

N-Iodosuccinimide as a Precatalyst for C–N Bond-Forming Reactions from Alcohols under Mild Reaction Conditions

Njomza Ajvazi ^{1,*} and Stojan Stavber ^{1,2}

¹ Department of Physical and Organic Chemistry, Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia

² Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

* Correspondence: njomza.ajvazi@rezonanca-rks.com; Tel.: +383-44-258-553

Supporting Information

Contents

General information.....	2
General procedure for new carbon-nitrogen bond formation in organic molecules mediated by NIS on half mmol scale.....	3
Optimizing the Reaction Conditions	4
Characterization Data of Isolated Final Products.....	7
References	14
¹ H NMR, ¹³ C NMR, and ¹⁹ F NMR spectra of isolated final products.....	15
Thermal Gravimetric (TG) analysis of the NIS.....	30

General information

All alcohol substrates were commercially available and were used without further purification. All reactions were performed in Mettler-Toledo Easymax 102 Advanced Synthesis Workstation using 25 mL closed reactor tubes at 85–115 °C for 21–24 h. All reactions were monitored by TLC (mobile phase: dichloromethane/hexane) and visualized by a UV lamp (254 nm). Column chromatography (CC) was performed using silica gel 60 (particle size: 0.063–0.200 mm), and purification of certain products was accomplished on preparative silica gel glass plates PLC Kieselgel 60 F254 with 2 mm layer thickness. Spectroscopic methods: nuclear magnetic resonance (Varian INOVA 300 NMR instrument, (300 MHz ^1H , 75 MHz ^{13}C , 285 MHz ^{19}F) at 25 °C. ^1H NMR spectra were obtained as solutions in CDCl_3 with TMS as an internal standard. ^{19}F NMR spectra were obtained as solutions in CDCl_3 with CFCl_3 as an internal standard. Melting points (open capillary tube methodology; uncorrected) were used for identification and structure elucidation.

The isolated known compounds were identified by comparing the spectroscopic data with the literature.

General procedure for new carbon-nitrogen bond formation in organic molecules mediated by NIS on half mmol scale: In 25 mL reactor tubes, a mixture of benzyl alcohol (0.5 mmol), acetonitrile or propionitrile (0.5 mL), water (0.5 mmol) and NIS (6–10 mol%), or a mixture of solid reaction components previously powdered in a mortar was transferred. The reactor tube was then heated at 85–115 °C for 21–24 h. The progress of the reaction mixture was monitored by TLC. After the completion of the reaction, the crude reaction mixture was cooled down to room temperature, diluted with ethyl acetate (15 mL), washed with Na₂S₂O₃ (6 mL), NaHCO₃ (6 mL), and water (10 mL), and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the crude reaction mixture obtained was analyzed by ¹H NMR. The pure final products were obtained after flash chromatography, column chromatography, or preparative thin-layer chromatography. Detailed experimental information, such as mediator loading, isolated yields, and spectroscopic and other identification data, are given below.

The isolated known compounds were identified by comparing the spectroscopic data with the literature.

The scale-up procedure for the synthesis of *N*-(phenyl(*p*-tolyl)methyl)acetamide 7: A mixture of phenyl(*p*-tolyl)methanol **6** (10 mmol, 1.98 g), 6 mol% NIS (135 mg, 0.06 mol), which had been powdered in a mortar, was transferred to a 25 mL reactor tubes, added eventual H₂O (10 mmol, 180 µl), and MeCN **2** (10 mL), and heated at 105 °C for 21 h, stirring 300 rpm.

The progress of the reaction mixture was followed by TLC. Upon completion of the reaction, the mixture was cooled to room temperature. Finally, the crude reaction mixture was -purified by column chromatography to obtain a pure product with excellent yield white solid, 2.2131 g, and 93%).

Optimizing the Reaction Conditions

Table S1. The catalytic effect of NIS on the conversion of diphenylmethanol **1** with acetonitrile solution **2** based on temperature ¹.

$ \begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{1} \end{array} \xrightarrow[\text{MeCN} + \text{H}_2\text{O}]{10 \text{ mol \% NIS}_{(\text{cat.})}} \begin{array}{c} \text{NHAc} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{3} \end{array} + \begin{array}{c} \text{O} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{4} \end{array} + \begin{array}{c} \text{Ph} \quad \text{Ph} \\ \diagdown \quad / \\ \text{C}-\text{O}-\text{C} \\ / \quad \diagdown \\ \text{Ph} \quad \text{Ph} \\ \mathbf{5} \end{array} $					
Entry	Temp. (°C)	Conversion ² (%) of 1	Relative distribution ² (%)		
			3	4	5
1	75	81	56	8	17
2	85	92	81	8	3
3	95	92	86	6	/
4	105	100	96	4	/

¹ Reaction conditions: diphenylmethanol **1** (0.5 mmol), MeCN **2** (1/2 mL), H₂O (0.5 mmol), 24 h.

² Determined from ¹H NMR spectra of isolated crude reaction mixtures.

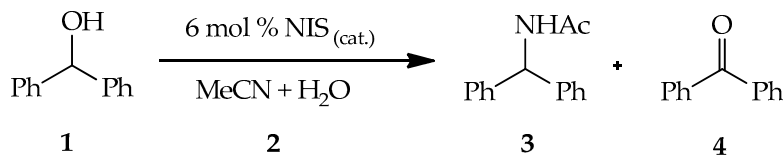
Table S2. The effect of loading of NIS as the mediator on the conversion of diphenylmethanol **1** with acetonitrile solution **2** ¹.

$ \begin{array}{c} \text{OH} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{1} \end{array} \xrightarrow[\text{MeCN} + \text{H}_2\text{O}]{\text{NIS}_{(\text{cat.})}} \begin{array}{c} \text{NHAc} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{3} \end{array} + \begin{array}{c} \text{O} \\ \\ \text{Ph}-\text{C}-\text{Ph} \\ \mathbf{4} \end{array} + \begin{array}{c} \text{Ph} \quad \text{Ph} \\ \diagdown \quad / \\ \text{C}-\text{O}-\text{C} \\ / \quad \diagdown \\ \text{Ph} \quad \text{Ph} \\ \mathbf{5} \end{array} $					
Entry	NIS (mol%)	Conversion ² (%) of 1	Relative distribution ² (%)		
			3	4	5
1	3	95	61	3	31
2	4	96	87	7	2
3	5	98	91	7	/
4	6	100	96	4	/

¹ Reaction conditions: diphenylmethanol **1** (0.5 mmol), MeCN **2** (1/2 mL), H₂O (0.5 mmol), 105 °C, 24 h.

² Determined from ¹H NMR spectra of isolated crude reaction mixtures.

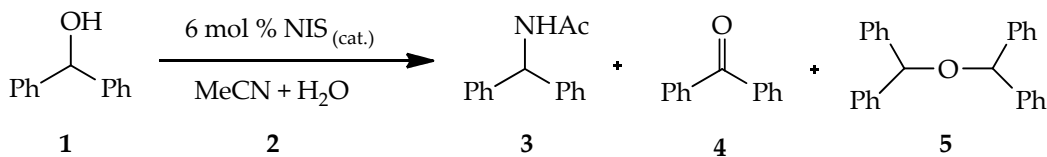
Table S3. The catalytic effect of NIS on the conversion of diphenylmethanol **1** with acetonitrile solution **2** based on time ¹.



Entry	Time (h)	Conversion ² (%) of 1	Relative distribution ² (%)	
			3	4
1	18	98	92	6
2	21	100	96	4
3	24	100	95	5

¹ Reaction conditions: diphenylmethanol **1** (0.5 mmol), MeCN **2** (1/2 mL), H₂O (0.5 mmol), 105 °C. ² Determined from ¹H NMR spectra of isolated crude reaction mixtures.

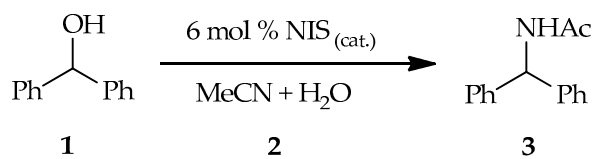
Table S4. The catalytic effect of NIS on the conversion of diphenylmethanol **1** with acetonitrile solution **2** based on mmol of water ¹.



Entry	mmol H ₂ O	Conversion ² (%) of 1	Relative distribution ² (%)		
			3	4	5
1	/	97	82	8	7
2	0.5	100	96	4	/
3	1	96	90	6	/
4	2	85	75	6	4

¹ Reaction conditions: diphenylmethanol **1** (0.5 mmol), MeCN **2** (1/2 mL), 105 °C, 21 h. ² Determined from ¹H NMR spectra of isolated crude reaction mixtures.

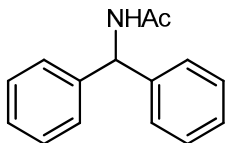
Table S5. The pH measurements on the conversion of diphenylmethanol **1** with acetonitrile solution **2** mediated by NIS.



Entry	Time (h)	pH
1	1	4
2	2	3
3	3	2.5
4	19	2
5	20	2
6	21	2

Characterization Data of Isolated Final Products

N-benzhydrylacetamide (3)[1]



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₅H₁₅NO (Mr = 225.29);

0.5 mmol diphenylmethanol **1** (92.1 mg), 0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl), 6 mol% NIS (6.7 mg, 0.06 mmol), 105°C, 21 h, stirring 300 rpm;

CC (SiO₂, EtOAc/3exane 9:1);

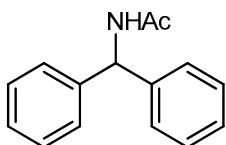
105 mg (94%), white solid;

126–127 °C, (lit. 128 °C);

δ (ppm) = 7.29 – 7.18 (m, 10H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 1.93 (s, 3H);

δ (ppm) = 169.5, 141.6, 128.6, 127.5, 127.4, 57.0, 23.2.

N-benzhydrylacetamide (3)[1] *From dimeric ether and MeCN*



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₅H₁₅NO (Mr = 225.29);

0.25 mmol (oxybis(methanetriyl))tetrabenzene **5** (87.6 mg), 0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl), 6 mol% NIS (6.7 mg, 0.06 mmol), 105°C, 21 h, stirring 300 rpm;

CC (SiO₂, EtOAc/hexane 9:1);

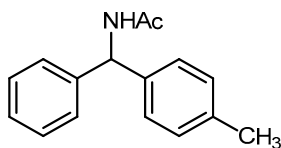
105 mg (93%), white solid;

126–127 °C, (lit. 128 °C);

δ (ppm) = 7.29 – 7.18 (m, 10H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 1.93 (s, 3H);

δ (ppm) = 169.5, 141.6, 128.6, 127.5, 127.4, 57.0, 23.2.

***N*-(phenyl(*p*-tolyl)methyl)acetamide (7)[2]**



Reaction conditions:

C₁₆H₁₇NO (Mr = 239.31);
0.5 mmol phenyl(*p*-tolyl)methanol **6** (99.1 mg),
0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl), 6 mol%
NIS (6.7 mg, 0.06 mmol), 105°C, 21 h, stirring 300
rpm;

Purification:

CC (SiO₂, EtOAc/hexane 9:1);

Yield:

113 mg (94%), white solid;

Mp.:

127–129 °C, (lit. 126–128 °C);

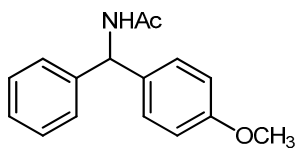
¹H NMR (300 MHz, CDCl₃):

δ (ppm) = 7.32 – 7.08 (m, 9H), 6.57 (d, *J* = 7.7 Hz,
1H), 6.16 (d, *J* = 8.1 Hz, 1H), 2.30 (s, 3H), 1.94 (s,
3H);

¹³C NMR (76 MHz, CDCl₃):

δ (ppm) = 169.4, 141.8, 138.7, 137.1, 129.3, 128.6,
127.5, 127.4, 127.3, 56.8, 23.2, 21.1.

***N*-((4-methoxyphenyl)(phenyl)methyl)acetamide (9)[2]**



Reaction conditions:

C₁₆H₁₇NO₂ (Mr = 255.31);
0.5 mmol (4-methoxyphenyl)(phenyl)methanol **8**
(107.1 mg), 0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl),
6 mol% NIS (6.7 mg, 0.06 mmol), 85°C, 21 h,
stirring 300 rpm;

Purification:

CC (SiO₂, EtOAc/Hexane 9:1);

Yield:

94 mg (73%), white solid;

Mp.:

157–159 °C, (lit. 154–156 °C);

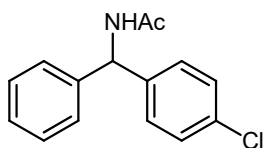
¹H NMR (300 MHz, CDCl₃):

δ (ppm) = 7.33 – 7.09 (m, 9H), 6.83 (s, 1H), 6.18 (d,
1H), 3.78 (s, 3H), 2.02 (s, 3H);

¹³C NMR (76 MHz, CDCl₃):

δ (ppm) = 169.2, 159.0, 141.9, 133.9, 128.8, 128.7,
127.4, 127.4, 114.1, 56.5, 55.4, 23.4.

***N*-((4-chlorophenyl)(phenyl)methyl)acetamide (**11**)**[3]



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₅H₁₄ClNO (Mr = 259.73);

0.5 mmol (4-chlorophenyl)(phenyl)methanol **10** (109.3 mg), 0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl), 10 mol% NIS (11.2 mg, 0.1 mmol), 105°C, 24 h, stirring 300 rpm;

CC (SiO₂, EtOAc/Hexane 9:1);

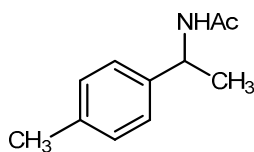
119 mg (92%), white solid;

134–136 °C, (lit. 133–135 °C);

δ (ppm) = 7.30 – 7.08 (m, 9H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.12 (d, *J* = 8.1 Hz, 1H), 1.90 (s, 3H);

δ (ppm) = 169.6, 141.2, 140.2, 133.1, 128.8, 128.8, 128.7, 127.7, 127.5, 56.4, 23.0.

***N*-(1-(*p*-Tolyl)ethyl)acetamide (**15**)**[4]



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₁H₁₅NO (Mr = 177.24);

0.5 mmol 1-(*p*-tolyl)ethanol **14** (68.9 μl), 0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl), 10 mol% NIS (11.2 mg, 0.1 mmol), 105°C, 24 h, stirring 300 rpm;

CC (SiO₂, EtOAc/hexane 9:1);

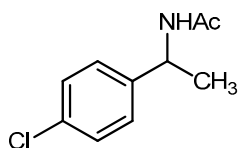
71 mg (80%), white solid;

76–78 °C, (lit. 80–82 °C);

δ (ppm) = 7.18 (dd, 4H), 5.90 (br, 1H), 5.08 (p, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 1.95 (s, 3H), 1.46 (d, *J* = 6.9 Hz, 3H);

δ (ppm) = 169.2, 140.3, 137.1, 129.4, 126.2, 48.6, 23.5, 21.8, 21.1.

***N*-(1-(4-chlorophenyl)ethyl)acetamide (17)**[5]



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₀H₁₂ClNO (Mr = 197.66);

0.5 mmol 1-(4-chlorophenyl)ethanol **16** (66.9 μl), 0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl), 10 mol% NIS (11.2 mg, 0.1 mmol), 105°C, 24 h, stirring 300 rpm;

TLC-preparative (EtOAc/hexane 9:1);

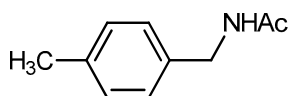
85 mg (86%), white solid;

96–98 °C, (lit. 98–99 °C);

δ (ppm) = 7.29 – 7.20 (m, 4H), 6.28 (d, *J* = 6.7 Hz, 1H), 5.04 (p, *J* = 7.1 Hz, 1H), 1.95 (s, 3H), 1.43 (d, *J* = 7.0 Hz, 3H);

δ (ppm) = 169.4, 142.0, 133.0, 128.7, 127.6, 48.3, 23.3, 21.8.

***N*-(4-methylbenzyl)acetamide (23)**[6]



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₀H₁₃NO (Mr = 163.22);

0.5 mmol *p*-tolylmethanol **22** (61.1 mg), 0.5 mL MeCN **2**, 0.5 mmol H₂O (9 μl), 10 mol% NIS (11.2 mg, 0.1 mmol), 115 °C, 21 h, stirring 300 rpm;

TLC-preparative (EtOAc/hexane 9:1);

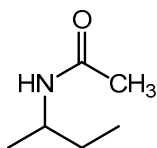
60 mg (73%), white solid;

103–105°C, (lit. 105–107 °C)

δ (ppm) = 7.14 (d, *J* = 3.1 Hz, 4H), 6.05 (s, 1H), 4.35 (d, *J* = 5.6 Hz, 2H), 2.32 (s, 3H), 1.98 (s, 3H);

δ (ppm) = 170.2, 137.3, 135.3, 129.4, 127.9, 43.5, 23.3, 21.2.

***N*-(*sec*-butyl)acetamide (27)[7]**



Reaction conditions:

Purification:

Yield:

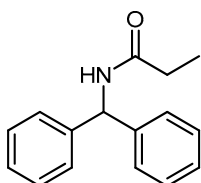
Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₆H₁₃NO (Mr = 115.17);
0.5 mmol butan-2-ol **26** (46 μl), 0.5 mL MeCN **2**,
0.5 mmol H₂O (9 μl), 10 mol% NIS (11.2 mg, 0.1
mmol), 105°C, 24 h, stirring 300 rpm;
CC (SiO₂, EtOAc/Hexane 9:1);
49 mg (85%), white solid;
115–117 °C, (lit.[8] 117–120 °C);
δ (ppm) = δ 5.25 (s, 1H), 4.00 – 3.79 (m, 1H), 1.96
(s, 3H), 1.50 – 1.41 (m, 2H), 1.12 (d, *J* = 6.6 Hz,
3H), 0.91 (t, *J* = 7.4 Hz, 3H);
δ (ppm) = 169.5, 46.8, 29.8, 23.7, 20.6, 10.4.

***N*-benzhydrylpropionamide (29)[9]**



Reaction conditions:

Purification:

Yield:

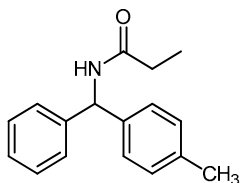
Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₆H₁₇NO (Mr = 239.31);
0.5 mmol diphenylmethanol **1** (92.1 mg), 0.5 mL
CH₃CH₂CN **28**, 0.5 mmol H₂O (9 μl), 6 mol% NIS
(6.7 mg, 0.06 mmol), 105°C, 21 h, stirring 300 rpm;
CC (SiO₂, EtOAc/hexane 9:1);
109 mg (91%), white solid;
141–143 °C, (lit. 144 °C);
δ (ppm) 7.33 – 7.16 (m, 10H), 6.43 (d, *J* = 8.0 Hz,
1H), 6.22 (d, *J* = 8.1 Hz, 1H), 2.21 (q, *J* = 7.6 Hz,
2H), 1.12 (t, *J* = 7.6 Hz, 3H);
δ (ppm) = 173.0, 141.8, 128.6, 127.5, 127.4, 56.8,
29.7, 9.9.

***N*-(phenyl(*p*-tolyl)methyl)propionamide (30)[10]**



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

C₁₇H₁₉NO (Mr = 253.34);

0.5 mmol phenyl(*p*-tolyl)methanol **6** (99.1 mg), 0.5 mL CH₃CH₂CN **28**, 0.5 mmol H₂O (9 μl), 6 mol% NIS (6.7 mg, 0.06 mmol), 105 °C, 21 h, stirring 300 rpm;

CC (SiO₂, EtOAc/hexane 9:1);

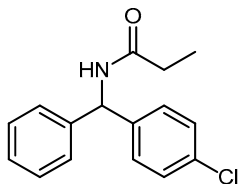
116 mg (92%), white solid;

118–120 °C;

δ (ppm) = 7.31 – 7.08 (m, 9H), 6.32 (s, 1H), 6.19 (d, *J* = 8.1 Hz, 1H), 2.31 (s, 3H), 2.22 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H);

δ (ppm) = 172.9, 141.9, 138.9, 137.1, 129.4, 128.6, 127.43, 127.39, 127.3, 56.6, 29.7, 21.1, 9.9.

***N*-((4-chlorophenyl)(phenyl)methyl)propionamide (31)**



Reaction conditions:

Purification:

Yield:

Mp.:

¹H NMR (300 MHz, CDCl₃):

¹³C NMR (76 MHz, CDCl₃):

HRMS (ESI):

C₁₆H₁₆ClNO (Mr = 273.76);

0.5 mmol (4-chlorophenyl)(phenyl)methanol **10** (109.3 mg), 0.5 mL CH₃CH₂CN **28**, 0.5 mmol H₂O (9 μl), 10 mol% NIS (11.2 mg, 0.1 mmol), 105 °C, 24 h, stirring 300 rpm;

CC (SiO₂, EtOAc/hexane 9:1);

128 mg (93%), white solid;

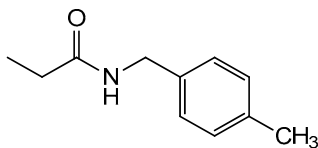
121–122 °C;

δ (ppm) = 7.32 – 7.10 (m, 9H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 2.20 (q, *J* = 7.6 Hz, 2H), 1.10 (t, *J* = 7.6 Hz, 3H);

δ (ppm) = 173.1, 141.2, 140.3, 133.2, 128.80, 128.79, 128.7, 127.7, 127.5, 56.3, 29.6, 9.9;

Calculated *m* / *z* = 274.0999 (MH⁺); found *m* / *z* = 274.0997 (MH⁺).

N-(4-methylbenzyl)propionamide (**32**)



Reaction conditions:

C₁₁H₁₅NO (Mr = 177.24);
0.5 mmol *p*-tolylmethanol **22** (61.1mg), 0.5 mL
CH₃CH₂CN **28**, 0.5 mmol H₂O (9 μl), 10 mol%
NIS (11.2 mg, 0.1 mmol), 115 °C, 21 h, stirring 300
rpm;

Purification:

CC (SiO₂, EtOAc/hexane 9:1);

Yield:

65 mg (74%), white solid;

Mp.:

85 °C;

¹H NMR (300 MHz, CDCl₃):

δ (ppm) = 7.14 (dd, *J* = 2.9 Hz, 4H), 5.94 (s, 1H),
4.36 (d, *J* = 5.7 Hz, 2H), 2.32 (s, 3H), 2.21 (q, *J* = 7.6
Hz, 3H), 1.15 (t, *J* = 7.6 Hz, 3H);

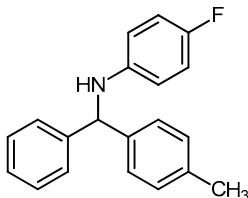
¹³C NMR (76 MHz, CDCl₃):

δ (ppm) = 173.7, 137.2, 135.5, 129.4, 127.9, 43.4,
29.7, 21.2, 10.0;

HRMS (ESI):

Calculated *m* / *z* = 178.1232 (MH⁺); found *m* / *z* =
178.1231 (MH⁺).

4-fluoro-*N*-(phenyl(*p*-tolyl)methyl)aniline (**34**)



Reaction conditions:

C₂₀H₁₈FN (Mr = 291.36);
0.5 mmol phenyl(*p*-tolyl)methanol **6** (99.1 mg),
0.55 mmol *p*-fluoroaniline **33** (52 μl), H₂O (9 μl),
10 mol% NIS (11.2 mg, 0.1 mmol), 105 °C, 24 h,
stirring 300 rpm;

Purification:

TLC-preparative (SiO₂, EtOAc/hexane 1:1);

Yield:

94 mg (65%), yellow oil;

¹H NMR (300 MHz, CDCl₃):

δ (ppm) = 7.27 (m, *J* = 26.7, 10.7, 7.3 Hz, 7H), 7.10
(d, *J* = 8.1 Hz, 2H), 6.78 (m, *J* = 8.7 Hz, 2H), 6.42
(m, *J* = 9.0, 4.4 Hz, 2H), 5.37 (s, 1H), 4.08 (s, 1H),
2.30 (s, 3H);

¹³C NMR (76 MHz, CDCl₃):

δ (ppm) = 157.5, 154.4, 143.87, 143.85, 143.1, 140.0,
137.2, 129.6, 128.9, 127.5, 127.4, 115.8, 115.5, 114.4,
114.3, 63.4, 21.2;

¹⁹F NMR (285 MHz, CDCl₃):

δ = -128.49 (m);

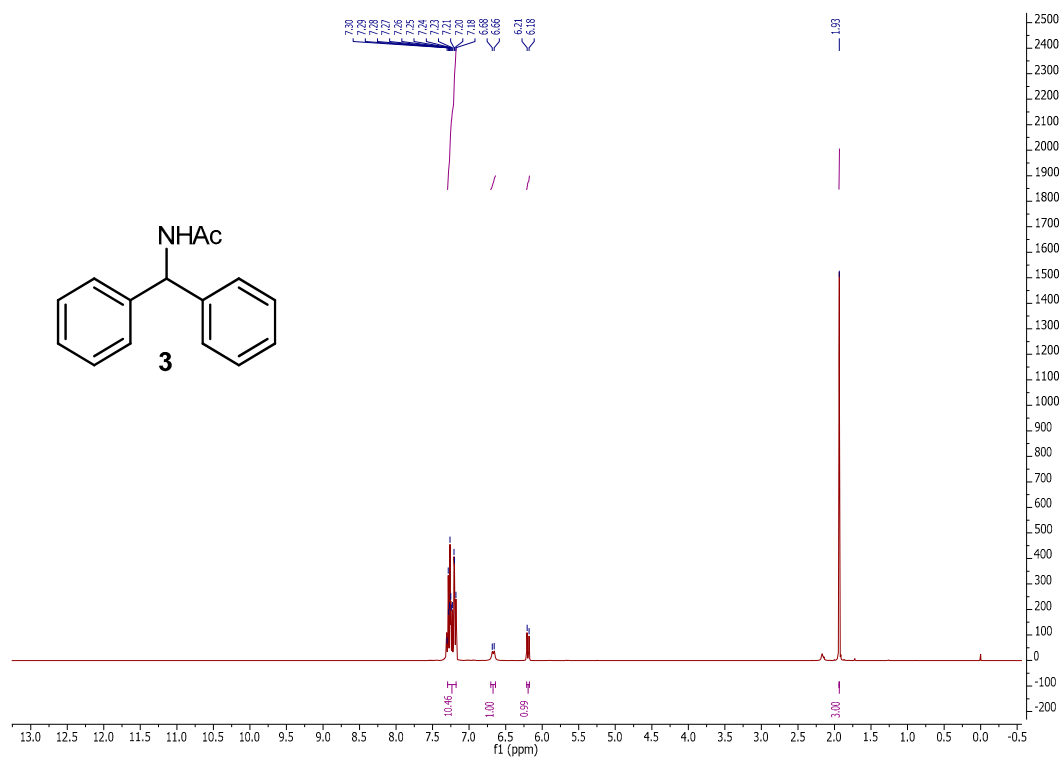
HRMS (ESI):

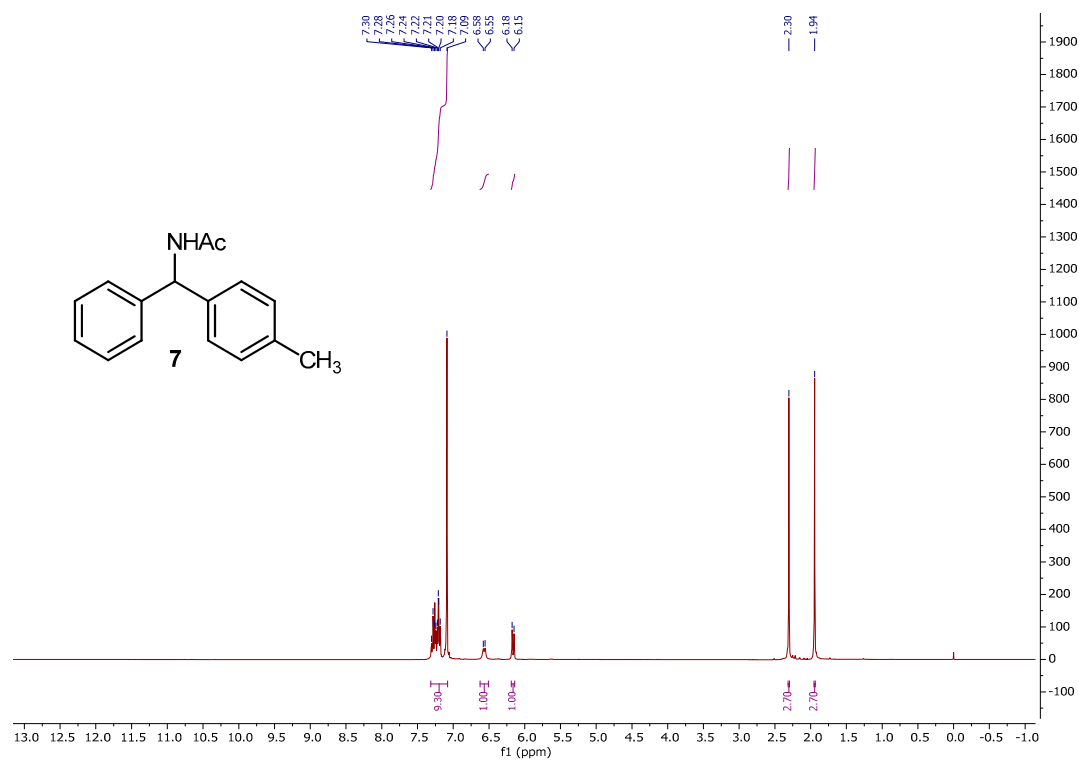
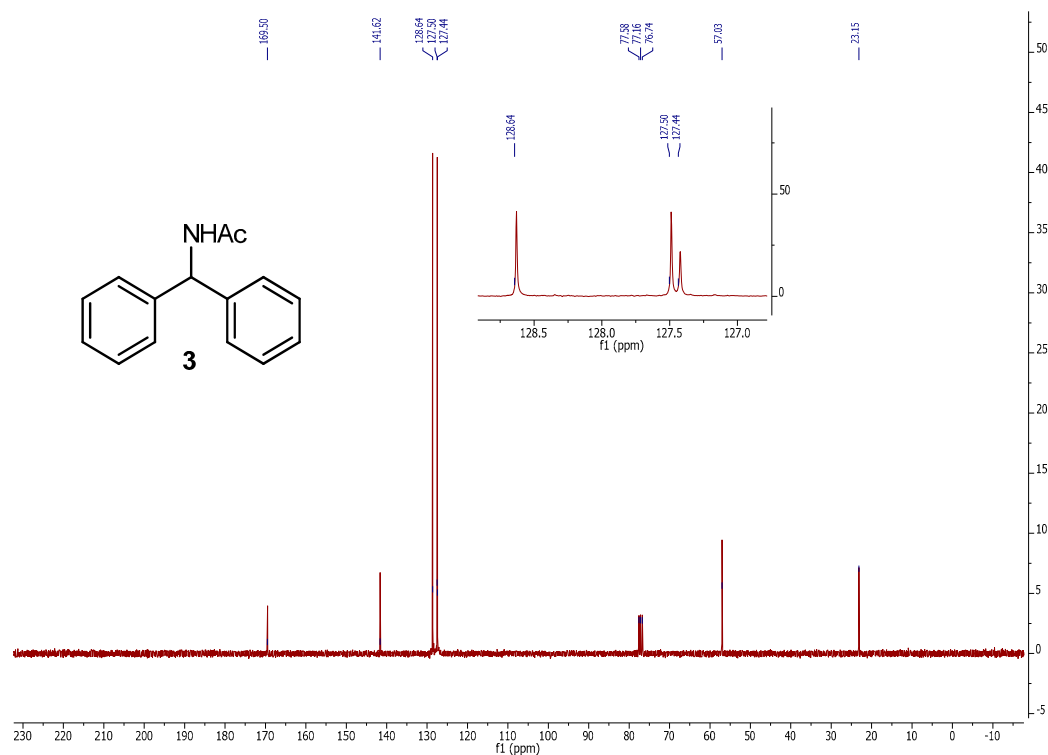
Calculated *m* / *z* = 290.1345 (MH⁺); found *m* / *z* =
290.1349 (MH⁺).

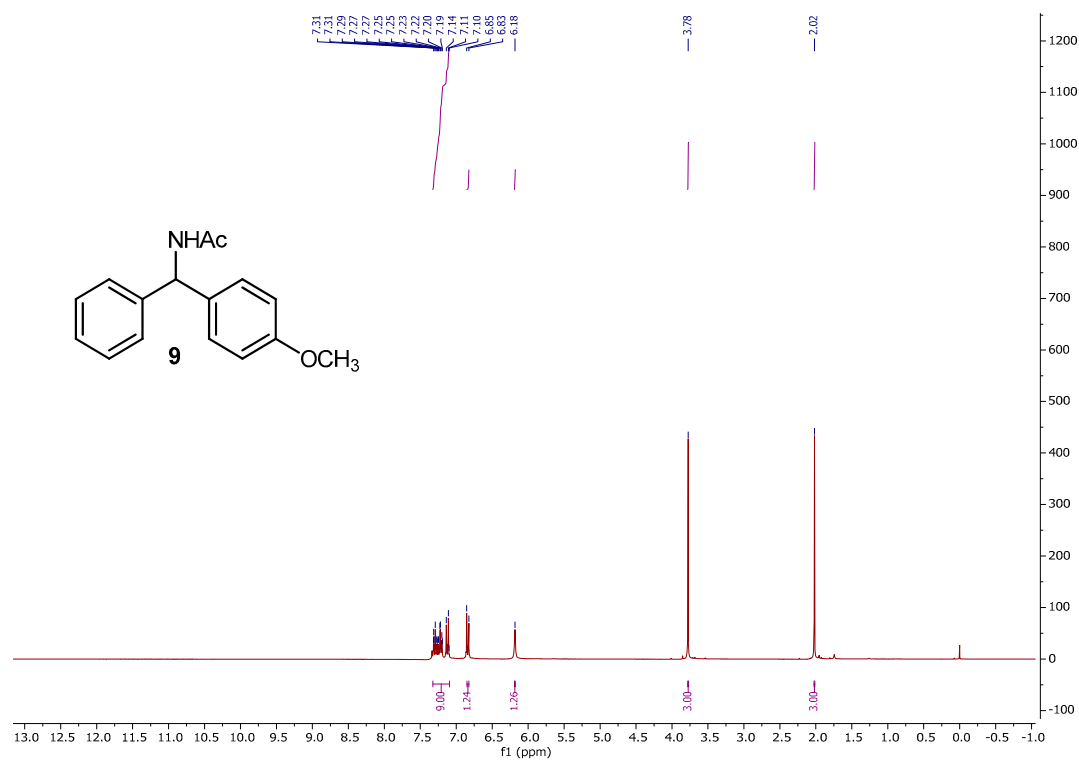
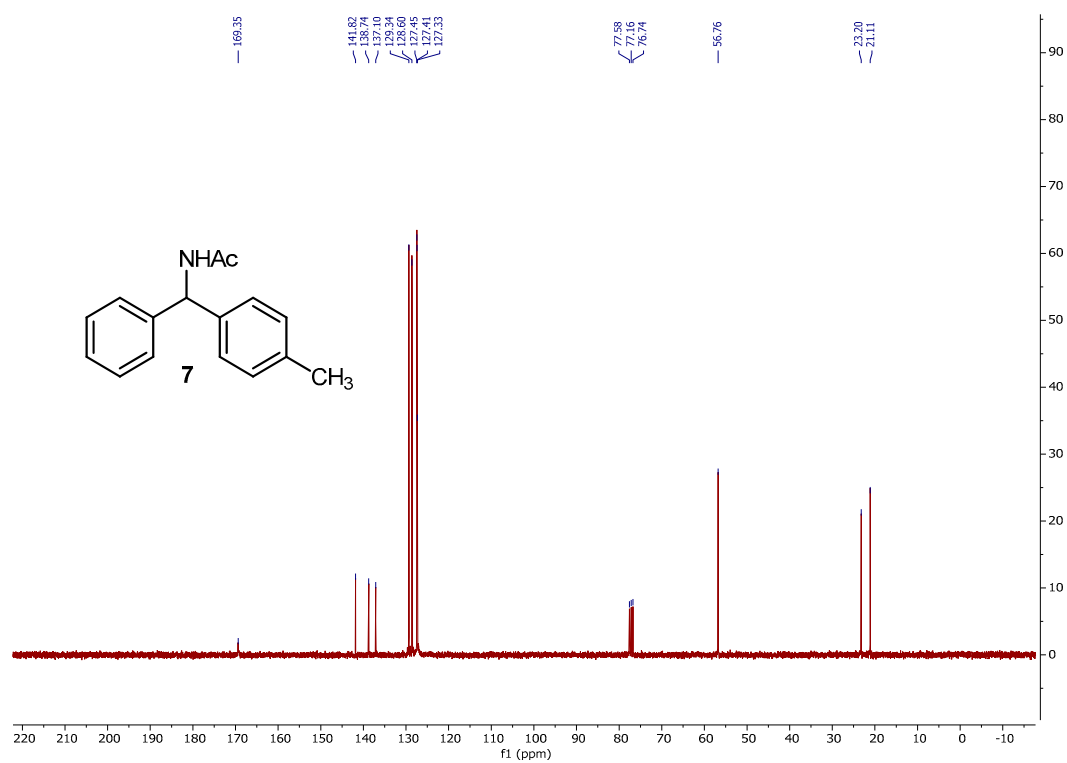
References

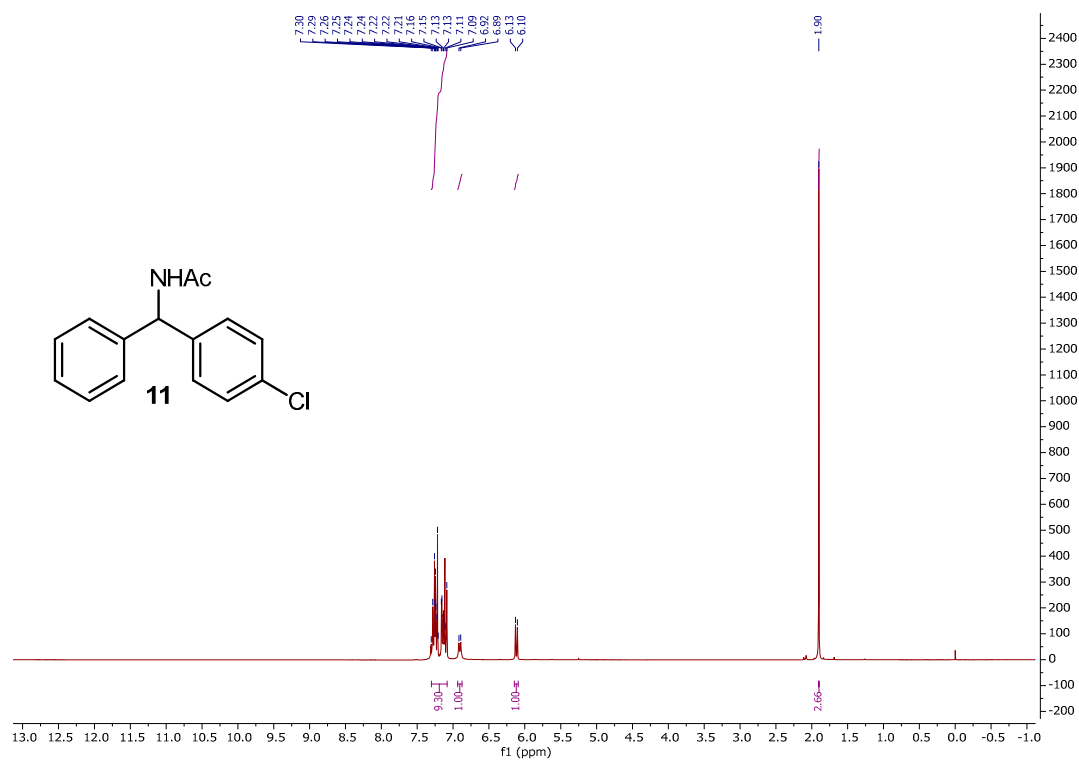
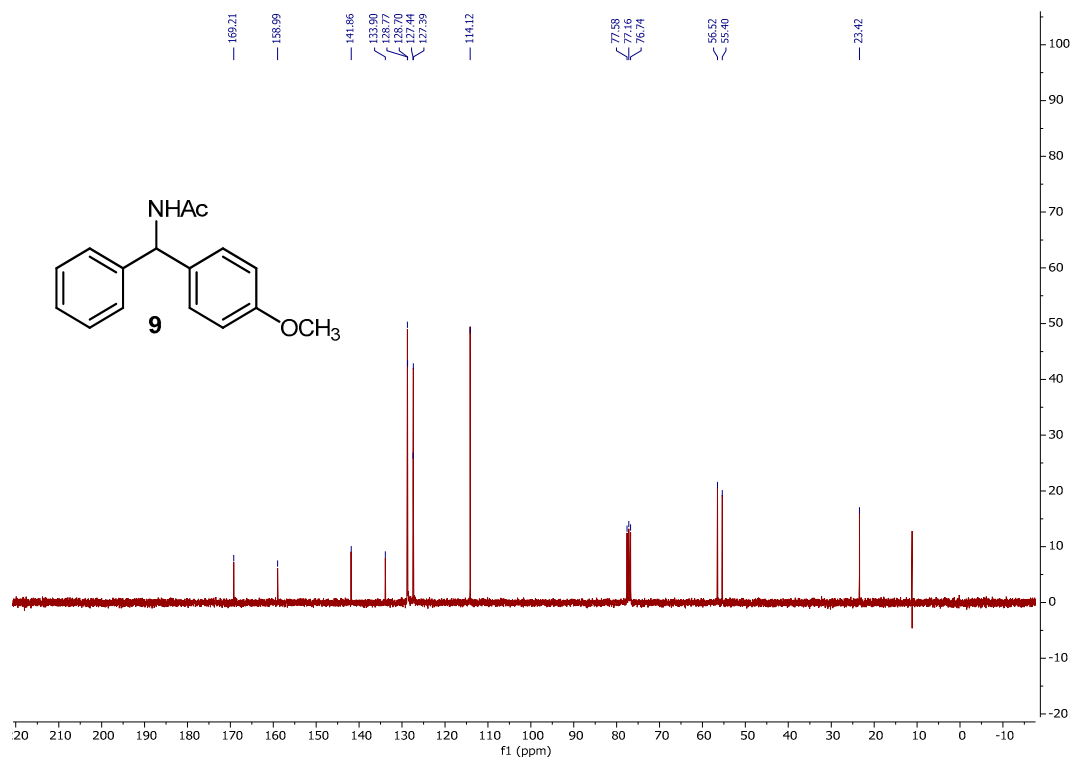
1. Ibrahim, N.; Hashmi, A.S.K.; Rominger, F. Gold Catalysis: Alkyl Migration in the Addition of Alcohols to Nitriles. *Adv. Synth. Catal.* **2011**, *353*, 461-468, doi:<https://doi.org/10.1002/adsc.201000779>.
2. Crampton, R.; Woodward, S.; Fox, M. Bis-Sulfamyl Imines: Potent Substrates for Asymmetric Additions of Arylboroxines under Rhodium Catalysis. *Adv. Synth. Catal.* **2011**, *353*, 903-906, doi:<https://doi.org/10.1002/adsc.201000838>.
3. Sanz, R.; Martínez, A.; Guilarte, V.; Álvarez-Gutiérrez, J.M.; Rodríguez, F. The Ritter Reaction under Truly Catalytic Brønsted Acid Conditions. *EurJOC* **2007**, *2007*, 4642-4645, doi:<https://doi.org/10.1002/ejoc.200700562>.
4. Li, G.; Antilla, J.C. Highly Enantioselective Hydrogenation of Enamides Catalyzed by Chiral Phosphoric Acids. *Org. Lett.* **2009**, *11*, 1075-1078, doi:<https://doi.org/10.1021/ol802860u>.
5. Yamamoto, Y.; Hasegawa, H.; Yamataka, H. Dynamic Path Bifurcation in the Beckmann Reaction: Support from Kinetic Analyses. *J. Org. Chem.* **2011**, *76*, 4652-4660, doi:<https://doi.org/10.1021/jo200728t>.
6. Yagafarov, N.Z.; Muratov, K.M.; Biriukov, K.; Usanov, D.L.; Chusova, O.; Perekalin, D.S.; Chusov, D. Ruthenium-Catalyzed Reductive Amidation without an External Hydrogen Source. *EurJOC* **2018**, *2018*, 557-563, doi:<https://doi.org/10.1002/ejoc.201701527>.
7. Singh, K.; Singh, K. N1,N3-Diacyl-3,4-dihydropyrimidin-2(1H)-ones: neutral acyl group transfer reagents. *Tetrahedron* **2009**, *65*, 10395-10399, doi:<https://doi.org/10.1016/j.tet.2009.10.037>.
8. White, E.H. Complex Salts of Monosubstituted Amides with the Hydrohalic Acids and the Halogens. *J. Am. Chem. Soc.* **1955**, *77*, 6215-6219, doi:<https://doi.org/10.1021/ja01628a046>.
9. Audiger, L.; Watts, K.; Elmore, S.C.; Robinson, R.I.; Wirth, T. Ritter Reactions in Flow. *ChemSusChem* **2012**, *5*, 257-260, doi:<https://doi.org/10.1002/cssc.201100372>.
10. Awano, T.; Ohmura, T.; Sugimoto, M. Inversion or Retention? Effects of Acidic Additives on the Stereochemical Course in Enantiospecific Suzuki–Miyaura Coupling of α -(Acetylamino)benzylboronic Esters. *J. Am. Chem. Soc.* **2011**, *133*, 20738-20741, doi:<https://doi.org/10.1021/ja210025q>.

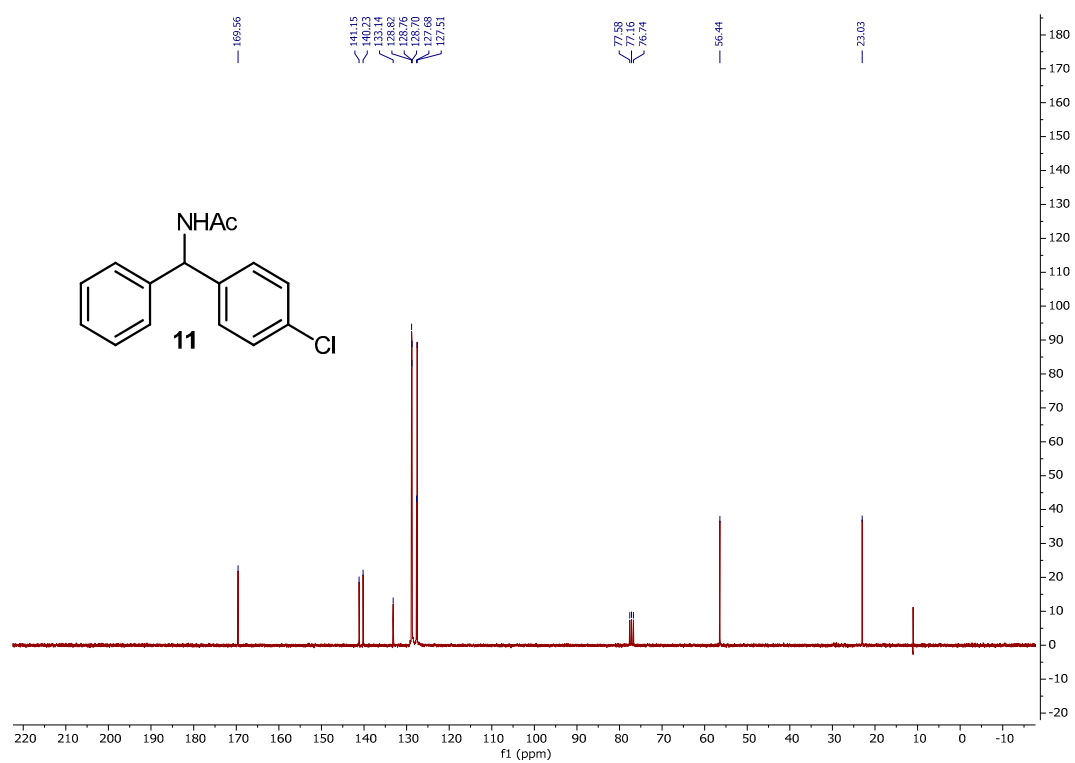
^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra of isolated final products

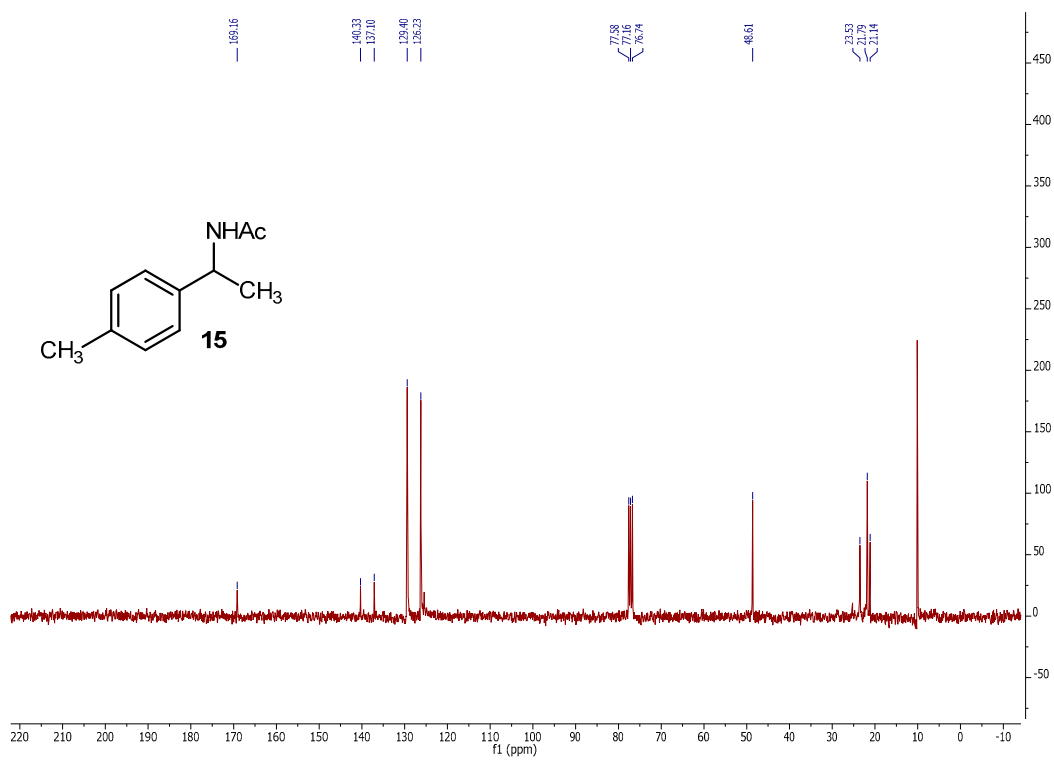
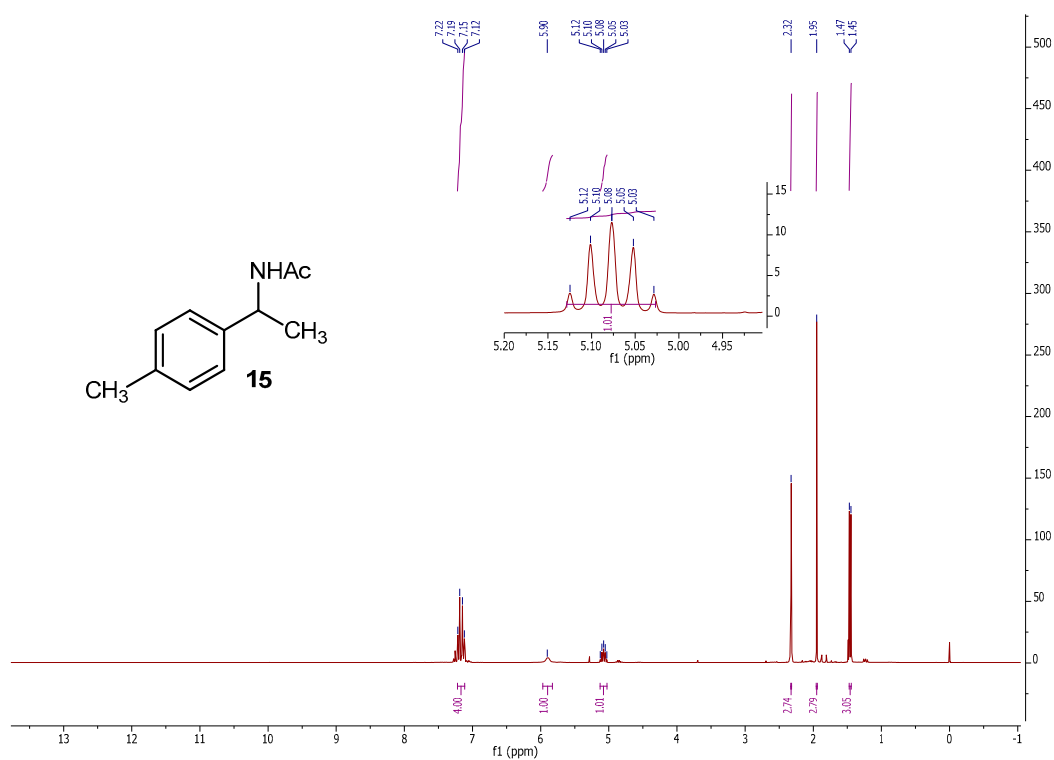


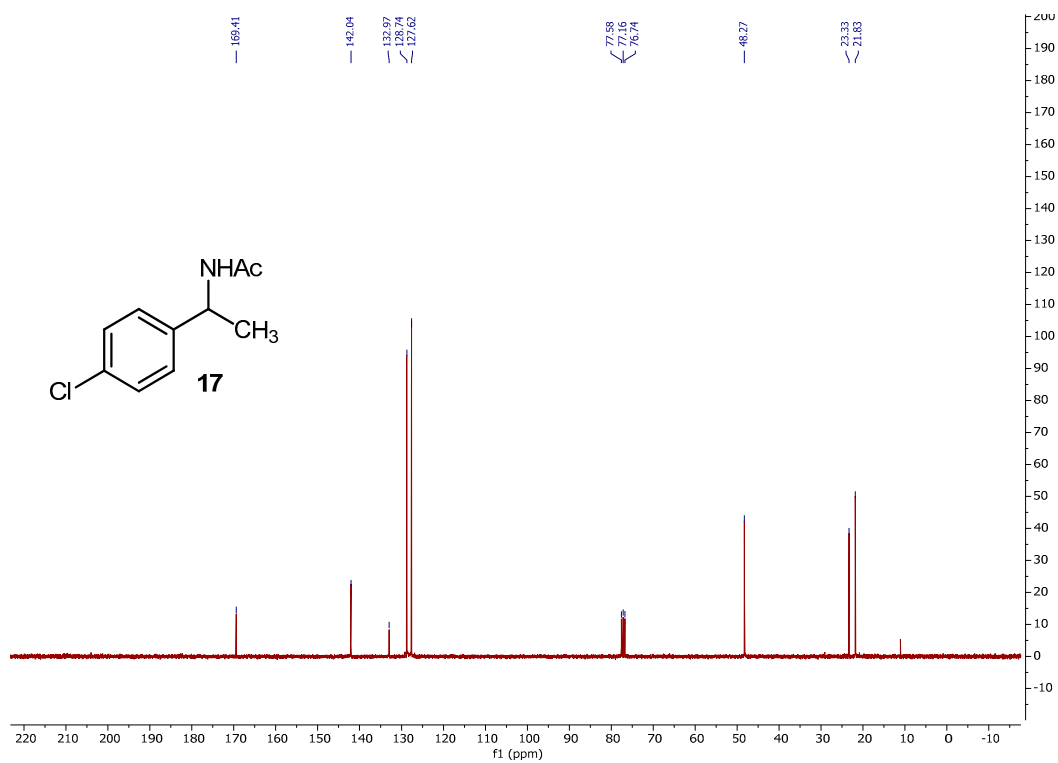
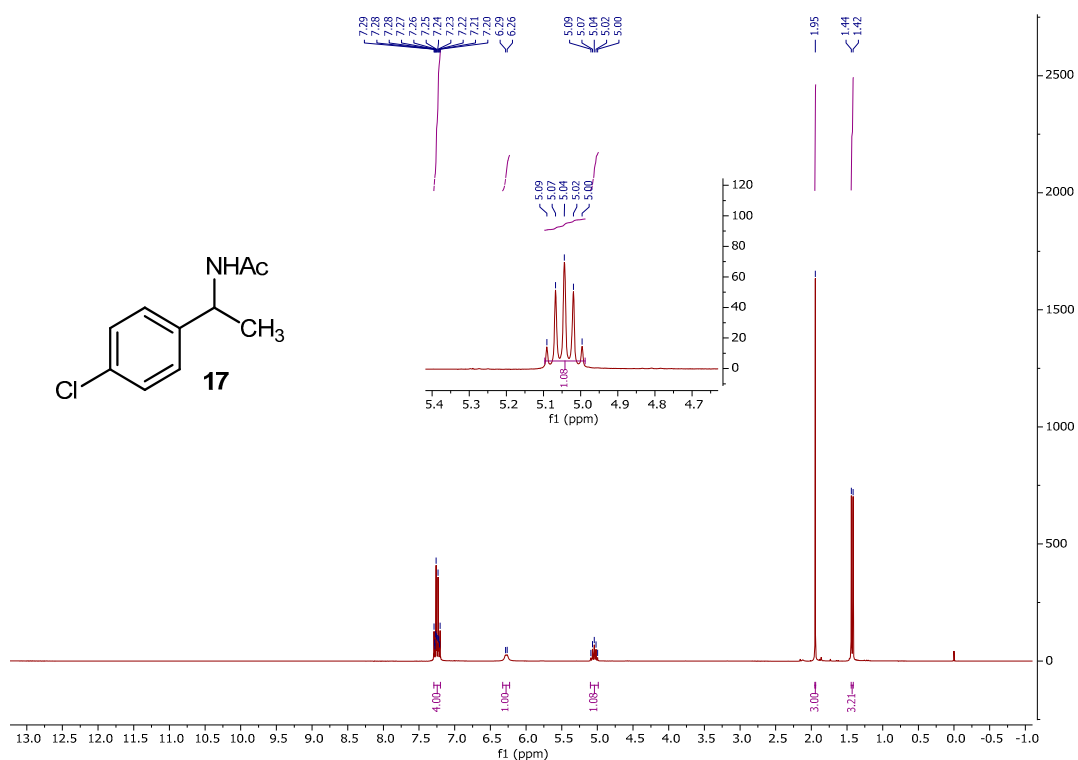


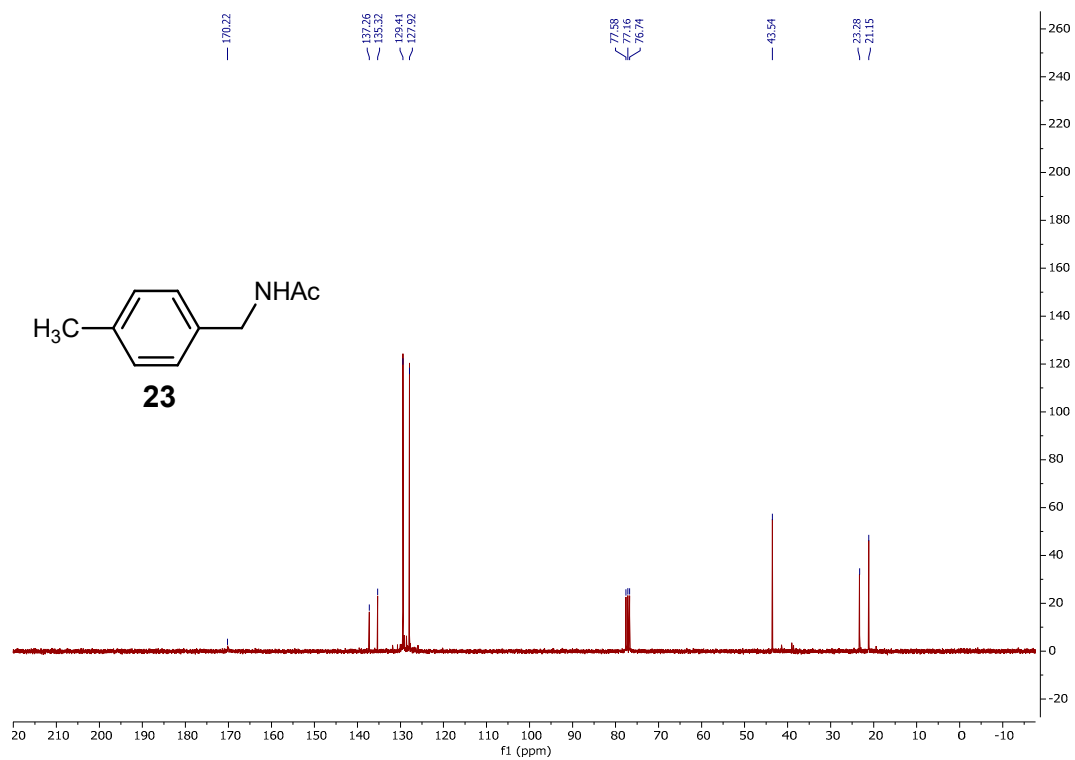
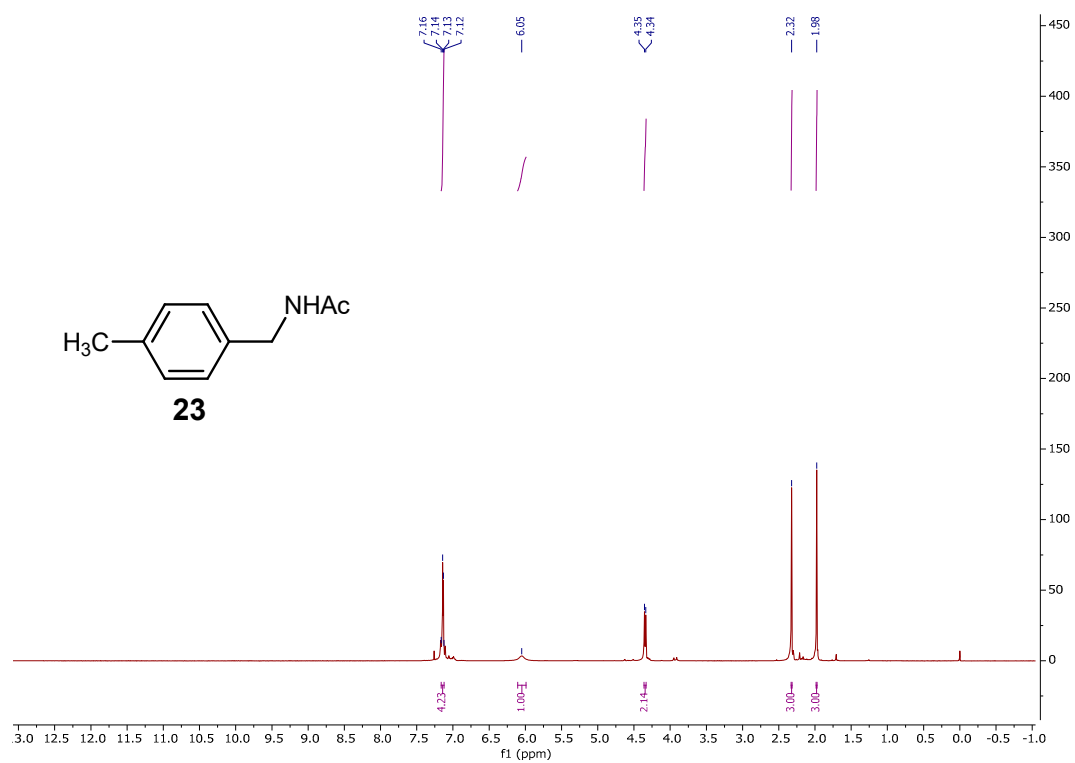


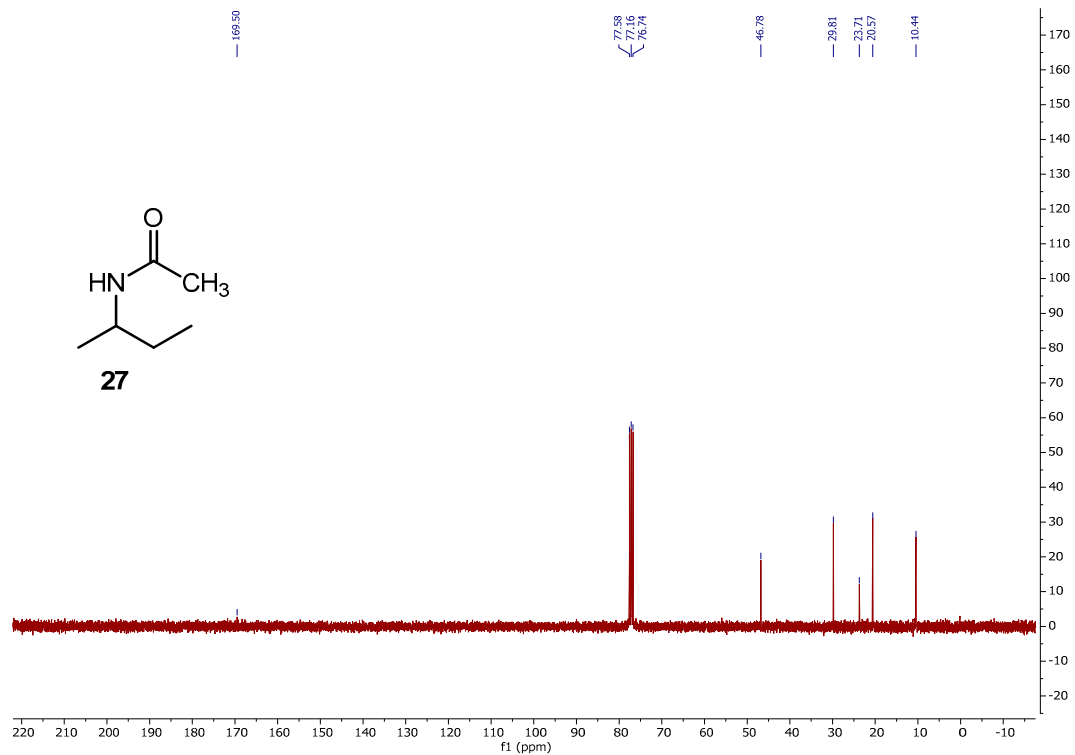
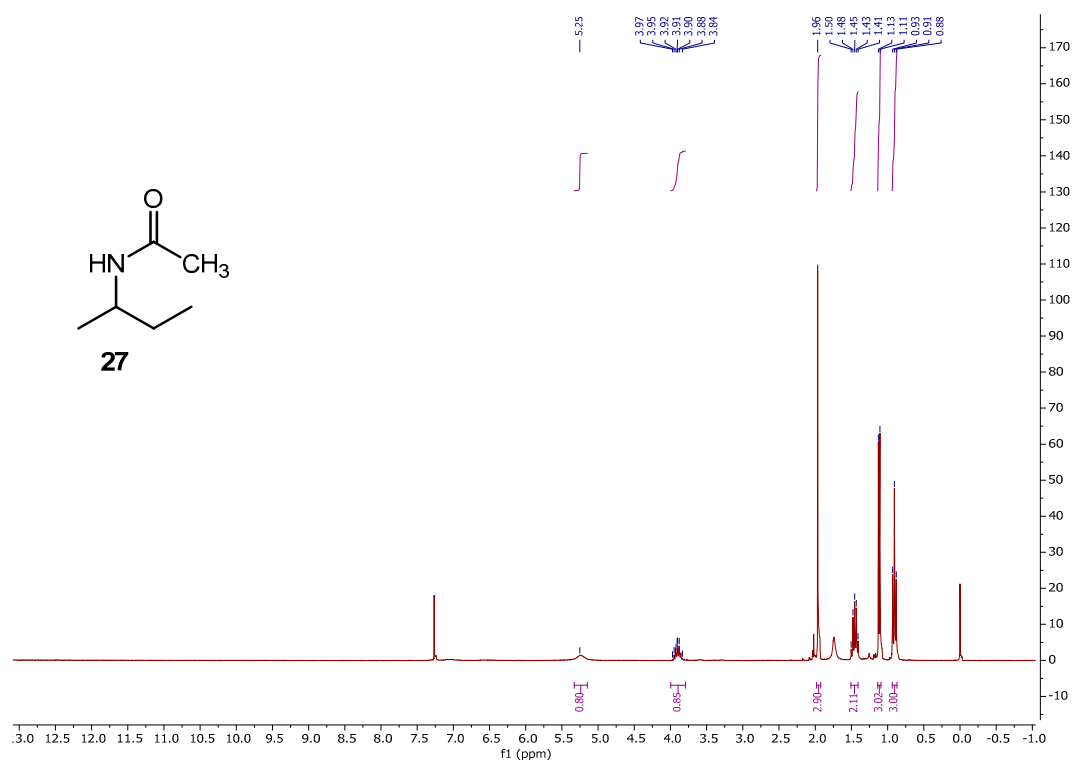


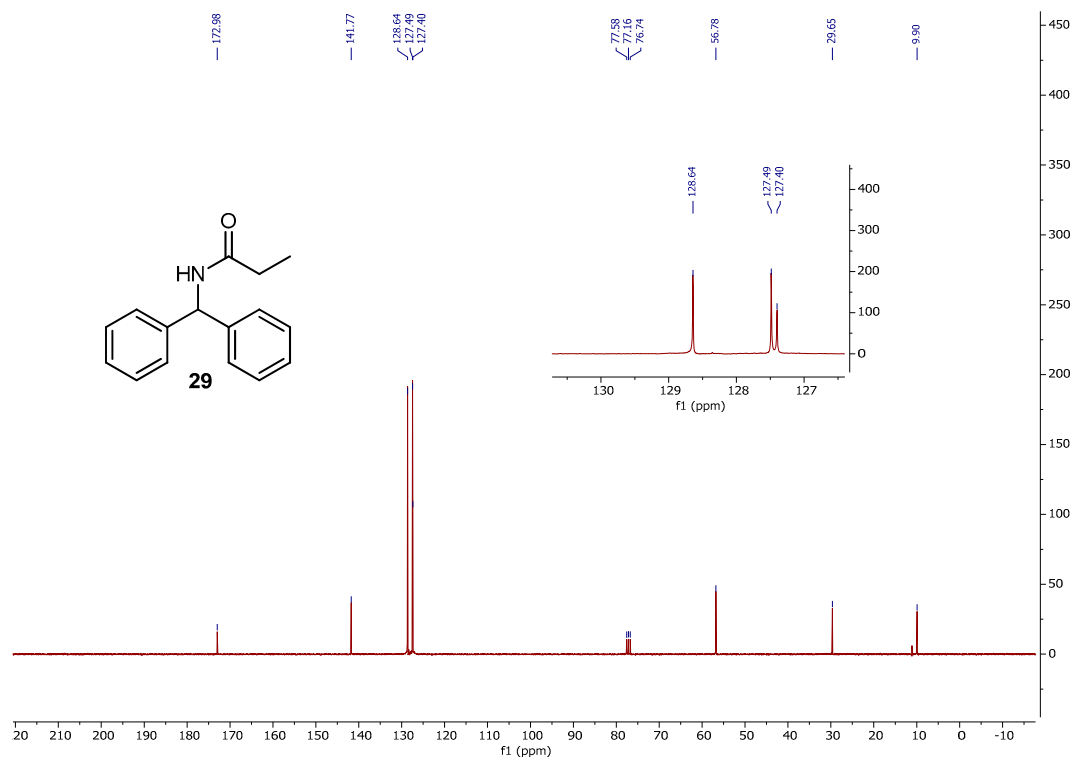
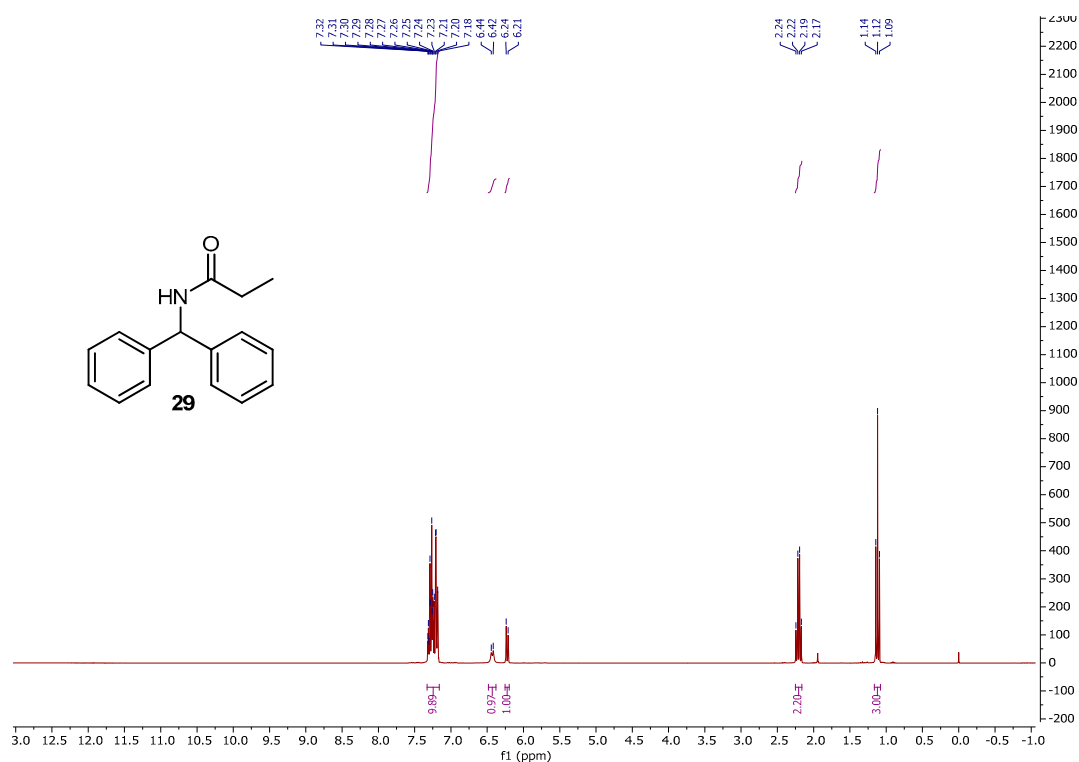


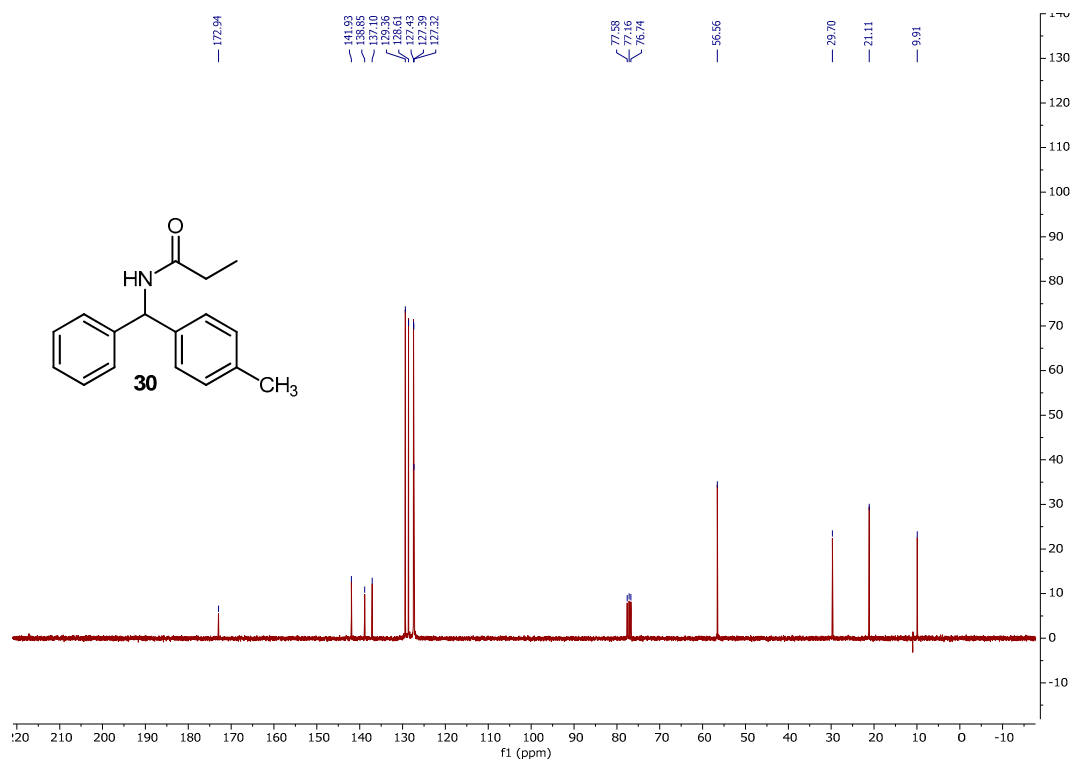
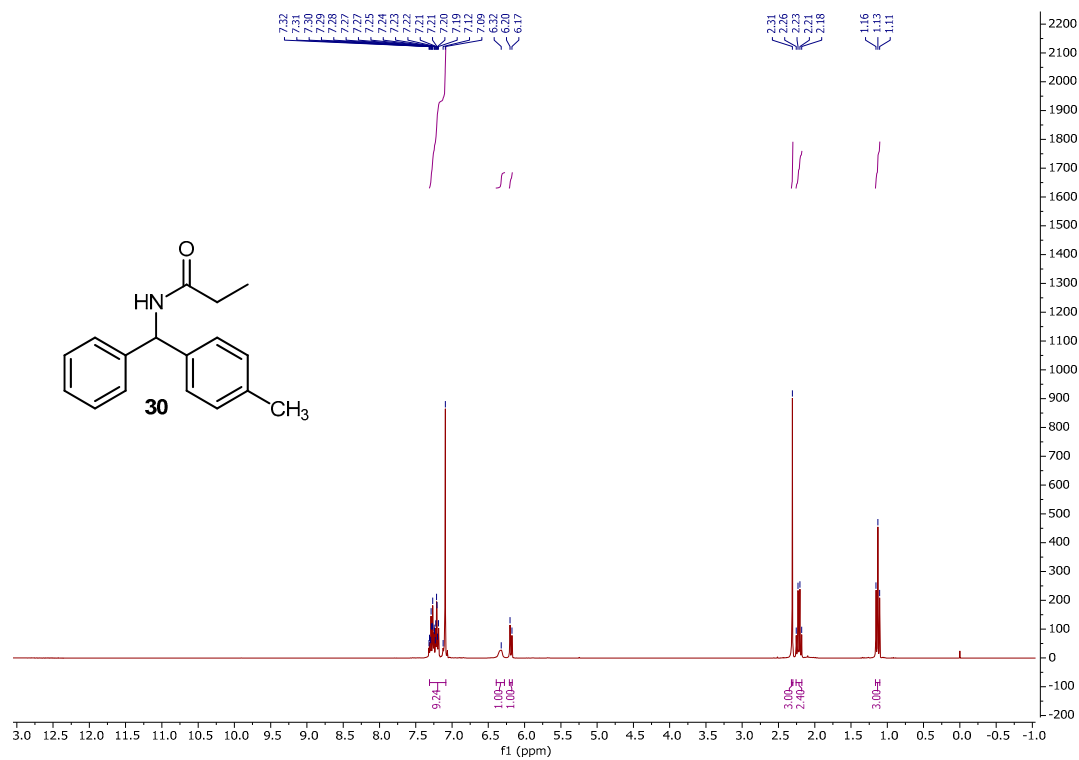


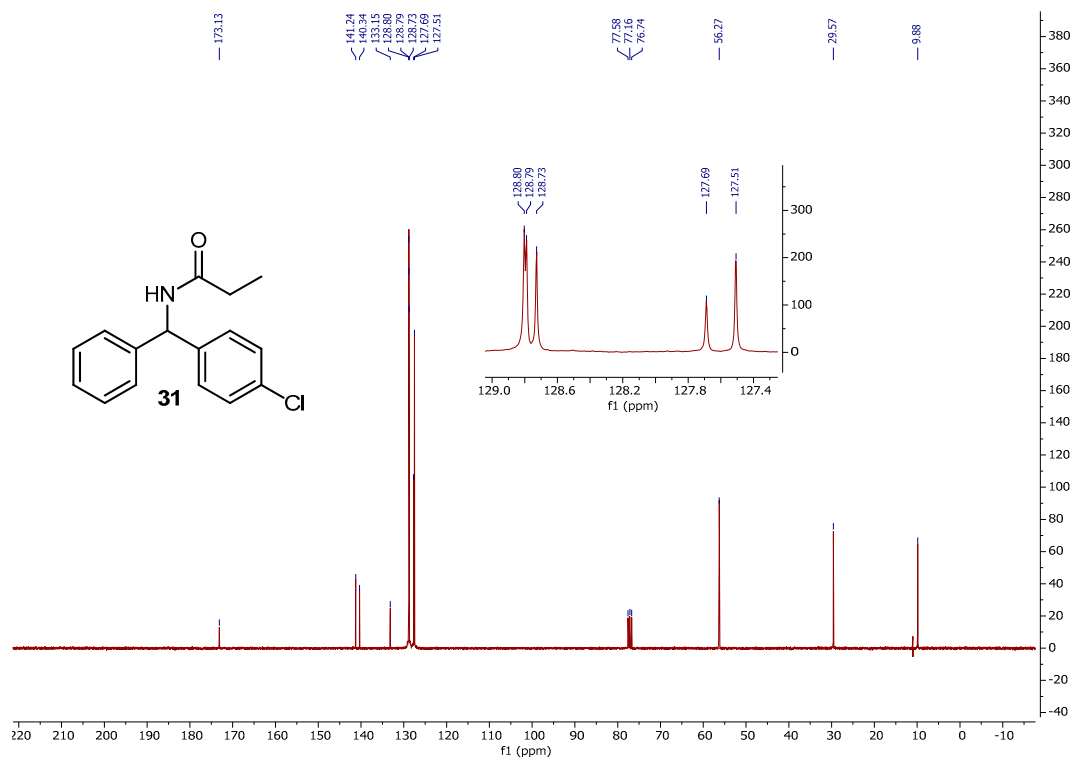
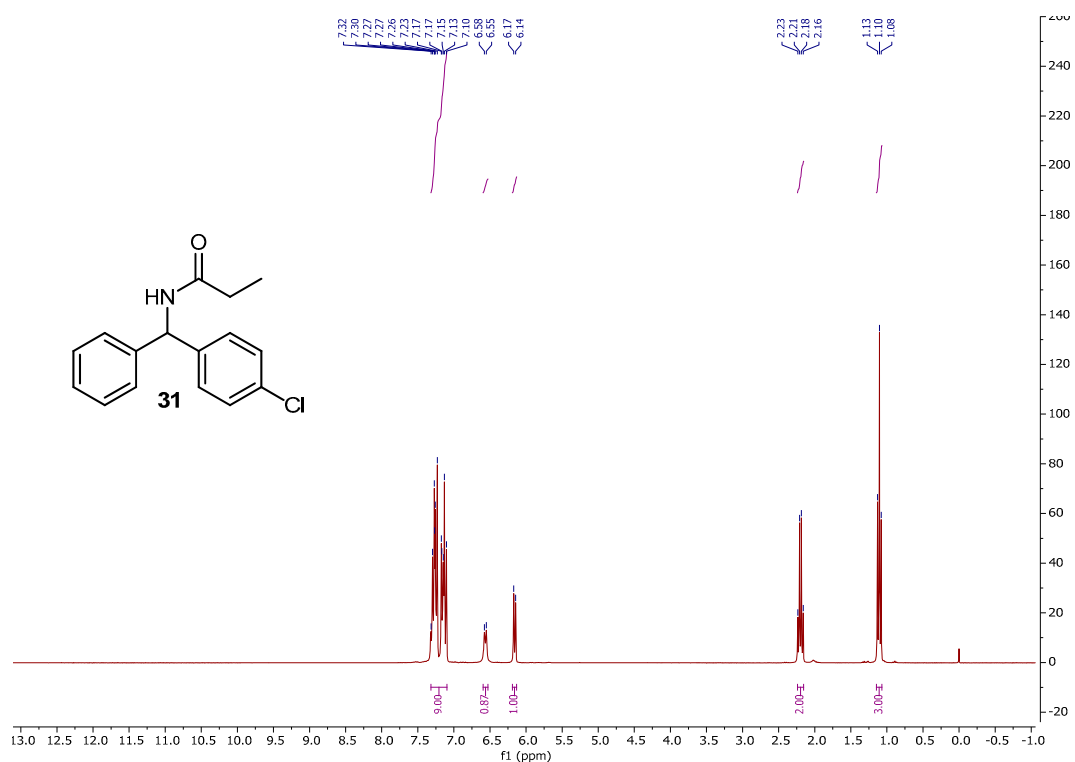


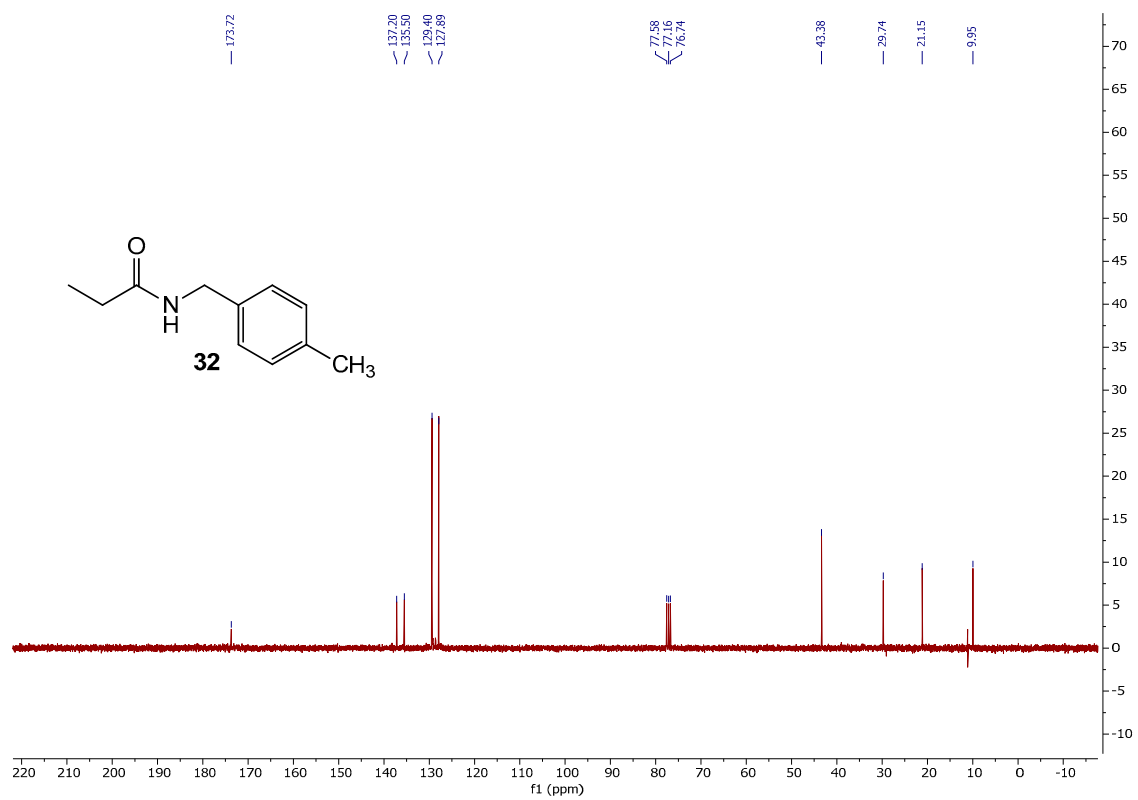
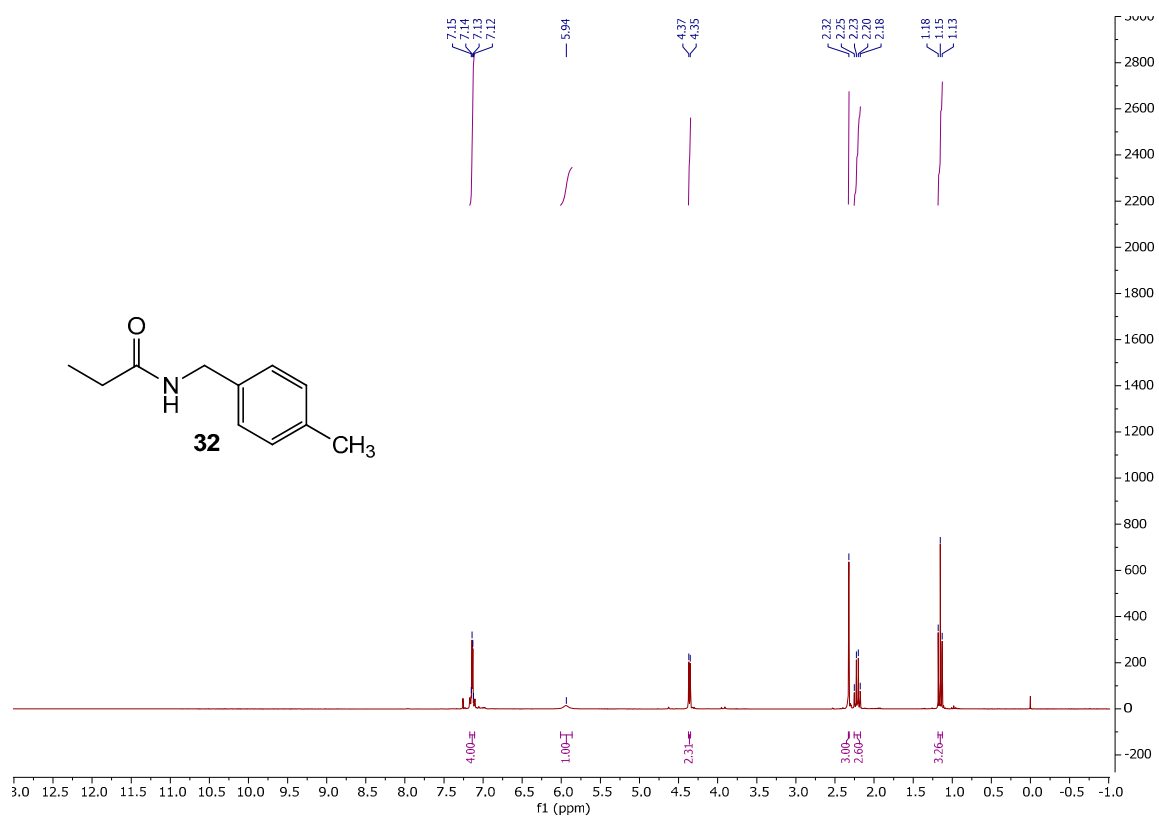


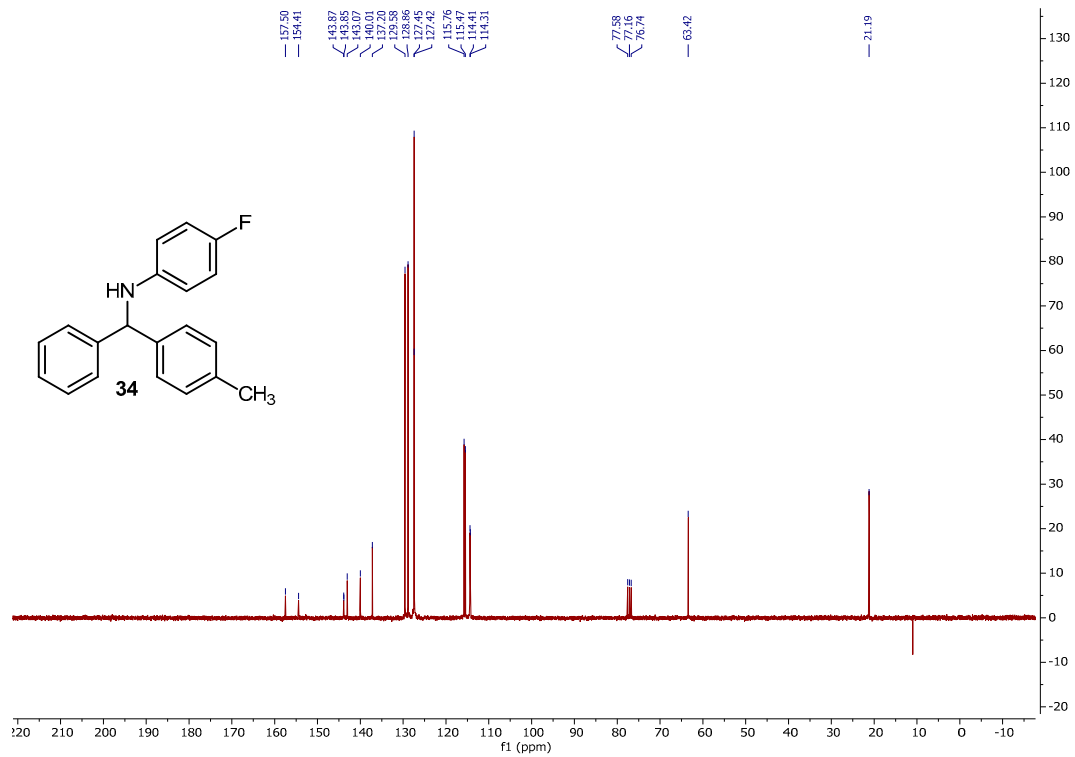
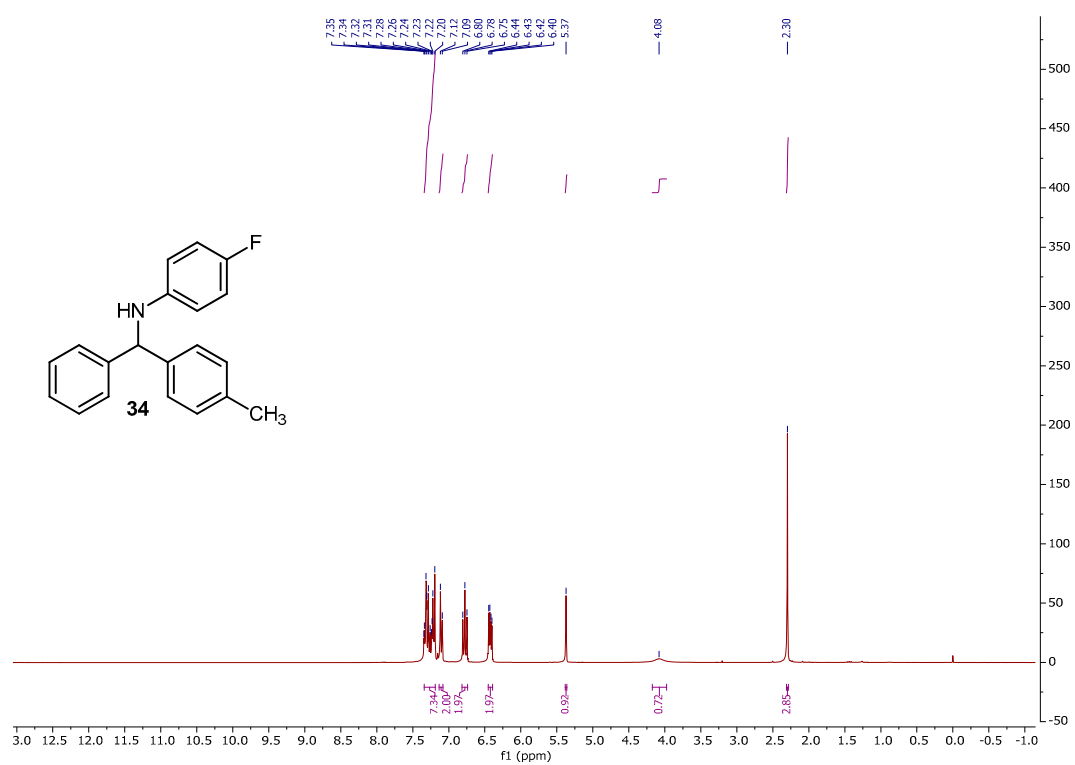


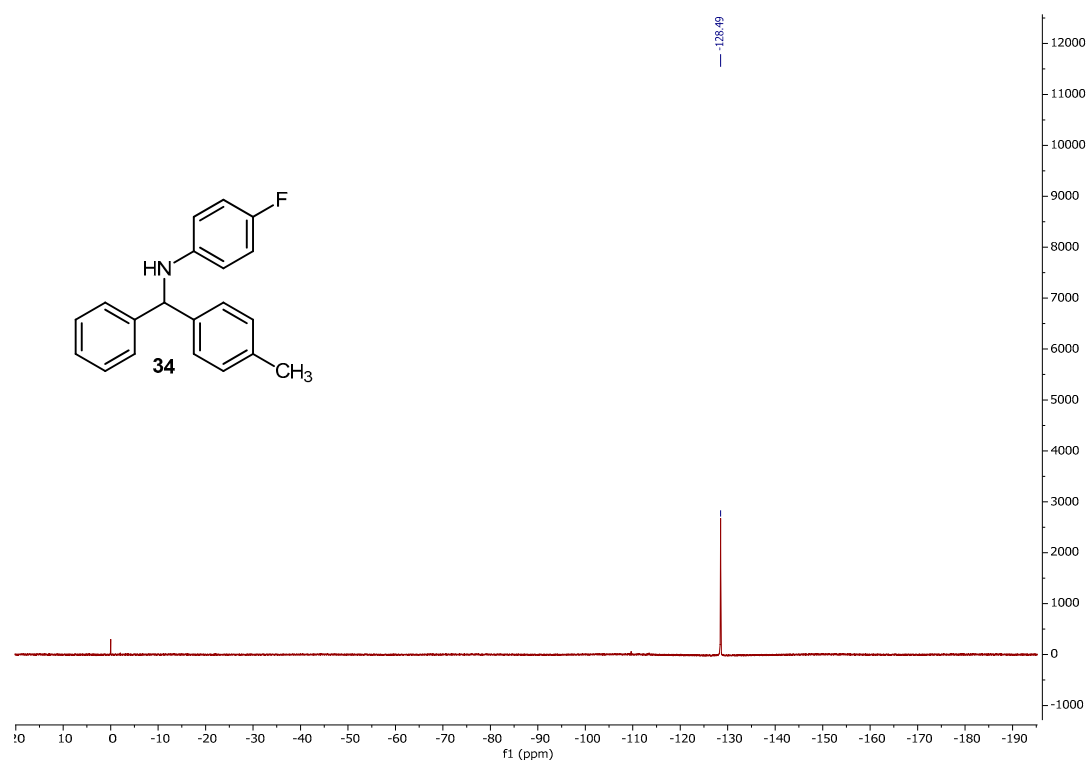












Experimental data related to thermal analysis

Instrument: Modular system for thermal analysis - Mettler Toledo, modules: TGA/SDTA 851, DSC 822

Experimental conditions:

- Temperature range: 25–200 degrees Celsius
- Platinum crucibles
- Heating rate: 10 st/min
- Atmosphere: air with flow rate 50 mL/min

Sample mass ca. 10 mg

