- Supplementary Information -

A quantitative empirical directing group scale for selectivity in iridium-catalysed hydrogen isotope exchange reactions

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1. General Experimental Details

General

For the synthetic procedures, standard Schlenk techniques under an inert gas atmosphere (Ar or N_2) were used, unless otherwise stated. Materials obtained from commercial sources were used without further purification. All glassware was flame dried and cooled under a stream of nitrogen.

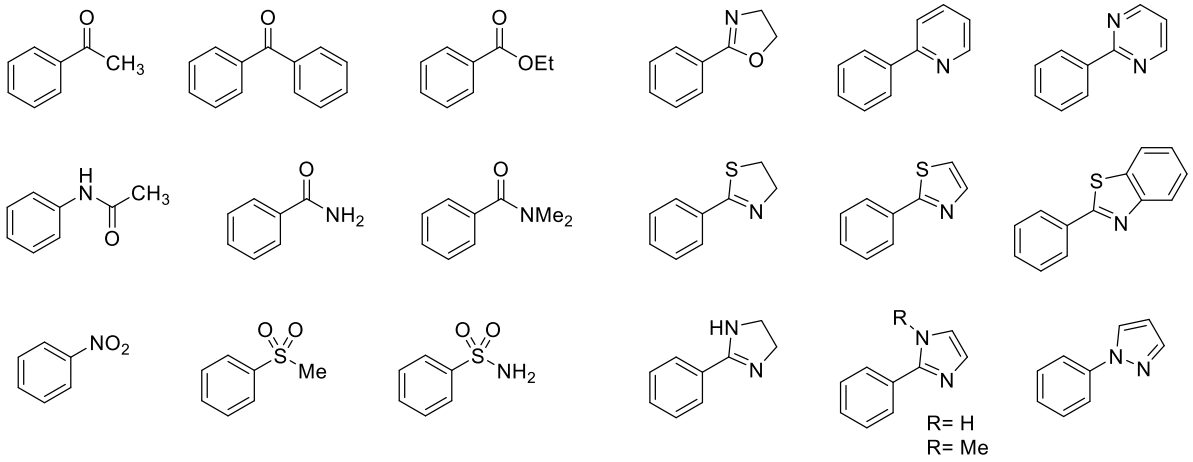
Materials

Dichloromethane, tetrahydrofuran, diethyl ether and toluene were obtained from a PureSolv SPS-400-5 Solvent Purification System. Ethyl acetate was dried over K_2CO_3, then distilled under a nitrogen atmosphere and stored over 3 Å molecular sieves. Dry organic solvents and distilled water used for cross-coupling reactions were additionally degassed by bubbling argon through the solvent for 30 min. For reactions/work-up procedures in air, p.a. grade solvents were used. Petroleum ether refers to alkanes with a boiling point range of 40-60°C.
(1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride,[S1] phenylthiazoline,[S2] and 1-methyl-2-phenylimidazole[S3] were synthesised according to literature procedures. 2-Phenylthiazole, 2-phenylpyrimidine, 2-(4-acetyl)phenylpyridine, and 2-(4-cyano)phenylpyridine were prepared by cross-coupling reactions of corresponding phenylboronic acids and heterobromides as described in section 2. 2-(4-Acetyl)phenyloxazoline and 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole were obtained from the reaction between corresponding aryl nitriles and amino alcohols catalysed by [Cu(Cl)(IPr)].[S4] Anhydrous Na[$BArF_{24}$] ($BArF_{24}$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)) was obtained following Bergman's synthesis,[S5] followed by recrystallising the crude Na[$BArF_{24}$]·*x*(solvent) prior to drying.[S6] Phosphine/NHC monodentate complex **Ir-1** with the $BArF_{24}$ counterion was synthesised from neutral chlorocarbene complex **Ir-2**[S7] in a procedure adapted from that published before for preparation of corresponding complexes with BF_4 and OTf counterions.[S8]
Flash column chromatography was carried out using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck silica plates coated with fluorescent indicator and visualised by UV light (254 nm)

Analysis

NMR Spectroscopy: ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz), ^{11}B (128 MHz) ^{19}F (376 MHz) and $^{31}P\{^{1}H\}$ (162 MHz) NMR spectra were obtained on a Bruker AV3-400 instrument with a liquid nitrogen Prodigy cryoprobe. The chemical shifts (δ) are reported in ppm relative to the residual protonated solvent for ^{1}H NMR or solvent signal for $^{13}C\{^{1}H\}$ NMR ($CDCl_3$: δ_H 7.26 ppm and δ_C 77.16 ppm; DMSO-d_6: δ_H 2.50 ppm and δ_C 39.51 ppm; C_6D_6: δ_H 7.16 ppm; acetone-d_6: δ_H 2.05 ppm).[S9] Coupling constants (*J*) are reported in Hz and refer to $^{3}J_{H\text{-}H}$ couplings, unless otherwise stated. Multiplicities are expressed with s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad signal). If no multiplicity is given for $^{13}C\{^{1}H\}$ data, the signal is a singlet. NMR assignments were made using additional 2D NMR experiments where necessary.
Infrared Spectroscopy: Infrared (IR) spectra were collected on a Shimadzu IRAffinity-1 Spectrophotometer with only major peaks being reported.
Elemental analysis was performed using a Perkin-Elmer CH2400 instrument.

a) For intermolecular competition experiments



b) For intramolecular competition experiments

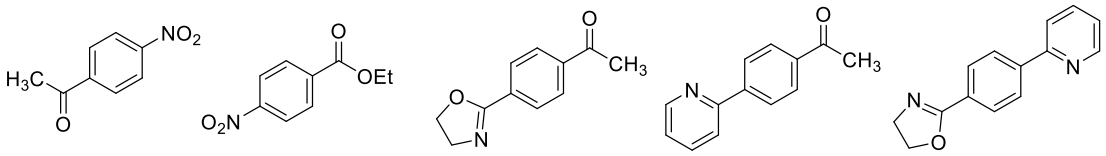


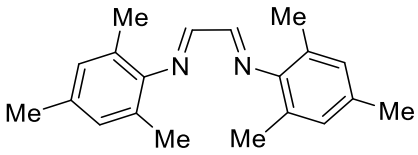
Figure S1. Scope of the substrates used in the study

2. Synthesis and Characterisation

2.1. Synthesis of Iridium (I) Complexes

Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl)[S1]

N,N'-dimesitylethanediimine



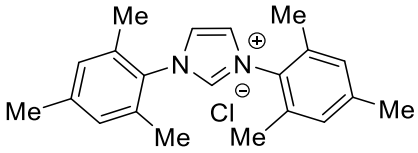
2,4,6-Trimethylaniline (84.2 mL, 0.60 mol, 2.0 equiv.) was dissolved in methanol (200 mL) and cooled to 0 °C, and a solution of 40% glyoxal in water (34.4 mL, 0.30 mol, 1.0 equiv.) with one or two drops of formic acid was added. The solution was warmed to room temperature and stirred for two days. The yellow suspension was filtrated and washed with a minimum volume of methanol and diethyl ether to afford *N,N'*-dimesitylethanediimine (78.5 g, 0.27 mol, 90%) as a yellow powder, which was used immediately in the next step.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (s, 2H, CH=N), 6.92 (s, 4H, ArH), 2.30 (s, 6H, *p*-CH_3), 2.17 (s, 12H, *o*-CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 163.6, 147.6, 134.4, 129.1, 126.7, 20.9, 18.3.

NMR data are consistent with the literature.[S10]

1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) [S1]



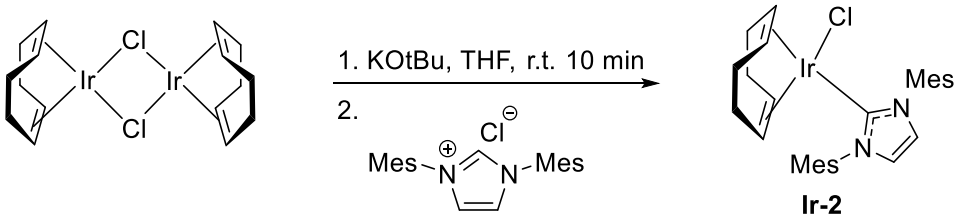
Paraformaldehyde (8.05g, 0.27 mol, 1.0 equiv.) was suspended in a solution of 4M hydrochloric acid in dioxane (94 mL, 0.38 mol, 1.4 equiv.) and stirred until complete dissolution of the white solid. THF (300 mL) was added, followed by the slow addition of *N,N'*-dimesitylethanediimine (78.5 g, 0.27 mol, 1.0 equiv.). The resulting solution was stirred at 40 °C for 2 days. The suspension was cooled to room temperature and the white precipitate was collected by filtration, and washed with THF (100 mL) and diethyl ether (100 mL) to afford the crude product, which was recrystallized from a DCM/Et_2O mixture to afford 1,3-bis-(2,4,6-trimethylphenyl)imidazolium chloride (36.6 g, 0.11 mol, 40%) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.64 (s, 1H, N-CH=N), 7.61 (d, *J* = 0.9 Hz, 2H), 7.02 (s, 4H, Ar), 2.33 (s, 6H, *p*-CH_3), 2.17 (s, 12H, *o*-CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 141.4, 139.2, 134.2, 130.7, 130.0, 124.8, 21.2, 17.7.

NMR data are consistent with the literature.[S1]

Synthesis of Chloro(η^4–cycloocta–1,5–diene)(1,3-dimesitylimidazoline-2-ylidene) iridium(I) [Ir(COD)(IMes)Cl][S7]



Bis(1,5-cyclooctadiene)diiridium(I) dichloride (500 mg, 0.75 mmol, 1 equiv.) and potassium *tert*-butoxide (167 mg, 1.50mmol, 2 equiv.) were added to a flame-dried Schlenk tube under argon and stirred under vacuum for 5 min. THF (12.5 mL) was added and the mixture was stirred under argon for 10 min. IMes·HCl (508 mg, 1.50 mmol, 2 equiv.) was then added and the resulting reaction mixture was stirred for 4 h. The solvent was removed *in vacuo*, and column chromatography (50% ethyl acetate in petroleum ether) afforded the title compound (730 mg, 1.14 mmol, 76 %) as yellow solid. The isolated catalyst was dried in a vacuum oven (40 °C, 1 mbar) for 24 h before use. This process was repeated batch-wise to obtain a of the quantity of **Ir-2** necessary for all competition studies and synthesis of **Ir-1** catalyst.

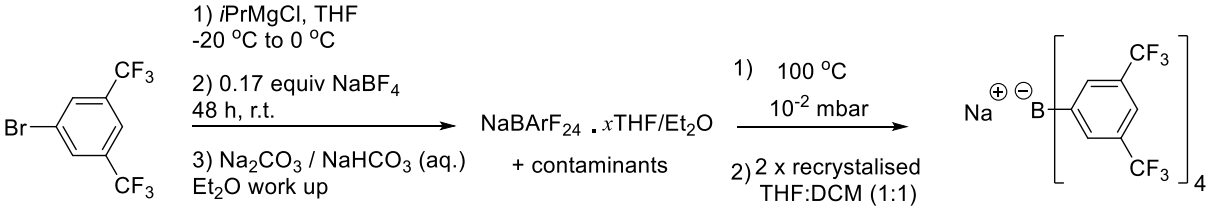
m.p. > 190 °C (decomposition)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.04 – 6.96 (m, 4H, Ar-H), 6.95 (s, 2H, NCH=CHN), 4.19 – 4.12 (m, 2H, COD CH), 3.01 – 2.94 (m, 2H, COD CH), 2.36 (s, 12H, *o*-CH_3Ar), 2.16 (s, 6H, *p*-CH_3Ar), 1.78 – 1.59 (m, 4H, COD CH_2), 1.39 – 1.20 (m, 4H, COD CH_2).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 180.9, 138.8, 137.5, 136.2, 134.5, 129.7, 128.3, 123.4, 82.7, 51.6, 33.6, 29.1, 21.3, 19.8, 18.4.

NMR data are consistent with the literature.[S7]

Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate [Na(BArF$_{24}$)][S5,S6]



A 2.0 M solution of *i*-PrMgCl in THF (100 mL, 0.20 mol, 6.6 equiv.) was added dropwise over 45 min to a stirred solution of 1-bromo-3,5-bistrifluoromethylbenzene (30 mL, 0.17 mol, 5.8 equiv.) in THF (150 mL) chilled to -20 °C. After the reaction was allowed to warm from -20 °C to 0 °C over 1 h, $NaBF_4$ (3.3 g, 0.03 mol, 1.0 equiv.) was quickly added as a solid under a stream of N_2. The mixture then stirred for 48 h at 23 °C (under N_2). All work-up and purification procedures were then carried out under air. The contents of the flask were poured into a solution of Na_2CO_3 (44 g) and $NaHCO_3$ (22 g) in water (600 mL). This mixture was stirred vigorously for 1 h and then extracted with diethyl ether (4 × 200 mL). The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. After filtration of the mixture and rotary evaporation of the filtrate, the crude Na[BArF$_{24}$]·*x*THF/Et$_2$O was dried at 100 °C/10^{-2} mbar for 10 h to yield a tacky brown/yellow solid. Dissolving the resulting oily crude material in a 1:1 mixture of dichloromethane and tetrahydrofuran (30 mL) and cooling the mixture at –23 °C for 48 h yielded an off-white crystalline solid, which was then recrystallised again under the same conditions. Anhydrous Na[BArF$_{24}$]·THF (12.7 g, 0.014 mmol, 48%) was obtained as white solid by drying the resulting crystalline solid under vacuum (< 10^{-2} mbar) for 10 h. Anhydrous Na[BArF$_{24}$] was stored under an atmosphere of argon.

^{1}H NMR (400 MHz, acetone-d_6) δ = 7.79 (br, 8H, *ortho*-Ar-H), 7.67 (br, 4H, *para*-Ar-H).

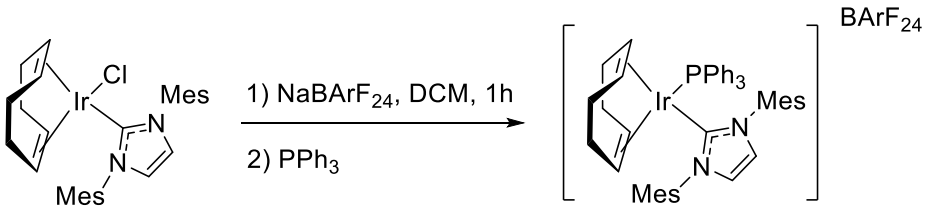
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ = 161.0 (q, $^1J_{C–B}$ = 49.9 Hz, *ipso*-C), 134.0 (br, *ortho*-C), 128.5 (qq, $^3J_{C–B}$ = 2.8 Hz, $^2J_{C–F}$ = 32.2 Hz, *meta*-C), 124.0 (q, $^1J_{C–F}$ = 272 Hz, CF_3), 117.5 (br, *para*-C).

^{11}B NMR (128 MHz, acetone-d_6) δ = -6.65.

^{19}F NMR (376 MHz, acetone-d_6) δ = -63.3.

NMR data are consistent with the literature.[S5]

Synthesis of η^4–cycloocta-1,5-diene(1,3-dimesitylimidazoline-2-ylidene)(triphenylphosphine)iridium(I)tetrakis [(3,5-rifluoromethylphenyl)]borate, [(COD)Ir(PPh$_3$)(IMes)]BArF$_{24}$ [S8]



Ir-2 **Ir-1**

[Ir(COD)Cl(IMes)], **Ir-2**, (200 mg, 0.31 mmol, 1.0 equiv.) and NaBArF$_{24}$ (275 mg, 0.31 mmol, 1.0 equiv.) were added to a flame-dried Schlenk tube under an argon atmosphere. The solids were then dissolved in anhydrous DCM (10 mL) and stirred for 30 min. The triphenylphosphine ligand (82 mg, 0.31 mmol, 1.0 equiv.) was then added slowly, initiating an orange to red colour change. After a further 30 min stirring, the reaction mixture was filtered through celite and concentrated *in vacuo*, resulting in a red oil. This residue was purified by column chromatography (50% DCM in petroleum ether) to afford the title compound as a red crystalline solid (365 mg, 0.21 mmol, 68 %). The isolated catalyst was dried in a vacuum oven (40 °C, 1 mbar) for 24 h before use. This process was repeated batch wise to obtain the quantities of **Ir-1** necessary for all competition studies.

m.p.: >150 °C (decomposition)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 – 7.69 (m, 8H, Ar- BArF$_{24}$), 7.51 (br, 4H, Ar-BArF$_{24}$), 7.45 – 7.39 (m, 3H, Ar-H), 7.31 – 7.24 (m, 8H, Ar-H and NCH=CHN), 7.15 – 7.07 (m, 6H, Ar-H), 7.02 (s, 2H, Ar-H), 6.66 (s, 2H, Ar-H), 4.39 – 4.32 (m, 2H, COD-CH), 3.38 – 3.31 (m, 2H, COD-CH), 2.34 (s, 6H, Ar-CH_3), 2.08 (s, 6H, Ar-CH_3), 1.75 (s, 6H, Ar-CH_3), 1.68 – 1.45 (m, 6H, COD-CH_2), 1.31 – 1.24 (m, 2H, COD-CH_2).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 178.1 (d, $^2J_{C–P}$ = 8.4 Hz), 161.9 (q, $^1J_{C–B}$ = 49.9 Hz), 140.2, 135.6, 135.2, 134.9, 134.8, 132.3, 132.2, 131.4, 131.3, 130.9, 130.6, 129.9, 129.5, 129.2, 128.9, 128.7, 128.6, 126.2, 124.7 (q, $^1J_{C–F}$ = 272 Hz), 117.6, 80.6, 80.5, 78.7, 31.9, 30.3, 30.2, 21.2, 20.9, 19.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ = - 6.64.

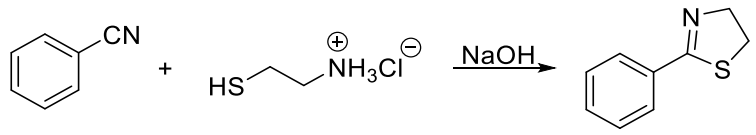
^{19}F NMR (376 MHz, $CDCl_3$) δ = - 62.4.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ = 16.4.

NMR data are consistent with the literature.[S8]

2.2. Synthesis of Substrates

2-Phenylthiazoline[S2]



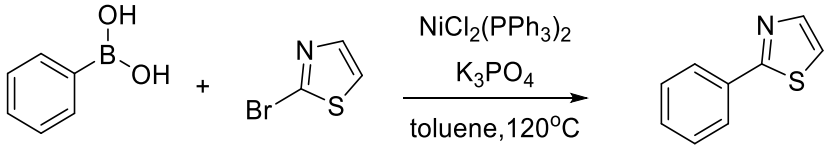
In air, a 10 mL round-bottom flask was charged with benzonitrile (0.50 g, 4.85 mmol), cysteamine hydrochloride (0.83 g, 7.28 mmol) and NaOH (40 mg, 0.97 mmol). The reaction was stirred at 80 °C for 2 hours under solvent-free conditions. The crude product was dissolved in ethyl acetate (2 mL) and water (10 mL) was added. The layers were separated and the aqueous layer was then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and dried under vacuum to give the title compound (0.76 g, 4.66 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 – 7.80 (m, 2H, Ar-H), 7.48 – 7.37 (m, 3H, Ar-H), 4.46 (t, *J* = 8.3 Hz, 2H, CH_2), 3.41 (t, *J* = 8.3 Hz, 2H, CH_2).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.0, 133.2, 131.4, 128.6, 128.5, 65.1, 33.7.

NMR data are consistent with the literature.[S2]

2-Phenylthiazole



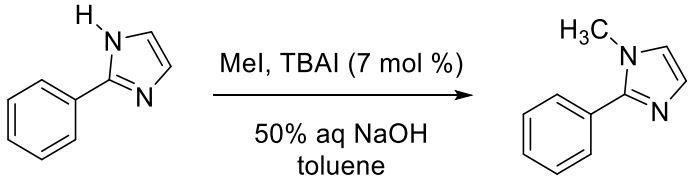
Phenylboronic acid (762 mg, 6.25 mmol, 1.25 equiv.), $[NiCl_2(PPh_3)_2]$ (262 mg, 0.40 mmol, 8 mol%), K_3PO_4 (1.59 g, 7.50 mmol, 1.5 equiv.) were added to a flame-dried two-necked round-bottom flask equipped with a stirrer bar and condenser. The system was evacuated for 5 minutes and filled with N_2, then dry toluene (10 mL) and 2-bromothiazole (820 mg, 5.0 mmol, 1 equiv.) were added. The reaction mixture was heated at reflux overnight (16 h) and was then cooled to room temperature before water (50 mL) and Et_2O (50 mL) were added. The aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was purified by column chromatography (10 % Et_2O in hexane) to afford the title compound as a yellow oil (163 mg, 1.01 mmol, 20 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.94 (m, 2H, Ar-H), 7.87 (d, *J* = 3.3 Hz, 1H, Ar-H), 7.48 – 7.41 (m, 3H, Ar-H), 7.33 (d, *J* = 3.3 Hz, 1H, CH).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.6, 143.8, 133.8, 130.1, 129.1, 126.7, 118.9.

NMR data are consistent with the literature.[S11]

1-Methyl-2-phenylimidazole[S3]



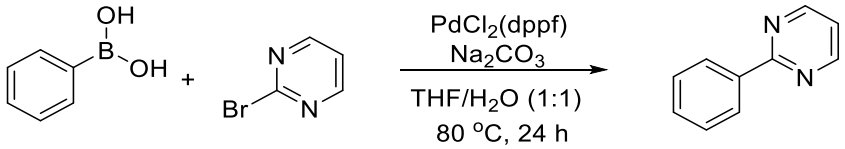
Methyl iodide (0.48 mL, 7.6 mmol) was added to the biphasic mixture obtained from 2-phenylimidazole (1.0 g, 6.9 mmol), tetra-*n*-butylammonium iodide (0.19 g, 0.51 mmol), 50% aqueous NaOH (30 mL) and toluene (30 mL). After stirring for 15 min at room temperature, the mixture was diluted with toluene (30 mL) and H_2O (30 mL). The organic phase was separated, dried ($MgSO_4$), and concentrated under reduced pressure to give pale yellow oil (1.03 g, 6.51 mmol, 97 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.60 (m, 2H, Ar-H), 7.48 – 7.37 (m, 3H, Ar-H), 7.12 (d, *J* = 1.2 Hz, 1H, CH), 6.97 (d, *J* = 1.2 Hz, 1H, CH), 3.19 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 147.9, 130.5, 128.8, 128.8, 128.7, 128.3, 122.5, 34.6.

NMR data are consistent with the literature. [S12]

2-Phenylpyrimidine



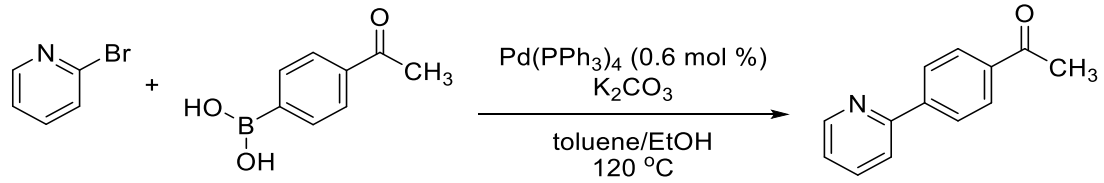
A flame dried 50 mL round-bottom flask was charged with [$PdCl_2$(dppf)] (40 mg, 0.05 mmol), phenylboronic acid (611 mg, 5.0 mmol), Na_2CO_3 (1.23 g, 12.0 mmol) and suspended in premixed 1:1 solution of THF/H_2O (60 mL). Subsequently, 2-bromopyrimidine (646 mg, 4.0 mmol) was added and the reaction mixture was stirred at 80 °C overnight (16 h), and then cooled to room temperature. H_2O (30 mL) was added to the reaction mixture. The aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was purified by column chromatography (20 % Et_2O in hexane) to afford the title compound as a yellow oil (331 mg, 2.12 mmol, 53 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 4.9 Hz, 2H, Ar-H), 8.49 – 8.42 (m, 2H, Ar-H), 7.52 – 7.47 (m, 3H, Ar-H), 7.18 (t, *J* = 4.8 Hz, 1H, Ar-H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 164.9, 157.4, 137.7, 130.9, 128.7, 128.3, 119.2.

NMR data are consistent with the literature.[S11]

2-(4-Acetyl)phenylpyridine



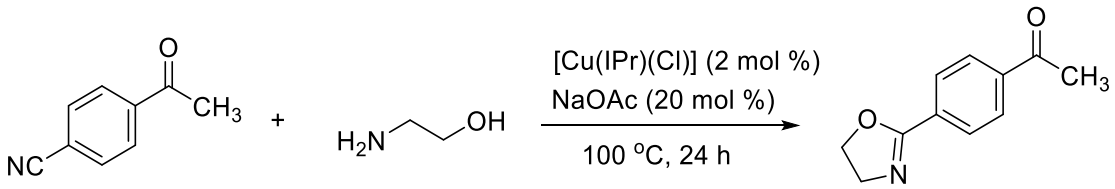
A flame dried 50mL round-bottom flask was charged with [$Pd(PPh_3)_4$] (21 mg, 0.018 mmol), 4-acetylphenylboronic acid (738 mg, 4.50 mmol), potassium carbonate (1.21 g, 9.0 mmol). The solids were suspended in premixed toluene/ethanol (3:2) (30 mL). Subsequently, 2-bromopyridine (0.28 mL, 3.0 mmol) was added and the reaction mixture was stirred for 24 h at 120 °C before being allowed to cool to room temperature. Water (100 mL) was added, the layers were separated, and the aqueous layer was extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and then the solvent was removed under vacuum yielding the crude yellow solid. The crude product was dissolved in DCM (5 mL) and passed through a short pad of silica which was then washed with further DCM. The solvent was evaporated, and the residue was crystallised from a DCM/pentane mixture to afford the product as a white solid (517 mg, 2.62 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 – 8.71 (m, 1H, Ar-H), 8.13 – 8.09 (m, 2H, Ar-H), 8.09 – 8.04 (m, 2H, Ar-H), 7.82 – 7.78 (m, 2H, Ar-H), 7.33 – 7.27 (m, 1H, Ar-H), 2.65 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 198.0, 150.1, 137.1, 129.0, 127.2, 123.1, 121.2, 26.9.

NMR data are consistent with the literature.[S13]

2-(4-Acetyl)phenyloxazoline[S5]



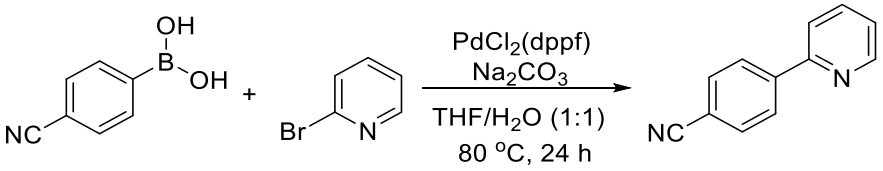
A flame dried vial was charged with [Cu(IPr)(Cl)] (10 mg, 0.02 mmol), 4-acetylbenzonitrile (145 mg,1.0 mmol) and NaOAc (16 mg, 0.2 mmol), and evacuated and backfilled with N_2. Ethanolamine (0.24 mL, 4.0 mmol) was added and the reaction was stirred at 100 °C for 16 h under solvent-free conditions. The reaction mixture was cooled to room temperature, dissolved in DCM and passed through a short pad of silica with DCM as the eluent. The solvent was removed under vacuum yielding a pale yellow solid (60 mg, 0.32 mmol, 32 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 7.97 (m, 4H, Ar-H), 4.47 (t, *J* = 9.6, 2H, CH_2), 4.10 (t, *J* = 9.6, 2H, CH_2), 2.63 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 197.7, 139.1, 132.0, 128.5, 128.4, 68.0, 55.3, 26.9.

NMR data are consistent with the literature.[S14]

2-(4-Cyano)phenylpyridine



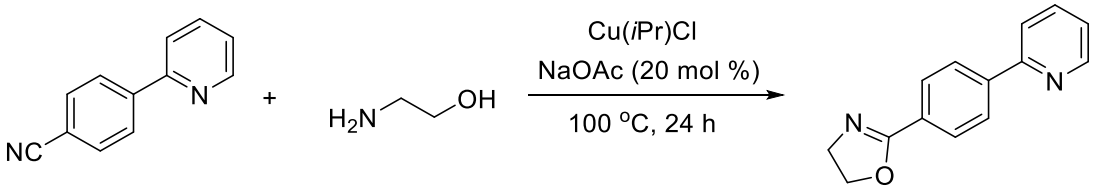
A flame dried 50 mL round-bottom flask was charged with [$PdCl_2$(dppf)] (31 mg, 0.03 mmol), 4-cyanophenylboronic acid (856 mg, 5.83 mmol), Na_2CO_3 (1.30 g, 12.0 mmol). The solids were suspended in premixed THF/H_2O (1:1) (40 mL). Subsequently, 2-bromopyridine (0.38 mL, 4.0 mmol) was added, the reaction mixture was stirred at 80 °C for 16 h and then cooled to room temperature. H_2O (30 mL) was added to the reaction mixture, the layers were separated, and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic solution was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by recrystallisation from a DCM/pentane mixture to afford the title compound as yellow solid (554 mg, 3.07 mmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.75 – 8.67 (m, 1H), 8.12 – 8.07 (m, 2H), 7.82 – 7.72 (m, 4H), 7.33 – 7.27 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 155.2, 150.1, 143.5, 137.2, 132.6, 127.5, 123.4, 121.1, 118.9, 112.5.

NMR data are consistent with the literature.[S15]

2-(4-(Pyridin-2-yl)phenyl)-4,5-dihydrooxazole [S4]



A flame dried vial was charged with [Cu(Cl)(IPr)] (135 mg, 0.27 mmol), 2-(4-cyano)phenylpyridine (500 mg, 2.77 mmol) and NaOAc (114 mg, 1.39 mmol), and evacuated and backfilled with N_2. Ethanolamine (0.34 mL, 4.0 mmol) was added and the reaction was stirred at 100 °C for 16 h under solvent-free conditions. The reaction mixture was cooled to room temperature, dissolved in DCM and transferred to a separating funnel containing brine (200 mL). The product was extracted with DCM (2 × 50 mL) and dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was purified by column chromatography (70 % EtOAc in hexane) to afford the title compound as pale pink solid (248 mg, 1.10 mmol, 40 %).

m.p.: 120-125 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 – 8.68 (m, 1H), 8.11 – 8.01 (m, 4H, Ar-H), 7.81 – 7.74 (m, 2H), 7.30 – 7.23 (m, 1H), 4.46 (t, *J* = 9.5, 2H, CH_2), 4.09 (t, *J* = 9.5, 2H, CH_2).

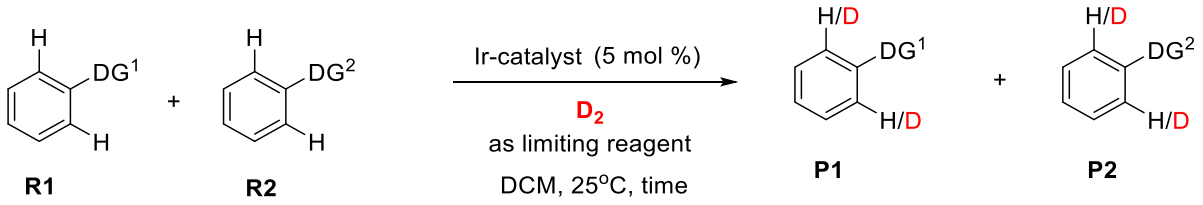
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ = 164.5, 156.5, 149.9, 142.0, 136.9, 128.7, 128.2, 126.9, 122.7, 120.9, 67.7, 55.1.

Anal. Calculated for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.28; H, 5.35; N, 12.34.

FTIR (neat): 3286, 3047, 2970, 2931, 2990, 2877, 1642, 1572, 1465, 1256, 1071, 1016, 940, 862, 785,731, 699, 615 cm^{-1}.

3. Intermolecular Competition Experiments

3.1. General Information



Reaction conditions

The relative rates of hydrogen-deuterium exchange reactions have been determined by competition experiments, where equimolar quantities of each of the two substrates bearing different DGs and catalytic amounts of iridium complexes were treated with a limiting amount of D_2 in DCM at 25°C. As a limiting amount of D_2 gas should be used to avoid full conversion of the substrates, its volume was controlled by adding the required amount of solvent.

The volume of 0.10 mmol of the D_2 gas can be calculated according to the ideal gas law (eq. S-1).

$$PV = nRT \qquad \text{(S-1)}$$

$n_{(max)} = 0.10$ mmol

$T = 298$ K (25 °C)

$R = 0.0821$ L·atm·K^{-1}·mol^{-1}

$P = 1$ atm

$V_{(max)} = nRT/P = 0.10 \times 0.0821 \times 298 / 1 = 2.45$ mL

As the volume of J. Young Schlenk flasks (Figure S2) used for the competition experiments is approximately 8 mL, the use of 6.0 mL of the solvent will lead to less than 1 equivalent of deuterium gas. None of the substrates in the study undergo complete deuteration under these conditions, which are quite different for those used in most HIE experiments where complete deuteration at one site is desired.

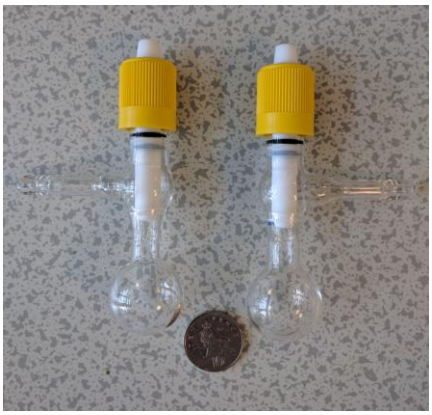


Figure S2. The J. Young Schlenk flasks used for competition experiments.

General Procedure (GP1)

The two substrates of interest (0.10 mmol each) were added to one J. Young Schlenk flask, along with the catalyst of choice (0.005 mmol, unless otherwise noted) in air. DCM (6 mL) was added in such a way to rinse the inner walls of the flask. The flask was then sealed (with the gas inlet left open) under air before being cooled in a dry ice–acetone bath. The flask was evacuated and flushed with deuterium three times *via* a balloon. The gas inlet was then closed with fast thread tap, creating a sealed atmosphere of deuterium. After sealing the flask, it was placed in the thermostated water bath, and the reaction timer was started. The reaction mixture was stirred at 25 °C (1 h for catalyst **Ir-1** and 16 h for catalyst **Ir-2**) before the removal of the excess deuterium and the opening of the flask to air. The reaction mixture was quenched with few drops of MeCN and transferred to a single necked flask together with washings (DCM) before removing the solvent under reduced pressure. For N<u>H</u>-containing substrates (benzamide, benzenesulfonamide, acetanilide, phenylimidazol(in)e) the residue was directly analysed by ^{1}H NMR. For other substrates, the residue was dissolved in a small portion of 1:1 mixture of petroleum ether and diethyl ether (or EtOAc) and passed through a short plug of silica, eluting with a 1:1 mixture of petroleum ether and diethyl ether (or EtOAc) (3 × 2 mL). The solvent was evaporated again under reduced pressure and the residue was analysed by ^{1}H NMR.

NMR spectrometer parameters are as follows: the relaxation delay was set to 20 s and the number of scans to four or higher when needed. After careful phasing and baseline correction, the integration of the signals was carried out manually.

Determination of Competition Rate Constants

The level of deuterium incorporation in the substrates was determined from the obtained ^{1}H NMR spectra (eq. S-2). The integrals were calibrated against a peak corresponding to a position which does not undergo labelling. In addition, the calibration signal was chosen to have as little overlap as possible with other peaks.

$$\%D = 100 - \left(\frac{\text{residual integral}}{\text{number of labelling sites}} \times 100\ \% \right) \tag{S-2}$$

Based on the ratio between the initial and remaining concentrations of non-deuterated substrates **R**, the competition constants κ were determined (eq. S-3).

$$\kappa = \frac{k_1}{k_2} = \frac{\log\left([\mathbf{R1}]_0 / [\mathbf{R1}]_t \right)}{\log\left([\mathbf{R2}]_0 / [\mathbf{R2}]_t \right)} \tag{S-3}$$

Initial concentrations of the substrates are defined by mass balance (eq. S-4).

$$[\mathbf{R}]_0 = [\mathbf{R}]_t + [\mathbf{P}]_t \tag{S-4}$$

The relative concentrations $[\mathbf{R}]_0$ and $[\mathbf{R}]_t$ were derived using equation (S-5) from the residual integral $I_{R(t)}$ of the peak corresponding to H/D positions, and the integral $I_{R(0)}$ of the peak used for calibration, which corresponds to both remaining starting material and deuterated product.

$$\frac{[\mathbf{R}]_0}{[\mathbf{R}]_t} = \frac{I_{R\,(0)} / N}{I_{R\,(t)} / N} \tag{S-5}$$

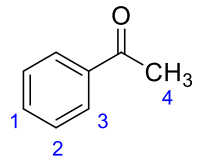
where N is the number of protons contributing to the corresponding peak.

Each combination was analysed three times, and the competition constants are the average of all runs. Standard error of the mean was determined for each averaged competition constant and are summarised in Tables S42-43).

The tables given below for each competition experiment (Table S1 to Table S41) summarize the amounts of the reagents used, integrals from the NMR spectra (Figures S3-S175) used to calculate the relative concentrations of substrates and the values of the competition constants κ.

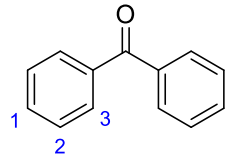
Spectral details for unlabelled substrates used in intermolecular competition studies

Acetophenone



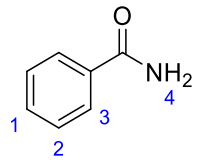
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.93 (m, 2H, H-3), 7.60 – 7.53 (m, 1H, H-1), 7.51 – 7.42 (m, 2H, H-2), 2.61 (s, 3H, H-4).
Incorporation expected at δ 7.99 – 7.93 ppm (H-3)
Determined against integral at δ 2.61 ppm (H-4)
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.98 – 7.94 (m, 2H, H-1), 7.67 – 7.61 (m, 1H, H-3), 7.55 – 7.50 (m, 2H, H-2), 2.58 (s, 3H, H-4).
Incorporation expected at δ 7.98 – 7.96 ppm (H-3)
Determined against integral at δ 2.58 ppm (H-4)

Benzophenone



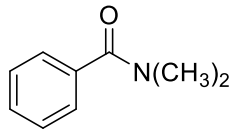
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.78 (m, 4H, H-3), 7.63 – 7.53 (m, 2H, H-1), 7.52 – 7.45 (m, 4H, H-2).
Incorporation expected at δ 7.84 – 7.78 ppm (H-3)
Determined against integral at δ 7.63 – 7.53 ppm (H-1)

Benzamide



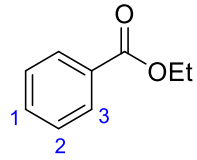
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.77 (m, 2H, H-3), 7.57 – 7.48 (m, 1H, H-1), 7.48 – 7.39 (m, 2H, H-2), 6.24 (bs, 2H, H-4)
Incorporation expected at δ 7.86 – 7.77 ppm (H-3)
Determined against integral at δ 7.48 – 7.39 ppm (H-2)
^{1}H NMR (400 MHz, DMSO- d_6) δ = 7.96 (bs, 1H, H-4), 7.90 – 7.85 (m, 2H, H-3), 7.54 – 7.48 (m, 1H, H-1), 7.48 – 7.41 (m, 2H, H-2), 7.35 (s, 1H, H-4)
Incorporation expected at δ 7.90 – 7.85 ppm (H-3)
Determined against integral at δ 7.48 – 7.41 ppm (H-2)

***N*,*N*-Dimethylbenzamide**



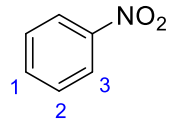
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.36 (m, 5H, Ar-H), 3.17 – 2.88 (m, 6H, 2 × CH_3).
Incorporation expected at δ 7.43 – 7.36 ppm
Determined against integral at δ 3.17 – 2.88 ppm

Ethylbenzoate



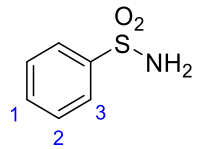
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 8.02 (m, 2H, H-3), 7.58 – 7.52 (m, 1H, H-1), 7.47 – 7.40 (m, 2H, H-2), 4.38 (q, *J* = 7.1 Hz, 2H, CH_2), 1.40 (t, *J* = 7.1 Hz, 3H, CH_3).
Incorporation expected at δ 8.07 – 8.03 ppm (H-3)
Determined against integral at δ 4.38 ppm (OC*H*$_2$CH$_3$)

Nitrobenzene



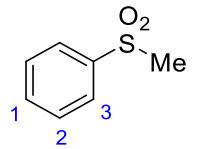
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 – 8.20 (m, 2H, H-3), 7.73 – 7.66 (m, 1H, H-1), 7.58 – 7.51 (m, 2H, H-2).
Incorporation expected at δ 8.26 – 8.20 ppm (H-3)
Determined against integral at δ 7.73 – 7.66 ppm (H-1)
^{1}H NMR (400 MHz, DMSO- d_6) δ = 8.30 – 8.16 (m, 2H, H-3), 7.90 – 7.79 (m, 1H, H-1), 7.73 – 7.61 (m, 2H, H-2).
Incorporation expected at δ 8.30 – 8.16 ppm (H-3)
Determined against integral at δ 7.73 – 7.61 ppm (H-2)

Benzenesulfonamide



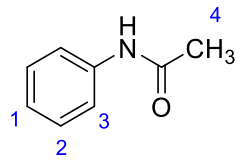
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.87 – 7.80 (m, 2H, H-3), 7.64 – 7.54 (m, 3H, H-1 and H-2), 7.36 (bs, 2H, NH_2)
Incorporation expected at δ 7.87 – 7.80 ppm (H-3)
Determined against integral at δ 7.64 – 7.54 ppm (H-1+H-2)

(Methylsulfonyl)benzene



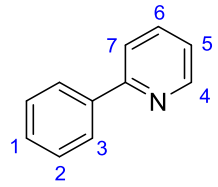
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.95 – 7.92 (m, 2H, H-3), 7.76 –7.72 (m, 1H, H-1), 7.68 – 7.64 (m, 2H, H-2), 3.21 (s, 3H, H-4).
Incorporation expected at δ 7.95 – 7.92 ppm (H-3)
Determined against integral at δ 7.68 – 7.64 ppm (H-2)

Acetanilide



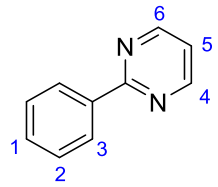
^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.90 (bs, 1H, NH), 7.60 – 7.55 (m, 2H, H-3), 7.30 – 7.24 (m, 2H, H-2), 7.04 – 6.99 (m, 1H, H-1), 2.04 (s, 3H, H-4).
Incorporation expected at δ 7.60 – 7.55 ppm (H-3)
Determined against integral at δ 2.04 ppm (H-4)

2-phenylpyridine



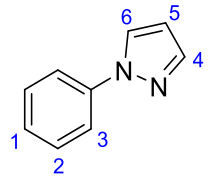
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 – 8.67 (m, 1H, H-4), 8.02 – 7.98 (m, 2H, H-3), 7.78 – 7.70 (m, 2H, H-6 and H-7), 7.51 – 7.45 (m, 2H, H-2), 7.45 – 7.39 (m, 1H, H-1), 7.25 – 7.21 (m, 1H, H-5).
Incorporation expected at δ 8.02 – 7.98 ppm (H-3)
Determined against integral at δ 8.73 – 8.67 ppm (H-4) or at δ 7.78 – 7.70 (H-6+H-7) depending on the competition partner.
^{1}H NMR (400 MHz, DMSO- d_6) δ = 8.69 – 8.65 (m, 1H, H-4), 8.11 – 8.06 (m, 2H, H-3), 7.97 – 7.93 (m, 1H, H-7), 7.90 – 7.84 (m, 1H, H-6), 7.52 – 7.46 (m, 2H, H-2), 7.46 – 7.41 (m, 1H, H-1), 7.38 – 7.32 (m, 1H, H-5).
Incorporation expected at δ 8.11 – 8.06 ppm (H-3)
Determined against integral at δ 7.90 – 7.84 ppm (H-6)

2-Phenylpyrimidine



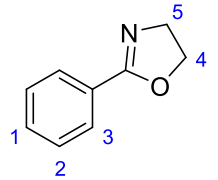
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 4.9 Hz, 2H, H-4), 8.48 – 8.43 (m, 2H, H-3), 7.52 – 7.48 (m, 3H, H-1 and H-2), 7.18 (t, *J* = 4.9 Hz, 1H, H-5)
Incorporation expected at δ 8.48 – 8.43 ppm (H-3)
Determined against integral at δ 7.18 ppm (H-5)

1-phenylpyrazole



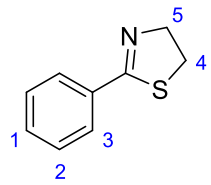
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 2.2 Hz, 1H, H-6), 7.75 – 7.68 (m, 3H, H-3 and H-4), 7.48 – 7.43 (m, 2H, H-2), 7.32 – 7.26 (m, 1H, H-1), 6.49 – 6.45 (m, 1H, H-5).
Incorporation expected at δ 7.75 – 7.68 ppm (H-3)
Determined against integral at δ 7.92 ppm (H-6)

2-phenyloxozoline



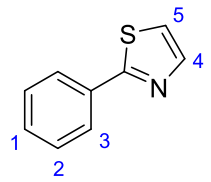
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 – 7.93 (m, 2H, H-3), 7.50 – 7.44 (m, 1H, H-1), 7.43 – 7.37 (m, 2H, H-2), 4.43 (t, *J* = 9.5 Hz, 2H, H-4), 4.06 (t, *J* = 9.5 Hz, 2H, H-5).
Incorporation expected at δ 7.97 – 7.93 ppm (H-3)
Determined against integral at δ 4.43 ppm (H-4)

2-phenylthiazoline



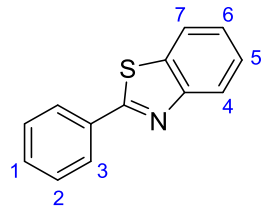
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 – 7.81 (m, 2H, H-3), 7.48 – 7.37 (m, 3H, H-1 and H-2), 4.46 (t, *J* = 8.3 Hz, 2H, H-4), 3.41 (t, *J* = 8.3 Hz, 2H, H-5).
Incorporation expected at δ 7.86 – 7.81 ppm (H-3)
Determined against integral at δ 4.46 ppm (H-4)

2-phenylthiazole



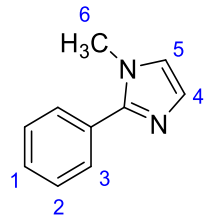
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.94 (m, 2H, H-3), 7.87 (d, *J* = 3.3 Hz, 2H, H-4), 7.48 – 7.42 (m, 3H, H-2 and H-1), 7.33 (d, *J* = 3.3 Hz, 2H, H-5).
Incorporation expected at δ 8.00 – 7.94 ppm (H-3)
Determined against integral at δ 7.87 or 7.33 ppm (H-4 or H-5)

2-phenylbenzothiazole



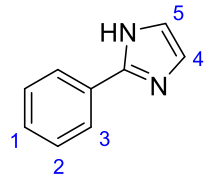
^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.14 – 8.06 (m, 3H, H-3 and H-4), 7.91 (d, *J* = 8.0 Hz, 1H, H-7), 7.53 – 7.48 (m, 4H, H-2 and H-5), 7.41-7.37 (m, 1H, H-6).
Incorporation expected at δ 8.14 – 8.06 ppm (H-3)
Incorporation determined against δ 7.91 ppm (H-7)

1-methyl-2-phenylimidazole



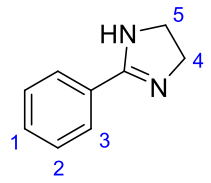
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.60 (m, 2H, H-3), 7.47 – 7.34 (m, 3H, H-1 and H-2), 7.12 (d, *J* = 1.2 Hz, 1H, H-5), 6.97 (d, *J* = 1.2 Hz, 1H, H-4), 3.19 (s, 3H, H-6).
Incorporation expected at δ 7.65 – 7.60 ppm (H-3)
Incorporation determined against δ 7.12 ppm (H-5)

2-phenylimidazole



^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.49 (bs, 1H, NH), 7.98 – 7.92 (m, 2H, H-3), 7.48 – 7.39 (2H, H-2), 7.36 – 7.29 (m, 1H, H-1), 7.13 (s, 2H, H-4 and H-5).
Incorporation expected at δ 7.98 – 7.92 ppm (H-3)
Incorporation determined against δ 7.13 ppm (H-4+H-5)

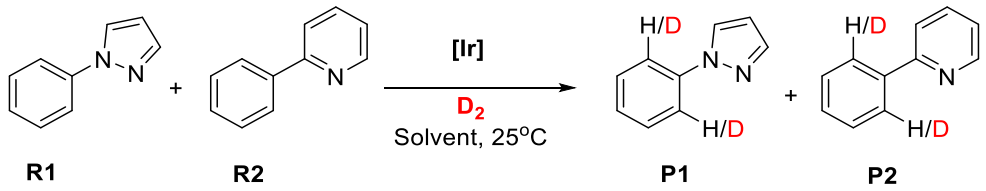
2-phenylimidazole



^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.86 – 7.80 (m, 2H, H-3), 7.49 – 7.36 (m, 3H, H-1 and H-2), 3.60 (s, 4H, H-4 and H-5).
Incorporation expected at δ 7.86 – 7.80 ppm (H-3)
Incorporation determined against δ 3.60 ppm (H-4+H-5)

3.2. Effects of the Reaction Conditions on Competition Rate Constants

The competition labelling of 2-phenylpyridine and 1-phenylpyrazole was chosen as a model reaction to test the influence of catalyst loading, reaction times and solvent on the competition rate constants κ.



Mass of reagents: 1-Phenylpyrazole (14.4 mg, 0.1 mmol); 2-Phenylpyridine (15.5 mg, 0.1 mmol); for catalyst **Ir-2** (2.1 mg for 2.5 mol %, 4.3 mg, 5 mol. %, 6.4 mg for 7.5 mol %, 8.6 mg for 10 mol %); for catalyst **Ir-1** (8.7 mg, 5 mol %); Volume (solvent) = 6.0 mL
Deuteration expected at δ (**R1**) = 7.78 – 7.67 ppm and at δ (**R2**) = 8.04 – 7.97 ppm
Determined against integral at δ 6.50 – 6.42 for **R1** and at δ 8.72 – 8.68 for **R2**
Spectral details of the reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72 – 8.68 (m, 1H, **R2**), 8.04 – 7.97 (m, 2H/D **R2**), 7.92 (d, *J* = 2.4 Hz, 1H, **R1**), 7.78 – 7.67 (m, 2H, **R2**, 1H, **R1**, 2H/D **R1**), 7.52 – 7.38 (3H, **R2** and 2H, **R1**), 7.31 – 7.26 (m, 1H, **R1**), 7.24 – 7.20 (m, 1H, **R2**), 6.50 – 6.42 (m, 1H, **R1**)

Catalyst loading

Competition experiments between 2-phenylpyridine and 1-phenylpyrazole with different loadings of the catalyst **Ir-2** (2.5 to 10 mol %) were performed in DCM (6.0 mL) following General Procedure GP1 for intermolecular competition experiments (time (t) = 16 h).

Table S1. Competition labelling of 1-phenylpyrazole and 2-phenylpyridine using different loadings of catalyst **Ir-2**.

Entry	catalyst loading (mol %)	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	2.5	1.40 [a]	1.00	30	1.32	0.86	23	1.35
2	5.0	1.29 [b]	1.00	36	1.22	0.85	28	1.32
3	7.5	1.48 [c]	1.00	26	1.43	0.94	24	1.10
4	10	1.17 [d]	1.00	42	1.09	0.91	40	1.05

[a] $I_{R1(t)} = 4.12–1.00–(0.86×2)$; [b] $I_{R1(t)} = 3.99−1.00−(0.85×2)$;

[c] $I_{R1(t)} = 4.36−1.00−(0.94×2)$; [d] $I_{R1(t)} = 3.99−1.00−(0.91×2)$

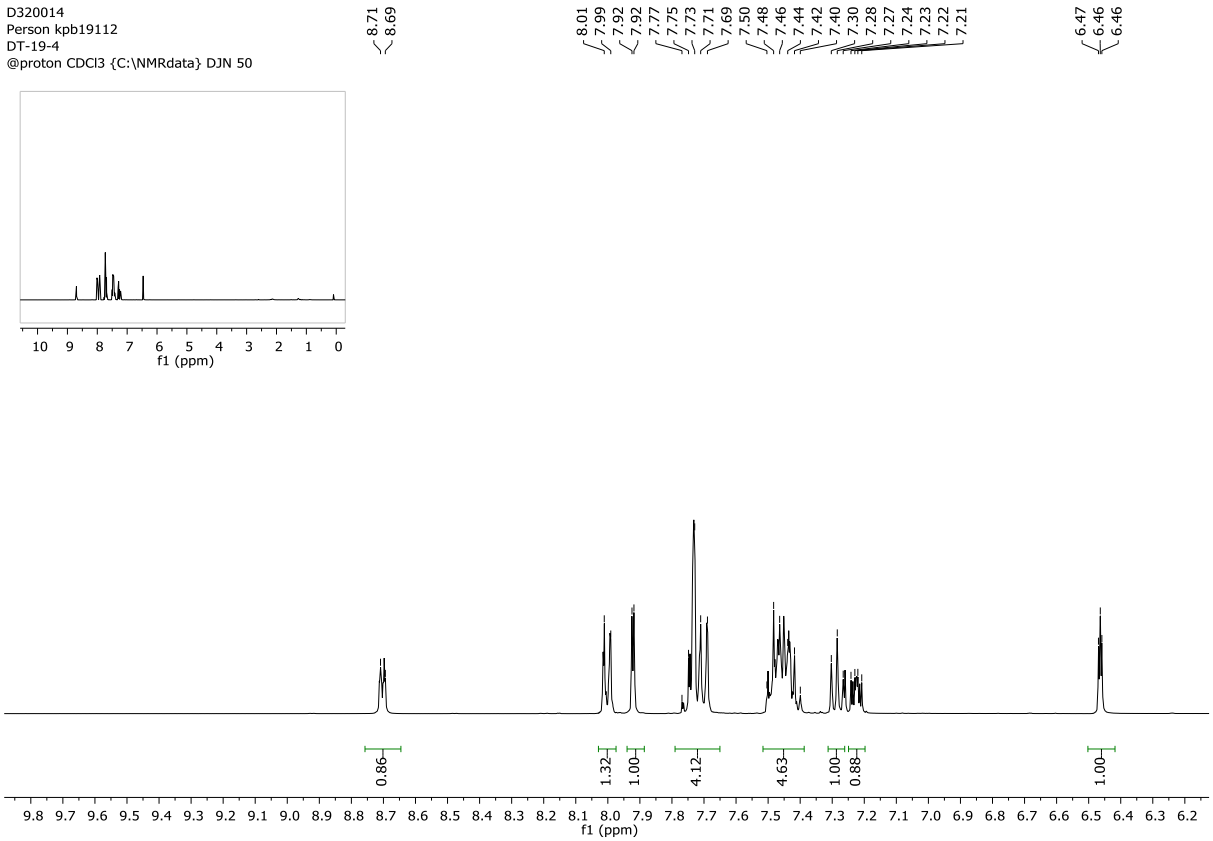


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 1, Table S1)

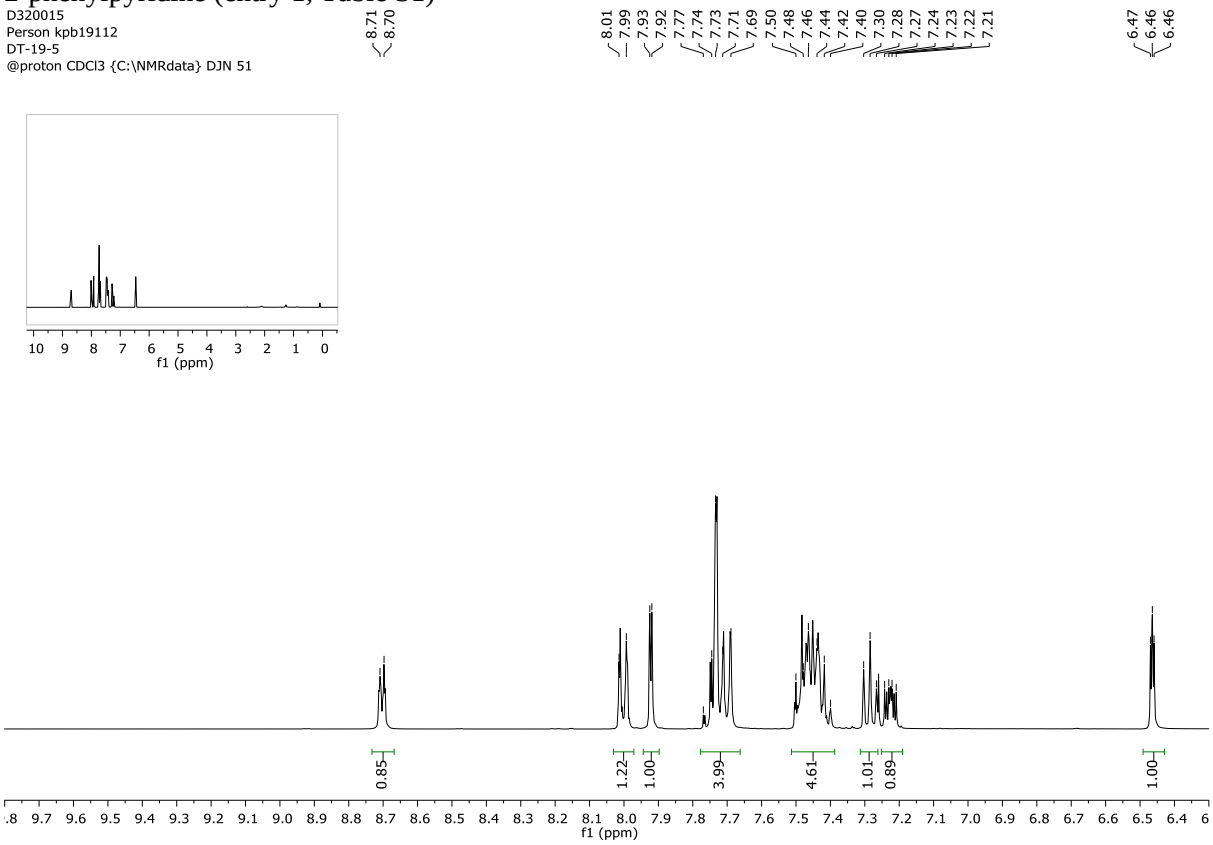


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 2, Table S1)

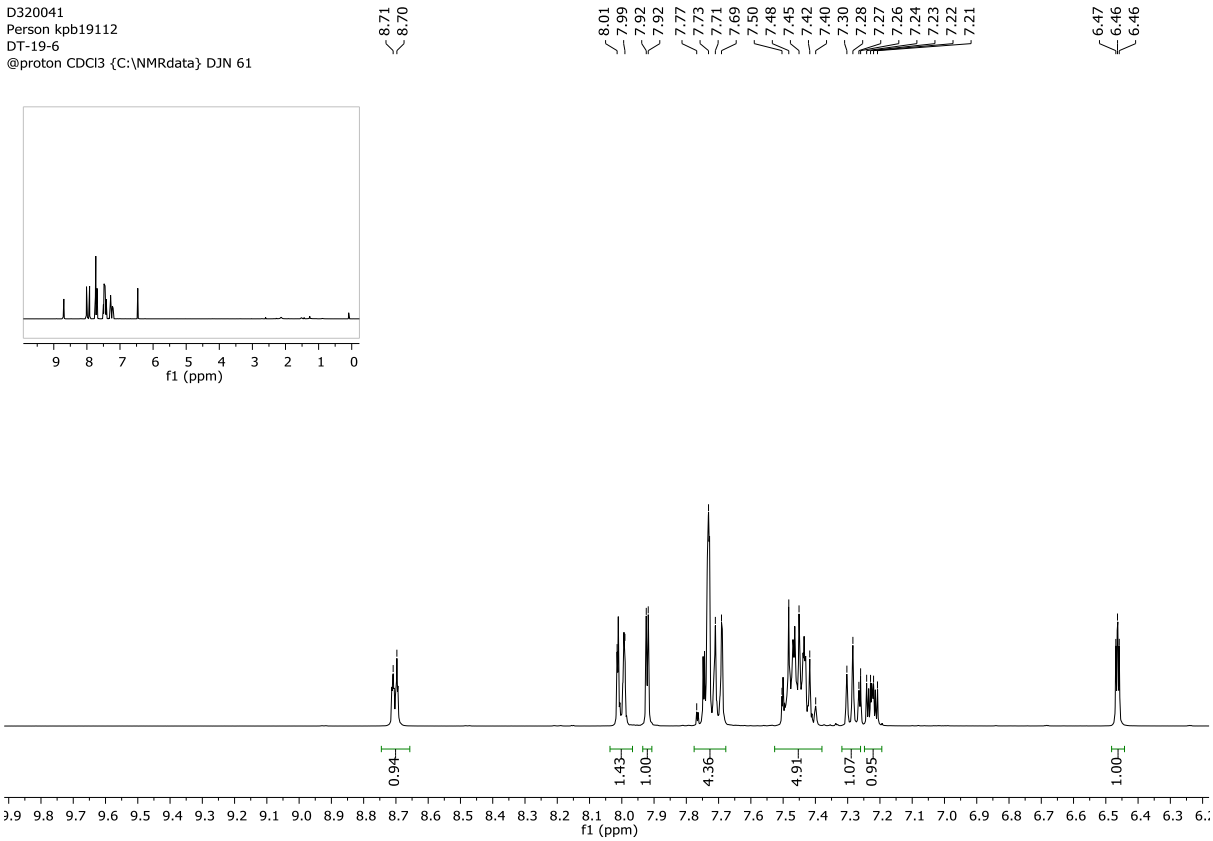


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 3, Table S1)

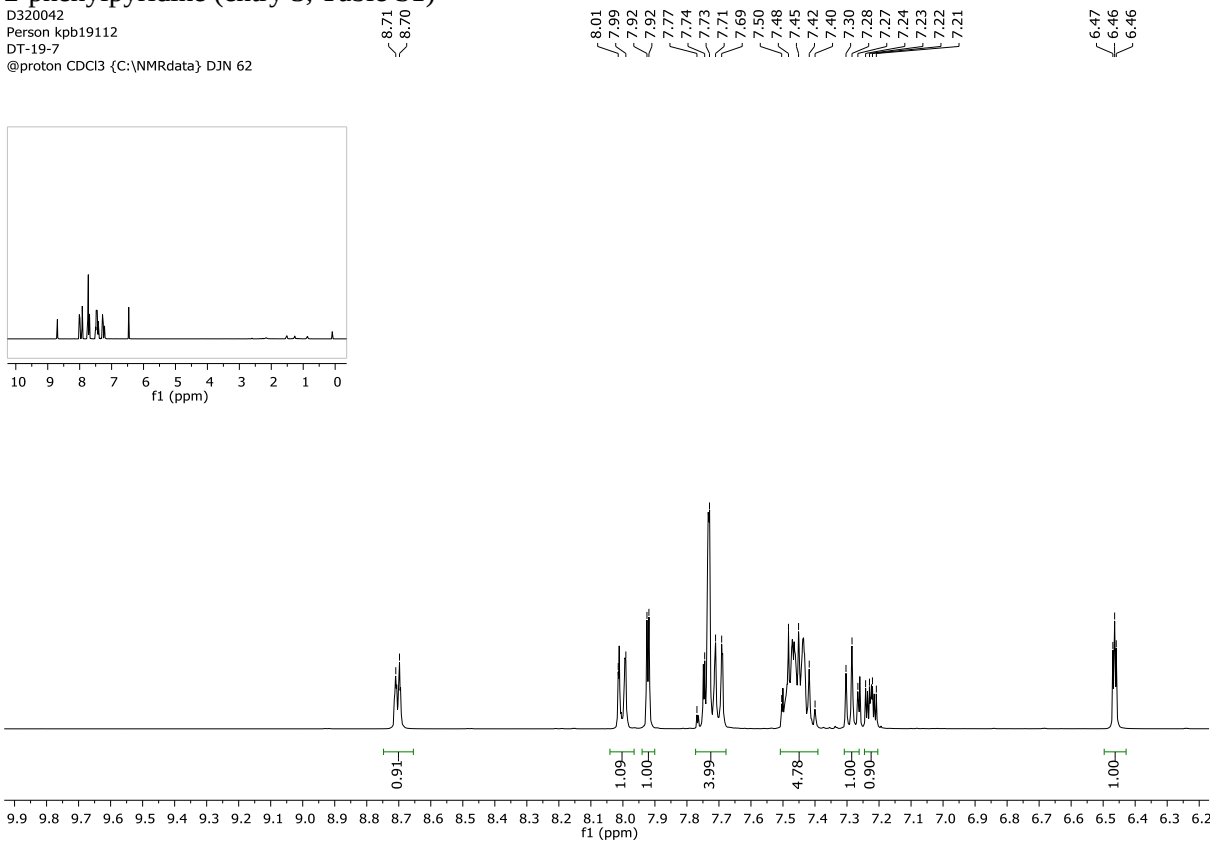


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 4, Table S1)

Time-dependence

Competition experiments between 1-phenylpyrazole and 2-phenylpyridine with the catalyst **Ir-2** (5 mol %) were performed in DCM (6.0 mL) over different time periods following the General Procedure GP1 for intermolecular competition experiments.

Table S2. Competition labelling of 1-phenylpyrazole and 2-phenylpyridine using catalyst **Ir-2** over different time periods.

Entry	reaction time	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	1h	1.92[a]	1.00	4	1.55	0.80	3	1.29
2	2h	1.89[b]	1.00	6	1.75	0.91	4	1.44
3	16h	1.65[c]	1.00	18	1.75	1.00	13	1.44

[a] $I_{R1(t)} = 4.52–1.00–(0.80\times2)$; [b] $I_{R1(t)} = 4.71-1.00-(0.91\times2)$; [c] $I_{R1(t)} = 4.65-1.00-(1.00\times2)$;

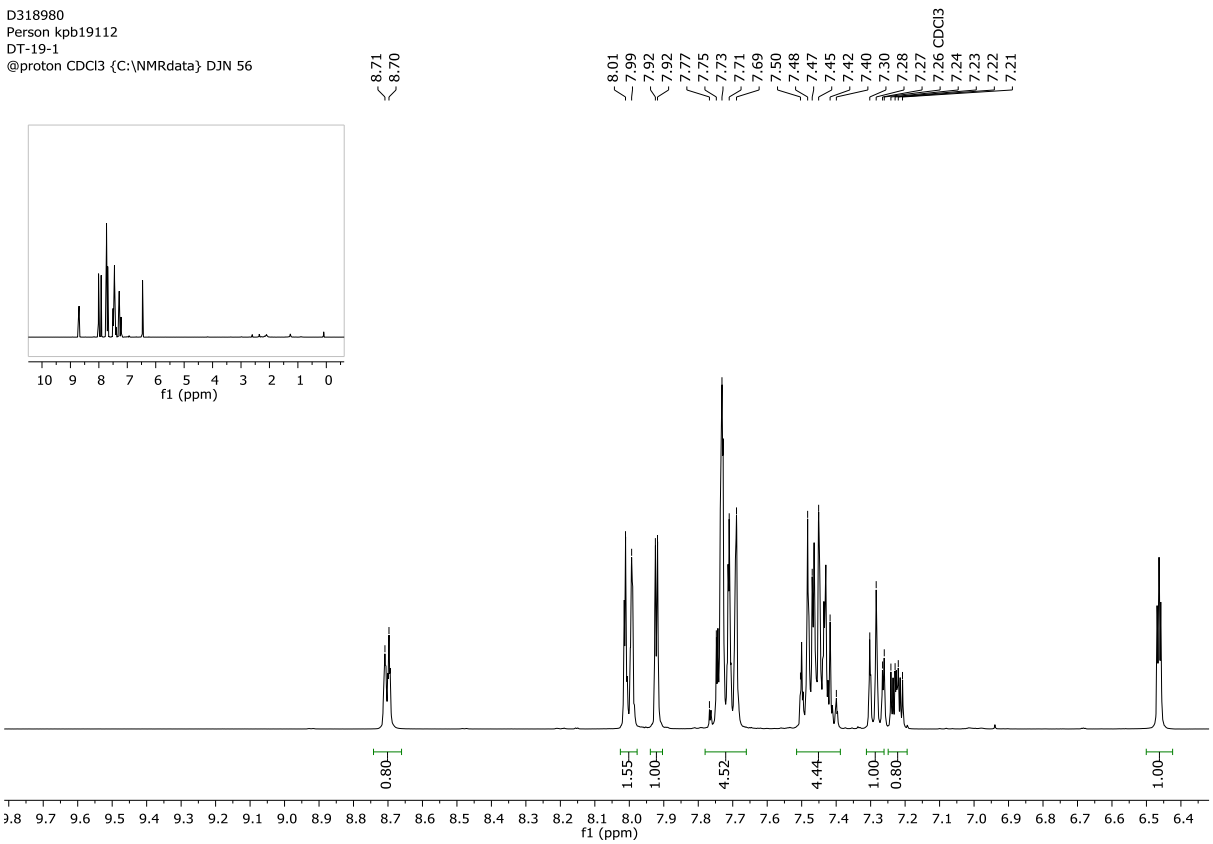


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 1, Table S2)

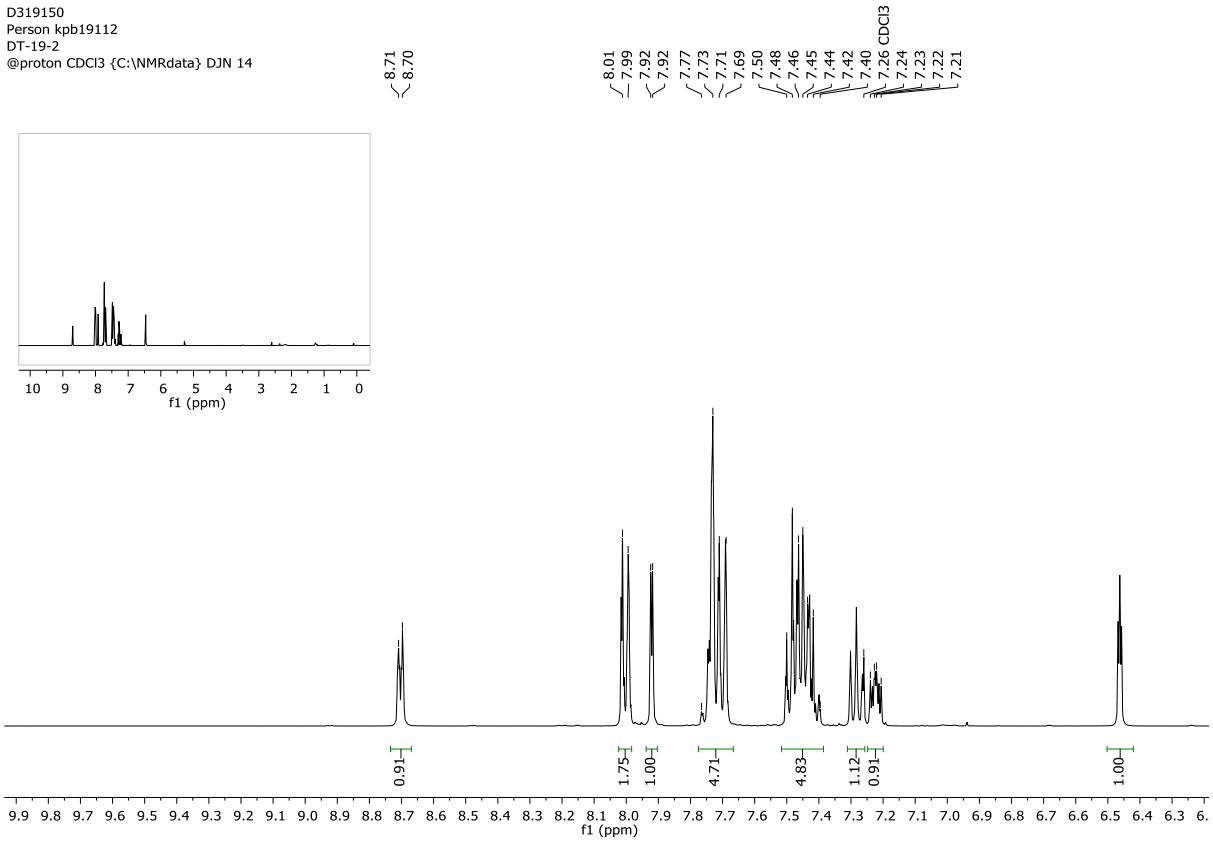


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 2, Table S2)

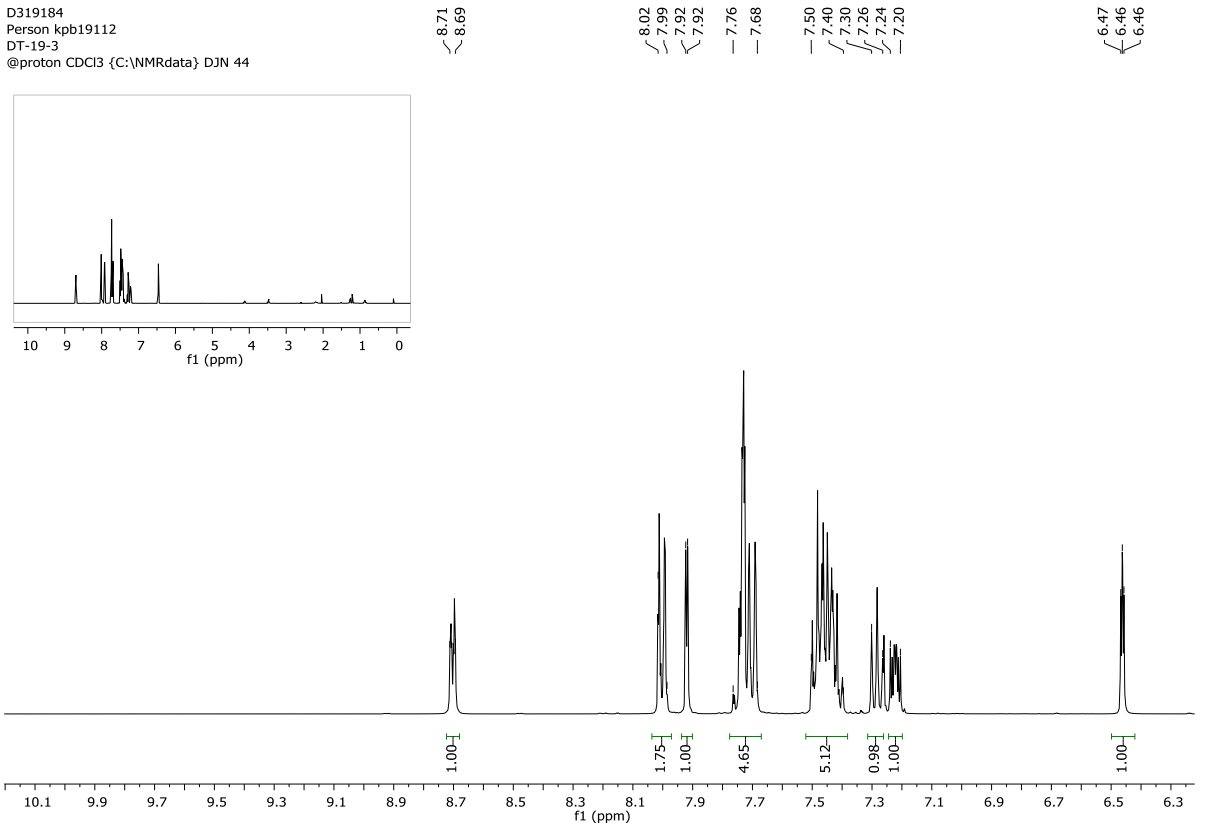


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 3, Table S2)

Solvent effects

Competition experiments between 1-phenylpyrazole and 2-phenylpyridine with the catalyst **Ir-1** (5 mol %) were performed in various solvents (6.0 mL) following the General Procedure GP1 for intermolecular competition experiments (time (t) = 1 h).

Table S3. Competition labelling of 1-phenylpyrazole and 2-phenylpyridine using catalyst **Ir-1** in different solvents.

Solvent	Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
DCM	1	1.26[a]	1.00	37	1.74	1.18	26	1.49
	2	0.90[b]	1.00	55	1.38	1.07	36	1.78
	3	0.92[c]	1.00	54	1.40	1.08	35	1.84
								Average κ = 1.71
[a] $I_{R1(t)}$ = 4.62–1.00–(1.18×2); [b] $I_{R1(t)}$ =4.04−1.00−(1.07×2); [c] $I_{R1(t)}$ = 4.08−1.00−(1.08×2);								
THF	1	1.15[a]	1.00	43	1.32	1.01	35	1.30
	2	1.22[b]	1.00	39	1.36	1.00	32	1.28
	3	0.95[c]	1.00	53	1.13	0.96	41	1.40
								Average κ = 1.33
[a] $I_{R1(t)}$ = 4.17–1.00–(1.01×2); [b] $I_{R1(t)}$ =4.22−1.00−(1.00×2); [c] $I_{R1(t)}$ = 3.87−1.00−(0.96×2);								
Et_2O	1	1.17[a]	1.00	42	1.39	1.05	34	1.30
	2	0.73[b]	1.00	64	0.91	0.97	53	1.33
	3	0.78[c]	1.00	61	1.03	0.96	46	1.51
								Average κ = 1.38
[a] $I_{R1(t)}$ = 4.27–1.00–(1.05×2); [b] $I_{R1(t)}$ = 3.67−1.00−(0.97×2); [c] $I_{R1(t)}$ = 3.66−1.00−(0.96×2);								
Toluene	1	0.98[a]	1.00	51	1.45	1.09	33	1.75
	2	0.98[b]	1.00	51	1.42	1.06	33	1.78
	3	1.11[c]	1.00	45	1.39	0.98	29	1.71
								Average κ = 1.75
[a] $I_{R1(t)}$ = 4.16–1.00–(1.09×2); [b] $I_{R1(t)}$ = 4.10−1.00−(1.06×2); [c] $I_{R1(t)}$ = 4.07−1.00−(0.98×2);								
EtOAc	1	1.38[a]	1.00	31	1.28	0.98	35	0.87
	2	0.90[b]	1.00	55	0.84	1.00	58	0.92
	3	0.88[c]	1.00	56	0.82	1.00	59	0.92
								Average κ = 0.90
[a] $I_{R1(t)}$ = 4.34–1.00–(0.98×2); [b] $I_{R1(t)}$ = 3.90−1.00−(1.00×2); [c] $I_{R1(t)}$ = 3.88−1.00−(1.00×2);								

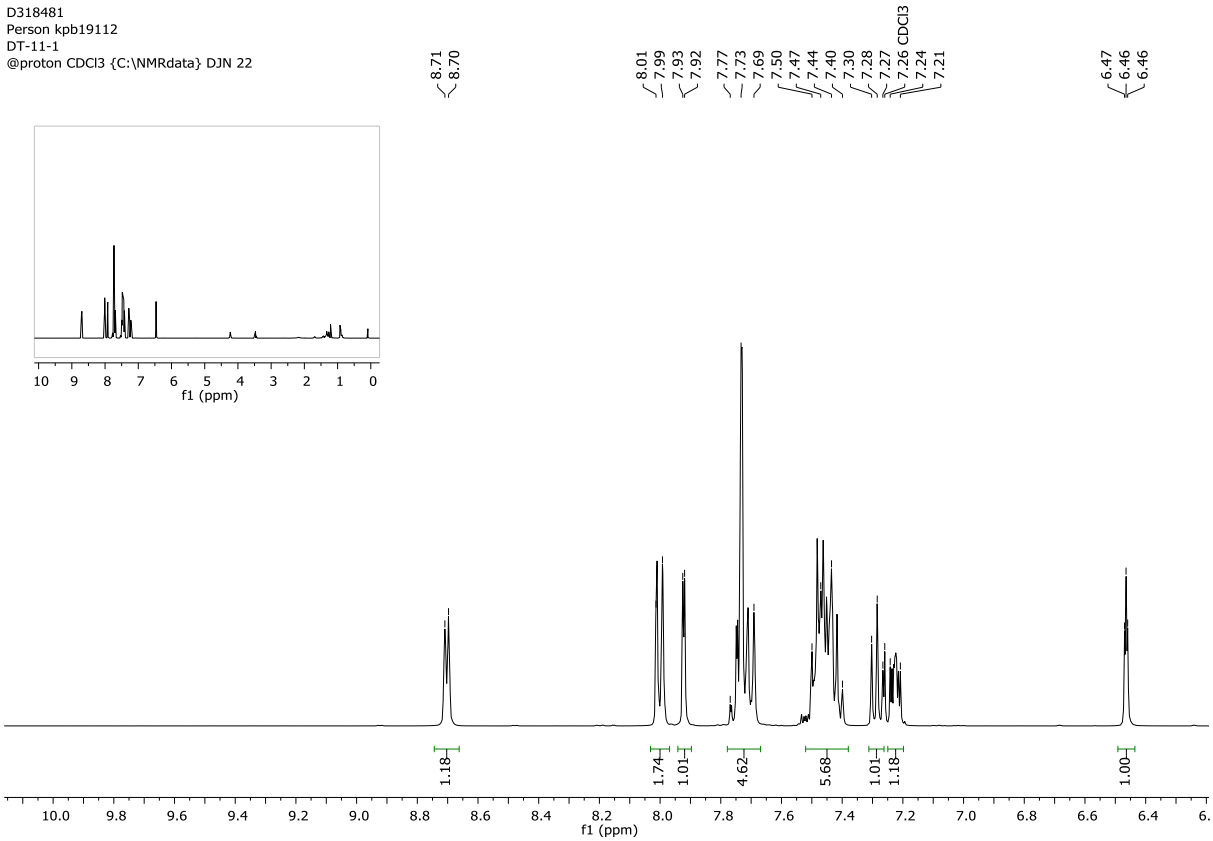


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (DCM-entry 1, Table S3)

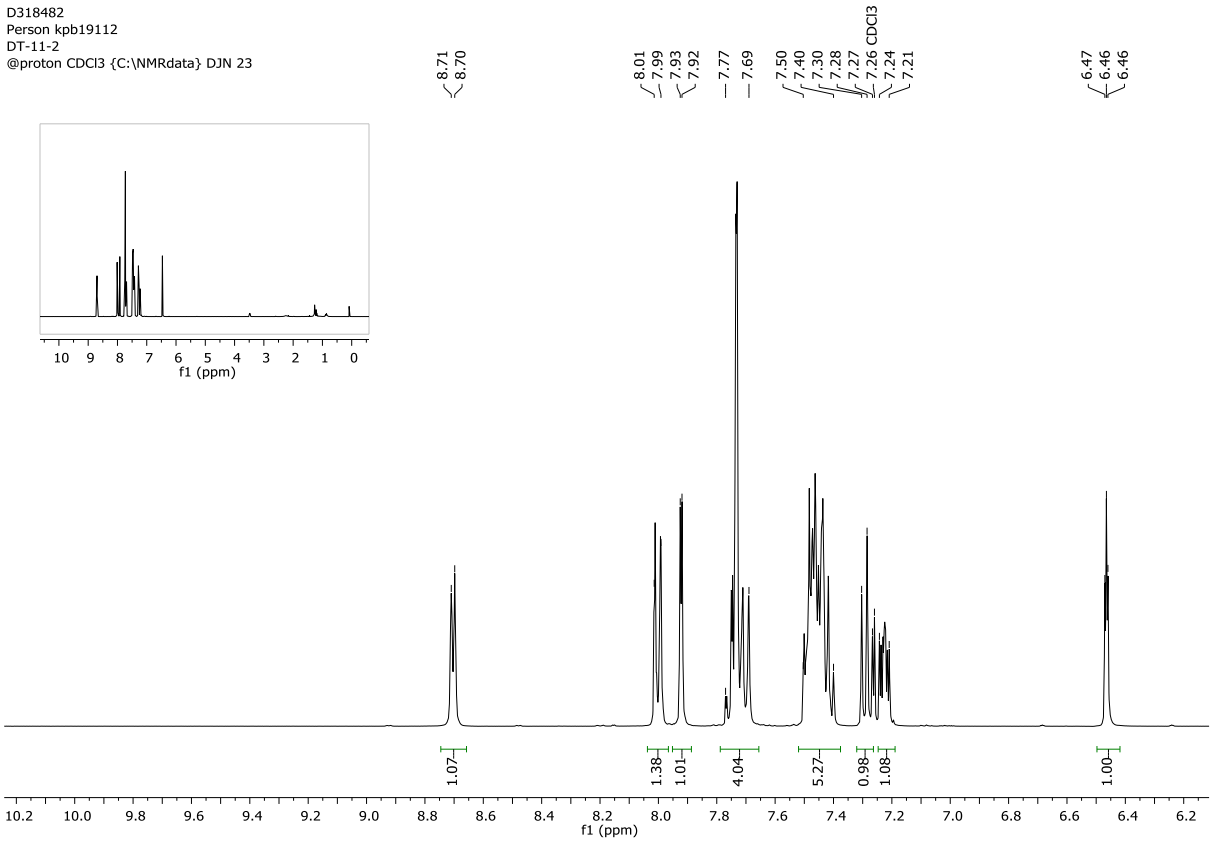


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (DCM-entry 2, Table S3)

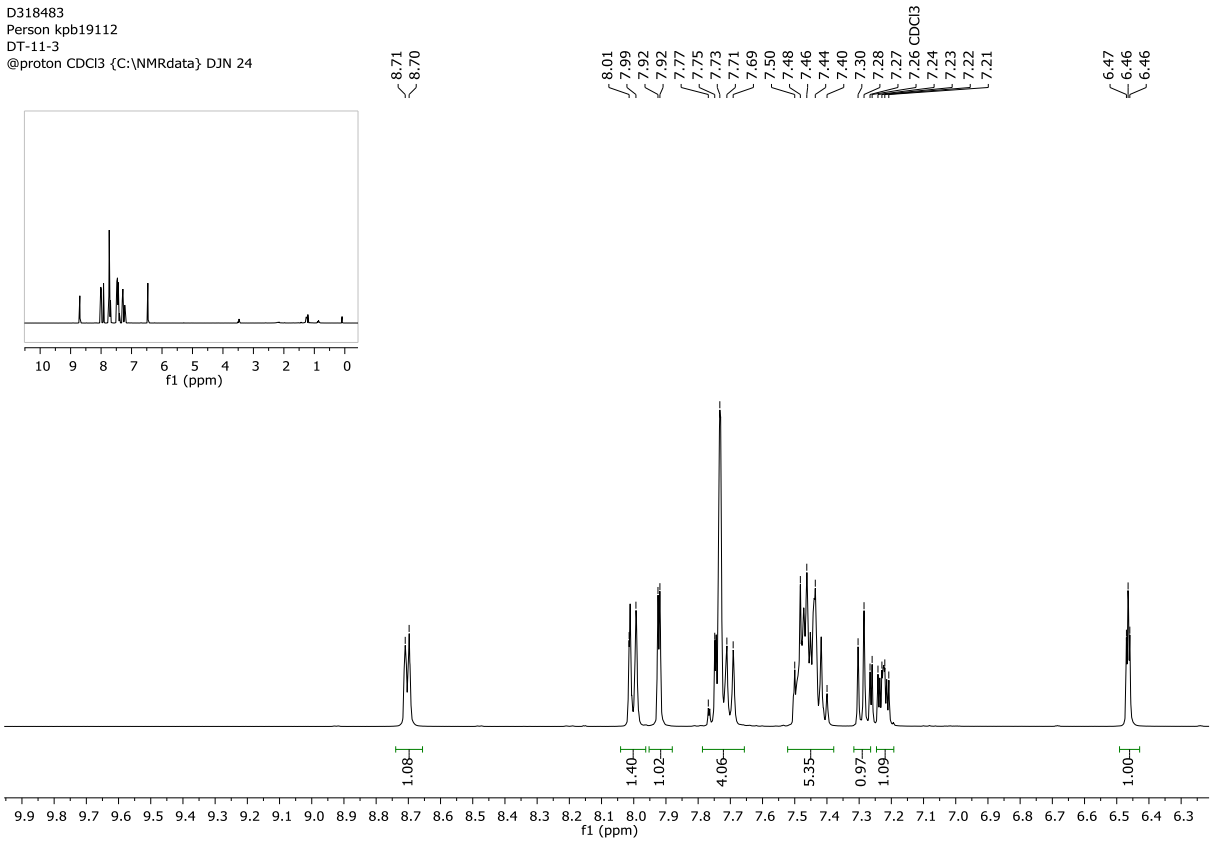


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (DCM-entry 3, Table S3)

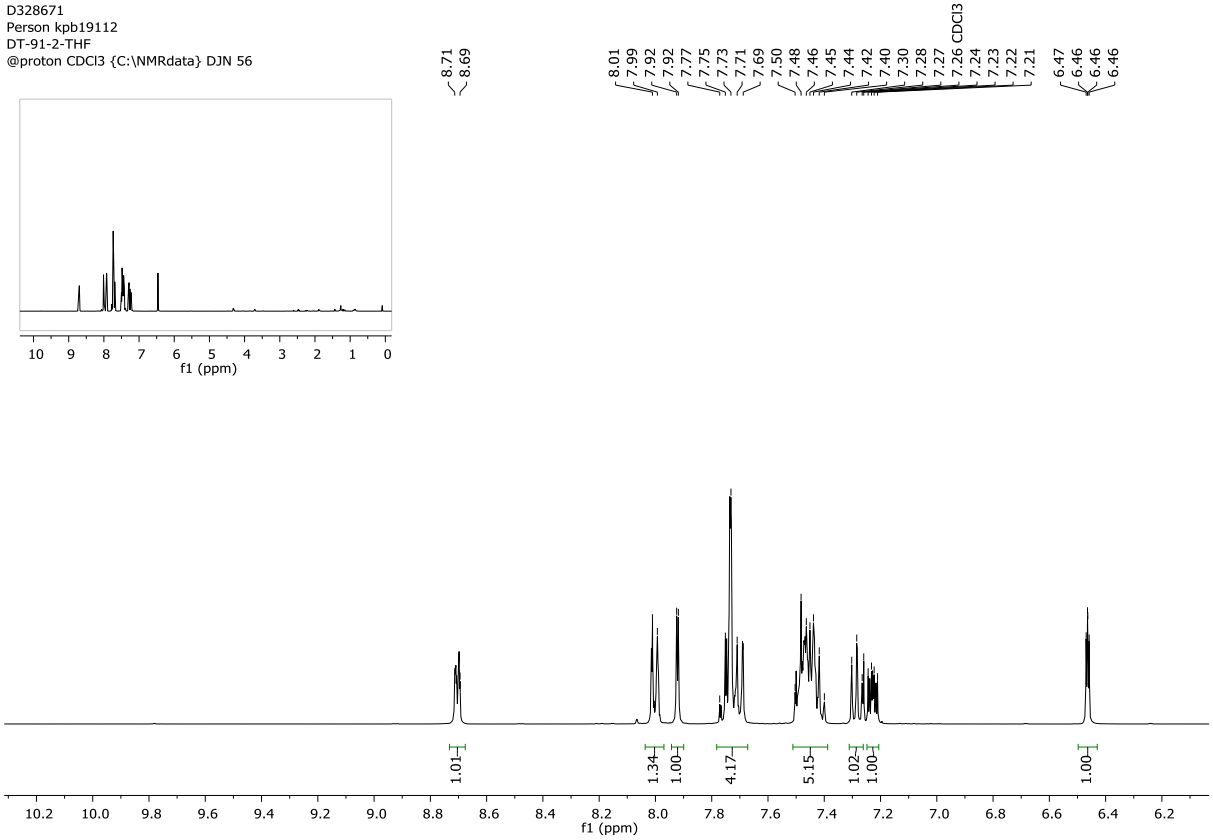


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (THF-entry 1, Table S3)

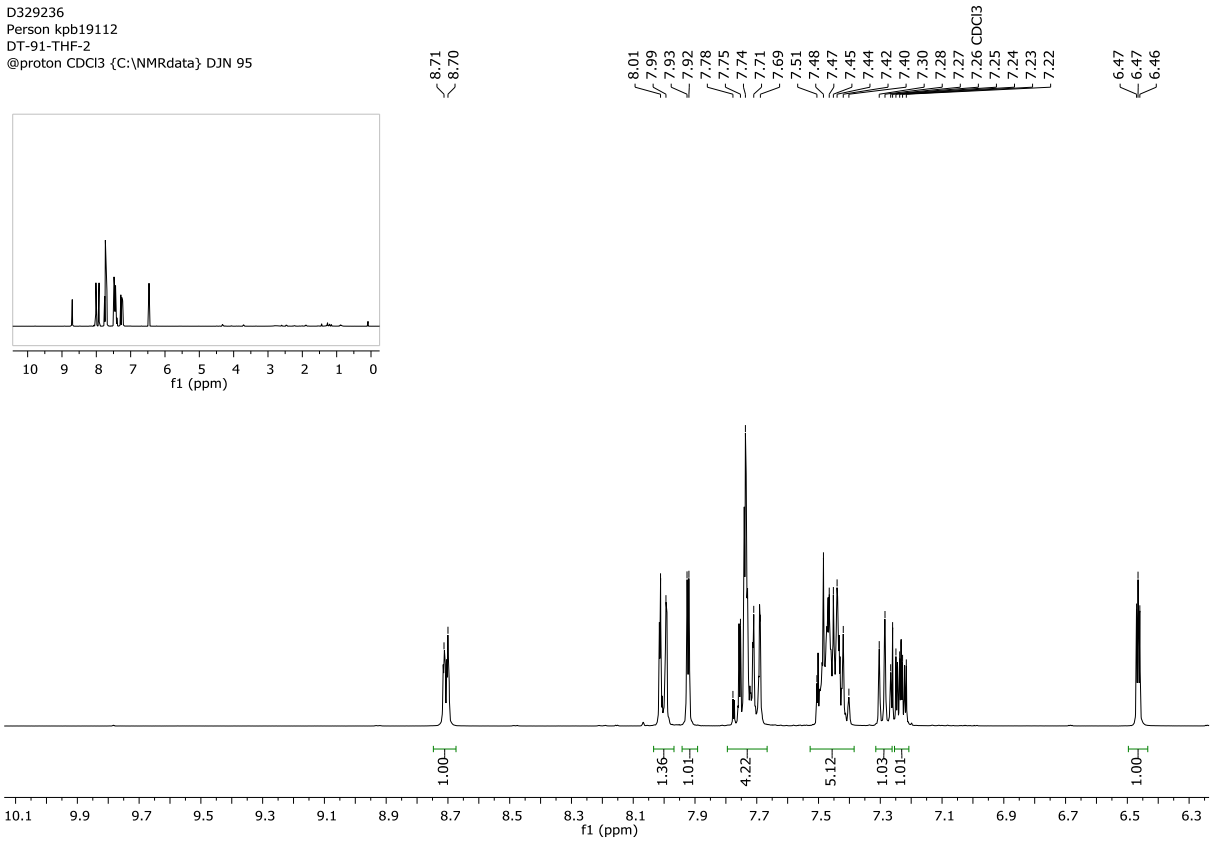


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (THF-entry 2, Table S3)

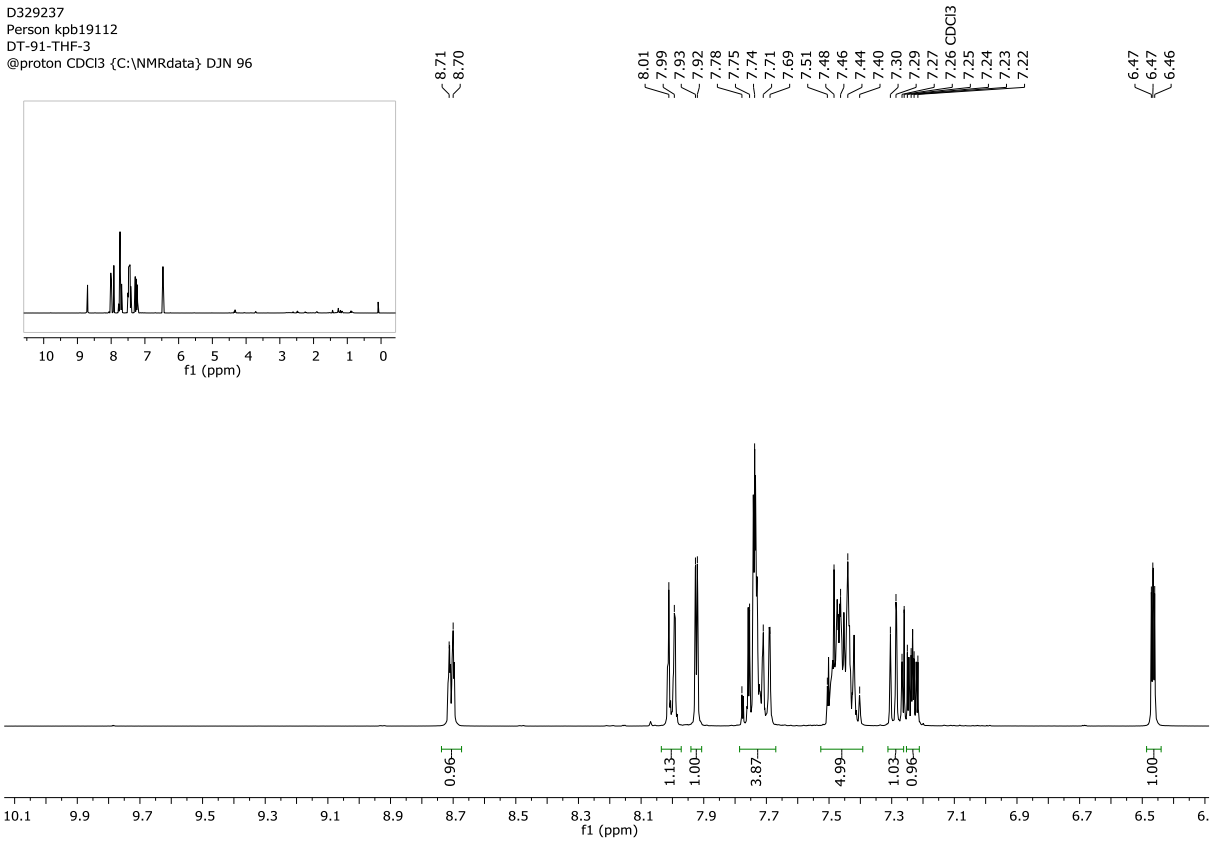


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (THF-entry 3, Table S3)

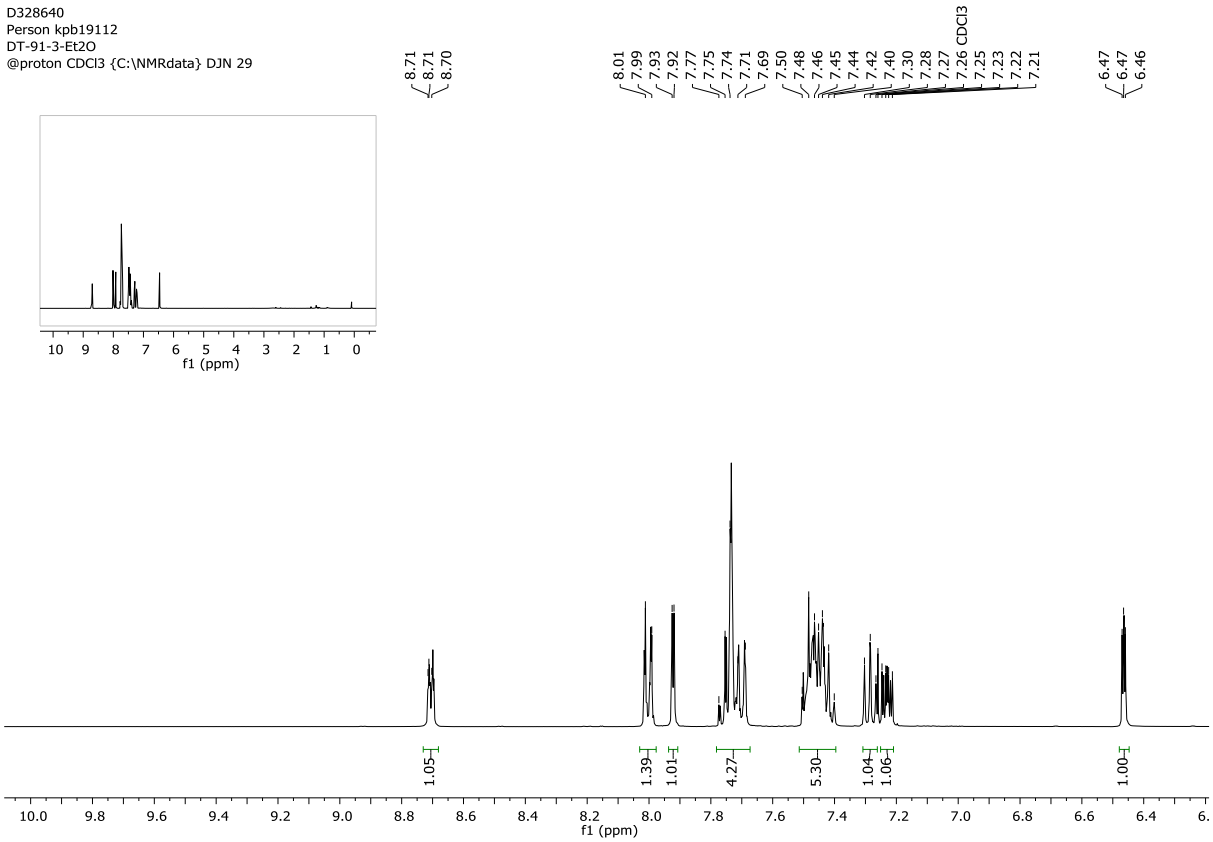


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (Et_2O-entry 1, Table S3)

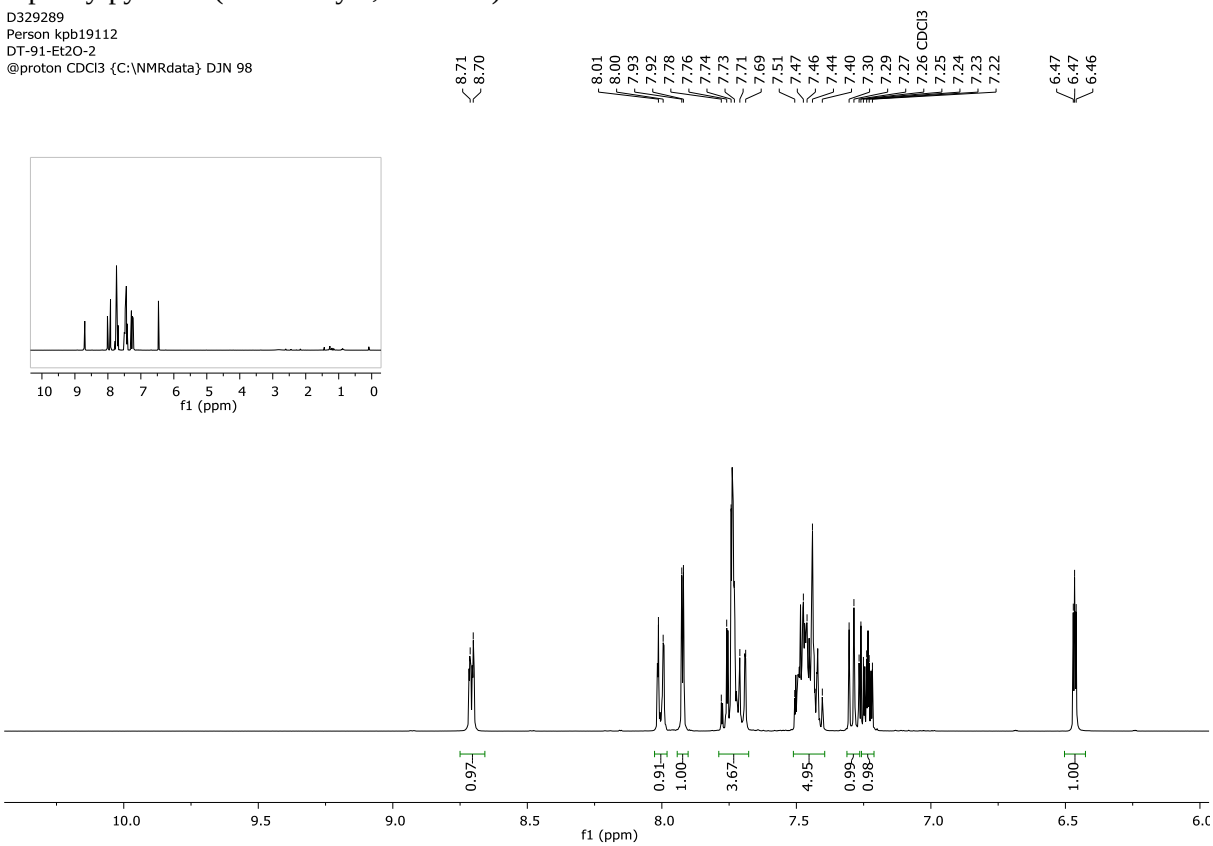


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (Et_2O-entry 2, Table S3)

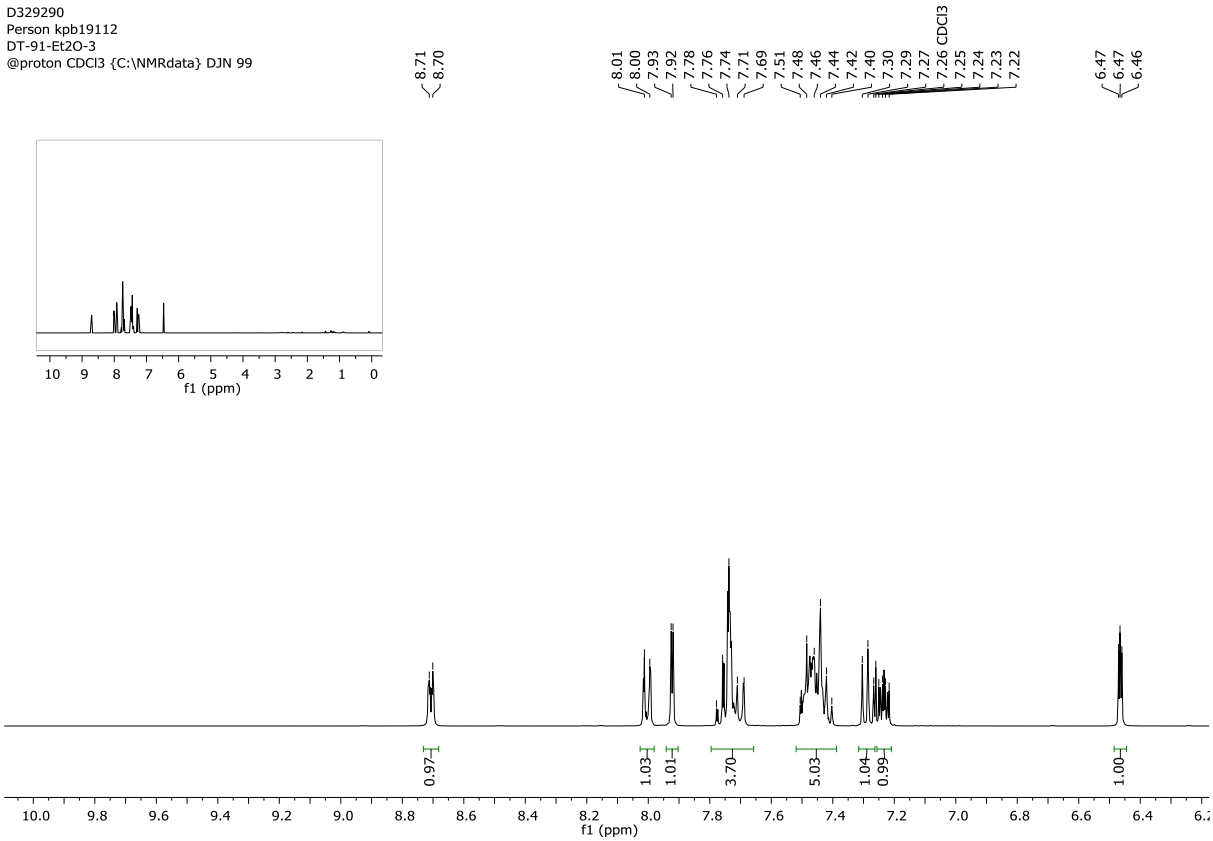


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (Et_2O-entry 3, Table S3)

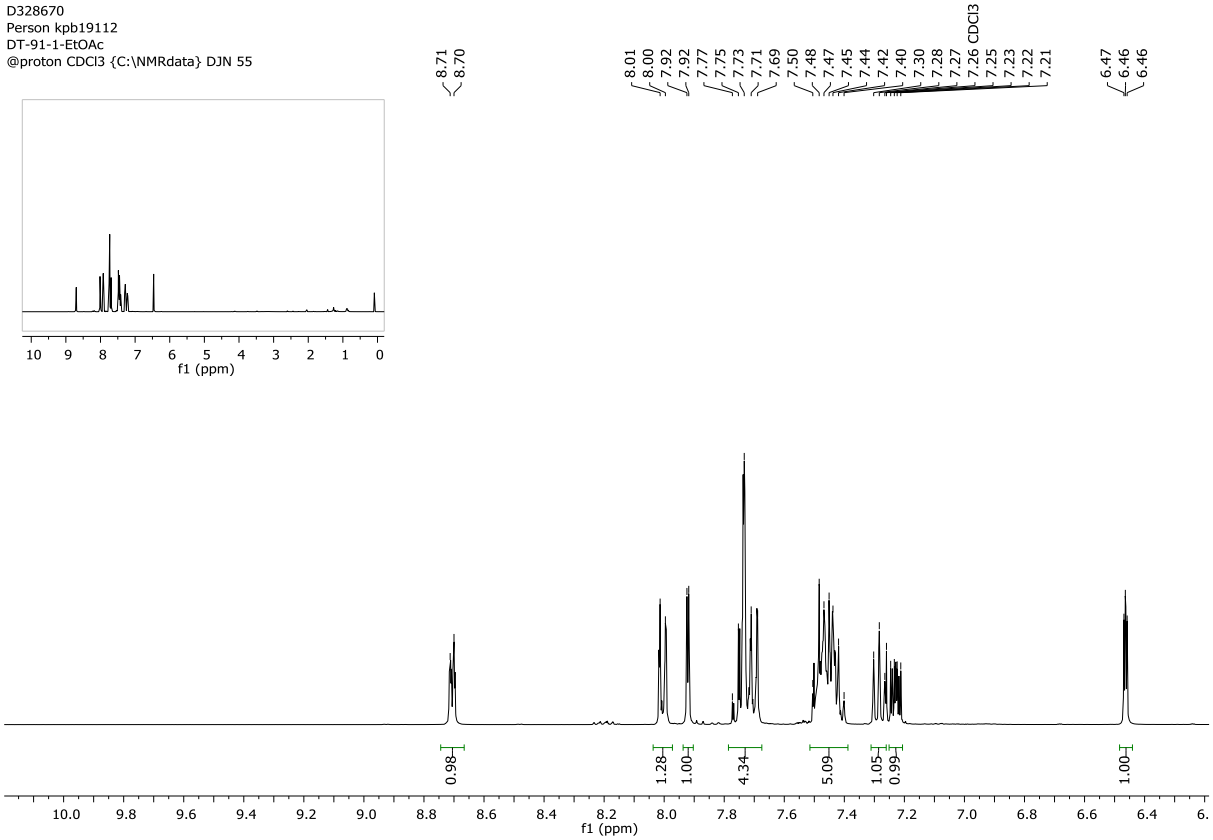


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (EtOAc-entry 1, Table S3)

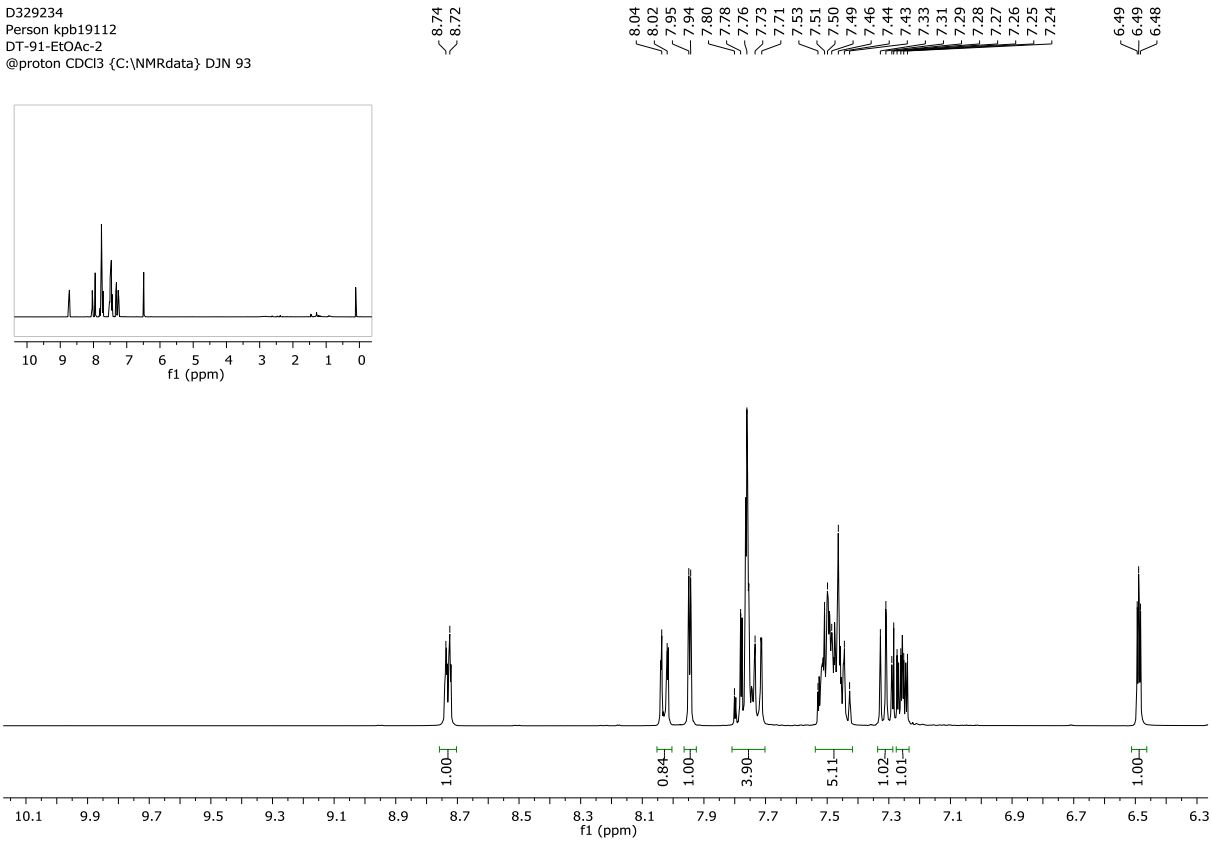


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (EtOAc-entry 2, Table S3)

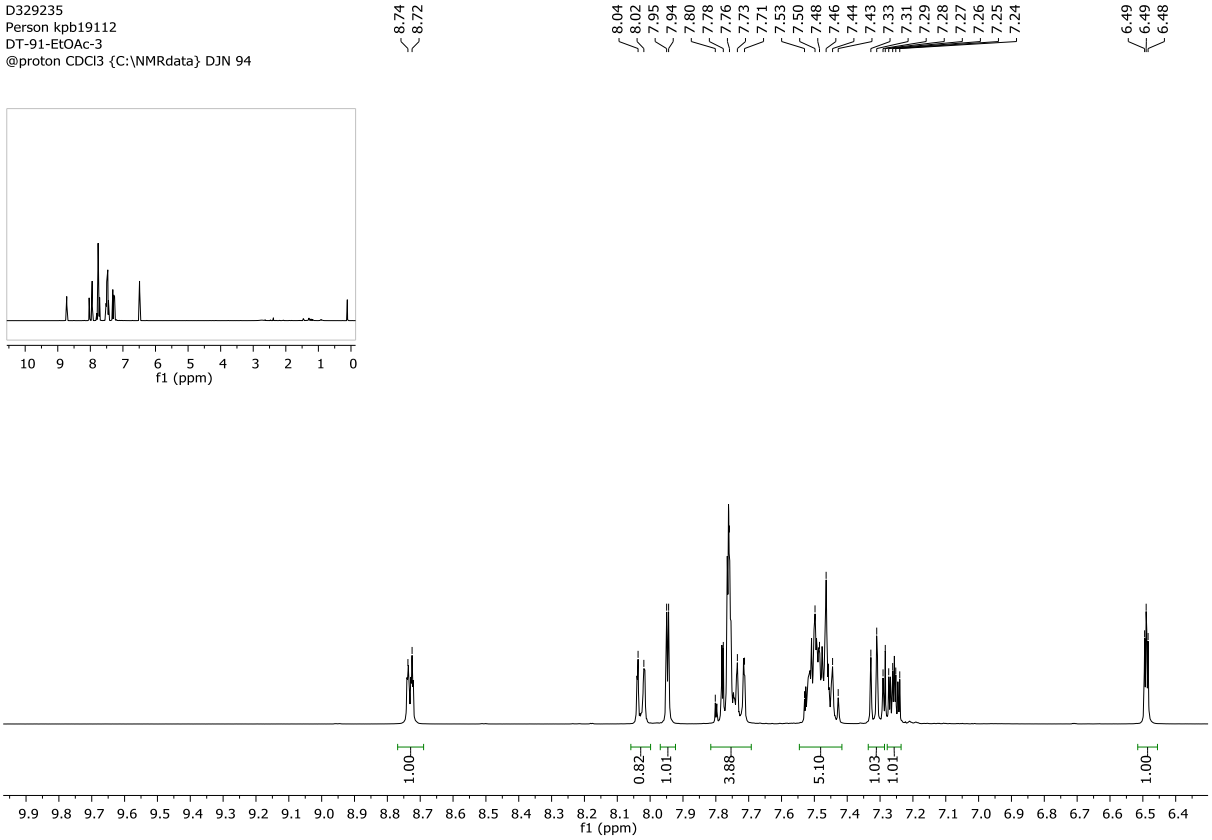


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (EtOAc-entry 3, Table S3)

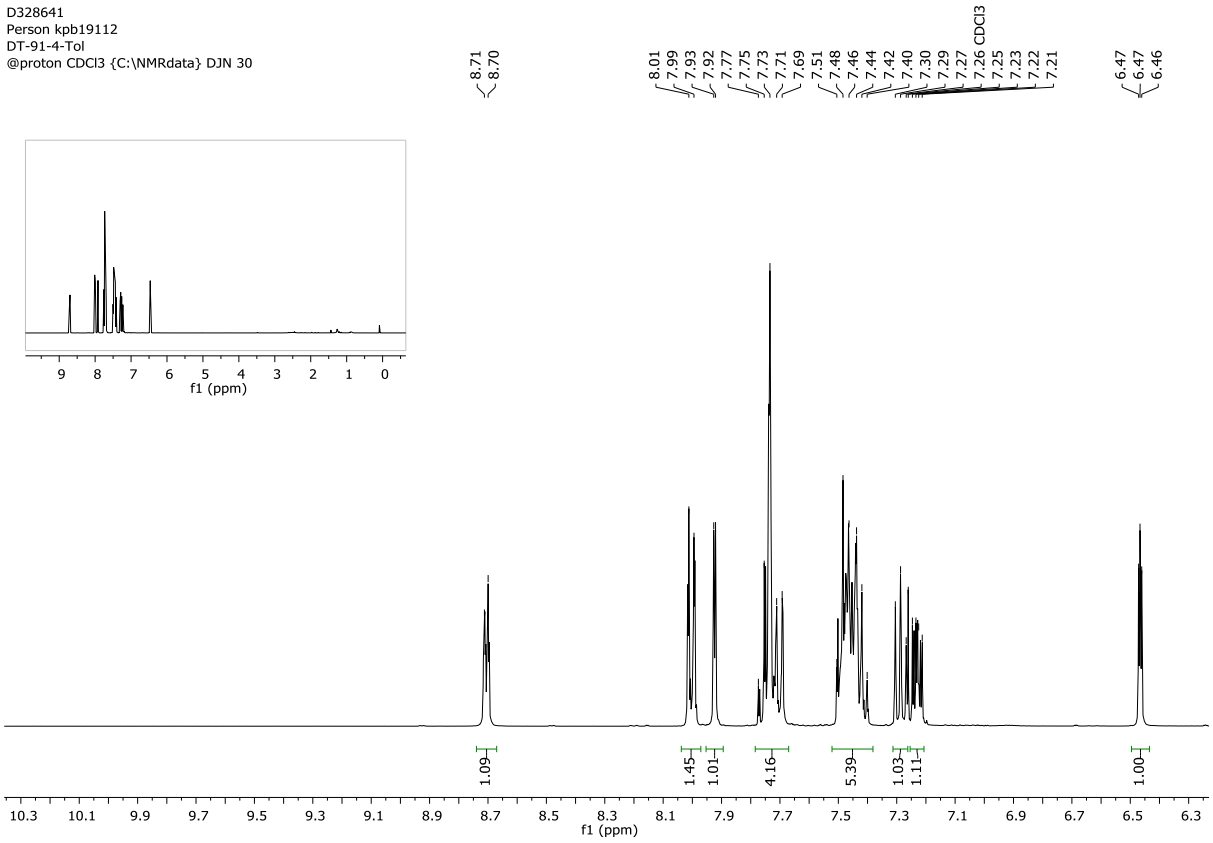


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (Toluene-entry 1, Table S3)

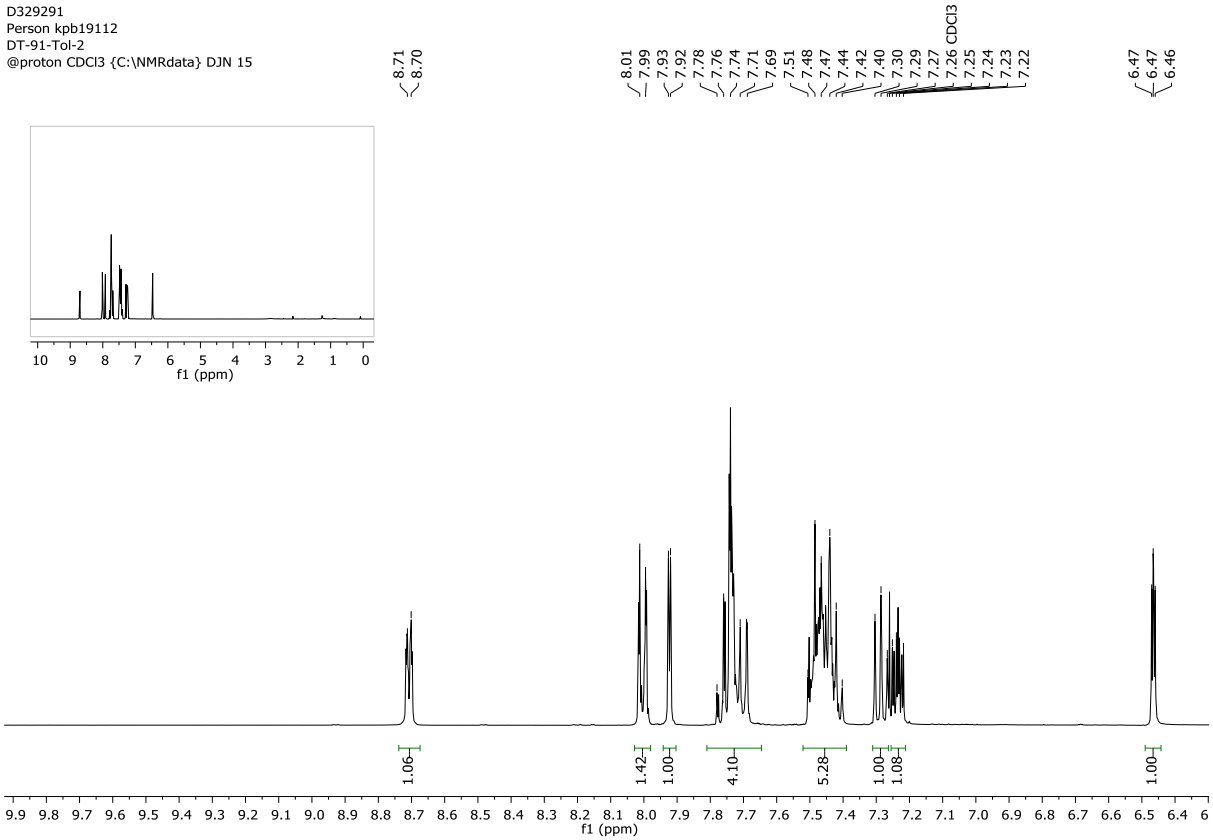


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (Toluene-entry 2, Table S3)

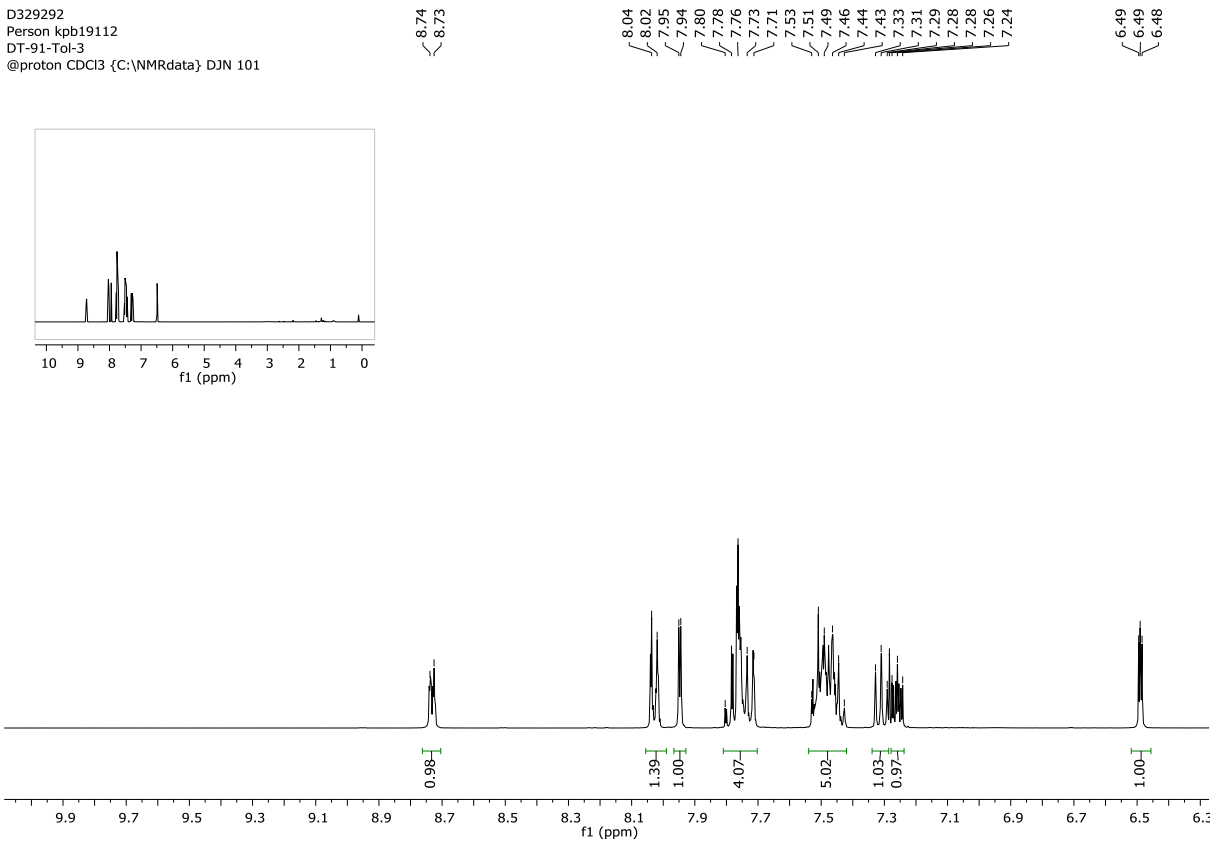
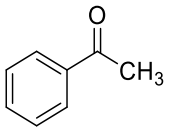
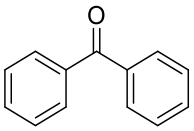


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (Toluene-entry 3, Table S3)

3.3. Competition Experiments with [(COD)Ir(IMes)PPh$_3$]BArF$_{24}$ (Ir-1)

Table S4. Determination of the competition rate constant κ from the labelling experiment between acetophenone and benzophenone

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh$_3$][BArF$_{24}$]
Mass	12.0 mg	18.2 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.99 – 7.93 ppm and at δ (**R2**) = 7.84 – 7.77 ppm
Determined against integral at δ (**R1**) = 2.61 ppm and at δ (**R2**) = 7.63 – 7.53 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.93 (m, 2H/D **R1**), 7.84 – 7.77 (m, 4H/D **R2**), 7.63 – 7.53 (m, 1H **R1** and 2H **R2**), 5.52 – 5.42 (m, 2H **R1** and 4H **R2**), 2.60 (s, 3H, **R1**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 4H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.39	3.00	31	3.07	2.22[a]	31	0.99
2	1.08	3.00	46	2.65	2.44[b]	46	1.01
3	1.01	3.00	50	2.18	2.12[c]	49	1.04
				Average κ = 1.01			

[a] $I_{R2(0)}$ = 3.22 – (3.00/3); [b] $I_{R2(0)}$ = 3.44 – (3.00/3); [c] $I_{R2(0)}$ = 3.12 – (3.00/3);

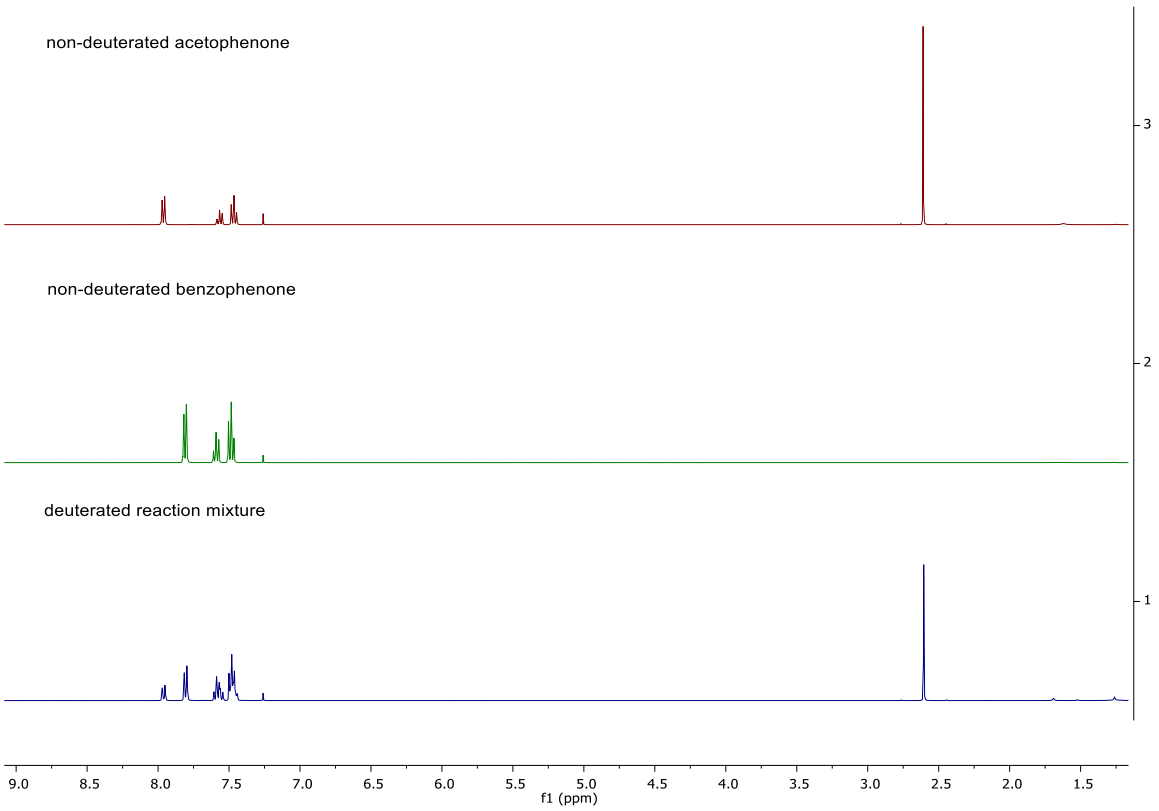


Figure S25. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

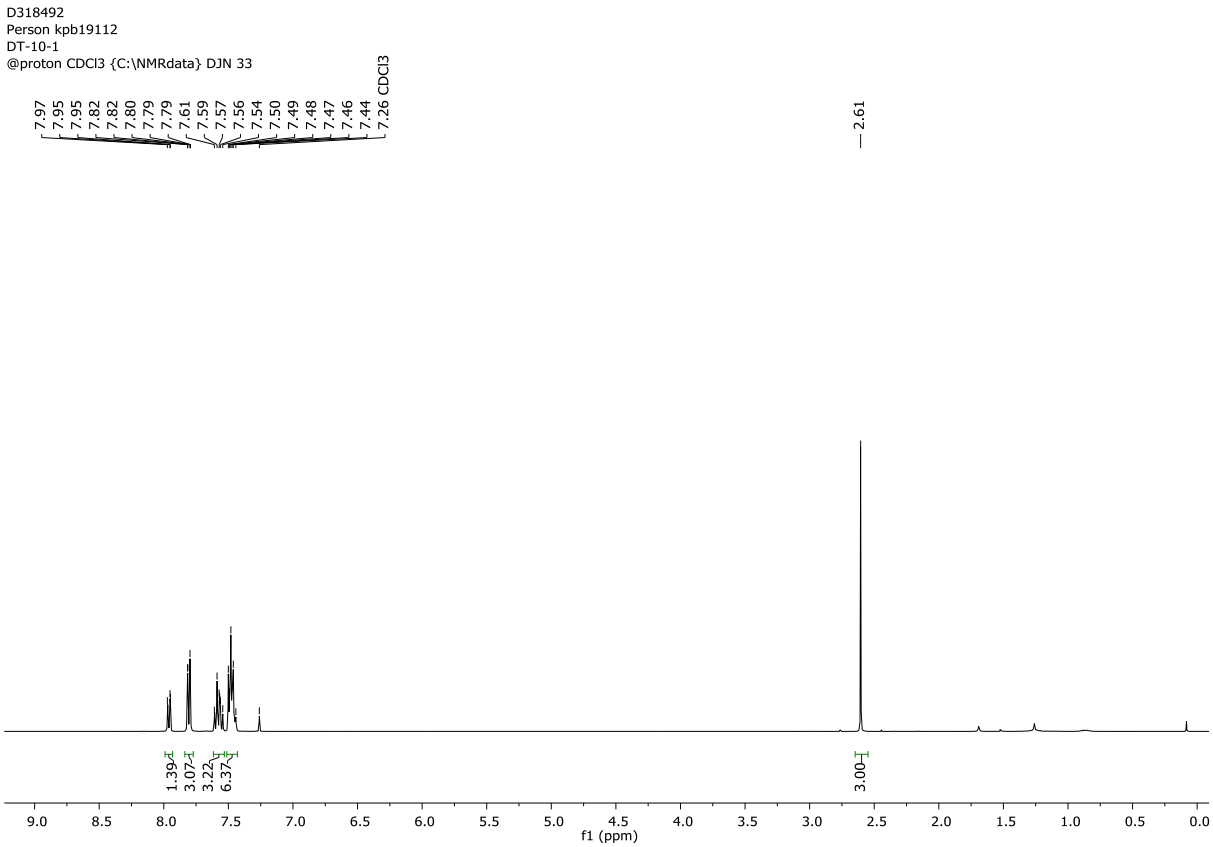


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzophenone (entry 1, Table S4).

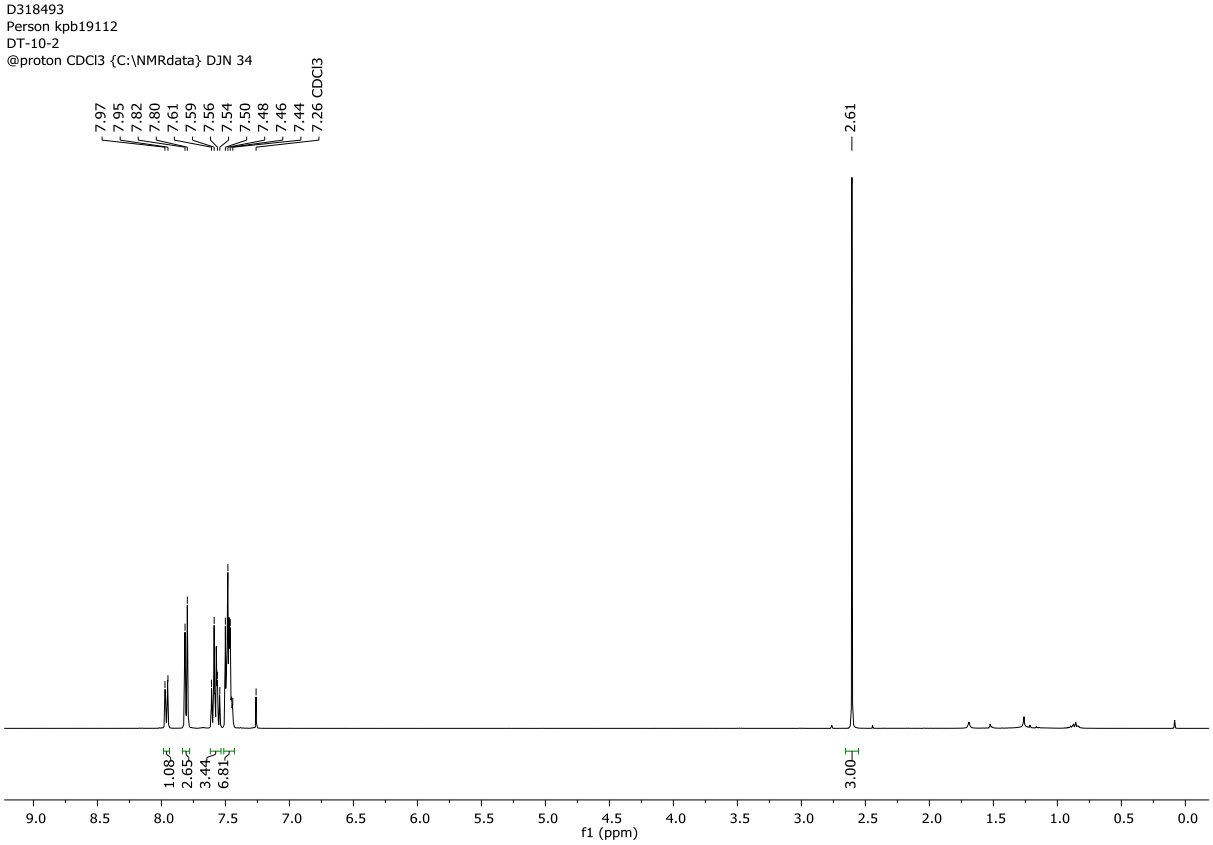


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzophenone (entry 2, Table S4).

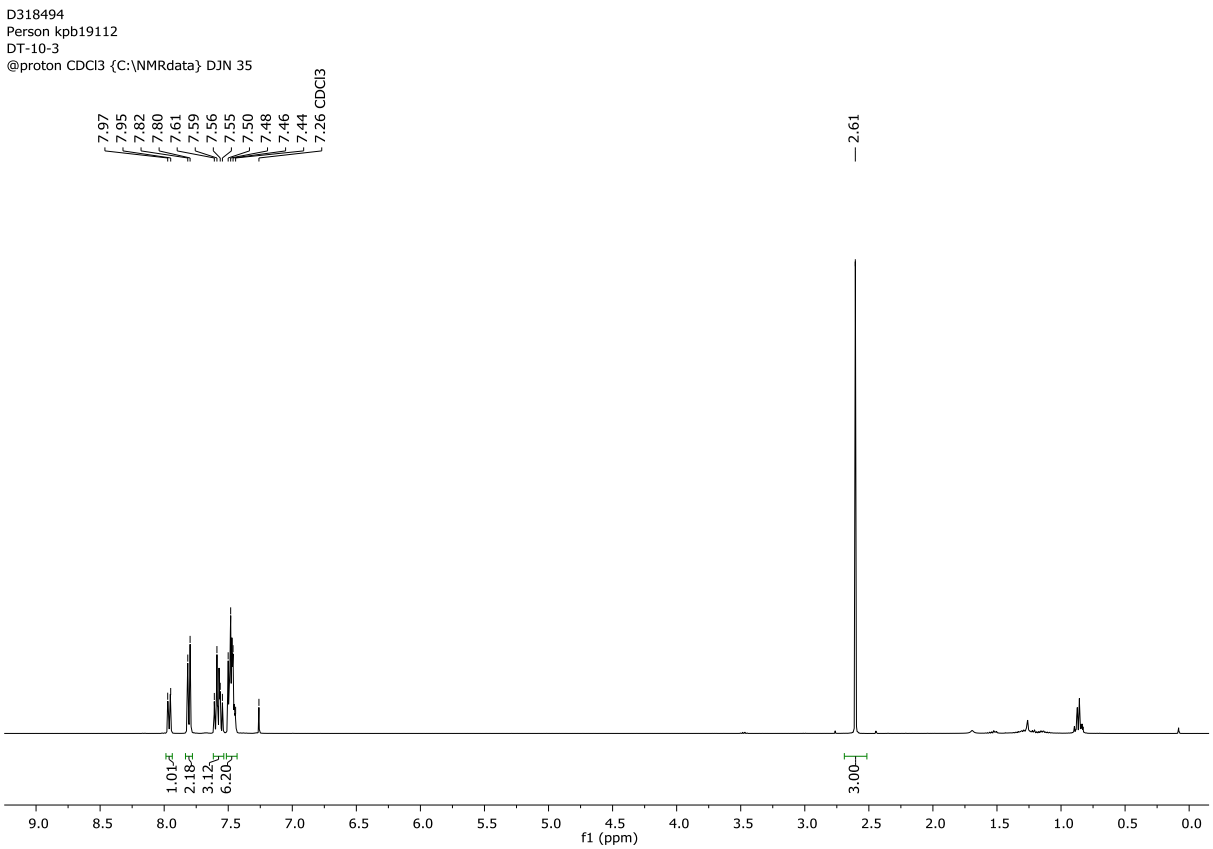
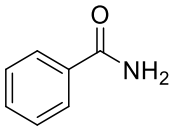
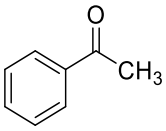


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzophenone (entry 3, Table S4).

Table S5. Determination of the competition rate constant κ from the labelling experiment between benzamide and acetophenone

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	12.1 mg	12.0 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.86 – 7.77 ppm and at δ (**R2**) = 7.99 – 7.93ppm
Determined against integral at δ (**R1**) = 7.59 – 7.39 ppm and at δ (**R2**) = 2.60 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.93 (m, 2H/D **R2**), 7.86 – 7.77 (m, 2H/D **R1**), 7.59 – 7.39 (m, 3H, **R1** and 3H, **R2**), 6.19 (br, 2H, **R1**), 2.60 (s, 3H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 3H	$\%D_{R2}$	κ
1	2.09	3.78[a]	17	1.94	3.00	3	6.14
2	1.57	3.84[b]	39	1.85	3.00	8	6.27
3	1.65	3.93[c]	37	1.86	3.00	7	6.37
				Average κ = 6.26			

[a] $I_{R1(0)}$ = 6.78 – 3.00; [b] $I_{R1(0)}$ = 6.84 – 3.00; [c] $I_{R1(0)}$ = 6.93 – 3.00;

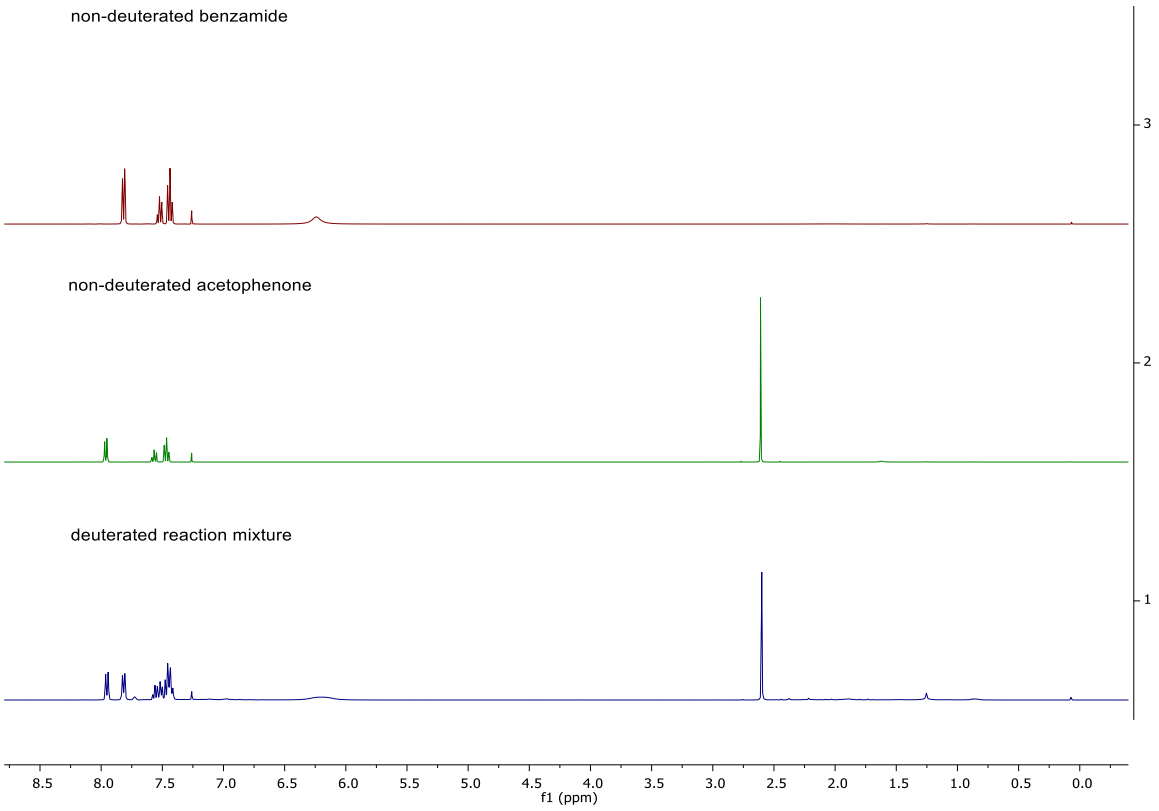


Figure S29. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

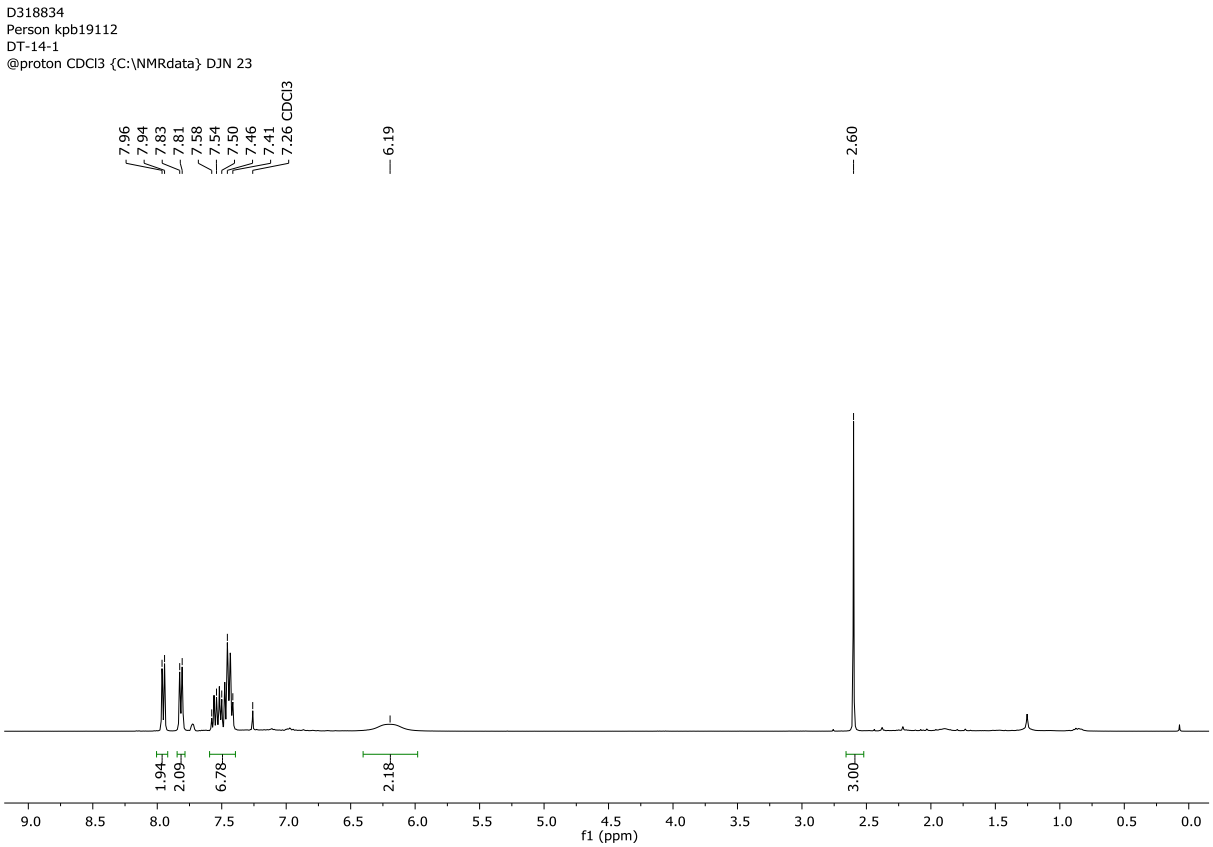


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzamide (entry 1, Table S5)

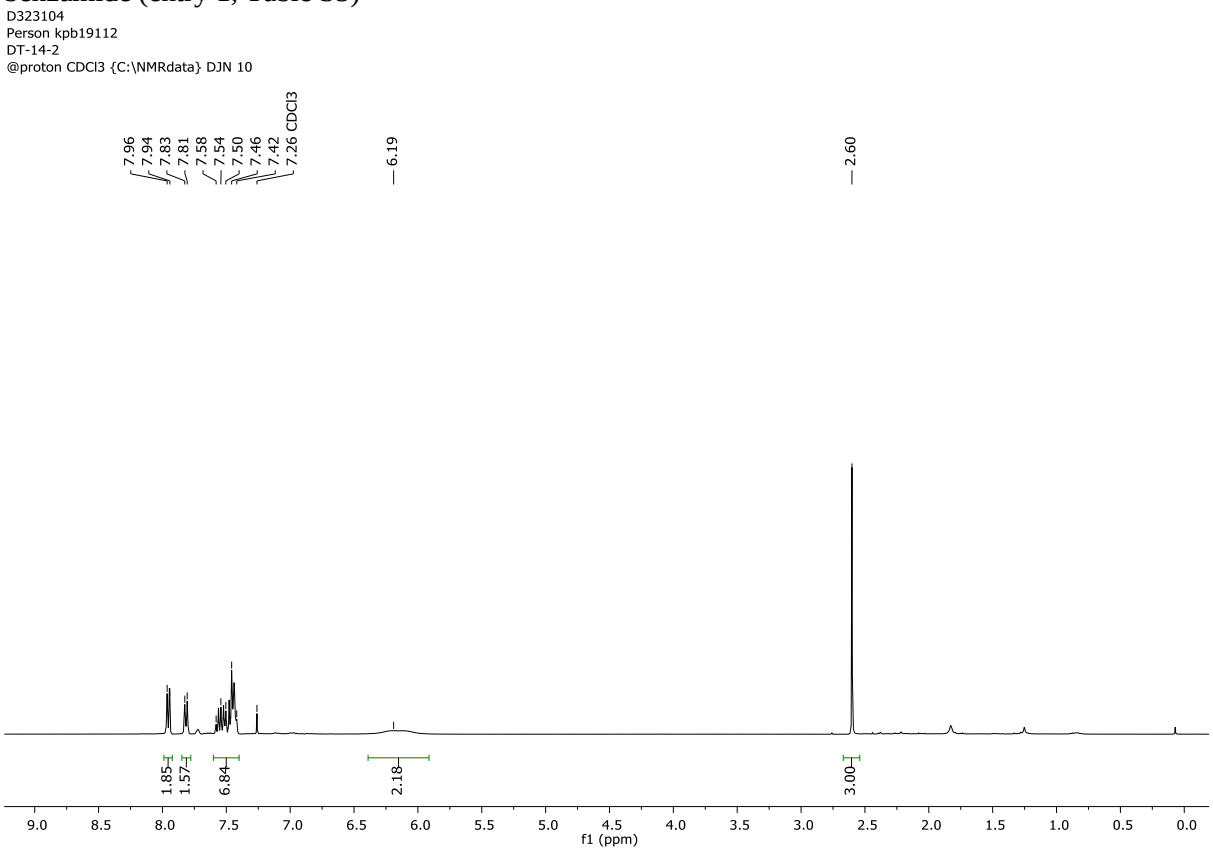


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzamide (entry 2, Table S5)

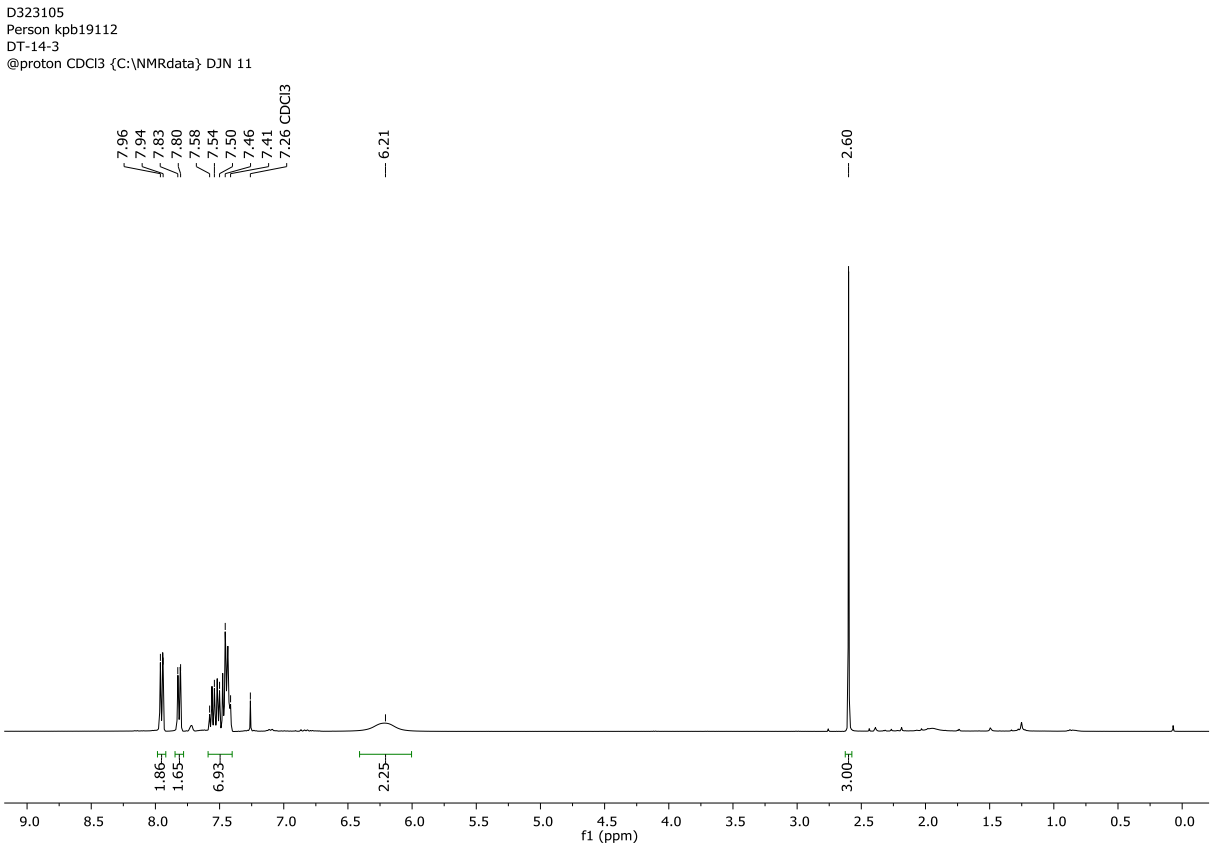
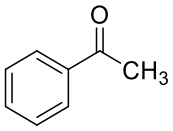
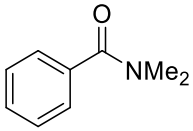


Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzamide (entry 3, Table S5)

Table S6. Determination of the competition rate constant κ from the labelling experiment between acetophenone and *N*,*N*-dimethylbenzamide.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	12.0 mg	14.9 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.99 – 7.93 ppm and at δ (**R2**) = 7.42 – 7.36 ppm
Determined against integral at δ (**R1**) = 7.57 – 7.54 ppm and at δ (**R2**) = 3.17 – 2.88 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.93 (m, 2H/D **R1**), 7.57 – 7.54 (m, 1H, **R1**), 7.47 – 7.43 (m, 2H, **R1**), 7.42 – 7.36 (m, 2H/D **R2** and 3H, **R2**), 3.17 – 2.88 (m, 6H, **R2**), 2.60 (s, **3H**, R1).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 6H	$\%D_{R2}$	κ
1	1.50	3.00	25	1.62[a]	5.32	9	3.18
2	1.54	3.00	23	1.96[b]	6.29	7	3.74
3	1.45	3.00	28	2.06[c]	6.59	6	4.82
Average *κ* = 3.91							

[a] $I_{R2(t)} = 4.28 – (5.32)/6×3$; [b] $I_{R2(t)} = 5.10 – (6.29)/6×3$; [c] $I_{R2(t)} = 5.35 – (6.59)/6×3$

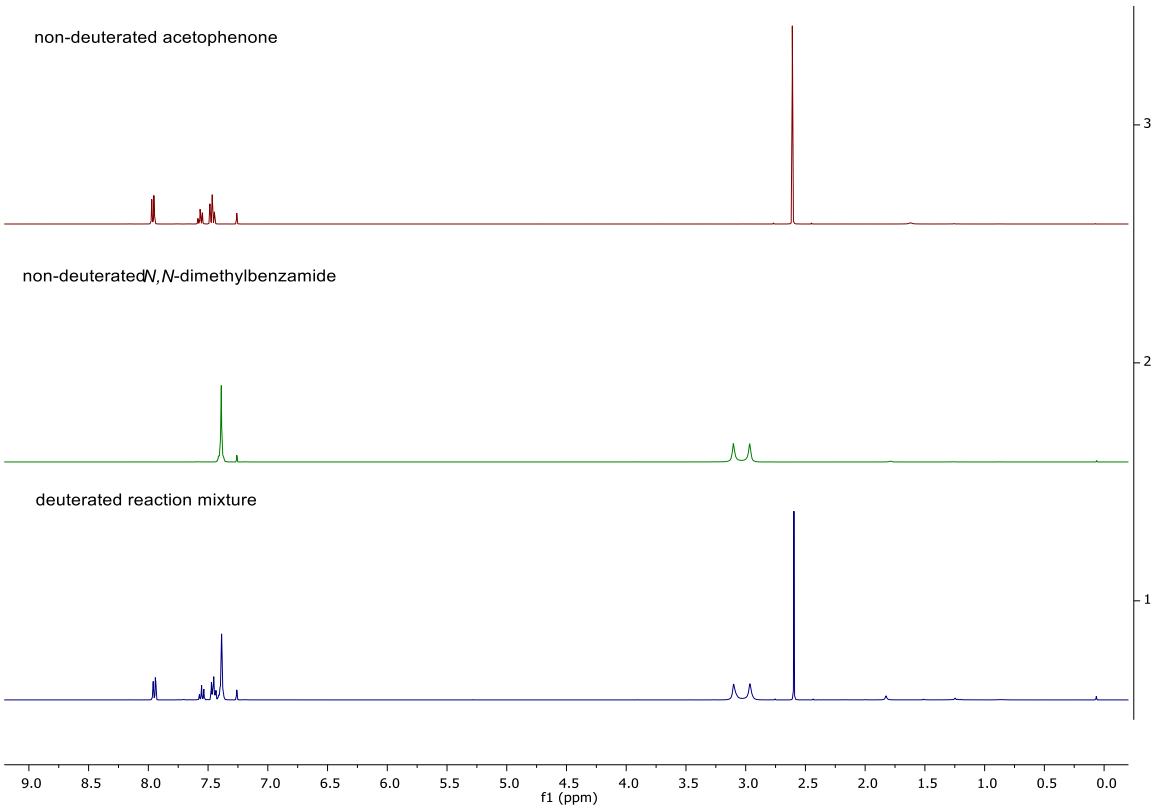


Figure S33. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

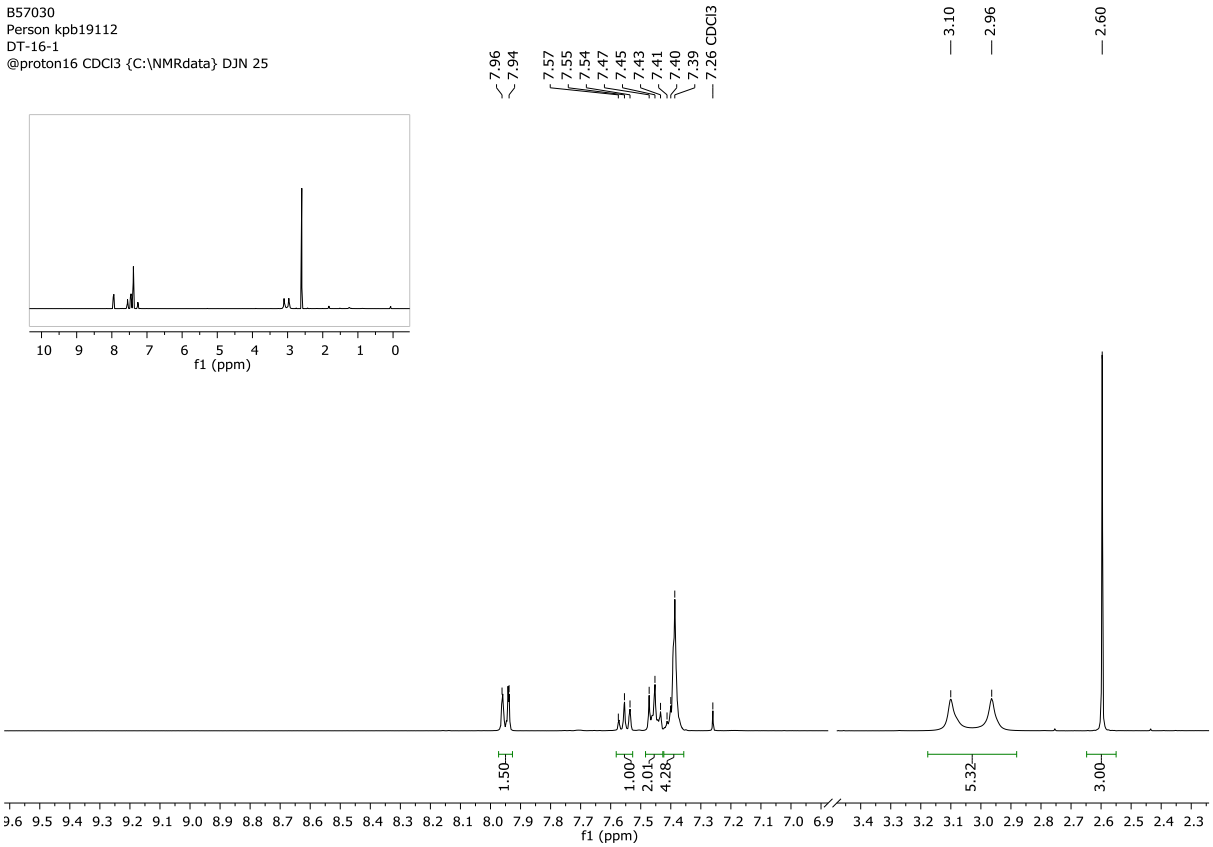


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and *N*,*N*-dimethylbenzamide (entry 1, Table S6).

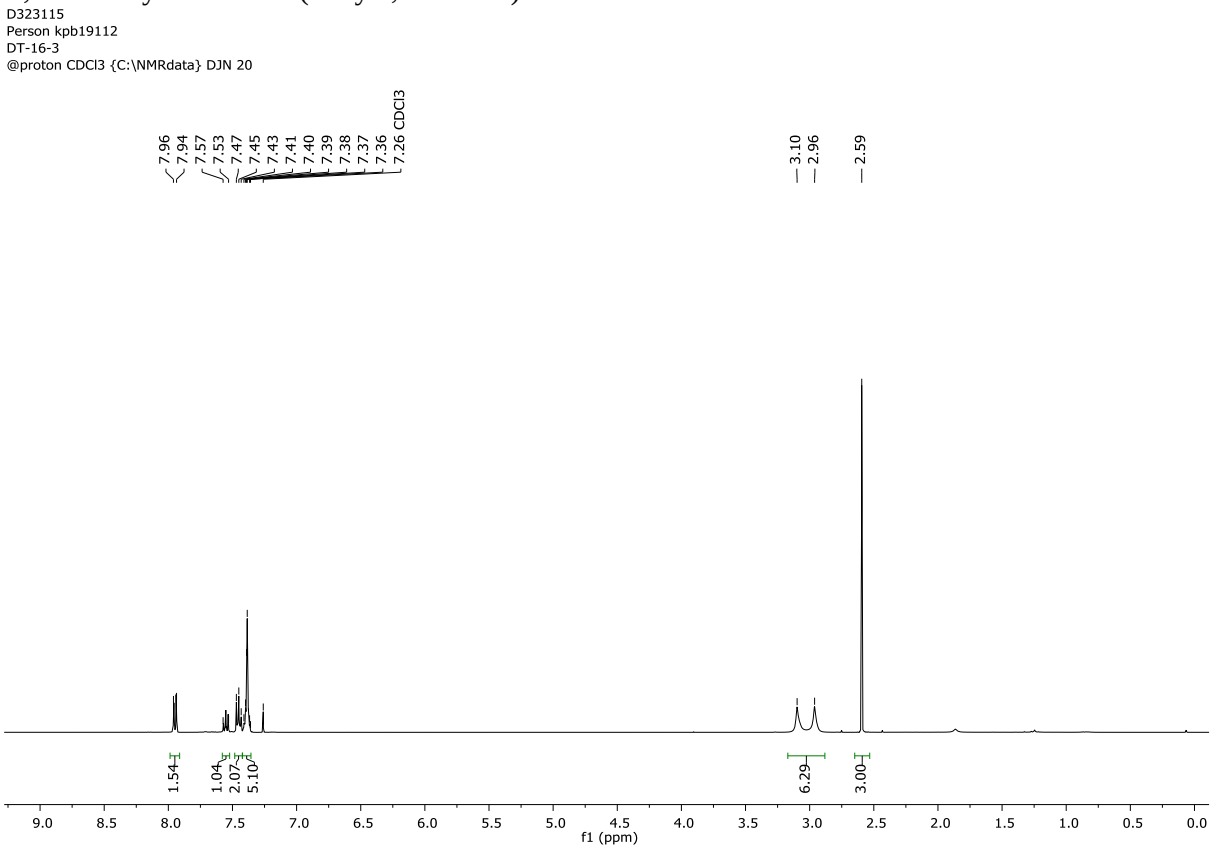


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and *N*,*N*-dimethylbenzamide (entry 2, Table S6).

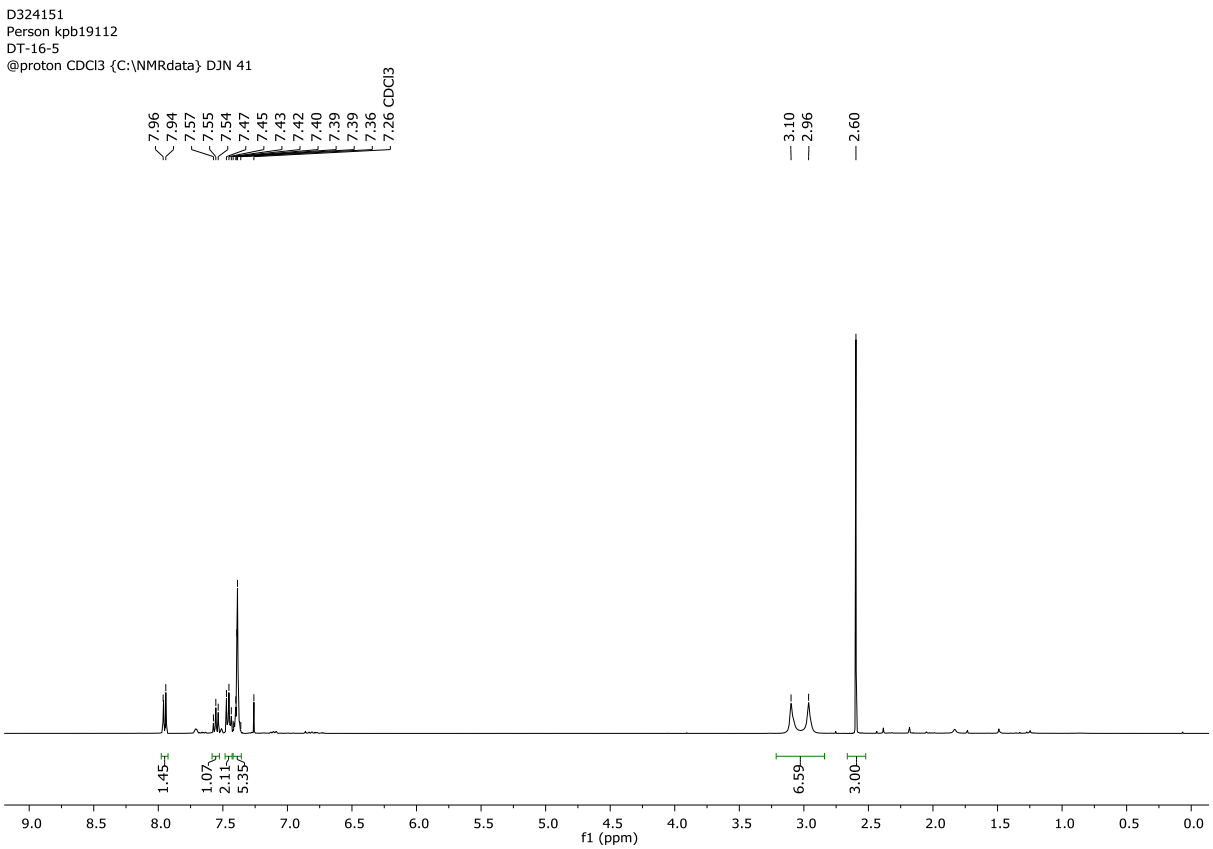
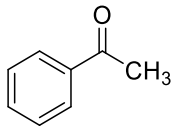
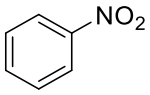


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and *N*,*N*-dimethylbenzamide (entry 3, Table S6).

Table S7. Determination of the competition rate constant κ from the labelling experiment between acetophenone and nitrobenzene.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	12.0 mg	12.3 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.99 – 7.93 ppm and at δ (**R2**) = 8.26 – 8.20 ppm
Determined against integral at δ (**R1**) = 2.61 ppm and at δ (**R2**) = 7.49 – 7.43 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 – 8.20 (m, 2H/D **R2**), 7.99 – 7.93 (m, 2H/D **R1**), 7.73 – 7.66 (m, 1H, **R2**), 7.59 – 7.51 (m, 1H, **R1** and 2H, **R2**), 7.49 – 7.43 (m, 2H, **R1**), 2.61 (s, 3H, CH_3).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.66	3.22	69	1.43	1.00	29	3.52
2	0.59	2.58	66	1.43	1.00	29	3.19
3	0.81	2.81	57	1.57	1.00	22	3.46
				Average κ = 3.39			

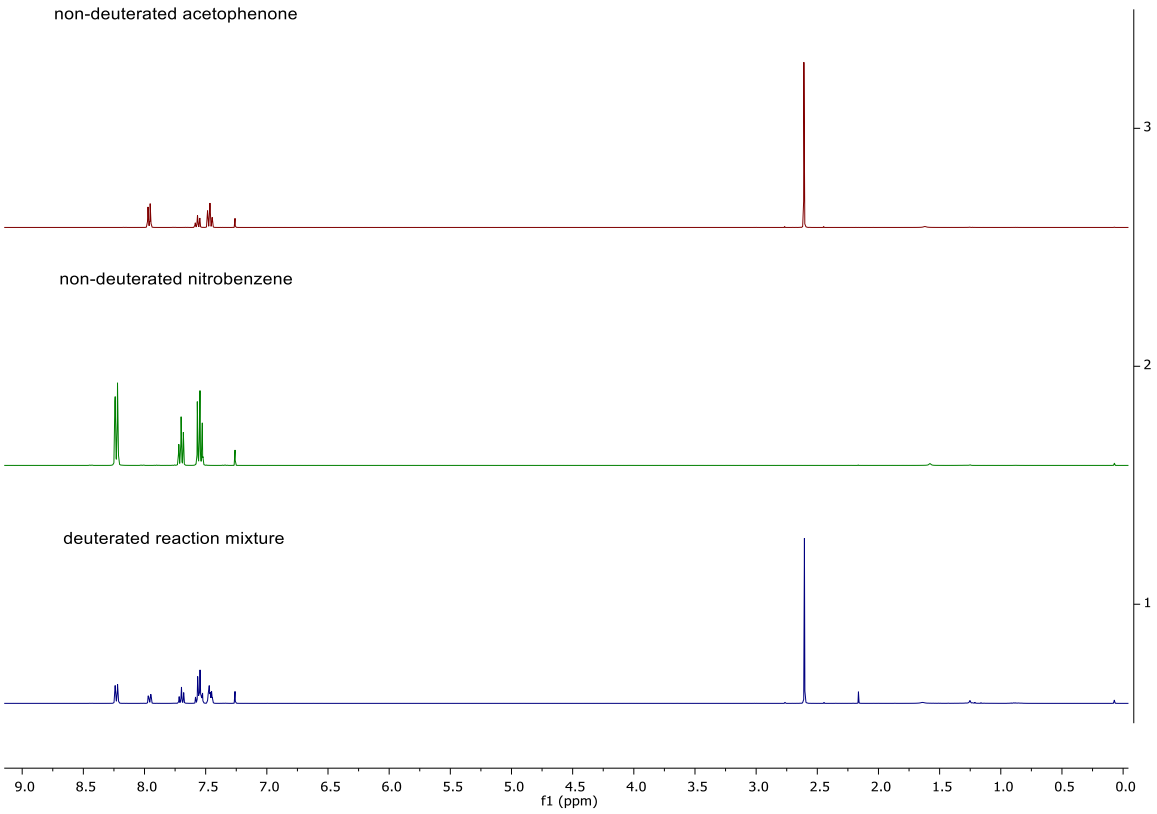


Figure S37. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

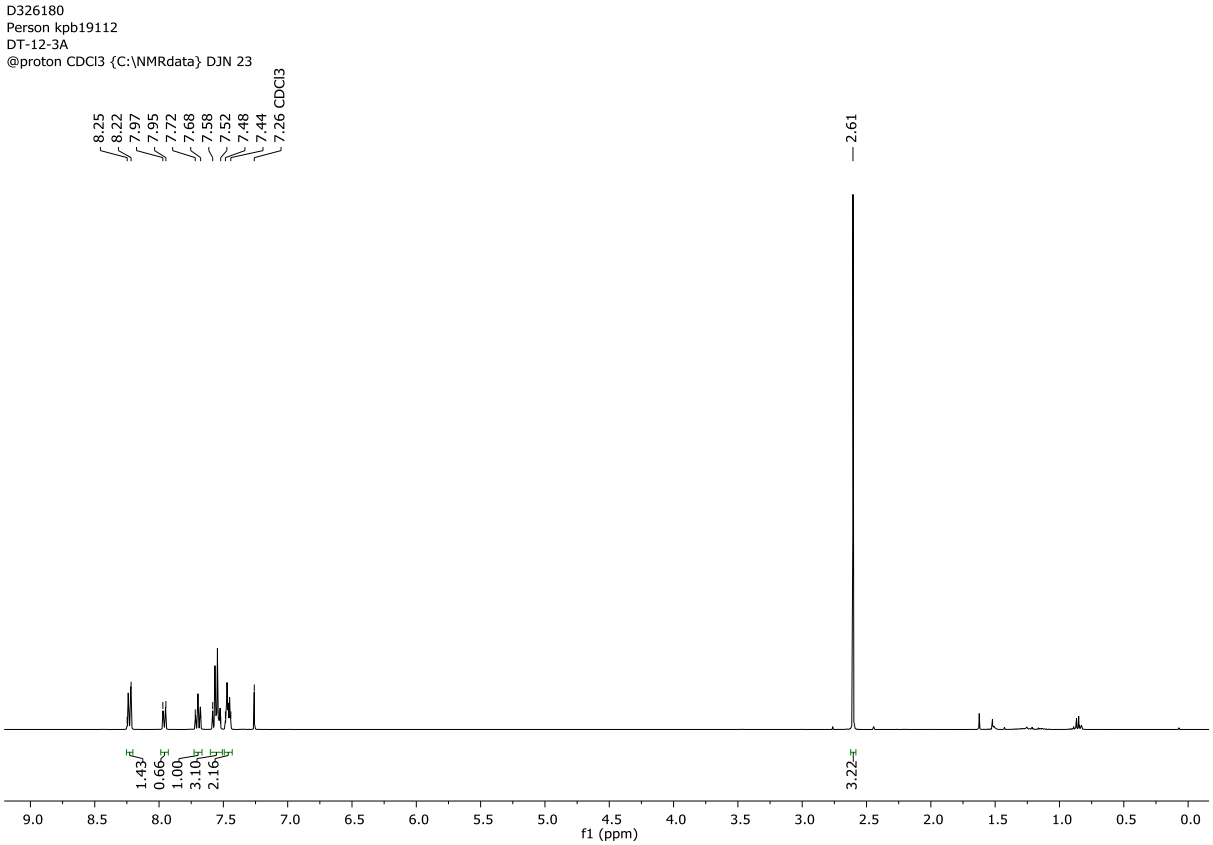


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and nitrobenzene (entry 1, Table S7).

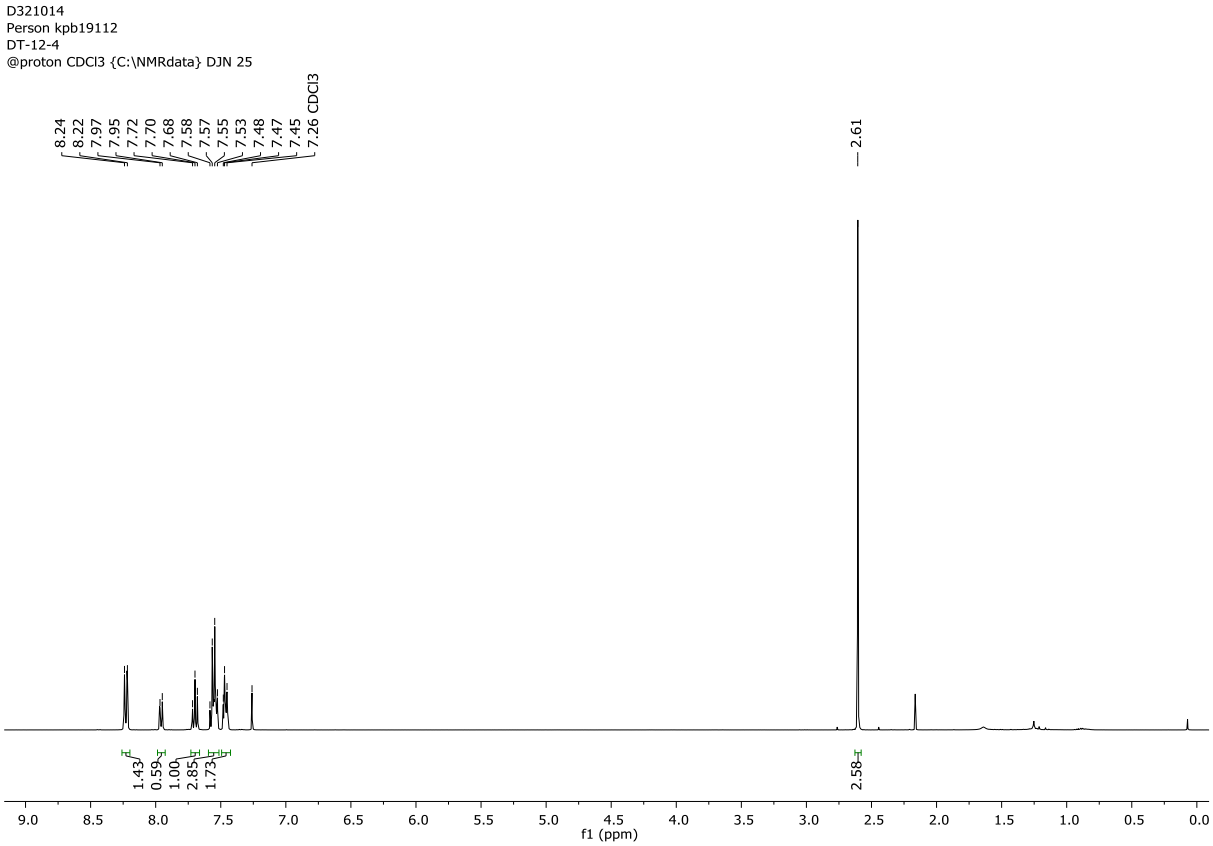


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and nitrobenzene (entry 2, Table S7).

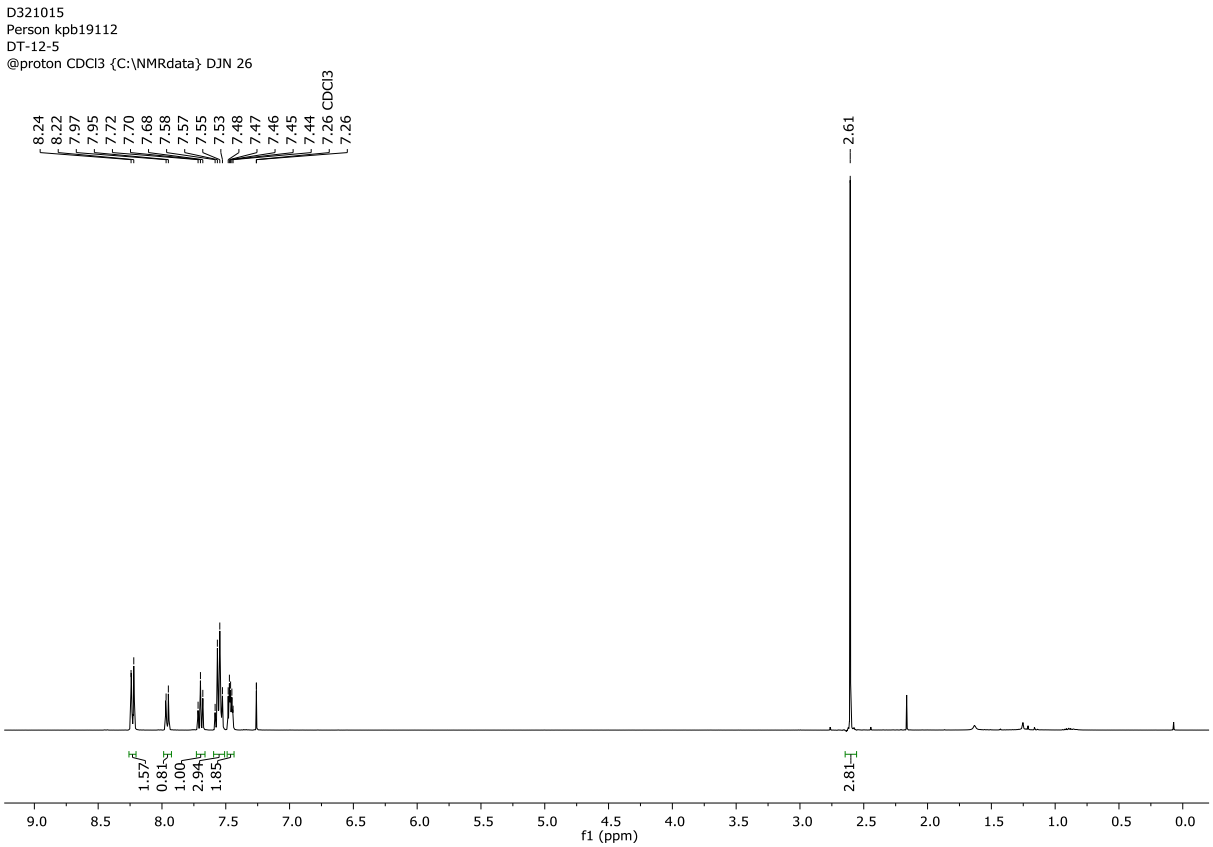
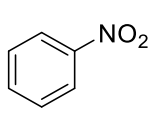
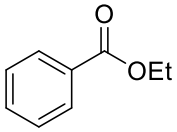


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and nitrobenzene (entry 3, Table S7).

Table S8. Determination of the competition rate constant κ from the labelling experiment between nitrobenzene and ethyl benzoate.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	12.3 mg	15.0 mg	8.7 mg

Deuteration expected at δ (**R1**) = 8.26 – 8.20 ppm and at δ (**R2**) = 8.08 – 8.02 ppm
Determined against integral at δ (**R1**) = 7.70 ppm and at δ (**R2**) = 4.38 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.26 – 8.20 (m, 2H/D, **R1**), 8.08 – 8.02 (m, 2H/D, **R2**), 7.70 (t, *J* = 7.4 Hz, 1H, **R1**), 7.59 – 7.51 (m, 2H, **R1** and 1H, **R2**), 7.43 (t, *J* = 7.6 Hz, 2H, **R2**), 4.38 (q, *J* = 7.1 Hz, 2H, **R2**), 1.39 (t, *J* = 7.1 Hz, 3H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	0.88	1.00	56	1.83	2.12	14	5.58
2	1.04	1.00	48	1.87	2.06	9	6.76
3	0.76	1.00	62	1.74	2.01	13	6.71
			Average κ = 6.35				

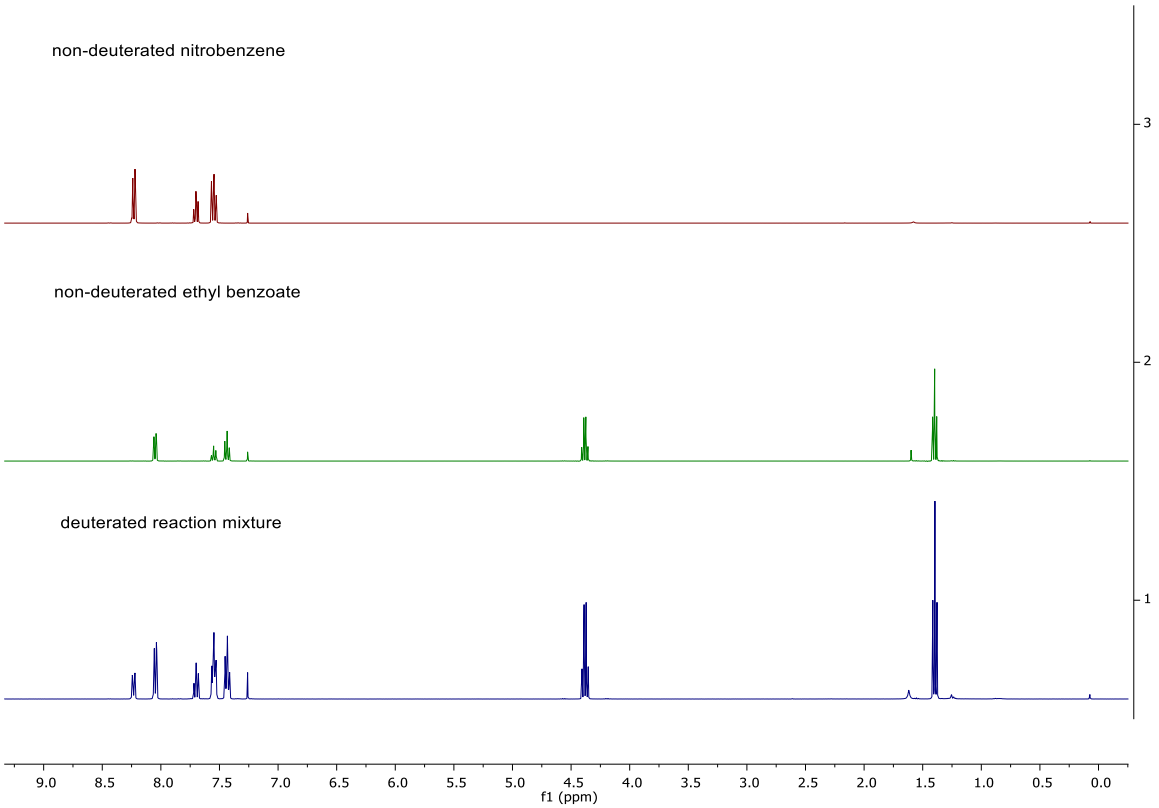


Figure S41. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

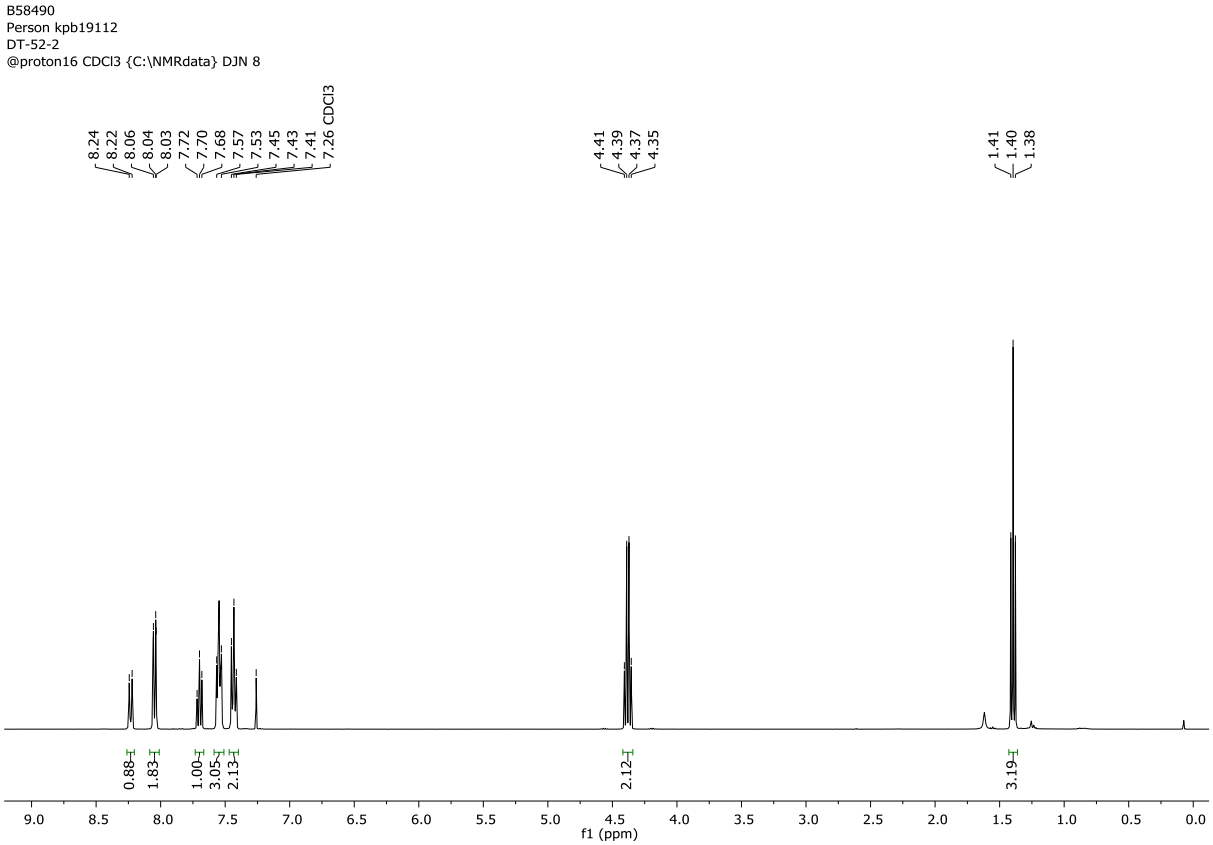


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between nitrobenzene and ethyl benzoate (entry 1, Table S8).

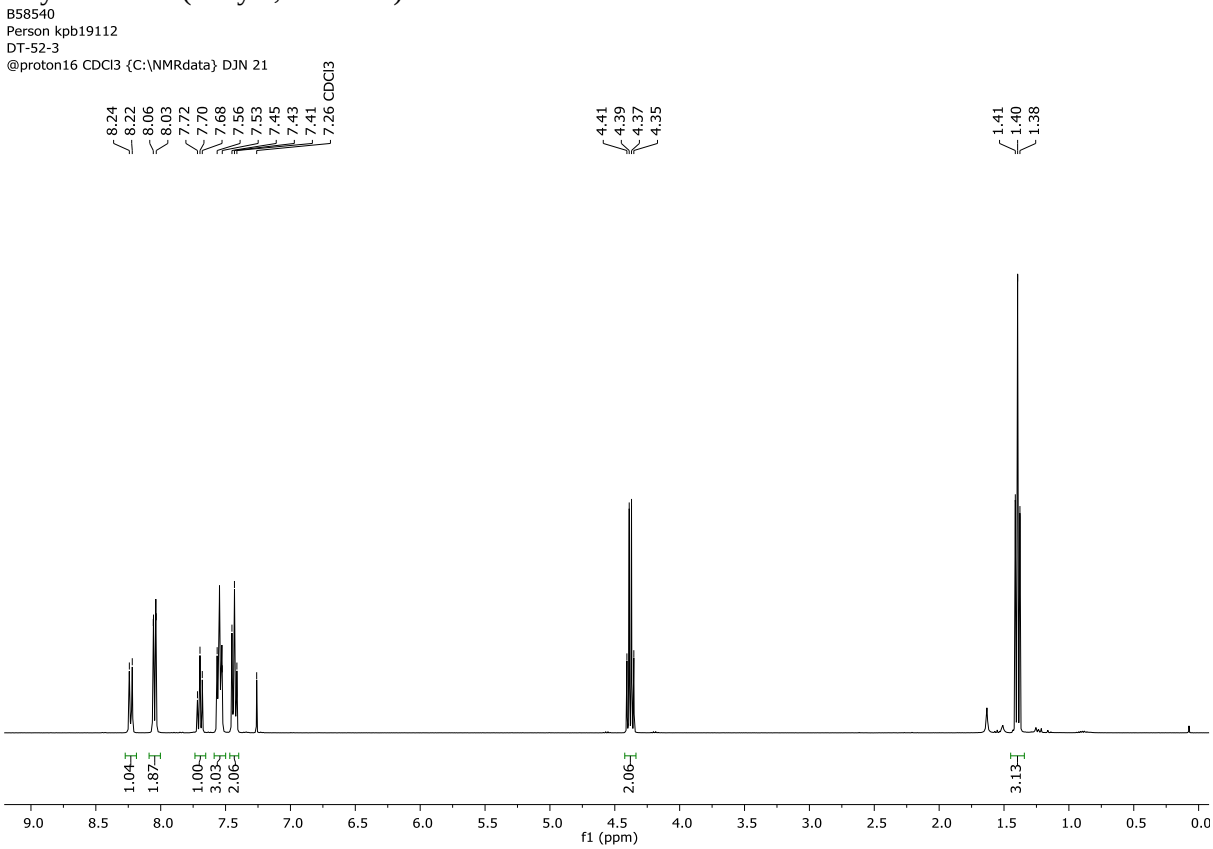


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between nitrobenzene and ethyl benzoate (entry 2, Table S8).

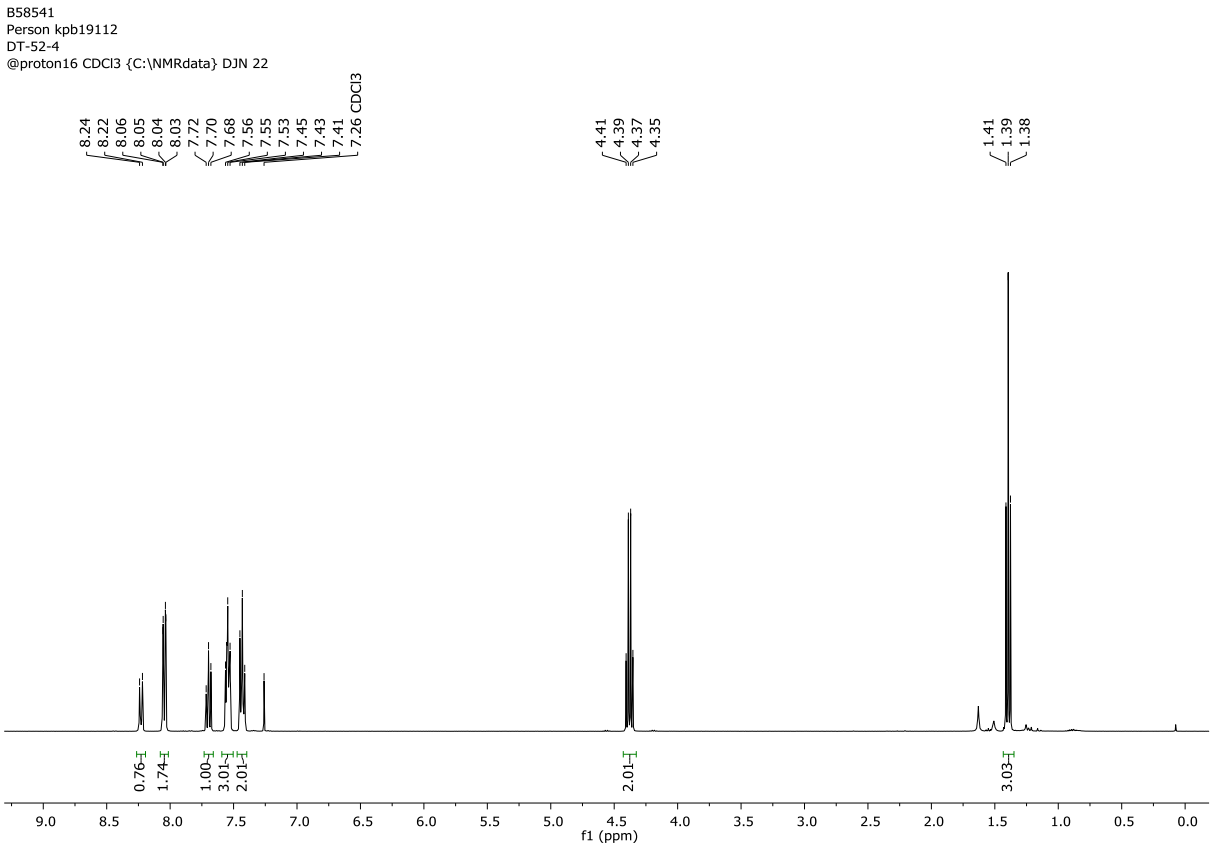
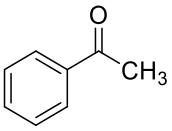
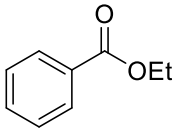


Figure S44. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between nitrobenzene and ethyl benzoate (entry 3, Table S8).

Table S9. Determination of the competition rate constant κ from the labelling experiment between acetophenone and ethyl benzoate.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	12.0 mg	15.0 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.99 – 7.93 ppm and at δ (**R2**) = 8.08 – 8.02 ppm
Determined against integral at δ (**R1**) = 2.61 ppm and at δ (**R2**) = 4.38 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 8.02 (m, 2H/D, **R2**), 7.99 – 7.93 (m, 2H/D **R1**), 7.59 – 7.52 (m, 1H, **R1** and 1H, **R2**), 7.49 – 7.40 (m, 2H, **R1** and 2H, **R2**), 4.38 (q, *J* = 7.1 Hz, 2H, **R2**), 2.61 (s, 3H, **R1**), 1.39 (t, *J* = 7.1 Hz, 3H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	0.74	3.00	63	1.93	2.14	10	9.63
2	0.59	3.00	71	2.37	2.66	11	10.58
3	0.54	3.00	73	1.89	2.13	11	10.95
			Average κ = 10.38				

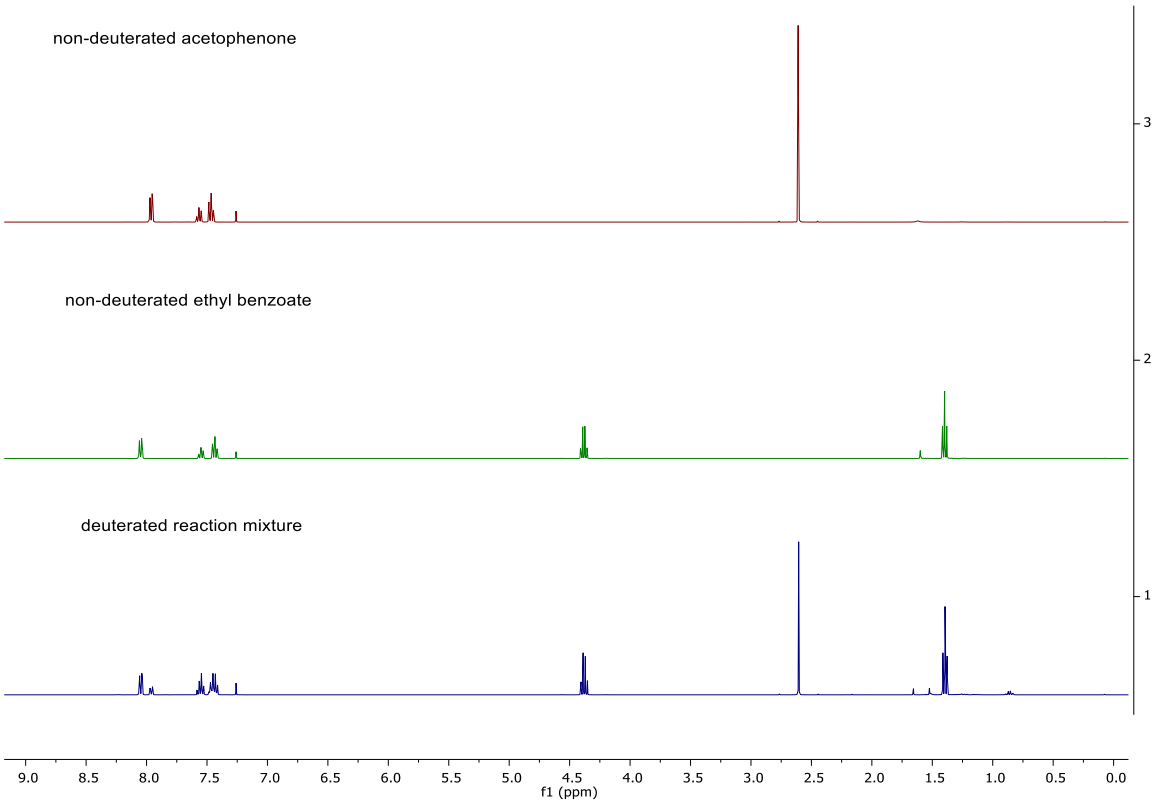


Figure S45. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

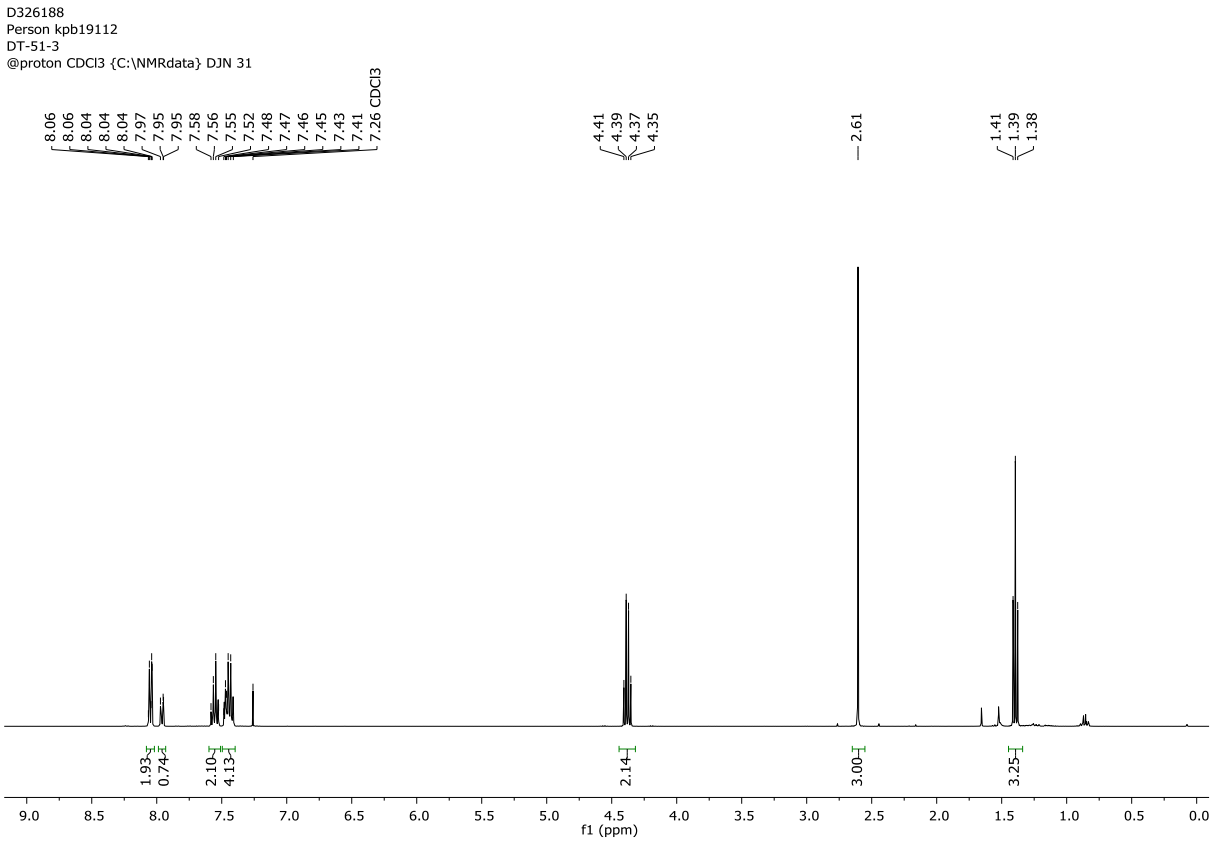


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and ethyl benzoate (entry 1, Table S9).

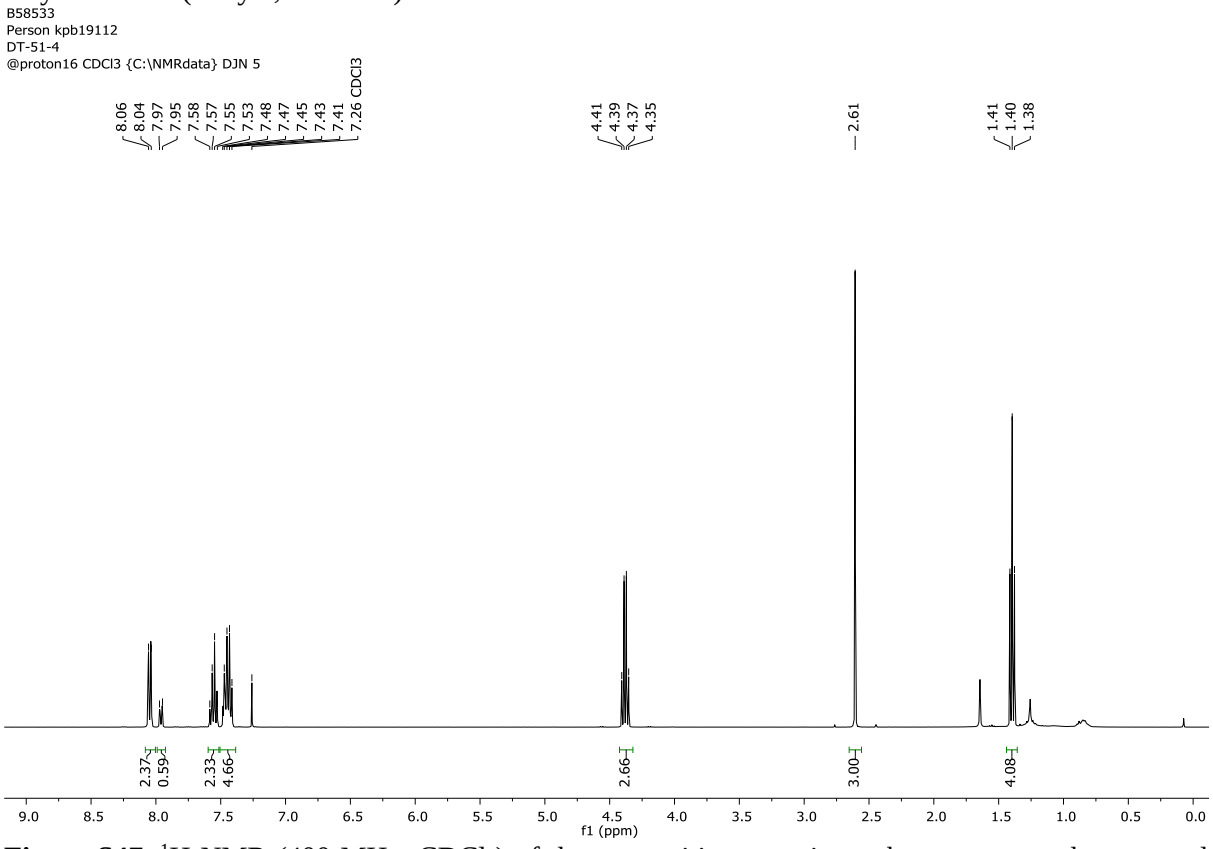


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and ethyl benzoate (entry 2, Table S9).

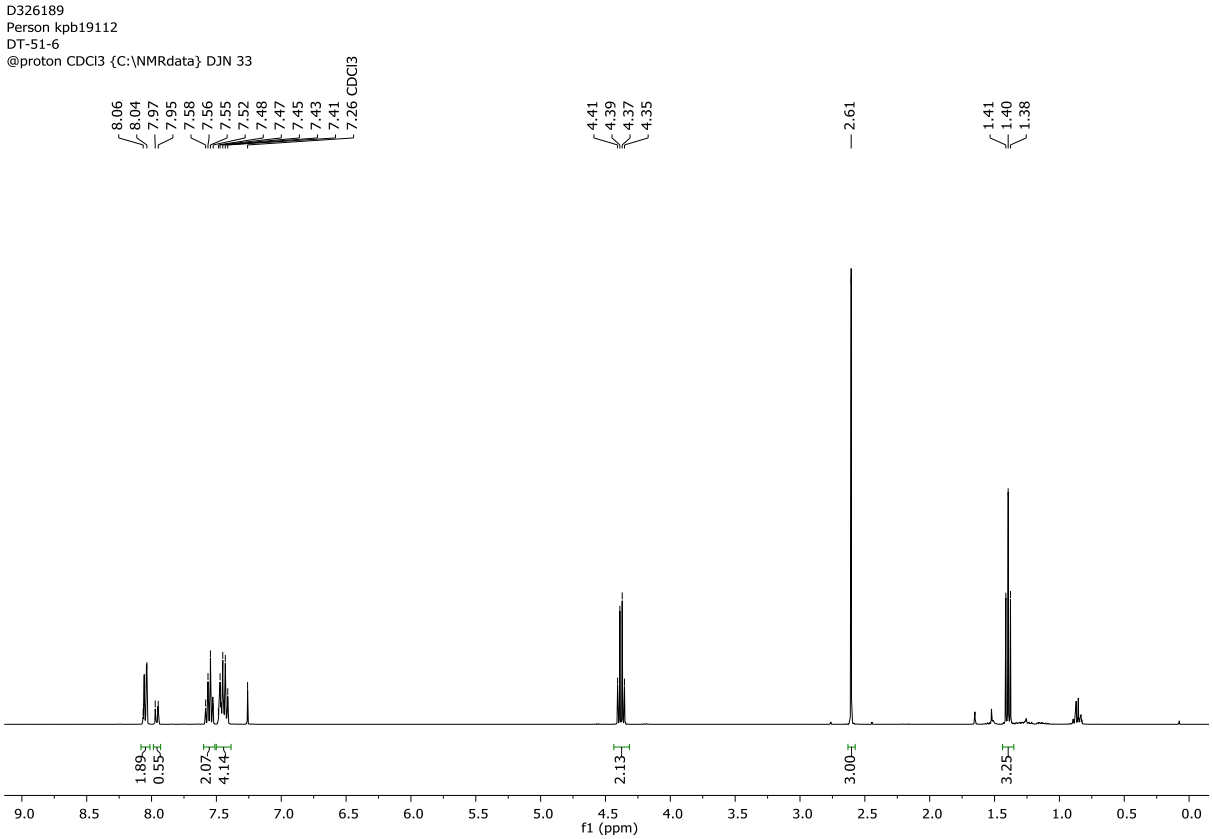
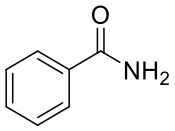
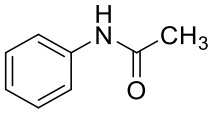


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and ethyl benzoate (entry 3, Table S9).

Table S10. Determination of the competition rate constant κ from the labelling experiment between acetanilide and benzamide.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	12.1 mg	13.5 mg	4.3 mg (2.5 mol %)

Deuteration expected at δ (**R1**) = 7.91 – 7.84 ppm and at δ (**R2**) = 7.60 – 7.55 ppm
Determined against integral at δ (**R1**) = 7.47 – 7.41 ppm and at δ (**R2**) = 7.30 – 7.24 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.90 (br, 1H, **R2**), 7.96 (br, 1H, **R1**), 7.91 – 7.84 (m, 2H/D, **R1**), 7.60 – 7.55 (m, 2H/D, **R2**), 7.54 – 7.41 (m, 1H, **R1**), 7.47 – 7.41 (m, 2H, **R1**), 7.35 (br, 1H, **R1**), 7.30 – 7.24 (m, 2H, **R2**), 7.04 –6.99 (m, 1H, R2), 2.04 (s, 3H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.75	1.93	9	1.86	2.00	7	1.35
2	1.76	1.98	11	1.86	2.00	7	1.62
3	1.72	1.96	12	1.85	2.00	8	1.68
				Average κ = 1.55			

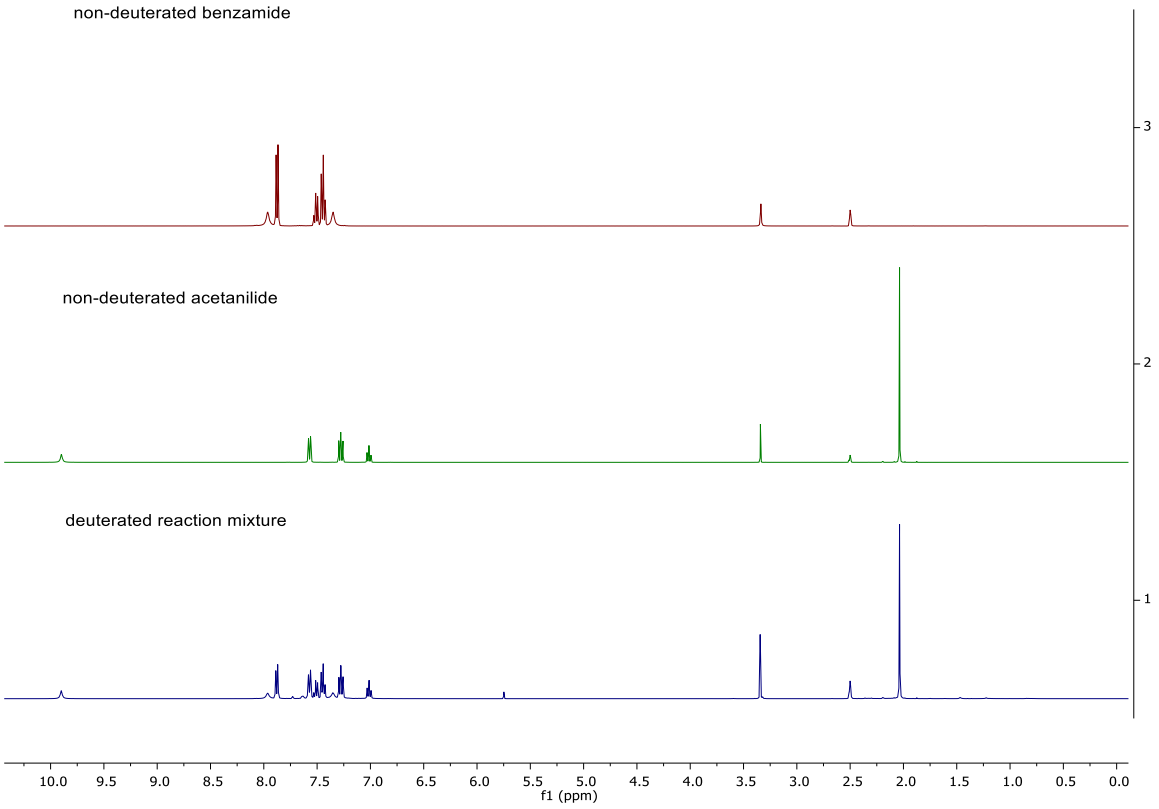


Figure S49. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

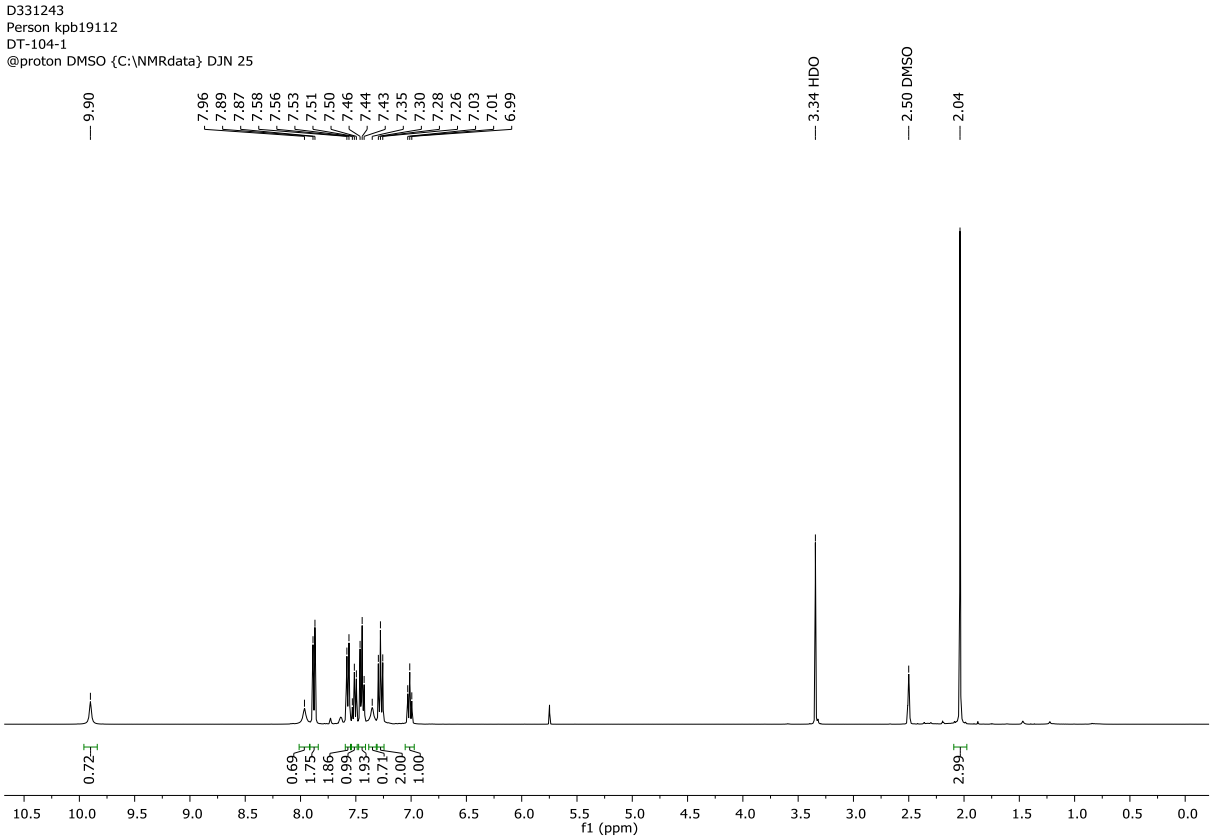


Figure S50. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between acetanilide and benzamide (entry 1, Table S10).

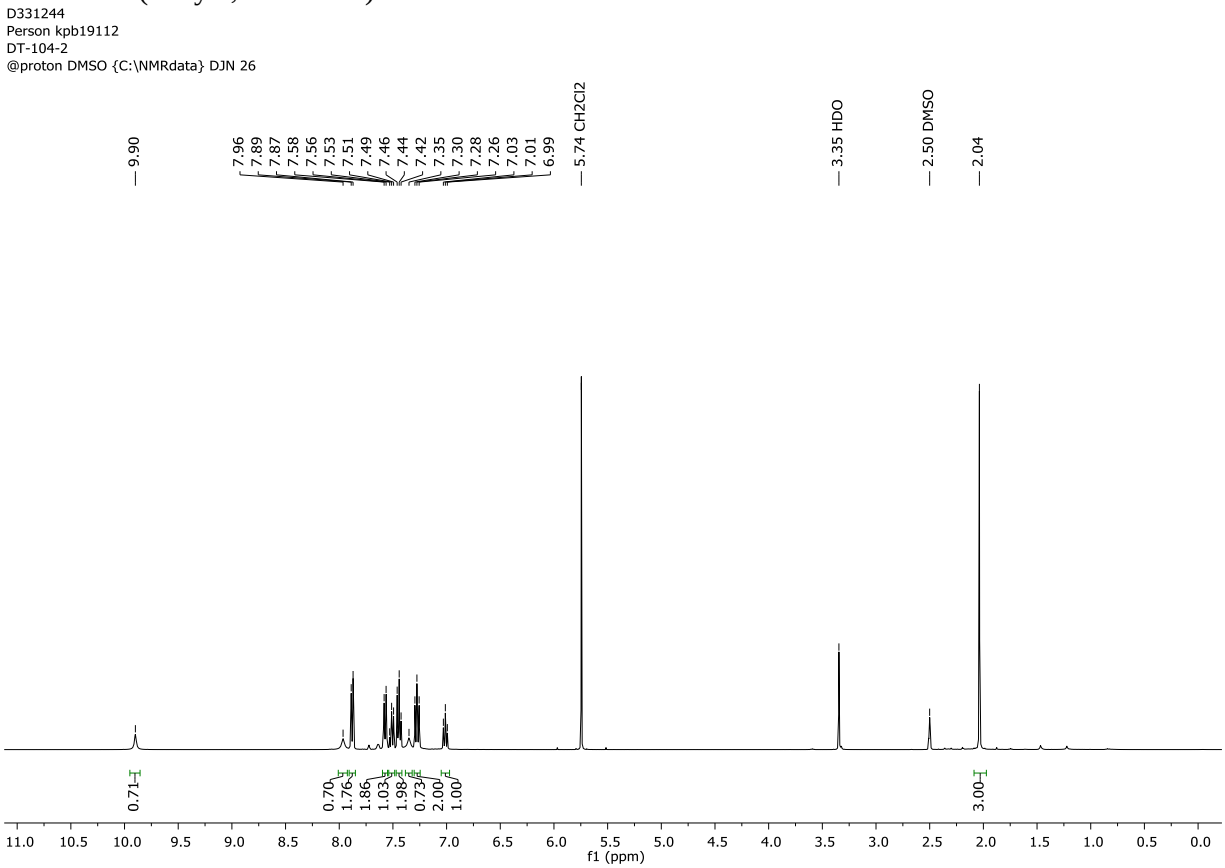


Figure S51. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between acetanilide and benzamide (entry 2, Table S10).

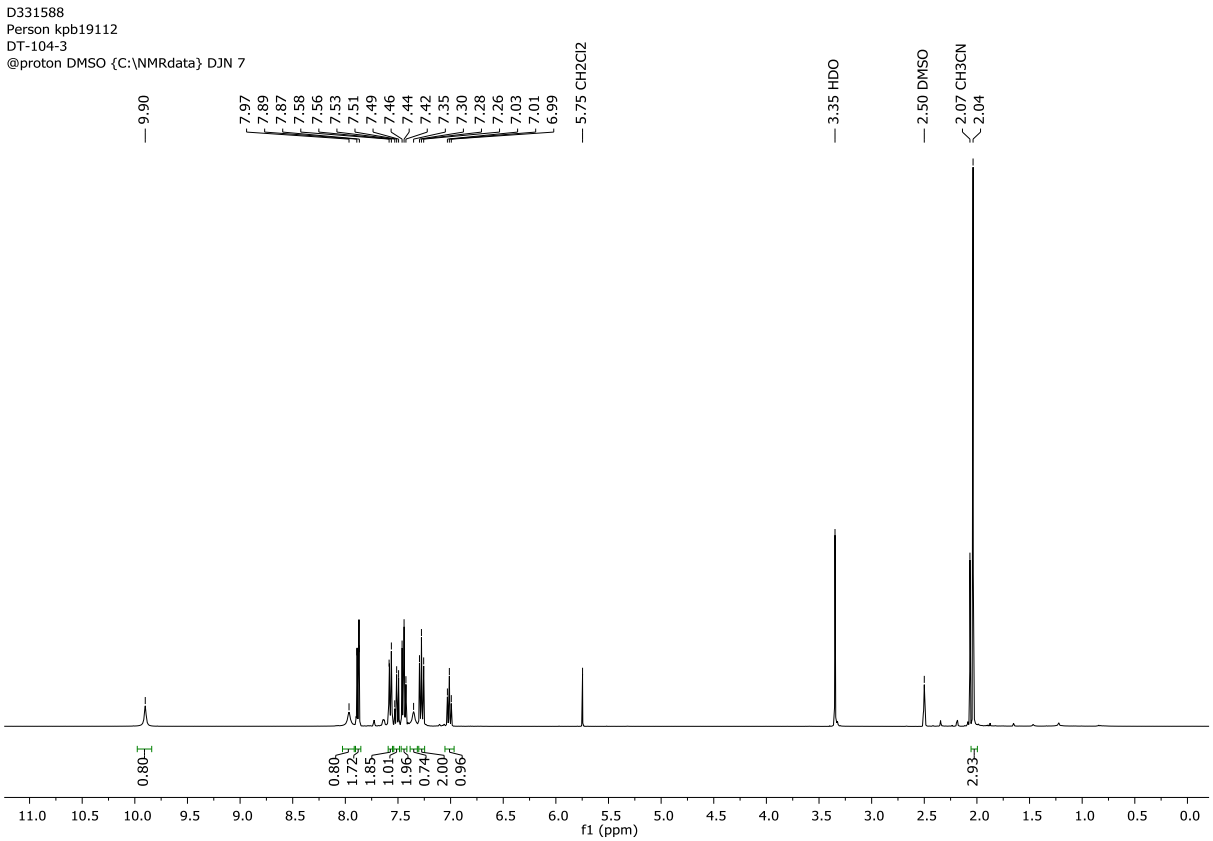
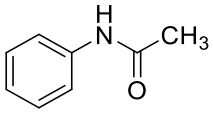
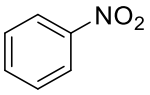


Figure S52. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between acetanilide and benzamide (entry 3, Table S10).

Table S11. Determination of the competition rate constant κ from the labelling experiment between acetanilide and nitrobenzene.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	13.5 mg	12.3 mg	4.3 mg (2.5 mol %)

Deuteration expected at δ (**R1**) =7.60 – 7.55 ppm and at δ (**R2**) = 8.26 – 8.20 ppm
Determined against integral at δ (**R1**) = 7.30 – 7.24 ppm and at δ (**R2**) = 7.87 – 7.81 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.90 (br, 1H, **R1**), 8.26 – 8.20 (m, 2H/D, **R2**), 7.87 – 7.81 (m, 1H, **R2**), 7.70 – 7.65 (m, 2H, **R2**), 7.60 – 7.55 (m, 2H/D, **R1**), 7.30 – 7.24 (m, 2H, **R1**), 7.04 –6.99 (m, 1H, **R1**), 2.04 (s, 3H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N =1H	$\%D_{R2}$	κ
1	1.11	2.00	45	1.75	0.91	4	15.01
2	0.81	2.00	60	1.68	0.89	6	15.63
3	0.94	2.00	53	1.73	0.91	5	14.89
			Average κ = 15.18				

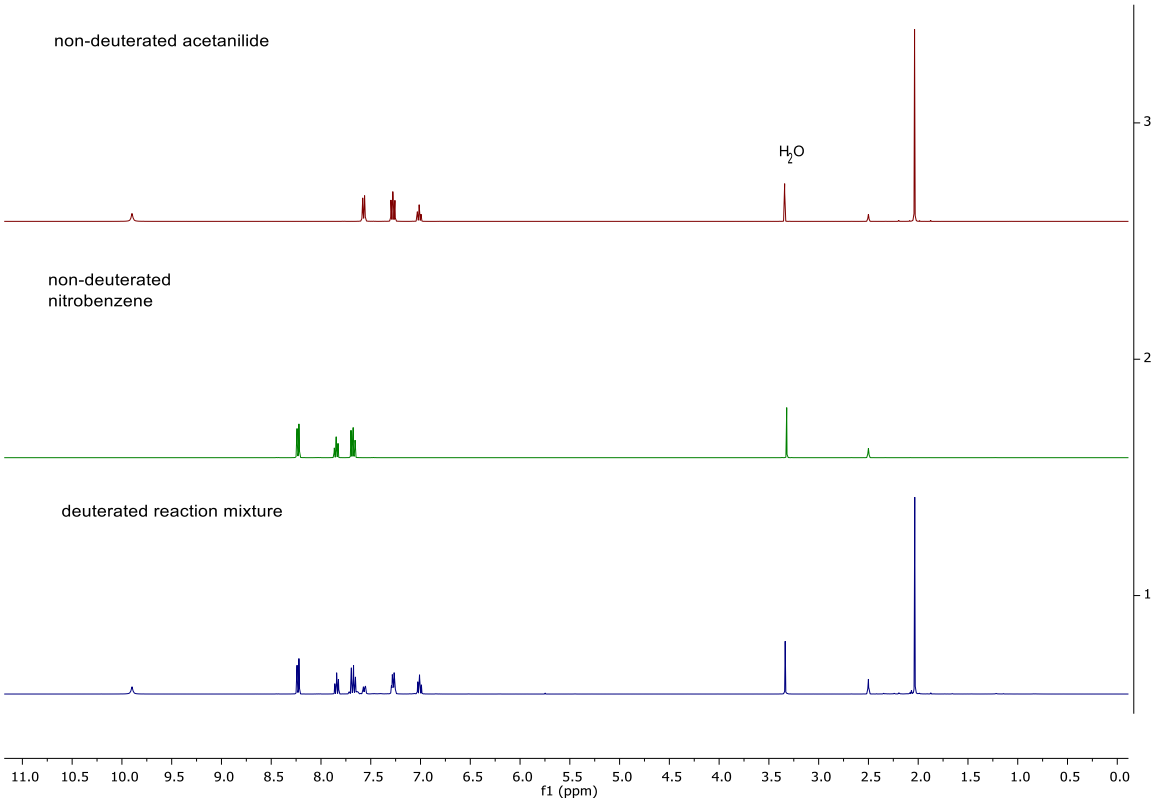


Figure S53. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

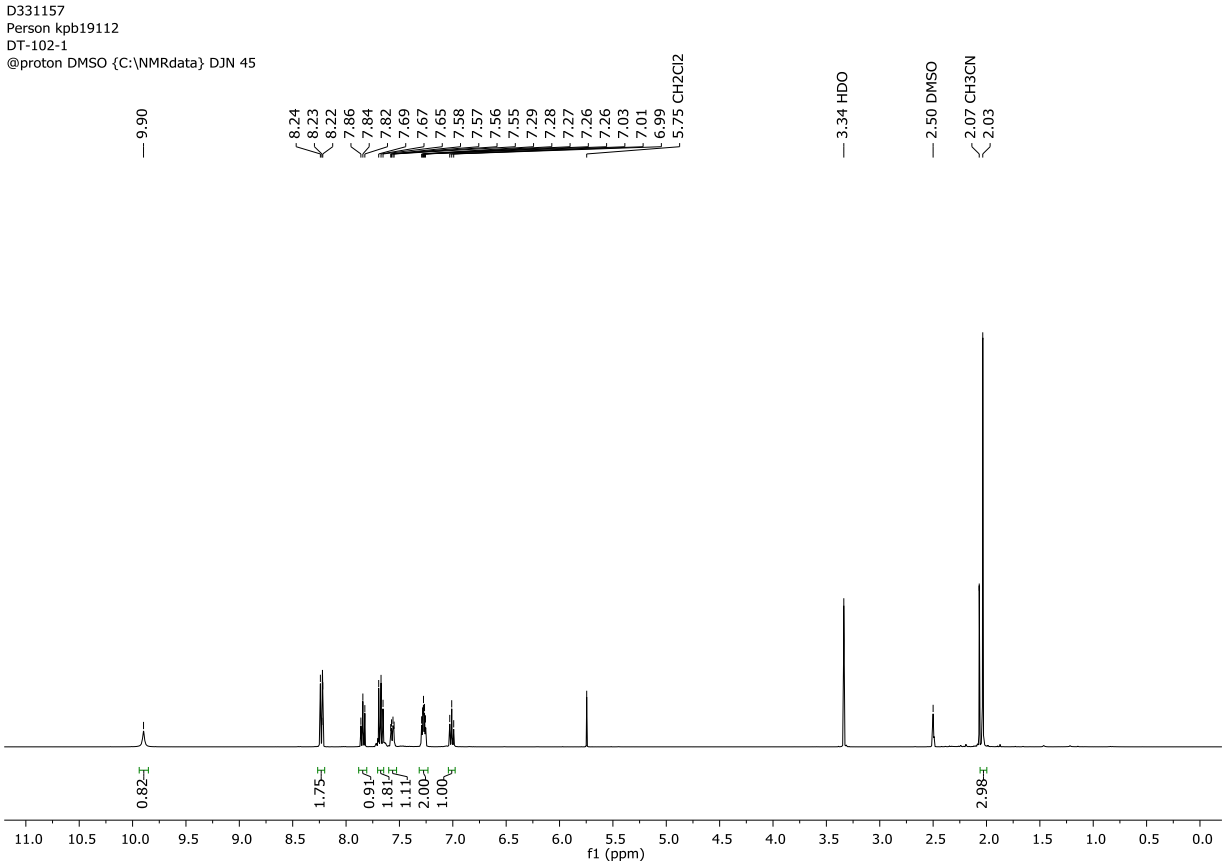


Figure S54. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between acetanilide and nitrobenzene (entry 1, Table S11).

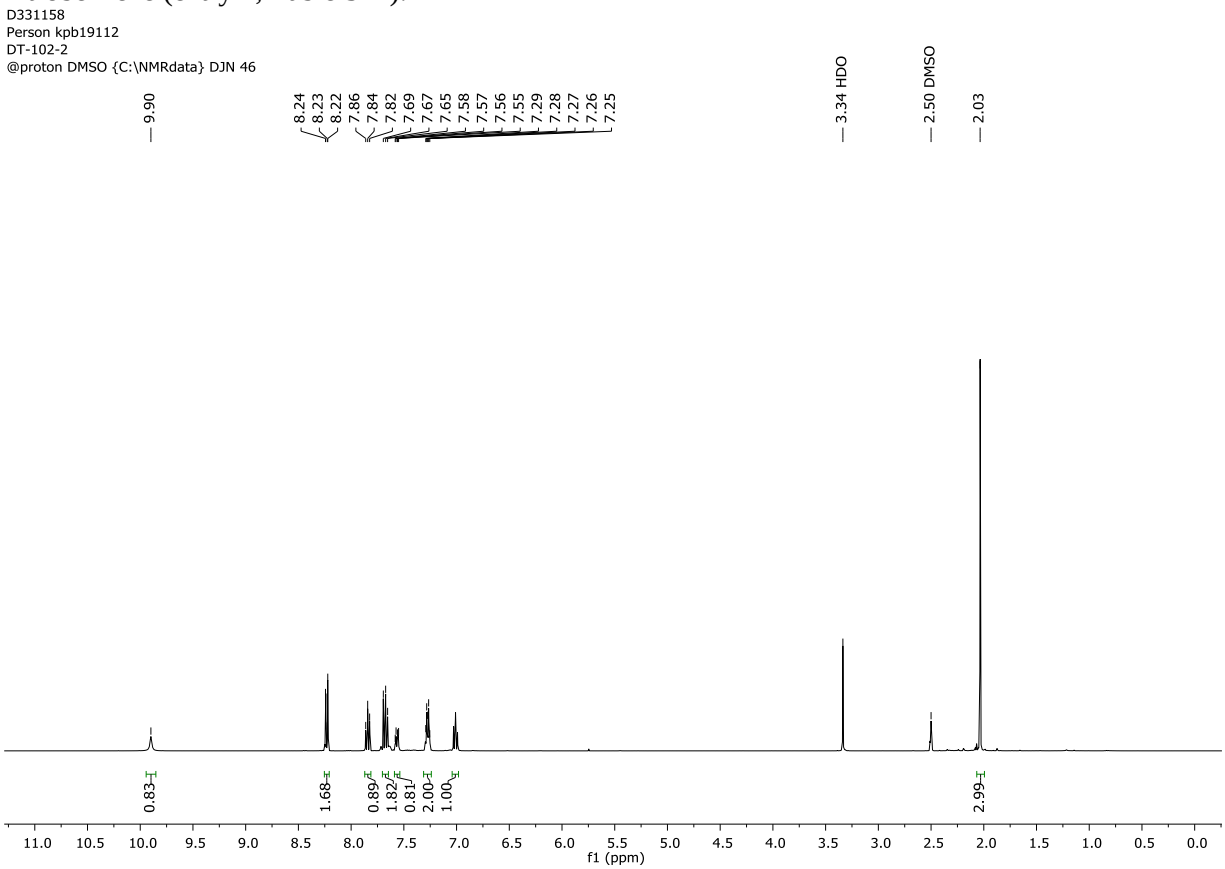


Figure S55. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between acetanilide and nitrobenzene (entry 2, Table S11).

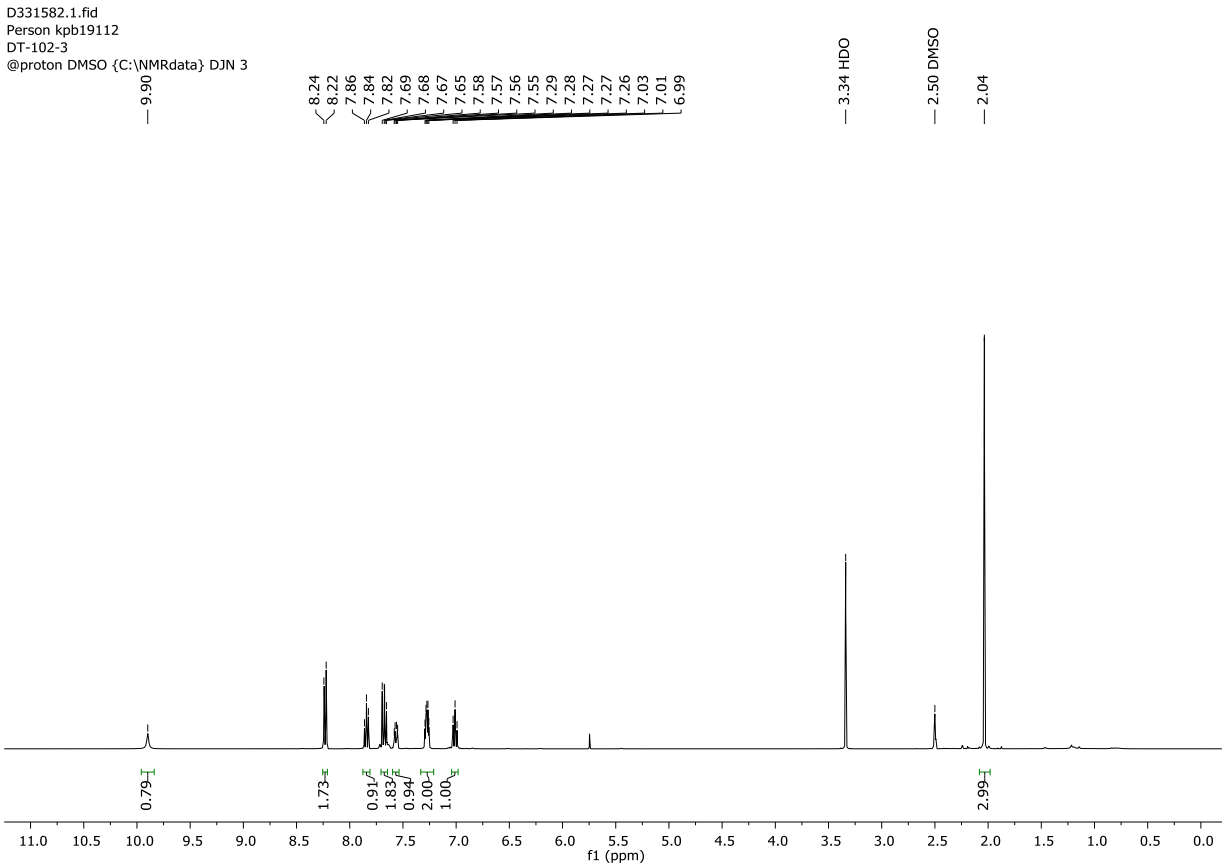
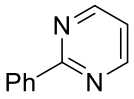
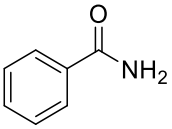


Figure S56. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between acetanilide and nitrobenzene (entry 3, Table S11).

Table S12. Determination of the competition rate constant κ from the labelling experiment between 2-phenylpyrimidine and benzamide.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	15.6 mg	12.1 mg	8.7 mg

Deuteration expected at δ (**R1**) = 8.48 – 8.43 ppm and at δ (**R2**) = 7.85 – 7.77 ppm
Determined against integral at δ (**R1**) = 8.81 ppm and at δ 7.55 – 7.39 ppm for **R2**
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.81 (d, *J* = 4.9 Hz, 2H, **R1**), 8.48 – 8.43 (m, 2H/D, **R1**), 7.85 – 7.77 (m, 2H/D, **R2**), 7.55 – 7.39 (m, 3H, **R1** and 3H, **R2**), 7.18 (t, *J* = 4.8 Hz, 1H, **R1**), 6.20 (br, 2H, **R2**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 3H	$\%D_{R2}$	κ
1	0.48	2.00	76	2.05	3.61 [a]	15	8.90
2	1.10	2.00	45	2.01	3.40 [b]	11	4.97
3	0.77	2.00	62	1.96	3.34 [c]	12	7.48
				Average κ = 7.12			

[a] $I_{R2(0)}$ = 6.61 – (2.00/2×3); [b] $I_{R2(0)}$ = 6.40 – (2.00/2×3); [c] $I_{R2(0)}$ = 6.34 – (2.00/2×3);

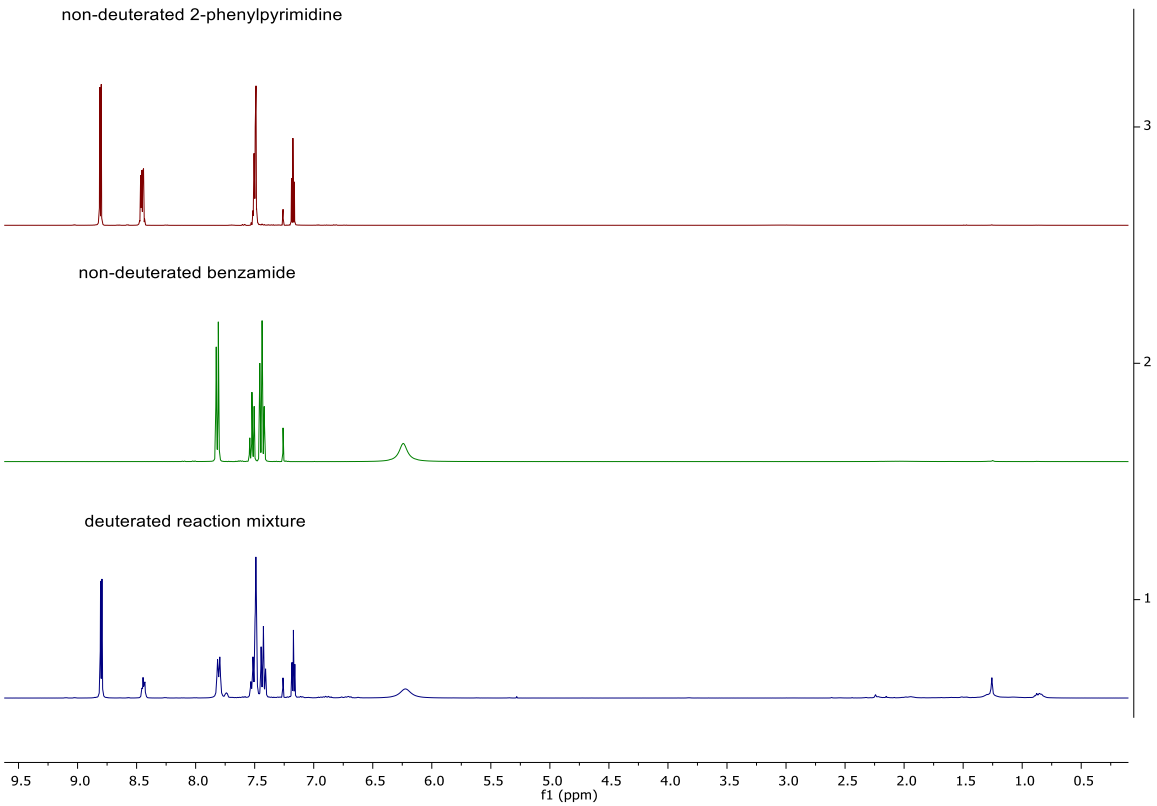


Figure S57. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

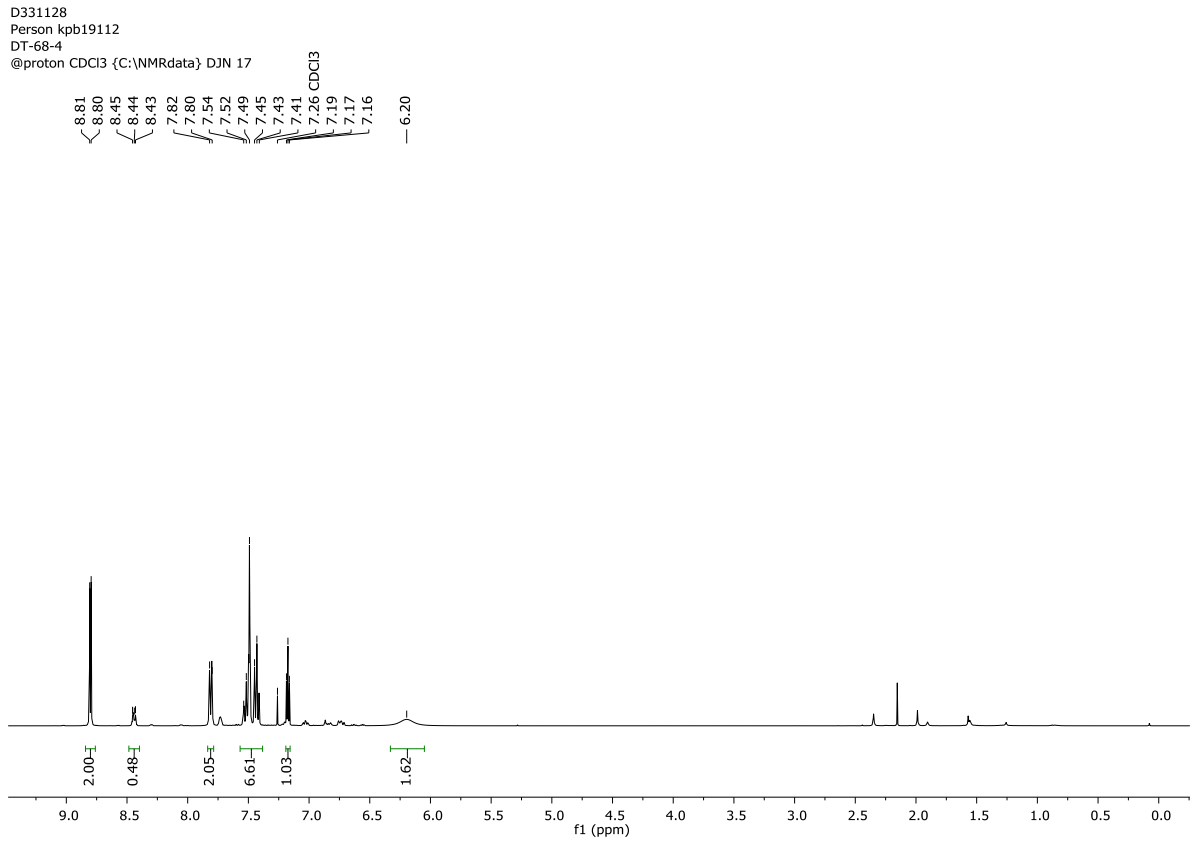


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyrimidine and benzamide (entry 1, Table S12).

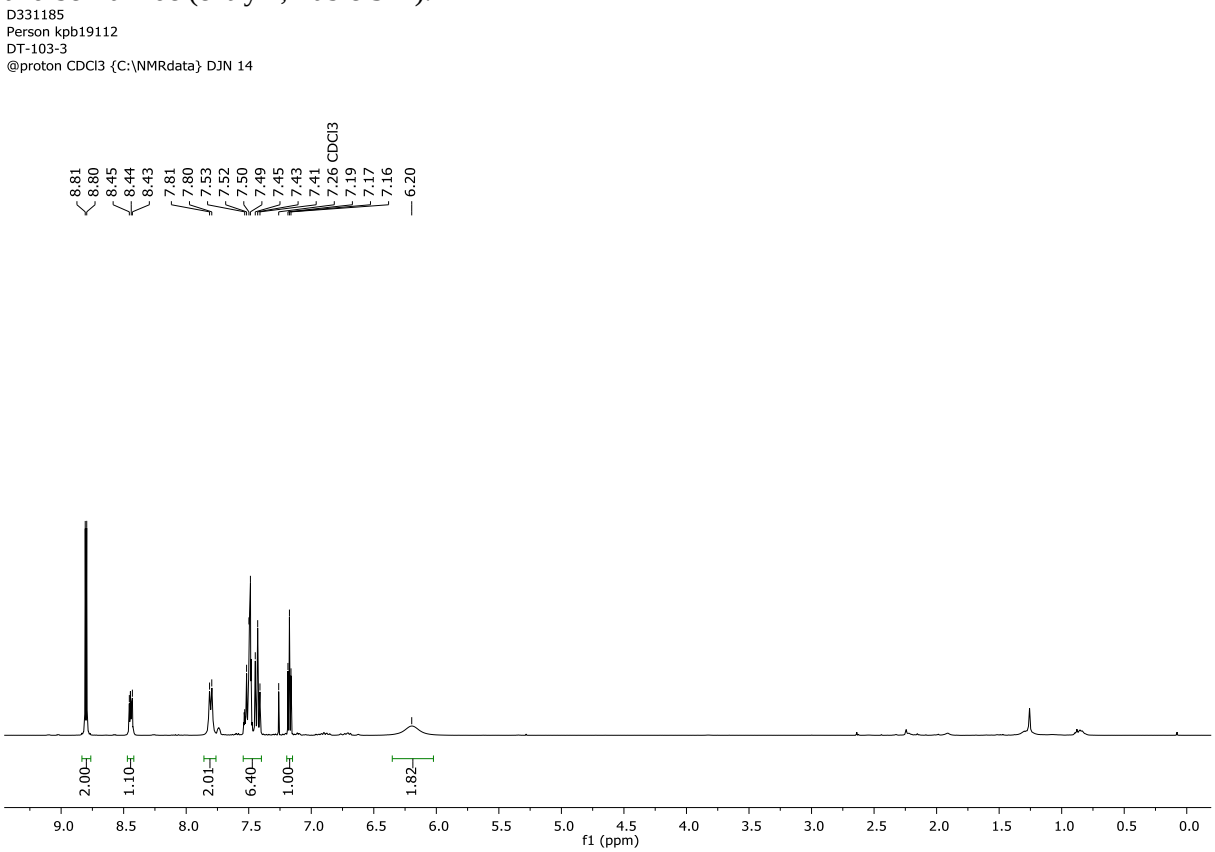


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyrimidine and benzamide (entry 2, Table S12).

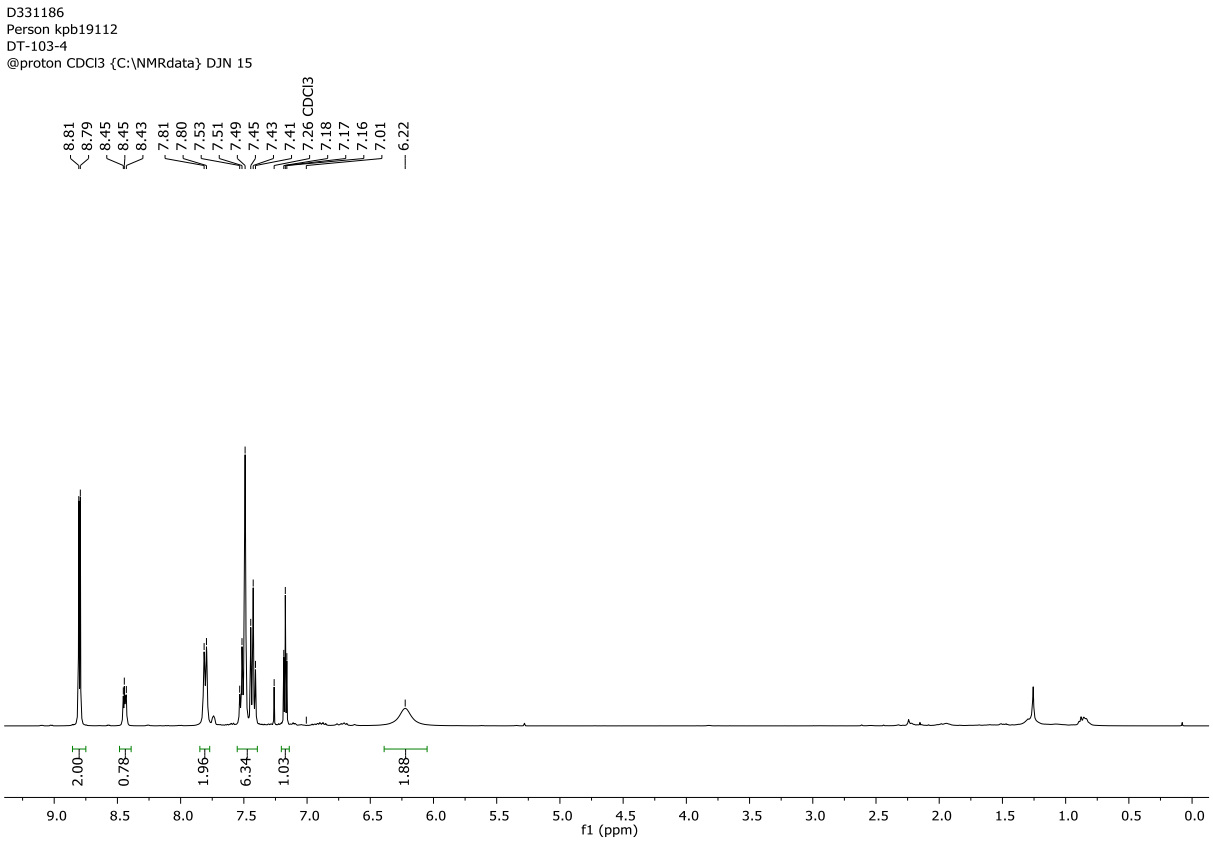
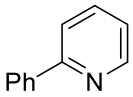
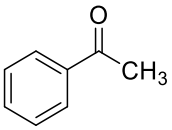


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyrimidine and benzamide (entry 3, Table S12).

Table S13. Determination of the competition rate constant κ from the labelling experiment between 2-phenylpyridine and acetophenone.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh$_3$][BArF$_{24}$]
Mass	15.5 mg	12.0 mg	8.7 mg

Deuteration expected at δ (**R1**) = 8.02 – 7.98 ppm and at δ (**R2**) = 7.98 – 7.94 ppm
Determined against integral at δ (**R1**) = 7.78 – 7.70 ppm and at δ (**R2**) = 2.60 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 – 8.66 (m, 1H, **R1**), 8.02 – 7.98 (m, 2H/D, **R1**), 7.98 – 7.94 (m, 2H/D, **R2**), 7.78 – 7.70 (m, 2H, **R1**), 7.59 – 7.53 (m, 1H, **R2**), 7.51 – 7.38 (m, 2H, **R2** and 3H, **R1**), 2.60 (s, 3H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 3H	$\%D_{R2}$	κ
1	1.75	2.26	23	1.97	3.00	2	16.92
2	1.62	2.26	28	1.96	3.00	2	16.48
3	1.60	2.25	29	1.96	3.00	2	16.88
Average κ = 16.76							

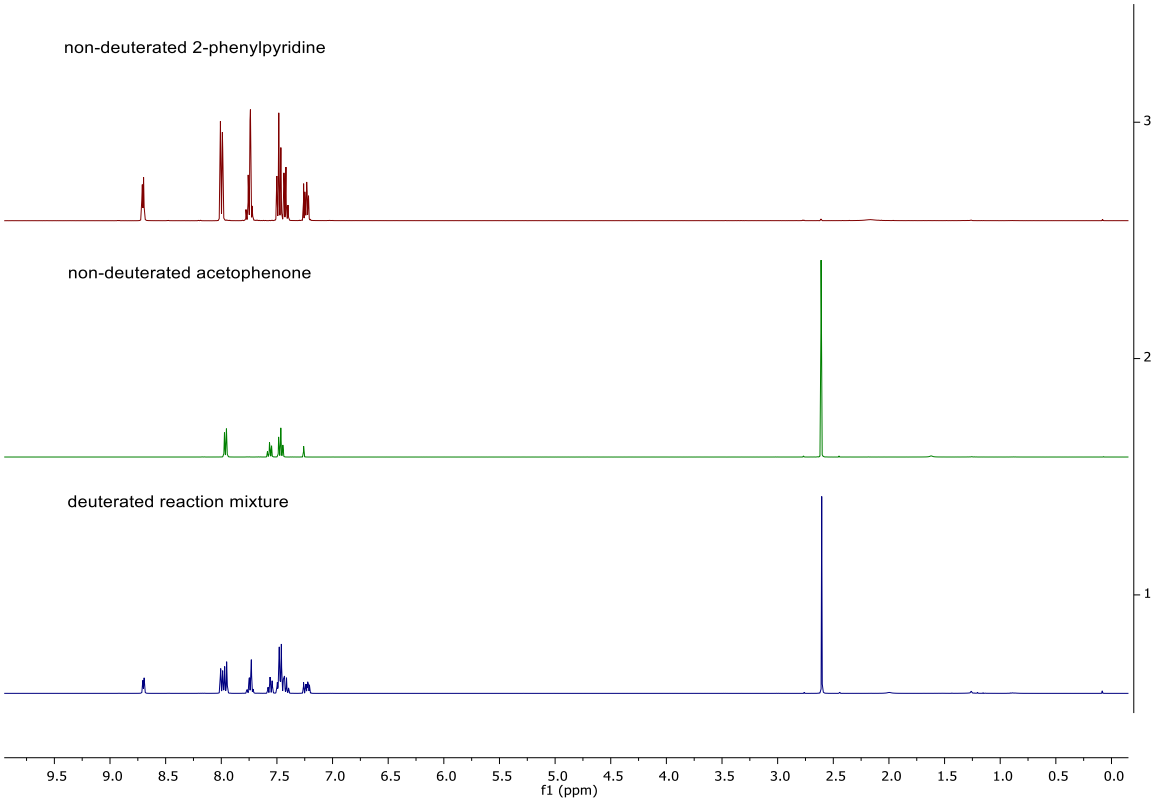


Figure S61. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

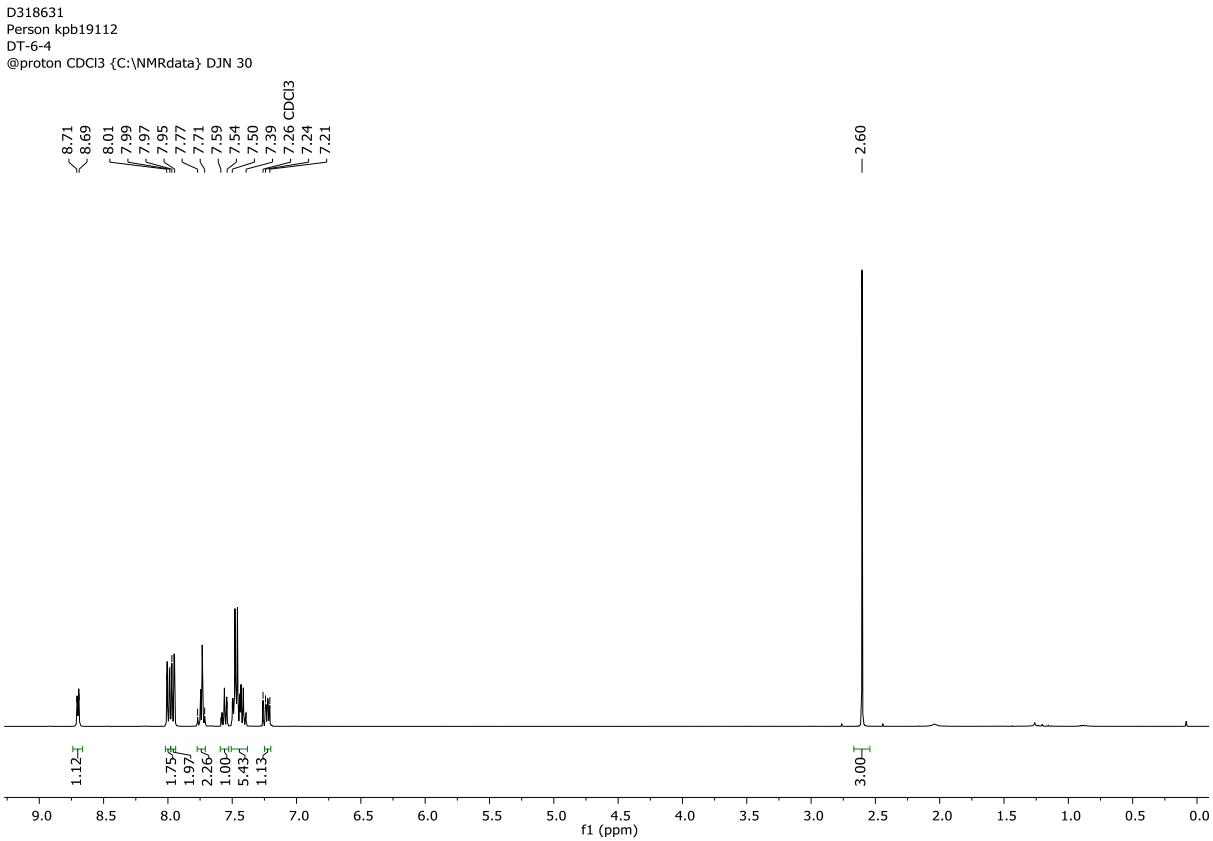


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between of 2-phenylpyridine and acetophenone (entry 1, Table S13).

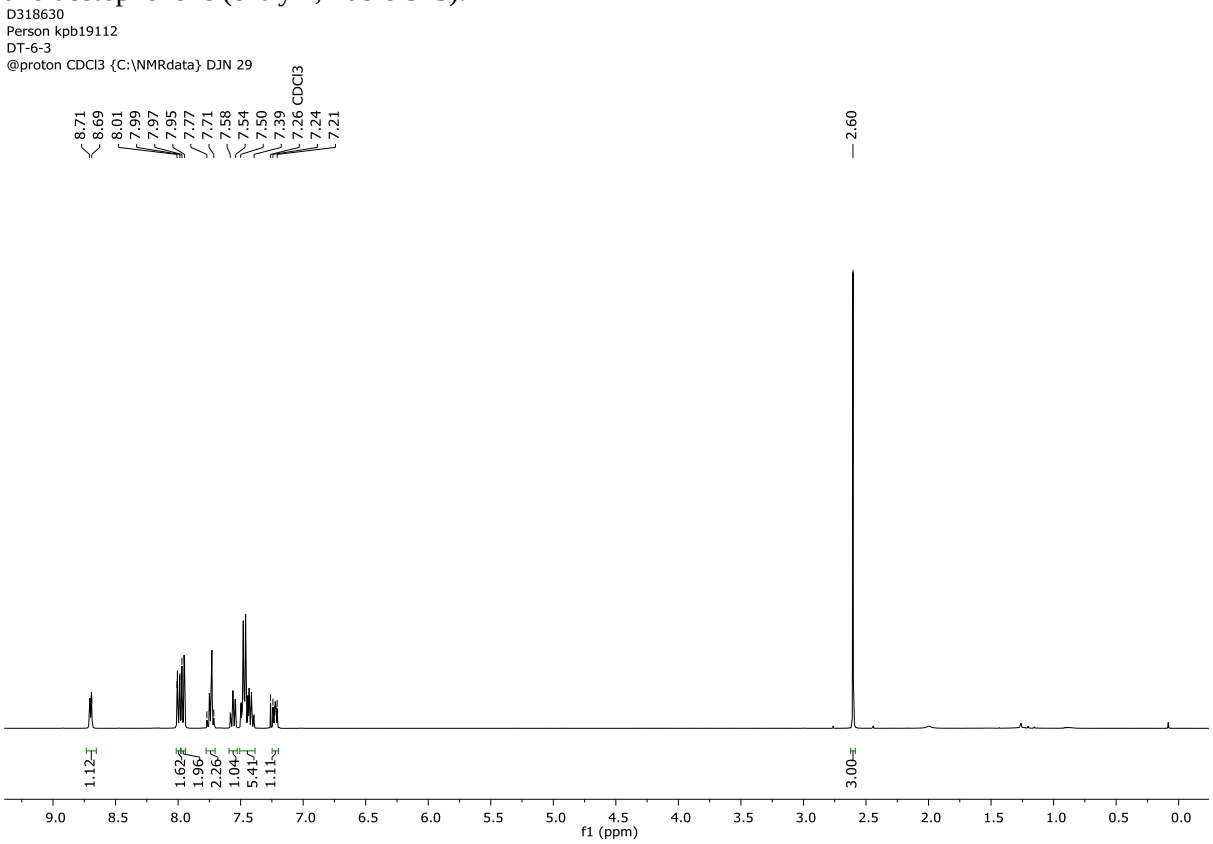


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between of 2-phenylpyridine and acetophenone (entry 2, Table S13).

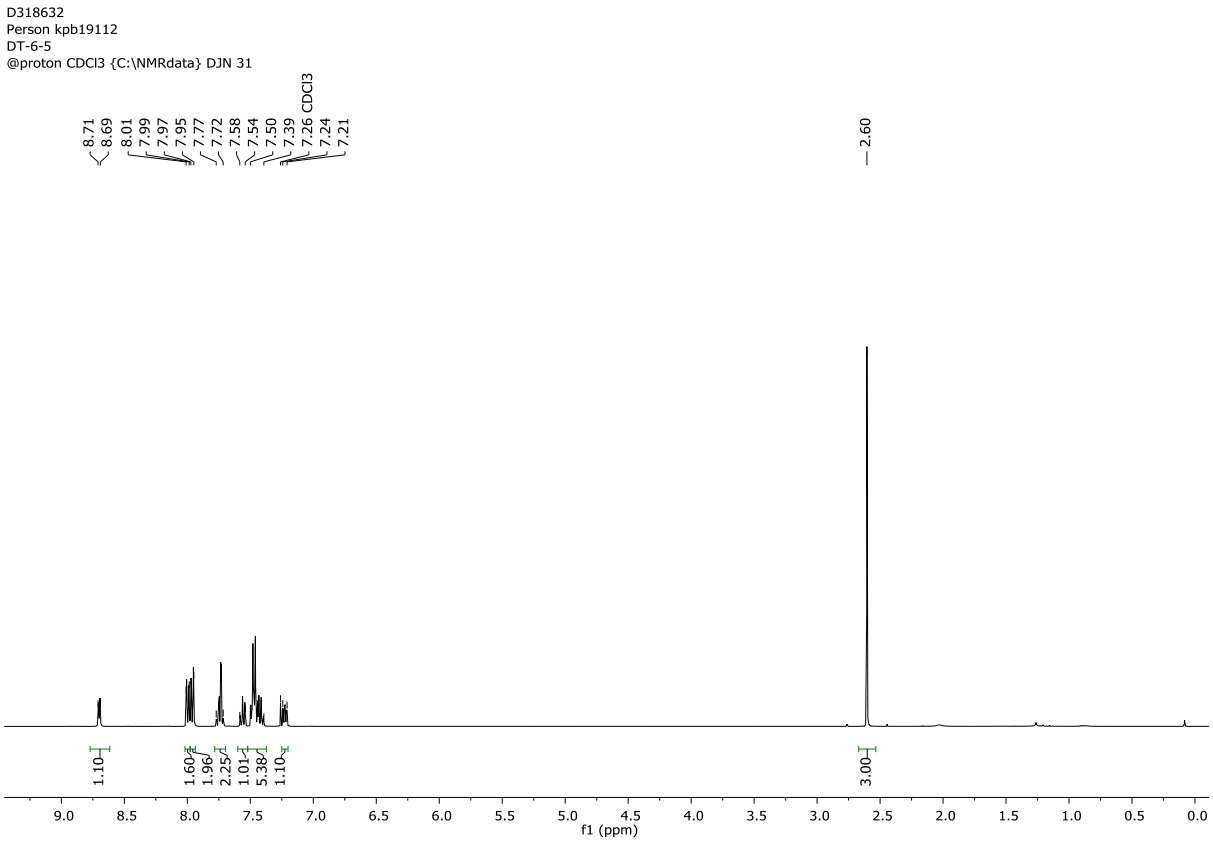
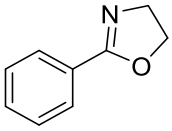
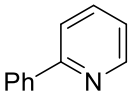


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between of 2-phenylpyridine and acetophenone (entry 3, Table S13).

Table S14. Determination of the competition rate constant κ from the labelling experiment between 2-phenyloxazoline and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	14.7 mg	15.5 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.97 – 7.93 ppm and at δ (**R2**) = 8.02 – 7.98 ppm
Determined against integral at δ (**R1**) = 4.44 ppm and at δ (**R2**) = 7.78 – 7.70 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 – 8.65 (m, 1H, **R2**), 8.02 – 7.98 (m, 2H/D **R1**), 7.97 – 7.93 (m, 2H/D **R2**), 7.78 – 7.70 (m, 2 **R2**), 7.51 – 7.37 (m, 3H, **R1** and 3H, **R2**), 7.25 – 7.20 (m, 1H, R2), 4.44 (t, *J* = 9.5 Hz, 2H, **R1**), 4.07 (t, *J* = 9.5 Hz, 2H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	0.61	1.36	55	1.40	2.00	30	2.25
2	0.72	1.36	47	1.59	2.00	21	2.77
3	0.44	1.59	72	1.41	2.00	30	3.68
			Average κ = 2.90				

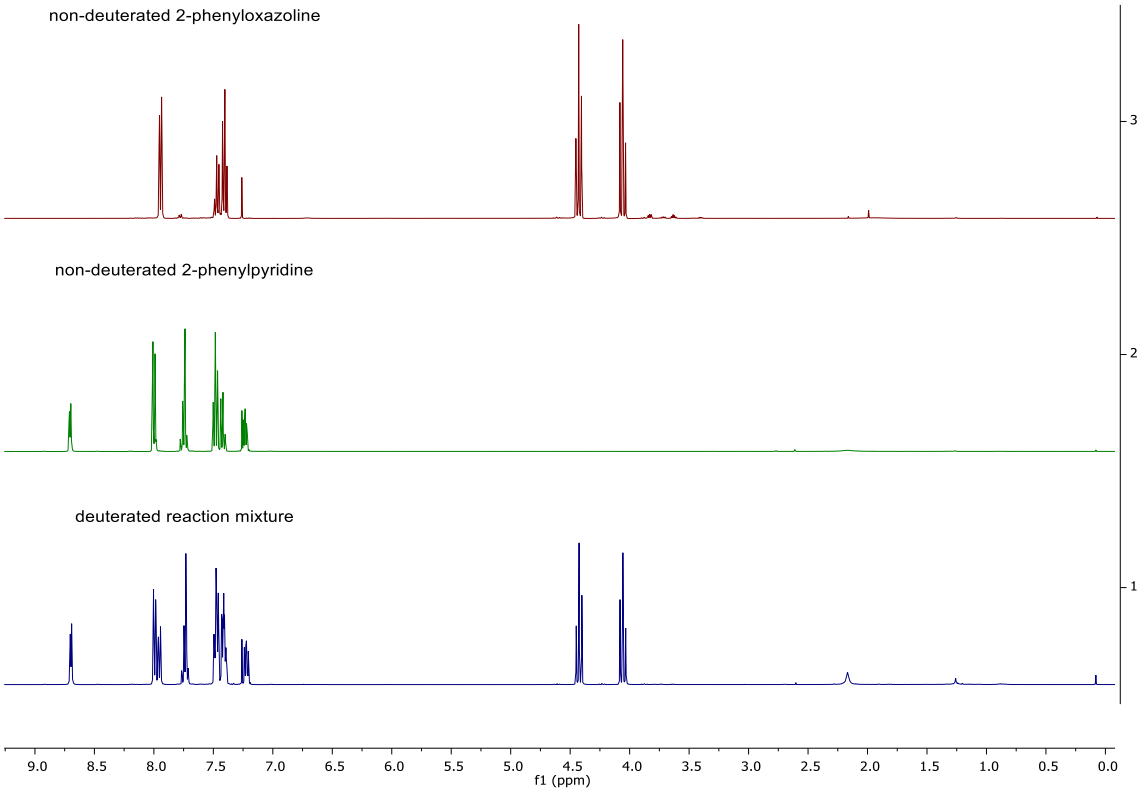


Figure S65. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

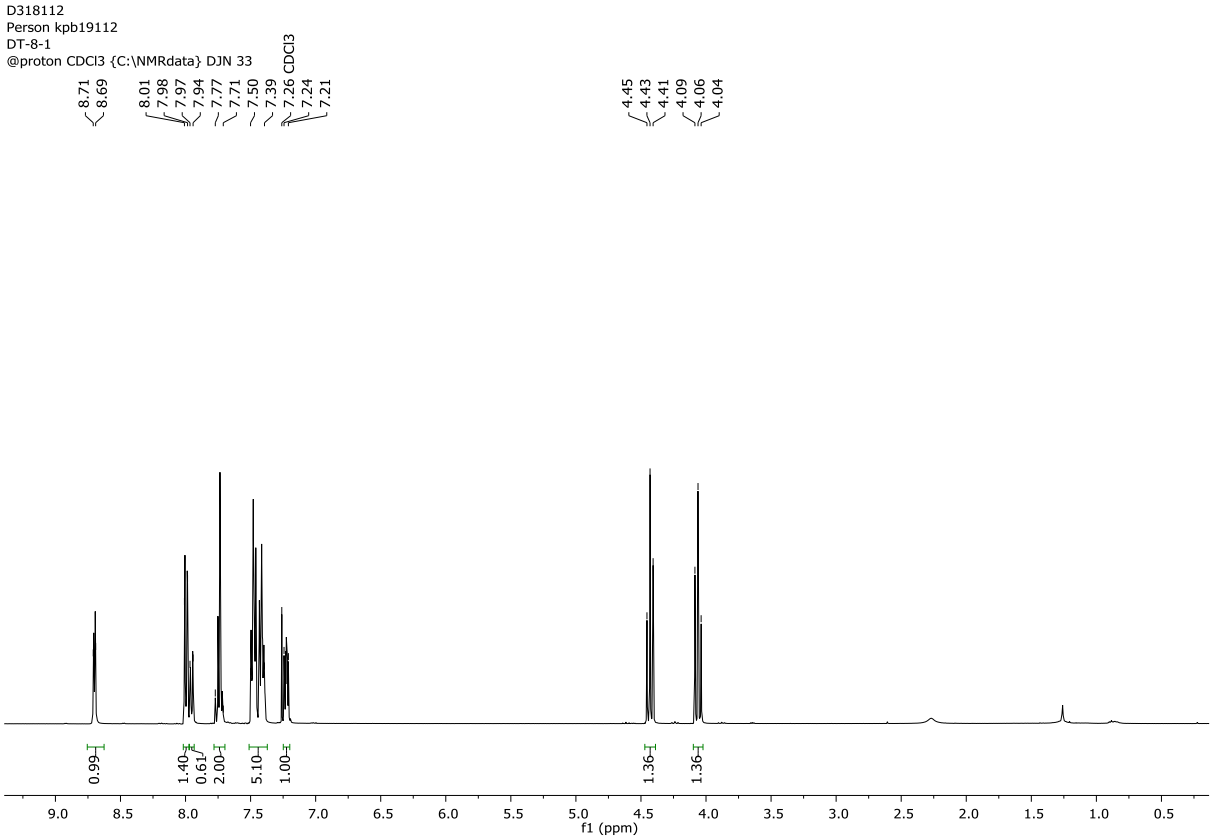


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylpyridine (entry 1, Table S14).

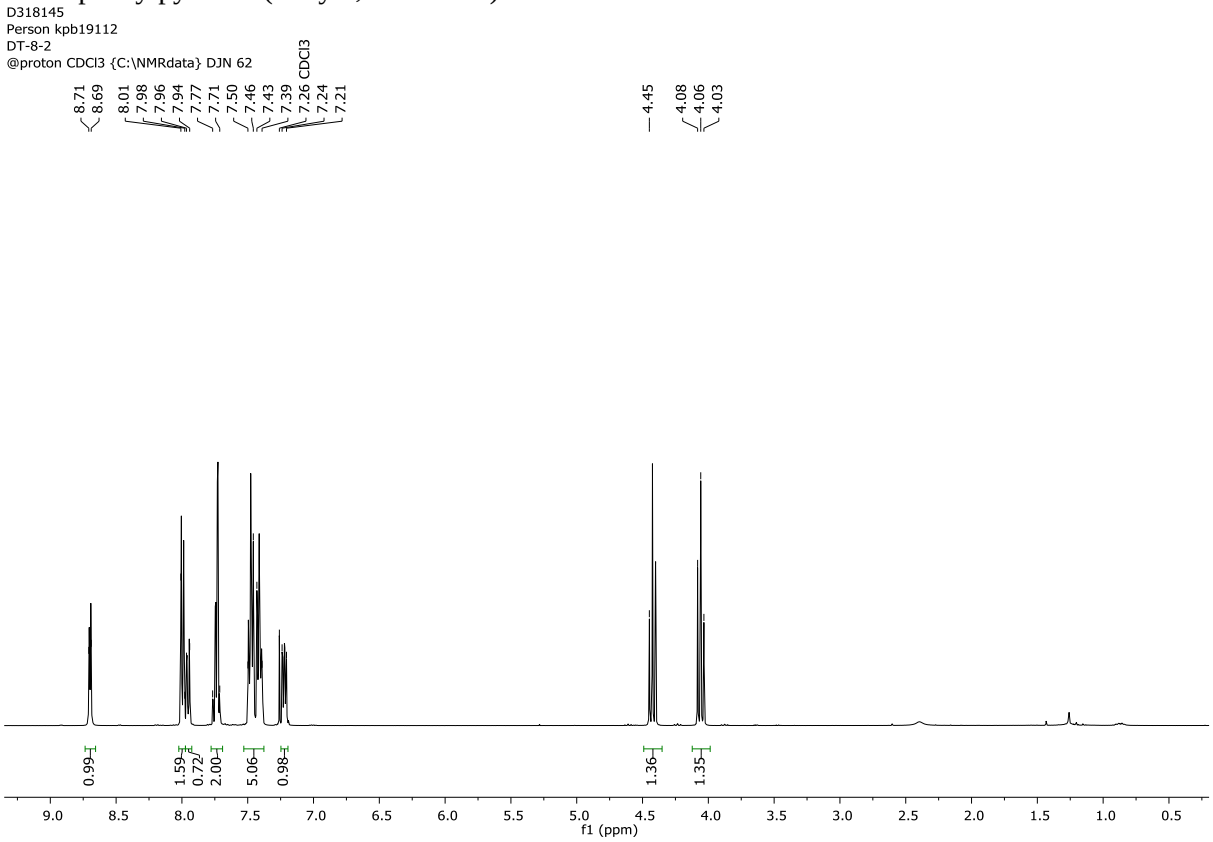


Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylpyridine (entry 2, Table S14).

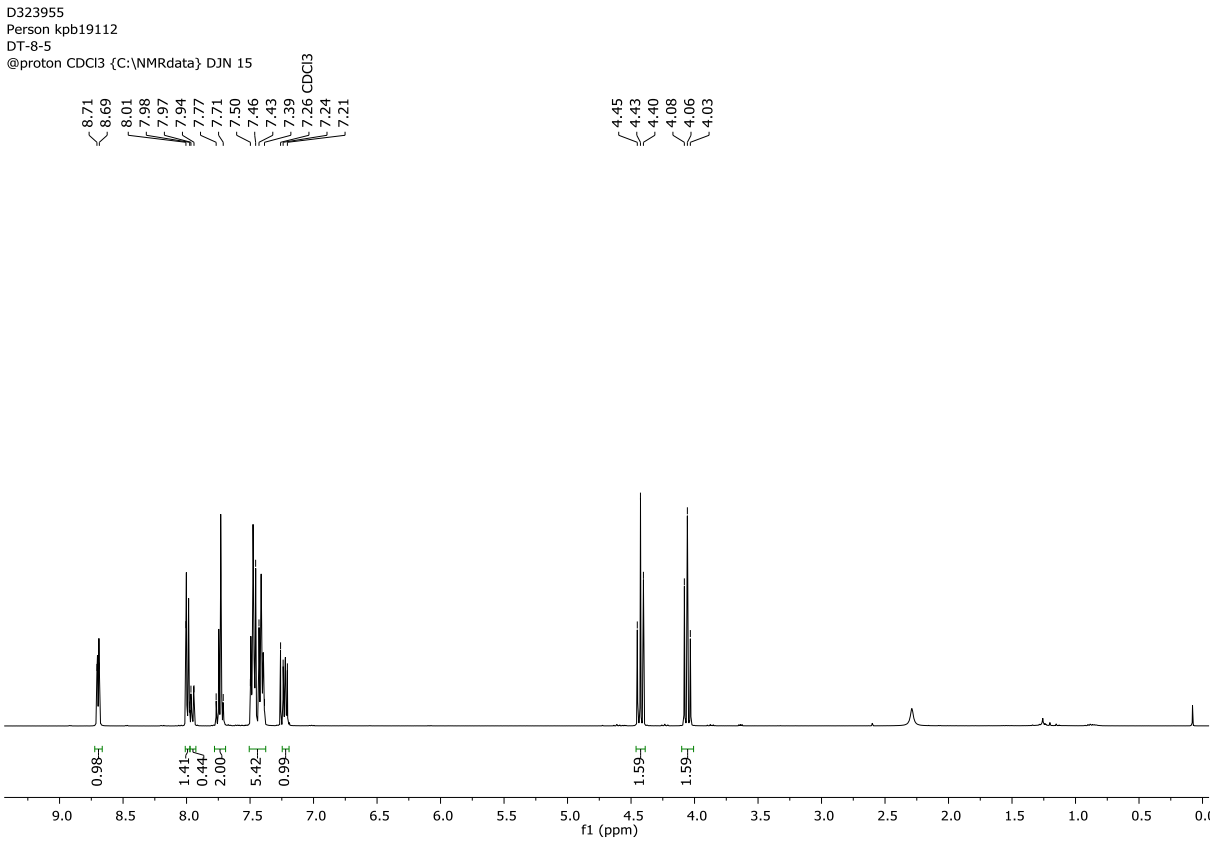
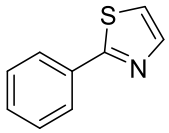
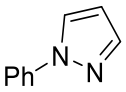


Figure S68. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylpyridine (entry 3, Table S14).

Table S15. Determination of the competition rate constant κ from the labelling experiment between 2-phenylthiazole and 1-phenylpyrazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh$_3$][BArF$_{24}$]
Mass	16.1 mg	14.4 mg	8.7 mg

Deuteration expected at δ (**R1**) = 8.00 – 7.95 ppm and at δ (**R2**) = 7.76 – 7.66 ppm
Determined against integral at δ (**R1**) = 7.87 ppm and at δ (**R2**) = 7.92 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.95 (m, 2H/D **R1**), 7.92 (d, *J* = 2.4 Hz, 1H, **R2**), 7.87 (d, *J* = 3.3 Hz, 1H, **R1**), 7.76 – 7.66 (m, 2H/D, **R2** and 1H, **R2**), 7.49 – 7.38 (m, 2H, **R2** and 3H, **R1**), 7.33 (d, *J* = 3.3 Hz, 1H, **R1**), 7.29 (t, *J* = 7.4 Hz, 1H, **R2**), 6.47 – 6.46 (m, 1H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.74	1.00	63	0.75[a]	1.00	63	1.01
2	0.87	1.00	57	0.90[b]	1.00	55	1.04
3	1.31	1.00	35	1.38[c]	1.00	31	1.14
				Average κ = 1.07			

[a] $I_{R2(t)}$ = 1.75 – 1.00; [b] $I_{R2(t)}$ = 1.90 – 1.00; [c] $I_{R2(t)}$ = 2.38 – 1.00;

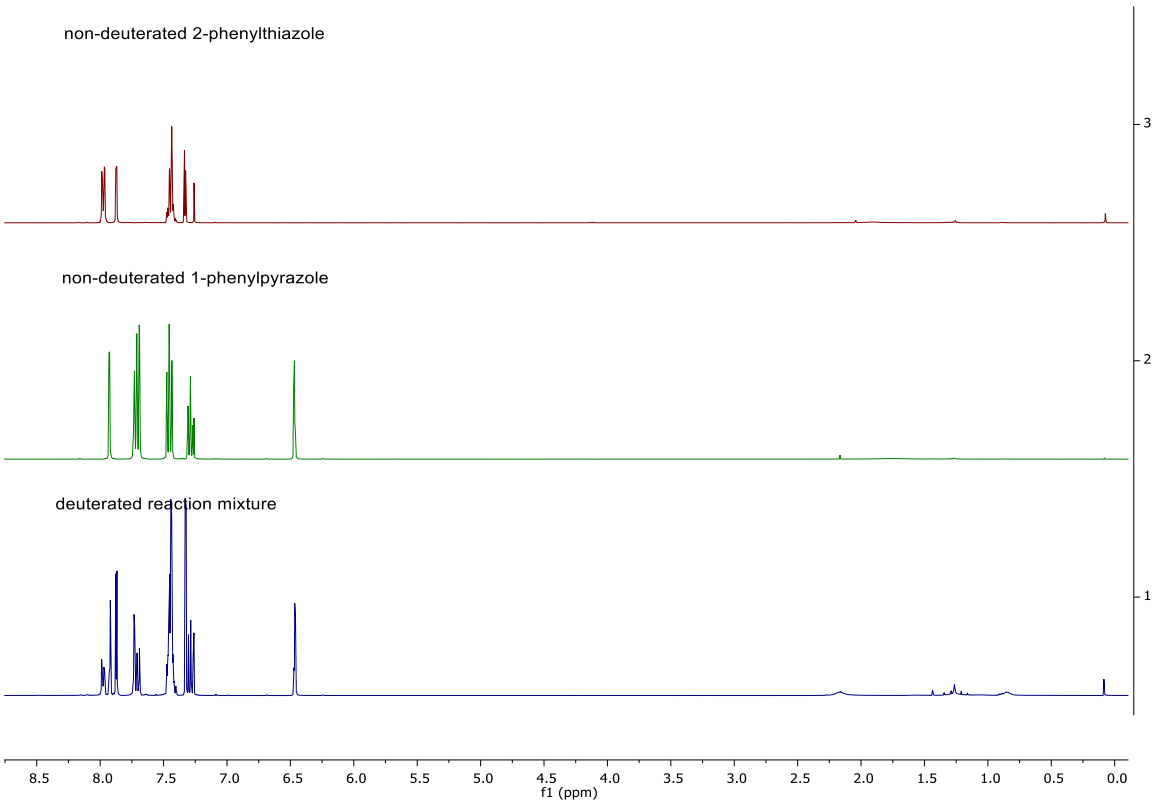


Figure S69. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

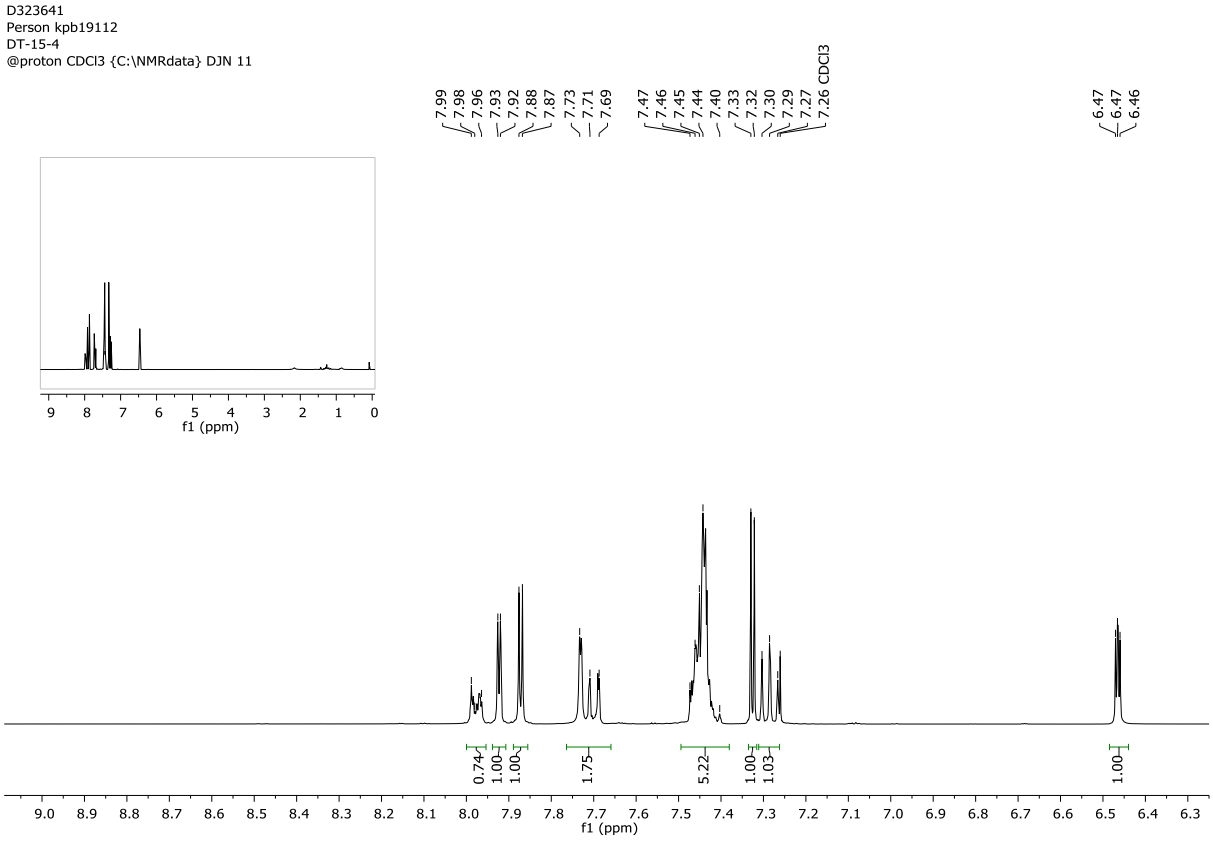


Figure S70. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazole and 1-phenylpyrazole (entry 1, Table S15).

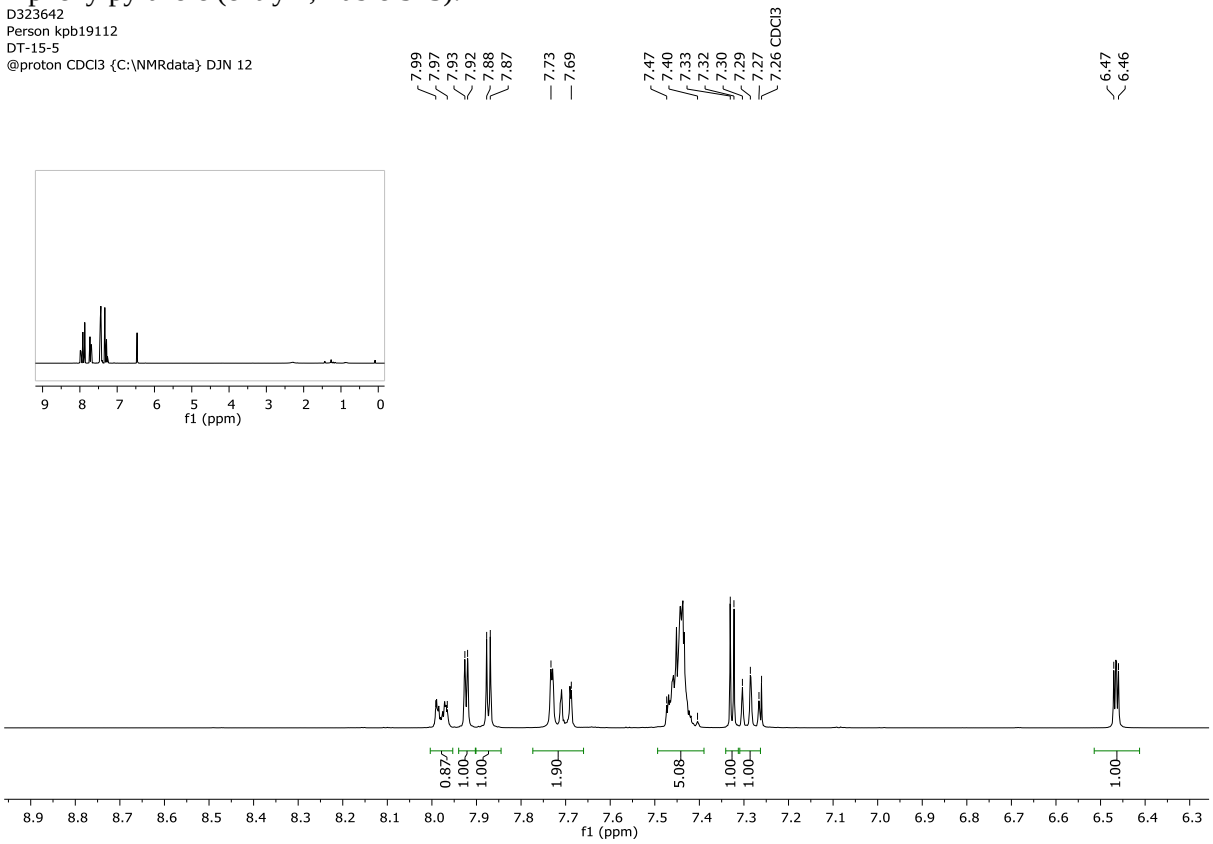


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazole and 1-phenylpyrazole (entry 2, Table S15).

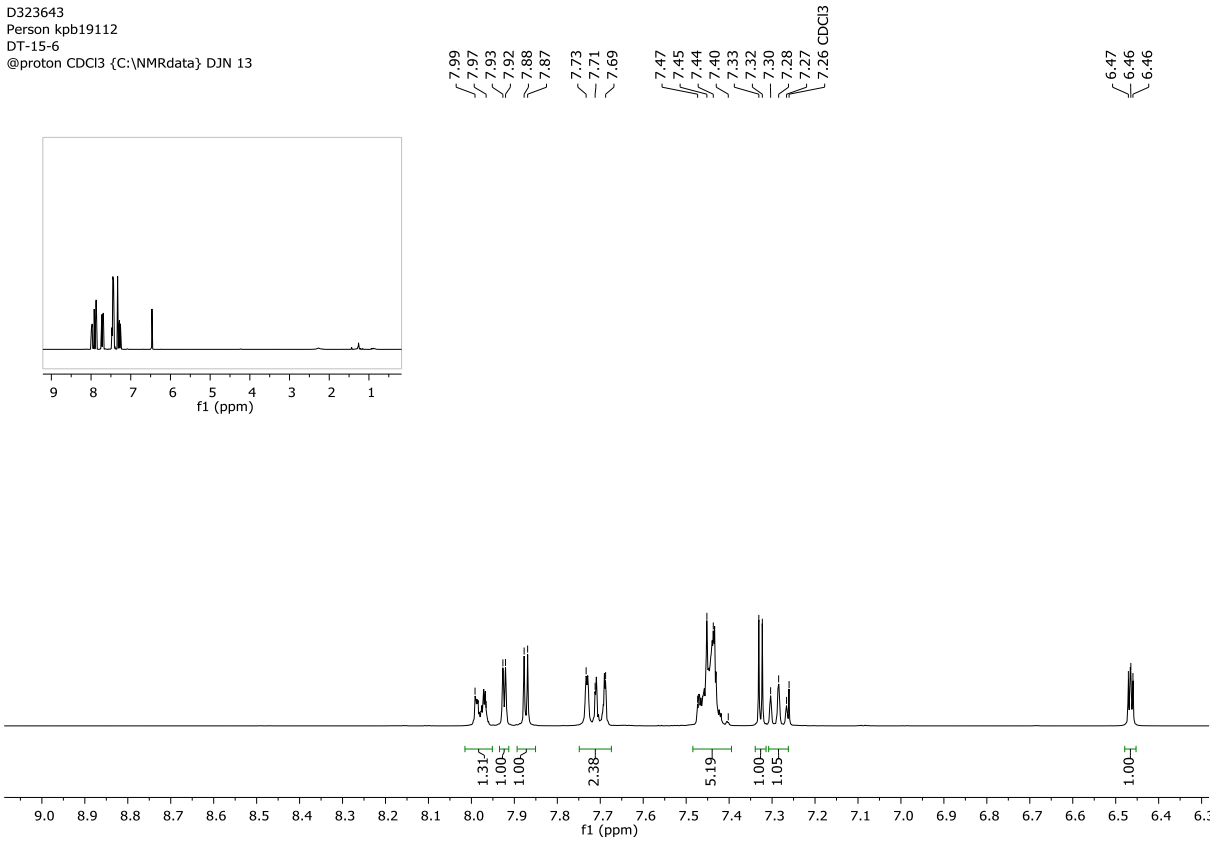
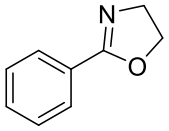
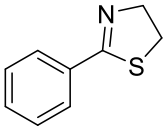


Figure S72. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazole and 1-phenylpyrazole (entry 3, Table S15).

Table S16. Determination of the competition rate constant κ from the labelling experiment between 2-phenyloxazoline and 2-phenylthiazoline.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	14.7 mg	16.3 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.98 – 7.93 ppm and at δ (**R2**) = 7.86 – 7.81 ppm
Determined against integral at δ (**R1**) = 4.06 ppm and at δ (**R2**) = 3.41 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.93 (m, 2H/D **R1**), 7.86 – 7.81 (m, 2H/D, **R2**), 7.51 – 7.36 (m, 3H, **R1** and 3H, **R2**), 4.49 – 4.38 (m, 2H, **R1** and 2H, **R2**), 4.06 (t, *J* = 9.5 Hz, 2H, **R1**), 3.41 (t, *J* = 8.4 Hz, 2H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.05	2.00	48	1.18	2.24	47	1.01
2	0.87	2.00	57	0.96	2.19	56	1.01
3	0.73	2.00	64	0.85	2.32	63	1.00
Average κ = 1.01							

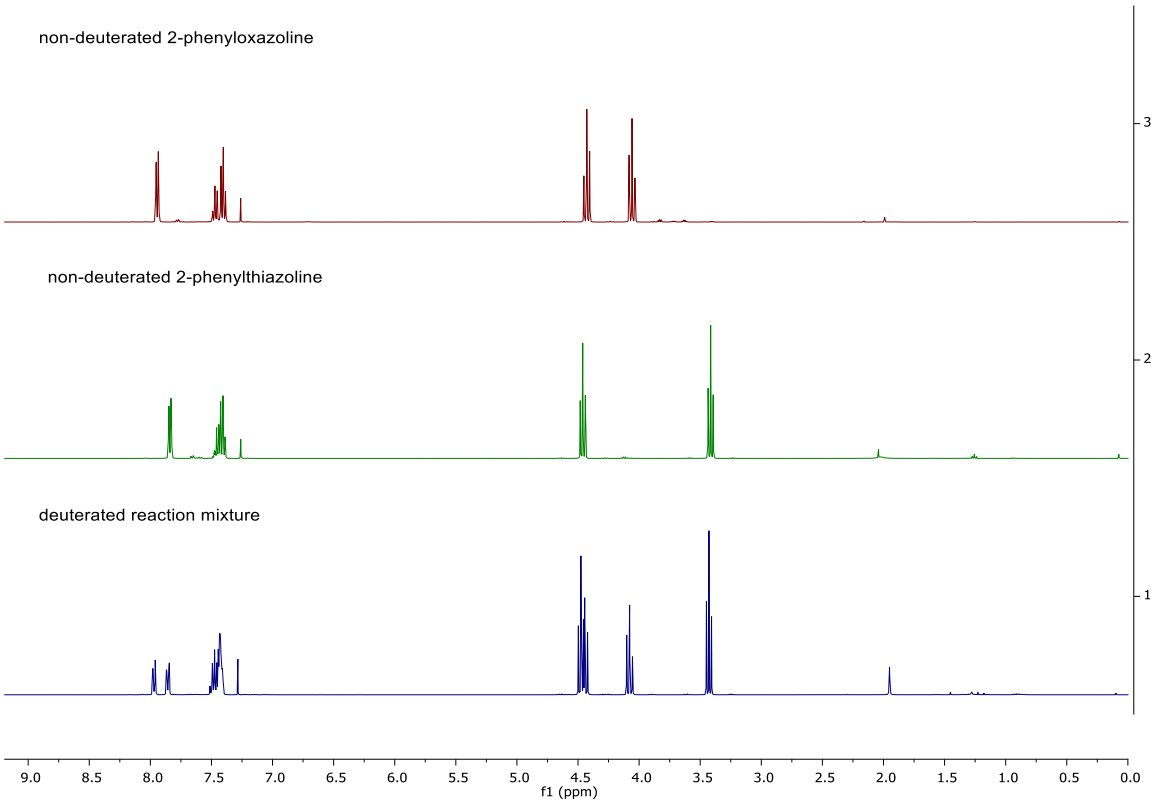


Figure S73. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

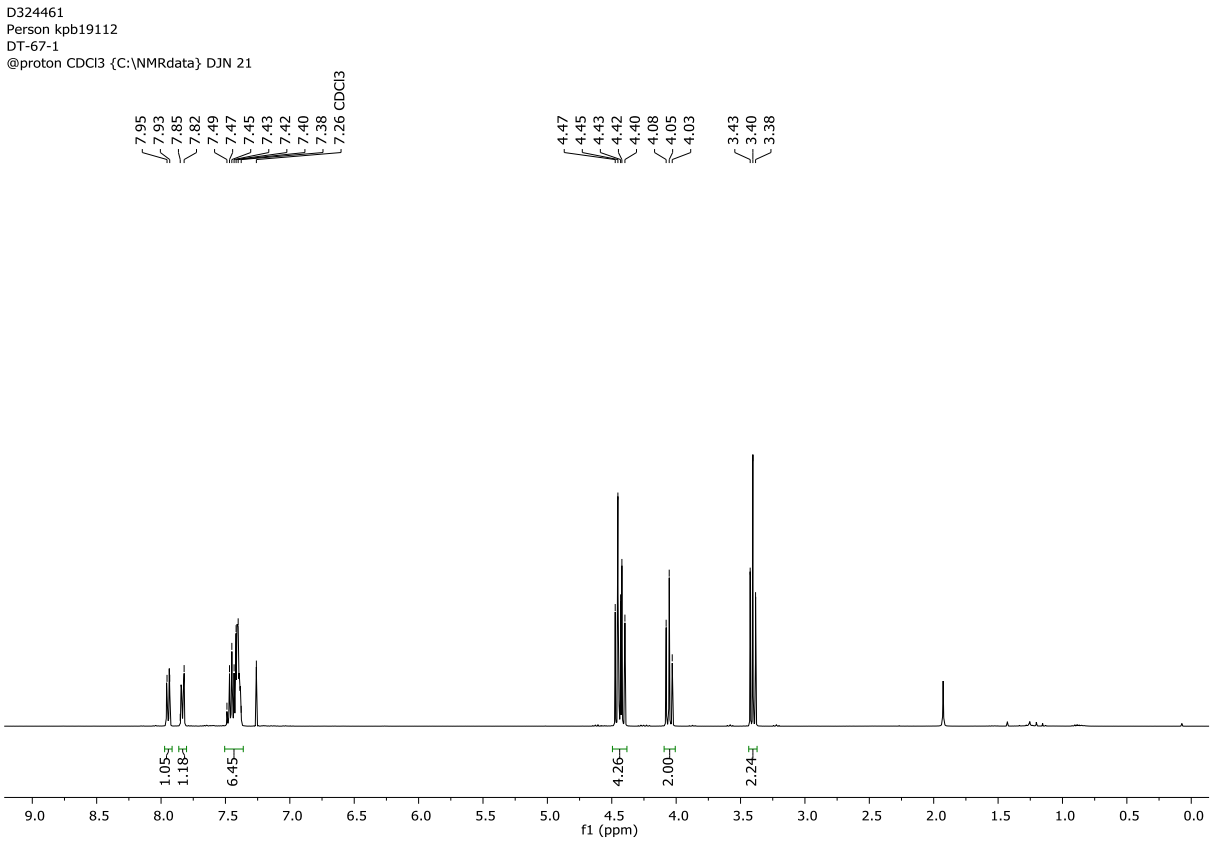


Figure S74. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylthiazoline (entry 1, Table S16).

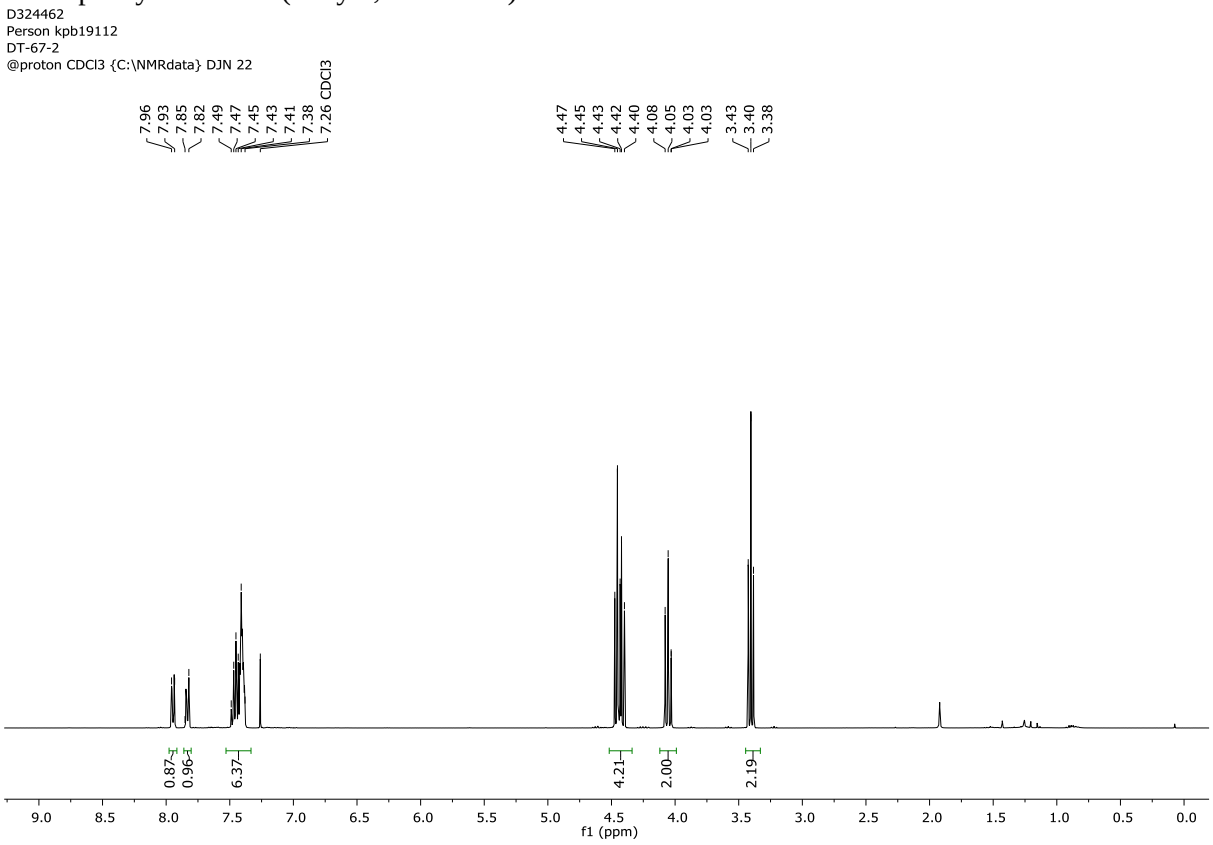


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylthiazoline (entry 2, Table S16).

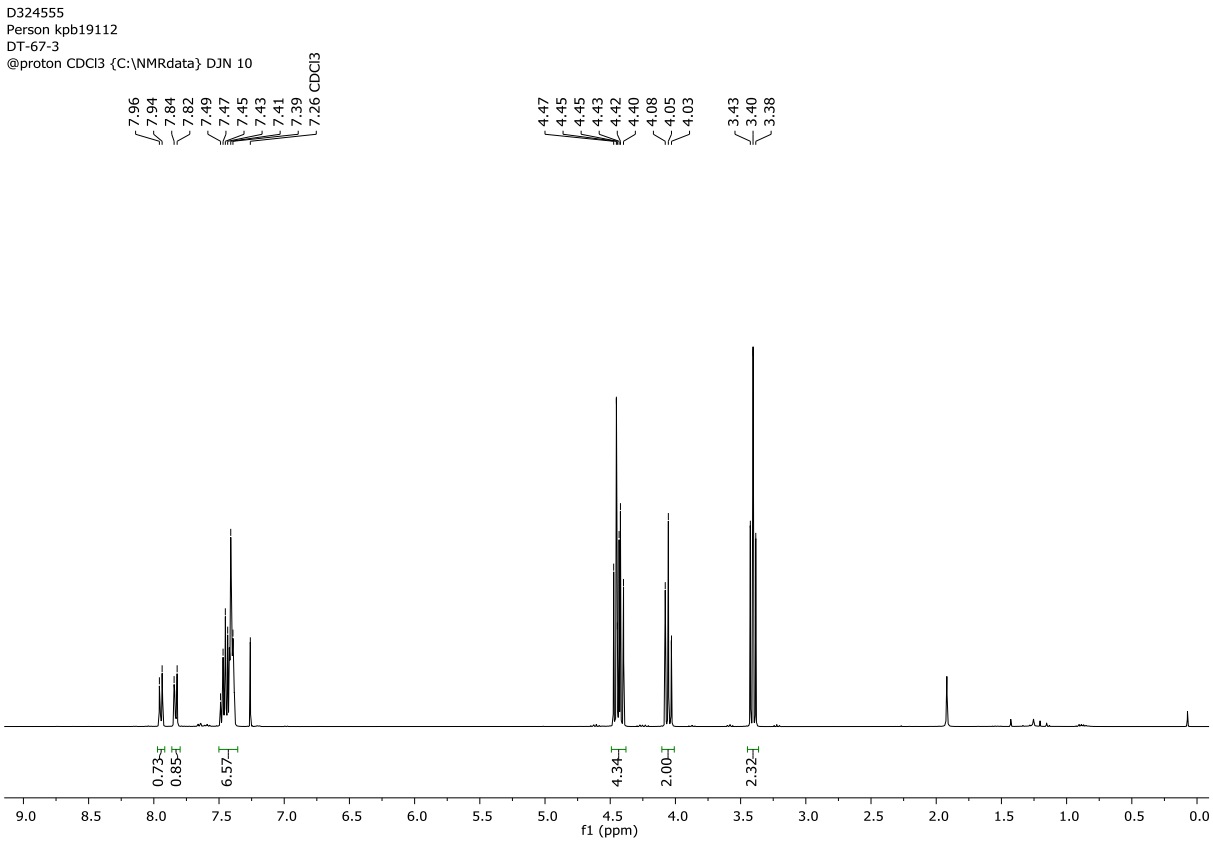
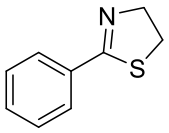
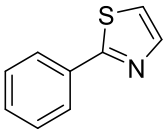


Figure S76. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylthiazoline (entry 3, Table S16).

Table S17. Determination of the competition rate constant κ from the labelling experiment between 2-phenylthiazoline and 2-phenylthiazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	16.3 mg	16.1 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.89 – 7.21 ppm and at δ (**R2**) = 8.00 – 7.94 ppm
Determined against integral at δ (**R1**) = 4.46 ppm and at δ (**R2**) = 7.33 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 – 7.94 (m, 2H/D **R2**), 7.89 – 7.21 (m, 2H/D, **R1** and 1H, **R2**), 7.49 – 7.37 (m, 3H, **R1** and 3H, **R2**), 7.33 (d, *J* = 3.3 Hz, 1H, **R2**), 4.46 (t, *J* = 8.3 Hz, 2H, **R1**), 3.41 (t, *J* = 8.3 Hz, 2H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.71[a]	1.96	64	0.75	1.00	63	1.04
2	0.68[b]	1.95	65	0.71	1.00	65	1.02
3	0.75[c]	1.93	61	0.80	1.00	60	1.03
Average κ = 1.03							

[a] $I_{R1(t)}$ = 1.71 – 1.00; [b] $I_{R1(t)}$ = 1.68 – 1.00; [c] $I_{R1(t)}$ = 1.75 – 1.00;

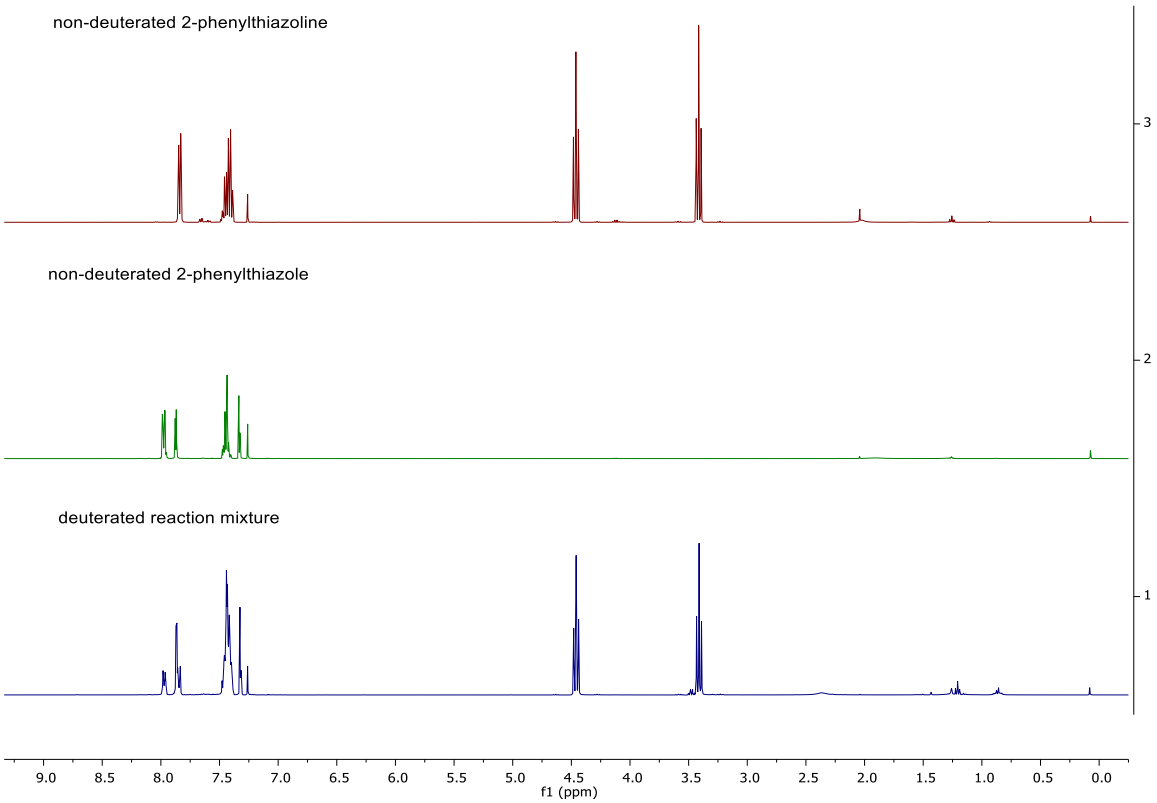


Figure S77. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

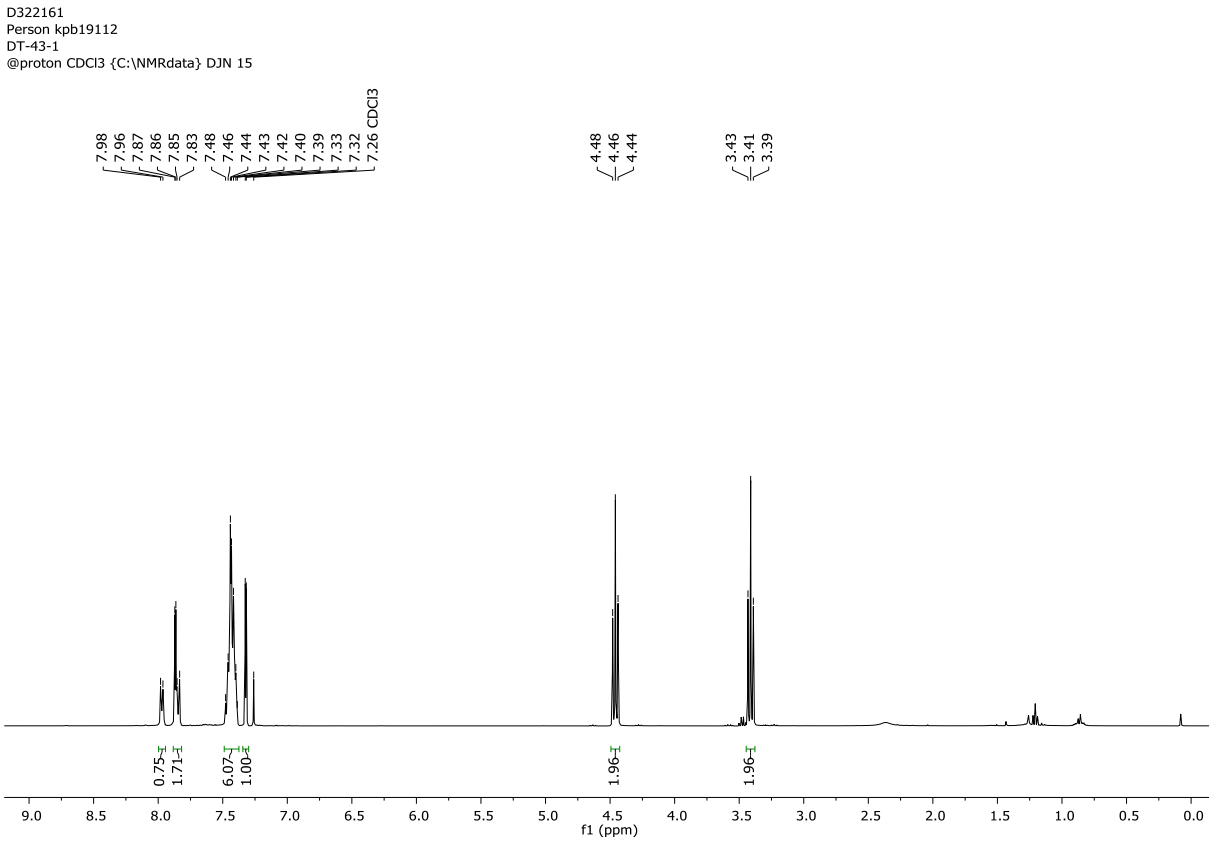


Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazoline and 2-phenylthiazole (entry 1, Table S17).

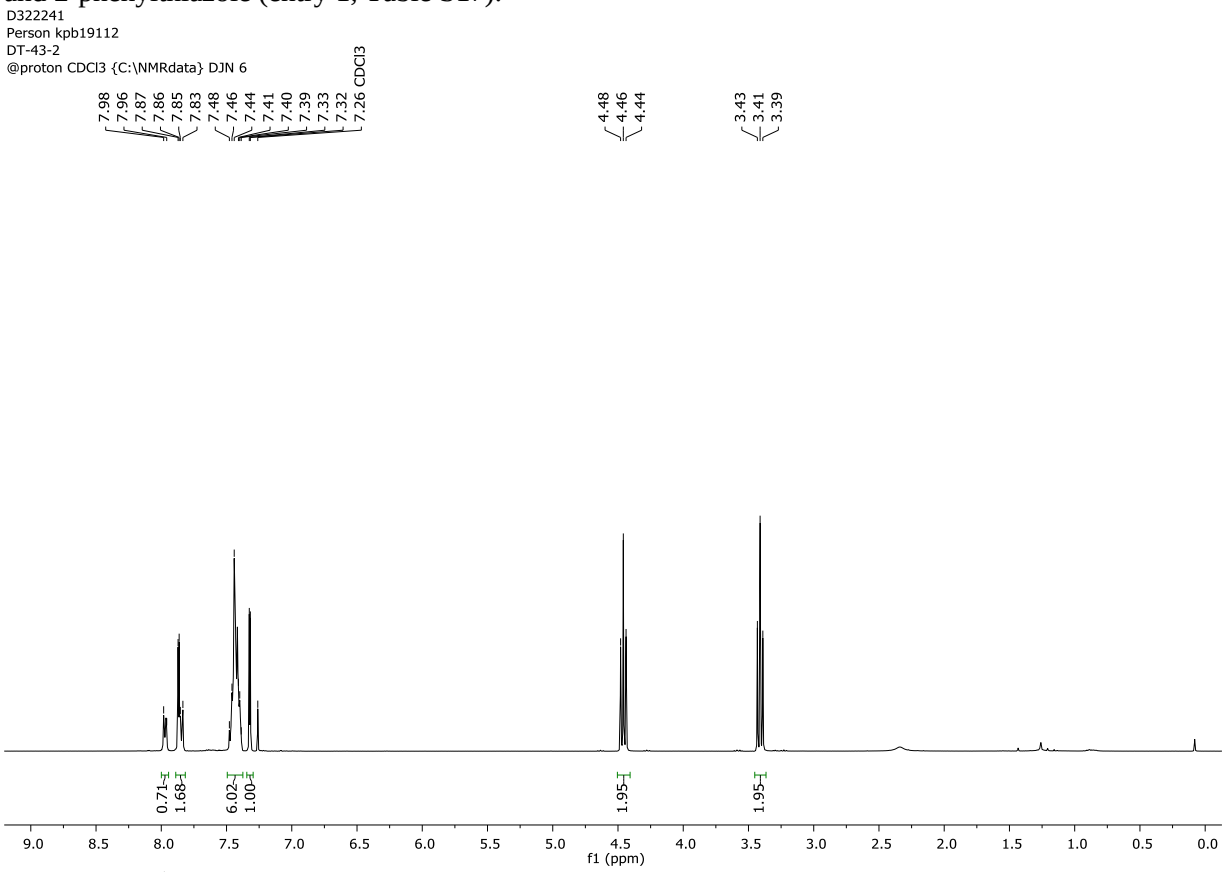


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazoline and 2-phenylthiazole (entry 2, Table S17).

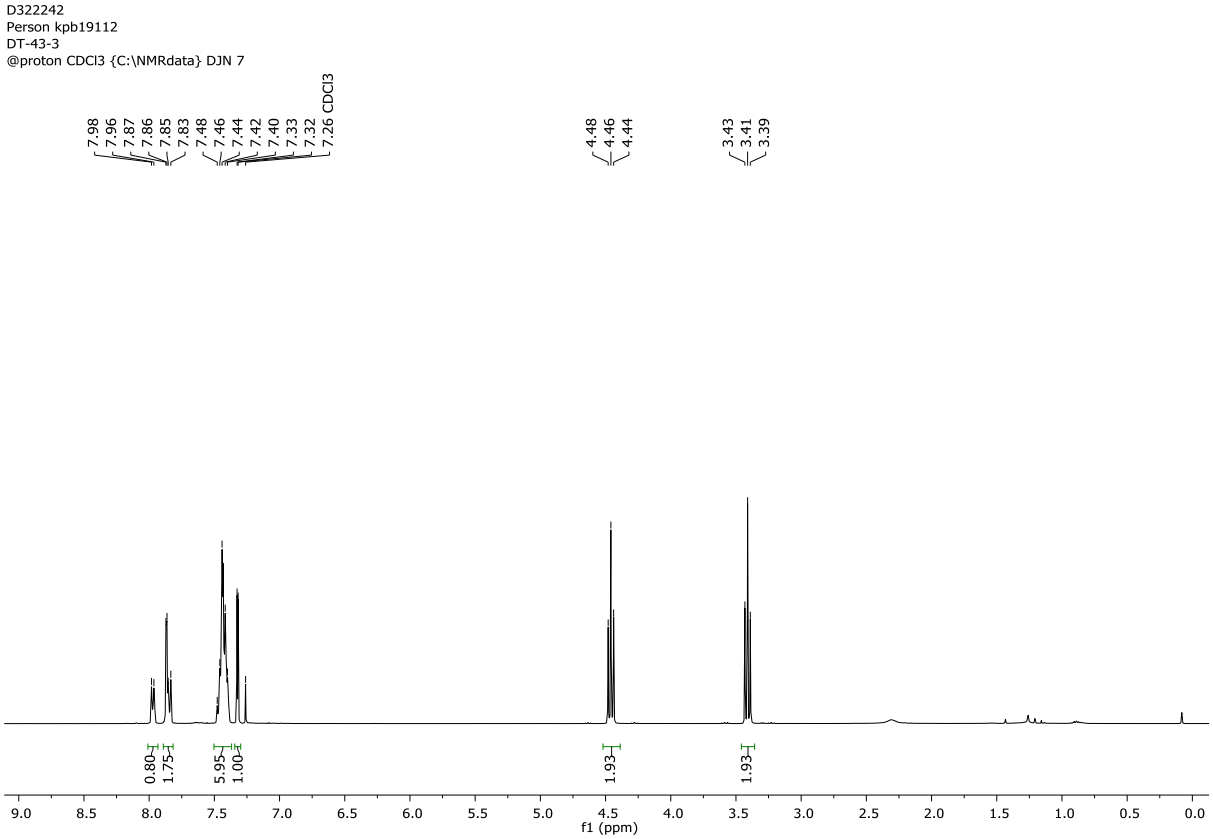
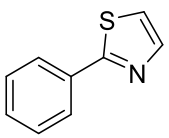
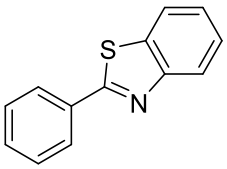


Figure S80. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazoline and 2-phenylthiazole (entry 3, Table S17).

Table S18. Determination of the competition rate constant κ from the labelling experiment between 2-phenylthiazole and 2-phenylbenzothiazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	16.1 mg	21.1 mg	8.7 mg

Deuteration expected at δ (**R1**) = 8.00 – 7.94 ppm and at δ (**R2**) = 8.14 – 8.06 ppm
Determined against integral at δ (**R1**) = 7.33 ppm and at δ (**R2**) = 7.93 – 7.85 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 – 8.06 (m, 2H/D, **R2** and 1H, **R2**), 8.00 – 7.94 (m, 2H/D **R1**), 7.93 – 7.85 (m, 1H, **R1** and 1H, **R2**), 7.54 – 7.35 (m, 3H, **R1** and 4H, **R2**), 7.33 (d, *J* = 3.3 Hz, 1H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.60	1.00	70	1.83[a]	1.08[d]	15	7.26
2	0.80	1.00	60	2.06[b]	1.16[e]	11	7.71
3	0.57	1.00	72	1.86[c]	1.10[f]	15	7.48
				Average κ = 7.48			

[a] $I_{R2(t)}$ = 2.91 – 1.00; [b] $I_{R2(t)}$ = 3.22 – 1.00; [c] $I_{R2(t)}$ = 2.96 – 1.00;
[d] $I_{R2(0)}$ = 2.08 – 1.00; [e] $I_{R2(0)}$ = 2.16 – 1.00; [f] $I_{R2(0)}$ = 2.10 – 1.00;

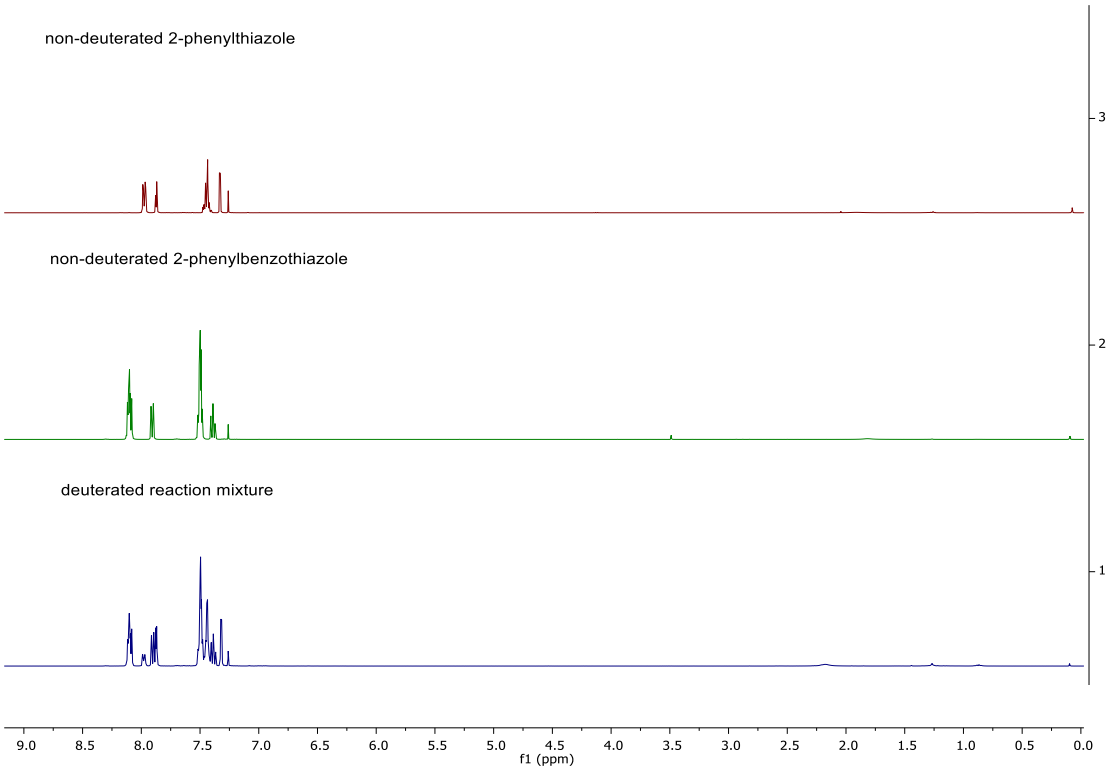


Figure S81. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

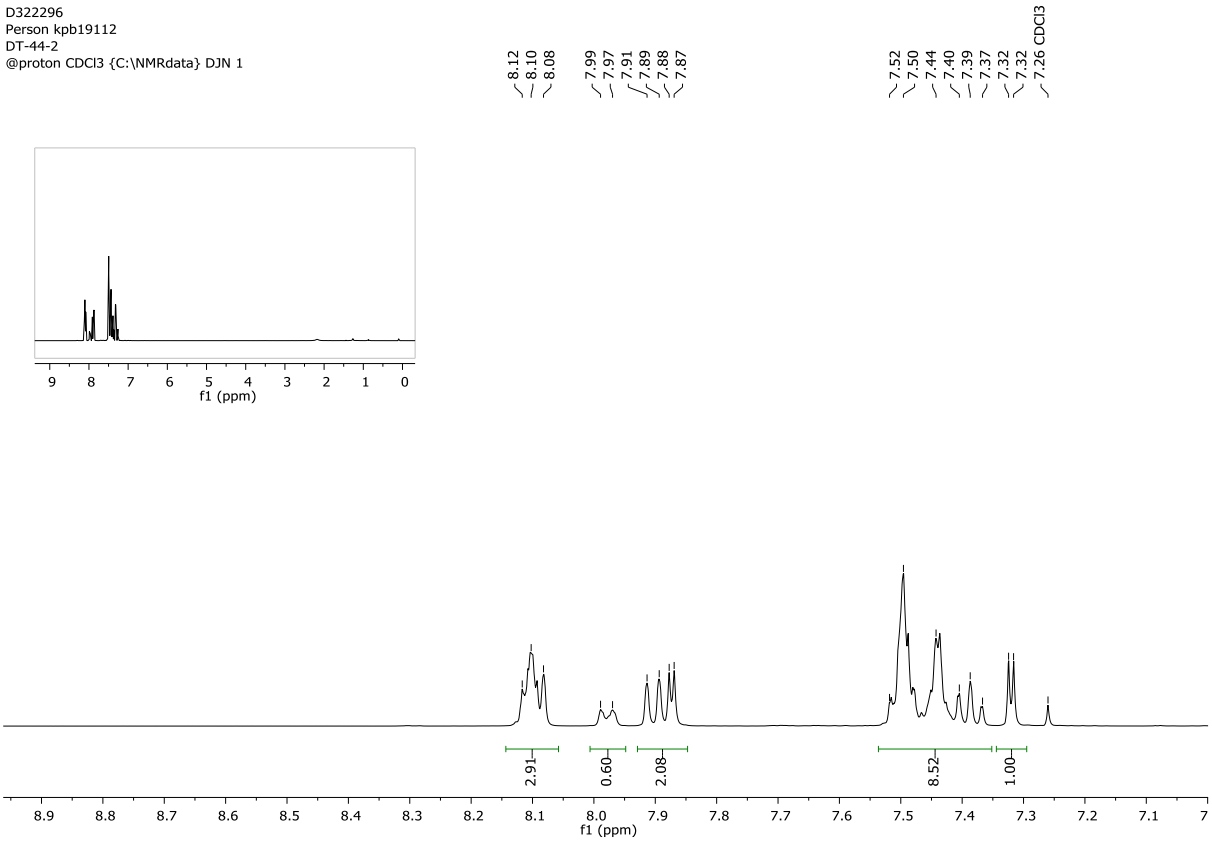


Figure S82. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazole and 2-phenylbenzothiazole (entry 1, Table S18)

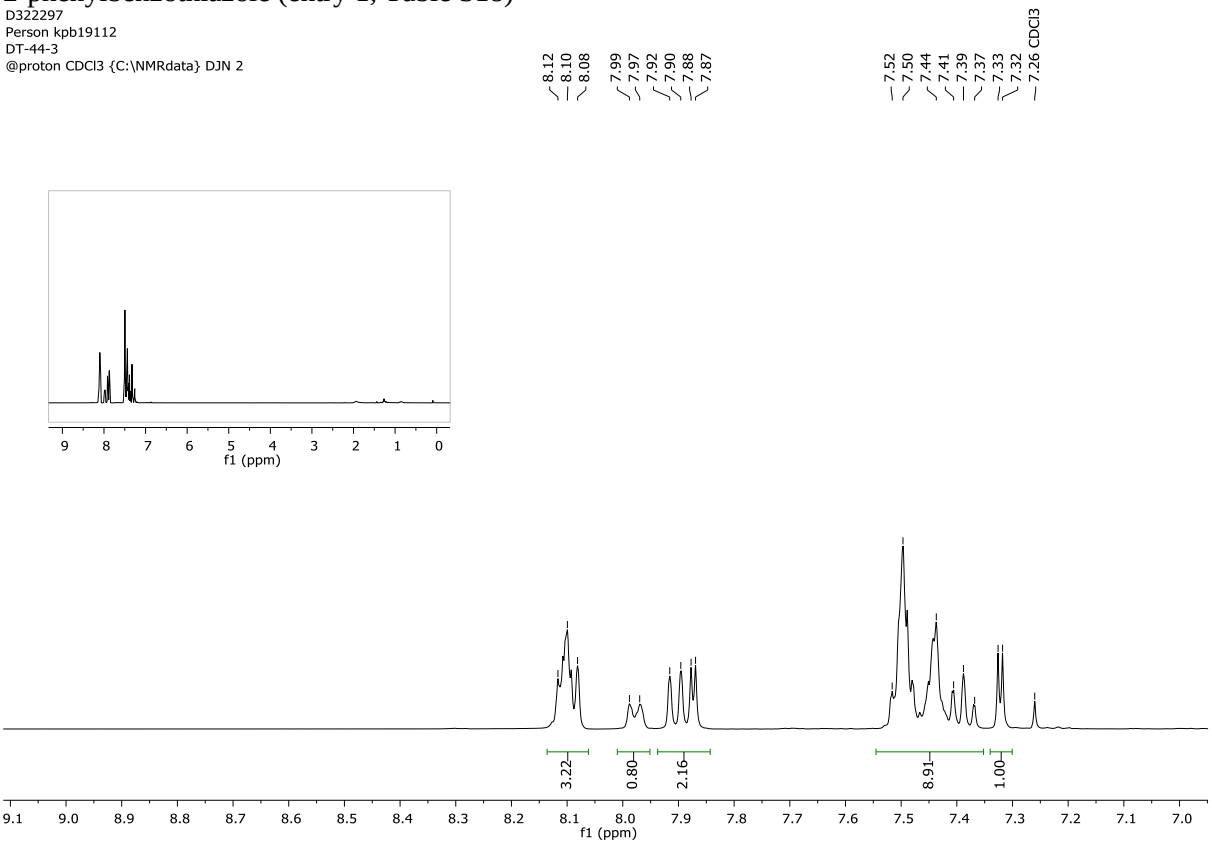


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazole and 2-phenylbenzothiazole (entry 2, Table S18).

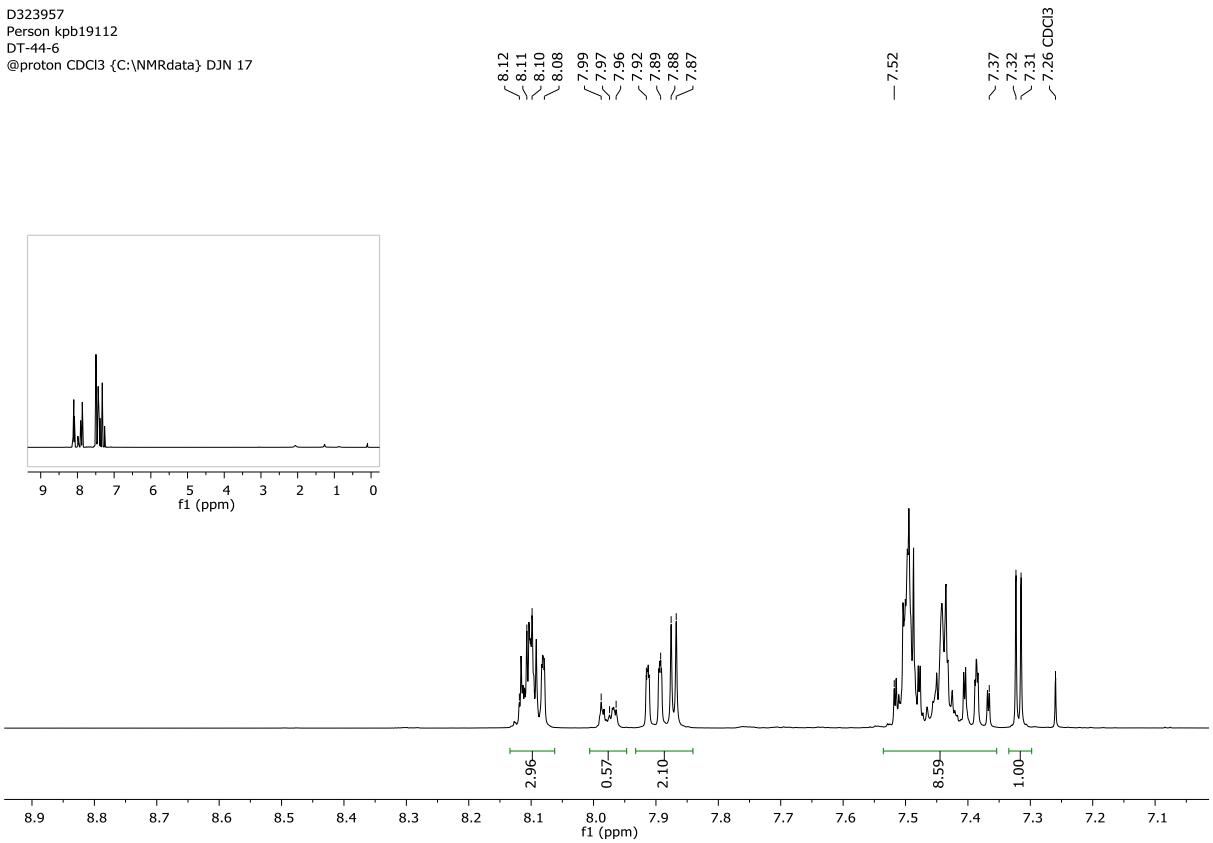
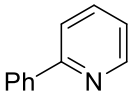
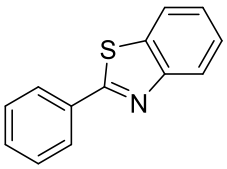


Figure S84. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazole and 2-phenylbenzothiazole (entry 3, Table S18).

Table S19. Determination of the competition rate constant κ from the labelling experiment between 2-phenylpyridine and 2-phenylbenzothiazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	15.5 mg	21.1 mg	8.7 mg

Deuteration expected at δ (**R1**) = 8.02 – 7.98 ppm and at δ (**R2**) = 8.14 – 8.06 ppm
Determined against integral at δ (**R1**) = 8.74 – 8.65 ppm and at δ (**R2**) = 7.93 – 7.85 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.74 – 8.65 (m, 1H, **R1**), 8.14 – 8.06 (m, 2H/D, **R2** and 1H, **R2**), 8.02 – 7.98 (m, 2H/D **R1**), 7.93 – 7.85 (m, 1H, **R2**), 7.77 – 7.71 (m, 2H, **R1**), 7.53 – 7.35 (m, 3H, **R1** and 4H, **R2**), 7.25 – 7.20 (m, 1H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	1.58	1.00	21	1.98[a]	1.06	7	3.45
2	1.60	1.00	20	2.12[b]	1.12	5	4.05
3	1.53	1.00	24	2.02[c]	1.09	7	3.51
Average κ = 3.67							

[a] $I_{R2(t)}$ = 3.04 – 1.06; [b] $I_{R2(t)}$ = 3.24 – 1.12; [c] $I_{R2(t)}$ = 3.11 – 1.09;

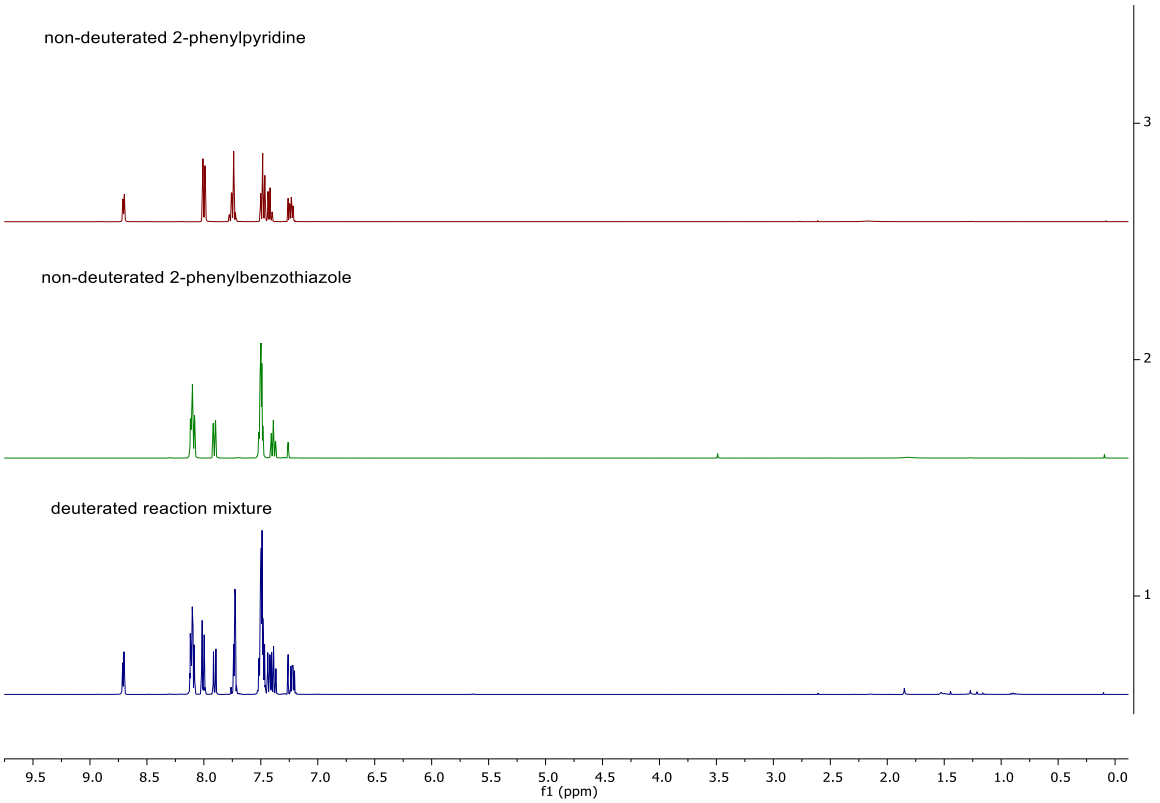


Figure S85. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

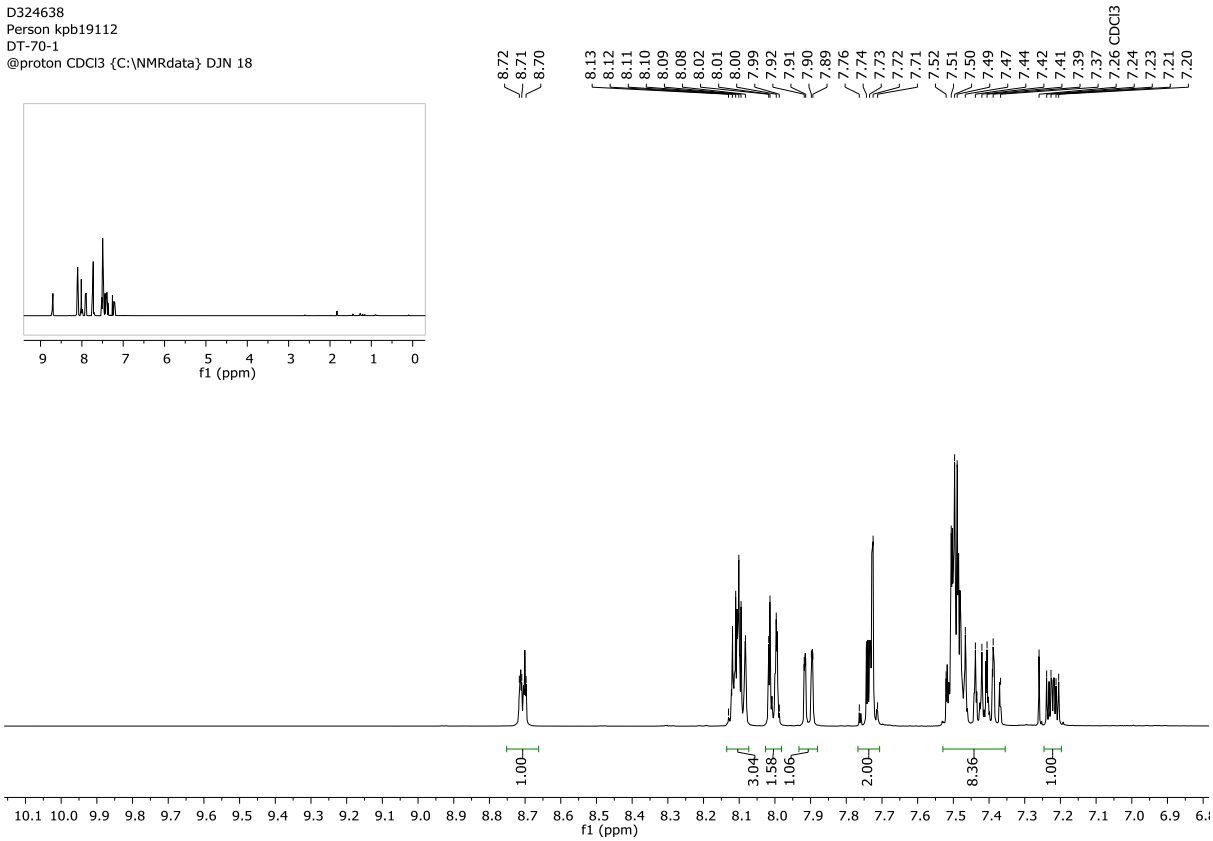


Figure S86. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyridine and 2-phenylbenzothiazole (entry 1, Table S19).

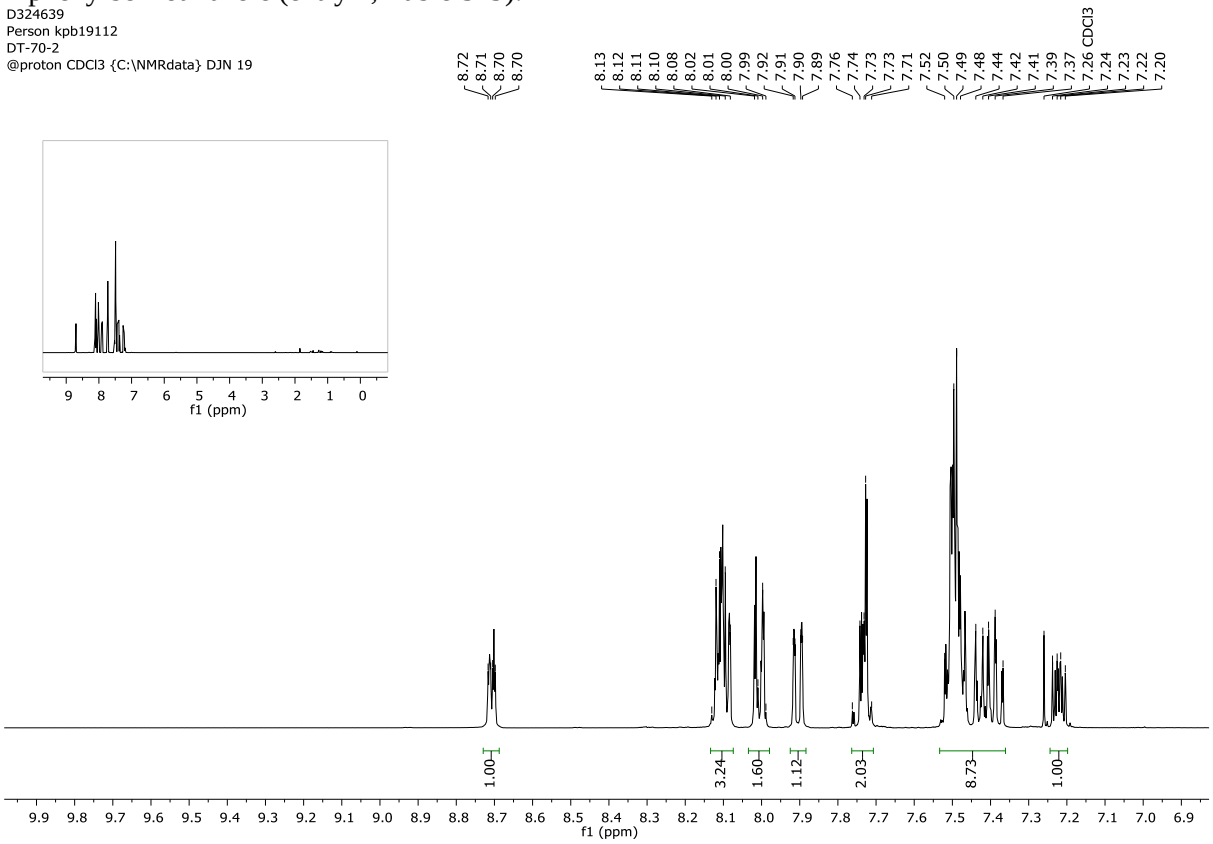


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyridine and 2-phenylbenzothiazole (entry 2, Table S19).

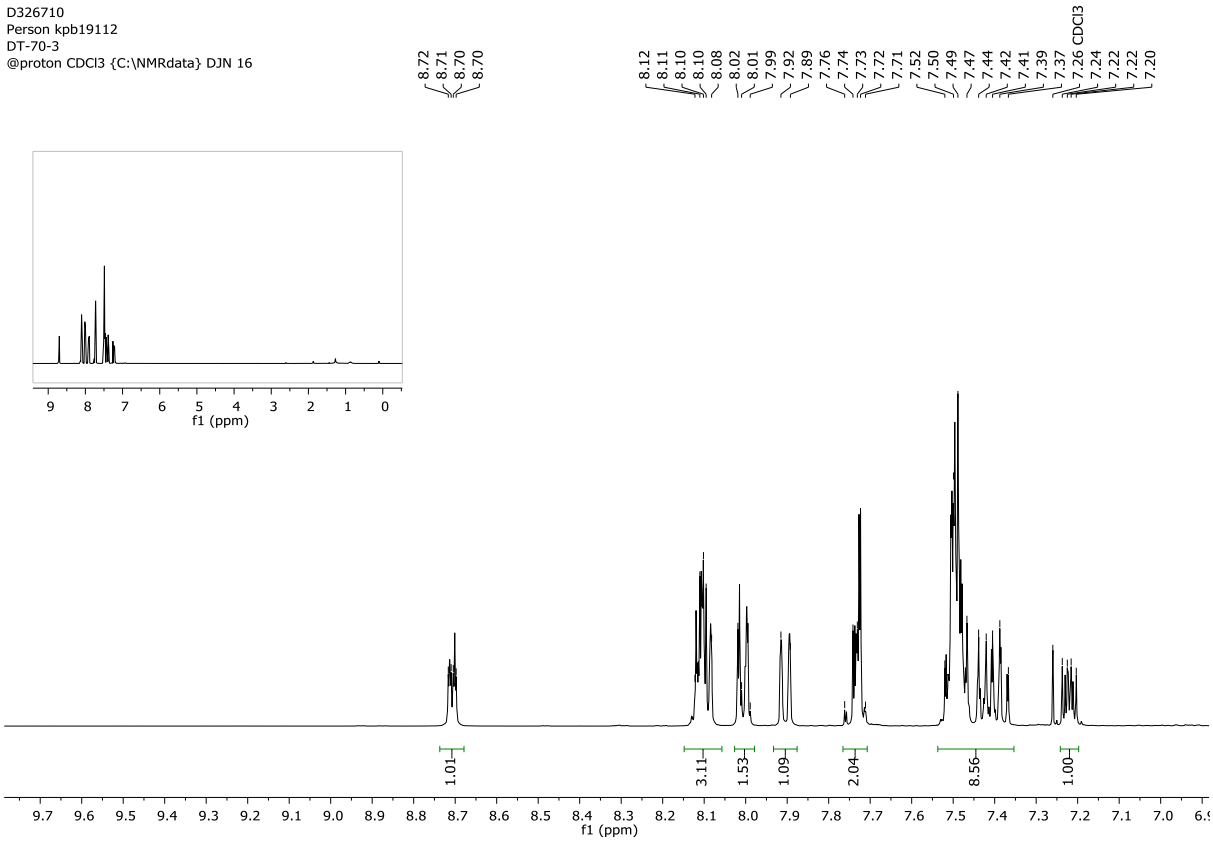
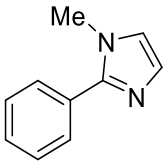
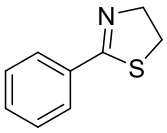


Figure S88. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyridine and 2-phenylbenzothiazole (entry 3, Table S19).

Table S20. Determination of the competition rate constant κ from the labelling experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	15.8 mg	16.3 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.65 – 7.60 ppm and at δ (**R2**) = 7.85 – 7.80 ppm
Determined against integral at δ (**R1**) = 7.12 ppm and at δ (**R2**) = 4.45 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 – 7.80 (m, 2H/D **R2**), 7.65 – 7.60 (m, 2H/D, **R1**), 7.48 – 7.36 (m, 3H, **R1** and 3H, **R2**), 7.12 (d, *J*=1.2 Hz, 1H, **R1**), 6.95 (d, *J*=1.2 Hz, 1H, **R1**), 4.45 (t, *J* = 8.3 Hz, 2H, **R2**), 3.73 (s, 3H, **R1**), 3.40 (t, *J* = 8.3 Hz, 2H, **R2**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	0.62	1.00	69	1.72	2.24	23	4.43
2	0.60	1.00	70	2.06	2.52	18	5.97
3	1.02	1.00	49	1.91	2.36	19	3.18
				Average κ = 4.53			

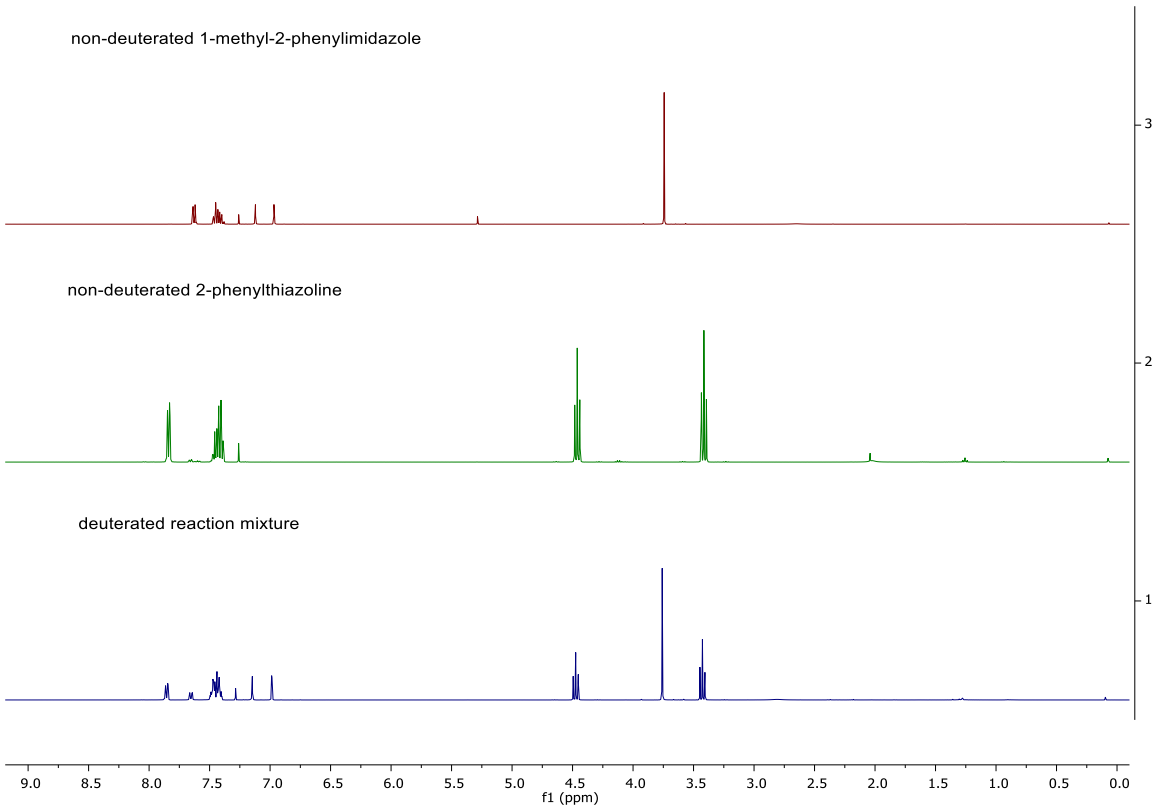


Figure S89. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

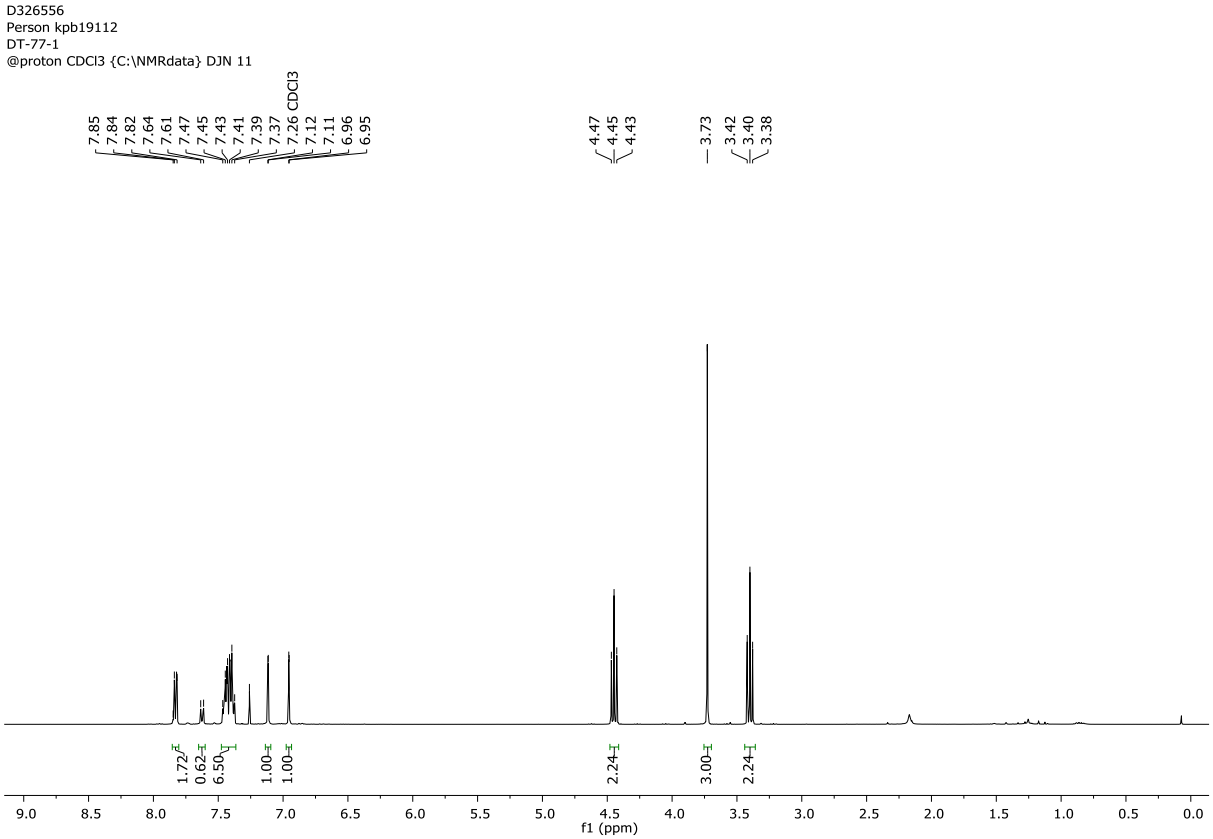


Figure S90. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline (entry 1, Table S20).

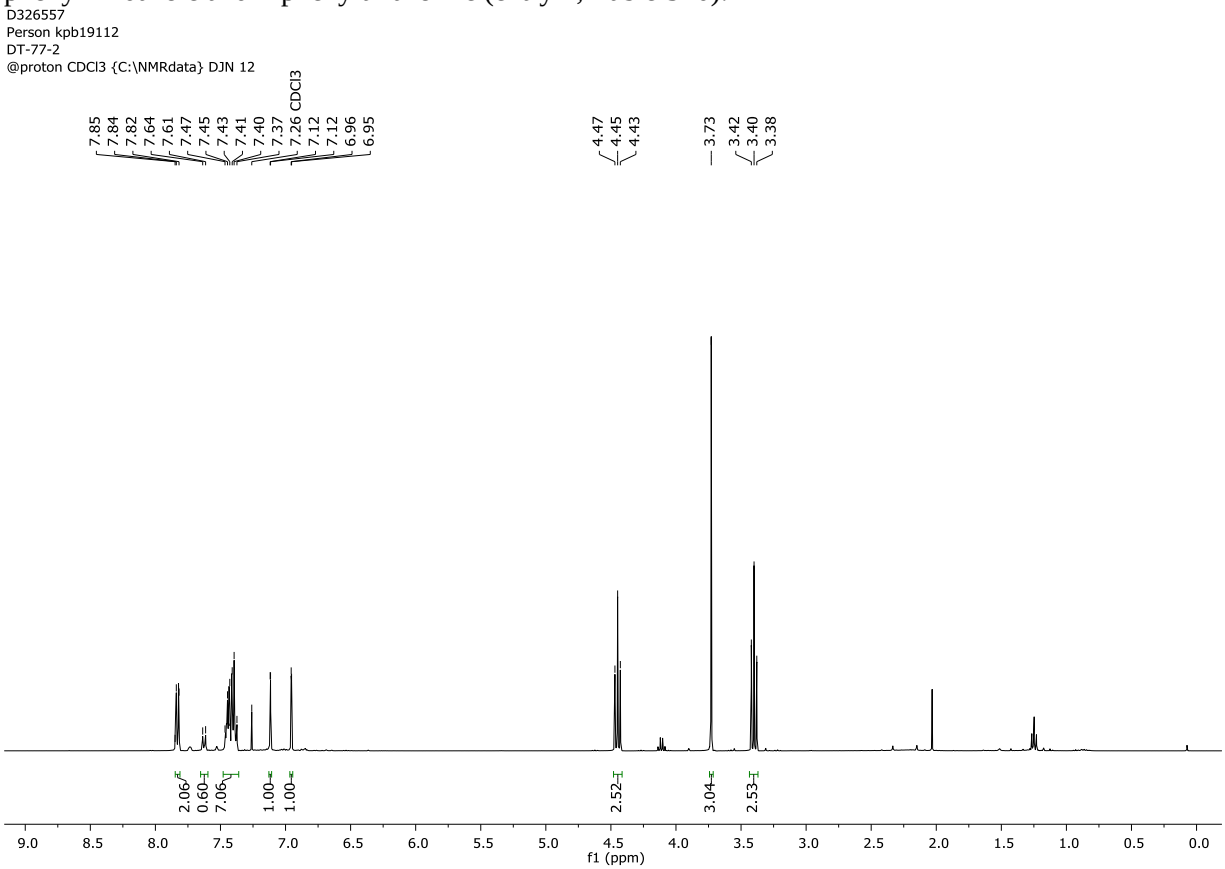


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline (entry 2, Table S20).

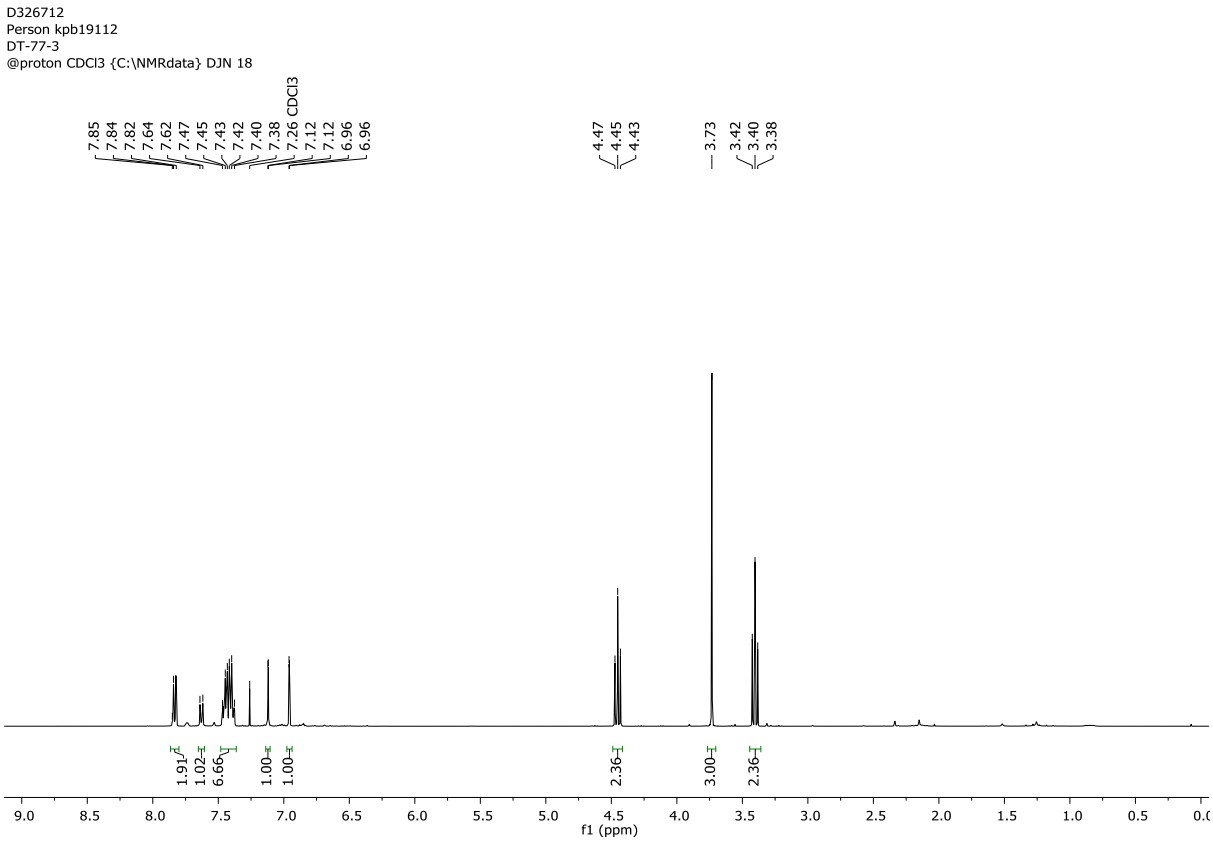
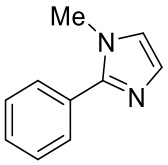
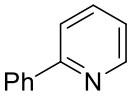


Figure S92. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline (entry 3, Table S20).

Table S21. Determination of the competition rate constant κ from the labelling experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	15.8 mg	15.5 mg	8.7 mg

Deuteration expected at δ (**R1**) = 7.65 – 7.60 ppm and at δ (**R2**) =8.02 – 7.96 ppm
Determined against integral at δ (**R1**) = 7.14 ppm and at δ (**R2**) = 8.73 – 8.66 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 – 8.66 (m, 1H, **R2**), 8.02 – 7.96 (m, 2H/D **R2**), 7.77 – 7.69 (m, 2H **R2**), 7.65 – 7.60 (m, 2H/D, **R1**), 7.50 – 7.36 (m, 3H, **R1** and 3H, **R2**), 7.24 – 7.18 (m, 1H, **R2**), 7.12 (d, *J*=1.2 Hz, 1H, **R1**), 6.95 (d, *J*=1.2 Hz, 1H, **R1**), 3.73 (s, 3H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.59	1.00	70	2.15	1.20	10	10.95
2	0.51	1.00	75	1.88	1.10	15	8.69
3	0.67	1.00	67	2.04	1.13	10	10.68
				Average κ = 10.11			

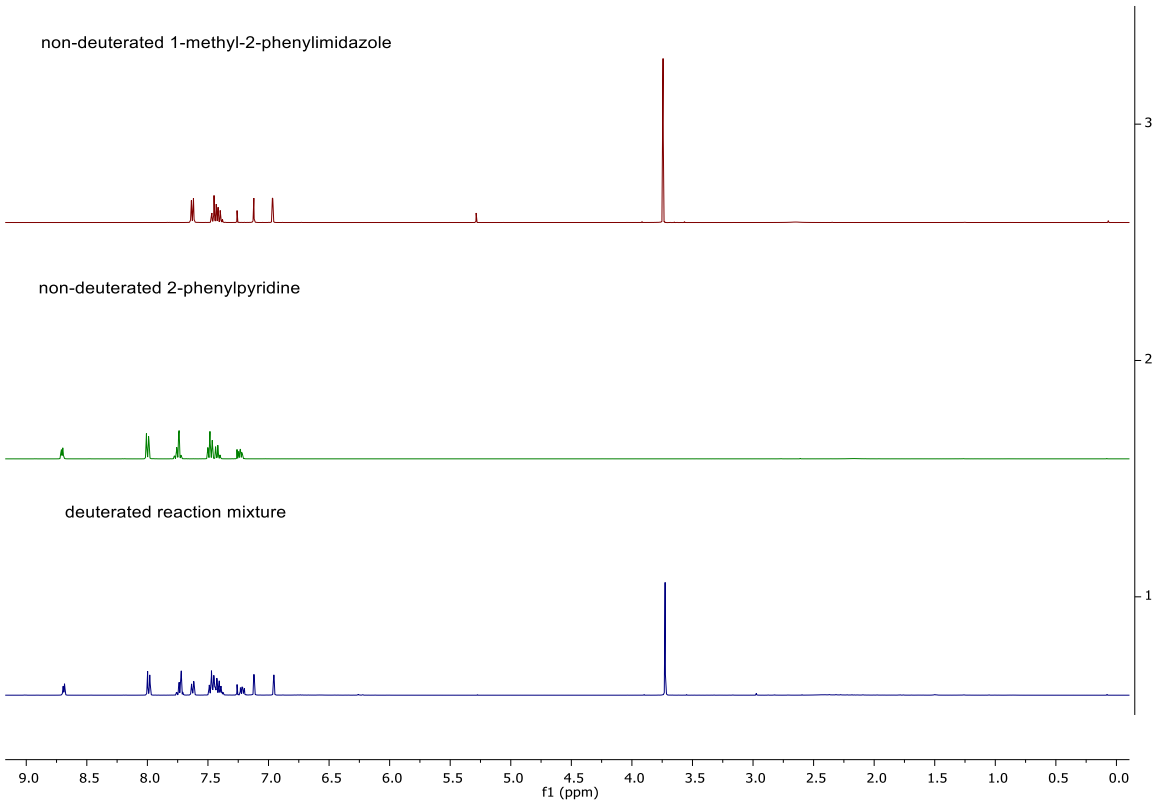


Figure S93. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

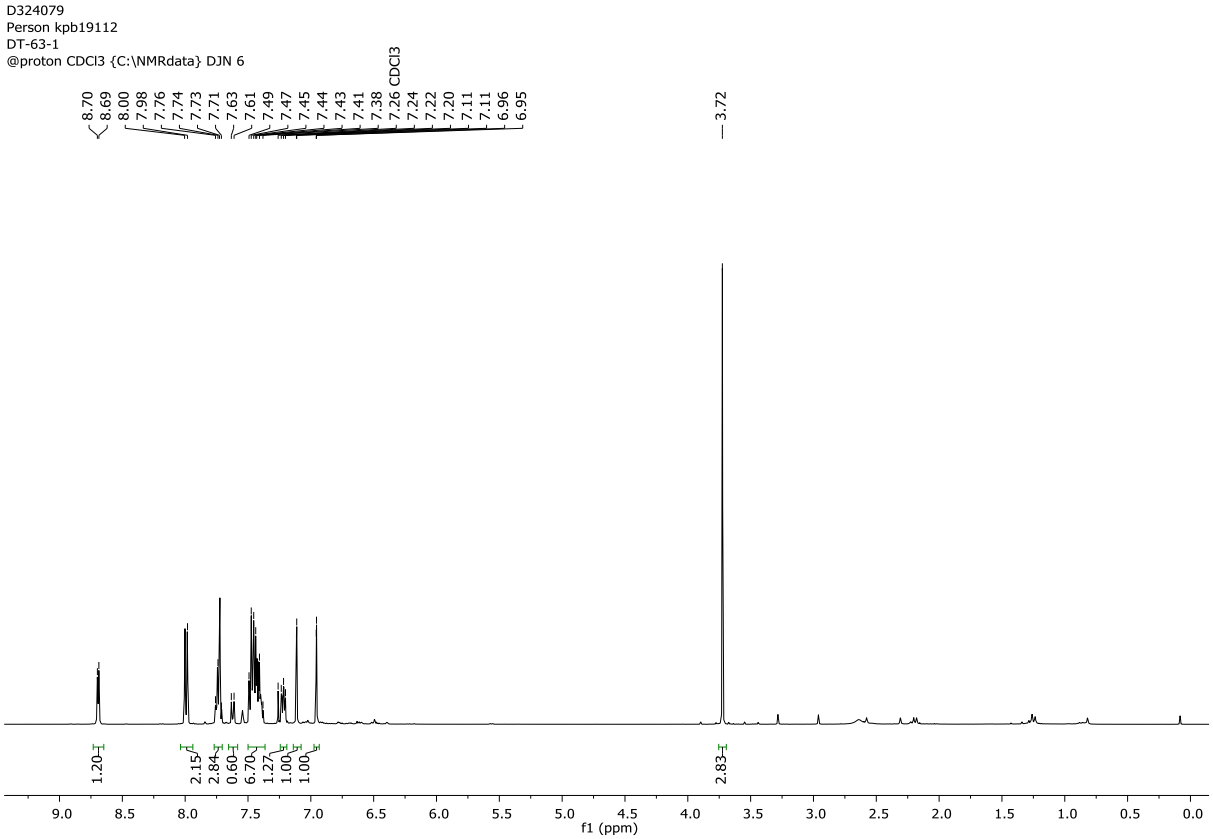


Figure S94. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine (entry 1, Table S21).

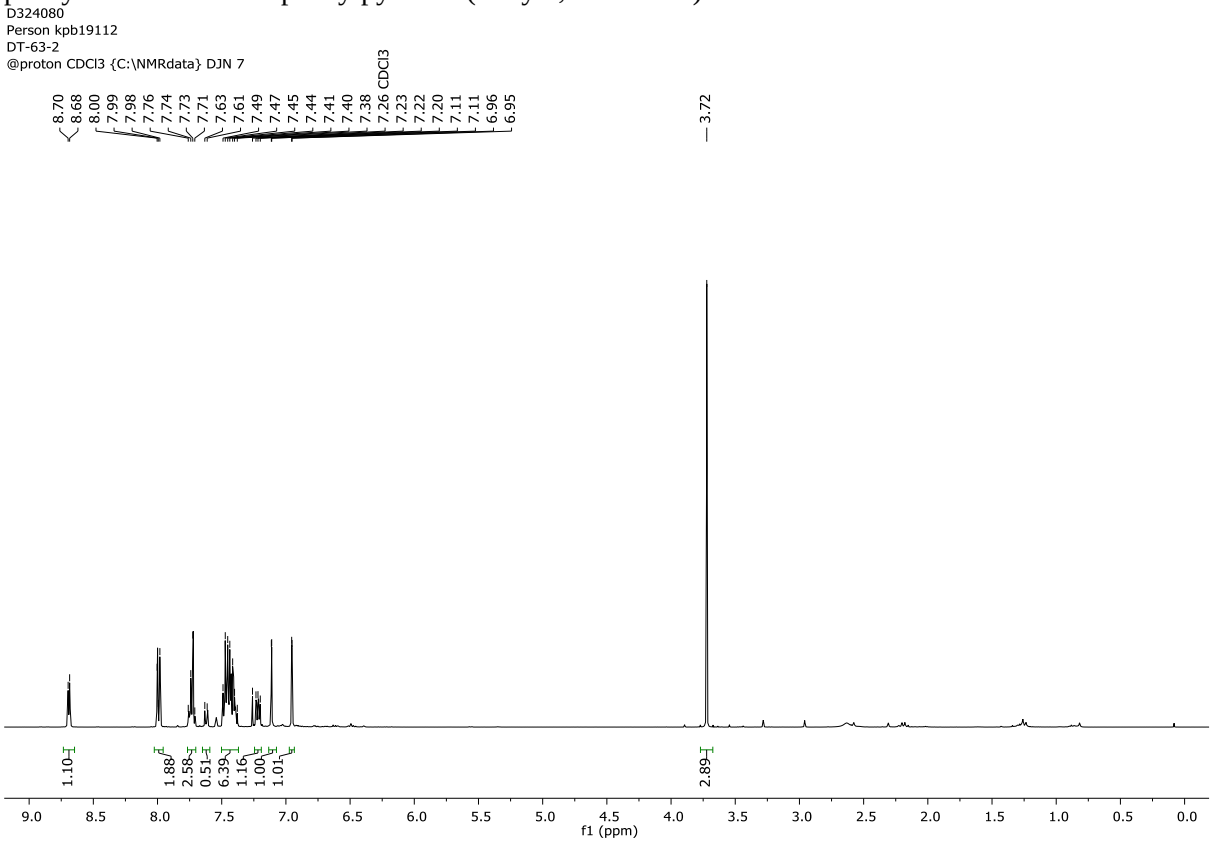


Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine (entry 2, Table S21).

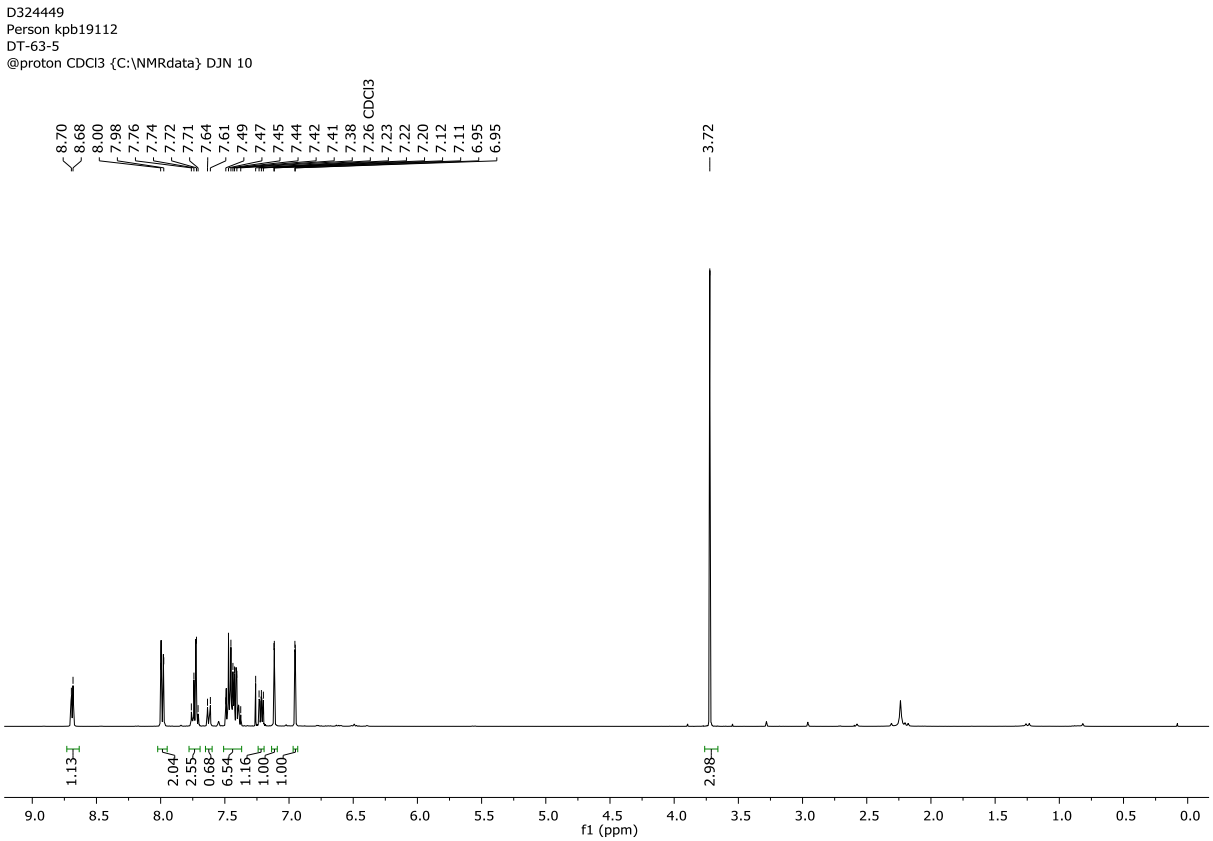
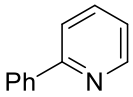
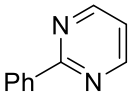


Figure S96. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine (entry 3, Table S21).

Table S22. Determination of the competition rate constant κ from the labelling experiment between 2-phenylpyridine and 2-phenylpyrimidine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-1** [(COD)Ir(IMes)PPh_3][$BArF_{24}$]
Mass	15.5 mg	15.6 mg	8.7 mg

Deuteration expected at δ (**R1**) = 8.02 – 7.97 ppm and at δ (**R2**) = 8.49 – 8.42 ppm
Determined against integral at δ (**R1**) = 7.77 – 7.70 ppm and at δ (**R2**) = 8.80 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 4.8 Hz, 2H, **R2**), 8.73 – 7.67 (m, 1H, **R1**), 8.49 – 8.42 (m, 2H/D, **R2**), 8.02 – 7.97 (m, 2H/D **R1**), 7.77 – 7.70 (m, 2H, **R1**), 7.52 – 7.39 (m, 3H, **R1** and 3H, **R2**), 7.25 – 7.20 (m, 1H, **R1**), 7.17 (t, *J* = 4.8 Hz, 1H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.39	1.94	28	1.54	2.00	23	1.28
2	1.58	1.88	16	1.71	2.00	15	1.11
3	1.59	1.85	14	1.76	2.00	12	1.18
			Average κ = 1.19				

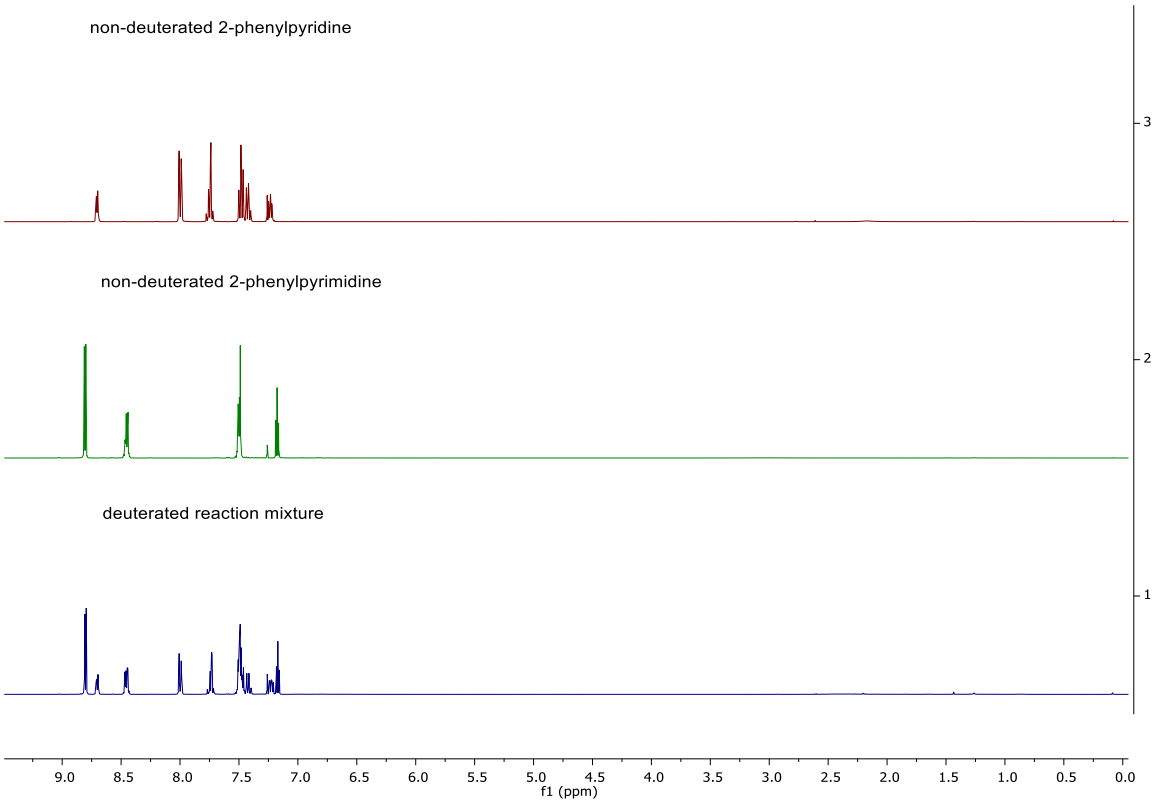


Figure S97. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

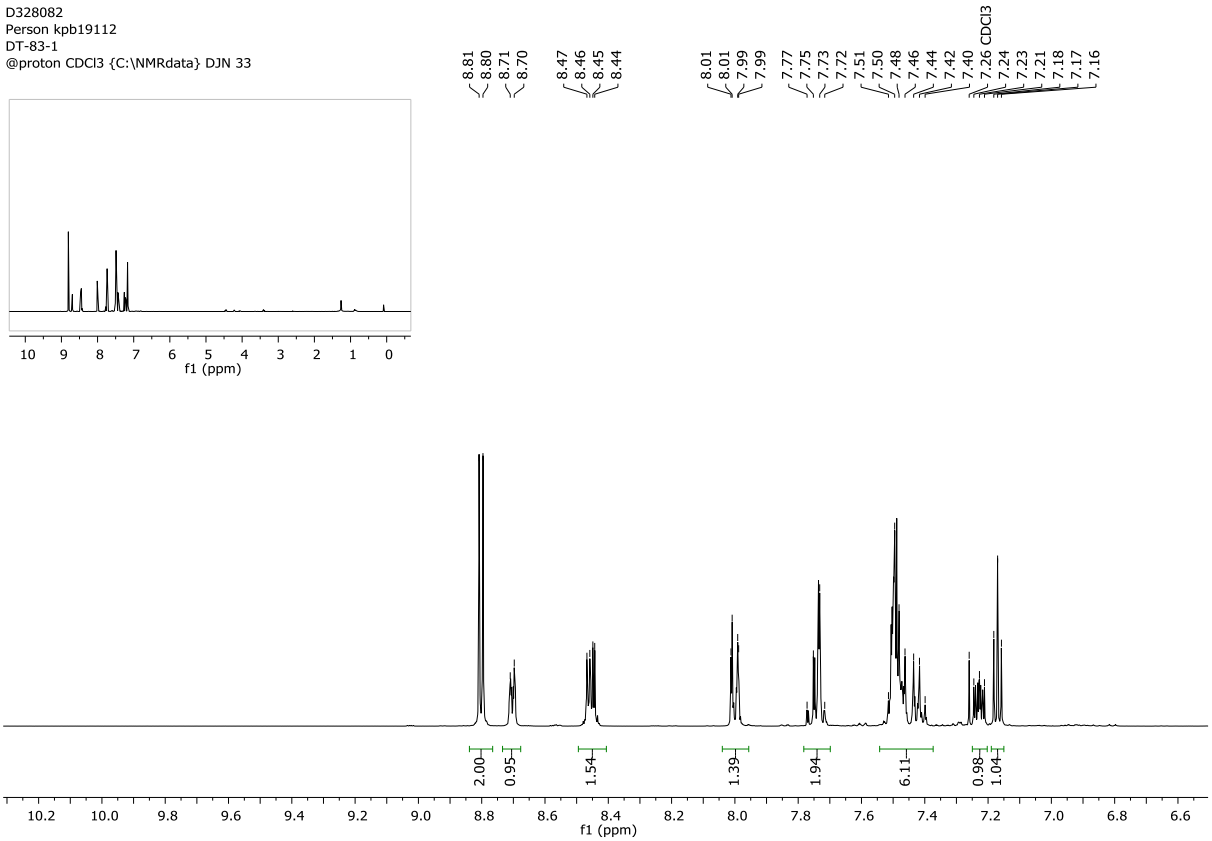


Figure S98. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyridine and 2-phenylpyrimidine (entry 1, Table S22).

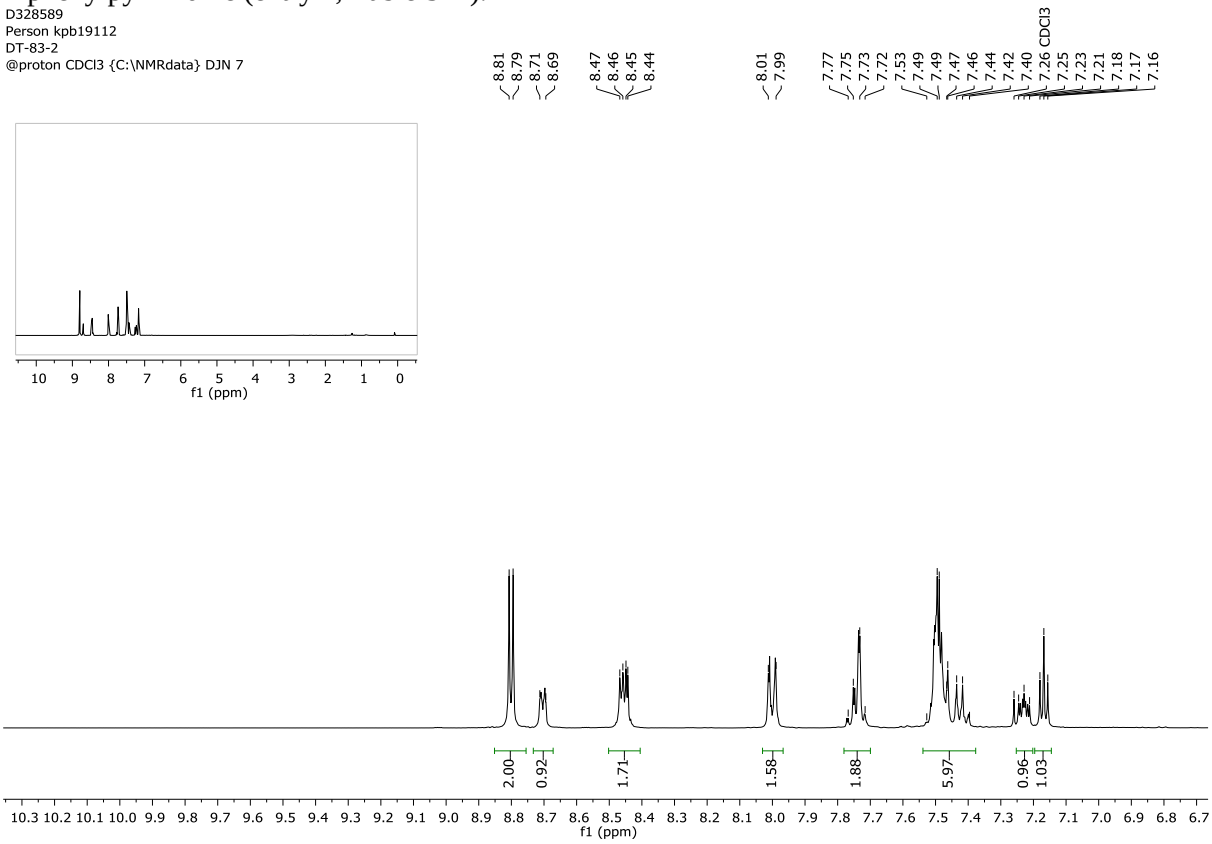


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyridine and 2-phenylpyrimidine (entry 2, Table S22).

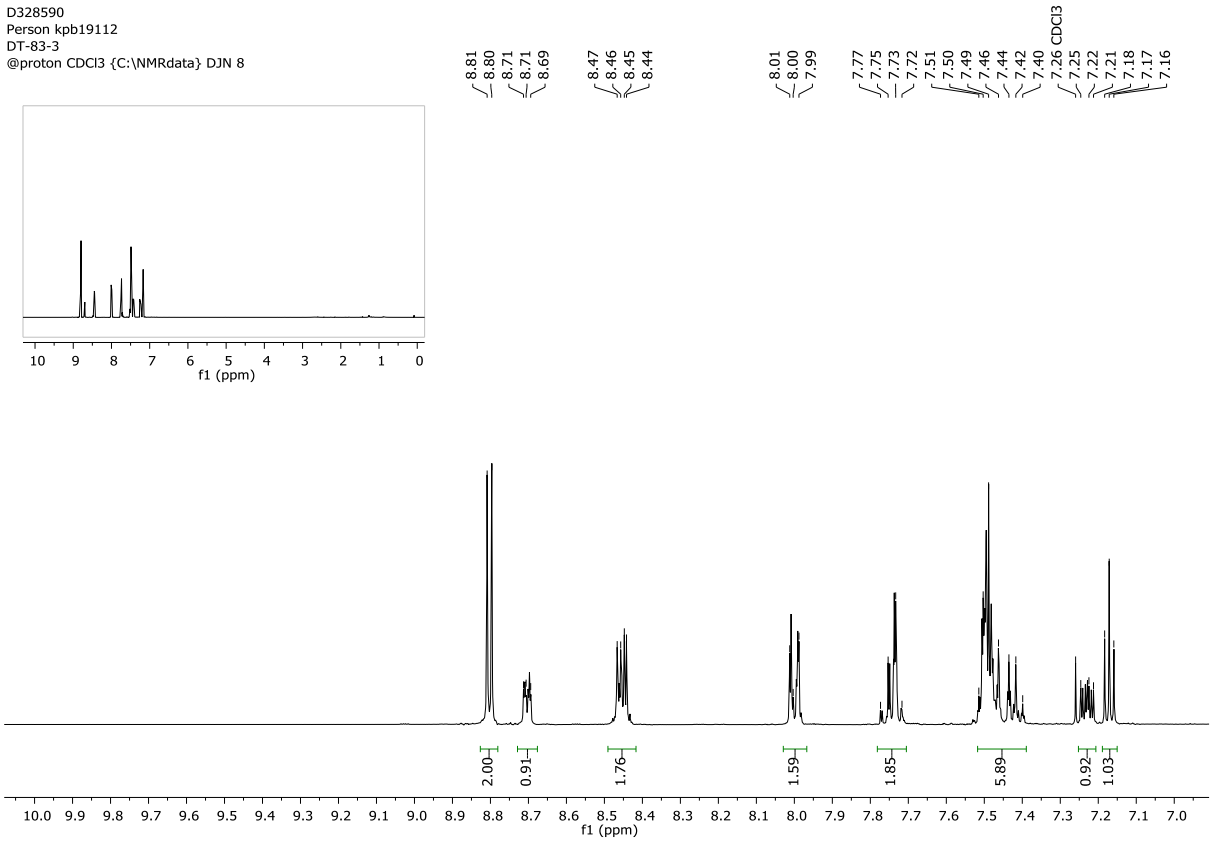
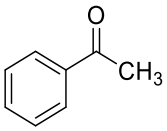
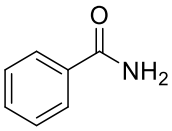


Figure S100. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyridine and 2-phenylpyrimidine (entry 3, Table S22).

3.4. Competition Experiments with (COD)Ir(IMes)Cl (Ir-2)

Table S23. Determination of the competition rate constant κ from the labelling experiment between acetophenone and benzamide.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	12.0 mg	12.1 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.95 ppm and at δ (**R2**) = 7.82 ppm
Determined against integral at δ (**R1**) = 2.60 ppm and at δ (**R2**) = 7.63 – 7.36 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 7.5 Hz, H/D **R1**), 7.82 (d, *J* = 7.4 Hz, H/D **R2**), 7.63 – 7.36 (m, 3H **R1** and 3H **R2**), 6.25 – 6.13 (bs, 2H, **R2**), 2.60 (s, 3H, **R1**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 3H	$\%D_{R2}$	κ
1	1.76	3.00	12	1.95	3.20[a]	9	1.42
2	1.71	3.00	15	1.76	2.93[b]	10	1.50
3	1.41	3.00	30	2.22	4.11[c]	19	1.66
				Average κ = 1.53			

[a] $I_{R2(0)}$ = 6.20 – 3.00; [b] $I_{R2(0)}$ = 5.93 – 3.00; [c] $I_{R2(0)}$ = 7.11 – 3.00;

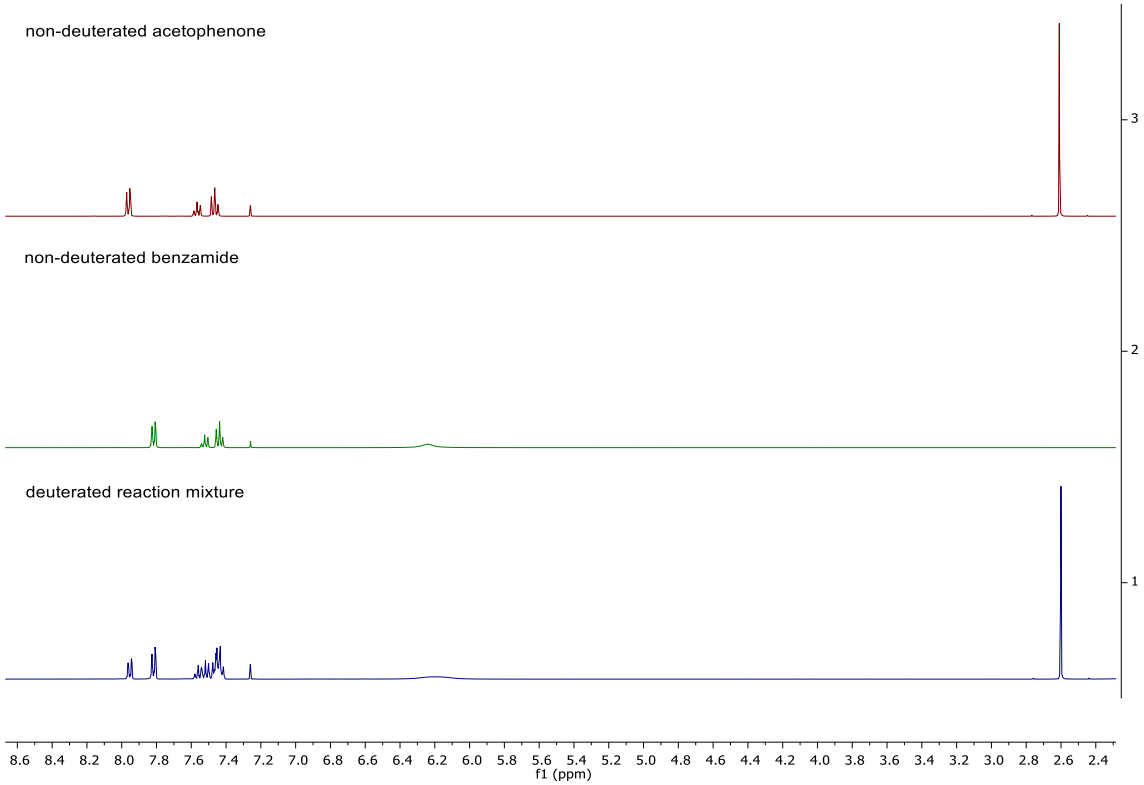


Figure S101. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture

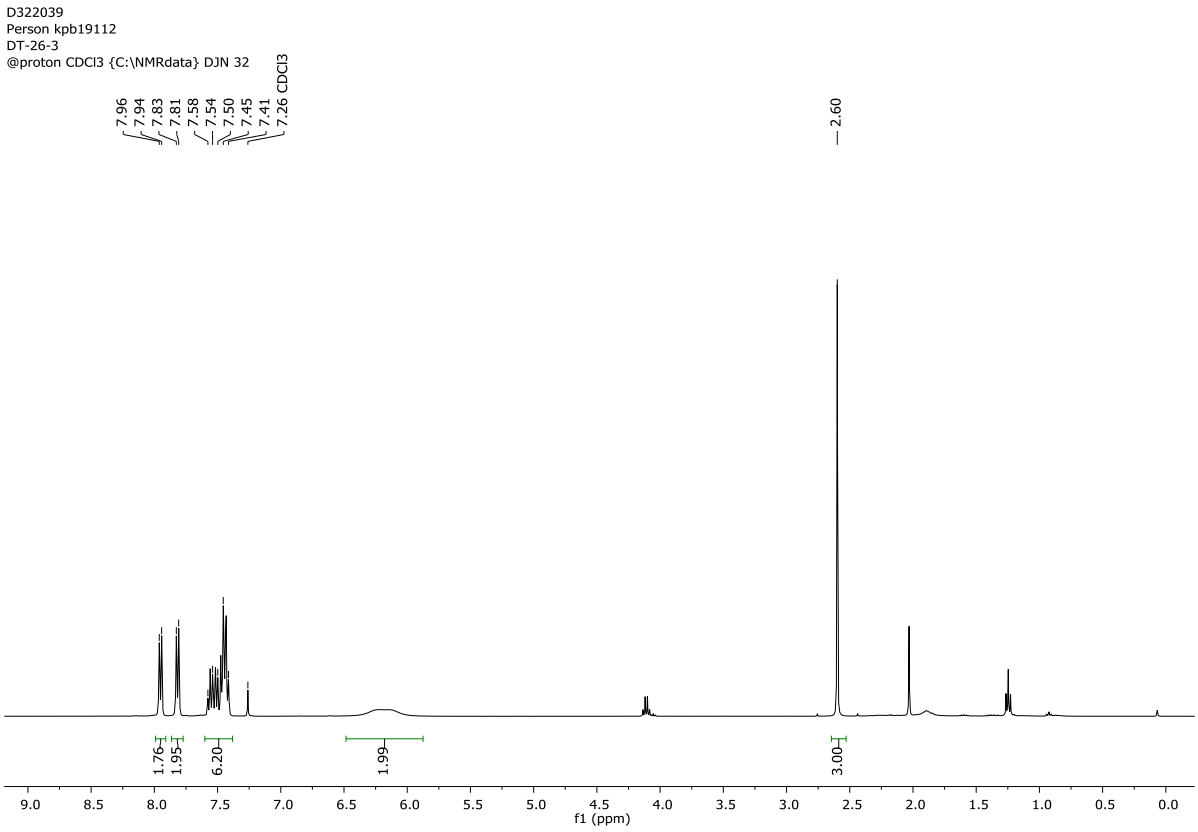


Figure S102. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzamide (entry 1, Table S23).

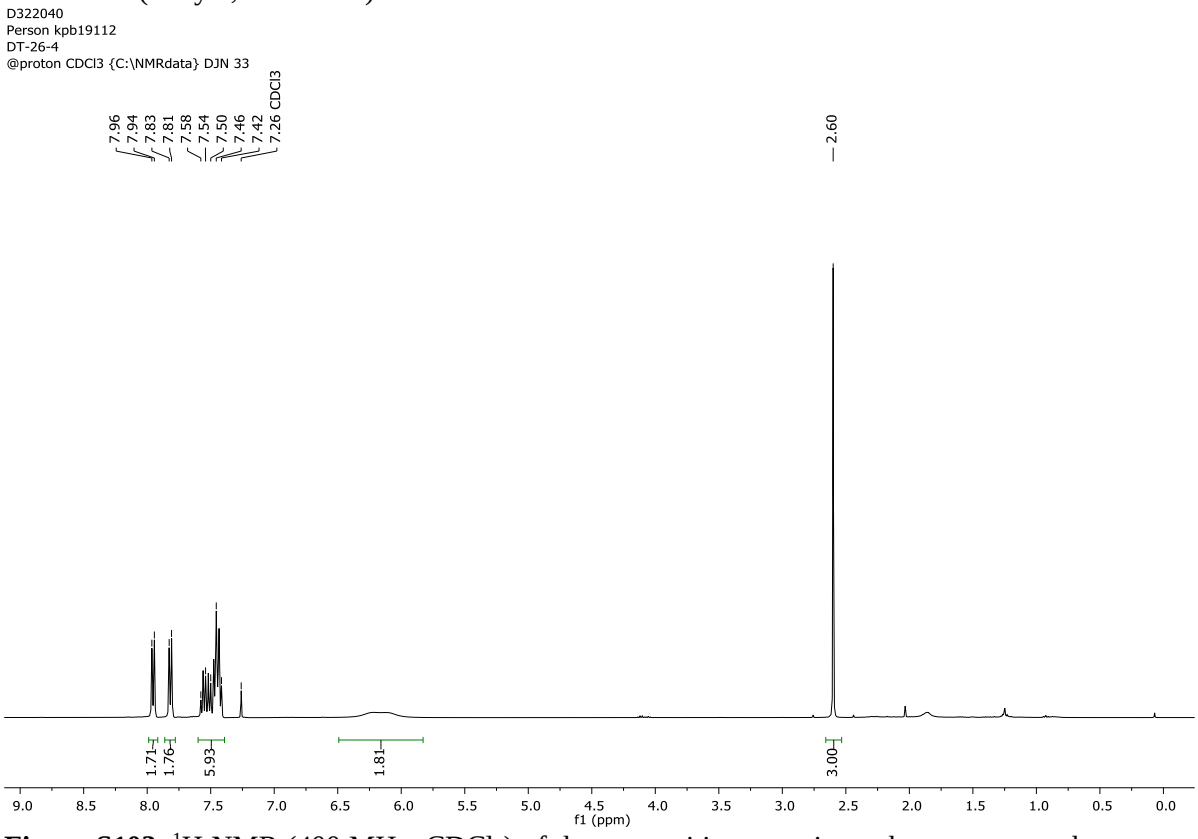


Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzamide (entry 2, Table S23).

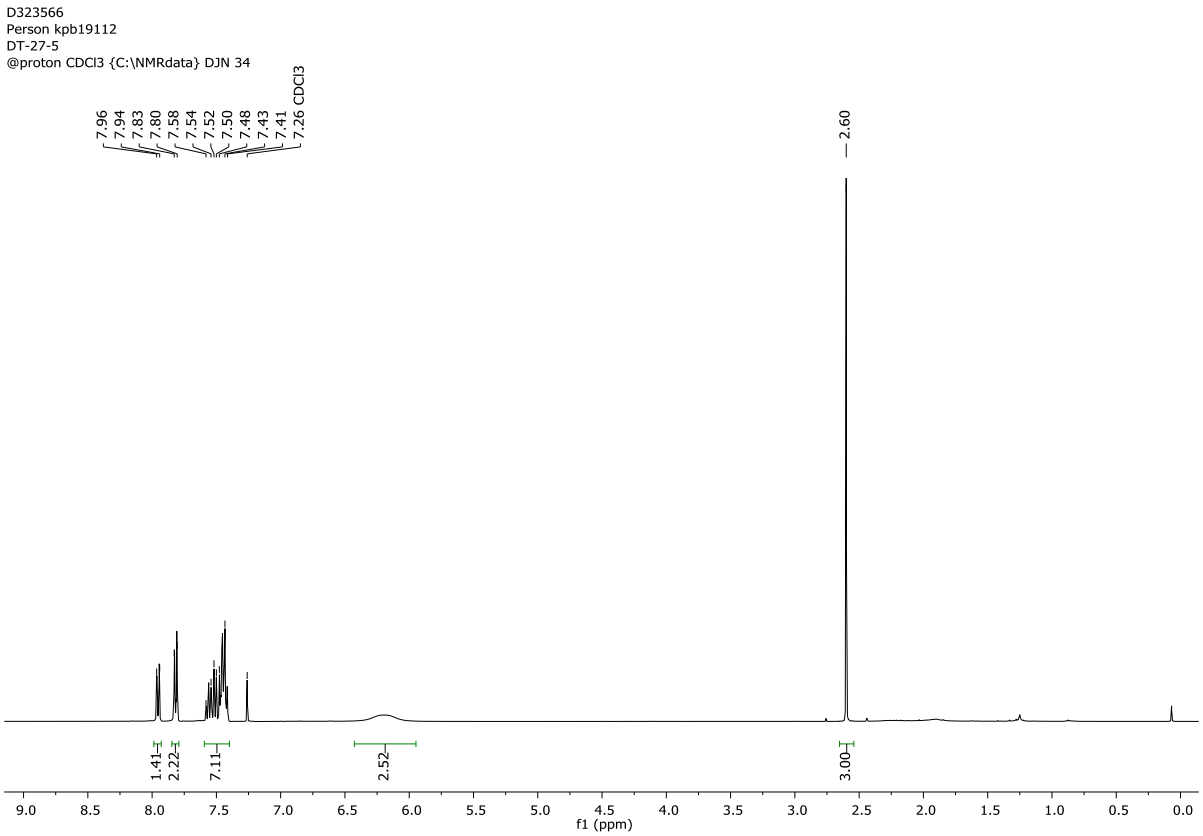
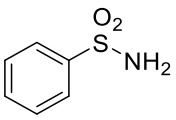
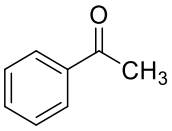


Figure S104. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and benzamide (entry 3, Table S23).

Table S24. Determination of the competition rate constant κ from the labelling experiment between benzenesulfonamide and acetophenone.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	15.7 mg	12.0 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.87 – 7.80 ppm and at δ (**R2**) = 7.99 – 7.93 ppm
Determined against integral at(**R1**) = 7.66 – 7.51 ppm and at δ (**R2**) = 2.58 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.99 – 7.93 (m, 2H/D **R2**), 7.87 – 7.80 (m, 2H/D **R1**), 7.67 – 7.49 (m, 3H **R1** and 3H **R2**), 7.35 (br, 2H, **R1**), 2.58 (s, 3H, **R2**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 3H	$\%D_{R2}$	κ
1	2.01	4.26[a]	29	1.45	3.00	28	1.07
2	1.50	3.80[b]	41	1.37	3.00	32	1.39
3	1.66	5.39[c]	54	1.09	3.00	46	1.27
Average κ = 1.24							

[a] $I_{R1(t)}$ = 7.26 – 3.00; [b] $I_{R1(t)}$ = 6.80 – 3.00; [c] $I_{R1(t)}$ = 8.39 – 3.00;

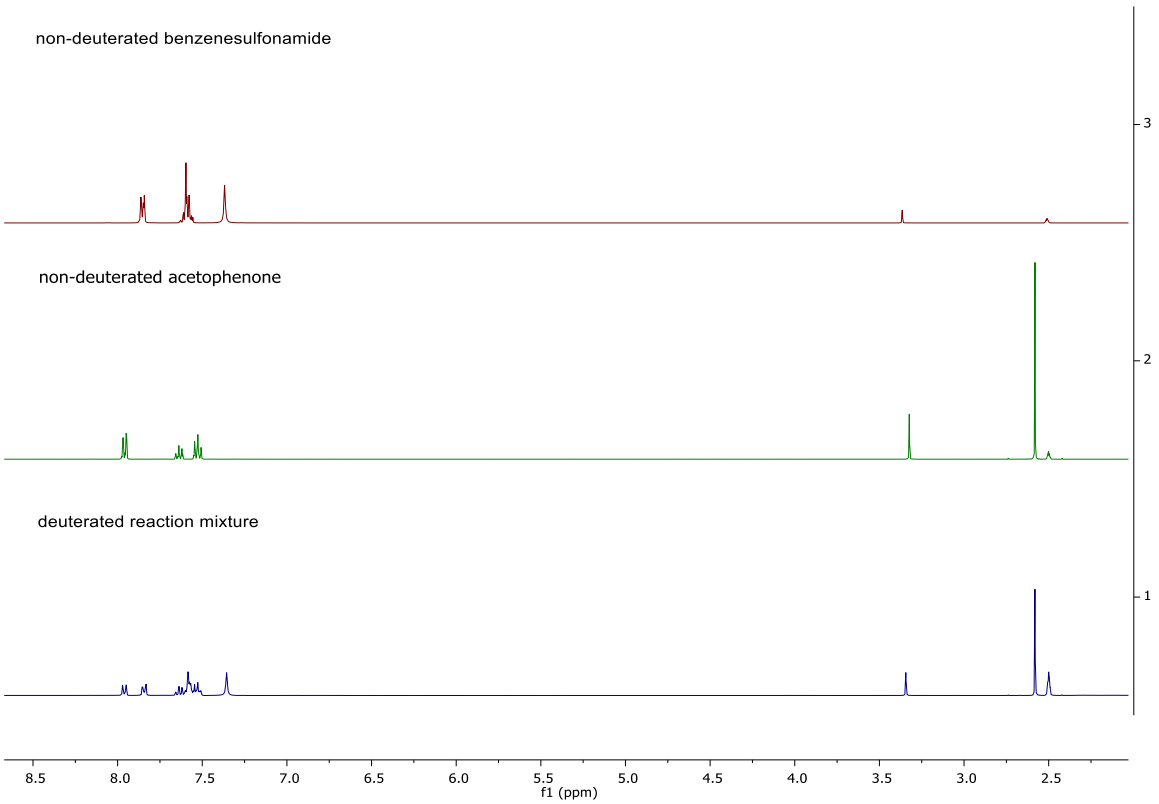


Figure S105. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

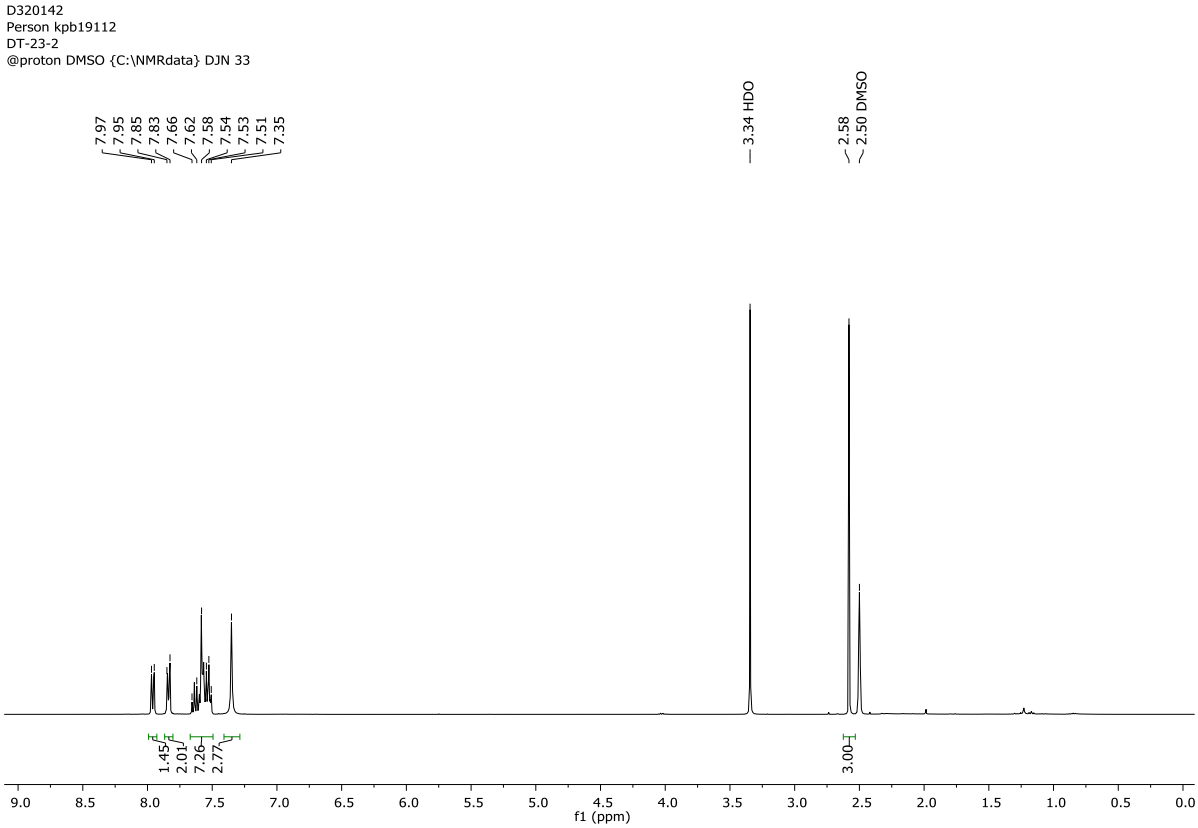


Figure S106. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and acetophenone (entry 1, Table S24).

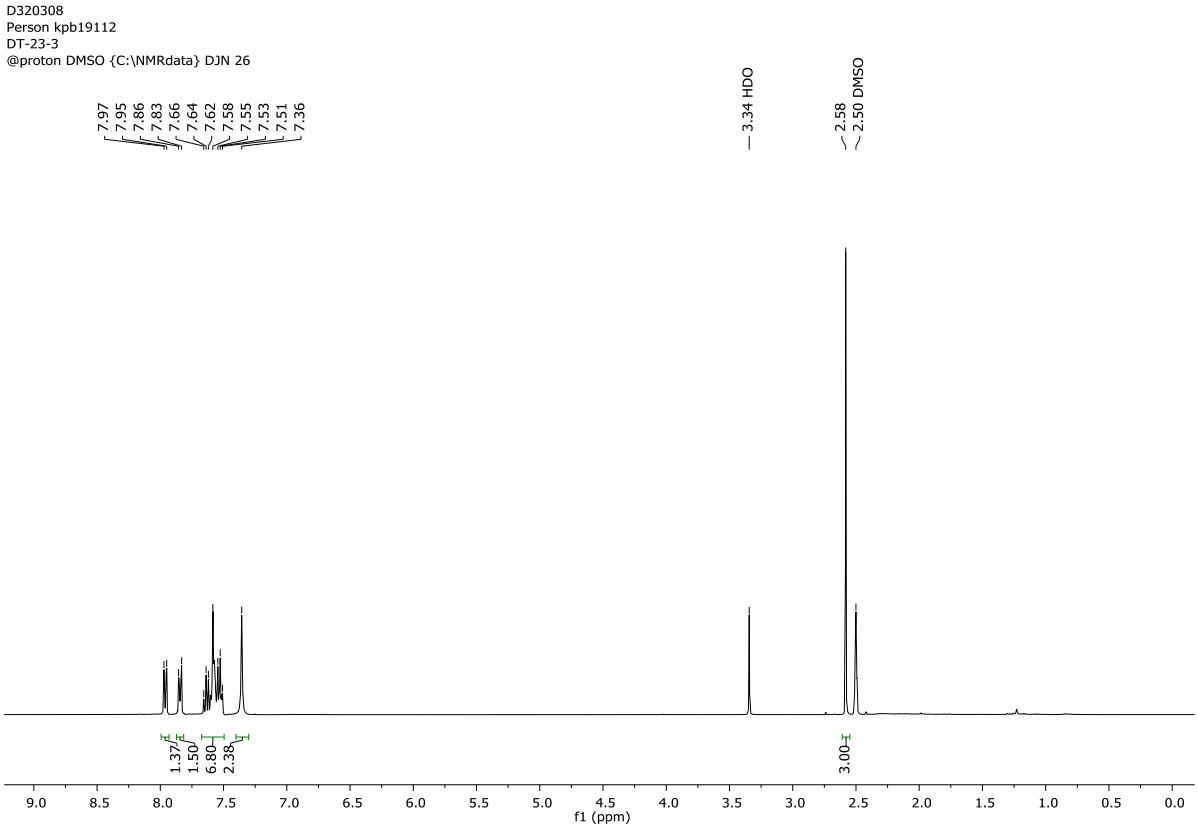


Figure S107. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and acetophenone (entry 2, Table S24).

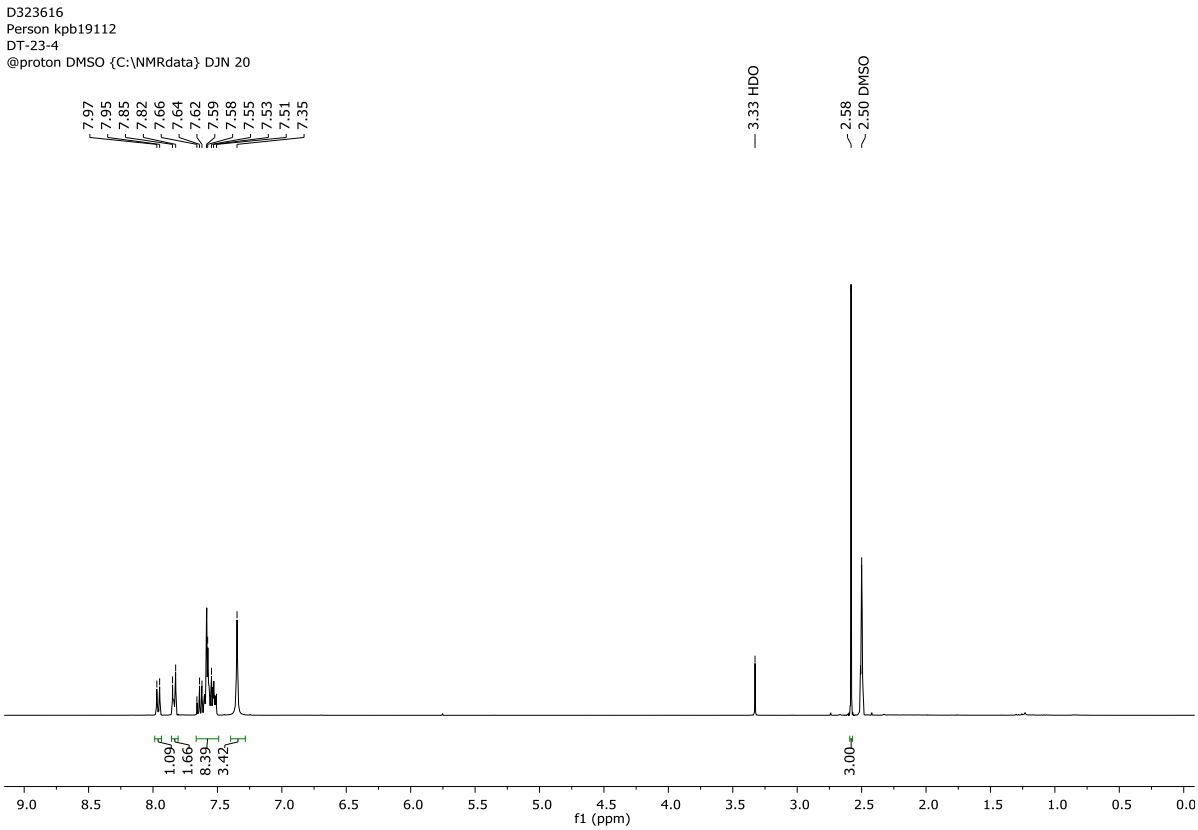
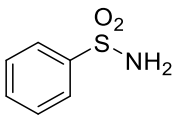
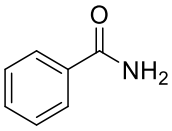


Figure S108. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and acetophenone (entry 3, Table S24).

Table S25. Determination of the competition rate constant κ from the labelling experiment between benzenesulfonamide and benzamide.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	15.7 mg	12.1 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.86 – 7.81 ppm and at δ (**R2**) = 7.90 – 7.86 ppm
Determined against integral at δ (**R1**) =7.63 – 7.54 ppm and at δ (**R2**) = 7.48 – 7.41 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.96 (bs, 1H, **R2**), 7.90 – 7.86 (m, 2H/D **R2**), 7.86 – 7.81 (m, 2H/D **R1**), 7.63 – 7.54 (m, 3H, **R1**), 7.54 – 7.49 (m, 1H, **R2**), 7.48 – 7.41 (m, 2H, **R2**), 7.35 (bs, 1H, **R2** and 2H, **R1**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.30	3.07	36	1.84	2.00	8	5.44
2	1.44	3.19	32	1.88	2.00	6	6.30
3	1.55	2.98	22	1.90	2.00	5	4.84
				Average κ = 5.53			

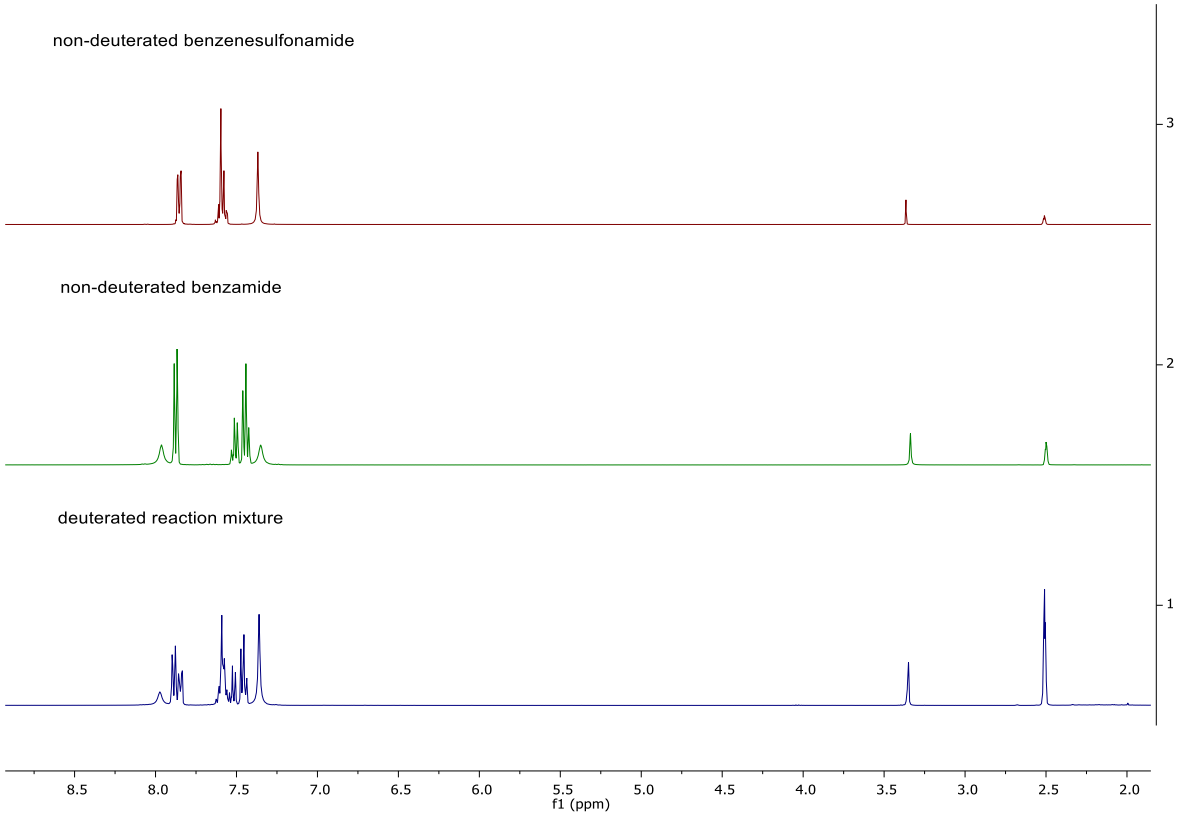


Figure S109. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

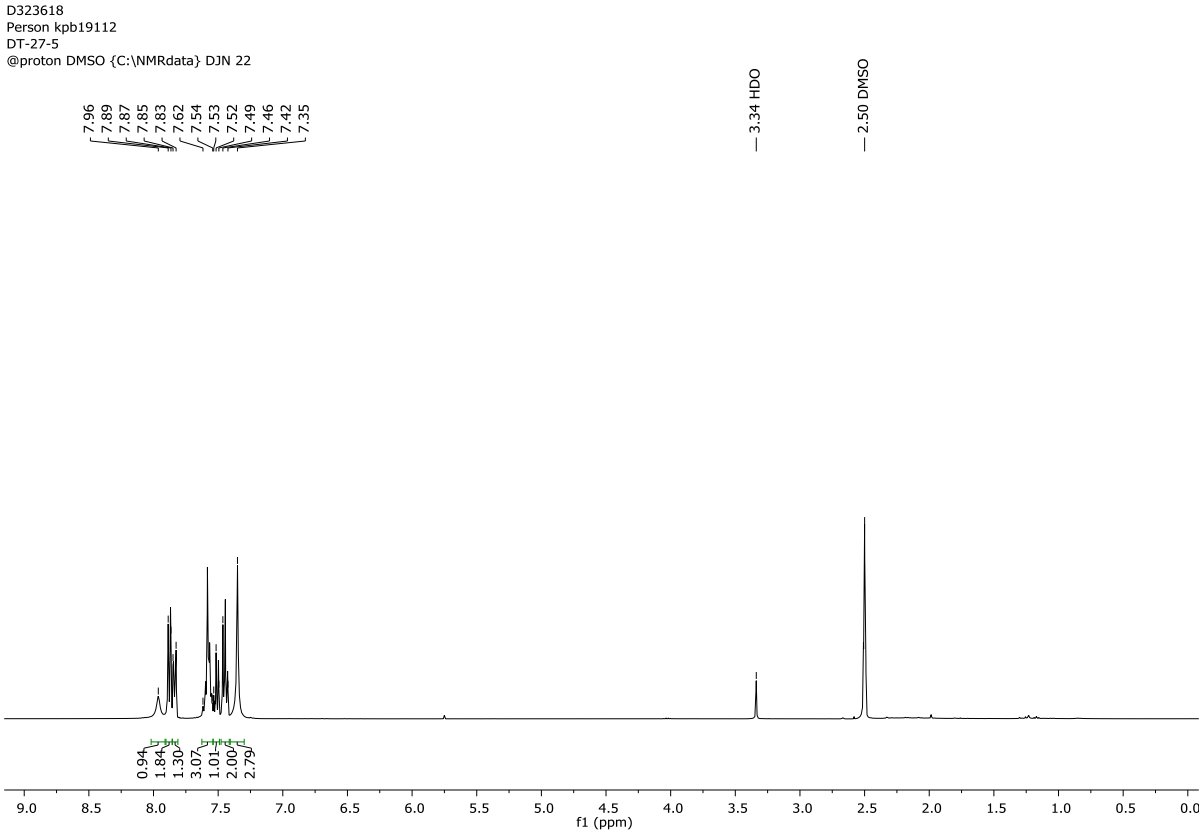


Figure S110. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and benzamide (entry 1, Table S25)**.**

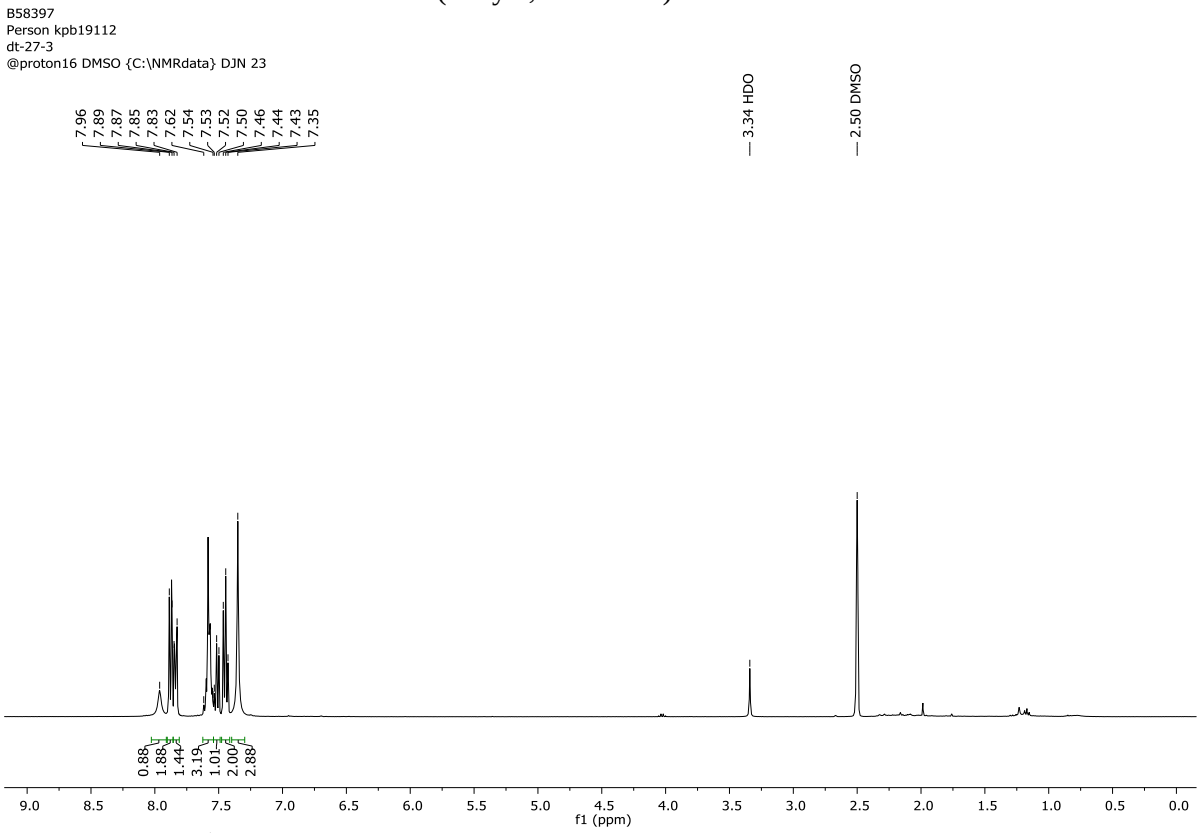


Figure S111. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and benzamide (entry 2, Table S25).

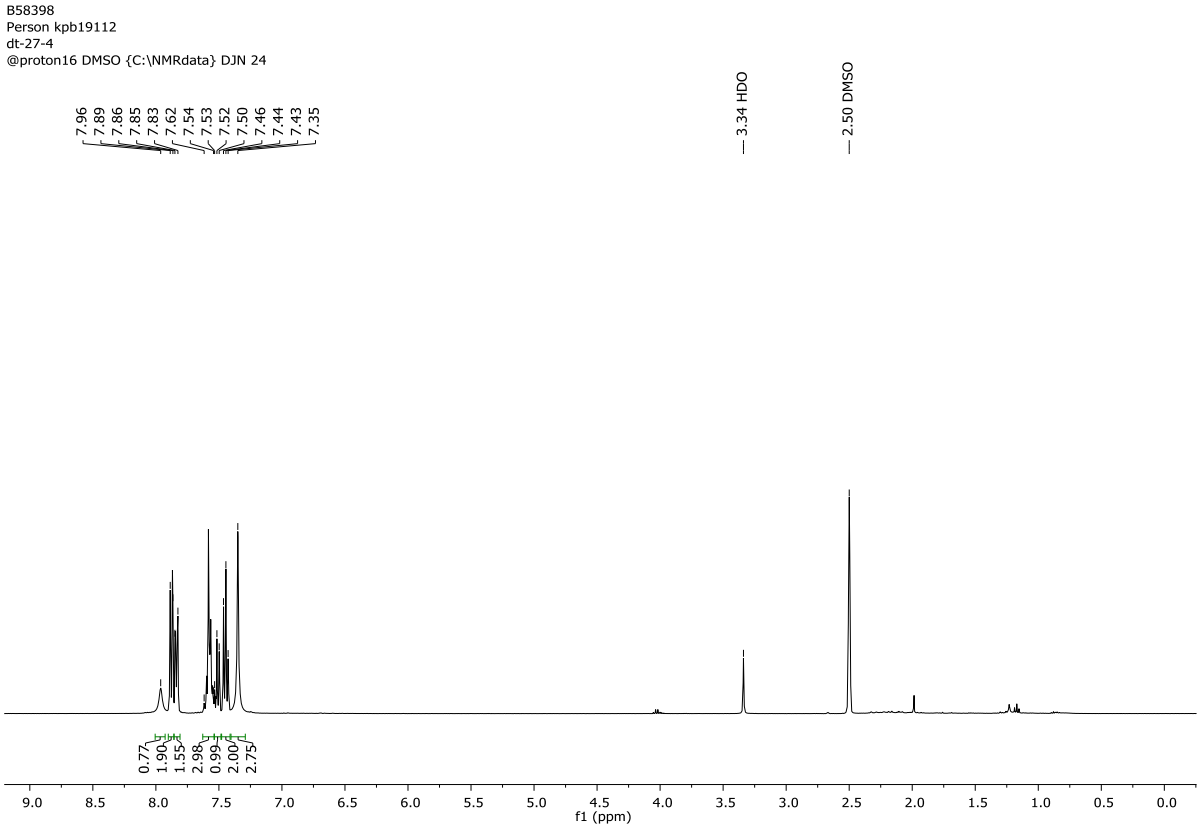
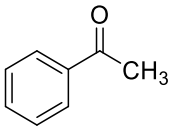
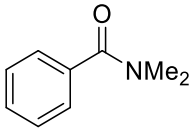


Figure S112. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and benzamide (entry 3, Table S25).

Table S26. Determination of the competition rate constant κ from the labelling experiment between acetophenone and *N*,*N*-dimethylbenzamide.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	12.0 mg	14.9 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.99 – 7.92 ppm and at δ (**R2**) = 7.42 – 7.35 ppm
Determined against integral at δ (**R1**) = 2.60 ppm and at δ (**R2**) = 3.18 – 2.88 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.92 (m, 2H/D **R1**), 7.58 – 7.53 (m, 1H, **R1**), 7.48 – 7.43 (m, 2H, **R1**), 7.42 – 7.35 (m, 2H/D **R2** and 3H, **R2**), 3.18 – 2.88 (m, 6H, **R2**), 2.60 (s, **3H**, R1)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 6H	$\%D_{R2}$	κ
1	0.83	3.00	59	2.99[a]	9.79	9	9.87
2	0.94	3.00	53	1.88[b]	6.12	8	9.24
3	1.04	3.00	48	2.12[c]	6.77	6	10.09
				Average κ = 9.73			

[a] $I_{R2(t)}$ = 7.88 – (9.79) / 6 × 3; [b] $I_{R2(t)}$ = 4.94 – (6.12) / 6 × 3; [c] $I_{R2(t)}$ = 5.50 – (6.77) / 6 × 3

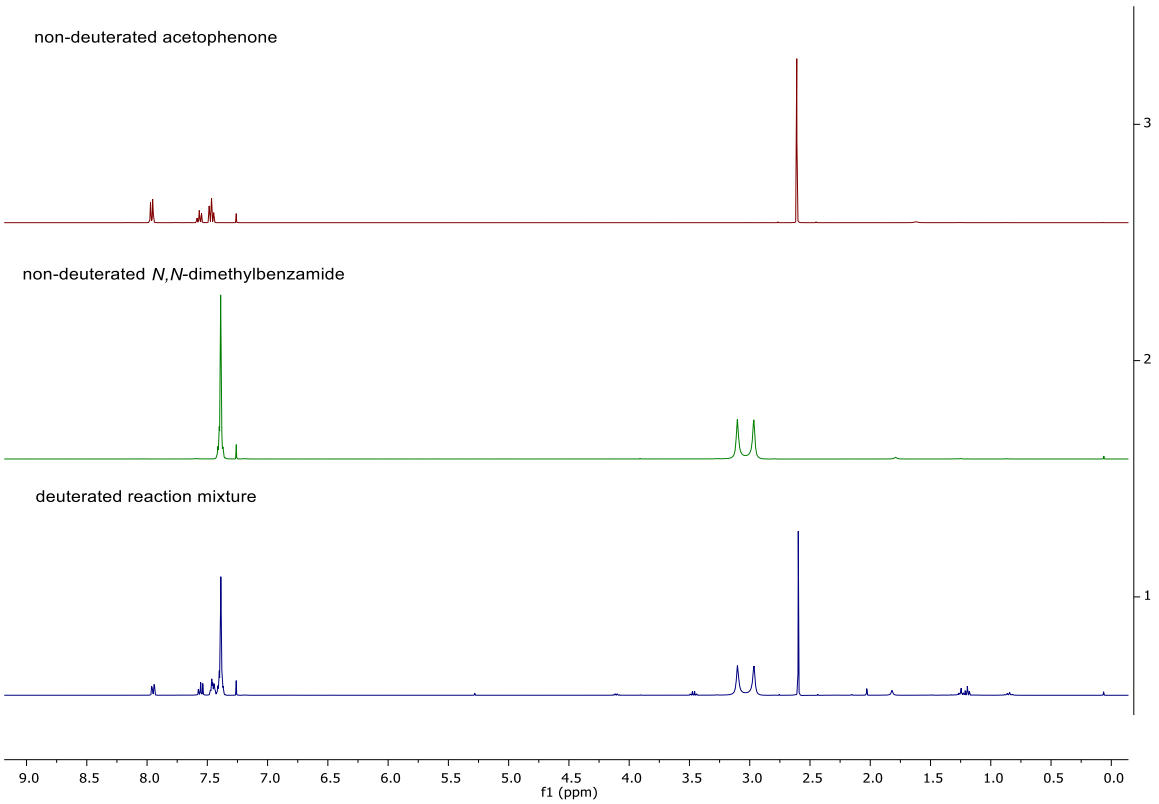


Figure S113. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

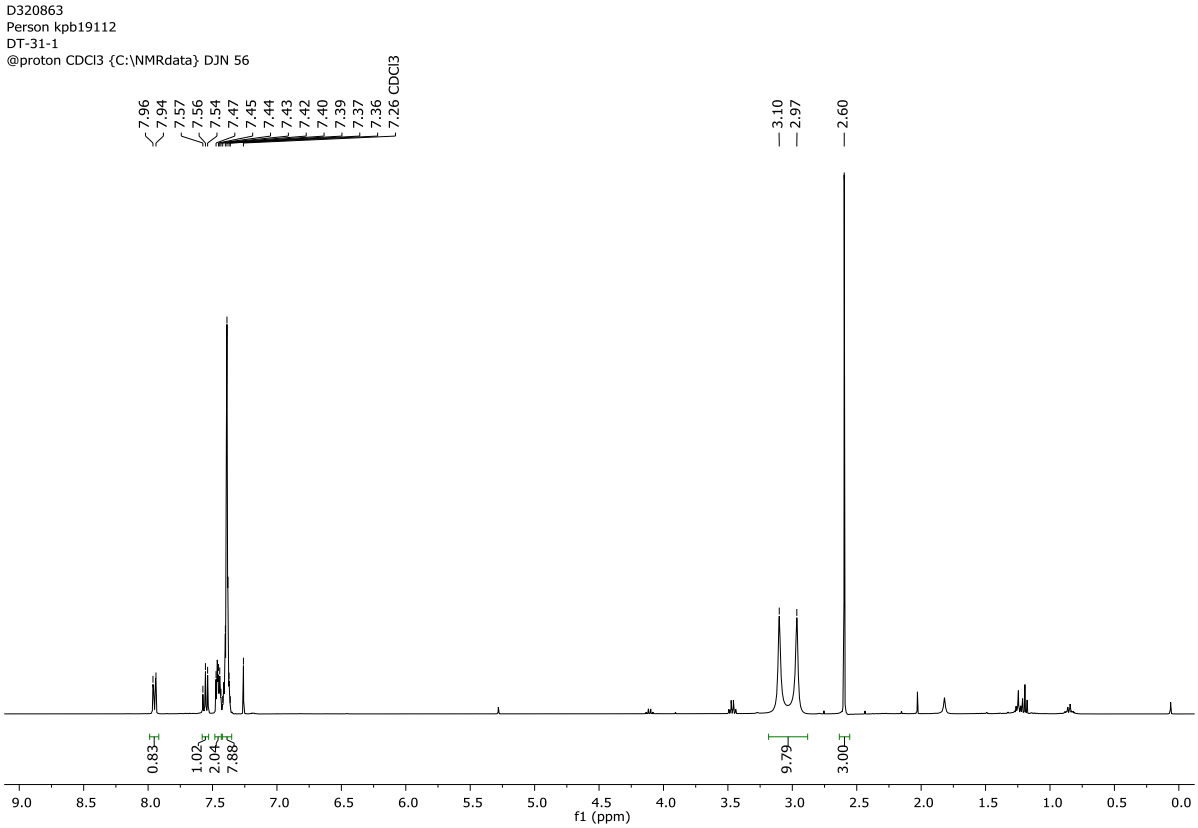


Figure S114. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and *N*,*N*-dimethylbenzamide (entry 1, Table S26).

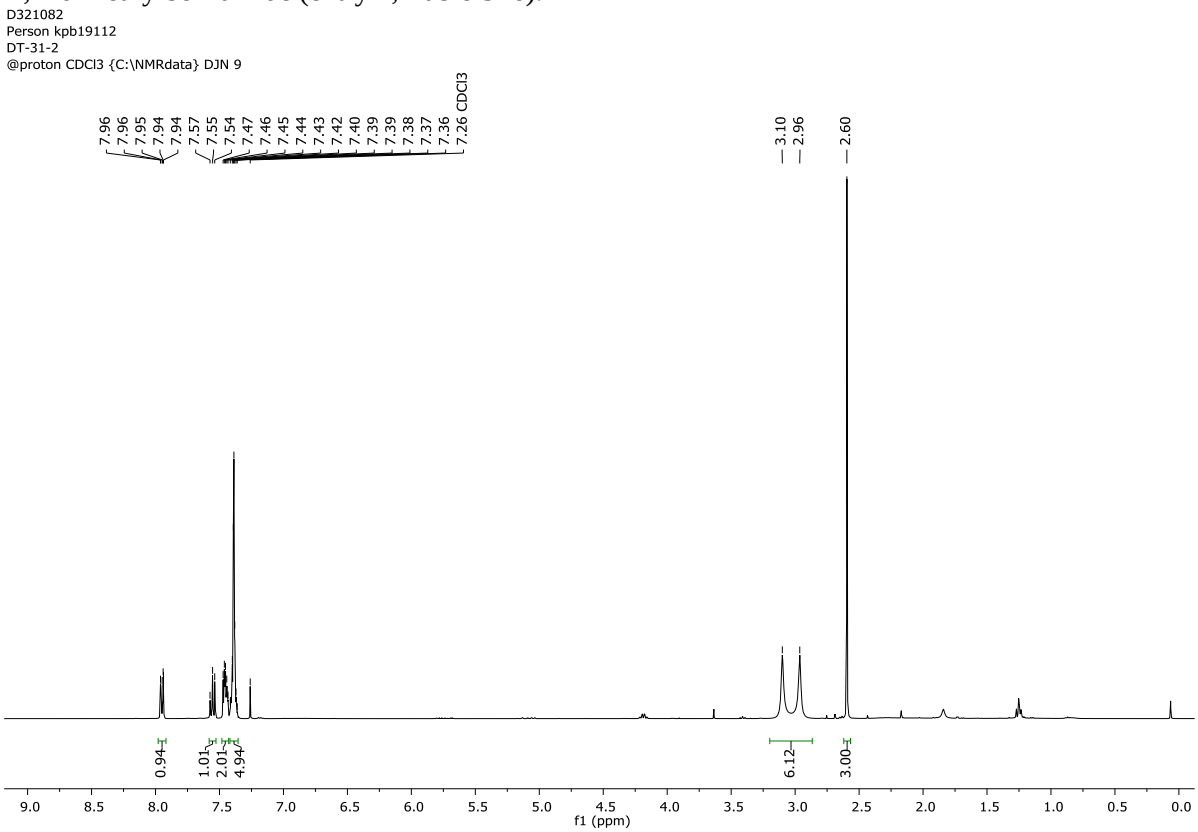


Figure S115. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and *N*,*N*-dimethylbenzamide (entry 2, Table S26).

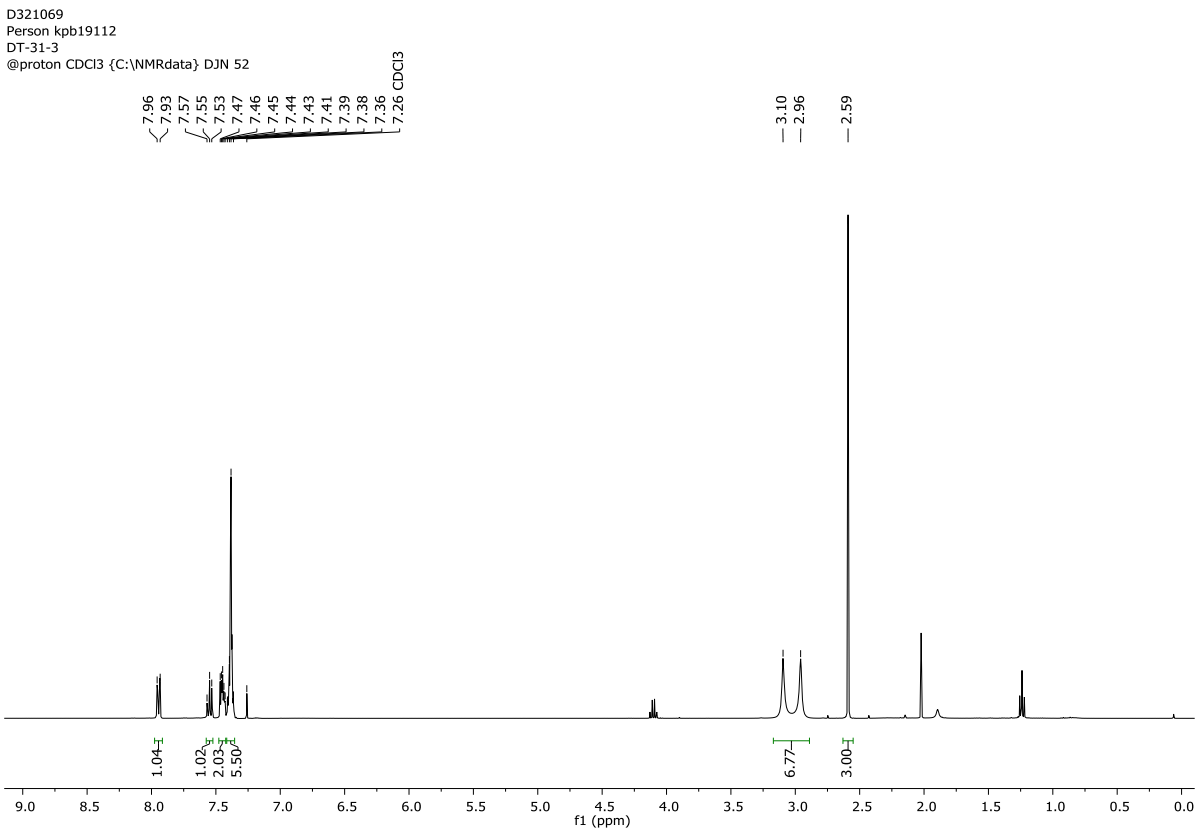
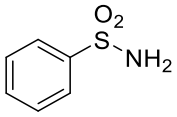
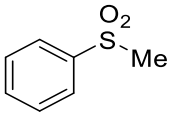


Figure S116. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between acetophenone and *N*,*N*-dimethylbenzamide (entry 3, Table S26).

Table S27. Determination of the competition rate constant κ from the labelling experiment between benzenesulfonamide and methylphenylsulfone.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	15.7 mg	15.6 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.85 – 7.83 ppm and at δ (**R2**) =7.95 – 7.93 ppm
Determined against integral at δ (**R1**) = 7.60 – 7.55 ppm and at δ (**R2**) = 7.64 – 7.62 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.95 – 7.93 (m, 2H/D **R2**), 7.85 – 7.83 (m, 2H/D **R1**), 7.76 – 7.72 (m, 1H, **R2**), 7.64 – 7.62 (m, 2H, **R2**), 7.60 – 7.55 (m, 3H, **R1**), 7.35 (bs, 2H, **R1**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 3H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.42	2.94	28	1.98	2.00	1	32.07
2	0.64	2.68	64	1.95	2.00	3	40.55
3	1.42	3.30	35	1.98	2.00	1	43.56
Average κ = 38.73							

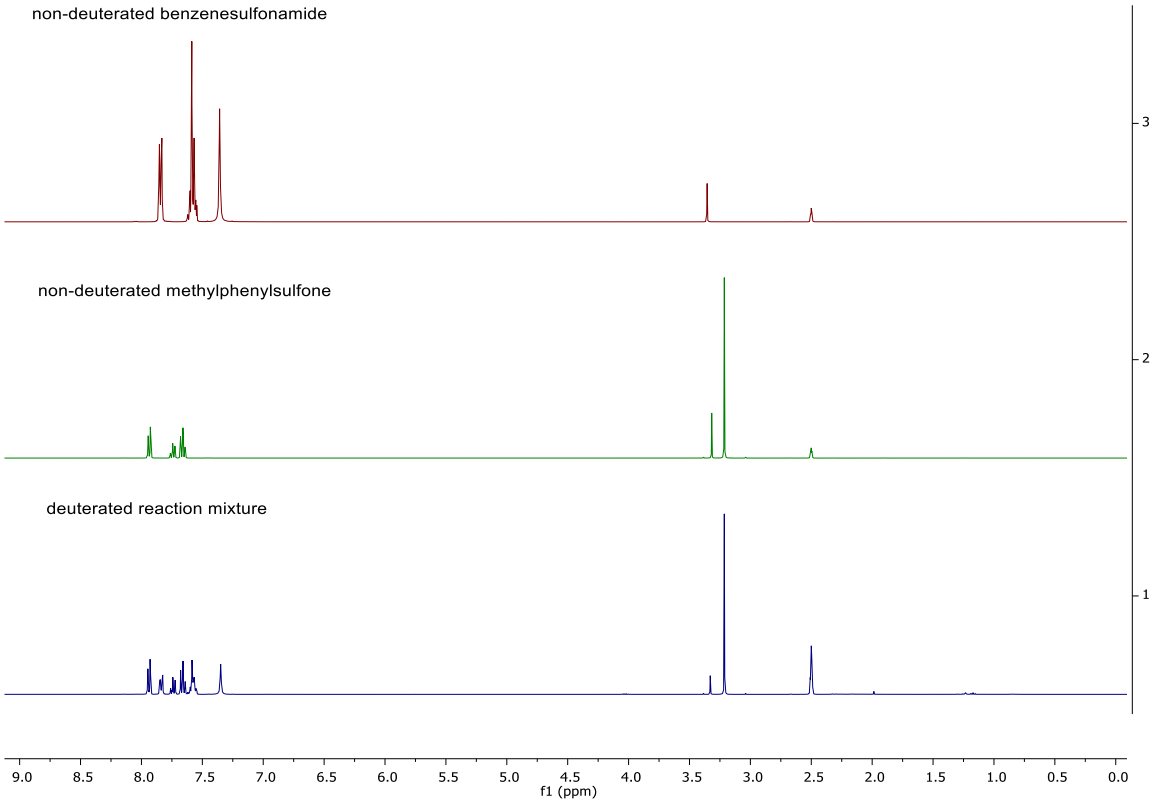


Figure S117. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

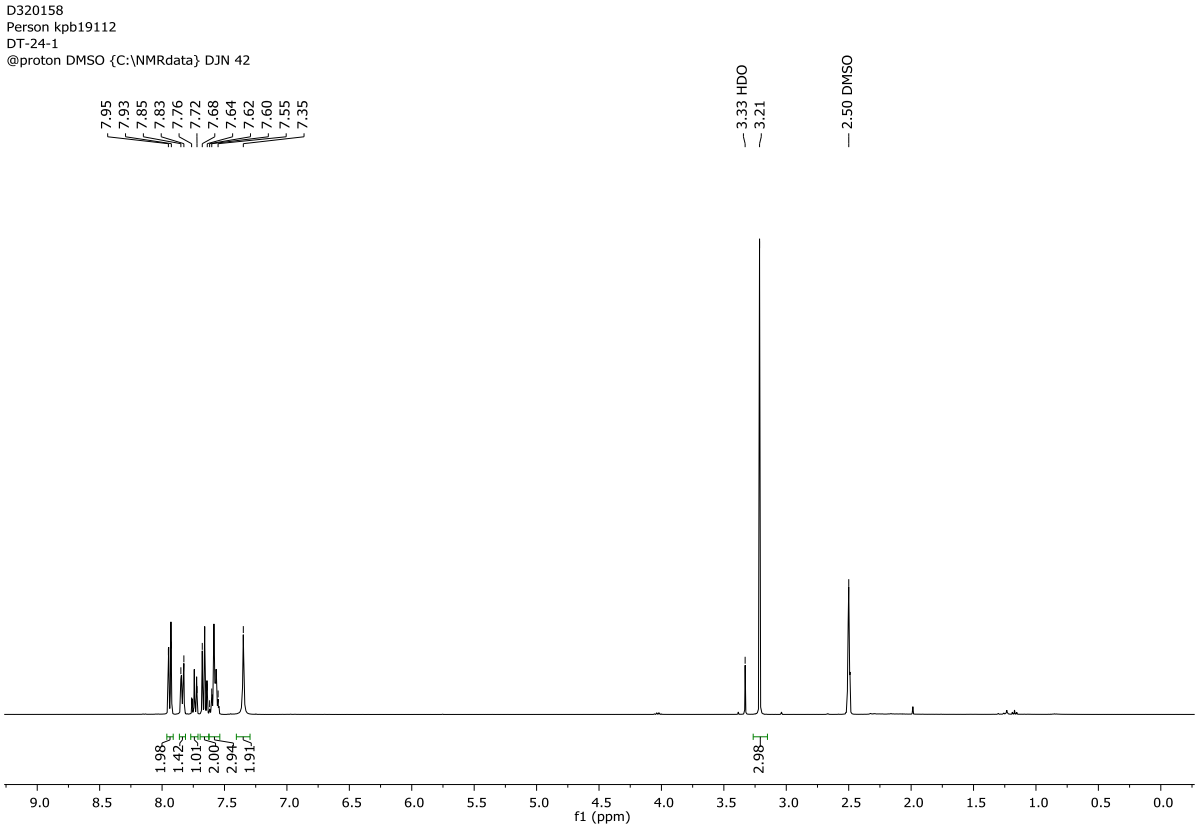


Figure S118. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and methylphenylsulfone (entry 1, Table S27).

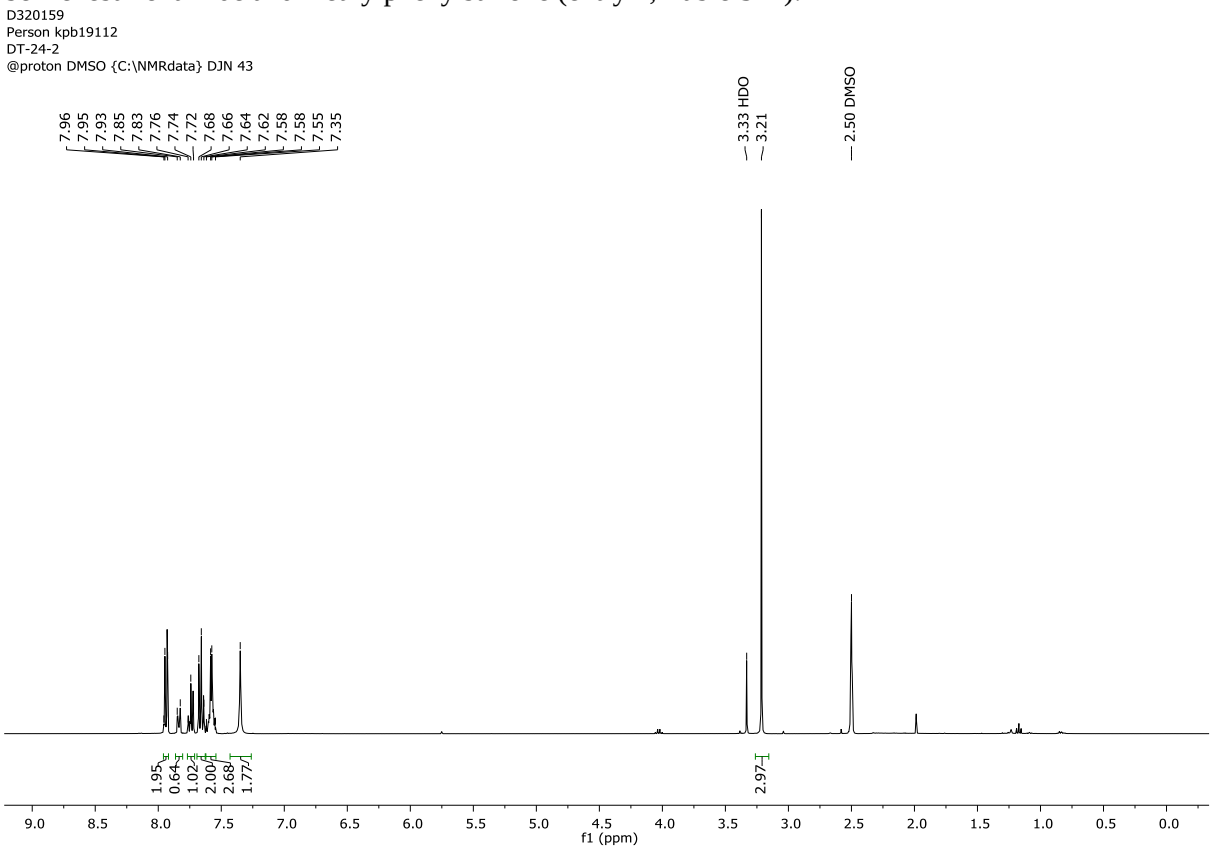


Figure S119. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and methylphenylsulfone (entry 2, Table S27).

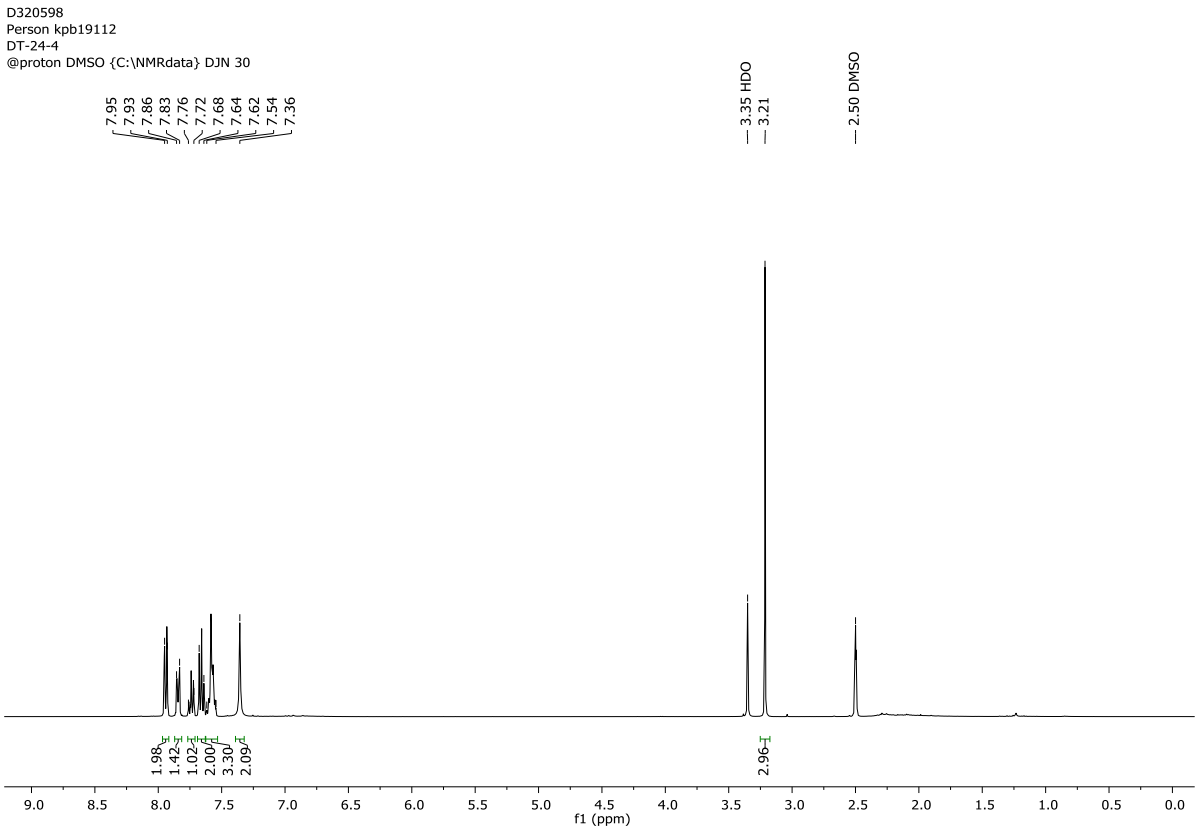
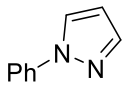
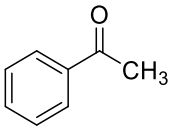


Figure S120. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between benzenesulfonamide and methylphenylsulfone (entry 3, Table S27).

Table S28. Determination of the competition rate constant κ from the labelling experiment between 1-phenylpyrazole and acetophenone.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	14.4 mg	12.0 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.73 – 7.69 ppm and at δ (**R2**) = 7.98 – 7.94 ppm
Determined against integral at δ (**R1**) = 6.48 – 6.42 ppm and at δ (**R2**) = 2.60 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.94 (m, 2H/D **R2**), 7.92 (d, *J* = 2.4 Hz, 1H, **R1**), 7.75 – 7.67 (m, 2H/D **R1** and 1H, **R1**), 7.60 – 7.53 (m, 1H, **R2**), 7.49 – 7.42 (m, 2H, **R1** and 2H, **R2**), 7.31 – 7.26 (m, 1H, **R1**), 6.48 – 6.45 (m, 1H, **R1**), 2.60 (s, 3H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 3H	$\%D_{R2}$	κ
1	0.99[a]	1.03	52	1.95	3.00	3	28.94
2	0.91[b]	1.43	68	1.92	3.00	4	28.05
3	0.93[c]	1.05	56	1.95	3.00	3	32.17
				Average κ = 29.72			

[a] $I_{R1(t)}$ = 2.02 – 1.03; [b] $I_{R1(t)}$ = 2.34 – 1.43; [c] $I_{R1(t)}$ = 1.98 – 1.05;

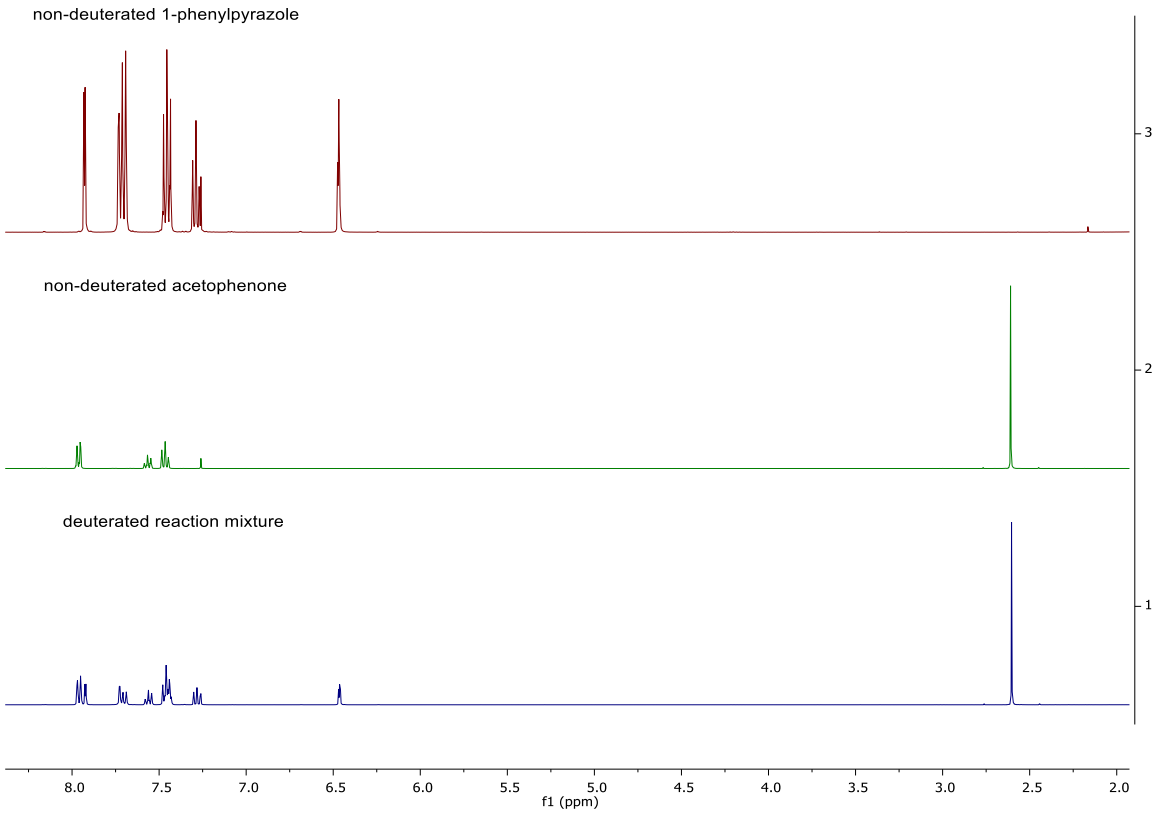


Figure S121. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

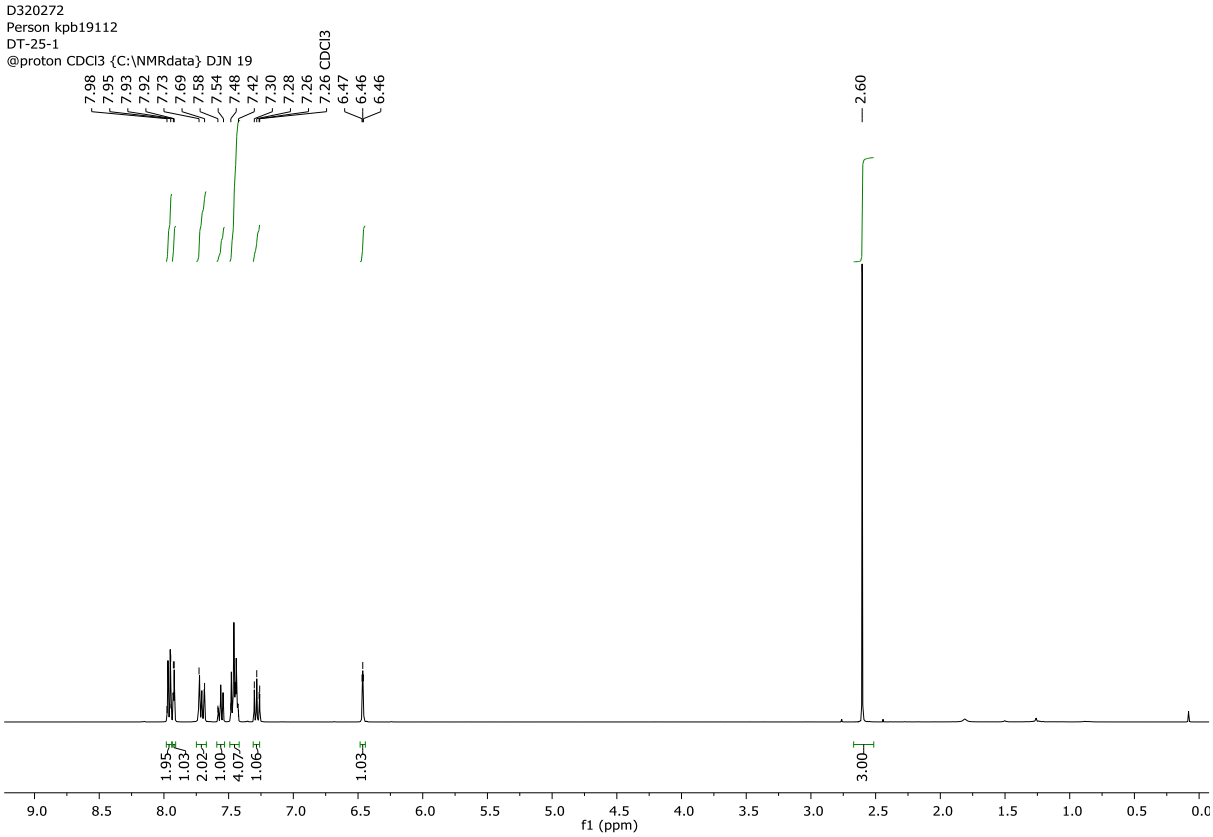


Figure S122. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and acetophenone (entry 1, Table S28).

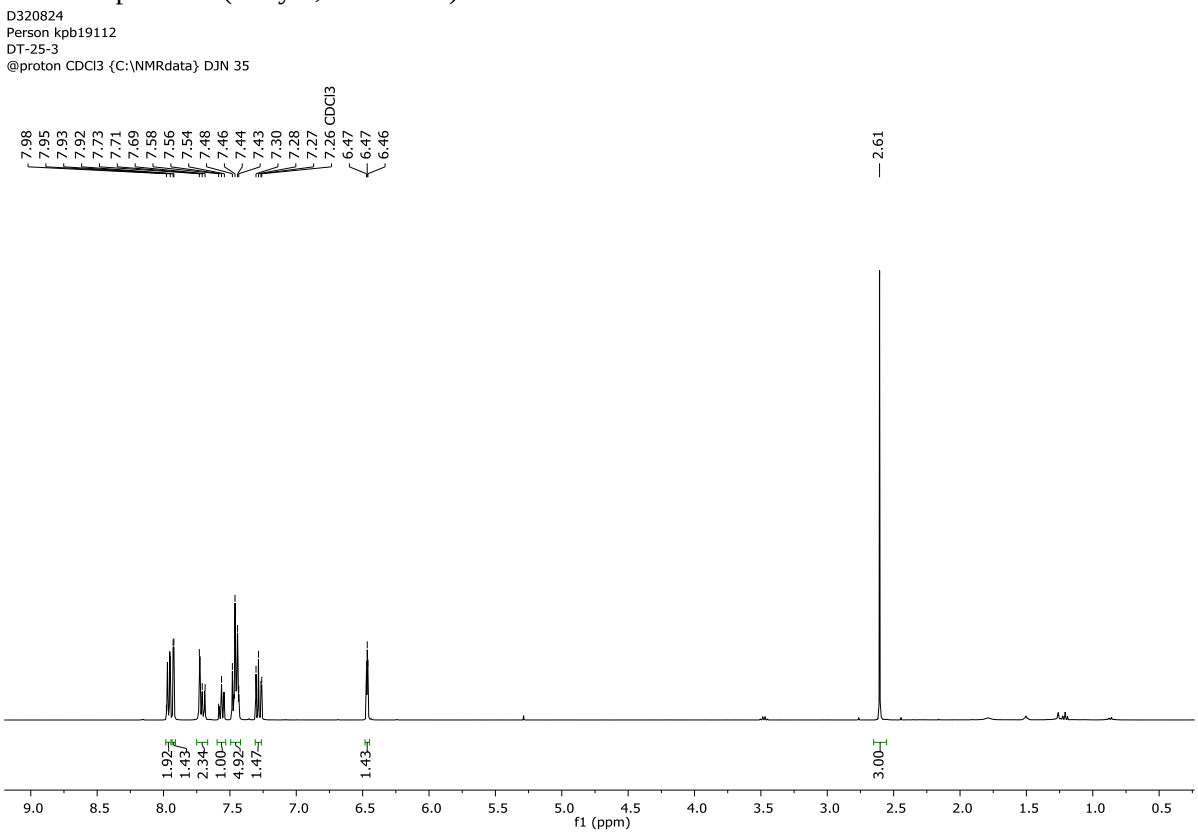


Figure S123. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and acetophenone (entry 2, Table S28).

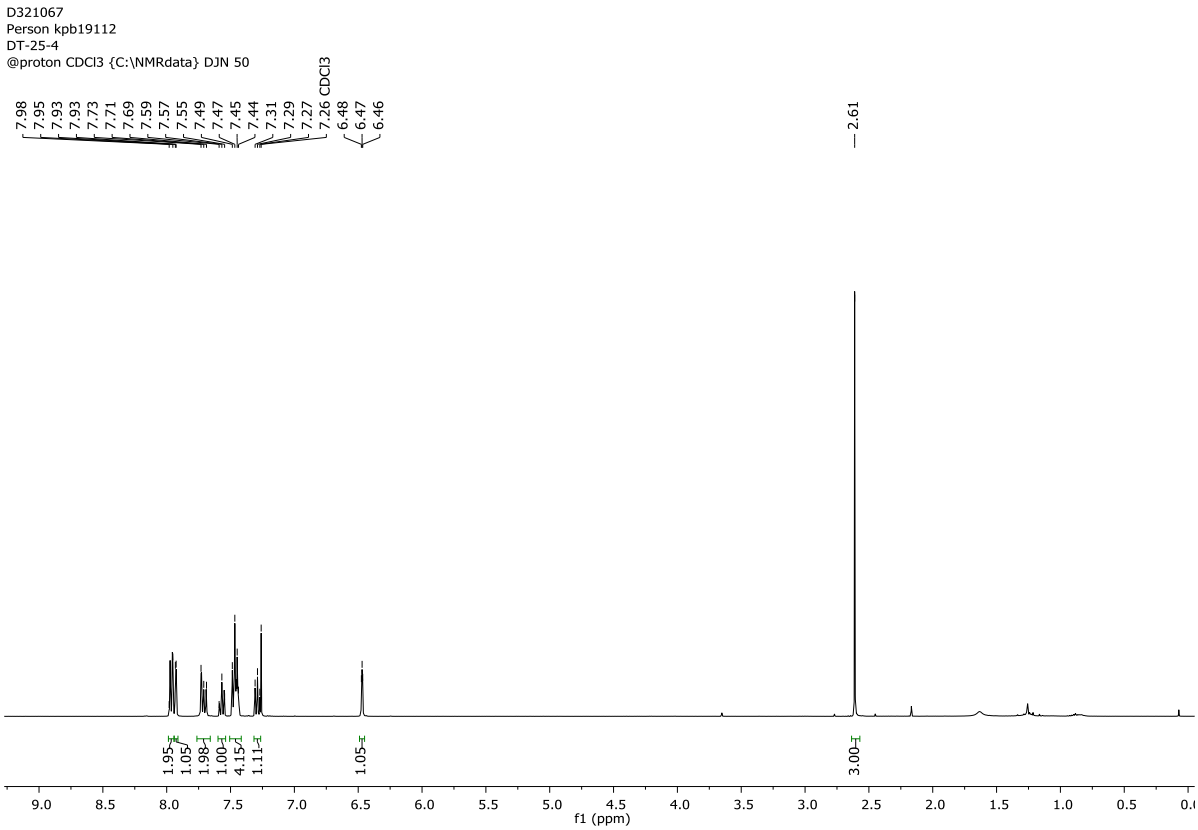
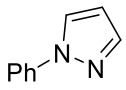
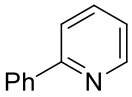


Figure S124. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and acetophenone (entry 3, Table S28).

Table S29. Determination of the competition rate constant κ from the labelling experiment between 1-phenylpyrazole and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	14.4 mg	15.5 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.78 – 7.67 ppm and at δ (**R2**) = 8.04 – 7.97 ppm
Determined against integral at δ (**R1**) = 6.50 – 6.42 ppm and at δ (**R2**) = 8.72 – 8.68 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.72 – 8.68 (m, 1H, **R2**), 8.04 – 7.97 (m, 2H/D **R2**), 7.92 (d, *J* = 2.4 Hz, 1H, **R1**), 7.78 – 7.67 (m, 2H, **R2**, 1H, **R1**, 2H/D **R1**), 7.52 – 7.38 (3H, **R2** and 2H, **R1**), 7.31 – 7.26 (m, 1H, **R1**), 7.24 – 7.20 (m, 1H, **R2**), 6.50 – 6.42 (m, 1H, **R1**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	1.65[a]	1.00	18	1.75	1.00	13	1.44
2	1.29[b]	1.00	36	1.22	0.85	28	1.32
3	1.23[c]	1.00	39	1.32	0.94	30	1.37
			Average κ = 1.38				

[a] $I_{R1(t)}$ =4.65–1.00–(1.00×2); [b] $I_{R1(t)}$ =3.99−1.00−(0.85×2); [c] $I_{R1(t)}$ = 4.11−1.00−(0.94×2)

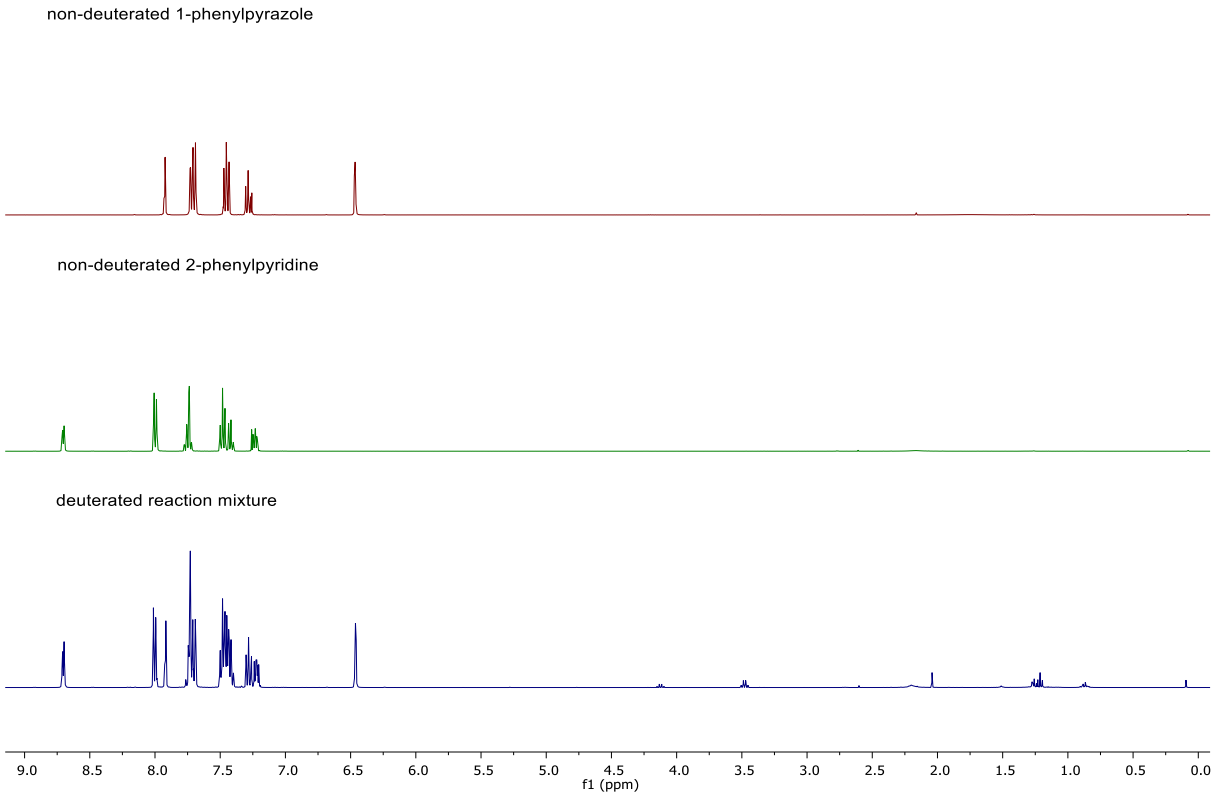


Figure S125. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

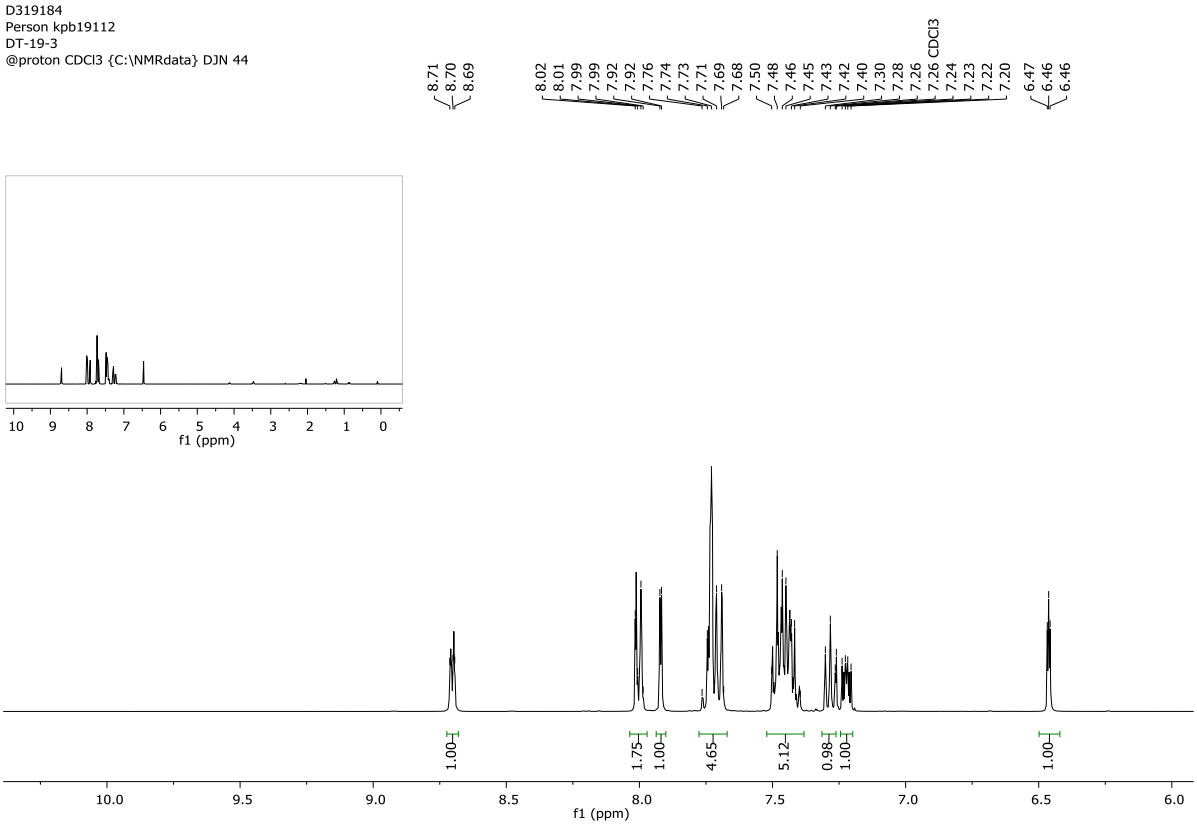


Figure S126. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 1, Table S29).

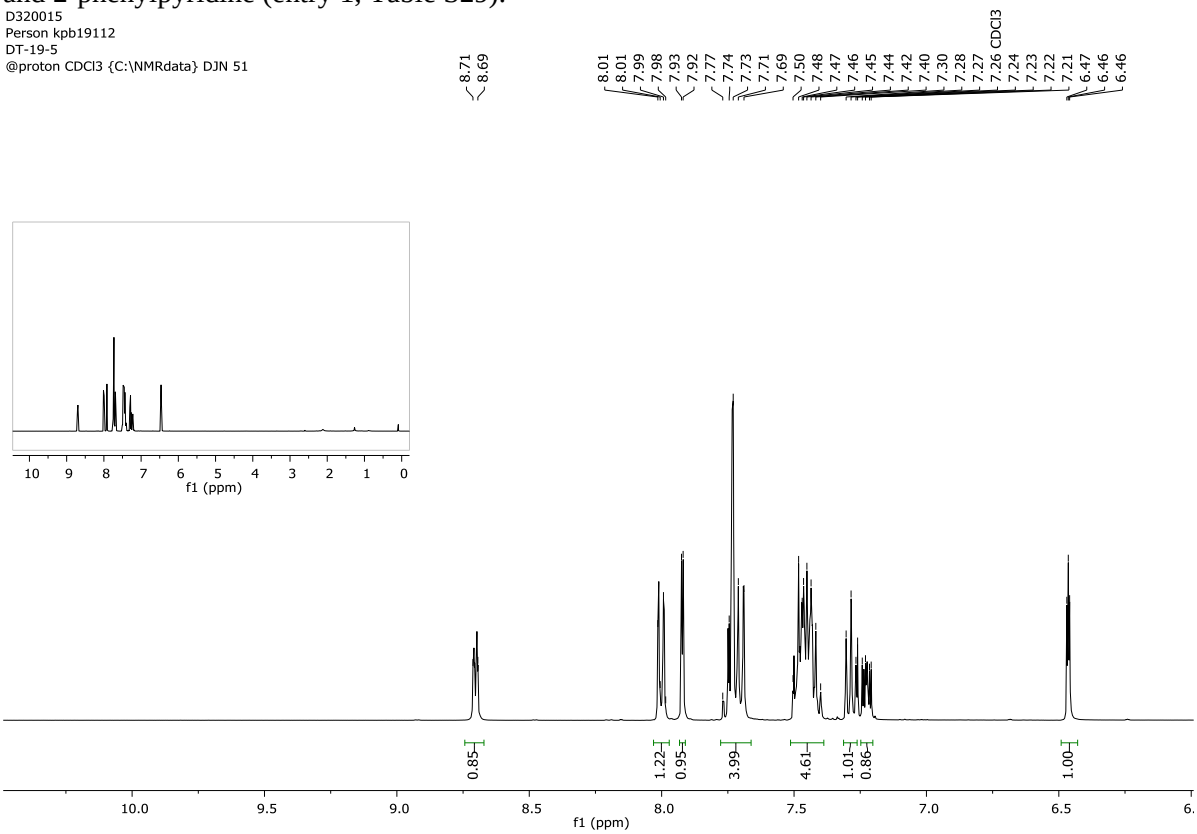


Figure S127. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 2, Table S29).

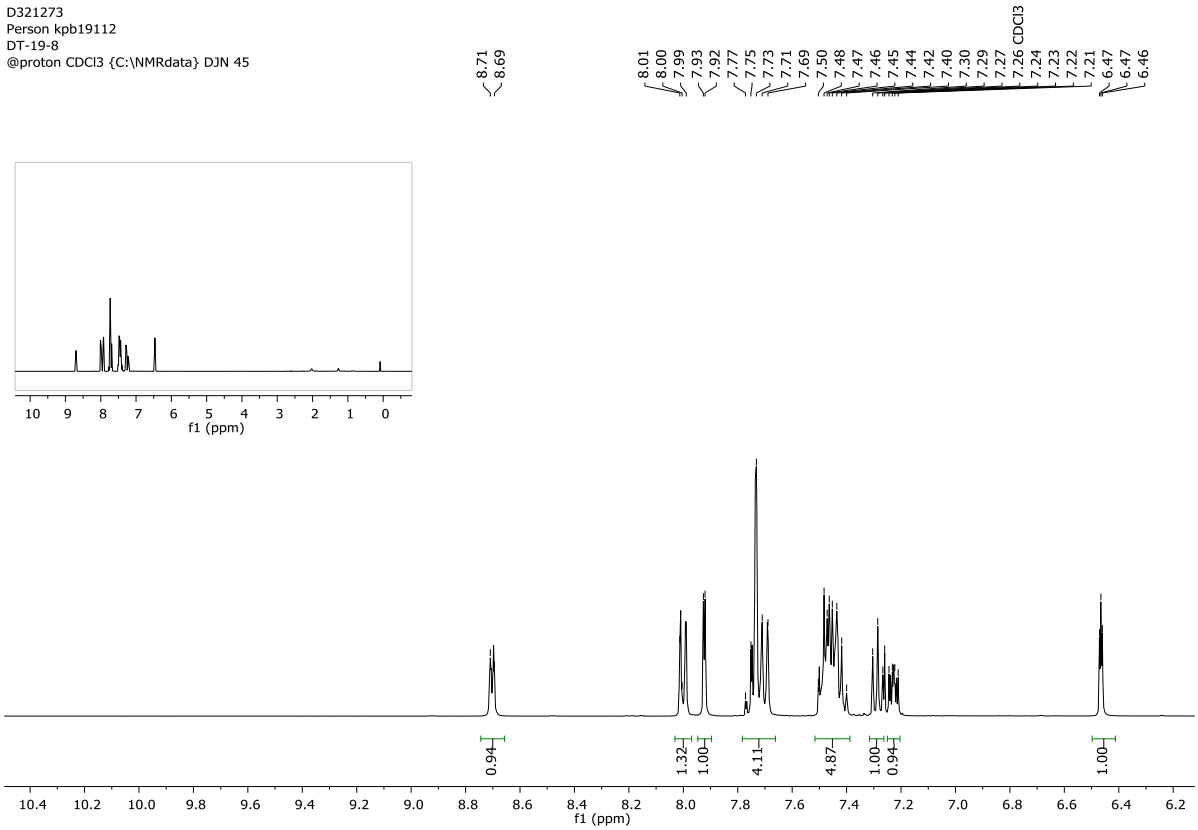
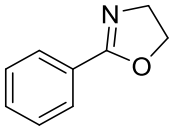
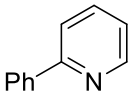


Figure S128. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylpyridine (entry 3, Table S29).

Table S30. Determination of the competition rate constant κ from the labelling experiment between 2-phenyloxazoline and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	14.7 mg	15.5 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.97 – 7.92 ppm and at δ (**R2**) = 8.02 – 7.97 ppm
Determined against integral at δ (**R1**) = 4.44 ppm and at δ (**R2**) = 8.73 – 8.66 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 – 8.66 (m, 1H, **R2**), 8.02 – 7.97 (m, 2H/D **R2**), 7.97 – 7.92 (m, 2H/D **R1**), 7.77 – 7.69 (m, 2H **R2**), 7.52 – 7.37 (m, 3H, **R1** and 3H, **R2**), 7.24 – 7.18 (m, 1H, **R2**), 4.44 (t, *J* = 9.5 Hz, 2H, **R1**), 4.07 (t, *J* = 9.5 Hz, 2H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	1.76	2.00	12	2.95	1.61	8	1.46
2	1.52	2.00	24	1.66	1.02	19	1.33
3	1.28	2.00	36	2.02	1.38	27	1.43
Average κ = 1.41							

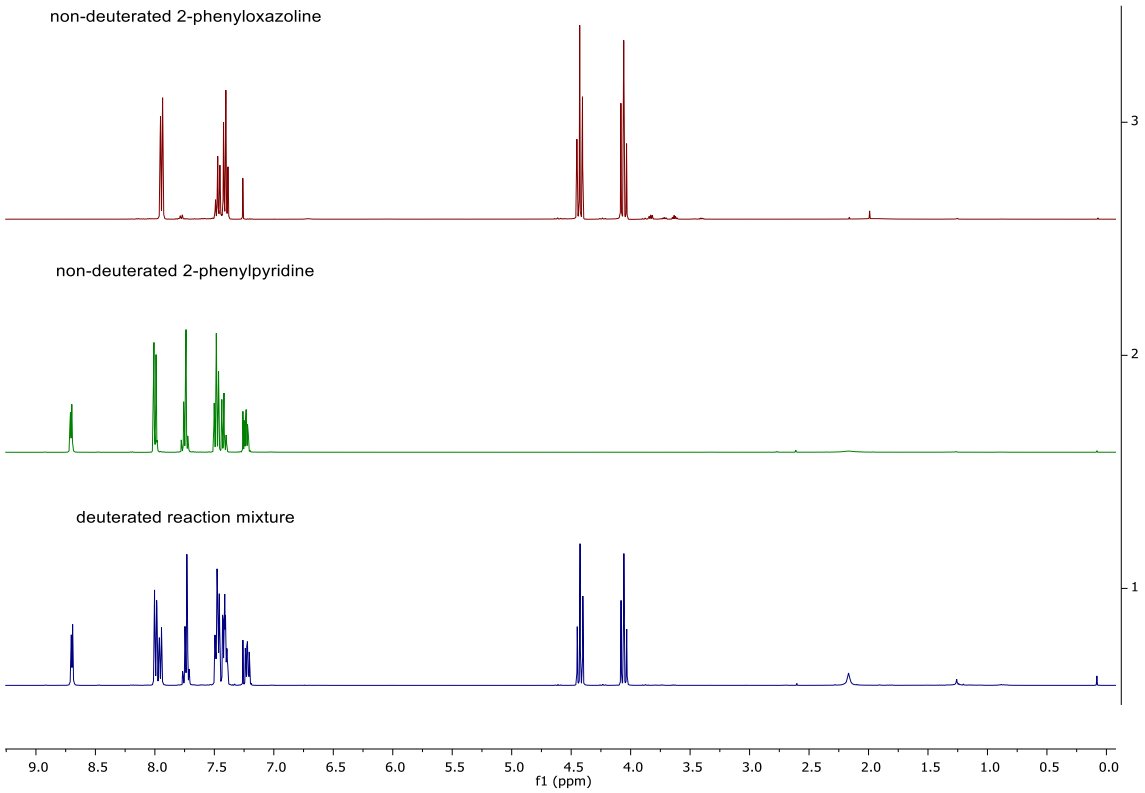


Figure S129. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

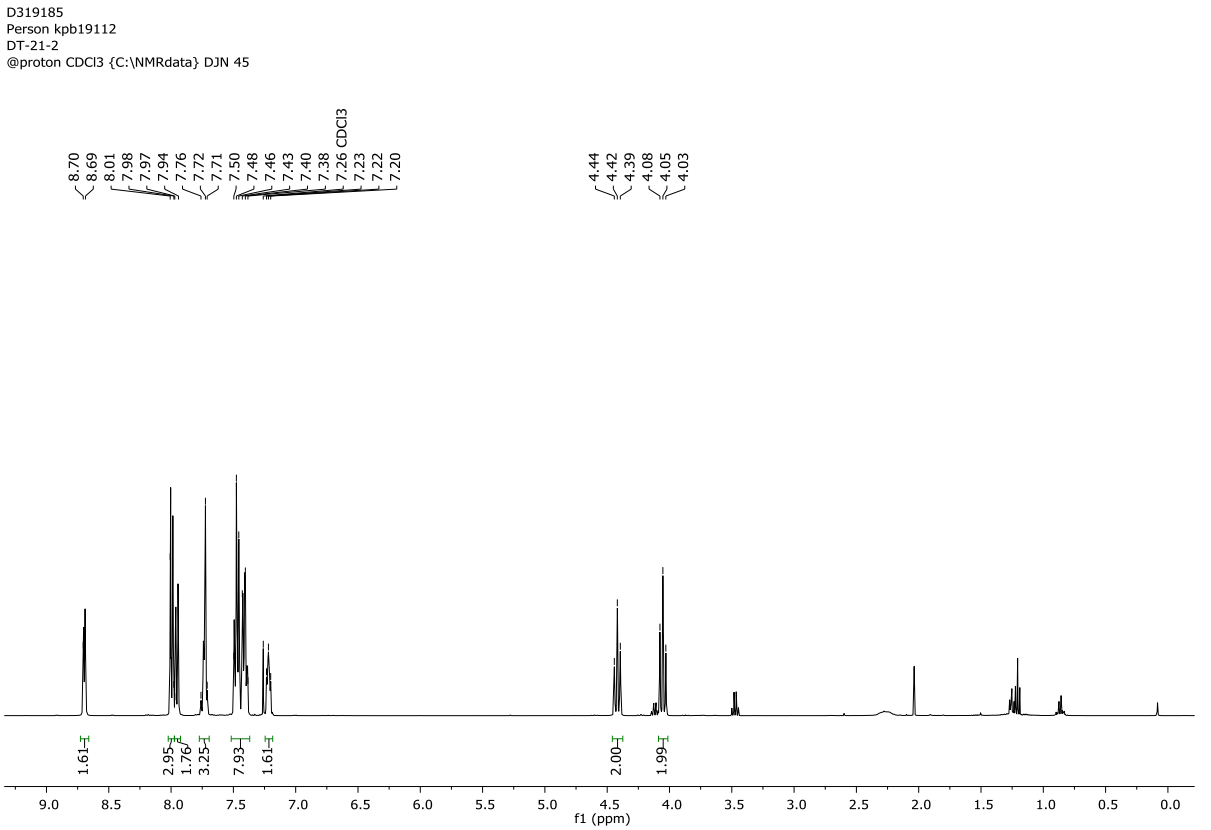


Figure S130. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylpyridine (entry 1, Table S30).

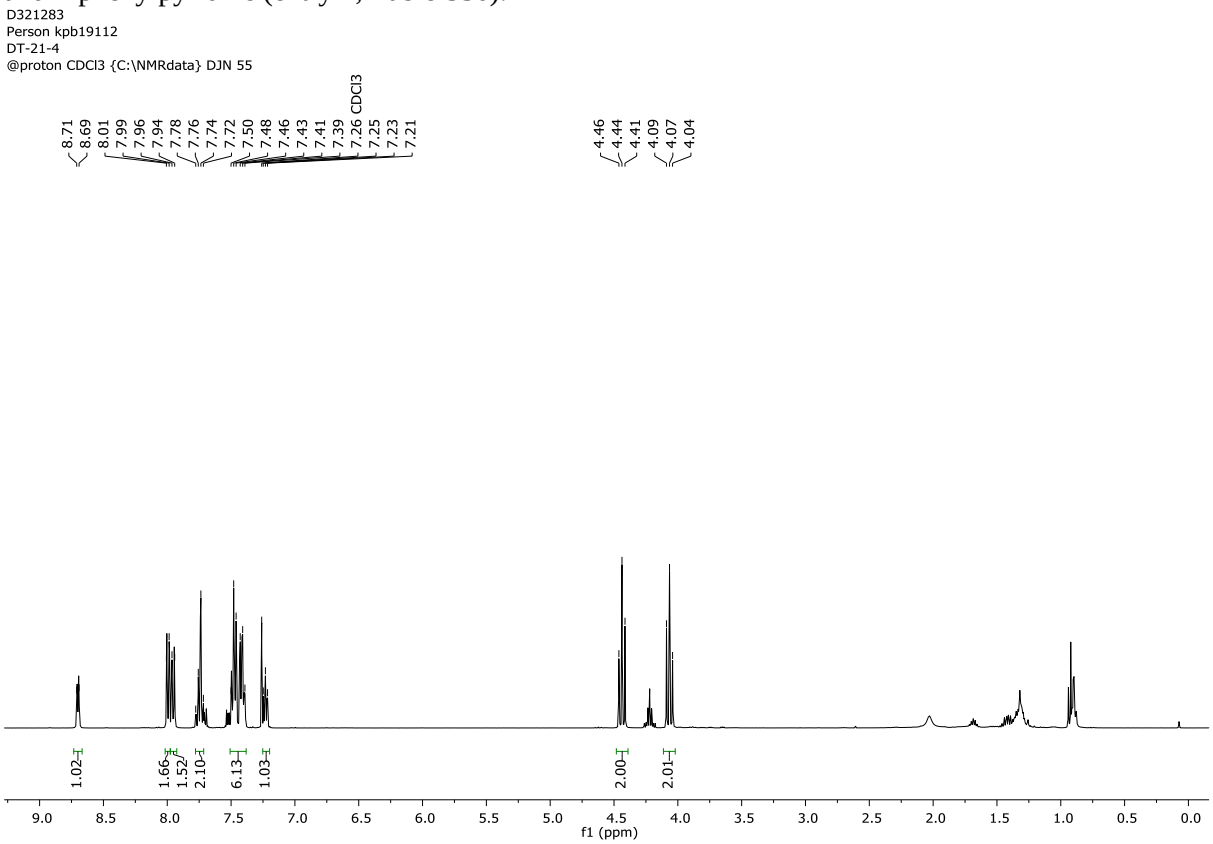


Figure S131. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylpyridine (entry 2, Table S30).

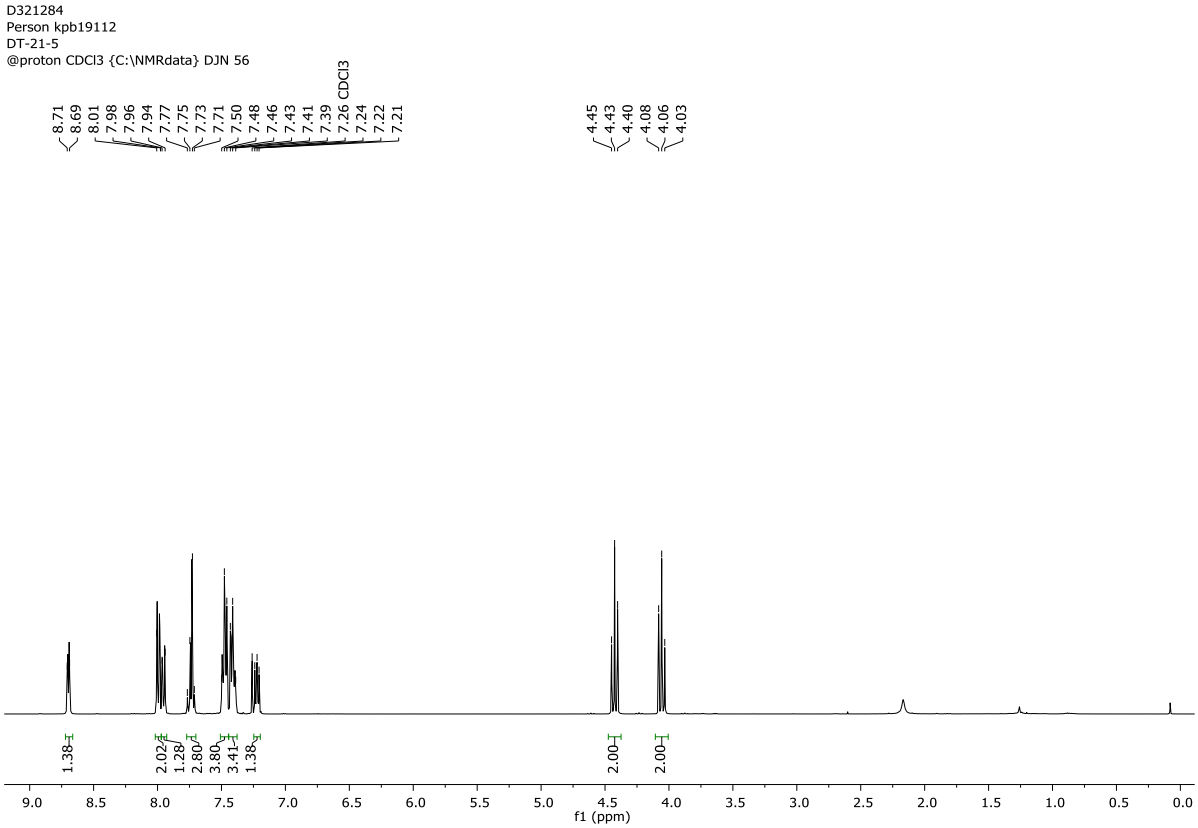
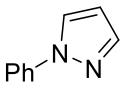
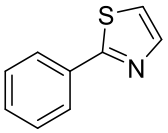


Figure S132. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenyloxazoline and 2-phenylpyridine (entry 3, Table S30).

Table S31. Determination of the competition rate constant κ from the labelling experiment between 1-phenylpyrazole and 2-phenylthiazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	14.4 mg	16.1 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.78 – 7.67 ppm ppm and at δ (**R2**) = 8.02 – 7.96 ppm
Determined against integral at δ (**R1**) = 6.49 – 6.43 ppm and at δ (**R2**) = 7.88 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 – 7.96 (m, 2H/D, **R2**), 7.92 (d, *J* = 2.4 Hz, 1H, **R1**), 7.88 (d, *J* = 3.3 Hz, 1H, **R2**), 7.76 – 7.66 (m, 2H/D, **R1** and 1H, **R1**), 7.49 – 7.39 (m, 2H, **R1** and 3H, **R2**), 7.33 (d, *J* = 3.3 Hz, 1H, **R2**), 7.29 (t, *J* = 7.4 Hz, 1H, **R1**), 6.49 – 6.43 (m, 1H, R1).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.82[a]	1.00	59	1.25	1.10	43	1.58
2	1.12[b]	1.00	44	1.52	1.05	28	1.79
3	1.19[c]	1.00	41	1.41	1.00	30	1.49
			Average κ = 1.62				

[a] $I_{R1(t)}$ = 1.82–1.00; [b] $I_{R1(t)}$ = 2.12−1.00; [c] $I_{R1(t)}$ = 2.19−1.00;

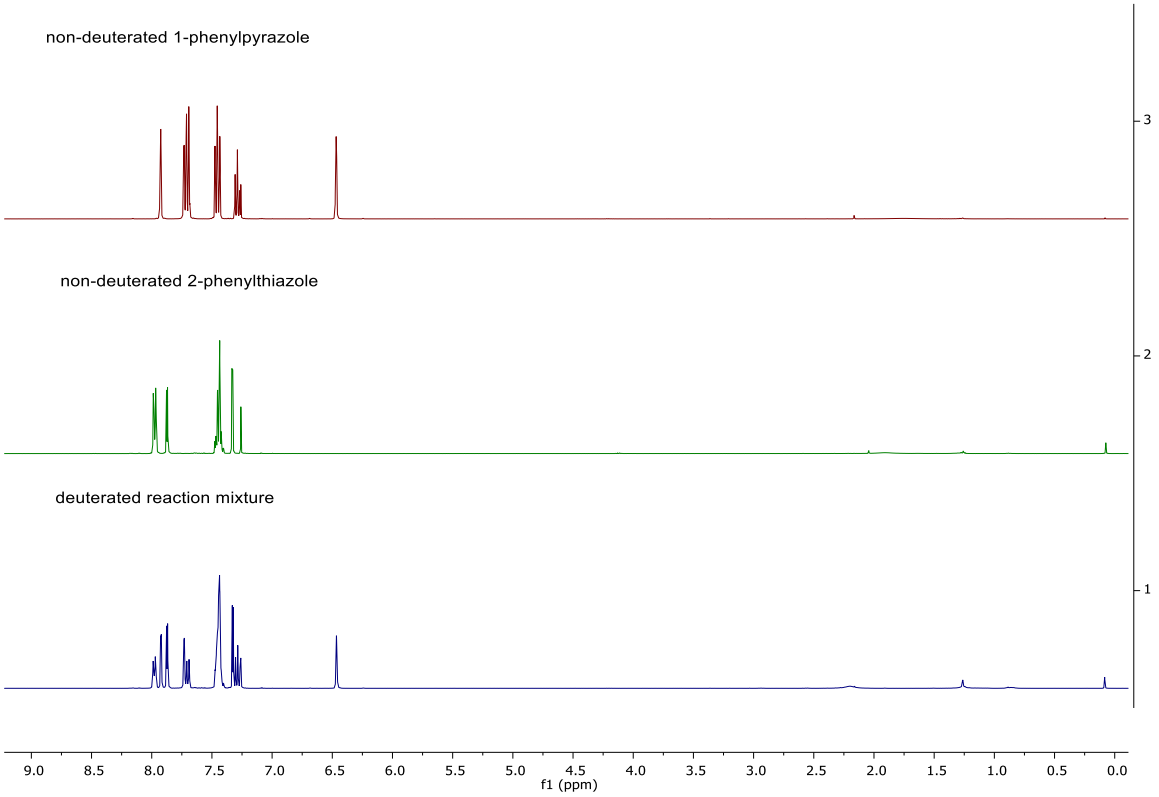


Figure S133. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

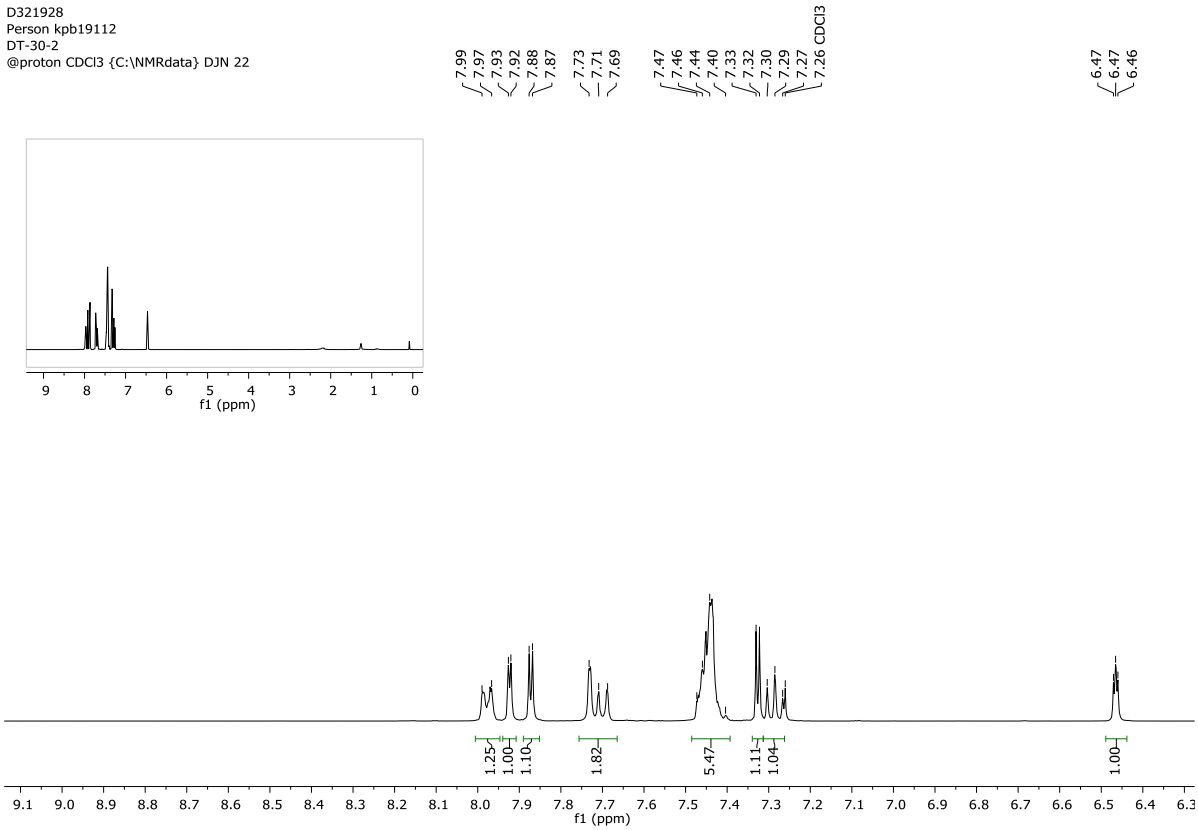


Figure S134. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylthiazole (entry 1, Table S31).

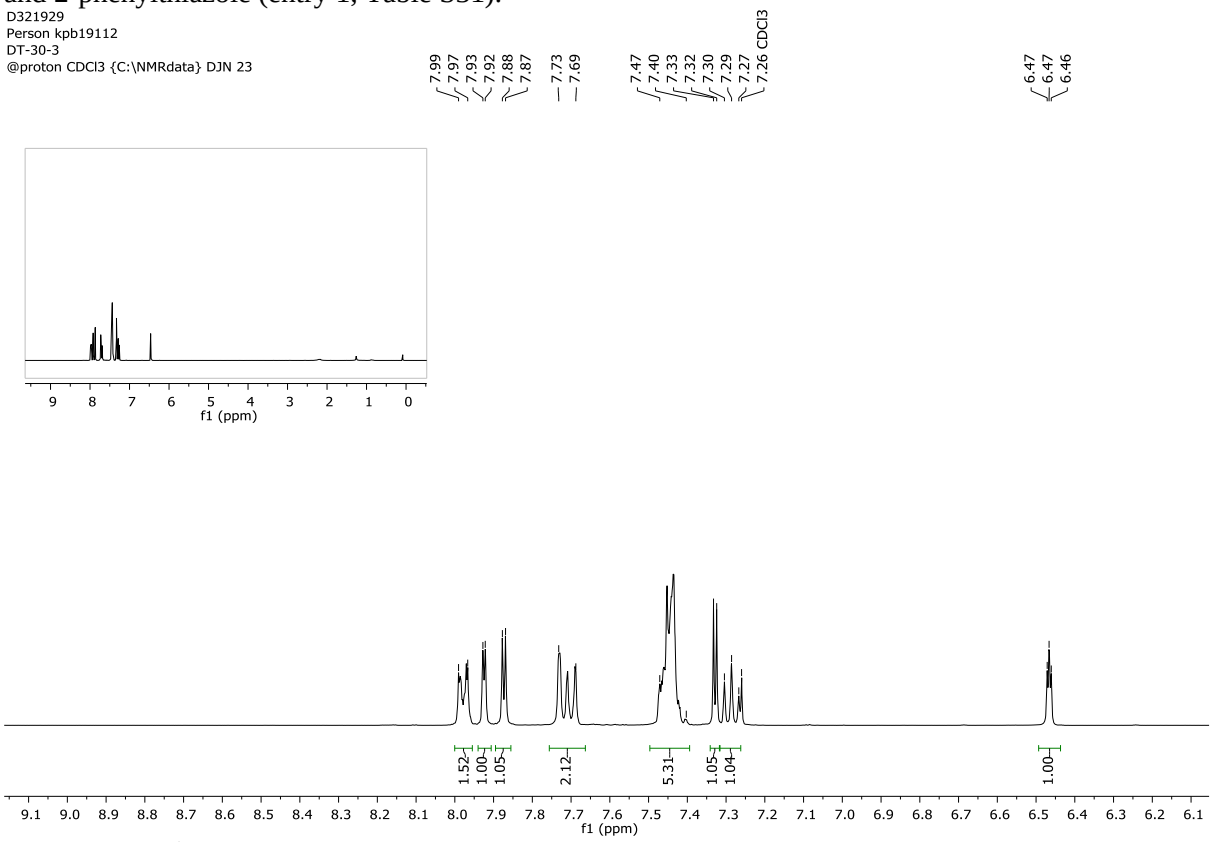


Figure S135. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylthiazole (entry 1, Table S31).

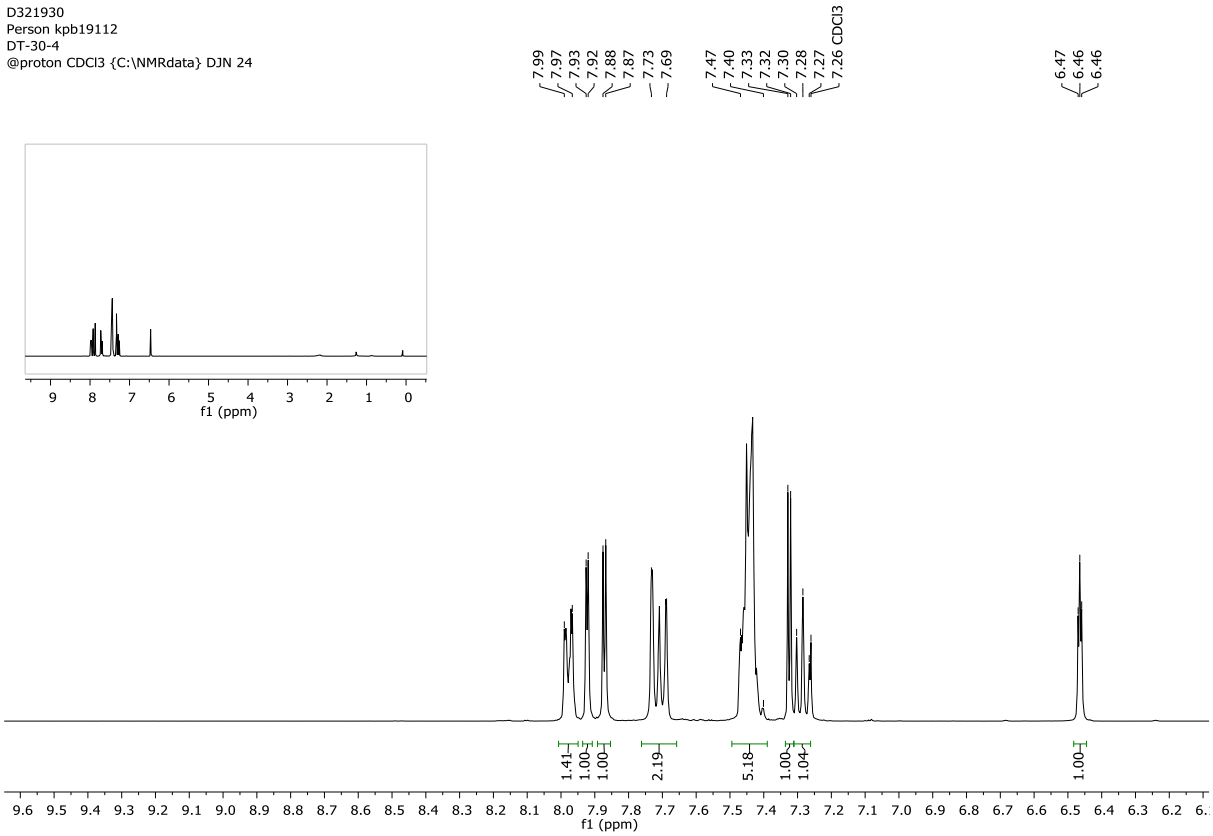
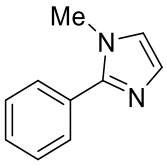
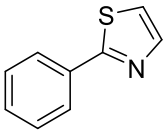


Figure S136. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-phenylpyrazole and 2-phenylthiazole (entry 1, Table S31).

Table S32. Determination of the competition rate constant κ from the labelling experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	15.8 mg	16.1 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.67 – 7.61 ppm and at δ (**R2**) =8.02 – 7.96 ppm
Determined against integral at δ (**R1**) = 7.12 ppm and at δ (**R2**) = 7.88 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 – 7.96 (m, 2H/D, **R2**), 7.88 (d, *J* = 3.3 Hz, 1H, **R2**), 7.67 – 7.61 (m, 2H/D, **R1**), 7.50 – 7.38 (m, 3H, **R1** and 3H, **R2**), 7.33 (d, *J* = 3.3 Hz, 1H, **R2**), 7.12 (d, *J* = 1.2 Hz, 1H, **R1**), 6.95 (d, *J* = 1.2 Hz, 1H, **R1**), 3.74 (s, 3H, **R1**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	1.10	1.00	45	1.91	1.00	5	12.98
2	0.63	1.00	69	1.90	1.03	8	14.29
3	0.71	1.00	65	1.95	1.06	8	12.39
				Average κ = 13.22			

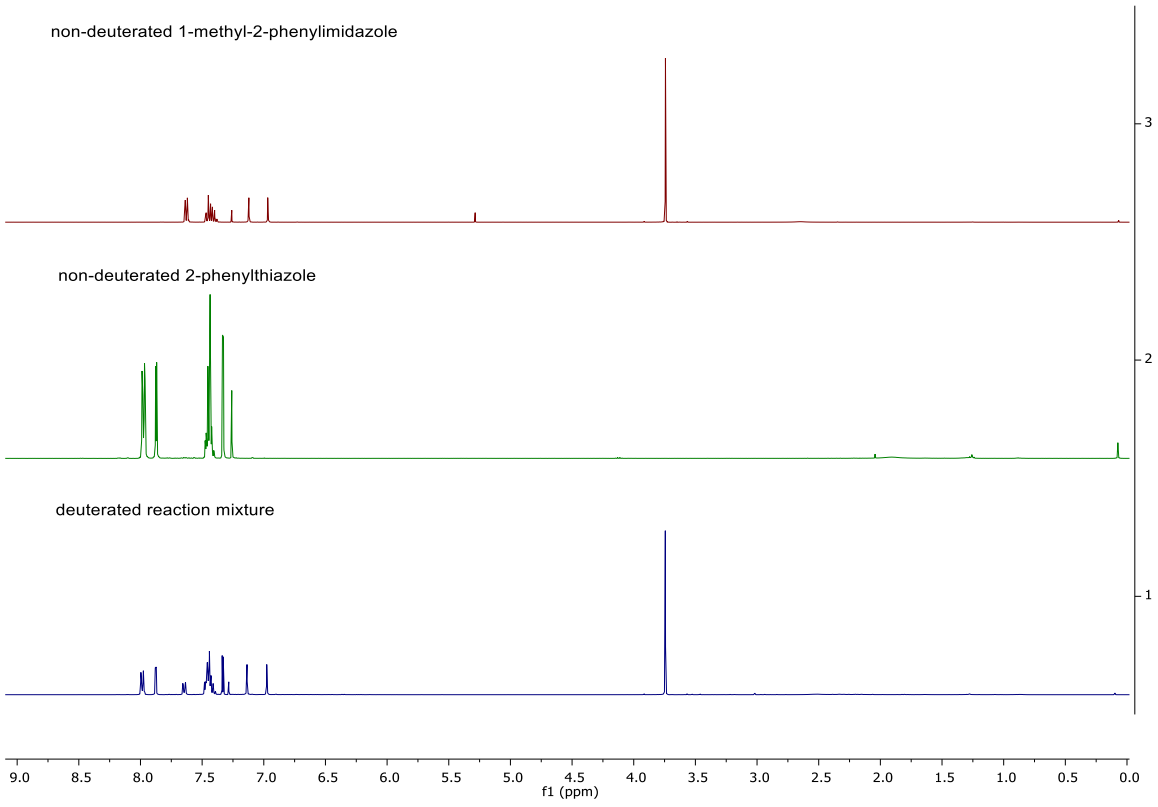


Figure S137. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

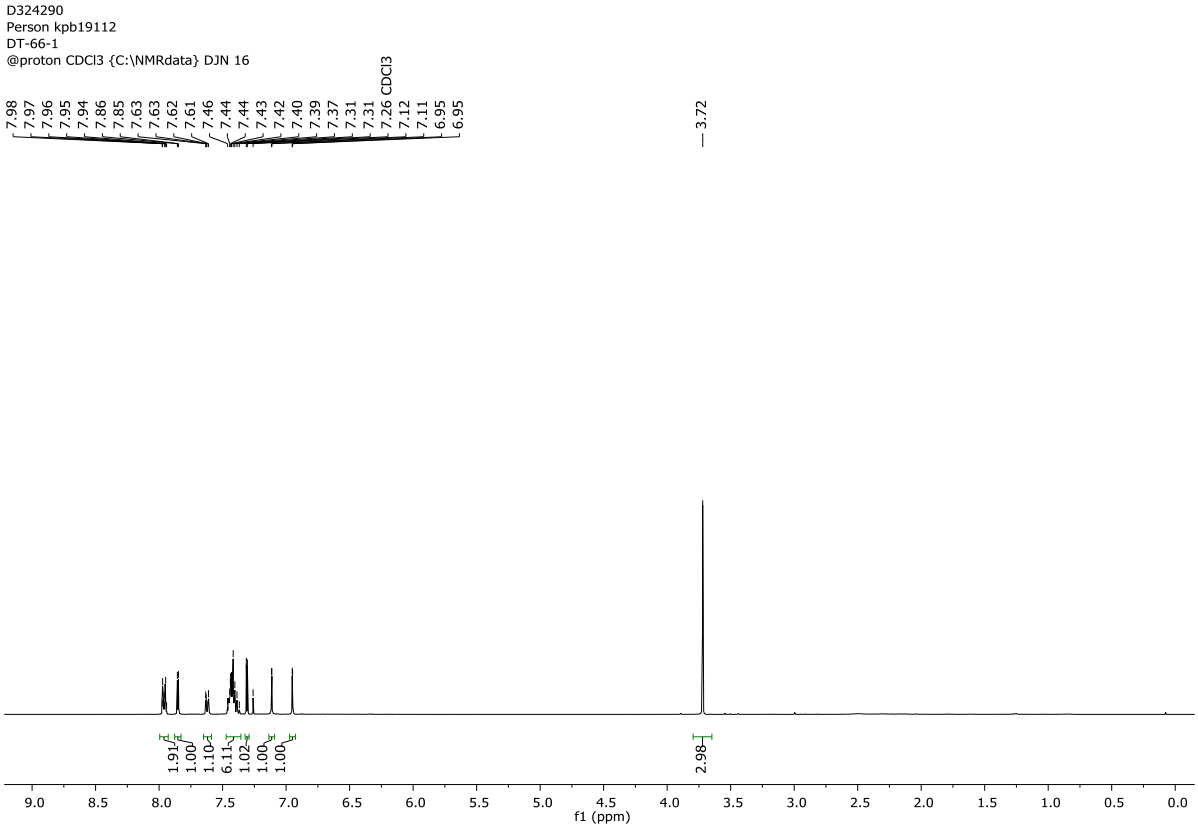


Figure S138. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazole (entry 1, Table S32).

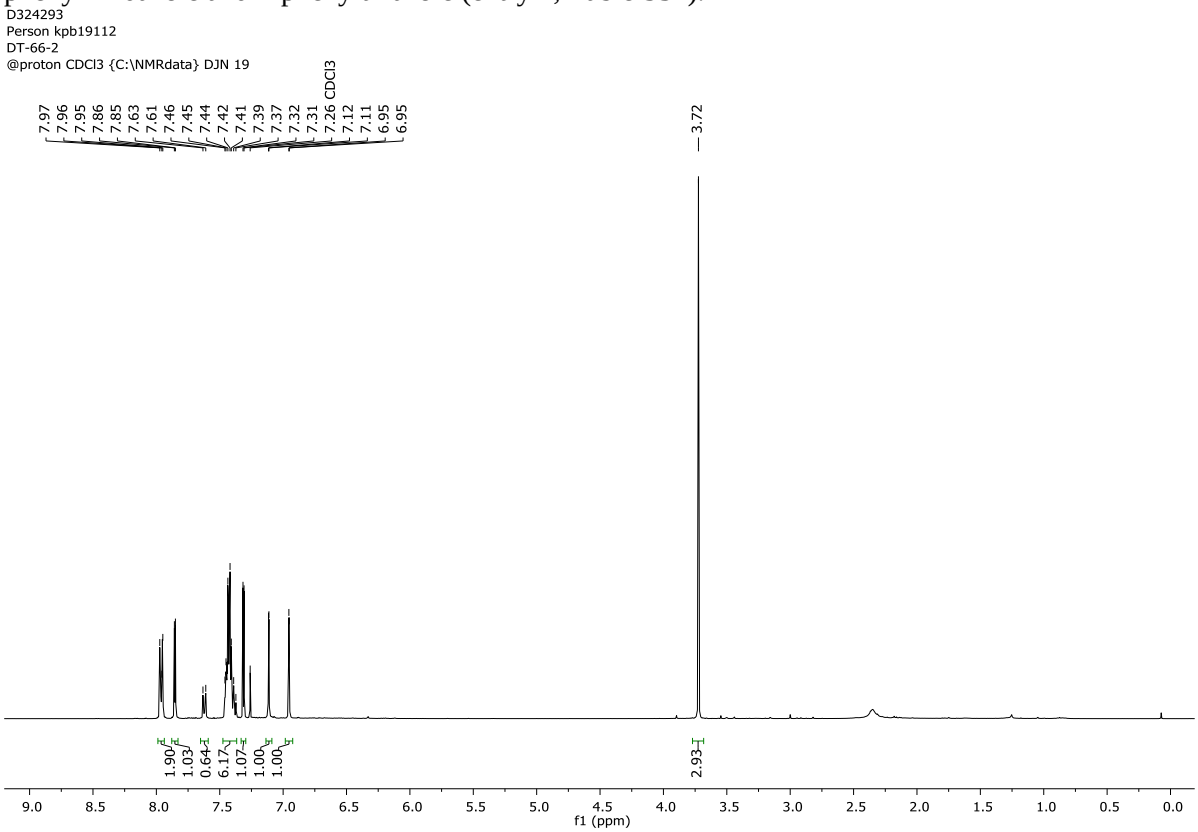


Figure S139. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazole (entry 2, Table S32).

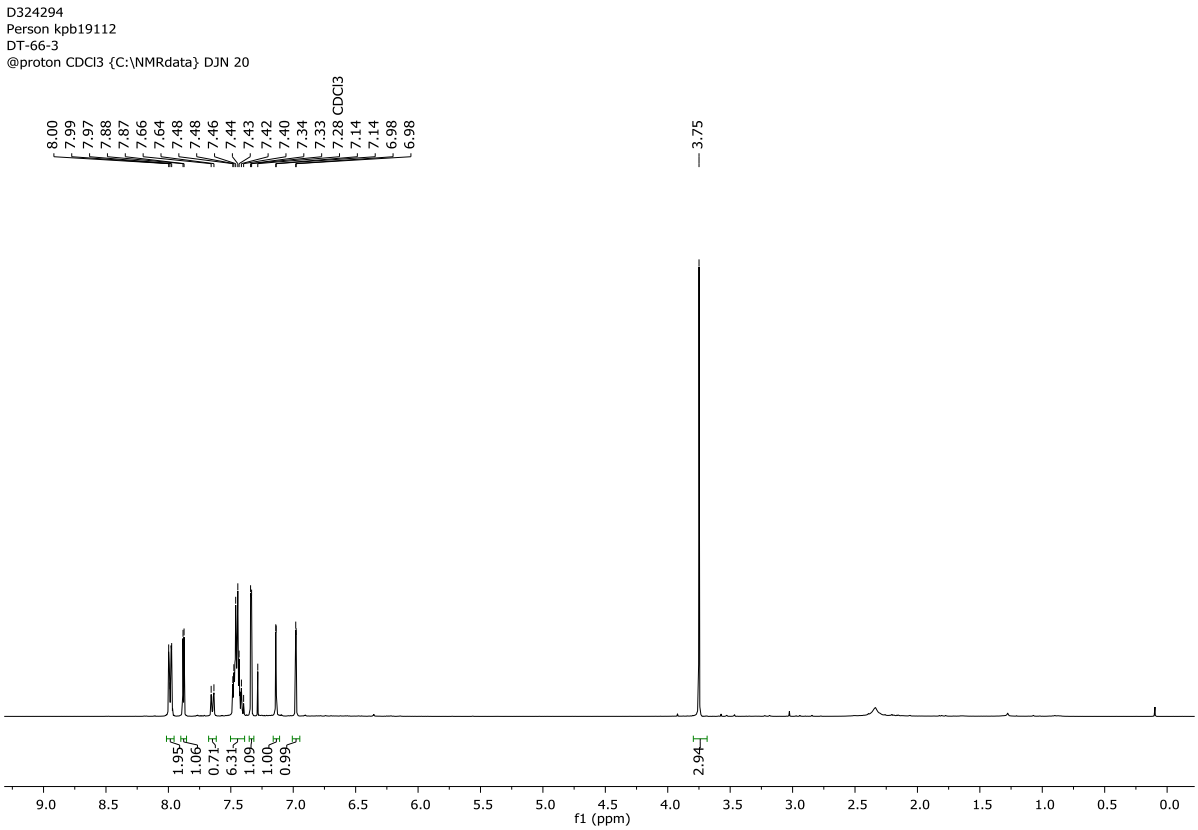
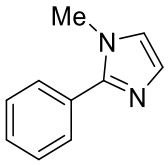
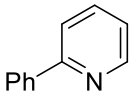


Figure S140. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazole (entry 3, Table S32).

Table S33 Determination of the competition rate constant κ from the labelling experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	15.8 mg	15.5 mg	3.2 mg

Note: Volume of DCM was increased to 4 mL to obtain higher conversion of both substrates.
Deuteration expected at δ (**R1**) = 7.67 – 7.61 ppm and at δ (**R2**) =8.02 – 7.96 ppm
Determined against integral at δ (**R1**) =7.12 ppm and at δ (**R2**) = 7.77 – 7.69 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 – 8.66 (m, 1H, **R2**), 8.02 – 7.96 (m, 2H/D **R2**), 7.77 – 7.69 (m, 2H **R2**), 7.67 – 7.61 (m, 2H/D, **R1**), 7.50 – 7.36 (m, 3H, **R1** and 3H, **R2**), 7.24 – 7.18 (m, 1H, **R2**), 7.12 (d, *J*=1.2 Hz, 1H, **R1**), 6.95 (d, *J*=1.2 Hz, 1H, **R1**), 3.73 (s, 3H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.58	1.00	21	2.09	2.32	10	2.26
2	1.60	1.00	20	2.02	2.28	11	1.84
3	1.36	0.87	22	1.76	2.00	12	1.93
Average κ = 2.01							

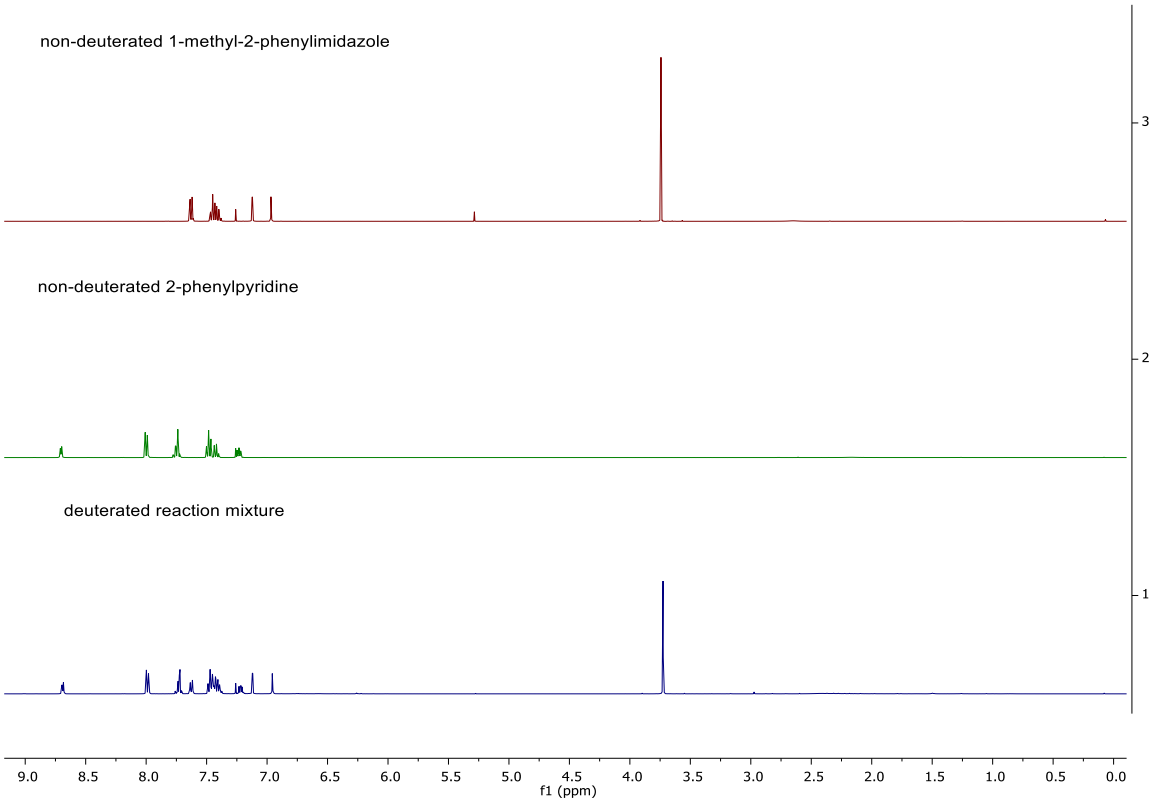


Figure S141. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

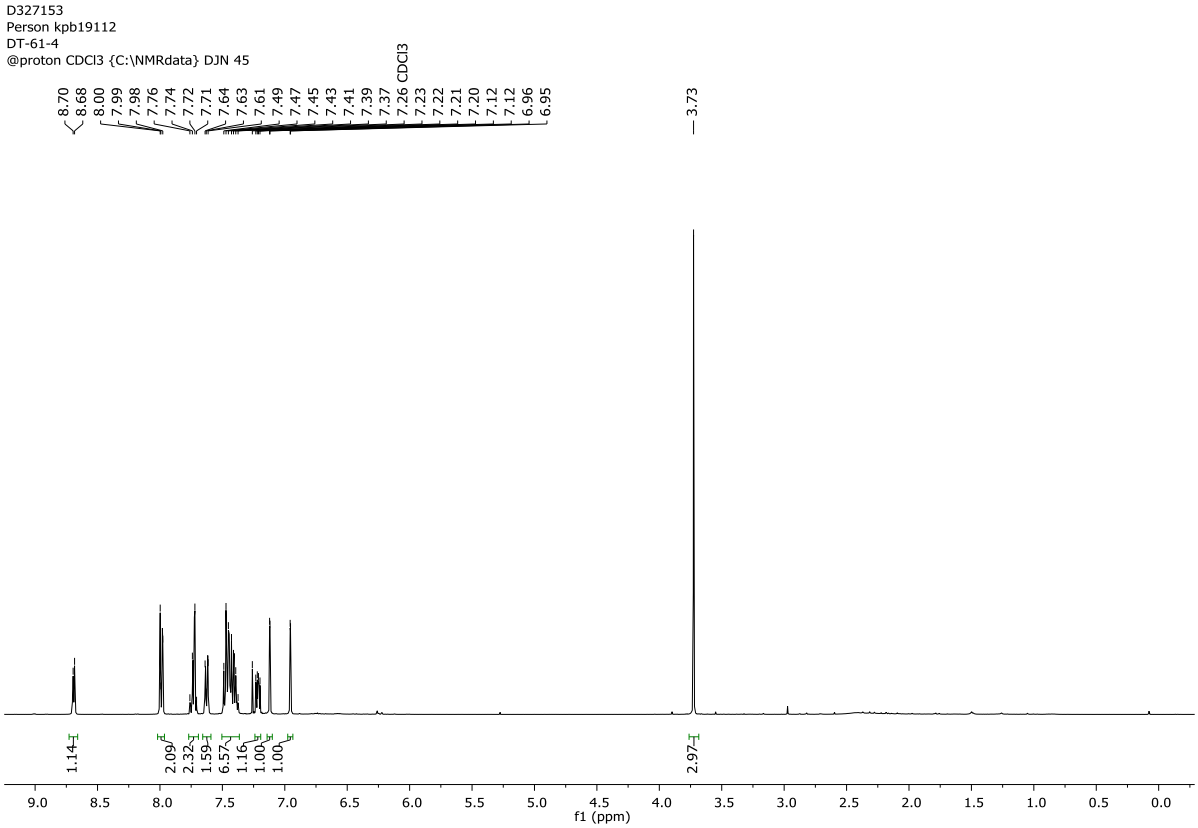


Figure S142. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine (entry 1, Table S33).

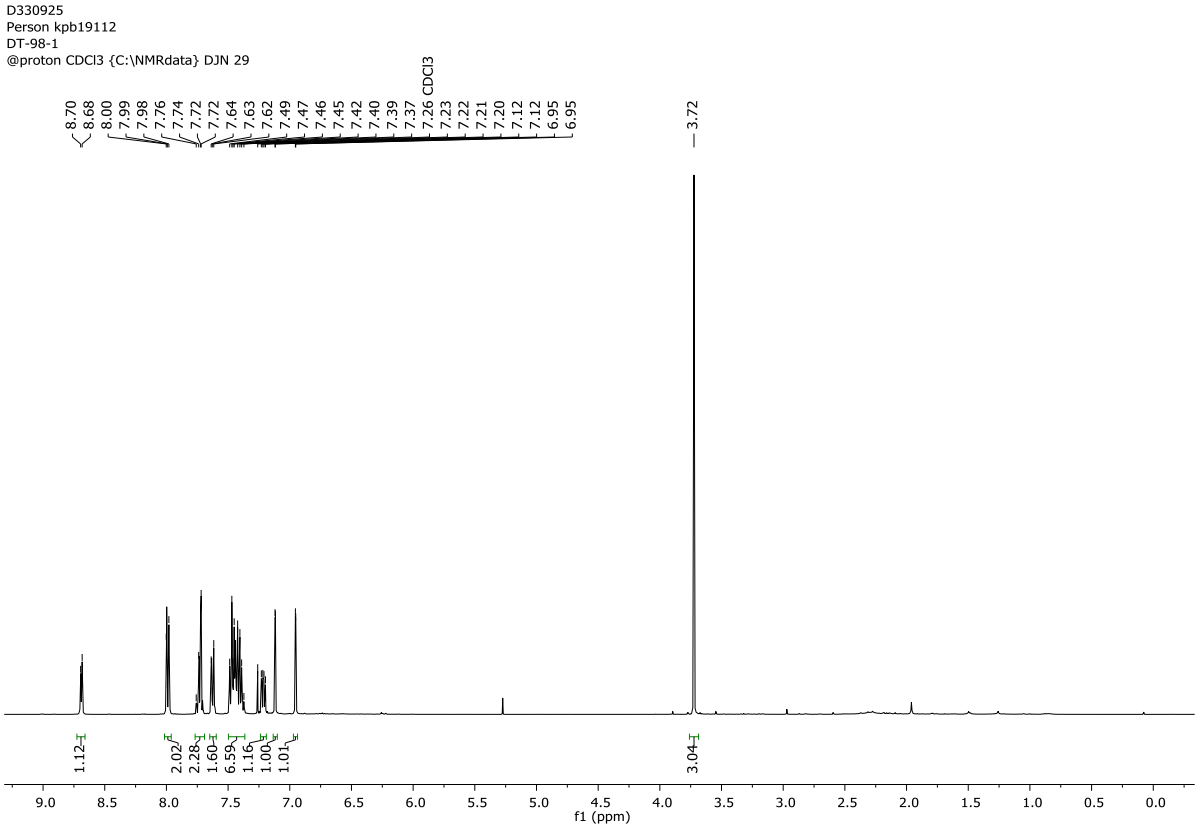


Figure S143. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine (entry 2, Table S33).

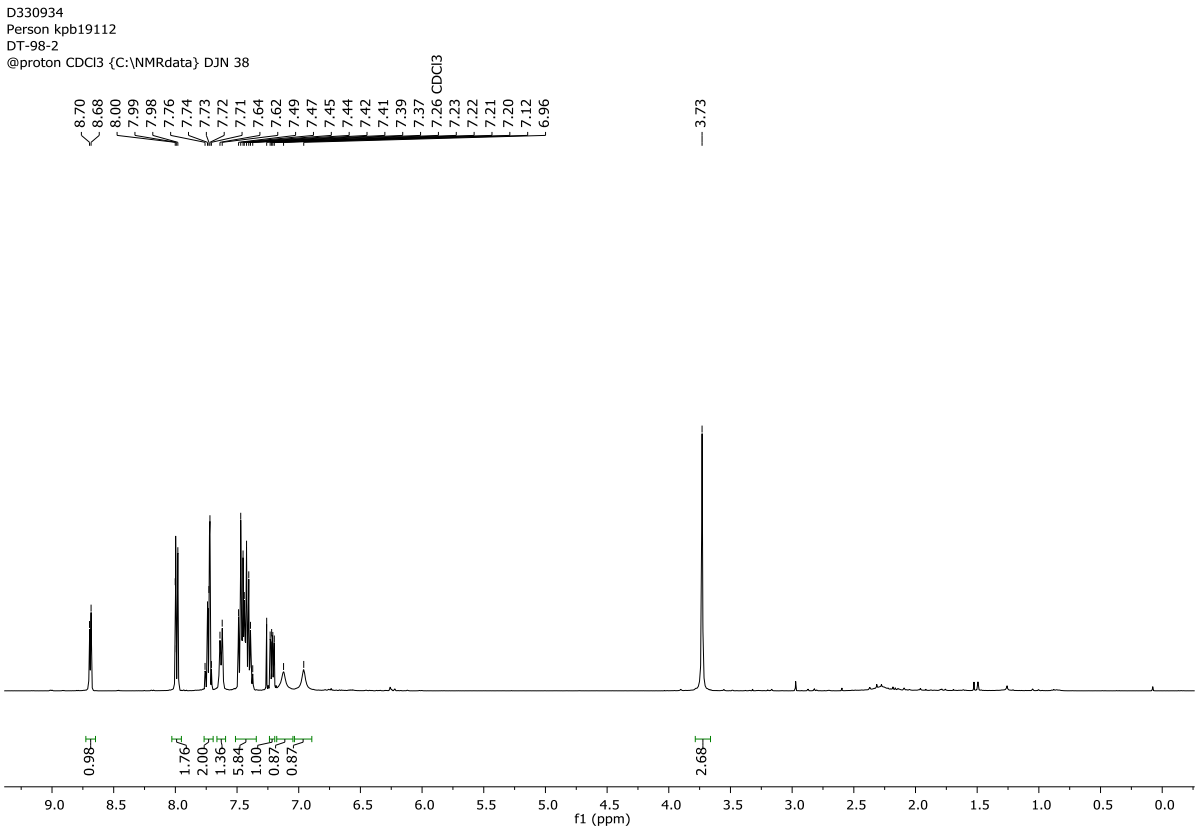
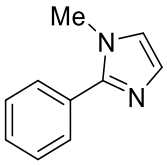
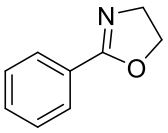


Figure S144. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylpyridine (entry 3, Table S33).

Table S34. Determination of the competition rate constant κ from the labelling experiment between 1-methyl-2-phenylimidazole and 2-phenyloxazoline.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	15.8 mg	14.7 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.67 – 7.61 ppm and at δ (**R2**) = 7.98 – 7.90 ppm
Determined against integral at δ (**R1**) = 7.12 ppm and at δ (**R2**) = 4.44 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.90 (m, 2H/D **R2**), 7.67 – 7.61 (m, 2H/D, **R1**), 7.50 – 7.36 (m, 3H, **R1** and 3H, **R2**), 7.12 (d, *J*=1.2 Hz, 1H, **R1**), 6.96 (d, *J*=1.2 Hz, 1H, **R1**), 4.43 (t, *J* = 9.5 Hz, 2H, **R2**), 4.06 (t, *J* = 9.5 Hz, 2H, **R2**), 3.74 (s, 3H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.03	0.73	29	1.92	2.00	4	8.55
2	1.31	0.93	30	1.91	2.00	5	7.61
3	1.76	1.05	16	1.96	2.00	2	8.74
				Average κ = 8.30			

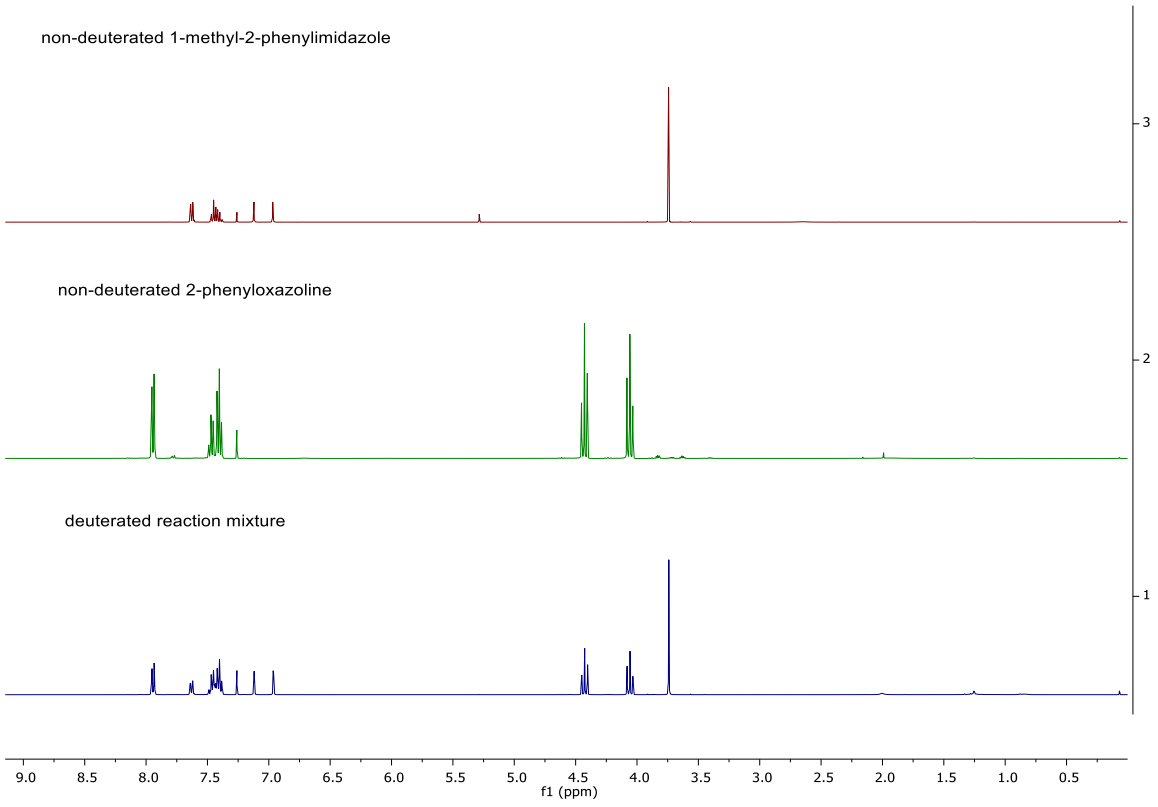


Figure S145. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

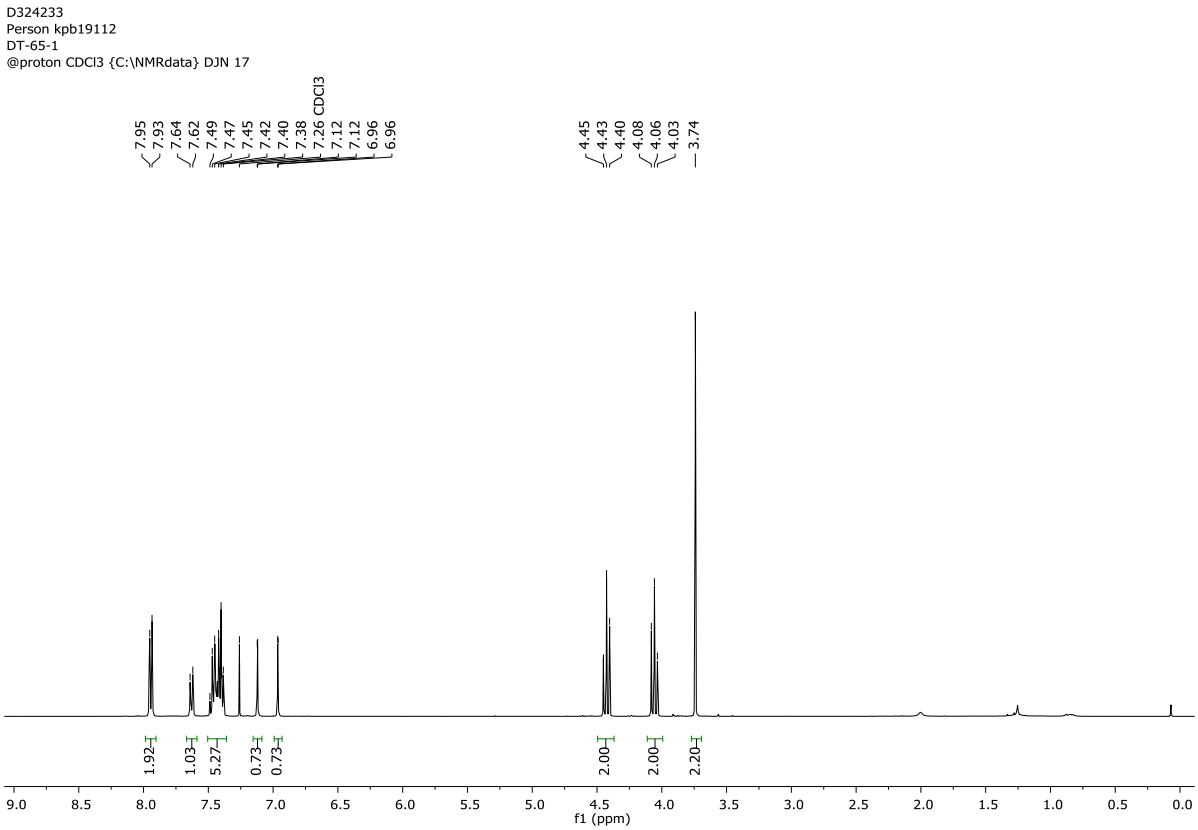


Figure S146. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenyloxazoline (entry 1, Table S34).

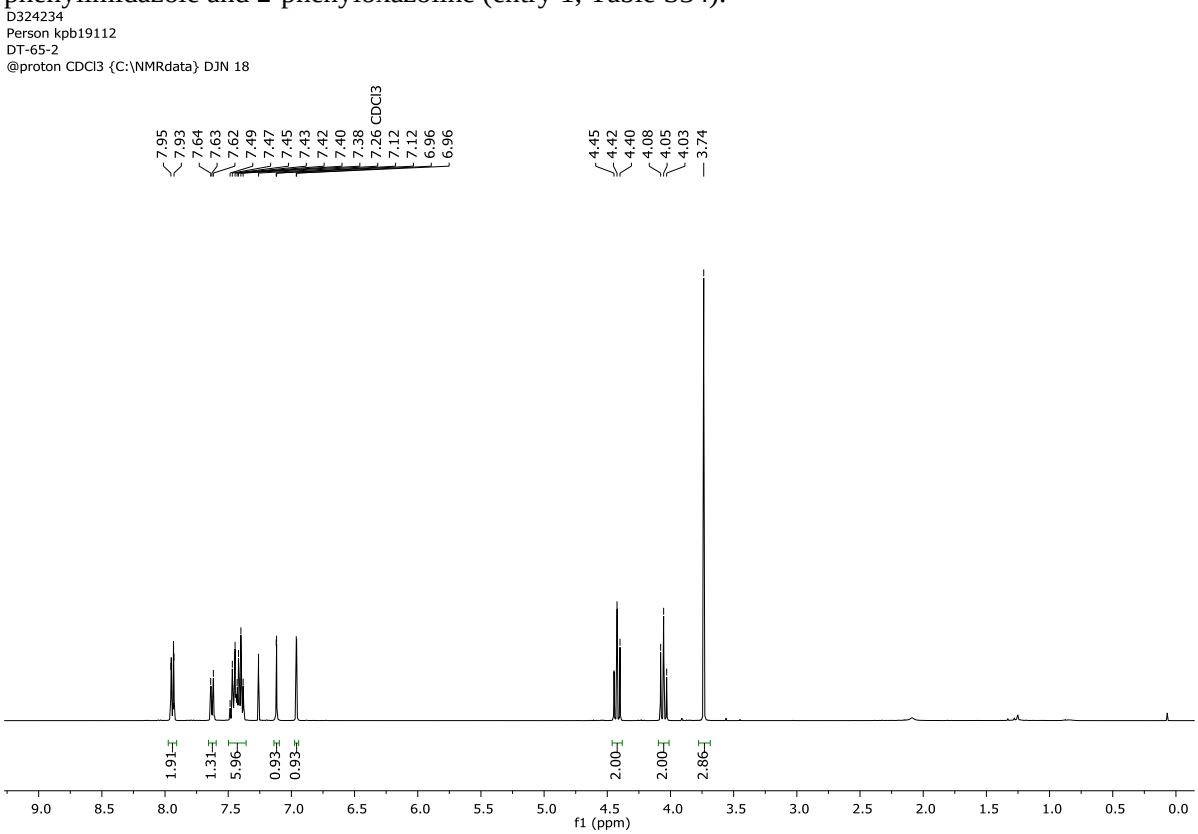


Figure S147. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenyloxazoline (entry 2, Table S34).

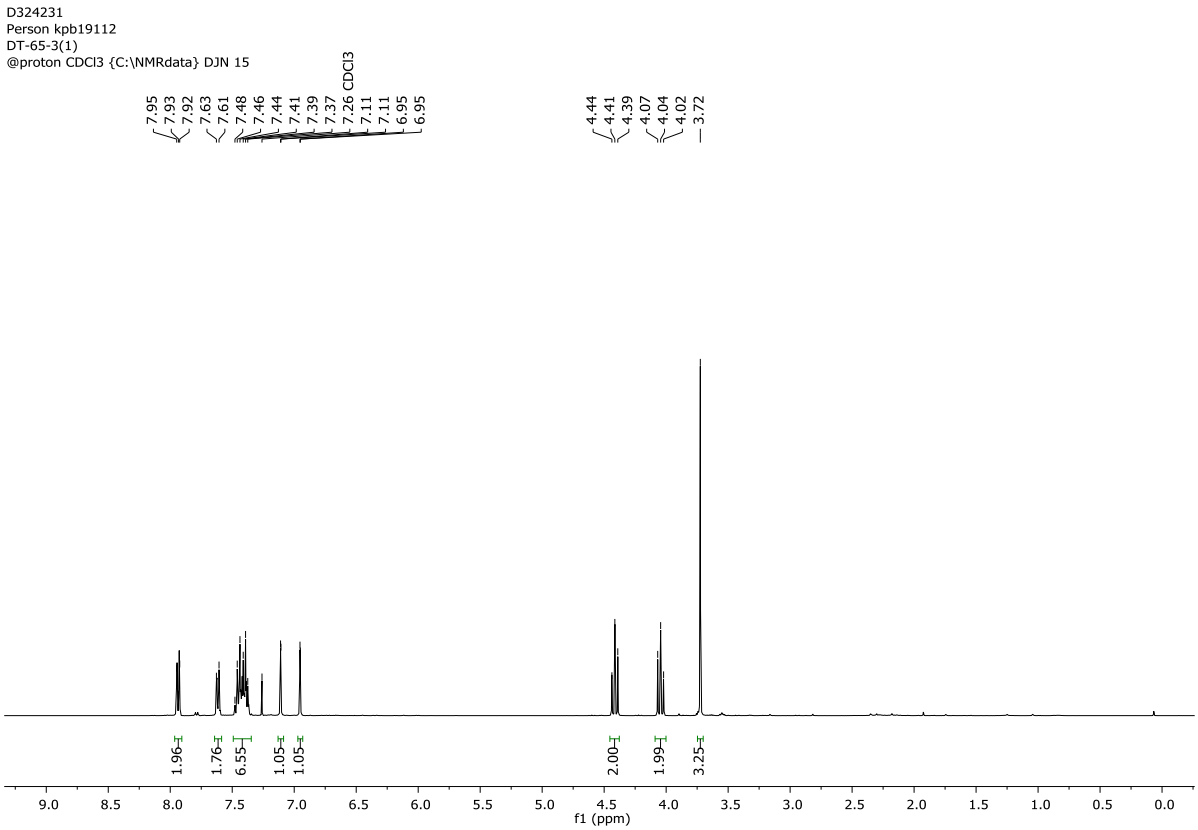
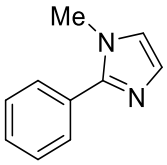
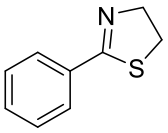


Figure S148. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenyloxazoline (entry 3, Table S34).

Table S35. Determination of the competition rate constant κ from the labelling experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	15.8 mg	16.3 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.65 – 7.60 ppm and at δ (**R2**) = 7.85 – 7.83 ppm
Determined against integral at δ (**R1**) = 7.12 ppm and at δ (**R2**) = 4.45 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 – 7.83 (m, 2H/D **R2**), 7.65 – 7.60 (m, 2H/D, **R1**), 7.48 – 7.36 (m, 3H, **R1** and 3H, **R2**), 7.12 (d, *J*=1.2 Hz, 1H, **R1**), 6.95 (d, *J*=1.2 Hz, 1H, **R1**), 4.45 (t, *J* = 8.3 Hz, 2H, **R2**), 3.73 (s, 3H, **R1**), 3.40 (t, *J* = 8.3 Hz, 2H, **R2**)

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 1H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	0.87	1.00	57	1.72	2.32	26	2.78
2	0.90	1.00	55	1.51	2.34	35	1.82
3	0.99	1.00	51	1.66	2.26	27	2.28
				Average κ = 2.29			

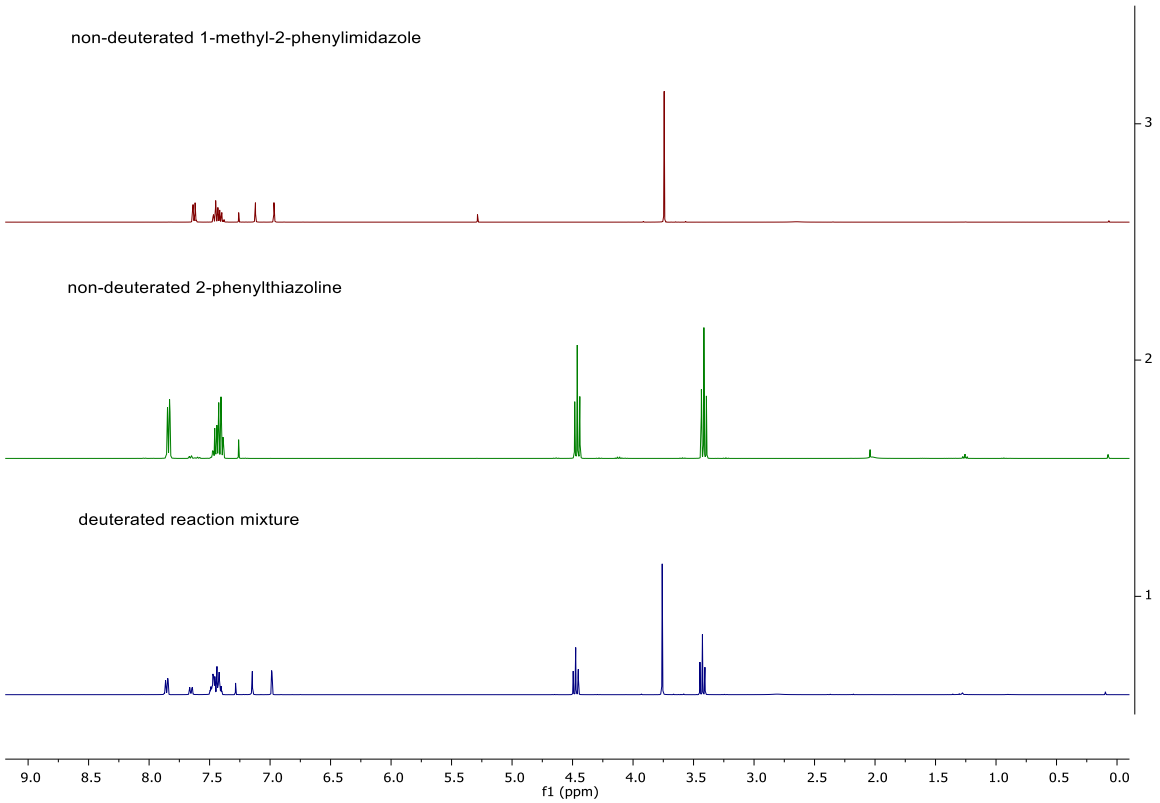


Figure S149. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

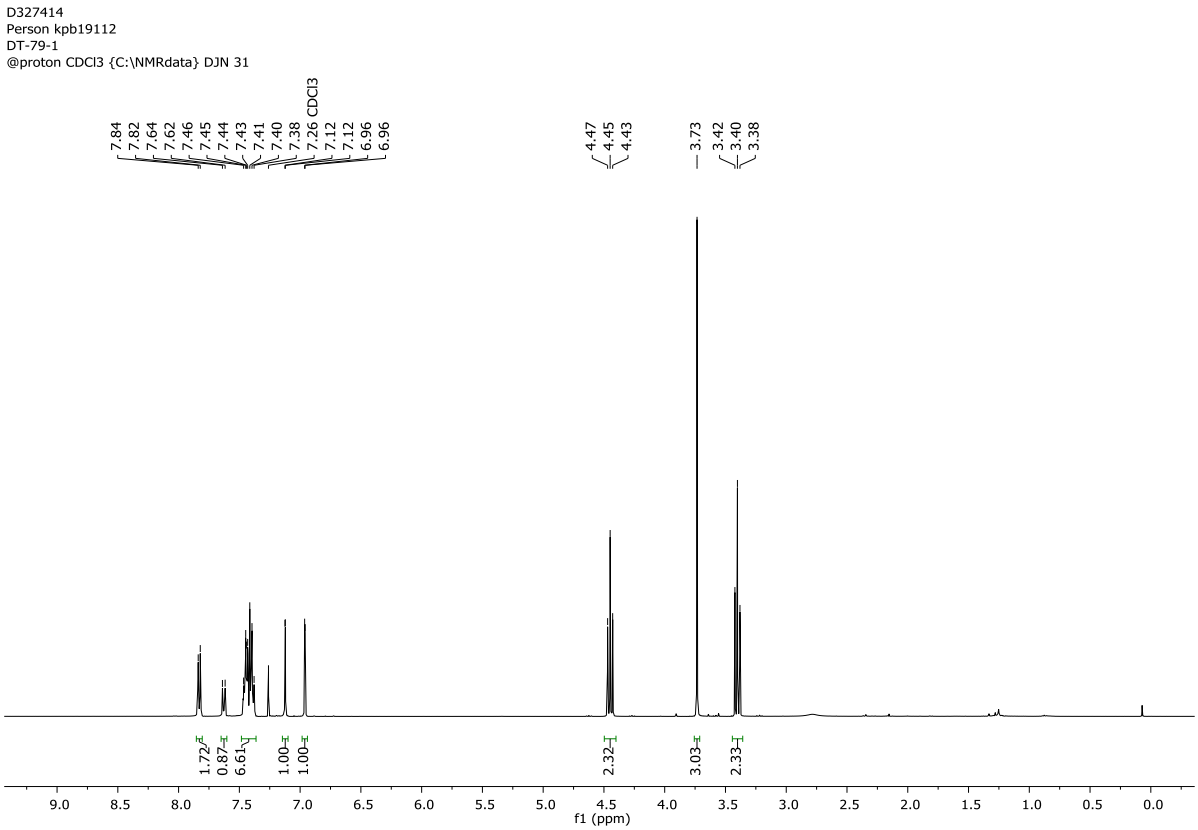


Figure S150. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline (entry 1, Table S35).

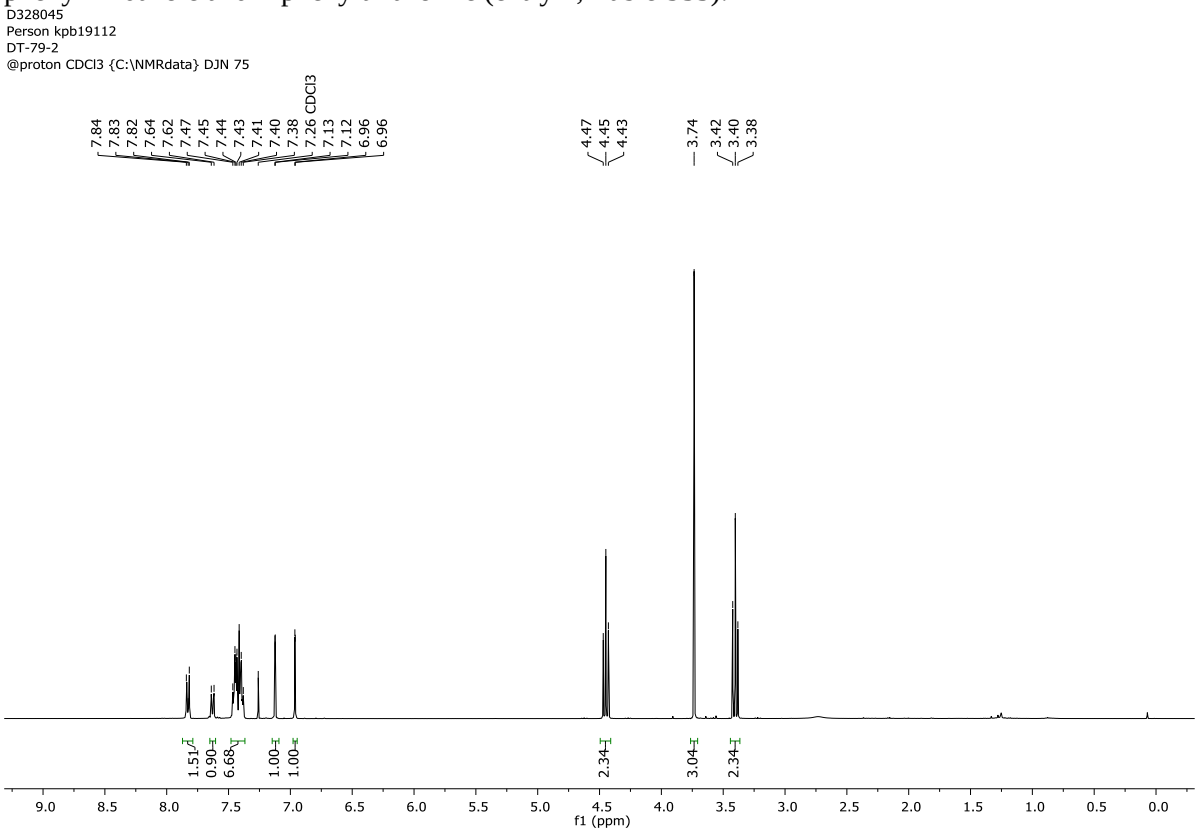


Figure S151. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline (entry 2, Table S35).

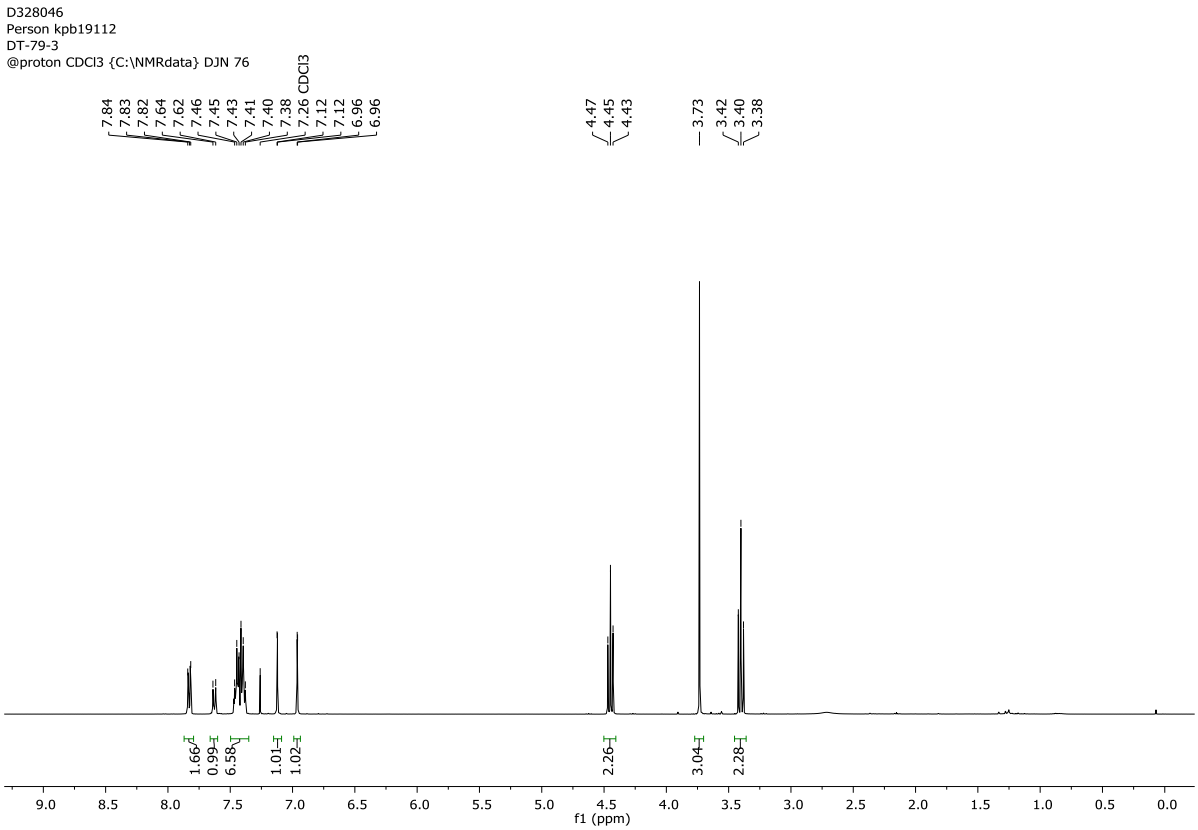
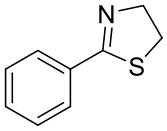
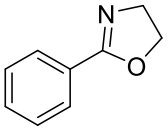


Figure S152. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 1-methyl-2-phenylimidazole and 2-phenylthiazoline (entry 3, Table S35).

Table S36. Determination of the competition rate constant κ from the labelling experiment between 2-phenylthiazoline and 2-phenyloxazoline.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	16.3 mg	14.7 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.86 – 7.81 ppm and at δ (**R2**) = 7.98 – 7.93 ppm
Determined against integral at δ (**R1**) = 3.41 ppm and at δ (**R2**) = 4.06 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.93 (m, 2H/D **R2**), 7.86 – 7.81 (m, 2H/D, **R1**), 7.51 – 7.36 (m, 3H, **R1** and 3H, **R2**), 4.49 – 4.40 (m, 2H, **R1** and 2H, **R2**), 4.06 (t, *J* = 9.5 Hz, 2H, **R2**), 3.41 (t, *J* = 8.4 Hz, 2H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.47	2.45	40	1.50	2.00	25	1.78
2	1.88	2.76	32	1.62	2.00	19	1.82
3	1.47	2.49	41	1.50	2.00	25	1.83
				Average κ = 1.81			

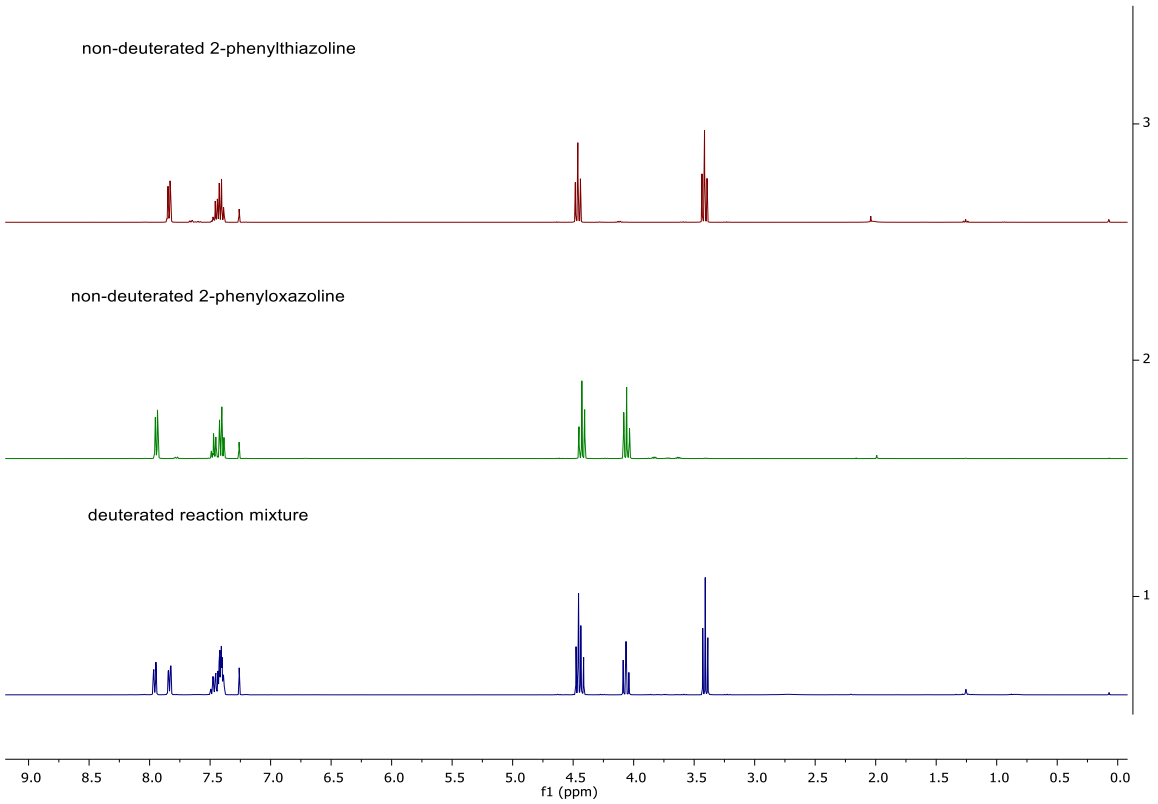


Figure S153. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

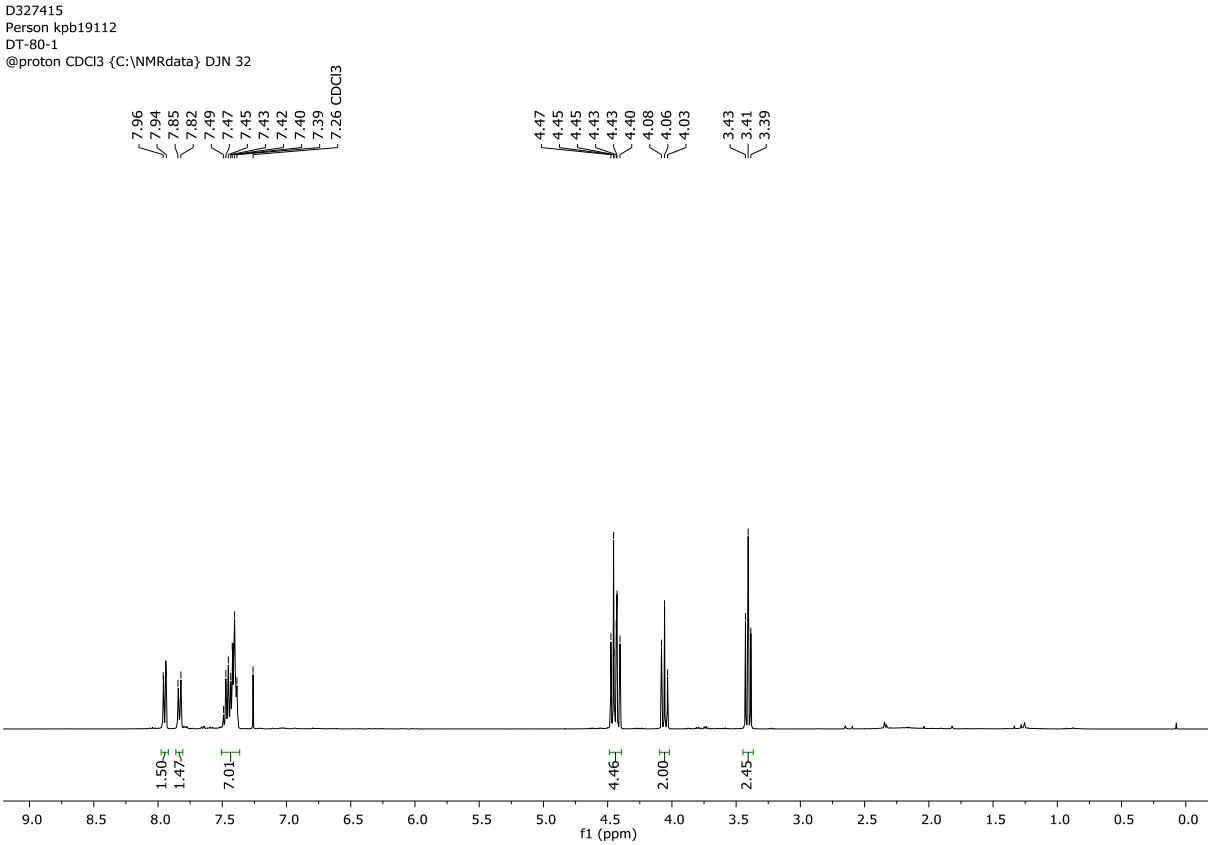


Figure S154. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazoline and 2-phenyloxazoline (entry 1, Table S36).

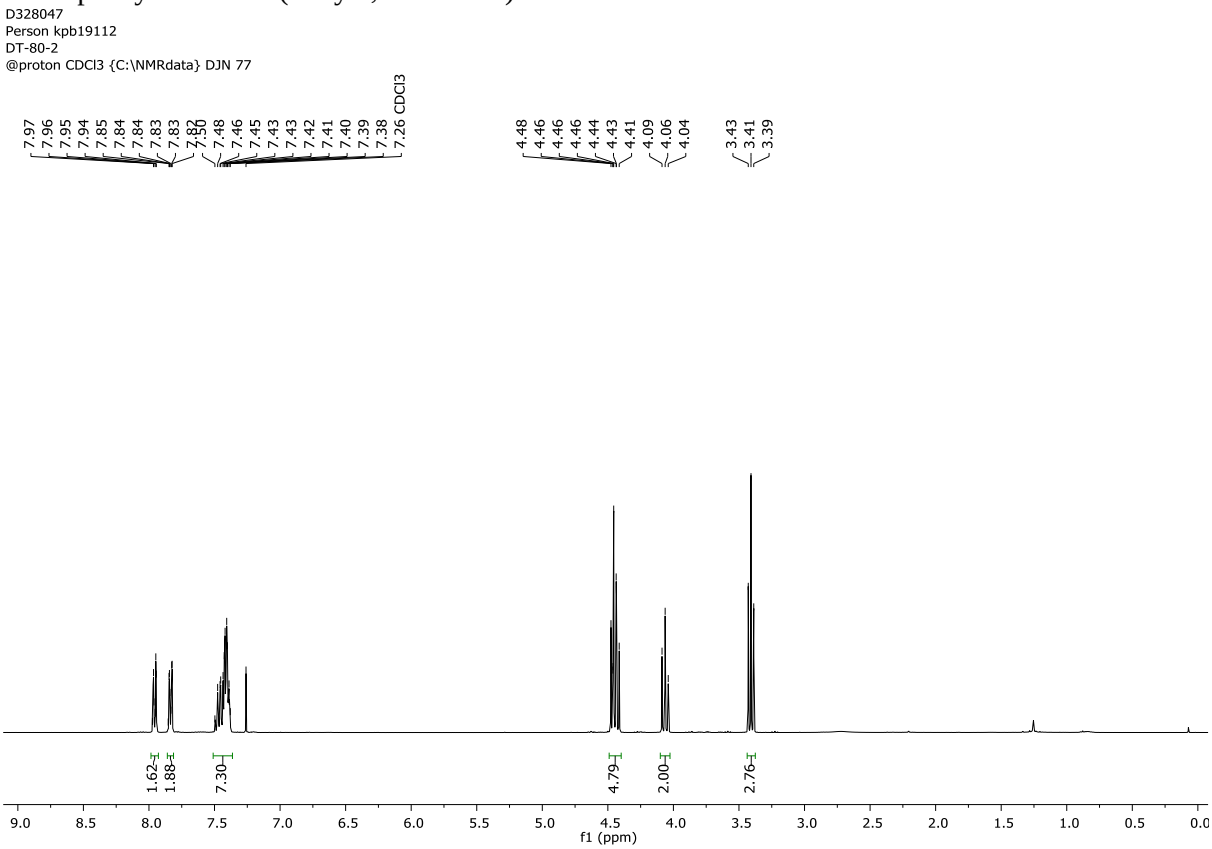


Figure S155. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazoline and 2-phenyloxazoline (entry 2, Table S36).

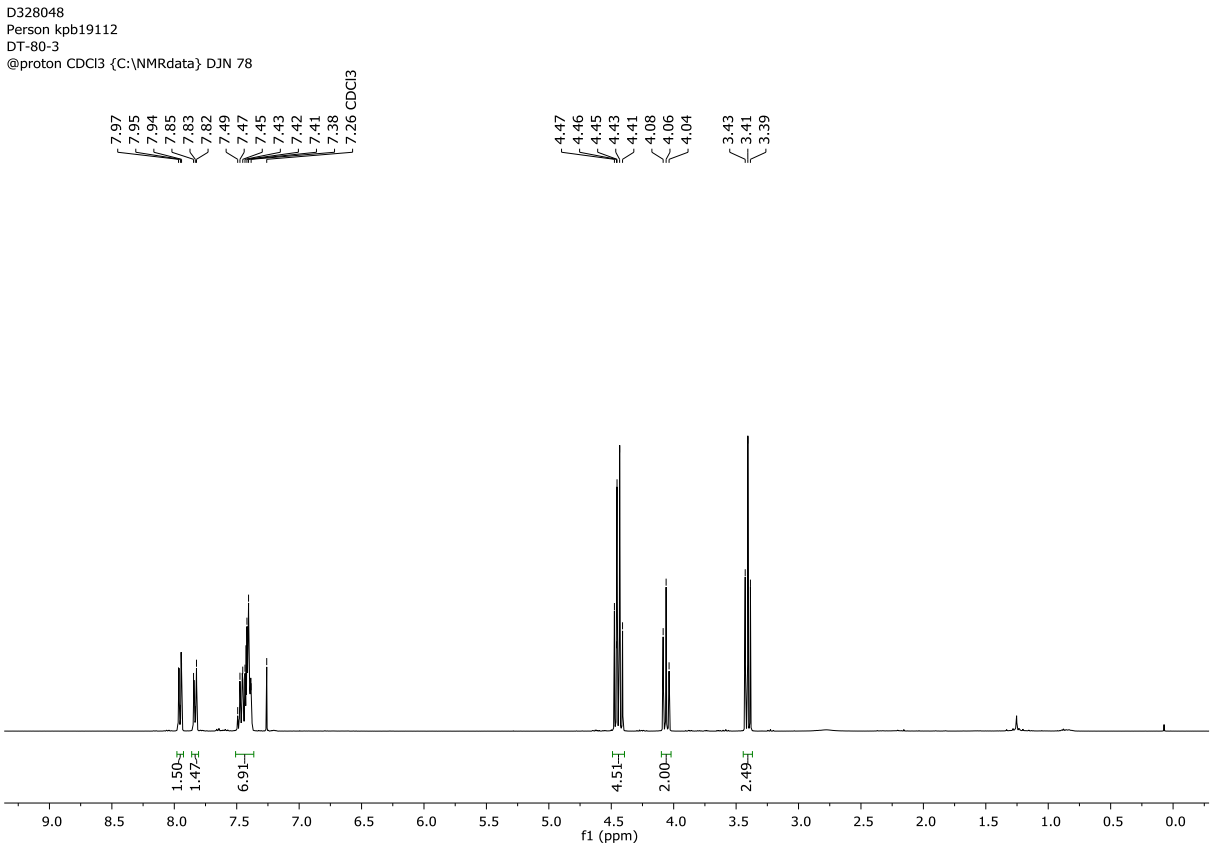
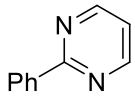
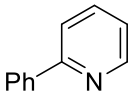


Figure S156. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylthiazoline and 2-phenyloxazoline (entry 3, Table S36).

Table S37. Determination of the competition rate constant κ from the labelling experiment between 2-phenylpyrimidine and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2 [(COD)Ir(IMes)Cl]**
Mass	15.6 mg	15.5 mg	3.2 mg

Deuteration expected at δ (**R1**) = 8.49 – 8.42 ppm and at δ (**R2**) = 8.02 – 7.97 ppm
Determined against integral at δ (**R1**) = 8.80 ppm and at δ (**R2**) = 7.77 – 7.70 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.80 (d, *J* = 4.8 Hz, 2H, **R1**), 8.73 – 7.67 (m, 1H, **R2**), 8.49 – 8.42 (m, 2H/D, **R1**), 8.02 – 7.97 (m, 2H/D **R2**), 7.77 – 7.70 (m, 2H, **R2**), 7.52 – 7.39 (m, 3H, **R1** and 3H, **R2**), 7.25 – 7.20 (m, 1H, **R2**), 7.17 (t, *J* = 4.8 Hz, 1H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 2H	$\%D_{R2}$	κ
1	1.70	2.00	15	1.75	2.01	13	1.17
2	1.52	2.00	24	1.58	1.96	19	1.27
3	1.56	2.00	22	1.66	2.00	17	1.33
			Average κ = 1.26				

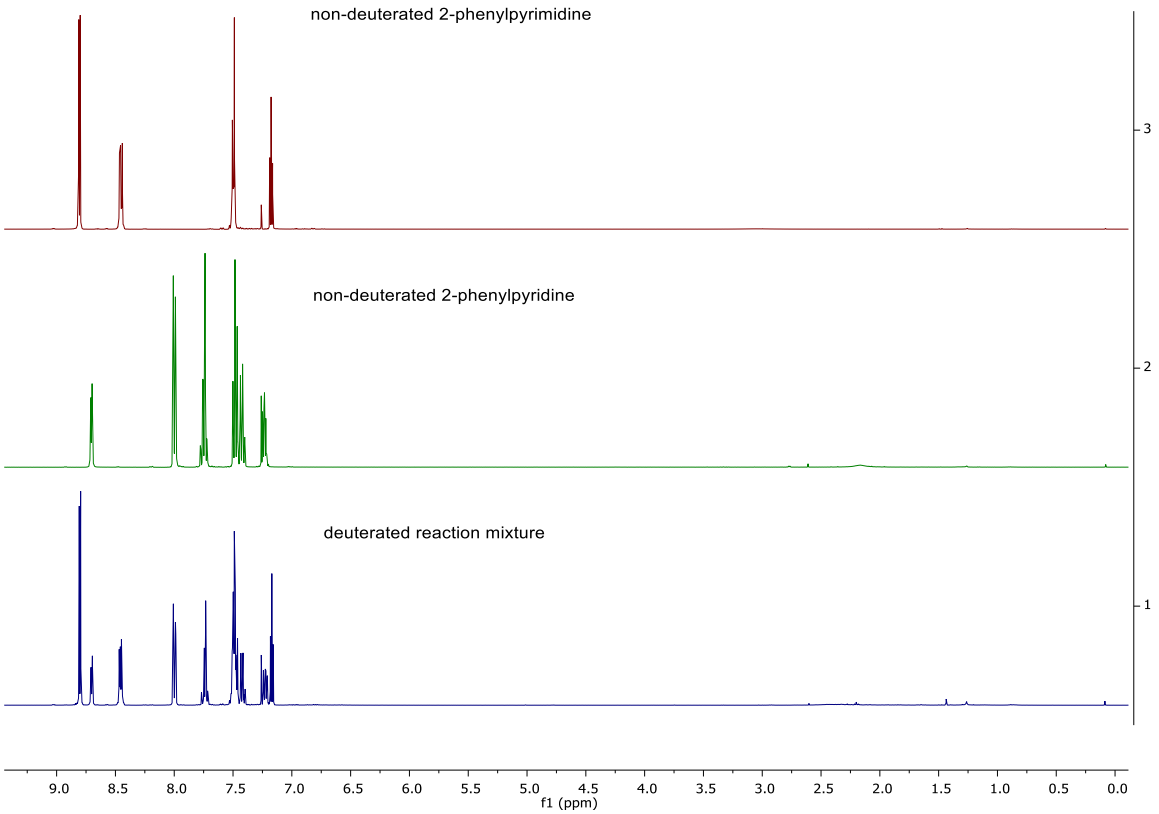


Figure S157. Stacked ^{1}H NMR (400 MHz, $CDCl_3$) of non-deuterated substrates and reaction mixture.

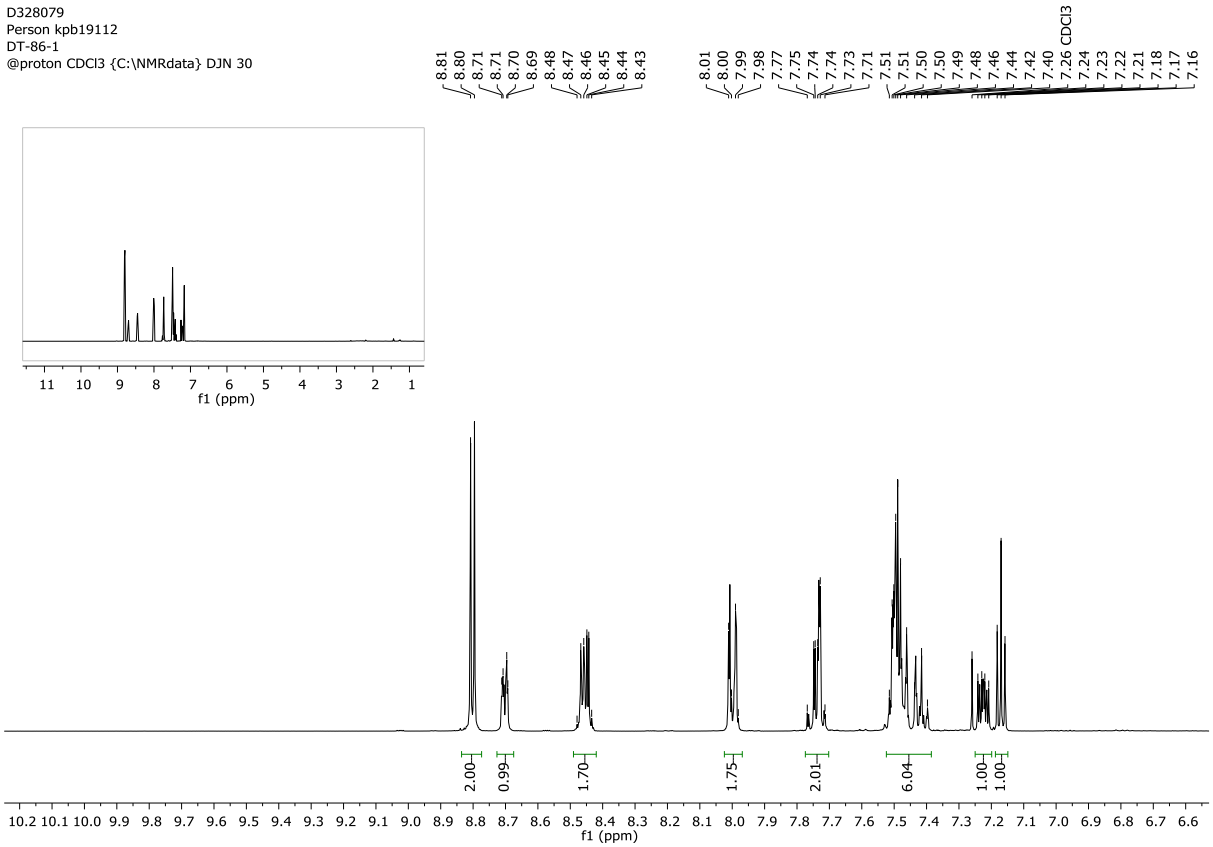


Figure S158. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyrimidine and 2-phenylpyridine (entry 1, Table S37).

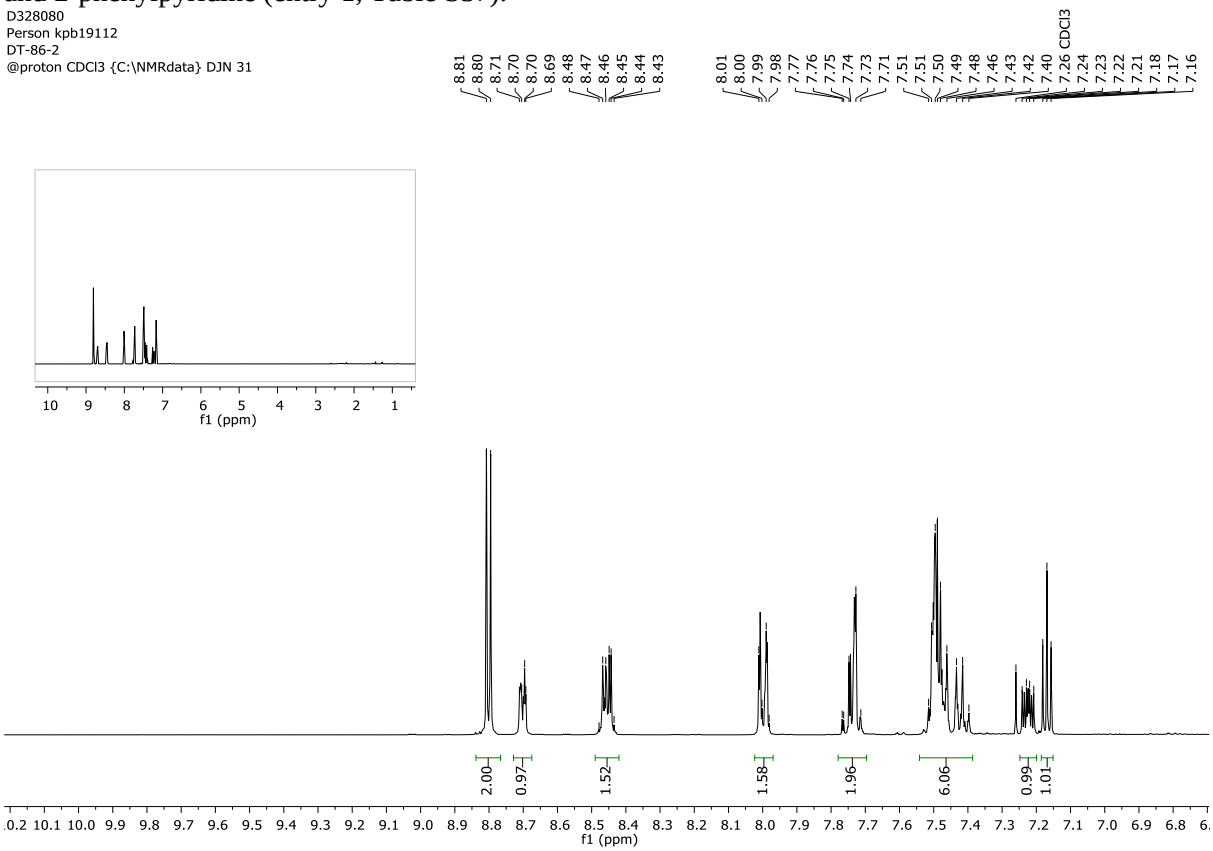


Figure S159. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyrimidine and 2-phenylpyridine (entry 2, Table S37).

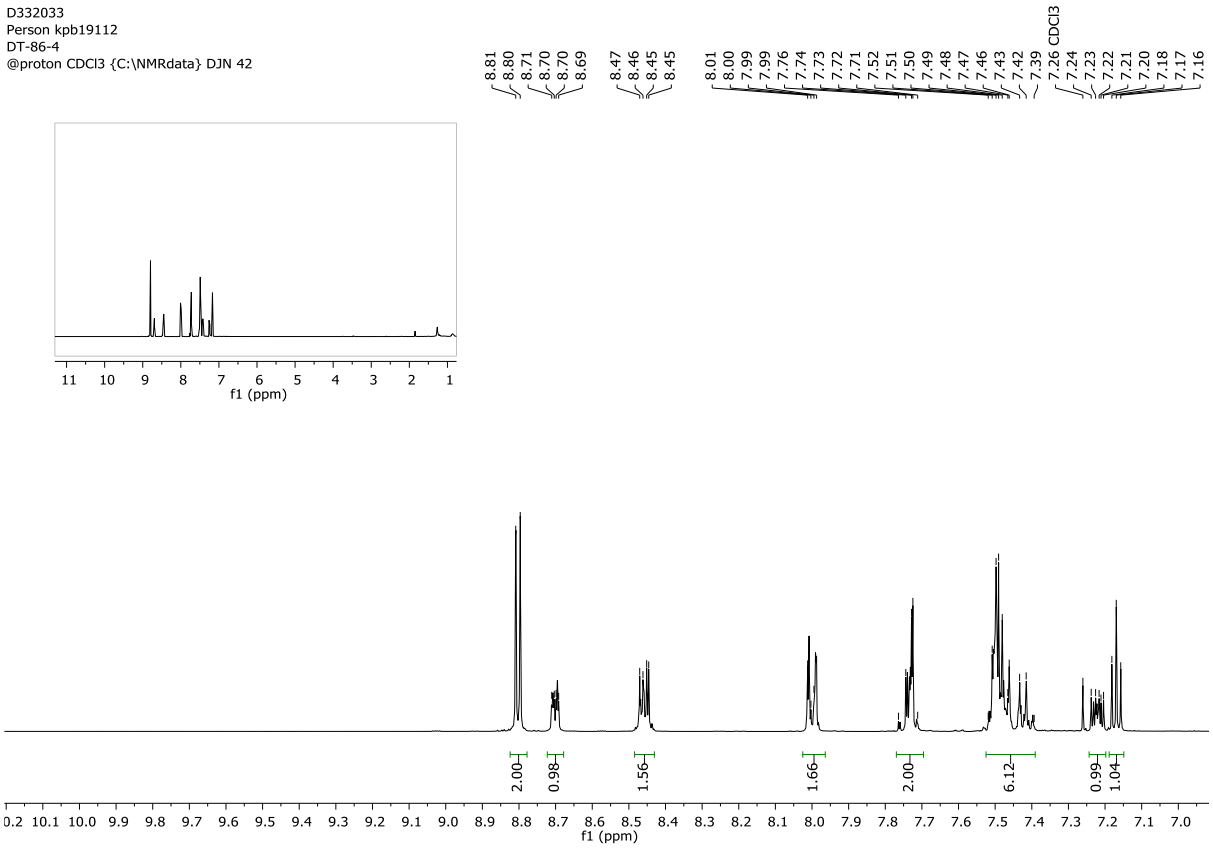
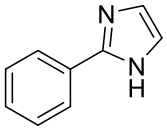
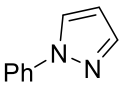


Figure S160. ^{1}H NMR (400 MHz, $CDCl_3$) of the competition experiment between 2-phenylpyrimidine and 2-phenylpyridine (entry 3, Table S37).

Table S38. Determination of the competition rate constant κ from the labelling experiment between 2-phenylimidazole and 1-phenylpyrazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** **[(COD)Ir(IMes)Cl]**
Mass	14.4 mg	14.4 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.98 – 7.90 ppm and at δ (**R2**) = 7.87 – 7.82 ppm
Determined against integral at δ (**R1**) = 7.52 – 7.41 ppm and at δ (**R2**) = 8.49 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.51 (br, 1H, **R1**), 8.49 (d, J = 2.5 Hz, 1H, **R2**), 7.98 – 7.90 (m, 2H/D, **R1**), 7.87 – 7.82 (m, 2H/D, **R2**), 7.74 (d, J = 1.5 Hz, 1H, **R1**), 7.52 – 7.41 (m, 2H, **R1** and 2H, **R2**), 7.36 – 7.29 (m, 1H, **R1** and 1H, **R2**), 7.14 (br, 2H, **R1**), 6.55 – 6.52 (m, 1H, **R2**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	1.08	2.23	52	1.87	1.00	6	10.79
2	1.04	2.11	51	1.87	1.00	6	10.53
3	1.06	2.15	51	1.88	1.00	6	11.43
			Average κ = 10.91				

[a] $I_{R1(t)}$ = 4.23–1.00×2; [b] $I_{R1(t)}$ = 4.11–1.00×2; [c] $I_{R1(t)}$ = 4.15–1.00×2;

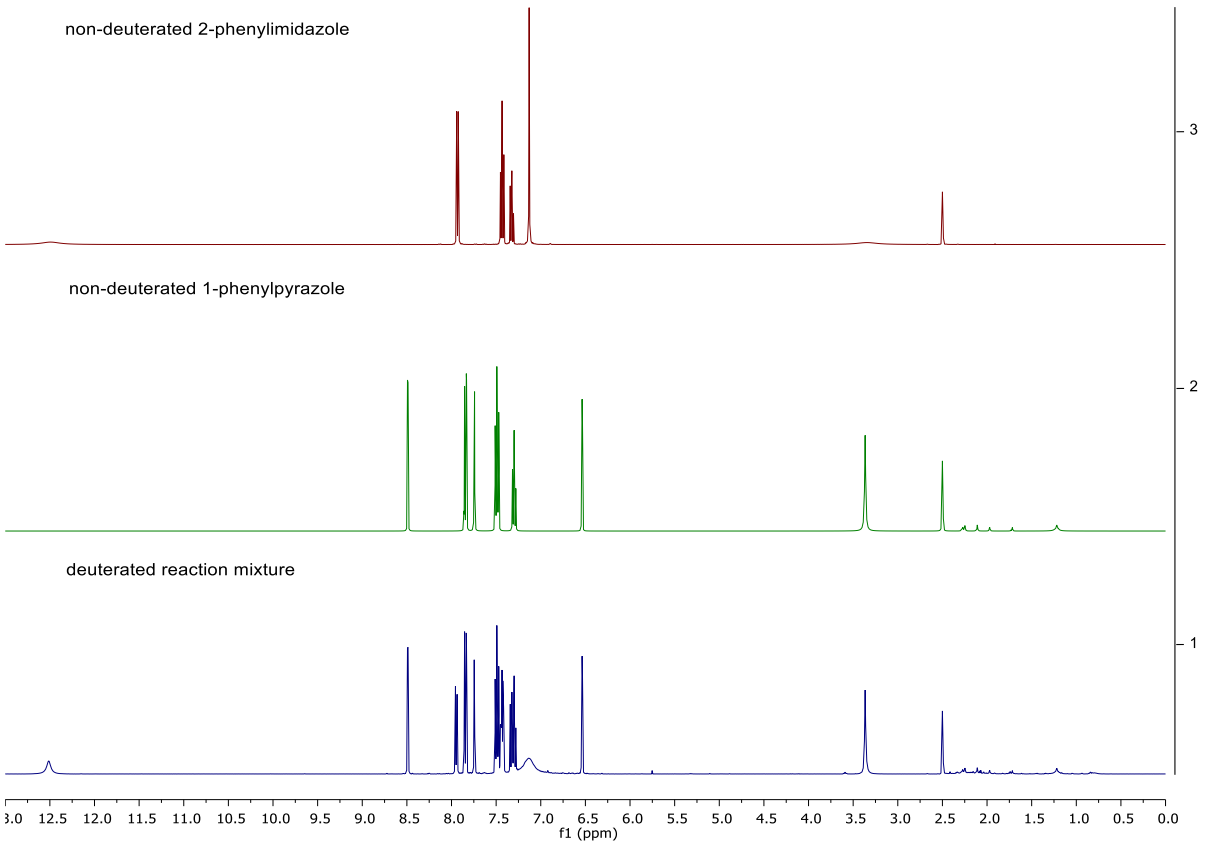


Figure S161. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

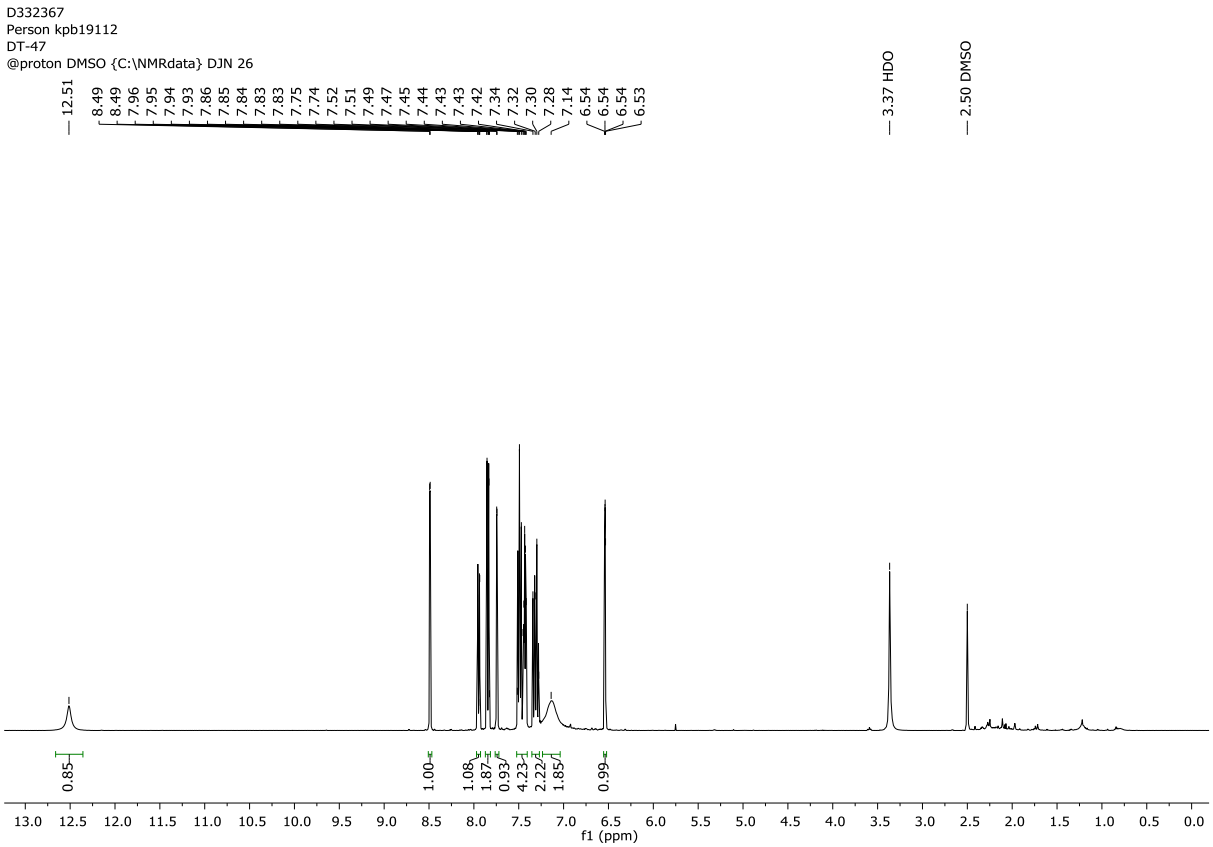


Figure S162. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazole and 1-phenylpyrazole (entry 1, Table S38).

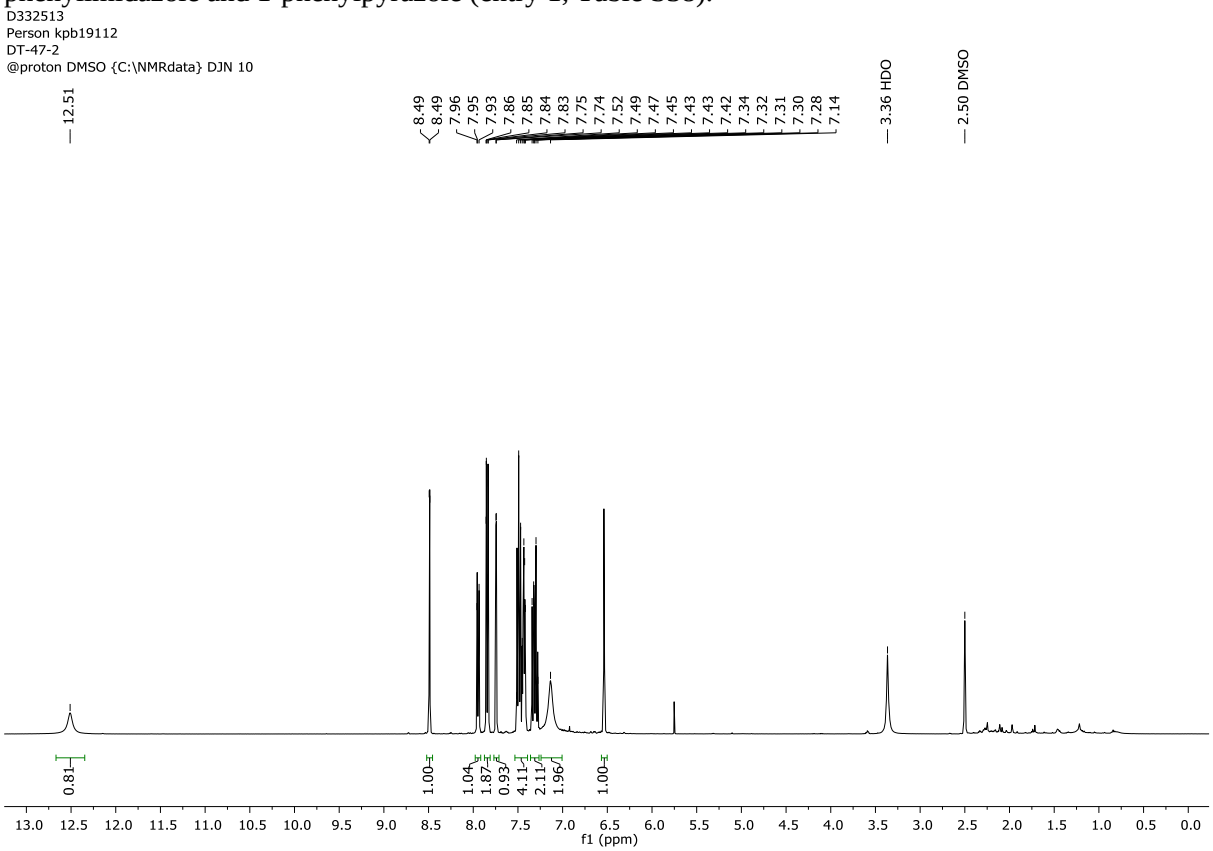


Figure S163. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazole and 1-phenylpyrazole (entry 2, Table S38).

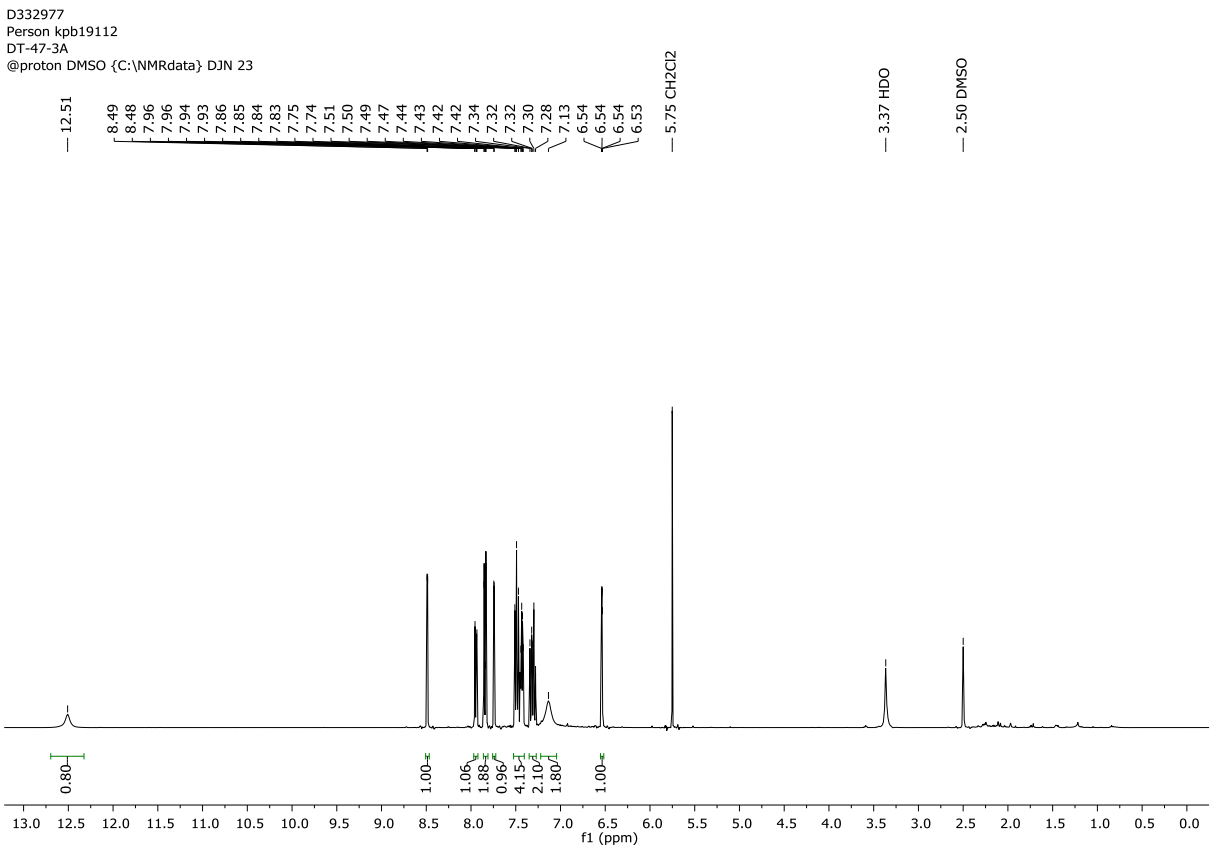
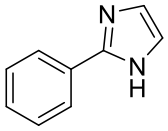
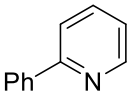


Figure S164. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazole and 1-phenylpyrazole (entry 3, Table S38).

Table S39. Determination of the competition rate constant κ from the labelling experiment between 2-phenylimidazole and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** **[(COD)Ir(IMes)Cl]**
Mass	14.4 mg	15.5 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.98 – 7.92 ppm and at δ (**R2**) = 8.11 – 8.06 ppm
Determined against integral at δ (**R1**) = 7.53 – 7.40 ppm and at δ (**R2**) = 7.90 – 7.84 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.51 (br, 1H, **R1**), 8.70 –8.65 (m, 1H, **R2**), 8.11 – 8.06 (m, H/D, **R2**), 7.98 – 7.92 (m, H/D, **R1** and 1H, **R2**), 7.90 – 7.84 (m, 1H, **R2**), 7.53 – 7.40 (m, 2H, **R1** and 3H, **R2**), 7.37 – 7.30 (m, 1H, **R1** and 1H, **R2**), 7.14 (br, 2H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 2H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.74[a]	2.06[d]	64	1.73	1.00	14	7.06
2	0.80[b]	2.06[e]	61	1.78	1.00	11	8.12
3	0.72[c]	1.94[f]	64	1.74	1.00	13	7.30
			Average κ = 7.49				

[a] $I_{R1(t)}$ = 1.74-1.00; [b] $I_{R1(t)}$ = 1.80-1.00; [c] $I_{R1(t)}$ = 1.72-1.00;

[d] $I_{R1(0)}$ = 5.06-1.00×3; [e] $I_{R1(0)}$ = 5.06-1.00×3; [f] $I_{R1(0)}$ = 4.99-1.00×3;

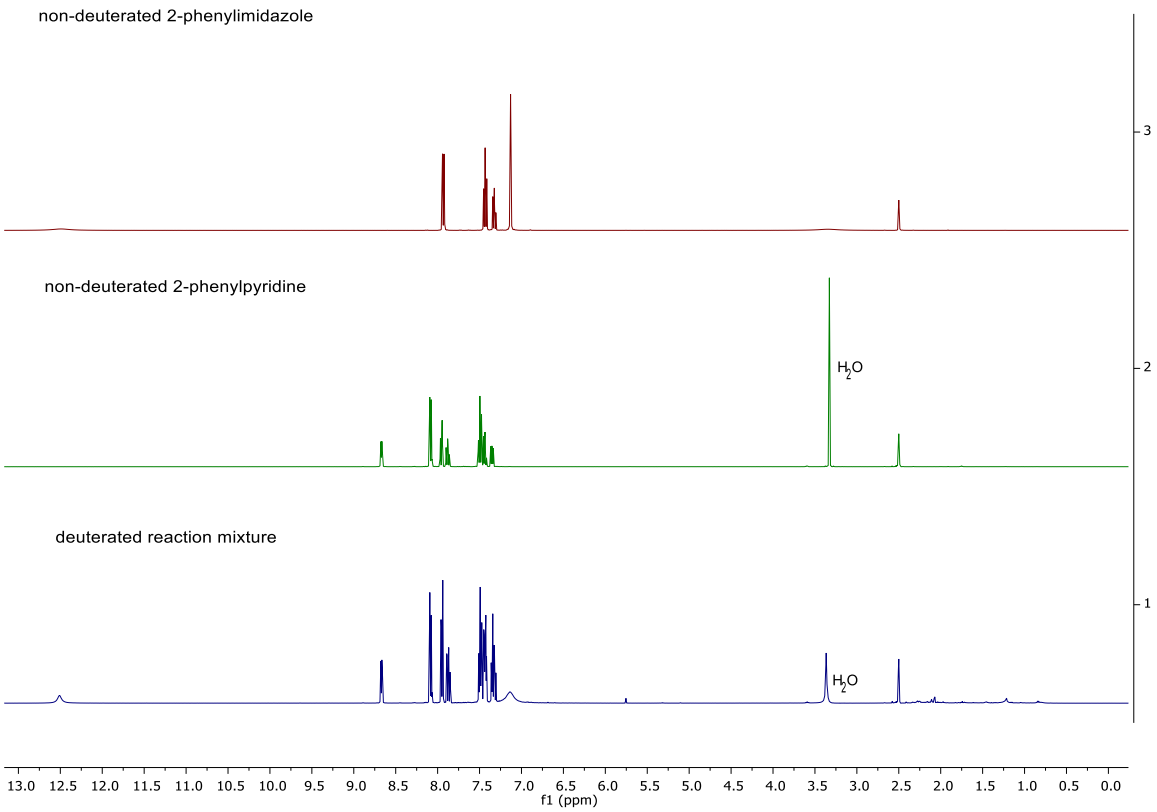


Figure S165. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

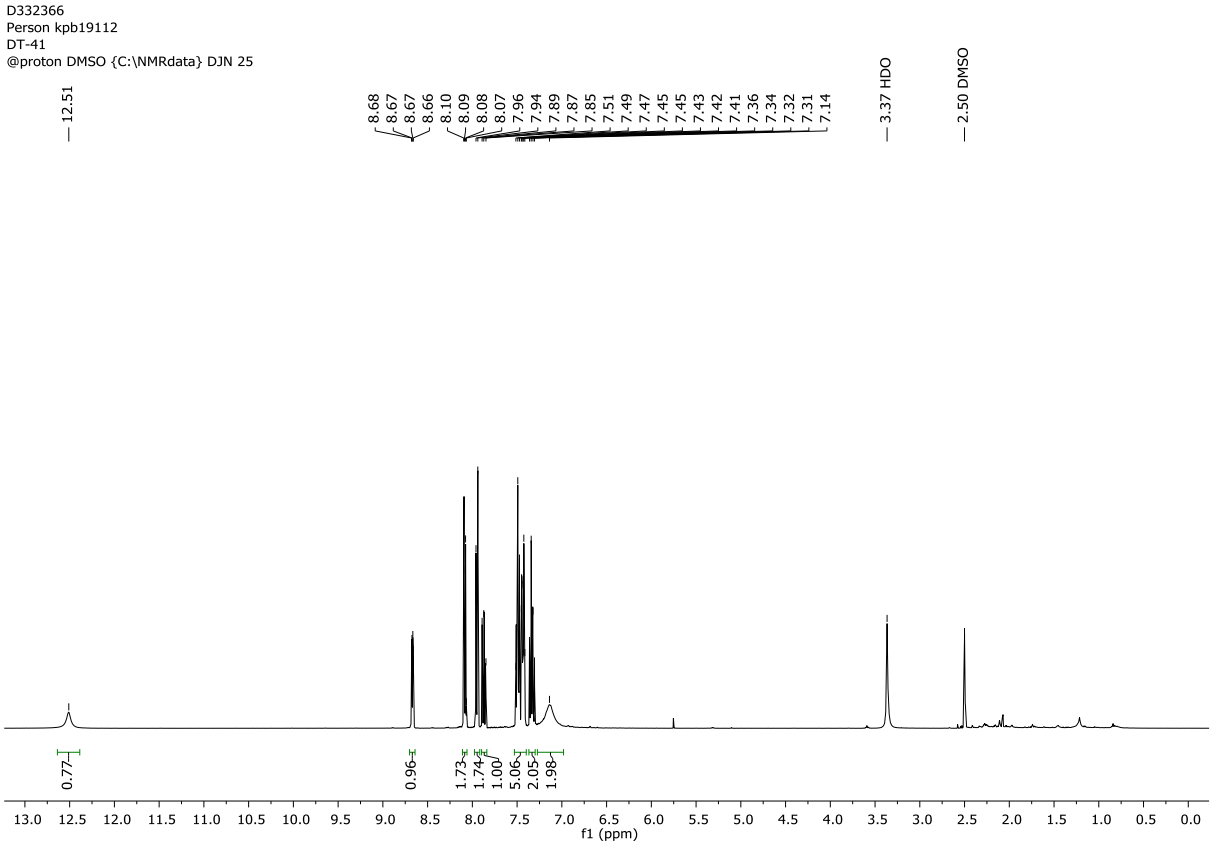


Figure S166. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazole and 1-phenylpyridine (entry 1, Table S39).

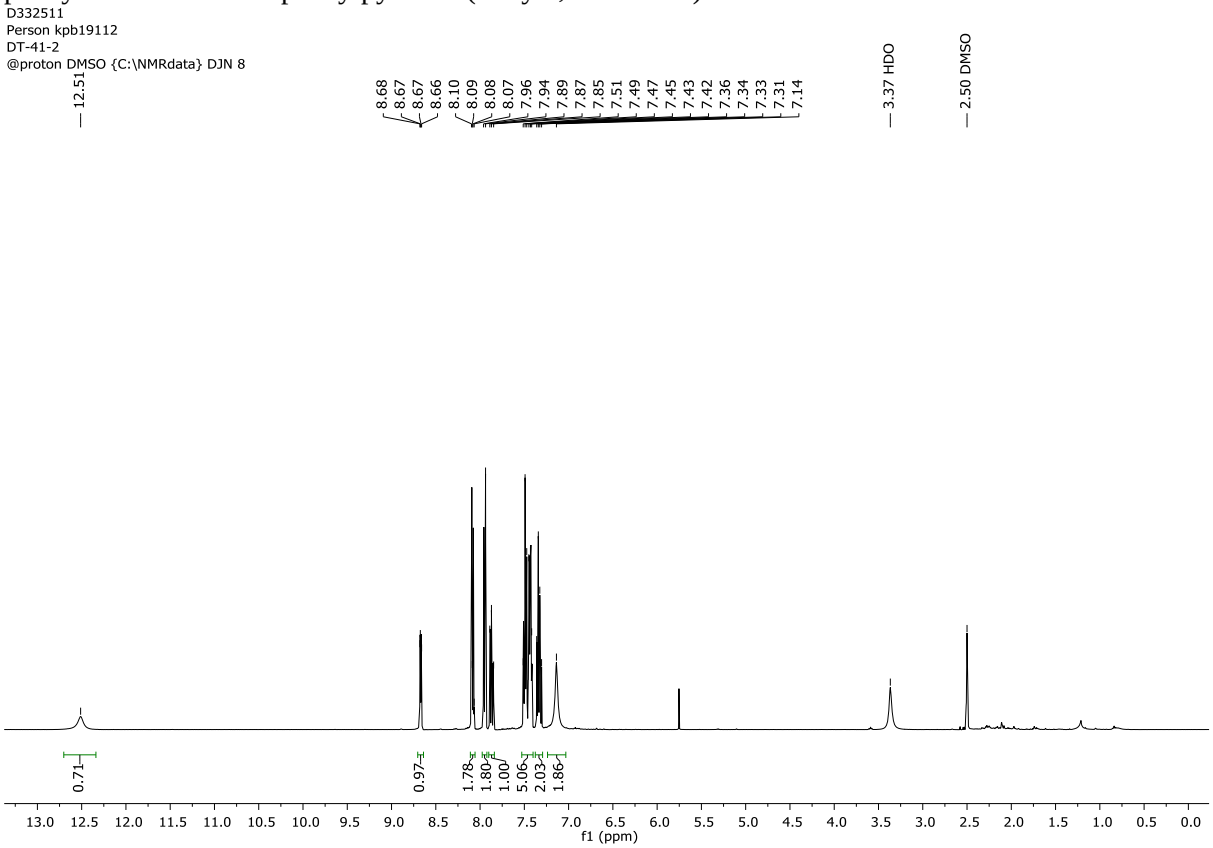


Figure S167. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazole and 1-phenylpyridine (entry 2, Table S39).

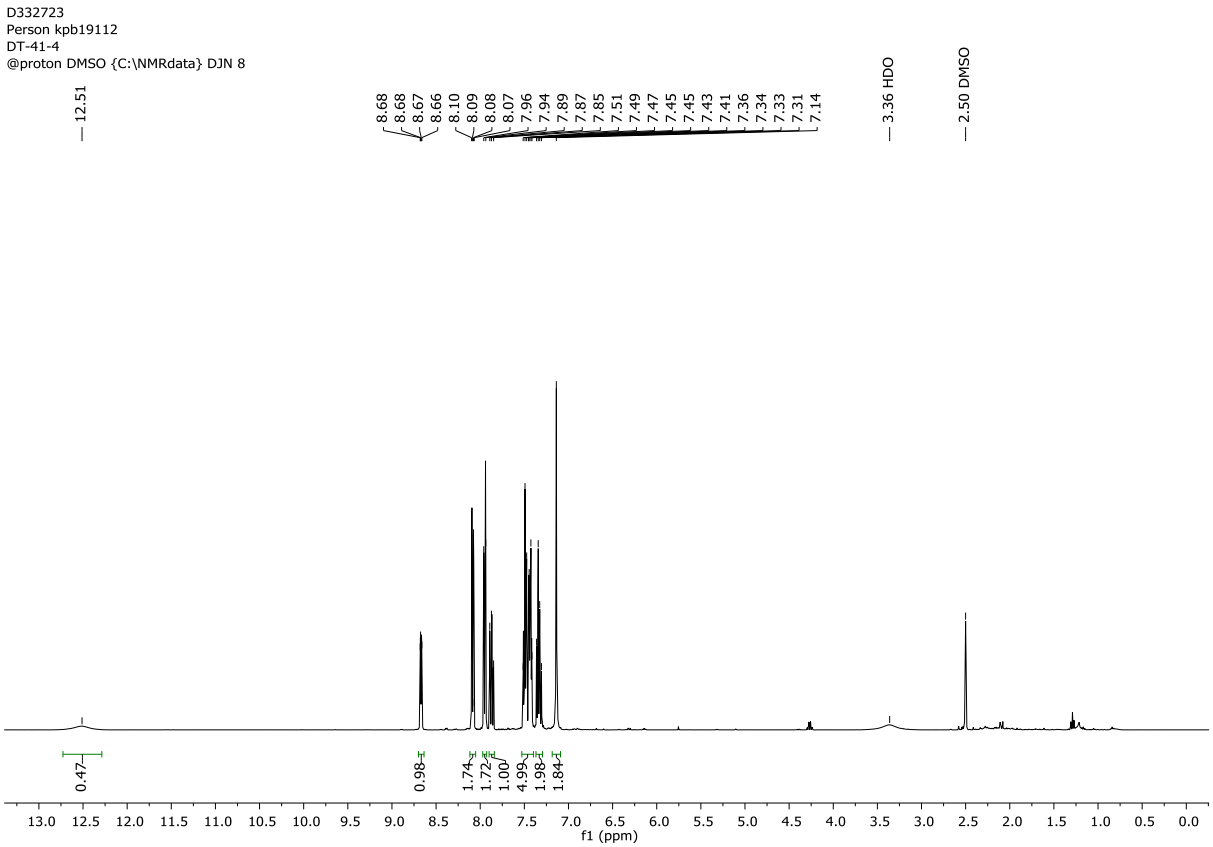
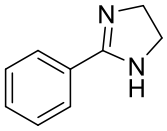
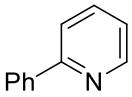


Figure S168. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazole and 1-phenylpyridine (entry 3, Table S39).

Table S40. Determination of the competition rate constant κ from the labelling experiment between 2-phenylimidazoline and 2-phenylpyridine.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	14.6 mg	15.5 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.90 – 7.81 ppm and at δ (**R2**) = 8.11 – 8.06 ppm
Determined against integral at δ (**R1**) = 3.61 ppm and at δ (**R2**) = 7.97 – 7.93 ppm
Spectral details of the deuterated reaction mixture:
^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.70 – 8.64 (m, 1H, **R2**), 8.11 – 8.06 (m, 2H/D, **R2**), 7.97 – 7.93 (m, 1H, **R2**), 7.90 – 7.81 (m, 2H/D, **R1** and 1H, **R2**), 7.53 – 7.39 (m, 3H, **R1** and 3H, **R2**), 7.36 – 7.29 (m, 1H, **R2**), 3.61 (m, 4H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 4H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	0.86 [a]	3.48	51	1.72	1.00	14	4.67
2	1.17 [b]	3.37	31	1.81	1.00	10	3.65
3	1.14 [c]	3.41	33	1.84	1.00	8	4.83
Average κ = 4.38							

[a] $I_{R1(0)}$ = 1.86-1.00; [b] $I_{R1(0)}$ = 2.17-1.00; [c] $I_{R1(0)}$ = 2.14-1.00;

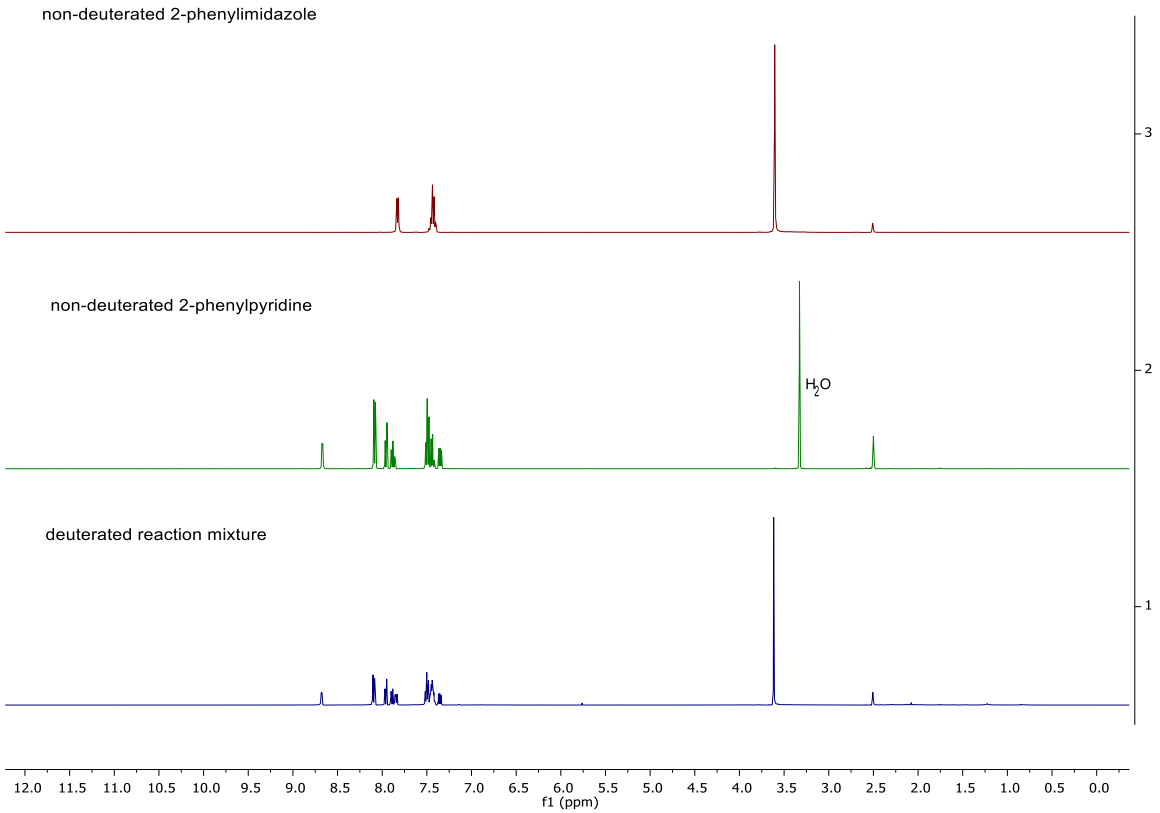


Figure S169. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

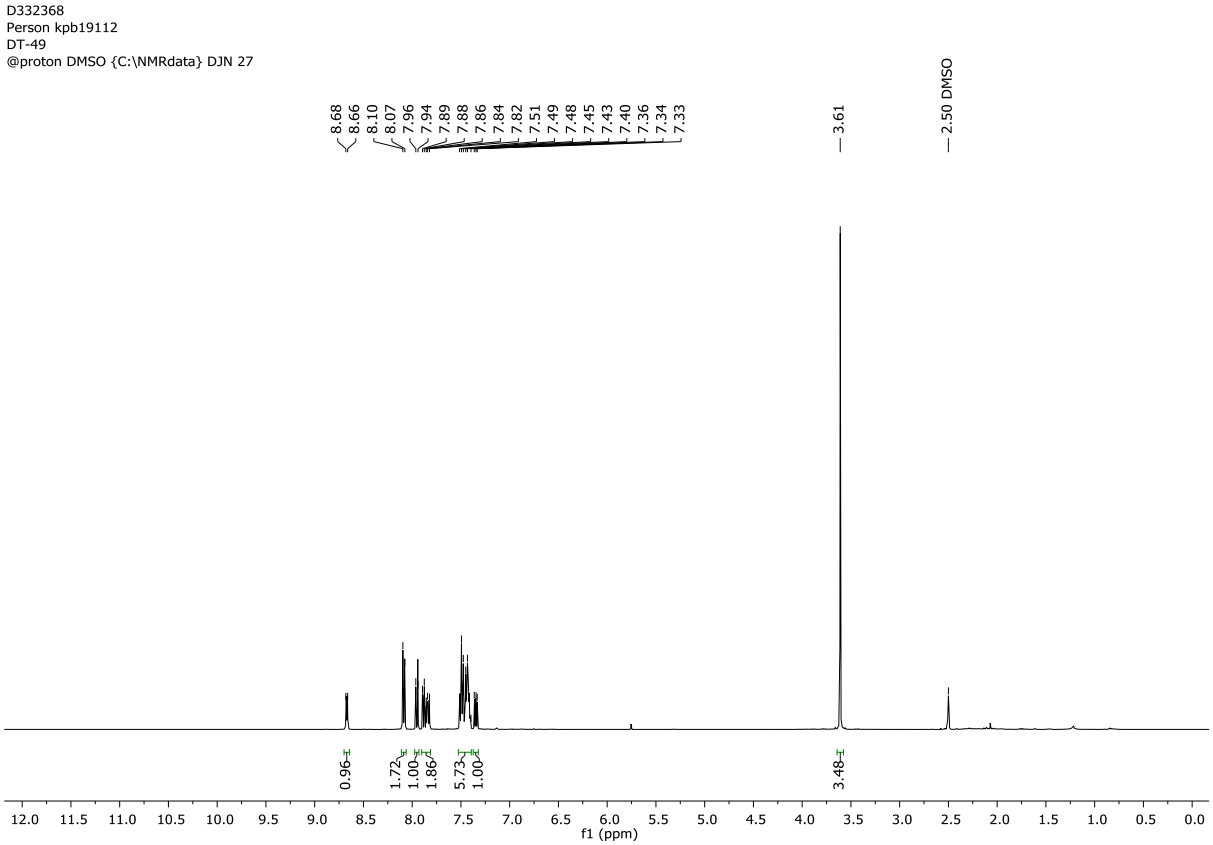


Figure S170. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazoline and 2-phenylpyridine (entry 1, Table S40).

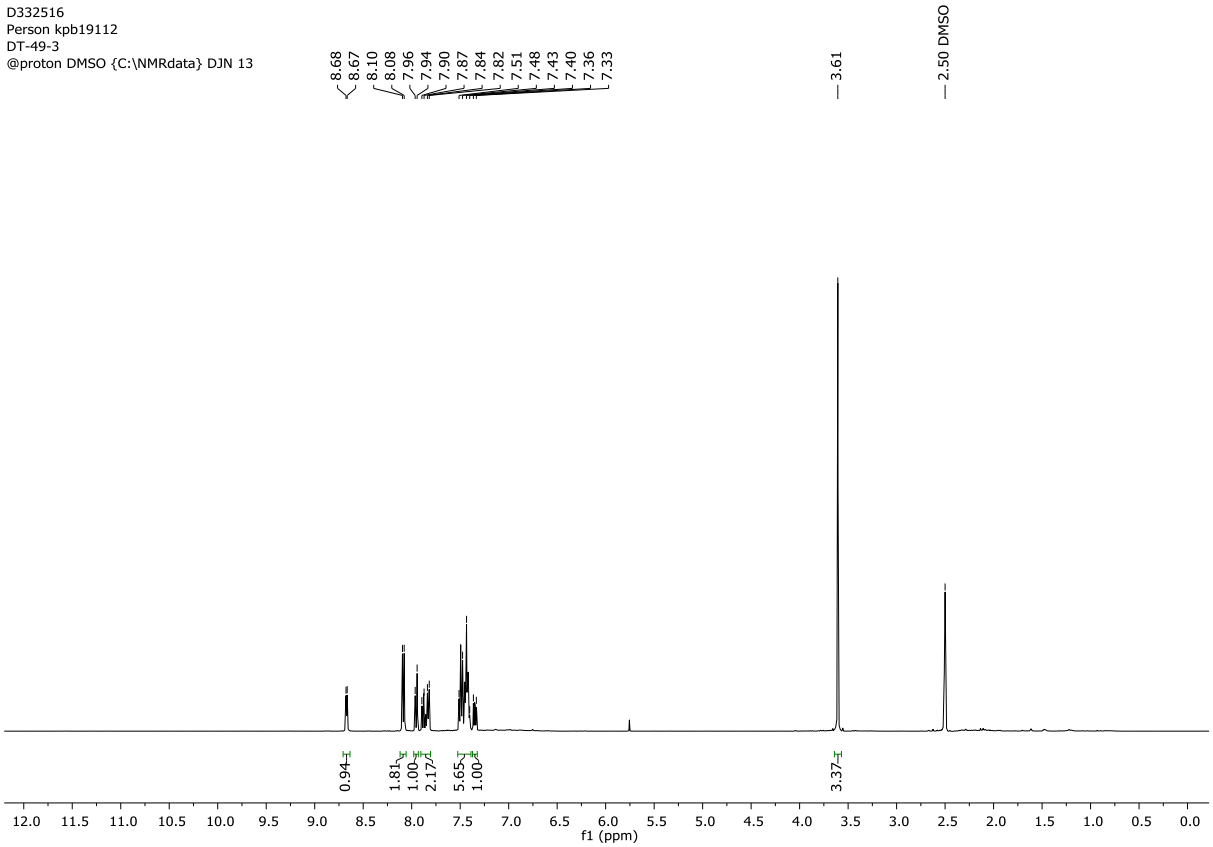


Figure S171. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazoline and 2-phenylpyridine (entry 2, Table S40).

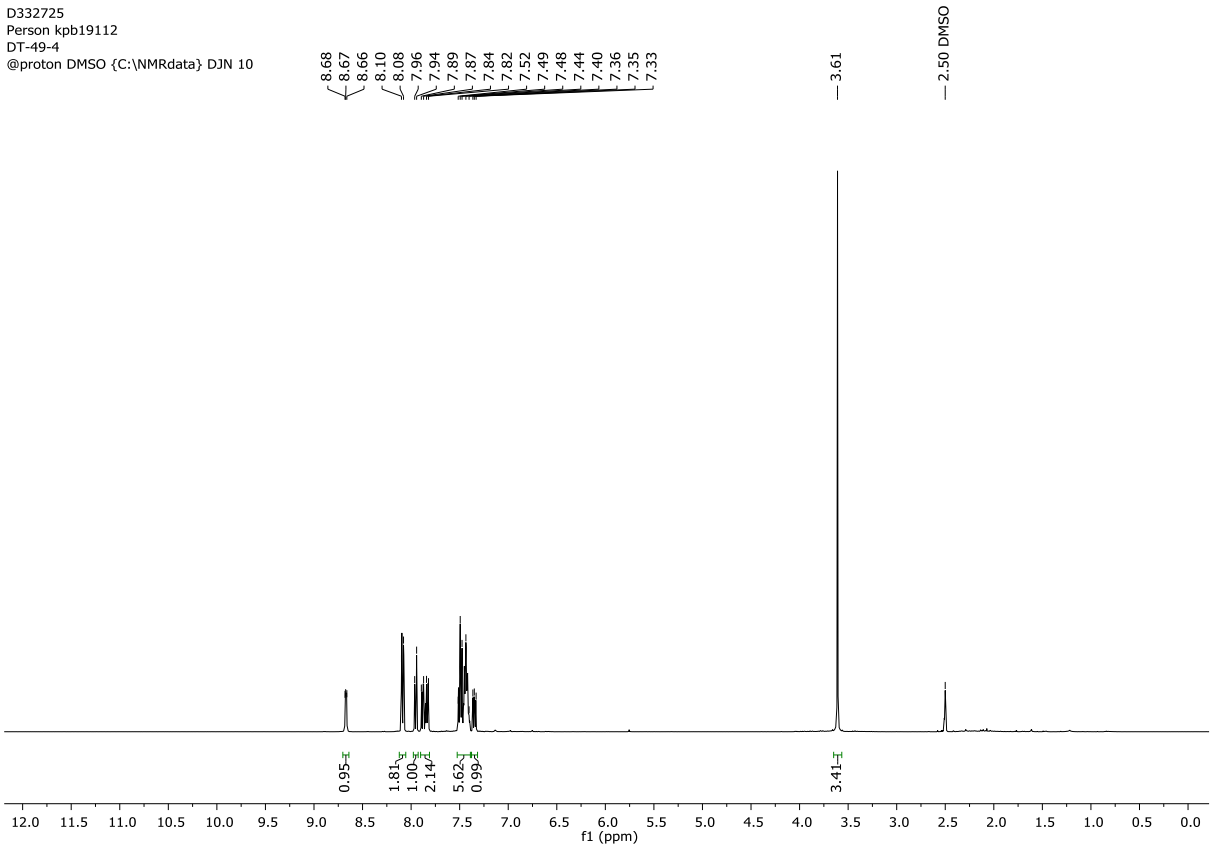
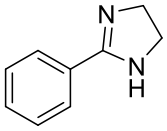
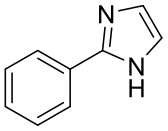


Figure S172. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazoline and 2-phenylpyridine *(*entry 3, Table S40).

Table S41. Determination of the competition rate constant κ from the labelling experiment between 2-phenylimidazoline and 2-phenylimidazole.

	Substrate **R1**	Substrate **R2**	Catalyst
			**Ir-2** [(COD)Ir(IMes)Cl]
Mass	14.6 mg	14.4 mg	3.2 mg

Deuteration expected at δ (**R1**) = 7.86 – 7.80 ppm and at δ (**R2**) = 7.98 – 7.90 ppm
Determined against integral at δ = 3.61 ppm for **R1** and at δ = 7.36 – 7.29 ppm for **R2**

Spectral details of the deuterated reaction mixture:

^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.98 – 7.90 (m, 2H/D, **R2**), 7.86 – 7.80 (m, 2H/D, **R1**), 7.50 – 7.38 (m, 3H, **R1** and 3H, **R2**), 7.36 – 7.29 (m, 1H, **R2**),7.13 (br, 2H, **R2**), 3.61 (s, 4H, **R1**).

Entry	$I_{R1(t)}$ N = 2H	$I_{R1(0)}$ N = 4H	$\%D_{R1}$	$I_{R2(t)}$ N = 2H	$I_{R2(0)}$ N = 1H	$\%D_{R2}$	κ
1	1.09	3.41	36	1.39	1.00	31	1.23
2	1.09	3.47	37	1.26	1.00	37	1.01
3	1.17	3.58	35	1.33	1.00	34	1.04
Average κ = 1.09							

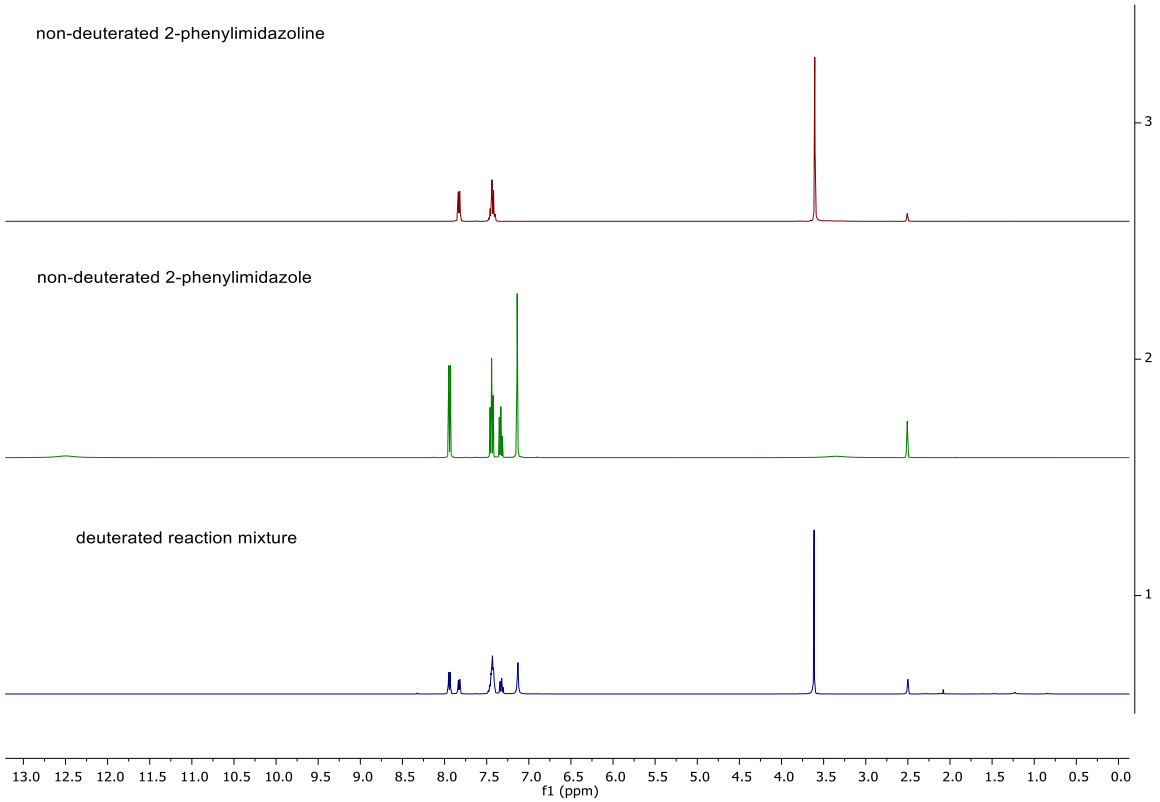


Figure S173. Stacked ^{1}H NMR (400 MHz, DMSO-d_6) of non-deuterated substrates and reaction mixture.

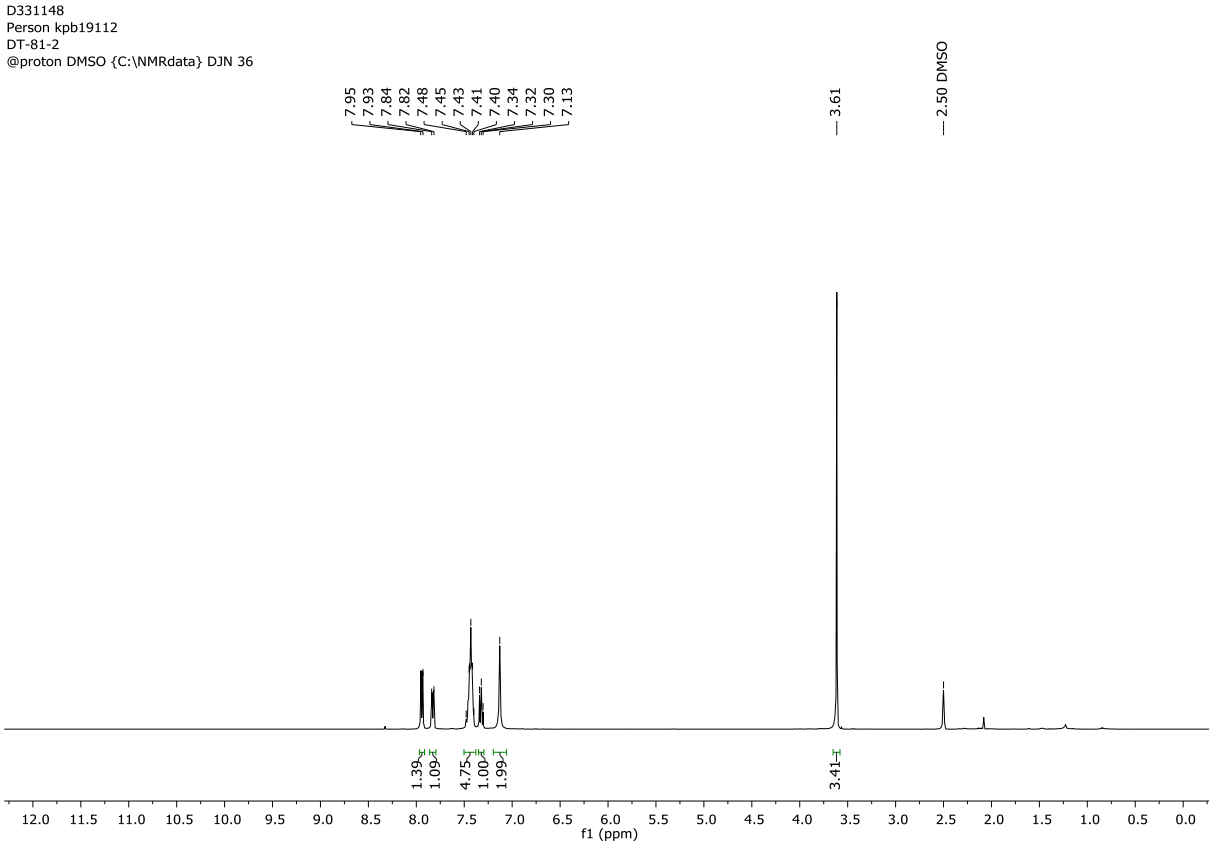


Figure S174. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazoline and 2-phenylimidazole (entry 1, Table S41).

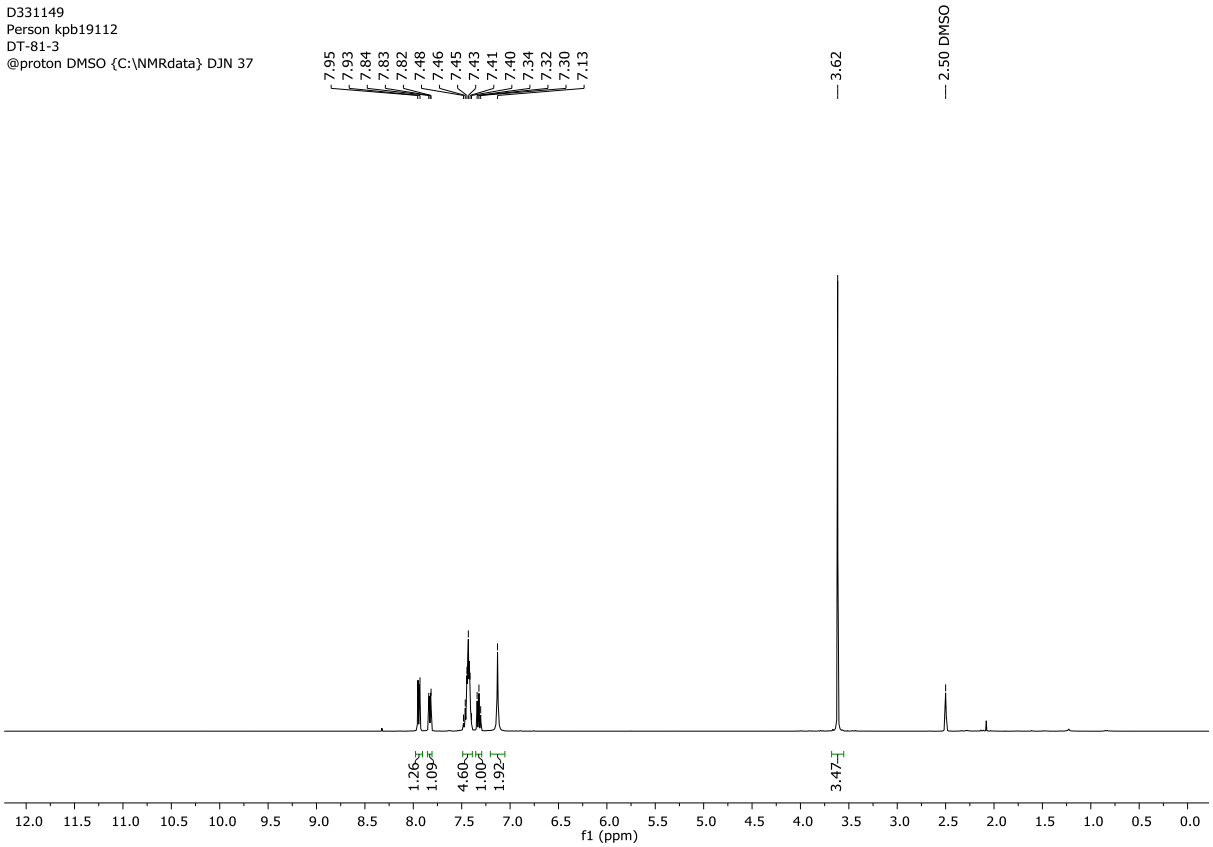


Figure S175. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazoline and 2-phenylimidazole (entry 2, Table S41).

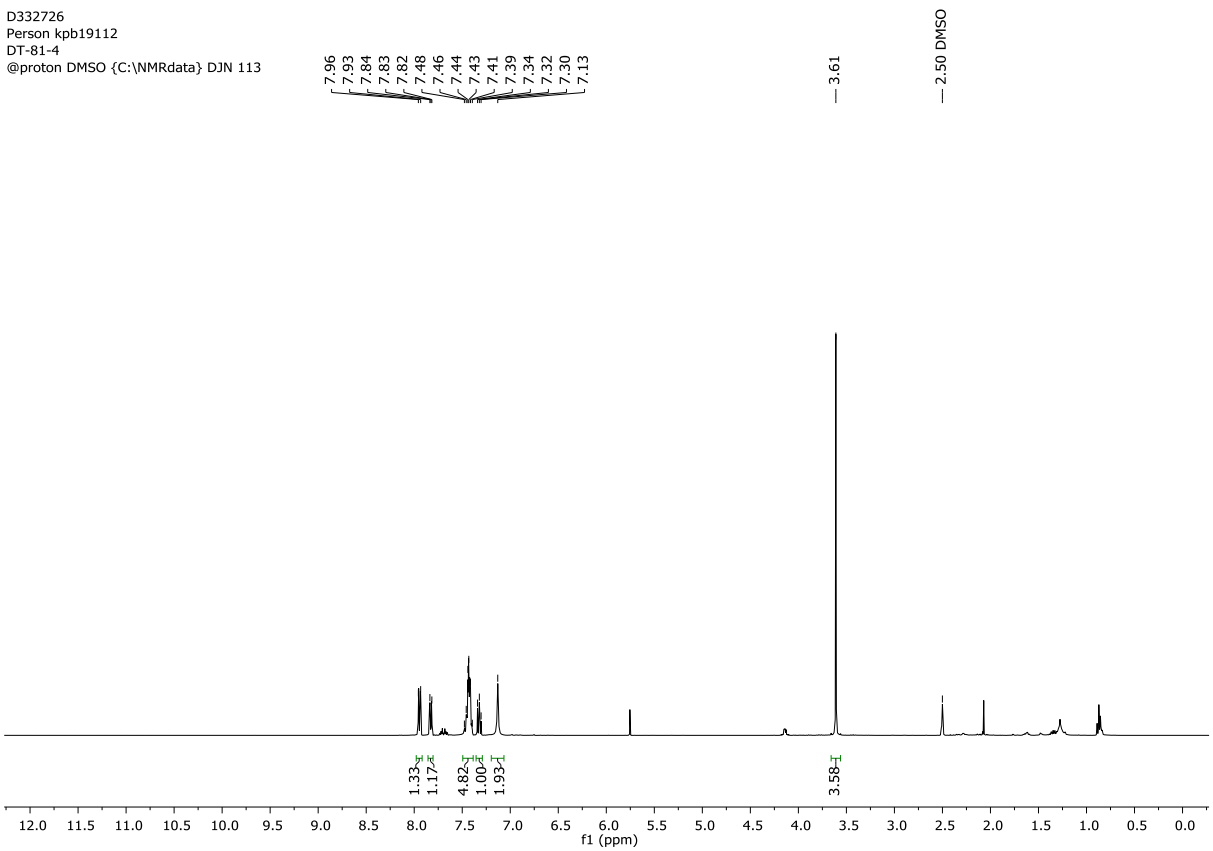


Figure S176. ^{1}H NMR (400 MHz, DMSO-d_6) of the competition experiment between 2-phenylimidazoline and 2-phenylimidazole (entry 3, Table S41).

3.5. Linear Regression Analysis.

Linear regression analysis of the experimentally obtained data set (κ^{exptl}) was performed to find the optimised k_{rel} values, which represent the relative rates of reaction of the different substrates, by minimising the sum of the squares of the errors $\Sigma\Delta^2$, where $\Delta^2 = \Sigma(\kappa^{exptl} - \kappa^{calcd})^2$ using Excel's Solver.

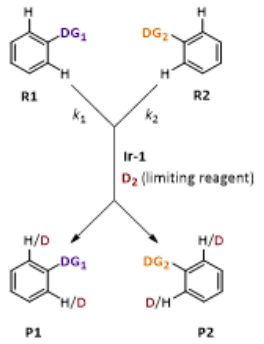
Calculated competition rate constants κ^{calcd} are expressed by equation (S-6)

$$\log \kappa = \log k_1 - \log k_2 \qquad \text{(S-6)}$$

The pyridine directing group was assigned as the reference substrate with $k_{rel} = 1$. All k_{rel} were constrained to be >= 0.001.

Solving the resulting overdetermined set of linear equations (eq. S-6) by least squares minimization yielded the k_{rel} values listed in Tables S42-S43.

Table S42. Linear regression analysis for k_{rel} determination for catalyst **Ir-1**.



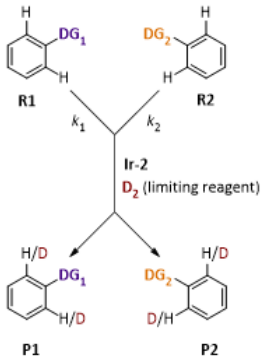
Substrates	k_{rel}
1-methyl-2-phenylimidazole	10.13
2-phenyloxazoline	2.80
2-phenylpyrimidine	2.66
2-phenylthiazoline	2.26
2-phenylthiazole	2.04
1-phenylpyrazole	1.77
2-phenylpyridine	1.00
acetanilide	0.48
benzamide	0.38
2-phenylbenzothiazole	0.27
acetophenone	0.06
benzophenone	0.06
nitrobenzene	0.03
N,N-dimethylbenzamide	0.02
ethylbenzoate	0.01

All k_{rel} constrained >= 0.001

	Catalyst: [(COD)Ir(IMes)PPh$_3$]BArF$_{24}$	Competition Rate Constants				Errors		Averaged	Standard Deviation	Standard Error	
		Expetrimental		Calculated from Solver							
		k^{exptl}	log k^{exptl}	log k^{calcd}	k^{calcd}	Δ (exptl - calcd)	(Δ (exptl - calcd))^2	k^{exptl}	(SD)	(SE)	k^{calcd}/k^{exptl}
DT-10	acetophenone vs benzophenone	0.99	-0.01	0.003	1.01	-0.02	0.00	**1.01**	0.02	0.01	1.00
		1.01	0.00			0.00	0.00				
		1.03	0.01			0.02	0.00				
DT-14	benzamide vs acetophenone	6.14	0.79	0.80	6.31	-0.17	0.03	**6.26**	0.11	0.07	1.01
		6.27	0.80			-0.04	0.00				
		6.37	0.80			0.06	0.00				
DT-16	acetophenone vs N,N-dimethylbenzamide	3.18	0.50	0.59	3.91	-0.73	0.54	**3.91**	0.84	0.48	1.00
		3.74	0.57			-0.18	0.03				
		4.82	0.68			0.91	0.83				
DT-52	nitrobenzene vs ethylbenzoate	5.58	0.75	0.76	5.75	-0.17	0.03	**6.35**	0.67	0.38	0.91
		6.76	0.83			1.01	1.02				
		6.71	0.83			0.96	0.92				
DT-12	acetophenone vs nitrobenzene	3.52	0.55	0.27	1.86	1.65	2.73	**3.39**	0.18	0.10	0.55
		3.19	0.50			1.33	1.76				
		3.46	0.54			1.60	2.56				
DT-51	acetophenone vs ethylbenzoate	9.63	0.98	1.03	10.71	-1.08	1.17	**10.38**	0.68	0.39	1.03
		10.58	1.02			-0.13	0.02				
		10.95	1.04			0.25	0.06				
DT-104	benzamide vs acetanilide	1.35	0.13	-0.11	0.78	0.57	0.33	**1.55**	0.18	0.10	0.50
		1.62	0.21			0.85	0.72				
		1.68	0.22			0.90	0.81				
DT-102	acetanilide vs nitrobenzene	15.01	1.18	1.18	15.14	-0.13	0.02	**15.18**	0.40	0.23	1.00
		15.63	1.19			0.49	0.24				
		14.89	1.17			-0.25	0.06				
DT-6	2-phenylpyridine vs acetophenone	16.92	1.23	1.22	16.78	0.14	0.02	**16.76**	0.24	0.14	1.00
		16.48	1.22			-0.30	0.09				
		16.88	1.23			0.10	0.01				
DT-103	2-phenylpyrimidine vs benzamide	8.90	0.95	0.85	7.07	1.82	3.32	**7.12**	1.99	1.15	0.99
		4.97	0.70			-2.10	4.41				
		7.48	0.87			0.41	0.17				
DT-11	1-phenylpyrazole vs 2-phenylpyridine	1.52	0.18	0.25	1.77	-0.25	0.06	**1.71**	0.17	0.10	1.03
		1.82	0.26			0.05	0.00				
		1.79	0.25			0.02	0.00				
DT-8	2-phenyloxazoline vs 2-phenylpyridine	2.25	0.35	0.45	2.80	-0.55	0.30	**2.90**	0.72	0.42	0.96
		2.77	0.44			-0.02	0.00				
		3.68	0.57			0.88	0.77				
DT-15	2-phenylthiazole vs 1-phenylpyrazole	1.01	0.01	0.06	1.15	-0.14	0.02	**1.07**	0.07	0.04	1.08
		1.04	0.02			-0.11	0.01				
		1.14	0.06			-0.01	0.00				
DT-43	2-phenylthiazoline vs 2-phenylthiazole	1.04	0.02	0.04	1.11	-0.07	0.01	**1.03**	0.01	0.01	1.08
		1.02	0.01			-0.09	0.01				
		1.03	0.01			-0.08	0.01				
DT-67	2-phenyloxazoline vs 2-phenylthiazoline	1.01	0.00	0.09	1.24	-0.23	0.05	**1.01**	0.00	0.00	1.23
		1.01	0.00			-0.23	0.05				
		1.00	0.00			-0.23	0.06				
DT-44	2-phenylthiazole vs 2-phenylbenzothiazole	7.26	0.86	0.87	7.48	-0.22	0.05	**7.48**	0.22	0.13	1.00
		7.71	0.89			0.23	0.05				
		7.48	0.87			0.00	0.00				
DT-70	2-phenylpyridine vs 2-phenylbenzothiazole	3.45	0.54	0.57	3.68	-0.23	0.05	**3.67**	0.33	0.19	1.00
		4.05	0.61			0.38	0.14				
		3.51	0.55			-0.16	0.03				
DT-77	1-methyl-2-phenylimidazole vs 2-phenylthiazoline	4.43	0.65	0.65	4.49	-0.05	0.00	**4.53**	1.40	0.81	0.99
		5.97	0.78			1.49	2.21				
		3.18	0.50			-1.30	1.70				
DT-63	1-methyl-2-phenylimidazole vs 2-phenylpyridine	10.95	1.04	1.01	10.13	0.82	0.67	**10.11**	1.23	0.71	1.00
		8.69	0.94			-1.43	2.05				
		10.68	1.03			0.55	0.31				
DT-83	2-phenylpyridine vs 2-phenylpyrimidine	1.28	0.11	-0.42	0.38	0.90	0.81	**1.19**	0.08	0.05	0.32
		1.11	0.05			0.73	0.54				
		1.18	0.07			0.81	0.65				

Sum of squares of errors:	32.51

Table S43. Linear regression analysis for k_{rel} determination for catalyst **Ir-2**.



Substrates	k_{rel}
2-phenylimidazole	7.11
2-phenylimidazoline	4.45
1-methyl-2-phenylimidazole	3.08
2-phenylpyrimidine	1.26
2-phenylthiazoline	1.02
2-phenylpyridine	1.00
1-phenylpyrazole	0.64
2-phenyloxazoline	0.39
2-phenylthiazole	0.24
benzenesulfonamide	0.05
acetophenone	0.02
benzamide	0.01
N,N-dimethylbenzamide	0.002
methylphenylsulfone	0.001

All k_{rel} constrained >=0.001

Catalyst: [(COD)Ir(IMes)Cl]	Competition Constants				Errors		Averaged	Standard Deviation	Standard Error	
	Expetrimental		Calculated from Solver							
	κ^{exptl}	$\log \kappa^{exptl}$	$\log \kappa^{calcd}$	κ^{calcd}	Δ (exptl - calcd)	(Δ (exptl - calcd))^2	κ^{exptl}	(SD)	(SE)	$\kappa^{calcd}/\kappa^{exptl}$
acetophenone vs benzamide	1.42	0.15	0.38	2.37	-0.95	0.90	**1.53**	0.12	0.07	1.55
	1.50	0.18			-0.87	0.75				
	1.66	0.22			-0.71	0.51				
benzenesulfonamide vs acetophenone	1.07	0.03	0.34	2.17	-1.09	1.19	**1.24**	0.16	0.09	1.74
	1.39	0.14			-0.78	0.61				
	1.27	0.10			-0.89	0.80				
acetophenone vs N,N-dimethylbenzamide	9.87	0.99	0.99	9.73	0.13	0.02	**9.73**	0.44	0.25	1.00
	9.24	0.97			-0.49	0.24				
	10.09	1.00			0.35	0.13				
benzenesulfonamide vs benzamide	5.44	0.74	0.71	5.14	0.30	0.09	**5.53**	0.74	0.42	0.93
	6.30	0.80			1.16	1.35				
	4.84	0.68			-0.30	0.09				
1-phenylpyrazole vs acetophenone	28.94	1.46	1.47	29.72	-0.78	0.61	**29.72**	2.17	1.25	1.00
	28.05	1.45			-1.67	2.79				
	32.17	1.51			2.45	6.00				
benzenesulfonamide vs methylphenylsulfone	32.07	1.51	1.59	38.73	-6.66	44.34	**38.73**	5.96	3.44	1.00
	40.55	1.61			1.82	3.33				
	43.56	1.64			4.83	23.37				
1-phenylpyrazole vs 2-phenylpyridine	1.44	0.16	-0.19	0.64	0.80	0.64	**1.38**	0.06	0.03	0.46
	1.32	0.12			0.68	0.47				
	1.37	0.14			0.74	0.54				
2-phenyloxazoline vs 2-phenylpyridine	1.46	0.16	-0.41	0.39	1.07	1.15	**1.41**	0.07	0.04	0.27
	1.33	0.12			0.95	0.89				
	1.43	0.16			1.04	1.09				
1-phenylpyrazole vs 2-phenylthiazole	1.58	0.20	0.43	2.70	-1.12	1.25	**1.62**	0.16	0.09	1.66
	1.79	0.25			-0.90	0.81				
	1.49	0.17			-1.21	1.46				
2-Phenylthiazoline vs 2-phenyloxazoline	1.78	0.25	0.42	2.64	-0.87	0.75	**1.81**	0.03	0.02	1.46
	1.82	0.26			-0.82	0.67				
	1.83	0.26			-0.81	0.65				
1-methyl-2-phenylimidazole vs 2-phenylpyridine	2.26	0.35	0.49	3.08	-0.82	0.67	**2.01**	0.22	0.13	1.53
	1.84	0.27			-1.24	1.53				
	1.93	0.28			-1.15	1.33				
1-methyl-2-phenylimidazole vs 2-phenyloxazoline	8.55	0.93	0.90	7.98	0.57	0.32	**8.30**	0.60	0.35	0.96
	7.61	0.88			-0.36	0.13				
	8.74	0.94			0.77	0.59				
1-methyl-2-phenylimidazole vs 2-phenylthiazole	12.98	1.11	1.11	13.00	-0.01	0.00	**13.22**	0.97	0.56	0.98
	14.29	1.15			1.29	1.66				
	12.39	1.09			-0.61	0.37				
1-methyl-2-phenylimidazole vs 2-phenylthiazoline	2.78	0.44	0.48	3.02	-0.24	0.06	**2.29**	0.48	0.28	1.32
	1.82	0.26			-1.20	1.43				
	2.28	0.36			-0.74	0.55				
2-Phenylpyrimidine vs 2-phenylpyridine	1.17	0.07	0.10	1.26	-0.09	0.01	**1.26**	0.08	0.05	1.00
	1.27	0.10			0.01	0.00				
	1.33	0.12			0.07	0.01				
2-phenylimidazoline vs 2-phenylimidazole	1.23	0.09	-0.20	0.63	0.60	0.36	**1.09**	0.12	0.07	0.57
	1.01	0.00			0.38	0.14				
	1.04	0.02			0.42	0.17				
2-phenylimidazole vs 2-phenylpyridine	7.06	0.85	0.85	7.11	-0.05	0.00	**7.49**	0.55	0.32	0.95
	8.12	0.91			1.01	1.02				
	7.30	0.86			0.19	0.04				
2-phenylimidazole vs 1-phenylpyrazole	10.79	1.03	1.05	11.13	-0.35	0.12	**10.91**	0.46	0.27	1.02
	10.53	1.02			-0.61	0.37				
	11.43	1.06			0.30	0.09				
2-phenylimidazoline vs 2-phenylpyridine	4.67	0.67	0.65	4.45	0.22	0.05	**4.38**	0.64	0.37	1.01
	3.65	0.56			-0.80	0.63				
	4.83	0.68			0.38	0.14				

Sum of squares of errors:	109.301

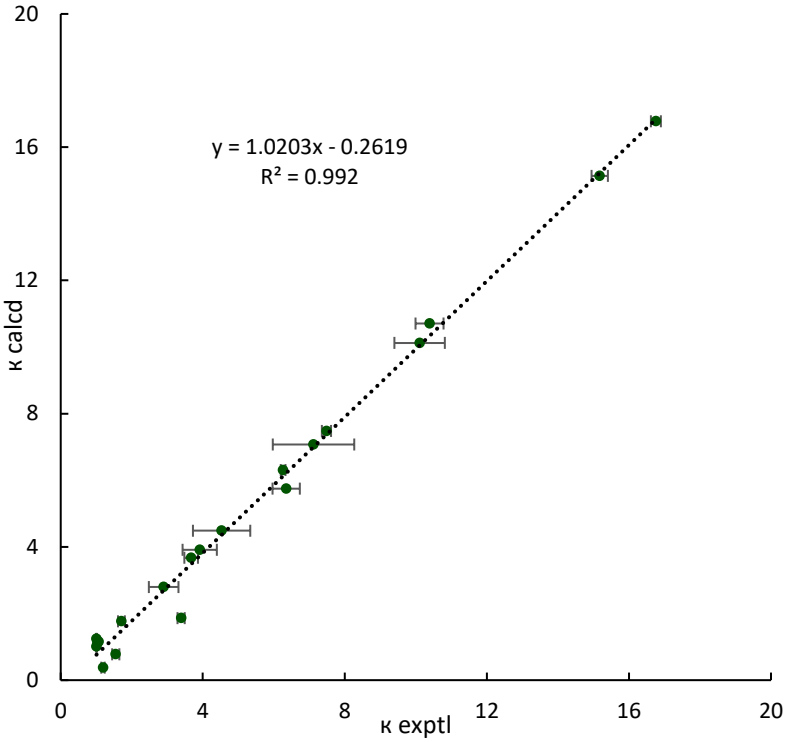


Figure S177. Plot of experimental *versus* calculated (from linear regression) competition constants κ for catalyst **Ir-1**. The error bars correspond to standard error on the mean.

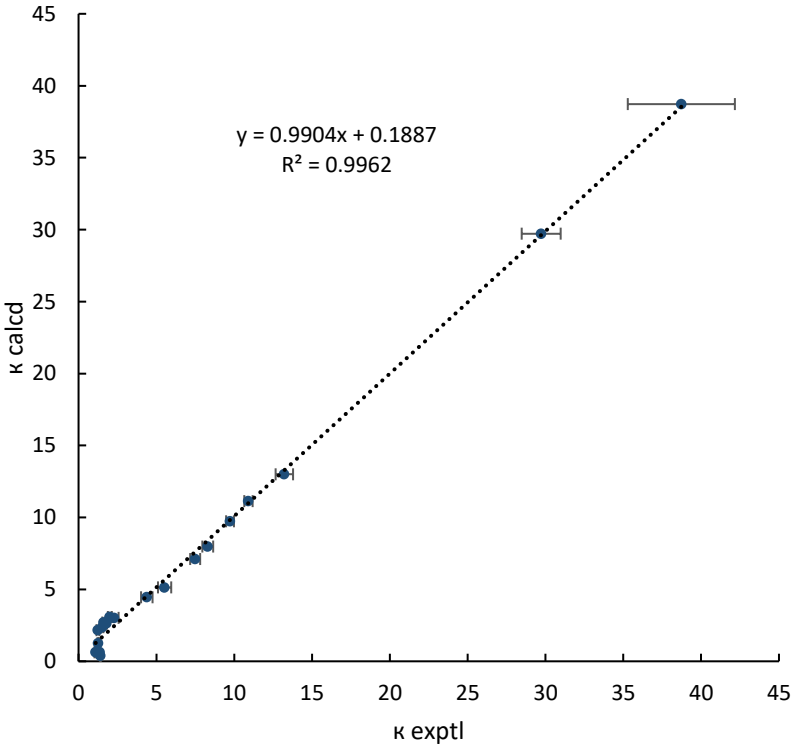
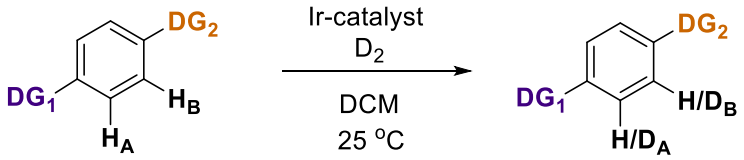


Figure S178. Plot of experimental *versus* calculated (from linear regression) competition constants κ for catalyst **Ir-2**. The error bars correspond to standard error on the mean.

4. Intramolecular Competition Experiments

4.1. General Information



General Procedure (GP2)

The substrate (0.10 mmol) and the catalyst (0.005 mmol) of choice were added to one J. Young Schlenk flask under air. The solvent, DCM (6 mL), was added in such a way to rinse the inner walls of the flask. The flask was then sealed (with gas inlet left open) under air before being cooled in a dry ice–acetone bath. The flask was evacuated and flushed with deuterium three times *via* a balloon. The gas inlet was then closed with fast thread tap, creating a sealed atmosphere of deuterium. After sealing the flask was placed in the thermostated water bath at 25 °C and the reaction timer was started. The reaction mixture was stirred for 1 h (for catalyst **Ir-1**) or 16 h (for catalyst **Ir-2**) before removing excess deuterium and replacing it with air. The reaction mixture was quenched with few drops of MeCN and transferred to a single necked flask together with washings (DCM) before removing the solvent under reduced pressure. The residue was dissolved in a small portion of 1:1 mixture of petroleum ether with diethyl ether (or ethyl acetate) and passed through a short plug of silica, eluting with a 1:1 mixture of petroleum ether and diethyl ether (3 × 2 mL), or a 1:1 mixture of petroleum ether with ethyl acetate where necessary, depending on the substrates used. The solvent was evaporated under reduced pressure and the residue was analysed directly by ^{1}H NMR spectroscopy.

Determination of Competition Rate Constants

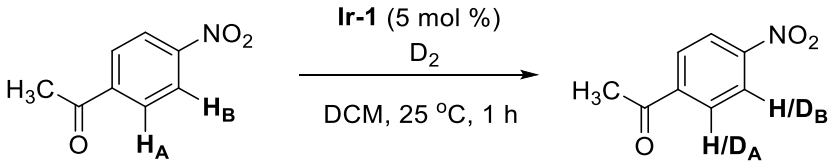
The level of deuterium incorporation (%D) in the substrates was determined by ^{1}H NMR. The integrals were calibrated against a peak corresponding to a position not expected to be labelled. Equations S-7 and S-8 were used to calculate the extent of labelling and competition rate constant κ':

$$\%D = 100 - \left(\frac{\text{residual integral}}{\text{number of labelling sites}} \times 100\ \% \right) \tag{S-7}$$

$$\kappa' = \frac{\%D_A}{\%D_B} = \frac{2 - \text{residual integral } H_A}{2 - \text{residual integral } H_B} \tag{S-8}$$

4.1. Competition Experiments with [(COD)Ir(IMes)PPh$_3$]BArF$_{24}$ (Ir-1)

Labelling of *p*-nitroacetophenone



According to GP2: 16.5 mg of substrate and 8.7 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.33 – 8.30 (m, 2H, H/D_B), 8.13 – 8.09 (m, 2H, H/D_A), 2.68 (s, 3H, CH_3)

Deuteration expected at δ (H_A) = 8.13 – 8.09 ppm and δ (H_B) = 8.33 – 8.30 ppm.

Determined against integral at δ = 2.68 ppm.

Table S44. Determination of the competition rate constant κ' from the labelling of *p*-nitroacetophenone.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	κ'
1	0.84	58	1.13	44	1.33
2	1.12	44	1.32	34	1.29
3	0.97	52	1.22	39	1.32
Average		**51**		**39**	**1.32**

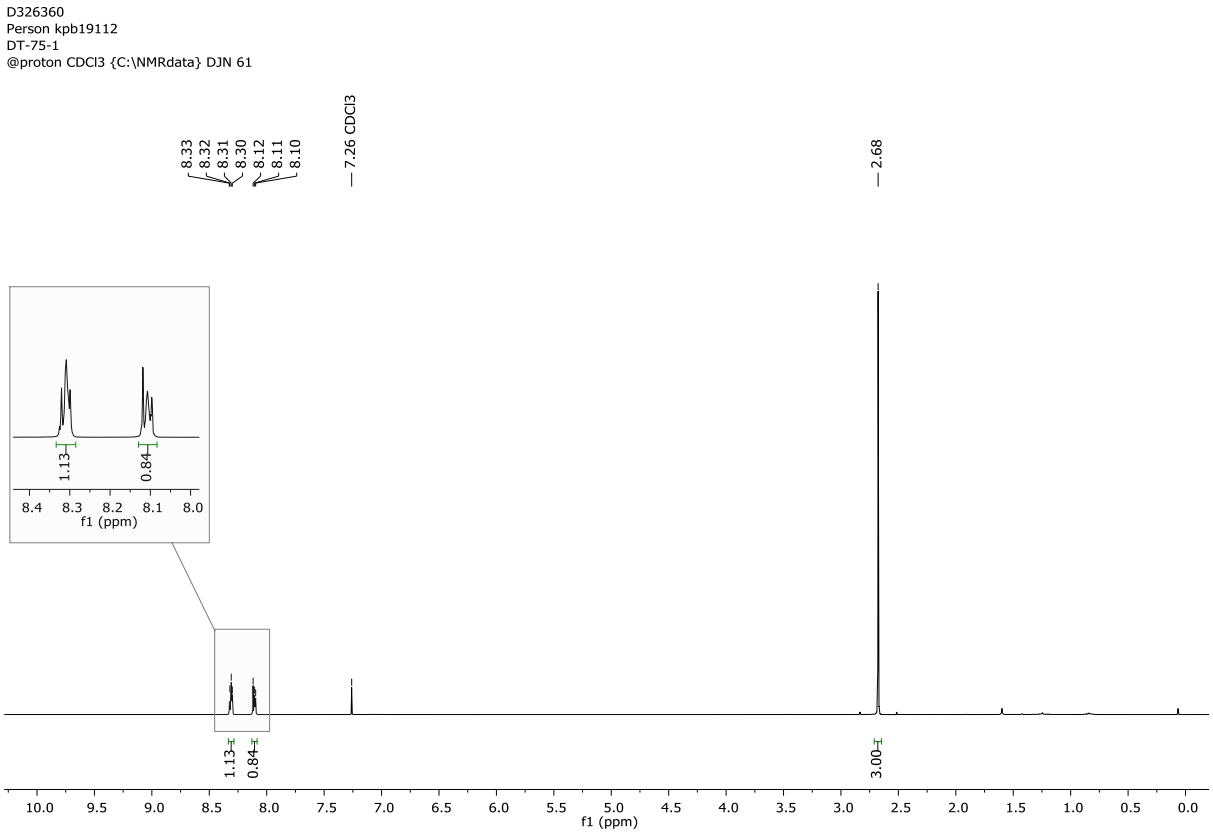


Figure S179. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled *p*-nitroacetophenone (entry 1, Table S44)

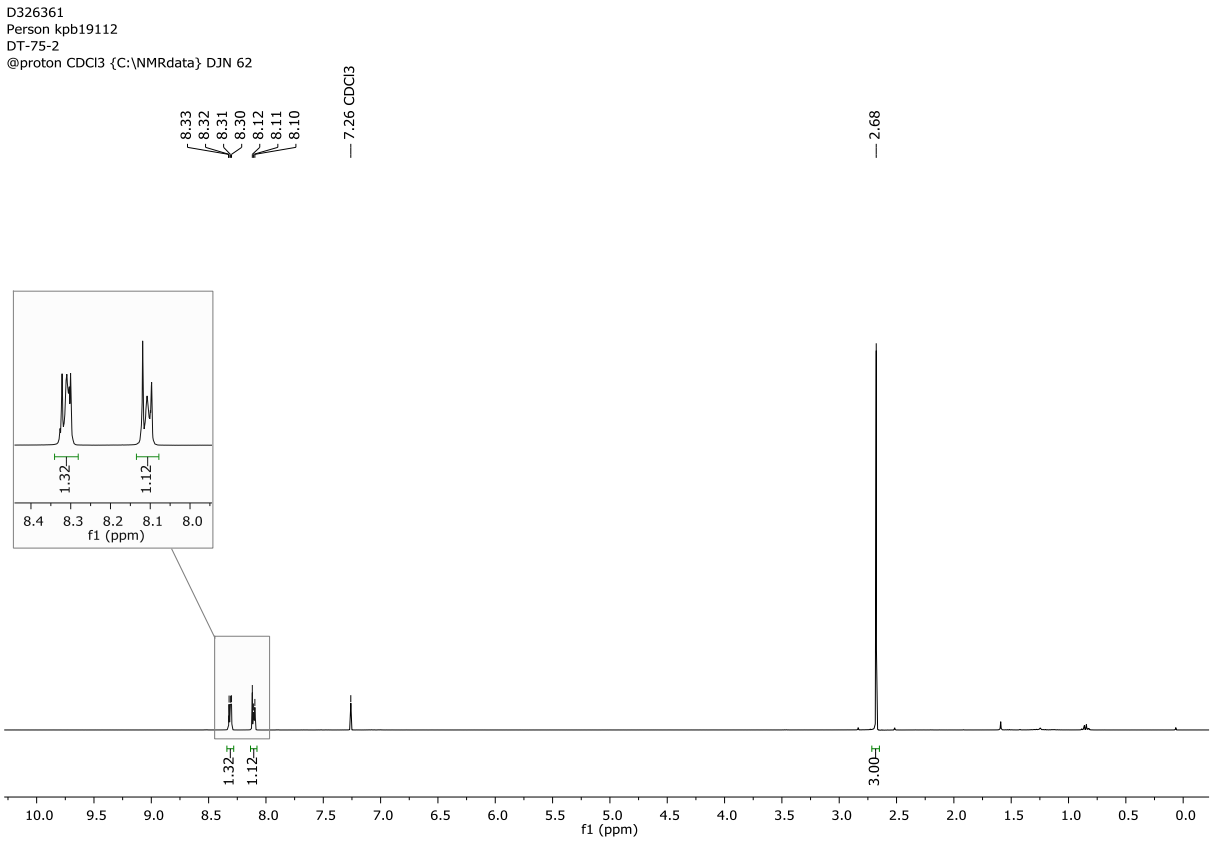


Figure S180. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled *p*-nitroacetophenone (entry 2, Table S44)

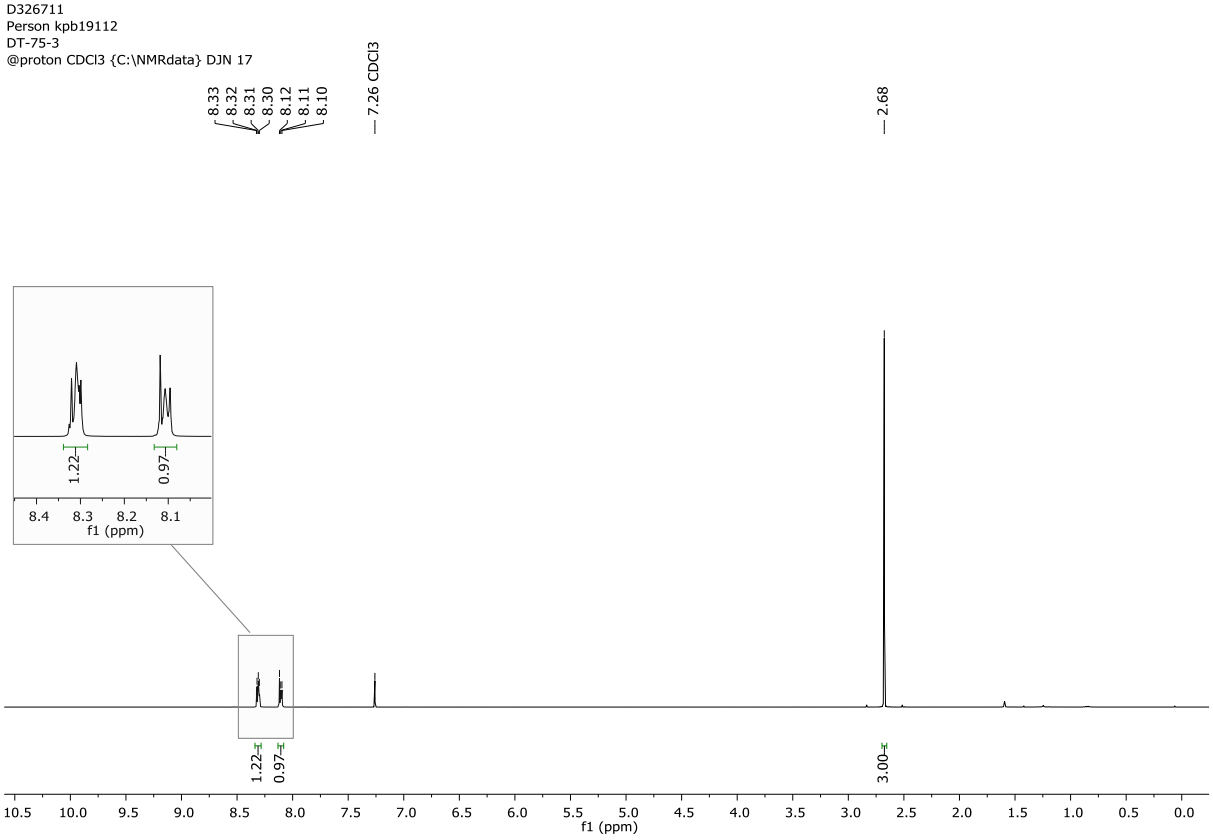
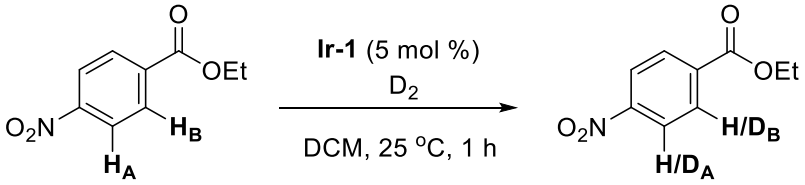


Figure S181. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled *p*-nitroacetophenone (entry 3, Table SX)

Labelling of ethyl 4-nitrobenzoate



According to GP2:19.5 mg of substrate and 8.7 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.26 (m, 2H, H/D_A), 8.23 – 8.18 (m, 2H, H/D_B), 4.43 (q, *J* = 7.1 Hz, 2H, CH_2), 1.42 (t, *J* = 7.1 Hz, 3H, CH_3).

Deuteration expected at δ (H_A) = 8.30 – 8.26 ppm and δ (H_B) = 8.23 – 8.18 ppm.

Determined against integral at δ = 4.43 ppm.

Table S45. Determination of the competition rate constant *κ′* from the labelling of ethyl 4-nitrobenzoate.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	*κ′*
1	0.85	58	1.09	46	1.26
2	0.81	60	1.11	45	1.34
3	1.23	39	1.34	33	1.17
Average		**52**		**41**	**1.26**

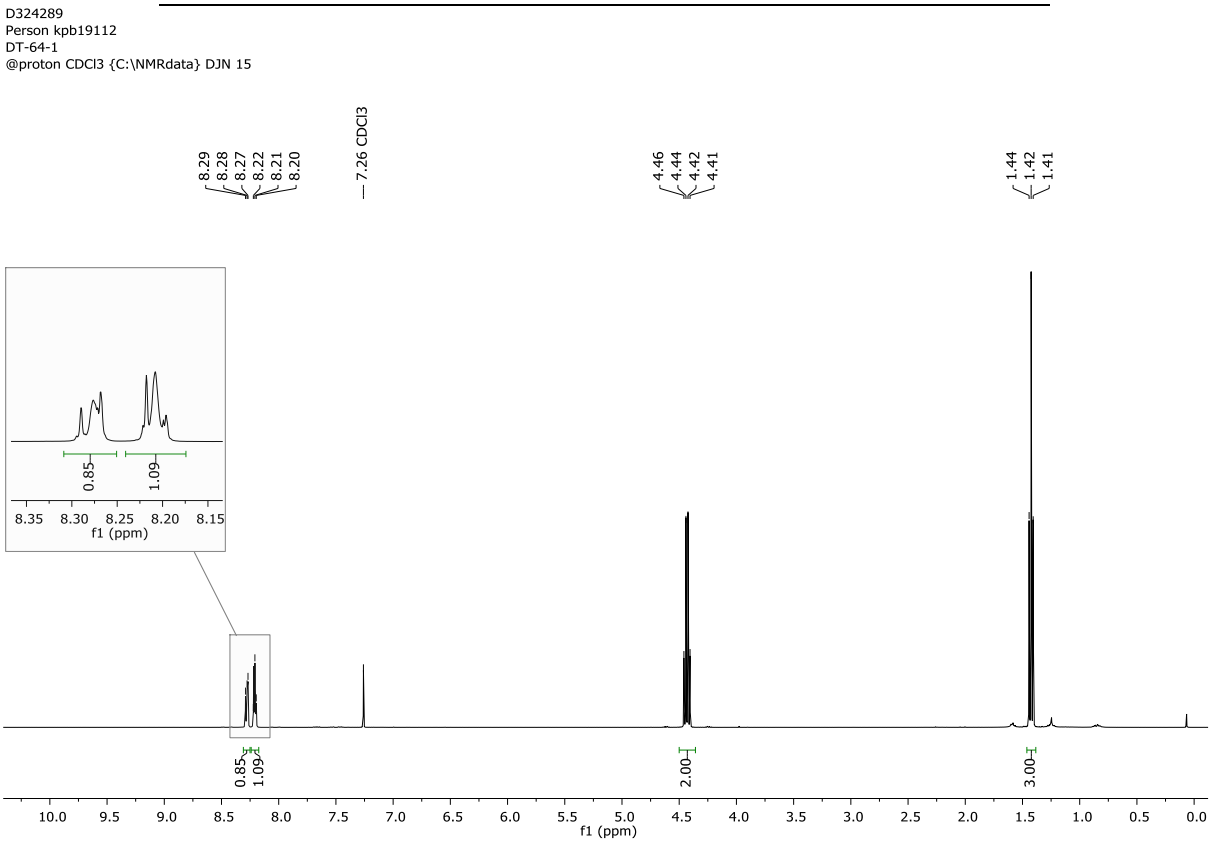


Figure S182. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled ethyl 4-nitrobenzoate (entry 1, Table S45)

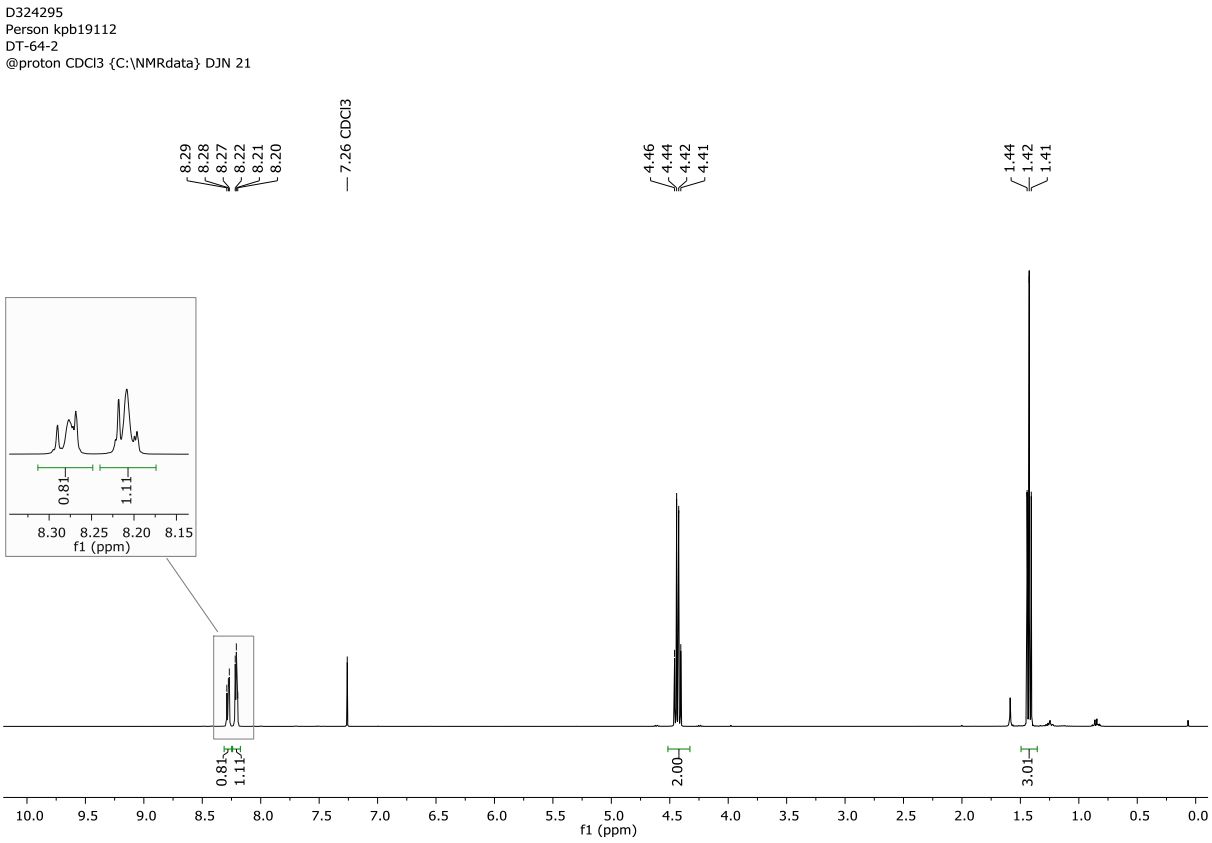


Figure S183. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled ethyl 4-nitrobenzoate (entry 2, Table S45)

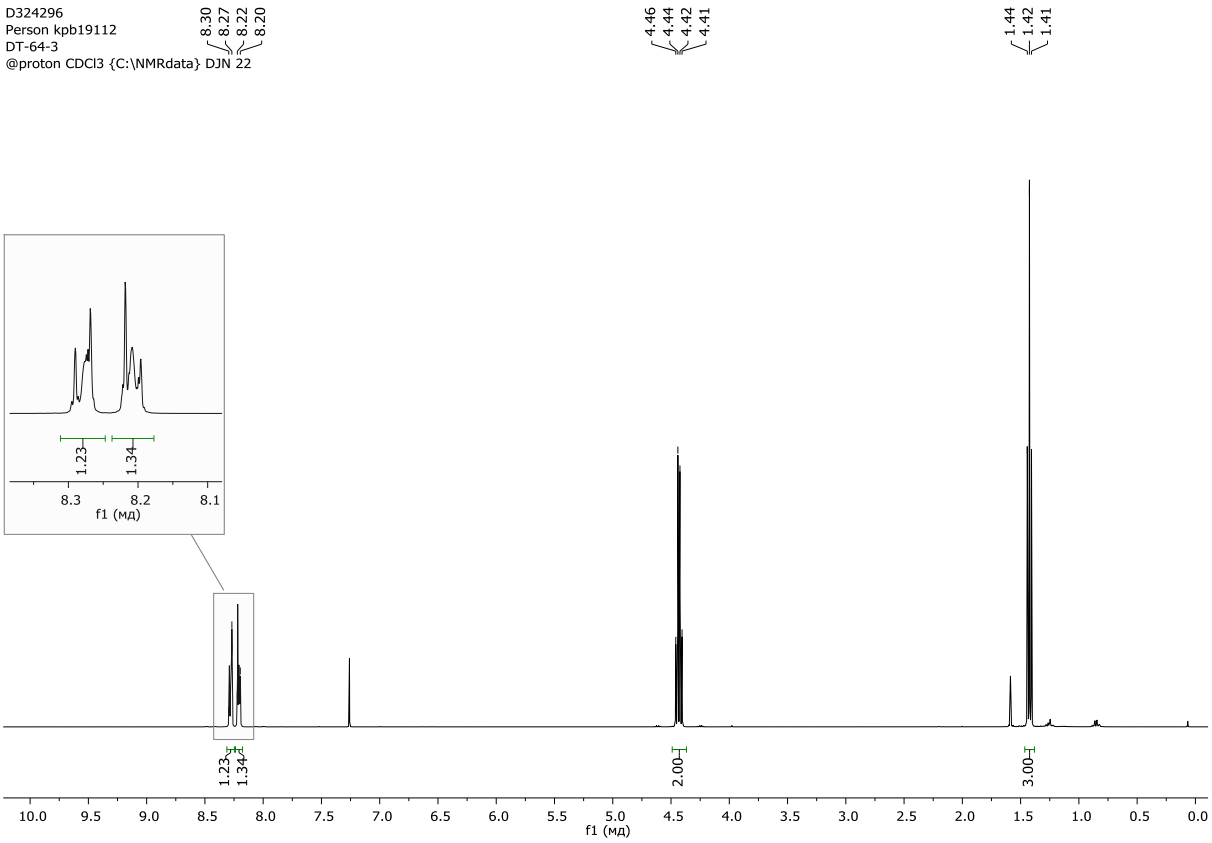
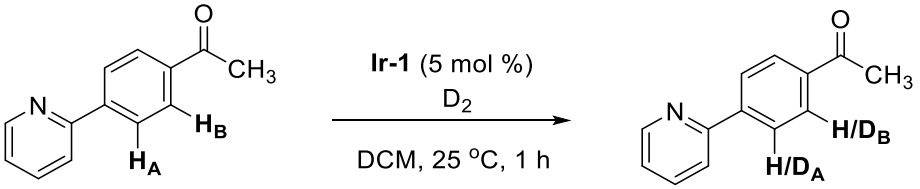


Figure S184. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled ethyl 4-nitrobenzoate (entry 3, Table S45)

Labelling of 4-acetyl-1-(pyridin-2-yl)benzene



According to GP2: 19.7 mg of substrate and 8.7 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 – 8.68 (m, 1H, Ar), 8.12 – 8.08 (m, 2H, H_A), 8.07 – 8.03 (m, 2H, H_B), 7.80 – 7.75 (m, 2H, Ar), 7.31 – 7.26 (m, 1H, Ar), 2.65 (s, 3H, CH_3).

Deuteration expected at δ (H_A) = 8.12 – 8.08 ppm and δ (H_B) = 8.07 – 8.03 ppm.

Determined against integral at δ = 2.65 ppm.

Note: Small signals, corresponding to the **Ir-1** catalyst, were present in the ^{1}H NMR spectra, however there is no overlap with the substrate signals.

Table S46. Determination of the competition rate constant κ' from the labelling of 4-acetyl-1-(pyridin-2-yl)benzene.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	κ'
1	1.51	25	1.97	1.5	16.33
2	1.66	17	1.98	1.0	17.00
3	1.55	23	1.97	1.5	15.00
Average		**21**		**1.3**	**16.11**

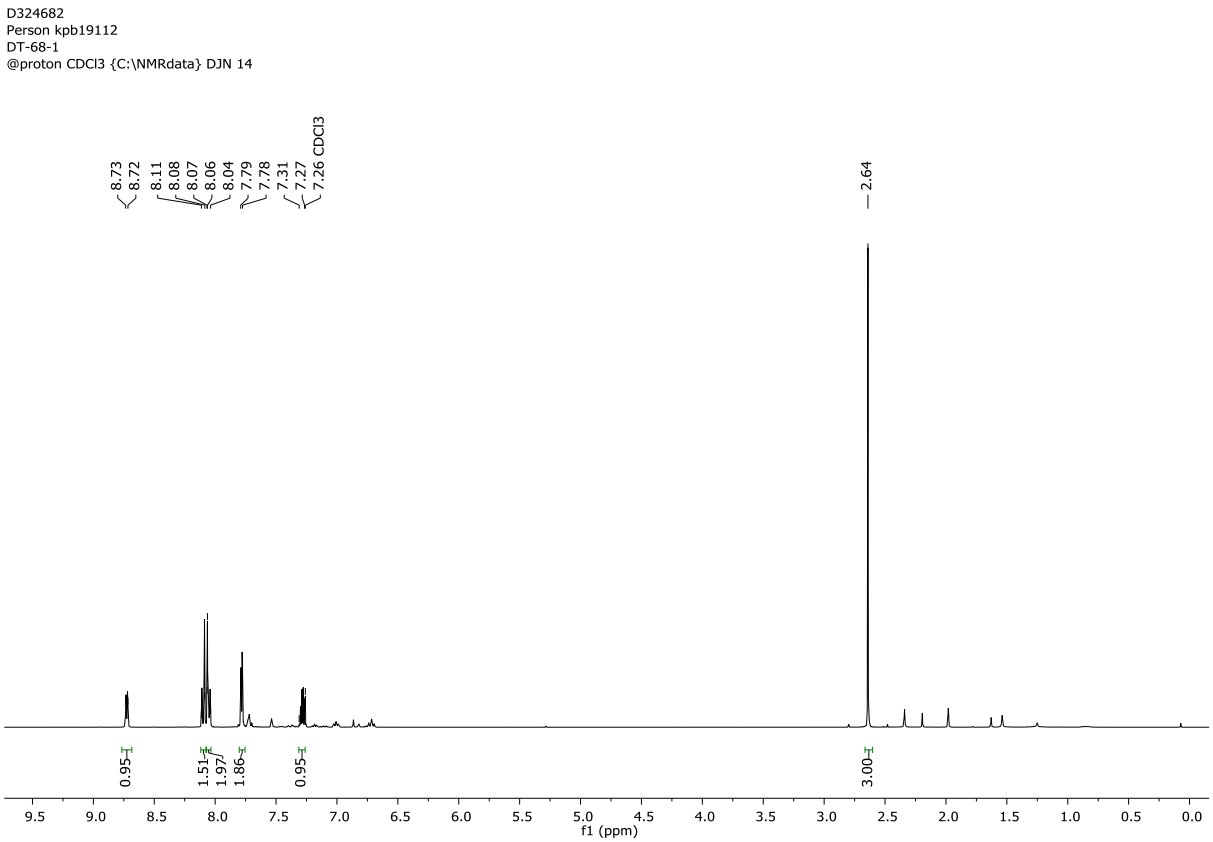


Figure S185. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 4-acetyl-1-(pyridin-2-yl)benzene (entry 1, Table S46)

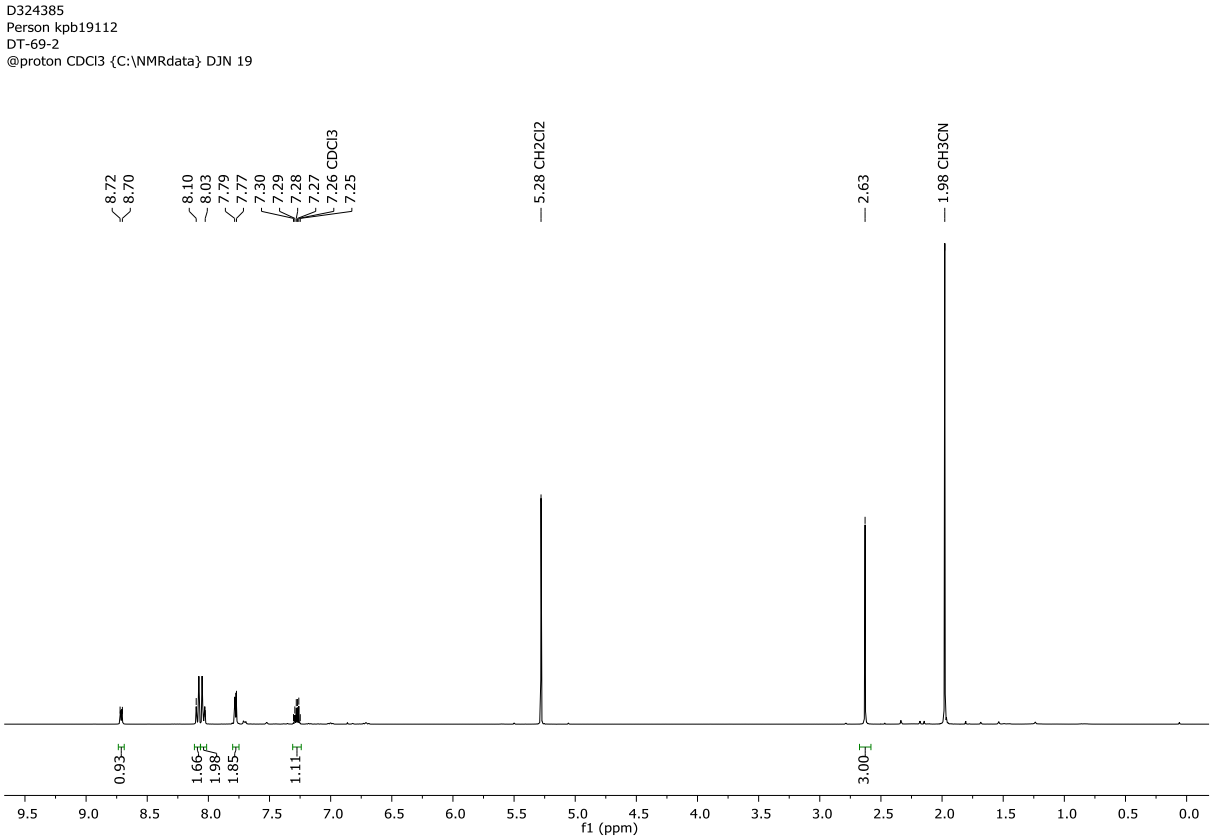


Figure S186. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 4-acetyl-1-(pyridin-2-yl)benzene (entry 2, Table S46)

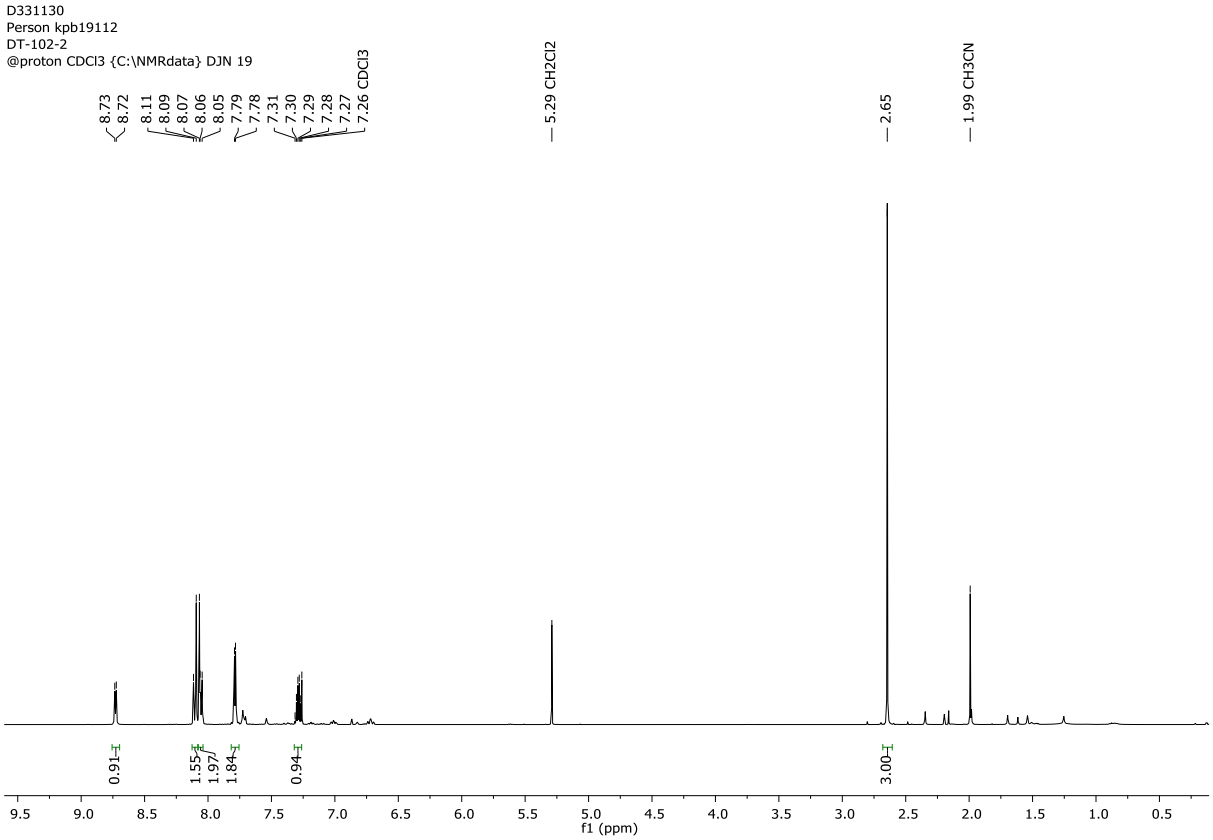
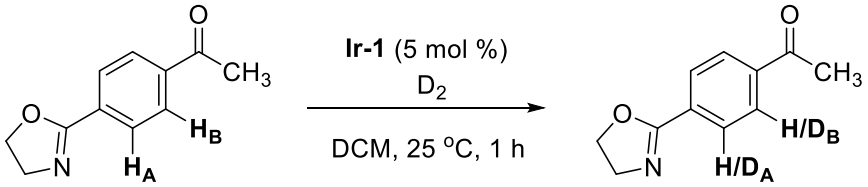


Figure S187. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 4-acetyl-1-(pyridin-2-yl)benzene (entry 3, Table S46)

Labelling of 2-(4-acetyl)phenyloxazoline



According to GP2: 18.9 mg of substrate and 8.7 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 8.01 (m, 2H, H_A), 8.01 – 7.96 (m, 2H, H_B), 4.47 (t, *J* = 9.6 Hz, 3H, CH_2), 4.10 (t, *J* = 9.6 Hz, 2H, CH_2), 2.62 (s, 3H, CH_3).

Deuteration expected at δ (H_A) = 8.06 – 8.01 ppm and δ (H_B) = 8.01 – 7.96 ppm.

Determined against integral at δ = 4.47 ppm.

Note: Small signals, corresponding to the **Ir-1** catalyst, were present in the ^{1}H NMR spectra, however they do not overlap with the substrate signals.

Table S47. Determination of the competition rate constant *κ′* from the labelling of 2-(4-acetyl)phenyloxazoline.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	*κ′*
1	0.41	80	1.96	2.0	39.75
2	0.44	78	1.96	2.0	39.00
3	0.76	62	1.97	1.5	41.33
Average		**73**		**1.8**	**40.03**

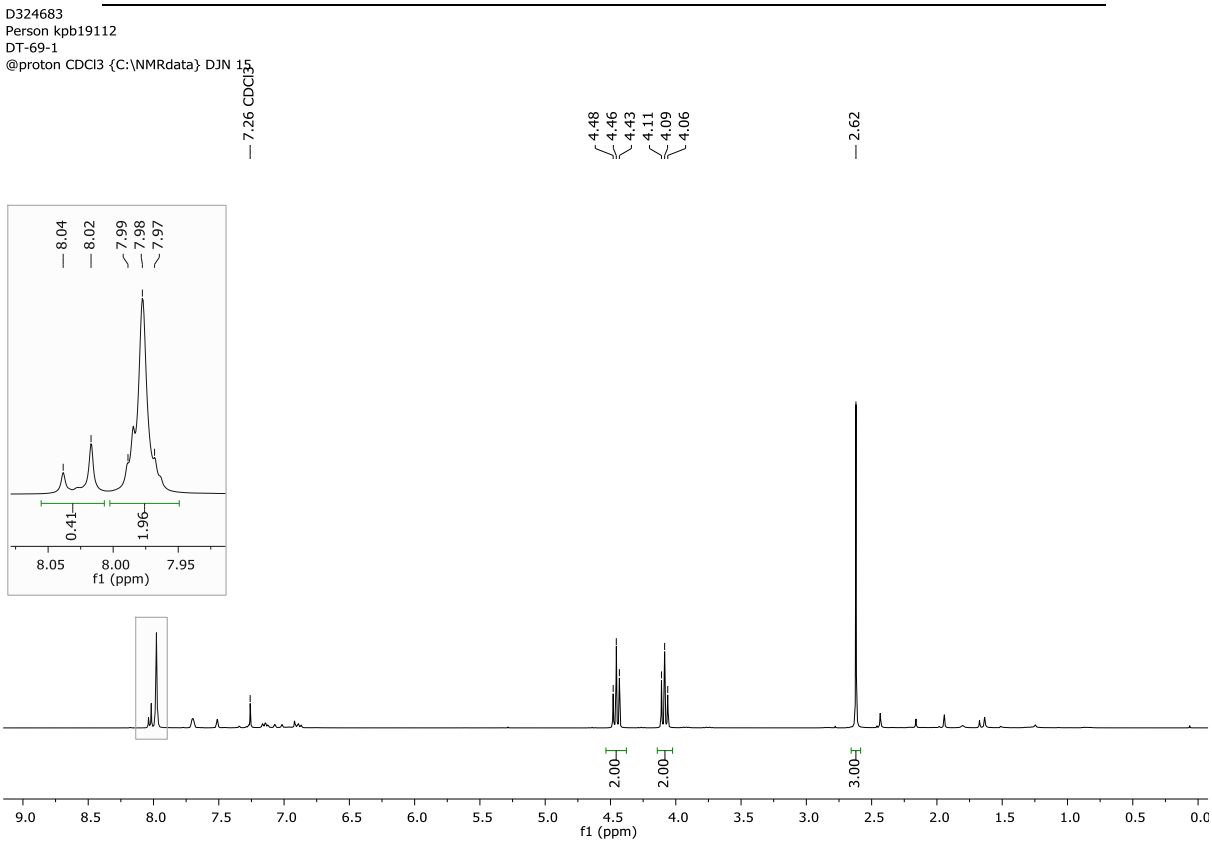


Figure S188. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 2-(4-acetyl)phenyloxazoline (entry 1, Table S47)

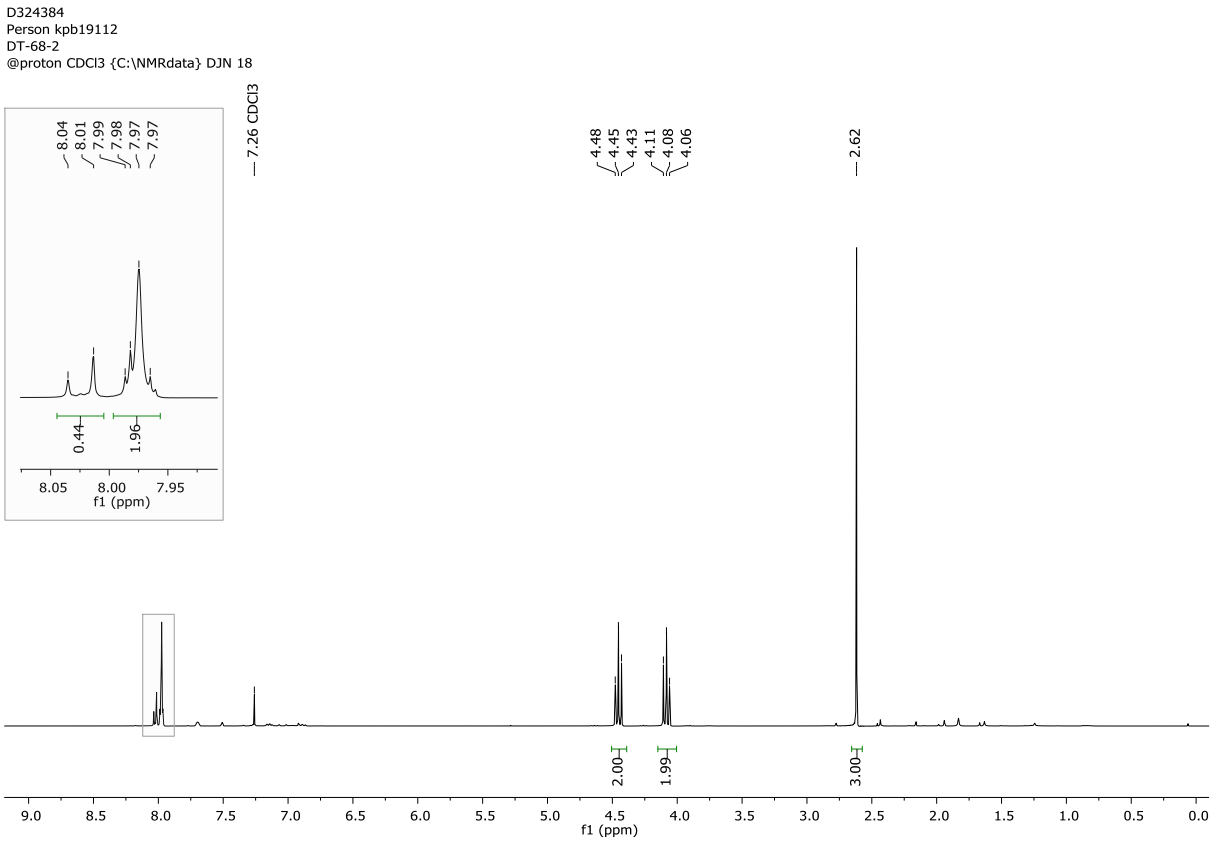


Figure S189. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 2-(4-acetyl)phenyloxazoline (entry 2, Table S47)

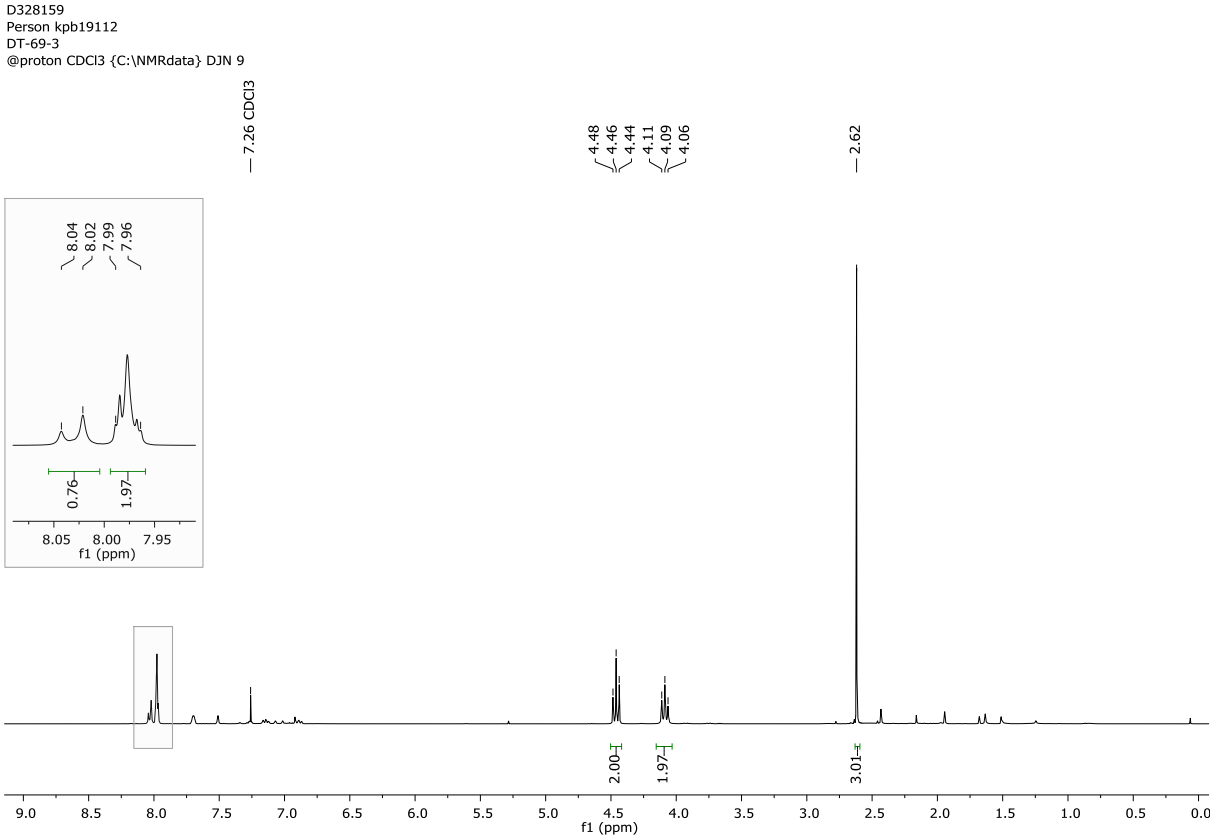
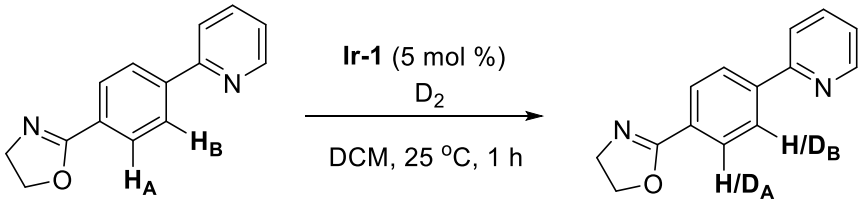


Figure S190. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 2-(4-acetyl)phenyloxazoline (entry 3, Table S47)

Labelling of 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole



According to GP2: 22.4 mg of substrate and 8.7 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, C_6D_6) δ = 8.56 – 8.51 (m, 1H, Ar-H), 8.36 – 8.32 (m, 1H, H_A), 8.17 – 8.11 (m, 2H, H_B), 7.25 – 7.21 (m, 1H, Ar-H), 7.11 – 7.04 (m, 1H, Ar-H), 6.66 – 6.61 (m, 1H, Ar-H), 3.77 – 3.69 (m, 2H, CH_2), 3.67 – 3.58 (m, 2H, CH_2).

Deuteration expected at δ (H_A) = 8.36 – 8.32 ppm and δ (H_B) = 8.17 – 8.11 ppm.

Determined against integral at δ = 6.66 – 6.61 ppm.

Note: Small signals, corresponding to the **Ir-1** catalyst, were present in the ^{1}H NMR spectra, however they do not overlap with the substrate signals.

Table S48. Determination of the competition rate constant κ' from the labelling of 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	κ'
1	0.80	60	1.45	28	2.18
2	0.42	79	1.57	22	3.67
3	0.48	76	1.62	19	4.00
Average		**72**		**23**	**3.29**

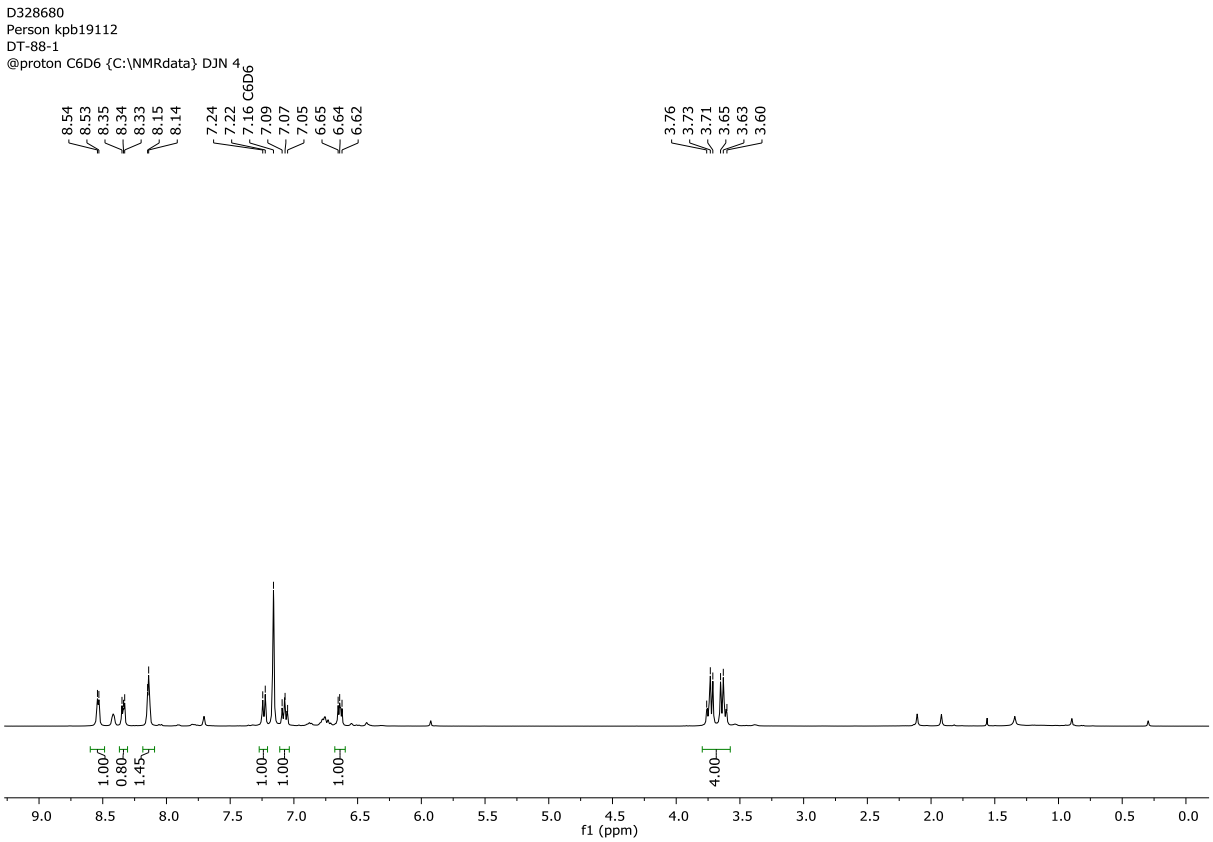


Figure S191. ^{1}H NMR (400 MHz, C_6D_6) of labelled 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole (entry 1, Table S48)

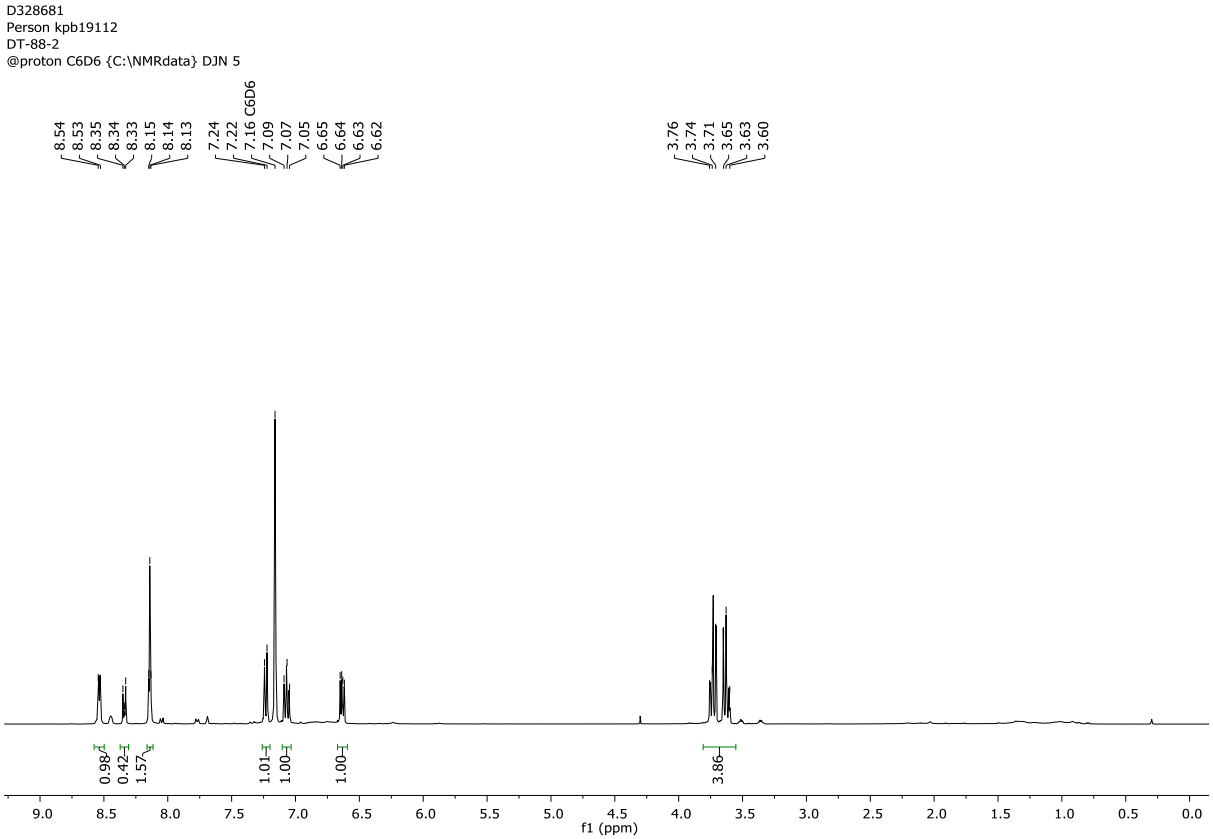


Figure S192. ^{1}H NMR (400 MHz, C_6D_6) of labelled 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole (entry 2, Table S48)

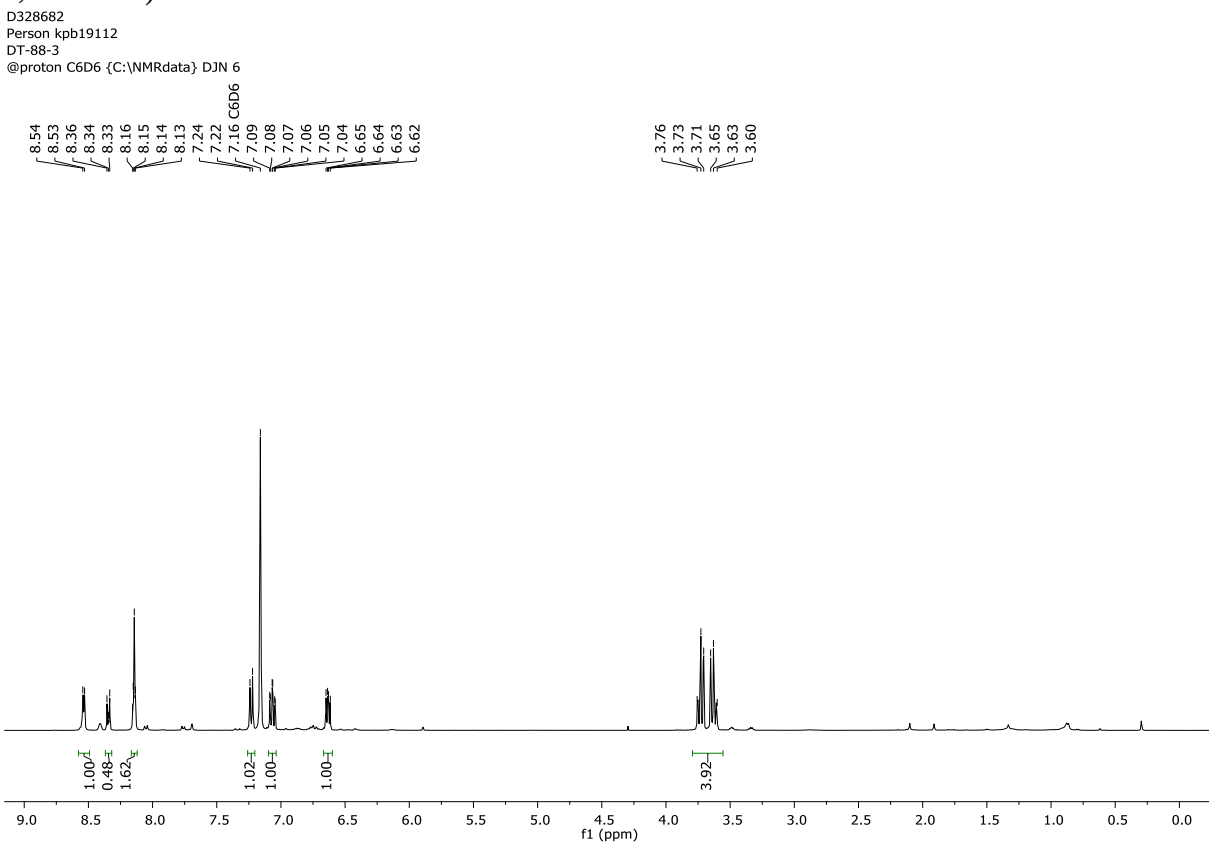
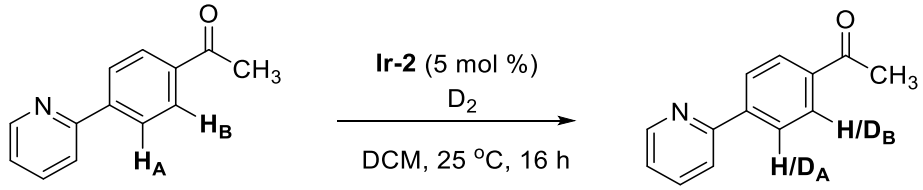


Figure S193. ^{1}H NMR (400 MHz, C_6D_6) of labelled 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole (entry 3, Table S48)

4.2. Competition Experiments with (COD)Ir(IMes)Cl (Ir-2)

Labelling of 4-acetyl-1-(pyridin-2-yl)benzene



According to GP2: 19.7 mg of substrate and 3.2 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 – 8.72 (m, 1H), 8.13 – 8.09 (m, 2H, H_A), 8.09 – 8.04 (m, 2H, H_B), 7.82 – 7.78 (m, 2H, Ar), 7.33 – 7.27 (m, 1H, Ar), 2.65 (s, 3H, CH_3).

Deuteration expected at δ (H_A) = 8.13 – 8.09 ppm and δ (H_B) = 8.09 – 8.04 ppm.

Determined against integral at δ = 2.65 ppm.

Table S49. Determination of the competition rate constant κ' from the labelling of 4-acetyl-1-(pyridin-2-yl)benzene.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	κ'
1	1.32	34	1.96	2	17.00
2	1.52	24	1.97	2	16.00
3	1.21	40	1.95	3	15.80
Average		**33**		**2**	**16.27**

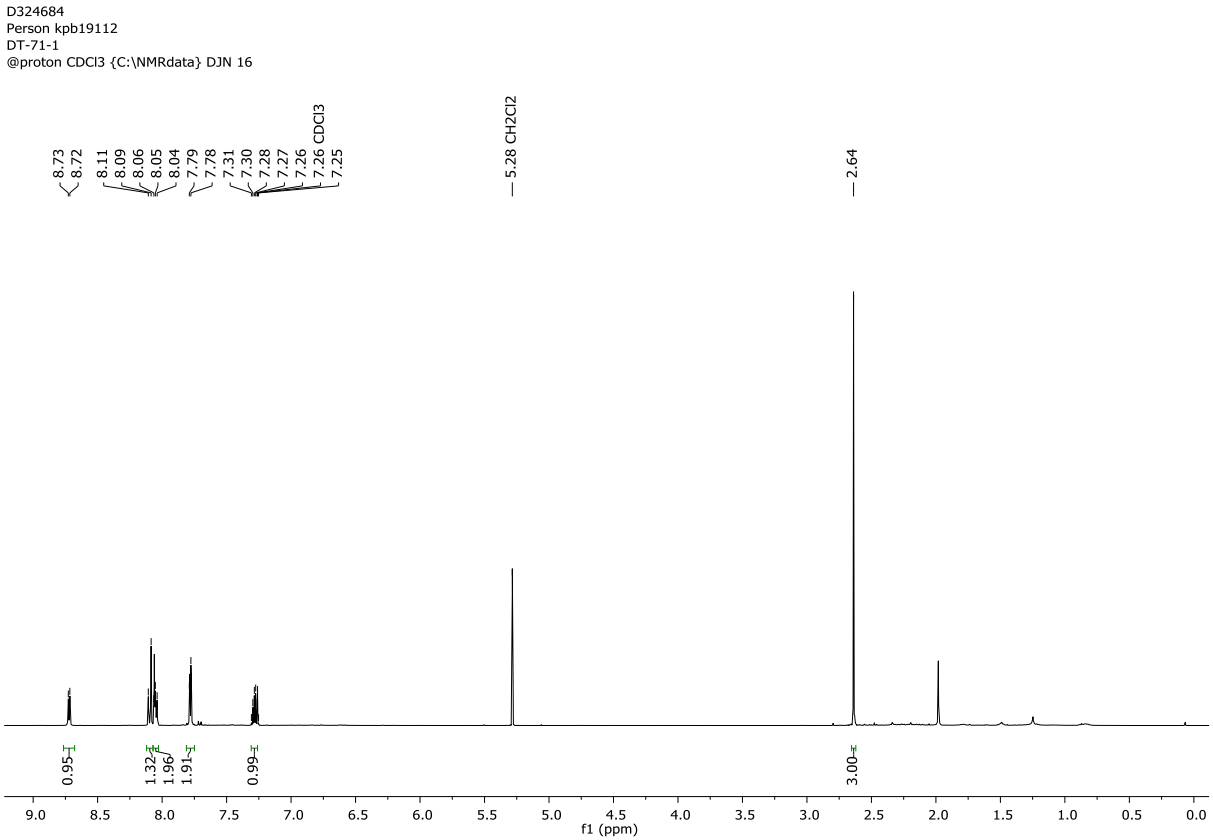


Figure S194. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 4-acetyl-1-(pyridin-2-yl)benzene (entry 1, Table S49).

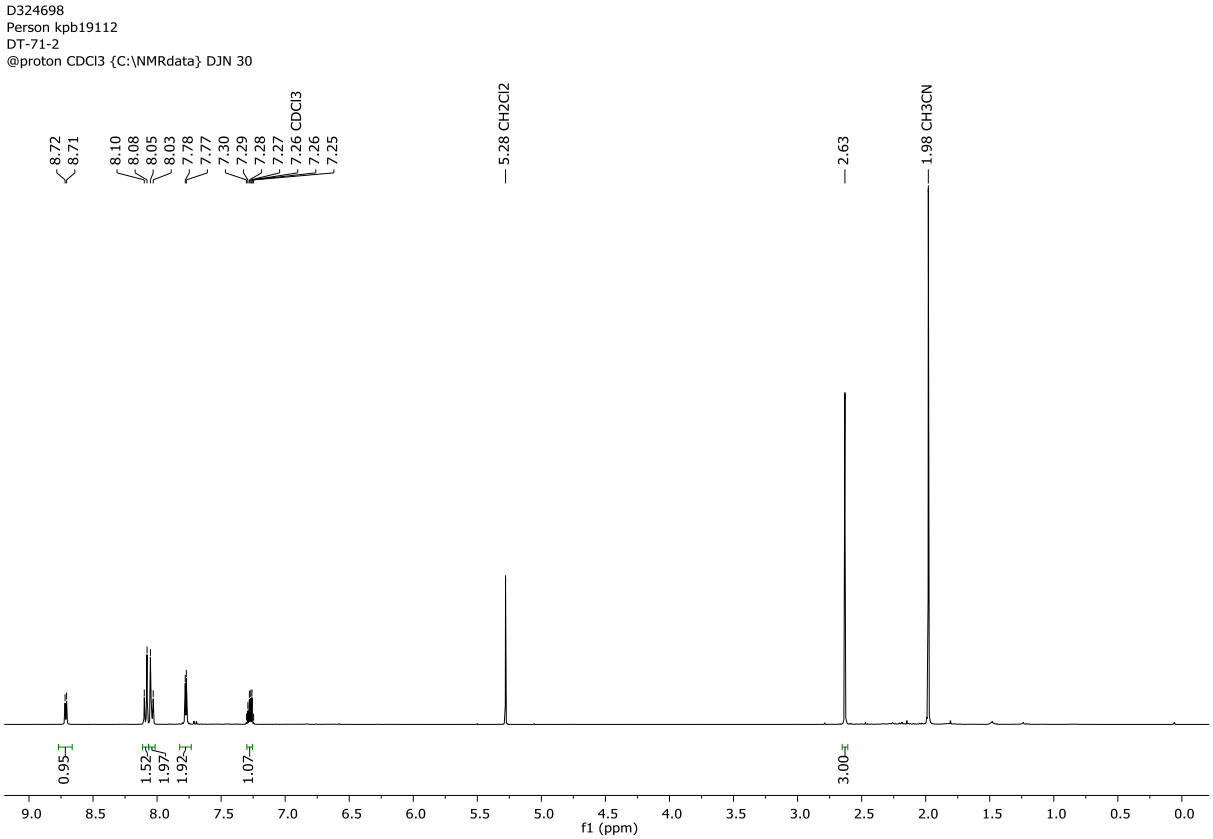


Figure S195. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 4-acetyl-1-(pyridin-2-yl)benzene (entry 2, Table S49).

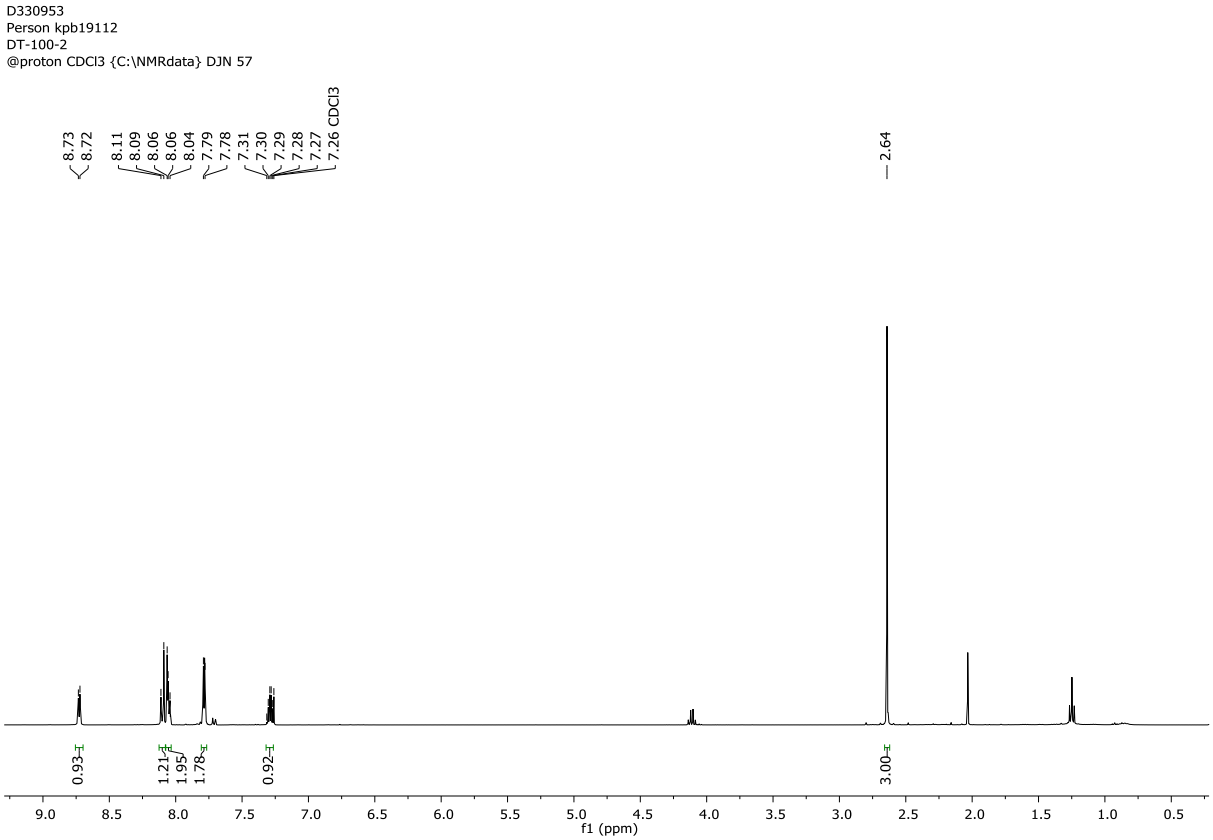
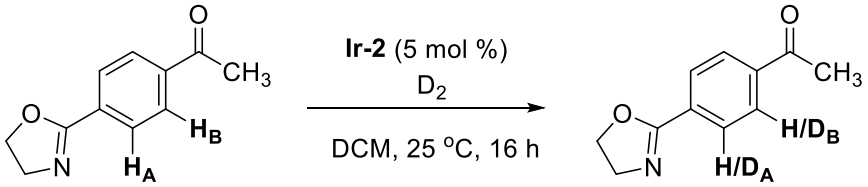


Figure S196. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 4-acetyl-1-(pyridin-2-yl)benzene (entry 3, Table S49).

Labelling of 2-(4-acetyl)phenyloxazoline



According to GP2: 18.9 mg of substrate and 3.2 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 – 8.01 (m, 2H, H_A), 8.01 – 7.96 (m, 2H, H_B), 4.47 (t, *J* = 9.6 Hz, 3H, CH_2), 4.10 (t, *J* = 9.6 Hz, 2H, CH_2), 2.62 (s, 3H, CH_3).

Deuteration expected at δ (H_A) = 8.06 – 8.01 ppm and δ (H_B) = 8.01 – 7.96 ppm.

Determined against integral at δ = 4.47 ppm.

Table S50. Determination of the competition rate constant *κ′* from the labelling of 2-(4-acetyl)phenyloxazoline.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	*κ′*
1	1.41	30	1.93	4	8.43
2	1.27	37	1.93	4	10.43
3	0.48	76	1.88	6	12.67
Average		**47**		**4**	**10.51**

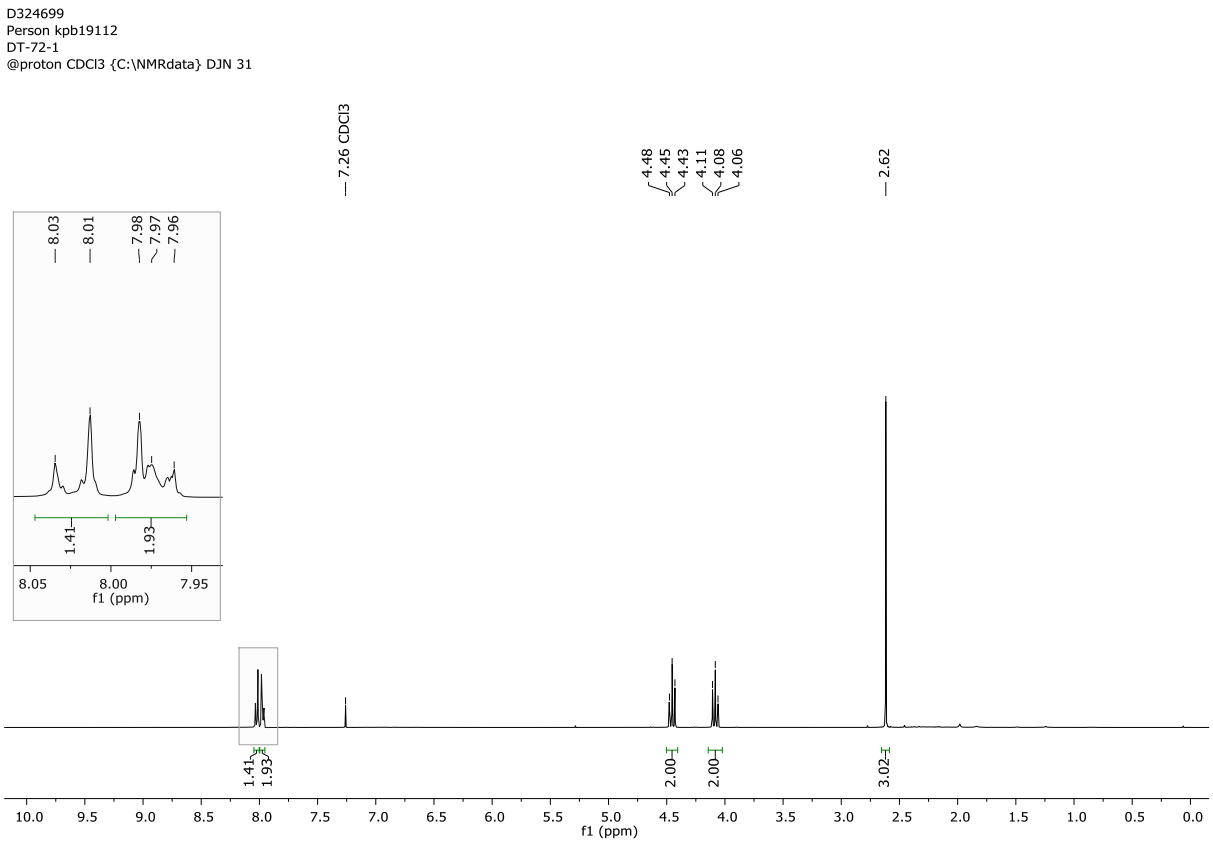


Figure S197. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 2-(4-acetyl)phenyloxazoline (entry 1, Table S50)

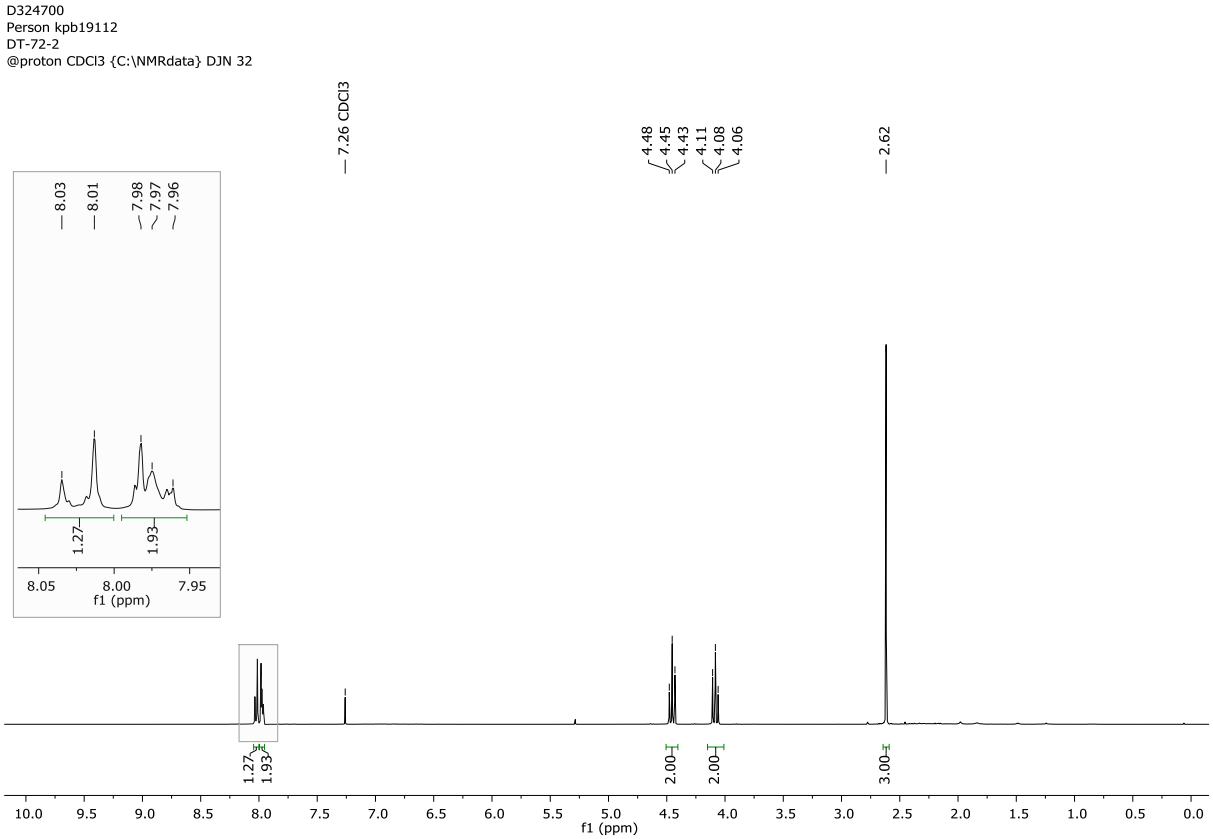


Figure S198. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 2-(4-acetyl)phenyloxazoline (entry 2, Table S50)

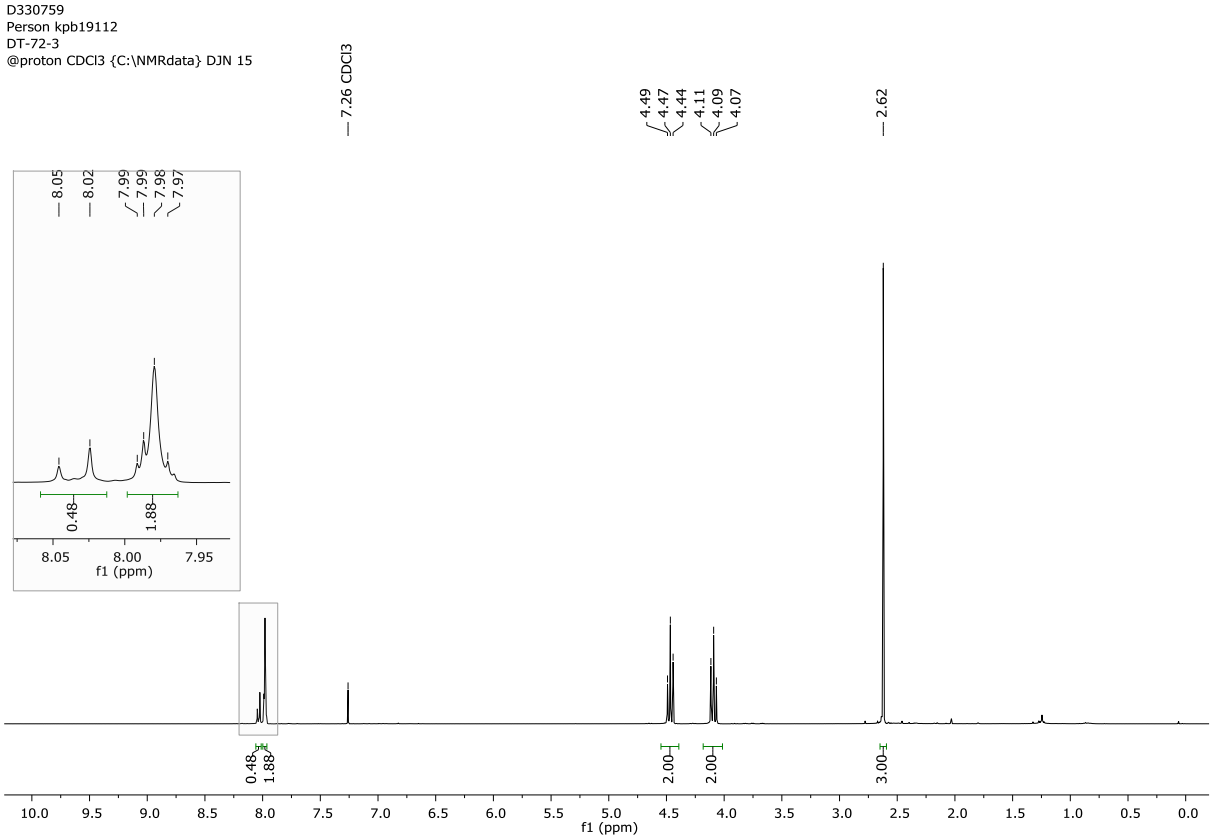
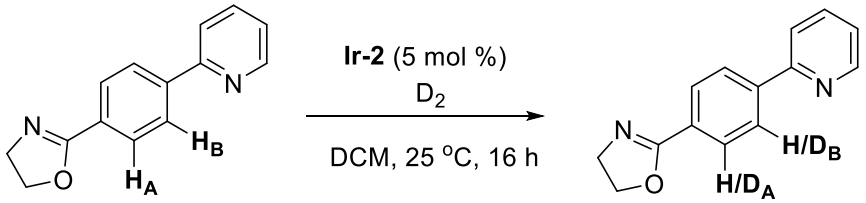


Figure S199. ^{1}H NMR (400 MHz, $CDCl_3$) of labelled 2-(4-acetyl)phenyloxazoline (entry 3, Table S50)

Labelling of 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole



According to GP2: 22.4 mg of substrate and 3.2 mg of catalyst

Spectral details of the reaction mixture:

^{1}H NMR (400 MHz, C_6D_6) δ = 8.56 – 8.51 (m, 1H, Ar-H), 8.36 – 8.32 (m, 1H, H_A), 8.17 – 8.11 (m, 2H, H_B), 7.25 – 7.21 (m, 1H, Ar-H), 7.11 – 7.04 (m, 1H, Ar-H), 6.66 – 6.61 (m, 1H, Ar-H), 3.77 – 3.58 (m, 4H, 2×CH_2).

Deuteration expected at δ (H_A) = 8.36 – 8.32 ppm and δ (H_B) = 8.17 – 8.11 ppm.

Determined against integral at δ = 6.66 – 6.61 ppm.

Table S51. Determination of the competition rate constant *κ*' from the labelling of 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole.

Entry	residual integral (H/D_A)	% D_A	residual integral (H/D_B)	% D_B	*κ'*
1	1.53	24	1.74	13	1.81
2	1.59	21	1.79	11	1.95
3	1.53	24	1.79	11	2.24
Average		**23**		**11**	**2.00**

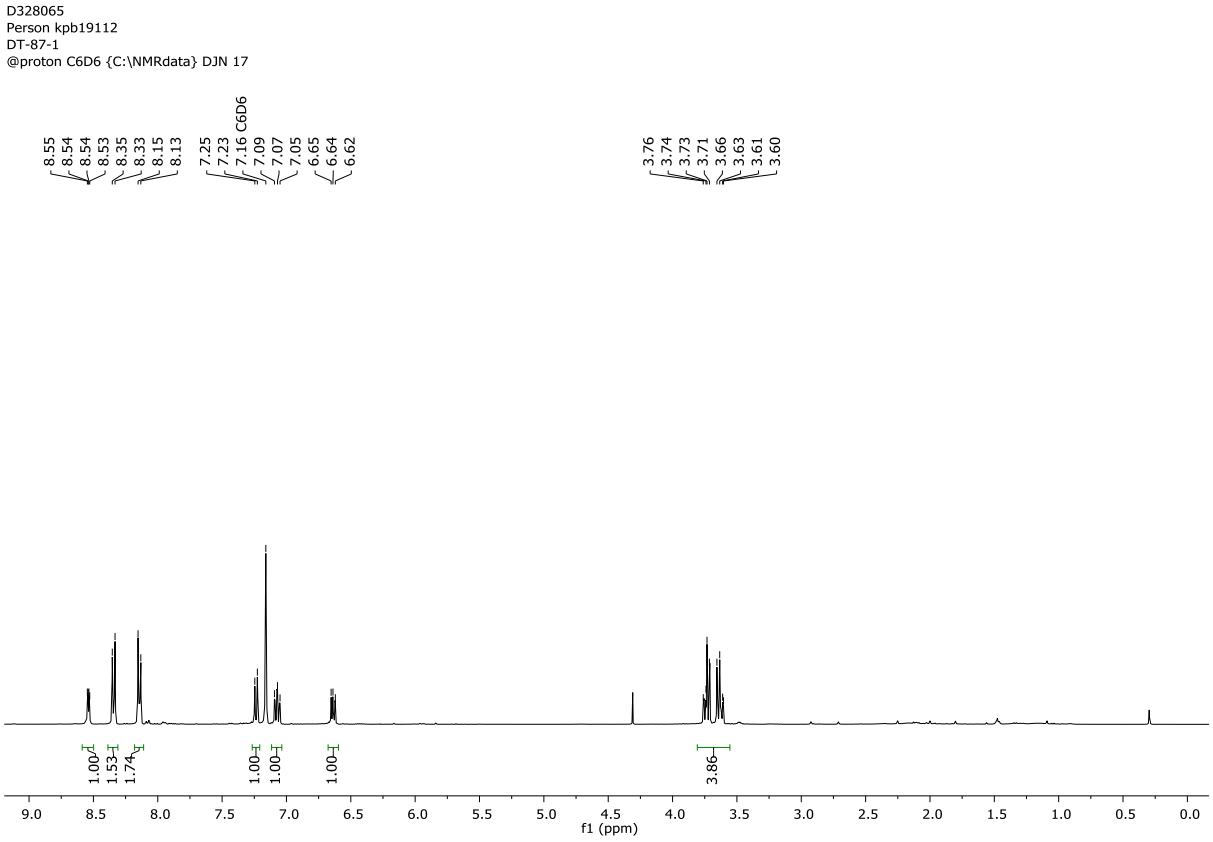


Figure S200. ^{1}H NMR (400 MHz, C_6D_6) of labelled 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole (entry 1, Table S51)

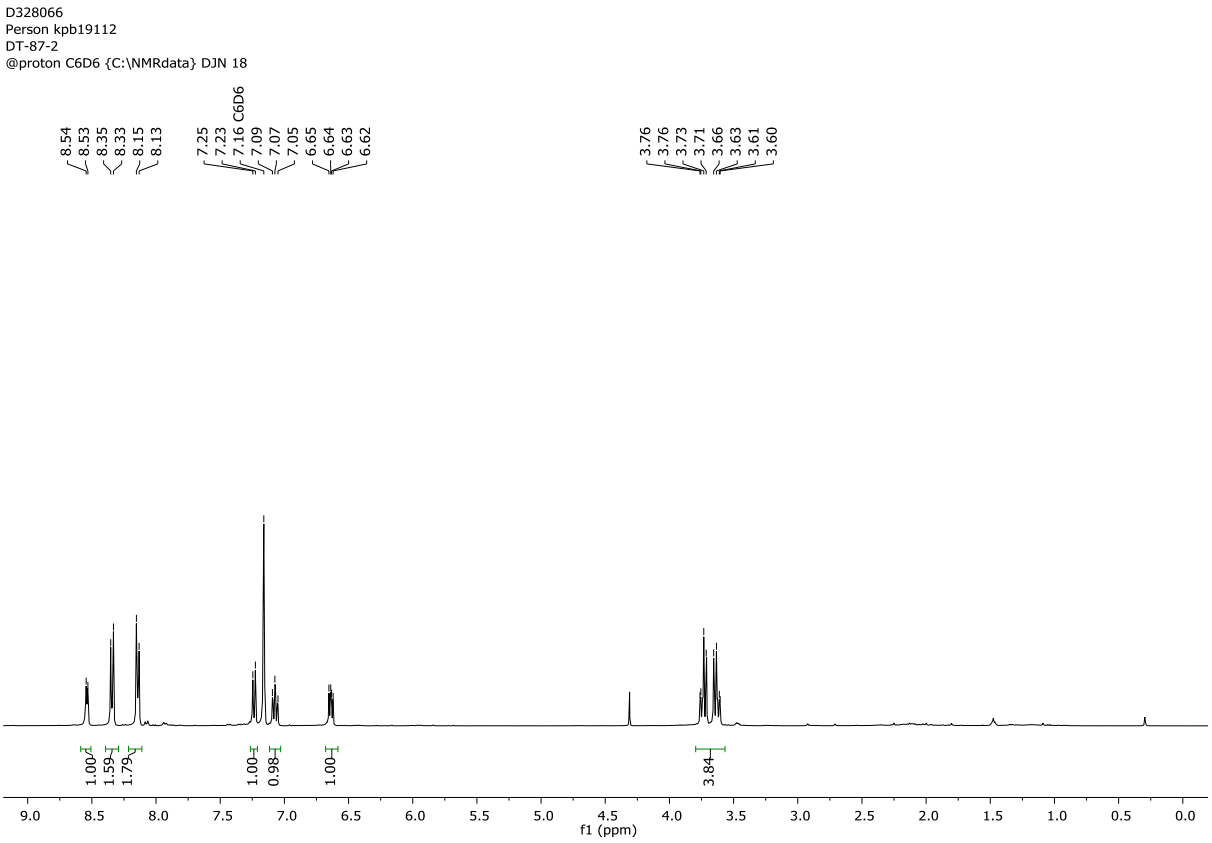


Figure S201. ^{1}H NMR (400 MHz, C_6D_6) of labelled 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole (entry 2, Table S51)

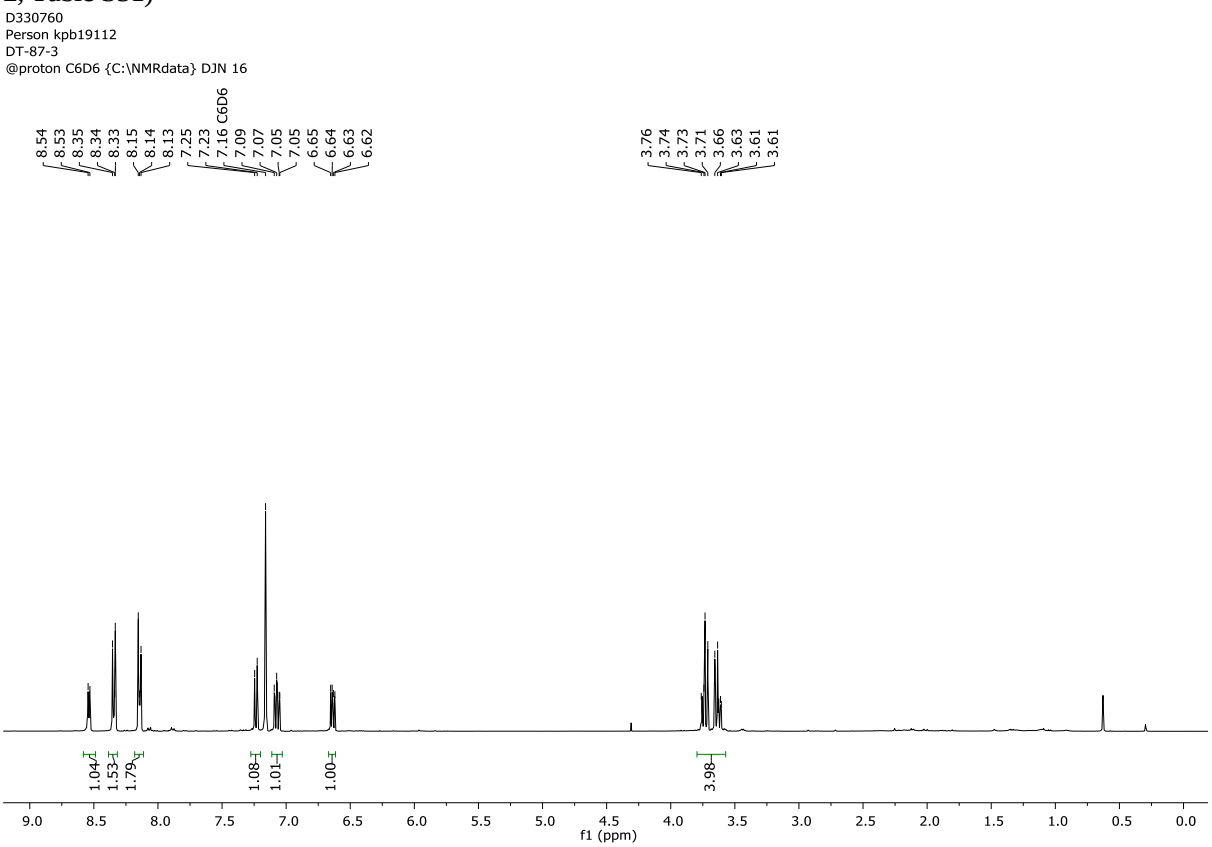


Figure S202. ^{1}H NMR (400 MHz, C_6D_6) of labelled 2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole (entry 3, Table S51)

5. References.

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6. Copies of NMR Spectra

6.1. ^{1}H and ^{13}C{^{1}H} NMR of synthesised substrates

N,N'-dimesitylethanediimine

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

D317246.1.fid
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DT-1
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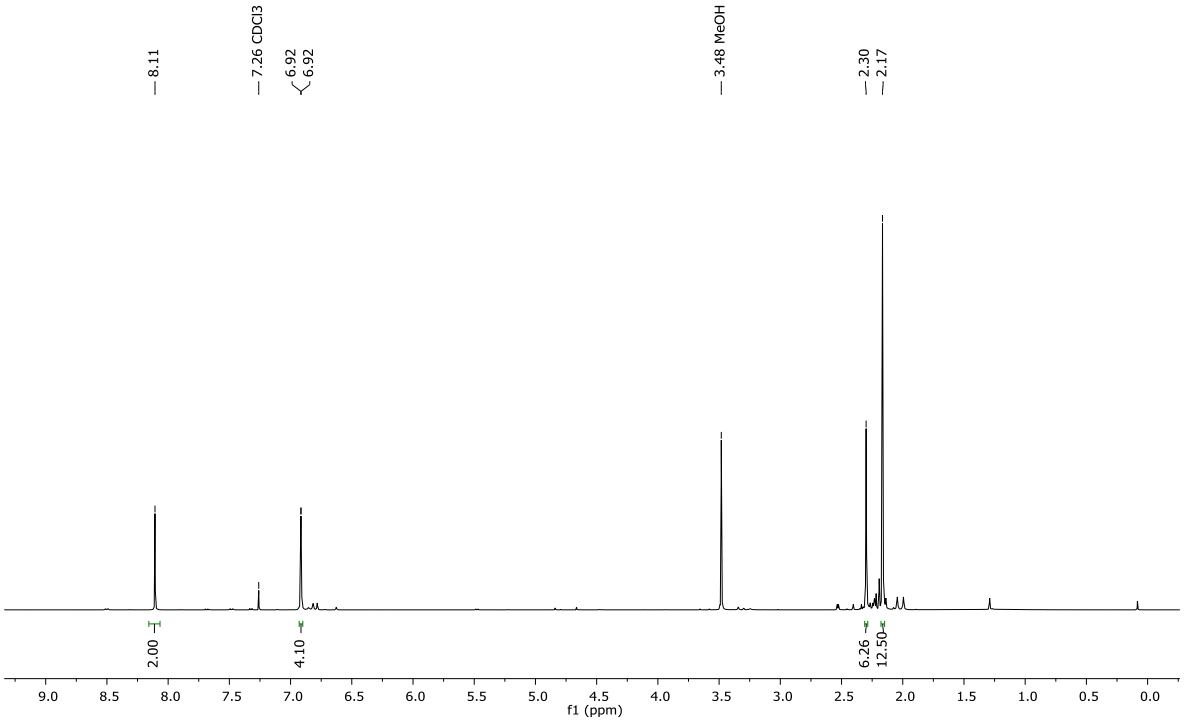
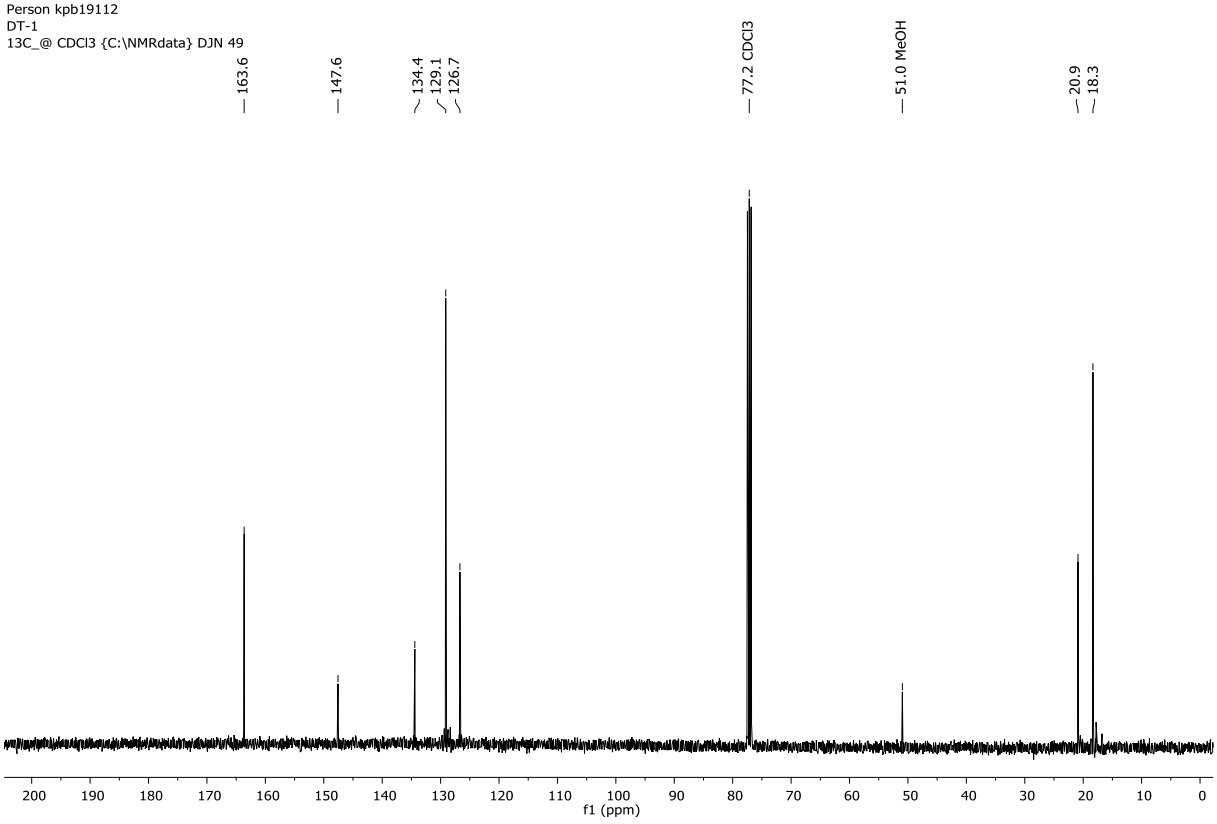


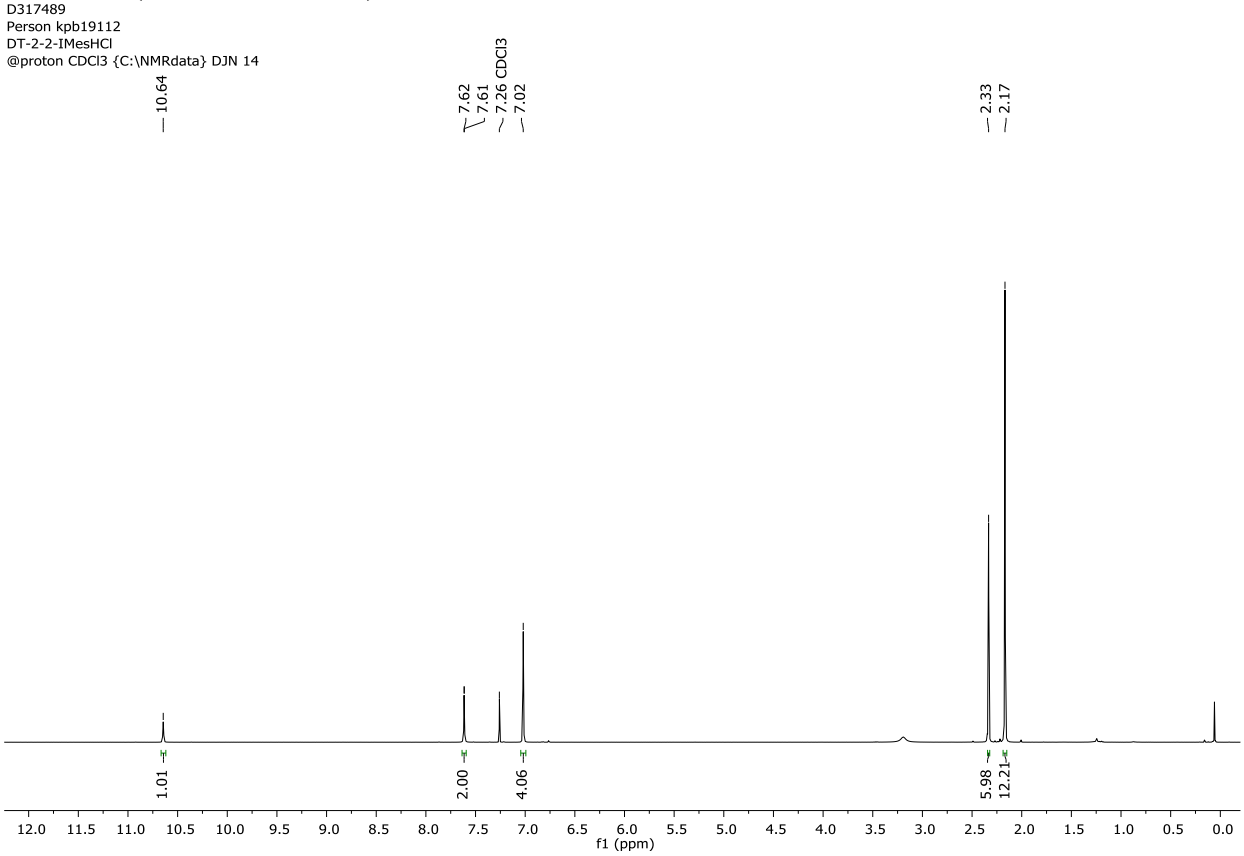
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

D317246.2.fid
Person kpb19112
DT-1
13C_@ CDCl3 {C:\NMRdata} DJN 49

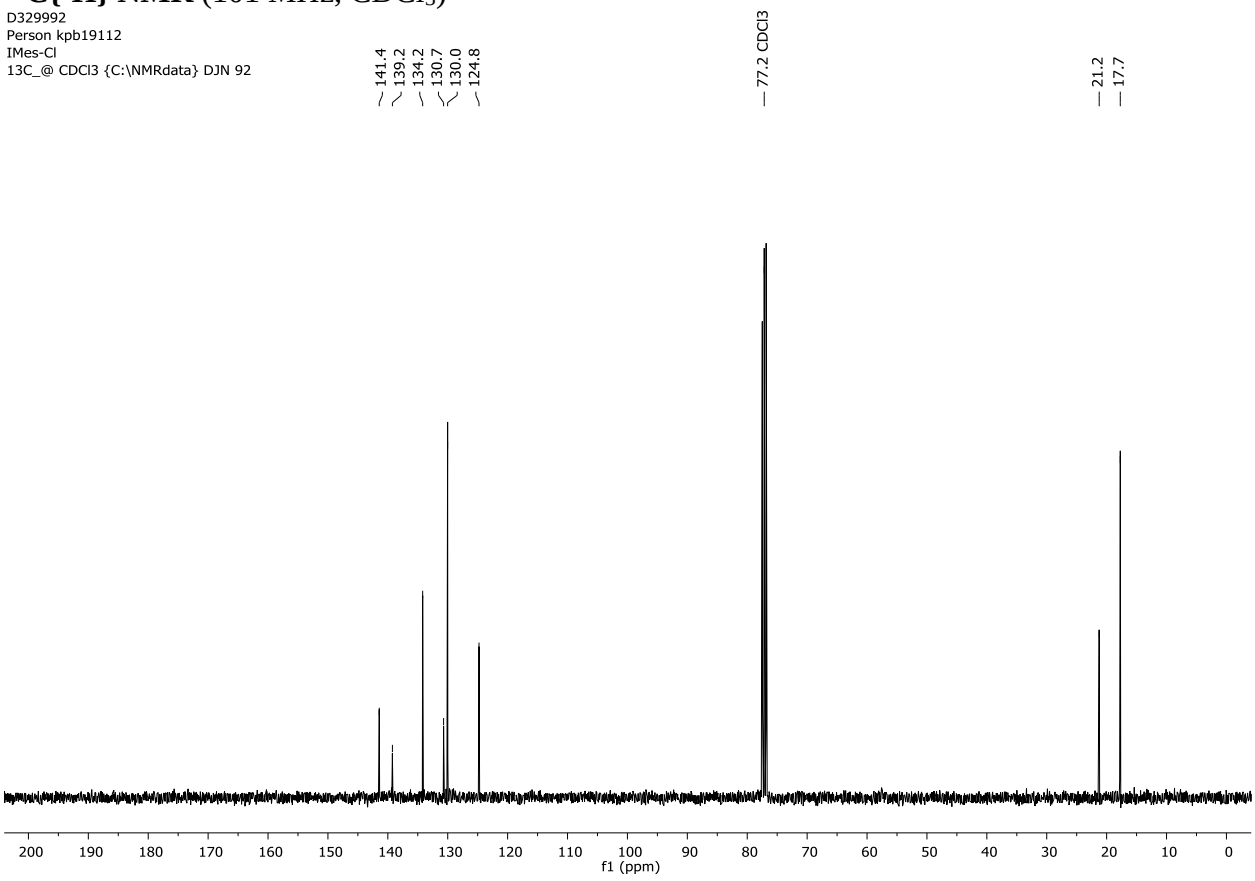


1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl)

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



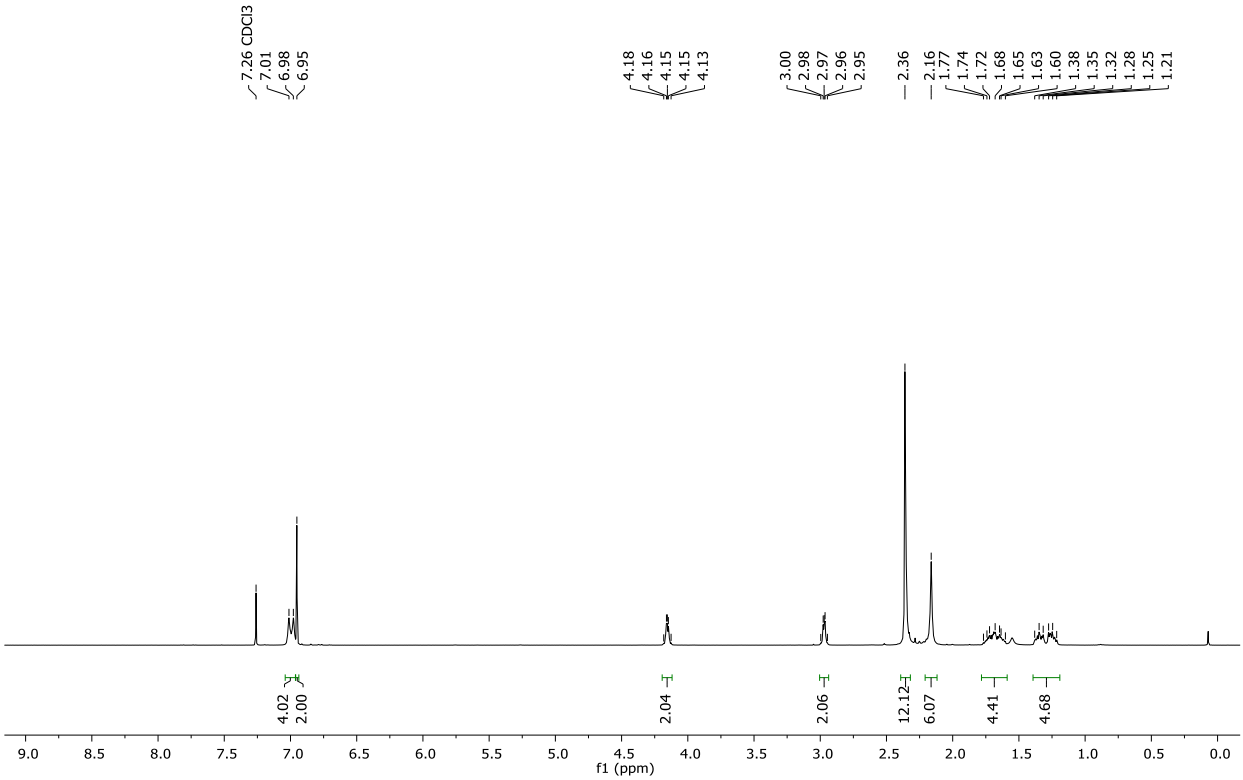
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



Chloro(η^4–cycloocta–1,5–diene)(1,3-dimesitylimidazoline-2-ylidene)iridium(I) **Ir-2**

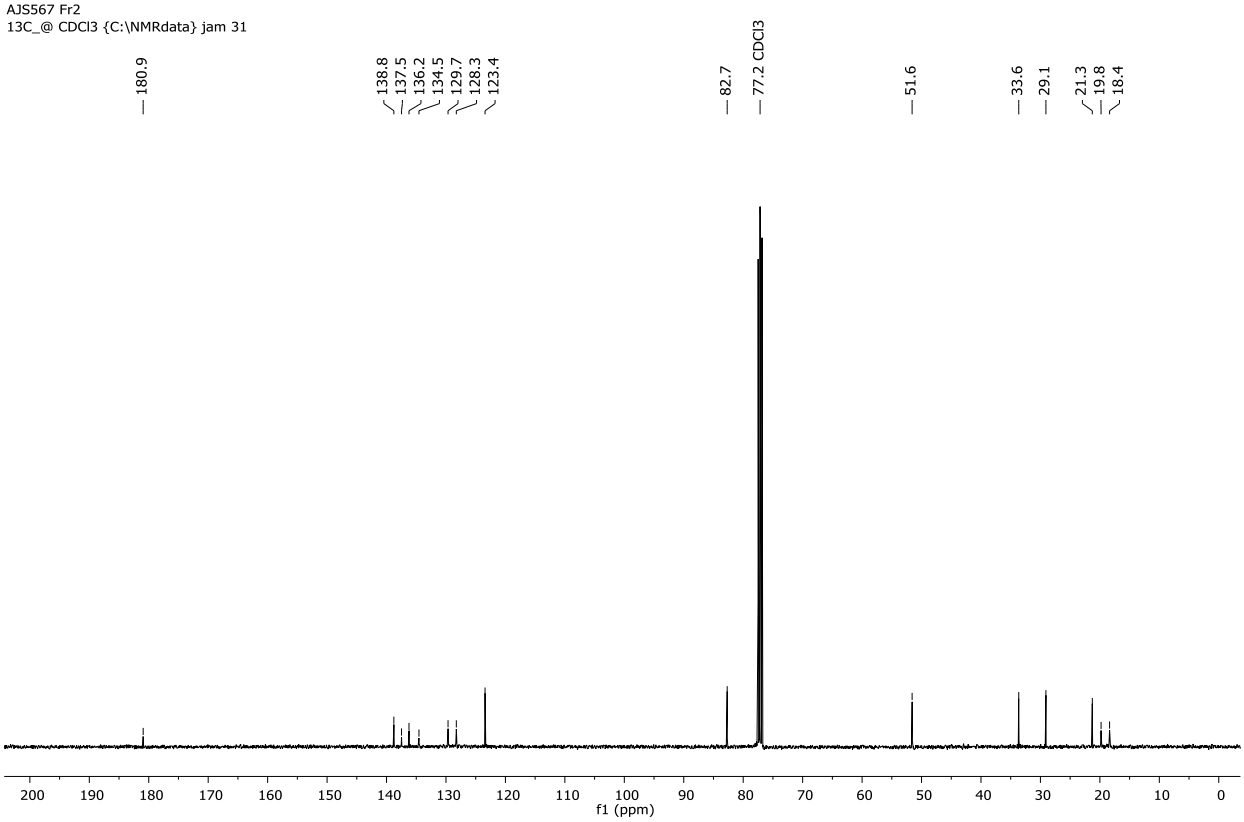
^{1}H NMR (400 MHz, $CDCl_3$)

D318954
Person kpb19112
DT-3
@proton CDCl3 {C:\NMRdata} DJN 32



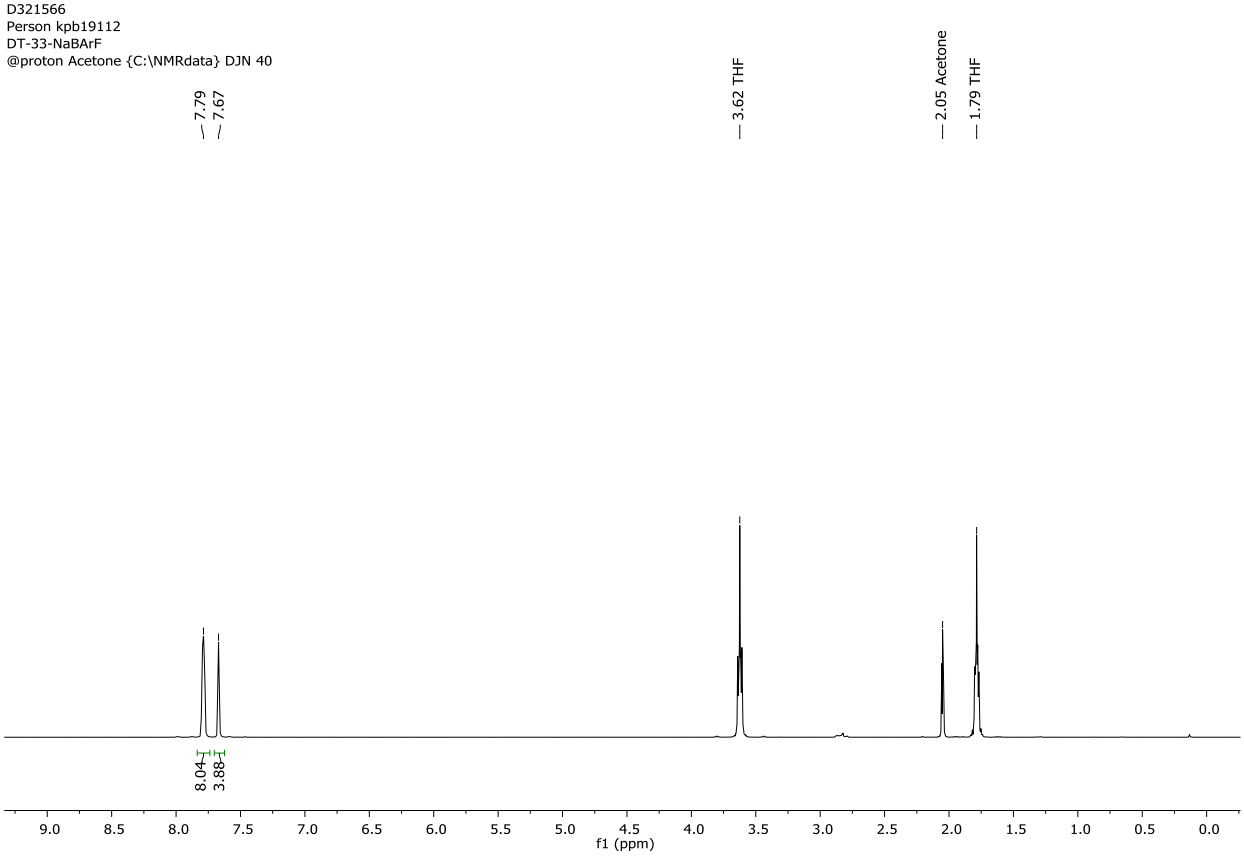
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

D318953
Person yxb10128
AJS567 Fr2
13C_@ CDCl3 {C:\NMRdata} jam 31

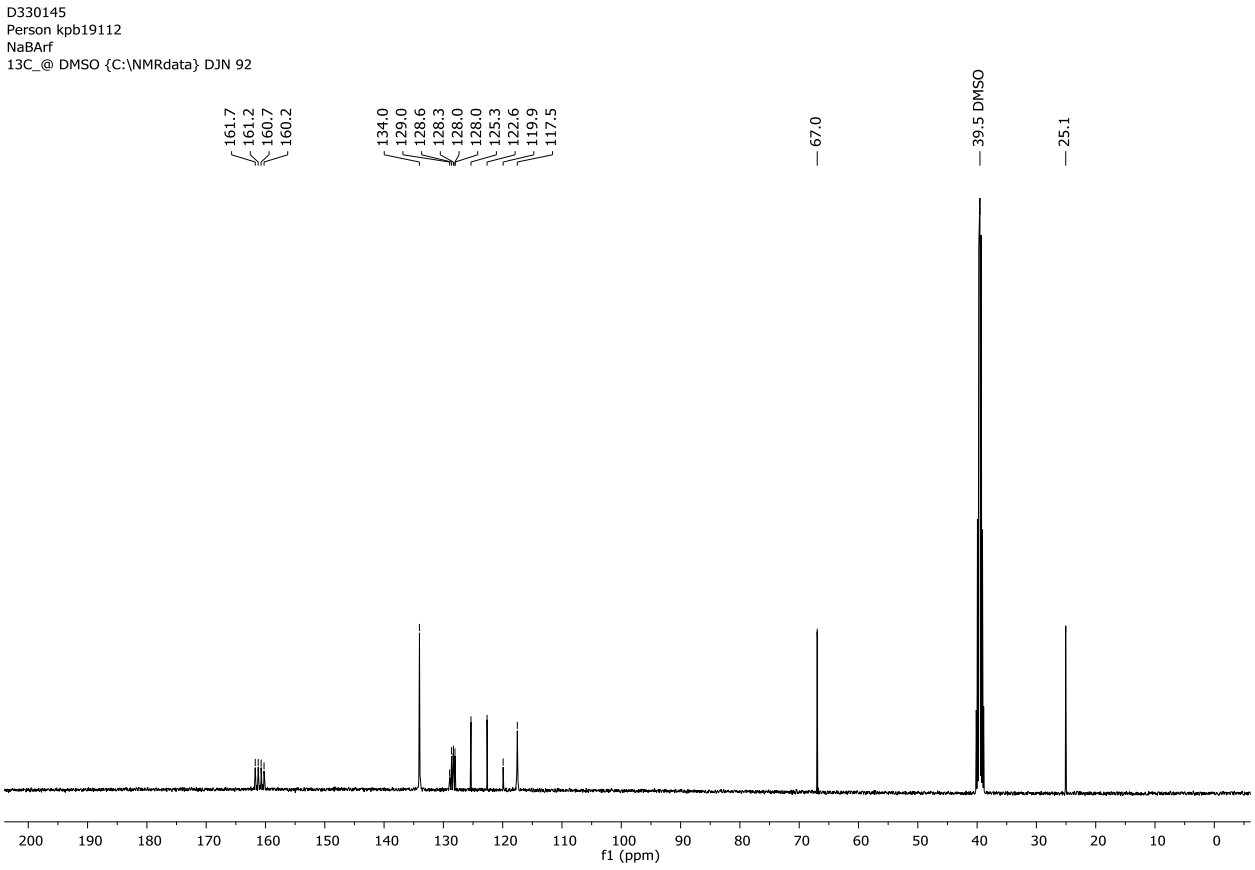


Soldium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Na[BArF$_{24}$])

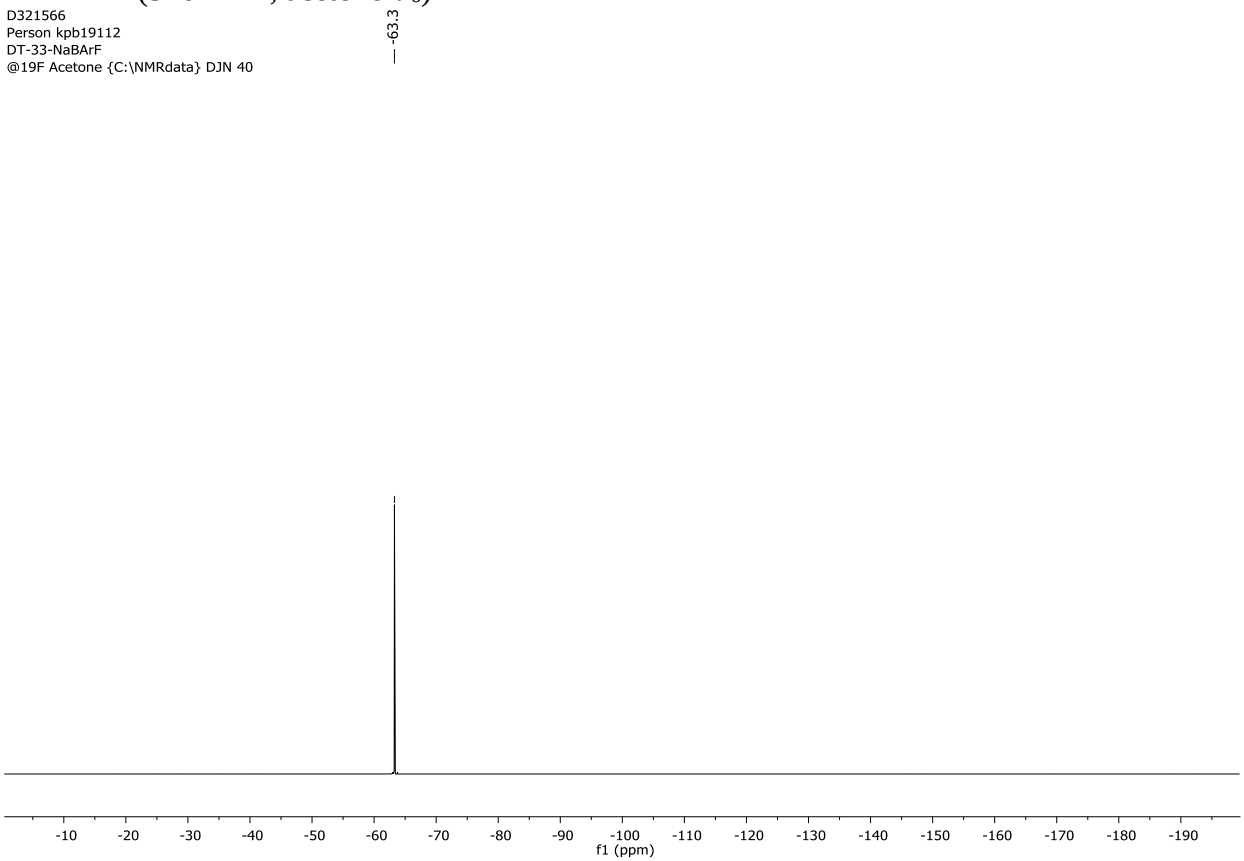
^{1}H NMR (400 MHz, acetone-d_6)



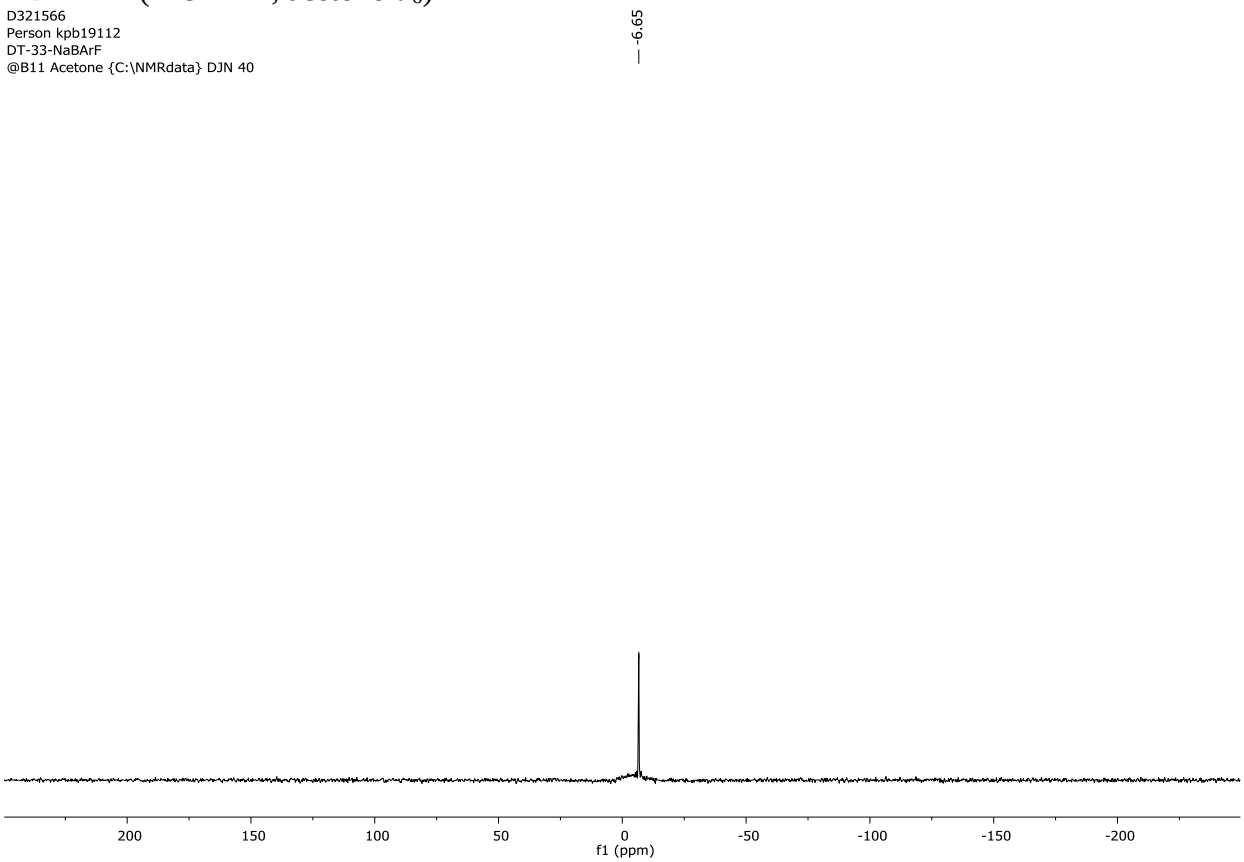
^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6)



^{19}F NMR (376 MHz, acetone-d_6)



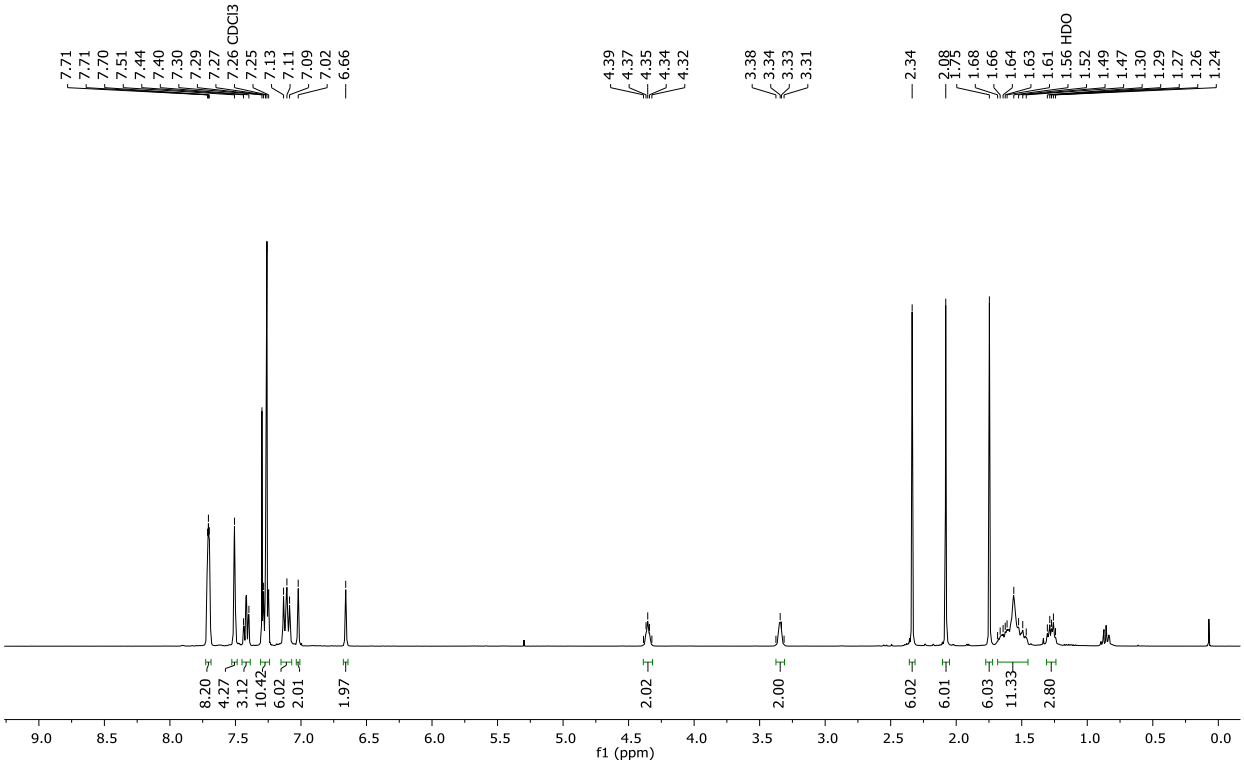
^{11}B NMR (128 MHz, acetone-d_6)



[(COD)Ir(IMes)(PPh$_3$)]BArF$_{24}$ **Ir-1**

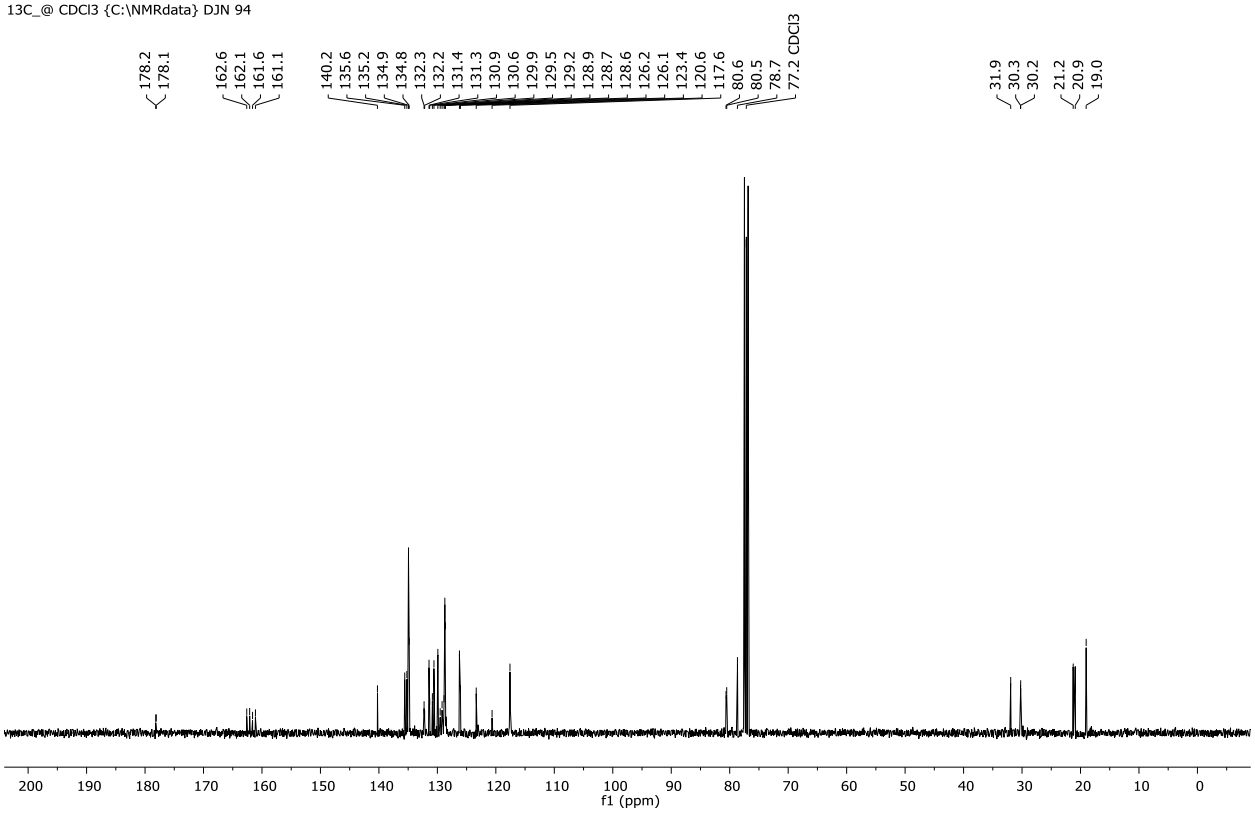
^{1}H NMR (400 MHz, $CDCl_3$)

D323541
Person kpb19112
DT-40-2a
@proton CDCl3 {C:\NMRdata} DJN 10



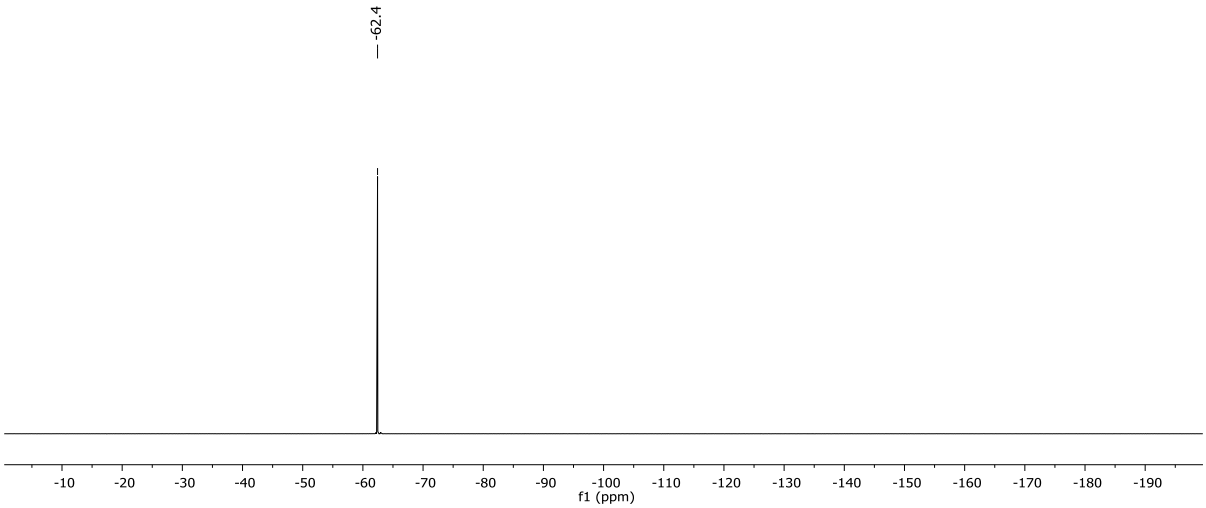
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

D330147
Person kpb19112
DT-89
13C_@ CDCl3 {C:\NMRdata} DJN 94



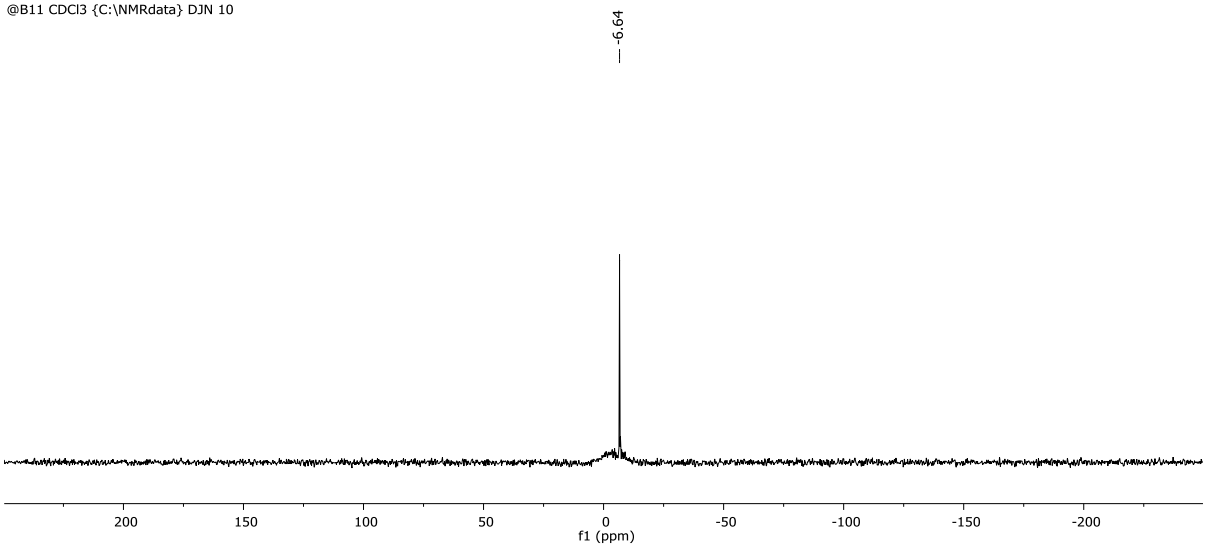
^{19}F NMR (376 MHz, $CDCl_3$)

D323541
Person kpb19112
DT-40-2a
@19F CDCl3 {C:\NMRdata} DJN 10



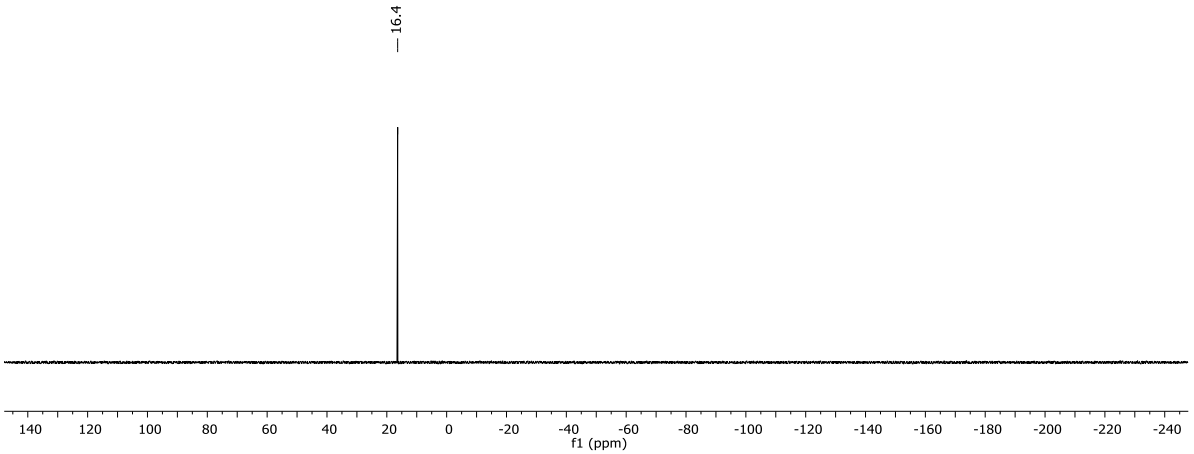
^{11}B NMR (128 MHz, $CDCl_3$)

D323541
Person kpb19112
DT-40-2a
@B11 CDCl3 {C:\NMRdata} DJN 10



^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$)

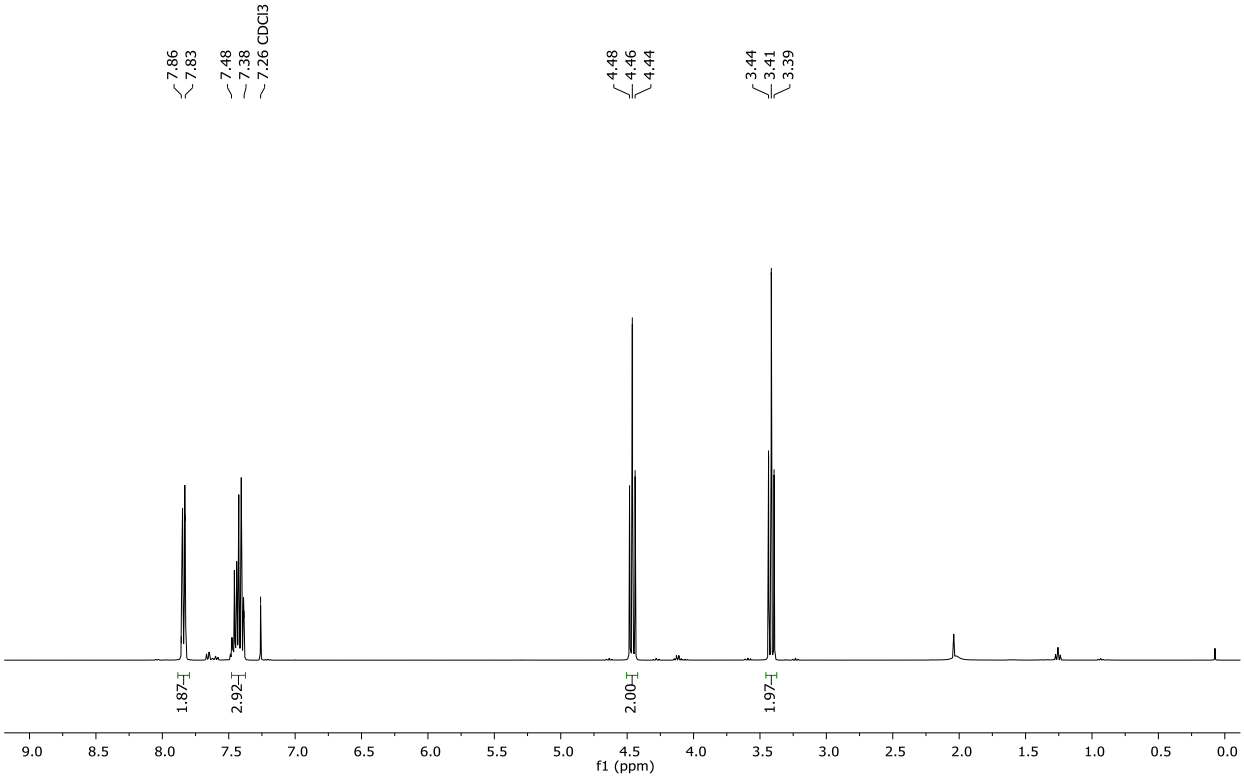
D323541
Person kpb19112
DT-40-2a
@31P_Hdec CDCl3 {C:\NMRdata} DJN 10



2-Phenylthiazoline

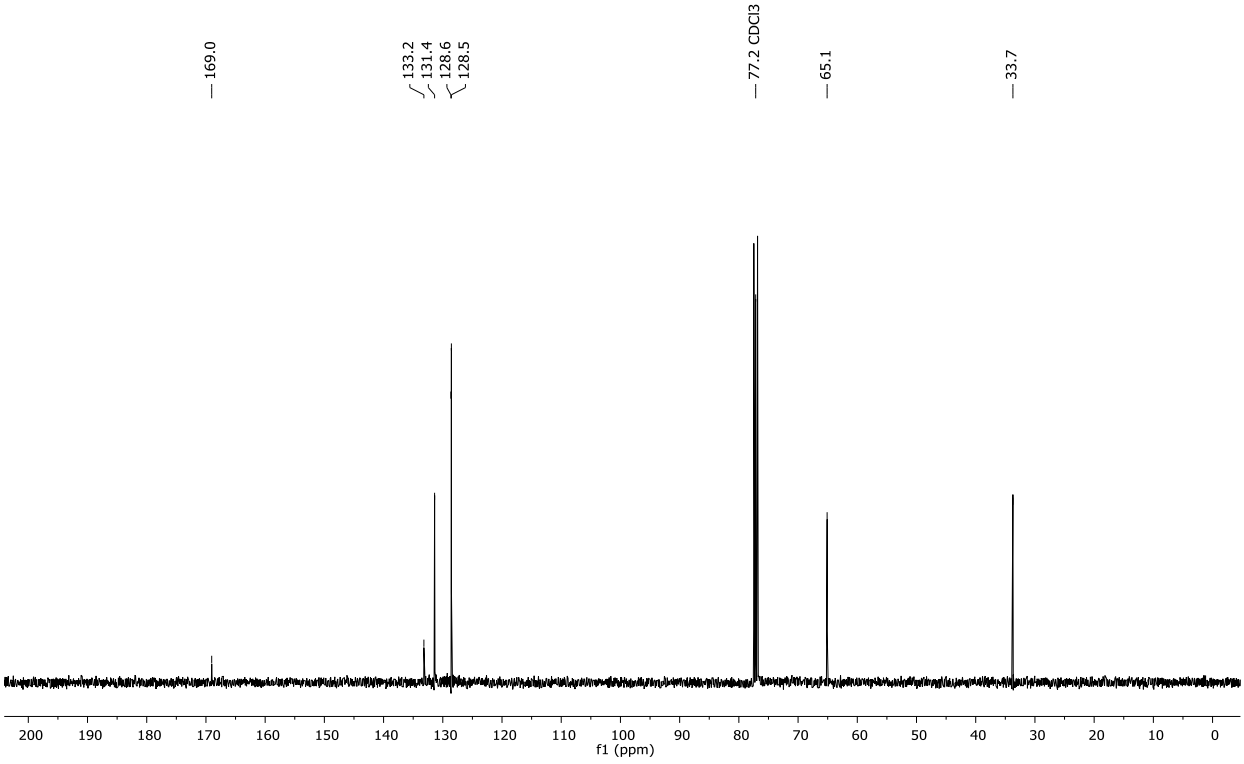
^{1}H NMR (400 MHz, $CDCl_3$)

D319916
Person kpb19112
DT-20-DG-15
@proton CDCl3 {C:\NMRdata} DJN 5



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

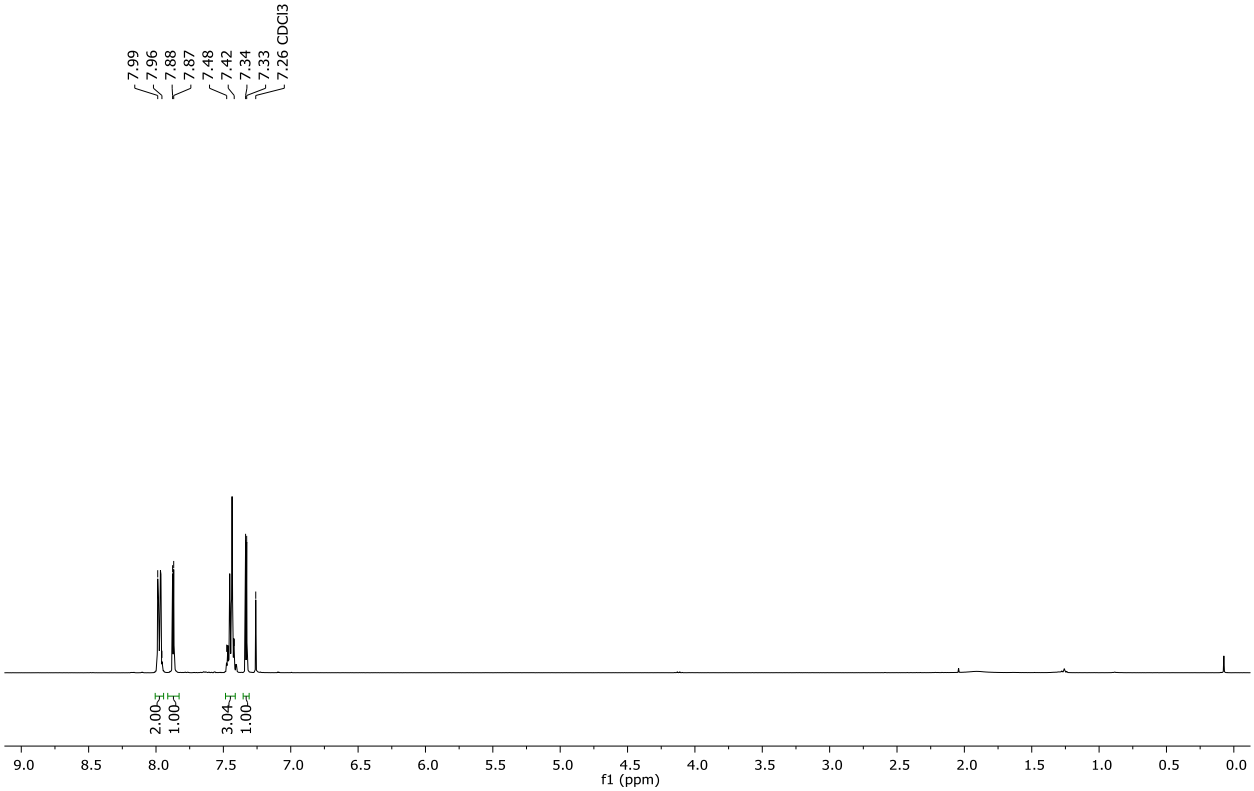
D329993
Person kpb19112
Ph-thiazoline
13C_@ CDCl3 {C:\NMRdata} DJN 27



2-Phenylthiazole

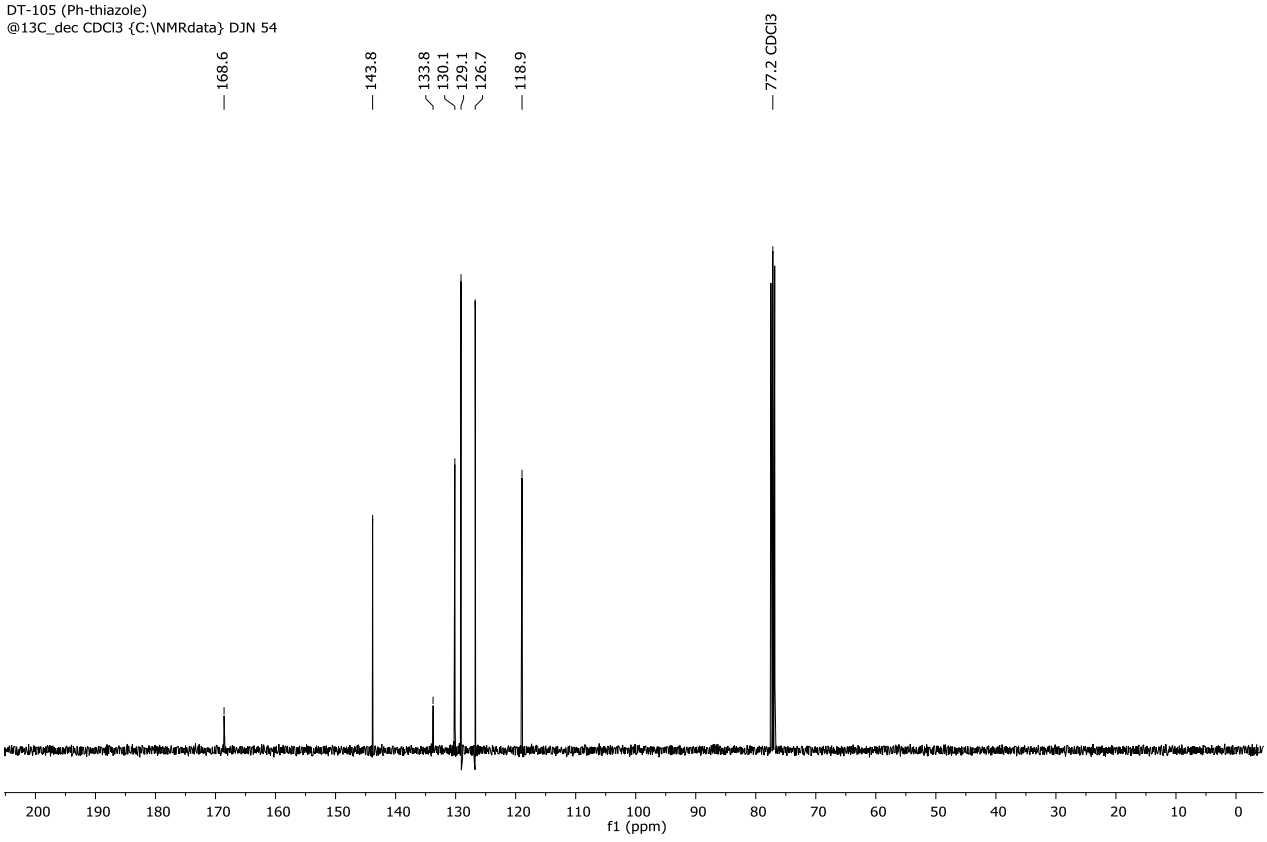
^{1}H NMR (400 MHz, $CDCl_3$)

D318663
Person kpb19112
DT-DG-10
@proton CDCl3 {C:\NMRdata} DJN 21



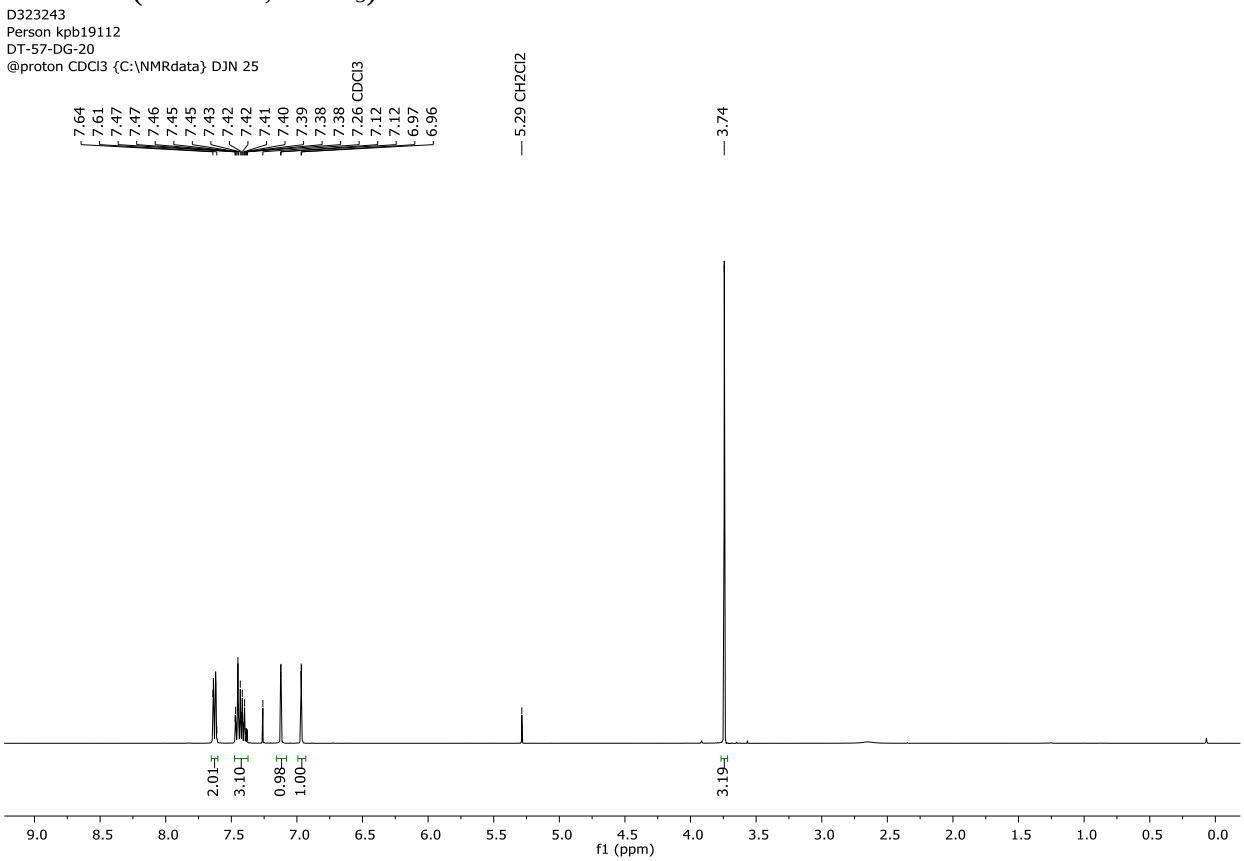
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

B61716
Person kpb19112
DT-105 (Ph-thiazole)
@13C_dec CDCl3 {C:\NMRdata} DJN 54

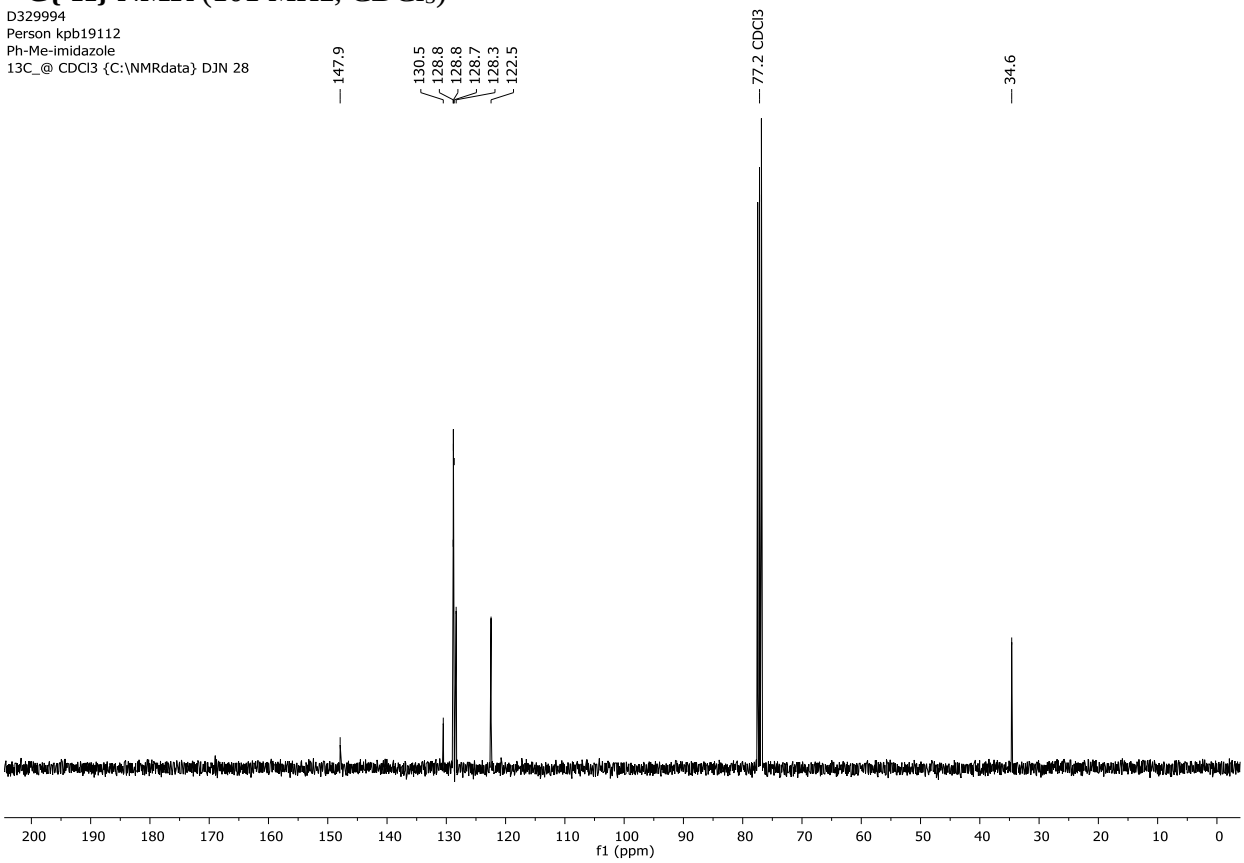


1-Methyl-2-phenylimidazole

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

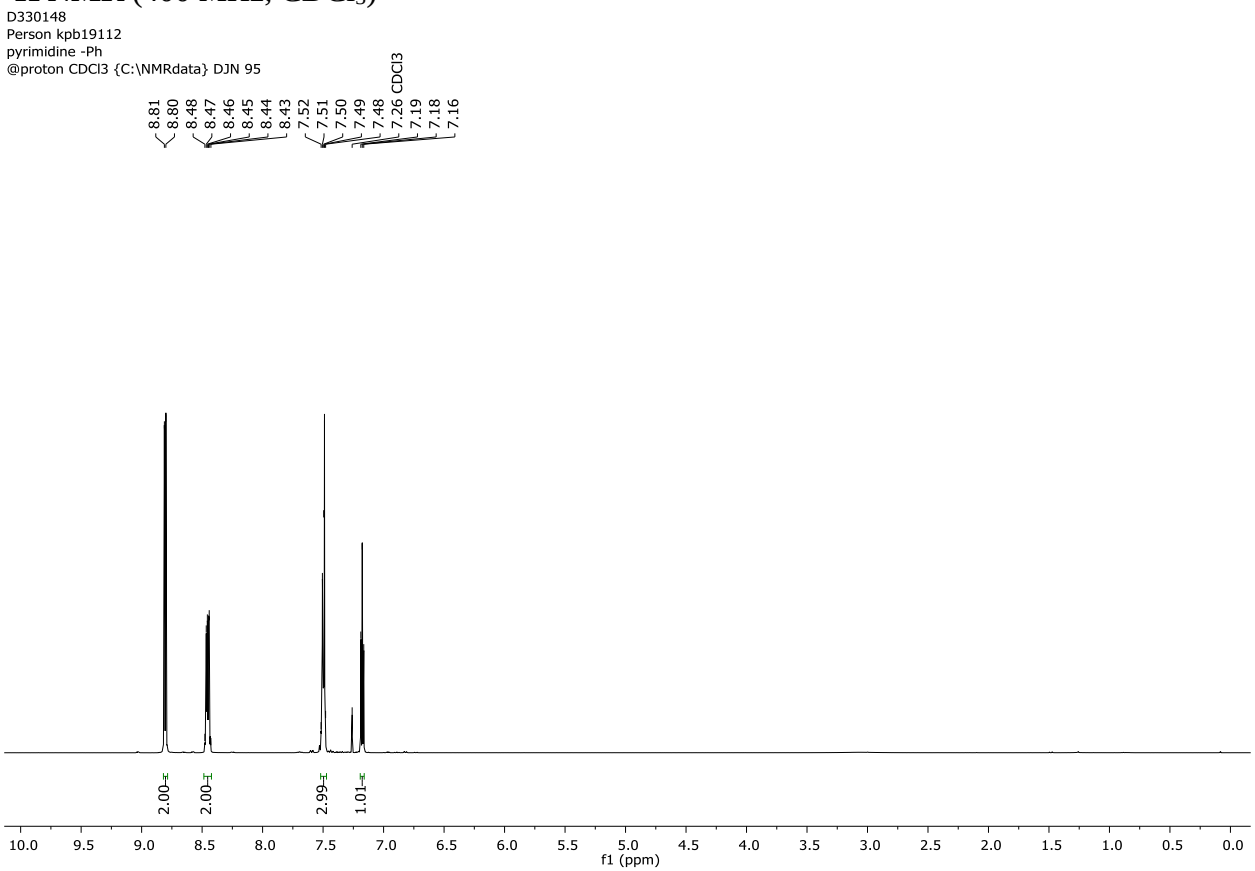


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

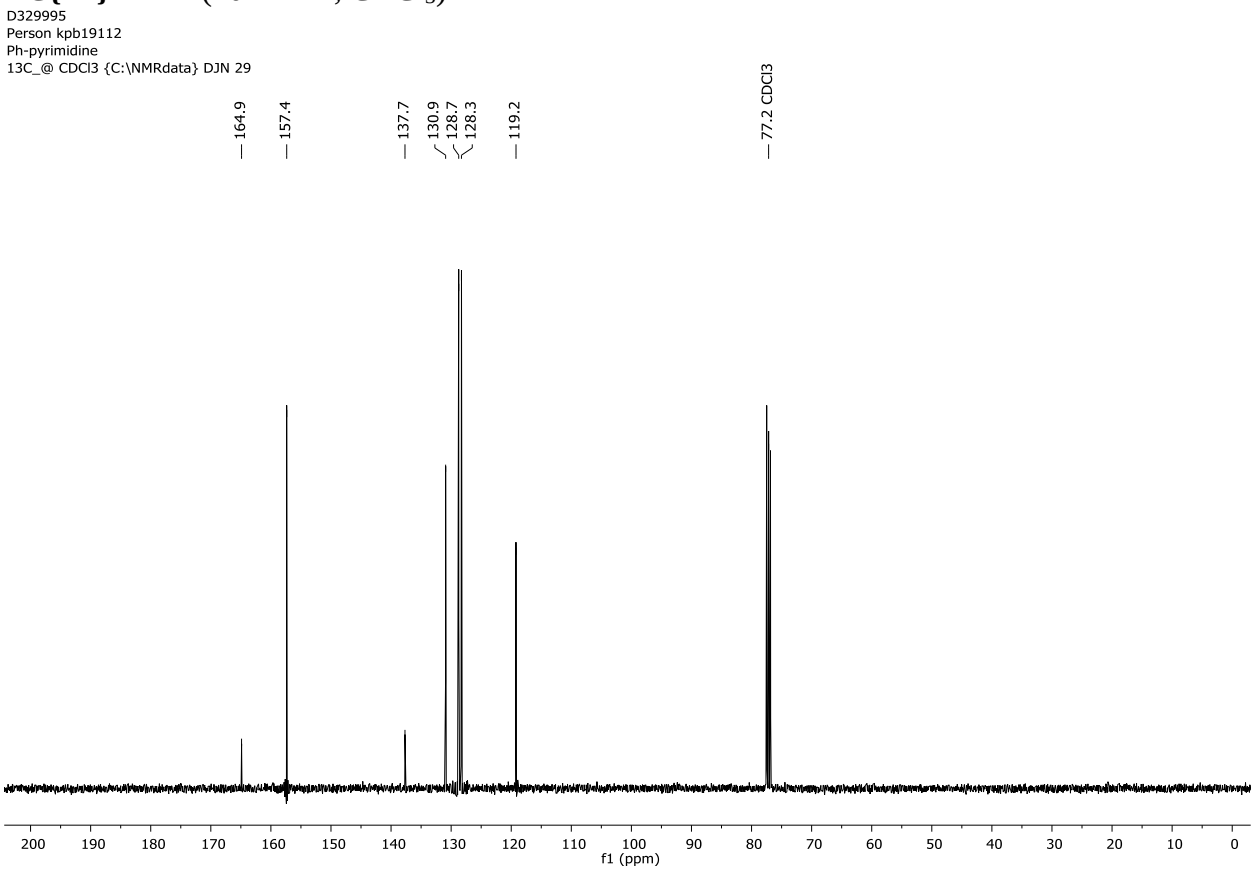


2-Phenylpyrimidine

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



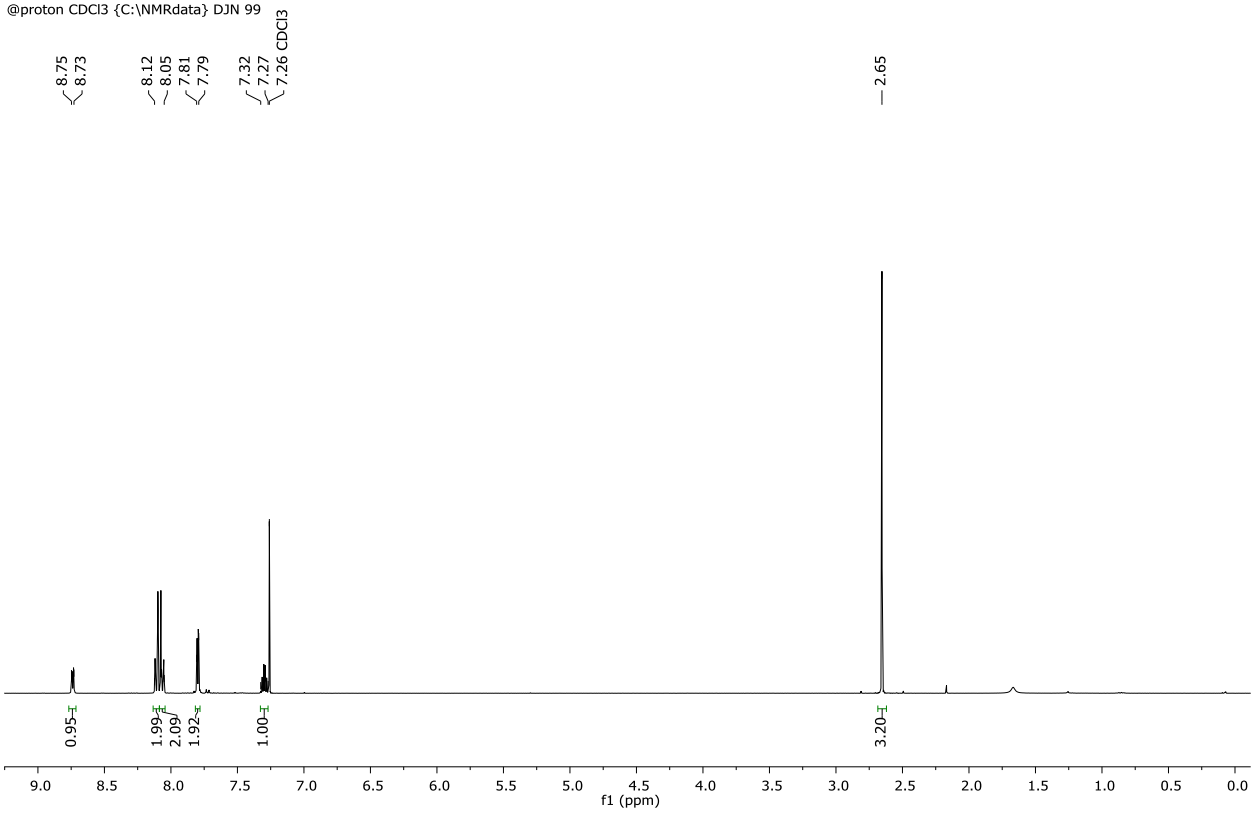
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



2-(4-acetyl)phenylpyridine

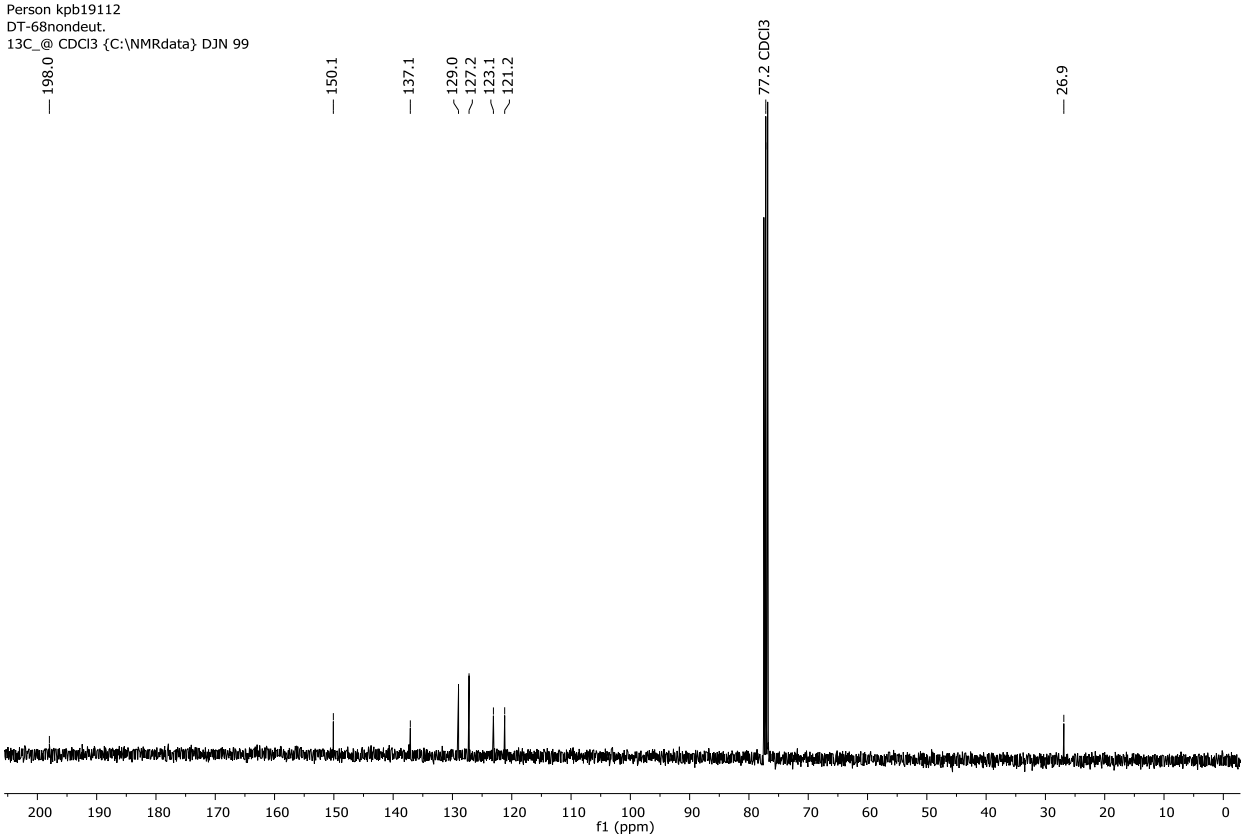
^{1}H NMR (400 MHz, $CDCl_3$)

D324484
Person kpb19112
DT-68nondeut.
@proton CDCl3 {C:\NMRdata} DJN 99



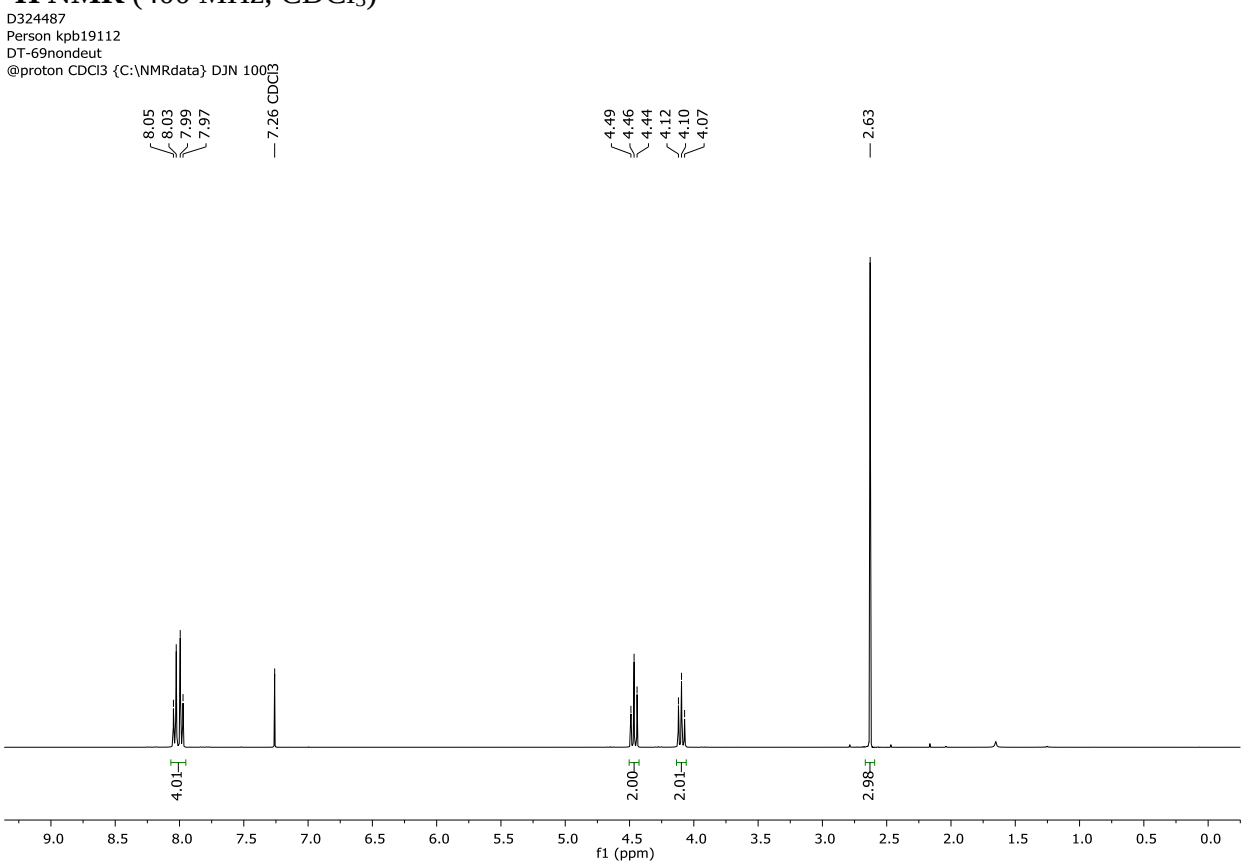
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

D324484
Person kpb19112
DT-68nondeut.
13C_@ CDCl3 {C:\NMRdata} DJN 99

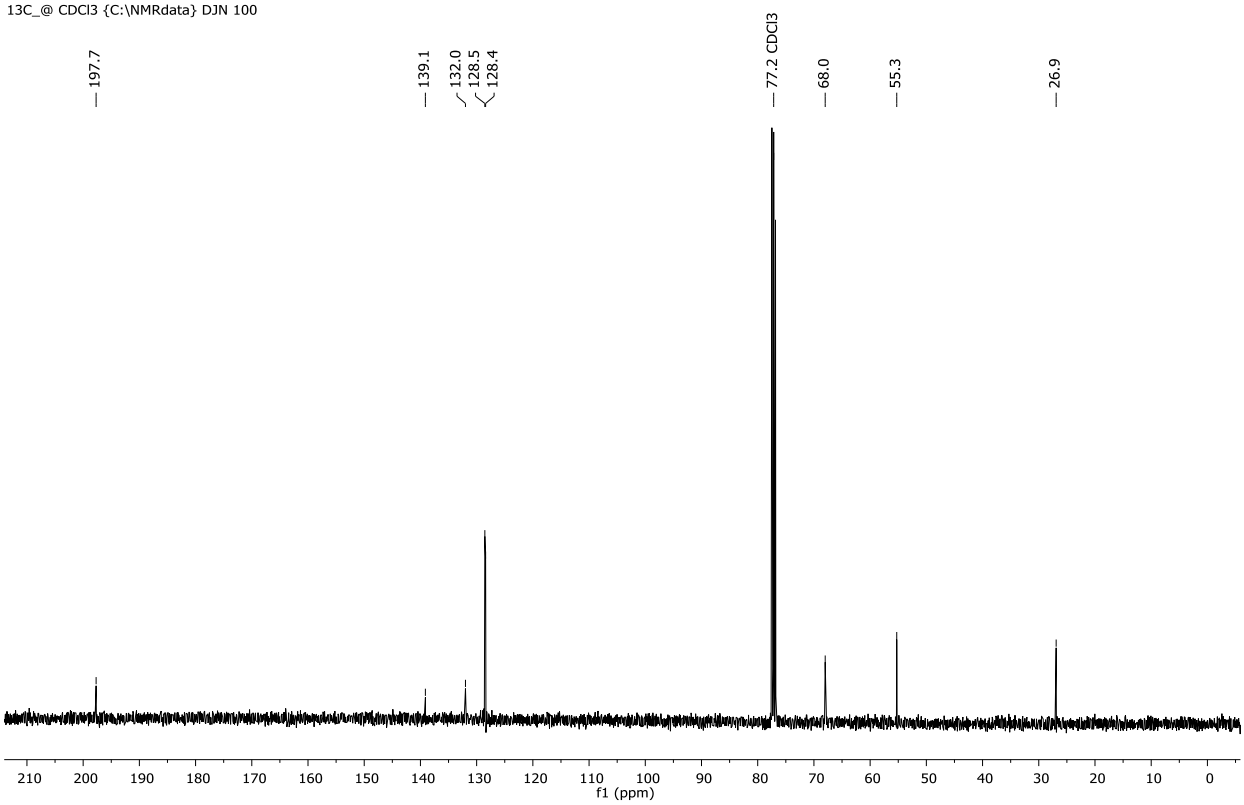


2-(4-acetyl)phenyloxazoline

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



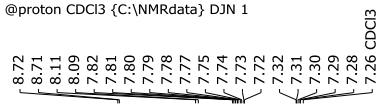
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

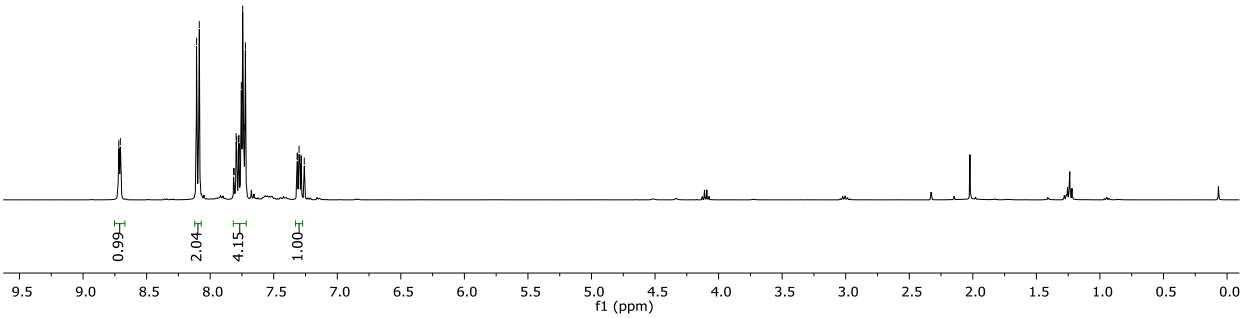


2-(4-cyano)phenylpyridine

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

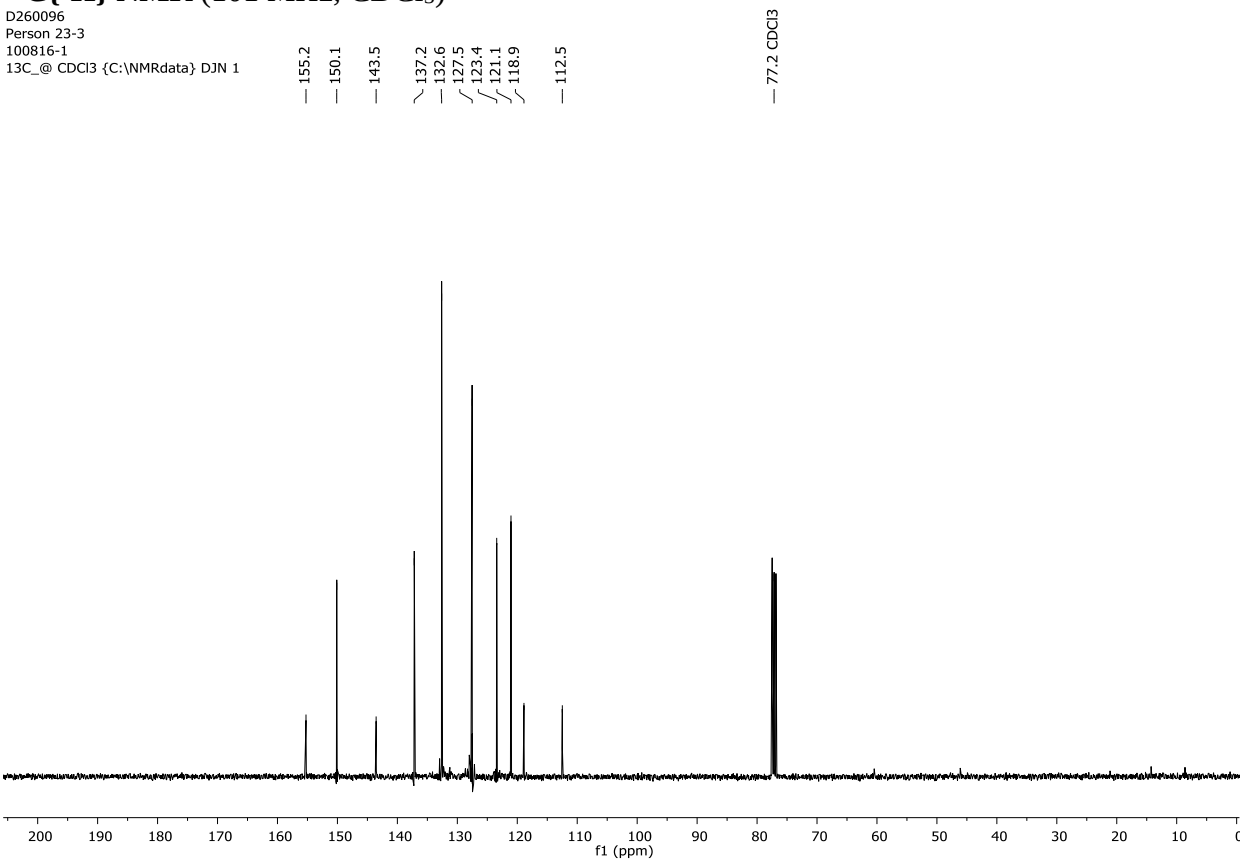
D260096
Person 23-3
100816-1
@proton CDCl3 {C:\NMRdata} DJN 1





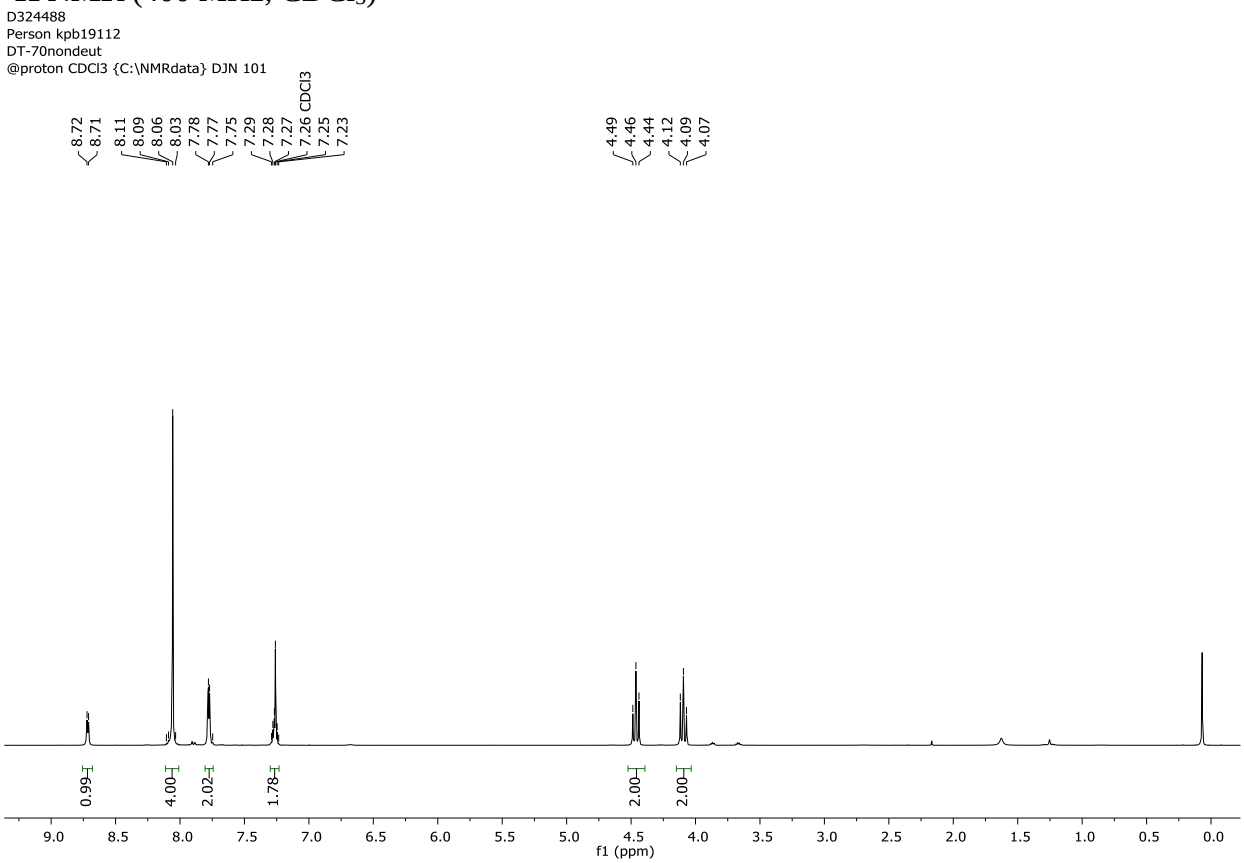
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

D260096
Person 23-3
100816-1
13C_@ CDCl3 {C:\NMRdata} DJN 1

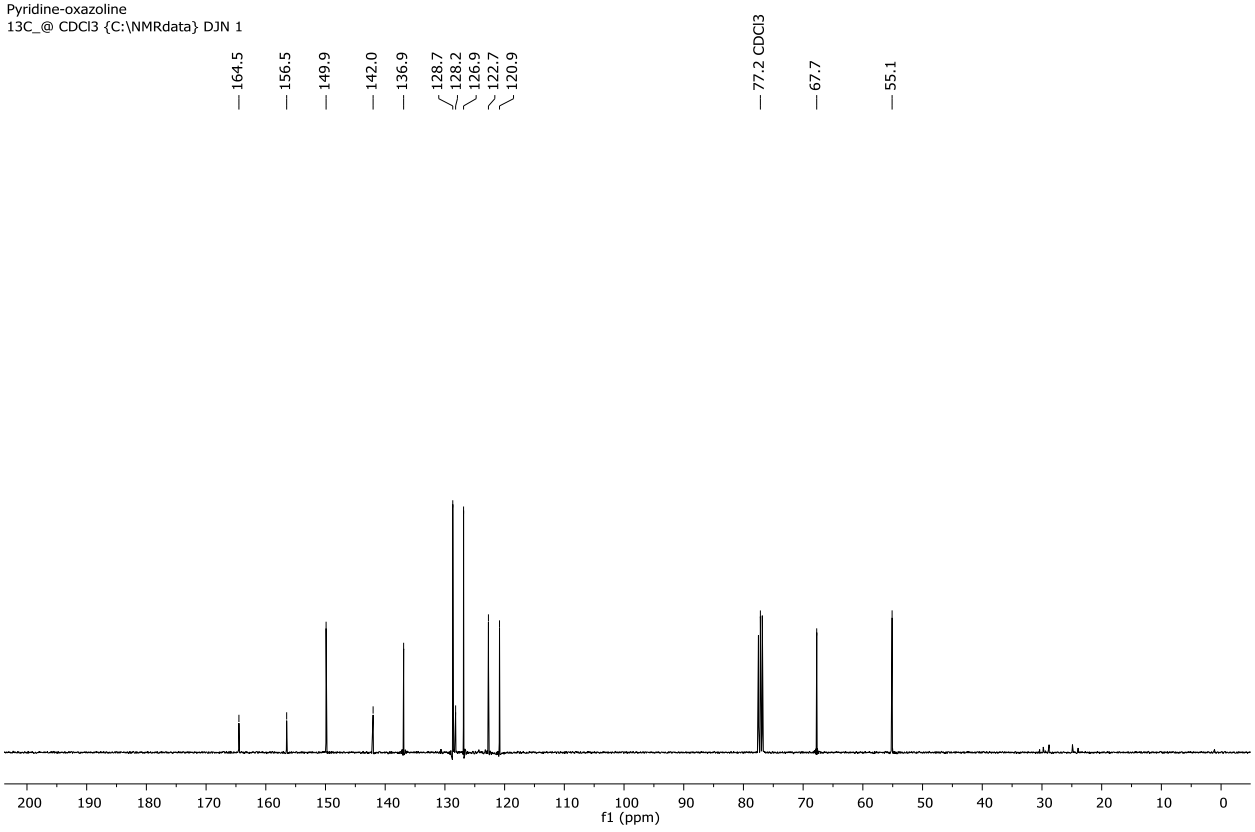


2-(4-(pyridin-2-yl)phenyl)-4,5-dihydrooxazole

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



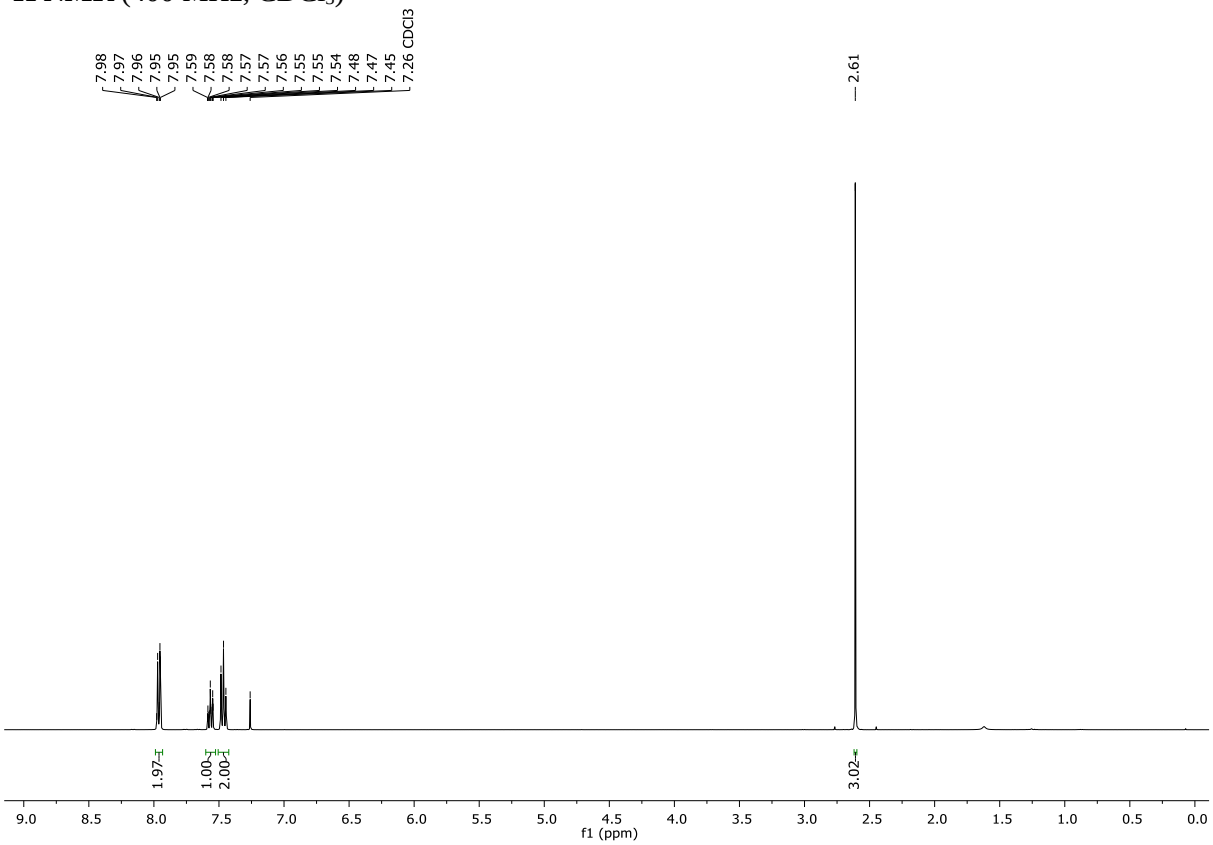
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



6.2. ^{1}H NMR of non-deuterated commercial substrates

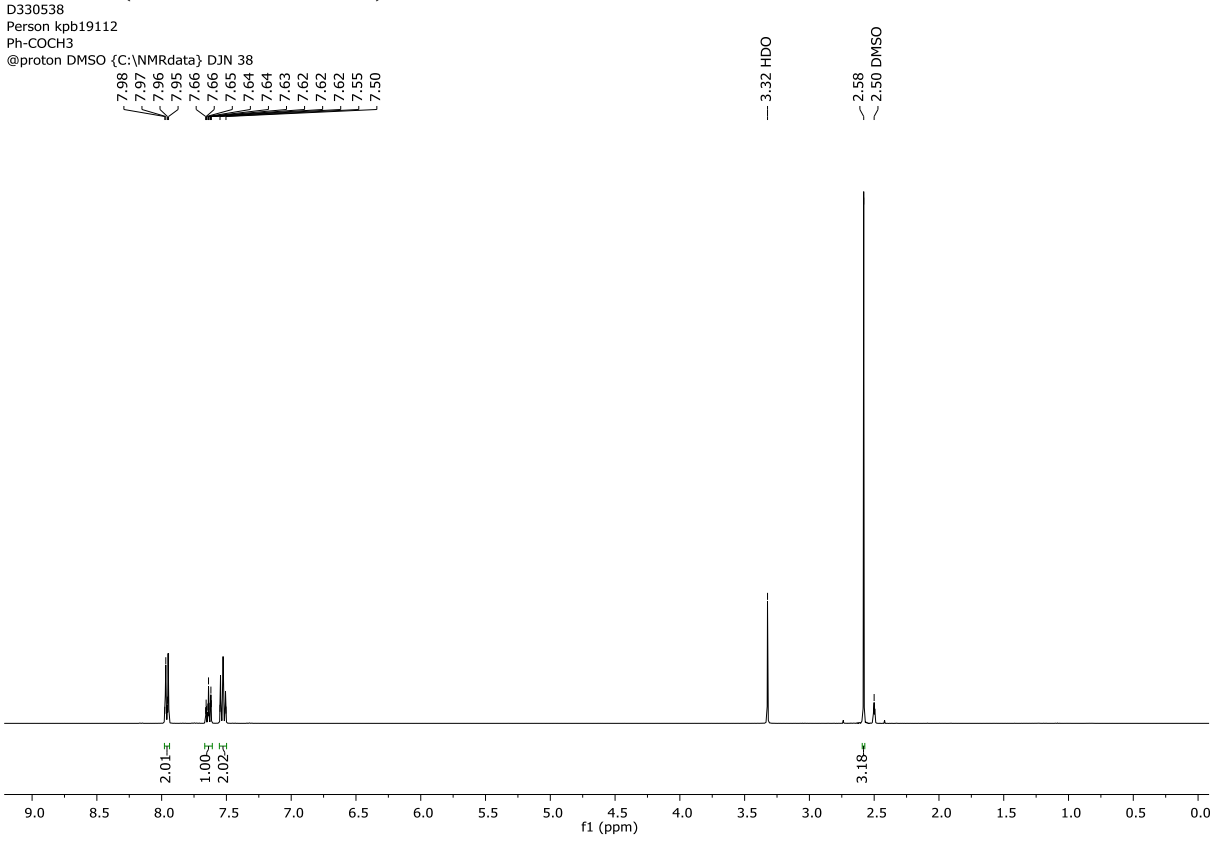
Acetophenone

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



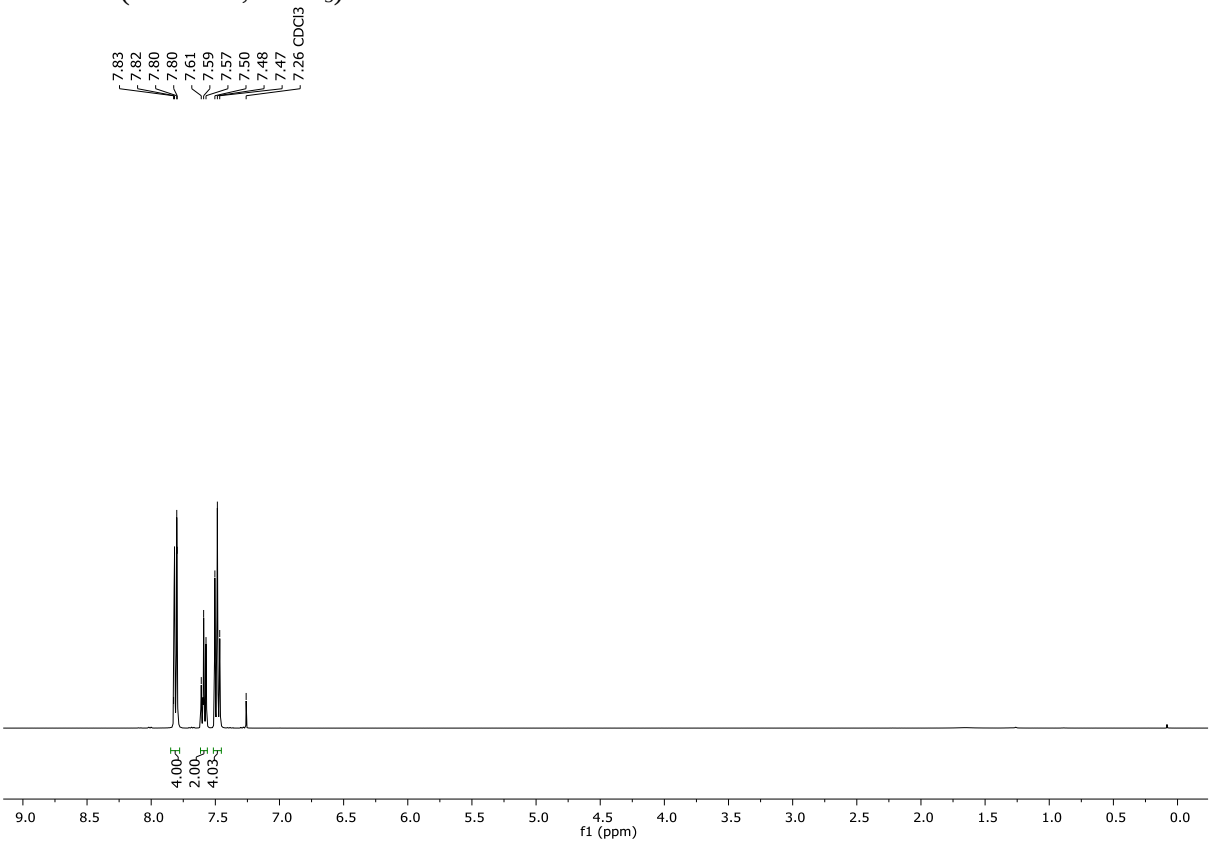
Acetophenone

^{1}H NMR (400 MHz, DMSO-d_6)



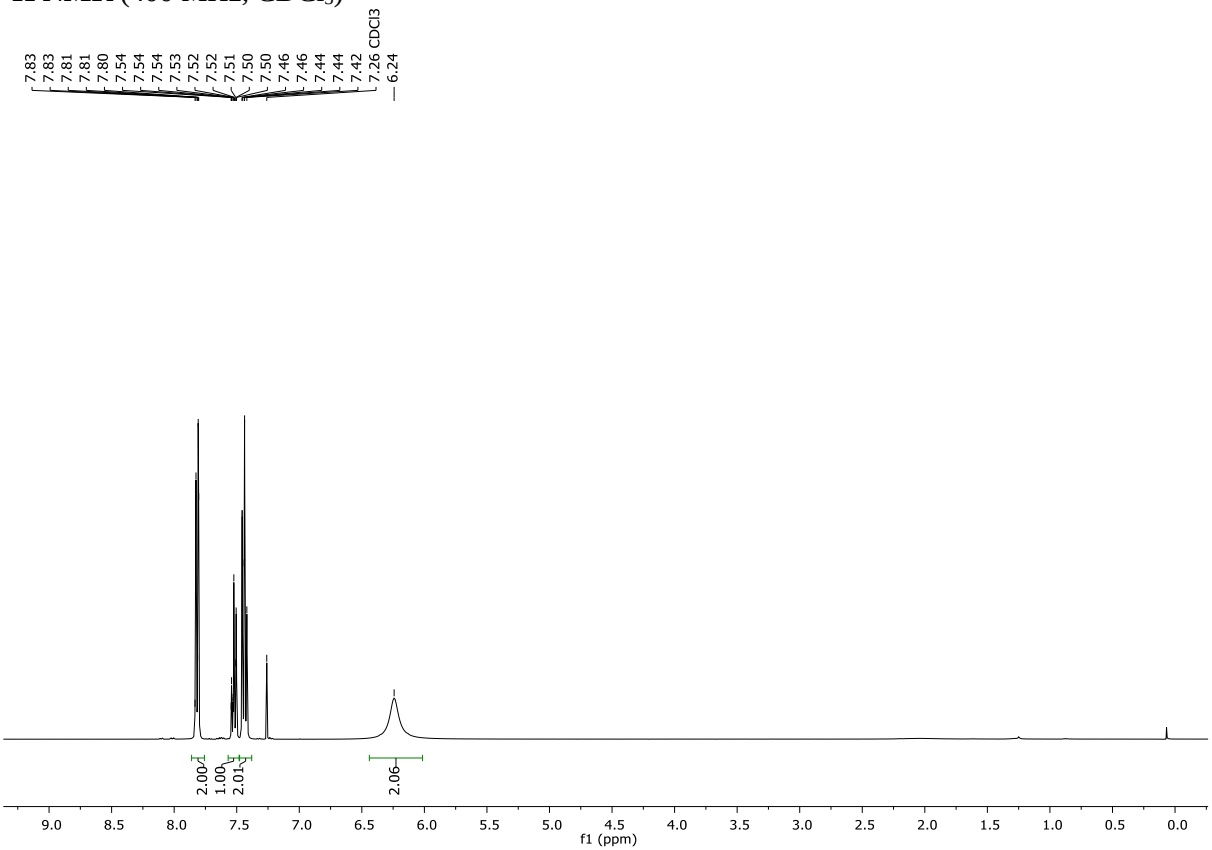
Benzophenone

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



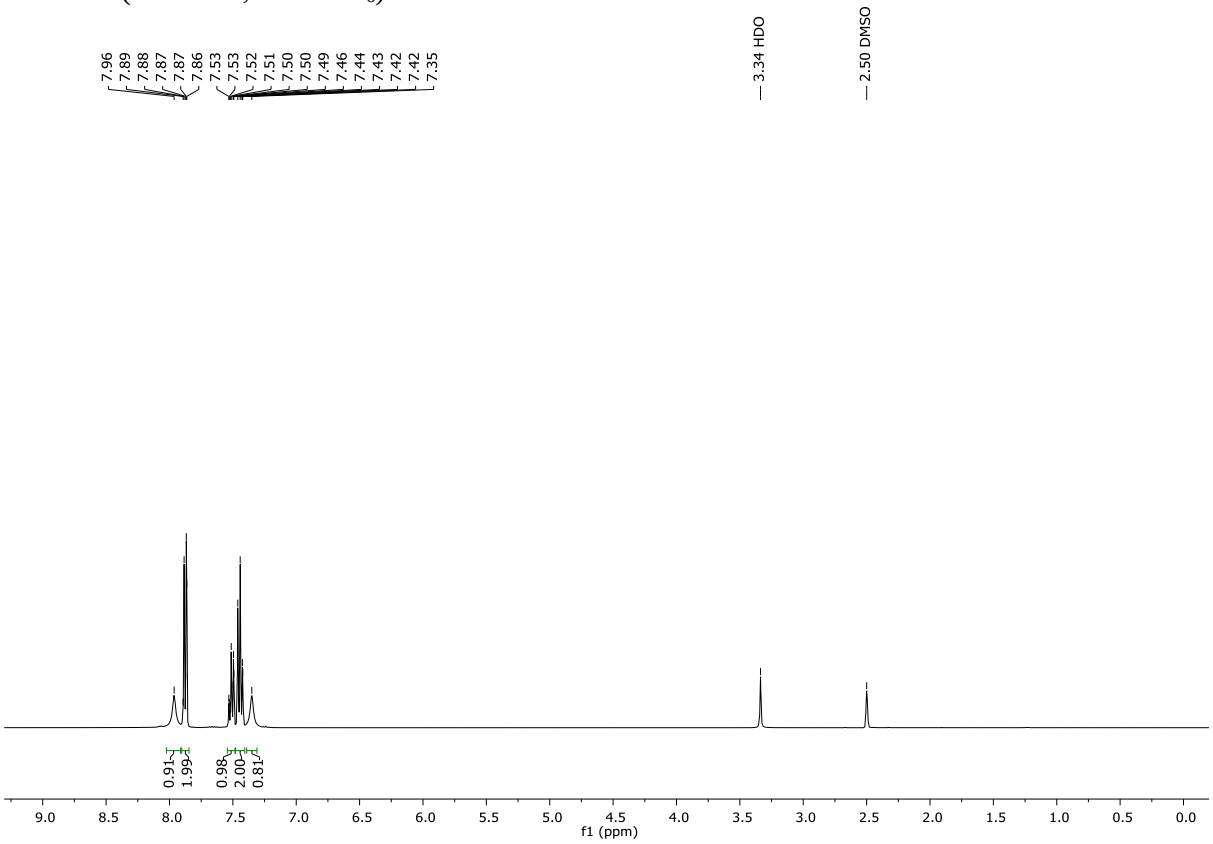
Benzamide

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



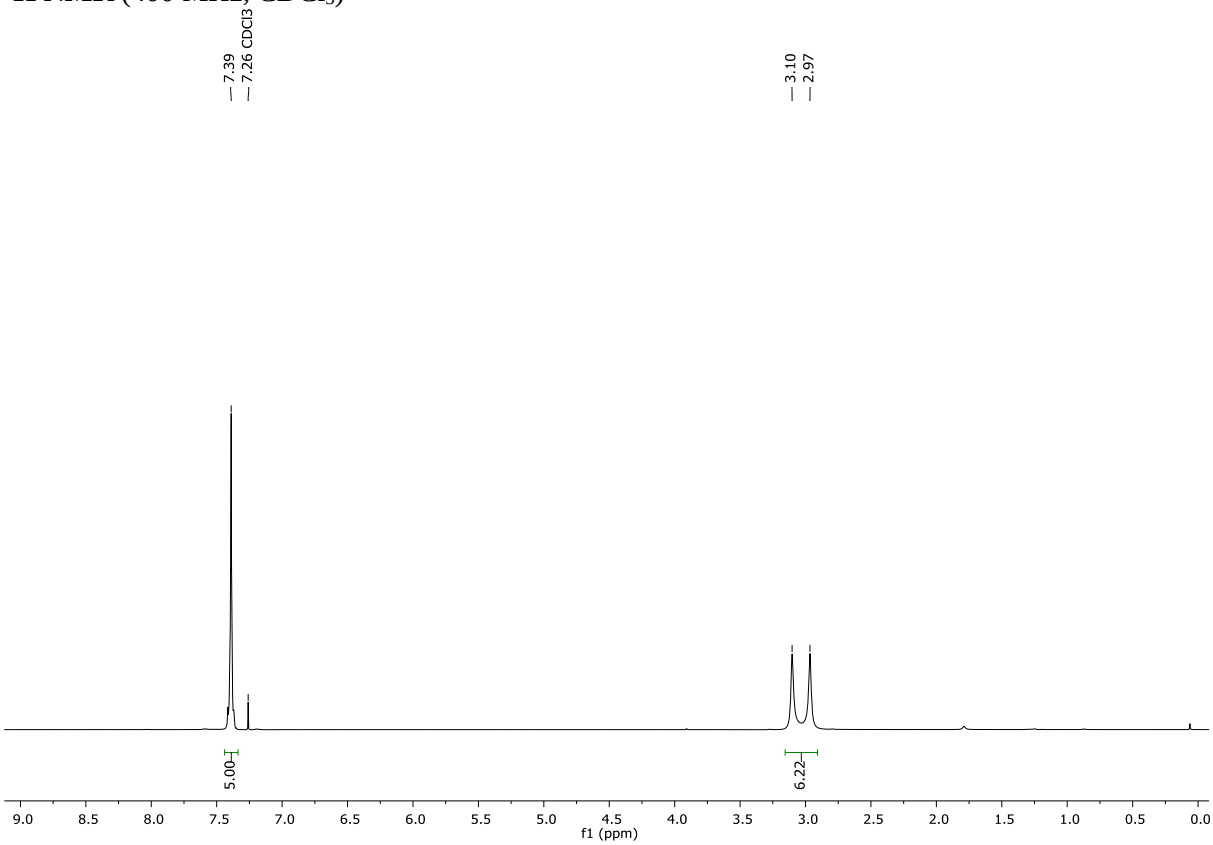
Benzamide

^{1}H NMR (400 MHz, DMSO-d_6)



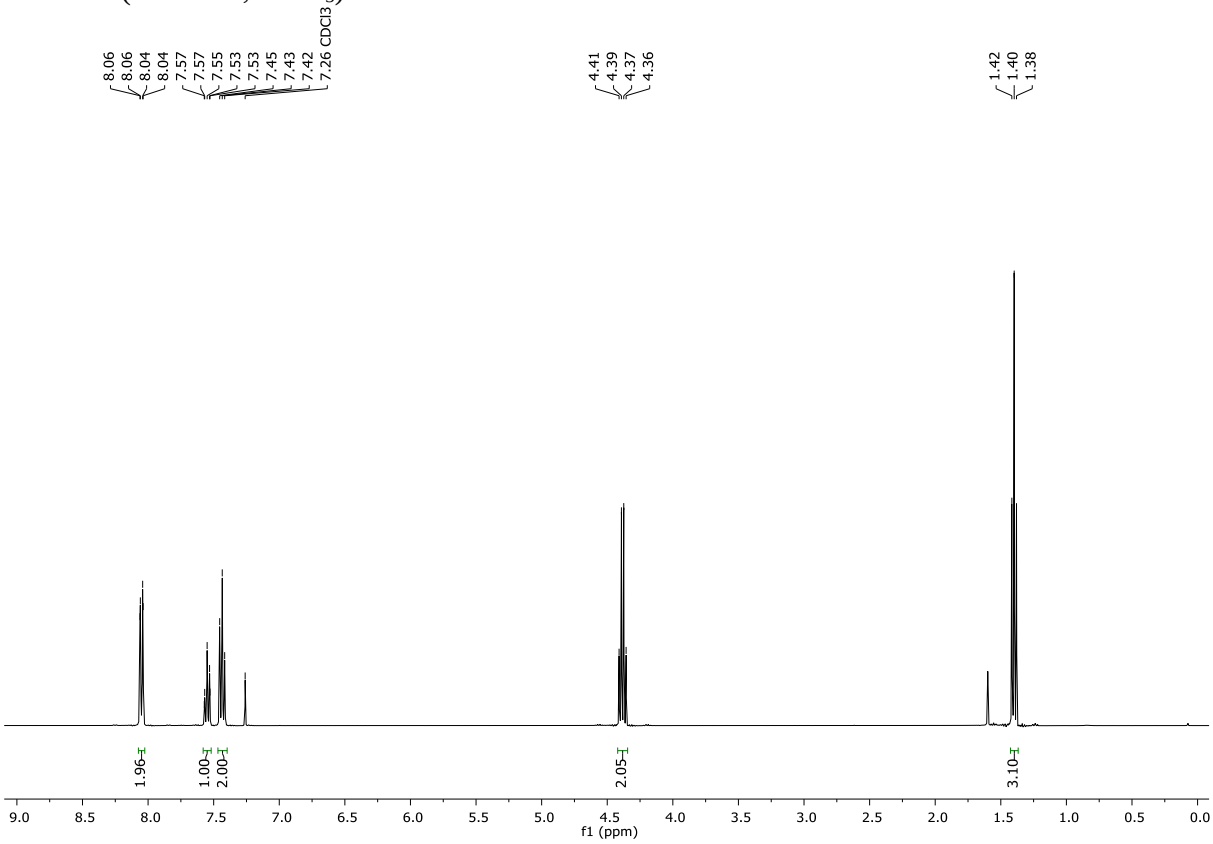
N,N-Dimethylbenzamide

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



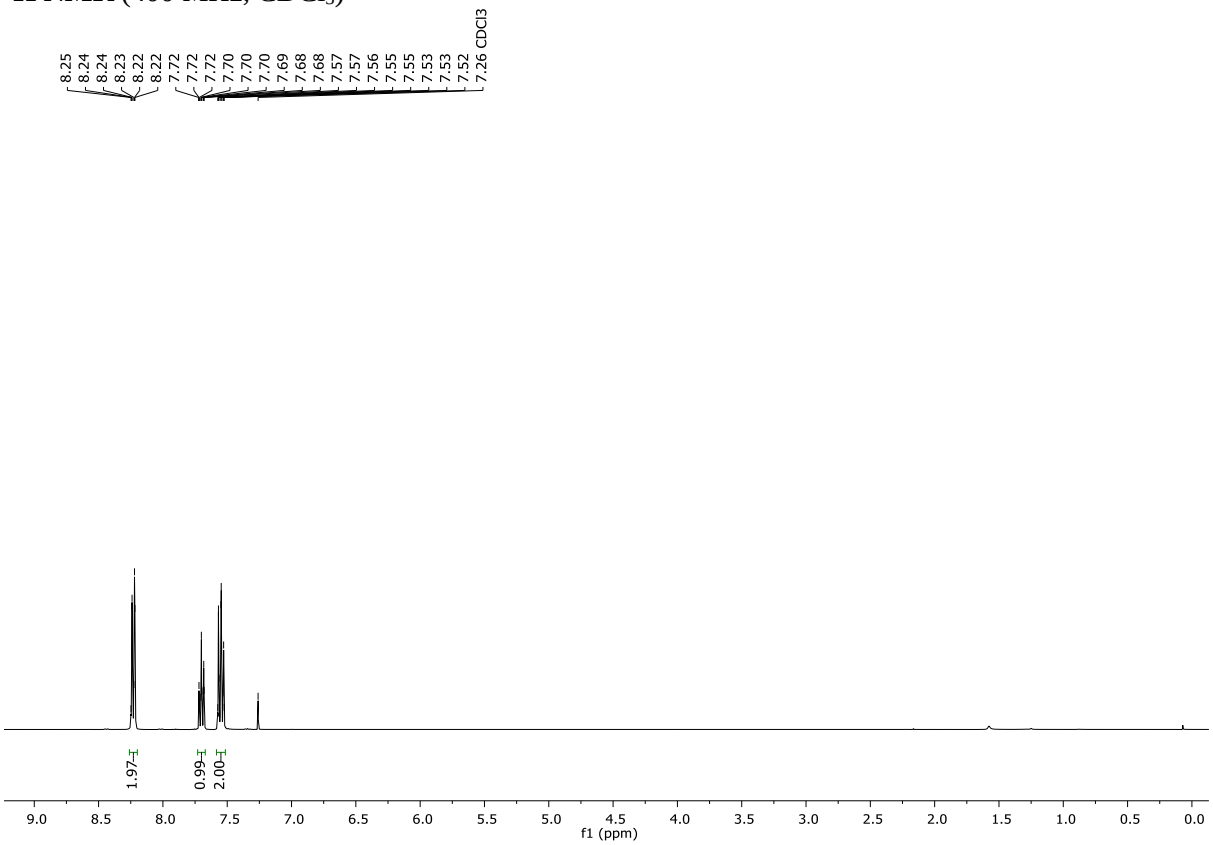
Ethyl benzoate

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



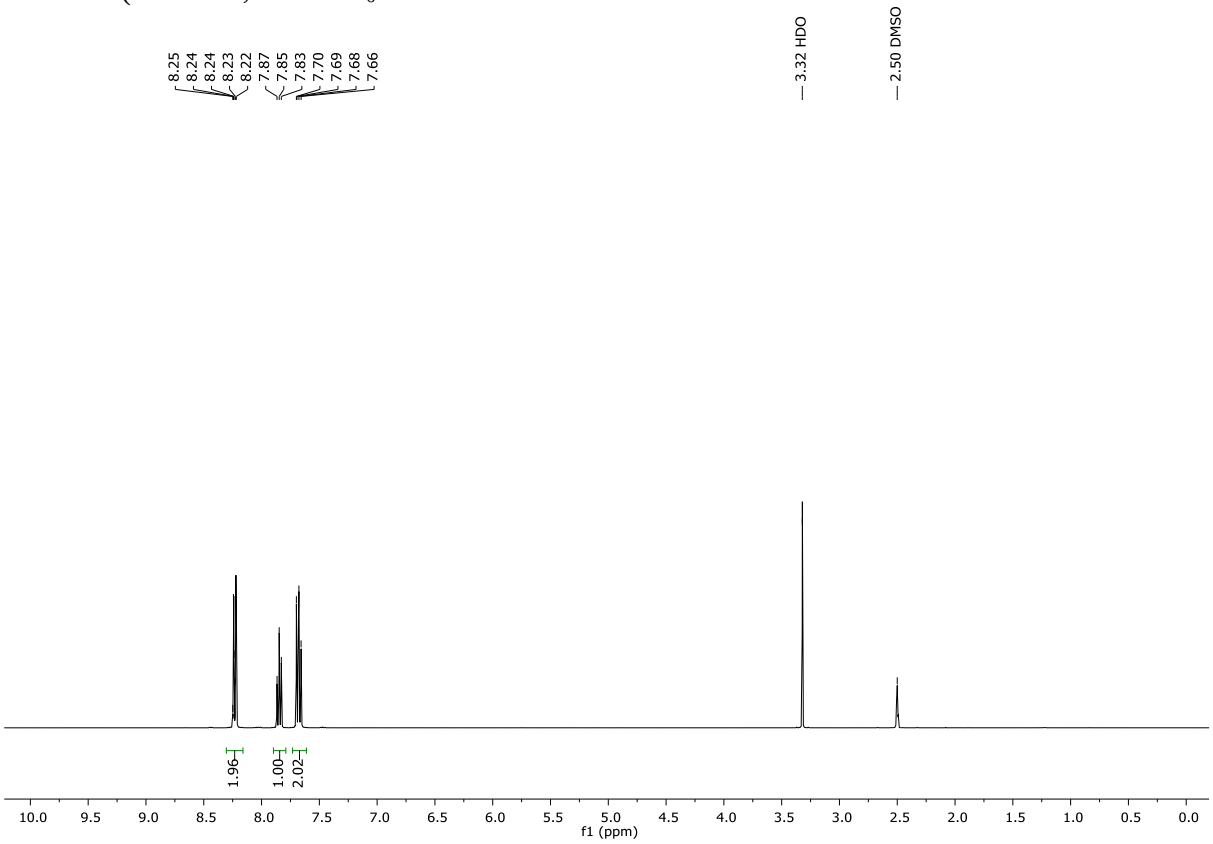
Nitrobenzene

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



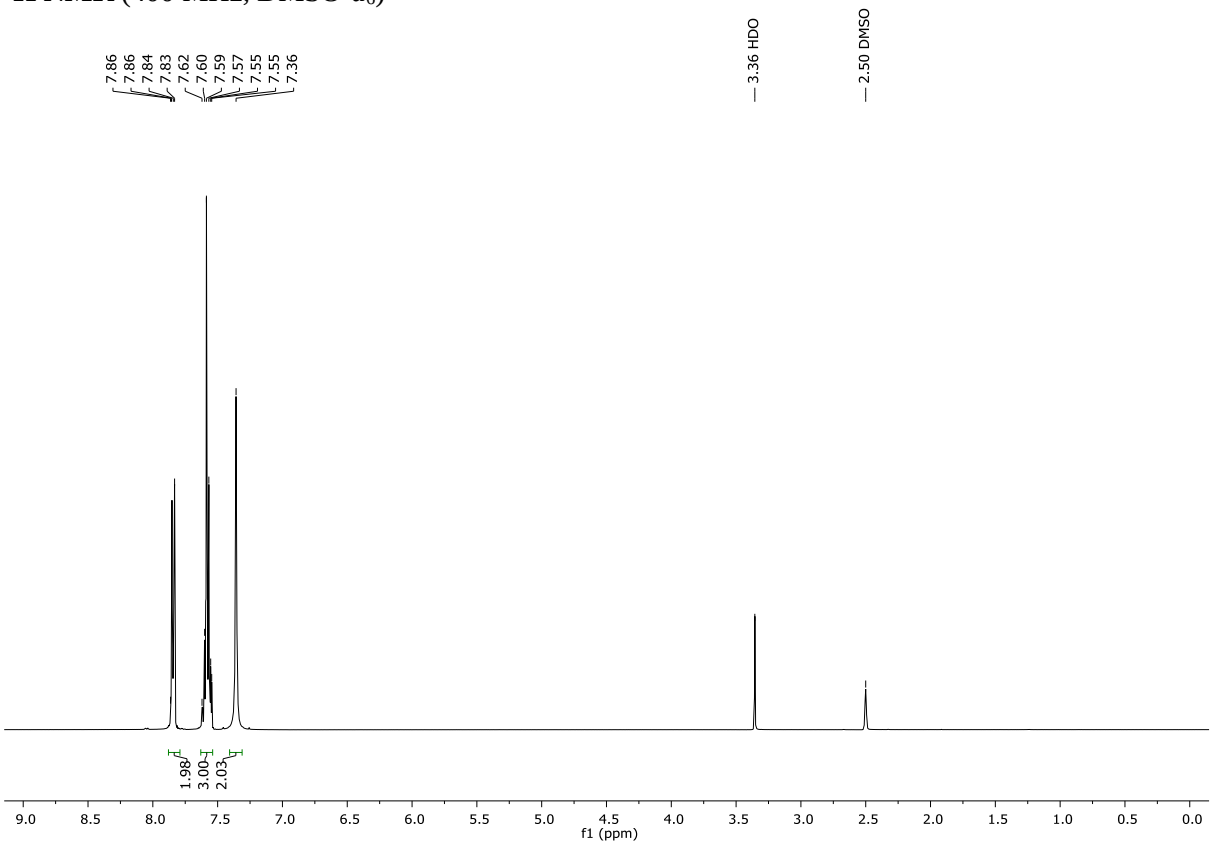
Nitrobenzene

^{1}H NMR (400 MHz, DMSO-d_6



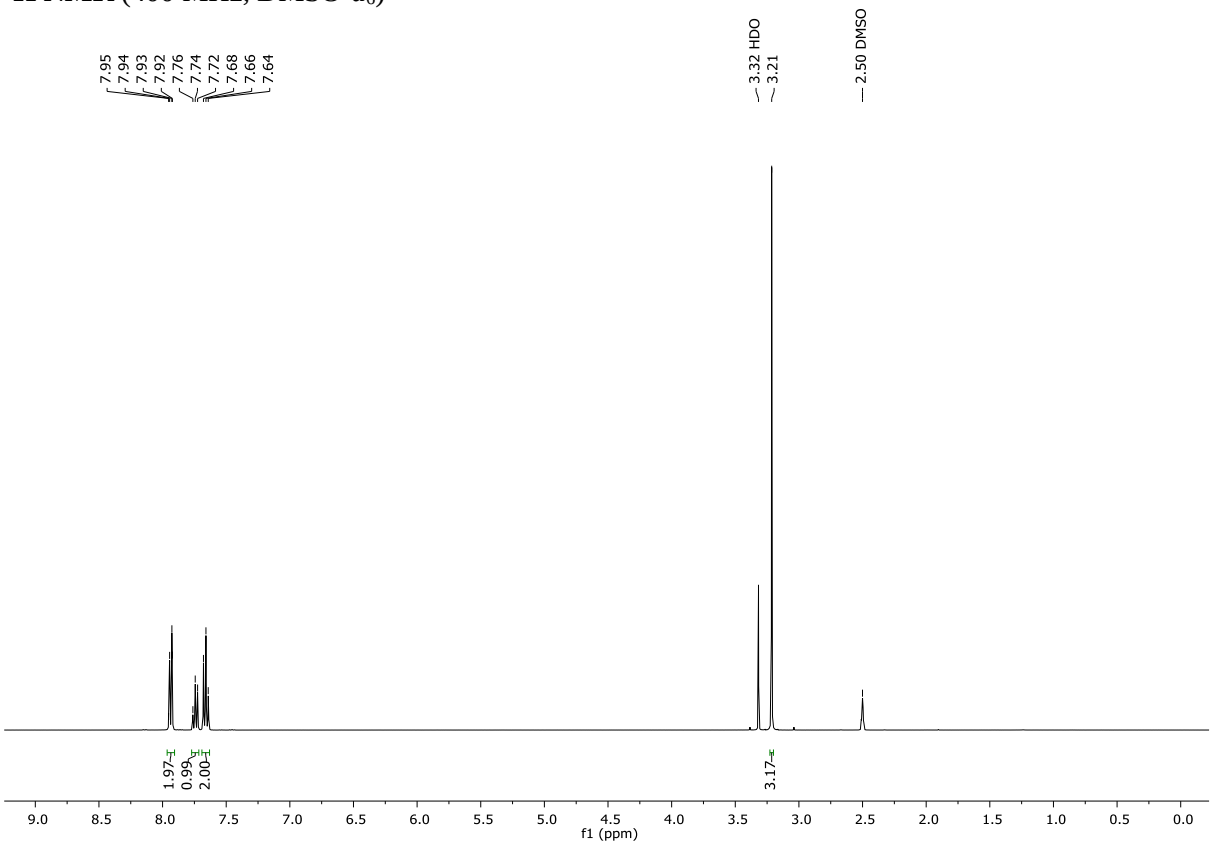
Benzenesulfonamide

^{1}H NMR (400 MHz, DMSO-d_6)



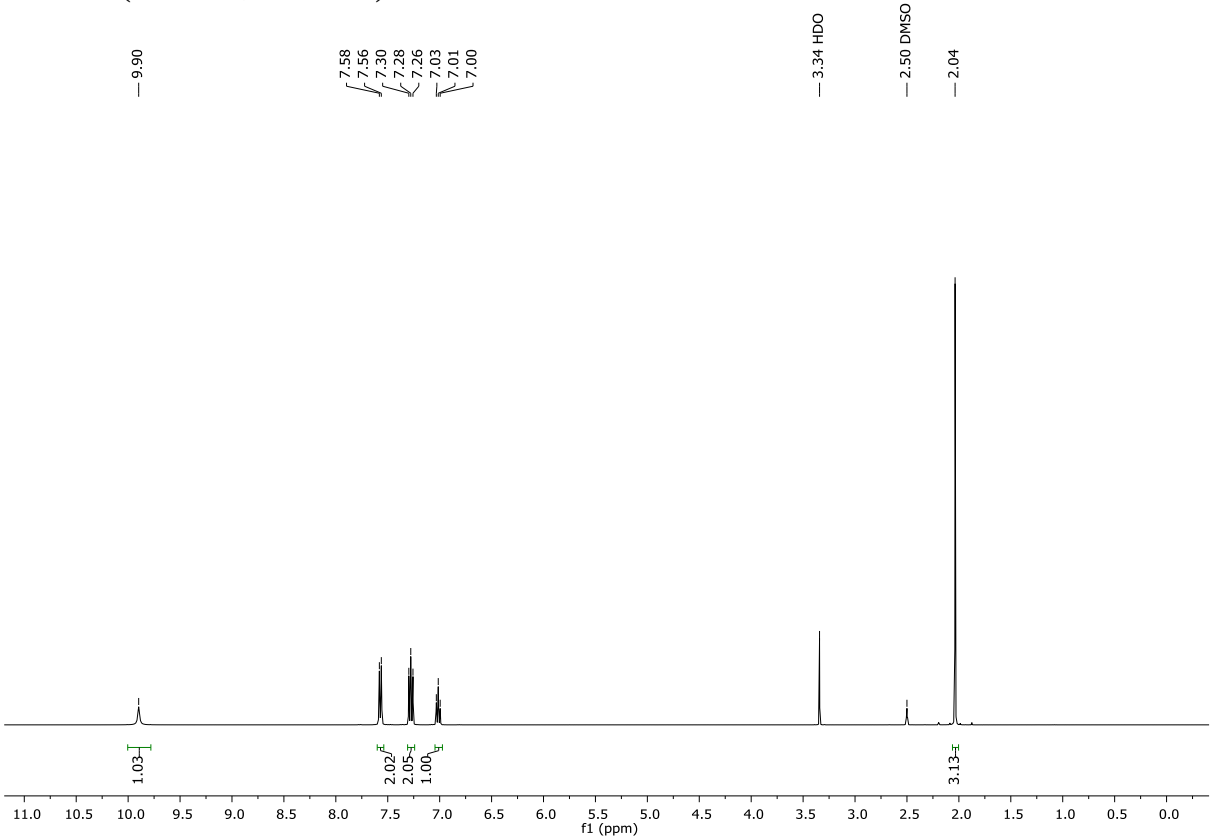
(Methylsulfonyl)benzene

^{1}H NMR (400 MHz, DMSO-d_6)



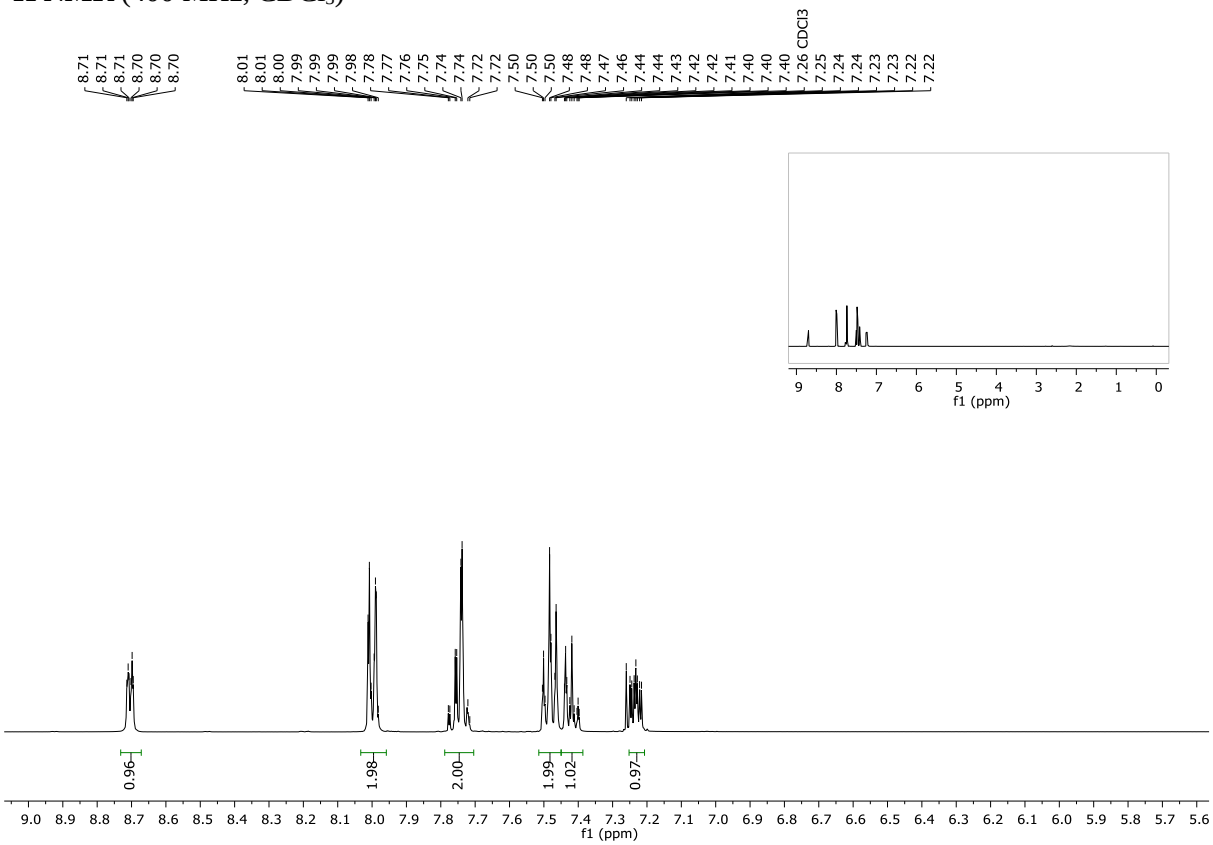
Acetanilide

^{1}H NMR (400 MHz, DMSO-d_6)



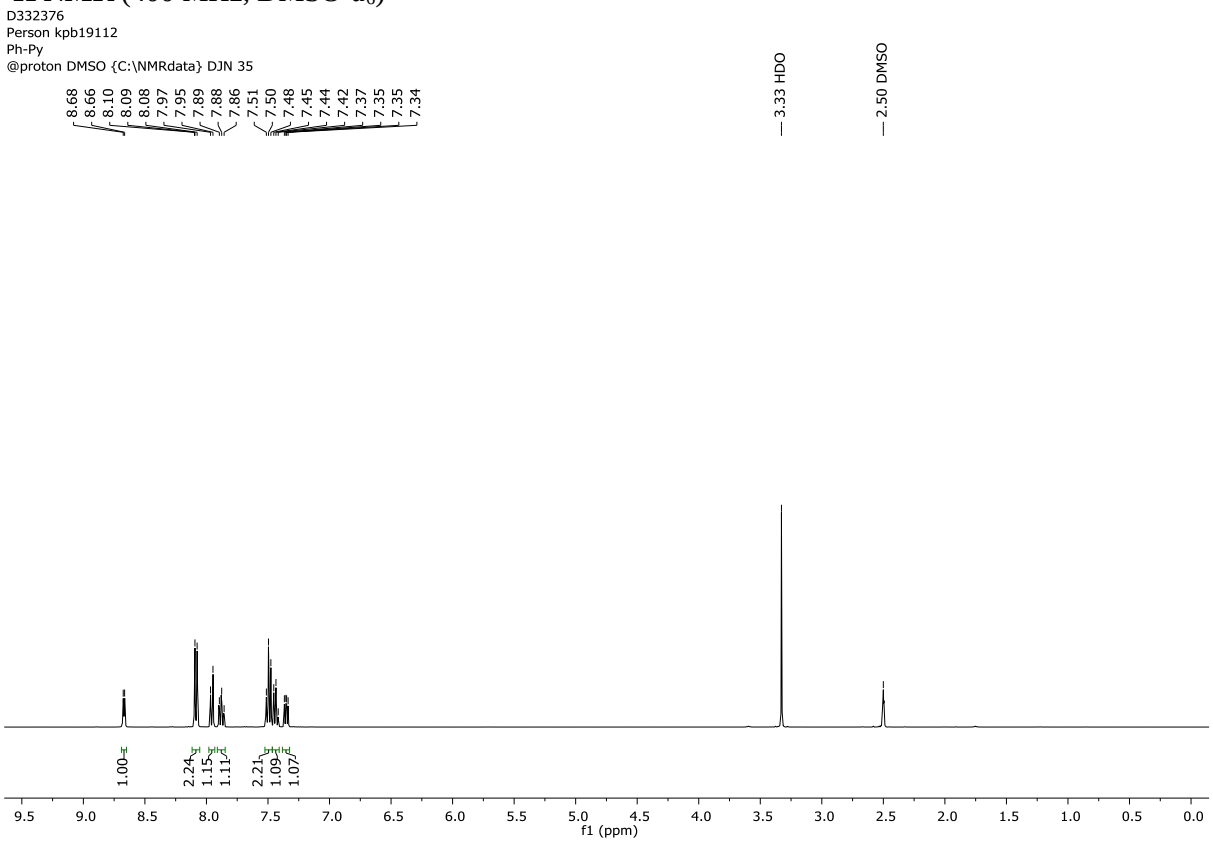
2-Phenylpyridine

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



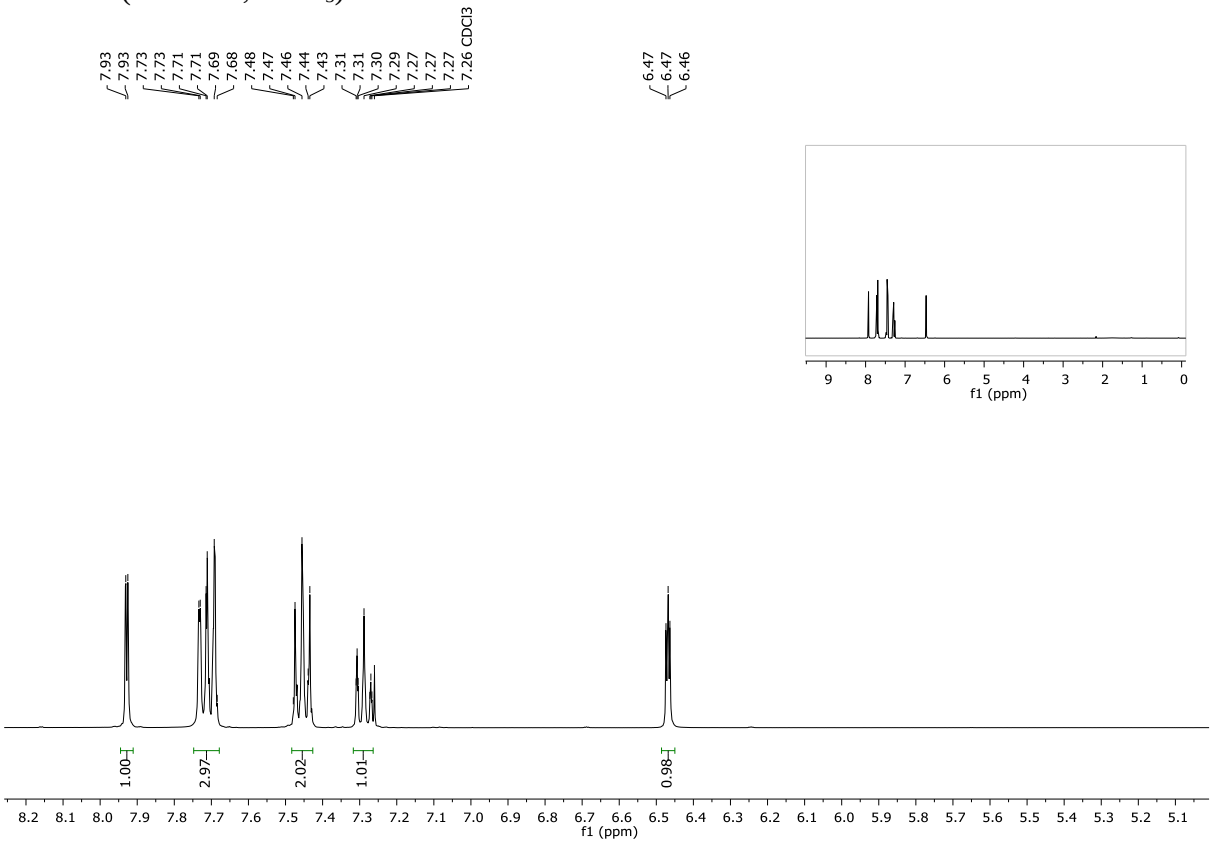
2-Phenylpyridine

^{1}H NMR (400 MHz, DMSO-d_6)



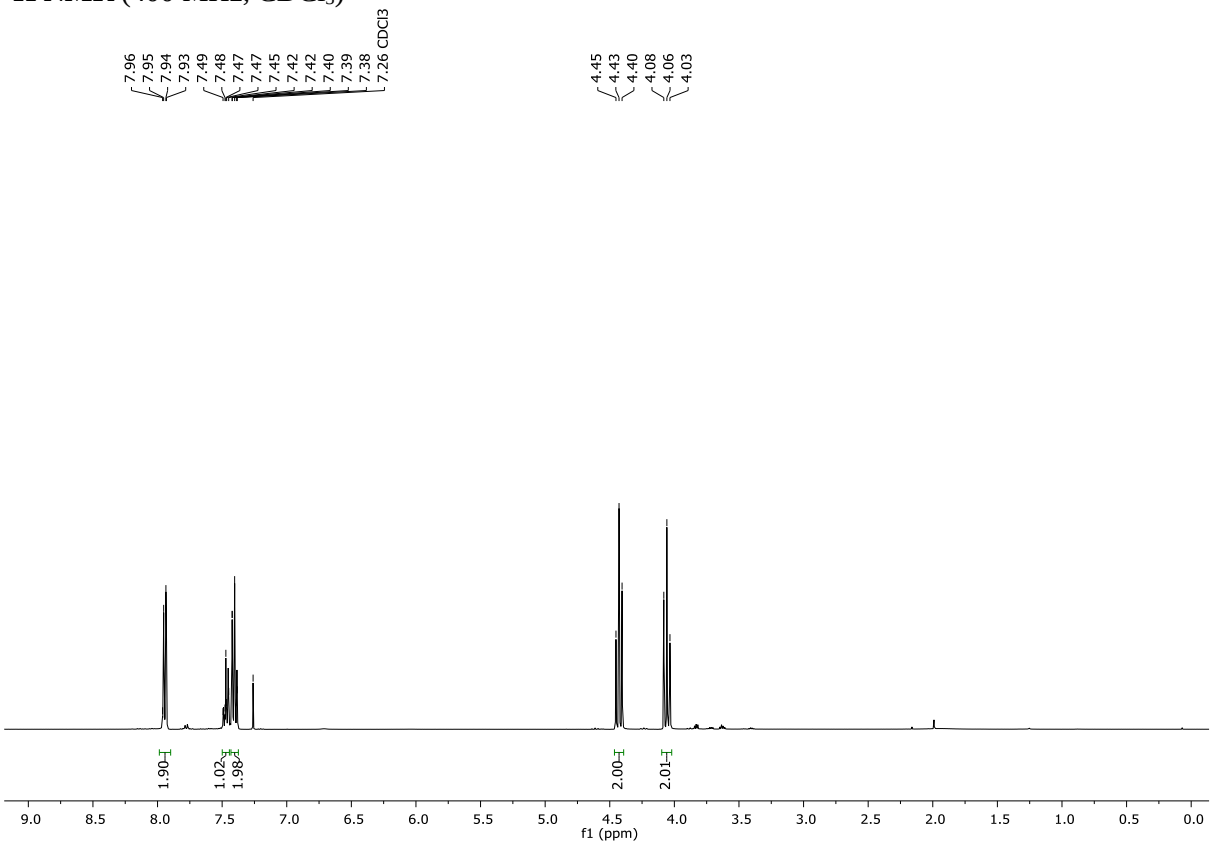
1-Phenylpyrazole

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



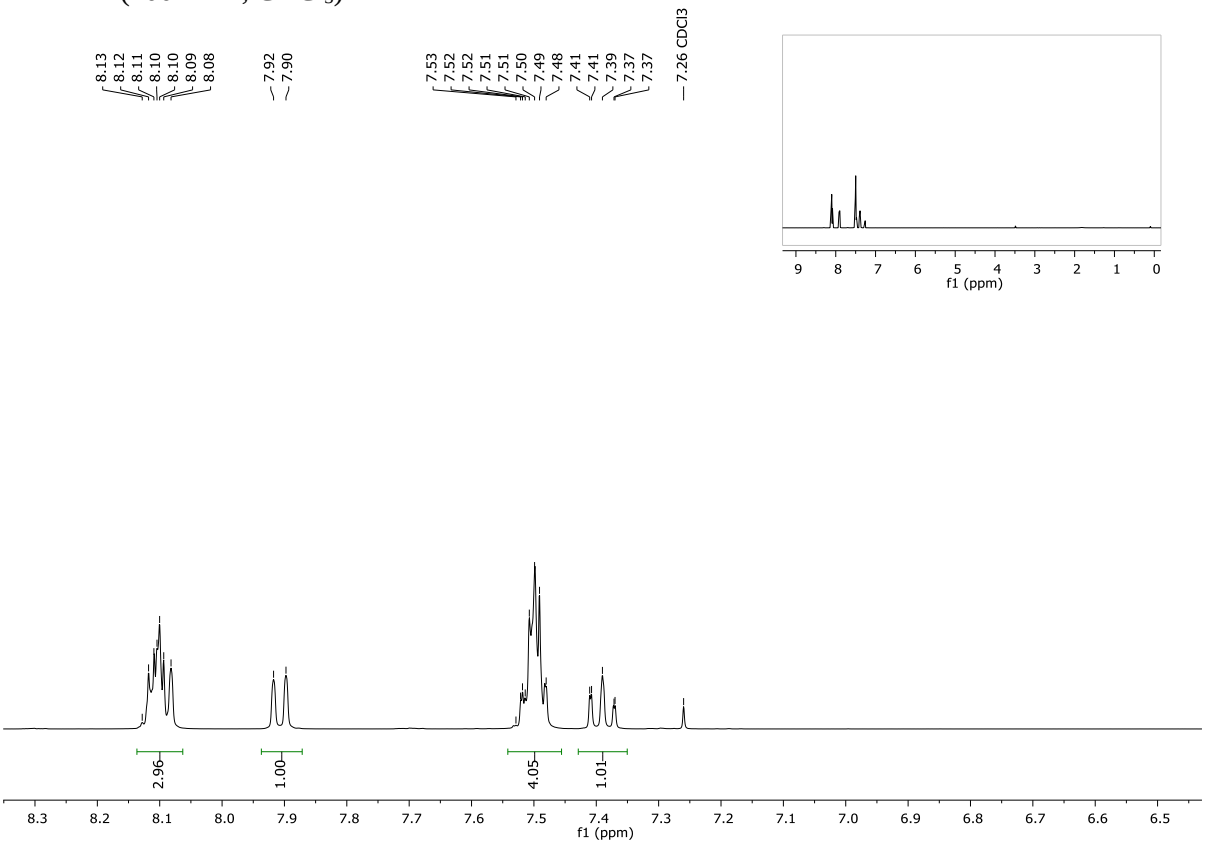
2-Phenyloxozoline

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



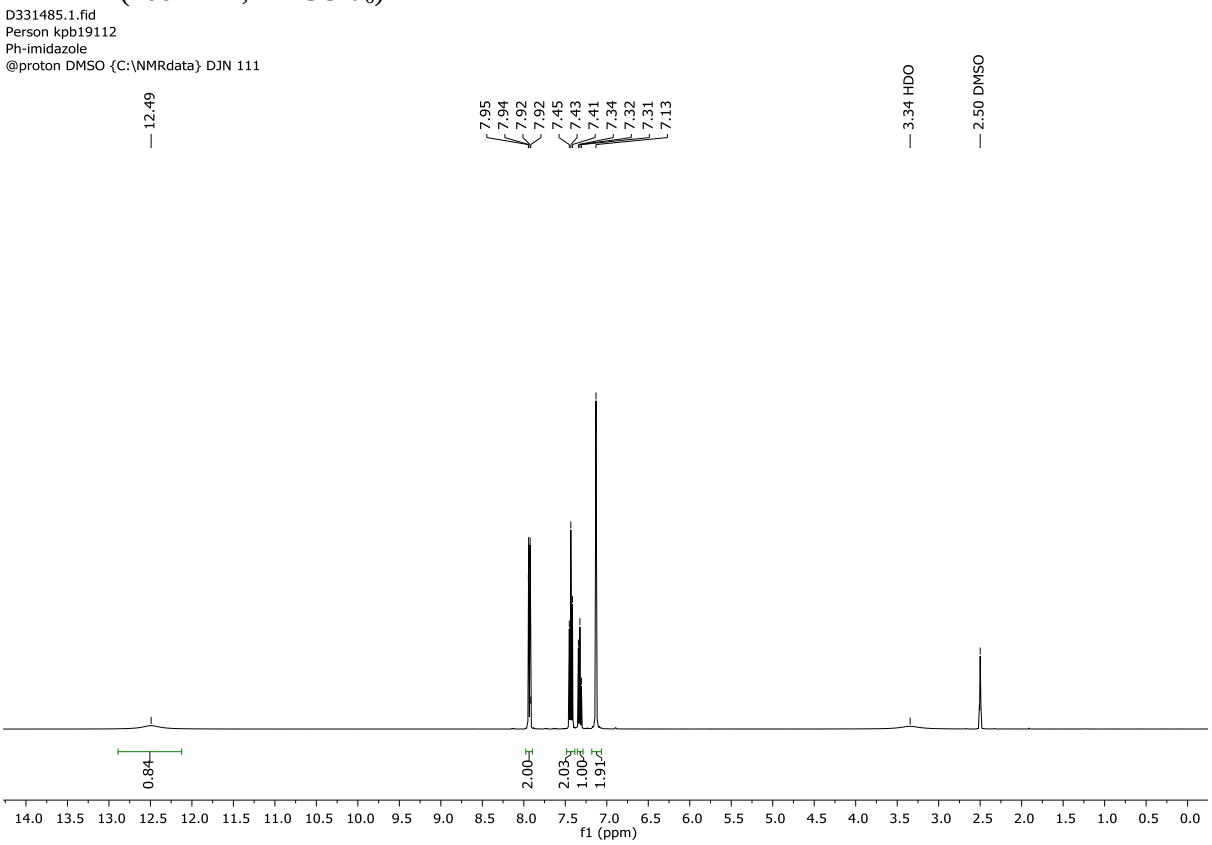
2-Phenylbenzothiazole

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



2-Phenylimidazole

^{1}H NMR (400 MHz, DMSO-d_6)



2-Phenylimidazoline

^{1}H NMR (400 MHz, DMSO-d_6