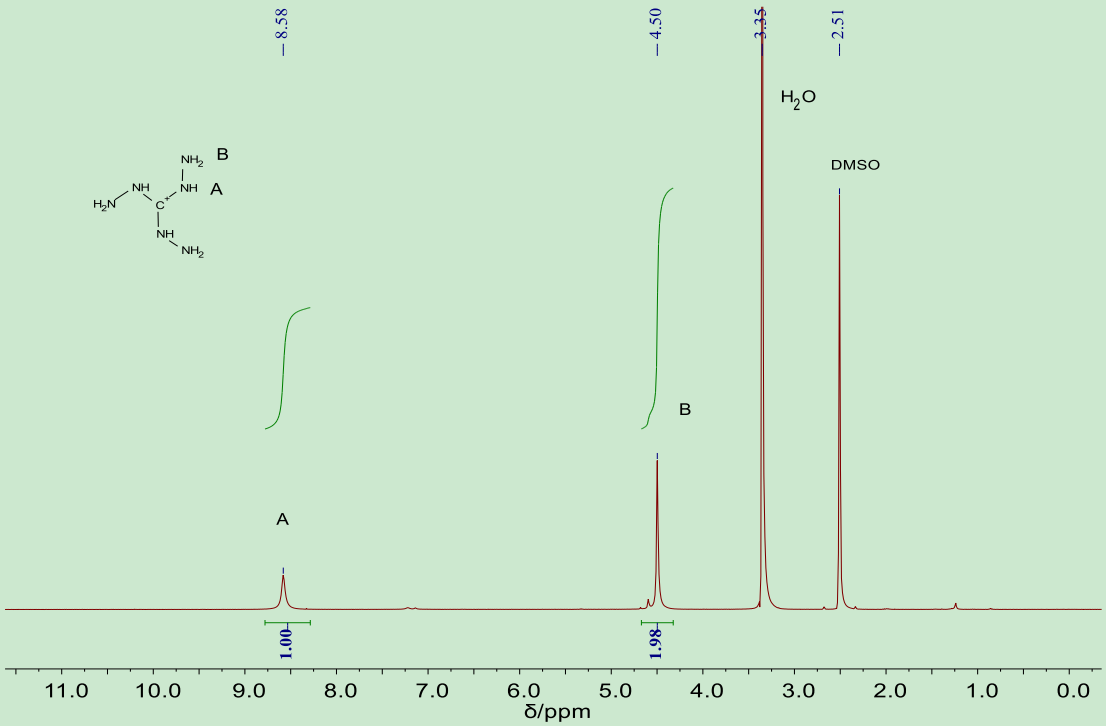


Fig. S1 ^1H NMR spectrum of triaminoguanidine hydrochloride in DMSO-d_6 (400 MHz).

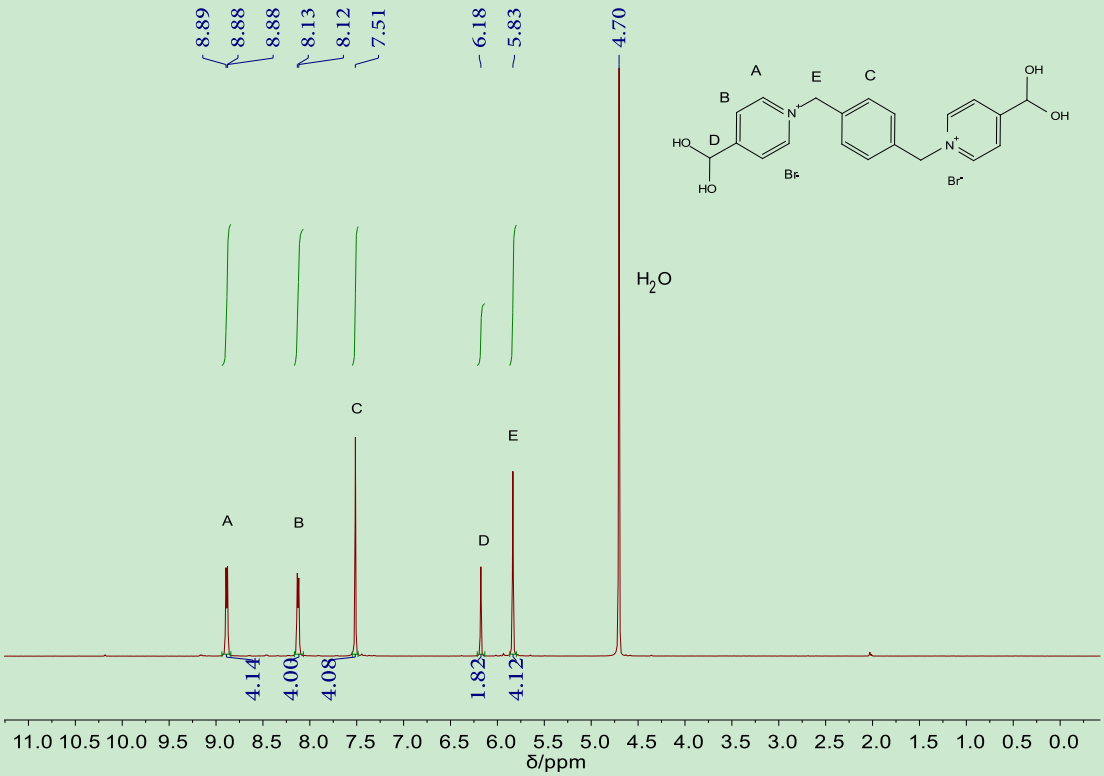


Fig. S2 ^{1}H NMR spectrum of 1,1′-(*p*-phenylenedimethylene)bis[4-formylpyridinium bromide] (PFB) in D_2O (400 MHz).

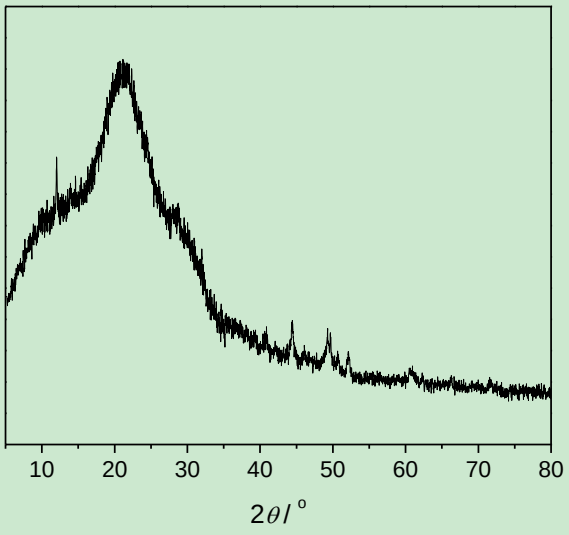


Fig. S3 Powder X-ray diffraction pattern of PT-OH aerogel.

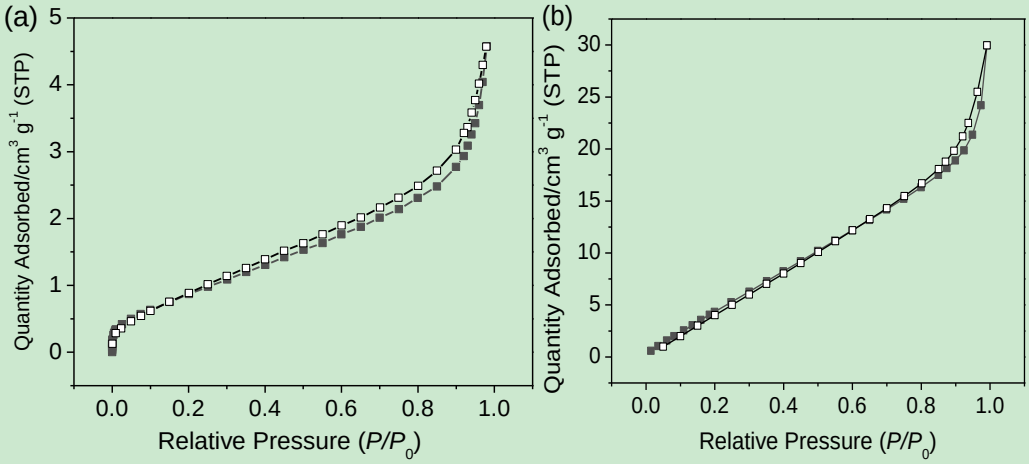


Fig. S4 N_2 adsorption-desorption isotherms of (a) PT and (b) PT-OH aerogels (adsorption, filled symbols; desorption, open symbols).

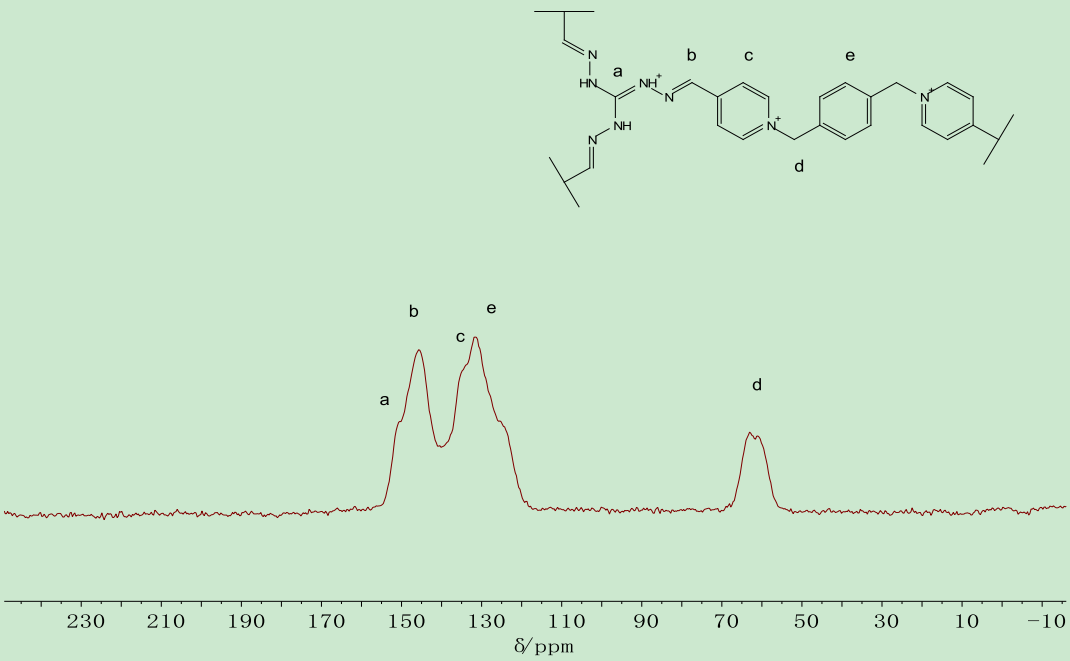


Fig. S5 Solid-state CP/MAS ^{13}C NMR spectrum of PT-OH aerogel (150 MHz).

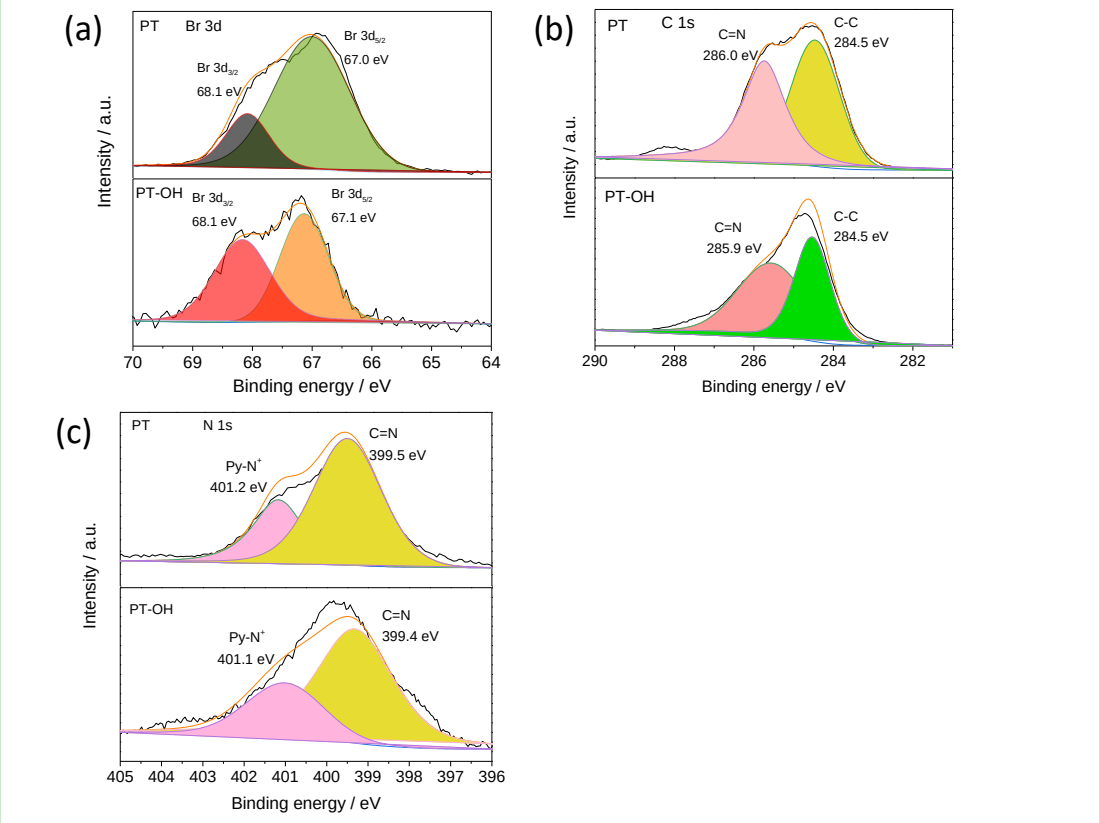


Fig. S6 (a) XPS Br 3d, (b) C 1s, and (c) N 1s spectra of PT aerogel and PT-OH aerogel.

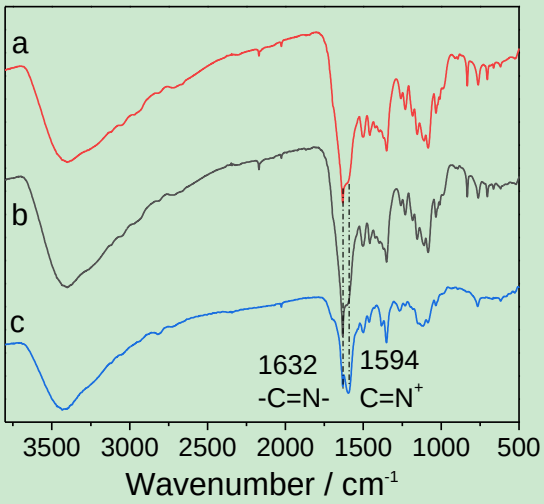


Fig. S7 FT-IR spectra of a) PT gel, b) PT gel in 1 mol L^{-1} HCl aqueous solution and c) PT gel in 1 mol L^{-1} KOH aqueous solution for 48 h.

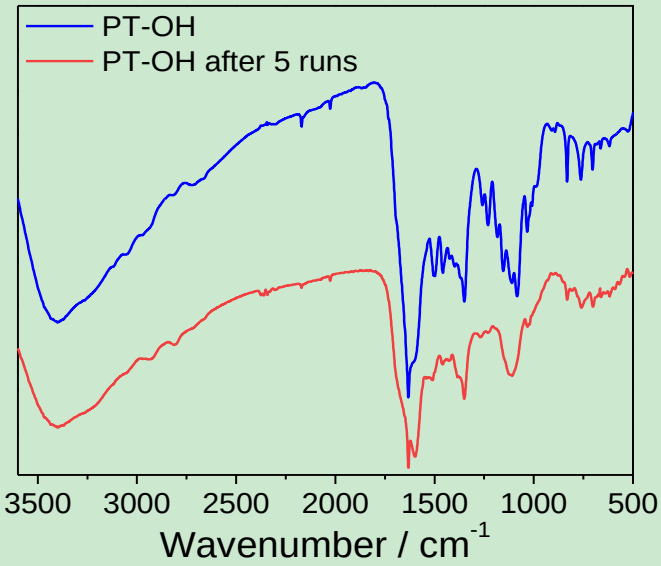


Fig. S8 FT-IR spectra of PT-OH and PT-OH after 5 runs.

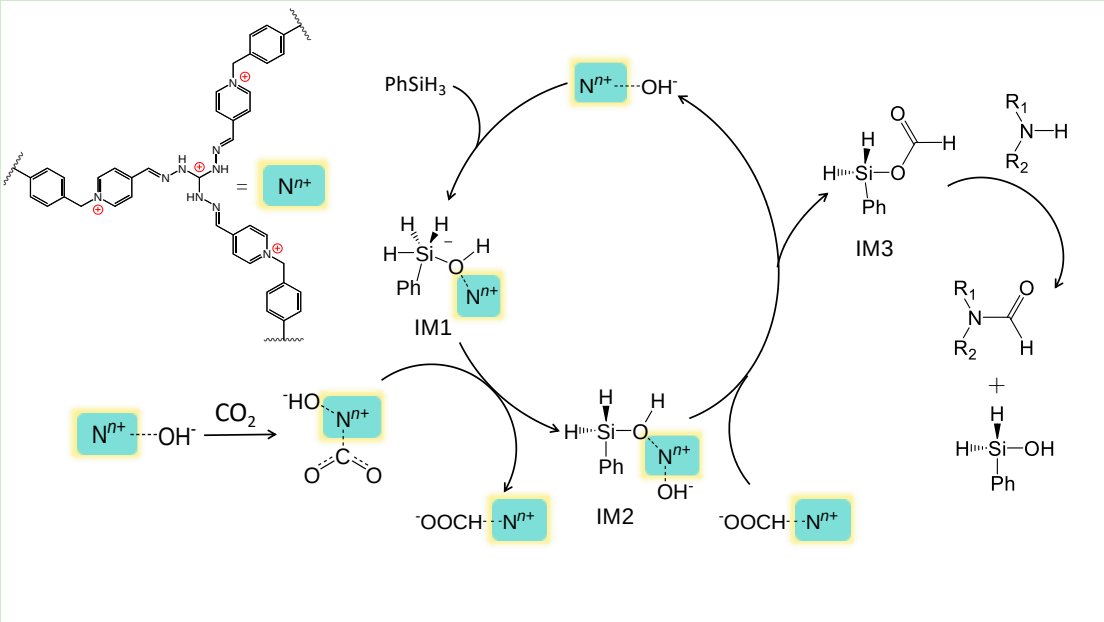


Fig. S9 Plausible mechanism of PT-OH-catalyzed *N*-formylation reaction of CO_2 with amine or amide.

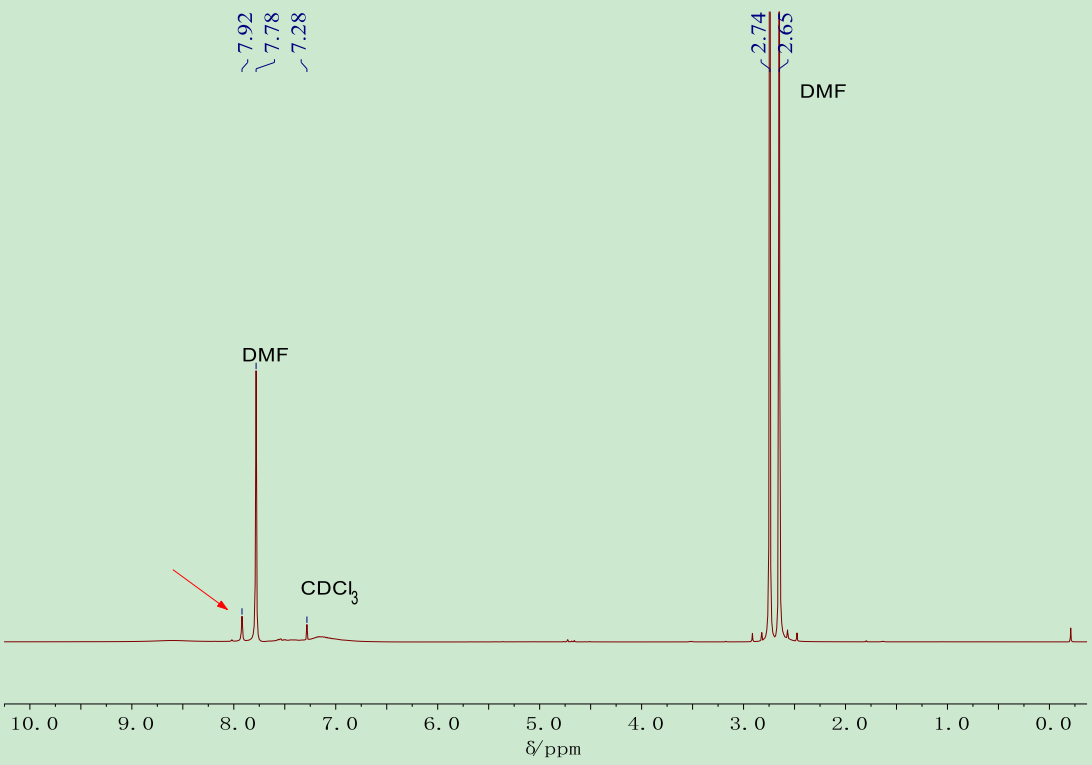


Fig. S10 ^{1}H NMR spectrum of the reaction mixture showing the presence of $HCOO^-$ ($CDCl_3$, 400 MHz). Reaction conditions: $PhSiH_3$ (3 mmol), PT-OH catalyst (0.1 mmol), DMF solvent (2 mL), RT, CO_2 (1 atm), 24 h.

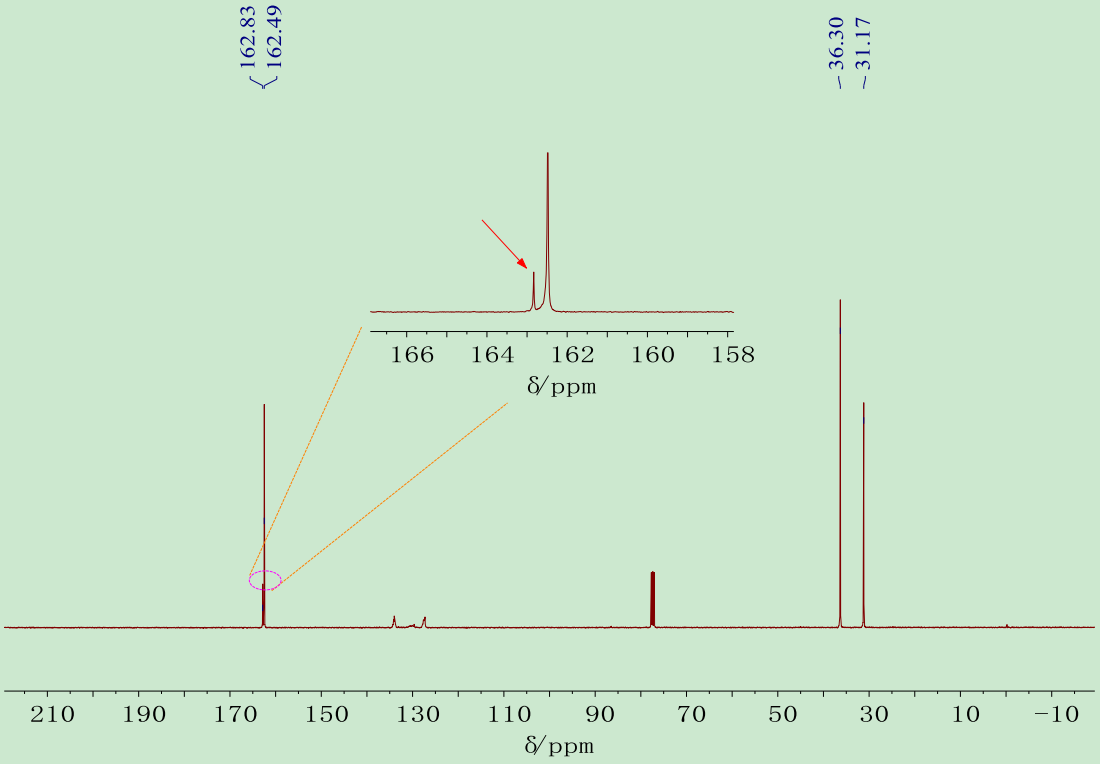
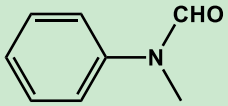
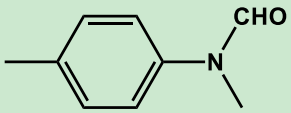


Fig. S11 ^{13}C NMR spectrum of the reaction mixture showing the presence of $HCOO^-$ ($CDCl_3$, 101 MHz). Reaction conditions: $PhSiH_3$ (3 mmol), PT-OH catalyst (0.1 mmol), DMF solvent (2 mL), RT, CO_2 (1 atm), 24 h.

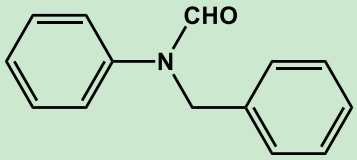
^{1}H and ^{13}C NMR data of products



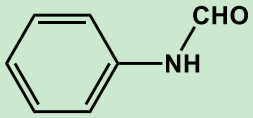
***N*-Methylformanilide** (**2a**), yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.54 (s, 1H), 7.47-7.40 (m, 2H), 7.38-7.32 (m, 2H), 7.30-7.24 (m, 1H), 3.22 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.53, 142.56, 129.91, 126.11 122.04, 31.53.



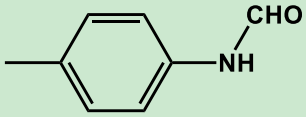
***N*,4'-Dimethylformanilide (2b)**, yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.47 (s, 1H), 7.21 (s, 4H), 3.19 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.36, 140.07, 135.49, 130.30, 122.15, 31.63, 20.79.



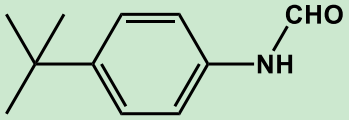
***N*-Benzyl-*N*-phenylformamide (2c)**, yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (s, 1H), 7.41-7.19 (m, 8H), 5.06 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.88, 141.19, 137.44, 129.91, 128.92, 127.72, 127.54, 126.47, 123.23, 47.16.



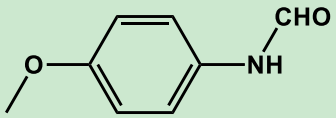
Formylaniline (2d), yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.16 (s, 1H), 8.96-8.05 (m, 1H), 7.84-6.83 (m, 5H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.98, 160.05, 138.69, 129.85, 129.31, 129.25, 124.09, 119.66, 119.61, 118.05.



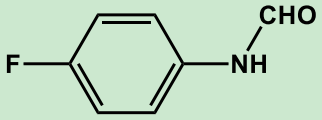
***N*-*p*-tolylformamide (2e)**, yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.05 (s, 1H), 8.49 (m, 1H), 7.70-6.62 (m, 5H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6):δ 162.92, 159.79, 136.22, 133.03, 130.24, 129.67, 119.61, 118.20, 20.89.



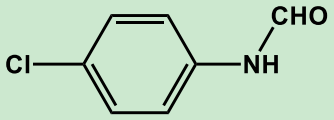
(4-(tert-butyl)phenyl)formamide (2f), yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.08 (s, 1H), 8.96-8.05 (m, 1H), 7.50 (d, J = 8.7 Hz, 1.5H), 7.38-7.30 (m, 2H), 7.11 (d, J = 8.6 Hz, 0.5H), 1.26 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.90, 159.80, 146.40, 136.16, 126.46, 125.85, 119.45, 117.98, 34.43, 31.59.



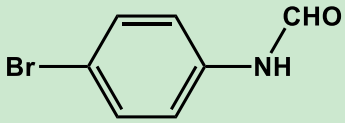
***N*-(4-methoxyphenyl) formamide (2g)**, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.08-9.81 (m, 1H), 8.66-8.14 (m, 1H), 7.31 (dd, J = 199.2, 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.06, 159.54, 156.49, 155.88, 131.88, 121.10, 120.20, 115.09, 114.44, 55.64.



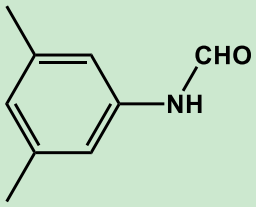
***N*-4-(fluorophenyl) formamide (2h)**, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (d, J = 42.6 Hz, 1H), 8.77-8.16 (m, 1H), 7.61 (dd, J = 8.9, 5.0 Hz, 2H), 7.40-7.03 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.18, 159.97, 157.41, 135.09, 135.06, 121.44, 121.36, 120.06, 119.98, 116.59, 116.37, 116.02, 115.80.



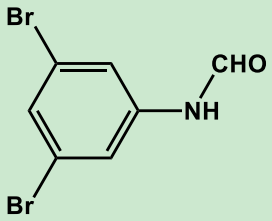
***N*-(4-chlorophenyl) formamide (2i)**, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.26 (d, J = 44.7 Hz, 1H), 8.94-8.25 (m, 1H), 7.61 (d, J = 8.8 Hz, 1.5H), 7.37 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.7 Hz, 0.5H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.02, 160.21, 137.60, 129.71, 129.24, 127.66, 121.21, 119.49.



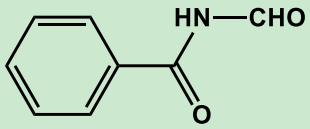
***N*-(4-bromophenyl)formamide (2j)**, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.33 (s, 1H), 8.79-8.30 (m, 1H), 7.58-7.49 (m, 3H), 7.17 (d, J = 8.8 Hz, 0.5H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.97, 160.24, 138.04, 132.16, 121.58, 119.85, 115.56.



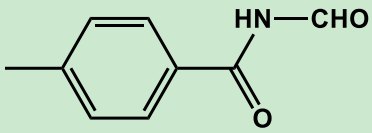
***N*-(3,5-dimethylphenyl)formamide (2k),** yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.99 (s, 1H), 8.91-7.90 (m, 1H), 7.23 (s, 1.5H), 6.76 (d, J = 41.7 Hz, 1.5H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 162.87, 159.90, 138.34, 125.60, 117.35, 115.72, 21.48.



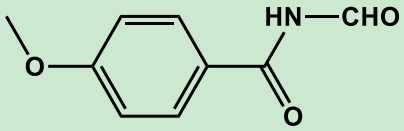
***N*-(3,5-dibromophenyl)formamide (2l)**, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 1H), 8.33 (s, 1H), 7.83 (d, J = 1.8 Hz, 1.5H), 7.60-7.32 (m,1.5H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 163.16, 160.80, 141.23, 128.67, 122.93, 121.01, 119.11.



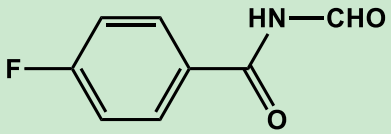
***N*-formylbenzamide** (**4a**), white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.74 (s, 1H), 9.27 (s, 1H), 8.11-7.95 (m, 2H), 7.74-7.64 (m, 1H), 7.56 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 168.02, 164.95, 133.97, 131.98, 129.19, 128.87.



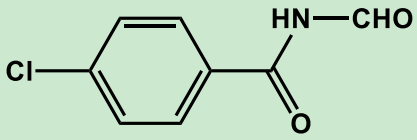
***N*-formyl-4-methylbenzamide (4b)**, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.67 (s, 1H), 9.26 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.77, 164.94, 144.44, 129.74, 128.96, 21.59.



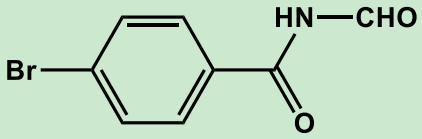
***N*-formyl-4-methoxybenzamide (4c)**, white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.62 (s, 1H), 9.25 (s, 1H), 8.03 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6): δ 167.08, 164.97, 163.89, 131.13, 123.95, 114.50, 56.08.



4-Fluoro-*N*-formylbenzamide (4d), white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.76 (s, 1H), 9.25 (s, 1H), 8.15 – 8.06 (m, 2H), 7.40 (t, J = 8.9 Hz, 2H).^{13}C NMR (101 MHz, DMSO-d_6): δ 166.93, 164.95, 131.97, 131.88, 116.43, 116.21.



4-Chloro-*N*-formylbenzamide (4e), white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.79 (d, J = 8.9 Hz, 1H), 9.25 (d, J = 8.8 Hz, 1H), 8.08 -7.99 (m, 2H), 7.70 -7.57 (m, 2H).^{13}C NMR (101 MHz, DMSO-d_6): δ 167.15, 164.91, 138.92, 130.85, 129.34.



4-Bromo-*N*-formylbenzamide (4f), white solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.78 (s, 1H), 9.25 (s, 1H), 7.95 (d, J = 8.6 Hz, 2H), 7.82-7.67 (m, 2H).^{13}C NMR (101 MHz, DMSO-d_6): δ 164.91, 132.28, 131.22, 130.94, 128.03.

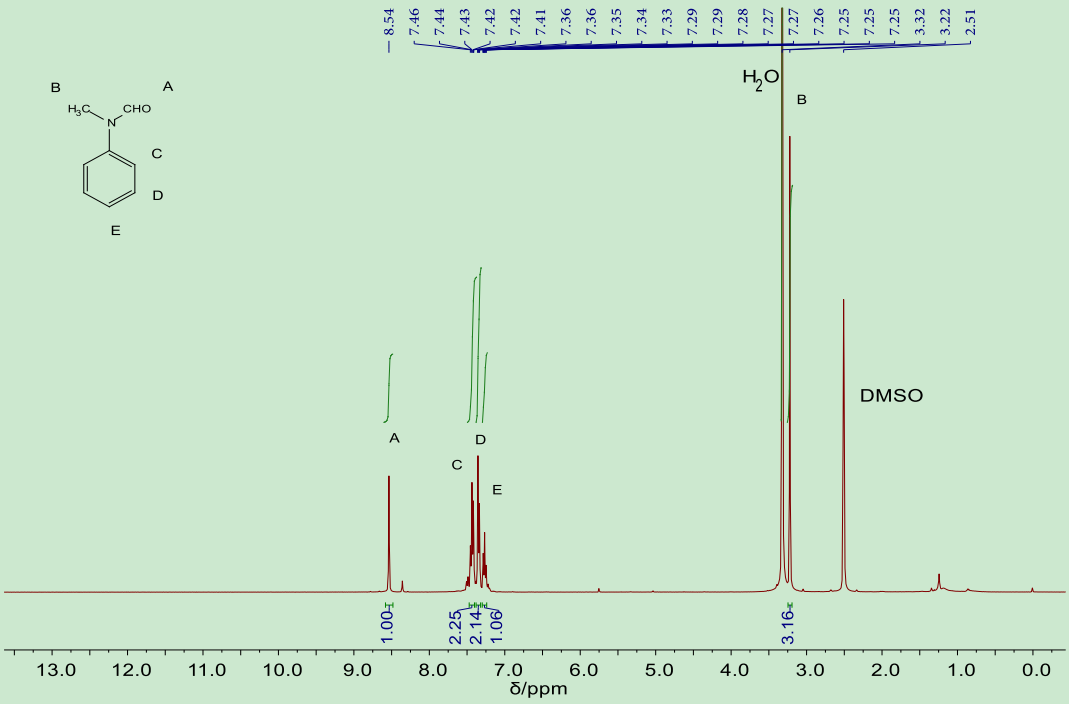


Fig. S12 ^{1}H NMR spectrum of **2a** in DMSO-d_6 (400 MHz).

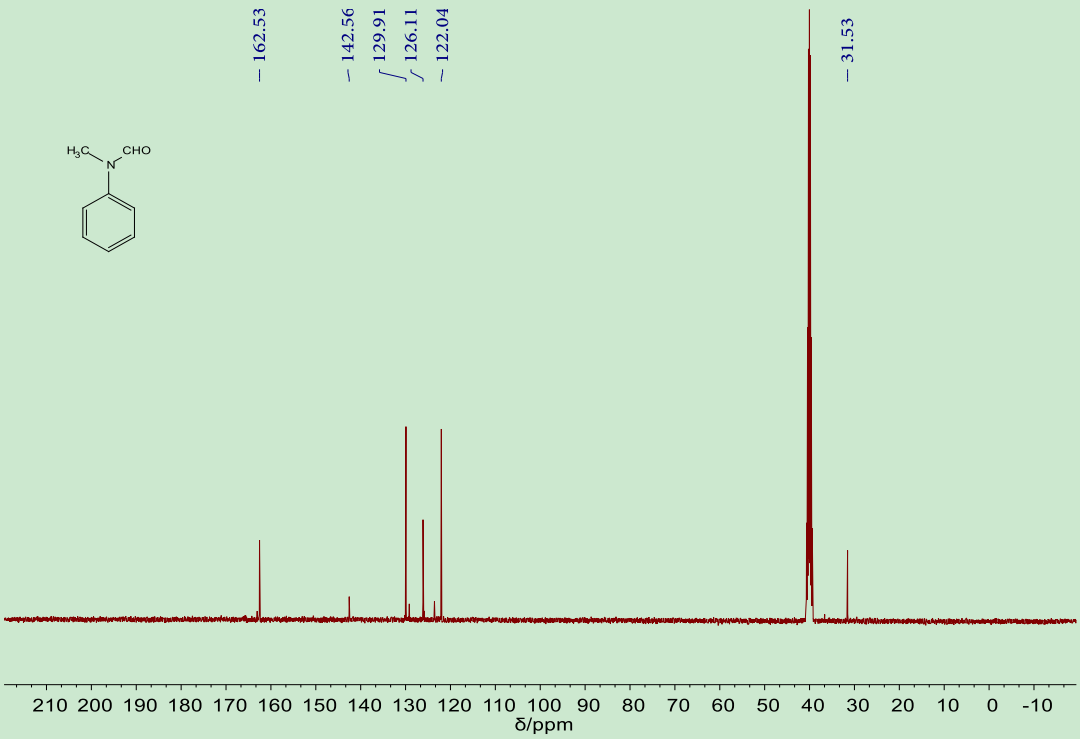


Fig. S13 ^{13}C NMR spectrum of **2a** in DMSO-d_6 (101 MHz).

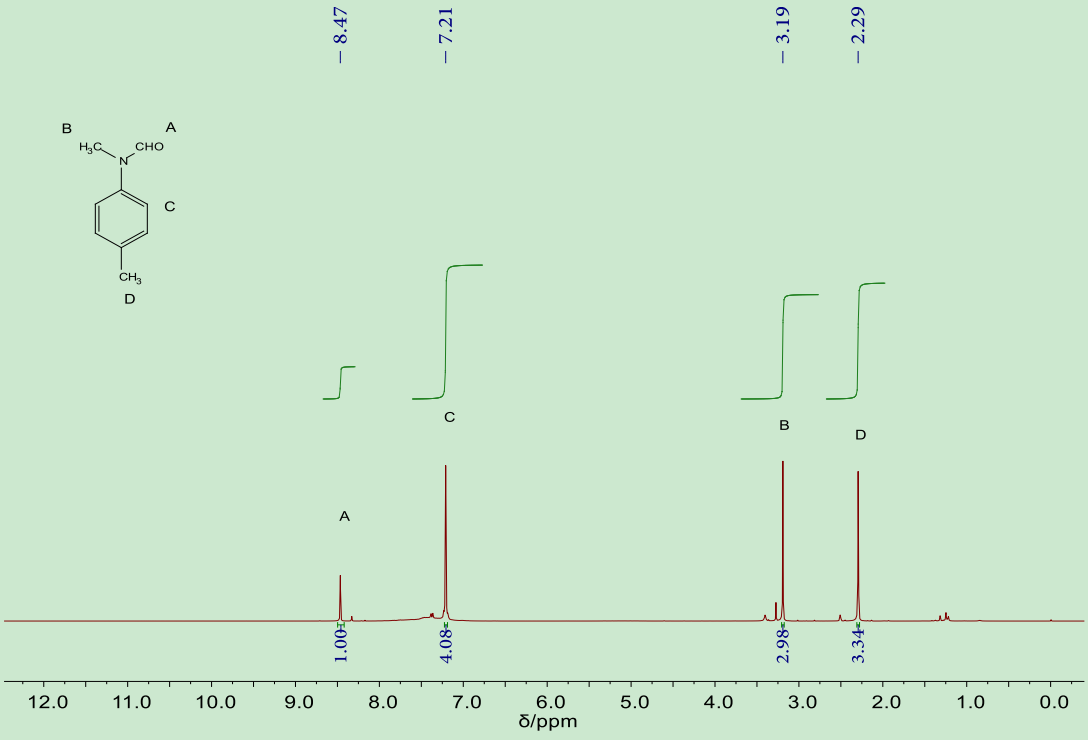


Fig. S14 ^{1}H NMR spectrum of **2b** in DMSO-d_6 (400 MHz).

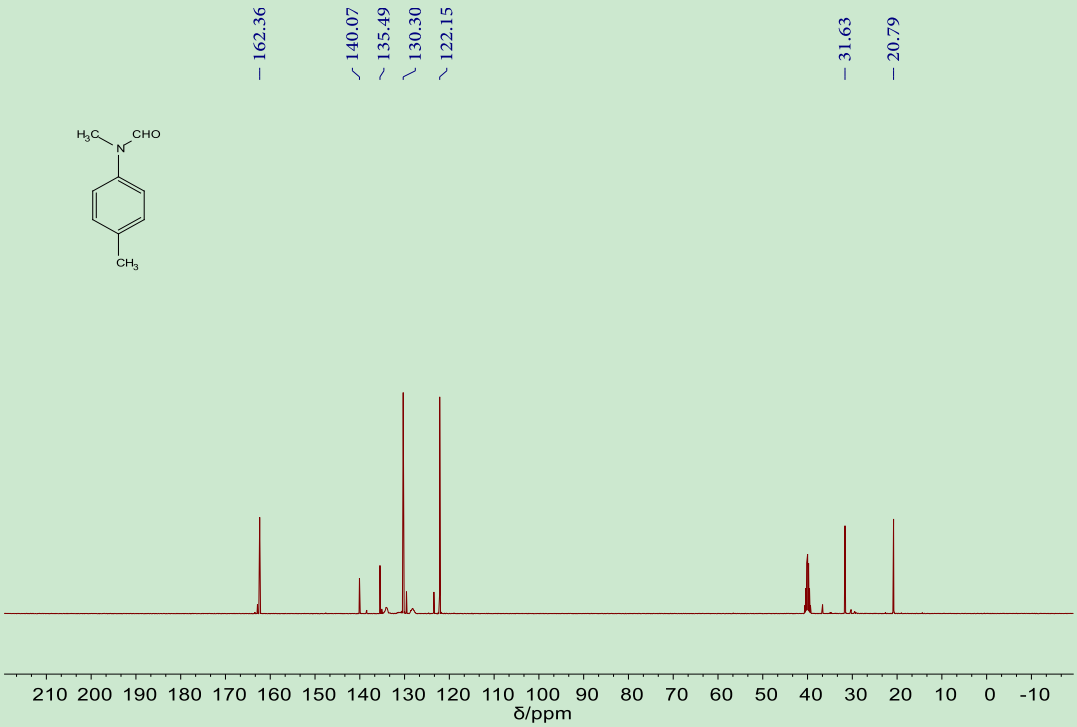


Fig. S15 ^{13}C NMR spectrum of **2b** in DMSO-d_6 (101 MHz).

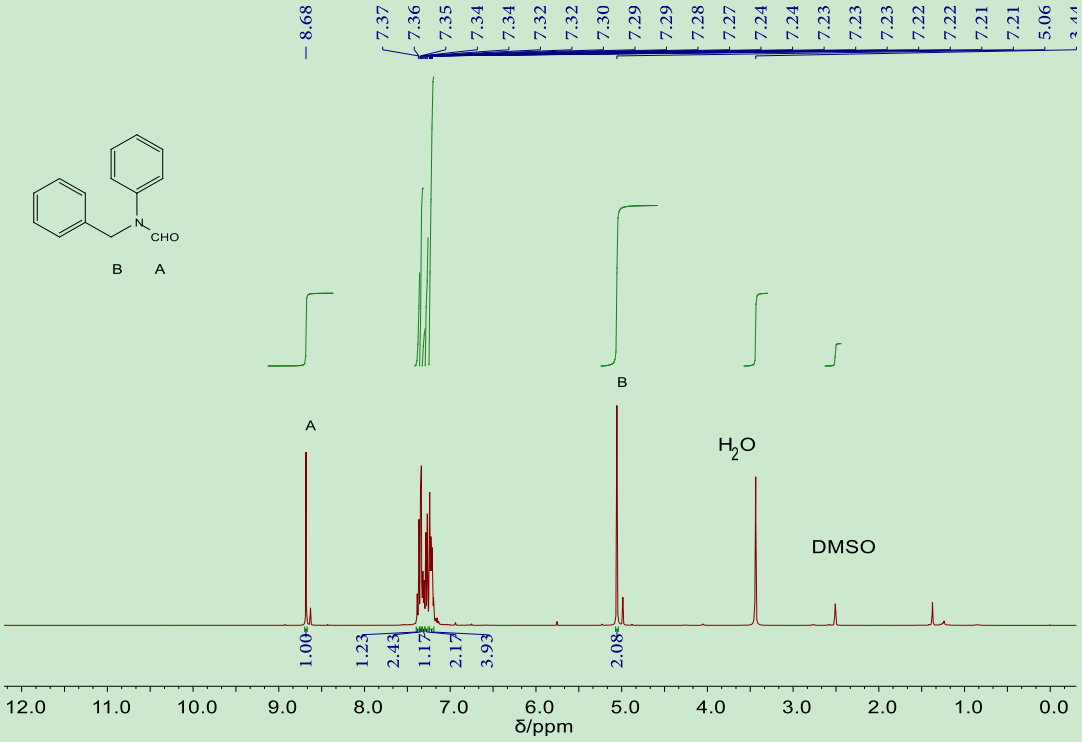


Fig. S16 ^{1}H NMR spectrum of **2c** in DMSO-d_6 (400 MHz).

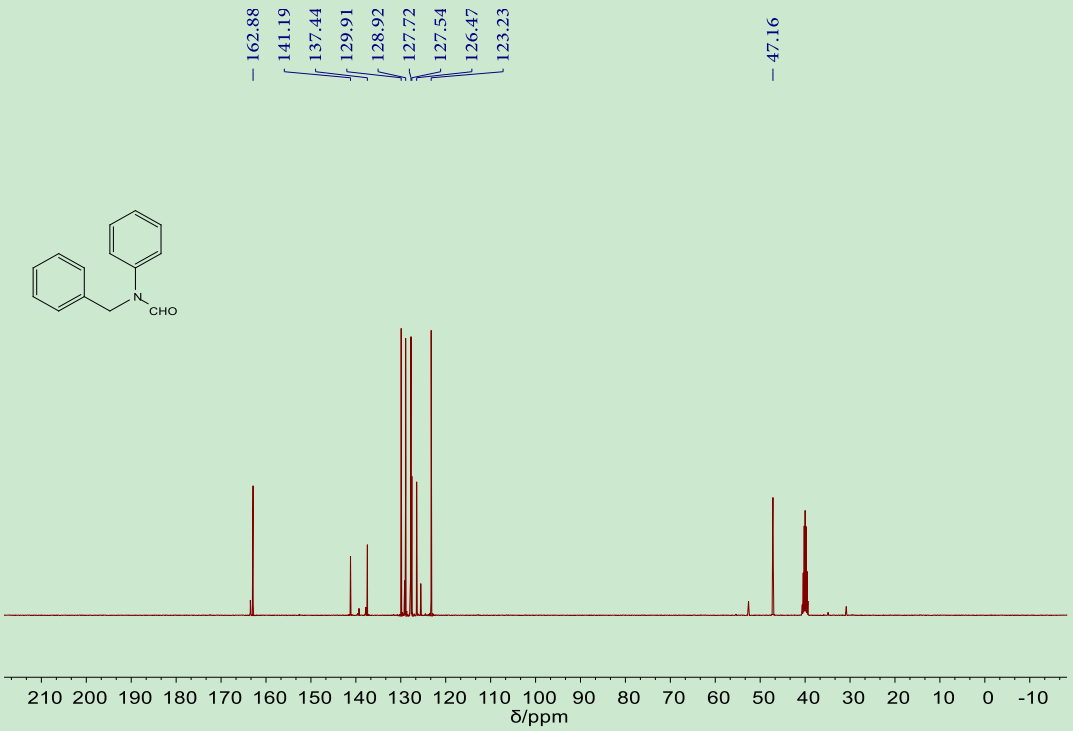


Fig. S17 ^{13}C NMR spectrum of **2c** in DMSO-d_6 (101 MHz).

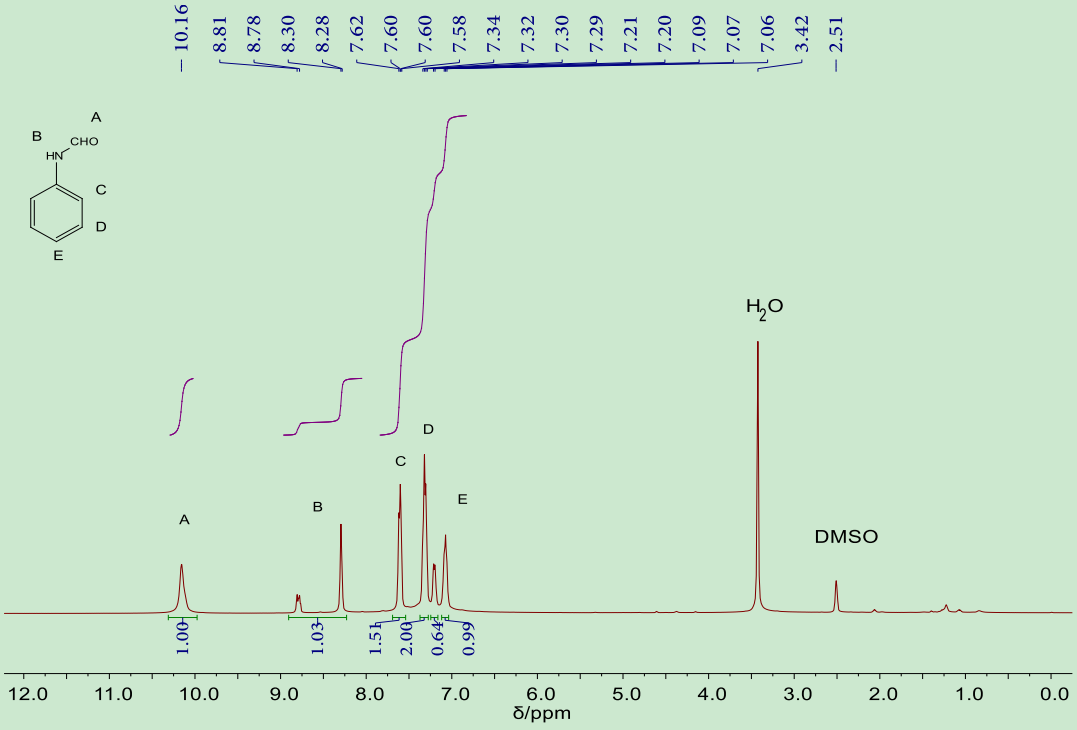


Fig. S18 ^{1}H NMR spectrum of **2d** in DMSO-d_6 (400 MHz).

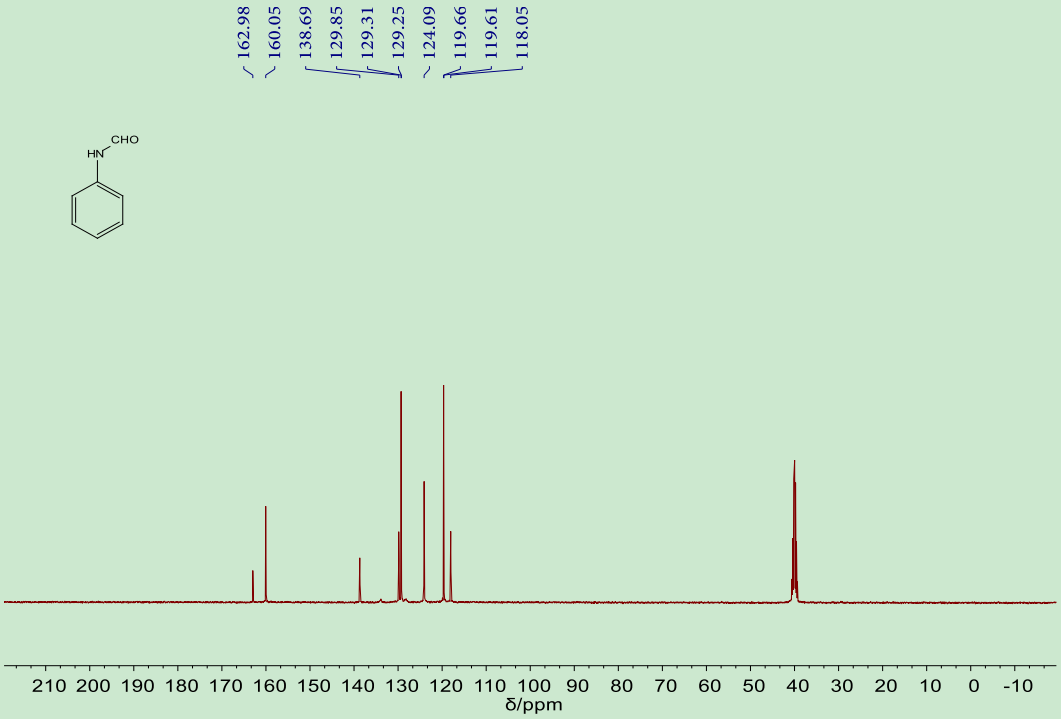


Fig. S19 ^{13}C NMR spectrum of **2d** in DMSO-d_6 (101 MHz).

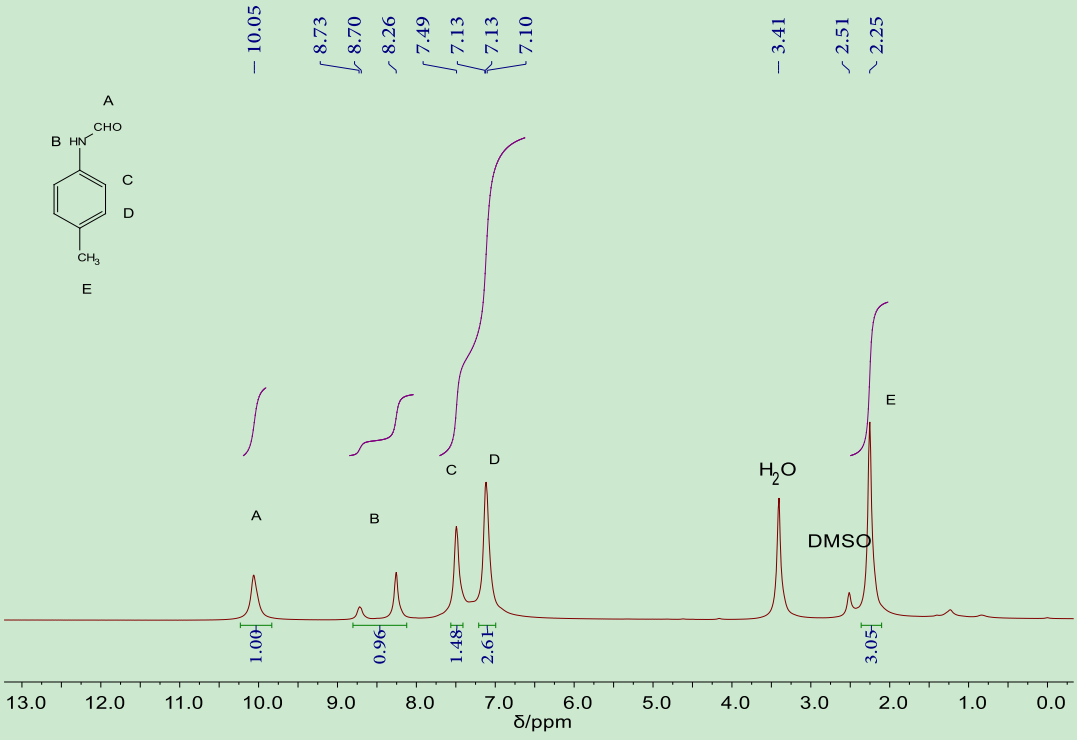


Fig. S20 ^{1}H NMR spectrum of **2e** in DMSO-d_6 (400 MHz).

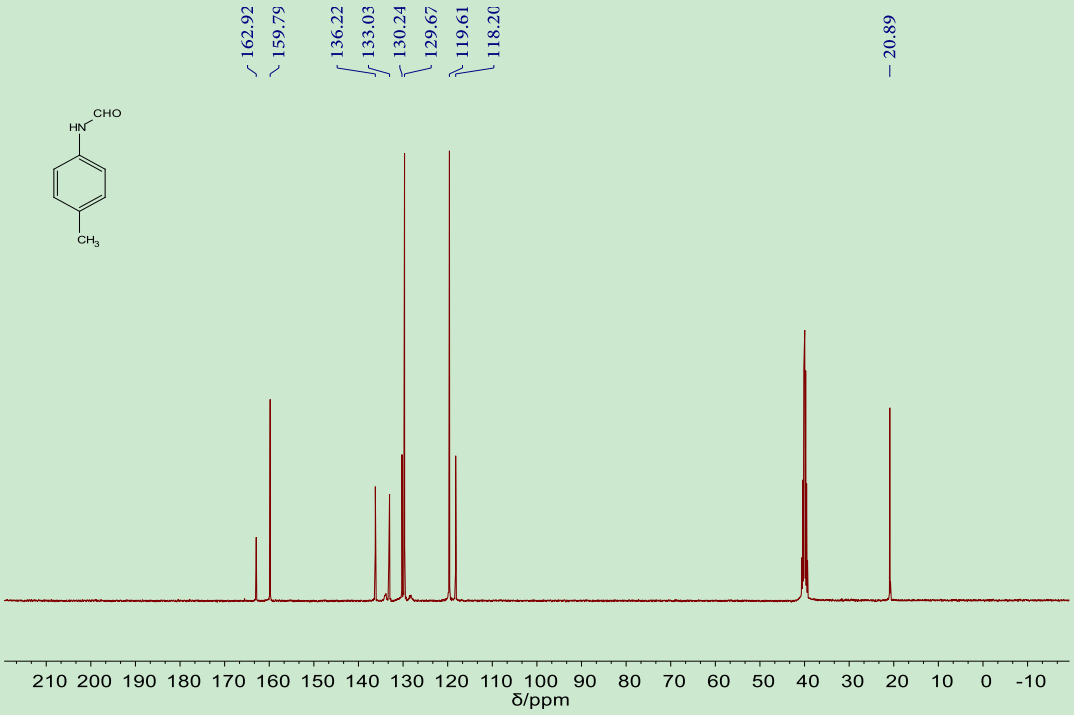


Fig. S21 ^{13}C NMR spectrum of **2e** in DMSO-d_6 (101 MHz).

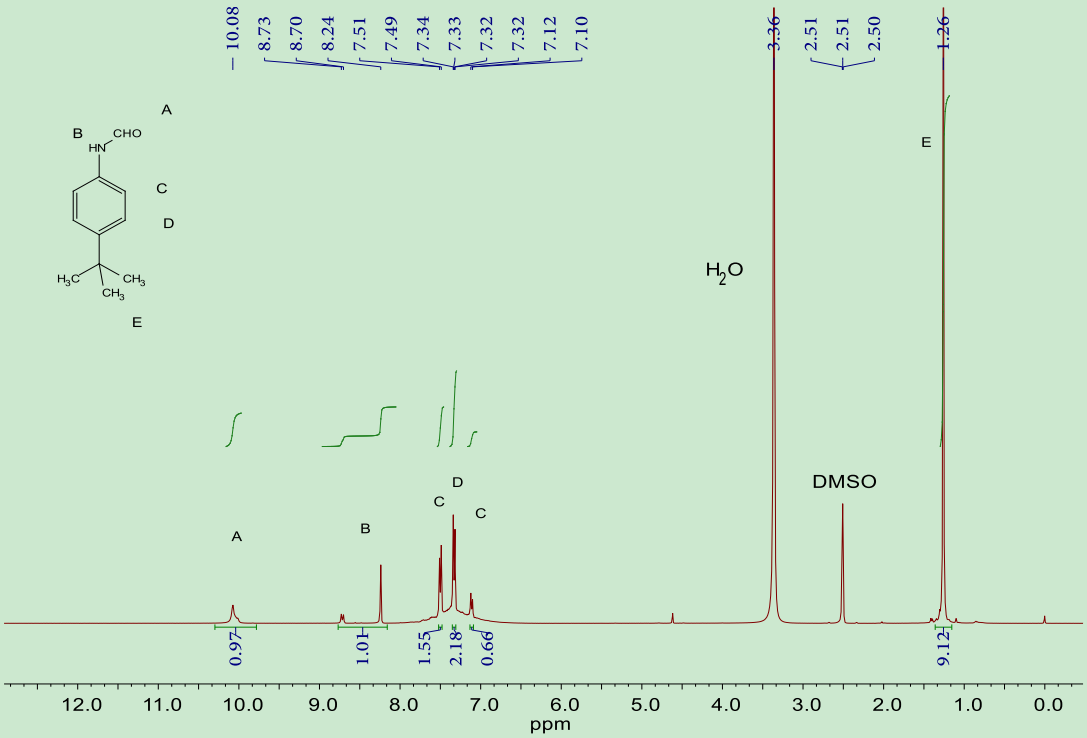


Fig. S22 ^{1}H NMR spectrum of **2f** in DMSO-d_6 (400 MHz).

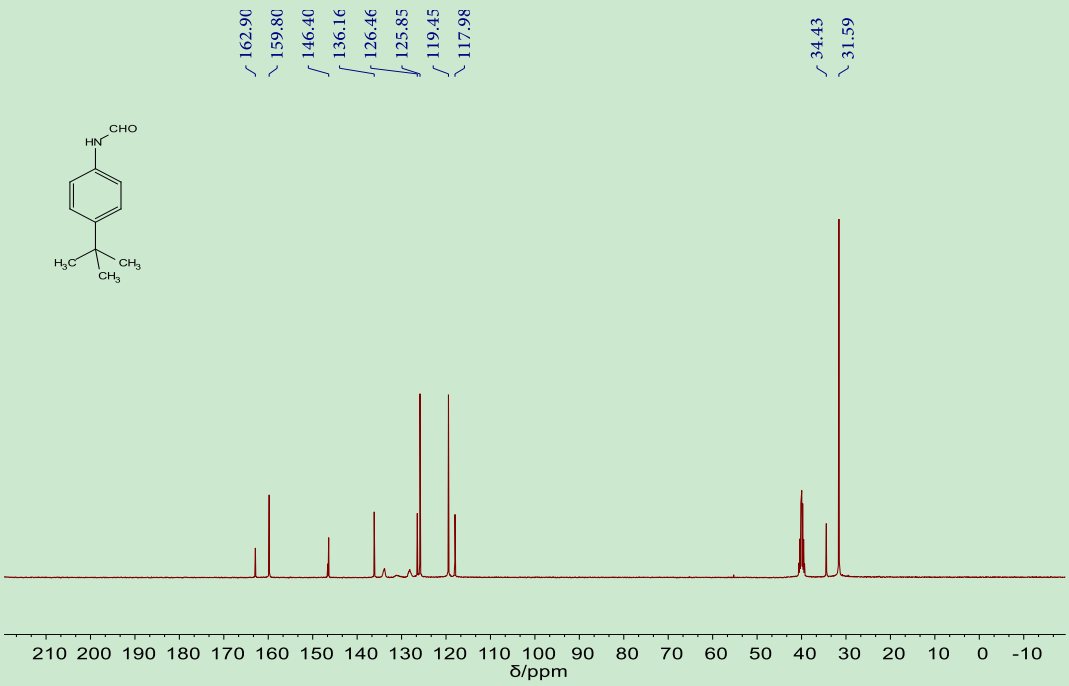


Fig. S23 ^{13}C NMR spectrum of **2f** in DMSO-d_6 (101 MHz).

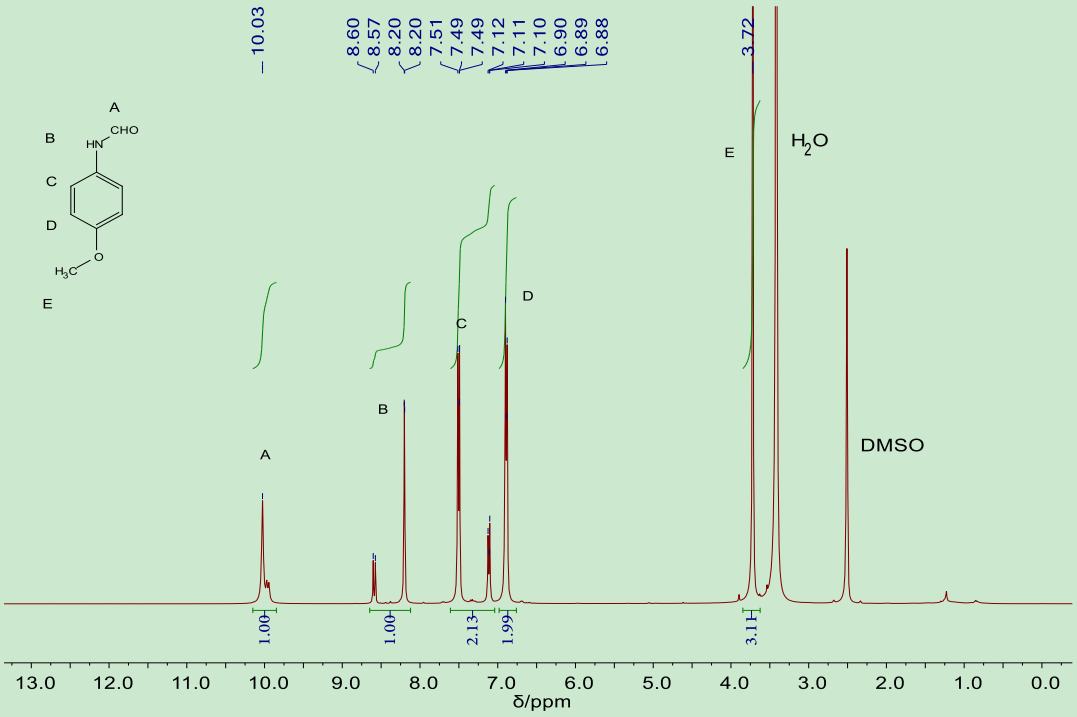


Fig. S24 ^{1}H NMR spectrum of **2g** in DMSO-d_6 (400 MHz).

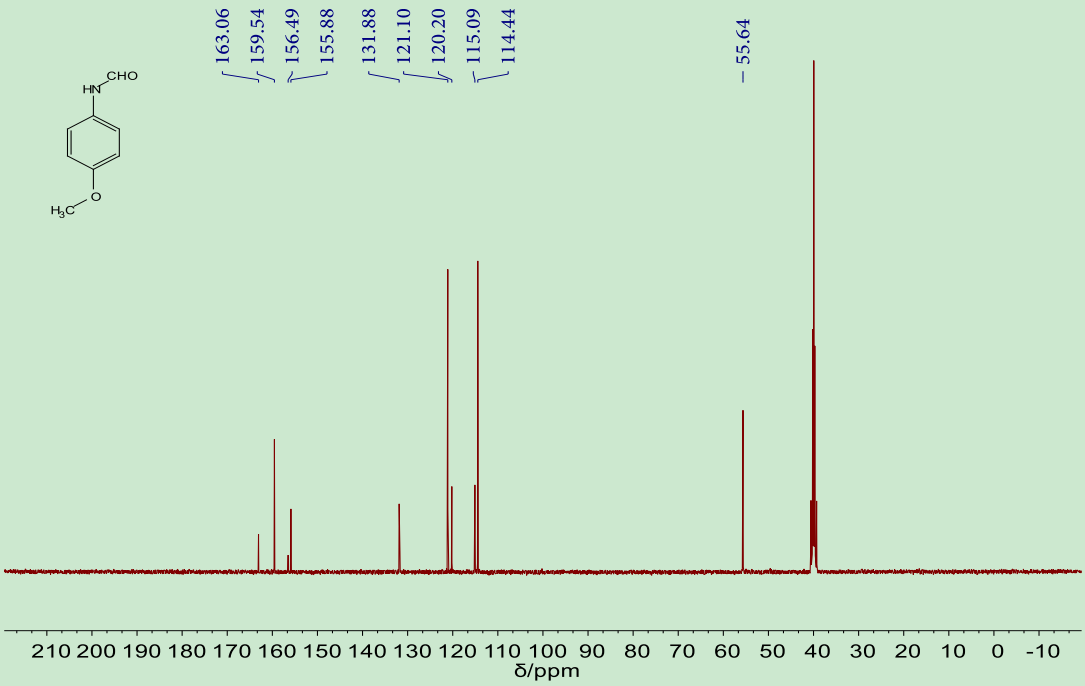


Fig. S25 ^{13}C NMR spectrum of **2g** in DMSO-d_6 (101 MHz).

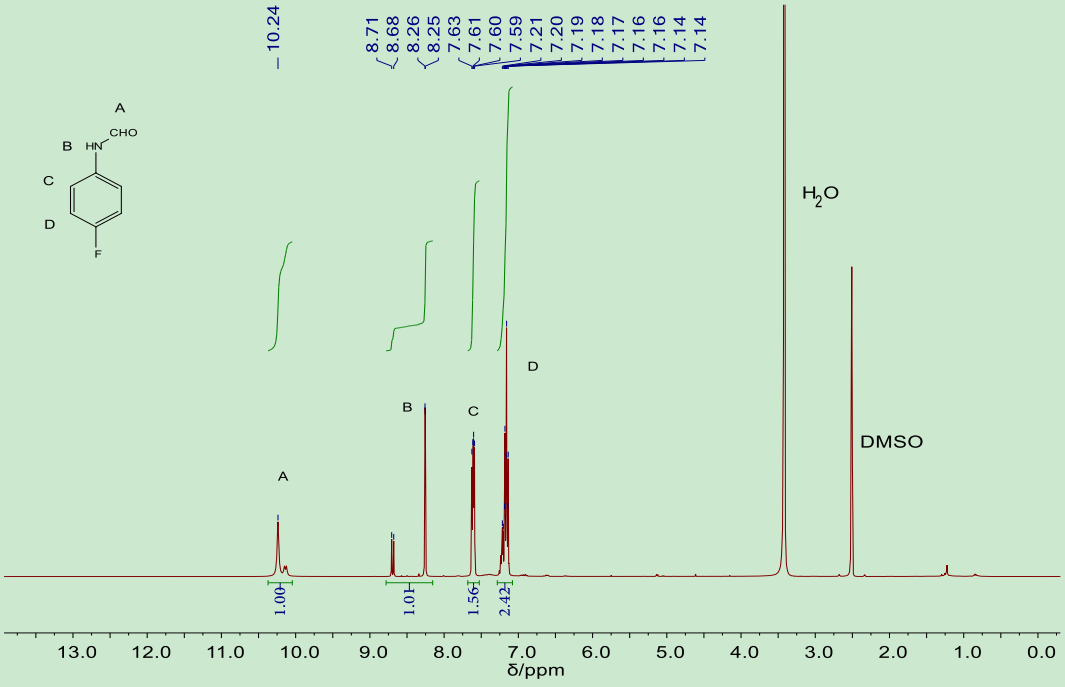


Fig. S26 ^{1}H NMR spectrum of **2h** in DMSO-d_6 (400 MHz).

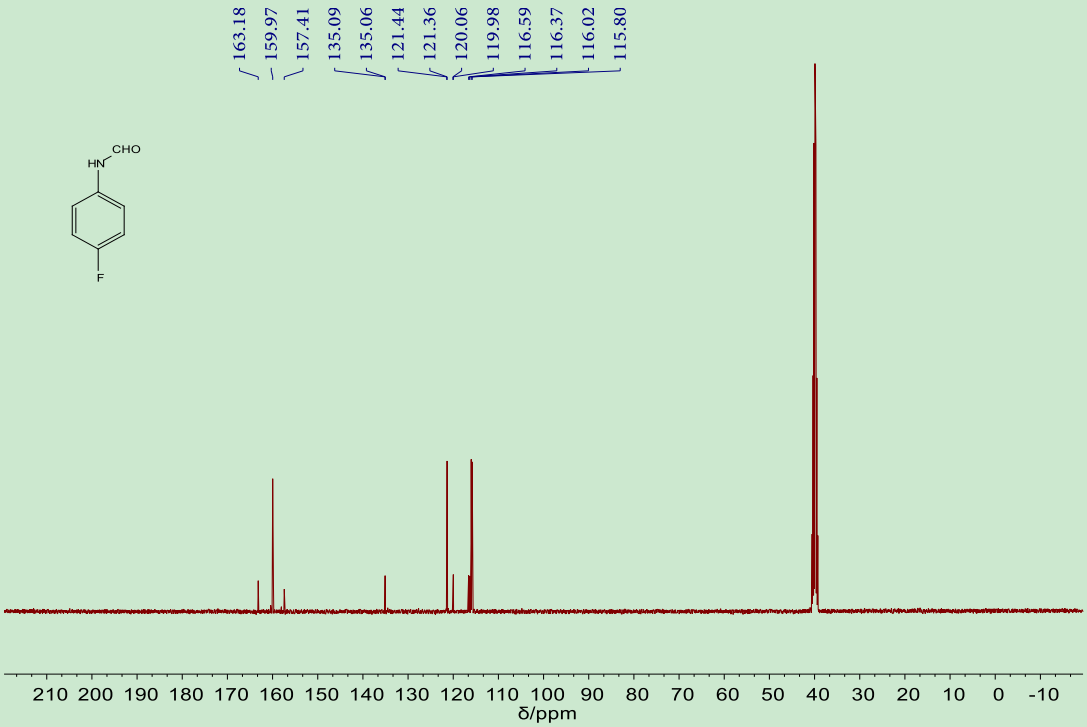


Fig. S27 ^{13}C NMR spectrum of **2h** in DMSO-d_6 (101 MHz).

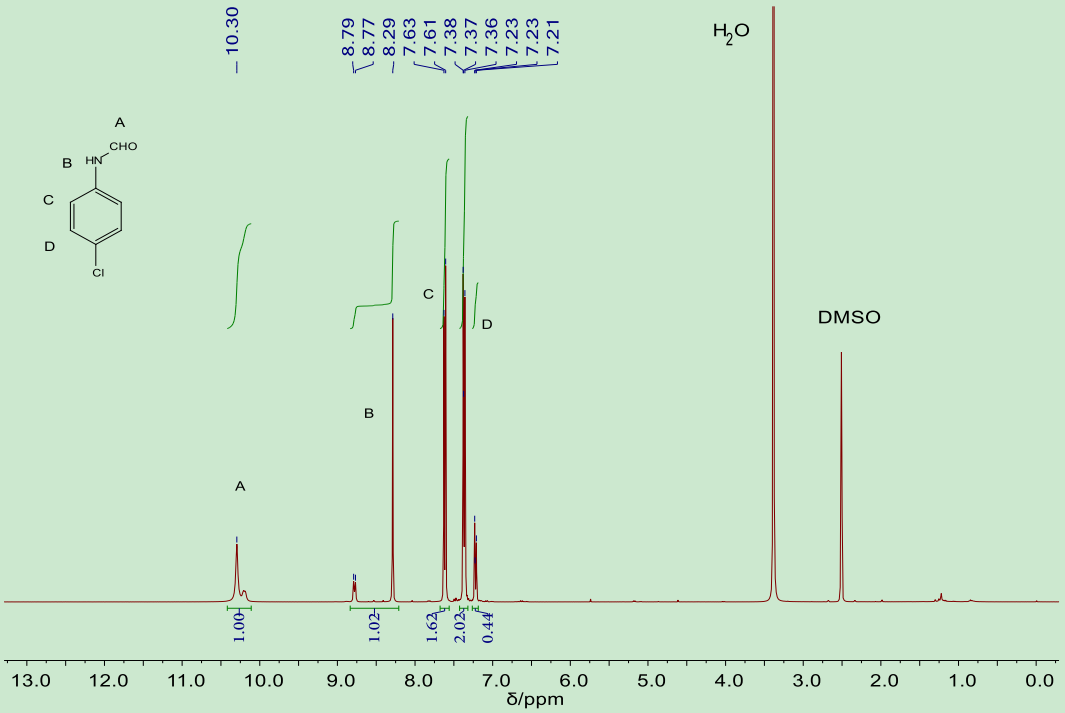


Fig. S28 ^{1}H NMR spectrum of **2i** in DMSO-d_6 (400 MHz).

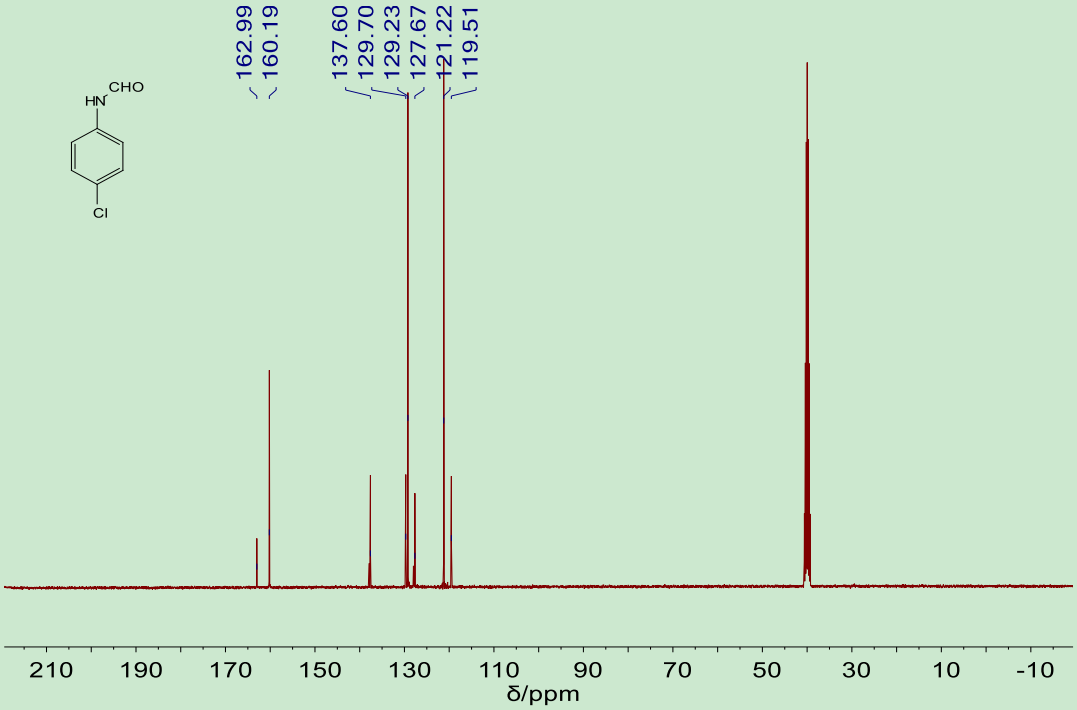


Fig. S29 ^{13}C NMR spectrum of **2i** in DMSO-d_6 (101 MHz).

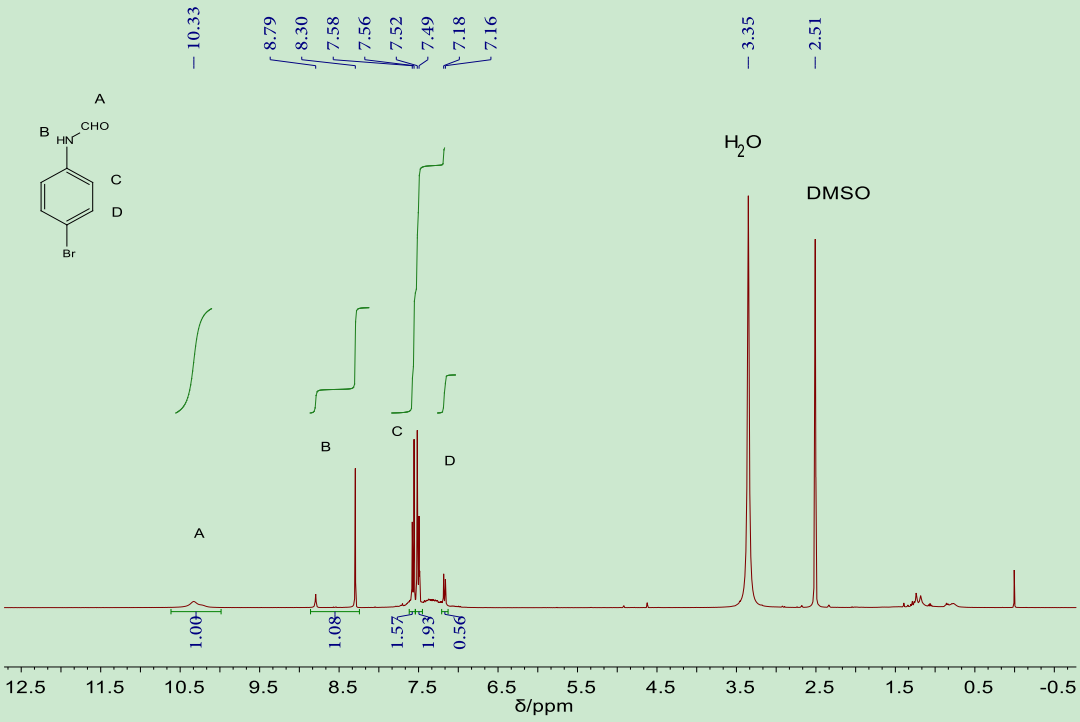


Fig. S30 ^{1}H NMR spectrum of **2j** in DMSO-d_6 (400 MHz).

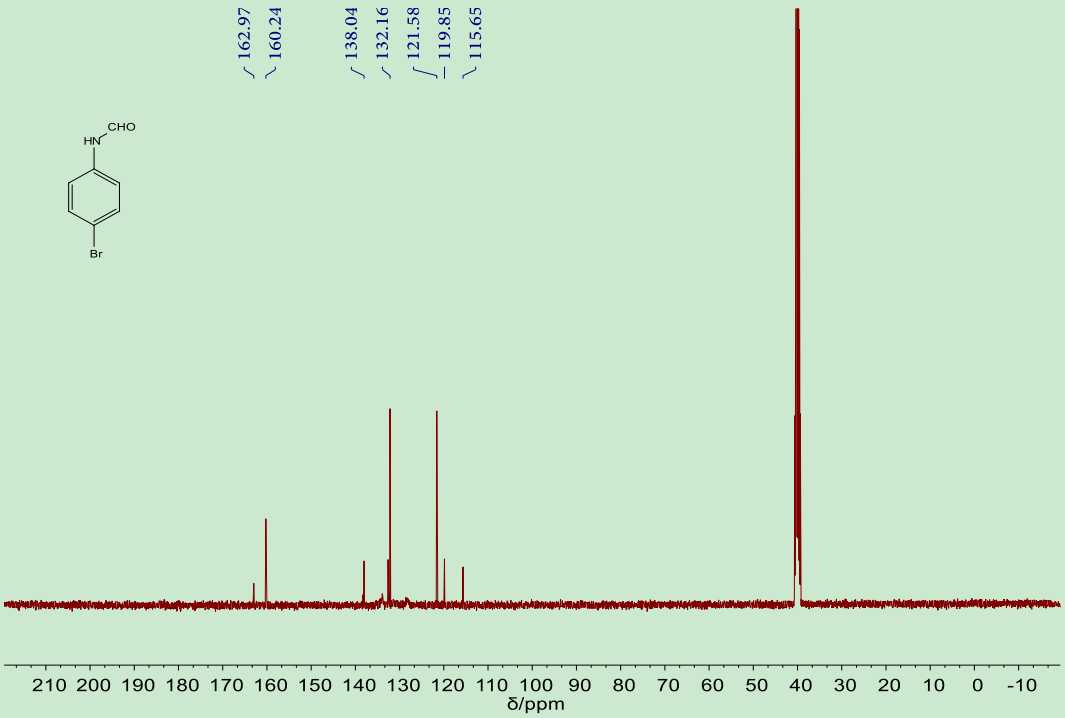


Fig. S31 ^{13}C NMR spectrum of **2j** in DMSO-d_6 (101 MHz).

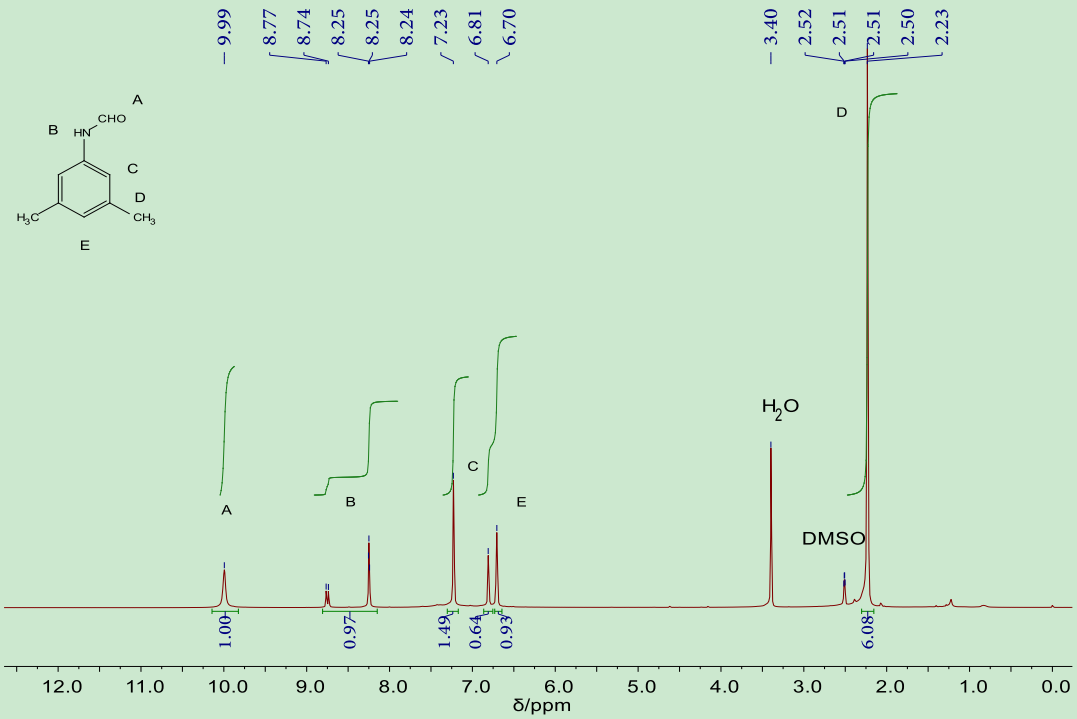


Fig. S32 ^{1}H NMR spectrum of **2k** in DMSO-d_6 (400 MHz).

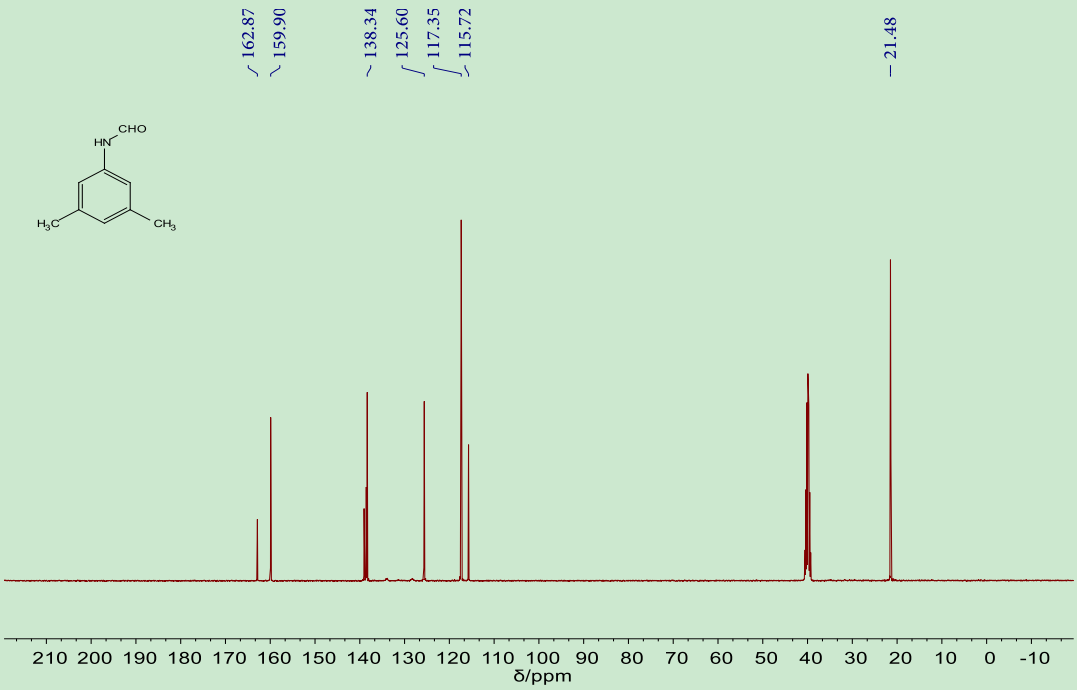


Fig. S33 ^{13}C NMR spectrum of **2k** in DMSO-d_6 (101 MHz).

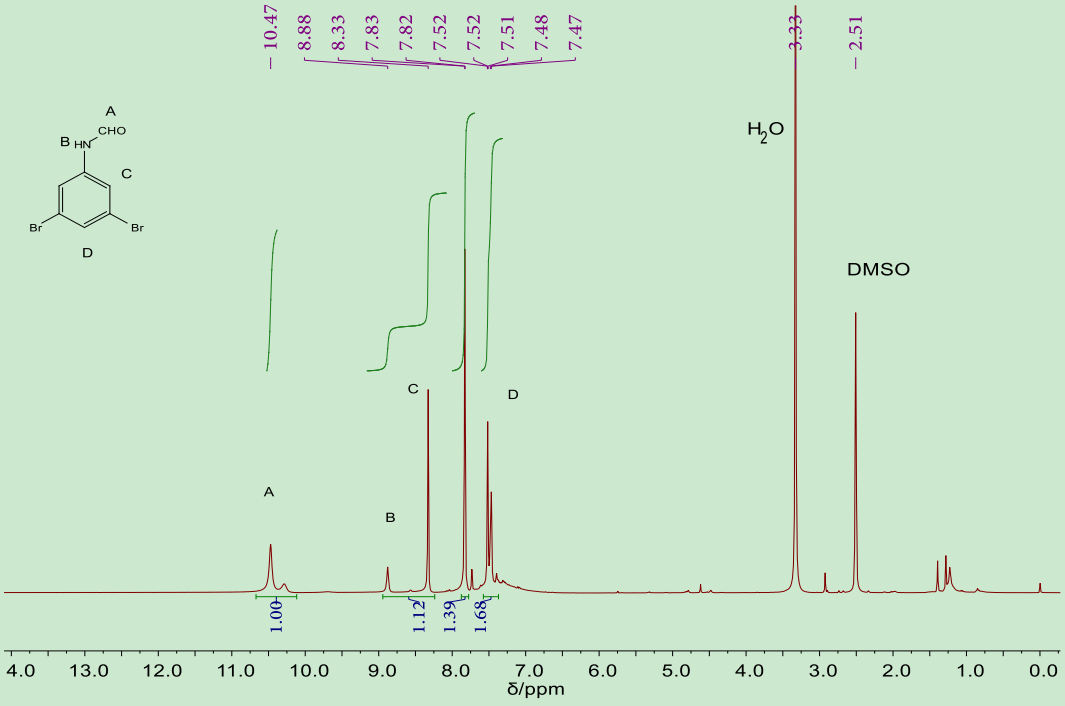


Fig. S34 ^{1}H NMR spectrum of **2l** in DMSO-d_6 (400 MHz).

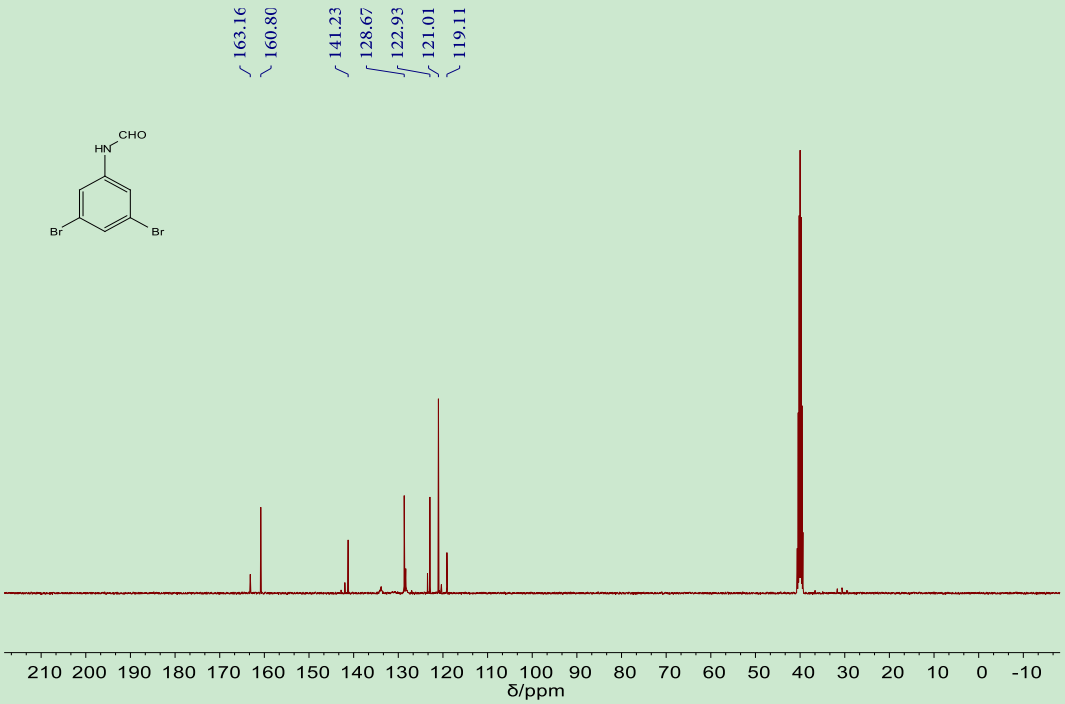


Fig. S35 ^{13}C NMR spectrum of **2l** in DMSO-d_6 (101 MHz).

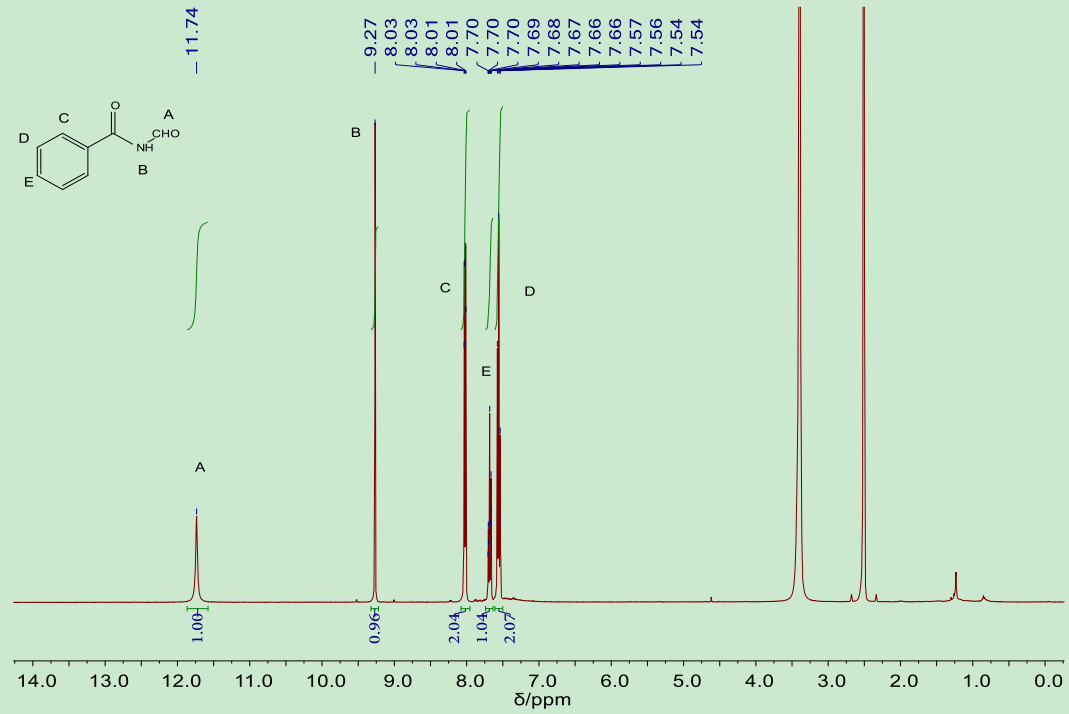


Fig. S36 ^{1}H NMR spectrum of **4a** in DMSO-d_6 (400 MHz).

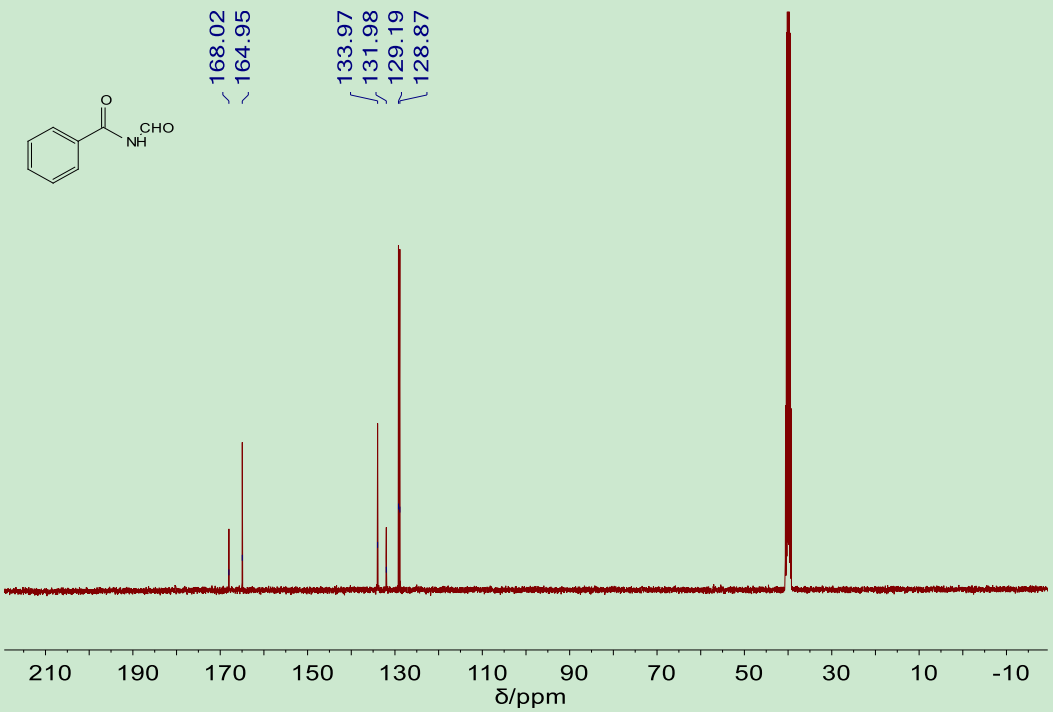


Fig. S37 ^{13}C NMR spectrum of **4a** in DMSO-d_6 (101 MHz).

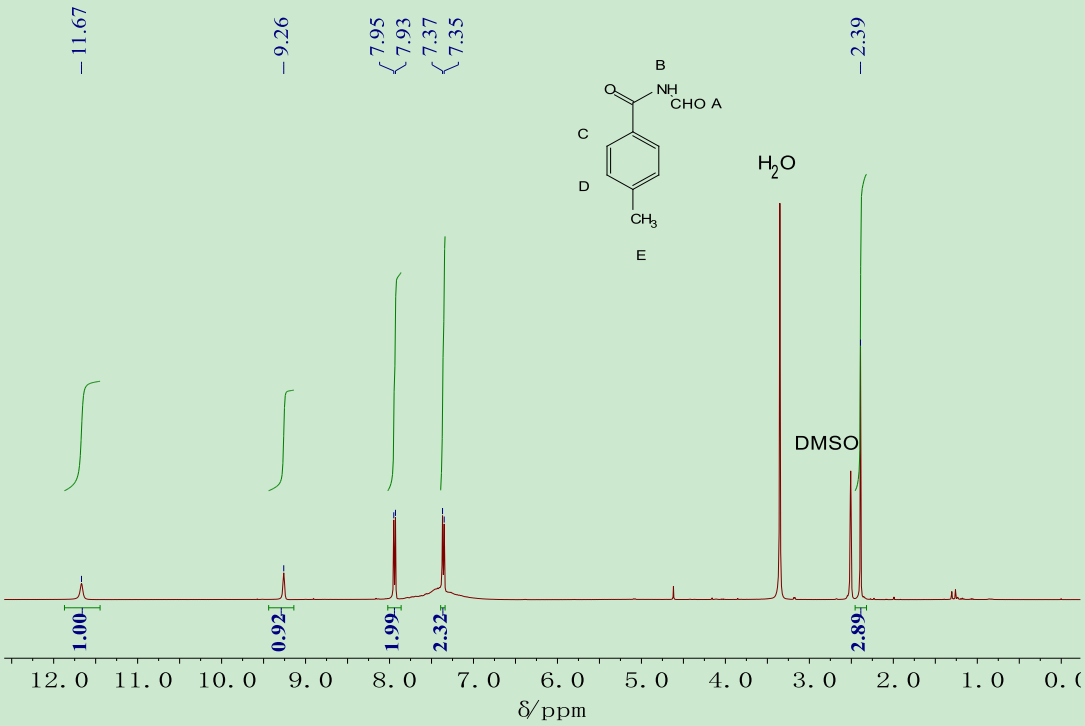


Fig. S38 ^{1}H NMR spectrum of **4b** in DMSO-d_6 (400 MHz).

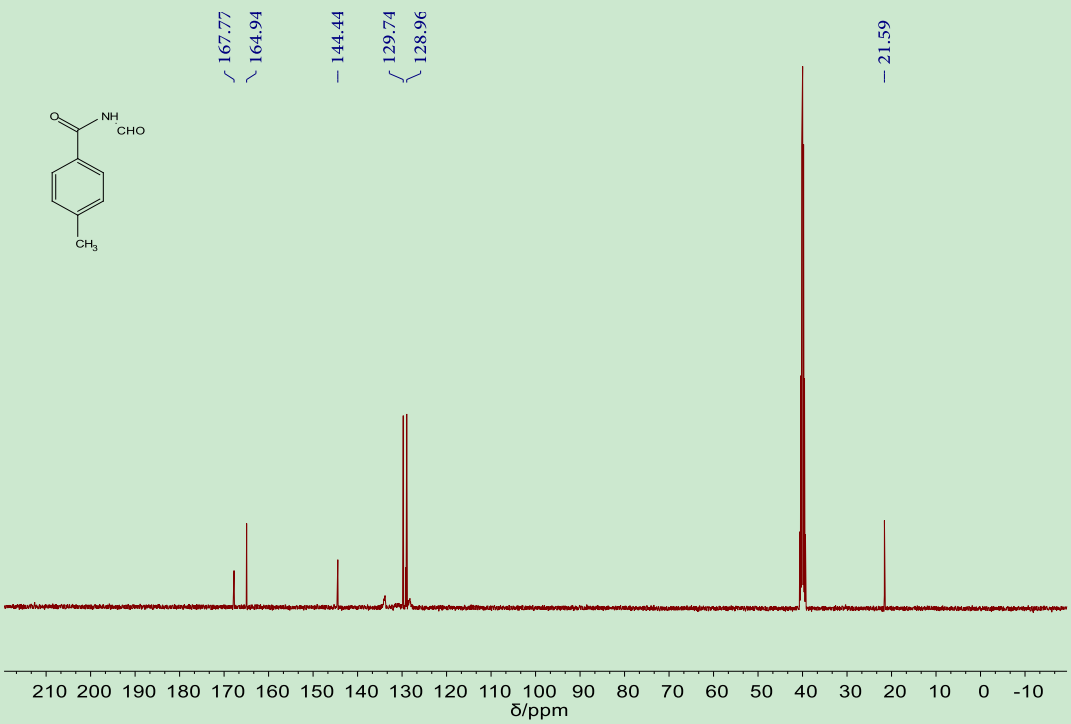


Fig. S39 ^{13}C NMR spectrum of **4b** in DMSO-d_6 (101 MHz).

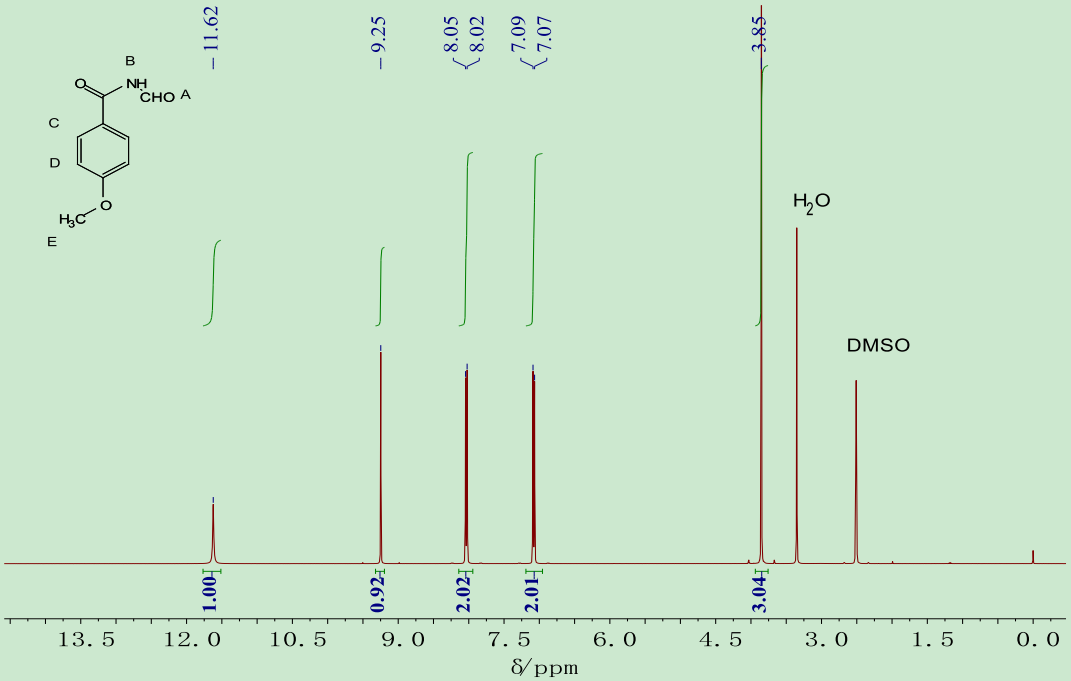


Fig. S40 ^{1}H NMR spectrum of **4c** in DMSO-d_6 (400 MHz).

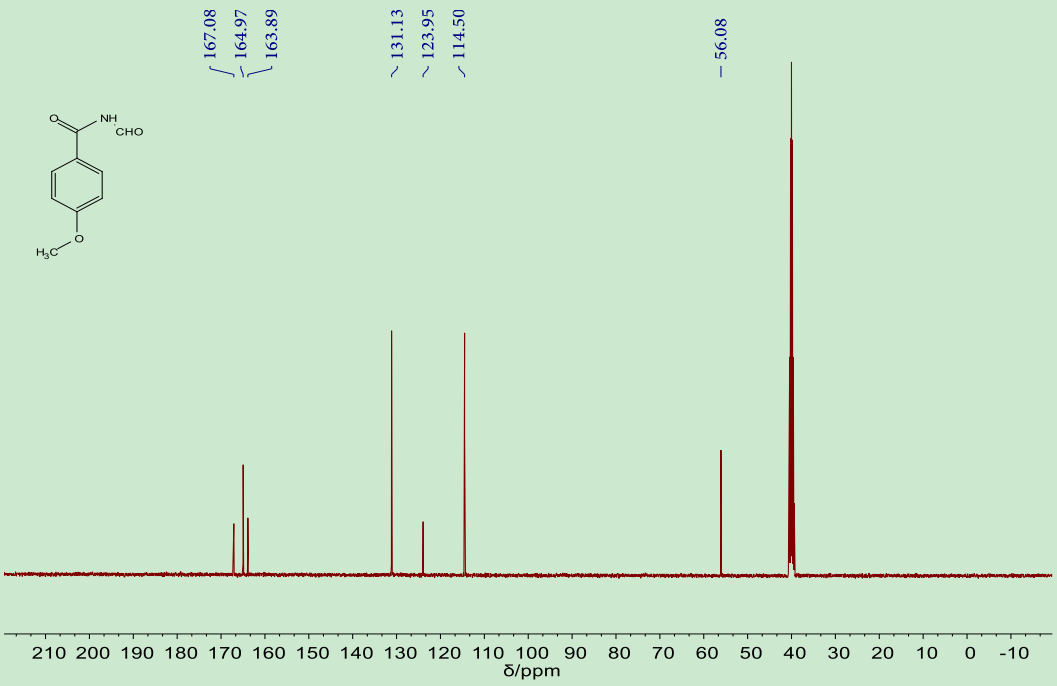


Fig. S41 ^{13}C NMR spectrum of **4c** in DMSO-d_6 (101 MHz).

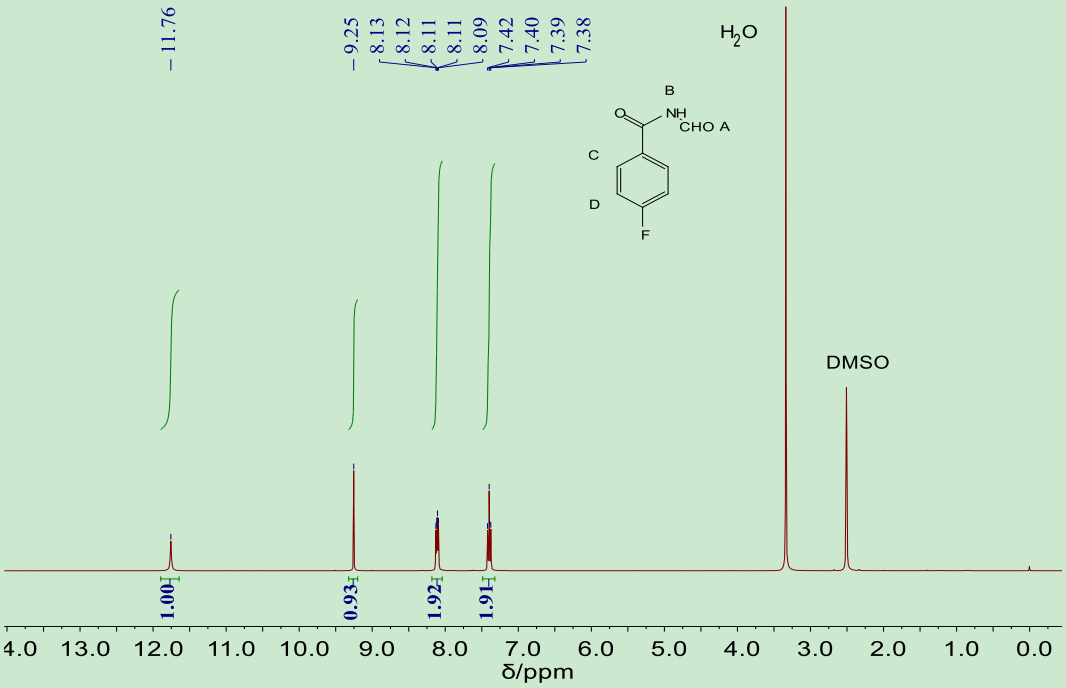


Fig. S42 ^{1}H NMR spectrum of **4d** in DMSO-d_6 (400 MHz).

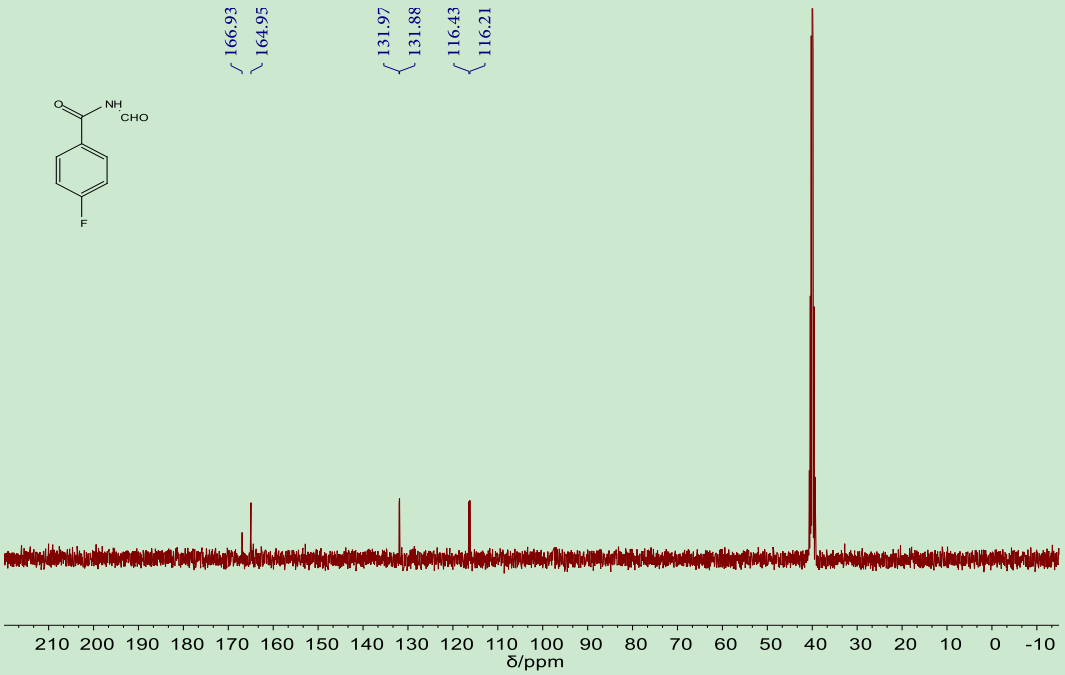


Fig. S43 ^{13}C NMR spectrum of **4d** in DMSO-d_6 (101 MHz).

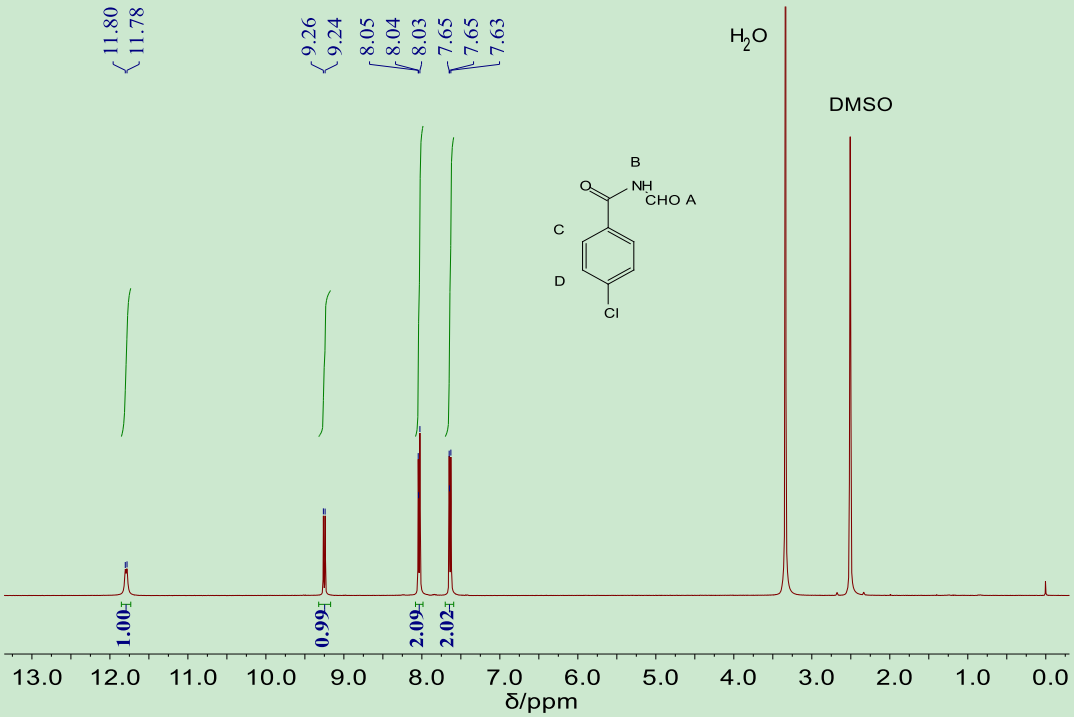


Fig. S44 ^{1}H NMR spectrum of **4e** in DMSO-d_6 (400 MHz).

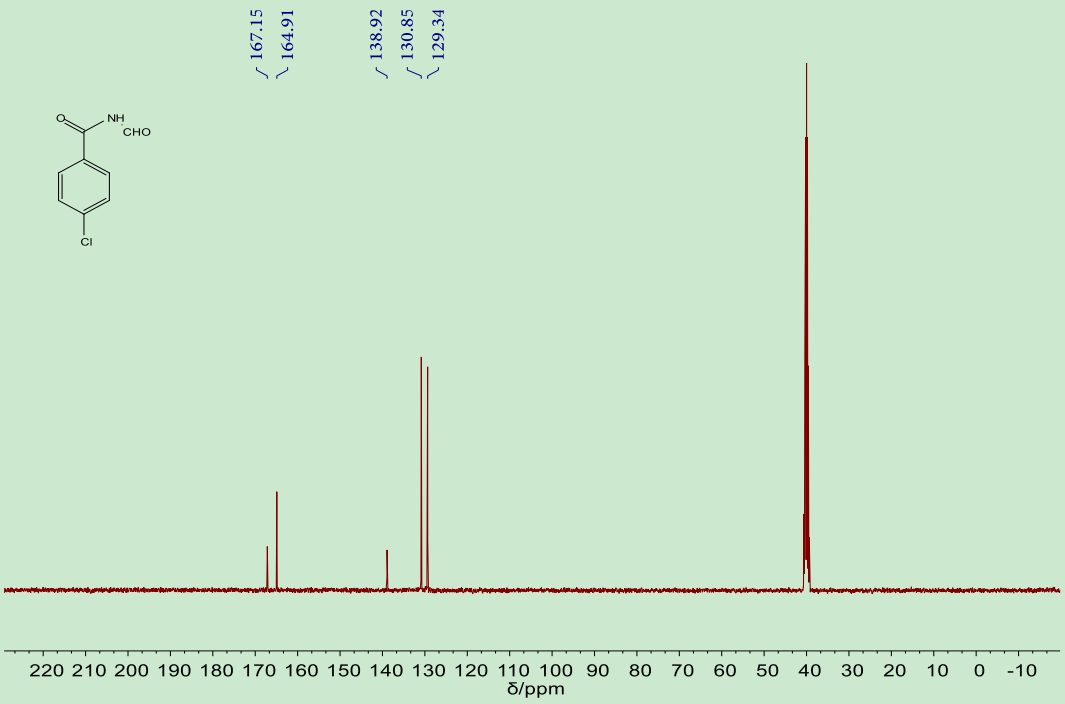


Fig. S45 ^{13}C NMR spectrum of **4e** in DMSO-d_6 (101 MHz).

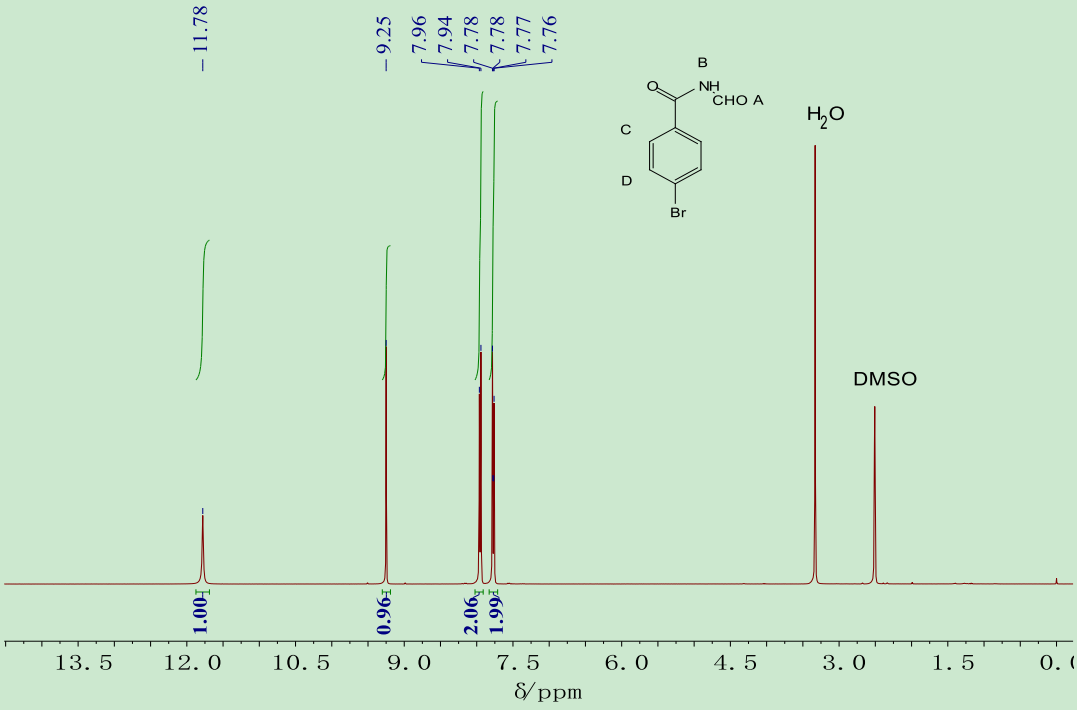


Fig. S46 ^{1}H NMR spectrum of **4f** in DMSO-d_6 (400 MHz).

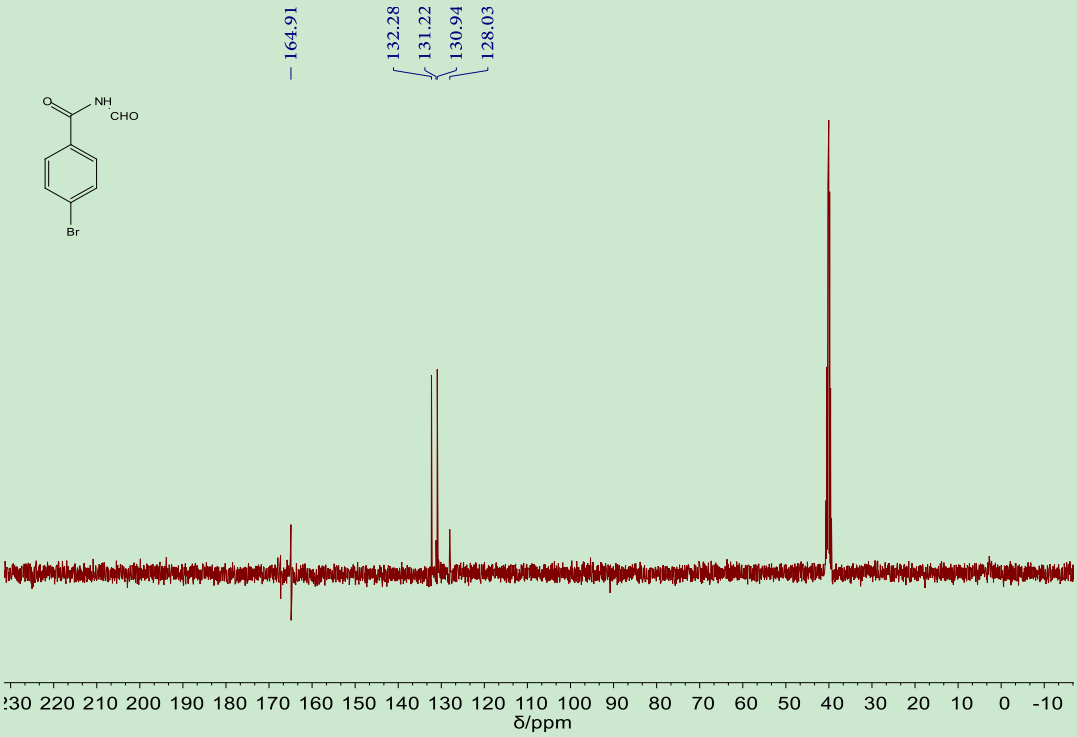


Fig. S47 ^{13}C NMR spectrum of **4f** in DMSO-d_6 (101 MHz).

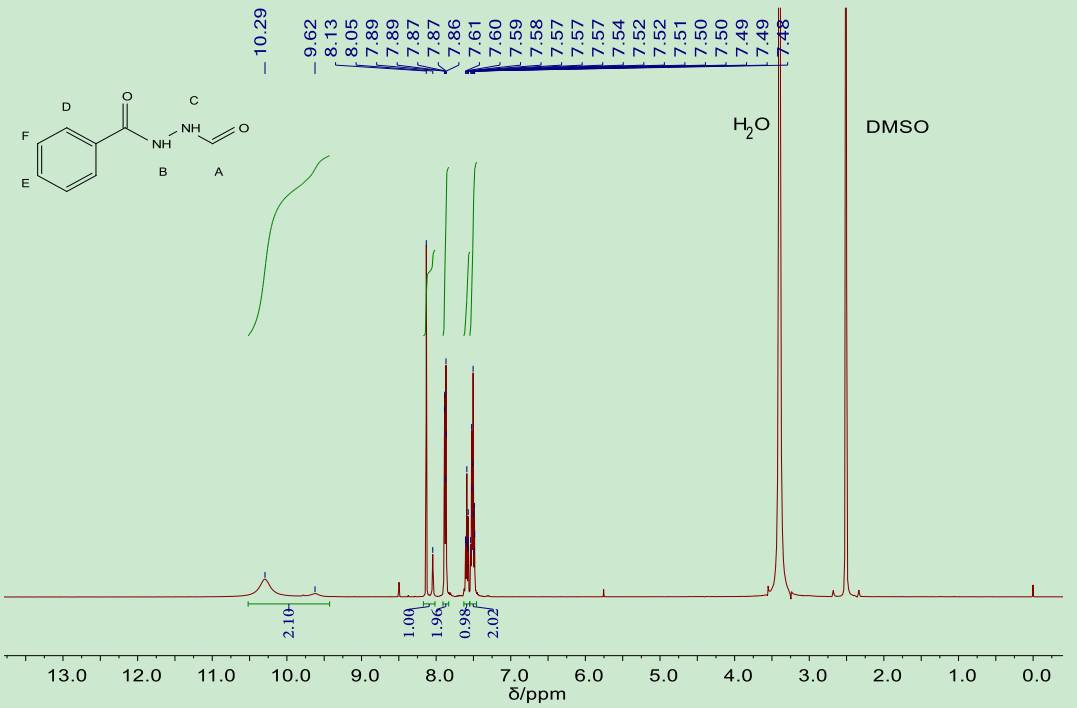


Fig. S48 ^{1}H NMR spectrum of **4g** in DMSO-d_6 (400 MHz).

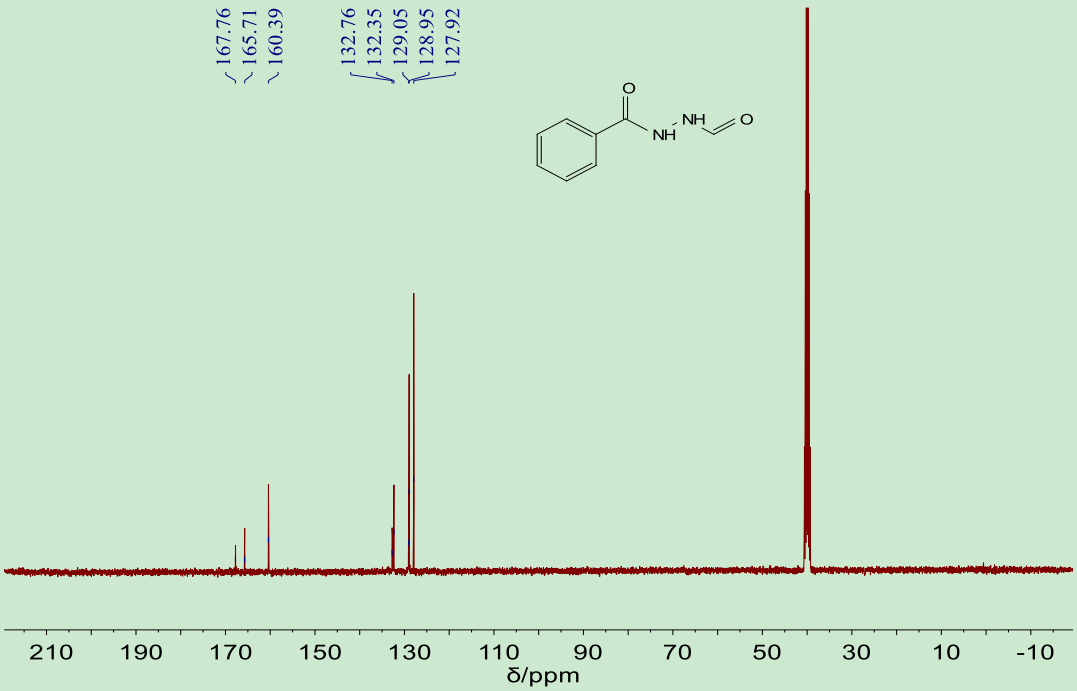


Fig. S49 ^{13}C NMR spectrum of **4g** in DMSO-d_6 (101 MHz).