Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ruthenium-catalysed cross-coupling reaction of ketones with transformable directing groups as alkenyl electrophiles

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Contents

Instrumentations

Nuclear magnetic resonance spectra were measured at 400 MHz for ^{1}H NMR and at 100 MHz for $^{13}C\{^{1}H\}$ NMR by Bruker Advanced III HD spectrometer. ^{1}H NMR chemical shifts were recorded in ppm relative to the resonance of tetramethylsilane (0.00 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), relative intensity. ^{13}C NMR chemical shifts were reported in ppm relative to the residual solvent signals at δ 77.16 for $CDCl_3$. High resolution mass spectra (HRMS) were recorded by APCI or ESI using a TOF by Bruker micrOTOF II or a JEOL JMS-T100LCS. Melting points were measured with Yanaco MP-S3. GC analysis was carried out using a capillary column (Agilent Technologies DB-1 (0.250 mm i.d. x 15 m length x 0.10 μm film) by Shimadzu GC-2010plus. GCMS analysis was carried out by Shimadzu QP-2010SE. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merck Silica gel 60 F254. Silica gel 60N (particle size 40–50 μm, KANTO KAGAKU) was used for flash column chromatographies. IR spectra were recorded on a Shimadzu IRAffinity-1S. All reactions were conducted under nitrogen atmosphere. Heating was performed with a KOIKE PRECISION INSTRUMENTS (KPI) HHE-19G-US II with aluminum blocks or EYELA oil bath OHB-1100G.

Chemicals

Unless otherwise noted, all materials were obtained from commercial suppliers (FUJIFILM Wako Pure Chemical Corporation (Wako), Kanto Chemical Co., Inc. (Kanto), Tokyo Chemical Industry Co., Ltd. (TCI), and Aldrich) and used without further purification.

***β*-Ketoamides 1**: were prepared from the corresponding *β*-ketoesters and amines, see the section "Preparation and Characterizations for *β*-Ketoamides **1**" in this supporting information for the detail.

***β*-Ketoesters**: ethyl 2-oxocyclohexanecarboxylate (Kanto), methyl 2-oxocyclopentane-1-carboxylate (Wako), methyl 2-oxocycloheptane-1-carboxylate (Aldrich), and ethyl 3-oxo-3-phenylpropanoate (Wako) were purchased from the commercial suppliers and used without further purification.

Amines: pyrrolidine (TCI), piperidine (Wako), azepane (TCI), morpholine (TCI), diethylamine (Wako), diisopropylamine (Wako), cyclohexylamine (Wako), aniline (Wako), isoindoline (TCI), benzylamine (Wako), thiophenol (Wako) were purchased from the commercial suppliers and used without further purification.

Organoboron compounds 2: prepared from organoboronic acid and diol in our previous paper,[1] were used without further purification.

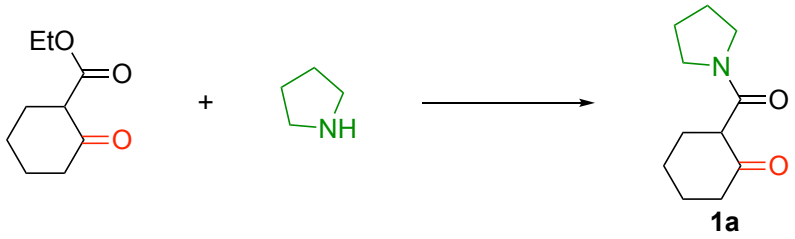
Catalyst: $Ru_3(CO)_{12}$ (Wako), $RuCl_2(PPh_3)_3$ (Wako), $RuHCl(CO)(PPh_3)_3$ (Aldrich), and $RuH_2(CO)(PPh_3)_3$ (TCI) were purchased from the commercial suppliers and used without further purification.

Solvents used in reactions: dry xylene (Kanto) and dry toluene (Kanto) were purchased as a dehydrated solvent from the commercial suppliers and used without further purification.

Others: potassium fluoride (spray dried) (Wako), anhydrous Na_2SO_4 (Wako), anhydrous $MgSO_4$ (Wako), molecular sieves 4A (Wako), hexane (Wako), EtOAc (Wako), NEt_3 (Wako), and chloroform-d_1 (99.8 atom% D with 0.03vol% TMS) (Kanto) were purchased from the commercial suppliers and used without further purification.

Preparation and Characterizations for β-Ketoamides 1

2-(Pyrrolidine-1-carbonyl)cyclohexan-1-one [CAS: 31150-04-6] (**1a**)



1a

Ethyl 2-oxocyclohexanecarboxylate (7.00 g, 41.2 mmol) and pyrrolidine (7.12 g, 100.1 mmol), potassium fluoride (spray dried) (5.84 g, 100.5 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry xylene (10 mL). The solution was then heated to 120 °C (oil bath) for 23 h and was cooled to 25 °C. To the solution was added water (20 mL). The solution was extracted with EtOAc (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 1:9) to give white solid (**1a**, 6.56 g, 82%).

R_f 0.52 (eluent: hexane/EtOAc = 1:9).

Mp 82–85 ºC.

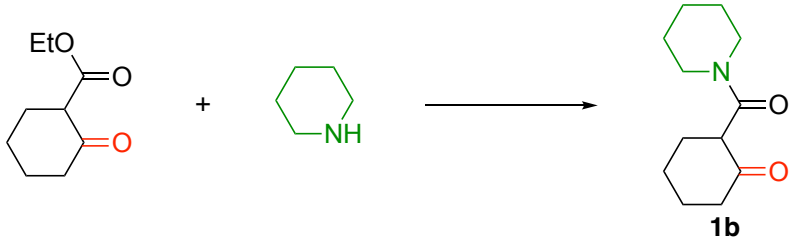
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.60–3.51 (m, 1H), 3.51–3.39 (m, 2H), 3.34 (t, J = 6.1 Hz, 2H), 2.64–2.54 (m, 1H), 2.39–2.28 (m, 1H), 2.28–2.15 (m, 1H), 2.12–1.76 (m, 8H), 1.74–1.60 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.6, 167.9, 56.3, 46.5, 45.9, 42.0, 29.9, 27.0, 26.1, 24.3, 23.4.

IR (neat) 1707, 1630, 1449, 1128 cm^{-1}.

Spectroscopic data for this compound matched the previously reported literature values.[2]

2-(Piperidine-1-carbonyl)cyclohexan-1-one [CAS: 6560-81-2] (**1b**)



1b

Ethyl 2-oxocyclohexanecarboxylate (3.48 g, 20.4 mmol) and piperidine (4.16 g, 48.8 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry toluene (20 mL). The solution was then heated to 120 °C (oil bath) for 20 h, and was cooled to 25 °C. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 3:1) to give pale yellow solid (**1b**, 3.40

g, 80%).

R_f 0.38 (eluent: hexane/EtOAc = 1:9).

Mp 65–67 ºC.

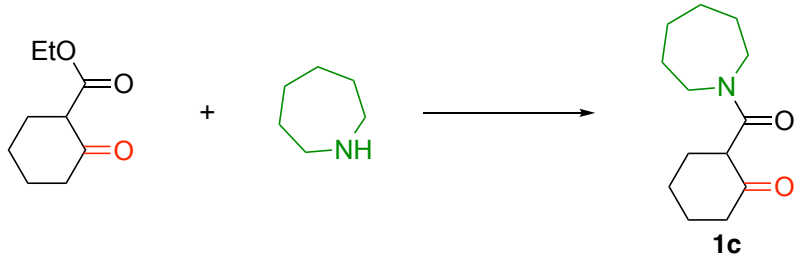
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.67–3.49 (m, 3H), 3.33–3.19 (m, 2H), 2.62–2.50 (m, 1H), 2.41–2.28 (m, 1H), 2.27–2.13 (m, 1H), 2.12–1.91 (m, 3H), 1.90–1.76 (m, 1H), 1.76–1.42 (m, 7H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.5, 167.7, 54.1, 46.8, 42.8, 41.8, 30.4, 27.1, 26.2, 25.5, 24.4, 23.5.

IR (neat) 1703, 1632, 1441 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{12}H_{20}NO_2^+$: 210.1489, found: 210.1492.

2-(Azepane-1-carbonyl)cyclohexan-1-one [CAS: 31150-03-5] (**1c**)



1c

Ethyl 2-oxocyclohexanecarboxylate (3.50 g, 20.6 mmol) and azepane (5.27 g, 53.1 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry xylene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 1:1) to give a yellow oil (**1c**, 2.67 g, 58%).

R_f 0.32 (eluent: hexane/EtOAc = 1:1).

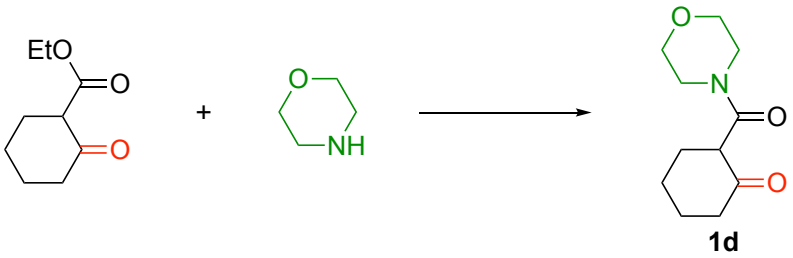
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.67–3.53 (m, 2H), 3.53–3.43 (m, 1H), 3.43–3.33 (m, 1H), 3.33–3.23 (m, 1H), 2.66–2.54 (m, 1H), 2.40–2.29 (m, 1H), 2.29–2.17 (m, 1H), 2.11–1.90 (m, 3H), 1.90–1.79 (m, 1H), 1.77–1.46 (m, 9H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.8, 169.2, 54.4, 47.9, 46.0, 41.9, 30.6, 29.2, 27.5, 27.3, 27.1, 26.5, 23.5.

IR (neat) 1709, 1656, 1450 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{13}H_{22}NO_2^+$: 224.1645, found: 224.1637.

2-(Morpholine-4-carbonyl)cyclohexan-1-one [CAS: 28637-51-6] (**1d**)



1d

Ethyl 2-oxocyclohexanecarboxylate (3.42 g, 20.1 mmol) and morpholine (4.46 g, 51.1 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry xylene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 1:4) to give white solid (**1d**, 3.57 g, 80%).

R_f 0.31 (eluent: hexane/EtOAc = 1:4).

Mp 75–78 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.88–3.78 (m, 1H), 3.70 (t, J = 4.9 Hz, 2H), 3.65 (t, J = 4.8 Hz, 2H), 3.56–3.45 (m, 2H), 3.40–3.26 (m, 2H), 2.60–2.50 (m, 1H), 2.40–2.28 (m, 1H), 2.28–2.15 (m, 1H), 2.14–1.95 (m, 3H), 1.90–1.76 (m, 1H), 1.75–1.60 (m, 1H).

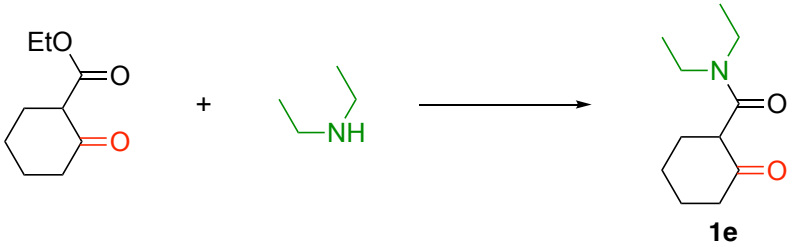
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.3, 168.0, 66.9, 66.6, 54.1, 46.3, 42.3, 42.0, 30.2, 27.1, 23.6.

IR (neat) 1708, 1639, 1437 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{11}H_{18}NO_3^+$: 212.1281, found: 212.1272.

Spectroscopic data for this compound matched the previously reported literature values.[2, 3]

***N*,*N*-Diethyl-2-oxocyclohexane-1-carboxamide** [CAS: 31150-05-7] (**1e**)



1e

Ethyl 2-oxocyclohexanecarboxylate (0.58 g, 3.39 mmol) and diethylamine (0.77 g, 10.6 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry toluene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 2:1) to give a yellow oil (**1e**, 0.41

g, 62%).

R_f 0.11 (eluent: hexane/EtOAc = 2:1).

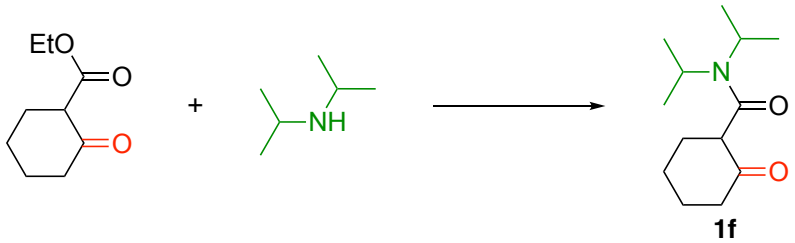
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.56–3.41 (m, 2H), 3.39–3.09 (m, 3H), 2.66–2.53 (m, 1H), 2.40–2.29 (m, 1H), 2.29–2.15 (m, 1H), 2.13–1.91 (m, 3H), 1.91–1.78 (m, 1H), 1.74–1.55 (m, 1H), 1.19–1.09 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 207.6, 168.6, 53.9, 41.8, 41.6, 40.0, 30.3, 26.8, 23.2, 14.3, 12.7.

IR (neat) 1711, 1636, 1450 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{11}H_{20}NO_2^+$: 198.1489, found: 198.1486.

***N,N*-Diisopropyl-2-oxocyclohexane-1-carboxamide** [CAS: 64425-73-6] (**1f**)



1f

Ethyl 2-oxocyclohexanecarboxylate (1.09 g, 6.38 mmol) and diisopropylamine (3.54 g, 35.0 mmol), potassium fluoride (spray dried) (1.47 g, 50.0 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry xylene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 23 h. and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 4:1) to give pale yellow solid (**1f**, 1.26 g, 87%).

R_f 0.07 (eluent: hexane/EtOAc = 4:1).

Mp 61–64 ºC.

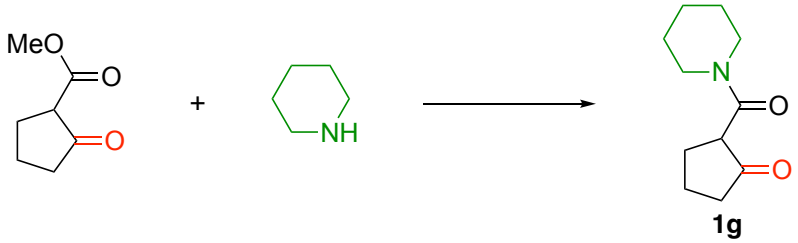
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.82–3.69 (m, 1H), 3.54–3.40 (m, 2H), 2.61–2.51 (m, 1H), 2.40–2.29 (m, 1H), 2.26–2.13 (m, 1H), 2.10–1.90 (m, 3H), 1.90–1.77 (m, 1H), 1.73–1.61 (m, 1H), 1.43 (d, J = 6.8 Hz, 3H), 1.38 (d, J = 6.8 Hz, 3H), 1.21–1.10 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 208.1, 168.2, 55.8, 48.8, 46.0, 42.0, 30.7, 27.3, 23.6, 21.1, 20.8, 20.7, 20.5.

IR (neat) 1713, 1628, 1441 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{13}H_{24}NO_2^+$: 226.1802, found: 226.1795.

2-(Piperidine-1-carbonyl)cyclopentan-1-one [CAS: 6560-62-9] (**1g**)



1g

Methyl 2-oxocyclopentane-1-carboxylate (0.58 g, 4.1 mmol) and piperidine (0.87 g, 10.3 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry toluene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 1:1) to give white solid (**1g**, 0.46 g, 58%).

R_f 0.29 (eluent: hexane/EtOAc = 1:1).

Mp 70–71 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.73–3.55 (m, 2H), 3.55–3.38 (m, 3H), 2.58–2.43 (m, 1H), 2.34–2.24 (m, 2H), 2.23–2.10 (m, 2H), 1.94–1.80 (m, 1H), 1.80–1.49 (m, 6H).

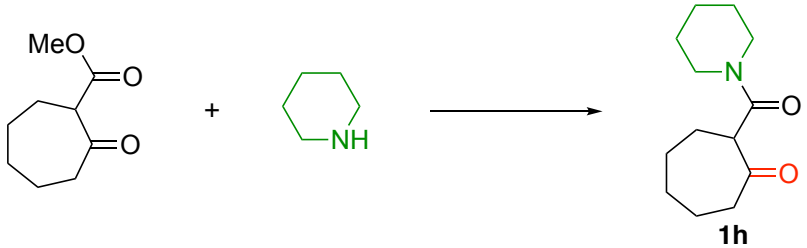
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 214.6, 166.7, 51.6, 47.3, 43.3, 38.6, 27.4, 26.6, 25.6, 24.6, 21.0

IR (neat) 1740, 1636, 1443 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{11}H_{18}NO_2^+$: 196.1332, found: 196.1340.

Spectroscopic data for this compound matched the previously reported literature values.[3]

2-(Piperidine-1-carbonyl)cycloheptan-1-one (**1h**)



1h

Methyl 2-oxocycloheptane-1-carboxylate (0.58 g, 4.1 mmol) and piperidine (0.87 g, 10.3 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry toluene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 1:1) to give a yellow oil (**1h**, 0.37 g, 40%).

R_f 0.39 (eluent: hexane/EtOAc = 1:1).

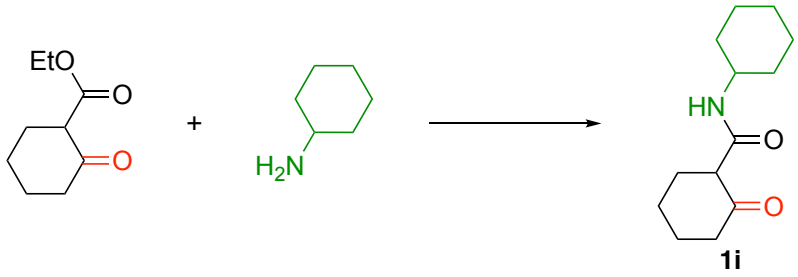
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 3.72–3.63 (m, 1H), 3.62–3.49 (m, 2H), 3.49–3.35 (m, 2H), 2.89–2.74 (m, 1H), 2.55–2.43 (m, 1H), 2.08–1.82 (m, 5H), 1.68–1.43 (m, 8H), 1.37–1.23 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 210.9, 168.3, 56.5, 47.1, 43.1, 42.8, 30.3, 28.0, 27.8, 26.4, 25.7, 25.5, 24.5.

IR (neat) 1701, 1638, 1439, 1238 cm^{-1}.

HRMS (APCI) *m*/*z* ($[M+H]^+$) calcd for $C_{13}H_{22}NO_2^+$: 224.1645, found: 224.1649.

***N*-Cyclohexyl-2-oxocyclohexane-1-carboxamide** [CAS: 82634-74-0] (**1i**)



1i

Ethyl 2-oxocyclohexanecarboxylate (0.58 g, 3.39 mmol) and cyclohexylamine (5.03 g, 50.7 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry toluene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 2:1) to give pale yellow solid (**1i**, 1.35 g, 30%).

R_f 0.25 (eluent: hexane/EtOAc = 2:1).

Mp 92–95 ºC.

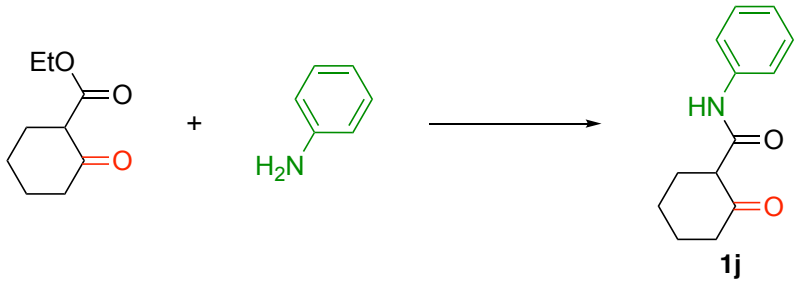
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 6.91 (s, 1H), 3.84–3.74 (m, 1H), 3.14 (ddd, J = 9.9, 5.5, 1.0 Hz, 1H), 2.49–2.33 (m, 3H), 2.03–1.56 (m, 10H), 1.43–1.30 (m, 2H), 1.25–1.12 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 211.1, 167.8, 55.8, 48.0, 42.2, 32.9 (2C), 31.7, 27.4, 25.6, 24.7(2C), 24.2.

IR (neat) 3283, 1713, 1551, 1449 cm^{-1}.

HRMS (APCI) *m*/*z* ($[M+H]^+$) calcd for $C_{13}H_{22}NO^+$: 224.1645, found: 224.1640.

2-Oxo-*N*-phenylcyclohexane-1-carboxamide [CAS: 51089-06-6] (**1j**)



Ethyl 2-oxocyclohexanecarboxylate (0.58 g, 3.39 mmol) and aniline (4.86 g, 52.2 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry toluene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 4:1) to give pale yellow solid (**1j**, 6.97 g, 63%).

R_f 0.10 (eluent: hexane/EtOAc = 4:1).

Mp 93–95 ºC.

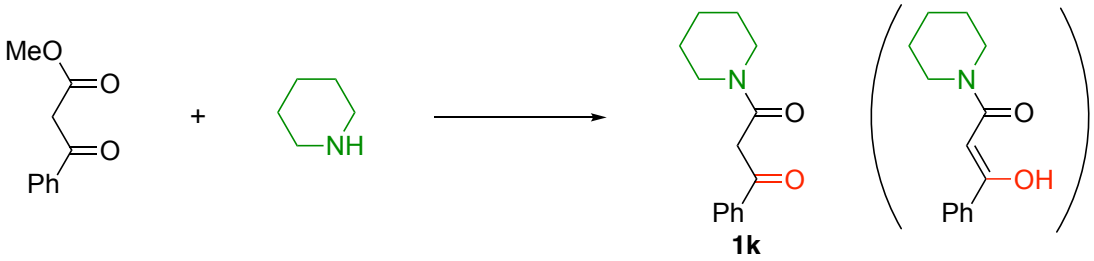
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.32 (s, 1H), 7.56 (d, J = 7.9 Hz, 2H), 7.32 (t, J = 8.0, 2H), 7.10 (t, J = 7.4 Hz, 1H), 3.36–3.26 (m, 1H), 2.62–2.37 (m, 3H), 2.15–1,90 (m, 3H), 1.90–1.69 (m, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 211.5, 167.1, 137.7, 129.0 (2C), 124.4, 120.2 (2C), 55.8, 42.5, 32.1, 27.5, 24.5.

IR (neat) 3291, 2943, 1709, 1672, 1598, 1549, 1497, 1445 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{13}H_{16}NO_2^+$: 218.1176, found: 218.1170.

1-Phenyl-3-(piperidin-1-yl)propane-1,3-dione [58792-29-3] (**1k**)



Ethyl 3-oxo-3-phenylpropanoate (0.76 g, 4.27 mmol) and piperidine (0.87 g, 10.2 mmol) was 50 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry toluene (20 mL). The solution was then heated to 120 ℃ (oil bath) for 20 h, and was cooled to 25 ℃. The solution was added water (20 mL). The solution was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc= 1:1) to give yellow oil (**1k**, 0.51 g, 2.20

mmol, 52%).

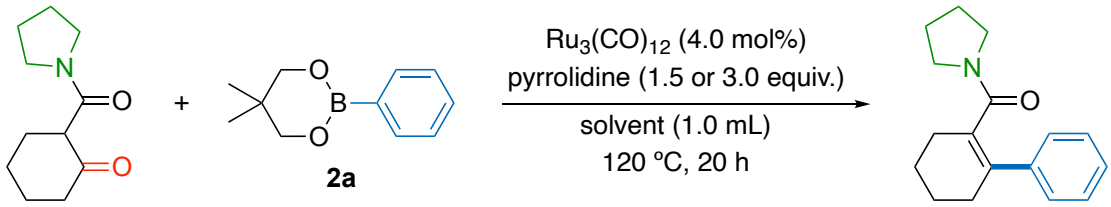
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 15.46 (s, 0.45H, enol), 8.05–8.03 (m, 1.09H, keto), 7.79–7.76 (m, 0.91H, enol), 7.61–7.57 (m, 0.55H, keto), 7.50–7.46 (m, 1.09H, keto), 7.44–7.38 (m, 1.36H, enol), 5.83 (s, 0.45H, enol), 4.1 (s, 1.09H, keto), 3.60–3.58 (m, 2.91H, keto + enol), 3.44–3.41 (m, 1.09H, keto), 1.71–1.53 (m, 6.00H, keto + enol).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.0 (keto), 171.5 (keto + enol), 165.0 (enol), 136.3, 135.3, 133.6, 130.5, 128.74, 128.72, 128.4, 125.9, 84.3, 47.7, 46.2, 43.1, 26.3, 26.0, 25.5, 24.6, 24.4.

Spectroscopic data for this compound matched the previously reported literature values.[4]

Optimization of Reaction Conditions of Ru-Catalysed Coupling of *β*-Ketoamides 1a with Organoboronate 2a

Standard Condition for the Optimization:

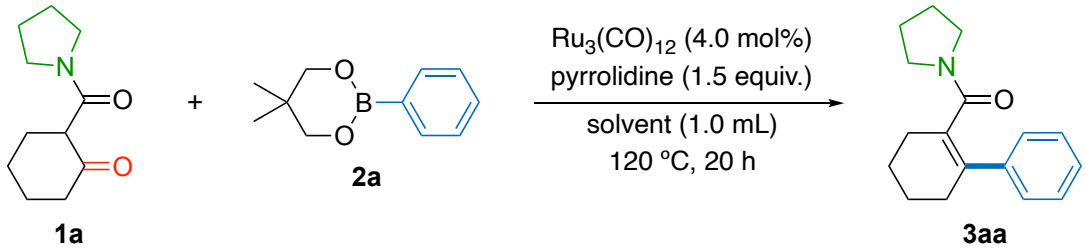


1a **3aa**

$Ru_3(CO)_{12}$ (5.1 mg, 0.008 mmol, 4.0 mol%) and 2-(pyrrolidine-1-carbonyl)cyclohexan-1-one (**1a**, 39.1 mg, 0.20 mmol, 1.0 equiv.) were placed in a 4 mL of two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry xylene (1.0 mL, 0.2 M) was added, pyrrolidine (42.7 mg, 0.3 or 6.0 mmol, 1.5 or 3.0 equiv.) was added into the flask through a septum by using a micro-syringe at 25 ℃. The solution was then heated to 120 ℃ (heat block). A separately prepared xylene solution (1.0 mL) of phenylboronate (**2a**, 57.0 or 114.0 mg, 0.30 or 0.60 mmol, 1.5 or 3.0 equiv.) was then added dropwise via a syringe pump to the solution over a 16 h period. After maintaining this temperature for an additional 20 h, the reaction mixture was cooled to 25 ℃. The reaction progress was monitored by GC analysis. The selected results of the optimization of the reactions were summarized below.

Effect of Solvents on the Reaction of **1a** with **2a**

Table S-1. Effect of Solvents on the Reaction of **1a** with **2a**.[a]

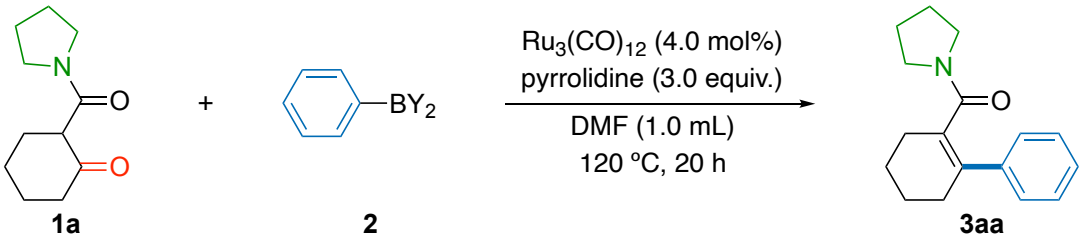


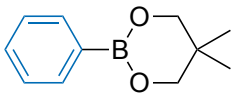
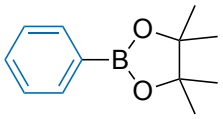
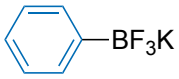
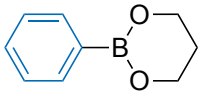
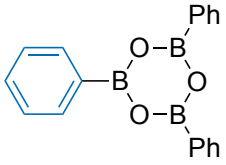
entry	**solvent**	conversion	yield (**3aa**)
1	**xylene**	**86%**	**37%**
2 [b]	THF	64%	19%
3	1,4-dioxane	64%	11%
4	DMF	53%	44%
5	NMP	>99%	17%
6	DMA	>99%	33%
7 [c]	DMI	>99%	23%
8	DMSO	48%	not detected
9	*tert*-AmylOH	<1%	not detected

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.3 mmol, 1.5 equiv., dropwise for 16 h), $Ru_3(CO)_{12}$ (0.008 mmol), and pyrrolidine (0.6 mmol) in solvent (1.0 mL) at 120 °C for 20 h. Yields of **3aa** were determined by GC analysis, using pentadecane as the internal standard. [b] The reaction was conducted at 80 °C. [c] 3.0 equiv. of amine was used.

Effect of Substituents on the Boron in Phenylboron **2** on the Reaction of **1a** with **2**

Table S-2. Effect of Substituents on the Boron in Phenylboron **2** on the Reaction of **1a** with **2**.[a]

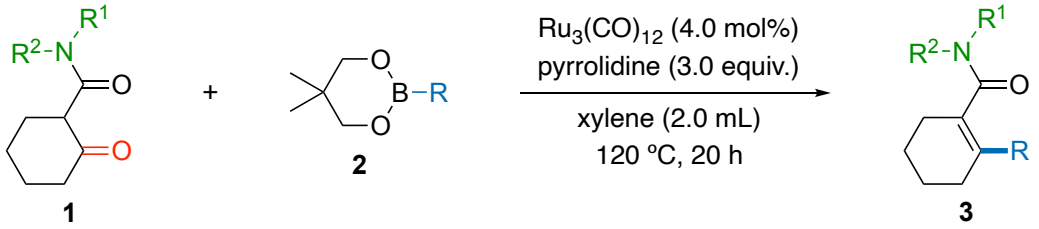


entry	phenylboron **2**	yield (**3aa**)
1		23%
2 [b]		6%
3		5%
4		27%
5		11%

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv., dropwise for 16 h), $Ru_3(CO)_{12}$ (0.008 mmol), and pyrrolidine (0.6 mmol) in solvent (1.0 mL) at 120 °C for 20 h. Yields of **3aa** were determined by GC analysis, using pentadecane as the internal standard. [b] Phenylboron **2** was added to the reaction vessel without dropwise.

Preparation and Characterization for Ruthenium-Catalysed Cross-Coupling of *β*-Ketoamides 1 with Organoboronates 2 (Tables 2 and 3).

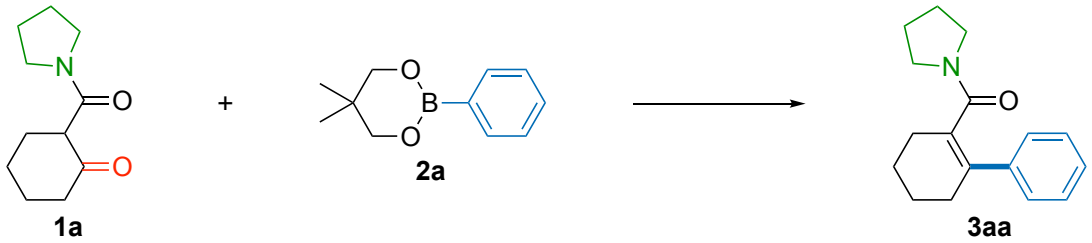
General Procedure A:



$Ru_3(CO)_{12}$ (5.1 mg, 0.008 mmol, 4.0 mol%), ketone **1** (0.2 mmol, 1.0 equiv.), and organoboronate **2** (0.6 mmol, 3.0 equiv.) were placed in a 4-mL two-necked flask equipped with a stirring bar under a nitrogen atmosphere. After dry xylene (2.0 mL, 0.1 M) and pyrrolidine (42.7 mg, 0.6 mmol, 3.0 equiv.) were added to the flask through a septum by using a micro-syringe at 25 °C, the mixture was heated to 120 °C (heat block). After this temperature was maintained for 20 h, the reaction mixture was cooled to 25 °C. The crude product **3** was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3) to afford the desired product **3**.

Scope of *β*-Ketoamides **1** (Table 2)

Pyrrolidin-1-yl(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (3aa)



1a **3aa**

The general procedure A was followed with use of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**, 114.6 mg, 0.6 mmol) and 2-(pyrrolidine-1-carbonyl)cyclohexan-1-one (**1a**, 39.0 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 33:67:1) to give a yellow oil (**3aa**, 10.7 mg, 21%).

R_f 0.27 (eluent: hexane/EtOAc = 1:2).

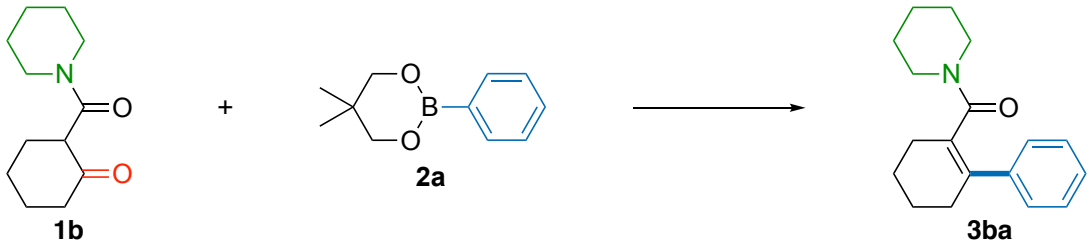
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.34–7.30 (m, 2H), 7.27 (t, J = 7.3 Hz, 2H), 7.21 (t, J = 7.1 Hz, 1H), 3.34–3.13 (m, 2H), 3.03–2.84 (m, 2H), 2.50–2.27 (m, 4H), 1.84–1.71 (m, 4H), 1.64–1.41 (m, 4H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 141.7, 134.8, 132.4, 127.9 (2C), 127.11, 127.07 (2C), 46.7, 44.8, 29.6, 27.1, 25.5, 24.1, 22.7, 22.0.

IR (neat) 1618, 1466, 1248 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{17}H_{22}NO^+$: 256.1696, found: 256.1699.

Piperidin-1-yl(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (3ba)



1b **3ba**

The general procedure A was followed with use of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**, 115.5 mg, 0.61 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 43.2 mg, 0.21 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 60:40:1) to give a pale yellow solid (**3ba**, 38.4 mg, 68%).

R_f 0.20 (eluent: hexane/EtOAc = 3:2).

Mp 63–65 ºC.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.33–7.27 (m, 4H), 7.23–7.19 (m, 1H), 3.51–3.46 (m, 1H), 3.25–3.19 (m, 1H), 3.13–2.99 (m, 2H), 2.62–2.58 (m, 2H), 2.25–2.04 (m, 2H), 1.82–1.72 (m, 4H), 1.41–1.31 (m, 3H),

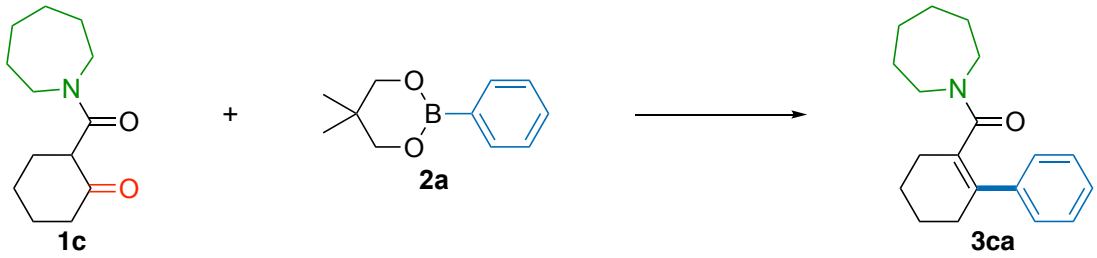
1.23–1.10 (m, 2H), 0.64–0.57 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 141.7, 134.4, 131.0, 128.0 (2C), 127.3 (2C), 127.1, 47.0, 41.7, 29.8, 27.8, 25.8, 25.0, 24.4, 22.7, 22.0.

IR (neat) 1616, 1439, 1283 cm^{-1}.

HRMS (APCI) *m/z* ([M+H]$^+$) calcd for $C_{18}H_{24}NO^+$: 270.1852, found: 270.1857.

Azepan-1-yl(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (3ca)



The general procedure A was followed with use of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**, 115.5 mg, 0.6 mmol) and 2-(azepane-1-carbonyl)cyclohexan-1-one (**1c**, 44.3 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 =75:25:1) to give a yellow oil (**3ca**, 38.0 mg, 67%).

R_f 0.27 (eluent: hexane/EtOAc = 3:1).

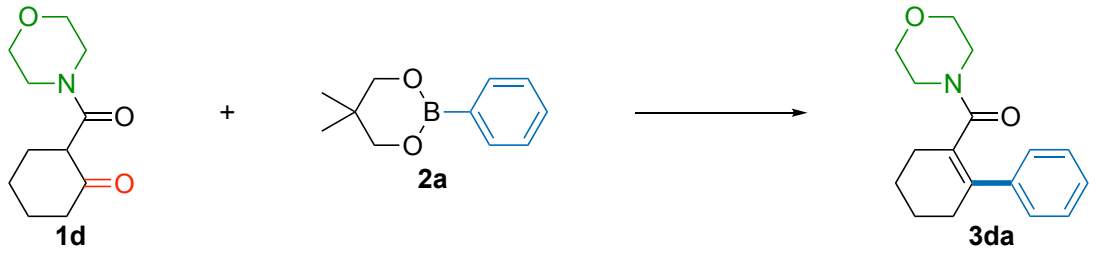
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35–7.33 (m, 2H), 7.28–7.25 (m, 2H), 7.22–7.18 (m, 1H), 3.31–3.21 (m, 3H), 3.00–2.94 (m, 1H), 2.60 (d, J = 15.8 Hz, 2H), 2.21 (t, J = 8.5 Hz, 1H), 2.09 (q, J = 5.9 Hz, 1H), 1.81–1.72 (m, 4H), 1.62–1.56 (m, 1H), 1.49–1.26 (m, 6H), 0.92 (t, J = 9.1 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.7, 141.8, 133.9, 131.7, 128.0 (2C), 127.4 (2C), 127.1, 48.1, 44.4, 29.8, 28.8, 28.2, 27.9, 27.1, 25.9, 22.8, 22.0.

IR (neat) 1611, 1493, 1092 cm^{-1}.

HRMS (APCI) *m/z* ([M+H]$^+$) calcd for $C_{19}H_{26}NO^+$: 284.2009, found: 284.2017.

Morpholino(3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (3da)



The general procedure A was followed with use of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**, 114.0 mg, 0.6 mmol) and 2-(morpholine-4-carbonyl)cyclohexan-1-one (**1d**, 42.2 mg, 0.20 mmol). The reaction

was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 60:40:1) to give a white solid (**3da**, 23.1 mg, 43%).

R_f 0.26 (eluent: hexane/EtOAc = 3:2).

Mp 71–74 °C.

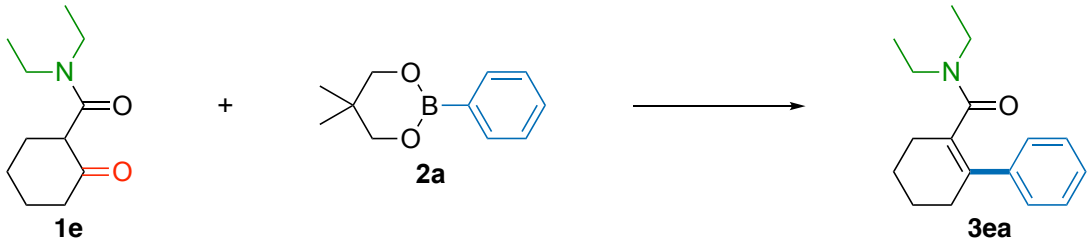
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.33–7.29 (m, 3H), 7.27–7.23 (m, 2H), 3.60–3.51 (m, 2H), 3.32–3.24 (m, 2H), 3.18–3.03 (m, 3H), 2.63–2.59 (m, 2H), 2.48–2.44 (m, 1H), 2.25–2.04 (m, 2H), 1.82–1.76 (m, 4H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 141.5, 135.6, 130.1, 128.3 (2C), 127.6, 127.3 (2C), 66.3, 66.2, 46.4, 41.3, 29.8, 27.7, 22.7, 21.9.

IR (neat) 1611, 1431, 1246 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{17}H_{22}NO_2^+$: 272.1645, found: 272.1645.

***N*,*N*-Diethyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxamide (3ea)**



The general procedure A was followed with use of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**, 114.0 mg, 0.6 mmol) and *N*,*N*-diethyl-2-oxocyclohexane-1-carboxamide (**1e**, 39.2 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 67:33:1) to give a yellow oil (**3ea**, 31.9 mg, 62%).

R_f 0.25 (eluent: hexane/EtOAc = 2:1)

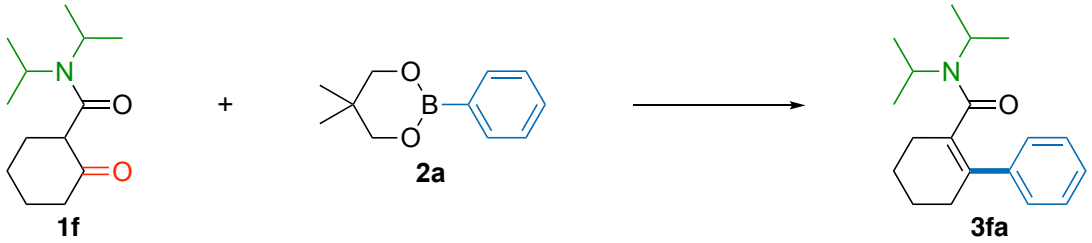
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.31–7.29 (m, 2H), 7.25–7.23 (m, 2H), 7.21–7.18 (m, 1H), 3.61–3.53 (m, 1H), 3.29–3.21 (m, 1H), 2.93–2.74 (m, 2H), 2.59–2.67 (m, 2H), 2.24–2.07 (m, 2H), 1.83–1.75 (m, 4H), 0.81–0.75 (m, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.1, 141.7, 134.2, 131.5, 128.0 (2C), 127.4 (2C), 127.0, 41.8, 37.7, 29.9, 27.9, 22.8, 22.0, 13.8, 11.8.

IR (neat) 1611, 1560, 1458 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{17}H_{24}NO^+$: 258.1852, found: 258.1842.

***N*,*N*-Diisopropyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxamide (3fa)**



The general procedure A was followed with use of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**, 114.6 mg, 0.6 mmol) and *N*,*N*-diisopropyl-2-oxocyclohexane-1-carboxamide (**1f**, 44.7 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 86:14:1) to give a yellow oil (**3fa**, 23.2 mg, 41%).

R_f 0.33 (eluent: hexane/EtOAc = 6:1).

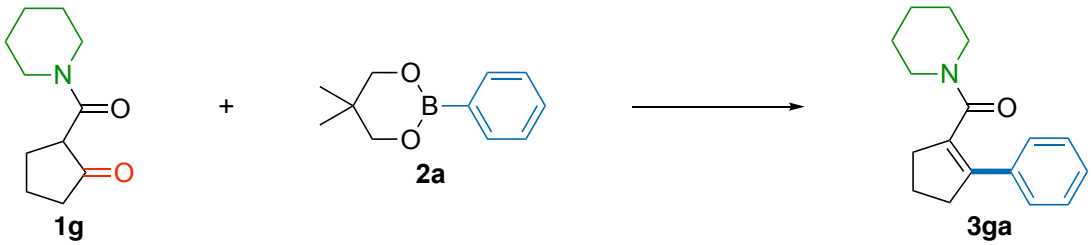
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.37 (d, J = 7.2 Hz, 2H), 7.25 (t, J = 7.2 Hz, 2H), 7.20–7.17 (m, 1H), 3.92 (septet, J = 6.7 Hz, 1H), 3.09 (septet, J = 7.8 Hz, 1H), 2.65–7.54 (m, 2H), 2.22–2.16 (m, 1H), 2.07–2.02 (m, 1H), 1.82–1.64 (m, 4H), 1.39 (d, J = 6.8 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H), 1.00 (d, J = 6.7 Hz, 3H), 0.31 (d, J = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.1, 141.8, 133.0, 132.3, 128.0 (2C), 127.9 (2C), 127.1, 50.0, 45.3, 29.7, 28.2, 22.9, 22.2, 21.7, 20.9, 19.8, 19.6.

IR (neat) 1611, 1439, 1325 cm^{-1}.

HRMS (APCI) *m*/*z* ([M+H]$^+$) calcd for $C_{19}H_{28}NO^+$: 286.2165, found: 286.2168.

(2-Phenylcyclopent-1-en-1-yl)(piperidin-1-yl)methanone (3ga)



The general procedure A was followed with use of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (**2a**, 115.4 mg, 0.6 mmol) and 2-(piperidine-1-carbonyl)cyclopentan-1-one (**1g**, 39.2 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 75:25:1) to give a white solid (**3ga**, 27.6 mg, 54%).

R_f 0.21 (eluent: hexane/EtOAc = 3:1).

Mp 101–103 °C.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.38–7.35 (m, 2H), 7.31–7.27 (m, 2H), 7.25–7.21 (m, 1H), 3.58 (s,

2H), 3.15 (t, J = 5.6 Hz, 2H), 2.88–2.84 (m, 2H), 2.80–2.76 (m, 2H), 2.10–2.02 (m, 2H), 1.48–1.47 (m, 4H), 1.04 (s, 2H).

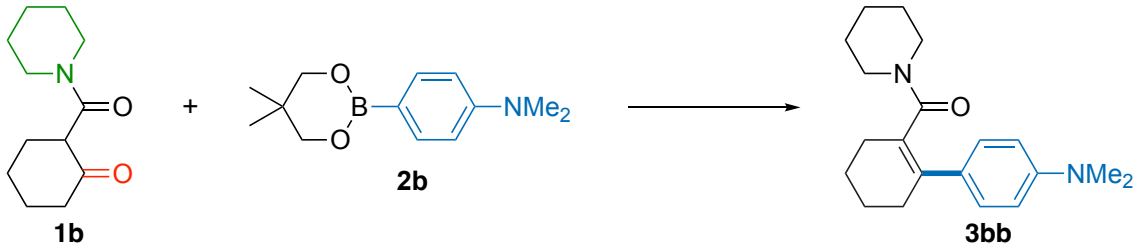
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.2, 138.8, 136.1, 133.2, 128.3 (2C), 127.6, 126.9 (2C), 47.1, 41.9, 37.1, 36.0, 26.0, 25.2, 24.5, 22.4.

IR (neat) 1611, 1439, 1279 cm^{-1}.

HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{17}H_{22}NO^+$: 256.1696, found: 256.1702.

Scope of Organoborons **2** (Table 3)

(4'-(Dimethylamino)-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(piperidin-1-yl)methanone (3bb)



The general procedure A was followed with use of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-*N*,*N*-dimethylaniline (**2b**, 140.5 mg, 0.6 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 42.8 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 60:40:1) to give a yellow oil (**3bb**, 30.6 mg, 49%).

R_f 0.24 (eluent: hexane/EtOAc = 3:2).

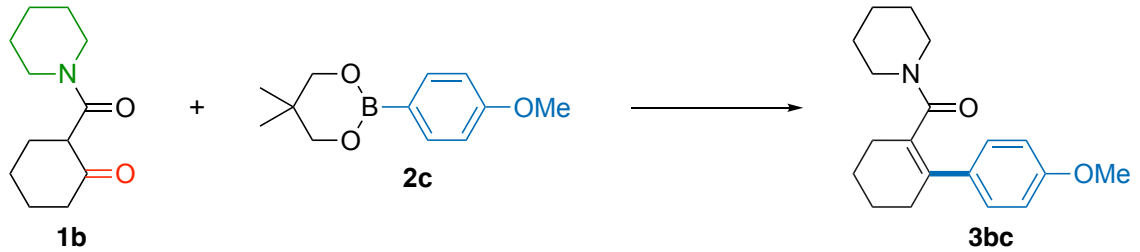
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.20–7.18 (d, J = 8.8 Hz, 2H), 6.66–6.64 (d, J = 8.8 Hz, 2H), 3.46–3.41 (m, 1H), 3.39–3.33 (m, 1H), 3.19–3.12 (m, 1H), 3.02–3.00 (m, 1H), 2.92 (s, 6H), 2.61–2.55 (m, 2H), 2.20–2.16 (m, 1H), 2.08–2.00 (m, 1H), 1.83–1.77 (m, 1H), 1.75–1.70 (m, 3H), 1.45–1.30 (m, 3H), 1.27–1.17 (m, 2H), 0.80–0.72 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.0, 149.7, 134.3, 130.0, 129.0, 128.1 (2C), 112.1 (2C), 47.0, 41.7, 40.6 (2C), 29.7, 28.0, 25.8, 25.2, 24.4, 22.9, 22.2.

IR (neat) 1611, 1520, 1441 cm^{-1}.

HRMS (APCI) *m*/*z* ($[M+H]^+$) calcd for $C_{20}H_{29}N_2O^+$: 313.2274, found: 313.2272.

(4'-Methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(piperidin-1-yl)methanone (3bc)



The general procedure A was followed with use of 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**2c**, 135.3 mg, 0.61 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 43.2 mg, 0.21 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 67:33:1) to give a white oil (**3bc**, 42.2 mg, 68%).

R_f 0.28 (eluent: hexane/EtOAc = 2:1).

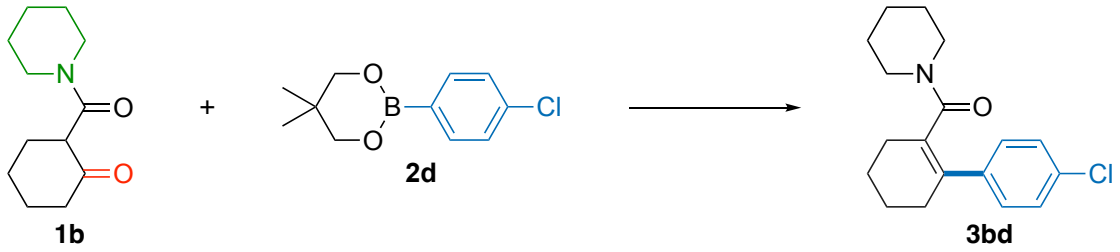
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.24 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 3.49–3.27 (m, 2H), 3.16–2.97 (m, 2H), 2.60–2.55 (m, 2H), 2.21–2.03 (m, 2H), 1.83–1.71 (m, 4H), 1.45–1.34 (m, 3H), 1.25–1.17 (m, 2H), 0.77–0.68 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.5, 158.7, 134.3, 133.9, 130.2, 128.5 (2C), 113.4 (2C), 55.3, 47.0, 41.7, 29.9, 27.9, 25.9, 25.1, 24.4, 22.8, 22.0.

IR (neat) 1609, 1510, 1439, 1252 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{19}H_{26}NO_2^+$: 300.1958, found: 300.1965.

(4'-Chloro-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)(piperidin-1-yl)methanone (3bd)



The general procedure A was followed with use of 2-(4-chlorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (**2d**, 154.0 mg, 0.69 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 41.1 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 67:33:1) to give a white solid (**3bd**, 29.8 mg, 49%).

R_f 0.25 (eluent: hexane/EtOAc = 2:1).

Mp 101–103 ºC.

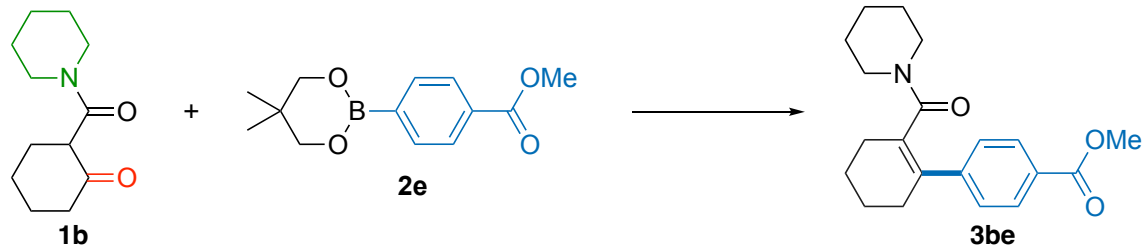
^{1}H NMR (100 MHz, $CDCl_3$) δ 7.25 (s, 4H), 3.42–3.31 (m, 2H), 3.17–2.96 (m, 2H), 2.56–2.52 (m, 2H), 2.21–2.04 (m, 2H), 1.83–1.69 (m, 4H), 1.41–1.40 (m, 3H), 1.25–1.19 (m, 2H), 0.78–0.75 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 140.1, 133.1, 132.9, 131.9, 128.7 (2C), 128.2 (2C), 47.0, 41.7, 29.7, 27.8, 26.0, 25.1, 24.3, 22.6, 21.9.

IR (neat) 1607, 1441, 1231 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{18}H_{23}ClNO^+$: 304.1463, found: 304.1467.

Methyl 6'-(piperidine-1-carbonyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylate (3be)



The general procedure A was followed with use of methyl 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzoate (**2e**, 143.9 mg, 0.58 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 41.1 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 50:50:1) to give a yellow oil (**3be**, 42.8 mg, 66%).

R_f 0.28 (eluent: hexane/EtOAc = 1:1).

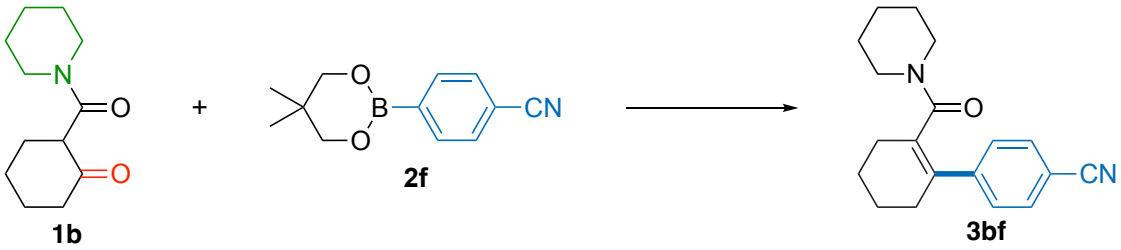
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.96 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 3.41–3.29 (m, 2H), 3.16–2.96 (m, 2H), 2.62–2.58 (m, 2H), 2.24–2.07 (m, 2H), 1.80–1.73 (m, 4H), 1.39–1.33 (m, 3H), 1.25–1.16 (m, 2H), 0.71–0.70 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0, 167.0, 146.5, 133.4, 132.7, 129.4 (2C), 128.7, 127.4 (2C), 52.1, 47.0, 41.7, 29.6, 27.9, 26.0, 25.0, 24.3, 22.6, 21.9.

IR (neat) 1722, 1607, 1437, 1279 cm^{-1}.

HRMS (APCI) m/z ($[M+H]^+$) calcd for $C_{20}H_{26}NO_3^+$: 328.1907, found: 328.1914.

6'-(Piperidine-1-carbonyl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (3bf)



The general procedure A was followed with use of 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)benzonitrile (**2f**, 174.60 mg, 0.81 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 42.2 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 60:40:1) to give a yellow oil (**3bf**, 38.8 mg, 0.132 mmol, 65 %).

R_f 0.22 (eluent: hexane/EtOAc = 3:2).

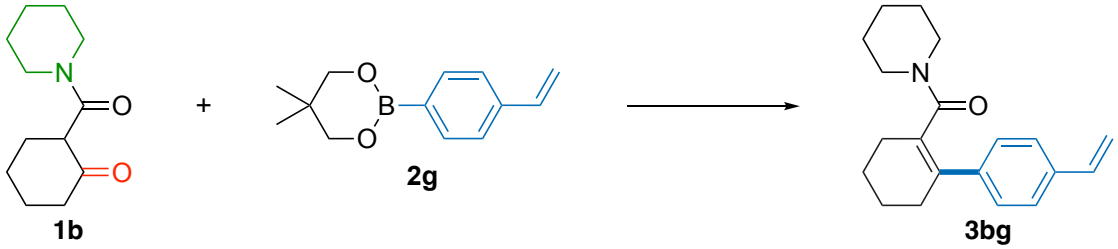
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 3.40–3.32 (m, 2H), 3.12–2.99 (m, 2H), 2.69–2.47 (m, 2H), 2.23–2.08 (m, 2H), 1.80–1.62 (m, 4H), 1.51–1.34 (m, 3H), 1.26–

1.15 (m, 2H), 0.80–0.62 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 146.6, 133.9, 132.7, 132.0 (2C), 128.2 (2C), 119.0, 110.8, 47.1, 41.9, 29.5, 27.9, 26.2, 25.2, 24.3, 22.6, 21.8.

IR (neat) 3460, 2226, 1700, 1616, 1442 cm^{-1}.

Piperidin-1-yl(4'-vinyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)methanone (3bg)



The general procedure A was followed with use of 5,5-dimethyl-2-(4-vinylphenyl)-1,3,2-dioxaborinane (**2g**, 130.6 mg, 0.6 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 41.1 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 60:40:1) to give a yellow oil (**3bg**, 27.8 mg, 47%).

R_f 0.24 (eluent: hexane/EtOAc = 3:2).

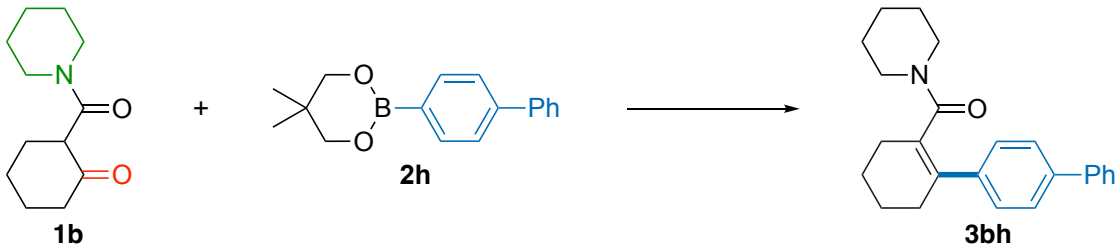
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.35–7.30 (m, 2H), 7.30–7.25 (m, 2H), 6.73–6.63 (m, 1H), 5.76–5.68 (m, 1H), 5.25– 5.19 (m, 1H), 3.43–3.31 (m, 2H), 3.18–3.12 (m, 1H), 3.00–2.95 (m, 1H), 2.62–2.57 (m, 2H), 2.27–2.14 (m, 1H), 2.12–2.00 (m, 1H), 1.80–1.72 (m, 4H), 1.43–1.34 (m, 3H), 1.25–1.18 (m, 2H), 0.76–0.72 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 141.4, 136.7, 136.5, 134.1, 131.3, 127.6 (2C), 126.0 (2C), 113.7, 47.1, 41.8, 29.8, 28.0, 26.0, 25.2, 24.5, 22.8, 22.1.

IR (neat) 1618, 1439, 1283 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{20}H_{26}NO^+$: 296.2009, found: 296.1999.

Piperidin-1-yl(3,4,5,6-tetrahydro-[1,1':4',1''-terphenyl]-2-yl)methanone (3bh)



The general procedure A was followed with use of 2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (**2h,** 164.8 mg, 0.62 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 41.4 mg,

0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 67:23:1) to give a white solid (**3bh**, 49.8 mg, 72%).

R_f 0.24 (eluent: hexane/EtOAc = 2:1).

Mp 98–100 ℃.

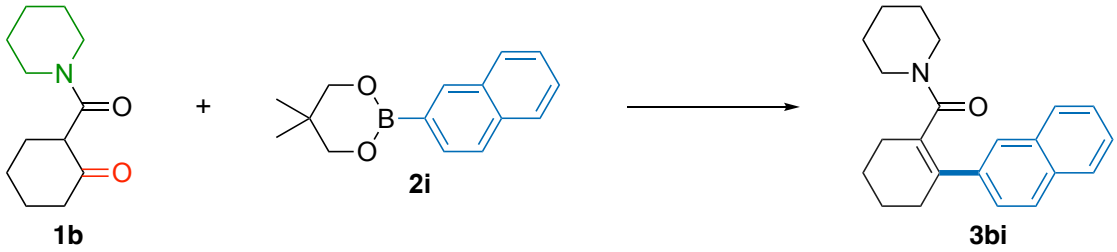
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.60–7.56 (m, 2H), 7.55–7.49 (m, 2H), 7.47–7.36 (m, 4H), 7.36–7.30 (m, 1H), 3.58–3.42 (m, 1H), 3.34–3.20 (m, 1H), 3.19–3.00 (m, 2H), 2.73–2.52 (m, 2H), 2.35–2.19 (m, 1H), 2.17–2.01 (m, 1H), 1.92–1.66 (m, 4H), 1.49–1.09 (m, 5H), 0.76–0.60 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 140.74, 140.72, 139.8, 133.9, 131.3, 128.8 (2C), 127.8 (2C), 127.3, 126.9 (2C), 126.7 (2C), 47.0, 41.8, 29.7, 27.9, 25.8, 25.0, 24.3, 22.7, 22.0.

IR (neat) 1612, 1439, 1283 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{24}H_{28}NO^+$: 346.2165, found: 346.2155.

(2-(Naphthalen-2-yl)cyclohex-1-en-1-yl)(piperidin-1-yl)methanone (3bi)



The general procedure A was followed with use of 5,5-Dimethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborinane (**2i,** 42.1 mg, 0.20 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 144.2 mg, 0.6 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 67:33:1) to give a colorless oil (**3bi**, 49.7 mg, 63%).

R_f 0.22 (eluent: hexane/EtOAc = 2:1).

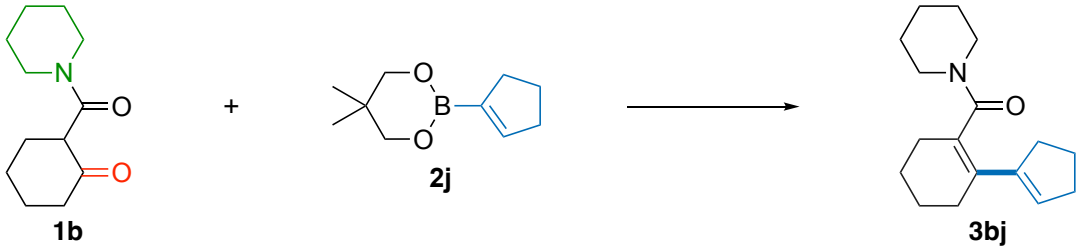
^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.83–7.71 (m, 4H), 7.49–7.38 (m, 3H), 3.39–3.24 (m, 2H), 3.23–3.11 (m, 1H), 3.01–2.88 (m, 1H), 2.78–2.60 (m, 2H), 2.39–2.24 (m, 1H), 2.19–2.07 (m, 1H), 1.93–1.70 (m, 4H), 1.39–1.25 (m, 2H), 1.21–1.10 (m, 2H), 1.08–0.96 (m, 1H), 0.68–0.54 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 134.3, 133.2, 132.5, 131.6, 128.2, 128.1, 127.5, 126.02, 125.98, 125.8, 125.7, 47.0, 41.7, 29.9, 28.0, 25.9, 25.0, 24.2, 22.8, 22.1.

IR (neat) 3854, 2933, 1614, 1442, 1265 cm^{-1}.

HRMS (ESI) *m/z* ($[M+Na]^+$) calcd for $C_{22}H_{25}NNaO^+$: 342.1828, found: 342.1838.

(2-(Cyclopent-1-en-1-yl)cyclohex-1-en-1-yl)(piperidin-1-yl)methanone (3bj)



The general procedure A was followed with use of 2-(cyclopent-1-en-1-yl)-5,5-dimethyl-1,3,2-dioxaborinane (**2j**, 109.2 mg, 0.61 mmol) and 2-(1-piperidinylcarbonyl)cyclohexan-1-one (**1b**, 42.0 mg, 0.20 mmol). The reaction was conducted for 20 h. The crude product was purified by flash column chromatography on silica gel (eluent: hexane/EtOAc/NEt_3 = 67:33:1) to give a yellow oil (**3bj**, 17.0 mg, 33%).

R_f 0.24 (eluent: hexane/EtOAc = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 5.76 (s, 1H), 3.71–3.66 (m, 1H), 3.44–3.35 (m, 2H), 3.27–3.21 (m, 1H), 2.44–2.37 (m, 3H), 2.36–2.28 (m, 3H), 2.25–2.16 (m, 2H), 2.04–1.99 (m, 1H), 1.87–1.78 (m, 2H), 1.67–1.58 (m, 4H), 1.56–1.43 (m, 5H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.3, 143.0, 130.5, 129.4, 128.3, 47.3, 41.7, 33.6, 32.5, 28.3, 27.8, 26.3, 25.3, 24.6, 23,7, 22.4, 22.1.

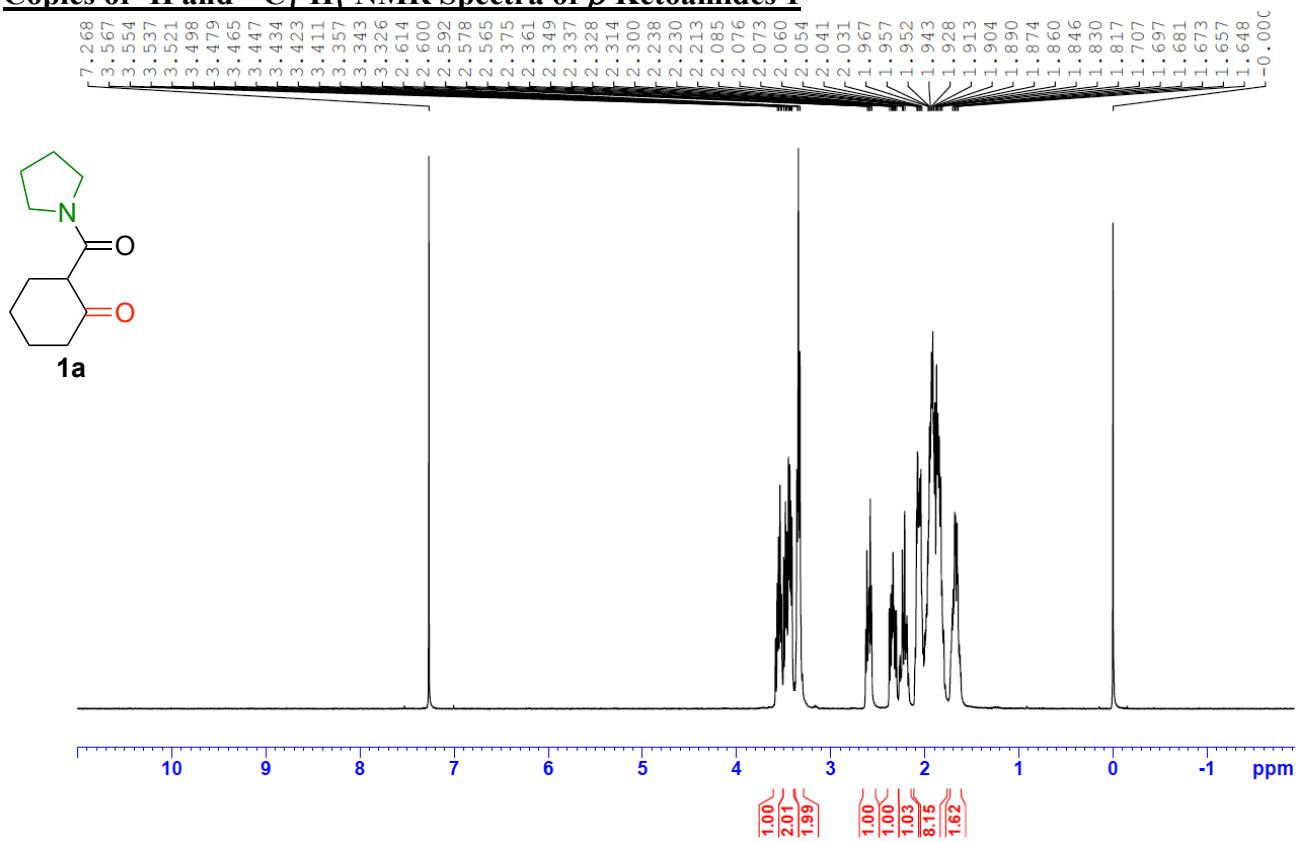
IR (neat) 1612, 1437, 1281 cm^{-1}.

HRMS (APCI) *m/z* ($[M+H]^+$) calcd for $C_{17}H_{26}NO^+$: 260.2009, found: 260.2014.

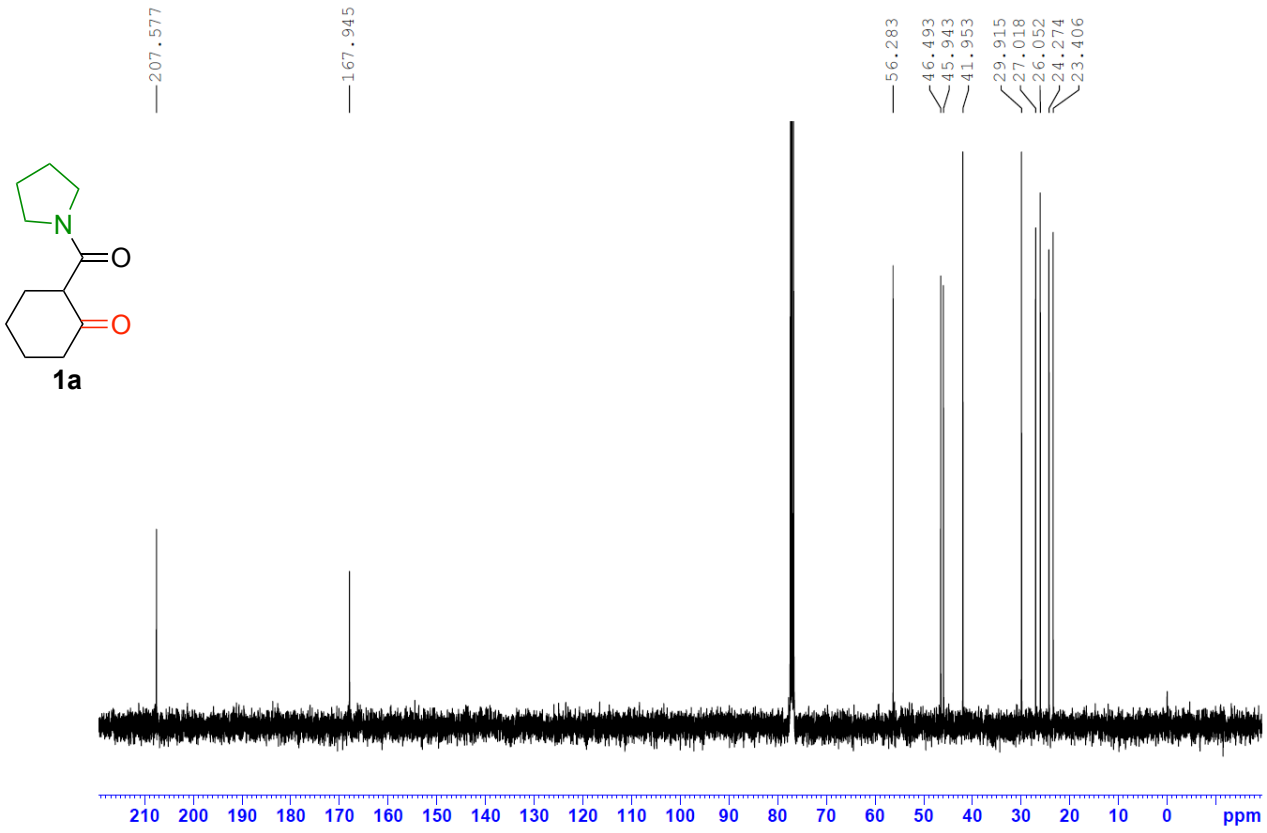
References

1. Y. Kogure and S. Ueno, *Org. Lett.*, 2022, **24**, 9233–9237.
2. P. Langer, E. Holtz and N. N. Saleh, *Chem. Eur. J.*, 2002, **8**, 917–928.
3. K. Dechira, A. Taleb, A. Benmaati, S. Hacini and H. Habib Zahmani, *Orient. J. Chem.*, 2018, **34**, 152–160.
4. D. Steinhuebel, Y. Sun, K. Matsumura, N. Sayo and T. Saito, *J. Am. Chem. Soc.*, 2009, **131**, 11316–11317.

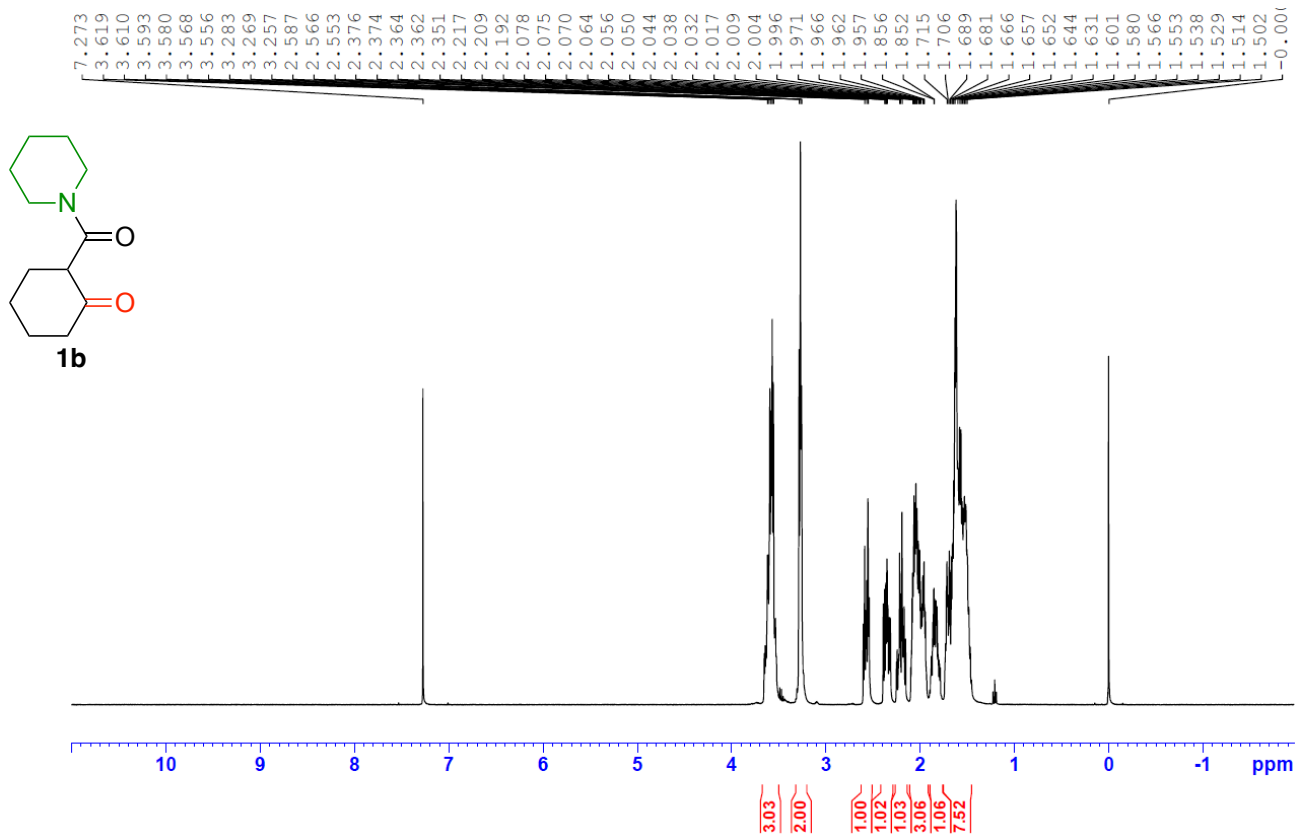
Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of *β*-Ketoamides 1



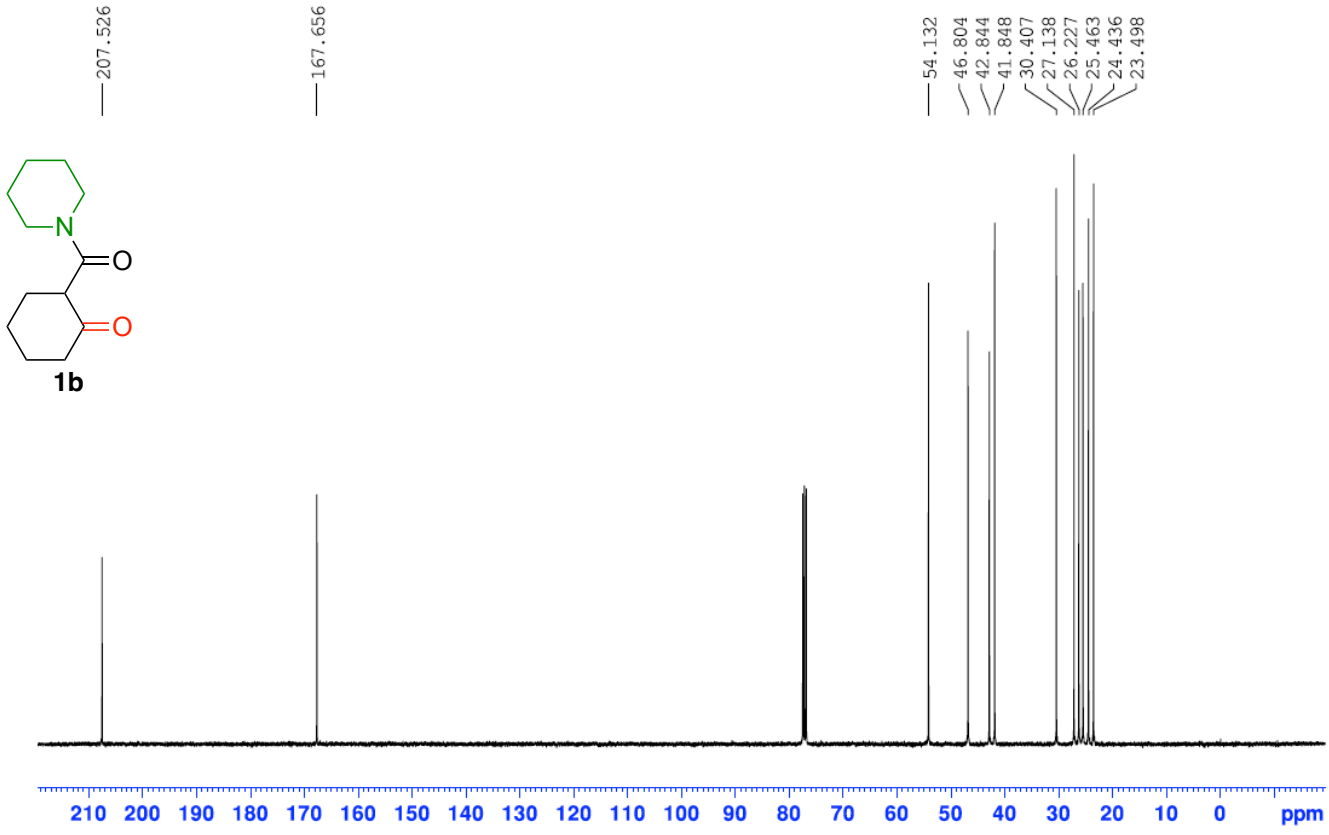
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1a**



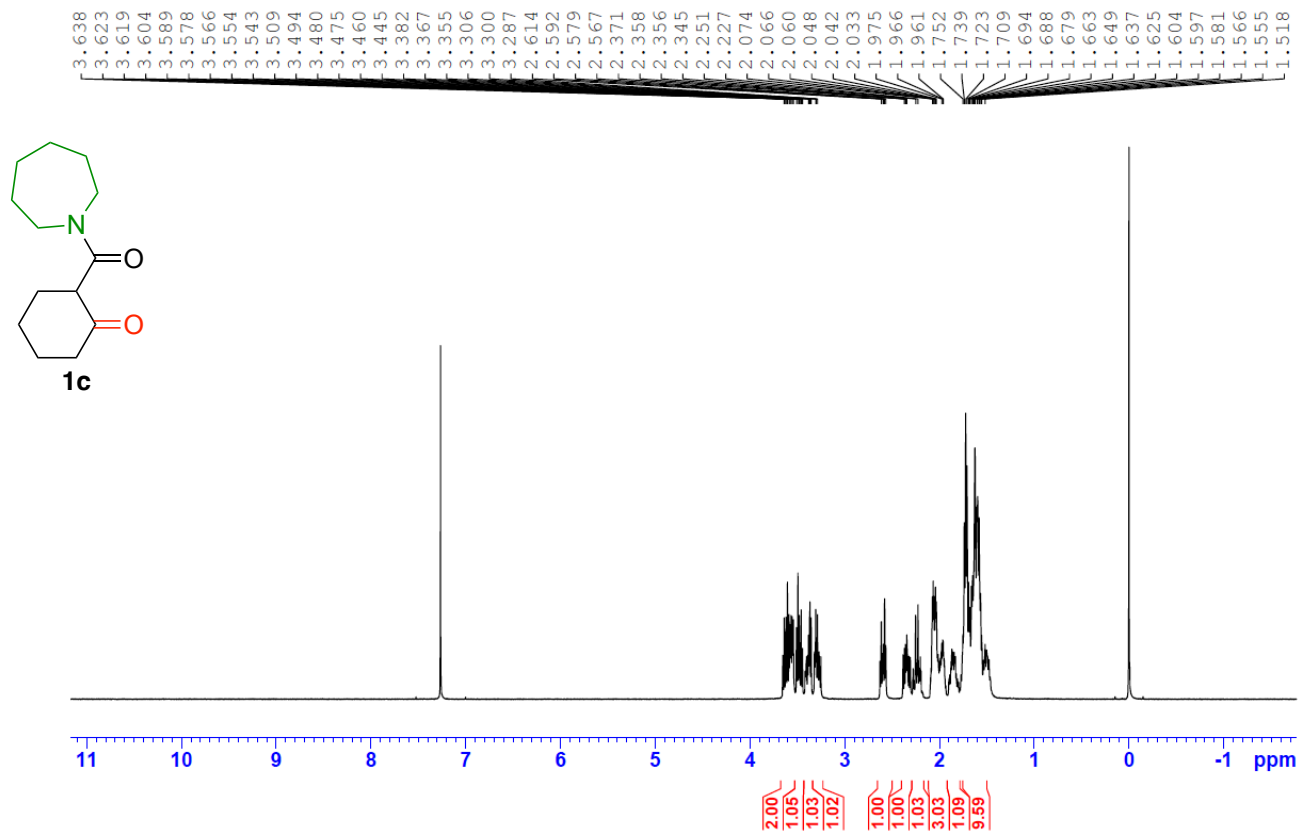
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **1a**



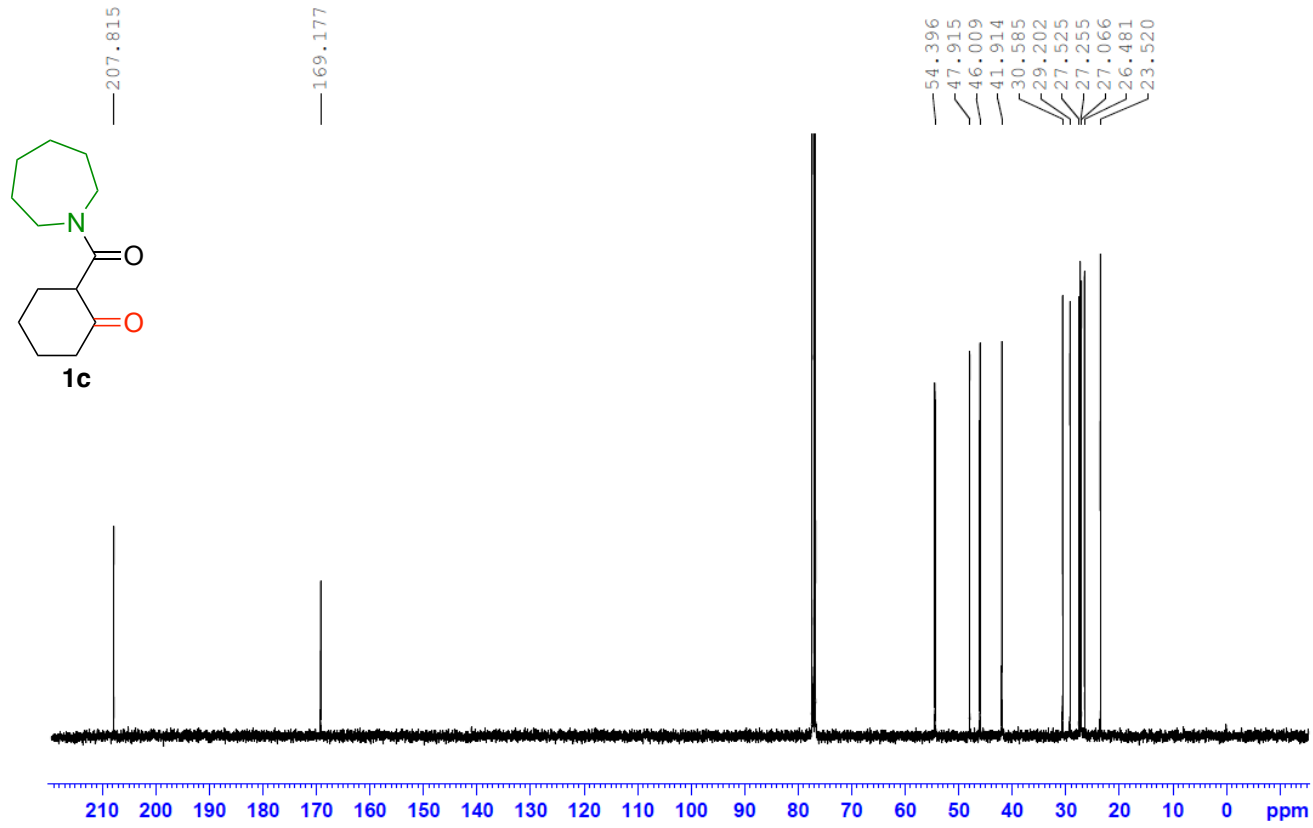
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1b**



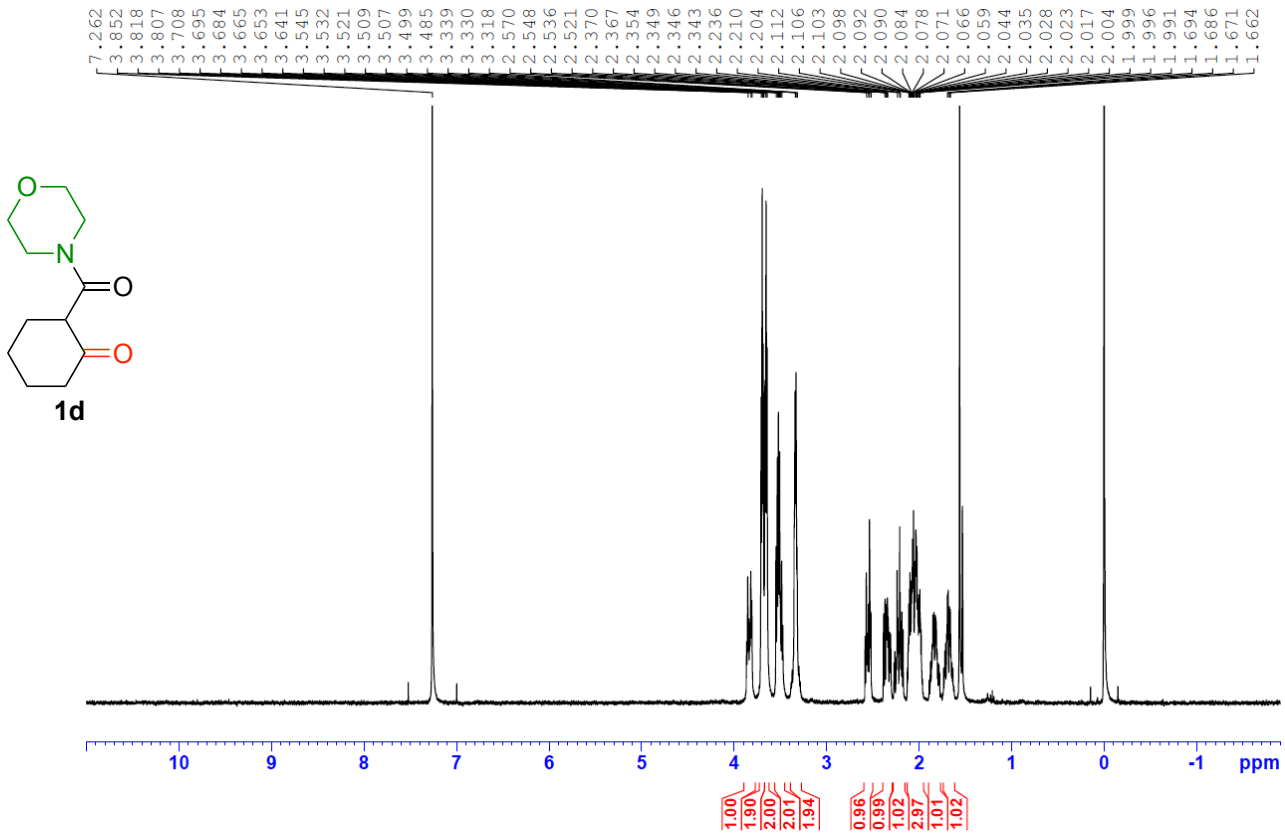
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1b**



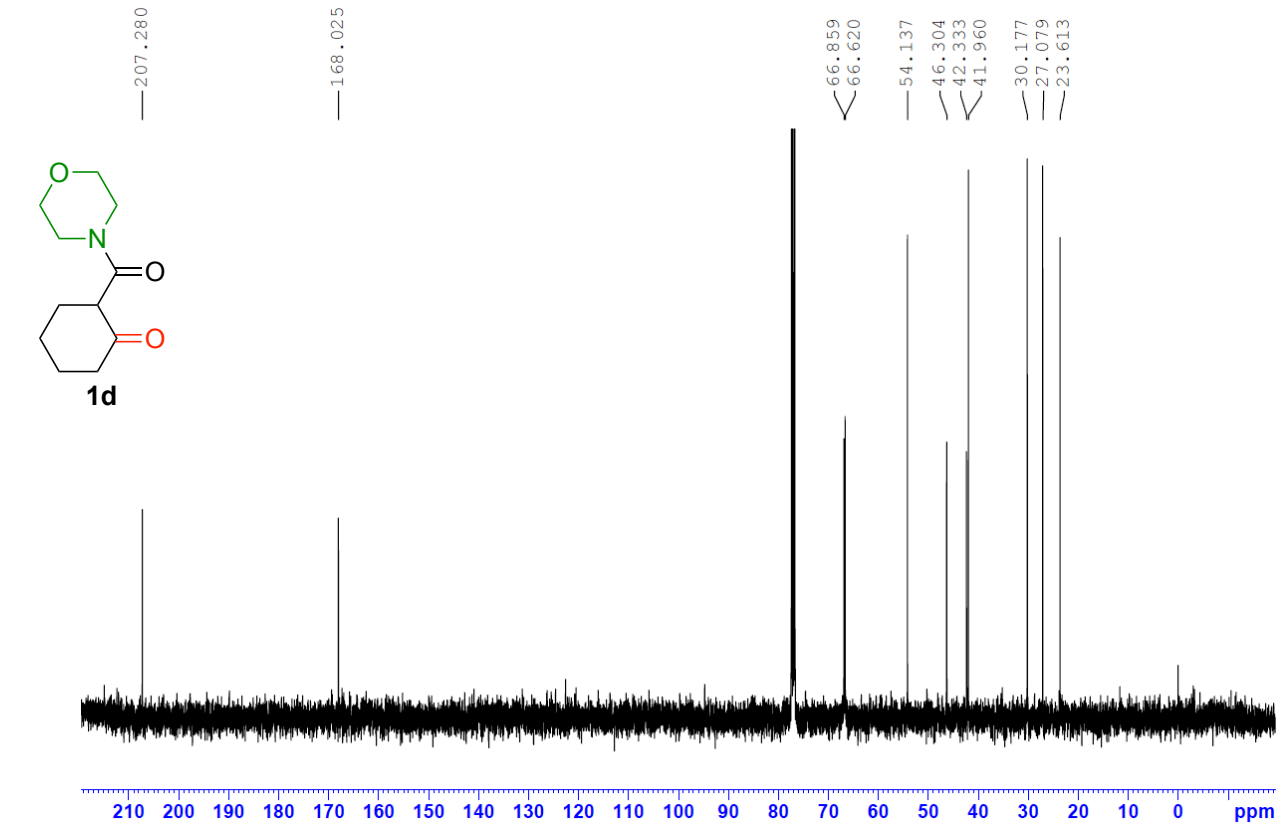
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1c**



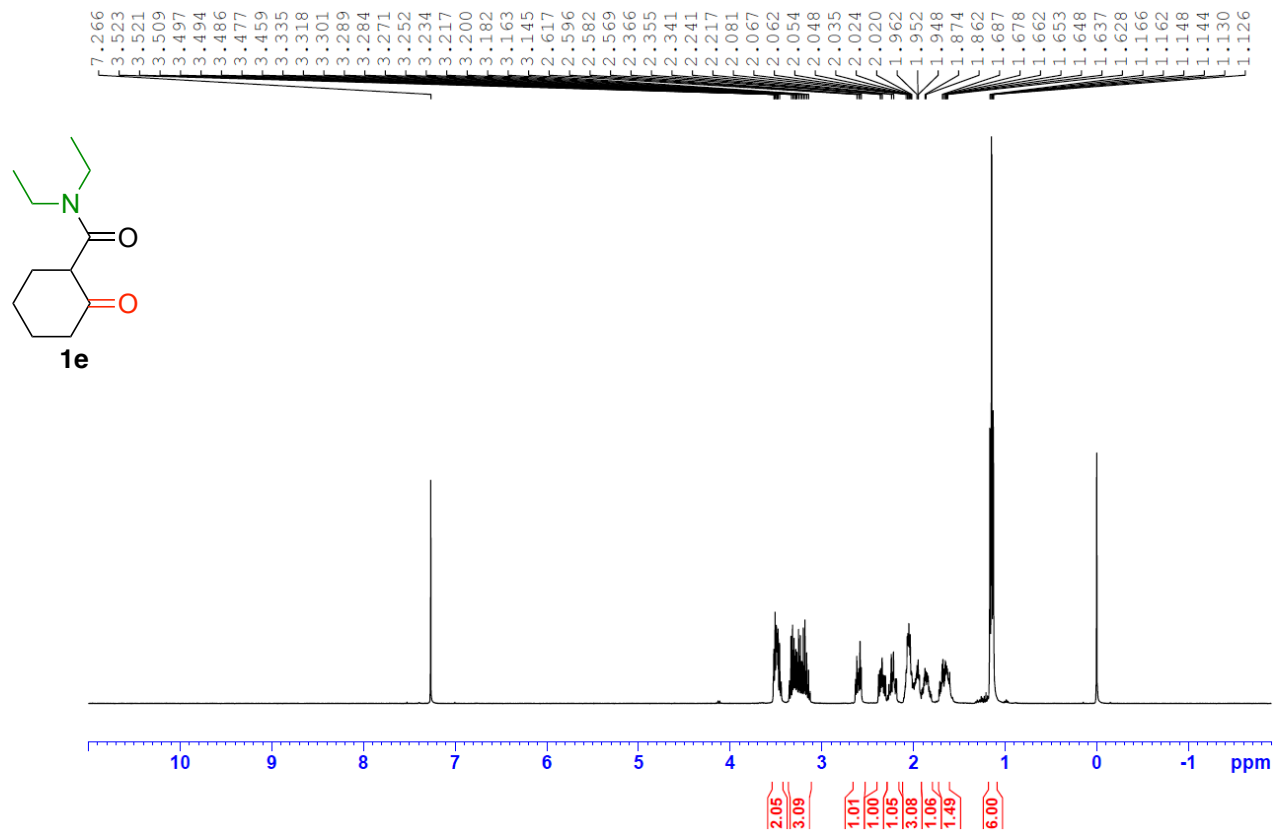
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1c**



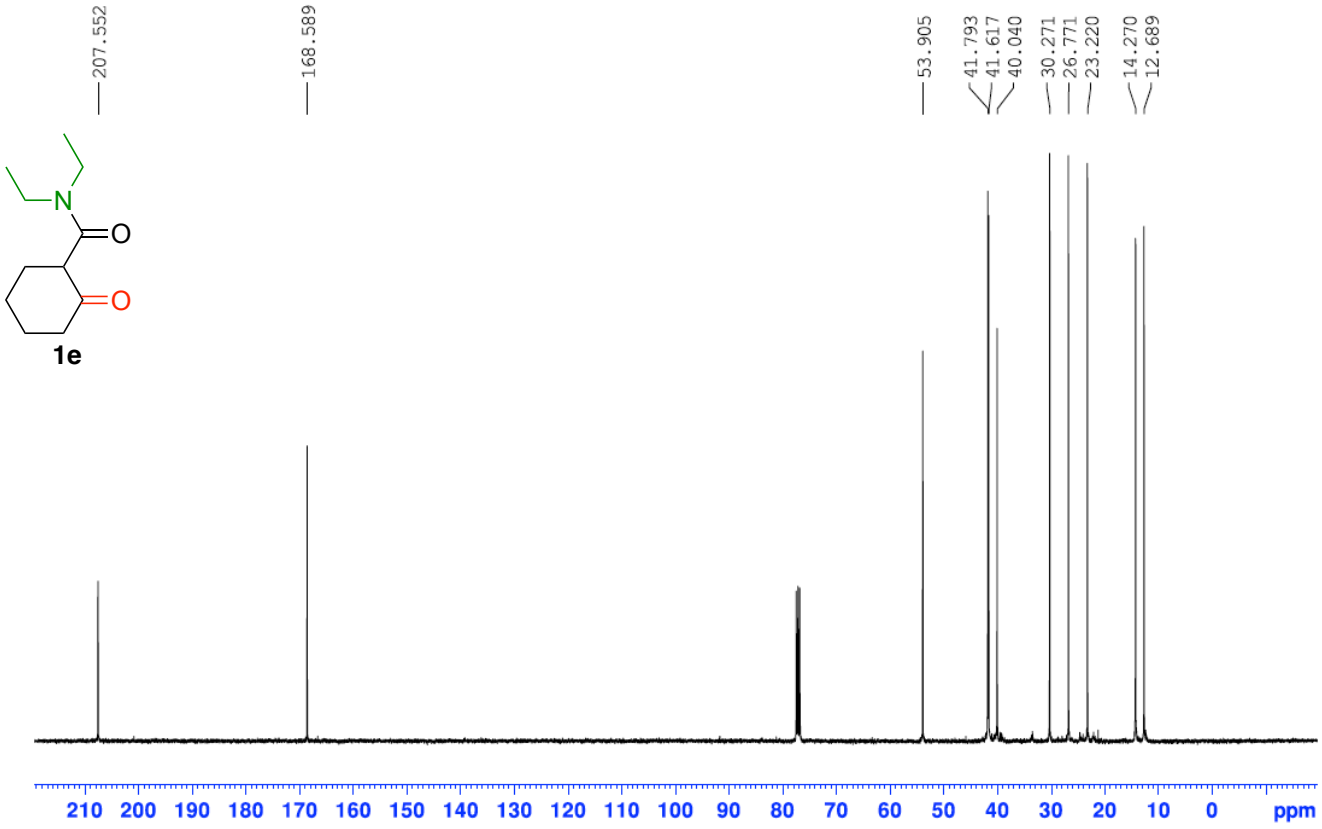
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1d**



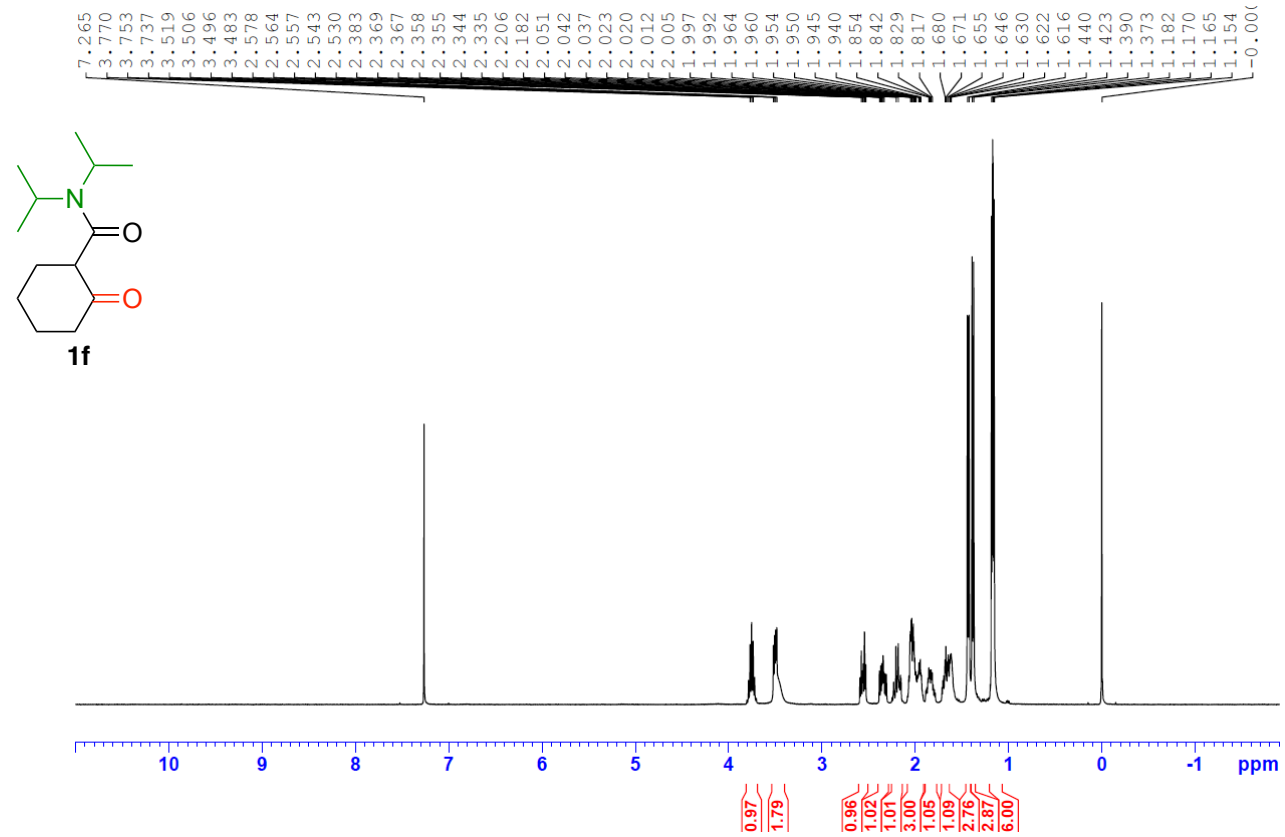
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1d**



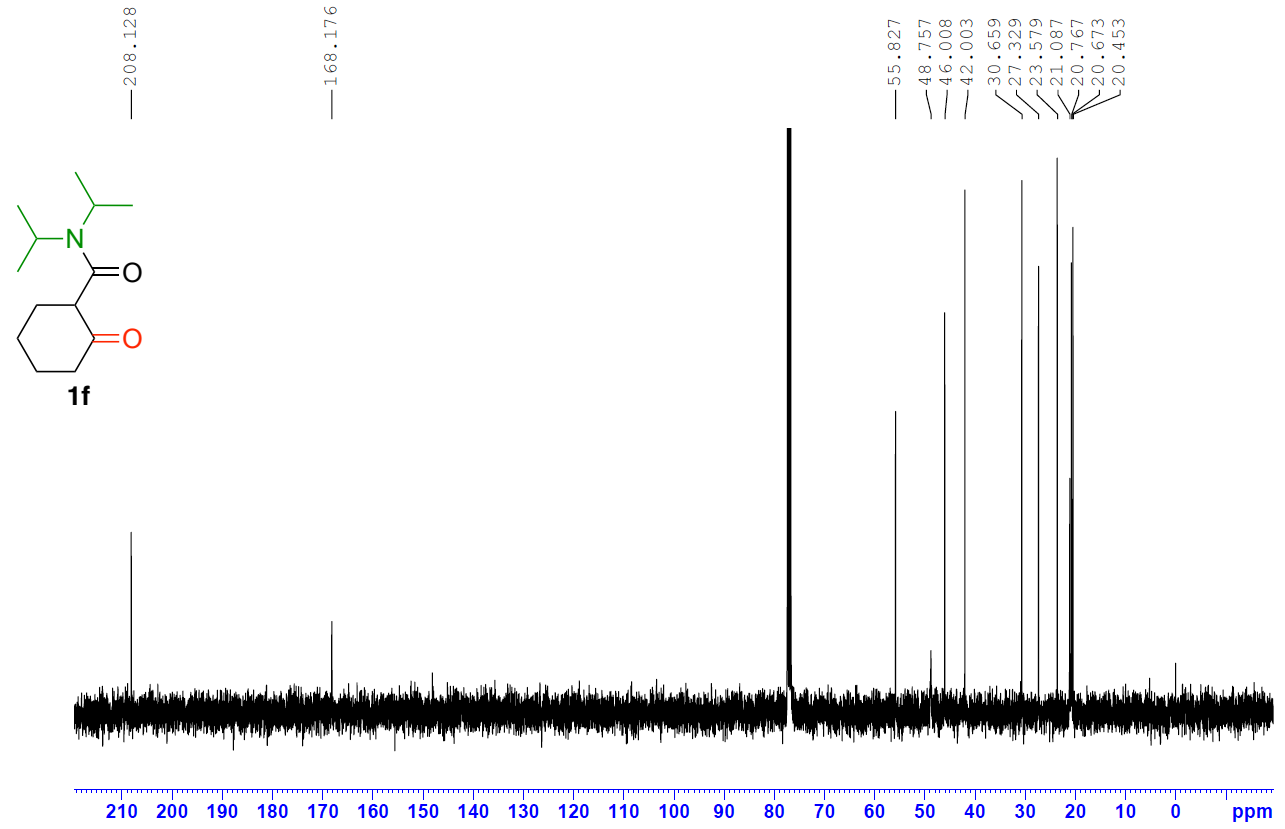
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1e**



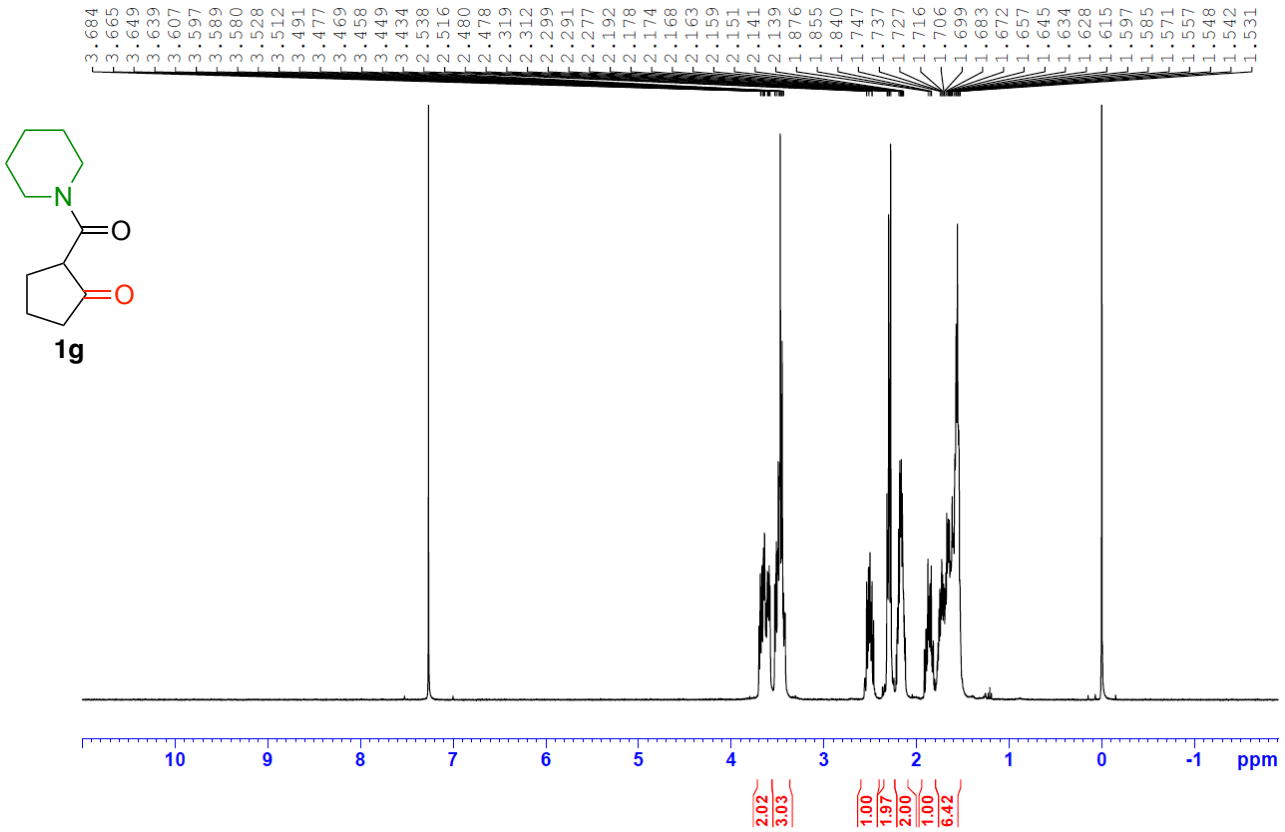
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1e**



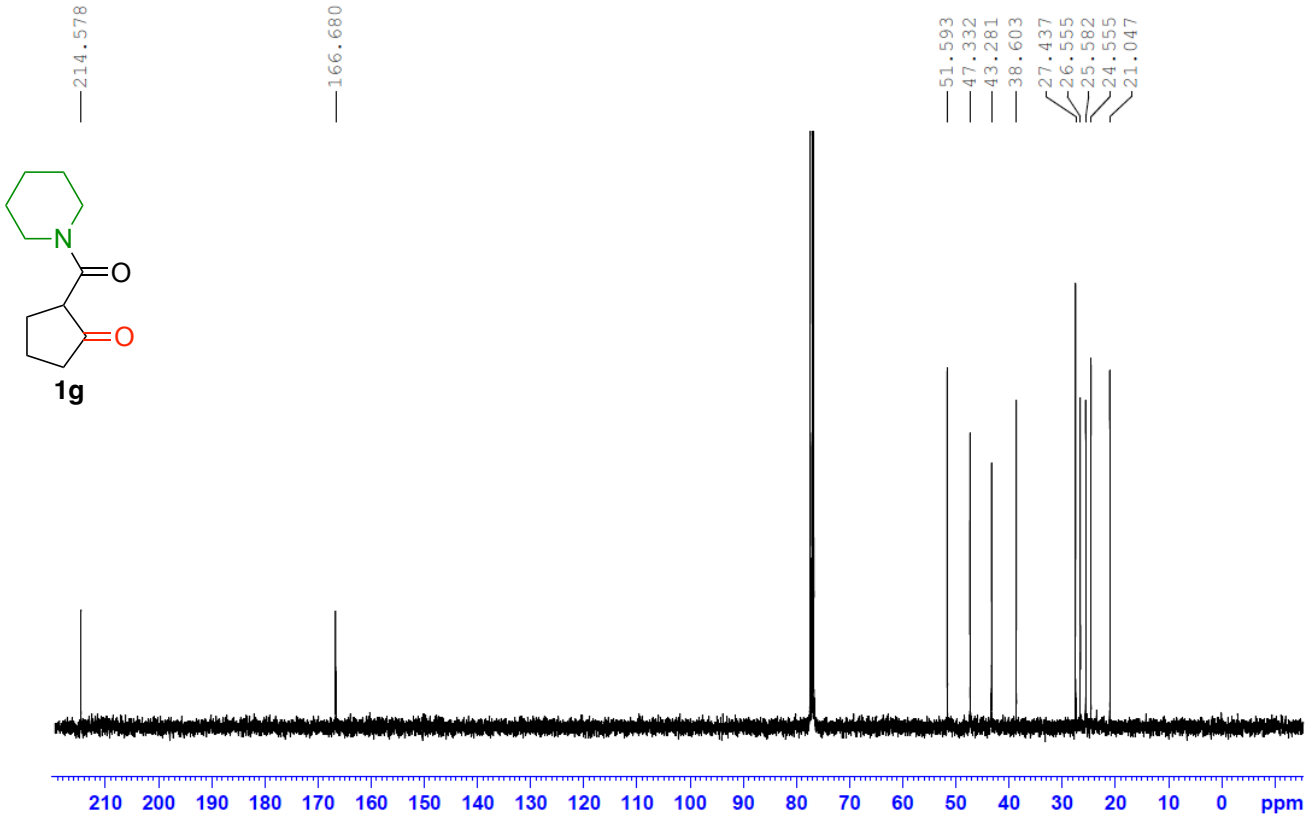
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1f**



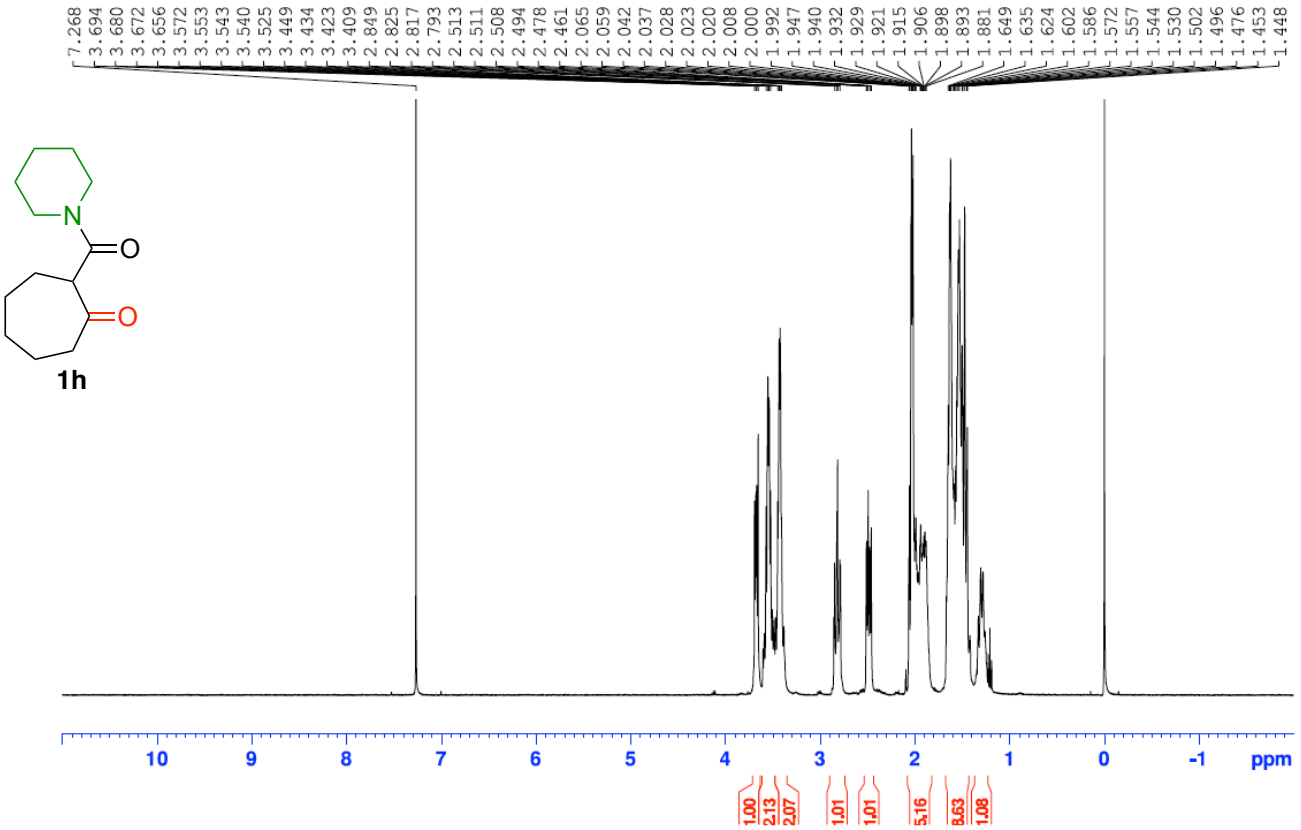
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1f**



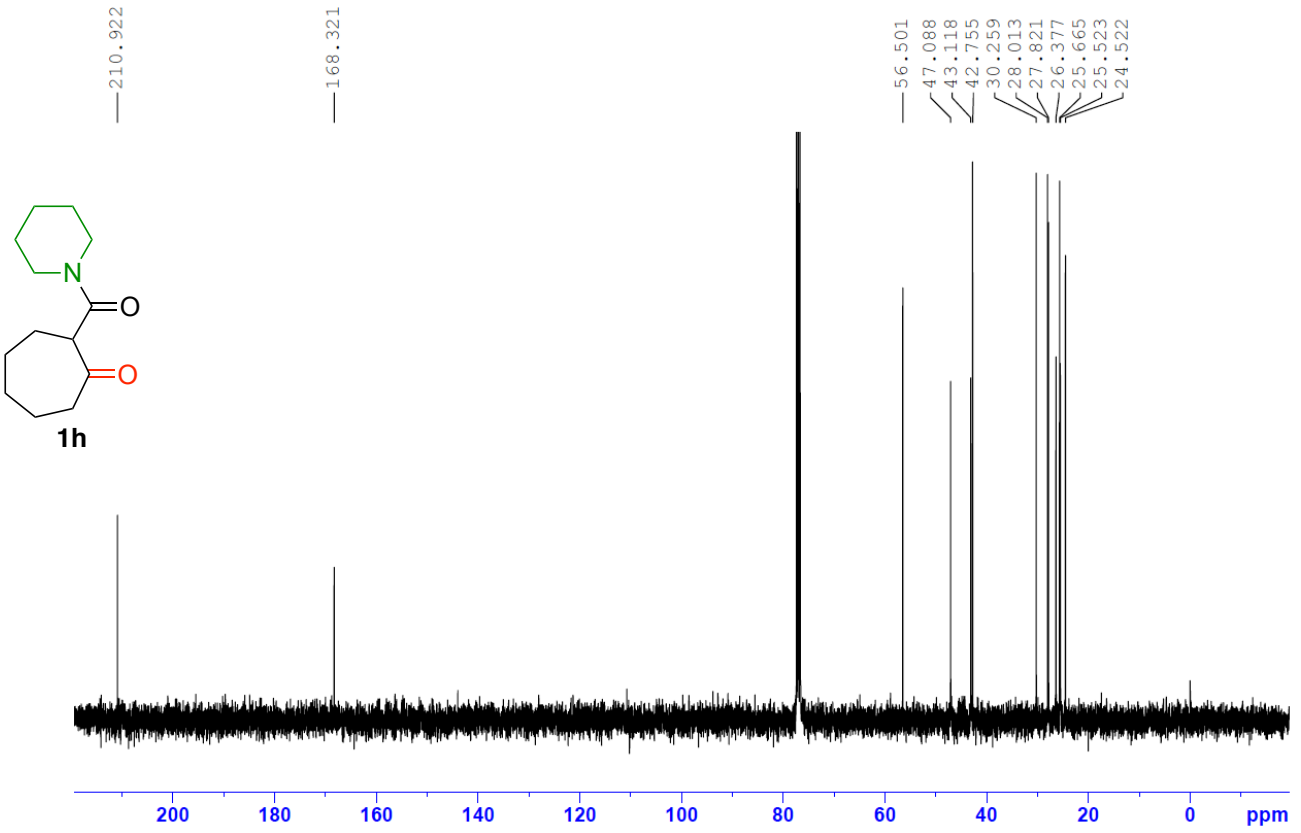
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1g**



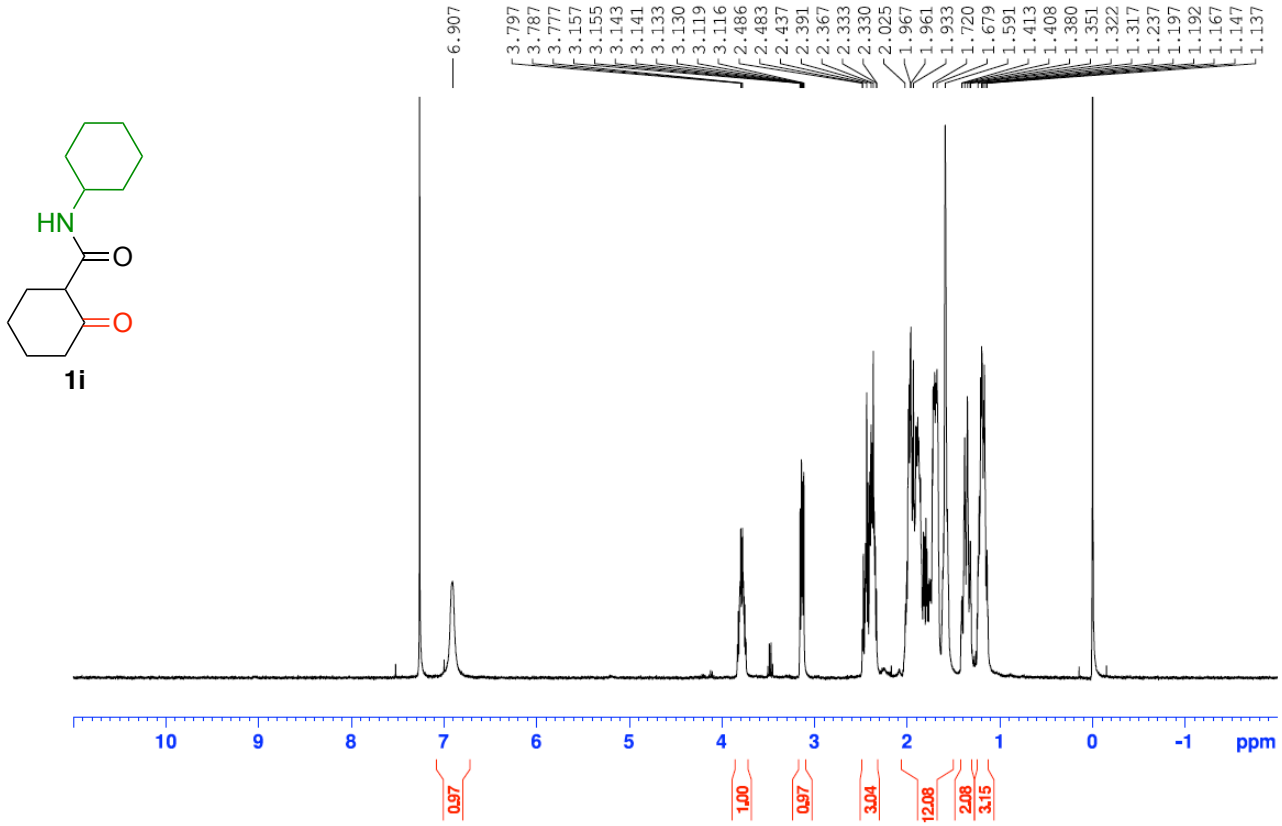
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1g**



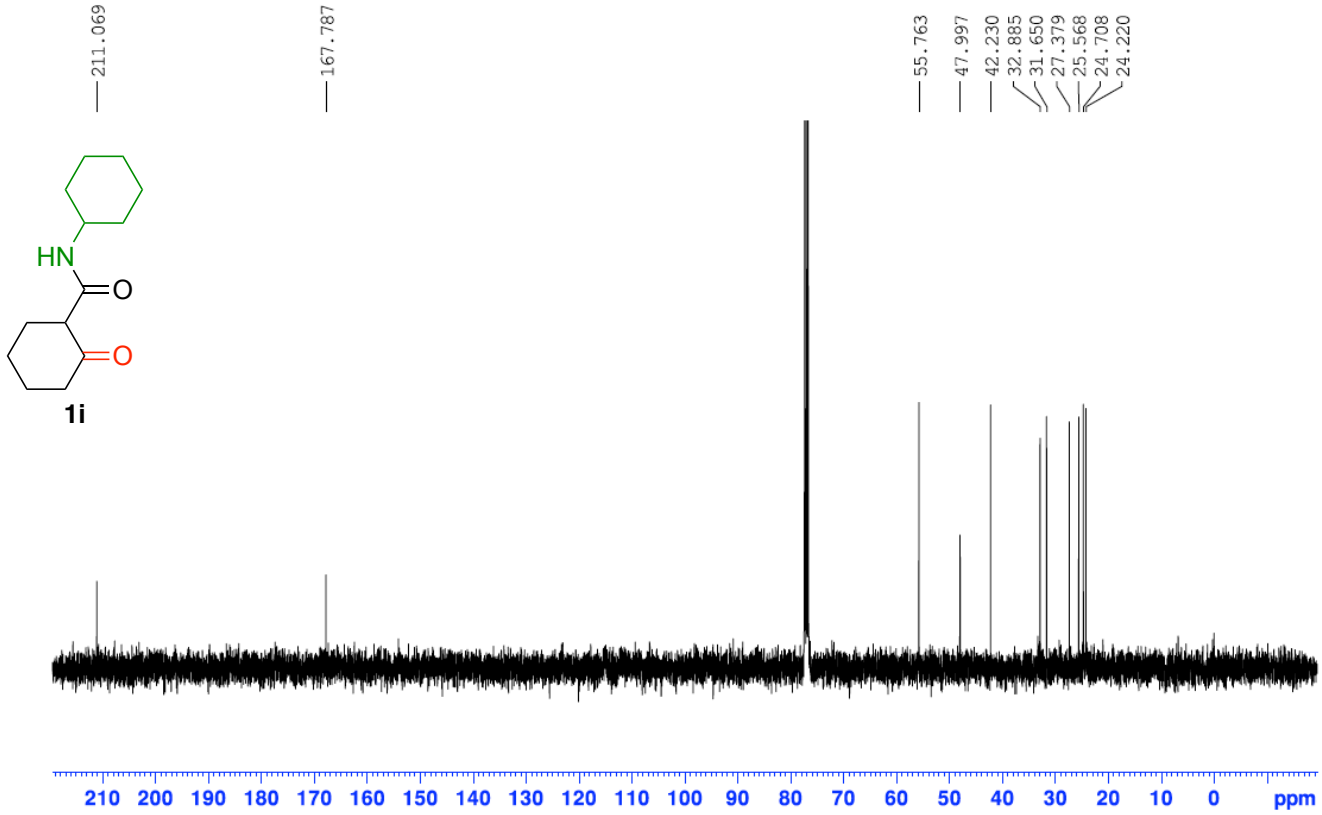
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1h**



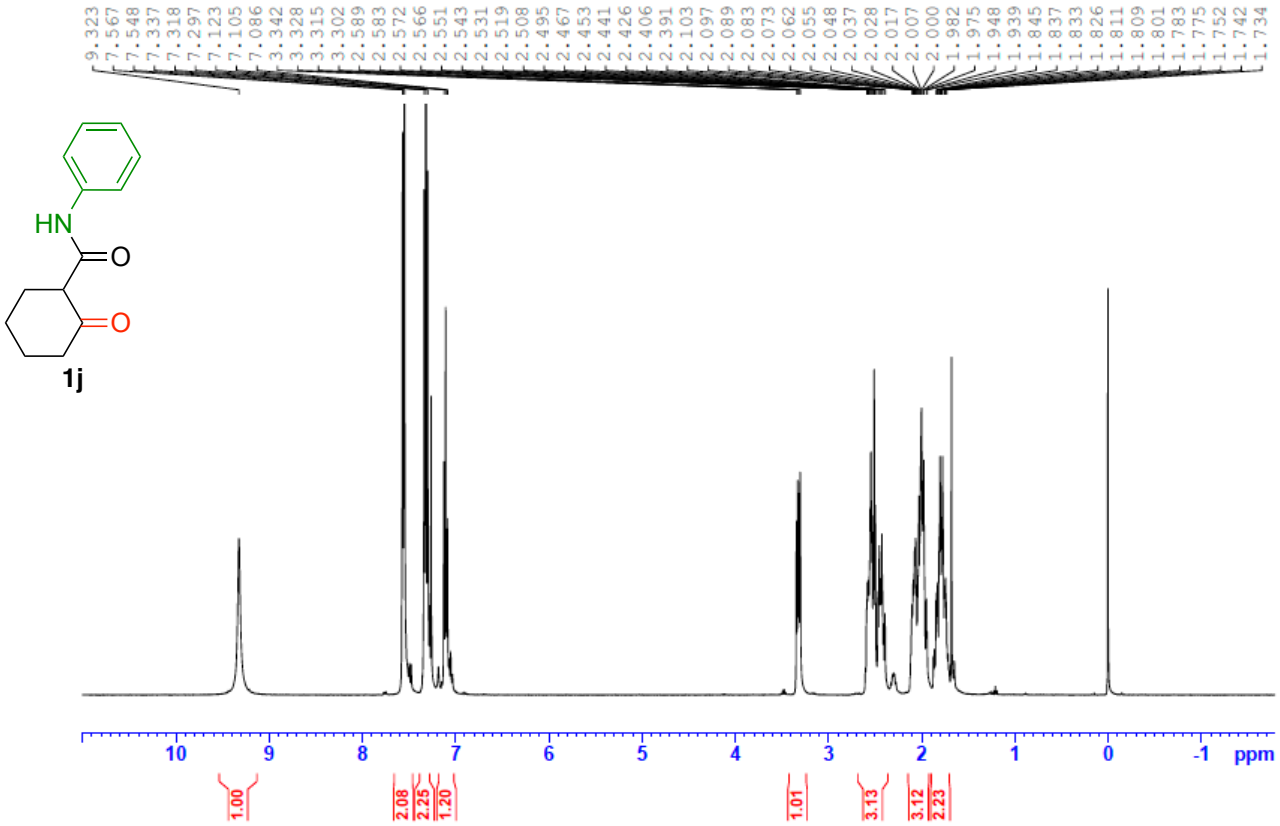
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1h**



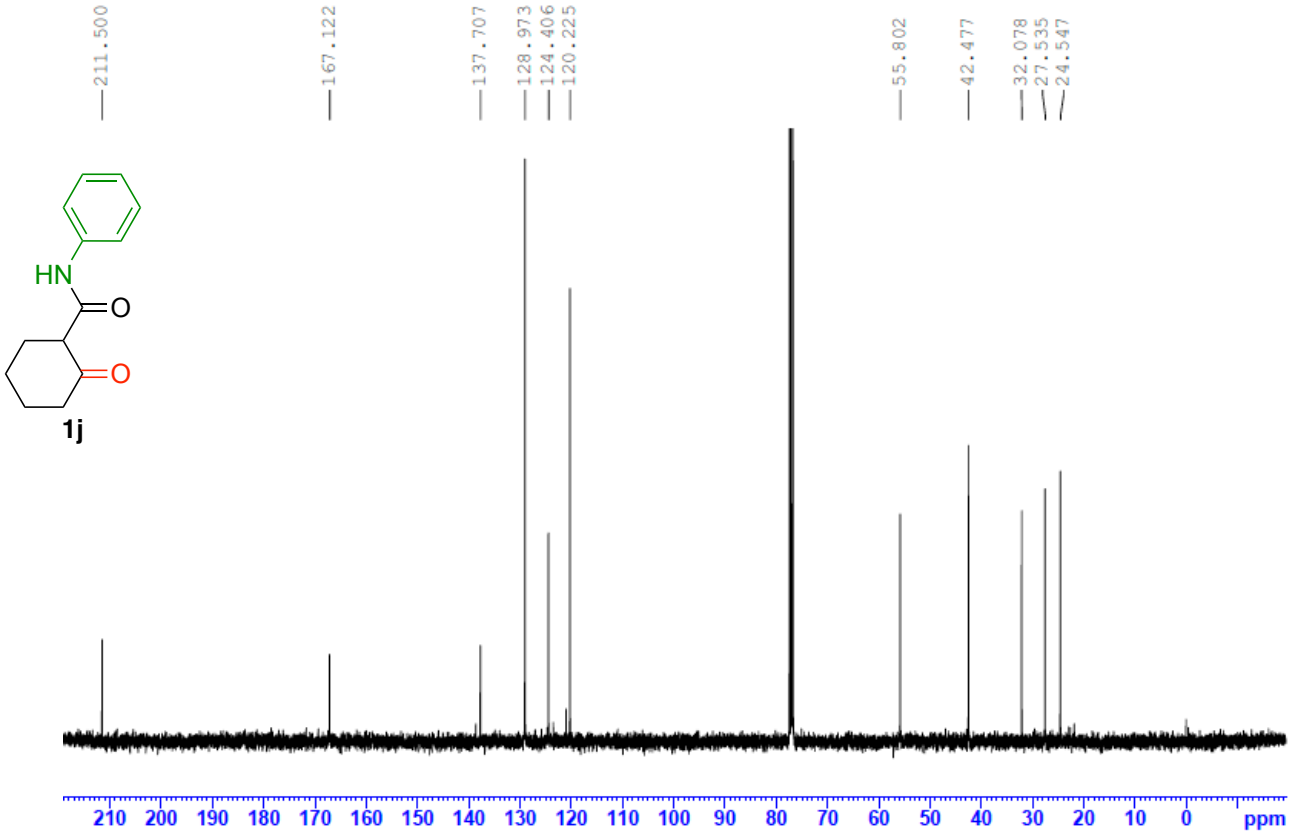
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1i**



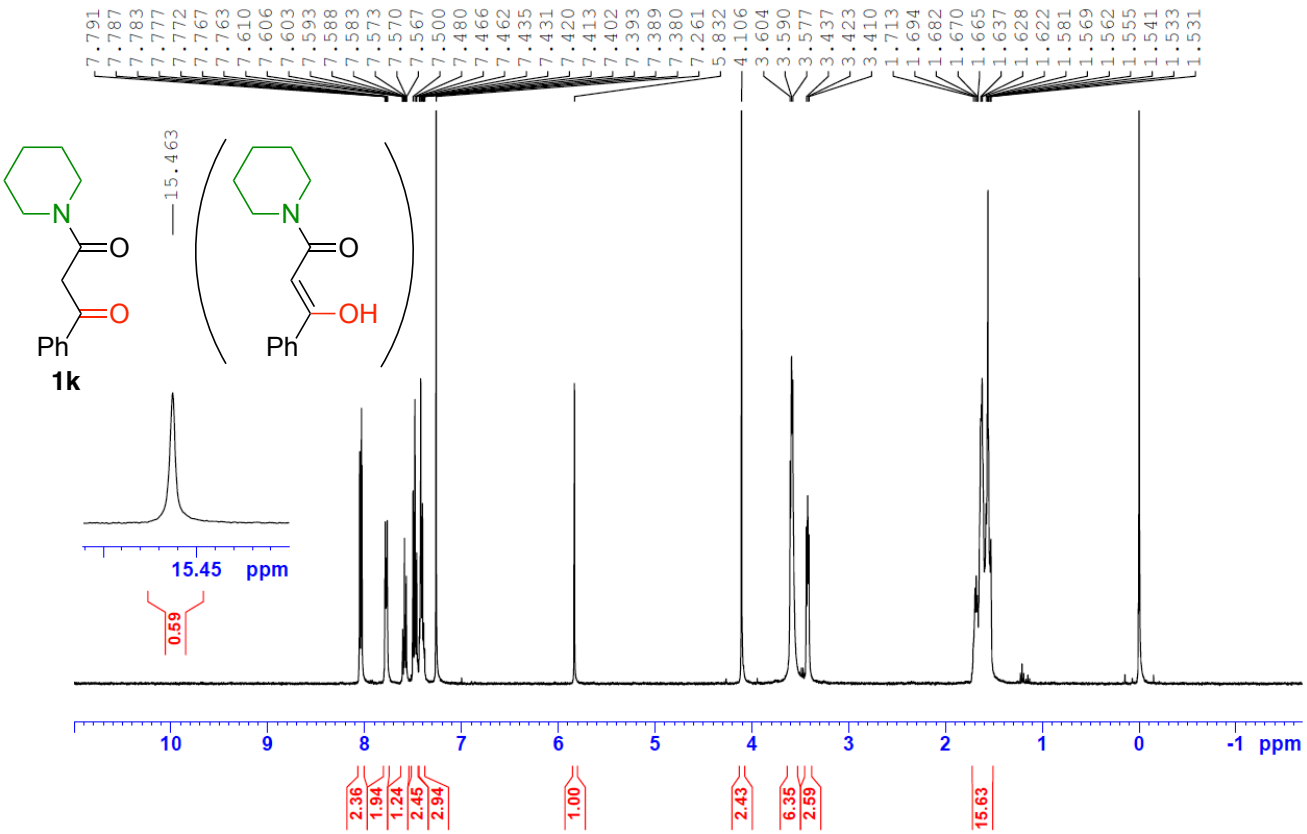
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1i**



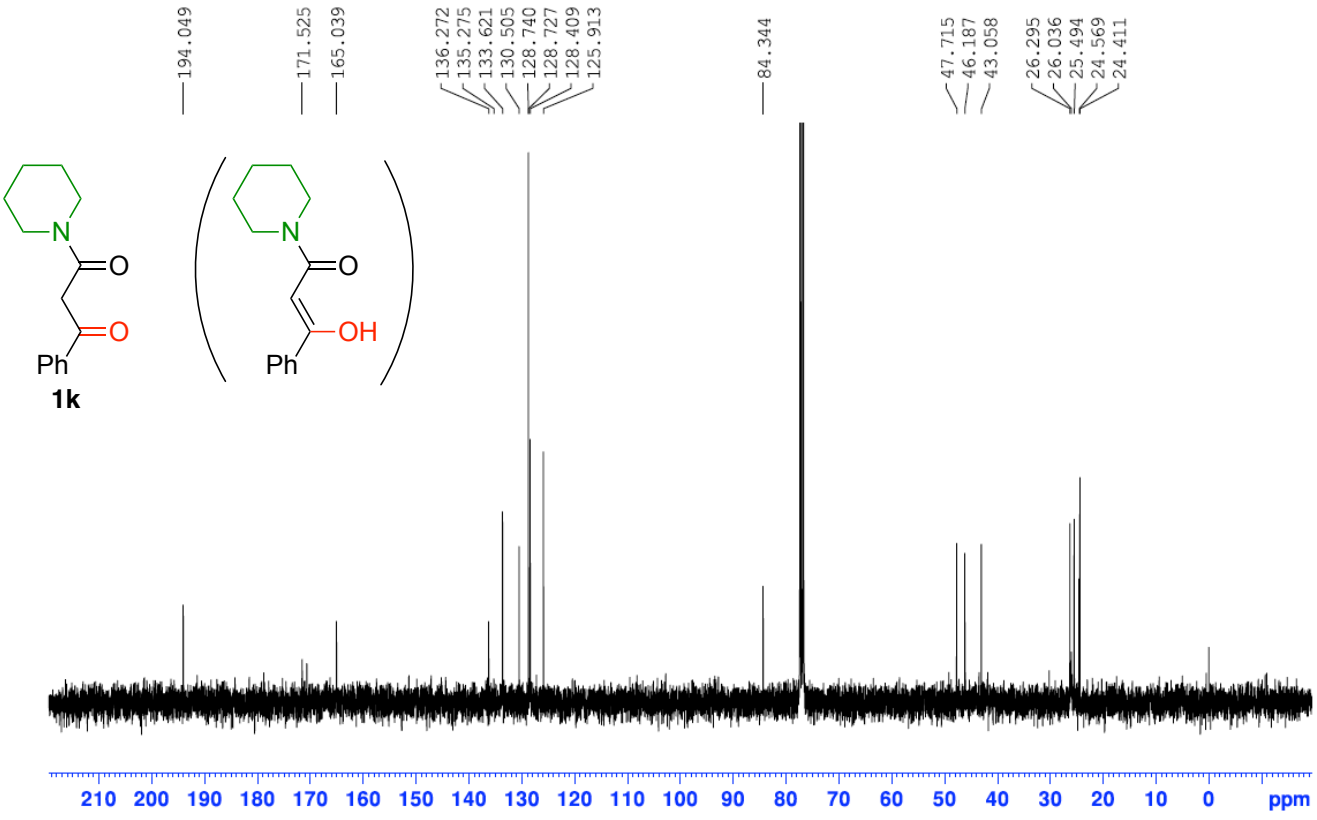
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1j**



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1j**

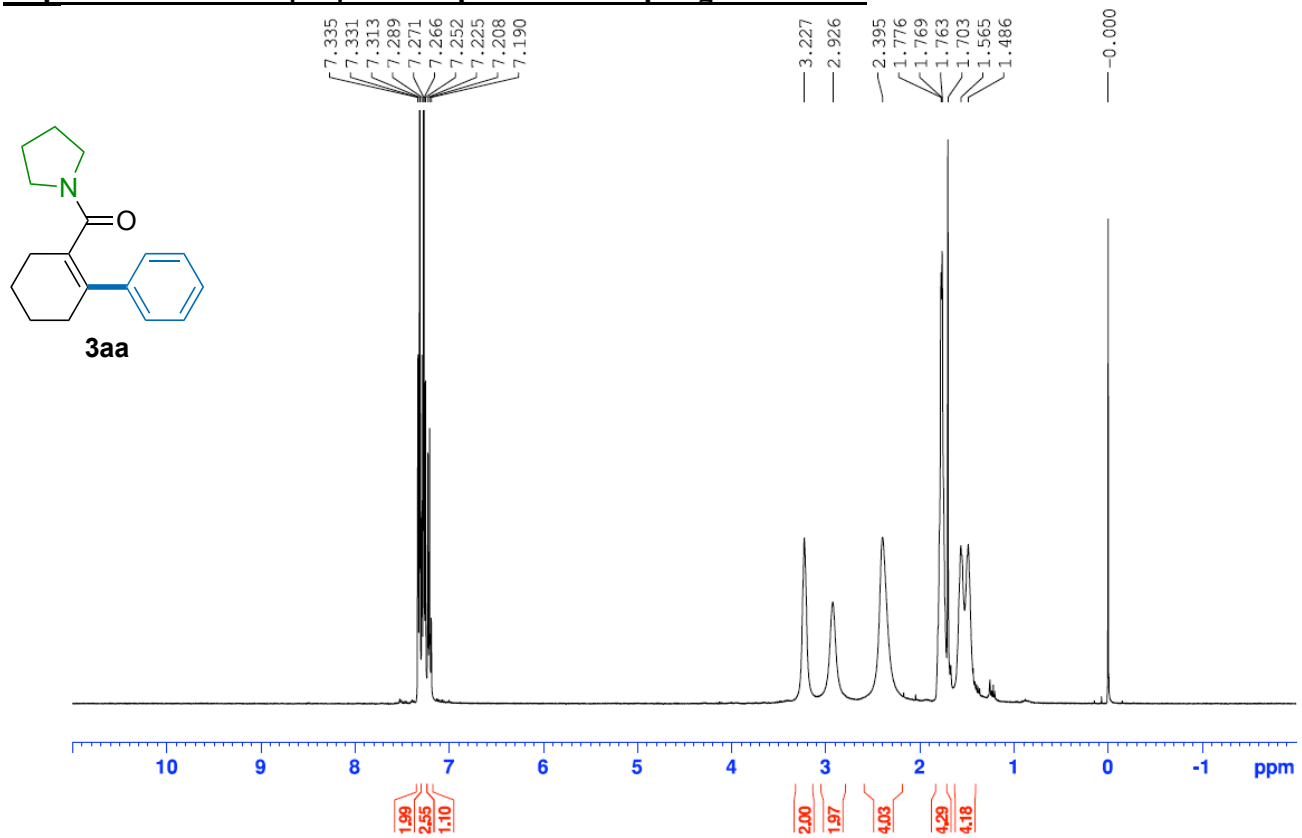


^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **1k**

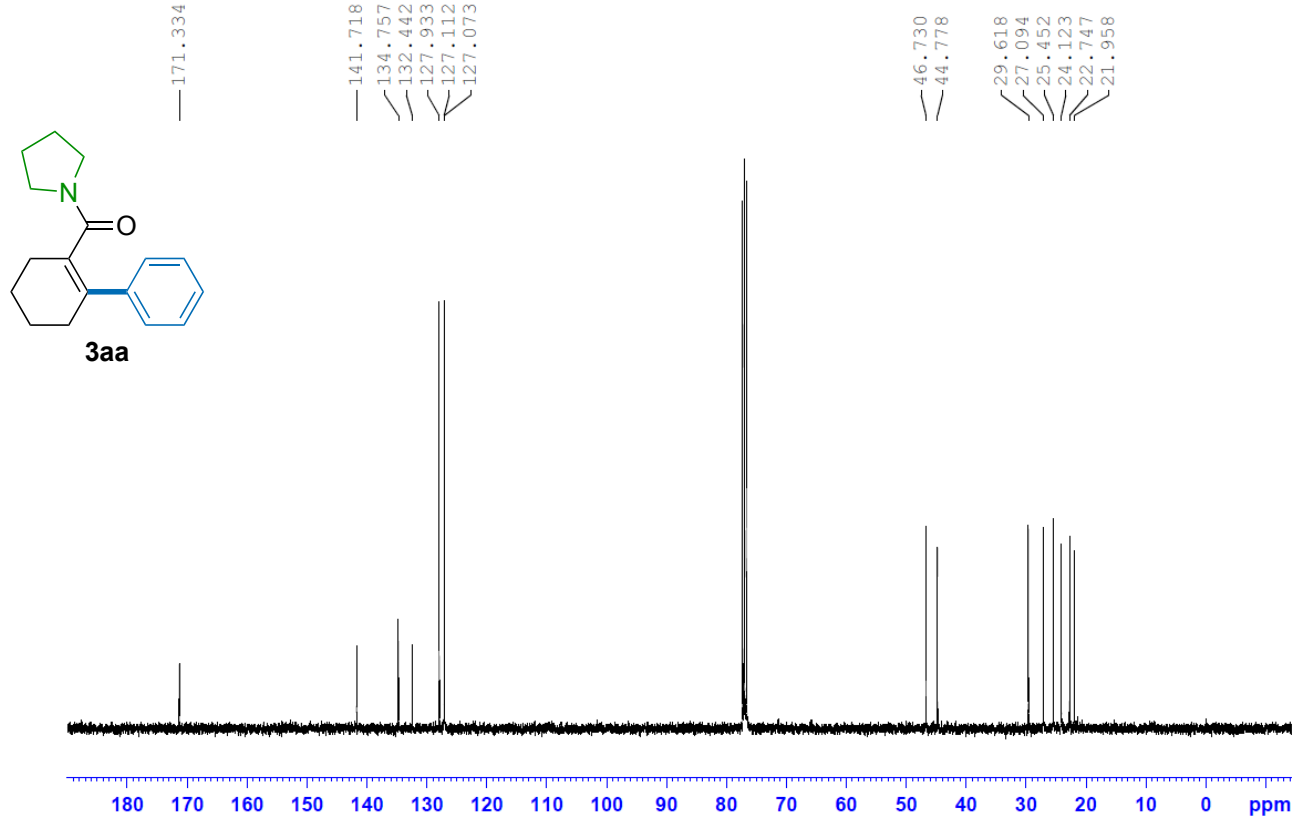


^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **1k**

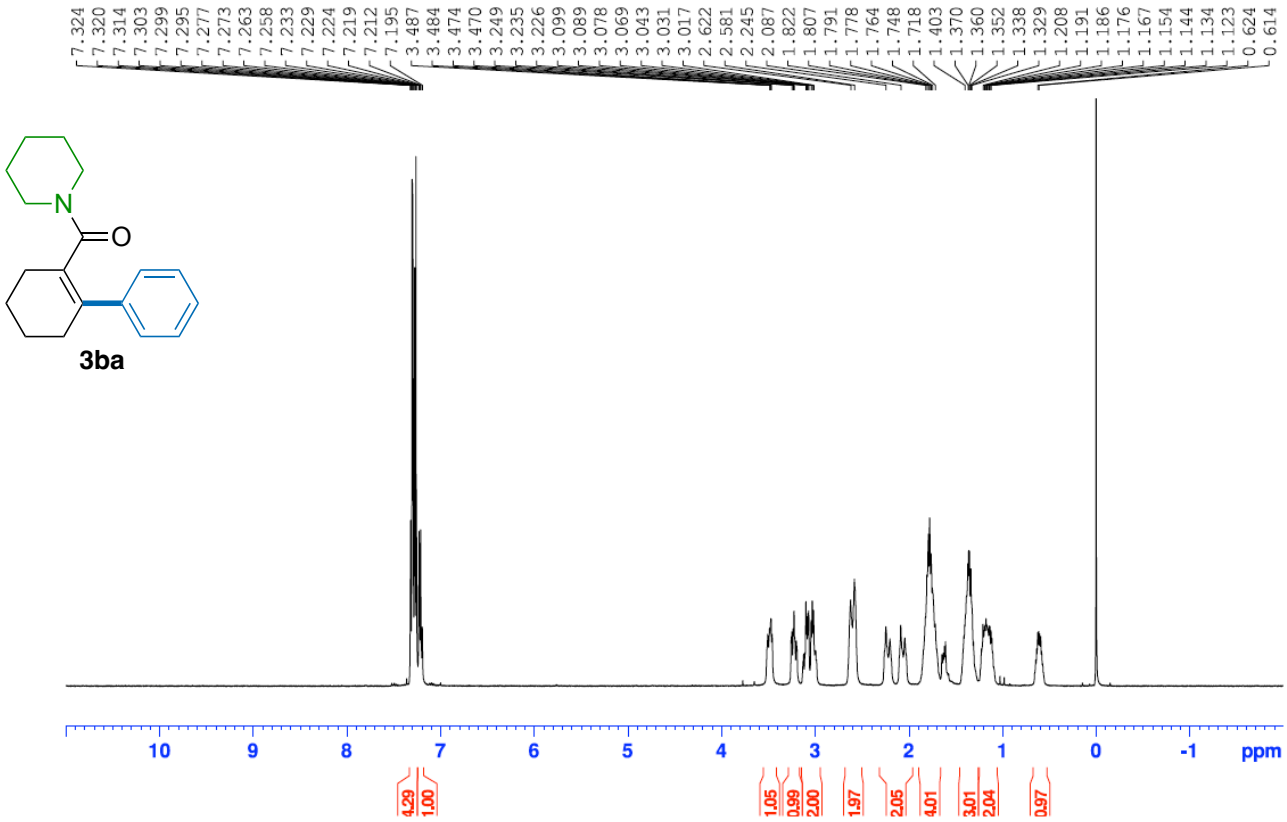
Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra of Coupling Products 3



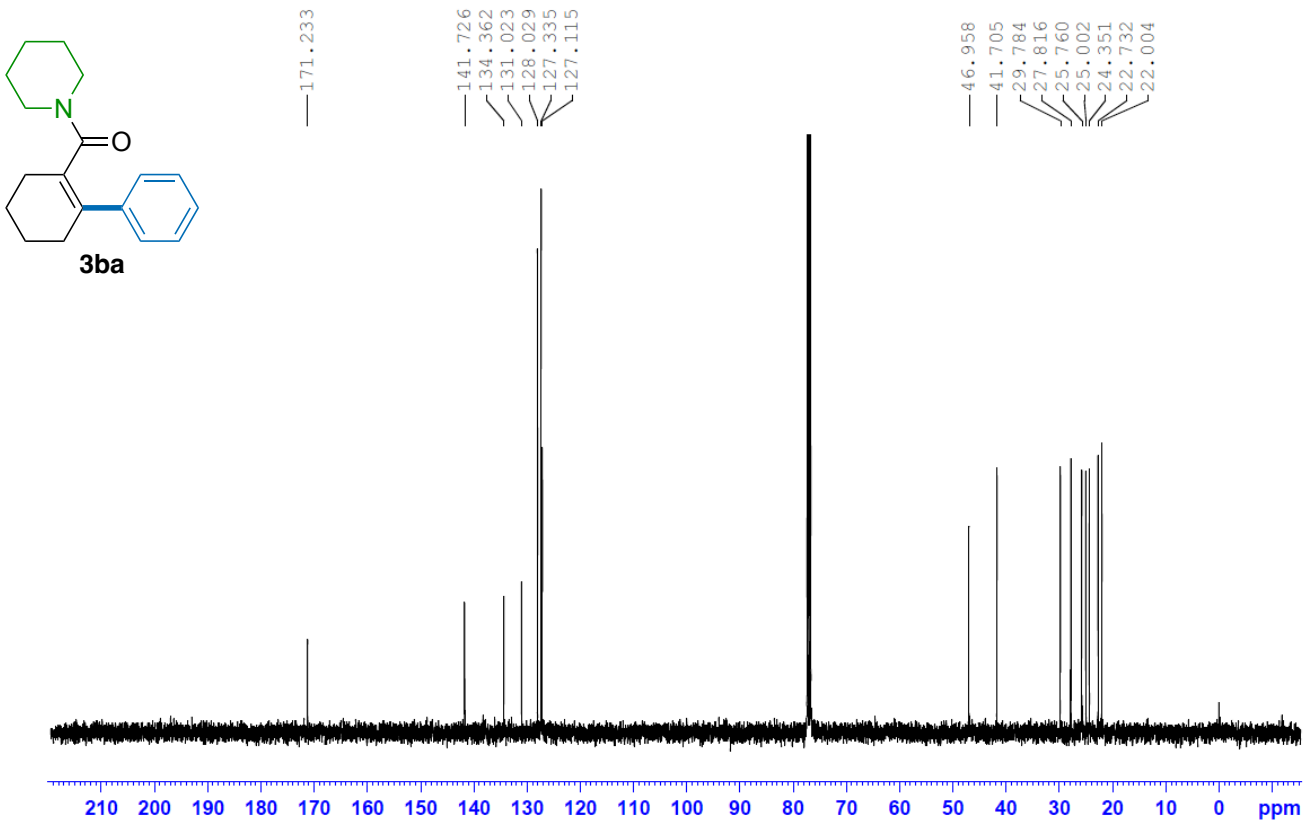
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3aa**



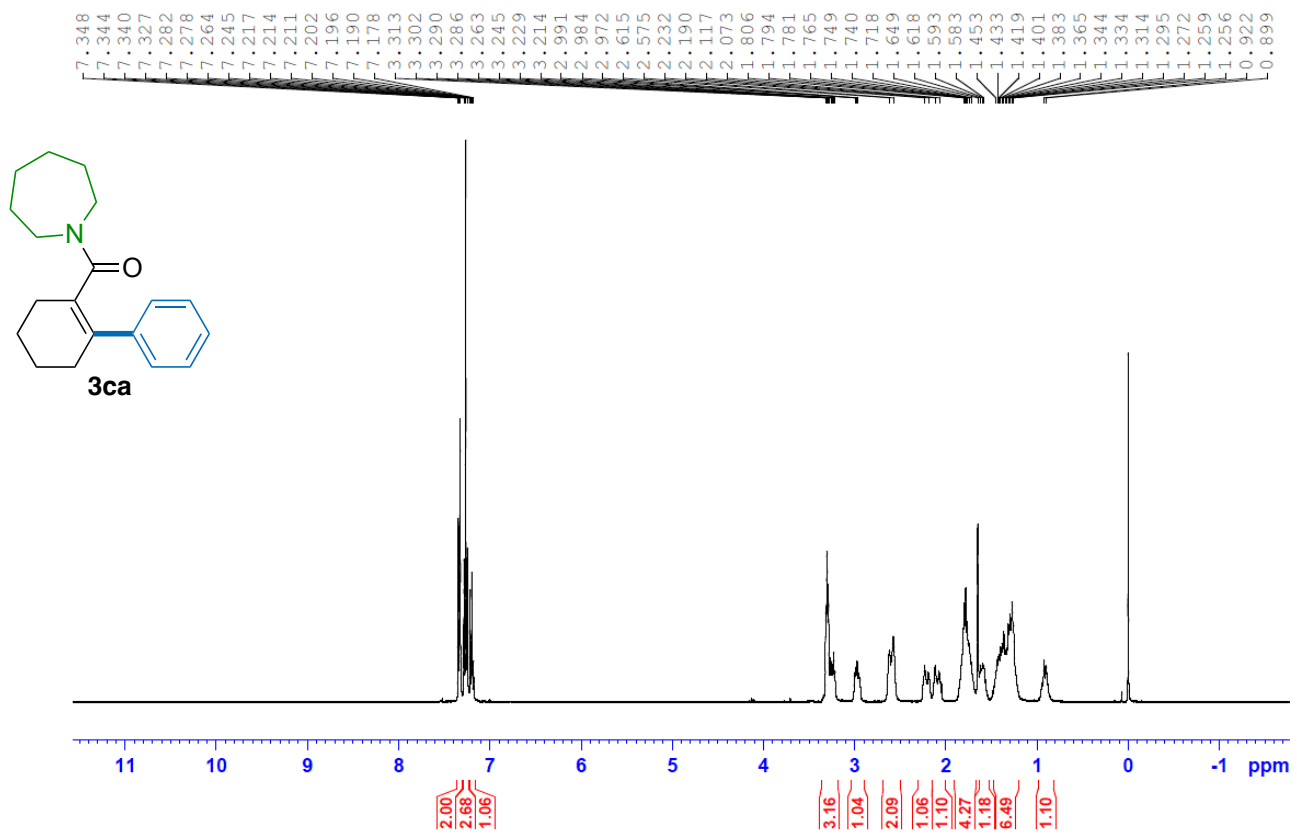
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of **3aa**



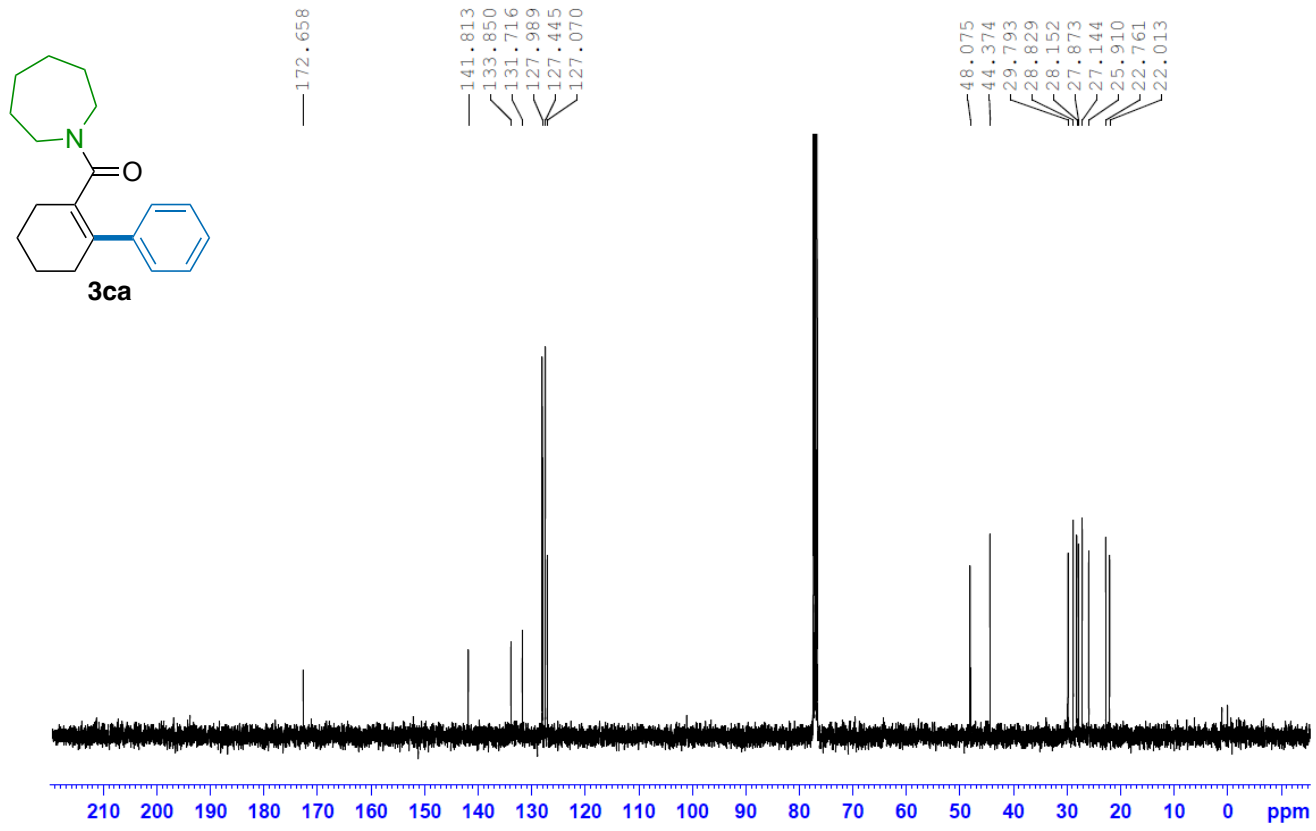
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3ba**



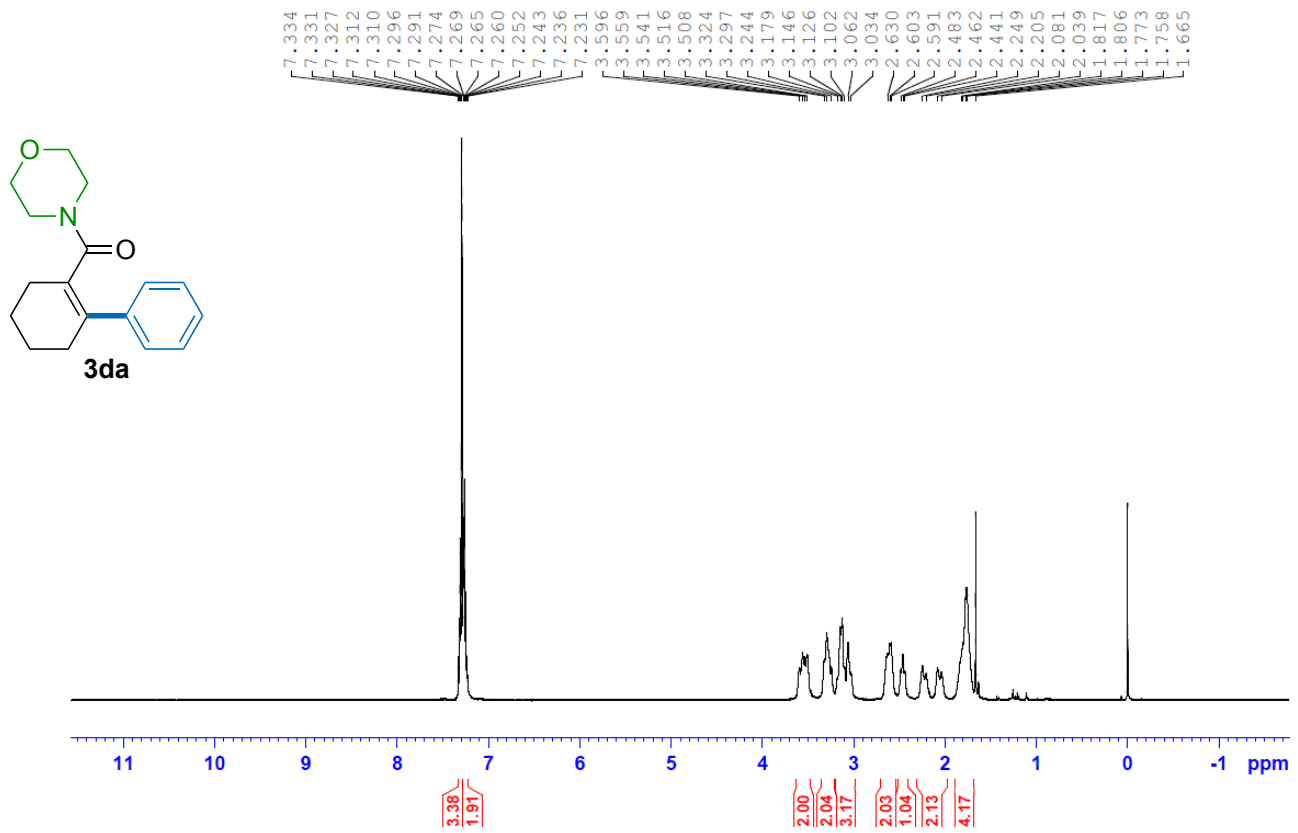
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3ba**



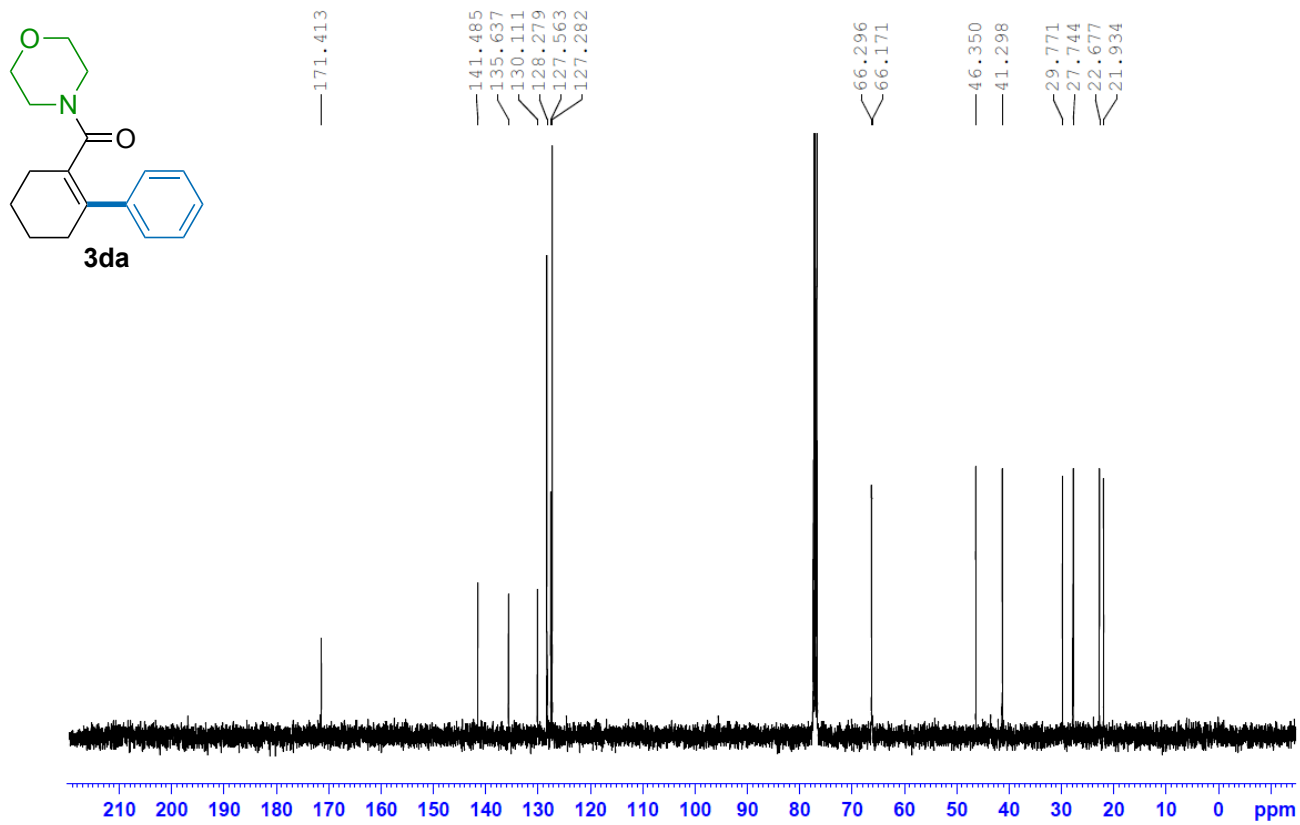
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3ca**



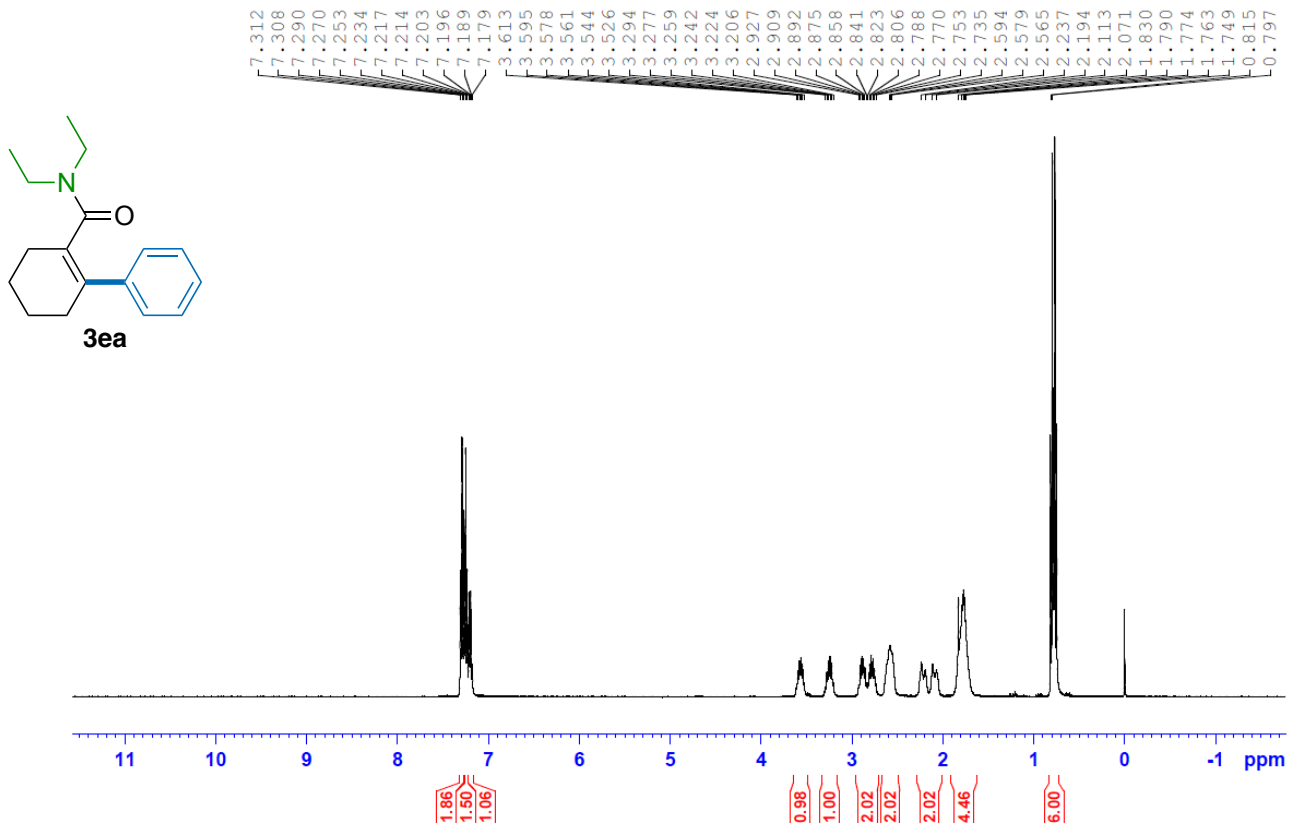
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3ca**



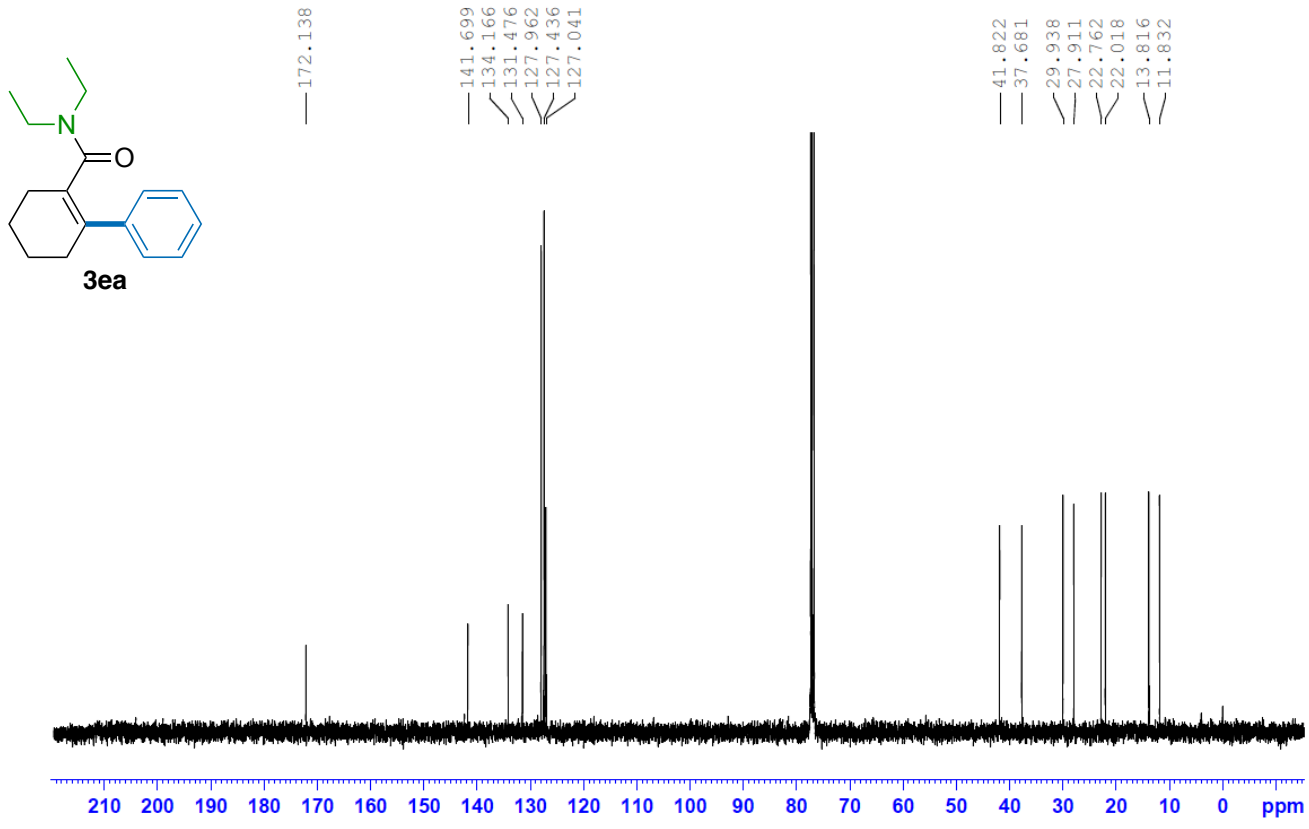
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3da**



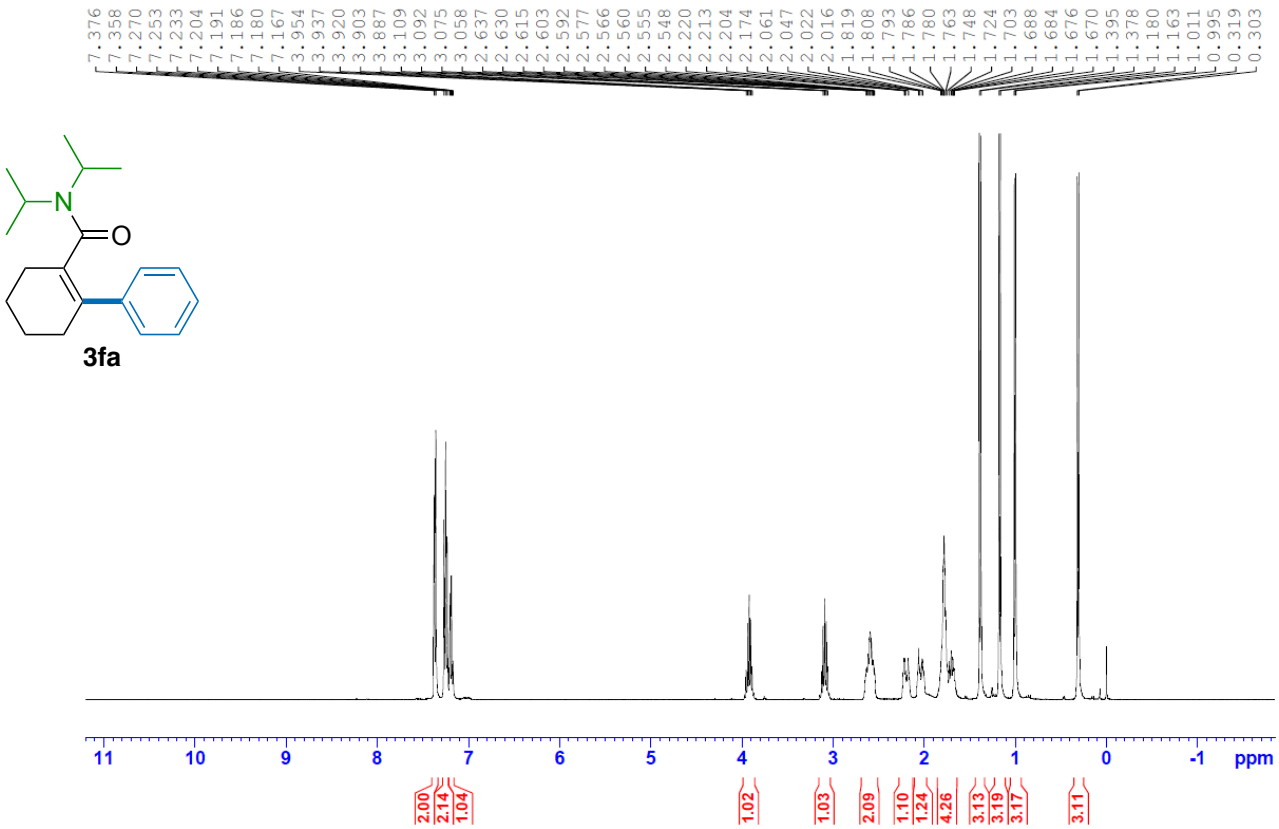
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3da**



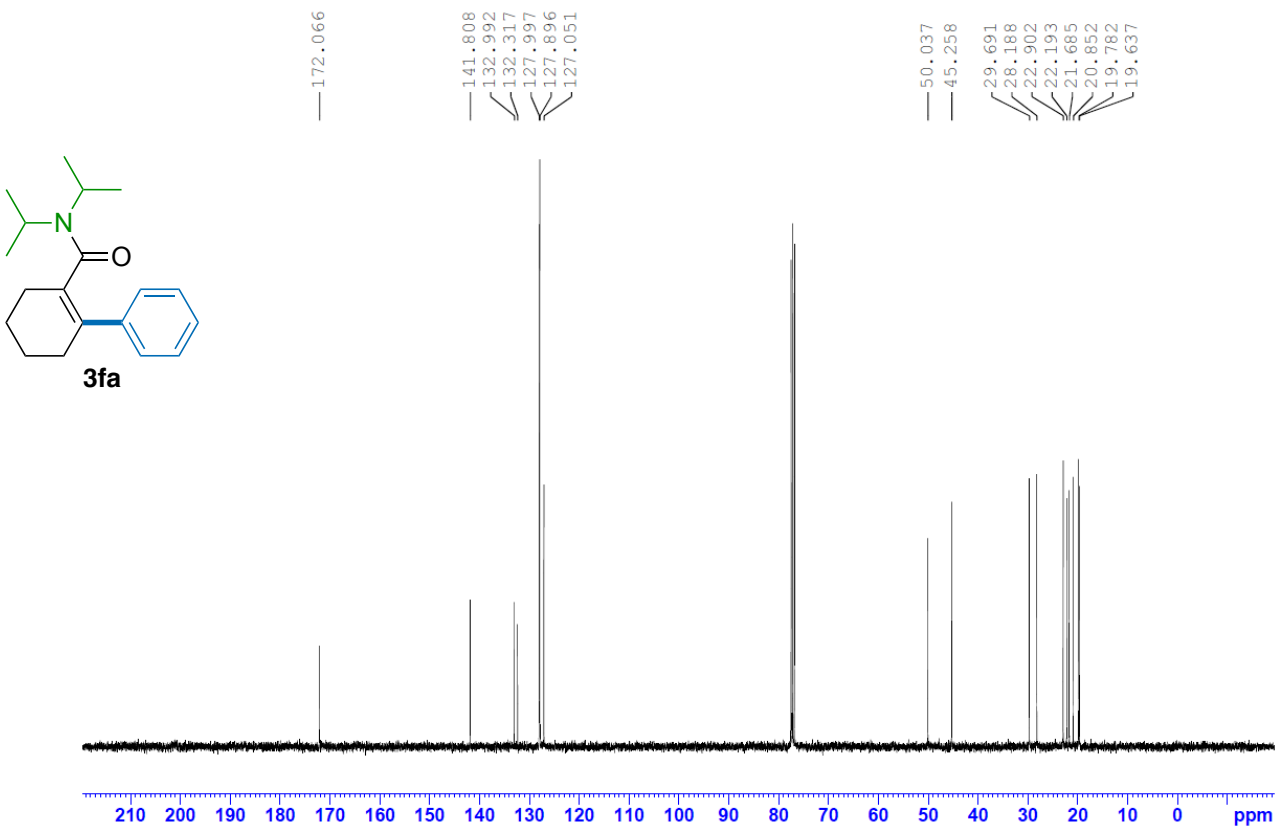
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3ea**



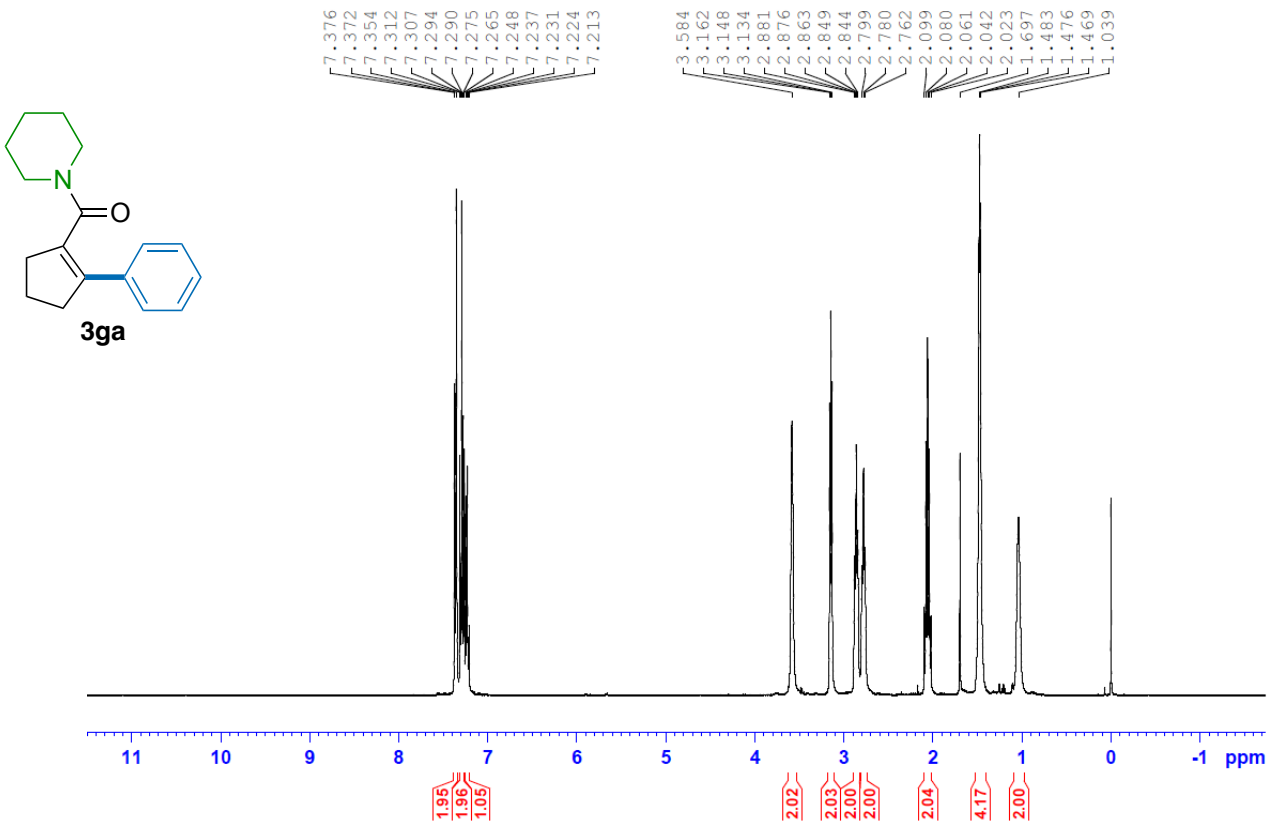
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3ea**



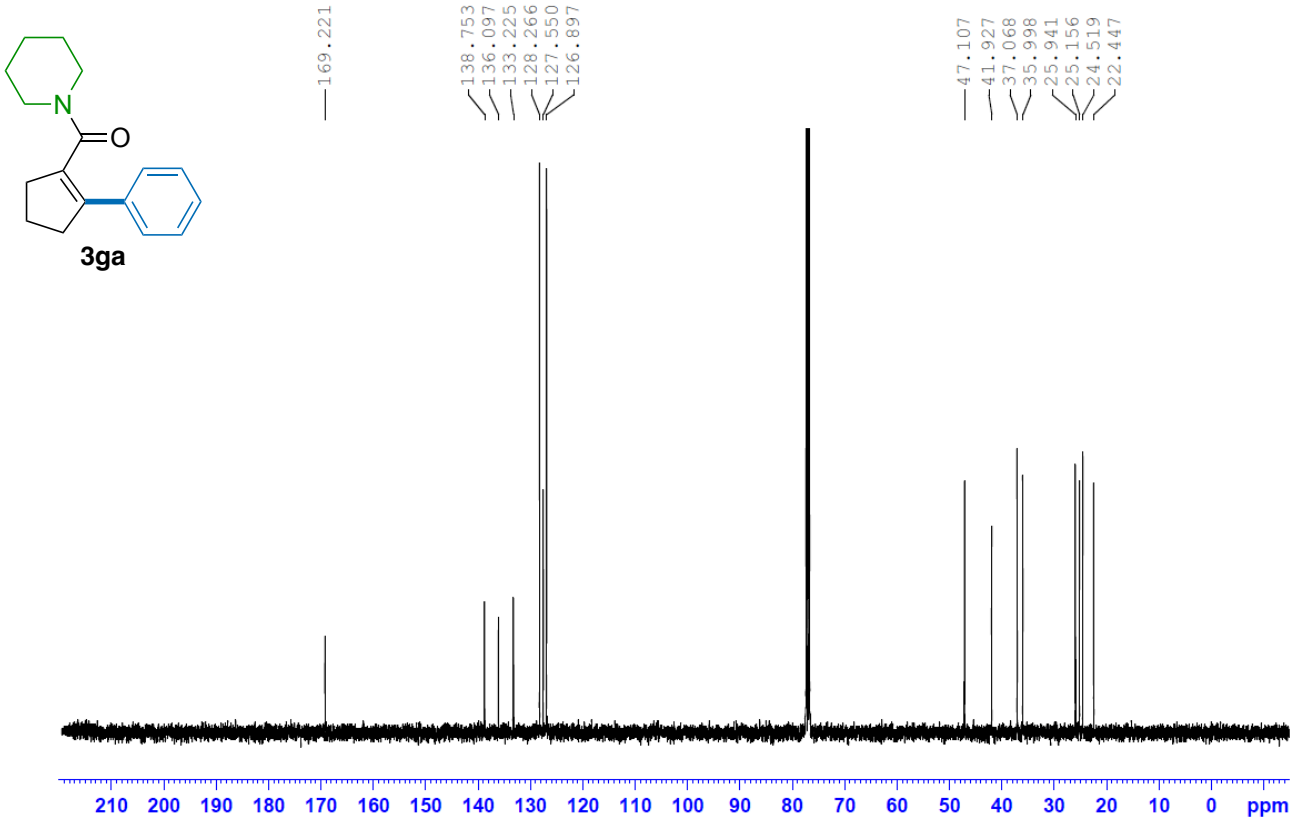
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3fa**



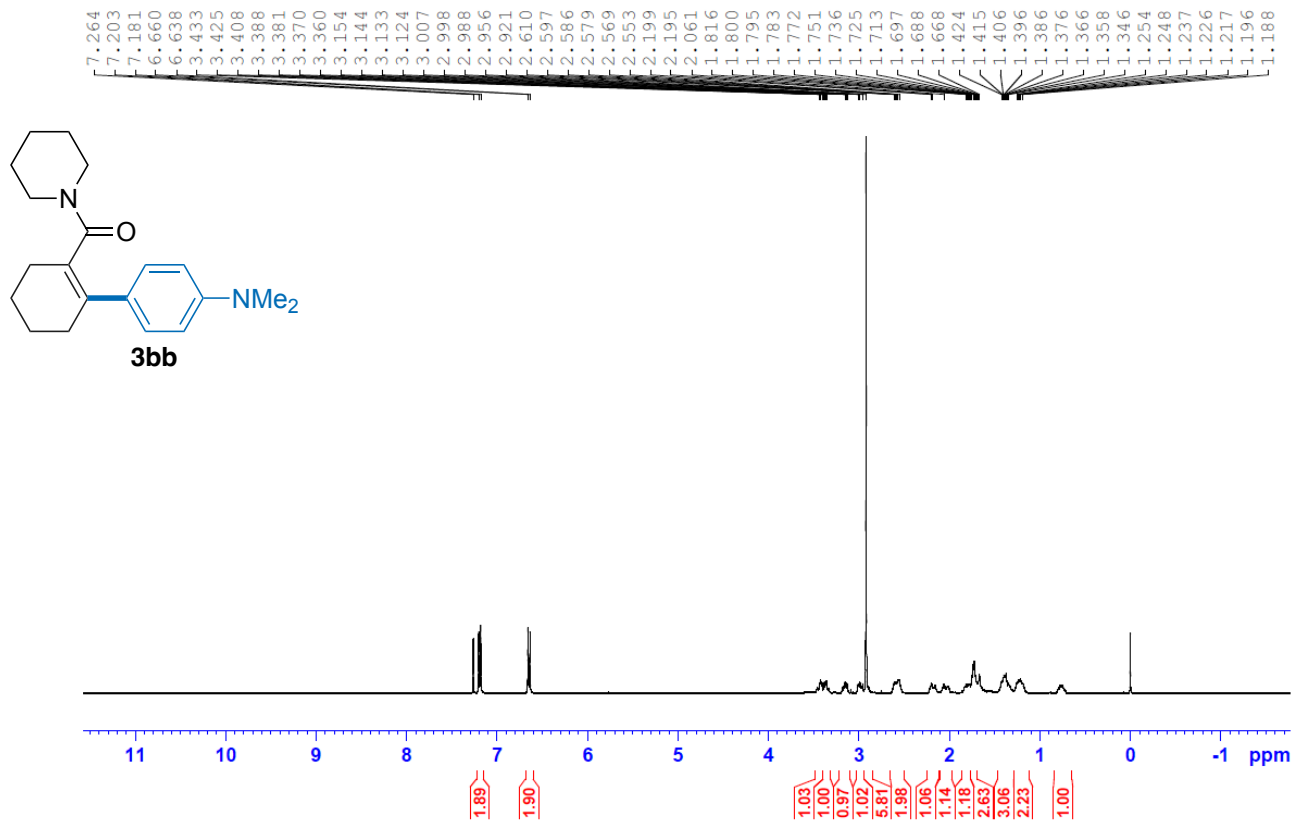
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3fa**



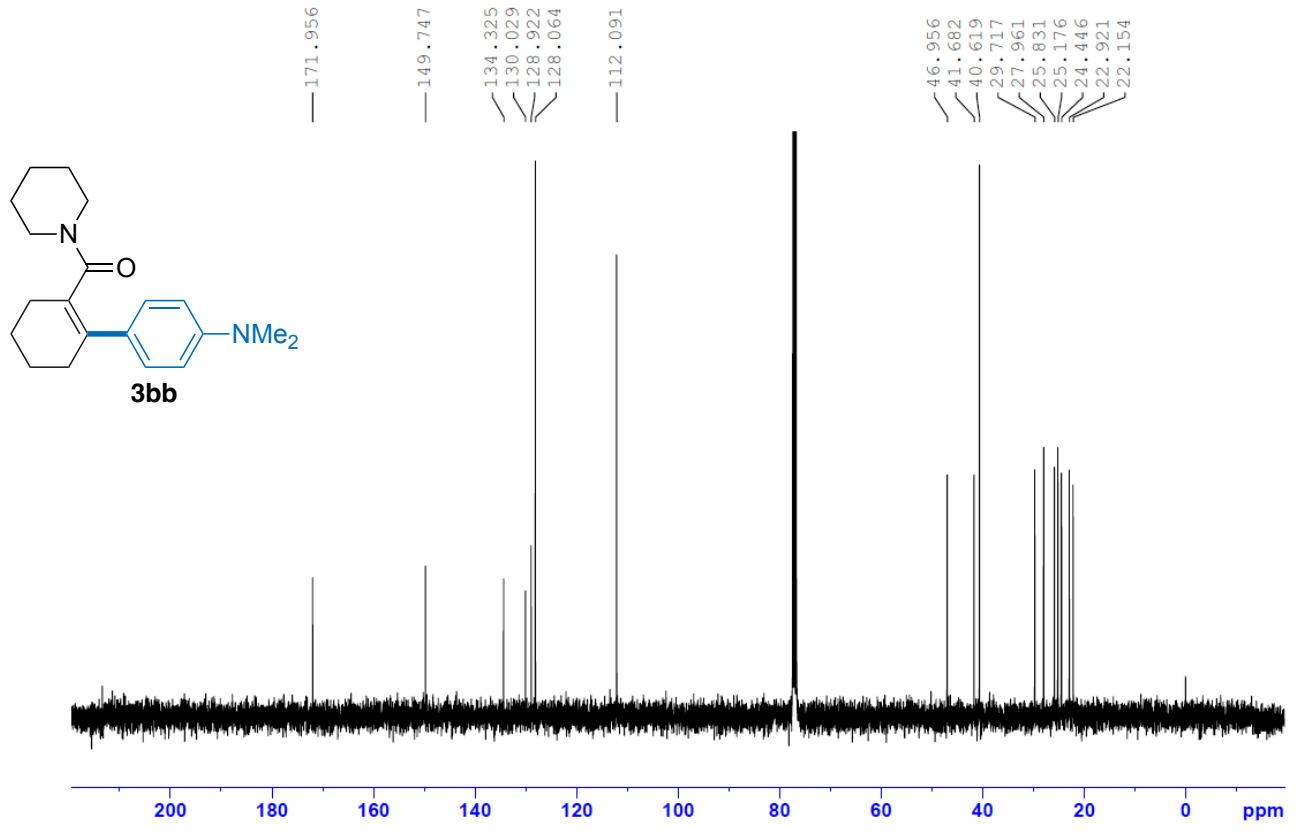
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3ga**



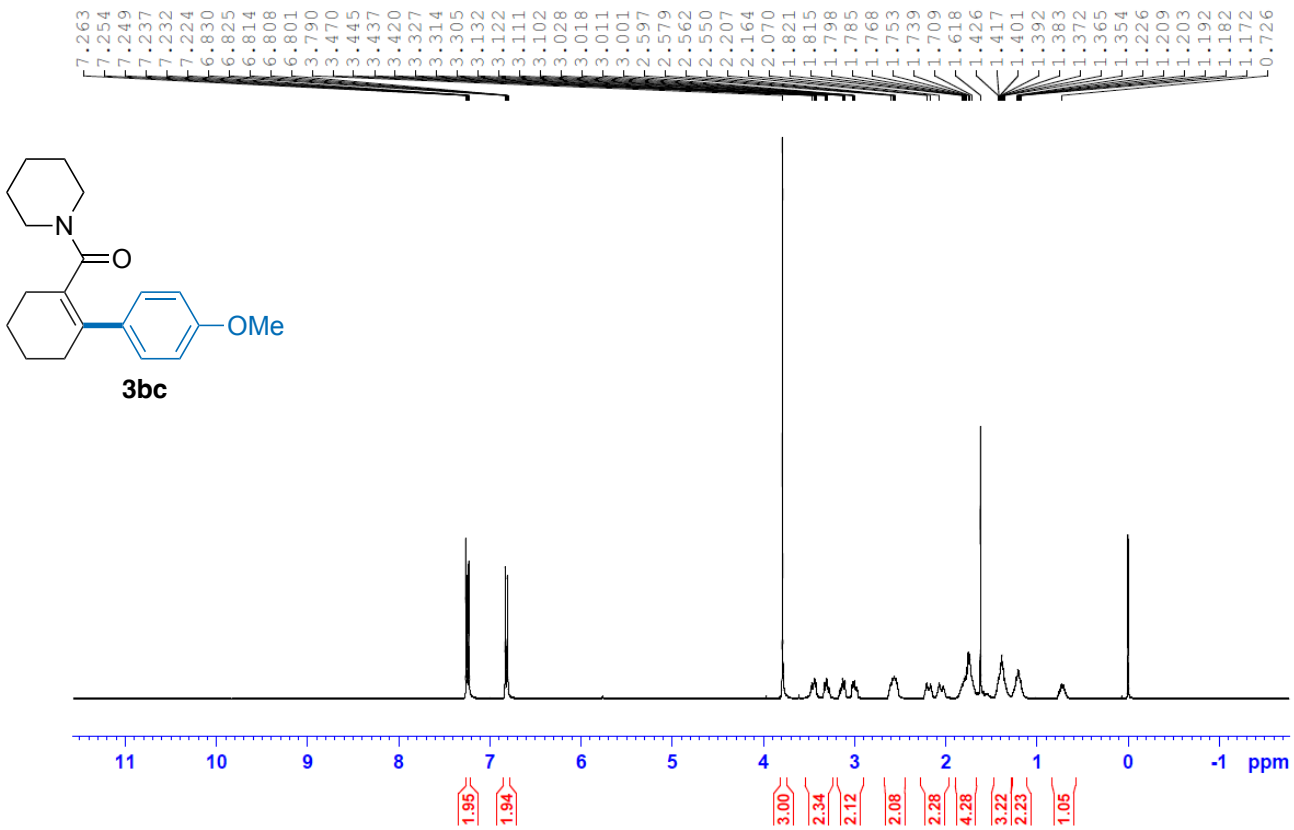
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3ga**



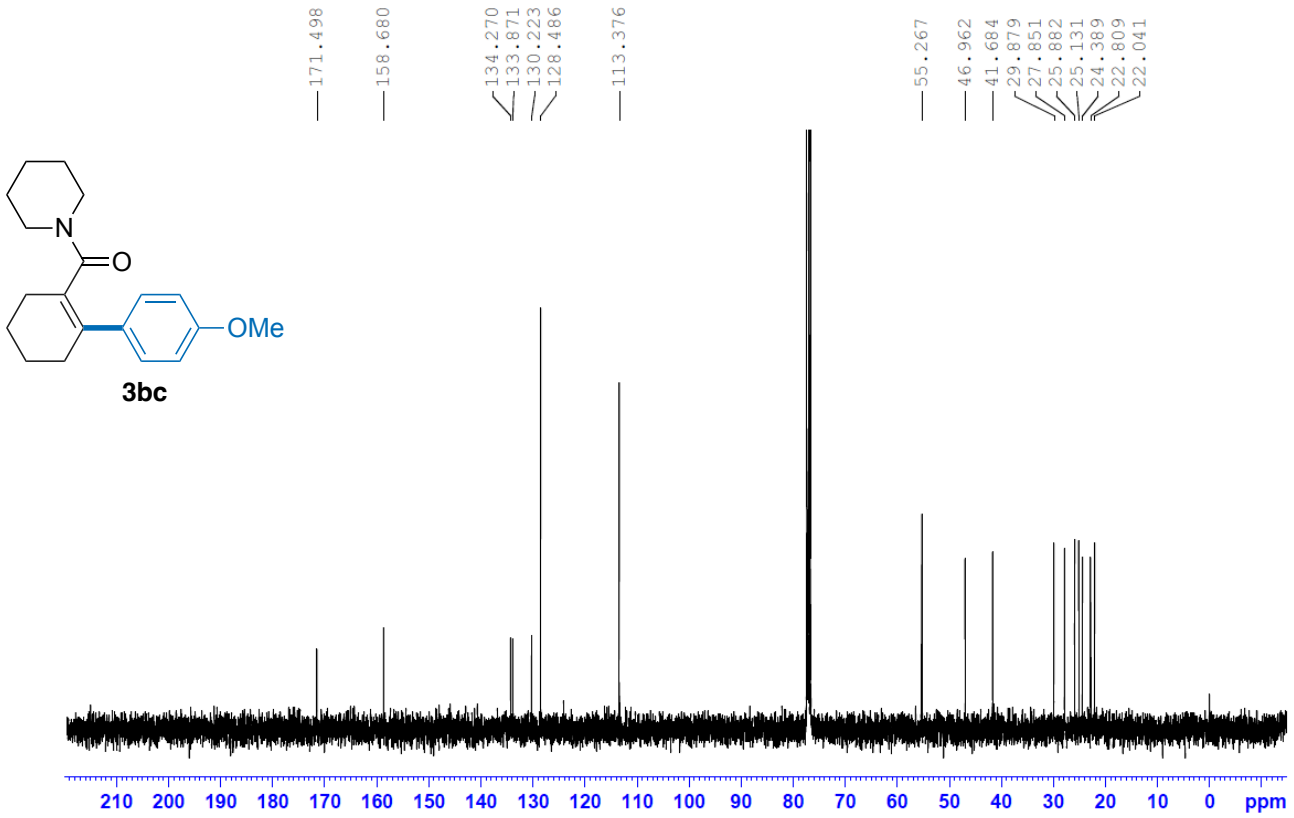
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bb**



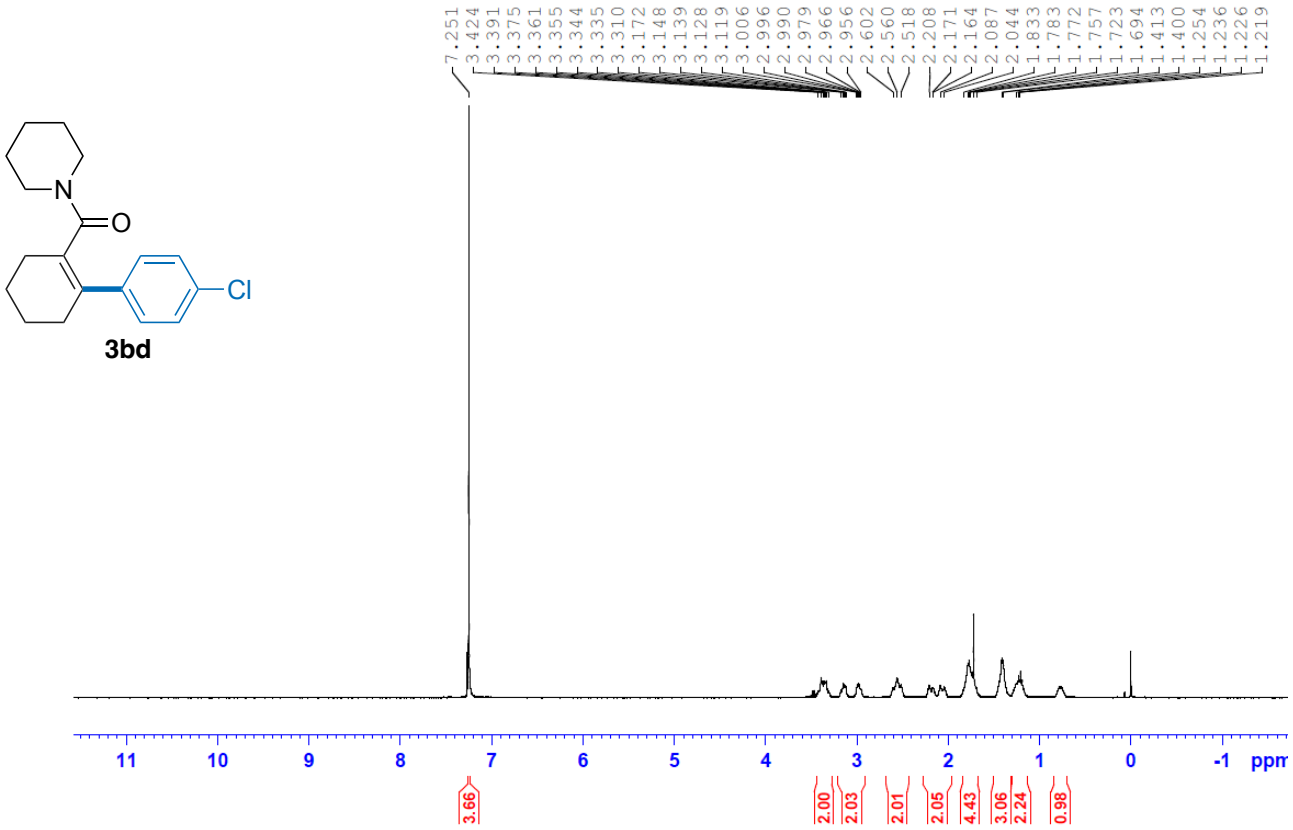
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bb**



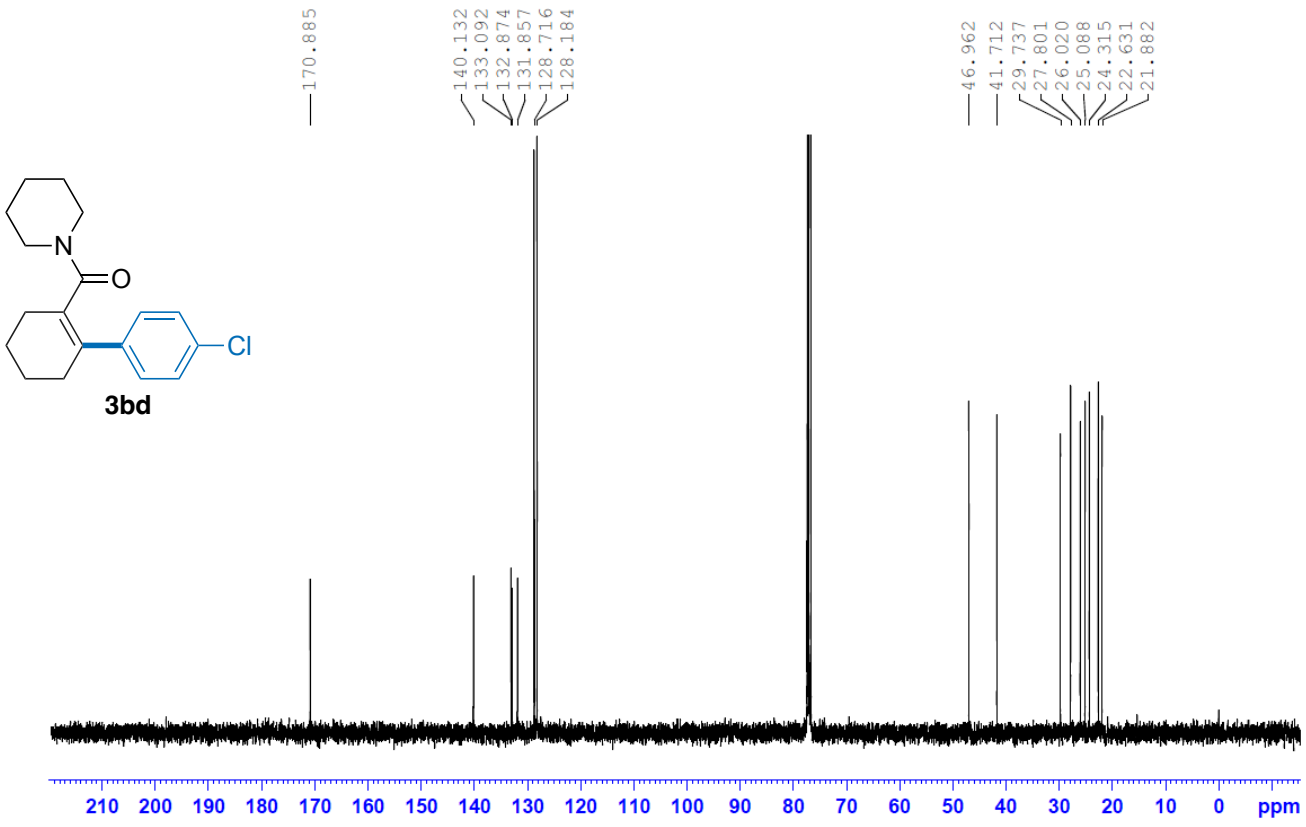
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bc**



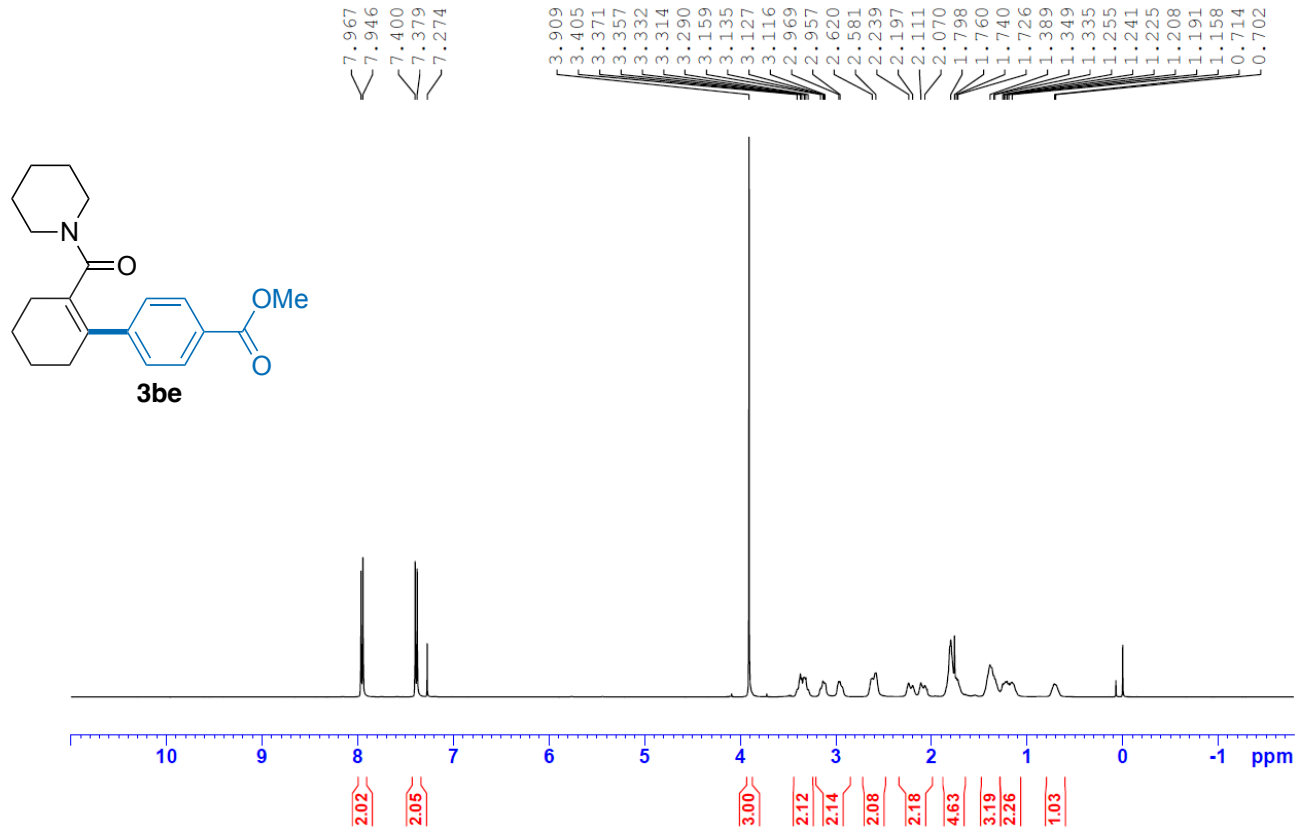
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bc**



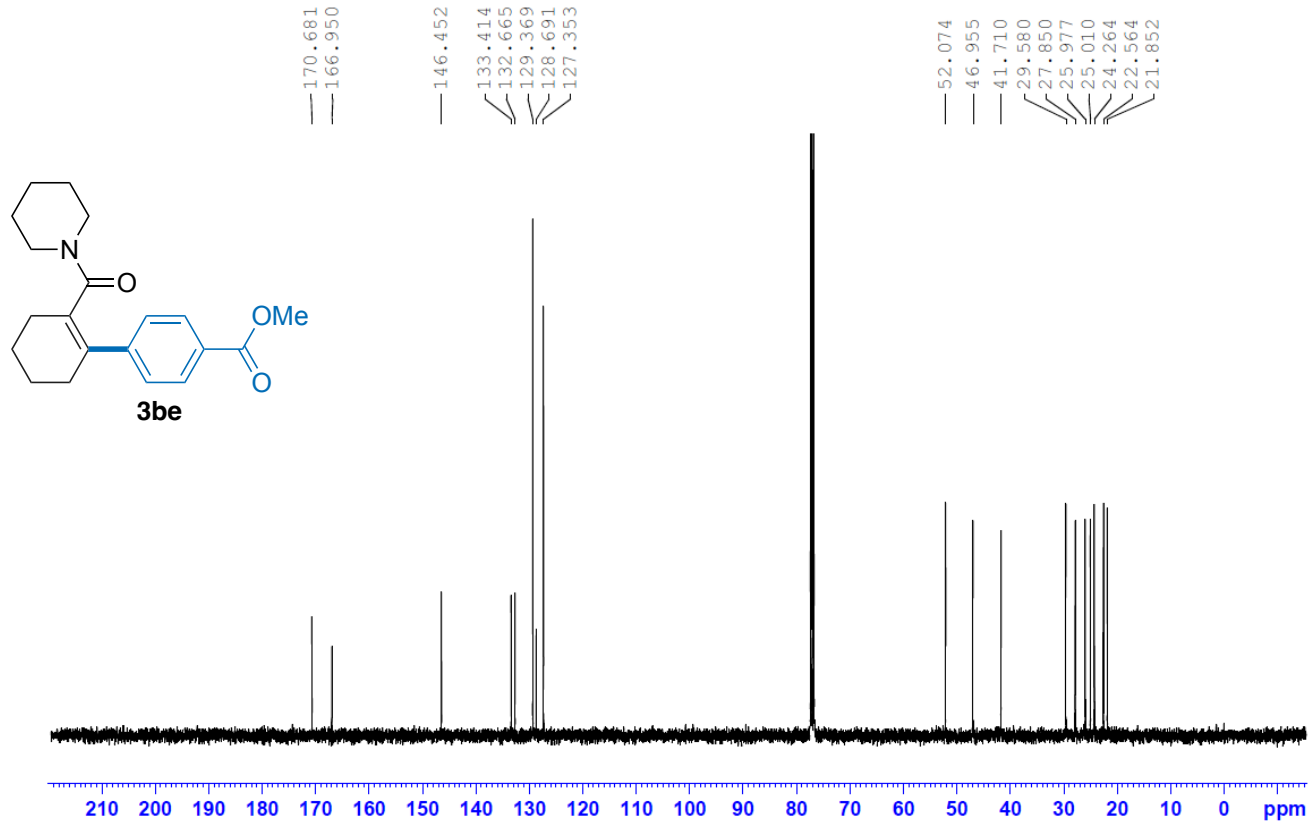
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bd**



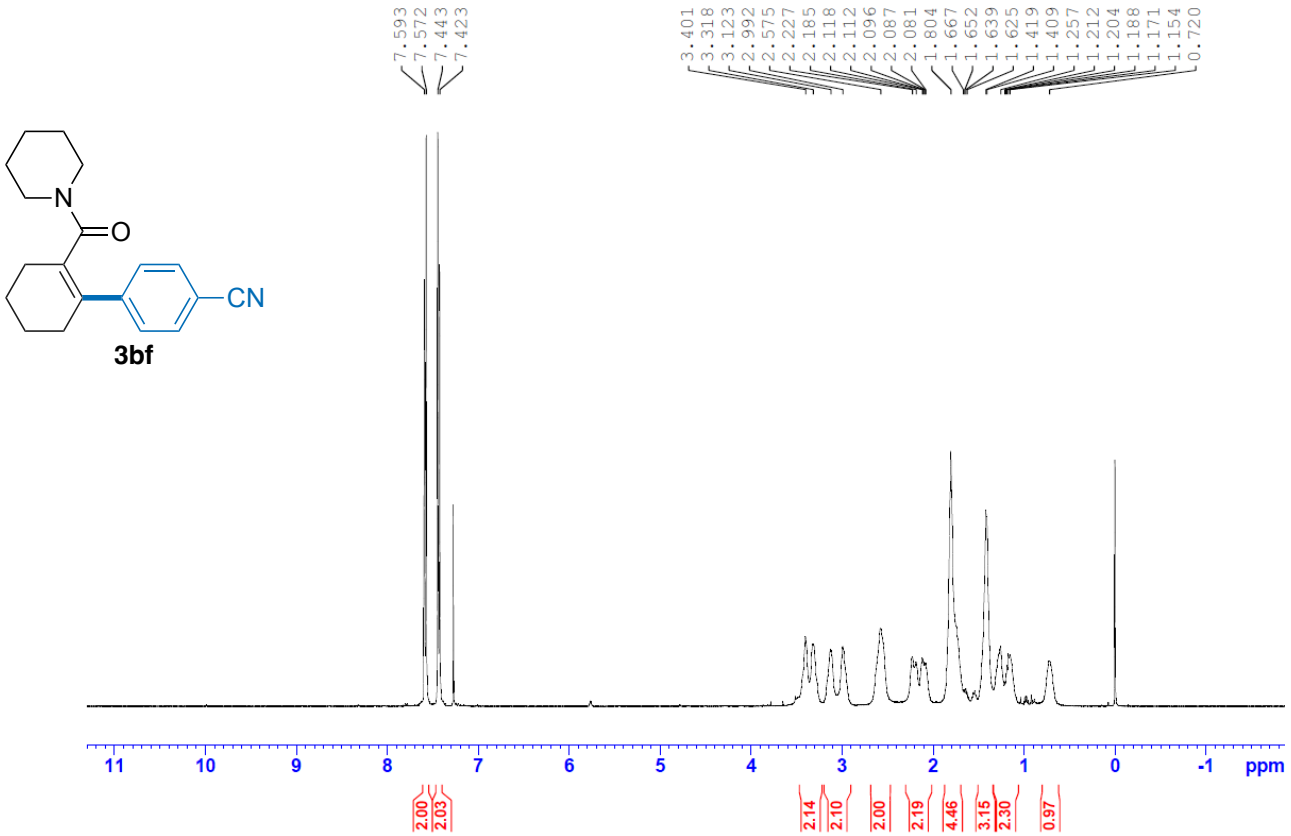
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bd**



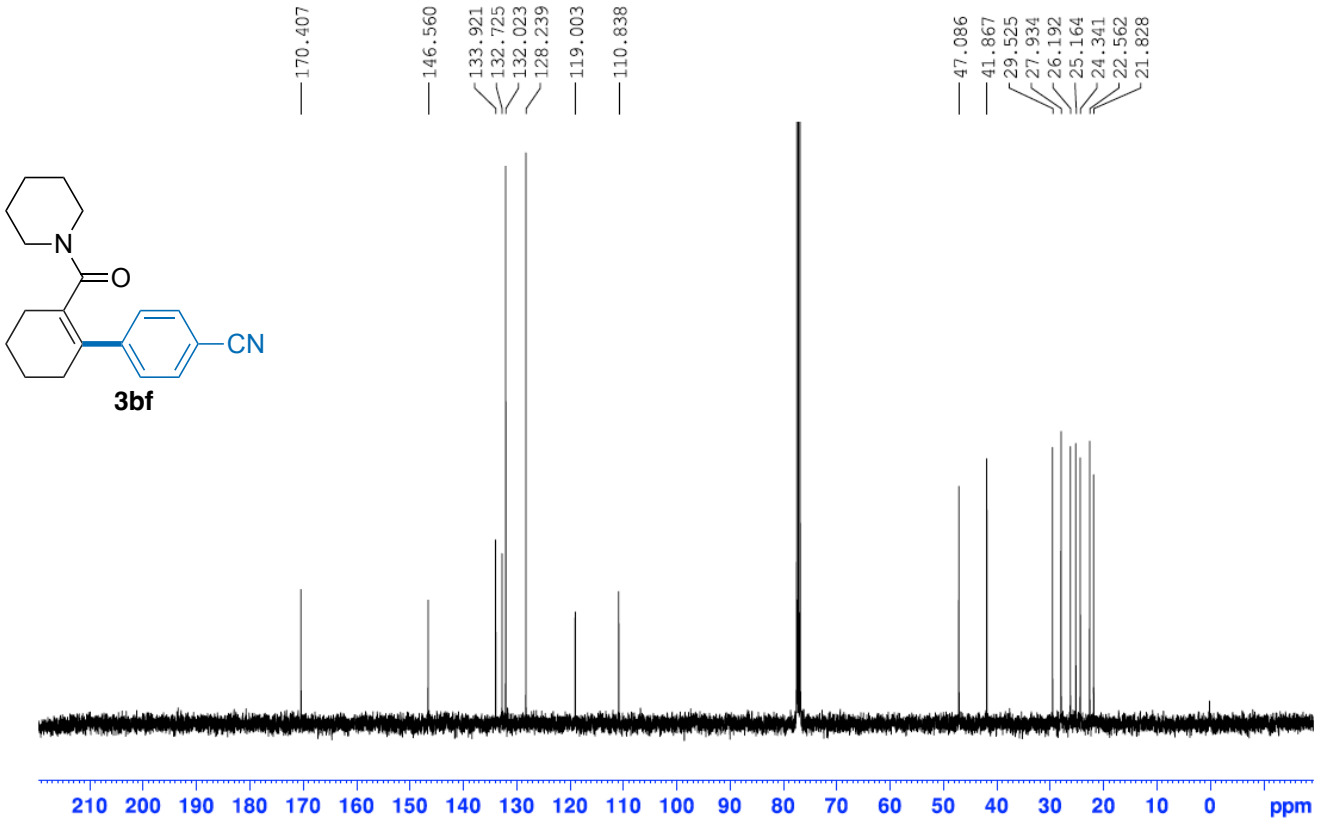
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3be**



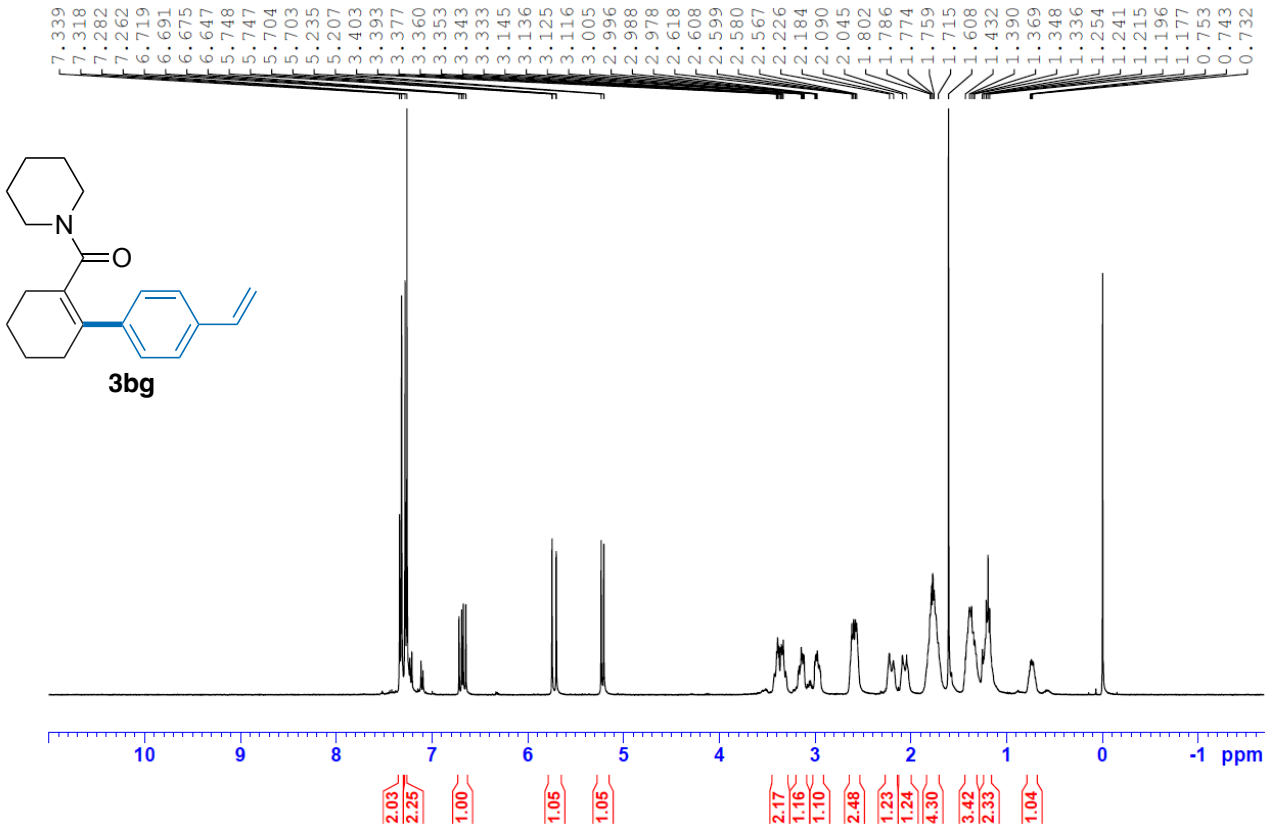
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3be**



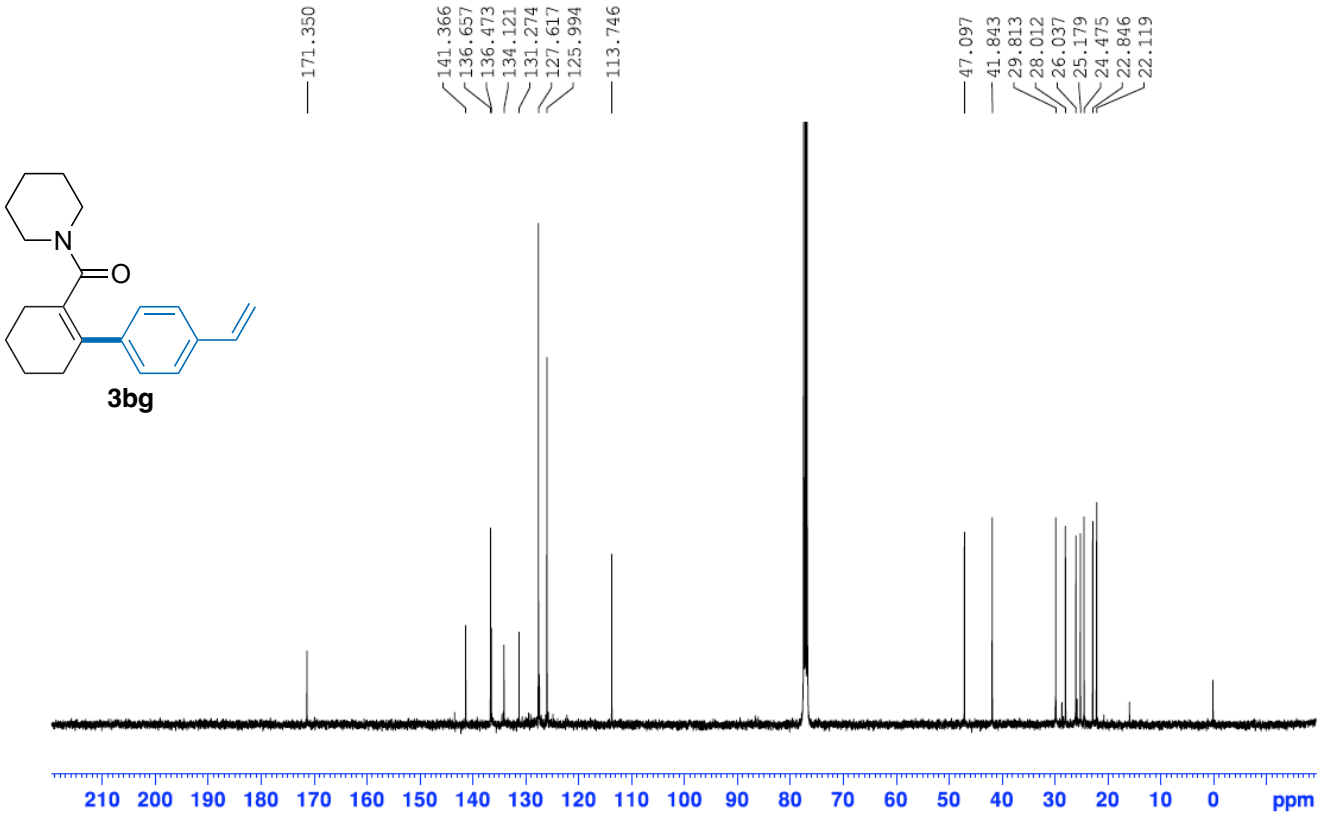
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bf**



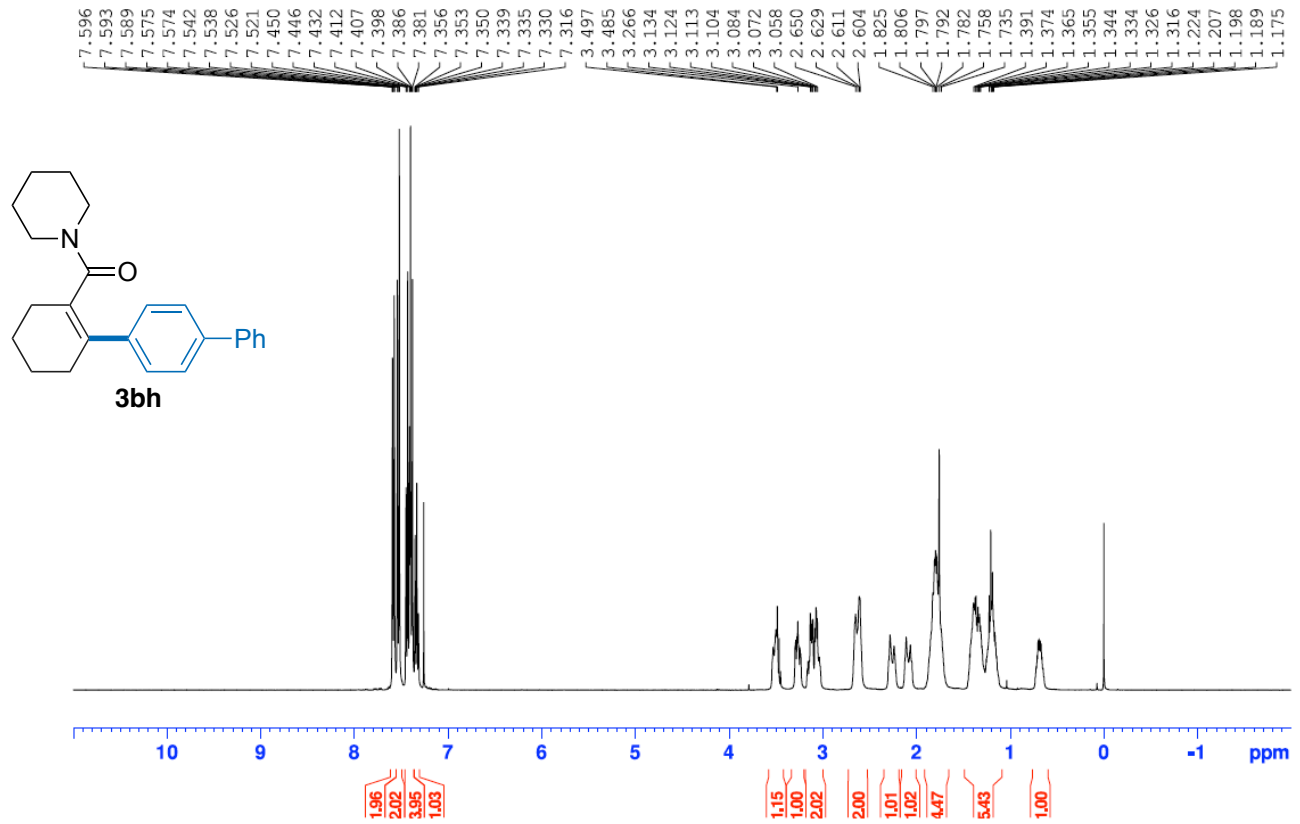
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bf**



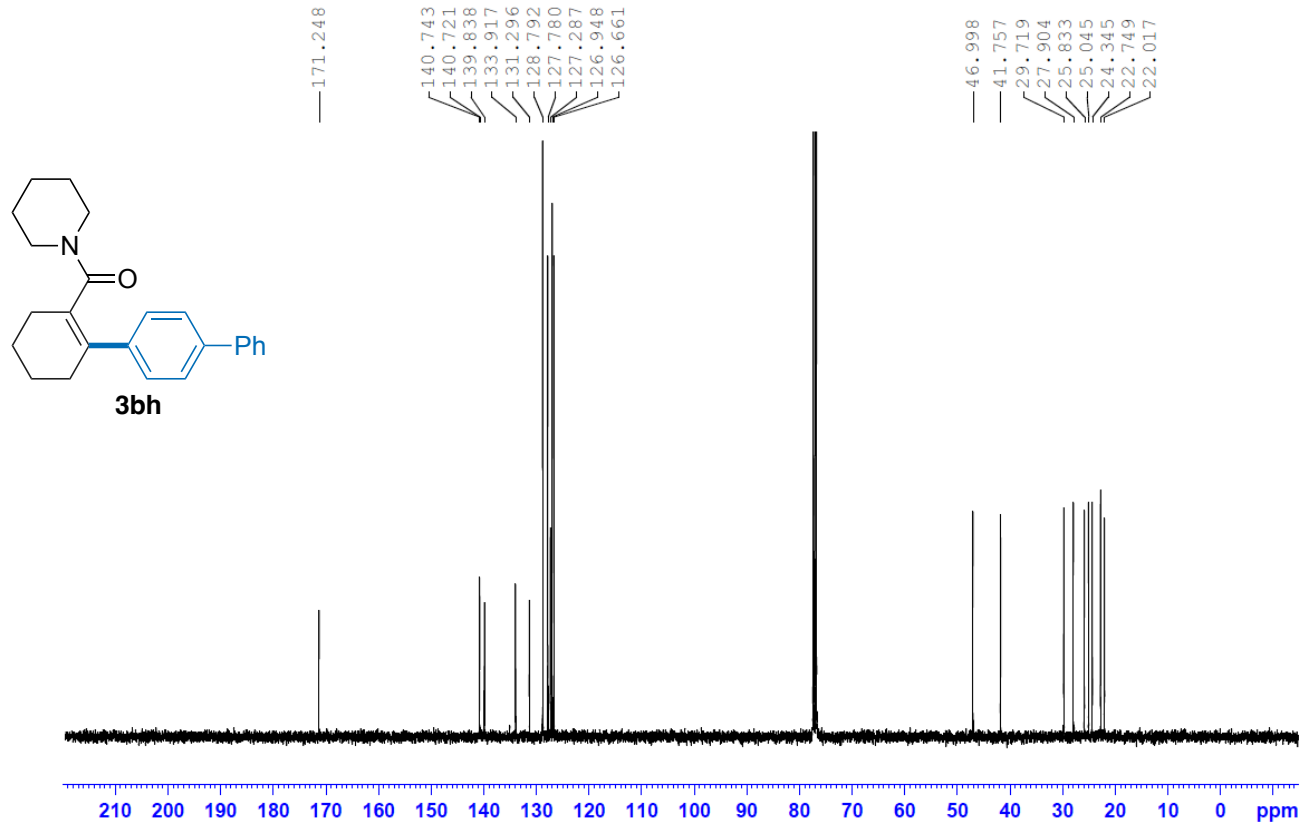
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bg**



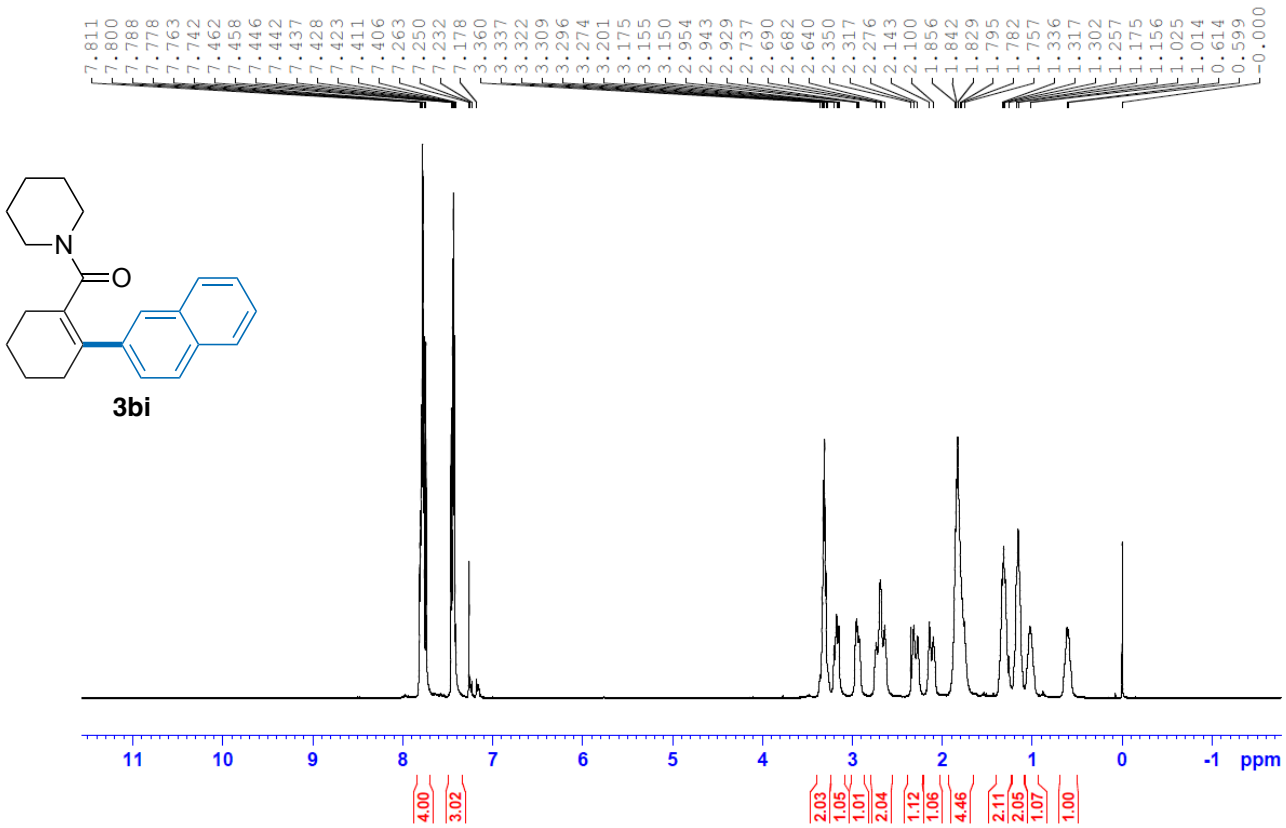
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bg**



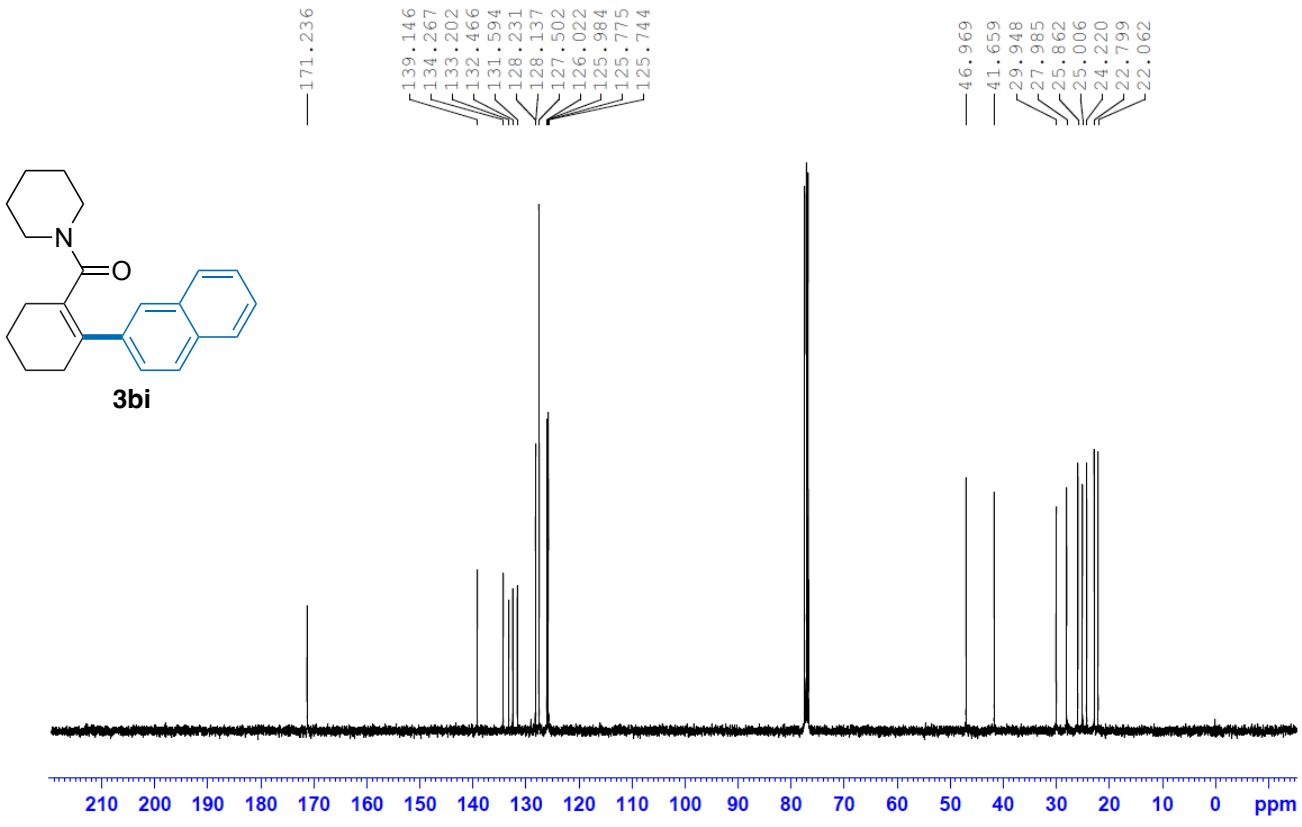
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bh**



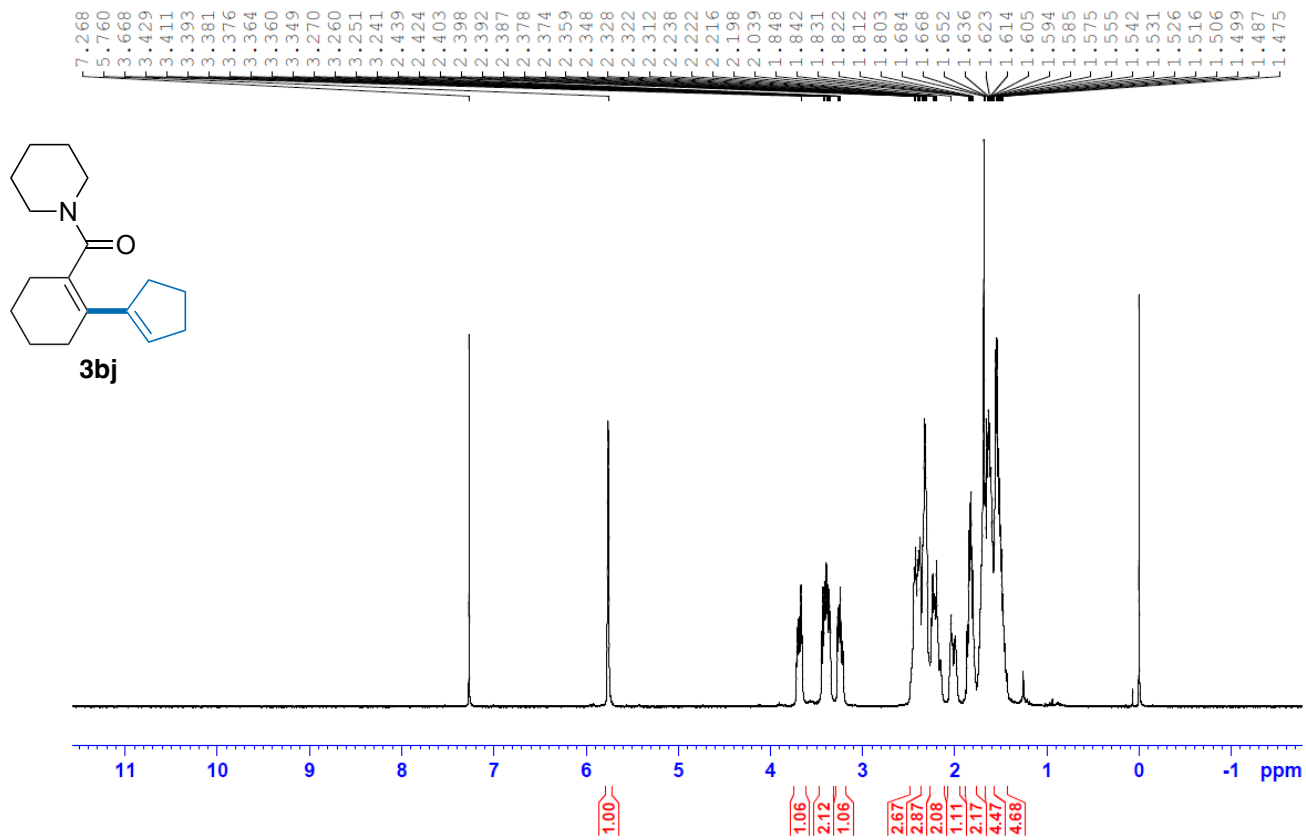
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bh**



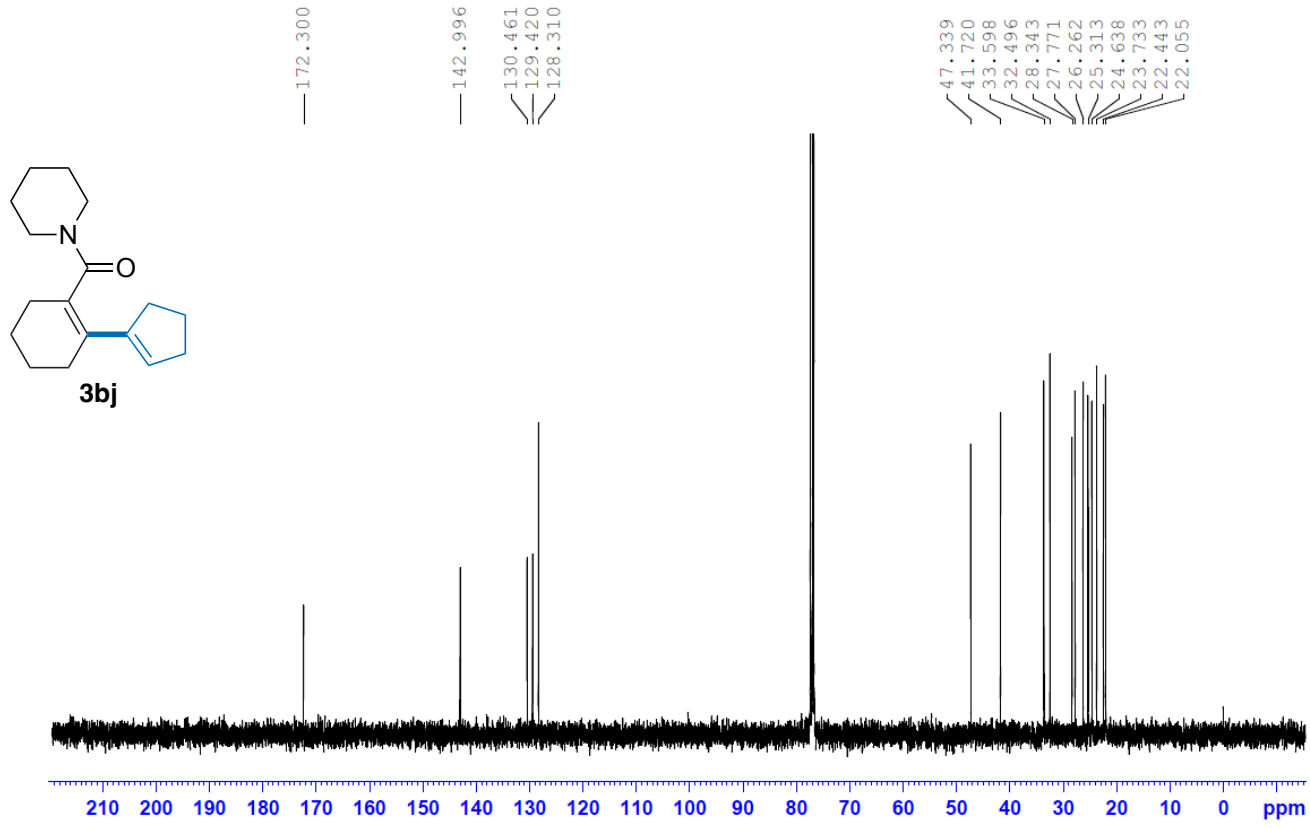
^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bi**



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bi**



^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS) of **3bj**



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **3bj**