Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information for:

A Modified Beckmann Rearrangement for the Facile Synthesis of Amidines and Imidates via Imidoyl Fluoride Intermediates

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1. General Information

NMR spectra were obtained on a Bruker 400 MHz (400.52 MHz for ^{1}H; 376.87 MHz for ^{19}F; 100.71 MHz for ^{13}C). ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative the residual solvent peak ($CDCl_3$: ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm. ^{19}F NMR spectra are referenced based on the internal standard 4-fluoroanisole. ^{1}H and ^{19}F multiplicities are reported as follows: singlet (s), broad singlet (br), doublet (d), triplet (t), quartet (q), pentet (pent) multiplet (m), sextet (sext), septet (sept), doublet of doublets (dd), doublet of triplets (dt), triplet of doublets (td), doublet of doublet of doublets (ddd), doublet of doublet of triplets (ddt), triplet of quartet of doublets (tqd). Coupling constants (*J*) are reported in Hz.

2. Methods and Materials

All reactions reported herein were performed without the exclusion of moisture or air unless otherwise noted. No dry solvents were used in any reactions for the synthesis of the sulfone iminium fluoride reagent or in the fluorination reactions using SIFs. All chemicals used throughout this work were purchased from commercial sources. The vendors used were: Sigma-Millipore, TCI America, Ambeed, Oakwood Chemical, Alfa Aesar and Acros Organics.

3. Synthesis of sulfone iminium fluoride reagent

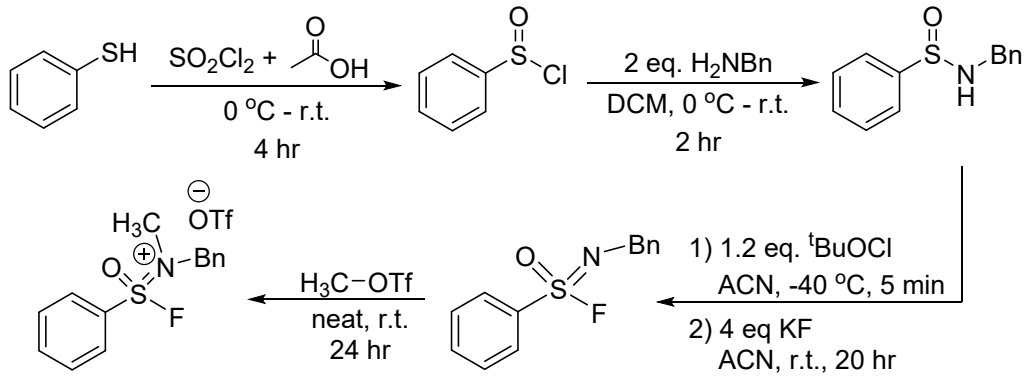


Figure S1. Synthesis of SIF reagent.

The following synthesis is modified from *Org. Lett.* **2022**, *24*, 5962.[1]

To a 100 mL round bottom flask, thiophenol (10.25 mL, 100 mmol) and acetic acid (5.75 mL, 100 mmol) were added with a stir bar and placed in an ice bath. Sulfuryl chloride (17.85 ml, 220 mmol) was added dropwise to the reaction at 0 °C. Vigorous bubbling was observed as well as a color change to orange-red. After the addition was complete, the reaction was stirred at room temperature for 4 hours, during which time bubbling continued. After 4 hours, acetyl chloride and excess sulfuryl chloride were removed under reduced pressure in a bath no higher than 10 °C. The product was isolated as a bright orange liquid and used without further purification.

To a 1000 mL round bottom flask, sulfinyl chloride (16.0 g, 0.10 mol) was added with a stir bar. DCM (400 mL) was added and the flask was placed in an ice bath. Once cooled, benzylamine (21.4 g, 0.20 mol) dissolved in DCM (100 mL) was added slowly to the reaction. An immediate white precipitate appeared along with a change to a colorless solution. The reaction was then stirred at room temperature for 2 hours. At this time, the reaction was filtered through a pad of celite followed by washing with H_2O (300 mL X 2). The organic layer was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to yield a white solid (21.7 g, 94% yield). The sulfinamide product was used in subsequent reactions without any further purification.

To a 250 mL round bottom flask, *N*-benzyl benzenesulfinamide (6.94 g, 30 mmol) was added with acetonitrile (100 mL). The flask was then set in a dry ice / acetonitrile bath (-40 °C) and allowed to cool for 5 minutes. *Tert*-butyl hypochlorite (3.89 g, 36 mmol, 1.2 equivalents) was dissolved in acetonitrile (10 mL) and added to the reaction flask slowly over the course of 10 minutes. The reaction was allowed to slowly warm to room temperature at which time potassium fluoride (6.96 g, 120 mmol, 4 equivalents) was added to the reaction. The reaction was then stirred for 20 hours at room temperature. At this time, the reaction was filtered through a pad of celite and the solvent was removed under reduced pressure. The crude sulfonimidoyl fluoride product was purified by silica gel column chromatography using hexane / ethyl acetate (0% → 20% gradient, 40 g silica gel column) as eluent. Following purification, the *N*-benzyl benzenesulfonimidoyl fluoride was isolated as a pale yellow liquid (5.38 g, 72%).

In a well-ventilated fume hood under normal atmospheric conditions, *N*-benzyl benzenesulfonimidoyl fluoride (3.74 g, 15.0 mmol) was added with a flea stir bar to a 20 mL scintillation vial. Methyl trifluoromethanesulfonate (1.80 mL, 16.5 mmol. 1.1 equivalents) was added to the reaction at room temperature. The reaction was then stirred for 24 hours at room temperature. After this time, the crude reaction mixture was washed with hexane (10 mL, 5 times) in order to remove excess methyl trifluoromethanesulfonate. The sulfone iminium fluoride product (5.89 g, 98%) was then used without further purification.

Handling of SIF Reagent

Once synthesized, the SIF reagent is stored in a freezer at -10 °C for long term stability. For all reactions, the SIF reagent is weighed out in a well-ventilated fume hood where the reaction is then conducted as well.

4. Synthesis of ketoxime substrates

Hydroxylamine hydrochloride (15.0 mmol, 1.5 eq.) was added to a 100 mL round bottom flask followed by ethanol (25 mL) and water (5 mL). Ketone (10.0 mmol, 1.0 eq.) was dissolved in THF (15 mL) and subsequently added to the reaction flask. The homogeneous mixture was stirred at room temperature until the ketone starting material was fully consumed (tracked by GC / MS). *Note*: benzophenone derivatives required heating to 90 °C for any appreciable formation of ketoxime product (labelled with * in figure below). Following the full consumption of starting material, the volatiles were removed under reduced pressure. The crude mixture was extracted into diethyl ether (50 mL) and washed with water (3 X 50 mL). The organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The ketoximes were used without further purification.

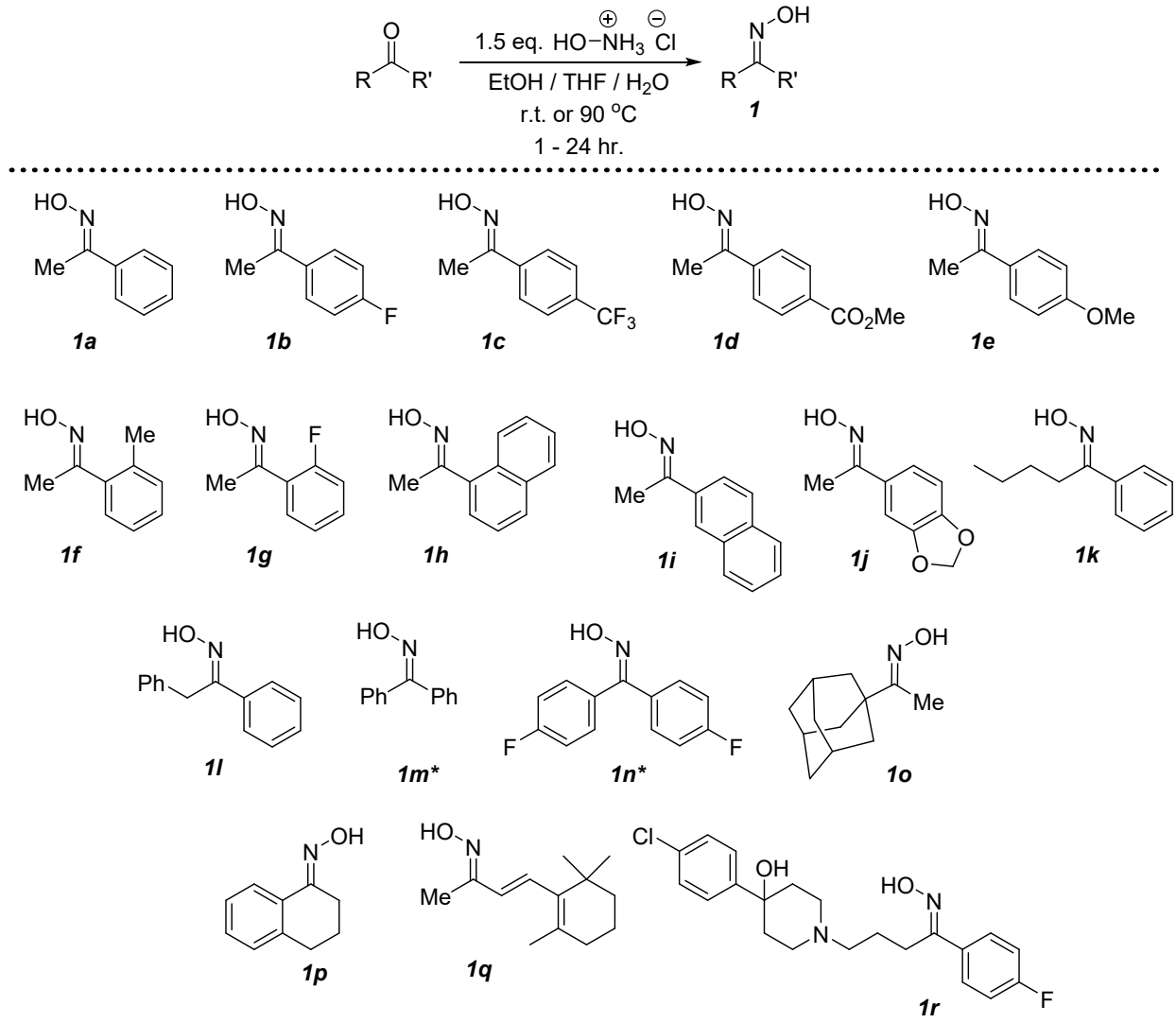


Figure S2. Synthesis of ketoxime substrates.

5. Optimization of imidoyl fluoride formation via SIF reagents

All reactions were performed on the benchtop without the exclusion of air or moisture.

To an 8 mL vial, acetophenone oxime, **1a**, (27.0 mg, 0.2 mmol), base (0.4 mmol, 2.0 eq.) and 4-fluoroanisole (25.2 mg, 0.2 mmol, 1.0 eq.) were added along with the requisite solvent (0.5 mL). SIF reagent (160.0 mg, 0.4 mmol, 2.0 eq.) was dissolved (0.25 mL) and added to the reaction vial at room temperature. The reaction was stirred for 60 seconds when it was transferred to an NMR tube and the yield was determined by ^{19}F NMR by comparison to the internal standard. The results of the optimization of both solvent and base are shown below in Table S1.

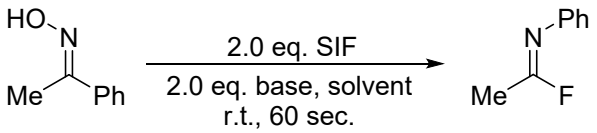


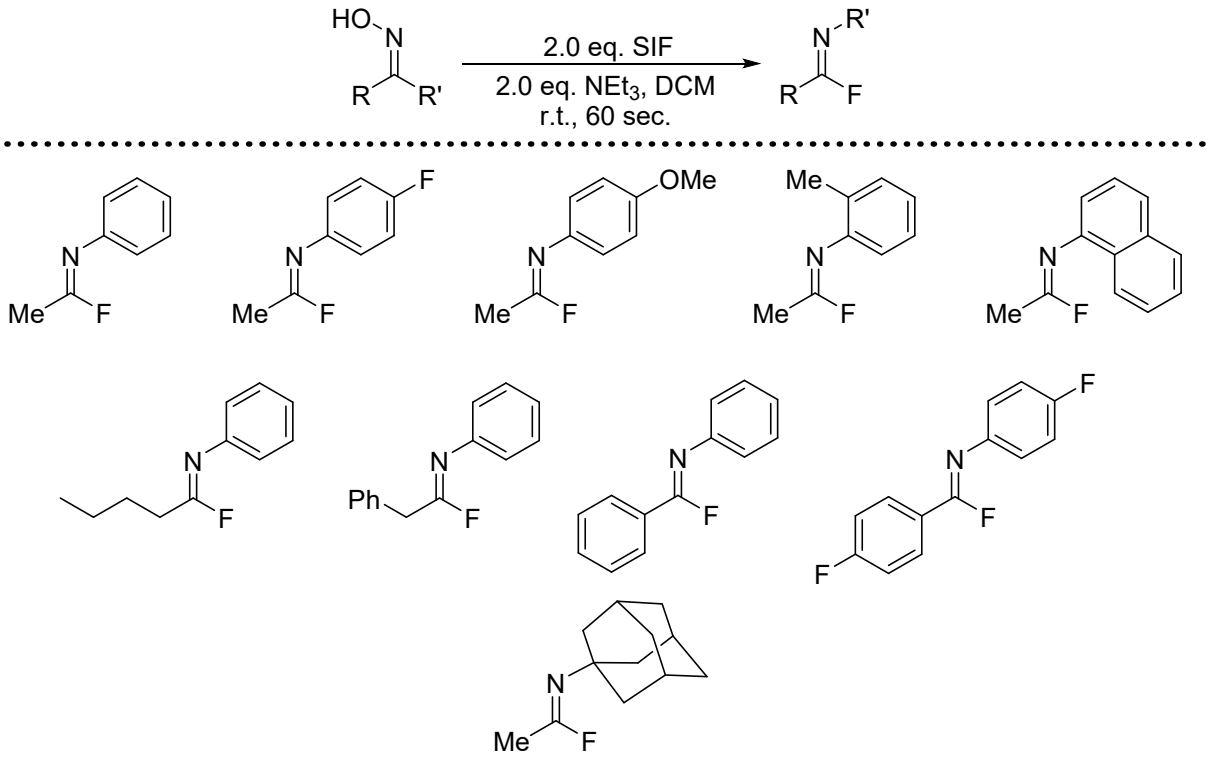
Table S1. Optimization for imidoyl fluoride formation using acetophenone oxime and SIF

Entry	Solvent	Base	^{19}F NMR Yield
1	DCM	DBU	92%
2	DCM	NEt_3	99%
3	DCM	Pyridine	62%
4	DCM	2,6-lutidine	34%
5	Acetonitrile	NEt_3	95%
6	THF	NEt_3	52%
7	Toluene	NEt_3	24%

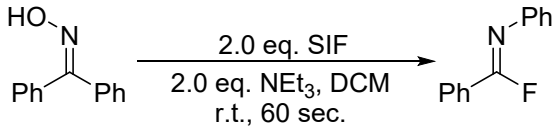
6. Scope of imidoyl fluoride formation from ketoximes

All reactions were performed on the benchtop without the exclusion of air or moisture.

To an 8 mL vial, ketoxime (0.2 mmol), NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) and 4-fluoroanisole (25.2 mg, 0.2 mmol, 1.0 eq.) were added along with DCM (0.5 mL). SIF reagent (160.0 mg, 0.4 mmol, 2.0 eq.) was dissolved (0.25 mL) and added to the reaction vial at room temperature. The reaction was stirred for 60 seconds when it was transferred to an NMR tube and the yield was determined by ^{19}F NMR by comparison to the internal standard. The imidoyl fluorides generated in this process are shown below in Figure S3. All conversions to imidoyl fluoride were >95% by ^{19}F NMR analysis.

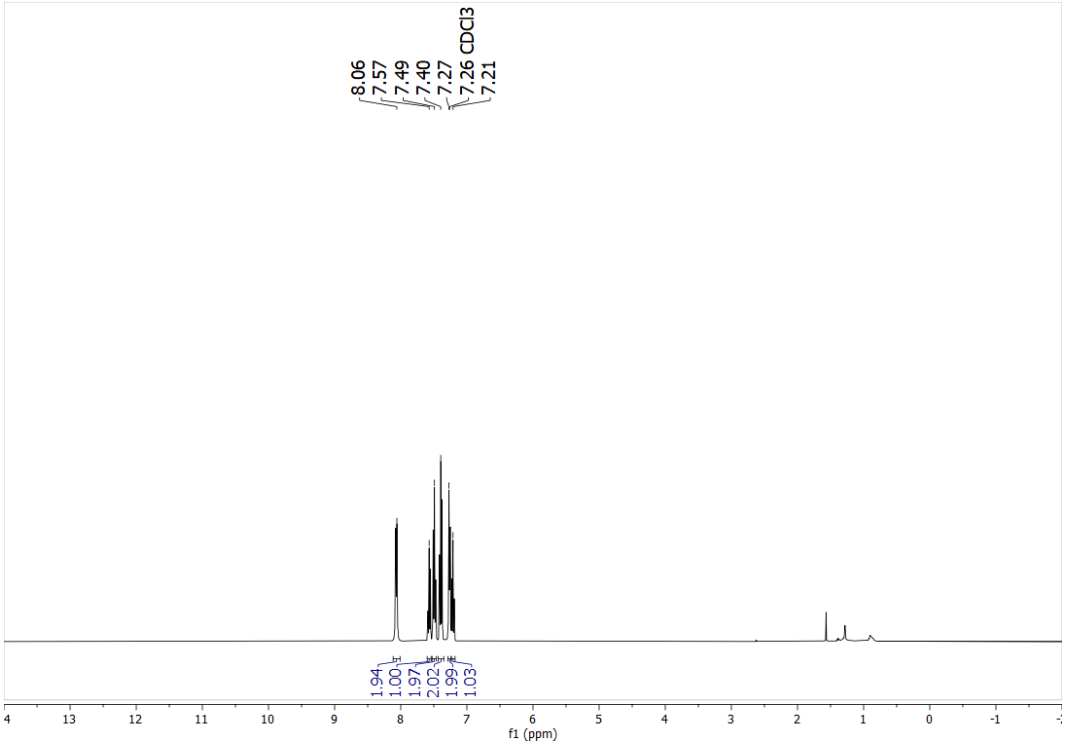


Isolation of imidoyl fluoride derived from benzophenone oxime

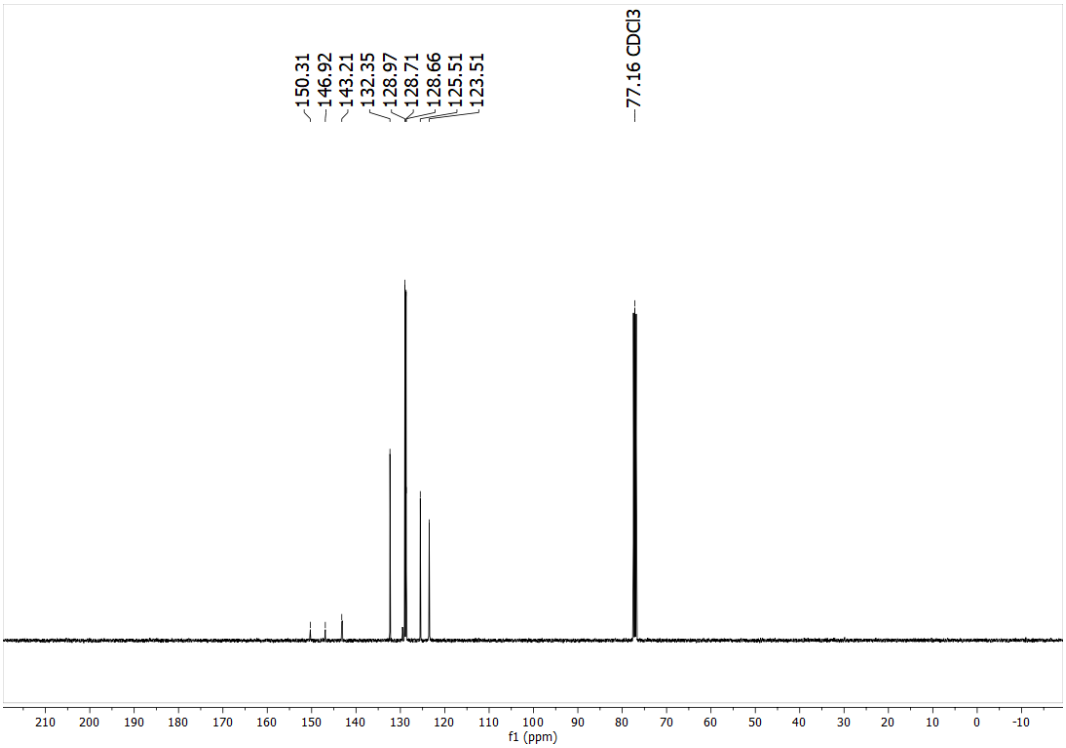


To an 8 mL vial, benzophenone oxime (39.4, 0.2 mmol), NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) and 4-fluoroanisole (25.2 mg, 0.2 mmol, 1.0 eq.) were added along with DCM (0.5 mL). SIF reagent (160.0 mg, 0.4 mmol, 2.0 eq.) was dissolved (0.25 mL) and added to the reaction vial at room temperature. The reaction was stirred for 60 seconds at which time the solvent was removed and the crude mixture was purified via silica gel chromatography (12 g silica gel column), using DCM and ethyl acetate as the eluent (0% → 30% gradient). The spectroscopic data (shown below) were consistent with those previously published in the literature.

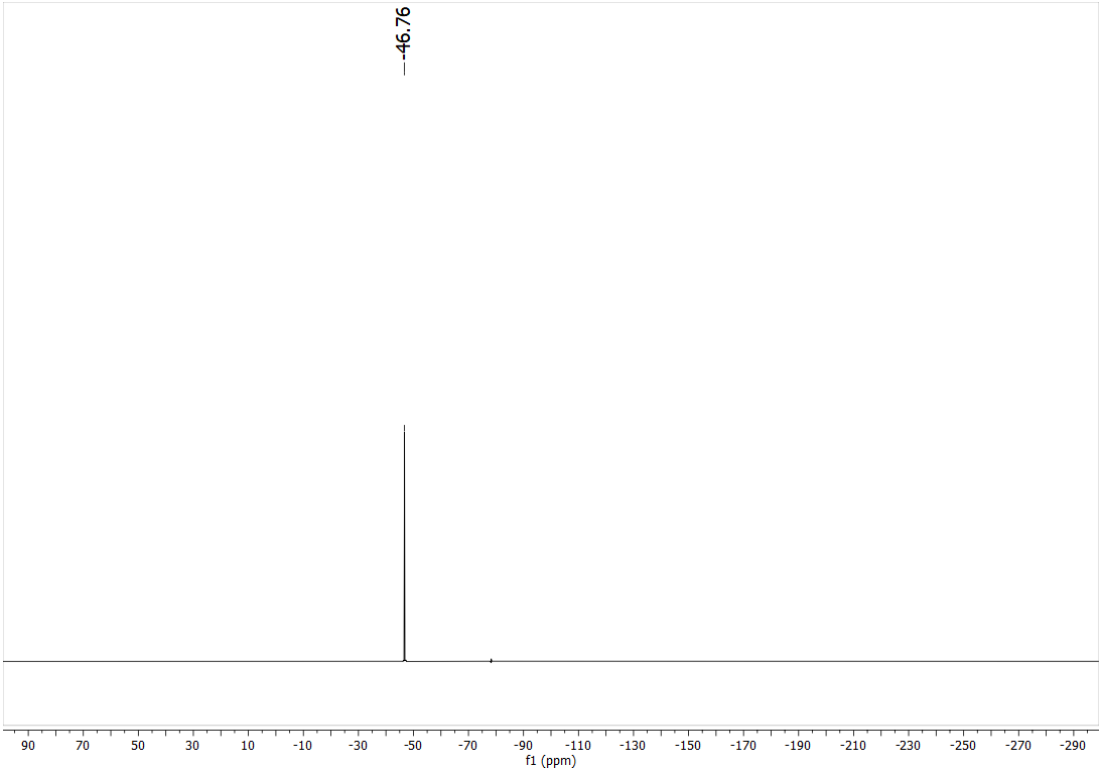
^{1}H NMR: 400 MHz in $CDCl_3$



^{13}C NMR: 101 MHz in $CDCl_3$



^{19}F NMR: 376 MHz in $CDCl_3$



7. Oxime substrate scope for the formation of amidines and imidates

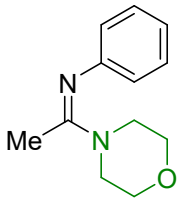
General Procedure A: for amidine synthesis using morpholine

To an 8 mL vial, ketoxime (0.2 mmol) and NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) were added along with DCM (0.5 mL). SIF reagent (160.0 mg, 0.4 mmol, 2.0 eq.) was dissolved (0.25 mL) and added to the reaction vial at room temperature. The reaction was stirred for 60 seconds at which time morpholine (34.8 mg, 0.4 mmol, 2.0 eq.) was added and the reaction was stirred for a further 10 minutes at room temperature. At this time, the solvent was removed under reduced pressure and the crude reaction mixture was purified via silica gel chromatography (12 g silica gel column), using DCM and ethyl acetate as the eluent (0% → 30% gradient).

General Procedure I: for imidate synthesis using 4-methoxyphenol

To an 8 mL vial, ketoxime (0.2 mmol) and NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) were added along with DCM (0.5 mL). SIF reagent (160.0 mg, 0.4 mmol, 2.0 eq.) was dissolved (0.25 mL) and added to the reaction vial at room temperature. The reaction was stirred for 60 seconds at which time 4-methoxyphenol (49.6 mg, 0.4 mmol, 2.0 eq.) and NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) were added and the reaction was stirred for a further 24 hours at room temperature. At this time, the solvent was removed under reduced pressure and the crude reaction mixture was purified via silica gel chromatography (12 g silica gel column), using hexane and ethyl acetate as the eluent (0% → 10% gradient).

(Z)-1-morpholino-N-phenylethanimine (2a-a)

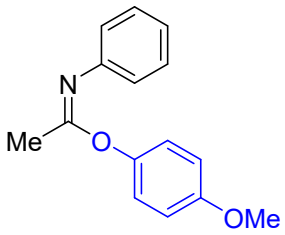


The reaction was performed using *General Procedure A* above with acetophenone oxime (27.0 mg, 0.2 mmol). Following silica gel chromatography, product **2a-a** was isolated as a white solid (38.0 mg, 93%). The isolated yield reported in the manuscript is the average of two runs (93% and 91% yield). The spectroscopic data were consistent with those previously published in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): 7.27 (t, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 2H), 3.77 (t, *J* = 4.9 Hz, 4H), 3.52 (t, *J* = 4.8 Hz, 4H), 1.87 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.1, 151.6, 128.9, 122.1, 121.9, 66.9, 45.4, 14.7 ppm.

4-methoxyphenyl (Z)-N-phenylacetimidate (2a-i)

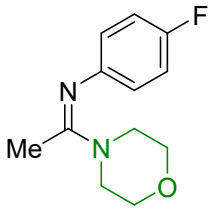


The reaction was performed using *General Procedure I* above with acetophenone oxime (27.0 mg, 0.2 mmol). Following silica gel chromatography, product **2a-i** was isolated as a white solid (43.4 mg, 90%). The isolated yield reported in the manuscript is the average of two runs (90% and 90% yield). The spectroscopic data were consistent with those previously published in the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$): 7.25 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 3H), 2.03 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.7, 156.8, 148.7, 146.4, 129.0, 123.2, 123.0, 121.0, 114.5, 55.7, 16.3 ppm.

(Z)-1-morpholino-N-(4-fluorophenyl)ethanimine (2b-a)



The reaction was performed using *General Procedure A* above with 4-fluoroacetophenone oxime (30.6 mg, 0.2 mmol). Following silica gel chromatography, product **2b-a** was isolated as a colorless oil (40.9 mg, 92%). The isolated yield reported in the manuscript is the average of two runs (92% and 89% yield).

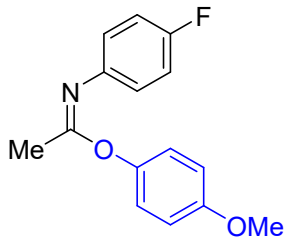
^{1}H NMR (400 MHz, $CDCl_3$): 6.93 (t, *J* = 8.7 Hz, 2H), 6.62 (m, 2H), 3.74 (t, *J* = 4.9 Hz, 4H), 3.48 (t, *J* = 4.8 Hz, 4H), 1.83 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 159.9, 157.6 (d), 147.7, 123.0 (d), 115.6 (d), 66.9, 45.4, 14.6 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -123.4 (m) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{12}H_{16}FN_2O$: 223.1246; found 223.1243

4-methoxyphenyl (Z)-N-(4-fluorophenyl)acetimidate (2b-i)



The reaction was performed using *General Procedure I* above with 4-fluoroacetophenone oxime (30.6 mg, 0.2 mmol). Following silica gel chromatography, product **2b-i** was isolated as a colorless oil (43.0 mg, 83%). The isolated yield reported in the manuscript is the average of two runs (83% and 77% yield).

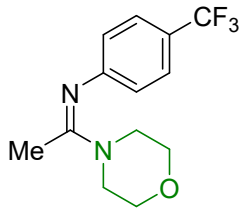
^{1}H NMR (400 MHz, $CDCl_3$): 7.01 (d, J = 9.0 Hz, 2H), 6.87 (t, J = 8.6 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 6.60 (m, 2H), 3.72 (s, 3H), 1.95 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 162.3, 160.5, 156.9, 146.3, 144.8, 128.6 (d), 122.9, 122.1 (d), 115.7 (d), 114.5, 55.7, 16.3 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -121.4 (m) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{15}FNO_2$: 260.1086; found 260.1086

(Z)-1-morpholino-N-(4-trifluoromethylphenyl)ethanimine (2c-a)



The reaction was performed using *General Procedure A* above with 4-trifluoromethylacetophenone oxime (40.6 mg, 0.2 mmol). Following silica gel chromatography, product **2c-a** was isolated as a colorless oil (52.3 mg, 96%). The isolated yield reported in the manuscript is the average of two runs (96% and 94% yield).

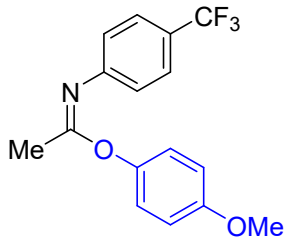
^{1}H NMR (400 MHz, $CDCl_3$): 7.47 (d, J = 8.2 Hz, 2H), 6.77 (d, J = 8.2 Hz, 2H), 3.75 (t, J = 4.8 Hz, 4H), 3.51 (t, J = 4.8 Hz, 4H), 1.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 156.9, 155.0, 126.2 (q), 124.0 (d), 123.5, 122.2, 66.8, 45.3, 14.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -61.5 (s) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{13}H_{16}F_3N_2O$: 273.1214; found 273.1211

4-methoxyphenyl (Z)-N-(4-trifluoromethylphenyl)acetimidate (2c-i)



The reaction was performed using *General Procedure I* above with 4-trifluoromethylacetophenone oxime (40.6 mg, 0.2 mmol). Following silica gel chromatography, product **2c-i** was isolated as a colorless oil (50.7 mg, 82%). The isolated yield reported in the manuscript is the average of two runs (82% and 81% yield).

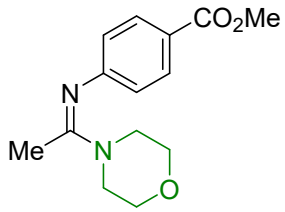
^{1}H NMR (400 MHz, $CDCl_3$): 7.50 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 3.80 (s, 3H), 2.04 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 162.1, 157.0, 151.9, 146.1, 126.3 (q), 125.9, 123.2, 122.9, 121.1, 114.6, 55.7, 16.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -61.8 (s) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{15}F_3NO_2$: 310.1054; found 310.1052

methyl (Z)-4-((1-morpholinoethylidene)amino)benzoate (2d-a)



The reaction was performed using *General Procedure A* above with methyl 4-acetylbenzoate oxime (38.6 mg, 0.2 mmol). Following silica gel chromatography, product **2d-a** was isolated as a white solid (44.1 mg, 84%). The isolated yield reported in the manuscript is the average of two runs (84% and 79% yield).

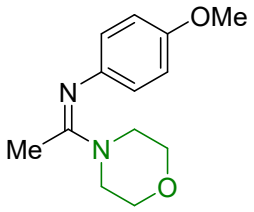
^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.1 Hz, 2H), 3.87 (s, 3H), 3.74 (t, *J* = 4.8 Hz, 4H), 3.51 (t, *J* = 4.8 Hz, 4H), 1.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 167.1, 156.2, 156.1, 130.5, 123.2, 121.6, 66.5, 51.6, 45.0, 14.6 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{14}H_{19}N_2O_3$: 263.1395; found 263.1395

Melting Point: 76 – 77 °C

(Z)-1-morpholino-N-(4-methoxyphenyl)ethanimine (2e-a)



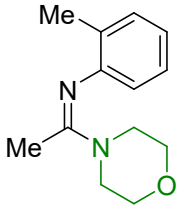
The reaction was performed using *General Procedure A* above with 4-methoxyacetophenone oxime (33.0 mg, 0.2 mmol). Following silica gel chromatography, product **2e-a** was isolated as a colorless oil (40.7 mg, 87%). The isolated yield reported in the manuscript is the average of two runs (87% and 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 6.80 (d, J = 8.9 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H), 3.77 (s, 3H), 3.74 (t, J = 4.8 Hz, 4H), 3.48 (t, J = 4.8 Hz, 4H), 1.84 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.7, 155.0, 144.8, 122.8, 114.3, 66.9, 55.6, 45.5, 14.6 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{13}H_{19}N_2O_2$: 235.1446; found 235.1447

(Z)-1-morpholino-N-(o-tolyl)ethanimine (2f-a)



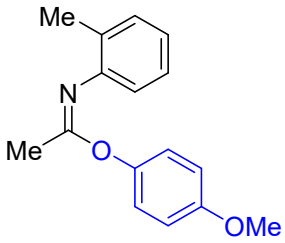
The reaction was performed using *General Procedure A* above with 2-methylacetophenone oxime (30.0 mg, 0.2 mmol). Following silica gel chromatography, product **2f-a** was isolated as a colorless oil (39.7 mg, 91%). The isolated yield reported in the manuscript is the average of two runs (91% and 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.20 (d, J = 7.4 Hz, 1H), 7.16 (t, J = 5.8 Hz, 1H), 7.09 (t, J = 6.0 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 3.81 (t, J = 4.9 Hz, 4H), 3.66 (t, J = 4.8 Hz, 4H), 2.15 (s, 3H), 1.94 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 160.1, 157.9, 132.4, 130.9, 127.0, 125.9, 124.7, 66.4, 46.8, 18.0, 15.5 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{13}H_{19}N_2O$: 219.1497; found 219.1496

4-methoxyphenyl (Z)-N-(o-tolyl)acetimidate (2f-i)



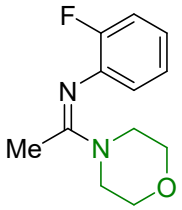
The reaction was performed using *General Procedure I* above with 2-methylacetophenone oxime (30.0 mg, 0.2 mmol). Following silica gel chromatography, product **2f-i** was isolated as a colorless oil (47.0 mg, 92%). The isolated yield reported in the manuscript is the average of two runs (92% and 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.08 – 7.14 (m, 4H), 6.90 – 6.95 (m, 3H), 6.63 (d, J = 7.5 Hz, 1H), 3.80 (s, 3H), 2.08 (s, 3H), 1.98 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.0, 156.8, 147.2, 146.5, 130.3, 128.7, 126.4, 123.2, 123.0, 120.2, 114.5, 55.6, 18.0, 16.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{18}NO_2$: 256.1337; found 256.1335

(Z)-1-morpholino-N-(2-fluorophenyl)ethanimine (2g-a)



The reaction was performed using *General Procedure A* above with 2-fluoroacetophenone oxime (30.6 mg, 0.2 mmol). Following silica gel chromatography, product **2g-a** was isolated as a colorless oil (40.9 mg, 92%). The isolated yield reported in the manuscript is the average of two runs (92% and 89% yield).

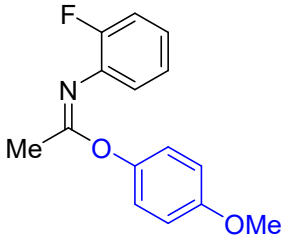
^{1}H NMR (400 MHz, $CDCl_3$): 6.99 – 7.04 (m, 2H), 6.88 – 6.94 (m, 1H), 6.80 (t, J = 8.3 Hz, 1H), 3.75 (t, J = 4.8 Hz, 4H), 3.55 (t, J = 4.8 Hz, 4H), 1.84 (d, J = 1.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 158.7, 155.5, 153.1, 139.2 (d), 124.9 (d), 124.3 (d), 122.8 (d), 115.9 (d), 66.8, 45.4, 15.1 (d) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -127.5 (m) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{12}H_{16}FN_2O$: 223.1246; found 223.1246

4-methoxyphenyl (Z)-N-(2-fluorophenyl)acetimidate (2g-i)



The reaction was performed using *General Procedure I* above with 2-fluoroacetophenone oxime (30.6 mg, 0.2 mmol). Following silica gel chromatography, product **2g-i** was isolated as a colorless oil (46.1 mg, 89%). The isolated yield reported in the manuscript is the average of two runs 89 and 84% yield).

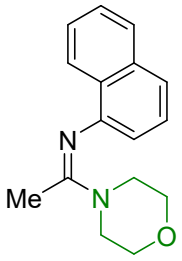
^{1}H NMR (400 MHz, $CDCl_3$): 7.13 (d, *J* = 8.9 Hz, 2H), 6.95 – 7.04 (m, 3H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.79 (t, *J* = 8.3 Hz, 1H), 3.79 (s, 3H), 2.04 (d, *J* = 1.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 163.7, 156.9, 154.6, 152.2, 146.3, 136.2 (d), 128.7 (d), 124.3 (d), 124.2, 123.6 (d), 122.9 (d), 115.8, 114.5, 55.7, 16.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -127.53 (m) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{15}FNO_2$: 260.1086; found 260.1087

(Z)-1-morpholino-N-(1-naphthyl)ethanimine (2h-a)



The reaction was performed using *General Procedure A* above with 1-acetonaphthone oxime (37.0 mg, 0.2 mmol). Following silica gel chromatography, product **2h-a** was isolated as a white solid (48.3 mg, 95%). The isolated yield reported in the manuscript is the average of two runs (95% and 94% yield).

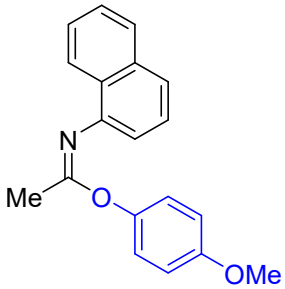
^{1}H NMR (400 MHz, $CDCl_3$): 7.86 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.45 (m, 3H), 6.74 (d, *J* = 8.4 Hz, 1H), 3.82 (t, *J* = 4.8 Hz, 4H), 3.63 (t, *J* = 4.7 Hz, 4H), 1.81 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.7, 148.3, 134.8, 128.7, 128.3, 126.5, 126.2, 125.3, 124.3, 122.2, 116.5, 67.3, 45.9, 15.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{19}N_2O$: 255.1497; found 255.1494

Melting Point: 90 – 91 °C

4-methoxyphenyl (Z)-N-(1-naphthyl)acetimidate (2h-i)



The reaction was performed using *General Procedure I* above with 1-acetonaphthone oxime (37.0 mg, 0.2 mmol). Following silica gel chromatography, product **2h-i** was isolated as a white solid (48.4 mg, 83%). The isolated yield reported in the manuscript is the average of two runs (83% and 80% yield).

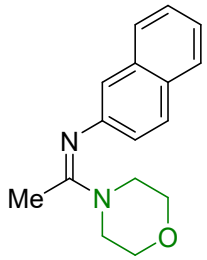
^{1}H NMR (400 MHz, $CDCl_3$): 7.75 – 7.81 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.48 (m, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 3H), 2.02 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 162.1, 156.9, 146.6, 144.9, 134.3, 128.0, 127.3, 126.1, 126.0, 125.5, 123.5, 123.3, 123.0, 115.4, 114.6, 55.7, 16.4 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{19}H_{18}NO_2$: 292.1337; found 292.1334

Melting Point: 86 – 88 °C

(Z)-1-morpholino-N-(2-naphthyl)ethanimine (2i-a)



The reaction was performed using *General Procedure A* above with 2-acetonaphthalene oxime (37.0 mg, 0.2 mmol). Following silica gel chromatography, product **2i-a** was isolated as a white solid (46.3 mg, 91%). The isolated yield reported in the manuscript is the average of two runs (91% and 86% yield).

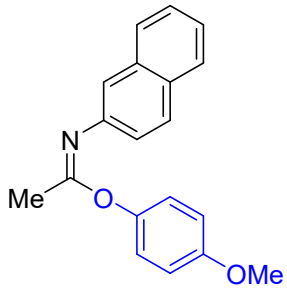
^{1}H NMR (400 MHz, $CDCl_3$): 7.69 – 7.76 (m, 2H), 7.41 (t, *J* = 6.4 Hz, 1H), 7.33 (t, *J* = 6.3 Hz, 1H), 7.08 (s, 1H), 6.97 (dd, *J* = 6.5, 1.1 Hz, 1H), 3.78 (t, *J* = 4.8 Hz, 4H), 3.54 (t, *J* = 4.7 Hz, 4H), 1.89 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.2, 149.4, 134.6, 129.9, 128.6, 127.7, 126.9, 126.0, 123.8, 123.7, 117.4, 66.9, 45.4, 14.8 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{19}N_2O$: 255.1497; found 255.1495

Melting Point: 88 – 90 °C

4-methoxyphenyl (Z)-N-(2-naphthyl)acetimidate (2i-i)



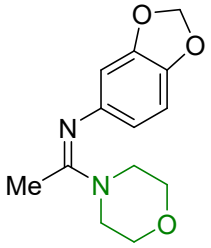
The reaction was performed using *General Procedure I* above with 2-acetonaphthalene oxime (37.0 mg, 0.2 mmol). Following silica gel chromatography, product **2i-i** was isolated as a colorless oil (49.6 mg, 85%). The isolated yield reported in the manuscript is the average of two runs (85% and 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.72 – 7.79 (m, 3H), 7.44 (t, *J* = 6.4 Hz, 1H), 7.37 (t, *J* = 6.3 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.13 (s, 1H), 6.93 – 6.98 (m, 3H), 3.81 (s, 3H), 2.08 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 162.0, 156.8, 146.4, 146.3, 134.2, 130.4, 128.8, 127.8, 127.2, 126.3, 124.4, 123.0, 122.1, 116.8, 114.5, 55.6, 16.4 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{19}H_{18}NO_2$: 292.1337; found 292.1337

(Z)-1-morpholino-N-(benzo[d][1,3]dioxol-5-yl)ethanimine (2j-a)



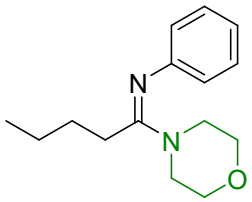
The reaction was performed using *General Procedure A* above with 3,4-methylenedioxyacetophenone oxime (35.8 mg, 0.2 mmol). Following silica gel chromatography, product **2j-a** was isolated as a colorless oil (43.7 mg, 88%). The isolated yield reported in the manuscript is the average of two runs (88% and 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 6.68 (d, *J* = 8.1 Hz, 1H), 6.26 (d, *J* = 2.1 Hz, 1H), 6.12 (dd, *J* = 6.0, 2.0 Hz, 1H), 5.90 (s, 2H), 3.73 (t, *J* = 4.8 Hz, 4H), 3.46 (t, *J* = 4.8 Hz, 4H), 1.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.8, 147.9, 146.4, 142.6, 113.9, 108.2, 103.7, 100.9, 66.9, 45.4, 14.6 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{13}H_{17}N_2O_3$: 248.1161; found 248.1160

(Z)-1-morpholino-N-phenylpentanimine (2k-a)



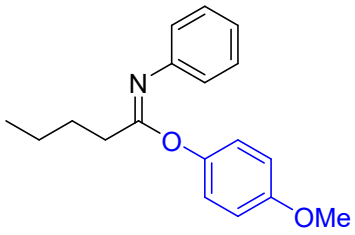
The reaction was performed using *General Procedure A* above with 1-phenylpentan-1-one oxime (35.4 mg, 0.2 mmol). Following silica gel chromatography, product **2k-a** was isolated as a colorless oil (45.3 mg, 92%). The isolated yield reported in the manuscript is the average of two runs (92% and 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.26 (t, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 2H), 3.77 (t, *J* = 4.8 Hz, 4H), 3.49 (t, *J* = 4.7 Hz, 4H), 2.24 (m, 2H), 1.44 (m, 2H), 1.22 (sext, *J* = 7.4 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 160.5, 151.5, 128.9, 122.0, 121.8, 67.0, 45.6, 30.0, 26.9, 22.7, 13.7 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{23}N_2O$: 247.1810; found 247.1809

4-methoxyphenyl (Z)-N-phenylpentanimidate (2k-i)



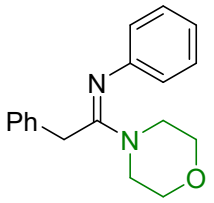
The reaction was performed using *General Procedure I* above with 1-phenylpentan-1-one oxime (35.4 mg, 0.2 mmol). Following silica gel chromatography, product **2k-i** was isolated as a colorless oil (50.0 mg, 88%). The isolated yield reported in the manuscript is the average of two runs (88% and 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.25 (t, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 9.0 Hz, 2H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 3H), 2.34 (t, *J* = 7.3 Hz, 2H), 1.69 (pent, *J* = 7.2 Hz, 2H), 1.35 (sext, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 164.2, 156.7, 148.4, 146.6, 128.9, 123.0, 122.9, 121.0, 114.5, 55.7, 29.5, 28.7, 22.5, 13.9 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{18}H_{22}NO_2$: 284.1650; found 284.1648

(Z)-1-morpholino-(N-phenyl)-2-phenylethanimine (2l-a)



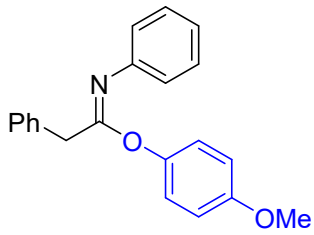
The reaction was performed using *General Procedure A* above with 1,2-diphenylethan-1-one oxime (42.2 mg, 0.2 mmol). Following silica gel chromatography, product **2l-a** was isolated as a colorless oil (53.3 mg, 95%). The isolated yield reported in the manuscript is the average of two runs (95% and 92% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.31 (t, *J* = 7.7 Hz, 2H), 7.16 – 7.24 (m, 5H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 2H), 3.71 (s, 2H), 3.59 (t, *J* = 4.8 Hz, 4H), 3.46 (t, *J* = 4.7 Hz, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.1, 151.2, 136.4, 129.0, 128.8, 127.9, 126.6, 122.1, 121.8, 66.8, 45.4, 33.7 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{18}H_{21}N_2O$: 281.1653; found 281.1651

4-methoxyphenyl (Z)-(N-phenyl)2-phenylacetimidate (2l-i)



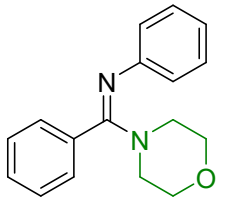
The reaction was performed using *General Procedure I* above with 1,2-diphenylethan-1-one oxime (42.2 mg, 0.2 mmol). Following silica gel chromatography, product **2l-i** was isolated as a colorless oil (57.8 mg, 91%). The isolated yield reported in the manuscript is the average of two runs (91% and 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.22 (t, *J* = 7.6 Hz, 2H), 7.16 – 7.20 (m, 5H), 6.97 (d, *J* = 9.0 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 3H), 3.61 (s, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.8, 156.8, 148.1, 146.5, 135.7, 129.1, 129.0, 128.7, 126.9, 123.3, 122.8, 121.2, 114.5, 55.6, 36.2 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{21}H_{20}NO_2$: 318.1494; found 318.1495

(Z)-1-morpholino-N,1-diphenylmethanimine (2m-a)



The reaction was performed using a modified version of *General Procedure A* above with benzophenone oxime (39.4 mg, 0.2 mmol). The reaction was allowed to stir for 24 hours at room temperature, instead of the usual 10 minutes. Following silica gel chromatography, product **2m-a** was isolated as a white solid (39.4 mg, 74%). The isolated yield reported in the manuscript is the average of two runs (74% and 70% yield).

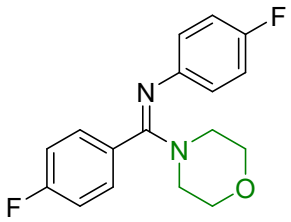
^{1}H NMR (400 MHz, $CDCl_3$): 7.20 – 7.26 (m, 3H), 7.10 – 7.15 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 7.4 Hz, 2H), 3.75 (t, *J* = 2.3 Hz, 4H), 3.42 (br, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 160.9, 150.6, 133.0, 129.2, 128.9, 128.4, 128.3, 122.9, 121.5, 66.9, 46.8 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{19}N_2O$: 267.1497; found 267.1495

Melting Point: 99 – 100 °C

(Z)-N,1-bis(4-fluorophenyl)-1-morpholinomethanimine (2n-a)



The reaction was performed using a modified version of *General Procedure A* above with 4,4'-difluorobenzophenone oxime (46.6 mg, 0.2 mmol). The reaction was allowed to stir for 24 hours at room temperature, instead of the usual 10 minutes. Following silica gel chromatography, product **2n-a** was isolated as a white solid (49.0 mg, 81%). The isolated yield reported in the manuscript is the average of two runs (81% and 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.06 (dd, *J* = 3.2, 3.1 Hz, 2H), 6.94 (t, *J* = 8.6 Hz, 2H), 6.71 (t, *J* = 8.6 Hz, 2H), 6.45 (dd, *J* = 3.5, 3.2 Hz, 2H), 3.73 (t, *J* = 2.4 Hz, 4H), 3.38 (br, 4H) ppm.

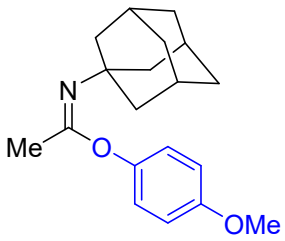
^{13}C NMR (101 MHz, $CDCl_3$): 164.0, 161.5, 160.3, 159.4, 157.0, 146.8 (d), 131.0 (d), 128.9 (d), 123.6 (d), 115.8 (d), 115.1 (d), 66.8, 46.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -111.1 (m, 1F), -123.2 (m, 1F) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{17}F_2N_2O$: 303.1309; found 303.1307

Melting Point: 91 – 93 °C

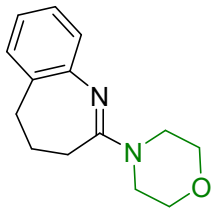
4-methoxyphenyl (Z)-N-((3s,5s,7s)-1-adamantanyl)acetimidate (2o-i)



The reaction was performed using *General Procedure I* above with 1-adamantyl methyl ketone oxime (38.6 mg, 0.2 mmol). Following the 60 second reaction, the solvent was removed under reduced pressure and toluene (21.2 µL, 0.2 mmol, 1.0 eq) was added to the reaction mixture as an internal standard. The mixture was then dissolved in $CDCl_3$ and the yield of **2o-i** reported in the manuscript (56%) was determined by comparison of the methoxy group and methyl group on the product compared to the methyl group of the internal standard in the ^{1}H NMR.

LRMS-EI (m/z): 300.2

4-(4,5-dihydro-3H-benzo[b]azepin-2-yl)morpholine (2p-a)



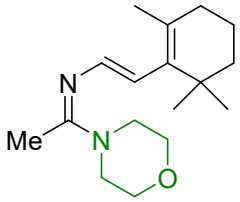
The reaction was performed using *General Procedure A* above with tetralone oxime (32.2 mg, 0.2 mmol). Following silica gel chromatography, product **2p-a** was isolated as a colorless oil (35.9 mg, 78%). The isolated yield reported in the manuscript is the average of two runs (78% and 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.19 (t, *J* = 9.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.89 – 6.95 (m, 2H), 3.77 (t, *J* = 4.8 Hz, 4H), 3.57 (t, *J* = 4.7 Hz, 4H), 2.52 (t, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.11 (pent, *J* = 7.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 163.3, 132.1, 128.8, 127.4, 123.8, 122.3, 121.0, 67.0, 45.7, 31.7, 30.6, 25.8 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{14}H_{19}N_2O$: 231.1497; found 231.1498

(Z)-1-morpholino-N-((E)-2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)ethan-1-imine (2q-a)



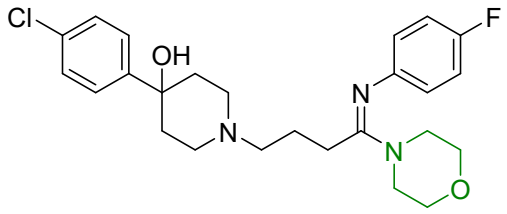
The reaction was performed using *General Procedure A* above with β-ionone oxime (41.5 mg, 0.2 mmol). Following silica gel chromatography, product **2q-a** was isolated as a colorless oil (36.5 mg, 66%). The isolated yield reported in the manuscript is the average of two runs (66% and 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 6.65 (d, *J* = 13.4 Hz, 1H), 5.86 (d, *J* = 13.3 Hz, 1H), 3.71 (t, *J* = 4.8 Hz, 4H), 3.49 (t, *J* = 4.7 Hz, 4H), 1.98 – 2.01 (m, 5H), 1.75 (s, 3H), 1.57 – 1.63 (m, 2H), 1.44 – 1.47 (m, 2H), 1.02 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.5, 138.8, 137.0, 127.9, 118.8, 67.0, 45.6, 39.8, 34.4, 33.2, 29.1, 22.2, 19.5, 13.1 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{29}N_2O$: 277.2280; found 277.2278

(Z)-4-(4-chlorophenyl)-1-(4-((4-fluorophenyl)imino)-4-morpholinobutyl)piperidin-4-ol (2r-a)



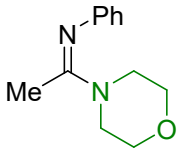
The reaction was performed using *General Procedure A* above with Haloperidol oxime (78.2 mg, 0.2 mmol). Following completion of the 10 minute reaction time, 4-fluoroanisole (52.0 mg, 0.4 mmol, 2.0 eq.) was added as an internal standard and the yield of **2r-a** reported in the manuscript (22%) was determined by ^{19}F NMR.

LRMS-EI (m/z): 460.1

8. Amine substrate scope for the formation of amidines from acetophenone oxime

General Procedure: To an 8 mL vial, acetophenone oxime (27.0 mg, 0.2 mmol, 1.0 eq.) and NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) were added along with DCM (0.5 mL). SIF reagent (160.0 mg, 0.4 mmol, 2.0 eq.) was dissolved (0.25 mL) and added to the reaction vial at room temperature. The reaction was stirred for 60 seconds at which time the amine nucleophile (0.4 mmol, 2.0 eq.) was added and the reaction was stirred for a further 10 minutes at room temperature. At this time, the solvent was removed under reduced pressure and the crude reaction mixture was purified via silica gel chromatography (12 g silica gel column), using DCM and ethyl acetate as the eluent (0% → 30% gradient).

(Z)-1-morpholino-N-phenylethanimine (3a)

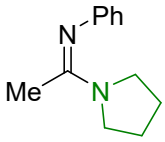


The reaction was performed using the *General Procedure* above with morpholine (34.8 mg, 0.4 mmol). Following silica gel chromatography, product **3a** was isolated as a white solid (38.0 mg, 93%). The isolated yield reported in the manuscript is the average of two runs (93% and 91% yield). The spectroscopic data were consistent with those previously published in the literature.[2] Product **3a** is the same as **2a-a** presented in Section 7.

^{1}H NMR (400 MHz, $CDCl_3$): 7.27 (t, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 2H), 3.77 (t, *J* = 4.9 Hz, 4H), 3.52 (t, *J* = 4.8 Hz, 4H), 1.87 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.1, 151.6, 128.9, 122.1, 121.9, 66.9, 45.4, 14.7 ppm.

(Z)-1-(pyrrolidinyl)-N-phenylethanimine (3b)

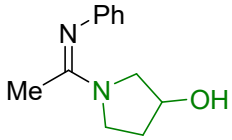


The reaction was performed using the *General Procedure* described above with pyrrolidine (28.4 mg, 0.4 mmol). Following silica gel chromatography, product **3b** was isolated as a colorless oil (35.4 mg, 95%). The isolated yield reported in the manuscript is the average of two runs (95% and 93% yield). The spectroscopic data were consistent with those previously published in the literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$): 7.29 – 7.39 (m, 5H), 3.64 (t, *J* = 6.9 Hz, 4H), 2.18 (s, 3H), 1.83 – 1.95 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.2, 136.6, 129.6, 128.1, 126.7, 51.0, 49.3, 25.0, 24.8, 17.5 ppm.

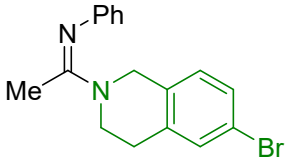
(Z)-1-(pyrrolidine-3-ol)-N-phenylethanimine (3c)



The reaction was performed using the *General Procedure* described above with 3-pyrrolidinol (34.8 mg, 0.4 mmol). Following the 60 second reaction, the solvent was removed under reduced pressure and toluene (21.2 µL, 0.2 mmol, 1.0 eq) was added to the reaction mixture as an internal standard. The mixture was then dissolved in $CDCl_3$ and the yield of **3c** reported in the manuscript (59%) was determined by comparison of the methyl group on the product with the methyl group of the internal standard in the ^1H NMR.

LRMS (m/z): 204.3

(Z)-1-(6-bromo-3,4-dihydroisoquinolin-2(1H)-yl)-N-phenylethanimine (3d)



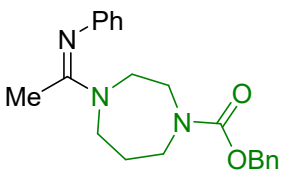
The reaction was performed using the *General Procedure* described above with 6-bromo-1,2,3,4-tetrahydroisoquinoline (84.8 mg, 0.4 mmol). Following silica gel chromatography, product **3d** was isolated as a colorless oil (50.0 mg, 76%). The isolated yield reported in the manuscript is the average of two runs (76% and 75% yield).

^1H NMR (400 MHz, $CDCl_3$): 7.33 (d, J = 6.9 Hz, 2H), 7.25 (t, J = 7.5 Hz, 2H), 7.05 (d, J = 8.7 Hz, 1H), 6.97 (t, J = 7.4 Hz, 1H), 6.73 (t, J = 7.5 Hz, 2H), 4.68 (s, 2H), 3.72 (t, J = 5.8 Hz, 2H), 2.91 (t, J = 5.8 Hz, 2H), 1.95 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 156.3, 151.8, 137.2, 133.3, 131.4, 129.5, 128.9, 128.4, 122.3, 121.8, 120.0, 46.7, 42.6, 29.3, 15.2 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{18}BrN_2$: 329.0653; found 329.0649

benzyl (Z)-4-(1-(phenylimino)ethyl)-1,4-diazepane-1-carboxylate (3e)



The reaction was performed using the *General Procedure* described above with benzyl-1-homopiperazinecarboxylate (93.7 mg, 0.4 mmol). Following silica gel chromatography, product **3e** was

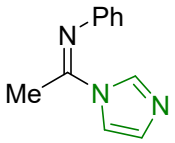
isolated as a colorless oil (42.2 mg, 60%). The isolated yield reported in the manuscript is the average of two runs (60% and 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.31 – 7.39 (m, 5H), 7.20 – 7.25 (m, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 2H), 5.18 (d, *J* = 3.4 Hz, 2H), 3.62 – 3.70 (m, 4H), 3.45 – 3.56 (m, 4H), 1.90 – 1.95 (m, 2H), 1.85 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 156.1, 155.9, 155.4, 151.8, 137.0, 136.9, 128.9, 128.6, 128.1, 128.0, 127.9, 122.3, 121.6, 67.2, 49.4, 49.1, 47.4, 46.5, 14.4 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{21}H_{26}N_3O_2$: 352.2025; found 352.2024

(Z)-1-(imidazolyl)-N-phenylethanimine (3f)



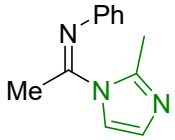
The reaction was performed using the *General Procedure* described above with imidazole (27.2 mg, 0.4 mmol). Following silica gel chromatography, product **3f** was isolated as a colorless oil (35.2 mg, 95%). The isolated yield reported in the manuscript is the average of two runs (95% and 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 8.18 (s, 1H), 7.65 (s, 1H), 7.36 (t, *J* = 6.4 Hz, 2H), 7.10 – 7.15 (m, 2H), 6.82 (d, *J* = 6.5 Hz, 2H), 2.31 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 149.6, 147.6, 135.7, 130.5, 129.3, 124.3, 120.2, 116.4, 15.9 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{11}H_{12}N_3$: 185.0952; found 185.0950

(Z)-1-(2-methylimidazolyl)-N-phenylethanimine (3g)



The reaction was performed using the *General Procedure* described above with 2-methylimidazole (32.8 mg, 0.4 mmol). Following silica gel chromatography, product **3g** was isolated as a white solid (37.1 mg, 93%). The isolated yield reported in the manuscript is the average of two runs (93% and 88% yield).

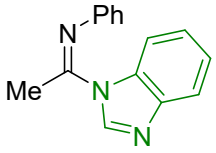
^{1}H NMR (400 MHz, $CDCl_3$): 7.36 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 1.2 Hz, 1H) 7.12 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 1.1 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 2H), 2.72 (s, 3H), 2.27 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 151.6, 148.2, 146.9, 129.3, 127.7, 124.1, 119.9, 117.5, 18.2, 17.6 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{12}H_{14}N_3$: 200.1187; found 200.1185

Melting Point: 58 – 59 °C

(Z)-1-(1H-benzo[d]imidazolyl)-N-phenylethanimine (3h)



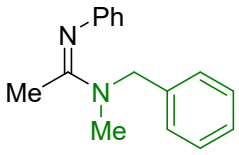
The reaction was performed using the *General Procedure* described above with benzimidazole (47.2 mg, 0.4 mmol). Following silica gel chromatography, product **3h** was isolated as a colorless oil (45.6 mg, 97%). The isolated yield reported in the manuscript is the average of two runs (97% and 96% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 8.45 – 8.50 (m, 1H), 8.40 (s, 1H), 7.81 – 7.86 (m, 1H), 7.37 – 7.42 (m, 4H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 2.49 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 150.9, 148.0, 144.6, 141.3, 132.4, 129.4, 125.1, 124.3, 124.2, 120.5, 120.4, 116.5, 16.7 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{14}N_3$: 236.1187; found 236.1186

(Z)-N-benzyl-N-methyl-N'-phenylethanimine (3i)



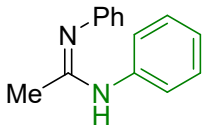
The reaction was performed using the *General Procedure* described above with *N*-methyl-*N*-benzylamine (48.5 mg, 0.4 mmol). Following silica gel chromatography, product **3i** was isolated as a colorless oil (40.5 mg, 85%). The isolated yield reported in the manuscript is the average of two runs (85% and 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.38 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.32 (m, 5H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 2H), 4.69 (s, 2H), 3.05 (s, 3H), 1.95 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 157.4, 152.5, 139.0, 129.2, 129.0, 127.5, 127.4, 122.8, 121.9, 53.6, 36.4, 15.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{19}N_2$: 239.1548; found 239.1545

(Z)-N,N'-diphenylacetimidamide (3j)



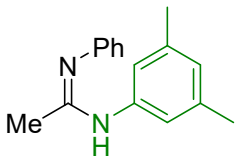
The reaction was performed using the *General Procedure* described above with aniline (37.2 mg, 0.4 mmol). Following silica gel chromatography, product **3j** was isolated as a colorless oil (20.2 mg, 48%). The isolated yield reported in the manuscript is the average of two runs (48% and 43% yield). The spectroscopic data were consistent with those previously published in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): 7.26 – 7.32 (m, 4H), 7.20 (br, 4H), 7.04 (t, *J* = 7.2 Hz, 2H), 6.24 (br, 1H), 1.99 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 152.4, 128.7, 123.2, 121.1, 19.6 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{14}H_{15}N_2$: 211.1235; found 211.1234

(Z)-N-(3,5-dimethylphenyl)-N'-phenylacetimidamide (3k)



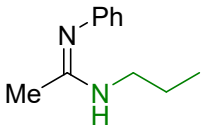
The reaction was performed using the *General Procedure* described above with 3,5-dimethylaniline (37.6 mg, 0.4 mmol). Following silica gel chromatography, product **3k** was isolated as a colorless oil (28.6 mg, 60%). The isolated yield reported in the manuscript is the average of two runs (60% and 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.30 (t, *J* = 6.5 Hz, 2H), 7.12 – 7.20 (m, 2H), 7.04 (t, *J* = 6.4 Hz, 1H), 6.82 (br, 2H), 6.70 (br, 1H), 5.30 (br, 1H) 2.30 (s, 6H), 1.99 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 153.2, 138.7, 129.1, 124.8, 122.8, 121.4, 119.2, 21.5, 18.9 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{19}N_2$: 239.1548; found 239.1550

(Z)-N'-phenyl-N-propylacetimidamide (3l)



The reaction was performed using the *General Procedure* described above with propylamine (23.6 mg, 0.4 mmol). Following silica gel chromatography, product **3l** was isolated as a white solid (18.0 mg, 51%). The isolated yield reported in the manuscript is the average of two runs (51% and 46% yield).

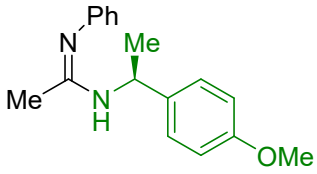
^{1}H NMR (400 MHz, $CDCl_3$): 7.25 (t, *J* = 7.4 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.4 Hz, 2H), 4.12 (br, 1H), 3.28 (br, 2H), 1.82 (br s, 3H), 1.59 (q, *J* = 7.7 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 153.1, 128.9, 124.5, 122.6, 122.0, 43.2, 22.8, 17.6, 12.1 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{11}H_{17}N_2$: 177.1391; found 177.1394

Melting Point: 59 – 61 °C

(S,Z)-N-(1-(4-methoxyphenyl)ethyl)-N'-phenylacetimidamide (3m)



The reaction was performed using the *General Procedure* described above with (S)-1-(4-methoxyphenyl)ethan-1-amine (60.4 mg, 0.4 mmol). Following silica gel chromatography, product **3m** was isolated as a colorless oil (43.0 mg, 80%). The isolated yield reported in the manuscript is the average of two runs (80% and 76% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.33 (br, 2H), 7.24 (br, 2H), 6.96 (br, 1H), 6.91 (d, J = 7.6 Hz, 2H), 6.75 (br, 2H), 5.17 (br, 1H), 4.52 (br, 1H), 3.81 (s, 3H), 1.76 (s, 3H), 1.53 (br, 3H) ppm.

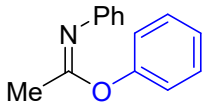
^{13}C NMR (101 MHz, $CDCl_3$): 158.7, 154.3, 151.8, 136.8, 129.0, 128.8, 127.5, 122.3, 121.8, 119.9, 114.0, 55.4, 49.4, 22.1, 17.6 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{21}N_2O$: 269.1653; found 269.1655

9. Alcohol substrate scope for the formation of imidates from acetophenone oxime

General Procedure: To an 8 mL vial, acetophenone oxime (27.0 mg, 0.2 mmol, 1.0 eq.) and NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) were added along with DCM (0.5 mL). SIF reagent (160.0 mg, 0.4 mmol, 2.0 eq.) was dissolved (0.25 mL) and added to the reaction vial at room temperature. The reaction was stirred for 60 seconds at which time the alcohol nucleophile (0.4 mmol, 2.0 eq.) and NEt_3 (40.0 mg, 0.4 mmol, 2.0 eq.) were added and the reaction was stirred for a further 24 hours at room temperature. At this time, the solvent was removed under reduced pressure and the crude reaction mixture was purified via silica gel chromatography (12 g silica gel column), using hexane and ethyl acetate as the eluent (0% → 10% gradient).

phenyl (Z)-N-phenylacetimidate (4a)



The reaction was performed using the *General Procedure* described above with phenol (37.6 mg, 0.4 mmol). Following silica gel chromatography, product **4a** was isolated as a white solid (39.3 mg, 93%). The isolated yield reported in the manuscript is the average of two runs (93% and 92% yield).

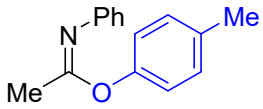
^{1}H NMR (400 MHz, $CDCl_3$): 7.39 (t, *J* = 7.3 Hz, 2H), 7.19 – 7.27 (m, 5H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.0 Hz, 2H), 2.06 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.2, 152.9, 148.6, 129.4, 129.0, 125.2, 123.3, 122.2, 120.9, 16.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{14}H_{14}NO$: 212.1075; found 212.1076

Melting Point: 52 – 53 °C

4-methylphenyl (Z)-N-phenylacetimidate (4b)



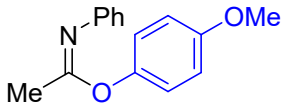
The reaction was performed using the *General Procedure* described above with *para*-cresol (43.2 mg, 0.4 mmol). Following silica gel chromatography, product **4b** was isolated as a colorless oil (40.1 mg, 89%). The isolated yield reported in the manuscript is the average of two runs (89% and 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.25 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 2.04 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.5, 150.7, 148.7, 134.7, 130.0, 128.9, 123.2, 121.9, 121.0, 21.0, 16.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{16}NO$: 226.1231; found 226.1229

4-methoxyphenyl (Z)-N-phenylacetimidate (4c)

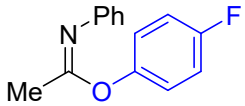


The reaction was performed using the *General Procedure* described above with 4-methoxyphenol (49.6 mg, 0.4 mmol). Following silica gel chromatography, product **4c** was isolated as a white solid (43.4 mg, 90%). The isolated yield reported in the manuscript is the average of two runs (90% and 90% yield). The spectroscopic data were consistent with those previously published in the literature. Product **4c** is the same as **2a-I** from Section 7.

^{1}H NMR (400 MHz, $CDCl_3$): 7.25 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 3H), 2.03 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.7, 156.8, 148.7, 146.4, 129.0, 123.2, 123.0, 121.0, 114.5, 55.7, 16.3 ppm.

4-fluorophenyl (Z)-N-phenylacetimidate (4d)



The reaction was performed using the *General Procedure* described above with 4-fluorophenol (44.8 mg, 0.4 mmol). Following silica gel chromatography, product **4d** was isolated as a colorless oil (35.3 mg, 77%). The isolated yield reported in the manuscript is the average of two runs (77% and 72% yield).

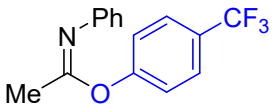
^{1}H NMR (400 MHz, $CDCl_3$): 7.26 (t, *J* = 7.6 Hz, 2H), 7.13 – 7.16 (m, 2H), 7.01 – 7.08 (m, 3H), 6.74 (d, *J* = 7.7 Hz, 2H), 2.05 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.3, 161.1, 158.7, 148.7 (d), 148.3, 129.1, 123.6 (d), 123.4, 120.8, 116.1 (d), 16.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -118.2 (m) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{14}H_{13}FNO$: 230.0981; found 230.0984

4-trifluoromethylphenyl (Z)-N-phenylacetimidate (4e)



The reaction was performed using the *General Procedure* described above with 4-trifluoromethylphenol (64.8 mg, 0.4 mmol). Following silica gel chromatography, product **4e** was isolated as a colorless oil (33.5 mg, 61%). The isolated yield reported in the manuscript is the average of two runs (61% and 52% yield).

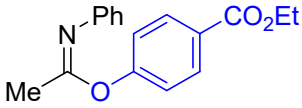
^{1}H NMR (400 MHz, $CDCl_3$): 7.65 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 2H), 2.09 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 160.8, 155.5, 147.9, 129.2, 127.5, 126.8 (q), 125.6 123.7, 122.7, 120.8, 16.2 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): -61.8 (s) ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{13}F_3NO$: 280.0949; found 280.0951

ethyl (Z)-4-(1-(phenylimino)ethoxy)benzoate (4f)



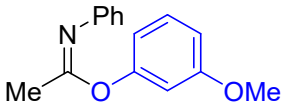
The reaction was performed using the *General Procedure* described above with ethyl 4-hydroxybenzoate (66.5 mg, 0.4 mmol). Following silica gel chromatography, product **4f** was isolated as a colorless oil (44.8 mg, 79%). The isolated yield reported in the manuscript is the average of two runs (79% and 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 8.08 (d, *J* = Hz, 2H), 7.25 – 7.30 (m, 4H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.08 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 166.2, 160.8, 156.7, 148.0, 131.1, 129.1, 127.3, 123.5, 122.2, 120.8, 61.0, 16.3, 14.5 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{18}NO_3$: 284.1286; found 284.1289

3-methoxyphenyl (Z)-N-phenylacetimidate (4g)



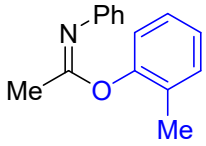
The reaction was performed using the *General Procedure* described above with 3-methoxyphenol (49.6 mg, 0.4 mmol). Following silica gel chromatography, product **4g** was isolated as a colorless oil (26.5 mg, 55%). The isolated yield reported in the manuscript is the average of two runs (55% and 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.20 – 7.25 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.69 – 6.74 (m, 4H), 3.77 (s, 3H), 2.01 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.1, 160.5, 153.9, 148.5, 129.8, 129.0, 123.3, 120.9, 114.6, 110.8, 108.4, 55.5, 16.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{16}NO_2$: 242.1181; found 242.1180

2-methylphenyl (Z)-N-phenylacetimidate (4h)



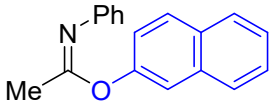
The reaction was performed using the *General Procedure* described above with *ortho*-cresol (43.2 mg, 0.4 mmol). Following silica gel chromatography, product **4h** was isolated as a colorless oil (29.3 mg, 65%). The isolated yield reported in the manuscript is the average of two runs (65% and 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.21 – 7.27 (m, 4H), 7.12 – 7.15 (m, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.73 (t, J = 7.4 Hz, 2H), 2.30 (s, 3H), 2.07 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 160.7, 151.6, 148.8, 131.1, 130.6, 129.0, 127.0, 125.6, 123.2, 122.4, 121.0, 16.6, 15.9 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{15}H_{16}NO$: 226.1232; found 226.1230

2-naphthyl (Z)-N-phenylacetimidate (4i)



The reaction was performed using the *General Procedure* described above with 2-naphthol (57.7 mg, 0.4 mmol). Following silica gel chromatography, product **4i** was isolated as a white solid (44.4 mg, 85%). The isolated yield reported in the manuscript is the average of two runs (85% and 80% yield).

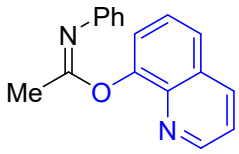
^{1}H NMR (400 MHz, $CDCl_3$): 7.68 – 7.74 (m, 3H), 7.51 (s, 1H), 7.26 – 7.36 (m, 3H), 7.14 (t, J = 7.5 Hz, 2H), 6.90 (t, J = 7.4 Hz, 1H), 6.65 (d, J = 7.5 Hz, 2H), 1.99 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.4, 150.7, 148.5, 134.2, 131.4, 129.2, 129.0, 127.9, 127.7, 126.4, 125.4, 123.3, 122.4, 120.9, 118.7, 16.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{18}H_{16}NO$: 262.1231; found 262.1232

Melting Point: 99 – 101 °C

8-quinolinyl (Z)-N-phenylacetimidate (4j)



The reaction was performed using the *General Procedure* described above with 8-hydroxyquinoline (58.1 mg, 0.4 mmol). Following silica gel chromatography, product **4j** was isolated as a white solid (43.5 mg, 83%). The isolated yield reported in the manuscript is the average of two runs (83% and 79% yield).

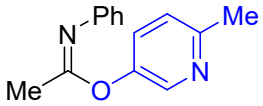
^{1}H NMR (400 MHz, $CDCl_3$): 8.99 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.69 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.55 – 7.62 (m, 2H), 7.44 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.4 Hz, 2H), 2.30 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 162.2, 150.1, 149.9, 148.7, 141.7, 136.2, 129.8, 128.9, 126.5, 125.2, 123.1, 122.0, 121.6, 120.9, 16.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{15}N_2O$: 263.1184; found 263.1185

Melting Point: 104 – 105 °C

6-methyl-3-pyridinyl (Z)-N-phenylacetimidate (4k)



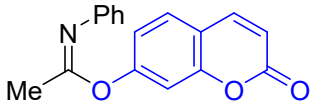
The reaction was performed using the *General Procedure* described above with 3-hydroxy-6-methylpyridine (43.6 mg, 0.4 mmol). Following silica gel chromatography, product **4k** was isolated as a colorless oil (33.5 mg, 74%). The isolated yield reported in the manuscript is the average of two runs (74% and 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 8.39 (d, *J* = 2.2 Hz, 1H), 7.46 (dd, *J* = 5.4, 2.3 Hz, 1H), 7.26 (t, *J* = 6.5 Hz, 2H), 7.15 (d, *J* = 7.1 Hz, 1H), 7.03 (t, *J* = 6.4 Hz, 1H), 6.71 (d, *J* = 6.5 Hz, 2H), 2.54 (s, 3H), 2.07 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.0, 154.9, 147.9, 147.3, 143.1, 130.3, 129.1, 123.5, 123.5, 120.7, 23.9, 16.1 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{14}H_{15}N_2O$: 227.1184; found 227.1183

2-oxo-2H-7-chromenyl (Z)-N-phenylacetimidate (4l)



The reaction was performed using the *General Procedure* described above with umbelliferone (64.8 mg, 0.4 mmol). Following silica gel chromatography, product **4l** was isolated as a white solid (41.9 mg, 75%). The isolated yield reported in the manuscript is the average of two runs (75% and 74% yield).

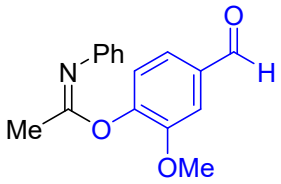
^{1}H NMR (400 MHz, $CDCl_3$): 7.67 (d, *J* = 9.5 Hz, 1H), 7.48 (d, *J* = 9.5 Hz, 1H), 7.26 – 7.32 (m, 3H), 7.20 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 2H), 6.38 (d, *J* = 9.4 Hz, 1H), 2.11 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 160.9, 160.8, 155.7, 154.9, 147.6, 143.2, 129.1, 128.5, 123.7, 120.7, 119.2, 116.2, 115.6, 111.0, 16.2 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{17}H_{14}NO_3$: 280.0973; found 280.0974

Melting Point: 127 – 128 °C

4-formyl-2-methoxyphenyl (Z)-N-phenylacetimidate (4m)



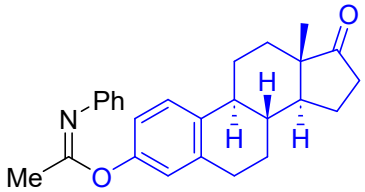
The reaction was performed using the *General Procedure* described above with vanillin (60.8 mg, 0.4 mmol). Following silica gel chromatography, product **4m** was isolated as a colorless oil (45.8 mg, 85%). The isolated yield reported in the manuscript is the average of two runs (85% and 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 9.93 (s, 1H), 7.49 – 7.52 (m, 2H), 7.34 (d, J = 7.4 Hz, 1H), 7.26 (t, J = 7.4 Hz, 2H), 7.03 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 7.5 Hz, 2H), 3.97 (s, 3H), 2.09 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 191.3, 160.4, 152.2, 148.2, 147.6, 134.7, 129.0, 125.3, 123.8, 123.5, 120.8, 111.0, 56.1, 15.7 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{16}NO_3$: 270.1130; found 270.1129

(Estrone) (Z)-N-phenylacetimidate (4n)



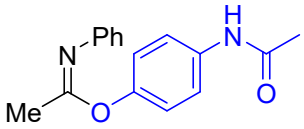
The reaction was performed using the *General Procedure* described above with estrone (108.2 mg, 0.4 mmol). Following silica gel chromatography, product **4n** was isolated as a colorless oil (44.9 mg, 58%). The isolated yield reported in the manuscript is the average of two runs (58% and 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.23 – 7.30 (m, 4H), 6.97 – 7.03 (m, 2H), 6.92 (s, 1H), 6.75 (d, J = 7.5 Hz, 2H), 290 – 2.93 (m, 2H), 2.51 (dd, J = 4.3, 1.5 Hz, 1H), 2.38 – 2.43 (m, 1H), 2.25 – 2.30 (m, 1H), 2.16 (t, J = 6.4 Hz, 1H), 1.95 – 2.07 (m, 7H), 1.50 – 1.62 (m, 9H), 0.90 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.5, 150.8, 148.8, 137.9, 136.6, 129.0, 126.4, 123.2, 122.1, 121.0, 119.5, 50.6, 48.1, 44.3, 38.2, 36.0, 31.7, 29.6, 26.6, 25.9, 21.7, 16.4, 14.0 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{26}H_{30}NO_2$: 388.2276; found 388.2278

4-acetamidophenyl (Z)-N-phenylacetimidate (4o)



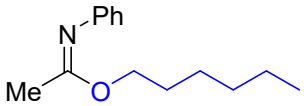
The reaction was performed using the *General Procedure* described above with acetaminophen (60.5 mg, 0.4 mmol). Following silica gel chromatography, product **4o** was isolated as a colorless oil (45.1 mg, 84%). The isolated yield reported in the manuscript is the average of two runs (84% and 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.44 (d, *J* = 8.9 Hz, 2H), 7.42 (br, 1H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 8.9 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 2H), 2.08 (s, 3H), 2.05 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 168.4, 161.8, 149.0, 148.3, 135.1, 129.1, 123.4, 122.5, 121.1, 120.9, 24.5, 16.3 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{16}H_{17}N_2O_2$: 269.1290; found 269.1287

1-hexyl (Z)-N-phenylacetimidate (4p)



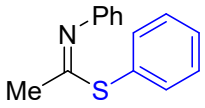
The reaction was performed using the *General Procedure* described above with 1-hexanol (0.50 mL , 4.0 mmol). Following silica gel chromatography, product **4p** was isolated as a colorless oil (15.3 mg, 35%). The isolated yield reported in the manuscript is the average of two runs (35% and 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$): 7.27 (t, *J* = 7.4 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 2H), 4.15 (t, *J* = 6.8 Hz, 2H), 1.82 (s, 3H), 1.71 (pent, *J* = 6.7 Hz, 2H), 1.32 – 1.43 (m, 6H), 0.92 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 161.6, 149.5, 129.1, 122.9, 121.3, 66.0, 31.8, 28.8, 26.0, 22.8, 16.3, 14.2 ppm.

HRMS ESI (m/z): [M + H] cald for $C_{14}H_{22}NO$: 220.1701; found 220.1703

Phenyl (Z)-N-phenylethanimidothioate (4q)



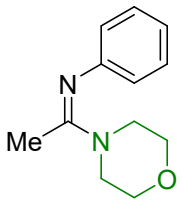
The reaction was performed using the *General Procedure* described above with thiophenol (44.1 mg , 0.4 mmol). Following silica gel chromatography, product **4q** was isolated as a colorless oil (38.1 mg, 84%). The isolated yield reported in the manuscript is the average of two runs (84% and 78% yield). The product was isolated as a 5:1 mixture of the Z and E isomers, respectively. The NMR information presented below is for the major Z isomer.

^{1}H NMR (400 MHz, $CDCl_3$): 7.53 (m, 2H), 7.38 (m, 5H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 2H), 2.12 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): 164.9, 150.3, 136.0, 129.6, 129.4, 129.2, 124.4, 120.0, 27.0 ppm.

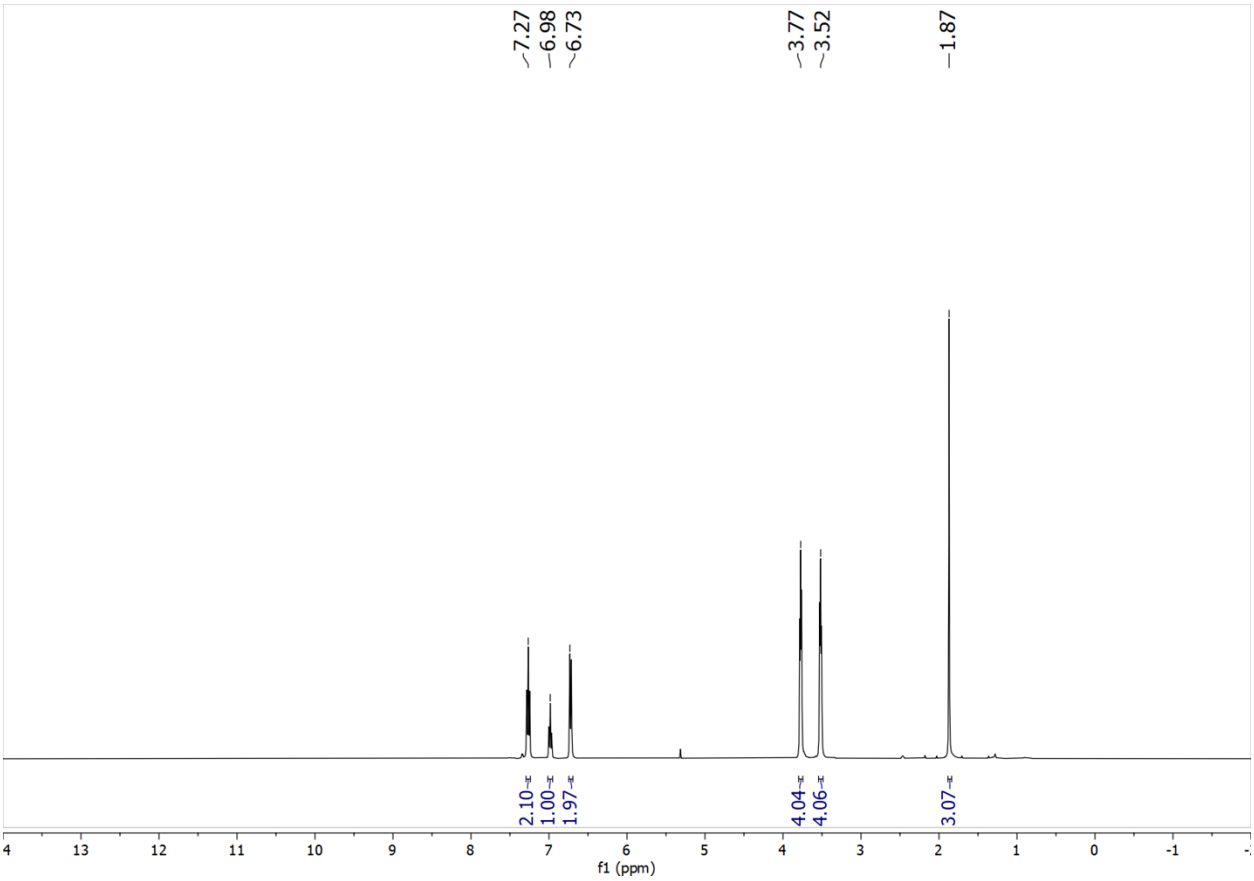
HRMS ESI (m/z): [M + H] cald for $C_{14}H_{14}NS$: 227.0769; found 227.0770

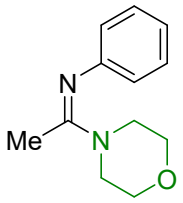
10. NMR spectra of isolated products



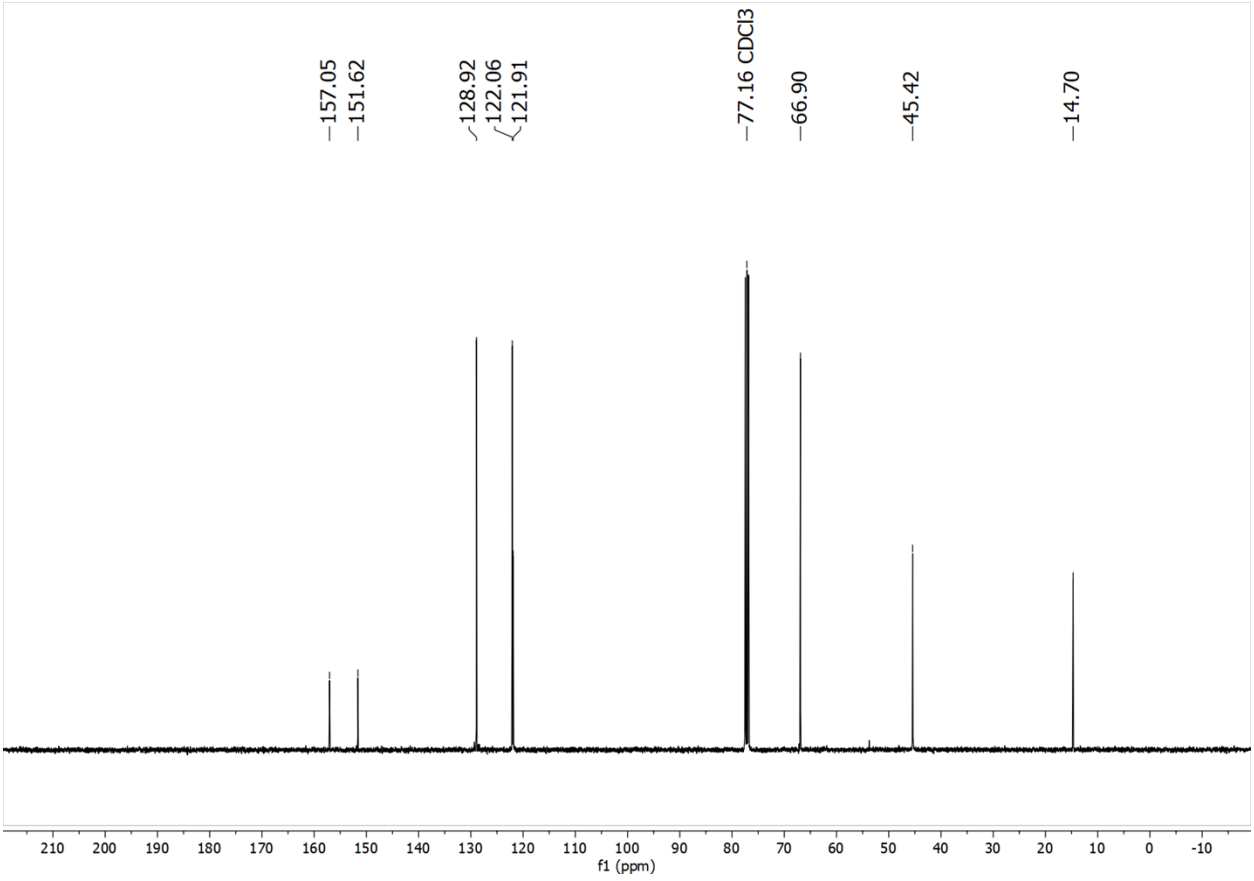
(Z)-1-morpholino-N-phenylethanimine (2a-a)

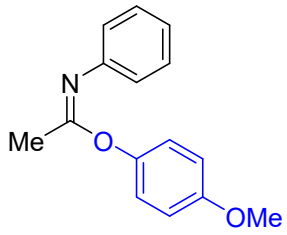
^{1}H NMR: 400 MHz in $CDCl_3$





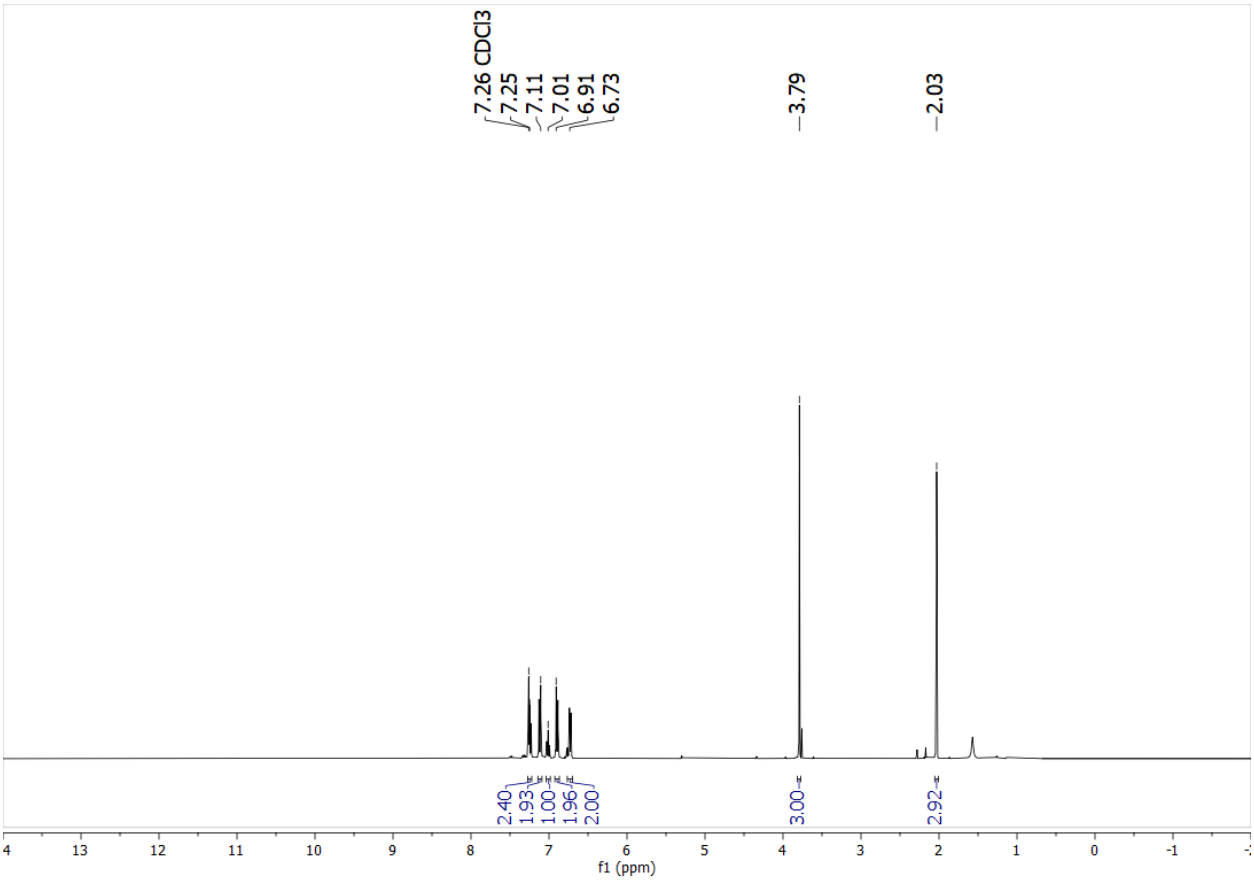
^{13}C NMR: 101 MHz in $CDCl_3$

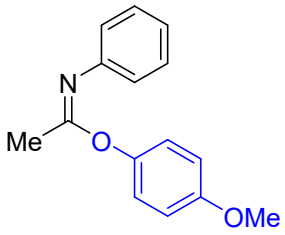




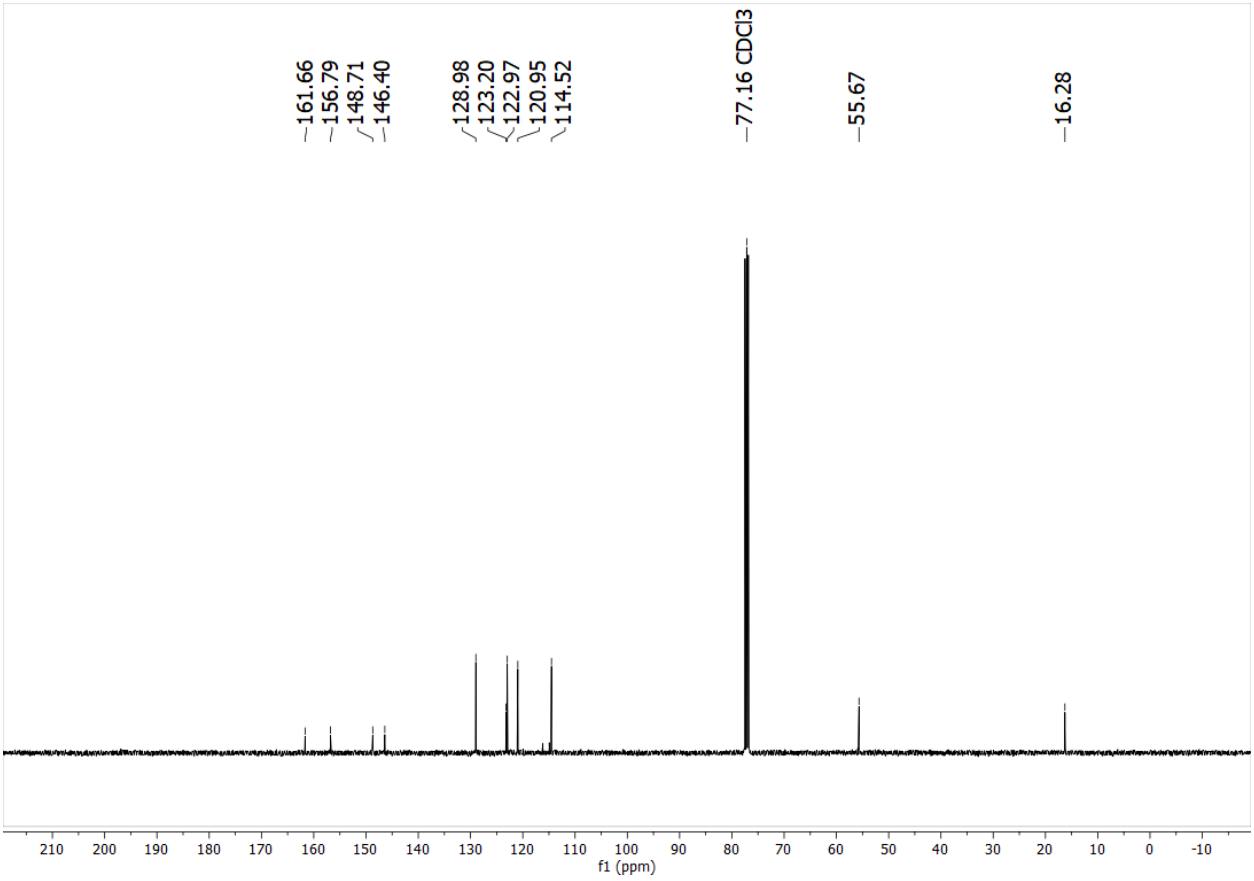
4-methoxyphenyl (Z)-N-phenylacetimidate (2a-i)

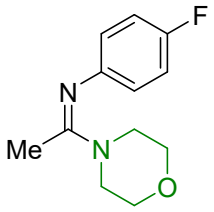
^{1}H NMR: 400 MHz in $CDCl_3$





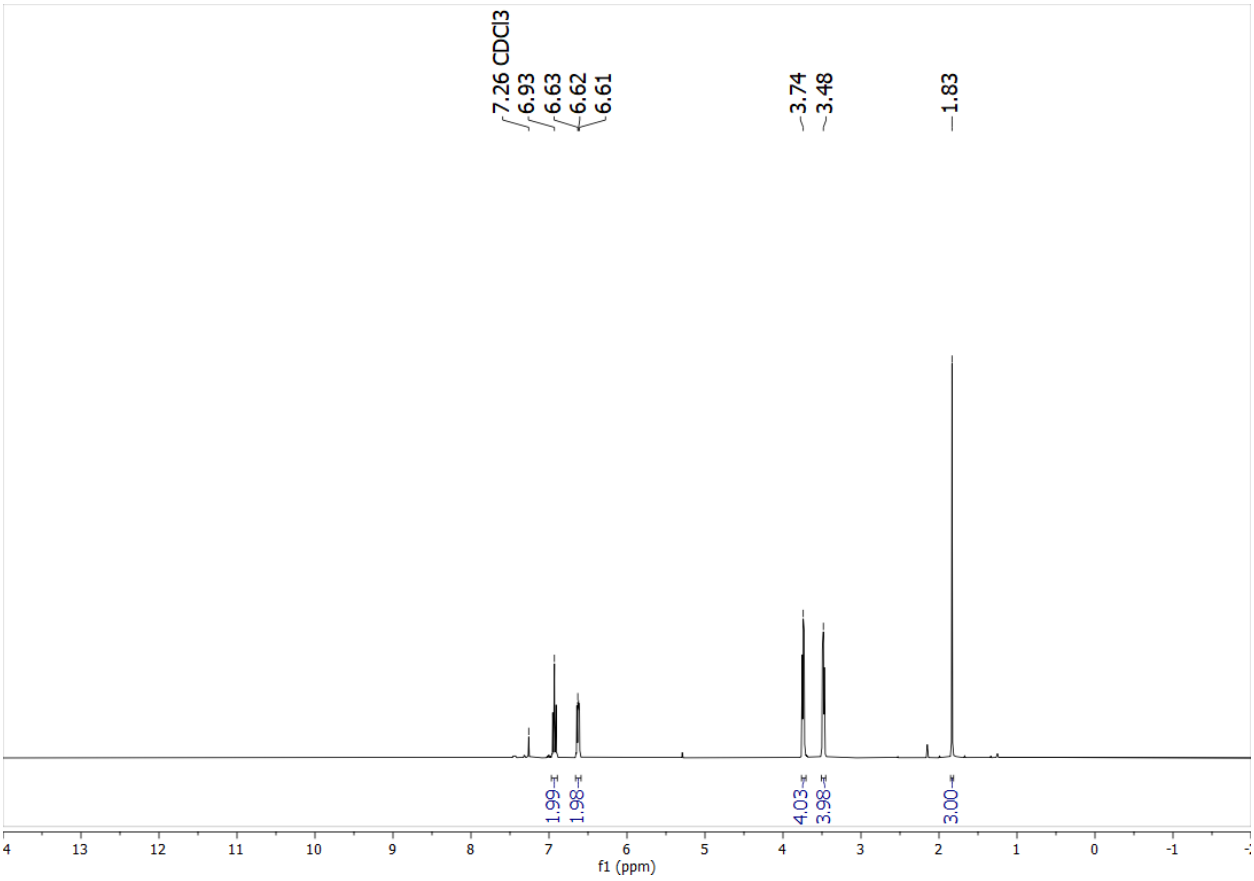
^{13}C NMR: 101 MHz in $CDCl_3$

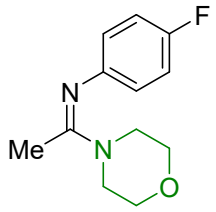




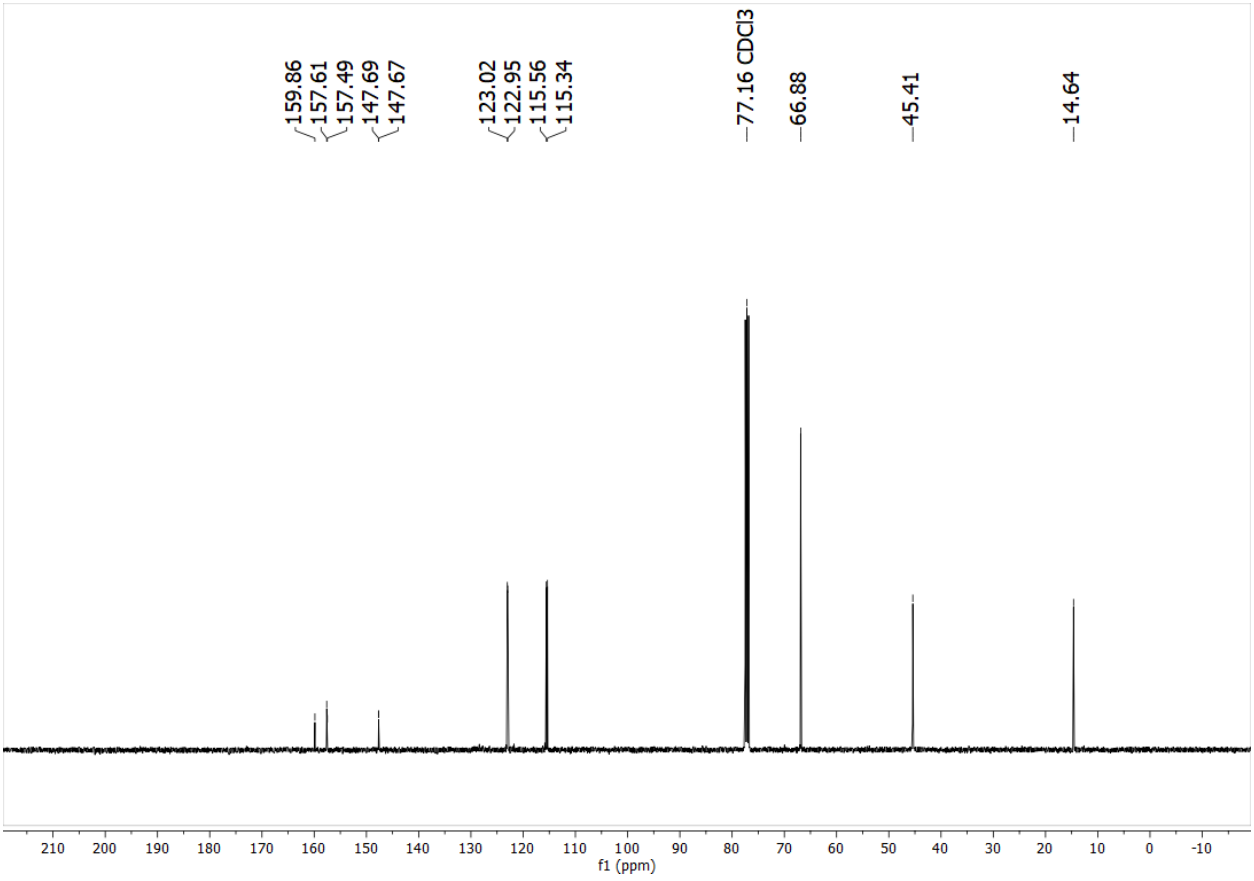
(Z)-1-morpholino-N-(4-fluorophenyl)ethanimine (2b-a)

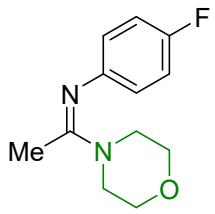
^{1}H NMR: 400 MHz in $CDCl_3$



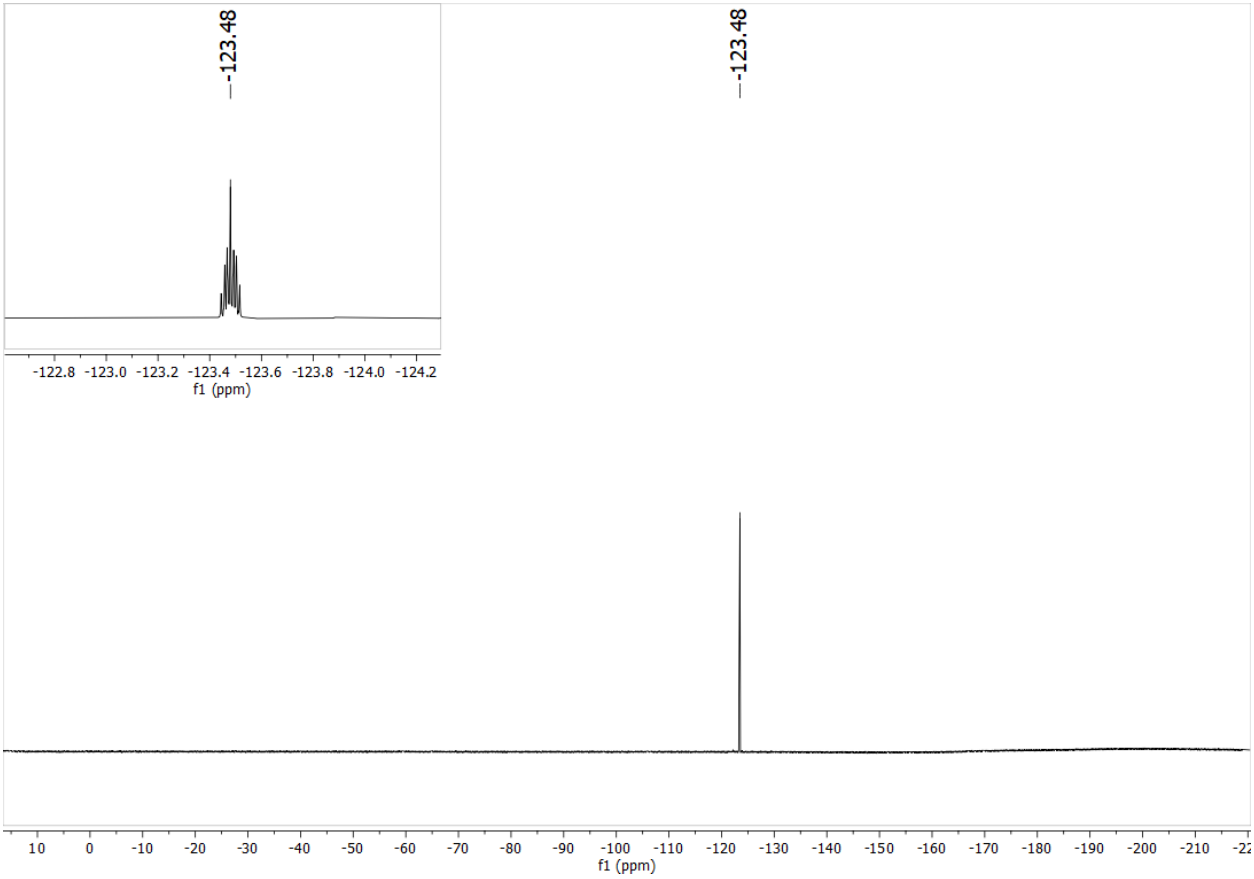


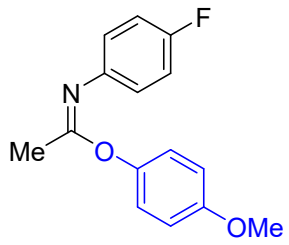
^{13}C NMR: 101 MHz in $CDCl_3$





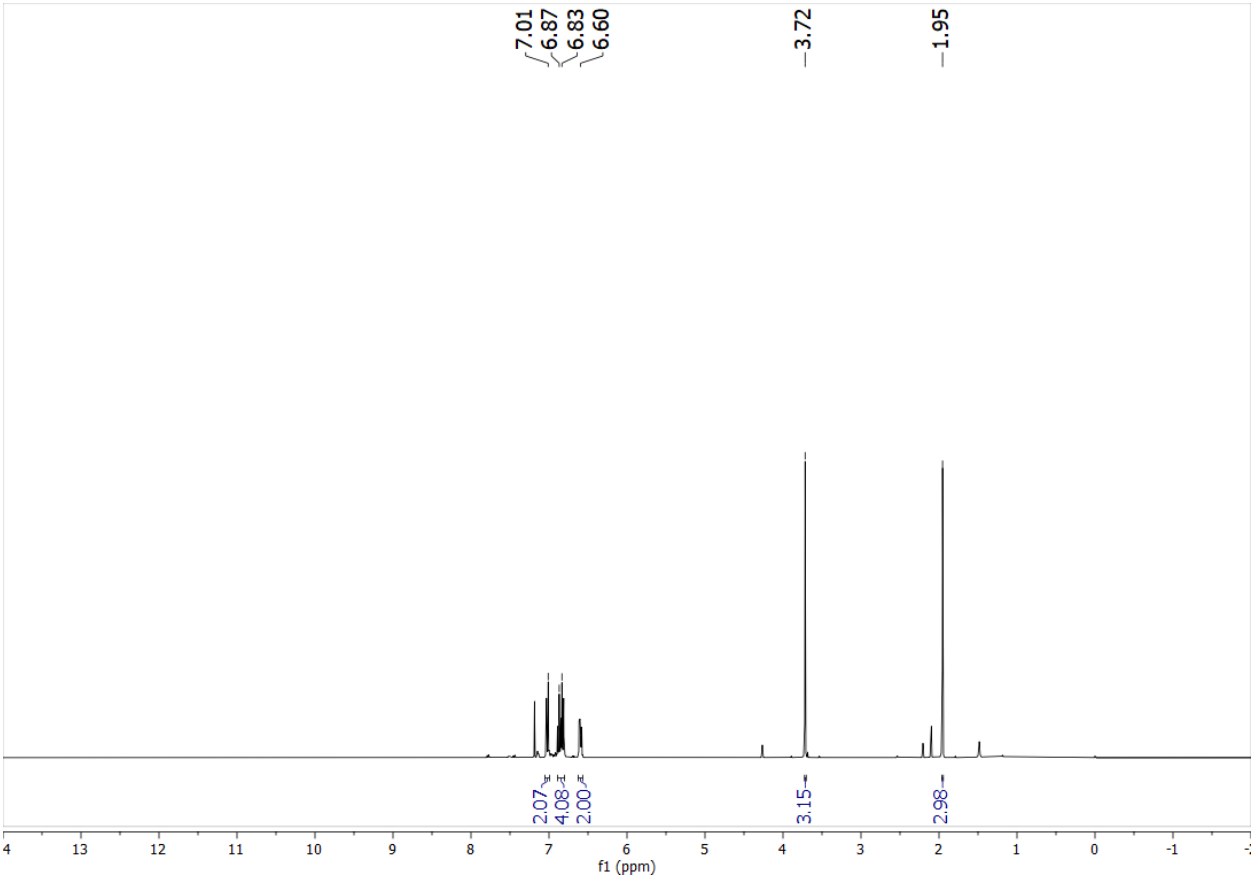
^{19}F NMR: 376 MHz in $CDCl_3$

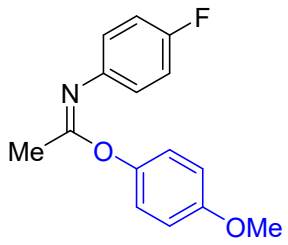




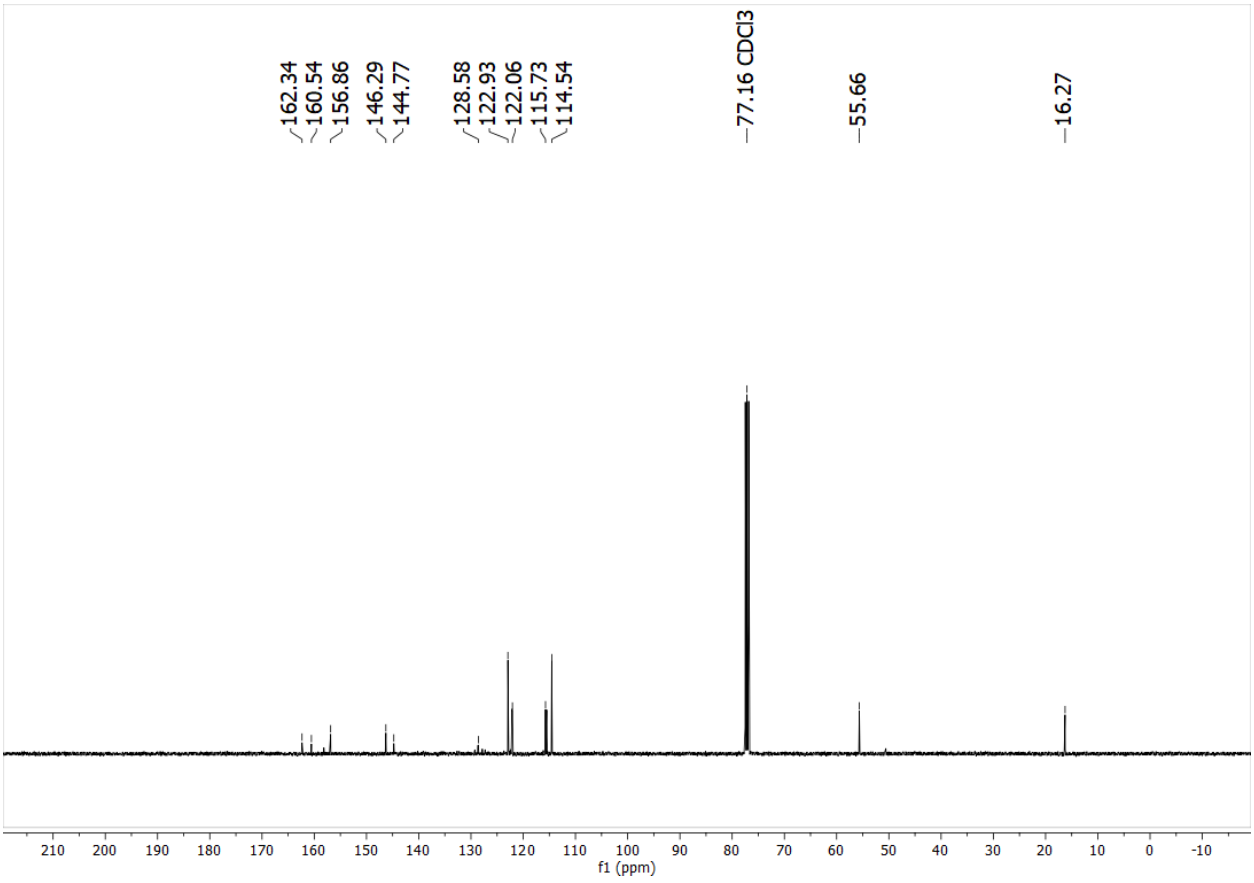
4-methoxyphenyl (Z)-N-(4-fluorophenyl)acetimidate (2b-i)

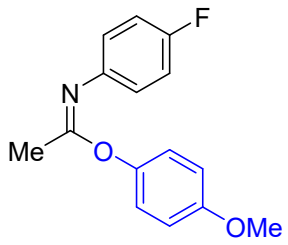
^{1}H NMR: 400 MHz in $CDCl_3$



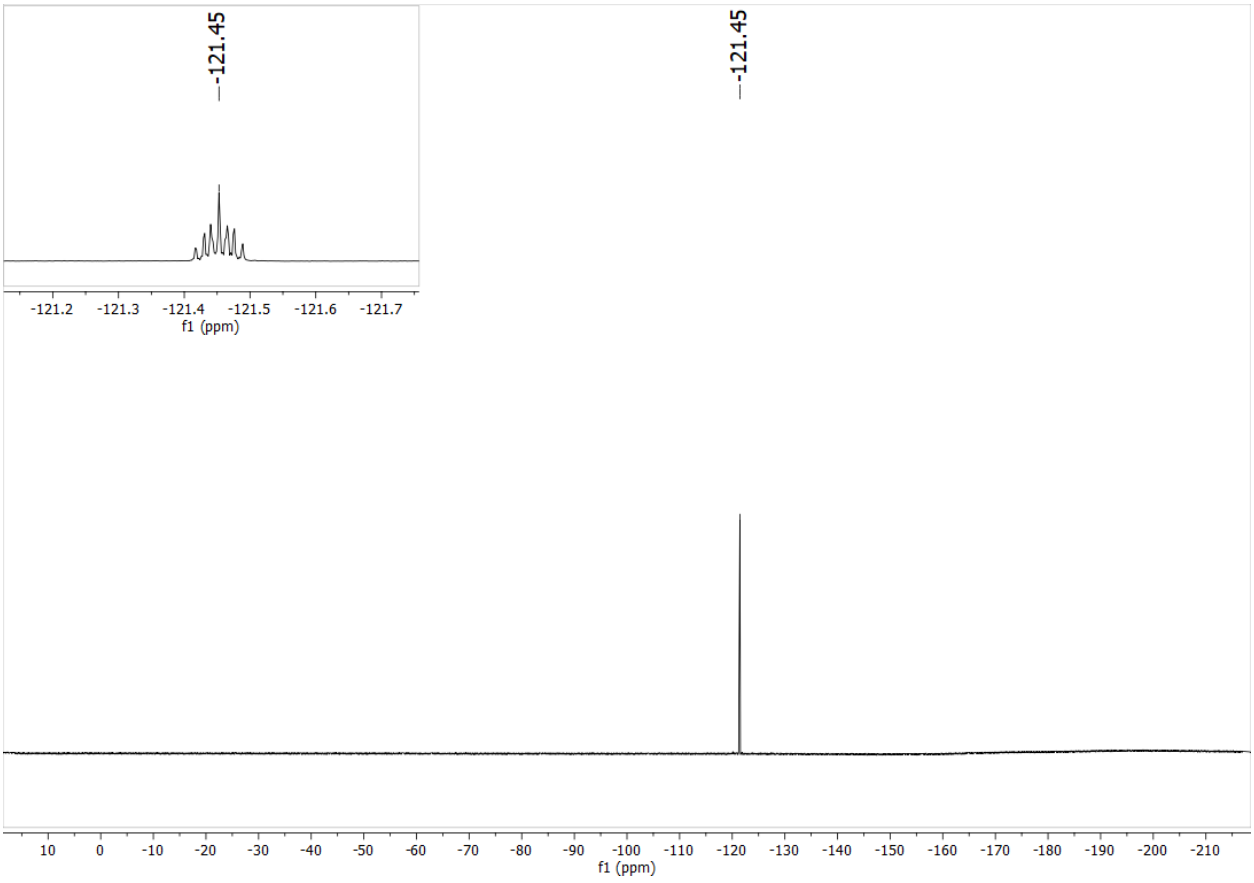


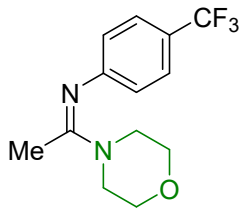
^{13}C NMR: 101 MHz in $CDCl_3$





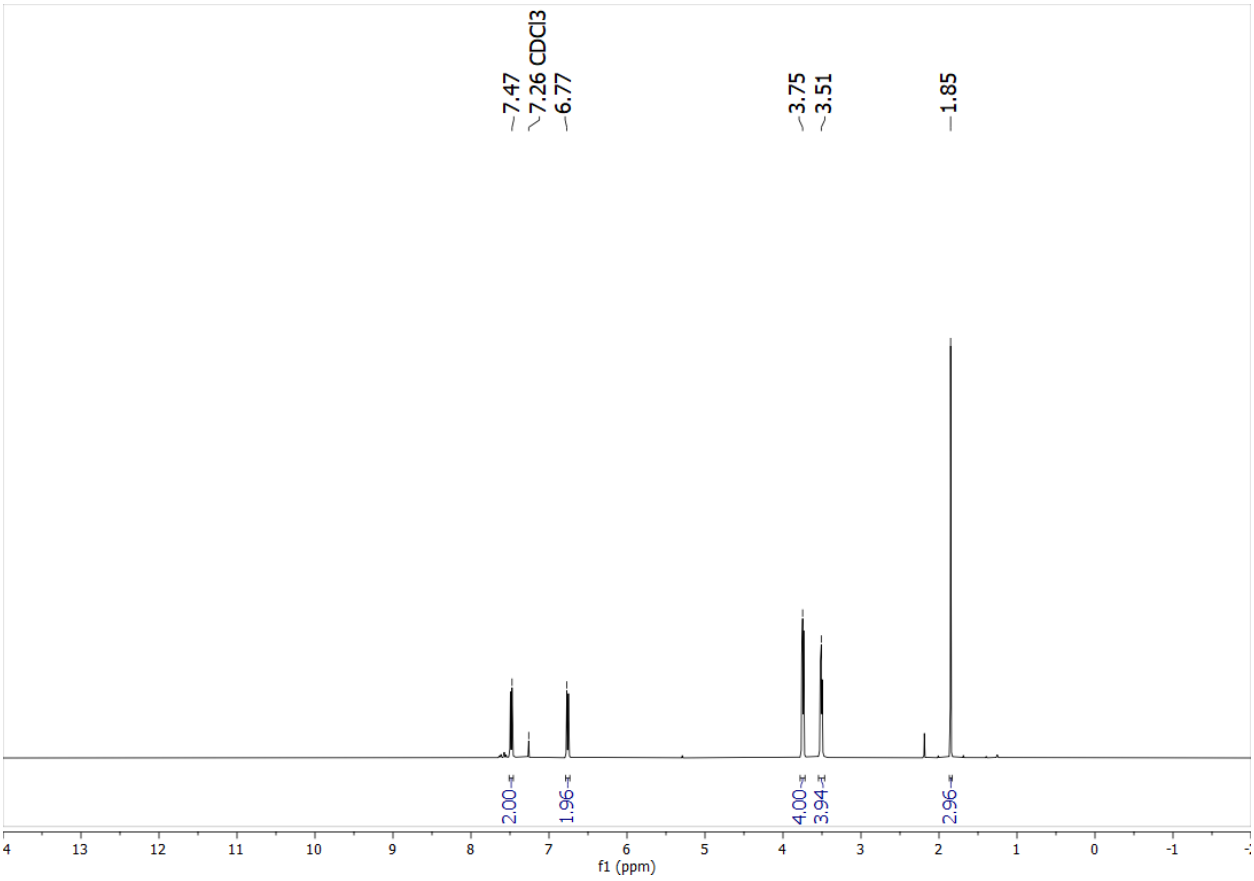
^{19}F NMR: 376 in $CDCl_3$

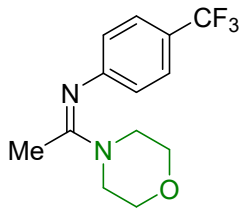




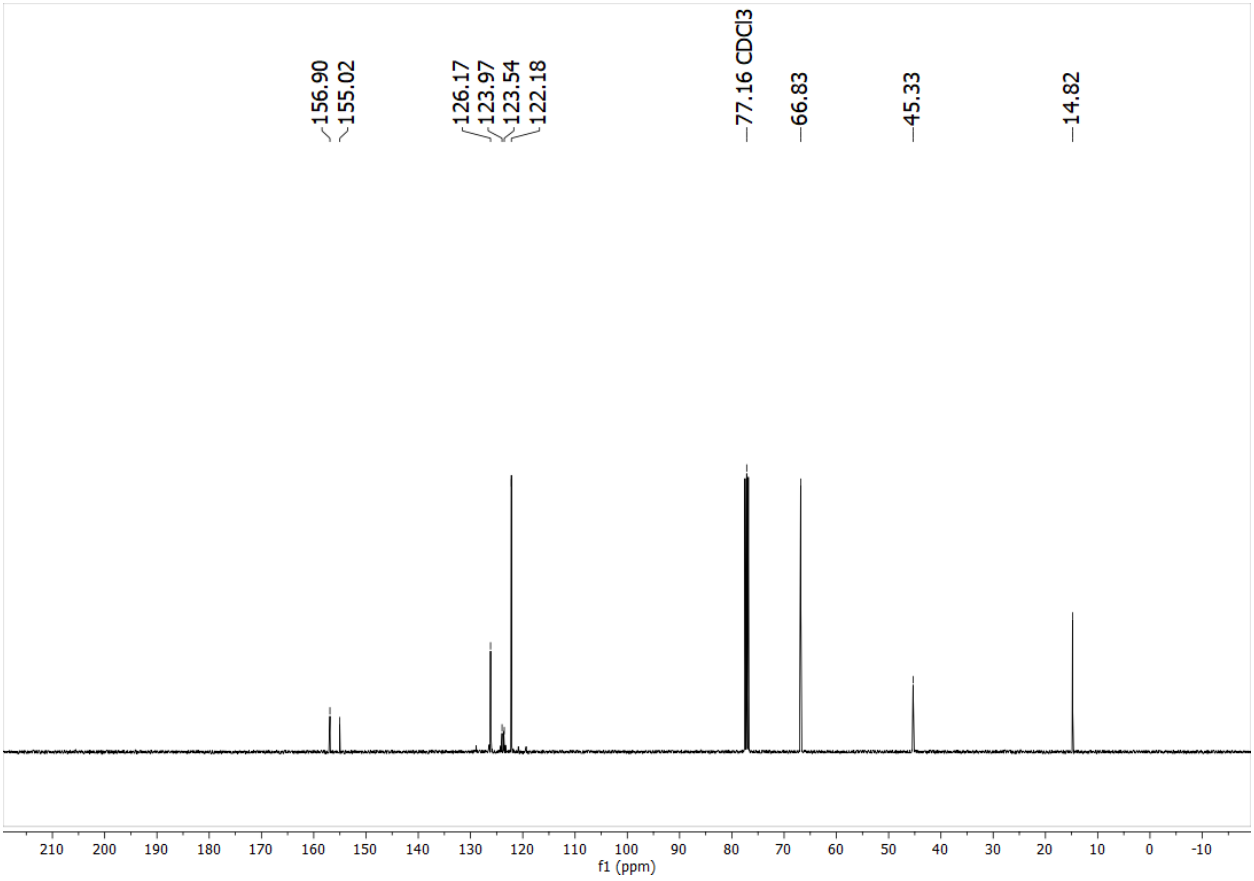
(Z)-1-morpholino-N-(4-trifluoromethylphenyl)ethanimine (2c-a)

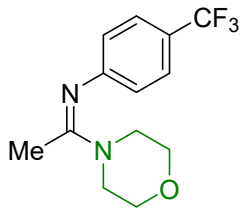
^{1}H NMR: 400 MHz in $CDCl_3$



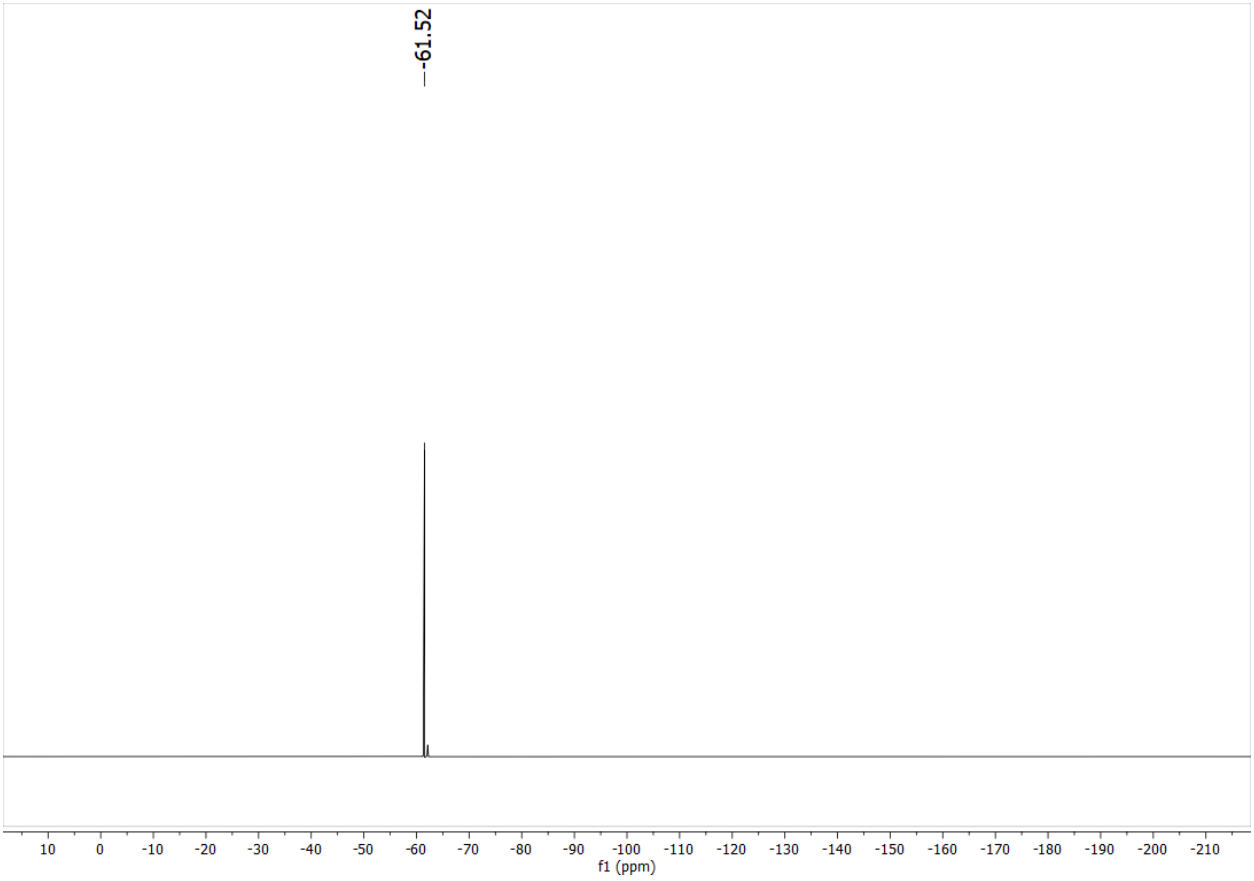


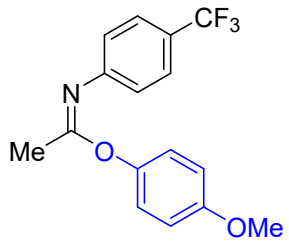
^{13}C NMR: 101 MHz in $CDCl_3$





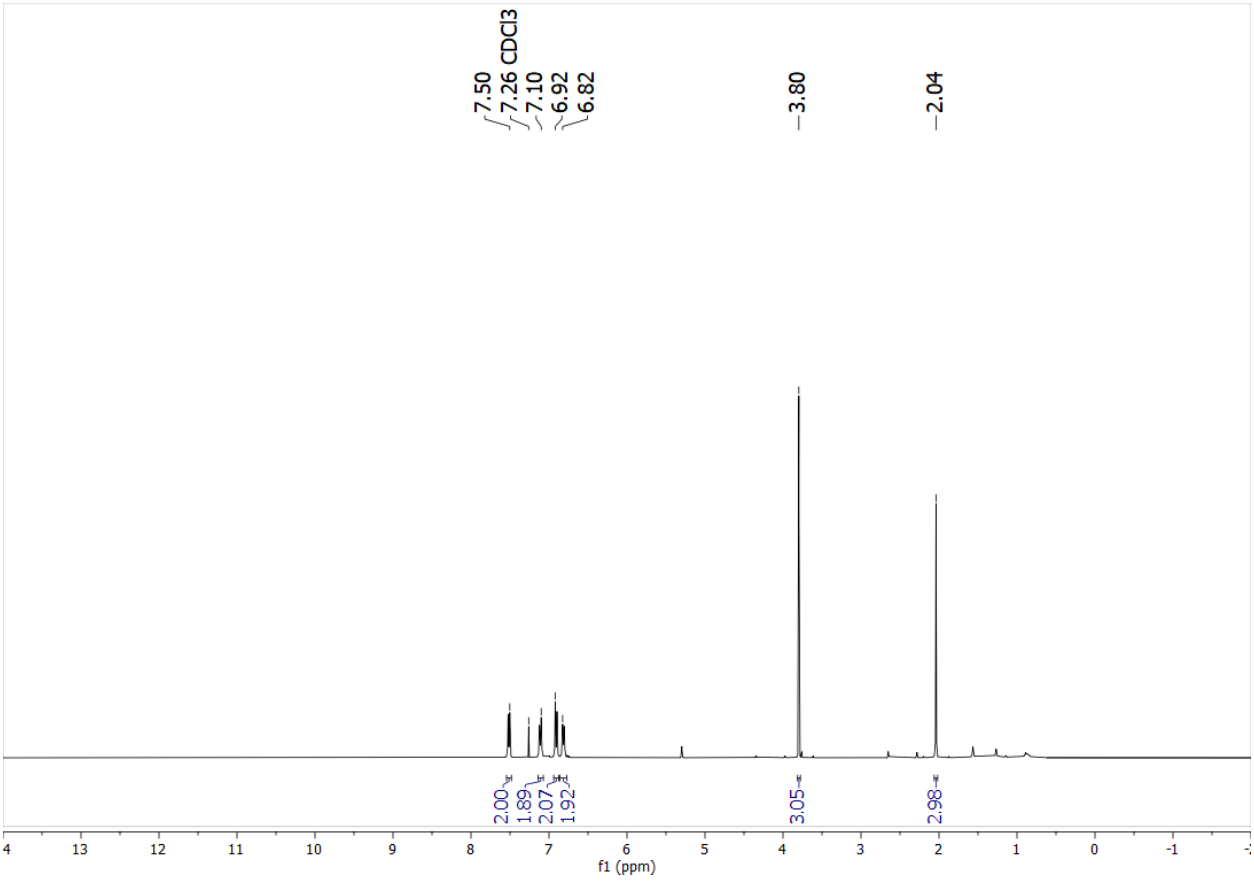
^{19}F NMR: 376 MHz in $CDCl_3$

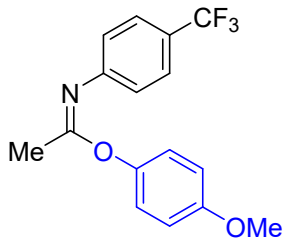




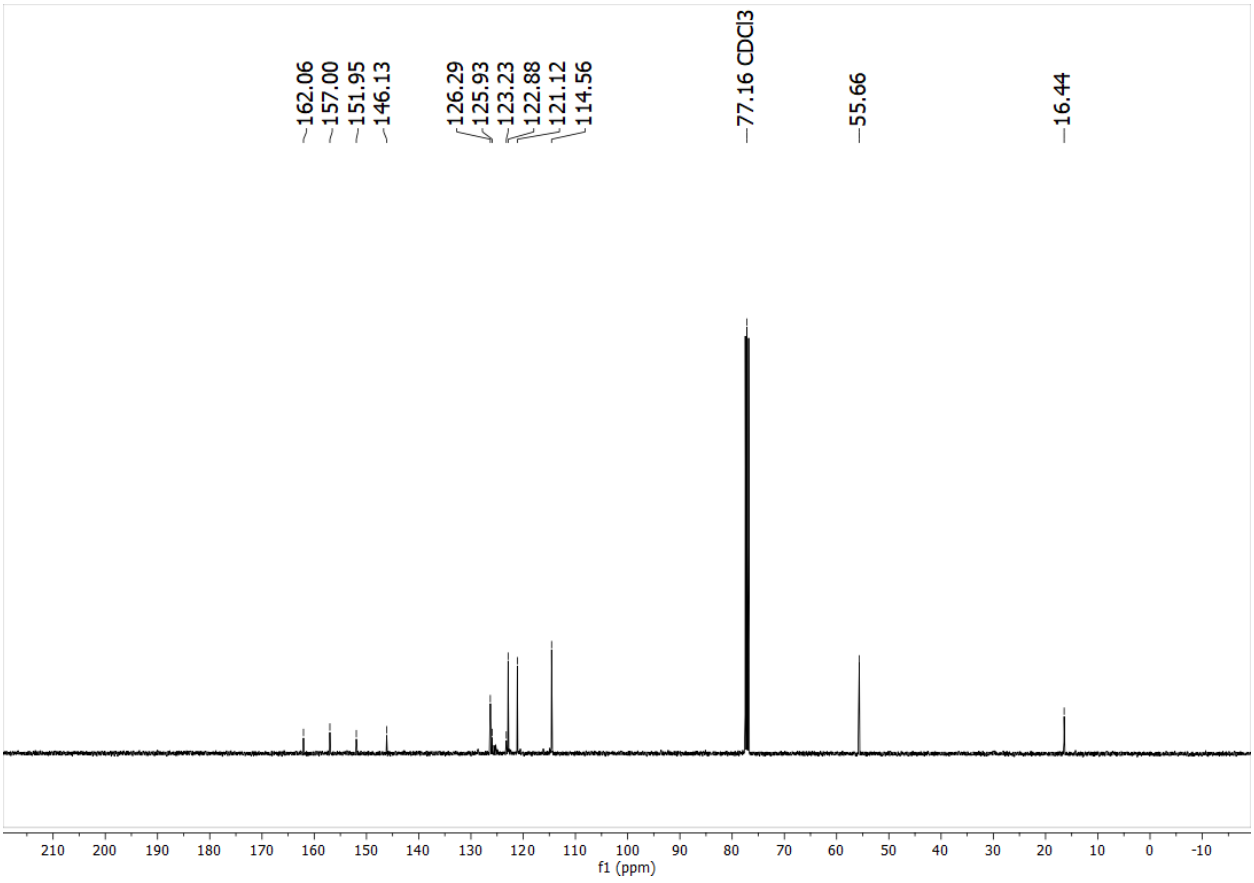
4-methoxyphenyl (Z)-N-(4-trifluoromethylphenyl)acetimidate (2c-i)

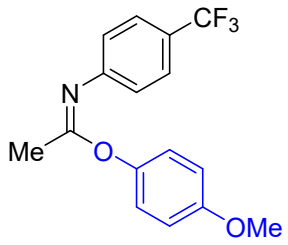
^{1}H NMR: 400 MHz in $CDCl_3$



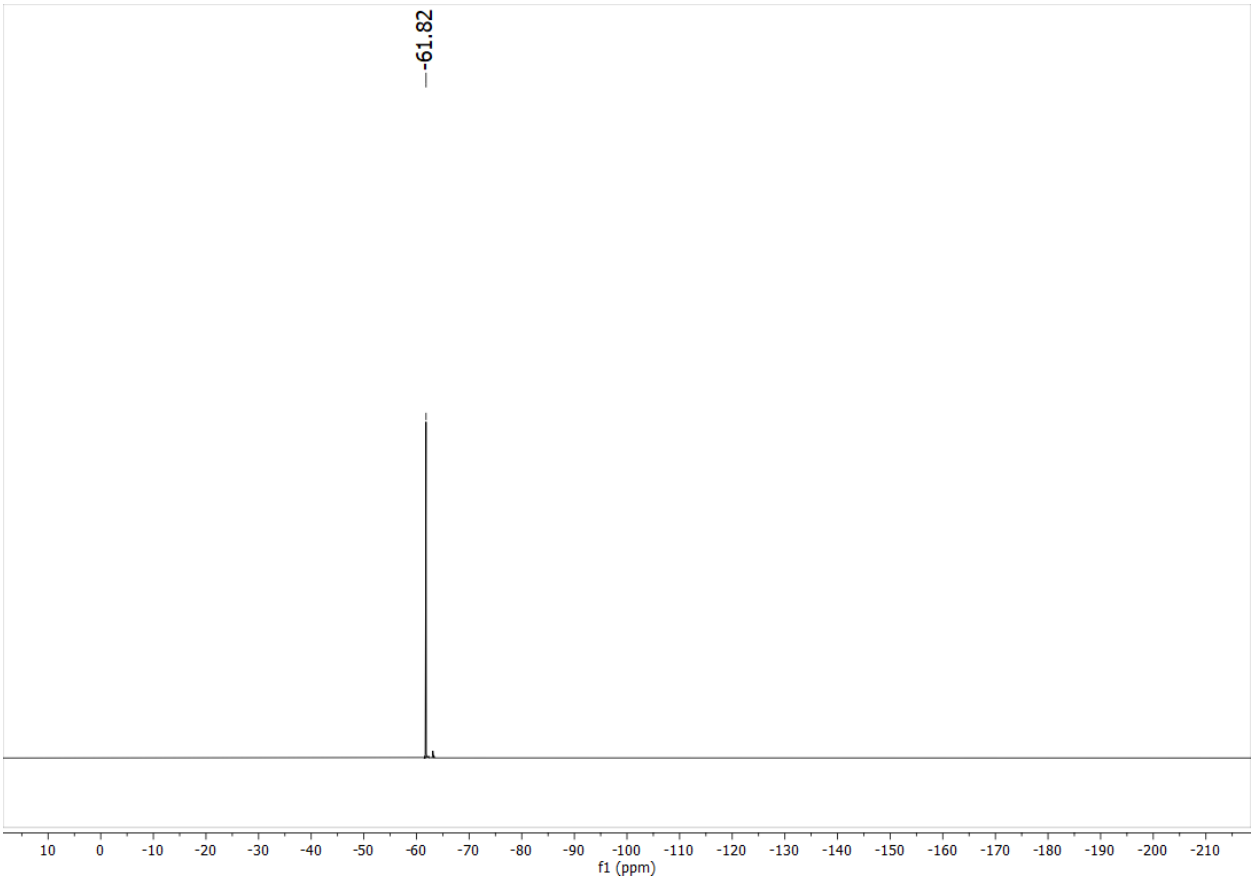


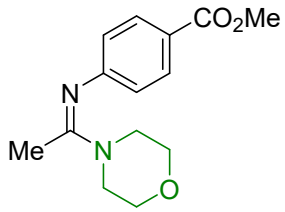
^{13}C NMR: 101 MHz in $CDCl_3$





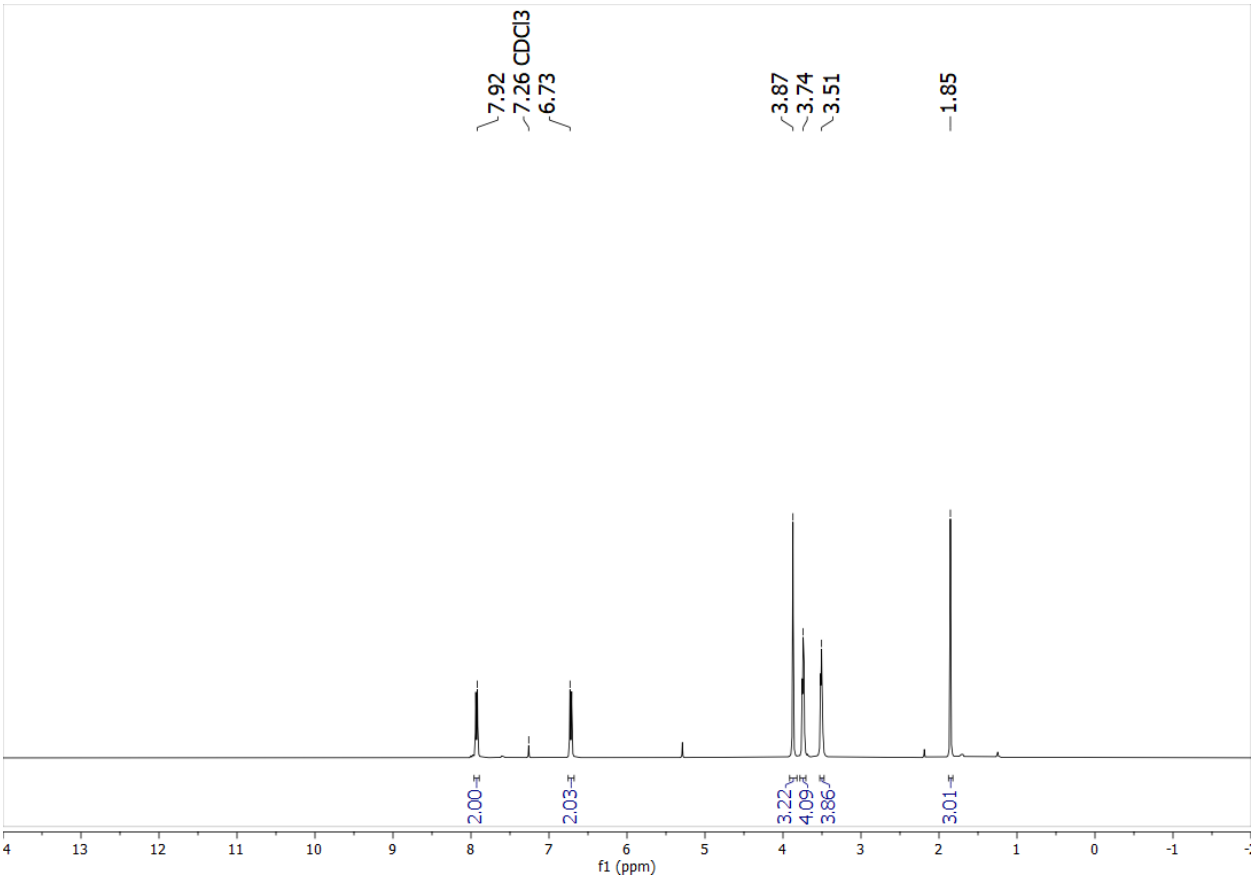
^{19}F NMR: 376 MHz in $CDCl_3$

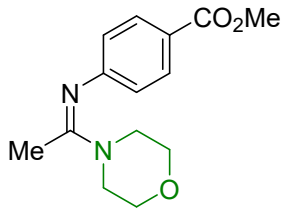




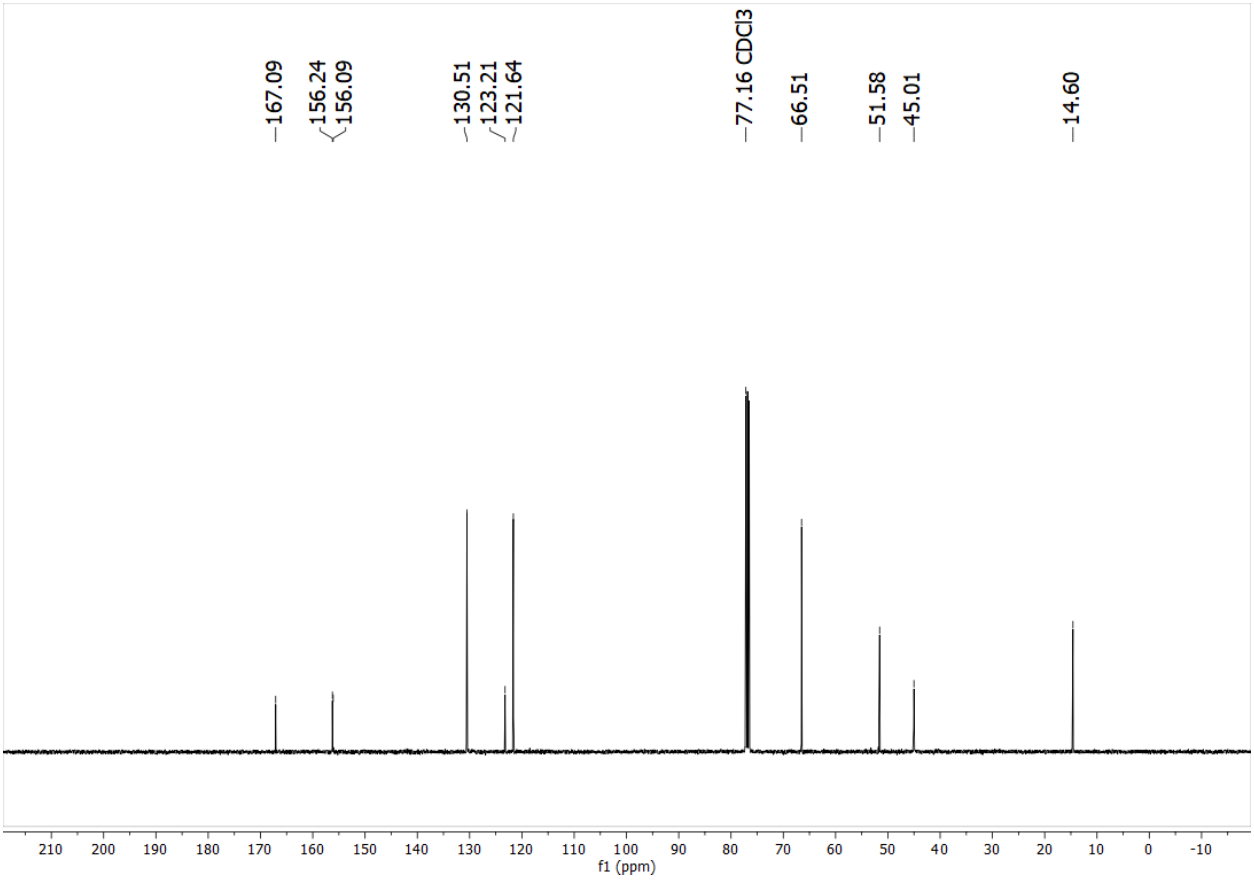
methyl (Z)-4-((1-morpholinoethylidene)amino)benzoate (2d-a)

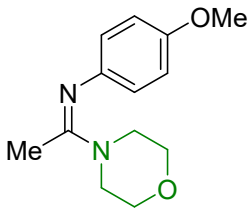
^{1}H NMR: 400 MHz in $CDCl_3$





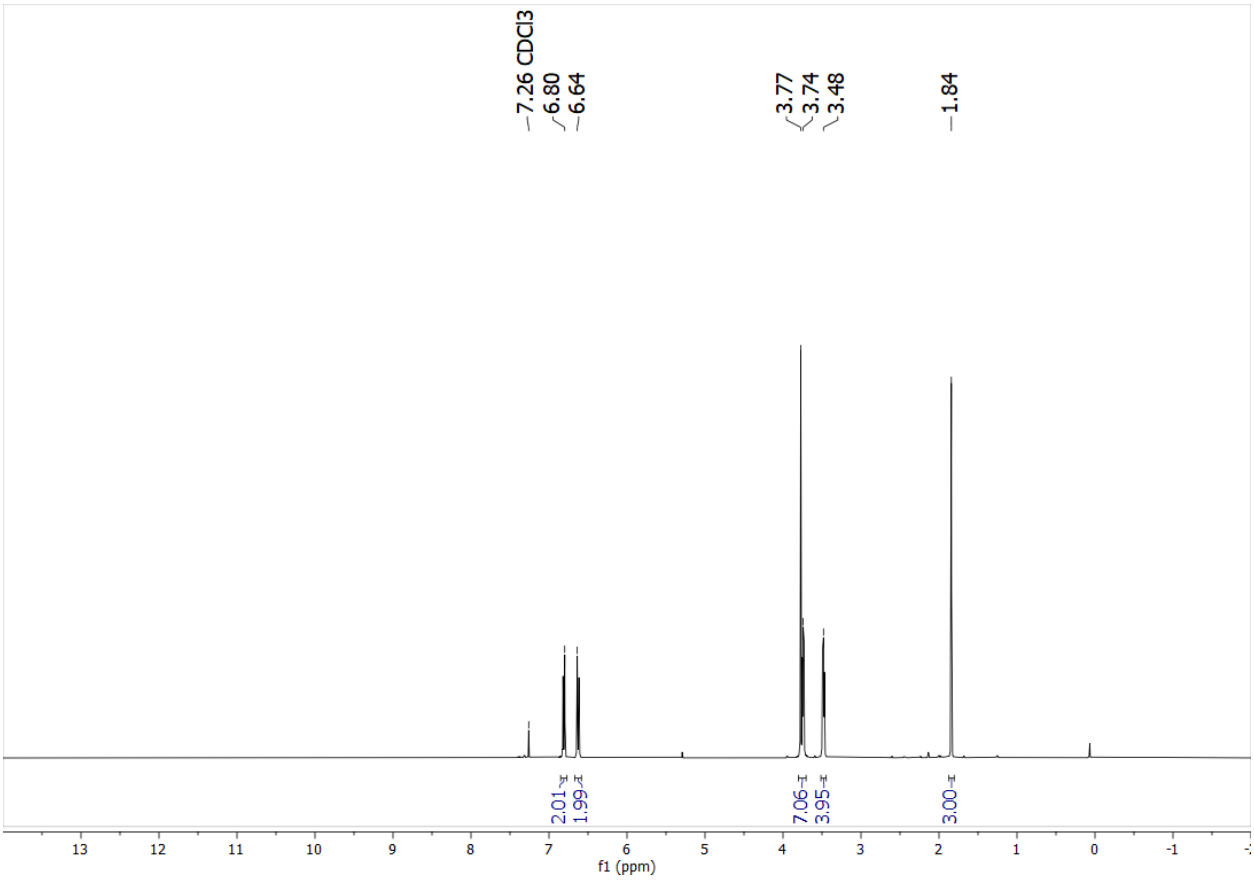
^{13}C NMR: 101 MHz in $CDCl_3$

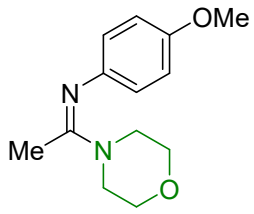




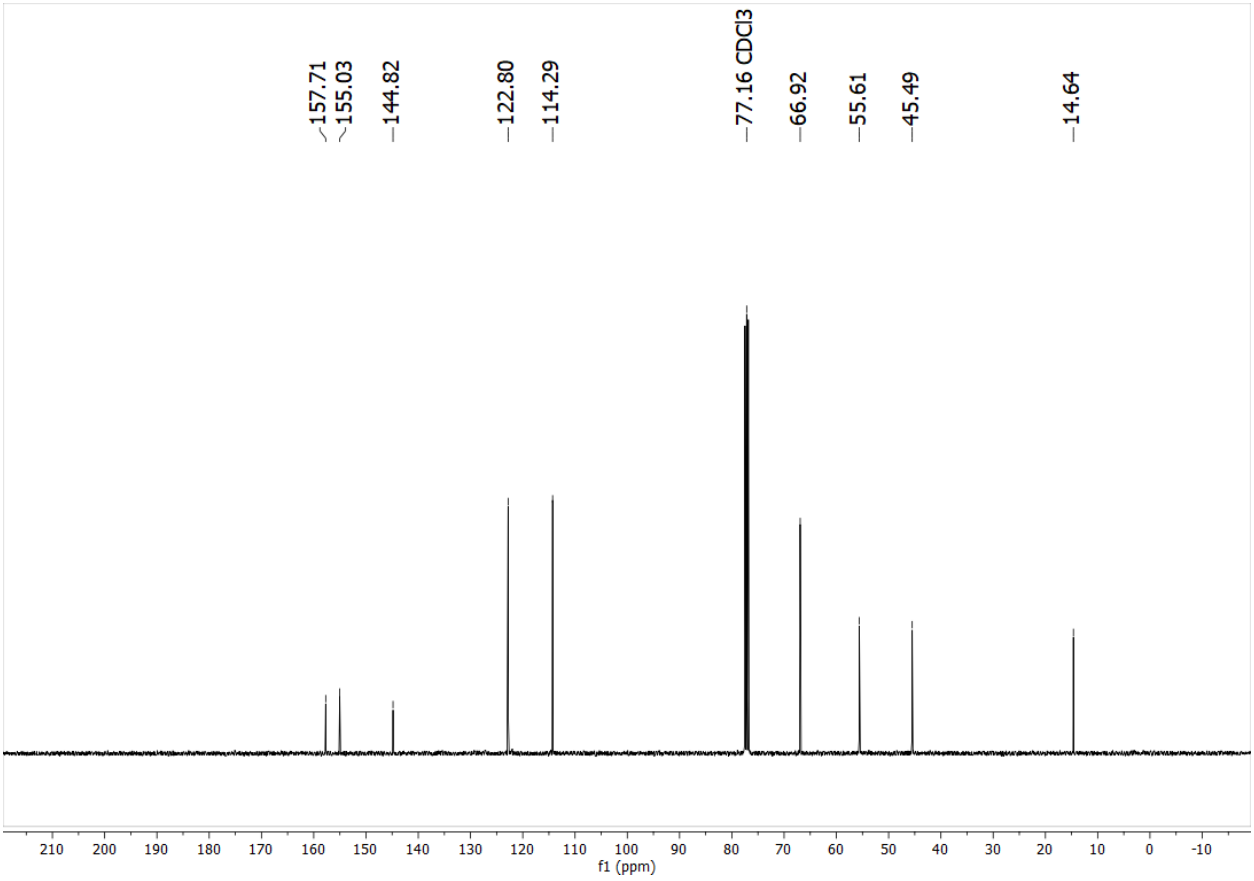
(Z)-1-morpholino-N-(4-methoxyphenyl)ethanimine (2e-a)

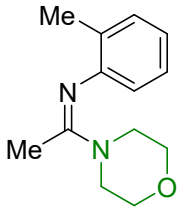
^{1}H NMR: 400 MHz in $CDCl_3$





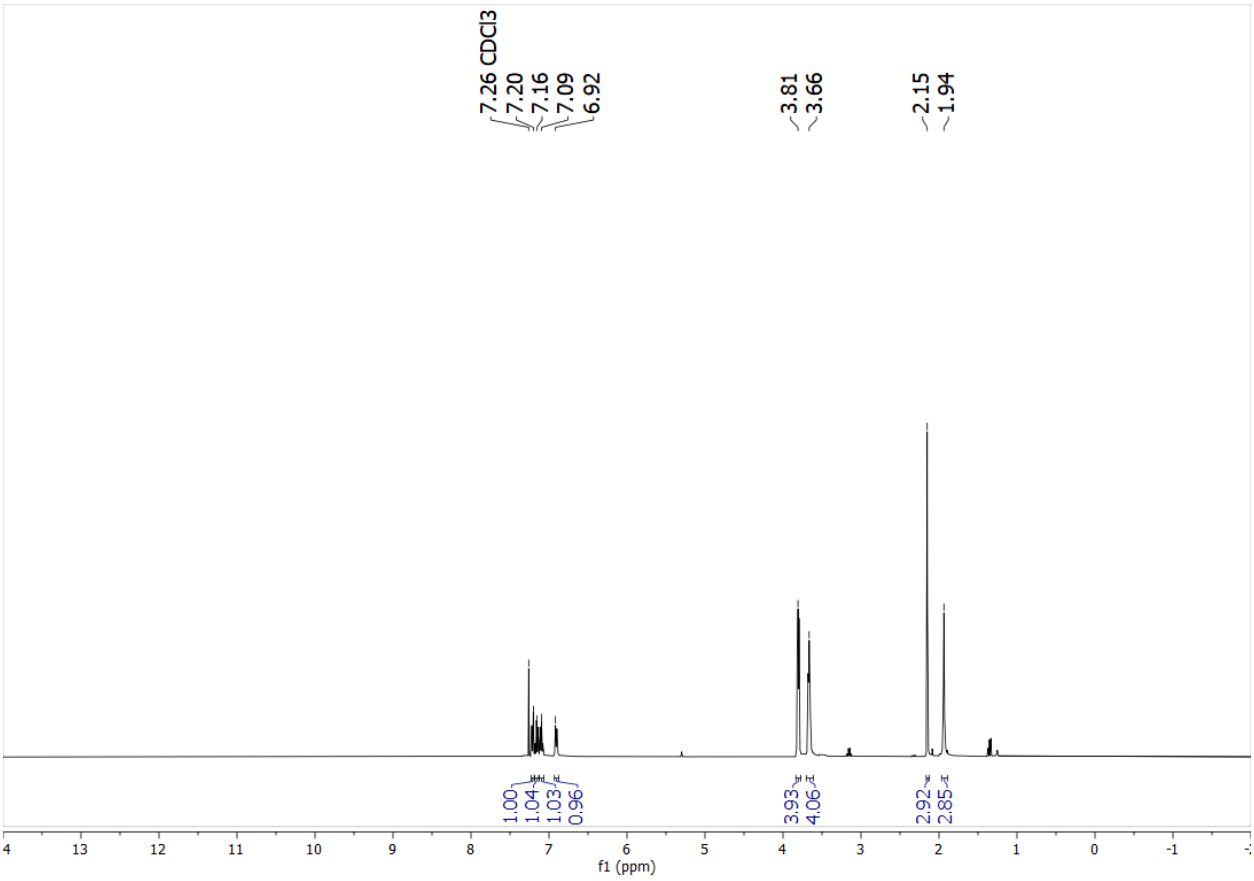
^{13}C NMR: 101 MHz in $CDCl_3$

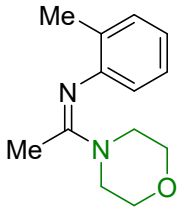




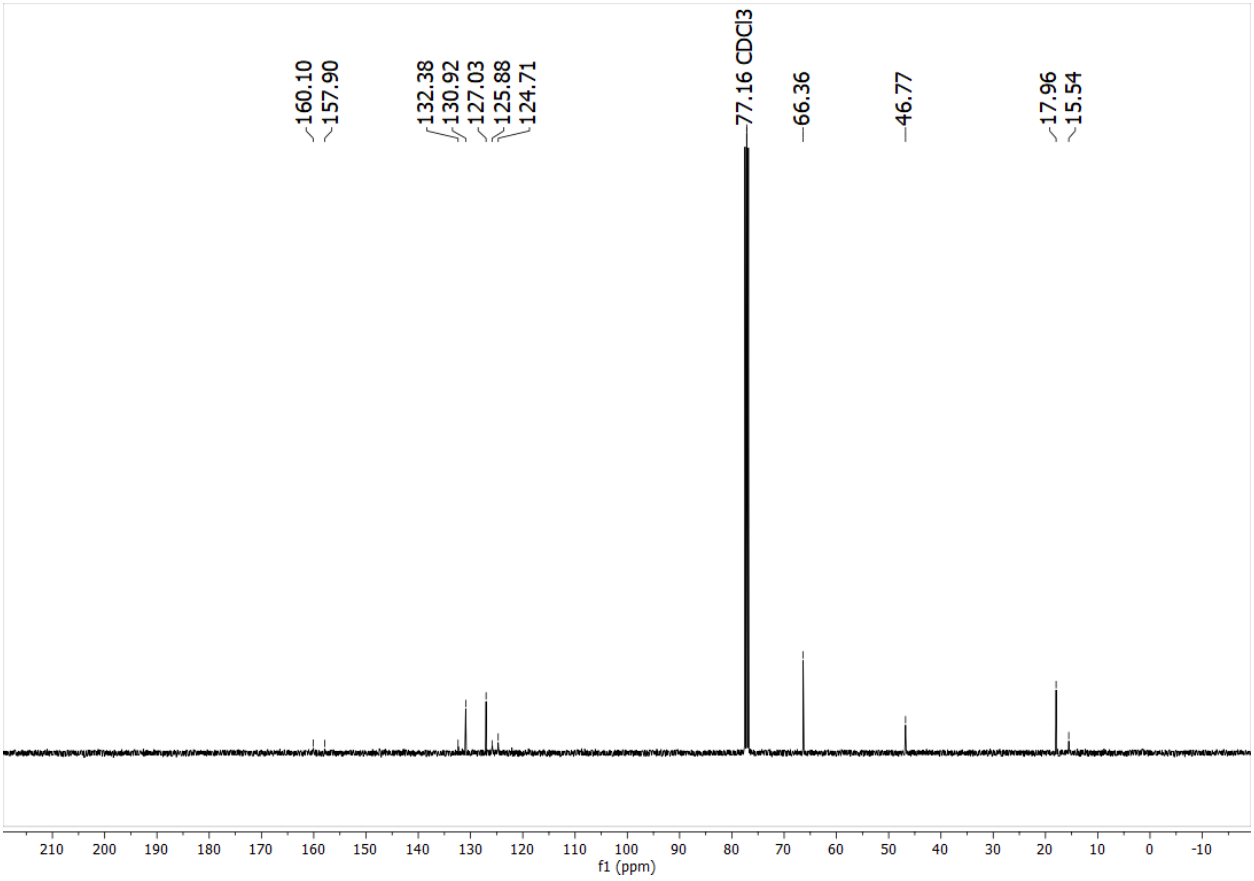
(Z)-1-morpholino-N-(o-tolyl)ethanimine (2f-a)

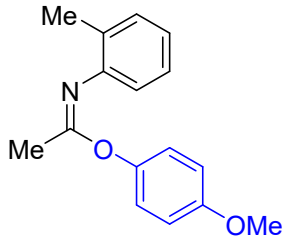
^{1}H NMR: 400 MHz in $CDCl_3$





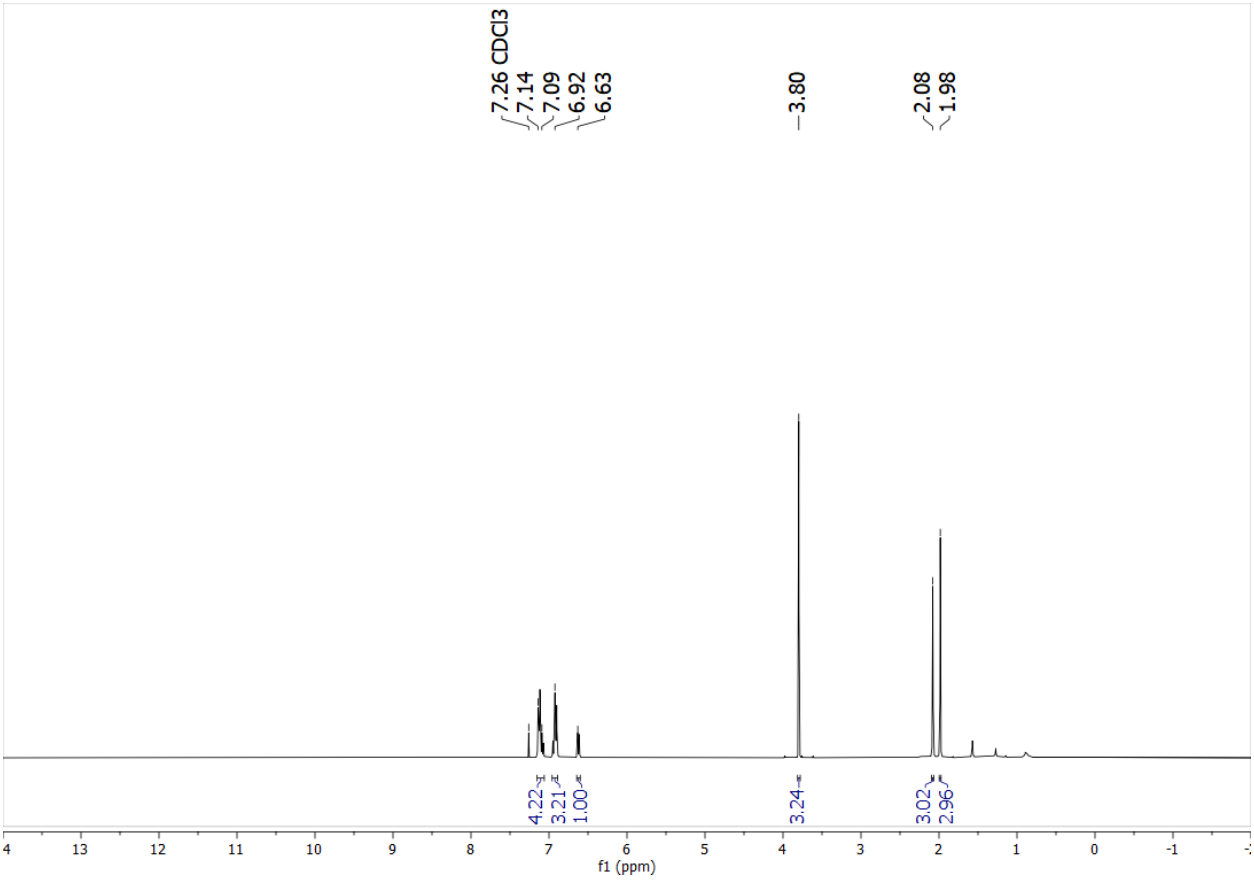
^{13}C NMR: 101 MHz in $CDCl_3$

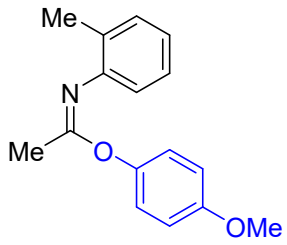




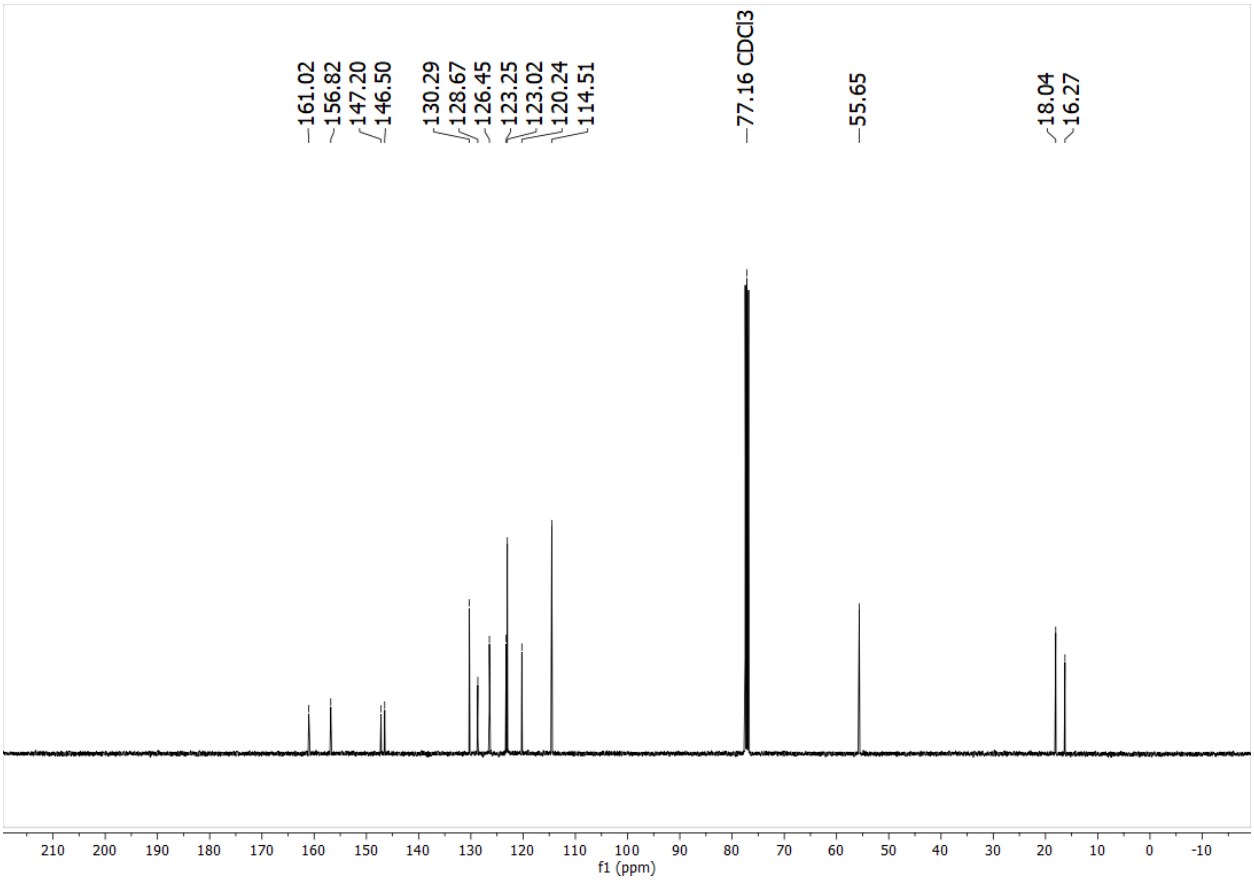
4-methoxyphenyl (Z)-N-(o-tolyl)acetimidate (2f-i)

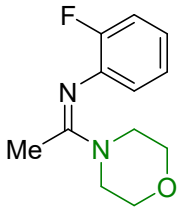
^{1}H NMR: 400 MHz in $CDCl_3$





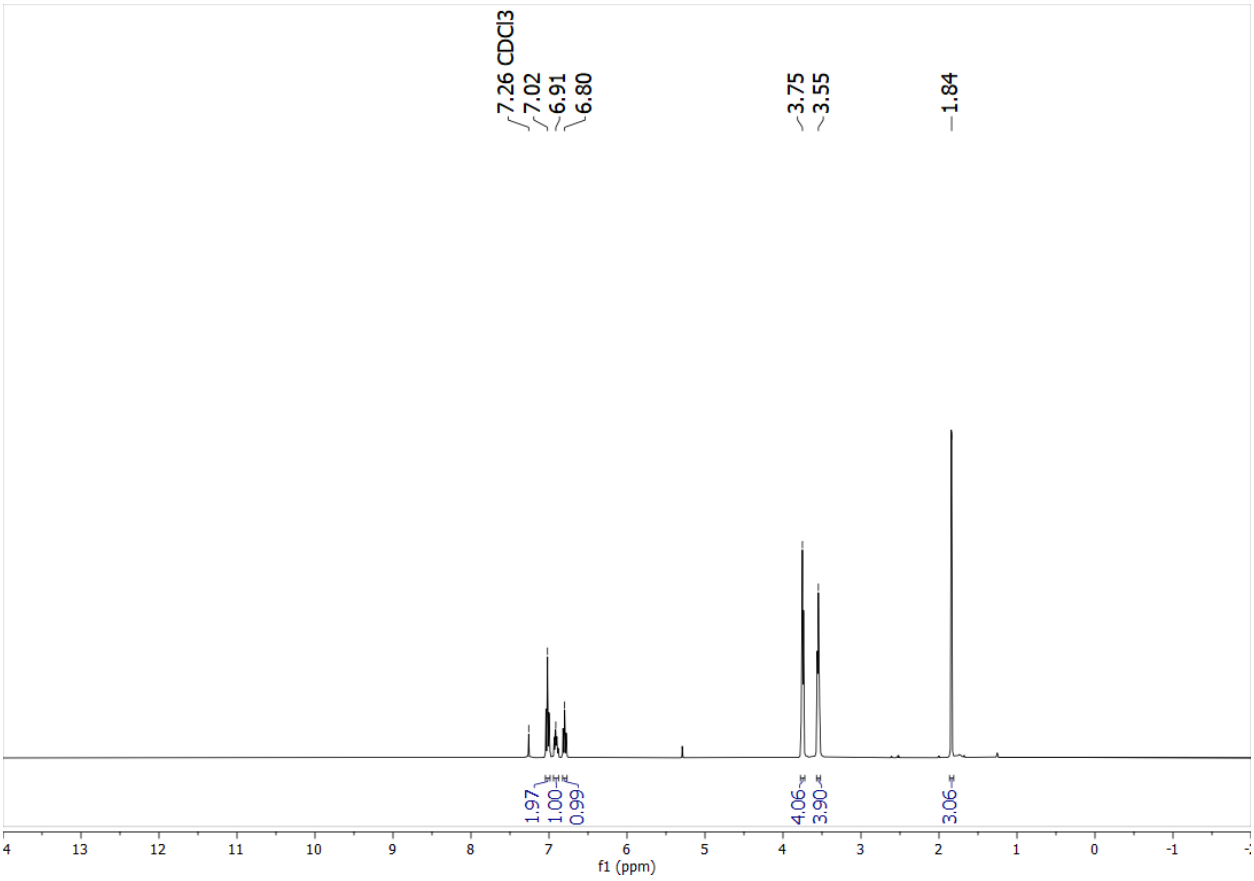
^{13}C NMR: 101 MHz in $CDCl_3$

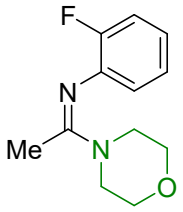




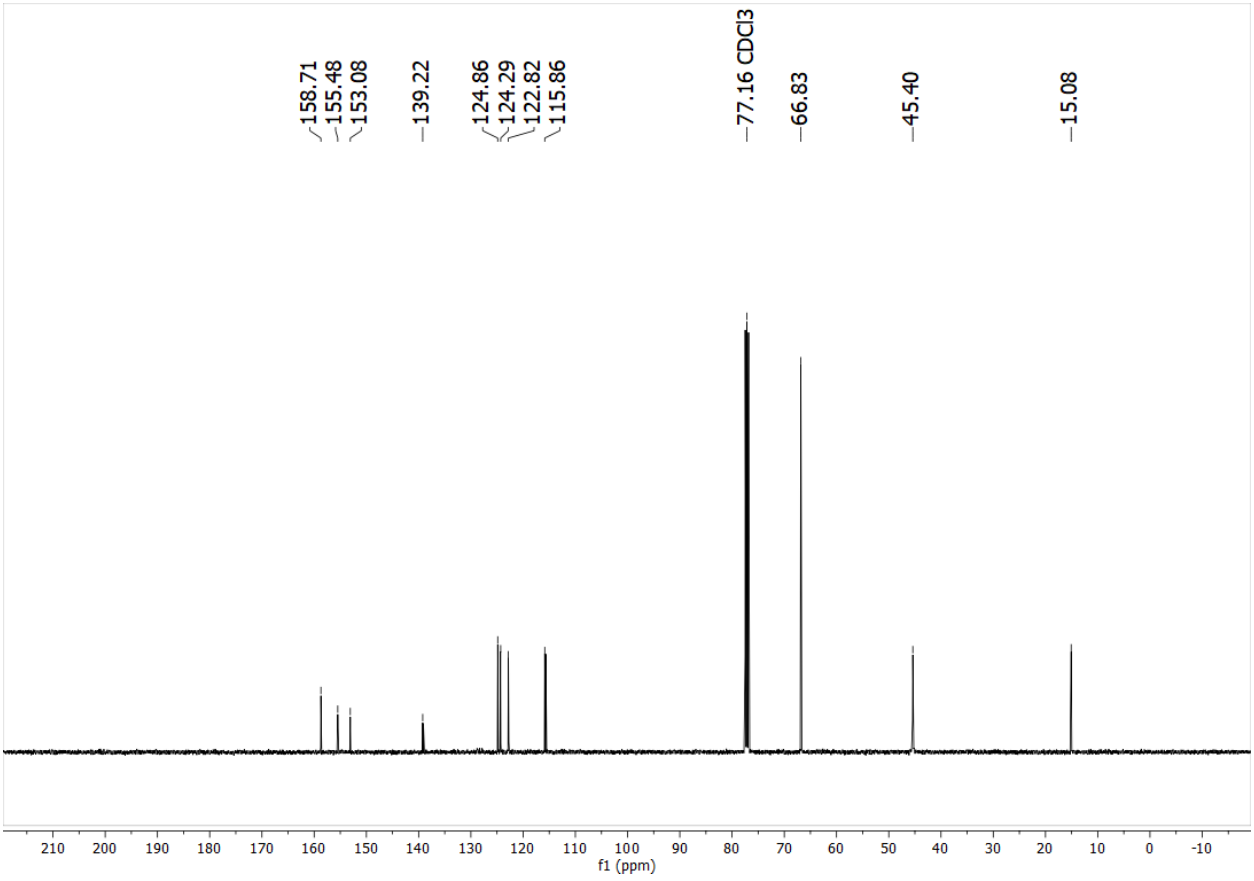
(Z)-1-morpholino-N-(2-fluorophenyl)ethanimine (2g-a)

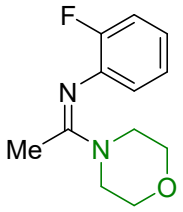
^{1}H NMR: 400 MHz in $CDCl_3$



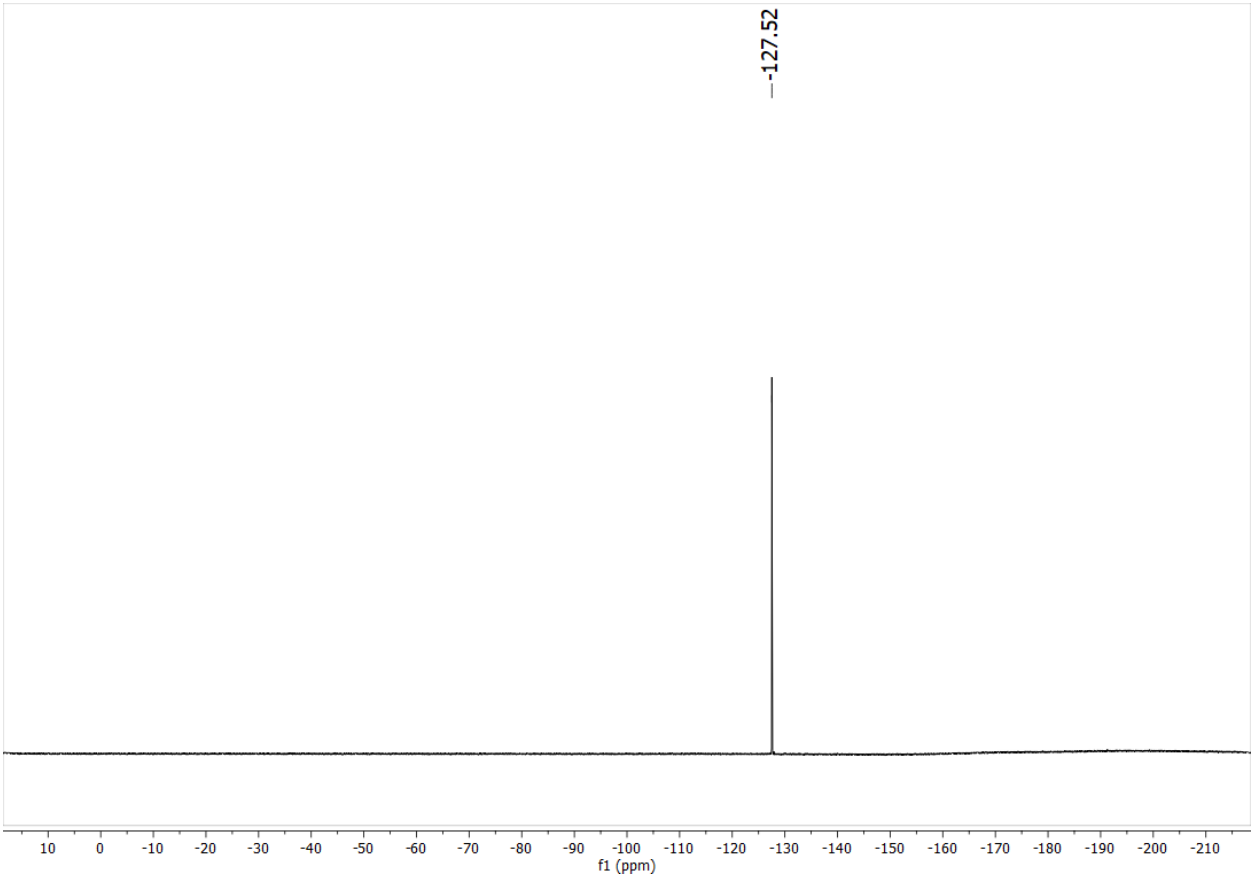


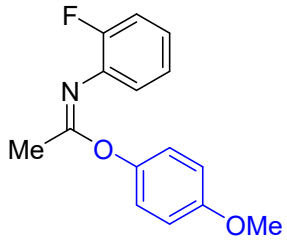
^{13}C NMR: 101 MHz in $CDCl_3$





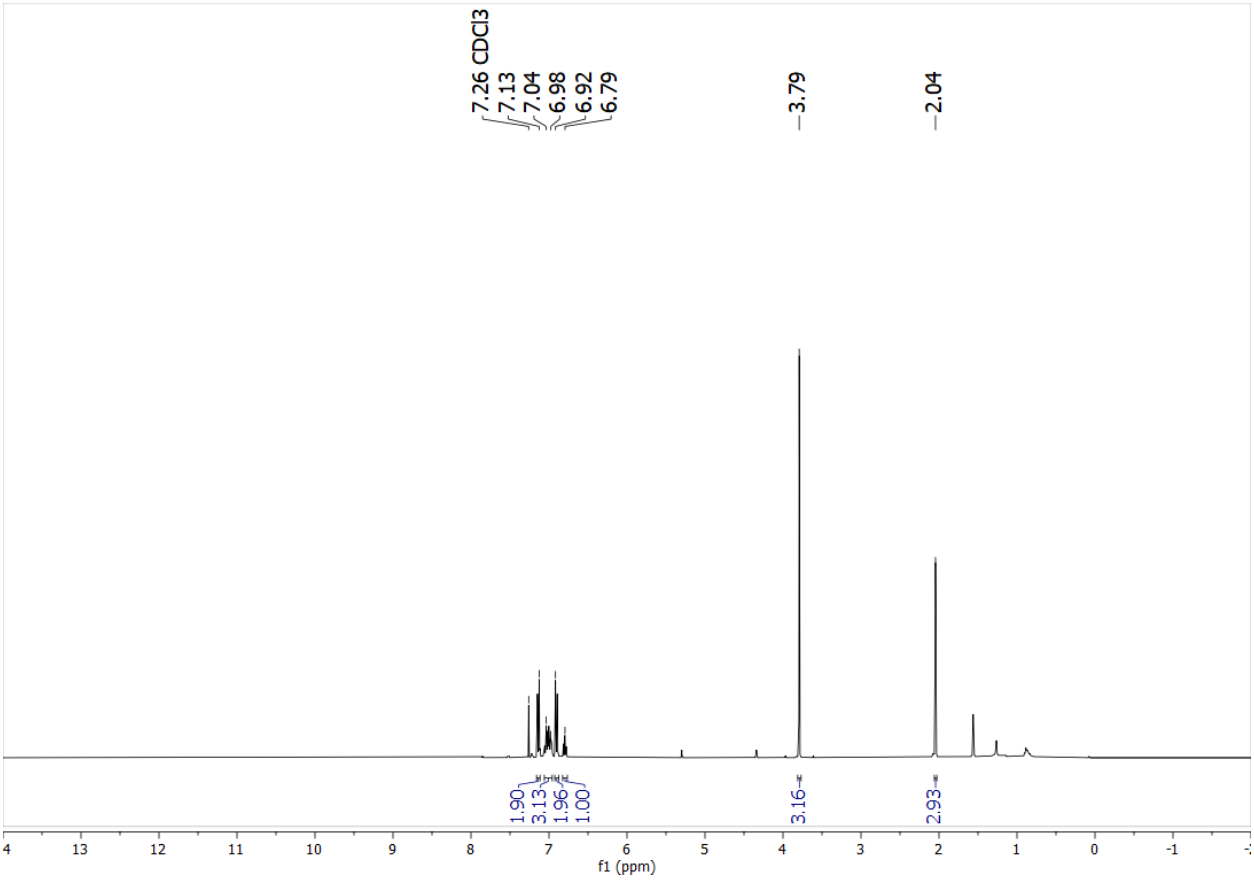
^{19}F NMR: 376 MHz in $CDCl_3$

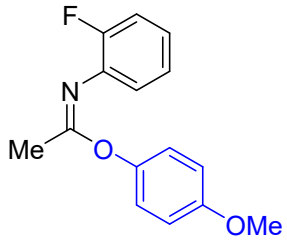




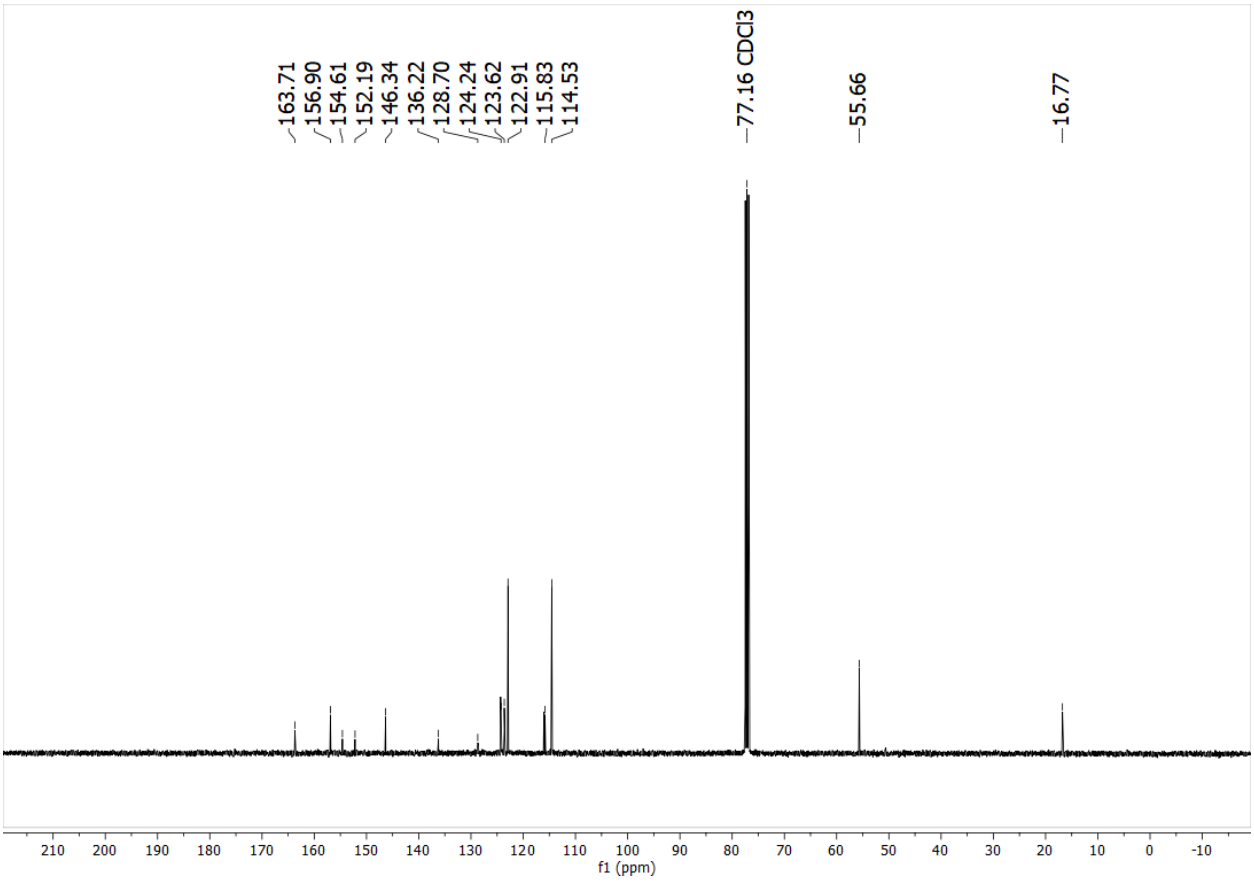
4-methoxyphenyl (Z)-N-(2-fluorophenyl)acetimidate (2g-i)

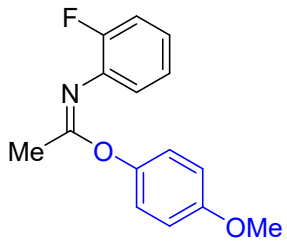
^{1}H NMR: 400 MHz in $CDCl_3$



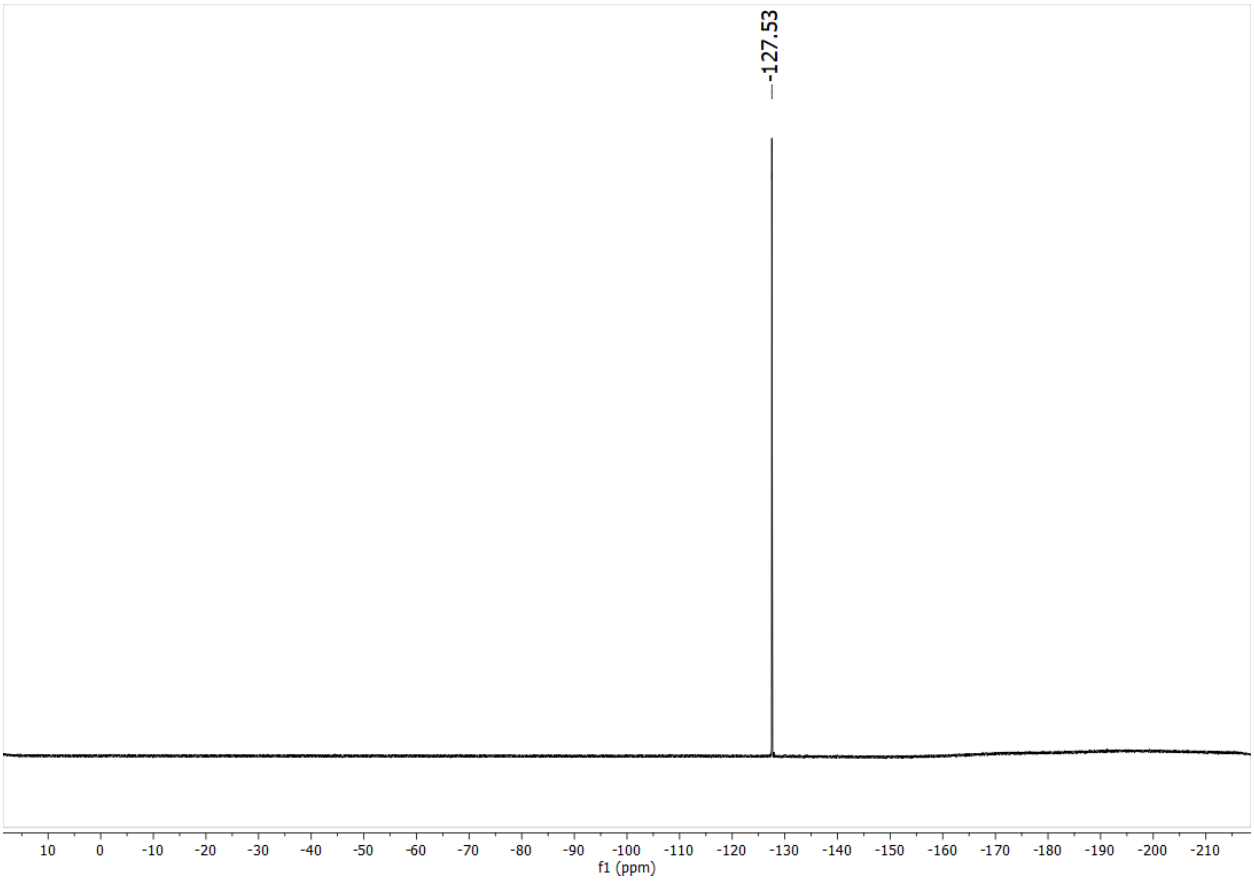


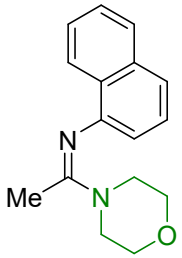
^{13}C NMR: 101 MHz in $CDCl_3$





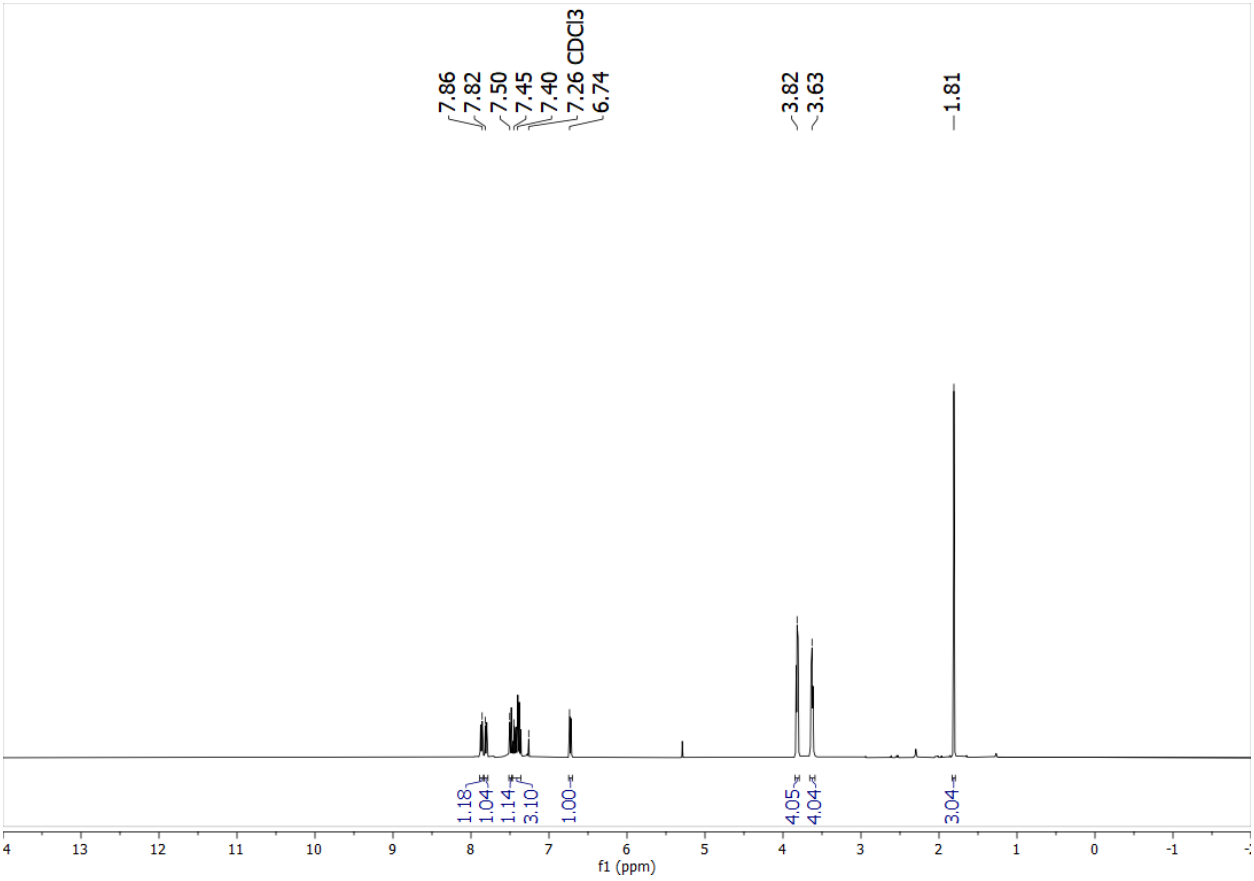
^{19}F NMR: 376 MHz in $CDCl_3$

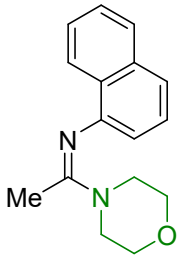




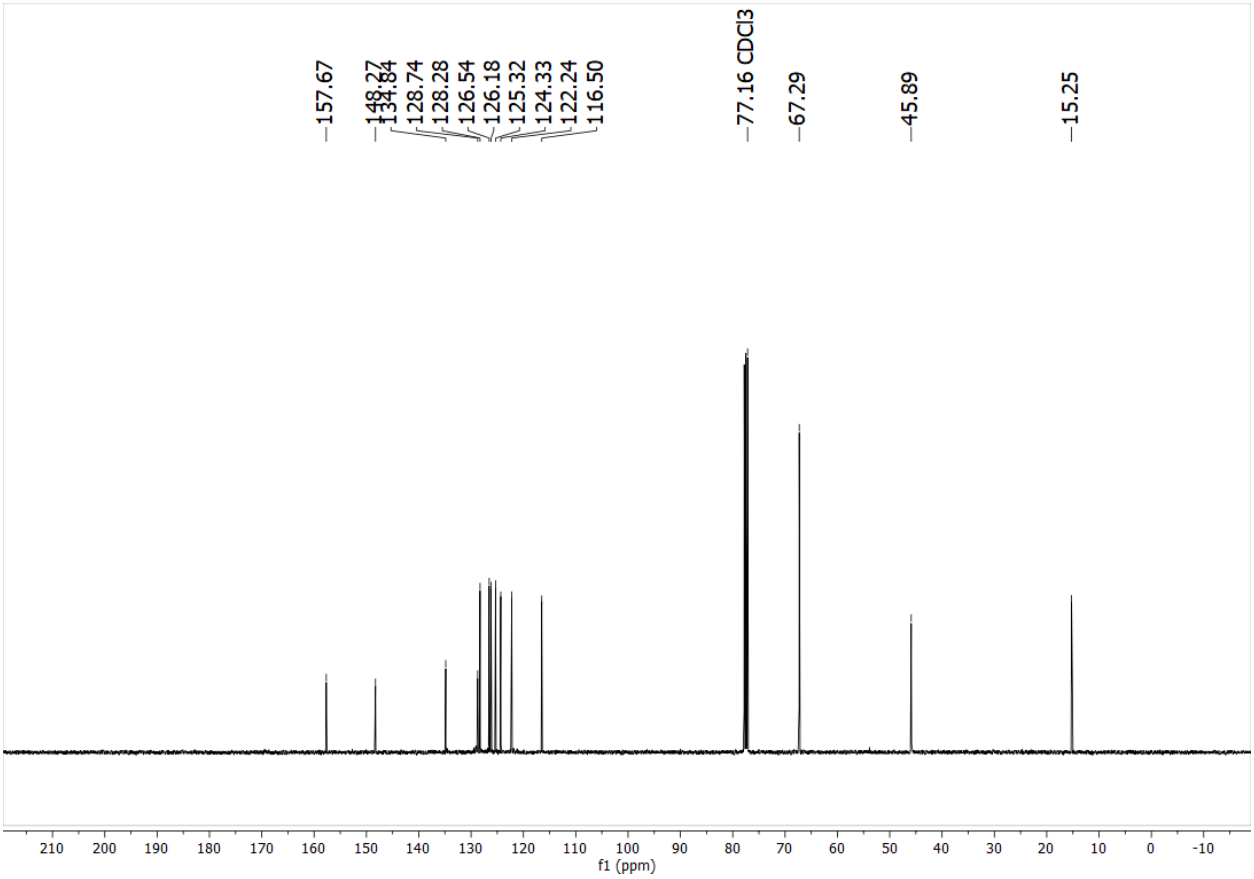
(Z)-1-morpholino-N-(1-naphthyl)ethanimine (2h-a)

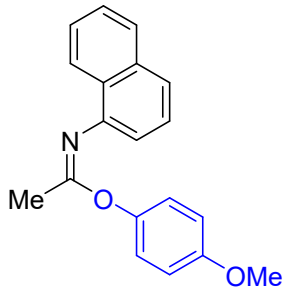
^{1}H NMR: 400 MHz in $CDCl_3$





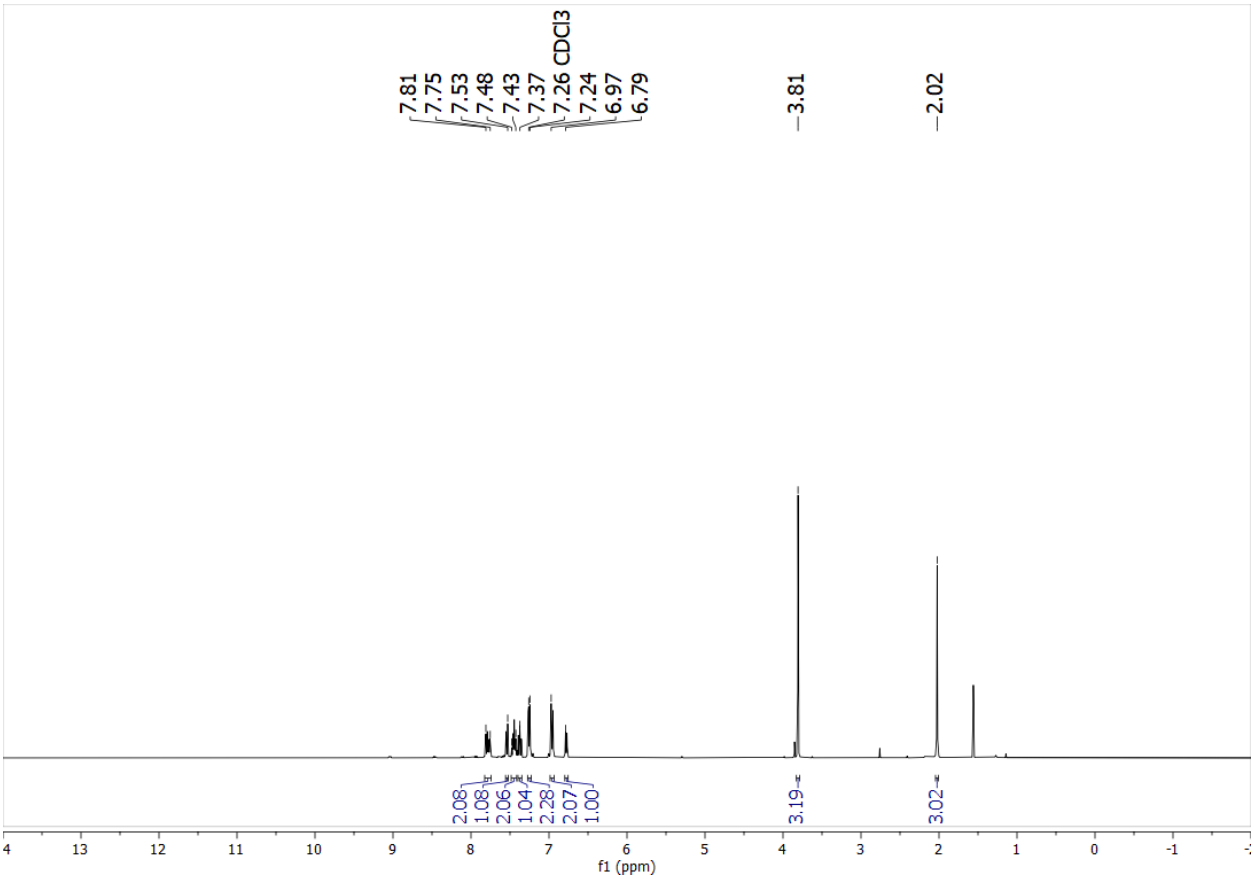
^{13}C NMR: 101 MHz in $CDCl_3$

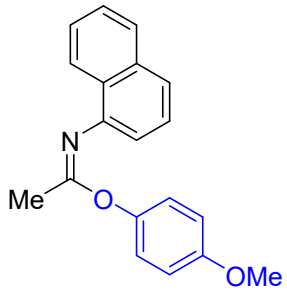




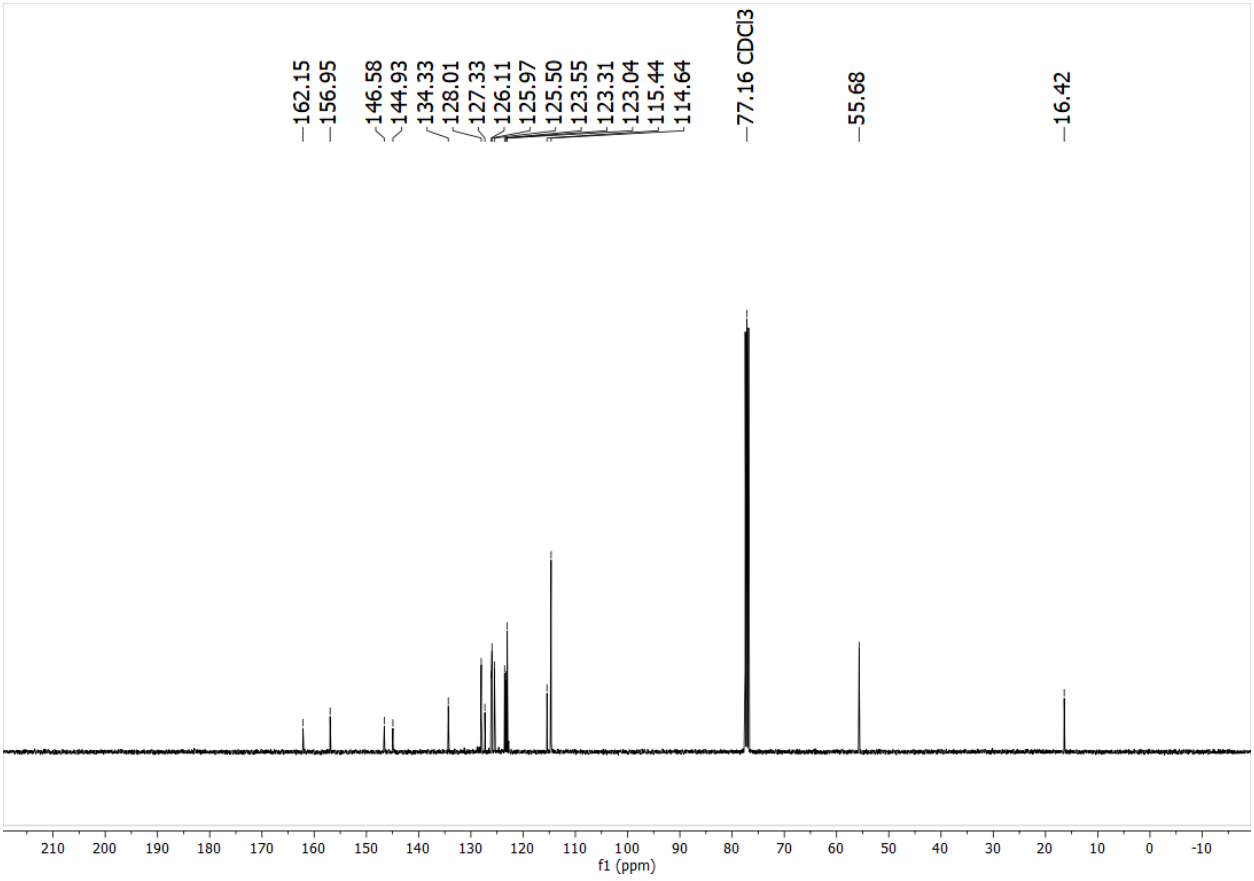
4-methoxyphenyl (Z)-N-(1-naphthyl)acetimidate (2h-i)

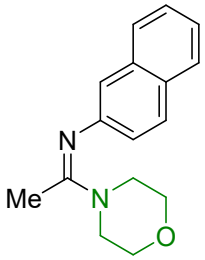
^{1}H NMR: 400 MHz in $CDCl_3$





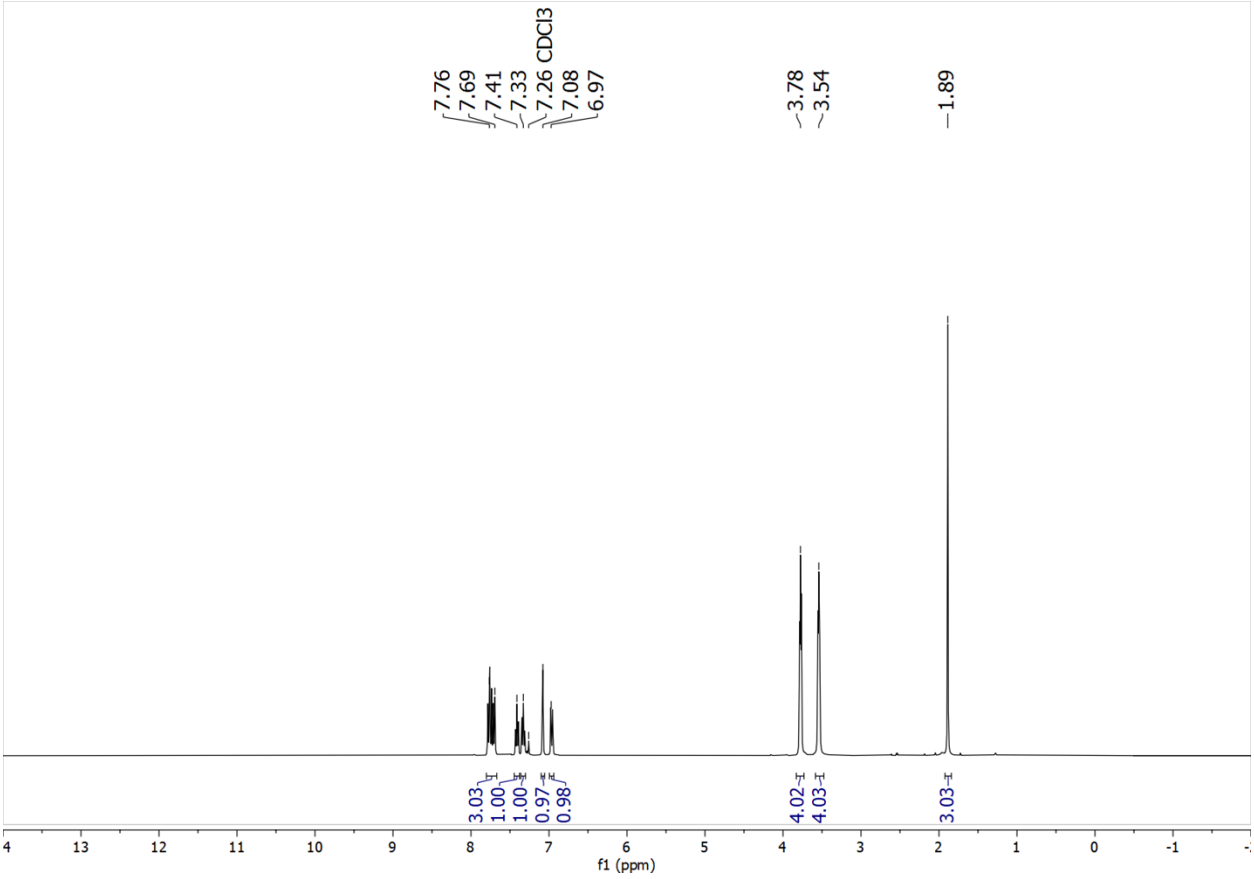
^{13}C NMR: 101 MHz in $CDCl_3$

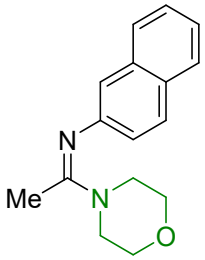




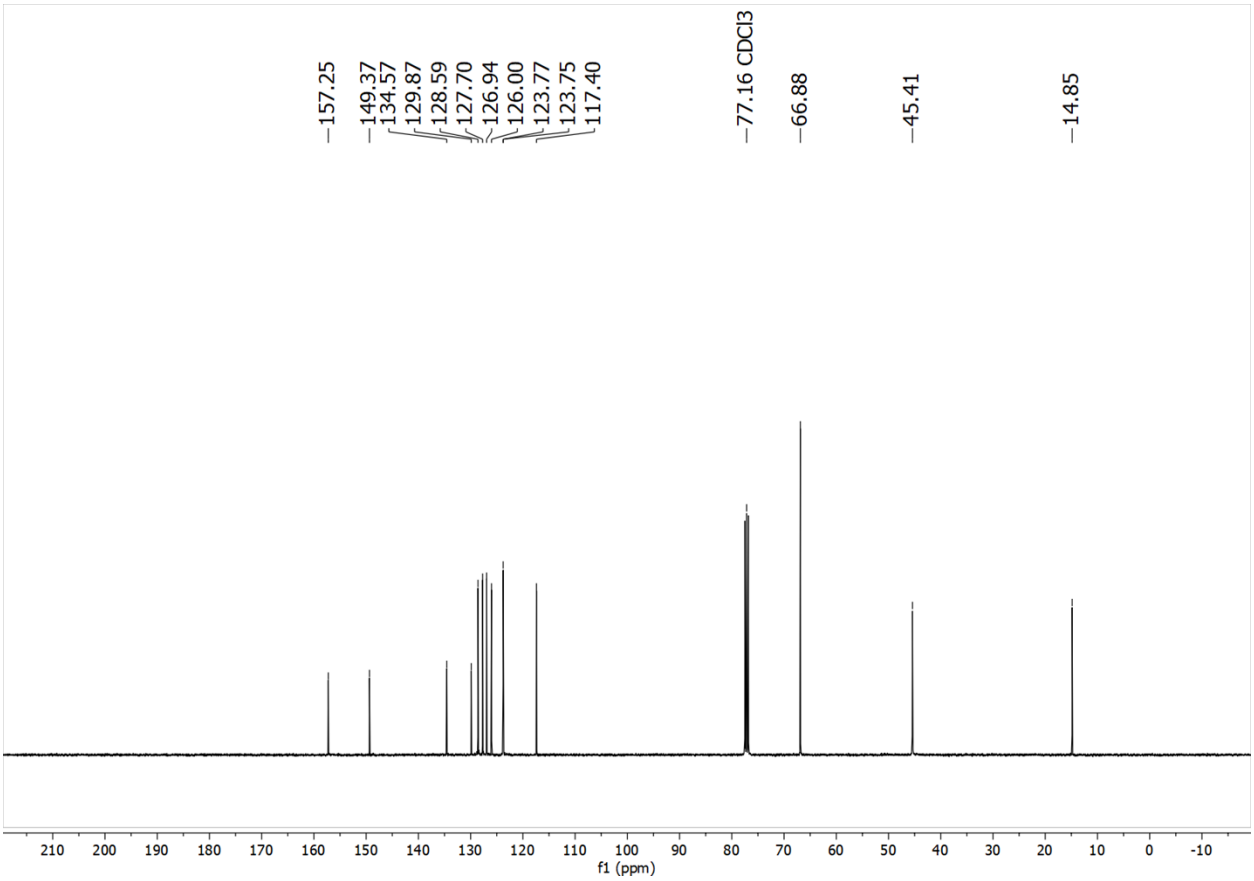
(Z)-1-morpholino-N-(2-naphthyl)ethanimine (2i-a)

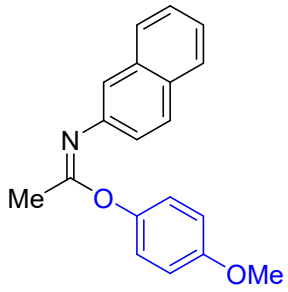
^{1}H NMR: 400 MHz in $CDCl_3$





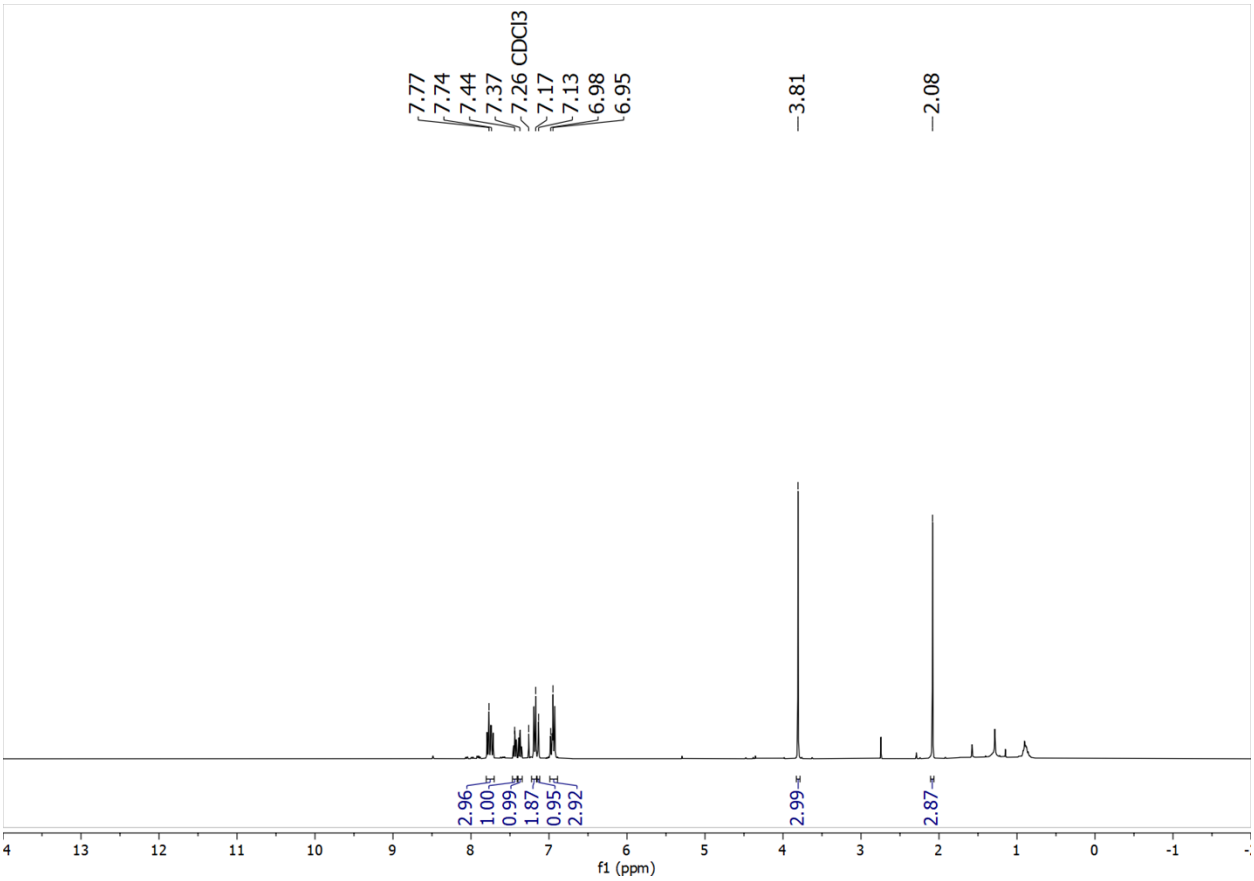
^{13}C NMR: 101 MHz in $CDCl_3$

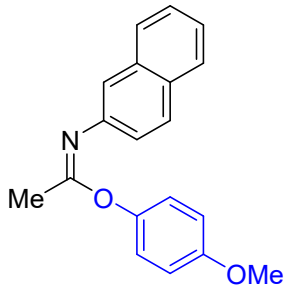




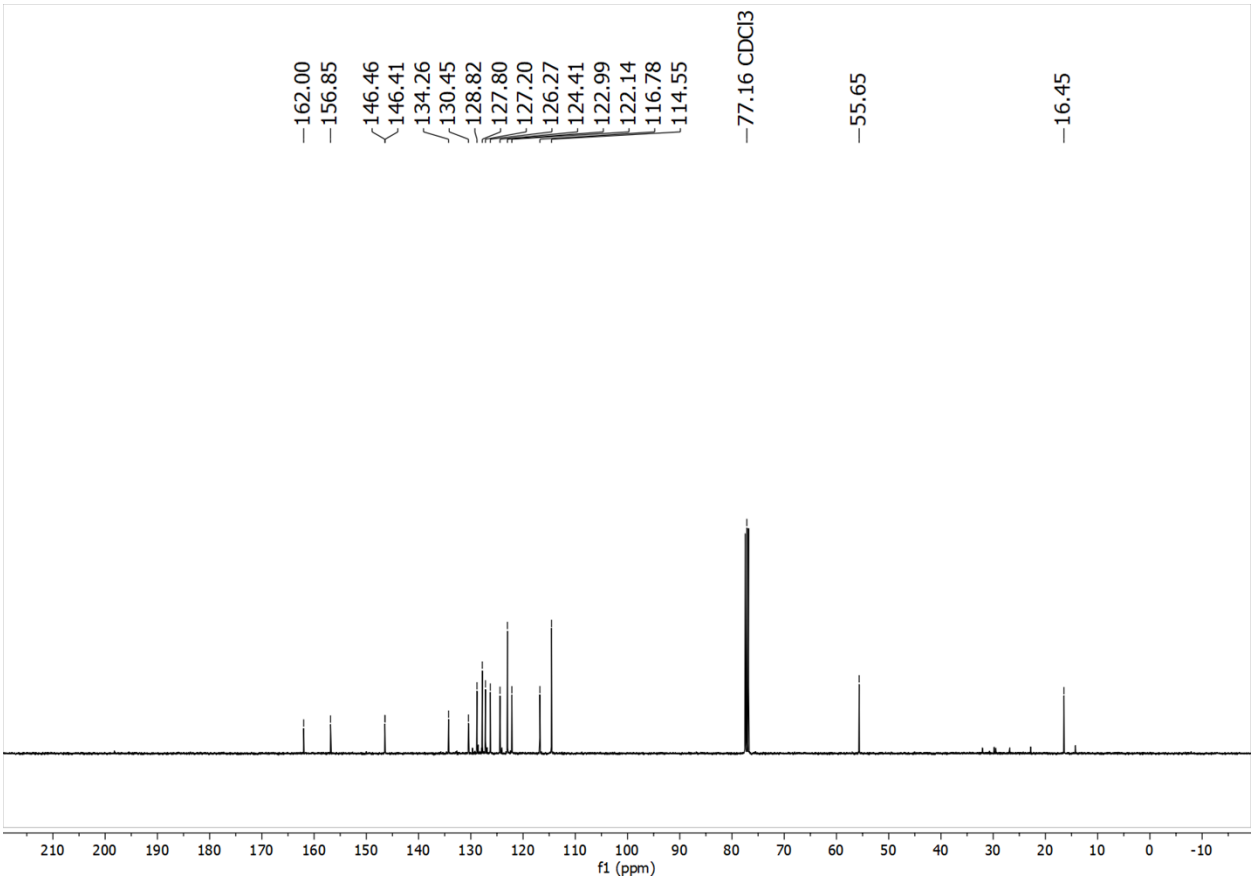
4-methoxyphenyl (Z)-N-(2-naphthyl)acetimidate (2i-i)

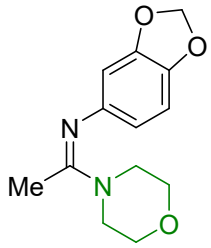
^{1}H NMR: 400 MHz in $CDCl_3$





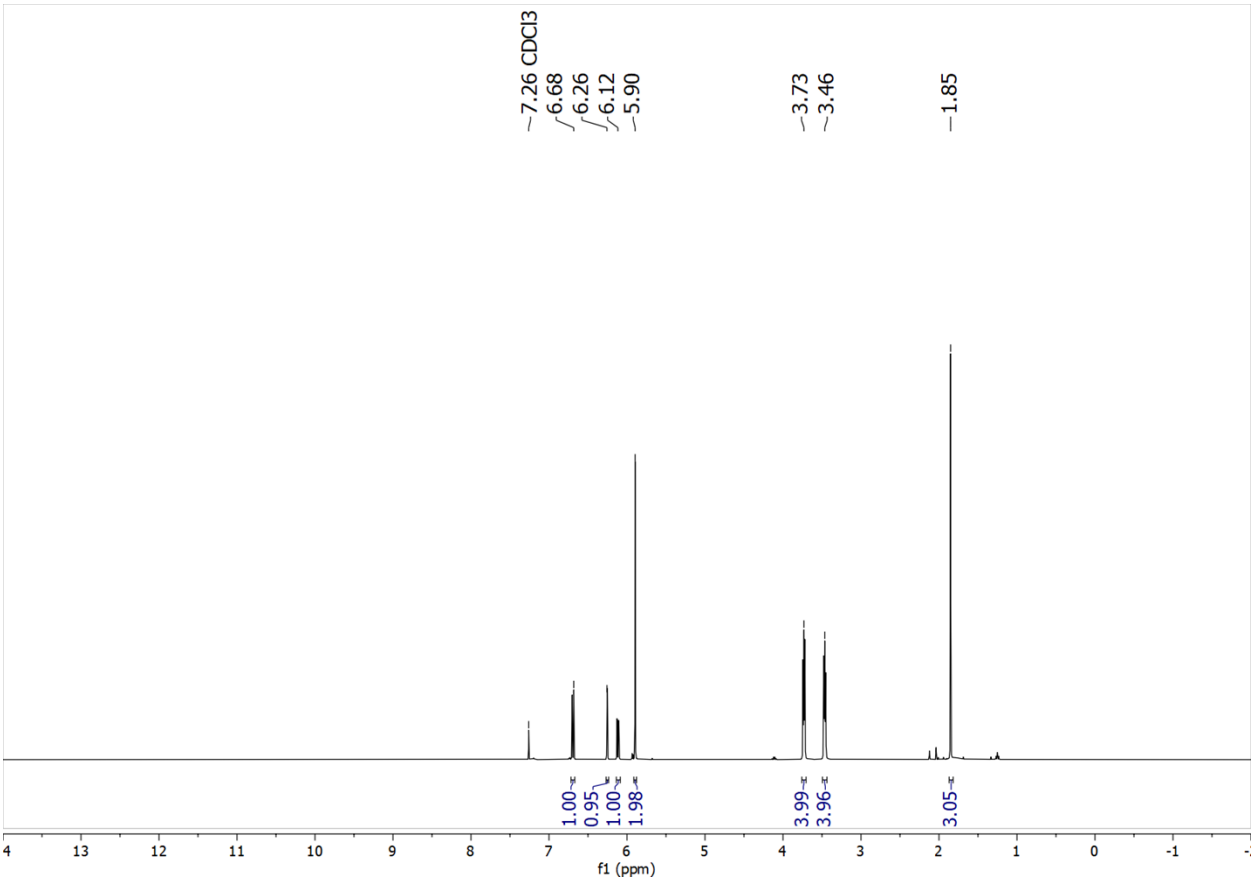
^{13}C NMR: 101 MHz in $CDCl_3$

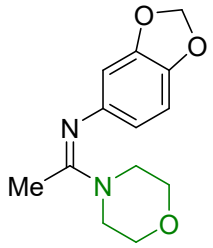




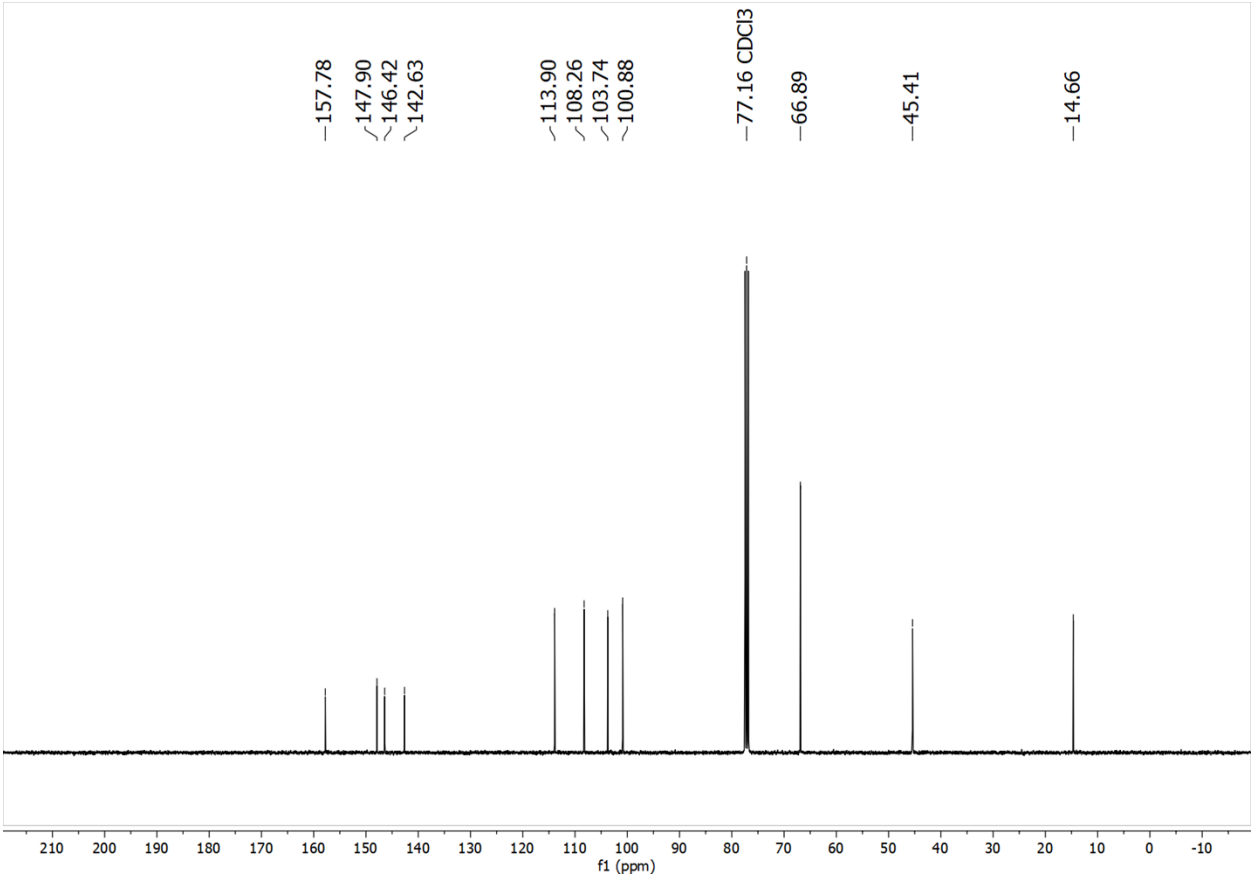
(Z)-1-morpholino-N-(benzo[d][1,3]dioxol-5-yl)ethanimine (2j-a)

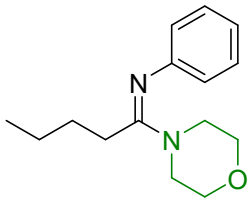
^{1}H NMR: 400 MHz in $CDCl_3$





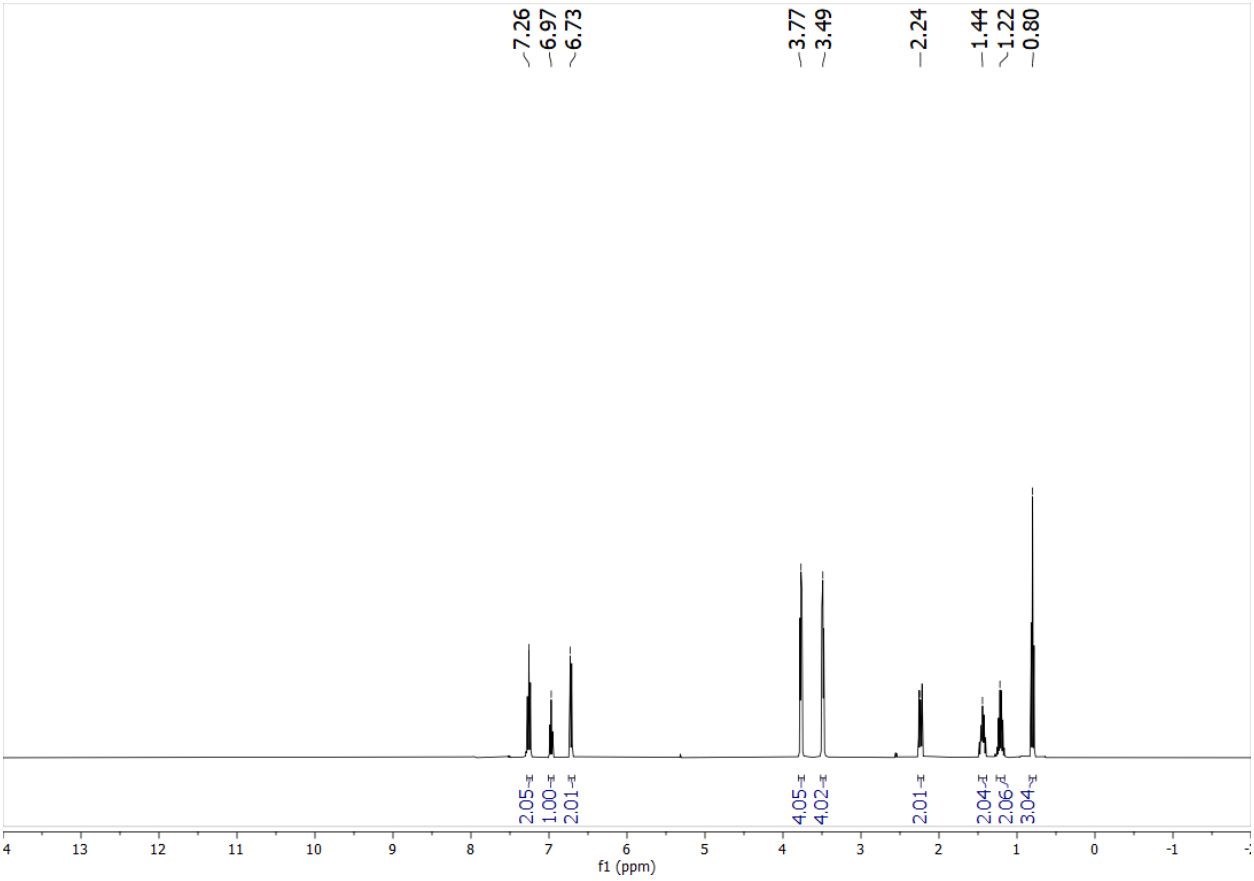
^{13}C NMR: 101 MHz in $CDCl_3$

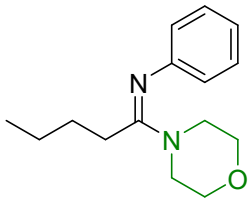




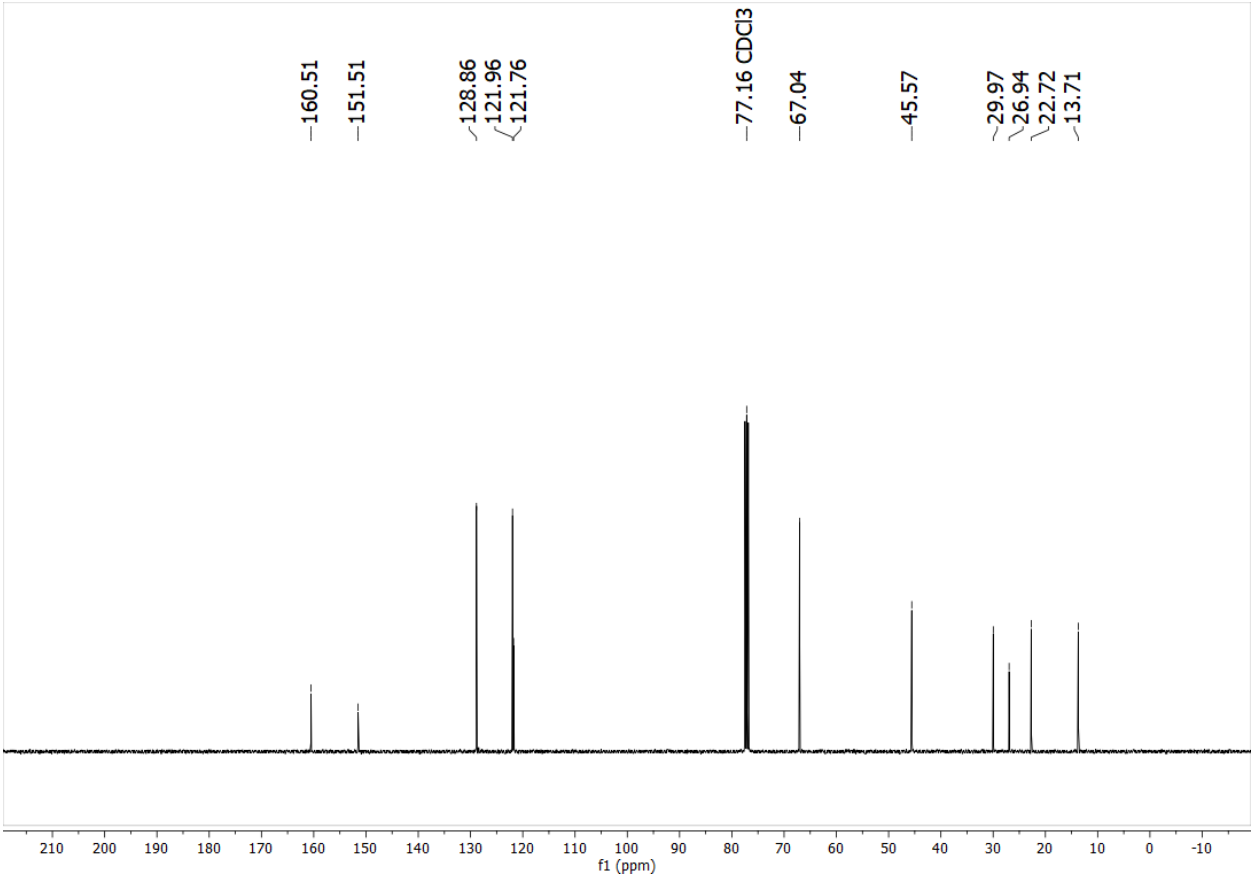
(Z)-1-morpholino-N-phenylpentanimine (2j-a)

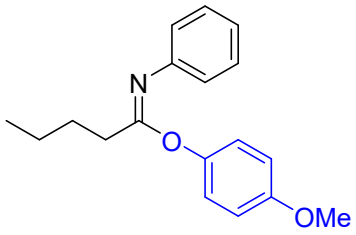
^{1}H NMR: 400 MHz in $CDCl_3$





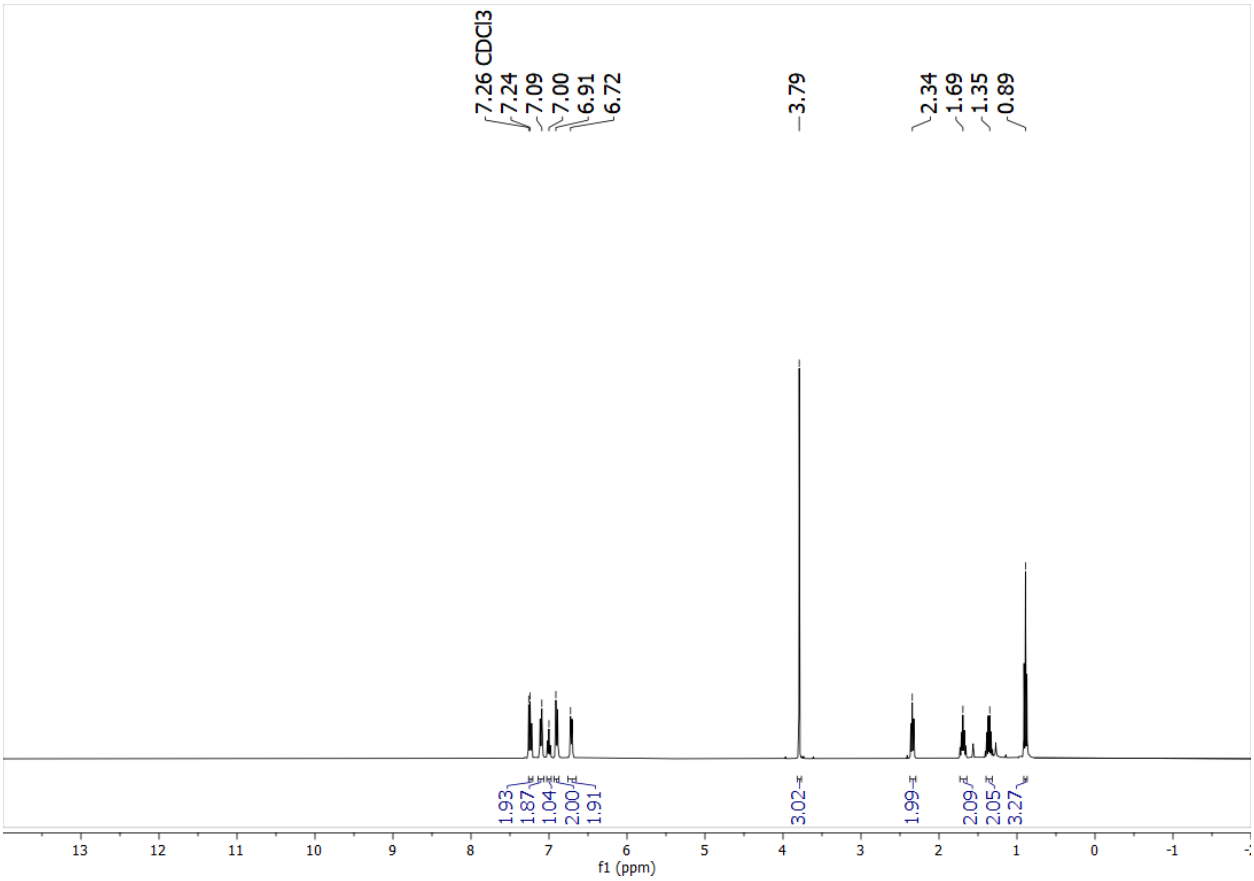
^{13}C NMR: 101 MHz in $CDCl_3$

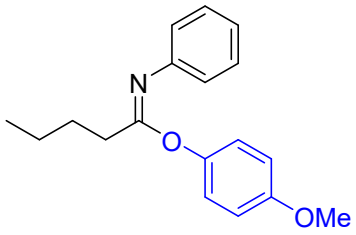




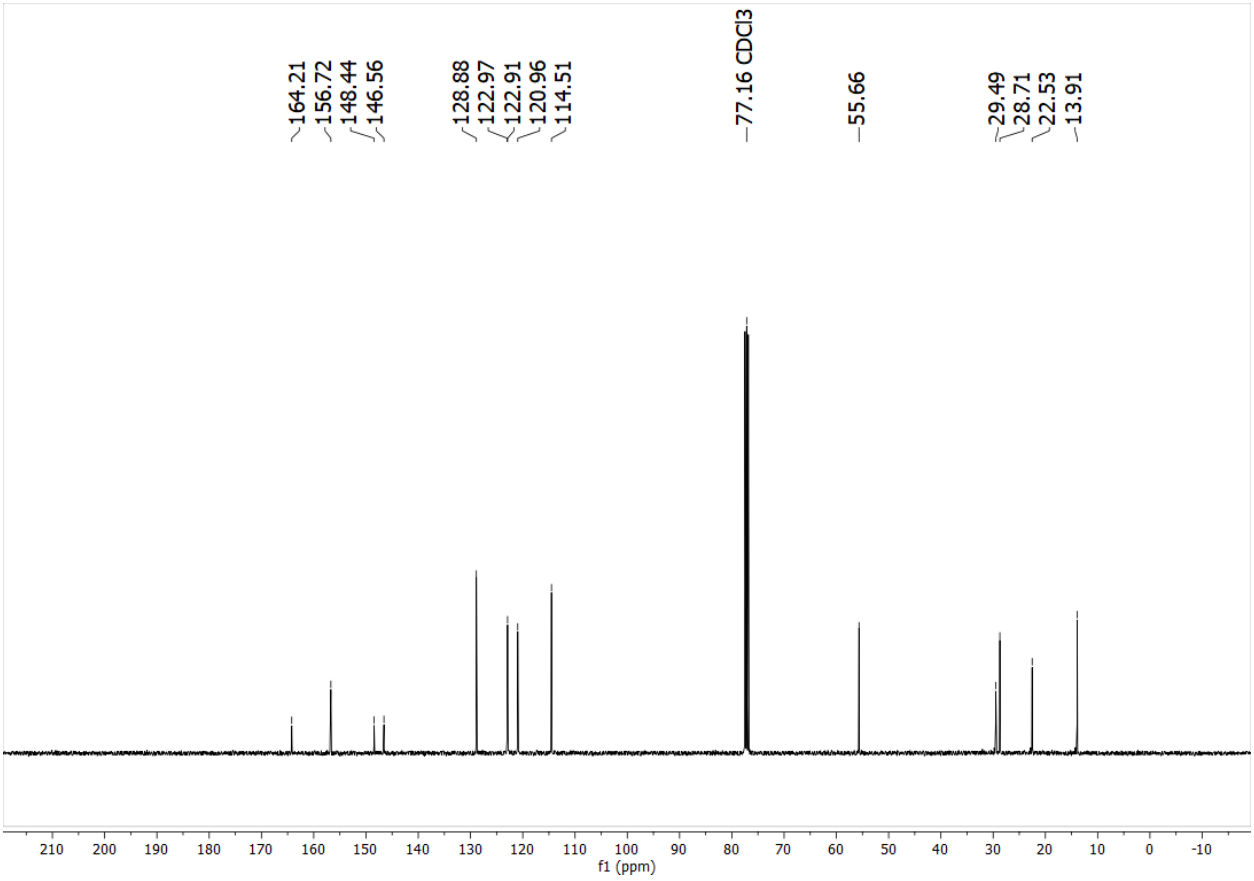
4-methoxyphenyl (Z)-N-phenylpentanimidate (2j-i)

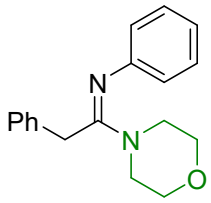
^{1}H NMR: 400 MHz in $CDCl_3$





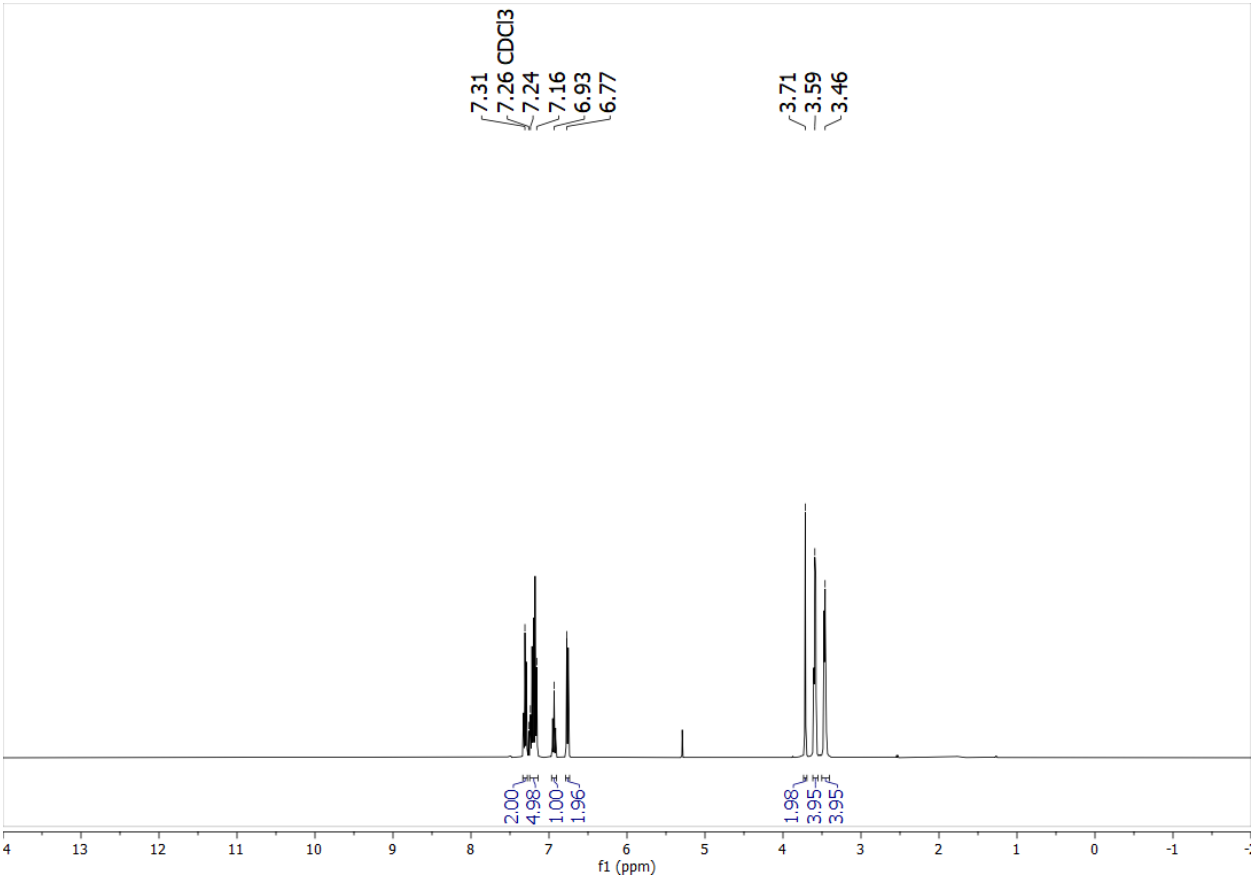
^{13}C NMR: 101 MHz in $CDCl_3$

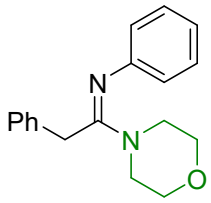




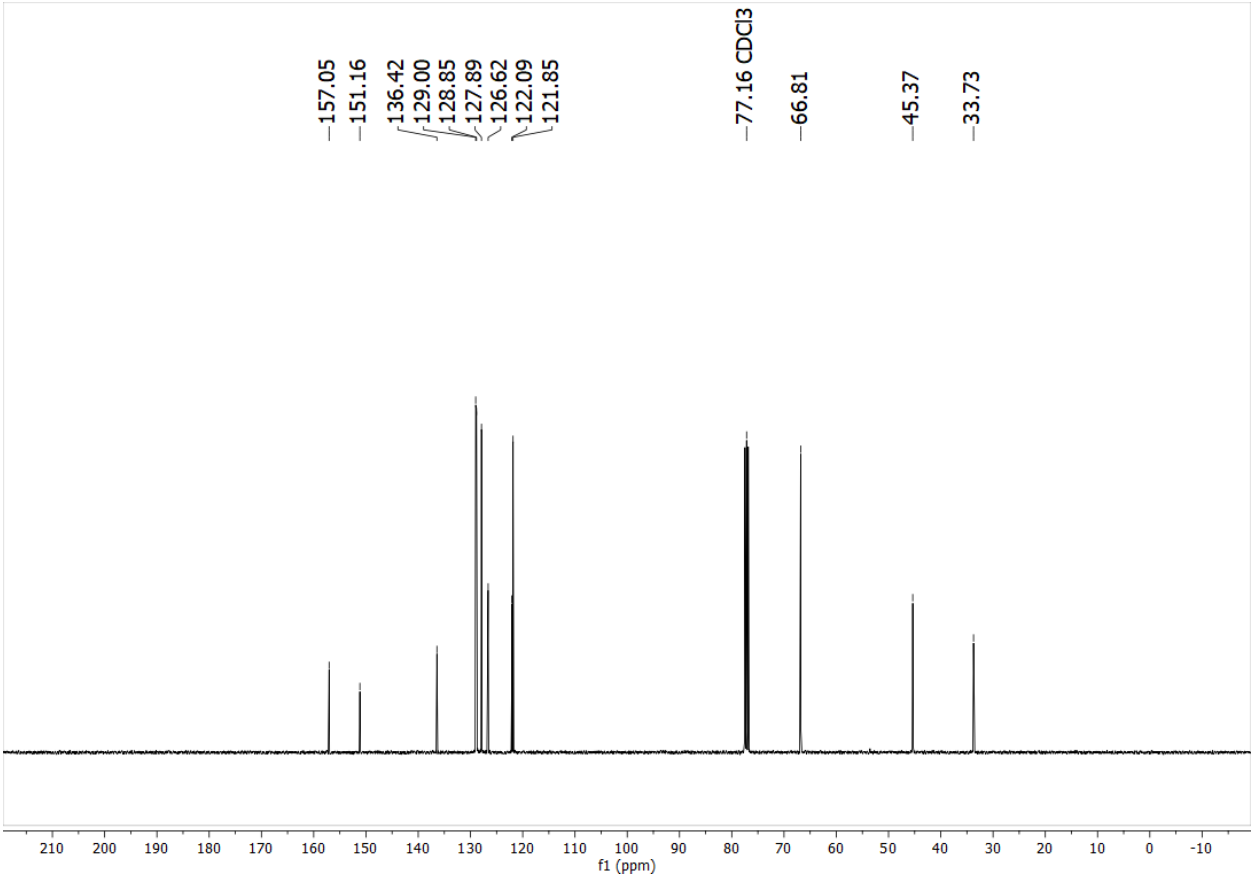
(Z)-1-morpholino-(N-phenyl)-2-phenylethanimine (2k-a)

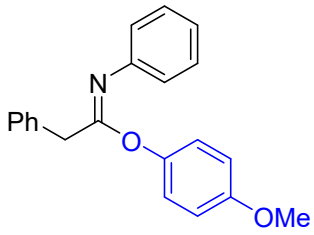
^{1}H NMR: 400 MHz in $CDCl_3$





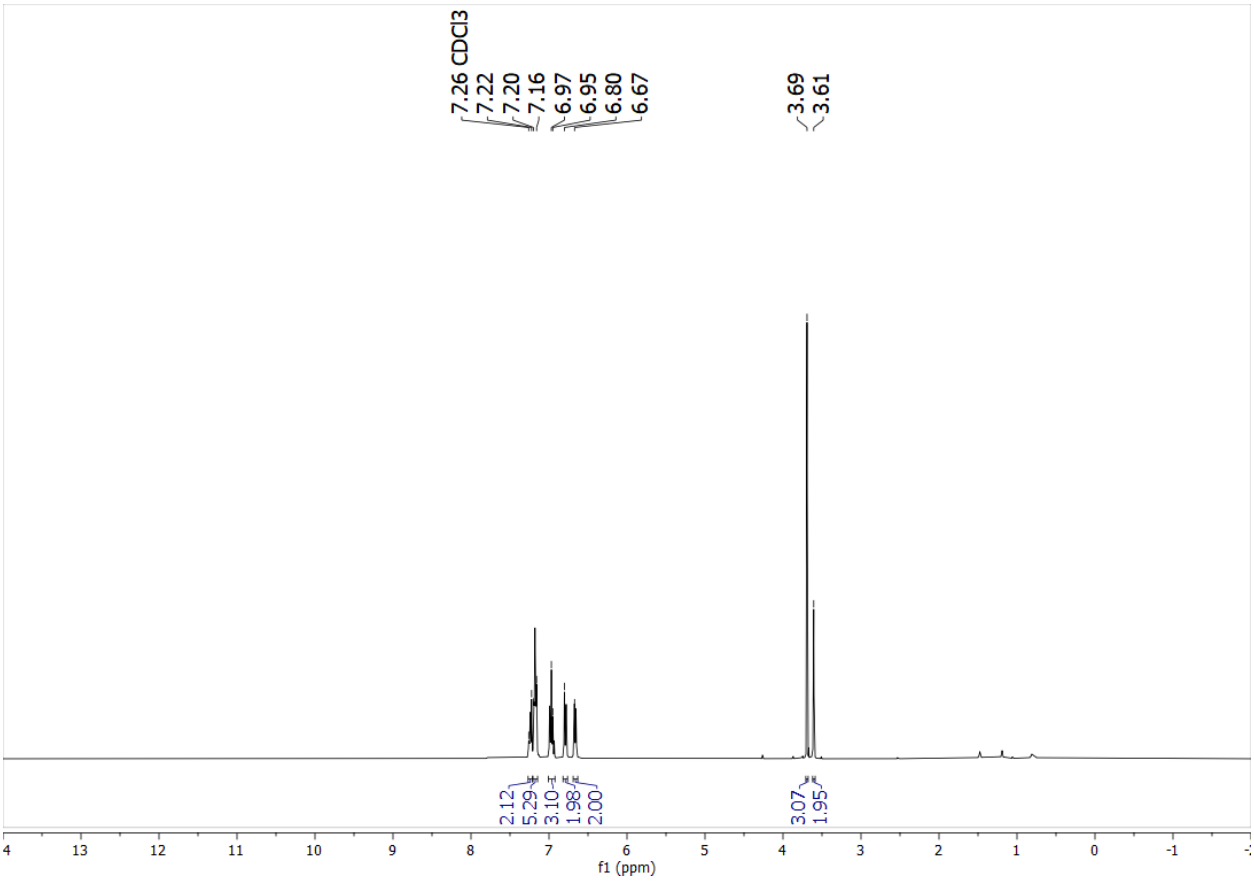
^{13}C NMR: 101 MHz in $CDCl_3$

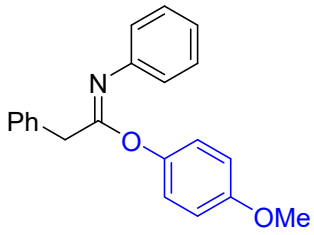




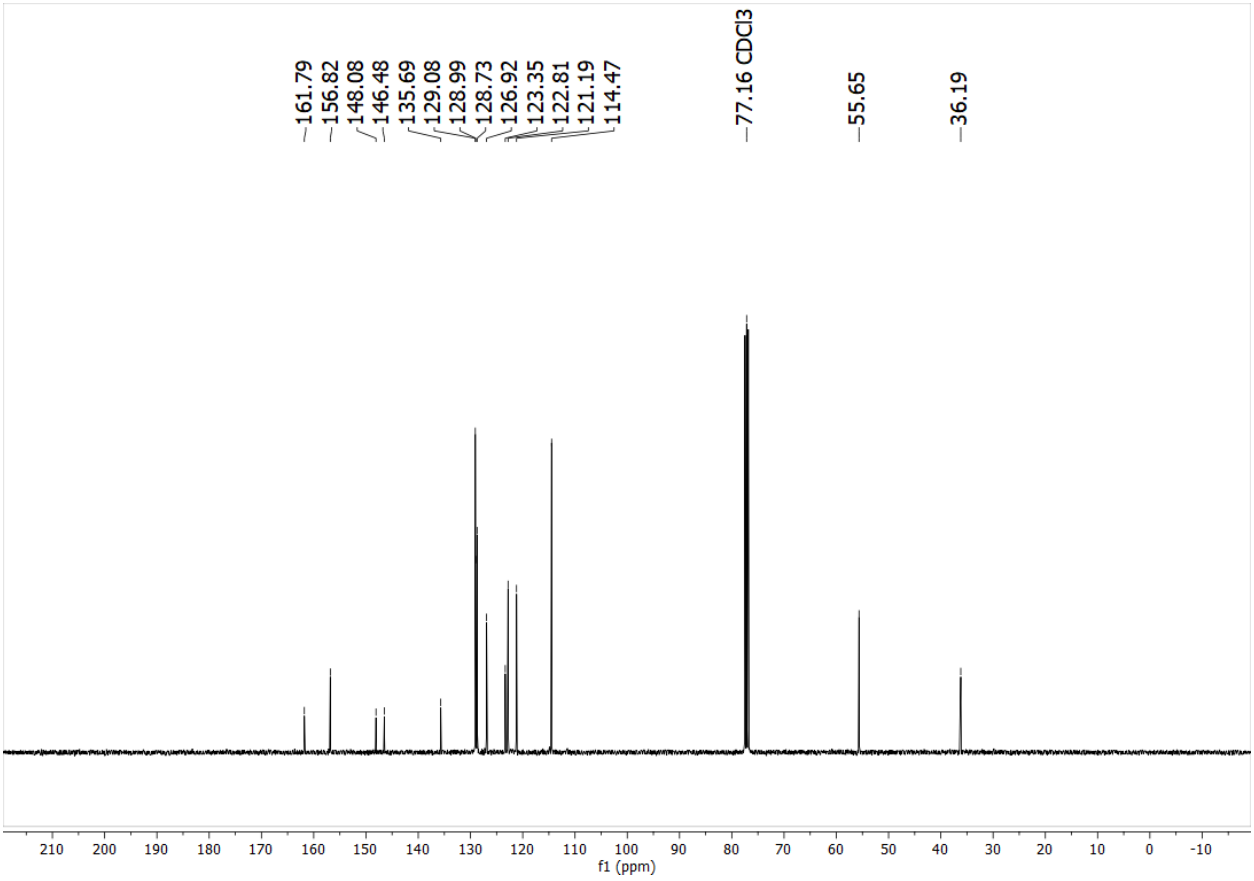
4-methoxyphenyl (Z)-(N-phenyl)2-phenylacetimidate (2k-i)

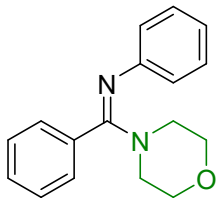
^{1}H NMR: 400 MHz in $CDCl_3$





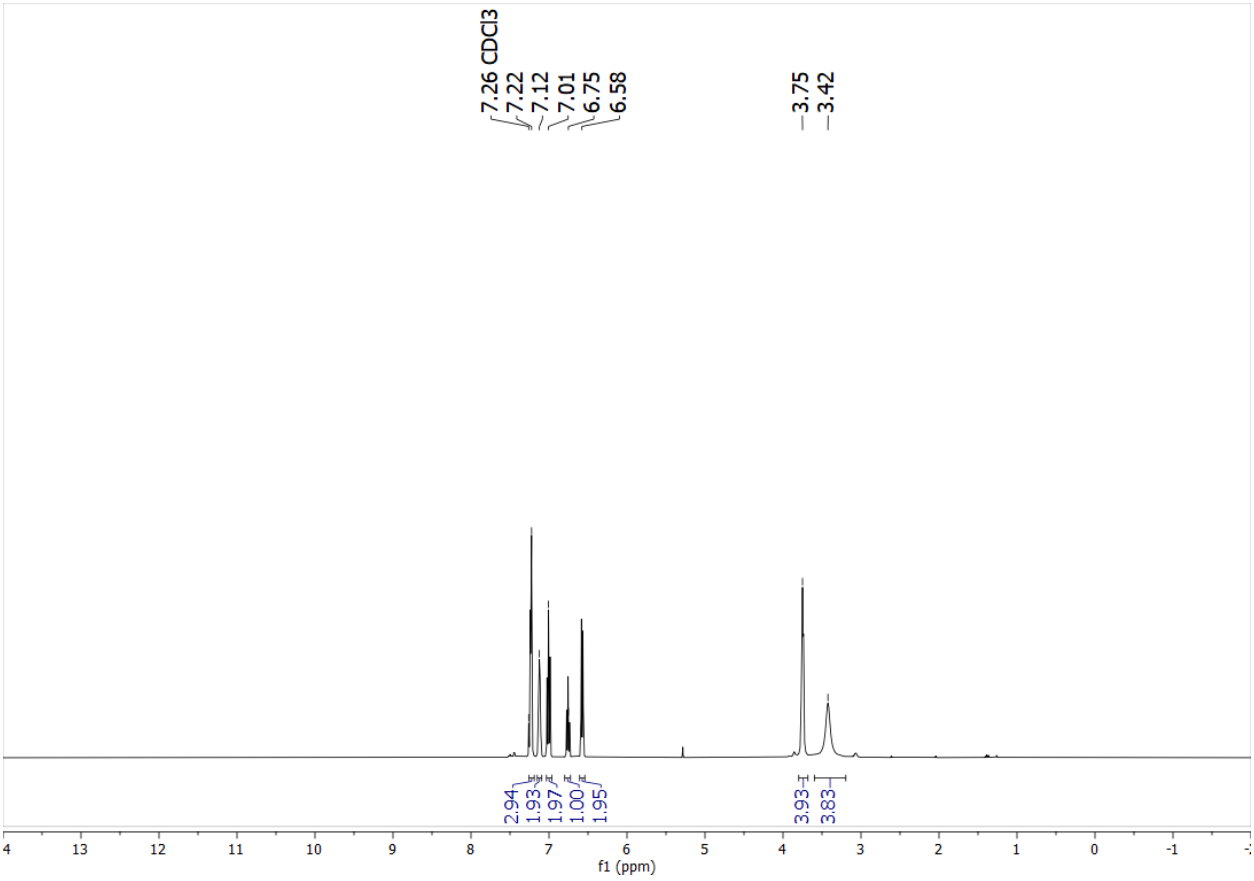
^{13}C NMR: 101 MHz in $CDCl_3$

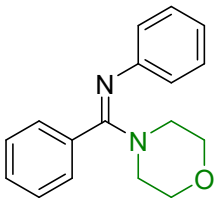




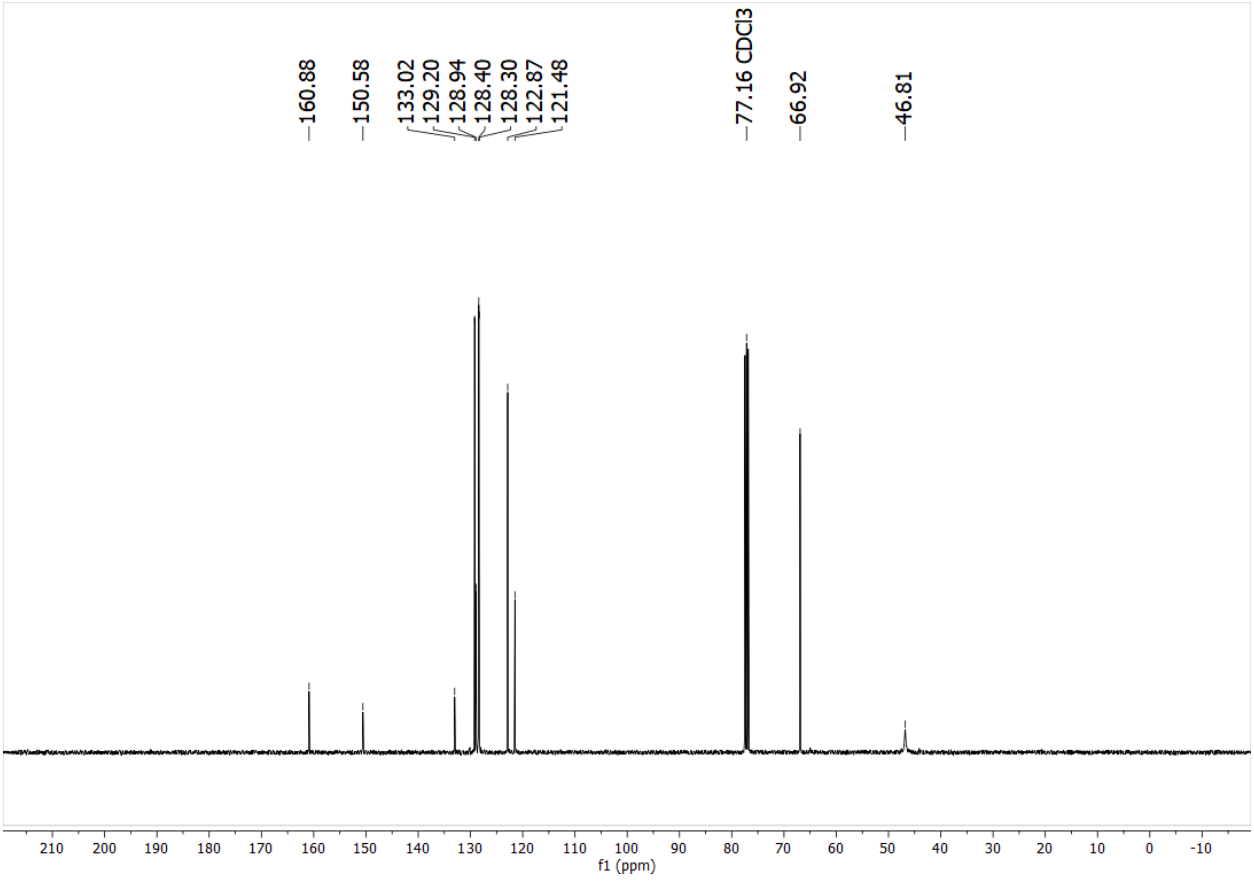
(Z)-1-morpholino-N,1-diphenylmethanimine (2m-a)

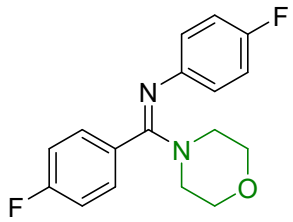
^{1}H NMR: 400 MHz in $CDCl_3$





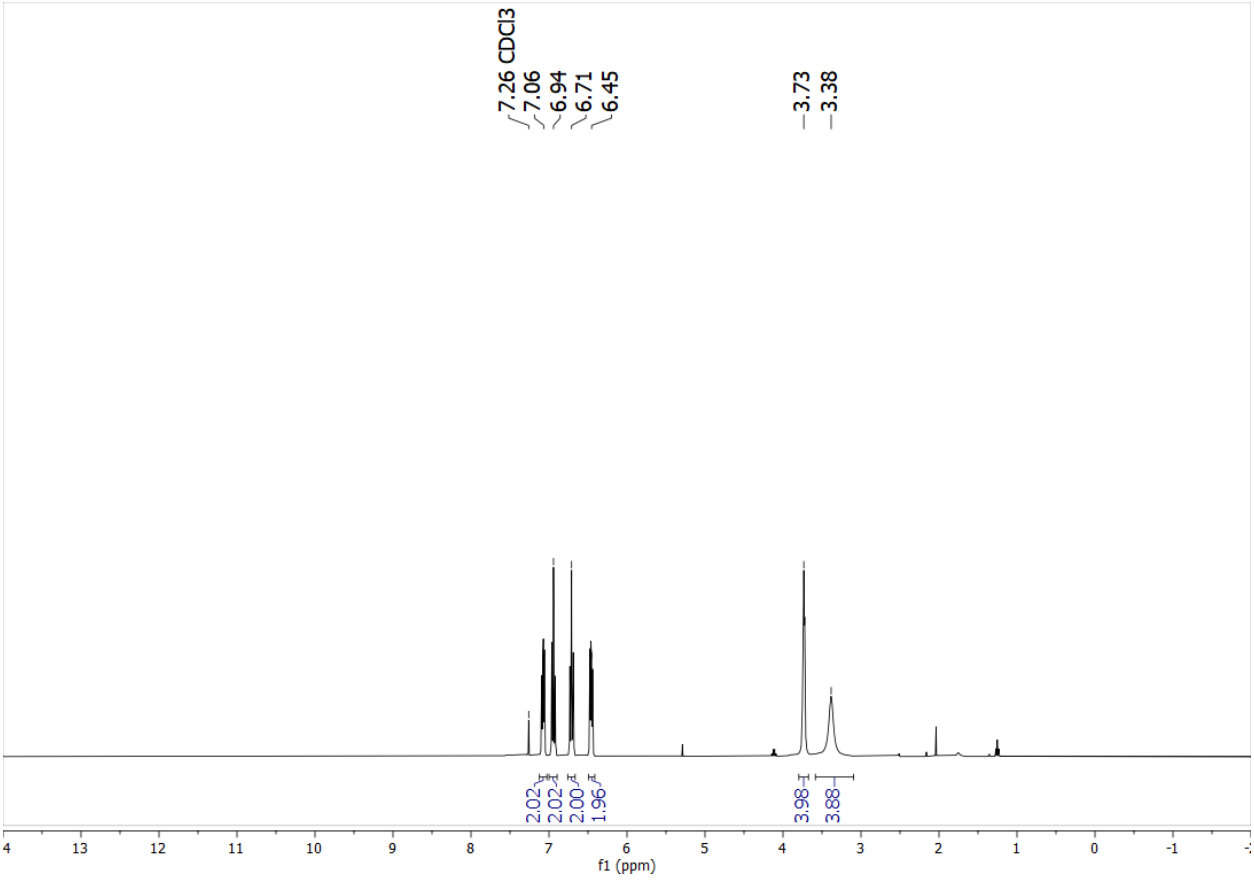
^{13}C NMR: 101 MHz in $CDCl_3$

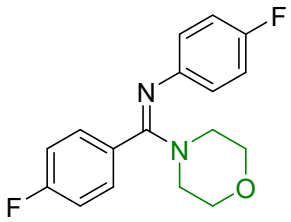




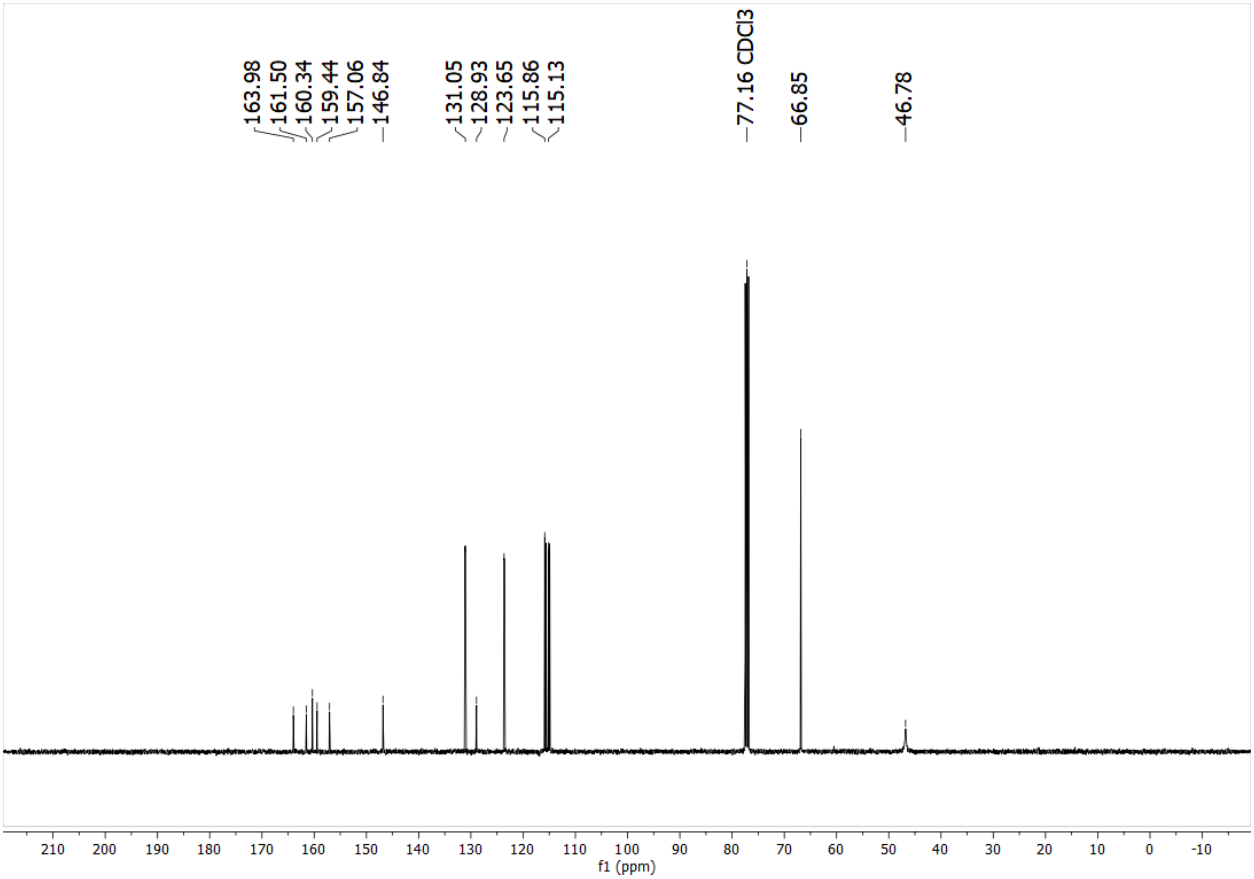
(Z)-N,1-bis(4-fluorophenyl)-1-morpholinomethanimine (2n-a)

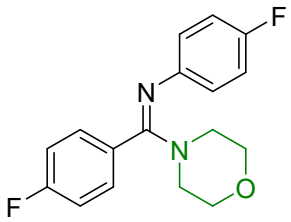
^{1}H NMR: 400 MHz in $CDCl_3$



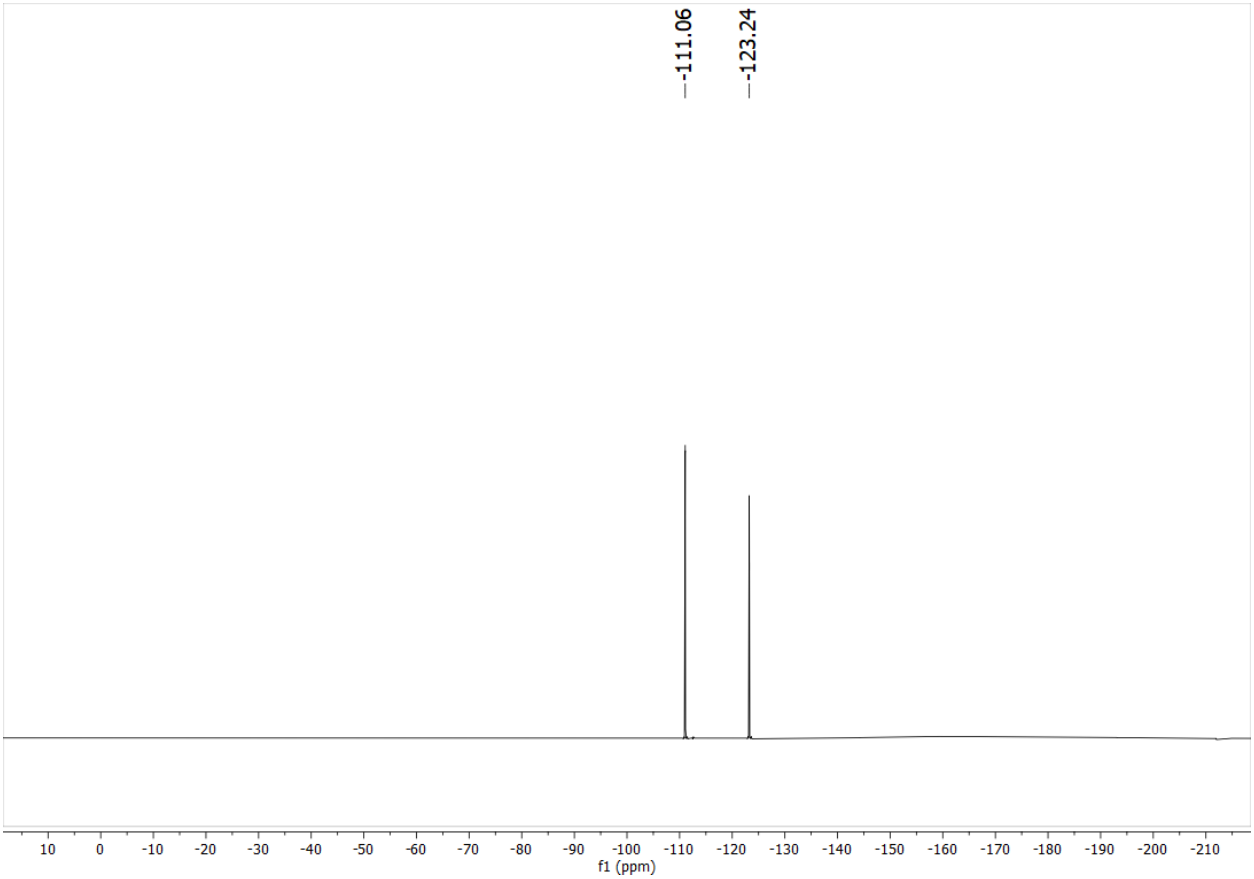


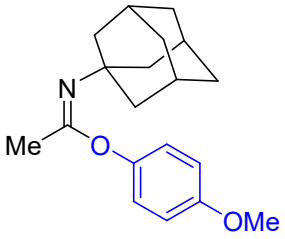
^{13}C NMR: 101 MHz in $CDCl_3$





^{19}F NMR: 376 MHz in $CDCl_3$

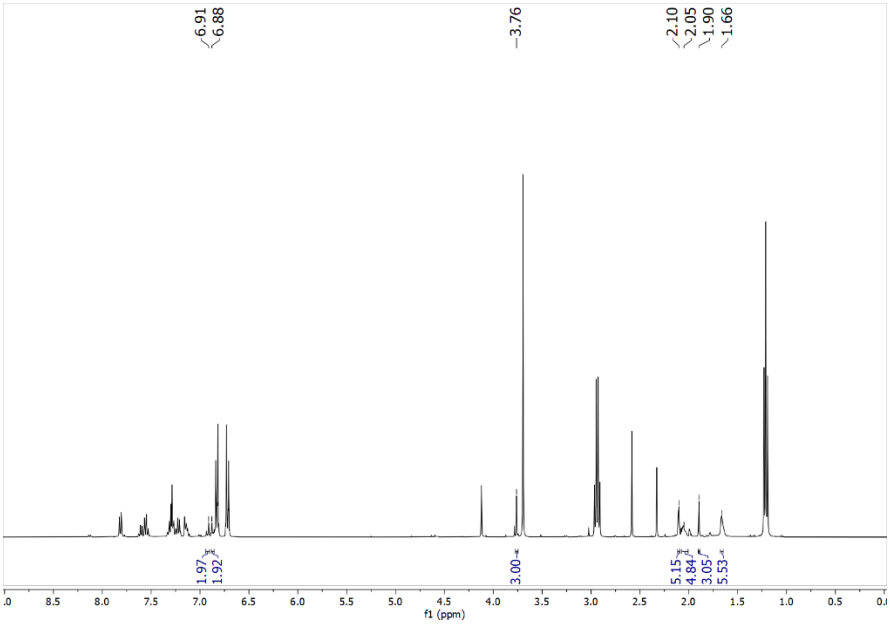




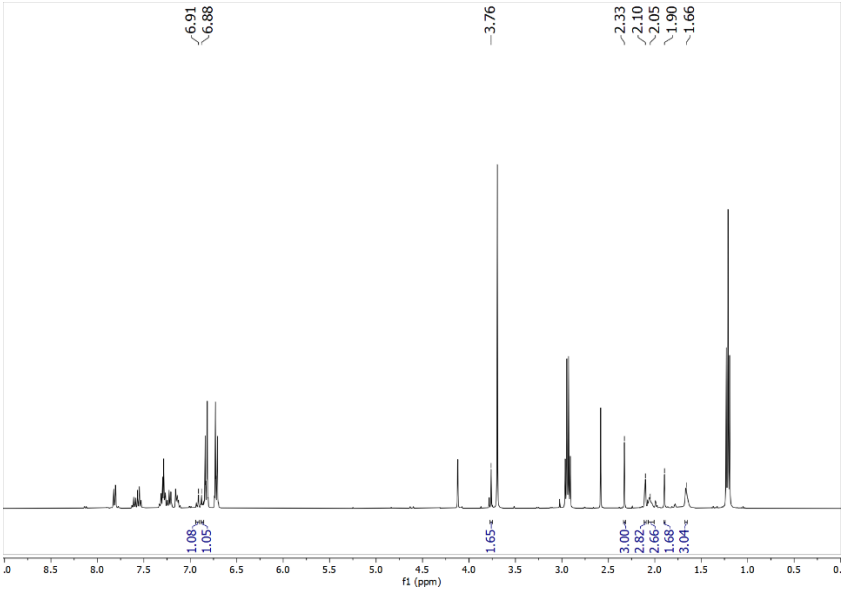
4-methoxyphenyl (Z)-N-((3s,5s,7s)-1-adamantanyl)acetimidate (2o-i)

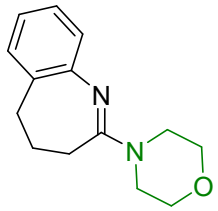
^{1}H NMR: 400 MHz in $CDCl_3$ with 1.0 equivalent of toluene as internal standard

Only product peaks have been highlighted / integrated in the following spectrum:



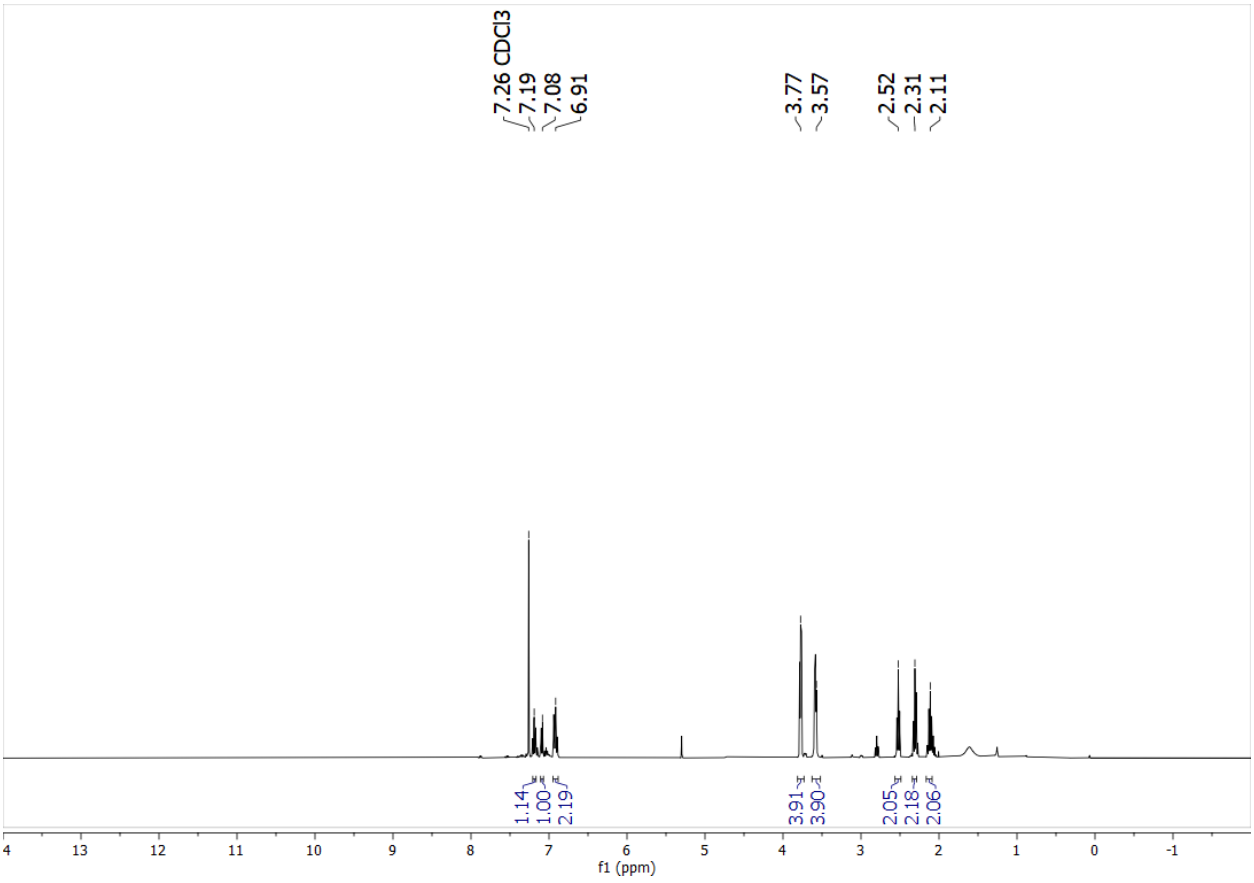
Both product peaks and the methyl group of toluene have been highlighted in the following spectrum:

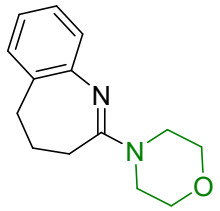




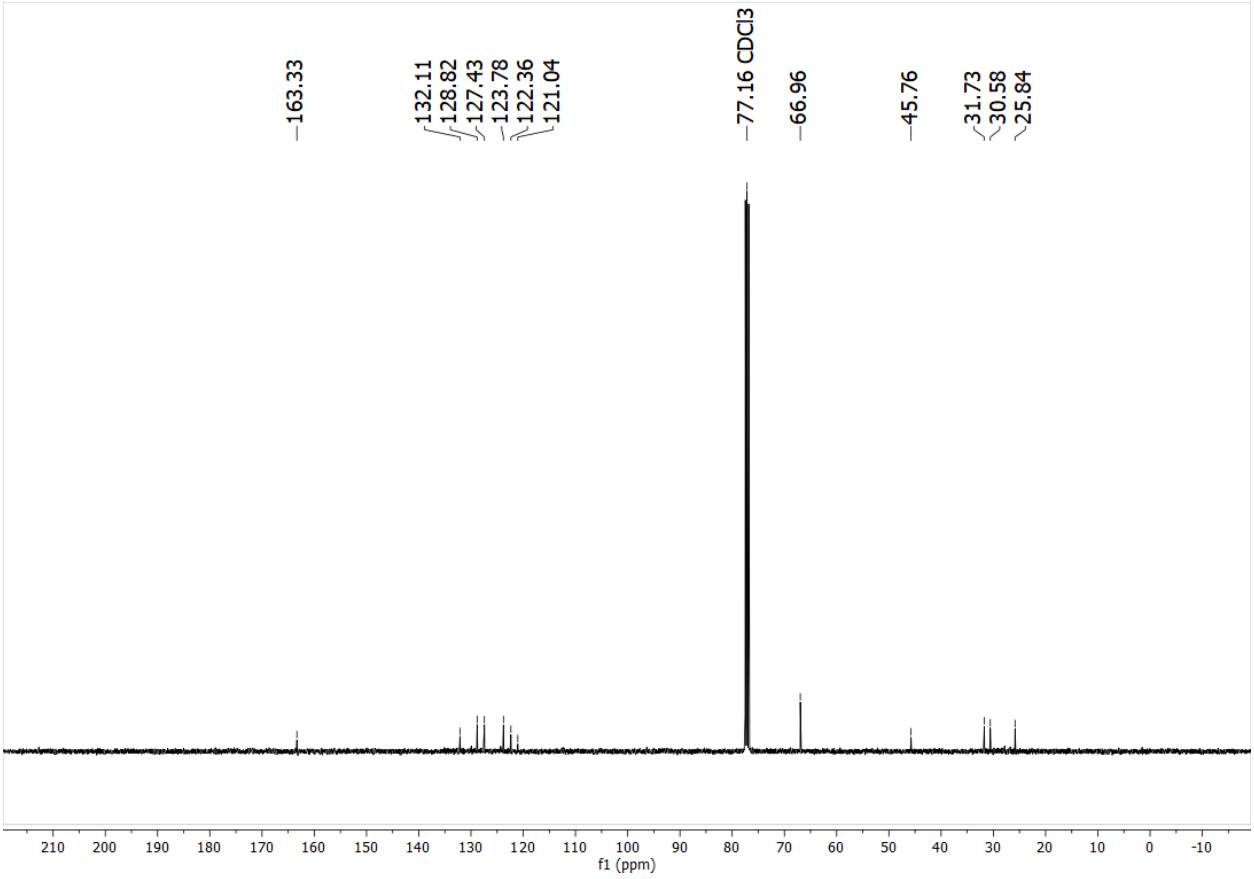
4-(4,5-dihydro-3H-benzo[b]azepin-2-yl)morpholine (2p-a)

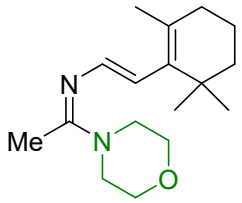
^{1}H NMR: 400 MHz in $CDCl_3$





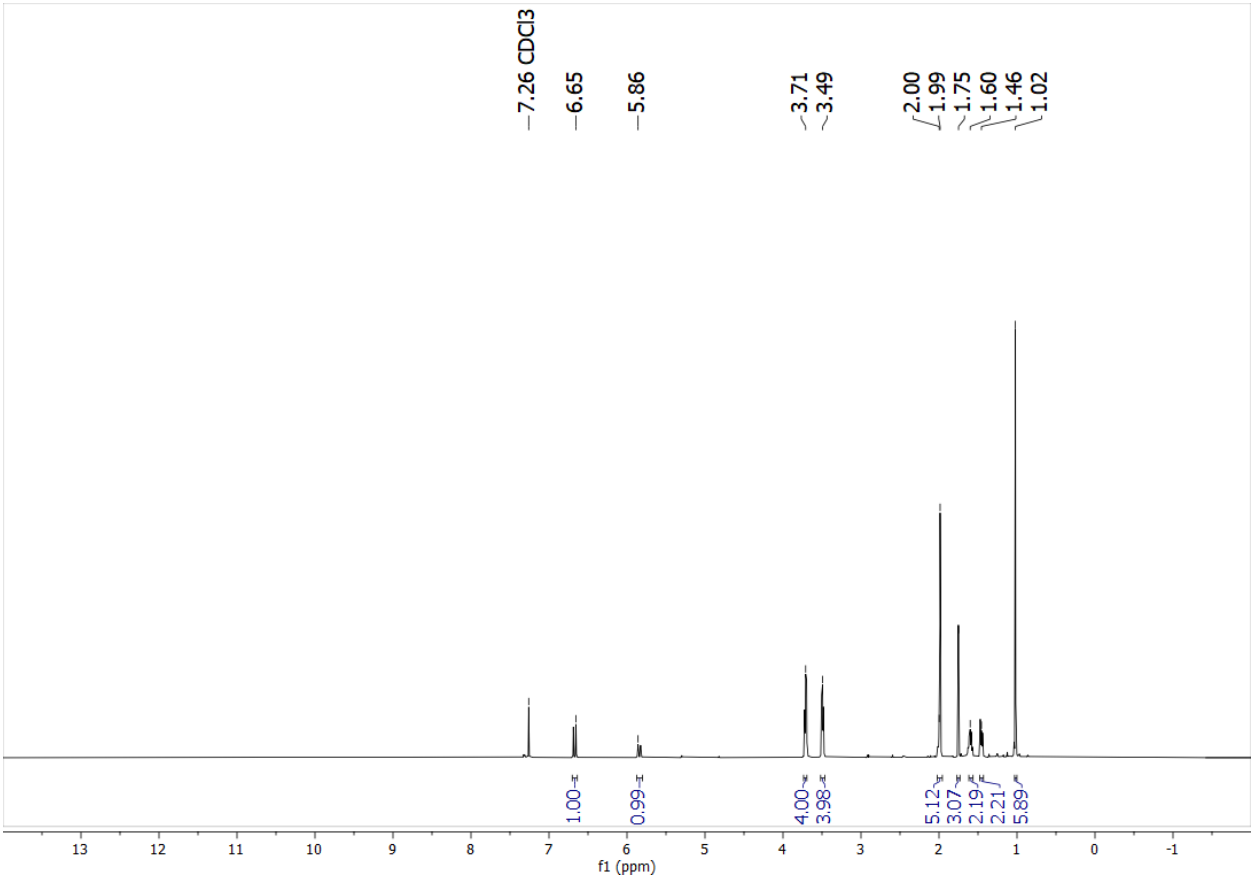
^{13}C NMR: 101 MHz in $CDCl_3$

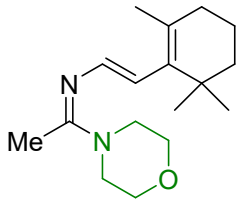




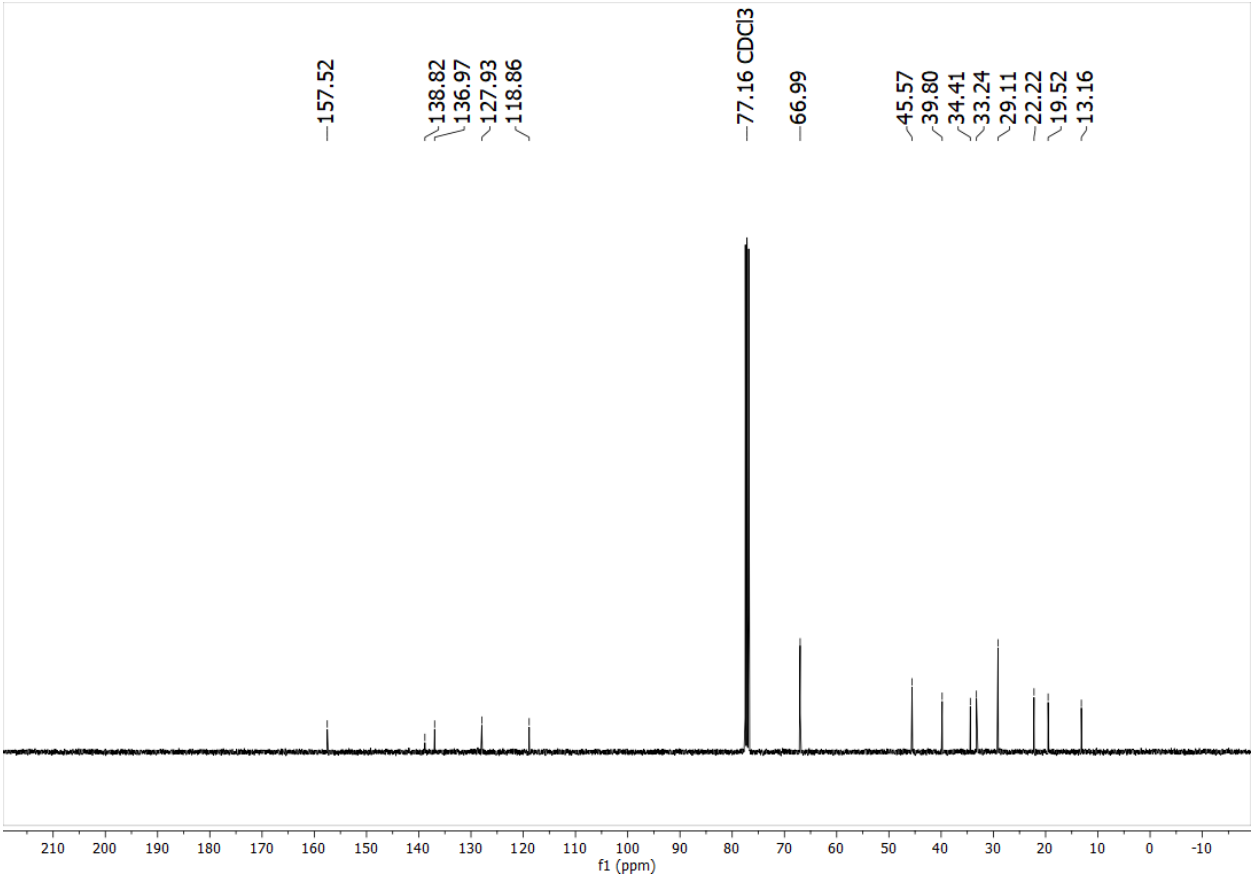
(Z)-1-morpholino-N-((E)-2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)ethan-1-imine (2q-a)

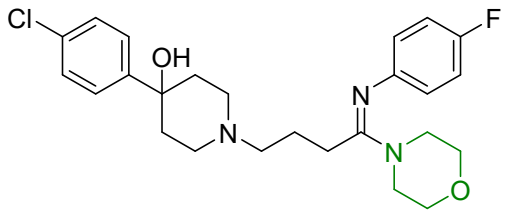
^{1}H NMR: 400 MHz in $CDCl_3$





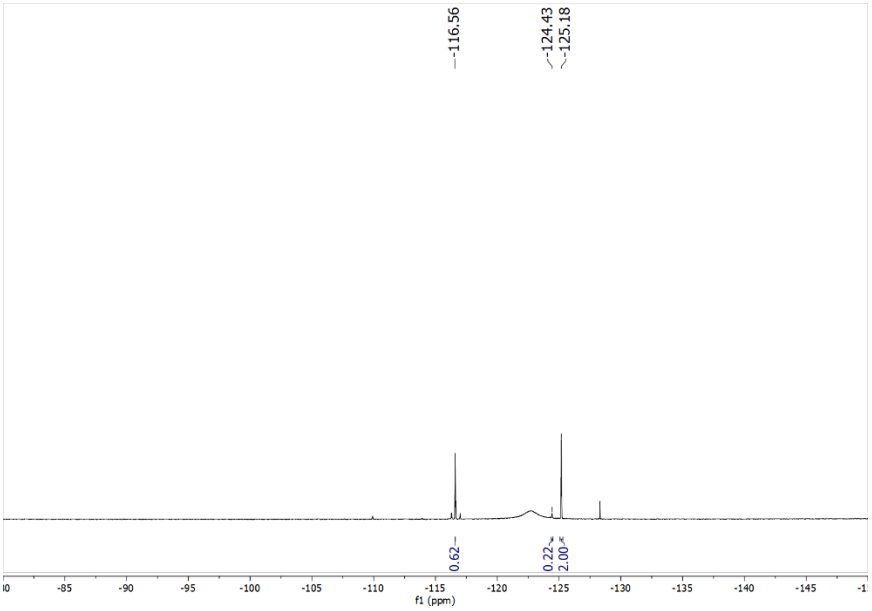
^{13}C NMR: 101 MHz in $CDCl_3$



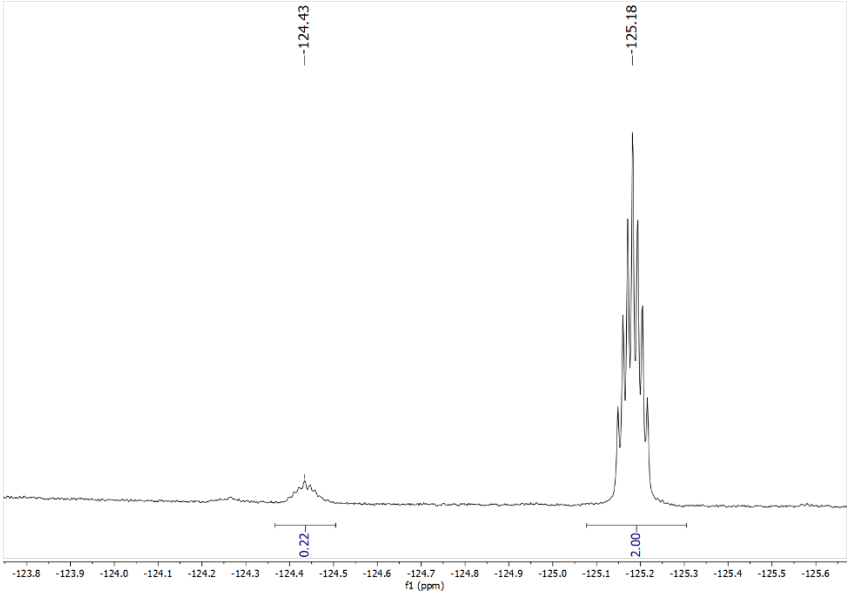


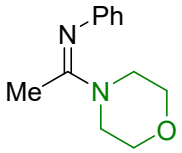
(Z)-4-(4-chlorophenyl)-1-(4-((4-fluorophenyl)imino)-4-morpholinobutyl)piperidin-4-ol (2r-a)

^{19}F NMR of crude reaction mixture with 2 equivalents of 4-fluoroanisole (peak at -125.18 ppm) and the product peak (-124.43 ppm) identified. Peak at -116.56 was identified to be amide by-product from degradation of the haloperidol imidoyl fluoride intermediated.



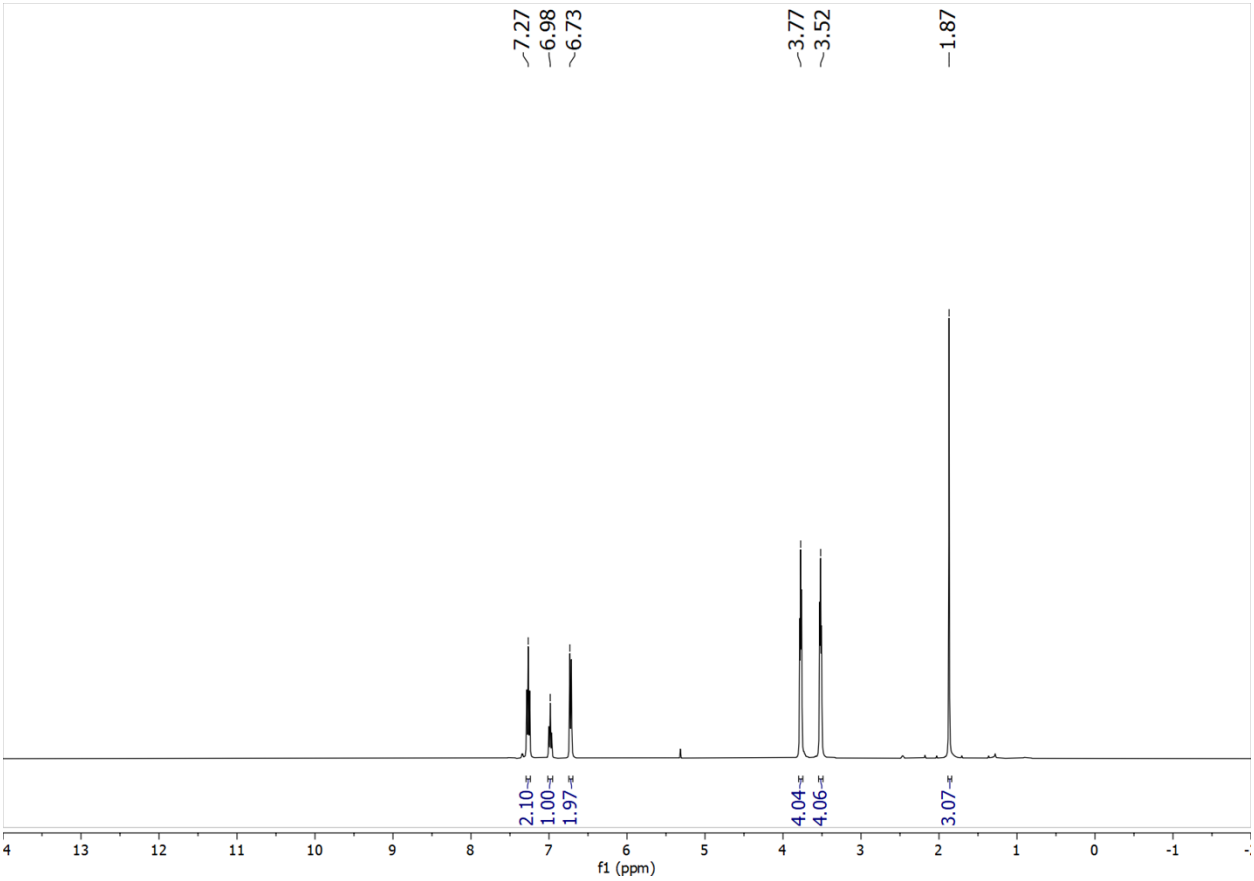
^{19}F NMR of crude reaction mixture, zoomed in on the product and internal standard region:

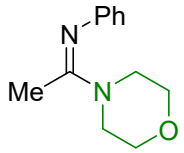




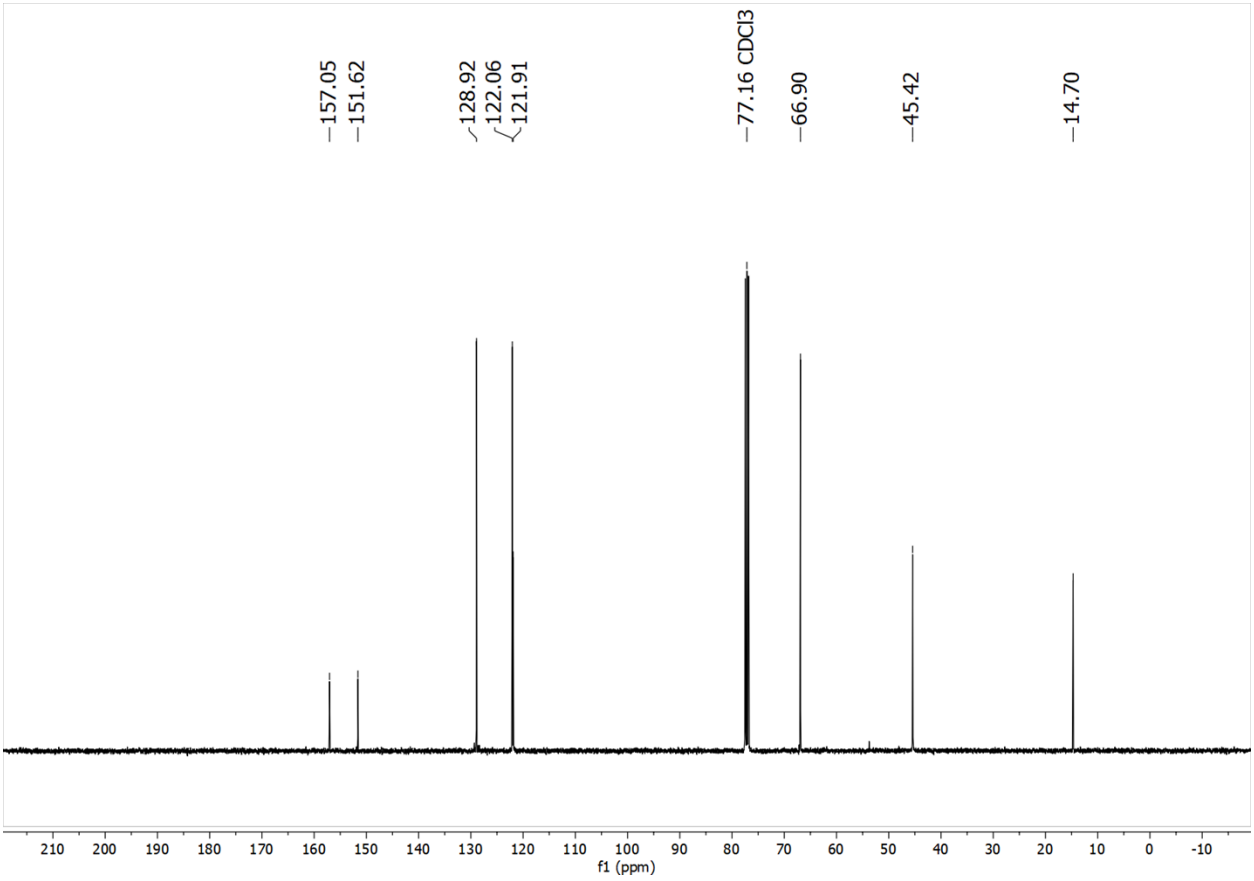
(Z)-1-morpholino-N-phenylethanimine (3a)

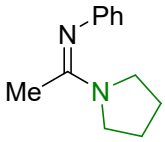
^{1}H NMR: 400 MHz in $CDCl_3$





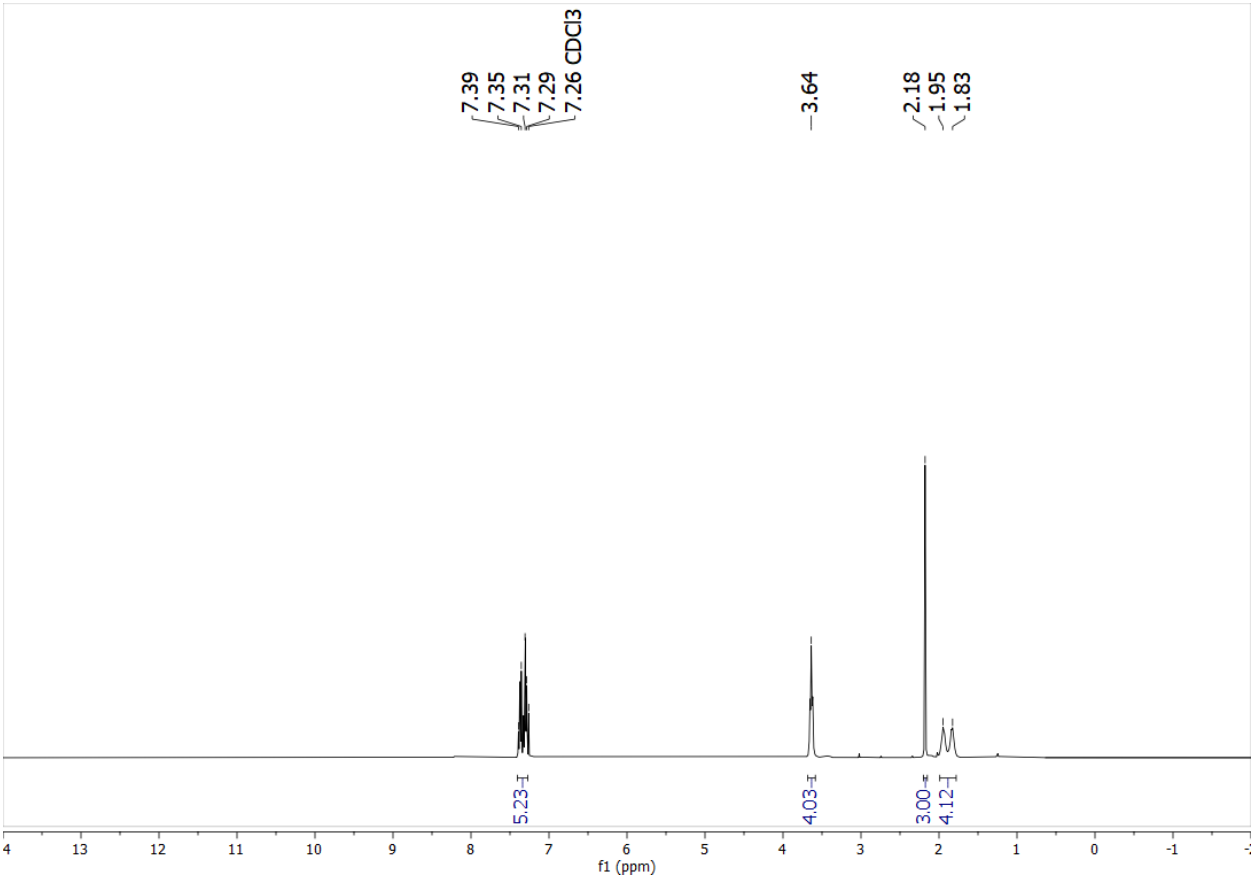
^{13}C NMR: 101 MHz in $CDCl_3$

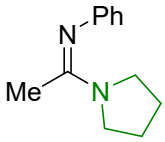




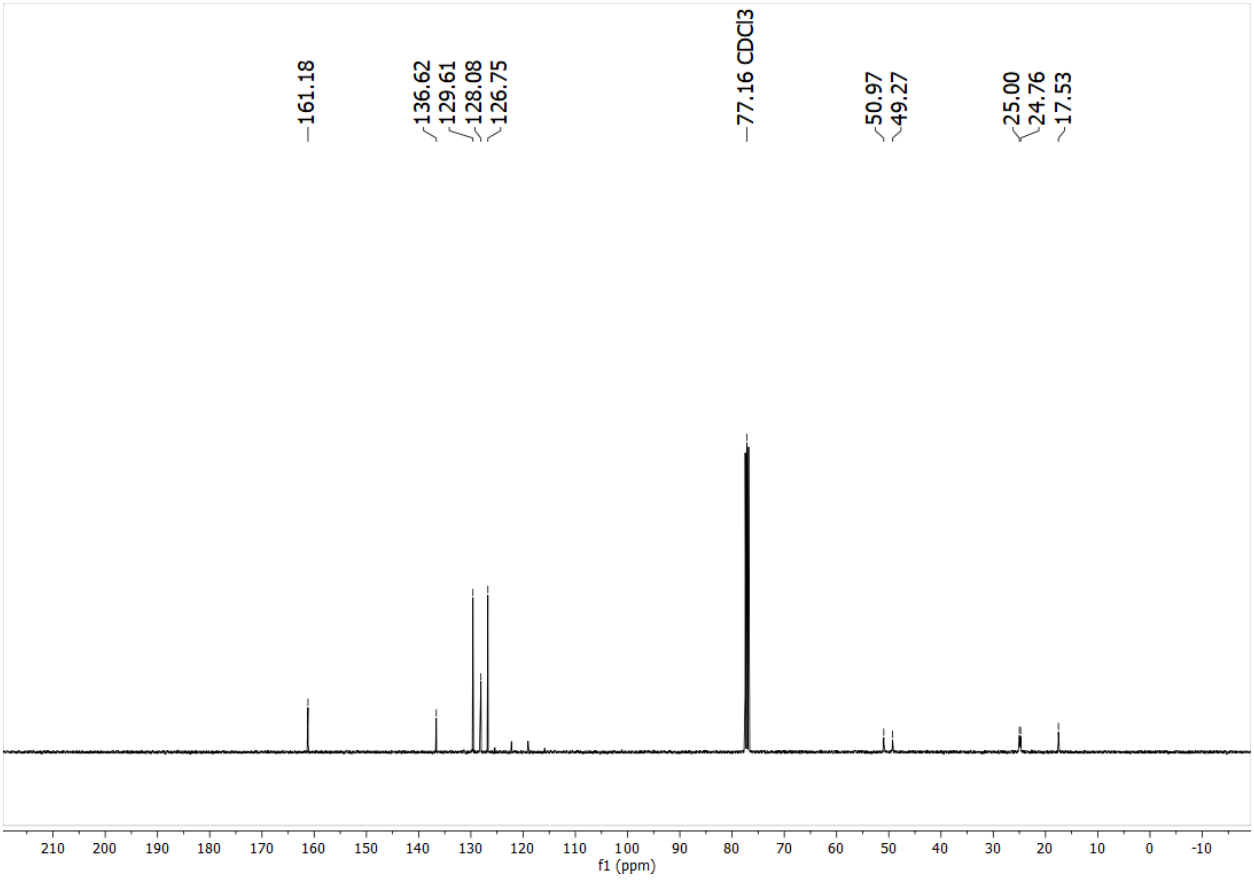
(Z)-1-(pyrrolidinyl)-N-phenylethanimine (3b)

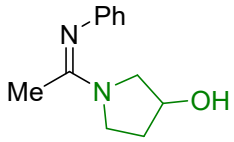
^{1}H NMR: 400 MHz in $CDCl_3$





^{13}C NMR: 101 MHz in $CDCl_3$

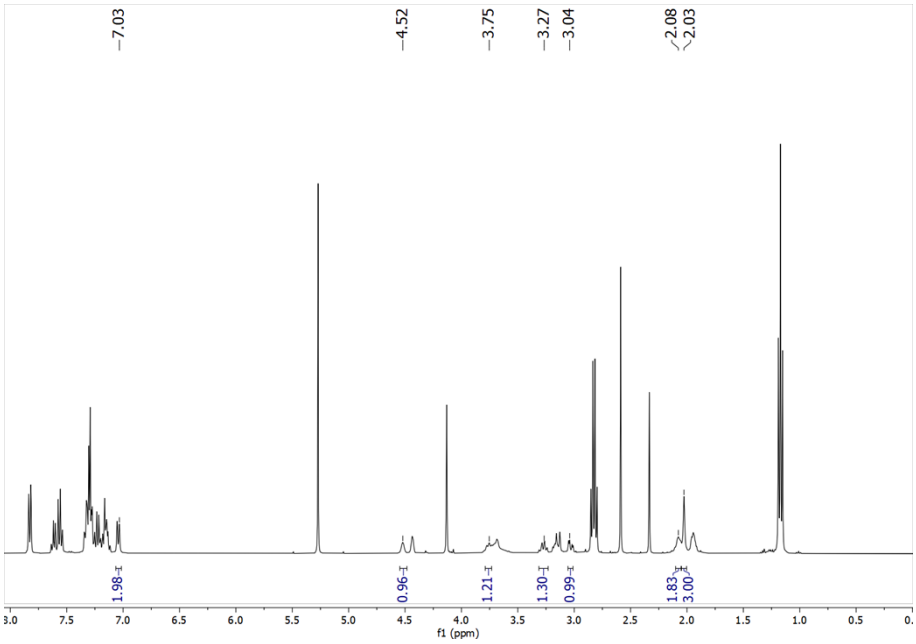




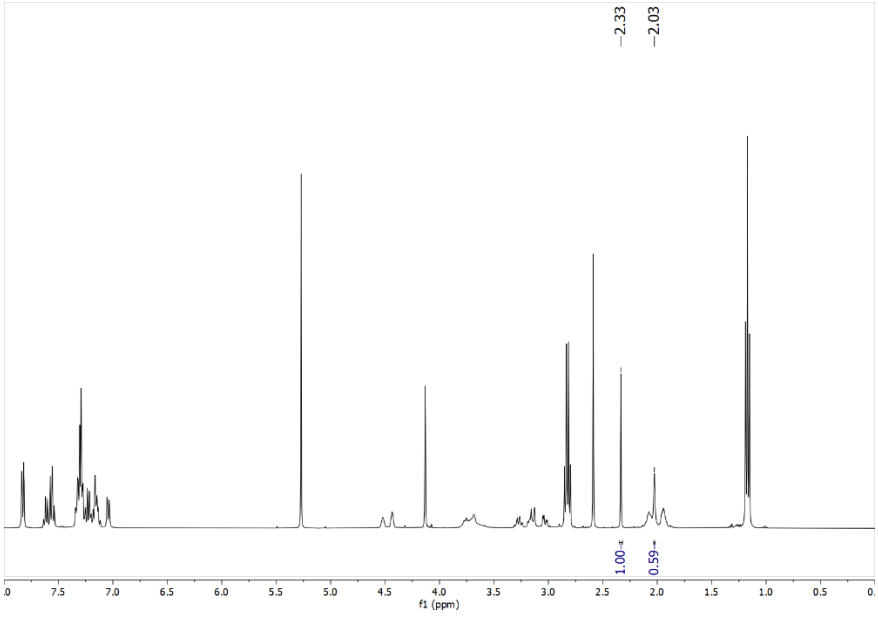
(Z)-1-(pyrrolidine-3-ol)-N-phenylethanimine (3c)

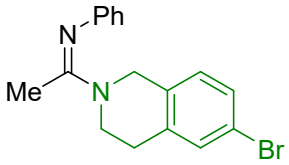
^{1}H NMR: 400 MHz in $CDCl_3$ with 1.0 equivalent of toluene as internal standard

Only product peaks have been highlighted / integrated in the following spectrum:



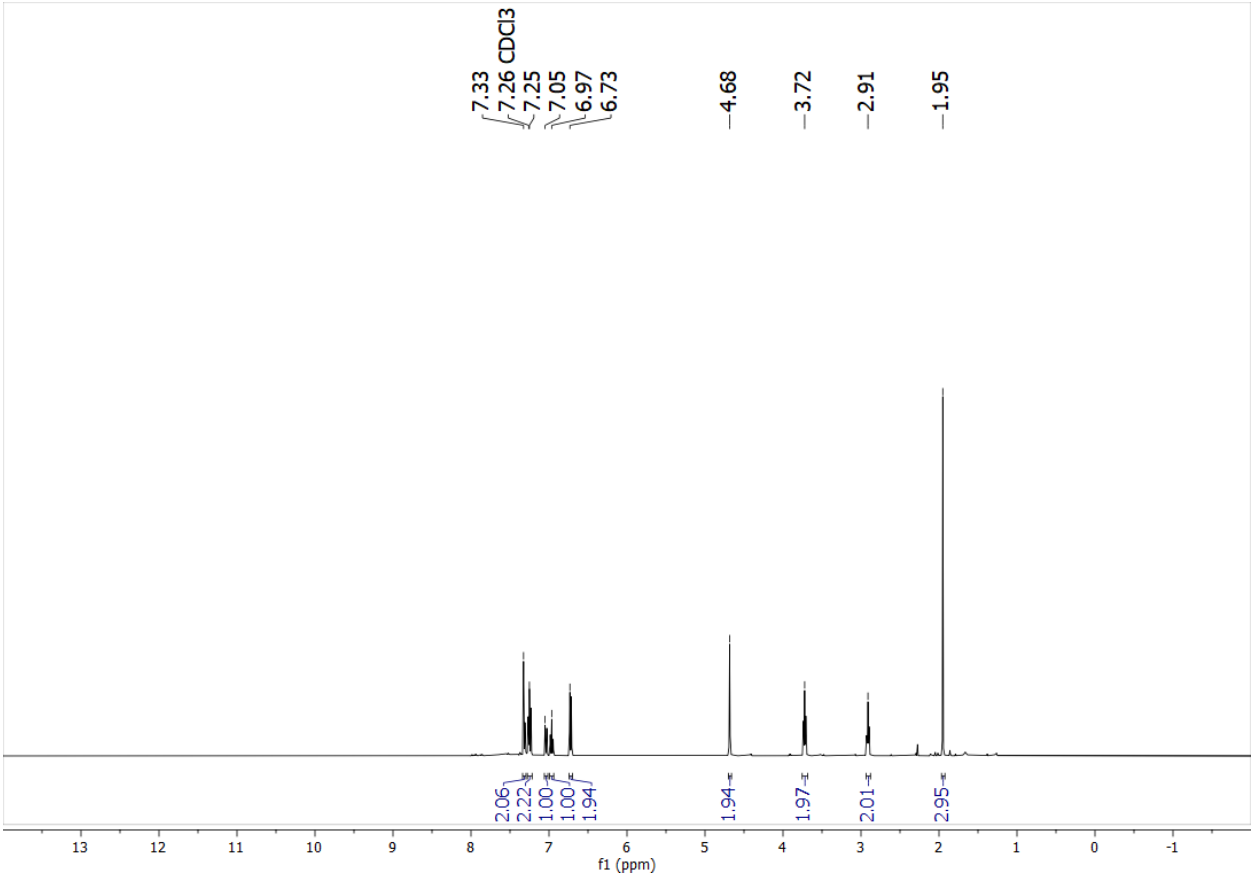
Internal standard (toluene) methyl peak is integrated to 1 (for 1.0 equivalent) and the methyl peak of the product is integrated (0.59) in the following spectrum:

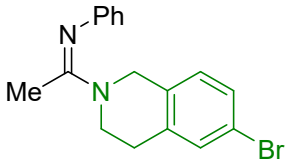




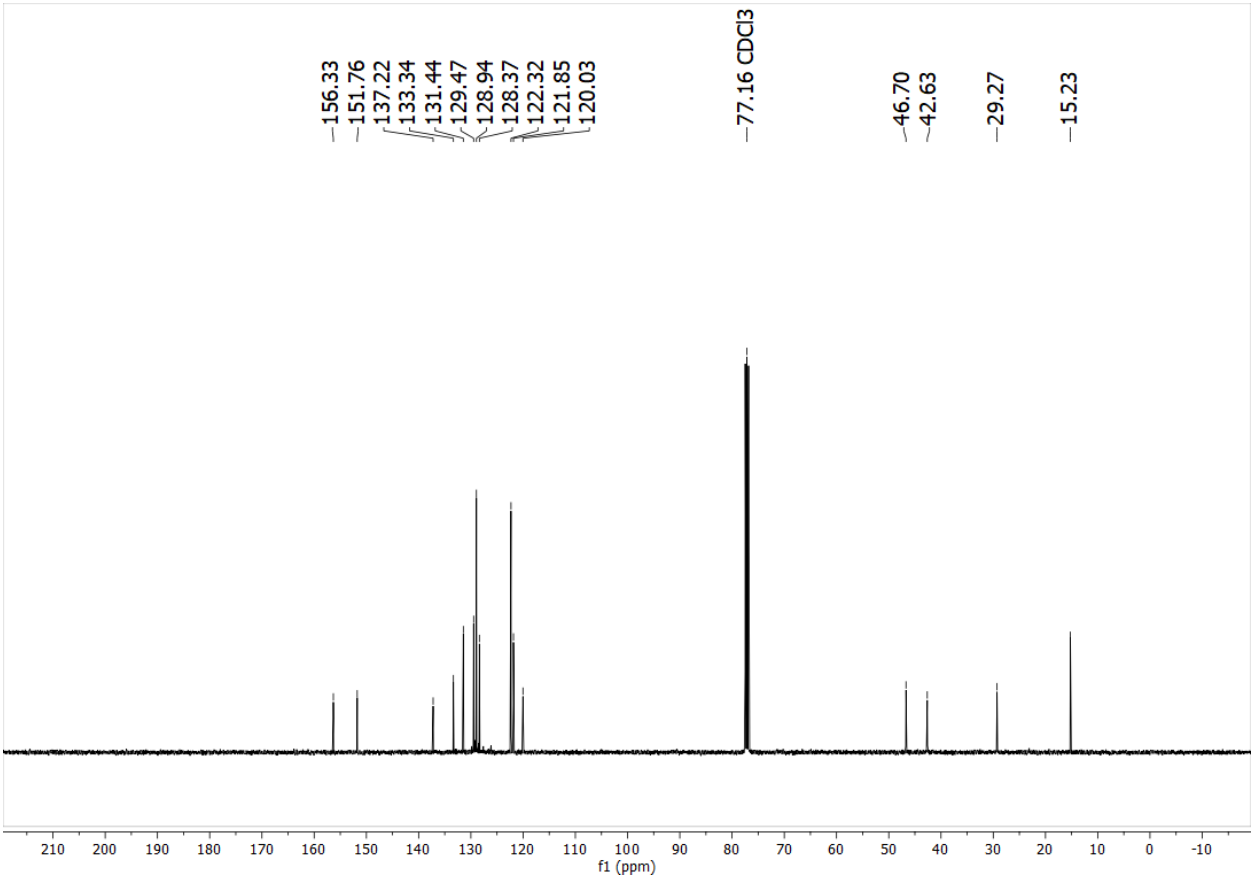
(Z)-1-(6-bromo-3,4-dihydroisoquinolin-2(1H)-yl)-N-phenylethanimine (3d)

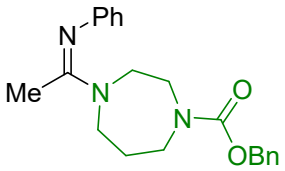
^{1}H NMR: 400 MHz in $CDCl_3$





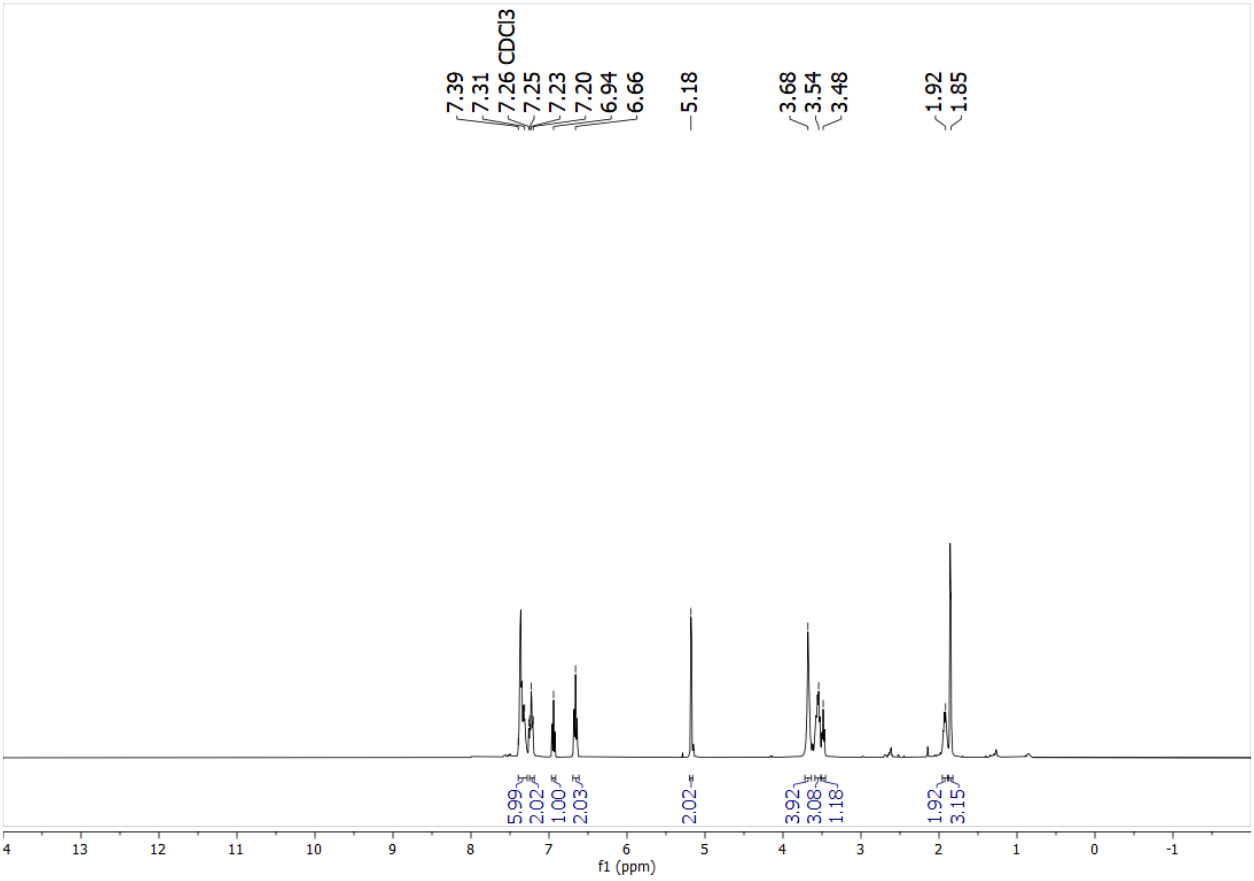
^{13}C NMR: 101 MHz in $CDCl_3$

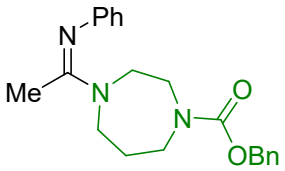




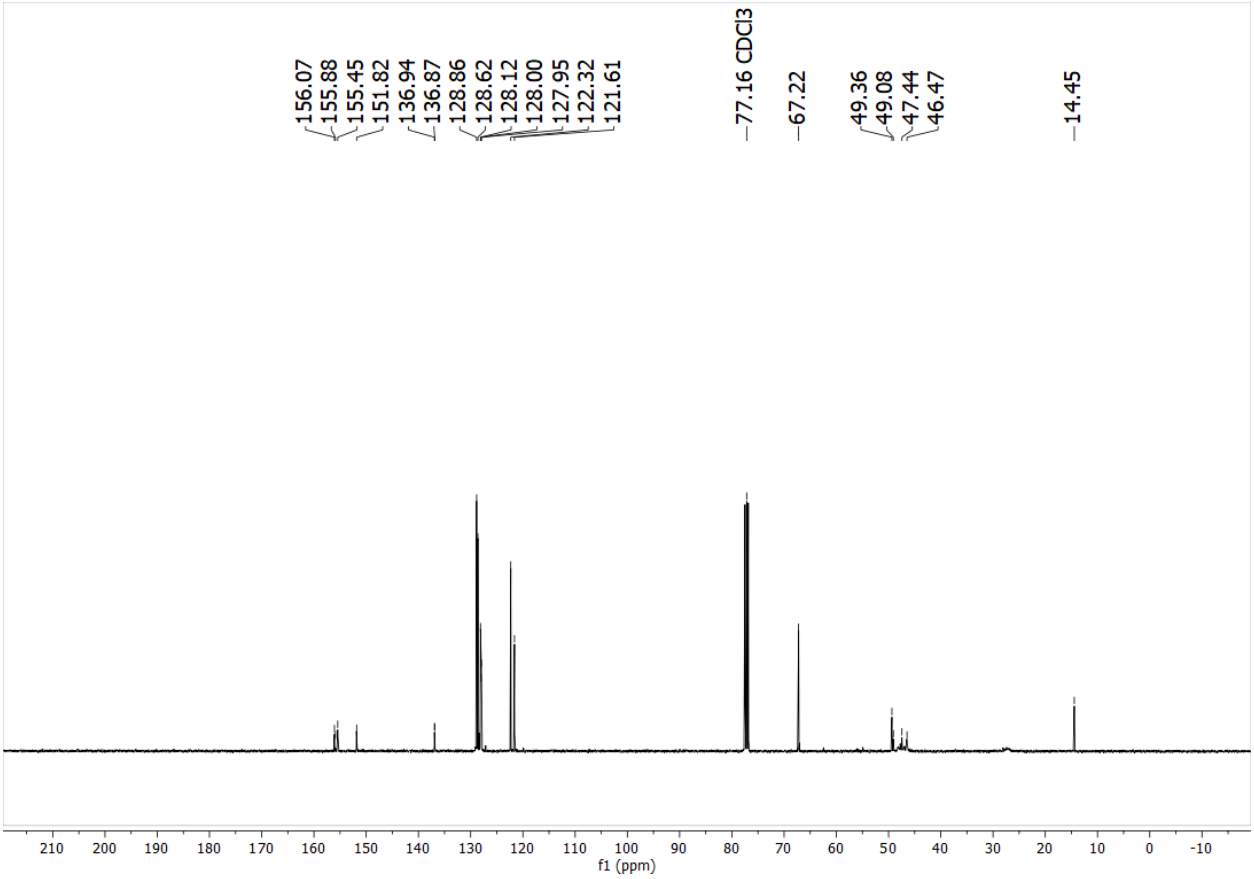
benzyl (Z)-4-(1-(phenylimino)ethyl)-1,4-diazepane-1-carboxylate (3e)

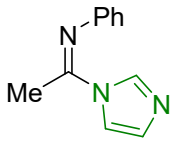
^{1}H NMR: 400 MHz in $CDCl_3$





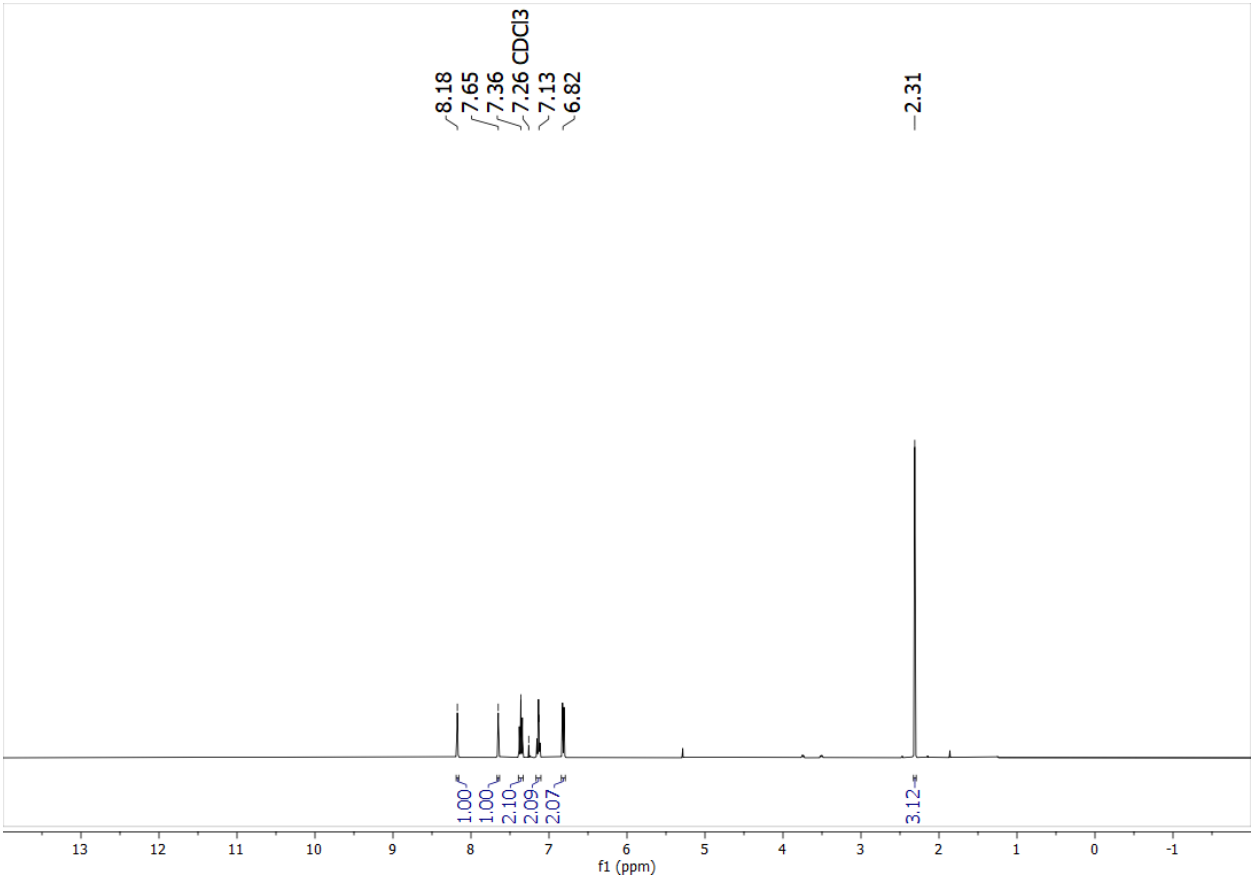
^{13}C NMR: 101 MHz in $CDCl_3$

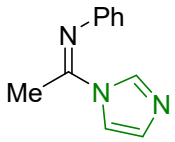




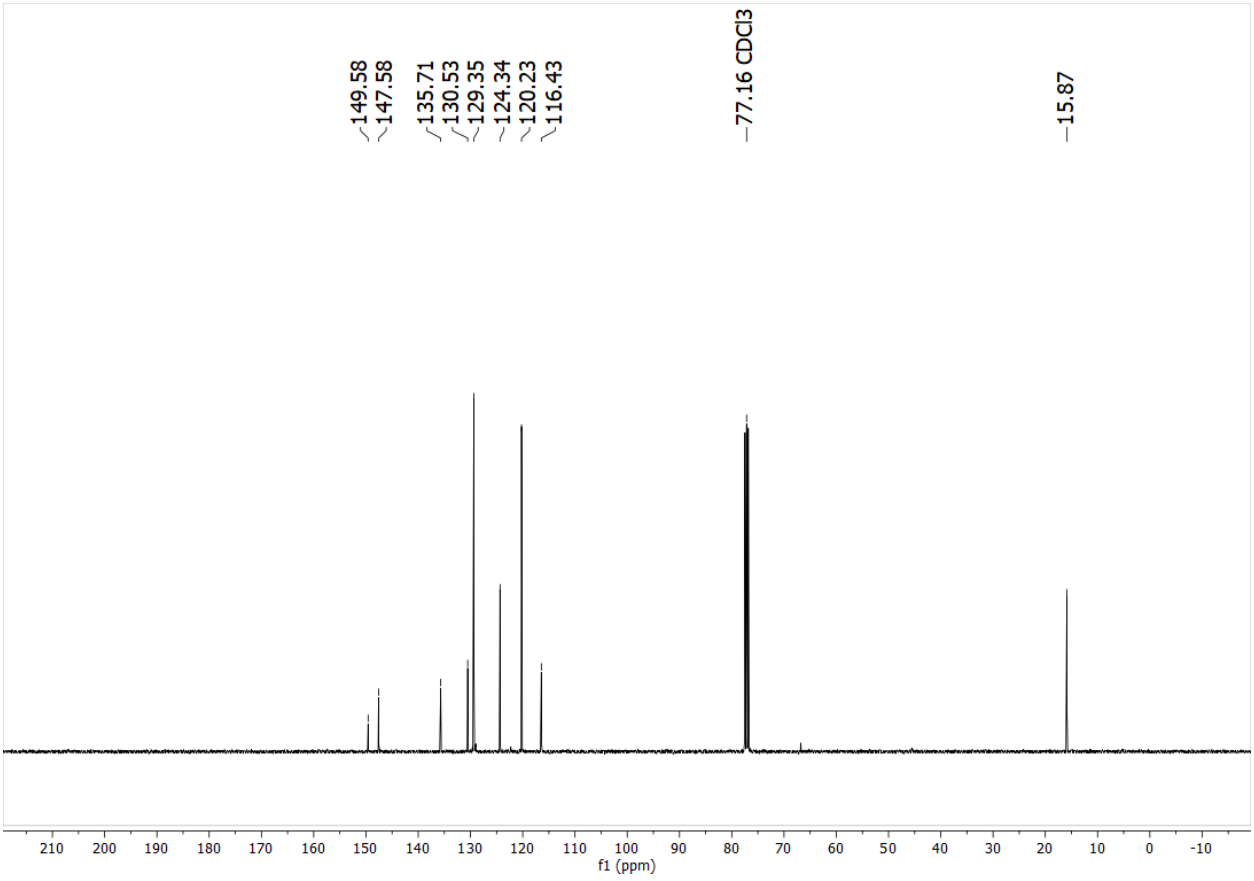
(Z)-1-(imidazolyl)-N-phenylethanimine (3f)

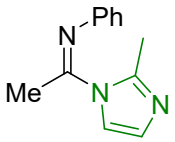
^{1}H NMR: 400 MHz in $CDCl_3$





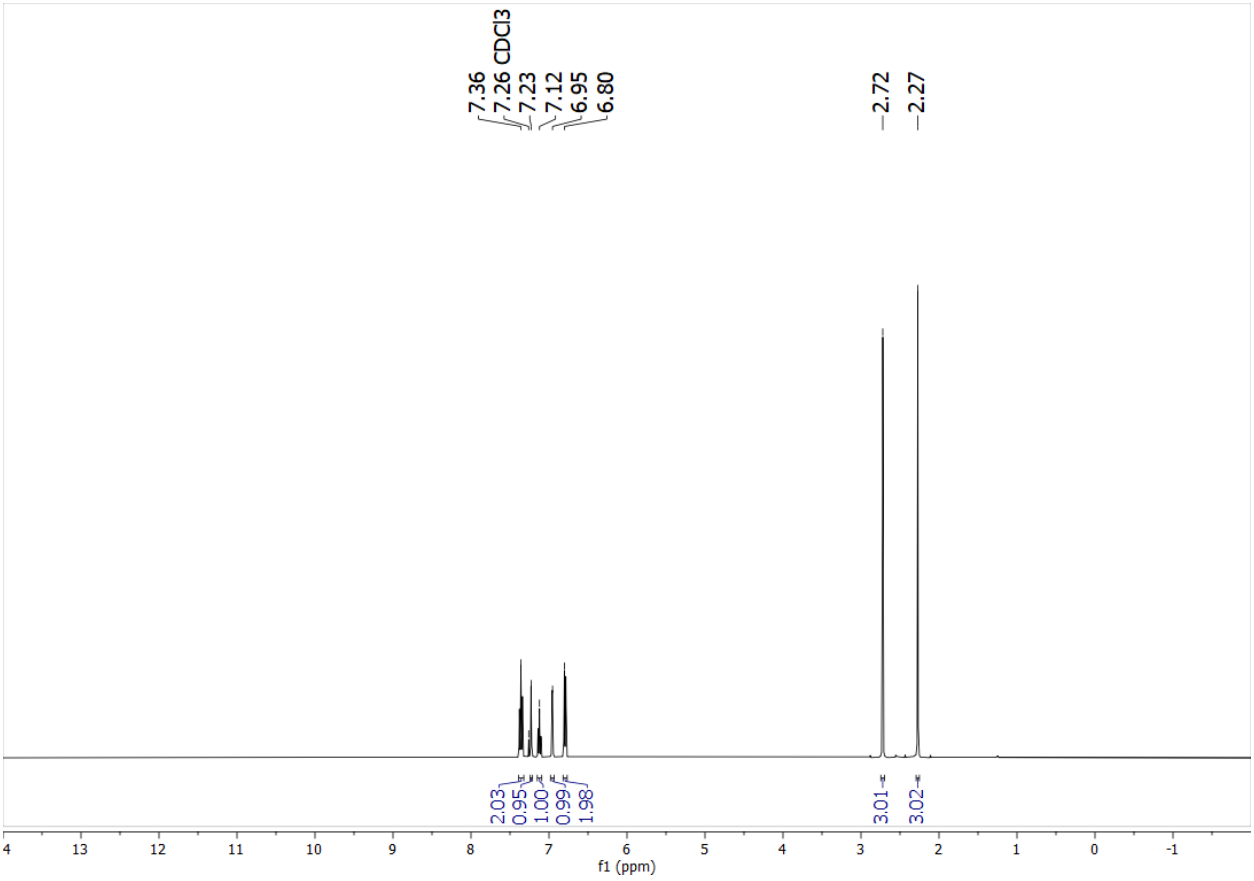
^{13}C NMR: 101 MHz in $CDCl_3$

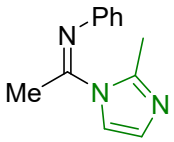




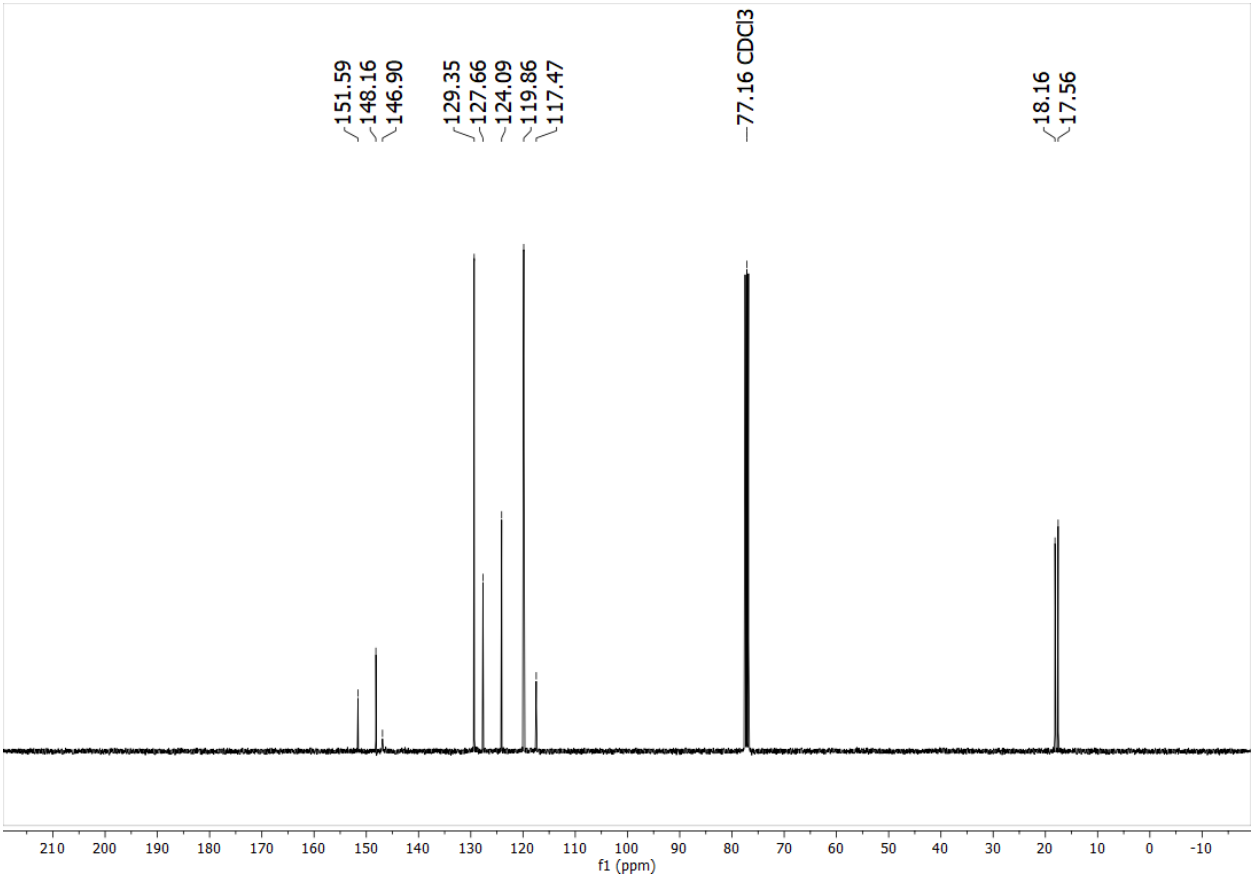
(Z)-1-(2-methylimidazolyl)-N-phenylethanimine (3g)

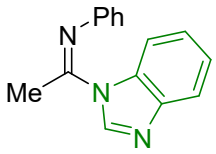
^{1}H NMR: 400 MHz in $CDCl_3$





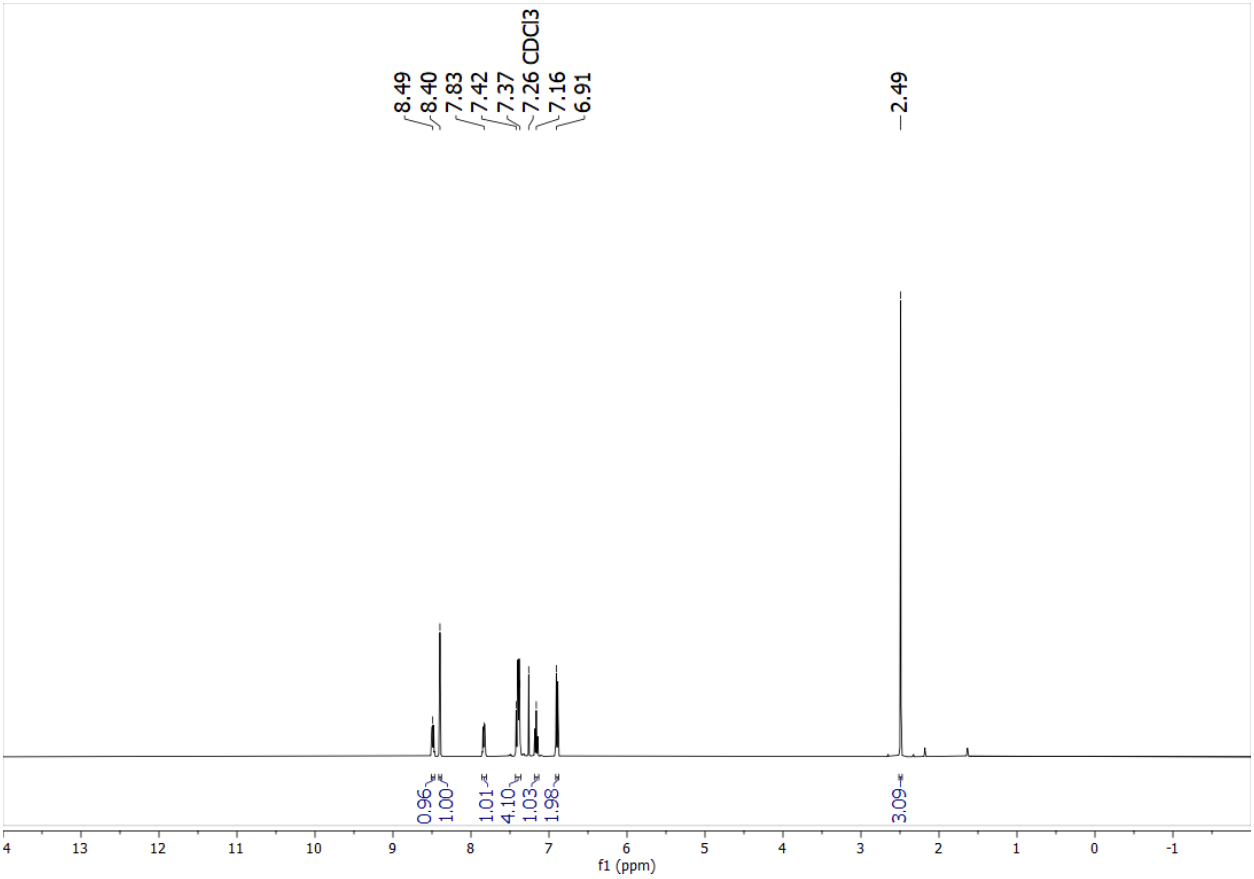
^{13}C NMR: 101 MHz in $CDCl_3$

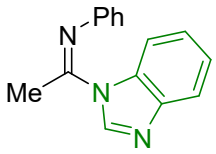




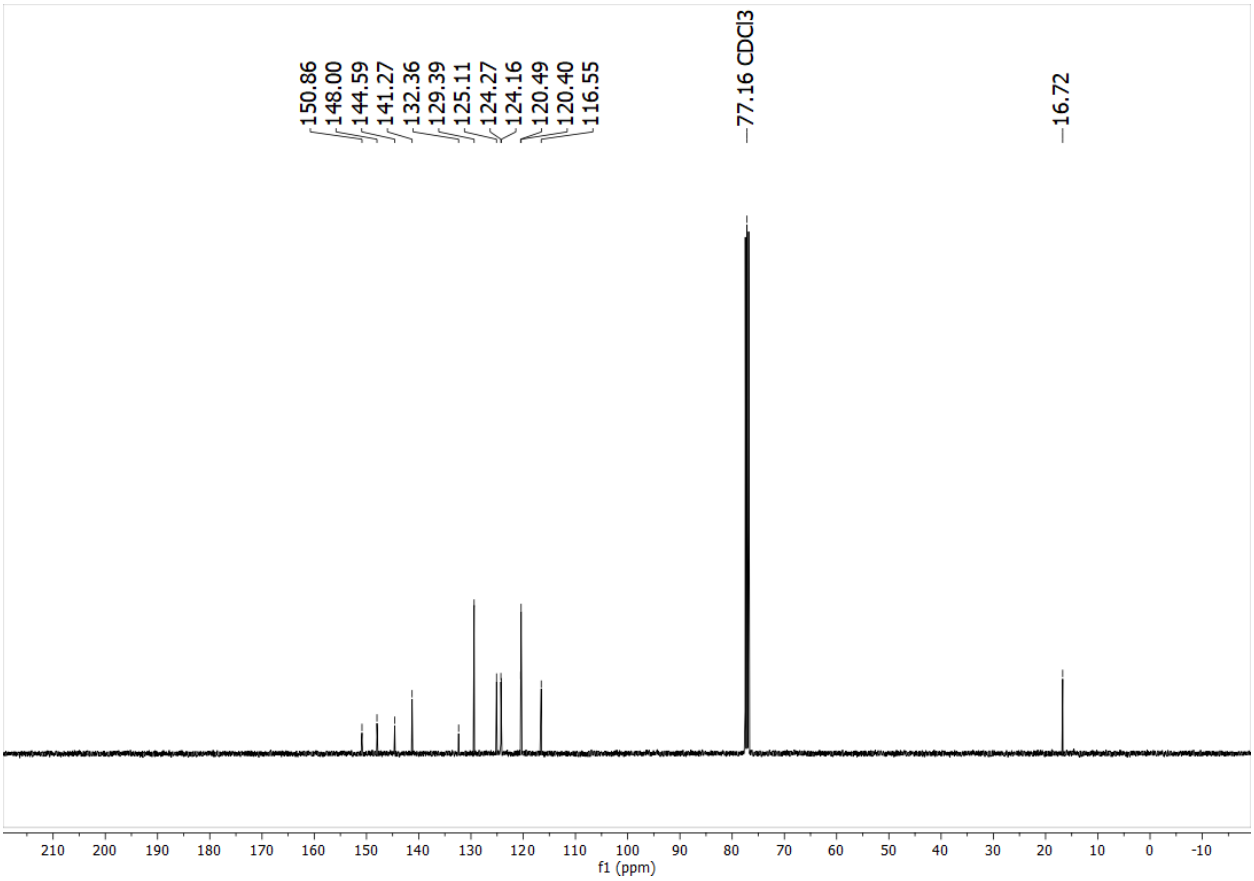
(Z)-1-(1H-benzo[d]imidazolyl)-N-phenylethanimine (3h)

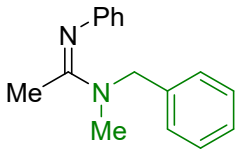
^{1}H NMR: 400 MHz in $CDCl_3$





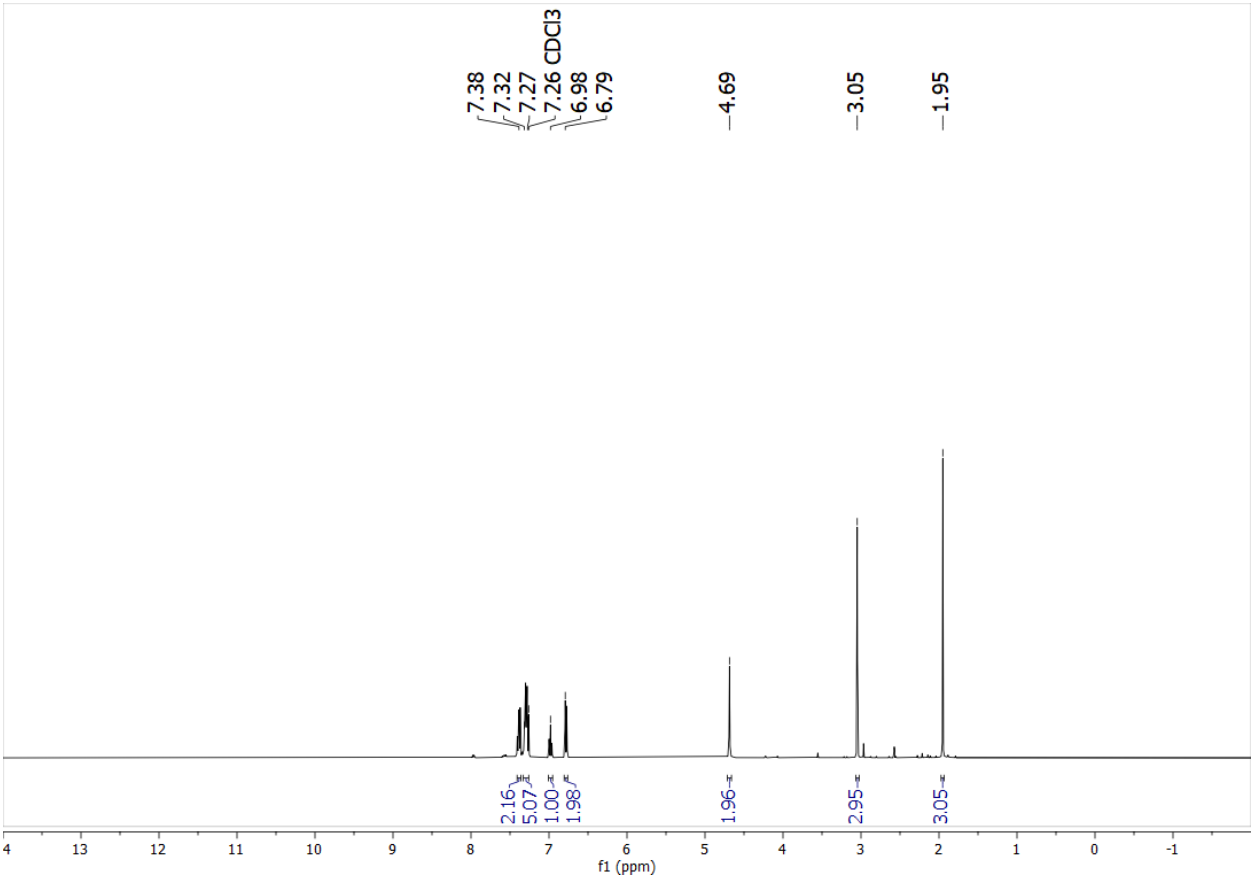
^{13}C NMR: 101 MHz in $CDCl_3$

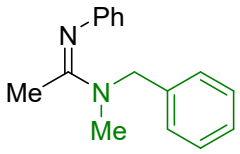




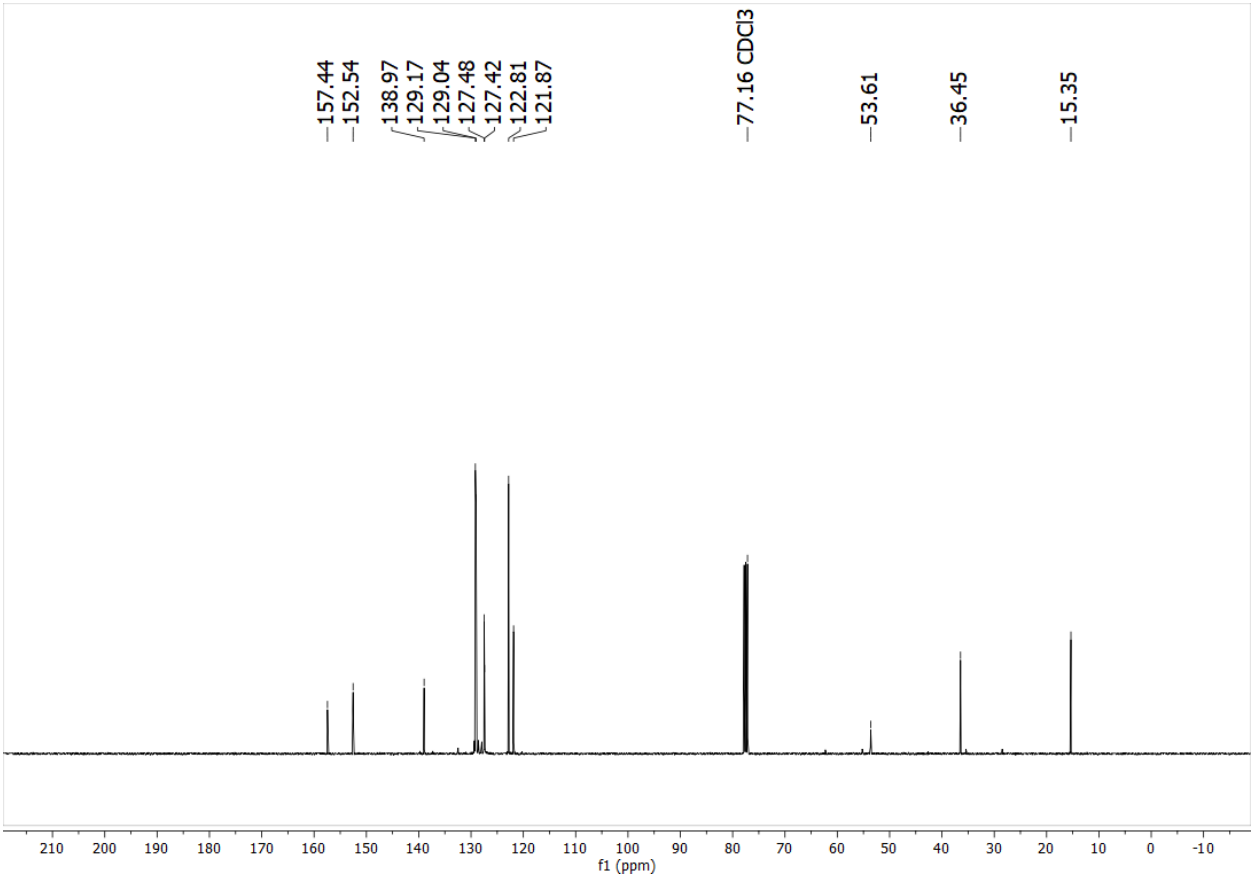
(Z)-N-benzyl-N-methyl-N'-phenylethanimine (3i)

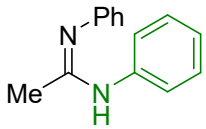
^{1}H NMR: 400 MHz in $CDCl_3$





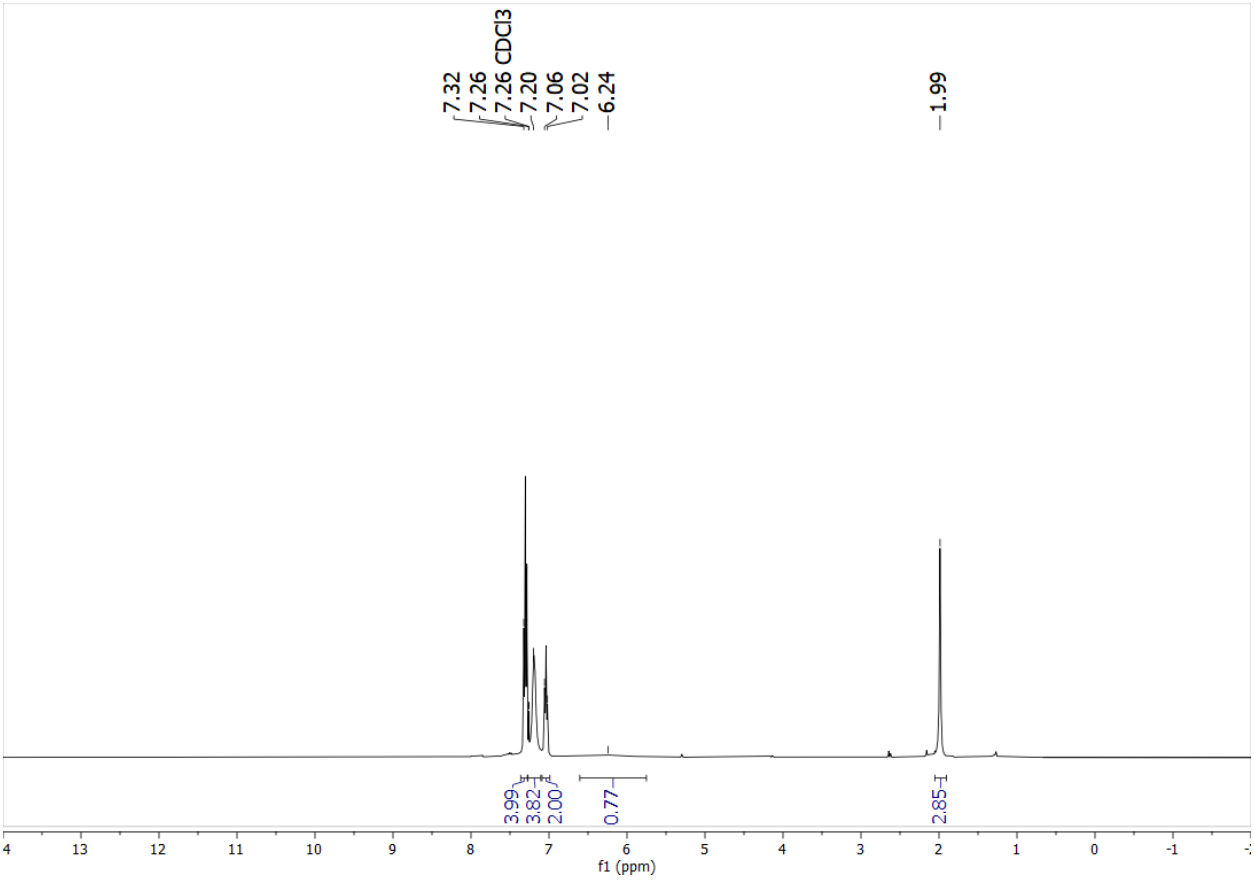
^{13}C NMR: 101 MHz in $CDCl_3$

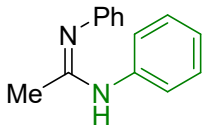




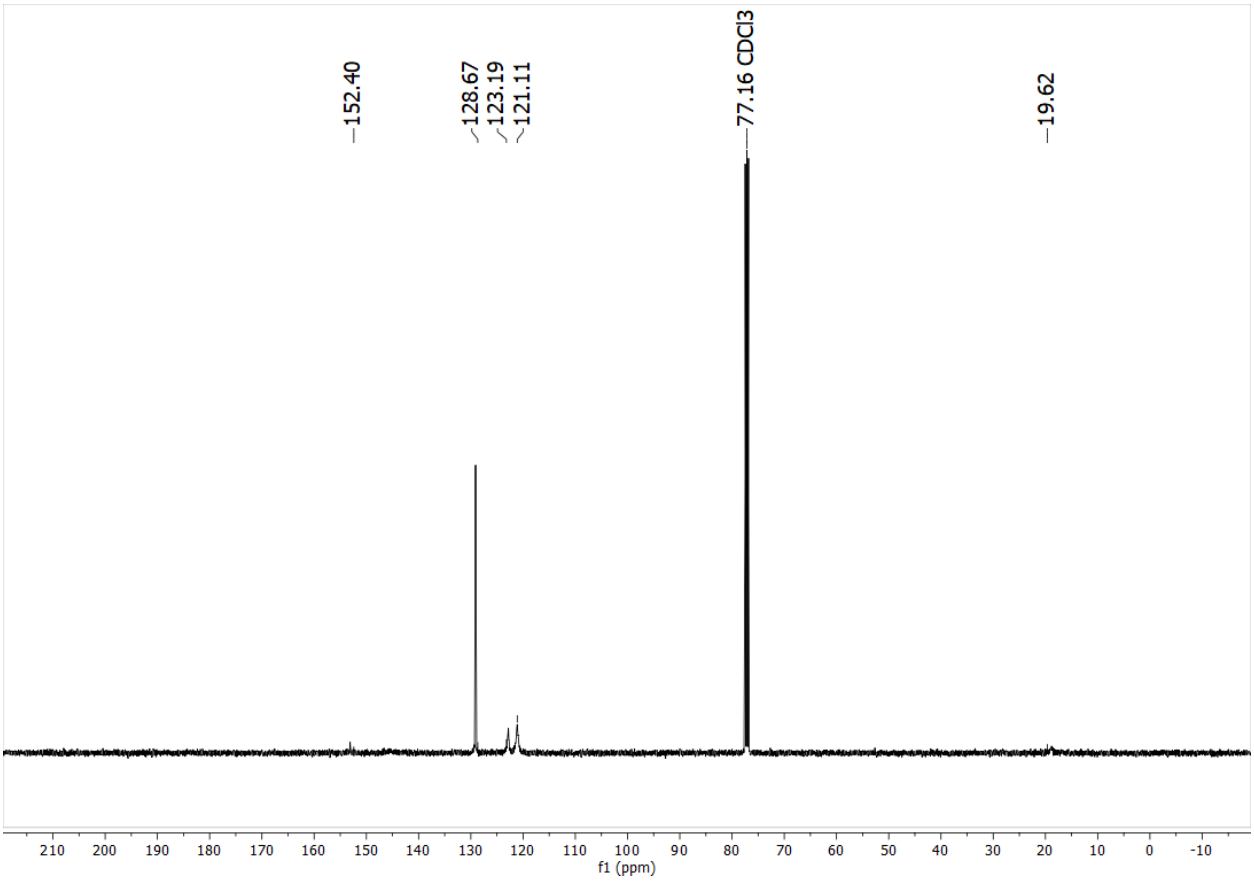
(Z)-N,N'-diphenylacetimidamide (3j)

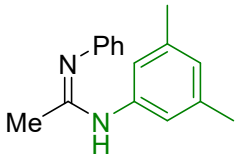
^{1}H NMR: 400 MHz in $CDCl_3$





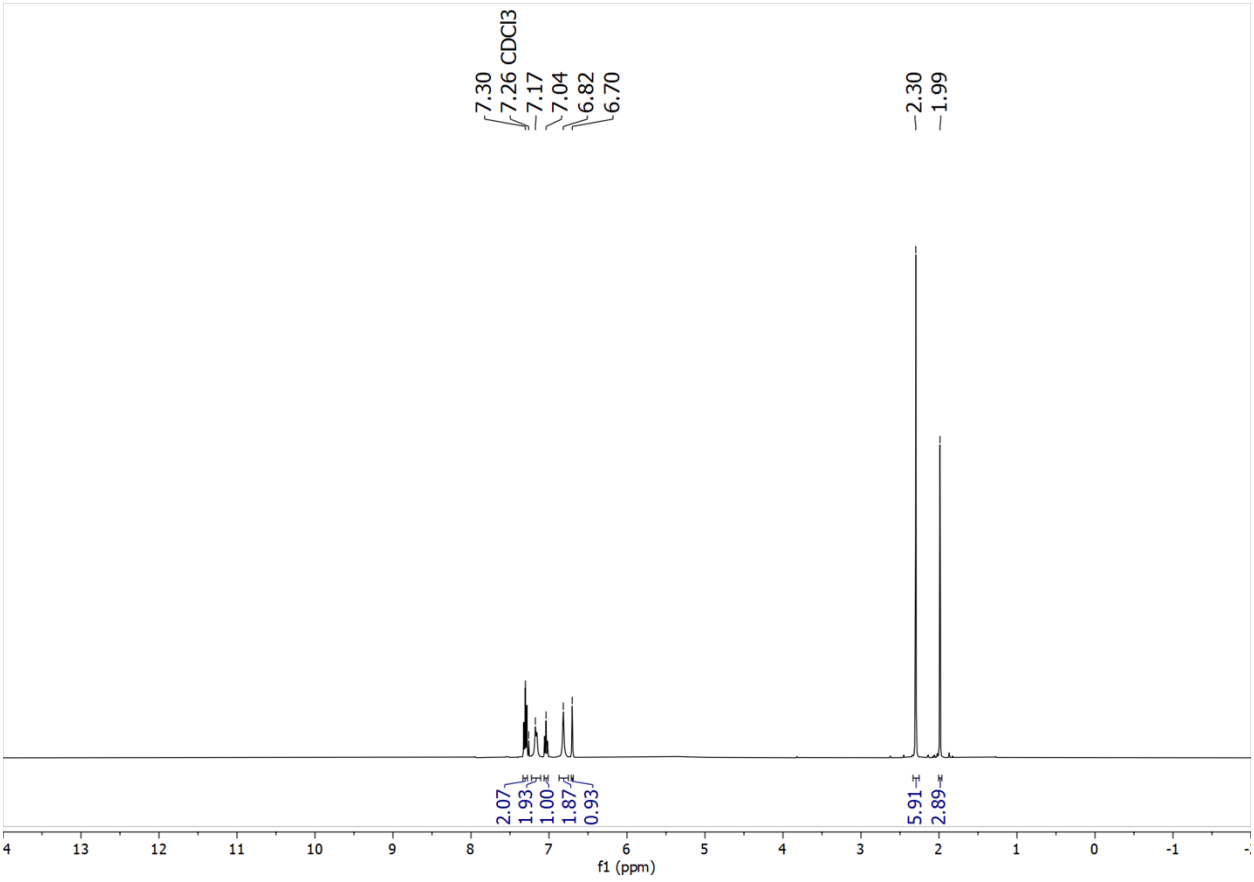
^{13}C NMR: 101 MHz in $CDCl_3$

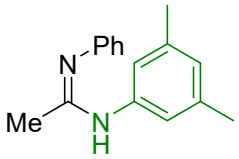




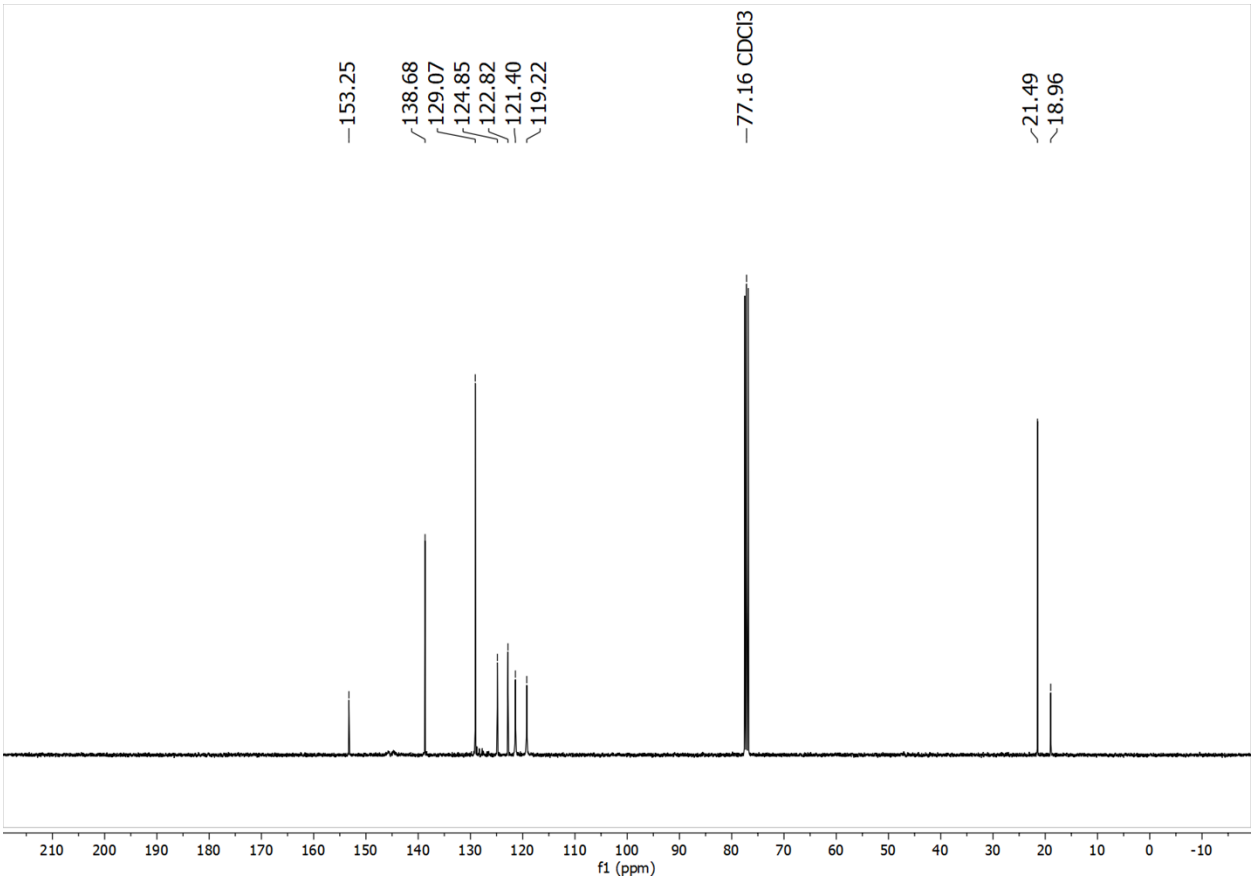
(Z)-N-(3,5-dimethylphenyl)-N'-phenylacetimidamide (3k)

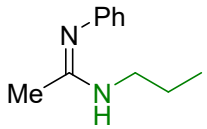
^{1}H NMR: 400 MHz in $CDCl_3$





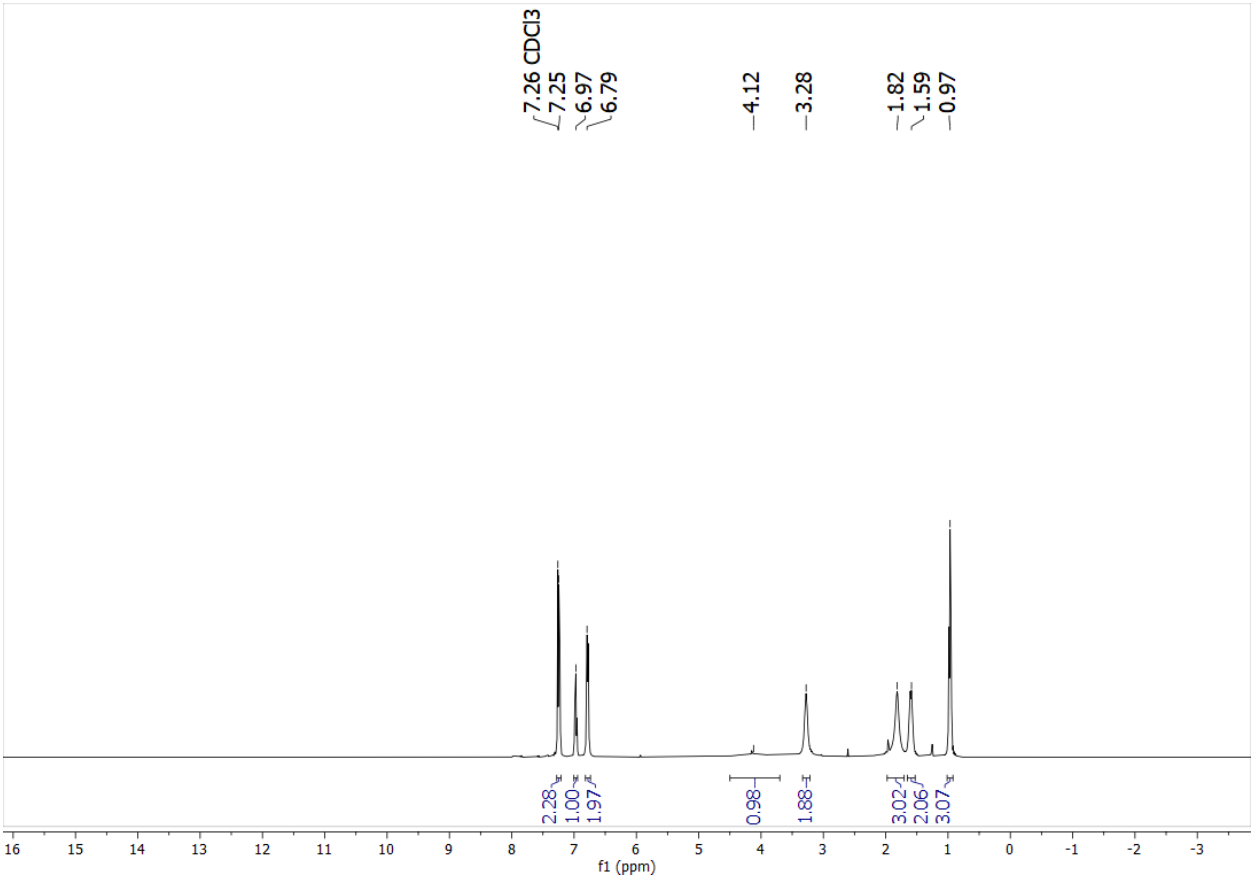
^{13}C NMR: 101 MHz in $CDCl_3$

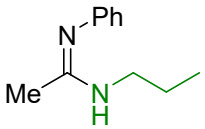




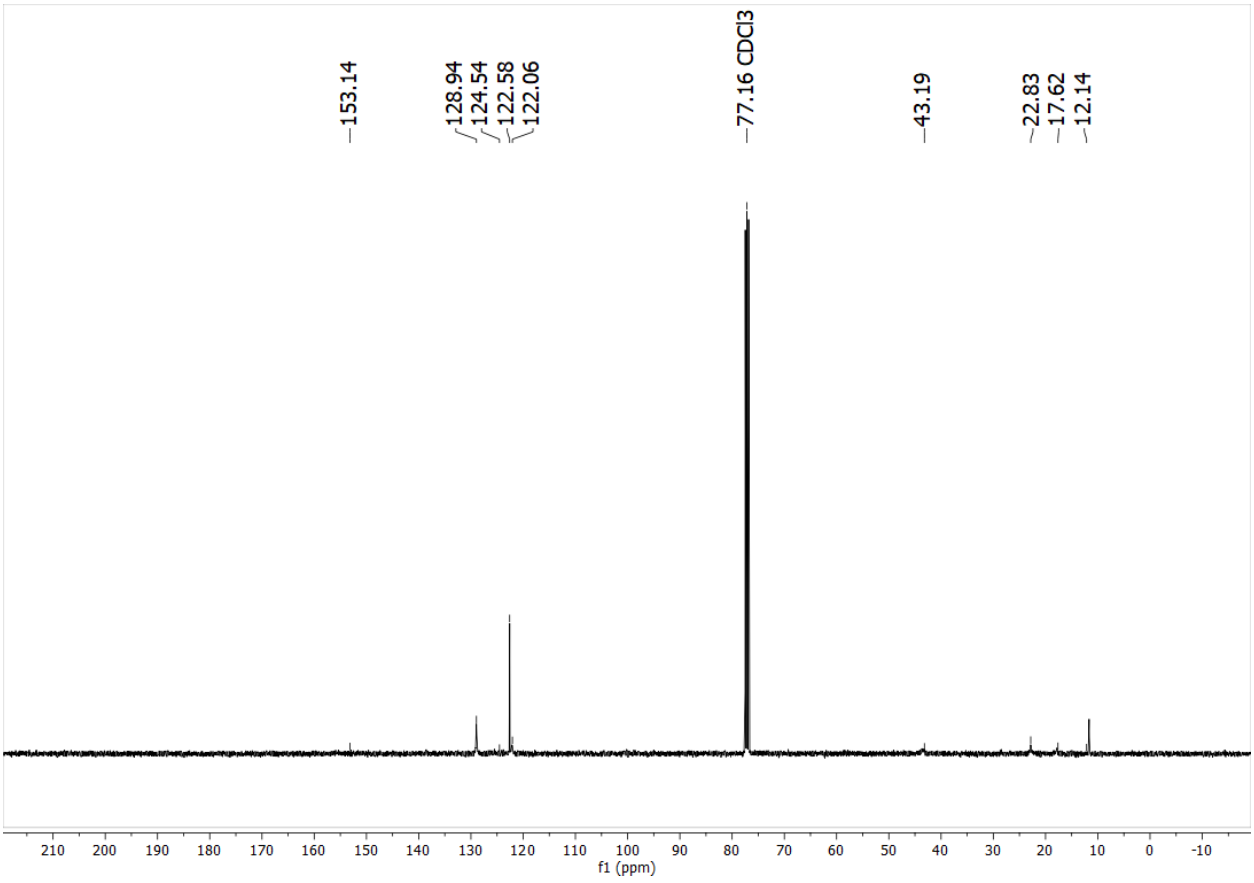
(Z)-N'-phenyl-N-propylacetimidamide (3l)

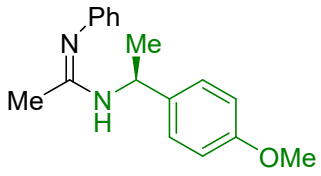
^{1}H NMR: 400 MHz in $CDCl_3$





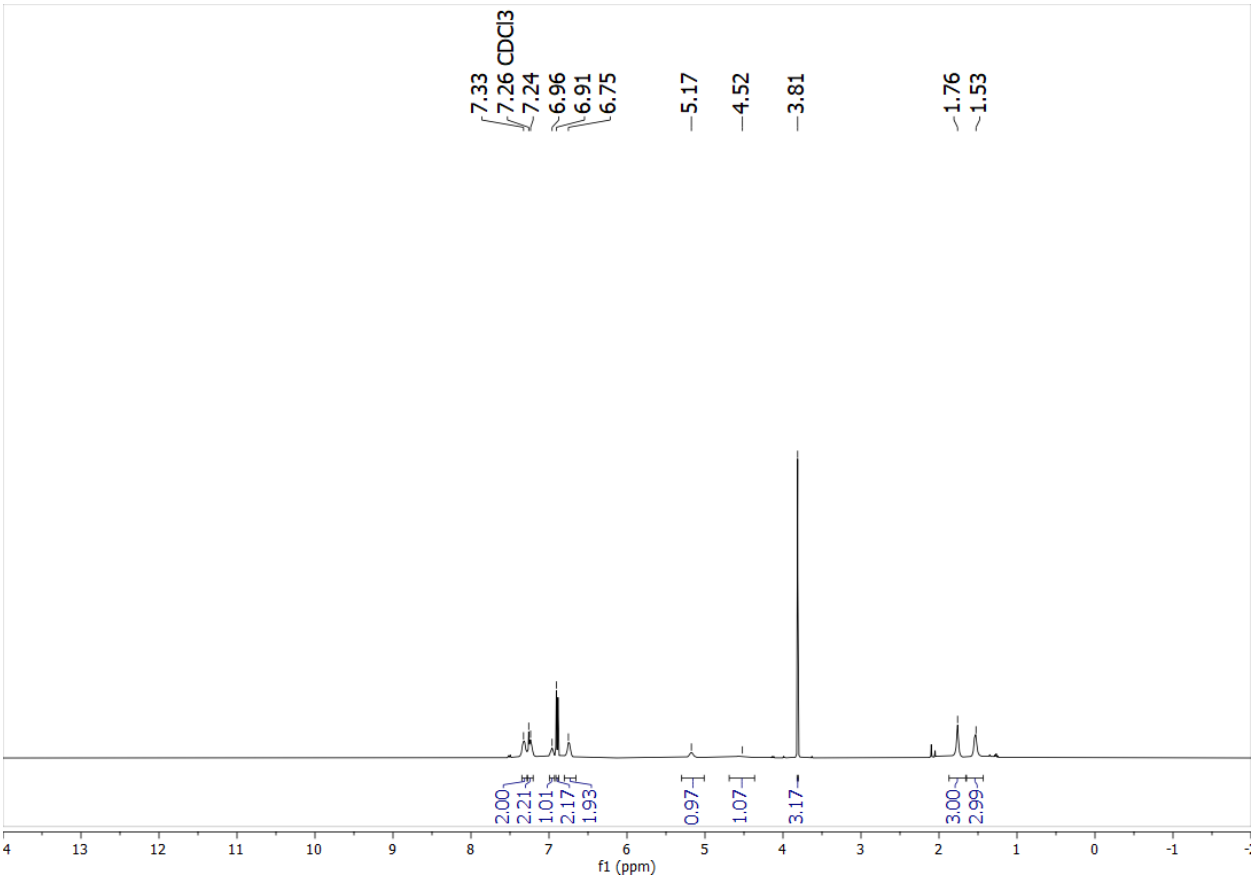
^{13}C NMR: 101 MHz in $CDCl_3$

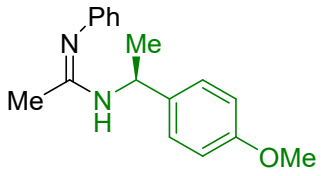




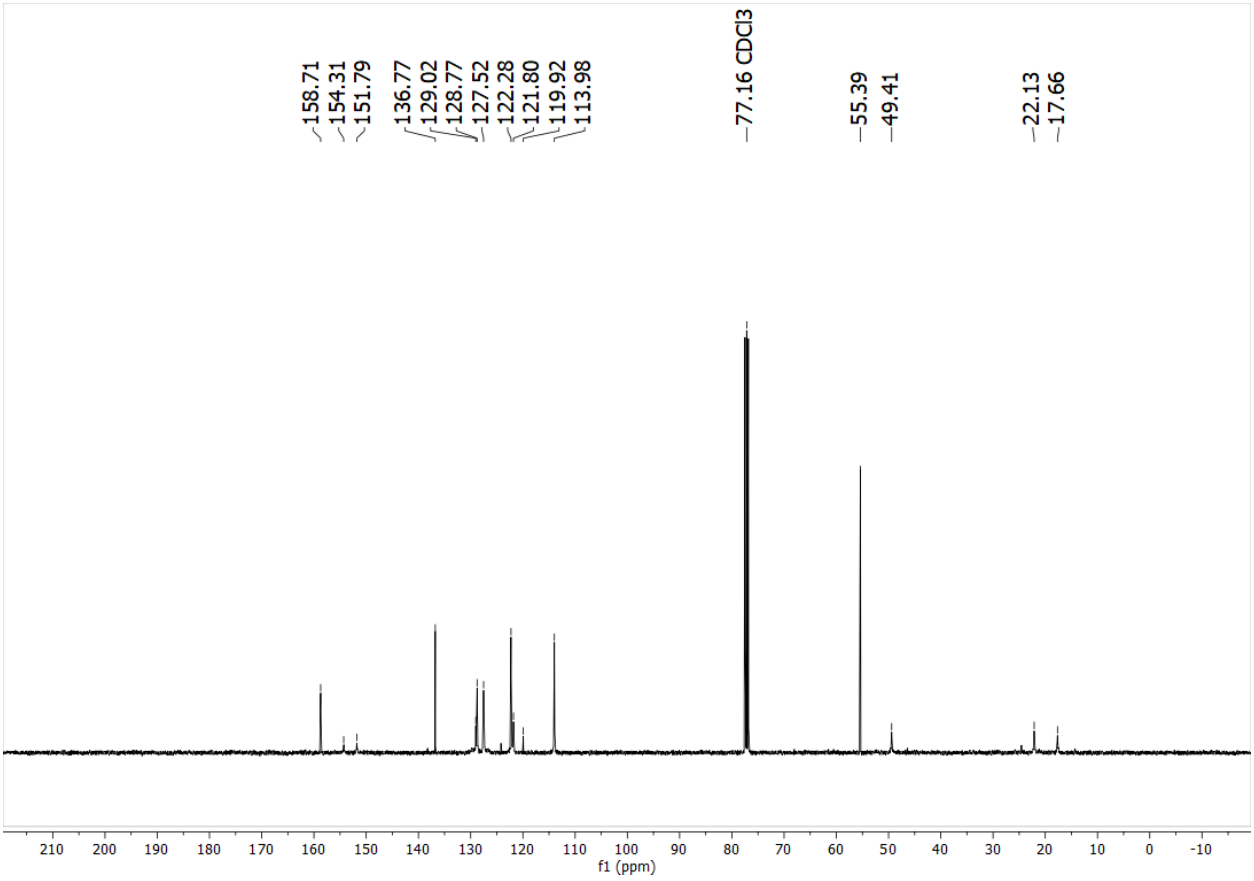
(S,Z)-N-(1-(4-methoxyphenyl)ethyl)-N'-phenylacetimidamide (3m)

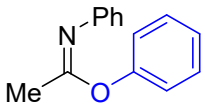
^{1}H NMR: 400 MHz in $CDCl_3$





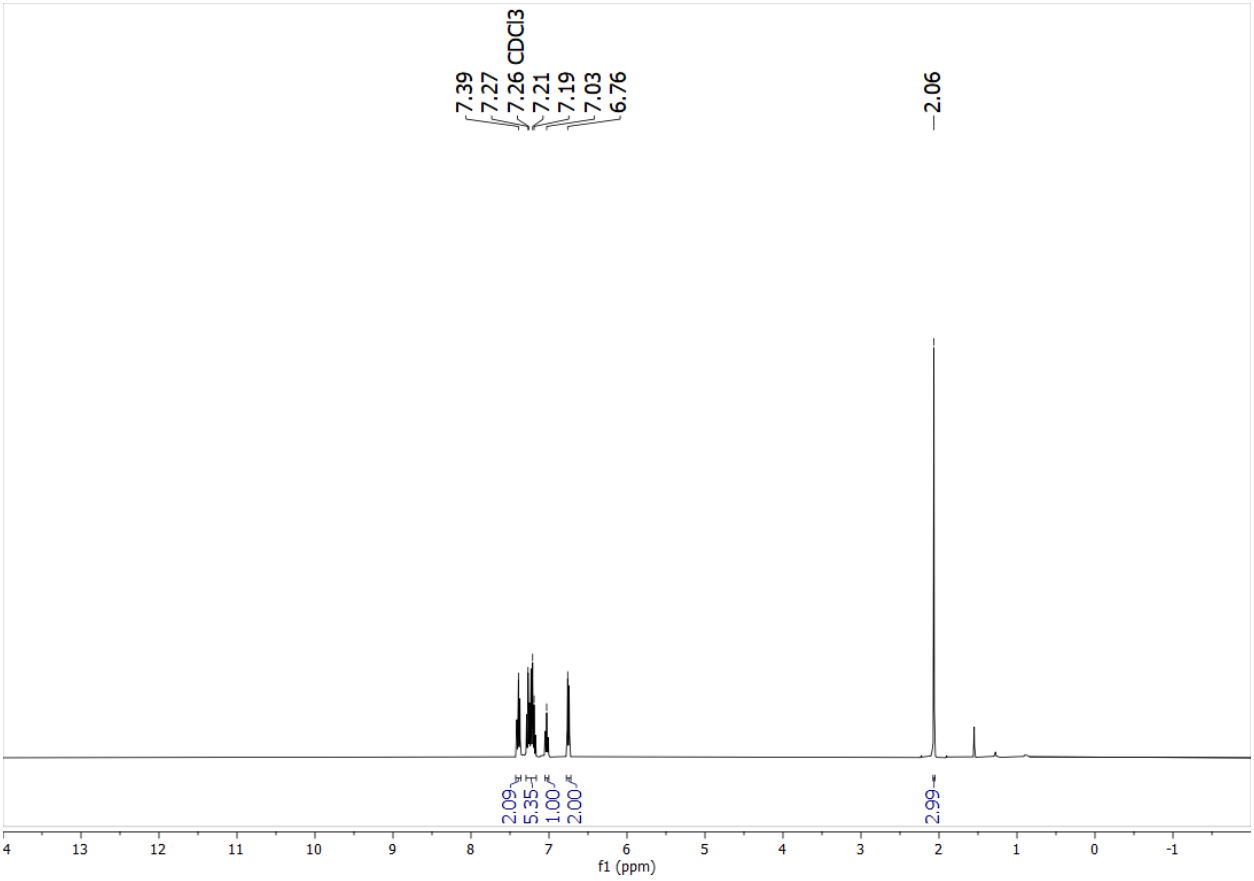
^{13}C NMR: 101 MHz in $CDCl_3$

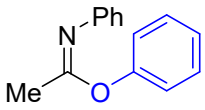




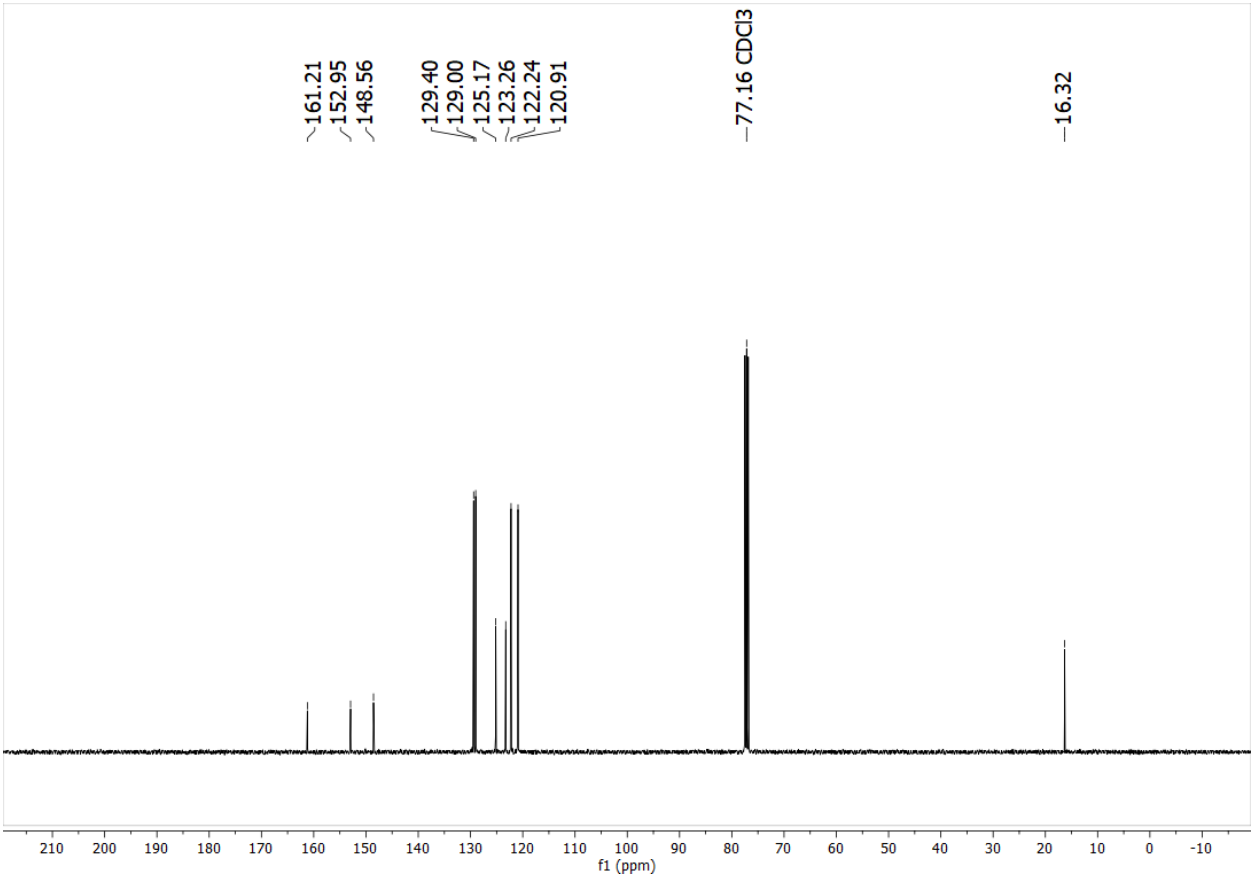
phenyl (Z)-N-phenylacetimidate (4a)

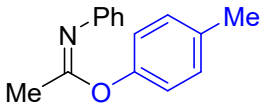
^{1}H NMR: 400 MHz in $CDCl_3$





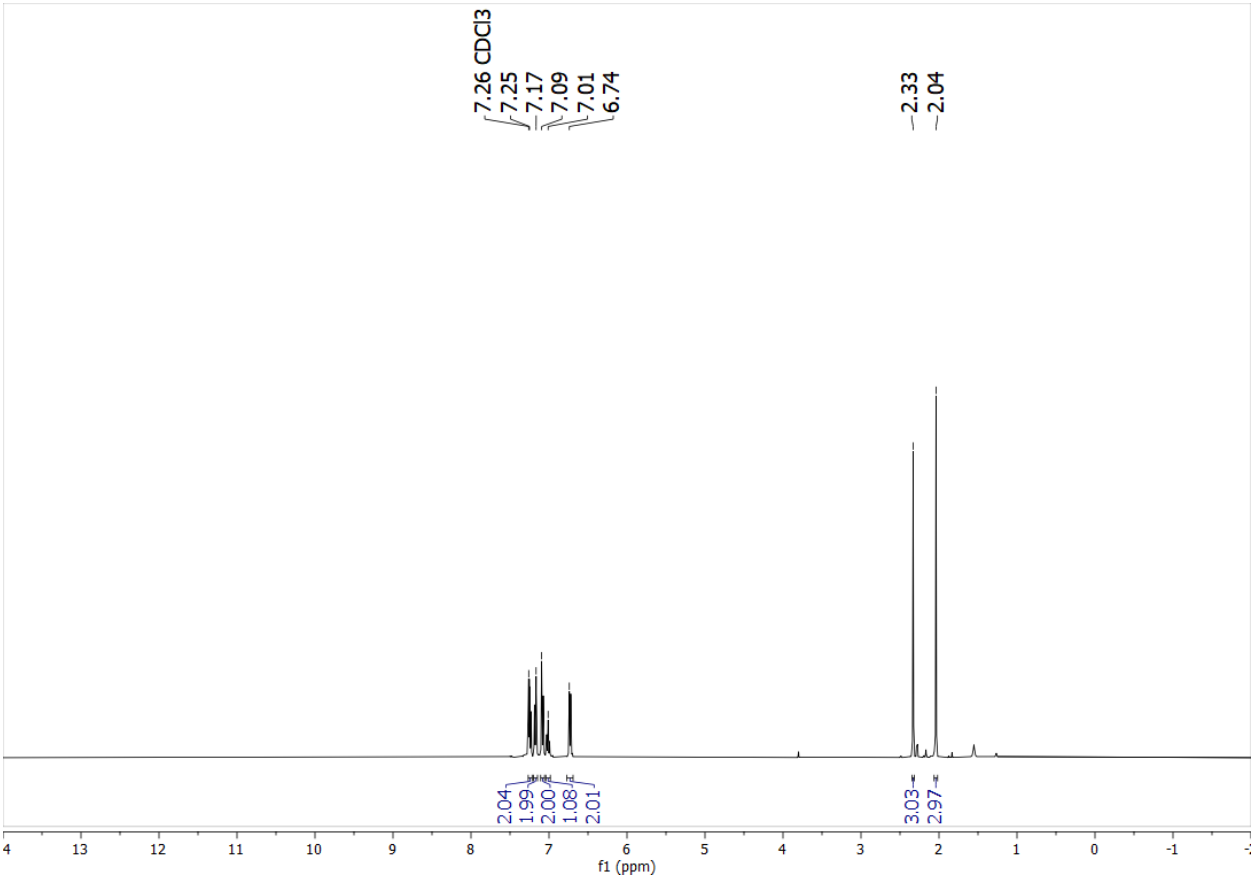
^{13}C NMR: 101 MHz in $CDCl_3$

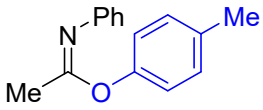




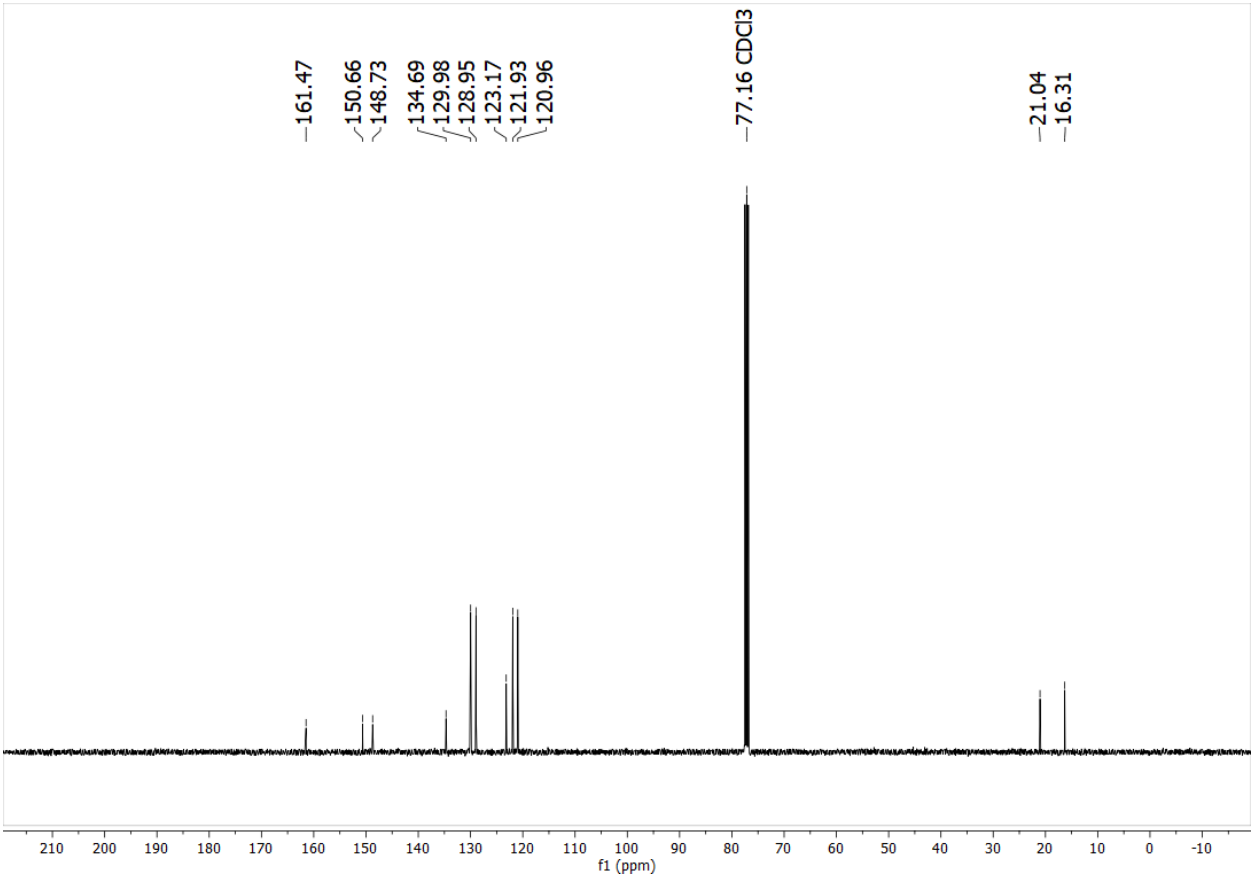
4-methylphenyl (Z)-N-phenylacetimidate (4b)

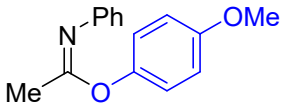
^{1}H NMR: 400 MHz in $CDCl_3$





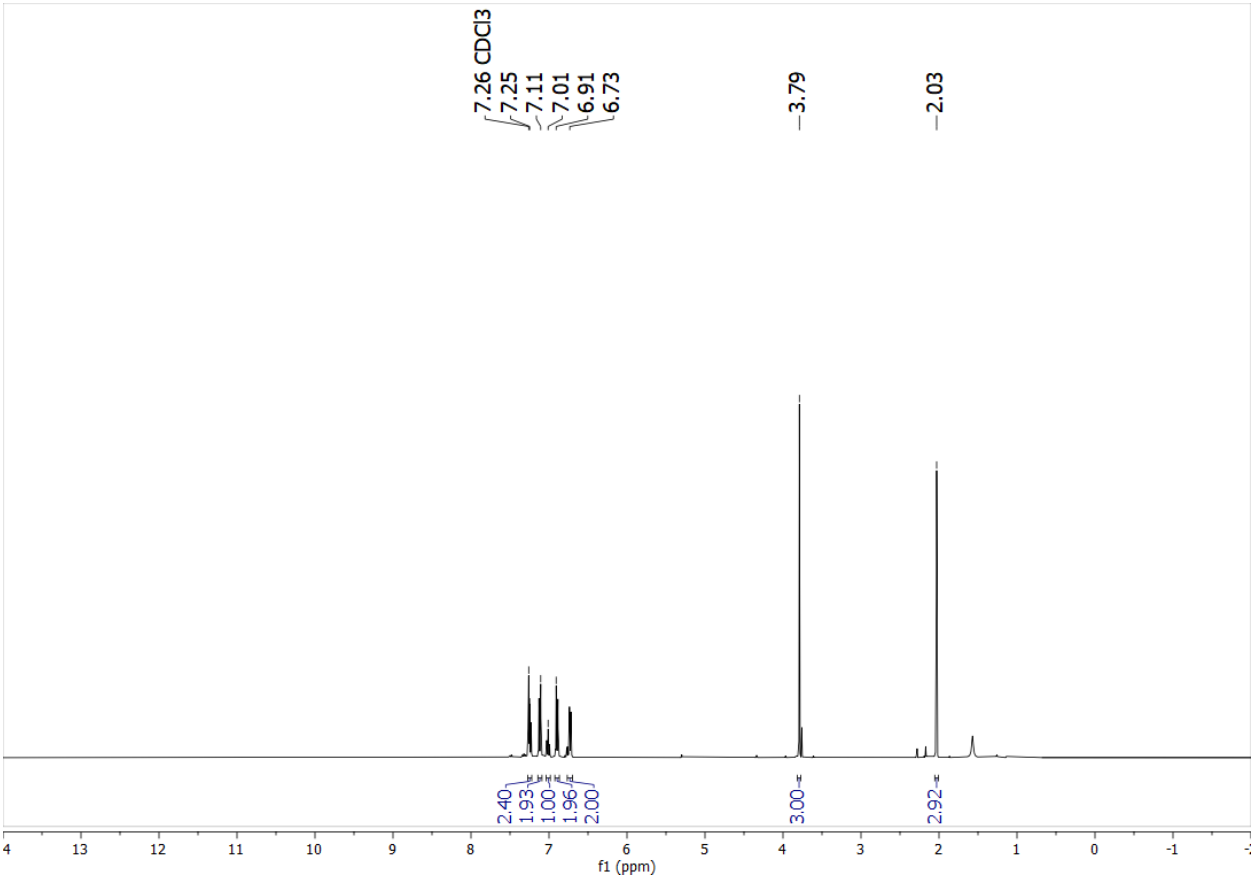
^{13}C NMR: 101 MHz in $CDCl_3$

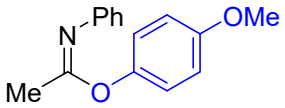




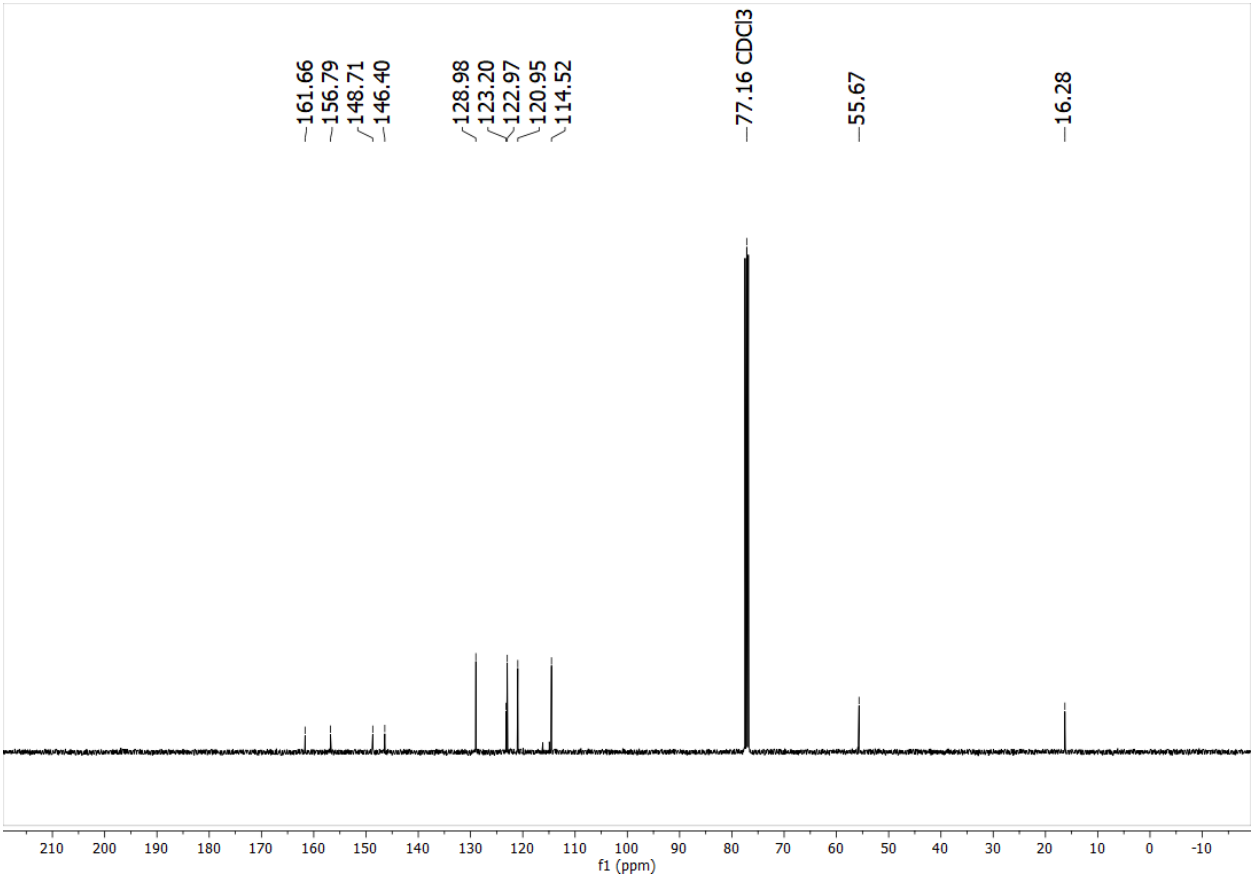
4-methoxyphenyl (Z)-N-phenylacetimidate (4c)

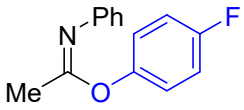
^{1}H NMR: 400 MHz in $CDCl_3$





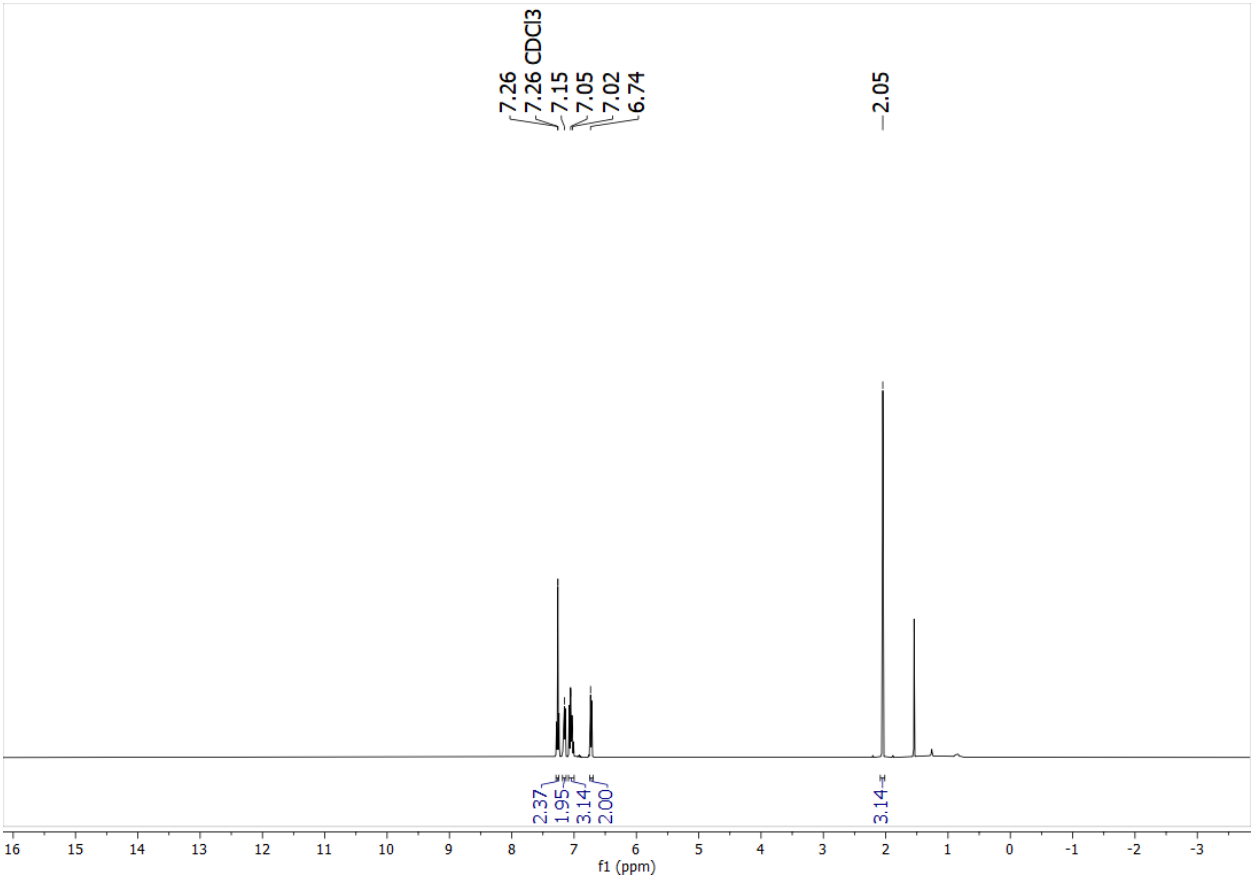
^{13}C NMR: 101 MHz in $CDCl_3$

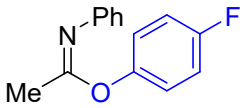




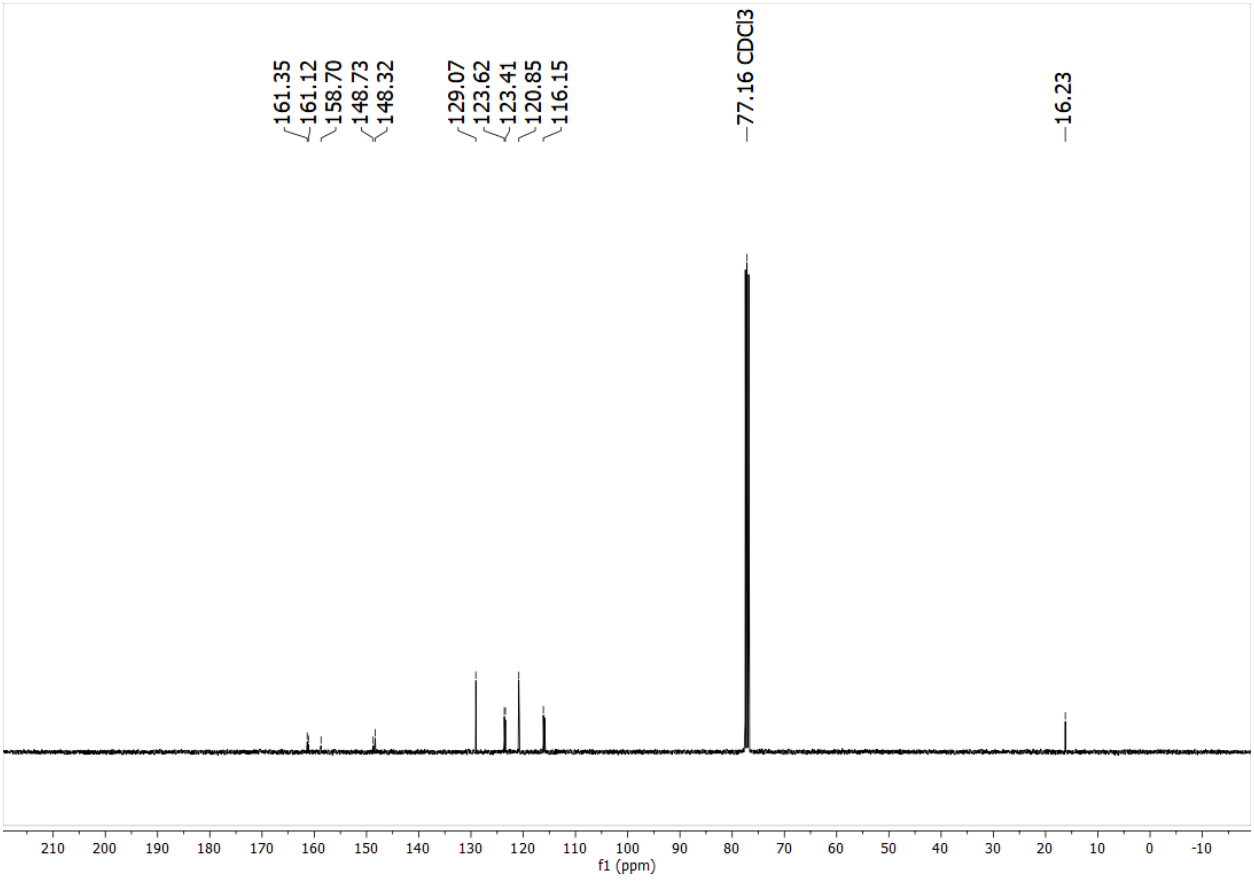
4-fluorophenyl (Z)-N-phenylacetimidate (4d)

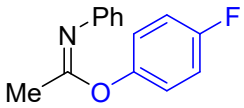
^{1}H NMR: 400 MHz in $CDCl_3$



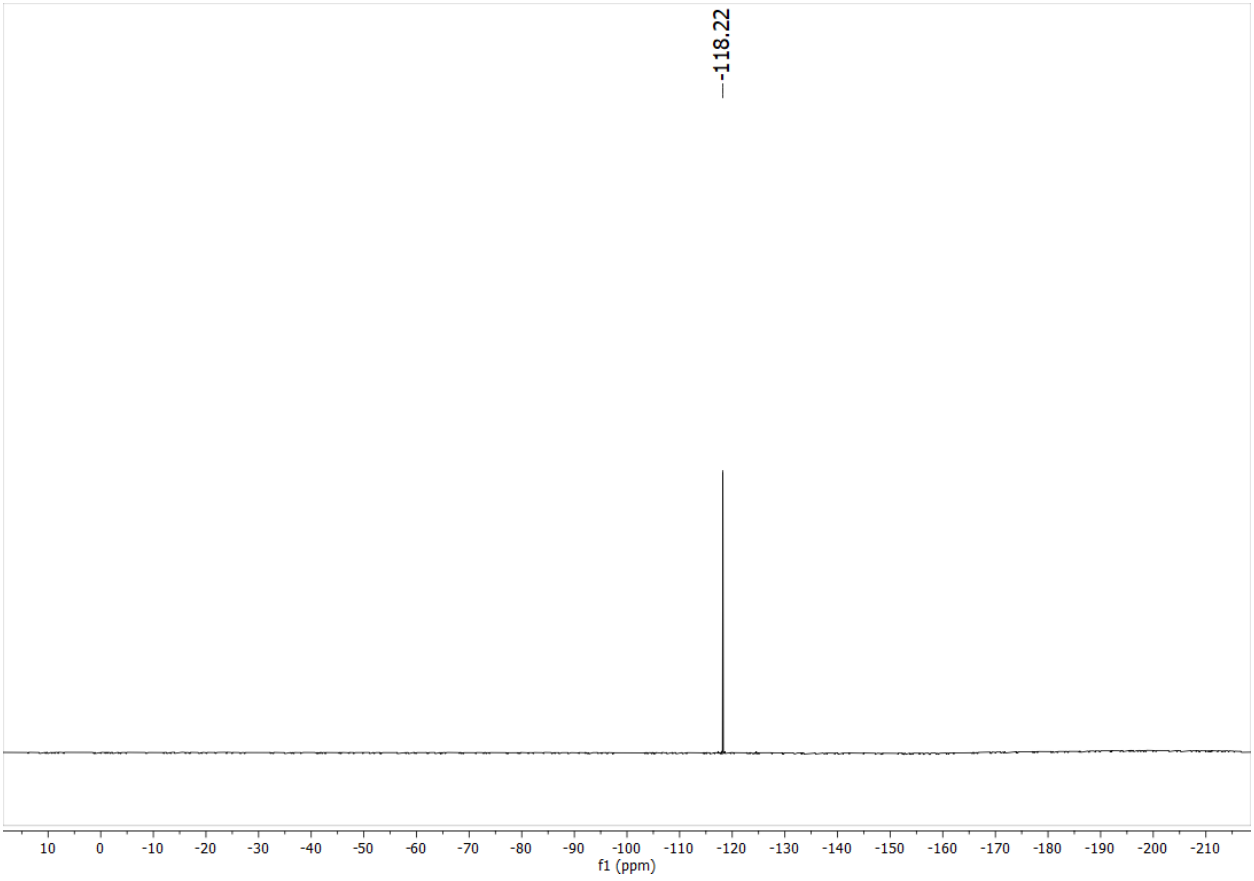


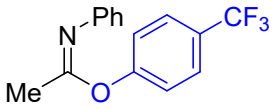
^{13}C NMR: 101 MHz in $CDCl_3$





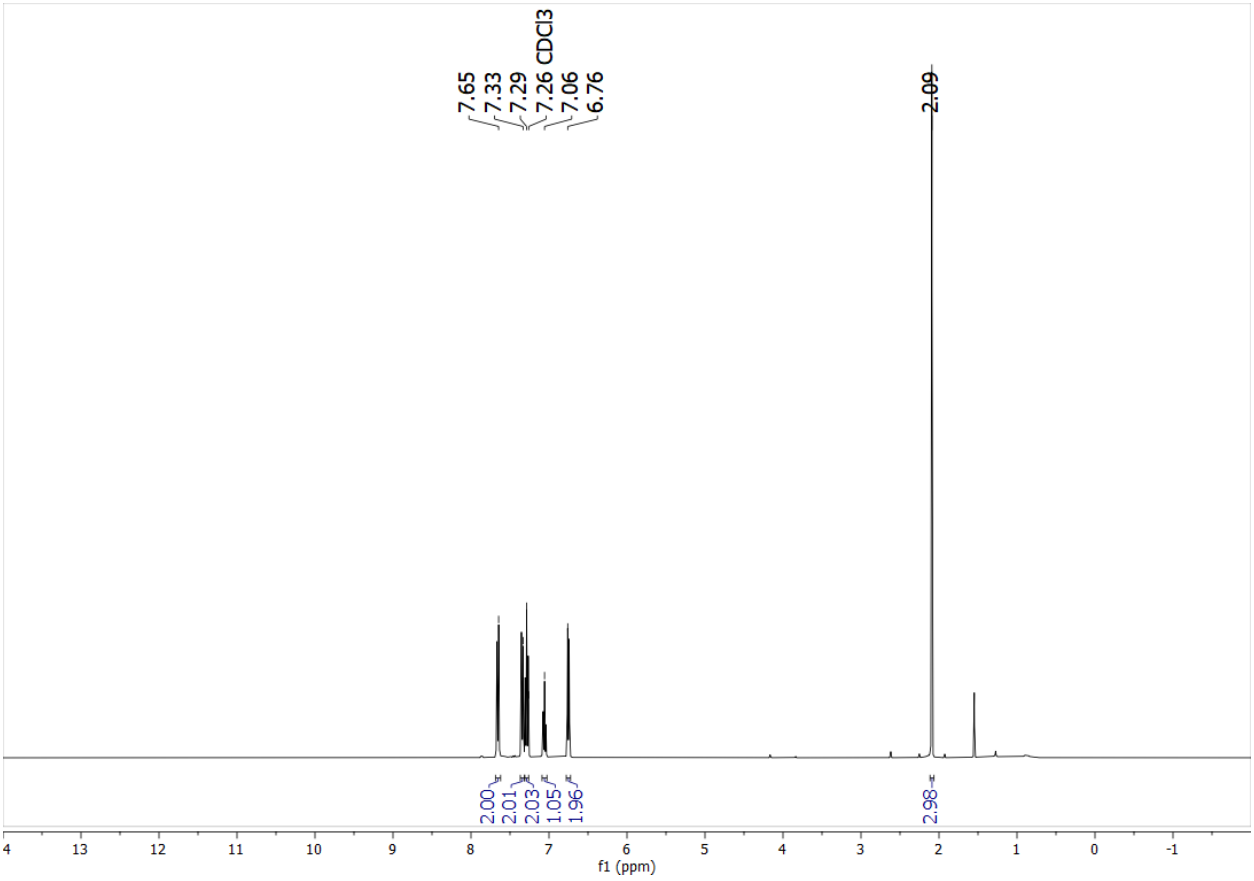
^{19}F NMR: 376 MHz in $CDCl_3$

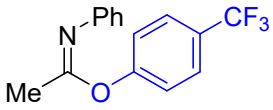




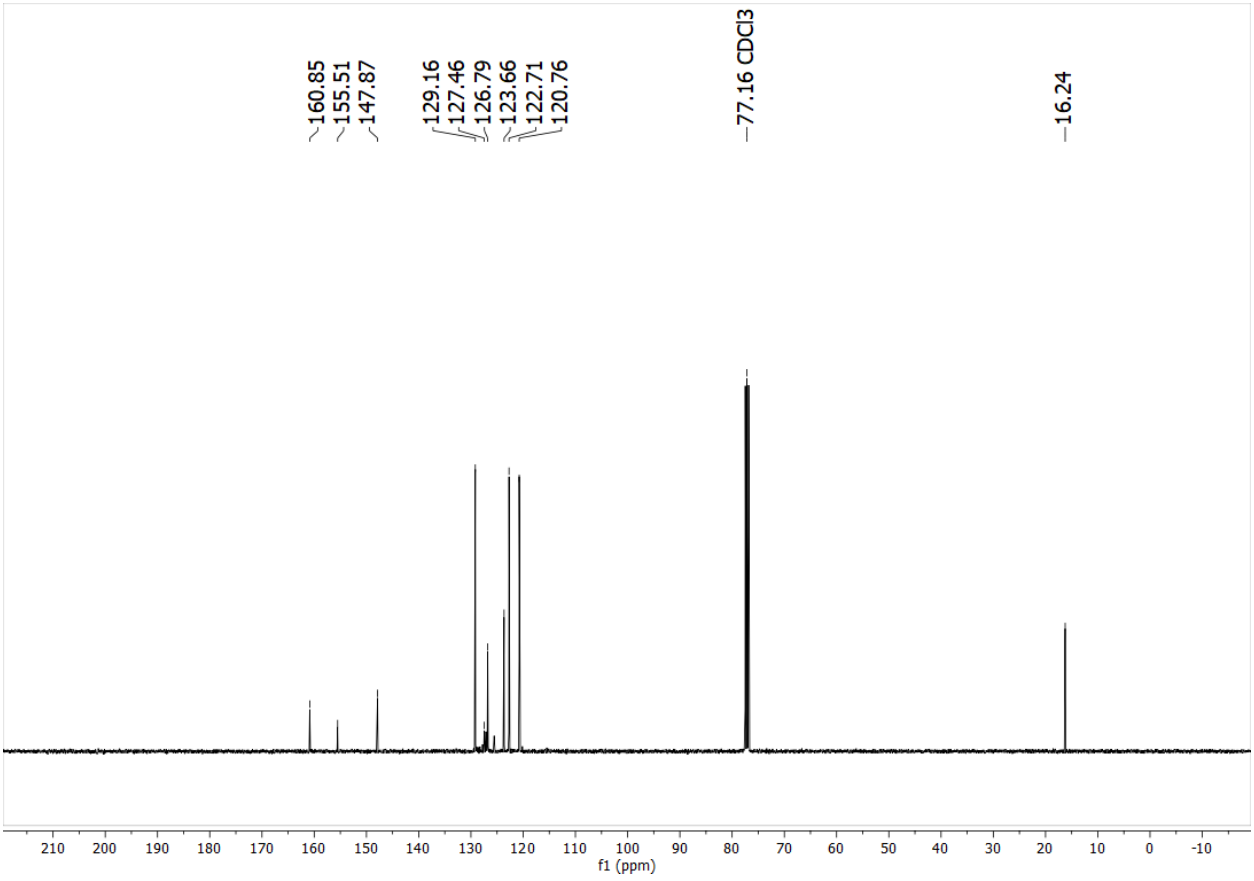
4-trifluoromethylphenyl (Z)-N-phenylacetimidate (4e)

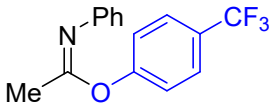
^{1}H NMR: 400 MHz in $CDCl_3$



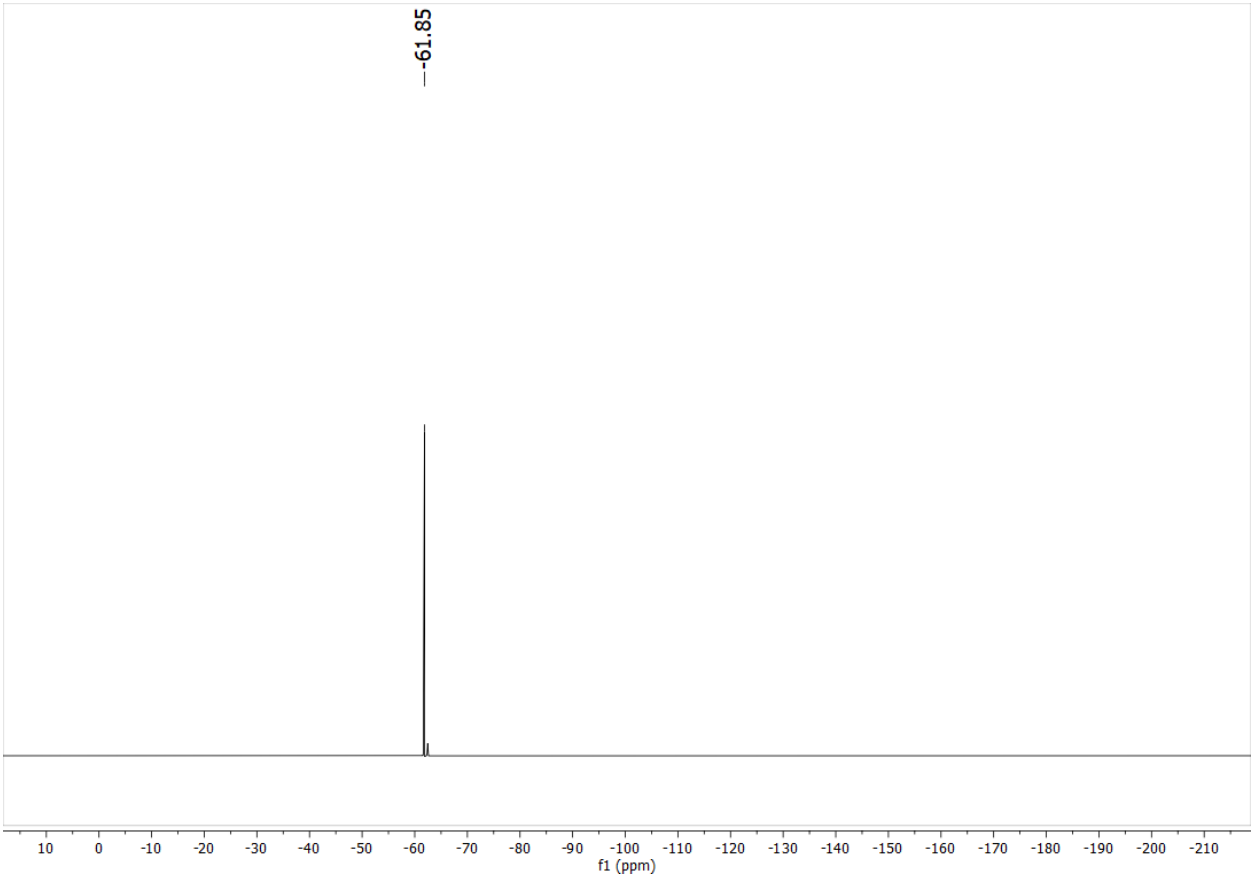


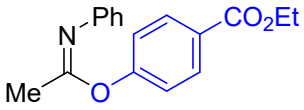
^{13}C NMR: 101 MHz in $CDCl_3$





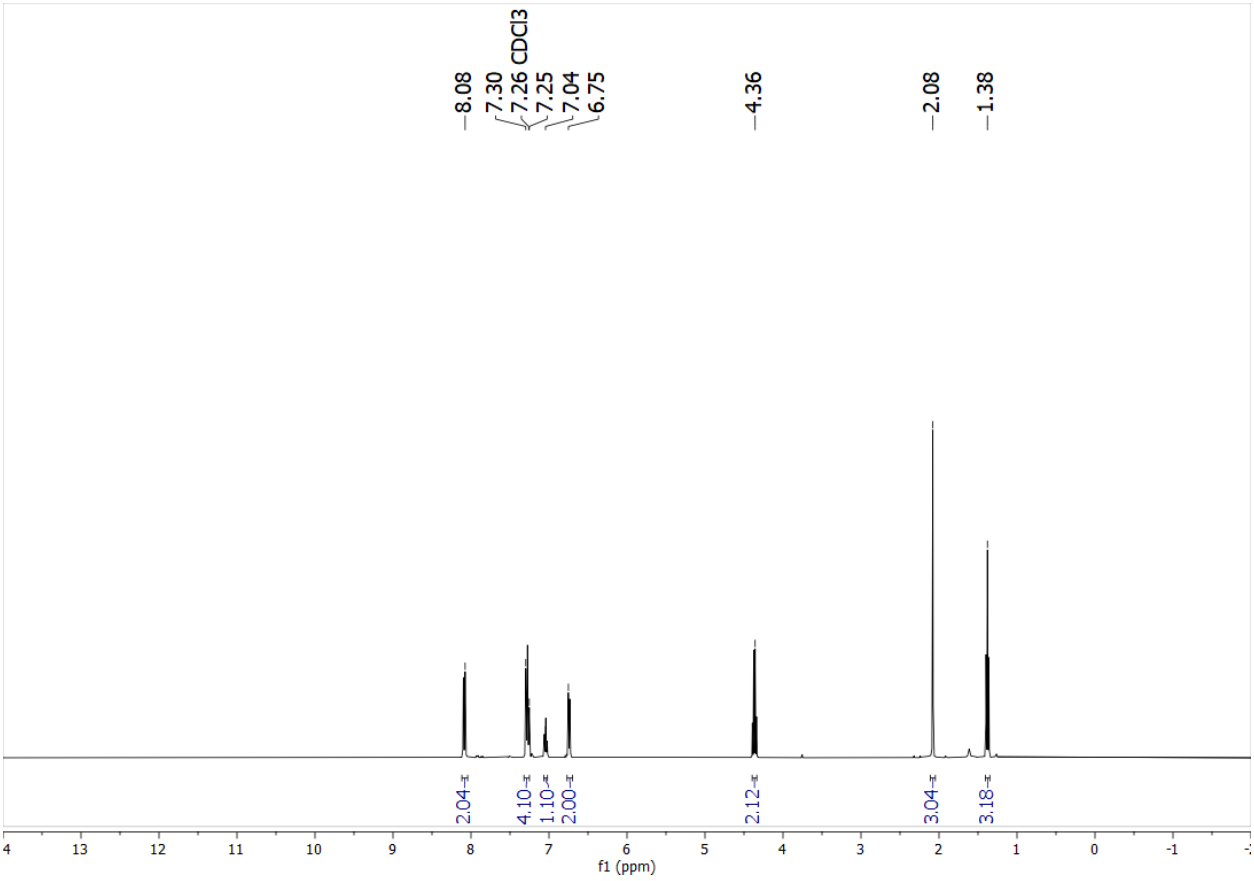
^{19}F NMR: 376 MHz in $CDCl_3$

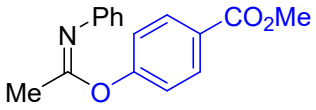




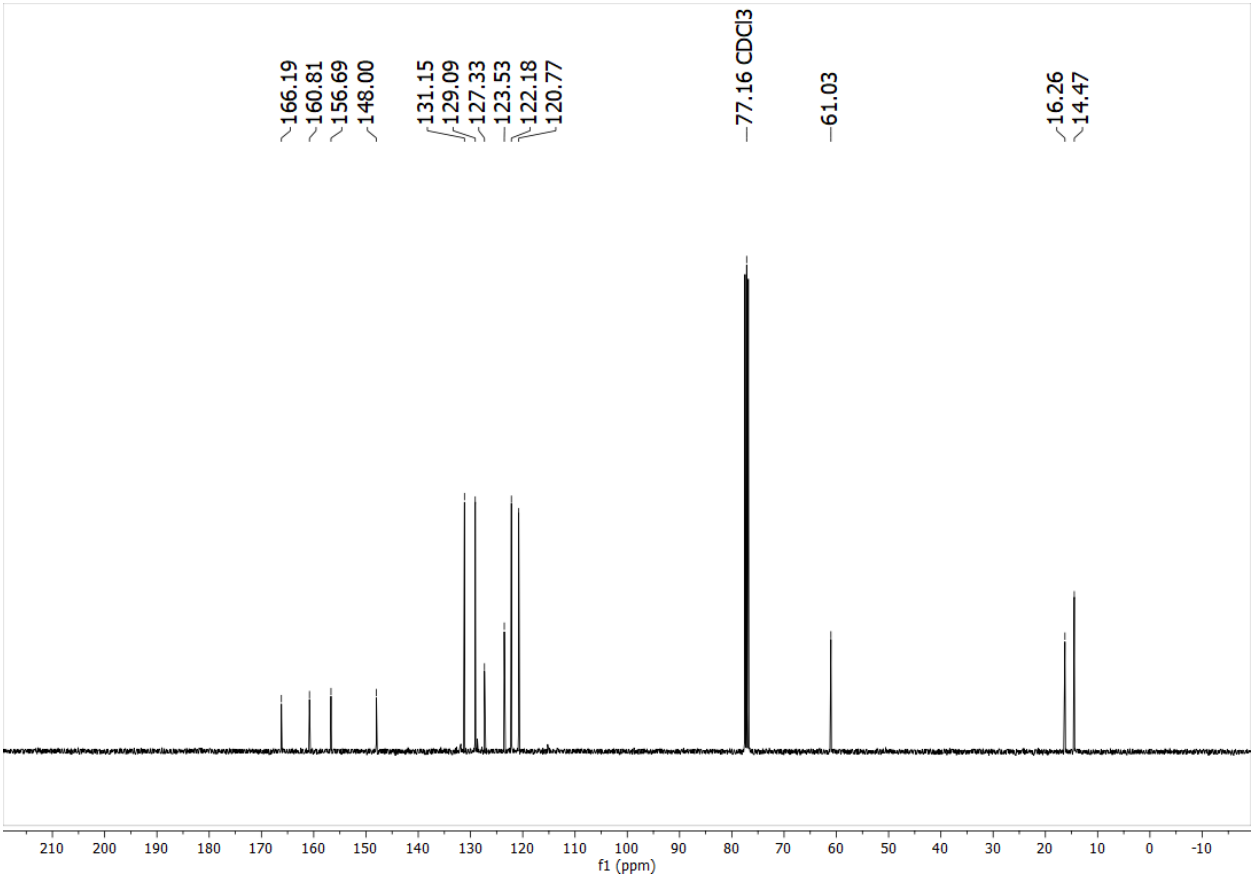
ethyl (Z)-4-(1-(phenylimino)ethoxy)benzoate (4f)

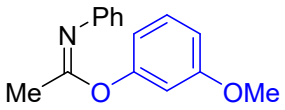
^{1}H NMR: 400 MHz in $CDCl_3$





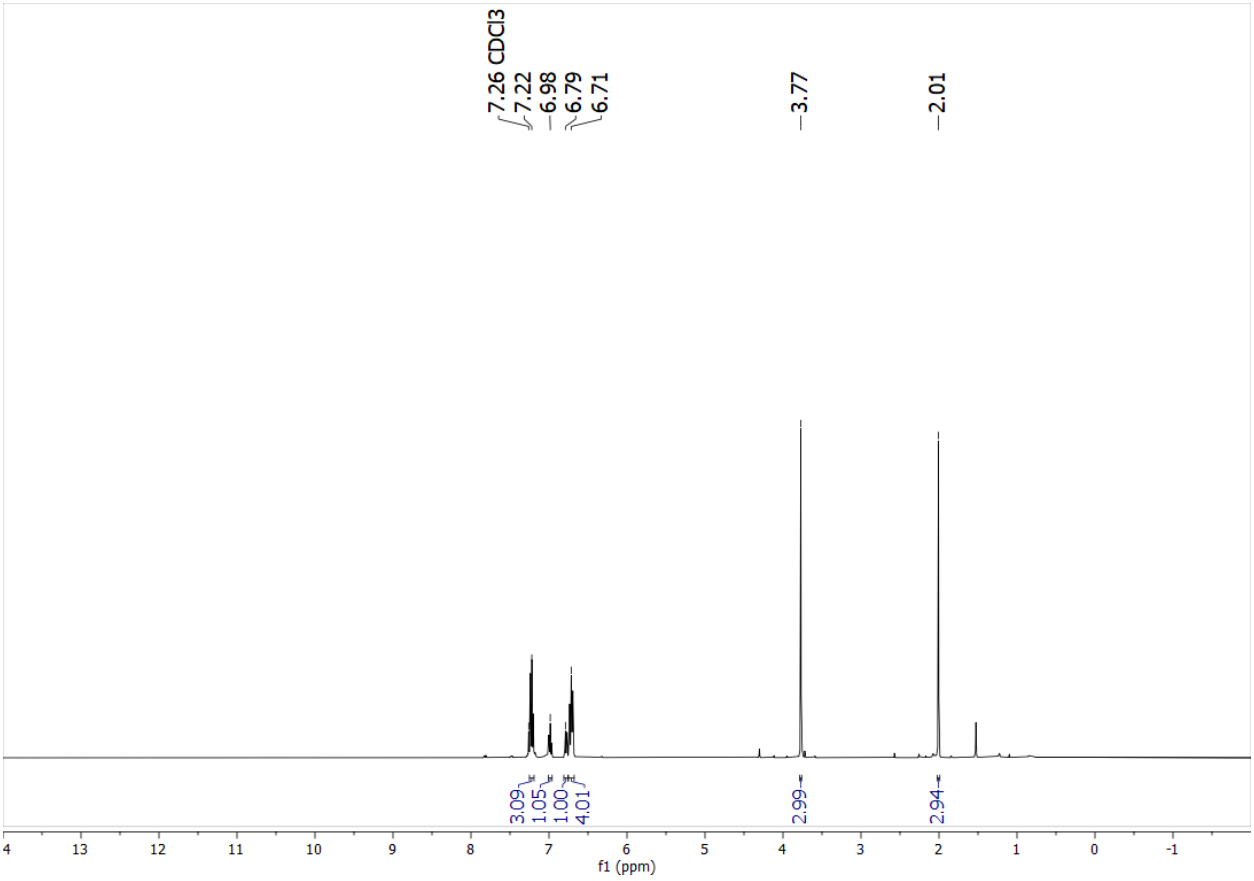
^{13}C NMR: 101 MHz in $CDCl_3$

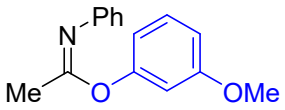




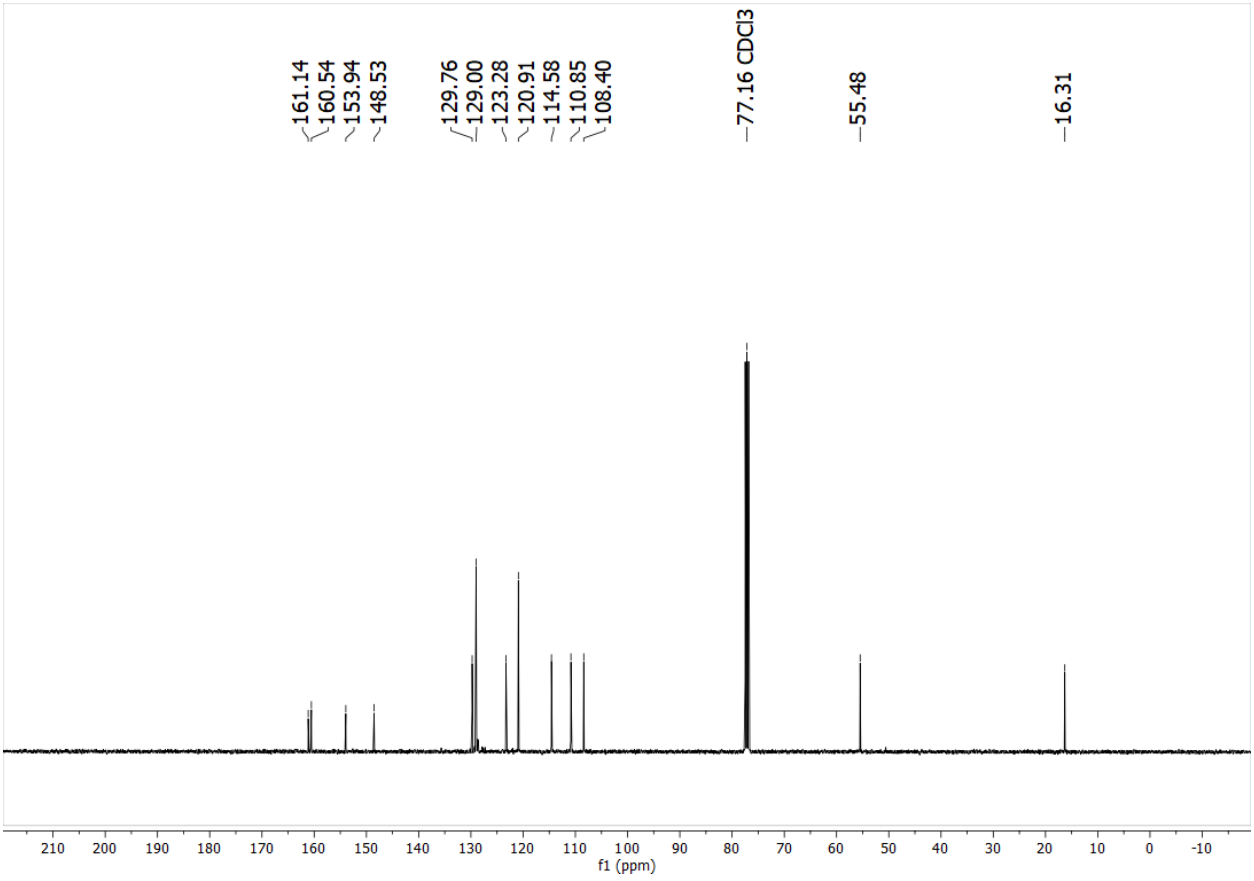
3-methoxyphenyl (Z)-N-phenylacetimidate (4g)

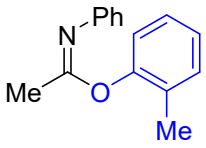
^{1}H NMR: 400 MHz in $CDCl_3$





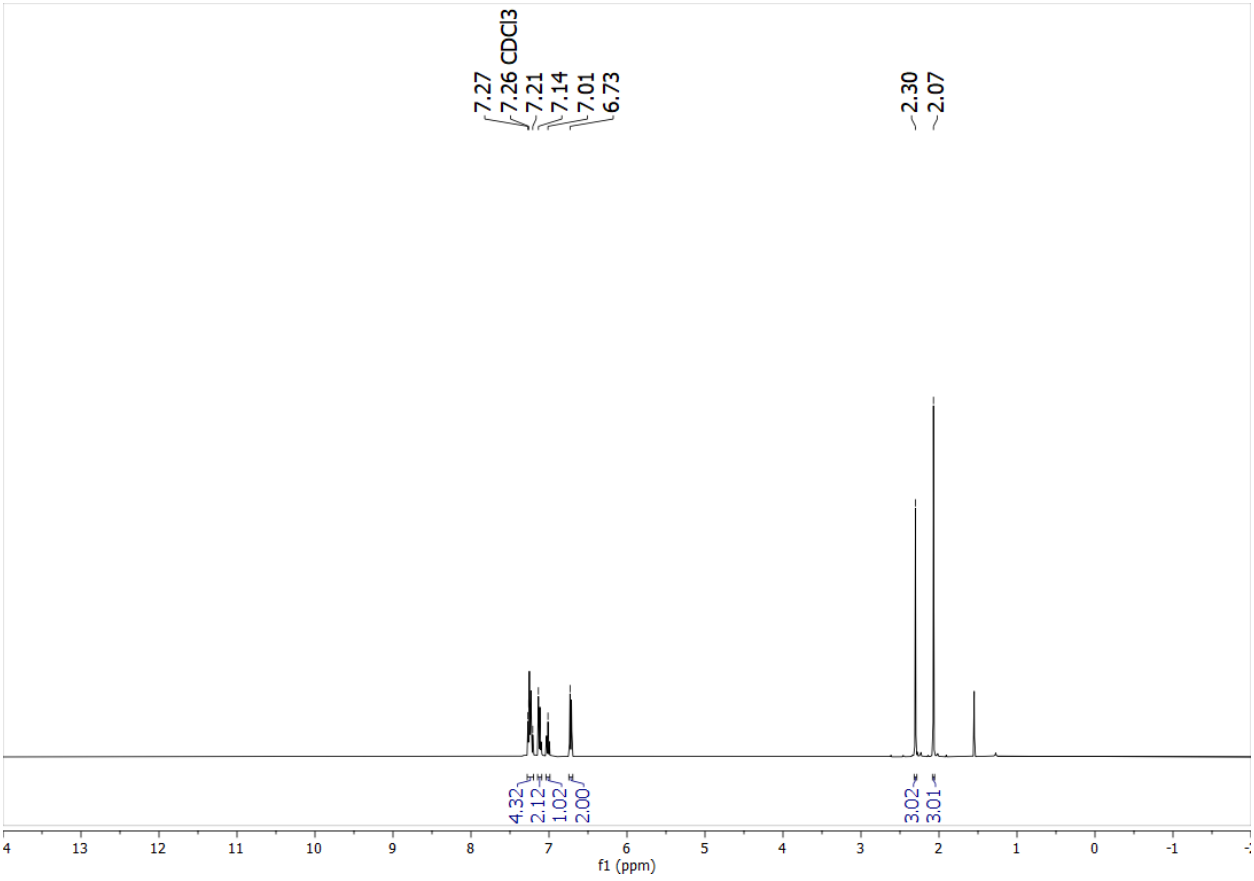
^{13}C NMR: 101 MHz in $CDCl_3$

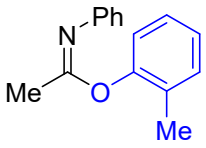




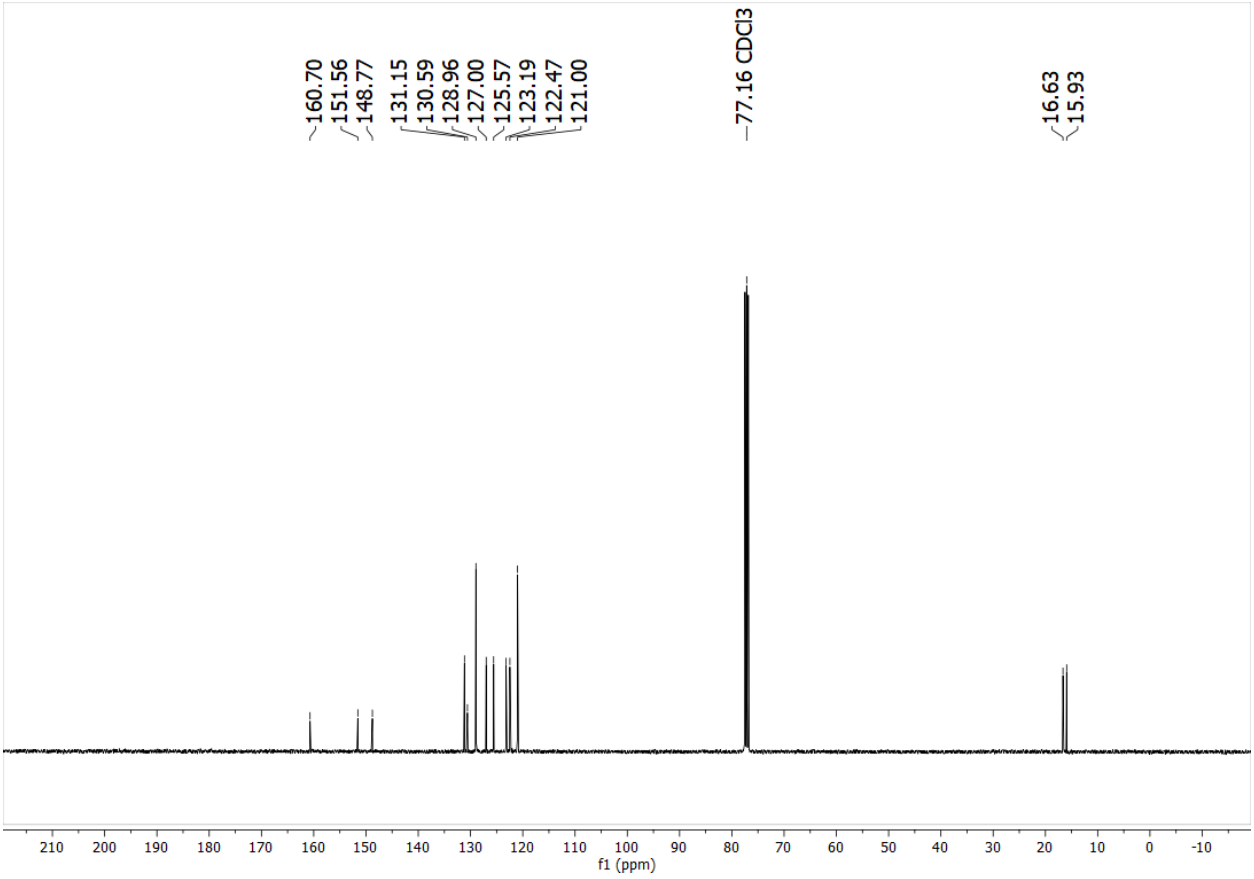
2-methylphenyl (Z)-N-phenylacetimidate (4h)

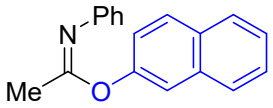
^{1}H NMR: 400 MHz in $CDCl_3$





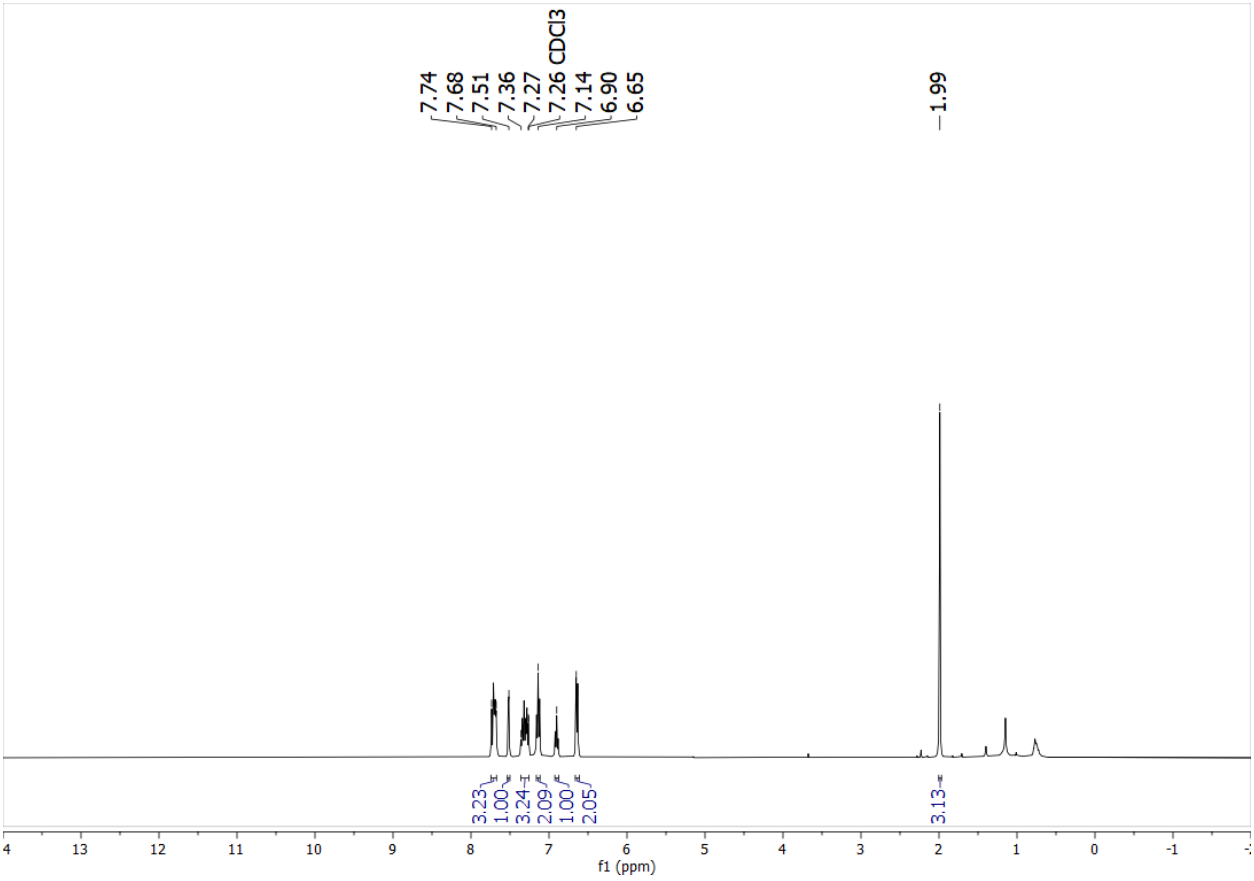
^{13}C NMR: 101 MHz in $CDCl_3$

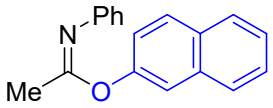




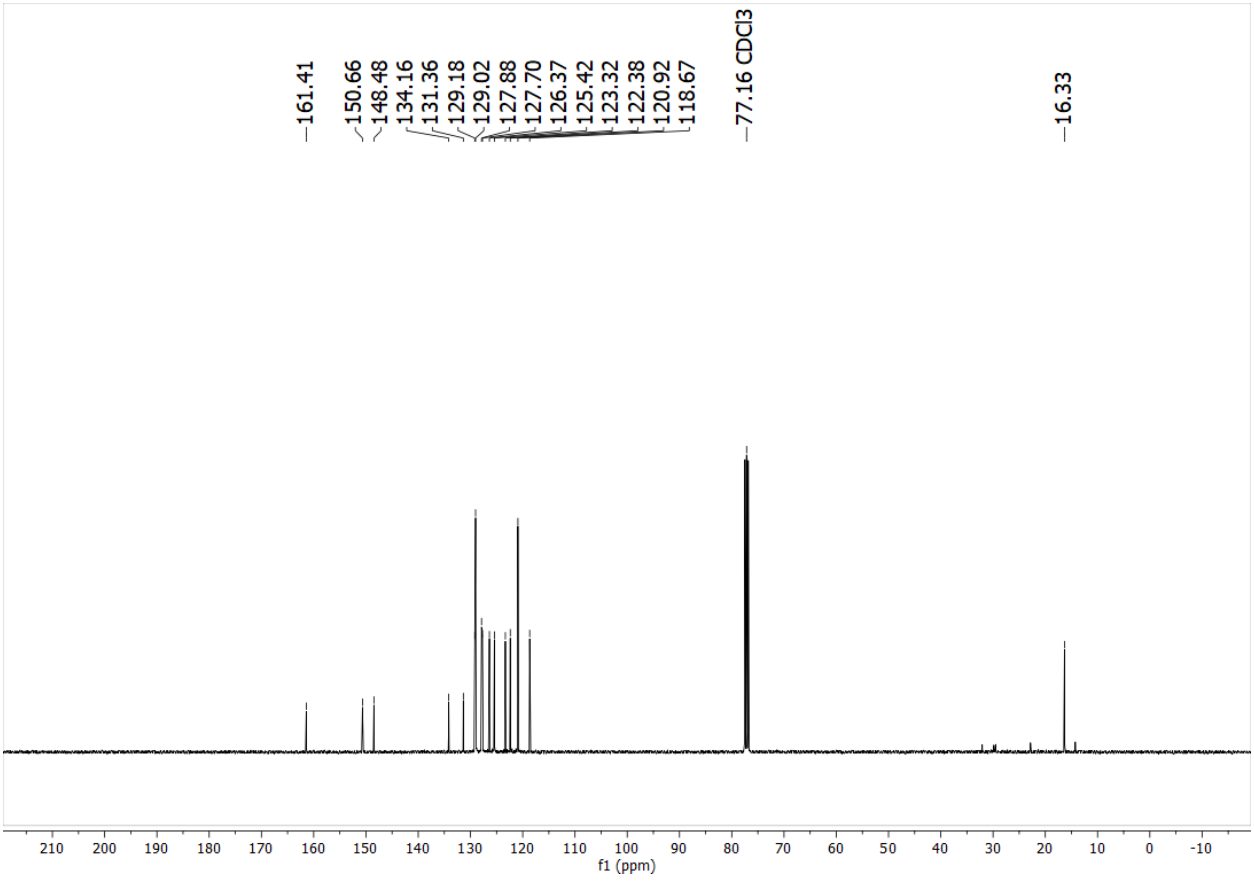
2-naphthyl (Z)-N-phenylacetimidate (4i)

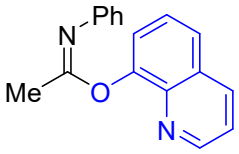
^{1}H NMR: 400 MHz in $CDCl_3$





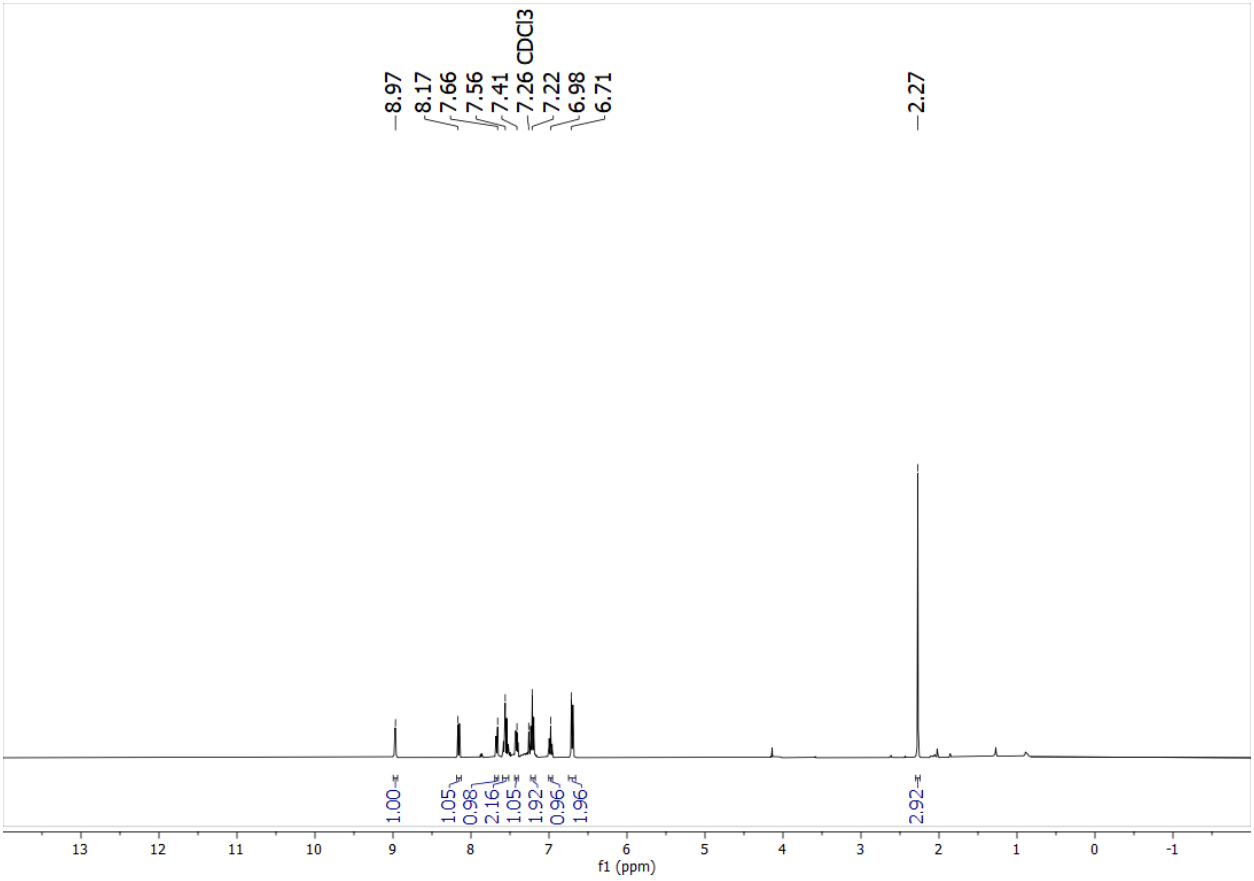
^{13}C NMR: 101 MHz in $CDCl_3$

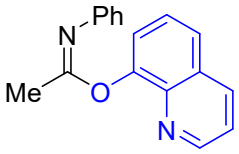




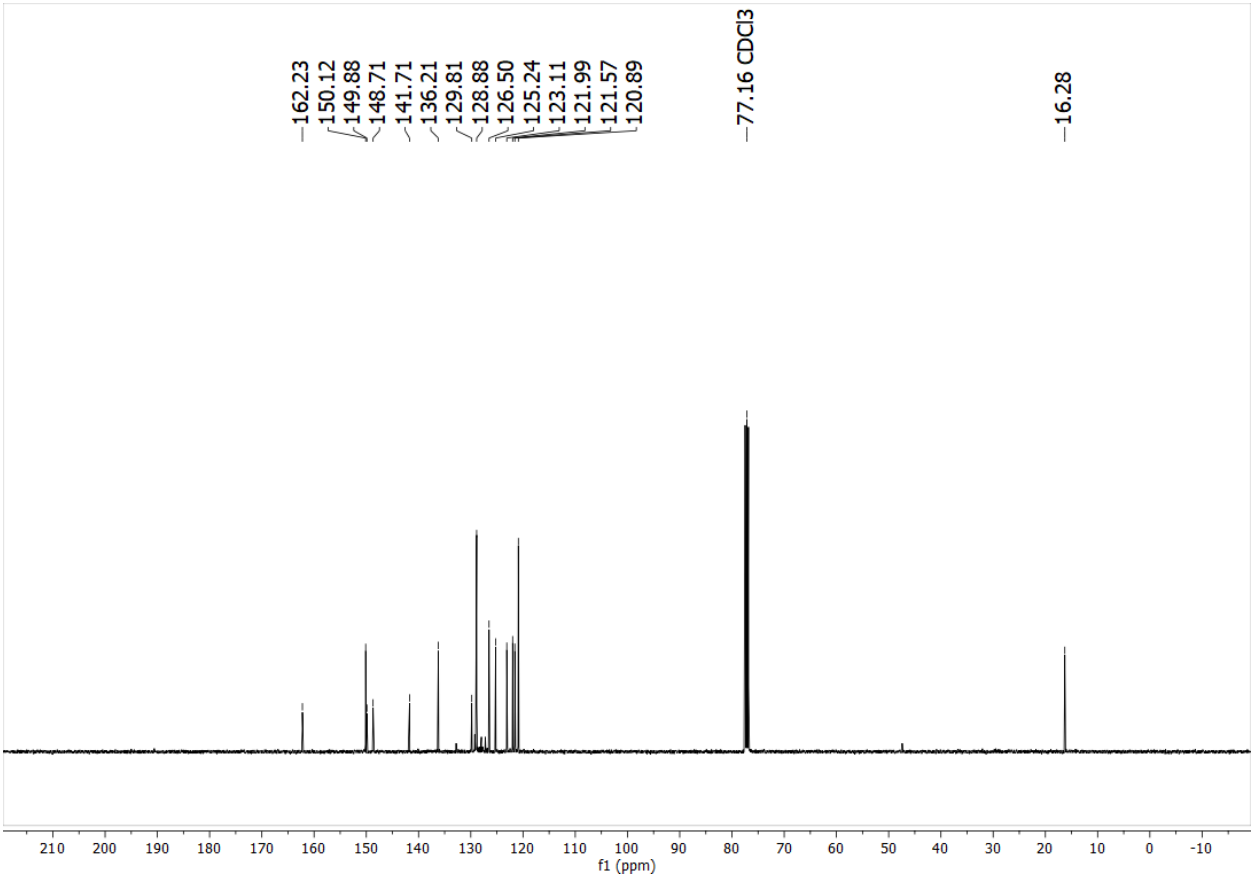
8-quinolinyl (Z)-N-phenylacetimidate (4j)

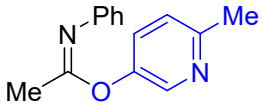
^{1}H NMR: 400 MHz in $CDCl_3$





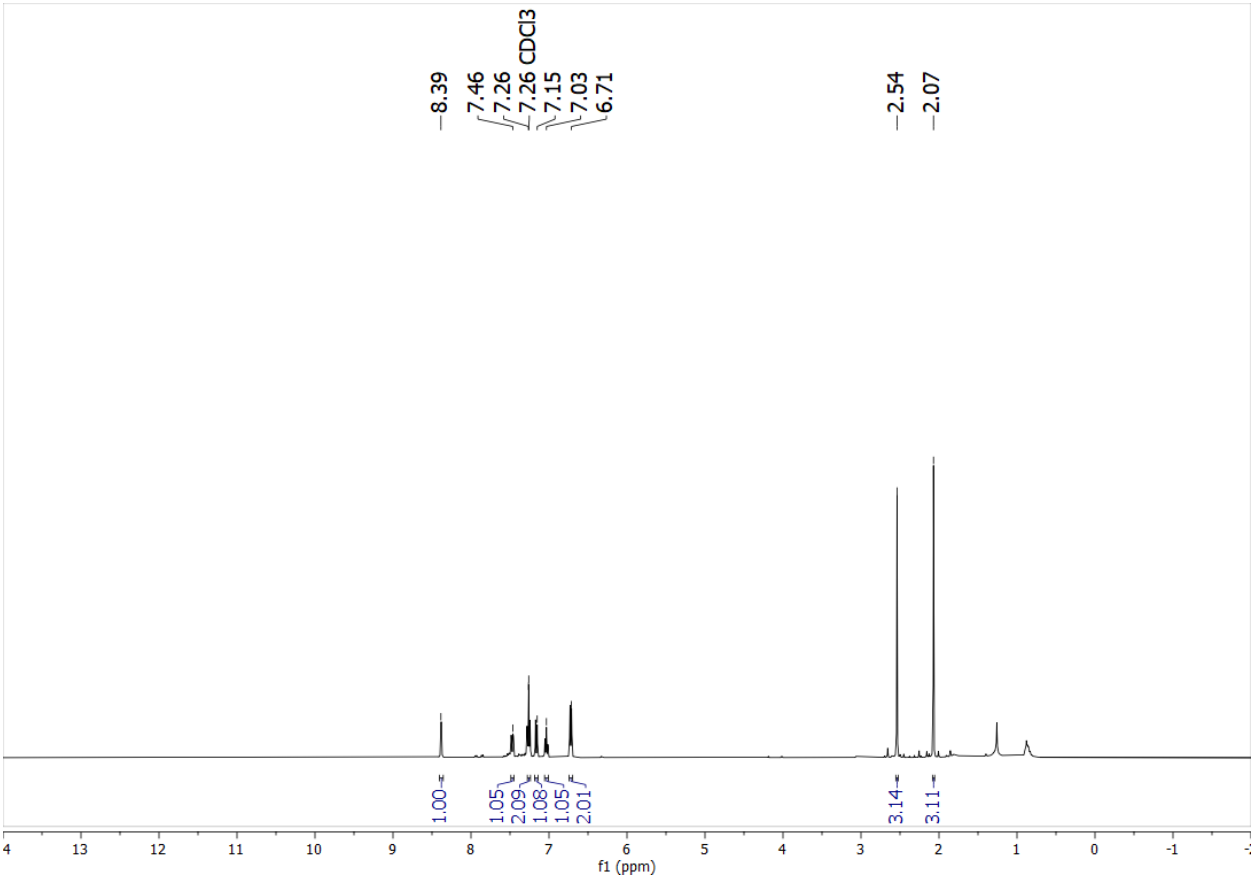
^{13}C NMR: 101 MHz in $CDCl_3$

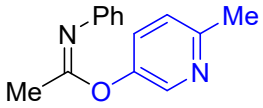




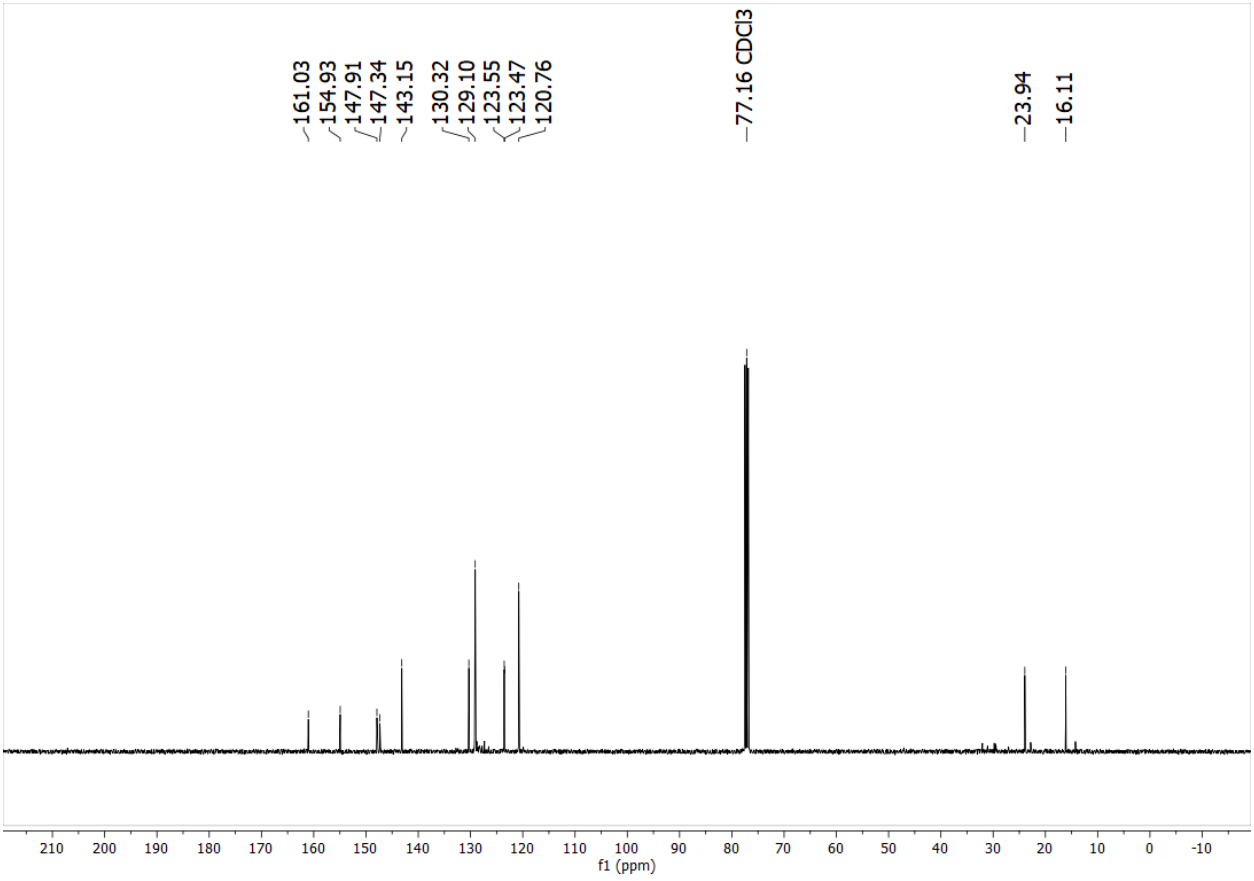
6-methyl-2-pyridinyl (Z)-N-phenylacetimidate (4k)

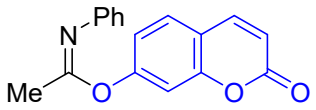
^{1}H NMR: 400 MHz in $CDCl_3$





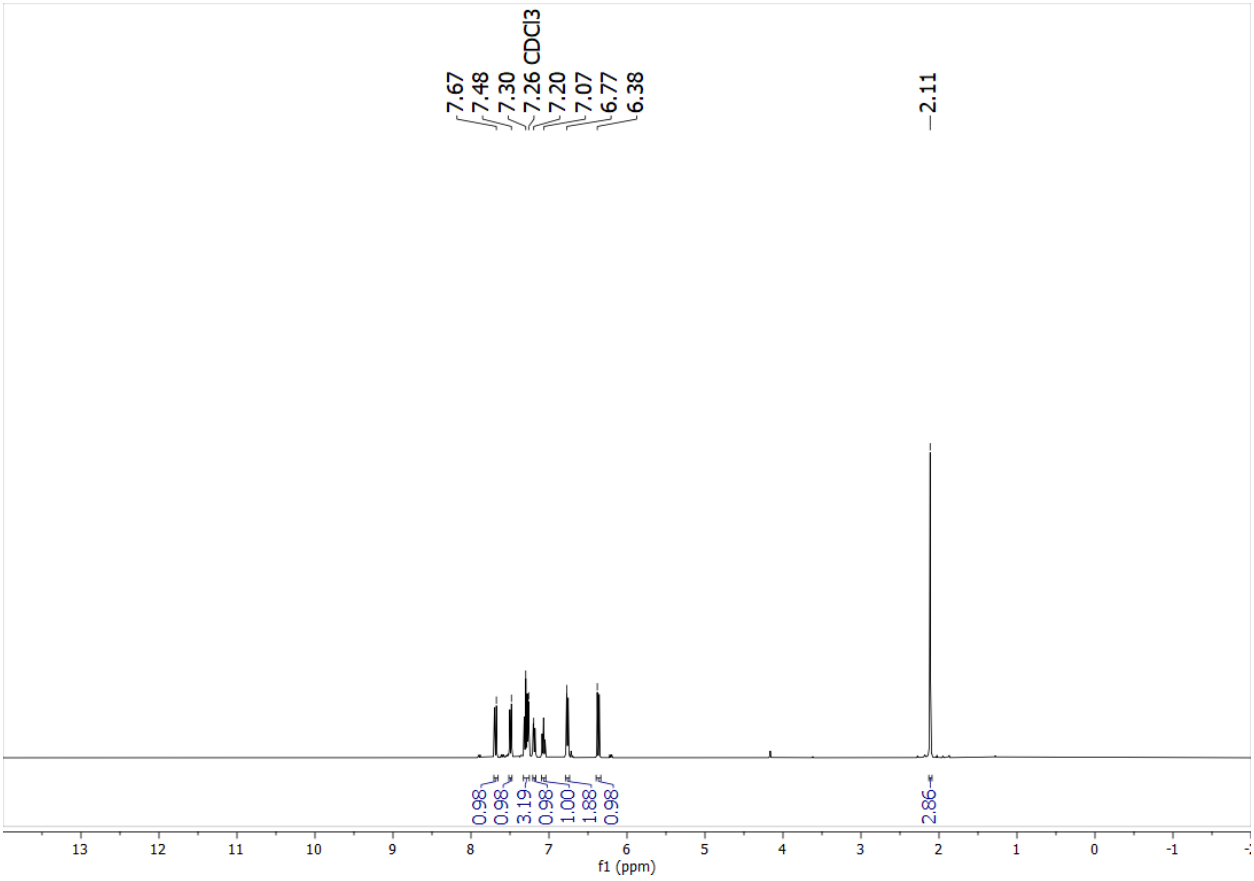
^{13}C NMR: 101 MHz in $CDCl_3$

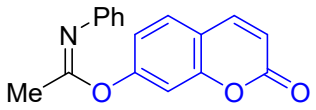




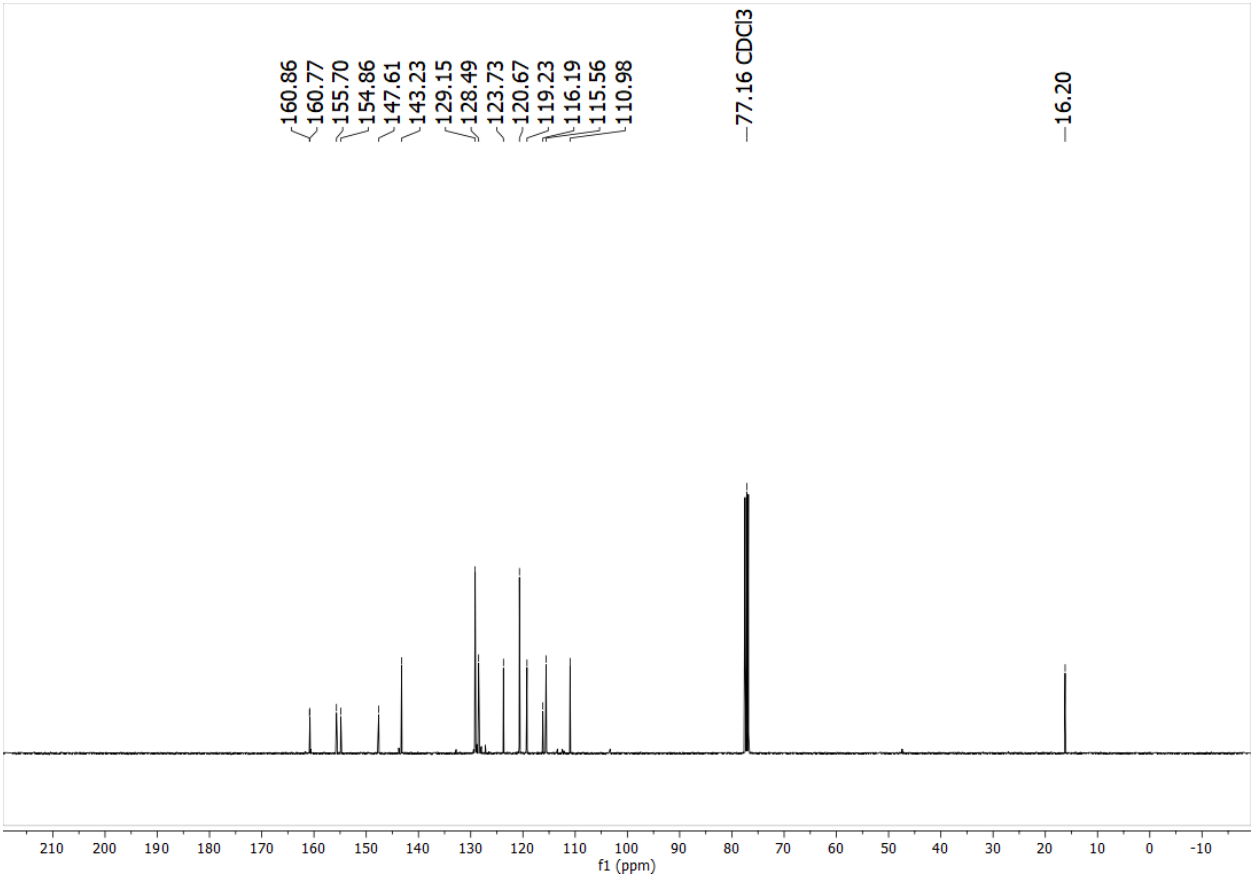
2-oxo-2H-7-chromenyl (Z)-N-phenylacetimidate (4l)

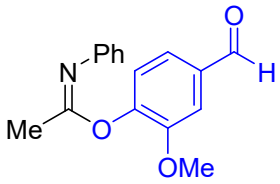
^{1}H NMR: 400 MHz in $CDCl_3$





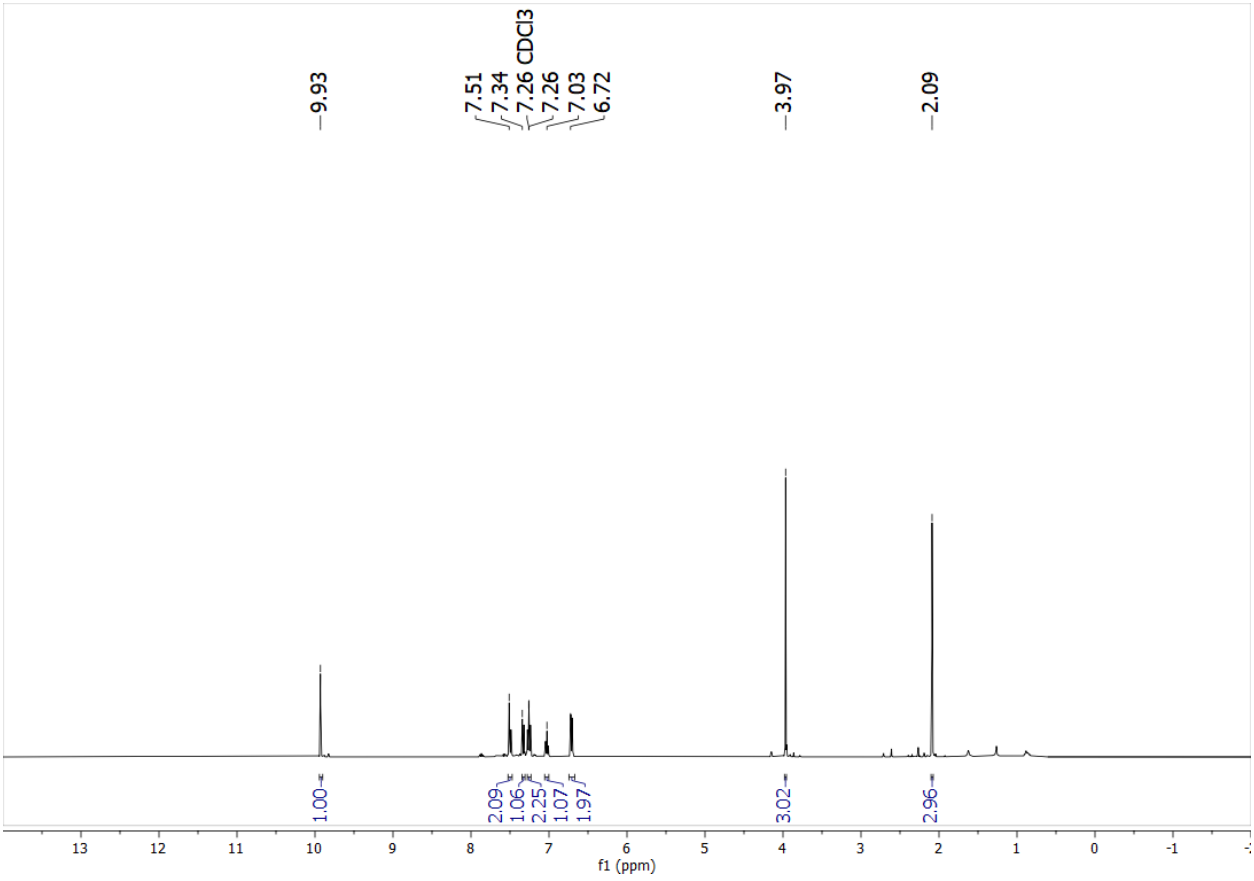
^{13}C NMR: 101 MHz in $CDCl_3$

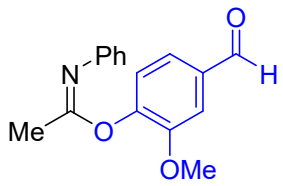




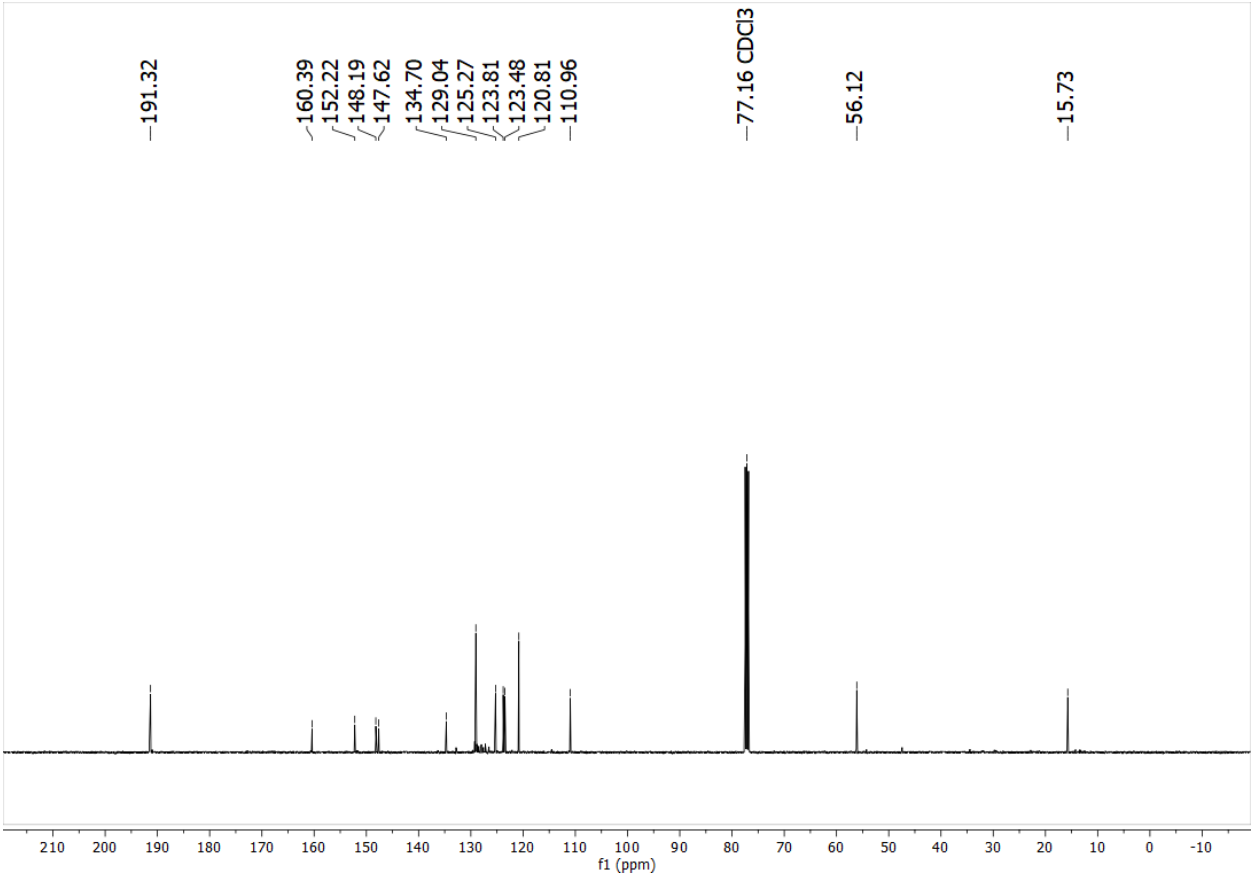
4-formyl-2-methoxyphenyl (Z)-N-phenylacetimidate (4m)

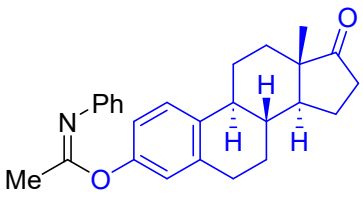
^{1}H NMR: 400 MHz in $CDCl_3$





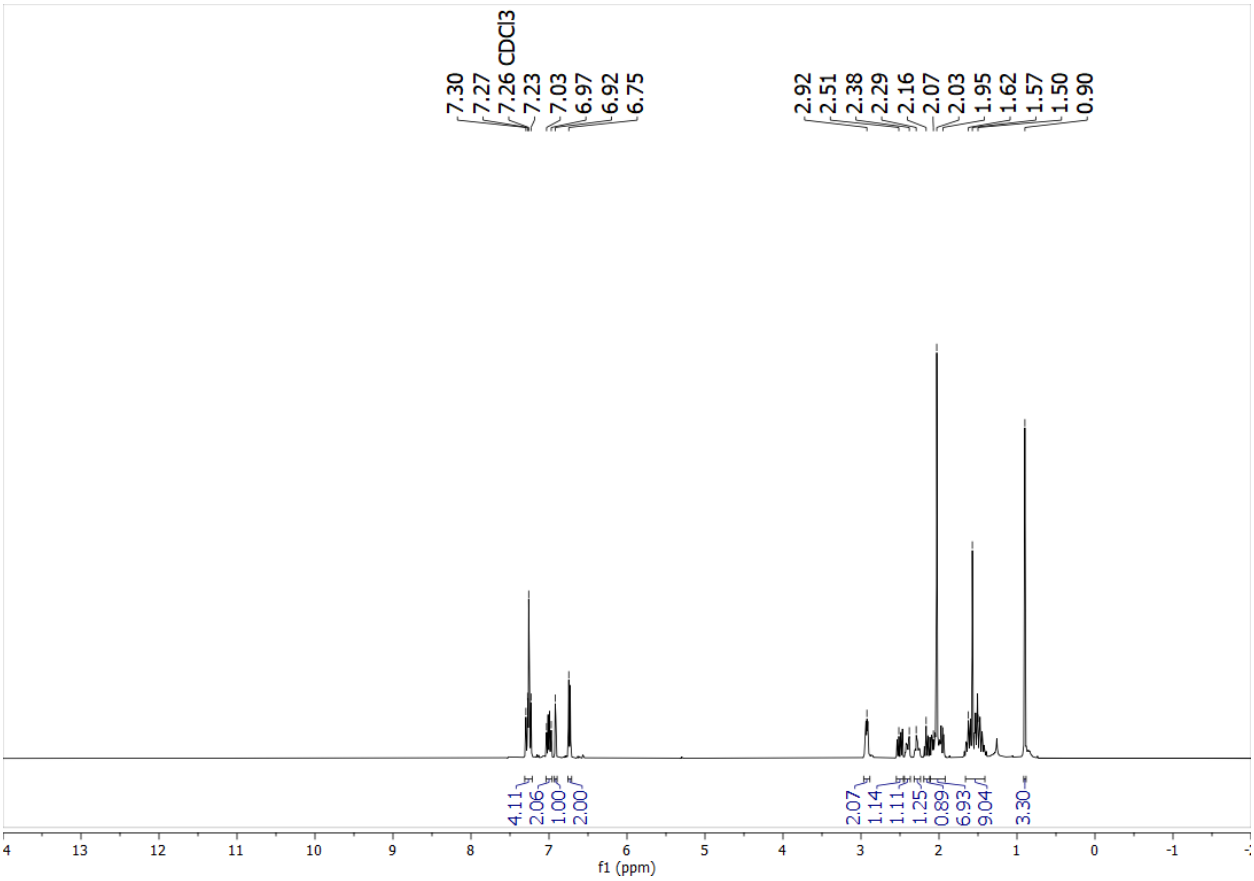
^{13}C NMR: 101 MHz in $CDCl_3$

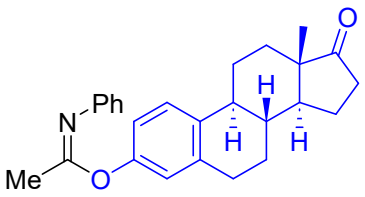




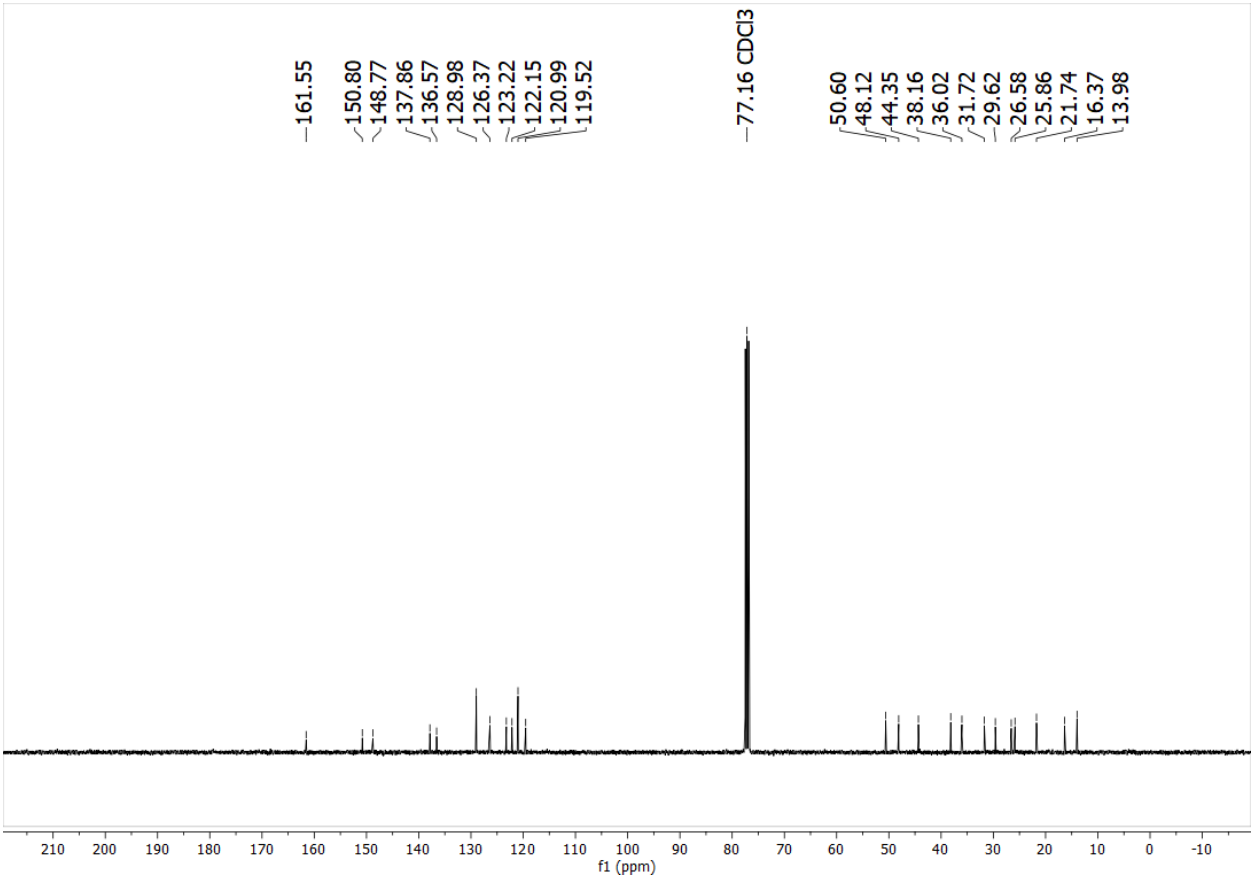
(Estrone) (Z)-N-phenylacetimidate (4n)

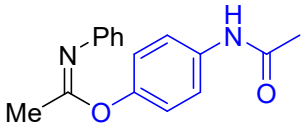
^{1}H NMR: 400 MHz in $CDCl_3$





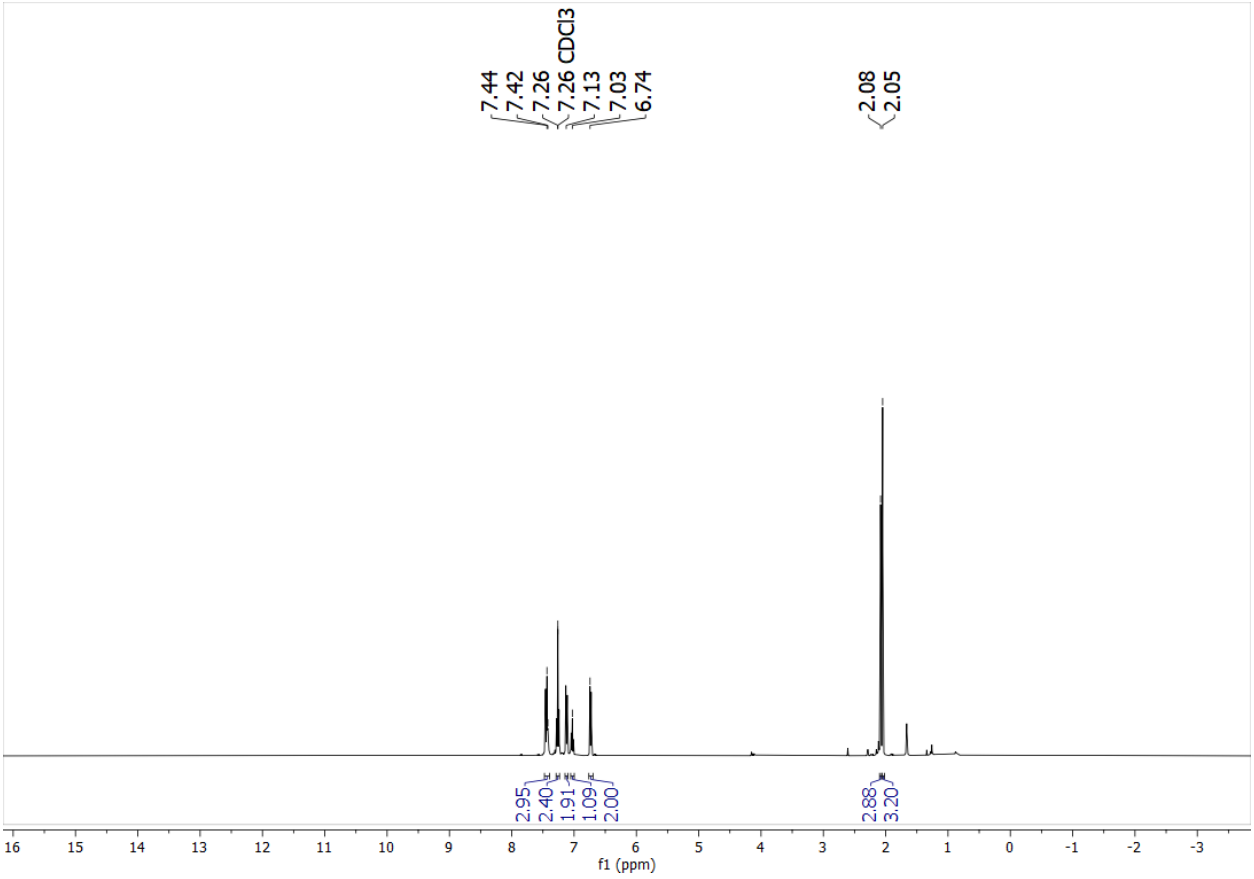
^{13}C NMR: 101 MHz in $CDCl_3$

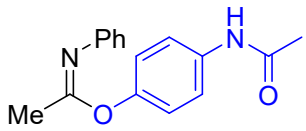




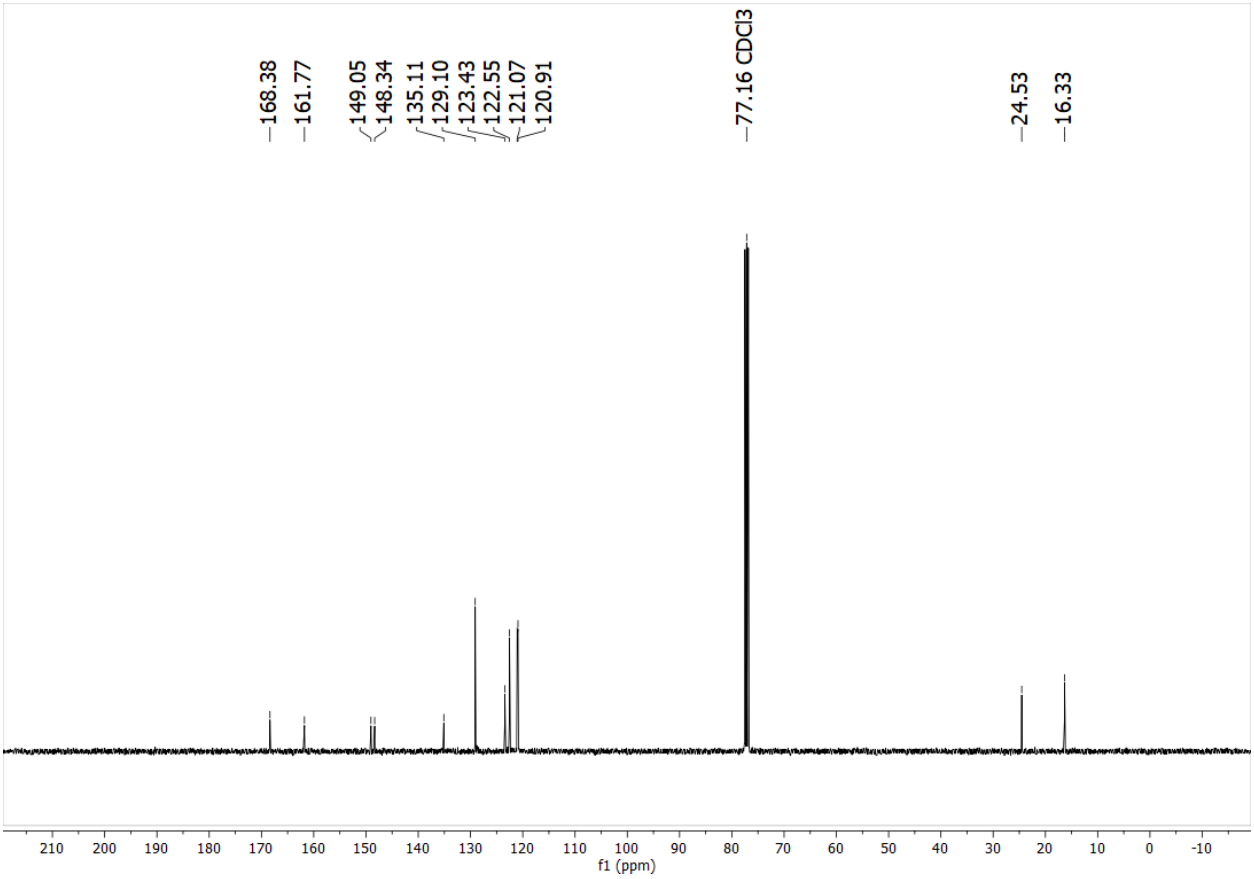
4-acetamidophenyl (Z)-N-phenylacetimidate (4o)

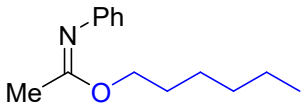
^{1}H NMR: 400 MHz in $CDCl_3$





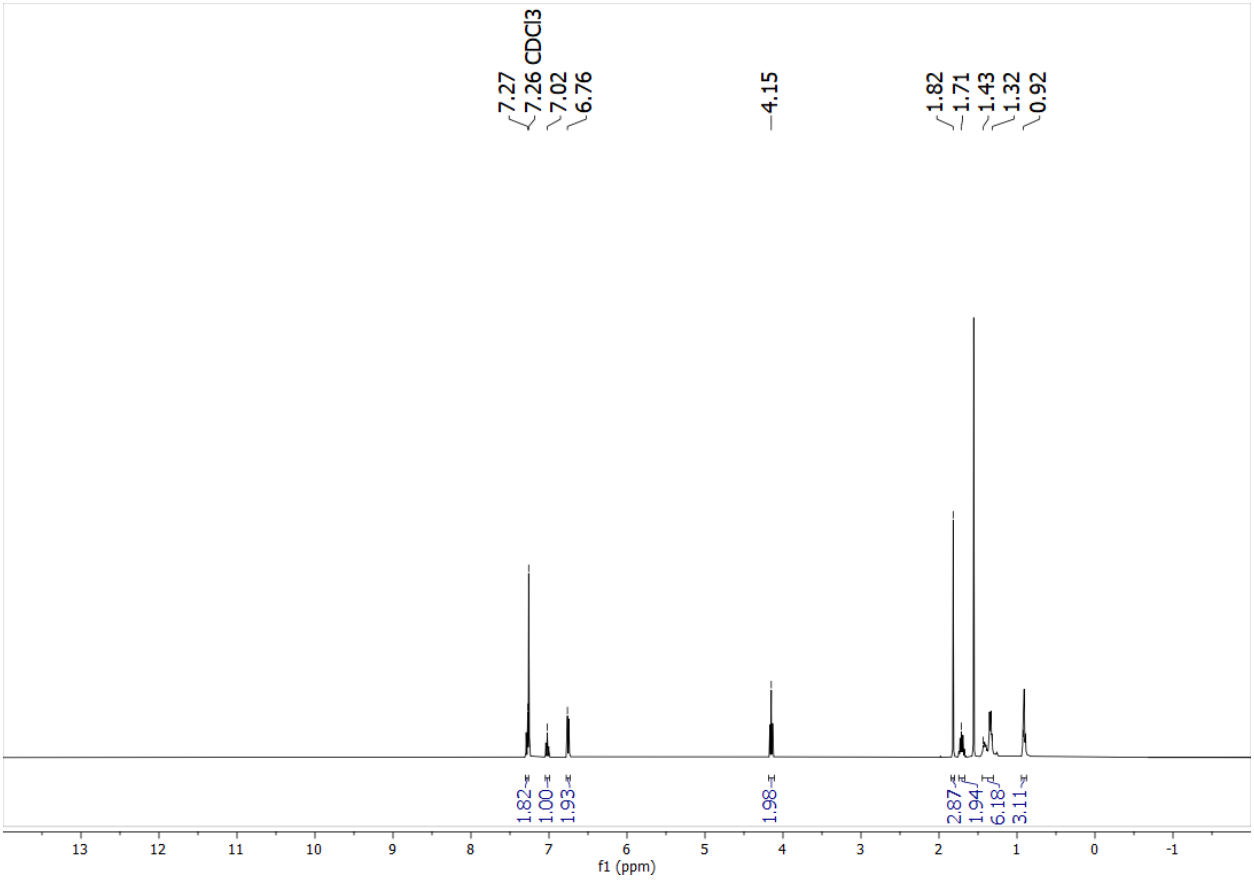
^{13}C NMR: 101 MHz in $CDCl_3$

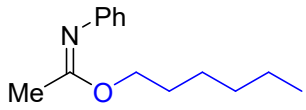




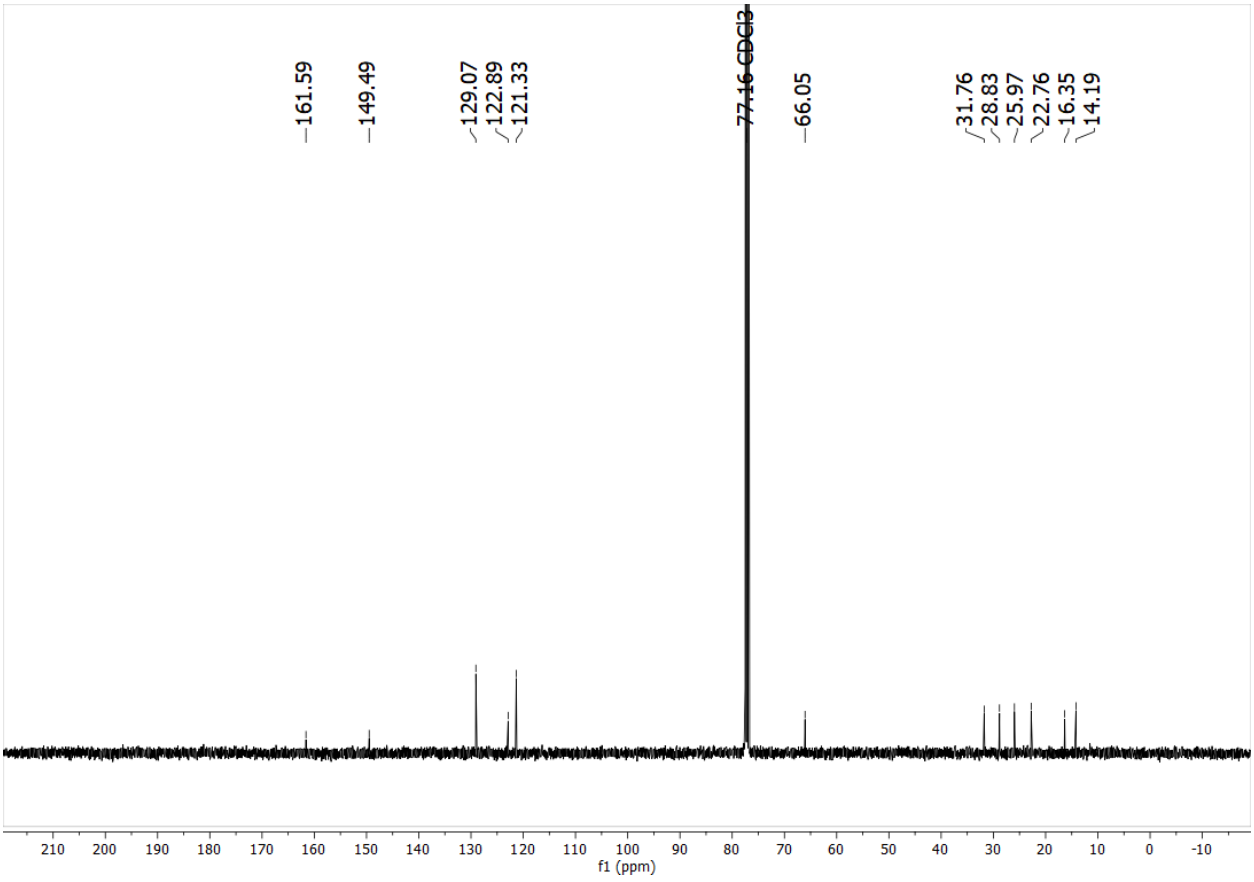
1-hexyl (Z)-N-phenylacetimidate (4p)

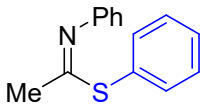
^{1}H NMR: 400 MHz in $CDCl_3$





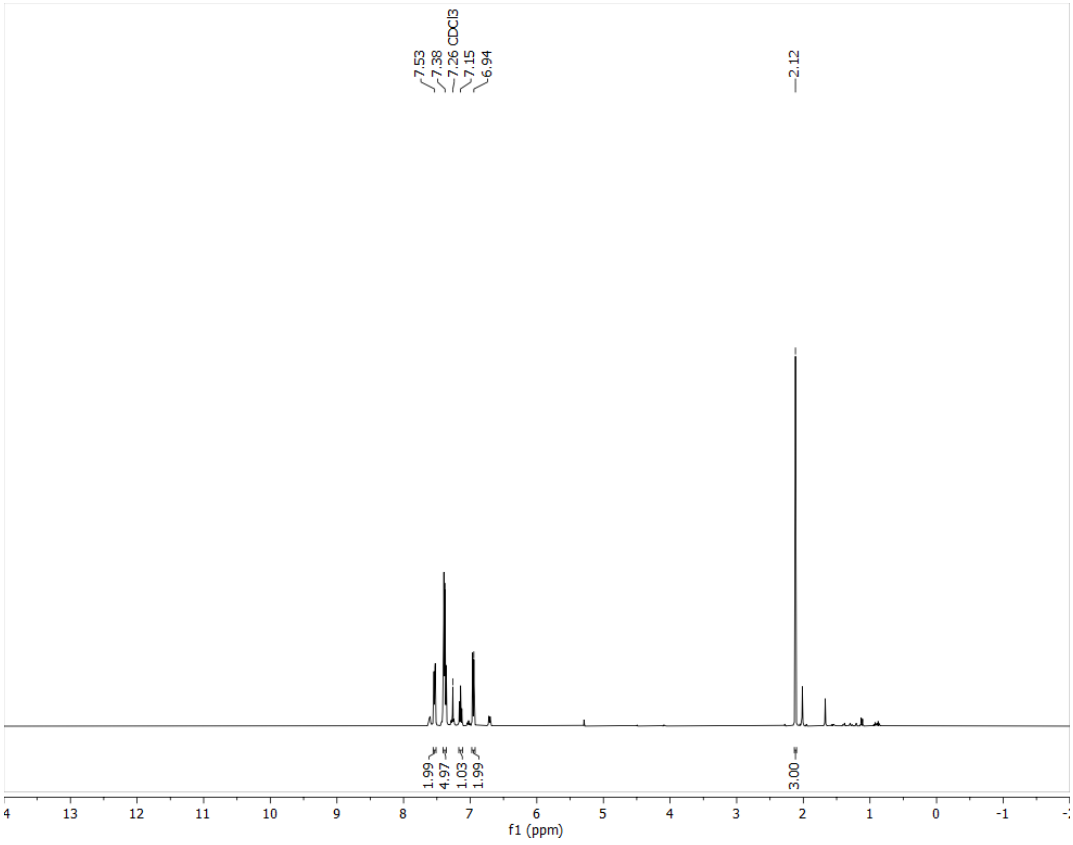
^{13}C NMR: 101 MHz in $CDCl_3$

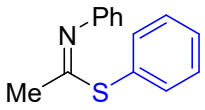




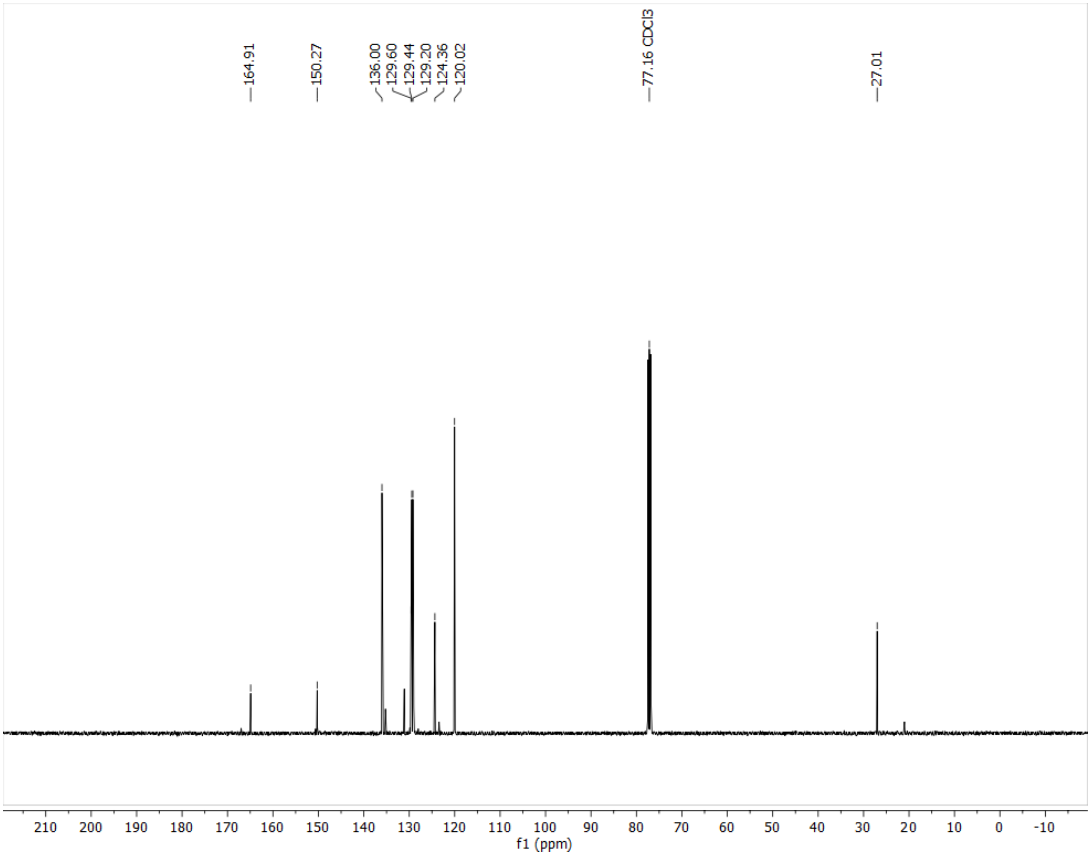
Phenyl (Z)-N-phenylethanimidothioate (4q)

^{1}H NMR: 400 MHz in $CDCl_3$ – only the Z isomer (major isomer) peaks are identified





^{13}C NMR: 101 MHz in $CDCl_3$ – only the Z isomer (major isomer) peaks are identified



11. References

(1) Vogel, J. A.; Hammami, R.; Ko, A.; Datta, H.; Eiben, Y. N.; Labenne, K. J.; McCarver, E. C.; Yilmaz, E. Z.; Melvin, P. R. Synthesis of Highly Reactive Sulfone Iminium Fluorides and Their Use in Deoxyfluorination and Sulfur Fluoride Exchange Chemistry. *Org. Lett.* **2022**, *24* (32), 5962-5966. DOI: 10.1021/acs.orglett.2c02232.
(2) Lu, Y.; Kasahara, A.; Hyodo, T.; Ohara, K.; Yamaguchi, K.; Otani, Y.; Ohwada, T. Isolation and Reactions of Imidoyl Fluorides Generated from Oxime Using the Diethylaminosulfur Trifluoride/Tetrahydrofuran (DAST–THF) System. *Org. Lett.* **2023**, *25* (19), 3482-3486. DOI: 10.1021/acs.orglett.3c01063.
(3) Strieth-Kalthoff, F.; Henkel, C.; Teders, M.; Kahnt, A.; Knolle, W.; Gómez-Suárez, A.; Dirian, K.; Alex, W.; Bergander, K.; Daniliuc, C. G.; et al. Discovery of Unforeseen Energy-Transfer-Based Transformations Using a Combined Screening Approach. *Chem* **2019**, *5* (8), 2183-2194. DOI: https://doi.org/10.1016/j.chempr.2019.06.004.