Supporting Information

N-Acyl pyrroles: chemoselective pyrrole dance vs. C–H functionalization/aroylation of toluenes

Huan Wang,[1,4,5] Jianyou Mao,[3,5] SuJuan Shuai,[4] Shuguang Chen,[2] Dong Zou,[4] Patrick J. Walsh*[2] and Jie Li*[1,4]

[1] School of Pharmaceutical Sciences, Hangzhou Medical College, Hangzhou, Zhejiang 311399, China
E-mail:lijie@zucc.edu.cn

[2]Roy and Diana Vagelos Laboratories, Penn/Merck Laboratory for High-Throughput Experimentation, University of Pennsylvania, Department of Chemistry, 231 South 34th Street, Philadelphia, Pennsylvania 19104, USA.
E-mail: pwalsh@sas.upenn.edu

[3]Technical Institute of Fluorochemistry (TIF), Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing 211800, P. R. China.

[4]College of Pharmaceutical Sciences, Zhejiang university, Hangzhou 310058, P. R. China.

[5]These authors contributed equally to this work

Table of Content

General Information

All reactions were conducted under an atmosphere of dry nitrogen with oven-dried glassware or vacuum line techniques. All anhydrous solvents were purchased from Sigma-Aldrich and directly used without further purification. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Sigma-Aldrich, TCI China, Acros, Alfa Aesar or J&K.

Progress of reactions was monitored by thin-layer chromatography using TLC plates and visualized by short-wave ultraviolet light. Flash chromatography was performed with Qingdao Haiyang flash silica gel (200–300 mesh). The NMR spectra were obtained using a Bruker AVANCE III 500 MHz spectrometers (Bruker Co., Switzerland) with TMS as the internal standard. The infrared spectra were obtained with KBr plates by using an FTIR650 FT-IR Spectrometer. High resolution mass spectrometry (HRMS) data were obtained on an Agilent Q-TOF 1290 LC/6224 MS system using electrospray ionization (ESI) in positive or negative mode. Melting points were determined on a Thermal Values analytical microscope and were uncorrected.

Preparation of *N*-acylpyrroles: *N*-acylpyrroles were prepared according to literature procedures.[1]

Preparation of 2,5-dimethyl-*N*-acylpyrroles: $KN(SiMe_3)_2$ (11.0 mL, 1.0 mol/L in THF, 1.1 equiv) was added dropwise to a cooled solution (–78 °C) of 2,5-dimethyl-1H-pyrrole (10 mmol, 1 equiv) in anhydrous THF (15 mL) under an argon atmosphere. After stirring at –78 °C for 1 h, a solution of benzoyl chloride (11 mmol, 1.1 equiv) in anhydrous THF (10 mL) was added dropwise. After stirring for 1 h, the reaction was warmed to room temperature and stirred for 12 h. The reaction mixture was quenched by aqueous saturated NH_4Cl (50 mL) and extracted with EtOAc (3 × 25 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated. The crude material was loaded onto a silica gel column and purified by flash chromatography.

Synthesis of 2-aroylpyrroles

General Procedure A

An oven-dried 10 mL vial equipped with a stir bar was charged with *N*-acylpyrroles (0.1 mmol) under a nitrogen atmosphere in a glovebox. Dry toluene (1 mL) was added to the reaction followed by addition of $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) by syringe at room temperature. The vial was capped, removed from the glovebox, and stirred for 3 h at 100 °C. After cooling to room temperature,

the reaction mixture was quenched with three drops of H_2O and the vial was opened to the air, passed through a short pad of silica gel and eluted with ethyl acetate (1 mL × 3). The combined organic solution was concentrated under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.

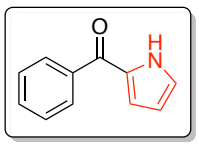
Synthesis of 1,2-diphenylethan-1-ones

General Procedure B

An oven-dried 10 mL vial equipped with a stir bar was charged with (2,5-dimethyl-1H-pyrrol-1-yl)(phenyl)methanone (0.1 mmol) under a nitrogen atmosphere in a glovebox. The toluene derivative (0.12 mmol) in 1 mL of dry THF was added to the reaction followed by addition of $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) by syringe at room temperature. Note that toluene derivatives (0.12 mmol) in a solid form were added to the reaction vial prior to (2,5-dimethyl-1H-pyrrol-1-yl)(phenyl)methanone. The vial was capped, removed from the glovebox, and stirred for 12 h at 100 °C. After cooling to room temperature, the reaction mixture was quenched with three drops of H_2O and the vial was opened to the air, passed through a short pad of silica gel and eluted with ethyl acetate (1 mL × 3). The combined organic solution was concentrated under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.

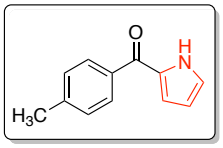
General Procedure C

An oven-dried 10 mL vial equipped with a stir bar was charged with 2,5-dimethyl-*N*-acylpyrroles (0.1 mmol) under a nitrogen atmosphere in a glovebox. Dry toluene (1 mL) was added to the reaction followed by addition of $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) by syringe at room temperature. The vial was capped, removed from the glovebox, and stirred for 12 h at 100 °C. After cooling to room temperature, the reaction mixture was quenched with three drops of H_2O and the vial was opened to the air, passed through a short pad of silica gel and eluted with ethyl acetate (1 mL × 3). The combined organic solution was concentrated under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.

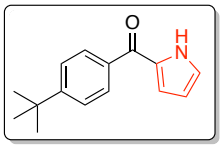


Phenyl(1*H*-pyrrol-2-yl)methanone (3a). The reaction was performed following General Procedure A with **1a** (17.1 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1)

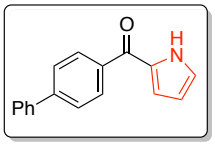
to give the product (13.9 mg, 81% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.92 – 7.90 (m, 2H), 7.59 – 7.55 (m, 1H), 7.51 – 7.47 (m, 2H), 7.17 – 7.15 (m, 1H), 6.91 – 6.89 (m, 1H), 6.36 – 6.34 (m, 1H). The NMR spectral data match the previously published data.[2]



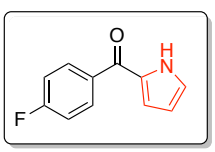
(1*H*-Pyrrol-2-yl)(*p*-tolyl)methanone (3b). The reaction was performed following General Procedure A with **1b** (18.5 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (12.6 mg, 68% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.73 (s, 1H), 7.84 – 7.82 (m, 2H), 7.30 – 7.28 (m, 2H), 7.14 – 7.13 (m, 1H), 6.90 – 6.89 (m, 1H), 6.35 – 6.33 (m, 1H), 2.44 (s, 3H). The NMR spectral data match the previously published data.[2]



(4-(*tert*-Butyl)phenyl)(1*H*-pyrrol-2-yl)methanone (3c). The reaction was performed following General Procedure A with **1c** (22.7 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (17.3 mg, 76% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.17 (s, 1H), 7.89 – 7.87 (m, 2H), 7.52 – 7.50 (m, 2H), 7.16 – 7.15 (m, 1H), 6.94 – 6.92 (m, 1H), 6.35 – 6.33 (m, 1H), 1.37 (s, 9H). The NMR spectral data match the previously published data.[3]

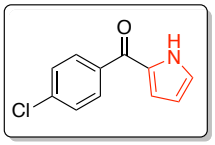


[1,1'-Biphenyl]-4-yl(1*H*-pyrrol-2-yl)methanone (3d). The reaction was performed following General Procedure A with **1d** (24.7 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (20.0 mg, 81% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.02 – 7.99 (m, 2H), 7.73 – 7.71 (m, 2H), 7.67 – 7.65 (m, 2H), 7.51 – 7.47 (m, 2H), 7.42 – 7.39 (m, 1H), 7.18 – 7.17 (m, 1H), 6.97 – 6.96 (m, 1H), 6.38 – 6.36 (m, 1H). The NMR spectral data match the previously published data.[4]

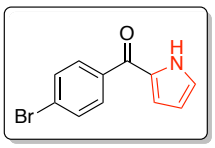


(4-Fluorophenyl)(1*H*-pyrrol-2-yl)methanone (3e). The reaction was performed following General Procedure A with **1e** (18.9 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted

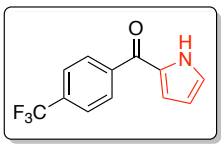
with hexanes:EtOAc = 20:1) to give the product (13.6 mg, 72% yield) as pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.18 (s, 1H), 7.97 – 7.93 (m, 2H), 7.19 – 7.14 (m, 3H), 6.88 – 6.87 (m, 1H), 6.36 – 6.34 (m, 1H). The NMR spectral data match the previously published data.[2]



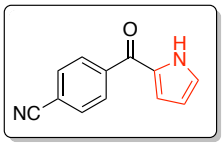
(4-Chlorophenyl)(1*H*-pyrrol-2-yl)methanone (3f). The reaction was performed following General Procedure A with **1f** (20.5 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (16.0 mg, 78% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.05 (s, 1H), 7.87 – 7.84 (m, 2H), 7.48 – 7.45 (m, 2H), 7.18 – 7.17 (m, 1H), 6.88 – 6.86 (m, 1H), 6.36 – 6.34 (m, 1H). The NMR spectral data match the previously published data.[5]



(4-Bromophenyl)(1*H*-pyrrol-2-yl)methanone (3g). The reaction was performed following General Procedure A with **1g** (24.9 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (18.4 mg, 74% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.42 (s, 1H), 7.80 – 7.77 (m, 2H), 7.64 – 7.61 (m, 2H), 7.20 – 7.18 (m, 1H), 6.88 – 6.86 (m, 1H), 6.35 – 6.33 (m, 1H). The NMR spectral data match the previously published data.[2]

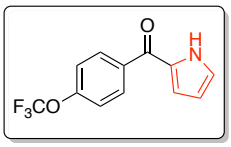


(1*H*-Pyrrol-2-yl)(4-(trifluoromethyl)phenyl)methanone (3h). The reaction was performed following General Procedure A with **1h** (23.9 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (16.7 mg, 70% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.85 (s, 1H), 8.00 – 7.98 (m, 2H), 7.77 – 7.75 (m, 2H), 7.21 – 7.20 (m, 1H), 6.88 – 6.86 (m, 1H), 6.38 – 6.36 (m, 1H). The NMR spectral data match the previously published data.[6]

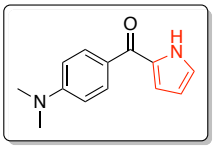


4-(1*H*-Pyrrole-2-carbonyl)benzonitrile (3i). The reaction was performed following General Procedure A with **1i** (19.6 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (14.7 mg, 75% yield) as white solid. ^{1}H NMR (500 MHz,

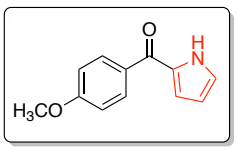
DMSO-d_6): δ 12.22 (s, 1H), 8.01 – 7.98 (m, 2H), 7.94 – 7.91 (m, 2H), 7.30 – 7.28 (m, 1H), 6.79 – 6.78 (m, 1H), 6.30 – 6.28 (m, 1H). The NMR spectral data match the previously published data.[7]



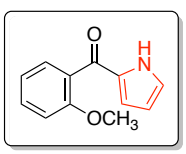
(1*H*-Pyrrol-2-yl)(4-(trifluoromethoxy)phenyl)methanone (3j). The reaction was performed following General Procedure A with **1j** (25.5 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (18.4 mg, 72% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.15 (s, 1H), 7.95 – 7.92 (m, 2H), 7.51 – 7.48 (m, 2H), 7.26 – 7.24 (m, 1H), 6.81 – 6.80 (m, 1H), 6.29 – 6.27 (m, 1H). The NMR spectral data match the previously published data.[6]



(4-(Dimethylamino)phenyl)(1*H*-pyrrol-2-yl)methanone (3k). The reaction was performed following General Procedure A with **1k** (21.4 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (18.0 mg, 84% yield) as yellow solid. mp = 130−132 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.97 – 7.94 (m, 2H), 7.10 – 7.08 (m, 1H), 6.92 – 6.90 (m, 1H), 6.73 – 6.70 (m, 2H), 6.33 – 6.32 (m, 1H), 3.06 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 183.4, 153.1, 131.6, 131.4, 125.7, 124.1, 117.7, 110.9, 110.5, 40.2; IR (thin film): 3260, 2919, 2856, 1611, 1576, 1541, 1127, 771 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}N_2O$ 215.1179; found 215.1179.

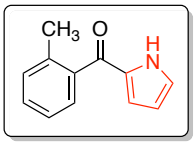


(4-Methoxyphenyl)(1*H*-pyrrol-2-yl)methanone (3l). The reaction was performed following General Procedure A with **1l** (20.1 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (14.5 mg, 72% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.96 – 7.93 (m, 2H), 7.13 – 7.12 (m, 1H), 7.00 – 6.97 (m, 2H), 6.90 – 6.89 (m, 1H), 6.35 – 6.33 (m, 1H), 3.89 (s, 3H). The NMR spectral data match the previously published data.[2]

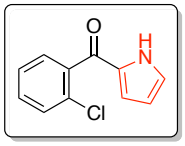


(2-Methoxyphenyl)(1*H*-pyrrol-2-yl)methanone (3m). The reaction was performed following General Procedure A with **1m** (20.1 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with

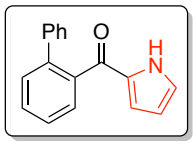
hexanes:EtOAc = 10:1) to give the product (16.9 mg, 84% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.46 – 7.42 (m, 2H), 7.12 – 7.10 (m, 1H), 7.02 – 6.99 (m, 2H), 6.65 – 6.63 (m, 1H), 6.28 – 6.26 (m, 1H), 3.83 (s, 3H). The NMR spectral data match the previously published data.[8]



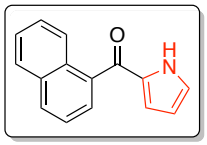
(1*H*-Pyrrol-2-yl)(*o*-tolyl)methanone (3n). The reaction was performed following General Procedure A with **1n** (18.5 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) and 12-crown-4 (52.9 mg, 0.3 mmol) dissolved in dry toluene (1 mL) at 120 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (9.4 mg, 51% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 11.09 (s, 1H), 7.56 – 7.54 (m, 1H), 7.42 – 7.39 (m, 1H), 7.33 – 7.27 (m, 2H), 7.20 – 7.19 (m, 1H), 6.68 – 6.66 (m, 1H), 6.32 – 6.30 (m, 1H), 2.49 (s, 3H). The NMR spectral data match the previously published data.[2]



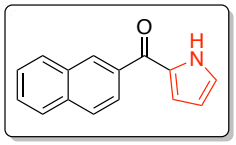
(2-Chlorophenyl)(1*H*-pyrrol-2-yl)methanone (3o). The reaction was performed following General Procedure A with **1o** (20.5 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (14.3 mg, 70% yield) as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.35 (s, 1H), 7.50 – 7.47 (m, 2H), 7.43 – 7.39 (m, 1H), 7.36 – 7.32 (m, 1H), 7.21 – 7.20 (m, 1H), 6.62 – 6.60 (m, 1H), 6.30 – 6.28 (m, 1H). The NMR spectral data match the previously published data.[2]



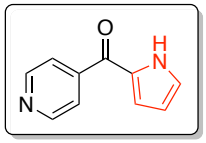
[1,1'-Biphenyl]-2-yl(1*H*-pyrrol-2-yl)methanone (3p). The reaction was performed following General Procedure A with **1p** (24.7 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 6 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (17.5 mg, 71% yield) as white solid. mp = 128−130 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.92 (s, 1H), 7.60 – 7.57 (m, 1H), 7.50 – 7.45 (m, 3H), 7.32 – 7.22 (m, 5H), 7.11 – 7.09 (m, 1H), 6.39 – 6.38 (m, 1H), 6.12 – 6.11 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 185.8, 140.4, 139.9, 139.2, 132.1, 130.2, 130.0, 128.6, 128.34, 128.29, 127.2, 127.0, 126.6, 119.8, 110.3; IR (thin film): 3261, 1623, 1543, 1402, 891 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NO$ 248.1070; found 248.1074.



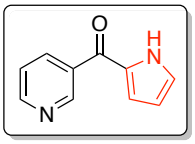
Naphthalen-1-yl(1*H*-pyrrol-2-yl)methanone (3q). The reaction was performed following General Procedure A with **1q** (22.1 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (18.8 mg, 85% yield) as pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.48 (s, 1H), 8.31 – 8.27 (m, 1H), 8.01 – 7.99 (m, 1H), 7.94 – 7.91 (m, 1H), 7.80 (dd, J = 7.0, 1.2 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.20 – 7.19 (m, 1H), 6.71 – 6.69 (m, 1H), 6.31 – 6.29 (m, 1H). The NMR spectral data match the previously published data.[9]



Naphthalen-2-yl(1*H*-pyrrol-2-yl)methanone (3r). The reaction was performed following General Procedure A with **1r** (22.1 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (17.0 mg, 77% yield) as pale yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.20 (s, 1H), 8.46 (s, 1H), 8.01 – 7.91 (m, 4H), 7.62 – 7.55 (m, 2H), 7.21 – 7.20 (m, 1H), 7.01 – 6.99 (m, 1H), 6.39 – 6.38 (m, 1H). The NMR spectral data match the previously published data.[9]

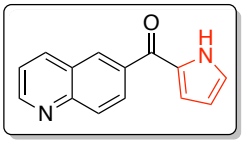


Pyridin-4-yl(1*H*-pyrrol-2-yl)methanone (3s). The reaction was performed following General Procedure A with **1s** (17.2 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) and 12-crown-4 (52.9 mg, 0.3 mmol) dissolved in dry toluene (1 mL) at 120 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (11.0 mg, 64% yield) as pale pink solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.27 (s, 1H), 8.76 – 8.75 (m, 2H), 7.68 – 7.67 (m, 2H), 7.31 – 7.30 (m, 1H), 6.83 – 6.82 (m, 1H), 6.30 – 6.28 (m, 1H). The NMR spectral data match the previously published data.[10]

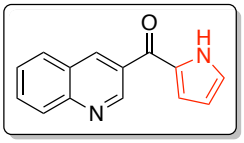


Pyridin-3-yl(1*H*-pyrrol-2-yl)methanone (3t). The reaction was performed following General Procedure A with **1t** (17.2 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (10.5 mg, 61% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.23

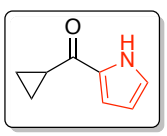
(s, 1H), 8.96 – 8.95 (m, 1H), 8.77 (dd, J = 4.8, 1.7 Hz, 1H), 8.17 – 8.15 (m, 1H), 7.55 – 7.53 (m, 1H), 7.29 – 7.27 (m, 1H), 6.83 – 6.81 (m, 1H), 6.29 – 6.28 (m, 1H). The NMR spectral data match the previously published data.[11]



(1*H*-Pyrrol-2-yl)(quinolin-6-yl)methanone (3u). The reaction was performed following General Procedure A with **1u** (22.2 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (16.2 mg, 73% yield) as white solid. mp = 181−183 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.19 (s, 1H), 9.01 (dd, J = 4.2, 1.8 Hz, 1H), 8.58 (dd, J = 8.3, 1.8 Hz, 1H), 8.53 (d, J = 1.6 Hz, 1H), 8.14 – 8.10 (m, 2H), 7.63 (dd, J = 8.3, 4.2 Hz, 1H), 7.29 – 7.28 (m, 1H), 6.94 – 6.93 (m, 1H), 6.32 – 6.31 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 183.1, 152.3, 148.8, 137.7, 136.3, 130.6, 129.7, 129.3, 128.8, 127.2, 126.9, 122.3, 120.1, 110.7; IR (thin film): 3436, 1735, 1637, 1552, 1399, 1137, 812 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{14}H_{11}N_2O$ 223.0866; found 223.0869.

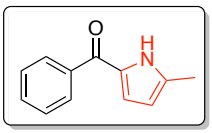


(1*H*-Pyrrol-2-yl)(quinolin-3-yl)methanone (3v). The reaction was performed following General Procedure A with **1v** (22.2 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (15.1 mg, 68% yield) as pale yellow solid. mp = 172−173°C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.28 (s, 1H), 9.22 (d, J = 2.1 Hz, 1H), 8.85 (d, J = 2.1 Hz, 1H), 8.19 (dd, J = 8.2, 1.3 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.71 – 7.67 (m, 1H), 7.32 – 7.31 (m, 1H), 6.98 – 6.96 (m, 1H), 6.33 – 6.32 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 181.8, 149.4, 148.6, 137.0, 131.4, 131.1, 130.6, 129.6, 128.7, 127.4, 127.2, 126.5, 120.2, 110.8; IR (thin film): 3184, 1625, 1398, 1147, 1124, 814 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{14}H_{11}N_2O$ 223.0881; found 223.0869.

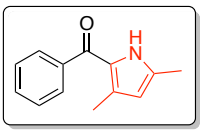


Cyclopropyl(1*H*-pyrrol-2-yl)methanone (3w). The reaction was performed following General Procedure A with **1w** (13.5 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) and 12-crown-4 (52.9 mg, 0.3 mmol) dissolved in dry toluene (1 mL) at 120 °C for 3 h. The crude material was purified by flash chromatography on silica gel

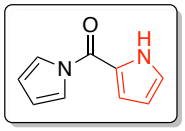
(eluted with hexanes:EtOAc = 20:1) to give the product (6.5 mg, 48% yield) as white solid. mp = 70−71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.44 (s, 1H), 7.08 – 7.02 (m, 2H), 7.30 – 7.29 (m, 1H), 2.50 – 2.45 (m, 2H), 1.23 – 1.19 (m, 1H), 0.99 – 0.95 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 190.7, 132.6, 124.8, 116.4, 110.6, 17.1, 10.7; IR (thin film): 3003, 2955, 1614, 1452, 1413, 929 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_8H_{10}NO$ 136.0757; found 136.0763.



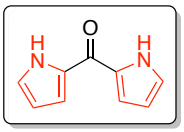
(5-Methyl-1*H*-pyrrol-2-yl)(phenyl)methanone (3x). The reaction was performed following General Procedure A with **1x** (18.5 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) and 12-crown-4 (52.9 mg, 0.3 mmol) dissolved in dry toluene (1 mL) at 120 °C for 13.5 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (11.7 mg, 63% yield) as brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.55 (s, 1H), 7.92 – 7.89 (m, 2H), 7.57 – 7.53 (m, 1H), 7.50 – 7.46 (m, 2H), 6.83 – 6.82 (m, 1H), 6.07 – 6.05 (m, 1H), 2.41 (s, 3H). The NMR spectral data match the previously published data.[12]



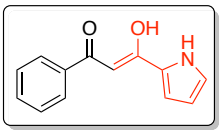
(3,5-Dimethyl-1*H*-pyrrol-2-yl)(phenyl)methanone (3y). The reaction was performed following General Procedure A with **1y** (19.9 mg, 0.1 mmol), $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) and 12-crown-4 (52.9 mg, 0.3 mmol) dissolved in dry toluene (1 mL) at 120 °C for 13.5 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (11.5 mg, 58% yield) as light brown solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.41 (s, 1H), 7.64 – 7.62 (m, 2H), 7.52 – 7.48 (m, 1H), 7.46 – 7.42 (m, 2H), 5.86 (d, J = 2.7 Hz, 1H), 2.30 (s, 3H), 1.92 (s, 3H). The NMR spectral data match the previously published data.[5]



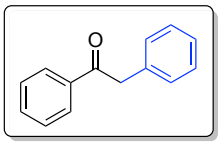
(1*H*-Pyrrol-1-yl)(1*H*-pyrrol-2-yl)methanone (3z). The reaction was performed following General Procedure A with **1z** (16.0 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 3 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (9.7 mg, 61% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 12.25 (s, 1H), 7.52 – 7.52 (m, 2H), 7.25 – 7.24 (m, 1H), 7.00 – 6.98 (m, 1H), 6.36 – 6.35 (m, 2H), 6.32 – 6.30 (m, 1H). The NMR spectral data match the previously published data.[13]



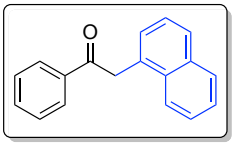
Di(1*H*-pyrrol-2-yl)methanone (3aa). The reaction was performed following General Procedure A with **1z** (16.0 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 120 °C for 13.5 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (8.0 mg, 50% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.81 (s, 2H), 7.09 – 7.05 (m, 4H), 6.23 – 6.21 (m, 2H). The NMR spectral data match the previously published data.[14]



(*Z*)-3-Hydroxy-1-phenyl-3-(1*H*-pyrrol-2-yl)prop-2-en-1-one (3Z). The reaction was performed following General Procedure A with **1Z** (21.3 mg, 0.1 mmol) and $LiN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in dry toluene (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 20:1) to give the product (18.7 mg, 88% yield) as yellow solid. mp = 108−109 °C. ^{1}H NMR (500 MHz, DMSO-d_6) [enol + keto]: δ 12.07 (s, 1H), 11.93 (s, 0.16H), 8.05 – 8.02 (m, 2H), 8.00 – 7.98 (m, 0.32H), 7.66 – 7.63 (m, 0.16H), 7.60 – 7.56 (m, 1H), 7.55 – 7.51 (m, 2.32H), 7.32 – 7.30 (m, 1H), 7.21 – 7.20 (m, 1H), 7.15 – 7.13 (m, 0.16H), 7.12 – 7.11 (m, 0.16H), 7.02 (s, 1H), 6.30 – 6.29 (m, 1H), 6.23 – 6.22 (m, 0.16H), 4.56 (s, 0.32H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) [enol + keto]: δ 195.3, 183.5, 181.4, 176.5, 136.4, 134.00, 133.5, 132.00, 131.6, 129.7, 128.77, 128.75, 128.5, 126.4, 126.3, 118.2, 116.5, 110.7, 110.2, 92.8, 49.1, one resonance was not observed due to coincidental overlap; IR (thin film): 3292, 3105, 1617, 1575, 1493, 1122, 744, 681 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{11}NNaO_2$ 236.0682; found 236.0689.

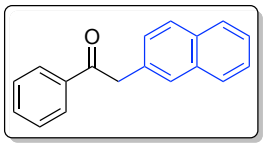


1,2-Diphenylethan-1-one (4aa). The reaction was performed following General Procedure C with **5a** (19.9 mg, 0.1 mmol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (16.3 mg, 83% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.08 (d, J = 7.5 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.54 – 7.51 (m, 2H), 7.33 – 7.29 (m, 4H), 7.25 – 7.21 (m, 1H), 4.40 (s, 2H). The NMR spectral data match the previously published data. [15]

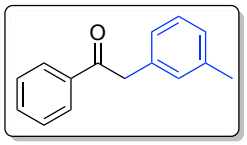


2-(Naphthalen-1-yl)-1-phenylethan-1-one (4ab). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2b** (17.0 mg, 0.12 mmol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved

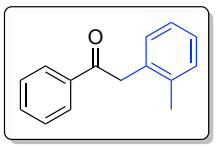
in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (21.9 mg, 89% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.15 – 8.13 (m, 2H), 7.95 – 7.93 (m, 1H), 7.86 – 7.84 (m, 2H), 7.70 – 7.66 (m, 1H), 7.59 – 7.56 (m, 2H), 7.52 – 7.43 (m, 4H), 4.91 (s, 2H). The NMR spectral data match the previously published data.[16]



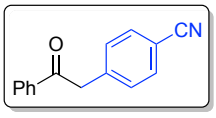
2-(Naphthalen-2-yl)-1-phenylethan-1-one (4ac). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2c** (17.0 mg, 0.12 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (14.3 mg, 58% yield) as colorless crystal. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.11 – 8.08 (m, 2H), 7.89 – 7.84 (m, 3H), 7.80 – 7.79 (m, 1H), 7.67 – 7.63 (m, 1H), 7.57 – 7.53 (m, 2H), 7.51 – 7.46 (m, 2H), 7.42 (dd, J = 8.5, 1.8 Hz, 1H), 4.58 (s, 2H). The NMR spectral data match the previously published data.[17]



1-Phenyl-2-(m-tolyl)ethan-1-one (4ad). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2d** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (15.3 mg, 73% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.05 – 8.03 (m, 2H), 7.65 – 7.62 (m, 1H), 7.55 – 7.51 (m, 2H), 7.20 – 7.17 (m, 1H), 7.07 – 7.03 (m, 3H), 4.34 (s, 2H), 2.27 (s, 3H). The NMR spectral data match the previously published data.[17]

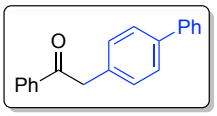


1-Phenyl-2-(*o*-tolyl)ethan-1-one (4ae). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2e** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (12.0 mg, 57% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.08 – 8.05 (m, 2H), 7.68 – 7.65 (m, 1H), 7.57 – 7.54 (m, 2H), 7.19 – 7.10 (m, 4H), 4.44 (s, 2H), 2.15 (s, 3H). The NMR spectral data match the previously published data.[16]

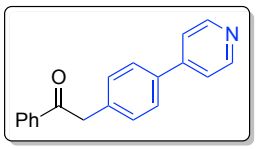


4-(2-Oxo-2-phenylethyl)benzonitrile (4af). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2f** (14.1 mg, 0.12

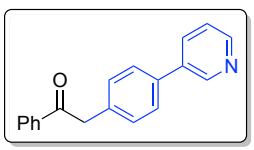
mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 50:1) to give the product (20.8 mg, 94% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.07 – 8.05 (m, 2H), 7.80 – 7.78 (m, 2H), 7.68 – 7.65 (m, 1H), 7.57 – 7.54 (m, 2H), 7.49 – 7.47 (m, 2H), 4.57 (s, 2H).[17]



2-([1,1'-Biphenyl]-4-yl)-1-phenylethan-1-one (4ah). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2h** (20.2 mg, 0.12 mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (17.1 mg, 63% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.09 – 8.07 (m, 2H), 7.67 – 7.60 (m, 5H), 7.56 – 7.53 (m, 2H), 7.47 – 7.43 (m, 2H), 7.37 – 7.33 (m, 3H), 4.45 (s, 2H).[18]

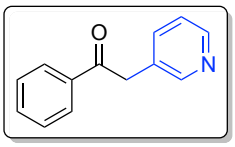


1-Phenyl-2-(4-(pyridin-4-yl)phenyl)ethan-1-one (4ai). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2i** (20.3 mg, 0.12 mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (24.8 mg, 91% yield) as pale yellow solid. mp = 154−156 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.63 – 8.61 (m, 2H), 8.09 – 8.07 (m, 2H), 7.78 – 7.75 (m, 2H), 7.71 – 7.70 (m, 2H), 7.68 – 7.64 (m, 1H), 7.57 – 7.54 (m, 2H), 7.44 – 7.42 (m, 2H), 4.49 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): δ 197.5, 150.2, 146.8, 136.5, 136.3, 135.3, 133.4, 130.7, 128.8, 128.4, 126.7, 121.1, 44.4; IR (thin film): 3034, 2920, 1686, 1596, 1405, 991, 786 cm^{-1}; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{15}NNaO$ 296.1046; found 296.1051.

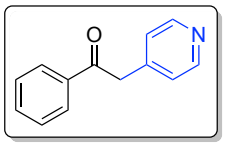


1-Phenyl-2-(4-(pyridin-3-yl)phenyl)ethan-1-one (4aj). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2j** (20.3 mg, 0.12 mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (22.4 mg, 82% yield) as pale yellow solid. mp = 113−115 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.89 (dd, J = 2.4, 0.9 Hz, 1H), 8.56 (dd, J = 4.7, 1.6 Hz, 1H), 8.09 – 8.05 (m, 3H), 7.70 – 7.64 (m, 3H), 7.57 – 7.53 (m, 2H), 7.49 – 7.46 (m, 1H),

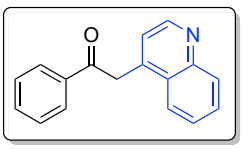
7.42 – 7.39 (m, 2H), 4.47 (s, 2H). $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-d_6): δ 197.6, 148.4, 147.6, 136.3, 135.3, 135.29, 135.25, 134.0, 133.4, 130.6, 128.8, 128.4, 126.8, 123.9, 44.3; IR (thin film): 3058, 2923, 1684, 1654, 1385, 995, 784 cm^{-1}; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{15}NNaO$ 296.1046; found 296.1047.



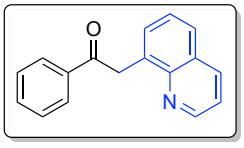
1-Phenyl-2-(pyridin-3-yl)ethan-1-one (4ak). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2k** (11.2 mg, 0.12 mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (18.7 mg, 95% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.87 – 8.85 (m, 2H), 8.49 – 8.45 (m, 1H), 8.10 – 8.03 (m, 3H), 7.73 – 7.70 (m, 1H), 7.62 – 7.59 (m, 2H), 4.80 (s, 2H). The NMR spectral data match the previously published data.[19]



1-Phenyl-2-(pyridin-4-yl)ethan-1-one (4al). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2l** (11.2 mg, 0.12 mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (17.1 mg, 87% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.52 – 8.51 (m, 2H), 8.08 – 8.05 (m, 2H), 7.68 – 7.65 (m, 1H), 7.57 – 7.54 (m, 2H), 7.31 – 7.29 (m, 2H), 4.50 (s, 2H). The NMR spectral data match the previously published data.[20]

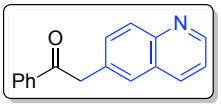


1-Phenyl-2-(quinolin-4-yl)ethan-1-one (4am). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2m** (17.2 mg, 0.12 mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (22.7 mg, 92% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.85 (d, J = 4.3 Hz, 1H), 8.16 – 8.14 (m, 2H), 8.06 (dd, J = 8.4, 1.2 Hz, 1H), 7.96 (dd, J = 8.3, 1.3 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.72 – 7.68 (m, 1H), 7.61 – 7.55 (m, 3H), 7.46 (d, J = 4.4 Hz, 1H), 5.02 (s, 2H). The NMR spectral data match the previously published data.[21]

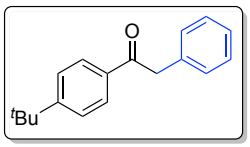


1-Phenyl-2-(quinolin-8-yl)ethan-1-one (4an). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2n** (17.2 mg, 0.12 mol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in

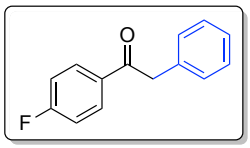
THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (18.5 mg, 75% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.83 (dd, J = 4.2, 1.8 Hz, 1H), 8.38 (dd, J = 8.3, 1.8 Hz, 1H), 8.12 – 8.10 (m, 2H), 7.92 (dd, J = 8.2, 1.5 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.60 – 7.54 (m, 3H), 7.52 (dd, J = 8.3. 4.2 Hz, 1H), 4.95 (s, 2H). The NMR spectral data match the previously published data.[22]



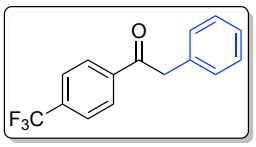
1-Phenyl-2-(quinolin-6-yl)ethan-1-one (4ao). The reaction was performed following General Procedure B with **5a** (19.9 mg, 0.1 mmol), **2o** (17.2 mg, 0.12 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in THF (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (18.0 mg, 73% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.87 (dd, J = 4.2, 1.7 Hz, 1H), 8.32 – 8.29 (m, 1H), 8.11 – 8.09 (m, 2H), 7.98 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 1.9 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.57 – 7.54 (m, 2H), 7.51 (dd, J = 8.3, 4.2 Hz, 1H), 4.64 (s, 2H). The NMR spectral data match the previously published data.[19]



1-(4-(*tert*-Butyl)phenyl)-2-phenylethan-1-one (4ba). The reaction was performed following General Procedure C with **5b** (25.5 mg, 0.1 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (22.7 mg, 90% yield) as pale yellow solid. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.90 – 7.87 (m, 2H), 7.41 – 7.38 (m, 2H), 7.27 – 7.15 (m, 5H), 4.19 (s, 2H), 2.16 (s, 9H). The NMR spectral data match the previously published data.[23]

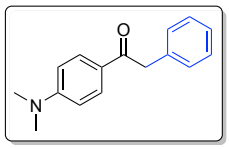


1-(4-Fluorophenyl)-2-phenylethan-1-one (4ca). The reaction was performed following General Procedure C with **5c** (21.7 mg, 0.1 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (16.7 mg, 78% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.16 – 8.11 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.21 (m, 3H), 4.39 (s, 2H). The NMR spectral data match the previously published data.[24]

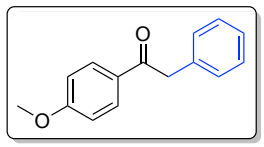


2-Phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (4da). The reaction was performed following General Procedure C with **5d** (26.7 mg, 0.1 mmol)

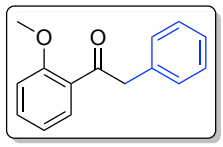
and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (16.6 mg, 63% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.23 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.2 Hz, 2H), 7.34 – 7.22 (m, 5H), 4.47 (s, 2H). The NMR spectral data match the previously published data.[25]



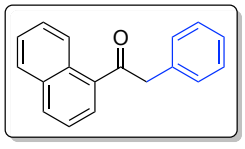
1-(4-(Dimethylamino)phenyl)-2-phenylethan-1-one (4ea). The reaction was performed following General Procedure C with **5e** (24.2 mg, 0.1 mmol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 50:1) to give the product (16.7 mg, 70% yield) as yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 – 7.92 (m, 2H), 7.33 – 7.28 (m, 4H), 7.24 – 7.20 (m, 1H), 6.66 – 6.63 (m, 2H), 4.19 (s, 2H), 3.04 (s, 6H). The NMR spectral data match the previously published data.[24]



1-(4-Methoxyphenyl)-2-phenylethan-1-one (4fa). The reaction was performed following General Procedure C with **5f** (22.9 mg, 0.1 mmol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (16.7 mg, 74% yield) as yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 – 7.99 (m, 2H), 7.34 – 7.23 (m, 5H), 6.94 – 6.91 (m, 2H), 4.24 (s, 2H), 3.86 (s, 3H). The NMR spectral data match the previously published data.[15]

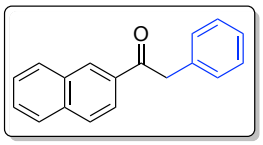


1-(2-Methoxyphenyl)-2-phenylethan-1-one (4ga). The reaction was performed following General Procedure C with **5g** (22.9 mg, 0.1 mmol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (17.8 mg, 79% yield) as colorless oil. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.54 – 7.50 (m, 2H), 7.30 – 7.27 (m, 2H), 7.23 – 7.15 (m, 4H), 7.02 – 6.99 (m, 1H), 4.25 (s, 2H), 3.90 (s, 3H). The NMR spectral data match the previously published data.[15]

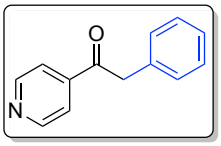


1-(Naphthalen-1-yl)-2-phenylethan-1-one (4ha). The reaction was performed following General Procedure C with **5h** (24.9 mg, 0.1 mmol) and $KN(SiMe_3)_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at

100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (16.7 mg, 68% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.43 – 8.41 (m, 1H), 8.25 (dd, J = 7.2, 1.2 Hz, 1H), 8.12 (d, J = 8.3 Hz, 1H), 8.00 – 7.98 (m, 1H), 7.63 – 7.54 (m, 3H), 7.32 – 7.28 (m, 4H), 7.23 – 7.20 (m, 1H), 4.48 (s, 2H). The NMR spectral data match the previously published data. [26]



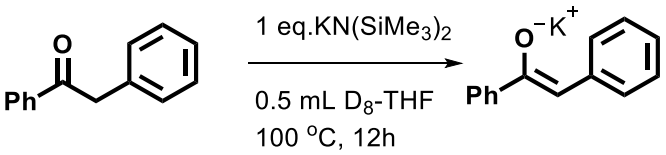
1-(Naphthalen-2-yl)-2-phenylethan-1-one (4ia). The reaction was performed following General Procedure C with **5i** (24.9 mg, 0.1 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 100:1) to give the product (11.1 mg, 45% yield) as pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.82 (d, J = 1.3 Hz, 1H), 8.15 (dd, J = 7.8, 1.4 Hz, 1H), 8.03 – 7.99 (m, 3H), 7.69 – 7.62 (m, 2H), 7.34 – 7.30 (m, 4H), 7.25 – 7.21 (m, 1H), 4.53 (s, 2H). The NMR spectral data match the previously published data.[24]



2-Phenyl-1-(pyridin-4-yl)ethan-1-one (4ja). The reaction was performed following General Procedure C with **5j** (20.0 mg, 0.1 mmol) and KN(SiMe$_3$)$_2$ (1.0 mol/L in THF, 0.3 mL, 0.3 mmol) dissolved in **2a** (1 mL) at 100 °C for 12 h. The crude material was purified by flash chromatography on silica gel (eluted with hexanes:EtOAc = 10:1) to give the product (10.0 mg, 51% yield) as white solid. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.82 – 8.81 (m, 2H), 7.90 – 7.89 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.23 (m, 3H), 4.45 (s, 2H). The NMR spectral data match the previously published data.[26]

Mechanism study

J-Young tube reaction for deprotonation of 1,2-diphenylethan-1-one

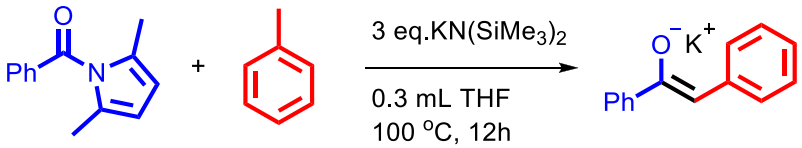


4aa **5aa**

An oven-dried 20 mL vial equipped with a stir bar was charged with 1,2-diphenylethan-1-one (**4aa**) (7.0 mg, 0.036 mmol) under a nitrogen atmosphere in the glovebox. A solution of KN(SiMe$_3$)$_2$ (7.2 mg, 0.036 mmol) in 0.5 mL of dry THF-D$_8$ was added at rt. After stirring for 5 min at 24 °C, the mixture was carefully transferred to J-Young tube. The J-Young NMR tube was sealed, removed from the glove box, and stirred for 12 h at 100 °C. After cooling to room temperature, ^{1}H and ^{13}C{^{1}H} NMR spectra were

acquired.

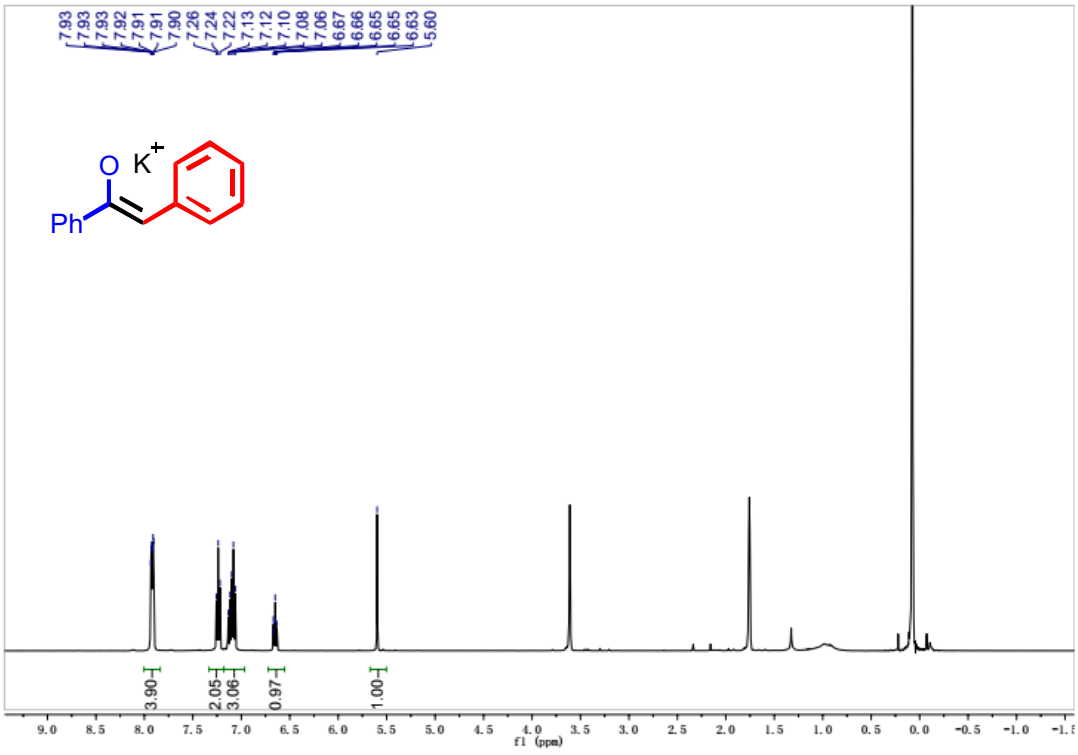
J-Young tube experiment of aroylation of toluene



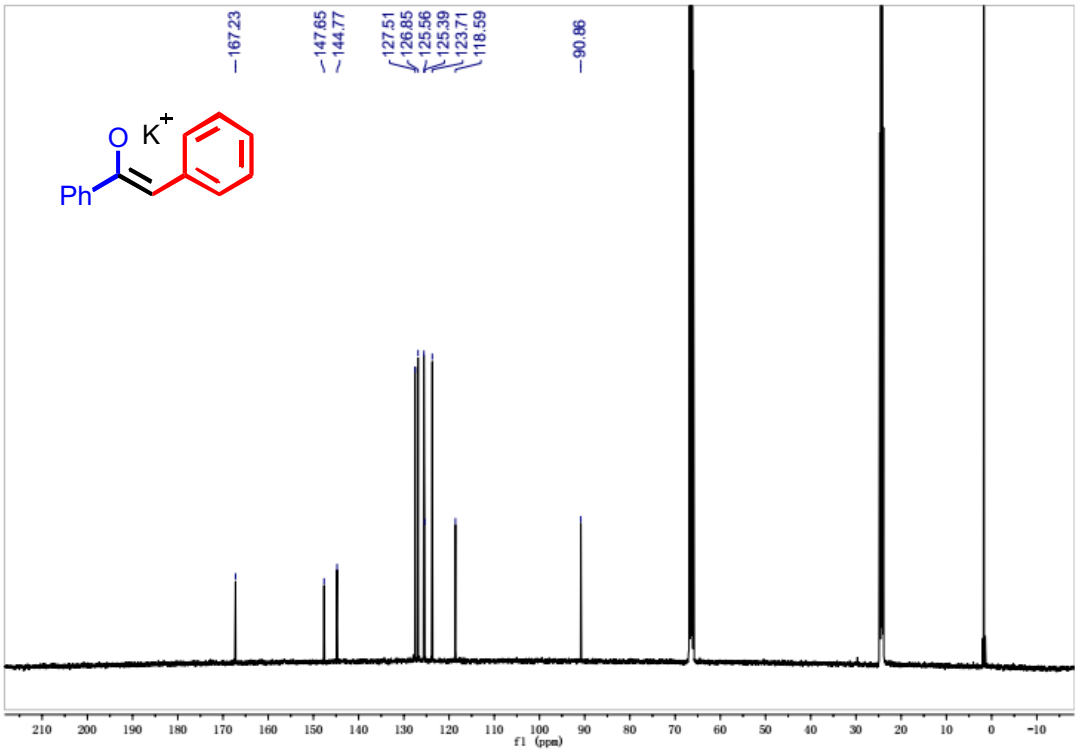
5a **2a** 1 mL **5aa**

To an oven dried scintillation vial equipped with a stir bar under a nitrogen atmosphere in the glove box were added **5a** (19.9 mg, 0.1 mmol), anhydrous toluene (1 mL), dry tertahydrofuran (0.3 mL) and $KN(SiMe_3)_2$ (59.7 mg, 0.3 mmol) at room temperature. The scintillation vial was sealed with cap and removed from the glove box. The reaction vessel was heated to 100 °C and stirred for 12 h. The scintillation vial was cool to room temperature and taken inside the glovebox. Removed the cap and the reuslting mixture was passed through a short pad of wiping paper loaded inside a pipet, and collected the solution using 20 mL vial and removed the combined solvent with oil pump in glovebox. The crude material was redissolved by 0.5 mL dry D_8-THF and the resulted mixture was transferred to the J-Young tube carefully with pipet. J-Young tube was removed outside the glovebox after sealing it tightly and transferred to take the NMR directly.

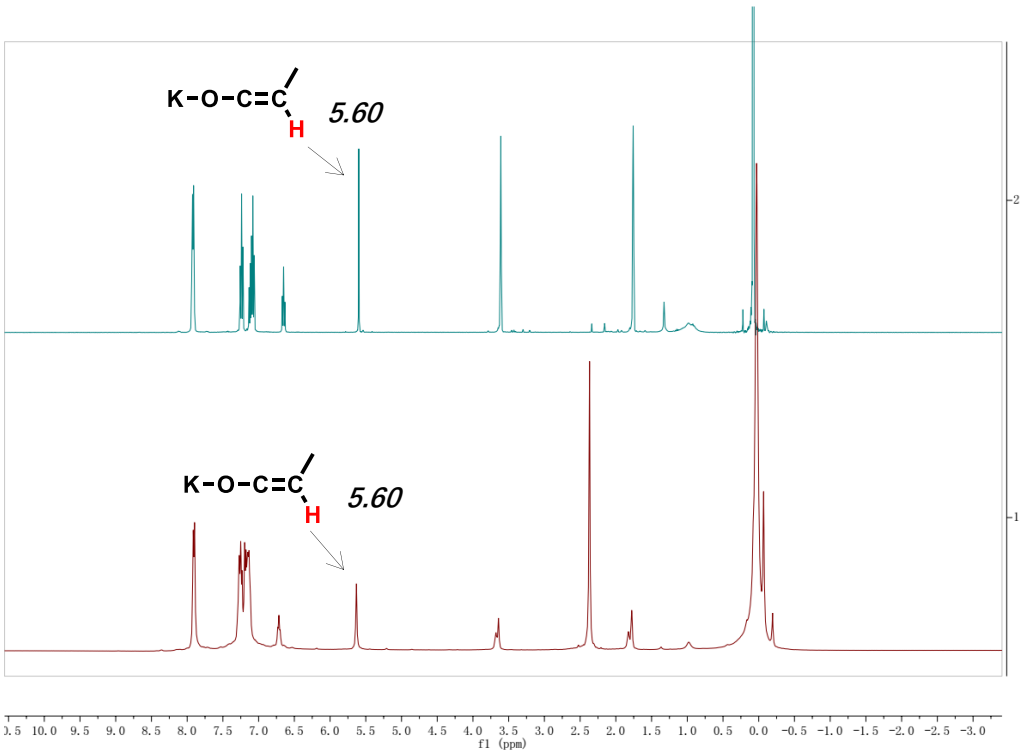
Supplementary Figure 1: ^{1}H-NMR deprotonated reaction in J-Young NMR tube.



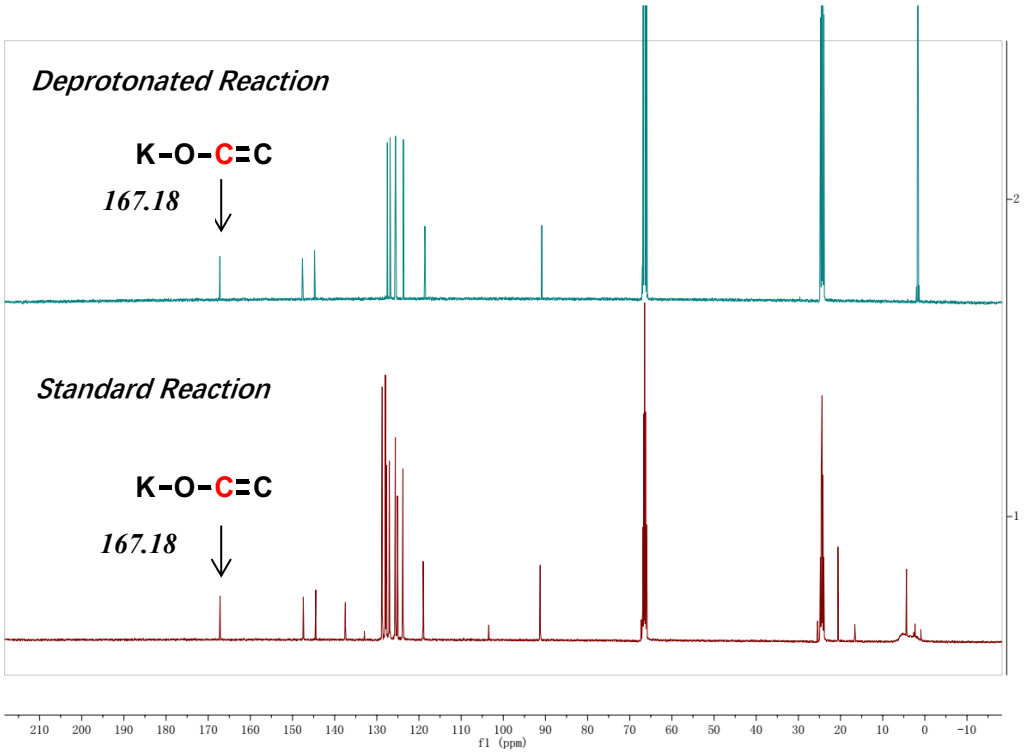
Supplementary Figure 2: ^{13}C-NMR deprotonated reaction in J-Young NMR tube.



Supplementary Figure 3: ^{1}H-NMR comparisons of deprotonated and standard reactions in J-Young tube.



Supplementary Figure 4: ^{13}C-NMR comparisons of deprotonated and standard reactions in J-Young tube.



References

1 Huang, P. Q. & Chen, H. Ni-Catalyzed cross-coupling reactions of *N*-acylpyrrole-type amides with organoboron reagents. *Chem. Commun. (Camb.)* **53**, 12584-12587 (2017).

2 Laha, J. K., Kaur Hunjan, M., Hegde, S. & Gupta, A. Aroylation of Electron-Rich Pyrroles under Minisci Reaction Conditions. *Org. Lett.* **22**, 1442-1447 (2020).

3 Gahman, T. C., Zhao, C., Lang, H. & Massari, M. E. Preparation of diazepine derivatives as cannabinoid receptor agonists. 20090062253 (2009).

4 Papastavrou, N., Chatzopoulou, M., Pegklidou, K. & Nicolaou, I. 1-Hydroxypyrazole as a bioisostere of the acetic acid moiety in a series of aldose reductase inhibitors. *Bioorg. Med. Chem.* **21**, 4951-4957 (2013).

5 Guo, Z., Wei, X., Hua, Y., Chao, J. & Liu, D. Synthesis of 2-benzoylpyrrole derivatives via C–H functionalization adjacent to nitrogen of pyrrole. *Tetrahedron Lett.* **56**, 3919-3922 (2015).

6 Maruta, K., Tsuchida, A. & Nagata, R. PPARδ agonists for treatment of hyperlipidemia and atherosclerosis. JP2003171275A (2003).

7 Sharma, R., Chouhan, M. & Nair, V. A. A novel one-pot synthesis of 2-benzoylpyrroles from benzaldehydes. *Tetrahedron Lett.* **51**, 2039-2043 (2010).

8 Kanakis, A. A. & Sarli, V. Total synthesis of (+/-)-marinopyrrole A via copper-mediated *N*-arylation. *Org. Lett.* **12**, 4872-4875 (2010).

9 Milen, M., Ábrányi-Balogh, P., Dancsó, A., Simig, G. & Volk, B. Synthesis of a new compound family, 1-aryl-3*H*-pyrrolo[2,1-*d*][1,2,5]triazepin-4(5*H*)-ones. *Tetrahedron* **70**, 465-476 (2014).

10 Li, L. *et al.* Iron and Manganese Complexes of 2-Carbonyl Pyrrolyls: Scorpionate Sandwich Anions and Extended Structures. *Organometallics* **34**, 2543-2549 (2015).

11 Zinc-mediated acylation and sulfonation of pyrrole and its derivatives. *Tetrahedron Lett.* **43**, 8133-8135 (2002).

12 Jacob, K., Treibs, A. & Waheeduddin Roomi, M. Benzoylierungen in der Pyrrol-Reihe. *Justus Liebigs Ann. Chem.* **724**, 137-142 (1969).

13 Shafi, S., Kędziorek, M. & Grela, K. Cross Metathesis of *N*-Allylamines and α,β-Unsaturated Carbonyl Compounds: A One-Pot Synthesis of Substituted Pyrroles. *Synlett*, 124-128 (2011).

14 Umasekhar, B., Ganapathi, E., Chatterjee, T. & Ravikanth, M. Synthesis, structure, and spectral, electrochemical and fluoride sensing properties of meso-pyrrolyl boron dipyrromethene. *Dalton Trans.* **44**, 16516-16527 (2015).

15 Yu, A., Li, J., Cui, M. & Wu, Y. Addition of arylboronic acids to nitriles in aqueous media catalyzed by a 2,2'-bipyridine-cyclopalladated ferrocenylimine complex. *Synlett*, 3063-3067 (2007).

16 Lu, H.-Y. *et al. N*-heterocyclic carbene-palladium-imine complex catalyzed α-arylation of ketones with aryl and heteroaryl chlorides under air atmosphere. *Tetrahedron Lett.* **61**, 152124 (2020).

17 Battace, A. *et al.* Heck Reactions of α- or β-Substituted Enol Ethers with Aryl Bromides Catalysed by a Tetraphosphane/Palladium Complex – Direct Access to Acetophenone or 1-Arylpropanone Derivatives. *Eur. J. Org. Chem.* **2007**, 3122-3132 (2007).

18 Gao, K., Yorimitsu, H. & Osuka, A. α-Arylation of Ketimines with Aryl Sulfides at a Low Palladium Catalyst Loading. *Angew. Chem. Int. Ed.* **55**, 4573-4576 (2016).

19 Quillen, A. *et al.* Palladium-Catalyzed Direct α-C(sp^3) Heteroarylation of Ketones under Microwave Irradiation. *J. Org. Chem.* **84**, 7652-7663 (2019).

20 Anders, E., Will, W. & Stankowiak, A. 1-Acyl-4-alkyliden-1,4-dihydropyridine, 7. Aktivierung durch Bortrifluorid: Intermolekulare Acylgruppenübertragung unter Bildung von 1-(4-Pyridyl)-2-alkanonen. *Chem. Ber.* **116**, 3192-3204 (1983).

21 Weiss, M. J. & Hauser, C. R. The Acylation and Carbethoxylation of Quinaldine, Lepidine and α-Picoline Using Sodium Amide or Potassium Amide. *J. Am. Chem. Soc.* **71**, 2023-2026 (1949).

22 Zhang, X., Qi, Z. & Li, X. Rhodium(III)-Catalyzed C-C and C-O Coupling of Quinoline *N*-Oxides with Alkynes: Combination of C-H Activation with O-Atom Transfer. *Angew. Chem. Int. Ed.* **53**, 10794-10798 (2014).

23 Zhang, S. *et al.* Cobalt(II)-Catalyzed Stereoselective Olefin Isomerization: Facile Access to Acyclic Trisubstituted Alkenes. *J. Am. Chem. Soc.* **142**, 8910-8917 (2020).

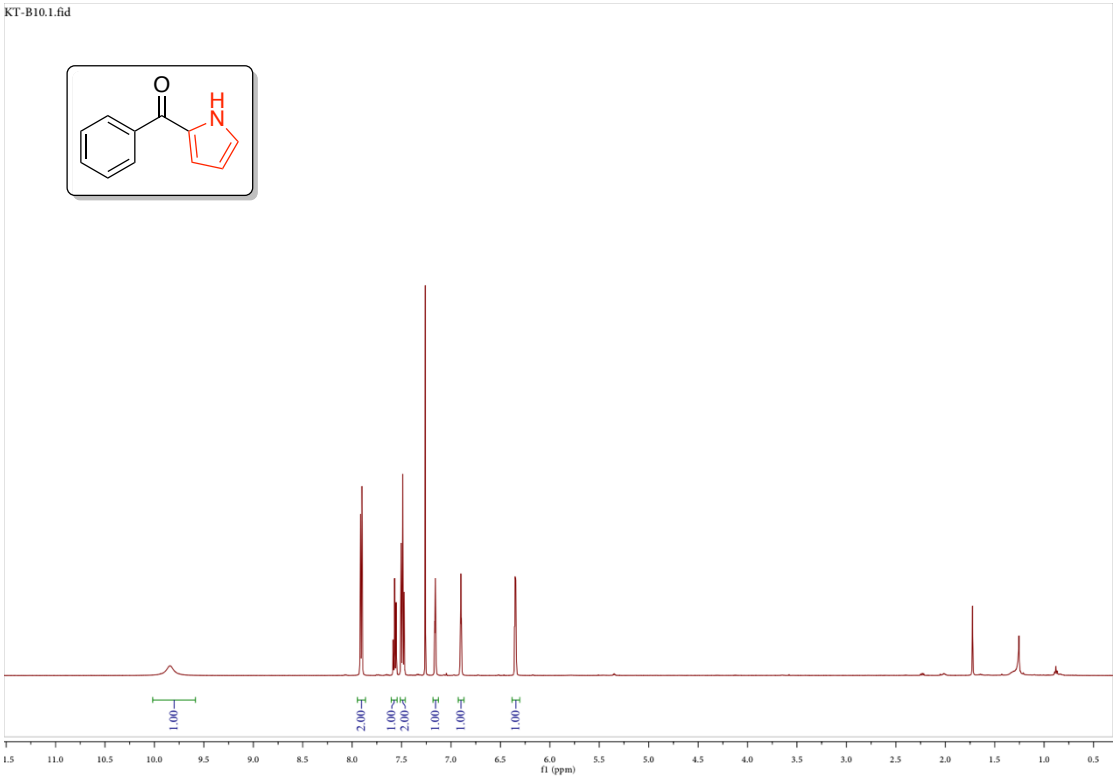
24 Simmons, B. J., Weires, N. A., Dander, J. E. & Garg, N. K. Nickel-Catalyzed Alkylation of Amide Derivatives. *ACS Catal.* **6**, 3176-3179 (2016).

25 Lee, B. & Chirik, P. J. Ketone Synthesis from Benzyldiboronates and Esters: Leveraging α-Boryl Carbanions for Carbon–Carbon Bond Formation. *J. Am. Chem. Soc.* **142**, 2429-2437 (2020).

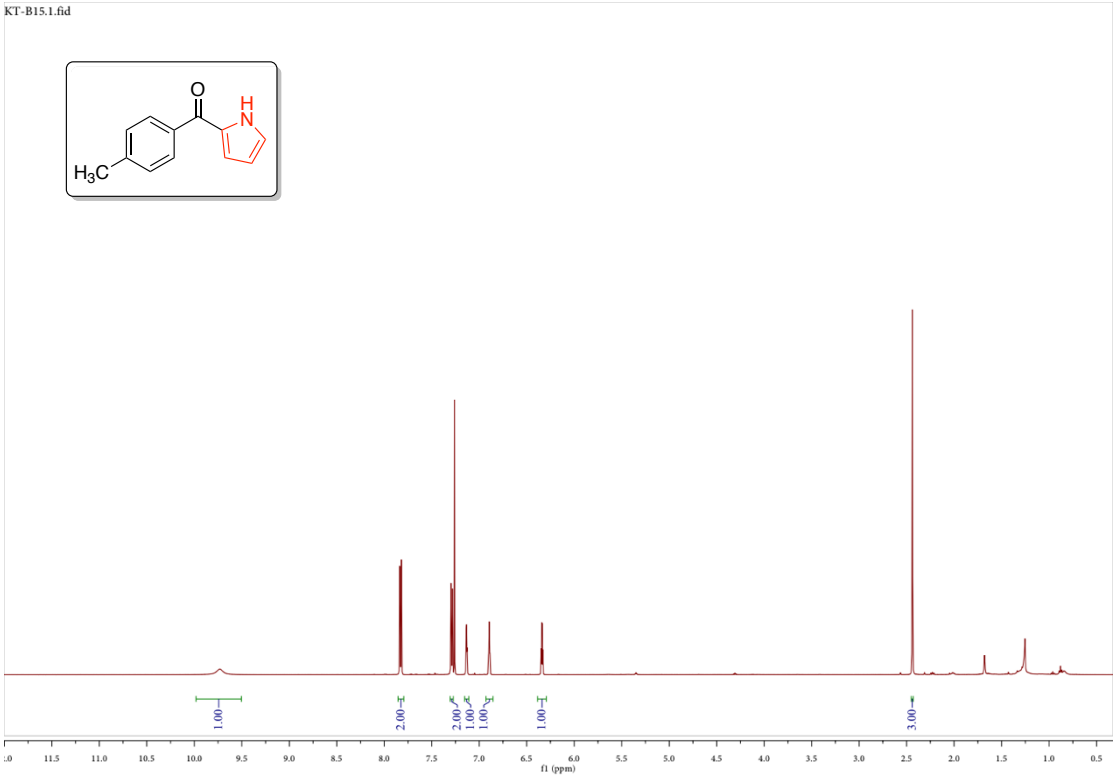
26 Moustafa, D., Sweet, C., Lim, H., Calalpa, B. & Kaur, P. Mn/Cu catalyzed addition of arylboronic acid to nitriles: Direct synthesis of arylketones. *Tetrahedron Lett.* **59**, 3816-3820 (2018).

NMR Spectra

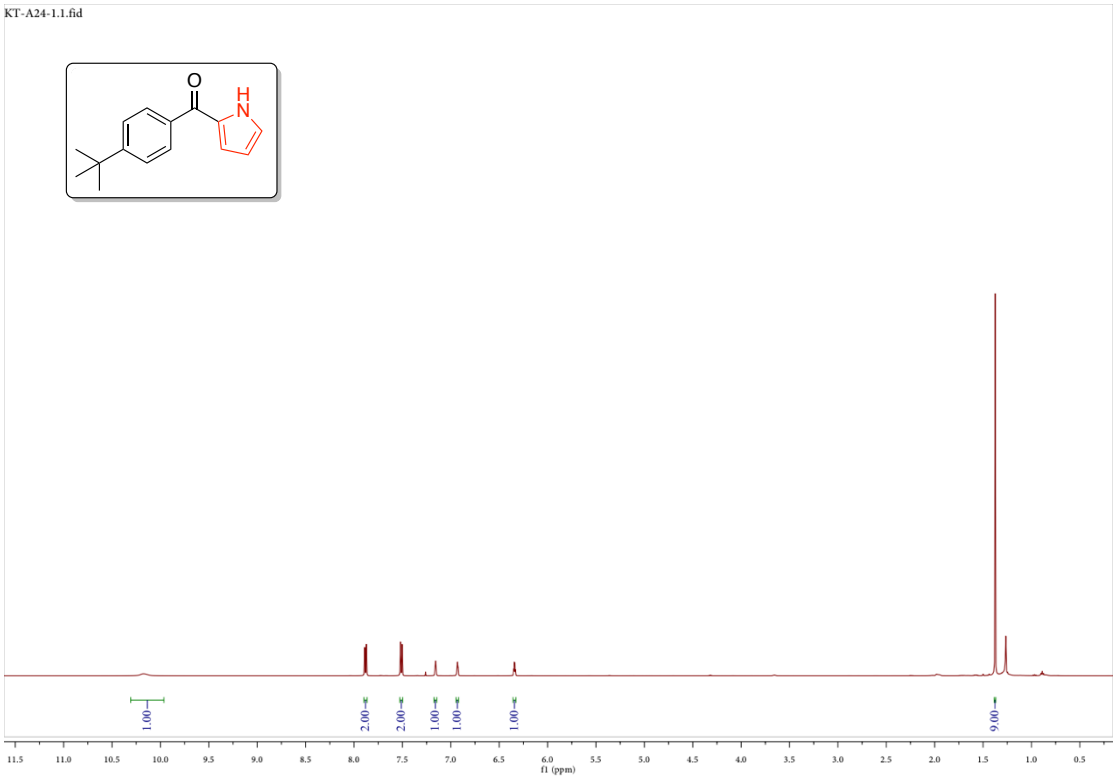
Supplementary Figure 5. ^{1}H NMR Spectrum of 3a (500 MHz, $CDCl_3$)



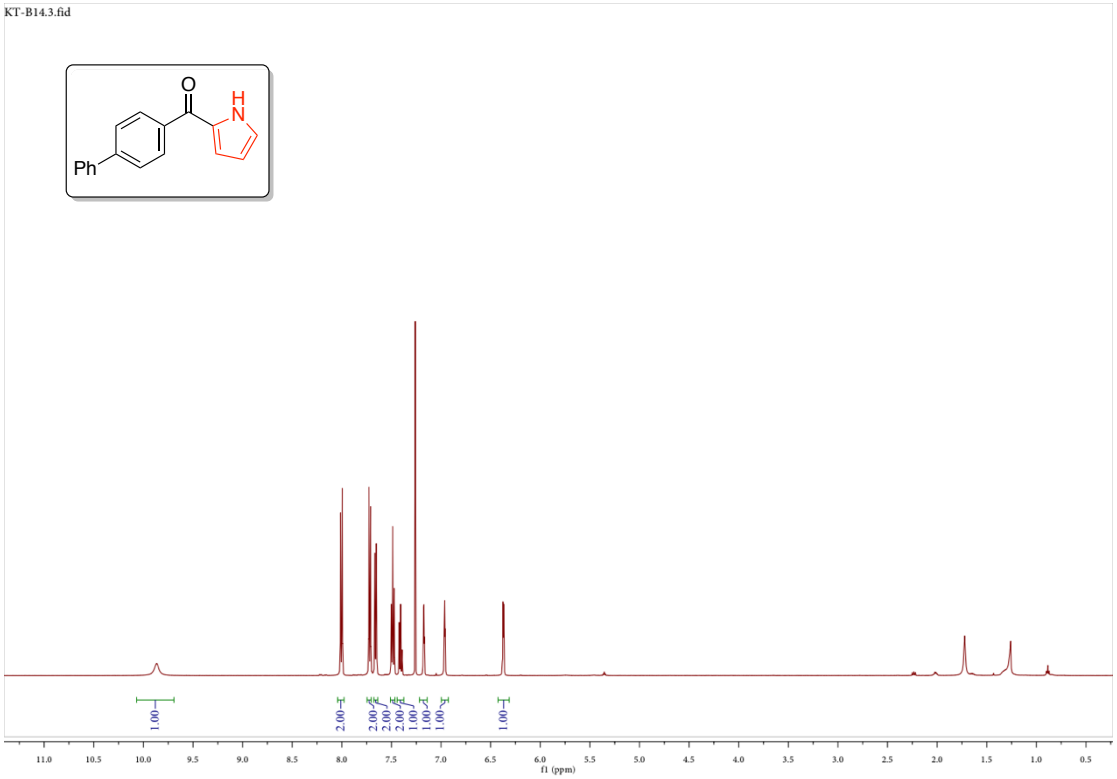
Supplementary Figure 6. ^{1}H NMR Spectrum of 3b (500 MHz, $CDCl_3$)



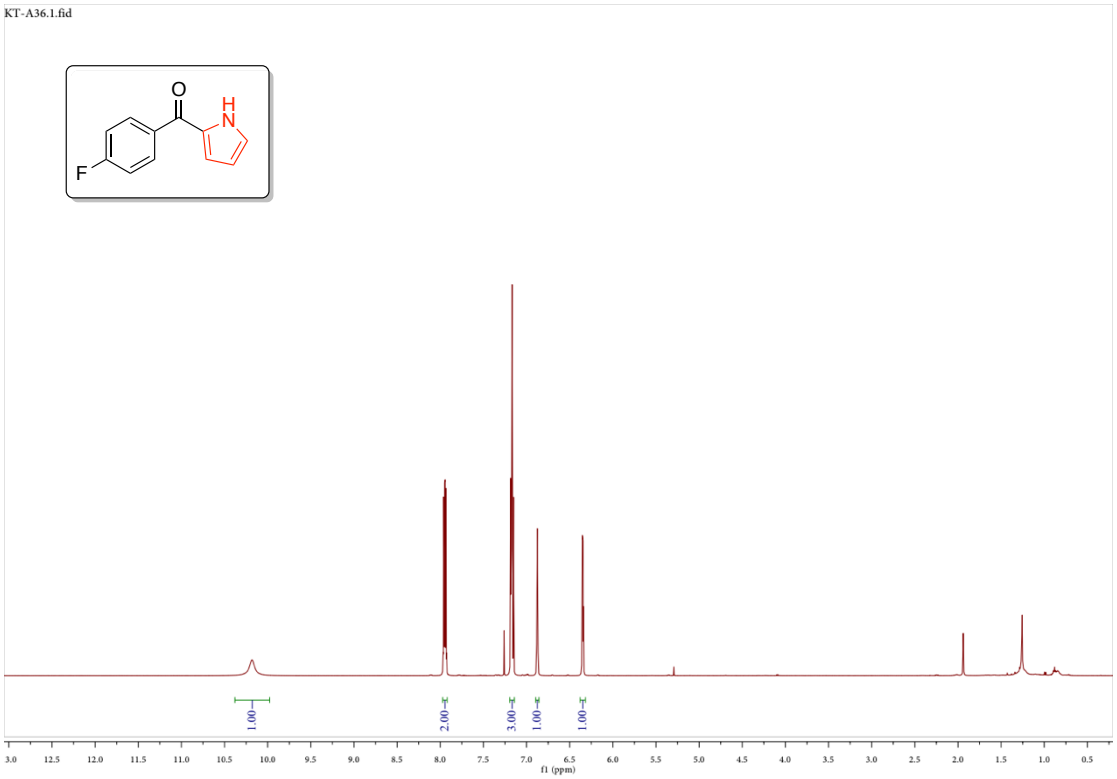
Supplementary Figure 7. ^{1}H NMR Spectrum of 3c (500 MHz, $CDCl_3$)



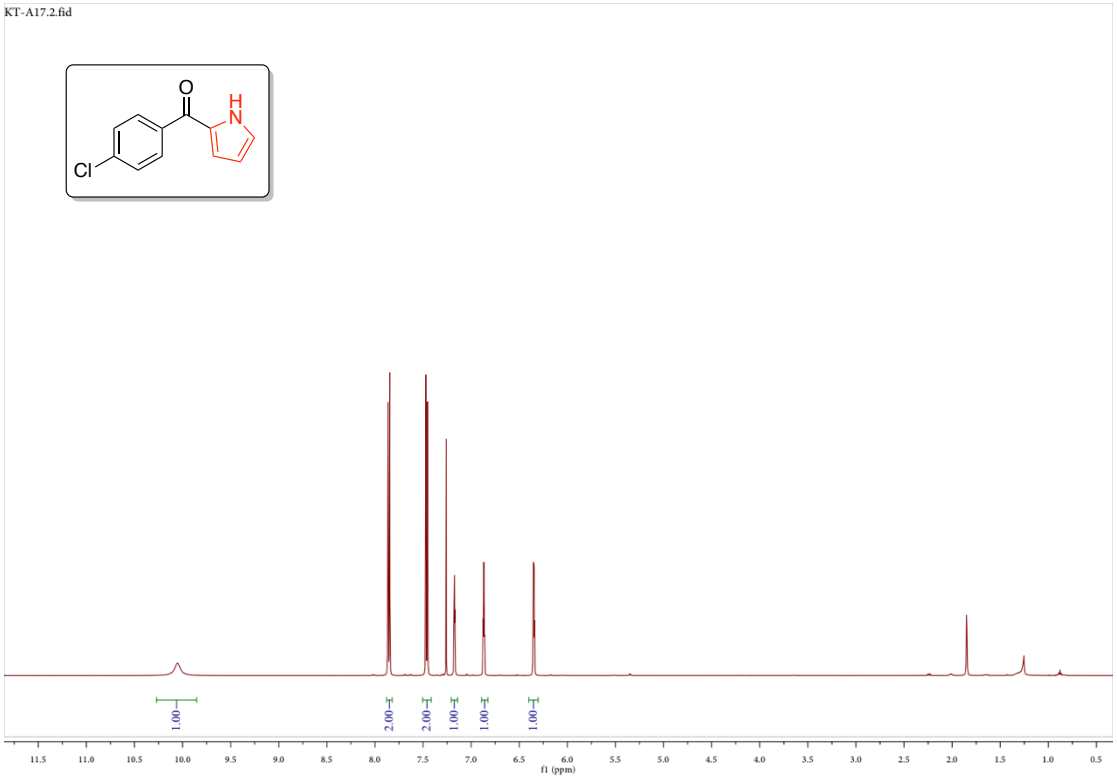
Supplementary Figure 8. ^{1}H NMR Spectrum of 3d (500 MHz, $CDCl_3$)



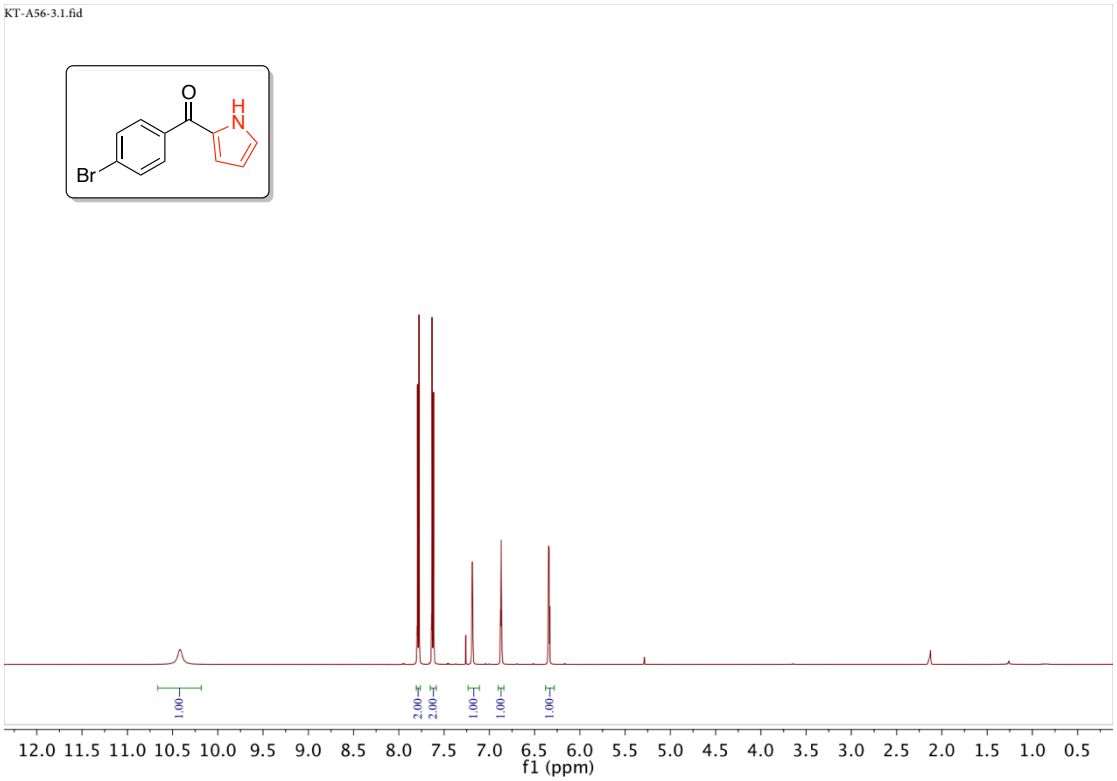
Supplementary Figure 9. ^{1}H NMR Spectrum of 3e (500 MHz, $CDCl_3$)



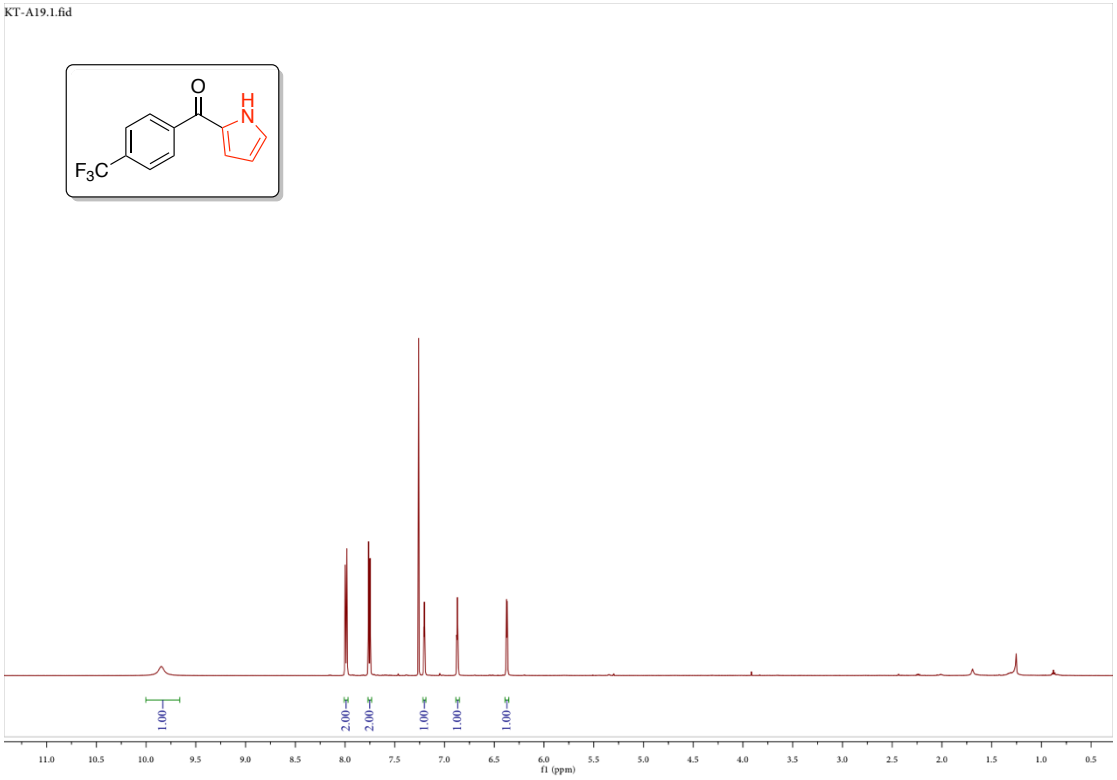
Supplementary Figure 10. ^{1}H NMR Spectrum of 3f (500 MHz, $CDCl_3$)



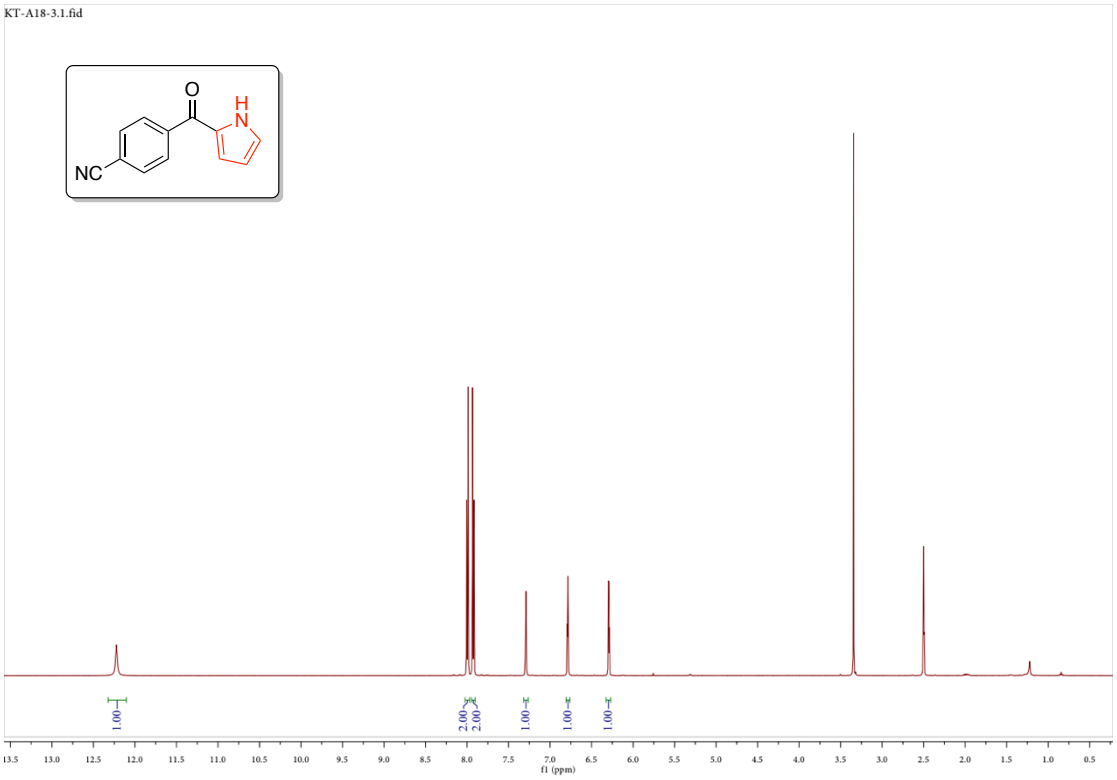
Supplementary Figure 11. ^{1}H NMR Spectrum of 3g (500 MHz, $CDCl_3$)



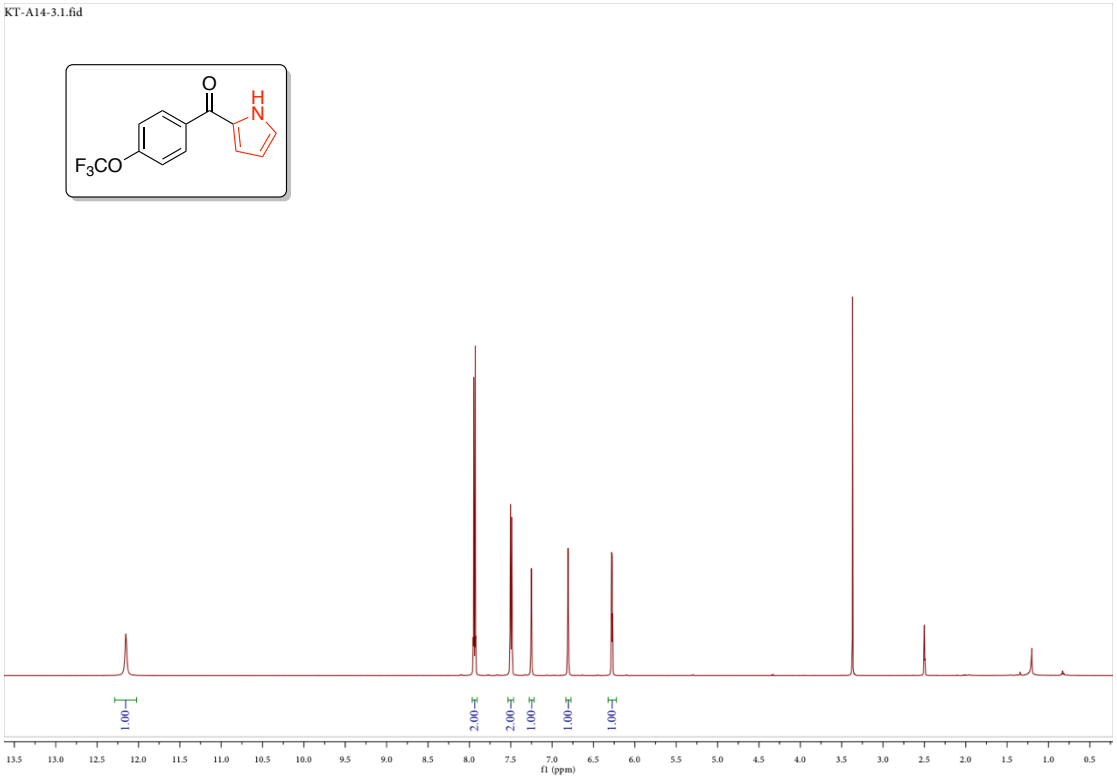
Supplementary Figure 12. ^{1}H NMR Spectrum of 3h (500 MHz, $CDCl_3$)



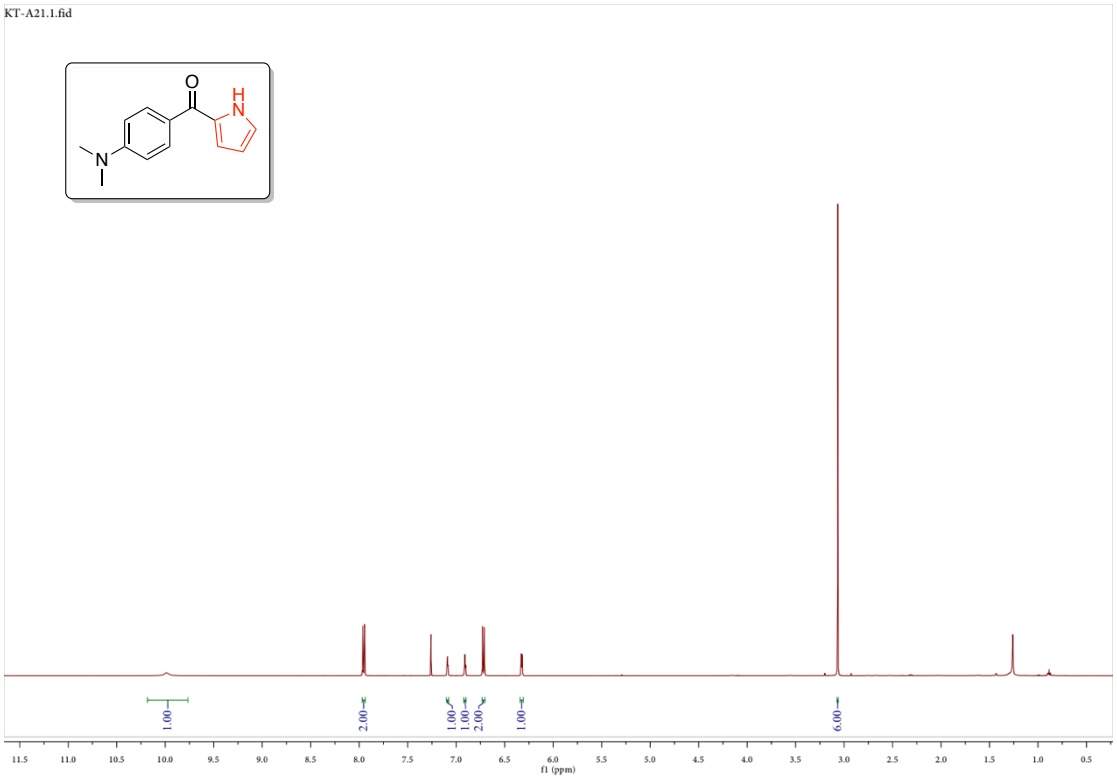
Supplementary Figure 13. ^{1}H NMR Spectrum of 3i (500 MHz, DMSO-d_6)



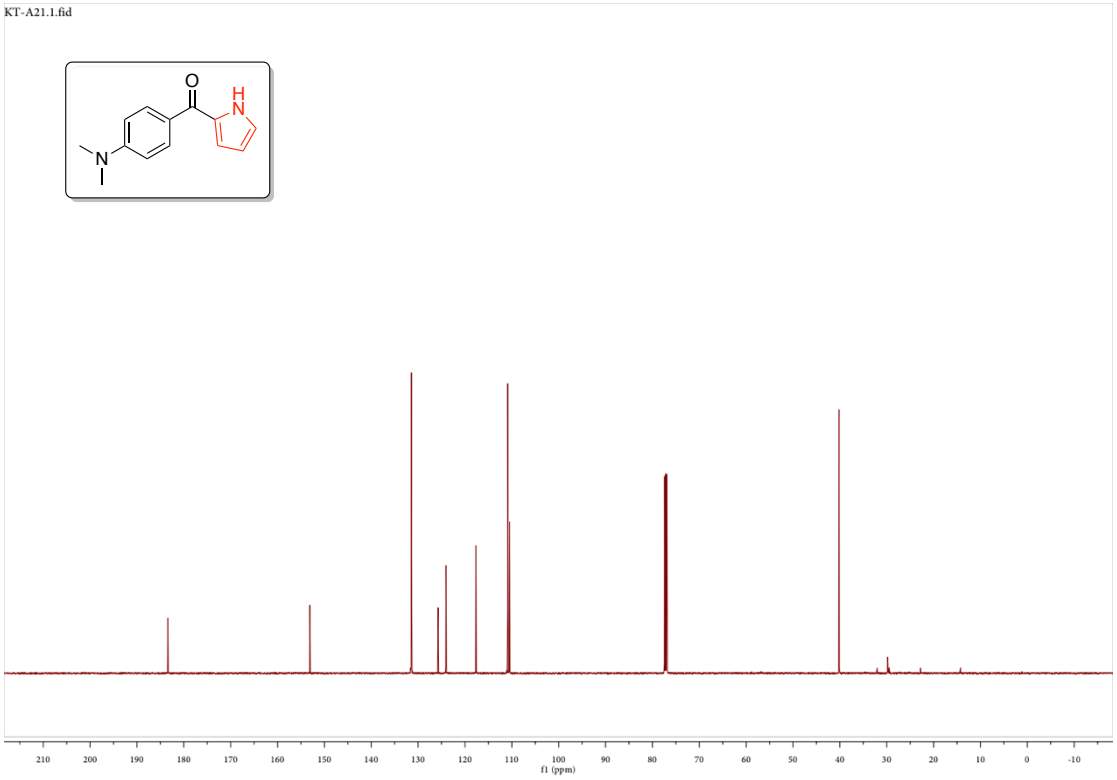
Supplementary Figure 14. ^{1}H NMR Spectrum of 3j (500 MHz, DMSO-d_6)



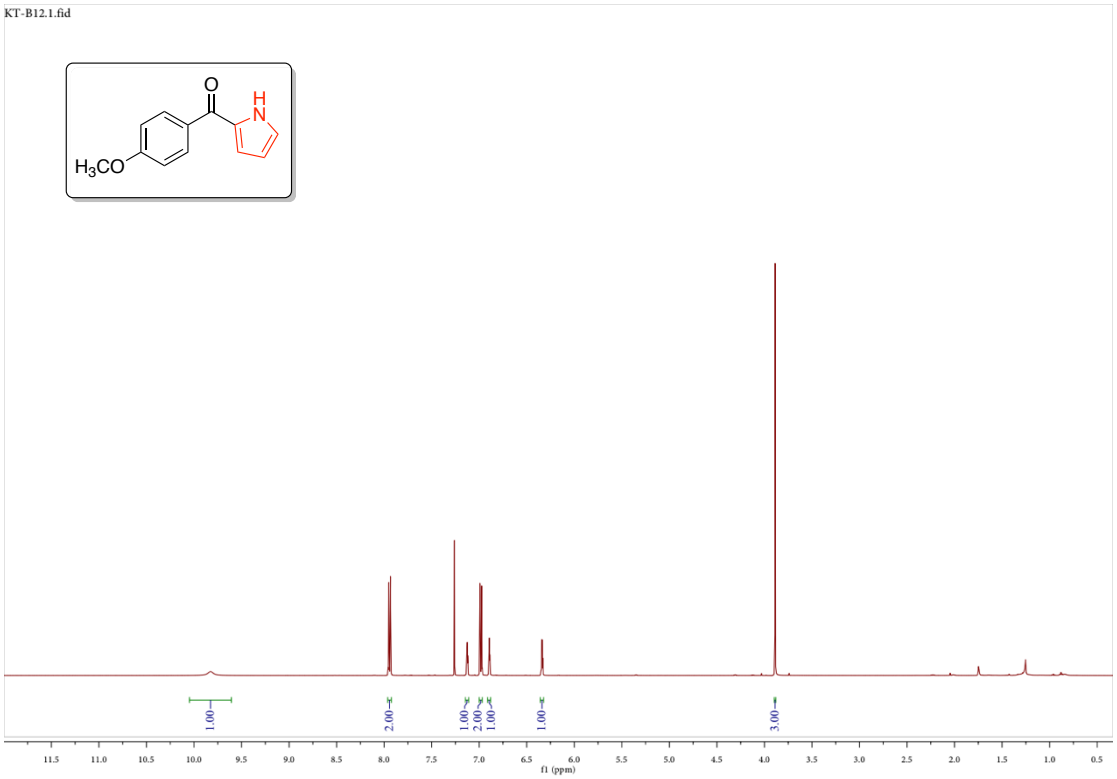
Supplementary Figure 15. ^{1}H NMR Spectrum of 3k (500 MHz, $CDCl_3$)



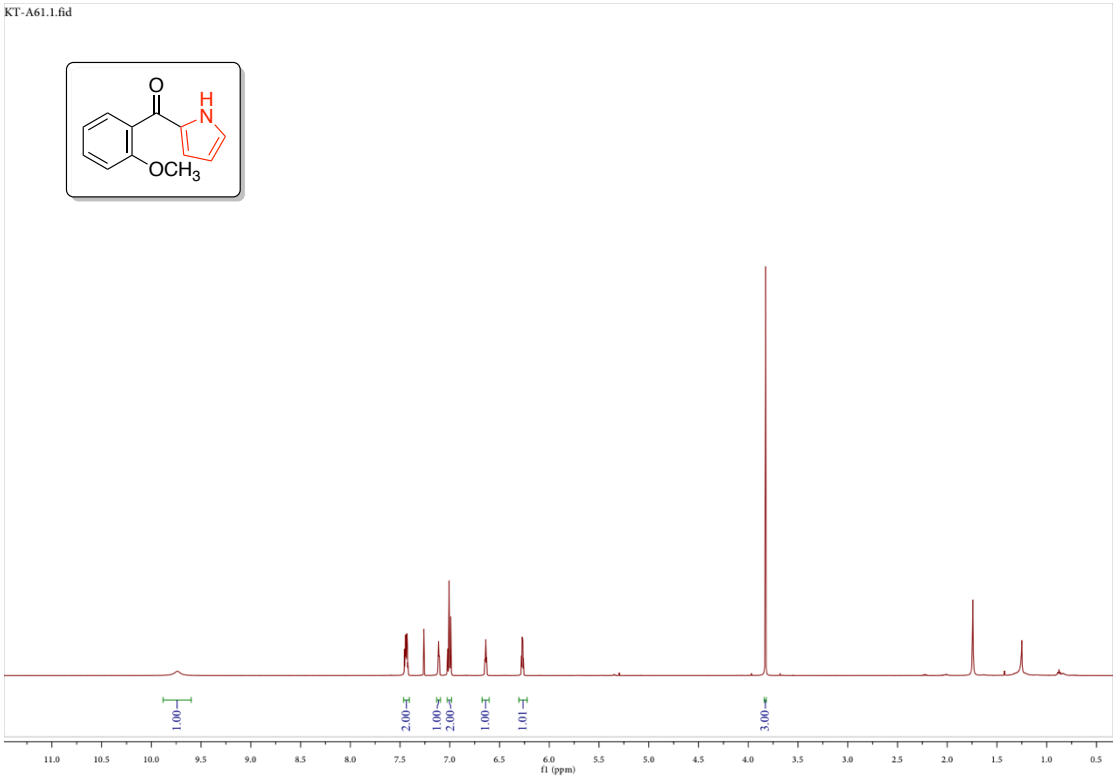
Supplementary Figure 16. ^{13}C NMR Spectrum of 3k (125 MHz, $CDCl_3$)



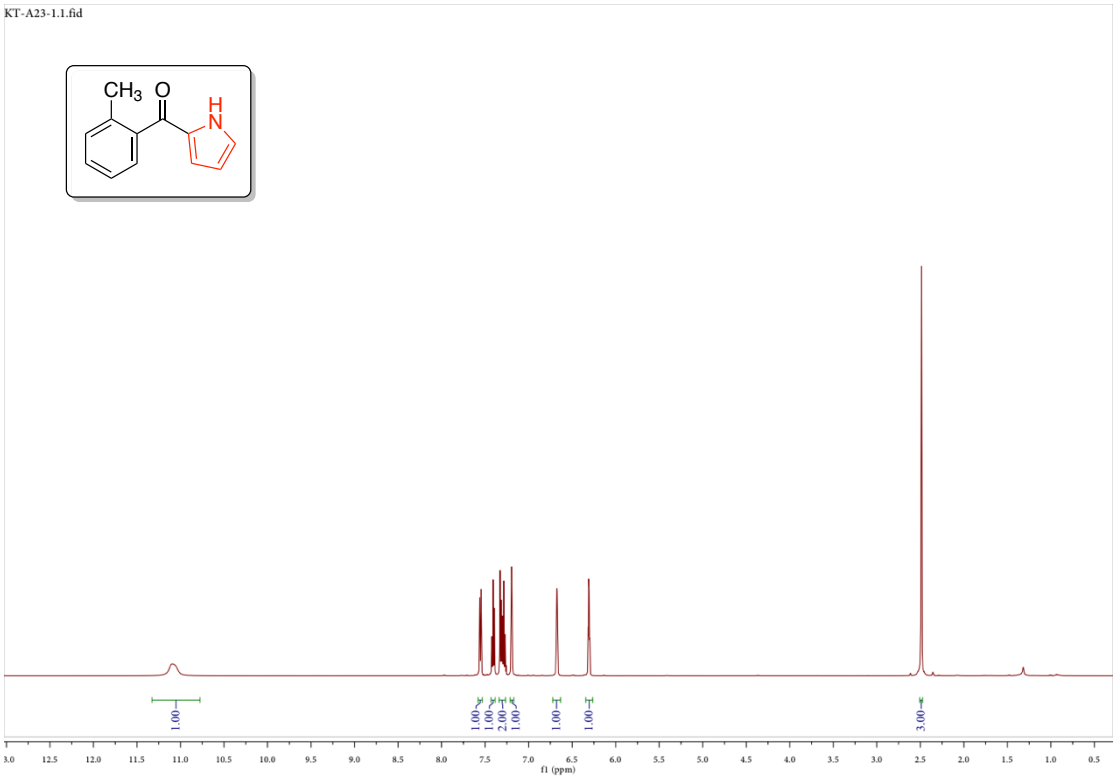
Supplementary Figure 17. ^{1}H NMR Spectrum of 3l (500 MHz, $CDCl_3$)



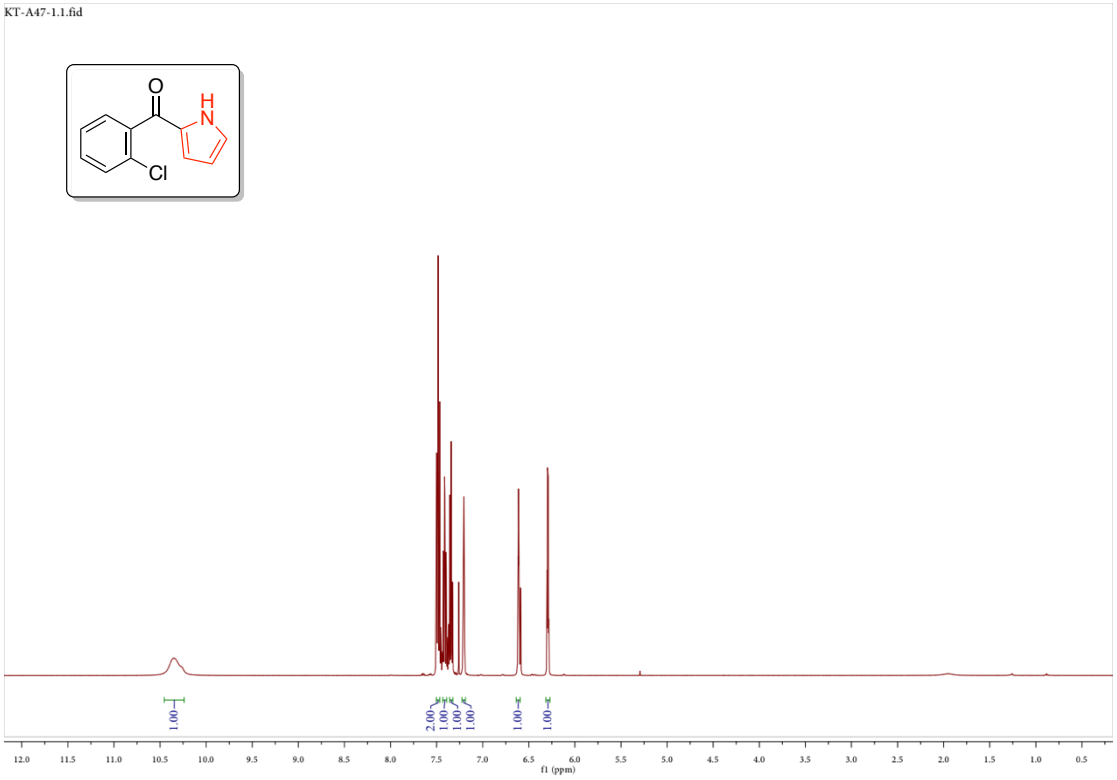
Supplementary Figure 18. ^{1}H NMR Spectrum of 3m (500 MHz, $CDCl_3$)



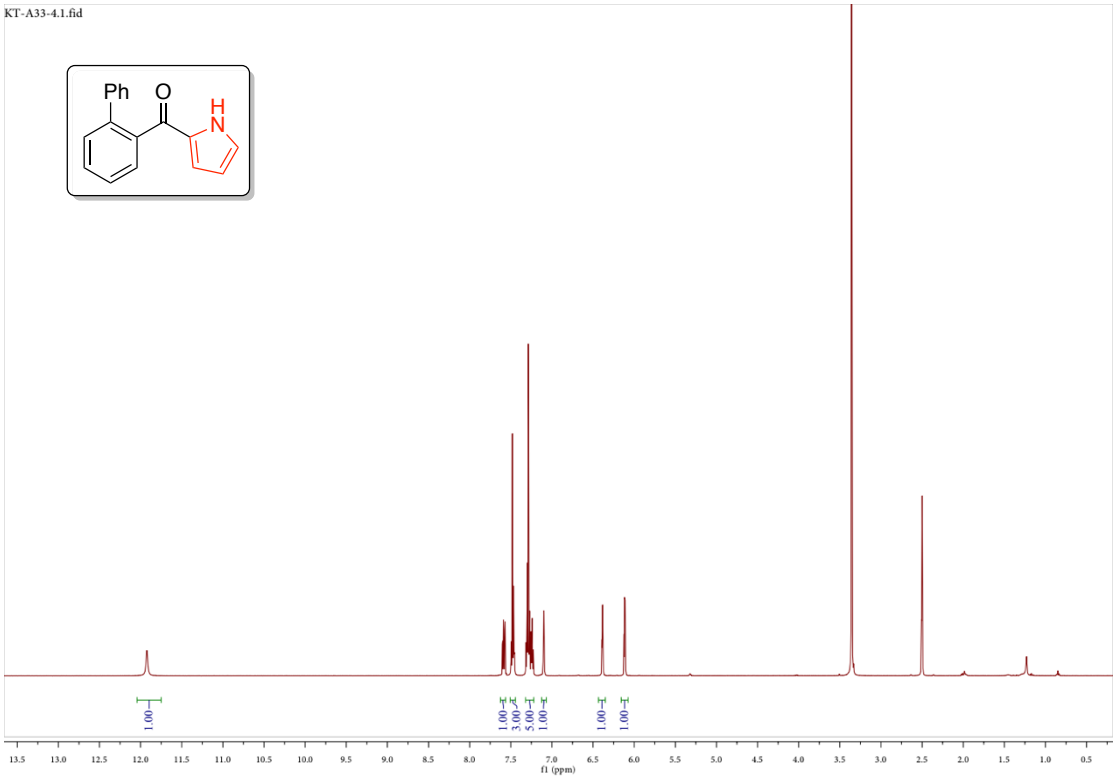
Supplementary Figure 19. ^{1}H NMR Spectrum of 3n (500 MHz, $CDCl_3$)



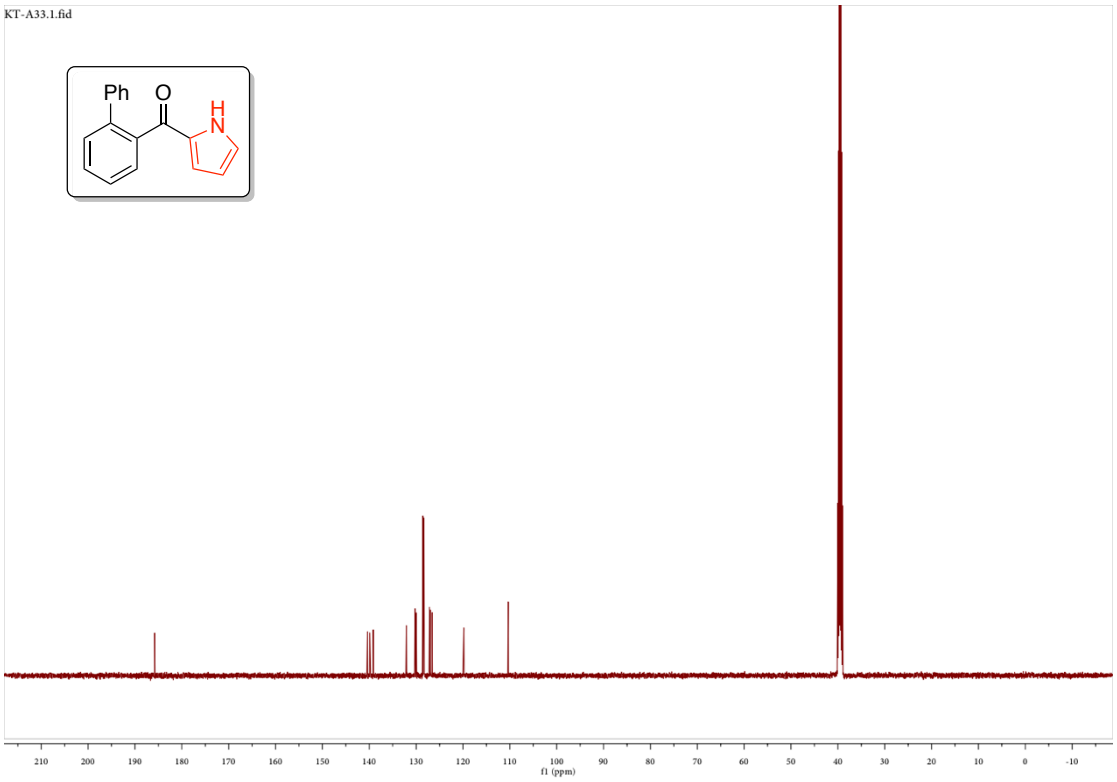
Supplementary Figure 20. ^{1}H NMR Spectrum of 3o (500 MHz, $CDCl_3$)



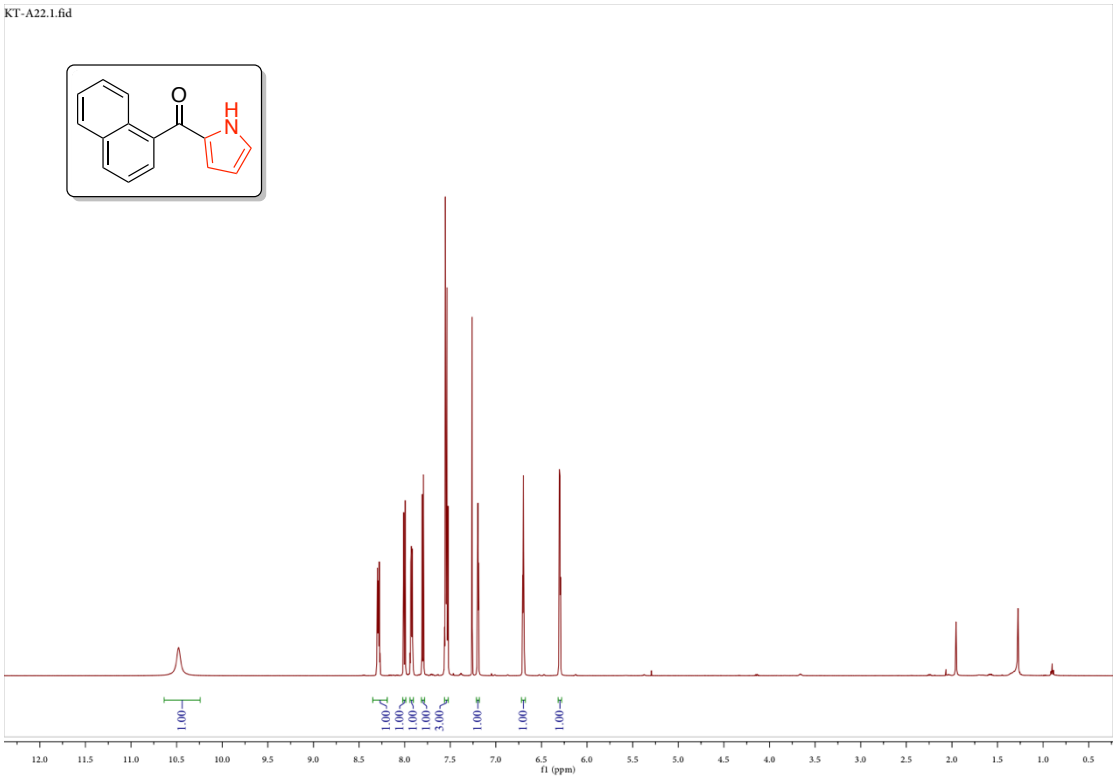
Supplementary Figure 21. ^{1}H NMR Spectrum of 3p (500 MHz, DMSO-d_6)



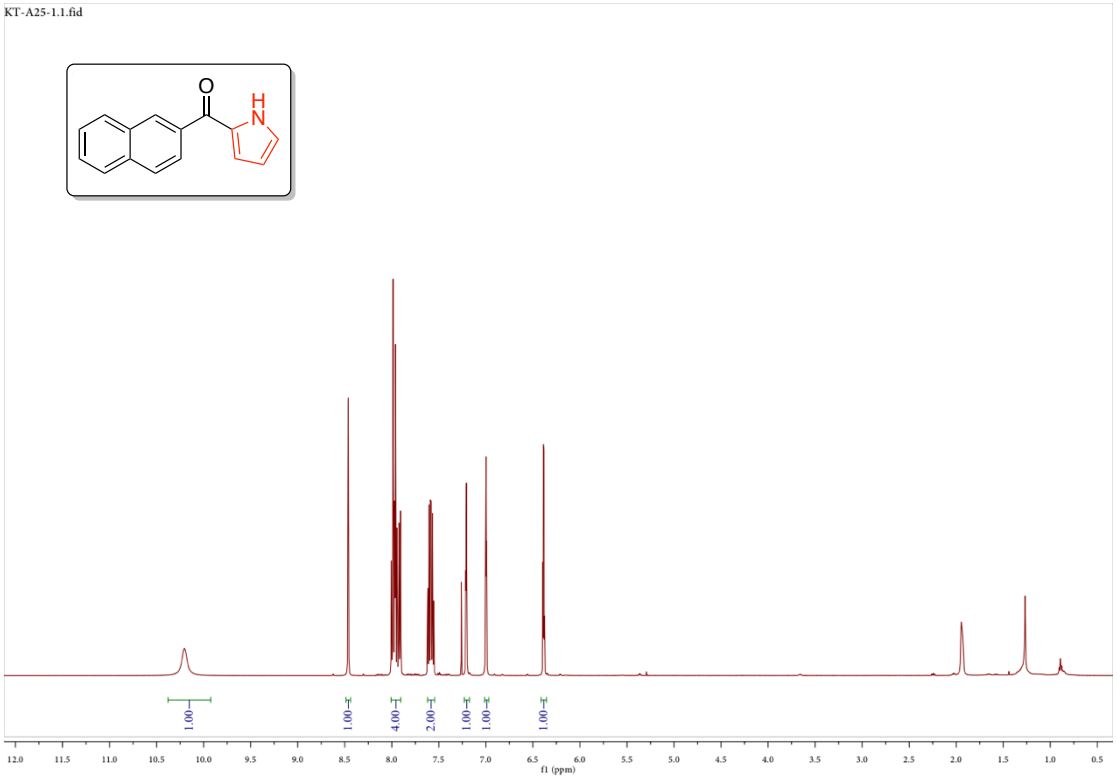
Supplementary Figure 22. ^{13}C NMR Spectrum of 3p (125 MHz, DMSO-d_6)



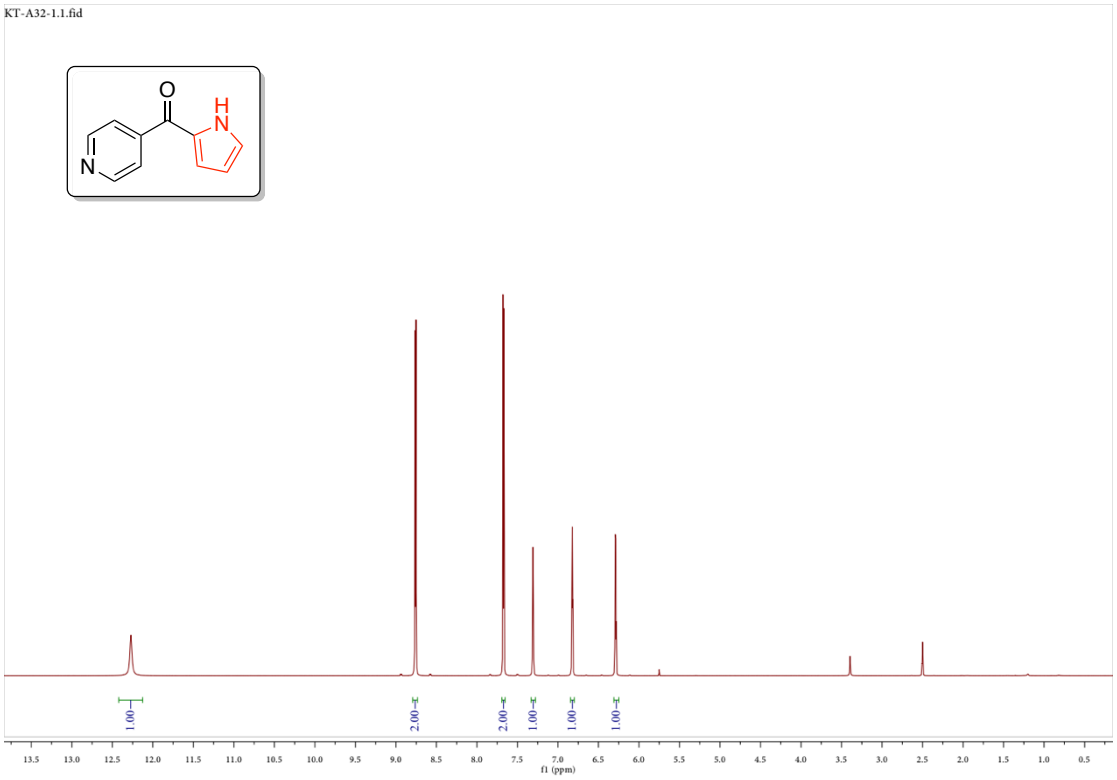
Supplementary Figure 23. ^{1}H NMR Spectrum of 3q (500 MHz, $CDCl_3$)



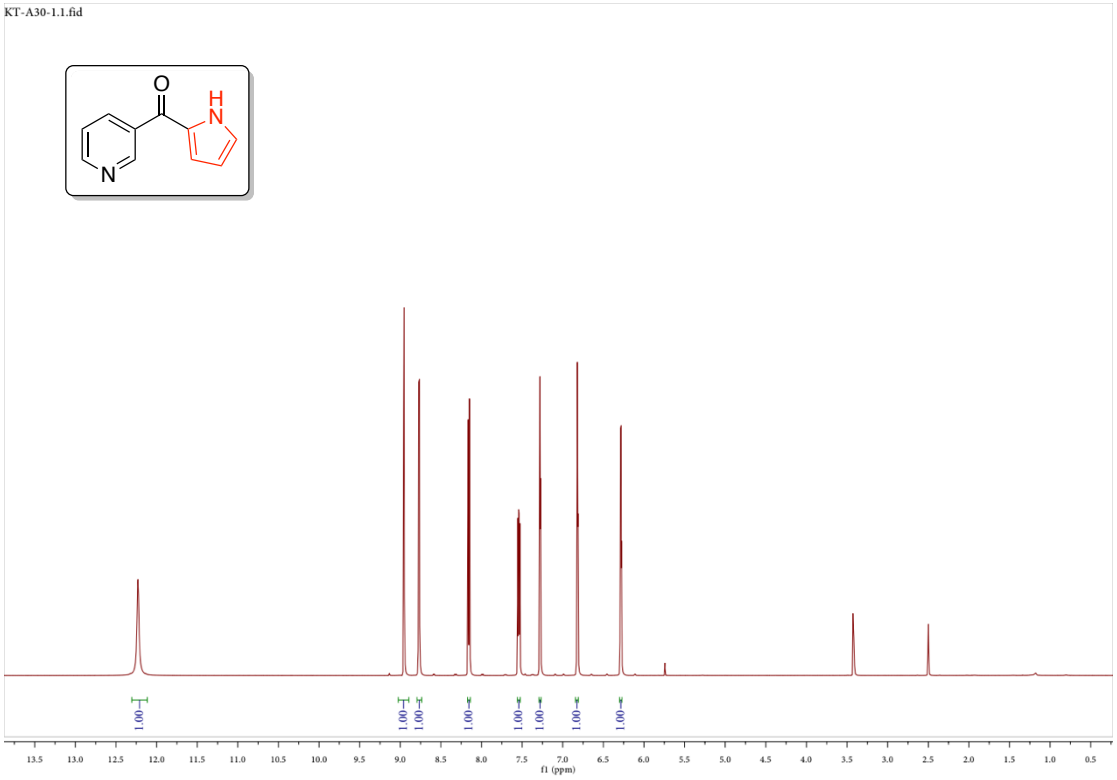
Supplementary Figure 24. ^{1}H NMR Spectrum of 3r (500 MHz, $CDCl_3$)



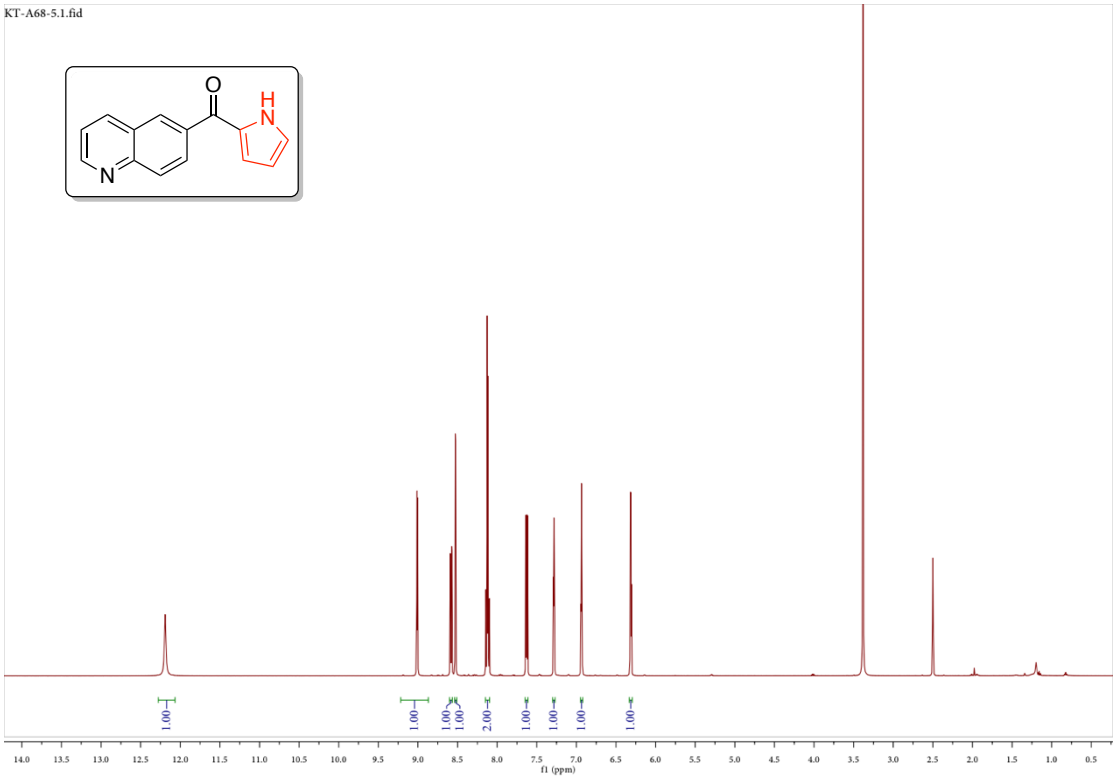
Supplementary Figure 25. ^{1}H NMR Spectrum of 3s (500 MHz, DMSO-*d*$_6$)



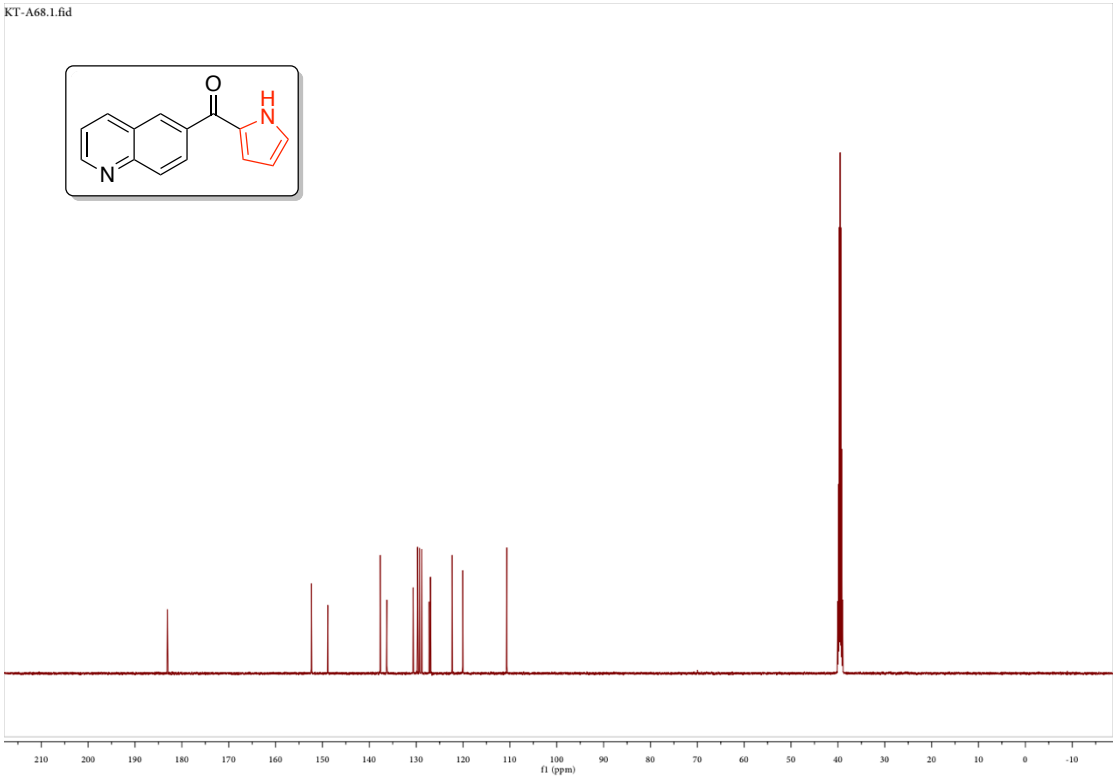
Supplementary Figure 26. ^{1}H NMR Spectrum of 3t (500 MHz, DMSO-*d*$_6$)



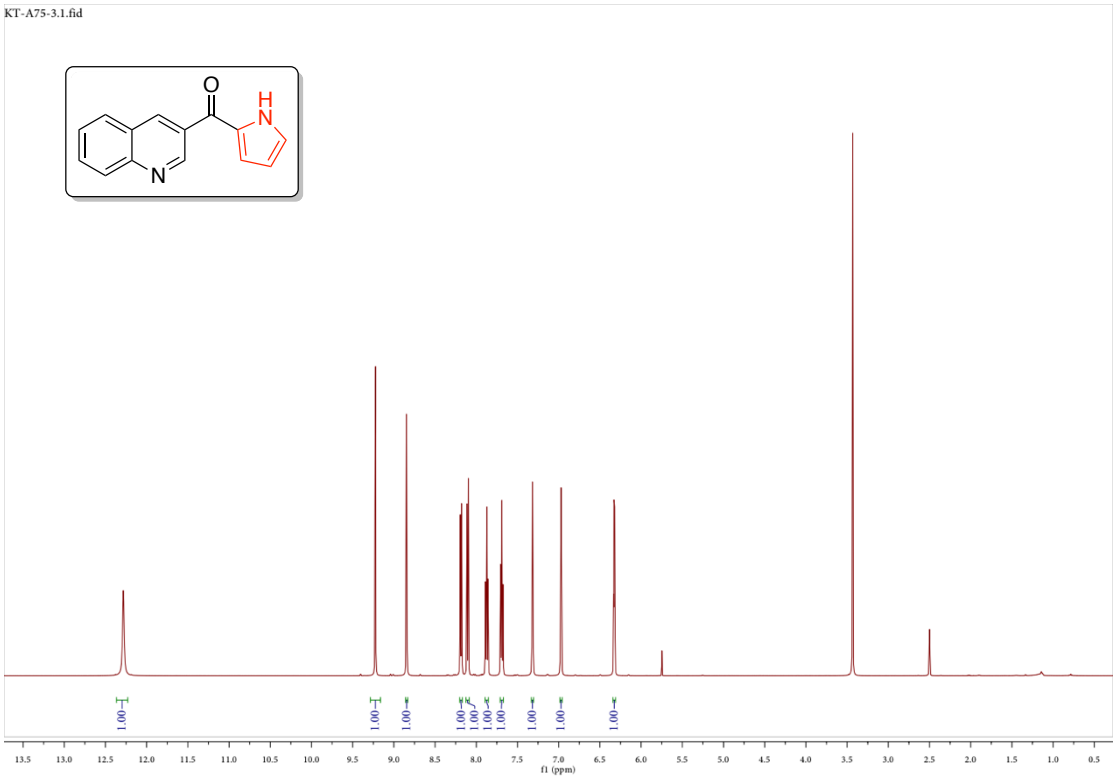
Supplementary Figure 27. ^{1}H NMR Spectrum of 3u (500 MHz, DMSO-d_6)



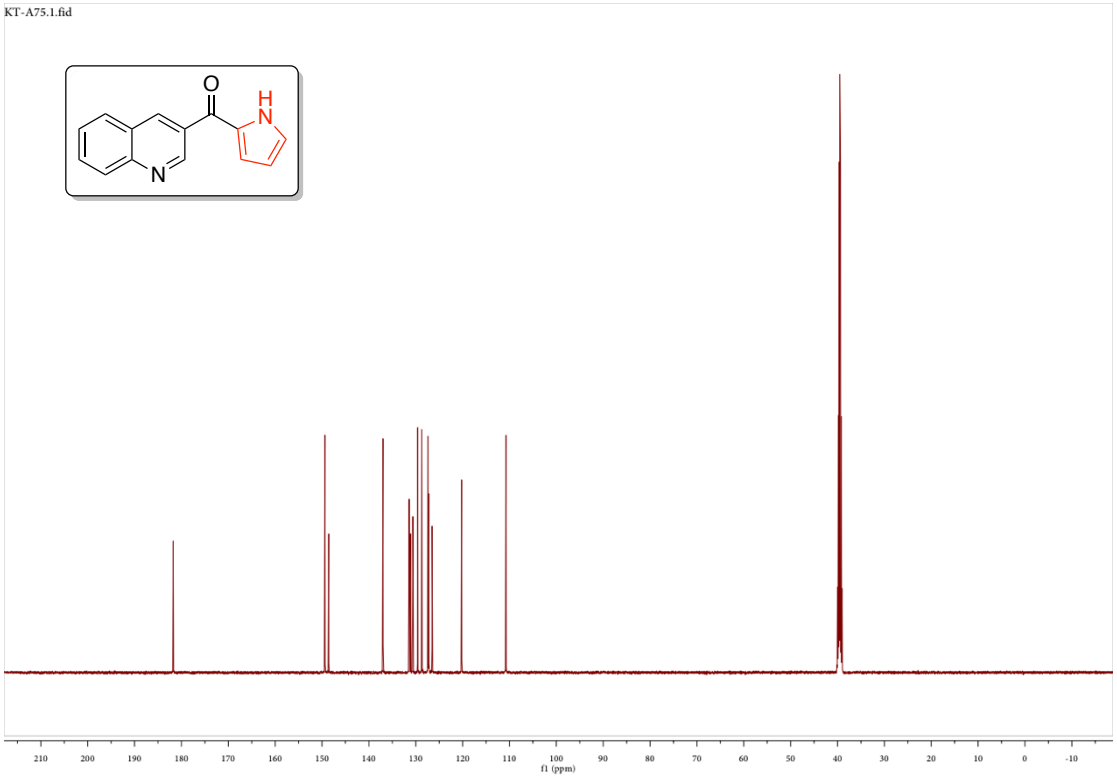
Supplementary Figure 28. ^{13}C NMR Spectrum of 3u (125 MHz, DMSO-d_6)



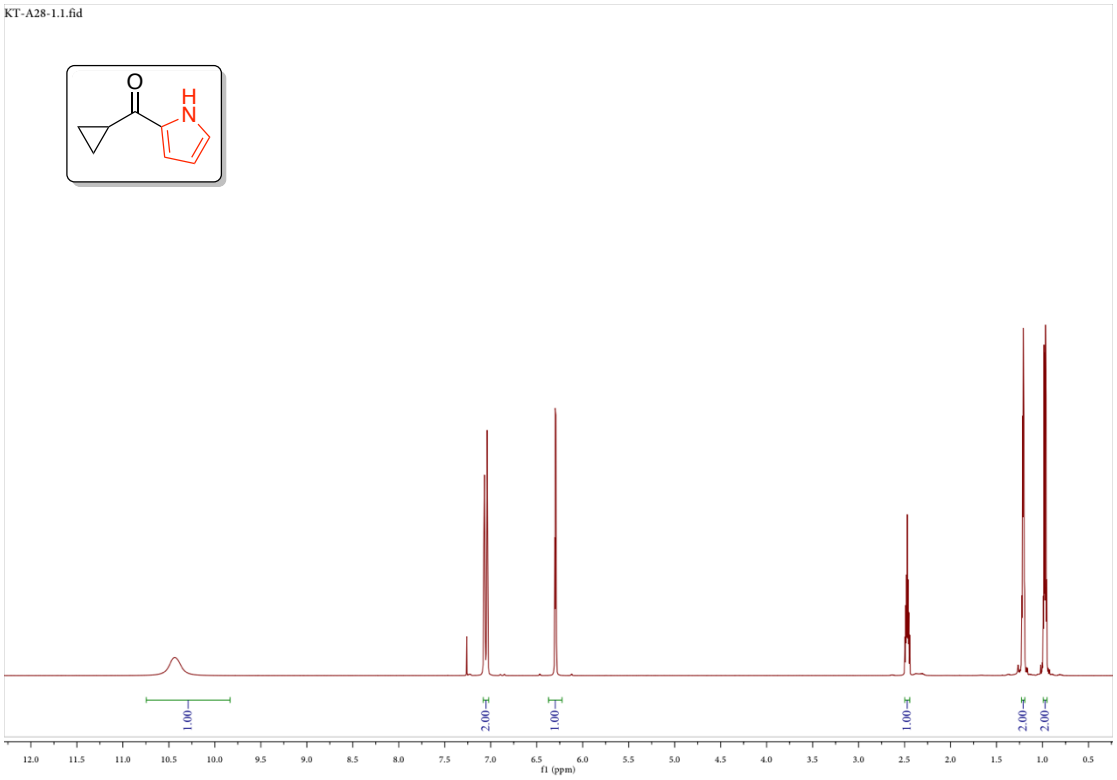
Supplementary Figure 29. ^{1}H NMR Spectrum of 3v (500 MHz, DMSO-d_6)



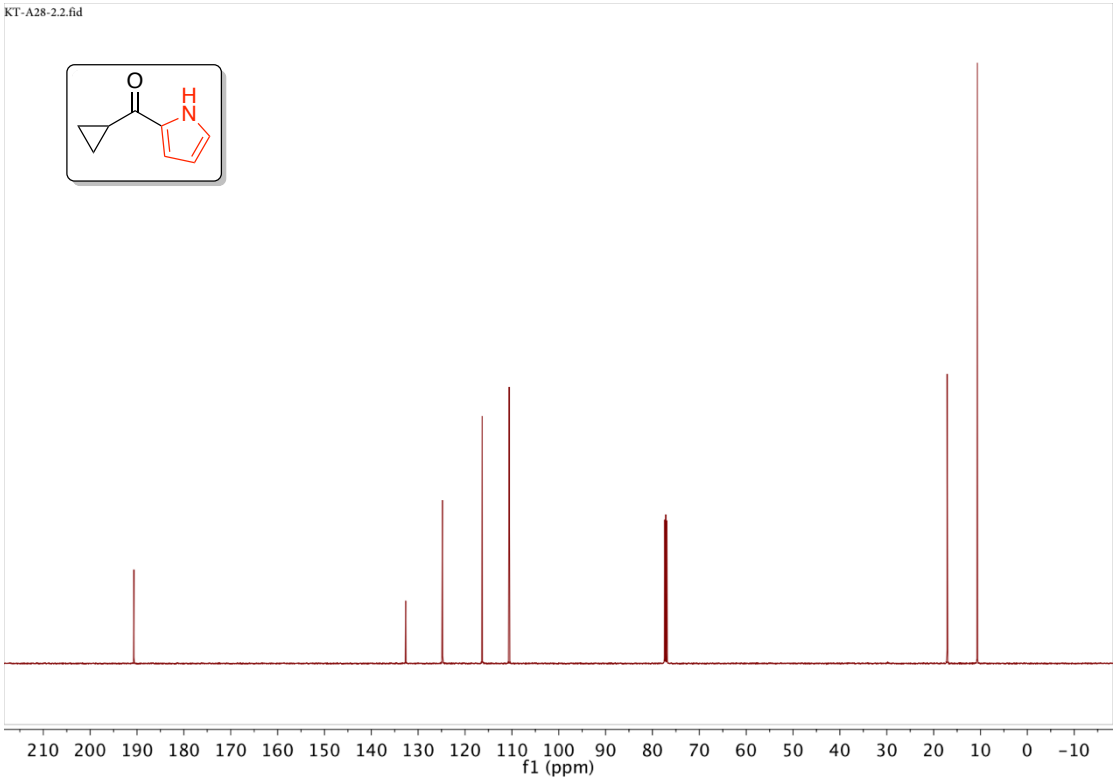
Supplementary Figure 30. ^{13}C NMR Spectrum of 3u (125 MHz, DMSO-d_6)



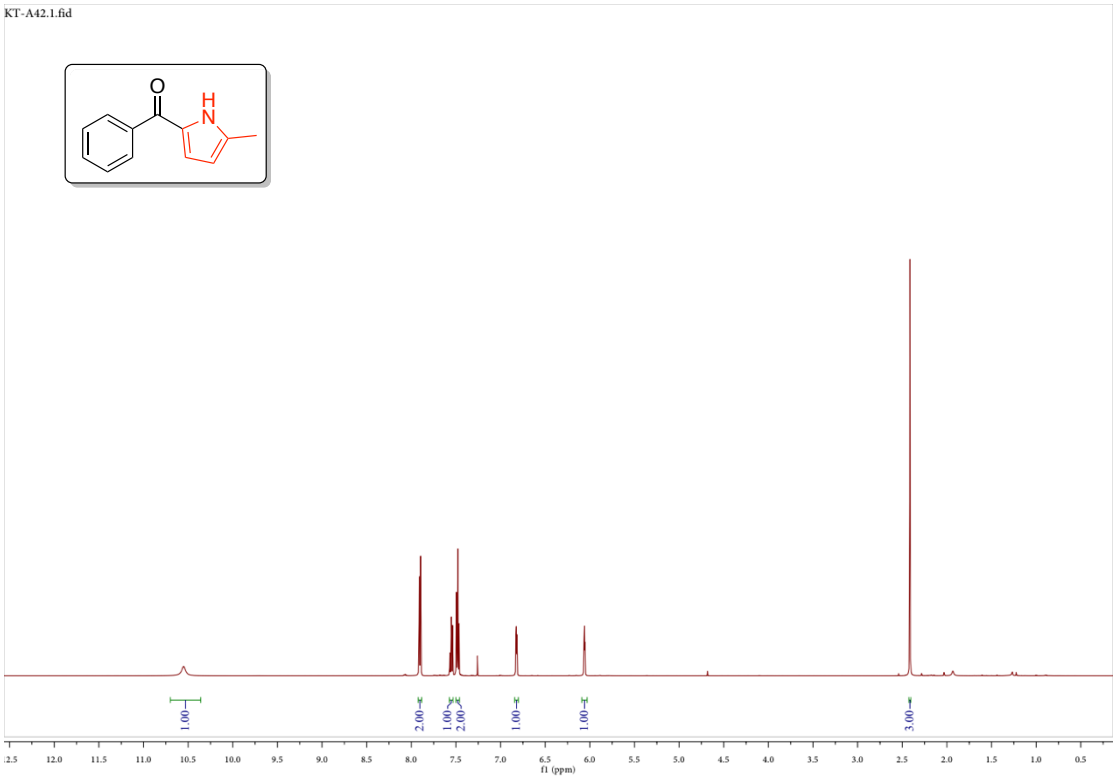
Supplementary Figure 31. ^{1}H NMR Spectrum of 3w (500 MHz, $CDCl_3$)



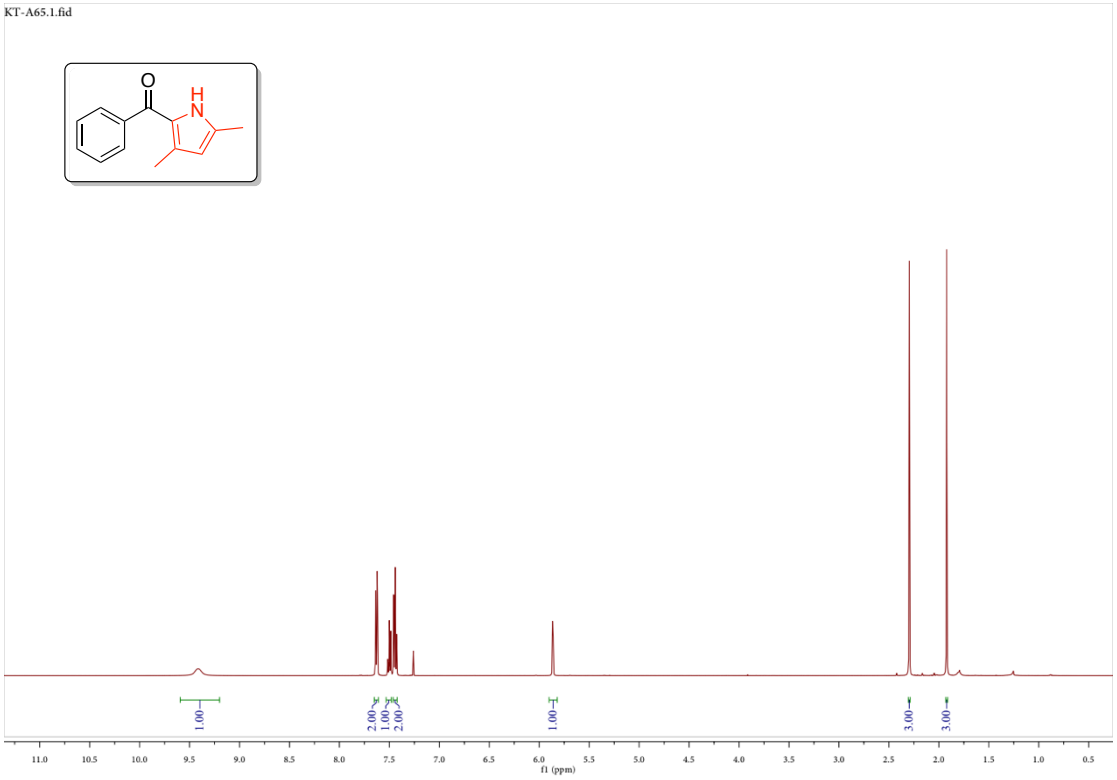
Supplementary Figure 32. ^{13}C NMR Spectrum of 3w (125 MHz, $CDCl_3$)



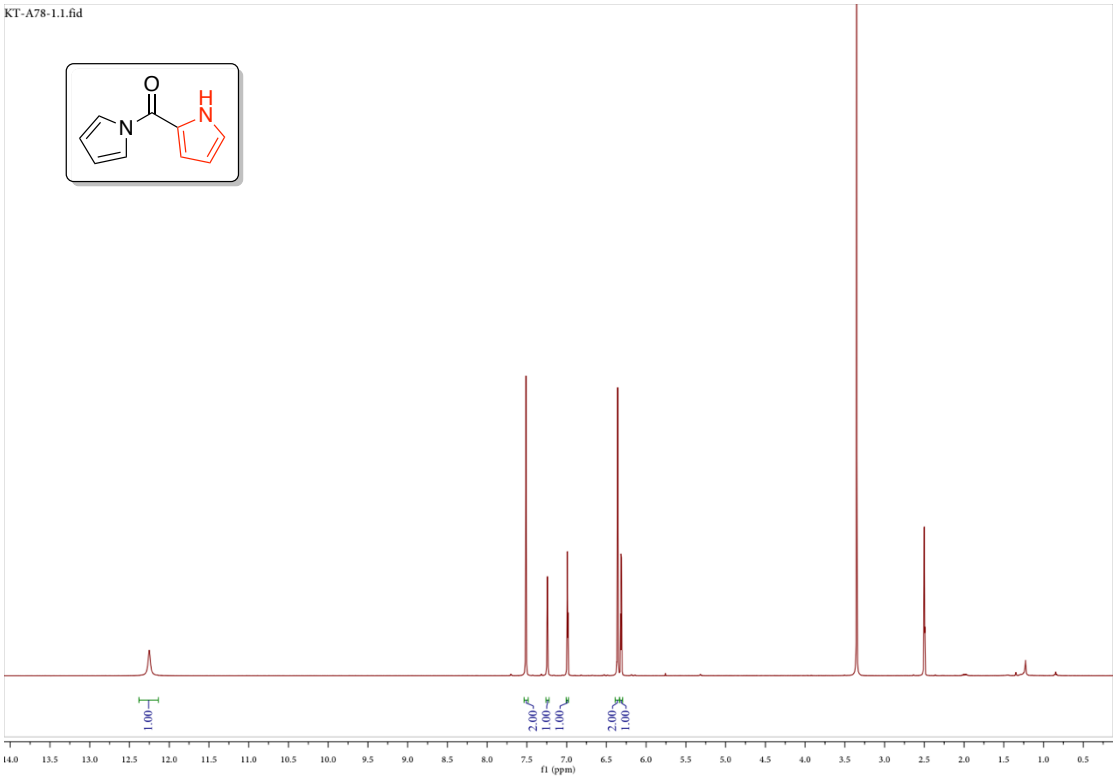
Supplementary Figure 33. ^{1}H NMR Spectrum of 3x (500 MHz, $CDCl_3$)



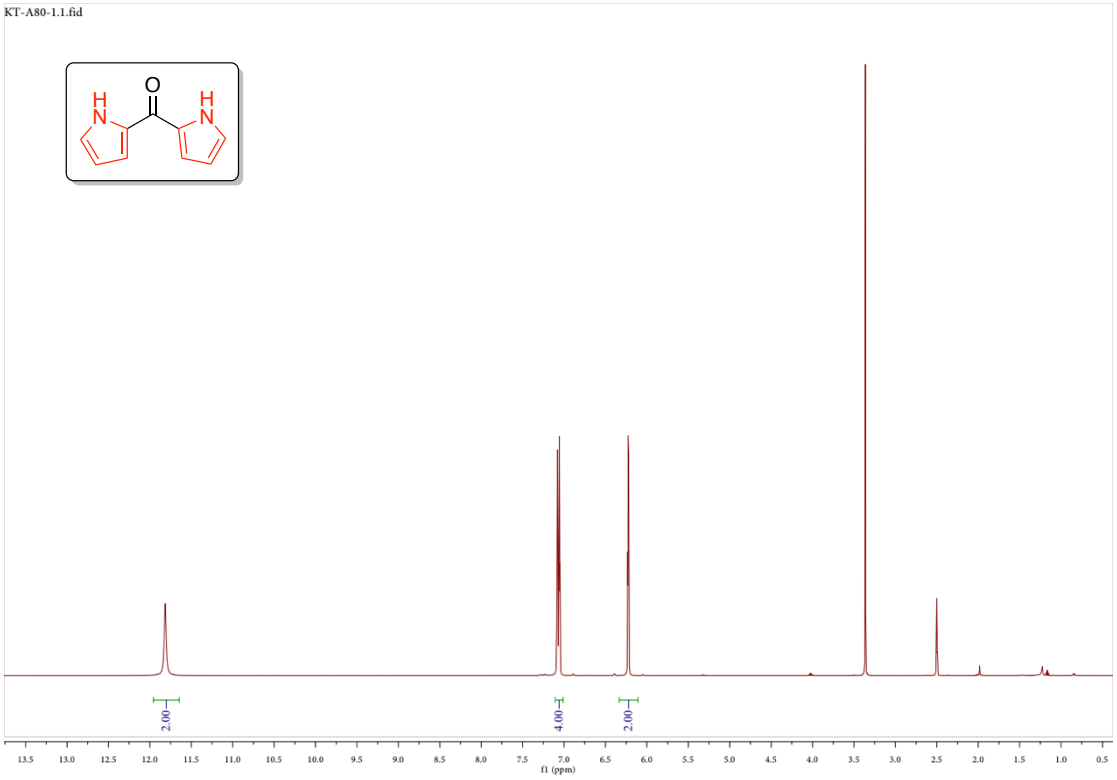
Supplementary Figure 34. ^{1}H NMR Spectrum of 3y (500 MHz, $CDCl_3$)



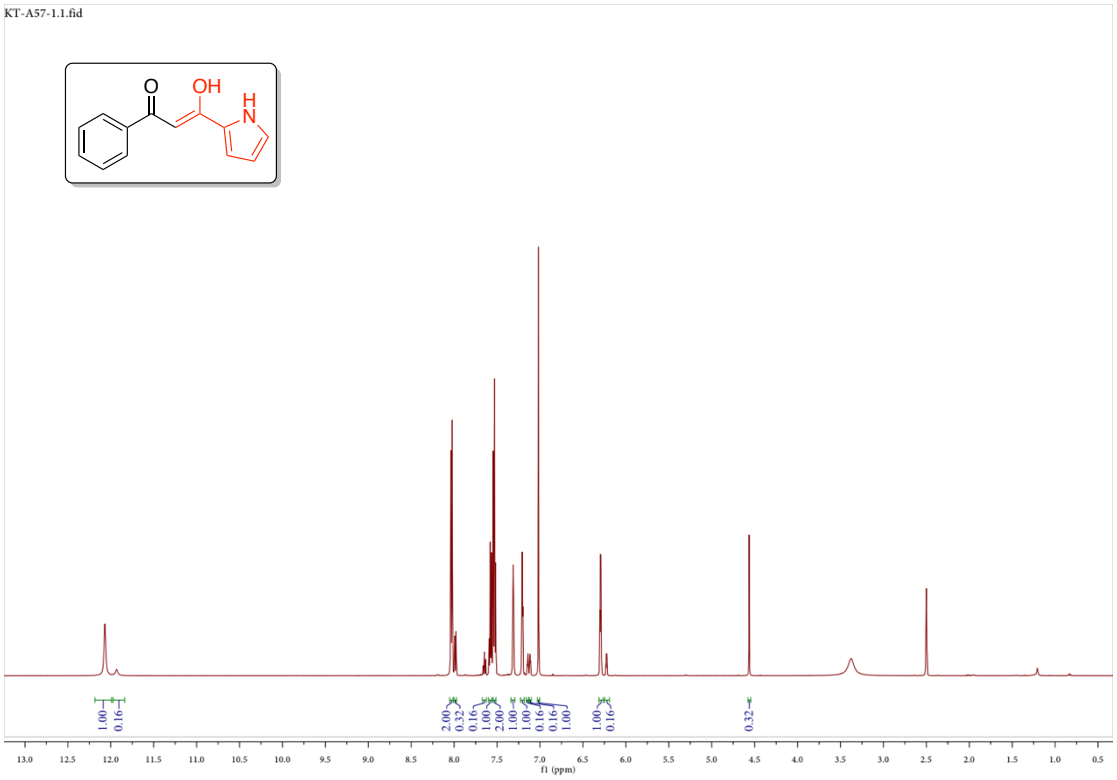
Supplementary Figure 35. ^{1}H NMR Spectrum of 3z (500 MHz, DMSO-d_6)



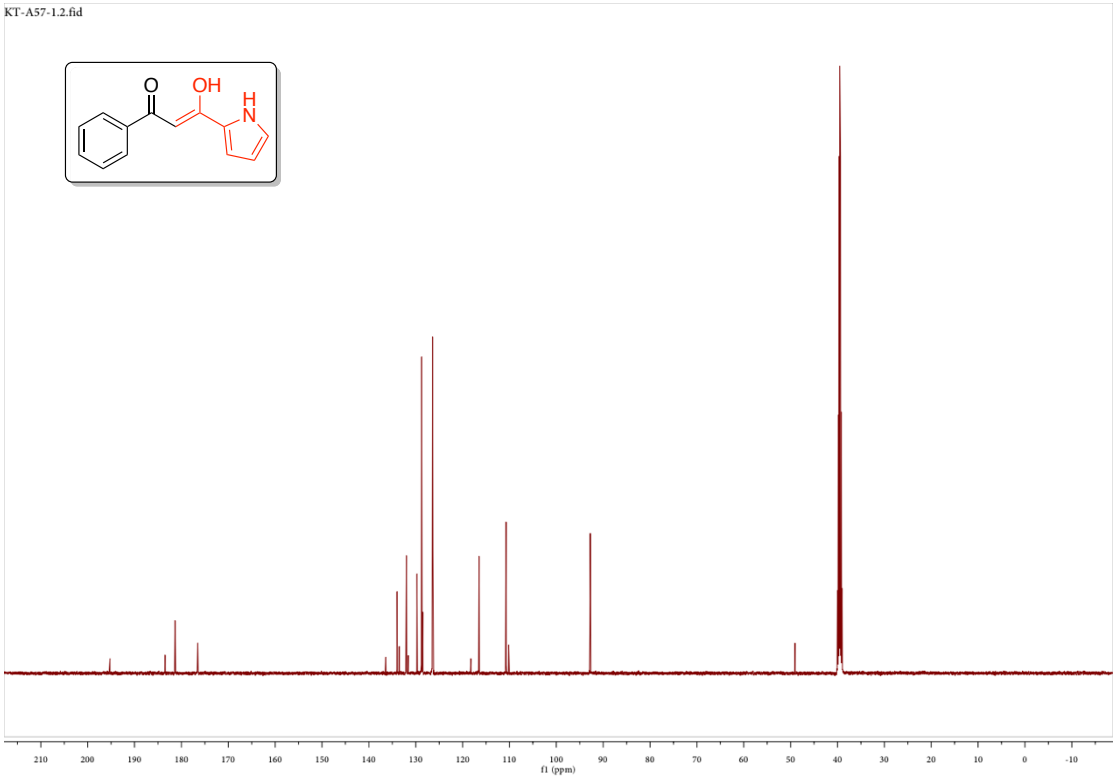
Supplementary Figure 36. ^{1}H NMR Spectrum of 3aa (500 MHz, DMSO-d_6)



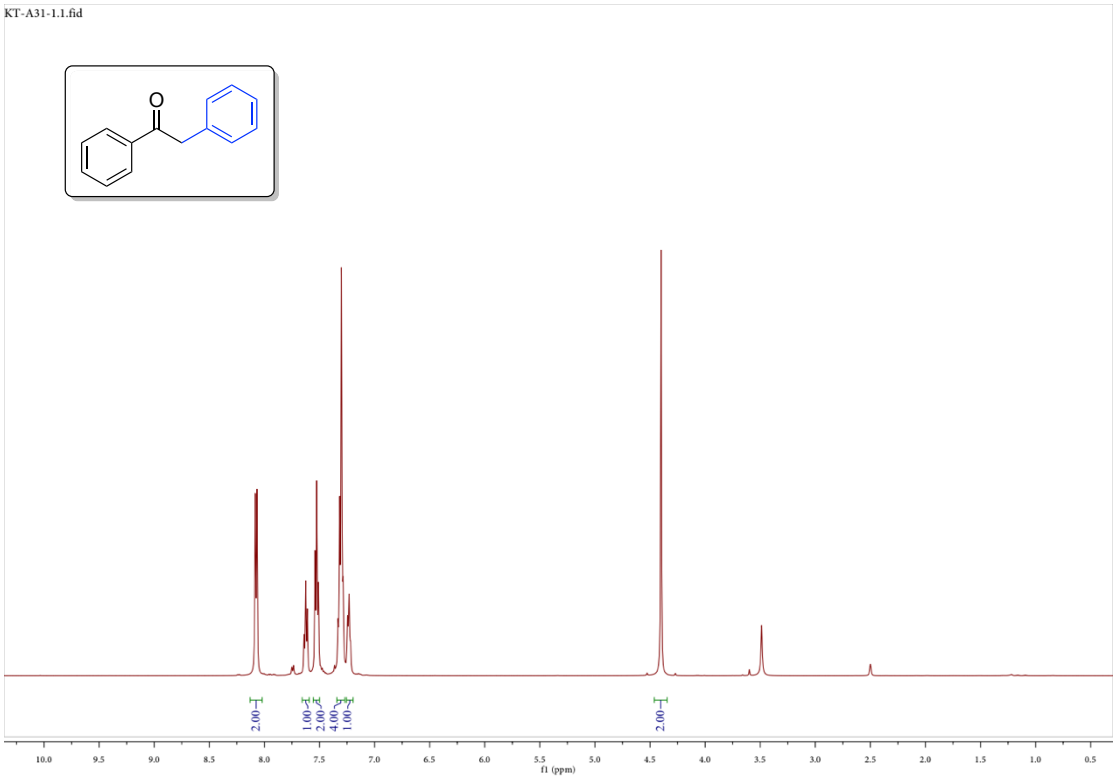
Supplementary Figure 37. ^{1}H NMR Spectrum of 3Z (500 MHz, DMSO-d_6)



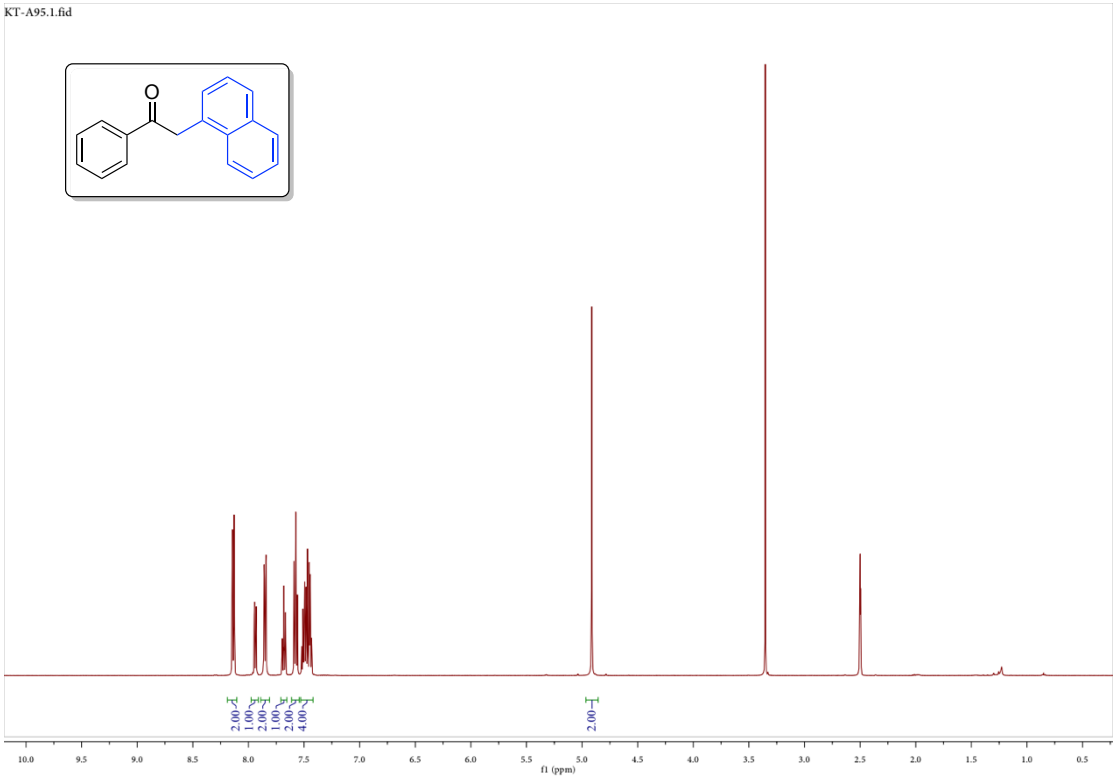
Supplementary Figure 38. ^{13}C NMR Spectrum of 3Z (125 MHz, DMSO-d_6)



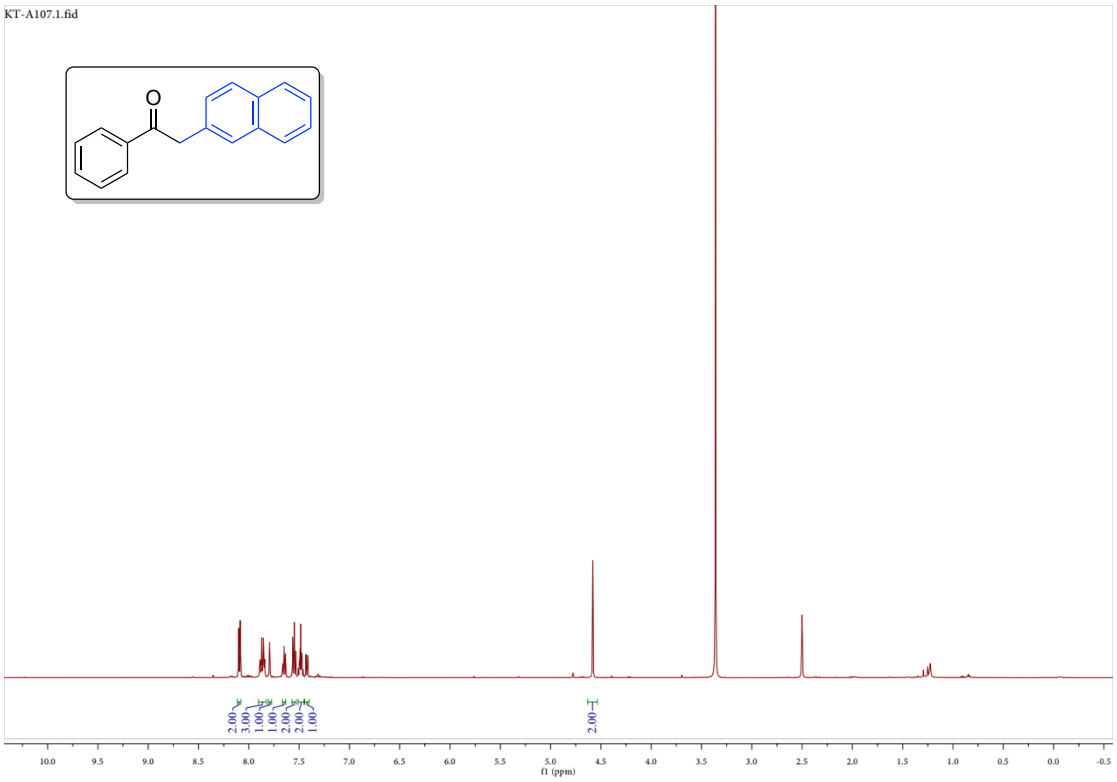
Supplementary Figure 39. ^{1}H NMR Spectrum of 4aa (500 MHz, DMSO-d_6)



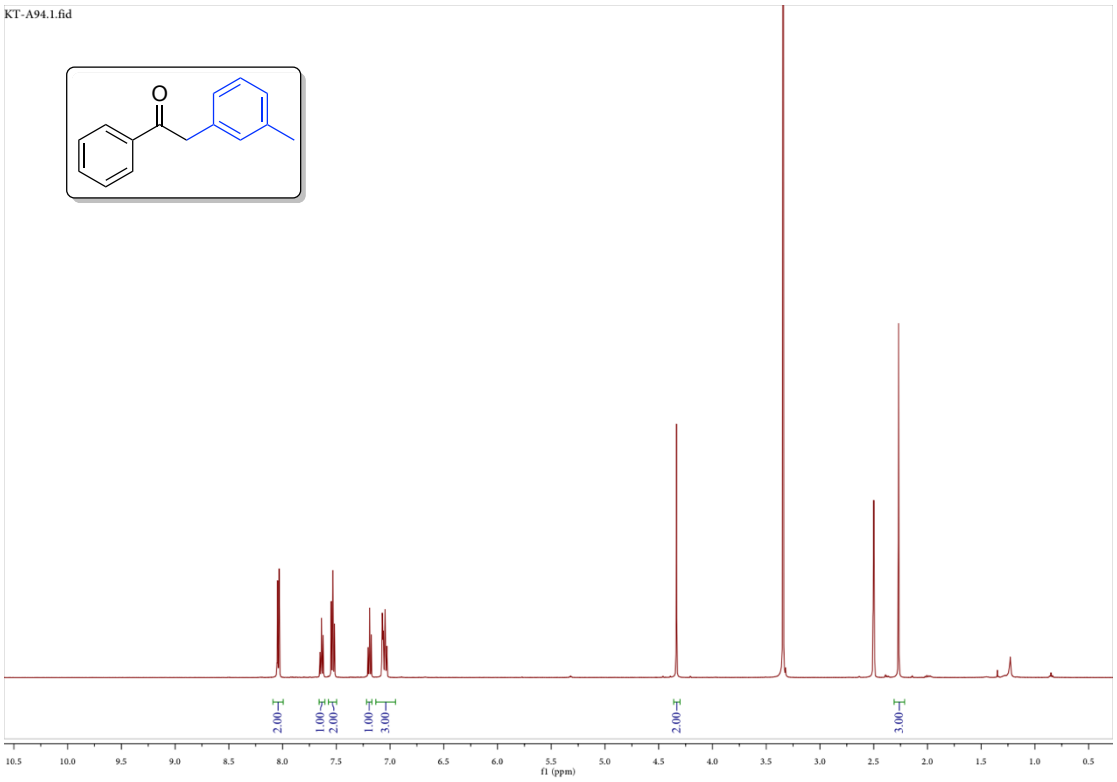
Supplementary Figure 40. ^{1}H NMR Spectrum of 4ab (500 MHz, DMSO-d_6)



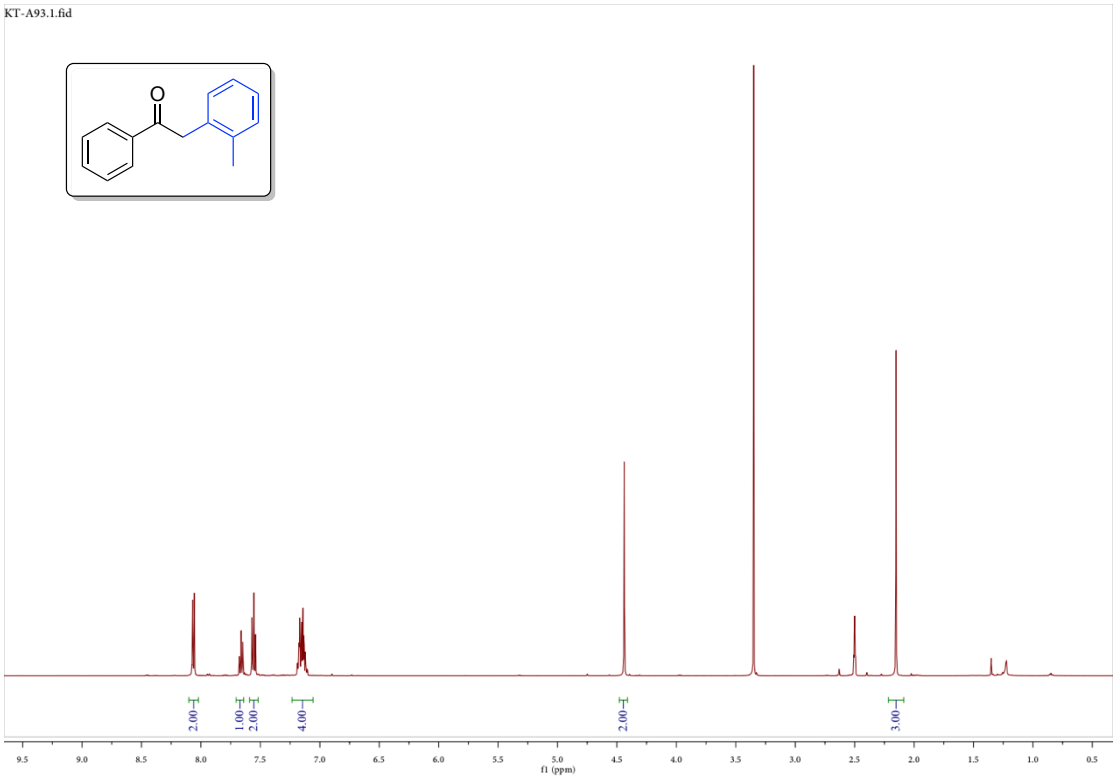
Supplementary Figure 41. ^{1}H NMR Spectrum of 4ac (500 MHz, DMSO-d_6)



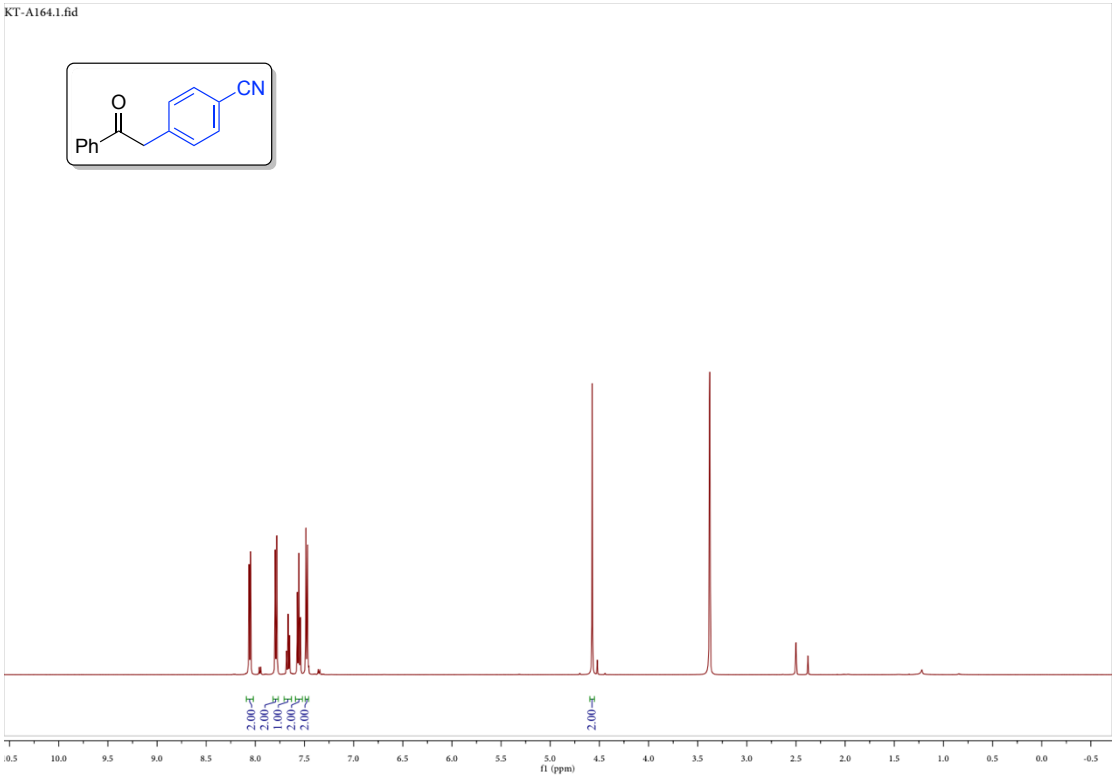
Supplementary Figure 42. ^{1}H NMR Spectrum of 4ad (500 MHz, DMSO-d_6)



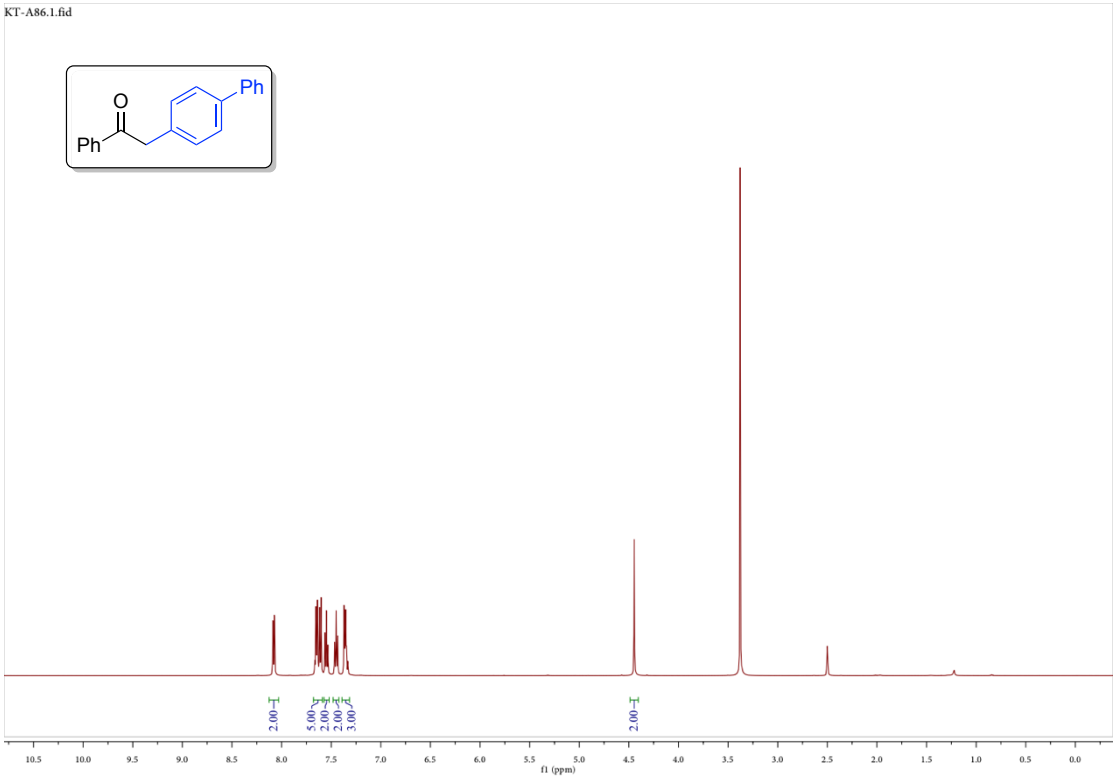
Supplementary Figure 43. ^{1}H NMR Spectrum of 4ae (500 MHz, DMSO-d_6)



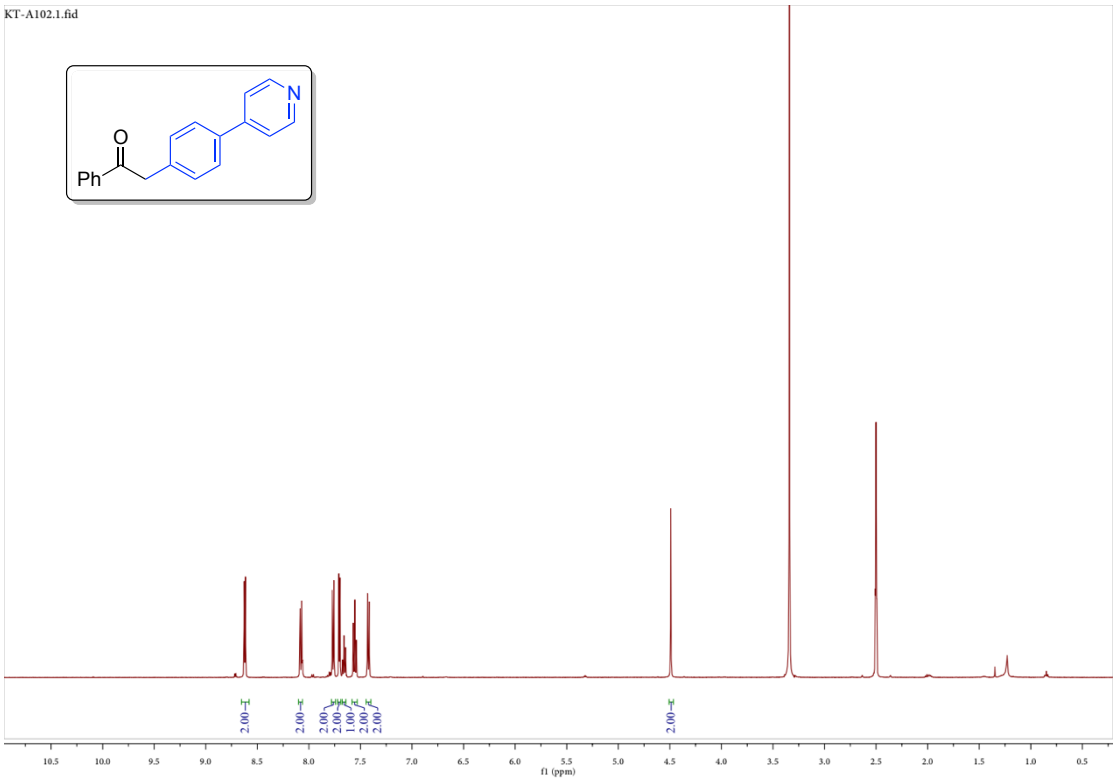
Supplementary Figure 44. ^{1}H NMR Spectrum of 4af (500 MHz, DMSO-d_6)



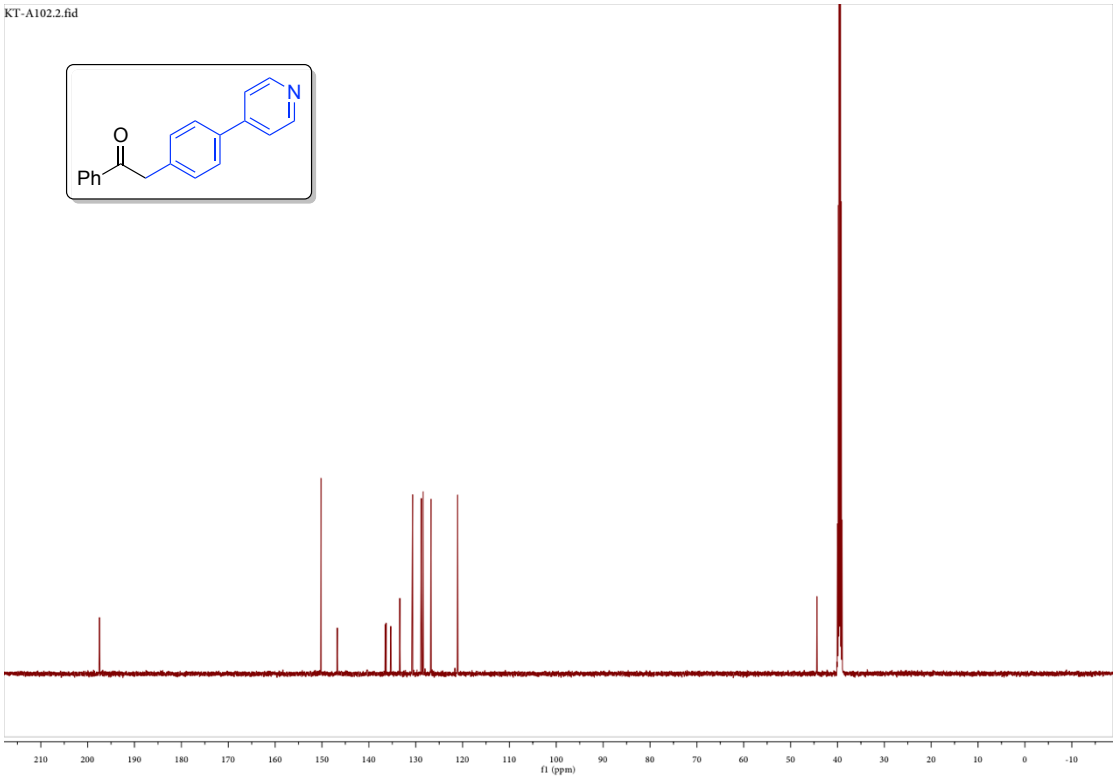
Supplementary Figure 45. ^{1}H NMR Spectrum of 4ah (500 MHz, DMSO-d_6)



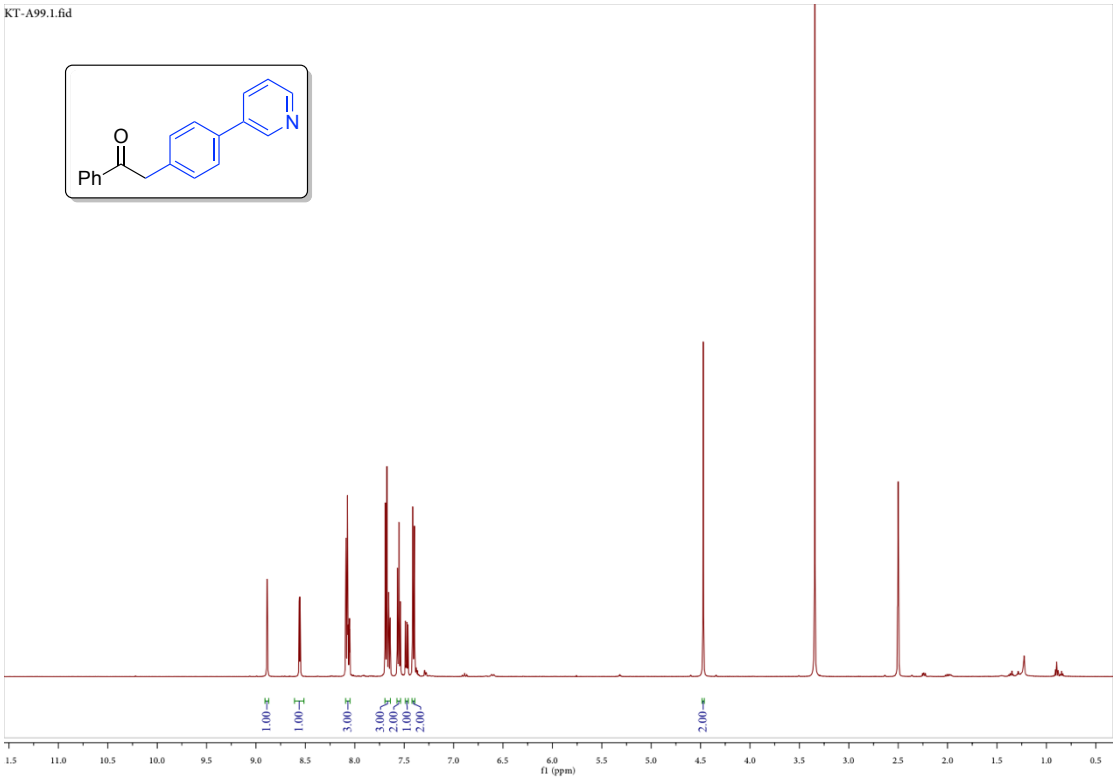
Supplementary Figure 46. ^{1}H NMR Spectrum of 4ai (500 MHz, DMSO-d_6)



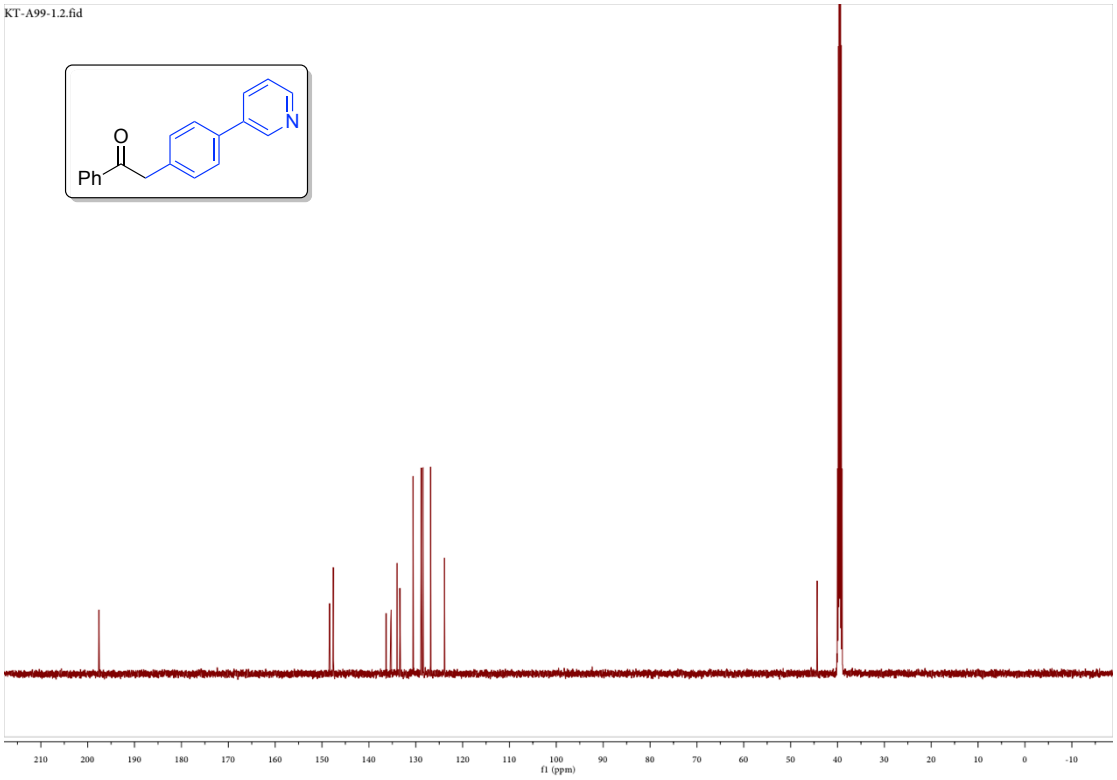
Supplementary Figure 47. ^{13}C NMR Spectrum of 4ai (125 MHz, DMSO-*d*$_6$)



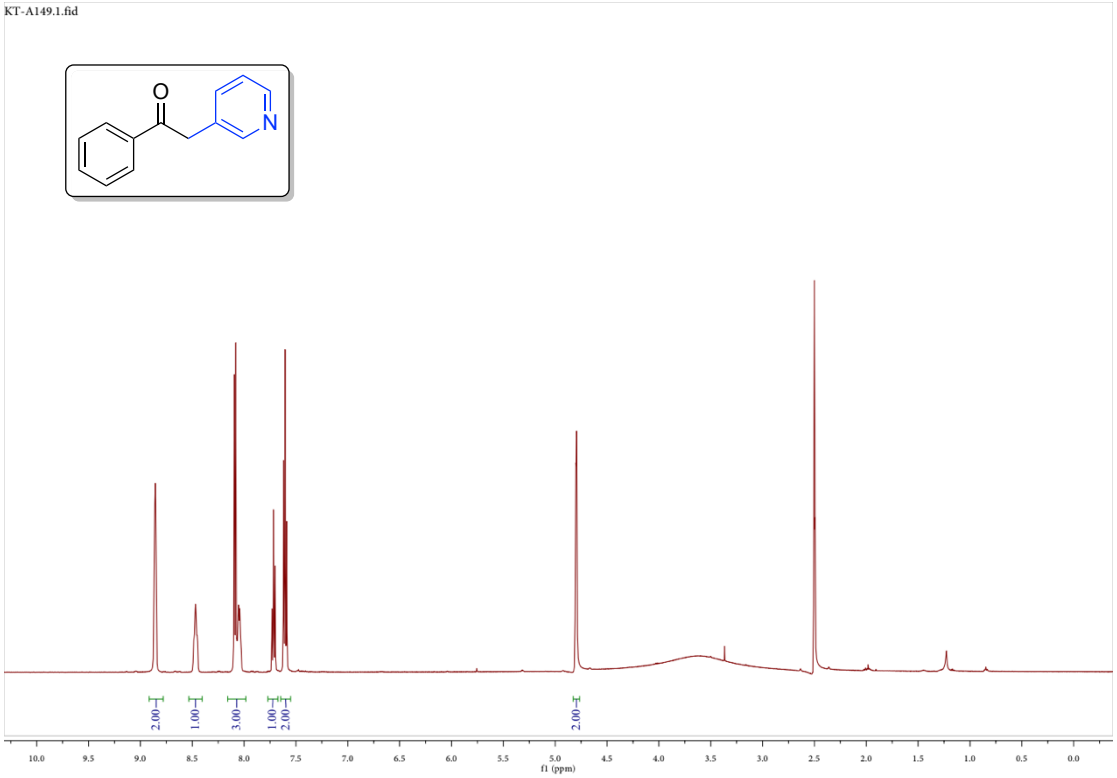
Supplementary Figure 48. ^{1}H NMR Spectrum of 4aj (500 MHz, DMSO-*d*$_6$)



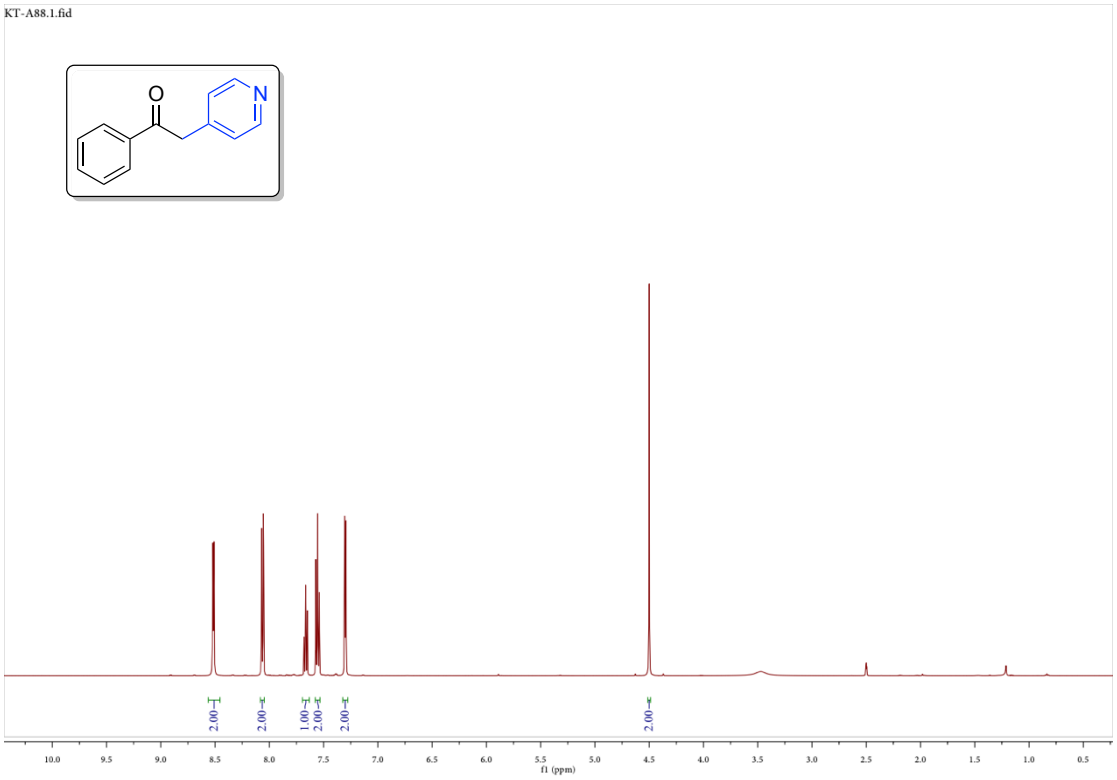
Supplementary Figure 49. ^{13}C NMR Spectrum of 4aj (125 MHz, DMSO-d_6)



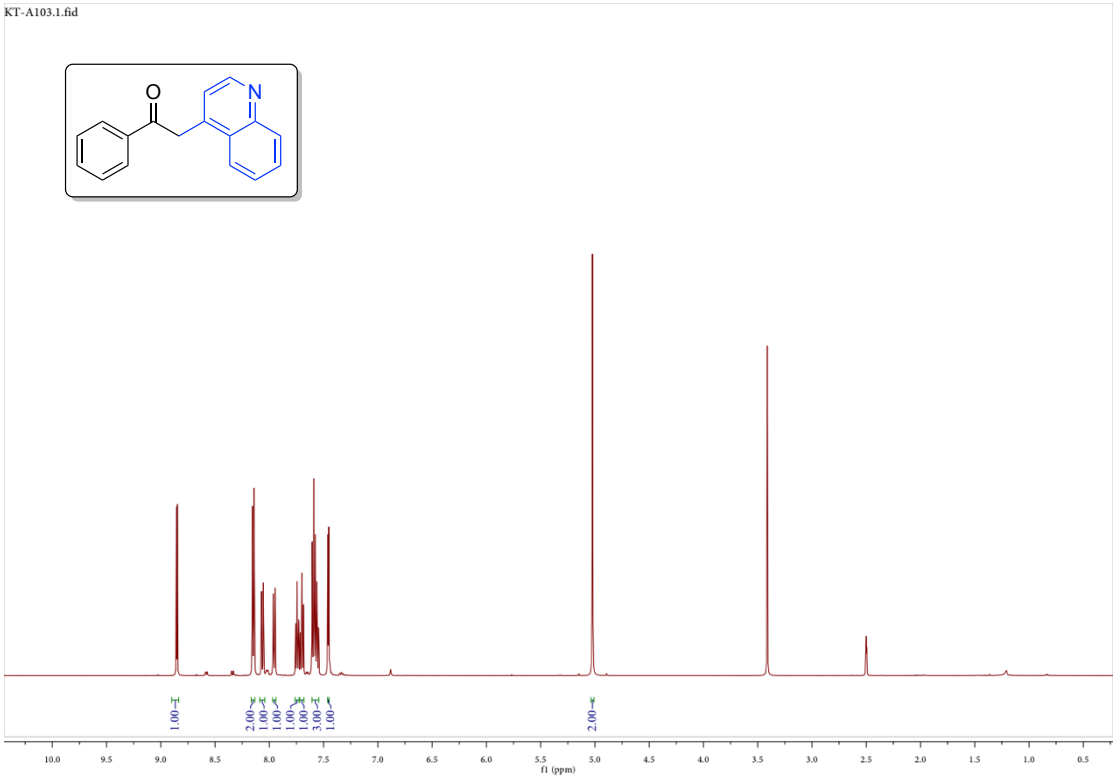
Supplementary Figure 50. ^{1}H NMR Spectrum of 4ak (500 MHz, DMSO-d_6)



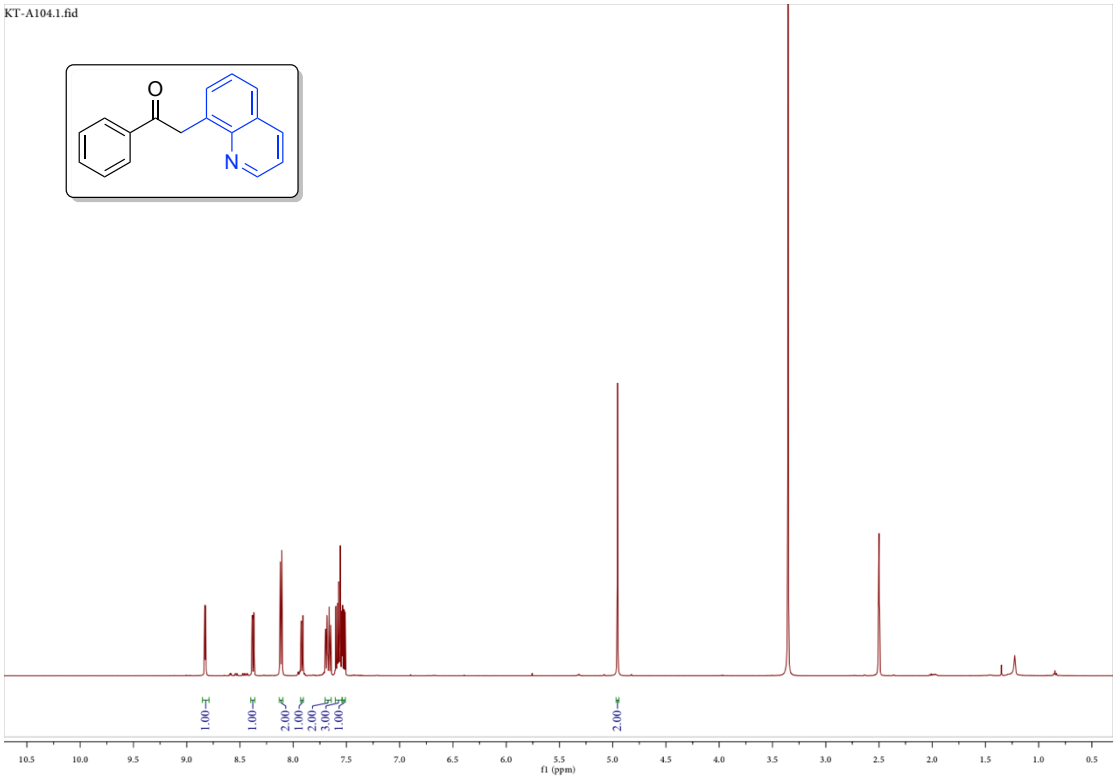
Supplementary Figure 51. ^{1}H NMR Spectrum of 4al (500 MHz, DMSO-d_6)



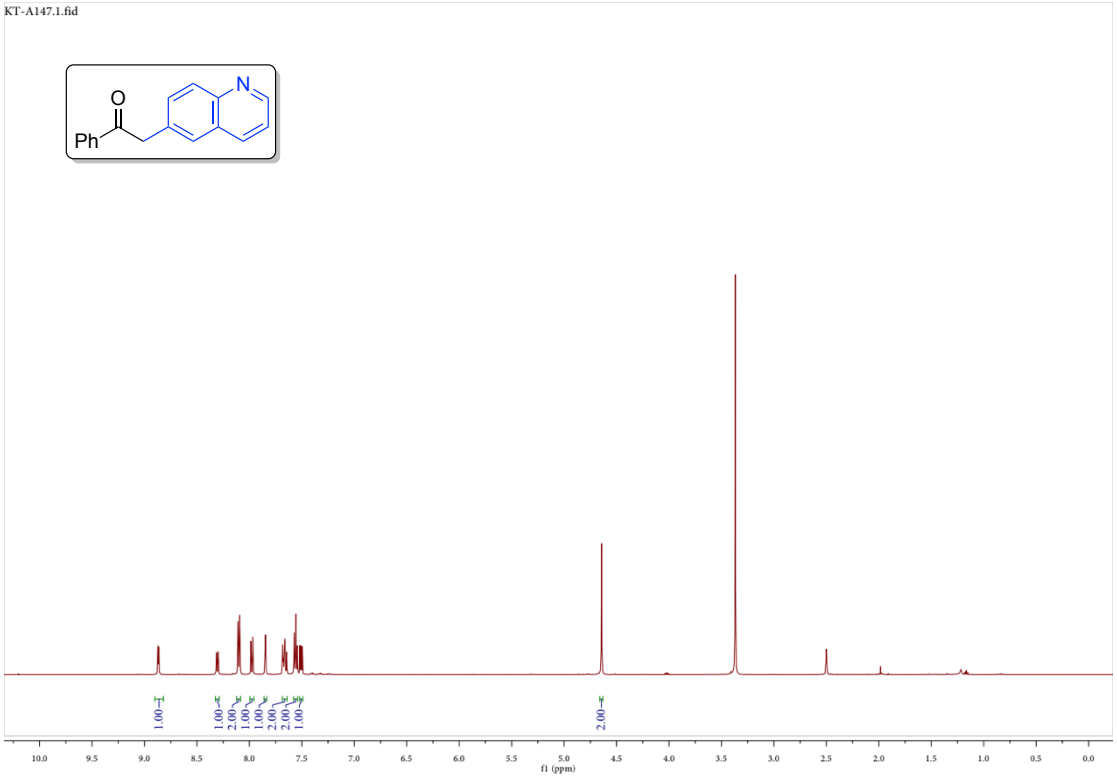
Supplementary Figure 52. ^{1}H NMR Spectrum of 4am (500 MHz, DMSO-d_6)



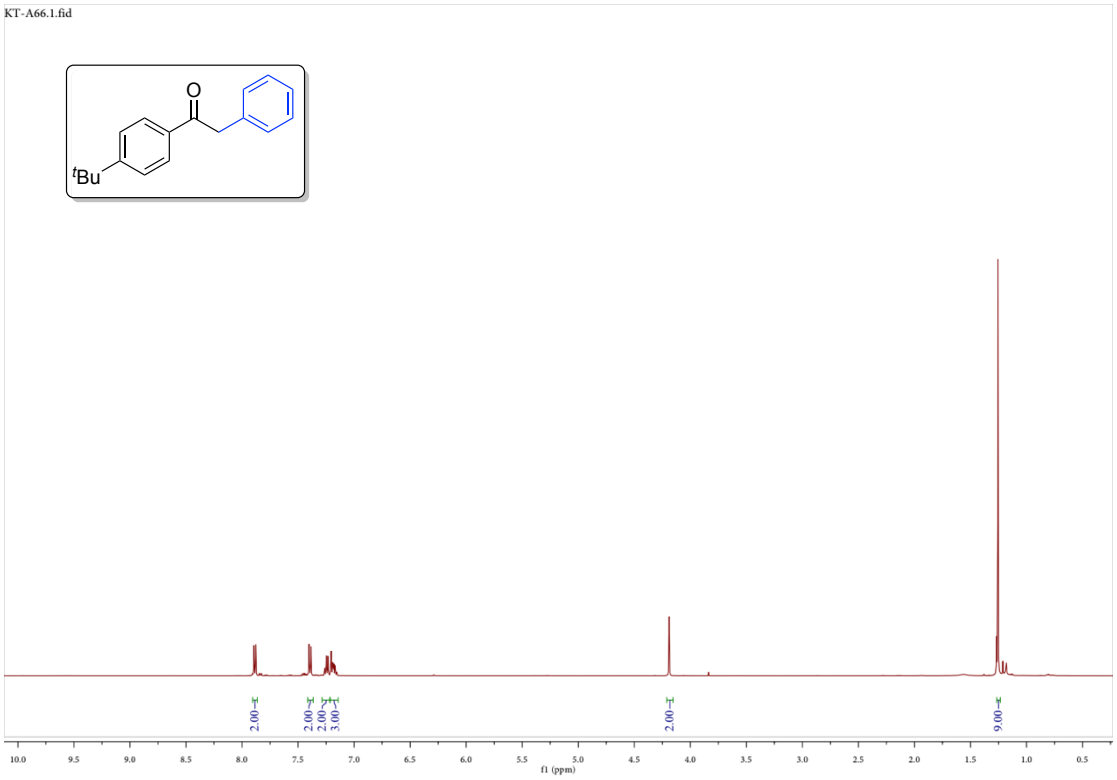
Supplementary Figure 53. ^{1}H NMR Spectrum of 4an (500 MHz, DMSO-d_6)



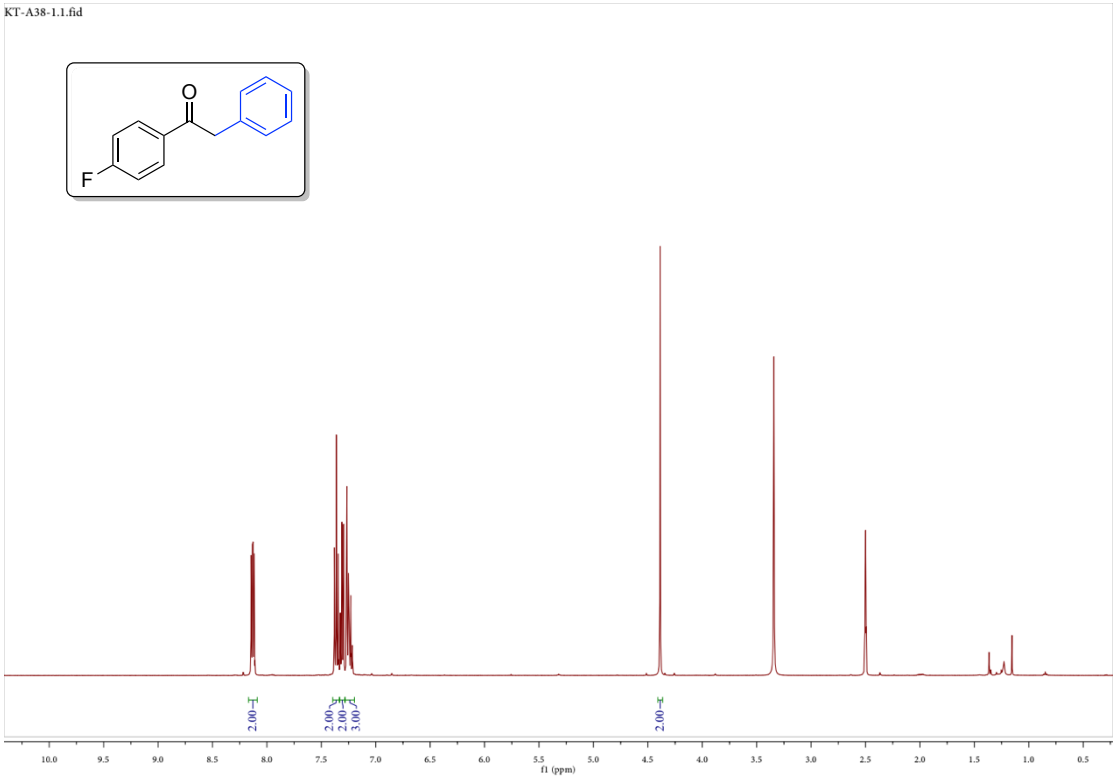
Supplementary Figure 54. ^{1}H NMR Spectrum of 4ao (500 MHz, DMSO-d_6)



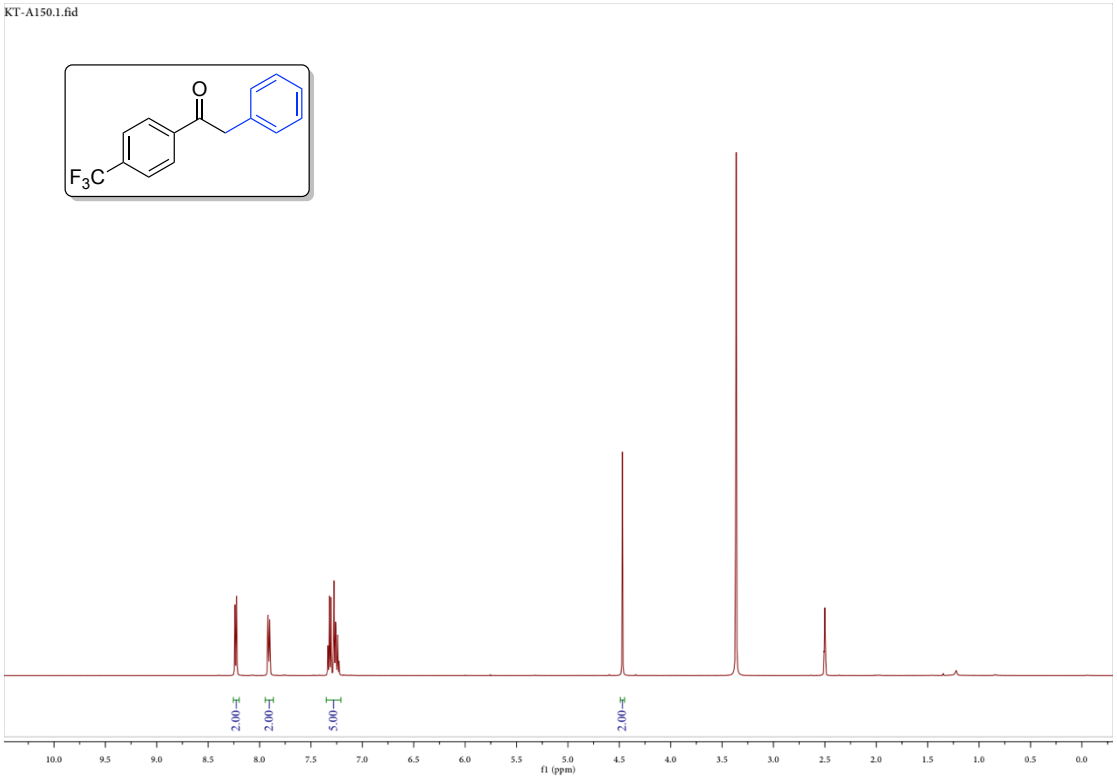
Supplementary Figure 55. ^{1}H NMR Spectrum of 4ba (500 MHz, $CDCl_3$)



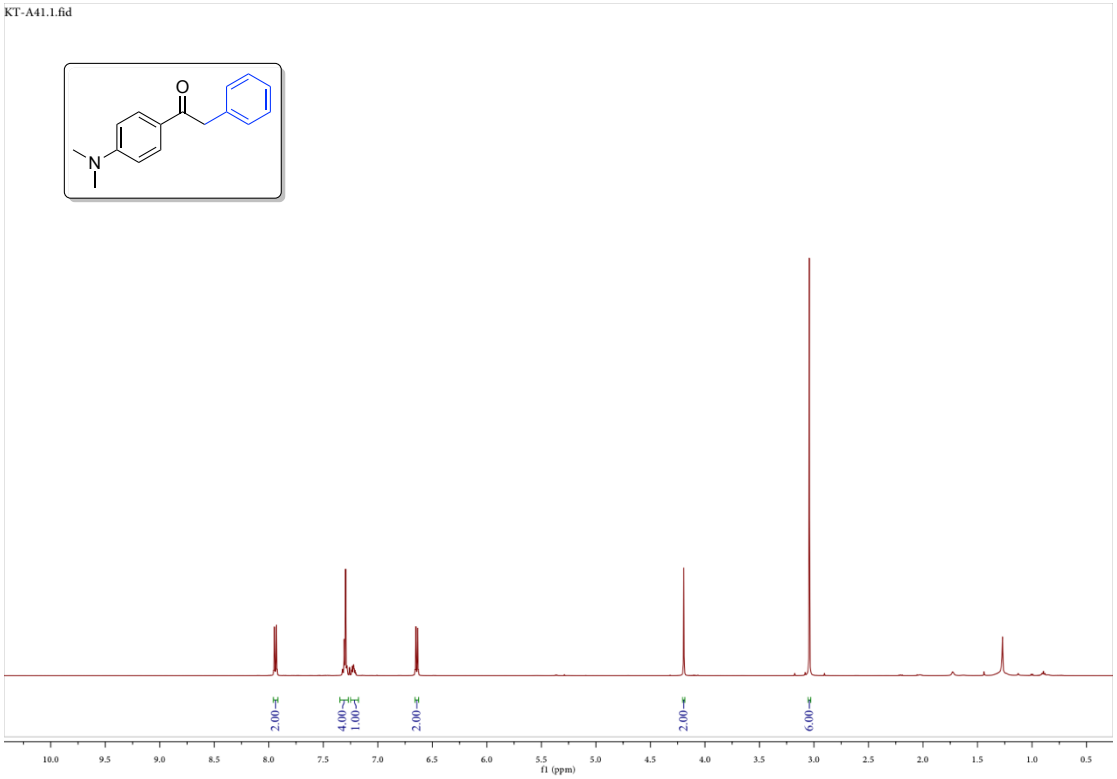
Supplementary Figure 56. ^{1}H NMR Spectrum of 4ca (500 MHz, DMSO-d_6)



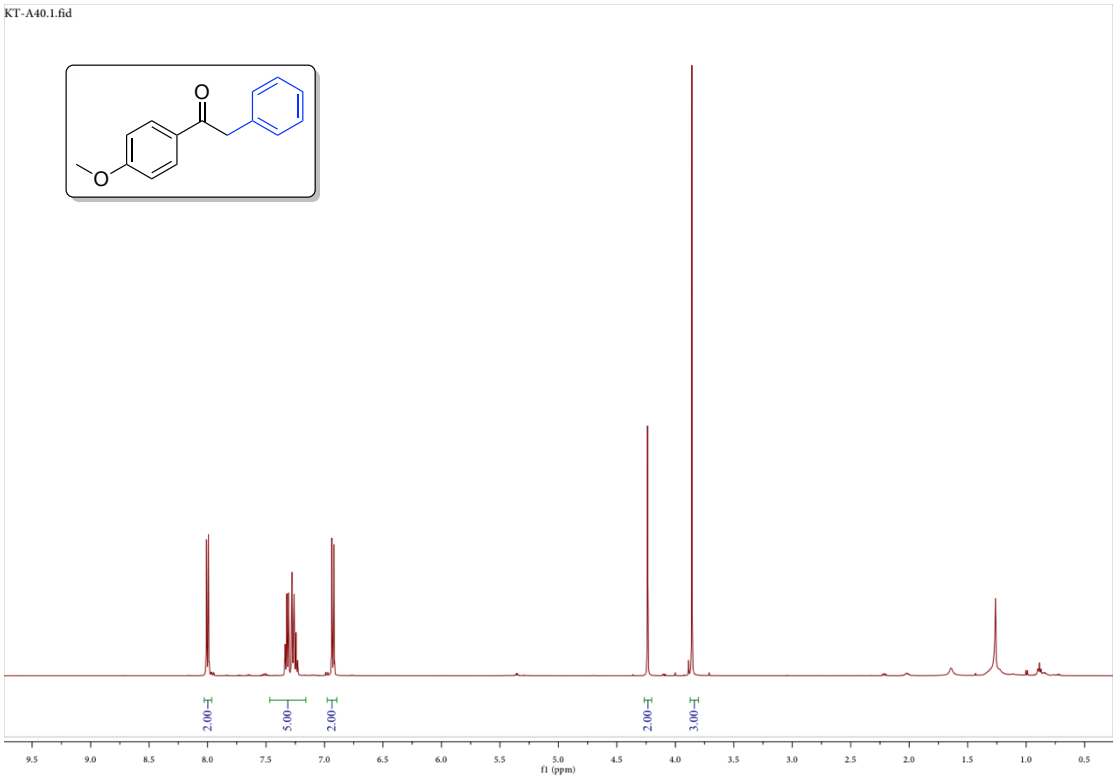
Supplementary Figure 57. ^{1}H NMR Spectrum of 4da (500 MHz, DMSO-d_6)



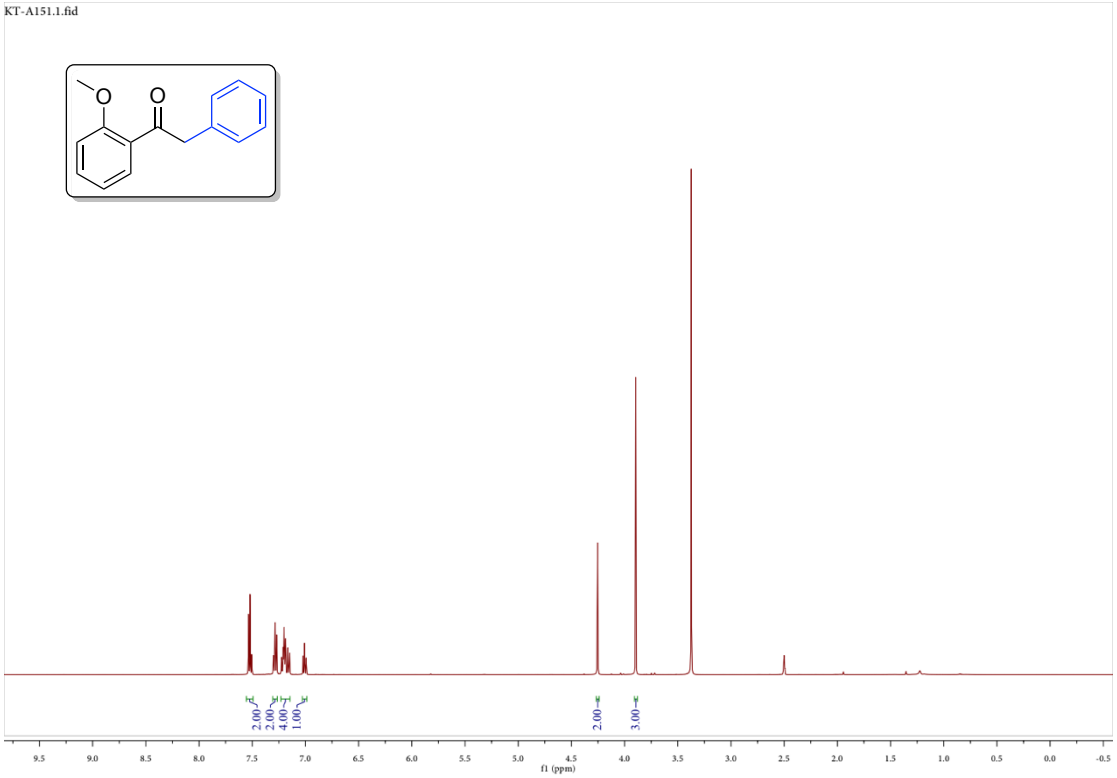
Supplementary Figure 58. ^{1}H NMR Spectrum of 4ea (500 MHz, $CDCl_3$)



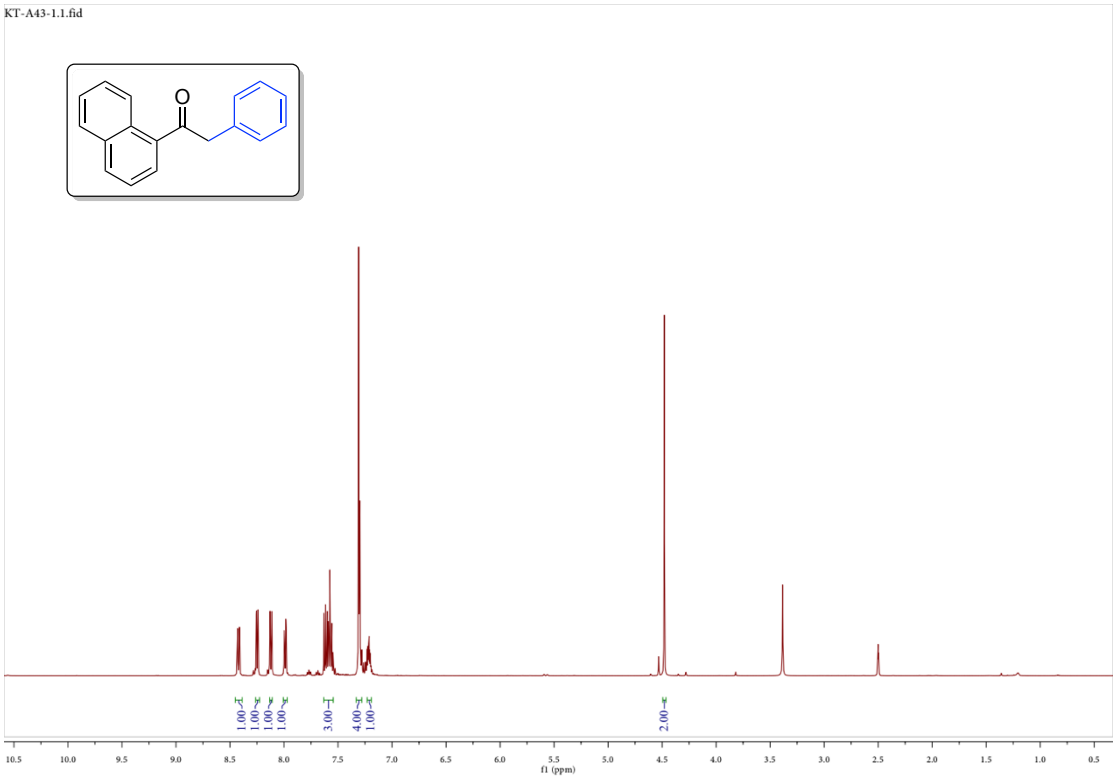
Supplementary Figure 59. ^{1}H NMR Spectrum of 4fa (500 MHz, $CDCl_3$)



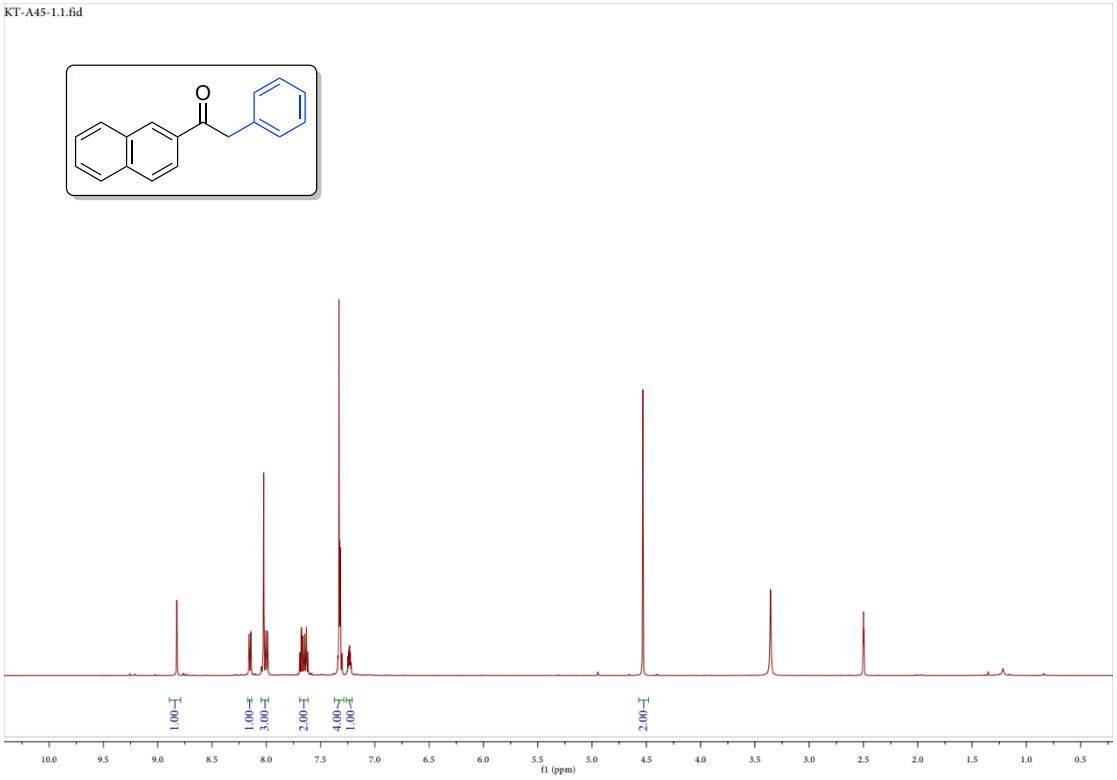
Supplementary Figure 60. ^{1}H NMR Spectrum of 4ga (500 MHz, DMSO-d_6)



Supplementary Figure 61. ^{1}H NMR Spectrum of 4ha (500 MHz, DMSO-d_6)



Supplementary Figure 62. ^{1}H NMR Spectrum of 4ia (500 MHz, DMSO-d_6)



Supplementary Figure 63. ^{1}H NMR Spectrum of 4ja (500 MHz, DMSO-*d*$_6$)