Supporting Information

Cobalt-Catalyzed Aminocarbonylation of (Hetero)Aryl Halides Promoted by Visible Light

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General Methods and Materials

Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker Avance III 600 CryoProbe (^{1}H NMR at 600 MHz and ^{13}C at 151 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CHCl_3$ at 7.260 ppm, DMSO-d_6 at 2.500 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52). ^{1}H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High-resolution mass spectrometry samples were analyzed with a hybrid LTQ FT (ICR 7T) (ThermoFisher, Bremen, Germany) mass spectrometer. Samples were introduced *via* a microelectrospray at a flow rate of 10 µL/min in methanol. Xcalibur (ThermoFisher, Breman, Germany) was used to analyze the data. Absorbance spectra were recorded on Varian Cary 50 Bio UV-Visible spectrophotometer with a scan rate of 300 nm/min. Samples were prepared using degassed tetrahydrofuran at a concentration of 10 µM $K[Co(CO)_4]$, transferred to a 4 mL quartz cell, and sealed with a PTFE-lined screw cap in an argon glovebox. The solvent absorbance background was subtracted from the reported spectra.

Analytical thin layer chromatography (TLC) was performed on SiliaPlate 250µm thick silica gel purchased from Silicycle. Visualization was accomplished with short-wave UV light (254 nm), or Hanessian's stain followed by heating when necessary. Purification of the reaction products was carried out by flash chromatography using Siliaflash P60 silica gel (40-63 µm) or SiliaFlash U60 silica gel (10-30 µm) purchased from Silicycle. Carbon monoxide, Research Purity 99.99% (part number CM R200) was purchased from Airgas. Tetrahydrofuran, diethyl ether, *N,N*-dimethylformamide, acetonitrile, and dichloromethane were dried by passage through a column of neutral alumina under nitrogen prior to use. *t*-Amyl alcohol was sparged with argon before storage over 3 Å molecular sieves in an argon filed glovebox. $Co_2(CO)_{10}$ was purchased from Strem Chemicals, stored in a glovebox at -30 °C, and used as received. $K[Co(CO)_4]$ was synthesized according to Ellis and co-workers.[1] $Ph_3Si[Co(CO)_4]$ was synthesized according to Coates and co-workers.[2] All liquid amine nucleophiles and 2,2,6,6-tetramethylpiperidine (TMP) were distilled prior to being stored in a glovebox. All other reagents were obtained from commercial sources and used without further purification, unless otherwise noted. In addition, all reactions were carried out under an atmosphere of dry argon in flame or oven-dried glassware with magnetic stirring. The glass tubes used were purchased from Ace Glass and the gas quick-connect adapters were obtained from Swagelok. PR160-370 nm and 390 nm LED lights were purchased from Kessil and set to 100% intensity (352mW/cm^2 measured from 1 cm distance).[3] An example of the carbonylation setup and photo-excitation setup is shown below.

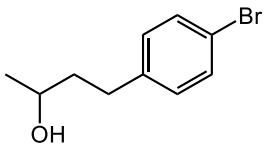
Swagelok setup for pressurizing reactions

Pressure tube and Kessil lights for aminocarbonylation
(Swagelok adapter not pictured)

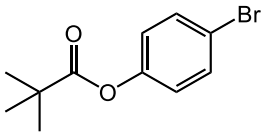
List of Abbreviations

DCM = dichloromethane
DMAP = 4-dimethylaminopyridine
DMSO = dimethyl sulfoxide
EtOAc = ethyl acetate
MeCN = acetonitrile
Pin = pinacol
Piv = pivalate
TEA = triethylamine
THF = tetrahydrofuran
TMP = 2,2,6,6-tetramethylpiperidine

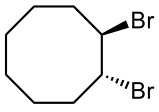
Substrate Preparation



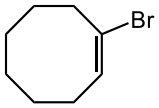
4-(4-bromophenyl)butan-2-ol (10) was prepared by dissolving 4-(4-bromophenyl)butan-2-one (2.59 g, 11.4 mmol) in methanol (38 mL) and cooling to 0 °C. Sodium borohydride (0.47 g, 12.5 mmol) was added portion-wise with stirring at 0 °C for 30 minutes. The mixture was warmed to room temperature, stirred for an additional 30 minutes, and then concentrated under reduced pressure. The mixture was brought up in water and DCM and the organic layer was separated. The aqueous layer was extracted twice with DCM and the organic layers were combined and washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by flash column chromatography in 25% EtOAc/hexanes to afford 2.5 g (96%) of **10** as a colorless oil. Physical and spectral data were in accordance with literature data.[4]



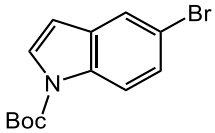
4-bromophenyl pivalate (11) was prepared according to a published procedure; physical and spectral data were in accordance with the literature.[5]



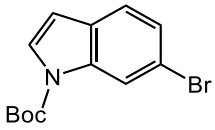
1,2-dibromocyclooctane (SI-19a) was prepared according to a published procedure and used without further purification; physical and spectral data were in accordance with the literature.[6]



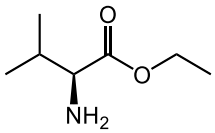
(E)-1-bromocyclooct-1-ene (19) was prepared by dissolving **SI-19a** (1.75 g, 6.48 mmol) in THF (2 mL) and slowly adding ^{t}BuOK (1.09 g, 9.72 mmol) as a solution in THF (2 mL). The mixture was stirred at room temperature overnight, then quenched with saturated ammonium chloride, and the organic layer were separated. The aqueous layer was extracted three times with DCM, and the organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by removing 1-cyclooctene under vacuum to produce 0.65 g (53%) of **19** as an orange oil. Physical and spectral data were in accordance with literature data.[7]



tert-butyl 5-bromo-1H-indole-1-carboxylate (26) was prepared according to published procedure; physical and spectral data were in accordance with literature data.[8]



tert-butyl 6-bromo-1H-indole-1-carboxylate (27) was prepared using a modified literature procedure.[8] To a solution of 6-bromo-1H-indole (0.50 g, 2.60 mmol) and DMAP (31 mg, 0.26 mmol) in MeCN (5 mL), di-tert-butyl dicarbonate (0.67 g, 3.10 mmol) was added in one portion. The reaction was stirred at room temperature for 30 minutes and monitored by TLC. When completed, the reaction was concentrated under reduced pressure, and purified by flash column chromatography in 2.5% EtOAc/hexanes to afford 0.72 g (95%) **27** as a yellow solid. Physical and spectral data were in accordance with literature data.[9]

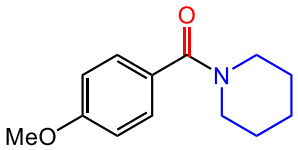


ethyl L-valinate (SI-44) was synthesized by cooling a stirred solution of L-valine (2.0 g, 17 mmol) in ethanol (50 mL) to -10 °C and adding $SOCl_2$ (4.1 g, 2.5 mL, 34 mmol) dropwise. The mixture was refluxed for 4 hours, left stirred at room temperature overnight, then concentrated under reduced pressure. The mixture was dissolved in DCM and washed with saturated sodium bicarbonate. The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography in EtOAc to produce 0.98 g (40%) **SI-44** as a pale-yellow oil. Physical and spectral data were in accordance with literature data.[10]

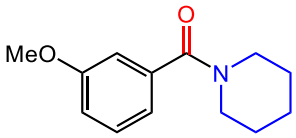
Cobalt-Catalyzed Aminocarbonylations

General Carbonylation Procedure A

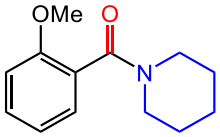
In a glovebox under an argon atmosphere, $Co_2(CO)_8$ (3.4 mg, 0.010 mmol) was combined with amine (0.26 mmol), TMP (68 µL, 0.40 mmol), and *t*-amyl alcohol (0.5 mL) in an Ace Glass pressure tube. The vessel was sealed with a septa and Teflon tape and removed from the glovebox. The aryl electrophile (0.20 mmol) was then added, and the septa was quickly replaced by a Swagelok connector cap. The tube was pressurized inside a fume hood with closed sashes with 5 atm CO, purged 5 times with CO to replace argon, set to 2 atm and stirred for 48 hours under irradiation at 390 nm. The reaction mixture was depressurized; 3 mL of EtOAc and 3 mL of 1M HCl were added. The mixture was extracted with EtOAc (3 x 2 mL), and the combined organic layers were allowed to sit open to air for two hours to decompose the cobalt complex as indicated by a color change from yellow to colorless. The combined organic layers were filtered through a plug of SiO_2, eluting with EtOAc, and concentrated under reduced pressure. The crude product was purified by flash column chromatography.



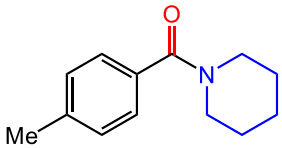
(4-methoxyphenyl)(piperidin-1-yl)methanone (SI-1) was obtained from 1-bromo-4-methoxybenzene using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 30–50% EtOAc/hexanes (R_f 0.38 in 50% EtOAc/hexanes) yielding **SI-1** as a yellow oil (43.5 mg, 99%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 3.64 (br s, 2H), 3.37 (br s, 2H), 1.64 (br s, 4H), 1.53 (br s, 2H). Physical and spectral data were in accordance with literature data.[11]



(3-methoxyphenyl)(piperidin-1-yl)methanone (SI-2) was obtained from 1-bromo-3-methoxybenzene using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.21 in 30% EtOAc/hexanes) yielding **SI-2** as a yellow oil (43.6 mg, 99%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 9.0, 7.5 Hz, 1H), 6.94 – 6.86 (m, 3H), 3.79 (s, 3H), 3.68 (br s, 2H), 3.31 (br s, 2H), 1.65 (br s, 4H), 1.48 (br s, 2H). Physical and spectral data were in accordance with literature data.[12]

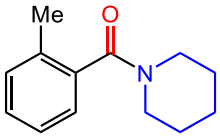


(2-methoxyphenyl)(piperidin-1-yl)methanone (SI-3) was obtained from 1-bromo-2-methoxybenzene using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 30–50% EtOAc/hexanes (R_f 0.41 in 50% EtOAc/hexanes) yielding **SI-3** as a yellow oil (44.6 mg, >99%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.34 – 7.23 (m, 1H), 7.18 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.79 (s, 3H), 3.75 (br s, 1H), 3.65 (br s, *J* = 13.0 Hz, 1H), 3.15 (dt, *J* = 6.3, 2.7 Hz, 2H), 1.67 – 1.56 (m, 4H), 1.48 (br s, 1H), 1.41 (br s, 1H). Physical and spectral data were in accordance with literature data.[13]

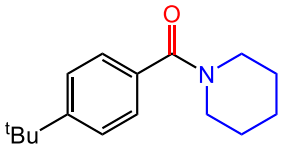


piperidin-1-yl(p-tolyl)methanone (SI-4) was obtained from 1-bromo-4-methylbenzene using General Carbonylation Procedure A. The crude product was purified *via* flash

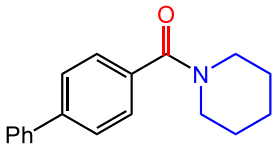
column chromatography using a gradient of 25–30% EtOAc/hexanes (R_f 0.26 in 30% EtOAc/hexanes) yielding **SI-4** as a yellow oil (38.6 mg, 95%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 3.67 (br s, 2H), 3.33 (br s, 2H), 2.34 (s, 3H), 1.65 (br s, 4H), 1.48 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]



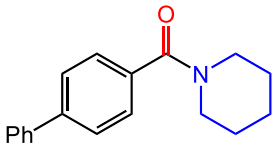
piperidin-1-yl(o-tolyl)methanone (SI-5) was obtained from 1-bromo-2-methylbenzene using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 15–30% EtOAc/hexanes (R_f 0.33 in 30% EtOAc/hexanes) yielding **SI-5** as a yellow oil (38.2 mg, 94%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 7.12 (d, *J* = 7.4 Hz, 1H), 3.79 (d, *J* = 12.6 Hz, 1H), 3.67 (d, *J* = 12.6 Hz, 1H), 3.19 – 3.10 (m, 2H), 2.28 (s, 3H), 1.63 (s, 4H), 1.43 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]



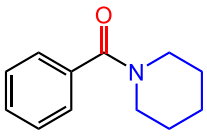
(4-(tert-butyl)phenyl)(piperidin-1-yl)methanone (SI-6) was obtained from 1-bromo-4-(tert-butyl)benzene using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 15–20% EtOAc/hexanes (R_f 0.30 in 20% EtOAc/hexanes) yielding **SI-6** as a yellow oil (51.5 mg, >99%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.68 (br s, 2H), 3.35 (br s, 2H), 1.65 (br s, 4H), 1.49 (br s, 2H), 1.30 (s, 9H). Physical and spectral data were in accordance with literature data.[11]



[1,1'-biphenyl]-4-yl(piperidin-1-yl)methanone (SI-7) was obtained from 4-bromo-1,1'-biphenyl *via* General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using a gradient of 20–25% EtOAc/hexanes (R_f 0.24 in 25% EtOAc/hexanes) yielding **SI-7** as a tan solid (53.8 mg, >99%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.64 – 7.57 (m, 4H), 7.49 – 7.42 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 3.73 (br s, 2H), 3.40 (br s, 2H), 1.68 (br s, 4H), 1.54 (br s, 2H). Physical and spectral data were in accordance with literature data.[11]

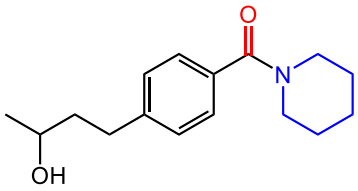


[1,1'-biphenyl]-4-yl(piperidin-1-yl)methanone (SI-8) was obtained from [1,1'-biphenyl]-4-yl trifluoromethanesulfonate *via* General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and 370 nm irradiation. The crude product was purified *via* flash column chromatography using a gradient of 15–30% EtOAc/hexanes (R_f 0.25 in 25% EtOAc/hexanes) yielding **SI-8** as a tan solid (56.2 mg, >99%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 4H), 7.49 – 7.43 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 3.73 (br s, 2H), 3.40 (br s, 2H), 1.69 (br s, 4H), 1.54 (br s, 2H). Physical and spectral data were in accordance with literature data.[11]

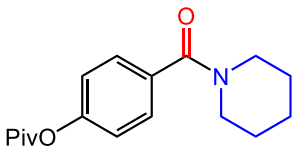


phenyl(piperidin-1-yl)methanone (SI-9) was obtained from bromobenzene using General Carbonylation Procedure A. The crude product was purified *via* flash column

chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.28 in 30% EtOAc/hexanes) yielding **SI-9** as a colorless oil (29.1 mg, 77%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.37 (s, 5H), 3.69 (br s, 2H), 3.32 (br s, 2H), 1.66 (br s, 4H), 1.49 (br s, 2H). Physical and spectral data were in accordance with literature data.[11]

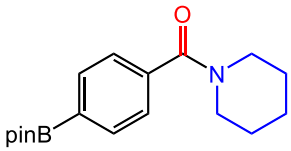


(4-(3-hydroxybutyl)phenyl)(piperidin-1-yl)methanone (SI-10) was obtained from **10** using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 40–75% EtOAc/hexanes (R_f 0.25 in 60% EtOAc/hexanes) yielding **SI-10** as a colorless oil (47.8 mg, 91%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.29 (d, J = 6.6 Hz, 2H), 7.20 (d, J = 6.9 Hz, 2H), 3.82 – 3.76 (m, 1H), 3.68 (br s, 2H), 3.34 (br s, 2H), 2.75 (dt, J = 14.0, 7.3 Hz, 1H), 2.70 – 2.63 (m, 1H), 1.89 (br s, 1H), 1.78 – 1.69 (m, 2H), 1.66 (br s, 4H), 1.50 (br s, 2H), 1.21 (dd, J = 6.1, 2.3 Hz, 3H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 170.6, 143.9, 133.8, 128.4, 127.0, 67.1, 48.9, 43.2, 40.6, 32.0, 26.6, 25.7, 24.6, 23.6. **HRMS** (ESI) calculated for $[C_{16}H_{23}NO_2+H]^+$ 262.180155, found 262.1814.

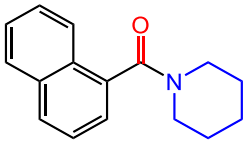


4-(piperidine-1-carbonyl)phenyl pivalate (SI-11) was obtained from **11** using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 20–25% EtOAc/hexanes (R_f 0.27 in 25% EtOAc/hexanes) yielding **SI-11** as a white solid (53.0 mg, 92%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.38 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 3.66 (br s, 2H), 3.32 (br s, 2H), 1.63 (br s, 4H), 1.47 (br s, 2H), 1.32 (s, 9H). **^{13}C NMR** (151 MHz, Chloroform-d) δ

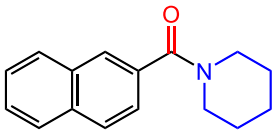
176.9, 169.6, 151.8, 133.8, 128.2, 121.6, 48.8, 43.2, 39.1, 27.1, 26.5, 25.6, 24.6. **HRMS** (ESI) calculated for $[C_{17}H_{23}NO_3+H]^+$ 290.175070, found 290.1763.



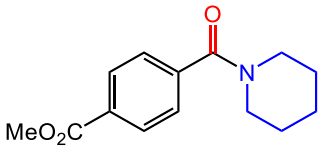
piperidin-1-yl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (SI-12) was obtained from 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.32 in 30% EtOAc/hexanes) yielding **SI-12** as a white solid (54.9 mg, 87%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.0 Hz, 2H), 7.34 (d, *J* = 7.0 Hz, 2H), 3.67 (br s, 2H), 3.26 (br s, 2H), 1.63 (br s, 4H), 1.45 (br s, 2H), 1.31 (s, 12H). Physical and spectral data were in accordance with literature data.[15]



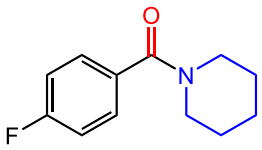
naphthalen-1-yl(piperidin-1-yl)methanone (SI-13) was obtained from 1-bromonaphthalene using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and 370 nm irradiation. The crude product was purified *via* flash column chromatography using a gradient of 25–30% EtOAc/hexanes (R_f 0.31 in 30% EtOAc/hexanes) yielding **SI-13** as a white solid (40.4 mg, 84%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.87 – 7.82 (m, 3H), 7.54 – 7.46 (m, 3H), 7.41 – 7.38 (m, 1H), 3.86 (tq, *J* = 13.0, 6.6, 5.5 Hz, 2H), 3.15 – 3.10 (m, 2H), 1.73 (p, *J* = 5.7, 5.0 Hz, 2H), 1.66 (p, *J* = 5.7 Hz, 2H), 1.44 – 1.33 (m, *J* = 7.8 Hz, 2H). Physical and spectral data were in accordance with literature data.[16]



naphthalen-2-yl(piperidin-1-yl)methanone (SI-14) was obtained from 2-bromonaphthalene using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and 370 nm irradiation. The crude product was purified *via* flash column chromatography using a gradient of 15–30% EtOAc/hexanes (R_f 0.28 in 25% EtOAc/hexanes) yielding **SI-14** as a white solid (37.4 mg, 78%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.85 (t, *J* = 8.9 Hz, 3H), 7.54 – 7.49 (m, 2H), 7.48 (dd, *J* = 8.4, 1.3 Hz, 1H), 3.76 (br s, 2H), 3.38 (br s, 2H), 1.69 (br s, 4H), 1.51 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]

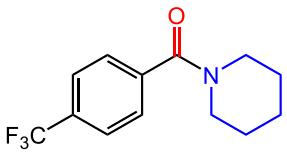


methyl 4-(piperidine-1-carbonyl)benzoate (SI-15) was obtained from methyl 4-bromobenzoate using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using a gradient of 30–40% EtOAc/hexanes (R_f 0.31 in 40% EtOAc/hexanes) yielding **SI-15** as a yellow solid (43.3 mg, 88%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 3.69 (br s, 2H), 3.26 (br s, 2H), 1.65 (br s, 4H), 1.48 (br s, 2H). Physical and spectral data were in accordance with literature data.[17]

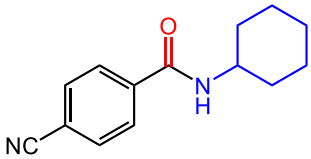


(4-fluorophenyl)(piperidin-1-yl)methanone (SI-16) was obtained from 1-bromo-4-fluorobenzene using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.30 in 30% EtOAc/hexanes) yielding **SI-16** as a yellow oil (39.8 mg, 96%). **^{1}H NMR** (600 MHz,

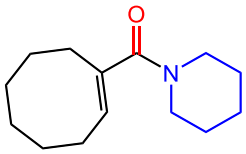
Chloroform-*d*) δ 7.42 – 7.32 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 3.67 (br s, 2H), 3.32 (br s, 2H), 1.65 (br s, 4H), 1.49 (br s, 2H). Physical and spectral data were in accordance with literature data.[11]



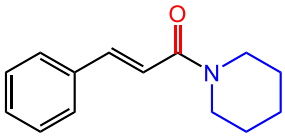
piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone (SI-17) was obtained from 1-bromo-4-(trifluoromethyl)benzene using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using a gradient of 15–25% EtOAc/hexanes (R_f 0.34 in 25% EtOAc/hexanes) yielding **SI-17** as a white solid (41.3 mg, 80%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 3.71 (br s, 2H), 3.28 (br s, 2H), 1.67 (br s, 4H), 1.50 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]



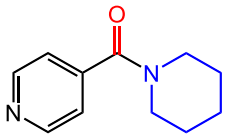
4-cyano-N-cyclohexylbenzamide (SI-18) was obtained from 4-bromobenzonitrile using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and 370 nm irradiation for 24 hours. The crude product was purified *via* flash column chromatography using a gradient of 15–20% EtOAc/hexanes (R_f 0.21 in 20% EtOAc/hexanes) yielding **SI-18** as a white solid (15.2 mg, 33%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 6.12 (s, 1H), 3.95 (ddt, *J* = 14.7, 10.8, 5.6 Hz, 1H), 2.01 (d, *J* = 9.5 Hz, 2H), 1.75 (d, *J* = 13.4 Hz, 2H), 1.65 (d, *J* = 13.0 Hz, 1H), 1.45 – 1.35 (m, 2H), 1.32 – 1.14 (m, 3H). Physical and spectral data were in accordance with literature data.[14]



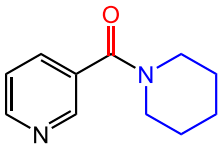
(E)-cyclooct-1-en-1-yl(piperidin-1-yl)methanone (SI-19) was obtained from **19** using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 10–20% EtOAc/hexanes (R_f 0.33 in 20% EtOAc/hexanes) yielding **SI-19** as a yellow oil (41.6 mg, 94%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 5.70 (t, J = 8.2 Hz, 1H), 3.48 (s, 4H), 2.32 – 2.28 (m, 2H), 2.17 – 2.13 (m, 2H), 1.64 – 1.58 (m, 4H), 1.56 – 1.47 (m, 10H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 172.4, 136.8, 130.1, 48.2, 42.6, 29.4, 29.2, 27.7, 26.5, 26.4, 26.2, 26.1, 25.8, 24.8. **HRMS** (ESI) calculated for $[C_{14}H_{23}NO+H]^+$ 222.185241, found 222.1863.



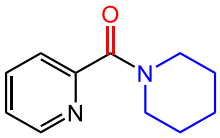
3-phenyl-1-(piperidin-1-yl)prop-2-en-1-one (SI-20) was obtained from (E)-(2-bromovinyl)benzene (85:15 *E:Z*) General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and 370 nm irradiation. The crude product was purified *via* flash column chromatography using a gradient of 20% EtOAc/hexanes (R_f 0.16 and 0.12 in 20% EtOAc/hexanes) yielding **SI-20** as a white solid (21.5 mg, 50%, 76:24 *E:Z*). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 15.4 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.24 (m, 9H), 6.90 (d, *J* = 15.4 Hz, 1H), 6.62 (d, *J* = 12.5 Hz, 1H), 6.03 (d, *J* = 12.5 Hz, 1H), 3.66 (s, 2H), 3.63 – 3.55 (m, 4H), 3.30 – 3.26 (m, 2H), 1.76 (s, 1H), 1.71 – 1.65 (m, 2H), 1.61 (s, 4H), 1.51 (s, 5H). Physical and spectral data were in accordance with literature data.[14]



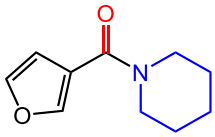
piperidin-1-yl(pyridin-4-yl)methanone (SI-21) was obtained from 4-bromopyridine hydrochloride using General Carbonylation Procedure A and quenched with 1M NaOH. The crude product was purified *via* flash column chromatography that was deactivated with 50% EtOAc/5% TEA/hexanes, then using a gradient of 60–95% EtOAc/hexanes (R_f 0.16 in 95% EtOAc/hexanes) yielding **SI-21** as a colorless oil (19.9 mg, 52%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.65 (dd, *J* = 4.5, 1.4 Hz, 2H), 7.24 (dd, *J* = 4.6, 1.4 Hz, 2H), 3.79 – 3.60 (m, 2H), 3.34 – 3.18 (m, 2H), 1.66 (br s, 4H), 1.49 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]



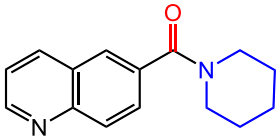
piperidin-1-yl(pyridin-3-yl)methanone (SI-22) was obtained from 3-bromopyridine using General Carbonylation Procedure A and quenched with 1M NaOH. The crude product was purified *via* flash column chromatography that was deactivated with 50% EtOAc/5% TEA/hexanes, then using a gradient of 50–90% EtOAc/hexanes (R_f 0.48 in 75% EtOAc/hexanes) yielding **SI-22** as a colorless oil (19.3 mg, 51%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 4.4 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.33 (dd, *J* = 7.7, 4.9 Hz, 1H), 3.69 (br s, 2H), 3.33 (br s, 2H), 1.67 (br s, 4H), 1.52 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]



piperidin-1-yl(pyridin-2-yl)methanone (SI-23) was obtained from 2-bromopyridine using General Carbonylation Procedure A and quenched with 1M NaOH. The crude product was purified *via* flash column chromatography using a gradient of 50–75% EtOAc/hexanes (R_f 0.28 in 75% EtOAc/hexanes) yielding **SI-23** as a yellow solid (27.7 mg, 73%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 3.7 Hz, 1H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.28 (dd, *J* = 7.3, 4.8 Hz, 1H), 3.70 (br s, 2H), 3.39 (br s, 0H), 1.65 (br s, 4H), 1.53 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]

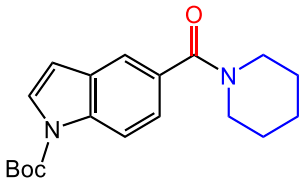


furan-3-yl(piperidin-1-yl)methanone (SI-24) was obtained from 3-bromofuran using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.22 in 30% EtOAc/hexanes) yielding **SI-24** as a yellow oil (27.6 mg, 77%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.65 (s, 1H), 7.38 (s, 1H), 6.50 (s, 1H), 3.61 (br s, 2H), 3.54 (br s, 2H), 1.70 – 1.61 (m, 2H), 1.57 (br s, 4H). Physical and spectral data were in accordance with literature data.[18]

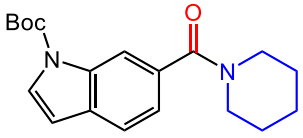


N-cyclohexylquinoline-6-carboxamide (SI-25) was obtained from 6-bromoquinoline using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and quenched with 1M NaOH. The crude product was purified *via* flash column chromatography using a gradient of 60–90% EtOAc/hexanes (R_f 0.28 in 90% EtOAc/hexanes) yielding **SI-25** as a

yellow oil (25.1 mg, 52%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.92 (s, 1H), 8.13 (dd, *J* = 32.7, 8.4 Hz, 2H), 7.86 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.42 (dd, *J* = 7.7, 3.8 Hz, 1H), 3.74 (br s, 2H), 3.35 (br s, 2H), 1.67 (br s, 4H), 1.51 (br s, 2H). Physical and spectral data were in accordance with literature data.[16]

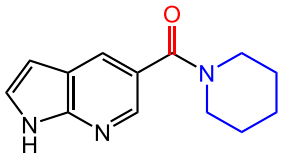


tert-butyl 5-(piperidine-1-carbonyl)-1H-indole-1-carboxylate (SI-26) was obtained from **26** using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.33 in 30% EtOAc/hexanes) yielding **SI-26** as a yellow oil (68.6 mg, >99%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.13 (s, 1H), 7.60 (s, 2H), 7.32 (d, J = 8.5 Hz, 1H), 6.56 (d, J = 3.4 Hz, 1H), 3.70 (br s, 2H), 3.35 (br s, 2H), 1.64 (s, 13H), 1.48 (br s, 2H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 170.9, 149.5, 135.5, 130.8, 130.3, 126.9, 123.1, 120.0, 114.9, 107.4, 84.1, 49.0, 43.3, 28.1, 26.6, 25.7, 24.6. **HRMS** (ESI) calculated for $[C_{19}H_{24}N_2O_3+H]^+$ 329.185969, found 329.1874.

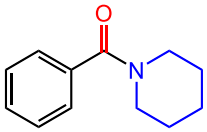


tert-butyl 6-(piperidine-1-carbonyl)-1H-indole-1-carboxylate (SI-27) was obtained from **27** using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using a gradient of 15–20% EtOAc/hexanes (R_f 0.20 in 20% EtOAc/hexanes) yielding **SI-27** as a colorless oil (54.7 mg, 83%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.21 (s, 1H), 7.63 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.25 (d, J = 7.4 Hz, 1H), 6.56 (s, 1H), 3.71 (br s, 2H), 3.38 (br s, 2H), 1.65 (s, 13H), 1.52 (br s, 2H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 171.0, 149.5, 134.7, 131.4, 127.3,

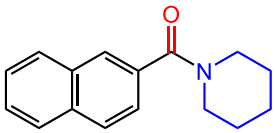
121.7, 121.0, 114.1, 84.1, 49.1, 43.4, 28.2, 26.6, 25.8, 24.7. **HRMS** (ESI) calculated for $[C_{19}H_{24}N_2O_3+H]^+$ 329.185969, found 329.1834.



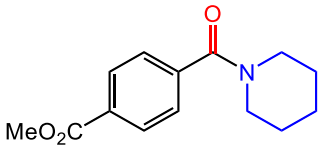
piperidin-1-yl(1H-pyrrolo[2,3-b]pyridin-5-yl)methanone (SI-28) was obtained from 5-bromo-1H-pyrrolo[2,3-b]pyridine using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and quenched with 1M NaOH. The crude product was purified *via* flash column chromatography using a gradient of 50–75% EtOAc/hexanes (R_f 0.17 in 75% EtOAc/hexanes) yielding **SI-28** as a tan solid (45.2 mg, 99%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 11.88 (s, 1H), 8.45 (s, 1H), 8.03 (d, J = 1.0 Hz, 1H), 7.41 (s, 1H), 6.59 – 6.47 (m, 1H), 3.74 (br s, 2H), 3.46 (br s, 2H), 1.68 (br s, 4H), 1.56 (br s, 2H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 169.6, 149.0, 141.5, 128.3, 126.9, 124.4, 119.8, 101.2, 49.3, 43.6, 26.7, 25.7, 24.6. **HRMS** (ESI) calculated for $[C_{13}H_{15}N_3O+H]^+$ 230.128789, found 230.1302.



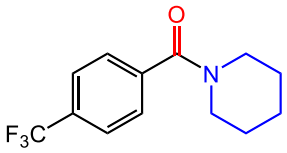
phenyl(piperidin-1-yl)methanone (SI-29) was obtained from chlorobenzene using General Carbonylation Procedure A with a 0.040 mmol $Co_2(CO)_8$ and 144 hours. The crude product was purified *via* flash column chromatography using a gradient of 20–25% EtOAc/hexanes (R_f 0.19 in 25% EtOAc/hexanes) yielding **SI-29** as a colorless oil (16.5 mg, 44%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.38 (s, 5H), 3.70 (br s, 2H), 3.33 (br s, 2H), 1.67 (br s, 4H), 1.50 (br s, 2H). Physical and spectral data were in accordance with literature data.[11]



naphthalen-2-yl(piperidin-1-yl)methanone (SI-30) was obtained from 2-chloronaphthalene using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 15–25% EtOAc/hexanes (R_f 0.27 in 25% EtOAc/hexanes) yielding **SI-30** as a white solid (38.5 mg, 80%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.85 (t, *J* = 8.2 Hz, 3H), 7.54 – 7.50 (m, 2H), 7.48 (dd, *J* = 8.4, 1.4 Hz, 1H), 3.76 (br s, 2H), 3.38 (br s, 2H), 1.69 (br s, 4H), 1.52 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]

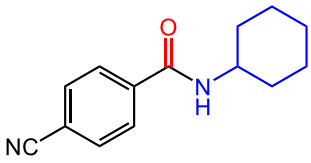


methyl 4-(piperidine-1-carbonyl)benzoate (SI-31) was obtained from methyl 4-chlorobenzoate using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and 370 nm irradiation. The crude product was purified *via* flash column chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.22 in 30% EtOAc/hexanes) yielding **SI-31** as a yellow solid (44.9 mg, 91%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 3.68 (br s, 2H), 3.25 (br s, 2H), 1.64 (br s, 4H), 1.47 (br s, 2H). Physical and spectral data were in accordance with literature data.[17]

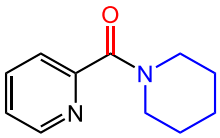


piperidin-1-yl(4-(trifluoromethyl)phenyl)methanone (SI-32) was obtained from 1-chloro-4-(trifluoromethyl)benzene using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$. The crude product was purified *via* flash column chromatography using

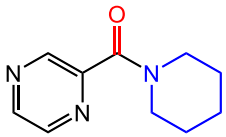
a gradient of 20–25% EtOAc/hexanes (R_f 0.31 in 25% EtOAc/hexanes) yielding **SI-32** as a white solid (30.1 mg, 59%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 3.71 (br s, 2H), 3.28 (br s, 2H), 1.67 (br s, 4H), 1.50 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]



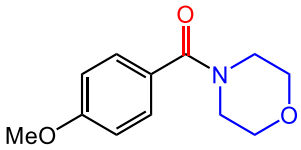
4-cyano-N-cyclohexylbenzamide (SI-33) was obtained from 4-chlorobenzonitrile using General Carbonylation Procedure A with 0.020 mmol $Co_2(CO)_8$ and 370 nm irradiation for 24 hours. The crude product was purified *via* flash column chromatography with fine-grade silica gel, using a gradient of 15–20% EtOAc/hexanes (R_f 0.19 in 20% EtOAc/hexanes) yielding **SI-33** as a white solid (19.5 mg, 43%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 6.04 (br s, 1H), 3.96 (dtq, *J* = 11.5, 8.1, 3.9 Hz, 1H), 2.03 (dd, *J* = 12.4, 3.1 Hz, 2H), 1.76 (dt, *J* = 13.3, 3.3 Hz, 2H), 1.72 – 1.62 (m, 1H), 1.49 – 1.34 (m, 2H), 1.32 – 1.15 (m, 3H). Physical and spectral data were in accordance with literature data.[14]



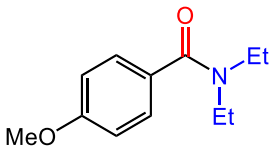
piperidin-1-yl(pyridin-2-yl)methanone (SI-34) was obtained from 2-chloropyridine using General Carbonylation Procedure A and quenched with 1M NaOH. The crude product was purified *via* flash column chromatography using a gradient of 50–75% EtOAc/hexanes (R_f 0.28 in 75% EtOAc/hexanes) yielding **SI-34** as a yellow solid (31.9 mg, 84%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 4.8 Hz, 1H), 7.74 (td, *J* = 7.7, 1.6 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 7.4, 5.0 Hz, 1H), 3.70 (br s, 2H), 3.42 – 3.31 (m, 2H), 1.64 (br s, 4H), 1.52 (br s, 2H). Physical and spectral data were in accordance with literature data.[14]



piperidin-1-yl(pyrazin-2-yl)methanone (SI-35) was obtained from 2-chloropyrazine using General Carbonylation Procedure A and quenched with 1M NaOH. The crude product was purified *via* flash column chromatography using a gradient of 30–70% EtOAc/hexanes (R_f 0.26 in 60% EtOAc/hexanes) yielding **SI-35** as a yellow oil (22.4 mg, 59%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 8.59 (d, *J* = 2.4 Hz, 1H), 8.55 – 8.49 (m, 1H), 3.73 (br s, 2H), 3.48 – 3.38 (m, 2H), 1.68 (br s, 4H), 1.58 (br s, 2H). Physical and spectral data were in accordance with literature data.[19]

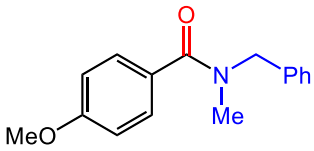


(4-methoxyphenyl)(morpholino)methanone (36) was obtained from General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 30–75% EtOAc/hexanes (R_f 0.21 in 50% EtOAc/hexanes) yielding **36** as a yellow oil (44.0 mg, 99%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.66 (br s, 8H). Physical and spectral data were in accordance with literature data.[20]

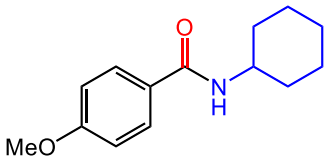


N,N-diethyl-4-methoxybenzamide (37) was obtained from General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 20–60% EtOAc/hexanes (R_f 0.43 in 50% EtOAc/hexanes) yielding **37** as a white solid (33.7 mg, 81%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.88

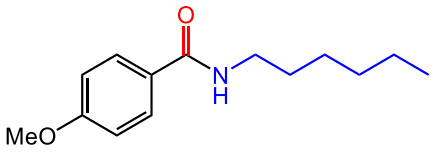
(d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 3.48 (br s, 2H), 3.30 (br s, 2H), 1.16 (br s, 6H). Physical and spectral data were in accordance with literature data.[21]



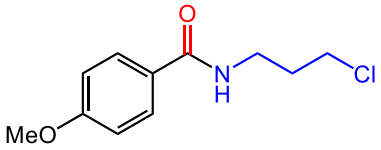
N-benzyl-4-methoxy-N-methylbenzamide (38) was obtained from General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 20–30% EtOAc/hexanes (R_f 0.23 in 30% EtOAc/hexanes) yielding **38** as a pink oil (41.4 mg, 81%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 3H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.19 (br s, 1H), 6.88 (br s, 2H), 4.73 (br s, 1H), 4.57 (br s, 1H), 3.80 (s, 3H), 2.95 (d, *J* = 48.7 Hz, 3H). Physical and spectral data were in accordance with literature data.[22]



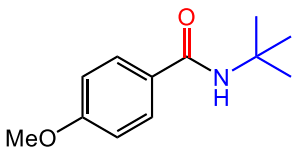
N-cyclohexyl-4-methoxybenzamide (39) was obtained from General Carbonylation Procedure A and was stopped after 24 hours. The crude product was washed with 1M NaOH and then purified *via* flash column chromatography using a gradient of 5–10% EtOAc/toluene (R_f 0.20 in 10% EtOAc/toluene) yielding **39** as a white solid (36.0 mg, 77%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.02 (s, 1H), 3.94 (ddp, *J* = 11.7, 8.0, 4.0 Hz, 1H), 3.82 (s, 3H), 2.08 – 1.93 (m, 2H), 1.73 (dt, *J* = 13.4, 3.4 Hz, 2H), 1.63 (dt, *J* = 12.8, 3.5 Hz, 1H), 1.46 – 1.32 (m, 2H), 1.30 – 1.11 (m, 3H). Physical and spectral data were in accordance with literature data.[21]



N-hexyl-4-methoxybenzamide (40) was obtained from General Carbonylation Procedure A and was stopped after 24 hours. The crude product was purified *via* flash column chromatography using a gradient of 5–15% EtOAc/toluene (R_f 0.33 in 15% EtOAc/toluene) yielding **40** as a white solid (35.1 mg, 75%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.35 (br s, 1H), 3.81 (s, 3H), 3.39 (q, *J* = 6.6 Hz, 2H), 1.57 (p, *J* = 7.2 Hz, 2H), 1.38 – 1.22 (m, 6H), 0.86 (t, *J* = 6.5 Hz, 3H). Physical and spectral data were in accordance with literature data.[21]

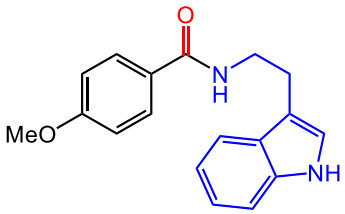


N-(3-chloropropyl)-4-methoxybenzamide (41) was obtained from General Carbonylation Procedure A and was stopped after 24 hours. The crude product was washed with 1M NaOH and then purified *via* flash column chromatography using a gradient of 25–30% EtOAc/hexanes (R_f 0.19 in 30% EtOAc/hexanes) yielding **41** as a yellow solid (21.9 mg, 48%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.73 (d, J = 5.7 Hz, 2H), 6.89 (d, J = 5.8 Hz, 2H), 6.56 (br s, 1H), 3.83 (s, 3H), 3.64 – 3.54 (m, 4H), 2.12 – 2.05 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 167.4, 162.3, 128.8, 126.7, 113.8, 55.5, 42.9, 37.6, 32.2. **HRMS** (ESI) calculated for $[C_{11}H_{14}ClNO_2+H]^+$ 228.079132, found 228.0796.

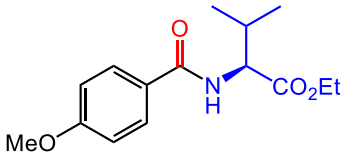


N-(tert-butyl)-4-methoxybenzamide (42) was obtained from General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a

gradient of 15–25% EtOAc/hexanes (R_f 0.46 in 25% EtOAc/hexanes) yielding **42** as a white solid (36.7 mg, 89%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.92 (s, 1H), 3.81 (s, 3H), 1.44 (s, 9H). Physical and spectral data were in accordance with literature data.[23]

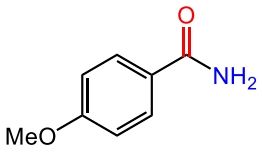


N-(2-(1H-indol-3-yl)ethyl)-4-methoxybenzamide (43) was obtained from General Carbonylation Procedure A and was stopped after 24 hours. The crude product was purified *via* flash column chromatography using a gradient of 30–50% EtOAc/hexanes (R_f 0.35 in 50% EtOAc/hexanes) yielding **43** as a yellow solid (55.0 mg, 93%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 8.67 (s, 1H), 7.65 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 6.99 (s, 1H), 6.84 (d, J = 8.7 Hz, 2H), 6.41 (s, 1H), 3.79 (s, 3H), 3.77 (q, J = 6.6 Hz, 2H), 3.06 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 167.3, 162.1, 136.5, 128.7, 127.4, 126.9, 122.4, 122.1, 119.4, 118.7, 113.7, 112.8, 111.5, 55.4, 40.4, 25.4. **HRMS** (ESI) calculated for $[C_{18}H_{18}N_2O_2+H]^+$ 295.144104, found 295.1454.



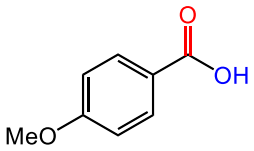
ethyl (4-methoxybenzoyl)-L-valinate (44) was obtained from **SI-44** using General Carbonylation Procedure A. The crude product was purified *via* flash column chromatography using a gradient of 5–10% EtOAc/toluene (R_f 0.32 in 10% EtOAc/toluene) yielding **44** as a white solid (42.7 mg, 76%). **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.76 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.61 (d, J = 8.3 Hz,

1H), 4.73 (dd, J = 8.6, 4.9 Hz, 1H), 4.21 (qq, J = 10.8, 7.1 Hz, 2H), 3.82 (s, 3H), 2.29 – 2.20 (m, 1H), 1.28 (t, J = 7.1 Hz, 3H), 0.97 (dd, J = 13.0, 6.9 Hz, 6H). **^{13}C NMR** (151 MHz, Chloroform-d) δ 172.4, 166.8, 162.4, 128.9, 126.5, 113.8, 61.4, 57.4, 55.5, 31.7, 19.1, 18.0, 14.3. **HRMS** (ESI) calculated for $[C_{15}H_{21}NO_4+H]^+$ 280.154335, found 280.1560.

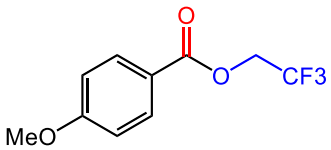


4-methoxybenzamide (45) was obtained from General Carbonylation Procedure A in the presence of 4 Å molecular sieves (ca. 50 mg) with $Co_2(CO)_8$ (6.8 mg, 0.020 mmol) and using ammonium carbamate (31.2 mg, 0.40 mmol) in place of the amine. The crude product was purified *via* flash column chromatography using a gradient of 50–75% EtOAc/hexanes (R_f 0.16 in 60% EtOAc/hexanes) yielding **45** as a white solid (13.9 mg, 46%). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.01 (br s, 1H), 5.80 (br s, 1H), 3.86 (s, 3H). Physical and spectral data were in accordance with literature data.[24]

Cobalt-Catalyzed Alkoxycarbonylations



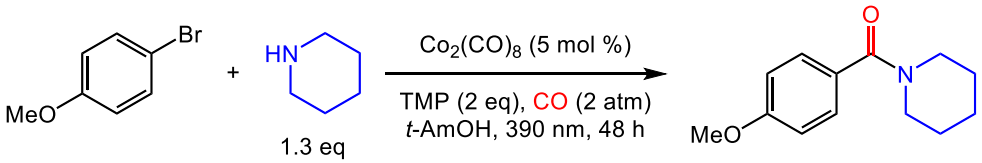
4-methoxybenzoic acid (46): In a glovebox under an argon atmosphere, $K[Co(CO)_4]$ (4.2 mg, 0.020 mmol) was combined with KOH (45 mg, 0.80 mmol), TMP (68 µL, 0.40 mmol), and *t*-amyl alcohol (0.5 mL) in an Ace Glass pressure tube. The vessel was sealed with a septa and Teflon tape and removed from the glovebox. 4-bromoanisole (25 µL, 0.20 mmol) was then added, and the septa was quickly replaced by a Swagelok connector cap. The tube was pressurized inside a fume hood with closed sashes with 5 atm CO, purged 5 times with CO to replace argon, set to 2 atm and stirred for 48 hours under irradiation at 390 nm. The reaction mixture was depressurized; 3 mL of EtOAc and 3 mL of 1M HCl were added. The mixture was extracted with EtOAc (3 x 1 mL), and the combined organic layers were allowed to sit open to air for two hours to decompose the cobalt complex as indicated by a color change from yellow to colorless. The combined organic layers were filtered through a plug of SiO_2, eluting with EtOAc, and concentrated under reduced pressure. The crude product was purified *via* recrystallization with toluene to yield **46** as a white solid (25.0 mg, 82%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H). Physical and spectral data were in accordance with literature data.[25]



2,2,2-trifluoroethyl 4-methoxybenzoate (47): In a glovebox under an argon atmosphere, $Ph_3Si[Co(CO)_4]$ (8.6 mg, 0.020 mmol) was combined with 2,2,2-trifluoroethanol (29 µL, 0.40 mmol), TMP (68 µL, 0.40 mmol), and *t*-amyl alcohol (0.5 mL) in an Ace Glass pressure tube. The vessel was sealed with a septa and Teflon tape and removed from the glovebox. The 4-bromoanisole (25 µL, 0.20 mmol) was then added,

and the septa was quickly replaced by a Swagelok connector cap. The tube was pressurized inside a fume hood with closed sashes with 5 atm CO, purged 5 times with CO to replace argon, set to 2 atm and stirred for 48 hours under irradiation at 390 nm. The reaction mixture was depressurized; 3 mL of EtOAc and 3 mL of 1M HCl were added. The mixture was extracted with EtOAc (3 x 1 mL), and the combined organic layers were allowed to sit open to air for two hours to decompose the cobalt complex as indicated by a color change from yellow to colorless. The combined organic layers were filtered through a plug of SiO_2, eluting with EtOAc, and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography using a gradient of 1–2.5% EtOAc/hexanes (R_f 0.19 in 2.5% EtOAc/toluene) yielding **47** as a yellow oil (32.1 mg, 69%). **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.67 (q, *J* = 8.5 Hz, 2H), 3.87 (s, 3H). Physical and spectral data were in accordance with literature data.[26]

Gram-Scale Aminocarbonylation



In a glovebox under an argon atmosphere, $Co_2(CO)_8$ (91.4 mg, 0.27 mmol) was combined with piperidine (0.69 mL, 6.95 mmol), TMP (1.80 mL, 10.7 mmol), and *t*-amyl alcohol (13.4 mL) in a 100 mL Ace Glass pressure tube. The vessel was sealed with a septa and Teflon tape and removed from the glovebox. 4-bromoanisole (0.67 mL, 1.0 g, 5.35 mmol) was then added, and the septa was quickly replaced by a Swagelok connector cap. The tube was pressurized inside a fume hood with closed sashes with 5 atm CO, purged 5 times with CO to replace argon, set to 2 atm and stirred for 48 hours under irradiation at 390 nm. The reaction mixture was depressurized; 50 mL of EtOAc and 50 mL of 1M HCl were added. The mixture was extracted with EtOAc (3 x 25 mL), and the combined organic layers were allowed to sit open to air for four hours to decompose the cobalt complex as indicated by a color change from yellow to colorless. The combined organic layers were filtered through a plug of SiO_2, eluting with EtOAc, and concentrated under reduced pressure. The crude product was purified *via* flash column chromatography using a gradient of 20–50% EtOAc/hexanes (R_f 0.41 in 50% EtOAc/hexanes) yielding **SI-1** as a colorless oil (1.13 g, 96%). Physical and spectral data were in accordance with literature data.[11]

UV-Vis Titration of $K[Co(CO)_4]$ with bromobenzene

The electron donor-acceptor complex was investigated by UV-Vis absorption spectra. Bromobenzene solution in THF (2.0 mM) was titrated into a solution with constant concentration of 10 μM $K[Co(CO)_4]$ and the change in the absorbance, compared to $K[Co(CO)_4]$ with no bromobenzene, was recorded (Table S1). The changes in absorbance were fit using a nonlinear modified Benesi–Hildebrand equilibrium model that was previously used to determine equilibrium constants of ion pairing.[27] These results are represented in Figure S1 and have been used to determine a binding constant of 3.31 $x10^5$ M^{-1} at 325 nm.

Table S1. K[Co(CO)4] and Bromobenzene association by UV-Vis

[PhBr] (M)	Δ Absorbance
0	0
2.01×10^{-6}	0.017
4.03×10^{-6}	0.505
6.04×10^{-6}	0.930
8.05×10^{-6}	1.274
10.1×10^{-6}	1.558
20.1×10^{-6}	1.840
50.3×10^{-6}	2.098
90.6×10^{-6}	2.278
151×10^{-6}	2.420

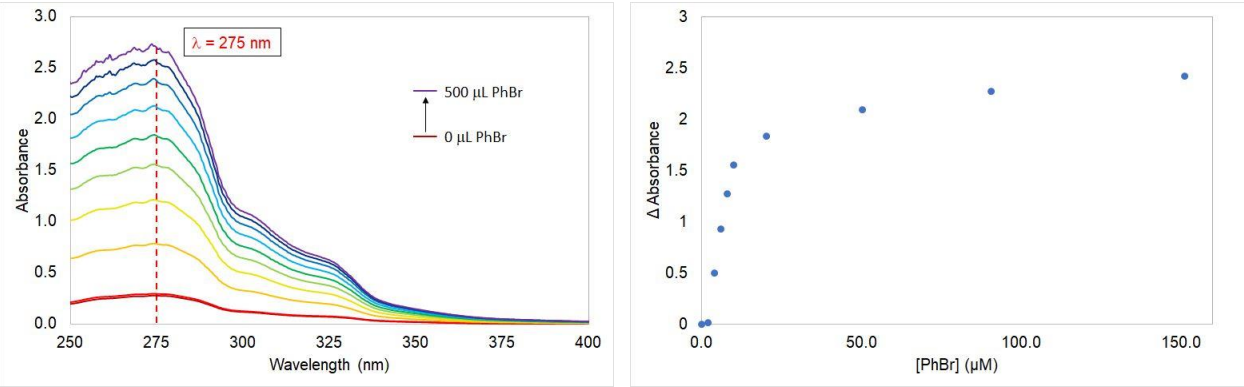


Figure S1. Absorption spectra of bromobenzene titration (left), and changes in absorbance monitored at 275 nm as a function of concentration of bromobenzene (right).

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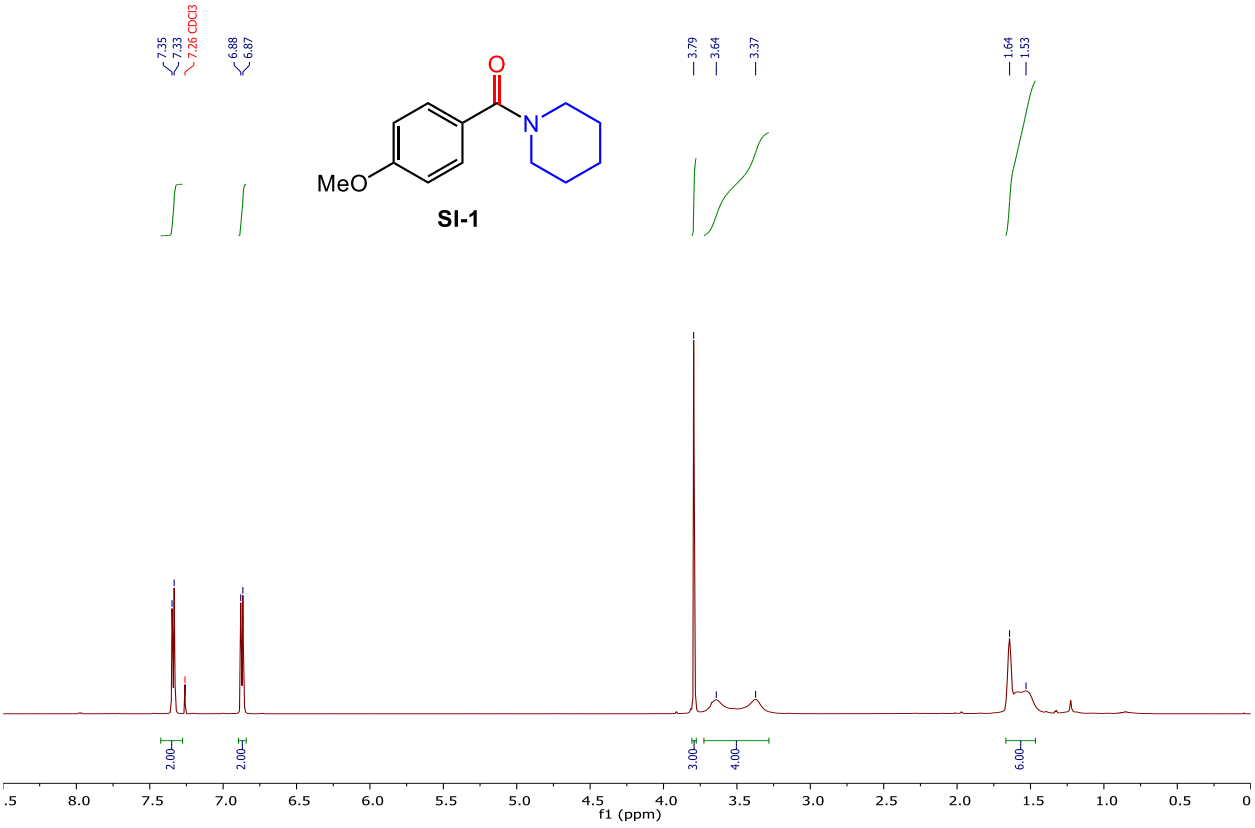
^{1}H and ^{13}C NMR Spectra



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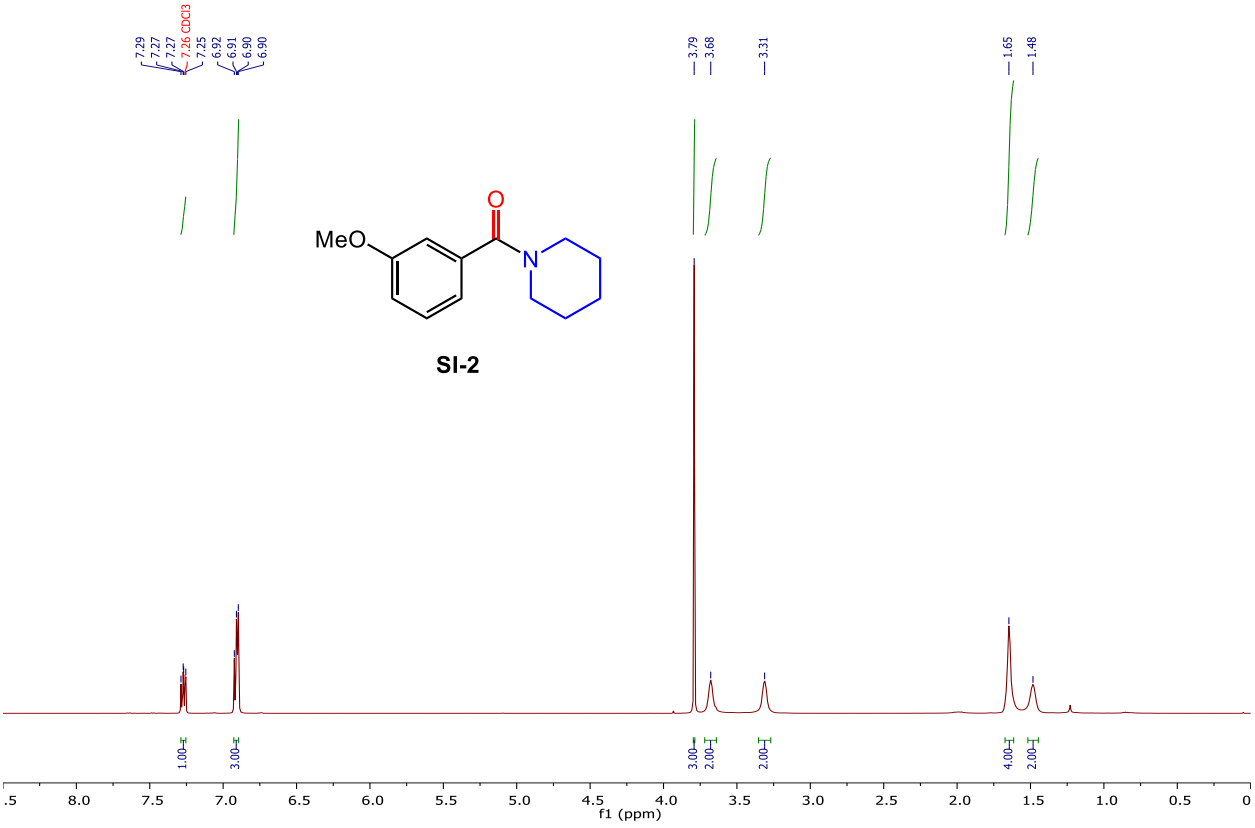

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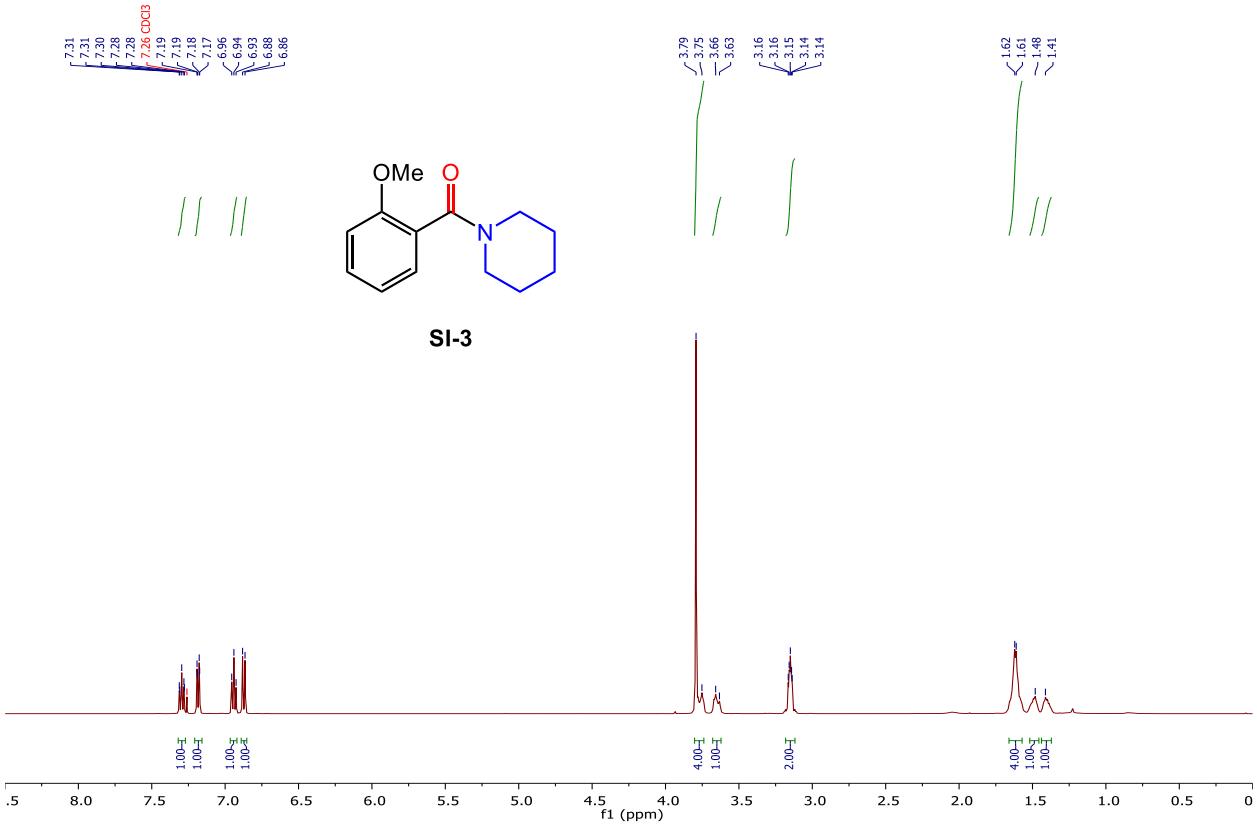
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7.19
7.18
7.17
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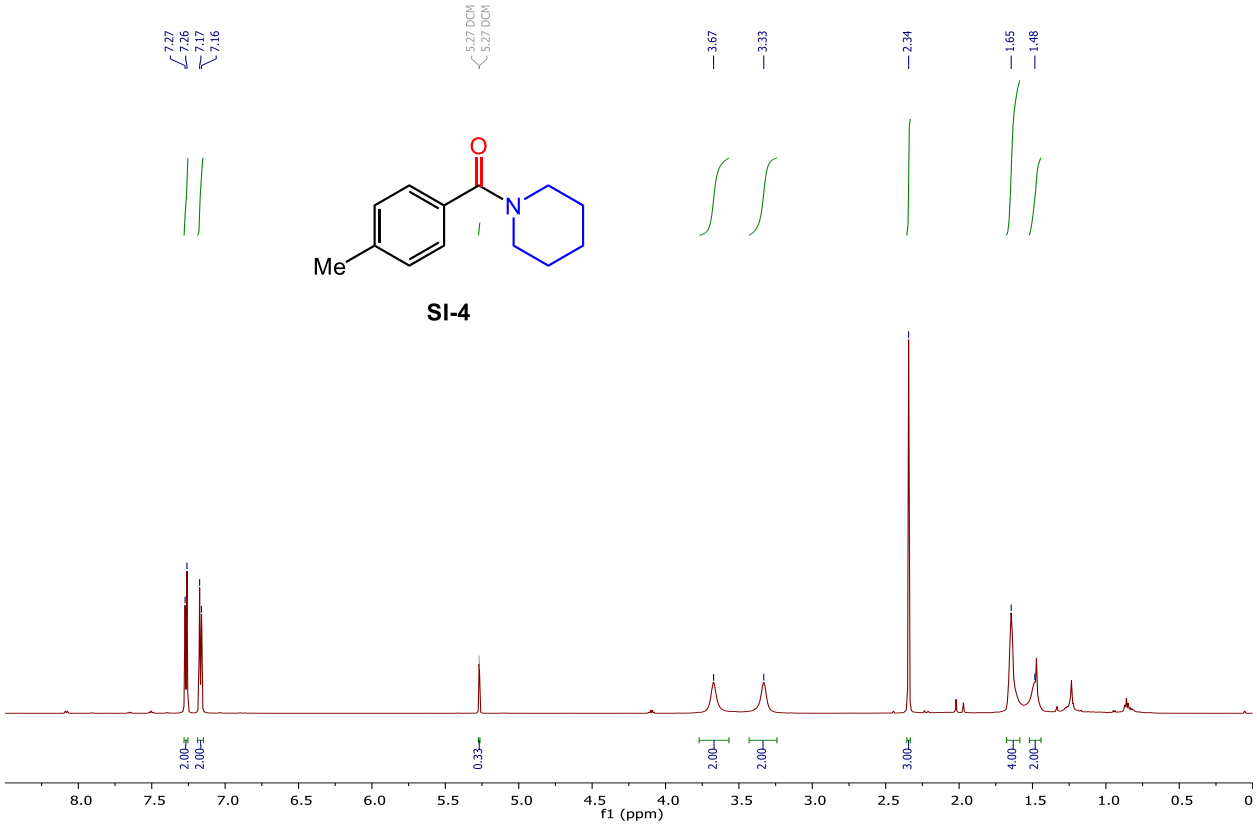
6.94
6.93
6.88
6.86
3.79
3.75
3.66
3.63
3.16
3.16
3.15
3.14
3.14
1.62
1.61
1.48
1.41
OMe
O
N
1.00
1.00
1.00
1.00
4.00
1.00
2.00
4.00
1.00
1.00
f1 (ppm)

SI-3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7.26
7.17
7.16
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5.27 DCM
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3.33
2.34
1.65
1.48
O
N
Me
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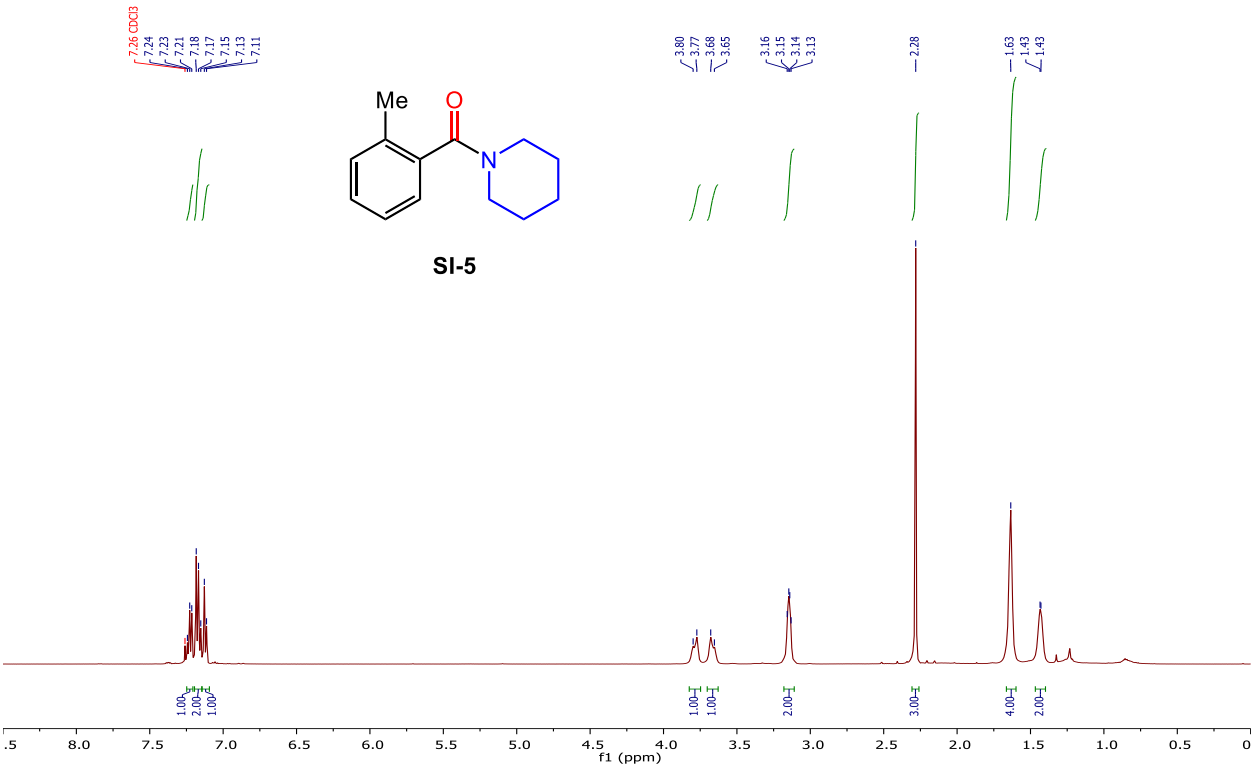
2.00
0.33
2.00
2.00
3.00
4.00
2.00
f1 (ppm)

SI-4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7.23
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7.17
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7.11
3.80
3.77
3.68
3.65
3.16
3.15
3.14
3.13
2.28
1.63
1.43
1.43
Me
O
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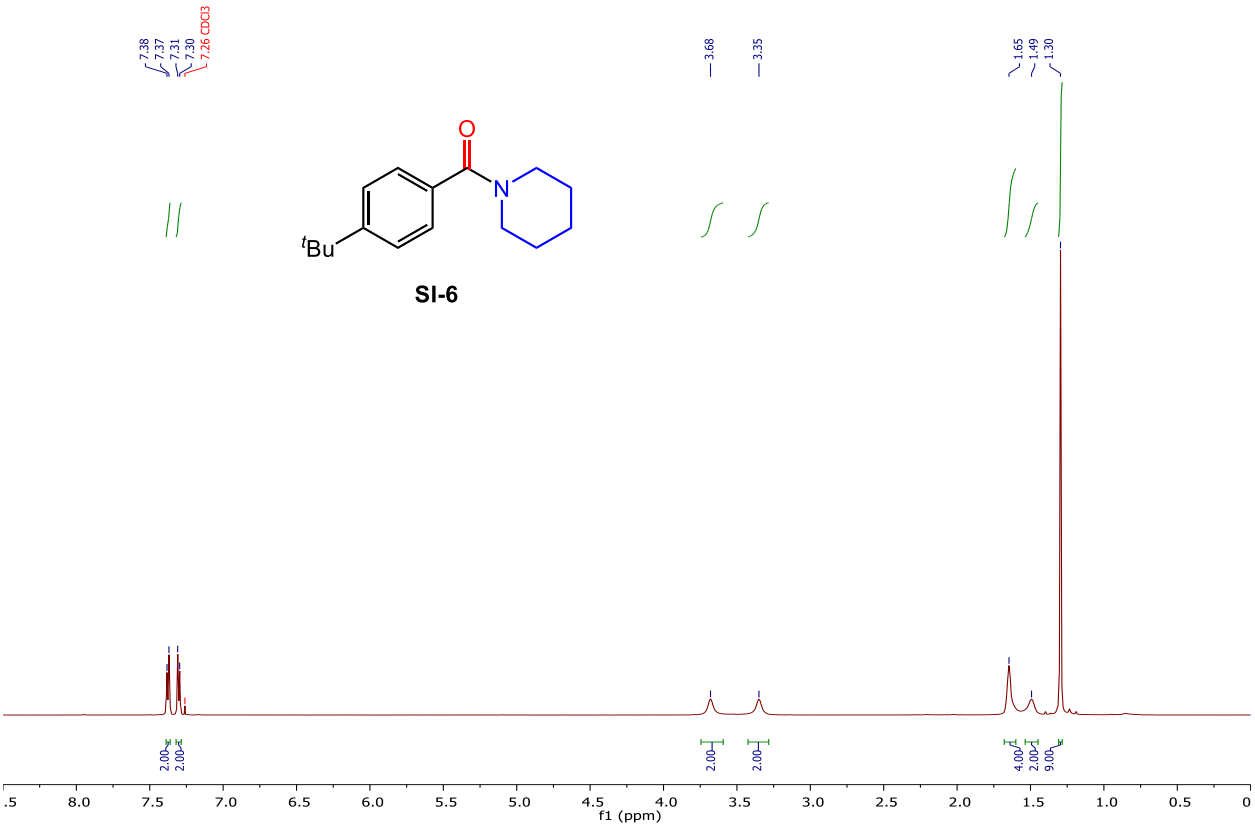
1.00
1.00
1.00
2.00
3.00
4.00
2.00
f1 (ppm)

SI-5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7.30
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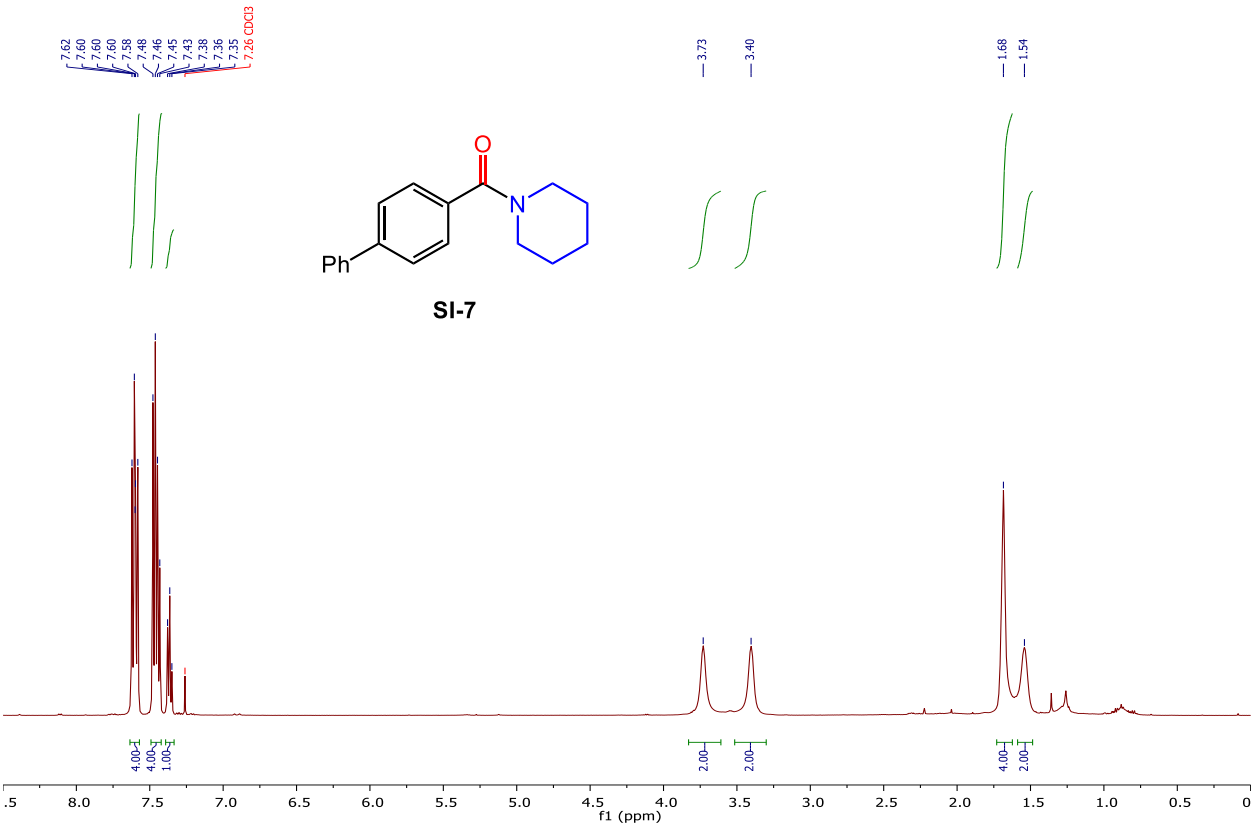
3.35
1.65
1.49
1.30
O
N
tBu
2.00
2.00
2.00
2.00
4.00
2.00
9.00
f1 (ppm)

SI-6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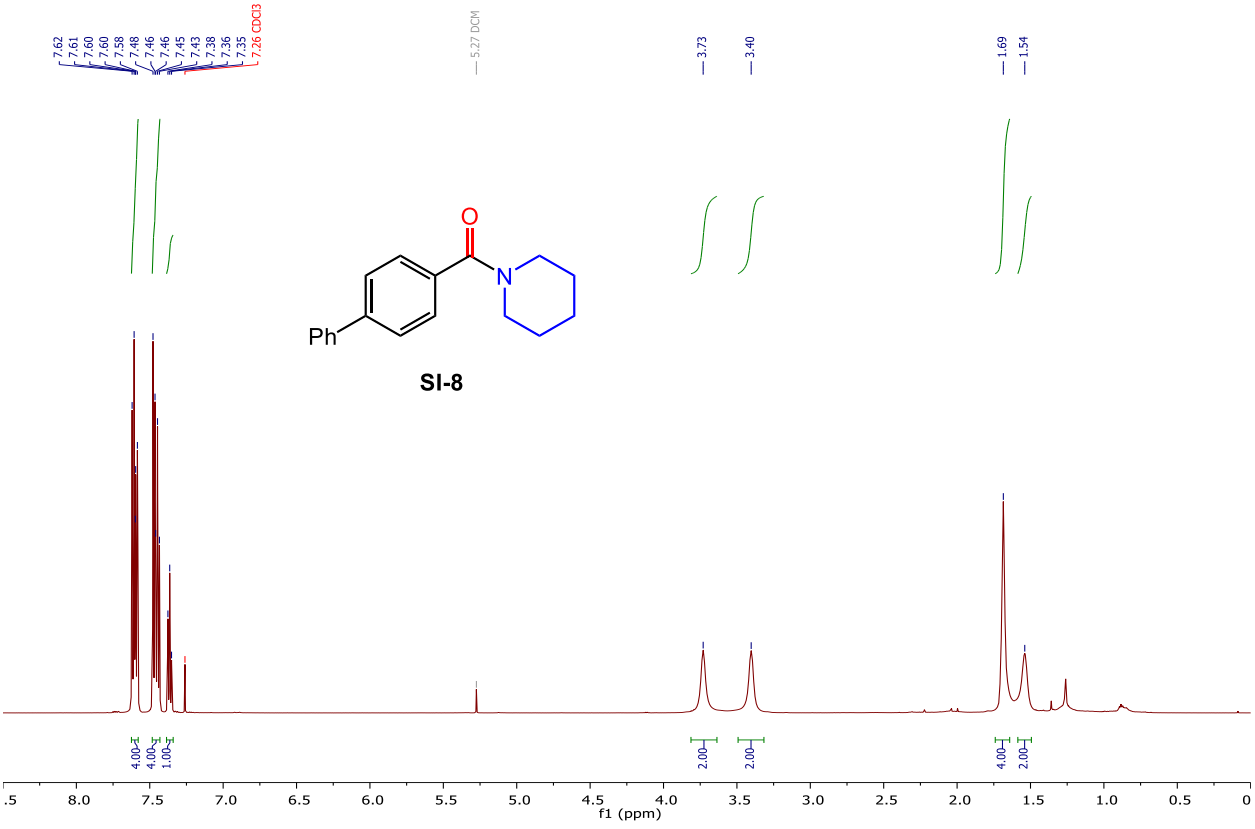
7.45
7.43
7.38
7.36
7.35
7.26 CDCl3
3.73
3.40
1.68
1.54
O
N
Ph
4.00
4.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

SI-7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7.46
7.45
7.43
7.38
7.36
7.35
7.26 CDCl3
5.27 DCM
3.73
3.40
1.69
1.54
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N
Ph
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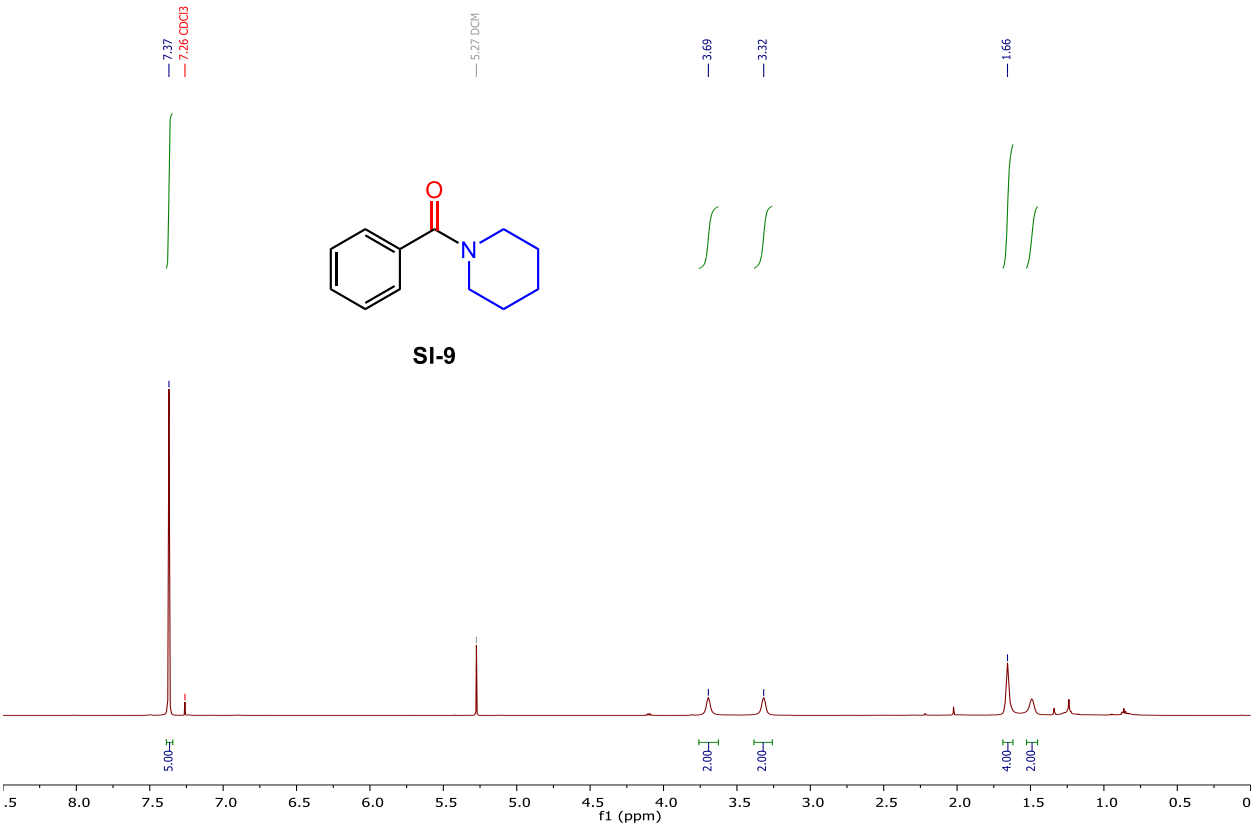
4.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

SI-8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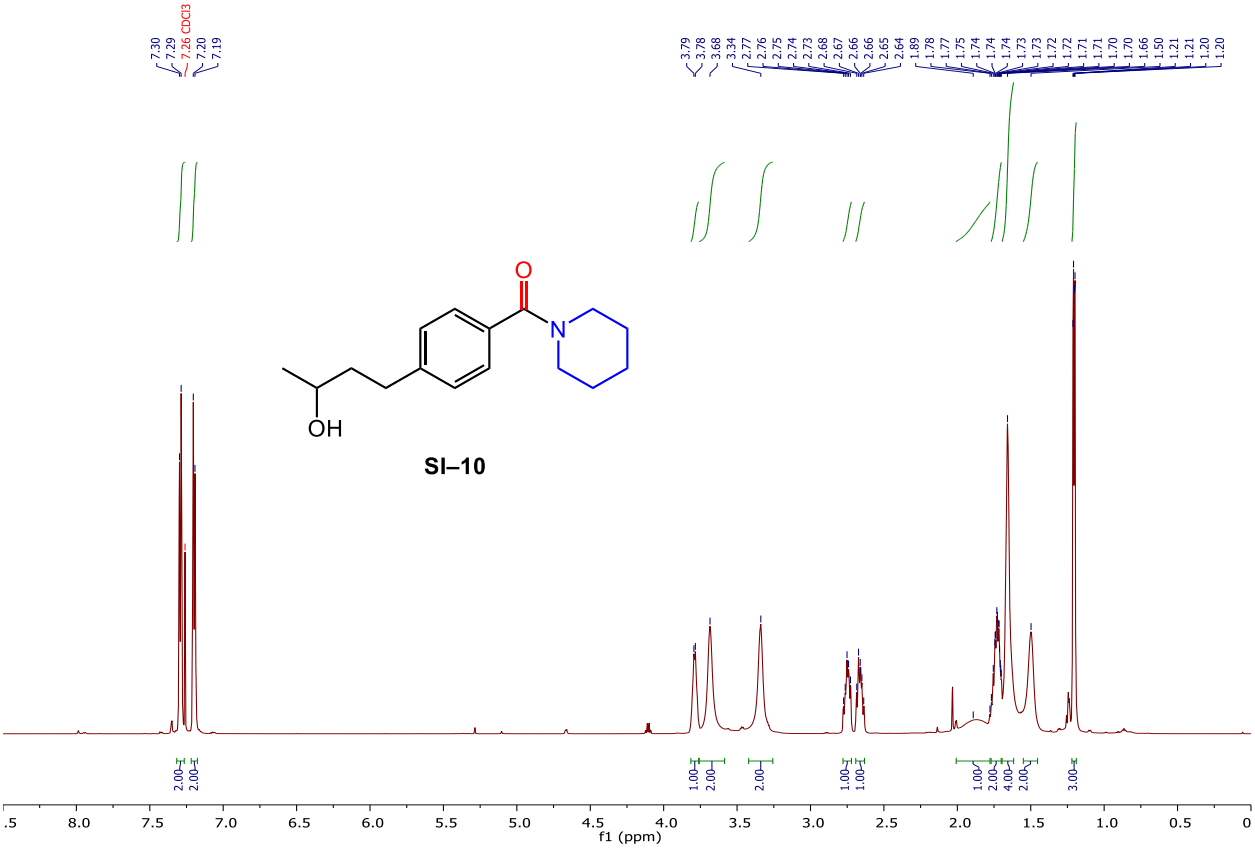
O
N
5.00
2.00
2.00
4.00
2.00
f1 (ppm)

SI-9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7.20
7.19
O
N
OH
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2.00
1.00
2.00
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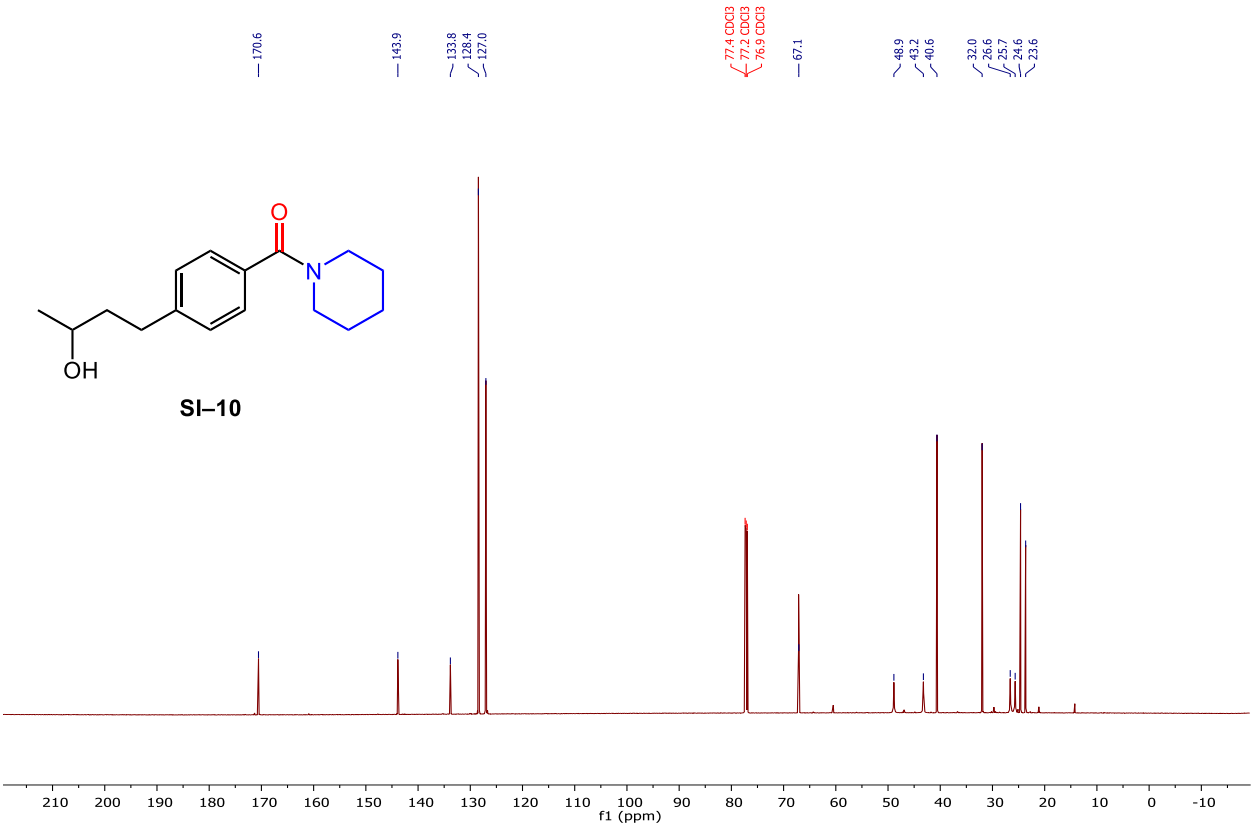
4.00
2.00
3.00
f1 (ppm)

SI–10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127.0
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77.2 CDCl3
76.9 CDCl3
67.1
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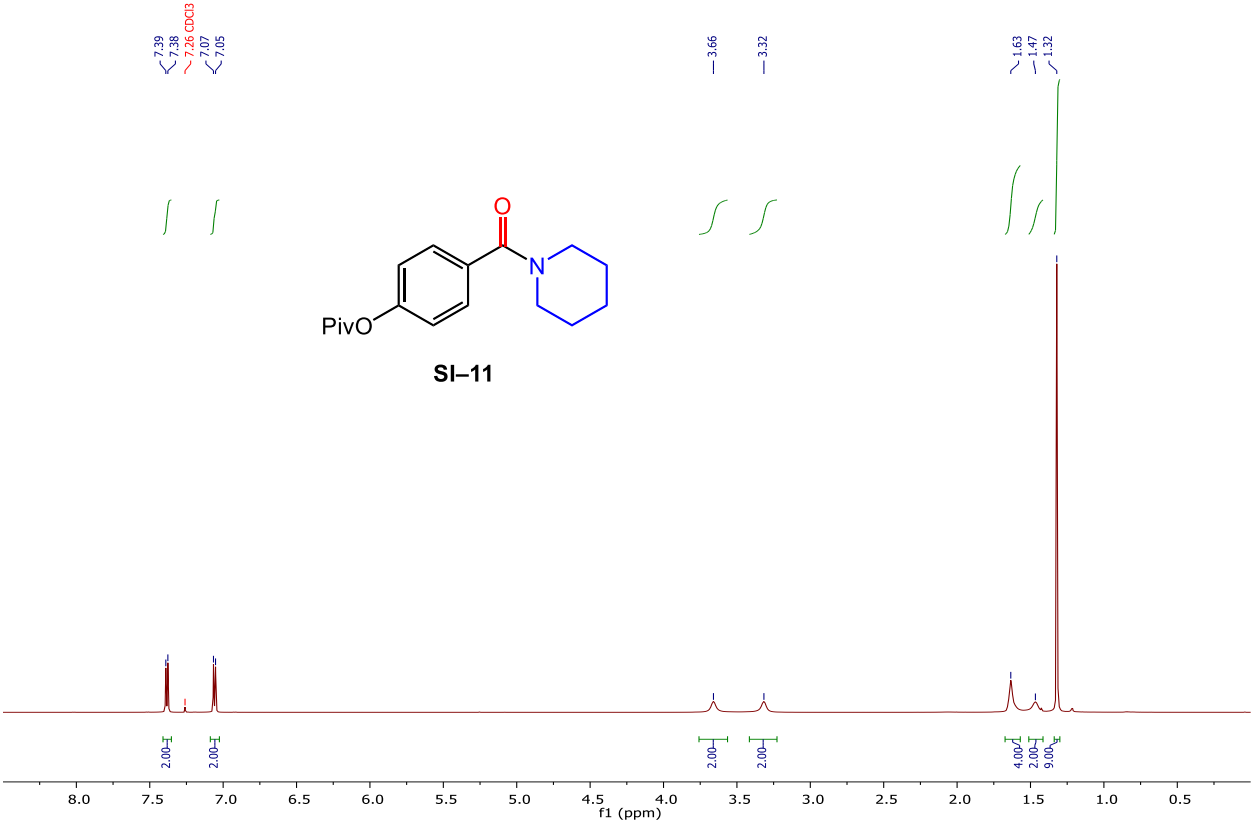
43.2
40.6
32.0
26.6
25.7
24.6
23.6
O
N
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

SI–10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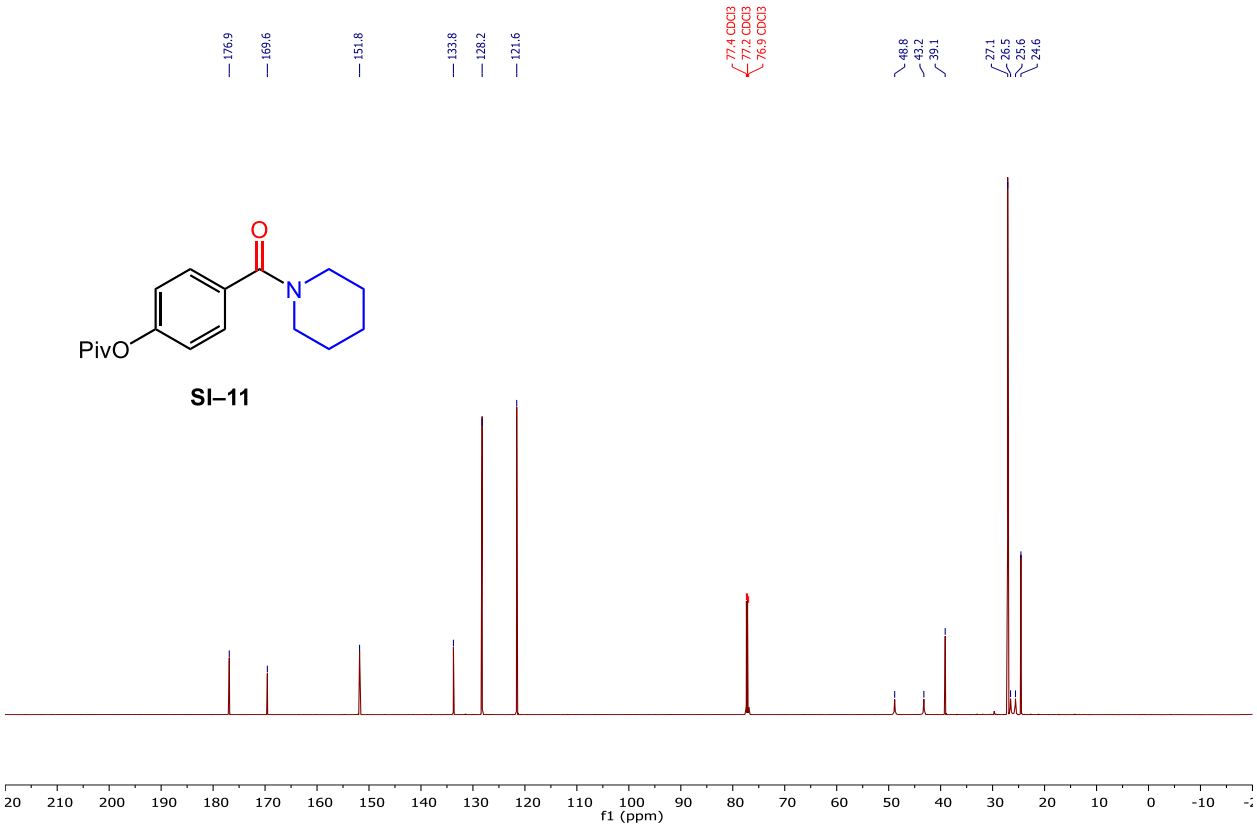
7.38
7.26 CDCl3
7.07
7.05
3.66
3.32
1.63
1.47
1.32
O
N
PivO
2.00
2.00
2.00
2.00
4.00
2.00
9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

SI–11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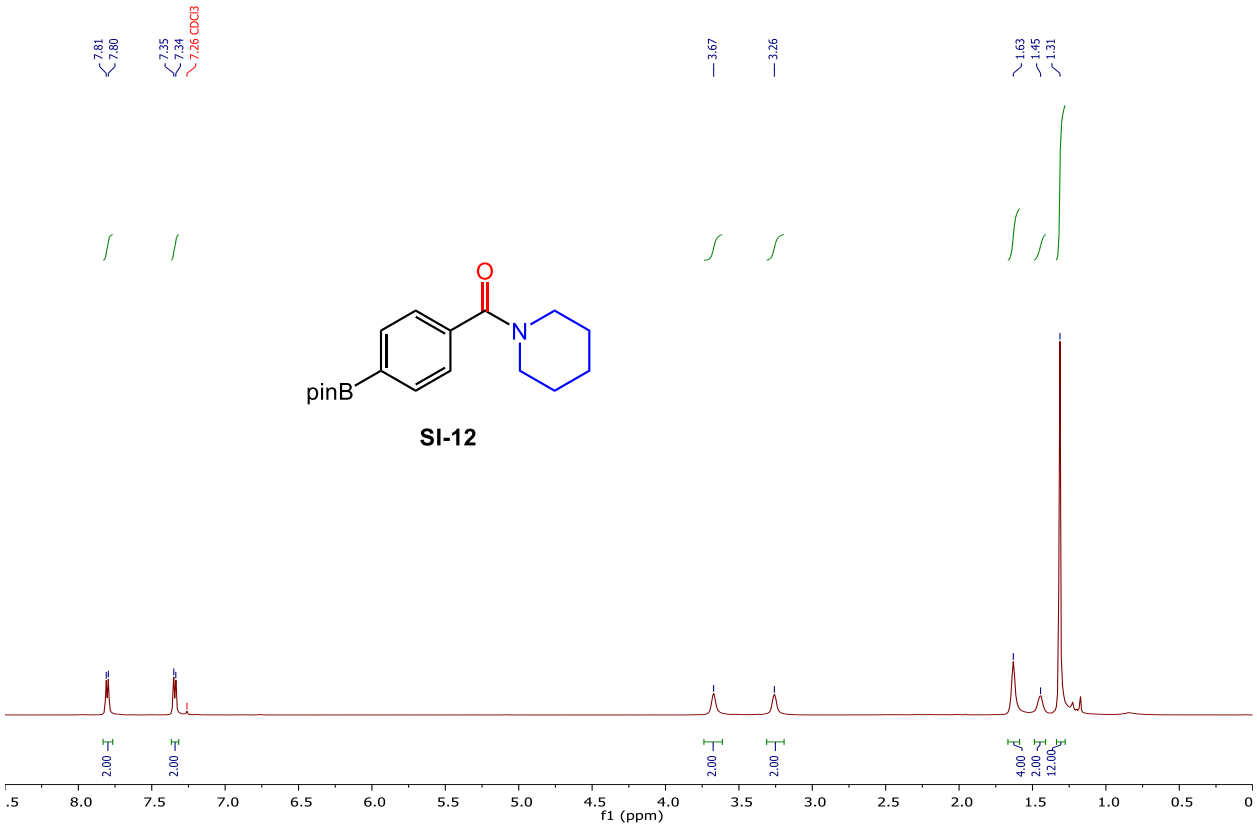
169.6
151.8
133.8
128.2
121.6
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
48.8
43.2
39.1
27.1
26.5
25.6
24.6
O
N
PivO
f1 (ppm)

SI–11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7.34
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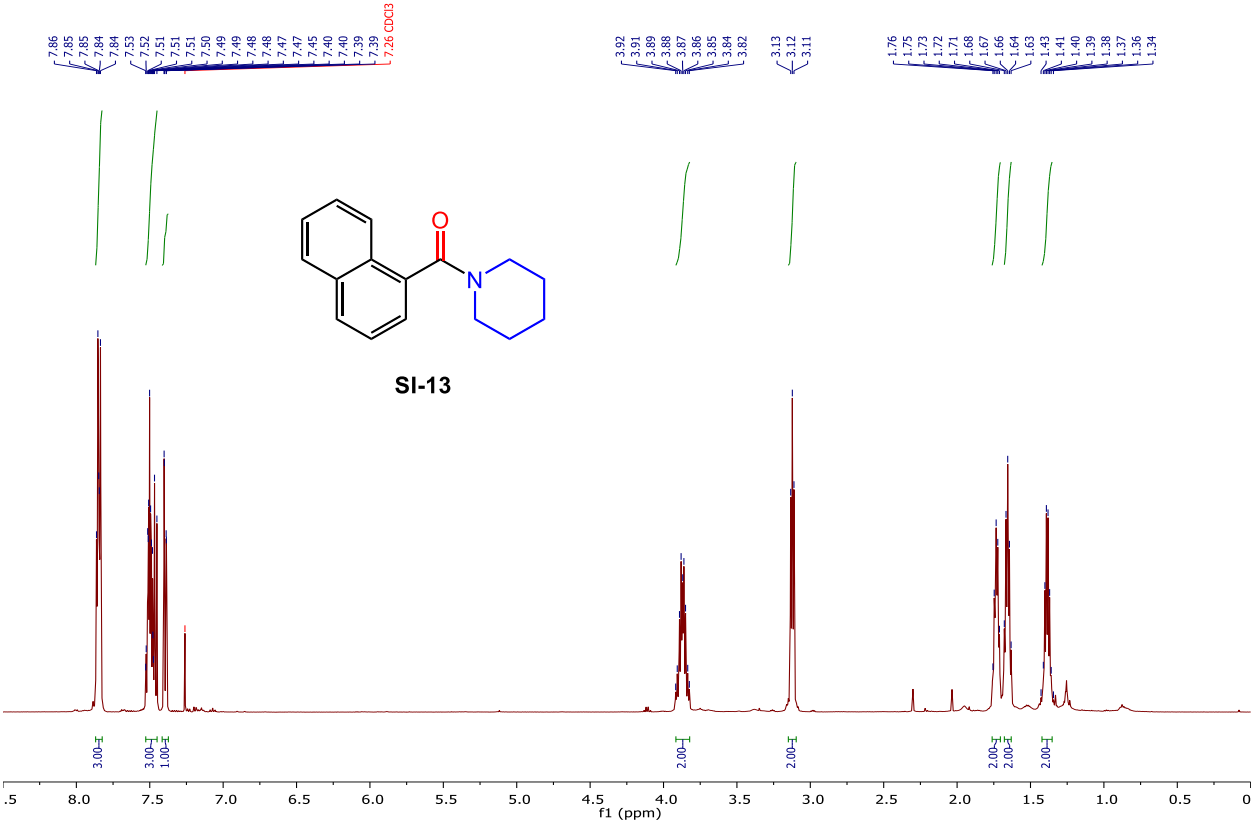
3.67
3.26
1.63
1.45
1.31
O
N
pinB
2.00
2.00
2.00
2.00
4.00
2.00
12.00
f1 (ppm)

SI-12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7.53
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.45
7.40
7.40
7.39
7.26 CDCl3
3.92
3.91
3.89
3.88
3.87
3.86
3.85
3.84
3.82
3.13
3.12
3.11
1.76
1.75
1.73
1.72
1.71
1.68
1.67
1.66
1.64
1.63
1.43
1.41
1.40
1.39
1.38
1.37
1.36
1.34
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3.00
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2.00
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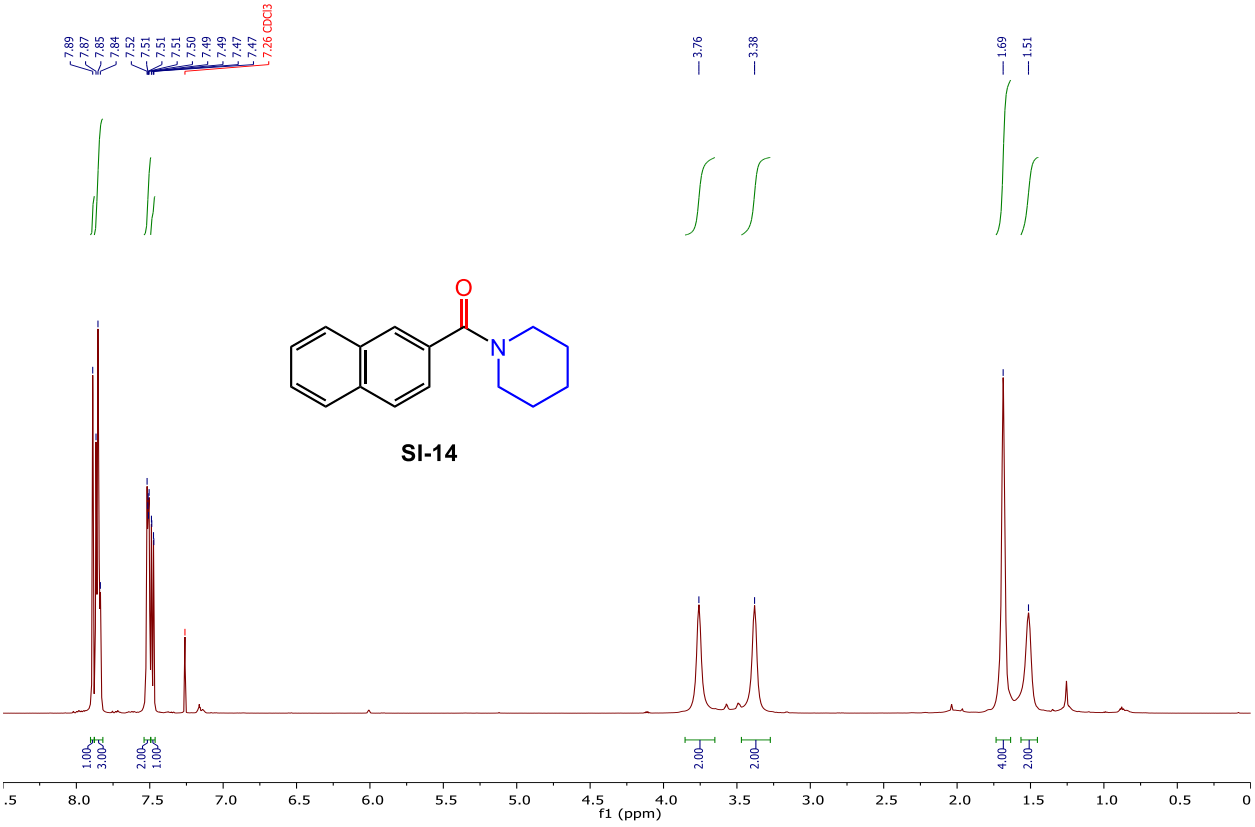
2.00
2.00
2.00
f1 (ppm)

SI-13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7.50
7.49
7.49
7.47
7.47
7.26 CDCl3
3.76
3.38
1.69
1.51
O
N
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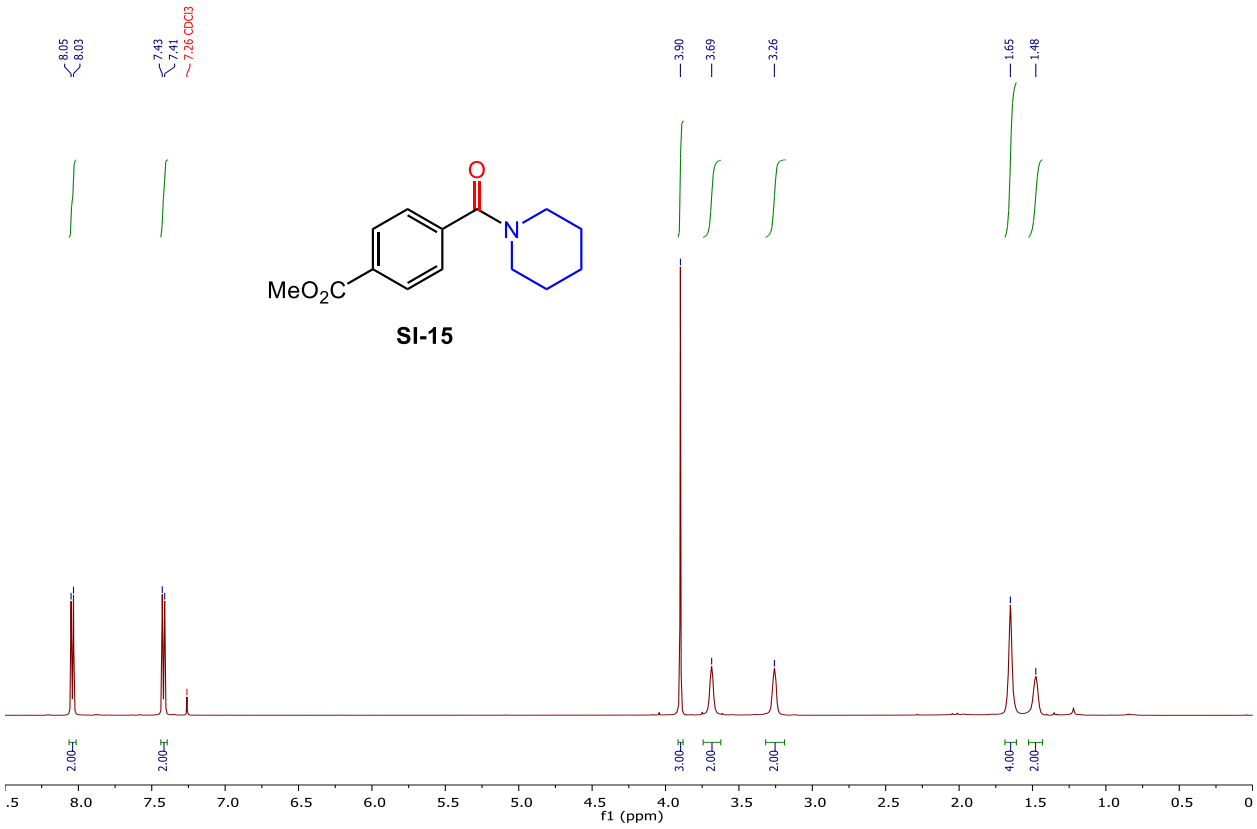
3.00
2.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

SI-14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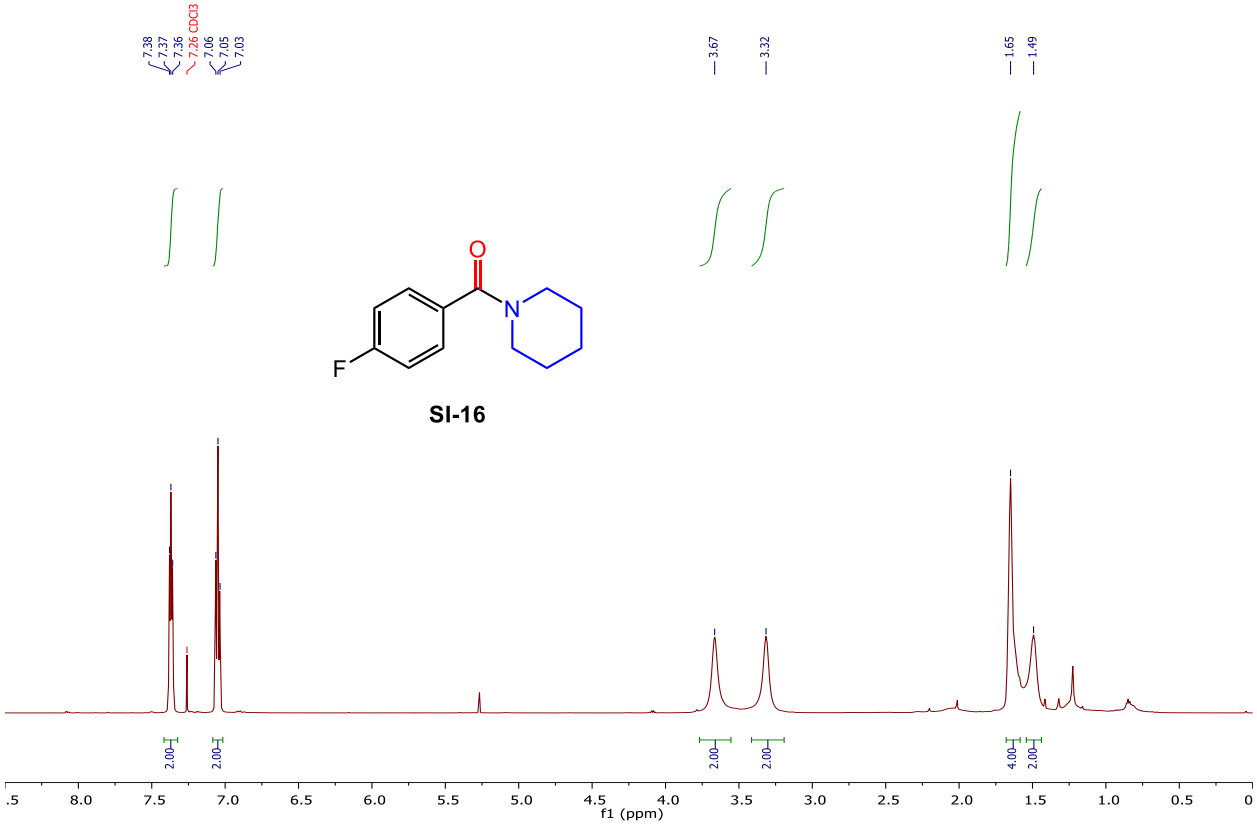
8.03
7.43
7.41
7.26 CDCl3
3.90
3.69
3.26
1.65
1.48
O
N
MeO2C
2.00
2.00
3.00
2.00
2.00
4.00
2.00
f1 (ppm)

SI-15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7.03
3.67
3.32
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1.49
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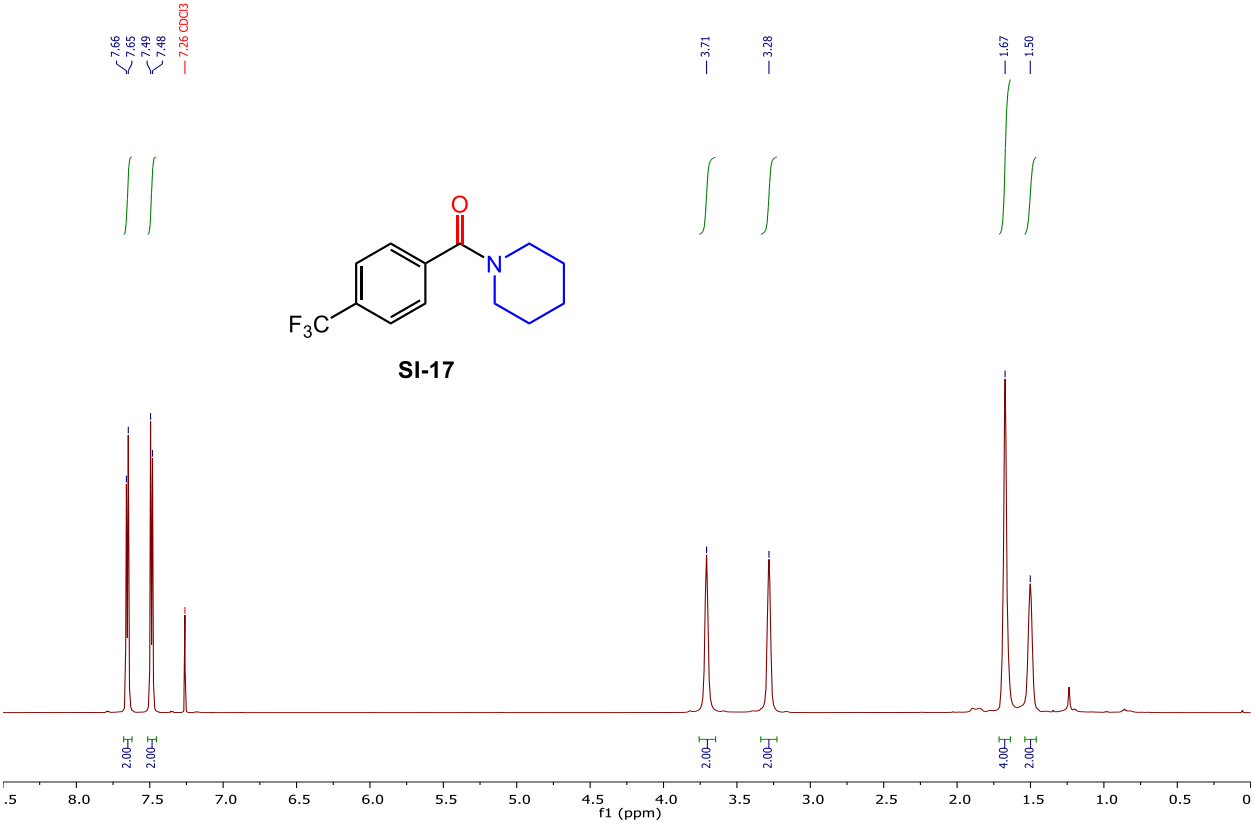
2.00
4.00
2.00
f1 (ppm)

SI-16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7.49
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N
F3C
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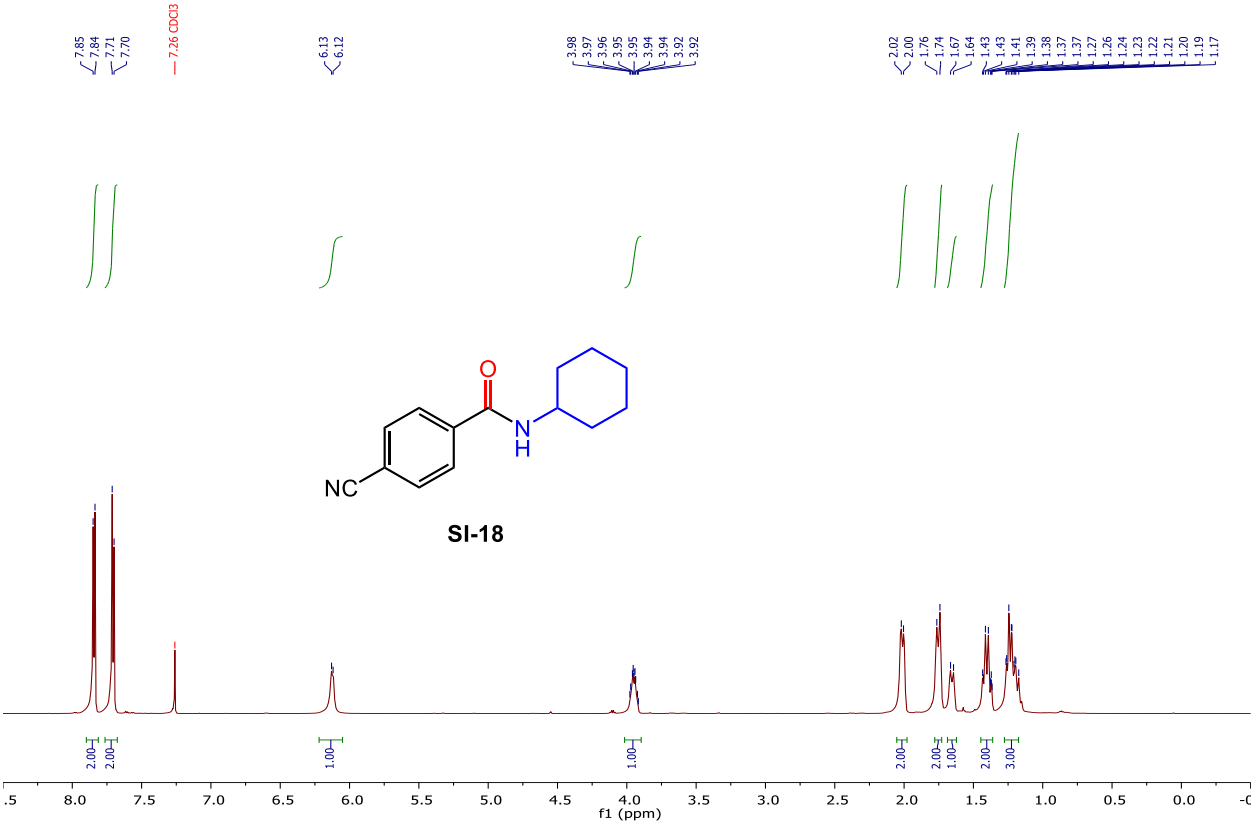
2.00
4.00
2.00
f1 (ppm)

SI-17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3.97
3.96
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3.95
3.94
3.94
3.92
3.92
2.02
2.00
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1.74
1.67
1.64
1.43
1.43
1.41
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1.38
1.37
1.37
1.27
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1.24
1.23
1.22
1.21
1.20
1.19
1.17
O
N
H
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1.00
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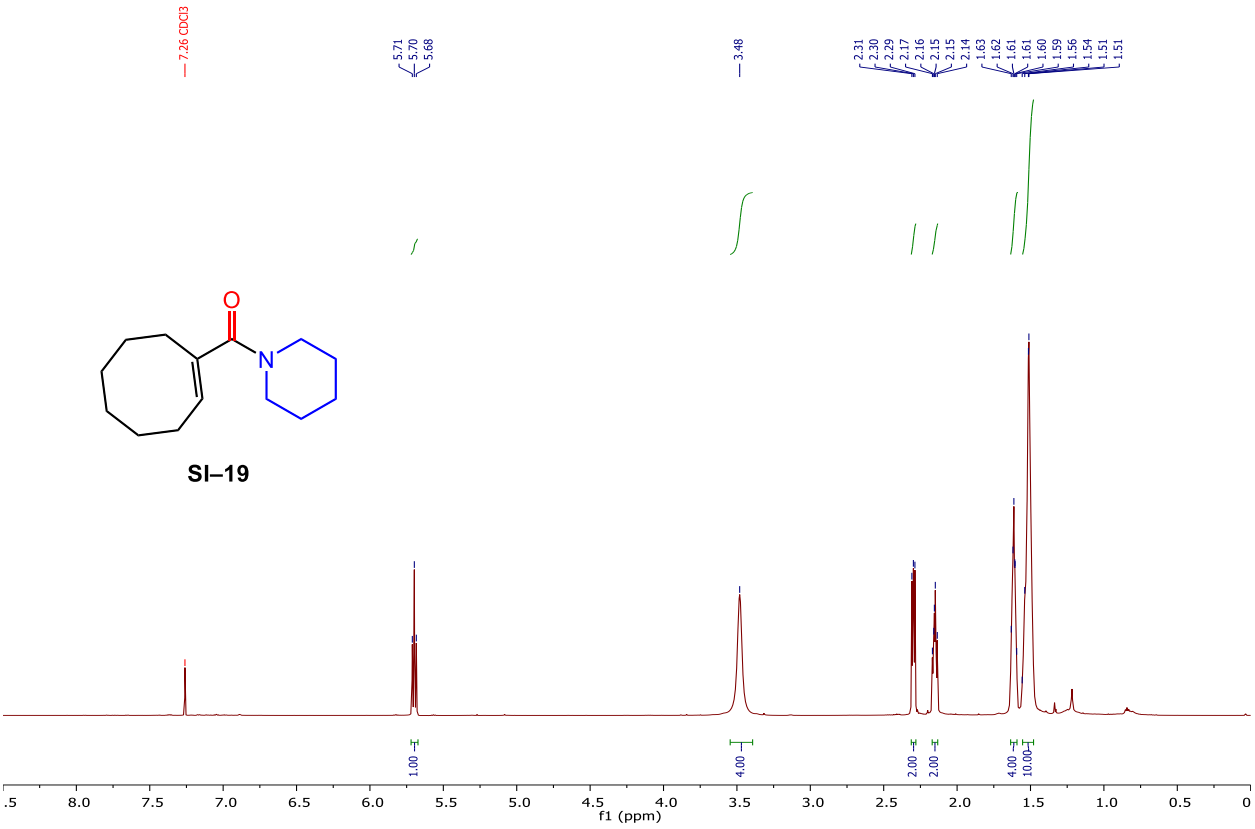
2.00
1.00
2.00
3.00
f1 (ppm)

SI-18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2.17
2.16
2.15
2.15
2.14
1.63
1.62
1.61
1.61
1.60
1.59
1.56
1.54
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N
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2.00
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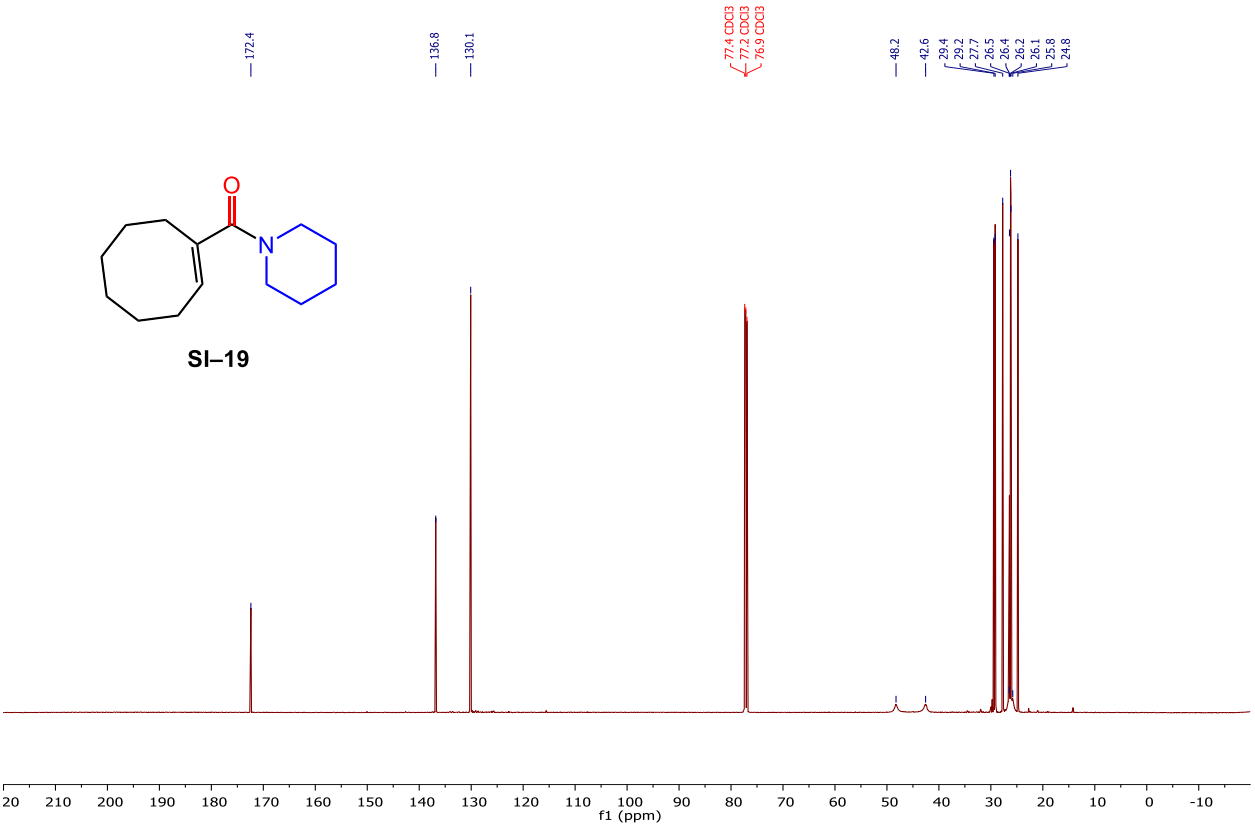
4.00
10.00
f1 (ppm)

SI–19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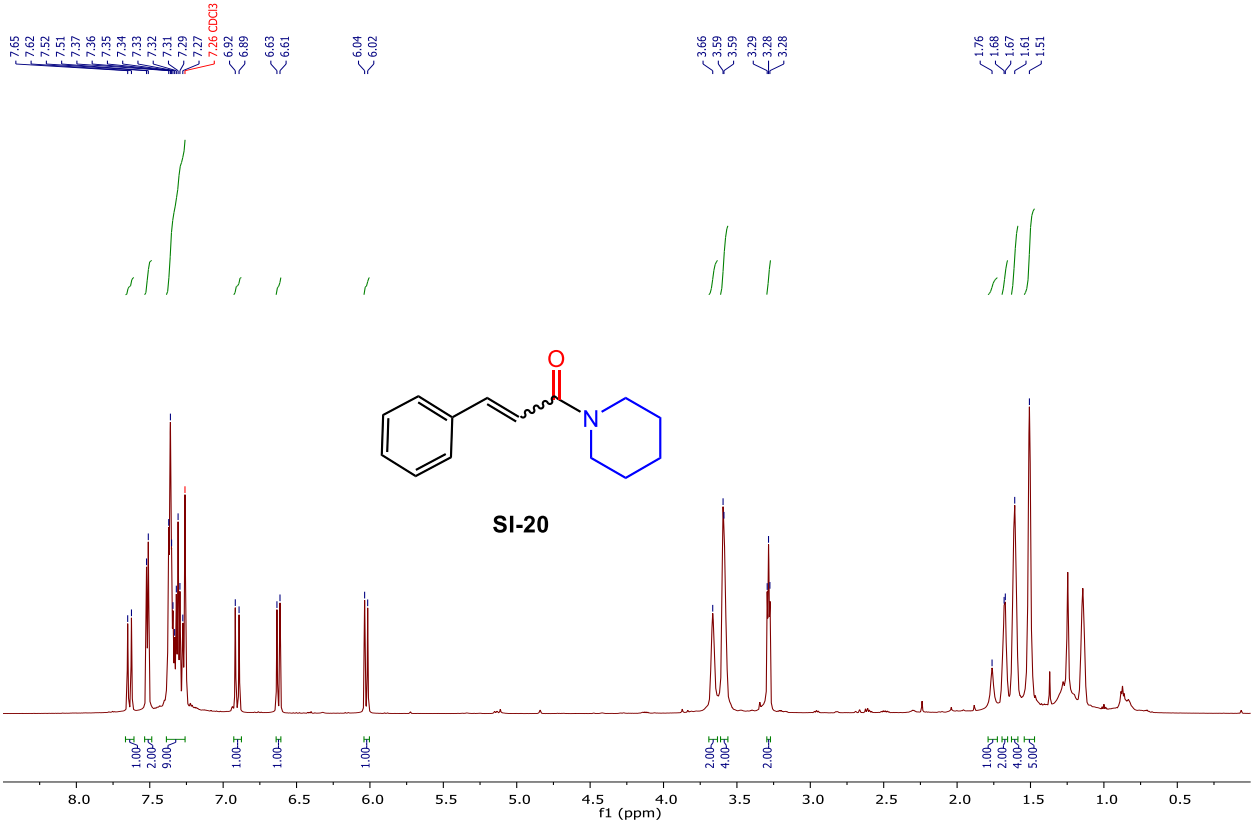
136.8
130.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
48.2
42.6
29.4
29.2
27.7
26.5
26.4
26.2
26.1
25.8
24.8
O
N
f1 (ppm)

SI–19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7.27
7.26 CDCl3
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6.89
6.63
6.61
6.04
6.02
3.66
3.59
3.59
3.29
3.28
3.28
1.76
1.68
1.67
1.61
1.51
O
N
SI-20
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9.00
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1.00
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4.00
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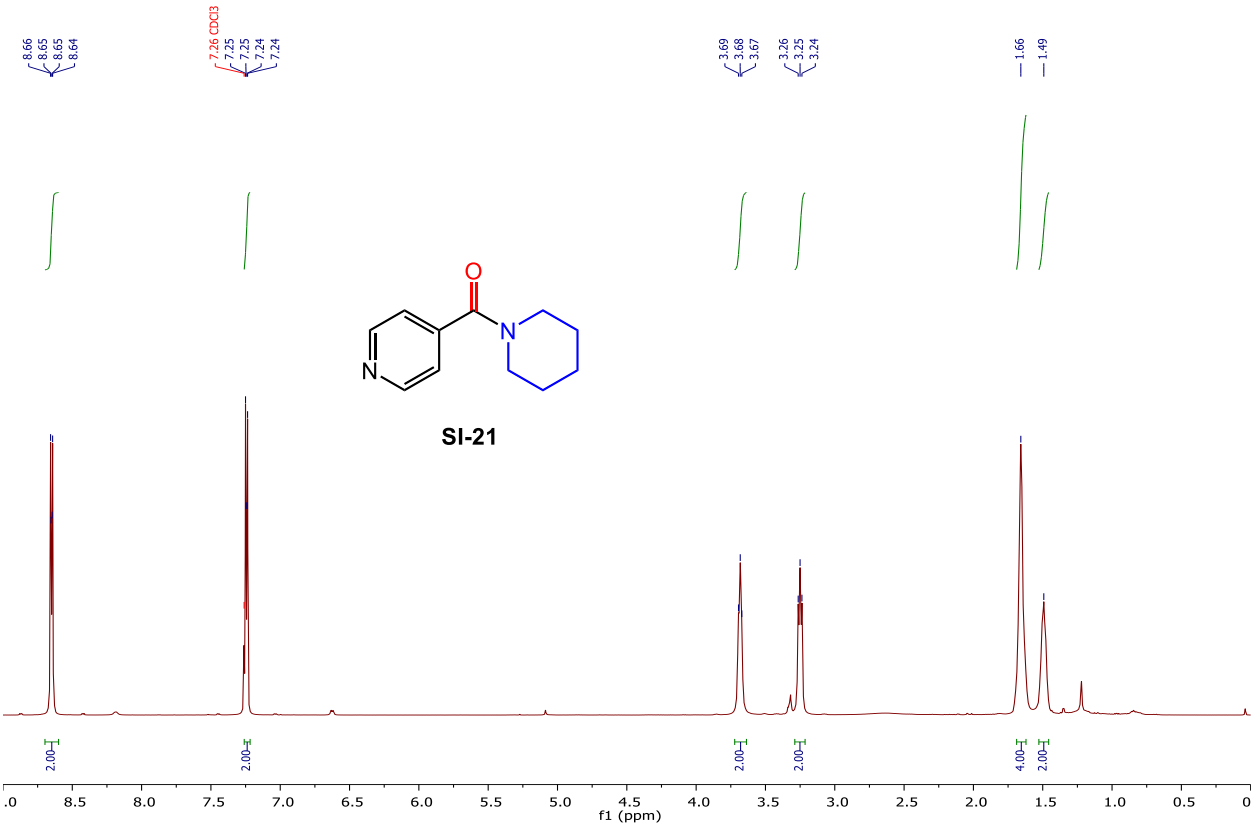
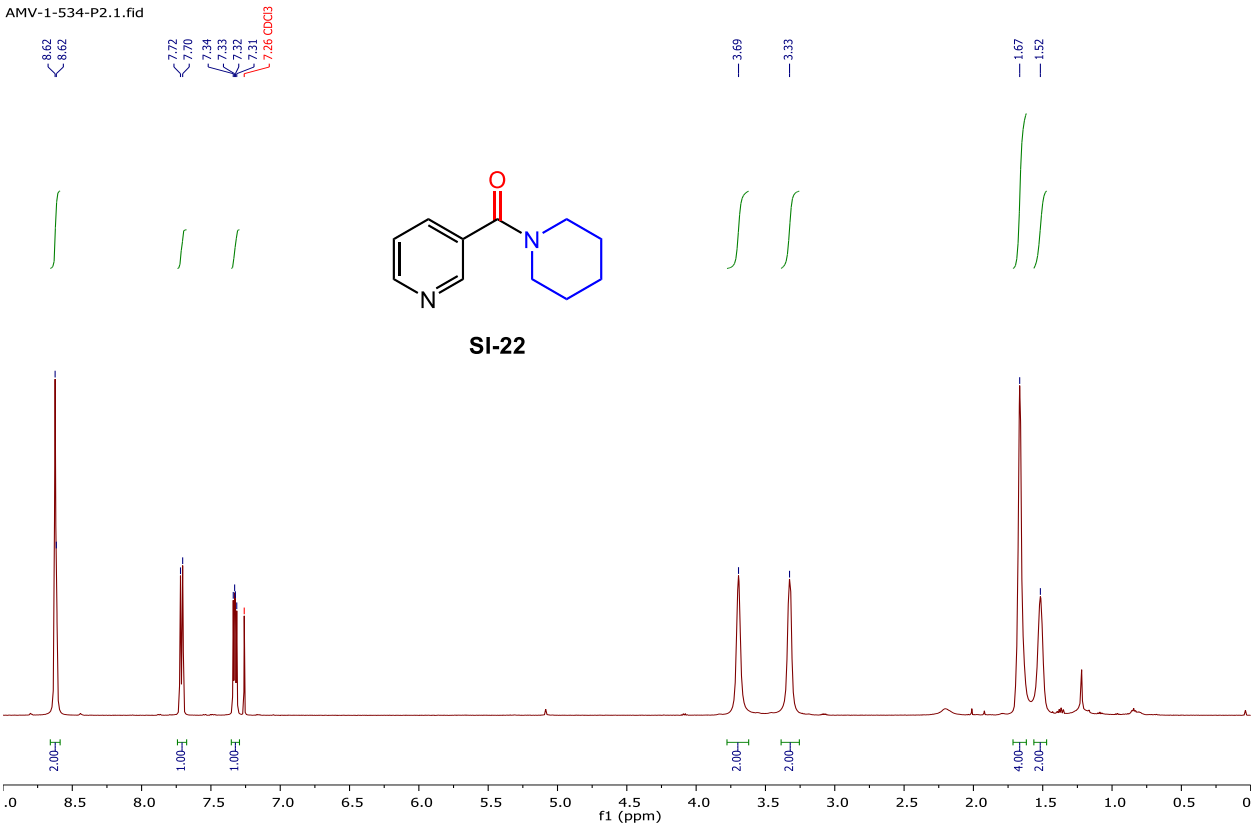
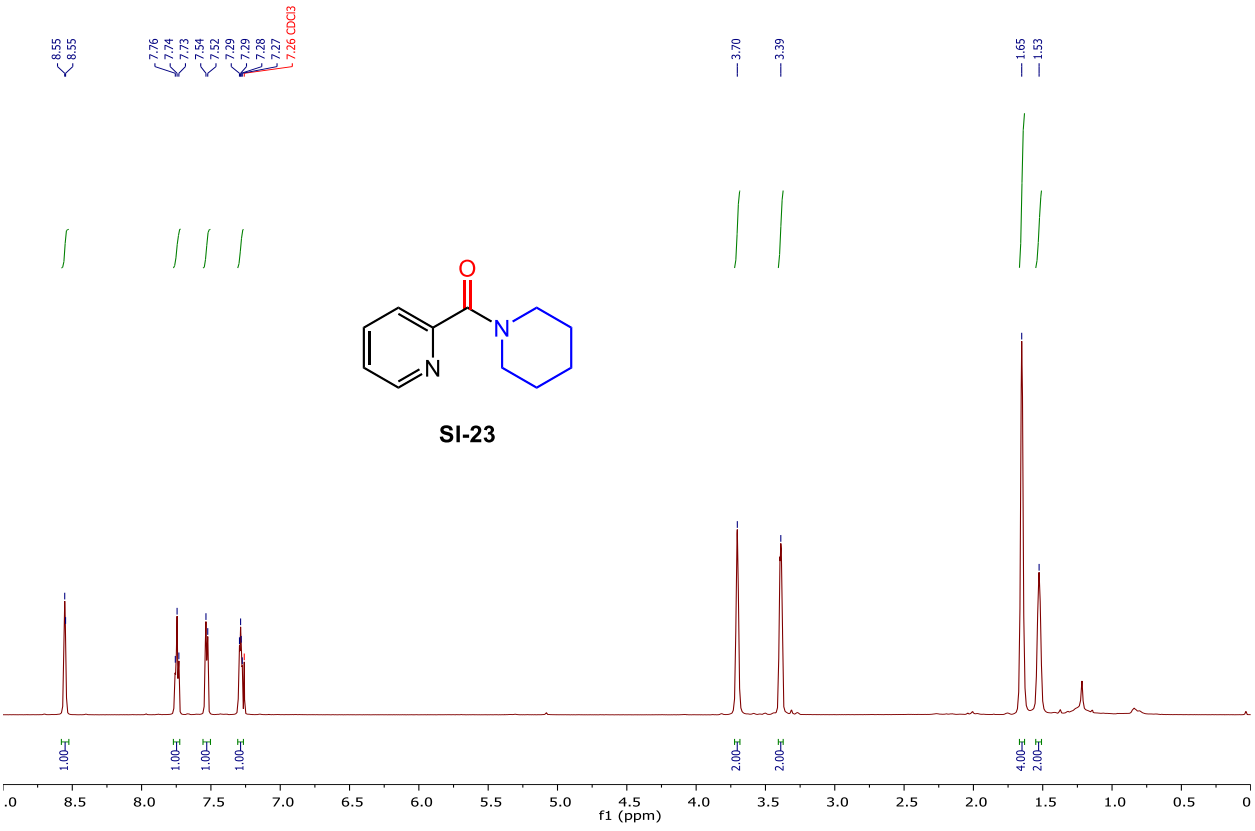
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

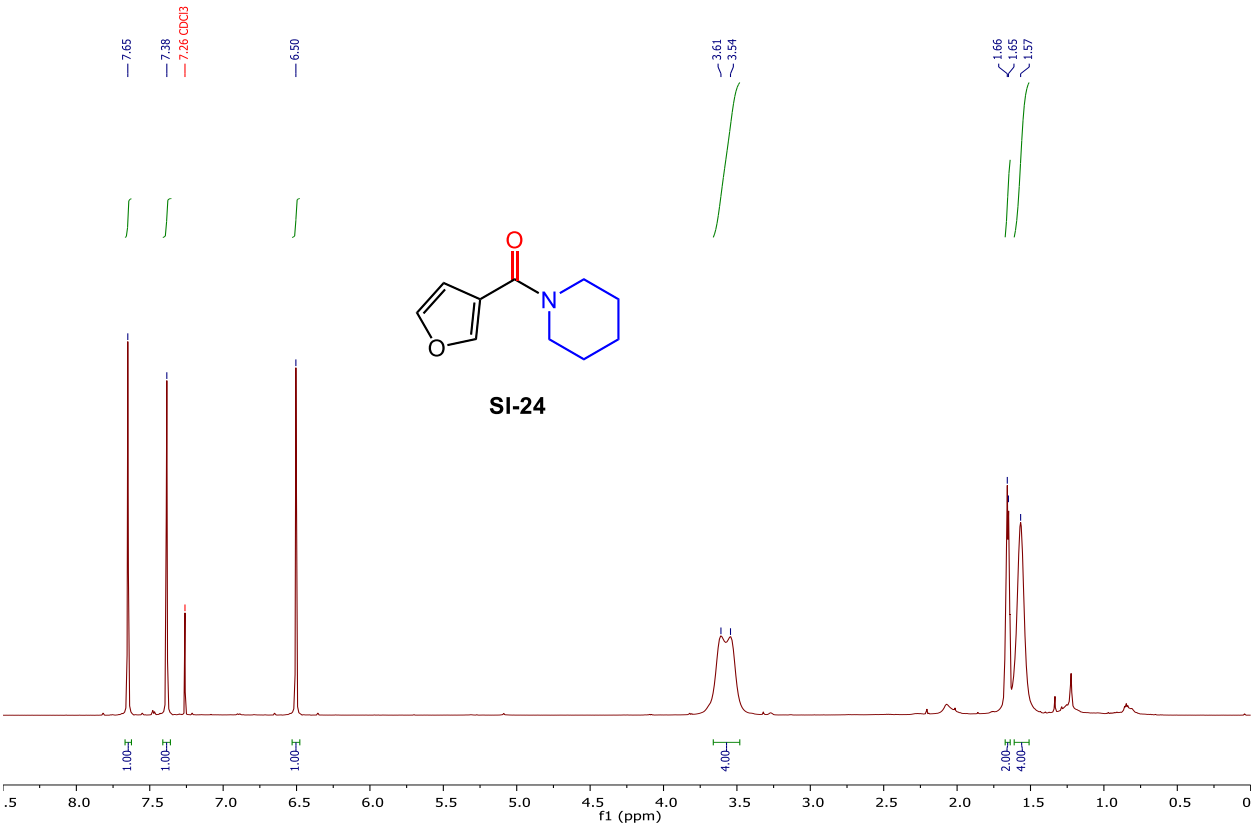

8.66
8.65
8.65
8.64
7.26 CDCl3
7.25
7.25
7.24
7.24
3.69
3.68
3.67
3.26
3.25
3.24
1.66
1.49
O
N
N
SI-21
2.00
2.00
2.00
2.00
4.00
2.00
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


AMV-1-534-P2.1.fid
8.62
8.62
7.72
7.70
7.34
7.33
7.32
7.31
7.26 CDCl3
3.69
3.33
1.67
1.52
O
N
N
2.00
1.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

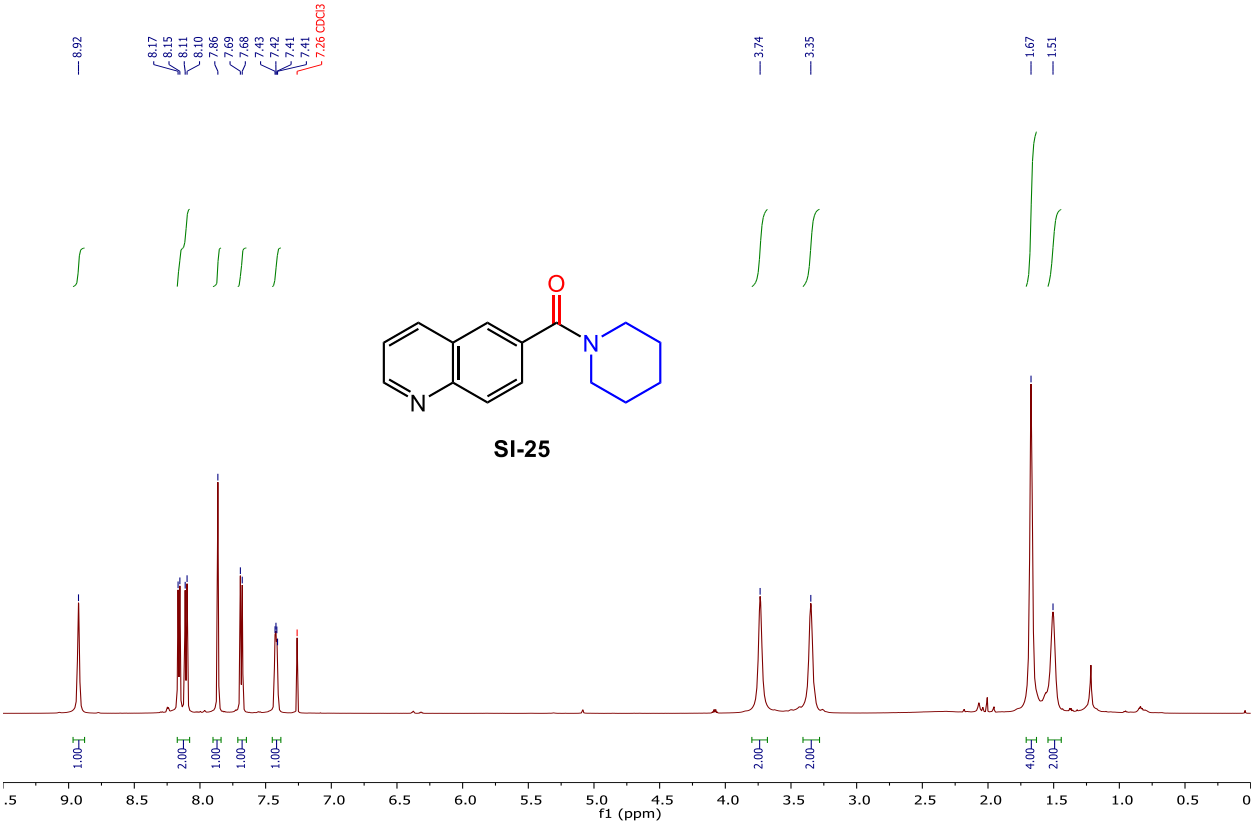
SI-22


8.55
8.55
7.76
7.74
7.73
7.54
7.52
7.29
7.29
7.28
7.27
7.26 CDCl3
3.70
3.39
1.65
1.53
O
N
N
1.00
1.00
1.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

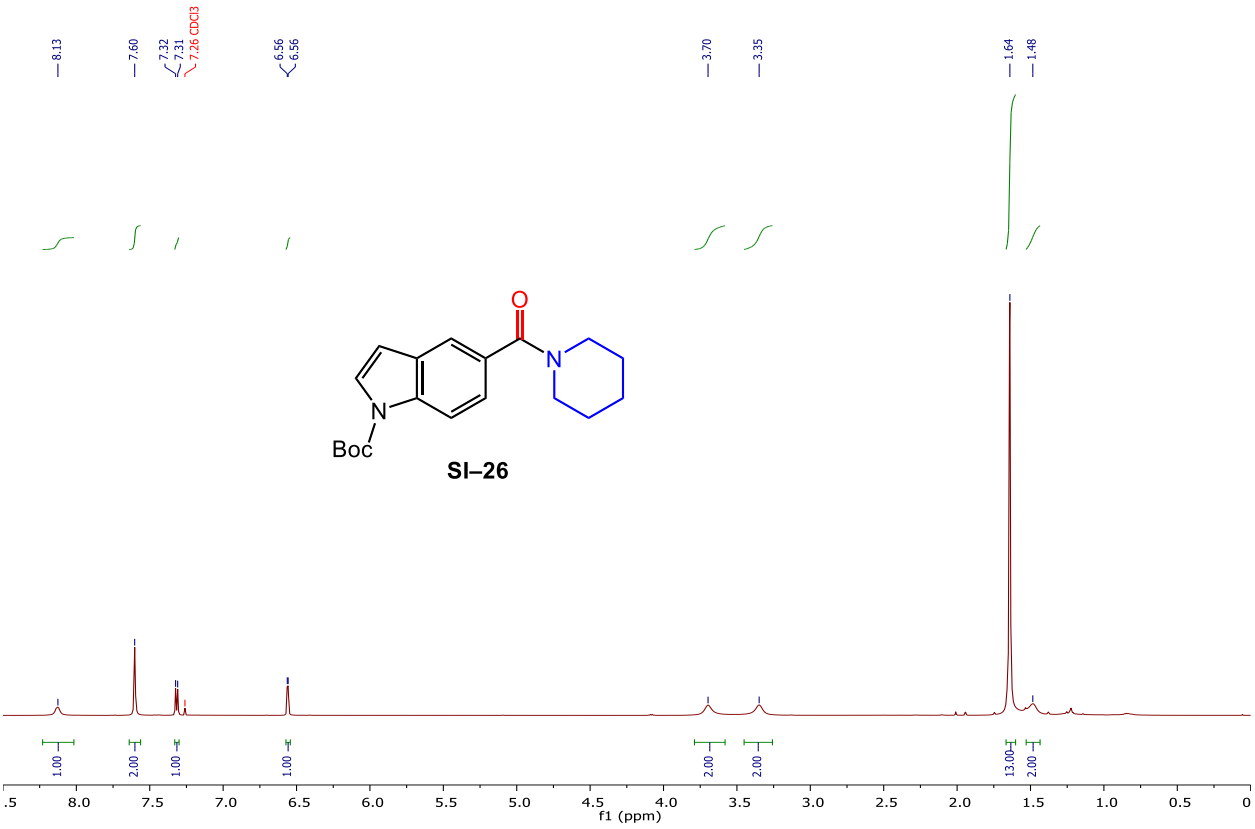
SI-23


7.65
7.38
7.26 CDCl3
6.50
3.61
3.54
1.66
1.65
1.57
1.00
1.00
1.00
4.00
2.00
4.00
f1 (ppm)

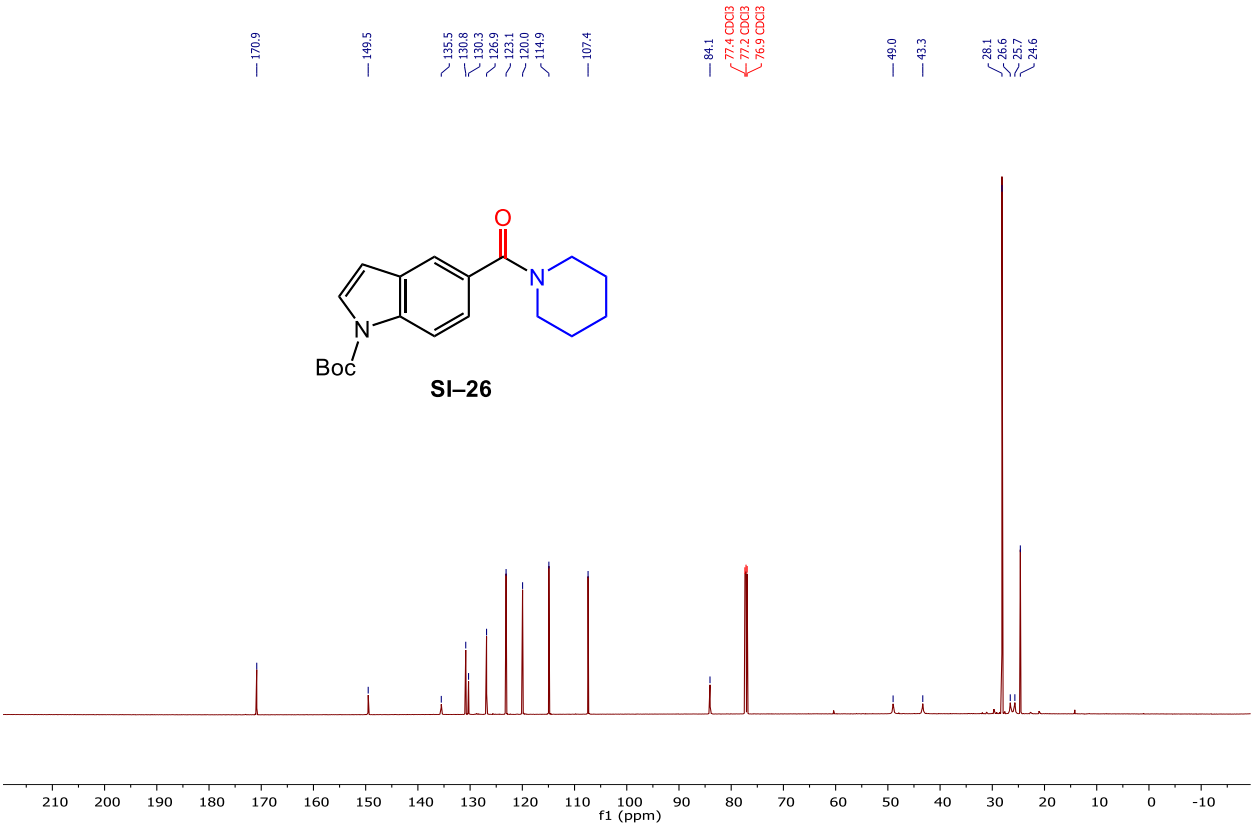
SI-24


8.92
8.17
8.15
8.11
8.10
7.86
7.69
7.68
7.43
7.42
7.41
7.41
7.26 CDCl3
3.74
3.35
1.67
1.51
1.00
2.00
1.00
1.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

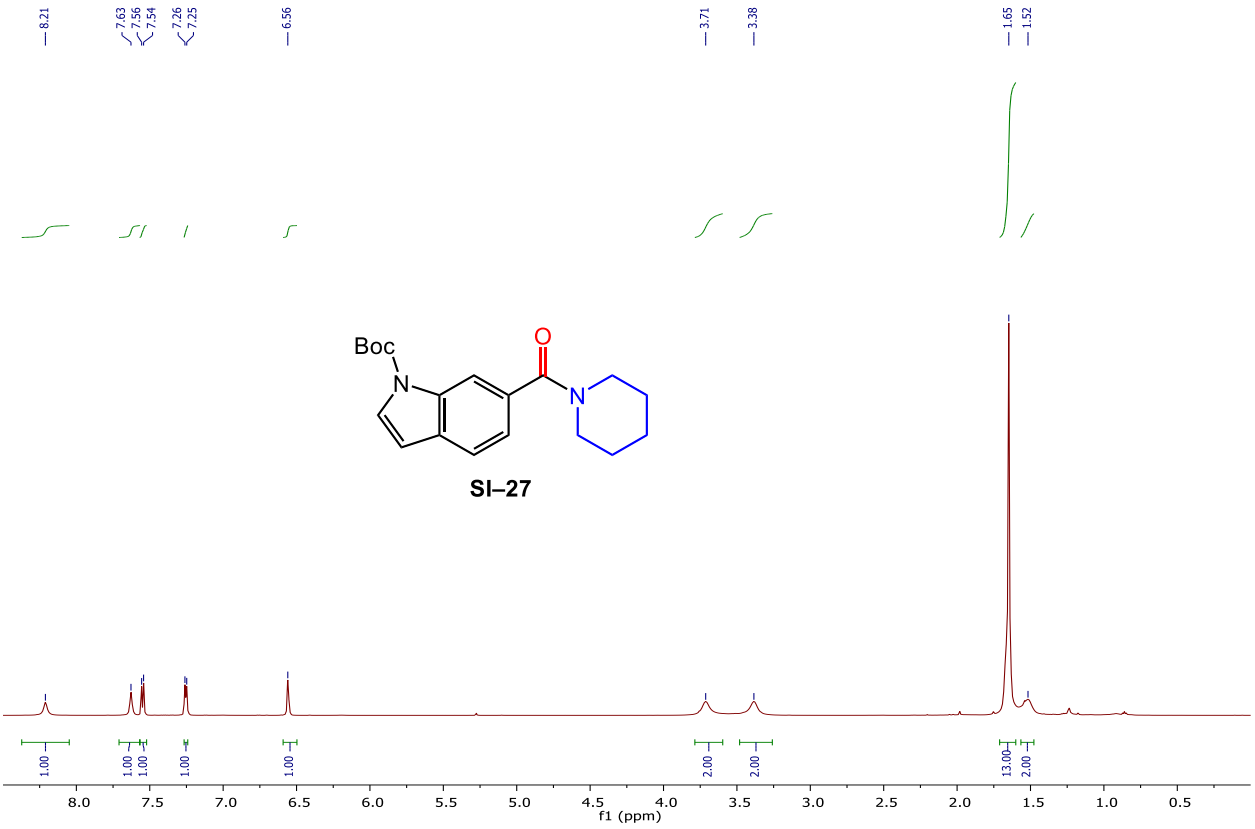
SI-25


8.13
7.60
7.32
7.31
7.26 CDCl3
6.56
6.56
3.70
3.35
1.64
1.48
O
N
N
Boc
1.00
2.00
1.00
1.00
2.00
2.00
13.00
2.00
f1 (ppm)

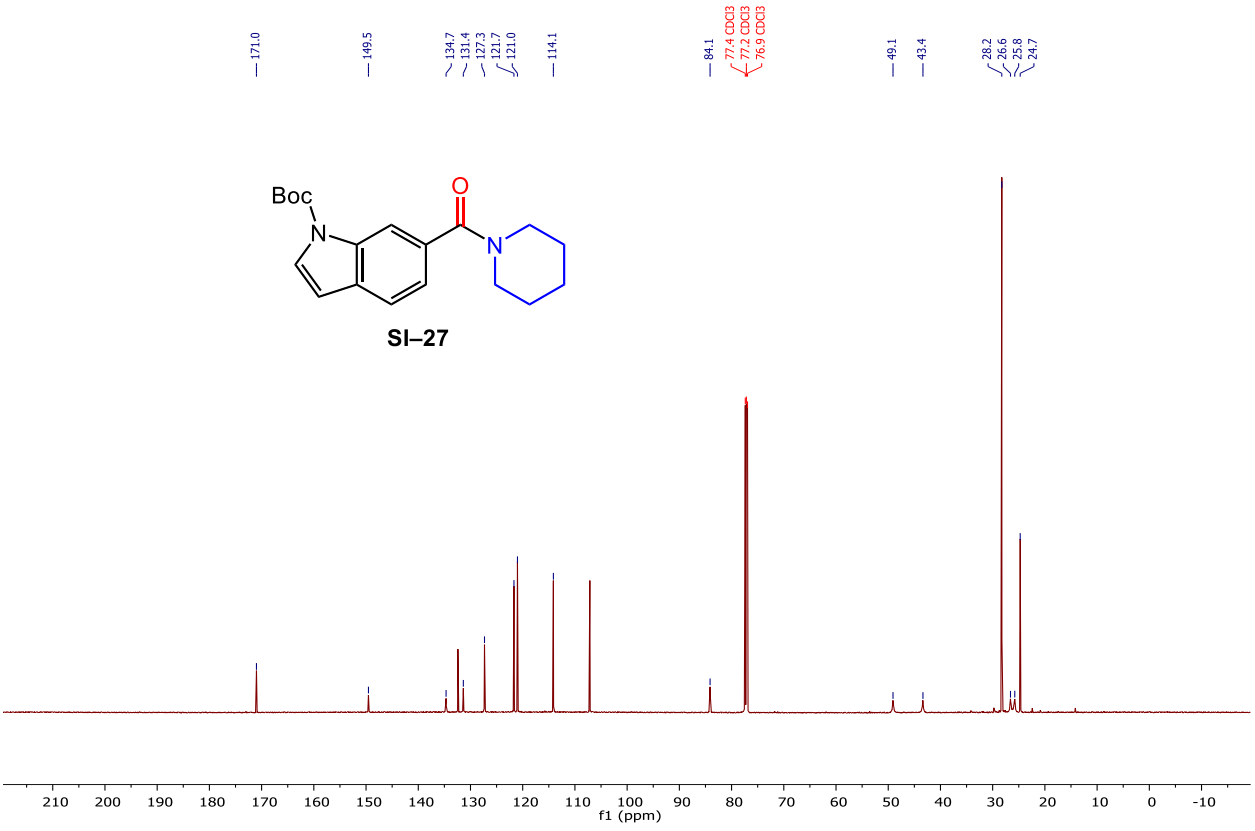
SI–26


170.9
149.5
135.5
130.8
130.3
126.9
123.1
120.0
114.9
107.4
84.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
49.0
43.3
28.1
26.6
25.7
24.6
O
N
N
Boc
f1 (ppm)

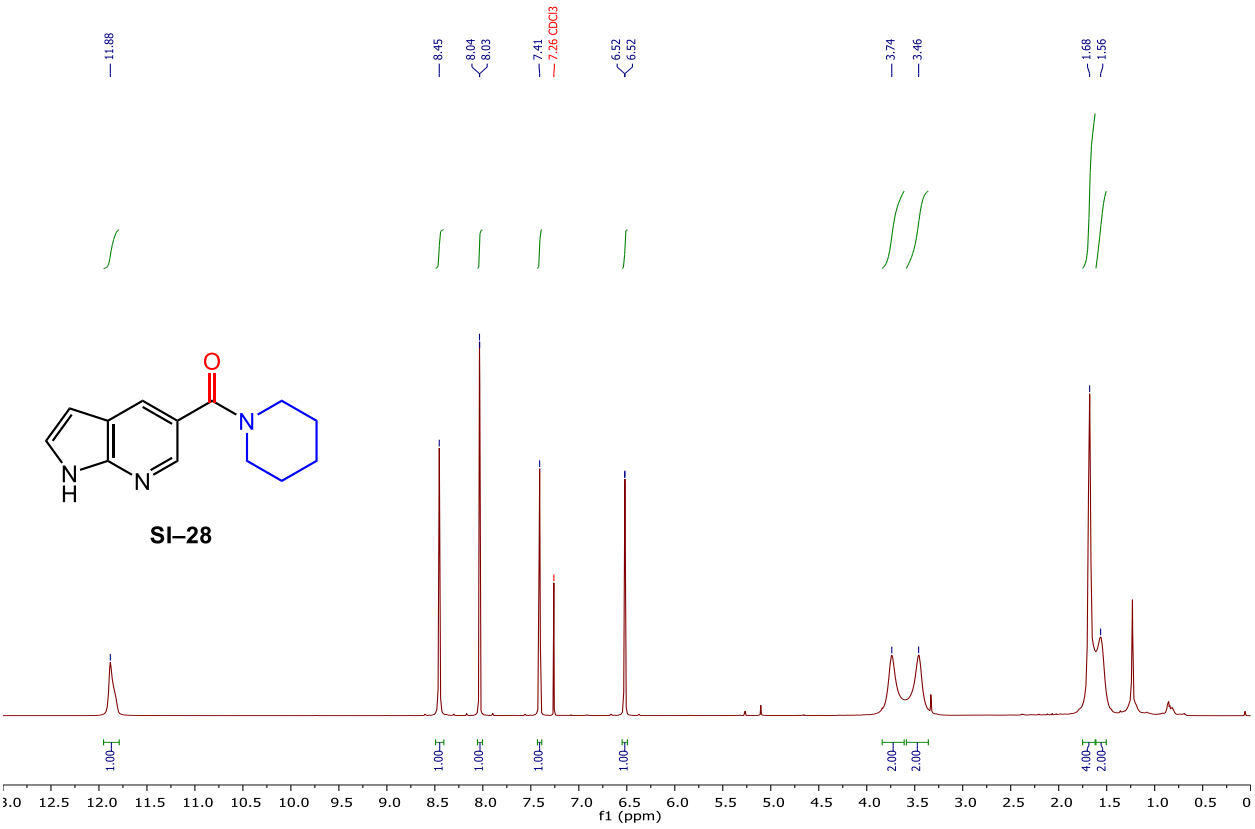
SI–26


8.21
7.63
7.56
7.54
7.26
7.25
6.56
3.71
3.38
1.65
1.52
Boc
N
O
N
1.00
1.00
1.00
1.00
1.00
2.00
2.00
13.00
2.00
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
f1 (ppm)

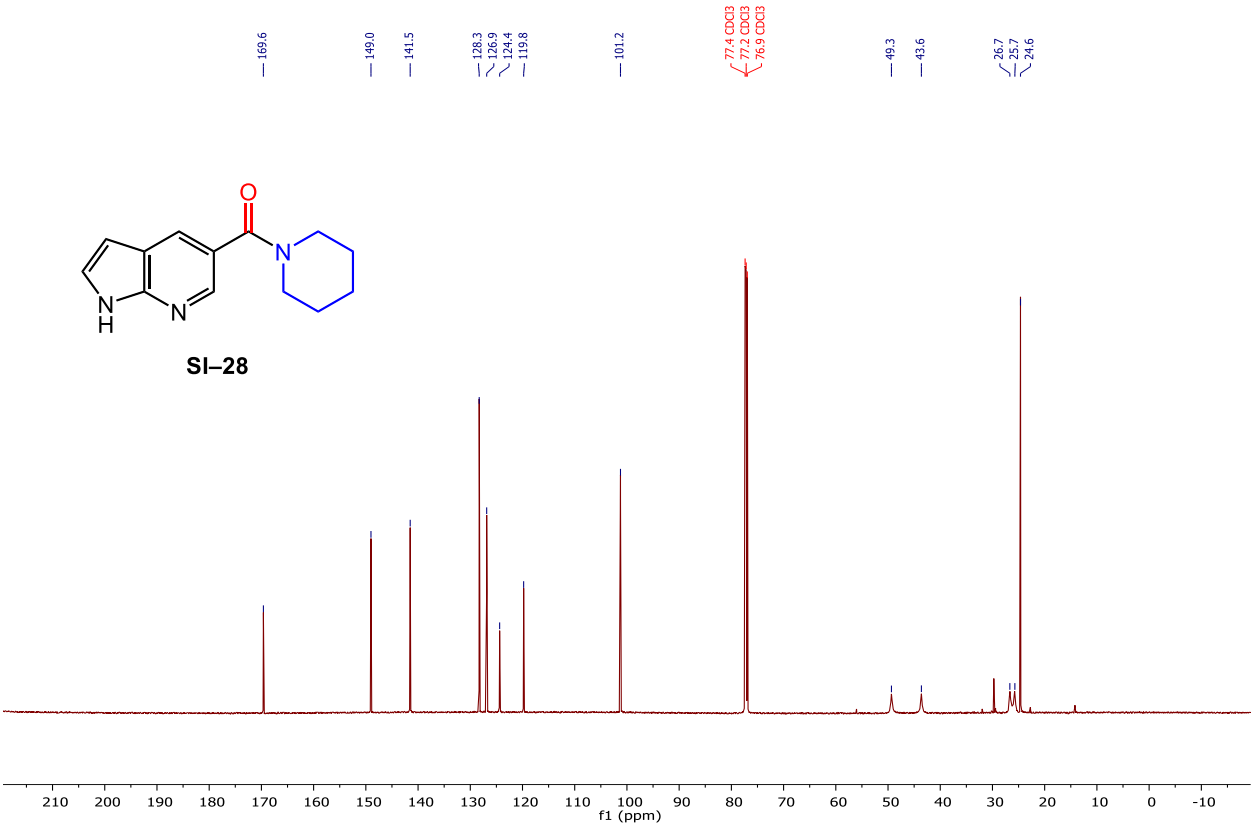
SI–27


171.0
149.5
134.7
131.4
127.3
121.7
121.0
114.1
84.1
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
49.1
43.4
28.2
26.6
25.8
24.7
Boc
N
O
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

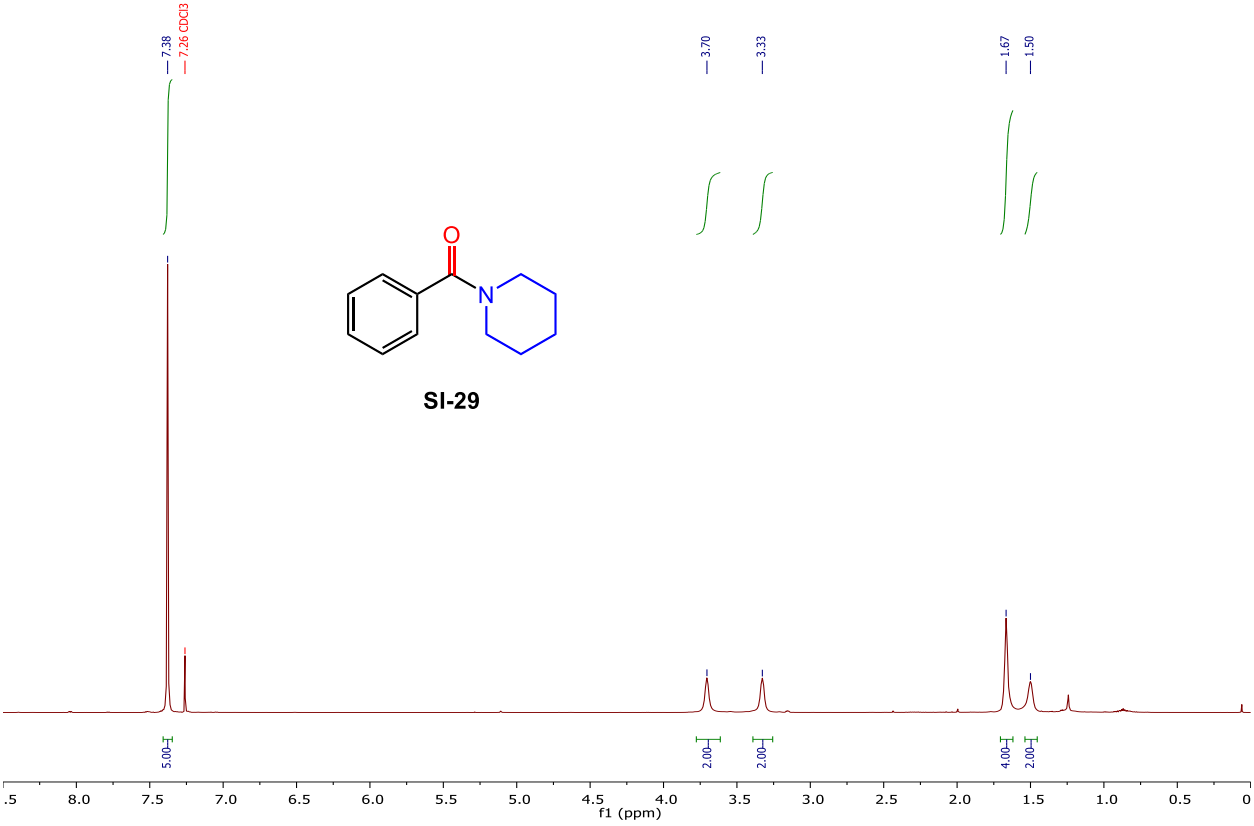
SI–27


11.88
8.45
8.04
8.03
7.41
7.26 CDCl3
6.52
6.52
3.74
3.46
1.68
1.56
O
N
N
H
N
1.00
1.00
1.00
1.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

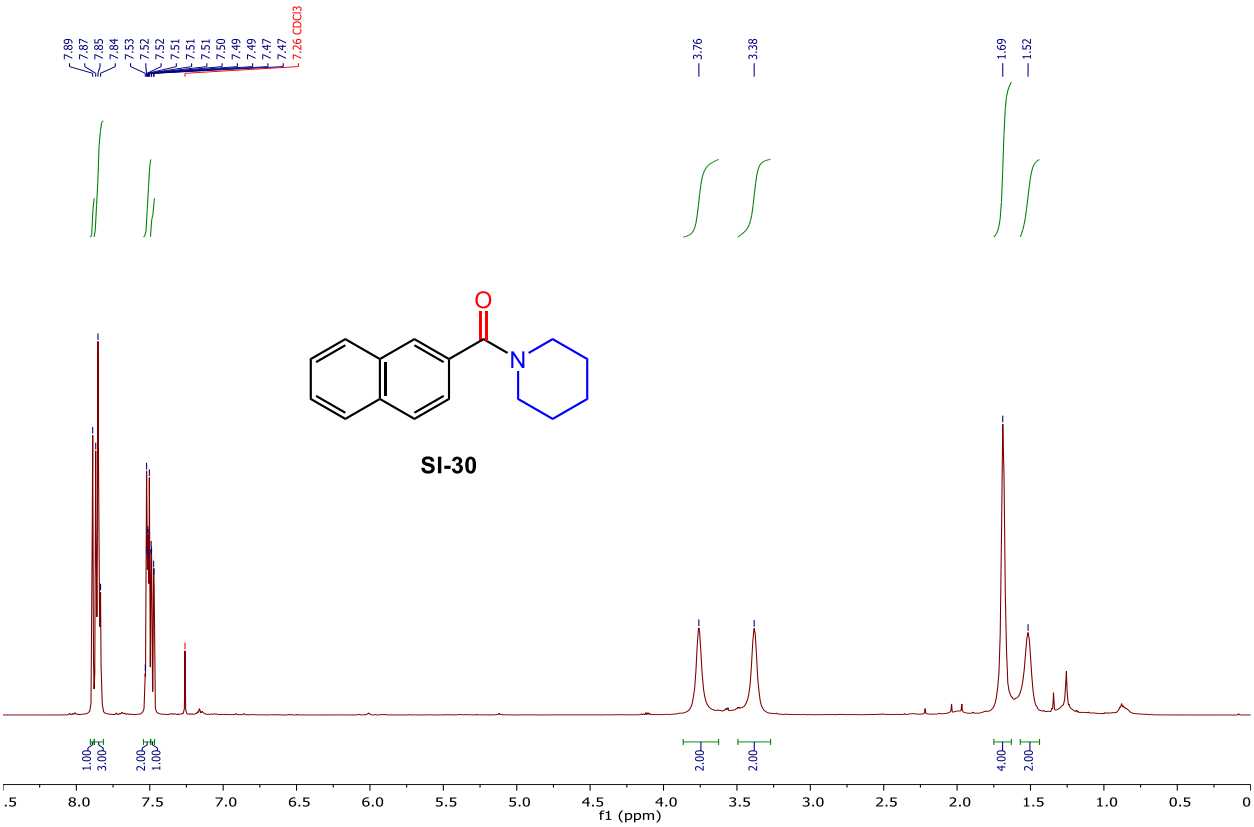
SI–28


169.6
149.0
141.5
128.3
126.9
124.4
119.8
101.2
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
49.3
43.6
26.7
25.7
24.6
O
N
N
H
f1 (ppm)

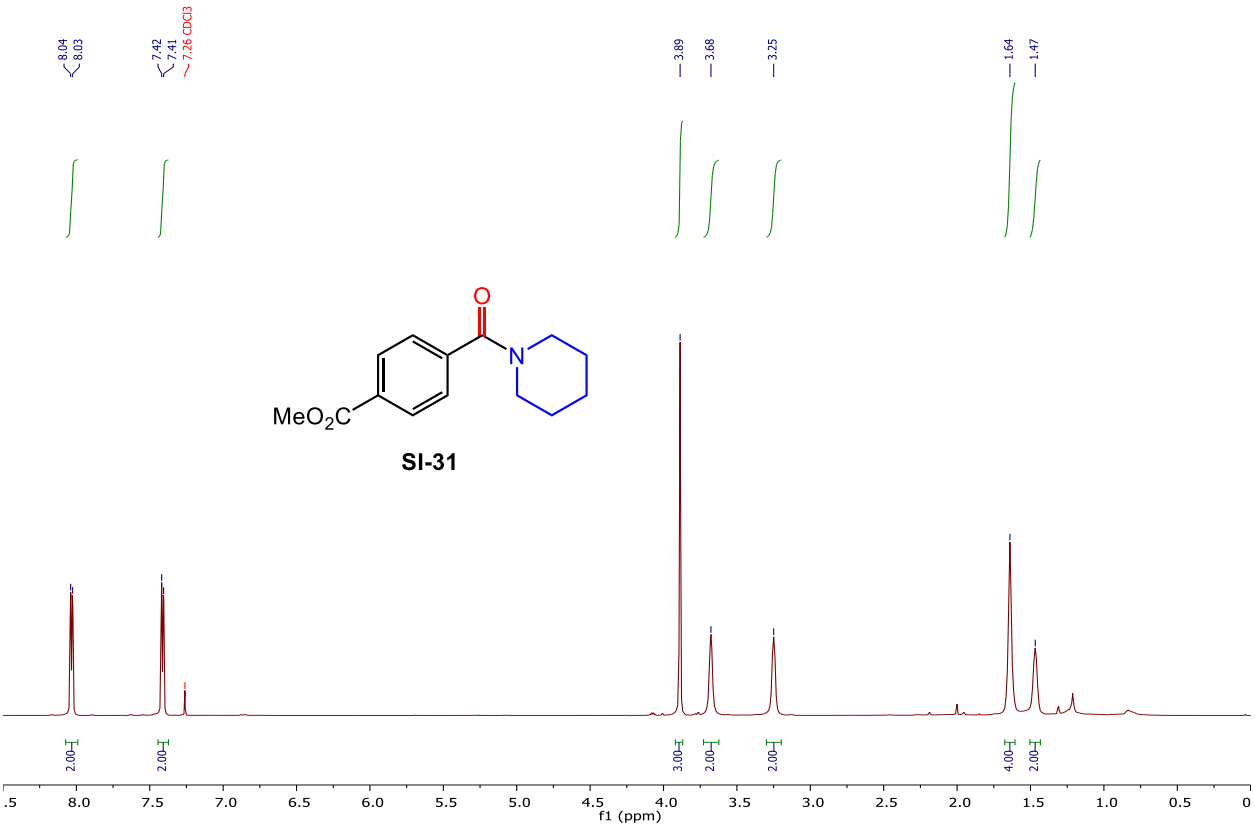
SI–28


7.38
7.26 CDCl3
3.70
3.33
1.67
1.50
O
N
5.00
2.00
2.00
4.00
2.00
f1 (ppm)

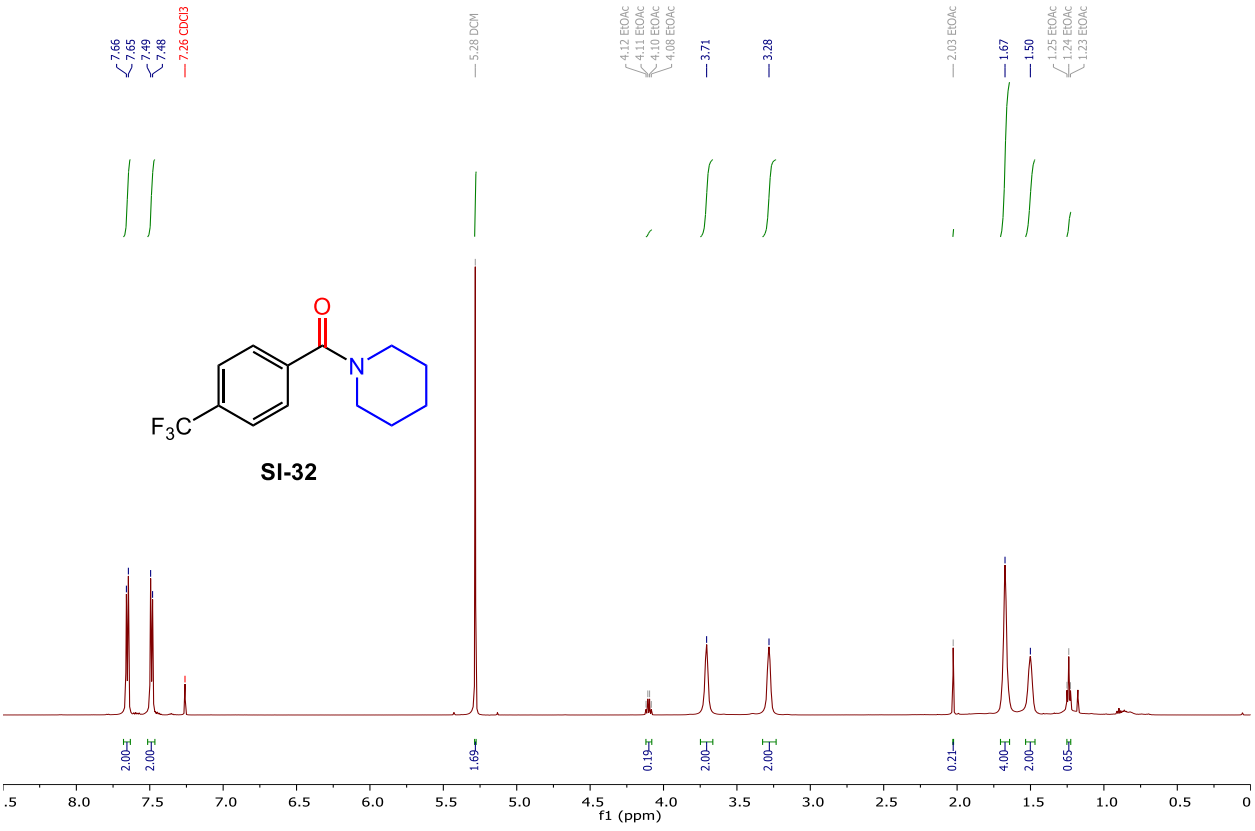
SI-29


7.89
7.87
7.85
7.84
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.49
7.49
7.47
7.47
7.26 CDCl3
3.76
3.38
1.69
1.52
O
N
1.00
3.00
2.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

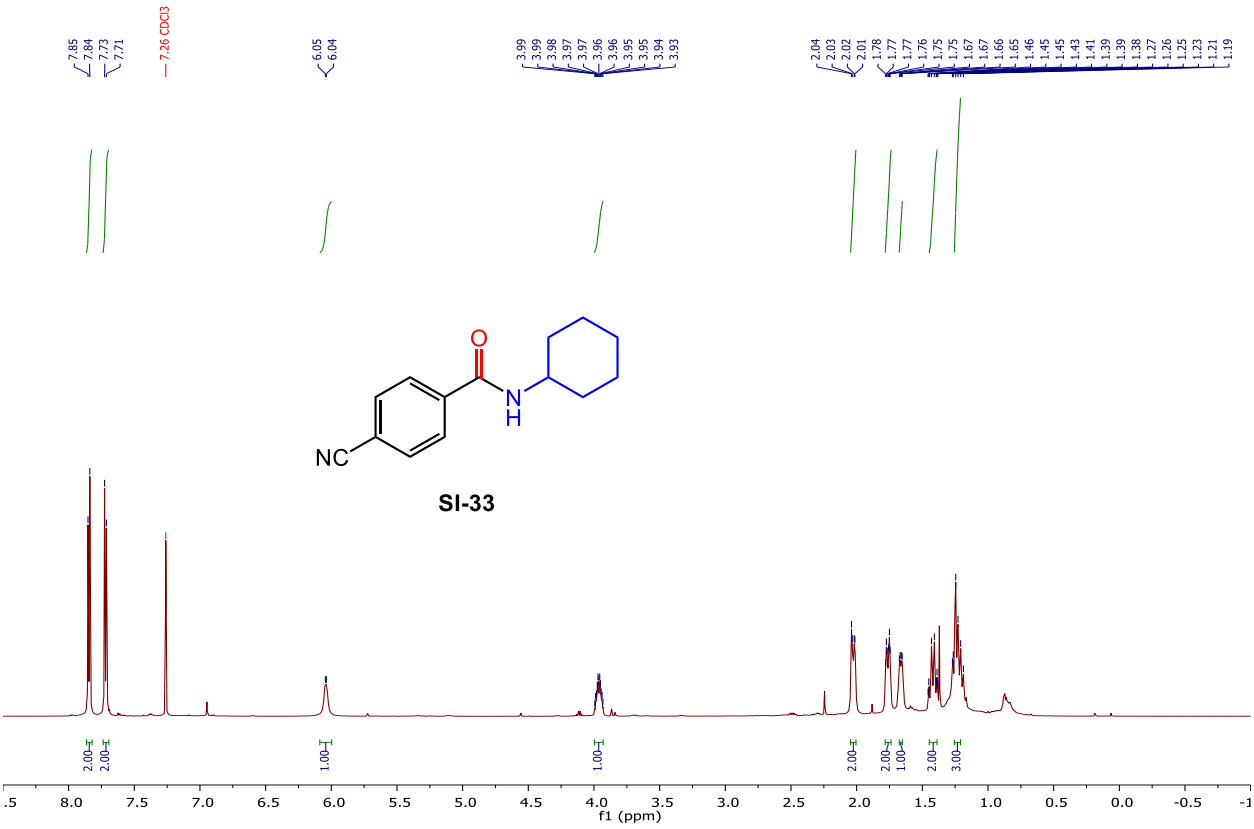
SI-30


8.04
8.03
7.42
7.41
7.26 CDCl3
3.89
3.68
3.25
1.64
1.47
O
N
MeO2C
2.00
2.00
3.00
2.00
2.00
4.00
2.00
f1 (ppm)

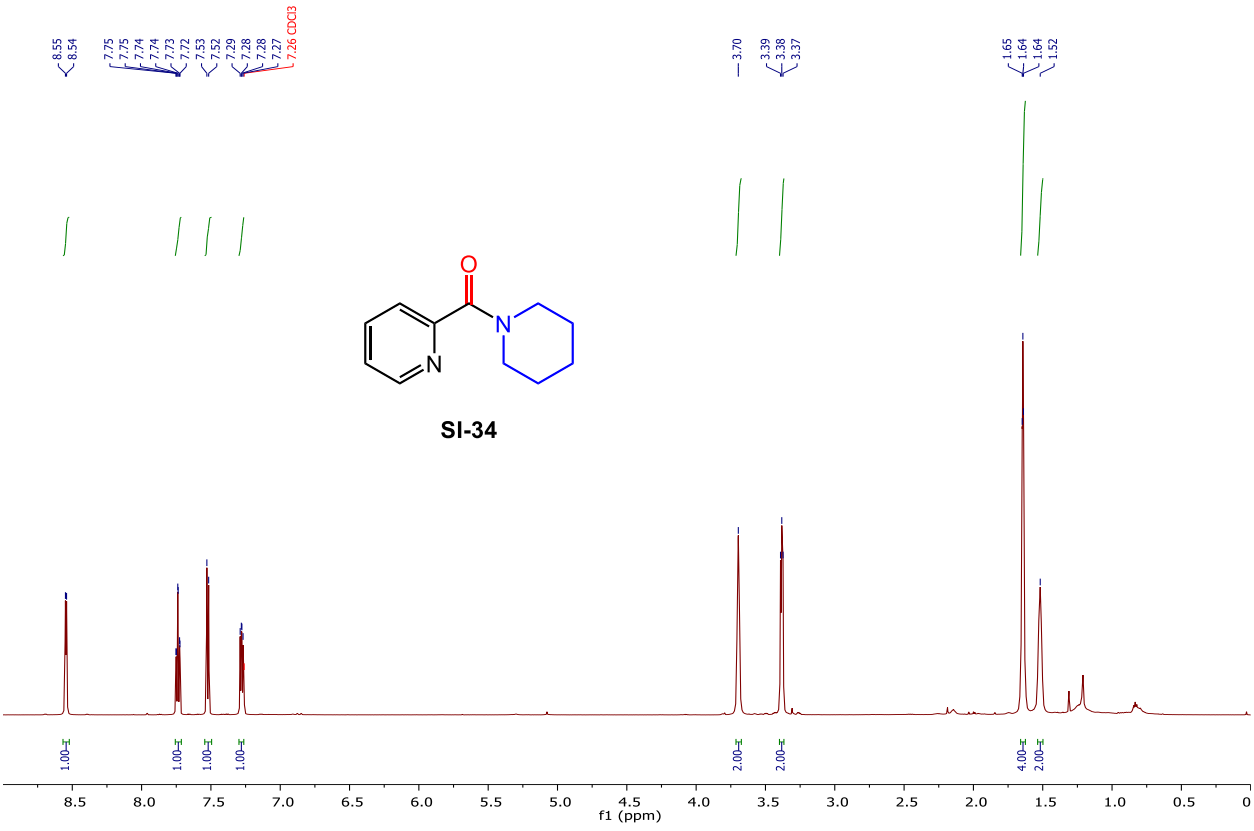
SI-31


7.66
7.65
7.49
7.48
7.26 CDCl3
5.28 DCM
4.12 EtOAc
4.11 EtOAc
4.10 EtOAc
4.08 EtOAc
3.71
3.28
2.03 EtOAc
1.67
1.50
1.25 EtOAc
1.24 EtOAc
1.23 EtOAc
O
N
F3C
2.00
2.00
1.69
0.19
2.00
2.00
0.21
4.00
2.00
0.65
f1 (ppm)

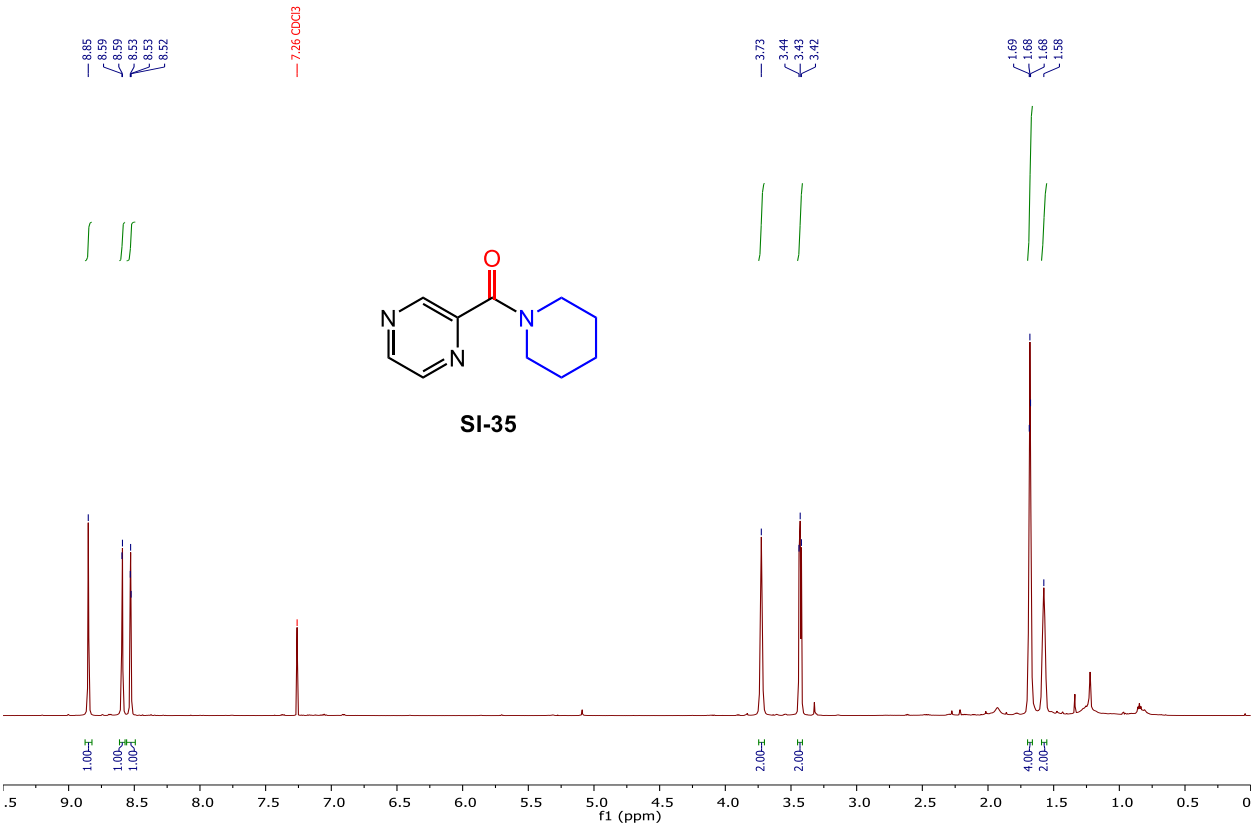
SI-32


7.85
7.84
7.73
7.71
7.26 CDCl3
6.05
6.04
3.99
3.99
3.98
3.97
3.97
3.96
3.96
3.95
3.95
3.94
3.93
2.04
2.03
2.02
2.01
1.78
1.77
1.77
1.76
1.75
1.75
1.67
1.67
1.66
1.65
1.46
1.45
1.45
1.43
1.41
1.39
1.39
1.38
1.27
1.26
1.25
1.23
1.21
1.19
O
N
H
NC
2.00
2.00
1.00
1.00
2.00
2.00
1.00
2.00
3.00
f1 (ppm)

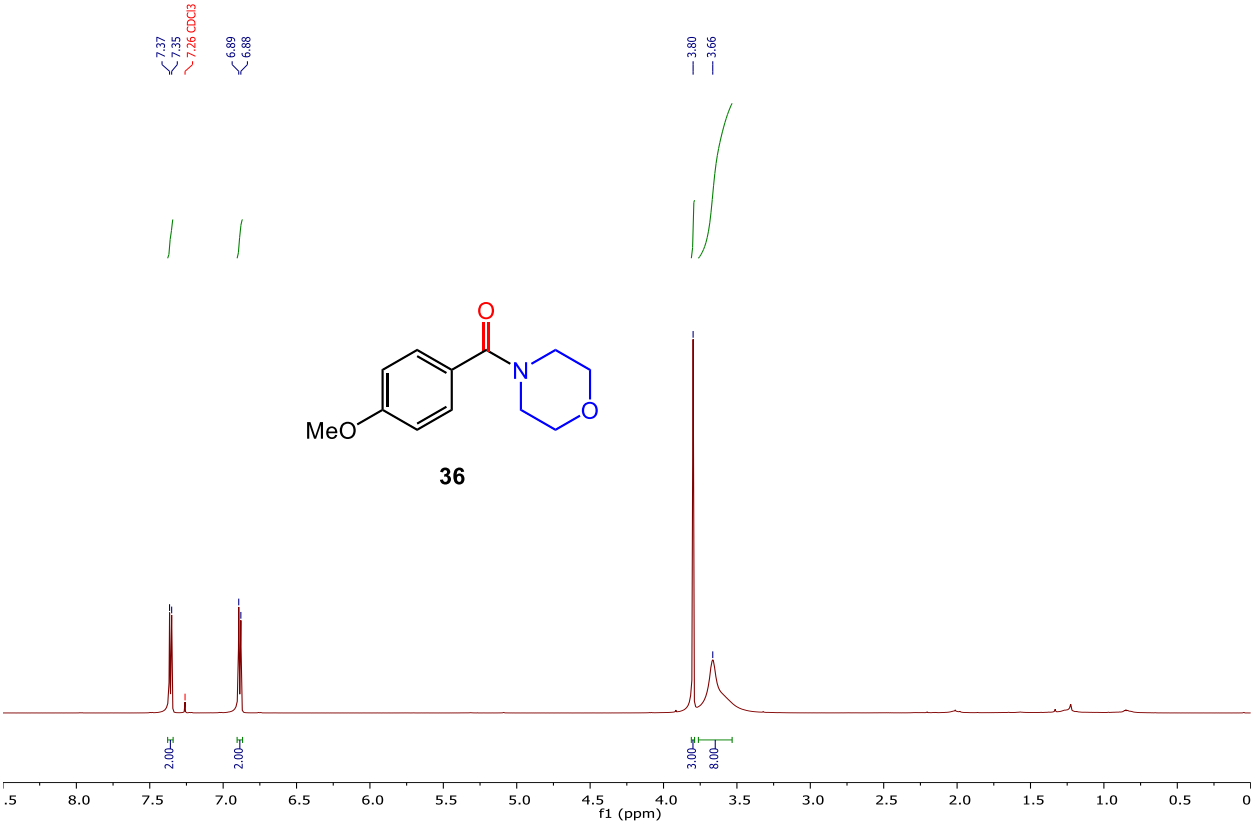
SI-33


8.55
8.54
7.75
7.75
7.74
7.74
7.73
7.72
7.53
7.52
7.29
7.28
7.28
7.27
7.26 CDCl3
3.70
3.39
3.38
3.37
1.65
1.64
1.64
1.52
O
N
N
1.00
1.00
1.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

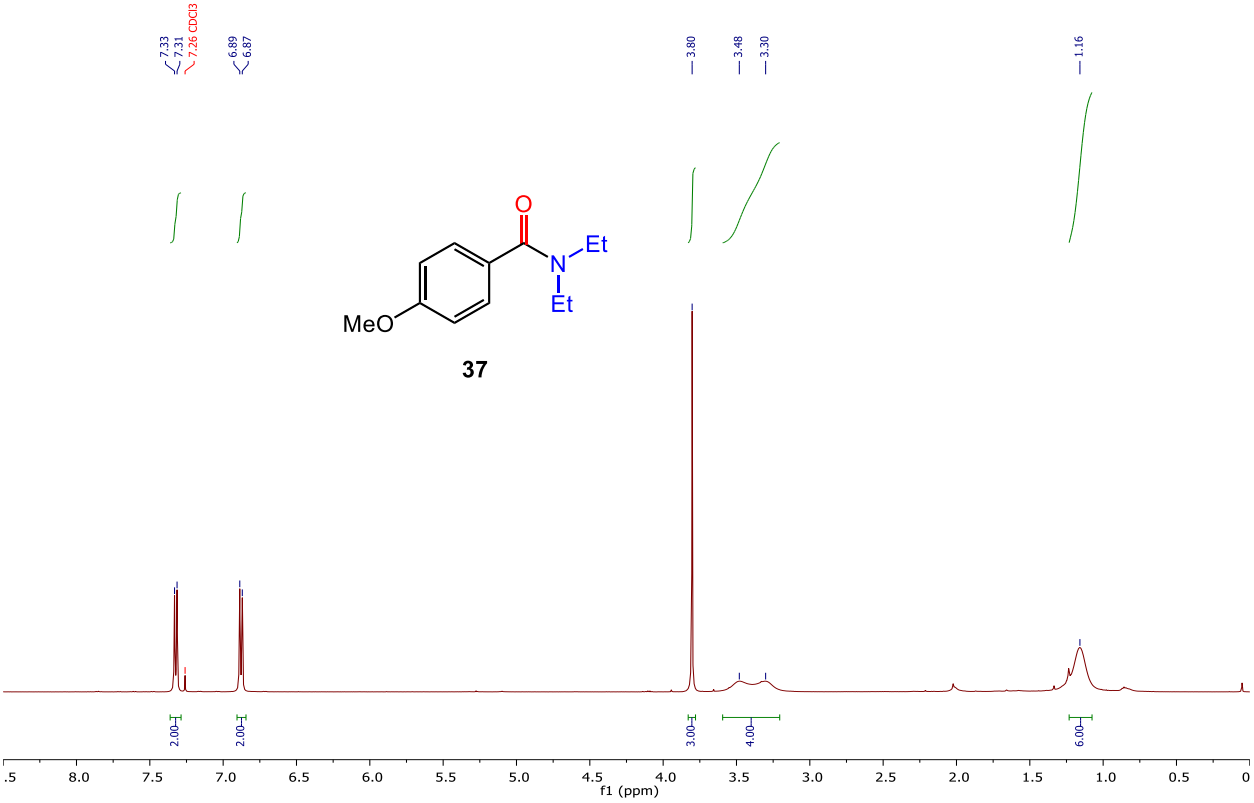
SI-34


8.85
8.59
8.59
8.53
8.53
8.52
7.26 CDCl3
3.73
3.44
3.43
3.42
1.69
1.68
1.68
1.58
O
N
N
N
1.00
1.00
1.00
2.00
2.00
4.00
2.00
f1 (ppm)

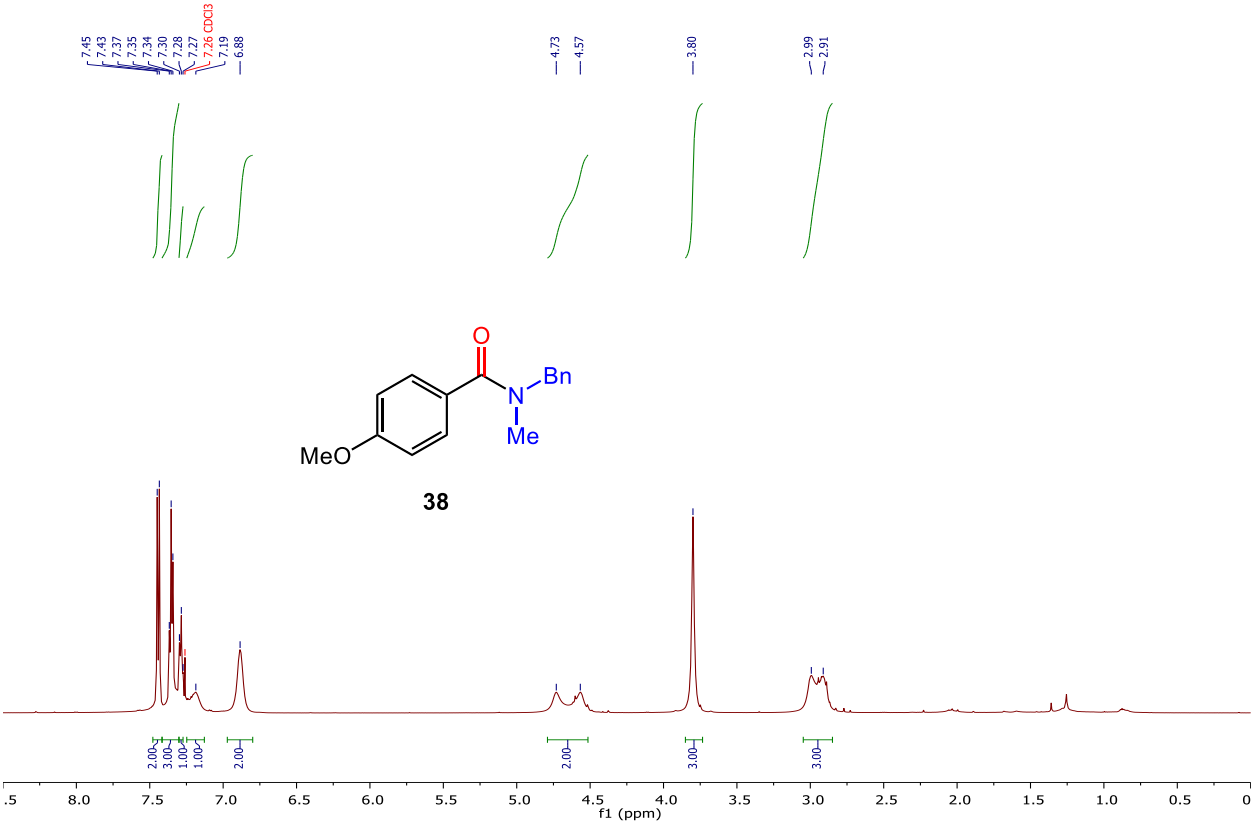
SI-35


7.37
7.35
7.26 CDCl3
6.89
6.88
3.80
3.66
O
N
O
MeO
2.00
2.00
3.00
8.00
f1 (ppm)

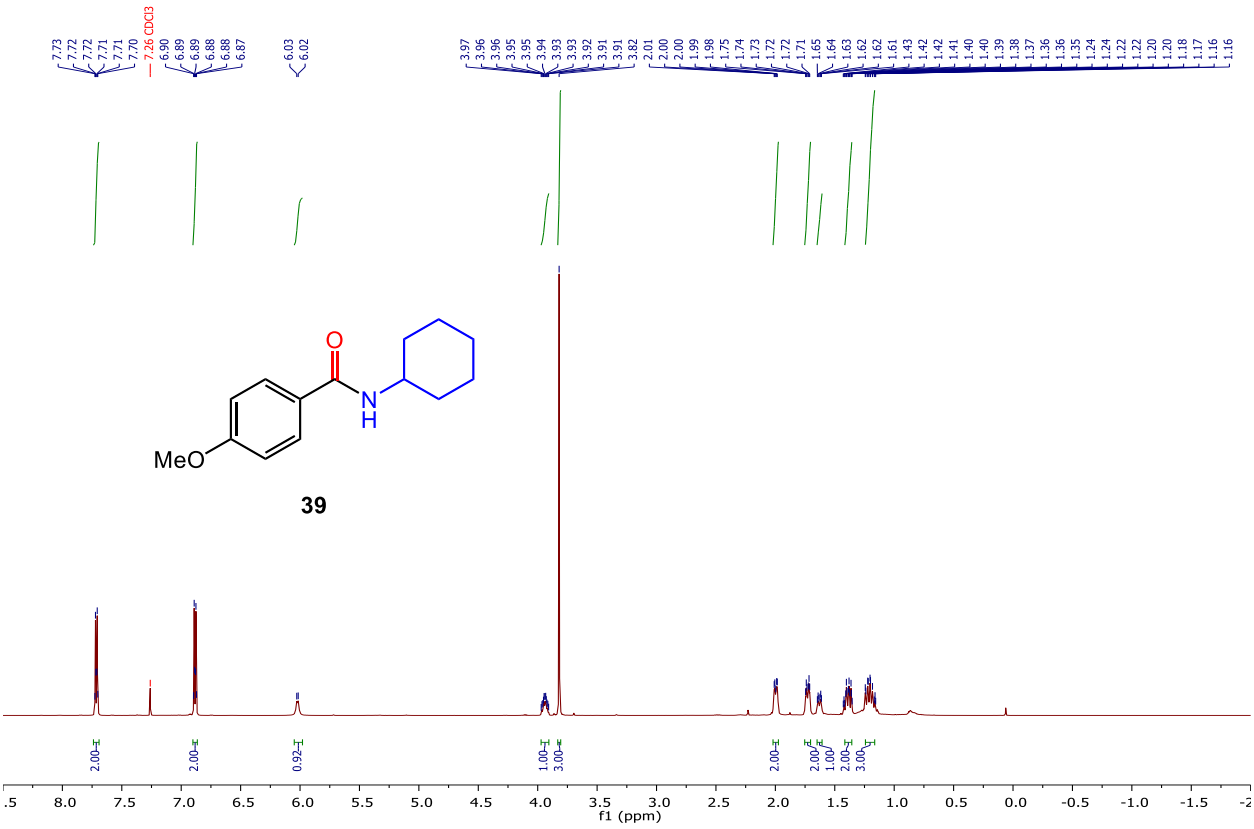
36


7.33
7.31
7.26 CDCl3
6.89
6.87
3.80
3.48
3.30
1.16
O
N
Et
Et
MeO
2.00
2.00
3.00
4.00
6.00
f1 (ppm)

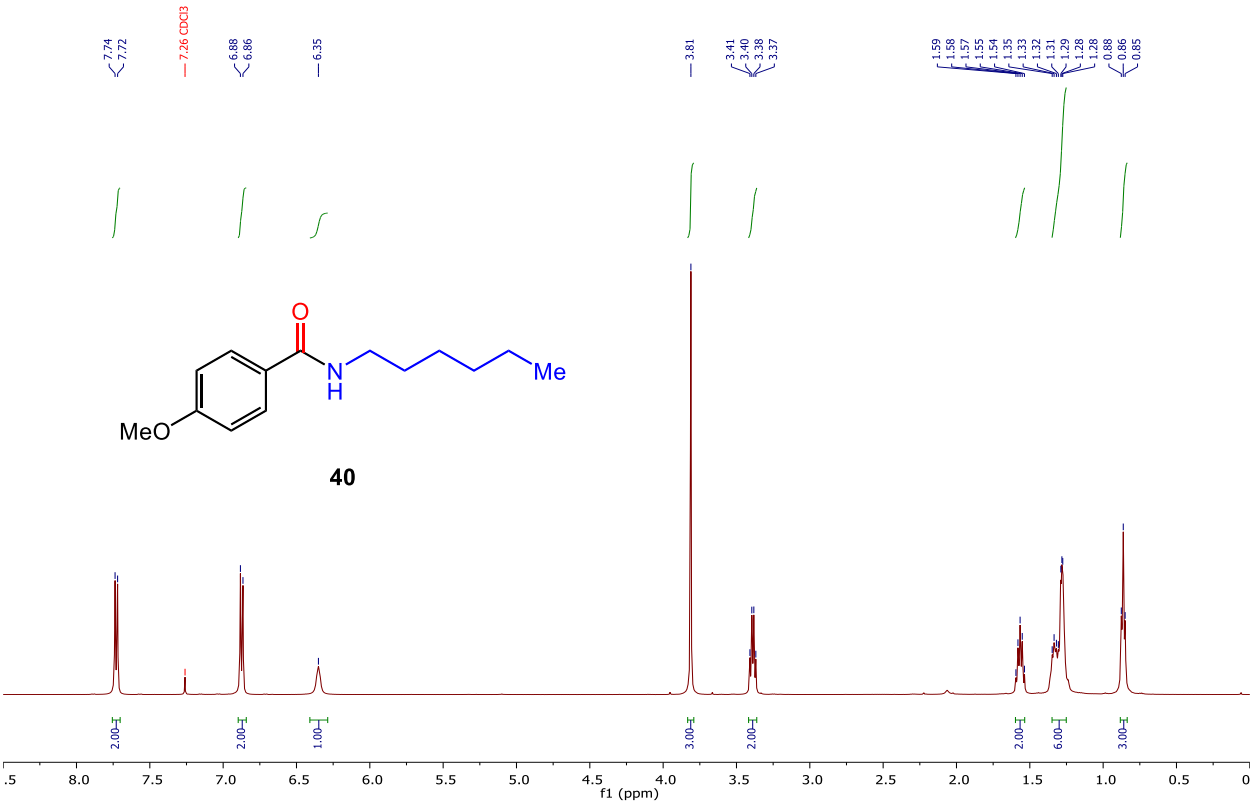
37


7.45
7.43
7.37
7.35
7.34
7.30
7.28
7.27
7.26 CDCl3
7.19
6.88
4.73
4.57
3.80
2.99
2.91
O
N
Bn
Me
MeO
2.00
3.00
1.00
1.00
2.00
2.00
3.00
3.00
f1 (ppm)

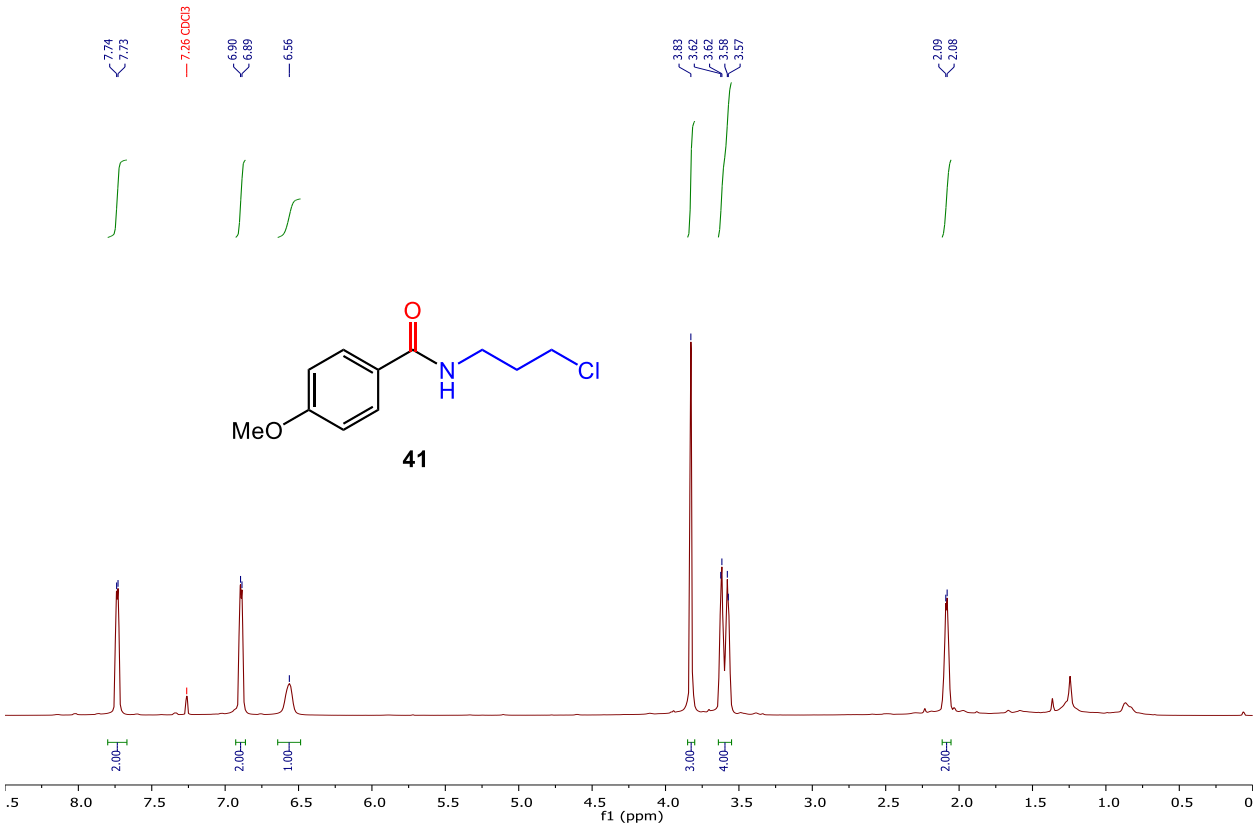
38

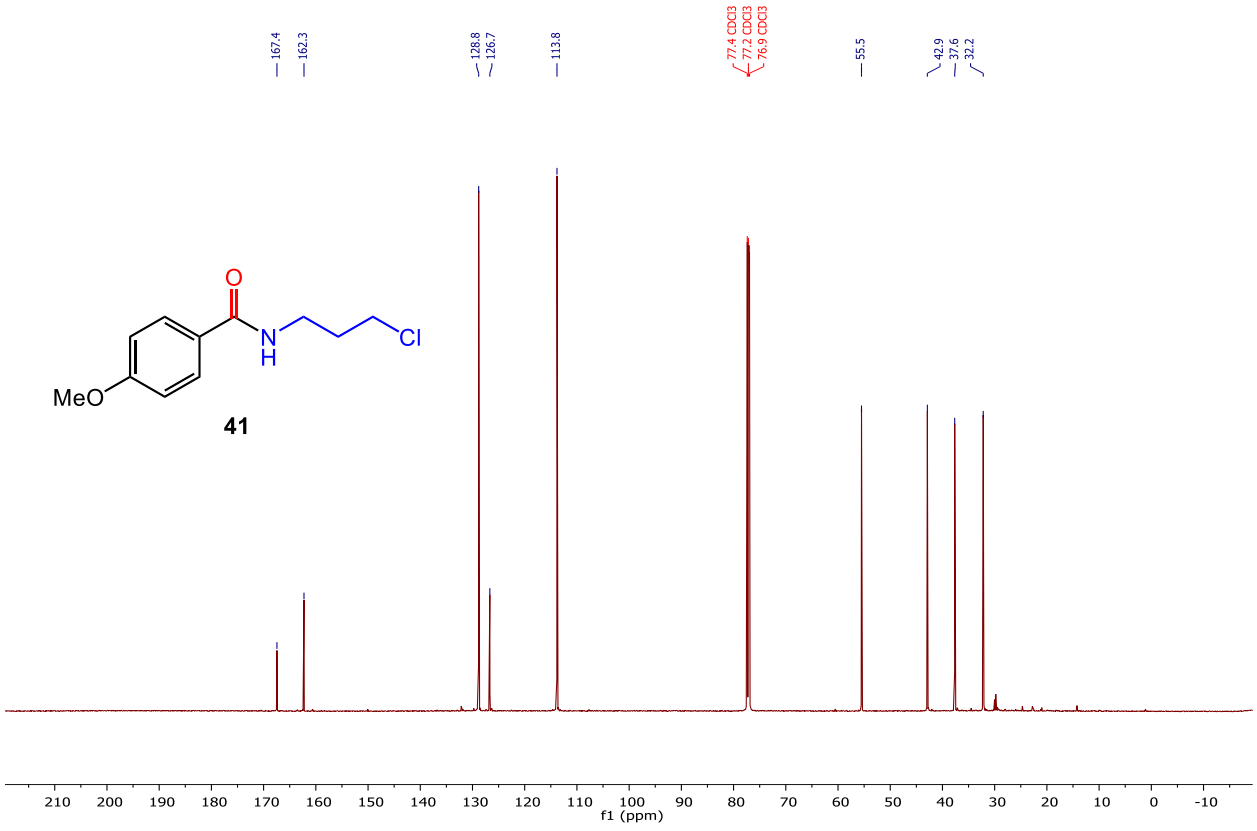

7.73
7.72
7.72
7.71
7.71
7.70
7.26 CDCl3
6.90
6.89
6.89
6.88
6.88
6.87
6.03
6.02
3.97
3.96
3.96
3.95
3.95
3.94
3.93
3.93
3.92
3.91
3.91
3.82
2.01
2.00
2.00
1.99
1.98
1.75
1.74
1.73
1.72
1.72
1.71
1.65
1.64
1.63
1.62
1.62
1.61
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.38
1.37
1.36
1.36
1.35
1.24
1.24
1.22
1.22
1.20
1.20
1.18
1.17
1.16
1.16
O
N
H
MeO
2.00
2.00
0.92
1.00
3.00
2.00
2.00
1.00
2.00
3.00
f1 (ppm)

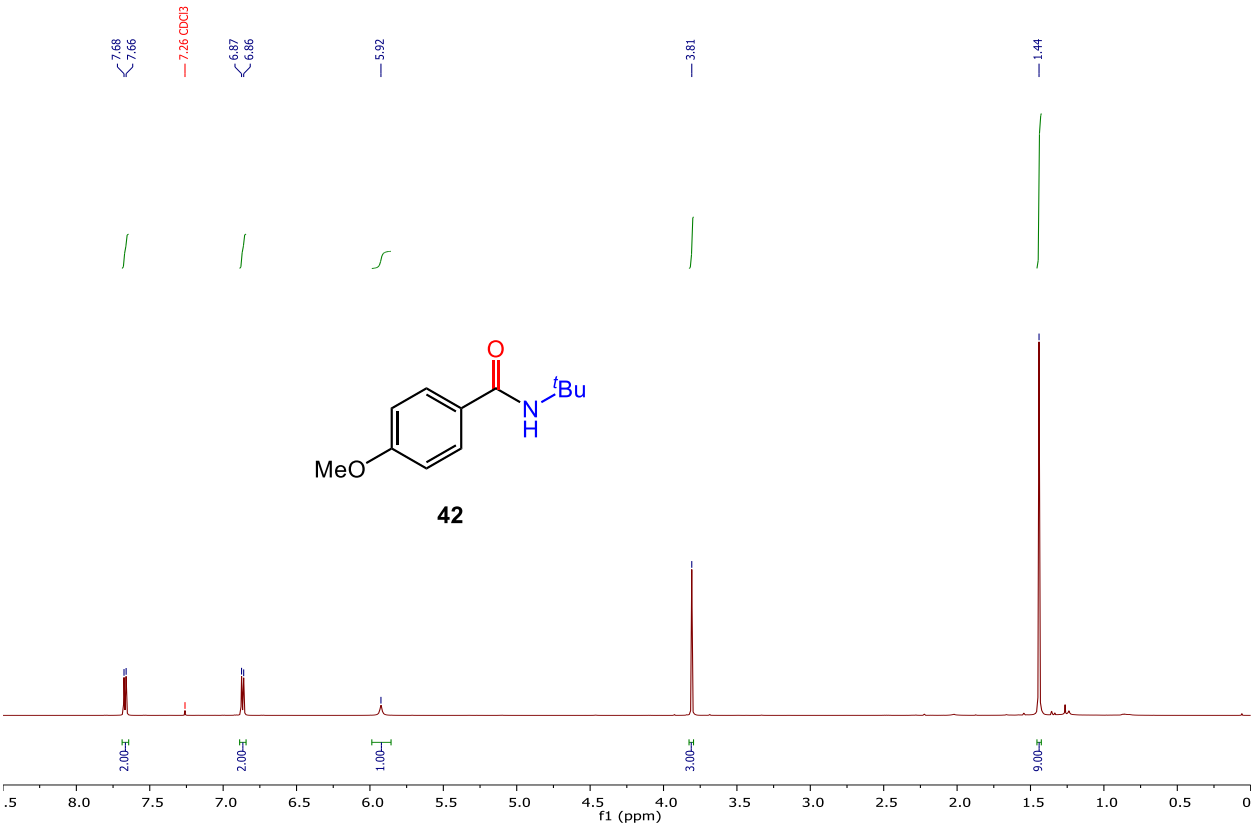
39


7.74
7.72
7.26 CDCl3
6.88
6.86
6.35
3.81
3.41
3.40
3.38
3.37
1.59
1.58
1.57
1.55
1.54
1.35
1.33
1.32
1.31
1.29
1.28
1.28
0.88
0.86
0.85
O
N
H
Me
MeO
2.00
2.00
1.00
3.00
2.00
2.00
6.00
3.00
f1 (ppm)

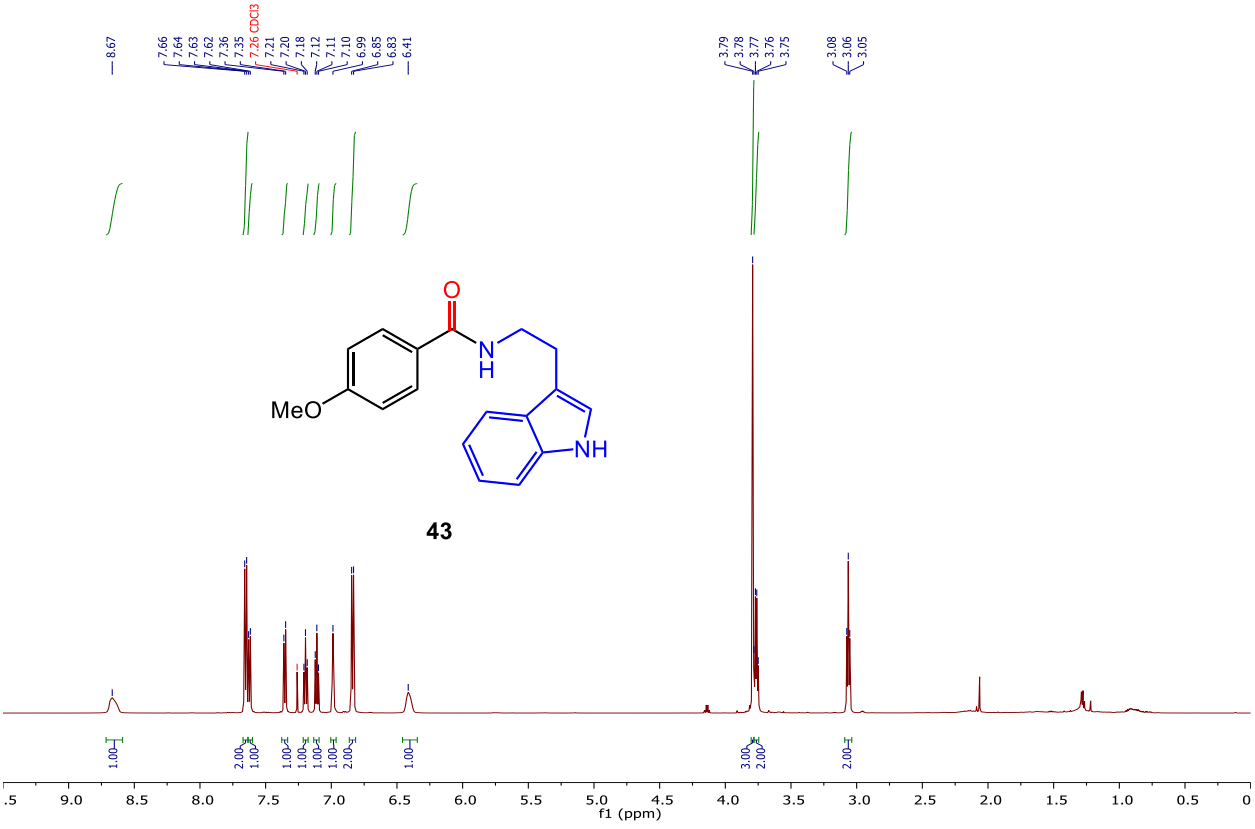
40


7.74
7.73
7.26 CDCl3
6.90
6.89
6.56
3.83
3.62
3.62
3.58
3.57
2.09
2.08
O
N
H
Cl
MeO
41
2.00
2.00
1.00
3.00
4.00
2.00
f1 (ppm)

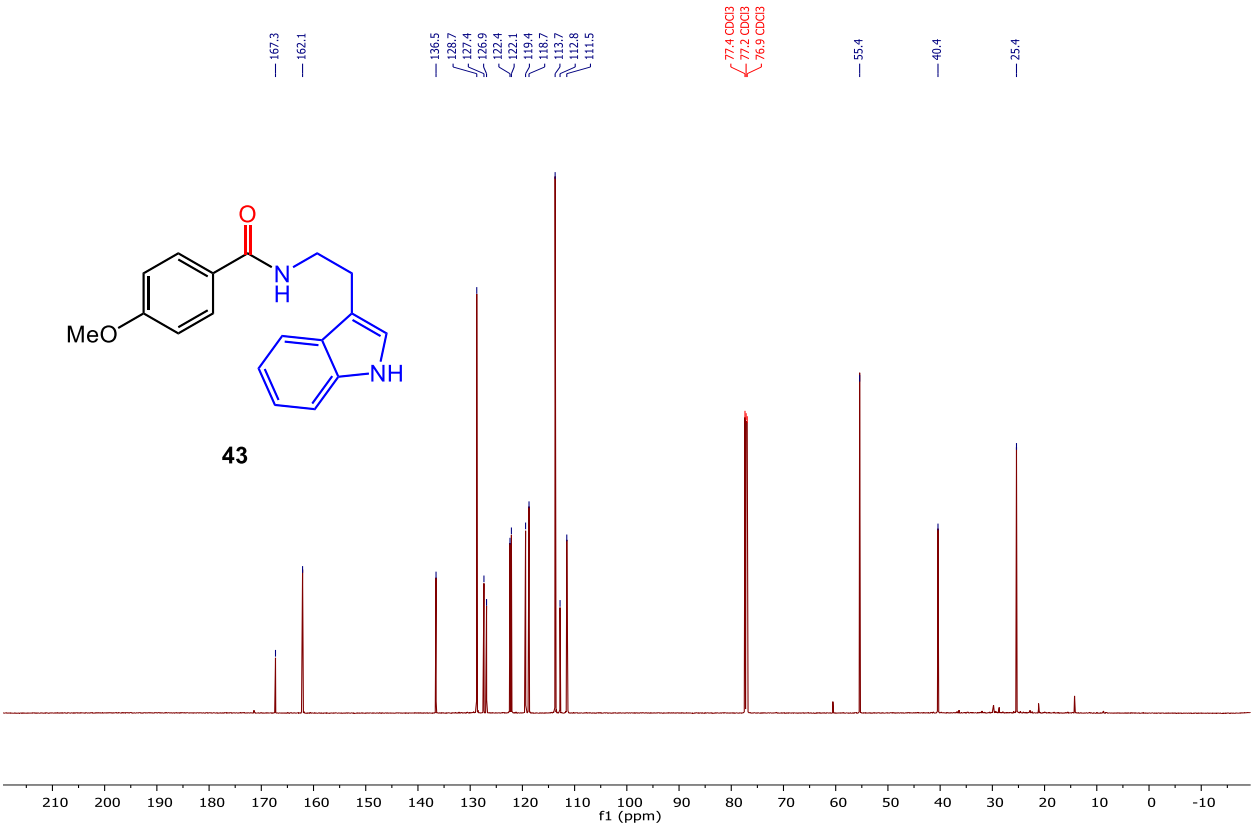

167.4
162.3
128.8
126.7
113.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
55.5
42.9
37.6
32.2
O
N
H
Cl
MeO
41
f1 (ppm)


7.68
7.66
7.26 CDCl3
6.87
6.86
5.92
3.81
1.44
O
N
H
tBu
MeO
2.00
2.00
1.00
3.00
9.00
f1 (ppm)

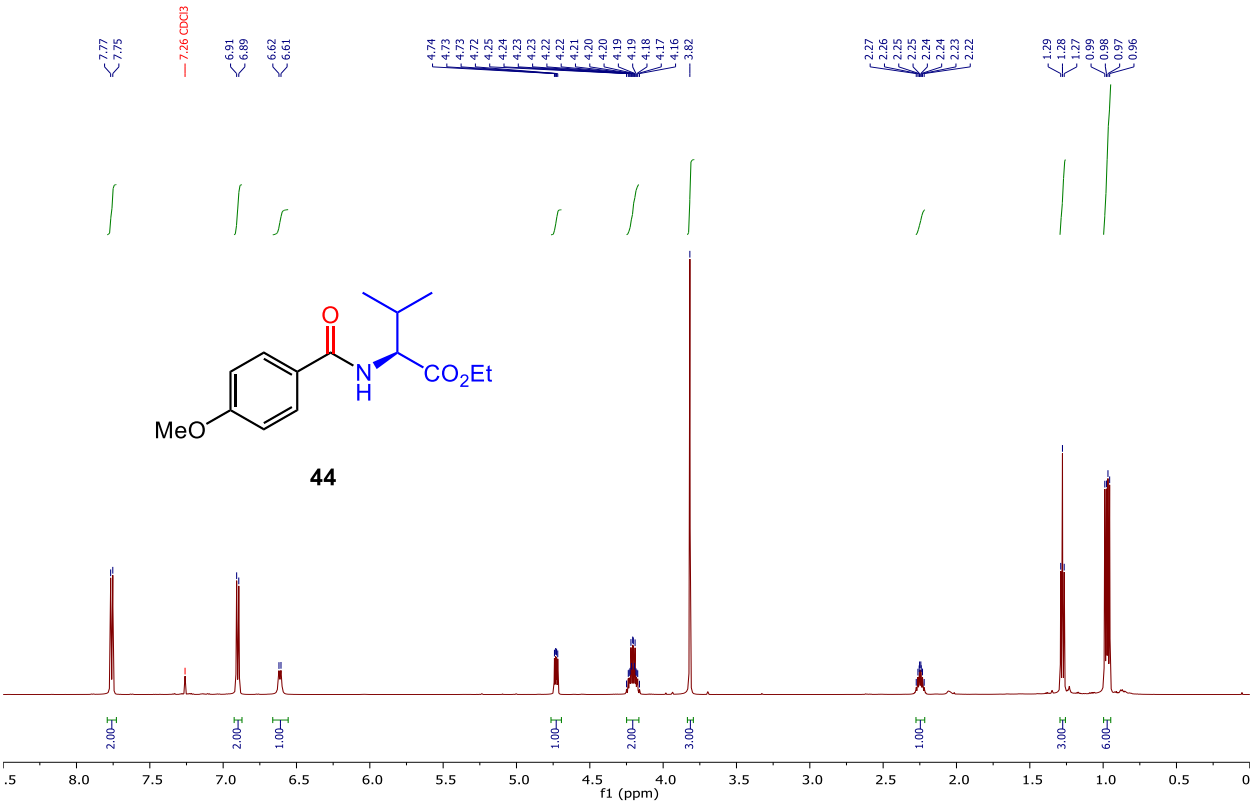
42


8.67
7.66
7.64
7.63
7.62
7.36
7.35
7.26 CDCl3
7.21
7.20
7.18
7.12
7.11
7.10
6.99
6.85
6.83
6.41
3.79
3.78
3.77
3.76
3.75
3.08
3.06
3.05
O
N
H
MeO
NH
1.00
2.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
2.00
2.00
f1 (ppm)

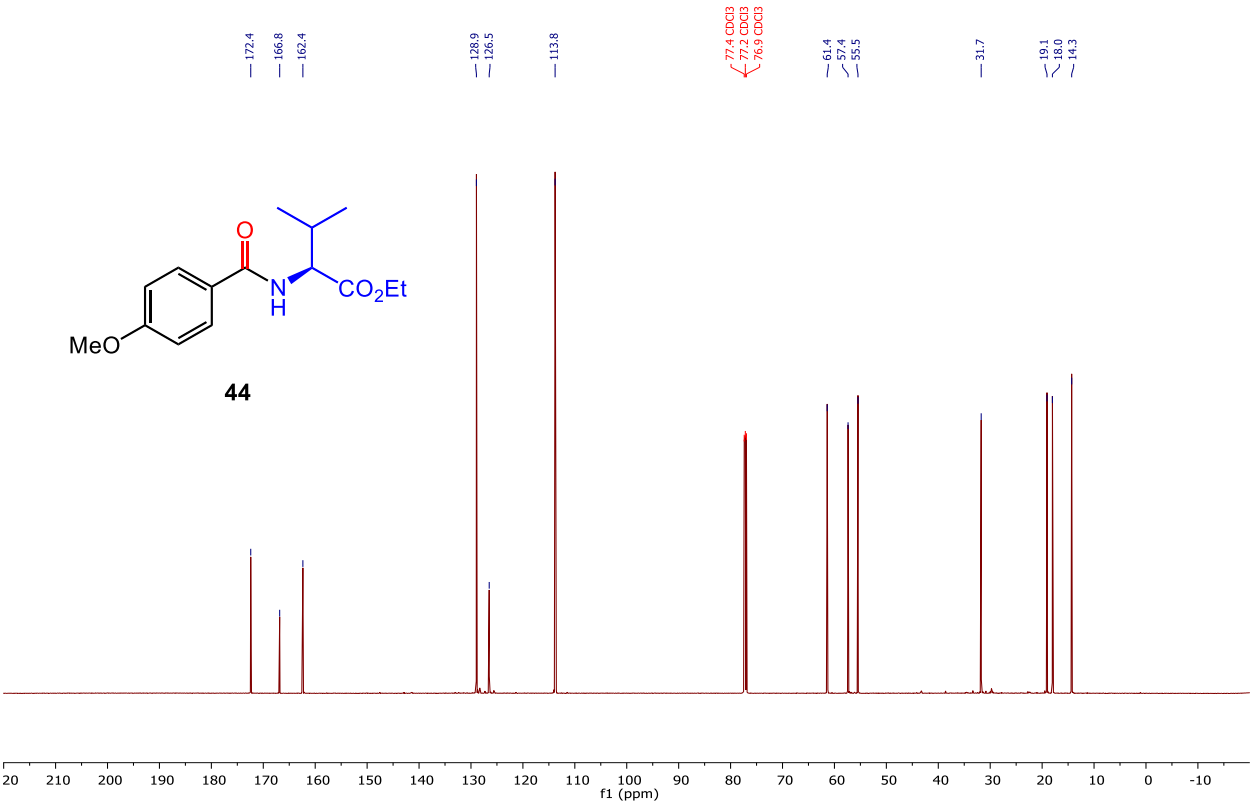
43


167.3
162.1
136.5
128.7
127.4
126.9
122.4
122.1
119.4
118.7
113.7
112.8
111.5
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
55.4
40.4
25.4
O
N
H
MeO
NH
f1 (ppm)

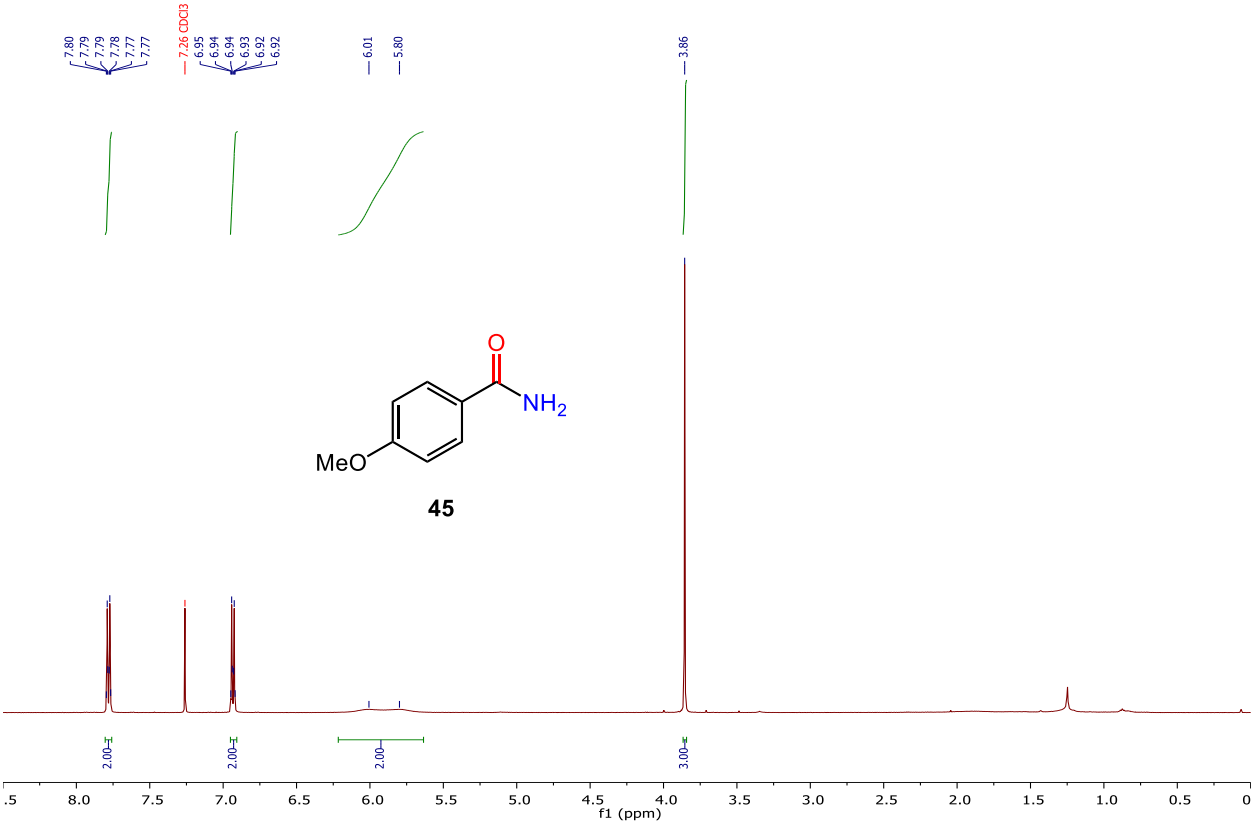
43


7.77
7.75
7.26 CDCl3
6.91
6.89
6.62
6.61
4.74
4.73
4.73
4.72
4.25
4.24
4.23
4.23
4.22
4.22
4.21
4.20
4.20
4.19
4.19
4.18
4.17
4.16
3.82
2.27
2.26
2.25
2.25
2.24
2.24
2.23
2.22
1.29
1.28
1.27
0.99
0.98
0.97
0.96
O
N
H
CO2Et
MeO
2.00
2.00
1.00
1.00
2.00
3.00
1.00
3.00
6.00
f1 (ppm)

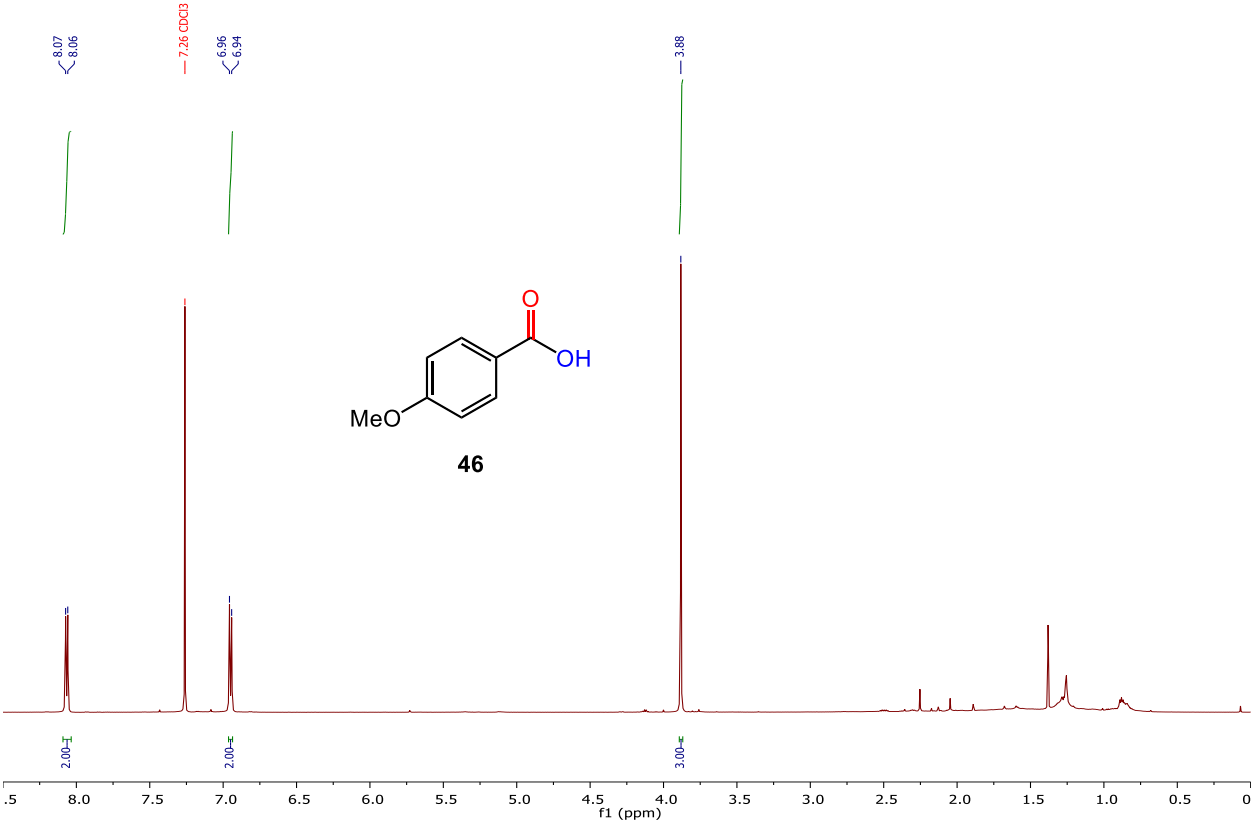
44


172.4
166.8
162.4
128.9
126.5
113.8
77.4 CDCl3
77.2 CDCl3
76.9 CDCl3
61.4
57.4
55.5
31.7
19.1
18.0
14.3
O
N
H
CO2Et
MeO
f1 (ppm)

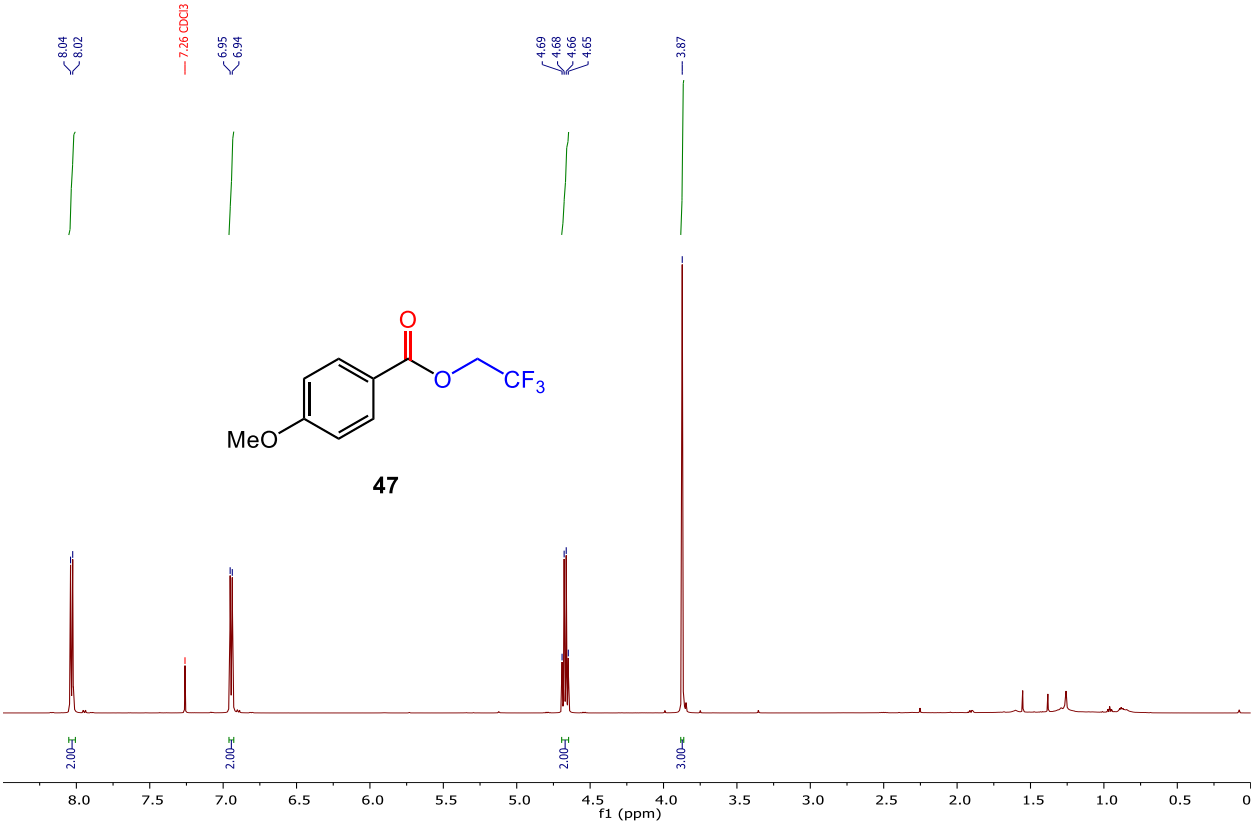
44


7.80
7.79
7.79
7.78
7.77
7.77
7.26 CDCl3
6.95
6.94
6.94
6.93
6.92
6.92
6.01
5.80
3.86
O
NH2
MeO
2.00
2.00
2.00
3.00
f1 (ppm)

45


8.07
8.06
7.26 CDCl3
6.96
6.94
3.88
O
OH
MeO
2.00
2.00
3.00
f1 (ppm)

46


8.04
8.02
7.26 CDCl3
6.95
6.94
4.69
4.68
4.66
4.65
3.87
O
O
CF3
MeO
2.00
2.00
2.00
3.00
f1 (ppm)

47