Copper-catalysed low-temperature water-gas shift reaction for selective deuteration of aryl halides

Wu Li, Ruiyang Qu, Weiping Liu, Florian Bourriquen, Stephan Bartling, Nils Rockstroh, Kathrin Junge,* and Matthias Beller*

Leibniz-Institut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany

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1. General remarks

Unless otherwise stated, reactions were performed in autoclaves. Solvents were used directly without further purification. Gas chromatography was performed on a HP 6890 with a HP5 column (Agilent) unless otherwise stated. NMR spectra were recorded on Bruker AV 300 and 400 spectrometers. All chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane (δ (ppm) = 0.0 for ¹H NMR in CDCl₃) and *d*-solvent peaks (δ (ppm) = 77.00 for ¹³C NMR, chloroform), respectively. Mass spectra were recorded on an AMD 402/3 or a HP 5973 mass selective detector.

The STEM micrographs were acquired at 200kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energydispersive x-ray-spectrometer (EDXS) including a silicon drift detector (dry SD60GV) for chemical analysis. General imaging was done with a high-angle annular dark field (HAADF) and an annular bright field (ABF) detector. The sample was deposited without any pretreatment on a holey carbon supported Ni-grid (mesh 300) and transferred to the microscope in a low background analytic specimen holder with a Be cradle.

The XPS (X-ray Photoelectron Spectroscopy) measurements were performed on an ESCALAB 220iXL (Thermo Fisher Scientific) with monochromated AI K α radiation (E = 1486.6 eV). Samples are prepared on a stainless-steel holder with conductive double-sided adhesive carbon tape. The electron binding energies were obtained with charge compensation using a flood electron source and referenced to the C 1s core level of carbon at 284.8 eV (C–C and C– H bonds). For quantitative analysis, the peaks were deconvoluted with Gaussian-Lorentzian curves using the software Unifit 2021. The peak areas were normalized by the transmission function of the spectrometer and the element specific sensitivity factor of Scofield.

The metal precursor Copper(II) acetate (99%, pure, anhydrous) was obtained from Acros and VULCAN® XC72R (Code XVC72R; CAS No. 1333-86-4) from Cabot Corporation. All reagents were used directly without further purification prior to use.

2. Procedure for the preparation of the catalyst



Carbon = VULCAN (XC72R)

Copper(II) acetate (99%, pure, anhydrous, 364 mg, 2.0 mmol) and 1, 10 phenanthroline monohydrate (Alfa Aesar, \geq 99%, 1188 mg, 6.0 mmol) (Cu:phenanthroline = 1:3 molar ratio) were stirred in ethanol (150 mL)) for 1 hour at 80 °C (rt to 80 °C). Then, carbon powder (4.0 g) (VULCAN® XC72R, Cabot Corporation Prod. Code XVC72R; CAS No. 1333-86-4) was added and the mixture was stirred at 80 °C for 15 hours. At the end of the reaction, the reaction mixture was cooled to room temperature and the ethanol was removed *in vacuo*. The black solid sample was dried under an oil pump vacuum for 6 hours, after which it was grinded to a fine powder. Then, the grinded powder was transferred into a ceramic crucible and placed in an oven (see below). The oven was evacuated to ca. 5 mbar and then flushed with argon, which was heated to 800 °C at a rate of 25 °C per minute and held at 800 °C for 2 hours under argon atmosphere. Then, heating was switched off and the oven allowed to cool to room temperature. During the whole process argon was constantly passed through the oven. (Elemental analysis: Cu= 2.4 wt%, C=78.0 wt%, H=0.3 wt%, N=1.6 wt%)



3. General procedure for deuteration (GPI)

In a 4 mL vial fitted with magnetic stirring bar and septum cap, copper catalyst (Cu-phen/C-800, 40 mg, 6 mol%) and substrate (0.25 mmol) were added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. After adding the solvent deuterium oxide (1.5 mL) and Et₃N (51 mg, 0.5 mmol), the vials (up to eight) were set in an alloy plate and then placed into a 300 mL steel Parr autoclave. The autoclave was flushed with carbon monoxide 6 times at 10 bar and finally pressurized to the desired value (40 bar). Then, it was placed into an aluminum block and heated to the desired temperature (120 °C). At the end of the reaction, the autoclave was quickly cooled down to room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and ethyl acetate was added to the crude benchmark reaction mixture as internal standard. The reaction mixture was centrifuged (see below), and the organic layer was analyzed at the GC-FID. In the other (hetero)arylhalides, the desired deuterated products were isolated by silica gel column chromatography (*n*-heptane/ethyl acetate mixtures=100/1).



4. General procedure for the large scale deuteration (GPII)

In a 300 mL steel Parr autoclave, Cu-phen/C-800 (4.8 g, 1.8 mmol Cu, 1.8 mol%) and substrate (100 mmol) were added. After adding deuterium oxide (100 mL) and Et_3N (20.2 g, 200 mmol, 2.0 eq.), the autoclave was flushed with carbon monoxide 6 times at 10 bar and finally

pressurized to the desired value (50 bar). Then, it was placed into an aluminum block and heated to the desired temperature (130 °C). Carbon monoxide was re-flushed every 12 h in case of the pressure decreasing (due to the gas consumption). At the end of the reaction, the autoclave was quickly cooled down to room temperature with an ice bath and vented. Finally, the mixture was removed from the autoclave, and ethyl acetate was added to the crude mixture for organic compounds extraction. In the cases of deuterated aniline-*d*, anisole-*d*, phenol- d_3 , anisole-*d*, benzaldehyde-*d*, the products were isolated by distillation.



Equipment for distillation

5. Reaction development and optimization

Table S1. Catalyst screening^a

	Br	[M] _{Cat.} (6 mol%)		₽
	MeO	CO, D ₂ O, Et ₃ N 120 °C, 24 h	MeO	
Entry	Catalyst	Additives	Temperature (°C)	Yield (%) ^b
1	Ru ₃ (CO) ₁₂	-	140	0
2	$Ru_3(CO)_{12}$	Xantphos	140	0
3	$Ru_3(CO)_{12}$	PPh ₃	140	0
4	Ru(acac) ₃	-	140	0
5	Ru(acac) ₃	Xantphos	140	0
6	RhH(CO)(PPh ₃) ₃	-	140	0
7	Cu(OAc) ₂	-	140	trace
8	Cu(OTf) ₂	-	140	trace
9	Cu(OAc) ₂	Phen	140	trace
10	Cu(OAc) ₂	PPh ₃	140	0
11	Cu(OAc) ₂	Xantphos	140	0
12	CuO	-	140	trace
13	Cu/Al ₂ O ₃ -800	-	140	16
14	Cu-phen/Al ₂ O ₃ -800	-	140	0
15	Co-phen/C-800	-	140	0
16	Co-Mel/TiO ₂	-	140	0
17	Fe-phen/C-800	-	140	9
18	Mn-phen/C-800	-	140	0
19	Ni-phen/SiO ₂ -800	-	140	0
20	Ni-phen/SiO ₂ -1000	-	140	0
21	Cu/C-800	-	140	trace
22	Cu-phen/C-800	-	140	77
23	Cu-phen/C-600	-	140	57
24	Cu-phen/C-900	-	140	43
25	Cu-phen/C-1000	-	140	28
26	Cu-phen/C-800 (5 °C/min)	-	140	63
27	Cu-phen/C-800	-	120	73
28	Cu-phen/C-800	-	120	92°
29	Pd/C	-	120	0 ^c
30	Pt/C	-	120	12°
31	Rh/C	-	120	0 <i>c</i>
32	Ru/C	-	120	0 <i>c</i>
33	Lindlar catalyst	-	120	13°
34	CuO/ZnO/Al ₂ O ₃ ^c	-	120	0 <i>c</i>
35	-	-	120	0 <i>°</i>

^aStandard conditions: 2-bromo-6-methoxynaphthalene (0.25 mmol, 1 equiv.), [M] catalyst (6 mol%), D₂O (1.5 mL), 40 bar CO, 120 °C, 24 h. ^bYields determined by GC-FID using *n*-dodecane as an internal standard. ^cCopper-based methanol synthesis catalyst. ^c48 h.

6. The measurement of CO₂ by GC

In a 300 mL steel Parr autoclave, Cu-phen/C-800 (4.8 g, 1.8 mmol Cu, 3.6 mol%) and 3bromoanisole (50 mmol) were added. After adding deuterium oxide (100 mL) and Et₃N (20.2 g, 200 mmol, 2.0 eq.), the autoclave was flushed with carbon monoxide 6 times at 10 bar and finally pressurized to the desired value (50 bar). Then, it was placed into an aluminum block and heated to the desired temperature (120 °C) and stay at 120 °C for 3 hours. Then, the autoclave was connected to a GC gas line for measurement and CO and CO₂ was detected (see below).

Data File C:\CHEM32\1\DATA\2020\2007\200703\SIG1004806.D
Sample Name: wu-8-362



7. Catalyst characterization by XPS and STEM

Photoelectron spectroscopy measurements have been applied to determine the oxidation state of copper. In Fig. S1 the Cu 2p spectra of the fresh catalyst, after one run, and after five runs is shown. The spectra consist of the Cu 2p3/2 and Cu 2p1/2 peaks around 933 eV and 953 eV, respectively. Additionally, a complex satellite peak structure depending on the oxidation state can be found from 940 eV to 945 eV as well as around 963 eV. In all three spectra two main Cu 2p3/2 peaks at 932.3 eV and 934.7 eV can be observed which are characteristic for Cu¹⁺/Cu⁰ and Cu²⁺ with its pronounced satellite features between 940 eV and 945 eV (M.C. Biesinger, Advanced Analysis of Copper X-ray Photoelectron (XPS) Spectra, *Surf. Interface Anal.* 49 (2017) 1325-1334). Unfortunately, Cu¹⁺ and Cu⁰ have nearly the same peak position so that a clear distinction is not possible. However, in the fresh catalyst only a small portion is present as Cu¹⁺/Cu⁰ and the dominating valence state seems to be 2+. After one run (Fig. S1b) the relative amount of Cu¹⁺/Cu⁰ increases and reaches its maximum after the fifth run so that a reduction of Cu²⁺ happens during the use of the catalyst. Furthermore, the surface concentration of Cu changes from 0.4 at.% for the fresh catalyst to 0.6 at.% after the first run to 0.3 at.% after the fifth run.



Fig. S1: High resolution XPS Cu 2p spectra of the fresh (a) catalyst, after one (b), and after 5 runs (c).



Fig. S2. Selected HAADF-STEM images of Cu-phen/C-800 after one use. It can be seen that the copper particles are smaller than in fresh Cu-phen/C-800.



Fig. S3. Selected EDX spectra of the marked areas of Cu-phen/C-800 after one use (left) are shown on the right. As expected, the brighter particle contains copper (spectrum 002), while it is negligible in the support. Moreover, comparison of the oxygen signals in both spectra reveals a higher intensity in the presence of copper, implying that copper is present in oxidic form(s).



Fig. S4. Selected HAADF-STEM images of Cu-phen/C-800 after five uses. Compared to fresh Cu-phen/C-800 and Cu-phen/C-800 after one use, the number of smaller copper containing particles seems increased.



Fig. S5. Selected EDX spectra of the marked areas of Cu-phen/C-800 after five uses (left) are shown on the right. Again, the brighter particle contains some copper (spectrum 001), while it is negligible in the support. The oxygen signal in the presence of copper is lower compared to the sample after 1 run, but also some sulfur could be found, which very likely stems from Vulcan XC72R. Based on this observation, copper could be present either in metallic or sulfidic form.



Catalysts Cu-phen/C-800 Cu/C-800 Cu-melamine/C-800	Yield (%) ^b					
Cu-phen/C-800	73					
Cu/C-800	trace					
Cu-melamine/C-800 49						
^a Conditions: 0.25 mmol substrate, 40 mg cata ^o C, 24 h. ^b Yields determined by GC-FID using	alyst, 51 mg NEt ₃ ,1.5 mL D ₂ O, 40 bar CO, 120 n -dodecane as an internal standard.					

8. Kinetic isotope effect investigations

All the experiments below used the same batch of copper catalyst and D_2O from the same bottle.



Fig. S6. Kinetic profile

In a 50 mL steel Parr autoclave (see above) loaded with Cu-phen/C catalyst (800 mg, 0.3 mmol), 3-bromoanisole (1000 mg, 5.3 mmol) and deuterium oxide 30.0 mL (1650 mmol) were added. The autoclave was flushed with CO 6 times at 10 bar and finally pressurized to the desired value (50 bar). Then, it was it placed into an equipment for the autoclave and heated to 120 °C (about 10 min). The first sample was taken 30 min after heating. Then, the other 8 samples were taken in 11 h, and ethyl acetate was added to the crude mixture. The reaction mixture was centrifuged, and the organic layer was analyzed at the GC-FID. Yields determined by GC-FID using *n*-hexadecane as an internal standard (see below).

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Primary KIE and secondary KIE

Fig. S7. Primary KIE and secondary KIE.

Primary kinetic isotope effects (both reactions are performed under identical conditions)

kD

Fig S8. Primary kinetic isotope effect

General procedure:

In a 50 mL steel Parr autoclave (see above) loaded with Cu-phen/C catalyst (800 mg, 0.3 mmol), 3-bromoanisole (1000 mg, 5.3 mmol) and deuterium oxide 30.0 mL (1650 mmol) were added. The autoclave was flushed with CO 6 times at 10 bar and finally pressurized to the desired value (50 bar). Then, it was it placed into an equipment for the autoclave and heated to 120 °C (about 10 min). The first sample was taken 20 min after heating. Then, the other 8 samples were taken in every 10 min, and ethyl acetate was added to the crude mixture. The reaction mixture was centrifuged, and the organic layer was analysed at the GC-FID. Yields determined by GC-FID using *n*-hexadecane as an internal standard (see below).

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General procedure:

In a 50 mL steel Parr autoclave (see above) loaded with Cu-phen/C catalyst (800 mg, 0.3 mmol), 3-bromoanisole (1000 mg, 5.3 mmol) and deuterium oxide 30.0 mL (1650 mmol) were added. The autoclave was flushed with CO 6 times at 10 bar and finally pressurized to the desired value (50 bar). Then, it was it placed into an equipment for the autoclave and heated to 120 °C (about 10 min). The first sample was taken 20 min after heating. Then, the other 8 samples were taken in every 10 min, and ethyl acetate was added to the crude mixture. The reaction mixture was centrifuged, and the organic layer was analyzed at the GC-FID. Yields determined by GC-FID using *n*-hexadecane as an internal standard (see below).

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Secondary KIE (both reactions are performed under identical conditions)

Fig. S9. Secondary kinetic isotope effect

General procedure:

In a 50 mL steel Parr autoclave (see above) loaded with Cu-phen/C catalyst (800 mg, 0.3 mmol), 4-bromoaniline (1066 mg, 6.2 mmol) and deuterium oxide 30.0 mL (1650 mmol) were added. The autoclave was flushed with CO 6 times at 10 bar and finally pressurized to the desired value (50 bar). Then, it was it placed into an equipment for the autoclave and heated to 120 °C (about 10 min). The first sample was taken 10 min after heating. Then, the other 8 samples were taken in every 10 min, and ethyl acetate was added to the crude mixture. The reaction mixture was centrifuged, and the organic layer was analyzed at the GC-FID. Yields determined by GC-FID using *n*-hexadecane as an internal standard (see below).

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In a 50 mL steel Parr autoclave loaded with Cu-phen/C catalyst (800 mg, 0.3 mmol), 4bromoaniline-2,6- d_2 (1079 mg, 6.2 mmol) and deuterium oxide 30.0 mL (1650 mmol) were added. The autoclave was flushed with CO 6 times at 10 bar and finally pressurized to the desired value (50 bar). Then, it was it placed into an equipment for the autoclave and heated to 120 °C (about 10 min). The first sample was taken 10 min after heating. Then, the other 8 samples were taken in every 10 min, and ethyl acetate was added to the crude mixture. The reaction mixture was centrifuged, and the organic layer was analyzed at the GC-FID. Yields determined by GC-FID using *n*-hexadecane as an internal standard (see below). Print of window 38: Current Chromatogram(s)

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9. Procedure for catalyst recycling (48 h)

In a 4 mL vial fitted with magnetic stirring bar and septum cap, copper catalyst (40 mg) and 2bromo-6-methoxynaphthalene (0.25 mmol) were added, independently. Then, a needle was inserted in the septum which allows gaseous reagents to enter. D₂O (1.5 mL) was added. The vials (up to eight) were set in an alloy plate and then placed into a 300 mL steel Parr autoclave. The autoclave was flushed with CO 6 times at 10 bar and finally pressurized to the desired value (40 bar). Then it was placed into an aluminium block and heated to the desired temperature (120 °C) from room temperature. The reaction was stirred for 48 hours at 120 °C. At the end of the reaction, the autoclave was quickly cooled down to room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and ethyl acetate was added. Dodecane (85 mg, 0.5 mmol) was added to the crude benchmark reaction mixture as internal standard. The reaction mixture was centrifuged, and the organic layer was analysed at the GC-FID. The catalyst was washed with ethanol and centrifuged for three times for regeneration. The ICP-MS results are summarized in section 10 and copper leaching into the liquid phase was observed with this heterogeneous copper catalyst. Additionally, no further reaction was observed, when the copper catalyst was filtered off and another 0.25 mmol of 2bromo-6-methoxynaphthalene was added to the solvent. Hence, the catalytically active species should not be derived from the leached copper.

Fig. S10. Catalyst recycling in 48 h

Procedure for catalyst recycling (6 h)

In order to see initial activity, we performed the catalyst recycling at low conversion regions. In a 4 mL vial fitted with magnetic stirring bar and septum cap, copper catalyst (40 mg) and 2bromo-6-methoxynaphthalene (0.25 mmol) were added, independently. Then, a needle was inserted in the septum which allows gaseous reagents to enter. D_2O (1.5 mL) was added. The vials (up to eight) were set in an alloy plate and then placed into a 300 mL steel Parr autoclave. The autoclave was flushed with CO 6 times at 10 bar and finally pressurized to the desired value (40 bar). Then it was placed into an aluminium block and heated to the desired temperature (120 °C) from room temperature. The reaction was stirred for 6 hours at 120 °C. At the end of the reaction, the autoclave was quickly cooled down to room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and ethyl acetate was added. Dodecane (85 mg, 0.5 mmol) was added to the crude benchmark reaction mixture as internal standard. The reaction mixture was centrifuged, and the organic layer was analysed at the GC-FID. The catalyst was washed with ethanol and centrifuged for three times for regeneration.

Fig. S11. Catalyst recycling in 6 h

10. ICP-OES analysis

ICP-OES (inductively coupled plasma optical emission spectrometry) for quantification analysis: Varian/Agilent 715-ES

In order to test the leaching of the catalyst, ICP-OES was performed (See below). Copper leaching could be observed from Table S3.

Table S3. ICP-OES results of the solution above after using (Section 9)

ICP-(DES ENERGEBNIS					
FILTER:		Wu, Li	9613		9619	*
ICP-Nr	Probe		EI El	r gebnis lement	erw.	gef(a) gef(b)
9613	WU-6-924-1	09.10.2019	g/l	Cu	-	0,0173 0,0173
9614	WU-6-924-2	09.10.2019	g/l	Cu	-	0,0422 0,0429
9615	WU-6-924-3	09.10.2019	g/l	Cu	-	0,0128 0,0133
9616	WU-6-924-4	09.10.2019	g/l	Cu	-	0,0021 0,0022
9617	WU-6-924-5	09.10.2019	g/l	Cu		nn nn

11. Characterization data for products

1b

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 2-bromo-6-methoxynaphthalene **1a** (67 mg, 0.28 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **1b** (41 mg, 0.26 mmol, 92%) was obtained as a white solid. ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.85 – 7.69 (m, 3H), 7.44 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.20 – 7.12 (m, 2H), 3.93 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 157.60, 134.59, 129.40, 127.56, 126.75, 126.28, 118.72, 105.77, 55.31.

HRMS (ESI-TOF) of 1b:

M Error mDa	
6 0.1	
).).6 0.1

2b

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 4-bromobenzamide **2a** (57 mg, 0.29 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **2b** (33 mg, 0.27 mmol, 94%) was obtained as a white solid.

¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) 7.94 – 7.84 (m, 2H), 7.50 – 7.42 (m, 2H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ 168.39, 168.33, 168.28, 134.72, 134.69, 134.66, 128.56, 127.91.

HRMS (ESI-TOF) of 2b:

ESI-TOF	ESI-TOF Accurate Mass Report										
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 14:00:33											
Sample S	ummary:										
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa		
329	20072023	WU-8-336	Wu Li	122.0590	C7H6[2H]ON	123.0668	123.0658	-8.1	-1.0		

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 2-bromobenzamide **3a** (46 mg, 0.23 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **3b** (25 mg, 0.20 mmol, 87%) was obtained as a white solid. ¹H NMR (300 MHz, DMSO- d_6) (ppm) 7.97 (s, 1H), 7.91 – 7.85 (m, 1H), 7.58 – 7.39 (m, 3H), 7.35 (s, 1H).

¹³C NMR (75 MHz, DMSO-*d*₆) (ppm) 168.34, 134.64, 131.66, 128.65, 128.54, 127.90.

HRMS (ESI-TOF) of 3b:

ESI-TOF	Accurate Mas	s Report								Page 1		
Results fil Last modi	iesults file: E:\Projects\2007.PRO\SampleDB\2007.rpt ast modified: Monday, July 20, 2020 13:46:14											
Sample S	ummary:											
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa			
353	20072047	WU-7-48	Wu Li	122.0590	C7H6[2H]ON	123.0668	123.0660	-6.5	-0.8			
D	4b	(13%) 0	%)									

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), (4-bromophenyl)acetamide **4a** (51 mg, 0.24 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **4b** (33 mg, 0.24 mmol, >99%) was obtained as a white solid. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.78 (s, 1H), 7.56 – 7.50 (m, 2H), 7.34 – 7.29 (m, 2H), 2.17 (s, 2.61H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 168.70, 137.98, 128.83, 124.44, 120.04, 24.50.

HRMS (ESI-TOF) of 4b:

ESI-TOF Accurate Mass Report											
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 14:01:05 											
oumpic of	anninary.										
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa		
342	20072036	WU-7-953	Wu Li	135.0684 136.0747	C8H9ON C8H8[2H]ON	136.0762 137.0825	136.0760	-1.5	-0.2		

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), (4-bromo-2-methylphenyl)acetamide **5a** (62 mg, 0.27 mmol), in D_2O (1.5 mL) and Et_3N (54 mg, 0.53 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **5b** (40 mg, 0.27 mmol, >99%) was obtained as a white solid.

¹H NMR (300 MHz, DMSO-*d*₆) δ 9.28 (s, 1H), 7.40 (dd, *J* = 8.0, 4.1 Hz, 1H), 7.21 – 7.12 (m, 2H), 2.20 (s, 3H), 2.15 – 1.87 (m, 2.73H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) 168.62, 136.97, 131.99, 130.58, 126.20, 125.46, 125.37, 23.73, 18.33.

HRMS (ESI-TOF) of 5b:

ESI-TOF Accurate Mass Report	Page 1
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 14:00:43	
Sample Summary:	

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
333	20072027	WU-8-315	Wu Li	150.0903	C9H10[2H]ON	151.0981	151.0984	2.0	0.3

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), (2-bromo-4-fluorophenyl)acetamide **6a** (56 mg, 0.24 mmol), in D₂O (1.5 mL) and Et₃N (50 mg, 0.49 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **6b** (36 mg, 0.23 mmol, 96%) was obtained as a white solid.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.69 (s, 1H), 7.45 – 7.41 (m, 1H), 7.00 – 6.96 (m, 2H), 2.14 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.65, 160.58, 158.16, 133.82, 121.92, 121.84, 121.71, 115.67, 115.58, 115.45, 115.36, 24.33.

¹⁹F NMR (282 MHz, DMSO-*d*₆) δ (ppm) -119.81.

HRMS (ESI-TOF) of 6b:

ESI-TOF A	ESI-TOF Accurate Mass Report										
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 13:38:28											
Sample S	ummary:										
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa		
350	20072044	WU-7-129	Wu Li	154.0653	C8H7[2H]OFN	155.0731	155.0731	0.0	0.0		

According to **GPI**, copper catalyst (Cu-phen/C-800, 42 mg), 5-bromo-2-morpholinobenzonitrile **7a** (57 mg, 0.21 mmol), in D_2O (1.5 mL) and Et_3N (50 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **7b** (40 mg, 0.21 mmol, >99%) was obtained as a colourless solid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.60 (d, J = 1.7 Hz, 1H), 7.52 (dd, J = 8.3, 1.7 Hz, 1H), 7.03 (dd, J = 8.4, 0.5 Hz, 1H), 3.99 – 3.88 (m, 4H), 3.29 – 3.14 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 155.49, 134.33, 133.79, 118.53, 118.29, 106.14, 66.94, 51.85.

HRMS (ESI-TOF) of 7b:

ESI-TOF	SI-TOF Accurate Mass Report										
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt .ast modified: Monday, July 20, 2020 14:01:07											
Sample S	ummary:										
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa		
343	20072037	WU-6-980	Wu Li	189.1012	C11H11[2H]ON2	190.1090	190.1094	2.1	0.4		

According to **GPI**, copper catalyst (Cu-phen/C-800, 41 mg), 2-bromo-6-morpholinobenzonitrile **8a** (67 mg, 0.25 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **8b** (45 mg, 0.24 mmol, 96%) was obtained as a white solid. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.50 (dd, *J* = 8.3, 7.5 Hz, 1H), 7.02 (ddd, *J* = 8.3, 6.8, 1.1 Hz, 2H), 3.97 – 3.84 (m, 4H), 3.29 – 3.10 (m, 4H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 144.72, 129.60, 126.81, 121.61, 117.13, 114.37, 42.08, 27.05, 22.25.

HRMS (ESI-TOF) of 8b:

ESI-TOF A	SI-TOF Accurate Mass Report											
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 14:00:27												
Sample Summary:												
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa			
327	20072021	WU-8-338	Wu Li	189.1012	C11H11[2H]ON2	190.1090	190.1097	3.7	0.7			

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 2-(4-bromophenyl)pyridine **9a** (79 mg, 0.34 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **9b** (47 mg, 0.30 mmol, 88%) was obtained as a colourless liquid. ¹H NMR (300 MHz, CDCl₃): δ (ppm) δ 8.71 (d, *J* = 4.5 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.85 – 7.64 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.21 (m, 1H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 157.36, 149.42, 137.08, 128.71, 128.50, 126.98, 122.20, 120.75.

HRMS (ESI-TOF) of 9b:

ESI-TOF Accurate Mass Report													
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 14:00:28													
Sample Summary:													
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa				
328	20072022	WU-8-349	Wu Li	156.0798	C11H8[2H]N	157.0876	157.0878	1.3	0.2				

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 2-(3-bromophenyl)pyridine **10a** (81 mg, 0.35 mmol), in D_2O (1.5 mL) and Et_3N (29 mg, 0.70 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **10b** (45 mg, 0.29 mmol, 83%) was obtained as a colourless liquid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.70 (d, *J* = 4.8 Hz, 1H), 8.07 – 7.94 (m, 2H), 7.78 – 7.68 (m, 2H), 7.53 – 7.38 (m, 2H), 7.26 – 7.17 (m, 1H).

¹³C NMR (75 MHz, CDCl₃): *δ* (ppm) 157.47, 149.64, 139.36, 136.82, 128.78, 128.50, 128.17, 126.94, 126.83, 122.13, 120.62.

HRMS (ESI-TOF) of 10b:

ESI-TOF	SI-TOF Accurate Mass Report Page														
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 13:33:10															
Sample Summary:															
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa						
348	348 20072042 WU-8-353 Wu Li 156.0798 C11H8[2H]N 157.0876 157.0881 3.2 0.5														

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 6-bromo-3,4-dihydroquinolin-2(1H)-one **11a** (55 mg, 0.24 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **11b** (34 mg, 0.23 mmol, 96%) was obtained as a white solid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.04 (s, 1H), 7.27 – 7.13 (m, 2H), 6.91 – 6.79 (m, 1H), 2.98 (s, 2H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 155.47, 133.93, 122.06, 118.55, 118.30, 106.03, 66.94, 51.84.

HRMS (ESI-TOF) of 11b:

ESI-TOF Accurate Mass Report													
Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 15:38:47													
Sample Summary:													
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa				
354 20072048 WU-6-960 Wu Li 147.0684 C9H9ON 148.0762 148.0762 0.0 0.0 148.0747 C9H8[2H]ON 149.0825													

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 5-bromophthalide **12a** (78 mg, 0.37 mmol), in D₂O (1.5 mL) and Et₃N (73 mg, 0.72 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **12b** (42 mg, 0.31 mmol, 84%) was obtained as a colourless liquid. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) 7.85 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.68 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 5.51 – 5.30 (m, 1.06H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) 171.15, 147.73, 134.68, 134.36, 134.03, 129.30, 125.44, 125.40, 125.36, 125.33, 123.35, 123.33, 123.30, 70.35.

HRMS (ESI-TOF) of 12b:

	Wh-8-329											
File : D:\Xd Full ms [12]	calibur\data\20 7.500 - 159.500	008\20080302chr)] - Range: 13	ei-av2.RAW 7.000 - 137.500									
Scan No. 1 o	of 1		-				0					
Mass	Absolute	Relative	Theoretical	Delta	Delta	KDB	Composition					
	Intensity	Intensity	Mass	[ppm]	[mmu]							
137.05519	927042	50.0	137.05506	0.9	0.1	6.0	C, H, 2H, O,					
137 13274	51062	2 8										

According to GPI, copper catalyst (Cu-phen/C-800, 40 mg), 3-bromo-5-methoxypyridine 13a (85 mg, 0.45 mmol), in D_2O (1.5 mL) and Et_3N (91 mg, 0.90 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product 13b (43 mg, 0.38 mmol, 84%) was obtained as a colorless liquid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.15 (s, 1H), 3.79 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 166.12, 137.38, 120.42, 55.52.

HRMS (ESI-TOF) of 13b:

According to GPI, copper catalyst (Cu-phen/C-800, 40 mg), 3-bromo-carbazole 14a (62 mg, 0.25 mmol), in D₂O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product 14b (41 mg, 0.24 mmol, 96%) was obtained as a white solid. ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) 11.26 (s, 1H), 8.19 – 8.04 (m, 2H), 7.50 (dd, J = 8.2, 0.7 Hz, 2H), 7.39 (dtd, J = 8.2, 3.5, 1.2 Hz, 2H), 7.16 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H). ¹³C NMR (101 MHz, DMSO- d_6) δ (ppm) 140.16, 140.01, 125.94, 125.84, 122.84, 122.80, 120.59, 120.48, 118.92, 111.37, 111.31.

HRMS (ESI-TOF) of 14b:

				We	1-8-	- 32P		#2(E11
File : D:\Xca	libur\data\20	08\20080303ahr	ei-av2.RAW					
Full ms [151.	500 - 173.500] - Range: 16	8.000 - 168.500					
Scan No. 1 of	1							
Mass	Absolute	Relative	Theoretical	Delta	Delta	RDB	Composition	
	Intensity	Intensity	Mass	[ppm]	[mmu]			
168.07918	871533	18.6	168.07923	-0.3	-0.0	9.0	C12 Hg 2H1 N1	

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 5-bromo-indole **15a** (47 mg, 0.24 mmol), in D_2O (1.5 mL) and Et₃N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **15b** (27 mg, 0.23 mmol, 95%) was obtained as a colourless liquid.

¹H NMR (300 MHz, CDCl₃): *δ* (ppm) 8.10 (s, 1H), 7.72 – 7.66 (m, 1H), 7.41 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.59 (ddt, *J* = 3.2, 1.3, 0.8 Hz, 0.63H).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 135.81, 124.18, 124.09, 124.01, 121.91, 120.66, 120.63, 111.06, 102.64, 102.57.

HRMS (ESI-TOF) of 15b:

ESI-TOF Accurate Mass Report													
Results fil Last modi	Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 13:54:32												
Sample S	Summary:												
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa				
347	20072041	WU-8-337	Wu Li	117.0563 119.0704	C8H5[2H]N C8H5[2H2]N	118.0641 120.0782	118.0648 120.0779	5.9 -2.5	0.7 -0.3				
		>											

According to **GPI**, copper catalyst (Cu-phen/C-800, 40 mg), 6-bromo-2-methylquinoline **16a** (56 mg, 0.25 mmol), in D_2O (1.5 mL) and Et_3N (51 mg, 0.5 mmol), CO (40 bar) were reacted at 120 °C for 48 h. The product **16b** (34 mg, 0.23 mmol, 93%) was obtained as a light yellow liquid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.97 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 1H), 2.99 (s, 0.67H).

¹³C NMR (75 MHz, CDCl₃): *δ* (ppm) 158.90, 147.64, 136.39, 129.45, 128.43, 127.40, 126.52, 122.04, 24.44.

HRMS (ESI-TOF) of 16b:

ESI-TOF	SI-TOF Accurate Mass Report Pag														
Results file Last modif	Results file: E:\Projects\2007.PRO\SampleDB\2007.rpt Last modified: Monday, July 20, 2020 13:54:26														
Sample Summary:															
Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa						
355 20072049 WU-8-311 Wu Li 147.0986 C10H5[2H4]N 148.1064 148.1056 -5.4 -0.8															

According to **GPII**, copper catalyst (Cu-phen/C-800, 4.8 g), 1-bromo-3-methoxybenzene **17a** (20.1 g, 107 mmol), in D₂O (100 mL) and Et₃N (22 g, 221 mmol), CO (40 bar) were reacted at 140 °C for 48 h. The product **17b** (6.8 g, 62 mmol, 58%) was obtained as a colourless liquid¹. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.37 – 7.29 (m, 1H), 7.05 – 6.88 (m, 3H), 3.84 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 159.58, 129.46, 120.55, 113.90, 113.80, 55.15.

18b

According to **GPII**, copper catalyst (Cu-phen/C-800 reused from **17b**), 1-bromo-2methoxybenzene **18a** (25.0 g, 134 mmol), in D₂O (100 mL) and Et₃N (23.1 g, 228 mmol), CO (40 bar) were reacted at 140 °C for 48 h. The product **18b** (8.3 g, 76 mmol, 57%) was obtained as a colourless liquid².

¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.40 – 7.29 (m, 2H), 7.04 – 6.90 (m, 2H), 3.84 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 159.51, 129.45, 129.35, 120.65, 113.94, 55.16.

19b

According to **GPII**, copper catalyst (Cu-phen/C-800 reused from **18b**), 1-bromo-2methoxybenzene **19a** (23.0 g, 124 mmol), in D_2O (100 mL) and Et_3N (23.5 g, 232 mmol), CO (40 bar) were reacted at 140 °C for 48 h. The product **19b** (7.5 g, 70 mmol, 65%) was obtained as a colourless liquid¹.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 10.03 (s, 1H), 7.99 – 7.86 (m, 2H), 7.59 – 7.47 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 192.40, 136.42, 134.49, 134.17, 133.85, 129.75, 128.90.

20b

According to **GPII**, copper catalyst (Cu-phen/C-800, 5.0 g), 1-bromo-4-methoxybenzene **20a** (36.3 g, 194 mmol), in D_2O (100 mL) and Et_3N (45 g, 445 mmol), CO (40 bar) were reacted at

130 °C for 6 days. The product **20b** (10.9 g, 99 mmol, 51%) was obtained as a colourless liquid².

¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.41 – 7.32 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 159.61, 129.39, 120.75, 120.43, 120.10, 113.93, 55.15.

According to **GPII**, copper catalyst (Cu-phen/C-800, 5.0 g), 4-bromophenol **21a** (35.3 g, 204 mmol), in D_2O (100 mL) and Et₃N (47 g, 465 mmol), CO (40 bar) were reacted at 130 °C for 6 days. The product **21b** (18.0 g, 186 mmol, 91%) was obtained as a colourless liquid.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.43 – 7.34 (m, 1H), 7.14 – 7.12 (m, 0.06H), 7.07 – 7.04 (m, 0.11H).

¹³C NMR (75 MHz, CDCl₃): *δ* (ppm) 155.14, 155.10, 129.94, 129.83, 121.31, 121.03, 120.71, 115.77, 115.71, 115.44, 115.12.

Elemental Composition Report

According to **GPII**, copper catalyst (Cu-phen/C-800, 5.0 g), 4-bromoaniline **22a** (34.8 g, 202 mmol), in D₂O (100 mL) and Et₃N (46 g, 455 mmol), CO (40 bar) were reacted at 130 °C for 6 days. The product **22b** (17.6 g, 188 mmol, 93%) was obtained as a colourless liquid¹. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.27 – 7.21 (m, 2H), 6.81 – 6.71 (m, 2H), 3.73 (s, 2H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 146.51, 129.37, 129.26, 129.15, 118.58, 115.18, 115.16.

According to **GPII**, copper catalyst (Cu-phen/C-800, 5.0 g), 1-bromo-4-methoxybenzene **23a** (23.2 g, 100 mmol), in D₂O (100 mL) and Et₃N (27 g, 267 mmol), CO (40 bar) were reacted at 130 °C for 6 days. The product **23b** (14.7 g, 94 mmol, 94%) was obtained as a white solid. ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.41 – 7.32 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 159.61, 129.39, 120.75, 120.43, 120.10, 113.93, 55.15. ¹⁹F NMR (282 MHz, DMSO-*d*₆) δ (ppm) -119.81.

12. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra for products

Original spectra for 1b:

Original spectra for 2b:

Original spectra for 3b:

Original spectra for 4b:

190813.f317.10.fid Li/ Wu-6-911 PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1908 17

2.17 2.15 2.15 2.15 2.15 2.15 1.94

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Original spectra for 5b:

7.42 7.41 7.40 7.20 7.15 7.15 7.15 7.15 7.15 7.13

2.52 2.51 2.51 2.55 2.50 2.05 2.05 2.05

Original spectra for 6b:

190828.416.10.fid Li Wu-7-129 Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1908 16 $\begin{array}{c} 7.69\\ 7.45\\ 7.45\\ 7.45\\ 7.45\\ 7.45\\ 7.42\\ 7.42\\ 7.42\\ 7.42\\ 7.42\\ 7.42\\ 7.01\\ 7.26\\ 6.99\\ 6.99\\ 6.99\\ 6.99\\ 6.97\\ 6.97\\ 6.97\\ 6.97\\ 6.97\\ 6.97\\ 6.97\\ 6.97\\ 6.96\\ 6.97\\ 6.96\\ 6.97\\ 6.95\\$

 $<^{2.14}_{2.14}$

200619.f308.12.fid Wu Li WU-8-335 19F(H-entk) DMSO {C:\Bruker\TopSpin3.6.0} 2006 8 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

Original spectra for 7b:

110 100 f1 (ppm) 210 200 190 180 170 160 150 140 130 120 -10

Original spectra for 8b:

200626.349.10.fid Wu Li WU-8-338 Au1H CDCI3 {C:\Bruker\TopSpin3.6.0} 2006 49

7.53 7.50 7.50 7.48 7.48 7.26 7.05 7.05 7.03 7.03 7.00 6.99

Original spectra for 9b:

270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Original spectra for 10b:

270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Original spectra for 11b:

Original spectra for 12b:

Original spectra for 14b:

			_						_						_						
220	210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10
										f1	(ppm)										

Original spectra for 15b:

Original spectra for 16b:

200612.323.20.fid Li/ Wu-8-311 Au1H CDCI3 {C:\Bruker\TopSpin3.6.0} 2006 23

____2.99

Original spectra for 17b:

200713.330.10.fid Wu Li WU-8-362-1 Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2007 30

7.38 7.35 7.35 7.35 7.35 7.35 7.35 7.35 6.97

— 3.87

270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Original spectra for 18b:

Original spectra for 19b:

201109.f364.10.fid	00080008800088000 0008000880008000 000800080008000000	85 84 85
Wu Li WU-8-534-4		ကိုကိုကို
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0}	2011 5	NY

Original spectra for 20b:

201118.323.10.fid 8 8 Wu Li WU-8-535-4 9 9 Au1H CDCl3 {C:\Bruker\TopSpin3.6.0} 2011 23

270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Original spectra for 21b:

Original spectra for 22b:

Original spectra for 23b:

200619.f308.10.fid 5 Wu Li WU-8-335 6 PROTON DMSO {C:\Bruker\TopSpin3.6.0} 2006 8

200619.f308.12.fid Wu Li WU-8-335 19F(H-entk) DMSO {C:\Bruker\TopSpin3.6.0} 2006 8 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)

13. References

- 1. C. Liu, S. Han, M. Li, X. Chong and B. Zhang, *Angew. Chem. Int. Ed.*, 2020, *59*, 18527–18531.
- 2. C. Liu, Z. Chen, C. Su, X. Zhao, Q. Gao, G. H. Ning, H. Zhu, W. Tang, K. Leng, W. Fu, B. Tian, X. Peng, J. Li, Q. H. Xu, W. Zhou and K. P. Loh, *Nat. Commun.*, 2018, **9**, 80.