Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

An Efficient Method for the Synthesis of 2-Pyridones *via* C-H Bond Functionalization

Shuguang Zhou,[a] Duan-Yang Liu,[b] Suo Wang,[a] Jie-Sheng Tian,*[a,b] and Teck-Peng Loh*[a,b,c]

[a]Institute of Advanced Synthesis (IAS), Northwestern Polytechnical University (NPU), Xi'an 710072, China. Yangtze River Delta Research Institute of NPU, Taicang Jiangsu, 215400, China.

[b]Institute of Advanced Synthesis (IAS), Nanjing Tech University (NanjingTech), Nanjing 211816, P. R. China.

[c]Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371

E-mail: ias_jstian@njtech.edu.cn, teckpeng@ntu.edu.sg

Table of Contents

1. General information

Materials:

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. HPLC grade CH_3OH was used directly. Toluene and THF were freshly distilled over Na/benzophenone before use. All chemicals were obtained from local suppliers or synthesized. The preparation of enaminones according to the previous procedure [1-4].

Methods:

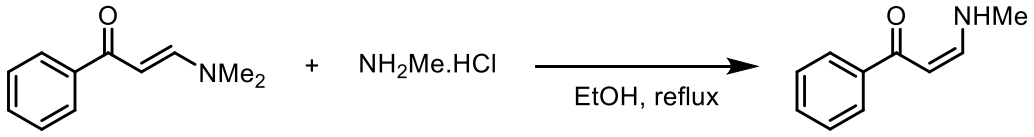
All $[Cp^*RhCl_2]_2$-catalyzed reactions were carried out with precautions to extrude moisture or oxygen. All reactions beyond room temperature (r.t.) were run in oil baths with the temperature calibrated with a thermometer. Prior to an experiment, the oil bath could equilibrate to the desired temperature for 15 min. ^1H, ^{13}C and ^{19}F-NMR spectra were recorded on a Bruker 400 (400 MHz for ^1H, 100 MHz for ^{13}C) or a JEOL ECX-400 (400 MHz for ^1H, 100 MHz for ^{13}C) or Bruker 500 (500 MHz for ^1H, 125 MHz for ^{13}C and 471 MHz for ^{19}F) spectrometer using residue solvent as internal reference. Silica gel (200~300 mesh) was used for flash column chromatography. High resolution mass analyses (ESI+) were performed on Waters mass spectrometer and Agilent 6224. Specific rotations were recorded on a Anton paer MCP 150. The following notations were used: br-broad, s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, dd – doublet of doublet, dt – doublet of triplet, td – triplet of doublet, ddd – doublet of doublet of doublet.

2. Synthesis and characterization of enaminones

2.1 General procedure for preparation of enaminone substrates:

Substrate **1a**-**1ab** synthesis:

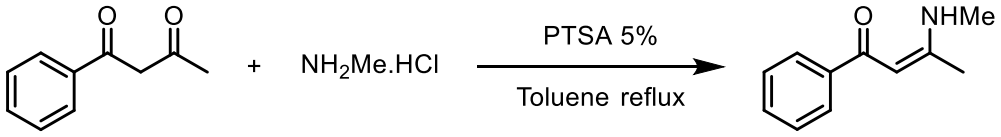
Example **1a**:



1a

A solution of (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (5 mmol) and methylamine hydrochloride (10 mmol) in ethanol (20 ml) was refluxed and it took 26-68 h to give the product **1a**.

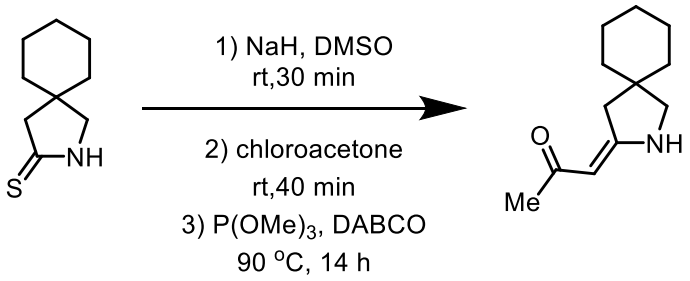
Substrate **1ac** synthesis[5]:



1ac

Enaminones **1ac** were prepared by heating of equimolar amounts of the corresponding β-diketone and $MeNH_2$ in the presence of cat. PTSA. The H_2O formed during the reaction was removed by azeotropic distillation until only clear toluene distilled. The toluene distilled off was continuously replaced by fresh toluene. After completion of the reaction, the solvent was evaporated in vacuo and the residue was purified by vacuum distillation or crystallisation.

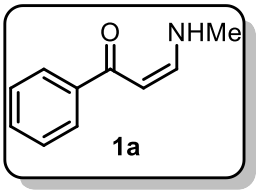
Substrate **1ad-1af** synthesis[6]:



General Procedure for substrate **1ad-1af** synthesis. To a solution of thioamide (1 mmol, 1.00 equiv) in DMSO (5 mL) was added NaH (95%) (1.1 mmol, 1.10 equiv), and the mixture was stirred at room temperature for 30 min under argon. The reaction mixture was treated with alkyl halide (1.05 mmol, 1.05 equiv), and after 30 min of stirring at rt, trimethyl phosphite (3 mmol, 3 equiv) and DABCO (3 mmol, 3 equiv) were added and the solution was allowed to stir at 90°C (internal temperature) until all alkylated species were consumed according to TLC (2-14 h). (In cases when chloroacetone was used as electrophile, 2 equiv of NaH and 2.5 equiv of chloroacetone gave the best results. Aryl halides were usually added in 1.1 equiv amounts, but in some cases 1.00 or 1.10 equiv was used. The actual amounts are specified below for each experiment.) After this time, the reaction mixture was poured into distilled water (50 mL) and extracted with CH_2Cl_2 (3×40 mL). The combined organic fractions were washed with water (5×80 mL), dried over Na_2SO_4, and evaporated under reduced pressure. Excess trimethyl phosphite and thioadducts were removed by coevaporation with ethanol. Crude products were usually solid, but in some cases the oily or semisolid crude material could be precipitated by addition of ethanol. Crude products were recrystallized from ethanol and oily products where purified by flash chromatography (EtOAc/Hep 1:4).

2.2 General procedure for characterization of enaminone substrates:

(*Z*)-3-(methylamino)-1-phenylprop-2-en-1-one (1a):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

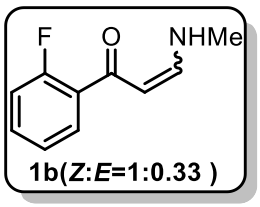
The title compound was obtained as a brown solid. Yield = 81% (652 mg) , mp: 138.2-139.1 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.90 – 7.80 (m, 2H), 7.46 – 7.36 (m, 3H), 6.92 (dd, *J* = 12.8, 7.4 Hz, 1H), 5.70 (d, *J* = 7.4 Hz, 1H), 3.07 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 155.7, 140.1, 131.1, 128.5, 127.3, 90.5, 35.6.

HRMS (ESI, m/z): Calcd. for $C_{10}H_{12}NO$: $[M+H]^+$, 162.0919. Found: *m/z* 162.0917.

1-(2-fluorophenyl)-3-(methylamino)prop-2-en-1-one (1b):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown solid in an inseparable state (1:0.33 by **^{1}H NMR**). Yield = 54% (484 mg), mp: 88.6-90.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.77-7.81 (m, 1H × 1 + 1H × 0.33), 7.35-7.38

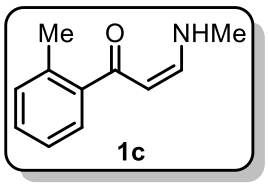
(m, 1H × 1 + 1H × 0.33), 7.16 – 7.20 (m, 1H × 1 + 1H × 0.33), 7.04-7.09 (m, 1H × 1 + 1H × 0.33), 6.89-6.94 (m, 1H × 1 + 1H × 0.33), 5.65-5.68 (m, 1H × 1 + 1H × 0.33),3.08 (d, *J* = 2.6 Hz, 3H × 1), 2.83 (s, 3H × 0.33).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 160.6 (d, *J* = 251.9 Hz) , 155.9, 132.06 (d, *J* = 8.8 Hz), 130.4 (d, *J* = 3.4 Hz), 128.6 (d, *J* = 13.2 Hz), 124.3 (d, *J* = 3.6 Hz), 116.5(d, *J* = 24.0 Hz) , 116.2 , 94.8 (dd, *J* = 9.5, 1.4 Hz), 35.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.50.

HRMS (ESI, m/z): Calcd. for $C_{10}H_{11}NOF$: $[M+H]^+$, 180.0825. Found: *m/z* 180.0826.

(*Z*)-3-(methylamino)-1-(o-tolyl)prop-2-en-1-one (1c):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

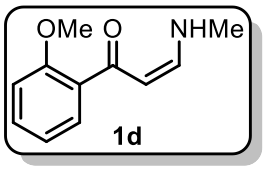
The title compound was obtained as a brown solid, Yield = 62% (543 mg), mp: 85.2-86.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.43 – 7.37 (m, 1H), 7.27 – 7.22 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.85 (dd, *J* = 12.9, 7.3 Hz, 1H), 5.31 (d, *J* = 7.3 Hz, 1H), 3.07 (d, *J* = 5.1 Hz, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 155.2, 141.8, 131.1, 129.2, 127.6, 125.6, 94.5, 35.6, 20.5.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO$: $[M+H]^+$, 176.1075. Found: *m/z* 176.1073.

(*Z*)-1-(2-methoxyphenyl)-3-(methylamino)prop-2-en-1-one (1d):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (3:1)

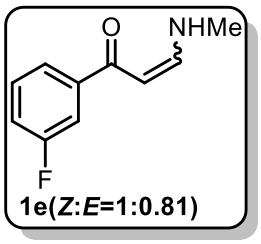
The title compound was obtained as a brown solid, Yield = 65% (621 mg), mp: 72.6-73.7 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.06 – 6.73 (m, 3H), 5.63 (d, *J* = 7.3 Hz, 1H), 3.84 (s, 3H), 3.03 (d, *J* = 5.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 157.2, 154.9, 131.2, 130.8, 129.8, 120.6, 111.5, 95.3, 55.7, 35.5.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO_2$: $[M+H]^+$, 192.1025. Found: *m/z* 192.1025.

1-(3-fluorophenyl)-3-(methylamino)prop-2-en-1-one (1e):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown solidin an inseparable state (1:0.81 by **^{1}H NMR**), Yield = 58% (519 mg), mp: 87.2-87.8 ºC.

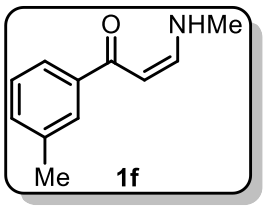
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, , 1H), 7.88-7.93 (m, 1H × 0.81) 7.54-7.67 (m, 2H × 1 + 2H × 0.81), 7.33-7.39 (m, 1H × 1 + 1H × 0.81), 7.10 – 7.17 (m, 1H × 1 + 1H × 0.81), 6.92-6.97 (m, 1H × 1), 5.79-5.82 (m, 1H × 0.81), 5.63-5.65 (m, 1H × 1),3.07 (d, *J* = 2.6 Hz, 3H × 1), 2.87 (s, 3H × 0.81).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3(*Z*), 188.0(*E*), 163.0 (d, *J* = 247.0 Hz)(*Z*), 162.9 (d, *J* = 247.2 Hz), 156.2(*Z*), 152.4(*E*), 142.8 (d, *J* = 5.9 Hz)(*E*), 142.3 (d, *J* = 6.2 Hz)(*Z*), 129.9 (d, *J* = 7.7, 3.5 Hz)(*ZE*), 123.3(*E*), 122.7 (d, *J* = 2.8 Hz)(*Z*), 118.0(d, *J* = 23.3 Hz)(*E*), 117.7(d, *J* = 22.1 Hz)(*Z*), 114.5(d, *J* = 21.6 Hz)(*E*), 114.0(d, *J* = 22.2 Hz)(*Z*), 92.2(*E*), 90.2(*Z*), 35.6(*Z*), 30.4(*E*).

^{19}F NMR (471 MHz, $CDCl_3$) δ -113.14.

HRMS (ESI, m/z): Calcd. for $C_{10}H_{11}NOF$: $[M+H]^+$, 180.0825. Found: *m/z* 180.0830.

(*Z*)-3-(methylamino)-1-(m-tolyl)prop-2-en-1-one (1f):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography:PE/EA (5:1)

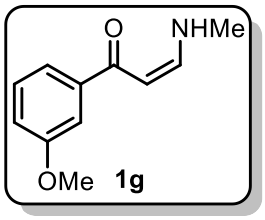
The title compound was obtained as a brown solid, Yield = 72% (630 mg), mp: 50.5-51.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.71 – 7.63 (m, 2H), 7.32 – 7.22 (m, 2H), 6.90 (dd, *J* = 12.8, 7.4 Hz, 1H), 5.69 (d, *J* = 7.4 Hz, 1H), 3.06 (d, *J* = 5.1 Hz, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 155.6, 140.0, 138.0, 131.8, 128.3, 127.8, 124.3, 90.5, 35.6, 21.6.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO$: $[M+H]^+$, 176.1075. Found: *m/z* 176.1077.

(*Z*)-1-(3-methoxyphenyl)-3-(methylamino)prop-2-en-1-one (1g):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (3:1)

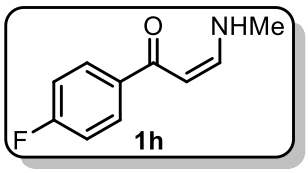
The title compound was obtained as a brown solid, Yield = 68% (650 mg), mp: 54.5-55.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.20 (s, 1H), 7.71 – 7.63 (m, 2H), 7.32 – 7.22 (m, 2H), 6.90 (dd, *J* = 12.8, 7.4 Hz, 1H), 5.69 (d, *J* = 7.4 Hz, 1H), 3.06 (d, *J* = 5.1 Hz, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.8, 159.9, 155.8, 141.5, 129.4, 119.7, 117.4, 111.9, 90.6, 55.5, 35.6.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO_2$: $[M+H]^+$, 192.1025. Found: *m/z* 192.1019.

(*Z*)-1-(4-fluorophenyl)-3-(methylamino)prop-2-en-1-one (1h):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown solid, Yield = 59% (528 mg), mp: 114.2-115.9 ºC.

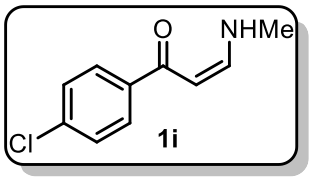
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.89 – 7.83 (m, 2H), 7.08 – 7.03 (m, 2H), 6.91 (ddd, *J* = 12.9, 7.3, 0.8 Hz, 1H), 5.63 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.06 (dd, *J* = 5.1, 1.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.6, 164.6(d, *J* = 251.3 Hz), 155.8, 136.2 (d, *J* = 3.1 Hz), 129.4 (d, *J* = 8.9 Hz), 115.3(d, *J* = 21.7 Hz), 90.0, 35.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -109.75.

HRMS (ESI, m/z): Calcd. for $C_{10}H_{11}NOF$: $[M+H]^+$, 180.0825. Found: *m/z* 180.0822.

(*Z*)-1-(4-chlorophenyl)-3-(methylamino)prop-2-en-1-one (1i):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

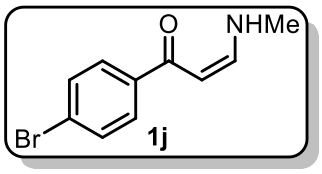
The title compound was obtained as a brown solid, Yield = 75% (732 mg),mp: 109.7-111.2 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 7.81 – 7.73 (m, 2H), 7.37 – 7.31 (m, 2H), 6.90 (dd, *J* = 12.9, 7.3 Hz, 1H), 5.62 (d, *J* = 7.3 Hz, 1H), 3.05 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 156.0, 138.3, 137.0, 128.6, 90.1, 35.7.

HRMS (ESI, m/z): Calcd. for $C_{10}H_{11}NOCl$: $[M+H]^+$, 196.0529. Found: *m/z* 196.0529.

(*Z*)-1-(4-bromophenyl)-3-(methylamino)prop-2-en-1-one (1j):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (3:1)

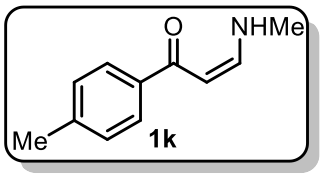
The title compound was obtained as a brown solid, Yield = 80% (956 mg), mp: 117.5-118.2 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 7.73 – 7.66 (m, 2H), 7.53 – 7.48 (m, 2H), 6.90 (dd, *J* = 12.9, 7.3 Hz, 1H), 5.61 (d, *J* = 7.3 Hz, 1H), 3.05 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 156.0, 138.7, 131.5, 128.8, 125.6, 90.0, 35.7.

HRMS (ESI, m/z): Calcd. for $C_{10}H_{11}NOBr$: $[M+H]^+$, 240.0024. Found: *m/z* 240.0024.

(*Z*)-3-(methylamino)-1-(p-tolyl)prop-2-en-1-one (1k):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

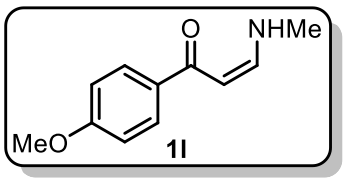
The title compound was obtained as a brown solid, Yield = 77% (674 mg), mp: 121.8-122.0 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 7.79 – 7.74 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.89 (dd, *J* = 12.8, 7.4 Hz, 1H), 5.68 (d, *J* = 7.4 Hz, 1H), 3.06 (d, *J* = 5.1 Hz, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 155.4, 141.3, 137.2, 129.1, 127.2, 90.2, 35.5, 21.6.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO$: $[M+H]^+$, 176.1075. Found: *m/z* 176.1077.

(*Z*)-1-(4-methoxyphenyl)-3-(methylamino)prop-2-en-1-one (1l):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

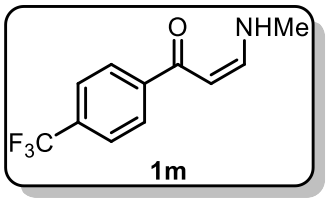
The title compound was obtained as a brown solid, Yield = 71% (679 mg), mp: 88.1-88.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 2H), 6.92 – 6.83 (m, 3H), 5.65 (d, *J* = 7.5 Hz, 1H), 3.83 (s, 3H), 3.04 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 162.0, 155.2, 132.7, 129.1, 113.6, 89.9, 55.5, 35.5.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO_2$: $[M+H]^+$, 192.1025. Found: *m/z* 192.1022.

(*Z*)-3-(methylamino)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one



1m

The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (3:1)

The title compound was obtained as a brown solid,Yield=53% (607mg), mp: 103.7-104.9 °C.

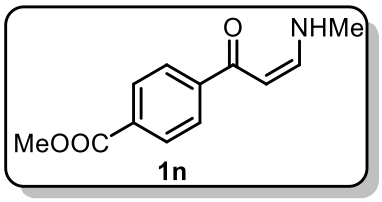
^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 7.9 Hz, 2H), 7.04 – 6.91 (m, 1H), 5.71 – 5.61 (m, 1H), 3.09 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.4, 156.4, 143.2, 132.4 (q, *J* = 32.3 Hz), 127.5, 126.4 (q, *J* = 273 Hz), 125.5 (q, *J* = 3.7 Hz), 90.5, 35.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.75.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{11}NOF_3$: $[M+H]^+$, 230.0787. Found: *m/z* 230.0795.

Methyl (*Z*)-4-(3-(methylamino)acryloyl)benzoate



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (3:1)

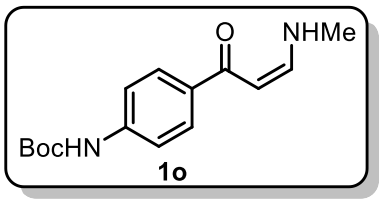
The title compound was obtained as a brown solid, Yield =43% (471mg), mp: 96.6-98.4 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.05 (dd, J = 6.7, 1.3 Hz, 2H), 7.92 – 7.84 (m, 2H), 7.02 – 6.88 (m, 1H), 5.74 – 5.64 (m, 1H), 3.91 (s, 3H), 3.09 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.7, 166.9, 156.3, 143.9, 132.0, 129.7, 127.1, 90.70, 52.4, 35.7.

HRMS (ESI, m/z): Calcd. for $C_{12}H_{14}NO_3$: $[M+H]^+$, 220.0968. Found: *m/z* 220.0971.

Tert-butyl (*Z*)-(4-(3-(methylamino)acryloyl)phenyl)carbamate



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (3:1)

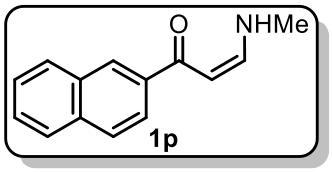
The title compound was obtained as a brown solid, Yield =35% (483mg), mp: 79.4-80.6 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.12 (s, 1H), 7.86 – 7.78 (m, 2H), 7.39 (d, J = 8.6 Hz, 2H), 6.88 (dd, J = 12.7, 7.4 Hz, 1H), 6.70 (s, 1H), 5.66 (d, J = 7.4 Hz, 1H), 3.05 (d, J = 5.0 Hz, 3H), 1.52 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.2, 155.4, 152.7, 141.1, 134.6, 128.5, 117.8, 90.2, 35.6, 29.9, 28.5.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{121}N_2O_3$: $[M+H]^+$, 277.1547. Found: *m/z* 277.1548.

(*Z*)-3-(methylamino)-1-(naphthalen-2-yl)prop-2-en-1-one (1p):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

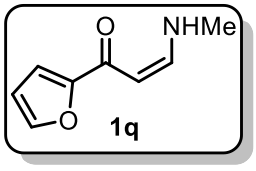
The title compound was obtained as a brown solid, Yield = 55% (581 mg), mp: 101.0-101.8 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.38 (s, 1H), 7.99 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.93 (dd, *J* = 6.6, 2.5 Hz, 1H), 7.86 (dd, *J* = 8.7, 6.6 Hz, 2H), 7.57 – 7.45 (m, 2H), 6.95 (dd, *J* = 12.8, 7.4 Hz, 1H), 5.85 (d, *J* = 7.4 Hz, 1H), 3.09 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 155.7, 137.3, 134.8, 133.0, 129.4, 128.1, 127.8, 127.6, 127.4, 126.4, 124.3, 90.6, 35.6.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{14}NO$: $[M+H]^+$, 212.1075. Found: *m/z* 212.1078.

(*Z*)-1-(furan-2-yl)-3-(methylamino)prop-2-en-1-one (1q):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown solid,Yield = 40% (302 mg), mp: 52.3-53.7 ^oC.

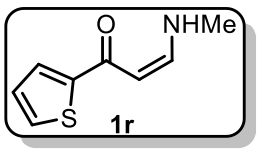
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.47 (dd, *J* = 1.6, 0.7 Hz, 1H), 6.98 (dd, *J* = 3.4,

0.7 Hz, 1H), 6.88 (dd, *J* = 12.9, 7.4 Hz, 1H), 6.46 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.61 (d, *J* = 7.4 Hz, 1H), 3.06 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 155.7, 154.3, 144.4, 112.9, 112.0, 90.1, 35.7.

HRMS (ESI, m/z): Calcd. for $C_8H_{10}NO_2$: $[M+H]^+$, 152.0712. Found: *m/z* 152.0710.

(*Z*)-3-(methylamino)-1-(thiophen-2-yl)prop-2-en-1-one (1r):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

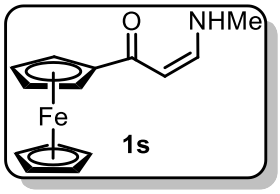
The title compound was obtained as a brown solid,Yield = 47% (393 mg), mp: 84.7-85.6 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.52 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.44 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.04 (dd, *J* = 4.9, 3.7 Hz, 1H), 6.84 (dd, *J* = 12.9, 7.3 Hz, 1H), 5.56 (d, *J* = 7.3 Hz, 1H), 3.03 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.0, 155.4, 146.9, 130.4, 128.0, 127.9, 90.2, 35.7.

HRMS (ESI, m/z): Calcd. for $C_8H_{10}NOS$: $[M+H]^+$, 168.0483. Found: *m/z* 168.0482.

(*Z*)-1-ferrocene-3-(phenylamino)prop-2-en-1-one (1s):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown solid,Yield = 38% (507 mg), mp: 136.9-137.5

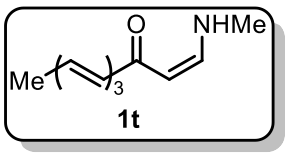
^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 6.71 (dd, *J* = 12.7, 7.5 Hz, 1H), 5.29 (d, *J* = 7.4 Hz, 1H), 4.72 (t, *J* = 1.9 Hz, 2H), 4.38 – 4.29 (m, 2H), 4.15 (s, 5H), 3.02 (d, *J* = 5.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 153.4, 91.7, 82.3, 71.0, 70.0, 68.6, 35.5.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{16}NOFe$: $[M+H]^+$, 268.0628. Found: *m/z* 268.0624.

(*Z*)-1-(methylamino)dec-1-en-3-one (1t):



1t

The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

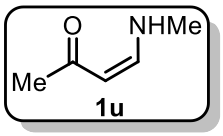
The title compound was obtained as a brown solid, Yield = 49% (434 mg), mp: 114.7-115.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.13 (s, 1H), 7.11 (dd, *J* = 15.1, 11.2 Hz, 1H), 6.76 (dd, *J* = 12.6, 7.2 Hz, 1H), 6.47 (dd, *J* = 14.8, 10.8 Hz, 1H), 6.28 – 6.05 (m, 3H), 5.86 (dq, *J* = 13.9, 6.8 Hz, 1H), 5.09 (d, *J* = 7.2 Hz, 1H), 3.02 (d, *J* = 5.0 Hz, 3H), 1.80 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 155.1, 139.3, 138.5, 133.5, 131.9, 131.0, 129.2, 94.9, 35.6, 18.8.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{16}NO$: $[M+H]^+$, 178.1232. Found: *m/z* 178.1233.

(*Z*)-4-(methylamino)but-3-en-2-one (1u):



1u

The synthetic method was followed the synthetic procedure of compound **1**a.

Flash chromatography: PE/EA (5:1)

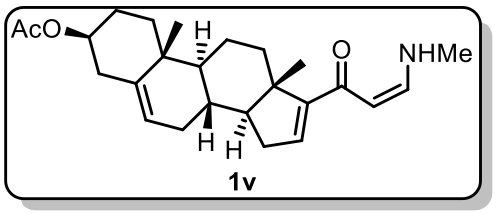
The title compound was obtained as a brown liquid, Yield = 51% (253 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 6.60 (dd, *J* = 12.8, 7.3 Hz, 1H), 4.96 (d, *J* = 7.3 Hz, 1H), 2.96 (d, *J* = 5.0 Hz, 3H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 154.0, 93.9, 35.4, 29.1.

HRMS (ESI, m/z): Calcd. for $C_5H_{10}NO$: $[M+H]^+$, 100.0762. Found: *m/z* 100.0762.

(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-((Z)-3-(methylamino) acryloyl)-2,3,4,7,8,9, 10,11,12,13,14,15-dodeca hydro-1H-cyclopenta [a] phenanthren-3-yl acetate (1v):



1v

The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown solid, Yield = 46% (914 mg), mp: 151.5-152.9 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 6.68 (dd, *J* = 12.7, 7.5 Hz, 1H), 6.39 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.38 (d, *J* = 5.0 Hz, 1H), 5.32 (d, *J* = 7.5 Hz, 1H), 4.62 – 4.57 (m, 1H), 2.98 (d, *J* = 5.1 Hz, 3H), 2.32 (d, *J* = 7.2 Hz, 3H), 2.05 – 2.00 (m, 6H), 1.88 (d, *J* = 3.3 Hz, 2H), 1.66 (d, *J* = 6.6 Hz, 2H), 1.63 – 1.56 (m, 5H), 1.43 (s, 1H), 1.13 (d, *J* = 4.1 Hz, 1H), 1.06 (s,

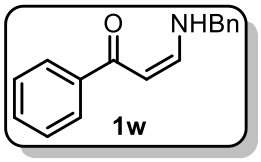
3H), 1.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 170.8, 156.4, 153.8, 140.4, 136.7, 122.5, 92.0, 74.2, 56.7, 50.7, 46.6, 38.4, 37.1, 37.0, 35.4, 35.2, 32.2, 31.8, 30.5, 28.0, 21.7, 21.0, 19.5, 16.5.

HRMS (ESI, m/z): Calcd. for $C_{25}H_{36}NO_3$: $[M+H]^+$, 398.2695. Found: *m/z* 398.2702.

Specific rotation: [α] = -33.600

(*Z*)-3-(benzylamino)-1-phenylprop-2-en-1-one (1w):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

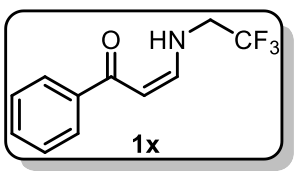
The title compound was obtained as a brown solid, Yield = 66% (783 mg), mp: 74.2-74.5 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.92 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.39 – 7.34 (m, 2H), 7.34 – 7.27 (m, 3H), 7.01 (dd, *J* = 12.7, 7.5 Hz, 1H), 5.79 (d, *J* = 7.5 Hz, 1H), 4.44 (d, *J* = 6.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 154.3, 139.7, 137.9, 131.2, 129.0, 128.4, 127.9, 127.4, 127.3, 90.9, 52.9.

HRMS (ESI, m/z): Calcd. for $C_{16}H_{16}NO$: $[M+H]^+$, 238.1232. Found: *m/z* 238.1230.

(*Z*)-1-phenyl-3-((2,2,2-trifluoroethyl)amino)prop-2-en-1-one (1x):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (3:1)

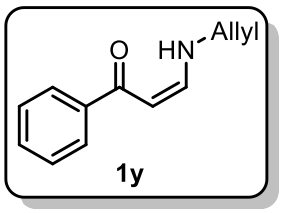
The title compound was obtained as a brown solid, Yield = 54% (619 mg), mp: 100.1-101.1 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (s, 1H), 7.94 – 7.84 (m, 2H), 7.54 – 7.34 (m, 3H), 6.85 (dd, *J* = 12.0, 7.8 Hz, 1H), 5.88 (d, *J* = 7.8 Hz, 1H), 3.80 – 3.61 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 153.5, 139.2, 131.8, 128.6, 127.6, 126.7(q, *J* = 280 Hz), 93.5, 50.2 (q, *J* = 34.34 Hz).

HRMS (ESI, m/z): Calcd. for $C_{11}H_{11}NOF_3$: $[M+H]^+$, 230.0793. Found: *m/z* 230.0798.

(*Z*)-3-(allylamino)-1-phenylprop-2-en-1-one (1y):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

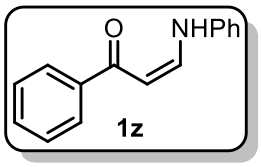
The title compound was obtained as a brown liquid, Yield =62% (580 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.39 (dd, J = 7.1, 5.8 Hz, 3H), 6.94 – 6.76 (m, 1H), 5.90 – 5.77 (m, 1H), 5.75 – 5.61 (m, 1H), 5.28 – 5.19 (m, 1H), 5.19 – 5.11 (m, 1H), 3.80 (d, J = 1.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 154.2, 139.7, 134.2, 130.9, 128.3, 127.1, 117.0, 90.7, 51.0.

HRMS (ESI, m/z): Calcd. for $C_{12}H_{14}NO$: $[M+H]^+$, 188.1070. Found: *m/z* 188.1073.

(*Z*)-1-phenyl-3-(phenylamino)prop-2-en-1-one (1z):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

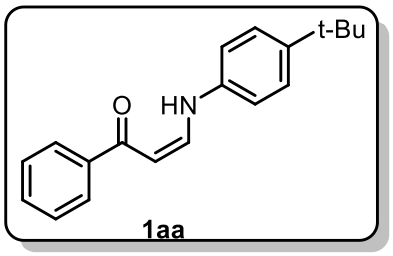
The title compound was obtained as a brown solid, Yield = 94% (1.05 g), mp: 139.8-140.3 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.16 (d, *J* = 11.3 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.60 – 7.42 (m, 4H), 7.35 (dd, *J* = 8.4, 7.5 Hz, 2H), 7.16 – 7.04 (m, 3H), 6.04 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 145.2, 140.4, 139.4, 131.8, 130.0, 128.7, 127.5, 123.9, 116.6, 93.9.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{14}NO$: $[M+H]^+$, 224.1075. Found: *m/z* 224.1072.

(*Z*)-3-((4-(tert-butyl)phenyl)amino)-1-phenylprop-2-en-1-one (1aa):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown solid, Yield =69% (963mg), mp: 139.8-140.3

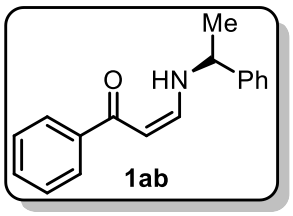
^{o}C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 12.18 (d, J = 12.1 Hz, 1H), 7.98 – 7.92 (m, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.43 (m, 2H), 7.39 – 7.35 (m, 2H), 7.06 (d, J = 8.7 Hz, 2H), 6.01 (d, J = 7.8 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 147.1, 145.5, 139.5, 137.9, 131.7, 128.6, 127.5, 126.8, 116.3, 93.5, 34.6, 31.6.

HRMS (ESI, m/z): Calcd. for $C_{19}H_{22}NO$: $[M+H]^+$, 280.1696. Found: *m/z* 280.1699.

(*R*,*Z*)-1-phenyl-3-((1-phenylethyl)amino)prop-2-en-1-one (1ab):



The synthetic method was followed the synthetic procedure of compound **1a**.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a brown oil, Yield = 38% (477 mg).

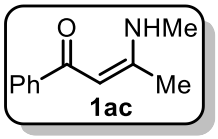
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 7.91 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.52 – 7.26 (m, 8H), 6.98 (dd, *J* = 12.8, 7.6 Hz, 1H), 5.76 (d, *J* = 7.6 Hz, 1H), 4.55 (p, *J* = 6.8 Hz, 1H), 1.65 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 152.8, 143.3, 139.8, 131.1, 129.0, 128.4, 127.8, 127.2, 126.3, 90.8, 57.9, 23.8.

HRMS (ESI, m/z): Calcd. for $C_{17}H_{18}NO$: $[M+H]^+$, 252.1388. Found: *m/z* 252.1385.

Specific rotation: [α] = -228.100

(*Z*)-3-(methylamino)-1-phenylbut-2-en-1-one (1ac):



This compound was prepared according to the literature procedure[5].

Flash chromatography: PE/EA (6:1)

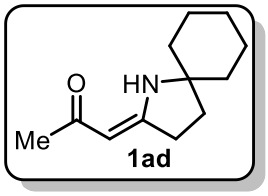
The title compound was obtained as a brown solid, Yield = 65% (569 mg), mp: 74.4-75.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.33 (s, 1H), 7.90 – 7.79 (m, 2H), 7.44 – 7.34 (m, 3H), 5.69 (s, 1H), 3.02 (d, *J* = 5.3 Hz, 3H), 2.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 166.2, 140.7, 130.6, 128.4, 127.1, 92.2, 29.9, 19.5.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO$: $[M+H]^+$, 176.1075. Found: *m/z* 176.1075.

(*Z*)-1-(2-azaspiro[4.5]decan-3-ylidene)propan-2-one (1ad):



This compound was prepared according to the literature procedure in 1mmol scale[6].

Flash chromatography: PE/EA (8:1)

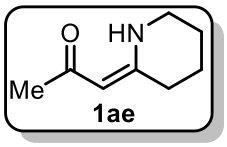
The title compound was obtained as a brown solid, Yield = 70% (136 mg), mp: 110.2-111.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 5.03 (s, 1H), 3.32 (s, 2H), 2.39 (s, 2H), 2.00 (s, 3H), 1.44 (d, *J* = 13.1 Hz, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 167.2, 90.4, 40.7, 37.1, 36.3, 28.9, 26.0, 23.5, 23.1.

HRMS (ESI, m/z): Calcd. for $C_{12}H_{20}NO$: $[M+H]^+$, 194.1545. Found: *m/z* 194.1544.

(*Z*)-1-(piperidin-2-ylidene)propan-2-one (1ae):



This compound was prepared according to the literature procedure in 1mmol scale[6].

Flash chromatography: PE/EA (8:1)

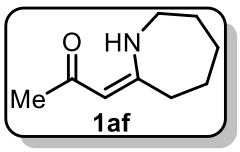
The title compound was obtained as a brown oil, Yield = 73% (102 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 4.85 (s, 1H), 3.30 – 3.33 (m, 2H), 2.31 – 2.35 (m, 2H), 1.97 (s, 3H), 1.65-1.79 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 164.4, 93.6, 41.2, 28.8, 28.6, 22.5, 19.5.

HRMS (ESI, m/z): Calcd. for $C_{18}H_{14}NO$: $[M+H]^+$, 140.1075. Found: *m/z* 140.1078.

(*Z*)-1-(azepan-2-ylidene)propan-2-one (1af):



This compound was prepared according to the literature procedure in 1mmol scale[6].

Flash chromatography: PE/EA (8:1)

The title compound was obtained as a brown oil, Yield = 75% (115 mg).

The title compound was obtained as a brown oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.84 (s, 1H), 4.94 (s, 1H), 4.07 – 4.13 (m, 2H), 3.18 – 3.24 (m, 2H), 2.27-2.31 (m, 2H), 1.98 (s, 3H), 1.35-1.65 (m, 4H).

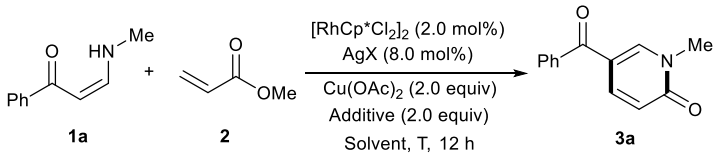
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.4, 169.8, 94.2, 44.3, 34.9, 30.6, 29.5, 28.9, 25.9.

HRMS (ESI, m/z): Calcd. for $C_9H_{16}NO$: $[M+H]^+$, 154.1232. Found: *m/z* 154.1232.

3. Optimization study

To verify this idea, we started our investigations by using (*Z*)-3-(methylamino)-1-phenylprop-2-en-1-one **1a** and widely existed methyl acrylate **2** as the model substrates. Firstly, several solvents were examined by using $[Cp^*RhCl_2]_2$ (2.0 mol%) as the catalyst precursor and $Cu(OAc)_2$ (2.0 equiv) as oxidant under nitrogen atmosphere at 100 °C for 12 h (Table S1, entries 2-5). To our delight, when methanol was used as the solvent, the 2-pyridone product **3a** was obtained in 45% yield (Table S1, entry 5). No desired product was detected in the absence of $[Cp^*RhCl_2]_2$ catalyst (Table S1, entry 1). We then varied the temperature in the range of 70-100 ^oC and found that 90 ^oC was most suitable temperature for this reaction (Table S1, entries 5-7). The screening of additives showed that potassium acetate (KOAc) was more efficient as compared with other tested additives (Table S1, entries 8-10) and could greatly increase the yield of **3a** to 75% (Table S1, entry 10). Moreover, it was observed that the catalytic system of $[Cp^*RhCl_2]_2$ (2.0 mol%) and silver salt (8.0 mol%) was more favorable to the formation of 2-pyridone **3a** (Table S1, entries 10-12). Therefore, $[Cp^*RhCl_2]_2$ (2.0 mol%), AgOAc (8.0 mol%), $Cu(OAc)_2$ (2.0 equiv), and KOAc (2.0 equiv) in methanol at 90 ^oC under N_2 atmosphere for 12 h were identified as the optimal reaction conditions.

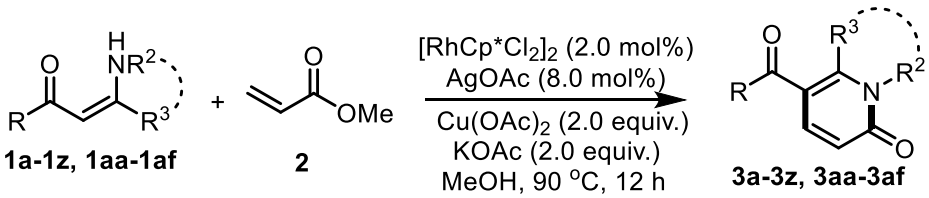
Table S1. Optimization study[a,b]



Entry	AgX	Additive	Solvent	T (^{o}C)	Yield (%)[b]
1	—	—	MeOH	100	0[c]
2	—	—	DCE	100	28
3	—	—	THF	100	trace
4	—	—	Toluene	100	trace
5	—	—	MeOH	100	45
6	—	—	MeOH	90	50
7	—	—	MeOH	70	26
8	—	HOAc	MeOH	90	47
9	—	PivOH	MeOH	90	48
10	—	KOAc	MeOH	90	75
11	AgOAc	KOAc	MeOH	90	81
12	$AgSbF_6$	KOAc	MeOH	90	78

[a]Reaction conditions: enaminone **1a** (0.2 mmol, 1.0 equiv), methyl acrylate **2** (0.3 mmol, 1.5 equiv), $Cu(OAc)_2$ (0.4 mmol, 2.0 equiv), additive (0.4 mmol, 2.0 equiv), solvent (1.0 mL), $[Cp^*RhCl_2]_2$ (2.0 mol%), AgX (8.0 mol%), 12 h. [b]Isolated yields. [c]Without $[Cp^*RhCl_2]_2$.

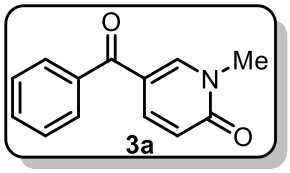
4. General procedure and characterization for [3+3] annulation into 2-pyridones



Typical procedure for [3+3] annulation into 2-pyridones: (*Z*)-3-(methylamino)-1-phenylprop-2-en-1-one **1a** and methyl acrylate **2** as the model substrates): To a 10 mL Schlenk flask equipped with magnetic stir bar was added (*Z*)-3-(methylamino)-1-phenylprop-2-en-1-one **1a** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mg, 0.004 mmol), AgOAc (2.7 mg, 0.016 mmol, 0.08 equiv), $Cu(OAc)_2$ (72.6 mg, 0.4 mmol, 2.0 equiv), KOAc (39.3 mg, 0.4 mmol, 2.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that methyl acrylate (**2**, 25.8 mg, 0.30 mmol, 1.5 equiv) in MeOH (1.0 mL)

was injected into the test tube via syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 90 °C for 12 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **3a**.

5-benzoyl-1-methylpyridin-2(1H)-one (3a)



Flash chromatography: PE/EA (6:1)

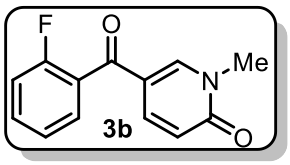
This compound was prepared by the general procedure described above, affording the desired product **3a** as a yellow solid (34.5 mg, 81%). mp: 183.0-183.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.3 Hz, 1H), 7.87 (d, *J* = 9.5 Hz, 1H), 7.67 (dd, *J* = 7.3, 0.8 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.52 – 7.46 (m, 2H), 6.59 (d, *J* = 9.5 Hz, 1H), 3.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 162.9, 145.3, 139.5, 137.4, 132.5, 129.2, 128.8, 119.7, 117.5, 38.6.

HRMS (ESI, m/z): Calcd. for $C_{13}H_{12}NO_2$: $[M+H]^+$, 214.0868. Found: *m/z* 214.0867.

5-(2-fluorobenzoyl)-1-methylpyridin-2(1H)-one (3b):



Flash chromatography: PE/EA (6:1)

This compound was prepared by the general procedure described above, affording the desired product **3b** as a yellow solid (20.8 mg, 45%). mp: 150.6-152.1 ºC.

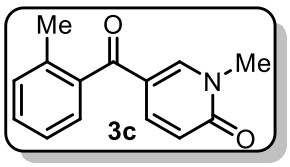
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 1.7 Hz, 1H), 7.83 (ddd, *J* = 9.5, 2.6, 1.4 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.29 (td, *J* = 7.6, 1.0 Hz, 1H), 7.21 – 7.14 (m, 1H), 6.58 (d, *J* = 9.6 Hz, 1H), 3.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 163.0, 159.6(d, *J* = 252.2 Hz), 145.6 (d, *J* = 2.1 Hz), 138.8 (d, *J* = 1.5 Hz), 133.5 (d, *J* = 8.3 Hz), 130.6 (d, *J* = 3.1 Hz), 126.2 (d, *J* = 15.5 Hz), 125.0 (d, *J* = 3.7 Hz), 119.8, 118.0 (d, *J* = 1.4 Hz), 116.6(d, *J* = 21.8 Hz), 38.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -112.02.

HRMS (ESI, m/z): Calcd. for $C_{13}H_{11}FNO_2$: $[M+H]^+$, 232.0774. Found: *m/z* 232.0778.

1-methyl-5-(2-methylbenzoyl)pyridin-2(1H)-one (3c):



Flash chromatography: PE/EA (6:1)

This compound was prepared by the general procedure described above, affording the desired product **3c** as a yellow solid (19.5 mg, 43%). mp: 142.5-143.2 ºC.

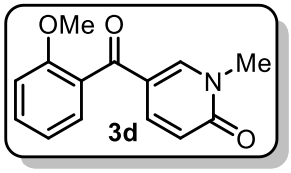
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.77 (m, 2H), 7.38 (ddd, *J* = 7.9, 5.3, 3.7 Hz, 1H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.25 (dd, *J* = 4.7, 1.2 Hz, 2H), 6.57 (d, *J* = 9.5 Hz, 1H), 3.53 (s, 3H),

2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 163.0, 145.8, 138.8, 137.7, 136.5, 131.5, 130.6, 127.7, 125.7, 119.9, 118.2, 38.6, 19.8.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{14}NO_2$: $[M+H]^+$, 228.1025. Found: *m/z* 228.1024.

5-(2-methoxybenzoyl)-1-methylpyridin-2(1H)-one (3d):



Flash chromatography: PE/EA (6:1)

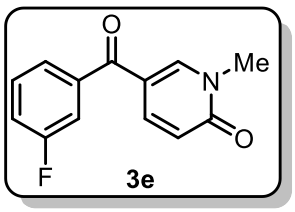
This compound was prepared by the general procedure described above, affording the desired product **3d** as a yellow solid (24.3 mg, 50%). mp: 135.6-137.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.5 Hz, 1H), 7.76 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.46 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H), 7.31 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.04 (td, *J* = 7.5, 0.8 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 9.5 Hz, 1H), 3.77 (s, 3H), 3.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 163.1, 156.9, 145.2, 139.2, 132.4, 129.5, 127.8, 121.1, 119.3, 118.4, 111.6, 55.8, 38.6.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{14}NO_3$: $[M+H]^+$, 244.0974. Found: *m/z* 244.0974.

5-(3-fluorobenzoyl)-1-methylpyridin-2(1H)-one (3e):



Flash chromatography: PE/EA (5:1)

This compound was prepared by the general procedure described above, affording the desired product **3e** as a yellow solid (21.3 mg, 46%). mp: 162.2-163.8 ºC.

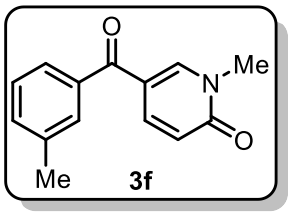
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87 (d, *J* = 9.4 Hz, 1H), 7.48 (dd, *J* = 12.4, 7.5 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 6.61 (d, *J* = 9.5 Hz, 1H), 3.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5 (d, *J* = 2.3 Hz), 162.8, 162.7(d, *J* = 250.3 Hz), 145.5, 139.4 (d, *J* = 6.4 Hz), 139.2, 130.6 (d, *J* = 7.9 Hz), 124.9 (d, *J* = 3.2 Hz), 119.9, 119.5(d, *J* = 21.4 Hz), 117.0, 116.1(d, *J* = 22.6 Hz), 38.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -111.08.

HRMS (ESI, m/z): Calcd. for $C_{13}H_{11}F\ NO_2$: $[M+H]^+$, 232.0774. Found: *m/z* 232.0773.

1-methyl-5-(3-methylbenzoyl)pyridin-2(1H)-one (3f):



3f

Flash chromatography: PE/EA (6:1)

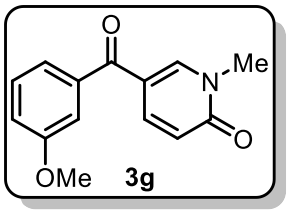
This compound was prepared by the general procedure described above, affording the desired product **3f** as a yellow solid (30.9 mg, 68%). mp: 147.6-149.2 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.4 Hz, 1H), 7.86 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.49 (s, 1H), 7.44 (d, *J* = 6.9 Hz, 1H), 7.41 – 7.33 (m, 2H), 6.58 (d, *J* = 9.5 Hz, 1H), 3.58 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.2, 162.9, 145.2, 139.53, 138.9, 137.5, 133.3, 129.7, 128.6, 126.4, 119.7, 117.6, 38.6, 21.6.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{14}NO_2$: $[M+H]^+$, 228.1025. Found: *m/z* 228.1025.

5-(3-methoxybenzoyl)-1-methylpyridin-2(1H)-one (3g):



Flash chromatography: PE/EA (5:1)

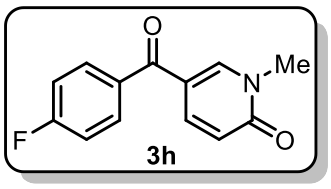
This compound was prepared by the general procedure described above, affording the desired product **3g** as a yellow solid (39.9 mg, 82%). mp: 133.7-134.5 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.5 Hz, 1H), 7.86 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.13 – 7.07 (m, 1H), 6.57 (d, *J* = 9.5 Hz, 1H), 3.84 (s, 3H), 3.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 162.9, 160.0, 145.3, 139.4, 138.8, 129.8, 121.6, 119.7, 118.6, 117.5, 114.0, 55.7, 38.6.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{14}NO_3$: $[M+H]^+$, 244.0974. Found: *m/z* 244.0977.

5-(4-fluorobenzoyl)-1-methylpyridin-2(1H)-one (3h):



Flash chromatography: PE/EA (5:1)

This compound was prepared by the general procedure described above, affording the desired product **3h** as a yellow solid (29.1 mg, 63%). mp: 182.7-184.2 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.5 Hz, 1H), 7.83 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.76

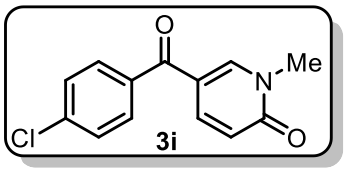
– 7.69 (m, 2H), 7.22 – 7.14 (m, 2H), 6.59 (d, *J* = 9.5 Hz, 1H), 3.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 165.4(d, *J* = 254.8 Hz), 162.9, 145.1 , 139.4, 133.7 (d, *J* = 3.3 Hz), 131.8 (d, *J* = 9.1 Hz), 119.8, 117.4, 116.1(d, *J* = 22.0 Hz), 38.7.

^{19}F NMR (471 MHz, $CDCl_3$) δ -105.79.

HRMS (ESI, m/z): Calcd. for $C_{13}H_{11}F\ NO_2$: $[M+H]^+$, 232.0774. Found: *m/z* 232.0777.

5-(4-chlorobenzoyl)-1-methylpyridin-2(1H)-one (3i):



Flash chromatography: PE/EA (5:1)

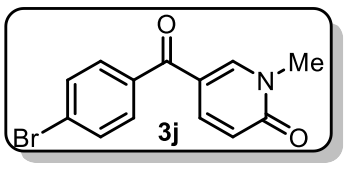
This compound was prepared by the general procedure described above, affording the desired product **3i** as a yellow solid (38.5 mg, 78%). mp: 187.9-189.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.81 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.48 – 7.43 (m, 2H), 6.57 (d, *J* = 9.5 Hz, 1H), 3.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 162.8, 145.2, 139.2, 138.9, 135.7, 130.6, 129.1, 119.9, 117.2, 38.7.

HRMS (ESI, m/z): Calcd. for $C_{13}H_{11}\ NO_2Cl$: $[M+H]^+$, 248.0478. Found: *m/z* 248.0480.

5-(4-bromobenzoyl)-1-methylpyridin-2(1H)-one (3j):



Flash chromatography: PE/EA (4:1)

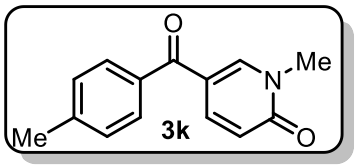
This compound was prepared by the general procedure described above, affording the desired product **3j** as a yellow solid (41.9 mg, 72%). mp: 191.0-191.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.82 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.57 – 7.52 (m, 2H), 6.58 (d, *J* = 9.5 Hz, 1H), 3.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 162.8, 145.3, 139.2, 136.2, 132.2, 130.8, 127.5, 119.9, 117.2, 38.7.

HRMS (ESI, m/z): Calcd. for $C_{13}H_{11}NO_2Br$: $[M+H]^+$, 291.9973. Found: *m/z* 291.9975.

1-methyl-5-(4-methylbenzoyl)pyridin-2(1H)-one (3k):



Flash chromatography: PE/EA (4:1)

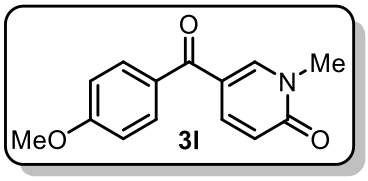
This compound was prepared by the general procedure described above, affording the desired product **3k** as a yellow solid (41.3 mg, 91%). mp: 185.6-186.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.4 Hz, 1H), 7.85 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.57 (d, *J* = 9.5 Hz, 1H), 3.58 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 145.0, 143.4, 139.6, 134.7, 129.5, 119.7, 117.7, 38.6, 21.8.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{14}NO_2$: $[M+H]^+$, 228.1025. Found: *m/z* 228.1027.

5-(4-methoxybenzoyl)-1-methylpyridin-2(1H)-one (3l):



Flash chromatography: PE/EA (3:1)

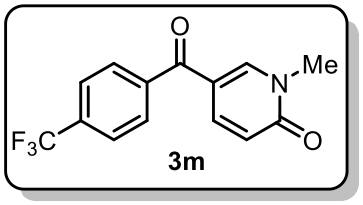
This compound was prepared by the general procedure described above, affording the desired product **3l** as a yellow solid (36.5 mg, 75%). mp: 182.7-183.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.81 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.00 – 6.92 (m, 2H), 6.56 (d, *J* = 9.5 Hz, 1H), 3.87 (s, 3H), 3.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 163.3, 162.9, 144.6, 139.7, 131.7, 129.8, 119.6, 117.9, 114.0, 55.7, 38.6.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{14}NO_3$: $[M+H]^+$, 244.0974. Found: *m/z* 244.0975.

1-methyl-5-(4-(trifluoromethyl)benzoyl)pyridin-2(1H)-one (3m):



Flash chromatography: PE/EA (3:1)

This compound was prepared by the general procedure described above, affording the desired product **3m** as a yellow solid (26.4 mg, 47%). mp: 173.7-175.3ºC.

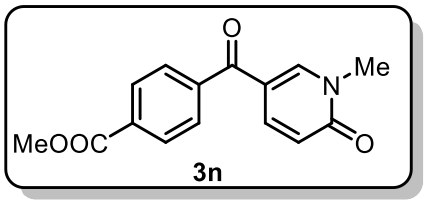
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.5 Hz, 1H), 7.82 (dt, *J* = 9.5, 2.5 Hz, 1H), 7.78 – 7.70 (m, 4H), 6.56 (dd, *J* = 9.5, 4.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 162.7, 145.7, 140.7, 138.9, 133.8(d, *J* = 33.0 Hz), 129.4, 125.9(q, *J* = 3.7 Hz),123.7 (d, *J* = 273.2 Hz), 120.0, 116.9, 38.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -63.04.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{11}NO_2F_3$: $[M+H]^+$, 282.0736. Found: *m/z* 282.0740.

Methyl 4-(1-methyl-6-oxo-1,6-dihydropyridine-3-carbonyl)benzoate (3n):



Flash chromatography: PE/EA (3:1)

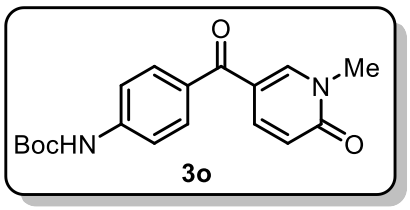
This compound was prepared by the general procedure described above, affording the desired product **3n** as a yellow solid (30.4 mg, 56%). mp: 171.3-173.0 ºC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 – 8.10 (m, 2H), 7.96 (d, J = 2.2 Hz, 1H), 7.85 (ddd, J = 9.5, 4.7, 2.6 Hz, 1H), 7.71 (dd, J = 8.2, 4.7 Hz, 2H), 6.59 (dd, J = 9.5, 6.5 Hz, 1H), 3.95 (s, 3H), 3.58 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.2, 166.3, 162.8, 145.6, 141.3, 139.1, 133.4, 130.0, 129.0, 120.0, 117.1, 52.8, 38.7

HRMS (ESI, m/z): Calcd. for $C_{15}H_{14}NO_4$: $[M+H]^+$, 272.0916. Found: *m/z* 272.0921.

Tert-butyl (4-(1-methyl-6-oxo-1,6-dihydropyridine-3-carbonyl)phenyl)carbamate



Flash chromatography: PE/EA (3:1)

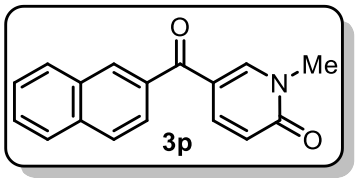
This compound was prepared by the general procedure described above, affording the desired product **3o** as a yellow viscous liquid (13.8 mg, 21%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.84 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 1H), 6.59 (d, *J* = 9.5 Hz, 1H), 3.59 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 163.0, 152.6, 144.8, 142.9, 139.7, 131.5, 130.9, 119.7, 117.9, 81.5, 38.6, 28.5.

HRMS (ESI, m/z): Calcd. for $C_{18}H_{21}N_2O_4$: $[M+H]^+$, 329.1496. Found: *m/z* 329.1488.

5-(2-naphthoyl)-1-methylpyridin-2(1H)-one (3p):



Flash chromatography: PE/EA (5:1)

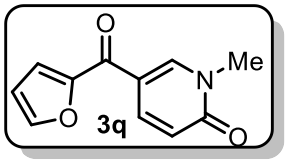
This compound was prepared by the general procedure described above, affording the desired product **3m** as a yellow solid (47.9 mg, 91%). mp: 128.3-128.9 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.04 (d, *J* = 2.5 Hz, 1H), 7.97 – 7.89 (m, 4H), 7.77 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.59 (dtd, *J* = 14.6, 6.9, 1.3 Hz, 2H), 6.61 (d, *J* = 9.5 Hz, 1H), 3.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 162.9, 145.3, 139.5, 135.3, 134.7, 132.4, 130.3, 129.4, 128.9, 128.6, 128.1, 127.3, 125.4, 119.8, 117.7, 38.6.

HRMS (ESI, m/z): Calcd. for $C_{17}H_{14}NO_2$: $[M+H]^+$, 262.1025. Found: *m/z* 264.1026.

5-(furan-2-carbonyl)-1-methylpyridin-2(1H)-one (3q):



Flash chromatography: PE/EA (5:1)

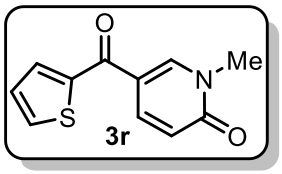
This compound was prepared by the general procedure described above, affording the desired product **3n** as a yellow solid (19.1 mg, 47%). mp: 190.8-191.5 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 2.5 Hz, 1H), 8.06 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.64 (d, *J* = 0.9 Hz, 1H), 7.30 (d, *J* = 3.2 Hz, 1H), 6.63 – 6.53 (m, 2H), 3.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 162.9, 152.7, 146.5, 144.9, 139.1, 119.7, 119.5, 116.8, 112.7, 38.7.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{10}NO_3$: $[M+H]^+$, 204.0661. Found: *m/z* 204.0661.

1-methyl-5-(thiophene-2-carbonyl)pyridin-2(1H)-one (3r):



Flash chromatography: PE/EA (5:1)

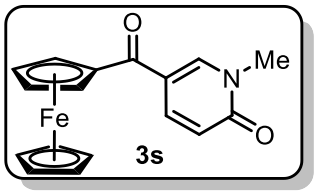
This compound was prepared by the general procedure described above, affording the desired product **3o** as a yellow solid (29.8 mg, 68%). mp: 174.2-175.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.5 Hz, 1H), 7.89 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.69 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.60 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.15 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.57 (d, *J* = 9.5 Hz, 1H), 3.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 182.9, 162.9, 144.1, 142.5, 139.1, 134.0, 133.3, 128.2, 119.8, 117.8, 38.6.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{10}NO_2S$: $[M+H]^+$, 220.0432. Found: *m/z* 220.0432.

5-(Ferrocene-carbonyl)-1-methylpyridin-2(1H)-one (3s):



Flash chromatography: PE/EA (5:1)

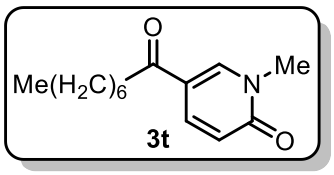
This compound was prepared by the general procedure described above, affording the desired product **3p** as a yellow solid (25.7 mg, 40%). mp: 170.5-171.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.4 Hz, 1H), 8.02 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.56 (d, *J* = 9.5 Hz, 1H), 4.83 – 4.78 (m, 2H), 4.59 – 4.53 (m, 2H), 4.19 (s, 5H), 3.61 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 163.0, 142.7, 138.9, 119.4, 119.1, 78.3, 72.6, 71.3, 70.4, 38.6.

HRMS (ESI, m/z): Calcd. for $C_{17}H_{16}NO_2Fe$: $[M+H]^+$, 320.0577. Found: *m/z* 320.0569.

1-methyl-5-octanoylpyridin-2(1H)-one (3t):



Flash chromatography: PE/EA (5:1)

This compound was prepared by the general procedure described above, affording the desired product **3q** as a yellow solid (26.3 mg, 56%). mp: 188.2-189.5 °C.

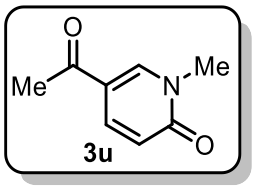
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.53 – 7.34 (m, 1H), 6.71 (d, *J* = 14.6 Hz, 1H), 6.67 – 6.59 (m, 1H), 6.55 (d, *J* = 9.3 Hz, 1H), 6.35 – 6.23 (m, 1H),

6.23 – 6.10 (m, 1H), 5.99 (dd, *J* = 14.3, 6.9 Hz, 1H), 3.61 (s, 3H), 1.83 (d, *J* = 5.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.2, 163.1, 145.5, 143.6, 143.2, 138.2, 136.7, 131.6, 128.2, 122.3, 119.8, 118.7, 38.7, 18.9.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{16}NO_2$: $[M+H]^+$, 230.1181. Found: *m/z* 230.1180.

5-acetyl-1-methylpyridin-2(1H)-one (3u):



Flash chromatography: PE/EA (5:1)

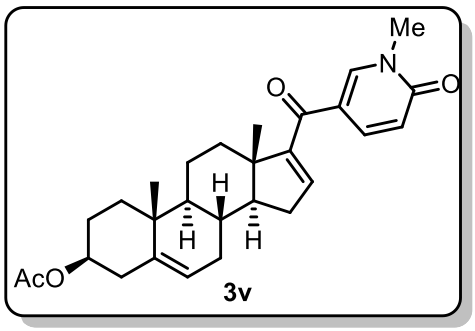
This compound was prepared by the general procedure described above, affording the desired product **3r** as yellow solid (19.9 mg, 66%). mp: 146.9-147.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 3.0 Hz, 1H), 7.85 (dd, *J* = 9.7, 2.8 Hz, 1H), 6.54 (d, *J* = 9.8 Hz, 1H), 3.60 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 163.0, 143.4, 138.0, 119.8, 117.9, 38.6, 26.0.

HRMS (ESI, m/z): Calcd. for $C_8H_{10}NO_2$: $[M+H]^+$, 152.0712. Found: *m/z* 152.0713.

(3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-(1-methyl-6-oxo-1,6-dihydropyridine-3-carbonyl)-2,3,4,7,8,9,10, 11,12,13,14,15-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl acetate (3v):



Flash chromatography: PE/EA (5:1)

This compound was prepared by the general procedure described above, affording the desired product **3s** as a yellow solid (43.1 mg, 48%). mp: 262.0-263.2 °C.

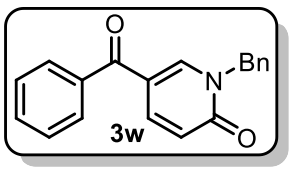
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.1 Hz, 1H), 7.80 (dd, *J* = 9.5, 2.3 Hz, 1H), 6.55 (d, *J* = 9.5 Hz, 1H), 6.37 (s, 1H), 5.39 (d, *J* = 4.5 Hz, 1H), 4.59 (dt, *J* = 10.4, 5.9 Hz, 1H), 3.59 (s, 3H), 2.45 – 2.29 (m, 3H), 2.22 – 2.03 (m, 3H), 2.03 (s, 3H), 1.86 (d, *J* = 10.1 Hz, 2H), 1.78 – 1.68 (m, 2H), 1.67 – 1.48 (m, 5H), 1.33 (td, *J* = 11.9, 6.2 Hz, 1H), 1.20 – 1.11 (m, 1H), 1.08 (d, *J* = 9.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.3, 170.8, 163.2, 153.2, 143.5, 140.5, 139.0, 122.2, 119.7, 119.2, 74.0, 56.5, 50.7, 48.0, 38.6, 38.3, 37.1, 37.0, 34.2, 33.1, 31.8, 30.3, 27.9, 21.7, 20.8, 19.5, 16.4.

HRMS (ESI, m/z): Calcd. for $C_{28}H_{36}NO_4$: $[M+H]^+$, 450.2644. Found: *m/z* 450.2649.

Specific rotation: [α] = -90.800

5-benzoyl-1-benzylpyridin-2(1H)-one (3w):



Flash chromatography: PE/EA (5:1)

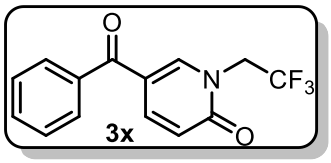
This compound was prepared by the general procedure described above, affording the desired product **3u** as a yellow solid (35.3 mg, 61%). mp: 131.6-132.2 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.7 Hz, 1H), 7.86 (dd, *J* = 9.4, 2.0 Hz, 1H), 7.56 (dd, *J* = 17.2, 7.4 Hz, 3H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.25 (m, 5H), 6.63 (d, *J* = 9.5 Hz, 1H), 5.15 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 162.4, 144.4, 139.2, 137.2, 135.5, 132.5, 129.3, 128.7, 128.7, 128.5, 120.3, 117.6, 52.8.

HRMS (ESI, m/z): Calcd. for $C_{19}H_{16}NO_2$: $[M+H]^+$, 290.1181. Found: *m/z* 290.1184.

5-benzoyl-1-(2,2,2-trifluoroethyl)pyridin-2(1H)-one (3x):



Flash chromatography: PE/EA (5:1)

This compound was prepared by the general procedure described above, affording the desired product **3v** as a yellow solid (33.7 mg, 60%). mp: 129.6-130.3 ºC.

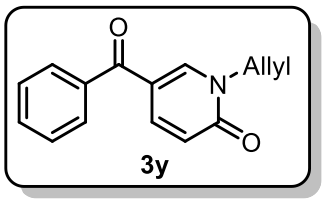
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (q, *J* = 2.5 Hz, 1H), 7.69 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 10.4 Hz, 1H), 4.64 (q, *J* = 8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 161.6, 144.3, 140.1, 137.0, 133.0, 129.4, 129.0, 126.2(d, *J* = 281.5 Hz), 120.9, 118.3, 48.3(q, *J* = 35.35 Hz).

^{19}F NMR (471 MHz, $CDCl_3$) δ -64.95.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{11}NO_2F_3$: $[M+H]^+$, 282.0742. Found: *m/z* 282.0740.

1-allyl-5-benzoylpyridin-2(1H)-one (3y):



Flash chromatography: PE/EA (5:1)

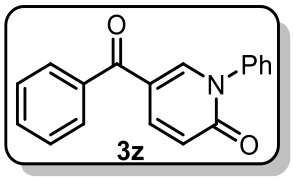
This compound was prepared by the general procedure described above, affording the desired product **3y** as a yellow solid (13.8 mg, 37%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.5 Hz, 1H), 7.82 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.63 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.45 (dd, *J* = 10.7, 4.5 Hz, 2H), 6.56 (d, *J* = 9.5 Hz, 1H), 5.26 (dd, *J* = 10.3, 1.0 Hz, 1H), 5.21 – 5.12 (m, 1H), 4.55 (dt, *J* = 5.9, 1.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 162.0, 144.1, 139.3, 137.3, 132.5, 131.8, 129.2, 128.7, 120.0, 119.6, 117.5, 51.8.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{14}NO_2$: $[M+H]^+$, 240.1019. Found: *m/z* 240.1027.

5-benzoyl-1-phenylpyridin-2(1H)-one (3z):



Flash chromatography: PE/EA (5:1)

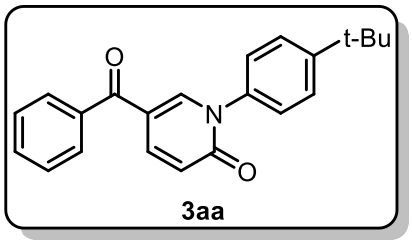
This compound was prepared by the general procedure described above, affording the desired product **3t** as a yellow solid (28.6 mg, 52%). mp: 125.5-126.3 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2H), 7.73 – 7.68 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.43 (m, 5H), 7.40 – 7.34 (m, 2H), 6.70 (d, *J* = 9.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 162.1, 144.9, 140.2, 139.6, 137.3, 132.6, 129.7, 129.3, 129.2, 128.8, 126.6, 121.0, 117.6.

HRMS (ESI, m/z): Calcd. for $C_{18}H_{14}NO_2$: $[M+H]^+$, 276.1025. Found: *m/z* 276.1024.

5-benzoyl-1-(4-(tert-butyl)phenyl)pyridin-2(1H)-one



Flash chromatography: PE/EA (5:1)

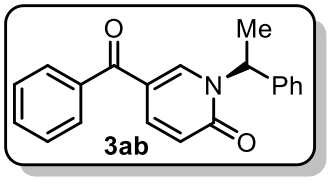
This compound was prepared by the general procedure described above, affording the desired product **3aa** as a yellow solid (39.1 mg, 59%). mp: 177.1-179.7 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 1H), 7.96 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.52 (m, 1H), 7.48 (ddd, *J* = 15.2, 7.0, 1.7 Hz, 4H), 7.29 (t, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 9.6 Hz, 1H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.9, 162.2, 152.3, 145.1, 139.4, 137.6, 137.4, 132.5, 129.2, 128.8, 126.7, 126.0, 121.0, 117.5, 34.9, 31.4.

HRMS (ESI, m/z): Calcd. for $C_{19}H_{22}NO$: $[M+H]^+$,332.1645. Found: *m/z* 332.1638.

(*R*)-5-benzoyl-1-(1-phenylethyl)pyridin-2(1H)-one (3ab):



Flash chromatography: PE/EA (5:1)

This compound was prepared by the general procedure described above, affording the

desired product **3w** as a yellow solid (15.2 mg, 25%). mp: 104.8-105.2 ºC.

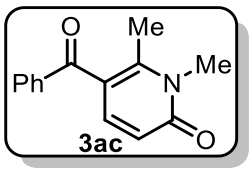
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.78 (d, *J* = 2.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 2H), 7.35 (ddd, *J* = 18.0, 9.0, 6.8 Hz, 7H), 6.64 (d, *J* = 9.5 Hz, 1H), 6.42 (q, *J* = 7.0 Hz, 1H), 1.71 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 162.3, 142.2, 139.5, 138.6, 137.2, 132.5, 129.4, 129.3, 128.7, 128.7, 127.8, 120.1, 117.6, 53.9, 19.2.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{18}NO_2$: $[M+H]^+$,304.1338. Found: *m/z* 304.1335.

Specific rotation: [α] = +30.300

5-benzoyl-1,6-dimethylpyridin-2(1H)-one (3ac):



Flash chromatography: PE/EA (5:1)

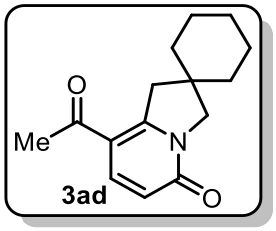
This compound was prepared by the general procedure described above, affording the desired product **3x** as a yellow solid (23.6 mg, 52%). mp: 133.2-134.5 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 9.5 Hz, 1H), 6.44 (d, *J* = 9.4 Hz, 1H), 3.62 (s, 3H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 163.1, 151.4, 139.9, 138.2, 133.3, 130.0, 128.8, 117.9, 115.7, 31.7, 18.8.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{21}O_4$: $[M+H]^+$, 228.1025. Found: *m/z*228.1022.

8'-acetyl-3'H-spiro[cyclohexane-1,2'-indolizin]-5'(1'H)-one (3ad):



Flash chromatography: PE/EA (5:1)

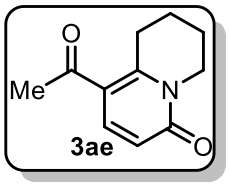
This compound was prepared by the general procedure described above, affording the desired product **3y** as a yellow solid (25.0 mg, 51%). mp: 105.6-107.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 9.5 Hz, 1H), 6.40 (d, *J* = 9.5 Hz, 1H), 3.92 (s, 2H), 3.34 (s, 2H), 2.44 (s, 3H), 1.60 – 1.43 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 162.1, 157.4, 140.3, 116.5, 114.2, 58.9, 47.0, 39.6, 36.5, 28.2, 25.6, 23.2.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{20}NO_2$: $[M+H]^+$, 246.1494. Found: *m/z* 246.1496.

1-acetyl-6,7,8,9-tetrahydro-4H-quinolizin-4-one (3ae):



Flash chromatography: PE/EA (5:1)

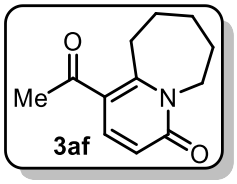
This compound was prepared by the general procedure described above, affording the desired product **3z** as a yellow solid (16.8 mg, 44%). mp: 98.4-100.1 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.6 Hz, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 4.13 – 3.93 (m, 2H), 3.31 (t, *J* = 6.7 Hz, 2H), 2.46 (s, 3H), 1.97 – 1.88 (m, 2H), 1.81 – 1.75 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 162.8, 155.8, 139.7, 115.8, 115.2, 43.0, 29.7, 27.6, 21.5, 18.4.

HRMS (ESI, m/z): Calcd. for $C_{11}H_{14}NO_2$: $[M+H]^+$, 192.1025. Found: *m/z* 192.1023.

1-acetyl-7,8,9,10-tetrahydropyrido[1,2-a]azepin-4(6H)-one (3af):



Flash chromatography: PE/EA (5:1)

This compound was prepared by the general procedure described above, affording the desired product **3aa** as a yellow solid (12.3 mg, 30%). mp: 103.7-104.8 °C.

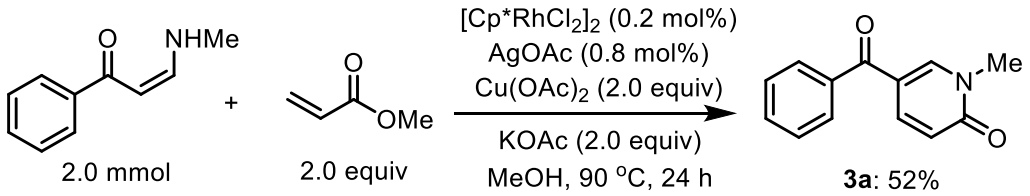
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.6 Hz, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 4.52 – 4.38 (m, 2H), 3.29 (s, 2H), 2.47 (s, 3H), 1.76 (dd, *J* = 10.1, 5.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 162.5, 158.3, 139.1, 117.4, 116.5, 43.6, 29.9, 29.5, 29.2, 27.3, 25.7.

HRMS (ESI, m/z): Calcd. for $C_{12}H_{16}NO_2$: $[M+H]^+$, 206.1181. Found: *m/z* 206.1180.

5. Practical utilities of [3+3] annulation into 2-pyridones

Low catalytic loading (0.2 mol%) on 2.0 mmol scale

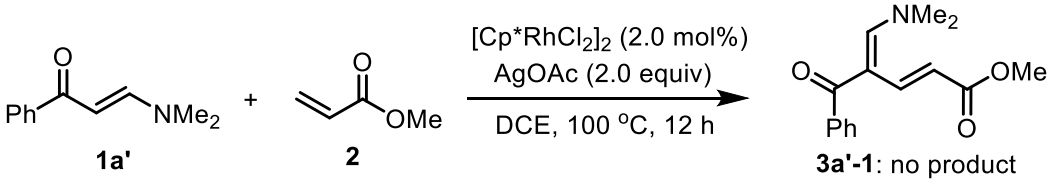


Typical procedure for [3+3] annulation into 2-pyridones: To a 25 mL Schlenk flask equipped with magnetic stirring bar was added (*Z*)-3-(methylamino)-1-phenylprop-2-en-1-one **1a** (2.0 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mg, 0.004 mmol), AgOAc (2.7 mg, 0.016 mmol, 0.08

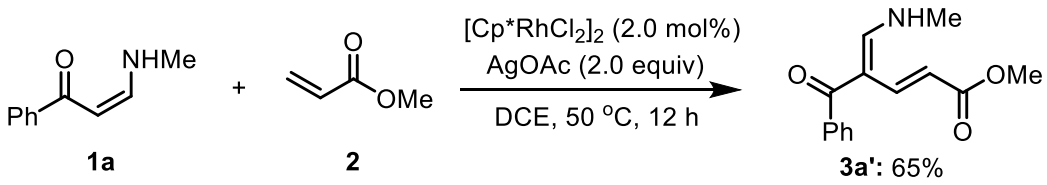
equiv), $Cu(OAc)_2$ (726 mg, 4.0 mmol, 2.0 equiv), KOAc (393 mg, 4.0 mmol, 2.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that methyl acrylate (**2**, 344 mg, 0.30 mmol, 2.0 equiv) in MeOH (10 mL) was injected into the test tube *via* syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 90 °C for 12 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **3a** (222mg, 52%).

6. Mechanistic study

6.1 Experiments for enaminones with the reactive sites

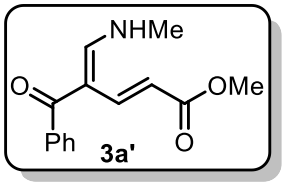


To a 10 mL Schlenk flask equipped with magnetic stirring bar was added (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one (**1a'**, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mg, 0.004 mmol), AgOAc (66.8 mg, 0.4 mmol, 2.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that methyl acrylate (**2**, 25.8 mg, 0.30 mmol, 1.5 equiv) in DCE (1.0 mL) was injected into the test tube via syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 100 °C for 12 h, during which time a constant checking by TLC was performed.



To a 10 mL Schlenk flask equipped with magnetic stirring bar was added (*Z*)-3-(methylamino)-1-phenylprop-2-en-1-one (**1a**, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mg, 0.004 mmol), AgOAc (66.8 mg, 0.4 mmol, 2.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that methyl acrylate (**2**, 25.8 mg, 0.30 mmol, 1.5 equiv) in DCE (1.0 mL) was injected into the test tube via syringe under N_2 atmosphere. The reaction mixture could stir at 50 °C for 12 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **3a'** (31.9 mg, 65%).

Methyl (2E,4Z)-4-benzoyl-5-(methylamino)penta-2,4-dienoate (3a'):



Flash chromatography: PE/EA (3:1)

Afford the desired product **3a'** as a yellow solid (31.9 mg, 65%). mp: 128.7-129.8 °C.

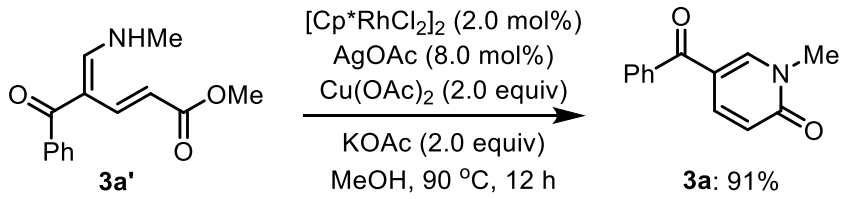
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.01 (s, 1H), 7.62 – 7.55 (m, 2H), 7.47 – 7.44 (m, 2H), 7.44 – 7.37 (m, 3H), 5.59 (d, *J* = 15.7 Hz, 1H), 3.65 (s, 3H), 3.20 (dd, *J* = 5.1, 0.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.2, 168.5, 157.6, 145.4, 140.4, 130.5, 128.4, 128.1, 105.4,

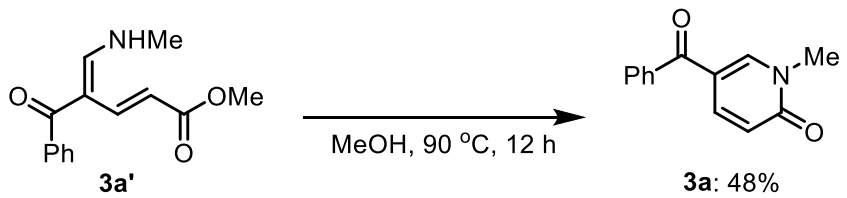
103.4, 51.4, 36.6.

HRMS (ESI, m/z): Calcd. for $C_{14}H_{16}NO_3$: $[M+H]^+$, 246.1130. Found: *m/z* 246.1128.

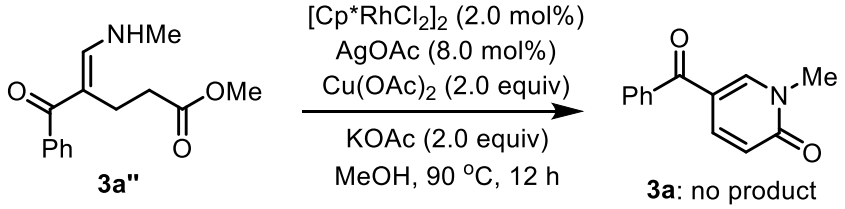
6.2 Experiments of intermediate cyclization



To a 10 mL Schlenk flask equipped with magnetic stirring bar was added methyl (2*E*,4*Z*)-4-benzoyl-5-(methylamino)penta-2,4-dienoate (**3a'**, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mg, 0.004 mmol), AgOAc (2.7 mg, 0.016 mmol, 0.08 equiv), $Cu(OAc)_2$ (72.6 mg, 4.0 mmol, 2.0 equiv), KOAc (39.3 mg, 4.0 mmol, 2.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that MeOH (1.0 mL) was injected into the test tube via syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 90 °C for 12 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **3a** (38.8 mg, 91%).

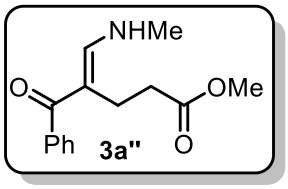


To a 10 mL Schlenk flask equipped with magnetic stirring bar was added methyl (2*E*,4*Z*)-4-benzoyl- 5-(methylamino)penta-2,4-dienoate (**3a'**, 0.2 mmol, 1.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that MeOH (1.0 mL) was injected into the test tube via syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 90 °C for 12 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **3a** (20.5 mg, 48%).



To a 10 mL Schlenk flask equipped with magnetic stir bar was added methyl (2*E*,4*Z*)-4-benzoyl-5-(methylamino)penta-2,4-dienoate (**3a''**, 0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (2.5 mg, 0.004 mmol), AgOAc (2.7 mg, 0.016 mmol, 0.08 equiv), $Cu(OAc)_2$ (72.6 mg, 4.0 mmol, 2.0 equiv), KOAc (39.3 mg, 4.0 mmol, 2.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that MeOH (1.0 mL) was injected into the test tube via syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 90 °C for 12 h, during which time a constant checking by TLC was performed.

Methyl (*Z*)-4-benzoyl-5-(methylamino)pent-4-enoate (3a''):



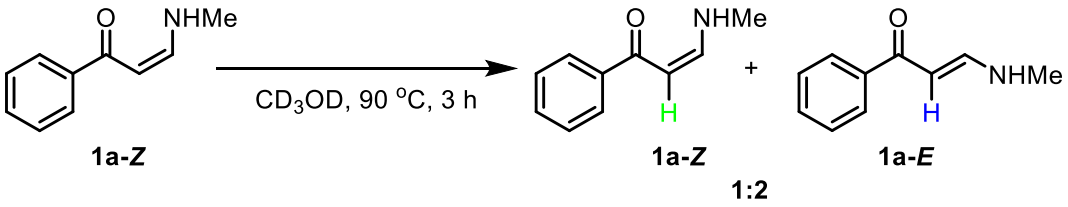
Flash chromatography: PE/EA (5:1)

Afford the desired product **3a''** as a yellow liquid (44.5 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.77 (s, 1H), 7.47 – 7.35 (m, 3H), 5.73 (d, *J* = 12.5 Hz, 1H), 3.69 (s, 3H), 3.60 (s, 2H), 3.01 (d, *J* = 74.3 Hz, 3H), 2.62 (t, *J* = 6.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.0, 171.4, 153.6, 140.4, 131.2, 128.3, 127.6, 93.2, 53.6, 52.2, 35.8, 33.9.

6.3 Deuterated experiments



To a 10 mL Schlenk flask equipped with magnetic stirring bar was added (*Z*)-3-(methylamino) -1-phenylprop-2-en-1-one (**1a**, 0.1 mmol, 1.0 equiv). Then the mixture was evacuated and backfilled with N_2 three times. After that CD_3OD (0.5 mL) was injected into the test tube *via* syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 90 °C for 3 h, the resulting reaction mixture was directly detected by NMR.

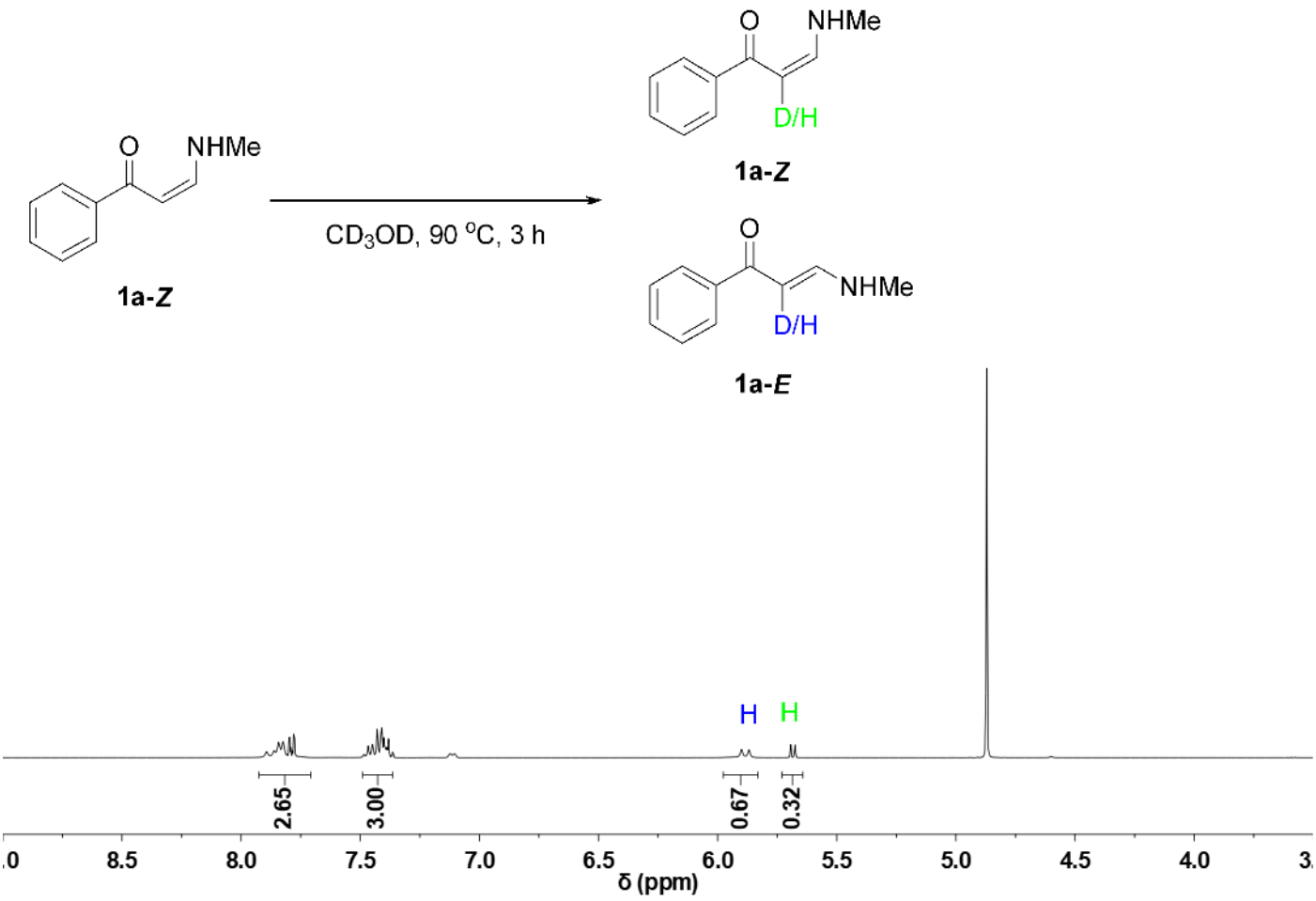
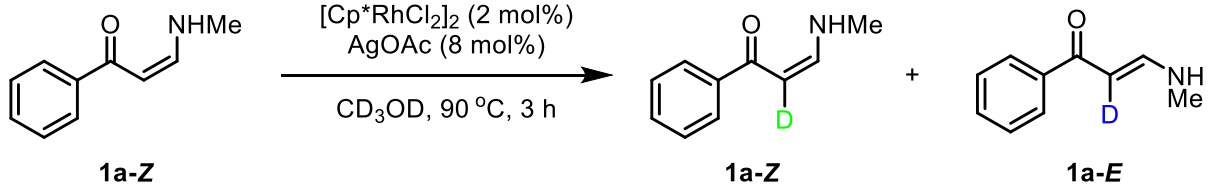


Fig. S1 ^{1}H-NMR of **1a** in CD_3OD



To a 10 mL Schlenk flask equipped with magnetic stirring bar was added (*Z*)-3-(methylamino) -1-phenylprop-2-en-1-one (**1a**, 0.1 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (1.2 mg, 0.002 mmol), AgOAc (1.3 mg, 0.008 mmol). Then the mixture was evacuated and backfilled with N_2 three times. After that CD_3OD (0.5 mL) was injected into the test tube via syringe under N_2 atmosphere. The reaction mixture was allowed to stir at 90 °C for 3 h, the

resulting reaction mixture was directly detected by NMR.

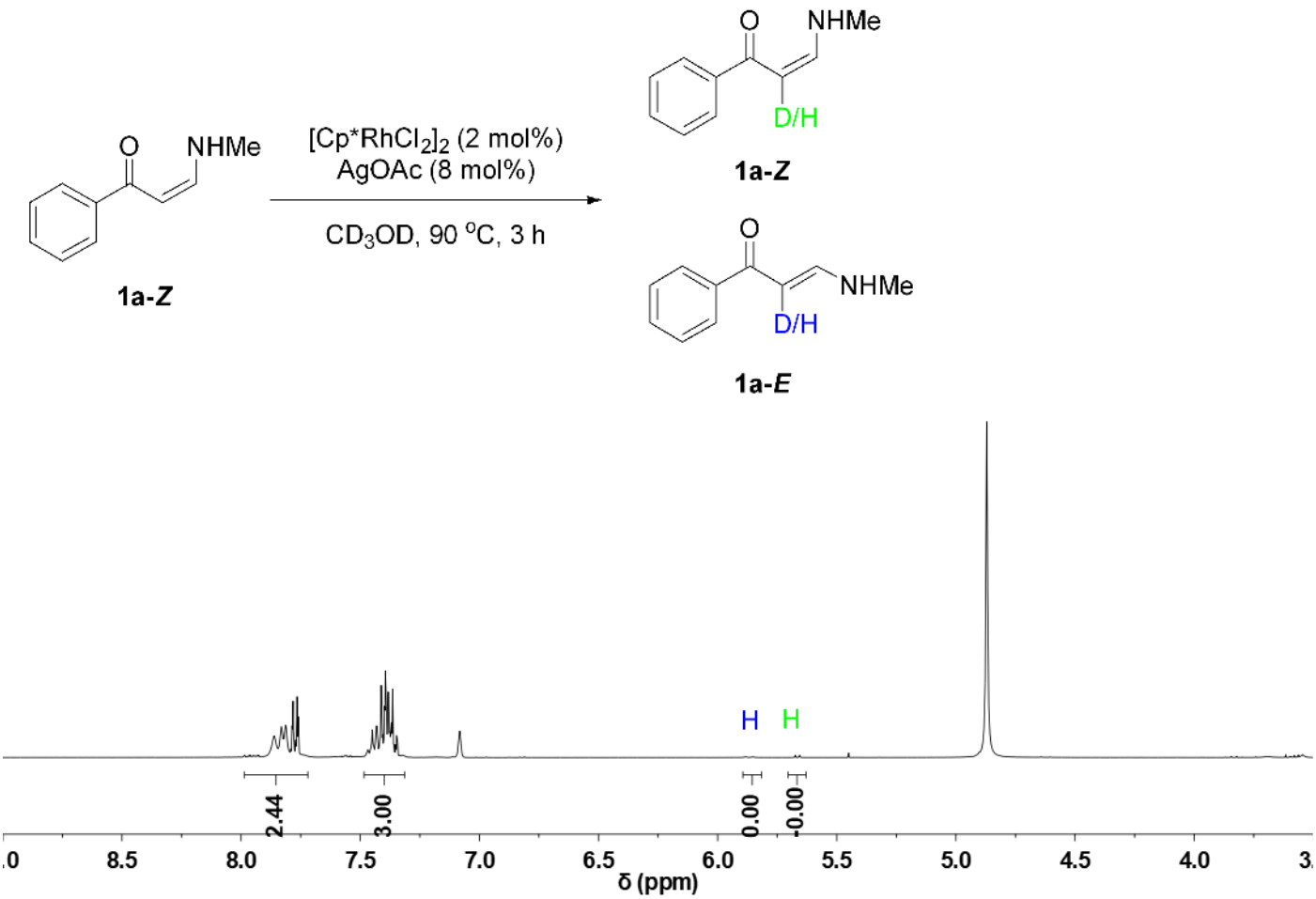


Fig. S2 Deuteration experiments of **1a**

Deuteration experiments were detected by ^{1}H NMR in CD_3OD as shown in **Fig. S1**. Enaminone **1a** with *Z* configuration can be converted to one with *E* configuration in CD_3OD at 90 °C for 3h. **Fig. S2** under $[Cp^*RhCl_2]_2$ and AgOAc catalytic system, hydrogen of enaminone **1a** at *α*-position can be almost completely deuterated.

7. References

1. S. Zhou, J. Wang, L. Wang, C. Song, K. Chen and J. Zhu, *Angew. Chem. Int. Ed., 2*016, **55**, 9384-9388.

2. A. S. Devi, M. C. Dutta, R. Nongkhlaw and J. N. Vishwakarma, *J. Indian. Chem. Soc*., 2010, **87**, 739-742.

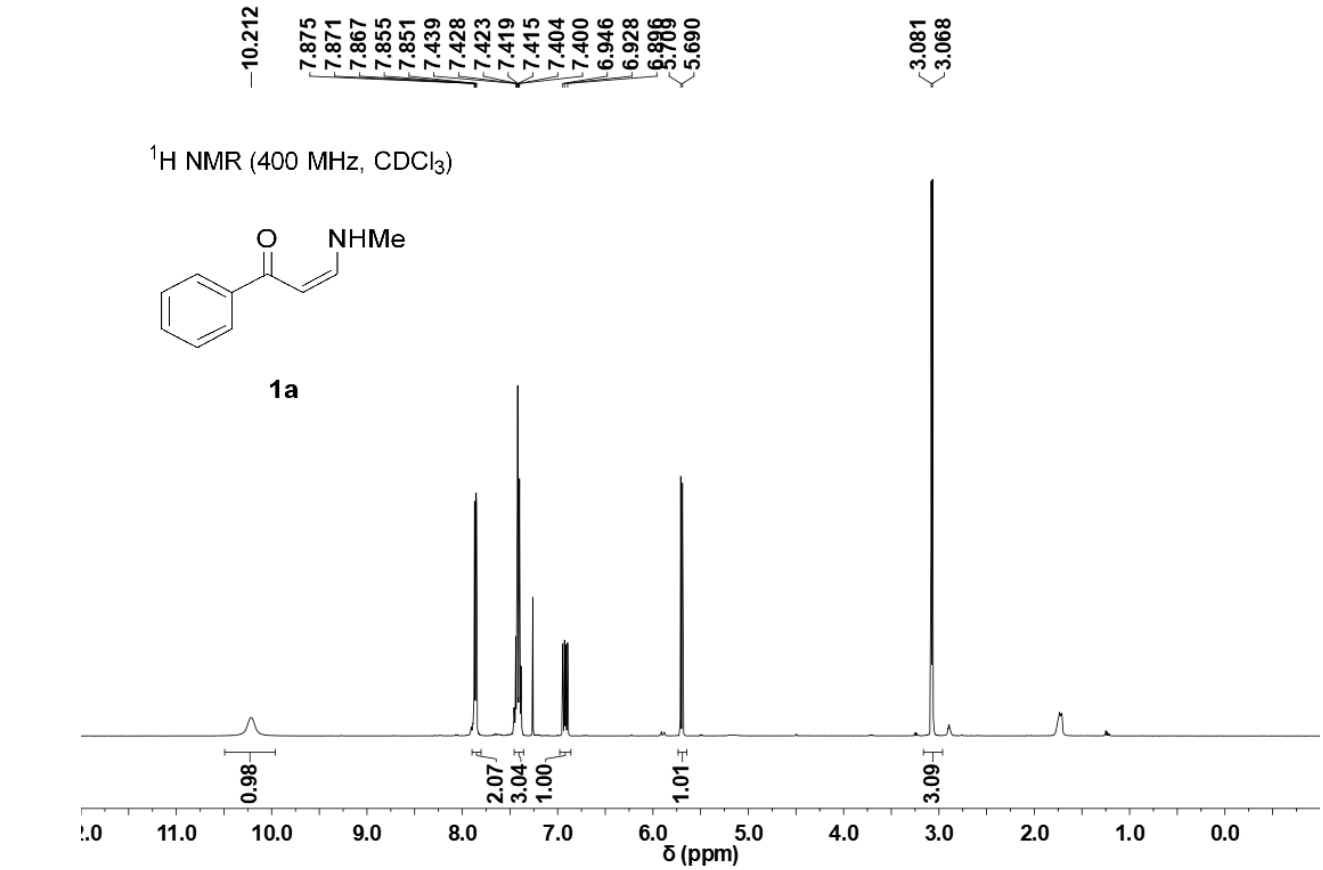
3. A. D. N. Brenno, A. M. L. Alexandre, B. B. Alinne and R. Dennis, *Tetrahedron.*, 2009, **65**, 2484-2496.

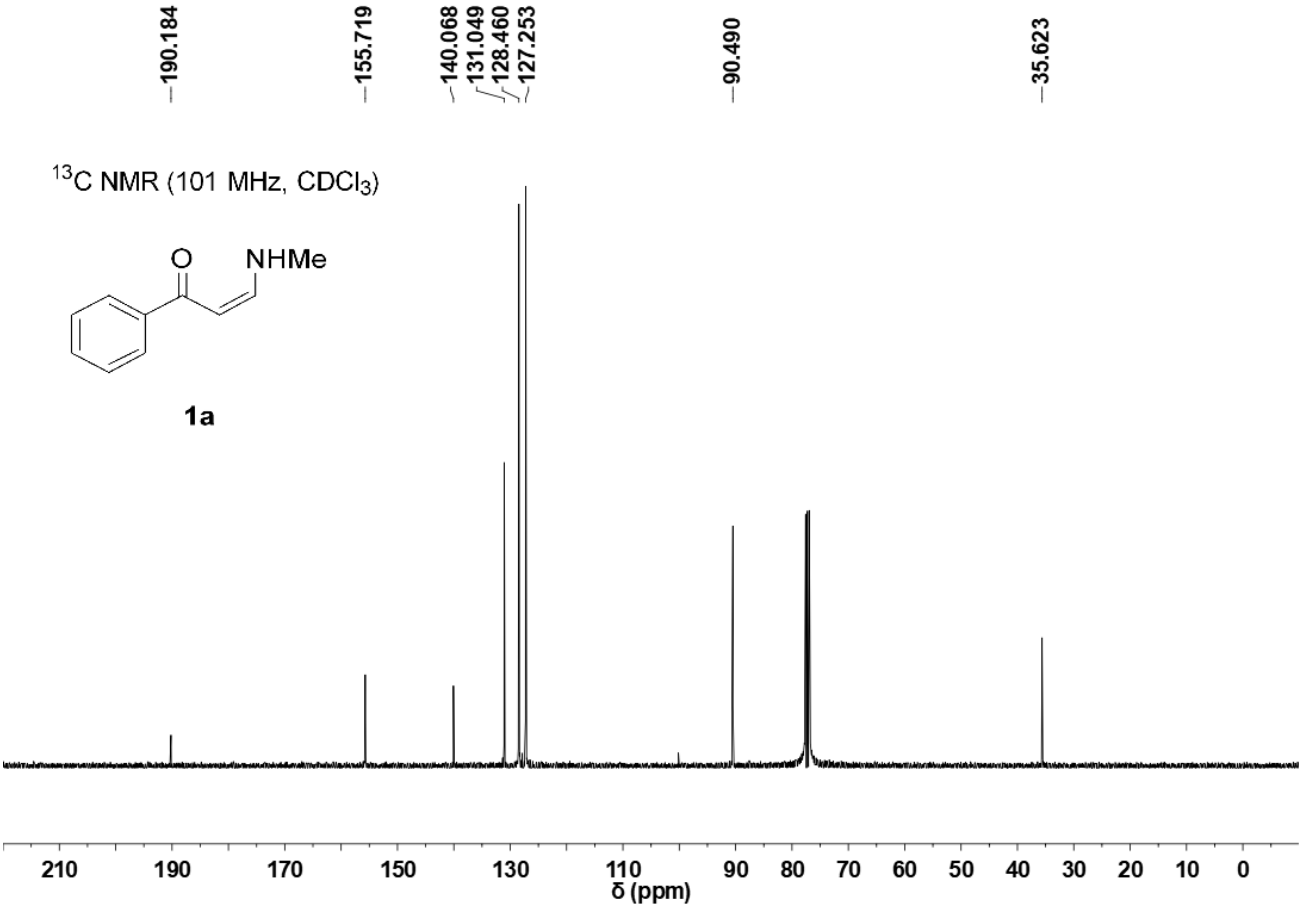
4. E. Philipped, B.Aniel, P. C. Jean, L. Gérard, *Can. J. Chem.*, 1991, **69**, 1201-1206.

5. P. Šimůnek, M. Svobodová, V. Bertolasi, V. Macháček, *Synthesis*, **2008**, *11*, 1761-1766.

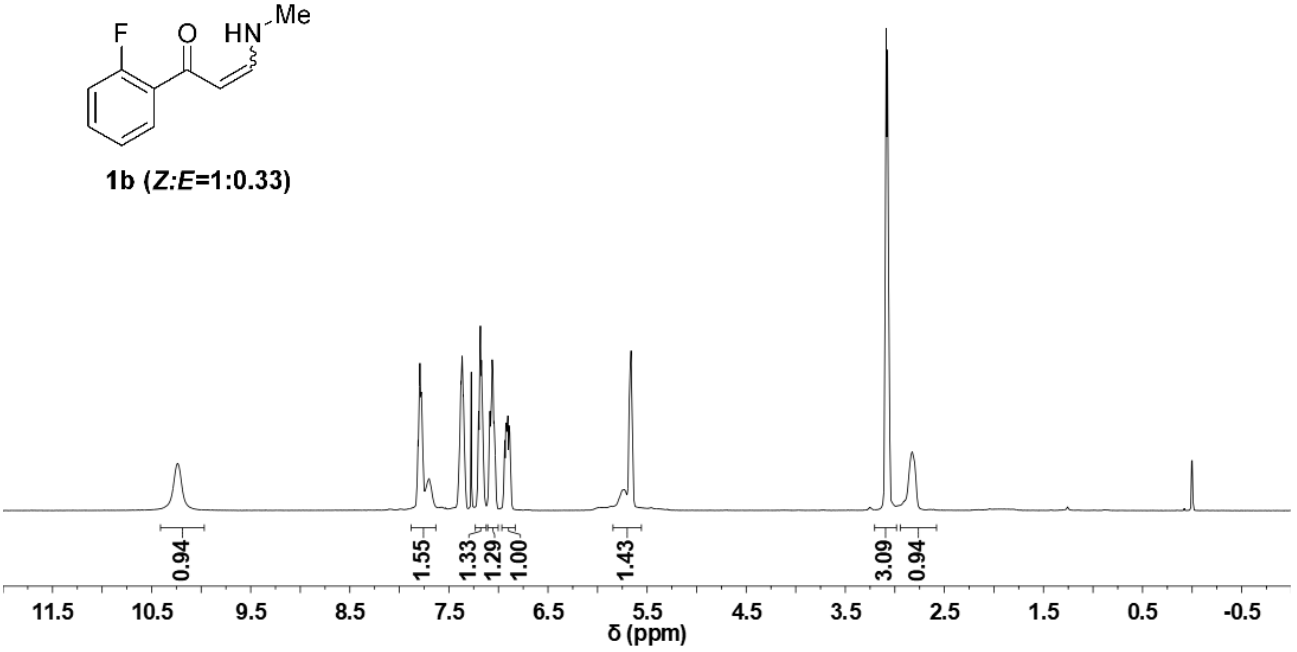
6. B. Pettersson, V. Hasimbegovic, J. Bergman, *J. Org. Chem.* **2011**, *76*, 1554-1561.

8. ^{1}H and ^{13}C NMR spectra

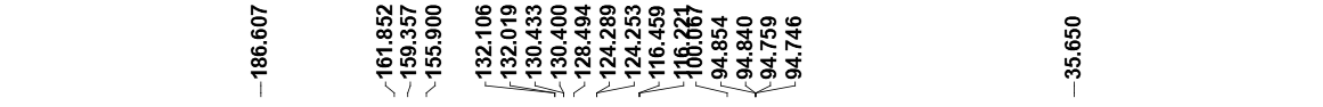




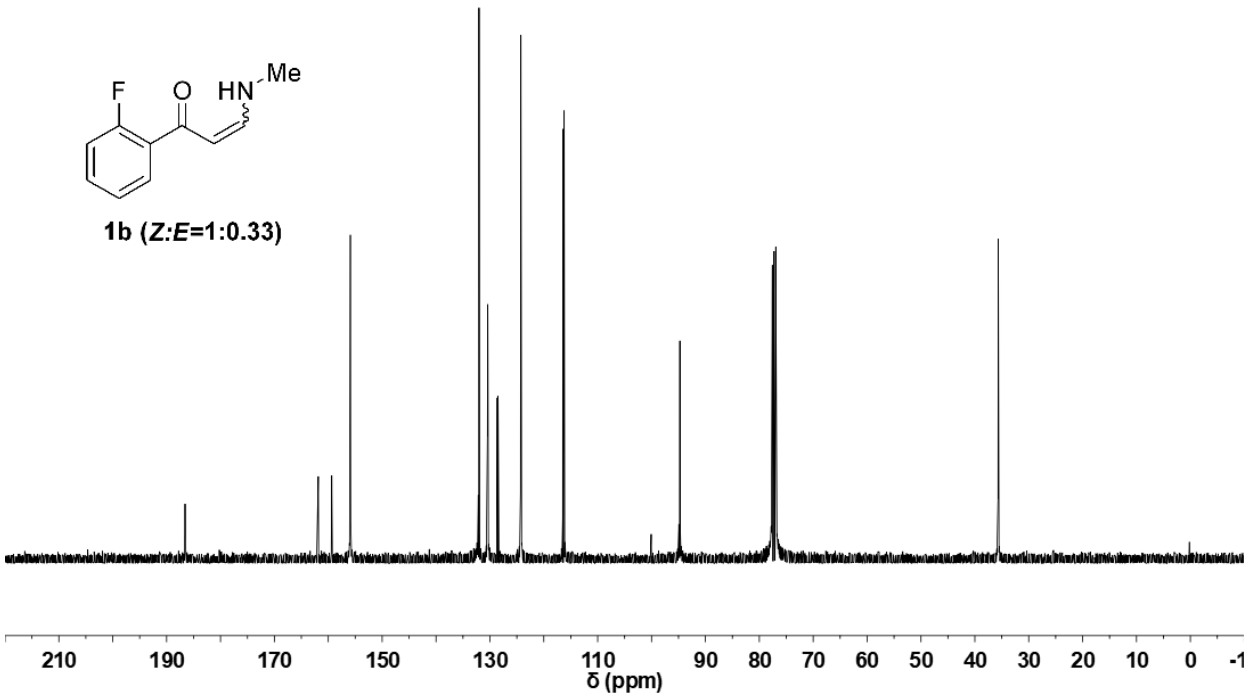
^{1}H NMR (400 MHz, $CDCl_3$)



1b (*Z*:*E*=1:0.33)

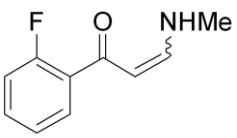


^{13}C NMR (101 MHz, $CDCl_3$)

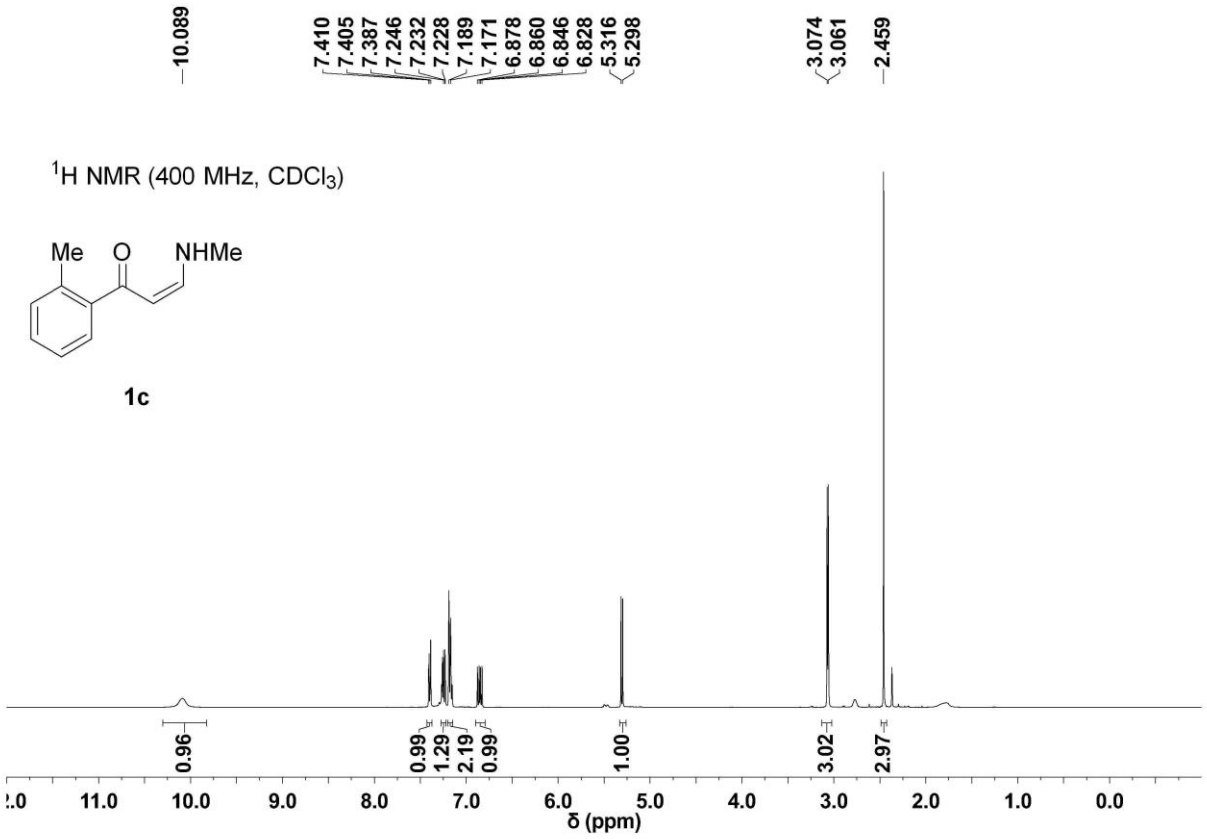


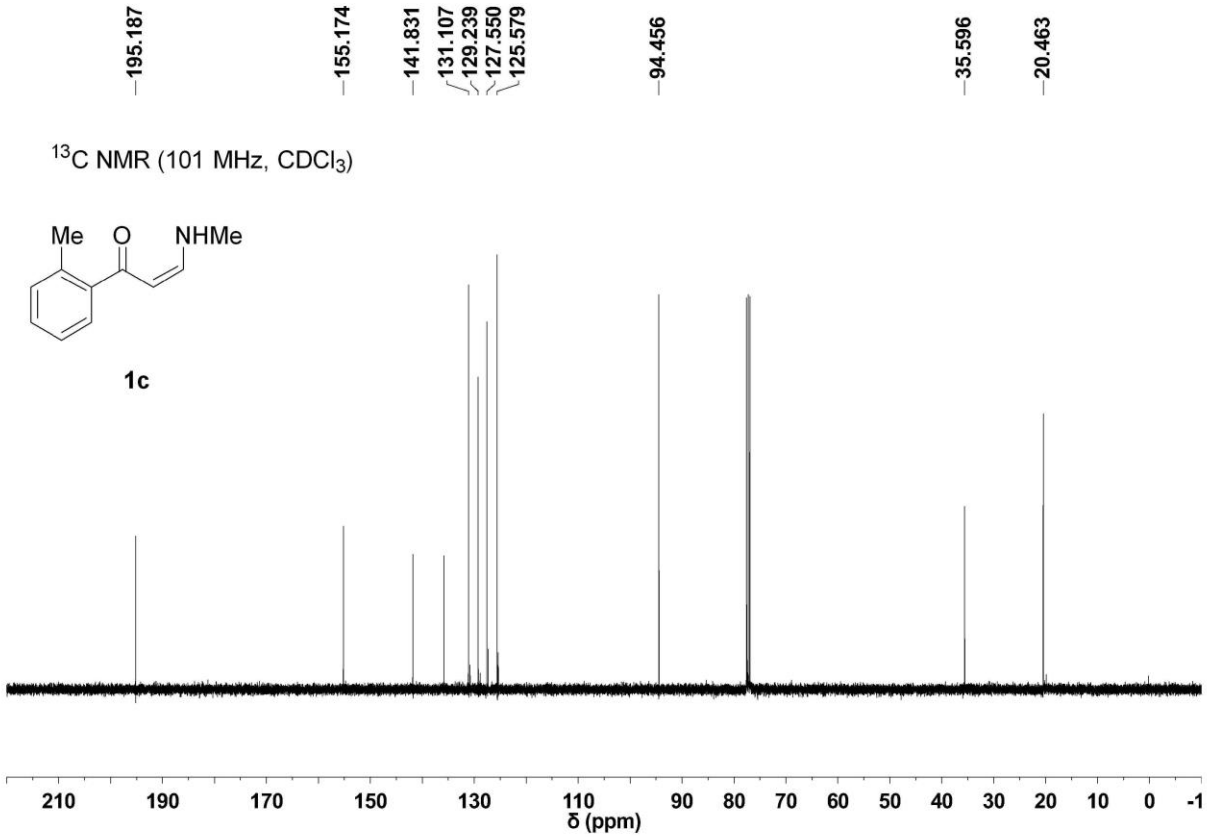
1b (*Z*:*E*=1:0.33)

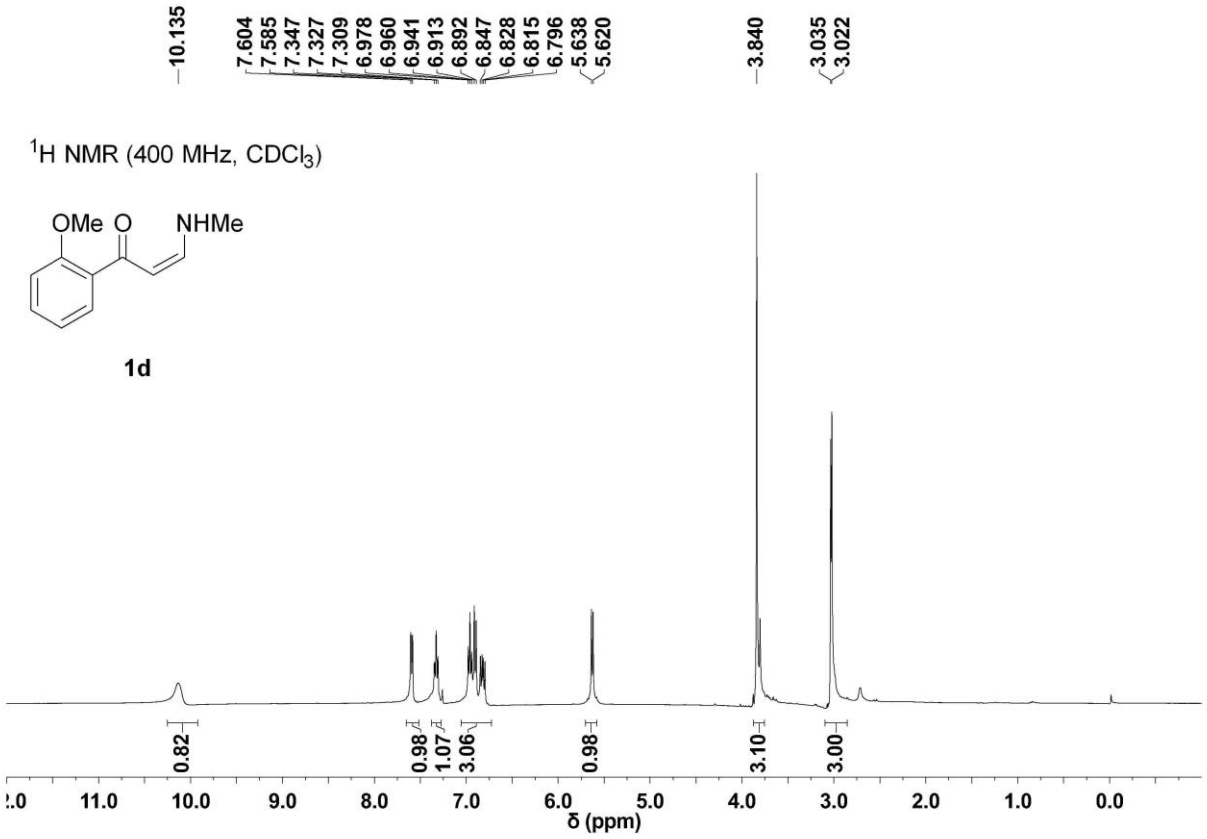
^{19}F NMR (471 MHz, $CDCl_3$)

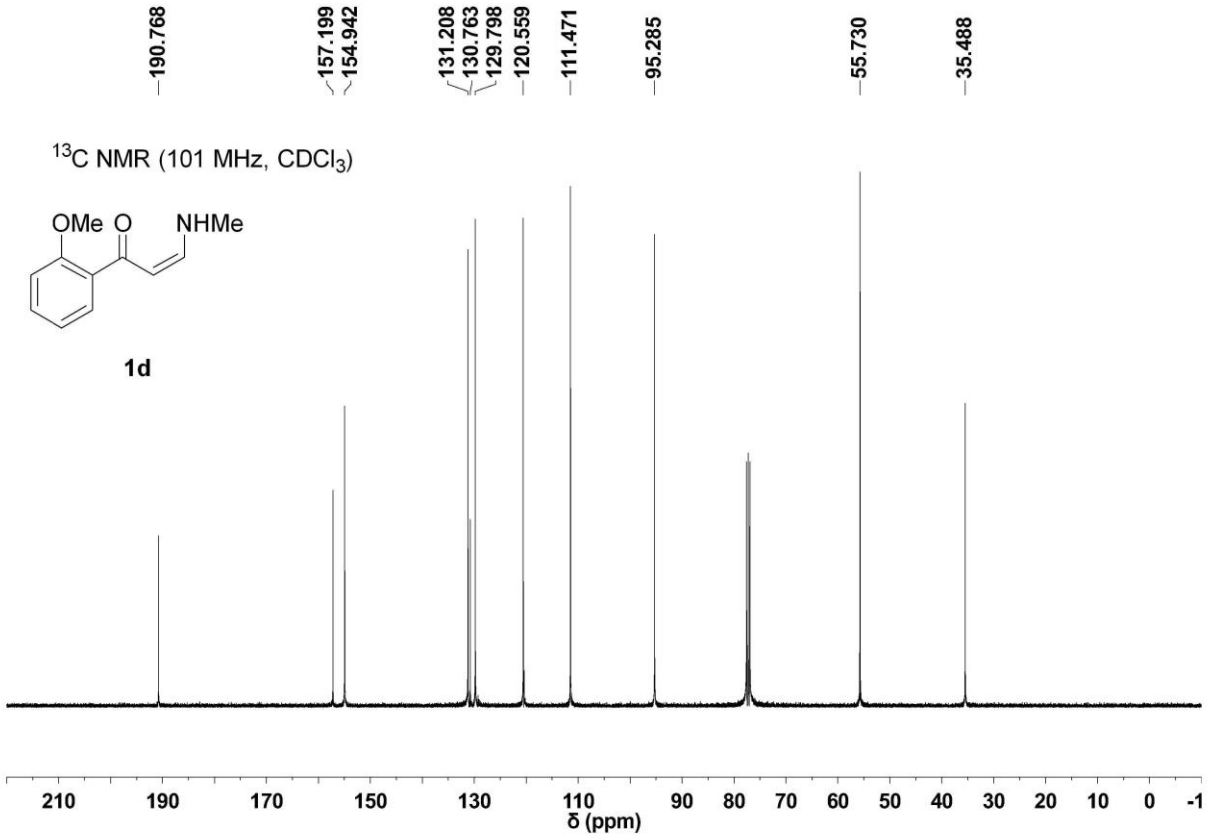


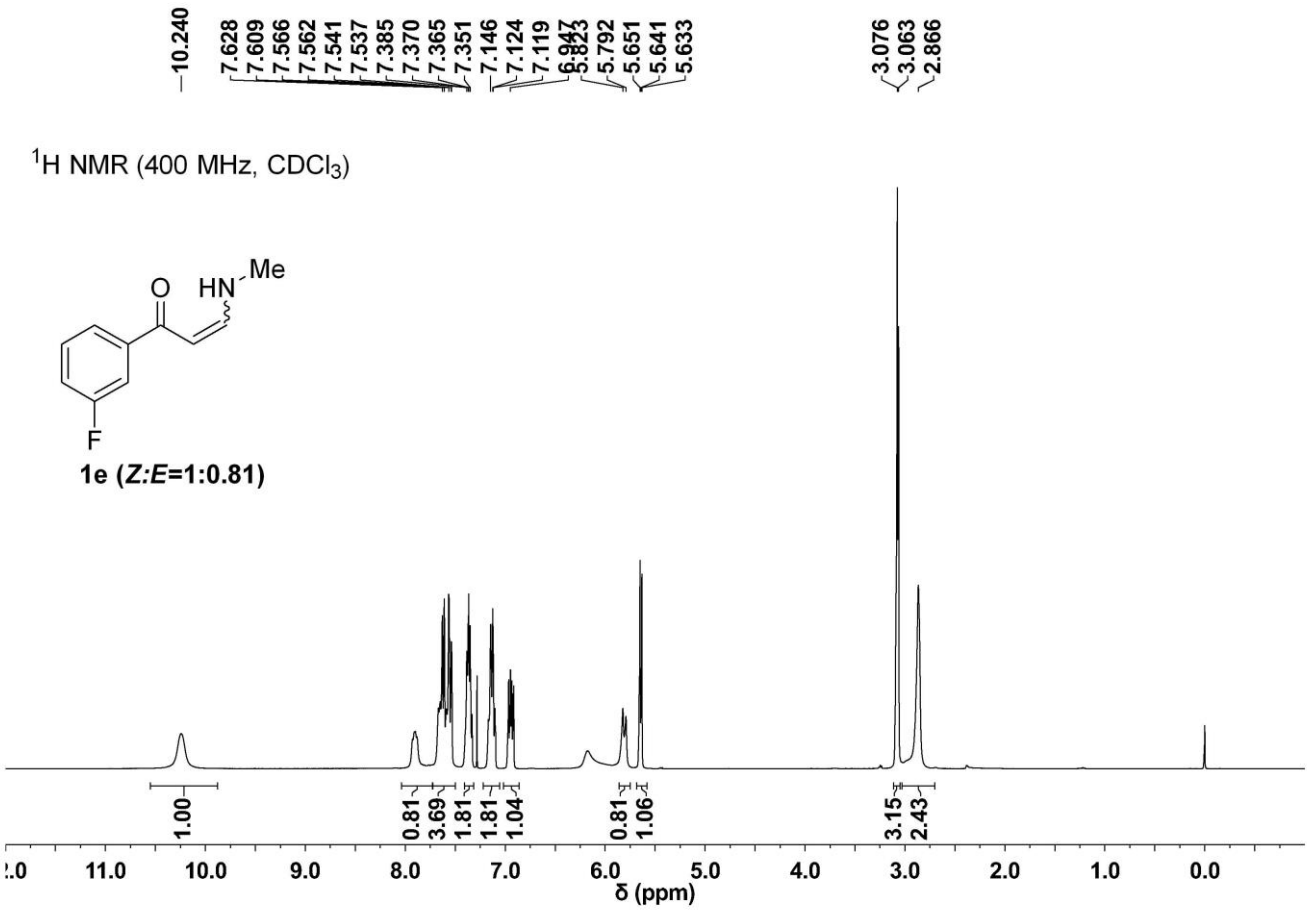
1b

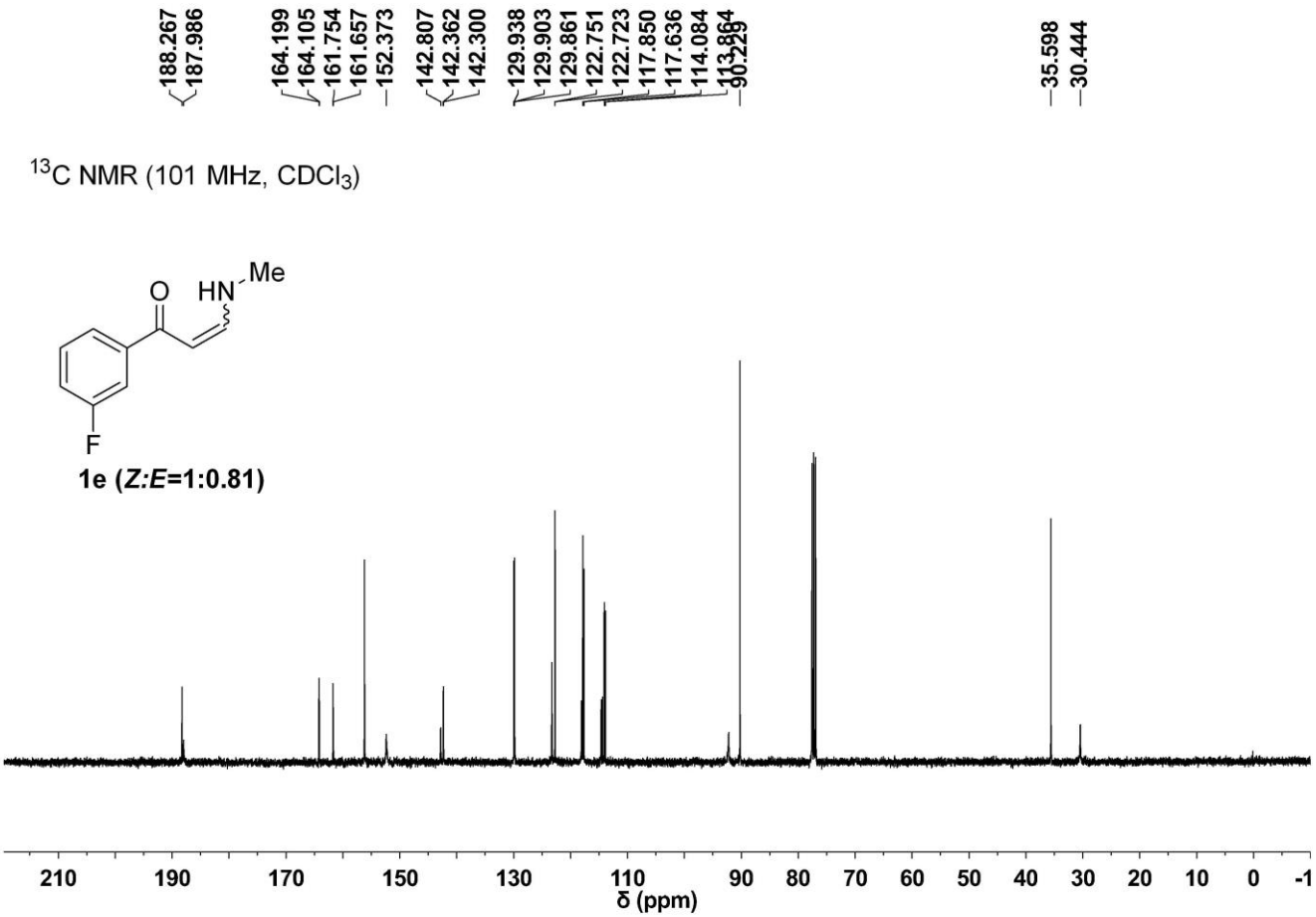

10.089
7.410
7.405
7.387
7.246
7.232
7.228
7.189
7.171
6.878
6.860
6.846
6.828
5.316
5.298
3.074
3.061
2.459
^{1}H NMR (400 MHz, $CDCl_3$)
Me
O
NHMe
1c
0.96
0.99
1.29
2.19
0.99
1.00
3.02
2.97
δ (ppm)


195.187
155.174
141.831
131.107
129.239
127.550
125.579
94.456
35.596
20.463
^{13}C NMR (101 MHz, $CDCl_3$)
Me
O
NHMe
1c
δ (ppm)


10.135
7.604
7.585
7.347
7.327
7.309
6.978
6.960
6.941
6.913
6.892
6.847
6.828
6.815
6.796
5.638
5.620
3.840
3.035
3.022
1H NMR (400 MHz, CDCl3)
OMe O
NHMe
1d
0.82
0.98
1.07
3.06
0.98
3.10
3.00
δ (ppm)

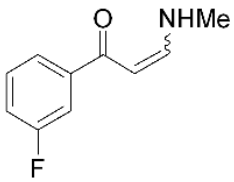

190.768
157.199
154.942
131.208
130.763
129.798
120.559
111.471
95.285
55.730
35.488
13C NMR (101 MHz, CDCl3)
OMe O
NHMe
1d
δ (ppm)


10.240
7.628
7.609
7.566
7.562
7.541
7.537
7.385
7.370
7.365
7.351
7.146
7.124
7.119
6.947
5.823
5.792
5.651
5.641
5.633
3.076
3.063
2.866
1H NMR (400 MHz, CDCl3)
O
HN
Me
F
1e (Z:E=1:0.81)
1.00
0.81
3.69
1.81
1.81
1.04
0.81
1.06
3.15
2.43
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

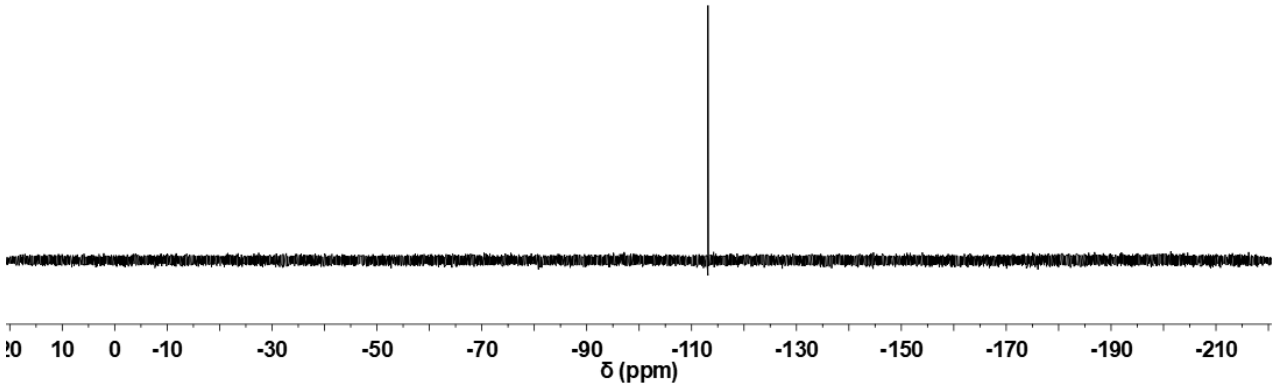

188.267
187.986
164.199
164.105
161.754
161.657
152.373
142.807
142.362
142.300
129.938
129.903
129.861
122.751
122.723
117.850
117.636
114.084
113.864
90.229
35.598
30.444
13C NMR (101 MHz, CDCl3)
O
HN
Me
F
1e (Z:E=1:0.81)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

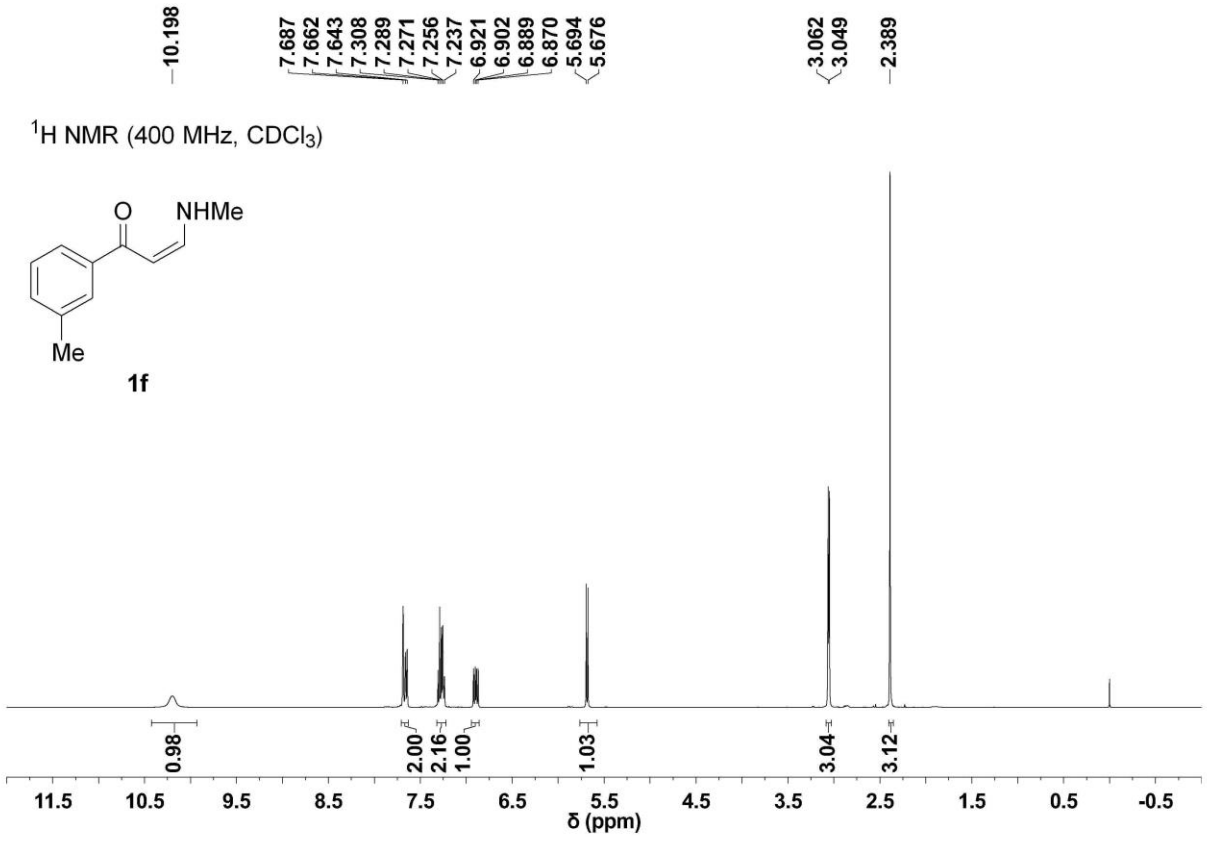
-113.136

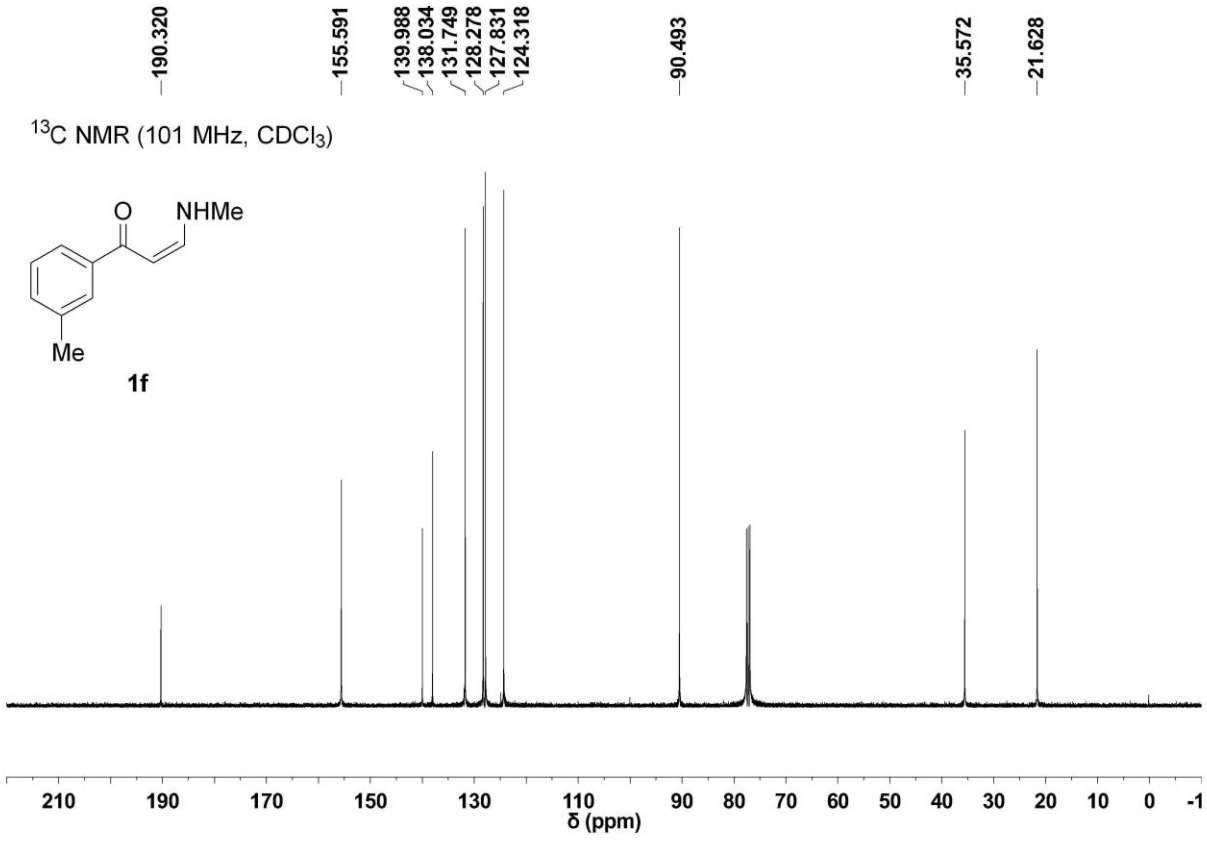
^{19}F NMR (471 MHz, $CDCl_3$)

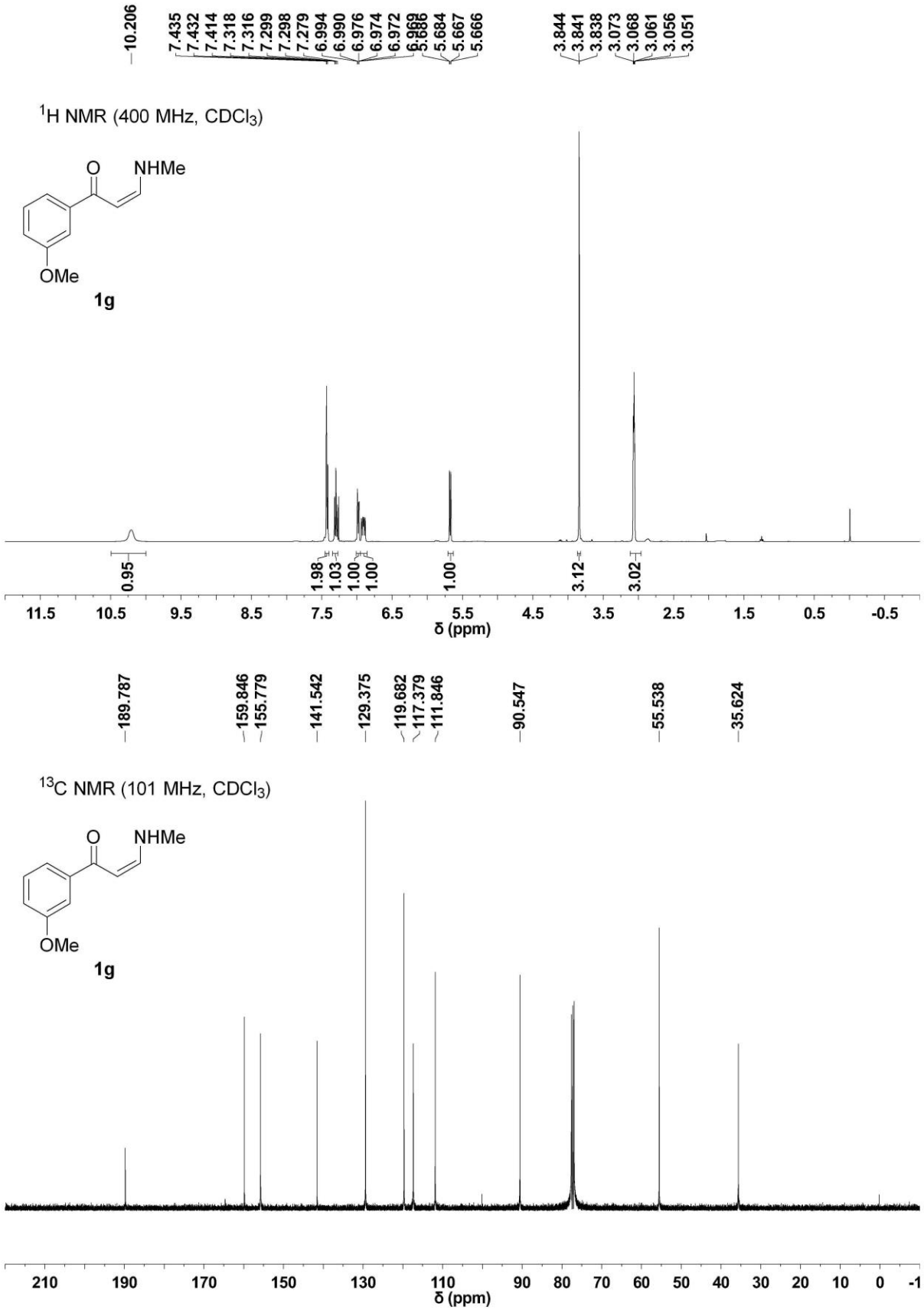


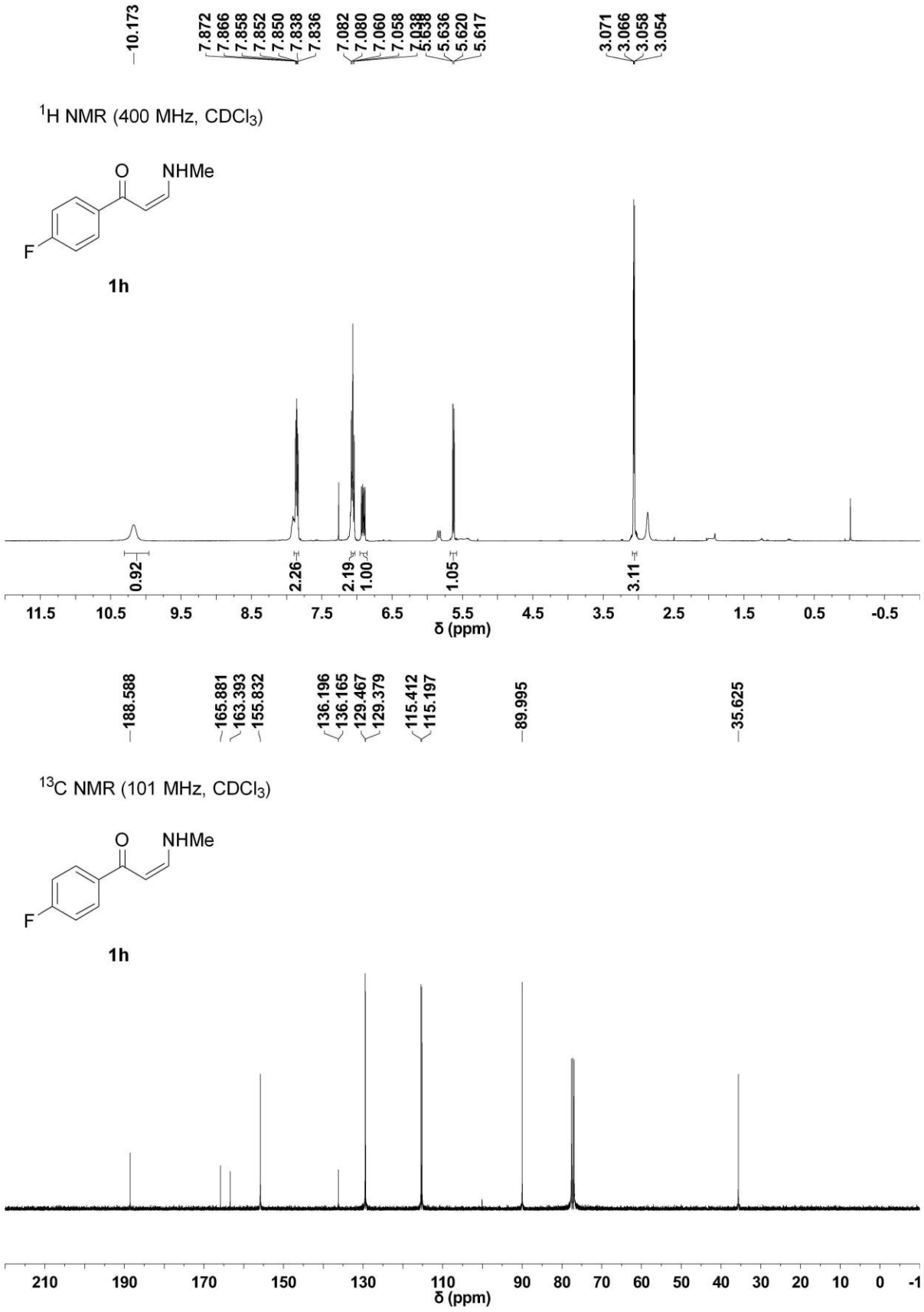
1e




10.198
7.687
7.662
7.643
7.308
7.289
7.271
7.256
7.237
6.921
6.902
6.889
6.870
5.694
5.676
3.062
3.049
2.389
1H NMR (400 MHz, CDCl3)
O
NHMe
Me
1f
0.98
2.00
2.16
1.00
1.03
3.04
3.12
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

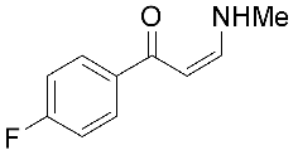

190.320
155.591
139.988
138.034
131.749
128.278
127.831
124.318
90.493
35.572
21.628
13C NMR (101 MHz, CDCl3)
O
NHMe
Me
1f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)


10.206
7.435
7.432
7.414
7.318
7.316
7.299
7.298
7.279
6.994
6.990
6.976
6.974
6.972
5.684
5.667
5.666
3.844
3.841
3.838
3.073
3.068
3.061
3.056
3.051
1H NMR (400 MHz, CDCl3)
O
NHMe
OMe
1g
0.95
1.98
1.03
1.00
1.00
1.00
3.12
3.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
189.787
159.846
155.779
141.542
129.375
119.682
117.379
111.846
90.547
55.538
35.624
13C NMR (101 MHz, CDCl3)
O
NHMe
OMe
1g
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

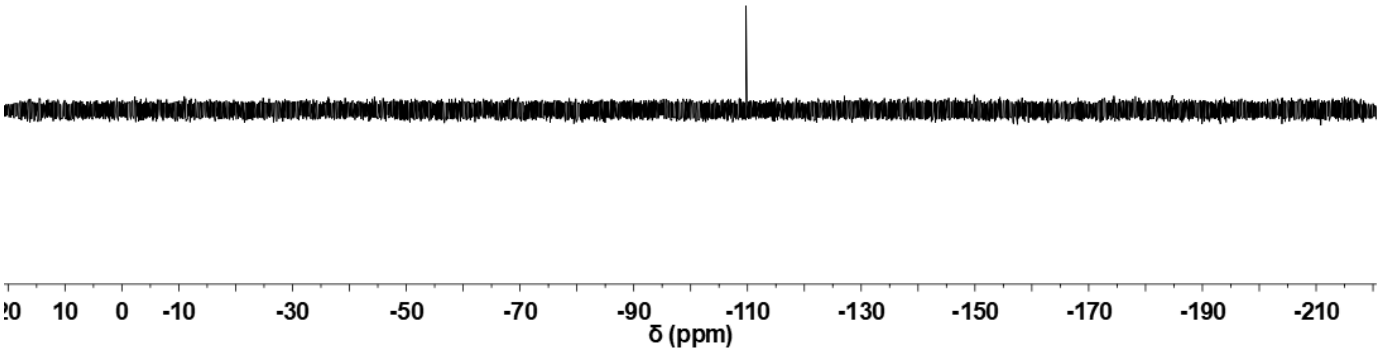

10.173
7.872
7.866
7.858
7.852
7.850
7.838
7.836
7.082
7.080
7.060
7.058
7.038
5.636
5.620
5.617
3.071
3.066
3.058
3.054
1H NMR (400 MHz, CDCl3)
O
NHMe
F
1h
0.92
2.26
2.19
1.00
1.05
3.11
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
188.588
165.881
163.393
155.832
136.196
136.165
129.467
129.379
115.412
115.197
89.995
35.625
13C NMR (101 MHz, CDCl3)
O
NHMe
F
1h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

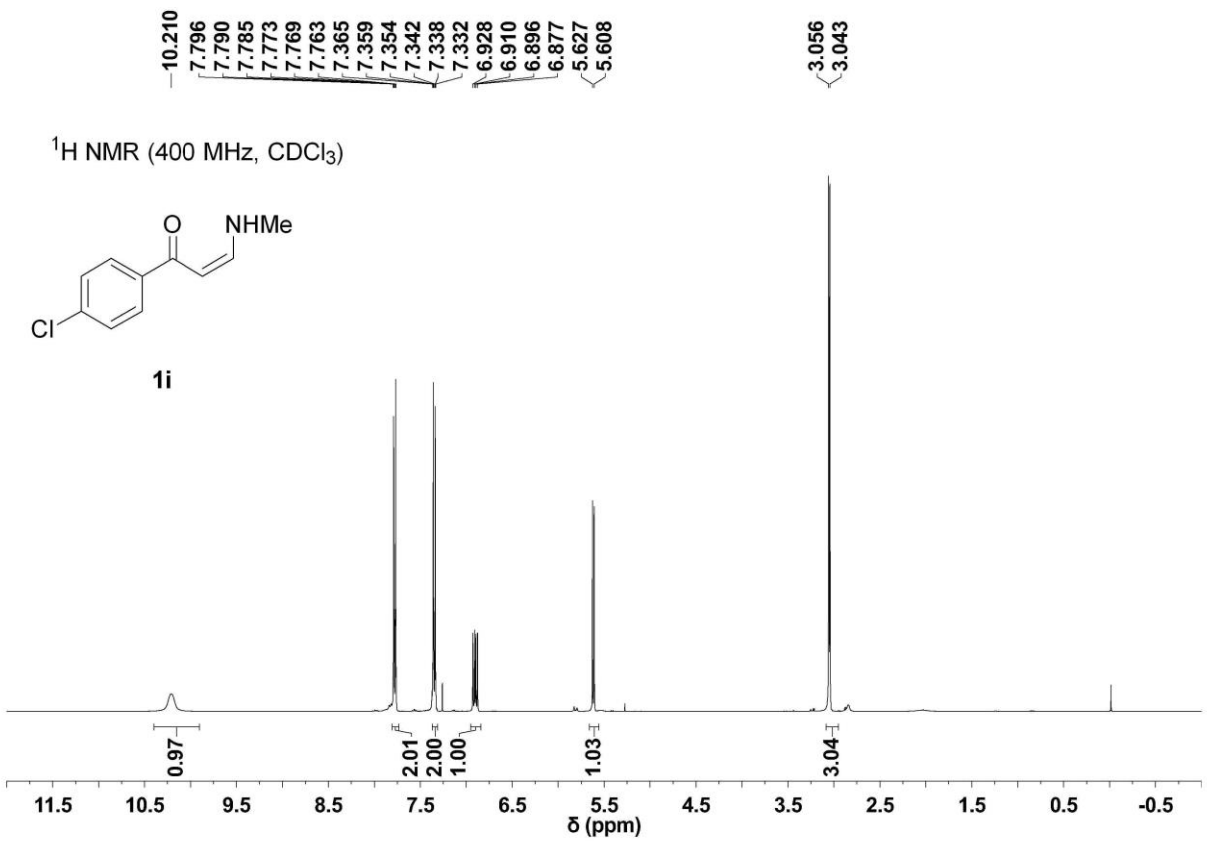
-109.750

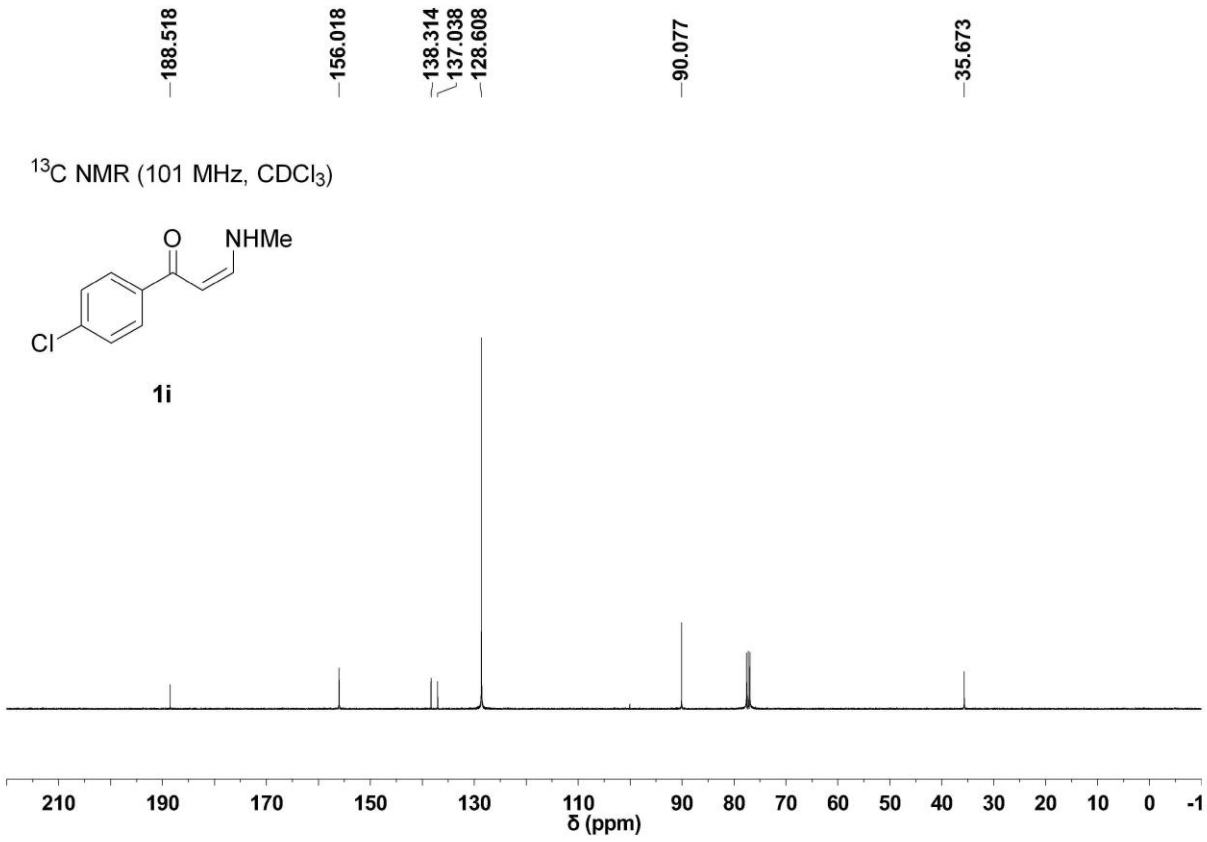
^{19}F NMR (471 MHz, $CDCl_3$)

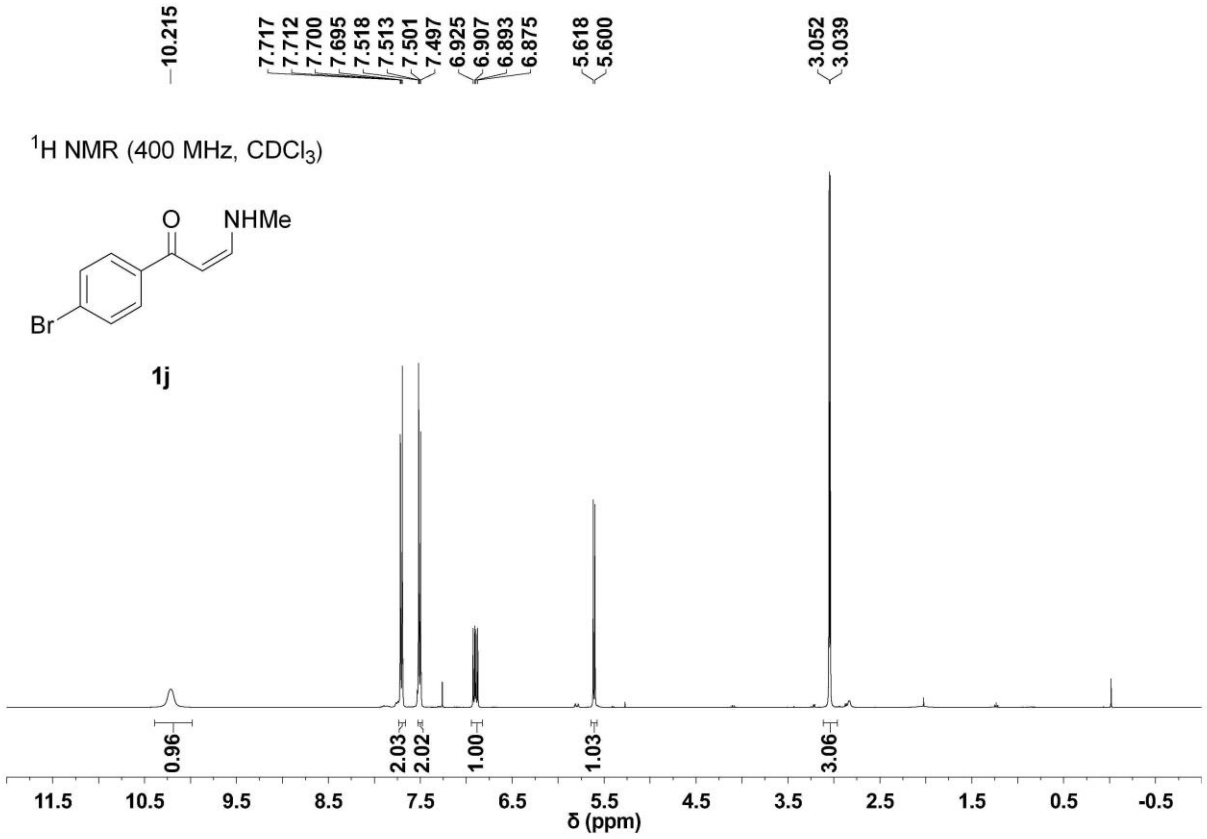


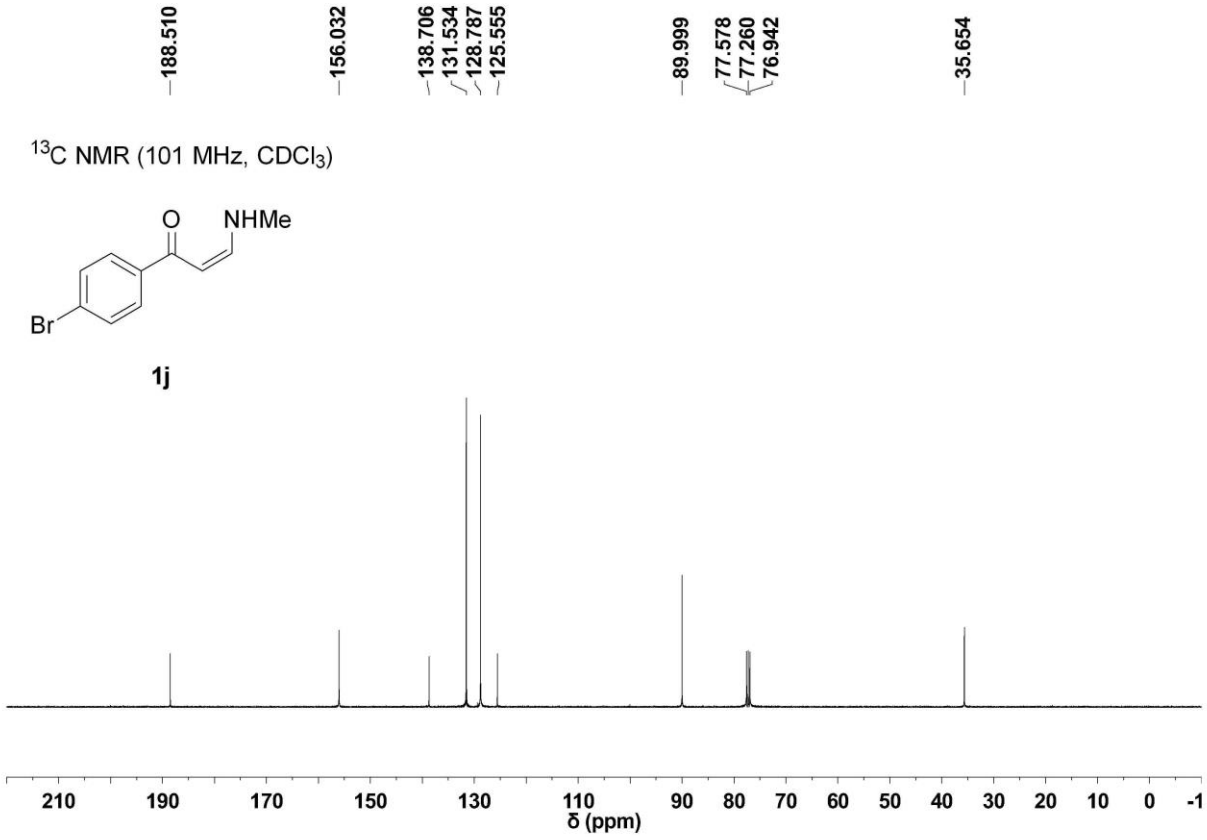
1h

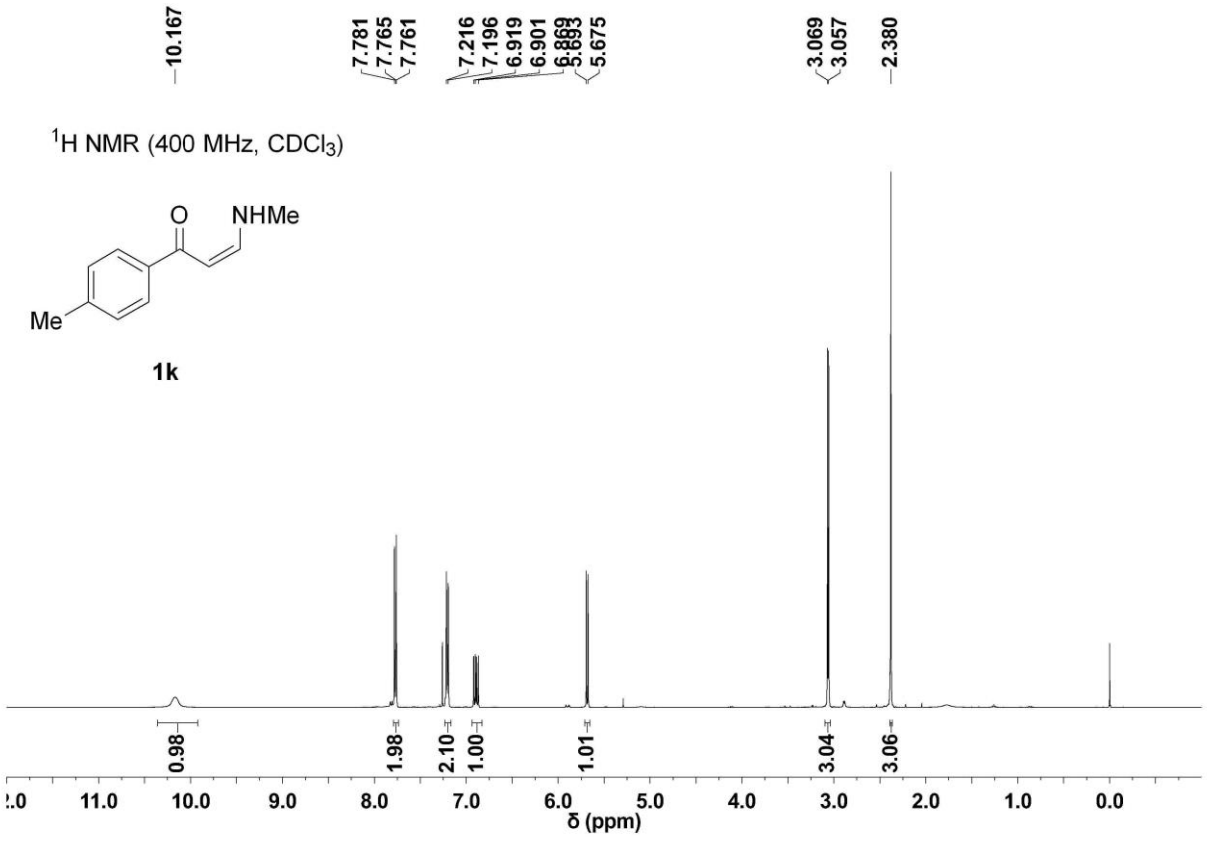


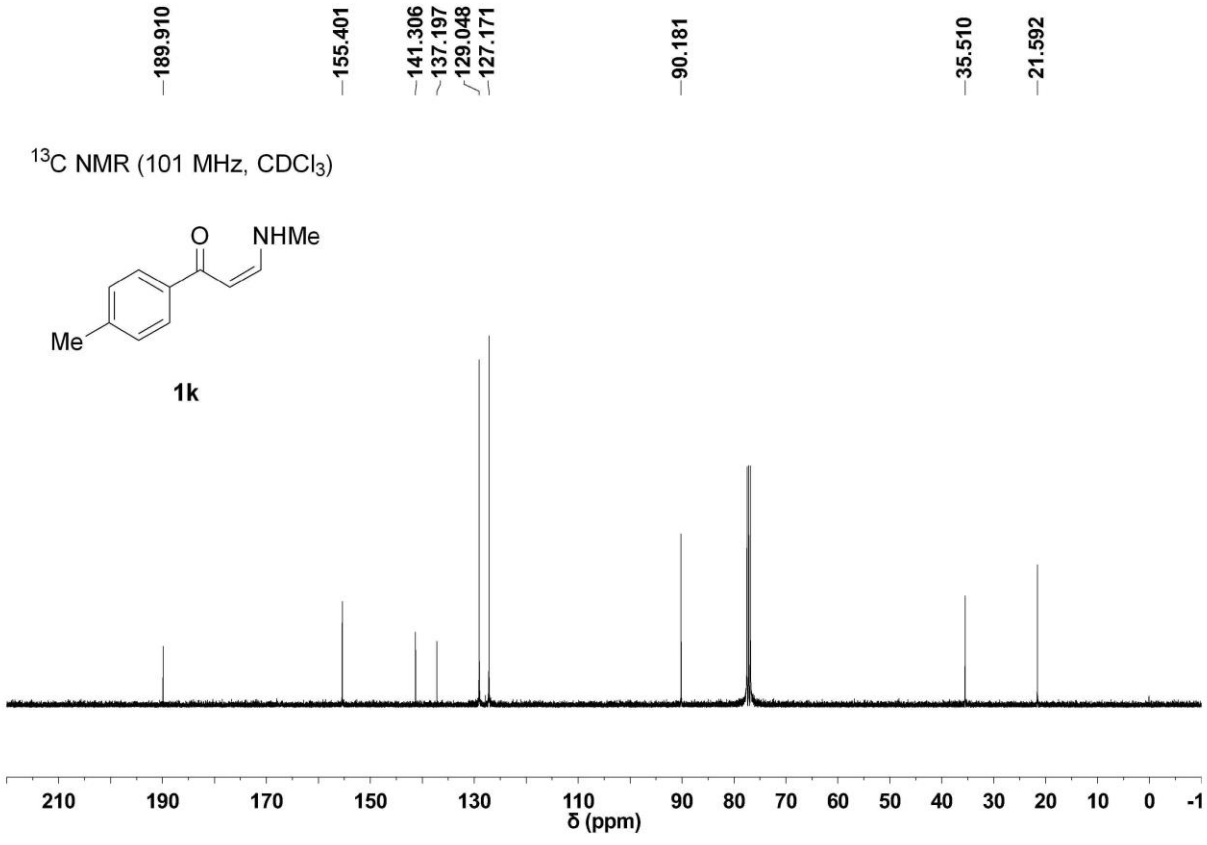

10.210
7.796
7.790
7.785
7.773
7.769
7.763
7.365
7.359
7.354
7.342
7.338
7.332
6.928
6.910
6.896
6.877
5.627
5.608
3.056
3.043
1H NMR (400 MHz, CDCl3)
O
NHMe
Cl
1i
0.97
2.01
2.00
1.00
1.03
3.04
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

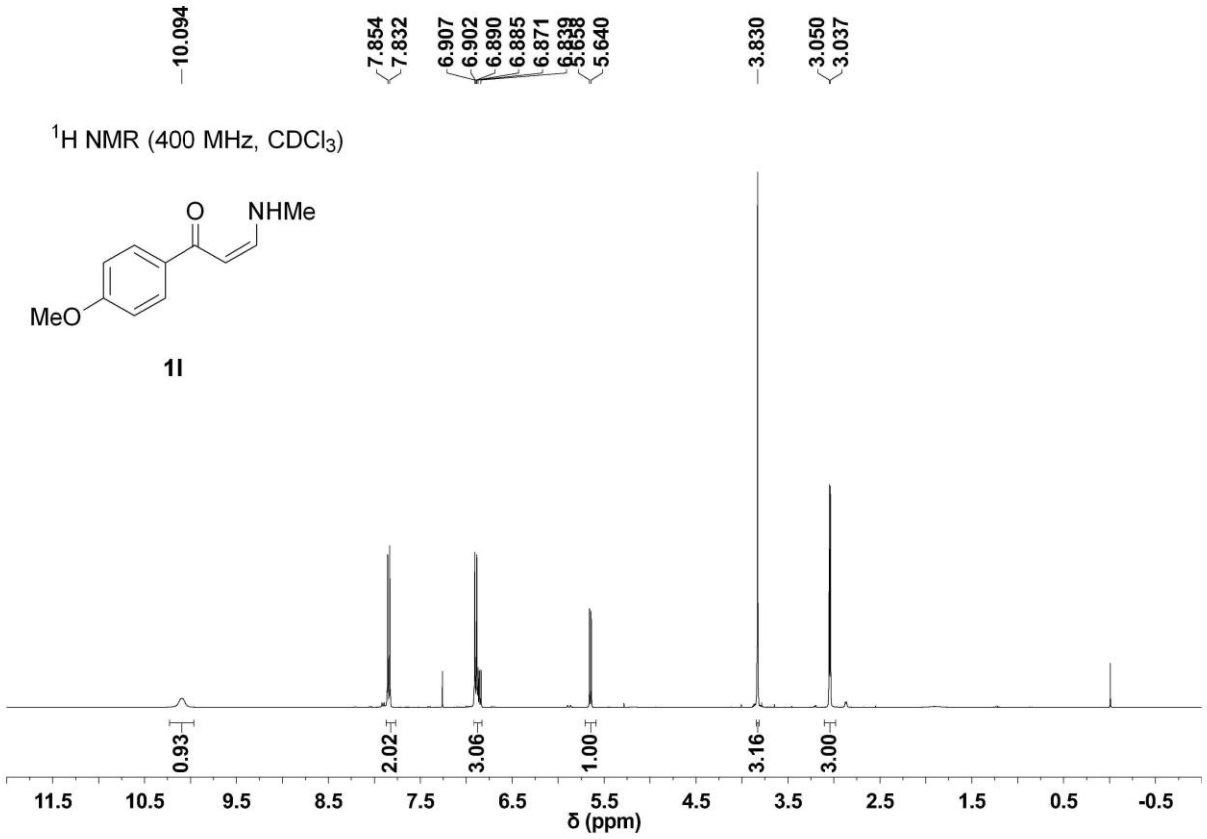

188.518
156.018
138.314
137.038
128.608
90.077
35.673
13C NMR (101 MHz, CDCl3)
O
NHMe
Cl
1i
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

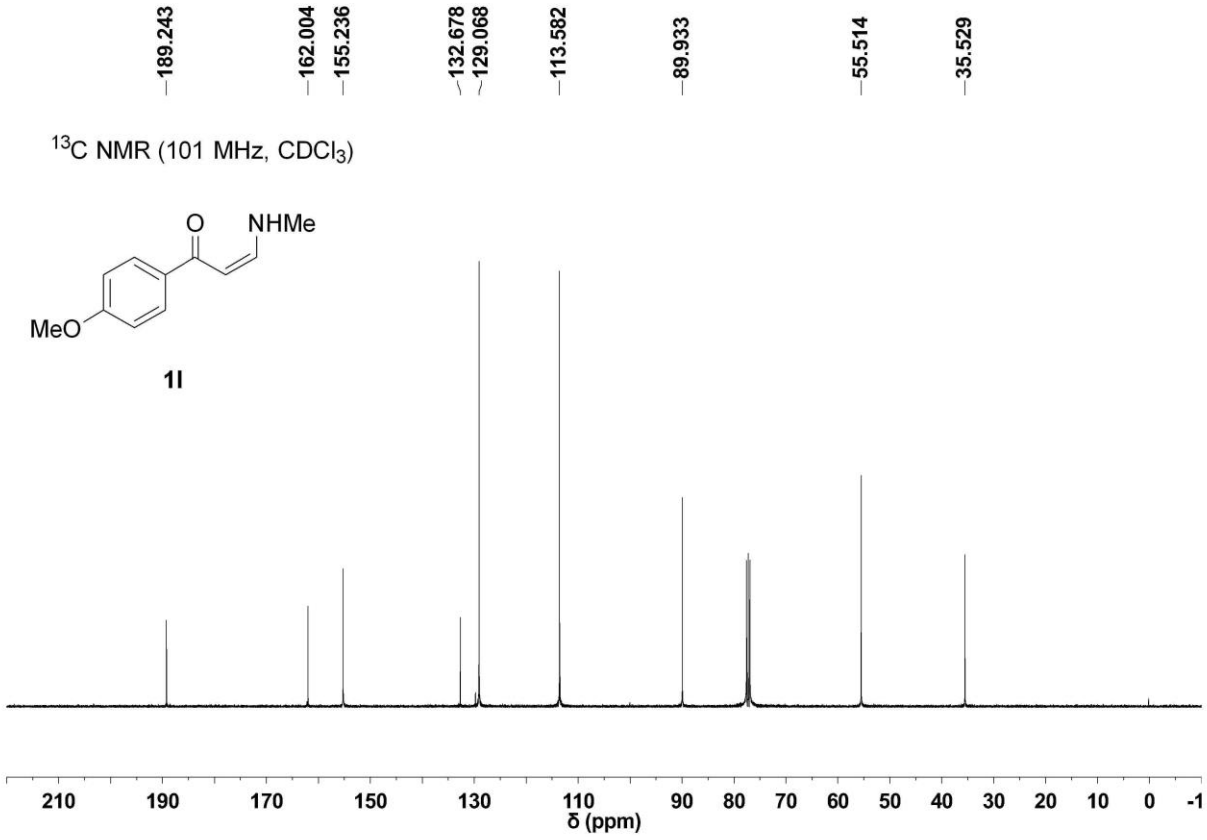

10.215
7.717
7.712
7.700
7.695
7.518
7.513
7.501
7.497
6.925
6.907
6.893
6.875
5.618
5.600
3.052
3.039
1H NMR (400 MHz, CDCl3)
O
NHMe
Br
1j
0.96
2.03
2.02
1.00
1.03
3.06
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

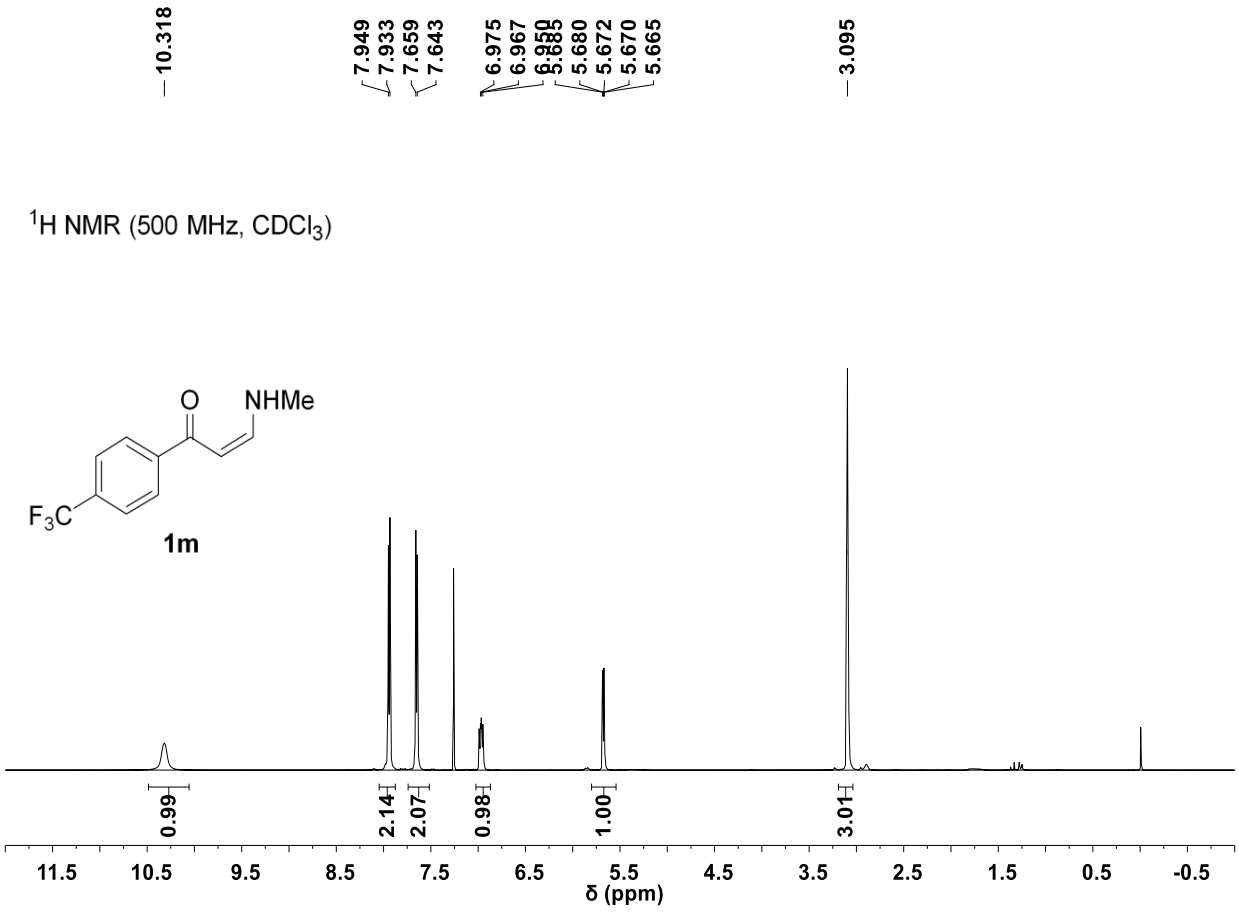

188.510
156.032
138.706
131.534
128.787
125.555
89.999
77.578
77.260
76.942
35.654
13C NMR (101 MHz, CDCl3)
O
NHMe
Br
1j
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

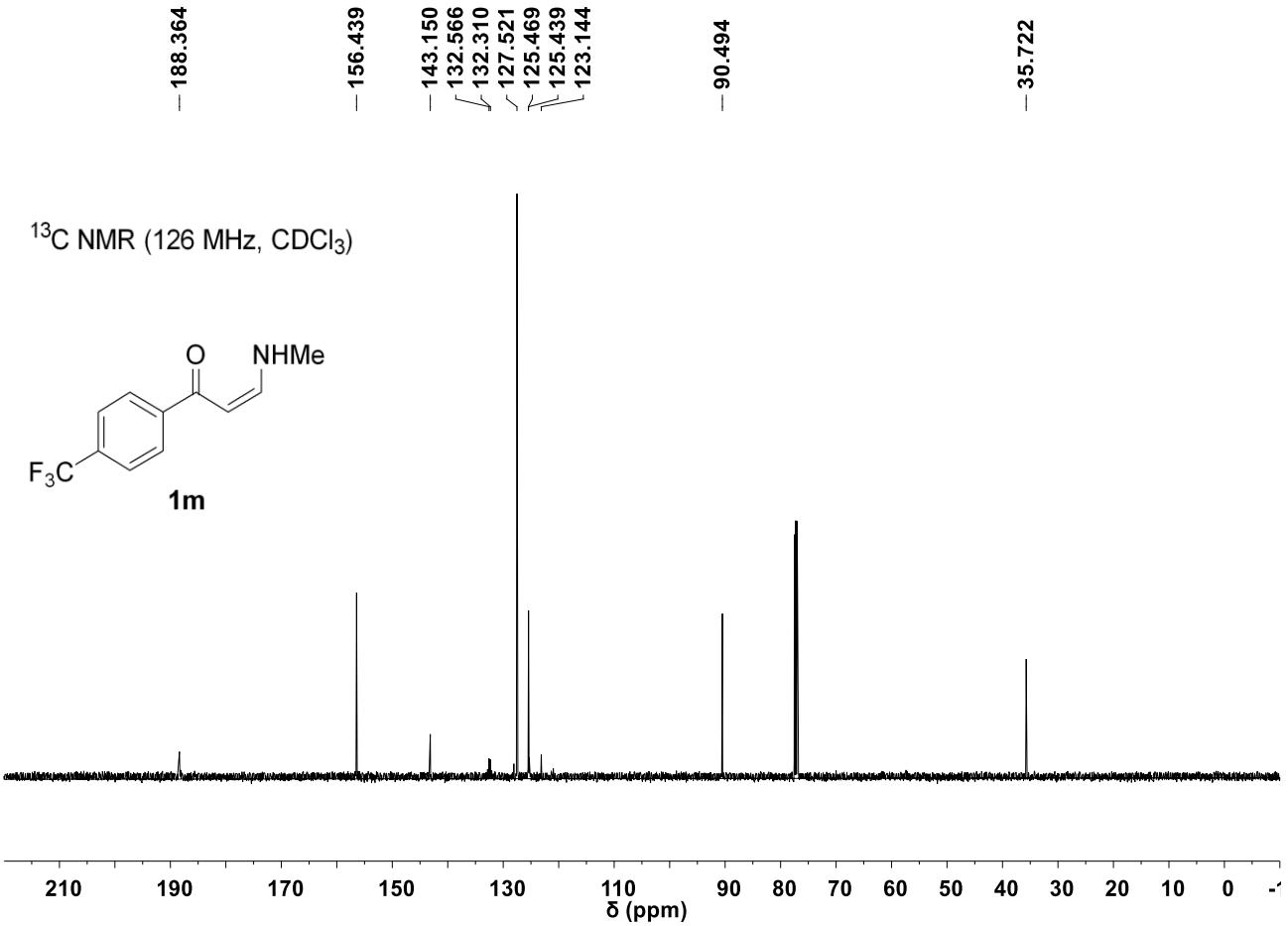

10.167
7.781
7.765
7.761
7.216
7.196
6.919
6.901
5.675
3.069
3.057
2.380
^{1}H NMR (400 MHz, $CDCl_3$)
O
NHMe
Me
1k
0.98
1.98
2.10
1.00
1.01
3.04
3.06
δ (ppm)


189.910
155.401
141.306
137.197
129.048
127.171
90.181
35.510
21.592
^{13}C NMR (101 MHz, $CDCl_3$)
O
NHMe
Me
1k
δ (ppm)

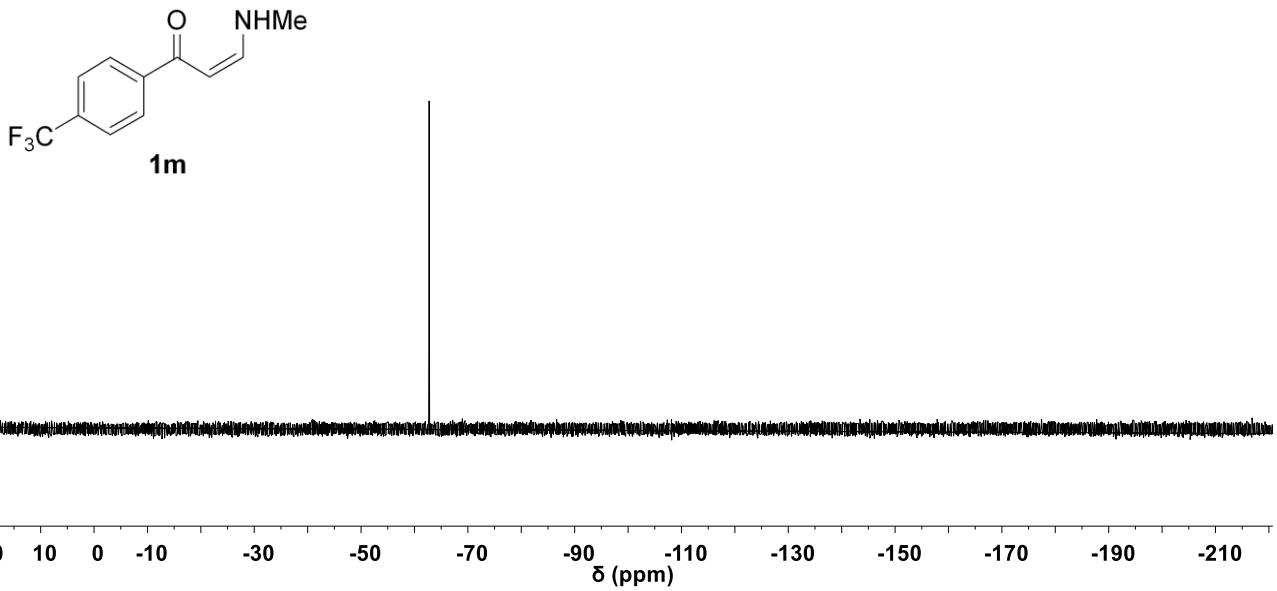

10.094
7.854
7.832
6.907
6.902
6.890
6.885
6.871
6.839
6.838
5.640
3.830
3.050
3.037
1H NMR (400 MHz, CDCl3)
O
NHMe
MeO
1l
0.93
2.02
3.06
1.00
3.16
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

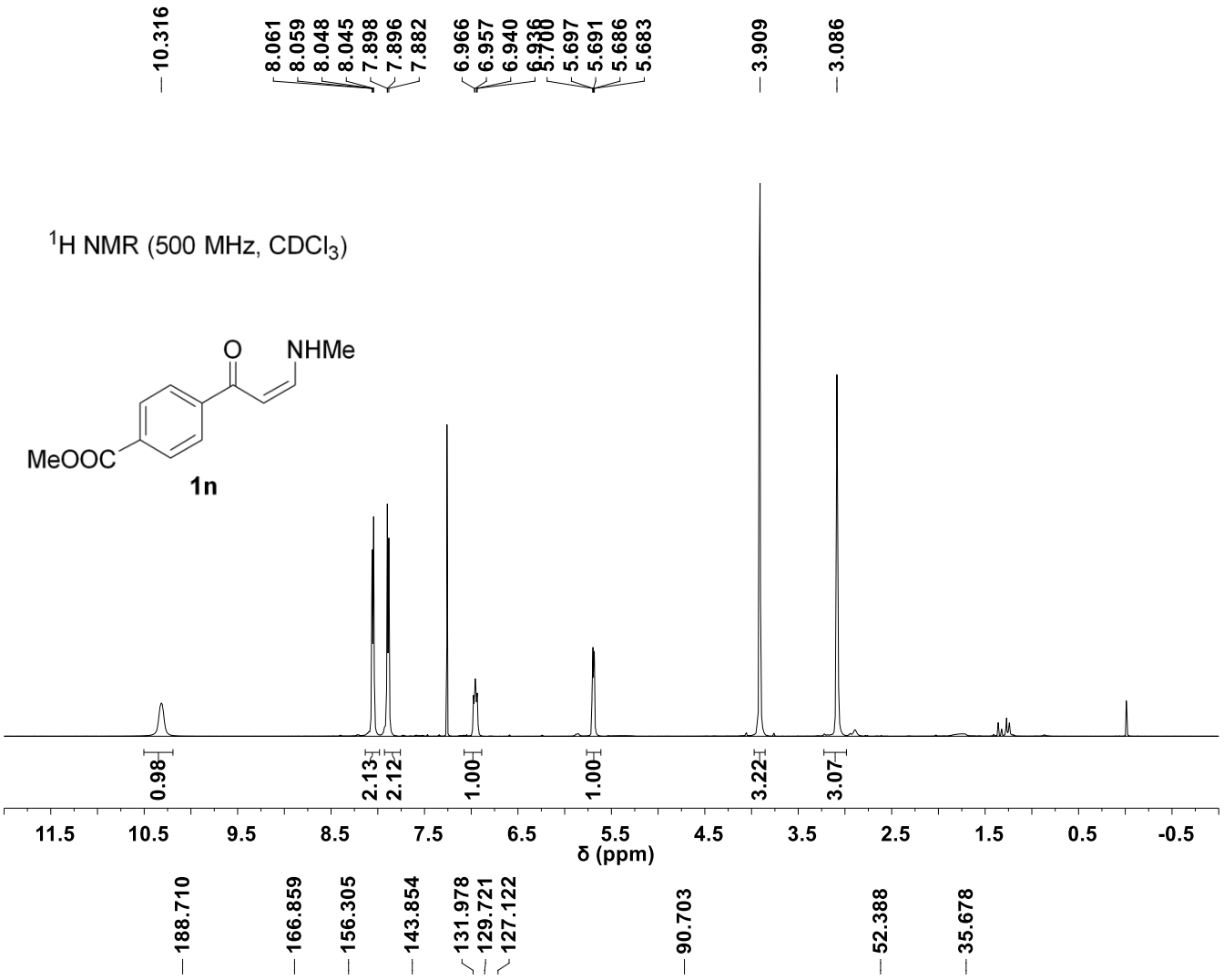

189.243
162.004
155.236
132.678
129.068
113.582
89.933
55.514
35.529
13C NMR (101 MHz, CDCl3)
O
NHMe
MeO
1l
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

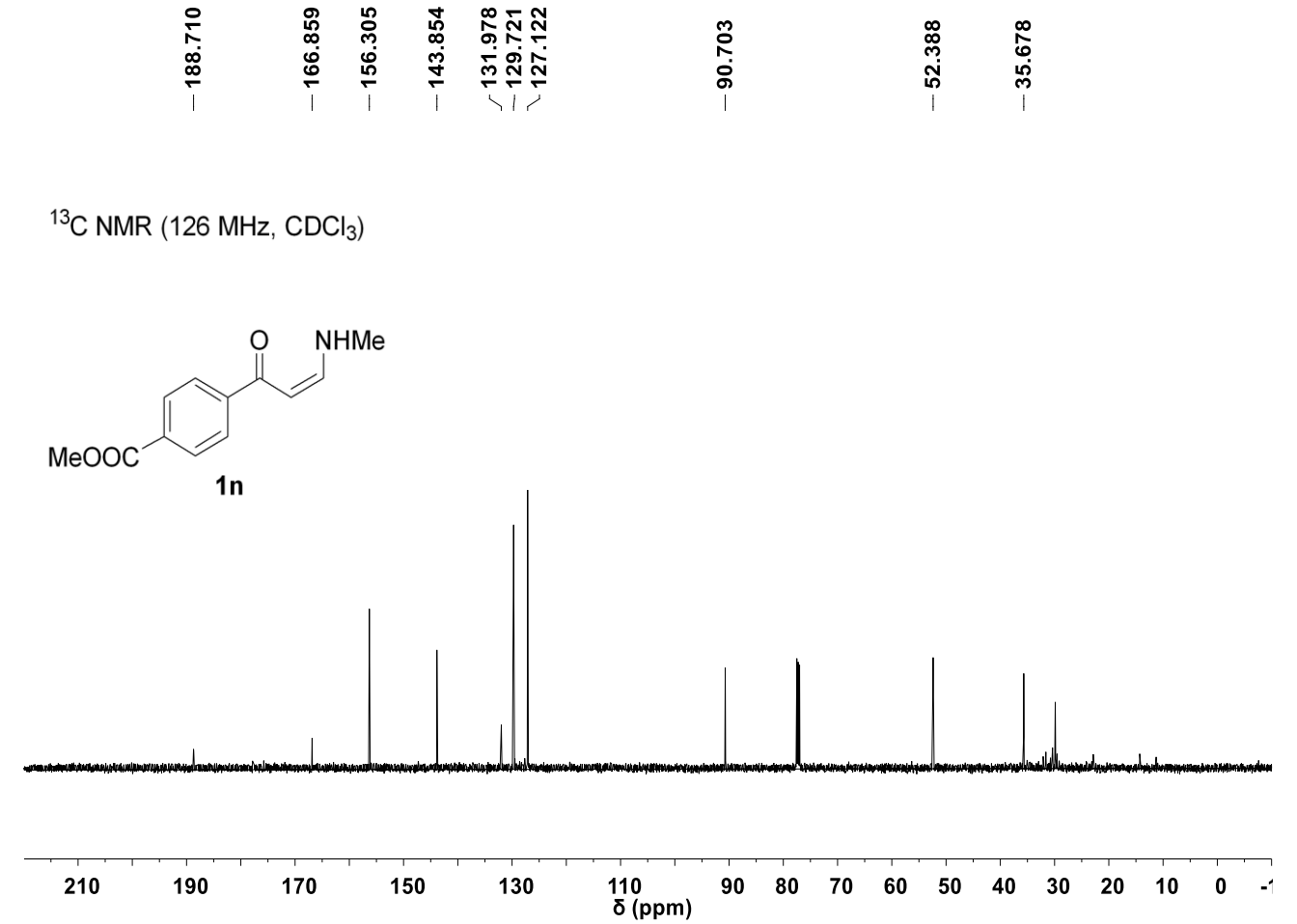

10.318
7.949
7.933
7.659
7.643
6.975
6.967
5.680
5.672
5.670
5.665
3.095
1H NMR (500 MHz, CDCl3)
O
NHMe
F3C
1m
0.99
2.14
2.07
0.98
1.00
3.01
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

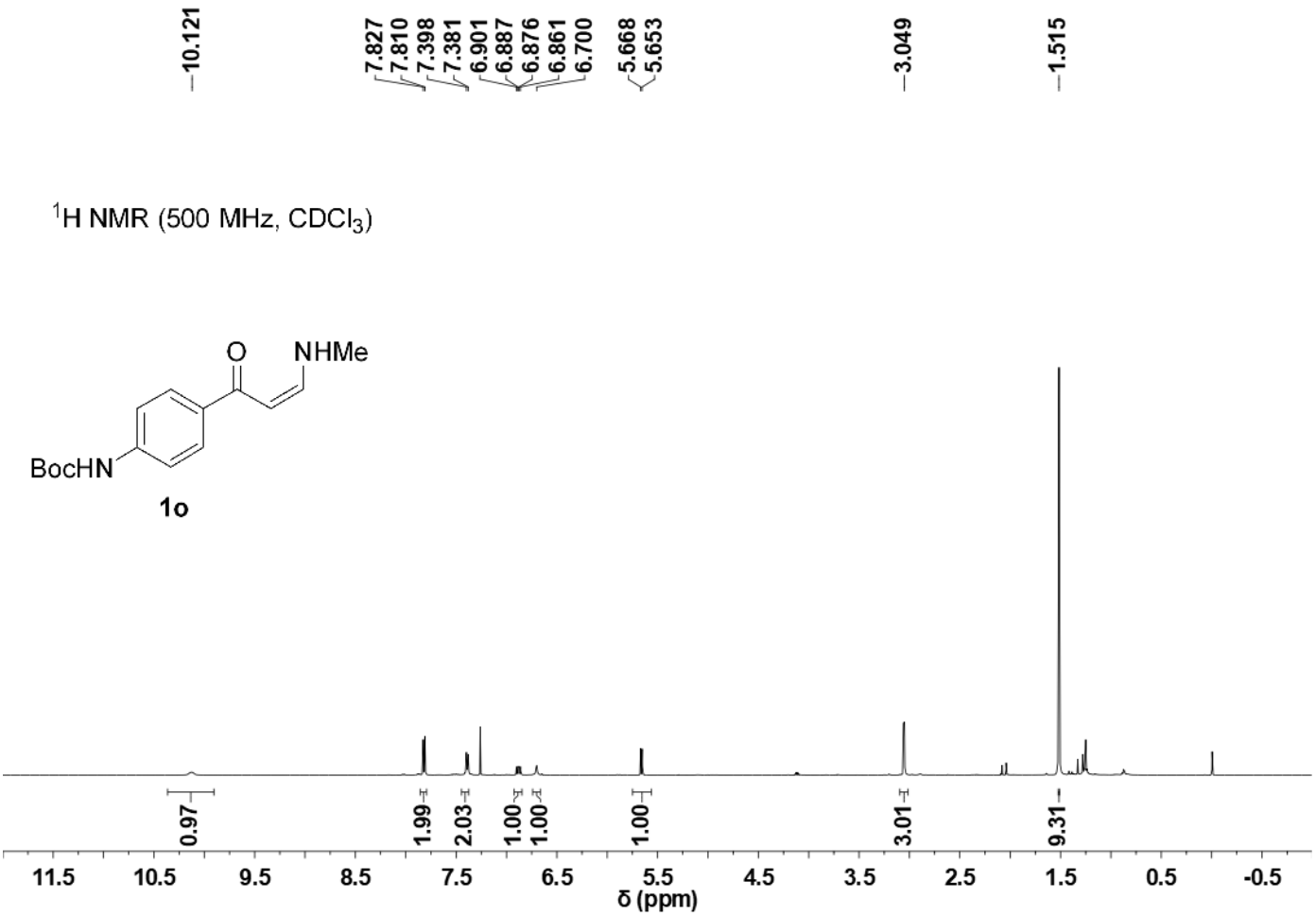

188.364
156.439
143.150
132.566
132.310
127.521
125.469
125.439
123.144
90.494
35.722
13C NMR (126 MHz, CDCl3)
O
NHMe
F3C
1m
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

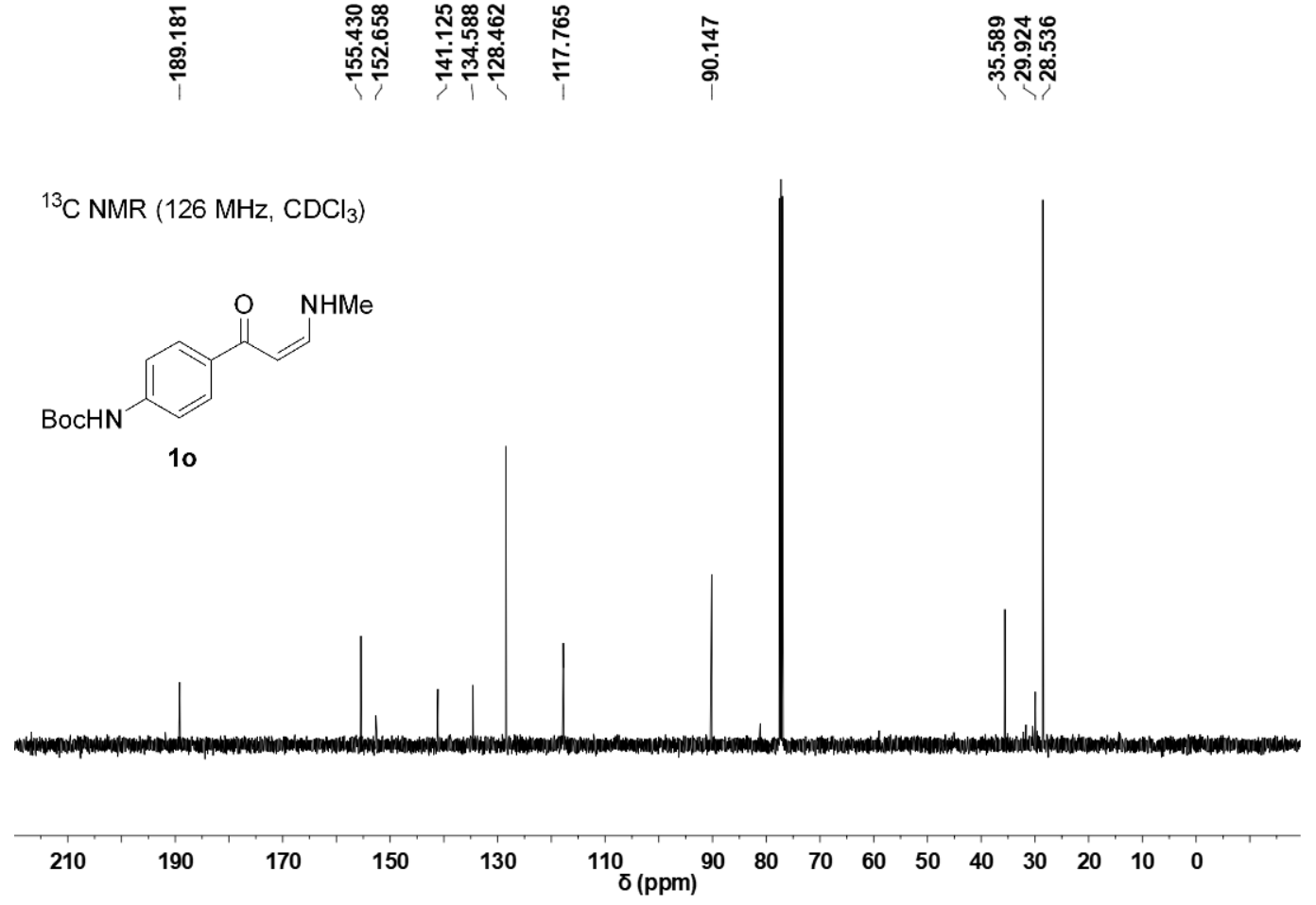
^{19}F NMR (471 MHz, $CDCl_3$)

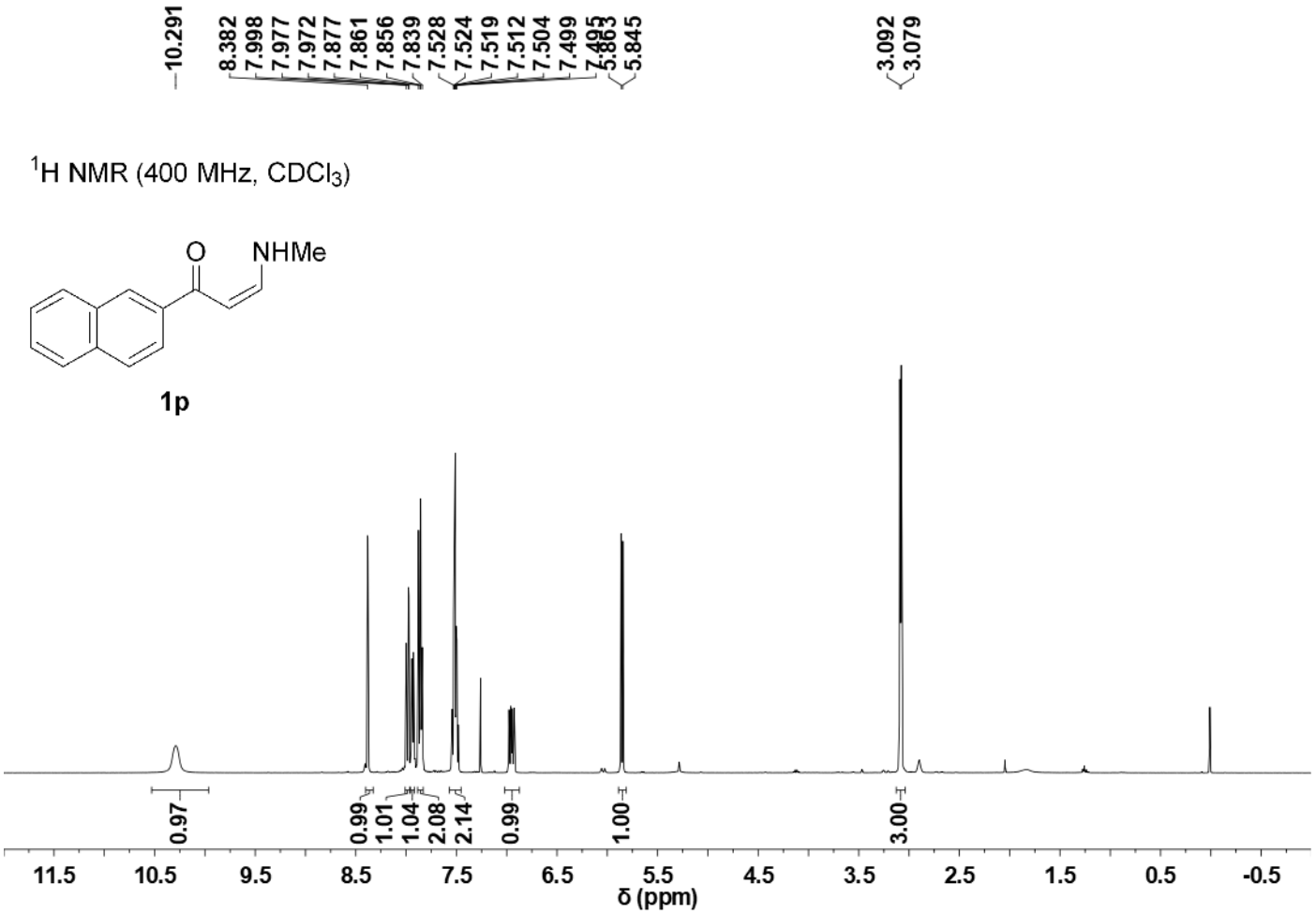



10.316
8.061
8.059
8.048
8.045
7.898
7.896
7.882
6.966
6.957
6.940
6.936
5.700
5.697
5.691
5.686
5.683
3.909
3.086
1H NMR (500 MHz, CDCl3)
O
NHMe
MeOOC
1n
0.98
2.13
2.12
1.00
1.00
3.22
3.07
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)


188.710
166.859
156.305
143.854
131.978
129.721
127.122
90.703
52.388
35.678
13C NMR (126 MHz, CDCl3)
O
NHMe
MeOOC
1n
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

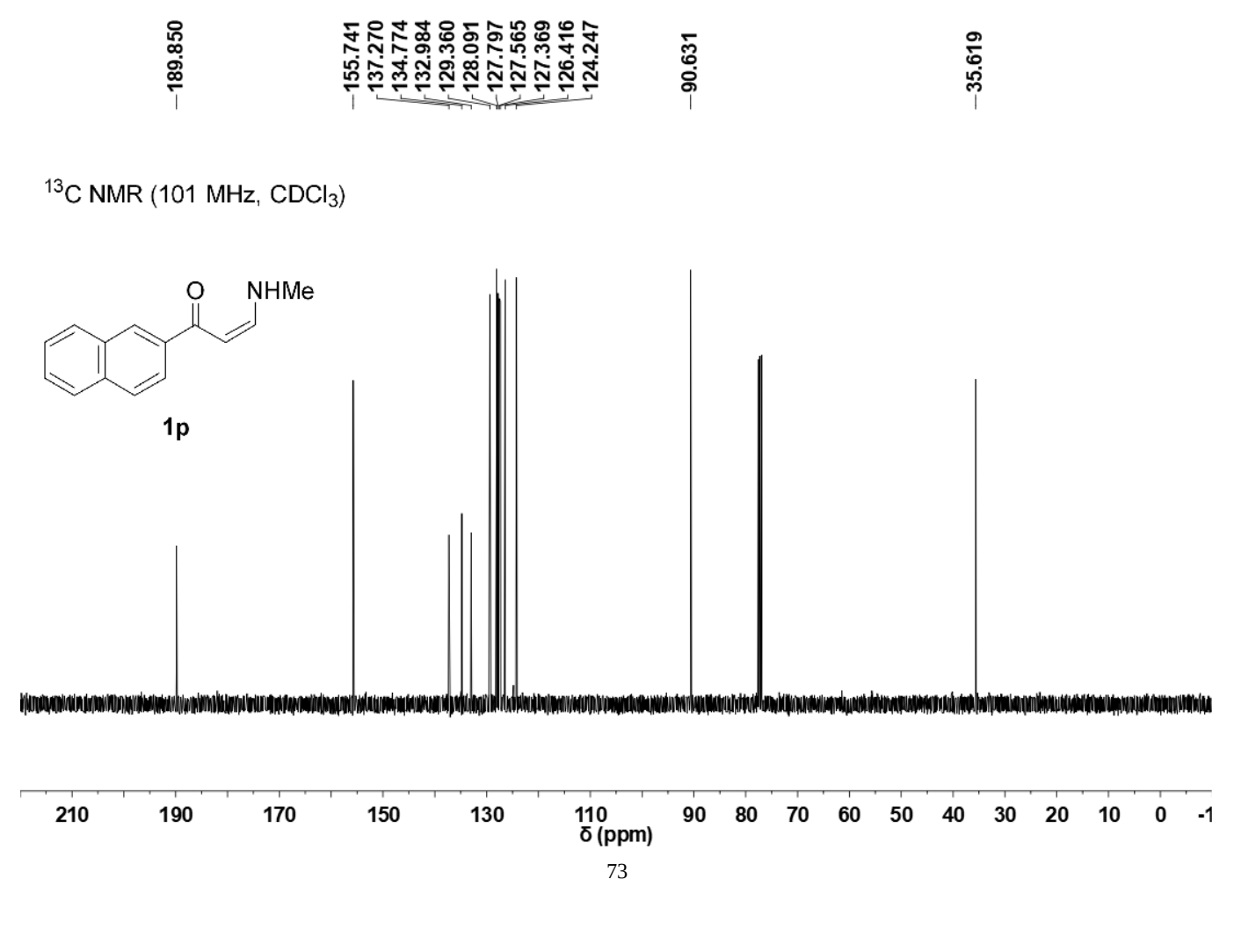

10.121
7.827
7.810
7.398
7.381
6.901
6.887
6.876
6.861
6.700
5.668
5.653
3.049
1.515
1H NMR (500 MHz, CDCl3)
O
NHMe
BocHN
1o
0.97
1.99
2.03
1.00
1.00
1.00
3.01
9.31
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)


189.181
155.430
152.658
141.125
134.588
128.462
117.765
90.147
35.589
29.924
28.536
13C NMR (126 MHz, CDCl3)
O
NHMe
BocHN
1o
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)



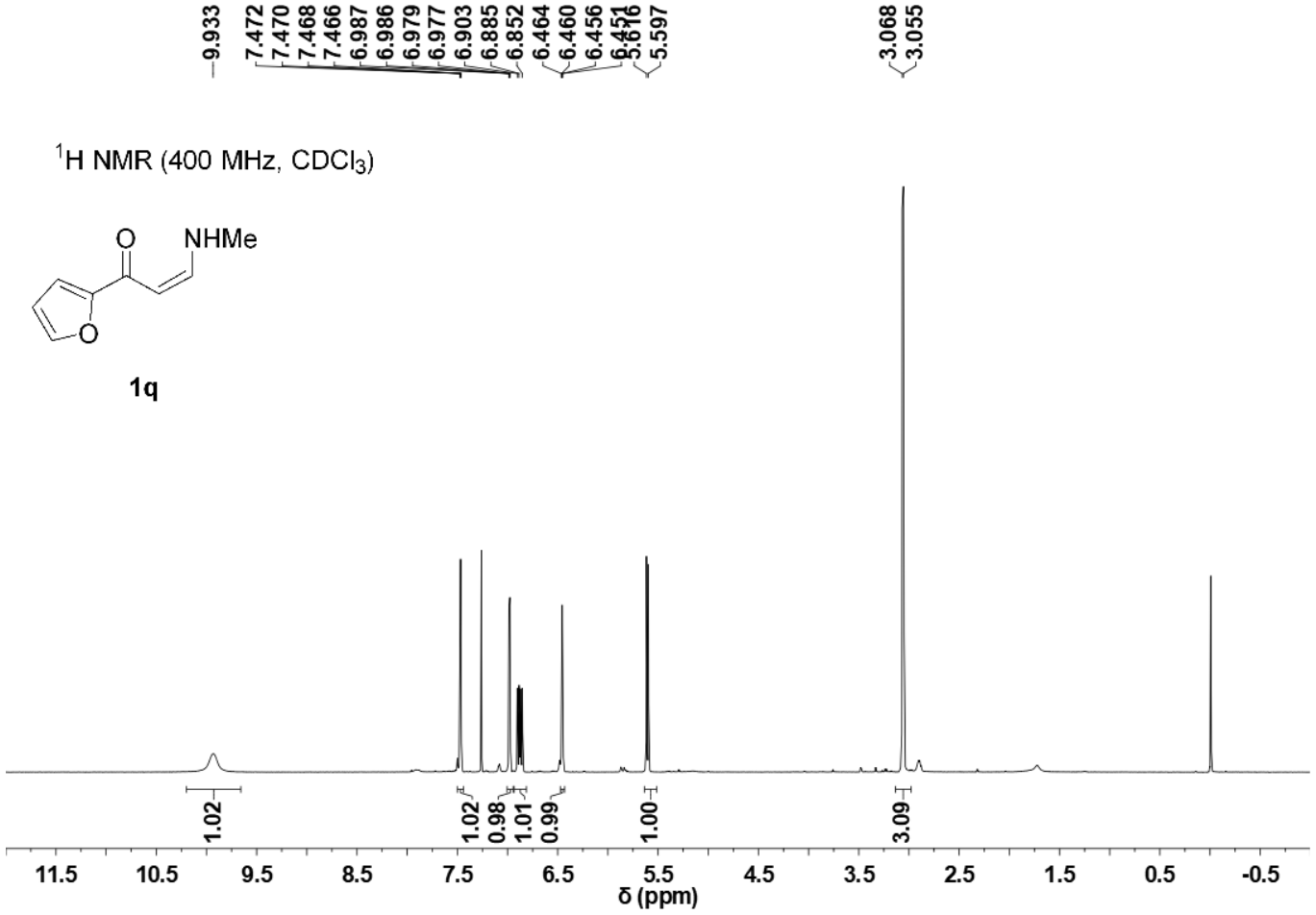
^{1}H NMR (400 MHz, $CDCl_3$)

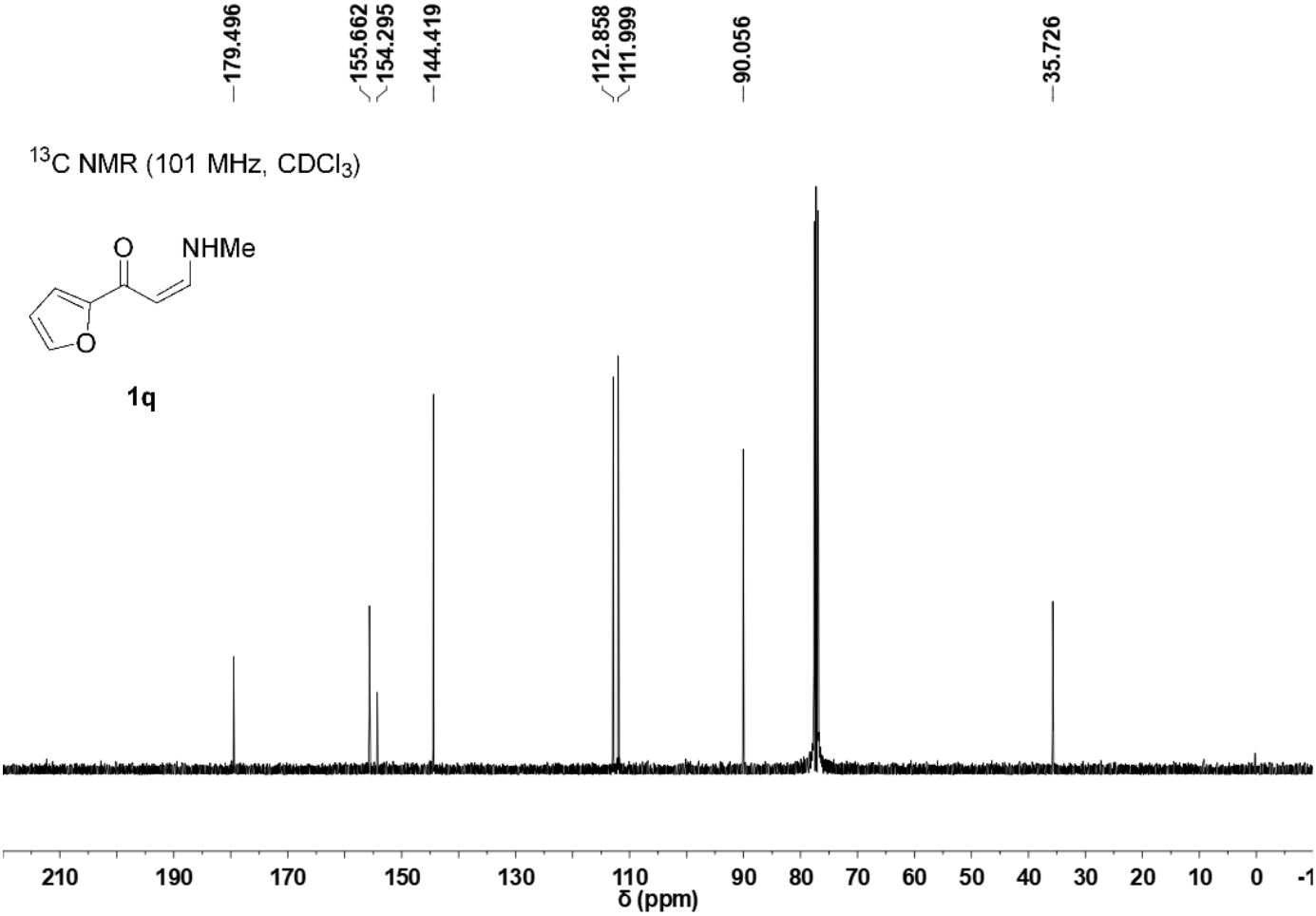
1p

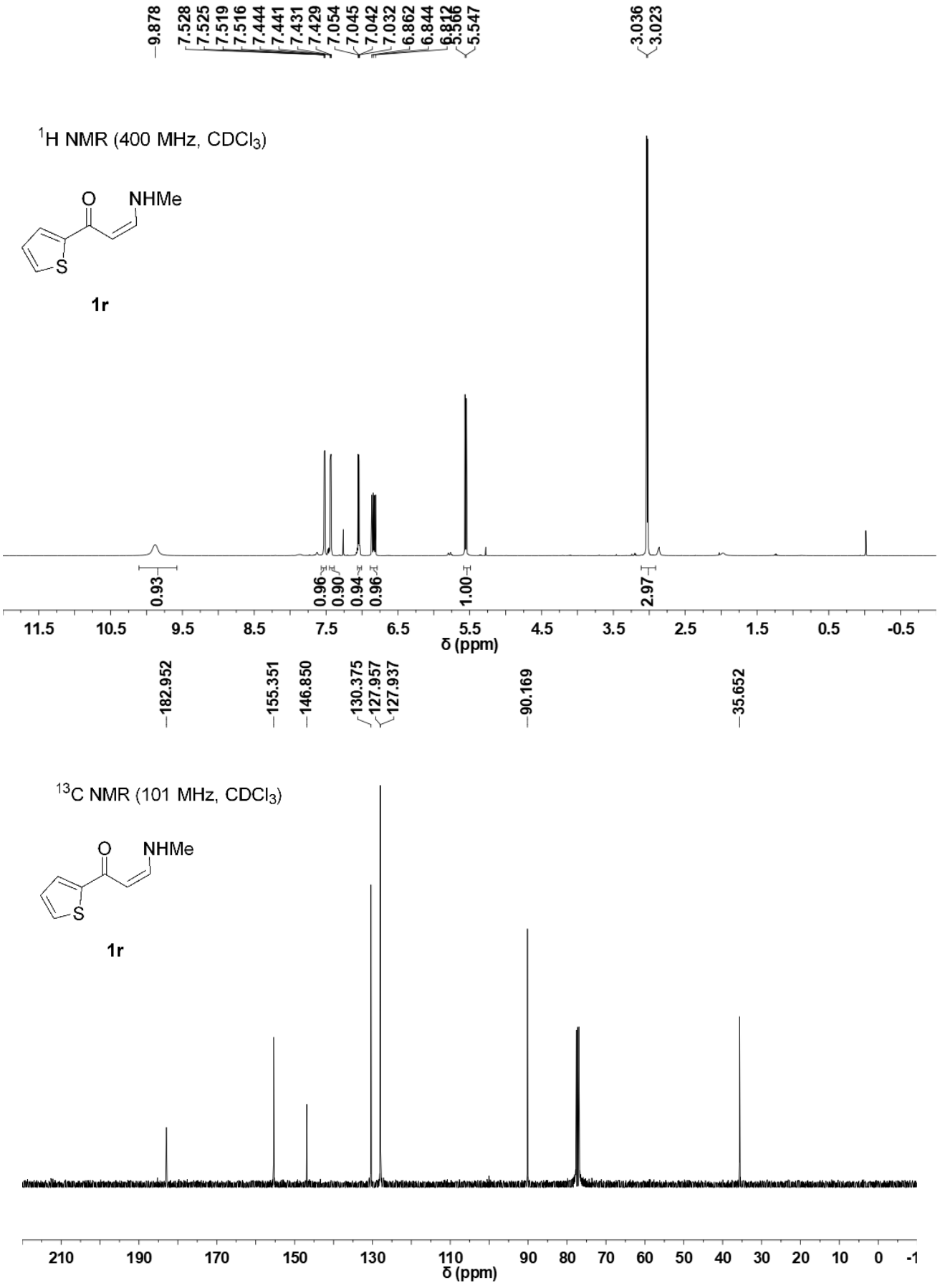


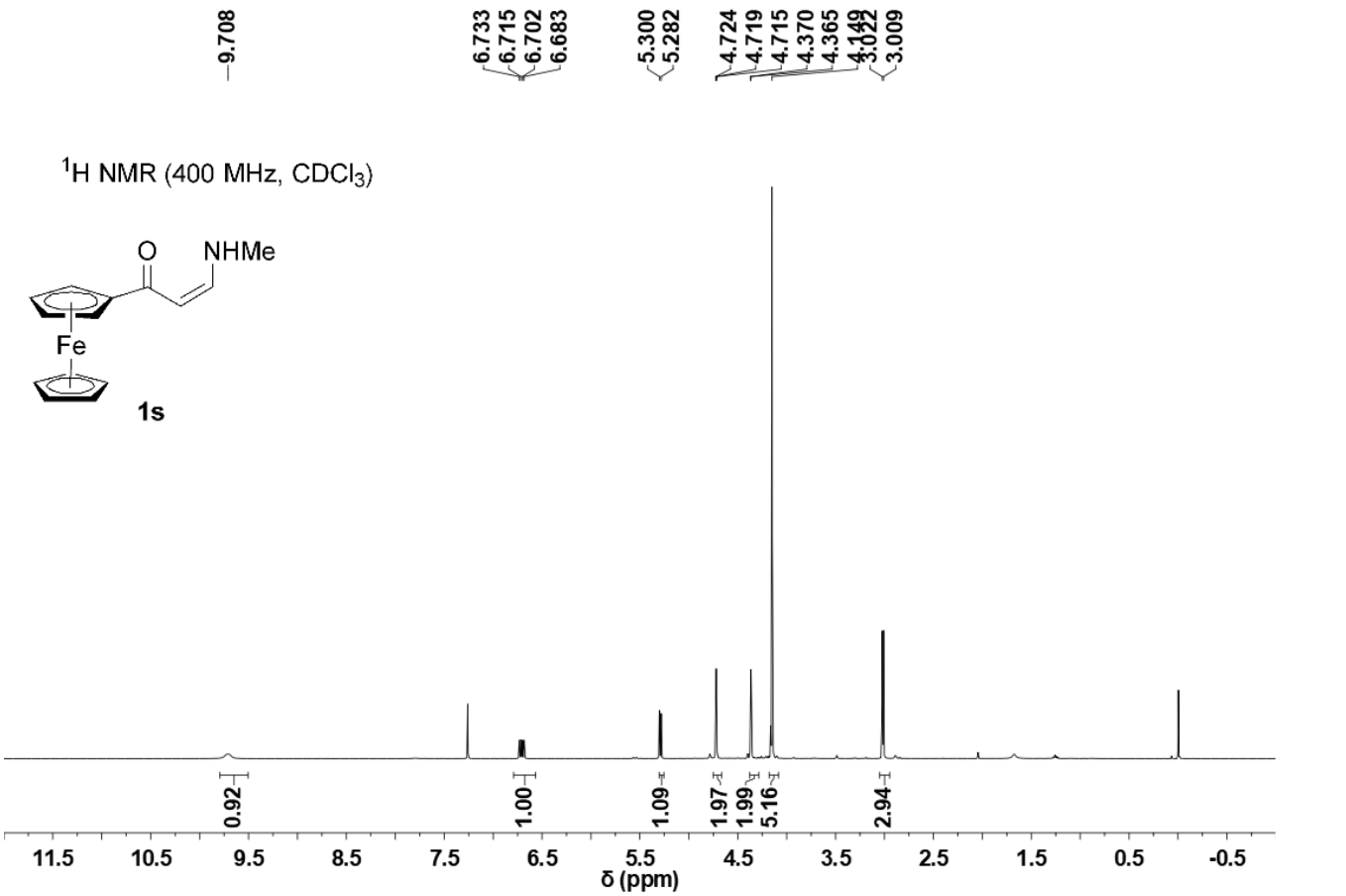
^{13}C NMR (101 MHz, $CDCl_3$)

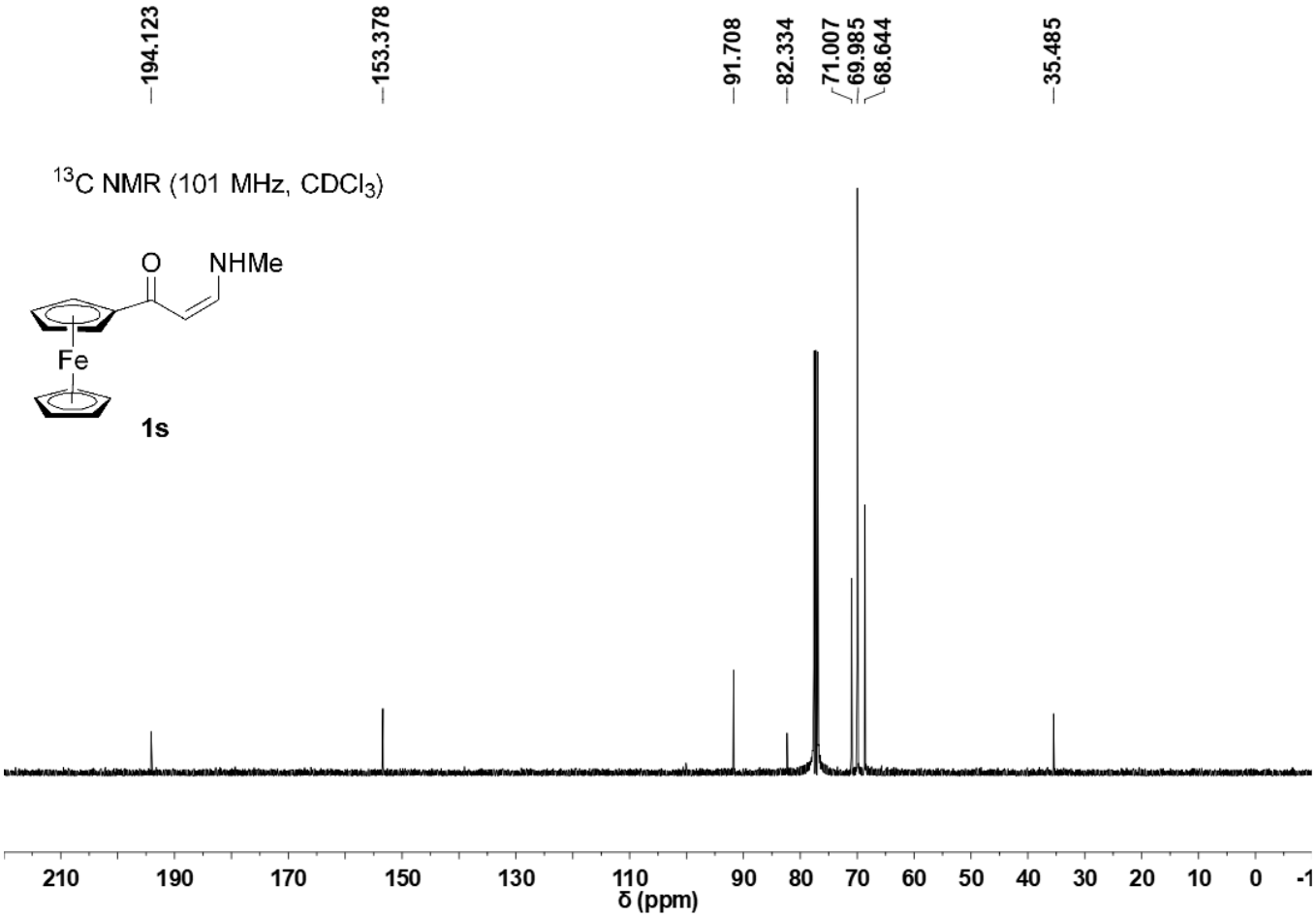
1p

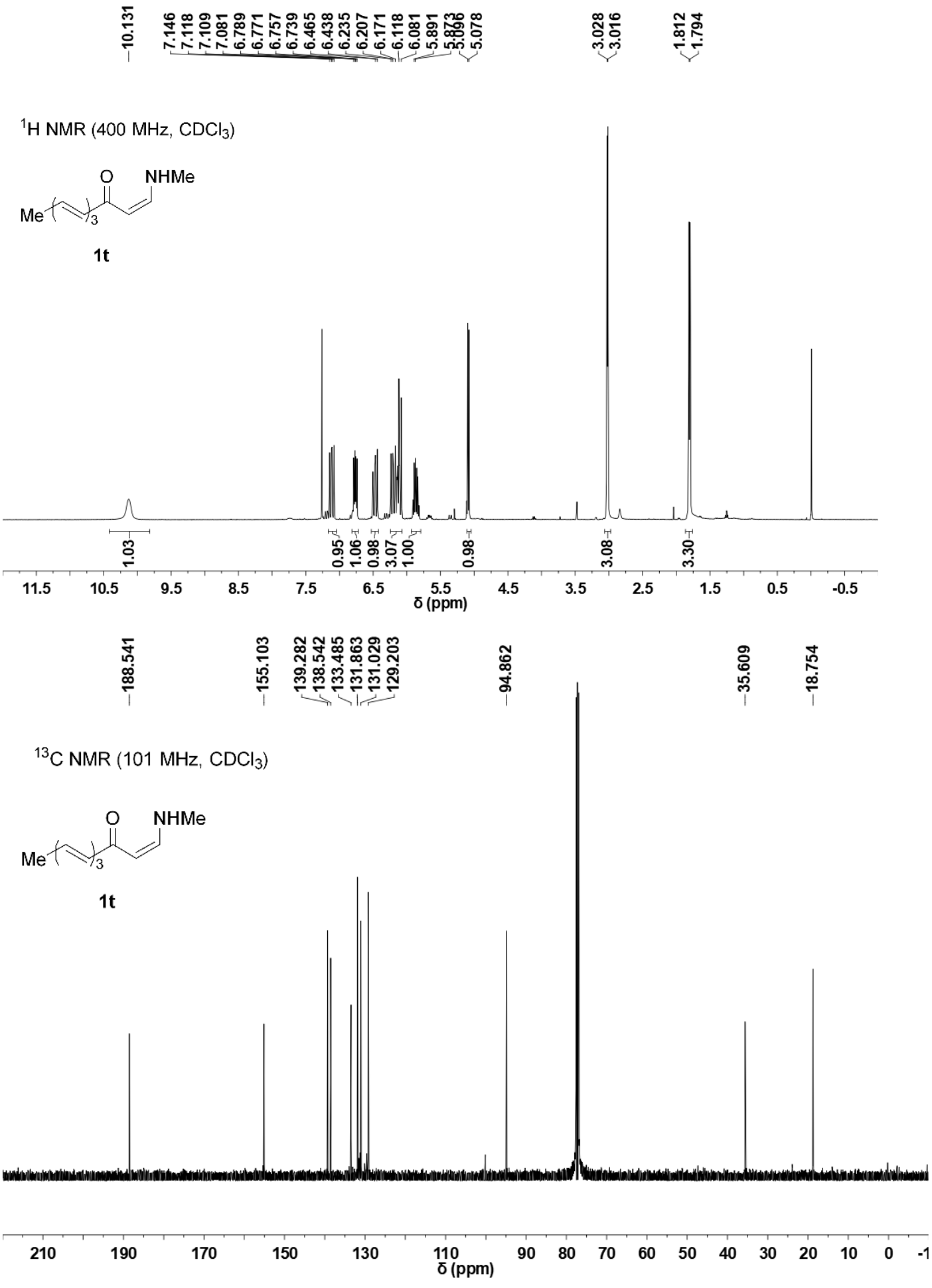

9.933
7.472
7.470
7.468
7.466
6.987
6.986
6.979
6.977
6.903
6.885
6.852
6.464
6.460
6.456
6.451
5.616
5.597
3.068
3.055
1H NMR (400 MHz, CDCl3)
O
NHMe
O
1q
1.02
1.02
0.98
1.01
0.99
1.00
3.09
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

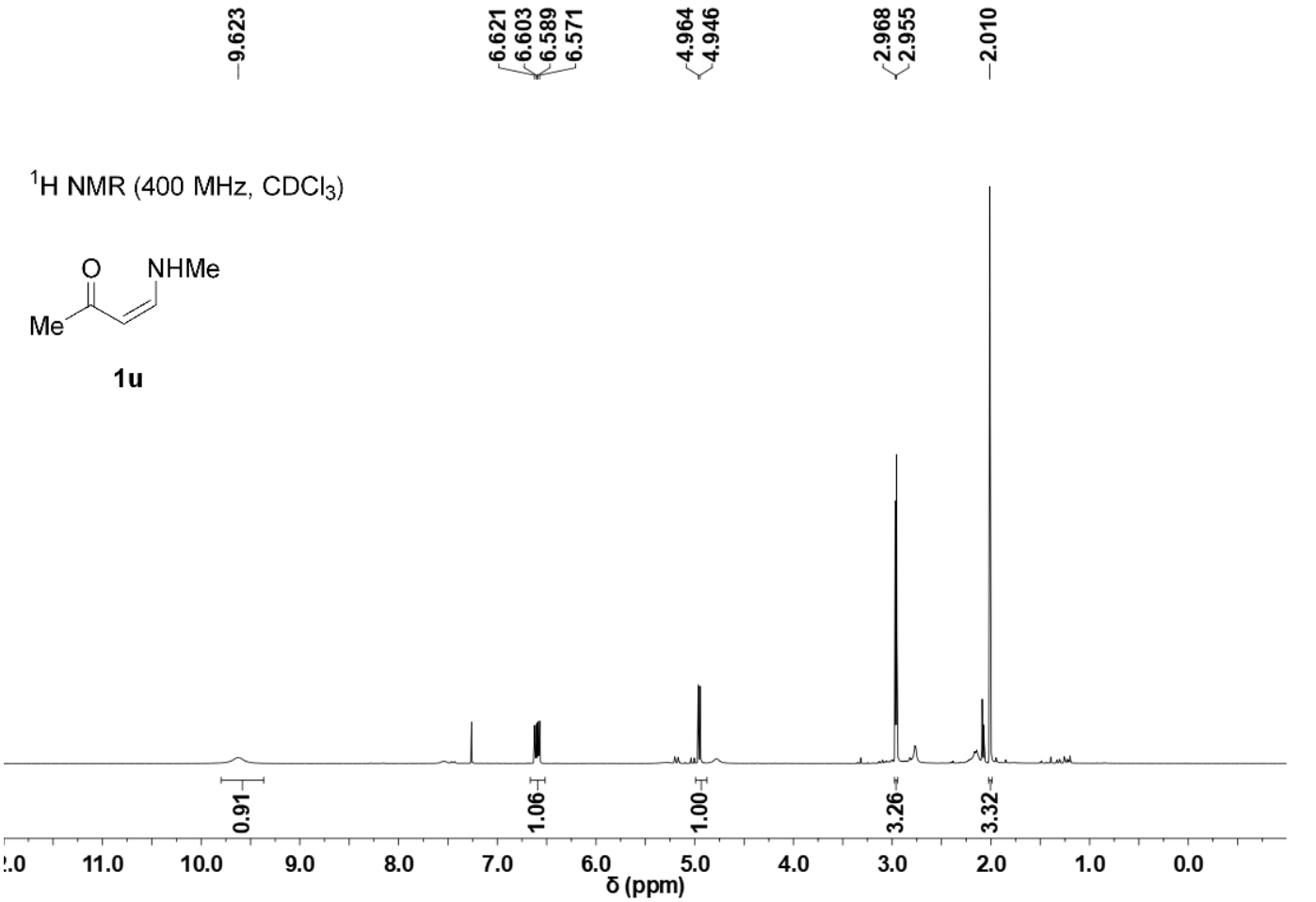

179.496
155.662
154.295
144.419
112.858
111.999
90.056
35.726
13C NMR (101 MHz, CDCl3)
O
NHMe
O
1q
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

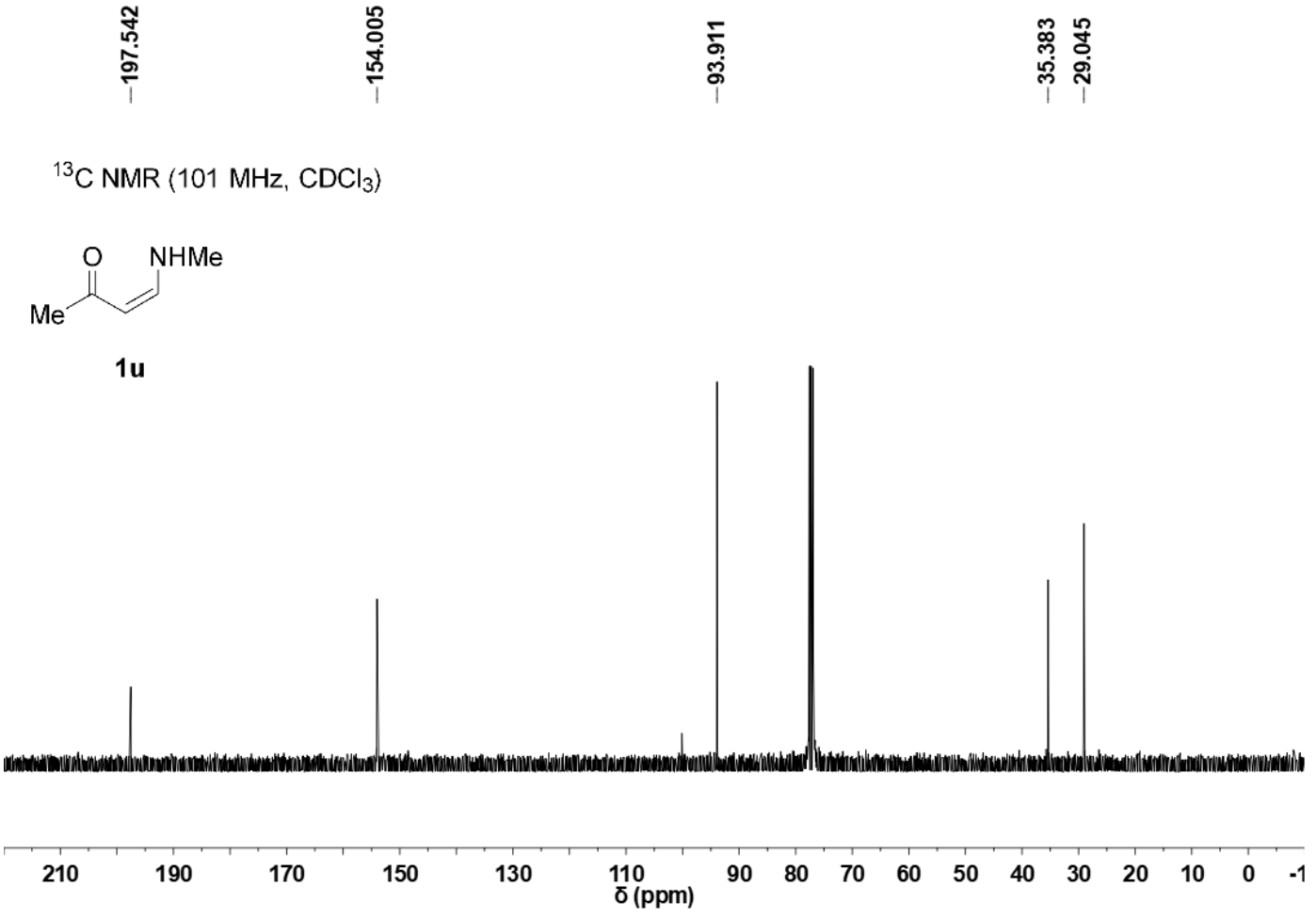

9.878
7.528
7.525
7.519
7.516
7.444
7.441
7.431
7.429
7.054
7.045
7.042
7.032
6.862
6.844
6.812
6.566
5.547
3.036
3.023
1H NMR (400 MHz, CDCl3)
O
NHMe
S
1r
0.93
0.96
0.90
0.94
0.96
1.00
2.97
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
182.952
155.351
146.850
130.375
127.957
127.937
90.169
35.652
13C NMR (101 MHz, CDCl3)
O
NHMe
S
1r
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

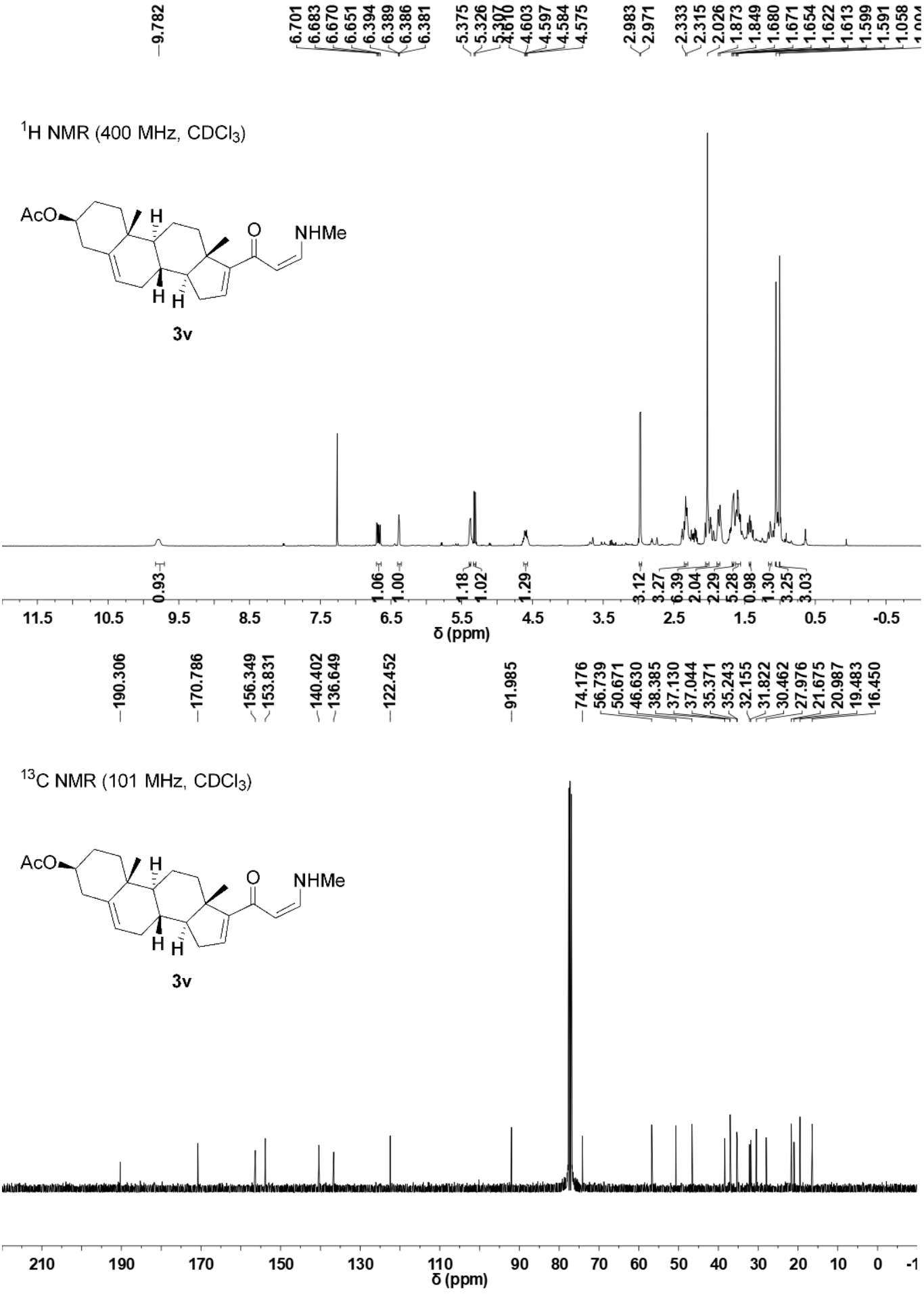

9.708
6.733
6.715
6.702
6.683
5.300
5.282
4.724
4.719
4.715
4.370
4.365
4.149
4.022
3.009
1H NMR (400 MHz, CDCl3)
O
NHMe
Fe
1s
0.92
1.00
1.09
1.97
1.99
5.16
2.94
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

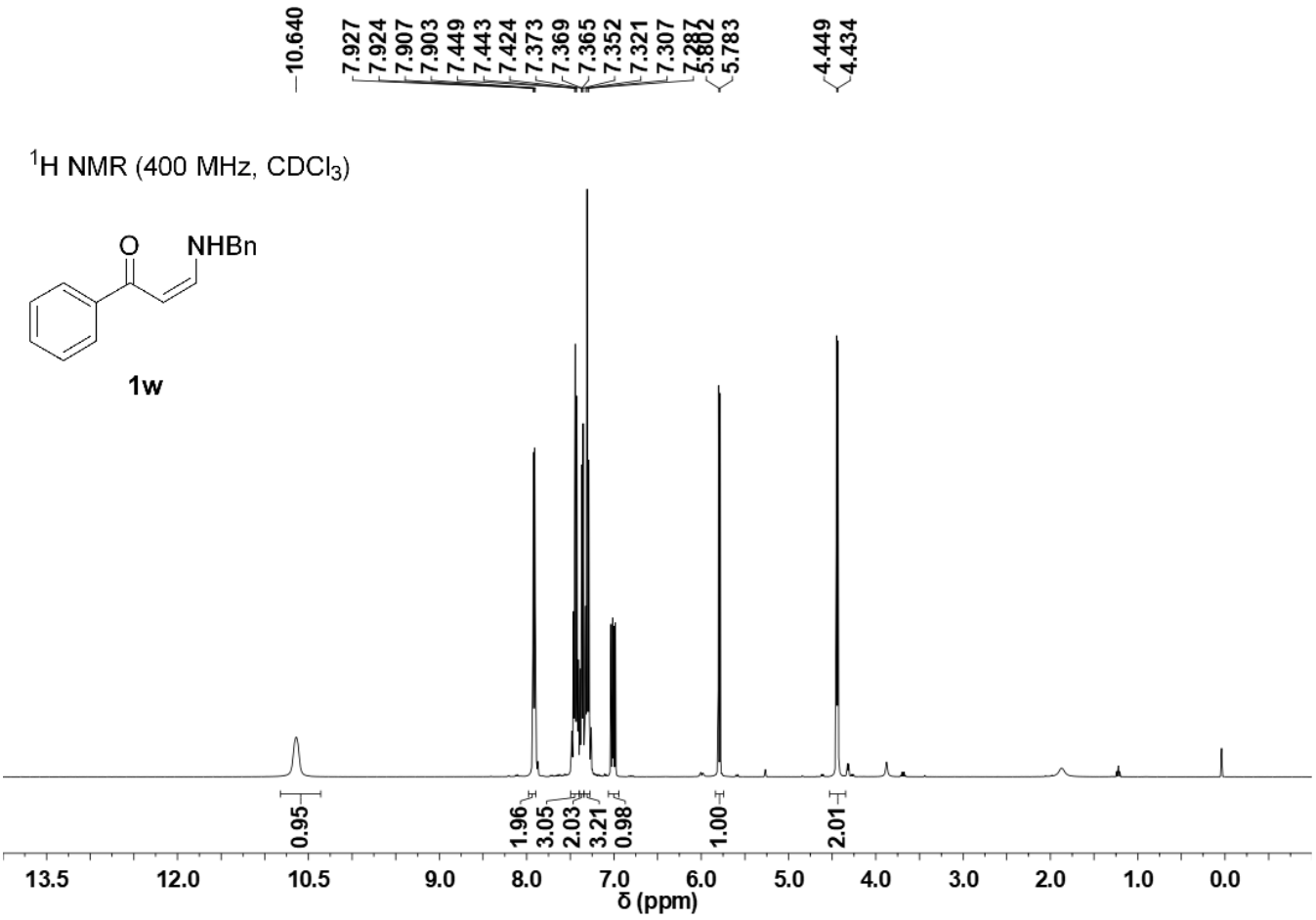

194.123
153.378
91.708
82.334
71.007
69.985
68.644
35.485
13C NMR (101 MHz, CDCl3)
O
NHMe
Fe
1s
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

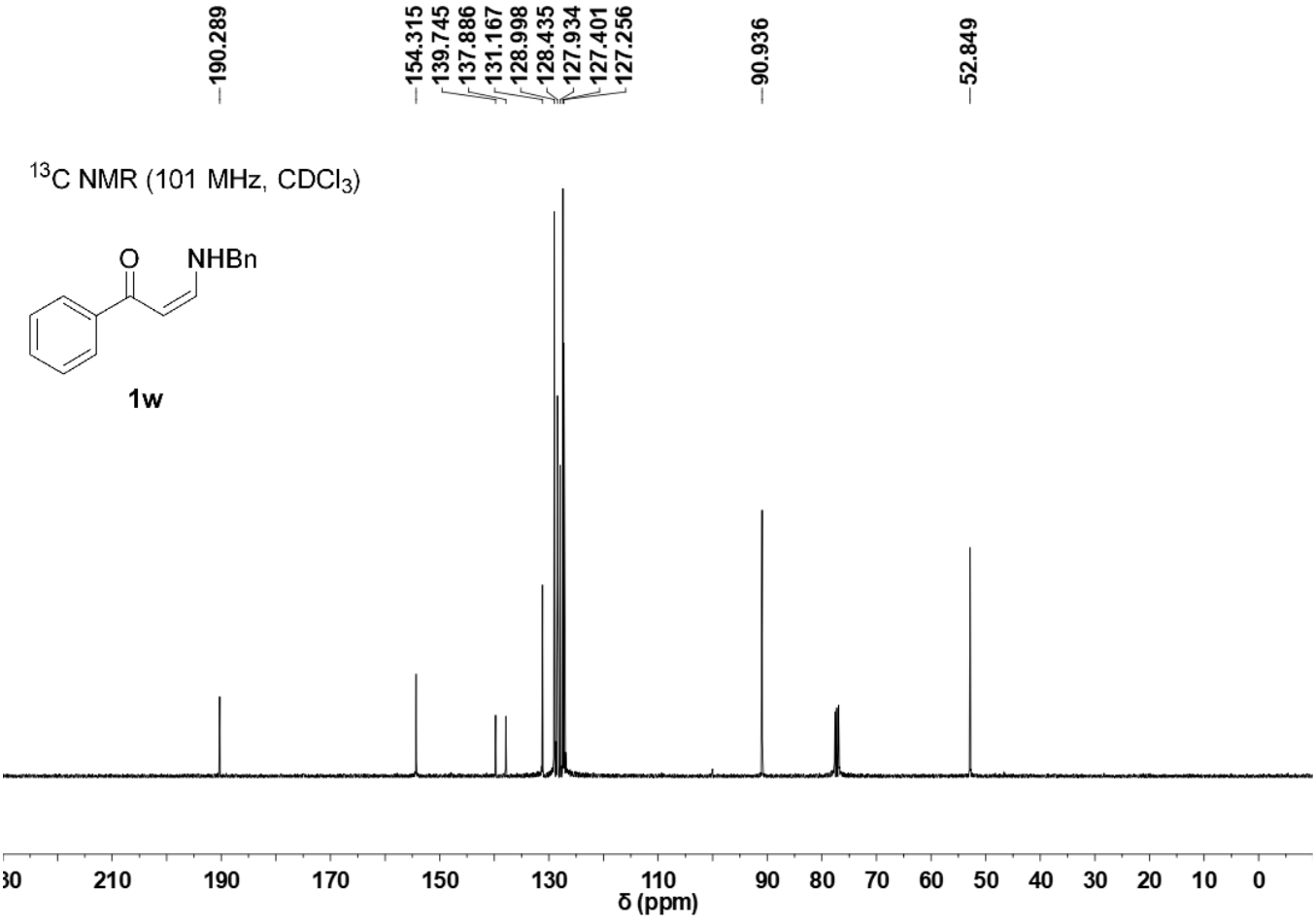

10.131
7.146
7.118
7.109
7.081
6.789
6.771
6.757
6.739
6.465
6.438
6.235
6.207
6.171
6.118
6.081
5.891
5.873
5.866
5.078
3.028
3.016
1.812
1.794
1H NMR (400 MHz, CDCl3)
O
NHMe
Me
3
1t
1.03
0.95
1.06
0.98
3.07
1.00
0.98
3.08
3.30
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
188.541
155.103
139.282
138.542
133.485
131.863
131.029
129.203
94.862
35.609
18.754
13C NMR (101 MHz, CDCl3)
O
NHMe
Me
3
1t
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

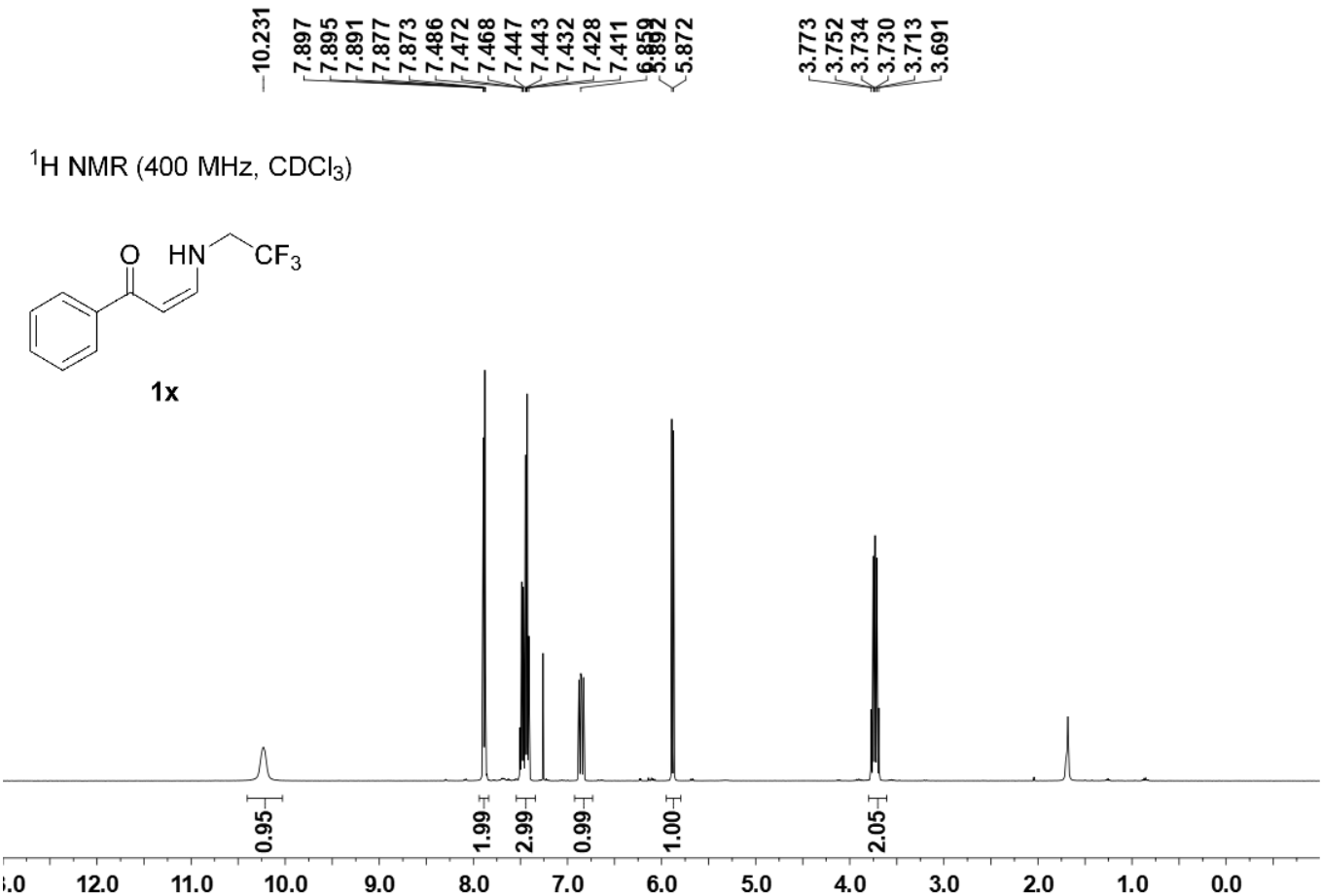

9.623
6.621
6.603
6.589
6.571
4.964
4.946
2.968
2.955
2.010
^{1}H NMR (400 MHz, $CDCl_3$)
O
NHMe
Me
1u
0.91
1.06
1.00
3.26
3.32
δ (ppm)

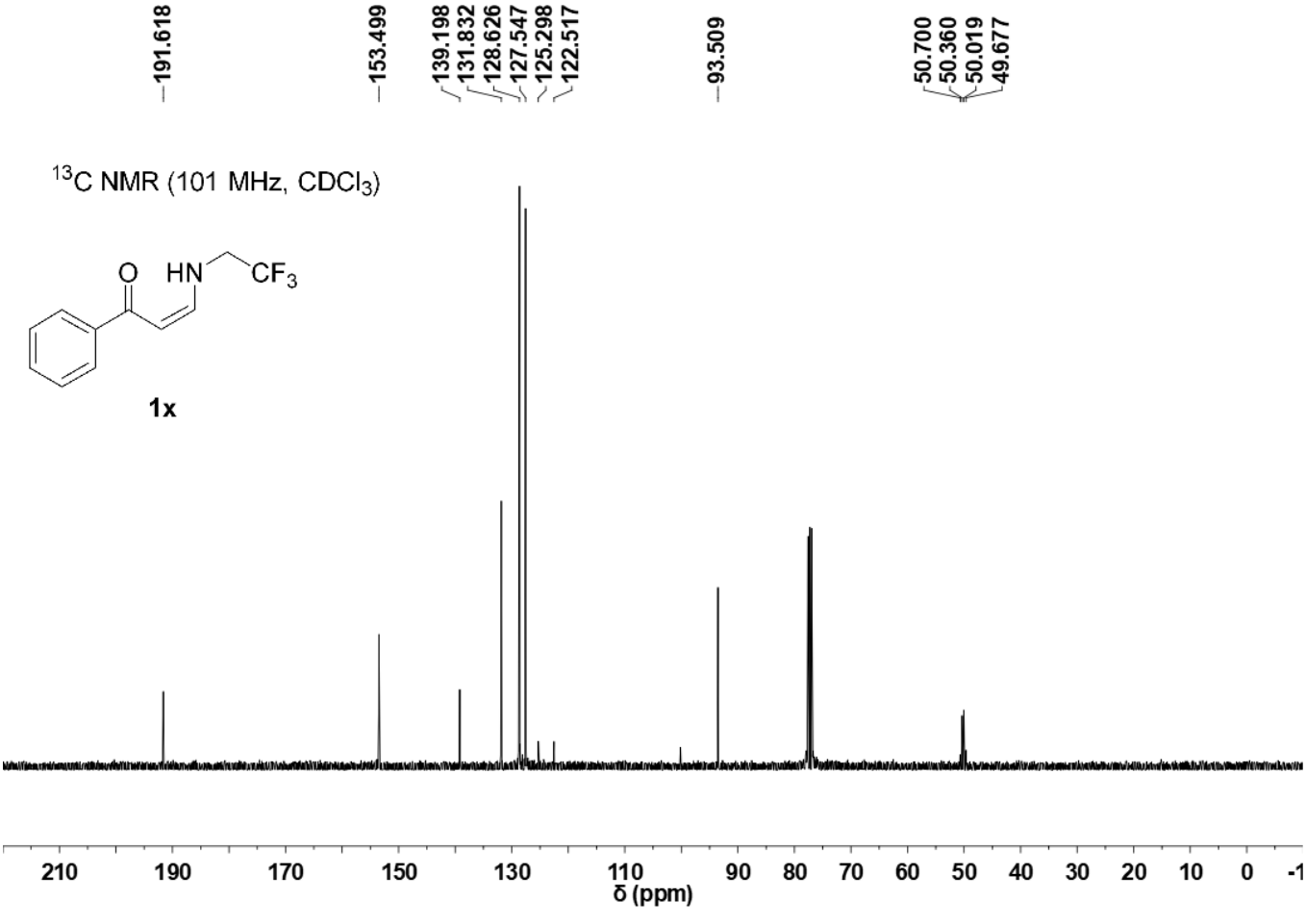

197.542
154.005
93.911
35.383
29.045
^{13}C NMR (101 MHz, $CDCl_3$)
O
NHMe
Me
1u
δ (ppm)


9.782
6.701
6.683
6.670
6.651
6.394
6.389
6.386
6.381
5.375
5.326
4.603
4.597
4.584
4.575
2.983
2.971
2.333
2.315
2.026
1.873
1.849
1.680
1.671
1.654
1.622
1.613
1.599
1.591
1.058
1H NMR (400 MHz, CDCl3)
AcO
H
O
NHMe
H
H
3v
0.93
1.06
1.00
1.18
1.02
1.29
3.12
3.27
6.39
2.04
2.29
5.28
0.98
1.30
3.25
3.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
190.306
170.786
156.349
153.831
140.402
136.649
122.452
91.985
74.176
56.739
50.671
46.630
38.385
37.130
37.044
35.371
35.243
32.155
31.822
30.462
27.976
21.675
20.987
19.483
16.450
13C NMR (101 MHz, CDCl3)
AcO
H
O
NHMe
H
H
3v
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


10.640
7.927
7.924
7.907
7.903
7.449
7.443
7.424
7.373
7.369
7.365
7.352
7.321
7.307
5.802
5.783
4.449
4.434
1H NMR (400 MHz, CDCl3)
O
NHBn
1w
0.95
1.96
3.05
2.03
3.21
0.98
1.00
2.01
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

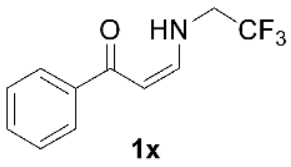

190.289
154.315
139.745
137.886
131.167
128.998
128.435
127.934
127.401
127.256
90.936
52.849
13C NMR (101 MHz, CDCl3)
O
NHBn
1w
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


10.231
7.897
7.895
7.891
7.877
7.873
7.486
7.472
7.468
7.447
7.443
7.432
7.428
7.411
5.872
3.773
3.752
3.734
3.730
3.713
3.691
1H NMR (400 MHz, CDCl3)
O
HN
CF3
1x
0.95
1.99
2.99
0.99
1.00
2.05
δ (ppm)

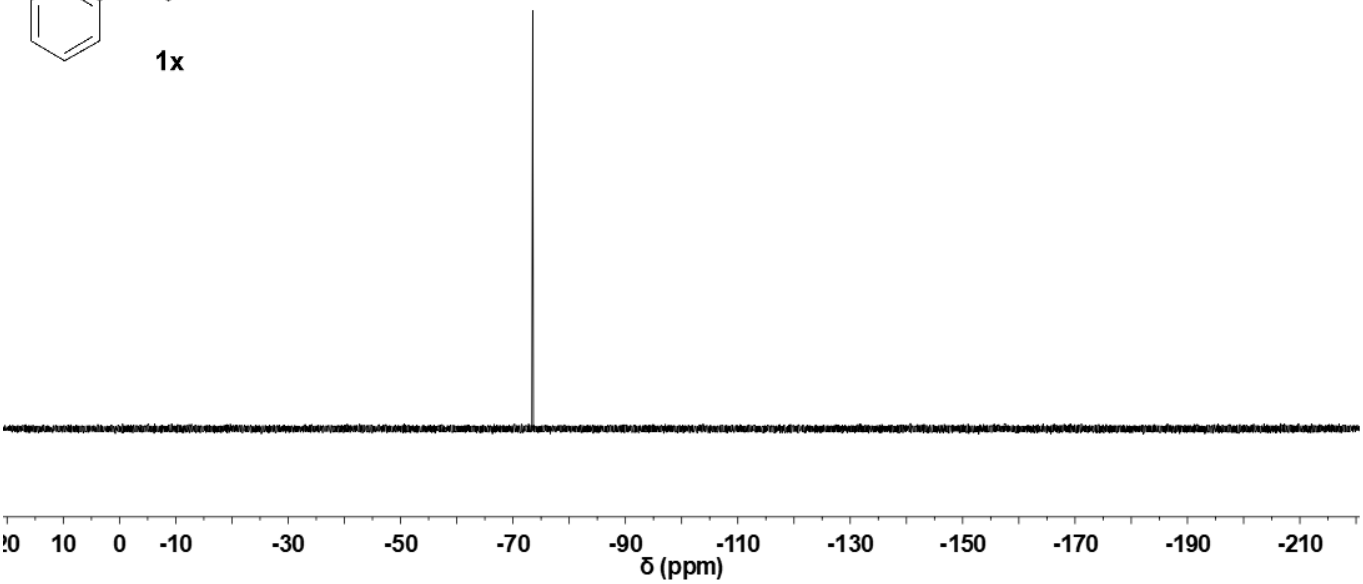

191.618
153.499
139.198
131.832
128.626
127.547
125.298
122.517
93.509
50.700
50.360
50.019
49.677
13C NMR (101 MHz, CDCl3)
O
HN
CF3
1x
δ (ppm)

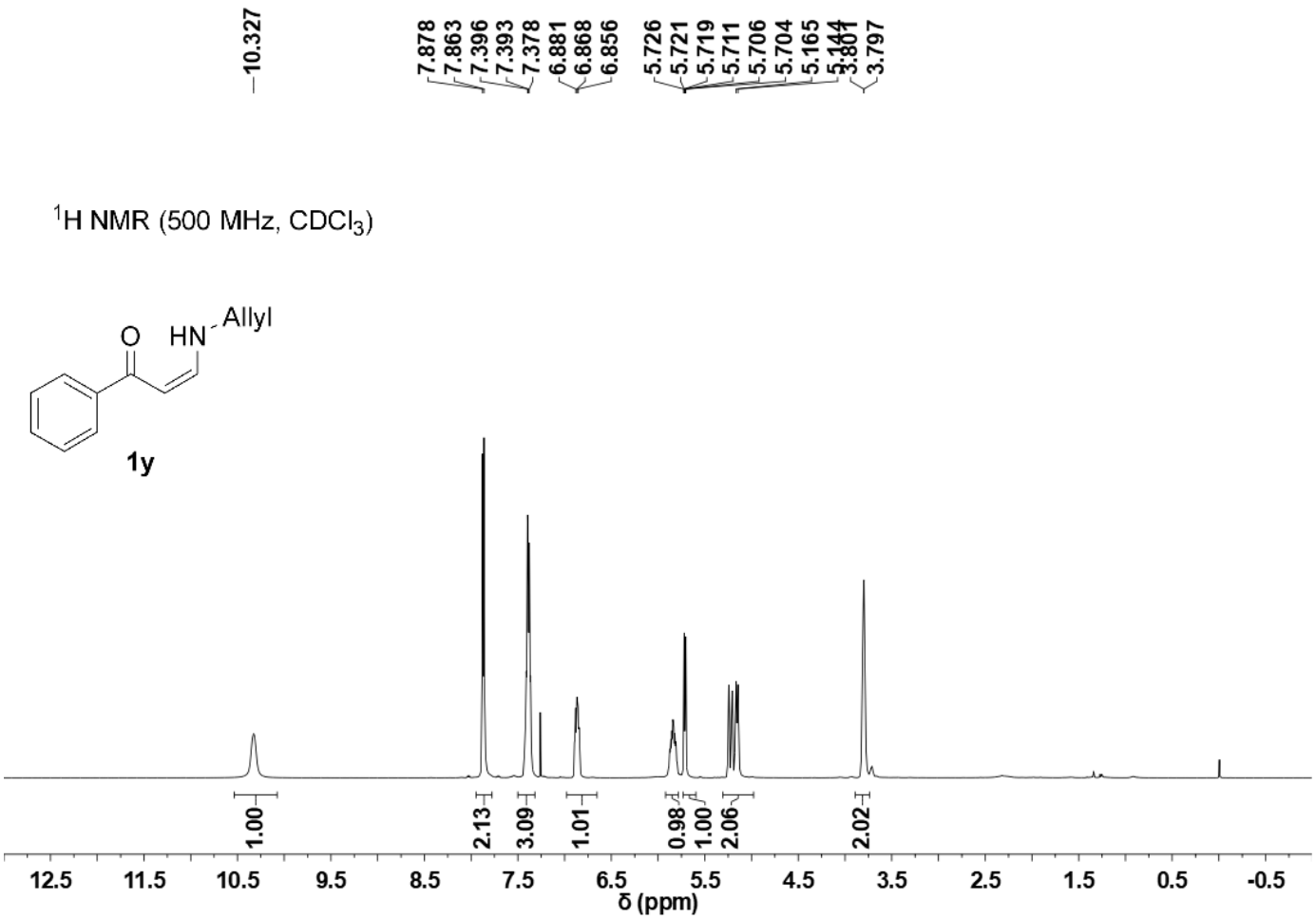
-73.510

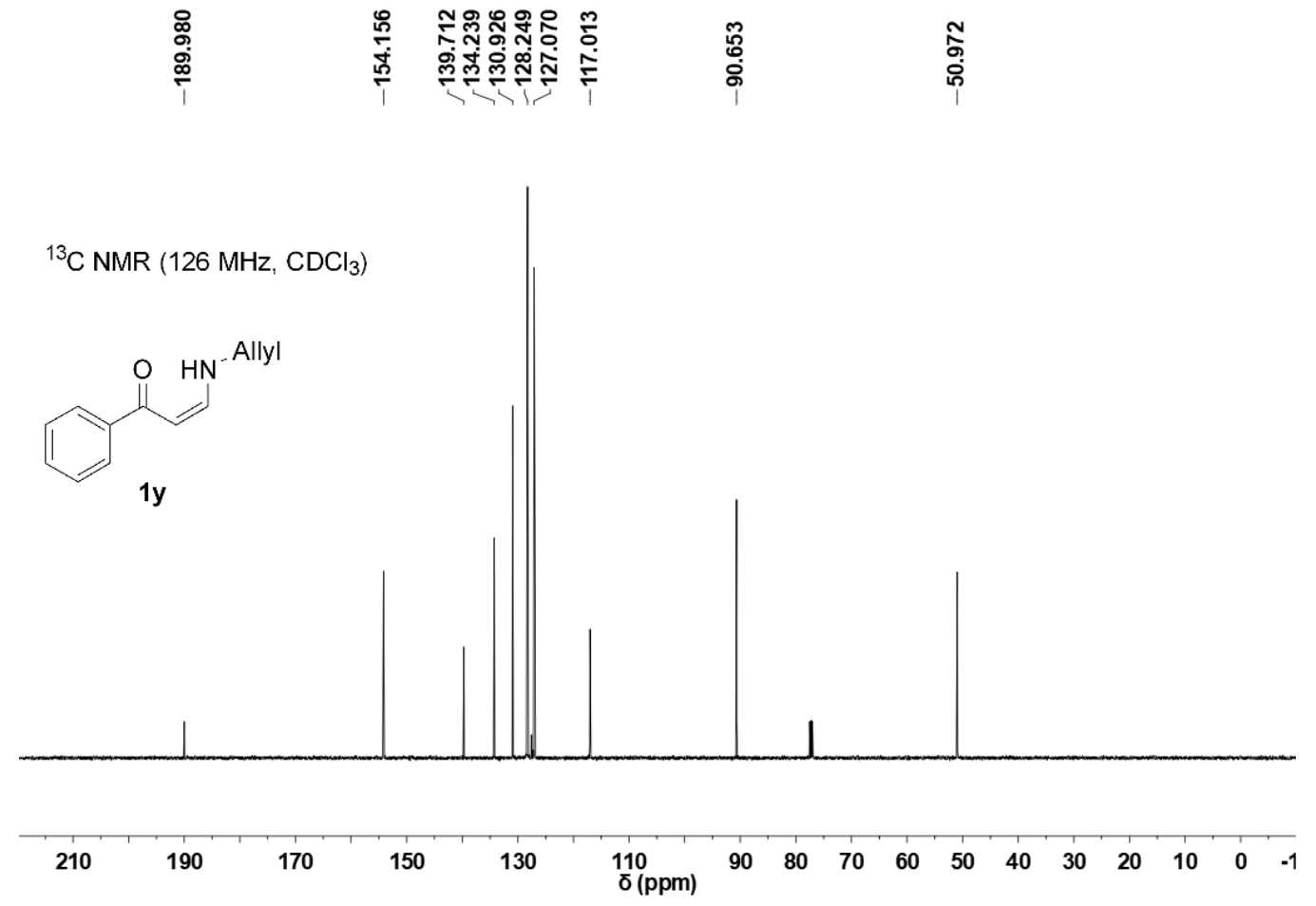
^{19}F NMR (471 MHz, $CDCl_3$)

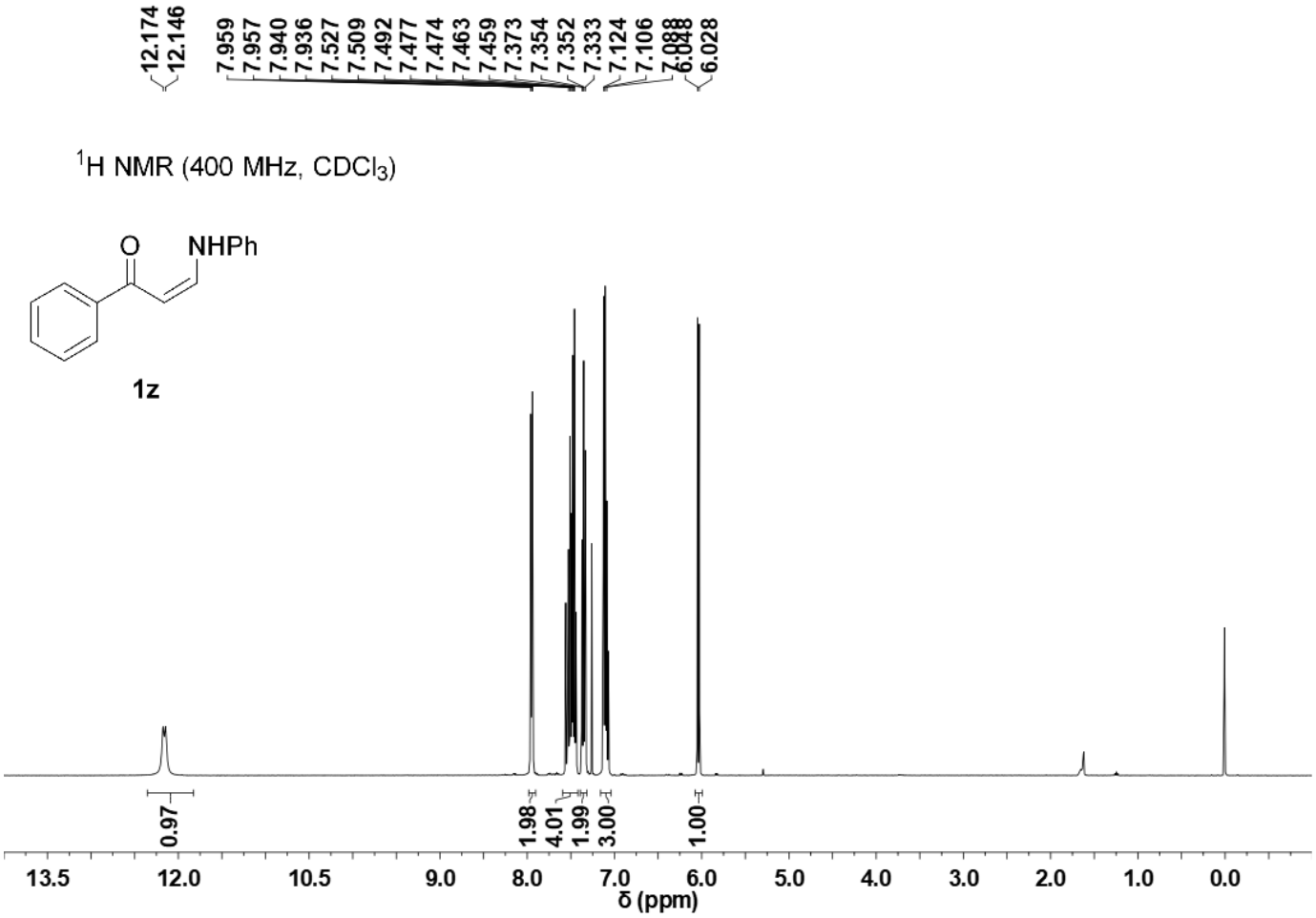


1x

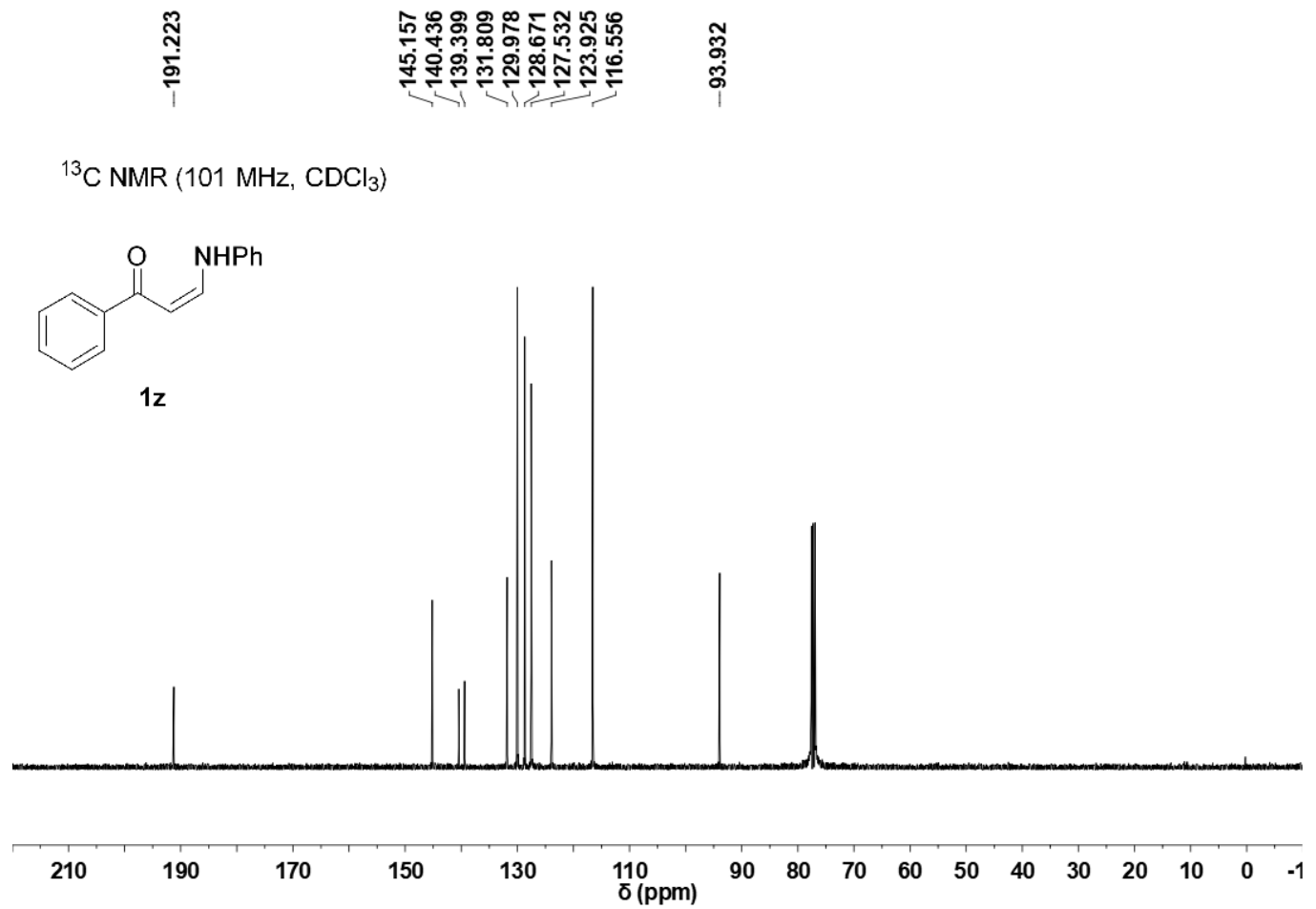



10.327
7.878
7.863
7.396
7.393
7.378
6.881
6.868
6.856
5.726
5.721
5.719
5.711
5.706
5.704
5.165
5.144
3.801
3.797
1H NMR (500 MHz, CDCl3)
O
HN
Allyl
1y
1.00
2.13
3.09
1.01
0.98
1.00
2.06
2.02
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)


189.980
154.156
139.712
134.239
130.926
128.249
127.070
117.013
90.653
50.972
13C NMR (126 MHz, CDCl3)
O
HN
Allyl
1y
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

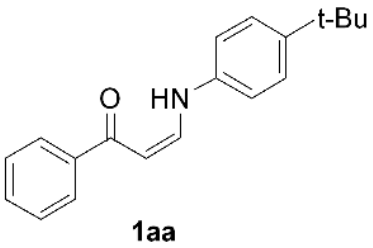


^{1}H NMR (400 MHz, $CDCl_3$)

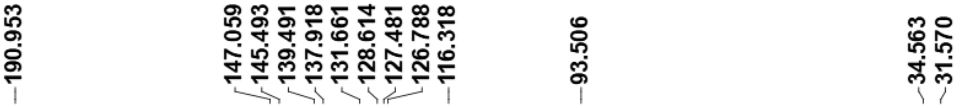


^{13}C NMR (101 MHz, $CDCl_3$)

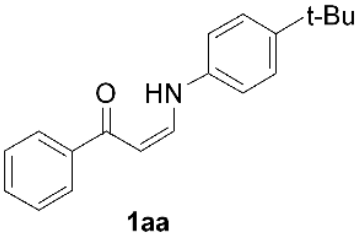
^{1}H NMR (500 MHz, $CDCl_3$)



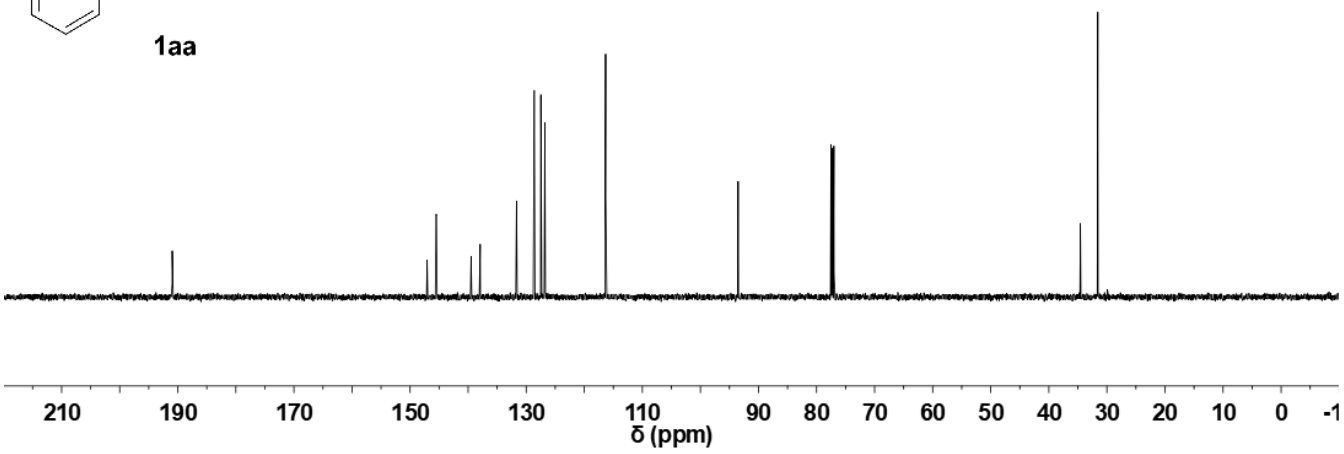
1aa

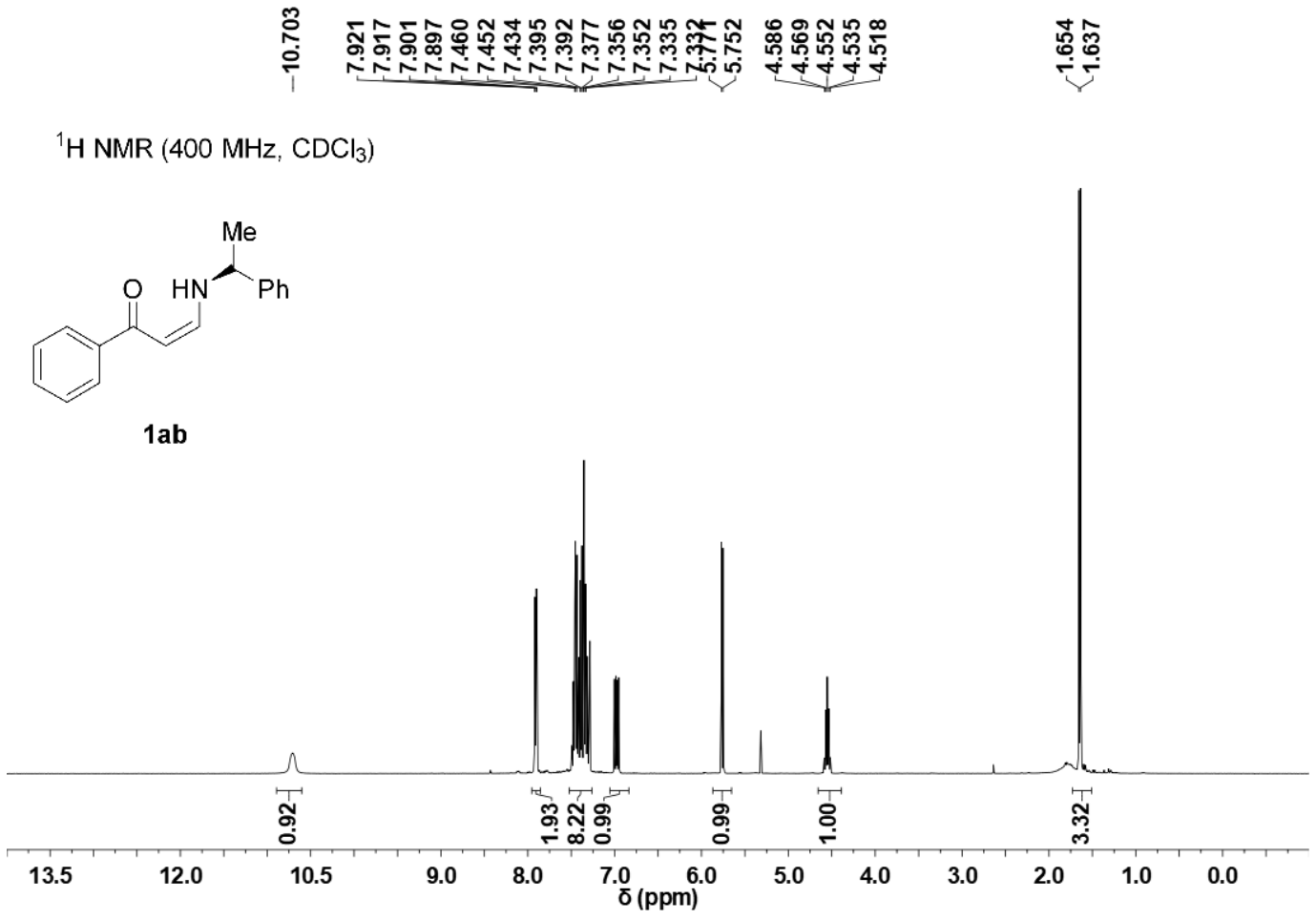


^{13}C NMR (126 MHz, $CDCl_3$)

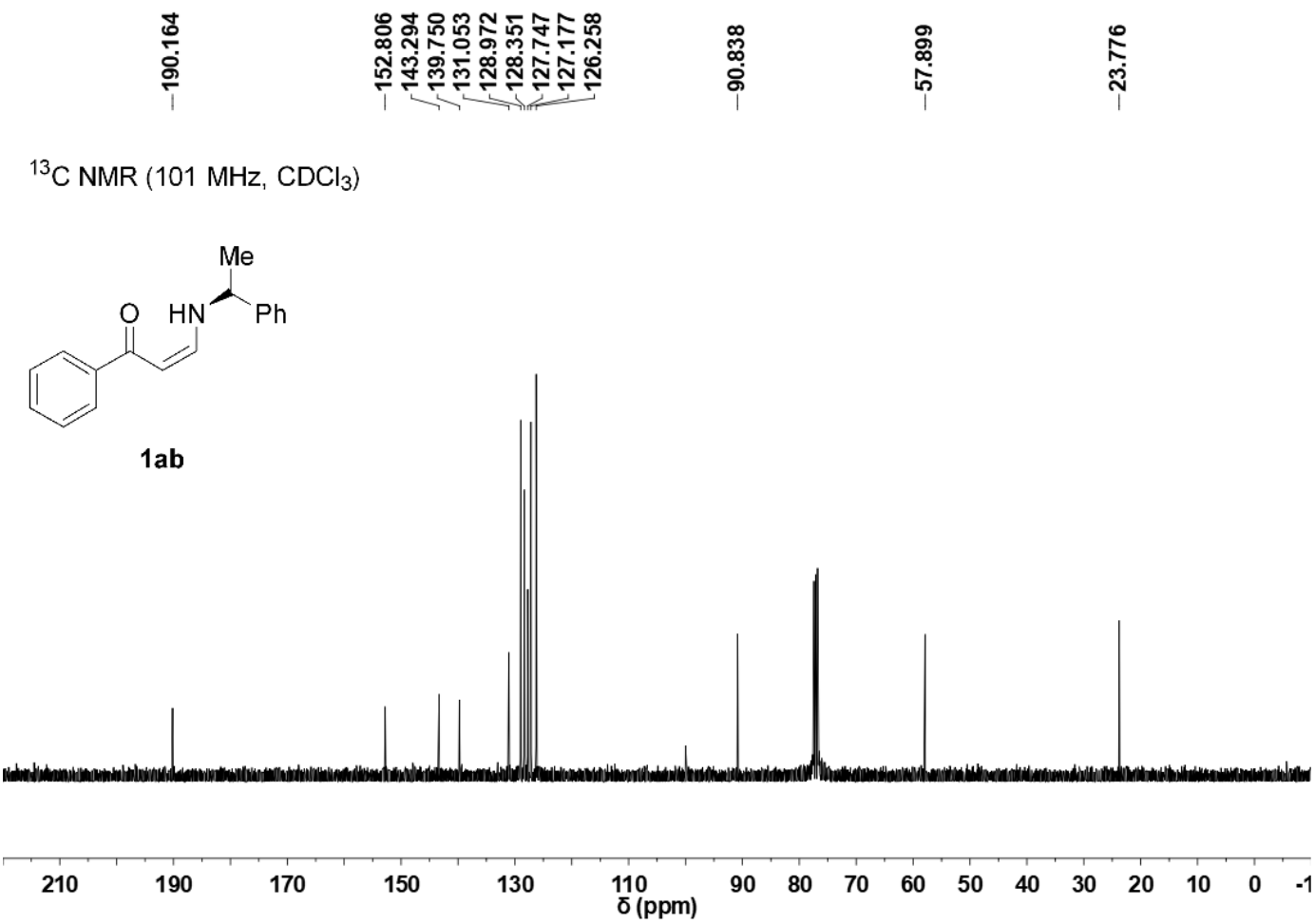


1aa

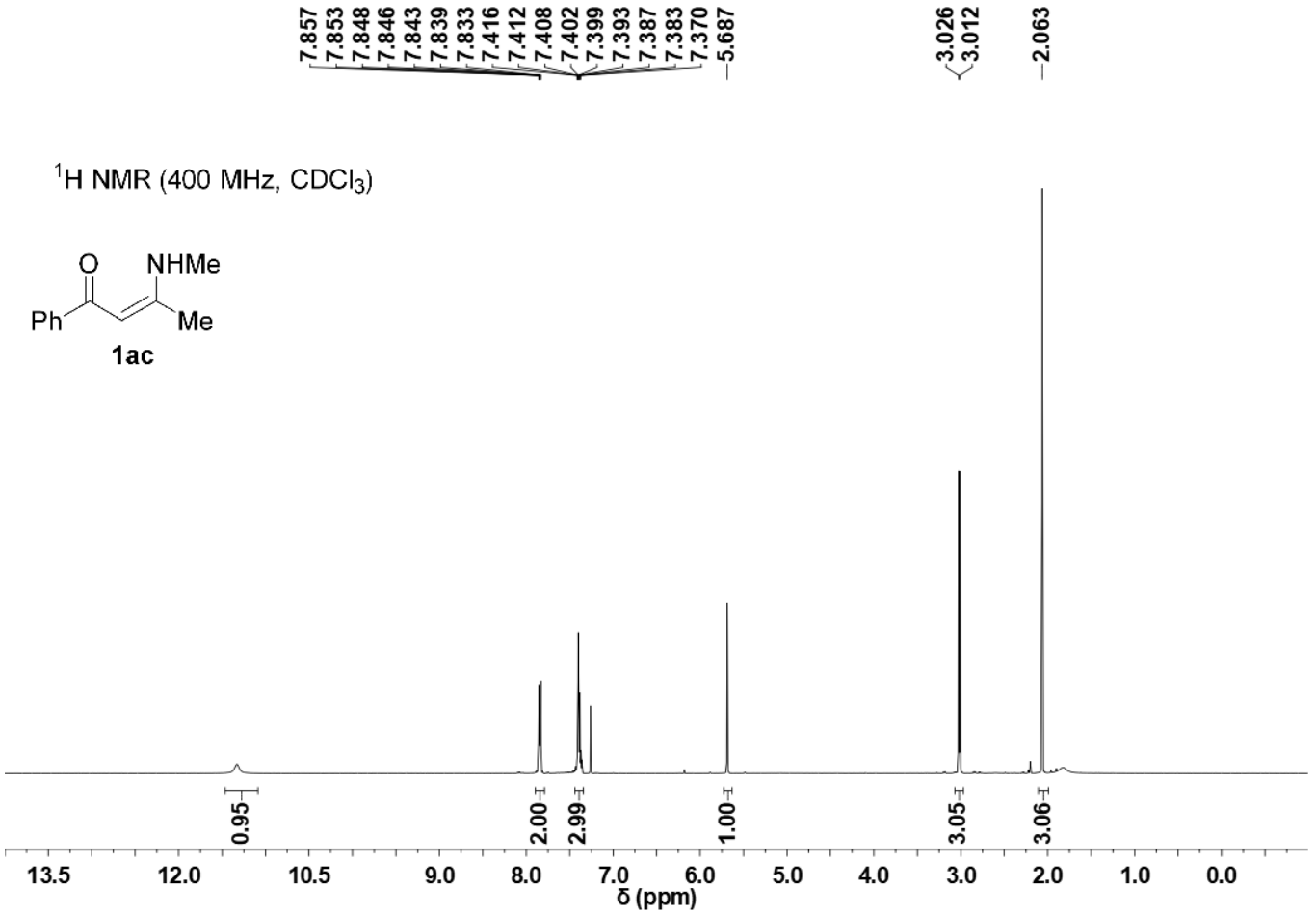


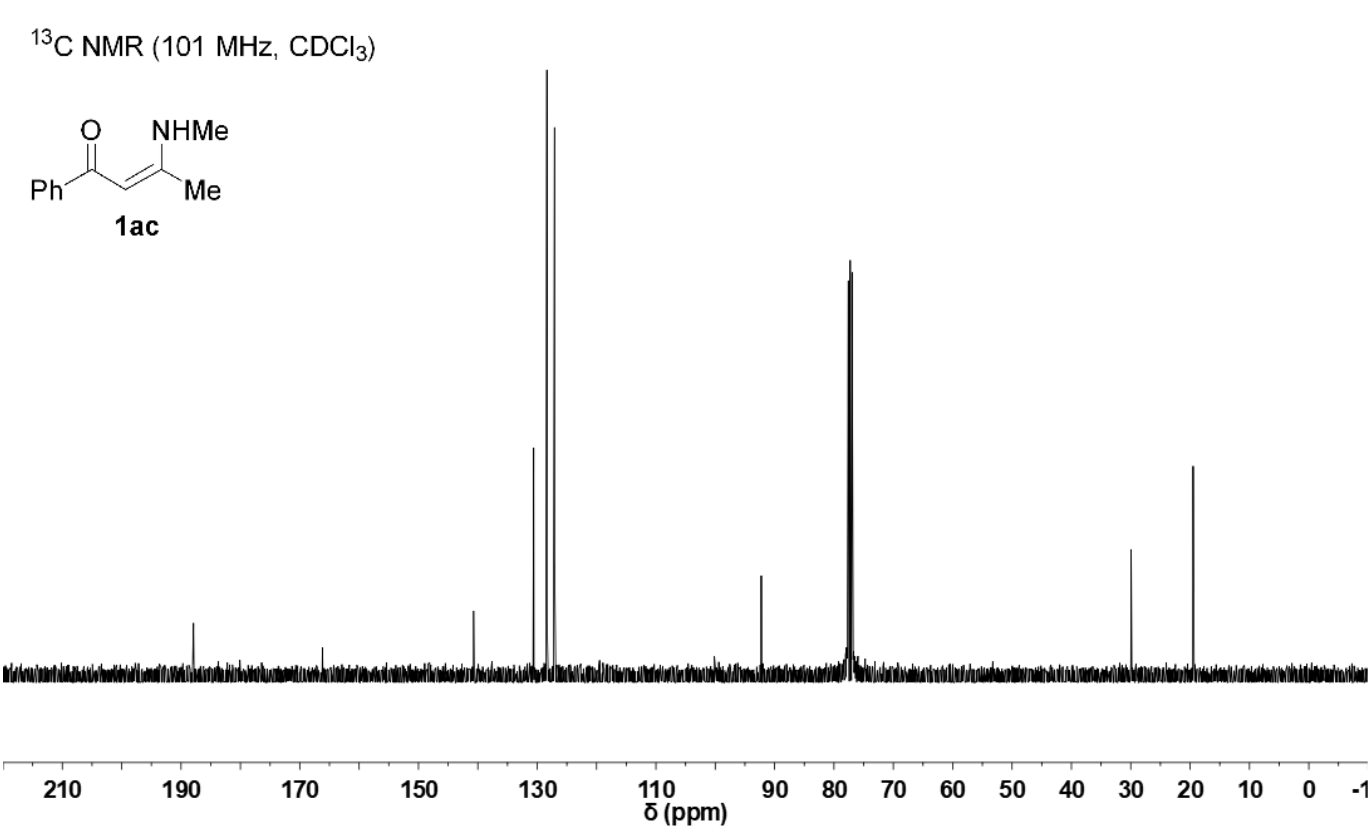


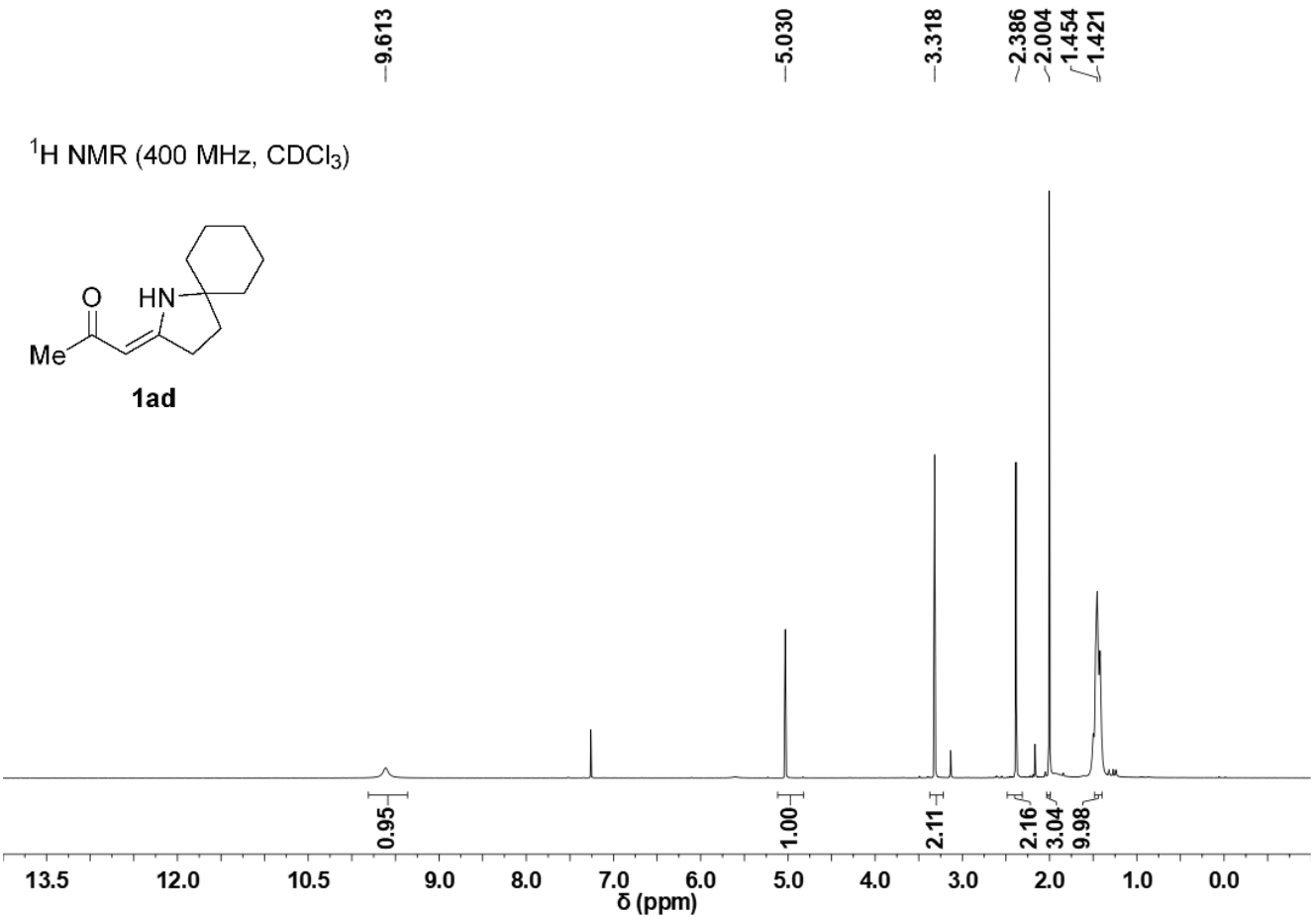
^{1}H NMR (400 MHz, $CDCl_3$)

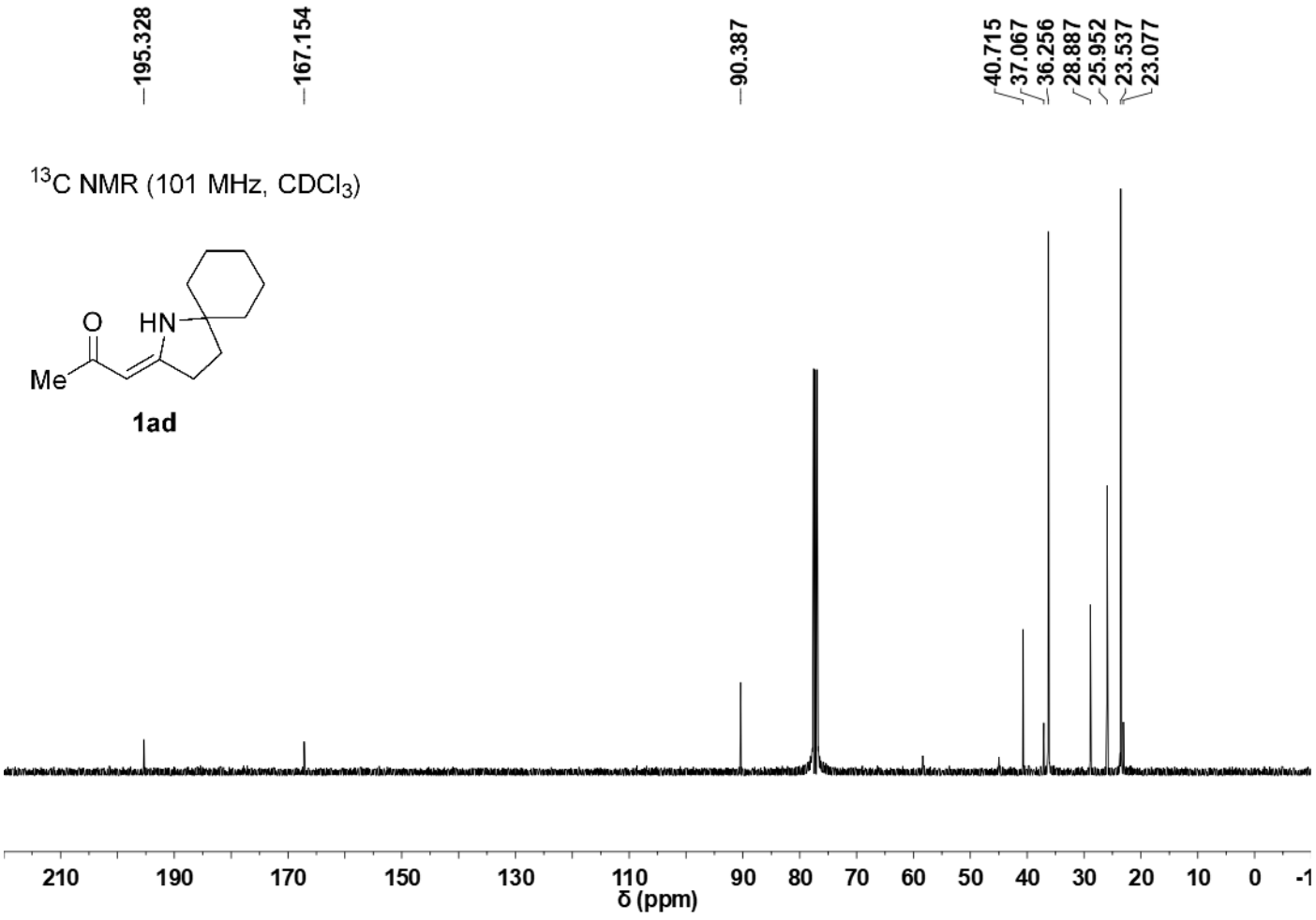


^{13}C NMR (101 MHz, $CDCl_3$)

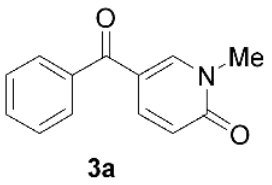

7.857
7.853
7.848
7.846
7.843
7.839
7.833
7.416
7.412
7.408
7.402
7.399
7.393
7.387
7.383
7.370
5.687
3.026
3.012
2.063
1H NMR (400 MHz, CDCl3)
O
NHMe
Ph
Me
1ac
0.95
2.00
2.99
1.00
3.05
3.06
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)


187.904
166.168
140.714
130.592
128.365
127.074
92.241
29.932
19.486
13C NMR (101 MHz, CDCl3)
O
NHMe
Ph
Me
1ac
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

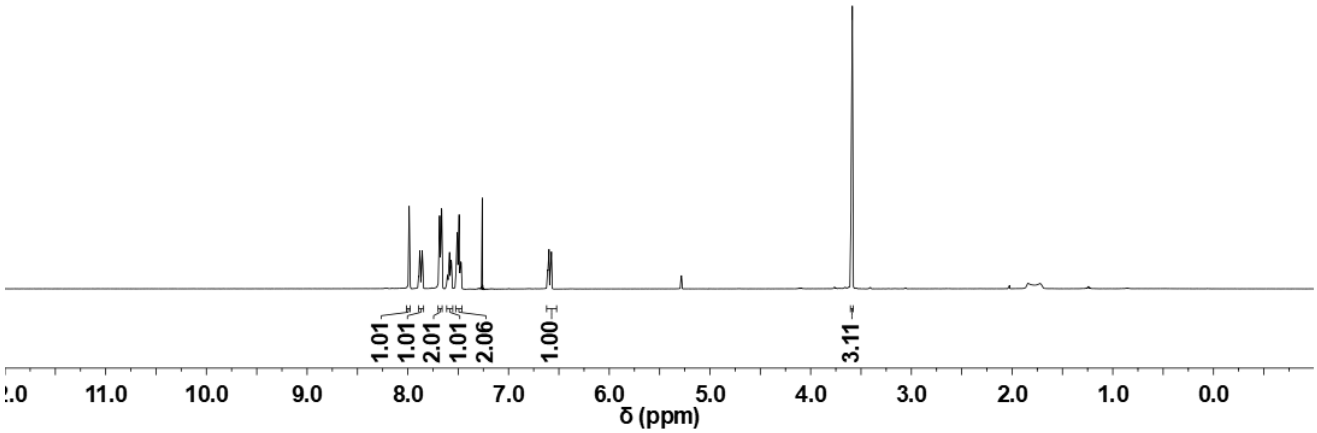

9.613
5.030
3.318
2.386
2.004
1.454
1.421
^{1}H NMR (400 MHz, $CDCl_3$)
O
HN
Me
1ad
0.95
1.00
2.11
2.16
3.04
9.98
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)


195.328
167.154
90.387
40.715
37.067
36.256
28.887
25.952
23.537
23.077
^{13}C NMR (101 MHz, $CDCl_3$)
O
HN
Me
1ad
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

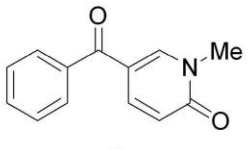
^{1}H NMR (400 MHz, $CDCl_3$)



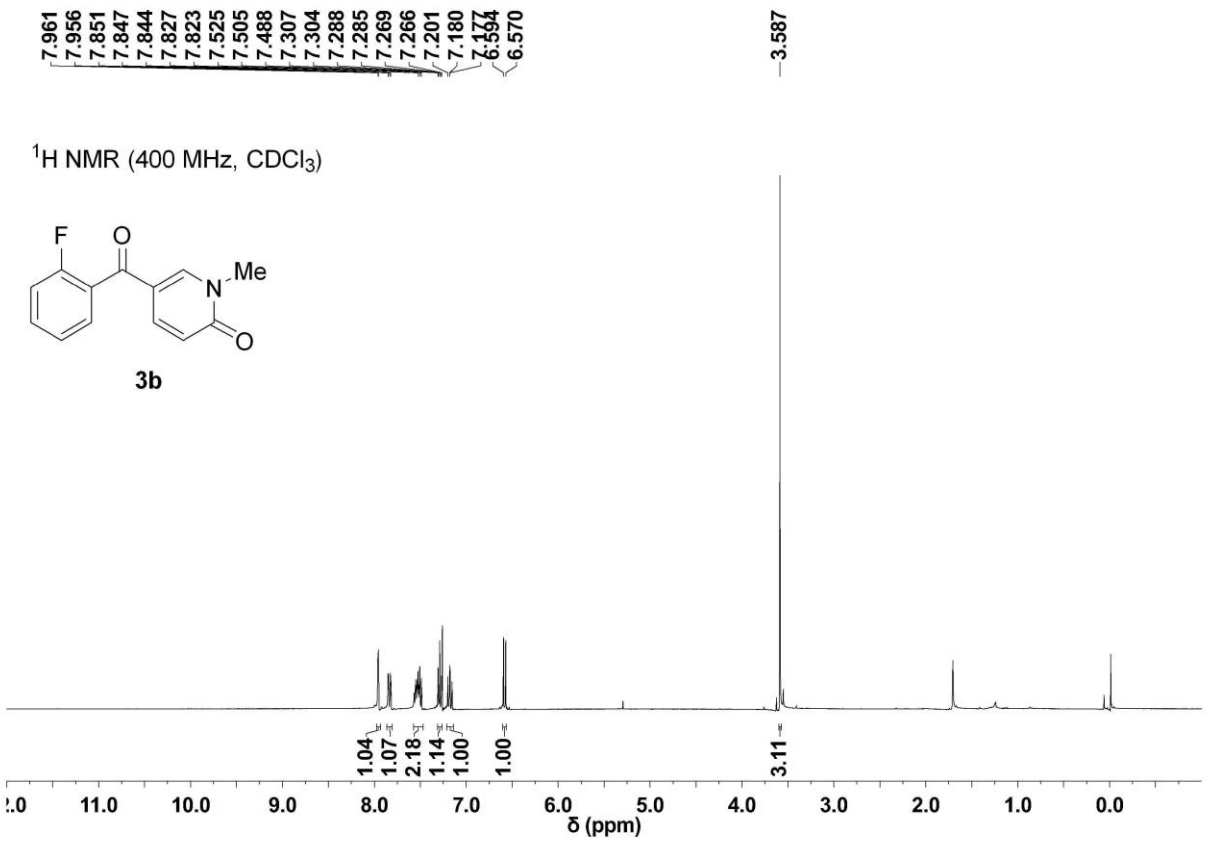
3a

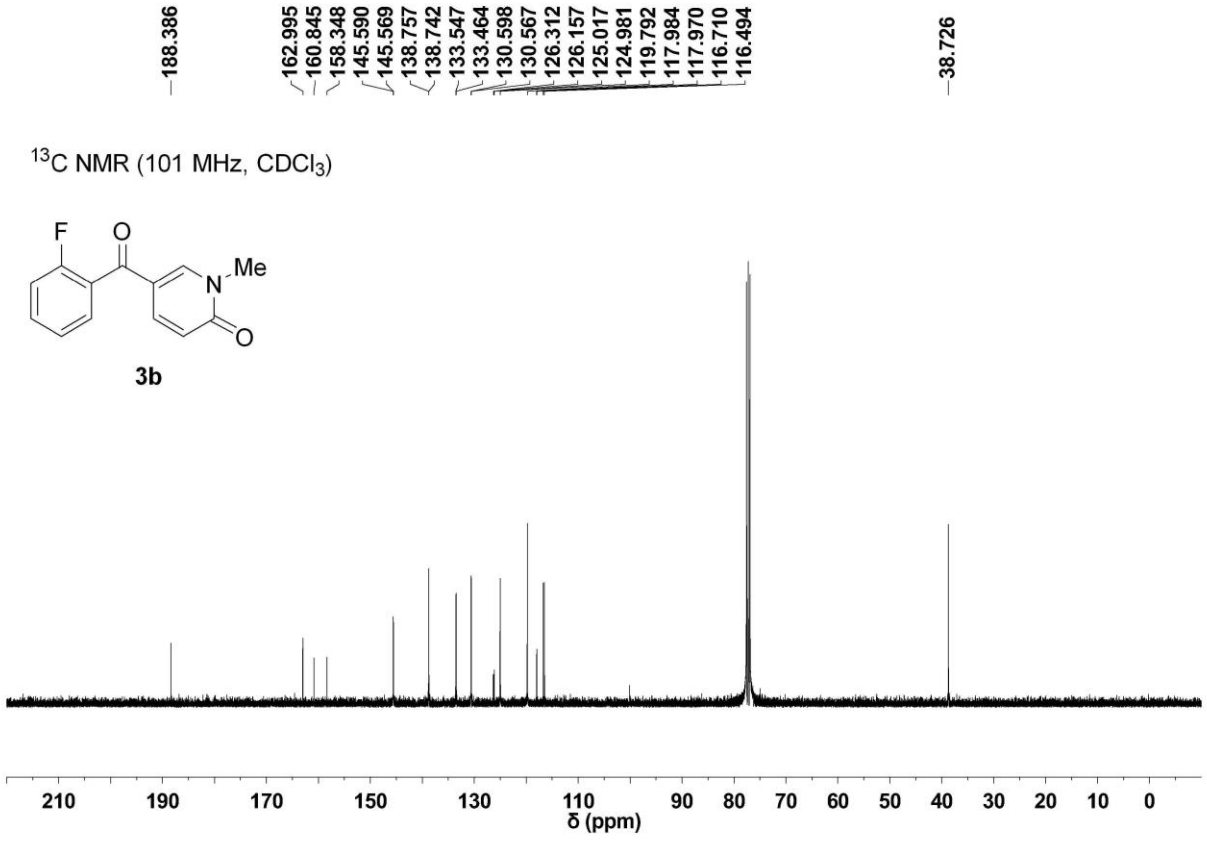


^{13}C NMR (101 MHz, $CDCl_3$)



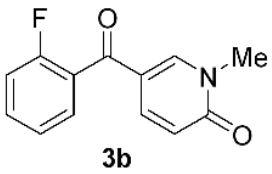
3a


7.961
7.956
7.851
7.847
7.844
7.827
7.823
7.525
7.505
7.488
7.307
7.304
7.288
7.285
7.269
7.266
7.201
7.180
7.177
6.594
6.570
3.587
1H NMR (400 MHz, CDCl3)
F
O
N
Me
O
3b
1.04
1.07
2.18
1.14
1.00
1.00
3.11
δ (ppm)

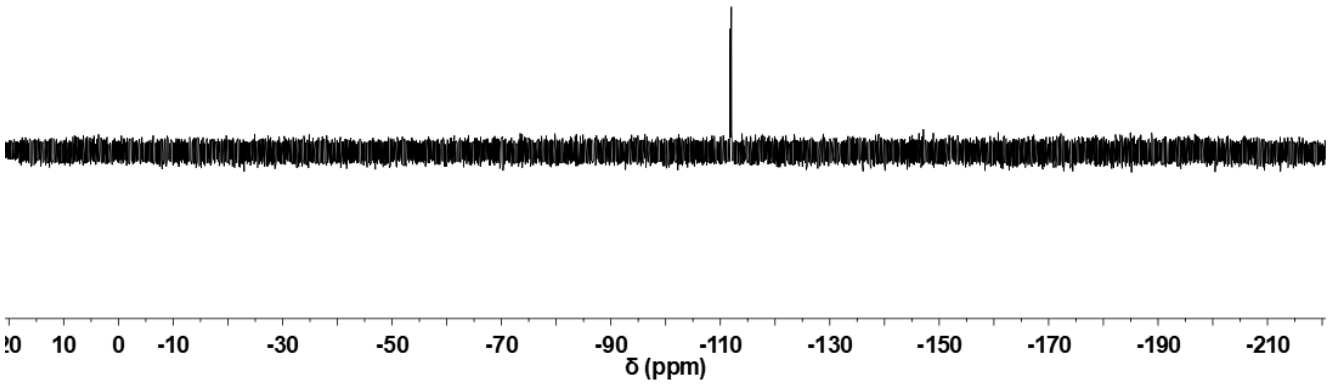

188.386
162.995
160.845
158.348
145.590
145.569
138.757
138.742
133.547
133.464
130.598
130.567
126.312
126.157
125.017
124.981
119.792
117.984
117.970
116.710
116.494
38.726
13C NMR (101 MHz, CDCl3)
F
O
N
Me
O
3b
δ (ppm)

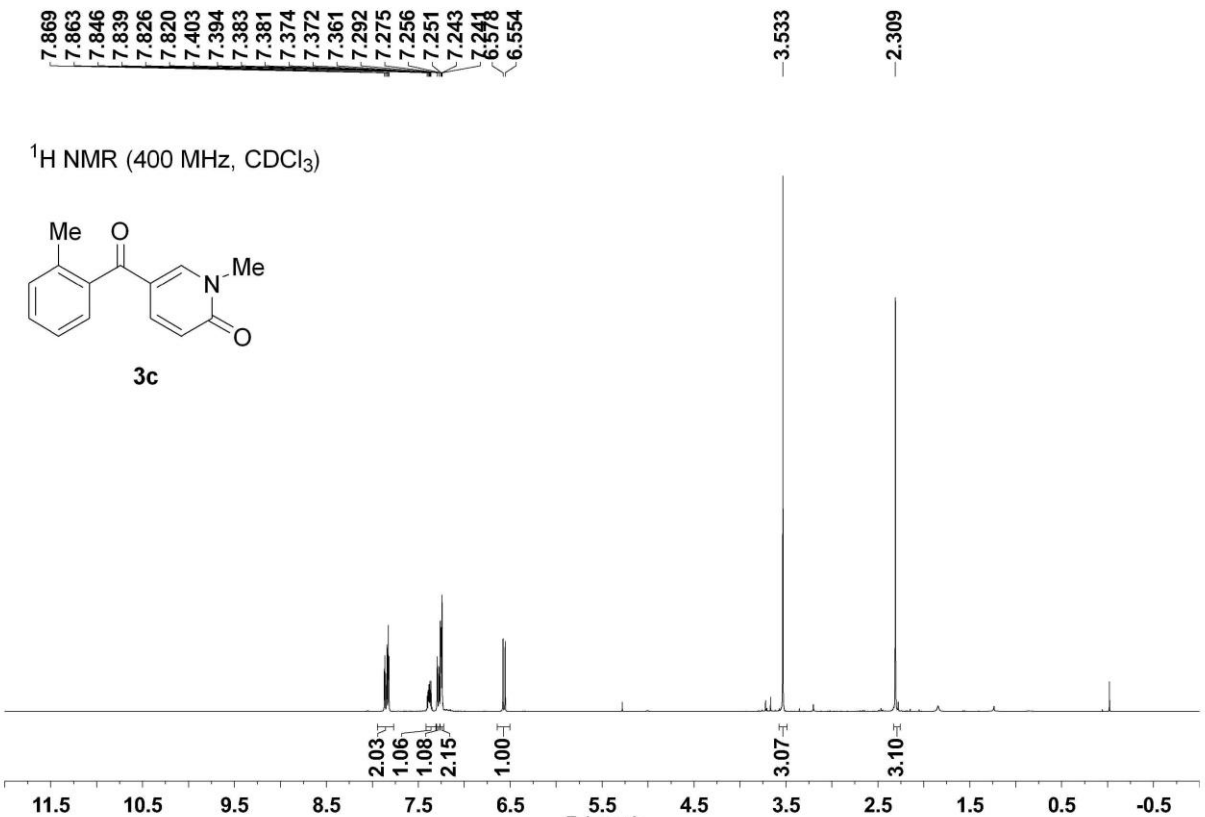
-112.018

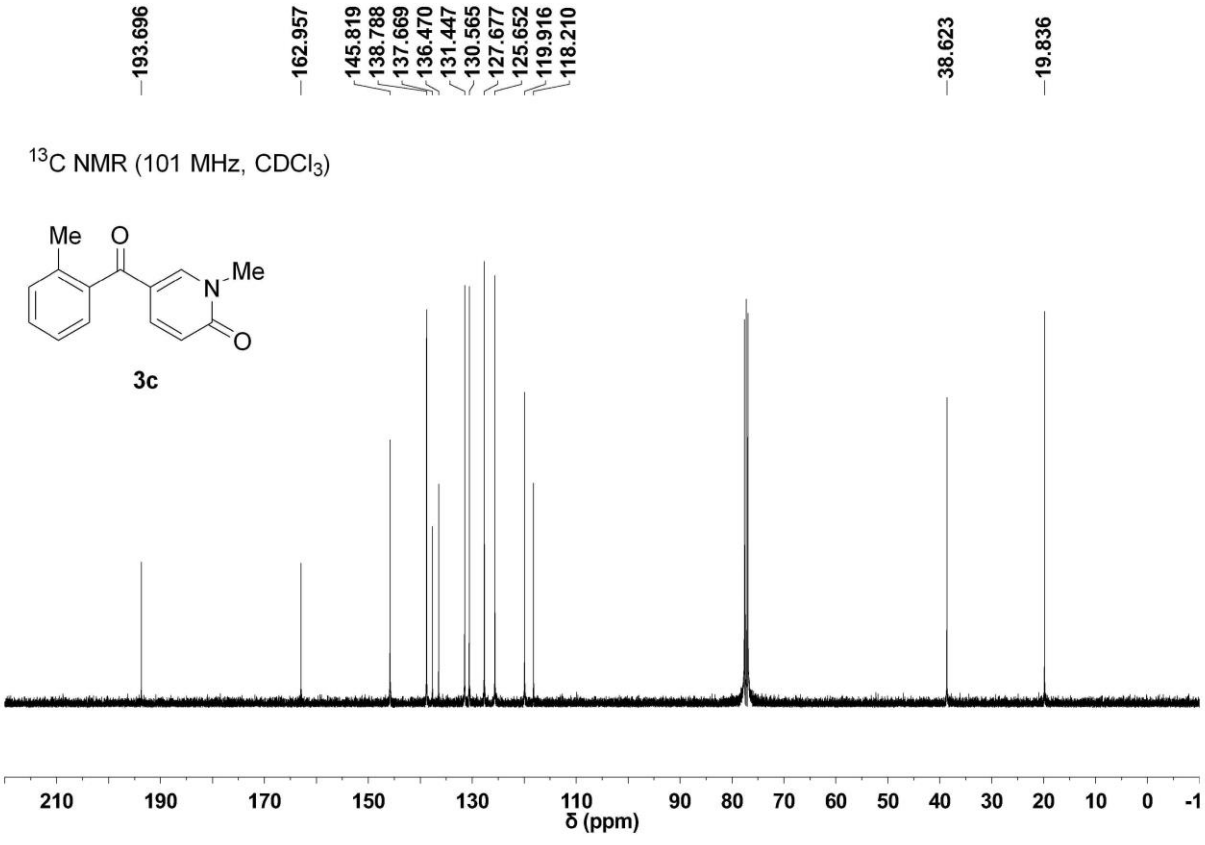
^{19}F NMR (471 MHz, $CDCl_3$)



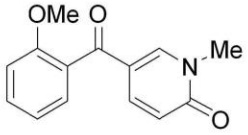
3b



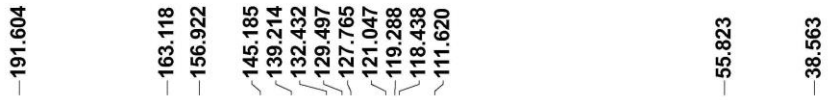

7.869
7.863
7.846
7.839
7.826
7.820
7.403
7.394
7.383
7.381
7.374
7.372
7.361
7.292
7.275
7.256
7.251
7.243
7.241
6.578
6.554
3.533
2.309
1H NMR (400 MHz, CDCl3)
Me
O
N
Me
O
3c
2.03
1.06
1.08
2.15
1.00
3.07
3.10
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)


193.696
162.957
145.819
138.788
137.669
136.470
131.447
130.565
127.677
125.652
119.916
118.210
38.623
19.836
13C NMR (101 MHz, CDCl3)
Me
O
N
Me
O
3c
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

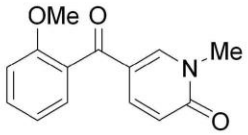
^{1}H NMR (400 MHz, $CDCl_3$)



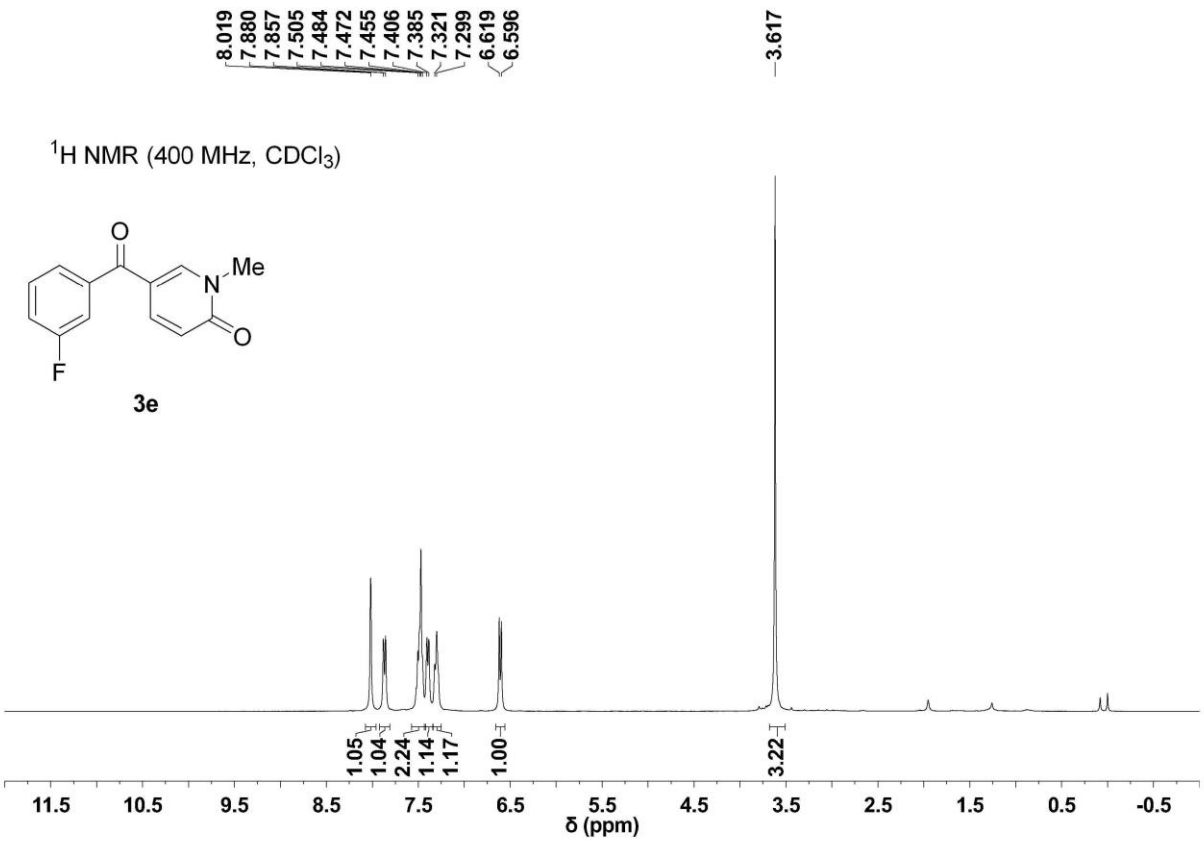
3d

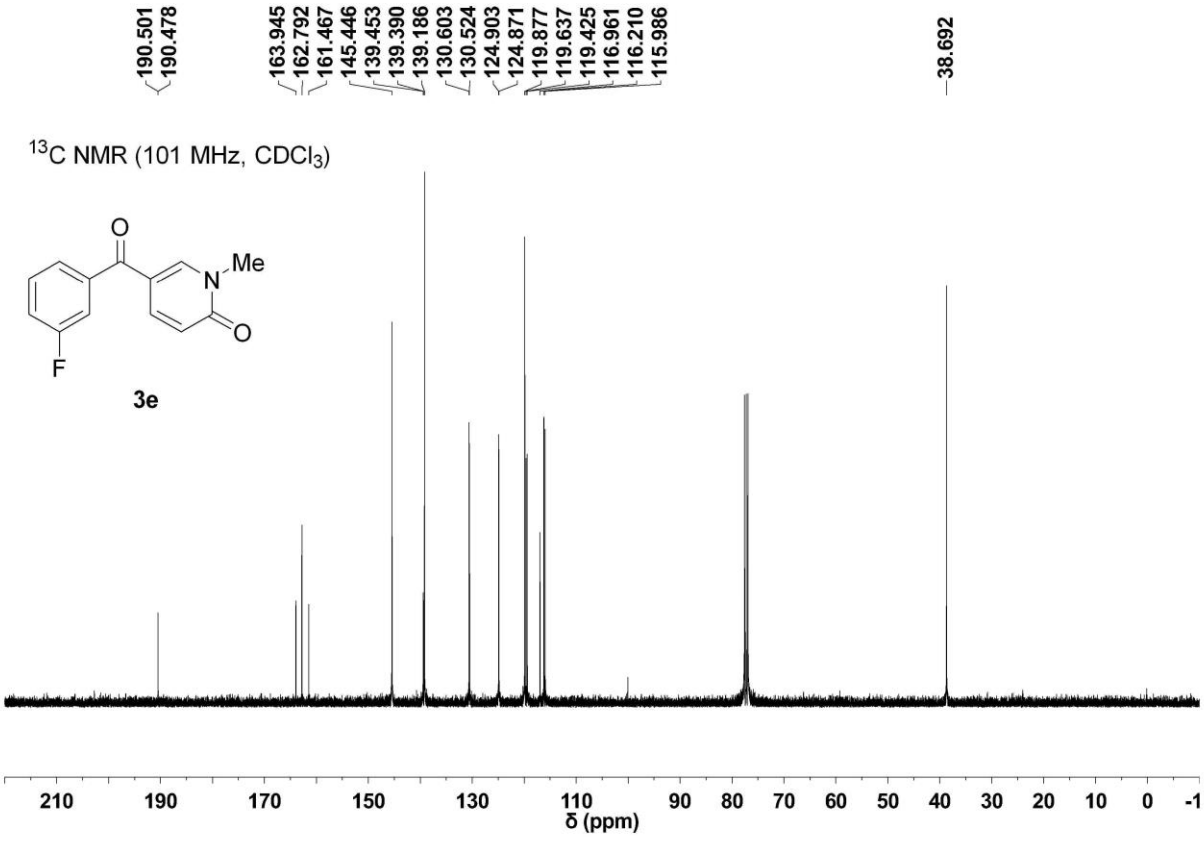


^{13}C NMR (101 MHz, $CDCl_3$)

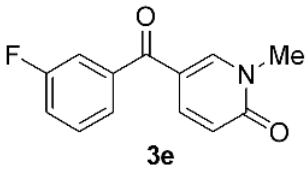


3d

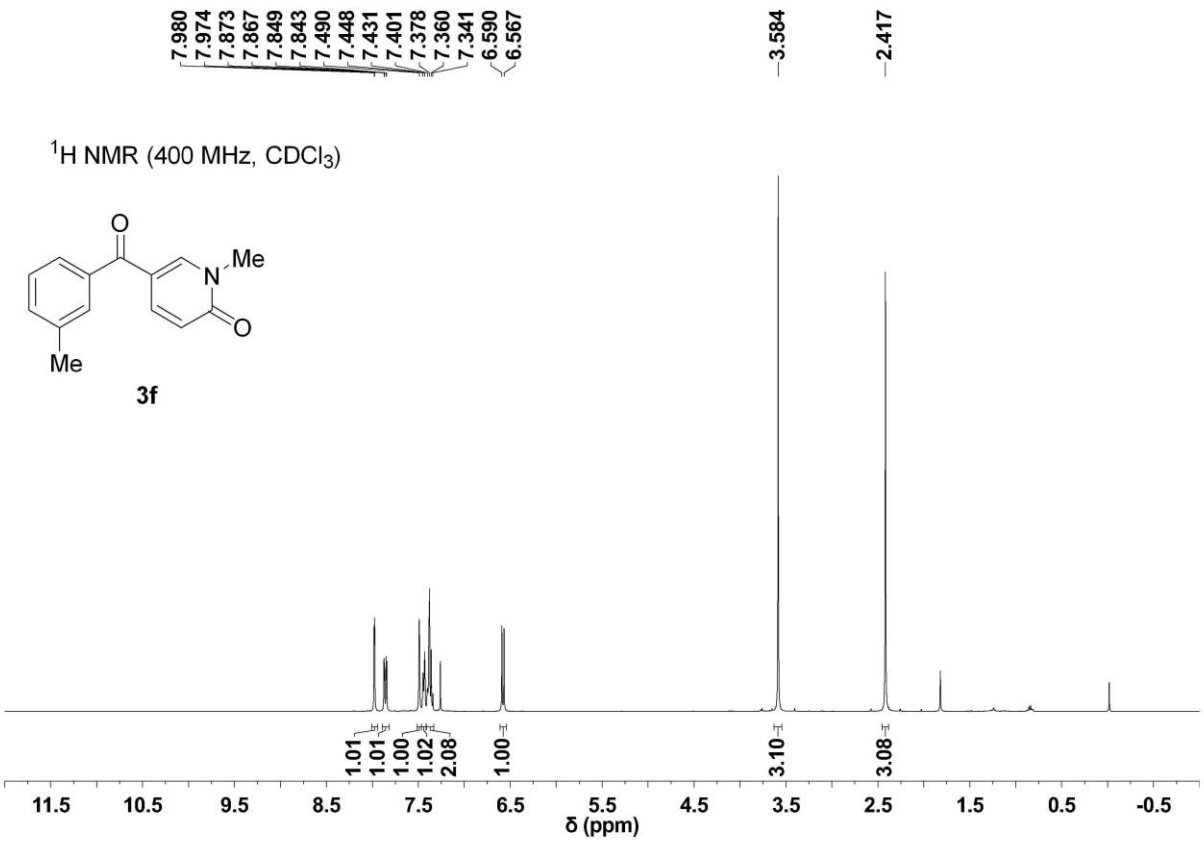

8.019
7.880
7.857
7.505
7.484
7.472
7.455
7.406
7.385
7.321
7.299
6.619
6.596
3.617
1H NMR (400 MHz, CDCl3)
O
N
Me
O
F
3e
1.05
1.04
2.24
1.14
1.17
1.00
3.22
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

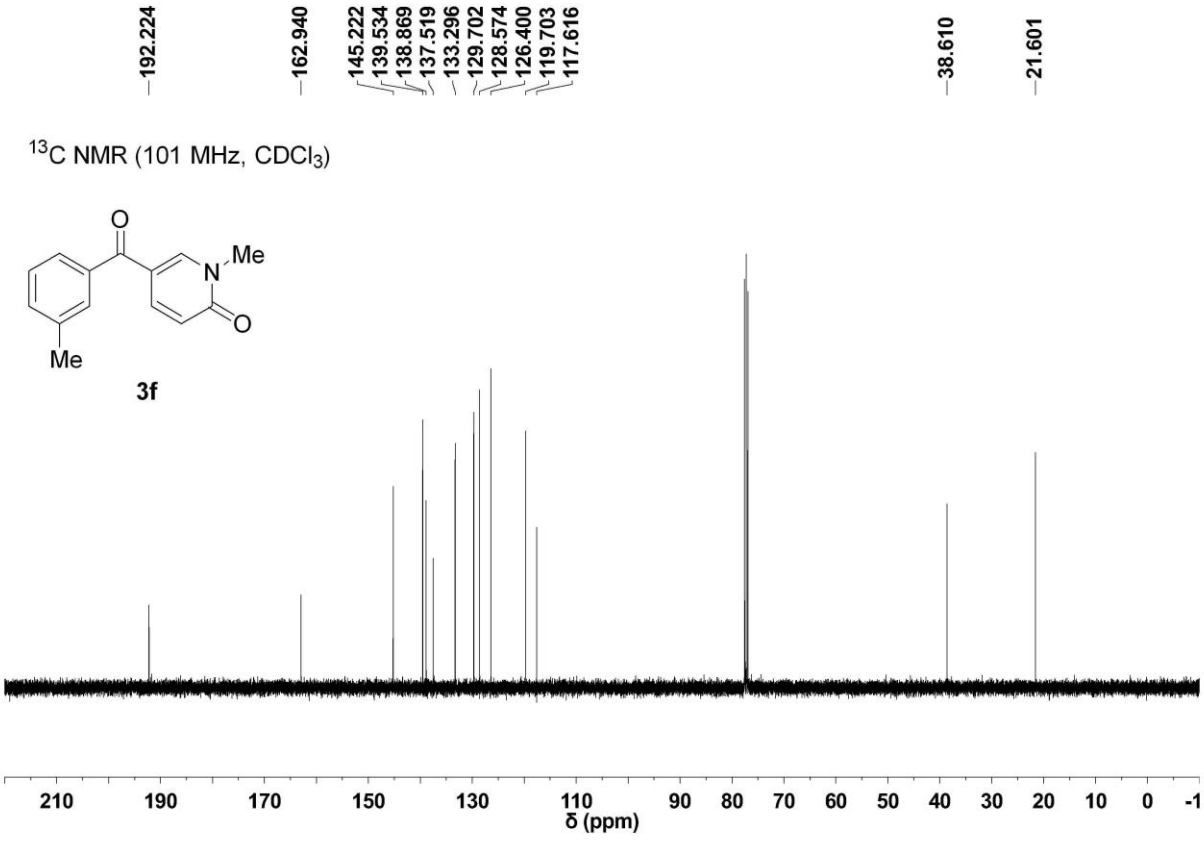

190.501
190.478
163.945
162.792
161.467
145.446
139.453
139.390
139.186
130.603
130.524
124.903
124.871
119.877
119.637
119.425
116.961
116.210
115.986
38.692
13C NMR (101 MHz, CDCl3)
O
N
Me
O
F
3e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

^{19}F NMR (471 MHz, $CDCl_3$)

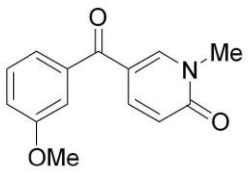


3e


7.980
7.974
7.873
7.867
7.849
7.843
7.490
7.448
7.431
7.401
7.378
7.360
7.341
6.590
6.567
3.584
2.417
1H NMR (400 MHz, CDCl3)
O
N
Me
O
Me
3f
1.01
1.01
1.00
1.02
2.08
1.00
3.10
3.08
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

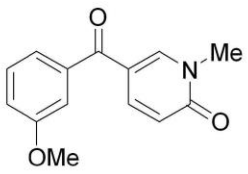

192.224
162.940
145.222
139.534
138.869
137.519
133.296
129.702
128.574
126.400
119.703
117.616
38.610
21.601
13C NMR (101 MHz, CDCl3)
O
N
Me
O
Me
3f
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

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

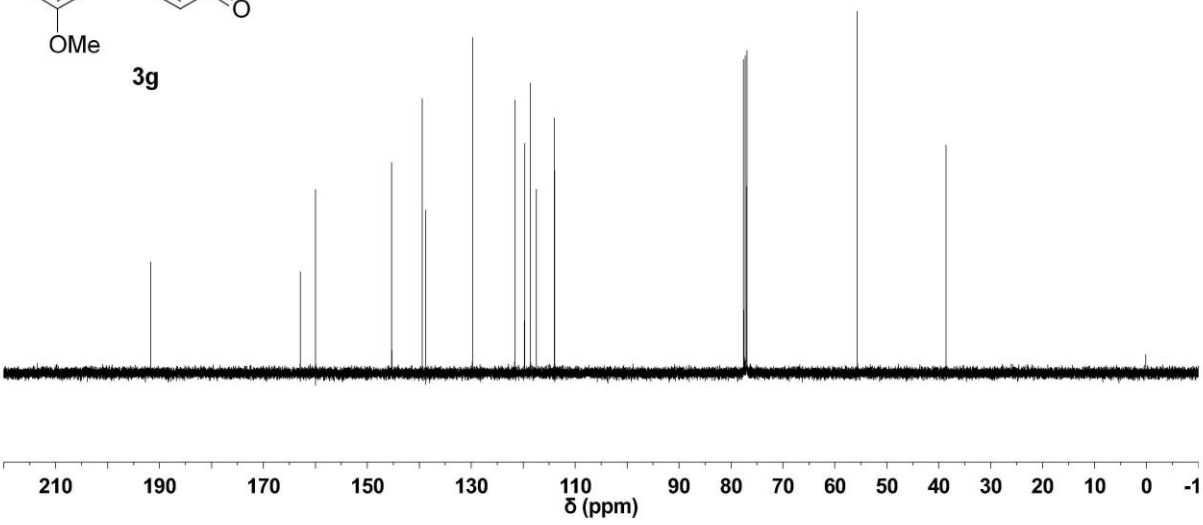


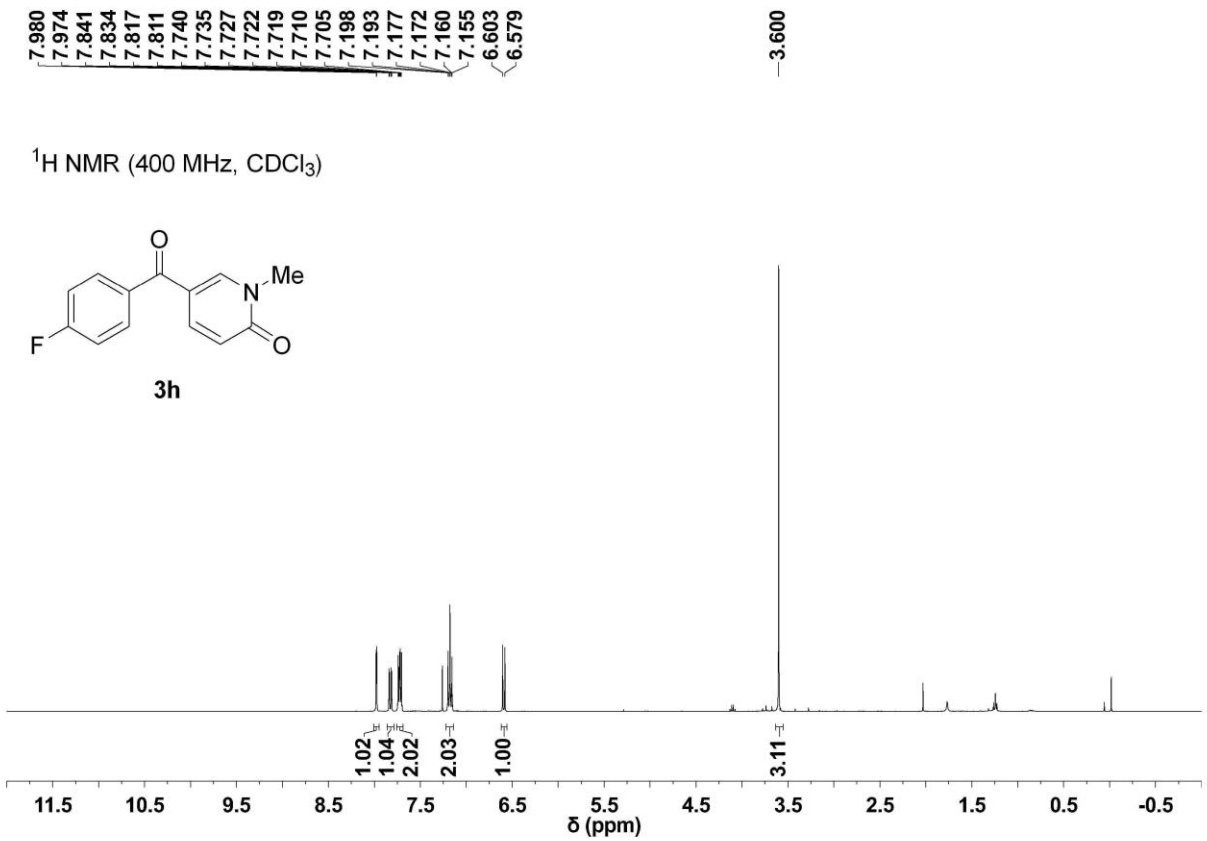
3g

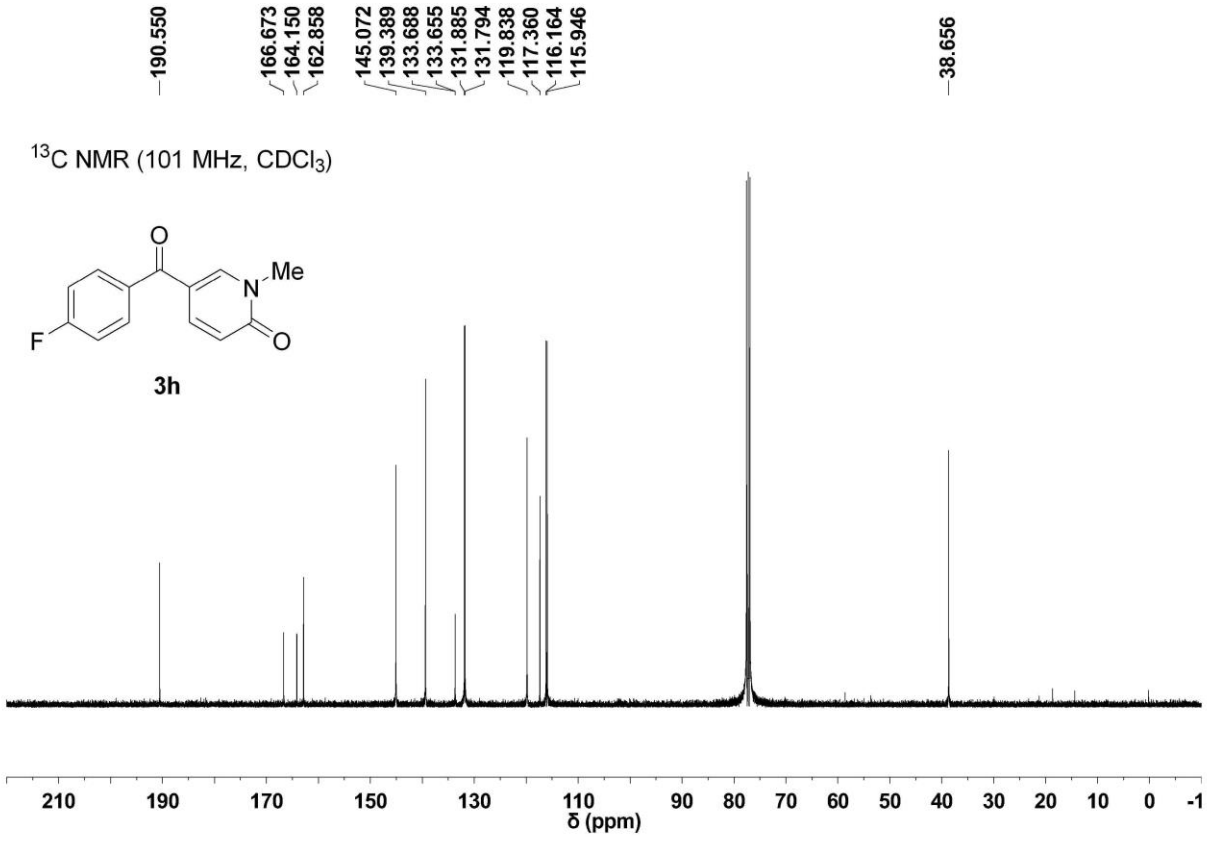
^{13}C NMR (101 MHz, $CDCl_3$)



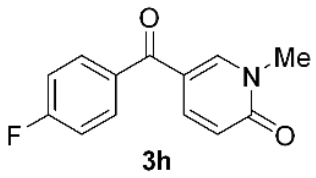
3g



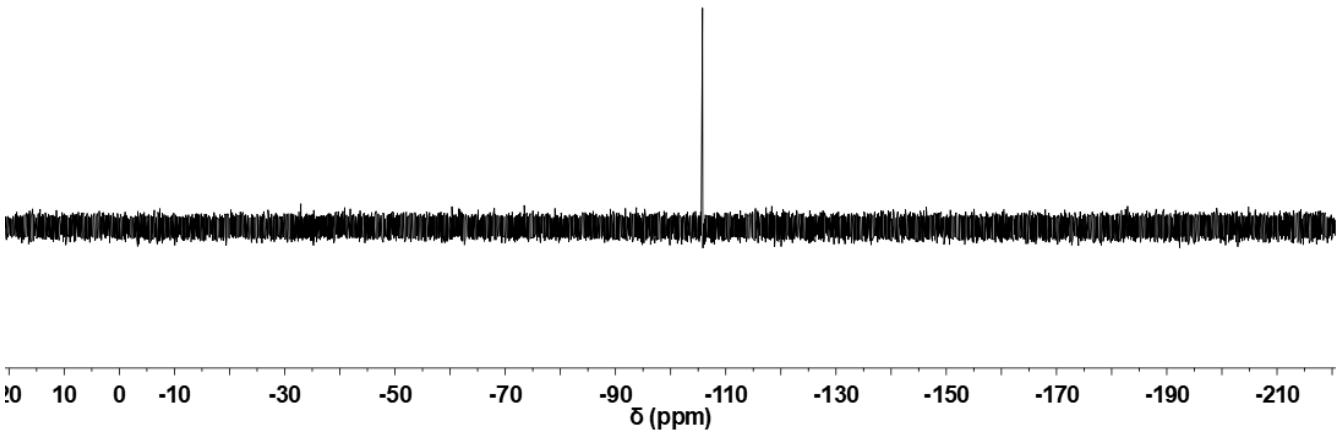

7.980
7.974
7.841
7.834
7.817
7.811
7.740
7.735
7.727
7.722
7.719
7.710
7.705
7.198
7.193
7.177
7.172
7.160
7.155
6.603
6.579
3.600
1H NMR (400 MHz, CDCl3)
O
N
Me
F
O
3h
1.02
1.04
2.02
2.03
1.00
3.11
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

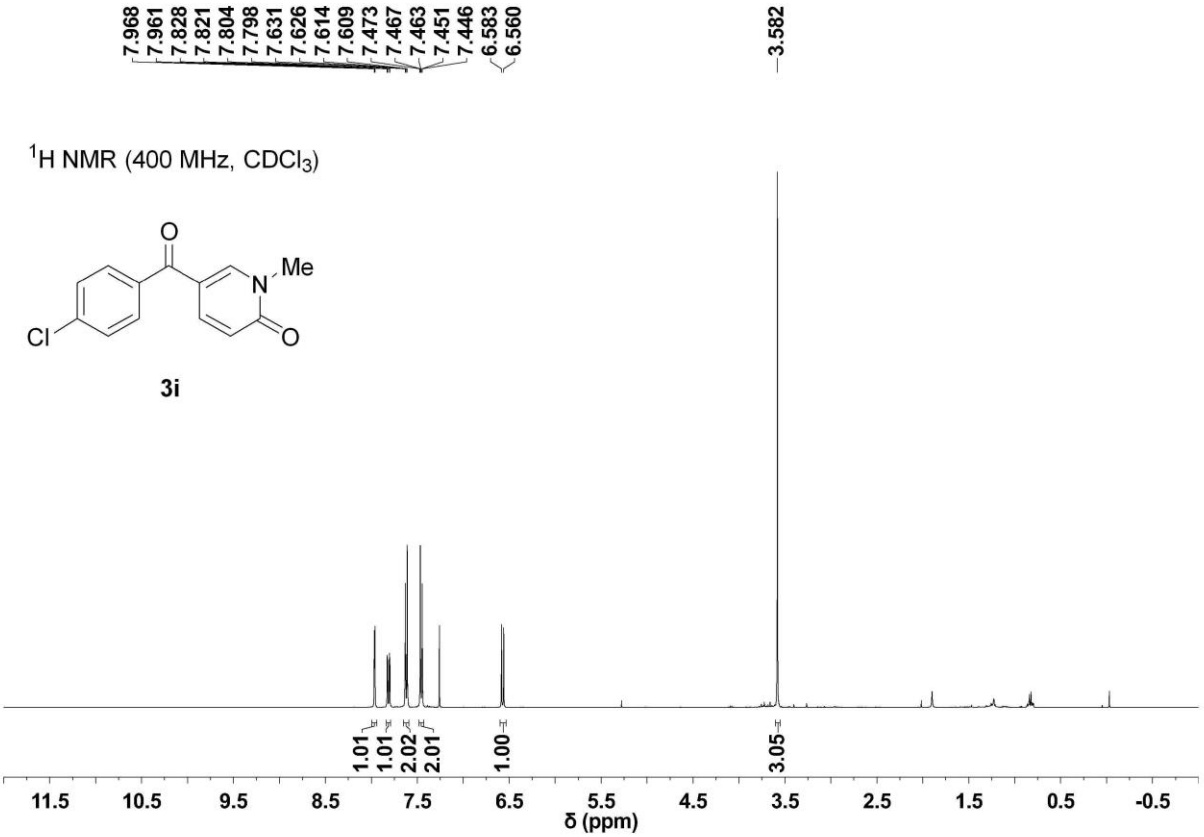

190.550
166.673
164.150
162.858
145.072
139.389
133.688
133.655
131.885
131.794
119.838
117.360
116.164
115.946
38.656
13C NMR (101 MHz, CDCl3)
O
N
Me
F
O
3h
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

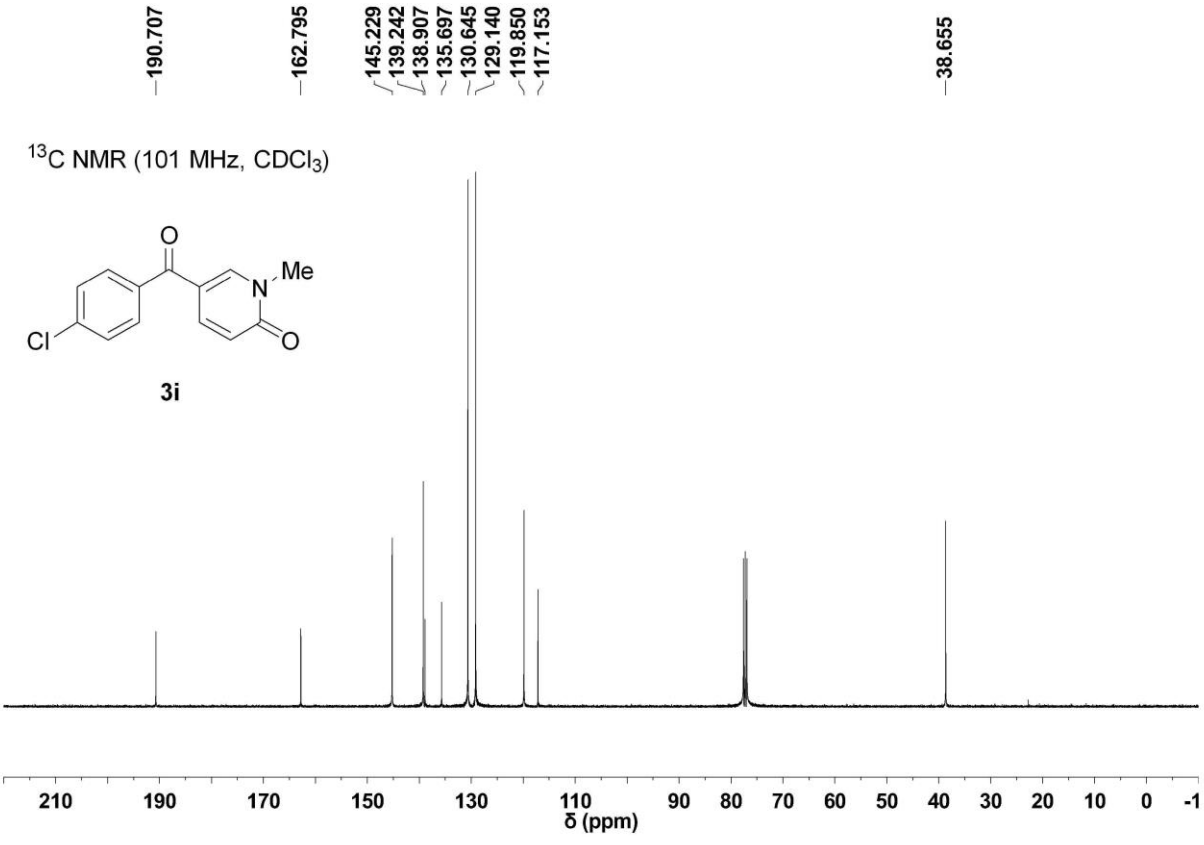
^{19}F NMR (471 MHz, $CDCl_3$)

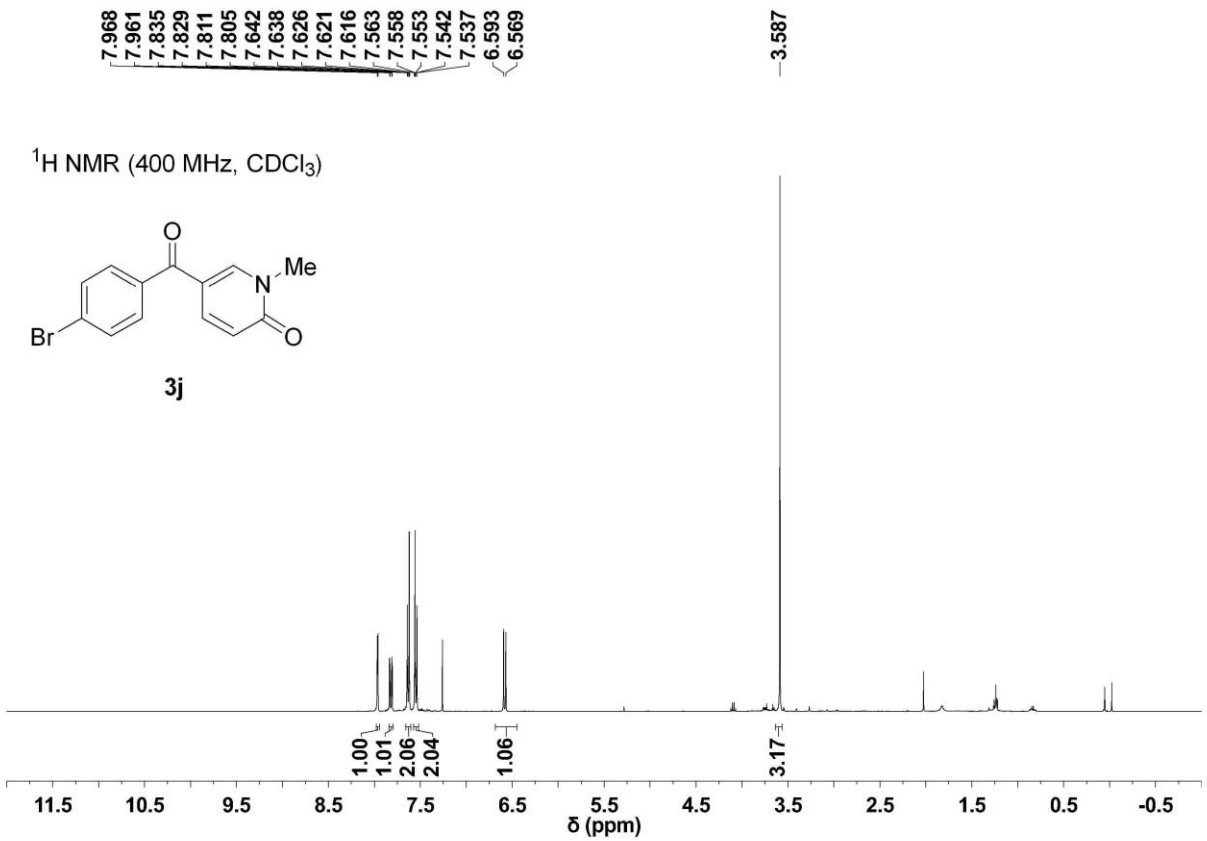


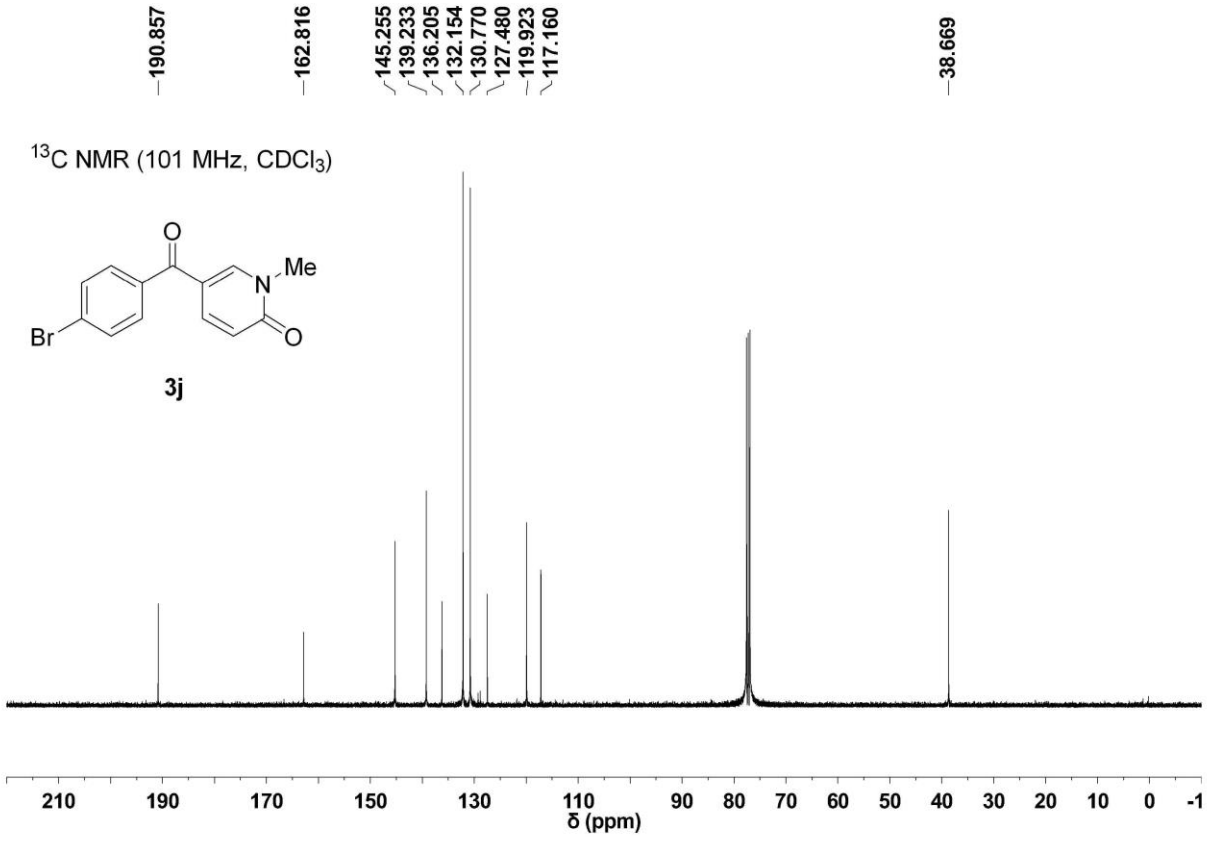
3h

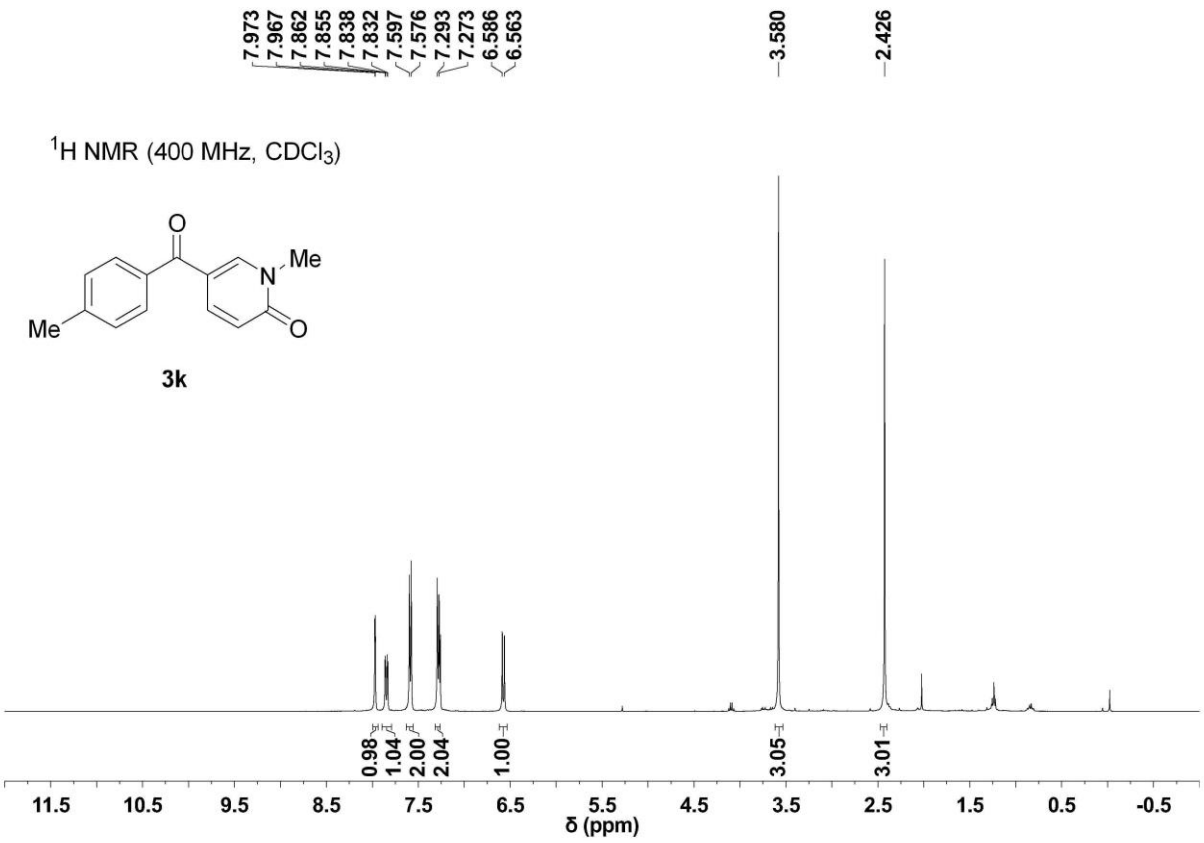


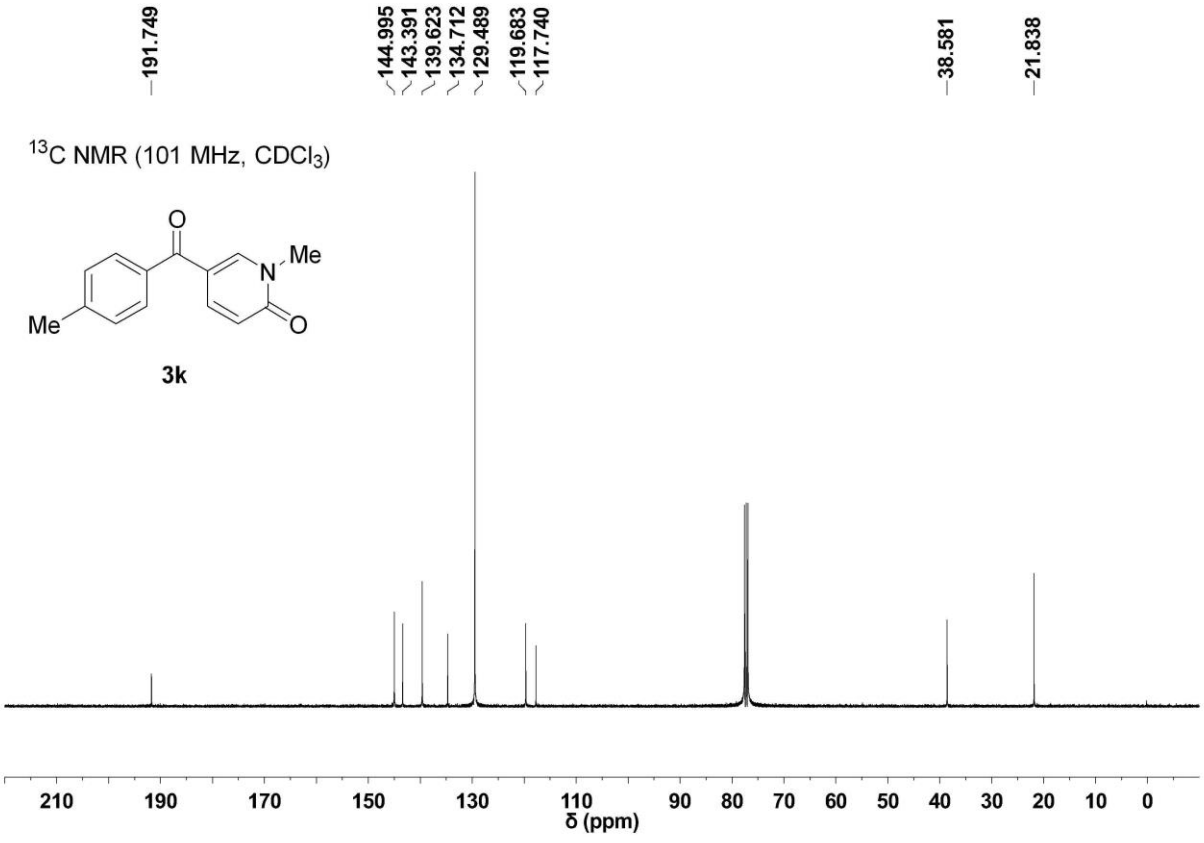

7.968
7.961
7.828
7.821
7.804
7.798
7.631
7.626
7.614
7.609
7.473
7.467
7.463
7.451
7.446
6.583
6.560
3.582
1H NMR (400 MHz, CDCl3)
O
N
Me
Cl
O
3i
1.01
1.01
2.02
2.01
1.00
3.05
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

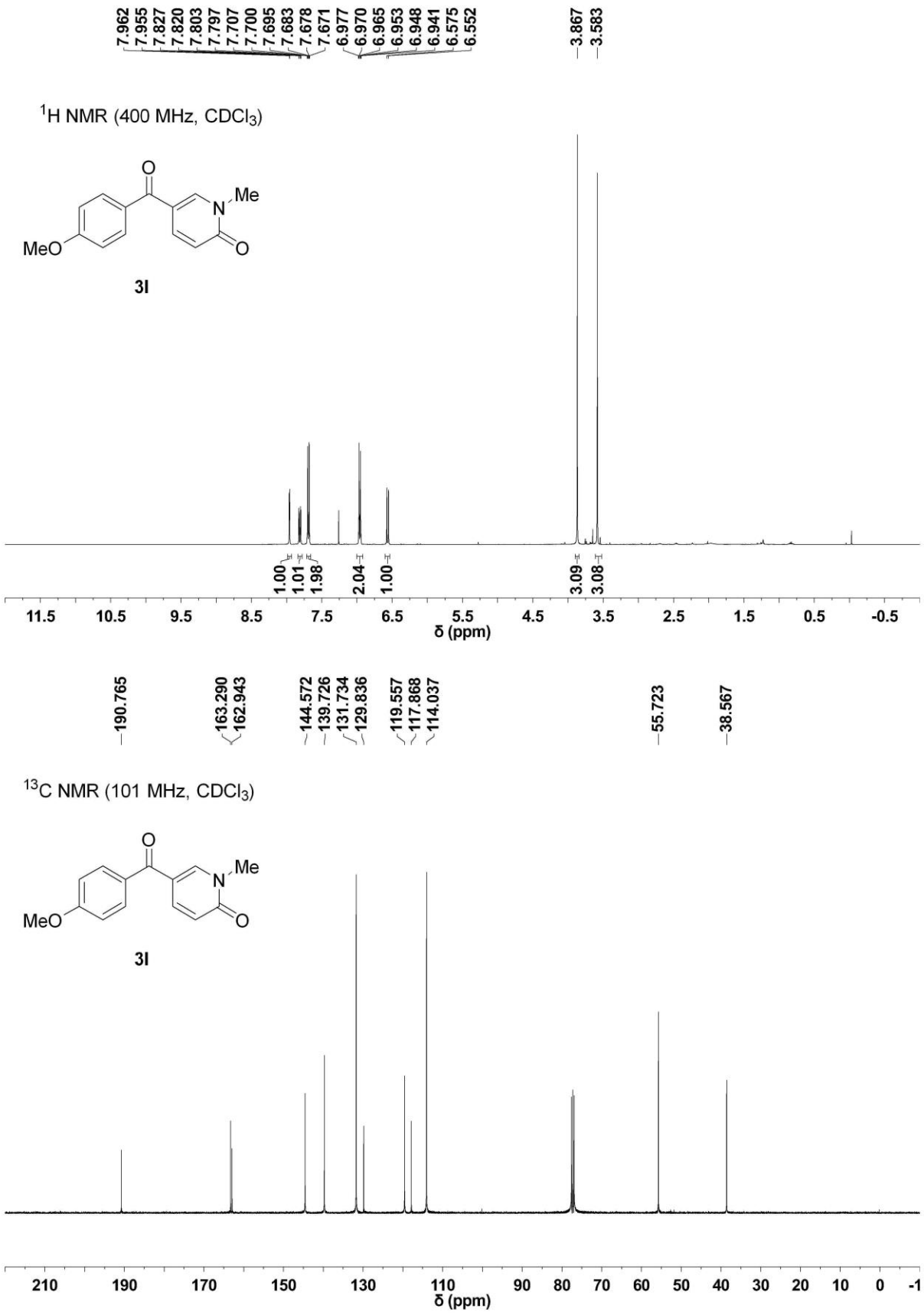

190.707
162.795
145.229
139.242
138.907
135.697
130.645
129.140
119.850
117.153
38.655
13C NMR (101 MHz, CDCl3)
O
N
Me
Cl
O
3i
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)


7.968
7.961
7.835
7.829
7.811
7.805
7.642
7.638
7.626
7.621
7.616
7.563
7.558
7.553
7.542
7.537
6.593
6.569
3.587
1H NMR (400 MHz, CDCl3)
O
N
Me
Br
O
3j
1.00
1.01
2.06
2.04
1.06
3.17
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

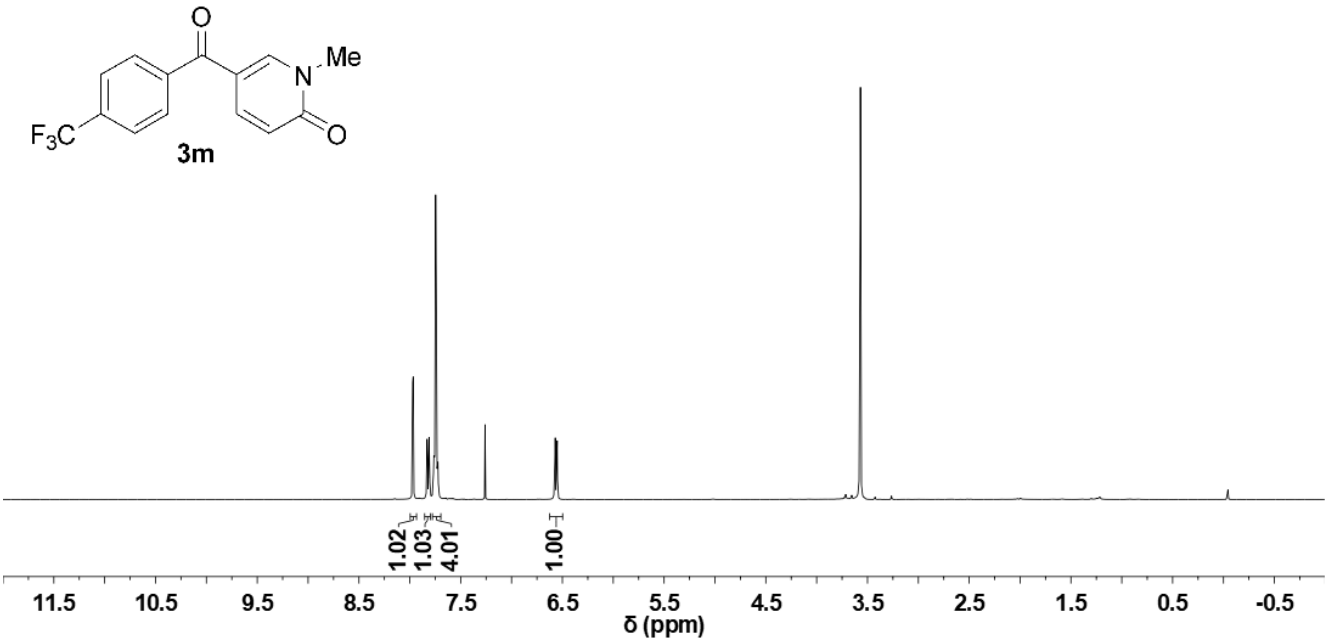

190.857
162.816
145.255
139.233
136.205
132.154
130.770
127.480
119.923
117.160
38.669
13C NMR (101 MHz, CDCl3)
O
N
Me
Br
O
3j
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

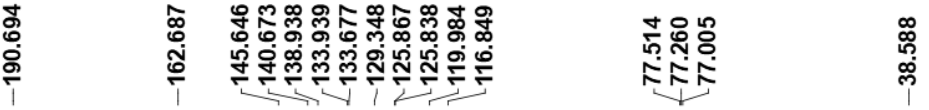

7.973
7.967
7.862
7.855
7.838
7.832
7.597
7.576
7.293
7.273
6.586
6.563
3.580
2.426
^{1}H NMR (400 MHz, $CDCl_3$)
O
N
Me
Me
O
3k
0.98
1.04
2.00
2.04
1.00
3.05
3.01
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)


191.749
144.995
143.391
139.623
134.712
129.489
119.683
117.740
38.581
21.838
^{13}C NMR (101 MHz, $CDCl_3$)
O
N
Me
Me
O
3k
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

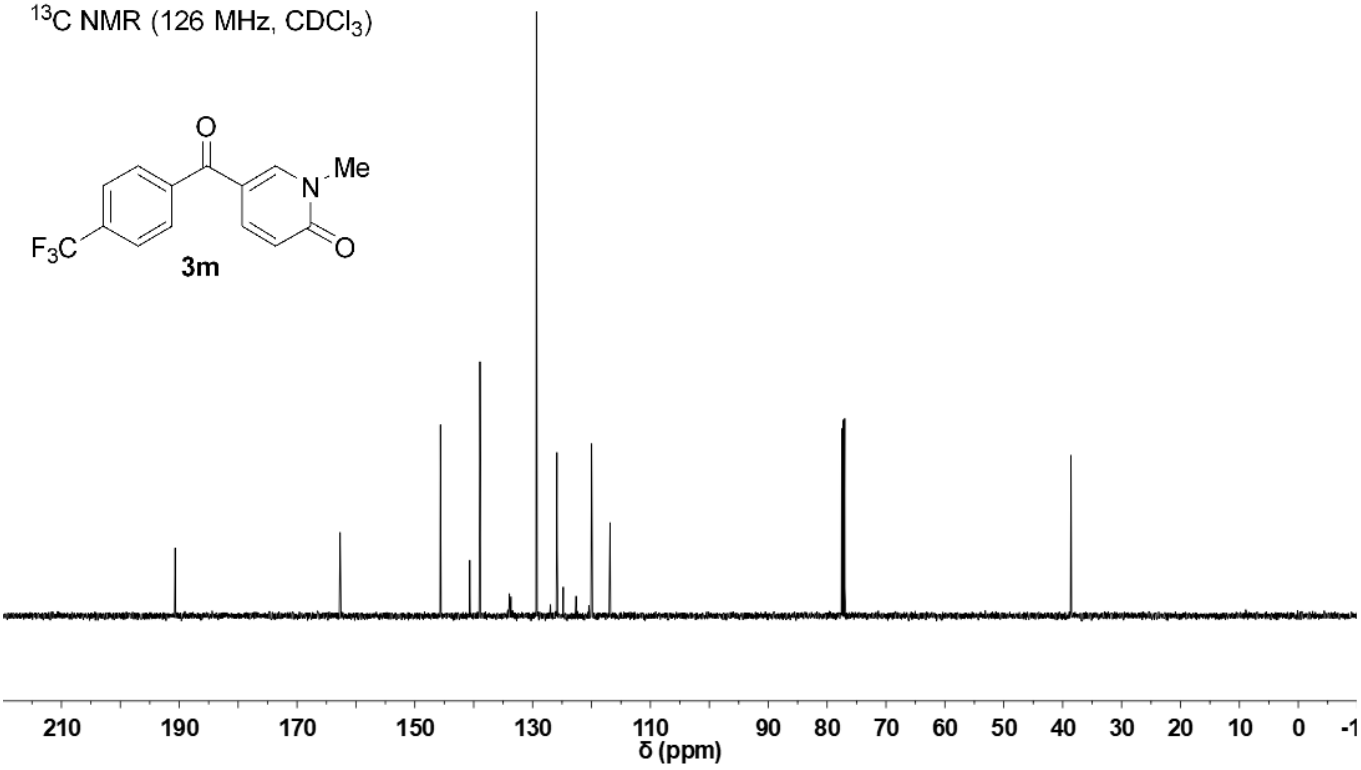

7.962
7.955
7.827
7.820
7.803
7.797
7.707
7.700
7.695
7.683
7.678
7.671
6.977
6.970
6.965
6.953
6.948
6.941
6.575
6.552
3.867
3.583
1H NMR (400 MHz, CDCl3)
O
N
Me
MeO
O
3l
1.00
1.01
1.98
2.04
1.00
3.09
3.08
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
190.765
163.290
162.943
144.572
139.726
131.734
129.836
119.557
117.868
114.037
55.723
38.567
13C NMR (101 MHz, CDCl3)
O
N
Me
MeO
O
3l
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

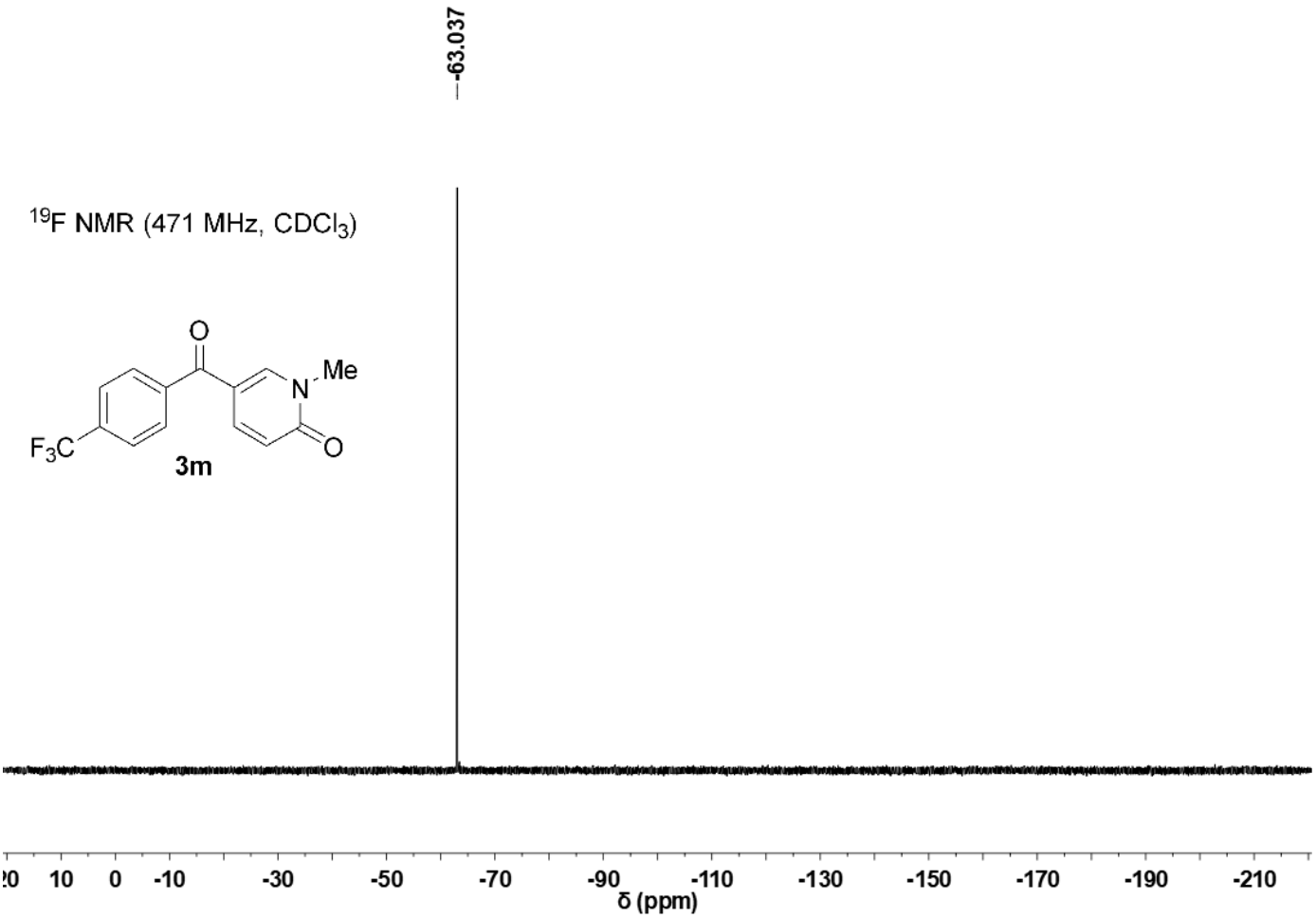
^{1}H NMR (500 MHz, $CDCl_3$)

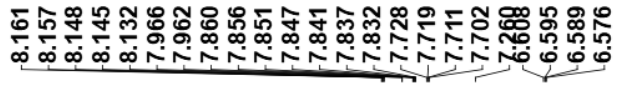




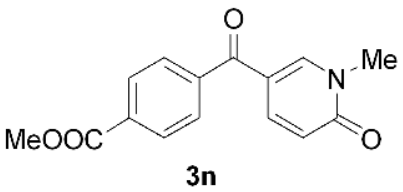
^{13}C NMR (126 MHz, $CDCl_3$)



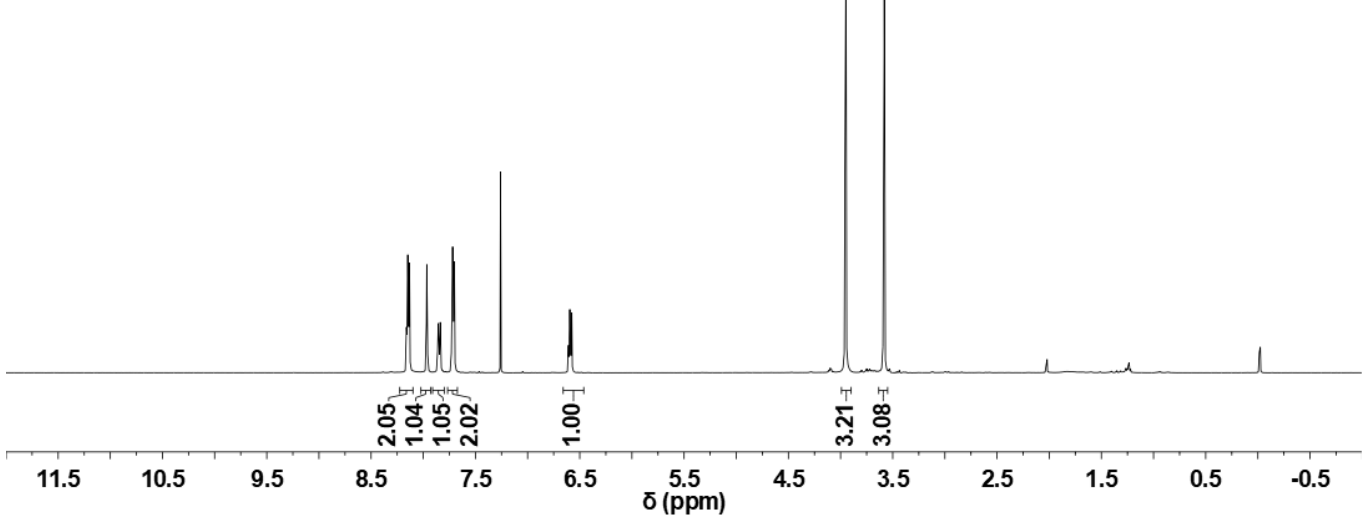

-63.037
19F NMR (471 MHz, CDCl3)
O
N
Me
O
F3C
3m
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
δ (ppm)

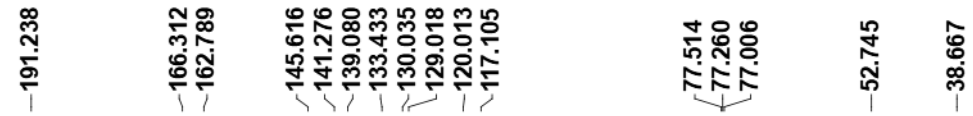


^{1}H NMR (500 MHz, $CDCl_3$)

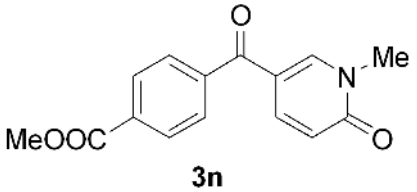


3n

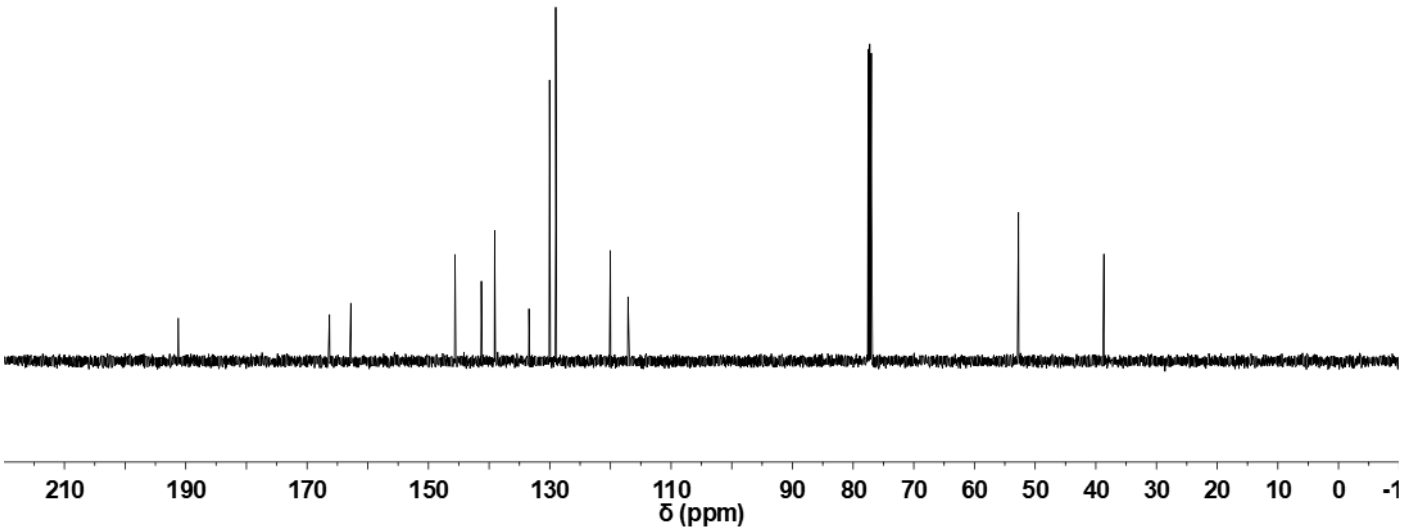




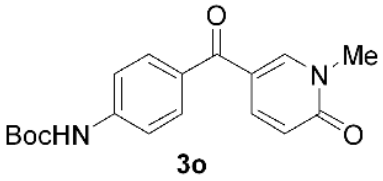
^{13}C NMR (126 MHz, $CDCl_3$)



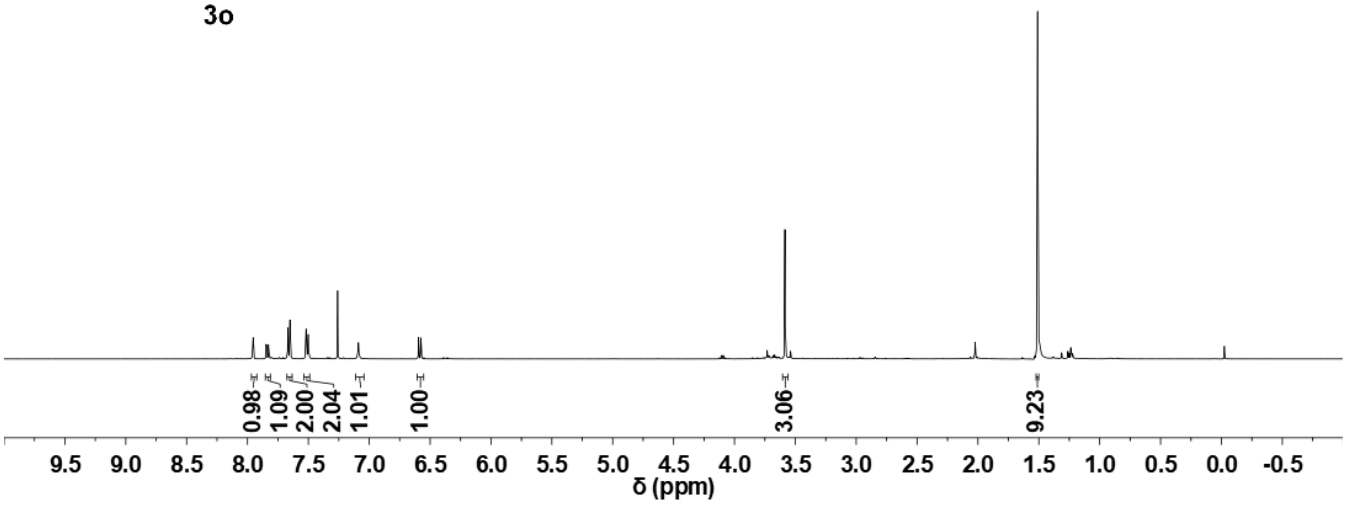
3n



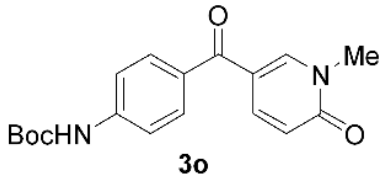
^{1}H NMR (500 MHz, $CDCl_3$)



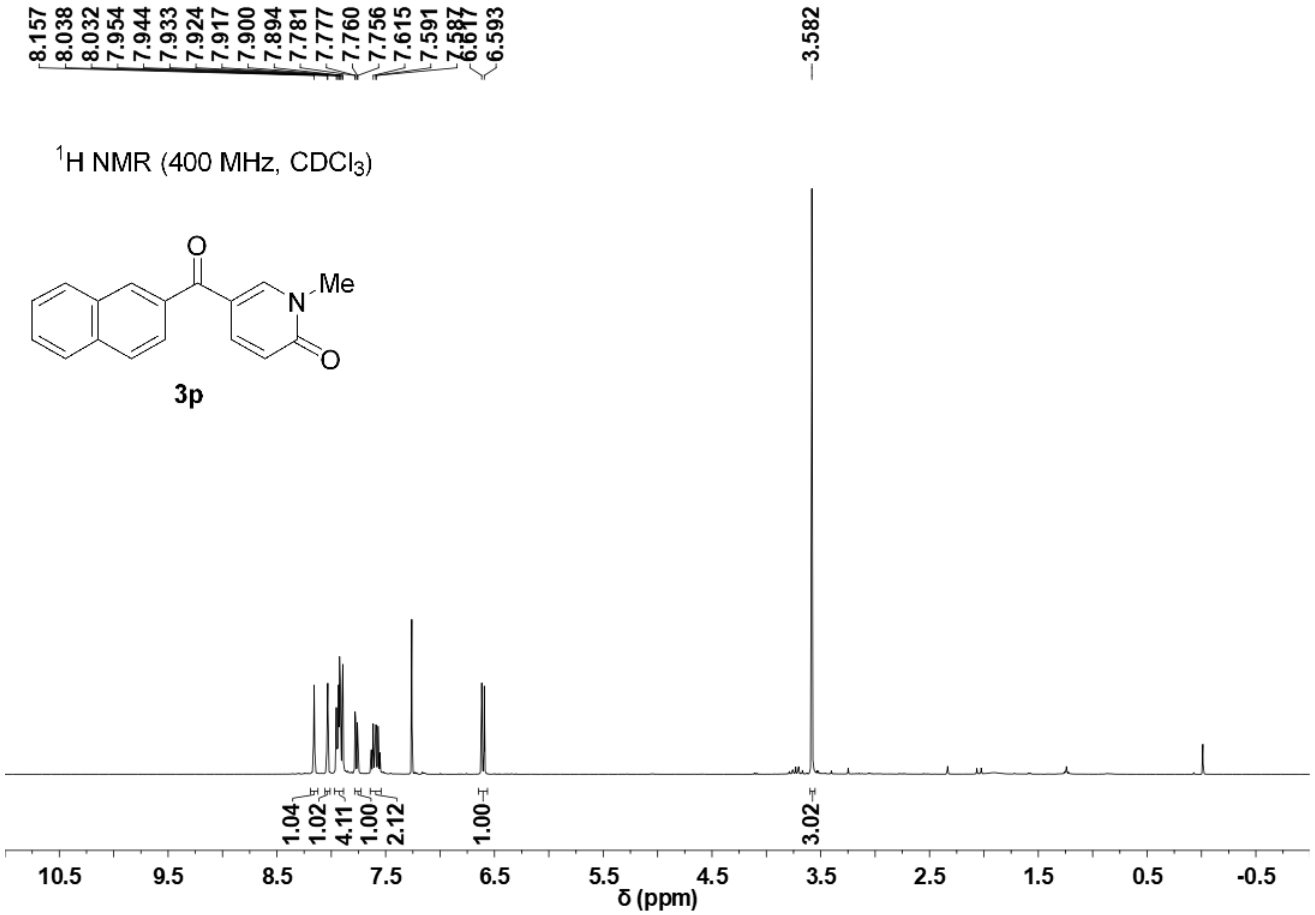
3o

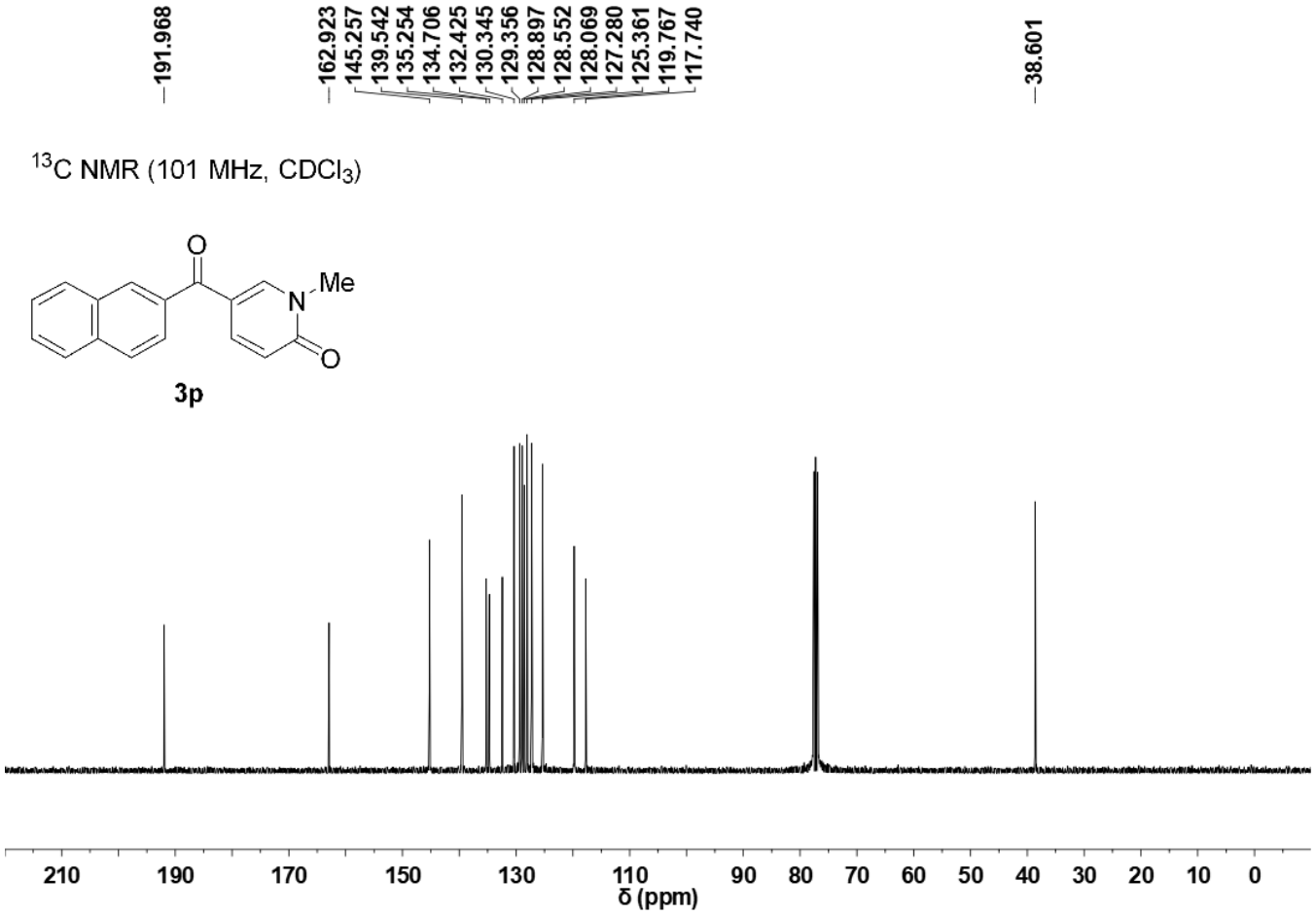


^{13}C NMR (126 MHz, $CDCl_3$)



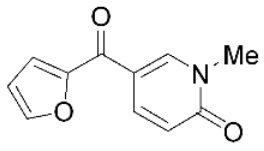
3o


8.157
8.038
8.032
7.954
7.944
7.933
7.924
7.917
7.900
7.894
7.781
7.777
7.760
7.756
7.615
7.591
7.587
6.617
6.593
3.582
1H NMR (400 MHz, CDCl3)
O
N
Me
O
3p
1.04
1.02
4.11
1.00
2.12
1.00
3.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

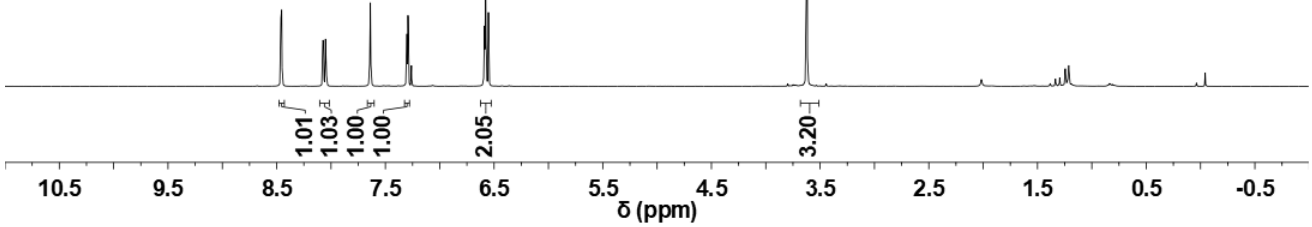

191.968
162.923
145.257
139.542
135.254
134.706
132.425
130.345
129.356
128.897
128.552
128.069
127.280
125.361
119.767
117.740
38.601
13C NMR (101 MHz, CDCl3)
O
N
Me
O
3p
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

8.460
8.454
8.075
8.069
8.051
8.045
7.640
7.638
7.300
7.292
6.591
6.587
6.582
6.577
6.552
3.623

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

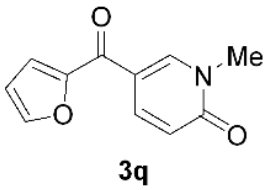


3q

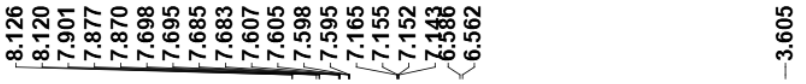


176.706
162.859
152.656
146.471
144.898
139.096
119.724
119.477
116.748
112.694
38.703

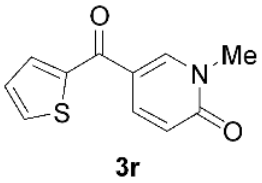
^{13}C NMR (101 MHz, $CDCl_3$)



3q

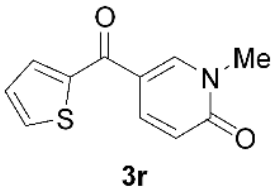


^{1}H NMR (400 MHz, $CDCl_3$)

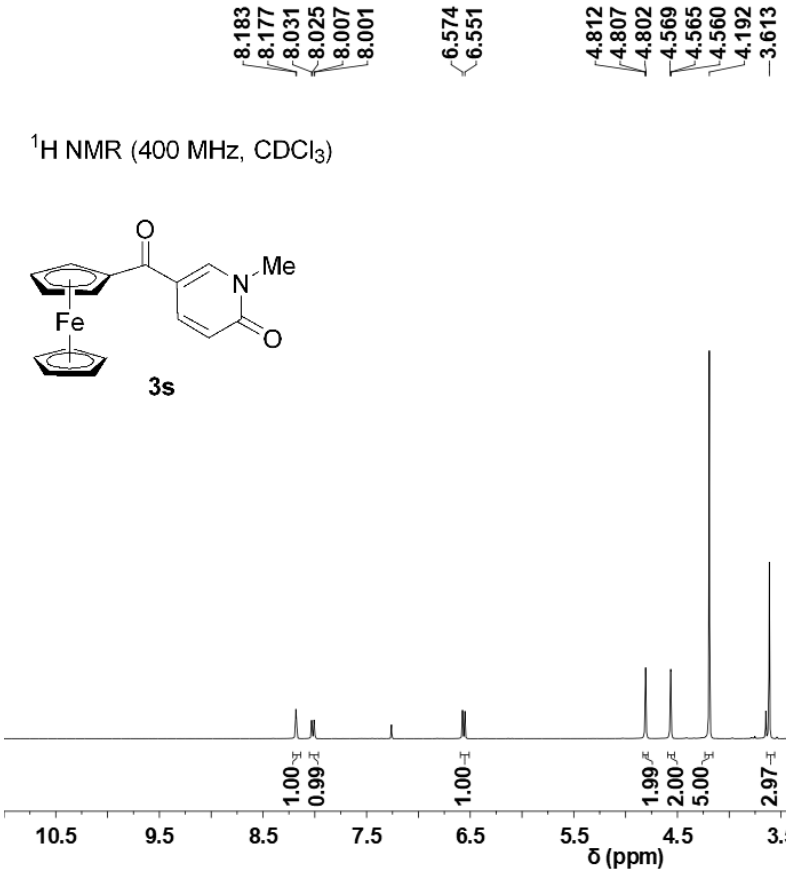


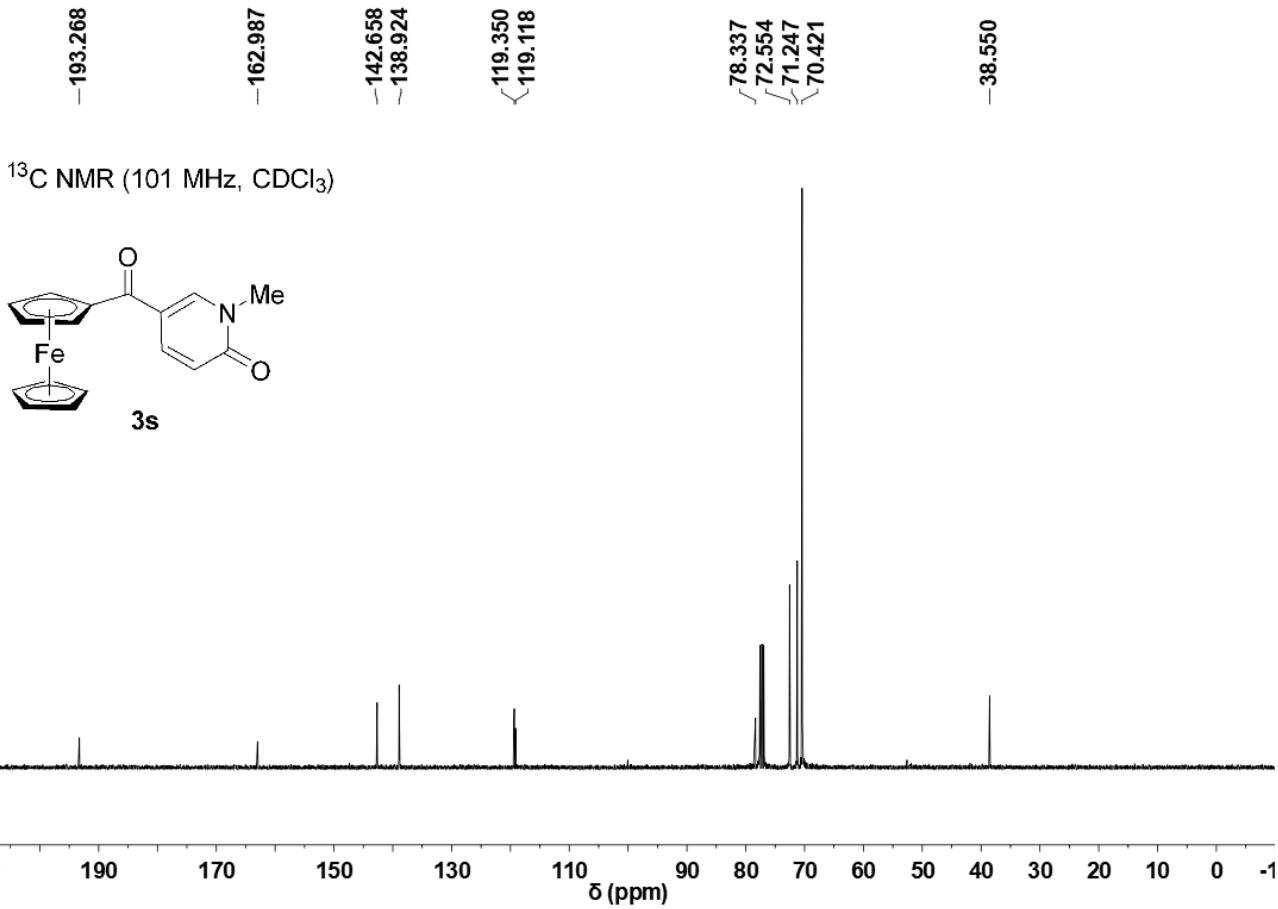
3r

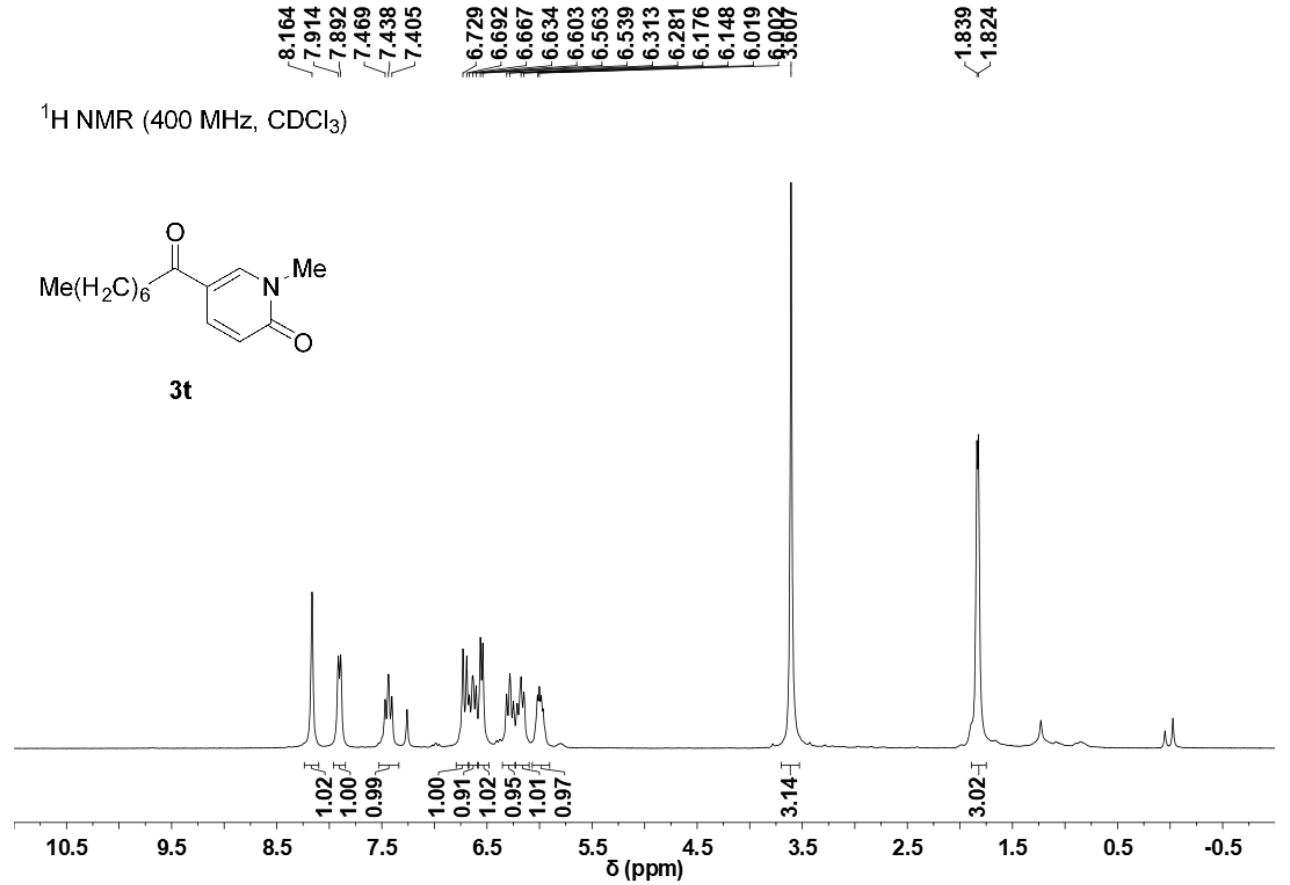
^{13}C NMR (101 MHz, $CDCl_3$)

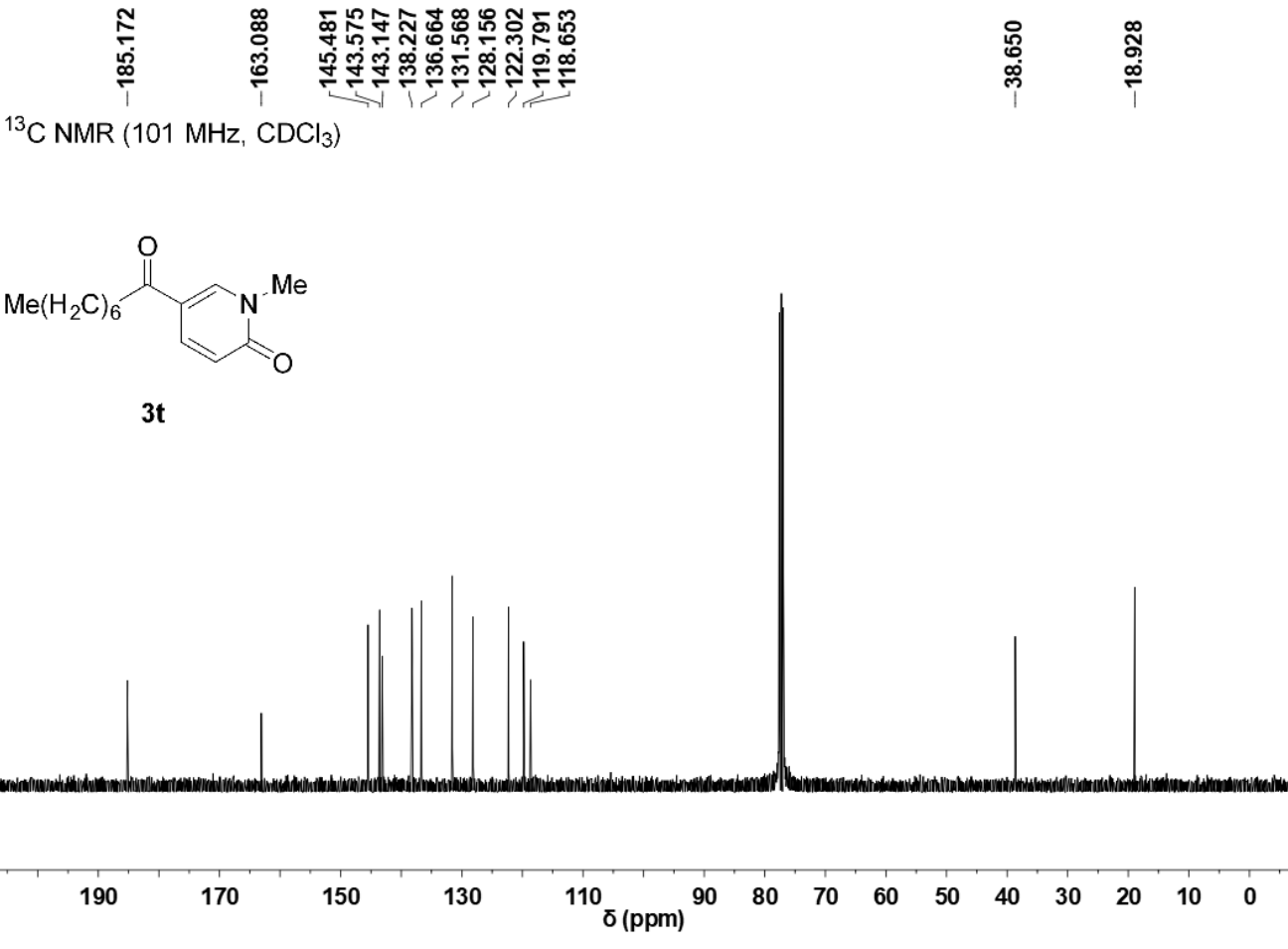


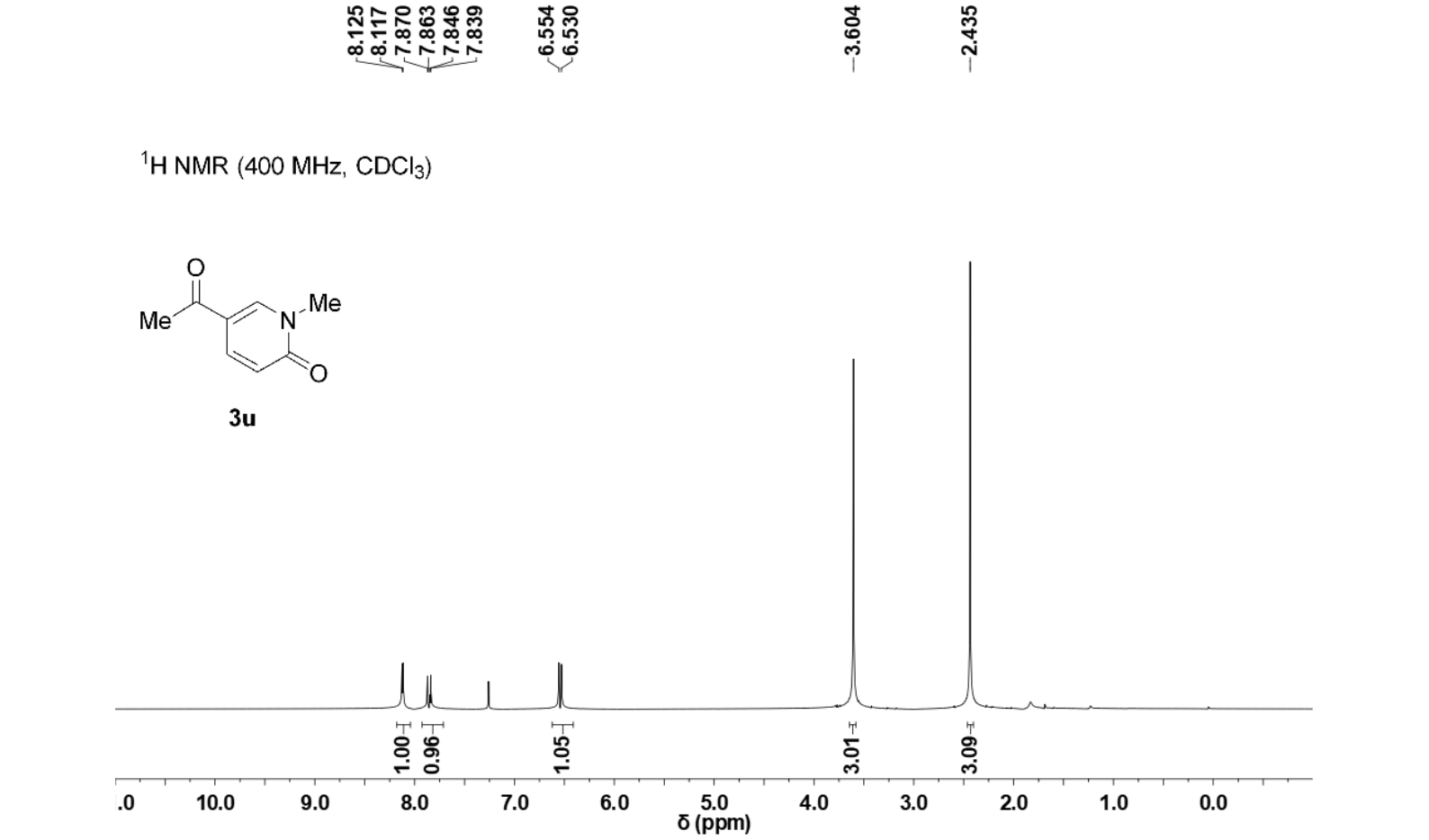
3r

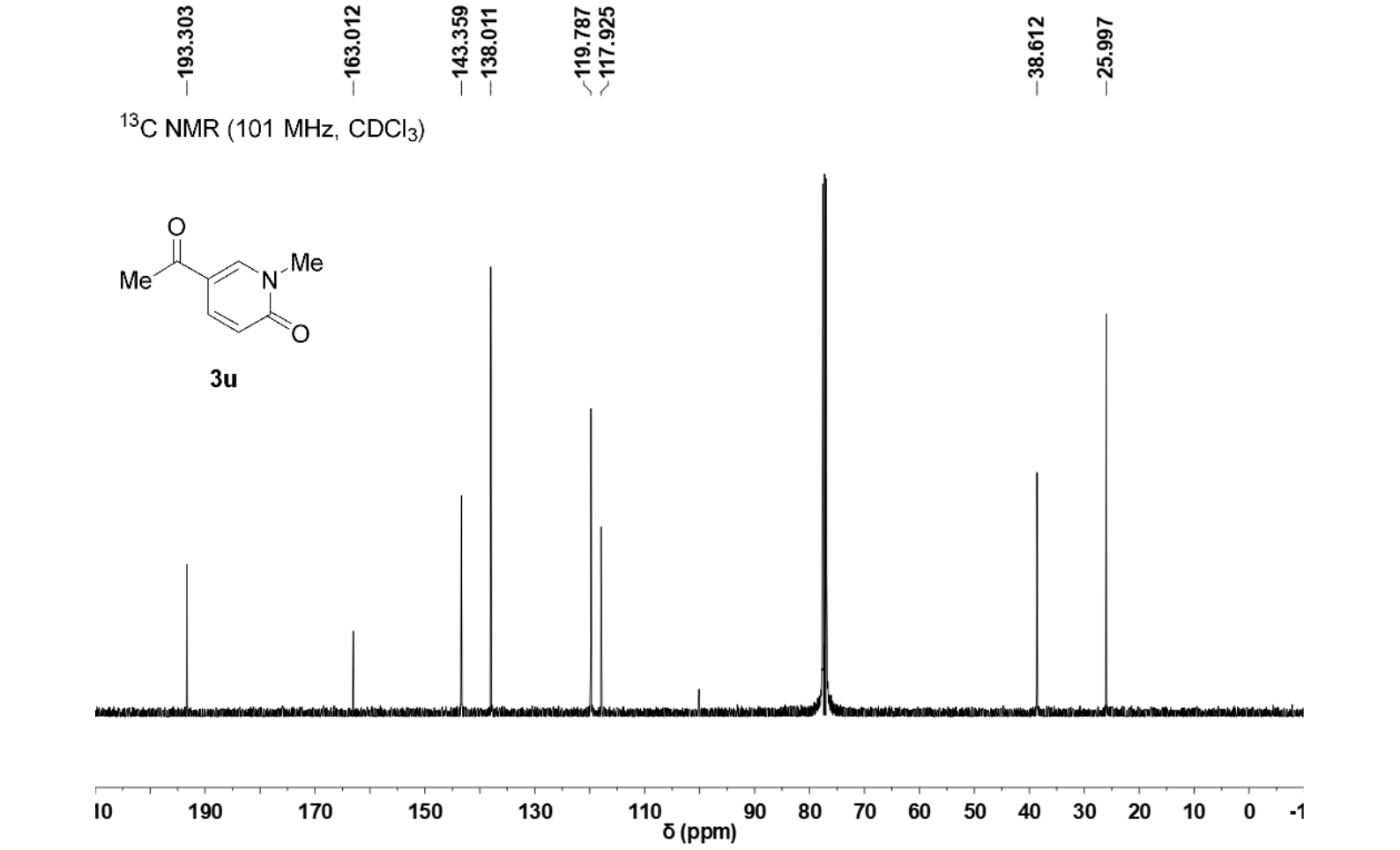

8.183
8.177
8.031
8.025
8.007
8.001
6.574
6.551
4.812
4.807
4.802
4.569
4.565
4.560
4.192
3.613
1H NMR (400 MHz, CDCl3)
O
N
Me
Fe
O
3s
1.00
0.99
1.00
1.99
2.00
5.00
2.97
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

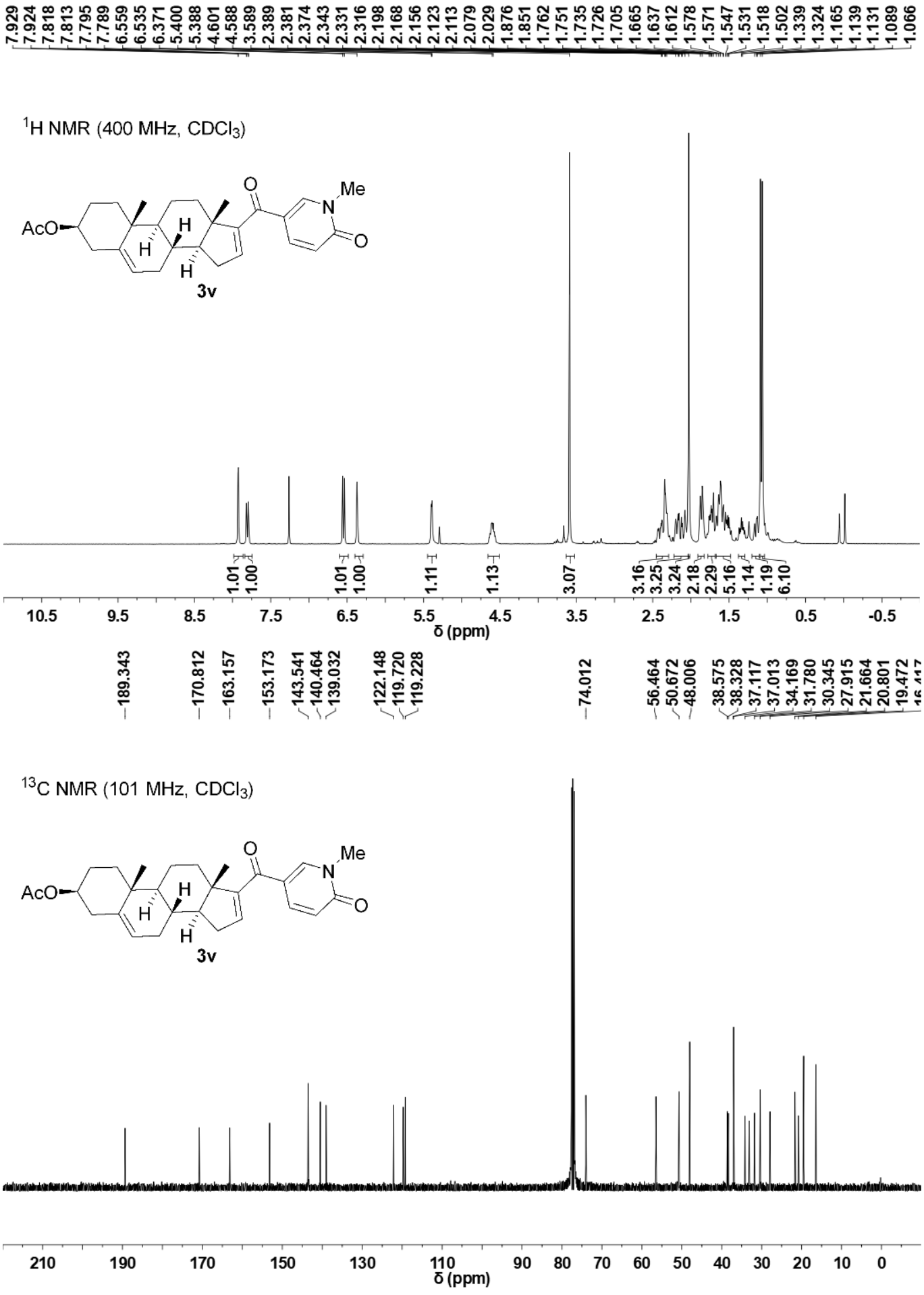

193.268
162.987
142.658
138.924
119.350
119.118
78.337
72.554
71.247
70.421
38.550
13C NMR (101 MHz, CDCl3)
O
N
Me
Fe
O
3s
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


8.164
7.914
7.892
7.469
7.438
7.405
6.729
6.692
6.667
6.634
6.603
6.563
6.539
6.313
6.281
6.176
6.148
6.019
3.807
1.839
1.824
1H NMR (400 MHz, CDCl3)
Me(H2C)6
N
Me
O
O
3t
1.02
1.00
0.99
1.00
0.91
1.02
0.95
1.01
0.97
3.14
3.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

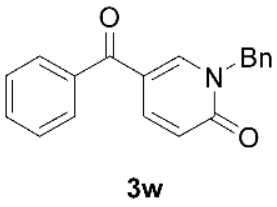

185.172
163.088
145.481
143.575
143.147
138.227
136.664
131.568
128.156
122.302
119.791
118.653
38.650
18.928
13C NMR (101 MHz, CDCl3)
Me(H2C)6
N
Me
O
O
3t
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


8.125
8.117
7.870
7.863
7.846
7.839
6.554
6.530
3.604
2.435
1H NMR (400 MHz, CDCl3)
O
Me
N
Me
O
3u
1.00
0.96
1.05
3.01
3.09
.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)

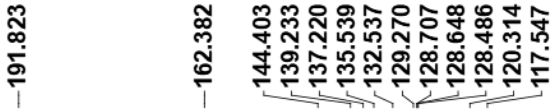

193.303
163.012
143.359
138.011
119.787
117.925
38.612
25.997
13C NMR (101 MHz, CDCl3)
O
Me
N
Me
O
3u
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


7.929
7.924
7.818
7.813
7.795
7.789
6.559
6.535
6.371
5.400
5.388
4.601
4.588
3.589
2.389
2.381
2.374
2.343
2.331
2.316
2.198
2.168
2.156
2.123
2.113
2.079
2.029
1.876
1.851
1.762
1.751
1.735
1.726
1.705
1.665
1.637
1.612
1.578
1.571
1.547
1.531
1.518
1.502
1.339
1.324
1.165
1.139
1.131
1.089
1.066
1H NMR (400 MHz, CDCl3)
AcO
H
H
H
O
N
Me
O
3v
1.01
1.00
1.01
1.00
1.11
1.13
3.07
3.16
3.25
3.24
2.18
2.29
5.16
1.14
1.19
6.10
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)
189.343
170.812
163.157
153.173
143.541
140.464
139.032
122.148
119.720
119.228
74.012
56.464
50.672
48.006
38.575
38.328
37.117
37.013
34.169
31.780
30.345
27.915
21.664
20.801
19.472
13C NMR (101 MHz, CDCl3)
AcO
H
H
H
O
N
Me
O
3v
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

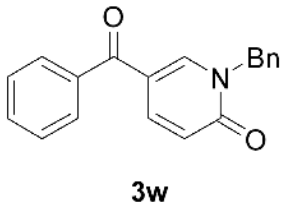
^{1}H NMR (400 MHz, $CDCl_3$)



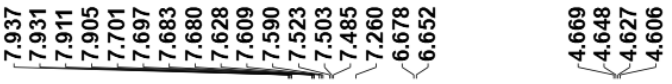
3w



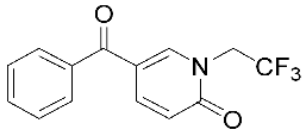
^{13}C NMR (101 MHz, $CDCl_3$)



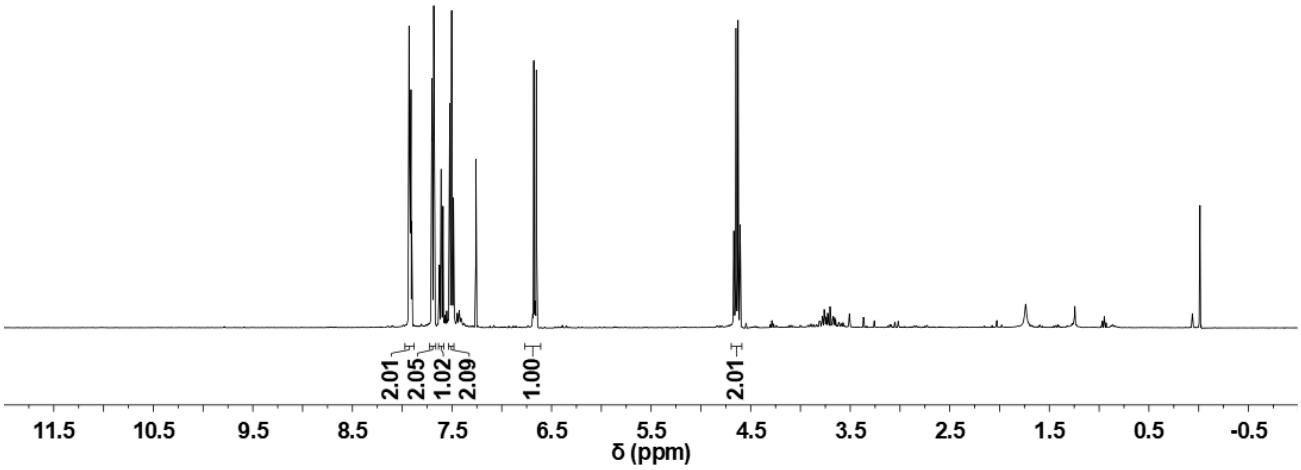
3w



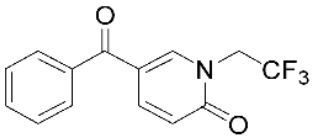
^{1}H NMR (400 MHz, $CDCl_3$)



3x



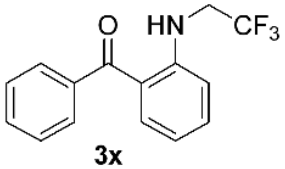
^{13}C NMR (101 MHz, $CDCl_3$)



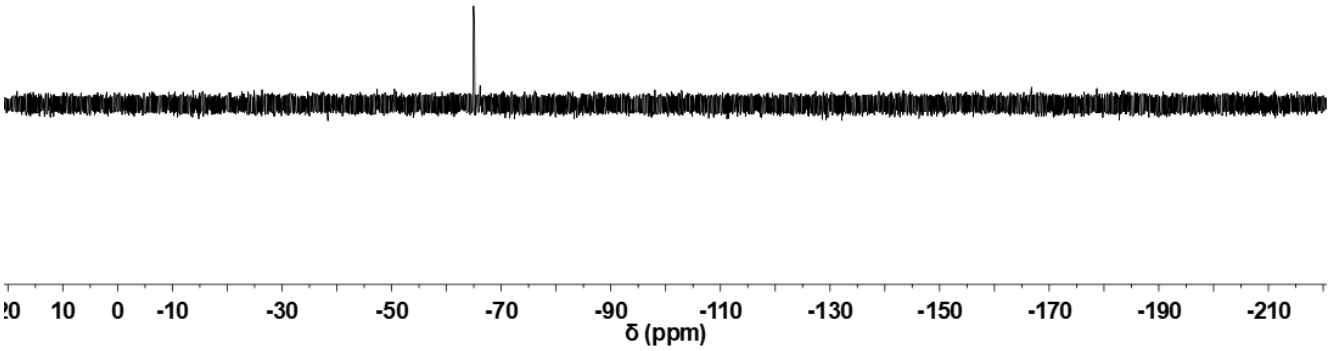
3x

-64.948

^{19}F NMR (471 MHz, $CDCl_3$)

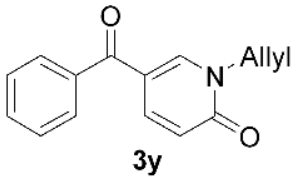


3x

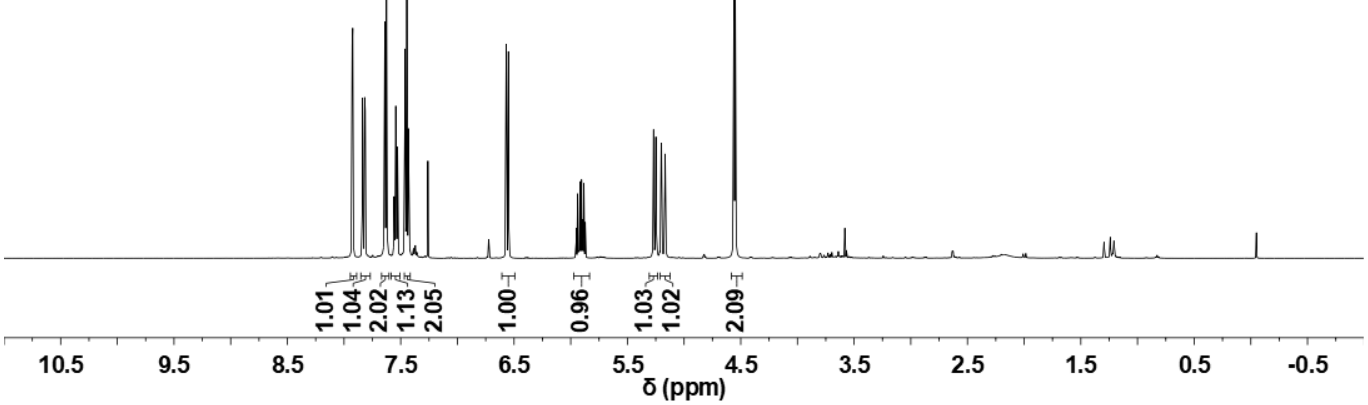


7.928 7.923 7.837 7.832 7.818 7.813 7.645 7.642 7.640 7.630 7.626 7.623 7.558 7.556 7.547 7.543 7.540 7.531 7.529 7.526 7.462 7.459 7.446 7.435 7.431 6.569 6.550 5.939 5.930 5.918 5.905 5.896 5.893 5.884 5.271 5.269 5.251 5.249 5.204 5.201 5.199 5.170 5.167 5.165 4.563 4.560 4.557 4.551 4.548 4.546

^{1}H NMR (500 MHz, $CDCl_3$)



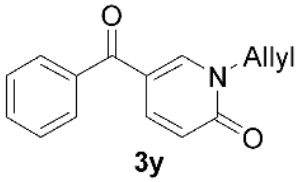
3y



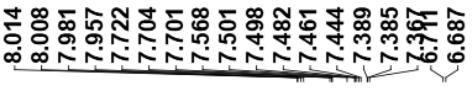
0906-z-9-2-2 cav C-1

191.783 162.043 144.129 139.246 137.323 132.462 131.753 129.174 128.691 120.030 119.570 117.505 51.769

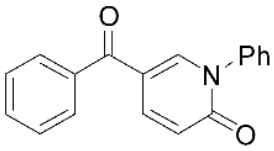
^{13}C NMR (126 MHz, $CDCl_3$)



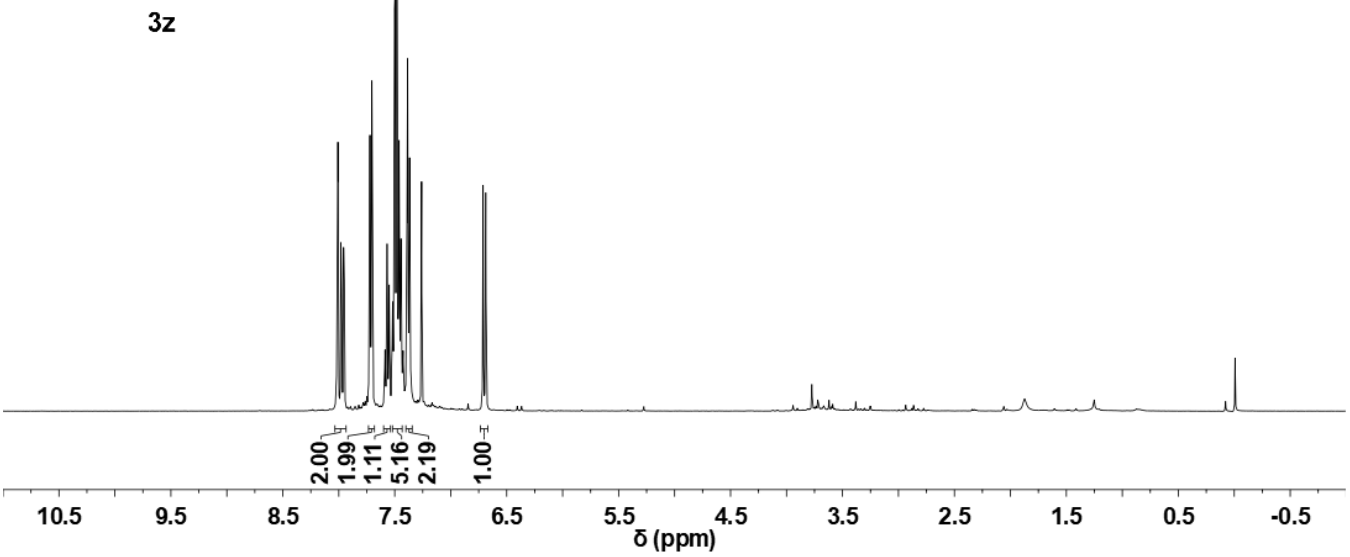
3y

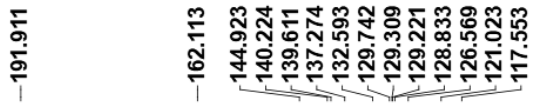


^{1}H NMR (400 MHz, $CDCl_3$)

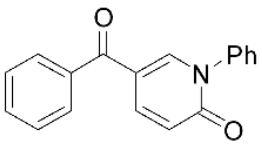


3z

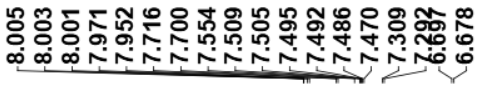




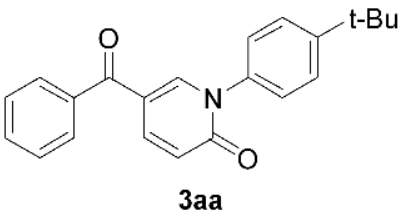
^{13}C NMR (101 MHz, $CDCl_3$)



3z

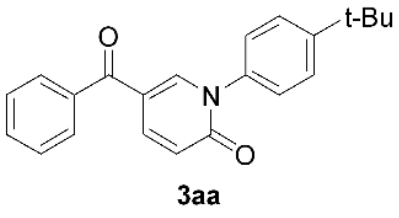


^{1}H NMR (500 MHz, $CDCl_3$)

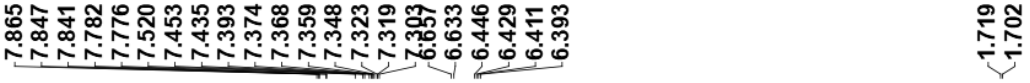


3aa

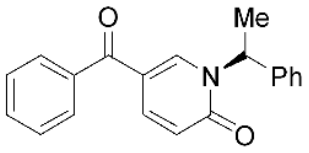
^{13}C NMR (126 MHz, $CDCl_3$)



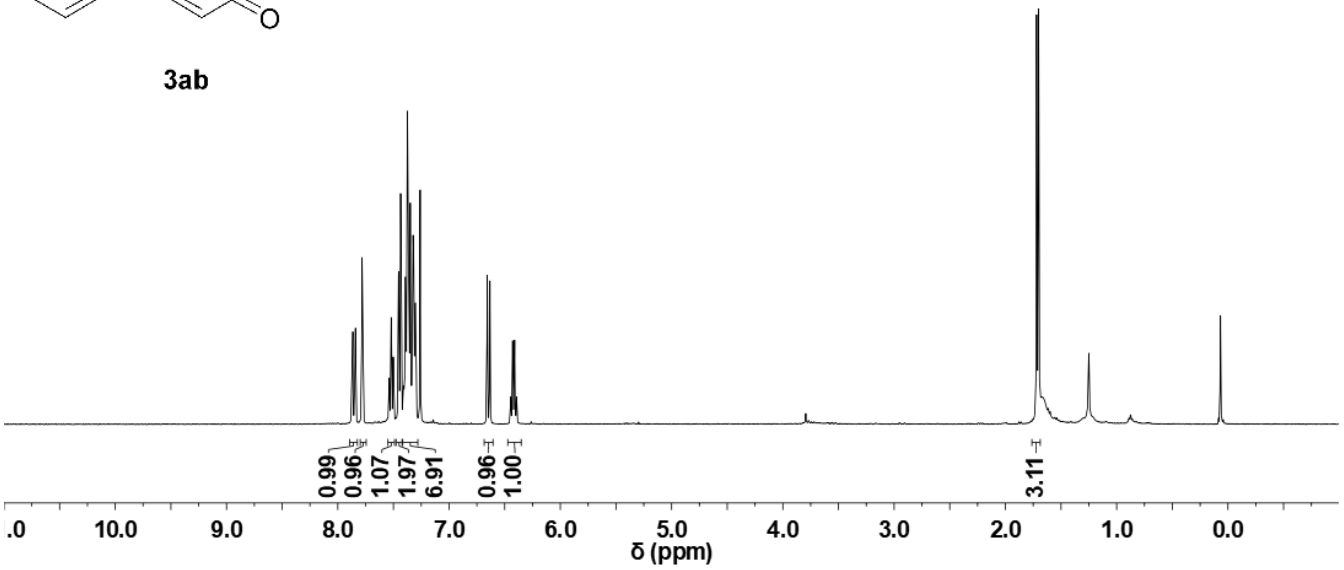
3aa



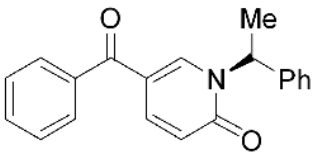
^{1}H NMR (400 MHz, $CDCl_3$)



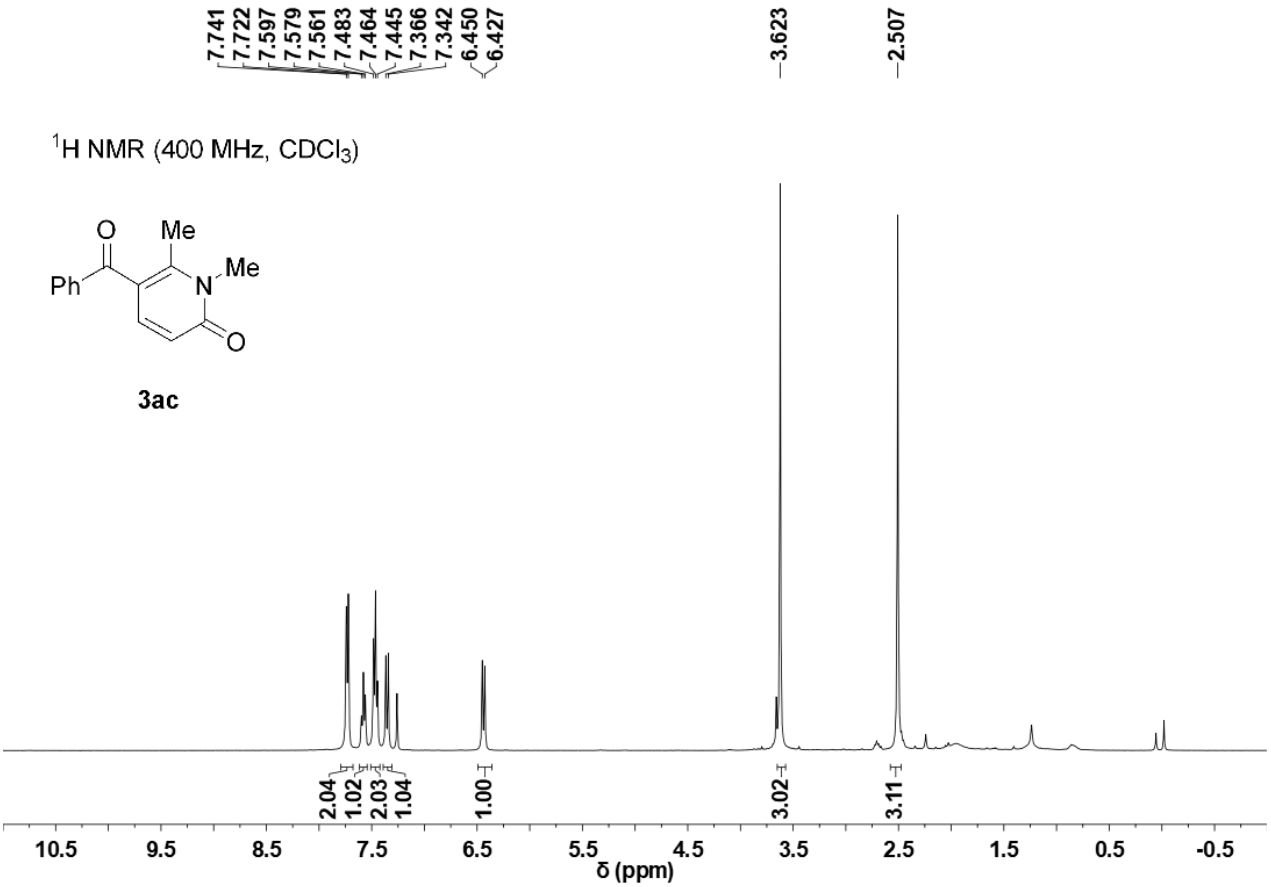
3ab

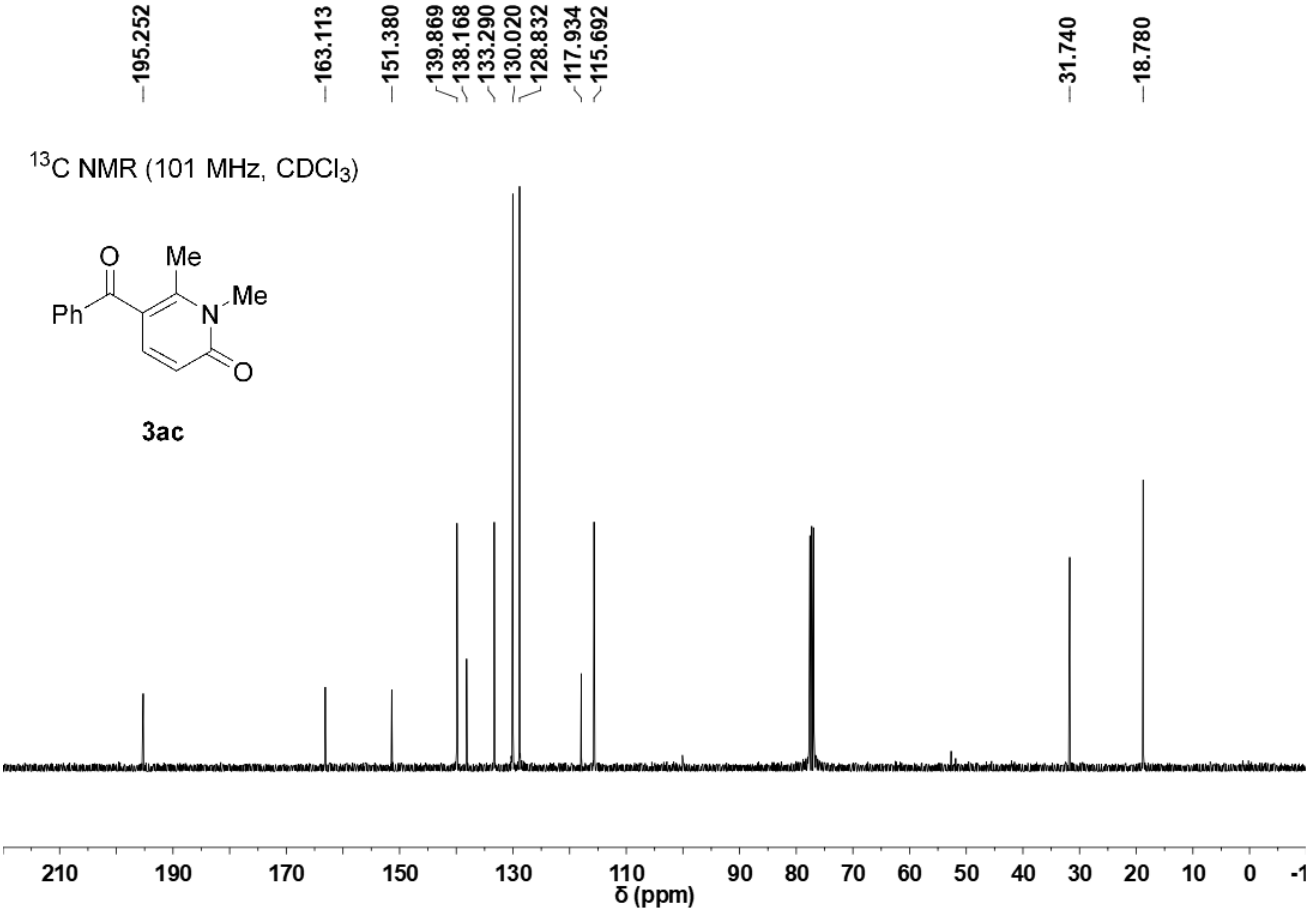


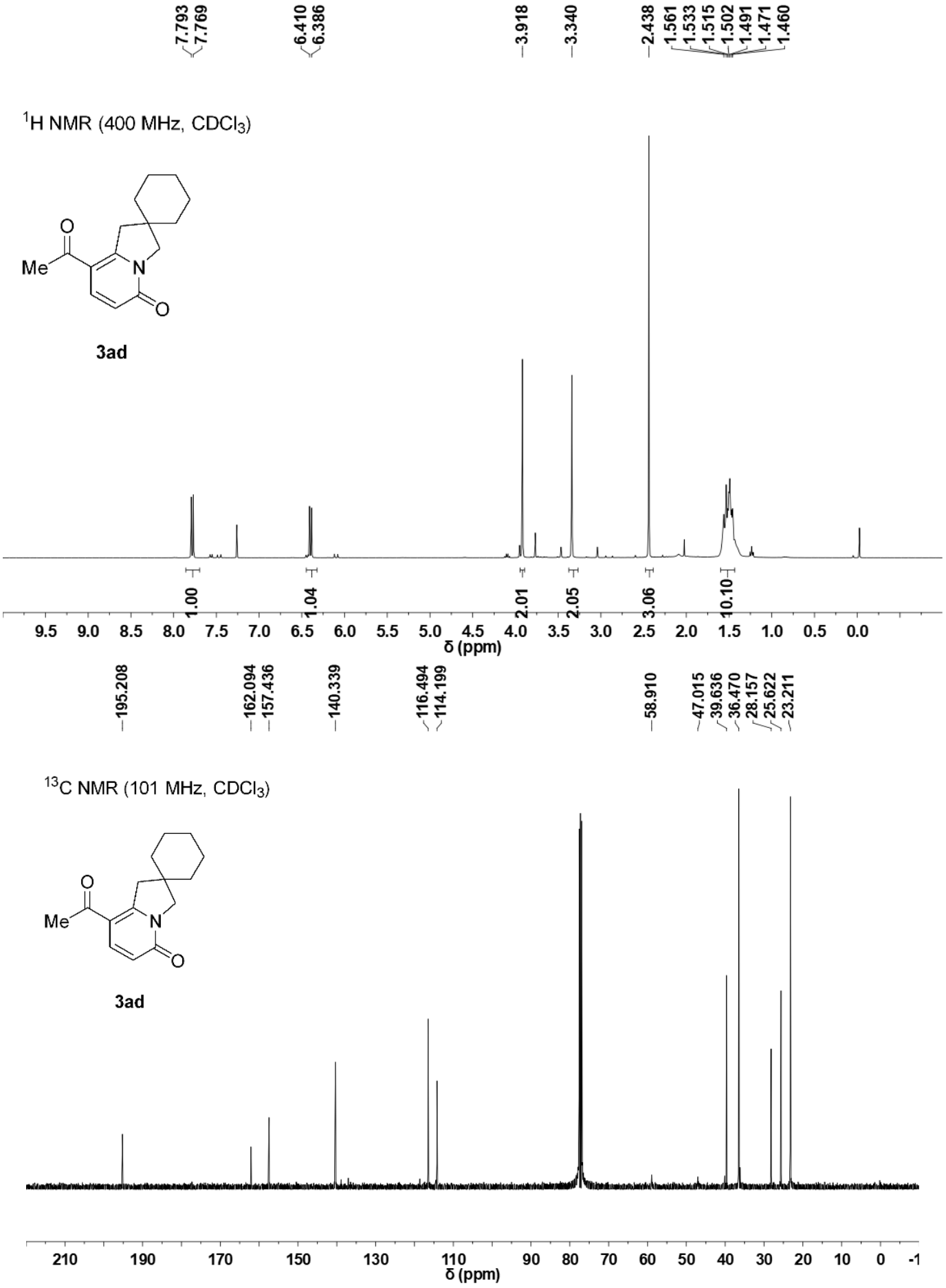
^{13}C NMR (101 MHz, $CDCl_3$)

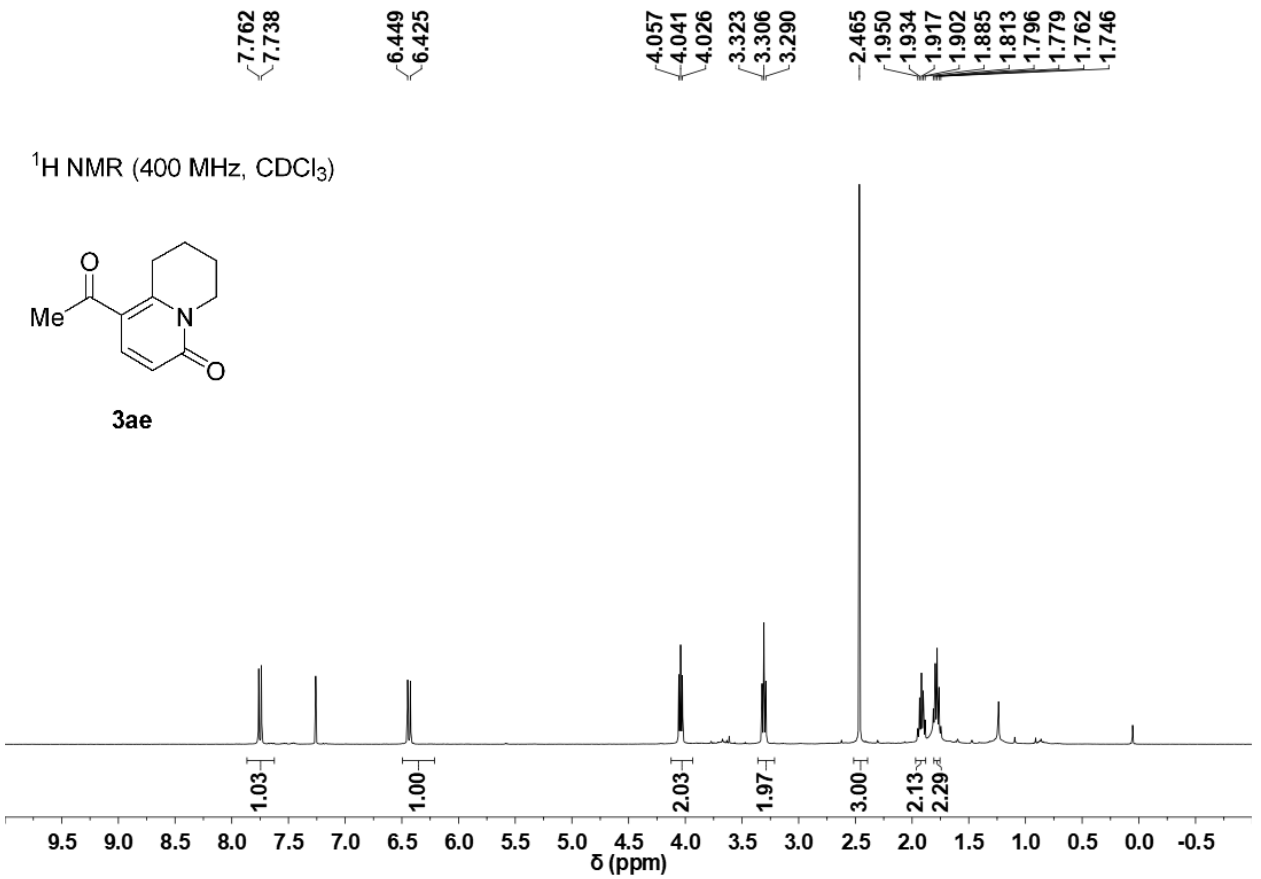


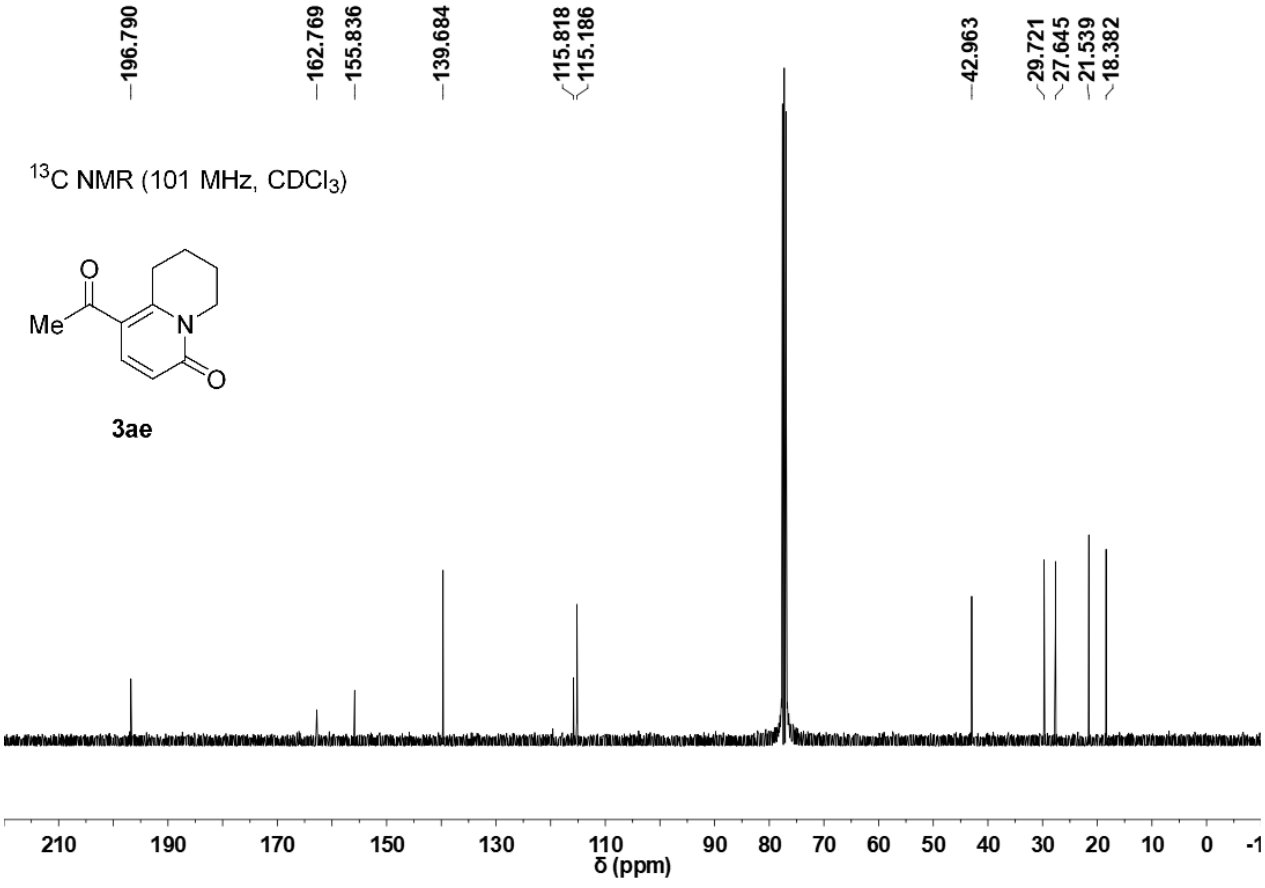
3ab

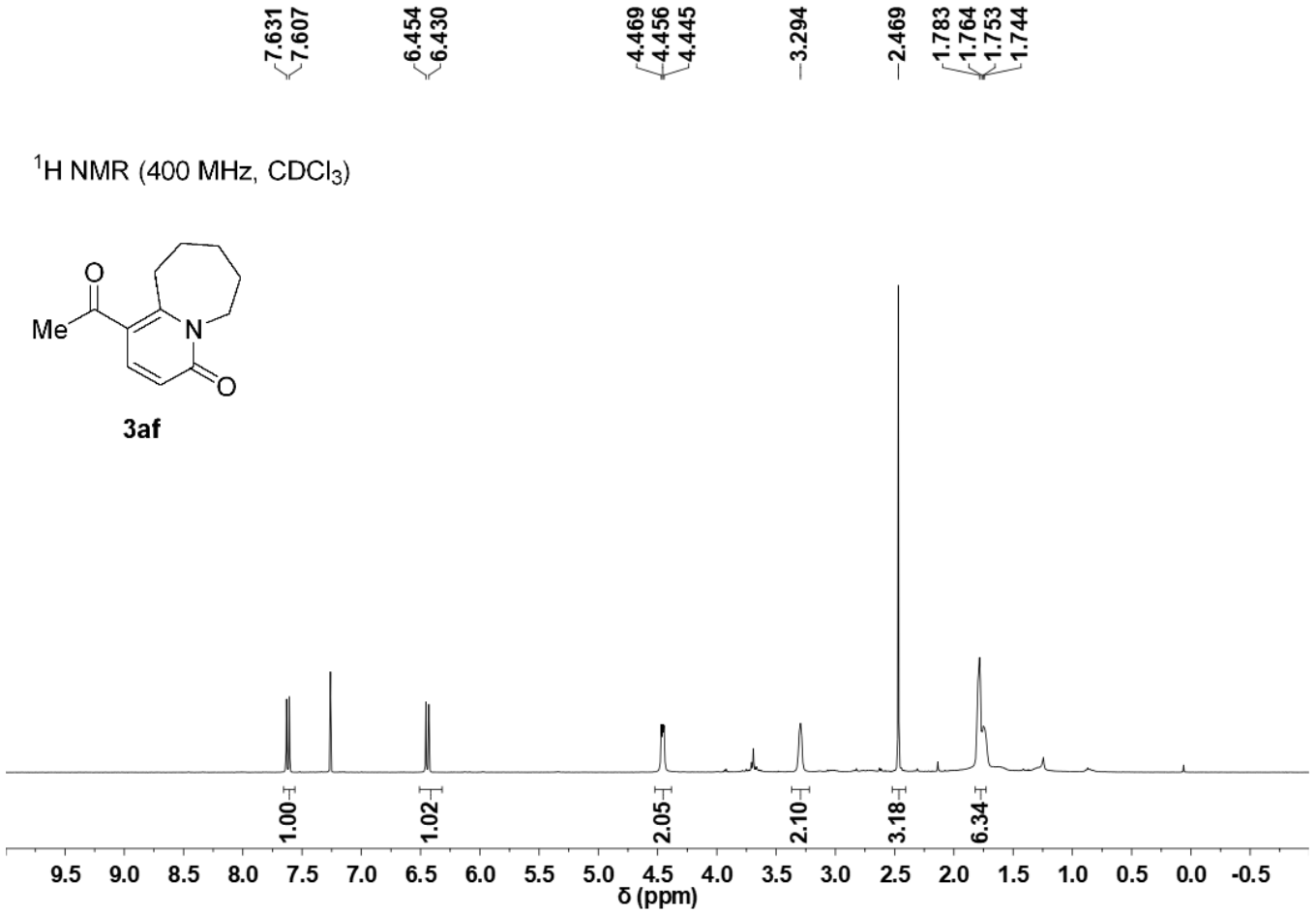

7.741
7.722
7.597
7.579
7.561
7.483
7.464
7.445
7.366
7.342
6.450
6.427
3.623
2.507
1H NMR (400 MHz, CDCl3)
O
Me
Ph
N
Me
O
3ac
2.04
1.02
2.03
1.04
1.00
3.02
3.11
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

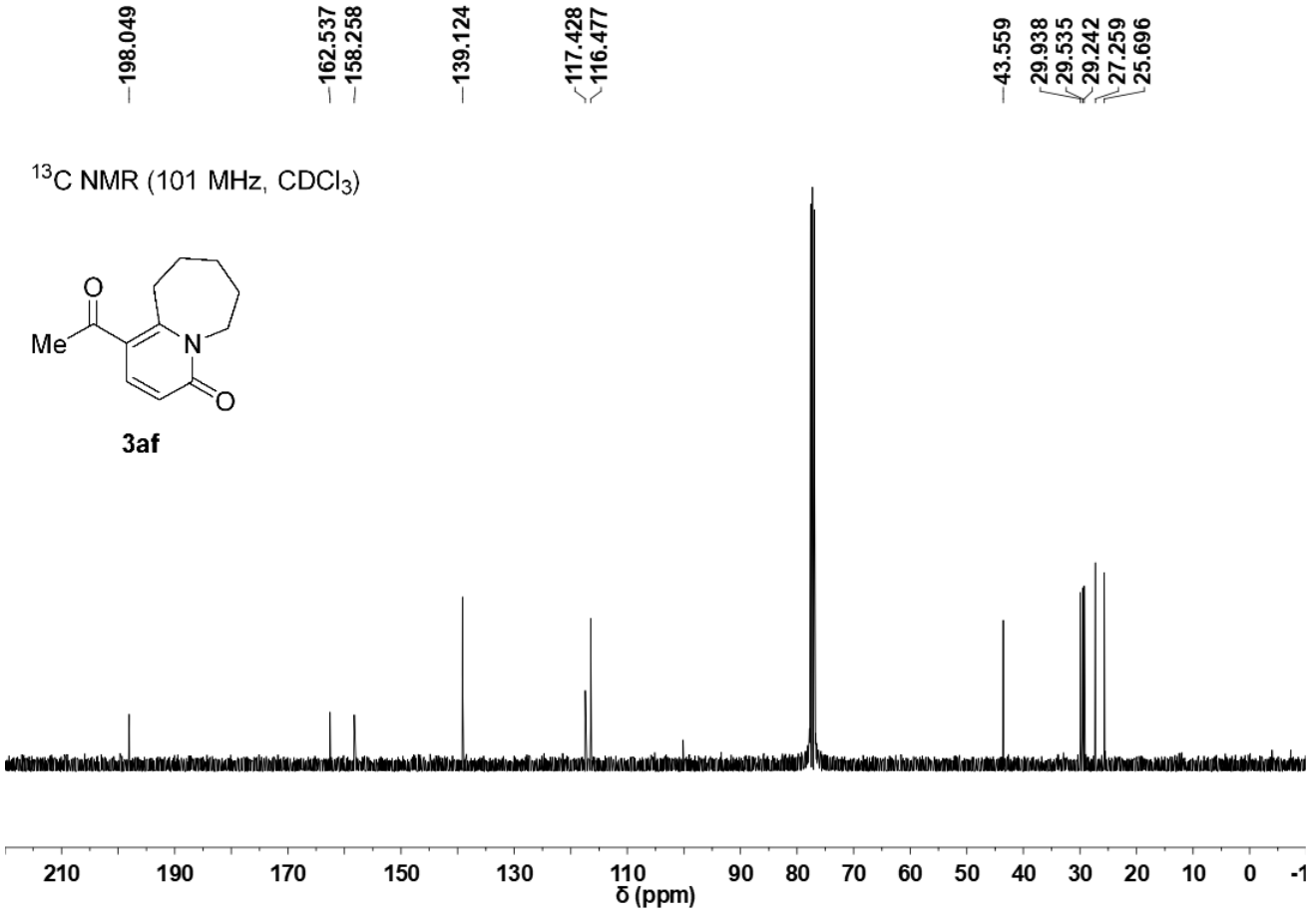

195.252
163.113
151.380
139.869
138.168
133.290
130.020
128.832
117.934
115.692
31.740
18.780
13C NMR (101 MHz, CDCl3)
O
Me
Ph
N
Me
O
3ac
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

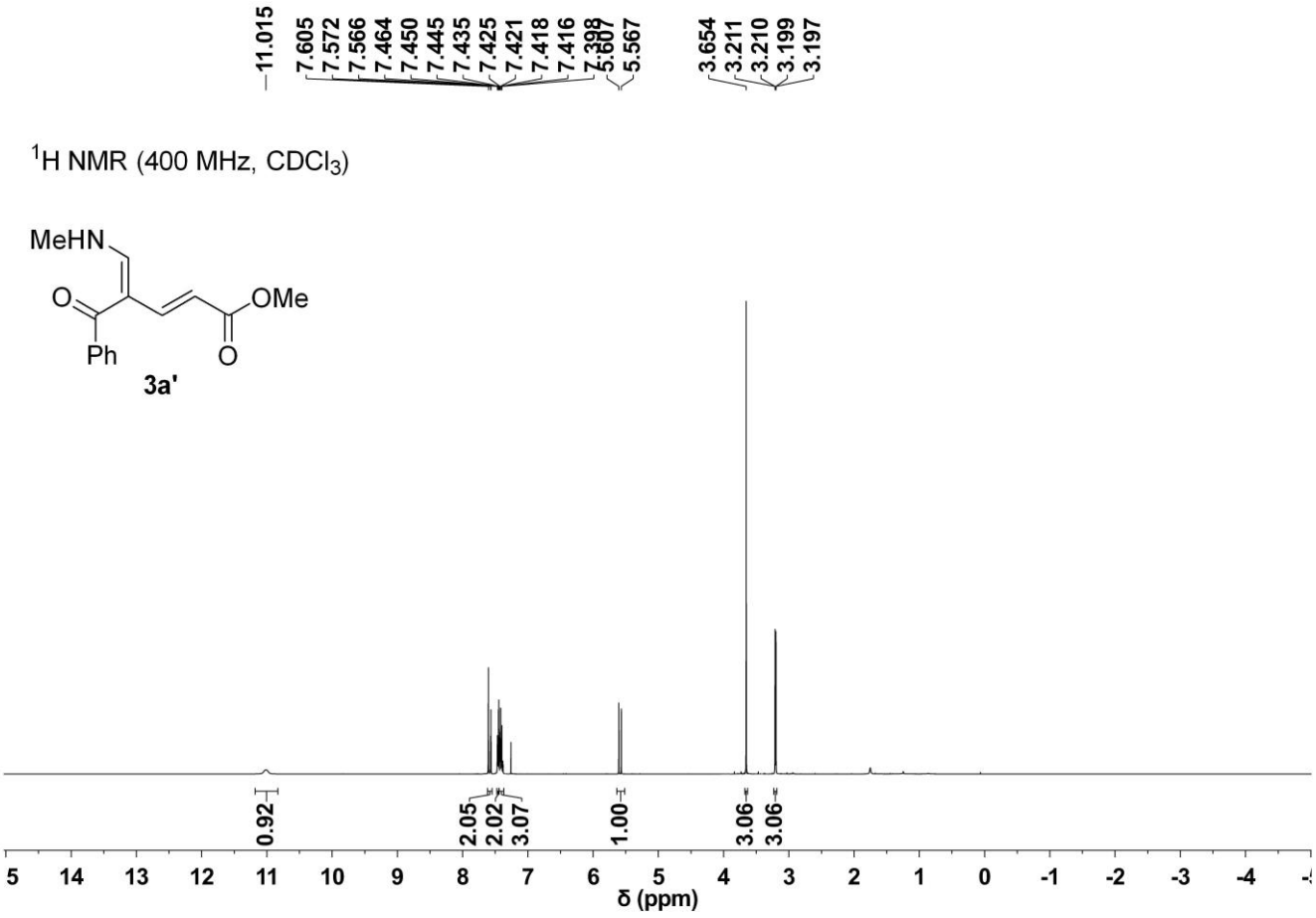

7.793
7.769
6.410
6.386
3.918
3.340
2.438
1.561
1.533
1.515
1.502
1.491
1.471
1.460
1H NMR (400 MHz, CDCl3)
O
Me
N
O
3ad
1.00
1.04
2.01
2.05
3.06
10.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)
195.208
162.094
157.436
140.339
116.494
114.199
58.910
47.015
39.636
36.470
28.157
25.622
23.211
13C NMR (101 MHz, CDCl3)
O
Me
N
O
3ad
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

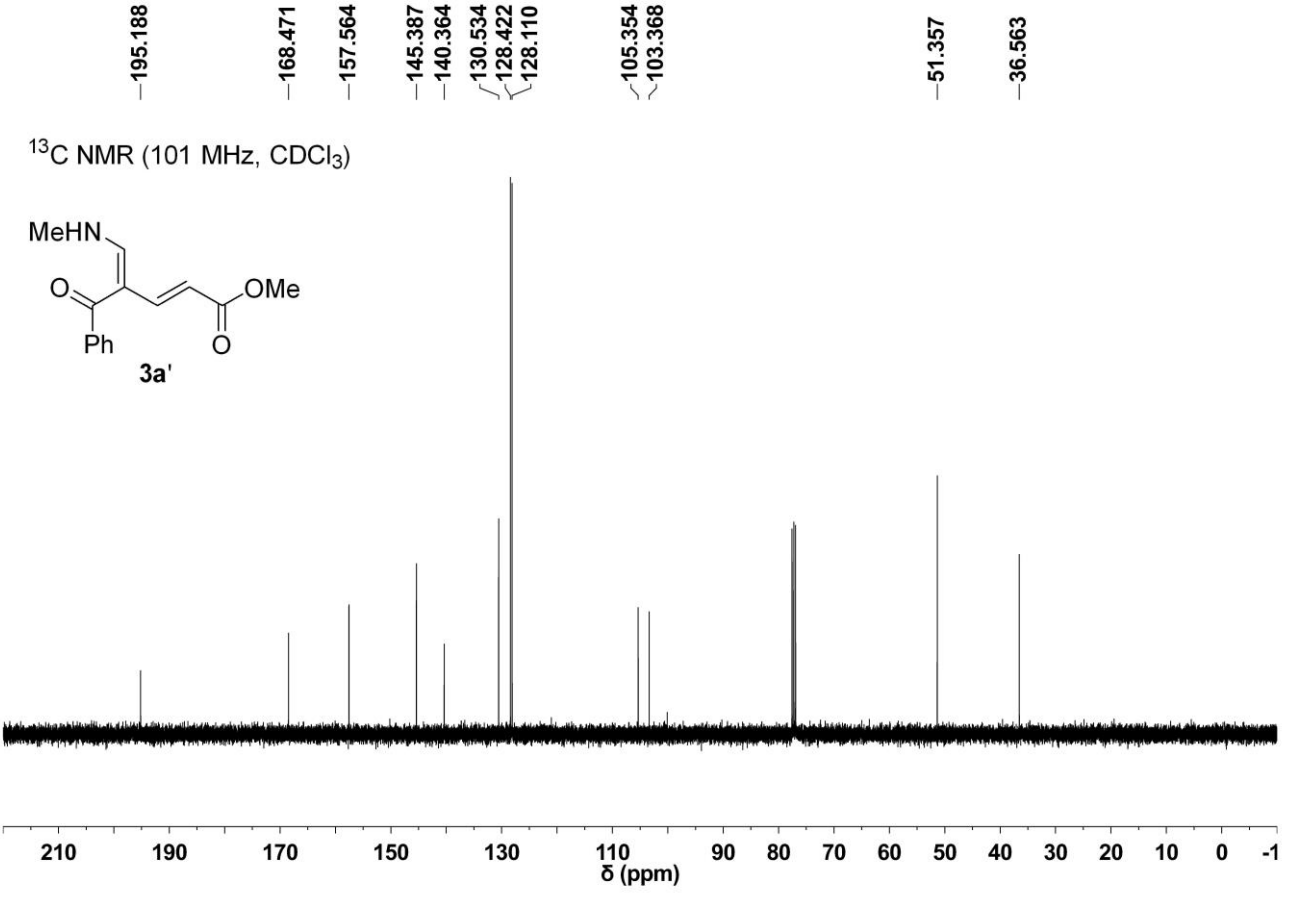

7.762
7.738
6.449
6.425
4.057
4.041
4.026
3.323
3.306
3.290
2.465
1.950
1.934
1.917
1.902
1.885
1.813
1.796
1.779
1.762
1.746
1H NMR (400 MHz, CDCl3)
Me
O
N
O
3ae
1.03
1.00
2.03
1.97
3.00
2.13
2.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


196.790
162.769
155.836
139.684
115.818
115.186
42.963
29.721
27.645
21.539
18.382
13C NMR (101 MHz, CDCl3)
Me
O
N
O
3ae
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

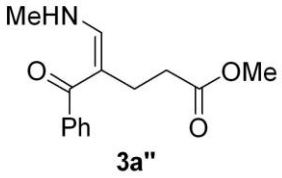

7.631
7.607
6.454
6.430
4.469
4.456
4.445
3.294
2.469
1.783
1.764
1.753
1.744
^{1}H NMR (400 MHz, $CDCl_3$)
O
Me
N
O
3af
1.00
1.02
2.05
2.10
3.18
6.34
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


198.049
162.537
158.258
139.124
117.428
116.477
43.559
29.938
29.535
29.242
27.259
25.696
^{13}C NMR (101 MHz, $CDCl_3$)
O
Me
N
O
3af
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)


11.015
7.605
7.572
7.566
7.464
7.450
7.445
7.435
7.425
7.421
7.418
7.416
5.567
3.654
3.211
3.210
3.199
3.197
1H NMR (400 MHz, CDCl3)
MeHN
O
OMe
Ph
O
3a'
0.92
2.05
2.02
3.07
1.00
3.06
3.06
δ (ppm)

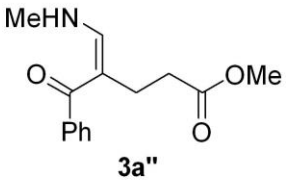

195.188
168.471
157.564
145.387
140.364
130.534
128.422
128.110
105.354
103.368
51.357
36.563
13C NMR (101 MHz, CDCl3)
MeHN
O
OMe
Ph
O
3a'
δ (ppm)

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



3a''

^{13}C NMR (101 MHz, $CDCl_3$)



3a''