Supporting Information for:

Catalytic Chemical Amide Synthesis at Room Temperature: One More Step Towards Peptide Synthesis

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Contents:

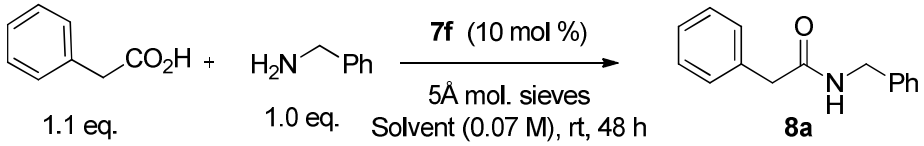
1. General Experimental Procedures for the Investigation of the Several Parameters in the Boronic Acid Catalyzed Amide Bond Formation

After identifying the optimal catalyst, (2-(thiophen-2-ylmethyl)phenyl)boronic acid **7f**, we proceeded to optimize the other reaction parameters including solvent, catalyst loading, dehydrating agent and its activation method using a model amidation reaction between benzyl amine and phenyl acetic acid according to the general procedure **D** for boronic acid catalyzed amidation.

1.1. Solvent screening

The optimal reaction solvent is dependent on the particular nature of the substrates employed. It is therefore preferable to optimize any new combination of substrates using different solvents (Table 1).

Table 1 : Solvent screening using catalyst **7f**.[a]



Entry	Solvent	Isolated Yield (%)
1	acetonitrile	0
2	toluene	36
3	chloroform	0
4	tetrahydrofuran	2
5	**dichloromethane**	**99**
6	1,2-dichloroethane	76
7	DMF	24
8	fluorobenzene	53.3
9	DCM/1,2-DCE 1:1	48

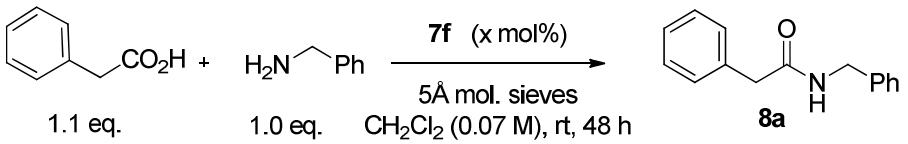
[a] Reaction conditions: phenyl acetic acid (75 mg, 0.55 mmol), boronic acid **7f** (10.9 mg, 0.05 mmol) and the amine (55 μL, 0.50 mmol) were stirred at room temperature (25 °C) for 48 h in dry solvent containing the powdered 5Å mol. sieves (1 g).

With the new catalyst **7f** and the chosen model substrates, CH_2Cl_2 appeared to be the best solvent (entry 5). Toluene (entry 2) and DMF (entry 7) provided low yields whereas no conversion was attained using THF (entry 4), Chloroform (entry 3) and acetonitrile (entry 1). Moderate yields were obtained using fluorobenzene (entry 8) and 1,2-DCE (entry 6). No further improvement was attained using a mixture DCM/1,2-DCE 1:1 (entry 9).

1.2. Optimization of catalyst loading

Optimization of the catalyst loading was carried out using the reaction between benzyl amine and phenyl acetic acid as a model reaction, **7f** as the catalyst, CH_2Cl_2 as the solvent and 5Å powdered molecular activated in Kugelrohr as the drying agent according to the general procedure **D** for boronic acid catalyzed amidation (Table 2).

Table 2: Optimization of the catalyst loading using catalyst **7f**.[a]



Entry	mol% of 7f	Isolated yield (%)
1[b]	2.5	36
2	5	53
3	7	62
4	**10**	**99**
5	20	100

[a] Reaction conditions: Phenyl acetic acid (75 mg, 0.55 mmol), boronic acid **7f** (2.5 to 10 mol%) and the benzyl amine (55 µL, 0.50 mmol) were stirred at room temperature (25 °C) for 48 h in dry CH_2Cl_2 containing the powdered 5Å mol. Sieves (1 g). [b] Reflux at 45 °C.

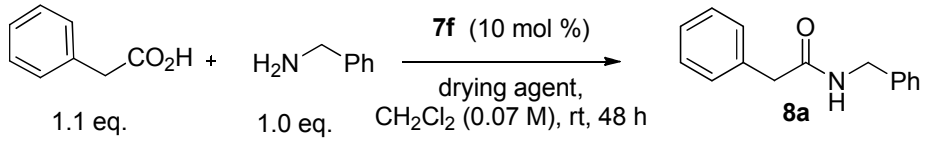
As shown by Table 2, catalyst loadings of 5 and 7 mol% provided moderate yields of the amide product **8a** (entries 2 and 3) whereas a 10 mol% catalyst loading resulted in excellent yield of amide **8a** (entry 4) at room temperature. Increasing the catalyst loading did not lead to any improvements in terms of the reaction time.

1.3. Dehydrating agent screening and its activation method

Another crucial factor in the boronic acid catalyzed amidation is the removal of water from the reaction medium as it inhibits the formation of the active reaction intermediates (entry1, Table 3). Screening of the different drying agents was performed using the reaction between

benzyl amine and phenyl acetic acid as a model reaction, **7f** as the catalyst (10 mol %), CH_2Cl_2 as the solvent and 1g of the dehydrating agent according to the general procedure **D** for boronic acid catalyzed amidation (Table 3).

Table 3: Comparison in the isolated yield of the amide product using different dehydrating agents.[a]



Entry	Drying agent	Activation method	Isolated Yield (%)
1	none	-	0
2	pwd lab grade $MgSO_4$	µW at P_{max} 30 min	0
3	pwd anhydrous $MgSO_4$	Kugelrohr 3 h at 250 °C	<5
4[b]	B_2O_3	-	28
5[b]	B_2O_3 without **7f**	-	23
6	pwd 4Å MS	µW at P_{max} 30 min	43
7	pwd 4Å MS	Kugelrohr 3 h at 250 °C	50
8	pwd 5Å MS	µW at P_{max} 30 min	0
9	**pwd 5Å MS**	**Kugelrohr 3 h at 250 °C**	**99**
10[b]	pwd 5Å MS / Soxhlet	Kugelrohr 3 h at 250 °C	85

[a] Reaction conditions: Phenyl acetic acid (75 mg, 0.55 mmol), boronic acid **7f** (2.5 to 10 mol%) and the benzyl amine (55 µL, 0.50 mmol) were stirred at room temperature (25 °C) for 48 h in dry CH_2Cl_2 containing the dehydrating agent (1g). [b] Reflux at 45 °C.

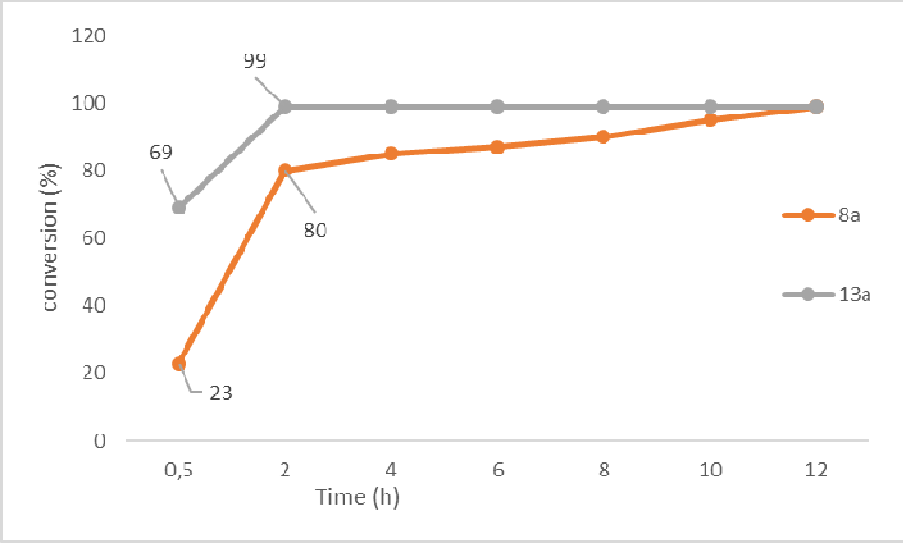
Screening of these different drying agents revealed that 5Å molecular sieves (activated powder) using Kugelrohr, ≈325 mesh particle size) was the most efficient dehydrating agent for this process with the possibility of their recycling (entry 10). 4Å molecular sieves activated either in Kugelrohr or microwave provided moderate yields (entries 6 and 7) while almost no conversion was attained with $MgSO_4$ (entries 2 and 3). B_2O_3 did not lead to any improvement in the yield where the same result was almost obtained in the presence or absence of the catalyst **7f** (entries 4 and 5).

The optimal reaction conditions were chosen to be 10 mol % of catalyst **7f**, 5Å powdered molecular sieves (1 g) activated in Kugelrohr, and CH_2Cl_2 as the solvent.

2. Studying the Kinetics of Catalyst **7f** with Two Different Carboxylic Acids

The progress of the reaction between the two carboxylic acids (phenylacetic acid and 4-methoxyphenylacetic acid) and benzylamine in the presence of the catalyst **7f** was monitored using 1,3,5-trimethoxybenzene as an internal standard. The results obtained are shown in figure 1.

Figure 1. Comparison between the rate constants of two different carboxylic acids where **8a** corresponds to the amide product resulting from the phenyl acetic acid and **13a** corresponds to the one formed using the *p*-methoxy phenyl acetic acid.



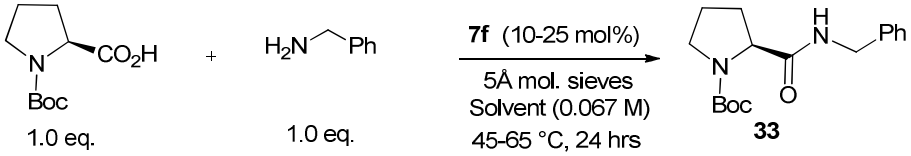
Title: Studying the % NMR yield of the amide products as a function of time.

This graph clearly shows that electron rich carboxylic acids are much more efficient providing a faster reaction compared to the phenyl acetic acid in the amide synthesis. Complete conversion was attained after just 2 hours using 4-methoxyphenylacetic acid (**13a**) while after 12 hrs with the phenylacetic acid (**8a**).

3. Optimization of the Amide Bond Formation using *N*- or *C*-protected Amino Acids in the Presence of Catalyst **7f**

In order to determine the optimal conditions for the coupling of one or two amino acids, a model reaction was carried out between (*S*)-N-Boc-proline and benzyl amine according to general procedure **E** for amide bond formation (Table 4).

Table 4. Optimization of reaction conditions for the direct amidation of amino acids.[a]



Entry	Solvent	Catalyst (mol %)	Temperature (°C)	Isolated yield (%)
1	CH_2Cl_2	10	65	10
2	PhF	10	45	26
3	PhF	10	65	57
4	PhF	25	45	45
5	**PhF**	**25**	**65**	**92**

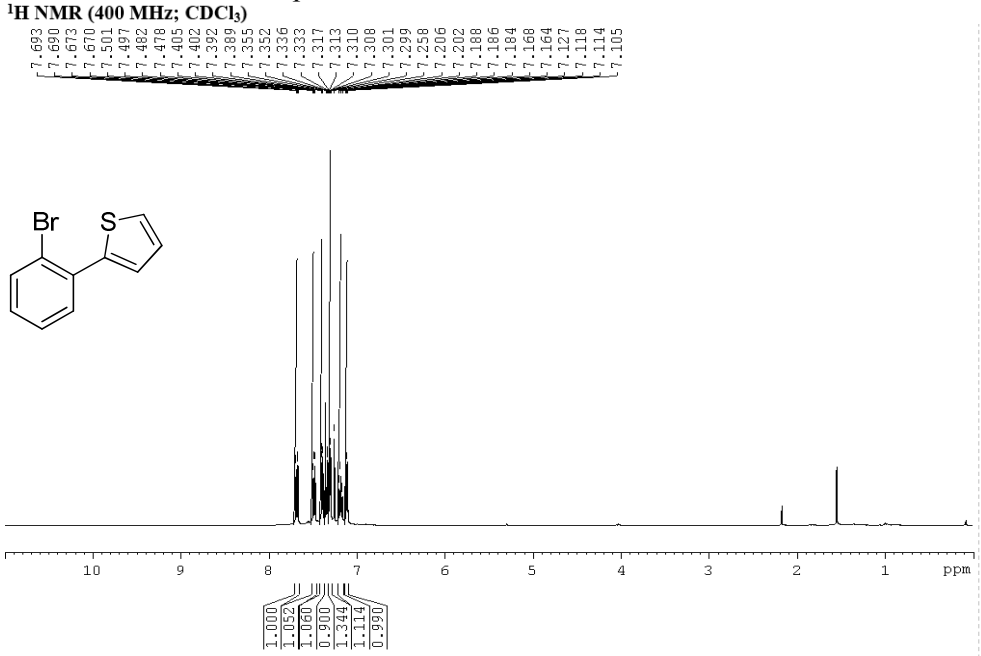
[a] Reaction conditions : (*S*)-N-Boc-proline (99 mg, 0.46 mmol), catalyst **7f** (10-25 mol%) and benzylamine (50.3 μL, 0.46 mmol) were stirred for 24 h containing the powdered 5Å mol. sieves (1 g).

As we have previously mentioned, non-polar solvents enhance the catalytic activity and tends to provide better azeotropic removal of water in the amidation reactions. Therefore, two non-polar solvents were tested. Fluorobenzene appeared to be the suitable solvent providing better solubilization of the starting Boc-proline and much higher yield of the desired amide **33** compared to CH_2Cl_2 (Table 1, Entries 1 and 2). In addition, temperature constituted another significant factor; decreasing the reaction temperature from 65 °C to 45 °C, led to a large decrease in the yield from 57% to 26% (Table 2, Entries 2 and 3).

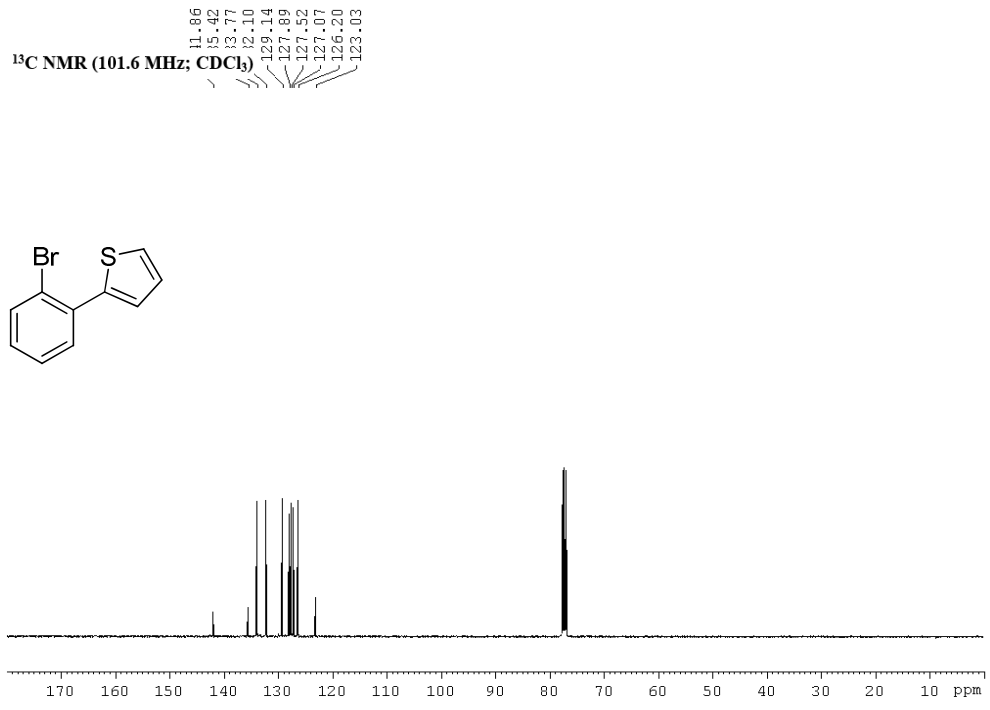
4. ^{1}H and ^{13}C Spectra of Aryl Bromides **9**

2-(2'-Bromophenyl)thiophene **9b**

^{1}H NMR (400 MHz; $CDCl_3$)

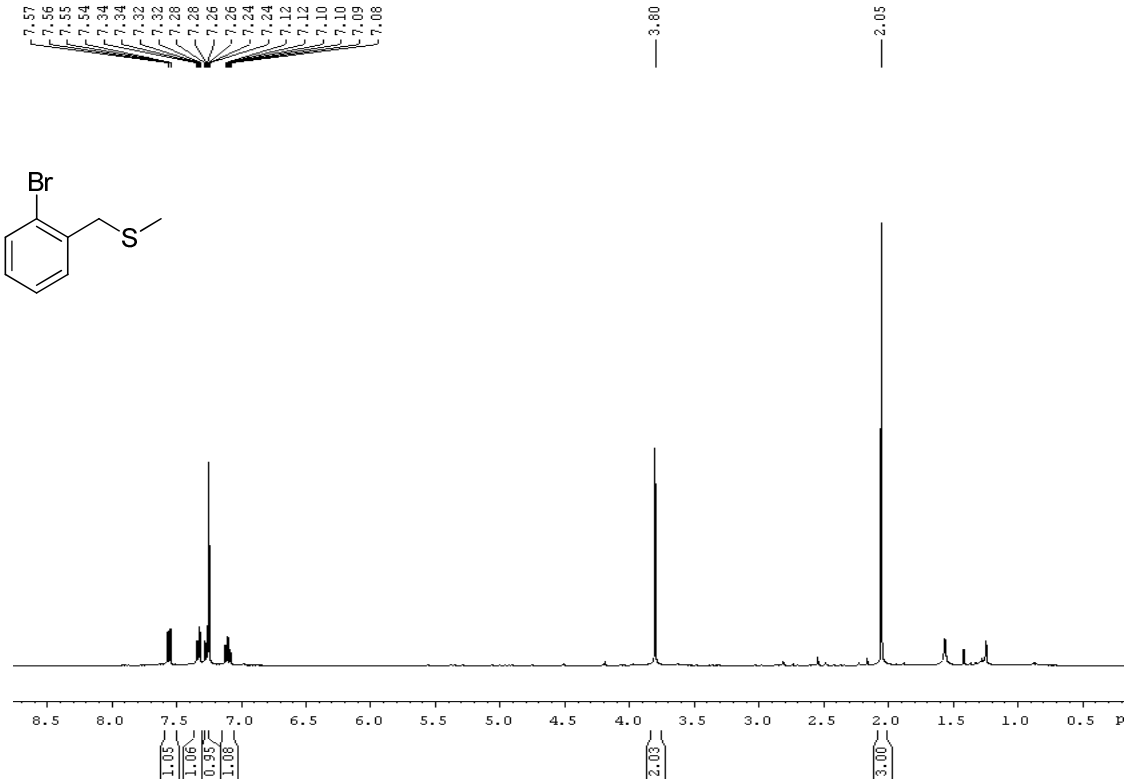


^{13}C NMR (101.6 MHz; $CDCl_3$)

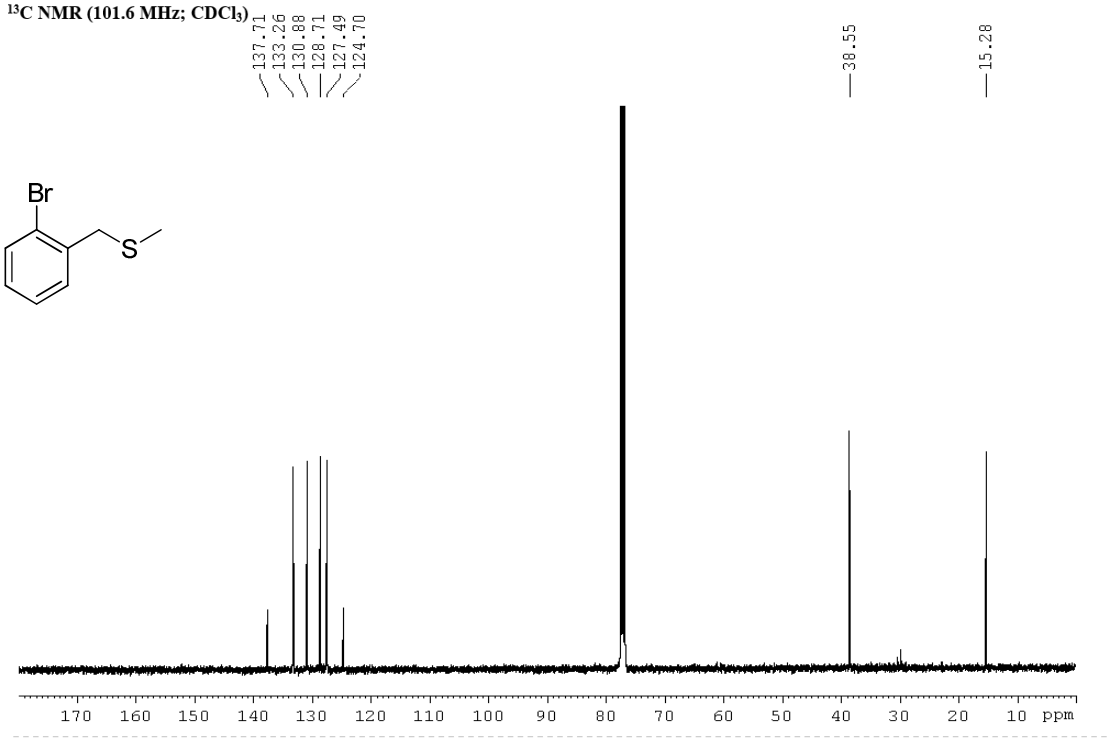


2-Bromobenzyl(methyl)sulfide **9c**

^{1}H NMR (400 MHz; $CDCl_3$)

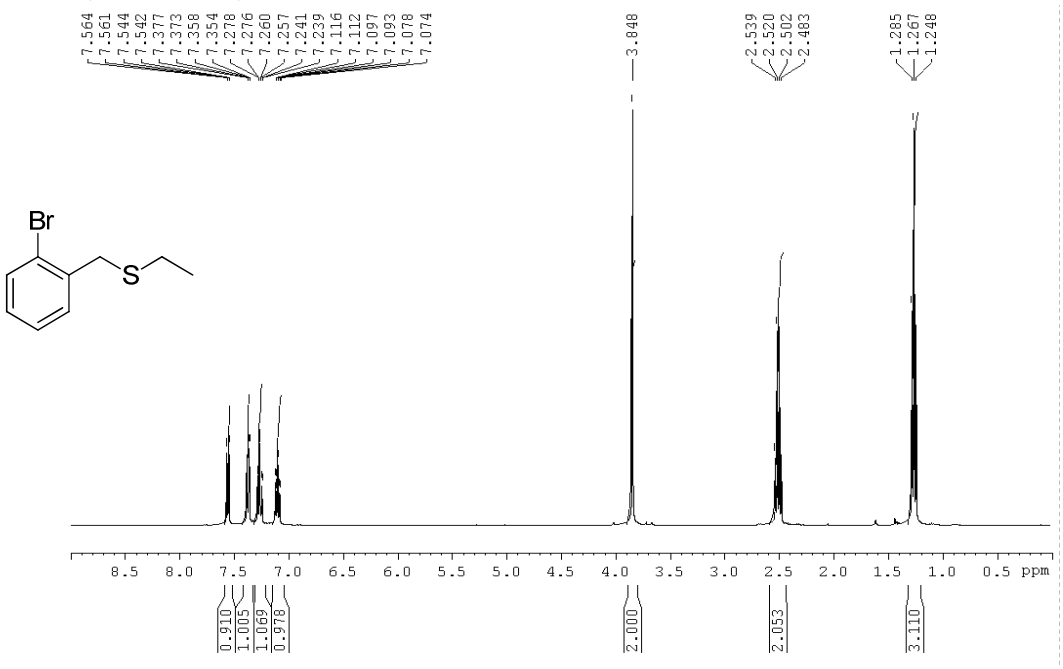


^{13}C NMR (101.6 MHz; $CDCl_3$)

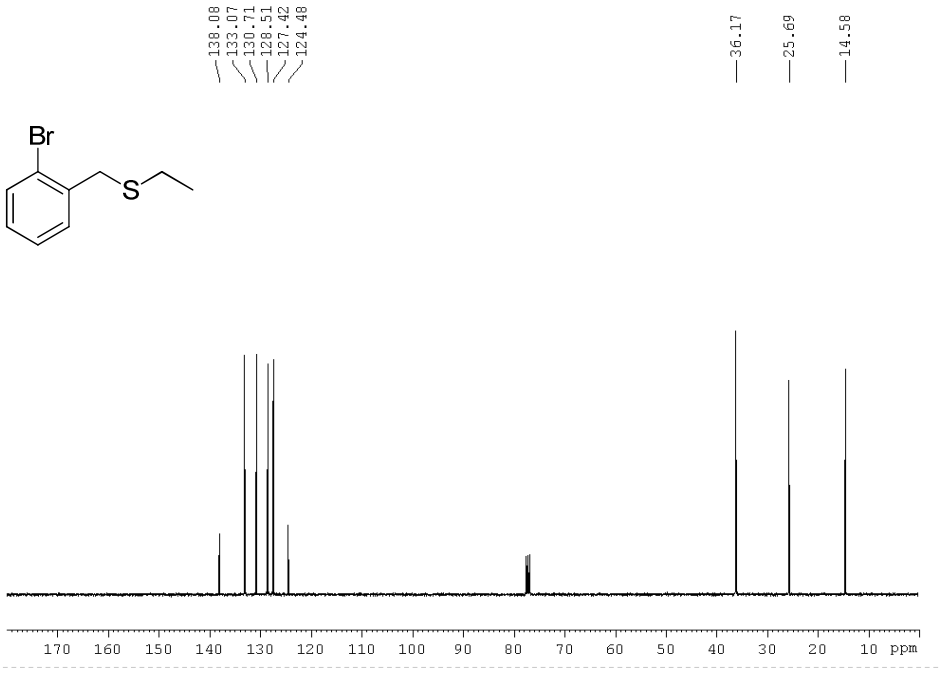


2-Bromobenzyl(ethyl)sulfide **9d**

^{1}H NMR (400 MHz; $CDCl_3$)

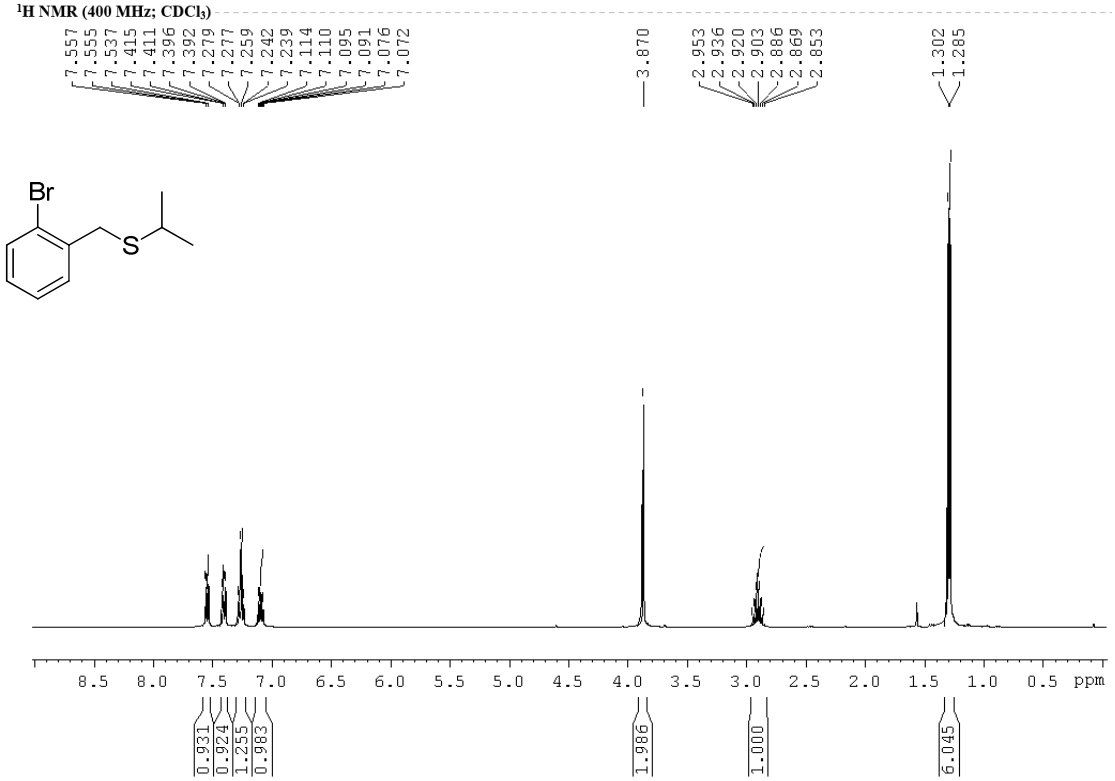


^{13}C NMR (101.6 MHz; $CDCl_3$)

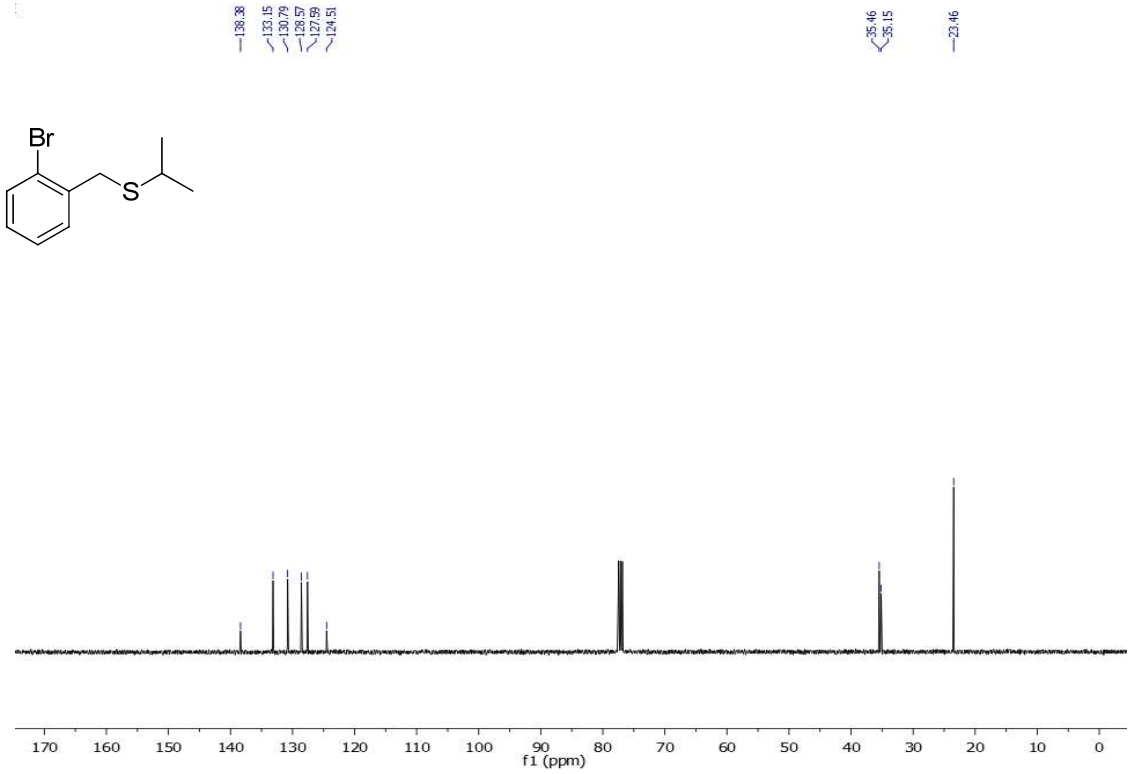


2-Bromobenzyl(isopropyl)sulfide **9e**

^{1}H NMR (400 MHz; $CDCl_3$)

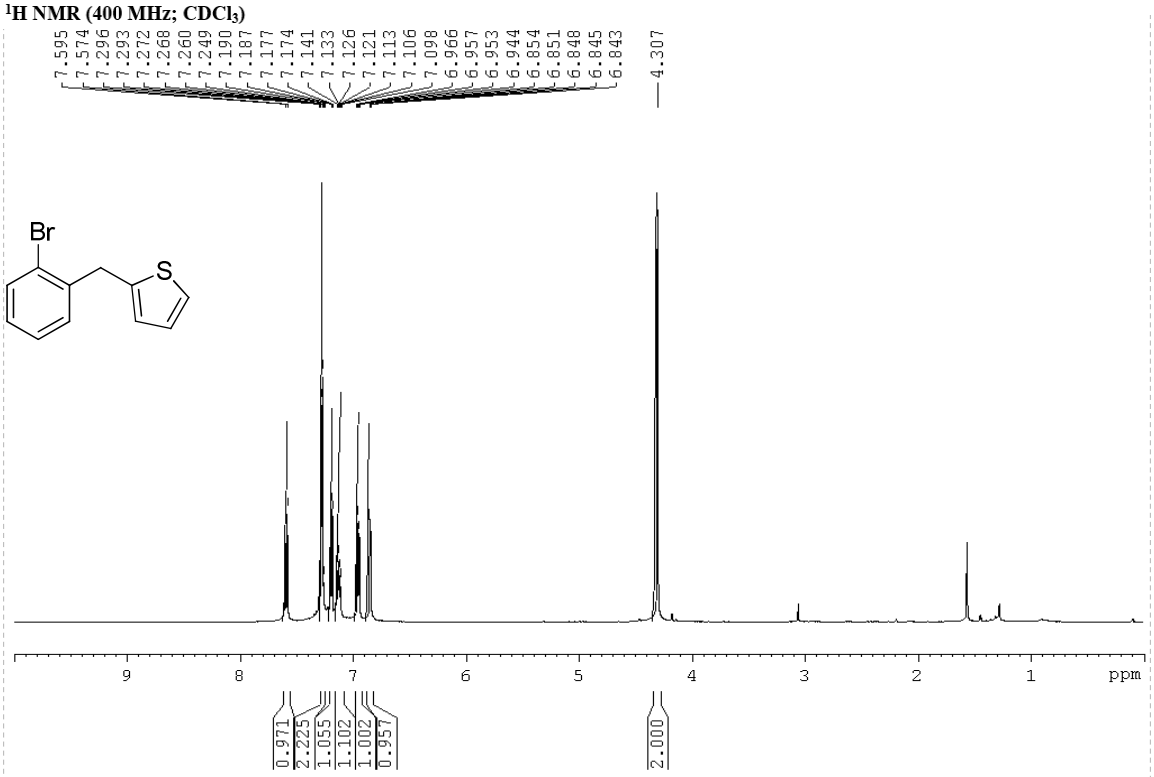


^{13}C NMR (101.6 MHz; $CDCl_3$)

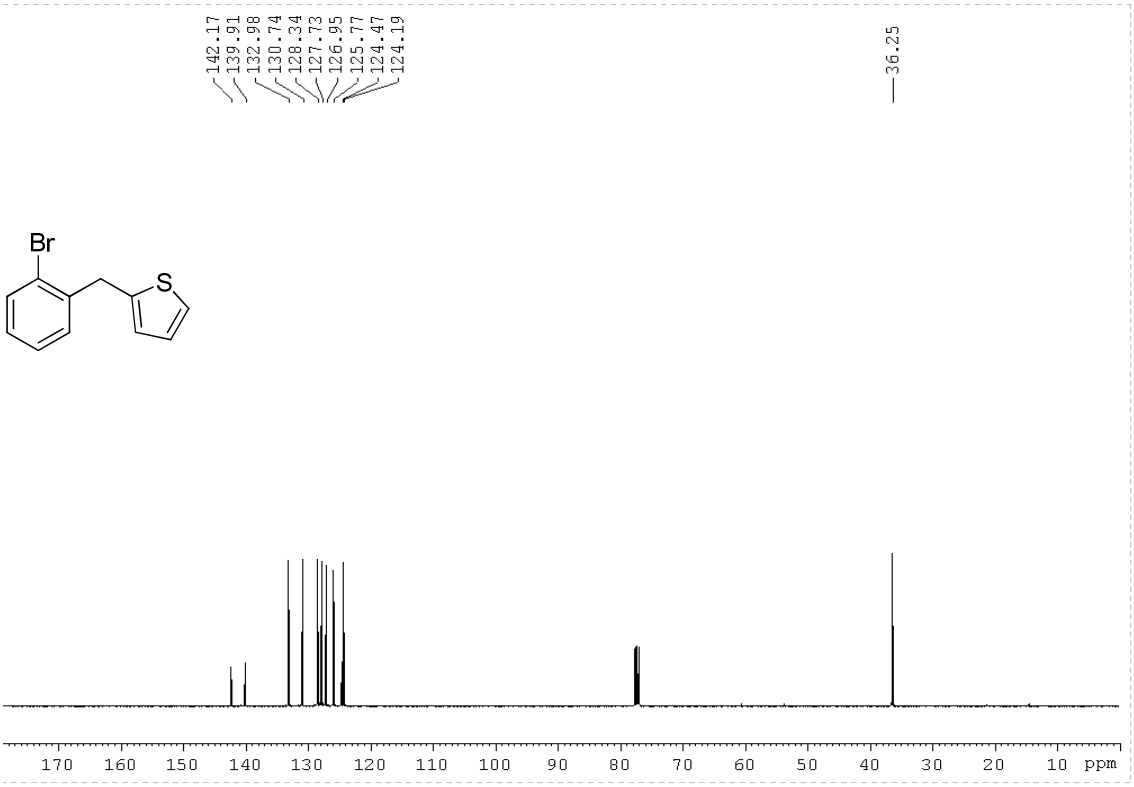


2-(2-Bromobenzyl)thiophene **9f**

^{1}H NMR (400 MHz; $CDCl_3$)

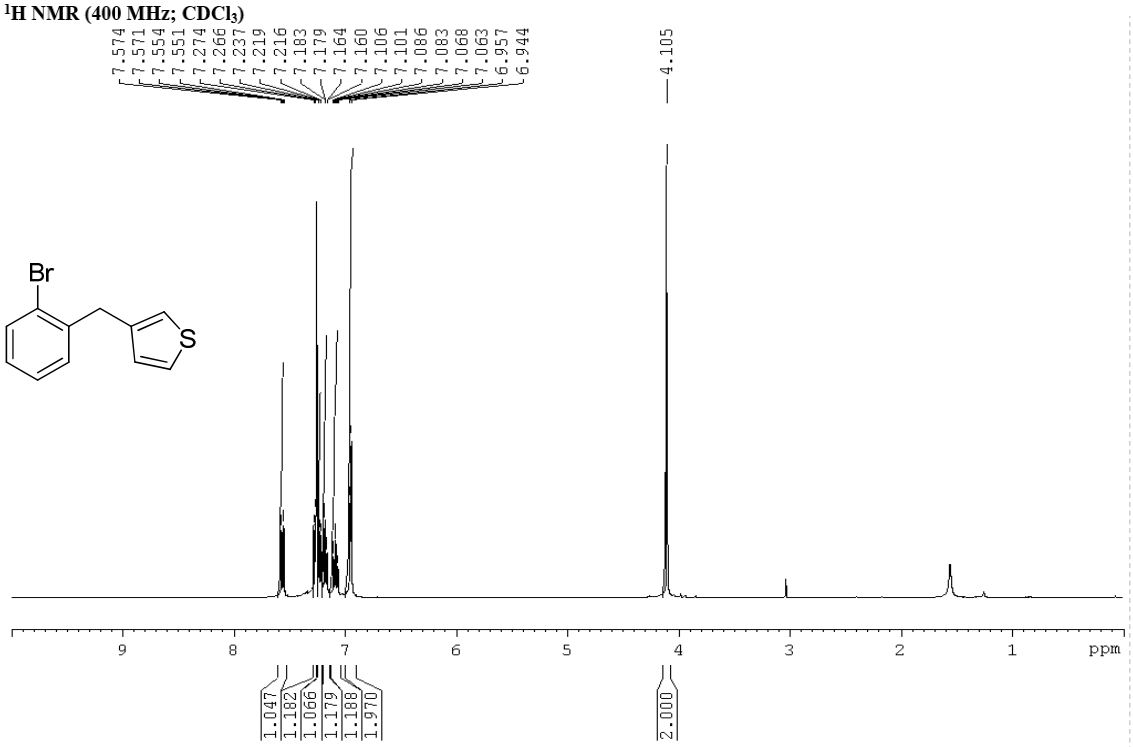


^{13}C NMR (101.6 MHz; $CDCl_3$)

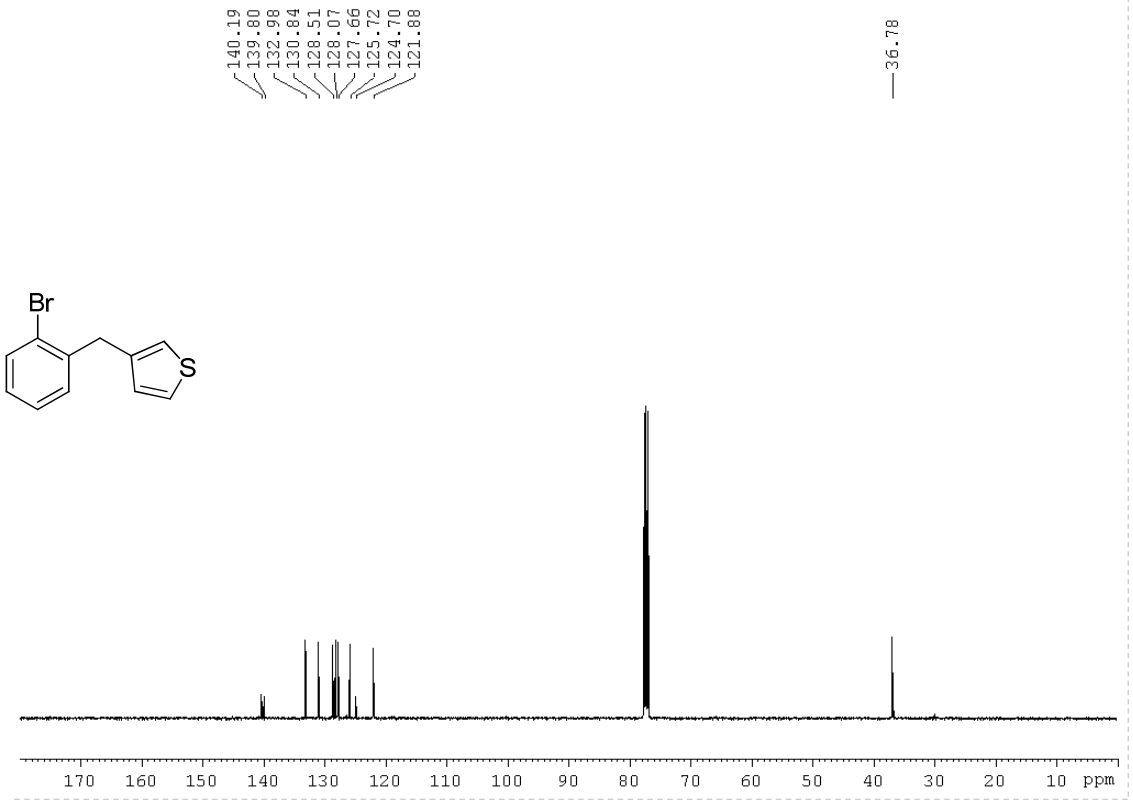


3-(2-Bromobenzyl)thiophene **9g**

^{1}H NMR (400 MHz; $CDCl_3$)

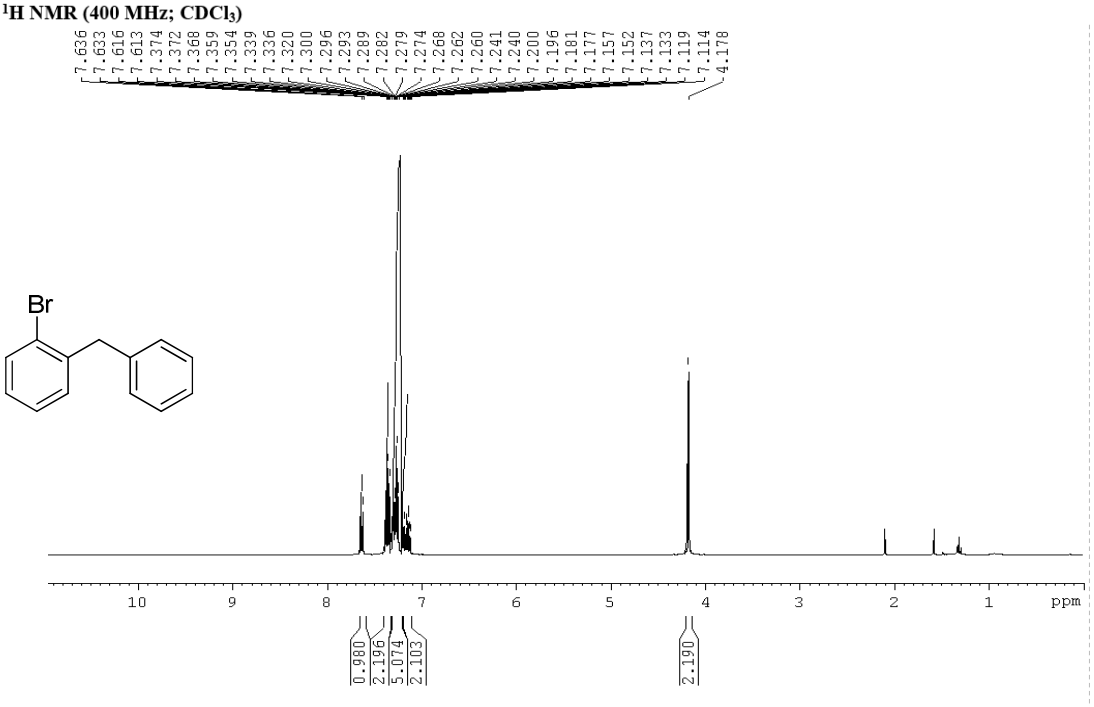


^{13}C NMR (101.6 MHz; $CDCl_3$)

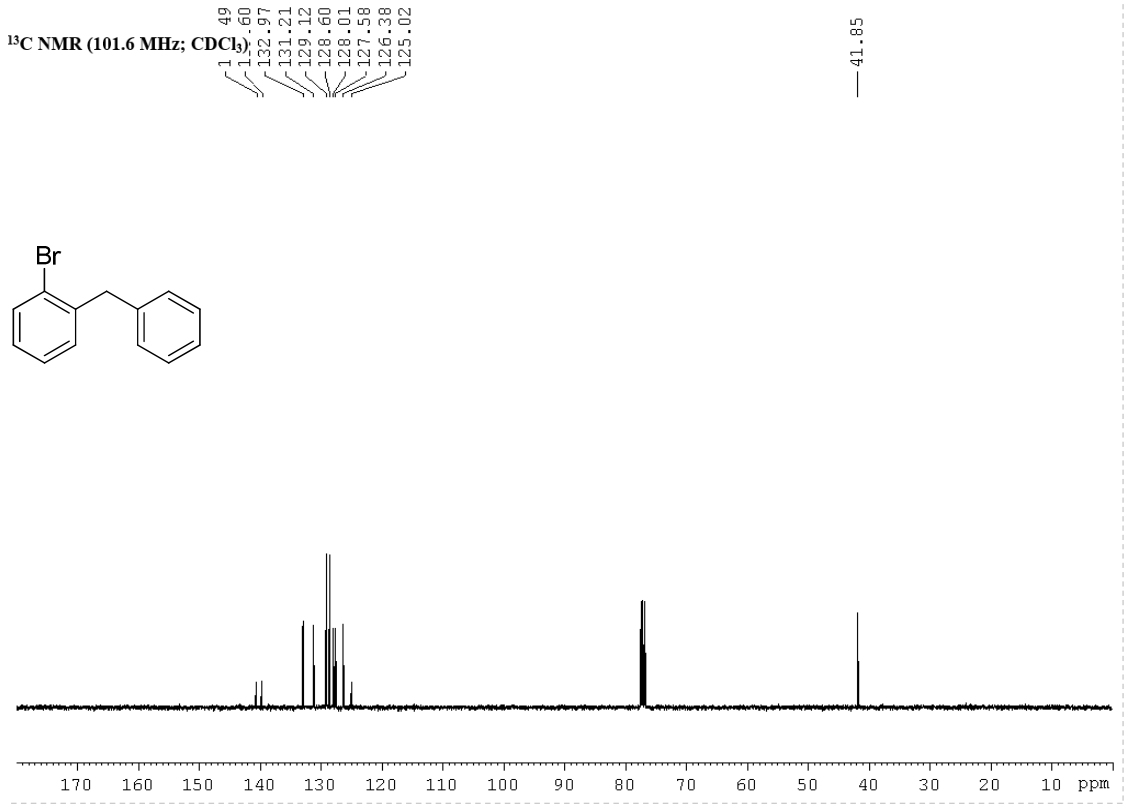


1-Benzyl-2-bromobenzene **9i**

^{1}H NMR (400 MHz; $CDCl_3$)

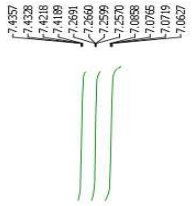


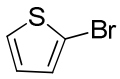
^{13}C NMR (101.6 MHz; $CDCl_3$)

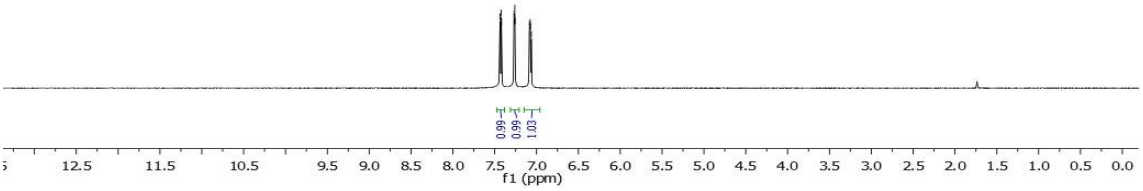


2-Bromothiophene **10**

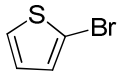
^{1}H NMR (400 MHz; $CDCl_3$)

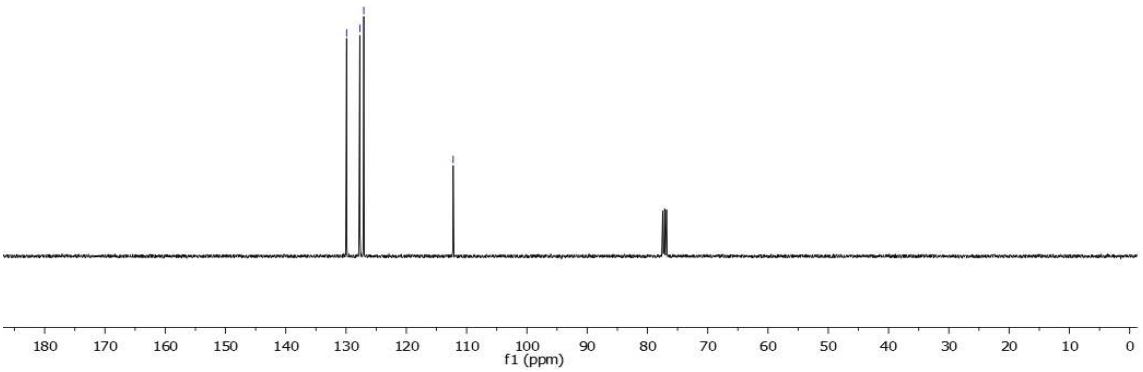






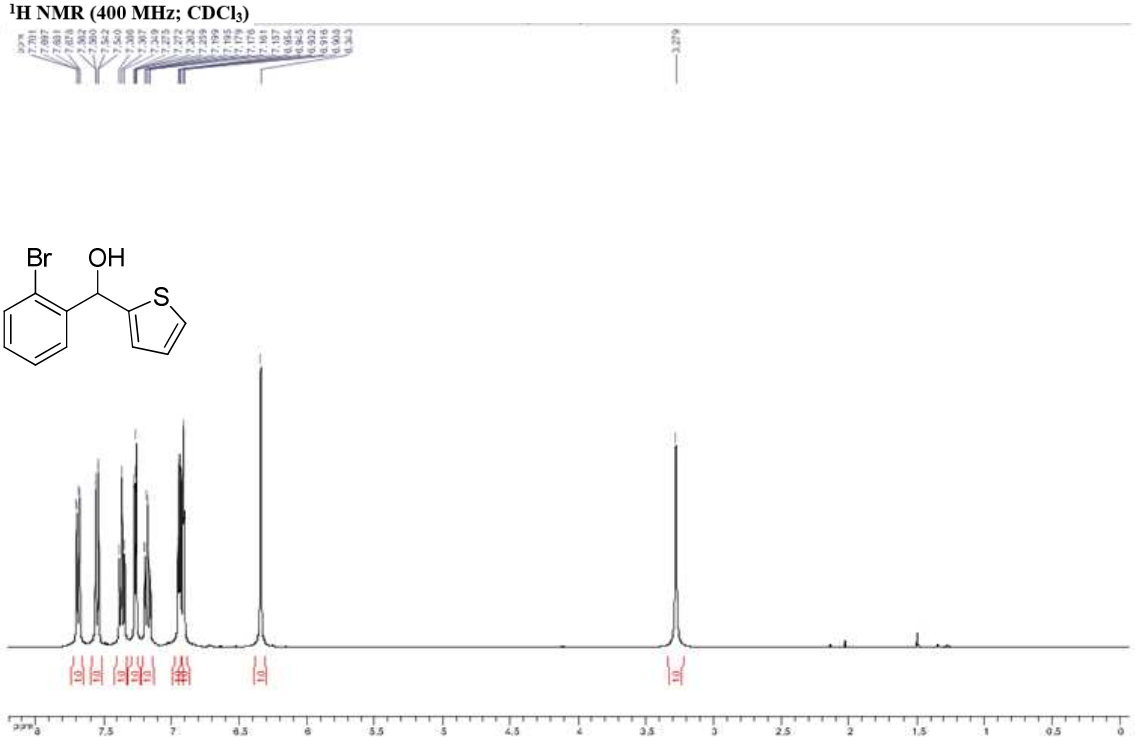
^{13}C NMR (101.6 MHz; $CDCl_3$)



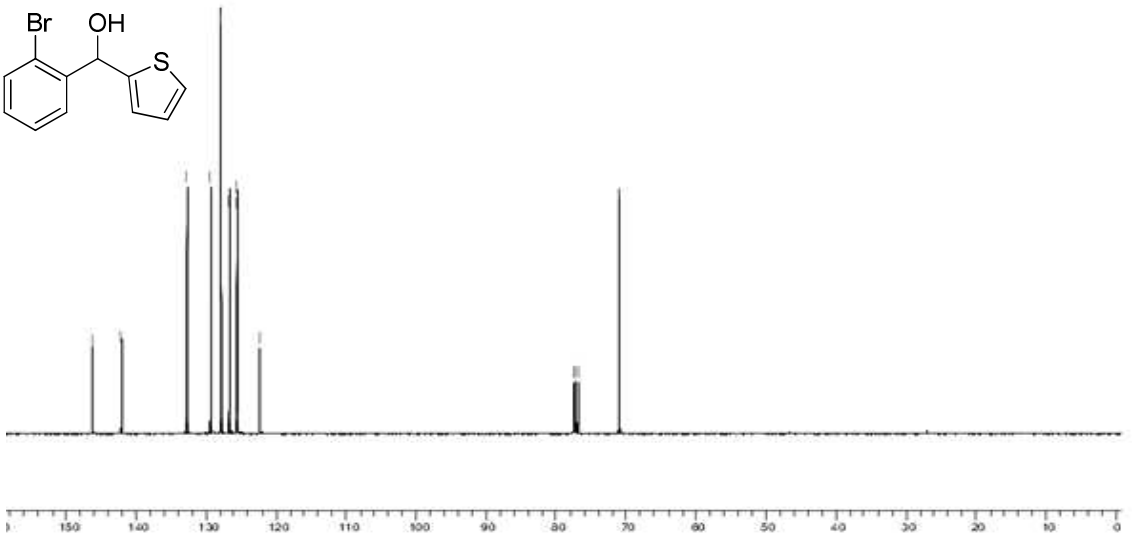


(2-Bromophenyl)(thiophen-2-yl)methanol **11**

^{1}H NMR (400 MHz; $CDCl_3$)

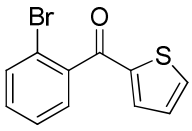


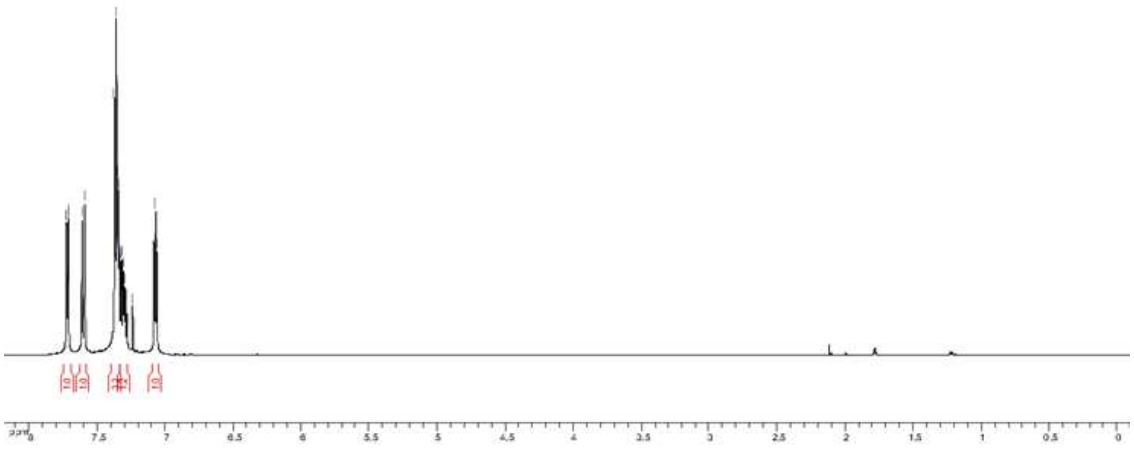
^{13}C NMR (101.6 MHz; $CDCl_3$)



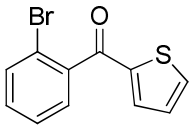
(2-Bromophenyl)(thiophen-2-yl)methanone **12**

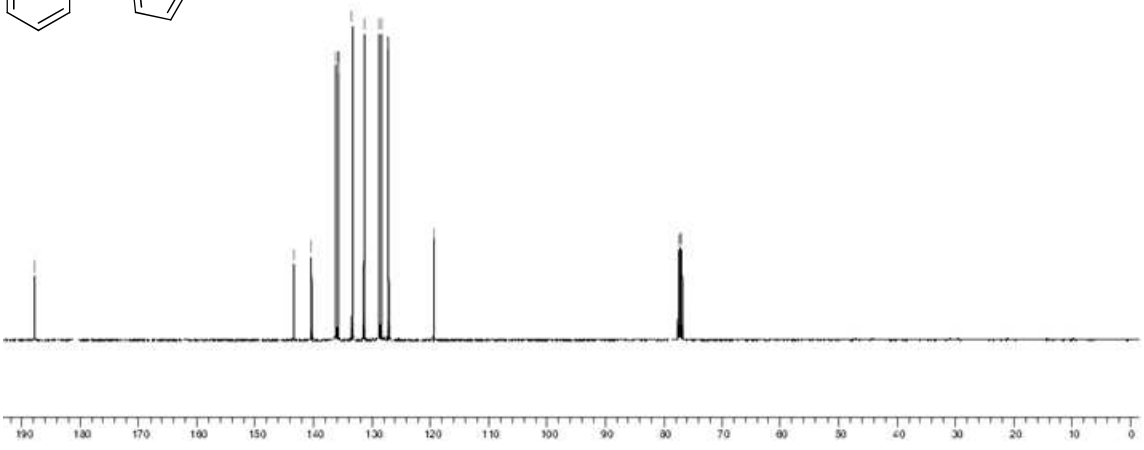
^{1}H NMR (400 MHz; $CDCl_3$)





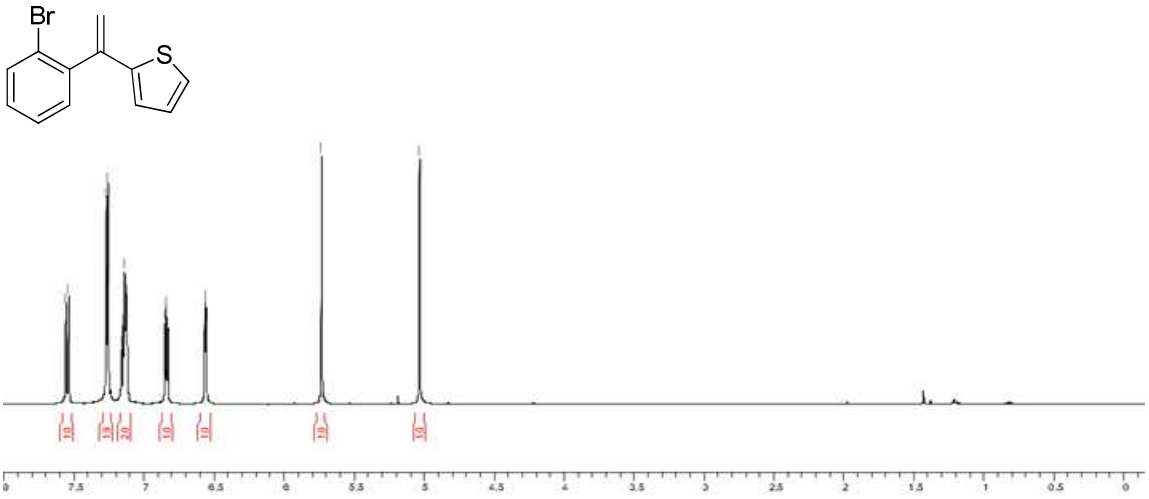
^{13}C NMR (101.6 MHz; $CDCl_3$)



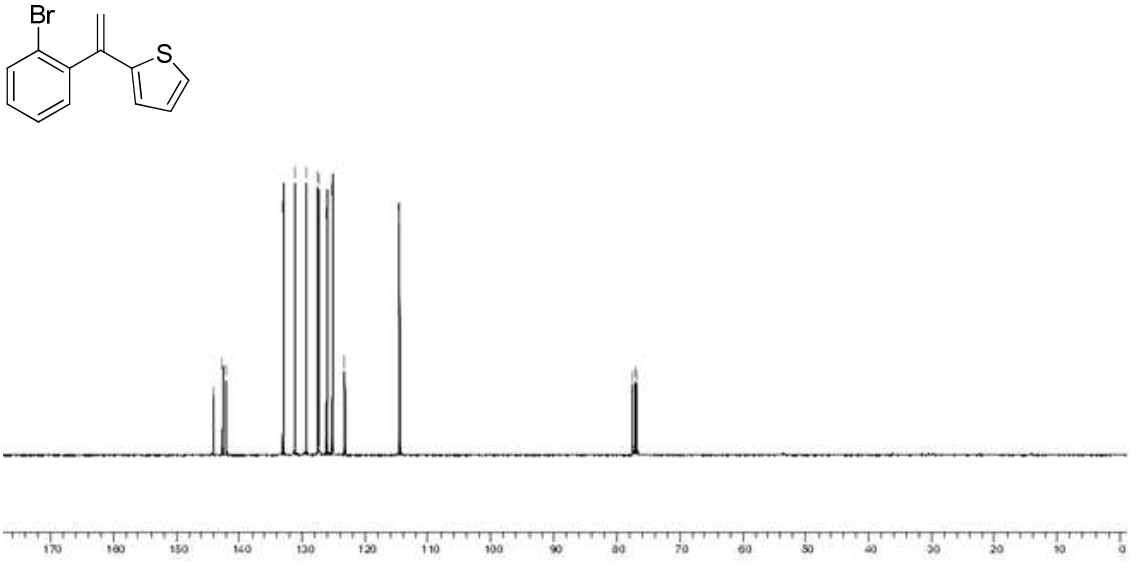


2-(1-(2-Bromophenyl)vinyl)thiophene **9j**

^{1}H NMR (400 MHz; $CDCl_3$)

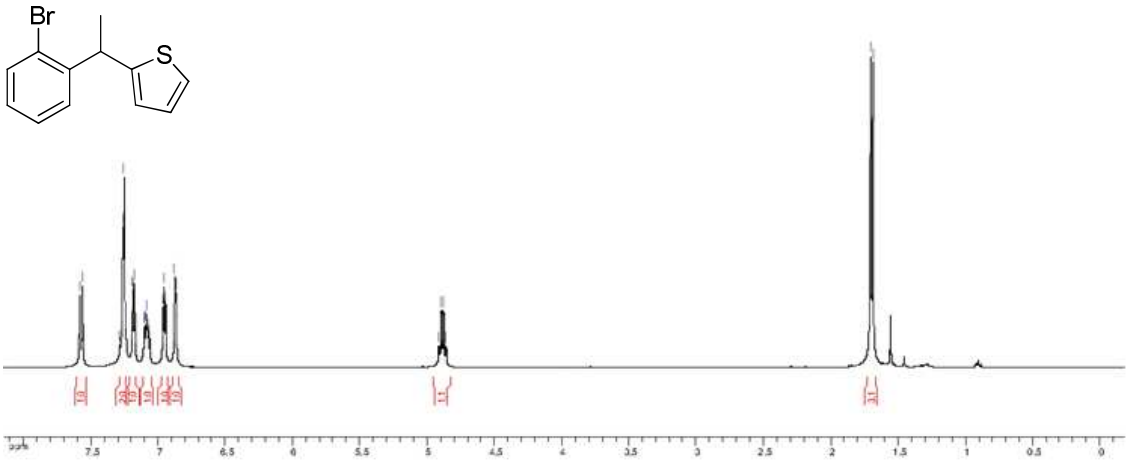


^{13}C NMR (101.6 MHz; $CDCl_3$)

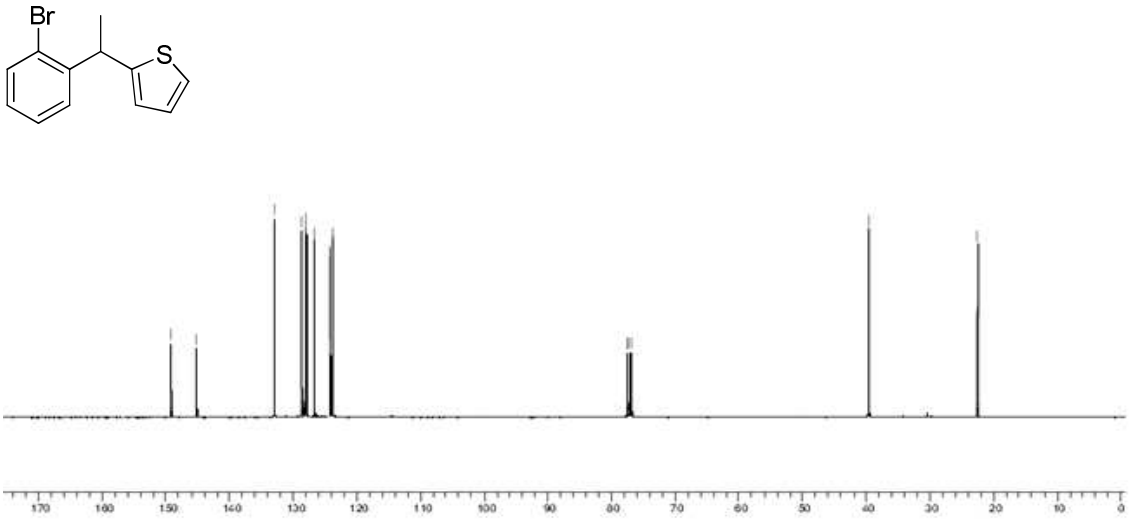


2-(1-(2-Bromophenyl)ethyl)thiophene **9k**

^{1}H NMR (400 MHz; $CDCl_3$)

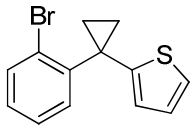


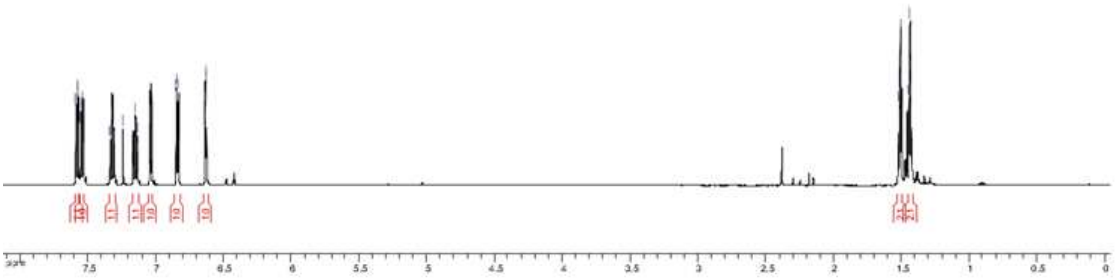
^{13}C NMR (101.6 MHz; $CDCl_3$)



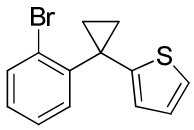
2-(1-(2-Bromophenyl)cyclopropyl)thiophene **9l**

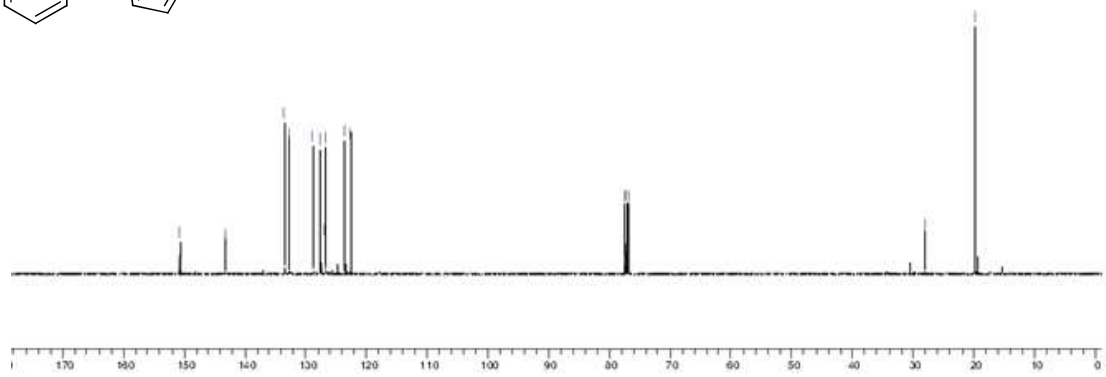
^{1}H NMR (400 MHz; $CDCl_3$)





^{13}C NMR (125.7 MHz; $CDCl_3$)

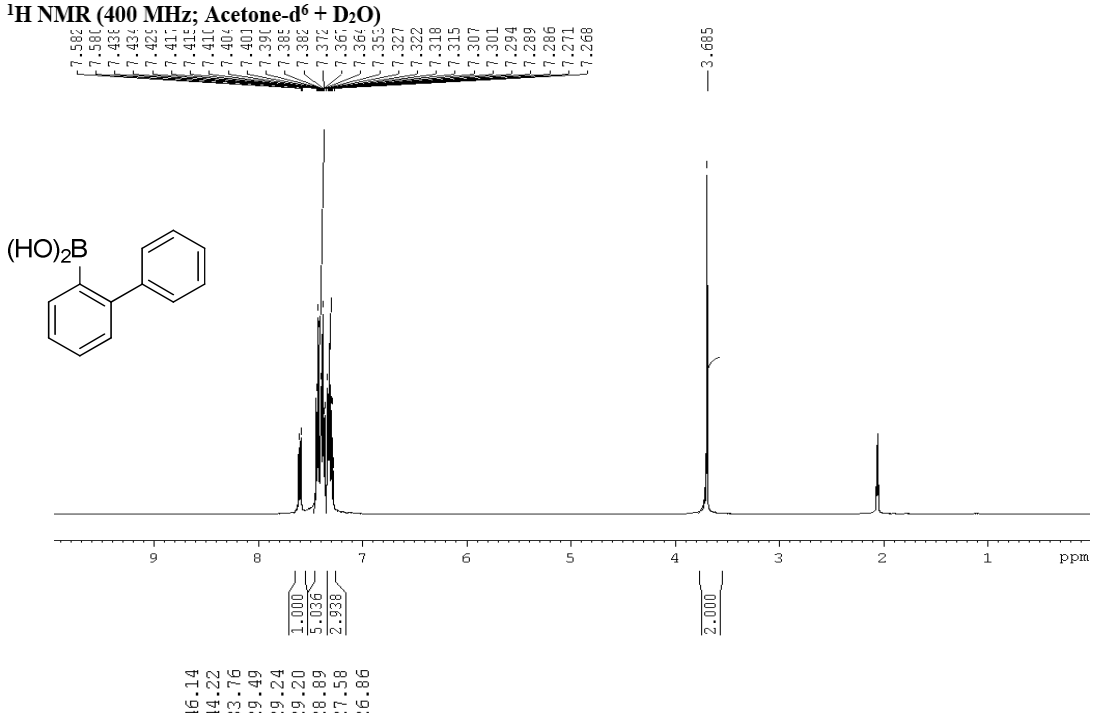




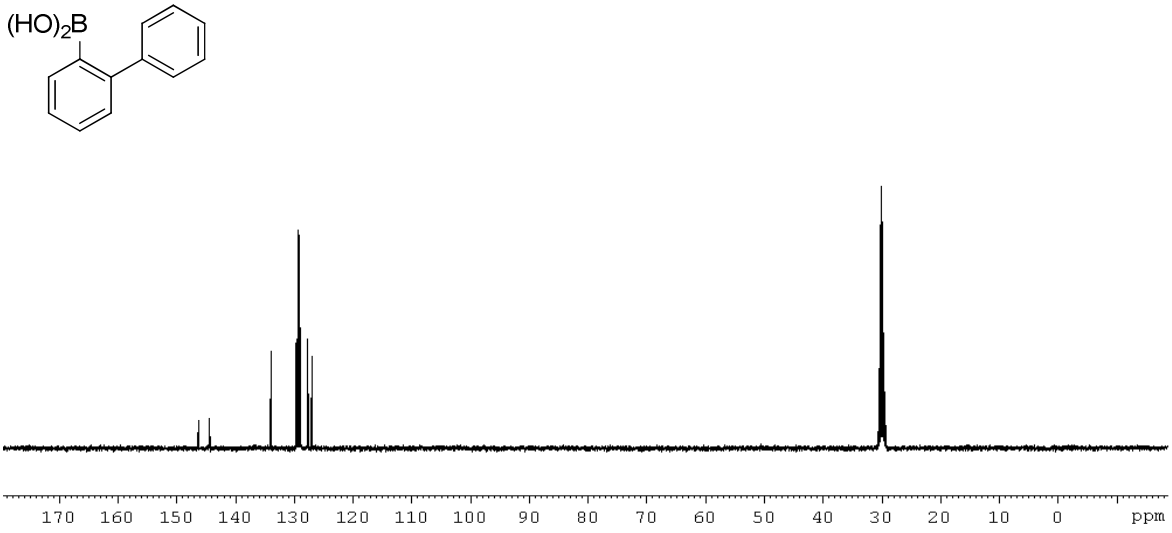
5. ^{1}H and ^{13}C Spectra of Boronic Acids

[1,1'-Biphenyl]-2-ylboronic acid **7a**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

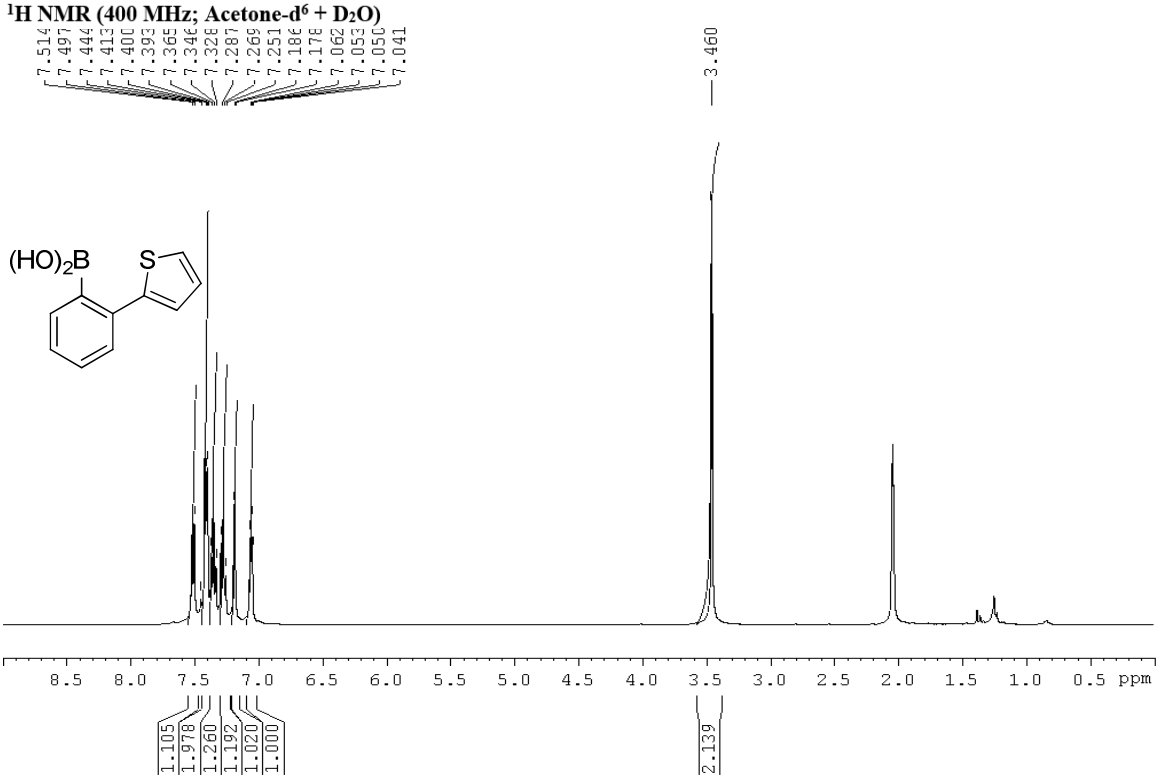


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

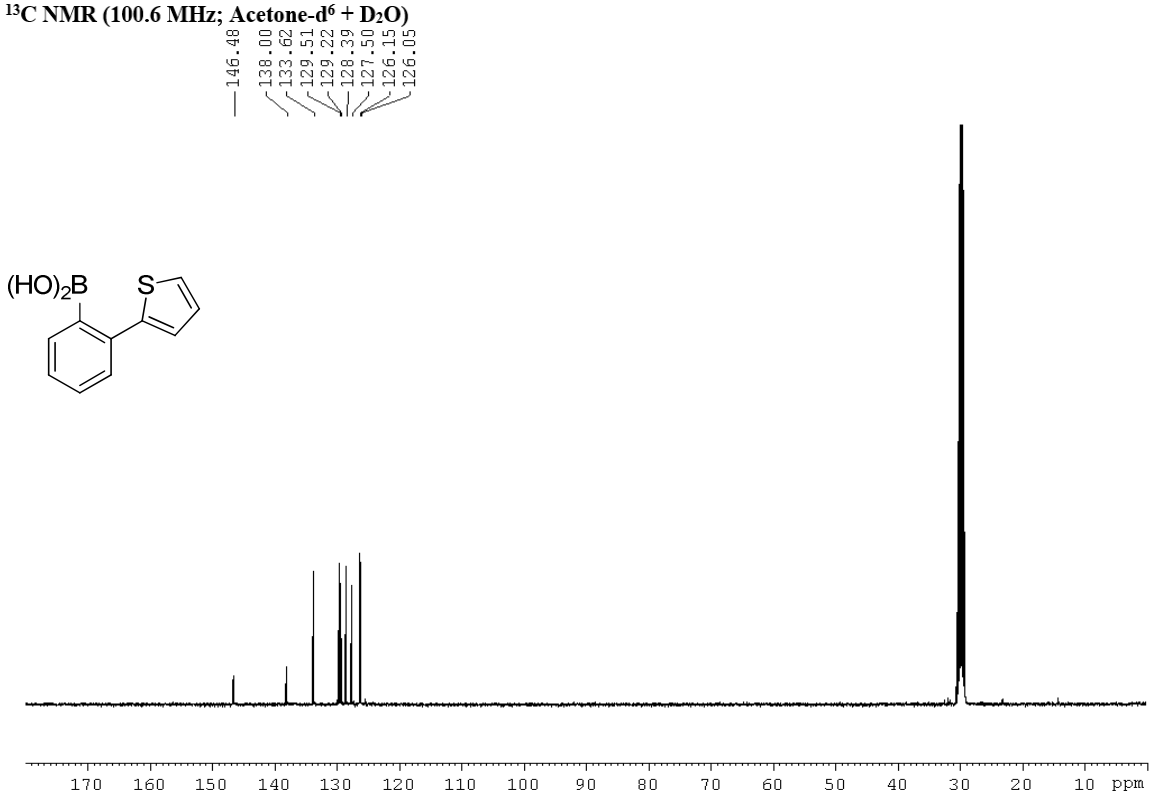


(2-(Thiophen-2-yl)phenyl)boronic acid **7b**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

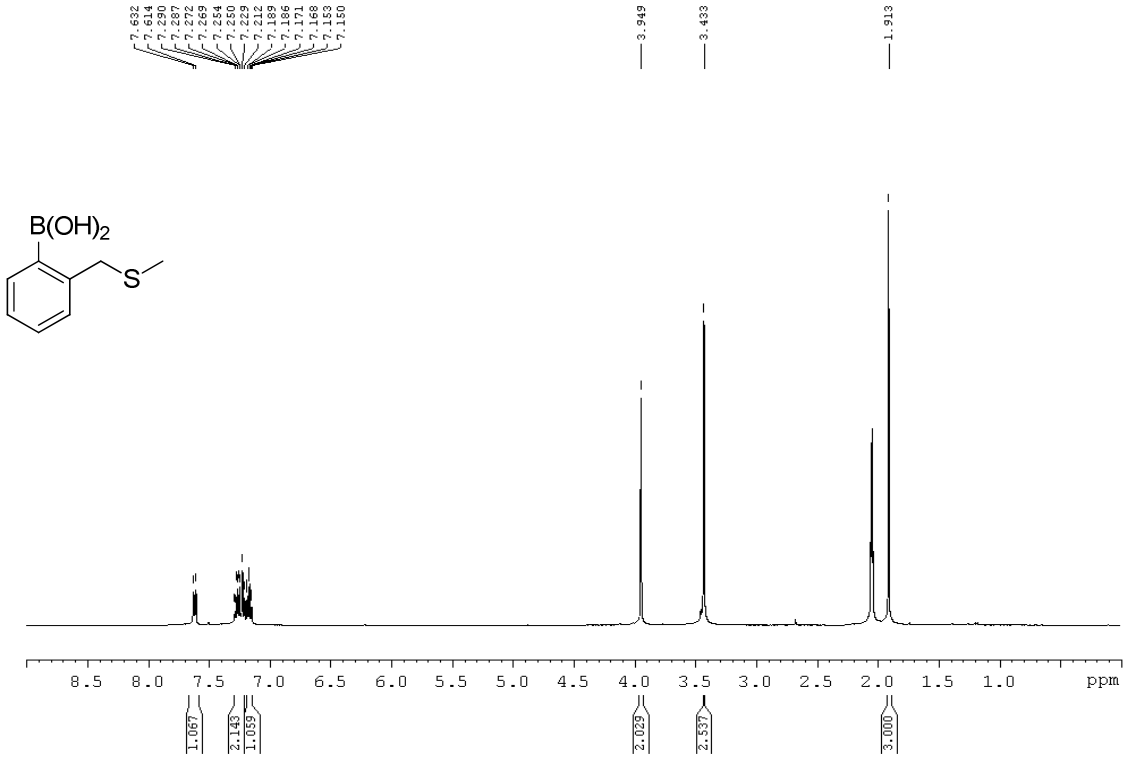


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

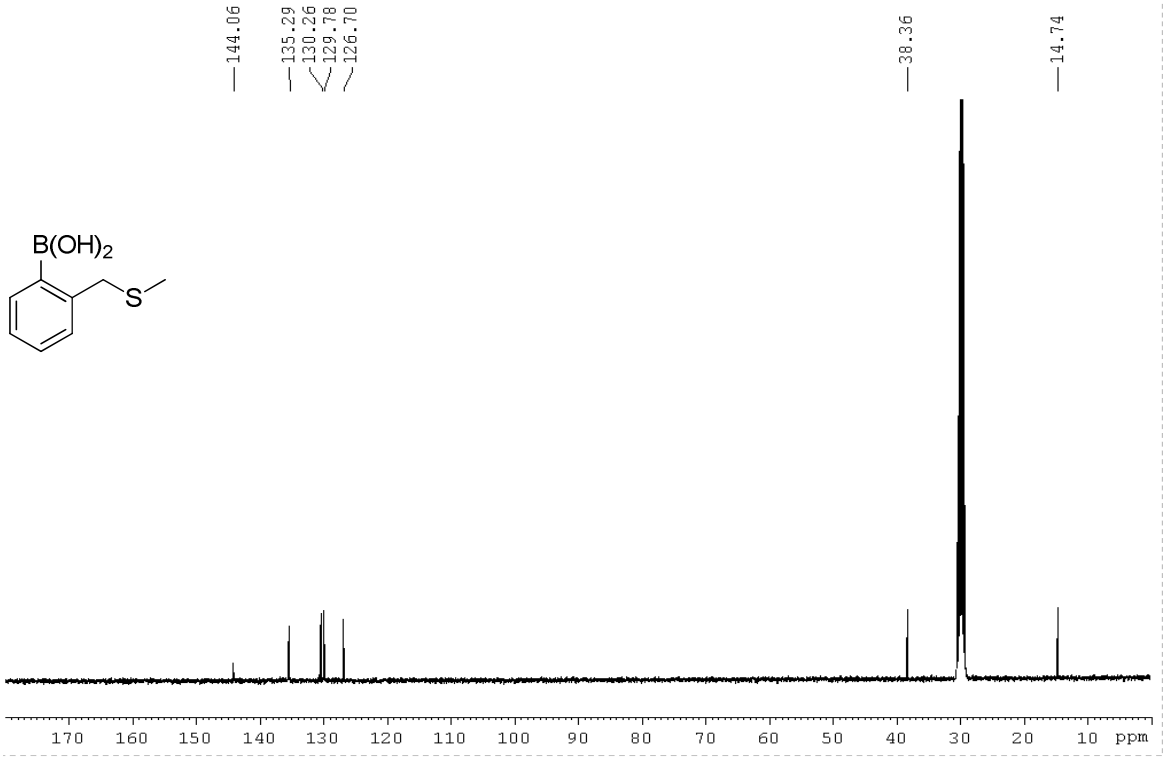


((Methyl)sulfide)phenylboronic acid **7c**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

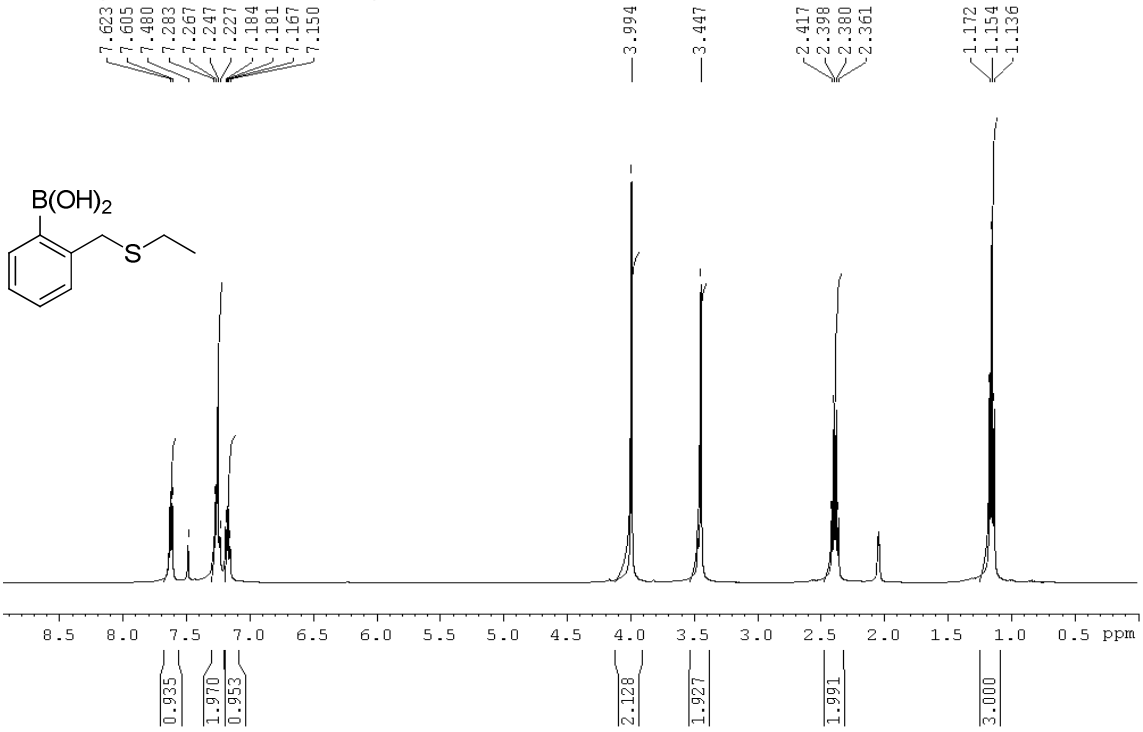


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

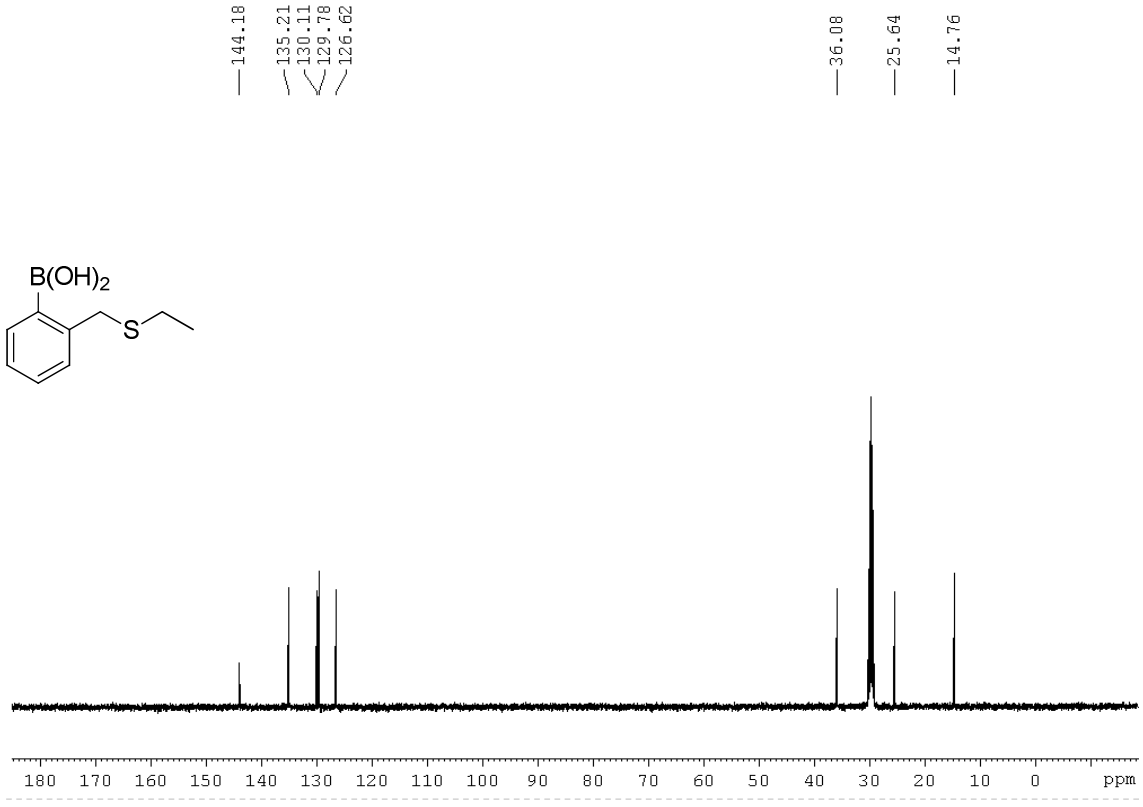


(2-((Ethylthio)methyl)phenyl)boronic acid **7d**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

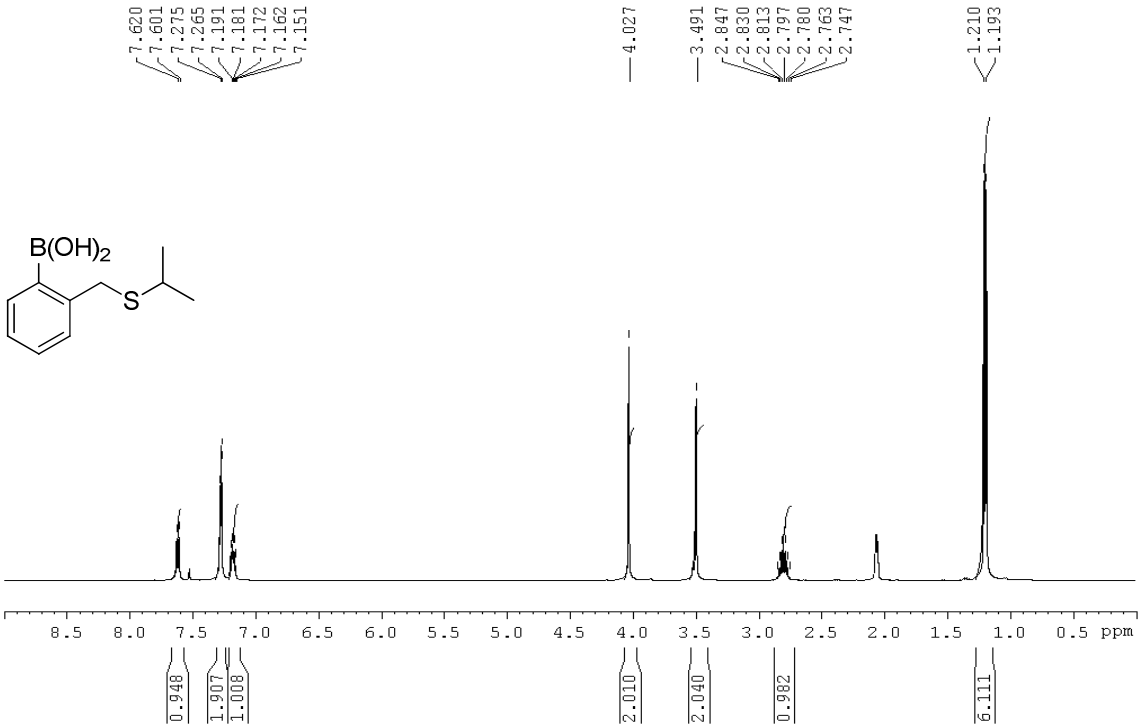


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

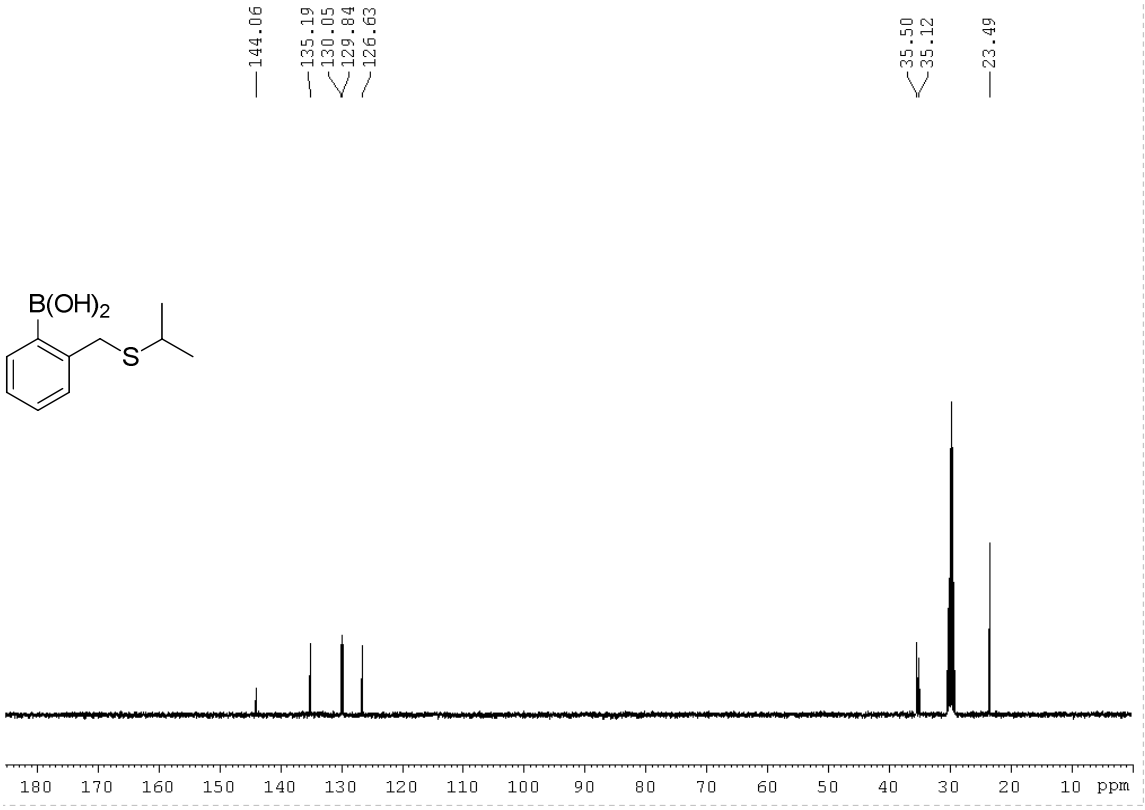


(2-((Isopropylthio)methyl)phenyl)boronic acid **7e**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

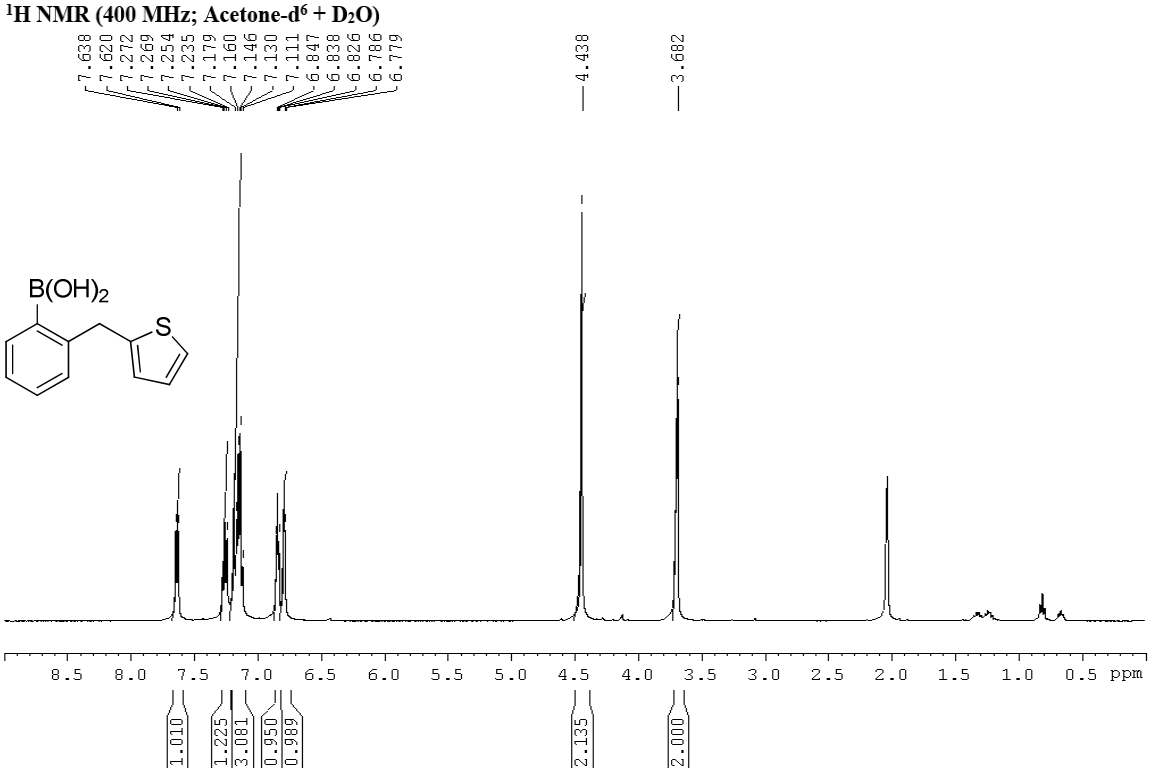


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

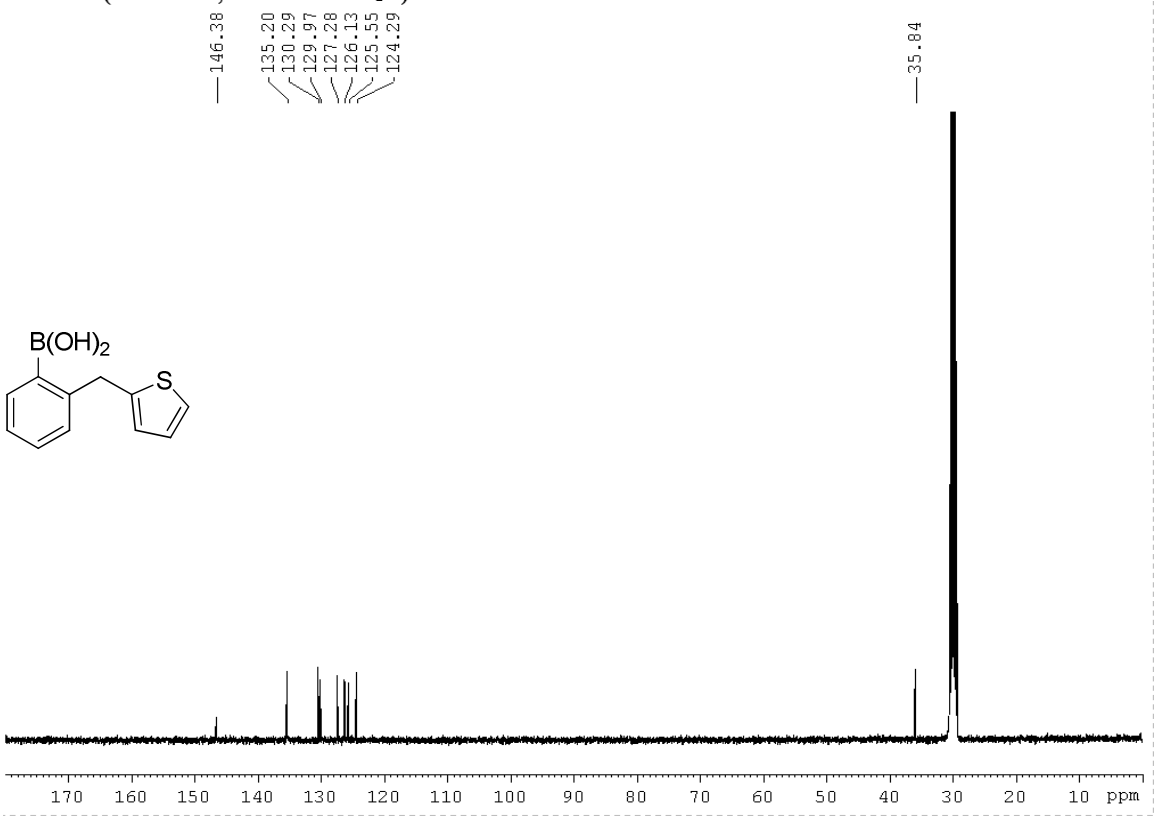


(2-(Thiophen-2-ylmethyl)phenyl)boronic acid **7f**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

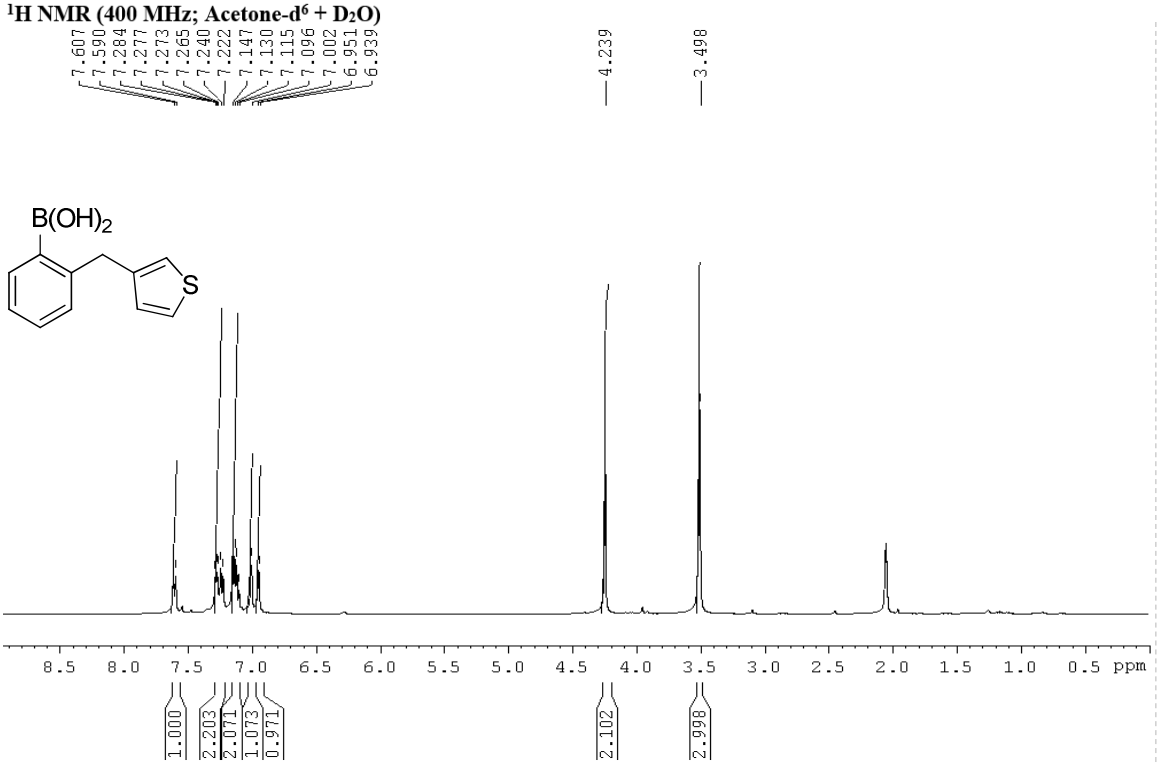


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

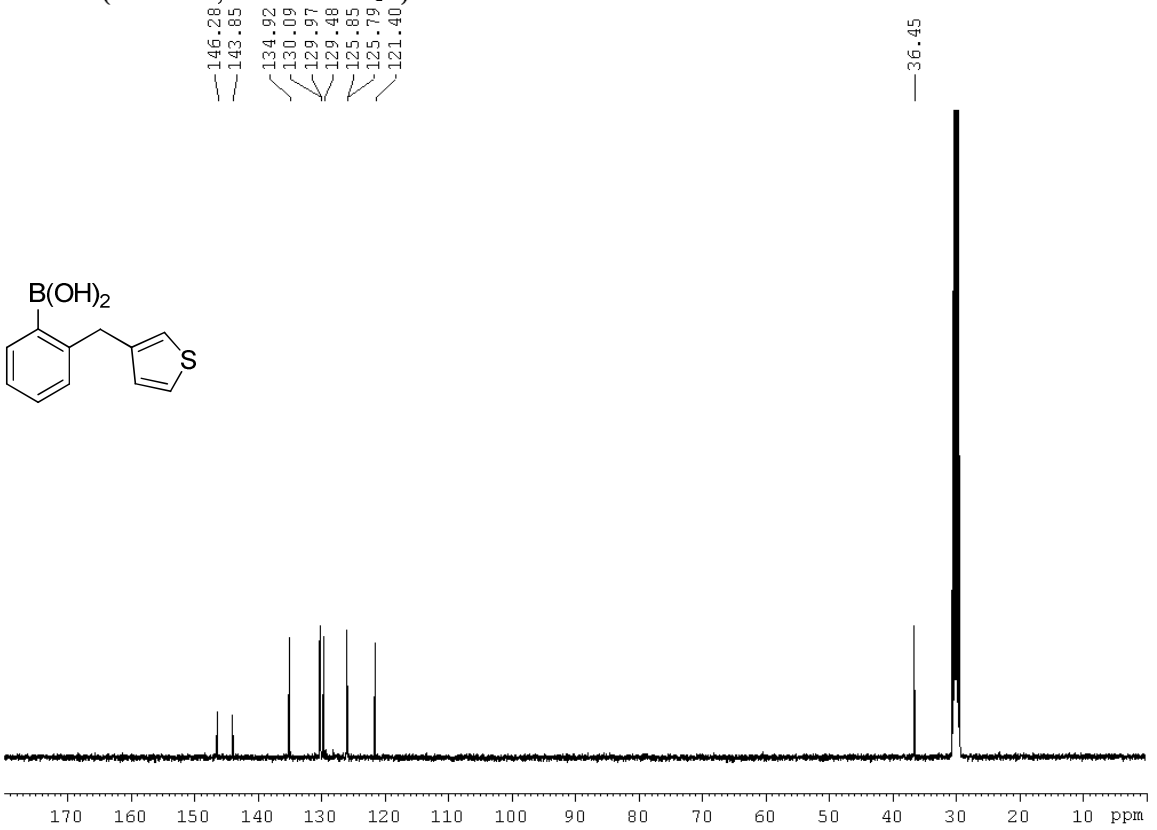


(2-(Thiophen-3-ylmethyl)phenyl)boronic acid **7g**

^{1}H NMR (400 MHz; Acetone-d^6 + D$_2$O)

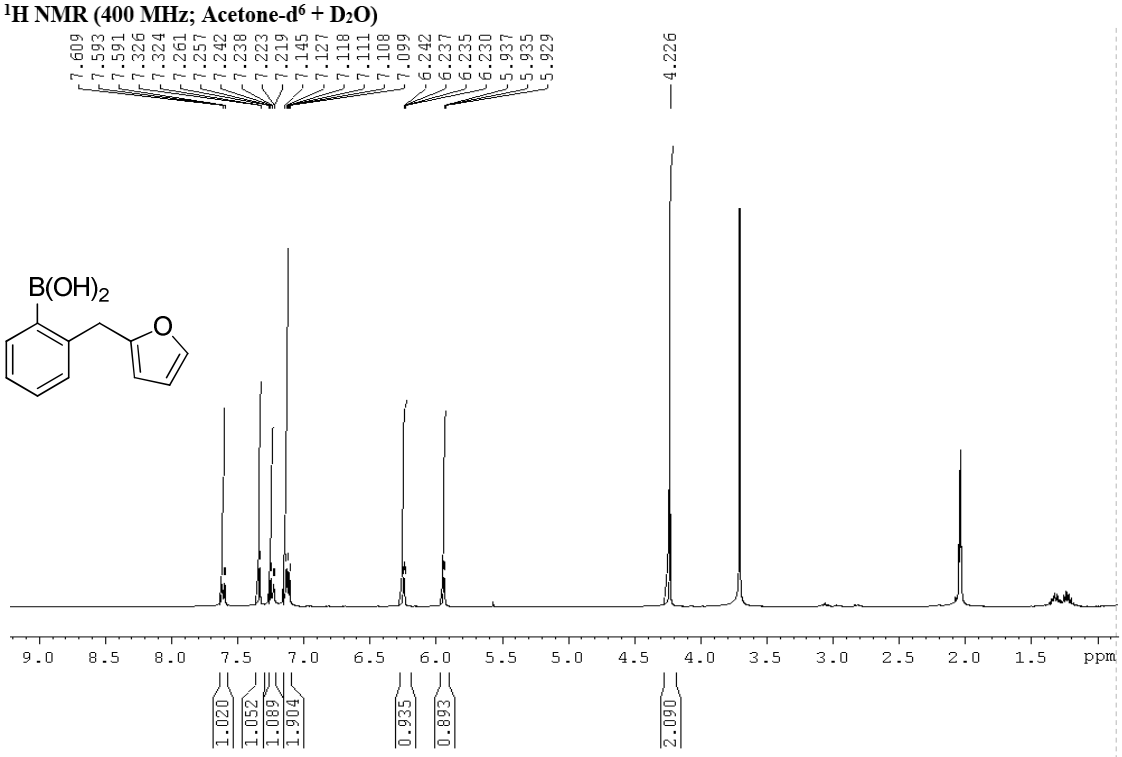


^{13}C NMR (100.6 MHz; Acetone-d^6 + D$_2$O)

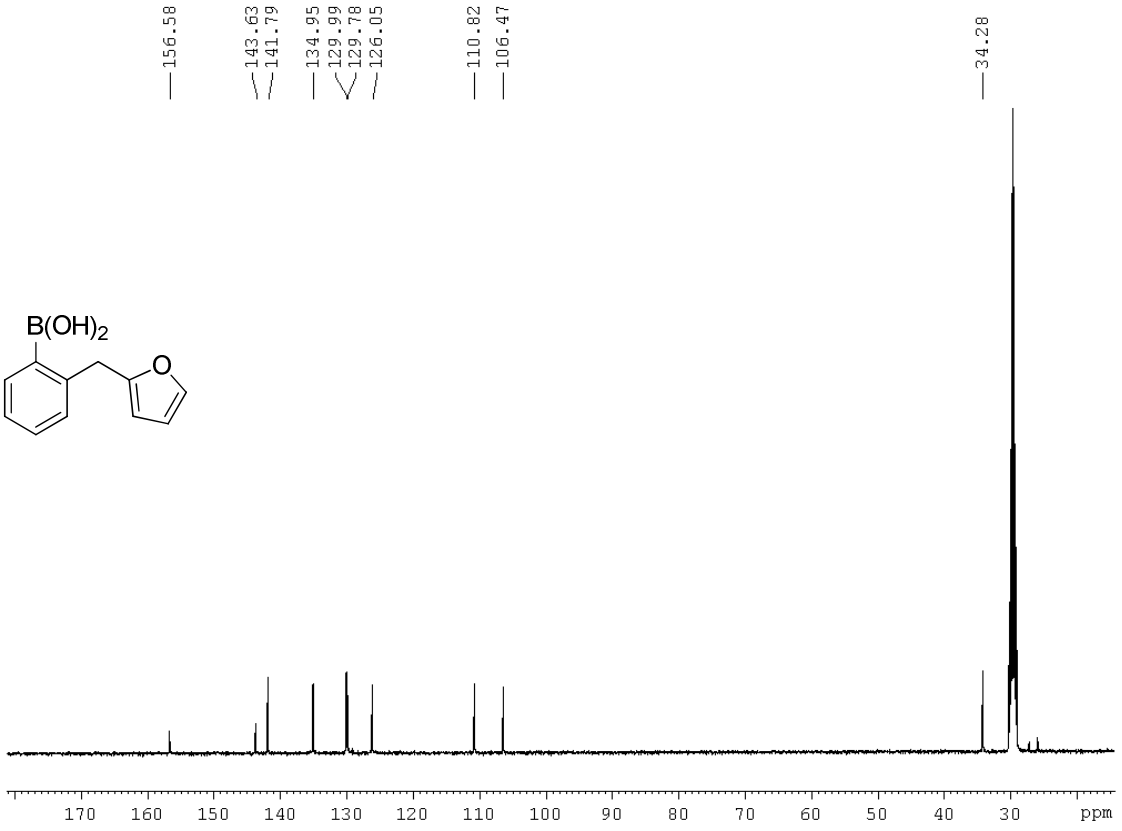


(2-(Furan-2-ylmethyl)phenyl)boronic acid **7h**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

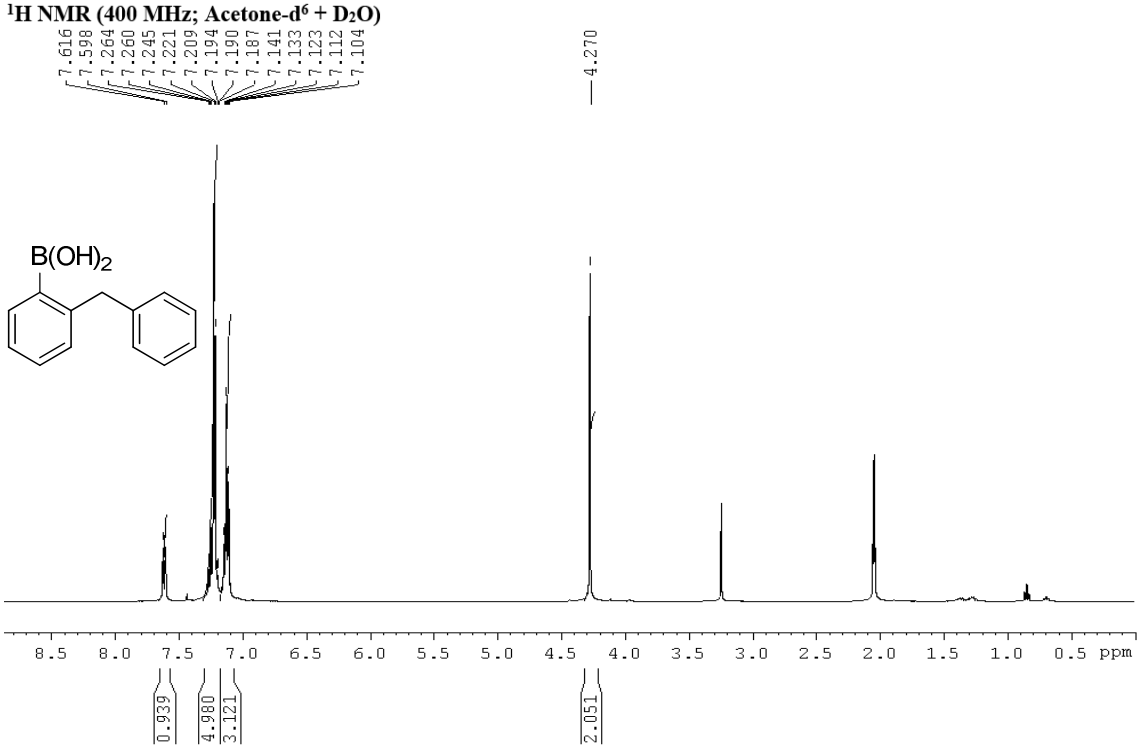


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

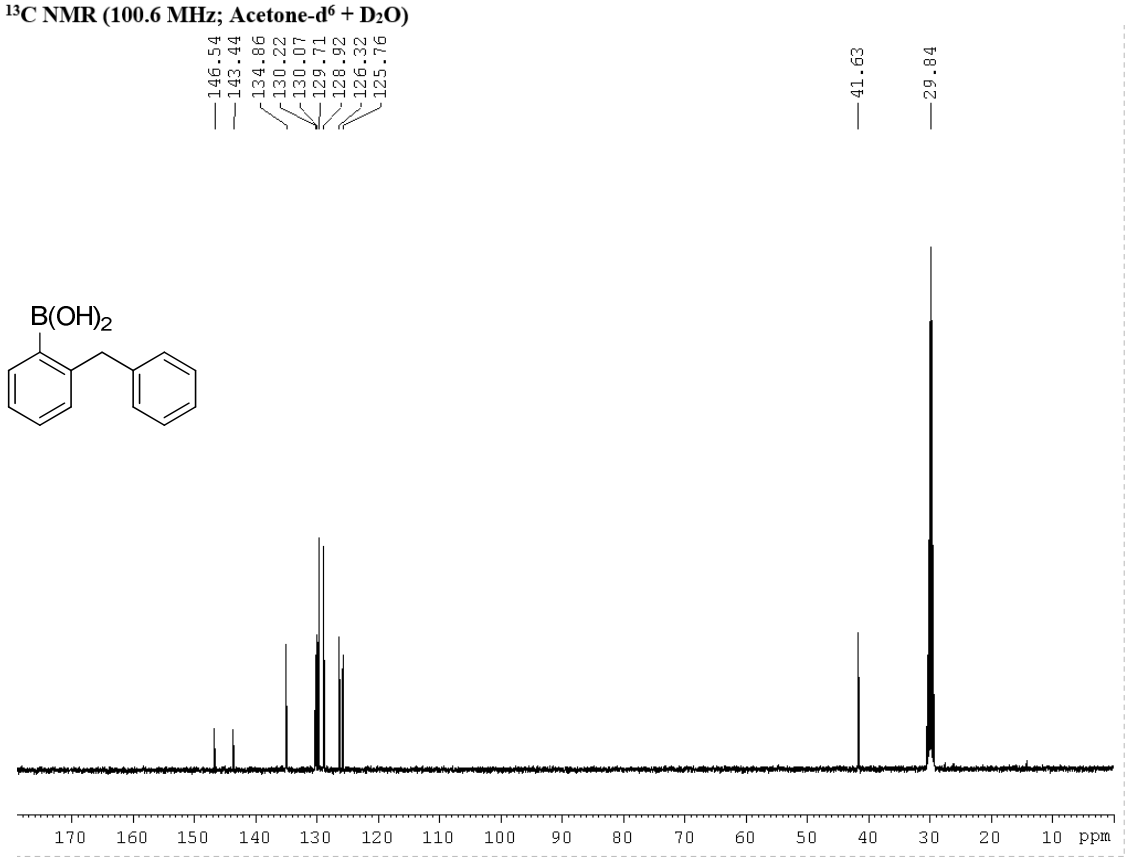


(2-Benzylphenyl)boronic acid **7i**

^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)

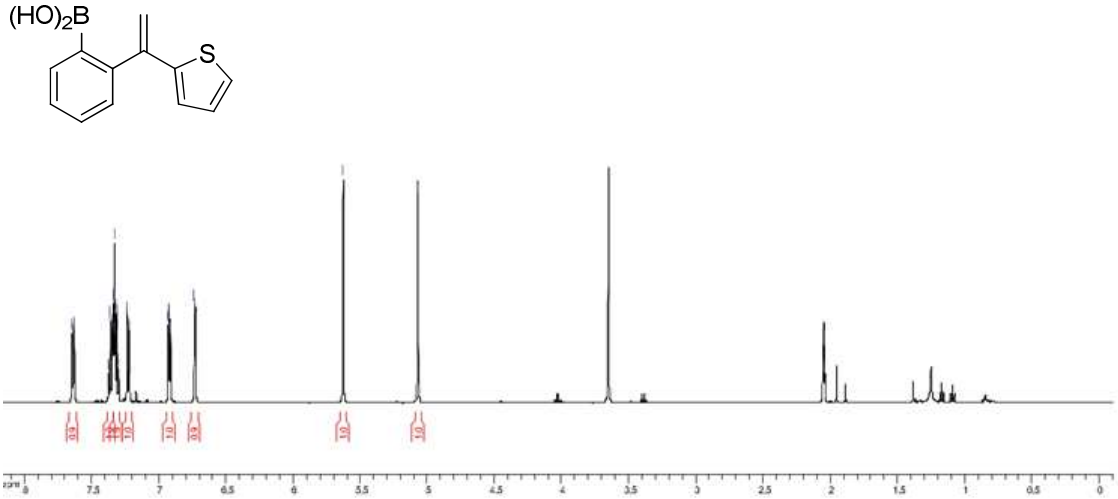


^{13}C NMR (100.6 MHz; Acetone-d^{6} + D$_2$O)

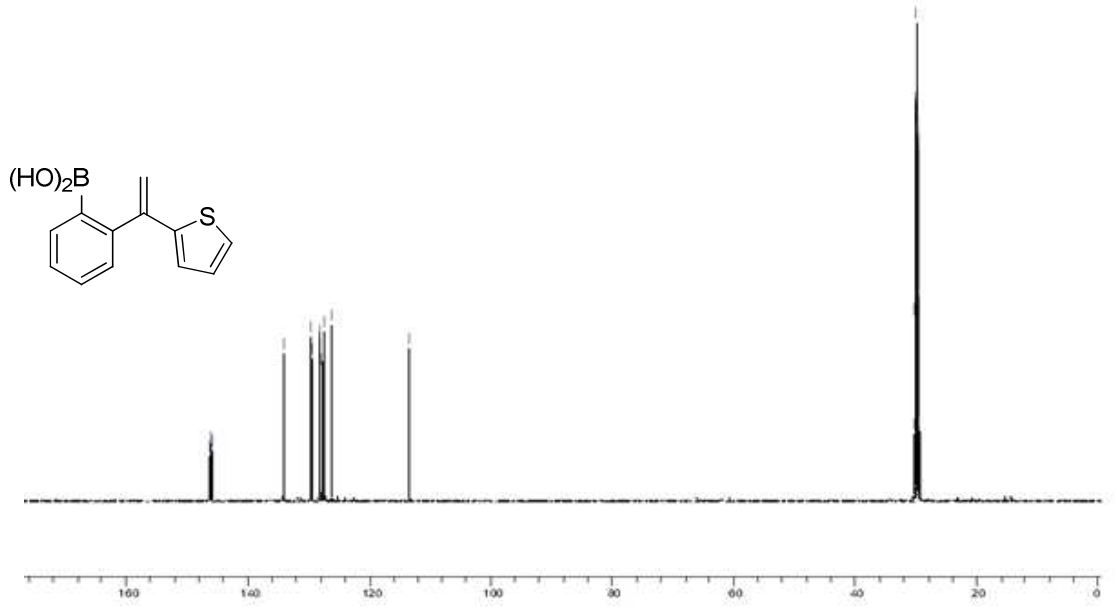


2-(1-(Thiophen-2-yl)vinyl)phenylboronic acid **7j**

^{1}H NMR (500 MHz; Acetone-d^{6} + D$_2$O)

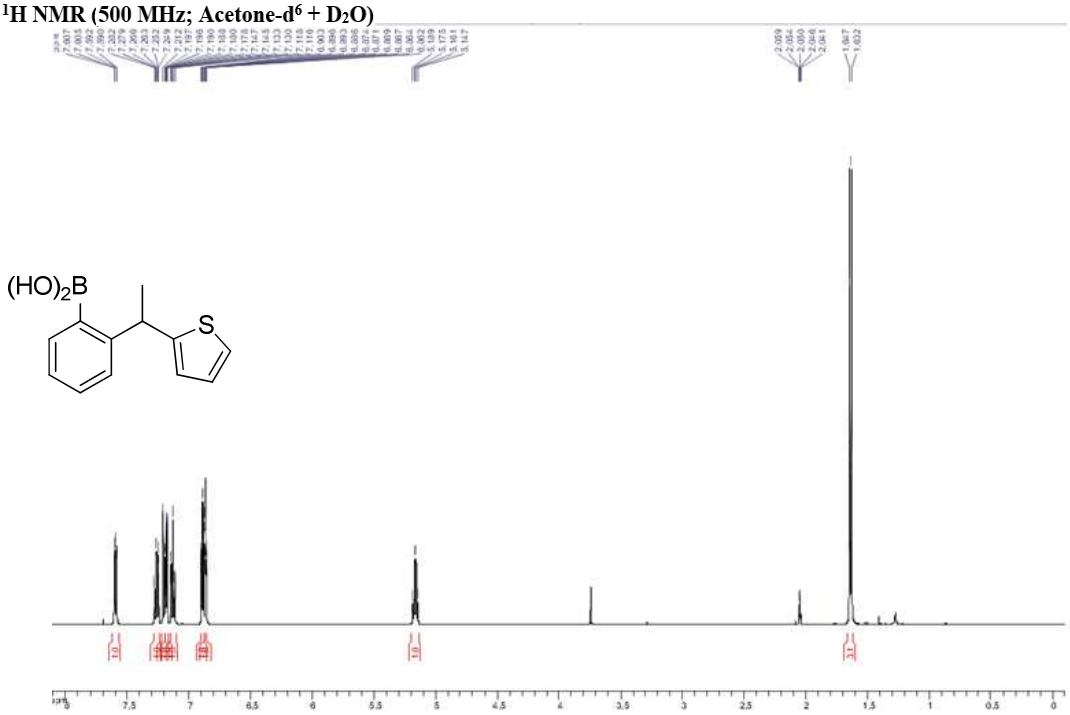


^{13}C NMR (125.7 MHz; Acetone-d^{6} + D$_2$O)

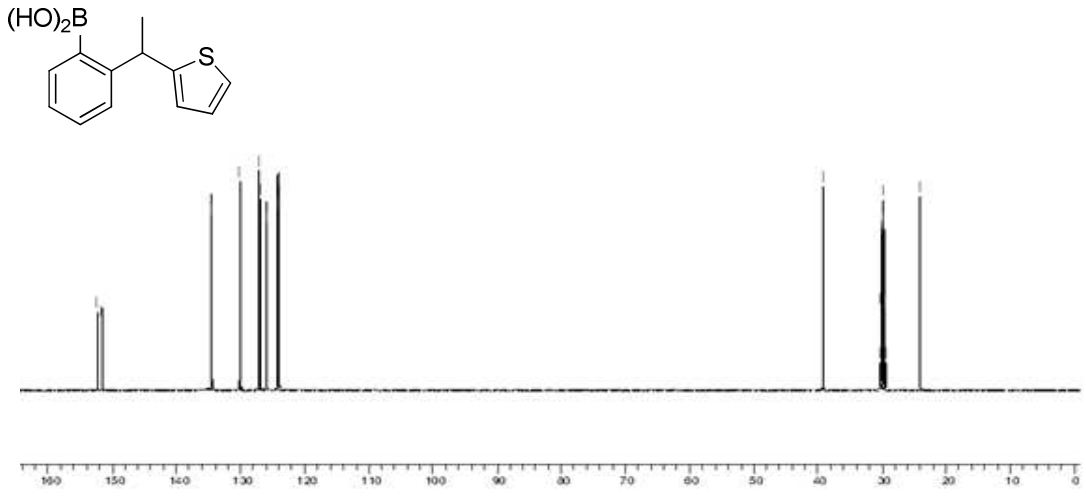


2-(1-(Thiophen-2-yl)ethyl)phenylboronic acid **7k**

^{1}H NMR (500 MHz; Acetone-d^{6} + D$_2$O)

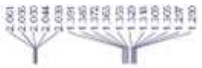


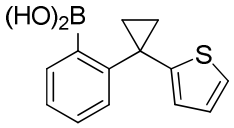
^{13}C NMR (125.7 MHz; Acetone-d^{6} + D$_2$O)

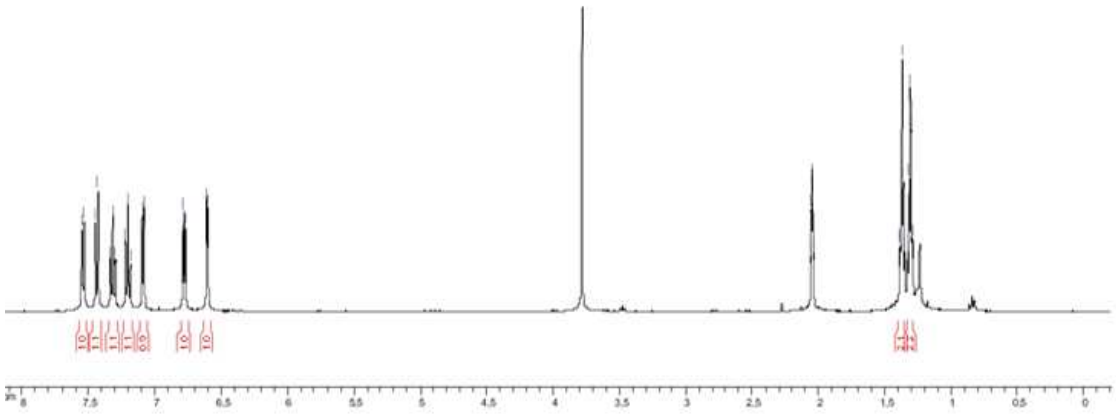


2-(1-(Thiophen-2-yl)cyclopropyl)phenylboronic acid **7l**

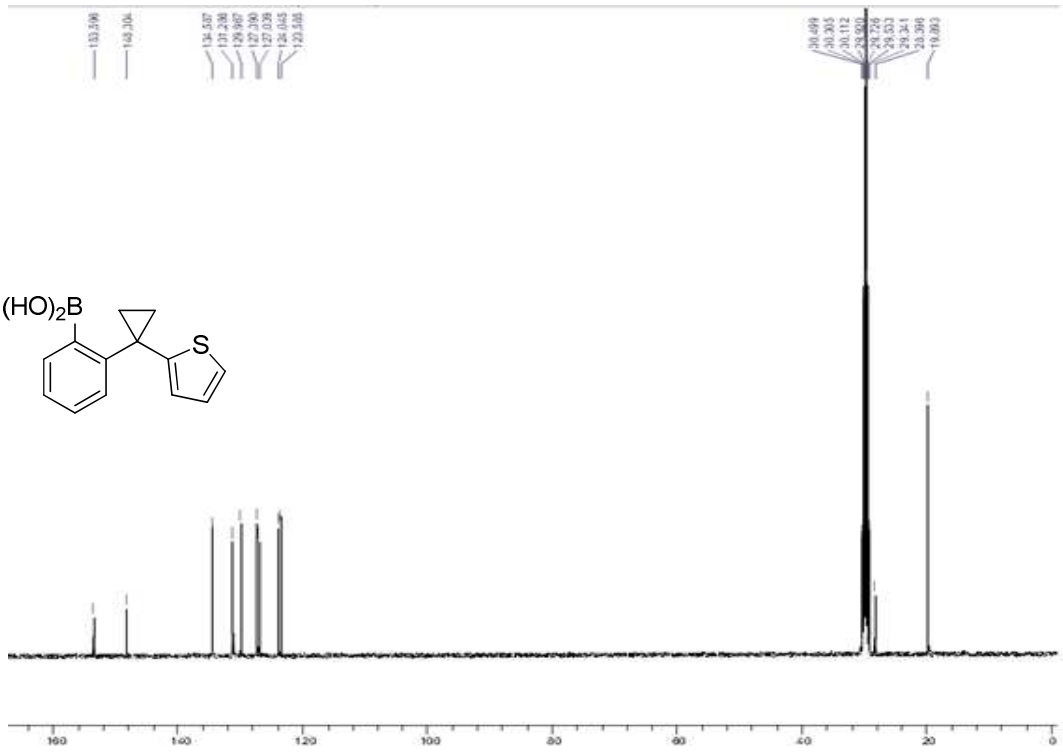
^{1}H NMR (400 MHz; Acetone-d^{6} + D$_2$O)







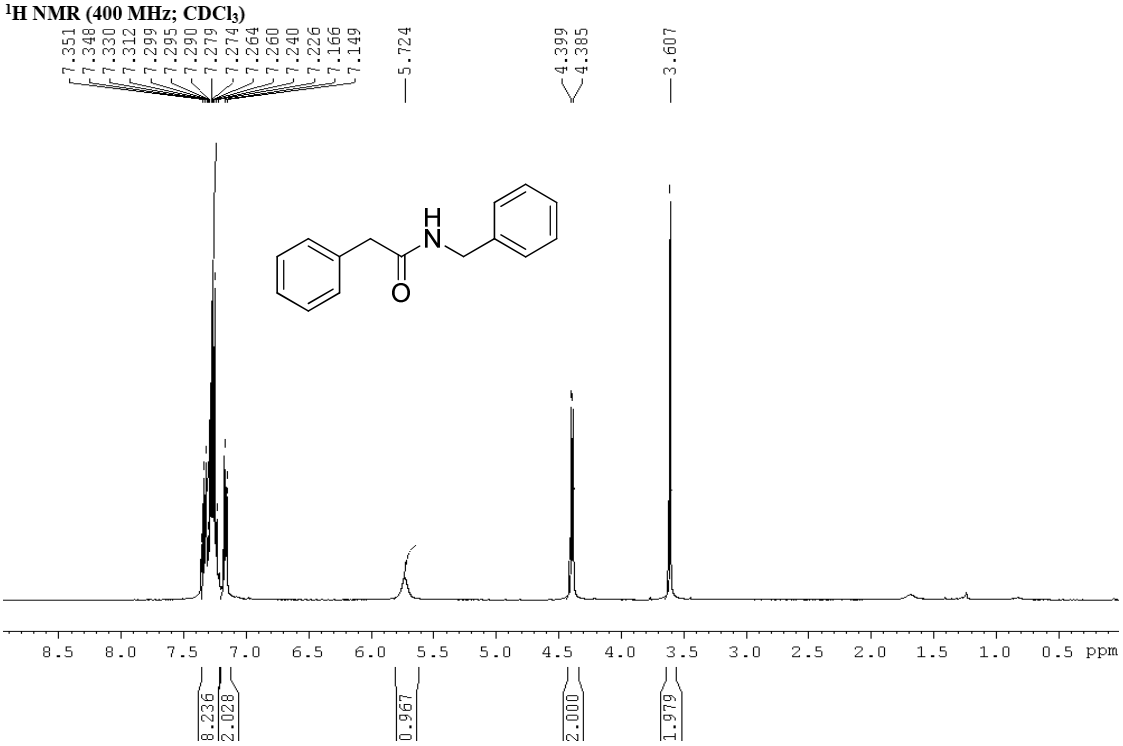
^{13}C NMR (125.7 MHz; Acetone-d^{6} + D$_2$O)



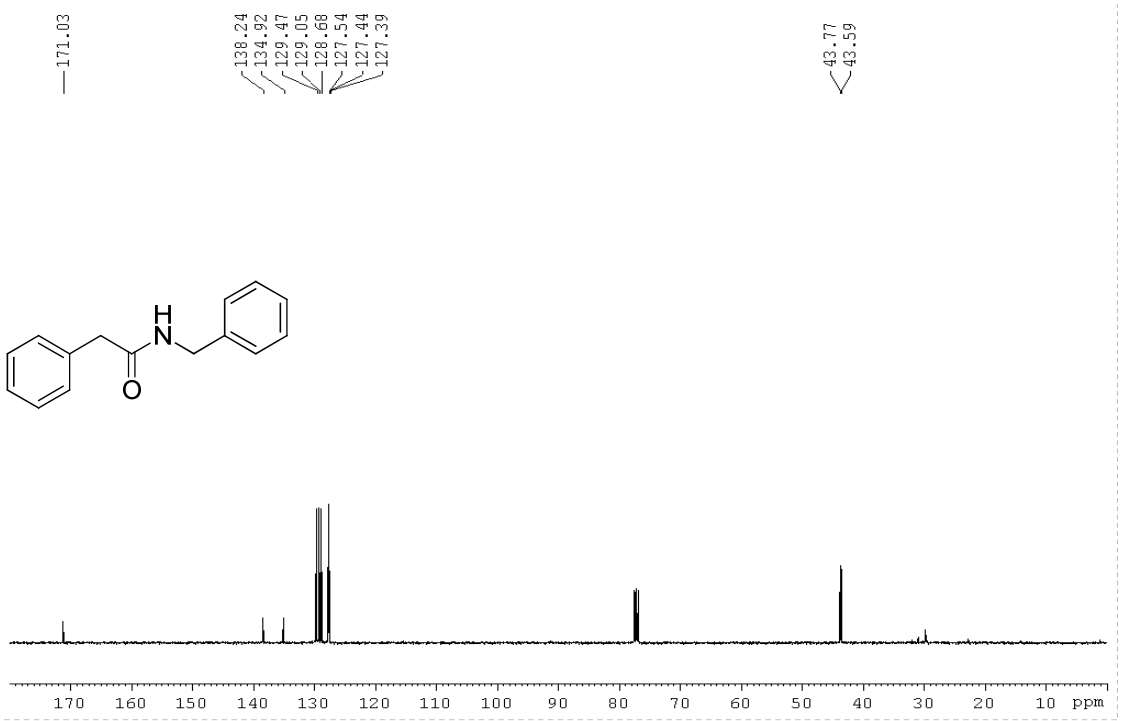
6. ^{1}H and ^{13}C Spectra of Synthesized Amides

N-benzyl-2-phenylacetamide **8a**

^{1}H NMR (400 MHz; $CDCl_3$)

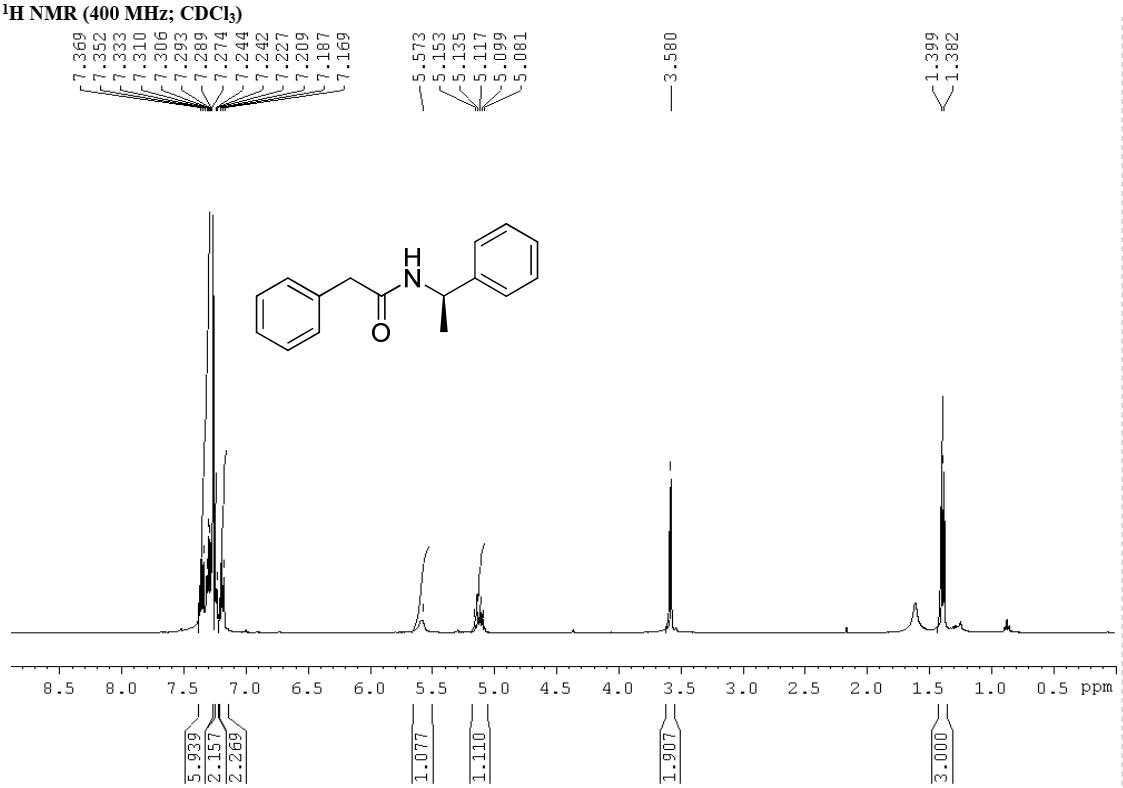


^{13}C NMR (101.6 MHz; $CDCl_3$)

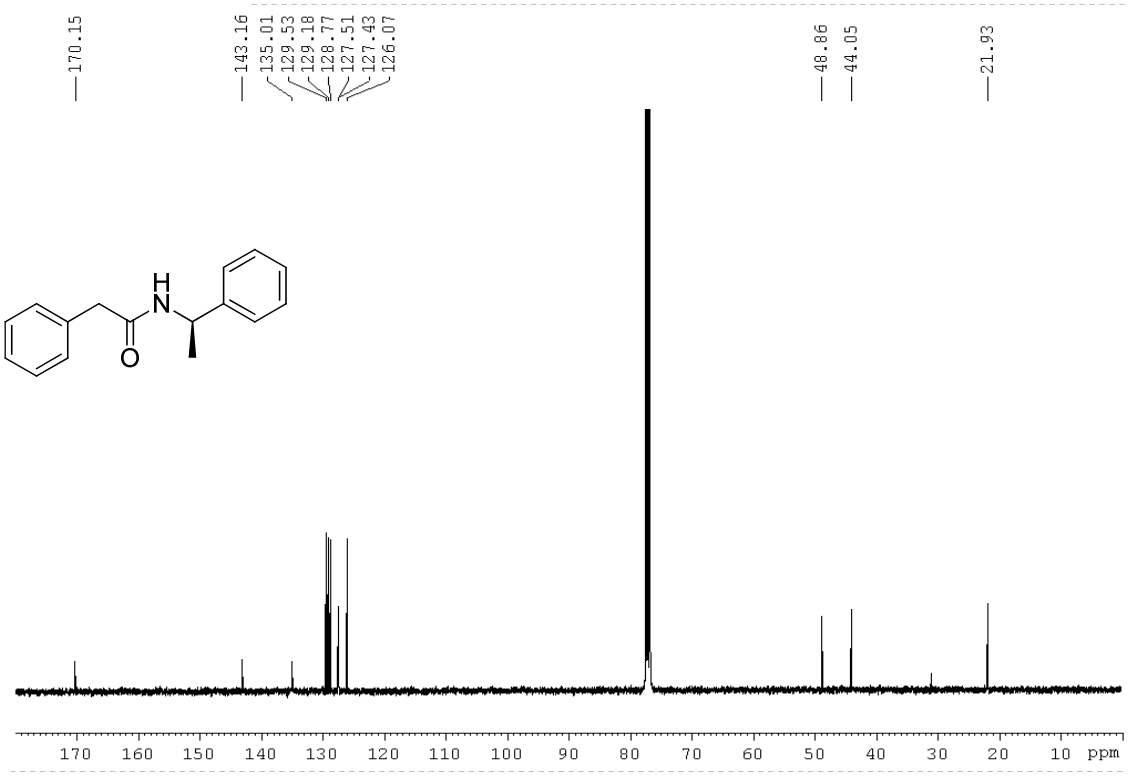


(*R*)-2-phenyl-N-(1-phenylethyl)acetamide **8b**

^{1}H NMR (400 MHz; $CDCl_3$)

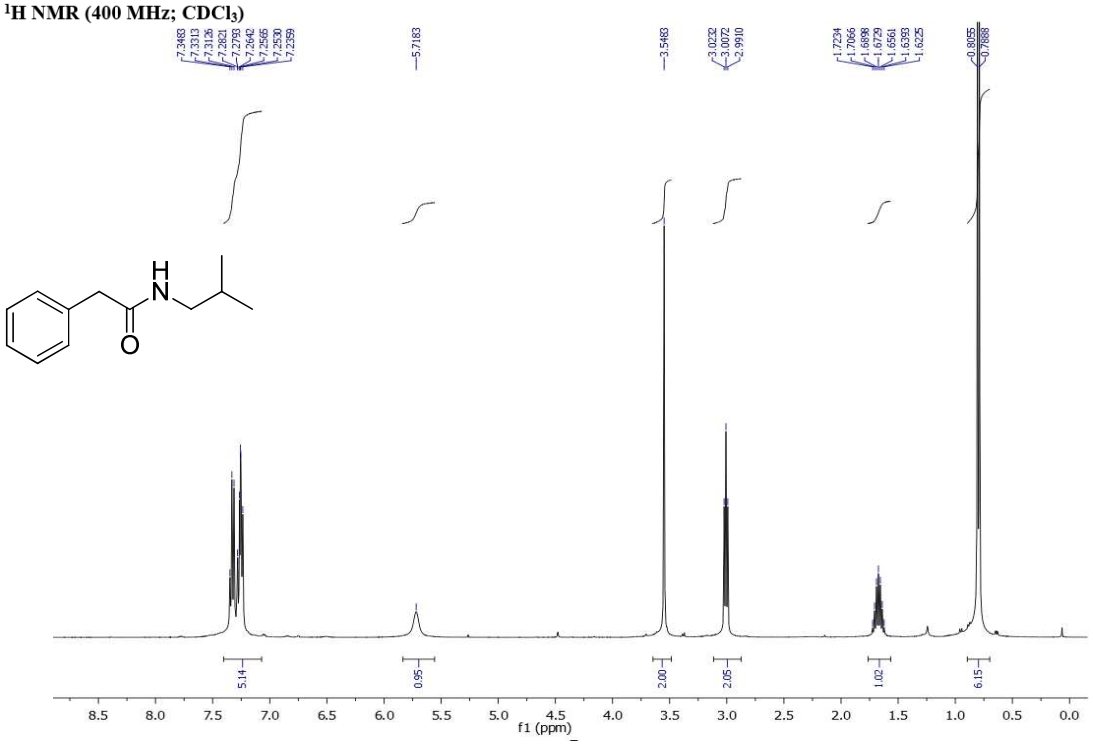


^{13}C NMR (101.6 MHz; $CDCl_3$)

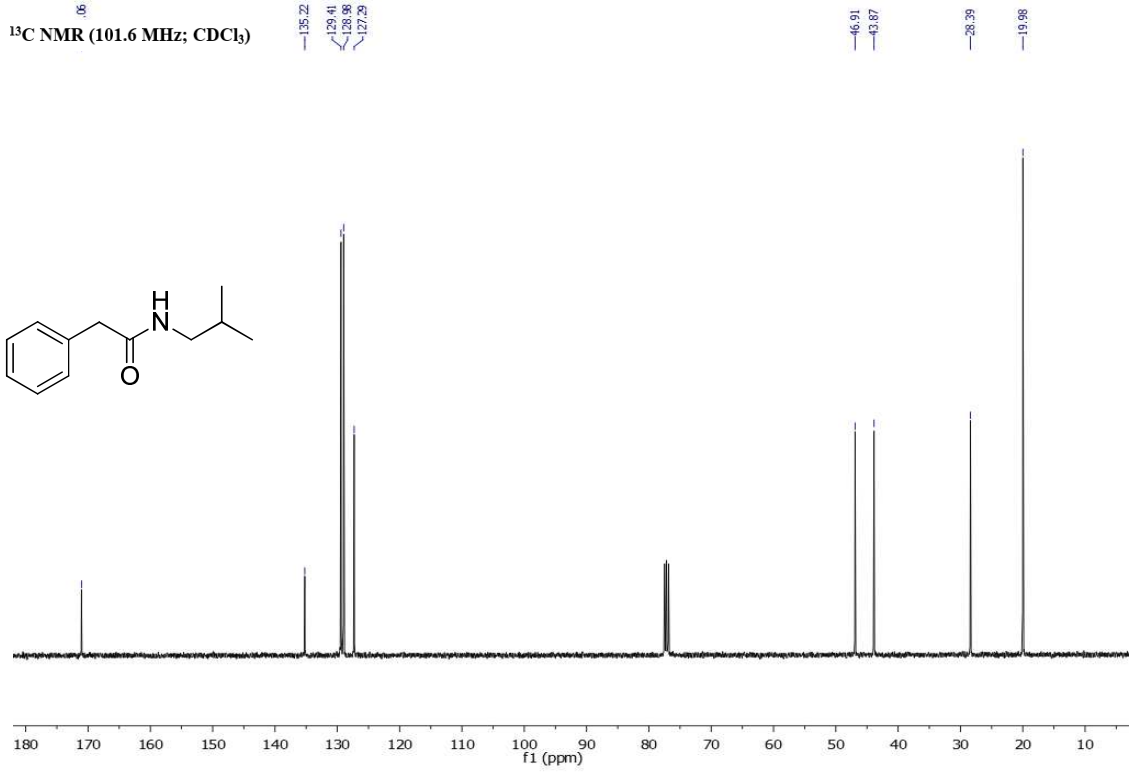


N-isobutyl-2-phenylacetamide **8c**

^{1}H NMR (400 MHz; $CDCl_3$)

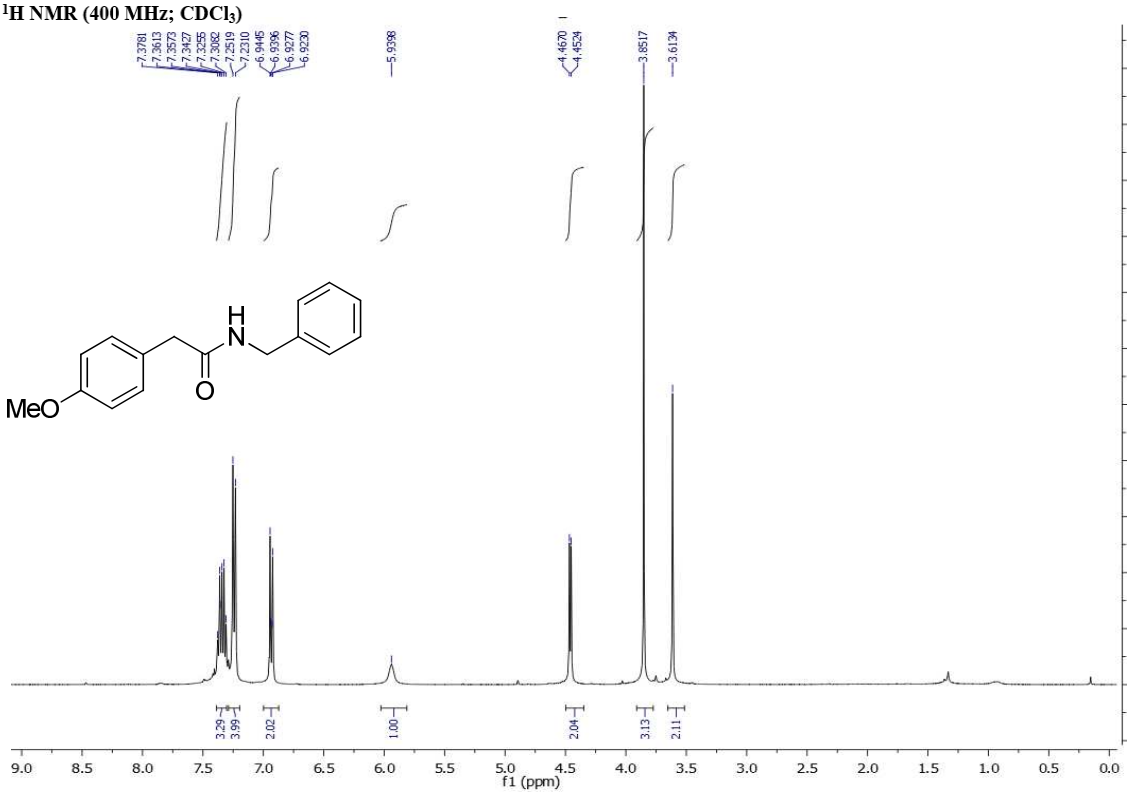


^{13}C NMR (101.6 MHz; $CDCl_3$)

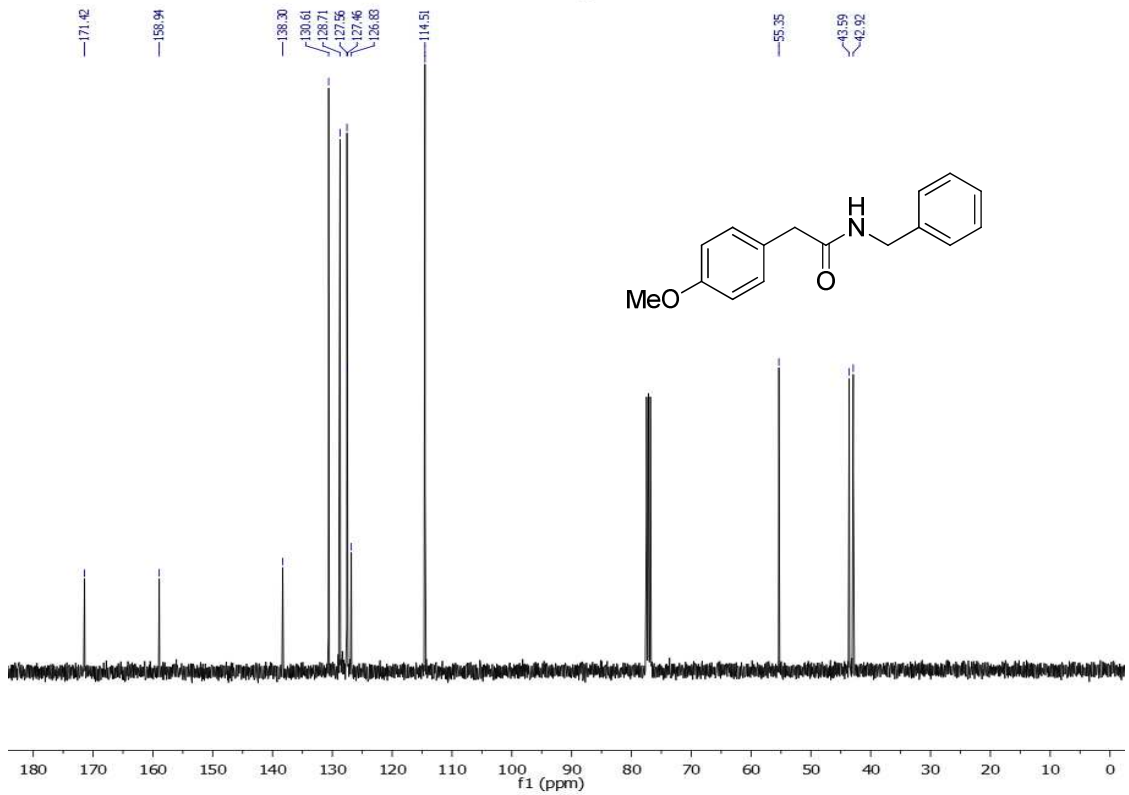


N-Benzyl-2-(4-methoxyphenyl)acetamide **13a**

^{1}H NMR (400 MHz; $CDCl_3$)

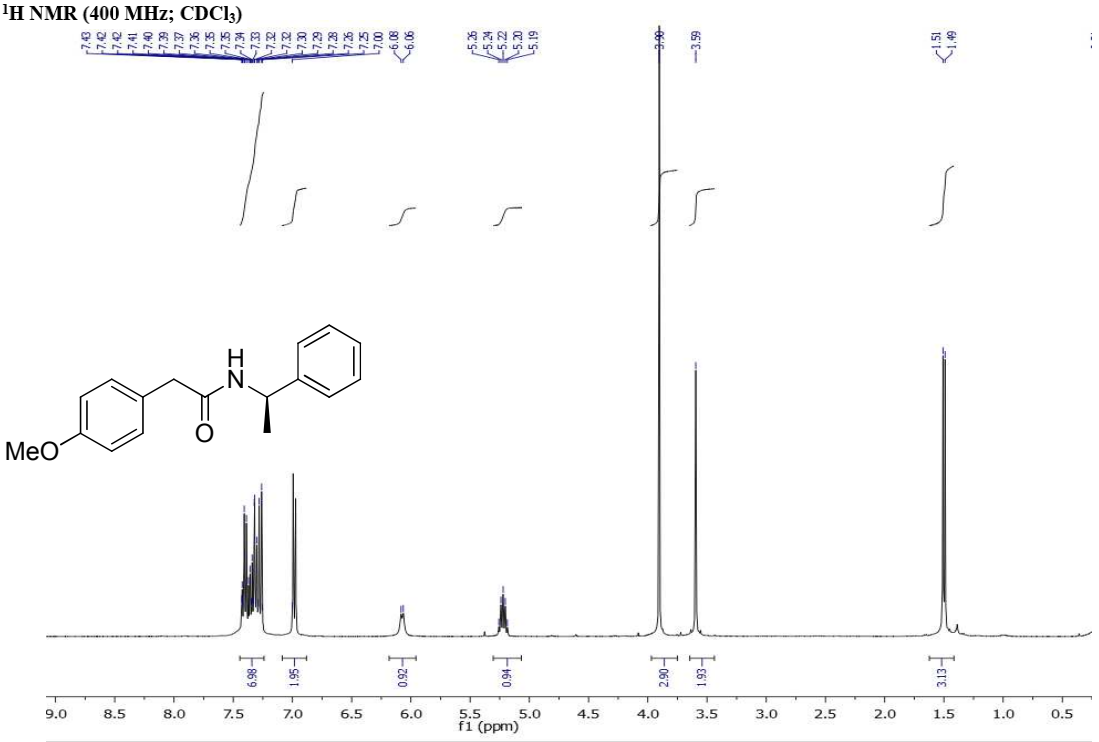


^{13}C NMR (101.6 MHz; $CDCl_3$)

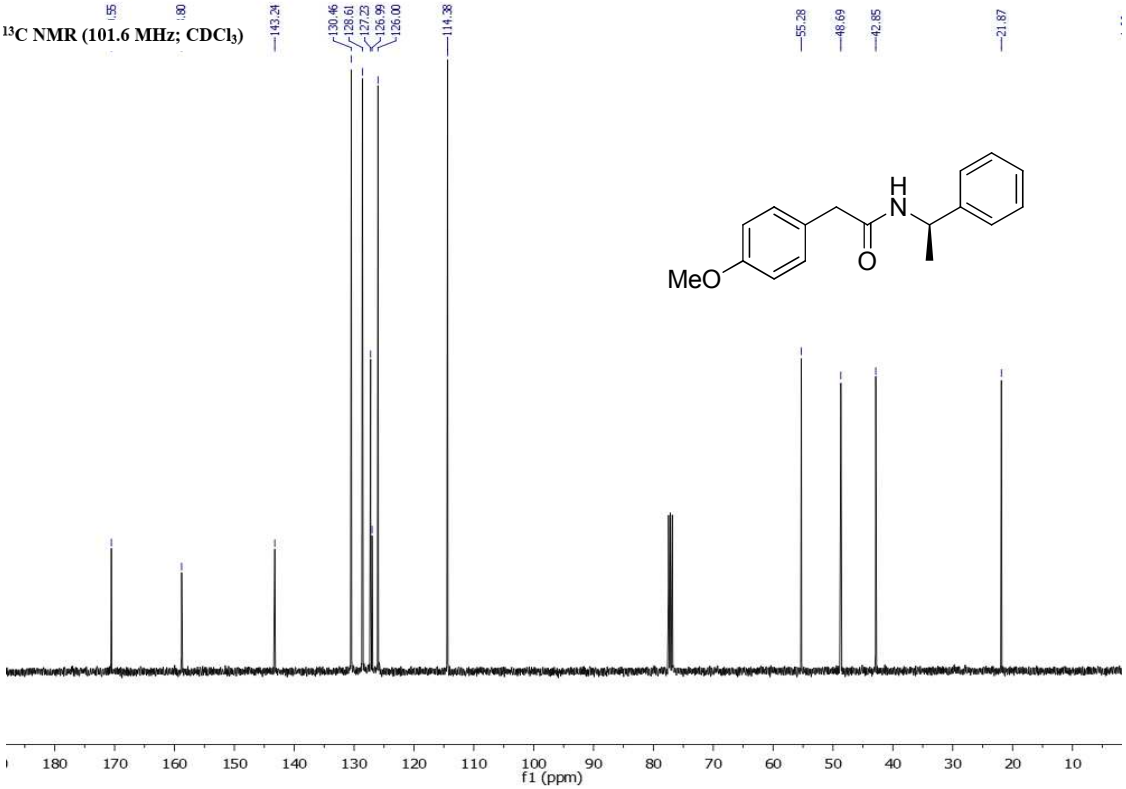


(*R*)-2-(4-methoxyphenyl)-N-(1-phenylethyl)acetamide **13b**

^{1}H NMR (400 MHz; $CDCl_3$)

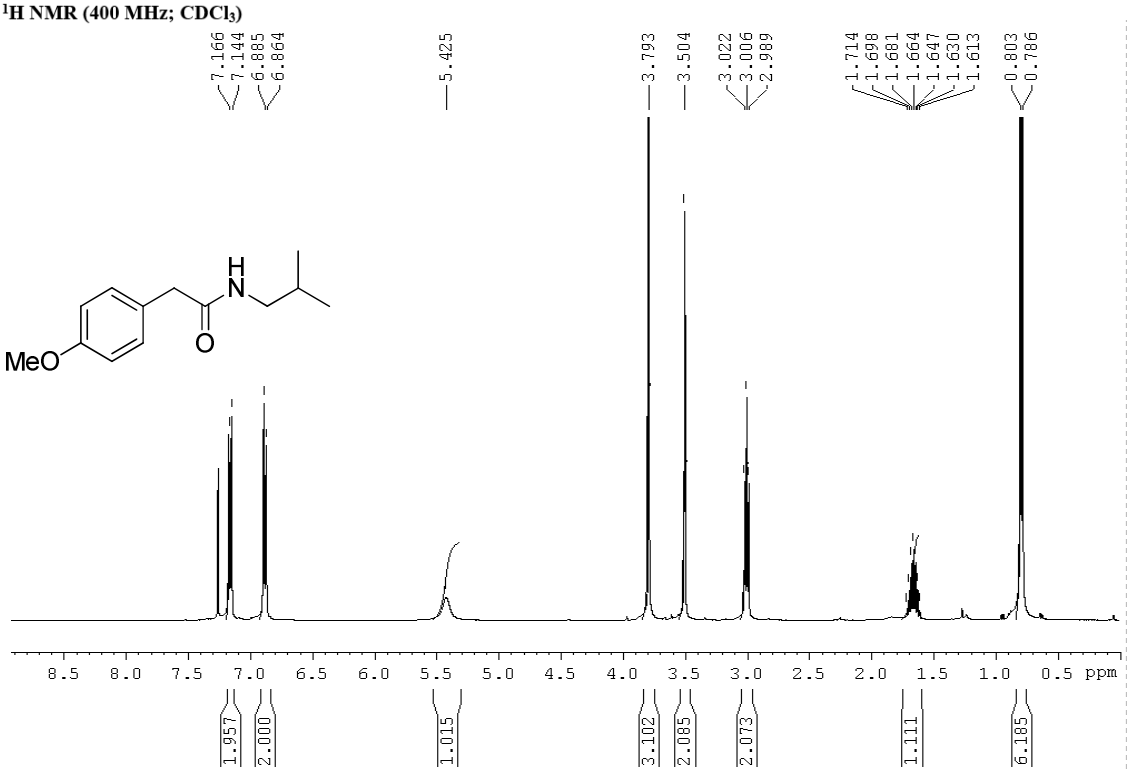


^{13}C NMR (101.6 MHz; $CDCl_3$)

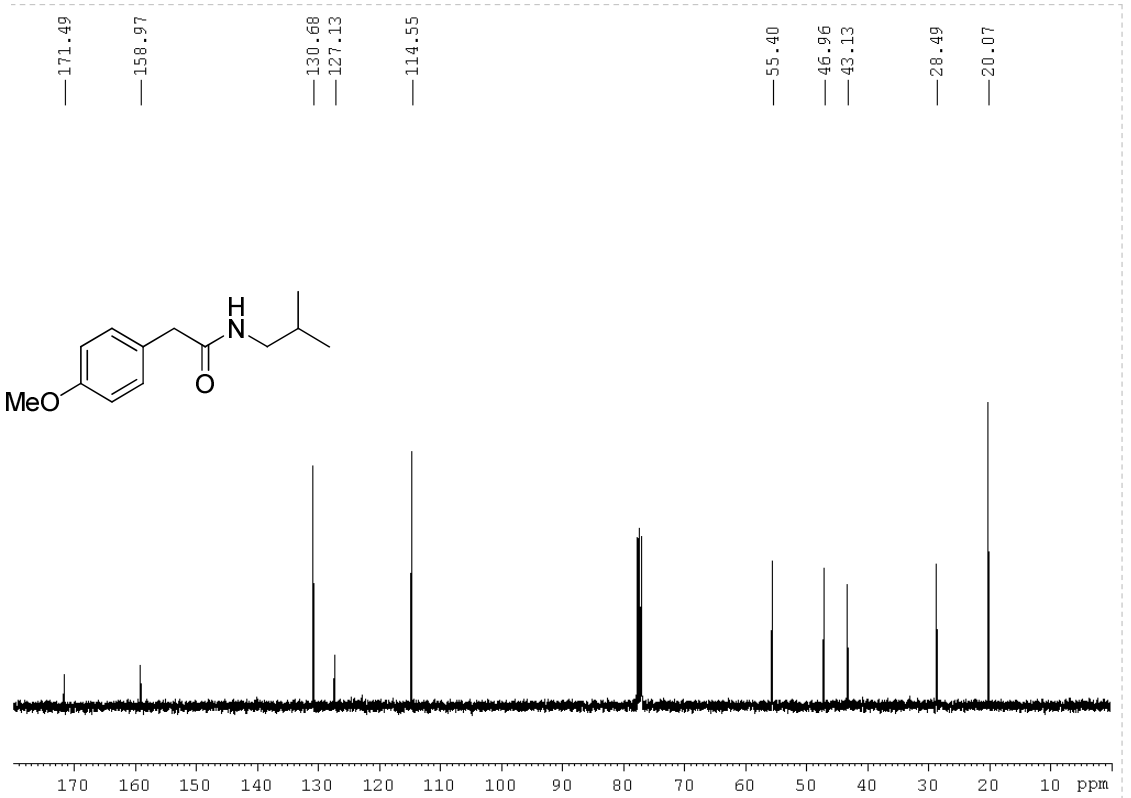


N-isobutyl-2-(4-methoxyphenyl)acetamide **13c**

^{1}H NMR (400 MHz; $CDCl_3$)

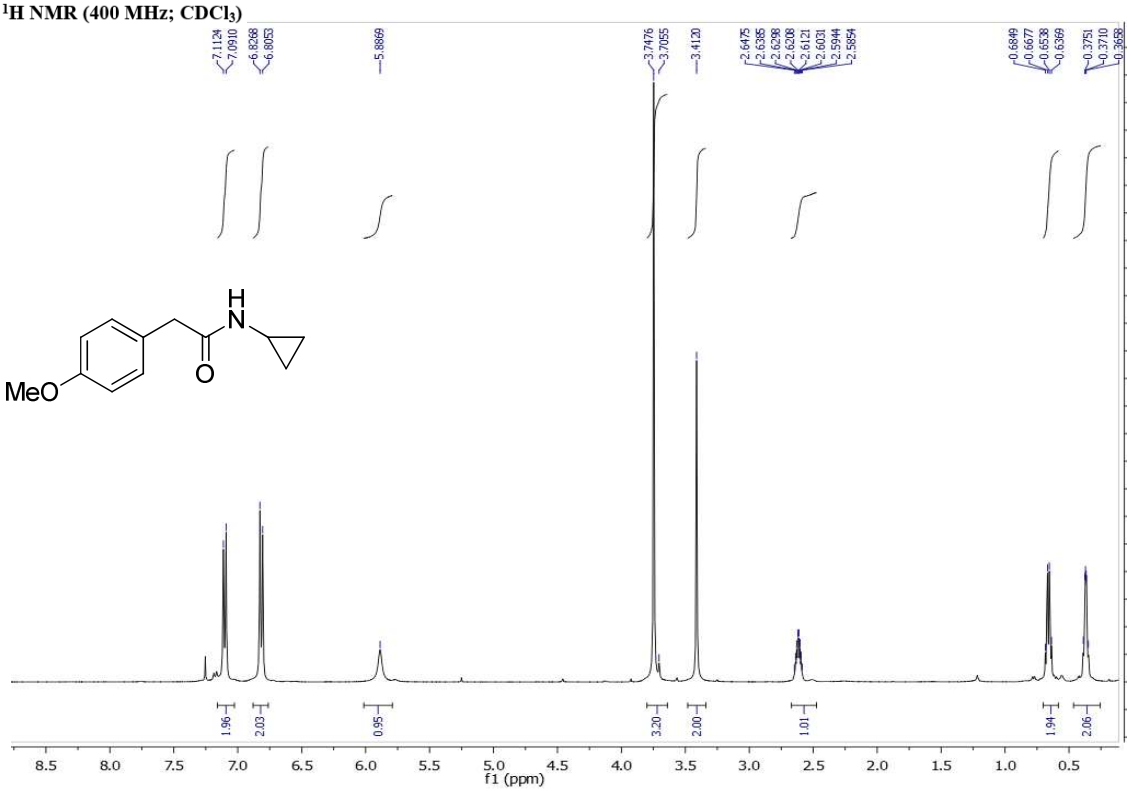


^{13}C NMR (101.6 MHz; $CDCl_3$)

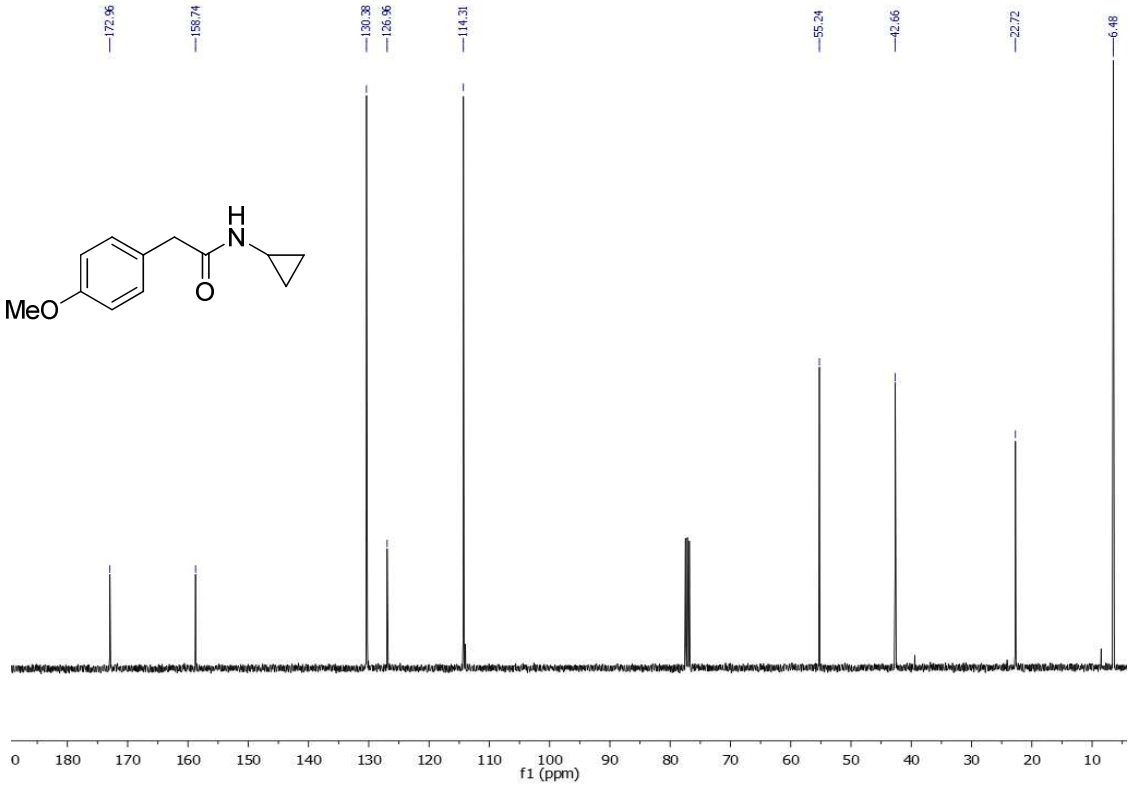


N-cyclopropyl-2-(4-methoxyphenyl)acetamide **13d**

^{1}H NMR (400 MHz; $CDCl_3$)

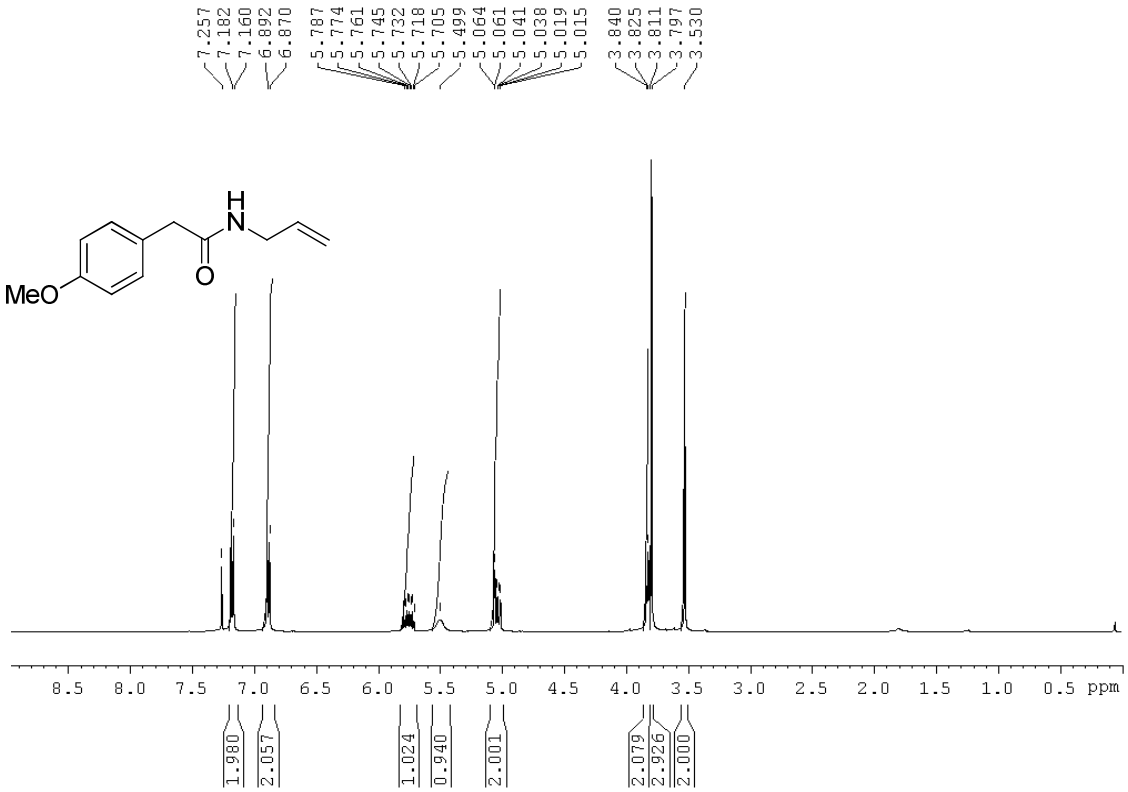


^{13}C NMR (101.6 MHz; $CDCl_3$)

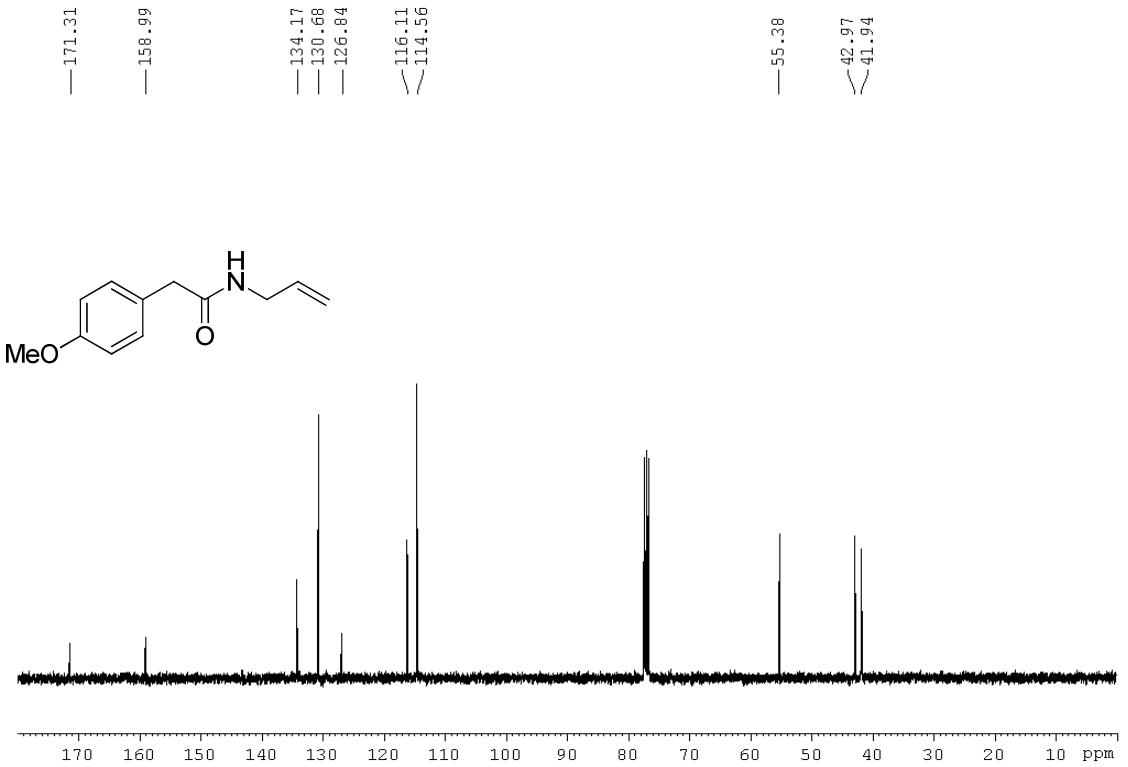


N-allyl-2-(4-methoxyphenyl)acetamide **13e**

^{1}H NMR (400 MHz; $CDCl_3$)

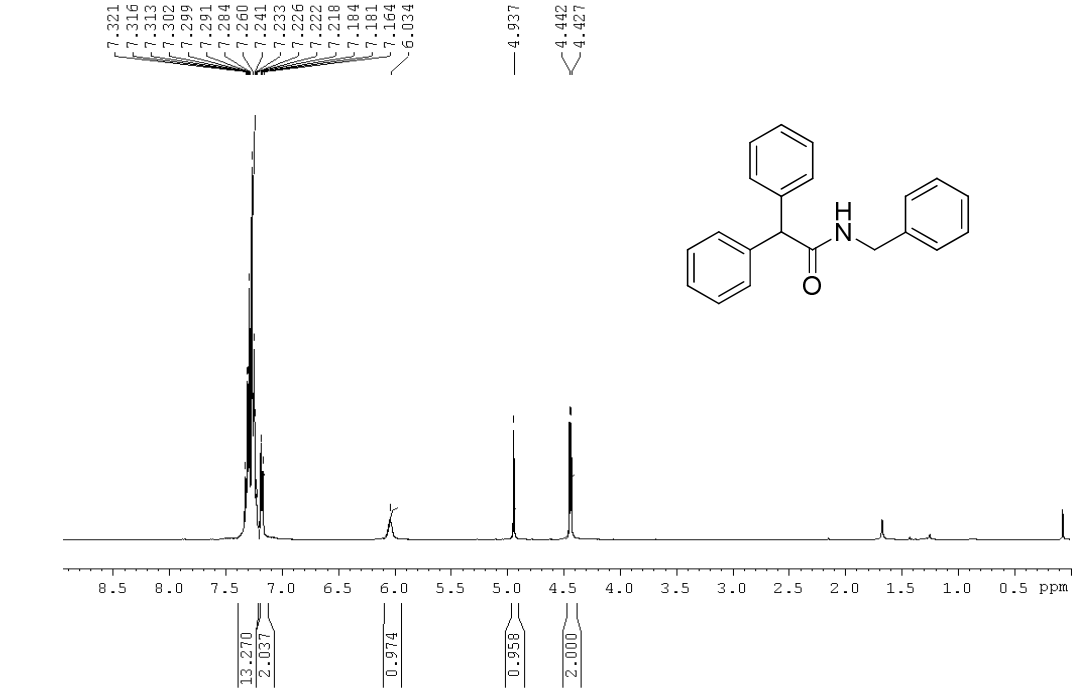


^{13}C NMR (101.6 MHz; $CDCl_3$)

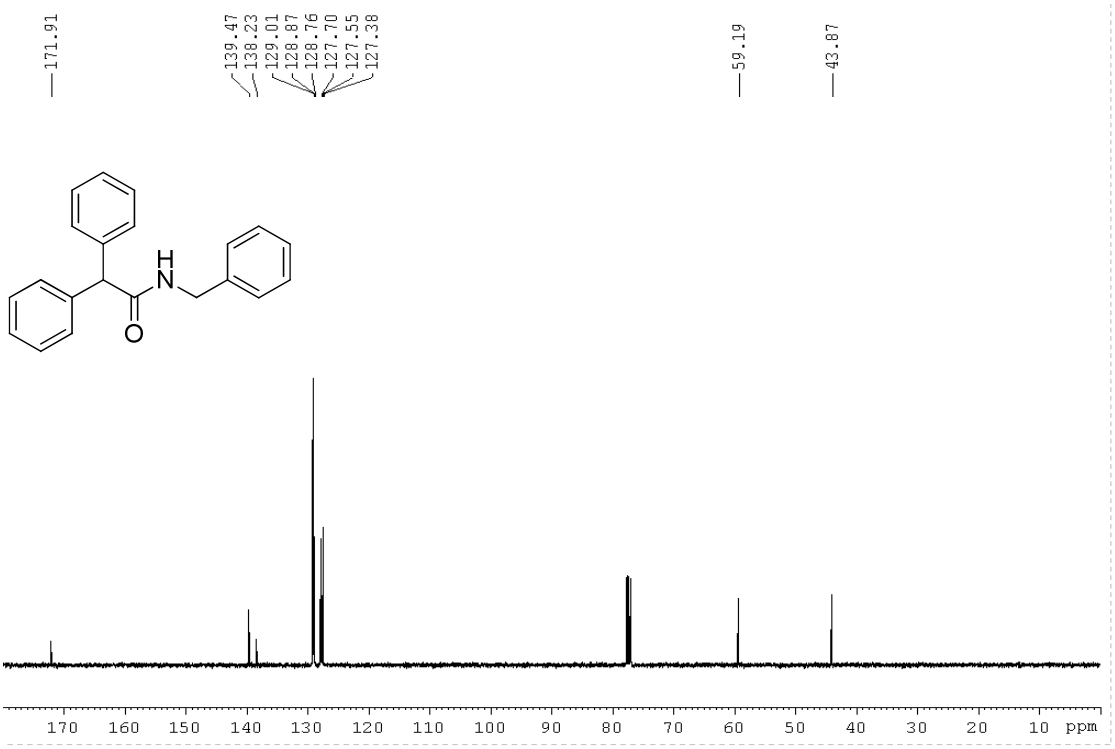


N-benzyl-2,2-diphenylacetamide **14a**

^{1}H NMR (400 MHz; $CDCl_3$)

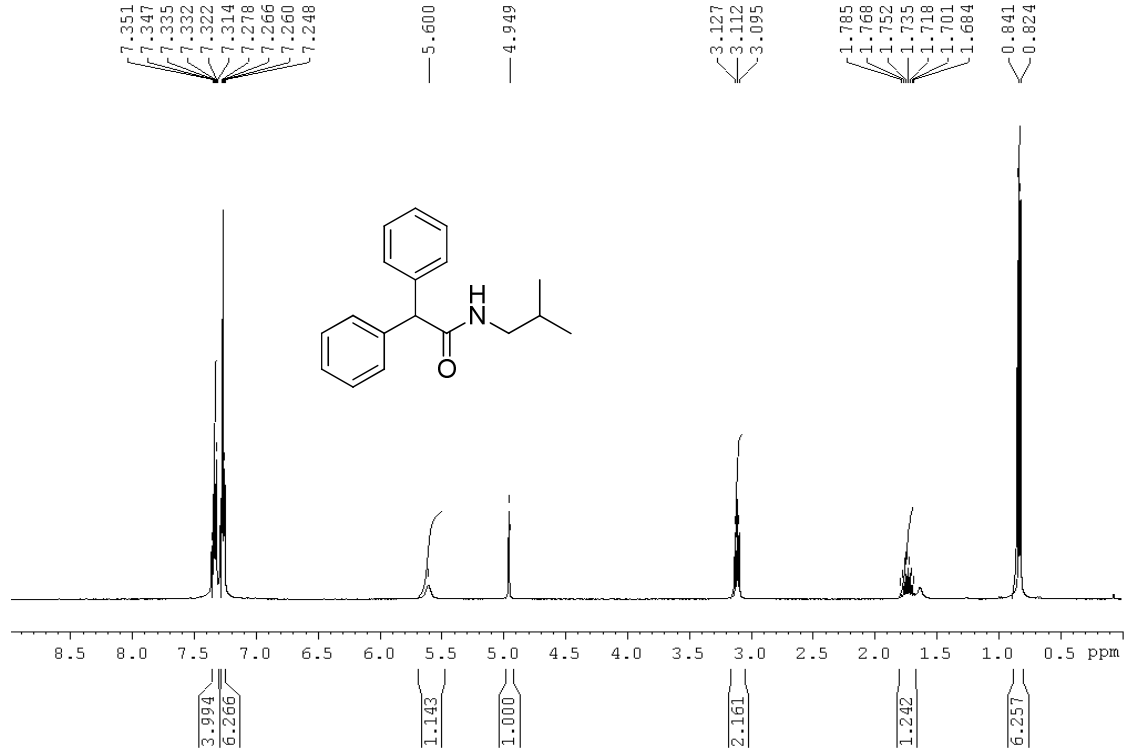


^{13}C NMR (101.6 MHz; $CDCl_3$)

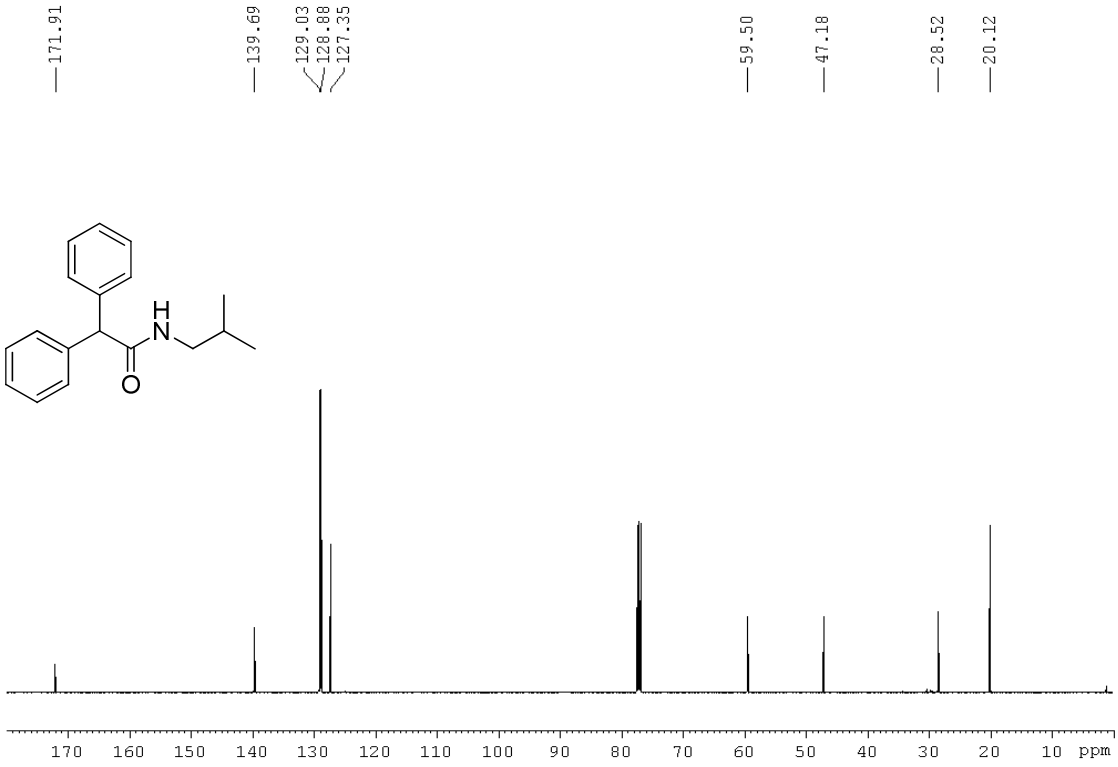


N-isobutyl-2,2-diphenylacetamide **14c**

^{1}H NMR (400 MHz; $CDCl_3$)

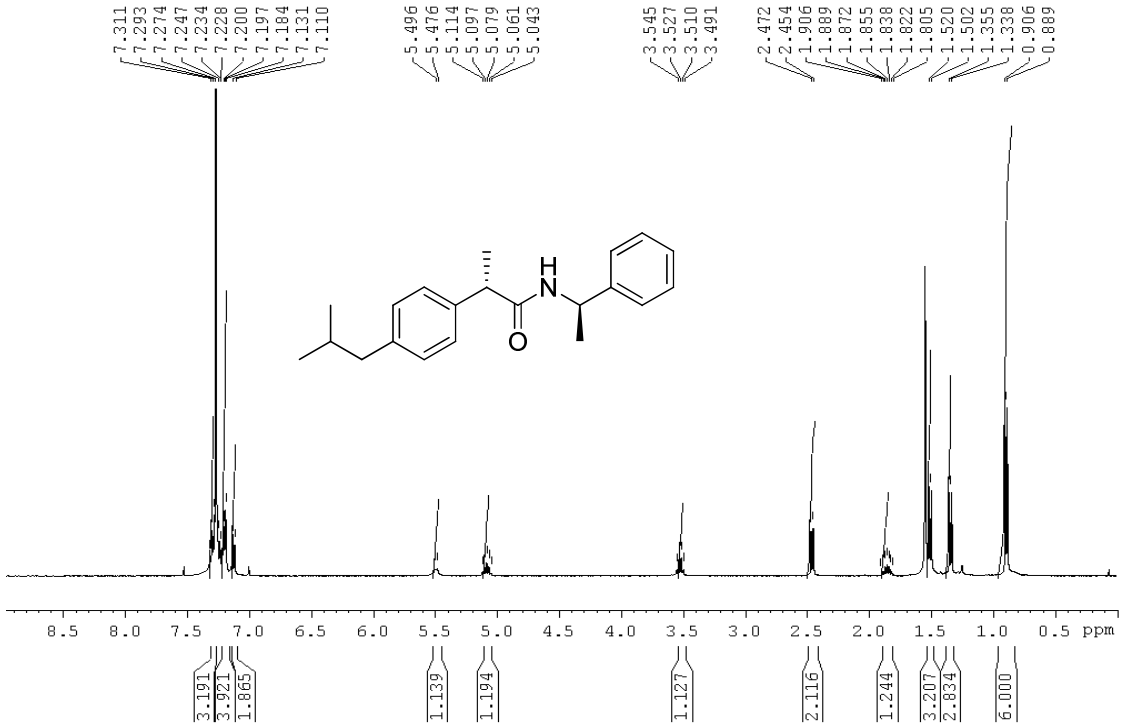


^{13}C NMR (101.6 MHz; $CDCl_3$)

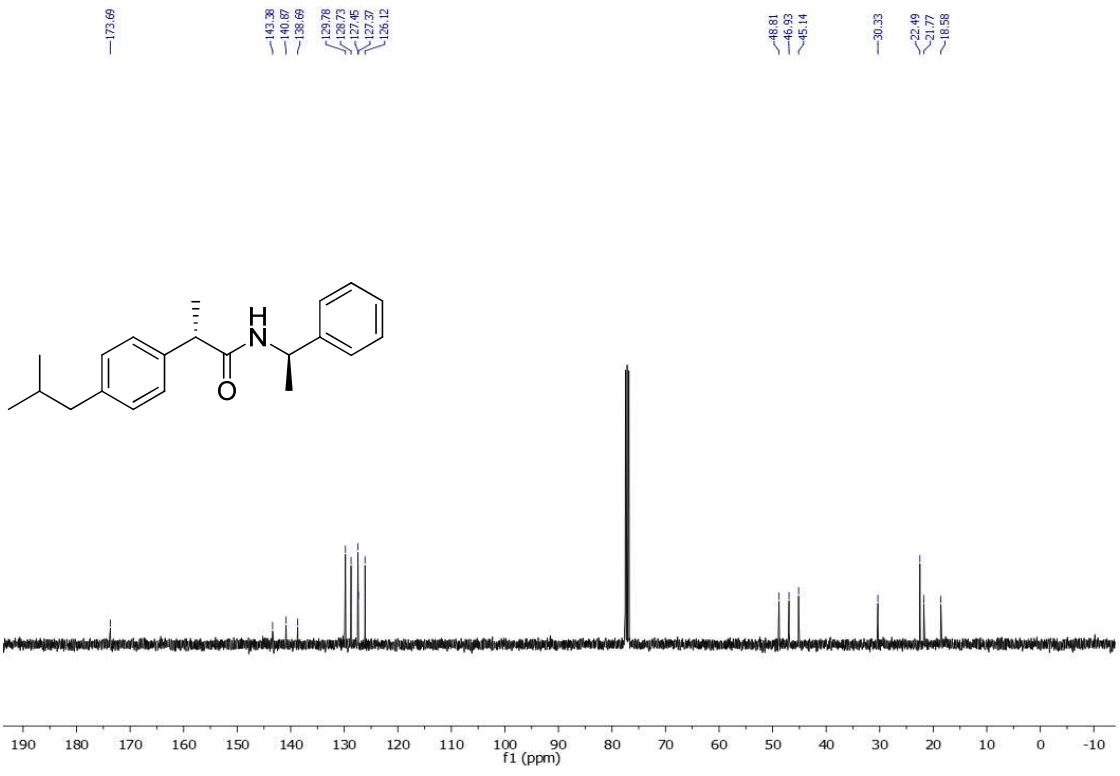


(*S*)-2-(4-isobutylphenyl)-N-((*R*)-1-phenylethyl)propanamide **15b**

^{1}H NMR (400 MHz; $CDCl_3$)

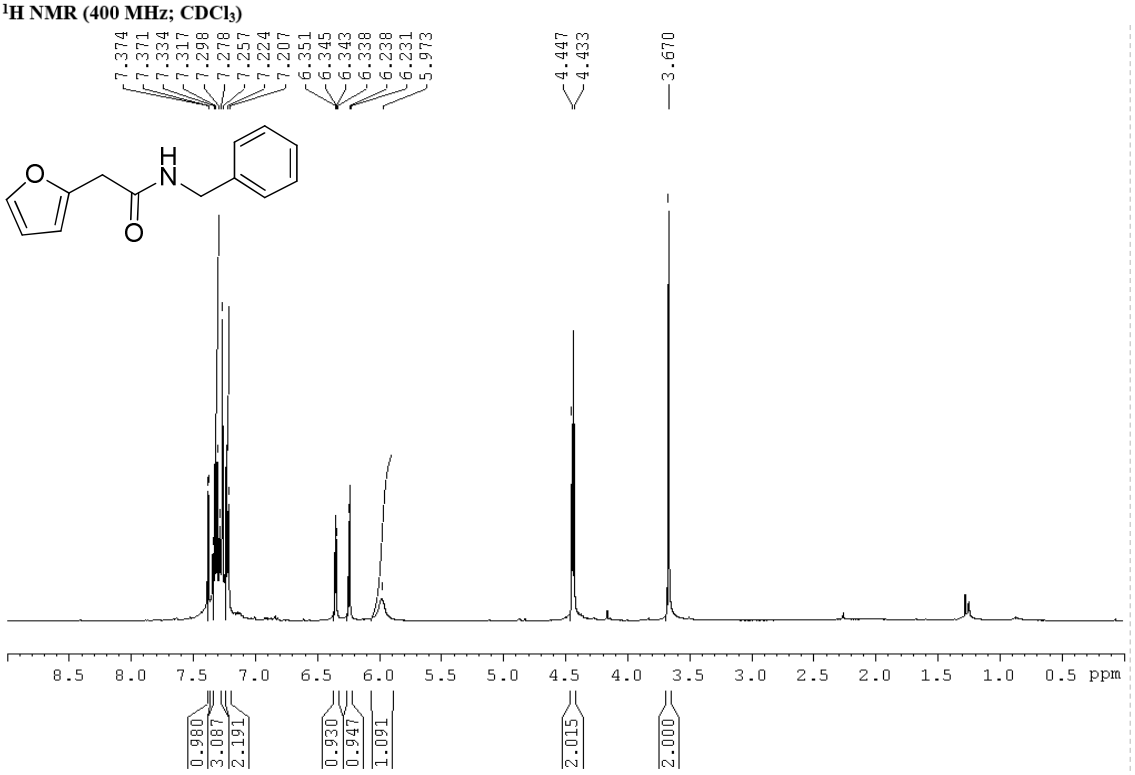


^{13}C NMR (101.6 MHz; $CDCl_3$)

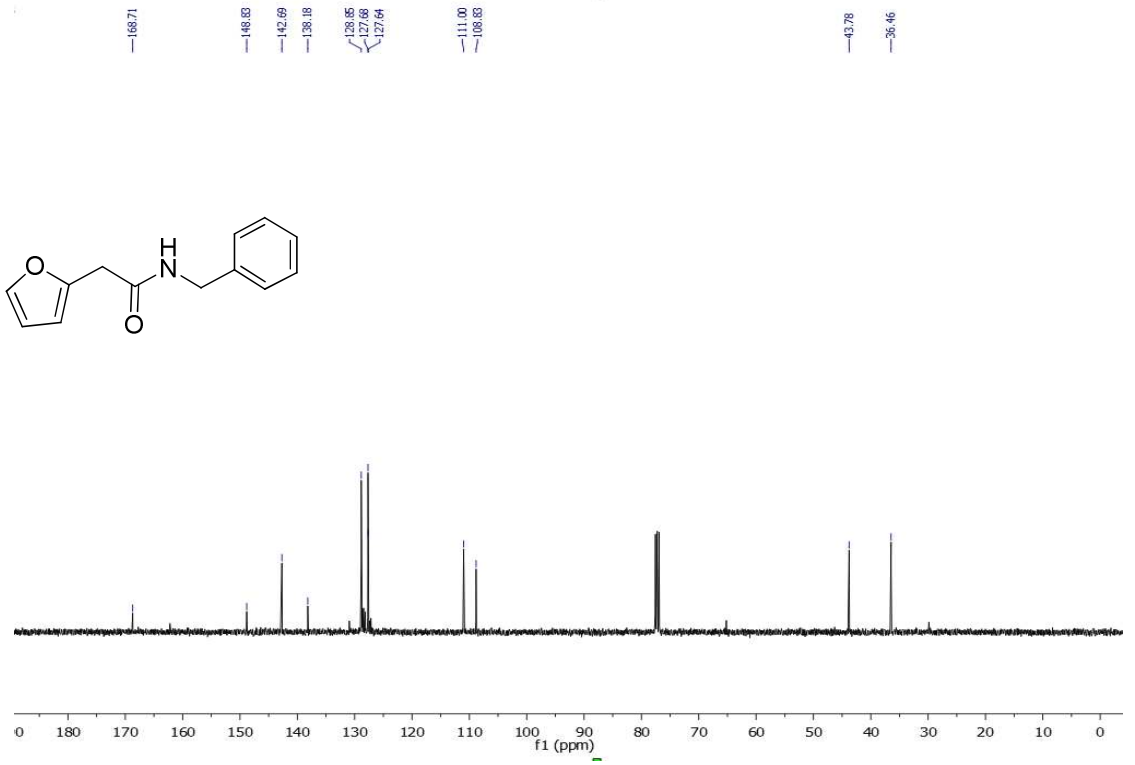


N-benzyl-2- (furan-2-yl)acetamide **16a**

^{1}H NMR (400 MHz; $CDCl_3$)

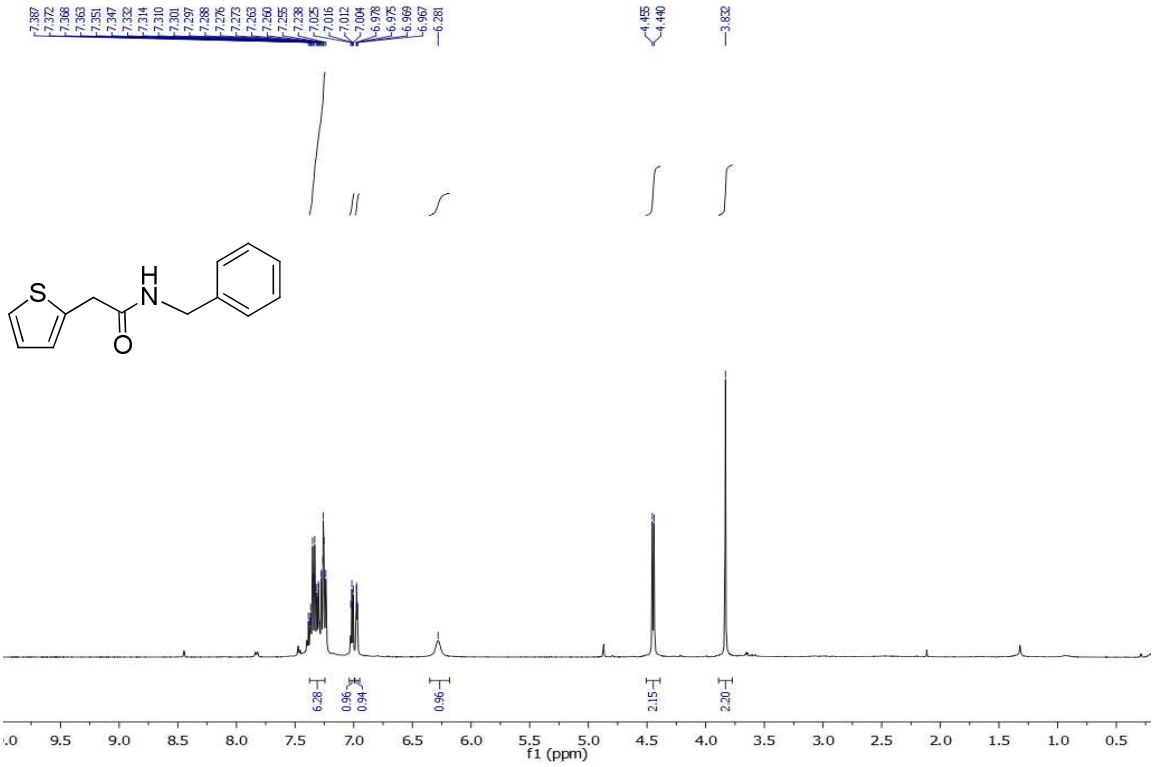


^{13}C NMR (101.6 MHz; $CDCl_3$)

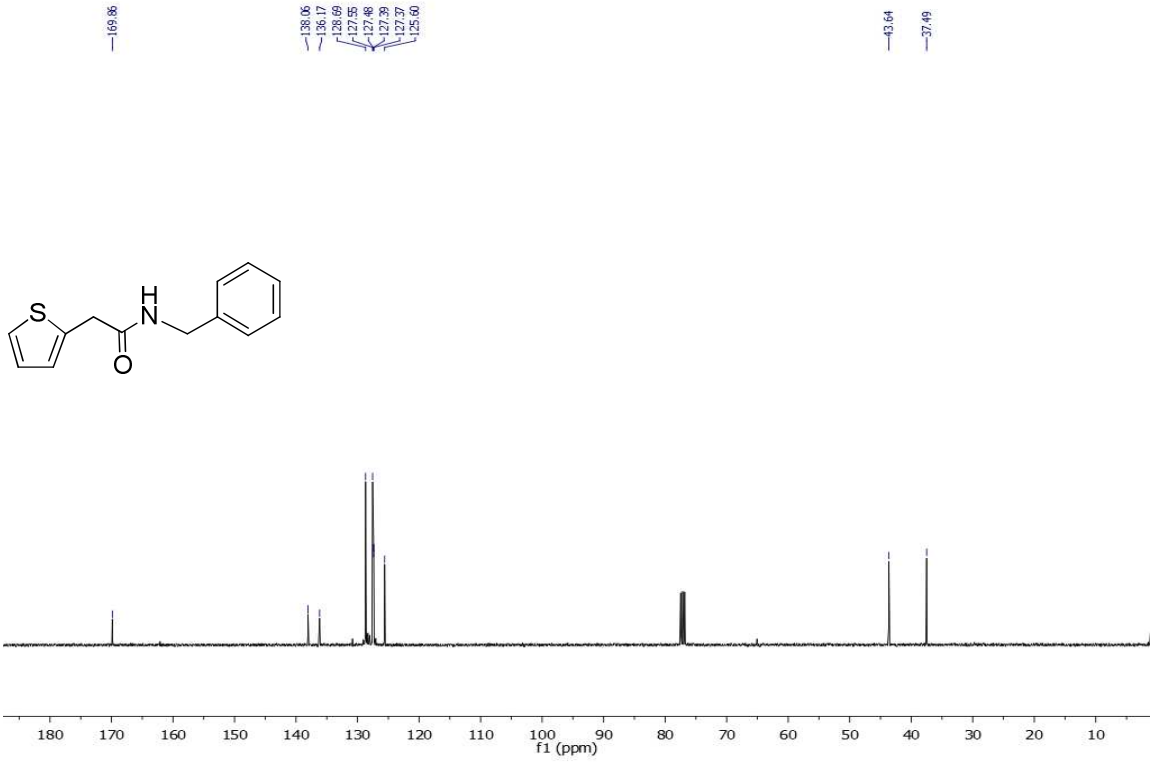


N-benzyl-2-(thiophen-2-yl)acetamide **17a**

^{1}H NMR (400 MHz; $CDCl_3$)

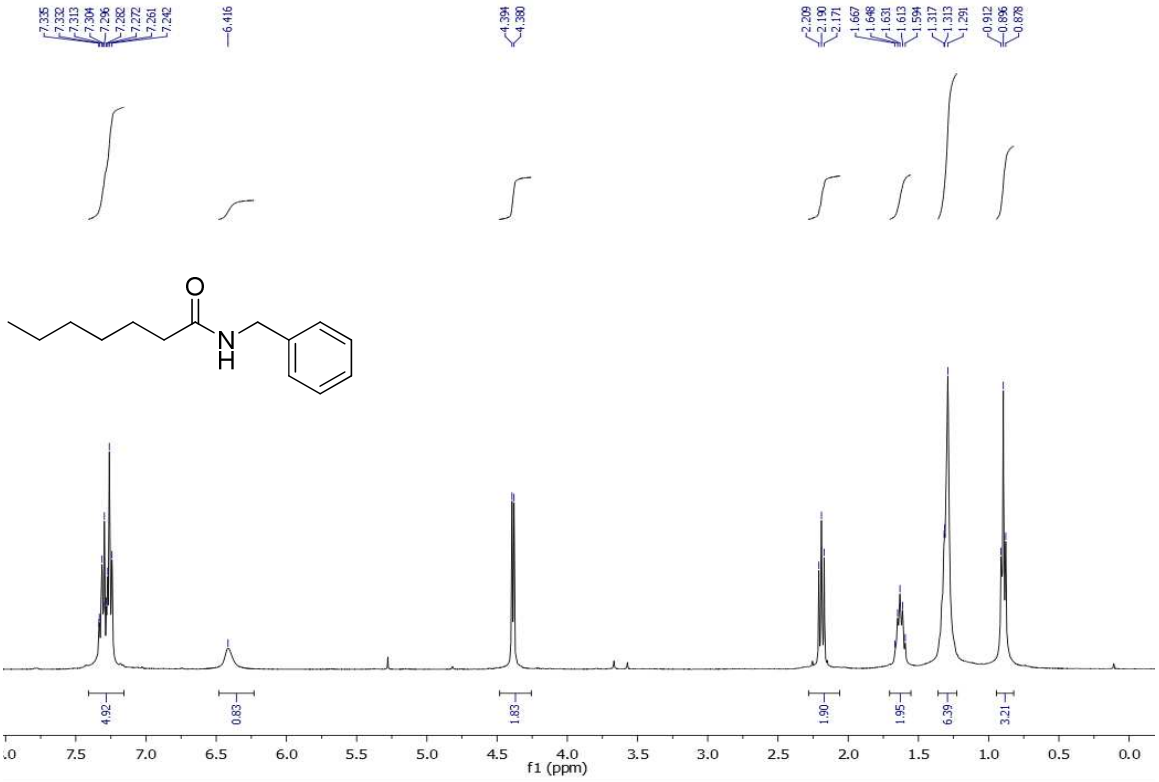


^{13}C NMR (101.6 MHz; $CDCl_3$)

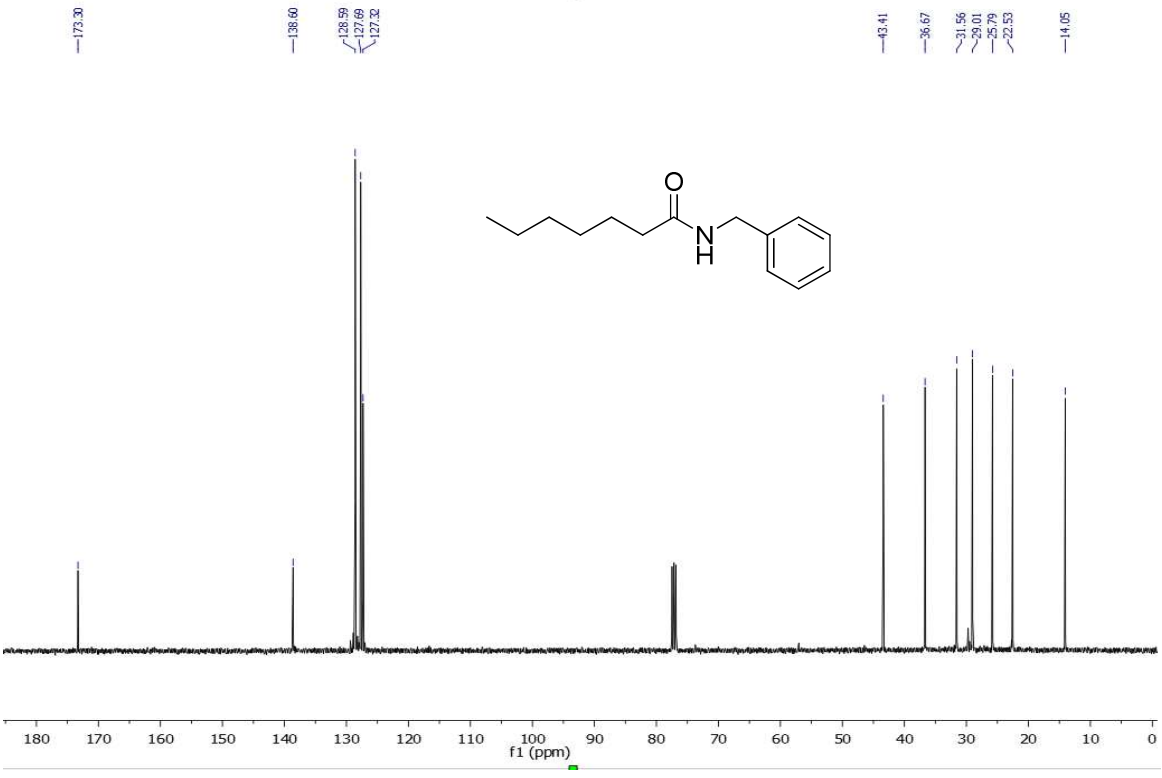


N-benzylheptanamide **18a**

^{1}H NMR (400 MHz; $CDCl_3$)

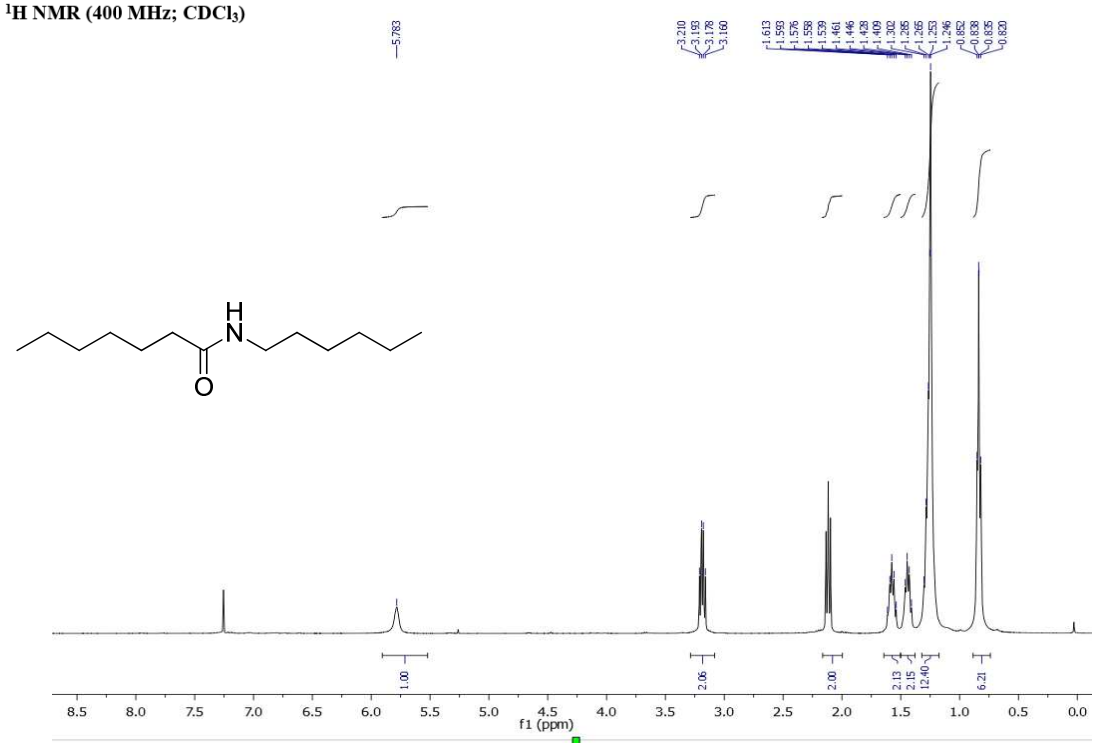


^{13}C NMR (101.6 MHz; $CDCl_3$)

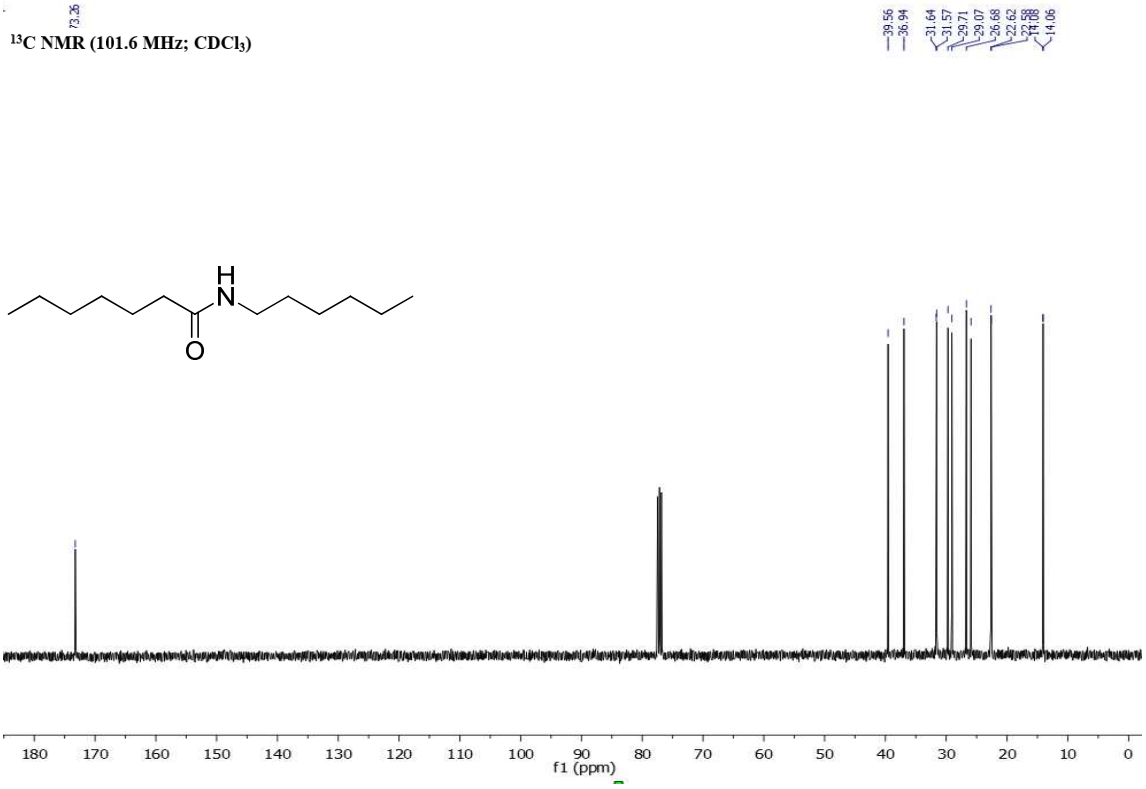


N-hexylheptanamide **19**

^{1}H NMR (400 MHz; $CDCl_3$)

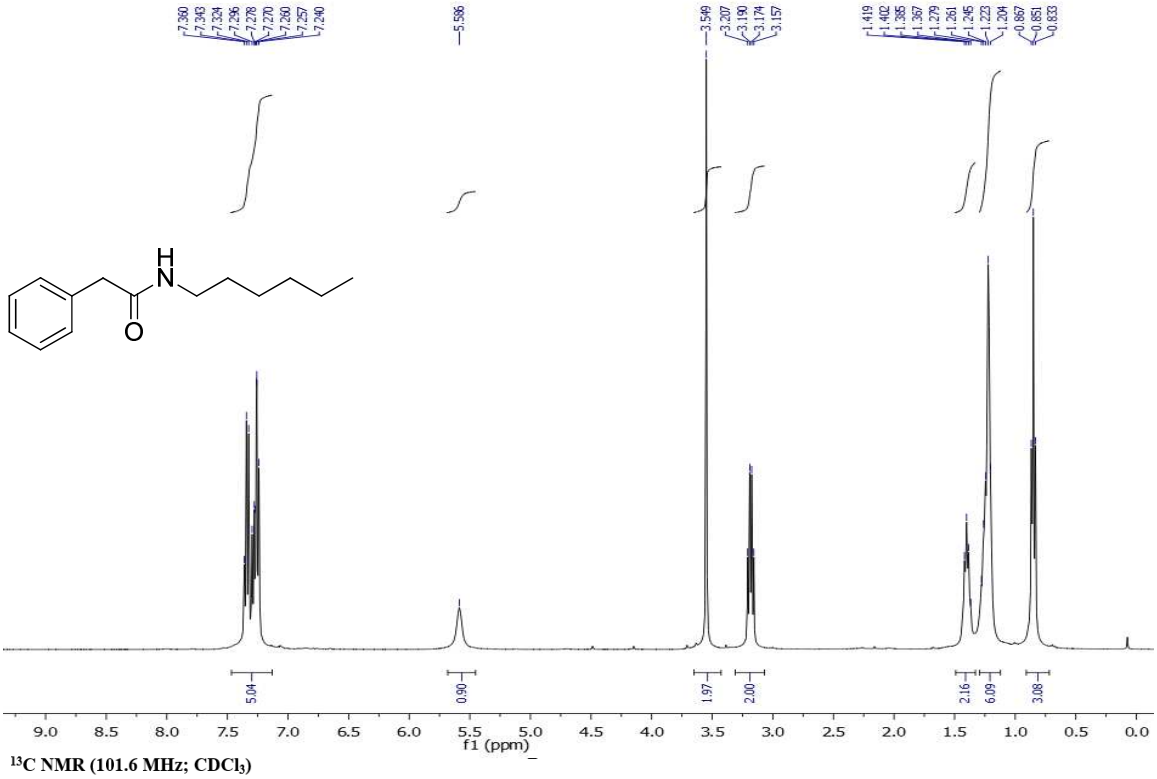


^{13}C NMR (101.6 MHz; $CDCl_3$)

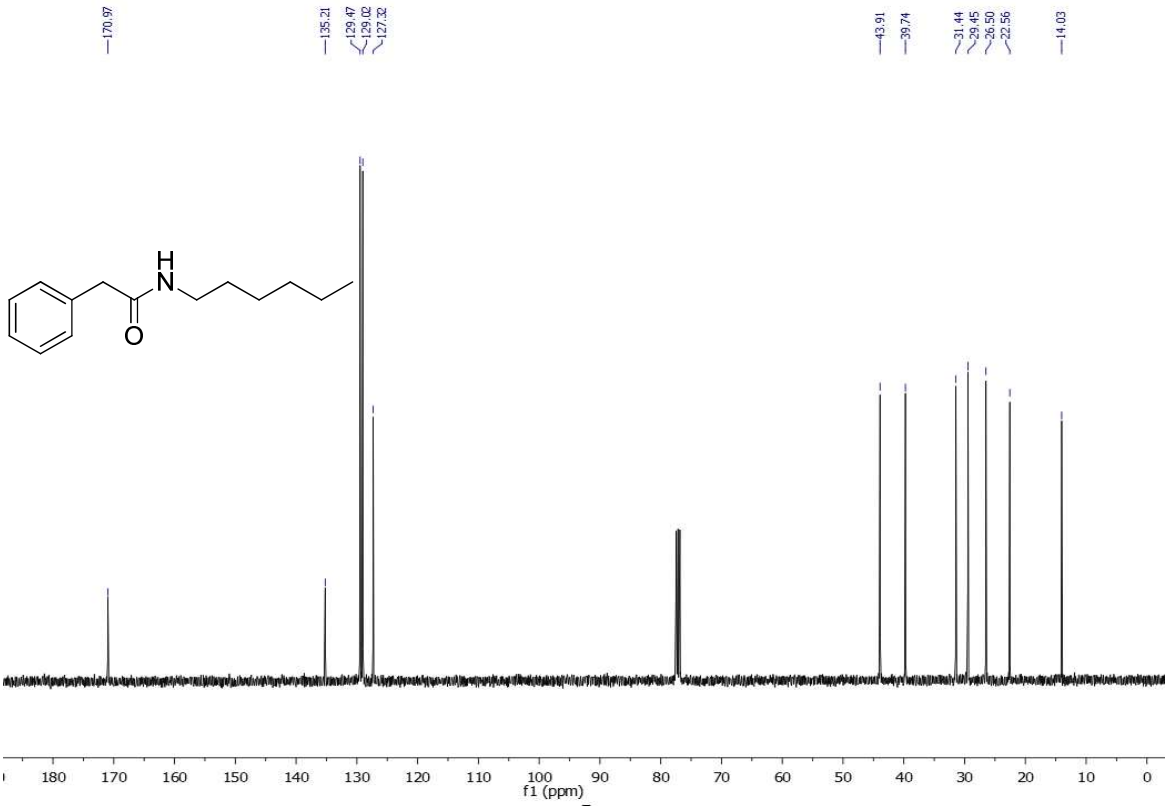


N-hexyl-2-phenylacetamide **20**

^{1}H NMR (400 MHz; $CDCl_3$)

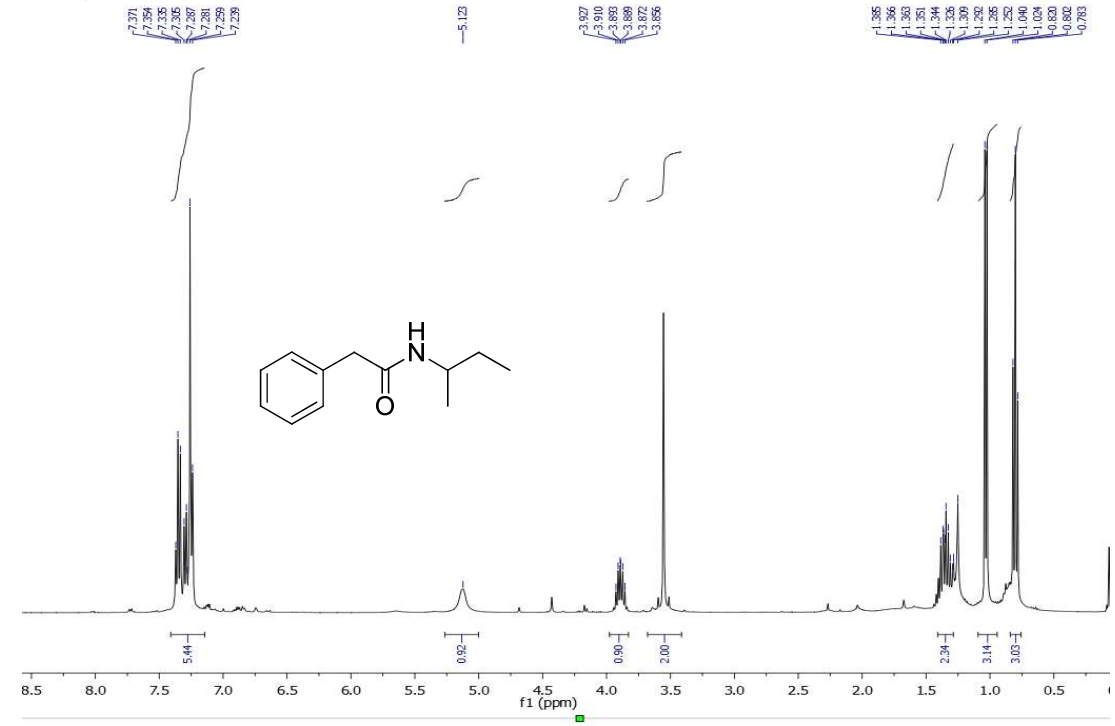


^{13}C NMR (101.6 MHz; $CDCl_3$)

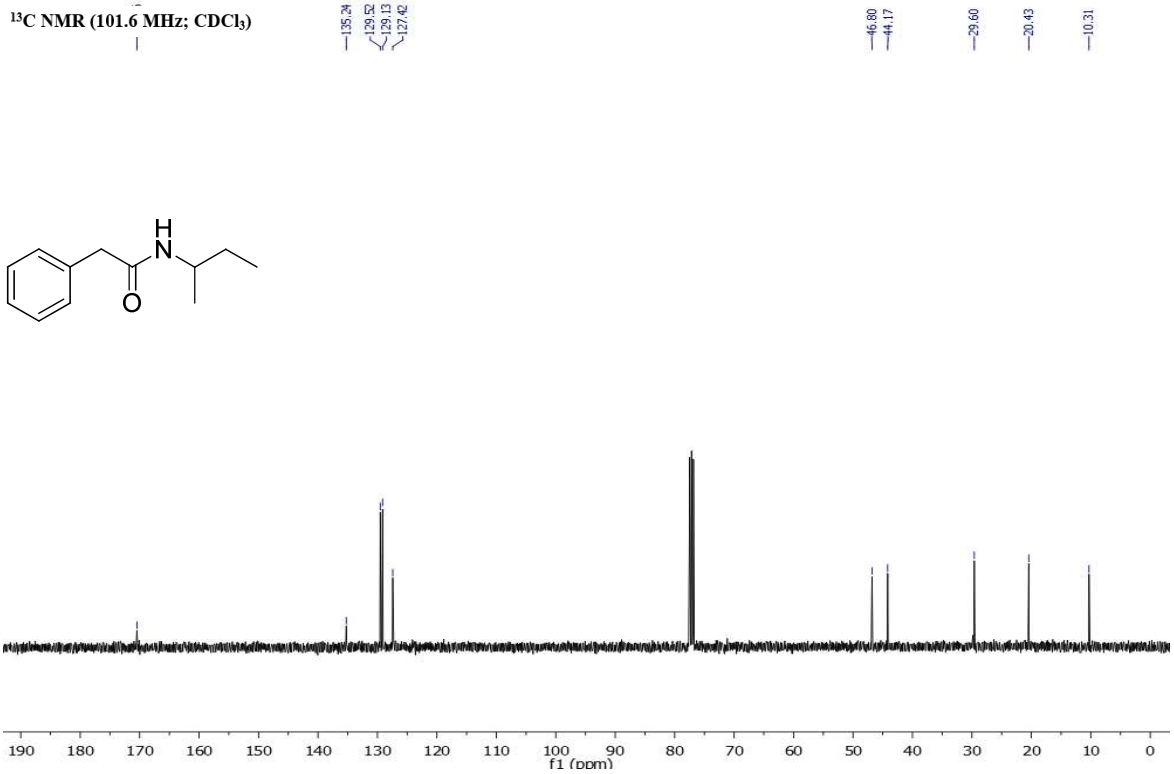


N-(sec-butyl)-2-phenylacetamide **21**

^{1}H NMR (400 MHz; $CDCl_3$)

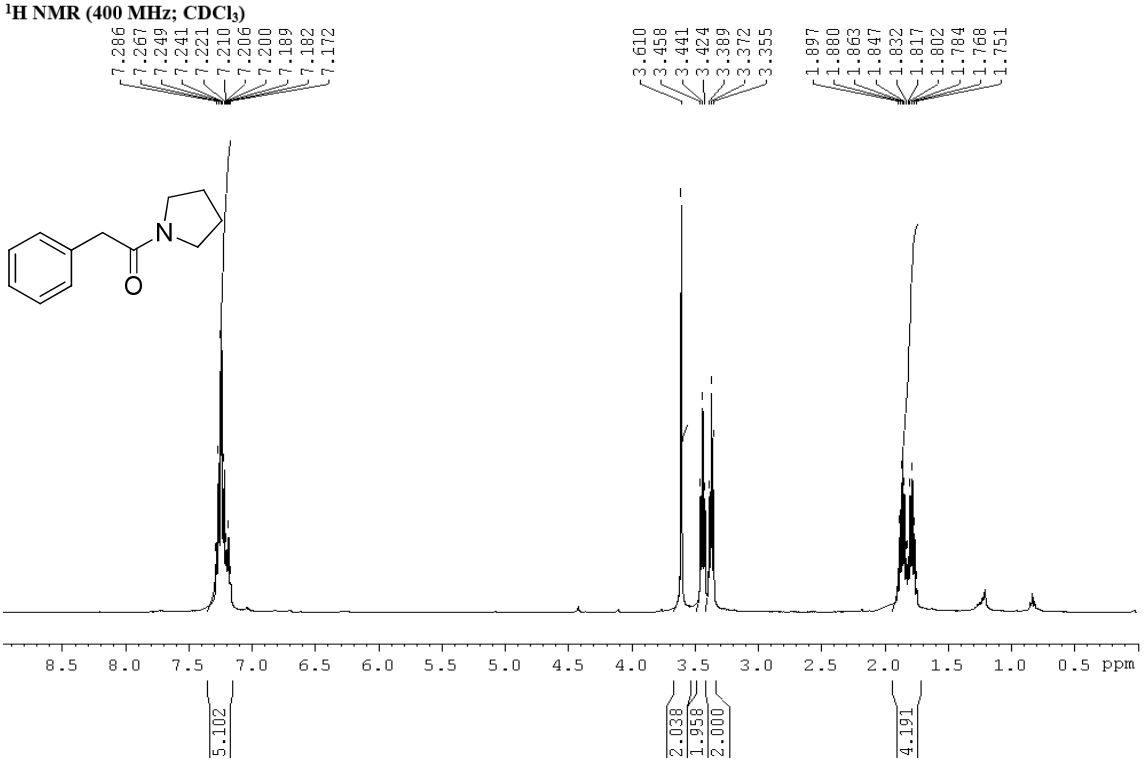


^{13}C NMR (101.6 MHz; $CDCl_3$)

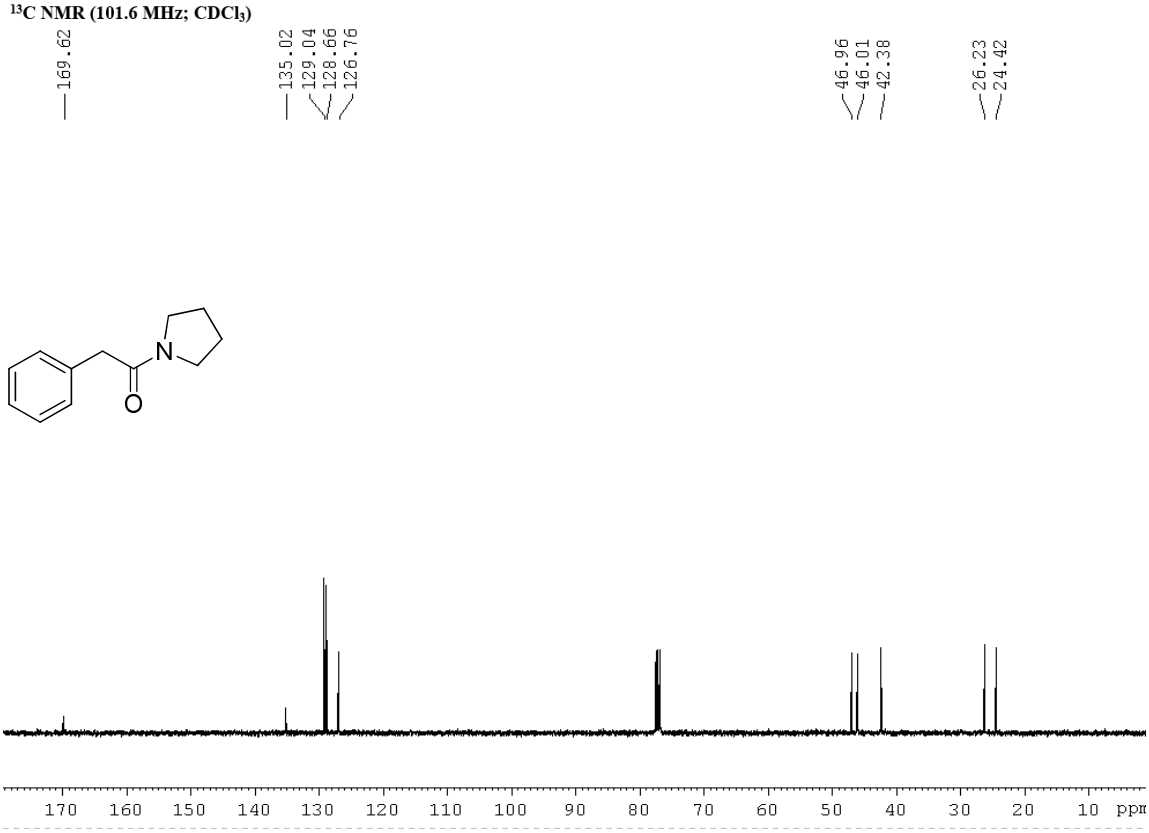


2-phenyl-1-(pyrrolidin-1-yl)ethanone **22**

^{1}H NMR (400 MHz; $CDCl_3$)

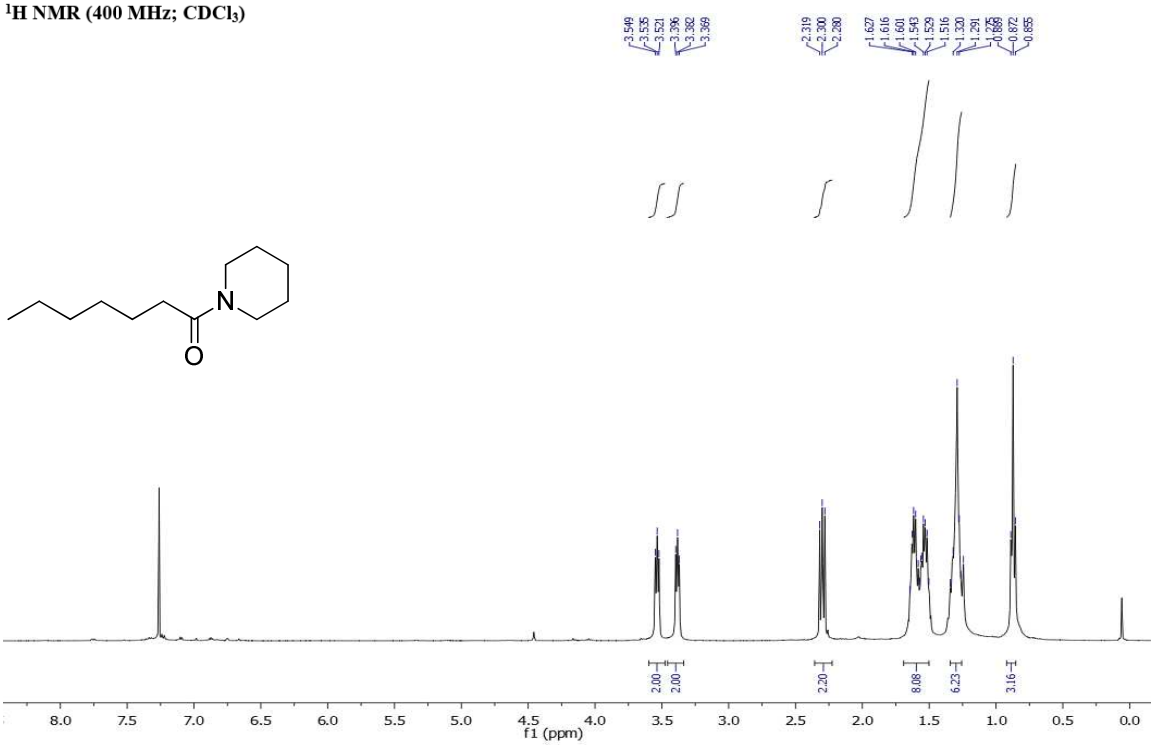


^{13}C NMR (101.6 MHz; $CDCl_3$)

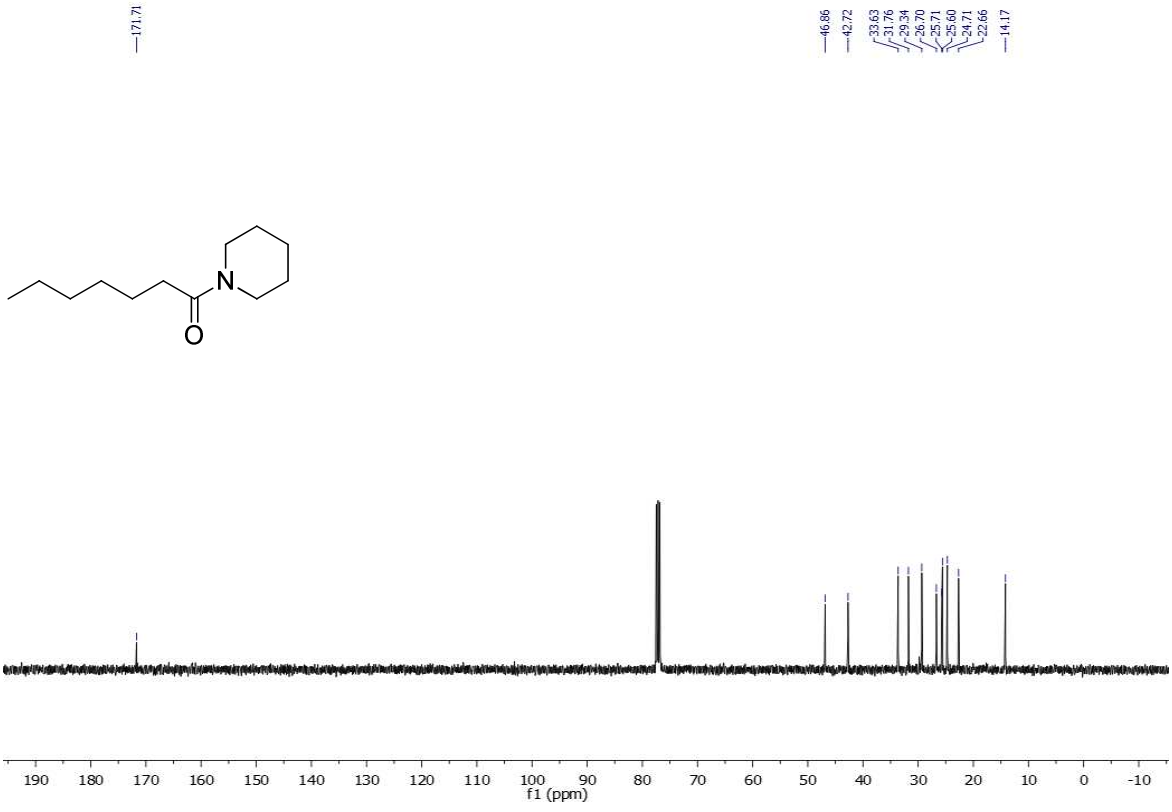


1-(piperidin-1-yl)heptan-1-one **23**

^{1}H NMR (400 MHz; $CDCl_3$)

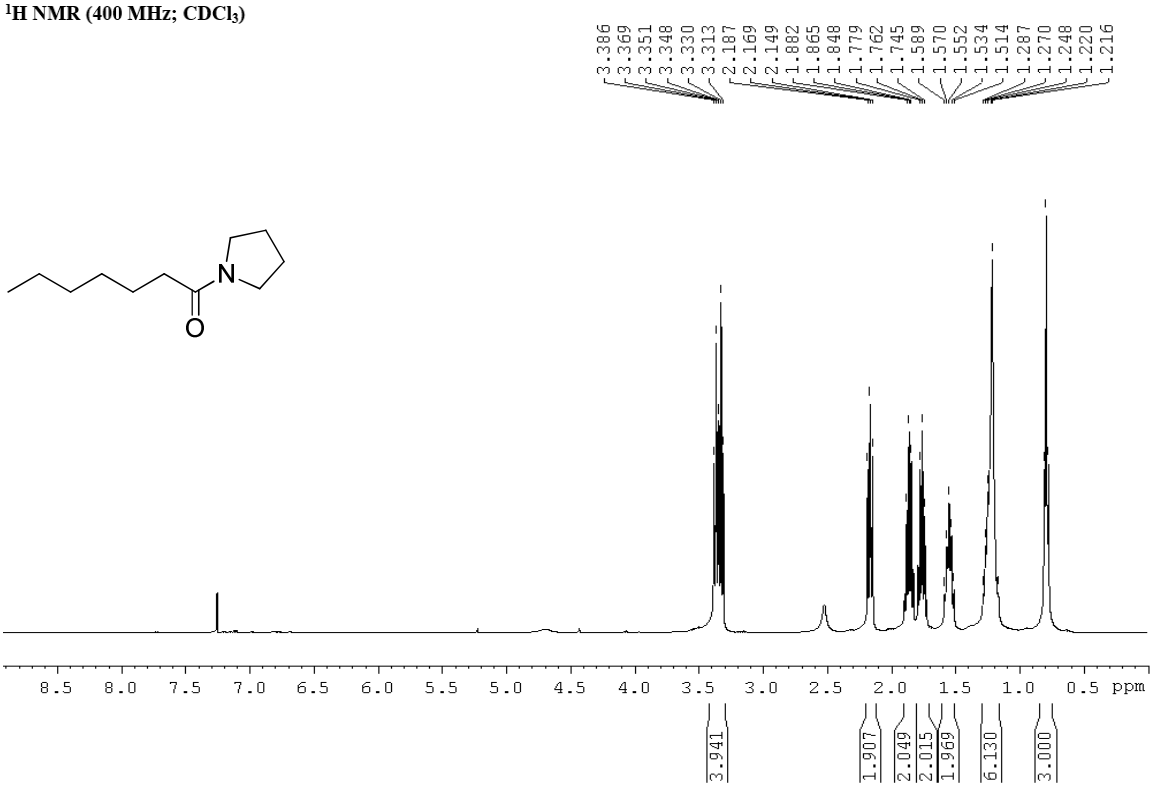


^{13}C NMR (101.6 MHz; $CDCl_3$)

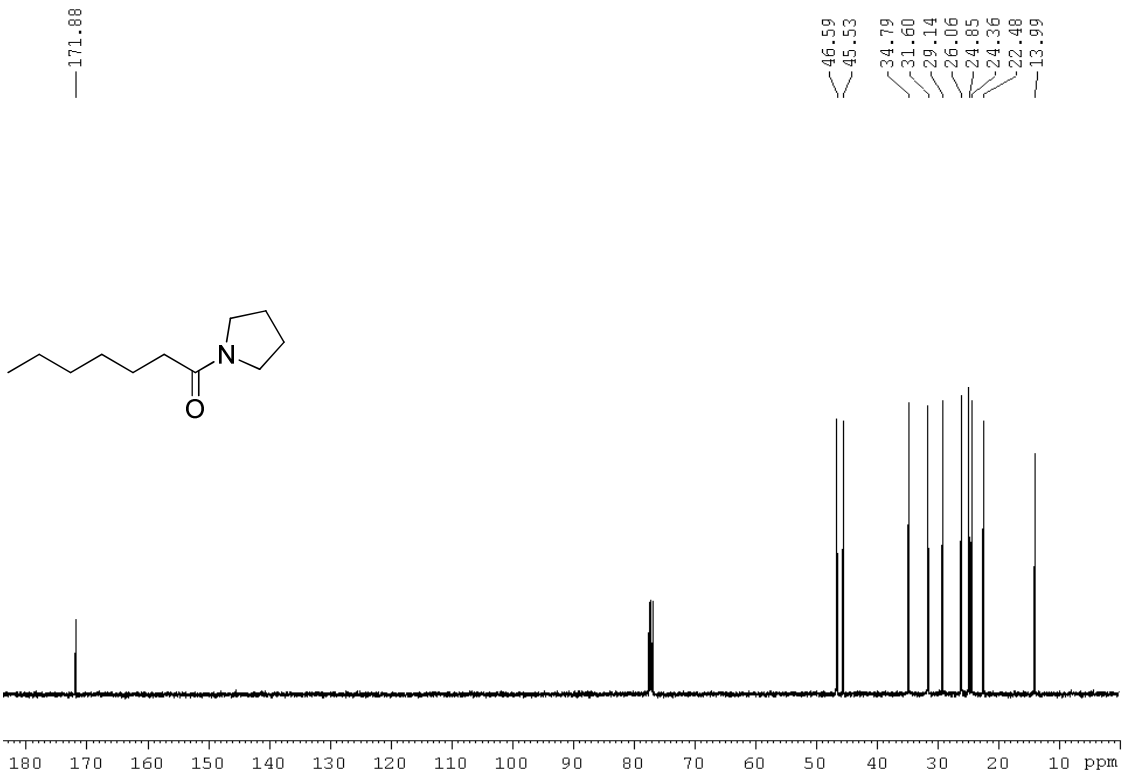


1-(pyrrolidin-1-yl)heptan-1-one **24**

^{1}H NMR (400 MHz; $CDCl_3$)

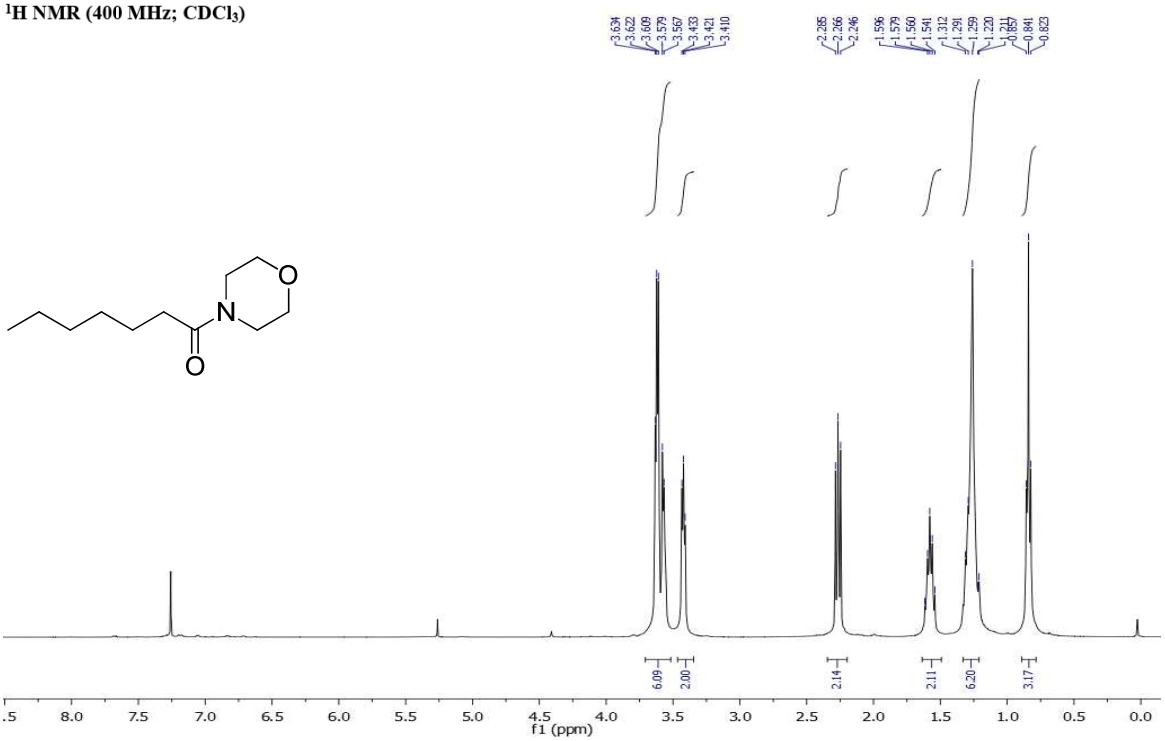


^{13}C NMR (101.6 MHz; $CDCl_3$)

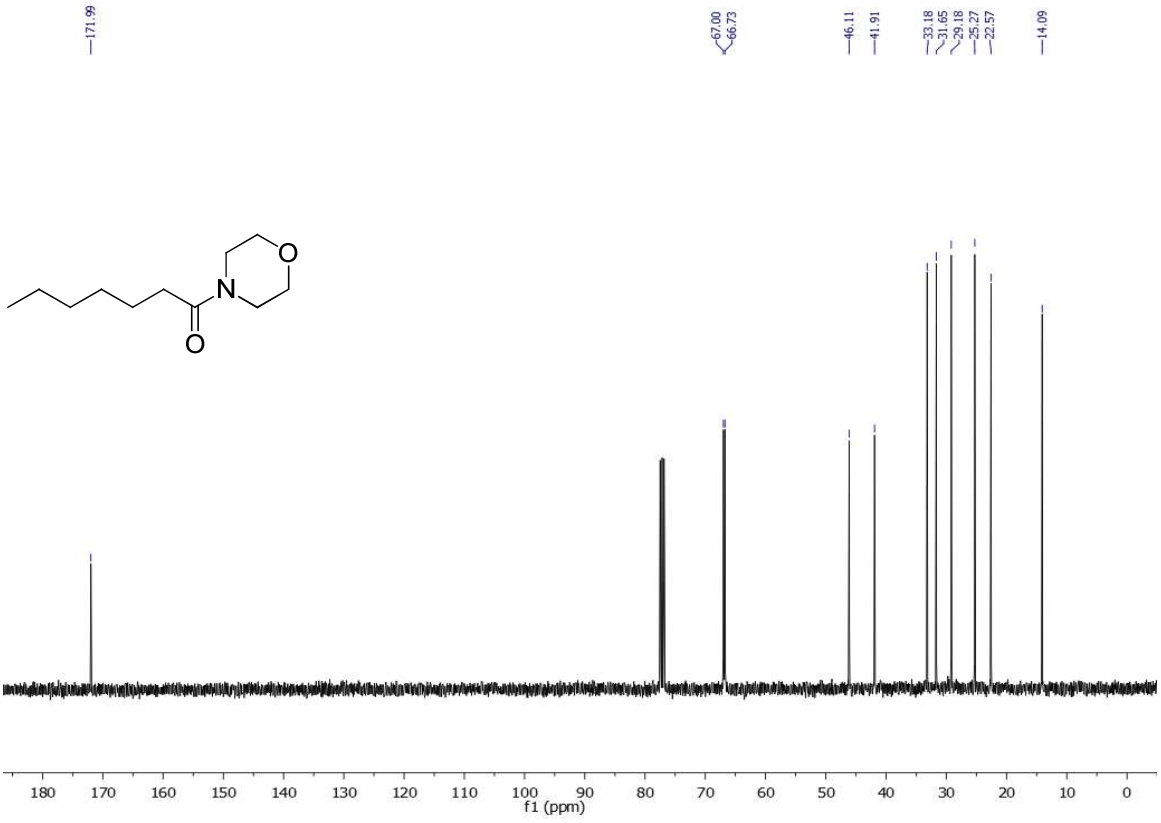


1-morpholinoheptan-1-one **25**

^{1}H NMR (400 MHz; $CDCl_3$)

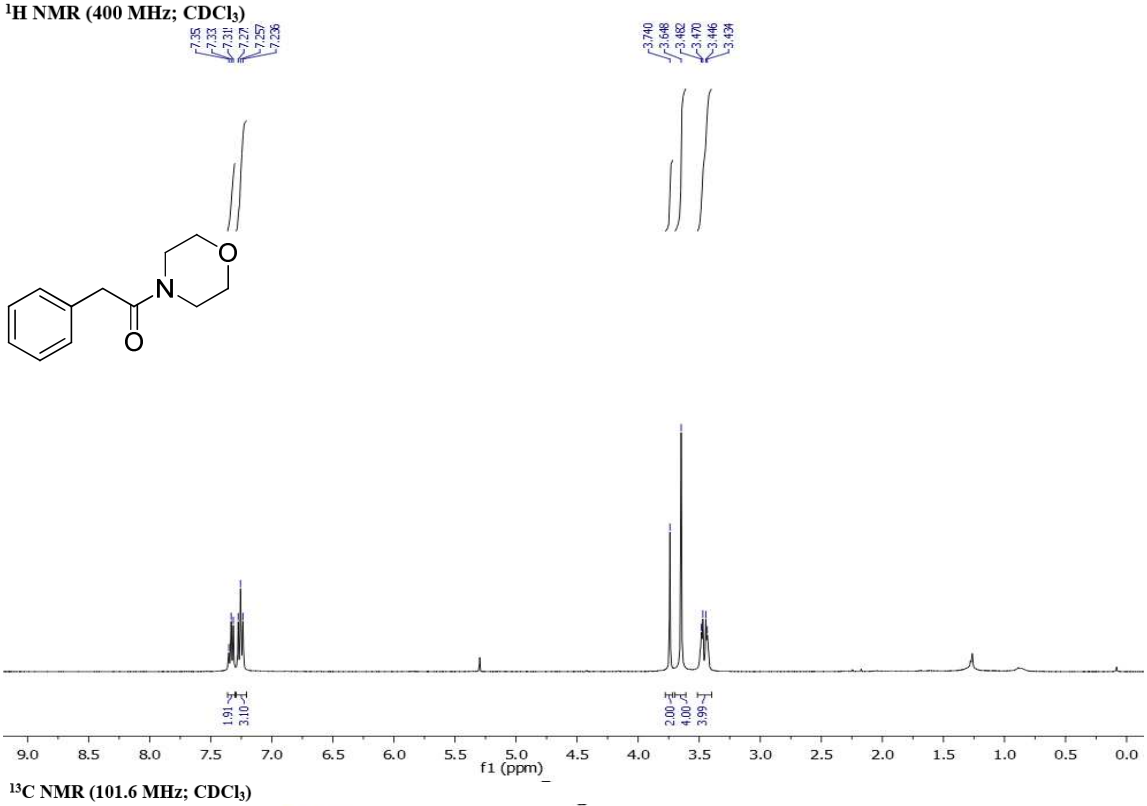


^{13}C NMR (101.6 MHz; $CDCl_3$)

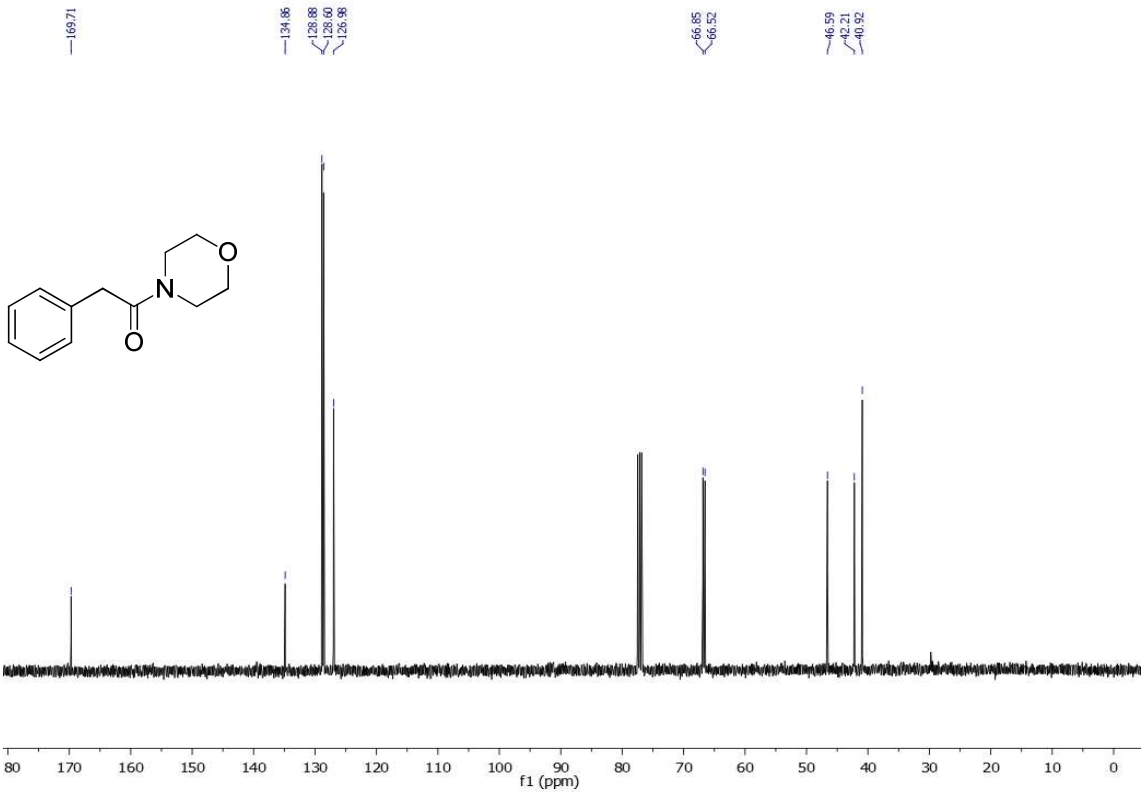


1-morpholino-2-phenylethanone **26**

^{1}H NMR (400 MHz; $CDCl_3$)

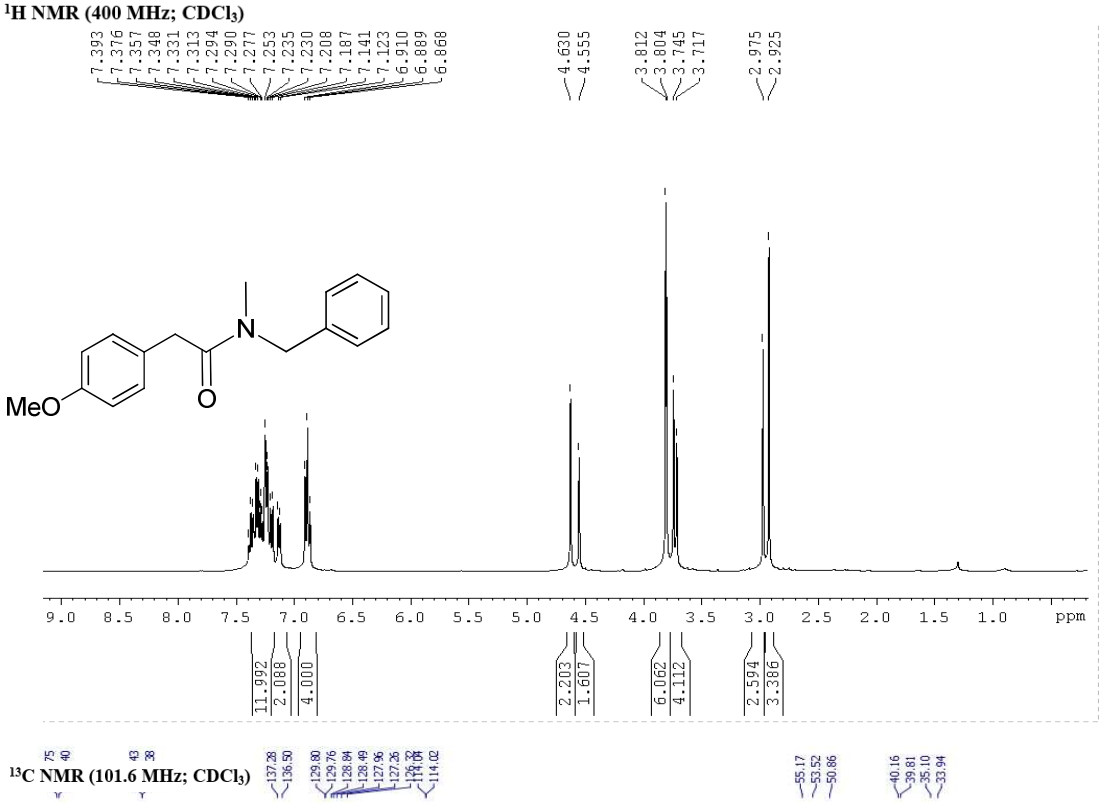


^{13}C NMR (101.6 MHz; $CDCl_3$)

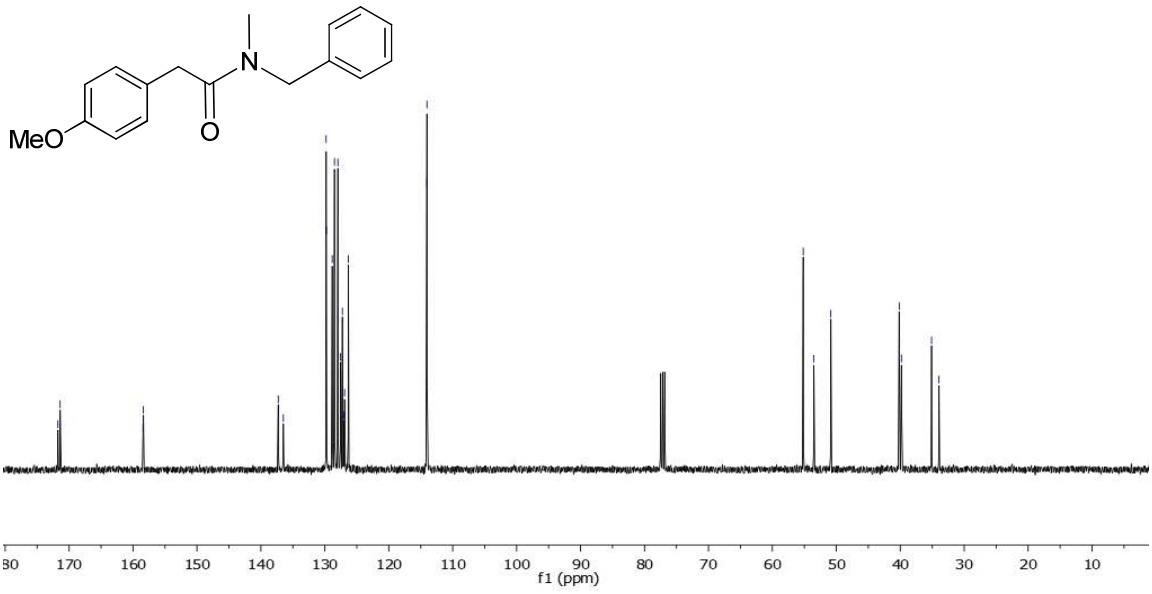


N-benzyl-2-(4-methoxyphenyl)-N-methylacetamide **27**

^{1}H NMR (400 MHz; $CDCl_3$)

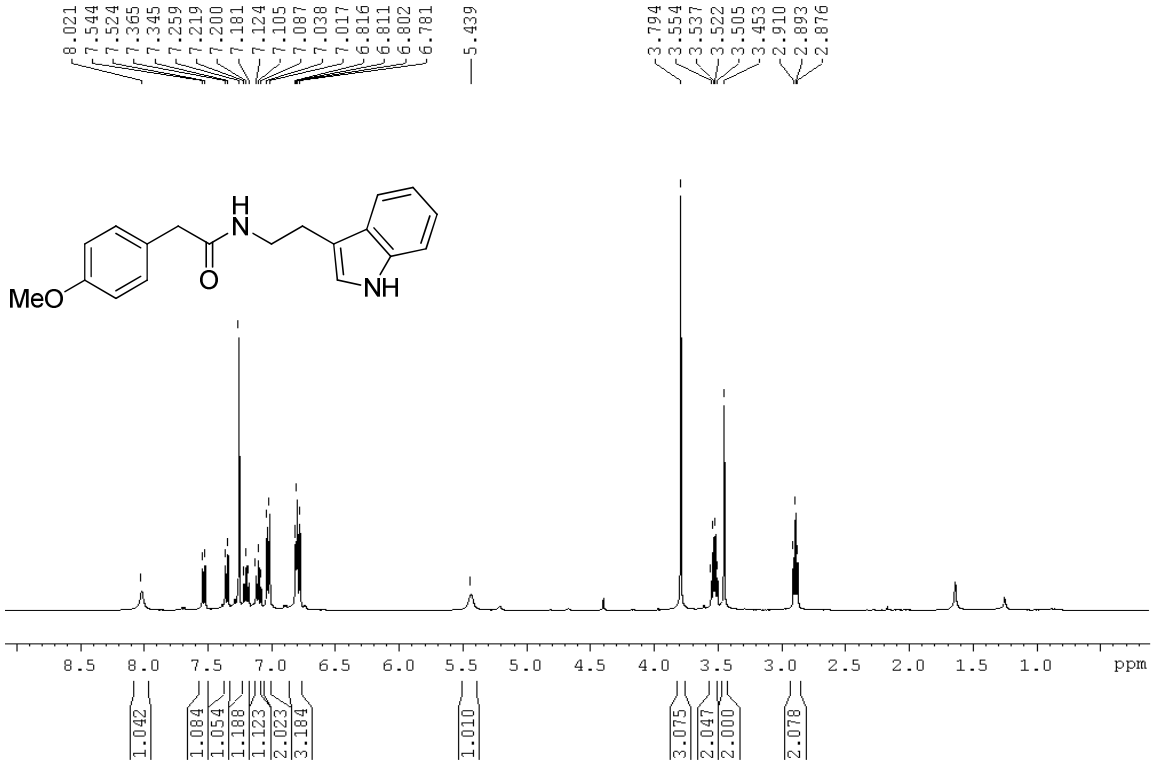


^{13}C NMR (101.6 MHz; $CDCl_3$)

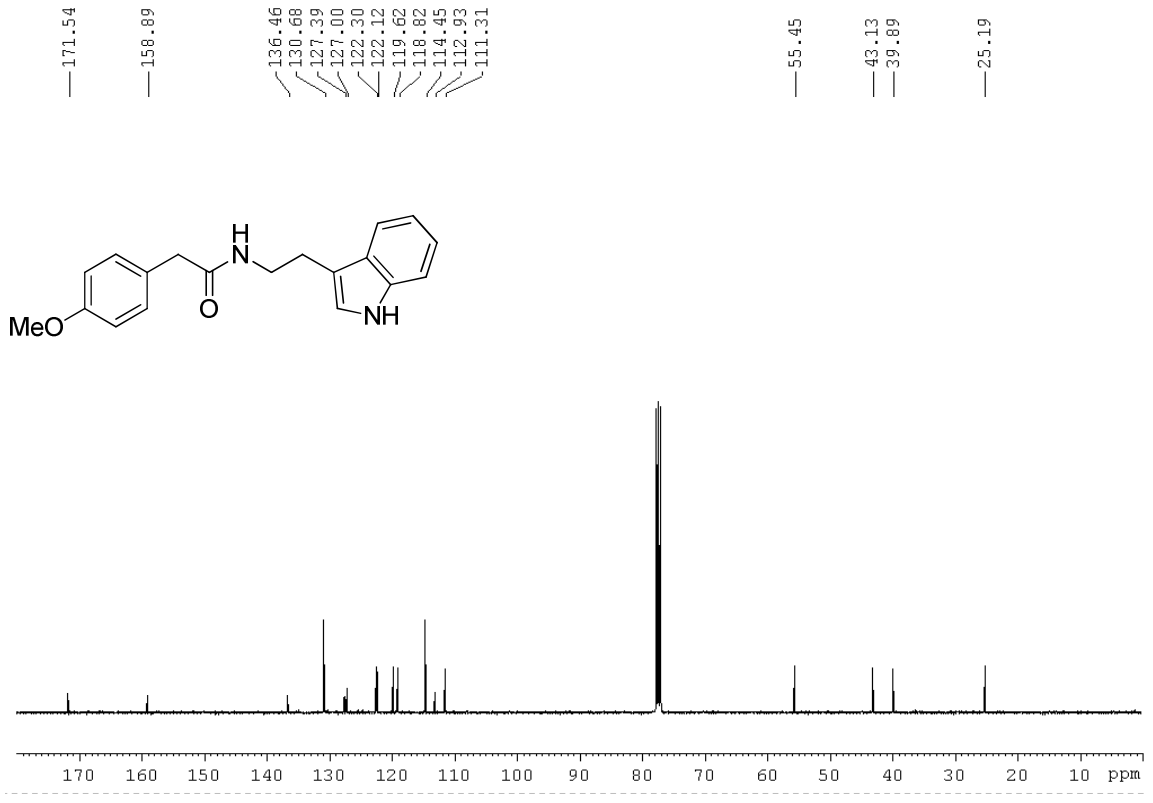


N-(2-(1H-indol-3-yl)ethyl)-2-(4-methoxyphenyl)acetamide **28**

^{1}H NMR (400 MHz; $CDCl_3$)

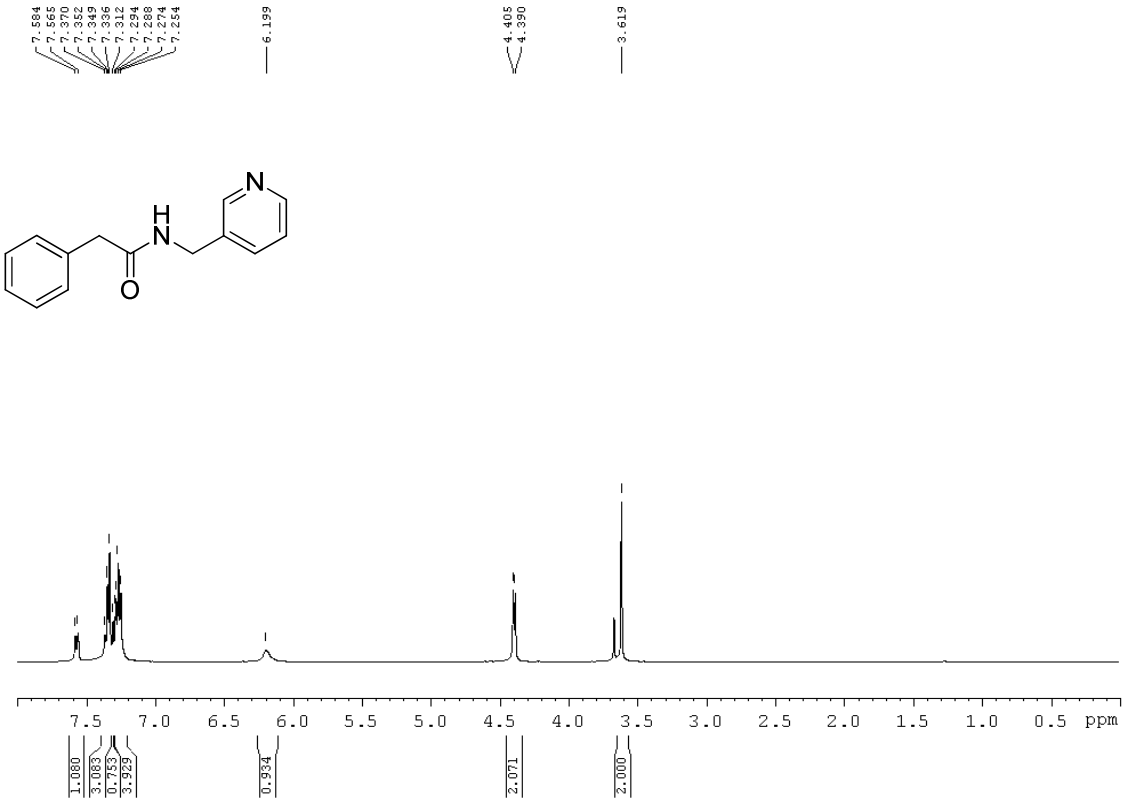


^{13}C NMR (101.6 MHz; $CDCl_3$)

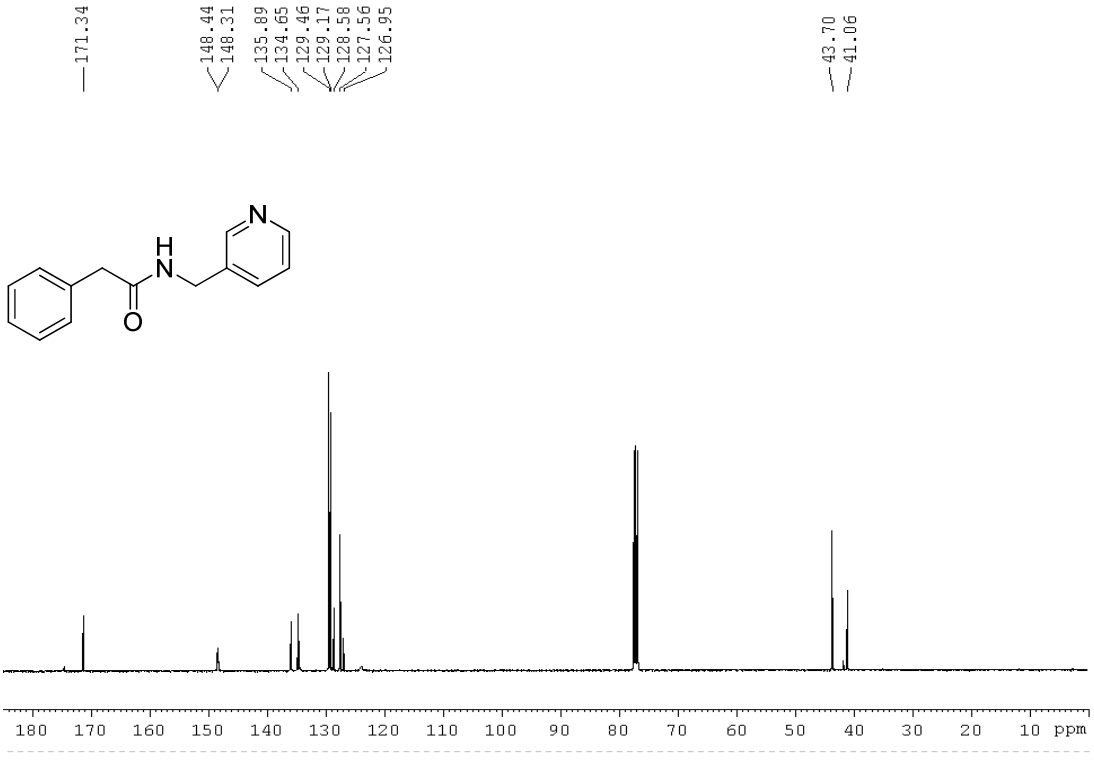


2-phenyl-N-((pyridin-3-yl)methyl)acetamide **29**

^{1}H NMR (400 MHz; $CDCl_3$)

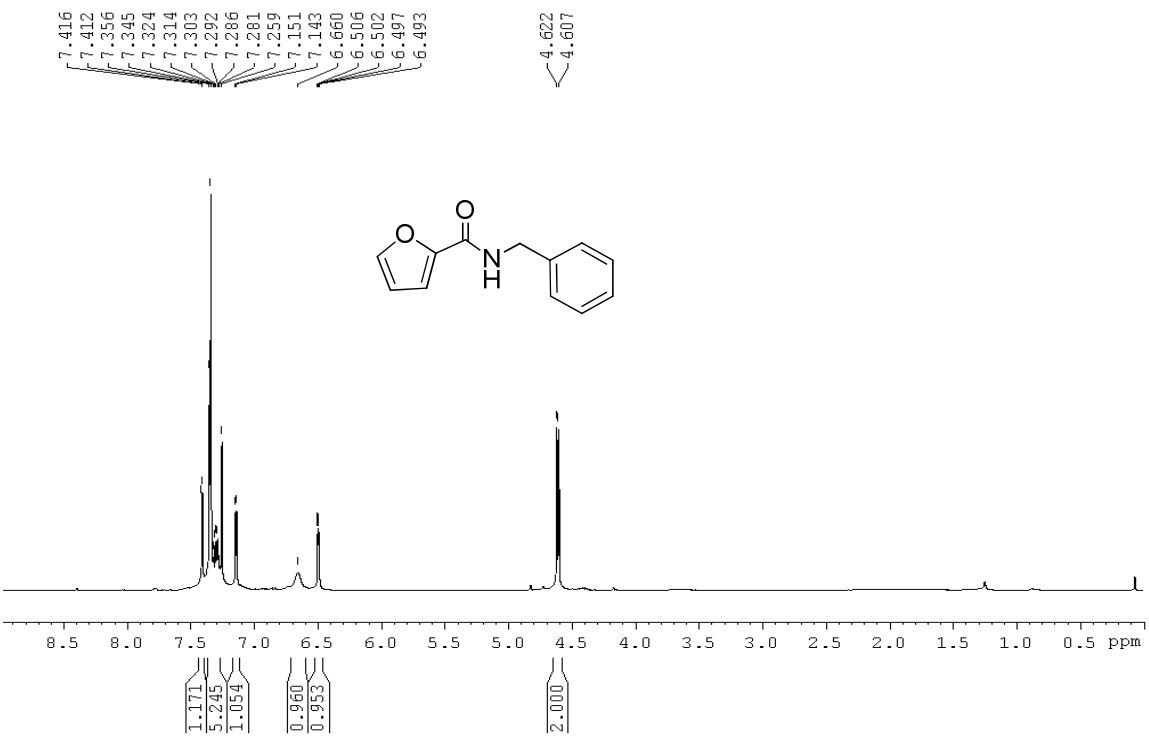


^{13}C NMR (101.6 MHz; $CDCl_3$)

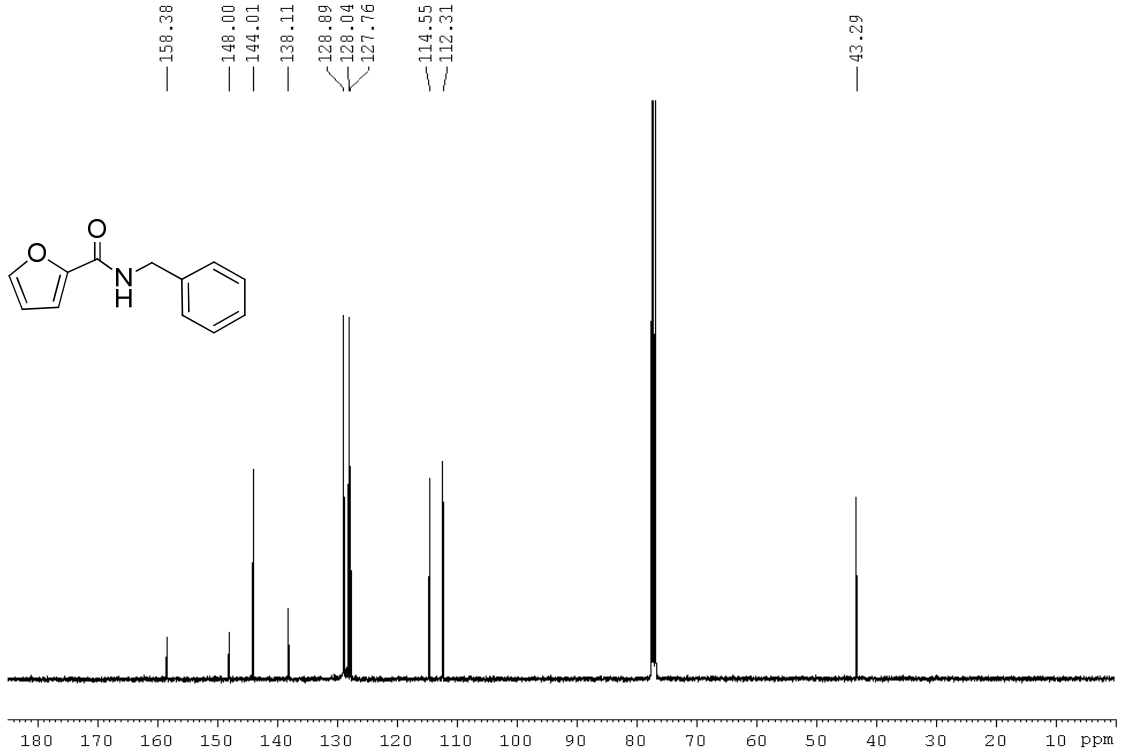


N-benzylfuran-2-carboxamide **30**

^{1}H NMR (400 MHz; $CDCl_3$)



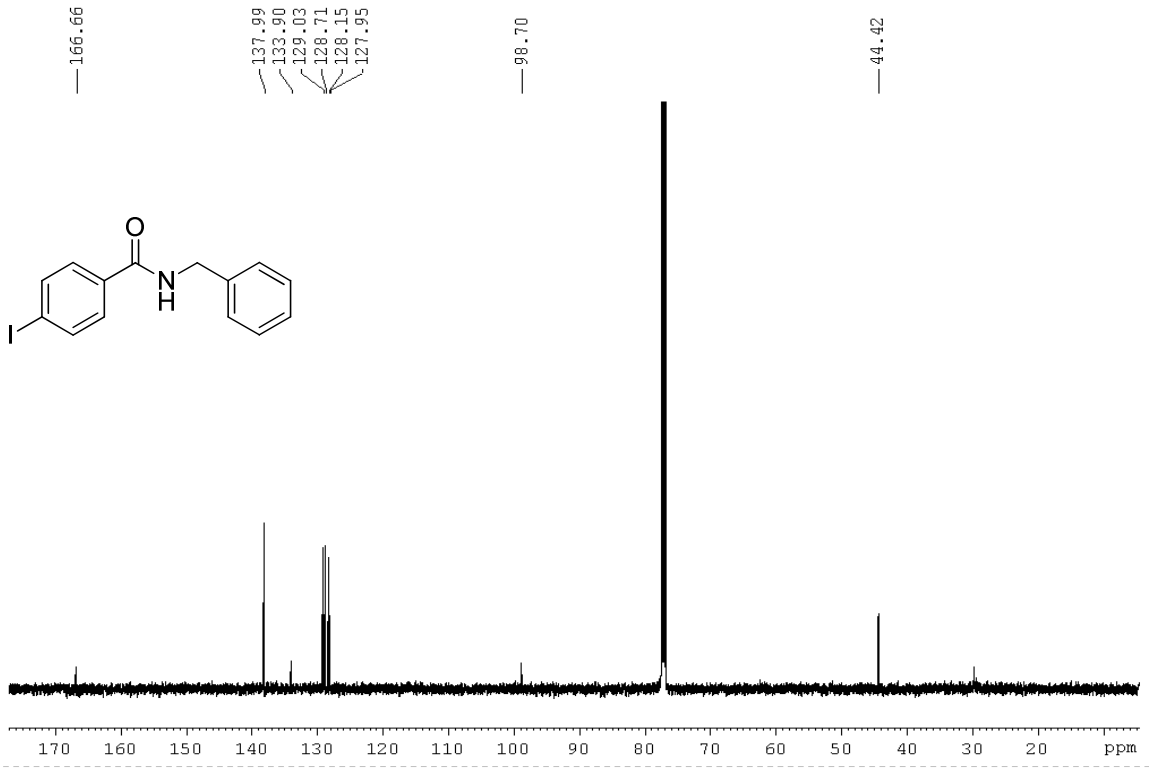
^{13}C NMR (101.6 MHz; $CDCl_3$)



N-benzyl-4-iodobenzamide **31**

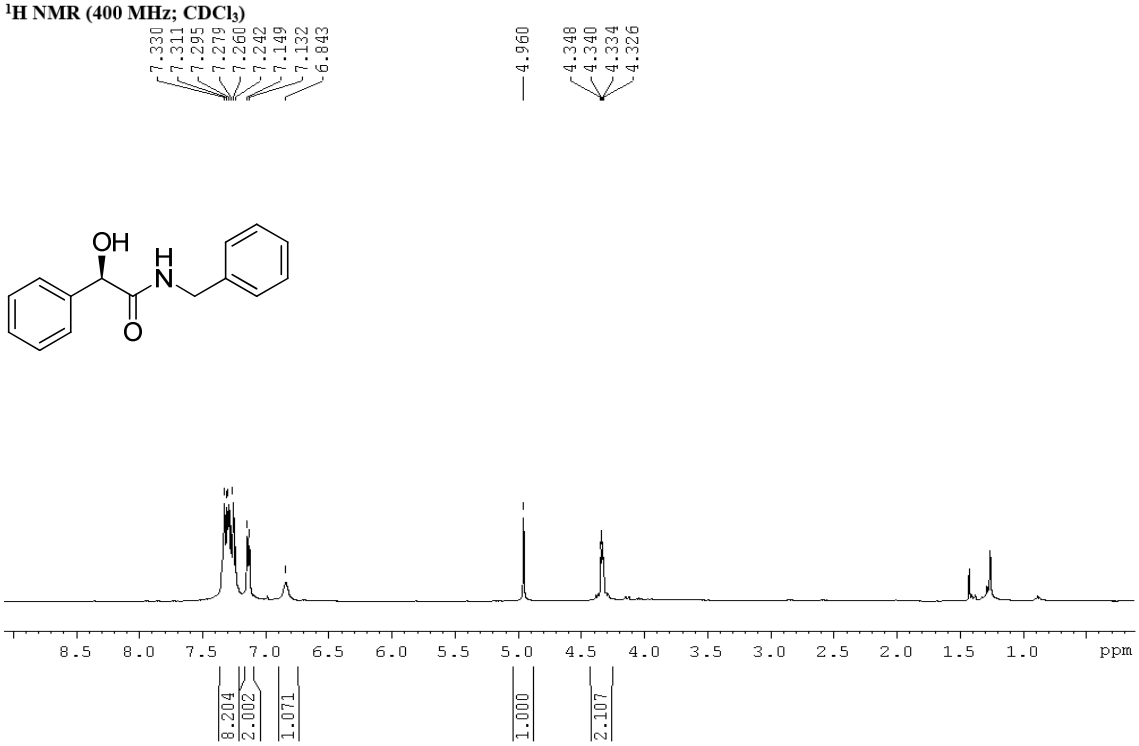
^{1}H NMR (400 MHz; $CDCl_3$)

^{13}C NMR (101.6 MHz; $CDCl_3$)

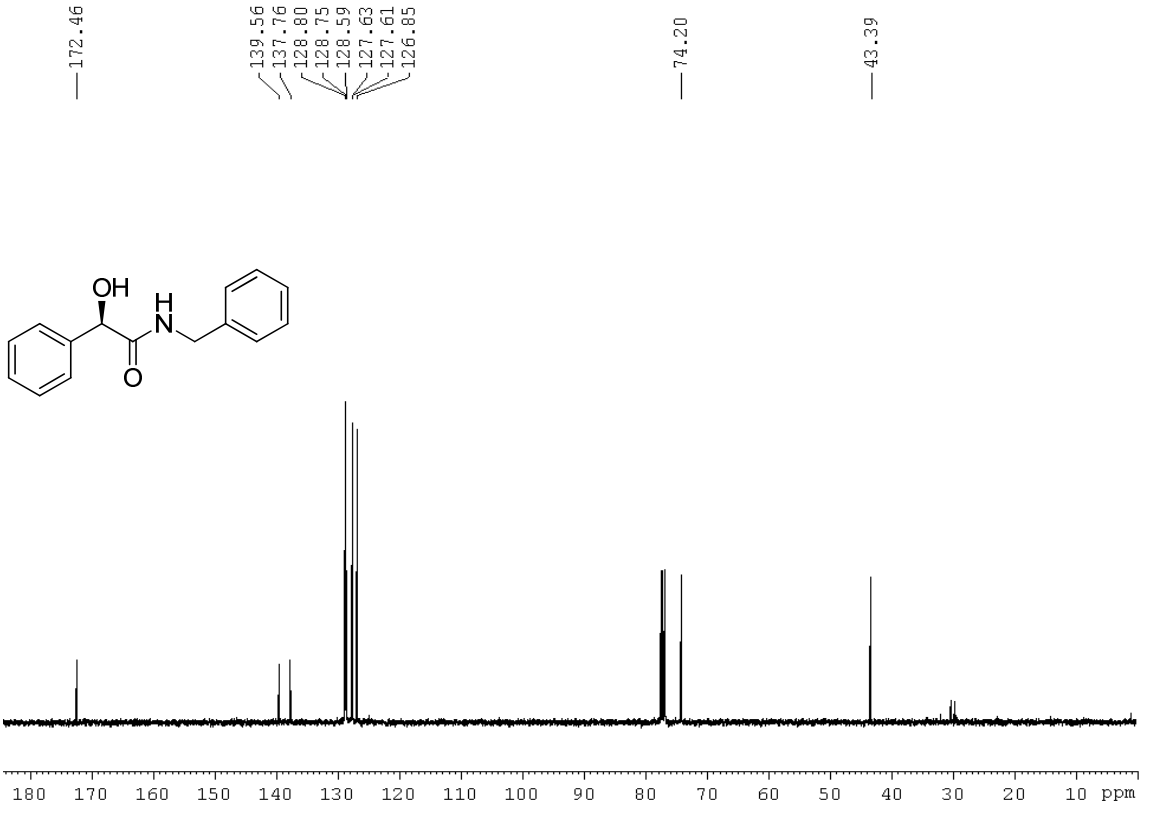


N-benzyl-2-hydroxy-2-phenylacetamide **32**

^{1}H NMR (400 MHz; $CDCl_3$)



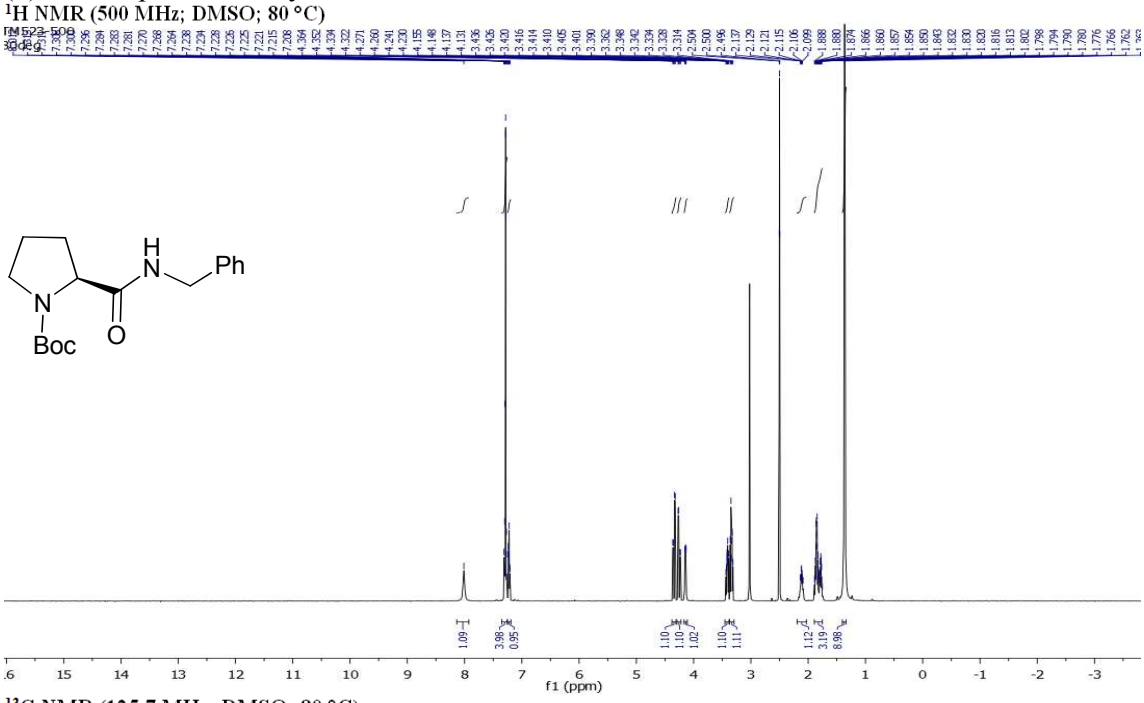
^{13}C NMR (101.6 MHz; $CDCl_3$)



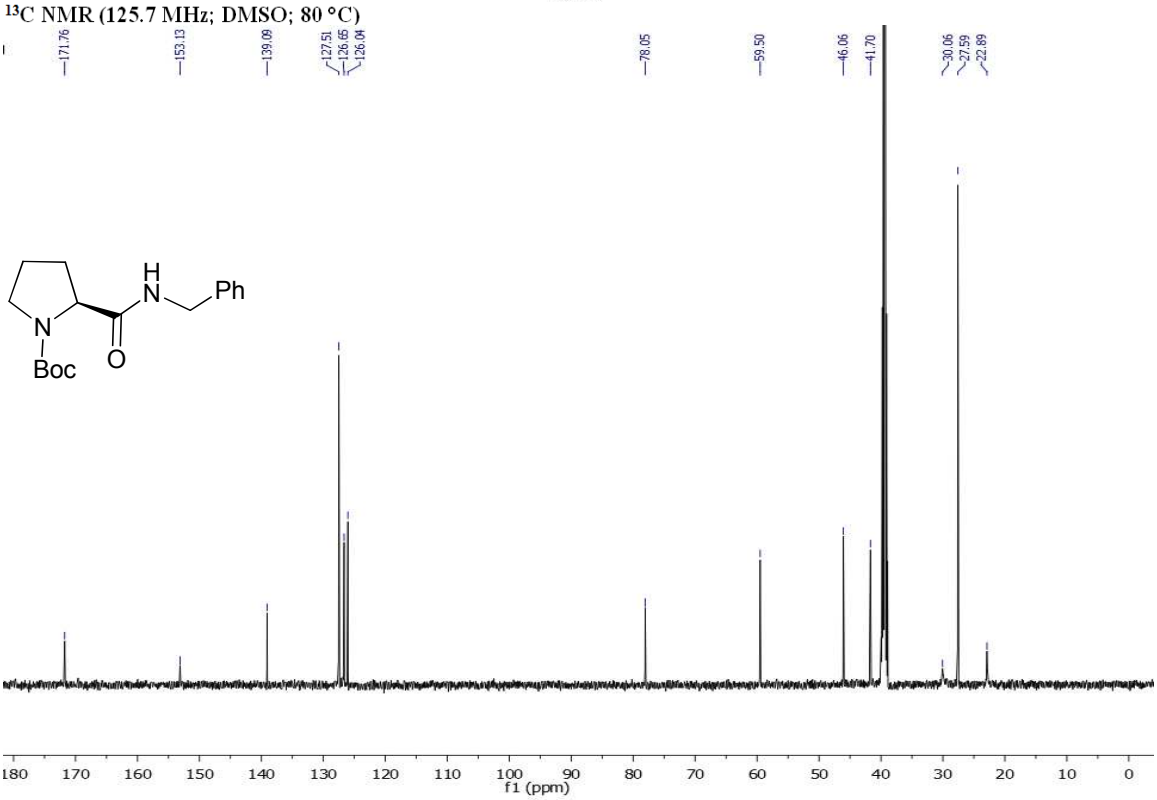
7. ^{1}H and ^{13}C Spectra of Amides Synthesized from *N*-Protected and/or *C*-Protected Amino Acids.

(*S*)-N-Boc-proline benzylamide **33**

^{1}H NMR (500 MHz; DMSO; 80 °C)

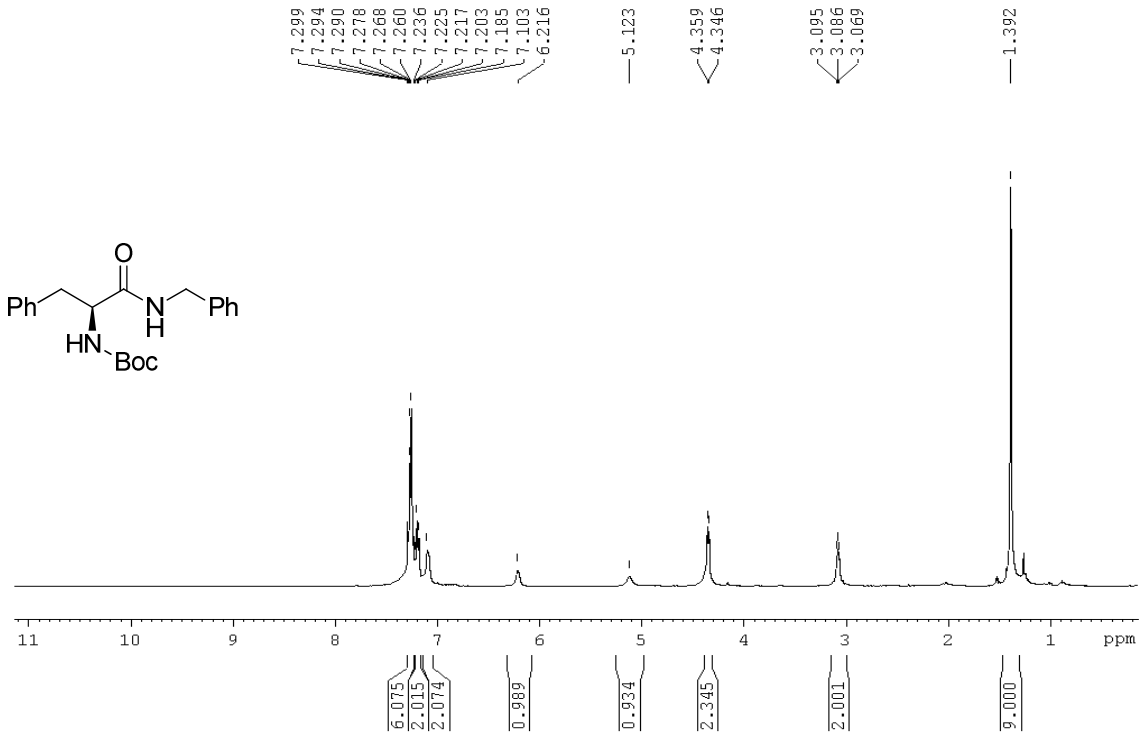


^{13}C NMR (125.7 MHz; DMSO; 80 °C)

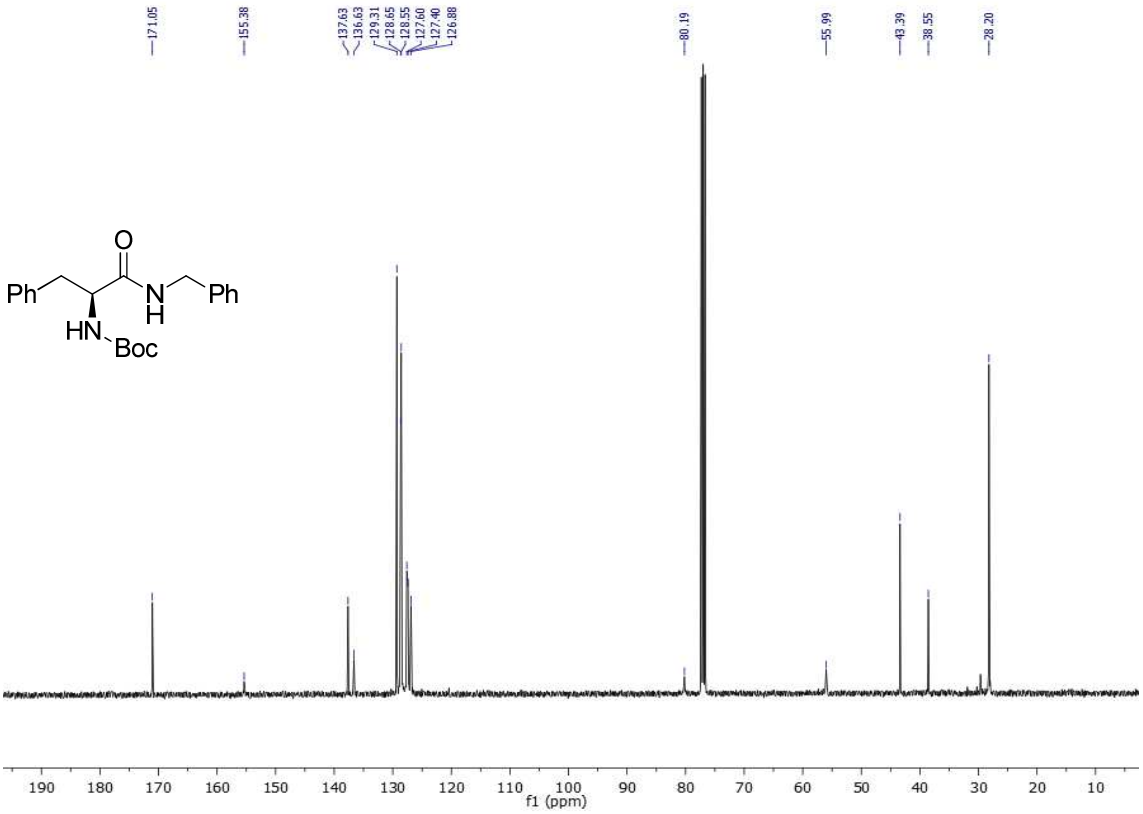


(*S*)-N-Boc-phenylalanine benzylamide **34**

^{1}H NMR (400 MHz; $CDCl_3$)

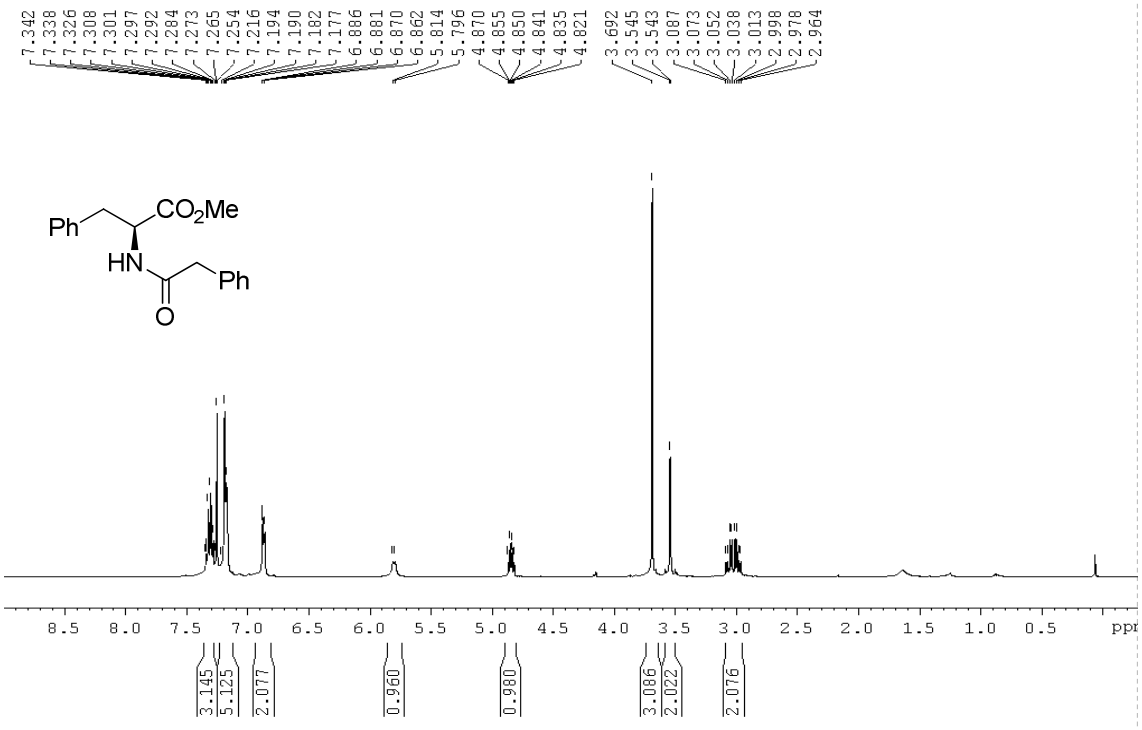


^{13}C NMR (101.6 MHz; $CDCl_3$)

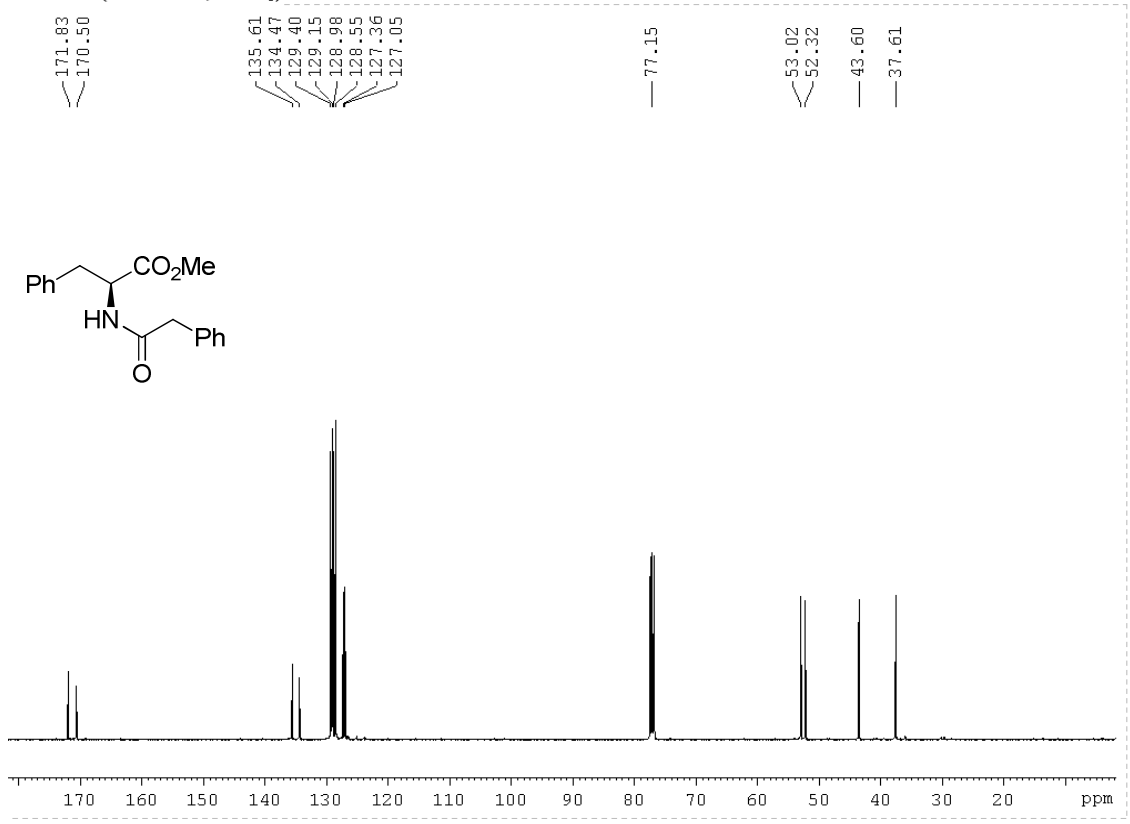


(*S*)-N-Phenylacetyl-phenylalanine Methyl ester **35**

^{1}H NMR (400 MHz; $CDCl_3$)

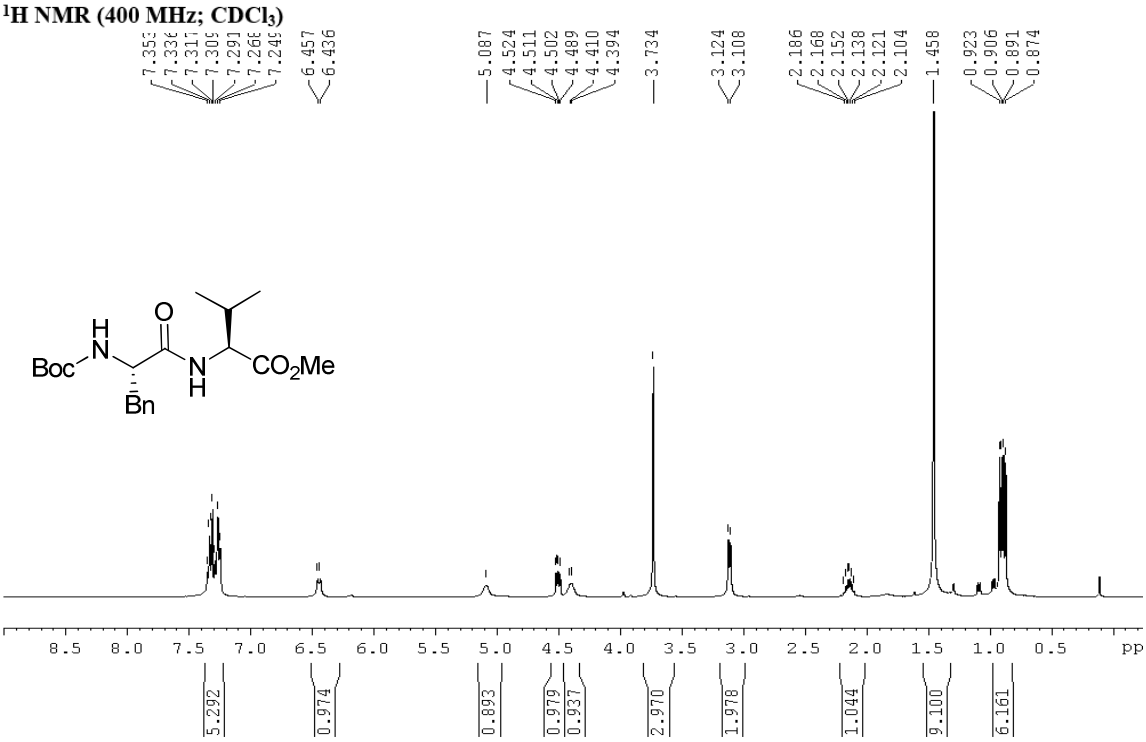


^{13}C NMR (101.6 MHz; $CDCl_3$)

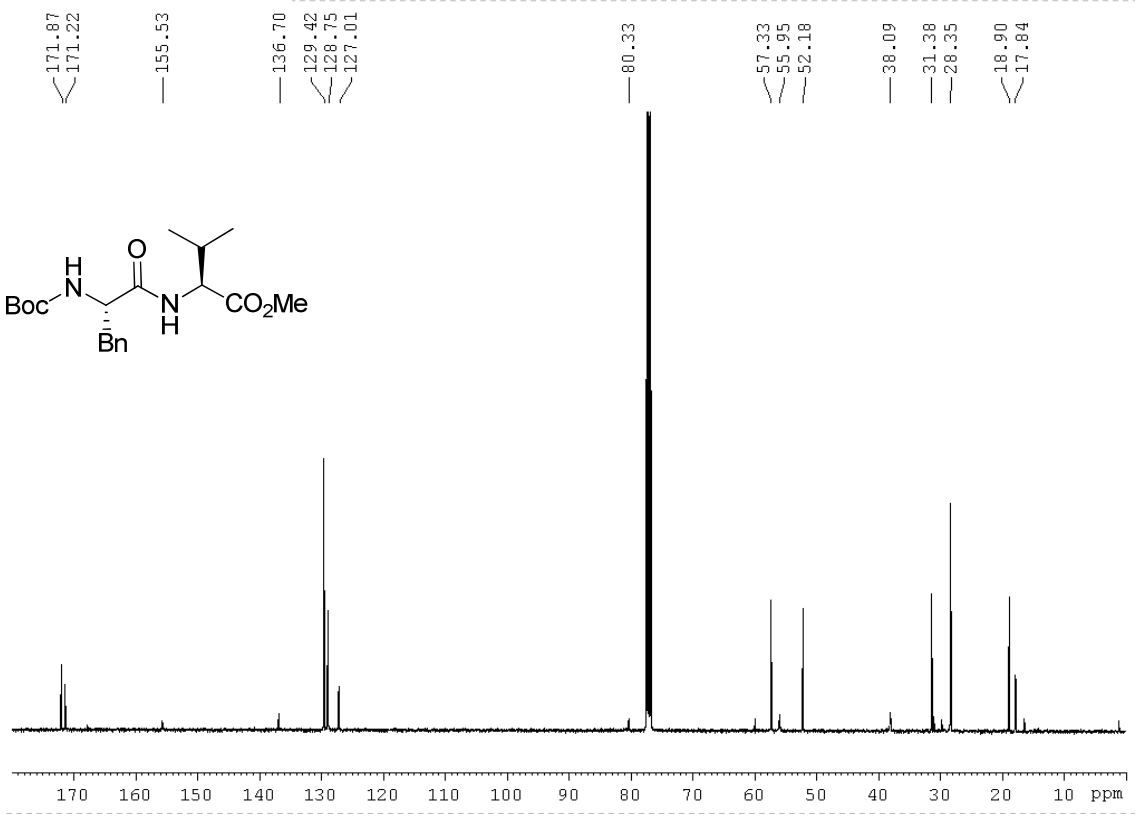


(*S*,*S*)-N-Boc-Phe-Val methyl ester **36**

^{1}H NMR (400 MHz; $CDCl_3$)

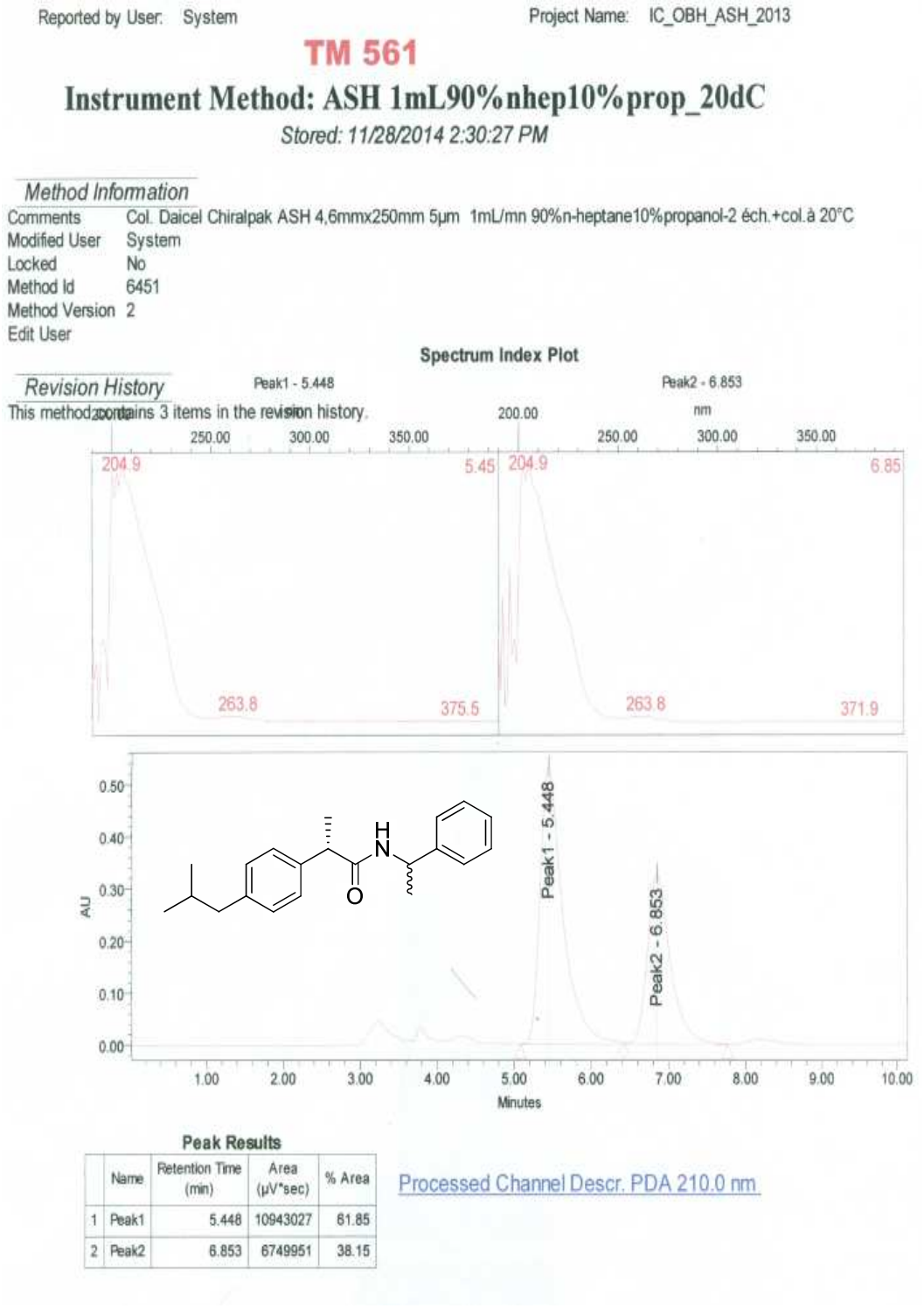


^{13}C NMR (101.6 MHz; $CDCl_3$)

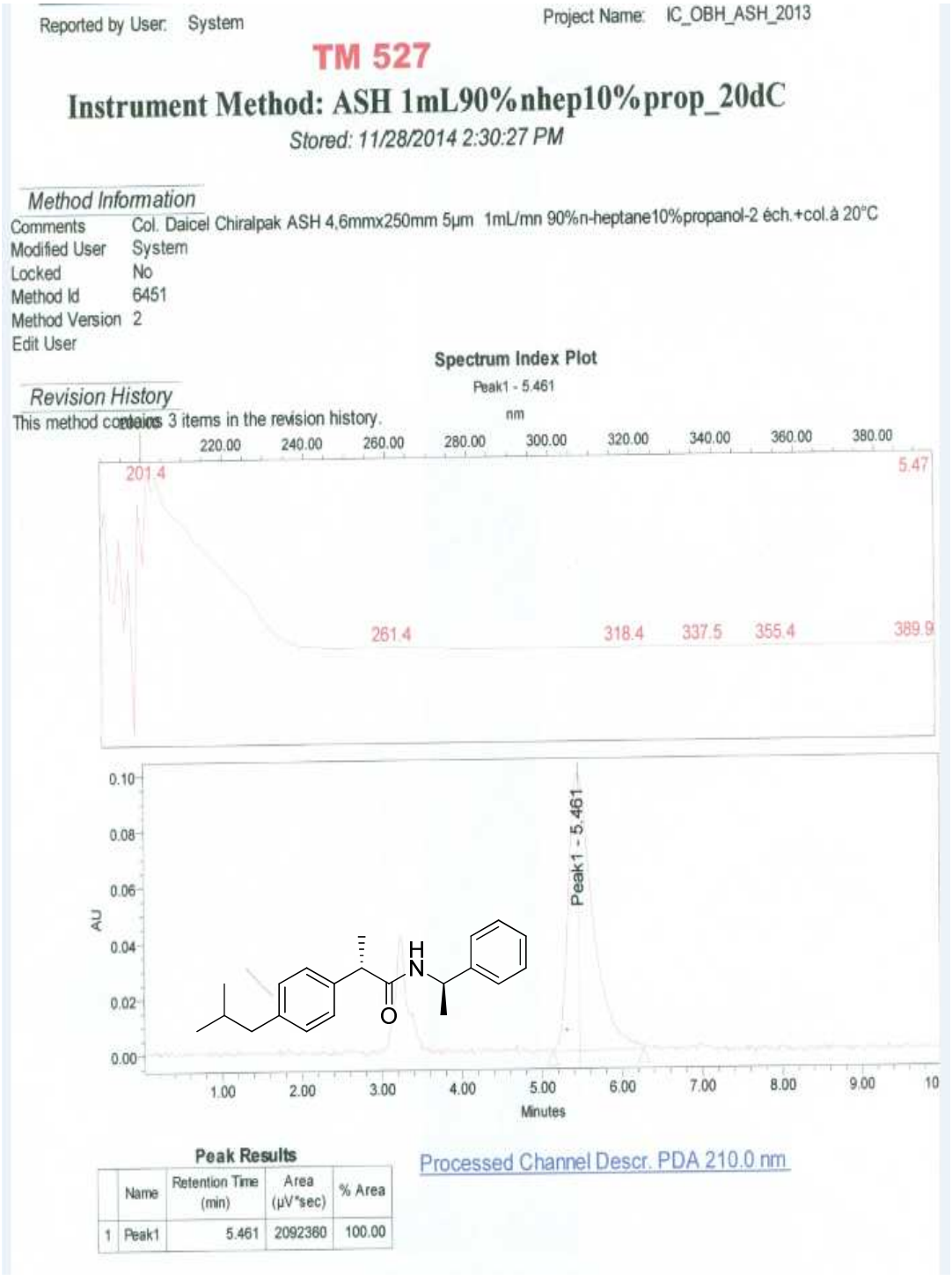


8. HPLC Spectra of Chiral Amides

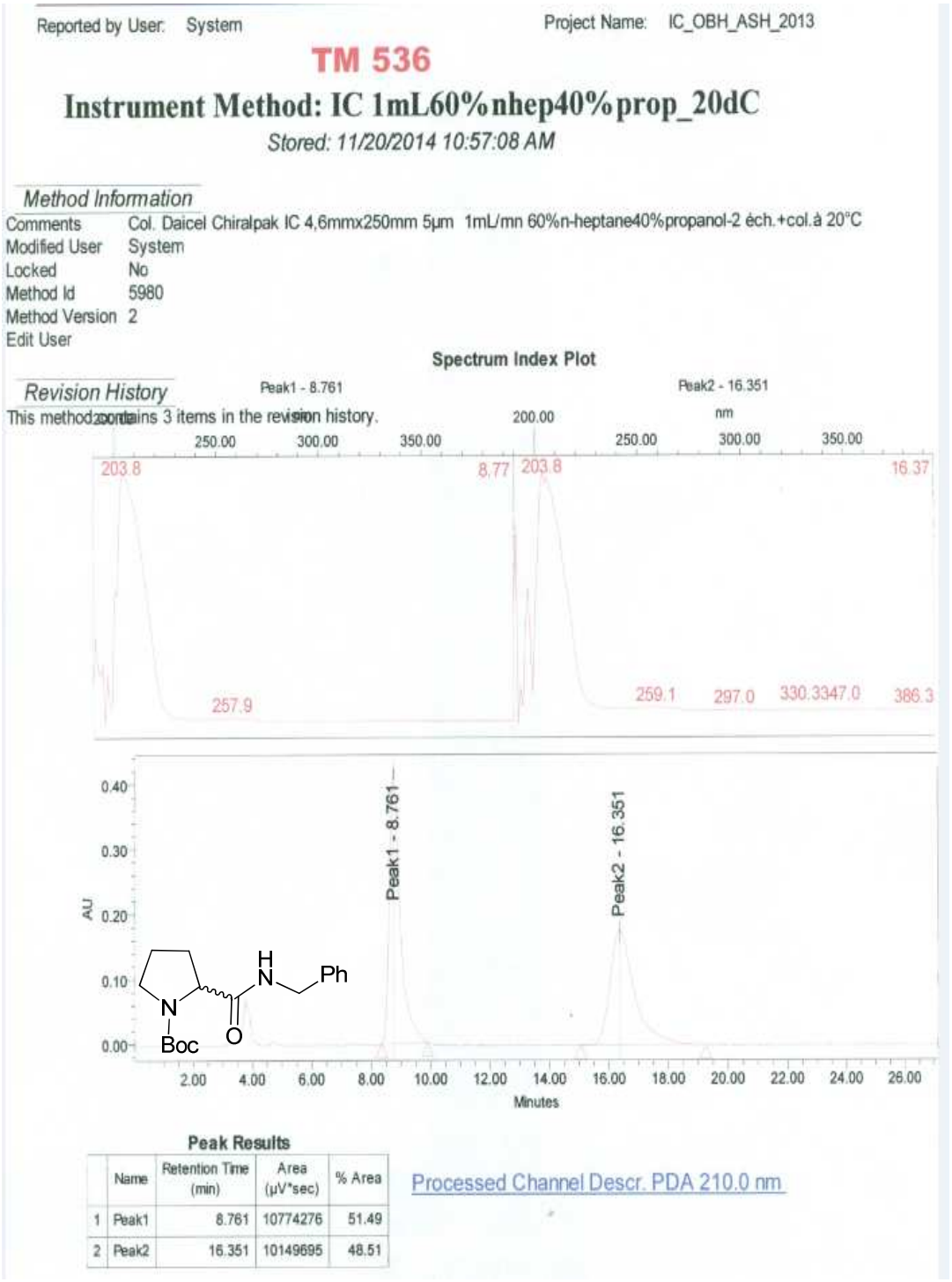
(2*S*)-2-(4-isobutylphenyl)- ((*R*,*S*)-1-phenylethyl)propanamide



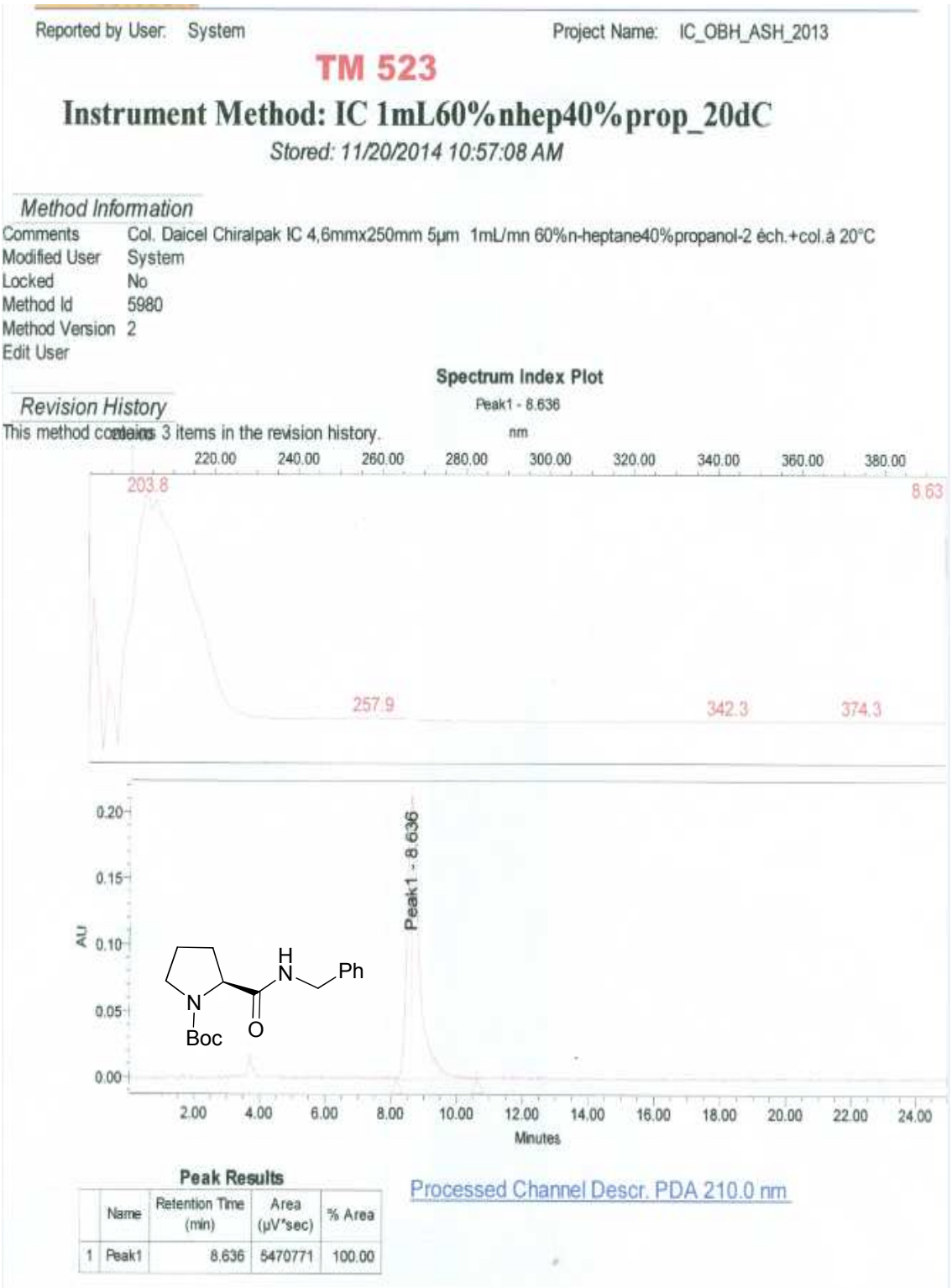
(*S*)-2-(4-isobutylphenyl)-N-((*R*)-1-phenylethyl)propanamide **15b**



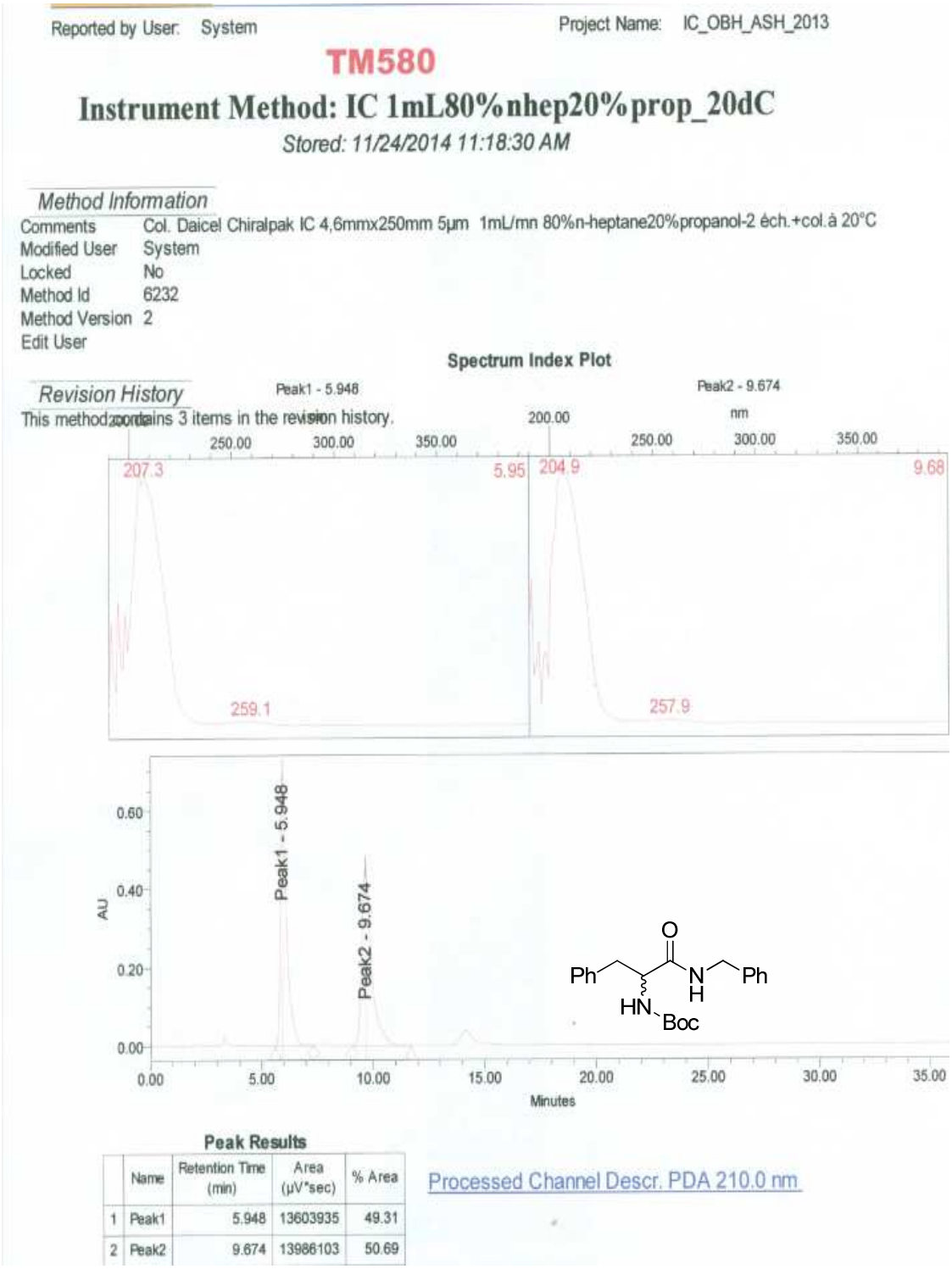
(*R*,*S*)-N-Boc-Proline Benzylamide



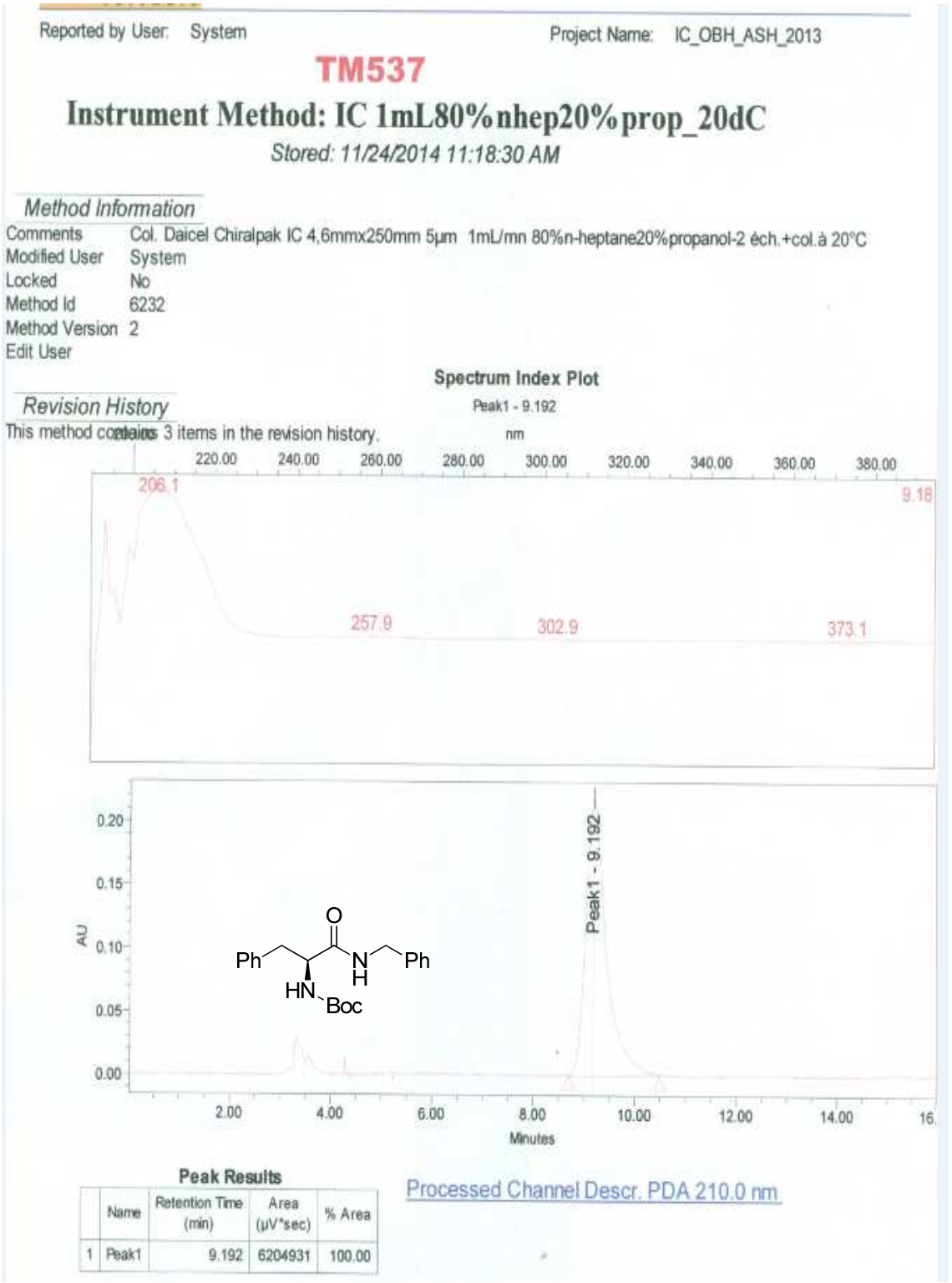
(*S*)-N-Boc-Proline Benzylamide **33**



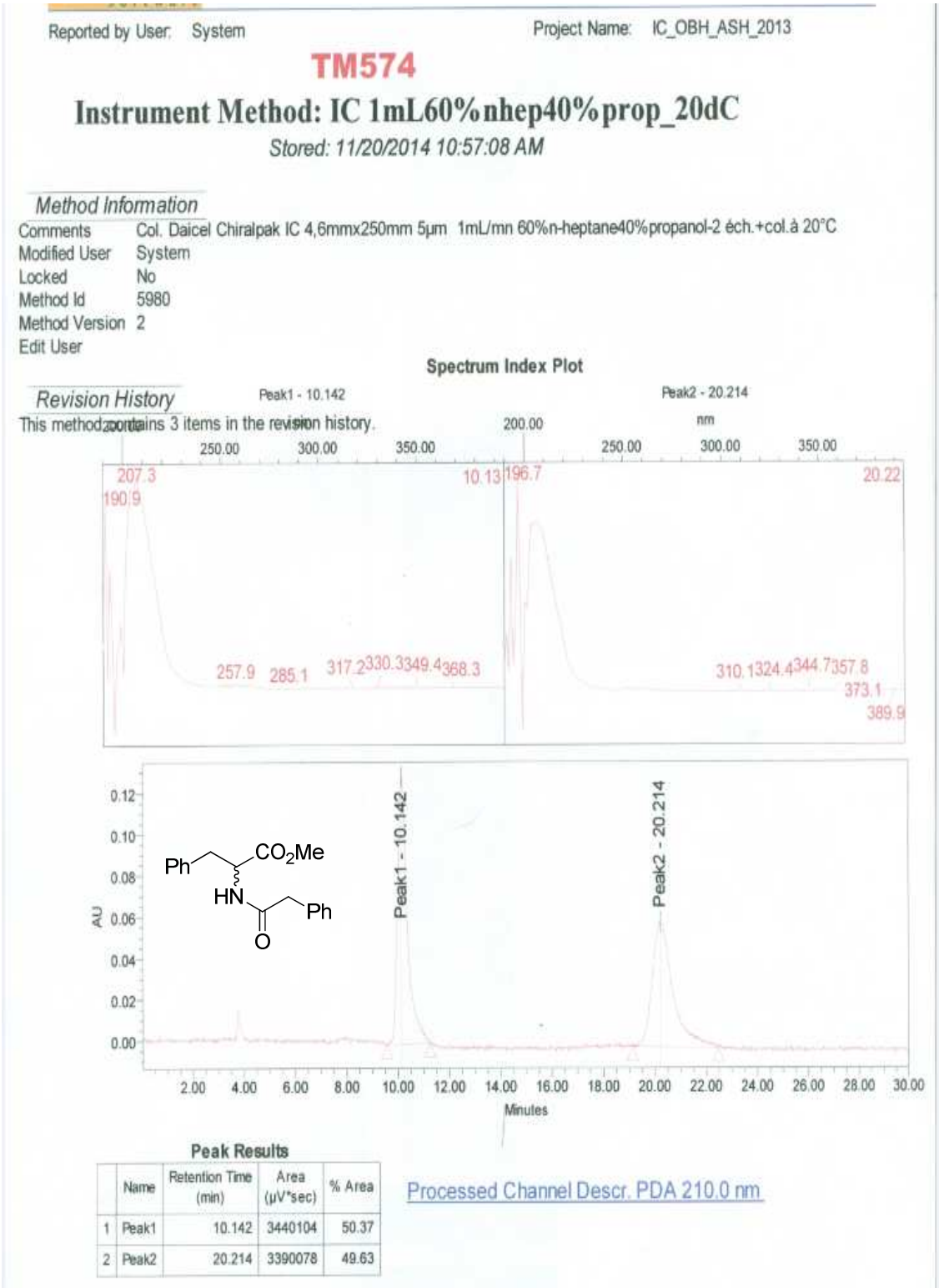
(*R*,*S*)-N-Boc-Phenylalanine Benzylamide



(*S*)-N-Boc-Phenylalanine Benzylamide **34**



(*R*,*S*)-N-Phenylacetyl-phenylalanine Methyl ester



(*S*)-N-Phenylacetyl-phenylalanine Methyl ester **35**