Mild Formamide Synthesis through Borinic Acid Catalysed Transamidation.

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Abstract: A highly efficient and mild transamidation of amides with amines co-catalysed by borinic acid and acetic acid is reported. A wide range of functionalized formamides was synthesized in excellent yields, including important chiral α-amino acid derivatives with minor racemisation being observed. Experiments suggest that the reaction rely on a cooperative catalysis involving an enhanced boron-derived Lewis acidity rather than an improved Brønsted acidity of acetic acid.

Formamides are important pharmacophore in various drugs such as leucovorin[1a], formoterol[1b], orlistat[1c]. They are also used in the synthesis of valuable heterocycles such as quinolone[2a] or imidazole[2b] and as precursors of isocyanides[3a-c] and formamidines[3d]. Formamides are also used as Lewis base organocatalysts in allylation and hydrosilylation reactions[4] and other transformations.[5] Moreover, the formyl group is a useful protecting group of the amine functionality.[6]

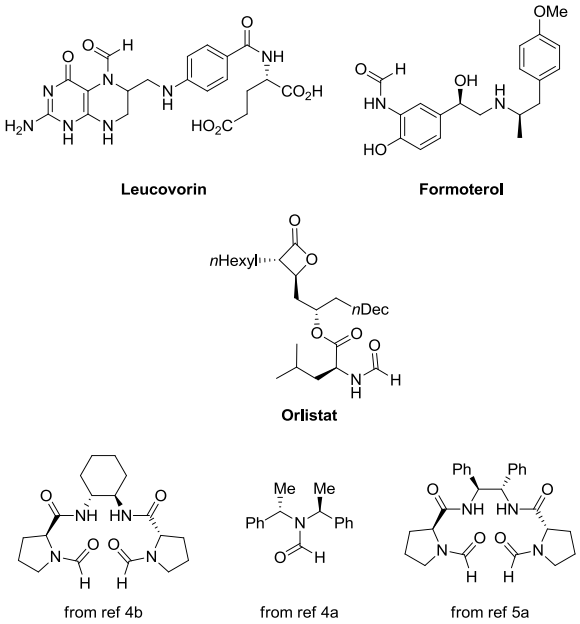
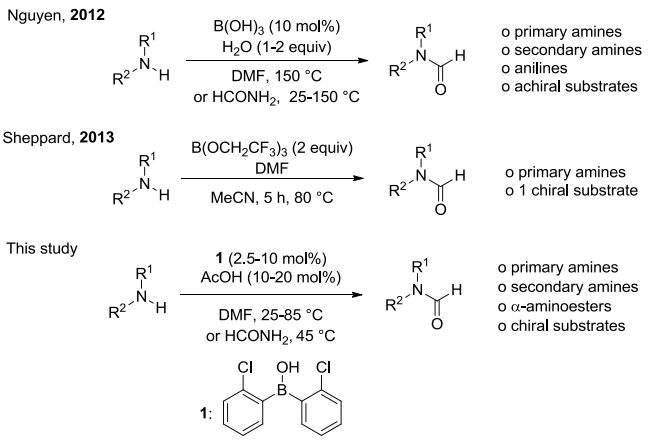


Figure 1. Relevant formamide-containing molecules

Beside the use of formic acid and its derivatives as amine formylating reagents[7], recent developments focused on the use of sub-stoichiometric amounts of a catalyst and a simpler formyl donor such as methanol,[8a-c] carbon monoxide[8d-e] and CO_2. [8f-i] However, these methodologies are significantly restricted to the use of expensive transition metals and high pressure of toxic gases.

Alternatively, transamidation[9] has been established via by recent formylating methodologies reported by Williams,[10a-b] Gamba-Sánchez[10c] and other groups[10d-f]. Unfortunately, despite of the advances achieved, most of these methods require excess amounts of activating reagents, high temperatures or extended reaction times to attain reasonable conversions along with a limited scope. In this context, the use of boron-based catalysts has appeared as an appealing approach (Scheme 1).[11] Evidences about the acceleration of intramolecular transamidation of glutamine by sodium borate were reported as early as 1949.[12] More recently, Sheppard reported a useful fluorinated boronate that is able to promote chromatography-free synthesis of formamides.[11b] Nevertheless, in both previous reports, the boron reagent had to be used in large excess. The first transamidation catalysed by substoichiometric amount of a boron derivative was reported by Nguyen in 2012 (10 mol % boric acid, solvent-free conditions).[11a] However, in most of the cases, temperatures as high as 150 °C were required limiting the scope to stable achiral amine substrates.[13]

In continuation to our recent developments in the field of boron-based catalysis aiming at developing metal-free alternatives for key chemical transformations,[14] we recently reported the borinic acid **1** as an efficient catalyst capable of achieving the challenging coupling between two non-activated amino acids.[14b]



Scheme 1. Formylating transamidations promoted by boron-based catalysts

In this project, the remarkable efficiency of borinic acid **1** in catalysing the transamidation of DMF with amines was recognized. As a first reaction, a combination of 10 mol % of **1** with 20 mol % of acetic acid was found to promote the unusual transamidation of DMF with benzylamine at room temperature in

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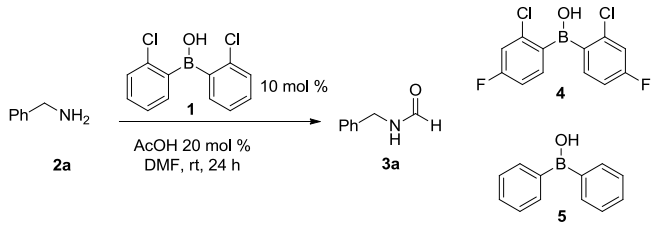
73% isolated yield. Intriguingly, under those conditions, the amide synthesis involving acetic acid was found to be completely unproductive [15] (Table 1, Entry 1)[16] . Notably, this result that was obtained under very mild conditions compared favorably with the state of art and prompted us to further investigate this reaction in details.

The efficiency of catalyst **1** was found to be significantly superior to that of borinic acids **4** and **5** (Table 1, Entries 2 and 3) as well as its analogue 2-chlorophenyl boronic acid **6** (Table 1, Entry 4). After optimisation, a gentle warming to 45 °C provided a quantitative yield while the duration of the reaction could be decreased to 4 hours upon warming to 65 °C (Table 1, Entries 6 and 7).

In the course of optimising the different reaction parameters, several test experiments were carried out and suggested a synergetic mechanism between the borinic acid **1** and acetic acid. In the absence of both acids, no conversion was observed (Table 1, Entry 8). However, the presence of borinic acid **1** alone resulted in a low yield of 34% whereas acetic acid alone led to an even further decrease in the yield. (Table 1, Entries 9-10). These results suggested a cooperation between the two acids and that a Lewis acid-assisted Brønsted acid (LBA) catalytic system could be at play.[17]

Table 1. Optimisation of the transamidation of DMF with benzylamine



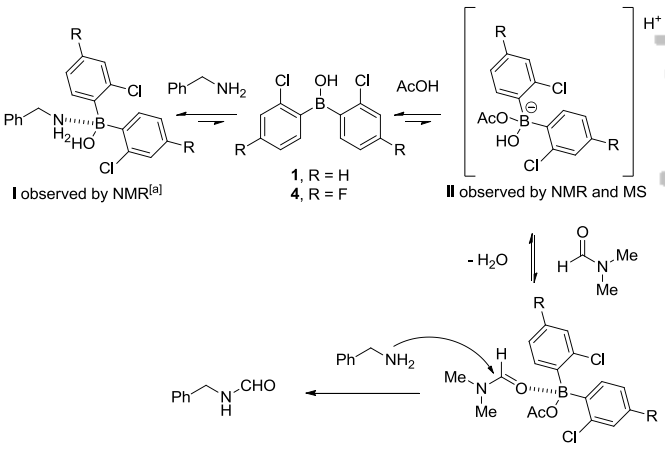
Entry	Deviation from standard conditions	Yield [%][a]
1	none	73
2	2-Cl-4-F-$(C_6H_3)_2$B(OH) **4**[b]	54
3	$Ph_2B(OH)$ **5**[b]	6
4	2-Cl-$C_6H_4B(OH)_2$ **6**[b]	22
5	reaction run for 72h	82
6	reaction run at 45 °C	98
7	reaction run at 65 °C for 4 h	99
8	no **1**, no AcOH	0
9	only **1**	34
10	only AcOH	19
11	only $BnCO_2H$[c]	15
12	only HCO_2H[c]	11
13	only CCl_3CO_2H[c]	9
14	only CF_3CO_2H[c]	1

[a] Isolated yields. [b] Instead of **1**. [c] Instead of AcOH.

However, upon examining the reactivity of different Brønsted acids (Table 1, Entries 11-14), the strongest trifluoroacetic acid afforded a barely detectable conversion despite of its higher Brønsted acidity (Table 1, Entry 14), thus rendering unlikely the initial hypothesis about the improvement of Brønsted acidity through the coordination of acetic acid with **1**.

In order to gain insight into the mechanism, the reaction was monitored using the borinic acid **4** as a fluorinated probe. Accordingly, aliquots of the reaction mixture were sequentially examined by means of ^{19}F NMR spectroscopy after the stepwise addition of the reagents. After the addition of acetic acid to borinic acid **4** in DMF, a single signal was observed at -110 ppm, corresponding to pure **4**. However, upon the addition of benzylamine **2a**, a new signal immediately appeared at -115.3 ppm, likely corresponding to the amine-borinic acid complex **I** (Scheme 2) that remained as the only detectable signal during 24 hours at 65 °C. A possible proto-deboronation of **4** during the reaction was ruled out since 2-chloro-4-fluorophenyl boronic acid **6** displayed a different signal at -108.3 ppm under similar conditions.[18]

Borinic acid **1** displayed a ^{11}B NMR signal at 38.7 ppm in DMF-d^7, representative of a trivalent boron species, and indicating the absence of any detectable interaction between DMF and the boron centre. Interestingly, upon the addition of two equivalents of acetic acid, a new signal appeared at 5.5 ppm in a 1 : 1 ratio, consistent with a tetravalent boron centre.[19] Any attempts to isolate this intermediate yielded back borinic acid **1** but direct ESI-TOF mass analysis of the mixture displayed a 309.0 *m/z* peak corresponding to $[M\text{-}H]^-$ of **1** complexed with acetic acid (**II**, Scheme 2). Unfortunately, no species involving the activation of DMF by the borinic acid **1** was detected. However, the observation of complex **II** suggested a mechanism where the borinic acid **1** was first converted to a mixed borinic-acetic anhydride possessing a higher Lewis acidity. This species would then activate DMF and promote the addition of benzylamine (Scheme 2).



Scheme 2. Second mechanistic hypothesis for the transamidation of DMF

With the optimal conditions in hand, the scope of DMF transamidation was further examined and it appeared that borinic acid **1** was efficiently able to formylate a wide range of

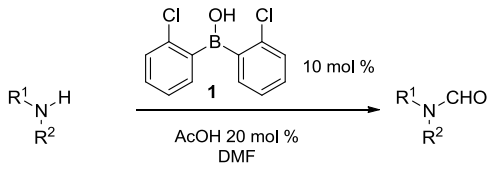
amines. The formylation of various primary amines was achieved at room temperature with good to excellent 77-99% yields (Table 2, Entries 1-5).

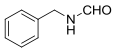
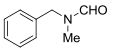
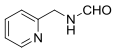
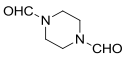
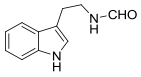
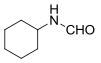
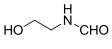
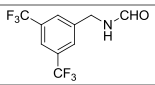
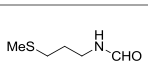
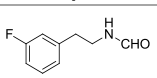
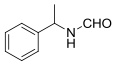
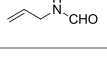
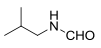
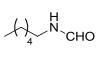
Noteworthy, only 5 equivalents of DMF were found to be sufficient for achieving room temperature formylation of primary amines functionalized with a pyridine, an indole, an unprotected alcohol or a methylthioether (Table 2, Entries 2-5). More difficult substrates required a slight warming to 65 °C to attain acceptable reaction rates. At this temperature, α-substituted primary amines and secondary amines gave 89-99% yields within 12-24 h (Table 2, Entries 6-10).

In some occasions, the starting amine was found to be poorly soluble in the reaction media resulting in the absence of conversion. However, in such cases, dilution with DMF led to higher yields. Thus, piperazine, cyclohexylamine and other amine substrates afforded excellent 96-99% yields with DMF being used in excess amounts (Table 2, Entries 11-17).

Among the tested primary amines, the hindered *t*-butylamine was the only to behave sluggishly, thus illustrating that steric hindrance played a significant role during the reaction (Table 2, Entry 18).

Table 2. Scope of the transamidation of DMF with the different amines.[a]

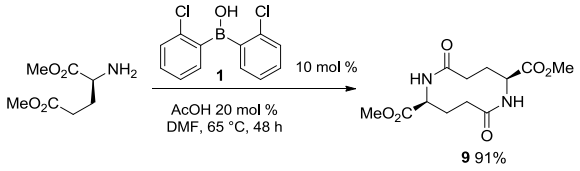


Entry	Formamide		T [°C]	t [h]	Yield [%][b]	Entry	Formamide		T [°C]	t [h]	Yield [%][b]
1		**3a**	20	72	86[c](99[d])	10		**3j**	65	12	99
2		**3b**	20	72	77[c]	11		**3k**	65	12	96[f]
3		**3c**	20	72	86[c]	12		**3l**	65	12	97[f]
4		**3d**	20	72	98 (90[e])	13		**3m**	65	12	99[f]
5		**3e**	20	72	99	14		**3n**	65	12	98[f]
6		**3f**	65	12	99	15		**3o**	65	24	99[f]
7		**3g**	65	12	99	16		**3p**	65	12	99[f]
8		**3h**	65	24	89	17		**3q**	65	12	98[f]
9		**3i**	65	24	96	18		**3r**	85	24	26[f,g]

[a] Reaction conditions: Borinic acid **1** (10 mol %), acetic acid (20 mol %), DMF (5 equiv.), reaction temperature and time as reported. [b] Isolated yields. [c] Quantitative yield at 65 °C. [d] Run on 5 mmol scale at 65 °C. [e] Run on 5 mmol scale at 20 °CT. [f] DMF was used as solvent. [g] NMR conversion.

Next, our attention was focused on the formylation of the more challenging α-amino esters. Indeed, this class of functionalized and racemisable substrates is generally underinvestigated with no precedent for a boron-derived catalysis being so far reported for the synthesis of *N*-formyl α-amino ester formamides.[20] As anticipated, glycine methyl ester reacted slowly a room temperature but afforded a quantitative yield at 65 °C. Encouraged by this result, several substituted chiral α-amino esters were tested. However, less reactive derivatives of alanine, phenylalanine, leucine, valine, methionine and proline required a substantial increase in the reaction temperature up to 85 °C to achieve yields of 78-99% (not reported in this paper).[21] However, considerable racemisation was recorded as formamides **8b**, **8c** and **8e** were obtained with

enantiomeric excesses of 25%, 47% and 80%, respectively while complete loss of the chiral integrity was observed with formamides **8f** and **8i**. Interestingly, the methyl glutamate diester provided the macrolactam **9** in 91% yield instead of the expected formamide **8j**, suggesting an unexpected activation of the side chain involving the ester moiety (scheme 3).[22]



Scheme 3. Synthesis of lactam **9** from the aspartic acid derivative.

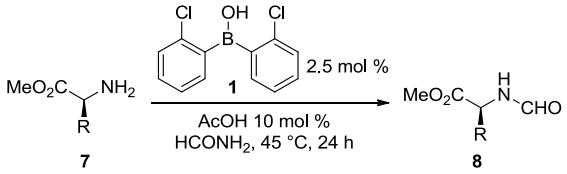
Consequently, milder conditions were sought and optimised to decrease racemisation during the transamidation process. Formamide ($HCONH_2$) was identified[23] as a useful alternative to DMF allowing transamidation at a lower temperature (45 °C) and using a lower catalyst loading (2.5 mol % of **1**).[24]

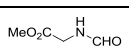
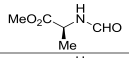
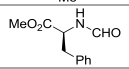
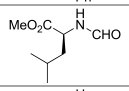
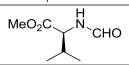
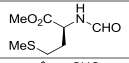
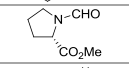
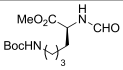
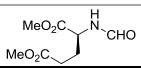
Upon using the new set of conditions, the reactions were noticeably faster with yields generally superior to 91% (Table 3, Entries 1-8). It is noteworthy to mention that these milder conditions strongly limited the racemization with enantiomeric excesses of 94%, 92% and 99% obtained respectively for formamides **8b**, **8c** and **8e** (determined by chiral HPLC, see Supporting Information). Additionally, racemisation in the case of formamides **8f** and **8i** was notably reduced to *ee* values superior to 90%. Remarkably, this method afforded a quantitative yield with acid sensitive Boc-protected lysine **8h** (Table3, Entry 8). Additionally, the methyl glutamate diester led chemoselectively to the desired formamide **8j**, however in a moderate yield of 57% with no traces of the cyclic dimer **9** detected by TLC and NMR (Table 3, Entry 10).

Finally, our study was completed by taking advantage of the mildness of our catalytic conditions to develop a one-pot procedure for the direct preparation of isocyanide **10** from benzylamine.[25] Among the various possible reagents that are able to dehydrate a formamide, the Burgess Reagent[26] was foreseen as being the most compatible upon using DMF as the solvent. Indeed, when Burgess Reagent and triethylamine were added after completion of the transamidation step of DMF with benzylamine and further reacted for 48 h, the corresponding benzyl isocyanide **10** was isolated in 65% yield (Scheme 4). Furthermore, when other amines were tested (α-methylbenzylamine, decylamine and cyclohexylamine), high conversions were observed by NMR. Unfortunately, the corresponding isocyanides rapidly decomposed invariably upon different purification attempts.

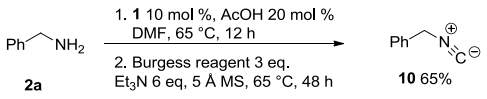
In conclusion, a new method for the *N*-formylation of amines using catalytic amounts of borinic acid **1** and acetic acid is reported. A short mechanistic study pointed towards a cooperative involvement of both species and a reactivity based on an improved Lewis acidity of the boron centre. More specifically, the *N*-formylation of amines was examined with a wide range of primary and secondary amines as well as functionalized α-amino esters. In the case of chiral substrates, the observed racemisation led to a switch of the formyl donor from DMF to $HCONH_2$ in order to keep racemisation at a low level. Additionally, our catalytic system was successfully extended to one-pot synthesis of isocyanides from their primary amines.

Table 3. Scope of the transamidation of $HCONH_2$ with α-aminoesters.[a]



Entry	Formamide		Yield [%][b]
1		**8a**	99
2		**8b**	99
3		**8c**	98
4		**8d**	97
5		**8e**	96 (97[c])
6		**8f**	91
7		**8g**	99
8		**8h**	99
10		**8i**	57

[a] Reaction conditions: Borinic acid **1** (2.5 mol %), acetic acid (10 mol %), $HCONH_2$ (5 equiv.). Reaction temperature and time as reported. [b] Isolated yields. [c] Run on 5 mmol scale (with 656 mg of **7e**).



Scheme 4. One pot synthesis of isocyanide **10** from benzylamine.

Experimental Section

General Procedure for the *N*-formylation of Amines using DMF. To a round-bottom flask kept under an argon atmosphere were added 2-chlorophenylborinic acid **1** (12.5 mg, 0.05 mmol, 0.1 equiv.), acetic acid (6 µL, 6 mg, 0.10 mmol, 0.2 equiv.) and dry DMF (0.19 mL or 7 mL as indicated). The mixture was vigorously stirred for 15 minutes at 25 °C, 65 °C or 85 °C, as indicated, and the amine (0.50 mmol, 1 equiv.) was then slowly added using a gastight syringe. The resulting mixture was stirred

for a further 12-72 h, as reported in table. DMF was removed using Kugelrohr distillation apparatus (55 °C) and the crude mixture was further purified by column chromatography to give the corresponding title compounds. For the amines with low boiling points, the reaction was set in a sealed tube.

General Procedure for the *N*-formylation of Amines using $HCONH_2$. To a sealed tube was added 2-chlorophenylborinic acid **1** (3 mg, 0.0125 mmol, 0.025 equiv.), $HCONH_2$ (0.10 mL, 2.5 mmol, 5 equiv.) and acetic acid (3 µL, 3 mg, 0.05 mmol, 0.1 equiv.). The mixture was vigorously stirred for 15 min at 45 °C and the α-amino methyl ester amine (0.50 mmol, 1 equiv.) was then slowly added using a gastight syringe. The resulting mixture was stirred for a further 24 h. The crude was purified using column chromatography to yield the corresponding title compounds.

Procedure for the One-Pot Synthesis of Isocyanide from Benzylamine. To a round-bottom flask kept under an argon atmosphere were added 2-chlorophenylborinic acid **1** (12.5 mg, 0.05 mmol, 0.1 equiv.), acetic acid (6 µL, 6 mg, 0.10 mmol, 0.2 equiv.) and dry DMF (7 mL) at 65 °C. The mixture was vigorously stirred for 15 minutes and benzylamine (0.50 mmol, 1 equiv.) was then slowly added using a gastight 100 µL syringe. The resulting mixture was stirred for 12 h at 65 °C. After 12 h, Burgess (360 mg, 1.5 mmol, 3 equiv.), triethylamine (418 µL, 3 mmol, 6 equiv.) and 5 Å powdered molecular sieves (1 g) were added and stirring was maintained for further 48 h. The reaction was quenched with water and extracted five times with Et_2O, washed with brine, dried over anhydrous $MgSO_4$ and concentrated under vacuum. Crude isocyanide **10** was purified by column chromatography.

Acknowledgements

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[15] Under condition reported in Table 1, Entry 1, benzyl acetamide resulting from the condensation of benzylamine and acetic acid was not observed neither by TLC nor ^1H NMR.

[16] For further details about optimisation, refer to the Supporting Information. Decreasing the catalyst loading of borinic acid **1** to 5 mol% led to a slightly lower yield while decreasing the acetic acid : borinic acid **1** ratio from 2 : 1 to 1 : 1 significantly lowered the yield of the reaction.

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[20] Isolated examples can be found in Ref. 7b-d and 8f. For a specific study see Ref 10f. In this latter report, benzylamine was found surprisingly less reactive than various α-amino esters.
[21] Reaction conditions: Borinic acid **1** (10 mol %), acetic acid (20 mol %) and DMF at 85 °C for 24h.
[22] With the same substrate, conditions used in Ref. 20 led to a partially racemised five-membered lactam in a low yield of 30% *via* an intramolecular cyclisation.
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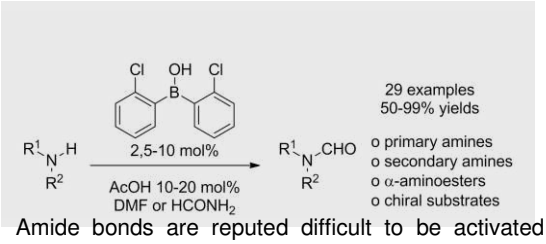
COMMUNICATION



Amide bonds are reputed difficult to be activated due to their high resonance stabilization. Herein, we report an unusual mild activation of dimethylformamide and formamide by borinic acid **1** illustrated by a general formylation of a wide range of amines, including chiral α-aminoesters.

*Tharwat Mohy El Dine, David Evans, Jacques Rouden, and Jérôme Blanchet**

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Mild Formamide Synthesis through Borinic Acid Catalysed Transamidation.

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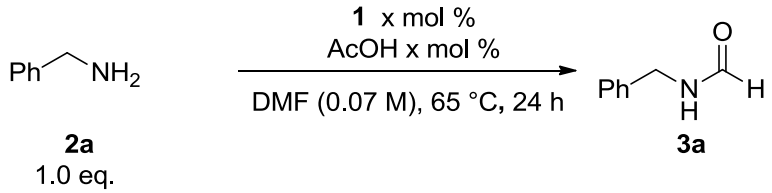
1. General Information

Unless otherwise stated, all reactions were performed under argon atmosphere using flame-dried glassware. Commercially available compounds were used without further purification. DMF was distilled from CaH_2. NMR experiments were performed in deuterated solvents. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F spectra were recorded on 400 and 500 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) relative to the residual protium in the solvents (^{1}H) or the solvent carbon (^{13}C) as internal standards. ^{1}H NMR spectral data features are tabulated in the following order: chemical shift in ppm (δ) (multiplicity, coupling constant, integration, type of H). The following abbreviations were used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplet; td, triplet of doublet; ddd, doublet of doublet of doublet; m, multiplet; sept, septet; quin, quintet. Because of their low intensity (resulting from quadruple coupling), ^{13}C signals arising from the quaternary carbon bearing the borinic acid group were not always observed and therefore were not always listed. Chromatographic separations were achieved on silica gel columns (Kieselgel 60, 40-63 µm). Detection was accomplished by irradiation with a UV lamp or staining with $KMnO_4$. IR Spectra were recorded on a FTIR spectrometer with frequencies expressed in cm^{-1}. HSQCETGP (2D H-1/X correlation via double inept transfer phase sensitive using Echo/Antiecho-TPPI gradient selection with decoupling during acquisition using trim pulses in inept transfer). HMBCGPLPNDQF (2D H-1/X correlation via heteronuclear zero and double quantum coherence optimized on long range couplings with low-pass J-filter to suppress one-bond correlations no decoupling during acquisition using gradient pulses for selection). DEPT135 (dept polarization transfer with 135 degree read pulse to give XH, XH_3 positive and XH_2 negative with decoupling during acquisition) were used to assign the NMR peaks. Mass Spectra and high-resolution mass spectra (HRMS) were obtained on a Q-Tof instrument were recorded using either electron impact (EI) or electrospray ionization (ESI) techniques. Powdered molecular sieves were dried for 3 hours under high vacuum (<1 mbar) at 250 °C using a Kugelrohr instrument.

2. Optimization Experiments

Table 1. Optimization of **1** loading and ratio AcOH:**1**[a]



2a
1.0 eq.

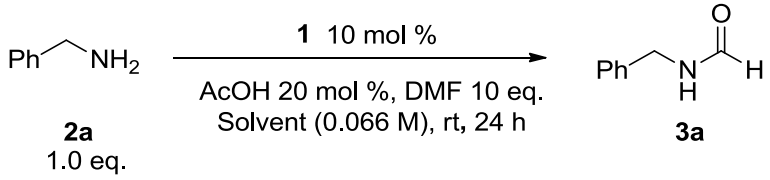
3a

Entry	AcOH (mol %)	1 (mol %)	Isolated Yield (%)
1	40	10	98
2	20	10	98
3		5	93
4	10	10	80

[a] Reaction conditions: Borinic acid **1** (5-10 mol %) and AcOH (10-40 mol %) in DMF (7 mL) were stirred at 65 °C for 15 min before the addition of benzylamine **2a** (55.5 µL, 0.50 mmol) and stirring was maintained for further 24 h.

As shown by Table 1, a catalyst loading of 10 mol % along with 40 mol % of AcOH provided the corresponding benzyl formamide **3a** in an excellent yield of 98% (Entry 1). Decreasing the amount of AcOH 20 mol % had no impact on the yield (Entry 2). Whereas, upon decreasing the catalyst loading to 5 mol % with 20 mol % AcOH, a slight decrease in the yield of **3a** was observed (93%, Entry 3). A further decrease for AcOH to 10 mol % greatly lowered the yield (80%, Entry 4). As a result, the optimal conditions appeared to involve a ratio of 2 : 1 AcOH/Borinic acid rather than a ratio of 1 : 1.

Table 2. Solvent screening using **1**[a]



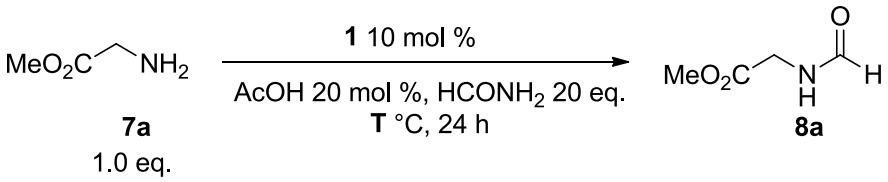
Entry	Solvent	Yield (%)
1	THF	15
2	CH_2Cl_2	8
3	MeCN	7
4	Toluene	5
5	AcOH	0
6	DMF	73

[a] Reaction conditions: Borinic acid **1** (10 mol %), AcOH (20 mol %) and DMF (10 eq.) in the chosen solvent (6.6 mL) were stirred at room temperature for 15 min before the addition of benzylamine **2a** (55.5 µL, 0.50 mmol) and stirring was maintained for further 24 h.

The results described in Table 2 showed that using DMF only as a reactant in the presence of another co-solvent significantly hindered the *N*-formylation of benzylamine **2a** (Entries1-4). However, using AcOH as a solvent completely inhibited the reaction (Entry 5). As a result, DMF was chosen as a solvent and reactant at the same time (Entry 6).

Optimization of *N*-formylation of glycine amino ester using $HCONH_2$

Table 3. Optimisation of temperature using **1**[a]

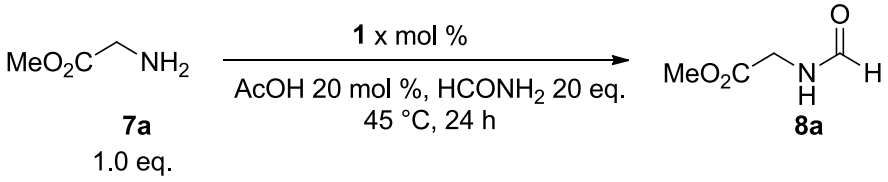


Entry	T (°C)	Isolated Yield (%)
1	65	99
2	45	99
3	20	80

[a] Reaction conditions: Borinic acid **1** (10 mol %) and AcOH (20 mol %) in $HCONH_2$ (20 eq.) were stirred at the specified temperature for 15 min before the addition of glycine methyl ester amine **7a** (40.0 µL, 0.50 mmol) and stirring was maintained for further 24 h.

Taking into account the previous optimal conditions used for the transamidation using DMF (Entry 1), we were able to reduce the temperature to 45 °C without affecting the yield of **8a** (Entry 2). Running the reaction at room temperature provided a lower yield of 80% (Entry 3).

Table 4. Optimisation of catalyst loading of **1**[a]

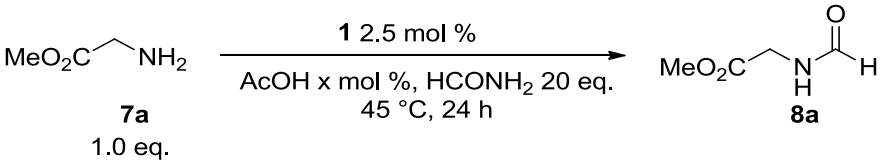


Entry	1 (mol %)	Isolated Yield (%)
1	10	99
2	5	99
3	2.5	99

[a] Reaction conditions: Borinic acid **1** (2.5-10 mol %) and AcOH (20 mol %) in $HCONH_2$ (20 eq.) were stirred at 45 °C for 15 min before the addition of glycine methyl ester amine **7a** (40.0 µL, 0.50 mmol) and stirring was maintained for further 24 h.

As shown by Table 4, a catalyst loading of 10 mol % provided **8a** in an excellent yield (Entry 1). Decreasing the loading of **1** to 5 mol % and even 2.5 mol % had no effect on the yield which remained quantitative (Entries 2 and 3). Thus, 2.5 mol% was chosen as the optimal catalyst loading for the *N*-formylation of α-amino esters using $HCONH_2$.

Table 5. Optimisation of **1**:AcOH ratio[a]

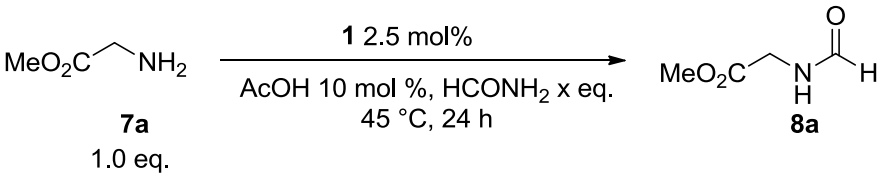


Entry	AcOH (mol %)	Ratio 1 : AcOH	Isolated Yield (%)
1	20	8 : 1	99
2	10	4 : 1	99
3	5	2 : 1	60

[a] Reaction conditions: Borinic acid **1** (2.5 mol %) and AcOH (5-20 mol %) in $HCONH_2$ (20 eq.) were stirred at 45 °C for 15 min before the addition of glycine methyl ester amine **7a** (40.0 µL, 0.50 mmol) and stirring was maintained for further 24 h.

As shown by Table 5, using 10 mol % or 20 mol % of AcOH provided **8a** in quantitative yield (Entries 1 and 2). Decreasing the loading of AcOH down to 05 mol % greatly lowered the yield of the reaction to 60% (Entry 3). Thus, the optimal ratio between AcOH and borinic acid was chosen to be 4 : 1.

Table 6. Optimisation of $HCONH_2$ equivalents using **1**[a]



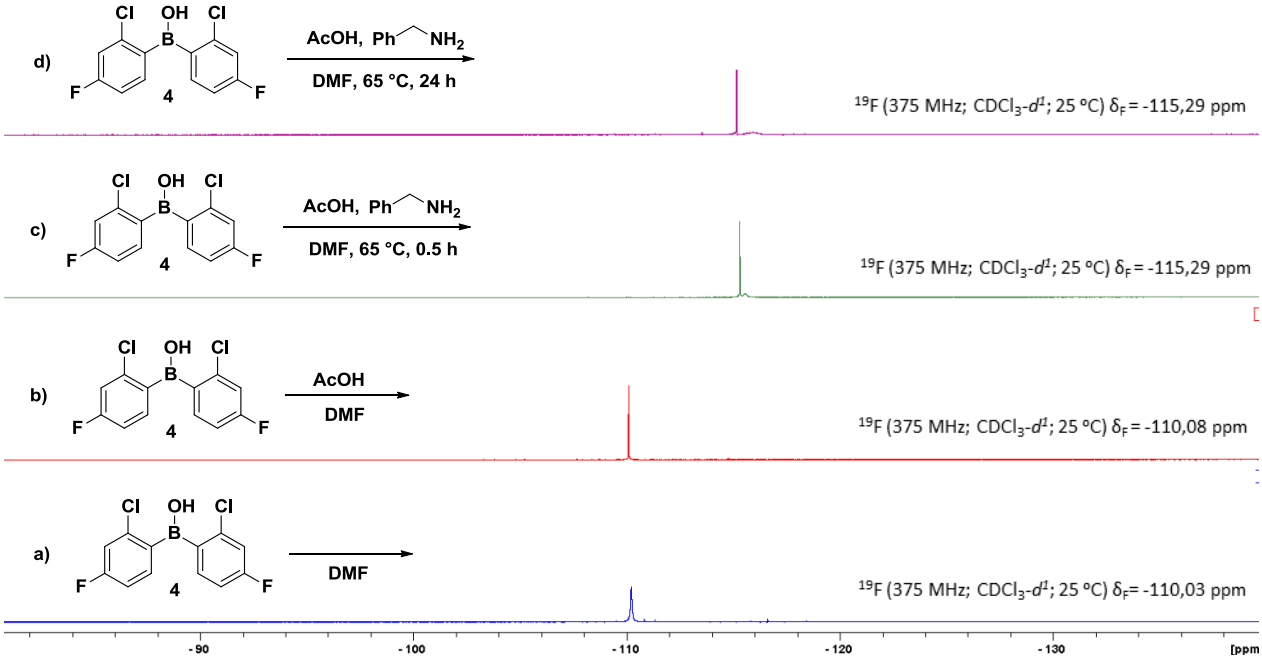
Entry	# eq of $HCONH_2$	Isolated Yield (%)
1	20	99
2	10	99
3	5	99

[a] Reaction conditions: Borinic acid **1** (2.5 mol %) and AcOH (10 mol %) in $HCONH_2$ (x eq.) were stirred at 45 °C for 15 min before the addition of glycine methyl ester amine **7a** (40.0 μL, 0.50 mmol) and stirring was maintained for further 24 h.

As shown by Table 6, the number of $HCONH_2$ equivalents can be decreased down to 5 eq. while providing the same quantitative yield of **8a** (Entries 1-3).

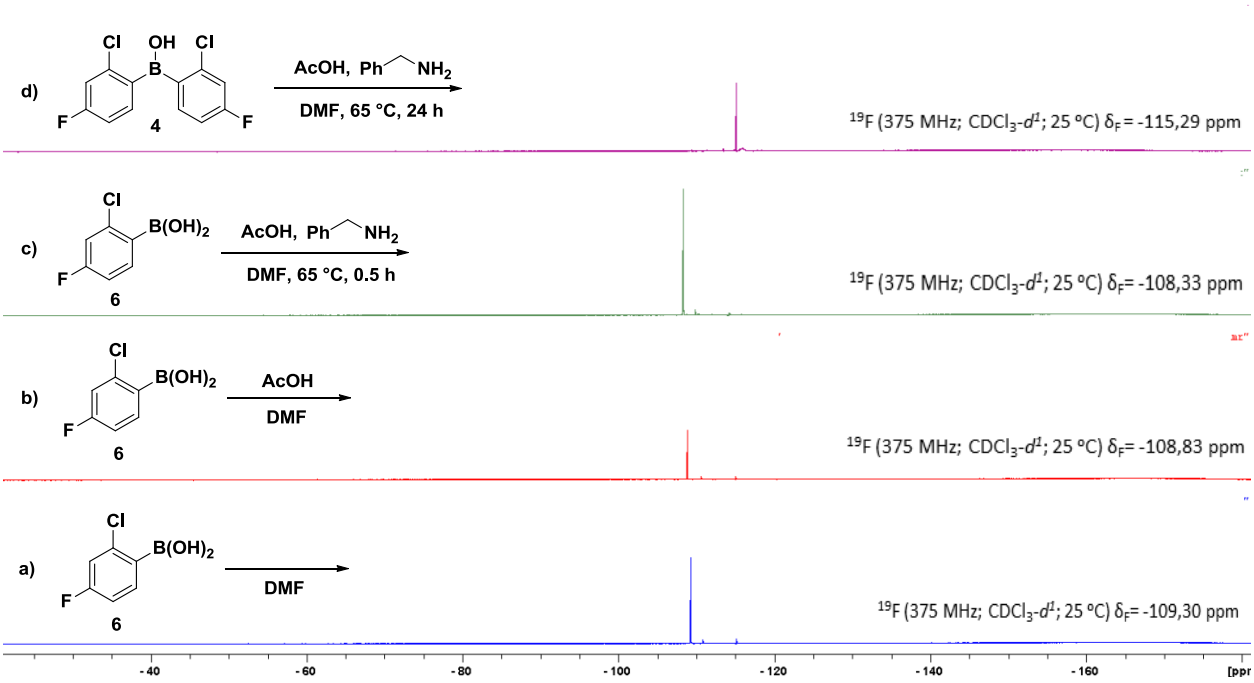
3. Mechanistic Studies

Scheme 1. Monitoring the progress of the reaction using **4** as a ^{19}F probe



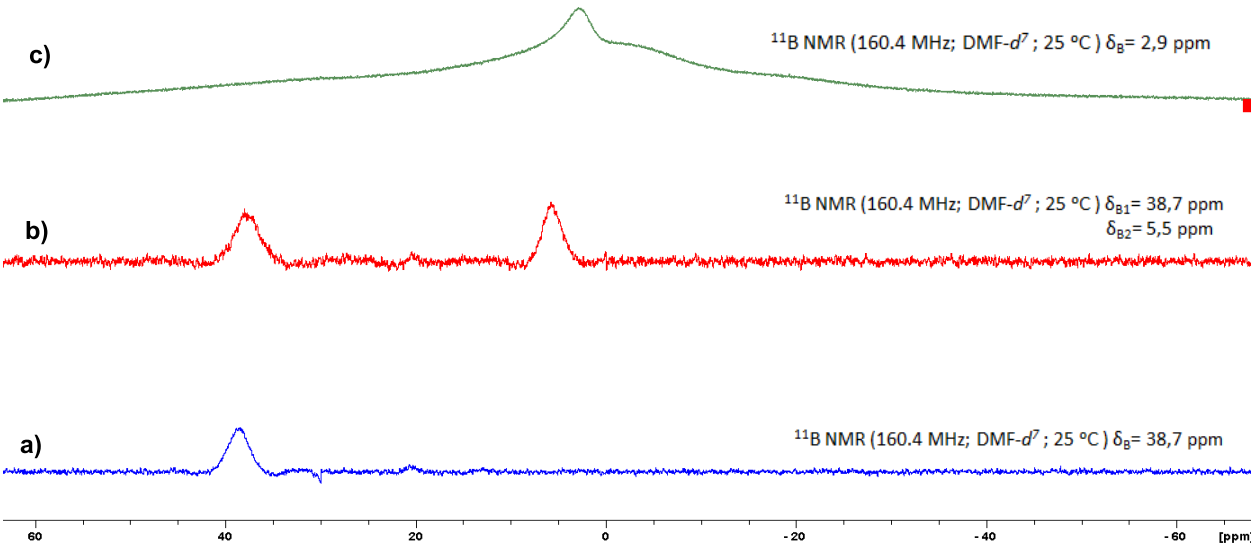
All the reactions were carried out at 65 °C in DMF (1 mL) the presence of 1,3,5-trimethoxybenzene as an internal standard (20 mol %). **(a) 4** (10 mol %). **(b) 4** (10 mol %) with AcOH (20 mol %). **(c) 4** (10 mol %) with AcOH (20 mol %) and benzylamine **2a** (50 mol %) after 30 min. **(d) 4** (10 mol %) with AcOH (20 mol %) and benzylamine **2a** (50 mol %) after 24 h.

Scheme 2. Studying the stability of **4** compared to boronic acid analogue **6**



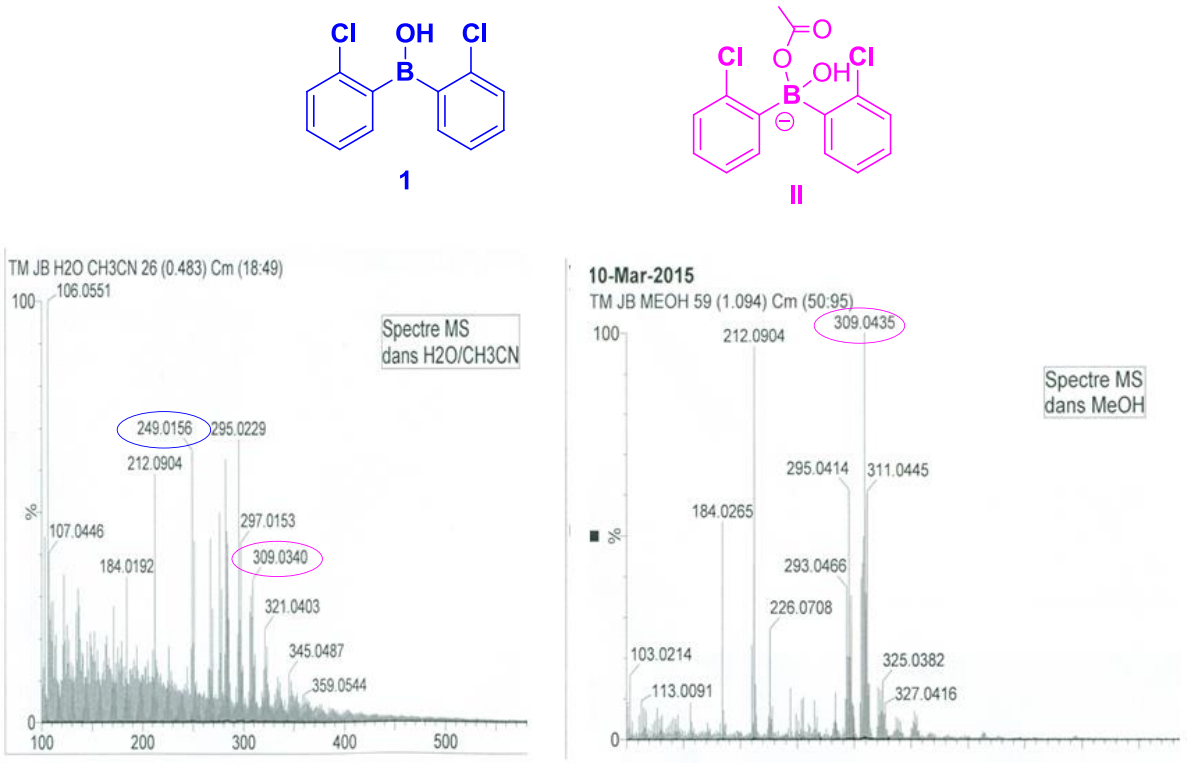
All the reactions were carried out at 65 °C in DMF (1 mL) the presence of 1,3,5-trimethoxybenzene as an internal standard (20 mol %). **(a) 6** (10 mol %). **(b) 6** (10 mol %) with AcOH (20 mol %). **(c) 6** (10 mol %) with AcOH (20 mol %) and benzylamine **2a** (50 mol %) after 24 h. **(d) 4** (10 mol %) with AcOH (20 mol %) and benzylamine **2a** (50 mol %) after 24 h.

Scheme 3. Monitoring the progress of the reaction using ^{11}B NMR of the borinic acid catalyst **1**



All the reactions were carried out in deuterated DMF-d^7 at RT. **(a) 1** alone. **(b) 1** with AcOH (20-40 mol %). **(c) 1** with AcOH (40 mol %) and benzylamine **2a** (50 mol %).

Scheme 4. Monitoring the progress of the reaction using mass spectroscopy

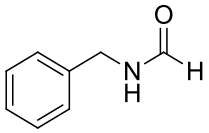


An equimolar mixture of **1** : **II** observed using LRMS (ESI-TOF) m/z: $[M - H]^-$

4. General Procedure A: *N*-Formylation of Amines using DMF

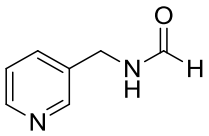
To a round-bottom flask under an argon atmosphere were added 2-chlorophenylborinic acid **1** (12.5 mg, 0.05 mmol, 0.1 equiv.), dry DMF (5 equiv. unless otherwise mentioned) and acetic acid (6 mg, 0.10 mmol, 6 µL, 0.2 equiv.). The mixture was vigorously stirred for 15 min at the given temperature (Table 2 main article) and the amine (0.50 mmol, 1 equiv.) was then slowly added using a gastight syringe. The resulting mixture was stirred for the given time. DMF was removed using Kugelrohr distillation apparatus (55 °C) and the residue was purified by column chromatography to give the title compounds. A sealed-pressure tube was used for the reactions involving low boiling points amines. When diluted conditions were required, 7 mL of dry DMF were used.

Benzylformamide (3a). Known and described.[1] The title compound was prepared according to the general procedure **A** at room temperature for 72 h using benzylamine (55.5 µL, 0.50 mmol). It was purified by column chromatography using CH_2Cl_2/EtOAc (70/30) as the eluent and isolated in the form of a colourless solid (58.2 mg, 0.43 mmol, 86%). Using a temperature of 65 °C provided a higher yield of **3a** within 12 h (67 mg, 0.50 mmol, 99%).



M.p: 62 – 64 °C (*lit*: 63-64).[2] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.37. The product was obtained in the form of 2 rotamers with a ratio of 9:1. The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.15 (br s, 0.9H_{CHO}), 8.07 (d, J = 12.0 Hz, 0.1H_{CHO}), 7.37 – 7.22 (m, 5H_{Ar}), 6.68 (br s, 0.9 H_{NH}), 6.39 (br s, 0.1H_{NH}), 4.41 (d, J = 6.0 Hz, 1.8H_{CH2}), 4.34 (d, J = 6.5 Hz, 0.2H_{CH2}). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.7 ($C{=}O_{\ minor}$), 161.1 ($C{=}O_{\ major}$) 137.6 (Cq_{Ar}), 129.0 ($CH_{Ar\ minor}$), 128.8 ($CH_{Ar\ major}$), 128.0 ($CH_{Ar\ minor}$) 127.8 ($CH_{Ar\ major}$), 127.7 ($CH_{Ar\ major}$), 127.0 ($CH_{Ar\ minor}$), 45.7 ($CH_{2\ minor}$) 42.2 ($CH_{2\ major}$).

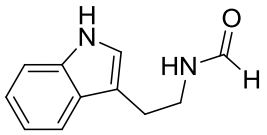
***N*-(Pyridine-2-yl)methylformamide (3b).** The title compound was prepared according to the general procedure **A** at room temperature for 72 h using 2-picolylamine (52 µL, 0.50 mmol). It was purified by column chromatography using CH_2Cl_2/EtOAc (60/40 to 50/50) as the eluent and isolated in the form of a yellow oil (52.4 mg, 0.385 mmol, 77%). Using a temperature of 65 °C provided a higher yield of **3b** within 12 h (67.3 mg, 0.49 mmol, 99%).



[1] R. Fu, Y. Yang, Z. Chen, W. Lai, Y. Ma, R. Yuan, Q. Wang, *Tetrahedron* **2014**, *70*, 9492–9499.
[2] R. Lanigan, R. Starkov, T. Sheppard, *J. Org. Chem.* **2013**, *78*, 4521–4523.

R_f (CH_2Cl_2/EtOAc: 60/40) = 0.10. The product was obtained in the form of 2 rotamers with a ratio of 9:1. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.54 (d, J = 4.8 Hz, 0.1H_{NH}), 8.50 (d, J = 4.3 Hz, 0.9H_{NH}), 8.29 (br s, 1H_{CHO}), 7.65 (td, J = 7.6, 1.5 Hz, 1H_{Ar}), 7.27-7.25 (m, 2H_{Ar}), 7.20-7.17 (m, 1H_{Ar}), 4.58 (d, J = 5.3 Hz, 1.8H_{CH2}), 4.51 (d, J = 6.3 Hz, 0.2H_{CH2}). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 161.2 (C=O), 155.8 (Cq_{Ar}), 148.8 (CH_{Ar}), 136.9 (CH_{Ar}), 122.4 (CH_{Ar}), 122.0 (CH_{Ar}), 42.9 ($CH_{2\ major}$), 29.6 ($CH_{2\ minor}$). υ_{max} (neat)/cm^{-1} 3284, 3012, 2929, 2863, 1663, 1593, 1572, 1531, 1477, 1437, 1385, 1242, 1216. HRMS (ESI$^+$ TOF) m/z: [M + H]$^+$ Calcd for $C_7H_9N_2O^+$: 137.0715; Found: 137.0714.

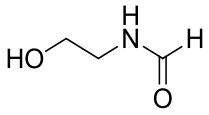
***N*-(2-(1*H*-Indol-3-yl)ethyl)formamide (3c).** The title compound was prepared according to the general procedure **A** at room temperature for 72 h using 2–(1*H*-indol-3-yl)ethanamine (94.1 mg, 0.50 mmol). It was purified by column chromatography using CH_2Cl_2/EtOAc (70/30) as the eluent and isolated in the form of a brown oil (81.0 mg, 0.43 mmol, 86%). Using a temperature of 65 °C provided the same yield of **3c** within 24 h (94.1 mg, 0.50 mmol, 99%).



R_f (CH_2Cl_2/EtOAc: 70/43) = 0.22. The product was obtained in the form of 2 rotamers with a ratio of 8:2. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.65 (br s, 1H_{NHAr}), 7.90 (br s, 0.8H_{CHO}), 7.69 (br d, J = 12.0 Hz, 0.2H_{CHO}), 7.51 (d, J = 7.8 Hz, 0.8H_{Ar}), 7.50-7.47 (m, 0.2H_{Ar}), 7.27 (d, J = 7.8 Hz, 1H_{Ar}), 7.13 (t, J = 7.2 Hz, 1H_{Ar}), 7.06-7.02 (m, 1H_{Ar}), 6.87 (s, 0.8H_{Ar}), 6.83 (s, 0.2H_{Ar}), 5.92 (br s, 1H_{NH}), 3.51 (q, J = 6.1 Hz, 1.5$H_{CH2\text{-}NH}$), 3.34 (q, J = 6.0 Hz, 0.5$H_{CH2\text{-}NH}$), 2.87 (t, J = 6.6 Hz, 1.5$H_{CH2\text{-}CH2\text{-}NH}$), 2.81 (t, J = 6.8 Hz, 0.5$H_{CH2\text{-}CH2\text{-}NH}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.7 (C=O $_{minor}$), 161.5 (C=O $_{major}$), 136.4 ($Cq_{Ar\ minor}$), 136.3 ($Cq_{Ar\ major}$), 127.1 ($Cq_{Ar\ major}$), 126.7 ($Cq_{Ar\ minor}$), 122.8 ($CH_{Ar\ minor}$), 122.3 ($CH_{Ar\ major}$), 122.0 ($CH_{Ar\ minor}$), 121.9 ($CH_{Ar\ major}$), 119.3 ($CH_{Ar\ minor}$), 119.2 ($CH_{Ar\ major}$), 118.4 ($CH_{Ar\ major}$), 118.2 ($CH_{Ar\ minor}$), 112.0 ($Cq_{Ar\ major}$), 111.5 ($CH_{Ar\ minor}$), 111.3 ($CH_{Ar\ major}$), 111.1 (s, $Cq_{Ar\ minor}$), 42.0 ($CH_{2\ minor}$), 38.3 ($CH_{2\ major}$), 27.1 ($CH_{2\ minor}$), 24.9 ($CH_{2\ major}$). υ_{max} (neat)/cm^{-1} 3289, 3059, 3010, 2928, 2872, 1660, 1515, 1457, 1435,

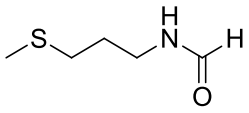
1385, 1339, 1216. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_{11}H_{12}ON_2Na^+$: 211.0847; Found: 211.0849.

***N*-(2-Hydroxyethyl)formamide (3d).** The title compound was prepared according to the general procedure **A** at room temperature for 72 h using 2-amino-ethan-1-ol (30 µL, 0.50 mmol). It was purified by column chromatography using CH_2Cl_2/MeOH (90/10 to 80/20) as the eluent and isolated in the form of a yellow oil (43.8 mg, 0.49 mmol, 98%).



R_f (CH_2Cl_2/MeOH: 80/20) = 0.18. The product was obtained in the form of 2 rotamers with a ratio of 9:1. ^{1}H NMR (400.0 MHz; MeOD-d^4) δ_H = 8.09 (br s, 0.9H$_{CHO}$), 8.01 (br s, 0.1H$_{CHO}$), 3.62 (t, J = 5.7 Hz, 1.6H$_{CH_2\text{-OH}}$), 3.59-3.58 (m, 0.4H$_{CH_2\text{-OH}}$), 3.35 (t, J = 5.6 Hz, 1.6H$_{CH_2\text{-NH}}$), 3.30 (t, J = 5.5 Hz, 0.4H$_{CH_2\text{-NH}}$). ^{13}C NMR (101.6 MHz; MeOD-d^4) δ_C = 167.9 (C=O $_{minor}$), 164.2 (C=O $_{major}$), 62.5 (CH$_2$ $_{minor}$), 61.5 (CH$_2$ $_{major}$), 45.4 (CH$_2$ $_{minor}$), 41.6 (CH$_2$ $_{major}$). υ_{max} (neat)/cm^{-1} 3313, 2940, 2879, 2468, 2387, 1737, 1643, 1536, 1427, 1380, 1228, 1064. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_3H_7NO_2Na^+$: 112.0374; Found: 112.0380.

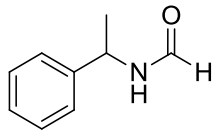
***N*-(3-(Methylthio)propyl)formamide (3e).** The title compound was prepared according to the general procedure **A** at room temperature for 72 h using 3-methylthiopropanamine (56 µL, 0.50 mmol). It was purified by column chromatography using CH_2Cl_2/EtOAc (80/20 to 70/30) as the eluent and isolated in the form of an orange oil (66.3 mg, 0.50 mmol, 99%).



R_f (CH_2Cl_2/EtOAc: 70/30) = 0.15. The product was obtained in the form of 2 rotamers with a ratio of 9:1. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.07 (br s, 0.9H$_{CHO}$), 7.97 (d, J = 12.0 Hz, 0.1H$_{CHO}$), 6.67 (br s, 0.9H$_{NH}$), 6.51 (br s, 0.1H$_{NH}$), 3.31 (q, J = 6.3Hz, 1.8H$_{CH_2\text{-NH}}$), 3.25-3.23 (m,

0.2H$_{CH_2\text{-NH}}$), 2.46 (t, J = 7.0 Hz, 2H$_{CH_2\text{-SMe}}$), 2.02 (s, 3H$_{CH_3}$), 1.79-1.72 (m, 2H$_{CH_2\text{-}CH_2\text{-}CH_2\text{-NH}}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.8 (C=O $_{minor}$), 161.5 (C=O $_{major}$), 40.1 ($CH_{2\ minor}$), 36.9 ($CH_{2\ major}$), 31.2 ($CH_{2\ major}$), 30.5 ($CH_{2\ minor}$), 29.5 ($CH_{2\ minor}$), 28.3 ($CH_{2\ major}$), 15.2 ($CH_{3\ major}$), 15.1 ($CH_{3\ minor}$). υ_{max} (neat)/cm^{-1} 3283, 3055, 2918, 2860, 1658, 1533, 1437, 1384, 1265, 1238, 1174, 1073. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_5H_{11}NONaS^+$: 156.0459; Found: 156.0458.

***N*-(1-Phenylethyl)formamide (3f)**. Known and described.[3] The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using 1-phenylethan-1-amine (65 µL, 0.50 mmol). It was purified by column chromatography using Pentane/EtOAc (90/10 to 60/40) as the eluent and isolated in the form of a yellow oil (73.9 mg, 0.50 mmol, 99%).

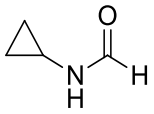


R_f (CH_2Cl_2/EtOAc: 80/20) = 0.68. The product was obtained in the form of 2 rotamers with a ratio of 8:2. The ^{1}H and ^{13}C data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.10 (br s, 0.8H$_{CHO}$), 8.08 (br s, 0.2H$_{CHO}$), 7.31-7.26 (m, 3H$_{Ar}$), 7.25-7.20 (m, 2H$_{Ar}$), 6.00 (br s, 0.2H$_{NH}$), 5.86 (br s, 0.8H$_{NH}$), 5.15 (quin, J = 7.3 Hz, 0.8H$_{CH}$), 4.63 (quin, J = 7.2 Hz, 0.2H$_{CH}$), 1.50 (d, J = 7.0 Hz, 0.6H$_{CH3}$), 1.46 (d, J = 6.9 Hz, 2.4H$_{CH3}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.1 (C=O $_{minor}$), 160.2 (C=O $_{major}$), 142.7 (Cq$_{Ar\ minor}$), 142.5 (Cq$_{Ar\ major}$), 128.9 (CH$_{Ar\ minor}$), 128.7 (CH$_{Ar\ major}$), 127.7 (CH$_{Ar\ minor}$), 127.5 (CH$_{Ar\ major}$), 126.1 (CH$_{Ar\ major}$), 125.7 (CH$_{Ar\ minor}$), 51.6 (CH $_{minor}$), 47.6 (CH $_{major}$), 23.6 ($CH_{3\ minor}$), 21.7 ($CH_{3\ major}$).

***N*-Cyclopropylformamide (3g)**. The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using cyclopropylamine (35 µL, 0.50 mmol) in a

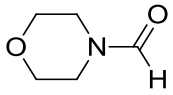
[3] T. Nakamura, K. Tateshi, S. Tsukagoshi, S. Hasimoto, S. Watanabe, V. A. Soloshonok, J. L. Acena, O. Kitagawa, *Tetrahedron* **2012**, *68*, 4013–4017.

sealed-pressure tube. It was purified by column chromatography using CH_2Cl_2/EtOAc (80/20 to 70/30) as the eluent and isolated in the form of a yellow oil (42.2 mg, 0.50 mmol, 99%).



R_f (CH_2Cl_2/EtOAc: 70/30) = 0.28. The product was obtained in the form of 2 rotamers with a ratio of 7:3. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.12 (d, J = 11.9 Hz, 0.3H_{CHO}), 8.00 (br s, 0.7H_{CHO}), 6.97 (br s, 0.7H_{NH}), 6.75 (br s, 0.3H_{NH}), 2.65-2.59 (m, 0.7$H_{CH\text{-}NH}$), 2.58-2.52 (m, 0.3$H_{CH\text{-}NH}$), 0.71-0.62 (m, 2H_{CH_2}), 0.56-0.52 (m, 0.6H_{CH_2}), 0.48-0.44 (m, 1.4H_{CH_2}). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 166.8 (C=O $_{minor}$), 162.8 (C=O $_{major}$), 22.7 (CH $_{minor}$), 21.2 (CH $_{major}$), 6.2 (CH_2 $_{minor}$), 6.0 (CH_2 $_{major}$). υ_{max} (neat)/cm^{-1} 3266, 3016, 2867, 1737, 1651, 1526, 1455, 1385, 1360, 1262, 1200. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_4H_7NONa^+$: 108.0425; Found: 108.0428.

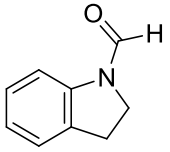
Morpholine-4-carbaldehyde (3h). Known and described.[4] The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 24 h using morpholine (43 µL, 0.50 mmol). It was purified by column chromatography using CH_2Cl_2/EtOAc (80/20 to 70/30) as the eluent and isolated in the form of a yellow oil (51.2 mg, 0.44 mmol, 89%).



R_f (CH_2Cl_2/EtOAc: 70/30) = 0.23. The ^{1}H and ^{13}C data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H 8.02 (br s, 1H_{CHO}), 3.67 (t, J = 4.7 Hz, 2$H_{O\text{-}CH_2\text{-}CH_2\text{-}N}$), 3.63 (t, J = 4.6 Hz, 2$H_{O\text{-}CH_2\text{-}CH_2\text{-}N}$), 3.54 (t, J = 5.1 Hz, 2$H_{O\text{-}CH_2\text{-}CH_2\text{-}N}$), 3.37 (t, J = 5.0 Hz, 2$H_{O\text{-}CH_2\text{-}CH_2\text{-}N}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 160.6 (C=O), 67.0 (CH_2), 66.2 (CH_2), 45.6 (CH_2), 40.4 (CH_2).

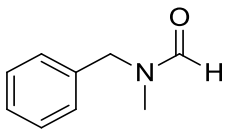
[4] Y. Zhao, S. Cai, J. Li, D. Zhigang, *Tetrahedron* **2013**, *69*, 8129–8131.

1-*H*-Indole-1-carbaldehyde (3i). The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 24 h using indole (56 µL, 0.50 mmol). It was purified by column chromatography using CH_2Cl_2/EtOAc (90/10) as the eluent and isolated in the form of a brown oil (70.6 mg, 0.48 mmol, 96%).



R_f (CH_2Cl_2/EtOAc: 90/10) = 0.26. The product was obtained in the form of 2 rotamers with a ratio of 8:2. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 9.03 (br s, 0.8H_{CHO}), 8.61 (br s, 0.2H_{CHO}), 7.36-7.25 (m, 3H_{Ar}), 7.17-7.13 (m, 1H_{Ar}), 4.21 (t, J = 8.4 Hz, 0.5$H_{CH_2\text{-}CH_2\text{-}N}$), 4.16 (td, J = 8.5, 0.9 Hz, 1.5$H_{CH_2\text{-}CH_2\text{-}N}$), 3.31-3.29 (m, 0.4$H_{CH_2\text{-}CH_2\text{-}N}$), 3.25 (m, 1.6$H_{CH_2\text{-}CH_2\text{-}N}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 159.3 (C=O $_{minor}$), 157.6 (C=O $_{major}$), 141.0 (Cq_{Ar}), 131.9 (Cq_{Ar}), 127.58 ($CH_{Ar\ minor}$), 127.57 ($CH_{Ar\ major}$), 126.0 ($CH_{Ar\ major}$), 124.8 ($CH_{Ar\ minor}$), 124.6 ($CH_{Ar\ minor}$), 124.3 ($CH_{Ar\ major}$), 116.7 ($CH_{Ar\ minor}$), 109.4 ($CH_{Ar\ major}$), 47.0 ($CH_{2\ minor}$), 44.6 ($CH_{2\ major}$), 27.7 ($CH_{2\ major}$), 27.2 ($CH_{2\ minor}$). υ_{max} (neat)/cm^{-1} 2918, 2851, 1668, 1595, 1494, 1463, 1405, 1363, 1338, 1293, 1267, 1173. HRMS (ESI$^+$ TOF) m/z: $[M + Na]^+$ Calcd for $C_9H_9NONa^+$: 170.0590; Found: 170.0582.

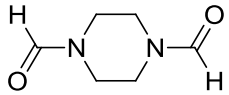
***N*-Benzyl-*N*-methylformamide (3j).** Known and described.[5] The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using *N*-methyl-1-phenylmethanamine (65 µL, 0.50 mmol). It was purified by column chromatography using pentane/EtOAc (80/20) as the eluent and isolated in the form of a yellow oil (74.4 mg, 0.50 mmol, 99%).



[5] L. Zhang, Z. Han, X. Zhao, Z. Wang, K. Ding, *Angew. Chem. Int. Ed*. **2015**, *54*, 6186–6189.

R_f (Pentane/EtOAc: 80/20) = 0.13. The product was obtained in the form of 2 rotamers with a ratio of 6:4. The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.21 (br s, $0.6H_{CHO}$), 8.08 (br s, $0.4H_{CHO}$), 7.32-7.22 (m, $3H_{Ar}$), 7.20-7.12 (m, $2H_{Ar}$), 4.44 (s, $0.8H_{CH_2}$), 4.31 (s, $1.2H_{CH_2}$), 2.76 (s, 1.2H, CH_3), 2.70 (s, 1.8H, CH_3). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 162.6 ($C{=}O_{\text{major}}$), 162.4 ($C{=}O_{\text{minor}}$), 135.8 ($Cq_{Ar\ \text{minor}}$), 135.5 ($Cq_{Ar\ \text{major}}$), 128.6 ($CH_{Ar\ \text{major}}$), 128.4 ($CH_{Ar\ \text{minor}}$), 128.0 ($CH_{Ar\ \text{major}}$), 127.8 ($CH_{Ar\ \text{minor}}$), 127.4 ($CH_{Ar\ \text{minor}}$), 127.2 ($CH_{Ar\ \text{major}}$), 53.2 ($CH_{2\ \text{major}}$), 47.5 ($CH_{2\ \text{minor}}$), 33.8 ($CH_{3\ \text{major}}$), 29.2 ($CH_{3\ \text{minor}}$).

Piperazine-1,4-carbaldehyde (3k). The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using piperazine (43.1 mg, 0.50 mmol) under the diluted conditions, purified by column chromatography using CH_2Cl_2/MeOH (90/10) and isolated in the form of a yellow oil (68.0 mg, 0.48 mmol, 96%).

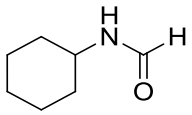


R_f (CH_2Cl_2/MeOH: 90/10) = 0.49. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.03 (br s, $2H_{CHO}$), 3.54-3.52 (m, $2H_{CH_2}$), 3.47 (s, $2H_{CH_2}$), 3.37 (s, $2H_{CH_2}$), 3.34-3.31 (m, $2H_{CH_2}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 160.8 (C=O), 160.6 (C=O), 45.8 (CH_2), 44.7 (CH_2), 40.2 (CH_2), 39.2 (CH_2). υ_{max} (neat)/cm^{-1} 3569, 2927, 2871, 2244, 1651, 1432, 1396, 1357, 1277, 1253, 1208, 1182, 1167. HRMS (ESI^+ TOF) m/z: $[M + Na]^+$ Calcd for $C_6H_{10}N_2O_2Na^+$: 165.0640; Found: 165.0647.

***N*-Cyclohexylformamide (3l).** Known and described.[6] The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using cyclohexylamine (57 µL, 0.50 mmol) under the diluted conditions. It was purified by column chromatography

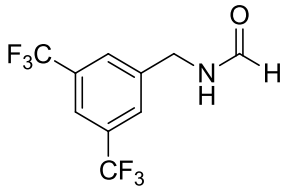
[6] O. Saidi, M. J. Bamford, A. J. Blacker, J. Lynch, S. P. Marsden, P. Plucinski, R. J. Watson, J. M. J. Williams, *Tetrahedron Lett.* **2010**, *51*, 5804–5806.

using CH_2Cl_2/EtOAc (90/10 to 80/20) as the eluent and isolated in the form of a yellow oil (61.3 mg, 0.48 mmol, 97%).



R_f (CH_2Cl_2/EtOAc: 80/20) = 0.26. The product was obtained in the form of 2 rotamers with a ratio of 8:2. The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.06 (br s, 0.2H_{CHO}), 8.02 (br s, 0.8H_{CHO}), 6.24 (br s, 0.2H_{NH}), 6.11 (br s, 0.8H_{NH}), 3.82-3.73 (m, 0.8H_{CH}), 3.25-3.23 (m, 0.2H_{CH}), 1.89-1.81 (m, 2H_{CH_2}), 1.68-1.63 (m, 2H_{CH_2}), 1.57-1.54 (m, 1H_{CH_2}), 1.34-1.24 (m, 2H_{CH_2}), 1.21-1.08 (m, 3H_{CH_2}). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 160.5 (C=O), 51.0 (CH), 47.0 (CH_2), 34.6 (CH_2), 32.9 (CH_2), 25.4 (CH_2), 24.7 (CH_2).

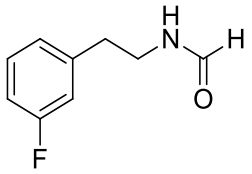
***N*-(3,5-bis(Trifluoromethyl)benzyl)formamide (3m).** The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using 3,5-bis(trifluoromethyl)-phenylmethanamine (122 mg, 0.50 mmol) under the diluted conditions. It was purified by column chromatography using CH_2Cl_2/EtOAc (70/30) as the eluent and isolated in the form of a colorless oil (135.4 mg, 0.50 mmol, 99%).



R_f (CH_2Cl_2/EtOAc: 70/30) = 0.42. The product was obtained in the form of 2 rotamers with a ratio of 9.5:0.5. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.25 (br s, 1H_{CHO}), 7.76 (s, 1H_{Ar}), 7.72 (s, 2H_{Ar}), 7.09 (br s, 1H_{NH}), 4.54 (d, J = 6.3 Hz, 2H_{CH_2}). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.8 (C=O $_{minor}$) 161.6 (C=O $_{major}$) 140.4 (Cq_{Ar}) 131.9 (q, $J_{C\text{-}F}$ = 33.4 Hz, Cq_{CF_3}) 127.6 (d, $J_{C\text{-}F}$ = 2.6 Hz, CH_{Ar}) 123.1 (d, $J_{C\text{-}F}$ = 272.8 Hz, Cq_F) 121.4 (quin, $J_{C\text{-}F}$ = 15.2 Hz, $CH_{Ar\ major}$) 119.0 ($CH_{Ar\ minor}$) 44.8 ($CH_{2\ minor}$) 41.1 ($CH_{2\ major}$). ^{19}F NMR (375 MHz; $CDCl_3$-d^1) δ_F = -62.9 (s). υ_{max}

(neat)/cm^{-1} 3287, 3054, 2877, 1662, 1529, 1381, 1351, 1274, 1167, 1120. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_{10}H_7NONa\ F_6^+$: 294.0330; Found: 294.0343.

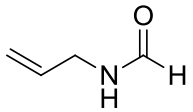
***N*-(3-Fluorophenethyl)formamide (3n).** The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using 2-(3-fluorophenyl)ethan-1-amine (65 µL, 0.50 mmol) under the diluted conditions. It was purified by column chromatography using CH_2Cl_2/EtOAc (70/30) as the eluent and isolated in the form of a colorless oil (82.1 mg, 0.49 mmol, 98%).



R_f (CH_2Cl_2/EtOAc: 70/30) = 0.25. The product was obtained in the form of 2 rotamers with a ratio of 9:1. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.05 (br s, 0.9H$_{CHO}$), 7.82 (d, J = 11.8 Hz, 0.1H$_{CHO}$), 7.23 (dd, J = 12.2, 5.5 Hz, 1H$_{Ar}$), 6.94 (d, J = 5.5 Hz, 1H$_{Ar}$), 6.90-6.86 (m, 2H$_{Ar}$), 6.20 (br s, 1H$_{NH}$), 3.50 (q, J = 6.8 Hz, 1.7H$_{CH_2\text{-}CH_2\text{-}NH}$), 3.42 (q, J = 6.7 Hz, 0.3H$_{CH_2\text{-}CH_2\text{-}NH}$), 2.79 (t, J = 7.0 Hz, 2H$_{CH_2\text{-}CH_2\text{-}NH}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.5 (C=O $_{minor}$), 162.8 (*d*, $J_{C\text{-}F}$ = 246.0 Hz, Cq$_{ArF}$), 161.3 (C=O $_{major}$), 141.0 (d, $J_{C\text{-}F}$ = 7.4 Hz, Cq$_{Ar\ major}$), 140.1 (d, $J_{C\text{-}F}$ = 7.2 Hz, Cq$_{Ar\ minor}$), 130.2 (d, $J_{C\text{-}F}$ = 8.3 Hz, CH$_{Ar\ minor}$), 130.0 (d, $J_{C\text{-}F}$ = 8.3 Hz, CH$_{Ar\ major}$), 124.5 (d, $J_{C\text{-}F}$ = 2.8 Hz, CH$_{Ar\ minor}$), 124.3 (d, $J_{C\text{-}F}$ = 2.8 Hz, CH$_{Ar\ major}$), 115.6 (d, $J_{C\text{-}F}$ = 21.1 Hz, CH$_{Ar\ minor}$), 115.48 (d, $J_{C\text{-}F}$ = 21.1 Hz, CH$_{Ar\ major}$), 113.7 (d, $J_{C\text{-}F}$ = 20.9 Hz, CH$_{Ar\ minor}$), 113.4 (d, $J_{C\text{-}F}$ = 21.1 Hz, CH$_{Ar\ major}$), 42.8 (CH$_{2\ minor}$), 38.9 (CH$_{2\ major}$), 37.2 (d, $J_{C\text{-}F}$ = 1.6 Hz, CH$_{2\ minor}$), 35.1 (d, $J_{C\text{-}F}$ = 1.6 Hz, CH$_{2\ major}$). ^{19}F NMR (375 MHz; $CDCl_3$-d^1) δ_F = -113.0 (s). υ_{max} (neat)/cm^{-1} 3281, 3056, 2936, 2866, 1657, 1616, 1588, 1488, 1449, 1383, 1250, 1140. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_9H_{10}NOFNa^+$: 190.0644; Found: 190.0654.

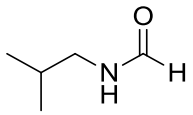
***N*-Allylformamide (3o).** The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 24 h using allylamine (96 µL, 0.50 mmol) under the diluted

conditions in a sealed-pressure tube. It was purified by column chromatography using CH_2Cl_2/EtOAc (90/10 to 70/30) as the eluent and isolated in the form of a colorless oil (42.6 mg, 0.50 mmol, 99%).



R_f (CH_2Cl_2/EtOAc: 90/10) = 0.11. The product was obtained in the form of 2 rotamers with a ratio of 9:1. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.12 (br s, 0.9H$_{CHO}$), 7.95 (d, J = 12.0 Hz, 0.1H$_{CHO}$), 6.68 (br s, 0.9H$_{NH}$), 6.38 (br s, 0.1H$_{NH}$), 5.83-5.70 (m, 1H$_{CH\text{-}CH_2\text{-}NH}$), 5.20-5.14 (m, 0.2H$_{(CH)_2\text{-}C=CH}$), 5.17-5.07 (m, 1.8H$_{(CH)_2\text{-}C=CH}$), 3.83 (t, J = 5.7 Hz, 1.8H$_{CH_2\text{-}NH}$), 3.79-3.76 (m, 0.2H$_{CH_2\text{-}NH}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.9 (C=O $_{minor}$), 161.3 (C=O $_{major}$), 134.2 (CH $_{minor}$), 133.4 (CH $_{major}$), 116.6 (CH $_{minor}$), 116.3 (CH $_{major}$), 43.8 (CH_2 $_{minor}$), 40.2 (CH_2 $_{major}$). υ_{max} (neat)/cm^{-1} 3284, 3055, 2924, 2867, 1658, 1644, 1532, 1421, 1383, 1338, 1232, 1145. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_4H_7NONa^+$: 108.0425; Found: 108.0429.

***N*-Isobutylformamide (3p).** Known and described.[7] The title compound was prepared according to the general procedure **B** at a temperature of 65 °C for 12 h using isobutylamine (50 µL, 0.50 mmol) under the diluted conditions in a sealed-pressure tube. It was purified by column chromatography using CH_2Cl_2/EtOAc (80/20) as the eluent and isolated in the form of a colorless oil (49.9 mg, 0.49 mmol, 99%).

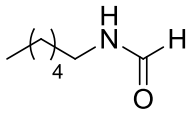


R_f (CH_2Cl_2/EtOAc: 80/20) = 0.21. The product was obtained in the form of 2 rotamers with a ratio of 9:1. The ^{1}H and ^{13}C data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.01 (br s, 0.9H$_{CHO}$), 7.84 (d, J = 11.9 Hz, 0.1H$_{CHO}$), 7.05 (br s,

[7] A. P. Johnson, R. W. A. Luke, A. N. Boa, *J. Chem. Soc., Perkin Trans.1* **1996**, *1*, 895–905.

1H_{NH}), 2.94 (t, *J* = 6.5 Hz, 1.6H_{CH2}), 2.87 (t, *J* = 6.5 Hz, 0.4H_{CH2}), 1.70-1.56 (m, 1H_{CH}), 0.79 (d, *J* = 6.8 Hz, 2 x 3H_{CH3}). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 165.0 (C=O $_{minor}$), 161.5 (C=O $_{major}$), 49.1 ($CH_{2\ minor}$), 45.1 ($CH_{2\ major}$), 29.2 (CH $_{minor}$), 28.0 (CH $_{major}$), 19.7 ($CH_{3\ major}$), 19.2 ($CH_{3\ minor}$).

***N*-Hexylformamide (3q).** Known and described.[8] The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 12 h using hexylamine (66 µL, 0.50 mmol) under the diluted conditions. It was purified by column chromatography using CH_2Cl_2/EtOAc (70/30) as the eluent and isolated in the form of a yellow oil (63.2 mg, 0.49 mmol, 98%).



R_f (CH_2Cl_2/EtOAc: 70/30) = 0.42. The product was obtained in the form of 2 rotamers with a ratio of 8:2. The ^{1}H and ^{13}C data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.16 (br s, 0.8H_{CHO}), 8.04 (d, *J* = 12.0 Hz, 0.2 H_{CHO}), 5.60 (br s, 1H_{NH}), 3.30 (q, *J* = 6.9 Hz, 1.5$H_{CH2\text{-}NH}$), 3.21 (q, *J* = 6.8 Hz, 0.5$H_{CH2\text{-}NH}$), 1.52 (qiun, *J* = 7.2 Hz, 2$H_{CH2\text{-}CH2\text{-}NH}$), 1.30 (s, 3 x 2$H_{CH2}$), 0.89 (t, *J* = 6.7 Hz, 3H_{CH3}). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 164.8 (C=O $_{minor}$), 161.3 (C=O $_{major}$), 41.8 ($CH_{2\ minor}$), 38.1 ($CH_{2\ major}$), 31.3 ($CH_{2\ major}$), 31.2 ($CH_{2\ minor}$), 31.0 ($CH_{2\ minor}$), 29.3 ($CH_{2\ major}$), 26.4 ($CH_{2\ major}$), 25.9 ($CH_{2\ minor}$), 22.41 ($CH_{2\ major}$), 22.38 ($CH_{2\ minor}$), 13.9 ($CH_{3\ major}$), 13.8 ($CH_{3\ minor}$).

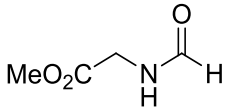
6. General Procedure B: *N*-formylation of α-amino esters using $HCONH_2$

To a sealed tube was added 2-chlorophenylborinic acid **1** (3 mg, 0.0125 mmol, 0.025 equiv.), $HCONH_2$ (0.10 mL, 2.5 mmol, 5 equiv.) and acetic acid (3 mg, 0.05 mmol, 3 µL, 0.1 equiv.). The mixture was vigorously stirred for 15 min at 45 °C and the α-amino ester amine (0.50 mmol, 1 equiv.) was then slowly added using a gastight syringe. The resulting mixture was stirred for a

[8] N. Ortega, C. Richter, F. Glorius, *Org. Lett.* **2013**, *15*, 1776–1779.

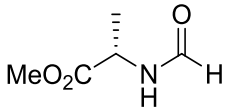
further 24 h. The reaction mixture was directly purified using column chromatography using CH_2Cl_2/EtOAc (90/10 to 80/20 and 70/30) as the eluent, unless otherwise stated, to yield the corresponding title compounds in good to excellent yields. It should be noted that the density of each free amine was determined prior to its addition and the volume was accordingly calculated.

Methyl-*N*-formyl-glycinate (8a). The title compound was prepared according to the general procedure **B** using glycine methyl ester (40 µL, 0.50 mmol) and isolated in the form of a yellow oil (58.2 mg, 0.50 mmol, 99%).



R_f (CH_2Cl_2/EtOAc: 70/30) = 0.26. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.23 (s, $1H_{CHO}$), 6.45 (br s, $1H_{NH}$), 4.08 (d, J = 5.4 Hz, $2H_{CH2}$), 3.75 (s, $3H_{OCH3}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 169.9 ($C{=}O_{ester}$), 161.2 (C=O), 52.4 (CH_3), 39.7 (CH_2). υ_{max} (neat)/cm^{-1} 3316, 3054, 2957, 2251, 1745, 1662, 1521, 1439, 1385, 1370, 1207, 1183, 1008. HRMS (ESI$^+$ TOF) m/z: [M + Na]$^+$ Calcd for $C_4H_7NO_3Na^+$: 140.0324; Found: 140.0327.

(*S*)-Methyl-*N*-formyl-alinate (8b). Known and described.[9] The title compound was prepared according to the general procedure **B** using of (*S*)-alanine methyl ester (54 µL, 0.50 mmol) and isolated in the form of a brown oil (65.6 mg, 0.50 mmol, 99%, *ee*: 94%).

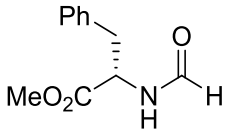


$[\alpha]_D^{25}$ - 53.1° (*c* 0.6, EtOH), $[\alpha]_D^{25}$ (*lit*) - 54.4° (*c* 0.6, EtOH).[10] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.21. The ^{1}H and ^{13}C data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz;

[9] M. Suchý, A. A. H. Elmehriki, R. H. E. Hudson, *Org. Lett.* **2011**, *13*, 3952–3955.
[10] T. V. Q. Nguyen, W.-J. Yoo, S. Kobayashi, *Angew. Chem.* **2015**, *127*, 9341 – 9344.

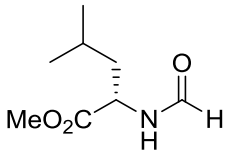
$CDCl_3$-d^1) δ_H = 8.14 (br s, $1H_{CHO}$), 6.63 (br s, $1H_{NH}$), 4.63 (q, *J* = 7.2 Hz, $1H_{CH}$), 3.72 (s, $3H_{OCH_3}$), 1.40 (d, *J* = 7.2 Hz, $3H_{CH_3}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 172.9 (C=O), 160.5 (C=O), 52.4 (CH_3), 46.6 (CH), 18.2 (CH_3).

(*S*)-Methyl-*N*-formyl-phenylalinate (8c). Known and described.[11] The title compound was prepared according to the general procedure **B** using of (*S*)-phenylalanine methyl ester (82 µL, 0.50 mmol) and isolated in the form of a colorless oil (101.9 mg, 0.49 mmol, 98%, *ee*: 92%).



$[\alpha]_D^{25}$ + 82.3° (*c* 2.0, EtOH), $[\alpha]_D^{25}$ (*lit*) + 86.1° (*c* 2.0, EtOH).[12] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.38. The ^{1}H and ^{13}C data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.11 (br s, $1H_{CHO}$), 7.30-7.22 (m, $3H_{Ar}$), 7.11-7.09 (m, $2H_{Ar}$), 6.39 (d, *J* = 6.3 Hz, $1H_{NH}$), 4.94 (q, *J* = 7.6 Hz, $1H_{CH\text{-}CH_2}$), 3.72 (s, $3H_{OCH_3}$), 3.15 (dd, *J* = 13.9, 6.6 Hz, $1H_{CH\text{-}CH_2}$), 3.09 (dd, *J* = 13.9, 5.6 Hz, $1H_{CH\text{-}CH_2}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 171.5 ($C{=}O_{ester}$), 160.6 (C=O), 135.4 (Cq_{Ar}), 129.1, (CH_{Ar}), 128.5 (CH_{Ar}), 127.1 (CH_{Ar}), 52.3 (CH_3), 51.7 (CH), 37.5 (CH_2).

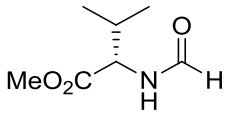
(*S*)-Methyl-*N*-formyl-leucinate (8d). The title compound was prepared according to the general procedure **B** using of (*S*)-leucine methyl ester (72 µL, 0.50 mmol) and isolated in the form of a yellow oil (83.9 mg, 0.484 mmol, 97%).



[11] D. W. Carney, J. V. Truong, J. K. Sello, *J. Org. Chem.*, **2011**, *76*, 10278–10285.
[12] J.-G. Kim, D. O. Jang, *Synlett* **2010**, 1231–1234

$[\alpha]_D^{25}$ + 4.2° (*c* 1.0, $CHCl_3$), $[\alpha]_D^{25}$ (*lit*) + 4.1° (*c* 1.0, $CHCl_3$).[13] R_f (CH_2Cl_2/EtOAc: 90/10) = 0.26. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.18 (br s, $1H_{CHO}$), 6.46 (br s, $1H_{NH}$), 4.69 (td, *J* = 8.8, 4.5 Hz, $1H_{CH_2\text{-}CH\text{-}NH}$), 3.71 (s, $3H_{OCH_3}$), 1.66-1.58 (m, $2H_{CH_2\text{-}CH\text{-}NH}$), 1.56-1.51 (m, $1H_{(CH_3)_2CH}$), 0.92 (m, 2 x $3H_{CH_3}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 173.1 ($C{=}O_{ester}$), 160.8 (C=O), 52.3 (CH_3), 49.2 (CH), 41.4 (CH_2), 24.7 (CH), 22.6 (CH_3), 21.7 (CH_3). υ_{max} (neat)/cm^{-1} 2924, 2957, 1744, 1661, 1531, 1437, 1384, 1076. HRMS (ESI^+ TOF) m/z: $[M + Na]^+$ Calcd for $C_8H_{15}NO_3Na^+$: 196.0950; Found: 196.0954.

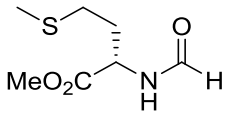
(*S*)-Methyl-*N*-formyl-valinate (8e). The title compound was prepared according to the general procedure **B** using of (*S*)-valine methyl ester (70 µL, 0.50 mmol) and isolated in the form of a yellow oil (76.7 mg, 0.48 mmol, 96%, *ee*> 99%).



$[\alpha]_D^{25}$ + 22.2° (*c* 1.0, $CHCl_3$), $[\alpha]_D^{25}$ (*lit*) + 28.2° (*c* 1.0, $CHCl_3$).[14] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.33. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.21 (br s, $1H_{CHO}$), 6.64 (d, *J* = 5.5 Hz, $1H_{NH}$), 4.60 (dd, *J* = 9.0, 4.9 Hz, $1H_{CH_2\text{-}CH\text{-}NH}$), 3.70 (s, $3H_{OCH_3}$), 2.19-2.11- (m, $1H_{(CH_3)_2CH}$), 0.92 (d, *J* = 6.8 Hz, $3H_{CH_3}$), 0.87 (d, *J* = 6.8 Hz, $3H_{CH_3}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 172.1 ($C{=}O_{ester}$), 161.1 (C=O), 55.5 (CH), 52.1 (CH_3), 31.0 (CH), 18.8 (CH_3), 17.5 (CH_3). υ_{max} (neat)/cm^{-1} 3303, 2968, 2877, 2251, 1739, 1662, 1520, 1466, 1437, 1384, 1372, 1268, 1182, 1138. HRMS (ESI^+ TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}NO_3Na^+$: 182.0793; Found: 182.0803.

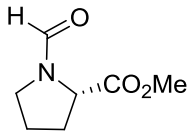
[13] A. Karim, A. Mortreux, F. Petit, G. Buono, G. Pfeiffer, C. Siv, *J. Organomet. Chem*. **1986**, *317*, 93–104.
[14] M. Aitali, S. Allaoud, A. Karim, C. Meliet, A. Mortreux, *Tetrahedron: Asymmetry* **2000**, *11*, 1367–1374.

(*S*)-Methyl-*N*-formylmethioninate (8f). Known and described.[9] The title compound was prepared according to the general procedure **B** using of (*S*)-methionine methyl ester (75 µL, 0.50 mmol) and isolated in the form of a yellow oil (87.1 mg, 0.456 mmol, 91%, *ee*: 90%).



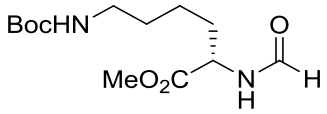
$[\alpha]_D^{25}$ + 39.4° (*c* 1.0, $CHCl_3$), $[\alpha]_D^{25}$ (*lit*) + 38.8° (*c* 1.0, $CHCl_3$).[9] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.54. The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; $CDCl_3$-*d*^{1}) δ_H = 8.17 (s, 1H_{CHO}), 6.85 (d, *J* = 6.4 Hz, 1H_{NH}), 4.76-4.71 (m, 1$H_{CH_2\text{-}CH\text{-}NH}$), 3.71 (s, 3$H_{OCH_3}$), 2.47 (t, *J* = 7.5 Hz, 2$H_{SMe\text{-}CH_2\text{-}CH_2\text{-}CH}$), 2.17-2.08 (m, 1$H_{SMe\text{-}CH_2\text{-}CH_2\text{-}CH}$), 2.04 (s, 3$H_{SCH_3}$), 2.0-1.93 (m, 1$H_{CH_2\text{-}CH_2\text{-}CH}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-*d*^{1}) δ_C = 172.0 ($C{=}O_{ester}$), 161.0 (C=O), 52.5 (CH_3), 49.9 (CH), 31.3 (CH_2), 29.7 (CH_2), 15.2 (CH_3).

(*S*)-Methyl-*N*-formylprolinate (8g). Known and described.[9] The title compound was prepared according to the general procedure **B** using of (*S*)-proline methyl ester (60 µL, 0.50 mmol) and isolated in the form of a yellow oil (78.2 mg, 0.50 mmol, 99%).



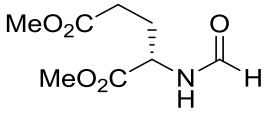
$[\alpha]_D^{25}$ – 109.7° (*c* 1.0, $CHCl_3$), $[\alpha]_D^{25}$ (*lit*) -89.5° (*c* 1.0, $CHCl_3$).[9] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.32. The product was obtained in the form of 2 rotamers with a ratio of 6:4. The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; $CDCl_3$-*d*^{1}) δ_H = 8.22 (br s, 0.6H_{CHO}), 8.18 (br s, 0.4H_{CHO}), 4.40-4.38 (m, 1H_{CH}) 3.70 (s, 1.2H_{OCH_3}), 3.67 (s, 1.8H_{OCH_3}) 3.63-3.53 (m, 1$H_{CH_2\text{-}N}$), 3.48-3.45 (m, 1$H_{CH_2\text{-}N}$), 2.24-2.13 (m, 2$H_{CH_2\text{-}CH_2\text{-}CH}$), 2.00-1.85 (m, 2$H_{CH_2\text{-}CH_2\text{-}CH}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-*d*^{1}) δ_C = 172.0 ($C{=}O_{ester\ minor}$), 171.9 ($C{=}O_{ester\ major}$), 161.4 ($C{=}O_{minor}$), 160.6 (s, $C{=}O_{major}$), 58.4 (CH_{major}), 56.2 (CH_{minor}), 52.5 ($CH_{3\ minor}$), 52.1 ($CH_{3\ major}$), 46.1 ($CH_{2\ major}$), 43.7 ($CH_{2\ minor}$), 29.4 ($CH_{2\ minor}$), 29.2 ($CH_{2\ major}$), 23.8 ($CH_{2\ major}$), 22.6 ($CH_{2\ minor}$).

(*S*)-Methyl-N^6-Boc-*N*-formyllysinate (8h). Known and described.[9] The title compound was prepared according to the general procedure **B** using of (*S*)-lysine methyl ester (130.2 mg, 0.50 mmol) and isolated in the form of a yellow oil (143.8 mg, 0.50 mmol, 99%).



$[\alpha]_D^{25}$ + 10.2° (*c* 1.0, $CHCl_3$), $[\alpha]_D^{25}$ (*lit*) + 12.6° (*c* 1.0, $CHCl_3$).[9] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.20. The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.18 (br s, $1H_{CHO}$), 6.70 (d, *J* = 6.1 Hz, $1H_{NH}$), 4.72 (t, *J* = 5.3 Hz, $1H_{Boc\text{-}NH}$), 4.63-4.58 (m, $1H_{CH_2\text{-}CH\text{-}NH}$), 3.72 (s, $3H_{OCH_3}$), 3.08-3.06 (m, $2H_{BocNH\text{-}CH_2\text{-}CH_2}$), 1.90-1.82 (m, $1H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$), 1.75-1.65 (m, $1H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$), 1.52-1.44 (m, $2H_{BocNH\text{-}\ CH_2\text{-}CH_2\text{-}CH_2}$), 1.40 (s, $9H_{(CH_3)_3C=O}$), 1.36-1.30 (m, $2H_{BocNH\text{-}CH_2\text{-}CH_2\text{-}CH_2}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C =172.4 ($C{=}O_{ester}$), 160.9 (C=O), 156.2 ($C{=}O_{Boc}$), 79.1 (Cq), 52.4 (CH_3), 50.6 (CH), 39.6 (CH_2), 31.4 (CH_2), 29.4 (CH_2), 28.3 (CH_3), 22.1 (CH_2).

(*S*)-Dimethyl-*N*-formylglutamate (8i). The title compound was prepared according to the general procedure **B** using of (*S*)-glutamate dimethyl ester (87.6 µL, 0.50 mmol) and isolated in the form of a yellow oil (58.2 mg, 0.29 mmol, 57%).

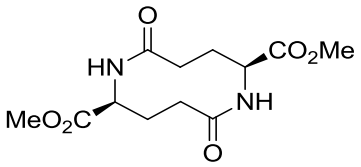


$[\alpha]_D^{25}$ + 66.9° (*c* 1.4, $CHCl_3$), $[\alpha]_D^{25}$ (*lit*) + 69.7° (*c* 1.4, $CHCl_3$).[15] R_f (CH_2Cl_2/EtOAc: 70/30) = 0.24. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 8.21 (br s, $1H_{CHO}$), 6.55 (d, *J* = 4.6 Hz, $1H_{NH}$), 4.73-4.68 (m, $1H_{CH\text{-}NH}$), 3.75 (s, $3H_{OCH_3}$), 3.66 (s, $3H_{OCH_3}$), 2.48-2.35 (m, $2H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$), 2.27-2.19 (m, $1H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$), 2.06-1.97 (m, $1H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 173.1 ($C{=}O_{ester}$), 171.9 ($C{=}O_{\text{ester next to (CH)}}$), 160.8 (C=O), 52.6 ($CH_3$), 51.8 ($CH_3$), 50.2 (CH), 29.8

[15] A. G. Avent, H. M. E. Duggan, D. W. Young, *Org. Biomol. Chem.* **2005**, *3*, 2327-2332.

(CH_2), 27.2 (CH_2). υ_{max} (neat)/cm^{-1} 3322, 2956, 2927, 2857, 2254, 1733, 1668, 1525, 1437, 1384, 1335, 1260, 1204, 1172. HRMS (ESI^+ TOF) m/z: $[M + Na]^+$ Calcd for $C_8H_{13}NO_5Na^+$: 226.0691; Found: 226.0699.

(*S*,*S*)-Dimethyl-5,10-dioxo-1,6-diazecane-2,7-dicarboxylate (9). The title compound was prepared according to the general procedure **A** at a temperature of 65 °C for 48 h using of (*S*)-glutamate dimethyl ester (87.6 µL, 0.50 mmol) under the diluted conditions, purified by column chromatography using CH_2Cl_2/EtOAc (80/20) and isolated in the form of a yellow oil (65.1 mg, 0.23 mmol, 91%).



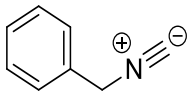
$[\alpha]_D^{25}$ + 0.69 ° (*c* 1.0, $CHCl_3$), (no reported $[\alpha]_D^{25}$ in *lit*). R_f (CH_2Cl_2/EtOAc: 80/20) = 0.26. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 6.82 (br s, $2H_{NH}$), 4.27-4.24 (m, 2 x $1H_{CH\text{-}NH}$), 3.76 (s, 2 x $3H_{CH_3}$), 2.51-2.41 (m, $2H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$), 2.39-2.28 (m, 2 x $2H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$), 2.25-2.18 (m, $2H_{CH_2\text{-}CH_2\text{-}CH\text{-}NH}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C =178.2 (C=O), 172.6 (C=O), 55.4 (CH), 52.6 (CH_3), 29.2 (CH_2), 24.8 (CH_2). υ_{max} (neat)/cm^{-1} 3231, 2956, 1739, 1694, 1437, 1378, 1205, 1152, 1113, 1042, 1023. HRMS (ESI^+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{18}N_2O_6Na^+$: 309.1064; Found: 309.1076.

7. Procedure C: One-Pot Synthesis of an Isocyanide from Benzylamine

To a round-bottom flask under an argon atmosphere were added 2-chlorophenylborinic acid **1** (12.5 mg, 0.05 mmol, 0.1 equiv.), dry DMF (7 mL) and acetic acid (6 mg, 0.10 mmol, 6 µL, 0.2 equiv.) at 65 °C. The mixture was vigorously stirred for 15 mins and the amine (0.50 mmol, 1 equiv.) was then slowly added using a gastight 100 µL syringe. The resulting mixture was stirred for 12 h at 65 °C. After 12 h, Burgess reagent (360 mg, 1.5 mmol, 3 equiv.), trimethylamine (418 µL, 3 mmol, 6 equiv.) and 5 Å powdered molecular sieves (1 g) were added and stirring was maintained for further 48 h. The reaction mixture was extracted five times with Et_2O and H_2O in order to remove DMF, washed with brine, dried over anhydrous $MgSO_4$ and concentrated under

vacuum. The crude mixture was purified by column chromatography using Pentane/EtOAc as the eluent to give the desired isocyanides.

Benzyl isocyanide (10). Known and described.[16] The title compound was prepared according to the procedure **C** using benzylamine (55 µL, 0.50 mmol). It was purified by column chromatography using Pentane /EtOAc (80/20 to 50/50) as the eluent to yield the title compound as an orange oil (43.9 mg, 0.33 mmol, 65%).

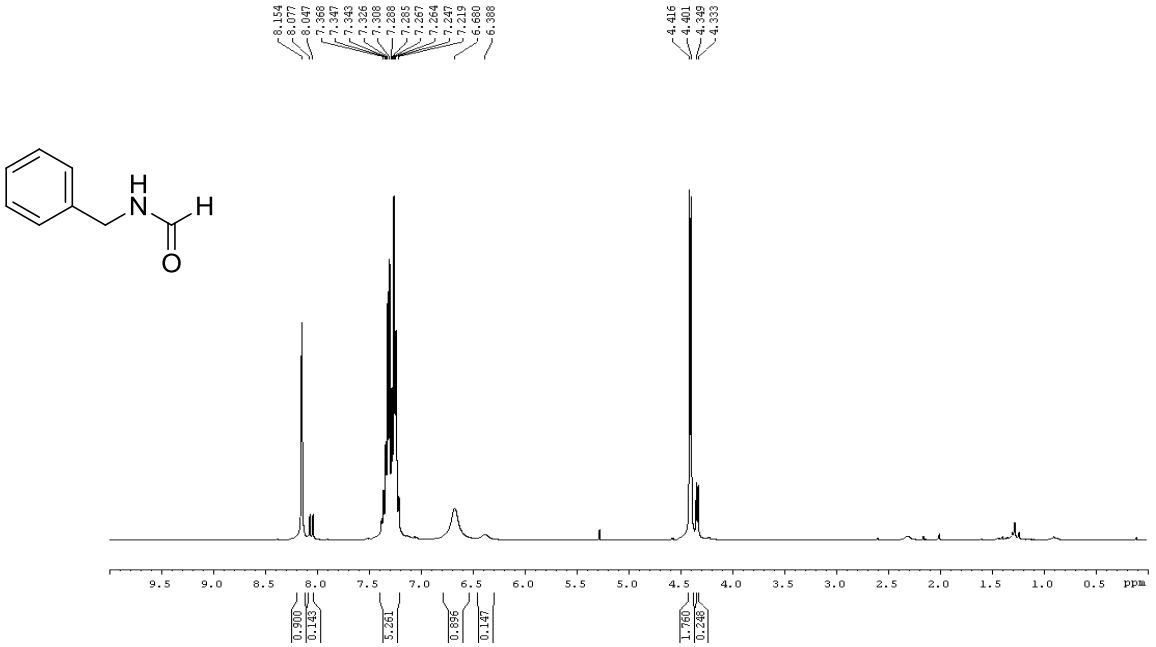


R_f (CH_2Cl_2/EtOAc: 95/5) = 0.55. The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; $CDCl_3$-d^1) δ_H = 7.43-7.34 (m, $5H_{Ar}$), 4.55 (s, $2H_{CH_2}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 157.7 (t, J = 5.4 Hz, CN), 132.3 (Cq_{Ar}), 129.0 (CH_{Ar}), 128.4 (CH_{Ar}), 126.6 (CH_{Ar}), 45.5 (t, J = 7.3 Hz, CH_2).

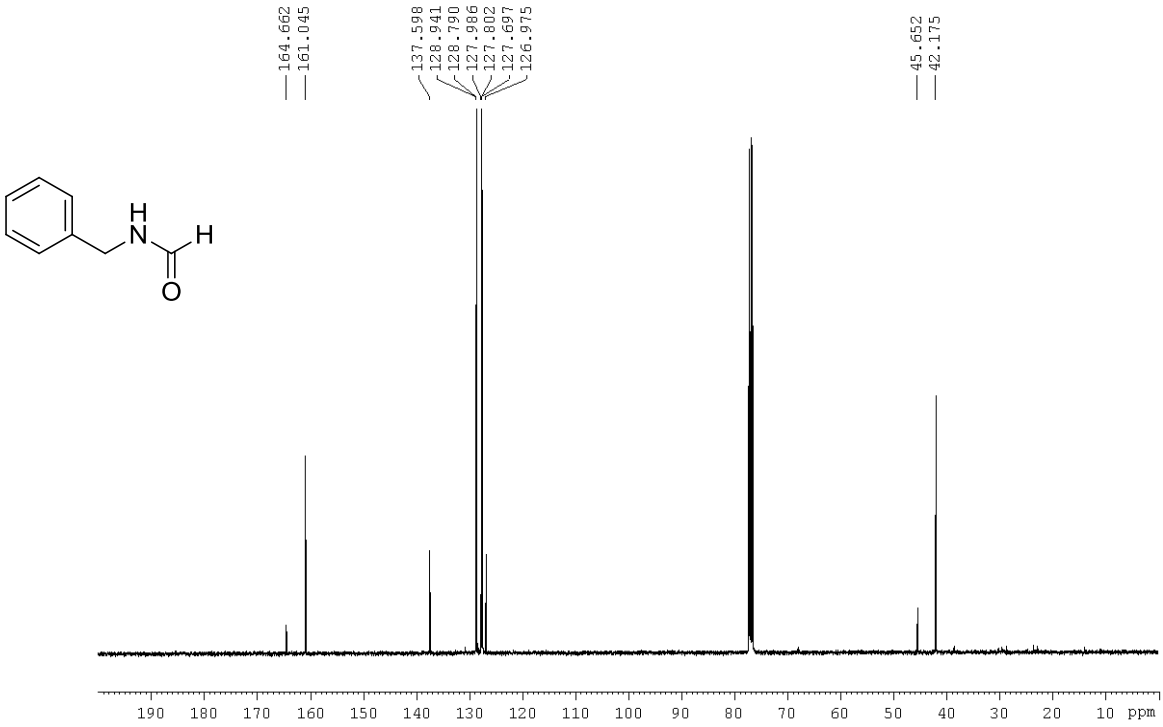
[16] M. Ketia, M. Vandamme, O. Mahé, J.-F. Paquin, *Tetrahedron Lett.* **2015**, *56*, 461–464.

8. ^{1}H and ^{13}C NMR Spectra of the Synthesised products

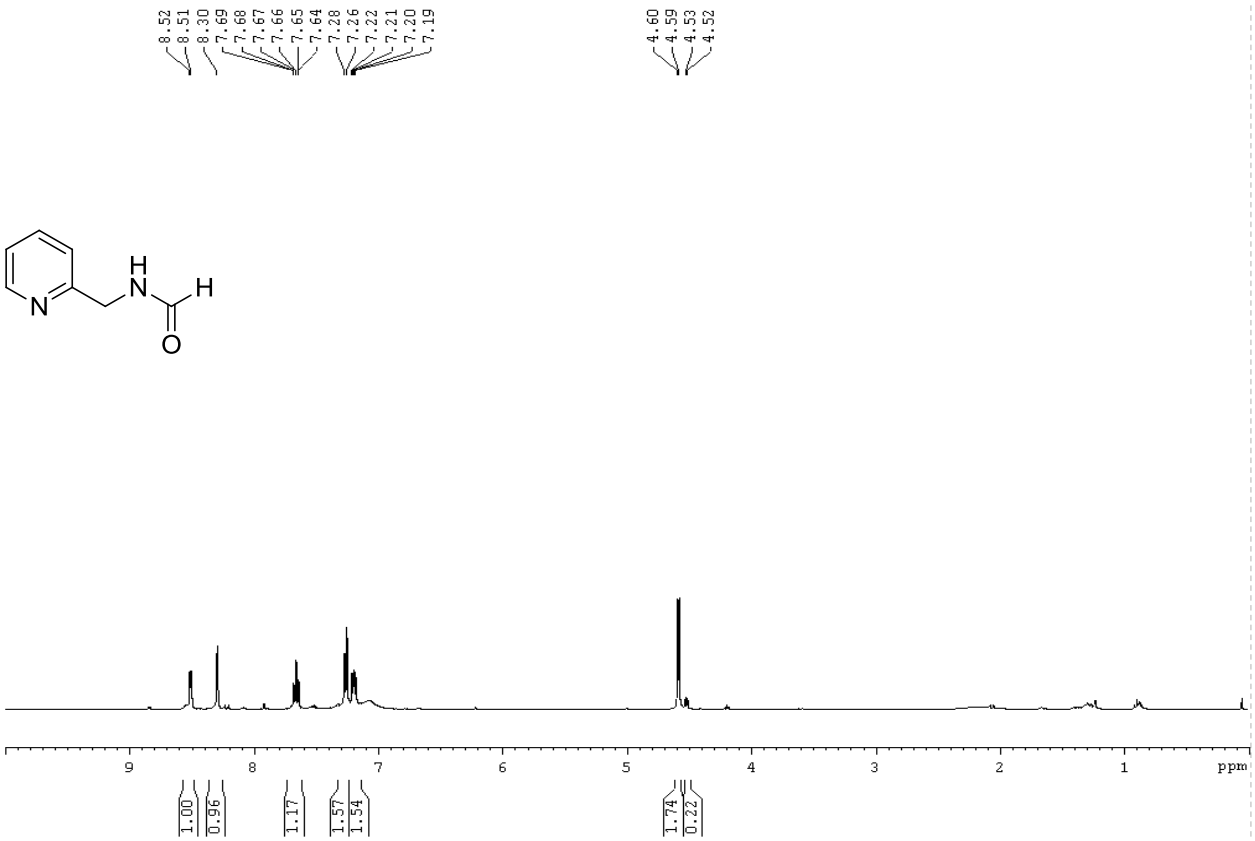
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3a**.



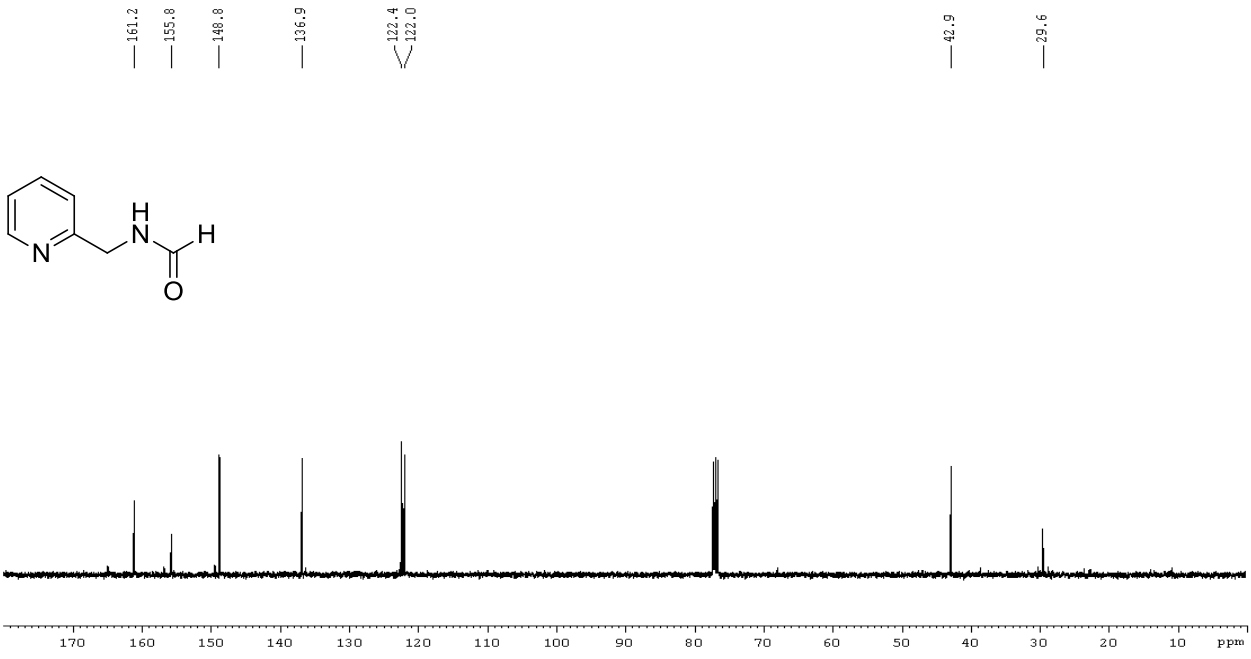
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3a**.



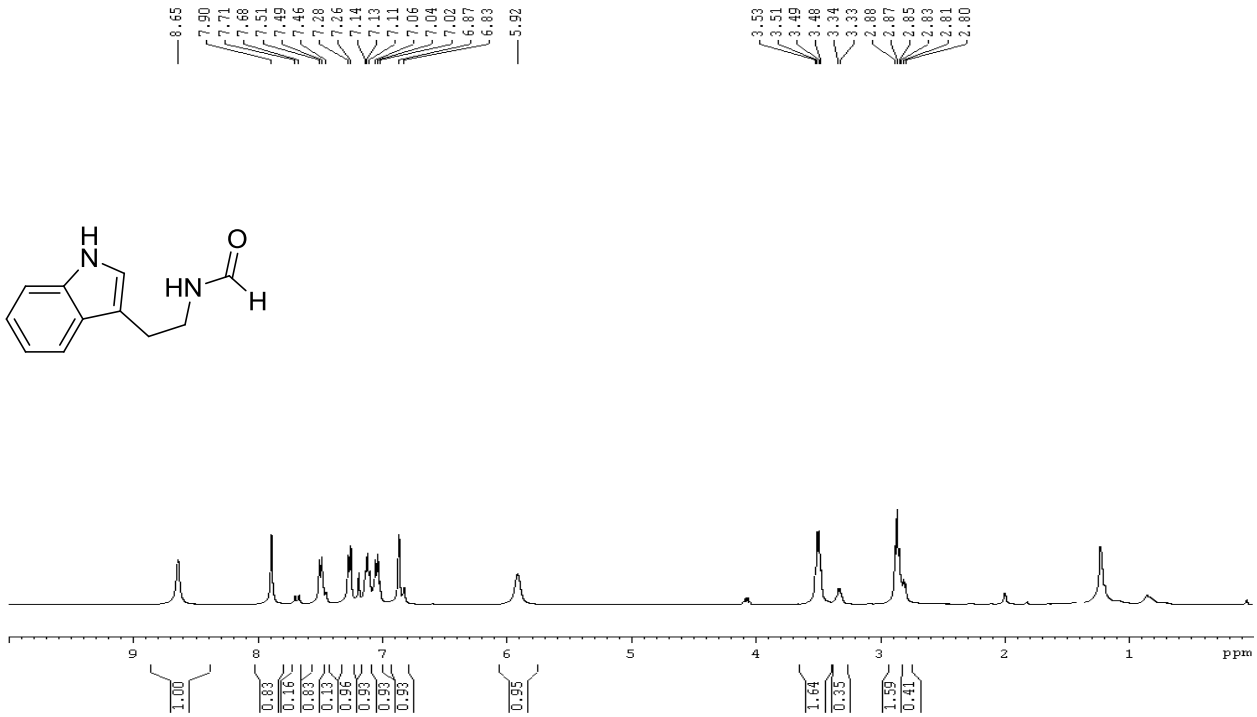
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3b**.



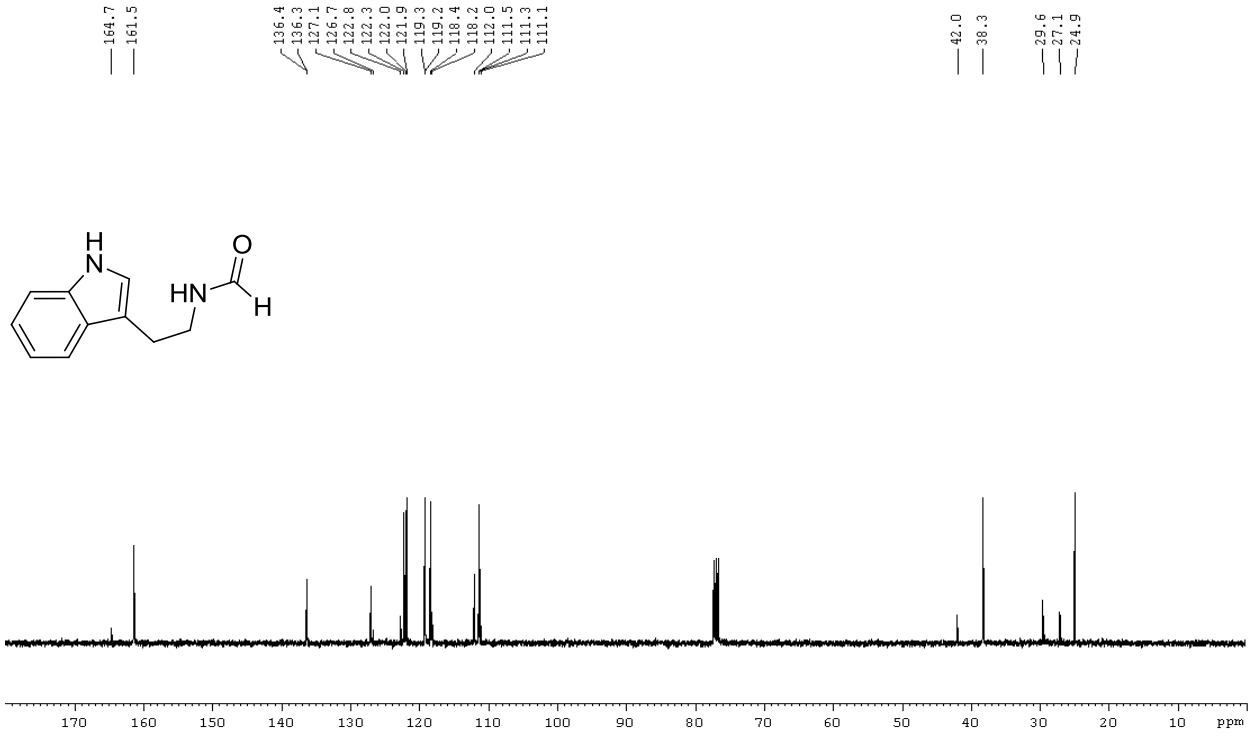
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3b**.



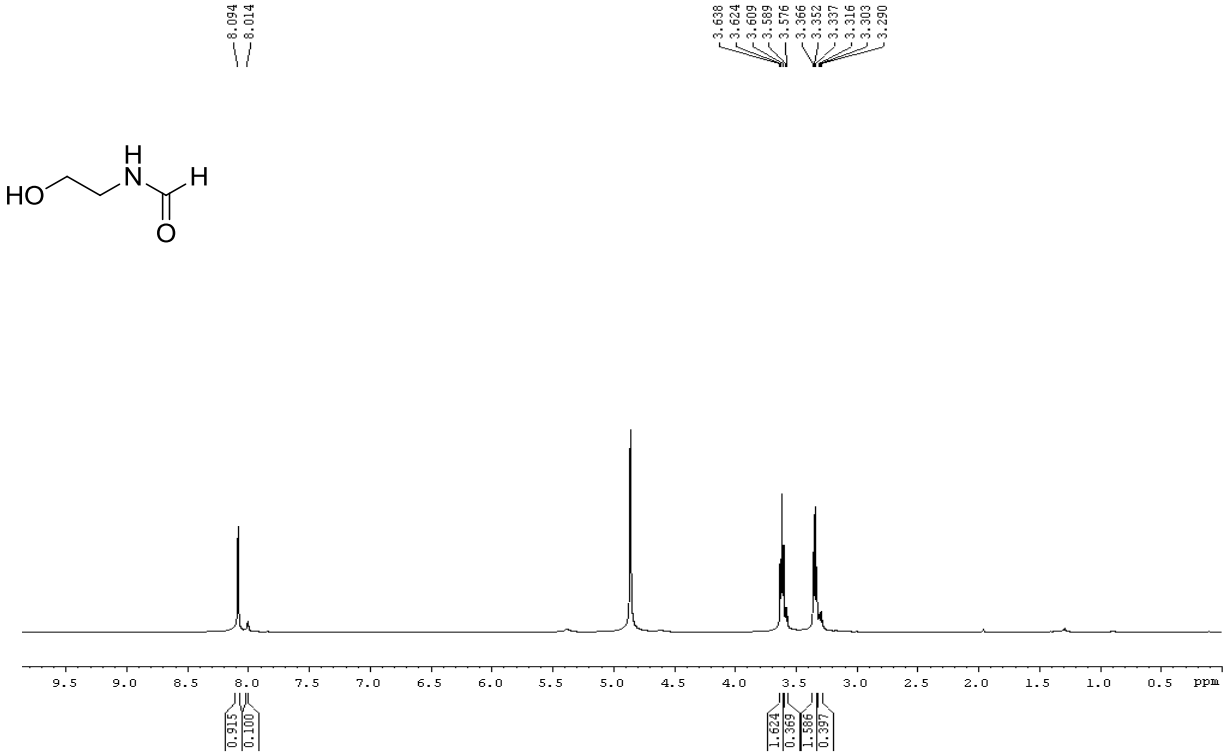
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3c**.



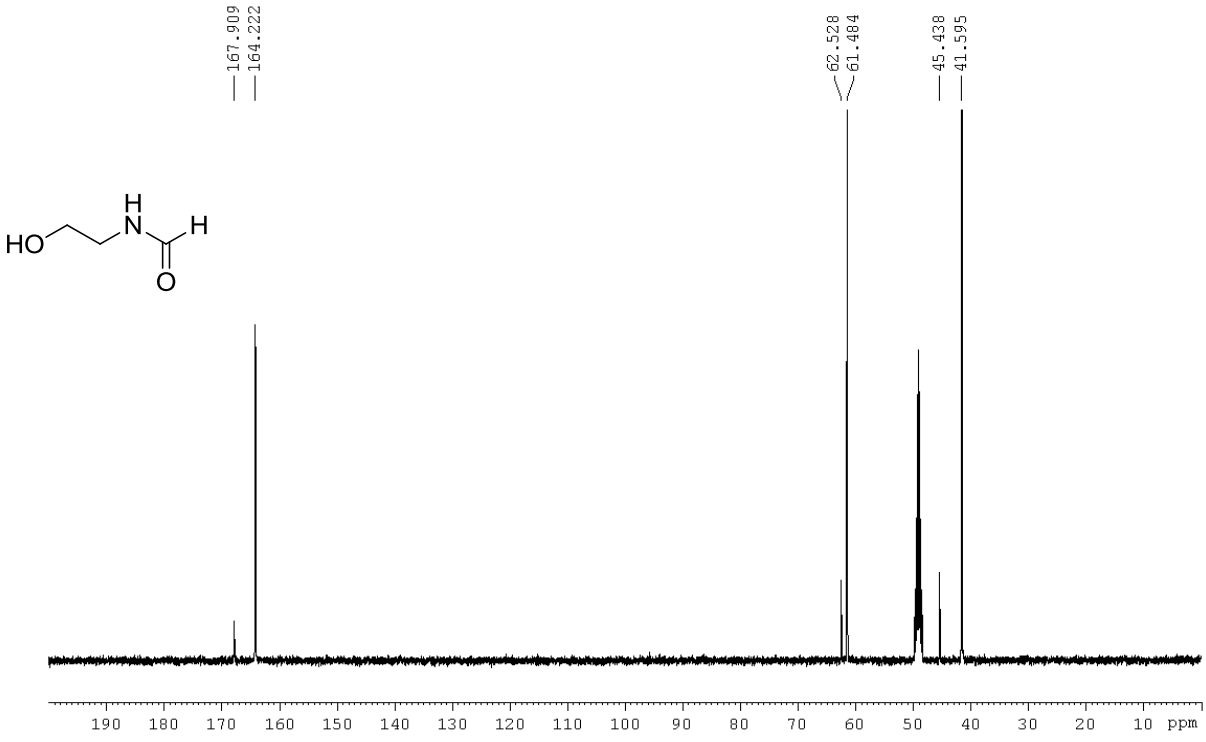
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3c**.



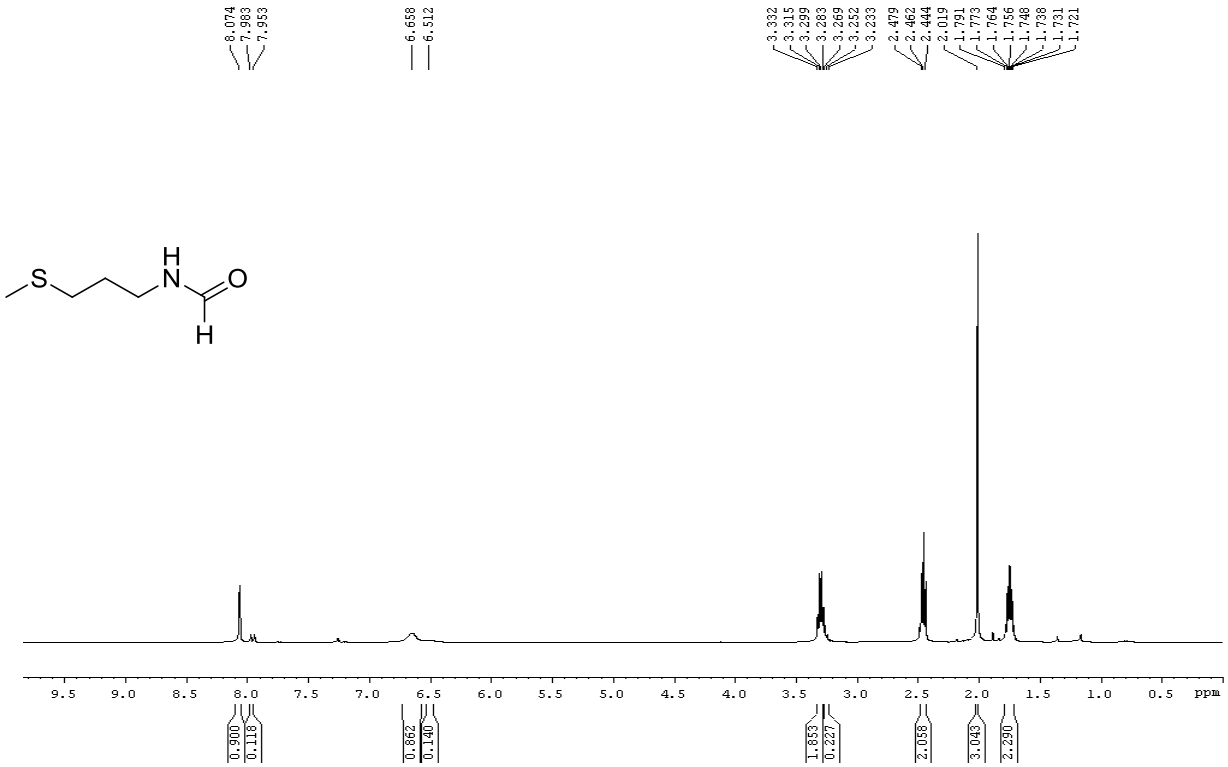
^{1}H NMR (400.0 MHz; MeOH-d^{4}) of **3d**.



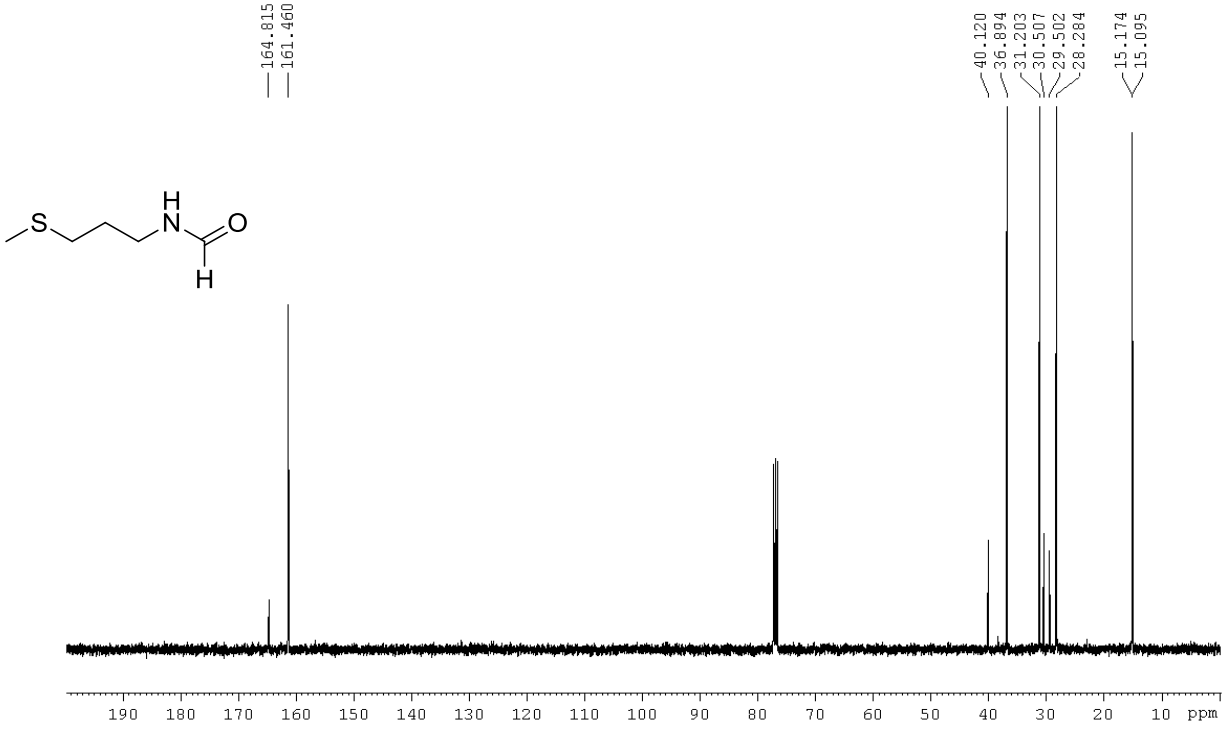
^{13}C NMR (100.0 MHz; MeOH-d^{4}) of **3d**.



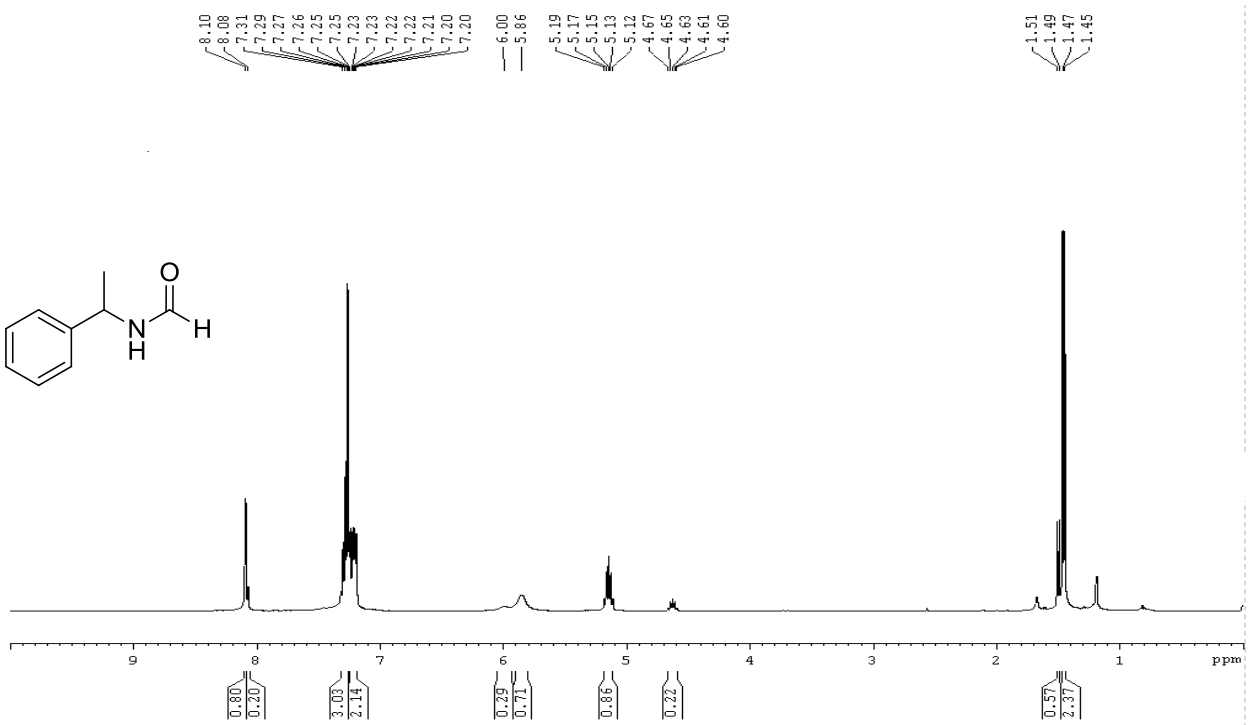
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3e**.



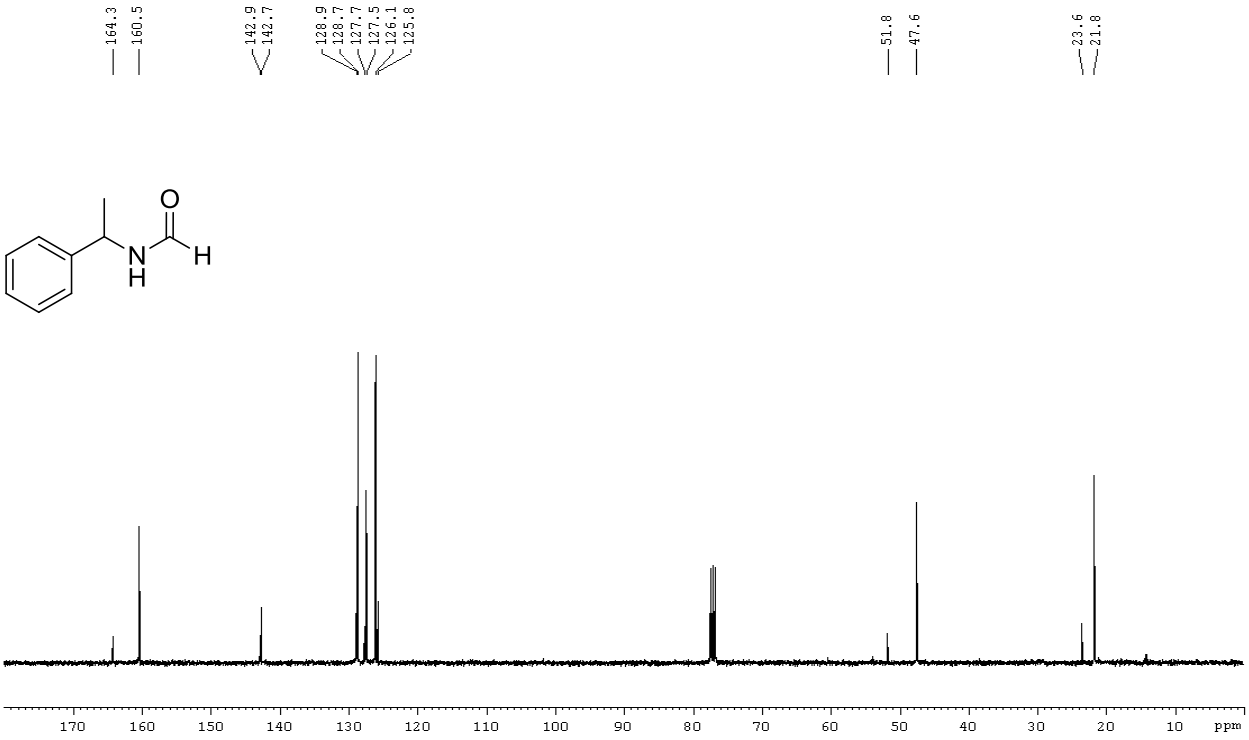
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3e**.



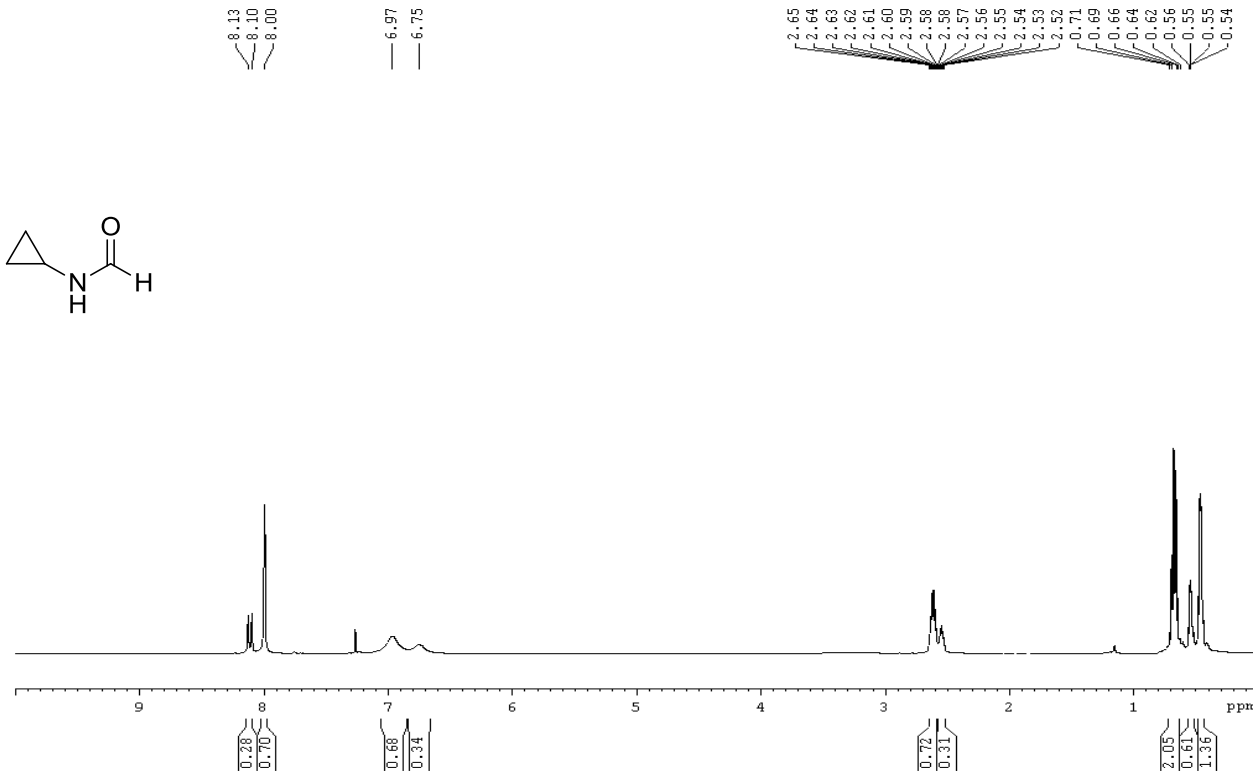
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3f**.



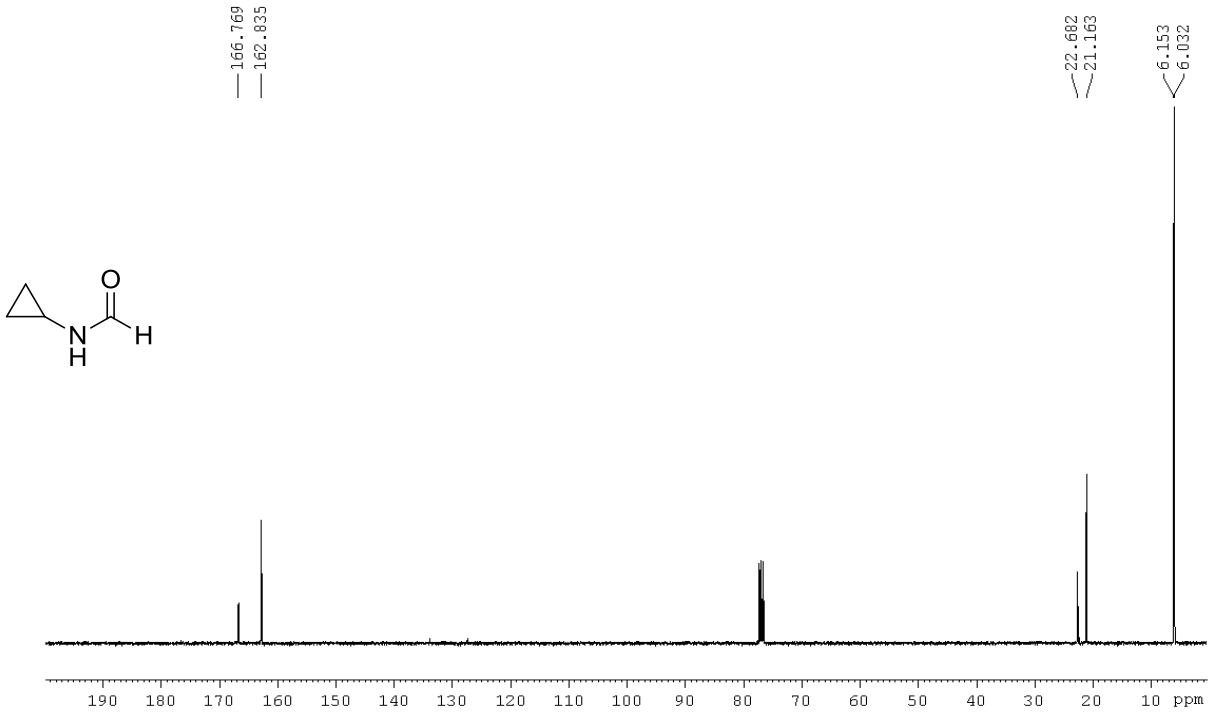
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3f**.



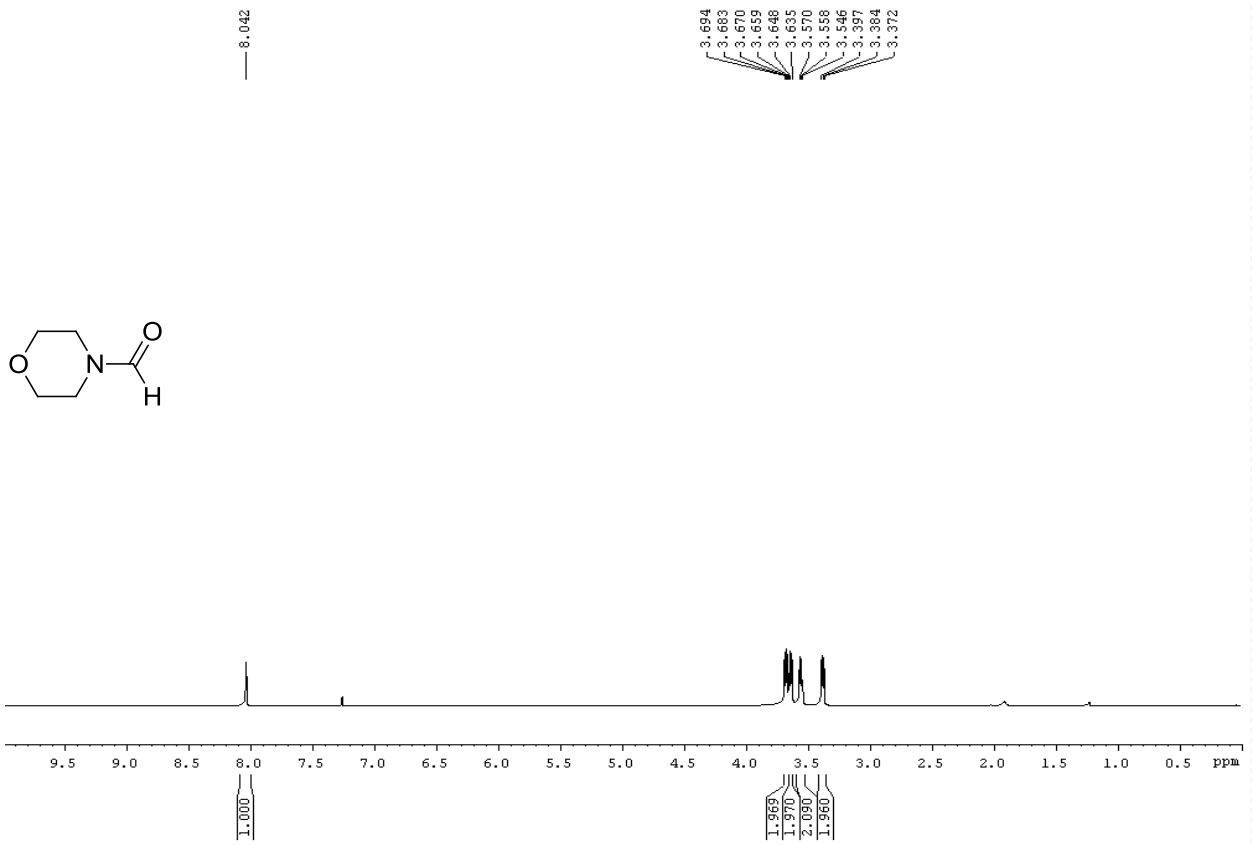
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3g**.



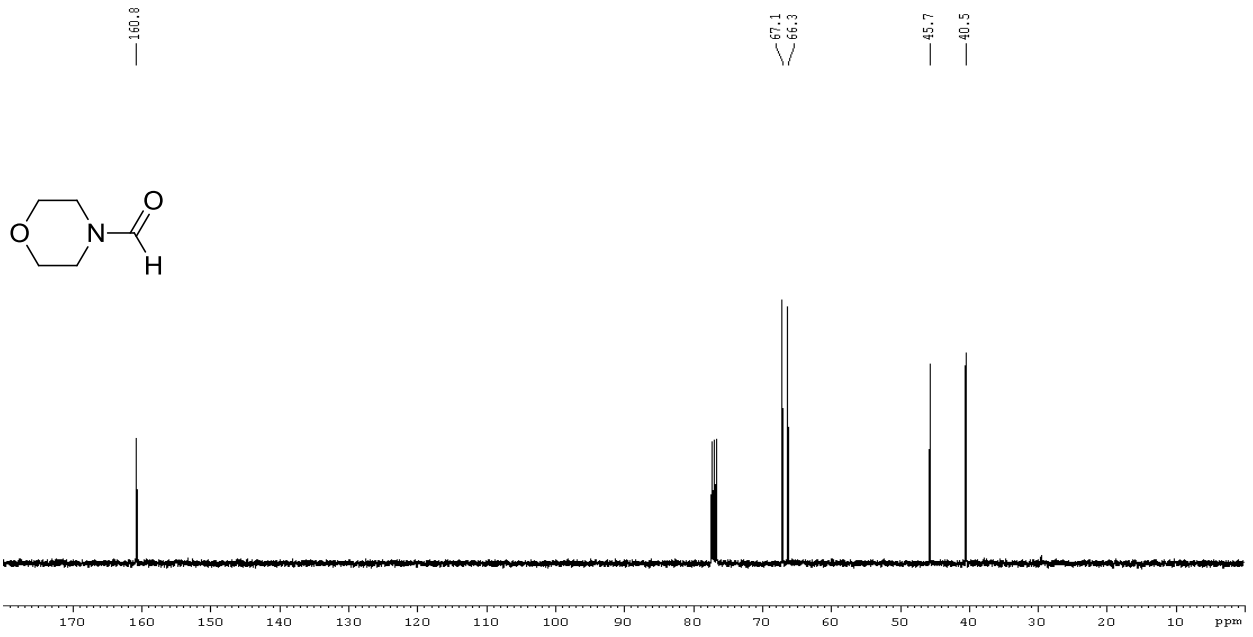
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3g**.



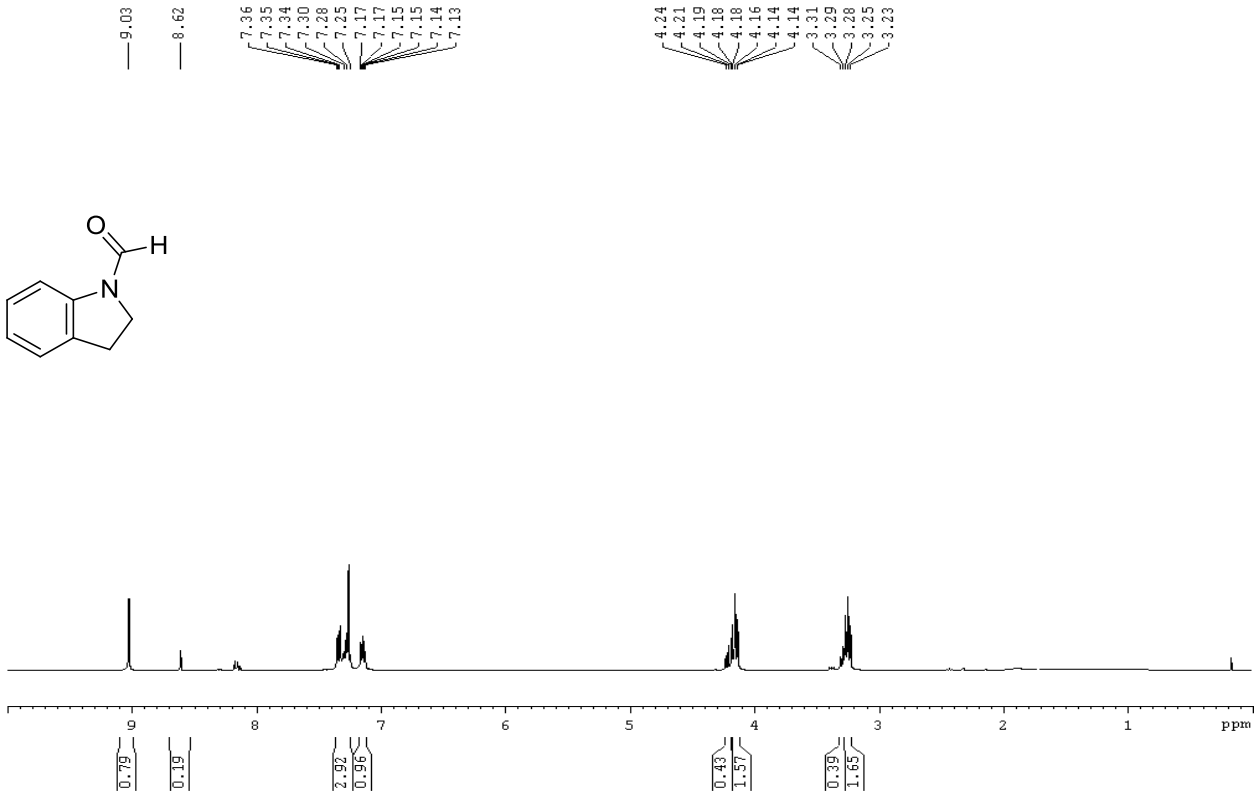
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3h**.



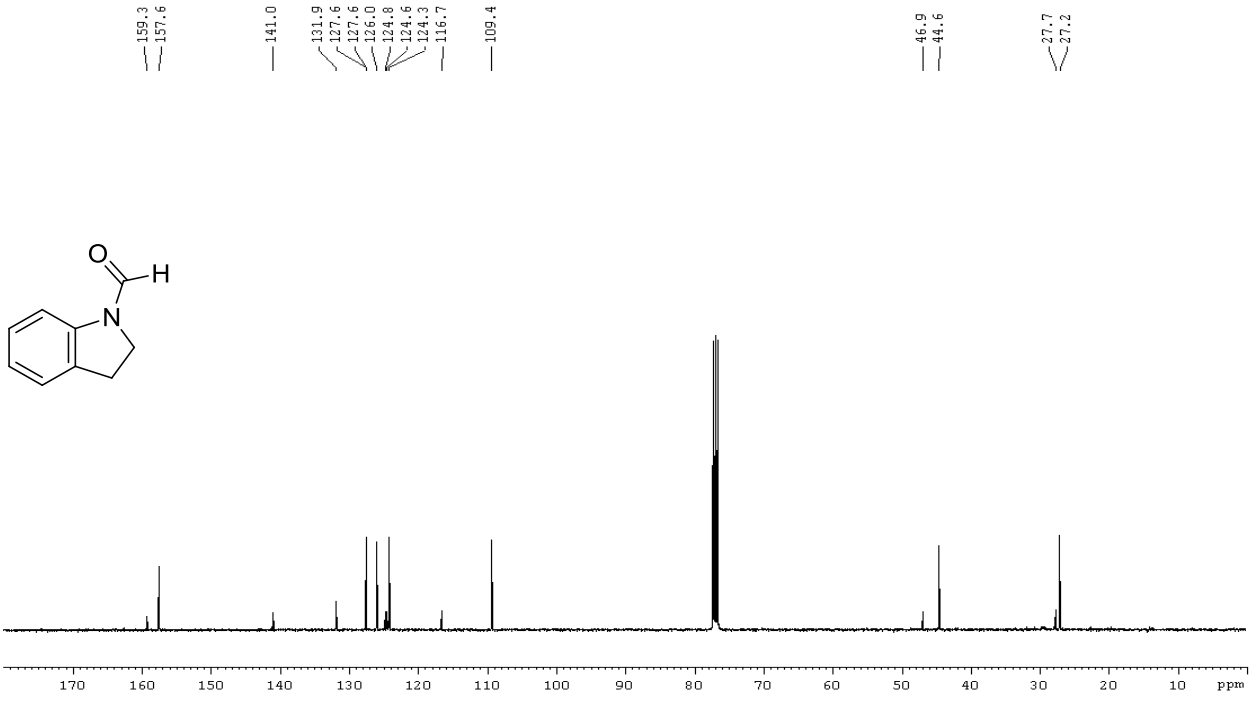
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3h**.



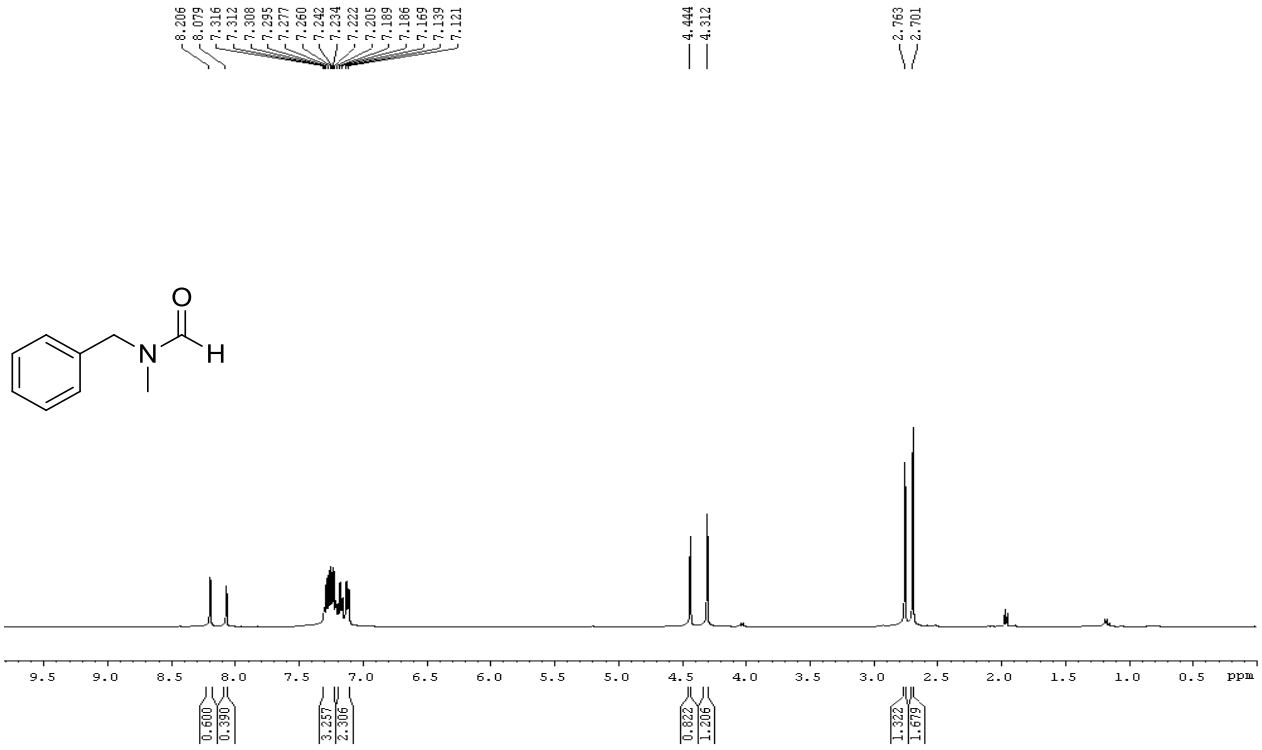
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3i**.



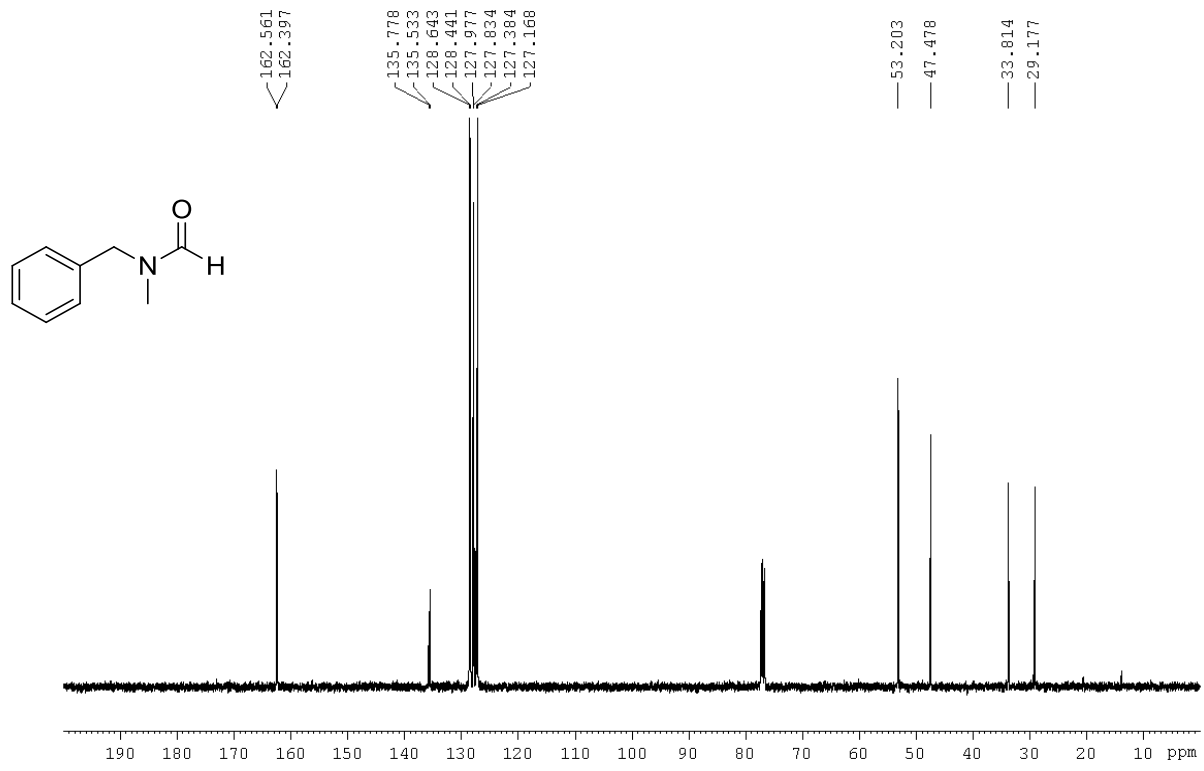
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3i**.



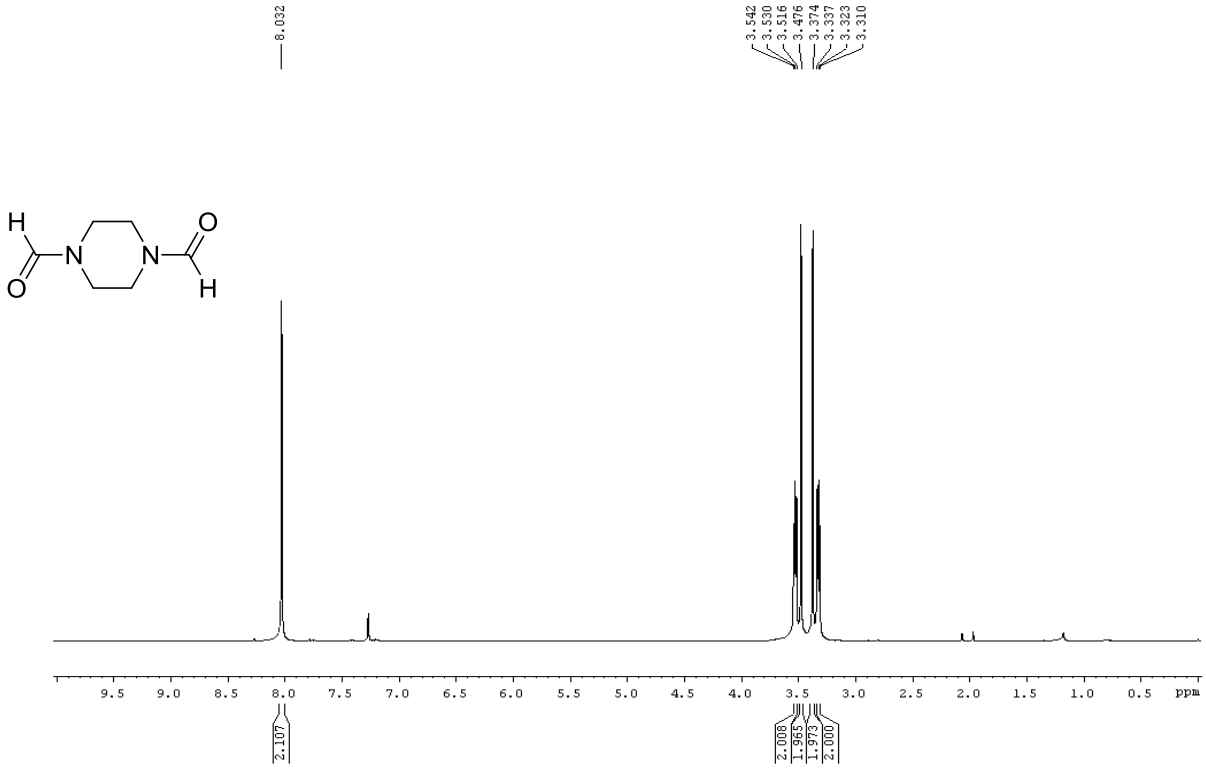
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3j**.



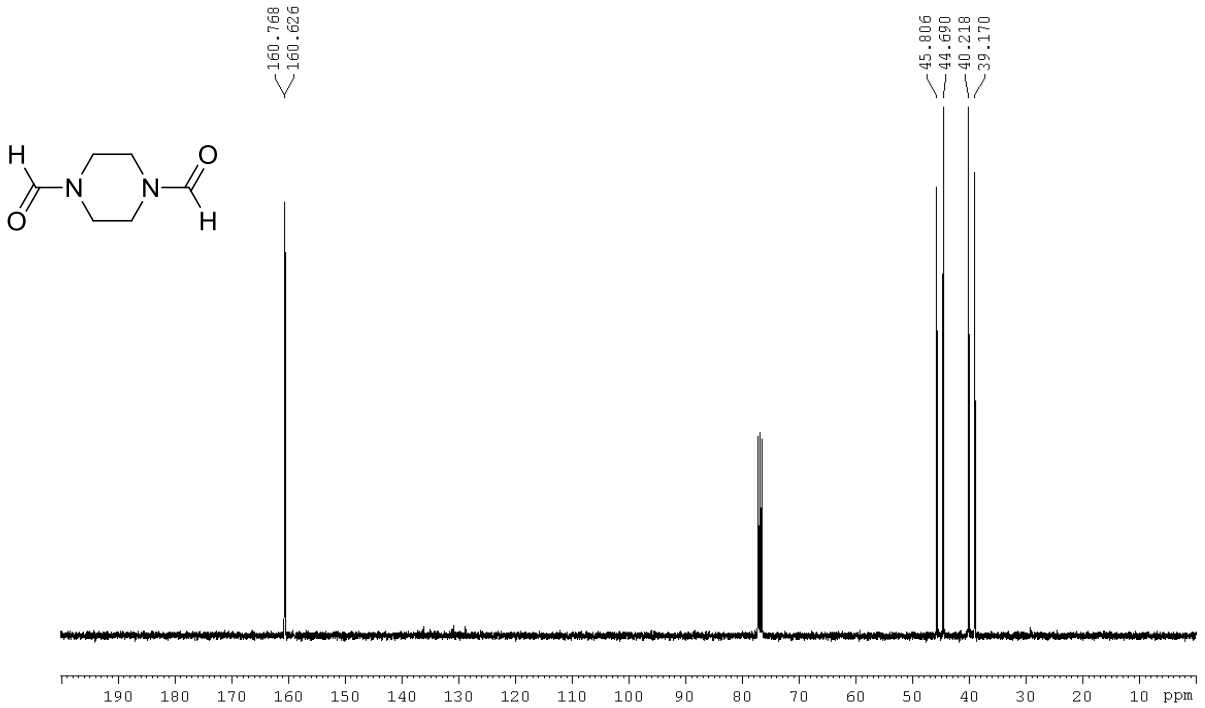
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3j**.



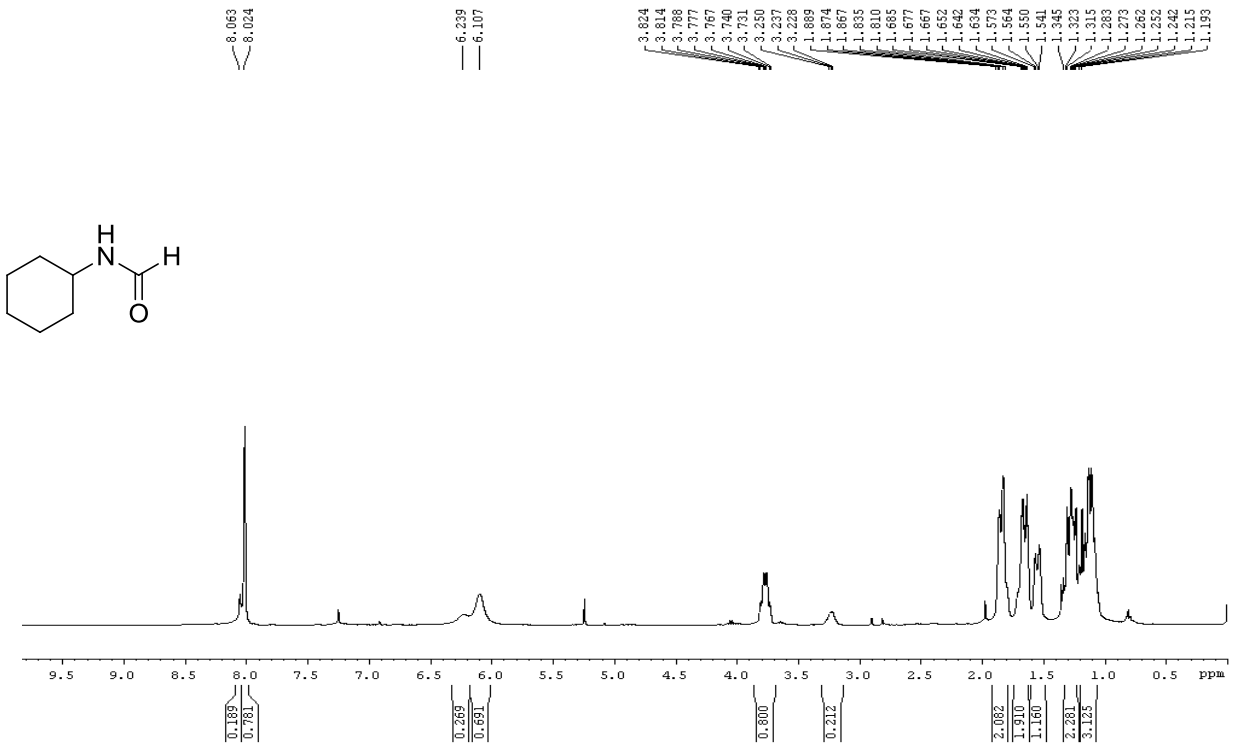
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3k**.



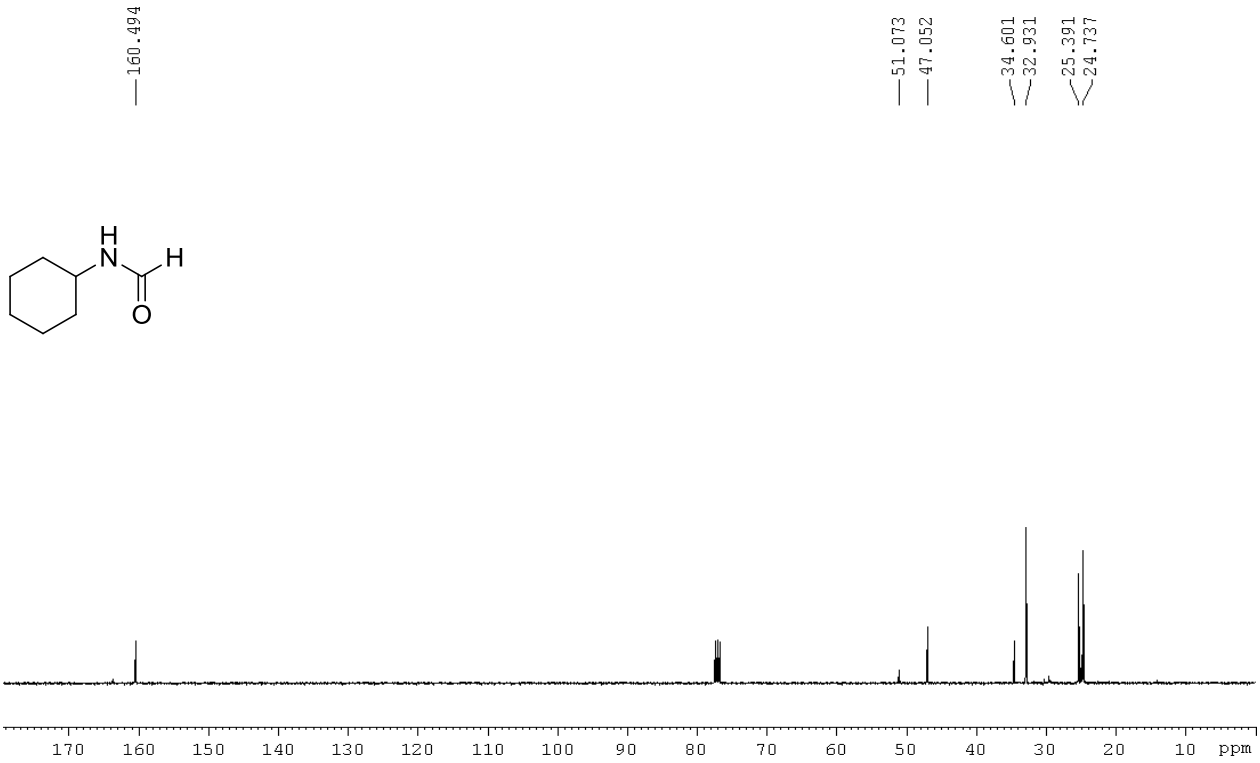
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3k**.



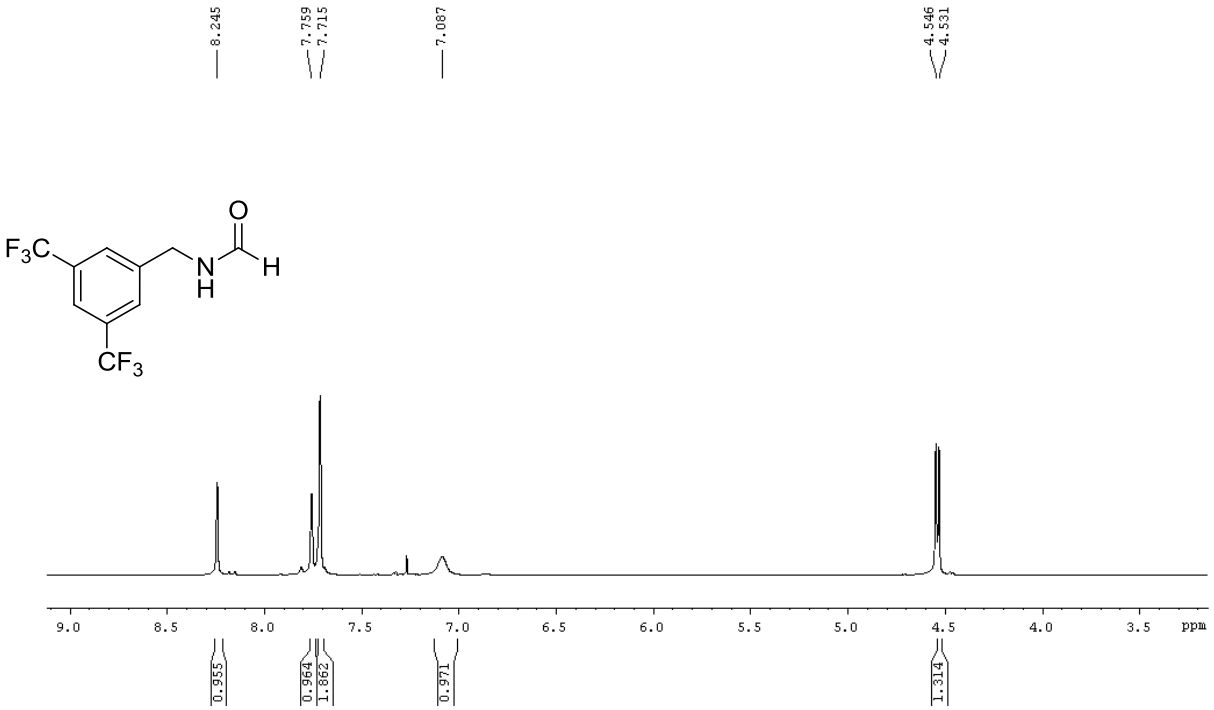
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3l**.



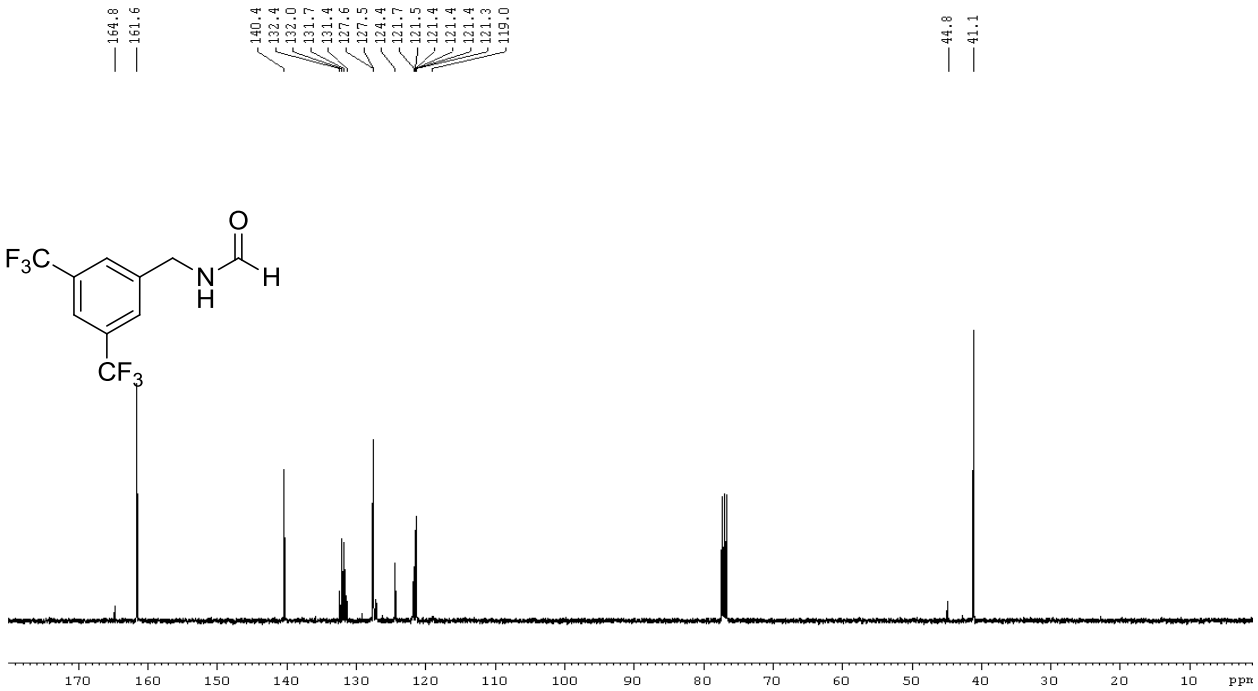
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3l**.



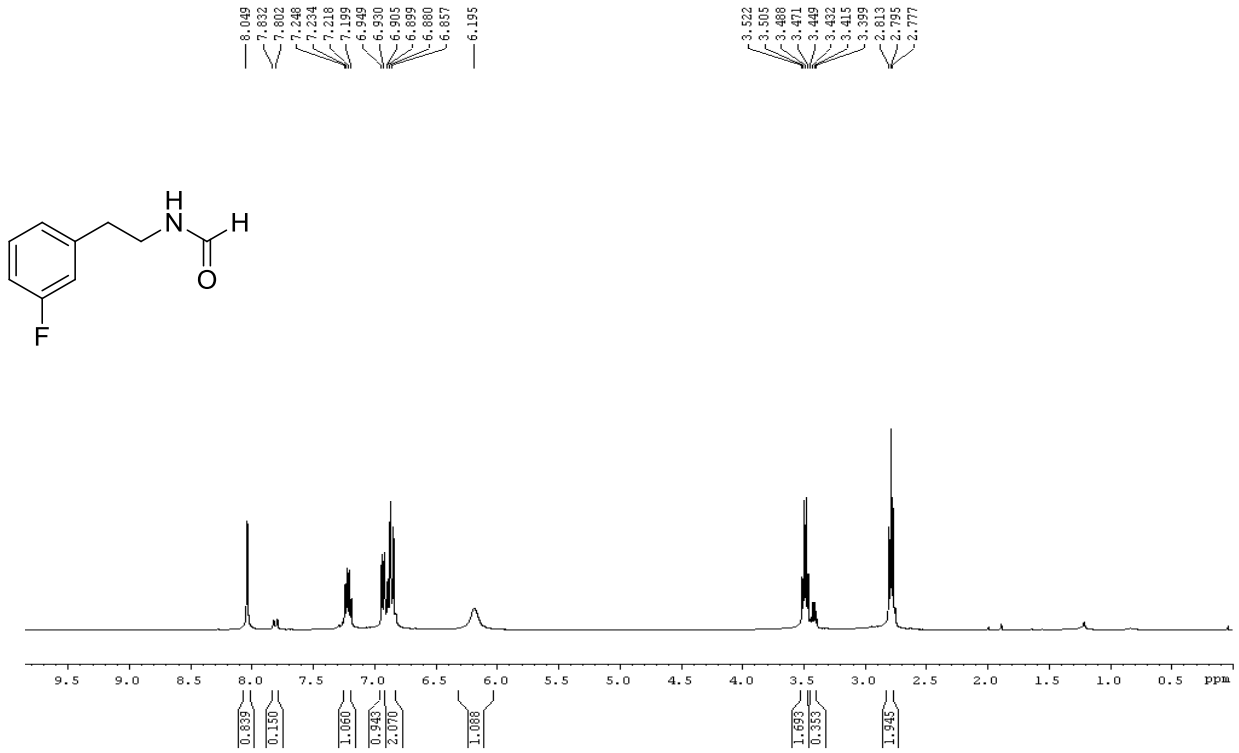
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3m**.



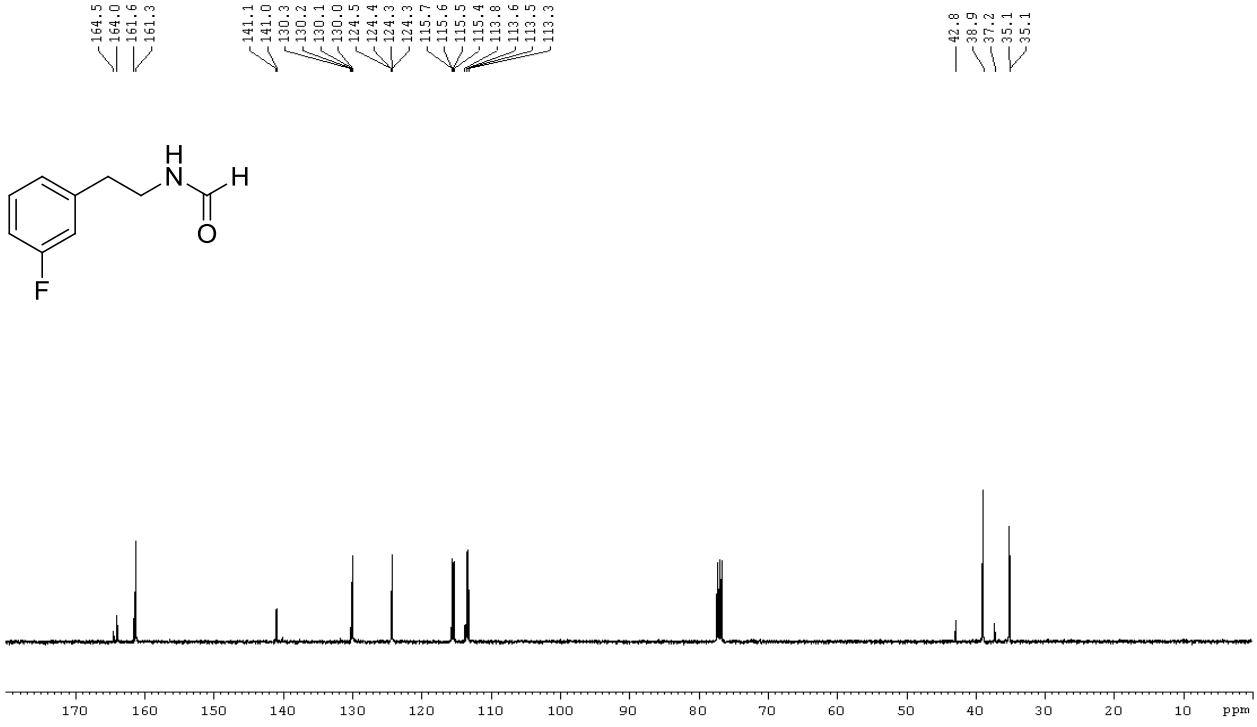
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3m**.



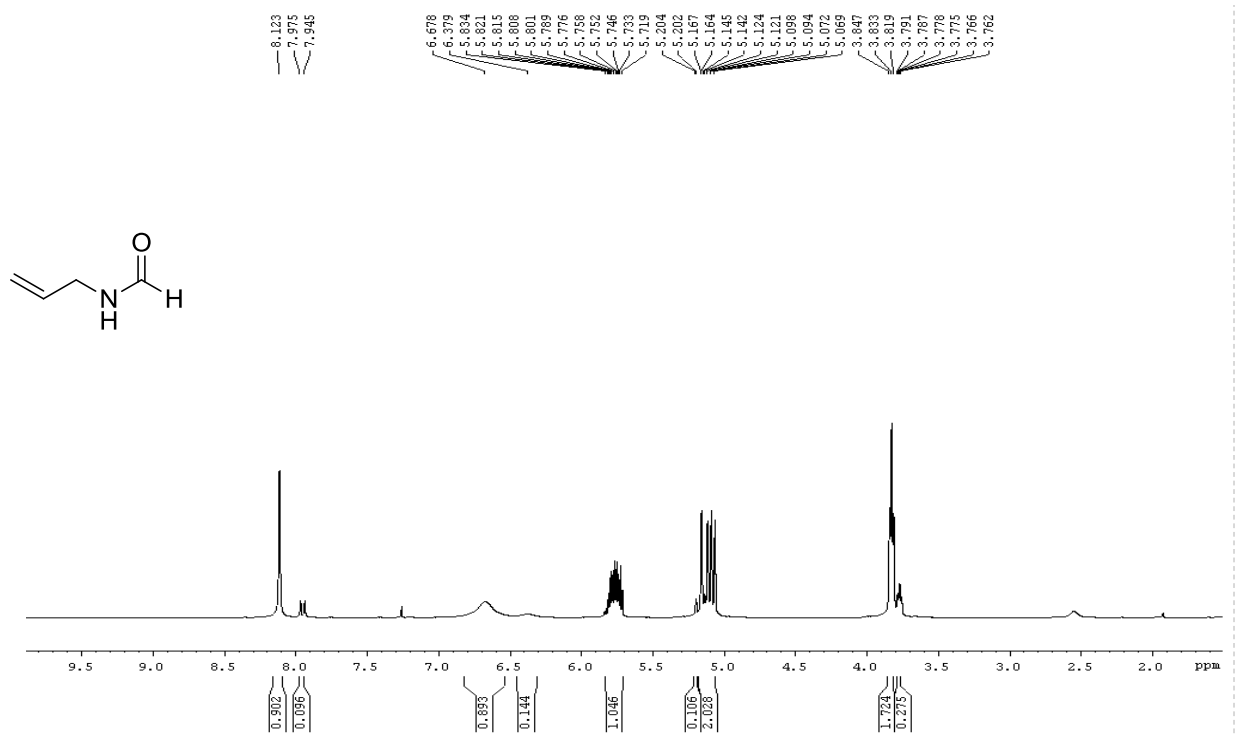
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3n**.



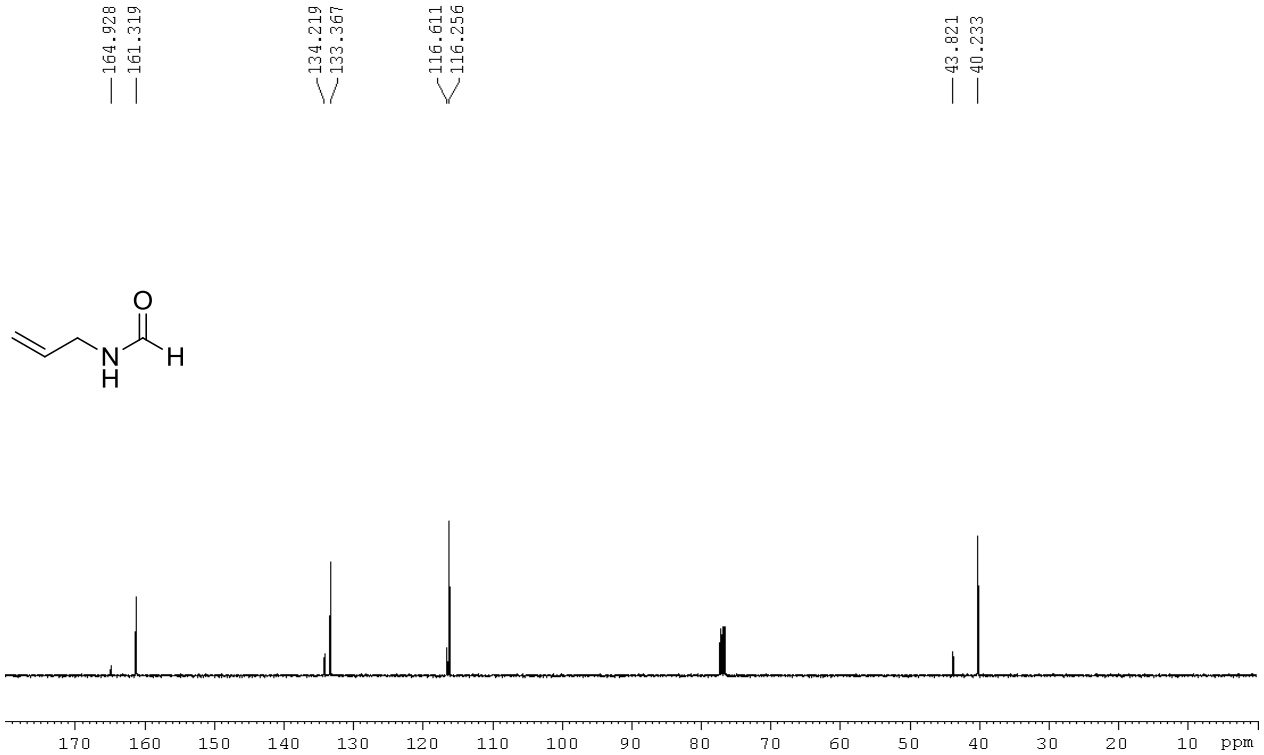
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3n**.



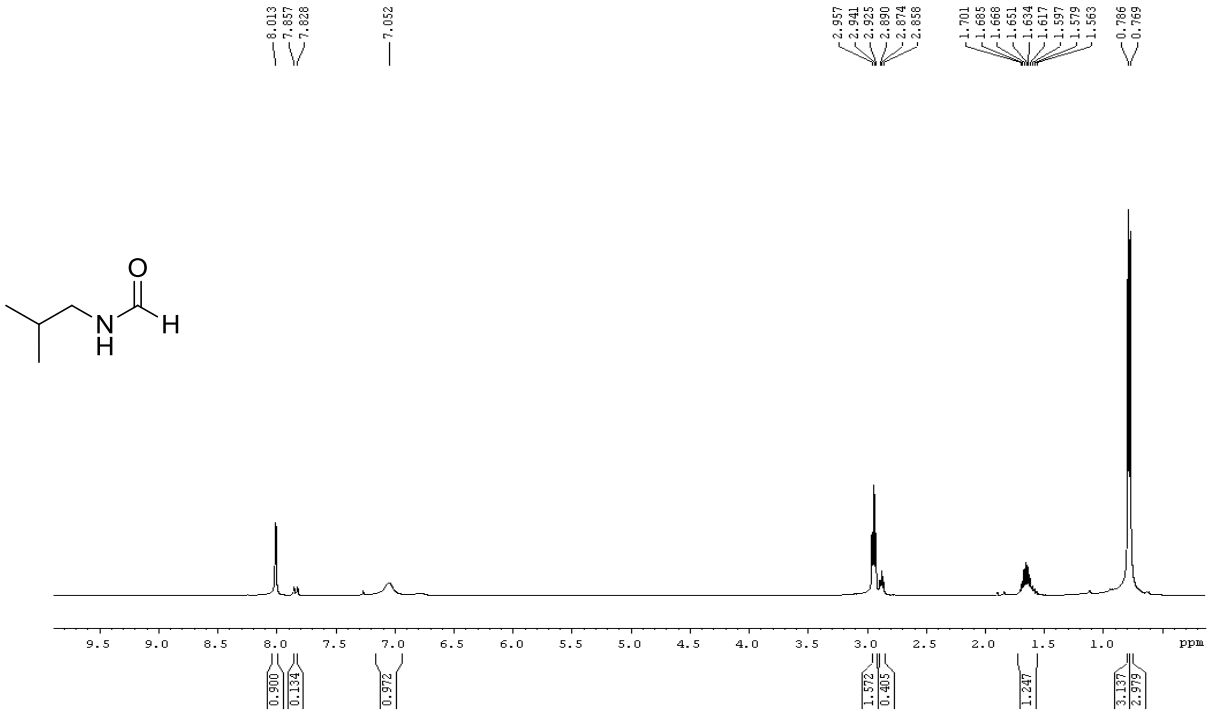
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3o**.



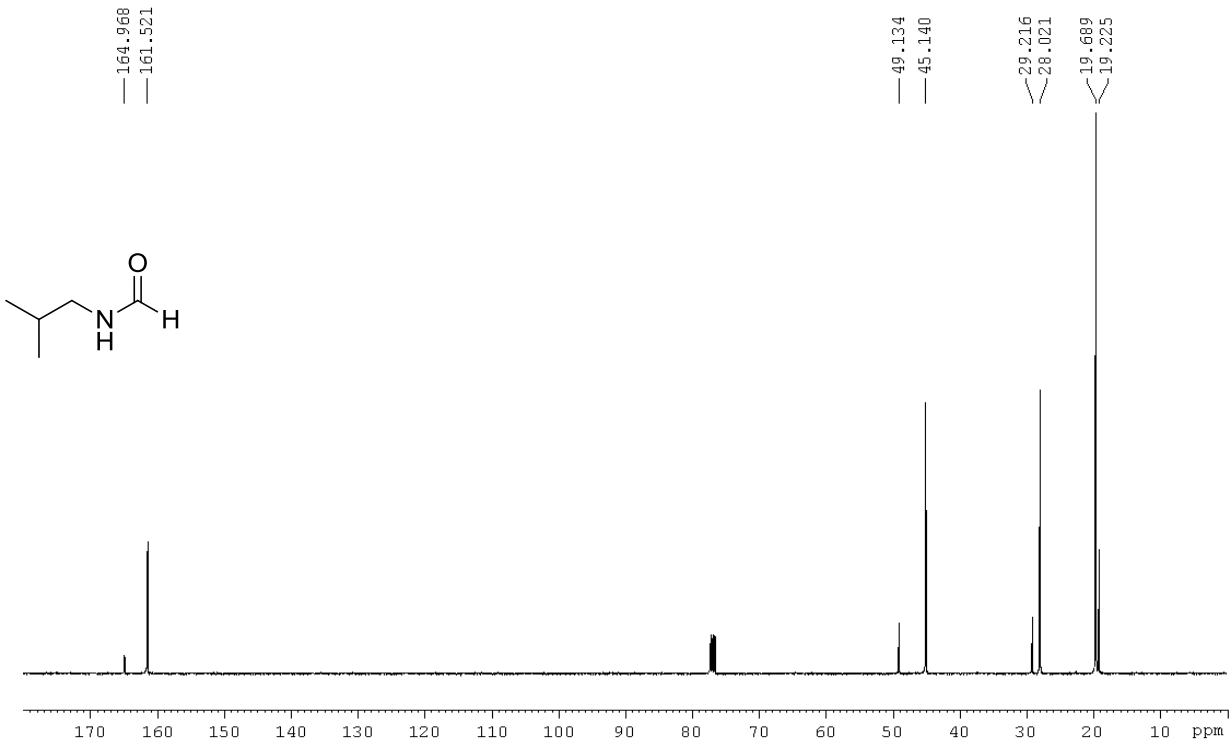
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3o**.



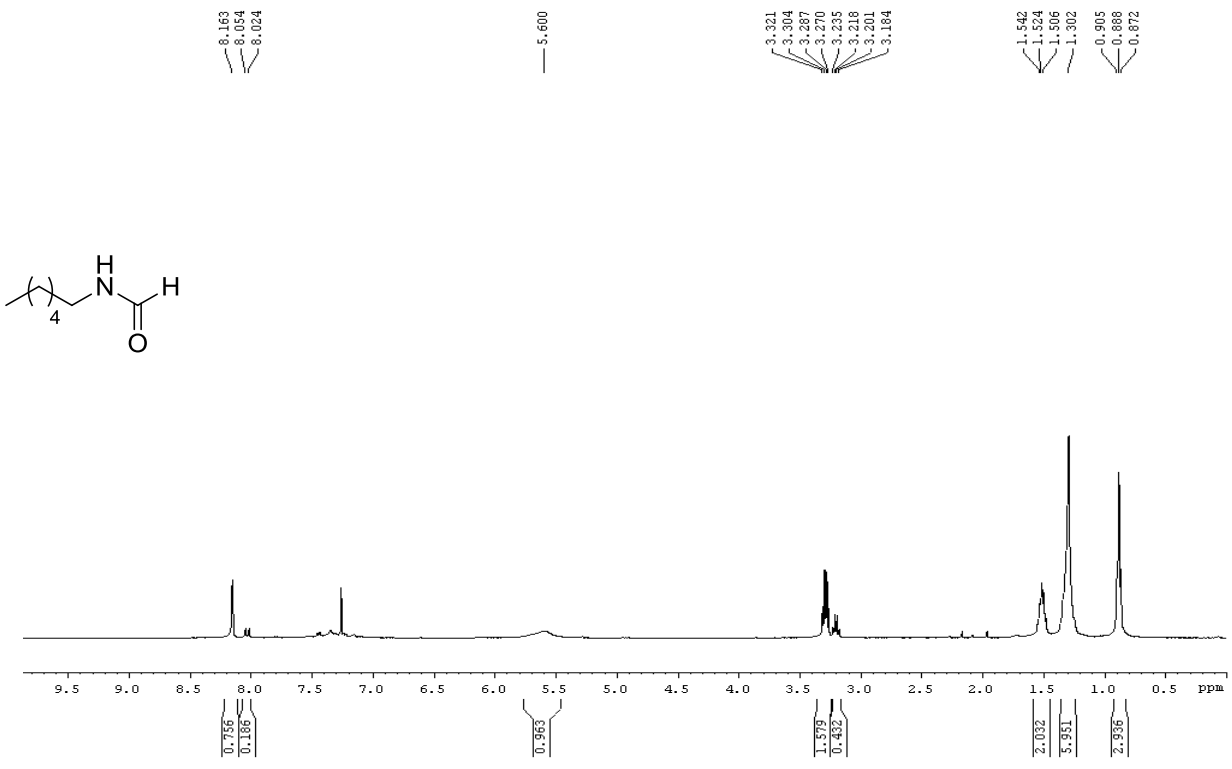
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3p**.



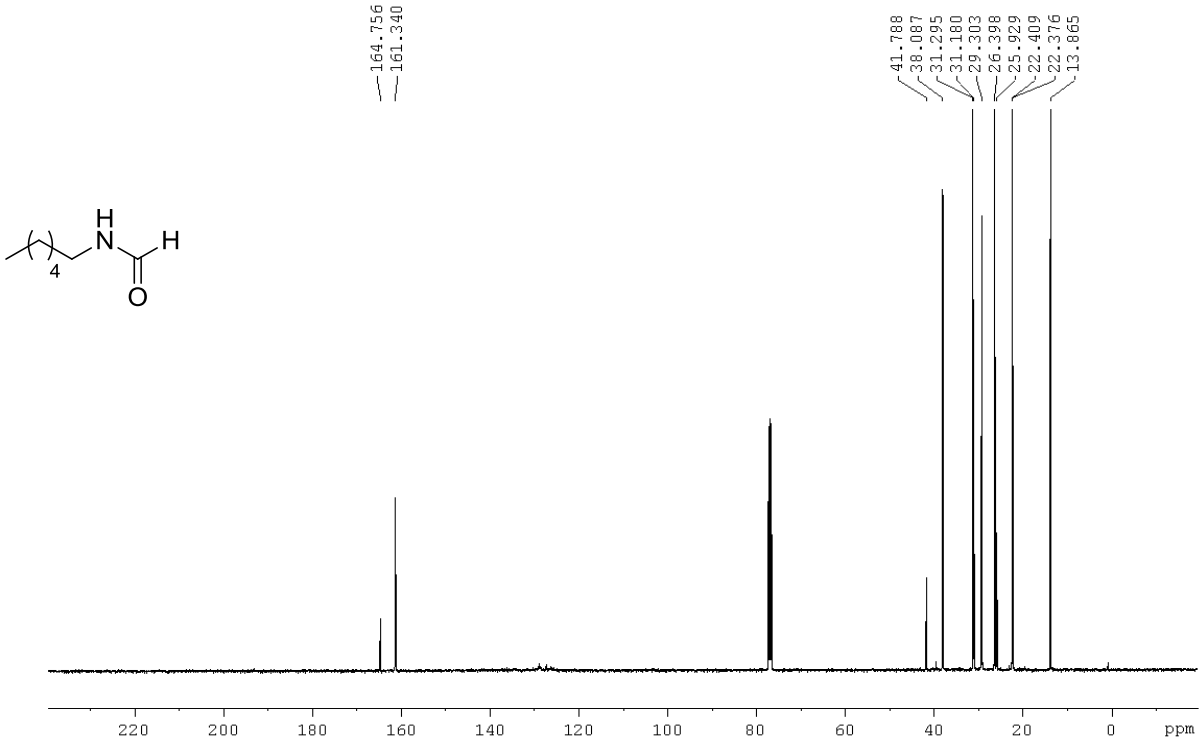
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3p**.



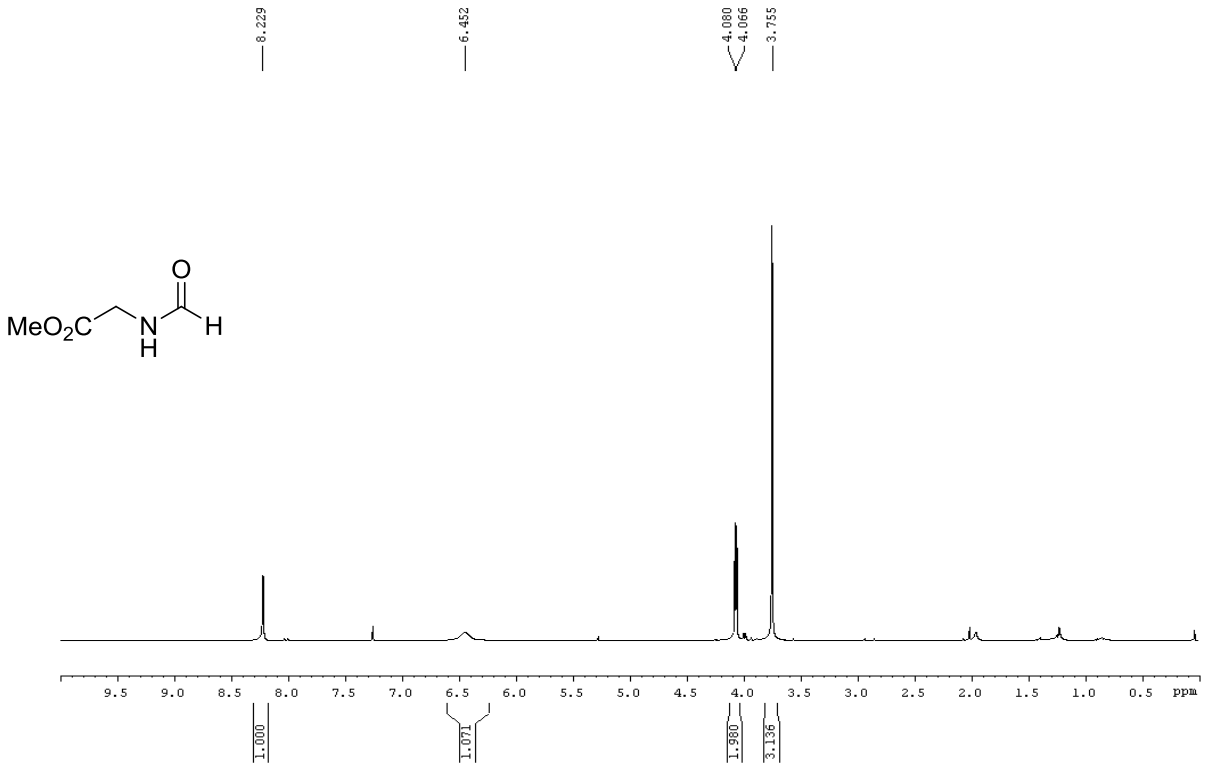
^{1}H NMR (400.0 MHz; $CDCl_3$) of **3q**.



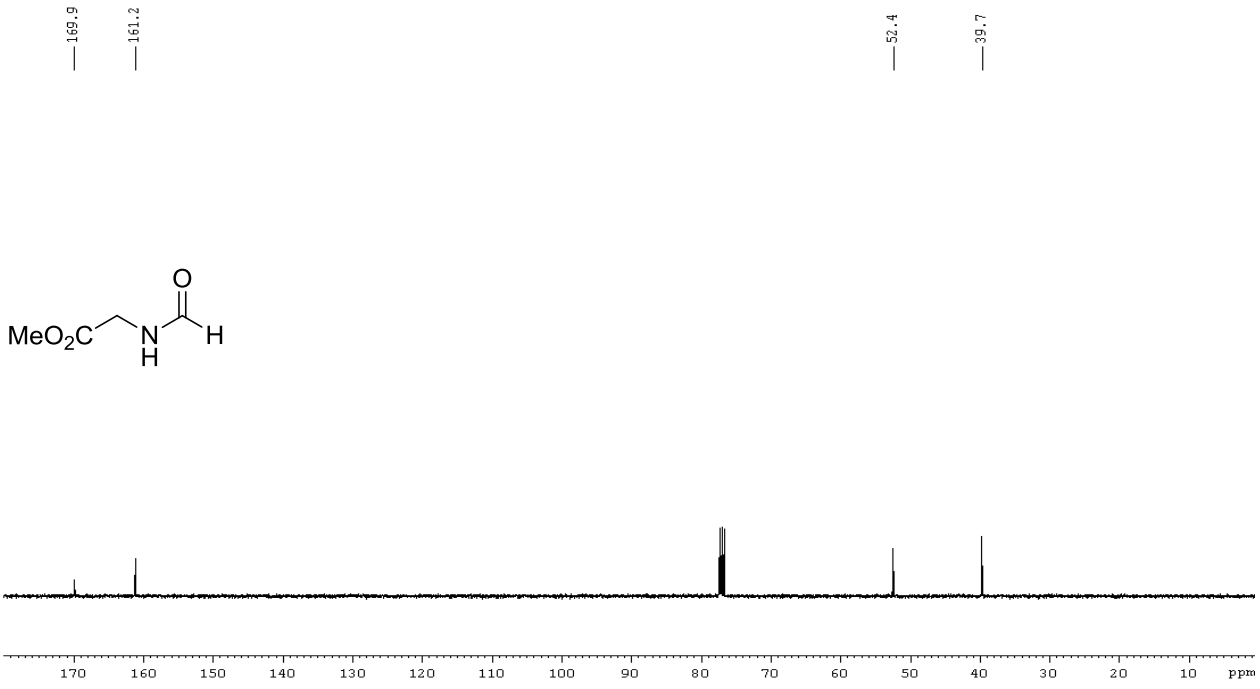
^{13}C NMR (100.0 MHz; $CDCl_3$) of **3q**.



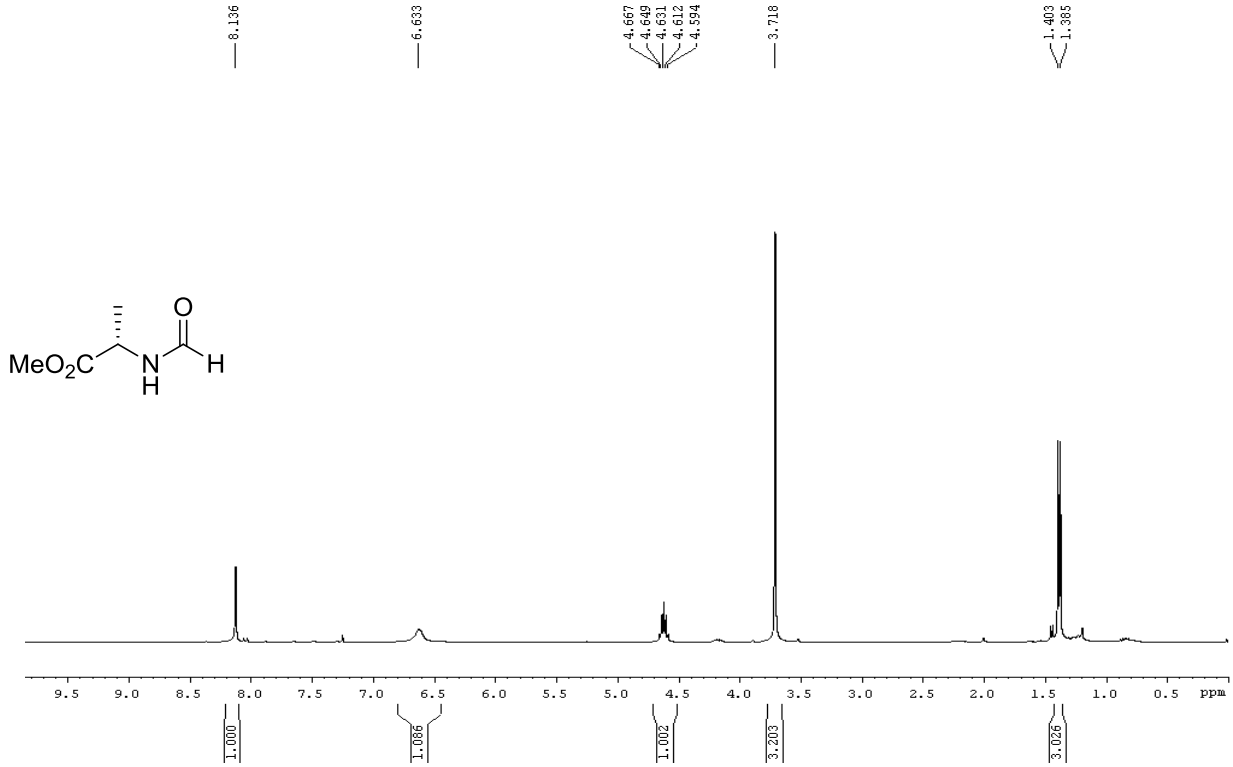
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8a**.



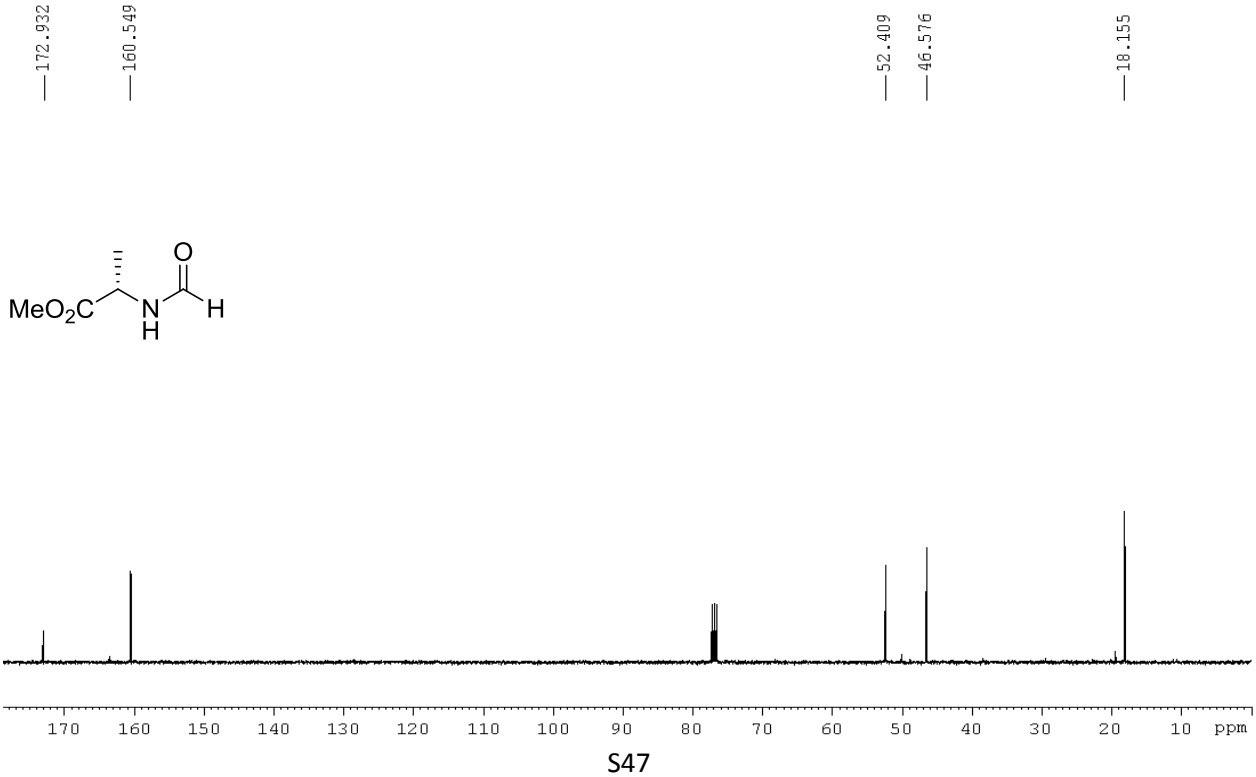
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8a**.



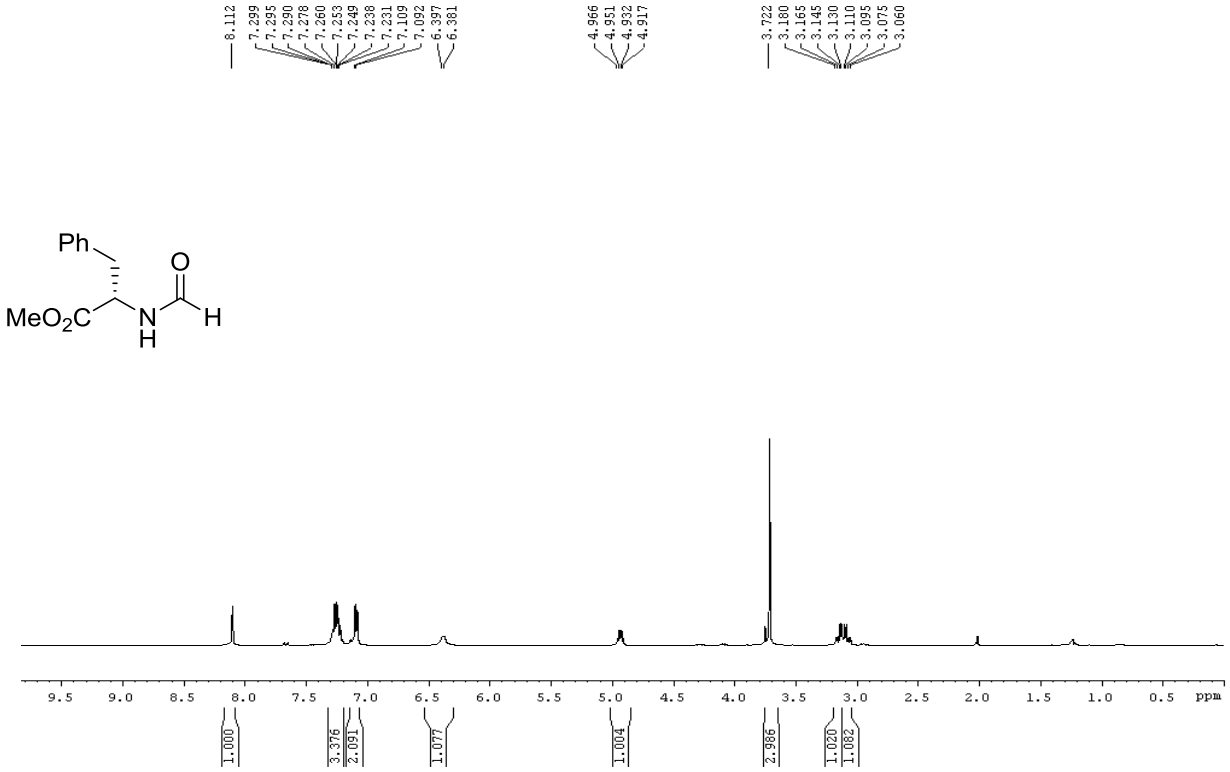
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8b**.



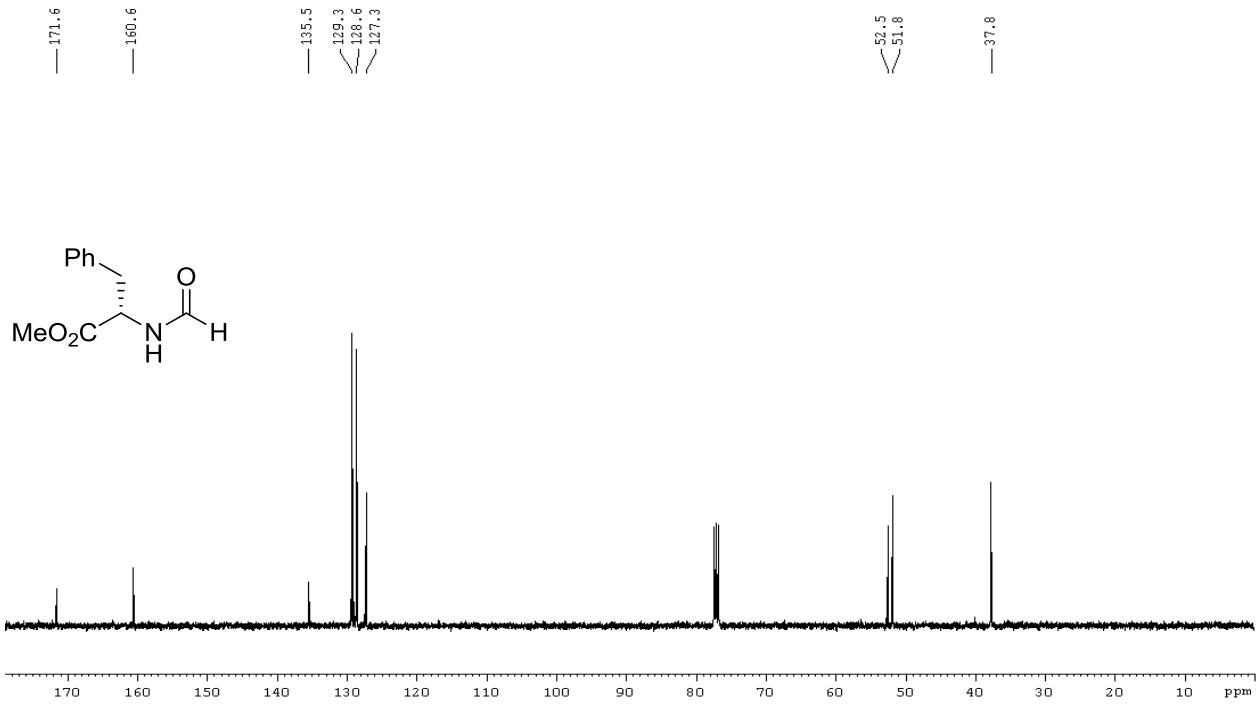
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8b**.



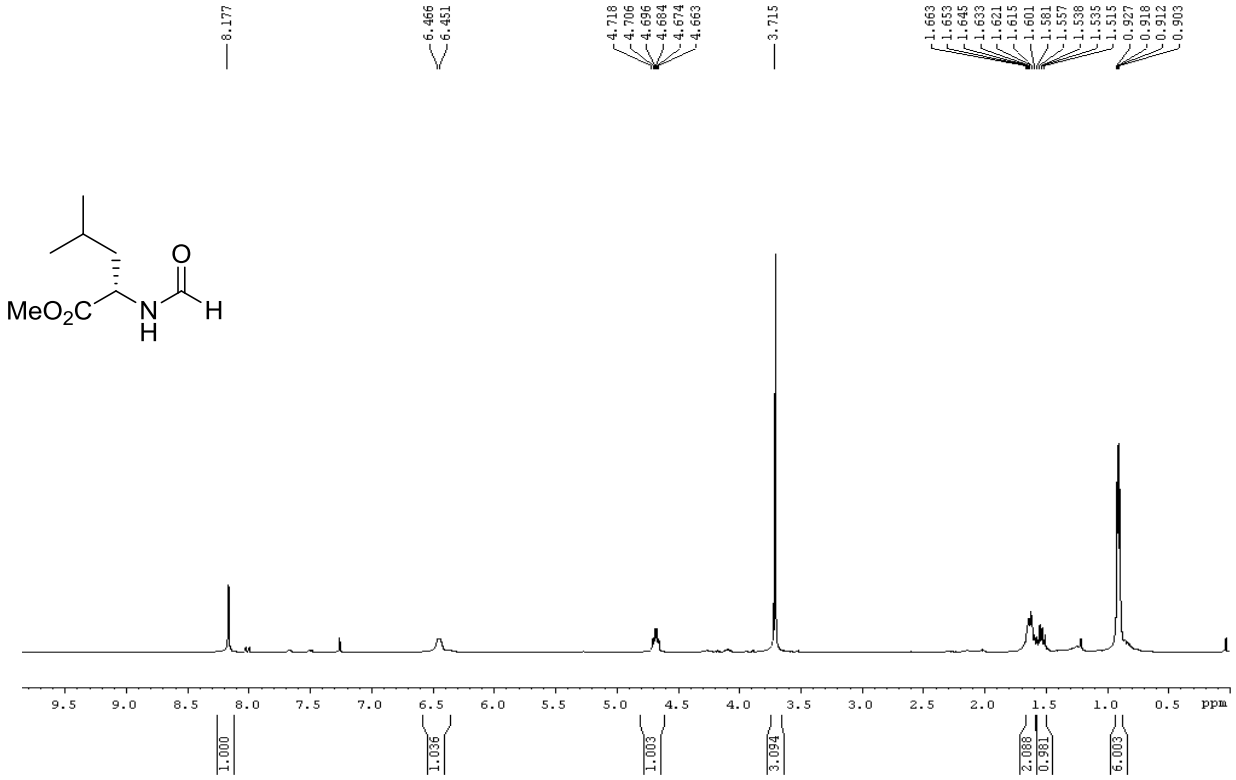
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8c**.



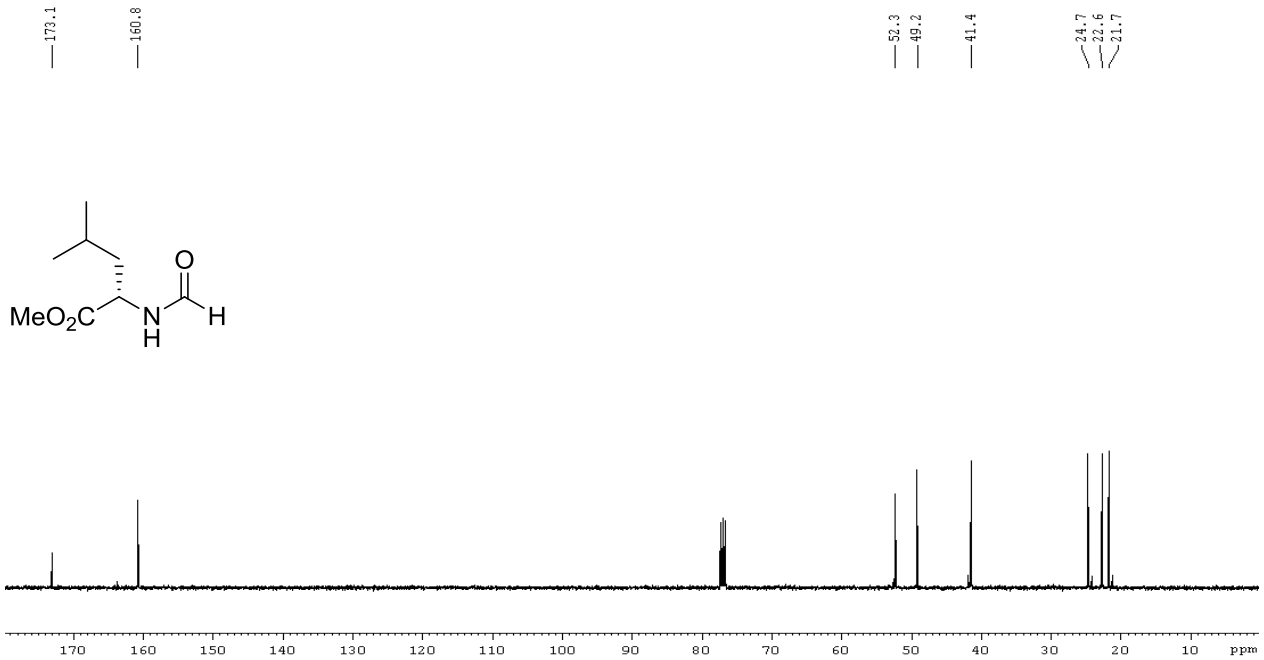
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8c**.



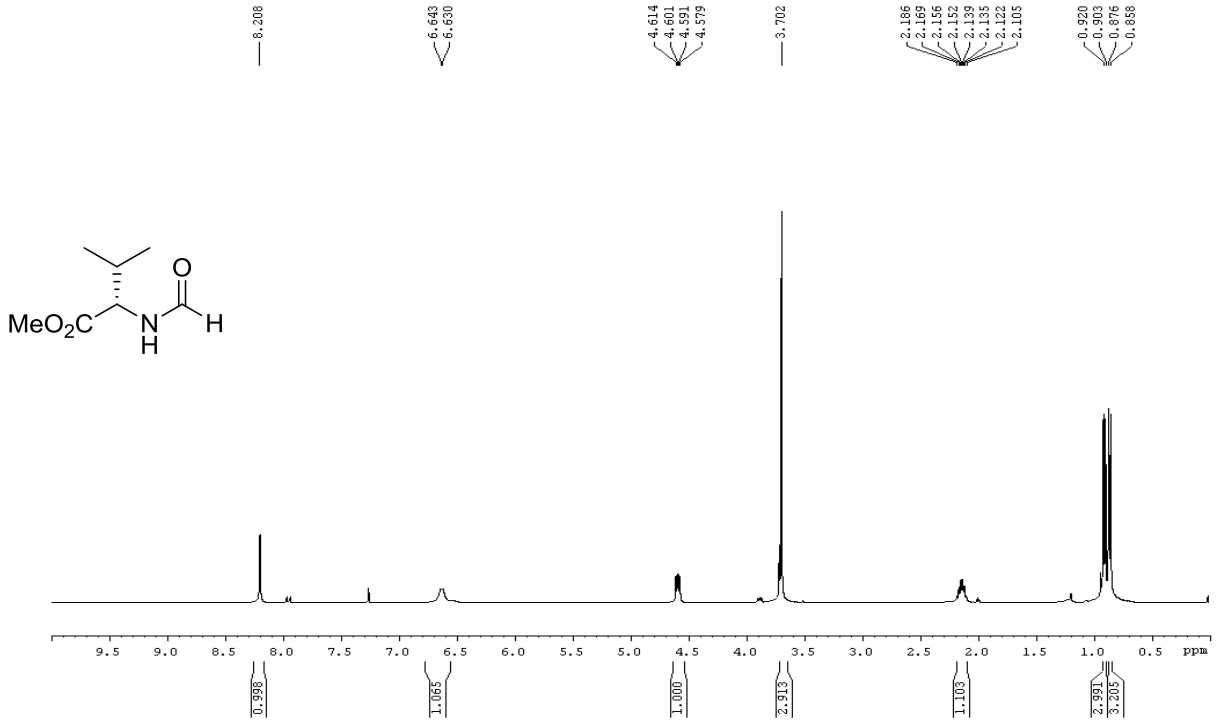
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8d**.



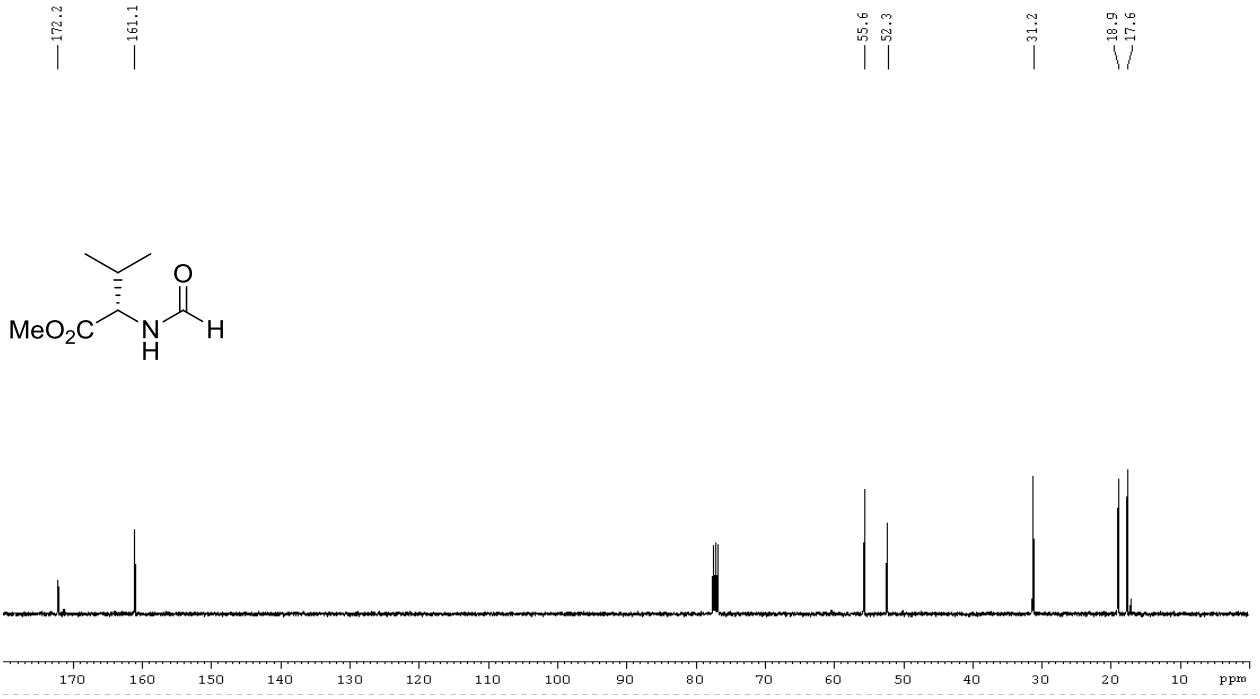
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8d**.



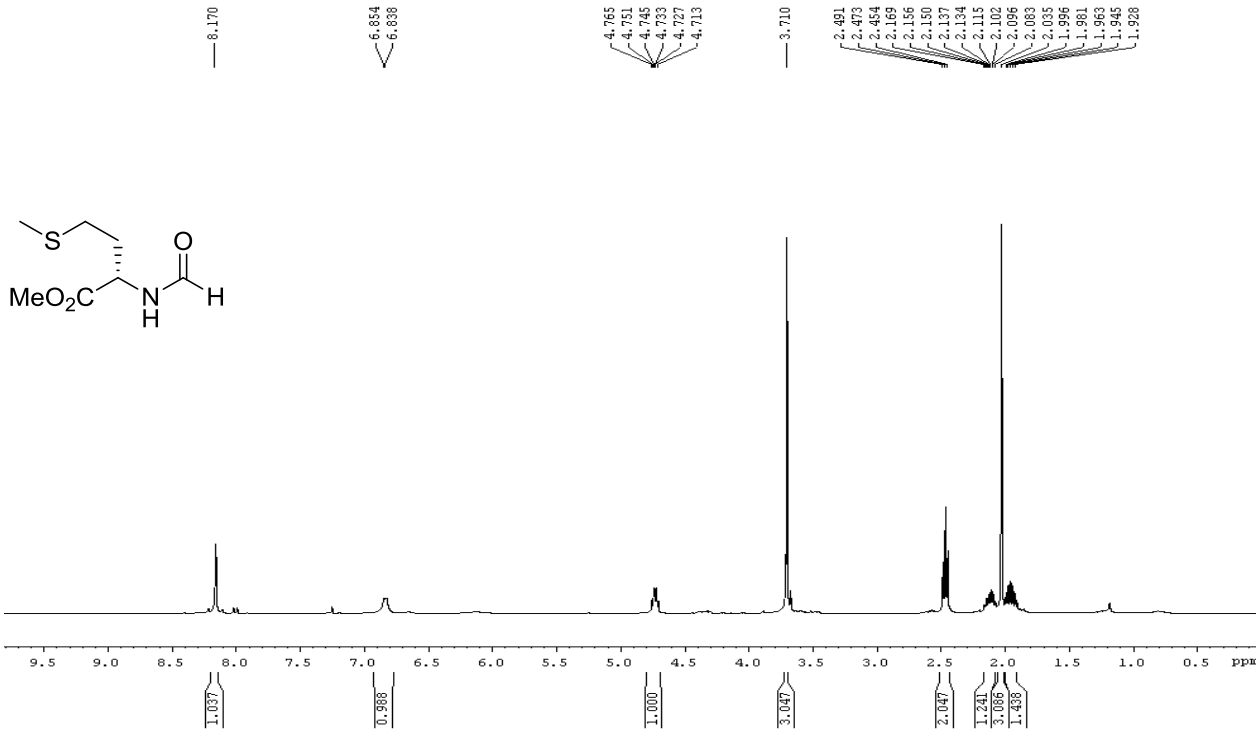
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8e**.



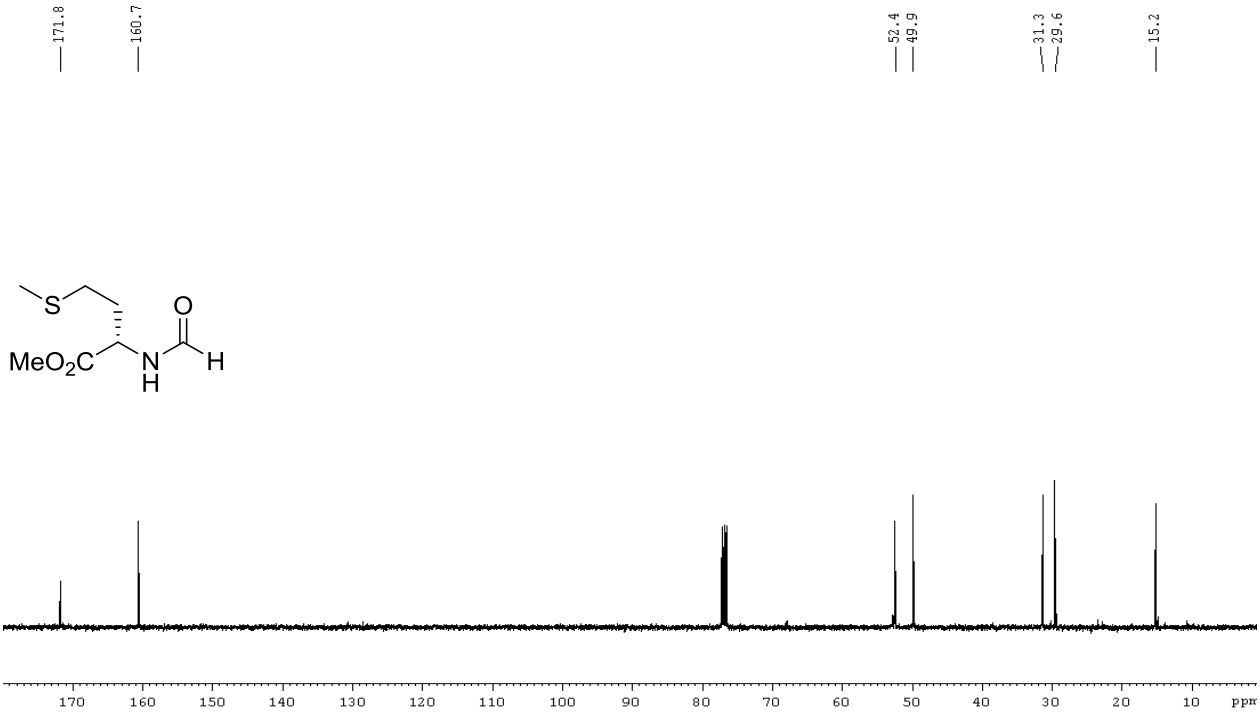
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8e**.



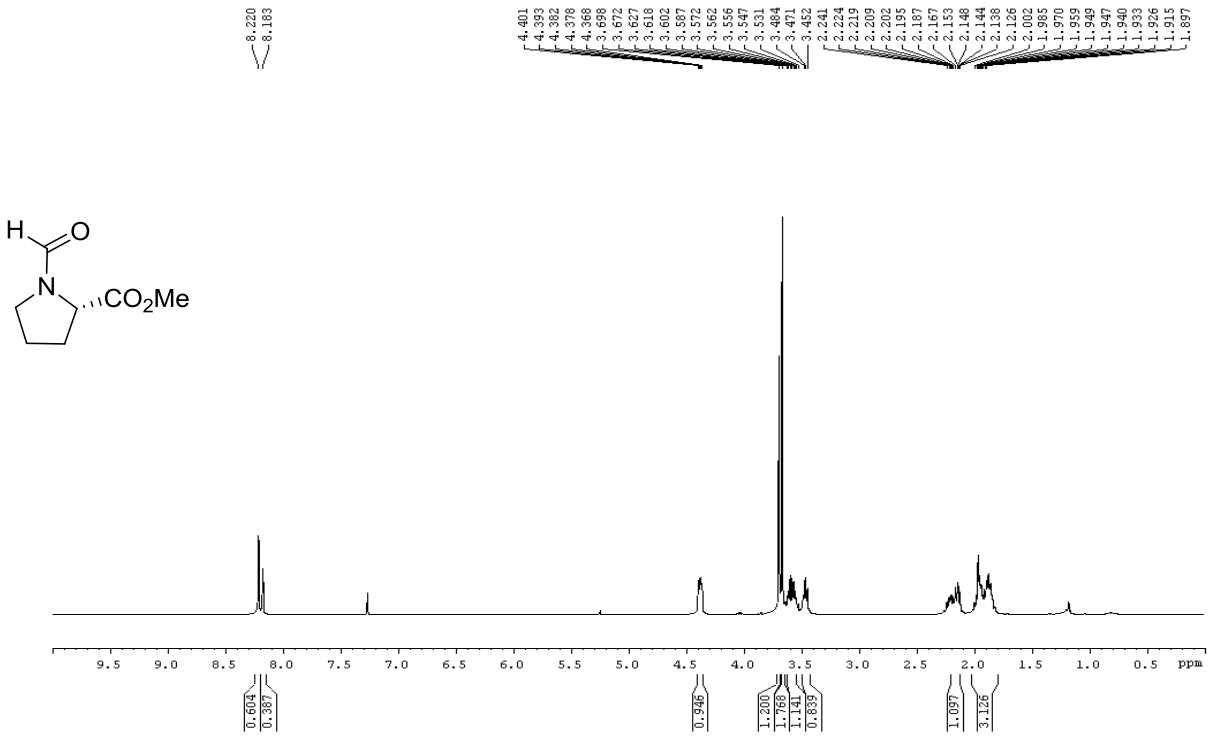
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8f**.



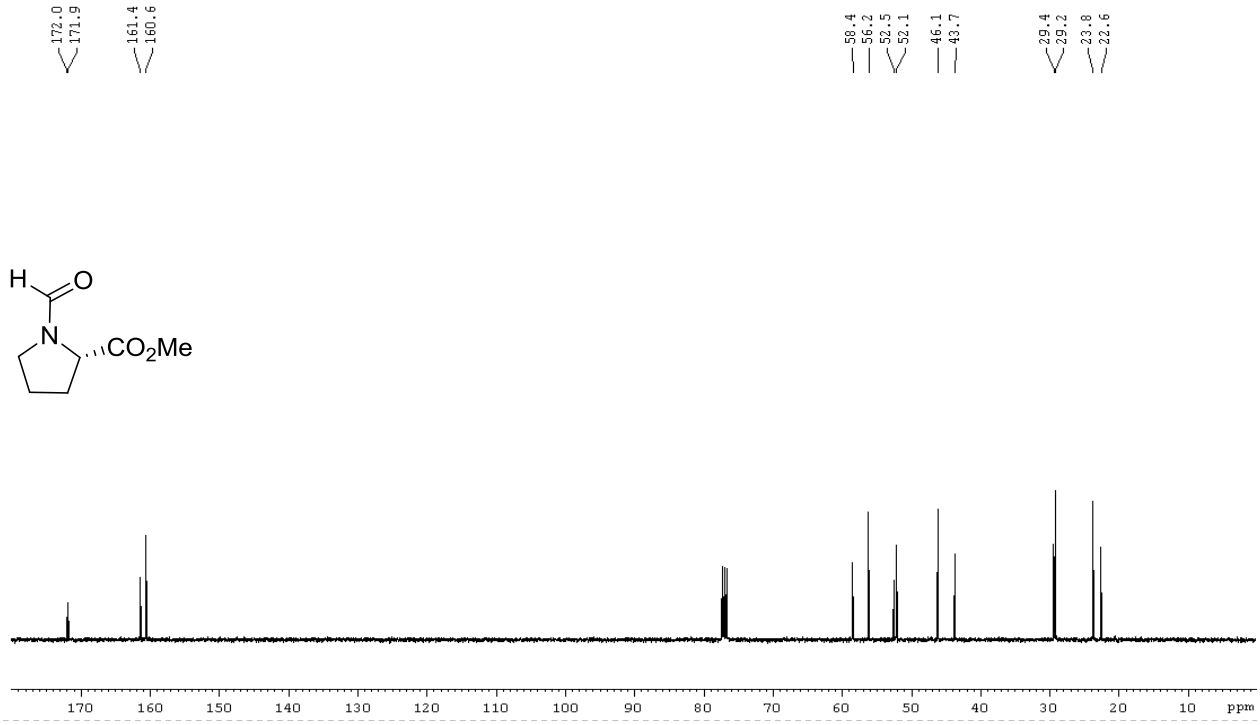
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8f**.



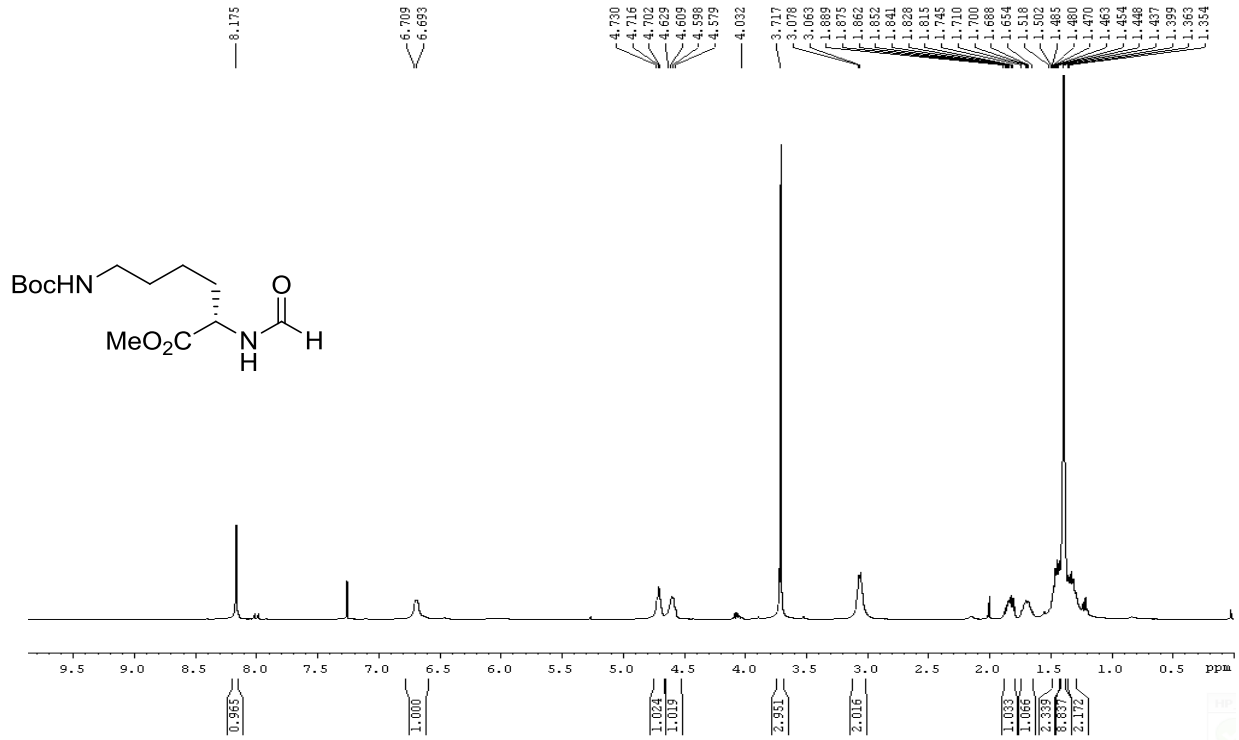
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8g**.



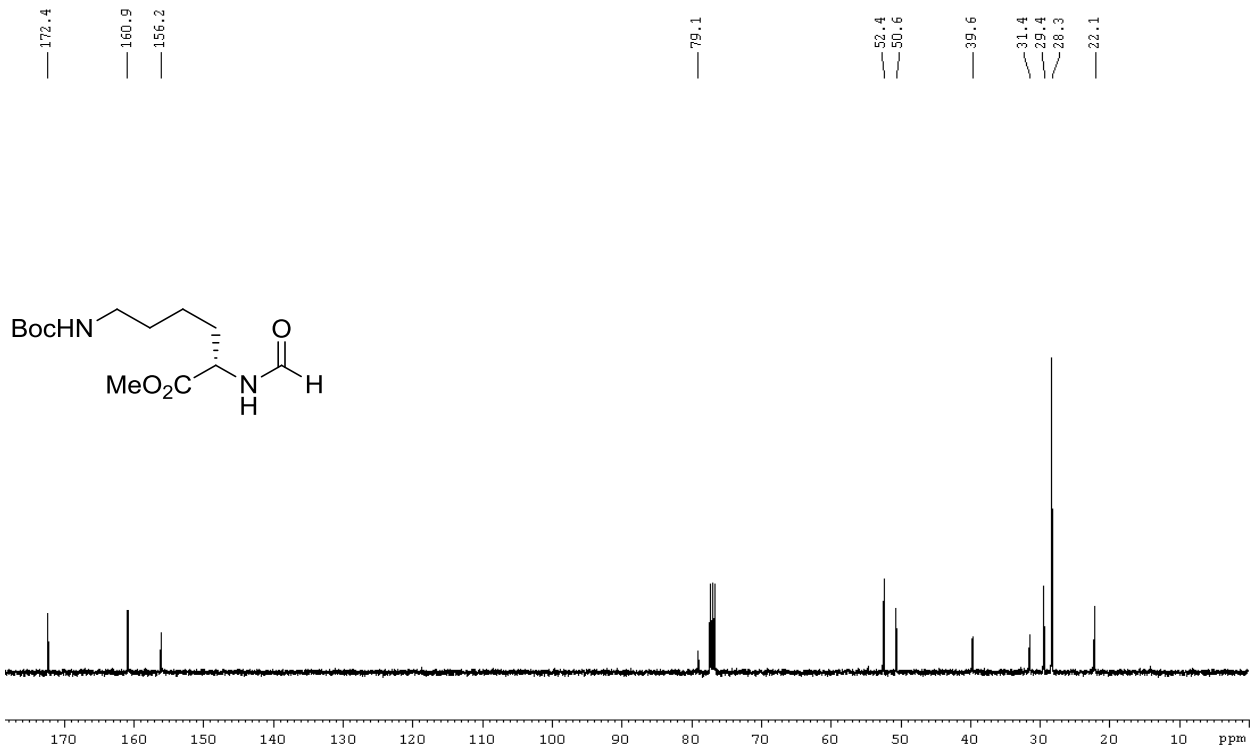
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8g**.



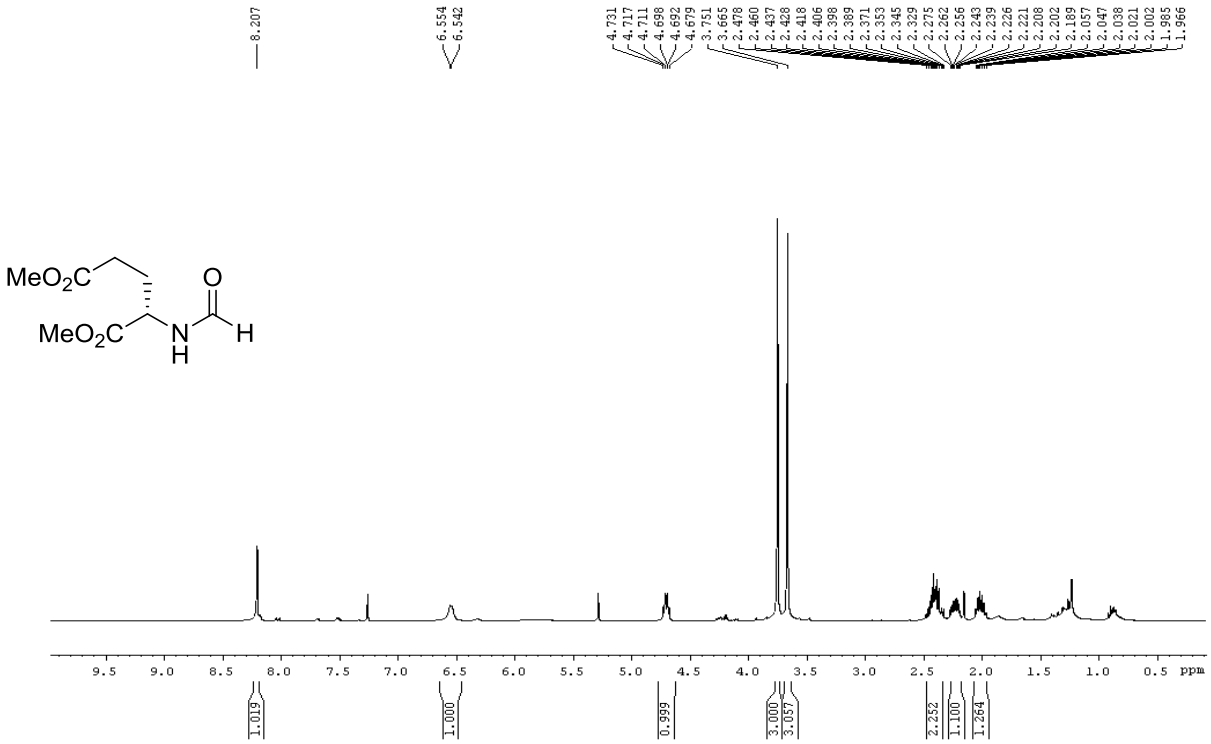
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8h**.



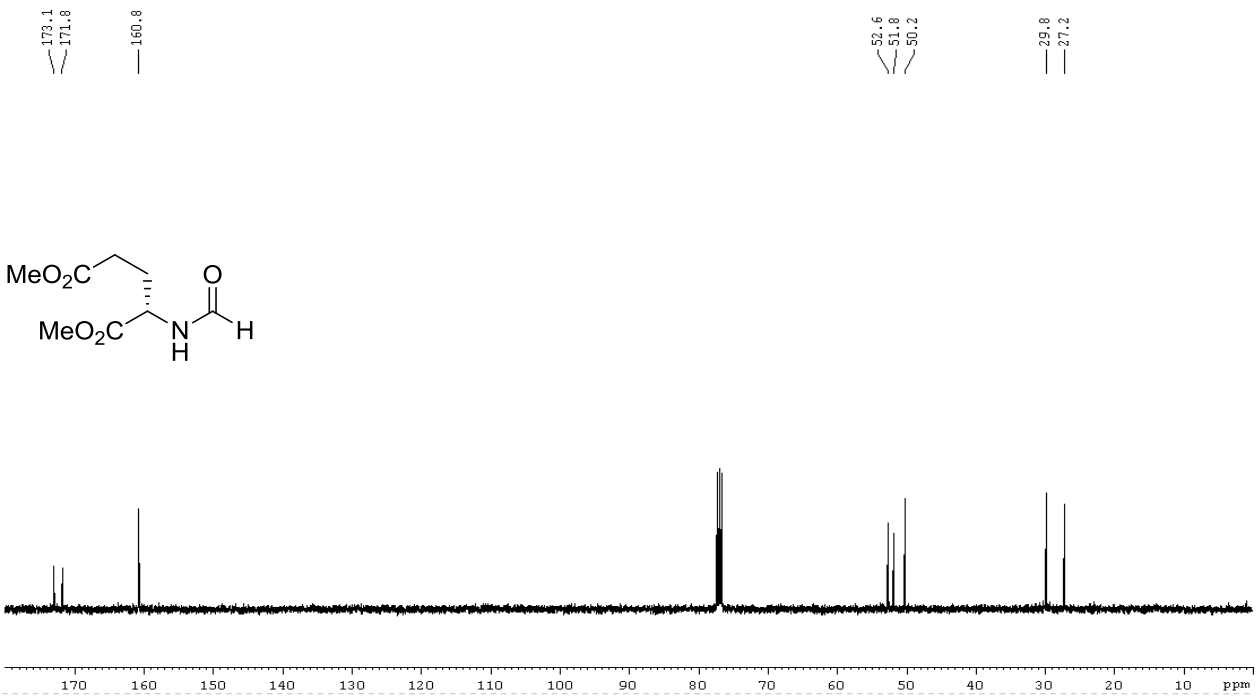
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8h**.



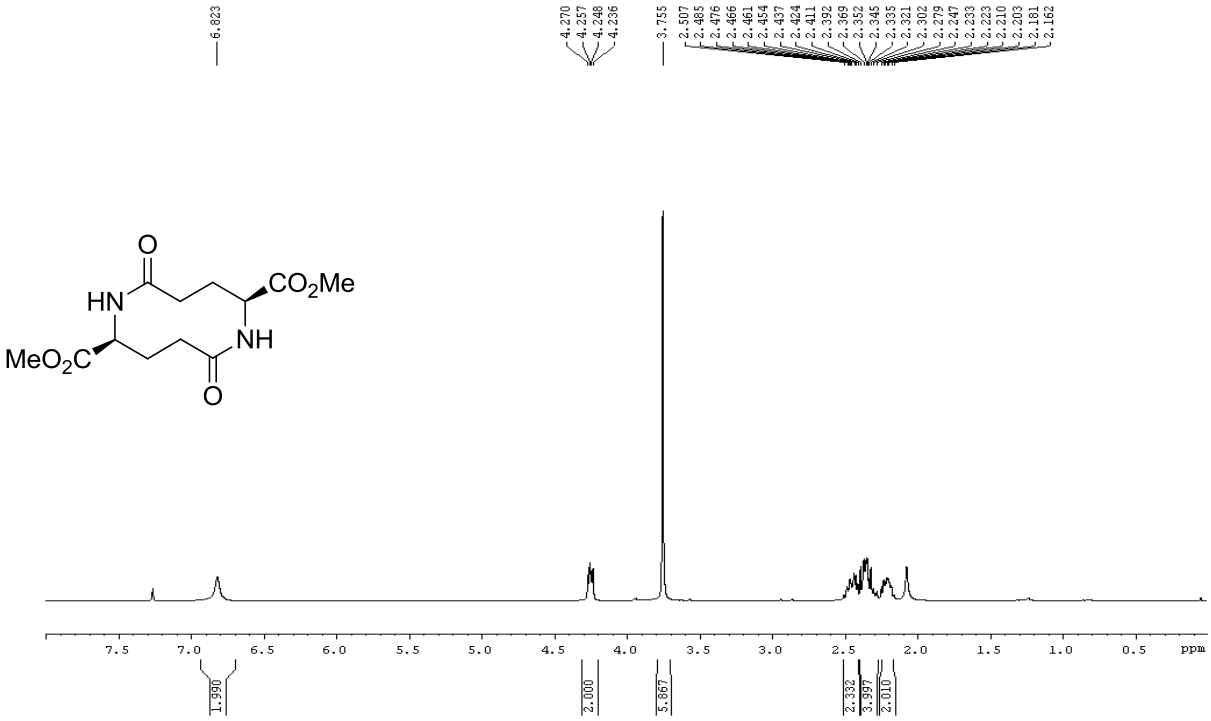
^{1}H NMR (400.0 MHz; $CDCl_3$) of **8i**.



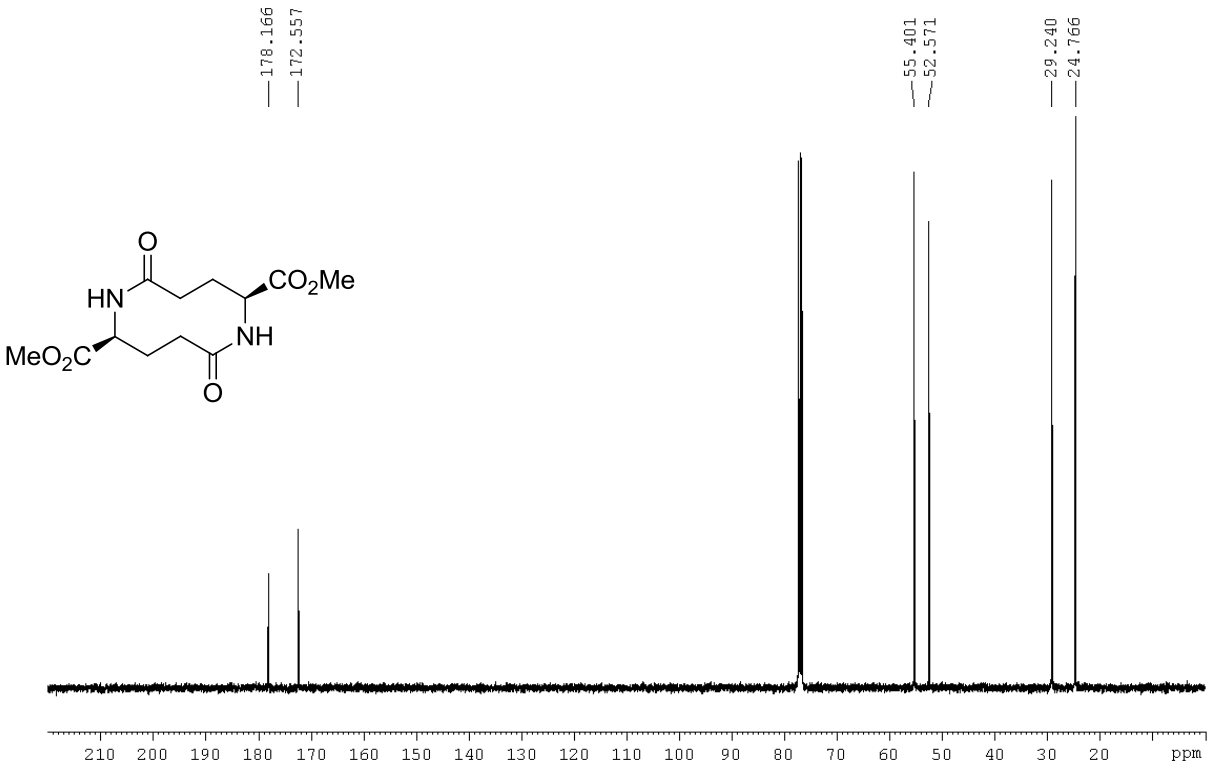
^{13}C NMR (100.0 MHz; $CDCl_3$) of **8i**.



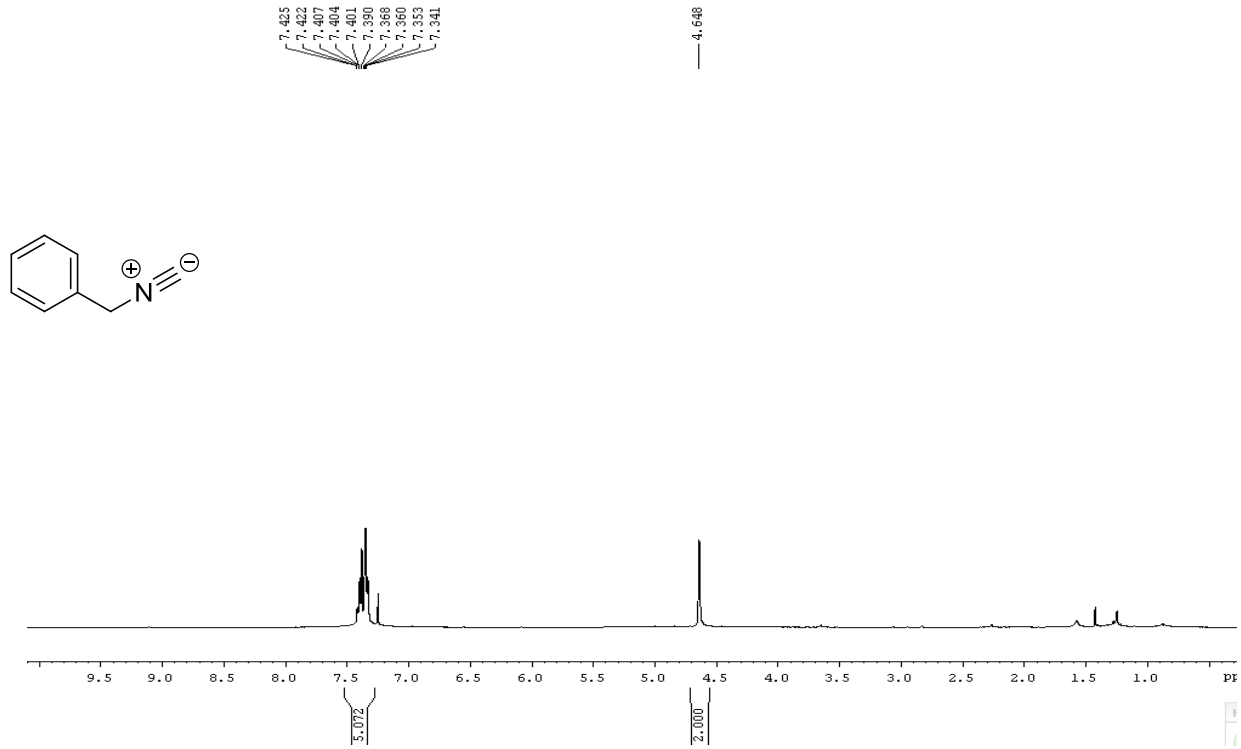
^{1}H NMR (400.0 MHz; $CDCl_3$) of **9**



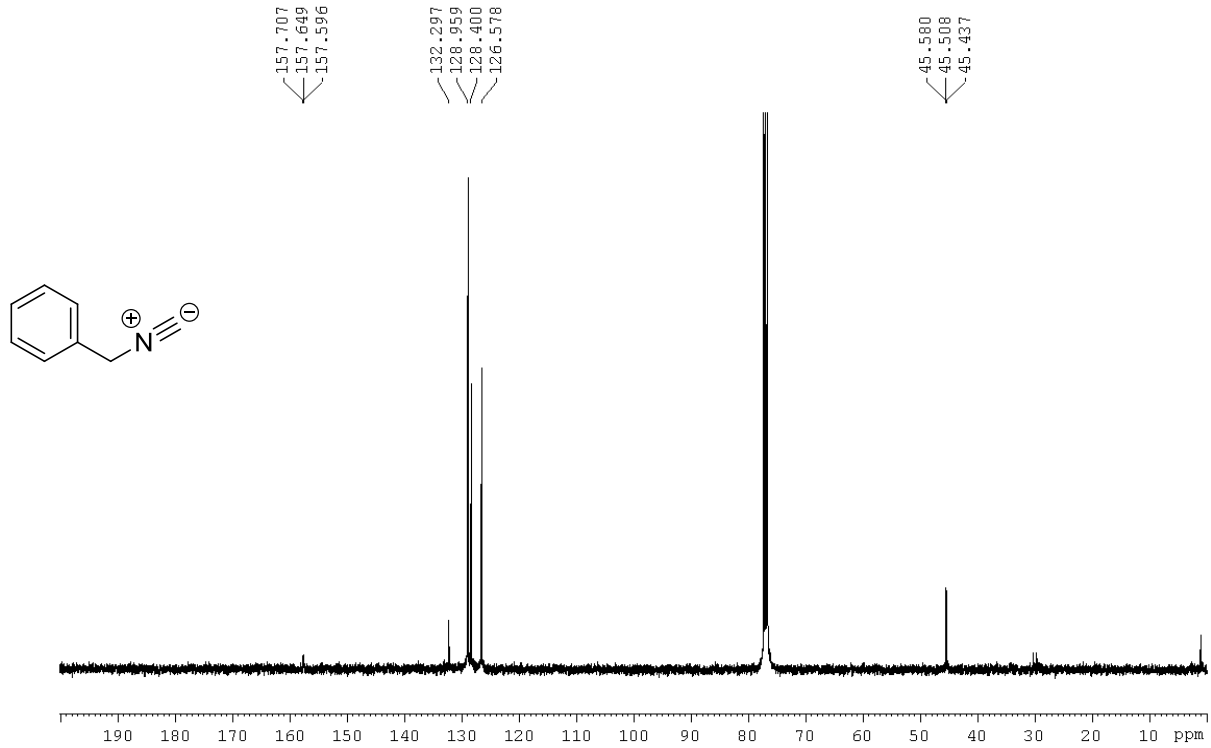
^{13}C NMR (100.0 MHz; $CDCl_3$) of **7**.



^{1}H NMR (400.0 MHz; $CDCl_3$) of **10**

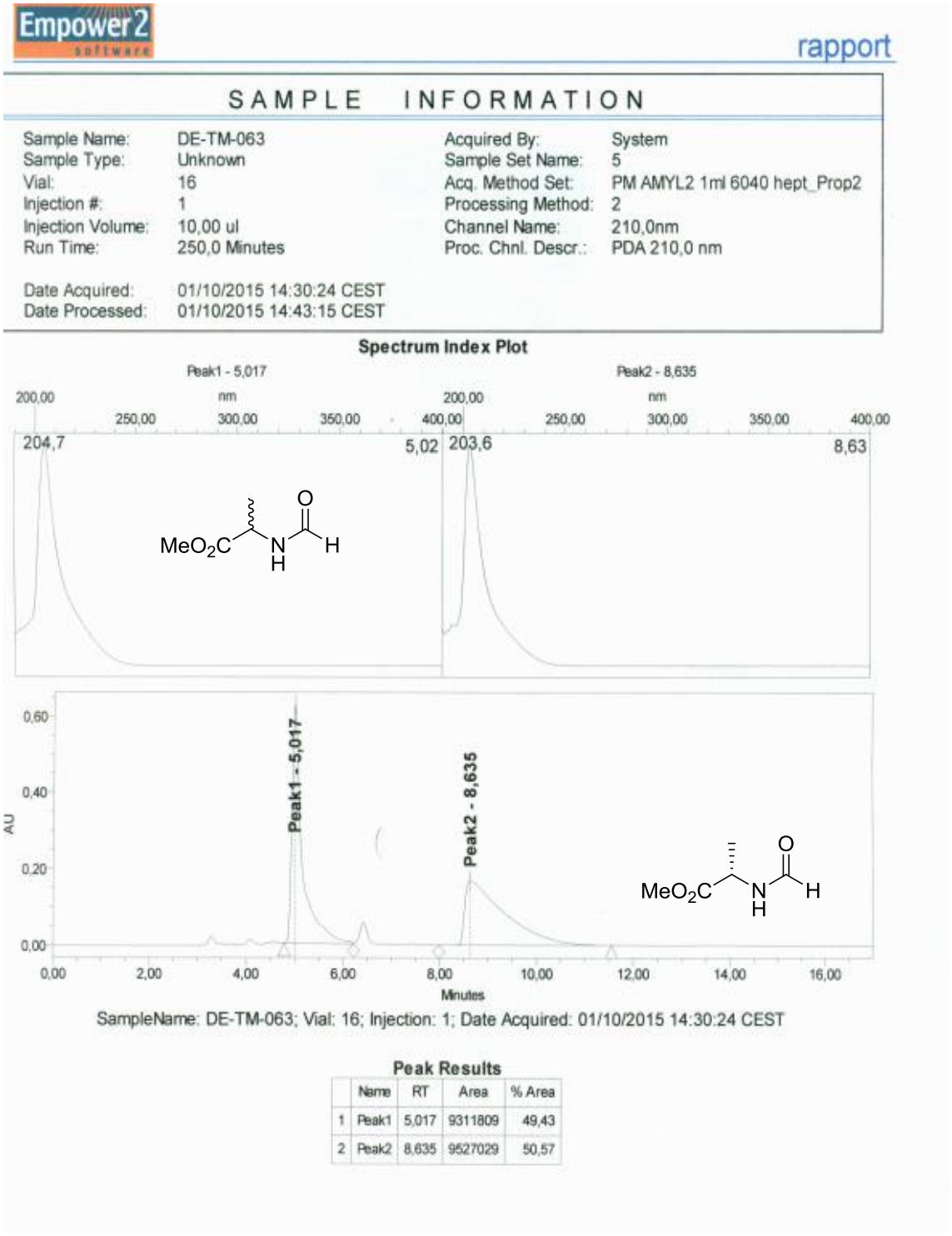


^{13}C NMR (100.0 MHz; $CDCl_3$) of **9**.

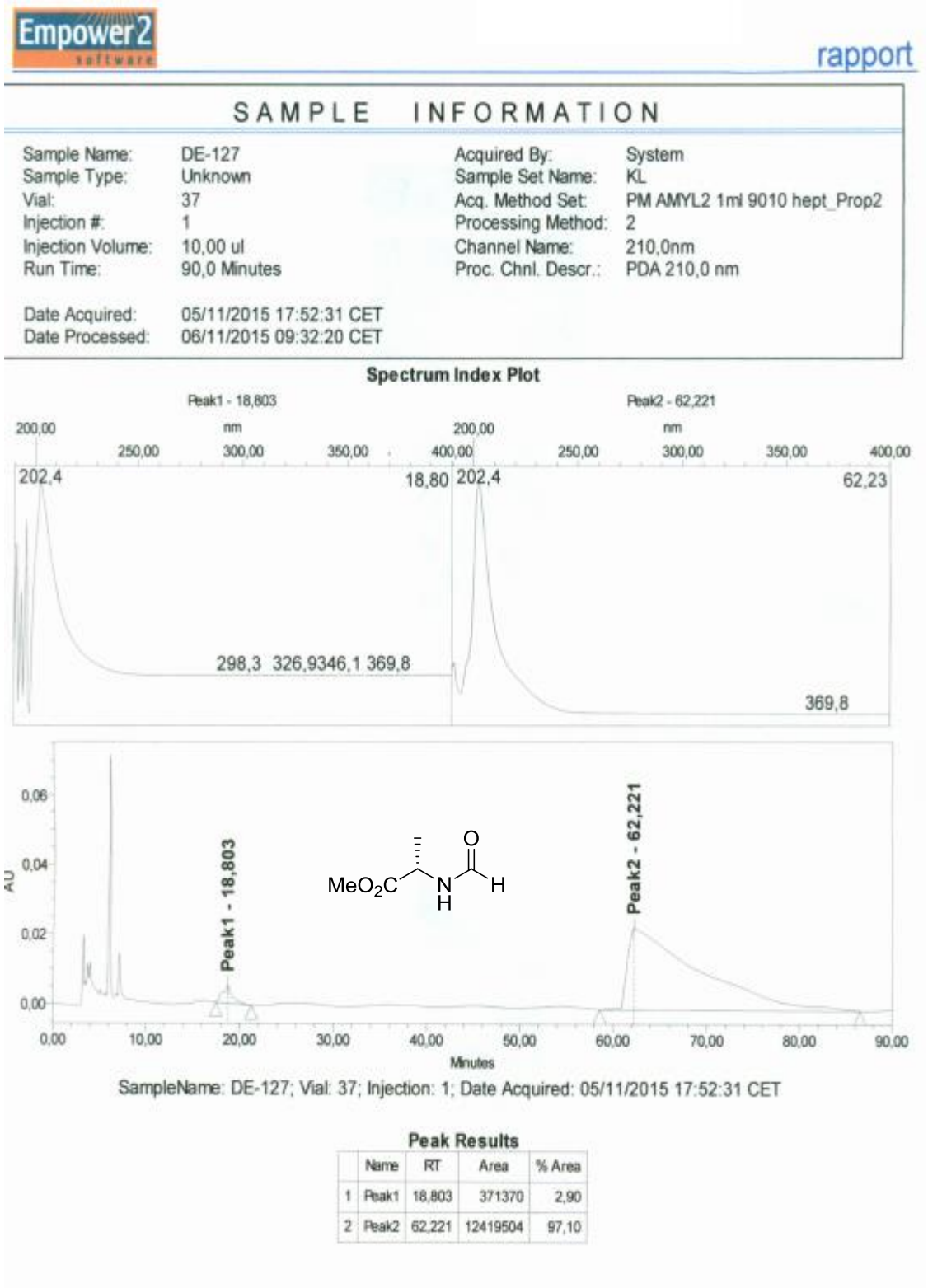


9. HPLC Spectra

Racemic-methyl-*N*-formyl-alinate **8b**



(*S*)-Methyl-*N*-formylalinate **8b** (Procedure **B**, $HCONH_2$ at 45 °C)



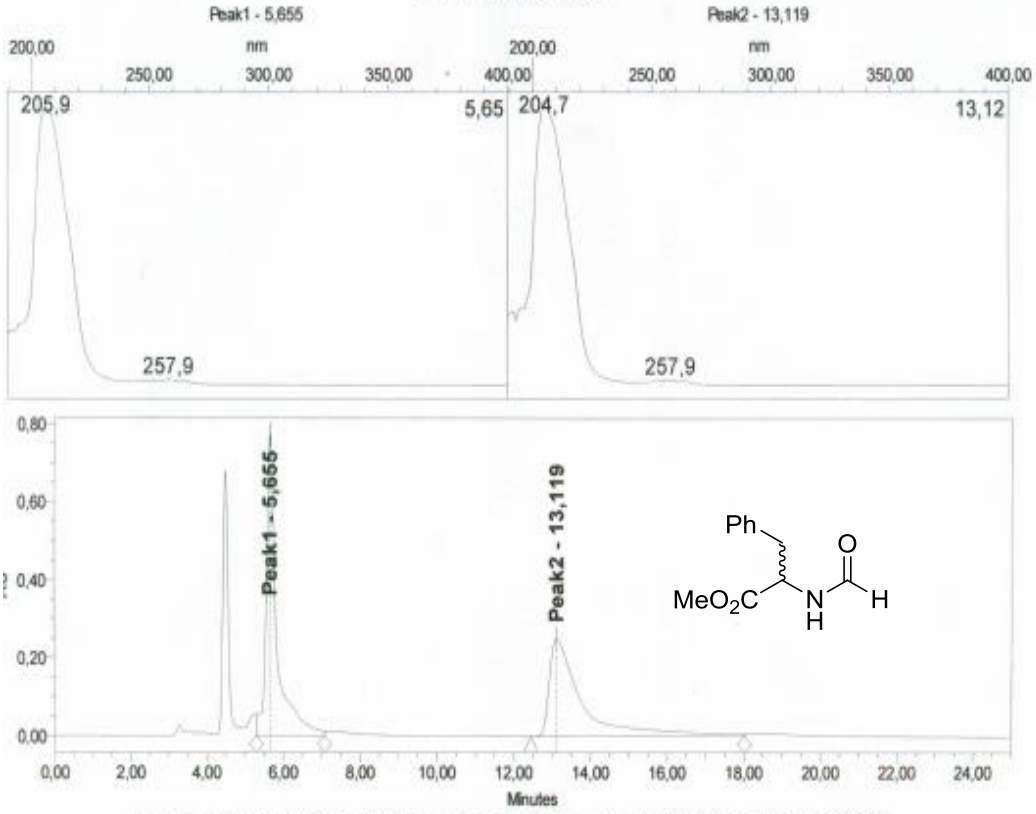
Rac-Methyl-*N*-formylphenylalinate

Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	DE-034	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	9	Acq. Method Set:	PM AMYL2 1ml 5050 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	240,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	02/09/2015 14:26:46 CEST		
Date Processed:	02/09/2015 15:29:13 CEST		



SampleName: DE-034; Vial: 9; Injection: 1; Date Acquired: 02/09/2015 14:26:46 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	5,655	14870677	50,49
2	Peak2	13,119	14582701	49,51

(*S*)-Methyl-*N*-formylphenylalinate **8c** (Procedure **B**, $HCONH_2$ at 45 °C)

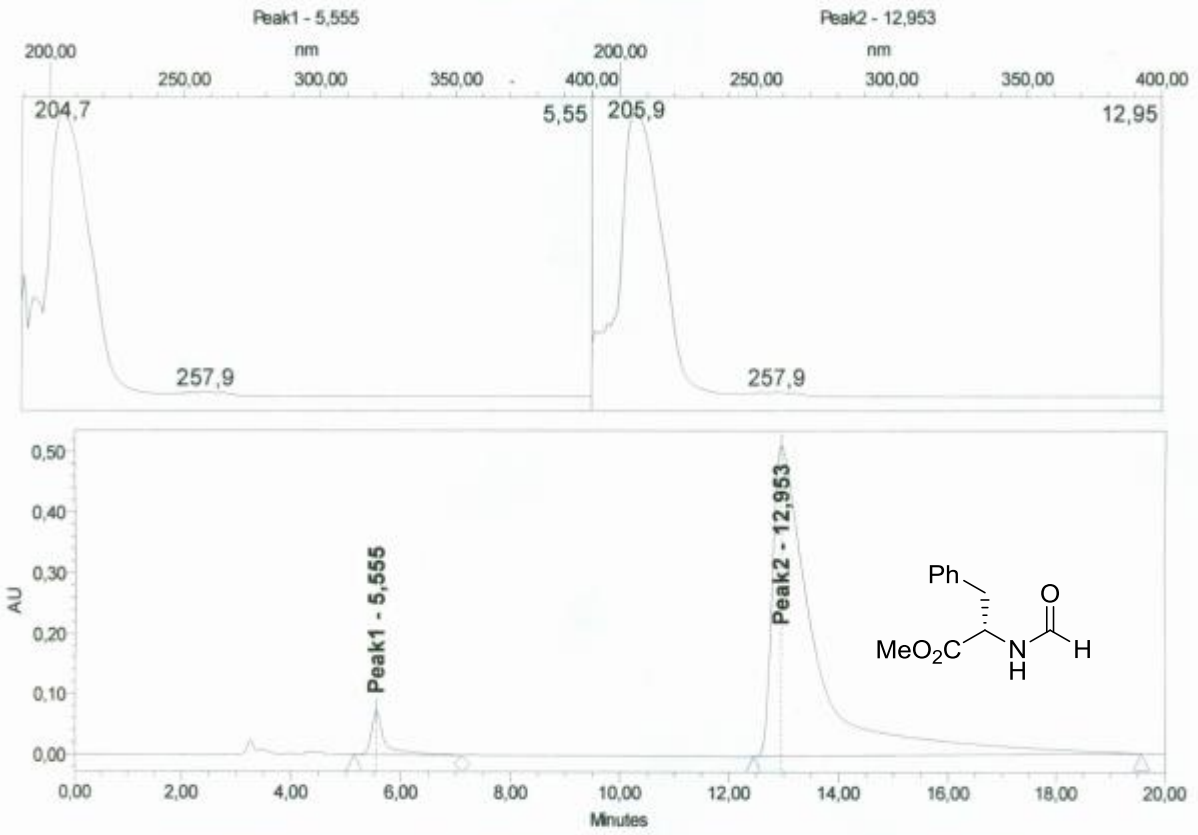
Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	DE-129	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	KL
Vial:	36	Acq. Method Set:	PM AMYL2 1ml 5050 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	20,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	05/11/2015 17:11:36 CET		
Date Processed:	06/11/2015 09:31:34 CET		

Spectrum Index Plot



SampleName: DE-129; Vial: 36; Injection: 1; Date Acquired: 05/11/2015 17:11:36 CET

Peak Results

	Name	RT	Area	% Area
1	Peak1	5,555	1215756	4,21
2	Peak2	12,953	27647722	95,79

Rac-Methyl-*N*-formylvalinate

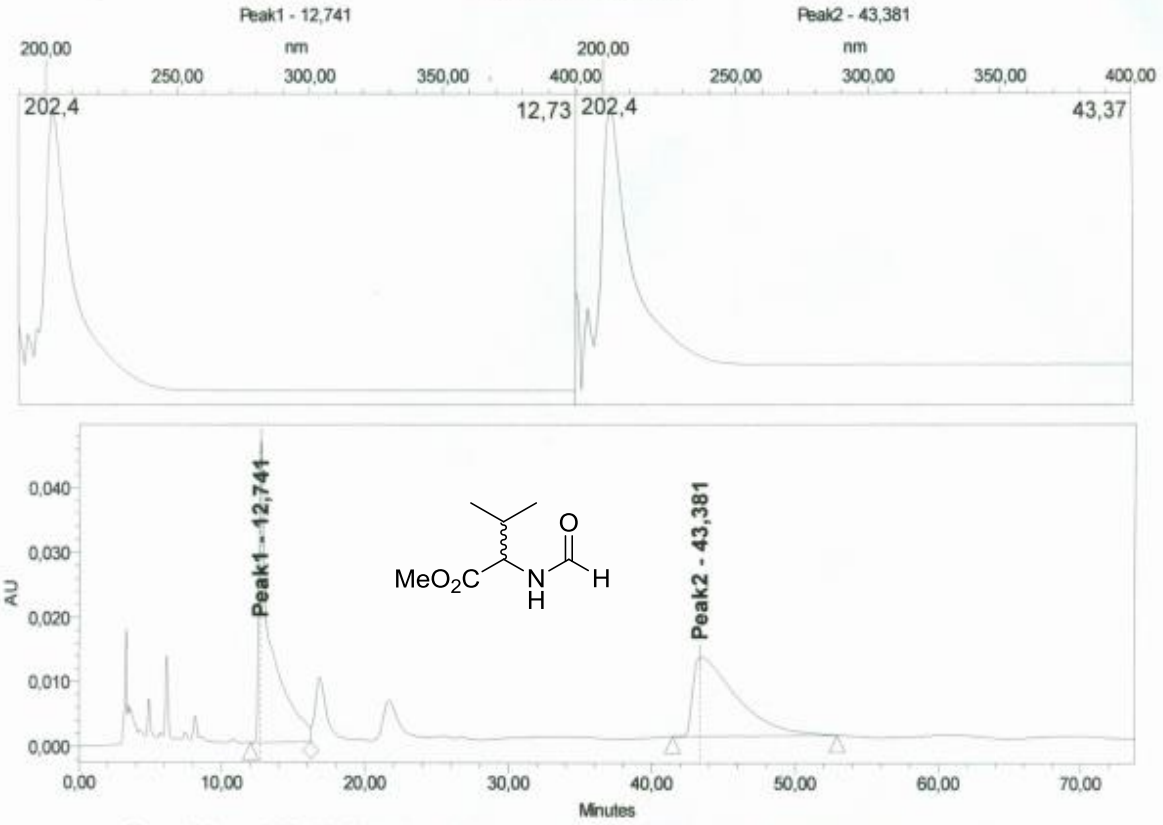
Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	DE-TM-067	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	26	Acq. Method Set:	PM AMYL2 1ml 9010 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	240,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	20/10/2015 14:37:54 CEST		
Date Processed:	21/10/2015 14:17:41 CEST		

Spectrum Index Plot



SampleName: DE-TM-067; Vial: 26; Injection: 1; Date Acquired: 20/10/2015 14:37:54 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	12,741	2616951	50,24
2	Peak2	43,381	2591644	49,76

(*S*)-Methyl-*N*-formylvalinate **8e** (Procedure **B**, $HCONH_2$ at 45 °C)

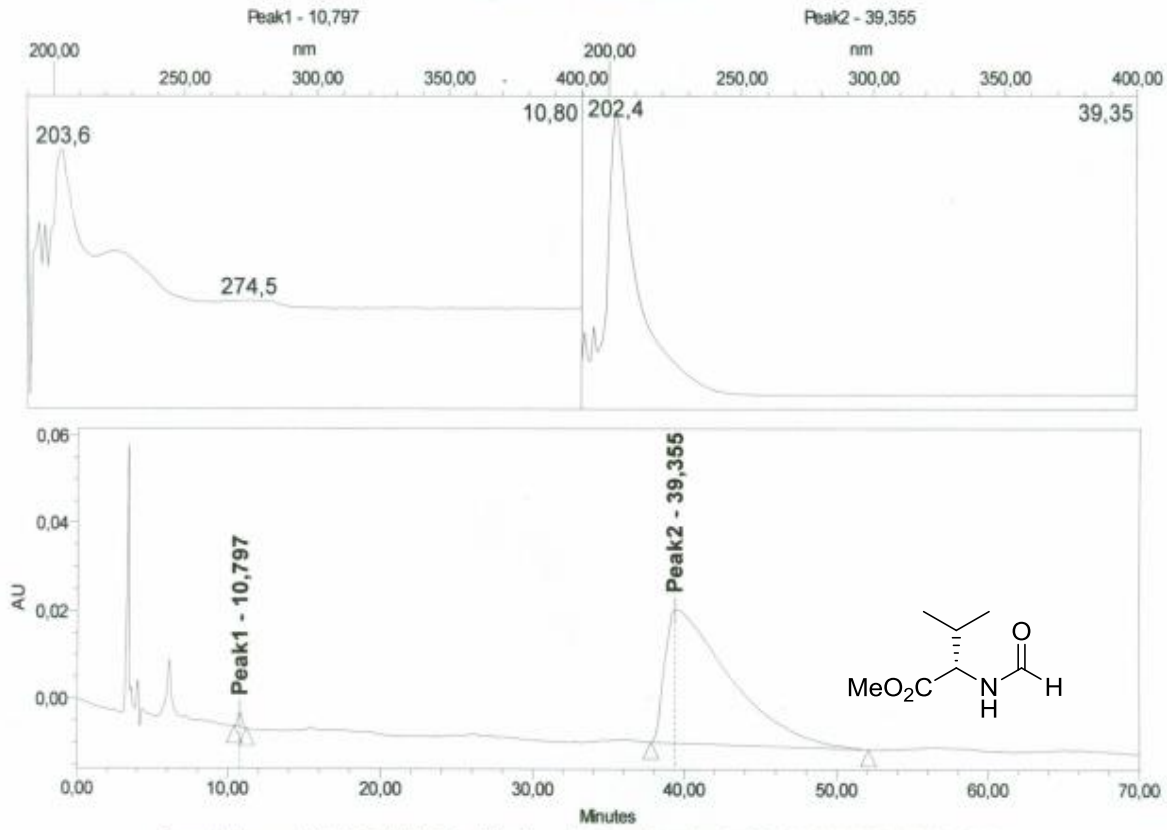
Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	DE-132	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	T
Vial:	38	Acq. Method Set:	PM AMYL2 1ml 9010 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	40,00 ul	Channel Name:	210,0nm
Run Time:	70,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	06/11/2015 09:53:09 CET		
Date Processed:	06/11/2015 10:46:47 CET		

Spectrum Index Plot



SampleName: DE-132; Vial: 38; Injection: 1; Date Acquired: 06/11/2015 09:53:09 CET

Peak Results

	Name	RT	Area	% Area
1	Peak1	10,797	64149	0,71
2	Peak2	39,355	9009750	99,29

Rac-Methyl-*N*-formylmethioninate

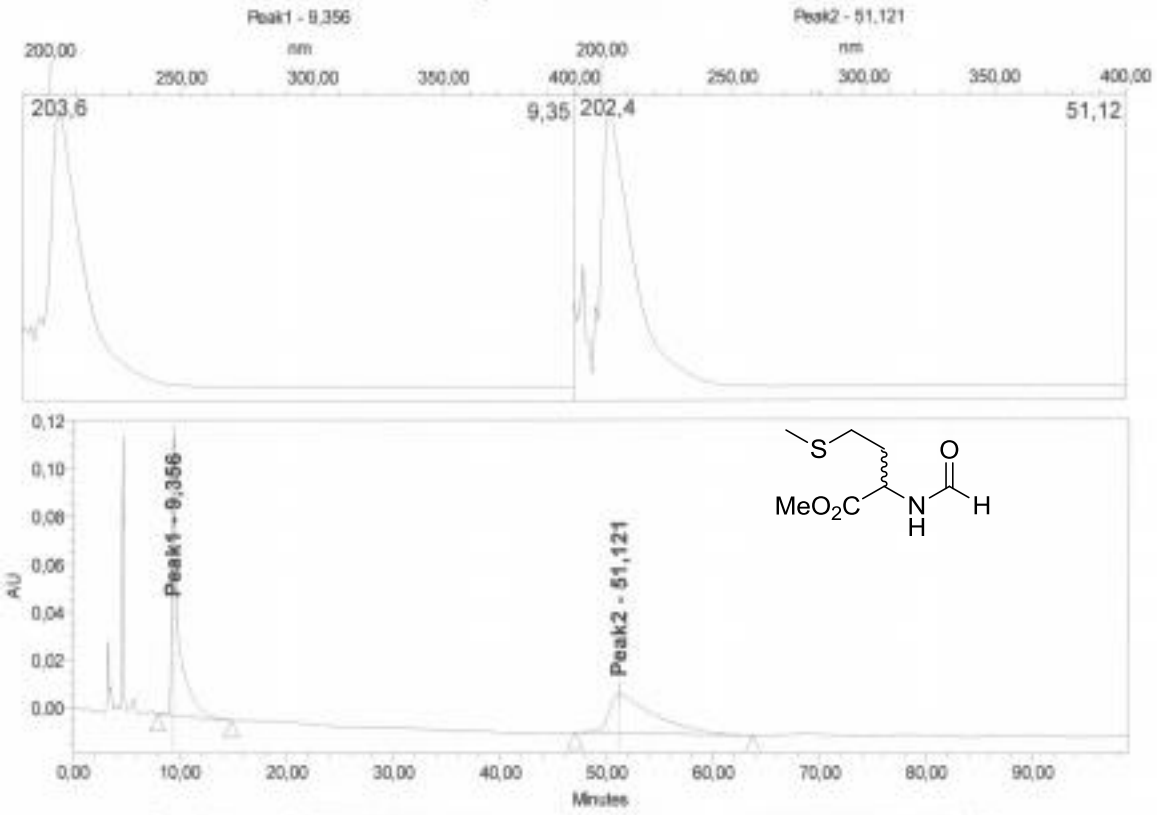
Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	DE TM 73	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	T
Vial:	37	Acq. Method Set:	PM AMYL2 1ml 6040 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	230,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	17/11/2015 12:04:10 CET		
Date Processed:	18/11/2015 10:38:30 CET		

Spectrum Index Plot



SampleName: DE TM 73; Vial: 37; Injection: 1; Date Acquired: 17/11/2015 12:04:10 CET

Peak Results

	Name	RT	Area	% Area
1	Peak1	9,356	4791117	50,25
2	Peak2	51,121	4744062	49,75

(*S*)- Methyl-*N*-formylmethioninate **8f** (Procedure **B**, $HCONH_2$ at 45 °C)