# A Purification-Free Method for the Synthese of Thiazolium Salts Using $P_2S_5$-$Py_2$ Complex or $P_4S_{10}$

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# Experimental Methods and Characterization Data

## 1.0 General Methods

All chemicals were obtained from commercial suppliers and used without further purification unless noted otherwise. Anhydrous solvents dichloromethane ($CH_2Cl_2$), toluene (PhMe), hexanes, and tetrahydrofuran (THF) were obtained from a Braun Solvent Purification System and stored under argon over activated 3 Å molecular sieves. Acetonitrile (MeCN), pyridine (py), and *N*,*N*-dimethyl formamide (DMF) were dried via distillation over $CaH_2$ and stored over activated 3 Å molecular sieves in Schlenk bottles. Unless otherwise noted all reactions were performed under an inert atmosphere of argon (4.8 grade). Reaction concentrations (molarities) are reported with respect to the limiting (*viz*. 1.00 equiv.) reagent.

Flash column chromatography (FCC) was performed according to Still *et al.* using EMD Millipore or Silicycle silica gel 60 (40-63 μm). Thin-layer chromatography (TLC) and was performed on Merck TLC Silica gel 60 $F_{254}$. UV light (254 nm), potassium permanganate ($KMnO_4$), ninhydrin, vanillin, phosphomolybdic acid (PMA), and/or iodine ($I_2$) on silica gel were used to visualize spots on the TLC plate. ACS grade solvents were used for column chromatography and TLC.

NMR spectra were measured in deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide (DMSO-$d_6$). The proton $^1$H NMR spectra were recorded using 500 or 600 MHz instruments, whereas carbon $^{13}$C NMR spectra were recorded on 125 or 150 MHz spectrometers. The $^1$H NMR and $^{13}$C NMR spectra were calibrated to residual solvent peaks at 7.26 ppm and 77.16 ppm and respectively for $CDCl_3$ and 2.5 ppm and 39.52 ppm respectively for DMSO-$d_6$. The $^1$H NMR chemical shifts and coupling constants were determined assuming first-order behavior. Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad), ap (apparent); the list of coupling constants (*J*) corresponds to the order of the multiplicity assignment.

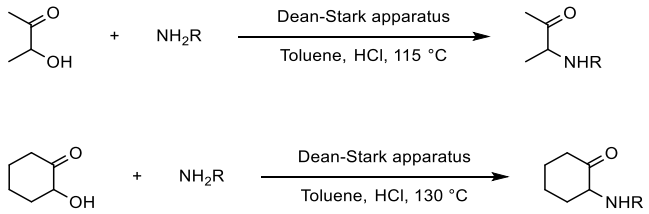
High-resolution mass spectra (HRMS) were recorded on a VG 70E double-focusing high-resolution spectrometer. Electrospray ionization (EI) was performed at 70 eV on a Qstar XL MS/MS system.

Infrared (IR) spectra were typically performed on a Fourier transform interferometer using a diffuse reflectance cell (DRIFT). Only diagnostic and/or intense peaks are reported. Spectra obtained using this method are typically acquired from samples prepared as thin-films on potassium bromide (KBr) pellets, or as suspended solids in a KBr pellet matrix. For some of the reactions, the yield was determined by $^1$HNMR with trichloroethylene (TCE) as an internal standard.

# 2.0 Procedures and Spectra for α-Formamido Ketones

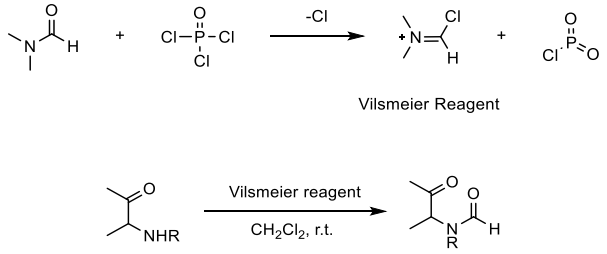
General procedure for the preparation of α-acylamino ketones

*Preparation of α-amino ketone*



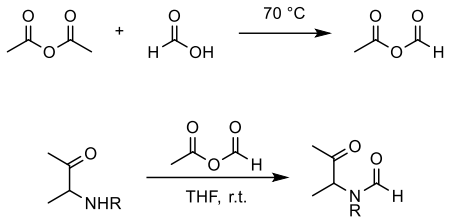

The appropriate amine (9.5 mmol) and α-hydroxy ketone (1.0 g, 11.4 mmol) were stirred in toluene (31.5 mL) at reflux temperature for 6 h with a Dean-Stark apparatus and 0.1 mL of conc. HCl as the catalyst. The obtained reaction mixture was concentrated and the α-amino ketone product was used in the formylation reaction without further purification.

*Preparation of α-acylamino ketones with Vilsmeier reagent (Route a)*




$POCl_3$ (2 equiv.) was added into DMF (5 equiv.) at 0 ℃ under argon, followed by stirring at room temperature for 30 min. The resulting Vilsmeier reagent was added dropwise to the appropriate α-amino ketone (1 equiv.) in $CH_2Cl_2$ (0.4 M) at 0 ℃ under argon. Generally, the reaction mixture turned dark brown over 4 hours. Once the reaction was completed as determined by TLC analysis, it was quenched with ice and then stirred until it warmed up to room temperature. 10 mL of $CH_2Cl_2$ and 20 mL of $H_2O$ were added to the flask for extraction. The aqueous layer first was washed with $CH_2Cl_2$ (5 × 10 mL). The aqueous layer was then basified to pH 8-9 using aq. $Na_2CO_3$ (sat.). The desired product was then extracted with $CH_2Cl_2$ (5 × 10 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure.

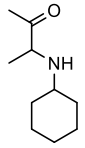
*Preparation of α-formamido ketones using mixed anhydride (Route b)*




**Scheme 5. 1** Preparation of α-formamido ketones using mixed anhydride

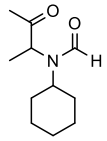
The acetic anhydride (2 equiv.) and formic acid (4 equiv.) were stirred at 70 ℃ for 2h. The obtained mixed anhydride was then added to the appropriate α-amino ketone solution (1 equiv.) in THF (0.5 M) followed by stirring at ambient temperature for 18 hours. The resulted crude compound was purified by column chromatography on silica gel, then concentrated under vacuum.

**Synthesis of 3-(cyclohexylamino)butan-2-one (S1)**



Synthesized according to the general procedure at 1.0 equiv. = 19.58 mmol scale using cyclohexylamine as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-cyclohexyl-*N*-(3-oxobutan-2-yl)formamide (15):**

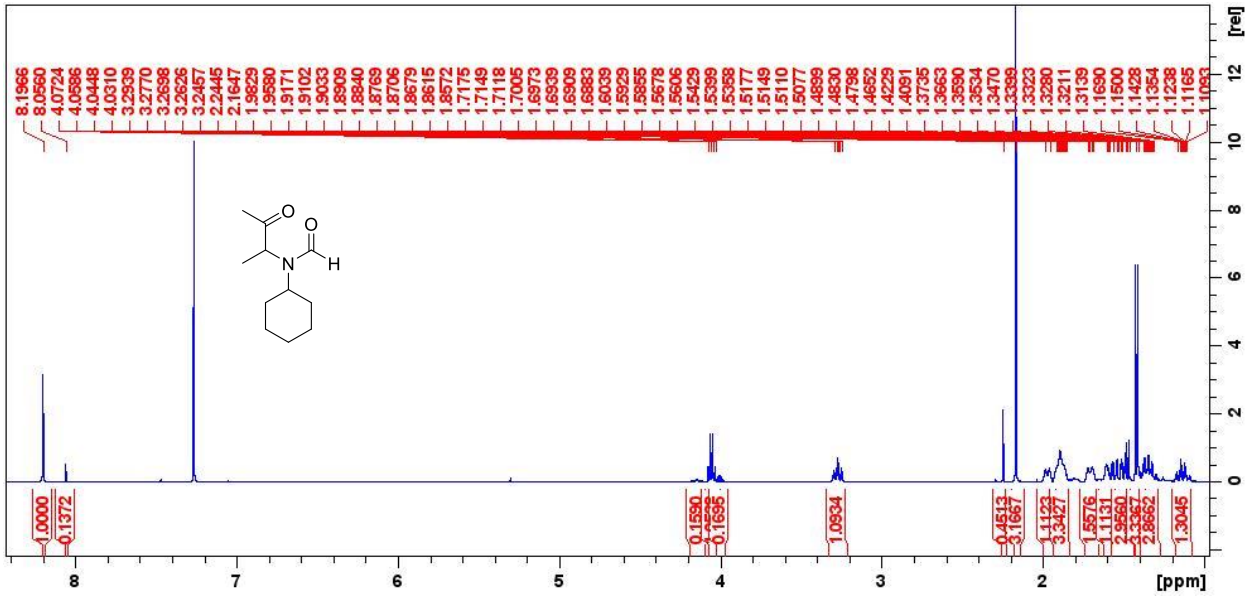


Synthesized according to Route b at 1.0 equiv. = 17.15 mmol scale using 3-(cyclohexylamino)butan-2-one as the starting material. The crude compound was purified by column chromatography (20% MeOH/$CH_2Cl_2$).

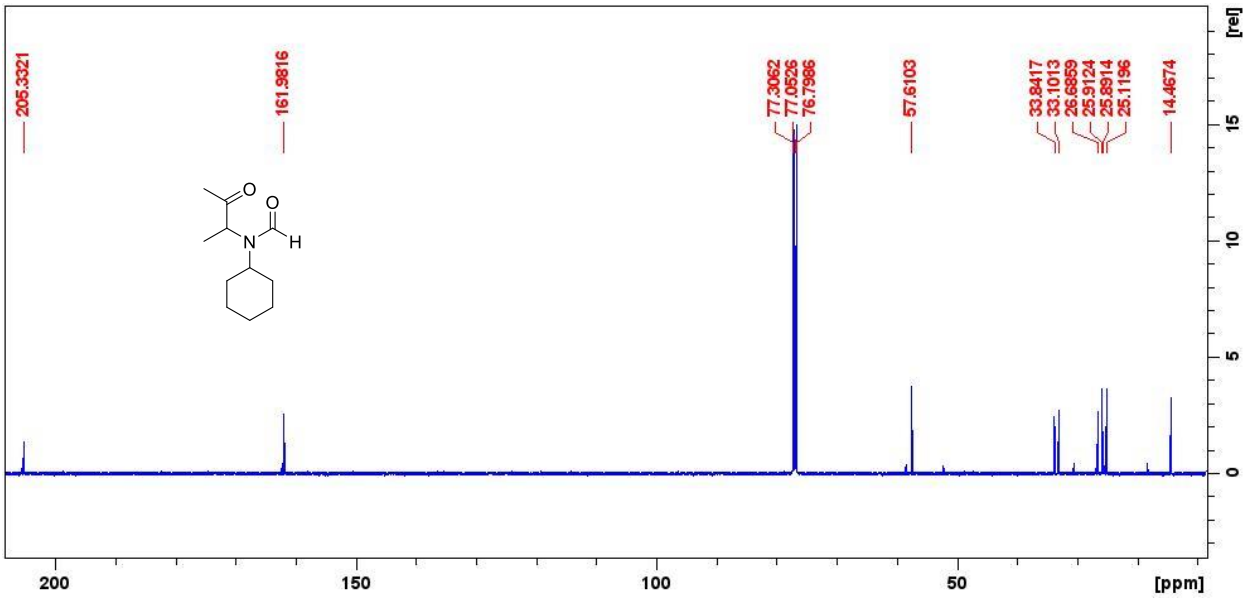
Compound **15** yield: 1.3 g (38% for two steps) as a light brown solid.

$R_f$ = 0.3 (15% EtOAc/ $CH_2Cl_2$); **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 8.20 (s, 1H), 3.07-4.02 (q, *J* = 6.9 Hz, 1H), 3.27 (tt, *J* = 12.1, 3.6 Hz, 1H), 2.16 (s, 3H), 2.01-1.94 (m, 1H), 1.94-1.83 (m, 3H), 1.74 – 1.63 (m, 1H), 1.58-1.44 (m, 3H), 1.42 (d, *J* = 6.9 Hz, 3H), 1.40-1.27 (m, 3H), 1.13 (qt, *J* = 13.2, 3.7 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.3, 162.3, 162.0, 58.6, 57.6, 57.6, 52.3, 33.8, 33.1, 30.6, 30.6, 26.9, 26.7, 25.9, 25.9, 25.7, 25.70 25.3, 25.1, 18.4, 14.5; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3397, 3302.05, 2939, 2926, 1076, 1658, 1448, 1428, 500; **HRMS** ($EI^+$) m/z calculated for $C_{11}H_{19}NO_2$ $[M]^+$: 198.1416; found: 198.1495

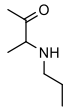
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum

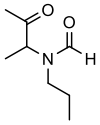


**Synthesis of 3-(propylamino)butan-2-one (S2)**



Synthesized according to the general procedure at 1.0 equiv. = 8.46 mmol scale using propylamine as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-(3-oxobutan-2-yl)-*N*-propylformamide (18): [1]**

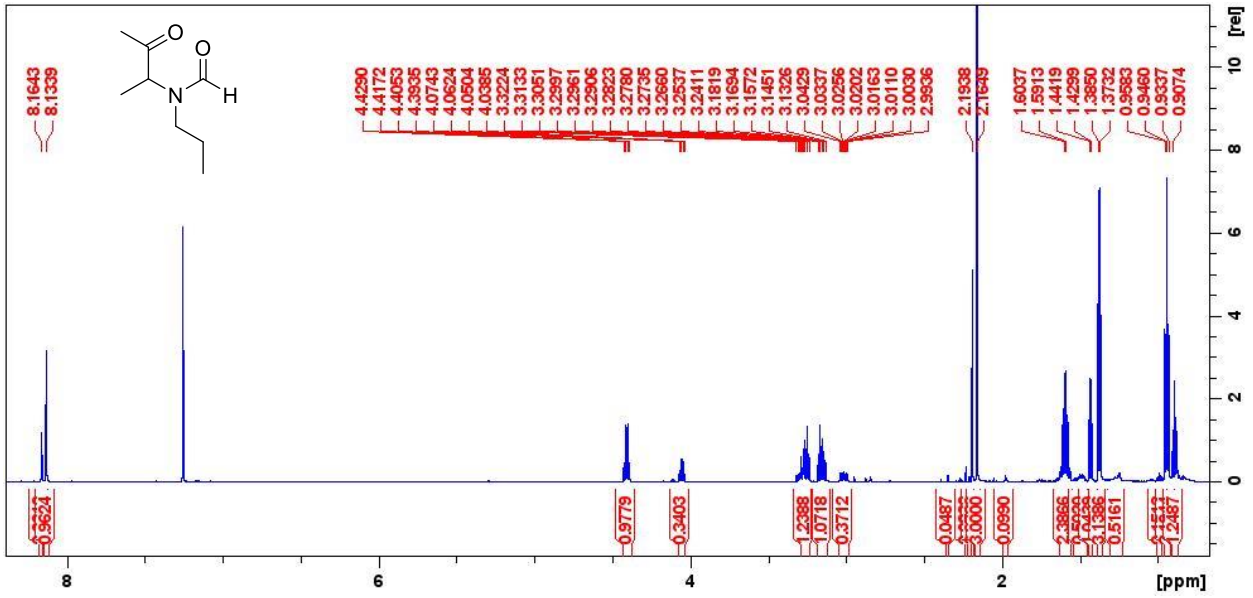


Synthesized according to Route a at 1.0 equiv. = 1.93 mmol scale using 3-(propylamino)butan-2-one as the starting material.

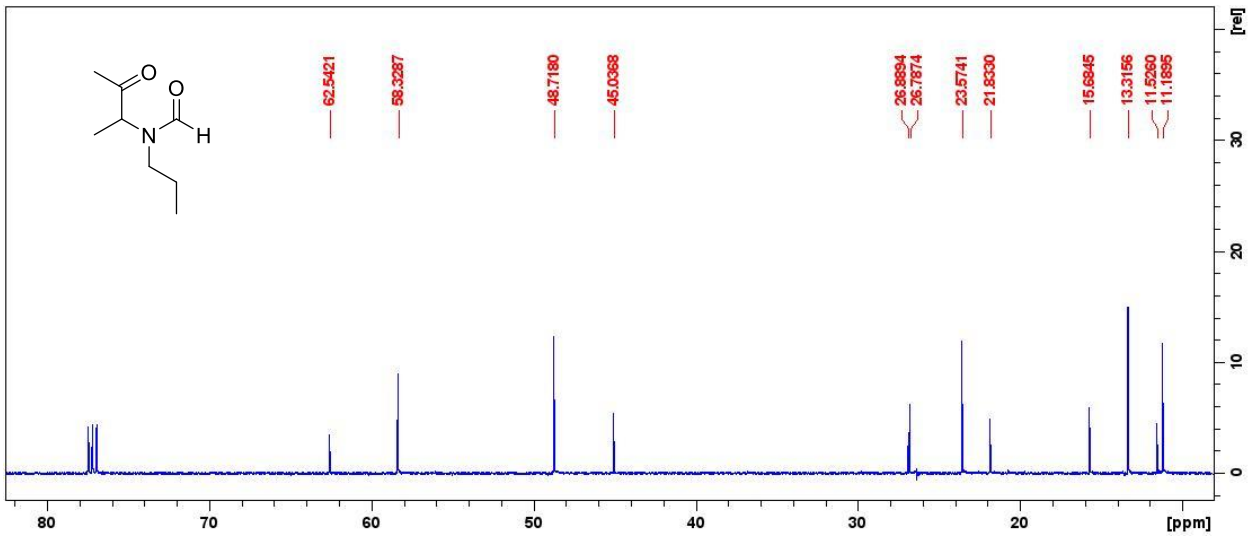
Compound **18** yield: 137 mg (45%) as a sticky brown liquid. All spectra are consistent with the literature.

$R_f$ = 0.3 (20% MeOH/ $CH_2Cl_2$) ; **$^1$H NMR** (600 MHz, $CDCl_3$) δ: 8.14 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 1H), 3.30-3.23 (m, 2H), 3.16 (dt, *J* = 14.7, 7.5 Hz, 1H), 2.16 (s, 3H), 1.64-1.56 (m, 2H), 1.38 (d, *J* = 7.08 Hz, 3H), 0.95 (t, *J* = 7.38 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.9, 205.6, 163.1, 62.5, 58.3, 48.7, 45.0, 26.9, 26.8, 23.6, 21.8, 15.7, 13.3, 11.5, 11.2

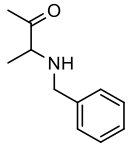
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum

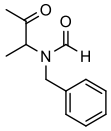


**Synthesis of 3-(benzylamino)butan-2-one (S3)**



Synthesized according to the general procedure at 1.0 equiv. = 9.98 mmol scale using benzylamine as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-benzyl-*N*-(3-oxobutan-2-yl)formamide (20):**

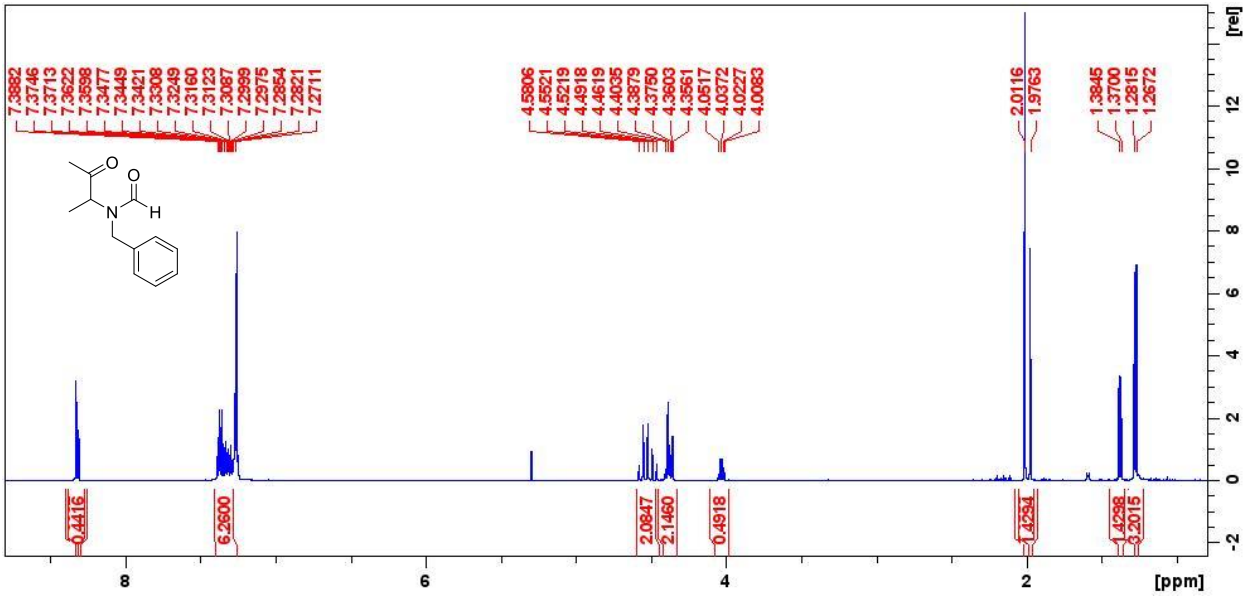


Synthesized according to Route b at 1.0 equiv. = 8.45 mmol scale using 3-(benzylamino)butan-2-one as the starting material. The crude compound was purified by column chromatography (5% MeOH/$CH_2Cl_2$).

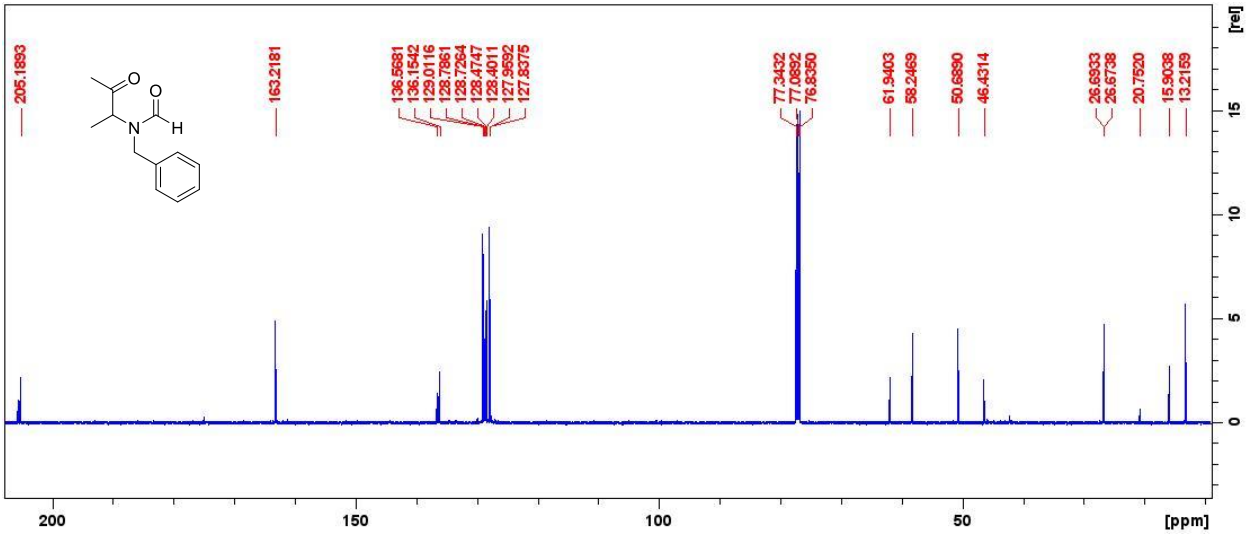
Compound **20** yield: 233 mg (20% yield for two steps) as a yellow liquid.

$R_f$ = 0.4 (5% MeOH/$CH_2Cl_2$); **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 8.33 (s, 1H), 7.40-7.24 (m, 5H), 4.59-4.45 (m, 1H), 4.44-4.36(m, 1H), 2.01 (s, 3H), 1.27 (d, *J* = 7.1 Hz, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.6, 205.2, 175.0, 163.2, 163.2, 136.6, 136.2, 129.0, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 127.7, 61.9, 58.3, 50.7, 46.4, 42.2, 26.7, 26.7, 20.8, 15.9, 13.2; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3324, 2988, 1720, 1666, 1428, 1357, 1206, 703, 590; **HRMS** ($EI^+$) m/z calculated for $C_{12}H_{15}NO_2$ $[M]^+$: 205.1103; found: 205.1109

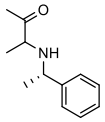
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum

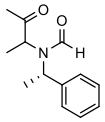


**Synthesis of *N*-(3-oxobutan-2-yl)-*N*-((S)-1-phenylethyl)formamide (S4)**



Synthesized according to the general procedure at 1.0 equiv. = 7.56 mmol scale using (S)-1-phenyl-ethylamine as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-(3-oxobutan-2-yl)-*N*-((S)-1-phenylethyl)formamide (22)**

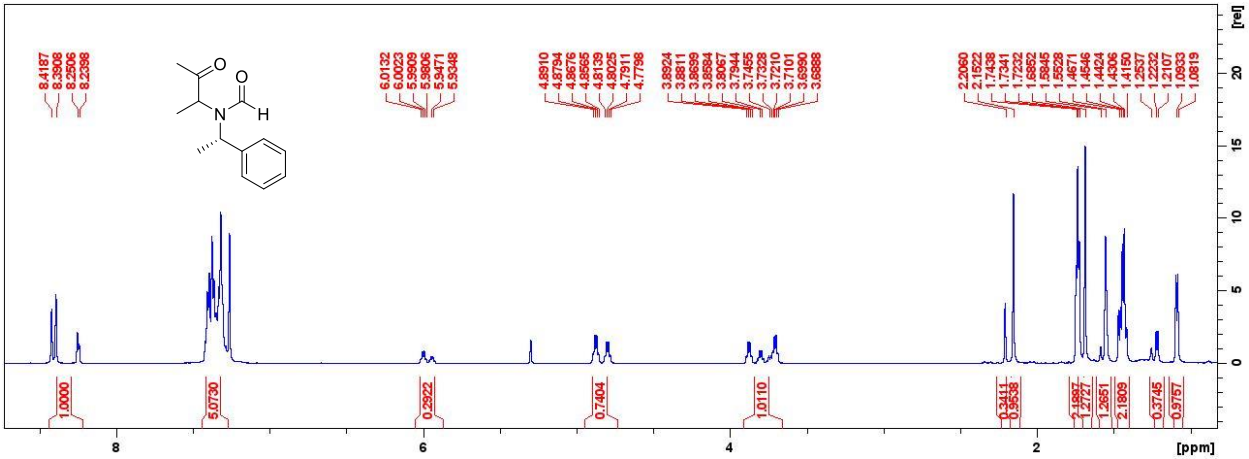


Synthesized according to Route b at 1.0 equiv. = 4.29 mmol scale using 3-(phenylamino)butan-2-one as the starting material. The crude compound was purified by column chromatography (2% MeOH/$CH_2Cl_2$).

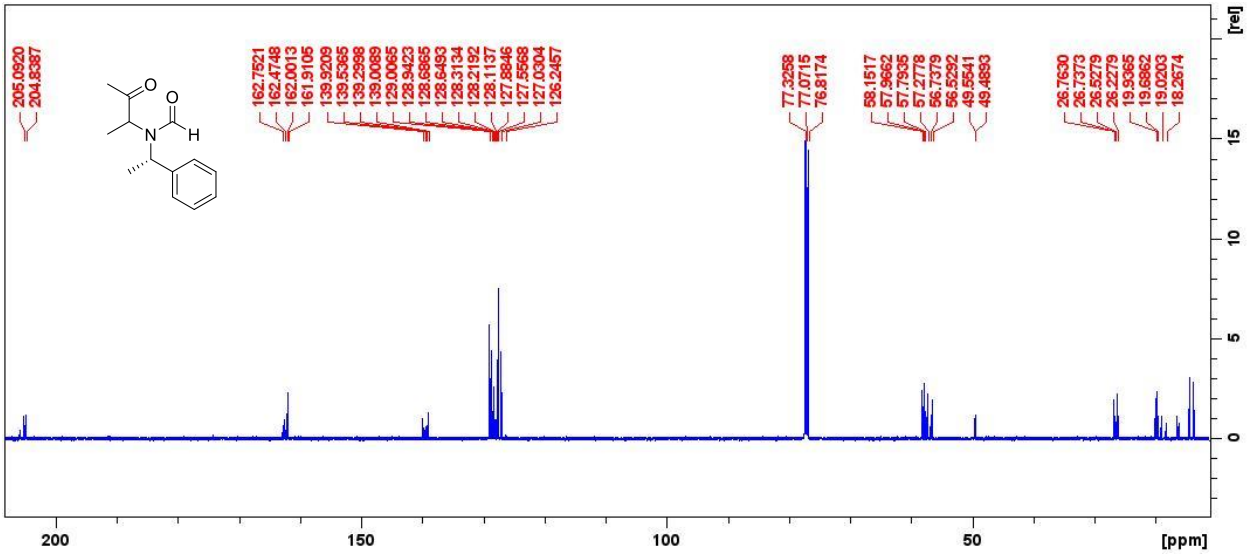
Compound **22** yield: 700 mg (42% yield for two steps) as a yellow liquid.

$R_f$ = 0.3 (5% MeOH/ $CH_2Cl_2$); **$^1$H NMR** (600 MHz, $CDCl_3$) δ: 8.41 (d, *J* = 16.7 Hz, 2H), 8.25 (d, *J* = 6.9 Hz, 1H), 7.43 – 7.29 (m, 15H), 7.26 (s, 1H), 6.00 (d, *J* = 7.3 Hz, 1H), 4.87 (q, *J* = 7.4 Hz, 1H), 4.80 (q, *J* = 7.3 Hz, 1H), 3.88 (q, *J* = 7.2 Hz, 1H), 3.80 (q, *J* = 7.5 Hz, 1H), 3.72 (dq, *J* = 13.8, 7.2 Hz, 2H), 2.21 (s, 1H), 2.15 (d, *J* = 2.3 Hz, 3H), 1.73 (t, *J* = 6.7 Hz, 7H), 1.57 – 1.53 (m, 4H), 1.44 (p, *J* = 8.5 Hz, 7H), 1.22 (d, *J* = 7.5 Hz, 1H), 1.09 (d, *J* = 7.0 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.8, 205.1, 204.8, 162.8, 162.5, 162.0, 161.9, 139.9, 139.5, 139.3, 139.0, 129.0, 129.0, 128.7, 128.7, 128.3, 128.2, 128.1, 127.9, 127.56, 127.0, 58.2, 58.0, 57.8, 57.3, 56.7, 56.5, 49.6, 49.5, 26.8, 26.7, 26.5, 26.2, 19.9, 19.7, 19.0, 18.3, 16.4, 16.1, 14.4, 13.8; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3320, 3064, 2938,2886, 1718, 1672, 1594, 1494, 1357, 1285, 1160, 1098, 700, 623; **HRMS** ($EI^+$) m/z calculated for $C_{13}H_{17}NO_2$ $[M]^+$: 219.1259; found: 219.1252

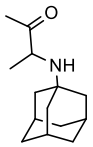
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum

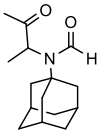


**Synthesis of 3-(((3s,5s,7s)-adamantan-1-yl)amino)butan-2-one (S5)**




Synthesized according to the general procedure at 1.0 equiv. = 5.71 mmol scale using adamantylamine as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-((3s,5s,7s)-adamantan-1-yl)-*N*-(3-oxobutan-2-yl)formamide (24)[2]**

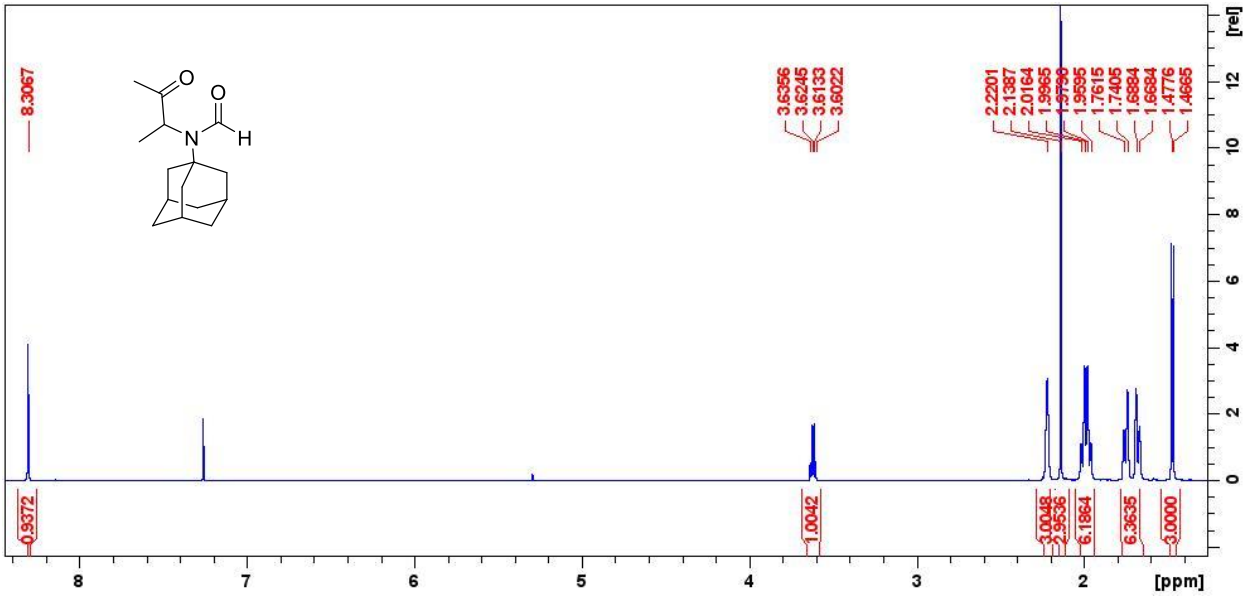



Synthesized according to Route b at 1.0 equiv. = 2.89 mmol scale using 3-(((3s,5s,7s)-adamantan-1-yl)amino)butan-2-one as the starting material. The crude compound was purified by column chromatography (2% MeOH/$CH_2Cl_2$).

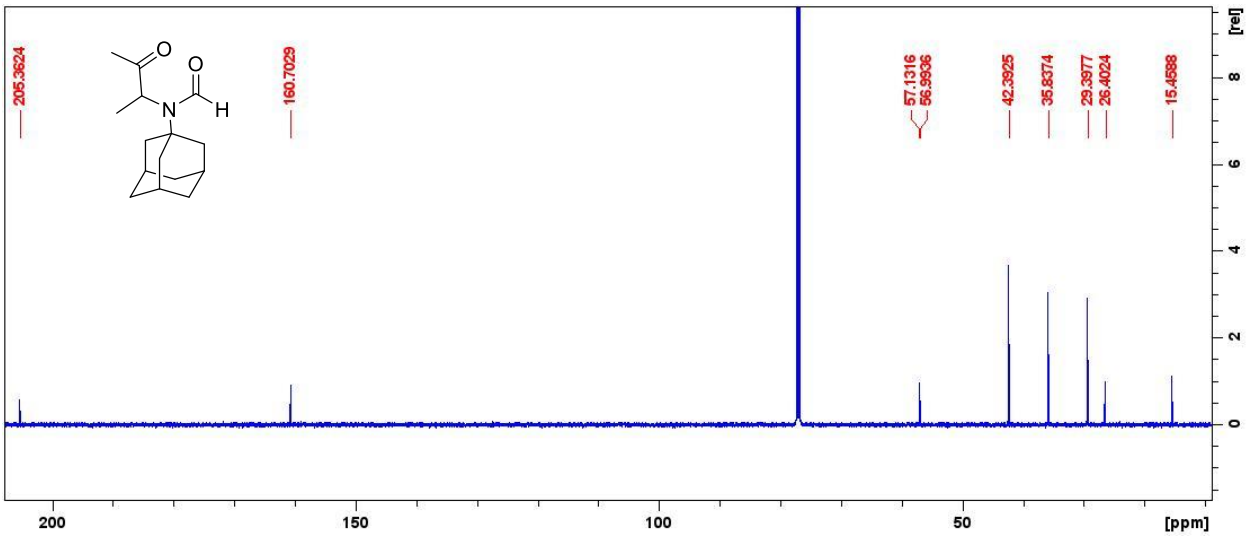
Compound **24** yield: 135 mg (13%) as a yellow solid. All spectra consistent with the literature.

$R_f$ = 0.3 (2% MeOH/$CH_2Cl_2$); **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 3.62 (q, *J* = 6.7, 1H), 2.22 (brs, 3H), 2.14 (s, 3H), 2.02-1.96 (m, 6H), 1.76-1.67 (m, 6H), 1.47 (d, *J* = 6.7 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.4, 160.7, 57.1, 57.0, 42.4, 35.8, 29.40, 26.4, 15.5

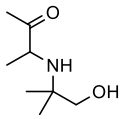
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum

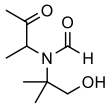


**Synthesis of 3-((1-hydroxy-2-methylpropan-2-yl)amino)butan-2-one (S6)**




Synthesized according to the general procedure at 1.0 equiv. = 11.22 mmol scale using 2-Amino-2-methyl-1-propanol as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-(1-hydroxy-2-methylpropan-2-yl)-*N*-(3-oxobutan-2-yl)formamide (26):**

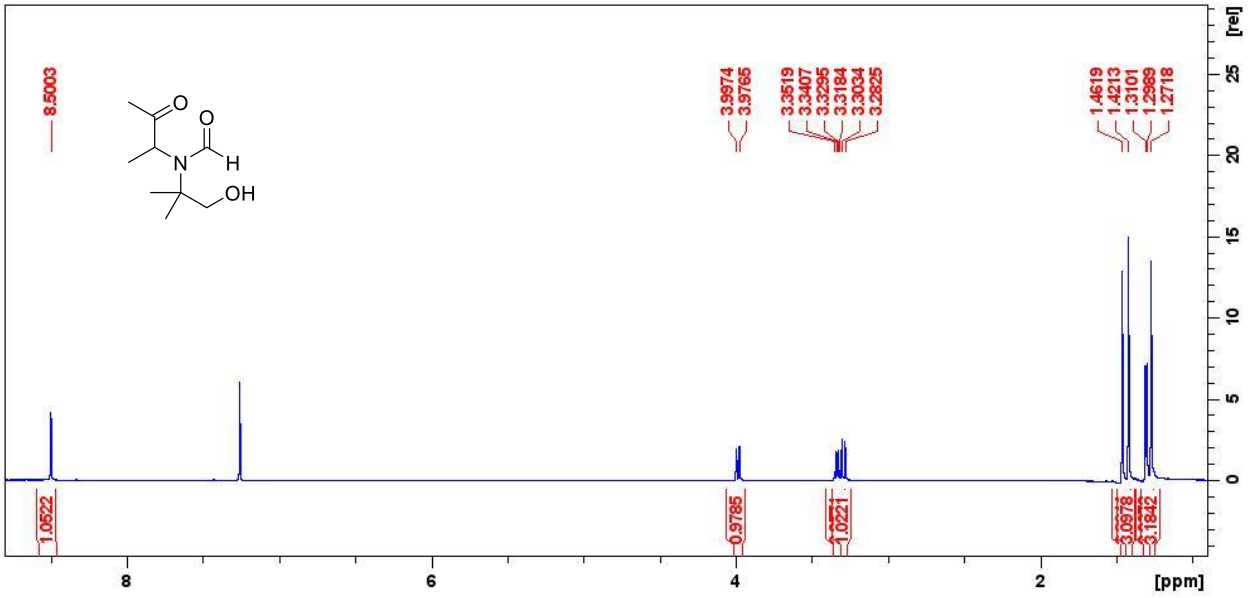



Synthesized according to Route b at 1.0 equiv. = 1.57 mmol scale using 3-((1-hydroxy-2-methylpropan-2-yl)amino)butan-2-one as the starting material. The crude compound was purified by column chromatography (20% MeOH/ $CH_2Cl_2$) followed by recrystallization with hot EtOAc.

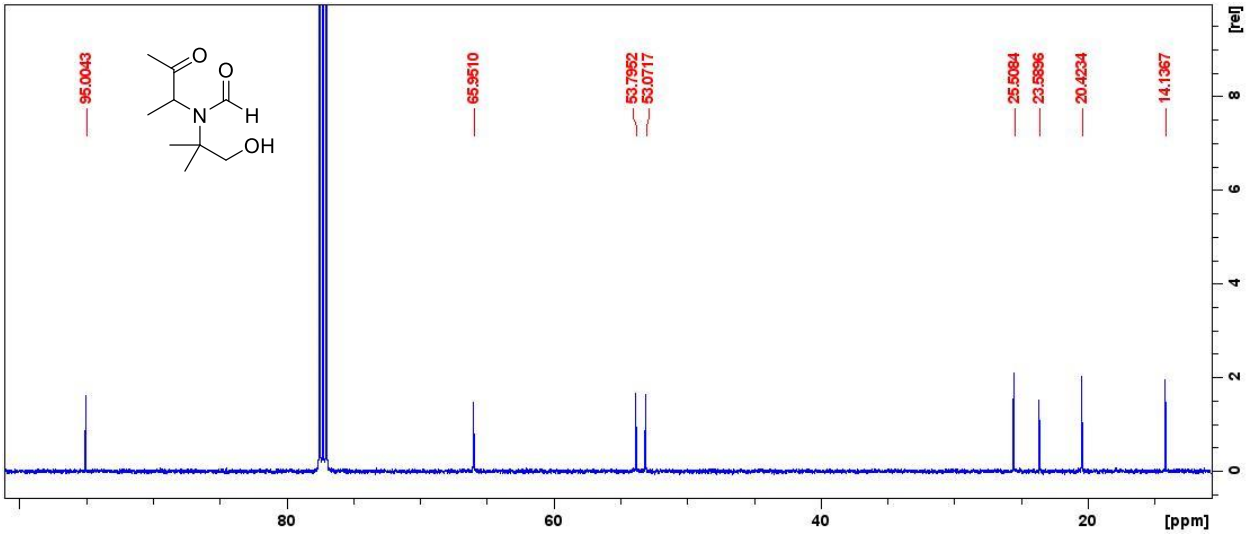
Compound **26** yield: 239 mg (81%) as a white solid.

$R_f$ = 0.4 (20% MeOH/$CH_2Cl_2$); **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.50 (s, 1H), 3.99 (d, *J* = 12.5 Hz, 1H), 3.34 (q, J = 6.7 Hz, 1H), 3.29 (d, *J* = 12.5 Hz, 1H), 1.46 (s, 3H), 1.42 (s, 3H), 1.30 (d, *J* = 6.7 Hz, 3H), 1.27 (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 169.3, 95.0, 66.0, 63.8, 53.8, 53.1, 25.5, 23.6, 20.4, 14.1

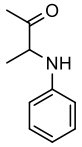
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum

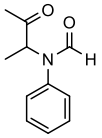


**Synthesis of 3-(phenylamino)butan-2-one (S7)**



Synthesized according to the general procedure at 1.0 equiv. = 16.98 mmol scale using aniline as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-(3-oxobutan-2-yl)-*N*-phenylformamide (28)[3]**

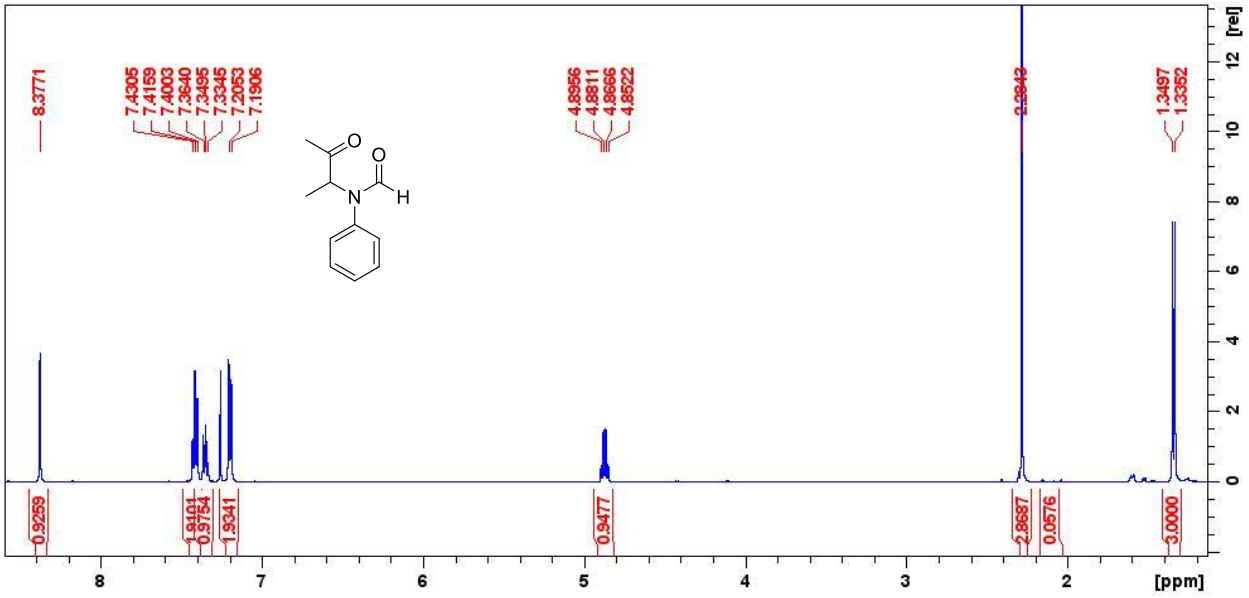


Synthesized according to Route b at 1.0 equiv. = 4.29 mmol scale using 3-(phenylamino)butan-2-one as the starting material. The crude compound was purified by column chromatography (2% MeOH/$CH_2Cl_2$)

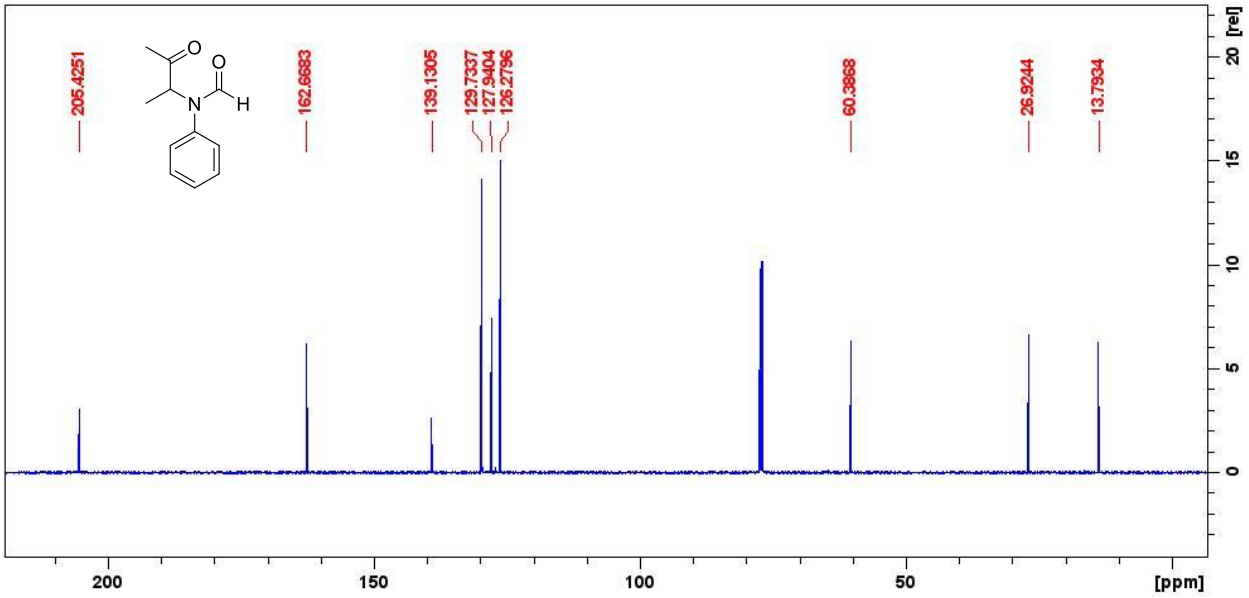
Compound **28** yield: 465 mg (55%) as a yellow solid. All spectra are consistent with the literature.

$R_f$ = 0.3 (30% EtOAc/Hexane); **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 8.38 (s, 1H), 7.42 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.20 (dd, *J* = 7.5, 1.8 Hz, 2H), 4.87 (q, *J* = 7.3 Hz, 1H), 2.28 (s, 3H), 1.34 (d, *J* = 7.2 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.4, 162.7, 139.1, 129.7, 127.9, 126.3, 60.4, 26.9, 13.8;

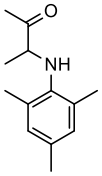
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum

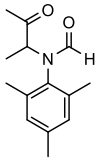


**Synthesis of 3-(mesitylamino)butan-2-one (S8)**



Synthesized according to the general procedure at 1.0 equiv. = 9.47 mmol scale using 2,4,6-trimethylaniline as the starting material. The crude compound was used in the next step without further purification.

**Synthesis of *N*-mesityl-*N*-(3-oxobutan-2-yl)formamide (30)[3]**

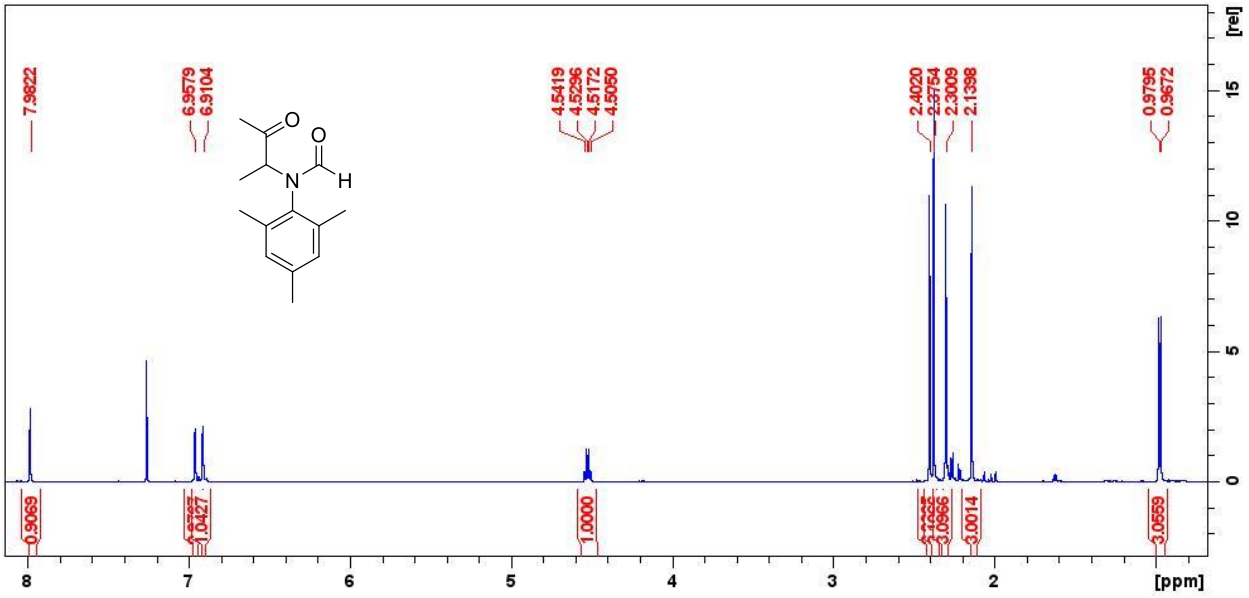


Synthesized according to Route b at 1.0 equiv. = 2.43 mmol scale using 3-(mesitylamino)butan-2-one as the starting material. The crude compound was purified by column chromatography (2% MeOH/$CH_2Cl_2$).

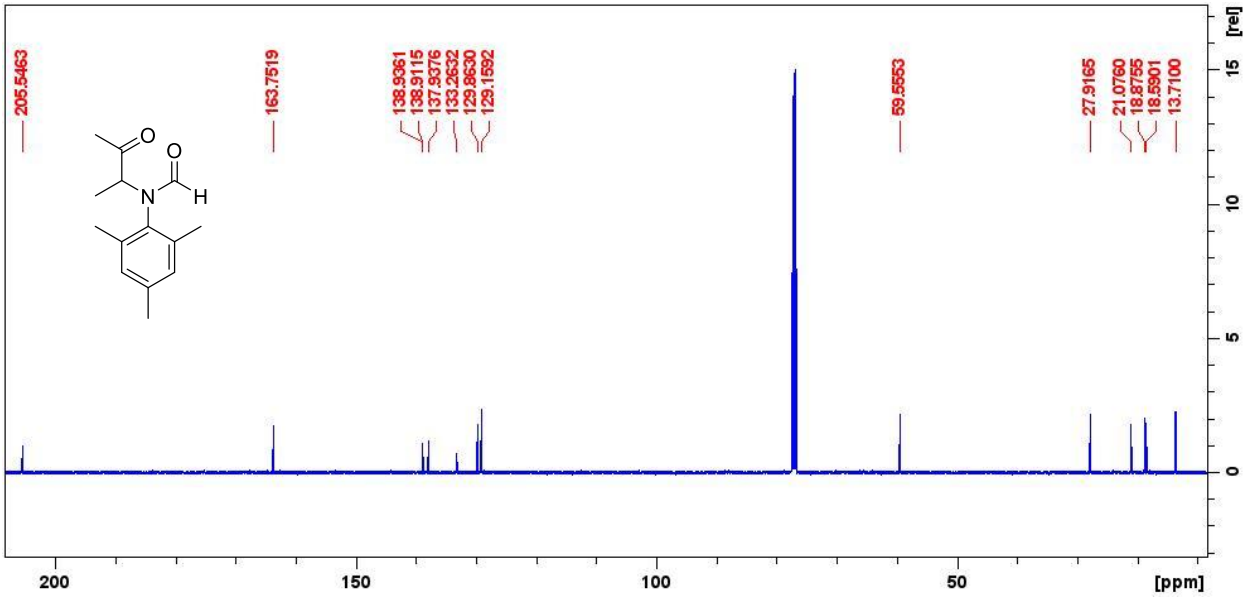
Compound **30** yield: 179 mg (40% for two steps) as a yellow solid. All spectra are consistent with the literature.

$R_f$ = 0.25 (1% MeOH/Hexane); **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 7.98 (s, 1H), 6.96 (s, 1H), 6.91(s, 1H), 4.52 (q, *J* = 7.4 Hz, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H), 2.14 (s,3H), 0.97 (d, *J* = 7.4 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.5, 163.8, 138.9, 138.9, 137.9, 133.3, 129.9, 129.2, 59.6, 27.9, 21.1, 18.9, 18.6, 13.7

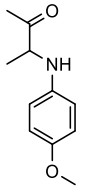
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



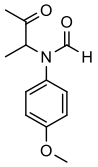
**Synthesis of 3-((4-methoxyphenyl)amino)butan-2-one (S9)**



Synthesized according to the general procedure at 1.0 equiv. = 2.03 mmol scale using 4-methoxyaniline as the starting material. The crude compound was purified by column chromatography (20% EtOAc/Hexanes).

Compound **S9** yield: 0.34g (86%) as a yellow solid

**Synthesis of *N*-(4-methoxyphenyl)-*N*-(3-oxobutan-2-yl)formamide (32):**

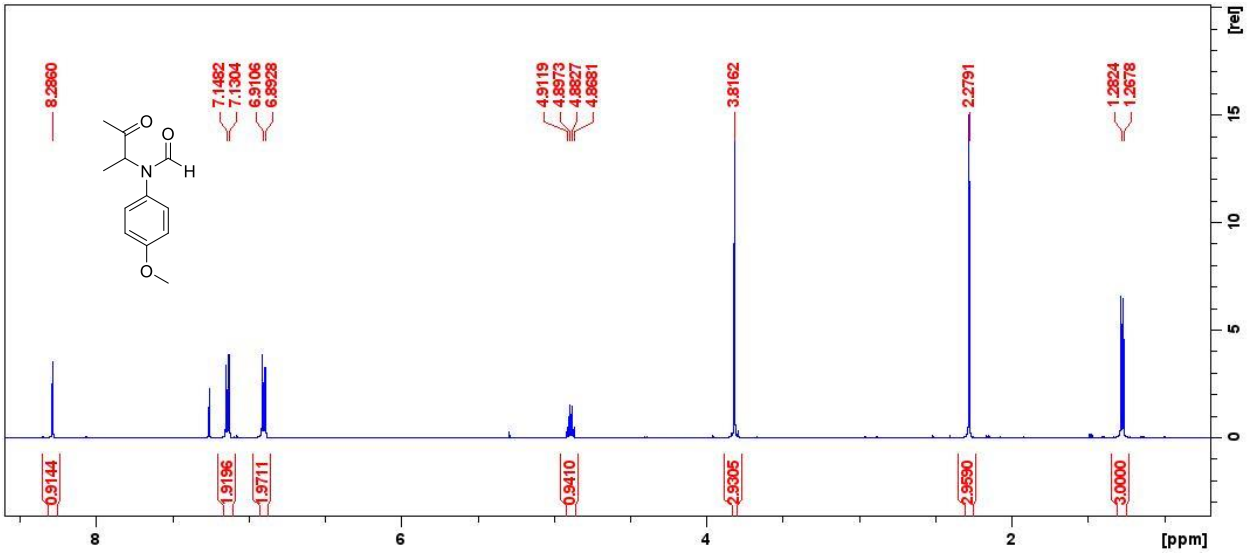


Synthesized according to the general procedure at 1.0 equiv. = 1.55 mmol scale using 3-(4-methoxyphenylamino)butan-2-one as the starting material. The crude compound was purified by column chromatography (25% EtOAc/Hexanes).

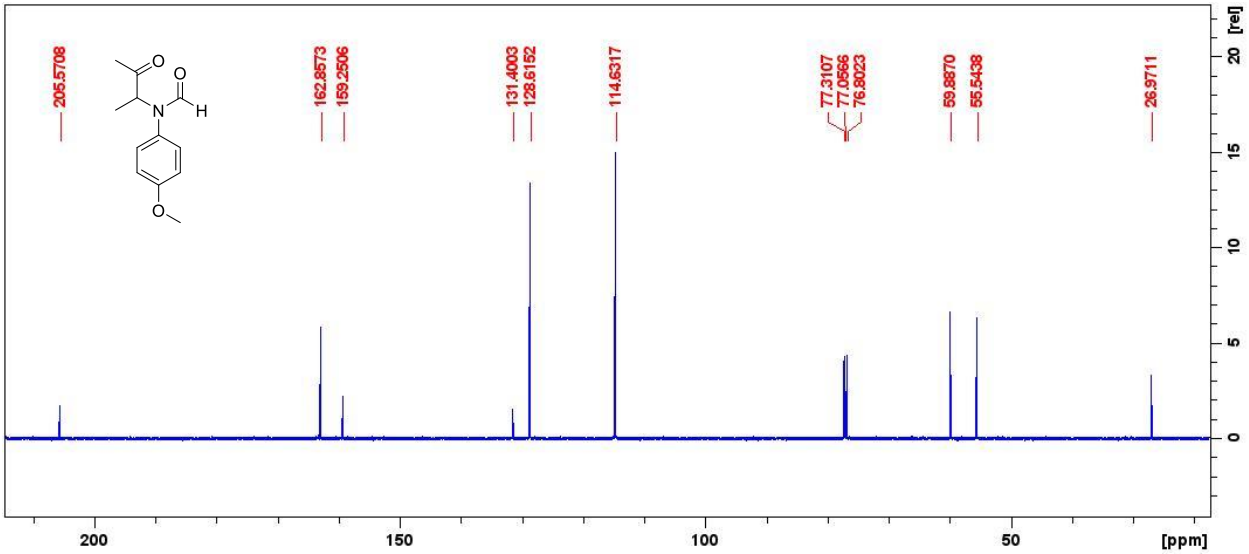
Compound **32** yield: 0.255g (74%) as a yellow solid

$R_f$ = 0.3 (20% EtOAc/ $CH_2Cl_2$); **$^1$H NMR** (600 MHz, $CDCl_3$) δ: 8.29 (s, 1H), 7.17 – 7.11 (m, 2H), 6.93 – 6.83 (m, 2H), 4.90 (q, *J* = 7.3 Hz, 1H), 3.82 (s, 3H), 2.28 (s, 3H), 1.28 (d, *J* = 7.3 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ:205.6, 162.9, 159.3, 131.4, 128.6, 114.6, 59.9, 55.5, 27.0, 13.8; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3045, 2989, 2938, 1721, 1671, 1511, 1355, 1245, 1030, 836, 562; **HRMS** ($EI^+$) m/z calculated for $C_{12}H_{15}NO_3$ $[M]^+$: 221.1052; found: 221.1050

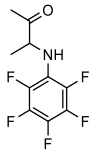
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 3-(perfluorophenylamino)butan-2-one (S10)[3]**

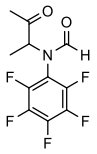


Synthesized according to the general procedure at 1.0 equiv. = 27.30 mmol scale using perfluoroaniline as the starting material. The crude compound was purified by column chromatography (20% EtOAc/Hexanes).

Compound **S10** yield: 5.70 g (82%) as a beige solid.

$R_f$ = 0.45 (30% EtOAc/Hexane); **$^1$H NMR** (600 MHz, $CDCl_3$) δ: 4.57 – 4.25 (m, 2H), 2.24 (s, 3H), 1.41 (d, *J* = 6.7 Hz, 3H)

**Synthesis of *N*-(3-oxobutan-2-yl)-*N*-(perfluorophenyl)formamide (34):**

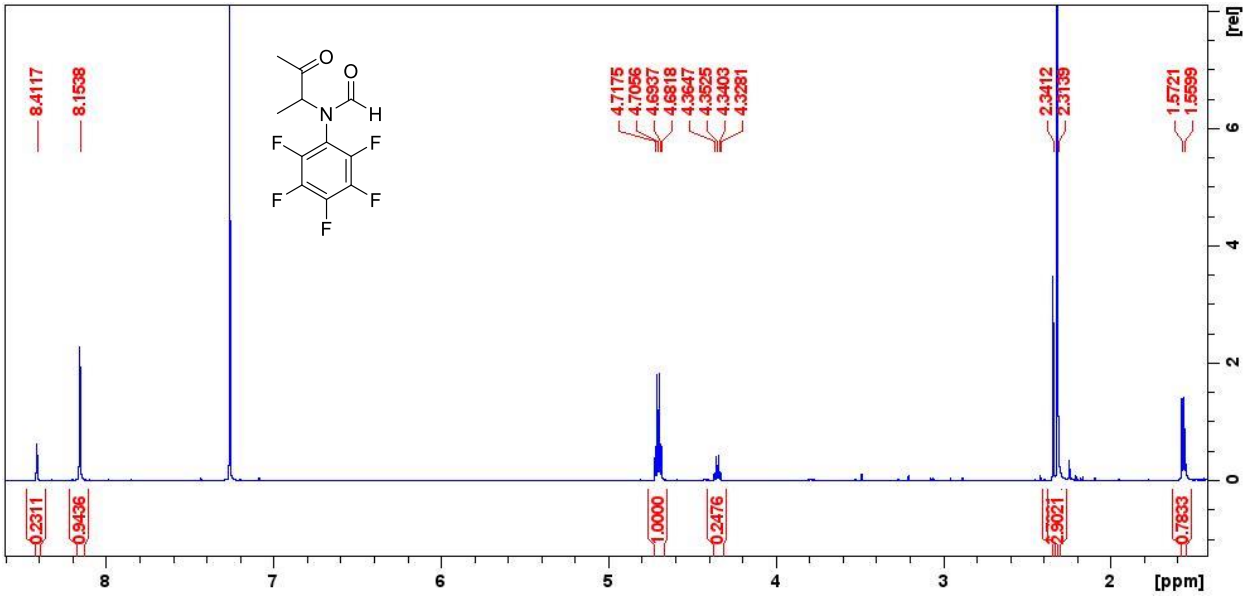


Synthesized according to the general procedure at 1.0 equiv. = 11.85 mmol scale using 3-(perfluorophenylamino)butan-2-one as the starting material. The crude compound was purified by column chromatography (30% EtOAc/Hexanes).

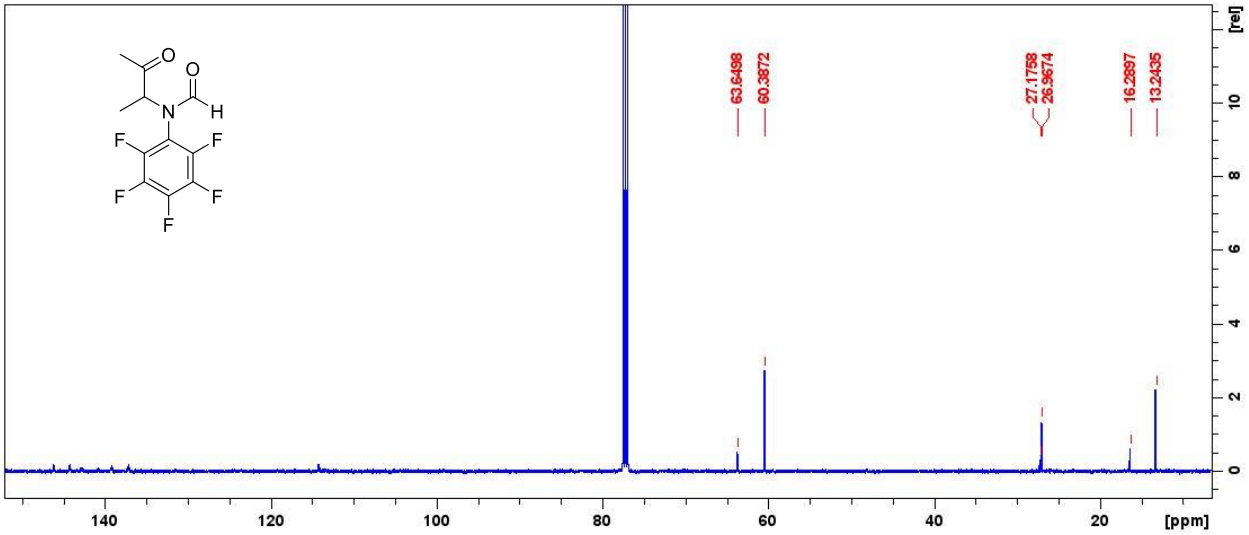
Compound **34** yield: 2.91 g (87%) as a white solid

$R_f$ = 0.31 (30% EtOAc/Hexane); **$^1$H NMR** (600 MHz, $CDCl_3$) δ: 8.15 (s, 1H), 4.70(q, J=7.14 Hz, 1H), 2.31(s, 3H), 1.33(d, J=7.14 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 203.4, 203.3, 162.3, 161.9, 146.2, 144.2, 139.2, 114.2, 63.7, 60.4, 27.2, 27.0, 17.0, 13.3; **FTIR** (KBr thin film) υmax ($cm^{-1}$):2985, 2325, 1731, 1710, 1361, 1264, 1108, 798; **HRMS** ($EI^+$) m/z calculated for $C_{11}H_8F_5NO_2$ $[M]^+$: 281.0475; found: 281.0482

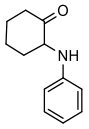
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 2-(phenylamino)cyclohexanone (S11)**

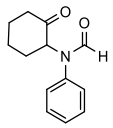


Synthesized according to the general procedure at 1.0 equiv. = 38.4 mmol scale using aniline as the starting material. The crude compound was purified by column chromatography (20% EtOAc/Hexanes).

Compound **S11** yield: 3.85 g (53%) as a brown solid.

$R_f$ = 0.26 (20% EtOAc/Hexanes); **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 7.23 – 7.13 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.66 – 6.58 (m, 2H), 4.90 (s, 1H), 4.01 (ddd, *J* = 12.2, 5.8, 1.4 Hz, 1H), 2.68 (ddq, *J* = 12.3, 6.1, 3.2 Hz, 1H), 2.59 (ddt, *J* = 13.5, 4.5, 2.3 Hz, 1H), 2.43 (tdd, *J* = 13.4, 6.3, 1.5 Hz, 1H), 2.17 (ddt, *J* = 12.8, 6.3, 3.0 Hz, 1H), 1.99 – 1.89 (m, 1H), 1.89 – 1.66 (m, 2H), 1.45 (qd, *J* = 12.8, 3.7 Hz, 1H)

**Synthesis of *N*-(2-oxocyclohexyl)-*N*-phenylformamide (36)**

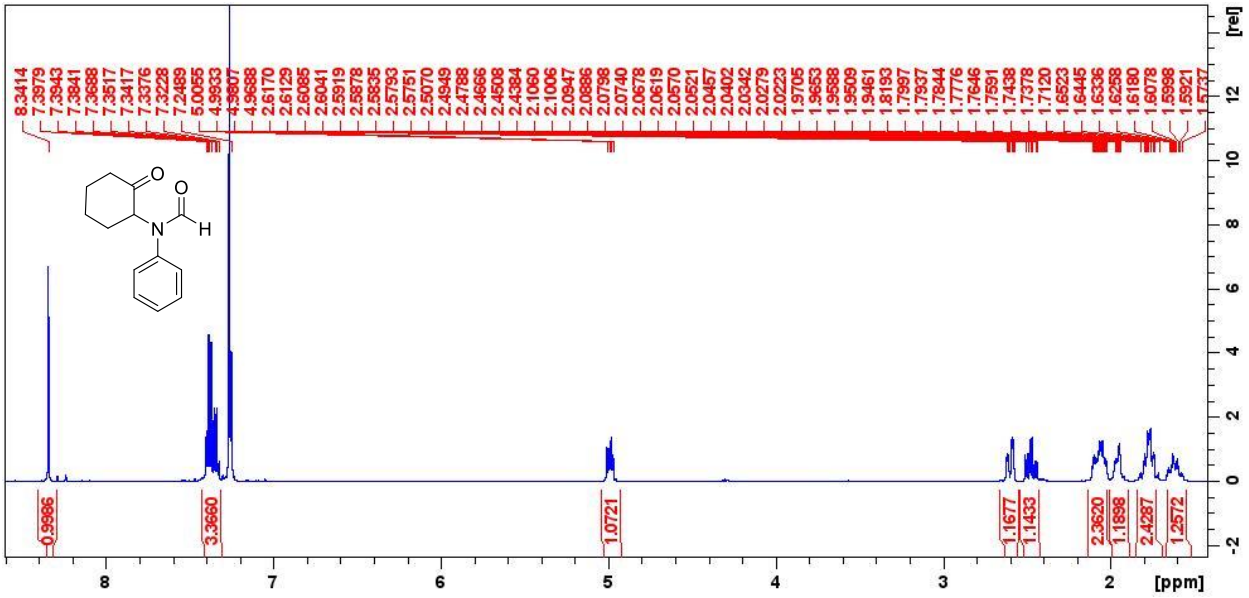


Synthesized according to the general procedure at 1.0 equiv. = 20.3 mmol scale using 2-(phenylamino)cyclohexanone as the starting material. The crude compound was purified by column chromatography (30% EtOAc/Hexanes).

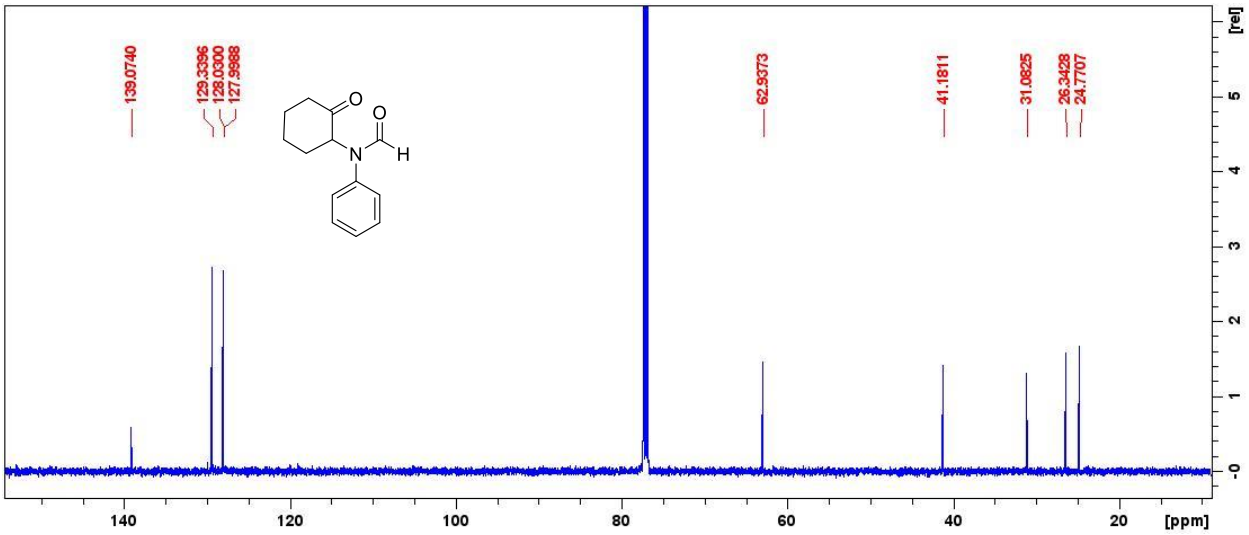
Compound **34** yield: 3.65 g (83%) as a dark brown solid

$R_f$ = 0.3 (2% MeOH/$CH_2Cl_2$); **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 8.34 (s, 1H), 7.40-7.36 (m, 2H), 7.35-7.32 (m, 1H), 7.27-7.24 (m, 2H), 4.98 (dd, *J* = 12.3, 6.1 Hz, 1H), 2.26-2.58 (m, 1H), 2.47 (td, *J* = 14.1, 6.1 Hz, 1H) , 2.12-2.00 (m, 2H), 1.99-1.89 (m, 1H), 1.84-1.69 (m, 2H), 1.67-1.54 (m, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 205.3, 162.3, 162.0, 58.6, 57.6, 57.6, 52.3, 33.8, 33.1, 30.6, 30.6, 26.9, 26.7, 25.9, 25.9, 25.7, 25.7, 25.3, 25.1, 18.4, 14.5; **FTIR** (KBr thin film) υmax ($cm^{-1}$):2940, 2867, 1681, 1594, 1494, 1270, 702; **HRMS** ($EI^+$) m/z calculated for $C_{13}H_{15}NO_2$ $[M]^+$: 217.1103; found: 217.1096

## $^{1}$H NMR spectrum

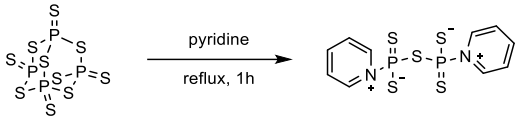



## $^{13}$C NMR spectrum



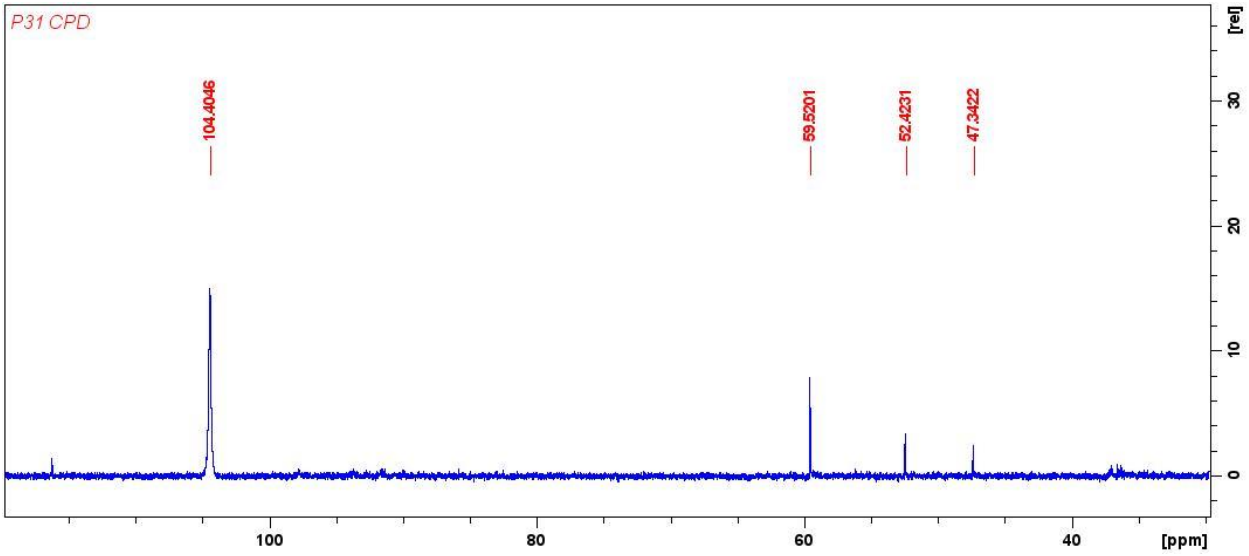
# 3.0 Preparation of $P_2S_5$-$Py_2$ Complex

*Preparation of* $P_2S_5$-$Py_2$ *complex with Svensson's procedure*



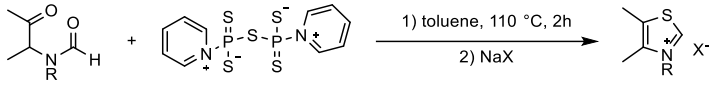

The $P_4S_{10}$ (4.5 g, 0.01mmol) was refluxed in dry pyridine (56mL) at 80 ℃ for 2 hours. The obtained clear yellow solution was left standing at ambient temperature overnight for crystallization. The resulting crystals were filtered and washed with dry acetonitrile (15 mL × 3) followed by dry hexane (15 mL), then dried under high vacuum for 2 hours to obtain a pale-yellow solid (6.4 g reaction mixture).

## $^{31}$P NMR spectrum



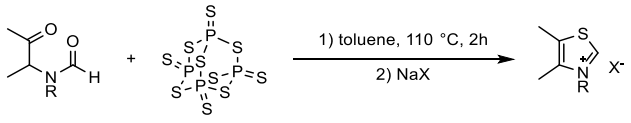
# 4.0 Procedures and Spectra for Thiazolium Salts

*Preparation of thiazolium pre-catalysts with* $P_2S_5$-$Py_2$ *complex (Route a)*



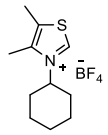

The appropriate α-formamido ketone (1 equiv.) and $P_2S_5$-$Py_2$ complex (3 equiv) were stirred in toluene at 110 ℃ for 2 hours. Over this period, the solution turned to yellow colour, and a sticky slurry precipitate formed. The soluble portion was then removed using a Pasteur pipette, and the precipitate was washed with hexane (3mL × 3). The precipitate was then dissolved in water at 65 ℃ over 20 min until it turned into a clear yellow solution. $NaBF_4$ (3 equiv.) or $NaBPh_4$ (1 equiv.) was added to the solution, followed by $CH_2Cl_2$. The biphasic mixture was stirred at room temperature for 15 minutes. After extraction with $CH_2Cl_2$ (10 mL × 3), the combined organic extracts were dried over $Na_2SO_4$ then concentrated under vacuum. If the obtained compound quickly turned green upon exposure to air, hexane (3 mL) was added to the product, then heated at 100 ℃ for 5 min, then concentrated while hot. This treatment was repeated three times.

*Preparation of thiazolium precursors with* $P_4S_{10}$ *reagent (Route b)*




The appropriate α-formamido ketones (1 equiv.) and $P_4S_{10}$ (1 equiv.) were stirred in toluene at 110 ℃ for two hours. Over this period, the solution turned to yellow, and a sticky slurry precipitate formed. The soluble portion was then removed using a Pasteur pipette, and the precipitate was washed with hexane (3mL × 3). The precipitate was then dissolved in water at 65 ℃ over 20 min until it turned into a clear yellow solution. $NaBF_4$ (3 equiv.) or $NaBPh_4$ (1 equiv.) was added to the solution, followed by $CH_2Cl_2$. The biphasic mixture was stirred at room temperature for 30 minutes. After extraction with $CH_2Cl_2$ (10 mL × 3), the combined organic extracts were dried over $Na_2SO_4$ then concentrated under vacuum. If the obtained compound quickly turned green upon exposure to air, hexane (3 mL) was added to the product, then heated at 100 ℃ for 5 min, then concentrated while hot. This treatment was repeated three times.

**Synthesis of 3-cyclohexyl-4,5-dimethylthiazol-3-ium tetrafluoroborate (16):**

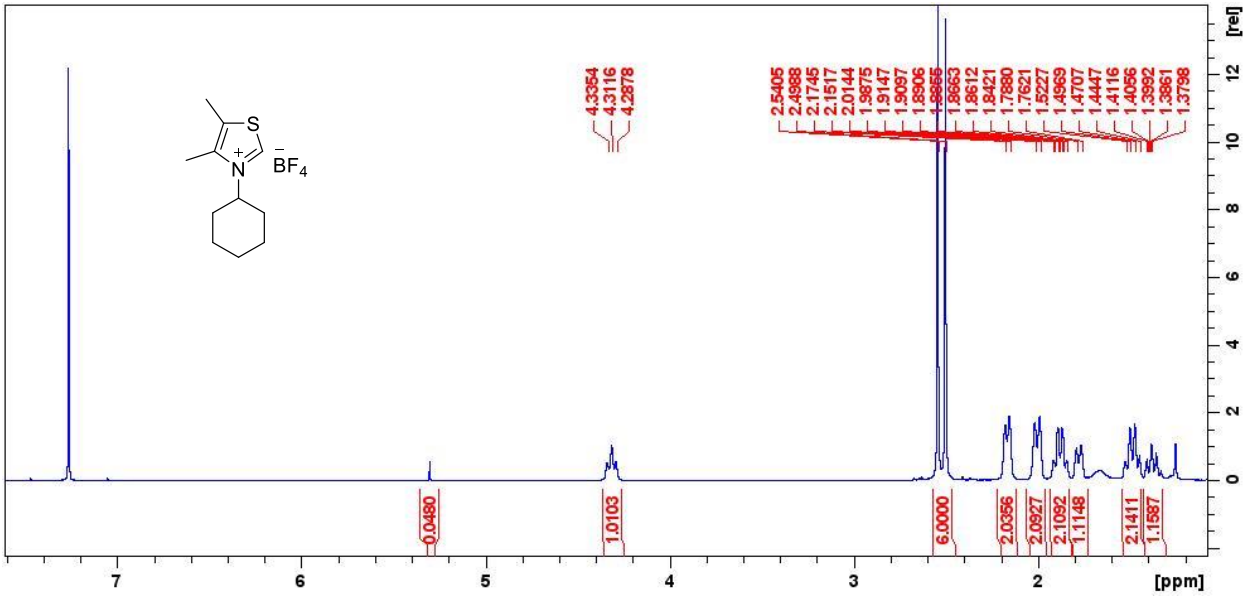



Synthesized according to Route a at 1.0 equiv. = 0.25 mmol scale, according to Route b at 1.0 equiv. =0.51 mmol scale using *N*-(3-oxobutan-2-yl)-*N*-propylformamide as the starting material.

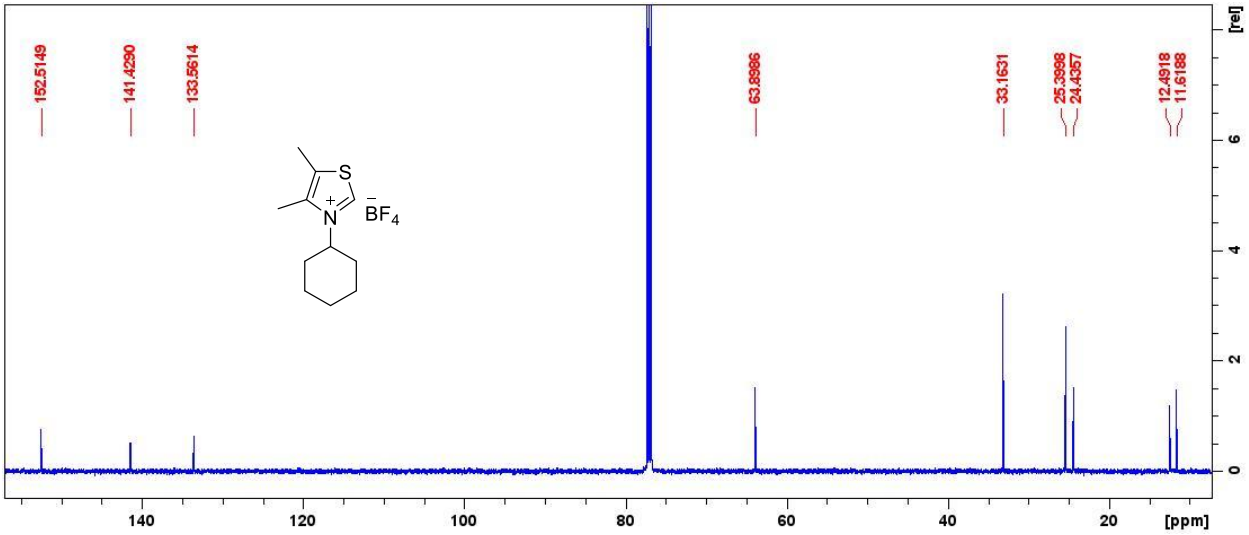
Compound **S7** yield: 60 mg (82% with $P_2S_5$-$Py_2$ complex) and 49 mg (68 % with $P_4S_{10}$) as a pale yellow solid. All spectra consistent with the literature.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ: 9.84 (s, 1H), 4.31 (tt, *J* = 12.1, 3.4 Hz, 1H), 2.54 (s, 3H), 2.50 (s, 3H), 2.16 (d, *J* = 11.9 Hz, 2H), 2.00 (dt, *J* = 13.7, 3.3 Hz, 2H), 1.88 (qd, *J* = 12.3, 3.5 Hz, 2H), 1.78 (dt, *J* = 13.2, 3.3 Hz, 1H), 1.48 (qt, *J* = 12.9, 3.3 Hz, 2H), 1.37 (qt, *J* = 13.2, 3.5 Hz, 1H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 152.5, 141.4, 133.6, 63.9, 33.2, 25.4, 24.4, 12.5, 11.6; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 2932, 2858, 1453, 1109, 533; **HRMS** ($EI^+$) m/z calculated for $C_{11}H_{18}NS^+$ $[M]^+$: 196.1154; found: 196.1151.

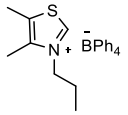
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 4,5-dimethyl-3-propylthiazol-3-ium tetraphenylborate (19):**

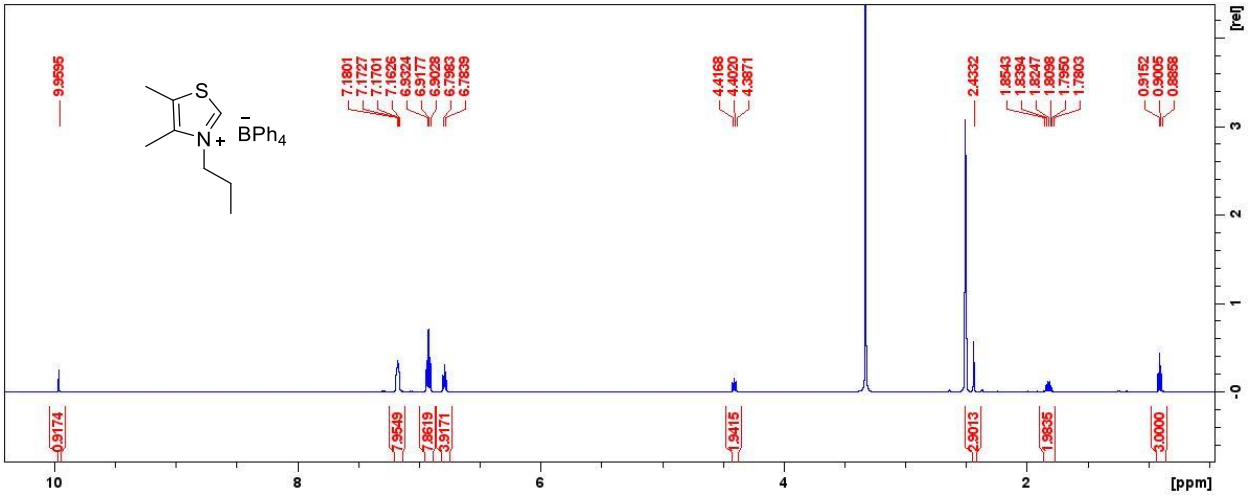



Synthesized according to Route a at 1.0 equiv. = 0.87 mmol scale , according to Route b at 1.0 equiv. =0.32 mmol scale using *N*-(3-oxobutan-2-yl)-*N*-propylformamide as the starting material.

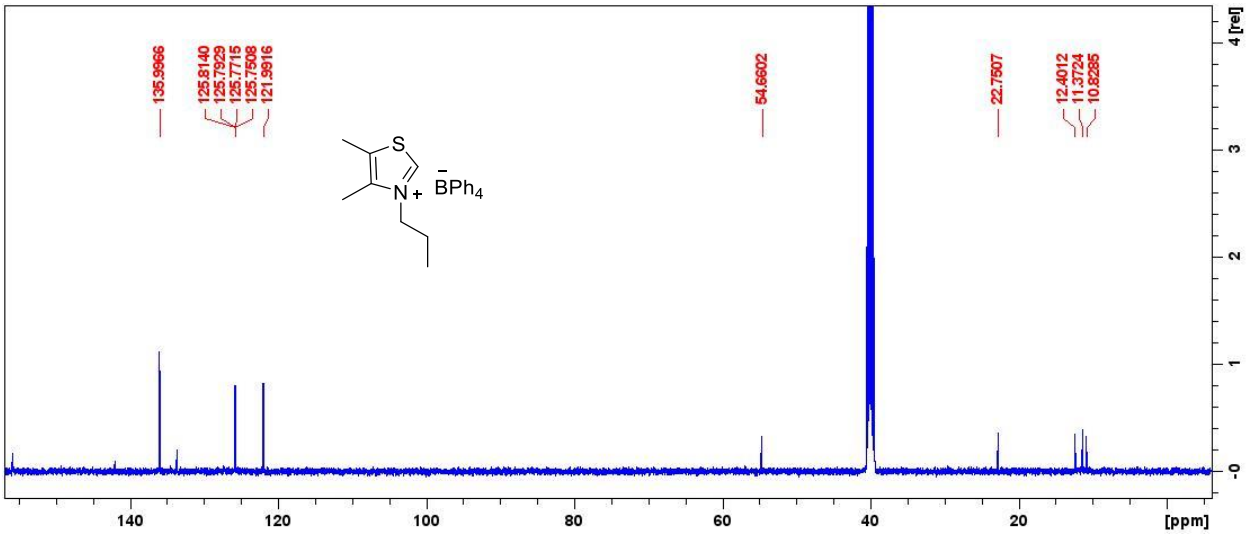
Compound **19** yield: 235 mg (57% with $P_2S_5$-$Py_2$ complex) and 22mg (29% with $P_4S_{10}$) as a light brown solid. All spectra consistent with the literature.

**$^1$H NMR** (600 MHz, DMSO-$d_6$) δ: 9.96 (s, 1H), 7.19-7.14 (m, 8H), 6.92 (t, *J* = 7.4 Hz, 8H), 6.78 (t, *J* = 7.17 Hz, 4H), 4.40 (t, *J* = 7.4 Hz, 2H), 2.43(s, 3H), 1.85-1.78 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 164.4, 164.0, 163.6, 155.9, 142.1, 136.0, 133.6, 125.8, 125.8, 125.8, 122.0, 54.7, 22.8, 12.4, 11.4, 10.8.

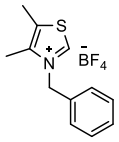
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 3-benzyl-4,5-dimethylthiazol-3-ium tetrafluoroborate (21)[4]**

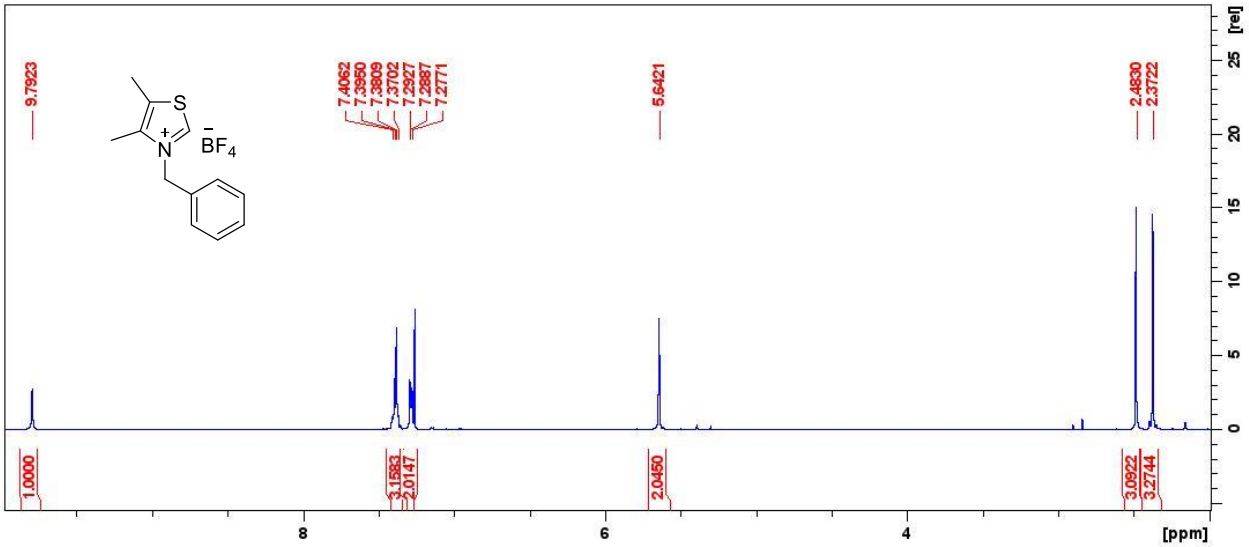



Synthesized according to Route a at 1.0 equiv. = 0.24 mmol scale, according to Route b at 1.0 equiv. = 0.24 mmol scale using *N*-benzyl-*N*-(3-oxobutan-2-yl)formamide as the starting material.

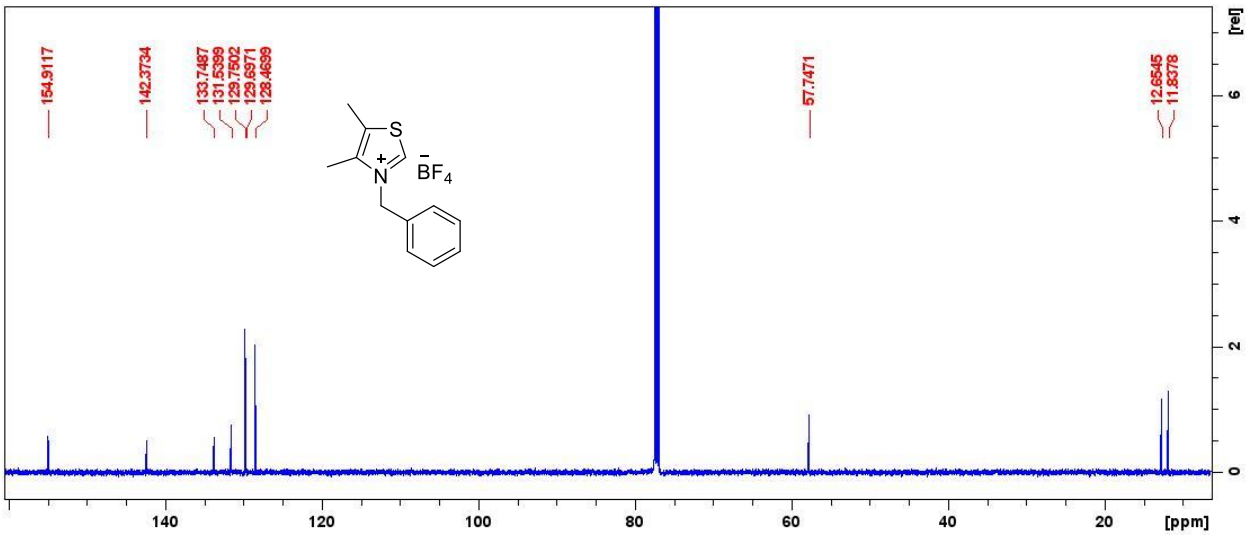
Compound **21** yield: 30 mg (43 % with $P_2S_5$-$Py_2$ complex) and 45 mg (65 % with $P_4S_{10}$) as a brown liquid. All spectra consistent with the literature.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ: 9.79 (s, 1H), 7.42-7.35 (m, 3H), 7.31-7.26 (m, 2H), 5.64 (s, 2H), 2.48 (s, 3H), 2.37 (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 154.9, 142.4, 133.8, 131.5, 129.8, 129.7, 128.5, 57.8, 12.7, 11.8.

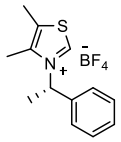
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of (S)-4,5-dimethyl-3-(1-phenylethyl)thiazol-3-ium tetrafluoroborate (23):**

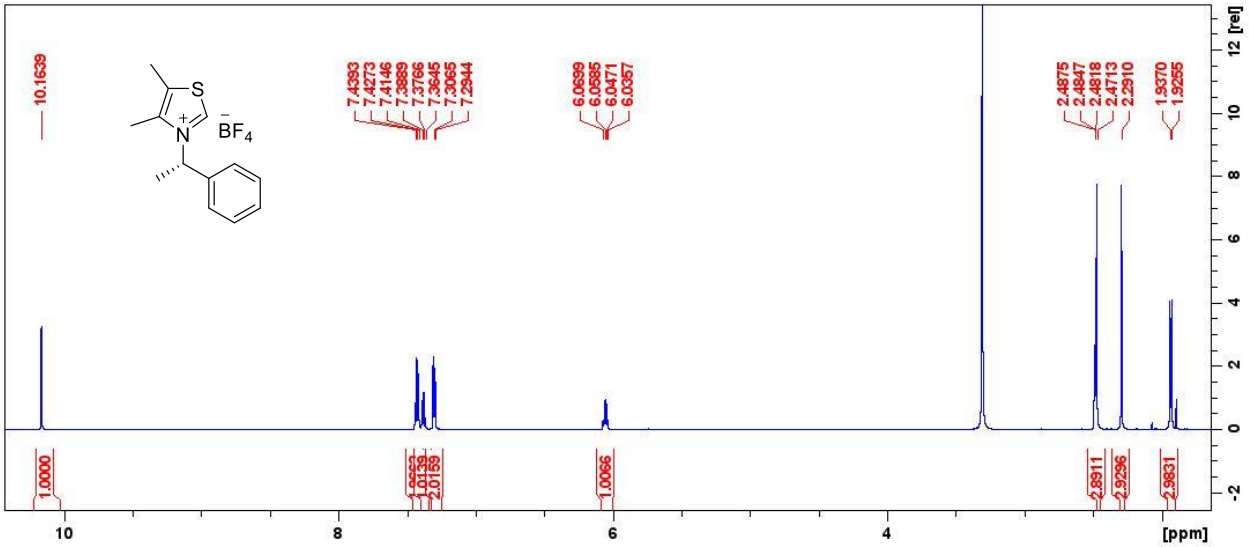



Synthesized according to Route a at 1.0 equiv. = 0.26 mmol scale, according to Route b at 1.0 equiv. = 0.23 mmol scale using *N*-(3-oxobutan-2-yl)-*N*-((S)-1-phenylethyl)formamide as the starting material.

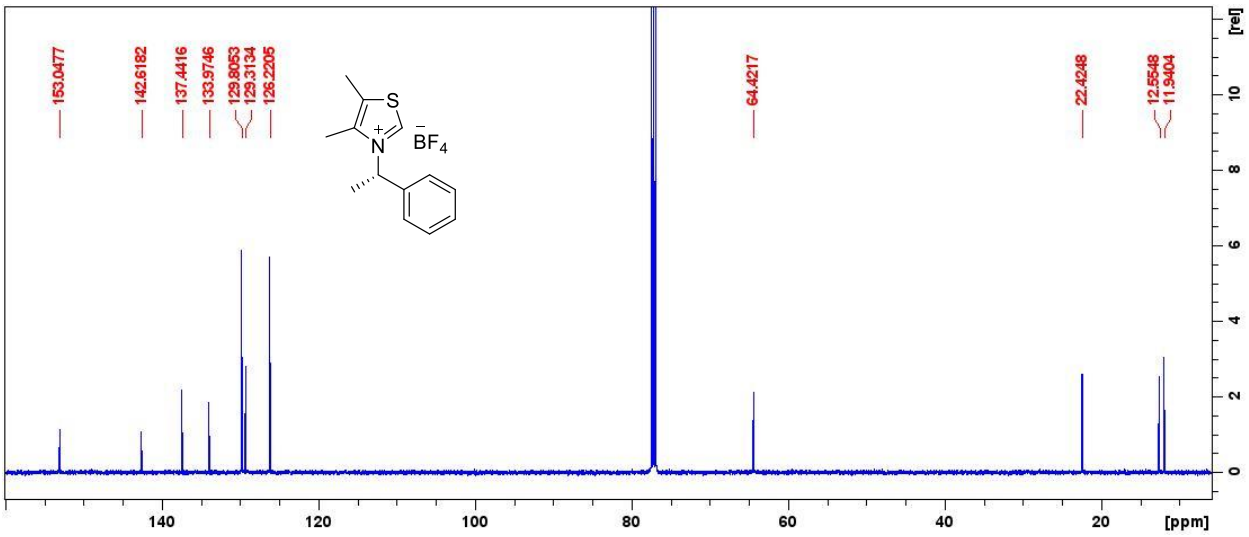
Compound **23** yield: 28 mg (36 % with $P_2S_5$-$Py_2$ complex) and 44 mg (69 % with $P_4S_{10}$) as a brown liquid. All spectra consistent with the literature.

**$^1$H NMR** (600 MHz, DMSO-$d_6$) δ: 10.16 (s, 1H), 7.43 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.30 (dd, *J* = 7.1, 1.8 Hz, 2H), 6.05 (q, *J* = 6.9 Hz, 1H), 2.47 (s, 3H), 2.29 (s, 3H), 1.93 (d, *J* = 7.0 Hz, 3H); **$^{13}$CNMR** (125 MHz, $CDCl_3$) δ: 153.1, 142.6, 137.5, 134.0, 129.8, 129.3, 126.2, 64.4, 22.4, 12.6, 11.9

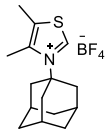
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 3-((3s,5s,7s)-adamantan-1-yl)-4,5-dimethylthiazol-3-ium tetrafluoroborate (25)**

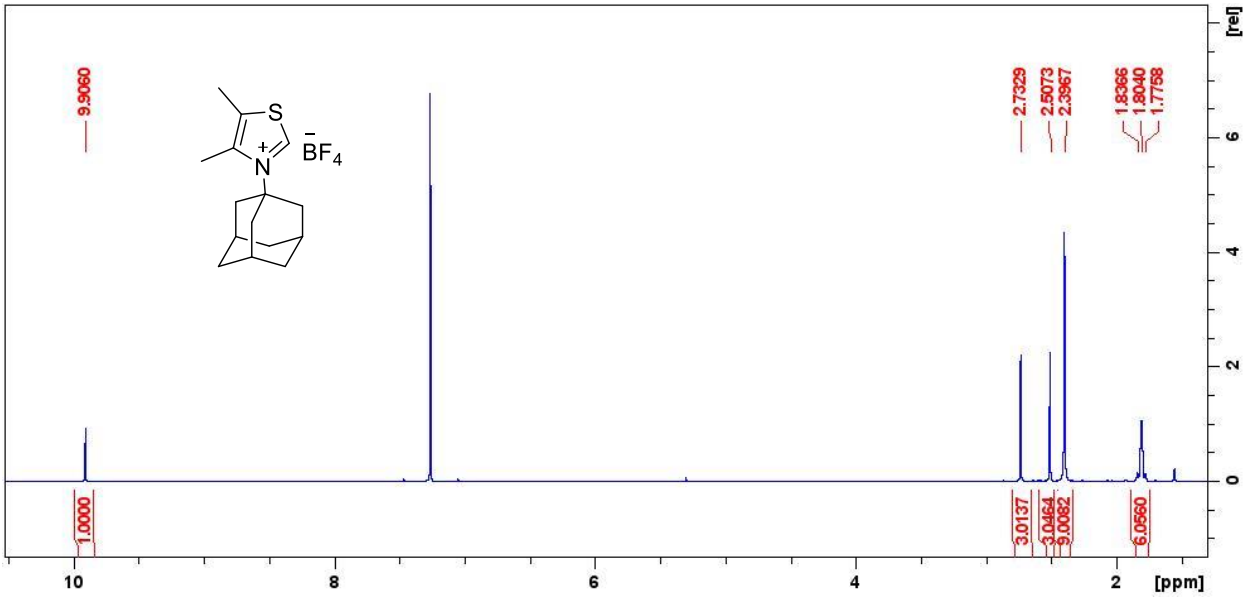



Synthesized according to Route a at 1.0 equiv. = 0.20 mmol scale, according to Route b at 1.0 equiv. = 0.06 mmol scale using N-((3s,5s,7s)-adamantan-1-yl)-N-(3-oxobutan-2-yl)formamide as the starting material.

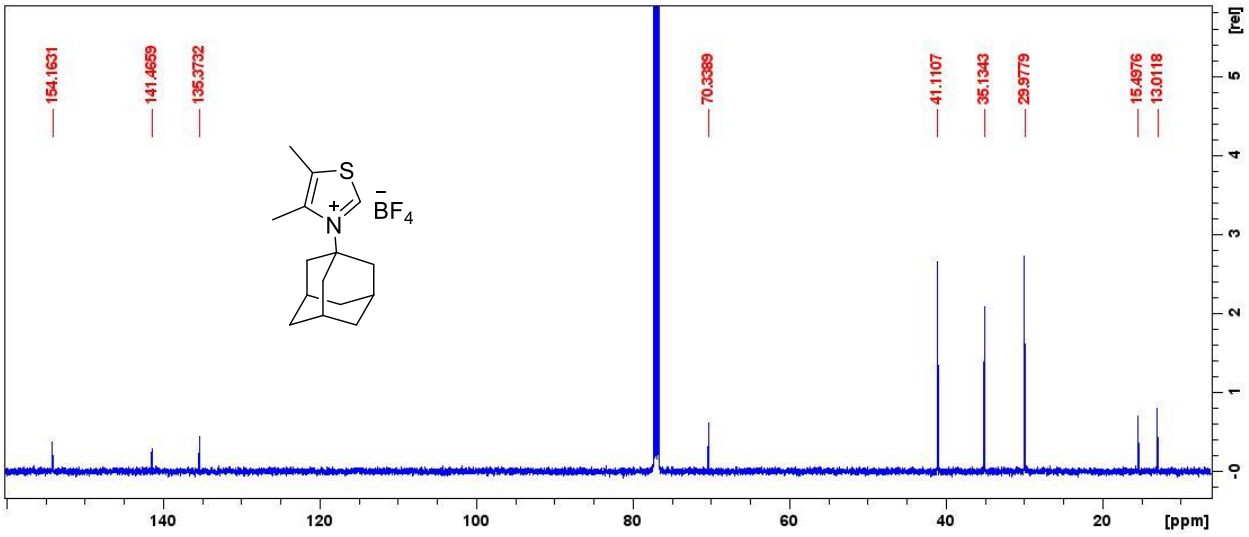
Compound **25** yield: 46 mg (67 % with $P_2S_5$-$Py_2$ complex) and 43 mg (63 % with $P_4S_{10}$) as a pale yellow solid. All spectra consistent with the literature.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ: 9.91 (s, 1H), 2.73 (s, 3H), 2.51 (s, 3H), 2.40 (s, 9H), 1.80 (s, 6H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 154.2, 141.5, 135.4, 70.3, 41.1, 35.1, 30.0, 15.5, 13.0; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3170, 2921, 2855, 1251, 1057, 802; **HRMS** ($EI^+$) m/z calculated for $C_{15}H_{22}NS^+$ $[M]^+$: 248.1467; found: 248.1461

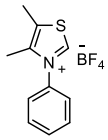
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 4,5-dimethyl-3-phenylthiazol-3-ium tetrafluoroborate (29):**

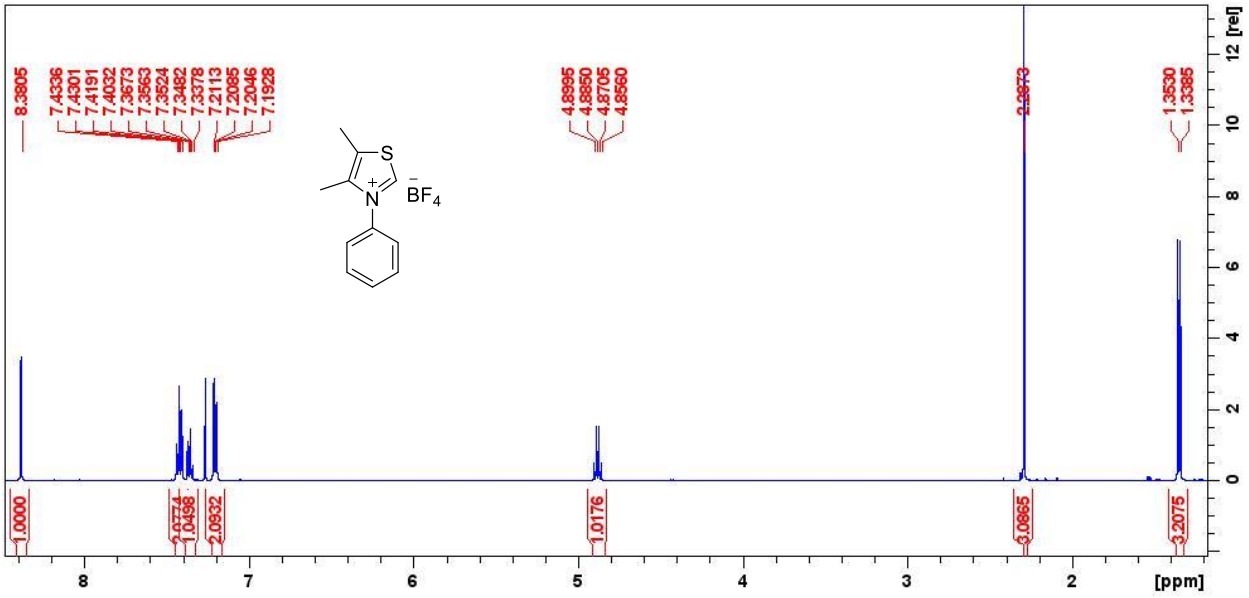



Synthesized according to Route a at 1.0 equiv. = 0.26 mmol scale, according to Route b at 1.0 equiv. = 0.21 mmol scale using *N*-(3-oxobutan-2-yl)-*N*-phenylformamide as the starting material.

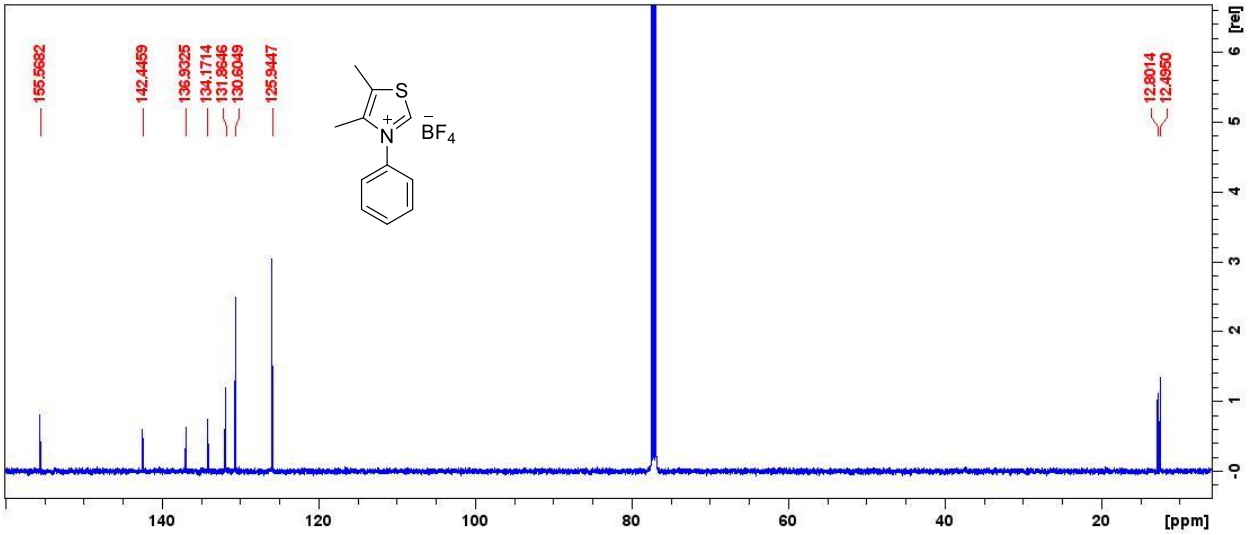
Compound **29** yield: 37 mg (52 % with $P_2S_5$-$Py_2$ complex) and 39 mg (54 % with $P_4S_{10}$) as a pale yellow solid. All spectra consistent with the literature.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ: 8.38 (s, 1H), 7.45-7.39 (m, 2H), 7.38-7.33 (m, 1H), 7.22-7.18 (m, 2H), 4.88 (q, *J* = 7.3 Hz, 1H), 2.29 (s, 3H), 1.35 (d, *J* = 7.3 Hz, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 155.6, 142.5, 136.9, 134.2, 131.9, 130.6, 126.0, 12.8, 12.5; **FTIR** (KBr thin film) υmax ($cm^{-1}$):3104, 2955, 1450, 1040, 706; **HRMS** ($EI^+$) m/z calculated for $C_{11}H_{12}NS^+$ $[M]^+$: 190.0658; found: 190.0694

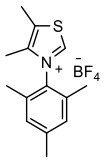
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



## Synthesis of 3-mesityl-4,5-dimethylthiazol-3-ium tetrafluoroborate (31):

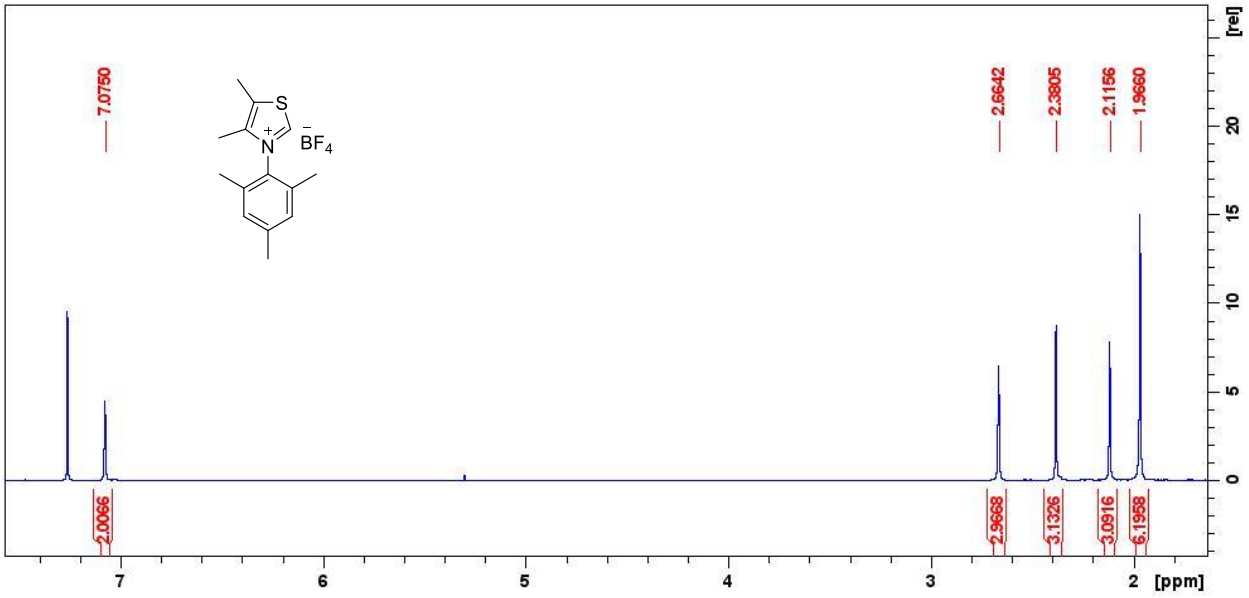



Synthesized according to Route a at 1.0 equiv. = 0.21 mmol scale, according to Route b at 1.0 equiv. = 0.21 mmol scale using *N*-mesityl-*N*-(3-oxobutan-2-yl)formamide as the starting material.

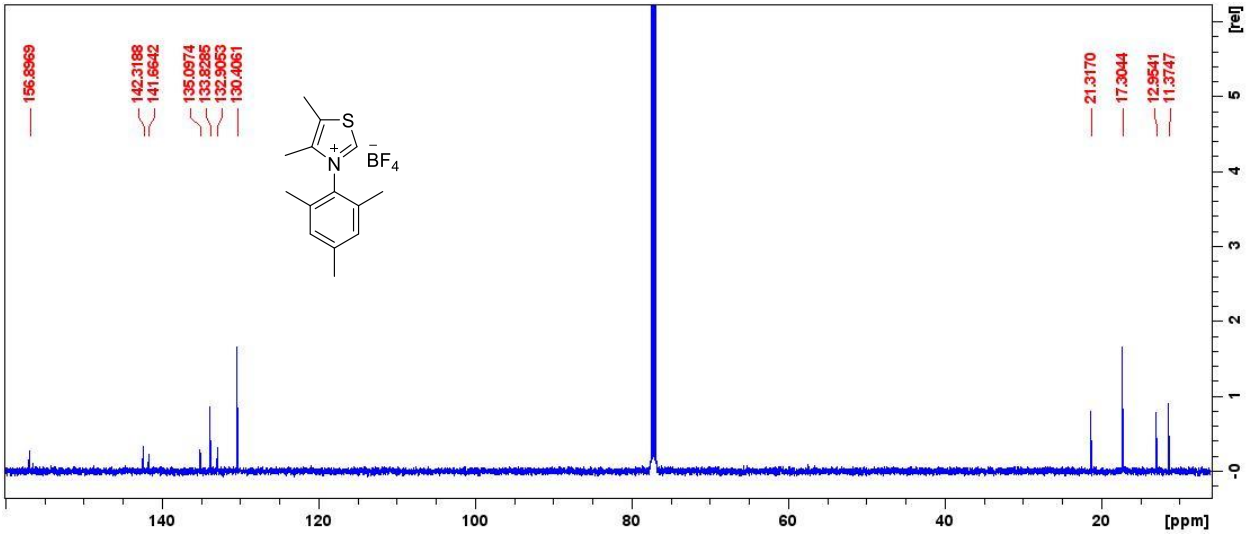
Compound **31** yield: 38 mg (55% with $P_2S_5$-$Py_2$ complex) and 50 mg (70 % with $P_4S_{10}$) as a white solid. All spectra consistent with the literature.

**$^1$H NMR** (600 MHz, $CDCl_3$) δ: 9.79 (s, 1H), 7.08 (s, 2H), 2.66 (s, 3H), 2.38 (s, 3H), 2.12 (s, 3H), 1.97 (s, 6H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 156.9, 142.3, 141.7, 135.1, 133.8, 132.9, 130.4, 21.3, 17.3, 13.0, 11.4; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3124, 2919, 1486, 1441, 1100, 1065, 533; **HRMS** ($EI^+$) m/z calculated for $C_{14}H_{18}NS^+$ $[M]^+$: 232.1154; found: 232.1148

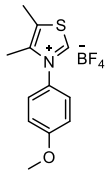
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 3-(4-methoxyphenyl)-4,5-dimethylthiazol-3-ium tetrafluoroborate (33)[5]**

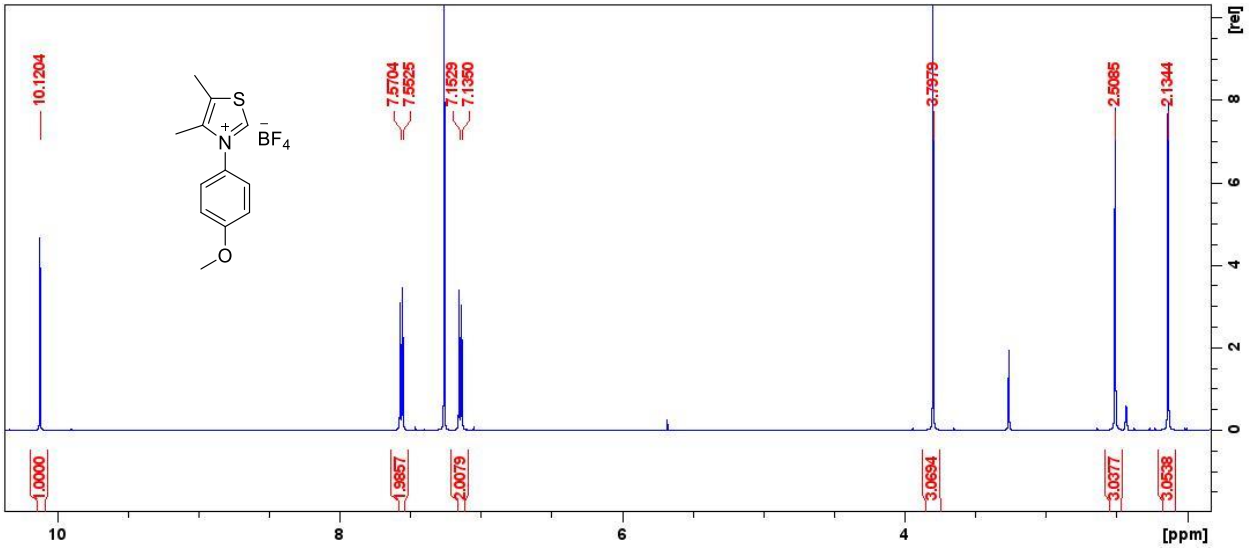



Synthesized according to Route a at 1.0 equiv. = 0.23 mmol scale, according to Route b at 1.0 equiv. = 0.23 mmol scale using N-(4-methoxyphenyl)-N-(3-oxobutan-2-yl)formamide as the starting material.

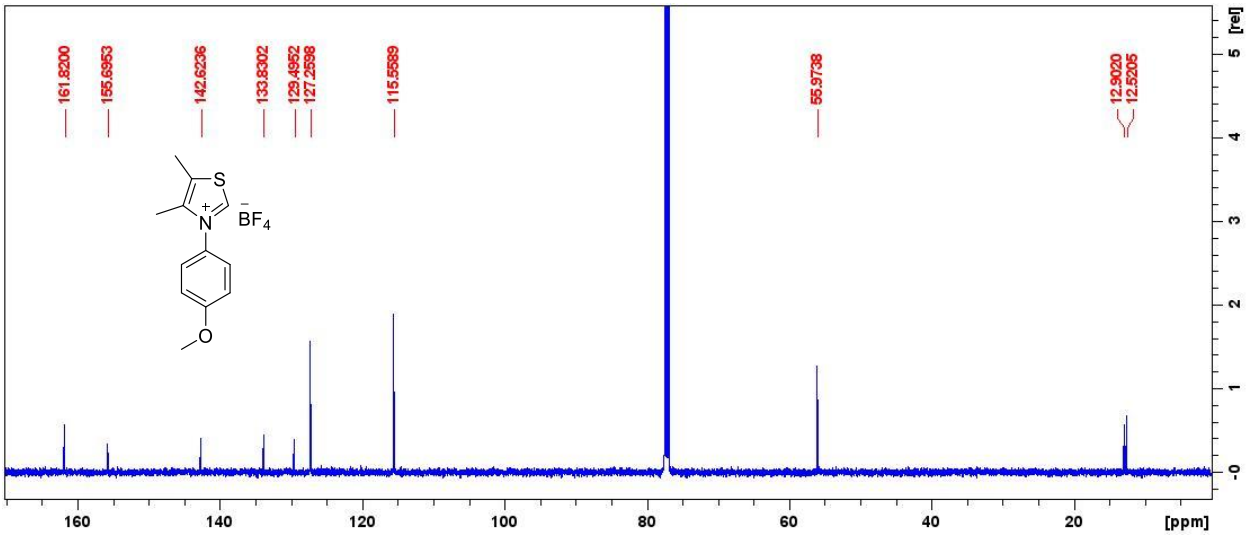
Compound **33** yield: 23 mg (33 % with $P_2S_5$-$Py_2$ complex) and 50 mg (72 % with $P_4S_{10}$) as a pale yellow solid. All spectra consistent with the literature.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ: 10.12 (s, 1H), 7.56 (d, *J* = 8.96 Hz, 2H), 7.14 (d, *J* = 8.96 Hz, 2H), 3.80 (s, 3H), 2.50 (s, 3H), 2.13 (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 161.8, 155.7, 142.6, 133.8, 129.5, 127.3, 115.6, 56.0, 12.9, 12.5.

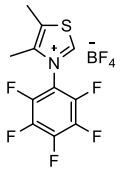
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 4,5-dimethyl-3-(perfluorophenyl)thiazol-3-ium tetrafluoroborate (35)[6]**

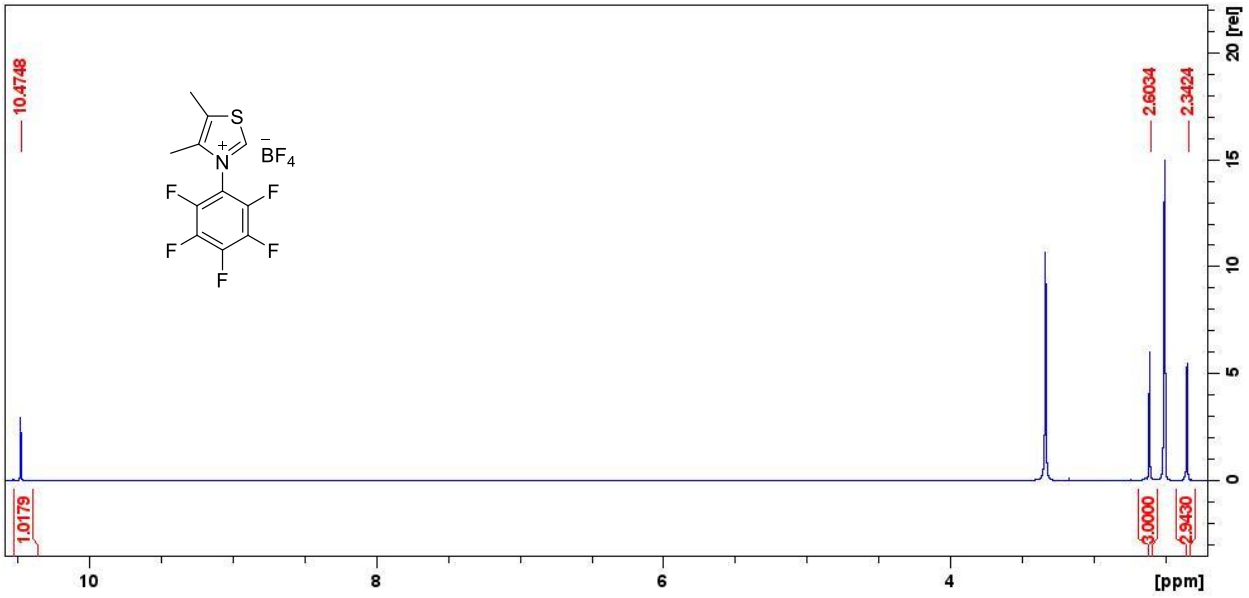



Synthesized according to Route a at 1.0 equiv. = 0.11 mmol scale using *N*-(3-oxobutan-2-yl)-*N*-(perfluorophenyl)formamide as the starting material.

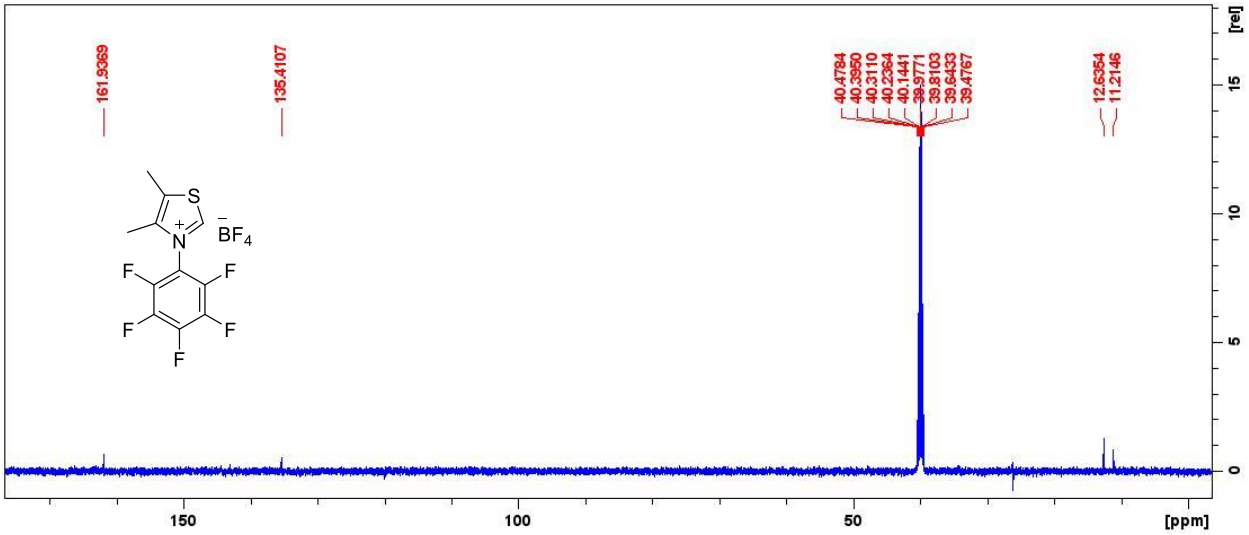
Compound **35** yield: 12 mg (30 % with $P_4S_{10}$) as a dark brown liquid. All spectra consistent with the literature.

**$^1$H NMR** (500 MHz, DMSO-$d_6$) δ: 10.47 (s, 1H), 2.60 (s, 3H), 2.34 (s, 3H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 161.9, 135.4, 12.6, 11.2; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3120, 2960. 1526, 1073, 1040, 730, 522; HRMS ($EI^+$) m/z calculated for $C_{11}H_7F_5NS^+$ $[M]^+$: 280.0214; found: 280.0221

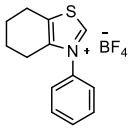
## $^{1}$H NMR spectrum




## $^{13}$C NMR spectrum



**Synthesis of 3-phenyl-4,5,6,7-tetrahydrobenzo[d]thiazol-3-ium tetrafluoroborate (37):**

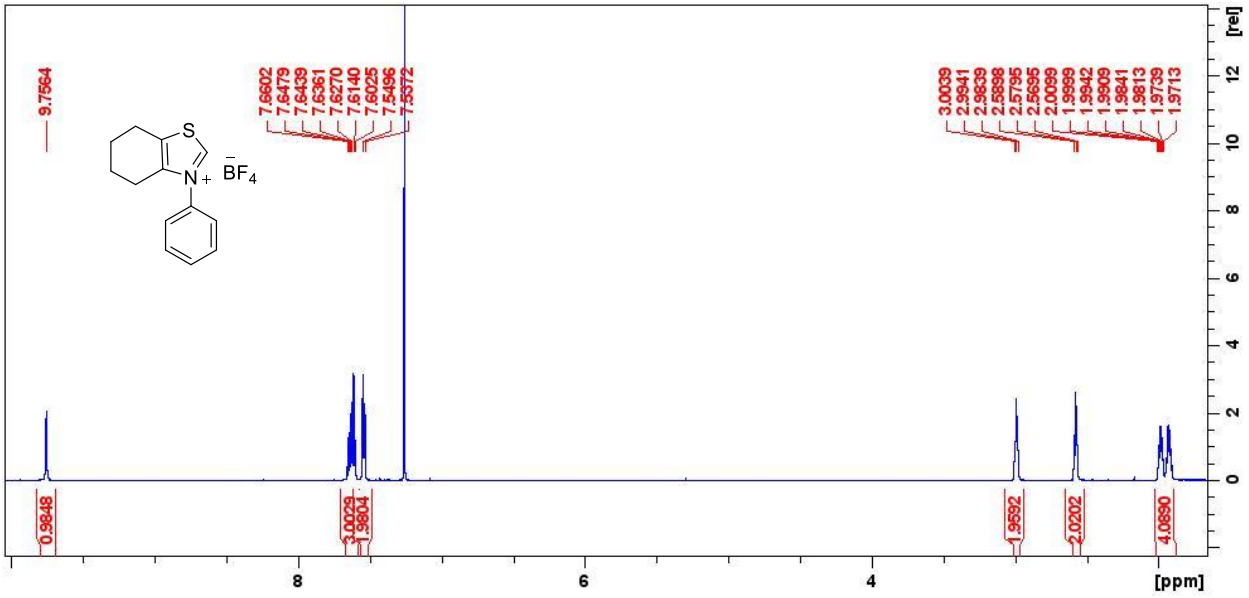


Synthesized according to Route a at 1.0 equiv. = 0.23 mmol scale, according to Route b at 1.0 equiv. = 0.23 mmol scale using *N*-(2-oxocyclohexyl)-*N*-phenylformamide as the starting material.

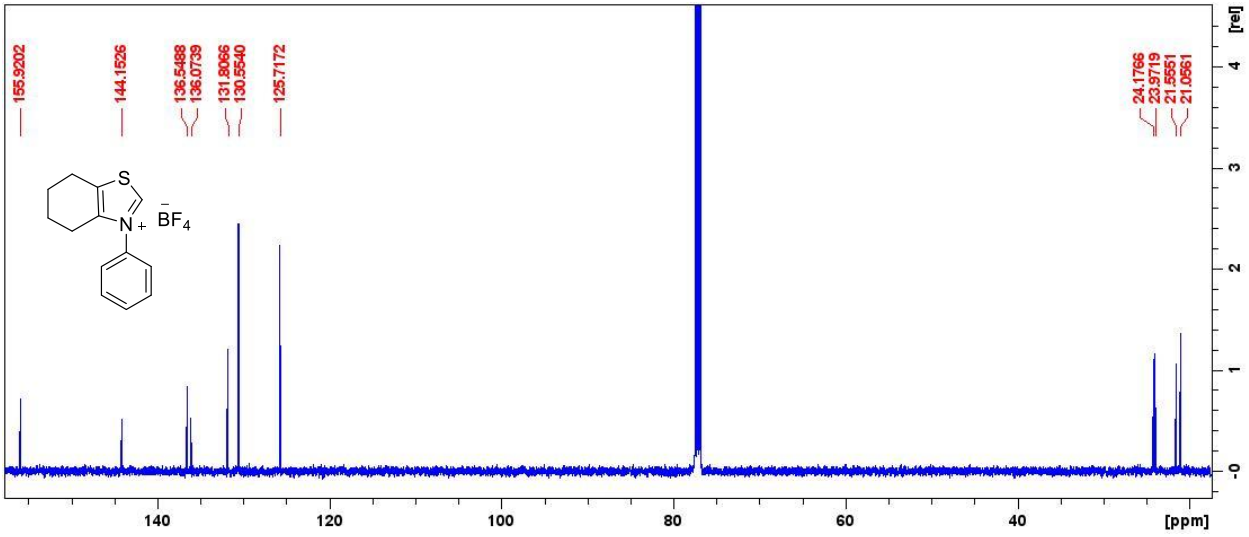
Compound **37** yield: 35 mg (49 % with $P_2S_5$-$Py_2$ complex) and 55 mg (79 % with $P_4S_{10}$) as a pale yellow solid. All spectra consistent with the literature.

**$^1$H NMR** (500 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.67-7.59 (m, 3H), 7.54 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 6.00 Hz, 2H), 2.58 (t, *J* = 6.09 Hz, 2H), 2.02-1.96 (m, 2H), 1.96-1.89 (m, 2H); **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ: 155.9, 144.2, 136.6, 136.1, 131.8, 130.6, 125.7, 24.2, 24.0, 21.6, 21.1; 522; **FTIR** (KBr thin film) υmax ($cm^{-1}$): 3421, 2940, 1492, 1031, 771, 696, 621, **HRMS** ($EI^+$) m/z calculated for $C_{13}H_{14}NS^+$ $[M]^+$: 216.0841; found: 216.0848

## $^{1}$H NMR spectrum

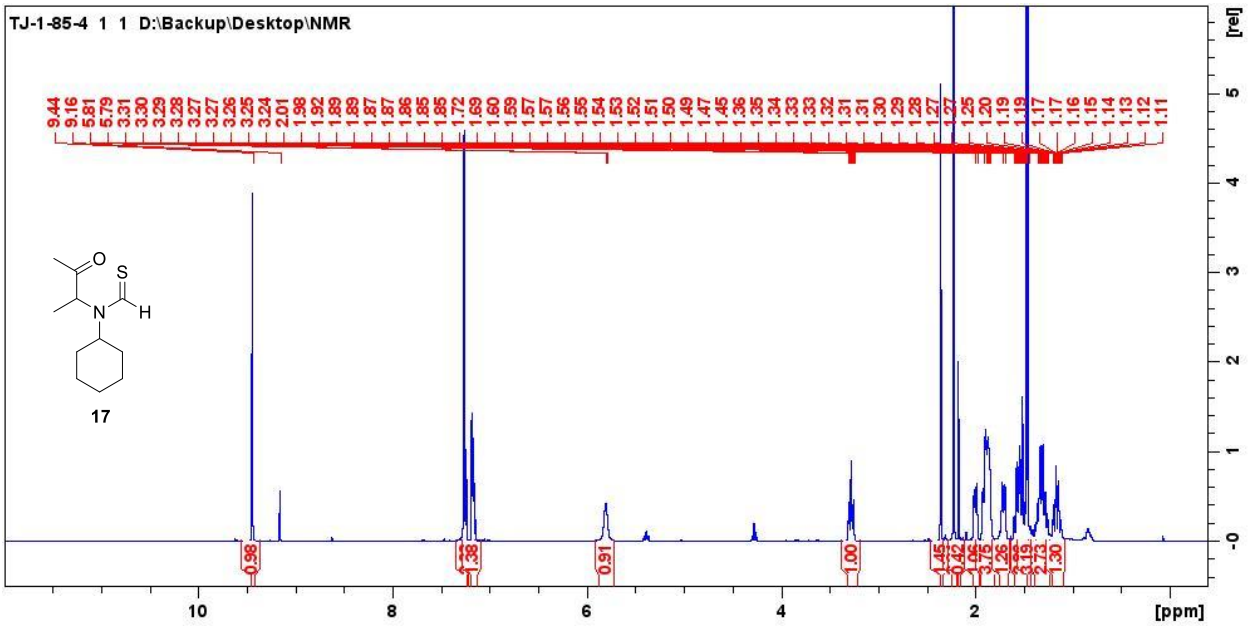



## $^{13}$C NMR spectrum

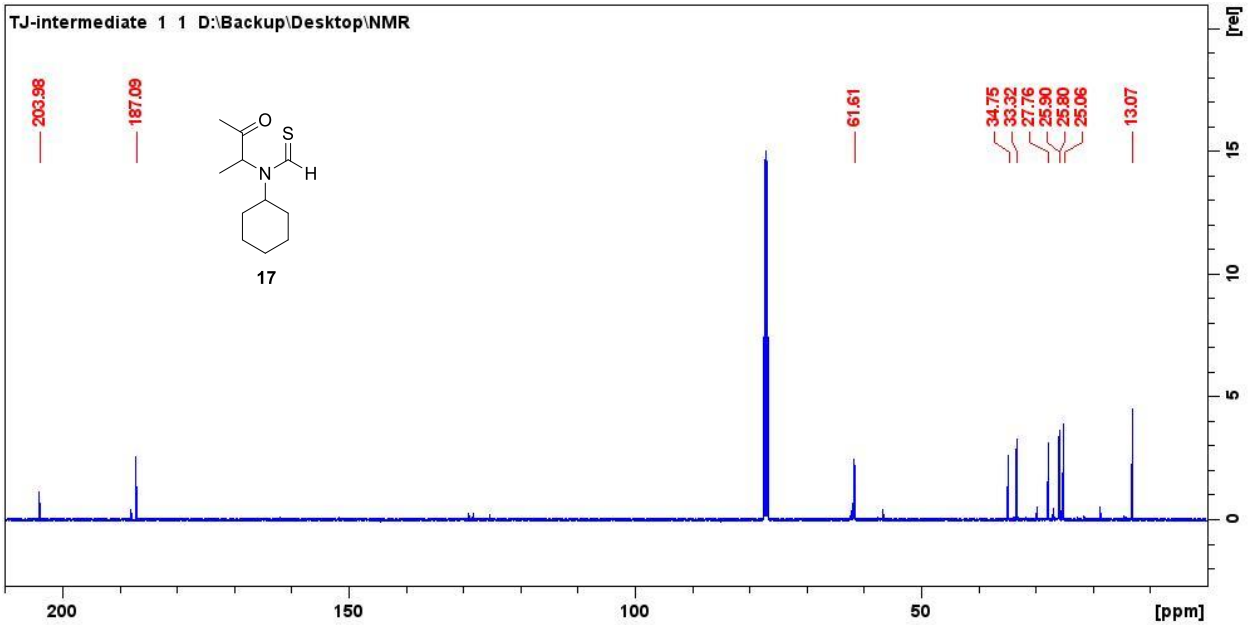


# 5.0 $^{1}$H NMR, $^{13}$C NMR, and HRMS Spectra for Intermediate 17

## $^{1}$H NMR




## $^{13}$C NMR

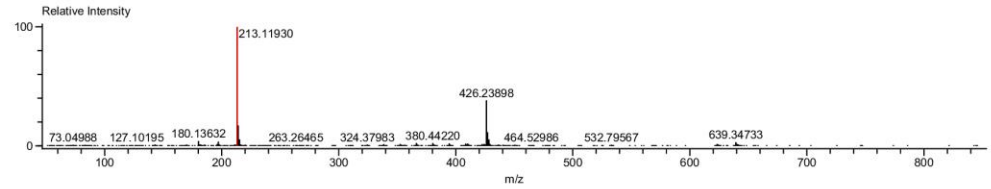


# High Resolution Mass Spectrum

Data:TJ-intermediate 2
Comment:
Description:
Ionization Mode:FD+(eiFi)
History:Centroid[Peak Detect[Centroid,10,Area]];Average(MS[1] 0.22..0.23)

Acquired:5/12/2021 9:07:54 AM
Operator:AccuTOF-PC
m/z Calibration File:PS cal Feb 2021
Created:5/12/2021 9:19:22 AM
Created by:AccuTOF-PC

Charge number:1
Tolerance:50.00[mDa]
Unsaturation Number:-10.0 .. 500.0 (Fraction:Both)
Element:$^{12}$C:1 .. 40, $^{1}$H:0 .. 500, $^{14}$N:0 .. 10, $^{16}$O:0 .. 5, $^{32}$S:0 .. 3




| Mass | Intensity | Calc. Mass | Mass Difference [mDa] | Mass Difference [ppm] | Possible Formula | Unsaturation Number |
|---|---|---|---|---|---|---|
| 213.11930 | 2256466.88 | 213.11942 | -0.13 | -0.59 | $^{12}C_5{}^{1}H_{25}{}^{16}O_4{}^{32}S_2$ | -6.5 |
| | | 213.11873 | 0.57 | 2.65 | $^{12}C_{11}{}^{1}H_{19}{}^{14}N_1{}^{16}O_1{}^{32}S_1$ | 3.0 |
| | | 213.11989 | -0.59 | -2.79 | $^{12}C_5{}^{1}H_{17}{}^{14}N_4{}^{16}O_5$ | -0.5 |
| | | 213.11855 | 0.75 | 3.51 | $^{12}C_3{}^{1}H_{15}{}^{14}N_7{}^{16}O_4$ | 0.0 |
| | | 213.11808 | 1.22 | 5.71 | $^{12}C_3{}^{1}H_{23}{}^{14}N_3{}^{16}O_3{}^{32}S_2$ | -6.0 |
| | | 213.12076 | -1.46 | -6.86 | $^{12}C_6{}^{1}H_{21}{}^{14}N_4{}^{32}S_2$ | -1.5 |
| | | 213.11739 | 1.91 | 8.95 | $^{12}C_9{}^{1}H_{17}{}^{14}N_4{}^{32}S_1$ | 3.5 |
| | | 213.12123 | -1.93 | -9.07 | $^{12}C_6{}^{1}H_{13}{}^{14}N_8{}^{16}O_1$ | 4.5 |
| | | 213.11721 | 2.09 | 9.81 | $^{12}C_1{}^{1}H_{13}{}^{14}N_{10}{}^{16}O_3$ | 0.5 |
| | | 213.11674 | 2.56 | 12.01 | $^{12}C_1{}^{1}H_{21}{}^{14}N_6{}^{16}O_2{}^{32}S_2$ | -5.5 |
| | | 213.12211 | -2.81 | -13.16 | $^{12}C_8{}^{1}H_{23}{}^{14}N_1{}^{16}O_1{}^{32}S_2$ | -2.0 |
| | | 213.11605 | 3.25 | 15.23 | $^{12}C_8{}^{1}H_{21}{}^{16}O_4{}^{32}S_1$ | -1.5 |
| | | 213.12257 | -3.27 | -15.37 | $^{12}C_8{}^{1}H_{15}{}^{14}N_6{}^{16}O_2$ | 4.0 |
| | | 213.11536 | 3.94 | 18.47 | $^{12}C_{14}{}^{1}H_{15}{}^{14}N_1{}^{16}O_1$ | 8.0 |
| | | 213.12326 | -3.97 | -18.61 | $^{12}C_2{}^{1}H_{21}{}^{14}N_4{}^{16}O_5{}^{32}S_1$ | -5.5 |
| | | 213.11471 | 4.59 | 21.53 | $^{12}C_6{}^{1}H_{19}{}^{14}N_3{}^{16}O_3{}^{32}S_1$ | -1.0 |
| | | 213.12392 | -4.62 | -21.67 | $^{12}C_{10}{}^{1}H_{17}{}^{14}N_2{}^{16}O_3$ | 3.5 |
| | | 213.12413 | -4.83 | -22.68 | $^{12}C_3{}^{1}H_{25}{}^{14}N_4{}^{32}S_3$ | -6.5 |
| | | 213.11402 | 5.28 | 24.77 | $^{12}C_{12}{}^{1}H_{13}{}^{14}N_4$ | 8.5 |
| | | 213.12460 | -5.30 | -24.88 | $^{12}C_3{}^{1}H_{17}{}^{14}N_8{}^{16}O_1{}^{32}S_1$ | -0.5 |
| | | 213.11337 | 5.93 | 27.83 | $^{12}C_4{}^{1}H_{17}{}^{14}N_6{}^{16}O_2{}^{32}S_1$ | -0.5 |

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