

## Supporting Information

### **New Transmetalation Reagents for the Gold-Catalyzed Visible-Light Enabled C(sp or sp<sup>2</sup>)-C(sp<sup>2</sup>) Cross-Coupling with Aryldiazonium Salts in the Absence of a Photosensitizer**

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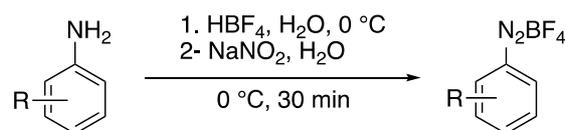
## 1. General information

All commercially available chemicals were purchased from suppliers (ABCR, Acros, Alfa Aesar, Chempur, Merck and Sigma Aldrich) or obtained from the chemical store of the University of Heidelberg and were used without further purifications. Dry solvents were dispensed from solvent purification system MB SPS-800-Benchtop. Deuterated solvents were supplied from Euriso-Top and used as received. The NMR spectra, if not noted otherwise, were recorded at room temperature on the following spectrometers: Bruker Avance III 300 (300 MHz), Bruker Avance DRX 300 (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz), Bruker Avance III 600 (600 MHz) or Fourier 300 (300 MHz). Chemical shifts  $\delta$  are quoted in parts per million (ppm) and coupling constants  $J$  in hertz (Hz).  $^1\text{H}$  and  $^{13}\text{C}$  spectra are calibrated in relation to the deuterated solvents, namely  $\text{CDCl}_3$  (7.26 ppm; 77.16 ppm).  $^{19}\text{F}$  spectra were calibrated in relation to the reference measurement of 1,2-difluorobenzene (-139 ppm). The following abbreviations were used to indicate the signal multiplicity: for the  $^1\text{H}$  NMR spectra: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), m (multiplet), as well as their combinations; for the  $^{13}\text{C}$  NMR spectra: s (quaternary carbon), d (tertiary carbon ( $\text{CH}$ )), t (secondary carbon ( $\text{CH}_2$ )) and q (primary carbon ( $\text{CH}_3$ )). All the  $^{13}\text{C}$  NMR spectra were measured with  $1\text{H}$ -decoupling and were interpreted with the help of DEPT135,  $^1\text{H}$ , $^1\text{H}$ -COSY and HMBC. All spectra were integrated and processed using TopSpin 3.5 software. Mass spectra (MS and HRMS) were determined in the chemistry department of the University Heidelberg under the direction of Dr. J. Gross.  $\text{EI}^+$ -spectra were measured on a JOEL JMS-700 spectrometer. For  $\text{ESI}^+$ -spectra a Bruker ApexQu FT-ICR-MS spectrometer was applied. Gas chromatography / Mass Spectroscopy (GC MS) was carried out on an Agilent 5975C Mass Selective Detector, coupled with an Agilent 7890A Gas Chromatograph. As a capillary column an OPTIMA 5 cross-linked Methyl Silicone column (30 m x, 0.32 mm, 0.25  $\mu\text{m}$ ) was employed, and nitrogen was used as the carrier gas. Flash Column Chromatography was accomplished using Silica gel 60 (0.04 – 0.063 mm / 230 – 400 mesh ASTM) purchased from Macherey-Nagel as stationary phase. As eluents the respectively mentioned proportions of petroleum ether (PE) and ethyl acetate (EA) were used. Analytical Thin Layer Chromatography (TLC) was carried out on precoated Macherey-Nagel POLYGRAM® SIL G/UV<sub>254</sub> or Merck TLC Silical Gel 60 F254 aluminium sheets. Detection was accomplished using UV-light (254 nm),  $\text{KMnO}_4$  (in 1.5M  $\text{Na}_2\text{CO}_3$  (aq.)), molybdato-phosphoric acid (5 % in ethanol), vanillin /  $\text{H}_2\text{SO}_4$  (in ethanol) or anisaldehyde / HOAc (in ethanol).

The aryldiazonium tetrafluoroborate were synthesized according to a modified procedure reported by König *et al.*<sup>[1]</sup> The neutral gold complexes were prepared after a procedure published by Hashmi *et al.*<sup>[2]</sup> and the synthesis of the cationic gold complexes proceeded after a modification of a literature report by Ogawa *et al.*<sup>[3]</sup>

## 2. General procedures

### General procedure for the synthesis of aryldiazonium tetrafluoroborate (GP1)



The corresponding aniline (10 mmol, 1.0 equiv.) was dissolved in a mixture of water (3.5 ml) and 3.5 ml of a 48 wt.% tetrafluoroboric acid solution in H<sub>2</sub>O. After cooling to 0 °C an aqueous solution of sodium nitrite (690 mg, 10 mmol, 1.0 equiv., in 1.0 ml H<sub>2</sub>O) was added dropwise over a course of 10 min. The reaction mixture was stirred for 30 min and the resulting precipitate was collected by filtration. The crude product was purified by dissolving in a minimum amount of acetone. The product was precipitated by addition of Et<sub>2</sub>O, which was again collected by filtration. For further purification, this can be repeated several times. After drying under high vacuum the corresponding diazonium tetrafluoroborate was obtained and stored at -20 °C.

### General procedure for the synthesis of gold complexes (GP2)

DMSAuCl (1.0 equiv.) was dissolved in DCM (40 mmol/l) and the corresponding ligand (1.0 equiv.) was added. After stirring for 2 hours at room temperature in the dark, the solvent was removed under reduced pressure at room temperature in the dark. The crude product was purified by dissolving in a minimum amount of DCM and the gold complex was precipitated by addition of *n*-pentane or PE. After filtration and drying under high vacuum in the dark, the corresponding gold complex was obtained and stored at -20 °C.

### General procedure for the synthesis of cationic gold complexes (GP3)

The corresponding gold complex of GP2 (1.0 equiv.) was dissolved in DCM (40 mmol/l) and AgNTf<sub>2</sub> (1.0 equiv.) was added. After the reaction mixture was stirred for 15 min at room temperature, the precipitated AgCl was removed by filtration through a Celite Pad. The

filtrate was concentrated under reduced pressure and the obtained cationic gold complex was dried under high vacuum.

### General procedure for visible-light enabled cross-coupling of arylboranes/-silanes and aryldiazonium salts (GP4)

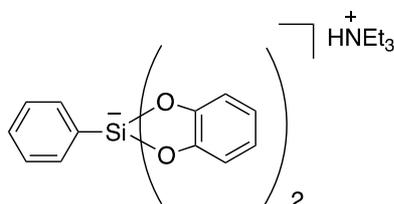
In a dried Pyrex screw-top reaction tube (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol %) and the corresponding arylborane/-silane (0.1 mmol, 1.0 equiv.) were dissolved in 0.5 ml MeOH. After adding the corresponding aryldiazonium salt (0.4 mmol, 4.0 equiv.) the reaction mixture was degassed under nitrogen by sparging for 5-10 min at -78 °C. The tubes were irradiated at room temperature with 29 W blue LEDs for 15-17 hours. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography.

### General procedure for visible-light enabled cross-coupling of silanes and aryldiazonium salts (GP5)

In a dried Pyrex screw-top reaction tube Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol %) and the corresponding silane (0.3 mmol, 1.0 equiv.) were dissolved in 1.5 ml MeCN. After adding the corresponding aryldiazonium salt (0.36 mmol, 1.2 equiv.) the reaction mixture was degassed under nitrogen by sparging for 5-10 min at -78 °C. The tubes were irradiated at room temperature with 29 W blue LEDs for 15-17 hours. The solvent was removed under reduced pressure and the resulting crude product was purified by column chromatography.

## 3. Substrate synthesis

### Synthesis of triethylammonium phenylbis(catecholato)silicate

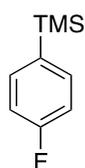


A microwave vial was charged 325 mg of pyrocatechol (2.95 mmol, 1.95 equiv.) and was sealed with a Teflon-coated septum cap. After purging with Ar and evacuation for three times, 3 ml of dry THF (0.5 M) and 0.25 ml of trimethylamine (1.82 mmol, 1.2 equiv.) were added. The resulting mixture was stirred at rt for 15 min before addition of 300 mg of trimethoxy(phenyl)silane (1.51 mmol, 1.0 equiv.). The vial was placed in the microwave

(Biotage, Initiator<sup>+</sup>) and heated at 80 °C for 16 h. After removal of the solvent under reduced pressure Et<sub>2</sub>O (0.1 M) was added. The mixture was sonicated for 15 min to allow the corresponding product to precipitate as a white powder, which was then filtrated and washed with Et<sub>2</sub>O to afford 583 mg of triethylammonium phenylbis(catecholato)silicate as a white solid (1.38 mmol, 91%).

**M.p** = 226-227 °C. **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ = 1.21 (t, *J* = 7.3 Hz, 9H), 3.17 (q, *J* = 7.3 Hz, 6H), 6.66-6.69 (m, 4H), 6.75-6.78 (m, 4H), 7.12-7.20 (m, 3H), 7.56-7.58 (m, 2H) ppm. **<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>): δ = 8.56 (q, 3C), 46.2 (t, 3C), 110.8 (d, 4C), 118.8 (d, 4C), 127.3 (s, 4C), 128.6 (s, 1C), 134.5 (d, 2C), 139.5 (d, 1C), 149.6 (d, 2C) ppm. **IR** (ATR):  $\tilde{\nu}$  = 3055, 2718, 1738, 1601, 1483, 1439, 1388, 1353, 1280, 1261, 1240, 1203, 1158, 1114, 1102, 1013, 928, 903, 890, 819, 762, 736, 723, 701 cm<sup>-1</sup>. **HRMS** (ESI (-)): *m/z* = 321.0587, calcd. for [C<sub>18</sub>H<sub>13</sub>O<sub>4</sub>Si]<sup>-</sup>: 321.0583.

### Synthesis of (4-fluorophenyl)trimethylsilane

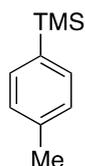


To a solution of 4-bromofluorobenzene (700 mg, 4 mmol) in anhydrous THF (10 mL) at -78 °C was added *n*-butyllithium (2.5 M in hexanes; 1.68 mL, 4.2 mmol) dropwise under an N<sub>2</sub> atmosphere. The solution was stirred at -78 °C for 1 h, then trimethylsilyl chloride (0.61 mL, 4.8 mmol) was added dropwise at -78 °C. The solution was stirred overnight at room temperature then quenched with H<sub>2</sub>O. The layers were separated then the aqueous layer was extracted with Et<sub>2</sub>O twice. The combined organic layer were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. Following purification by silica gel chromatography, the desired compound (415 mg, 62%) was obtained as a colorless liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 0.26 (s, 9H), 7.01-7.07 (m, 2H), 7.46-7.51 (m, 2H) ppm.

The data is consistent with the previous literature.<sup>[4]</sup>

### Synthesis of (4-methylphenyl)trimethylsilane

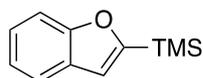


To a solution of 4-bromotoluene (684 mg, 4 mmol) in anhydrous THF (10 mL) at  $-78\text{ }^{\circ}\text{C}$  was added *n*-butyllithium (2.5 M in hexanes; 1.68 mL, 4.2 mmol) dropwise under an  $\text{N}_2$  atmosphere. The solution was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, then trimethylsilyl chloride (0.61 mL, 4.8 mmol) was added dropwise at  $-78\text{ }^{\circ}\text{C}$ . The solution was stirred overnight at room temperature then quenched with  $\text{H}_2\text{O}$ . The layers were separated then the aqueous layer was extracted with  $\text{Et}_2\text{O}$  twice. The combined organic layer were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. Following purification by silica gel chromatography, the desired compound (512 mg, 78%) was obtained as a colorless liquid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.26$  (s, 9H), 2.35 (s, 3H), 7.16-7.21 (m, 2H), 7.41-7.46 (m, 2H) ppm.

The data is consistent with the previous literature.<sup>[5]</sup>

### Synthesis of benzofuran-2-yltrimethylsilane



To a solution of 2,3-benzofuran (590 mg, 5 mmol) in anhydrous THF (10 mL) at  $-78\text{ }^{\circ}\text{C}$  was added *n*-butyllithium (2.5 M in hexanes; 2 mL, 5 mmol) dropwise under an  $\text{N}_2$  atmosphere. The solution was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, then trimethylsilyl chloride (0.698 mL, 5.5 mmol) was added dropwise at  $-78\text{ }^{\circ}\text{C}$ . The solution was stirred overnight at room temperature then quenched with  $\text{H}_2\text{O}$ . The layers were separated then the aqueous layer was extracted with  $\text{Et}_2\text{O}$  twice. The combined organic layer were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. Following purification by silica gel chromatography, the desired compound (461 mg, 48%) was obtained as a colorless liquid.

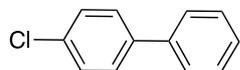
$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.36$  (s, 9H), 6.96 (d,  $J = 0.9$  Hz, 1H), 7.18 (dd,  $J = 1.0, 3.6$  Hz, 1H), 7.24-7.31 (m, 1H), 7.48-7.53 (m, 1H), 7.55-7.60 (m, 1H) ppm.

The data is consistent with the previous literature.<sup>[6]</sup>

## 4. Synthesis and characterization of cross-coupled products

### 4.1 Synthesis according to GP 4

#### Synthesis of 4-chloro-1,1'-biphenyl (**3a**)



According to GP4, 20.4 mg of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.1 mmol, 1.0 equiv.), 6.99 mg of  $(4\text{-CF}_3\text{-C}_6\text{H}_4)_3\text{PAuCl}$  (0.01 mmol, 10 mol%) and 91.0 mg of 4-chlorobenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC ( $\text{SiO}_2$ , 100% PE) to give 18.1 mg of **3a** (0.10 mmol, 96%) as a white solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.33\text{-}7.47$  (m, 5H),  $7.50\text{-}7.62$  (m, 4H) ppm.

The data is consistent with literature values.<sup>[7]</sup>

According to GP4, 23.3 mg of 4-methyl-2,6-dioxo-8-phenylhexahydro-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-ium-8-uide (0.1 mmol, 1.0 equiv.), 6.99 mg of  $(4\text{-CF}_3\text{-C}_6\text{H}_4)_3\text{PAuCl}$  (0.01 mmol, 10 mol%) and 91.0 mg of 4-chlorobenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC ( $\text{SiO}_2$ , 100% *n*-heptane) to give 17.4 mg of **3a** (0.09 mmol, 92%) as a white solid.

The data is consistent with the ones mentioned above.

According to GP4, 18.4 mg of potassium phenyltrifluoroborate (0.1 mmol, 1.0 equiv.), 6.99 mg of  $(4\text{-CF}_3\text{-C}_6\text{H}_4)_3\text{PAuCl}$  (0.01 mmol, 10 mol%) and 91.0 mg of 4 chlorobenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC ( $\text{SiO}_2$ , 100% *n*-heptane) to give 17.8 mg of **3a** (0.09 mmol, 94%) as a white solid.

The data is consistent with the ones mentioned above.

According to GP4, 19.8 mg of trimethoxy(phenyl)silane (0.1 mmol, 1.0 equiv.), 6.99 mg of  $(4\text{-CF}_3\text{-C}_6\text{H}_4)_3\text{PAuCl}$  (0.01 mmol, 10 mol%), 91.0 mg of 4-chlorobenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was

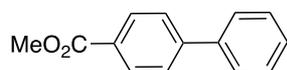
performed using PTLC (SiO<sub>2</sub>, 100% *n*-heptane) to give 17.8 mg of **3a** (0.09 mmol, 94%) as a white solid.

The data is consistent with the ones mentioned above.

According to GP4, 42.4 mg of triethylammonium phenylbis(catecholato)silicate (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 91.0 mg of 4-chlorobenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, 100% *n*-heptane) to give 17.3 mg of **3a** (0.09 mmol, 92%) as a white solid.

The data is consistent with the ones mentioned above.

### Synthesis of methyl [1,1'-biphenyl]-4-carboxylate (**3b**)



According to GP4, 20.4 mg of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 100 mg of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 19.3 mg of **3b** (0.09 mmol, 91%) as a white solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 3.90 (s, 3H), 7.33-7.46 (m, 3H), 7.58-7.70 (m, 4H), 8.05-8.09 (m, 2H) ppm.

The data is consistent with literature values.<sup>[7]</sup>

According to GP4, 23.3 mg of 4-methyl-2,6-dioxo-8-phenylhexahydro-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-ium-8-uide (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 100 mg of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 19.9 mg of **3b** (0.09 mmol, 94%) as a white solid.

The data is consistent with the ones mentioned above.

According to GP4, 18.4 mg of potassium phenyltrifluoroborate (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 100 mg of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted

in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 16.3 mg of **3b** (0.08 mmol, 77%) as a white solid.

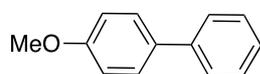
The data is consistent with the ones mentioned above.

According to GP4, 19.8 mg of trimethoxy(phenyl)silane (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 100 mg of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 17.3 mg of **3b** (0.08 mmol, 82%) as a white solid.

The data is consistent with the ones mentioned above.

According to GP4, 42.4 mg of triethylammonium phenylbis(catecholato)silicate (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 100 mg of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 17.7 mg of **3b** (0.08 mmol, 83%) as a white solid.

### Synthesis of 4-methoxy-1,1'-biphenyl (**3c**)



According to GP4, 20.4 mg of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 88.8 mg of 4-methoxybenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, PE/EA, 50:1) to give 6.00 mg of **3c** (0.03 mmol, 31%) as a white solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 3.86 (s, 3H), 6.96-7.01 (m, 2H), 7.27-7.33 (m, 1H), 7.39-7.44 (m, 2H), 7.51-7.57 (m, 4H) ppm.

The data is consistent with literature values.<sup>[8]</sup>

According to GP4, 23.3 mg of 4-methyl-2,6-dioxo-8-phenylhexahydro-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-4-ium-8-uide (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 88.8 mg of 4-methoxybenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was

performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 6.10 mg of **3c** (0.03 mmol, 33 %) as a white solid.

The data is consistent with the ones mentioned above.

According to GP4, 18.4 mg of potassium phenyltrifluoroborate (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 88.8 mg of 4-methoxybenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, PE/EA, 50:1) to give 6.50 mg of **3c** (0.04 mmol, 35%) as a white solid.

The data is consistent with the ones mentioned above.

According to GP4, 19.8 mg of trimethoxy(phenyl)silane (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 88.8 mg of 4-methoxybenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 3.80 mg of **3c** (0.02 mmol, 21%) as a white solid.

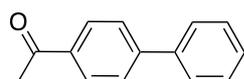
The data is consistent with the ones mentioned above.

According to GP4, 42.4 mg of triethylammonium phenylbis(catecholato)silicate (0.1 mmol, 1.0 equiv.), 6.99 mg of (4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>PAuCl (0.01 mmol, 10 mol%) and 88.8 mg of 4-methoxybenzenediazonium tetrafluoroborate (0.4 mmol, 4.0 equiv.) were reacted in 0.5 mL of MeOH. Purification was performed using PTLC (SiO<sub>2</sub>, *n*-heptane/EA, 20:1) to give 6.80 mg of **3c** (0.04 mmol, 37%) as a white solid.

The data is consistent with the ones mentioned above.

## 4.2 Synthesis according to GP 5

### Synthesis of 1-([1,1'-biphenyl]-4-yl)ethan-1-one (**5a**)



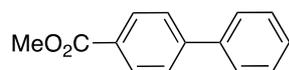
The reaction was carried out according to GP5, using 45.1 mg of trimethyl(phenyl)silane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 84.2 mg of 4-acetylbenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN.

After flash column chromatography (SiO<sub>2</sub>, PE/EA, 30:1), 35.8 mg of **5a** (0.18 mmol, 61%) were isolated as a pale yellow solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 2.63 (s, 3H), 7.37-7.50 (m, 3H), 7.60-7.71 (m, 4H), 8.01-8.05 (m, 2H) ppm.

The data is consistent with literature values.<sup>[8]</sup>

### Synthesis of methyl [1,1'-biphenyl]-4-carboxylate (**5b**)

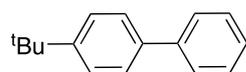


The reaction was carried out according to GP5, using 45.1 mg of trimethyl(phenyl)silane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 90.0 mg of 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, PE/EA, 20:1), 48.5 mg of **5b** (0.23 mmol, 76%) were isolated as a pale yellow solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 3.94 (s, 3H), 7.36-7.49 (m, 3H), 7.61-7.68 (m, 4H), 8.09-8.13 (m, 2H) ppm.

The data is consistent with literature values.<sup>[7]</sup>

### Synthesis of 4-(tert-butyl)-1,1'-biphenyl (**5c**)

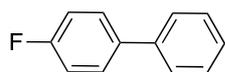


The reaction was carried out according to GP5, using 45.1 mg of trimethyl(phenyl)silane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 89.3 mg of 4-*tert*-butylbenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, 100% PE), 43.5 mg of **5c** (0.21 mmol, 69%) were isolated as an off-white solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 1.38 (s, 9H), 7.31-7.36(m, 1H), 7.41-7.50 (m, 4H), 7.53-7.62 (m, 4H) ppm.

The data is consistent with literature value.<sup>[9]</sup>

### Synthesis of 4-fluoro-1,1'-biphenyl (**5d**)

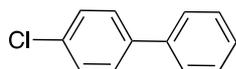


The reaction was carried out according to GP5, using 45.1 mg of trimethyl(phenyl)silane (0.3 mmol, 1.0 equiv.), 22.2 mg of  $\text{Ph}_3\text{PAuNTf}_2$  (0.03 mmol, 10 mol%), 75.6 mg of 4-fluorobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography ( $\text{SiO}_2$ , 100% PE), 43.8 mg of **5d** (0.25 mmol, 61%) were isolated as a colourless solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.09-7.16 (m, 2H), 7.31-7.37 (m, 1H), 7.41-7.47 (m, 2H), 7.51-7.61 (m, 4H) ppm.  $^{19}\text{F NMR}$  (283 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -115.90 (s, 1F) ppm.

The data is consistent with literature values.<sup>[10]</sup>

### Synthesis of 4-chloro-1,1'-biphenyl (**5e**)

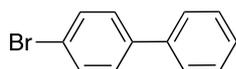


The reaction was carried out according to GP5, using 45.1 mg of trimethyl(phenyl)silane (0.3 mmol, 1.0 equiv.), 22.2 mg of  $\text{Ph}_3\text{PAuNTf}_2$  (0.03 mmol, 10 mol%), 81.5 mg of 4-chlorobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography ( $\text{SiO}_2$ , 100% PE), 44.0 mg of **5e** (0.23 mmol, 78%) were isolated as a colourless solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.33-7.47 (m, 5H), 7.49-7.58 (m, 4H) ppm.

The data is consistent with literature values.<sup>[7]</sup>

### Synthesis of 4-bromo-1,1'-biphenyl (**5f**)

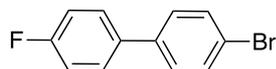


The reaction was carried out according to GP5, using 45.1 mg of trimethyl(phenyl)silane (0.3 mmol, 1.0 equiv.), 22.2 mg of  $\text{Ph}_3\text{PAuNTf}_2$  (0.03 mmol, 10 mol%), 97.5 mg of 4-bromobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography ( $\text{SiO}_2$ , 100% PE), 62.9 mg of **5f** (0.27 mmol, 90%) were isolated as a colourless solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 7.34-7.45 (m, 5H), 7.47-7.62 (m, 4H) ppm.

The data is consistent with literature values.<sup>[7]</sup>

### Synthesis of 4-bromo-4'-fluoro-1,1'-biphenyl (**5g**)

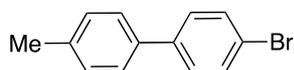


The reaction was carried out according to GP5, using 50.5 mg of (4-fluorophenyl)trimethylsilane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 97.5 mg of 4-bromobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, 100% PE), 70.1 mg of **5g** (0.28 mmol, 93%) were isolated as a colourless solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 7.09-7.15 (m, 2H), 7.39-7.43 (m, 2H), 7.47-7.59 (m, 4H) ppm.

The data is consistent with literature values.<sup>[11]</sup>

### Synthesis of 4-bromo-4'-methyl-1,1'-biphenyl (**5h**)

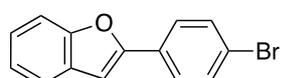


The reaction was carried out according to GP5, using 49.3 mg of trimethyl(*p*-tolyl)silane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 97.5 mg of 4-bromobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, 100% PE), 64.5 mg of **5h** (0.26 mmol, 87%) were isolated as a colourless solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 2.39 (s, 3H), 7.39-7.46 (m, 4H), 7.52-7.59 (m, 4H) ppm.

The data is consistent with literature values.<sup>[12]</sup>

### Synthesis of 2-(4-bromophenyl)benzofuran (**5i**)



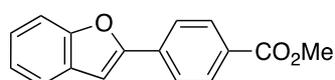
The reaction was carried out according to GP5, using 57.1 mg of benzofuran-2-yltrimethylsilane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%),

97.5 mg of 4-bromobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, 100% PE), 62.3 mg of **5i** (0.22 mmol, 71%) were isolated as a colourless solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.03 (d,  $J$  = 0.6 Hz, 1H), 7.21-7.24 (m, 1H), 7.26-7.33 (m, 1H), 7.48-7.63 (m, 4H), 7.71-7.75 (m, 2H) ppm.

The data is consistent with literature values.<sup>[13]</sup>

### Synthesis of methyl 4-(benzofuran-2-yl)benzoate (**5j**)

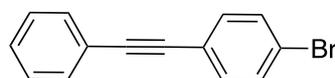


The reaction was carried out according to GP5, using 57.1 mg of benzofuran-2-yltrimethylsilane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 90.0 mg of 4-(methoxycarbonyl)tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, PE:EA, 20:1), 59.8 mg of **5j** (0.24 mmol, 79%) were isolated as a colourless solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.94 (s, 3H), 7.15 (d,  $J$  = 0.7 Hz, 1H), 7.22-7.25 (m, 1H), 7.27-7.35 (m, 1H), 7.54 (dd,  $J$  = 0.7, 8.2 Hz, 1H), 7.61 (dd,  $J$  = 0.7, 7.6 Hz, 1H), 7.91-7.94 (m, 2H) 8.09-8.13 (m, 2H) ppm.

The data is consistent with literature values.<sup>[14]</sup>

### Synthesis of 1-bromo-4-(phenylethynyl)benzene (**7a**)

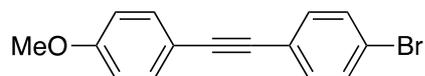


The reaction was carried out according to GP5, using 52.3 mg of trimethyl(phenylethynyl)silane (0.3 mmol, 59.0  $\mu$ L, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 97.5 mg of 4-bromobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, 100% PE), 62.3 mg of **7a** (0.24 mmol, 81%) were isolated as a colourless solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.33-7.40 (m, 5H), 7.45-7.53 (m, 4H) ppm.

The data is consistent with literature values.<sup>[15]</sup>

### Synthesis of 1-bromo-4-((4-methoxyphenyl)ethynyl)benzene (7b)

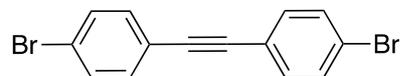


The reaction was carried out according to GP5, using 61.3 mg of ((4-methoxyphenyl)ethynyl)trimethylsilane (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 97.5 mg of 4-bromobenzenediazonium tetrafluoroborate (0.36 mmol, 1.2 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, PE/EA, 50:1), 36.2 mg of **7b** (0.13 mmol, 42%) were isolated as a pale yellow solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 3.83 (s, 3H), 6.85-6.90 (m, 2H), 7.34-7.38 (m, 2H), 7.44-7.48 (m, 4H) ppm.

The data is consistent with literature values.<sup>[16]</sup>

### Synthesis of 1,2-bis(4-bromophenyl)ethyne (7c)



The reaction was carried out according to GP5, using 51.1 mg of 1,2-bis(trimethylsilyl)ethyne (0.3 mmol, 1.0 equiv.), 22.2 mg of Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.03 mmol, 10 mol%), 194.5 mg of 4-bromobenzenediazonium tetrafluoroborate (0.72 mmol, 2.4 equiv.) and 1.5 mL of MeCN. After flash column chromatography (SiO<sub>2</sub>, 100% PE), 73.5 mg of **7c** (0.22 mmol, 73%) were isolated as a colourless solid.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 7.36-7.43 (m, 4H), 7.47-7.58 (m, 4H) ppm.

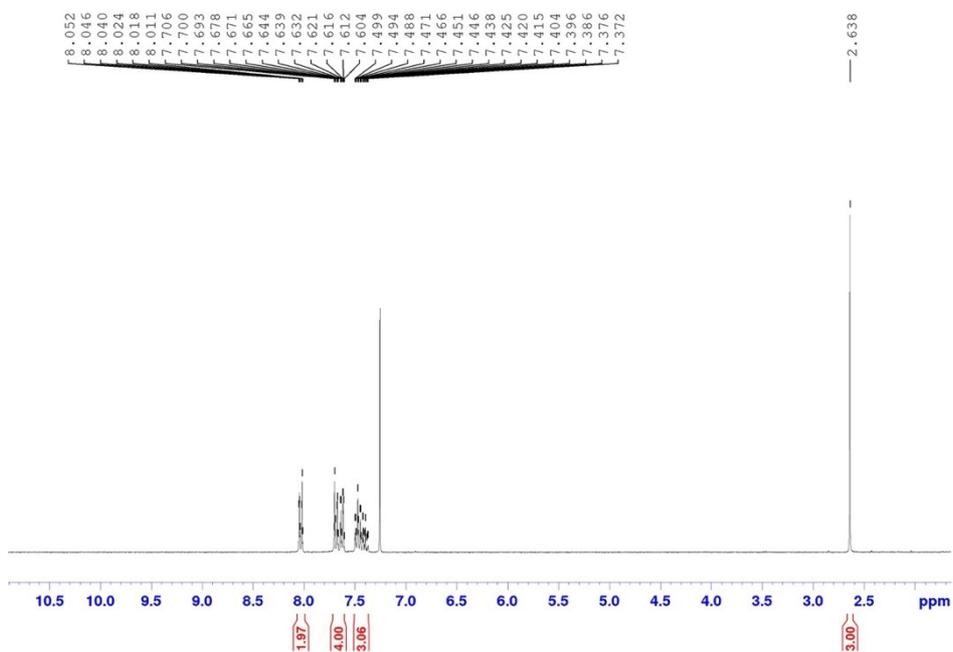
The data is consistent with literature values.<sup>[17]</sup>

As prove that this is not the homocoupling of the 4-bromobenzenediazonium tetrafluoroborate a HRMS was measured:

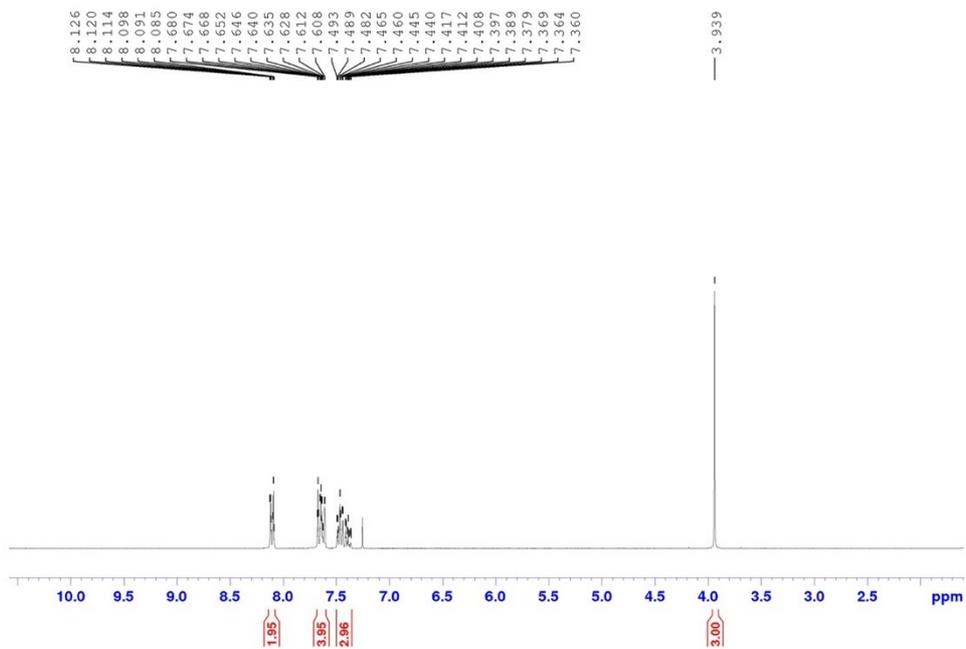
HRMS (EI (+)): *m/z* = 333.8973, calcd. for [C<sub>14</sub>H<sub>8</sub>Br<sub>2</sub>]<sup>+</sup>: 333.8993.

## 5. NMR spectra

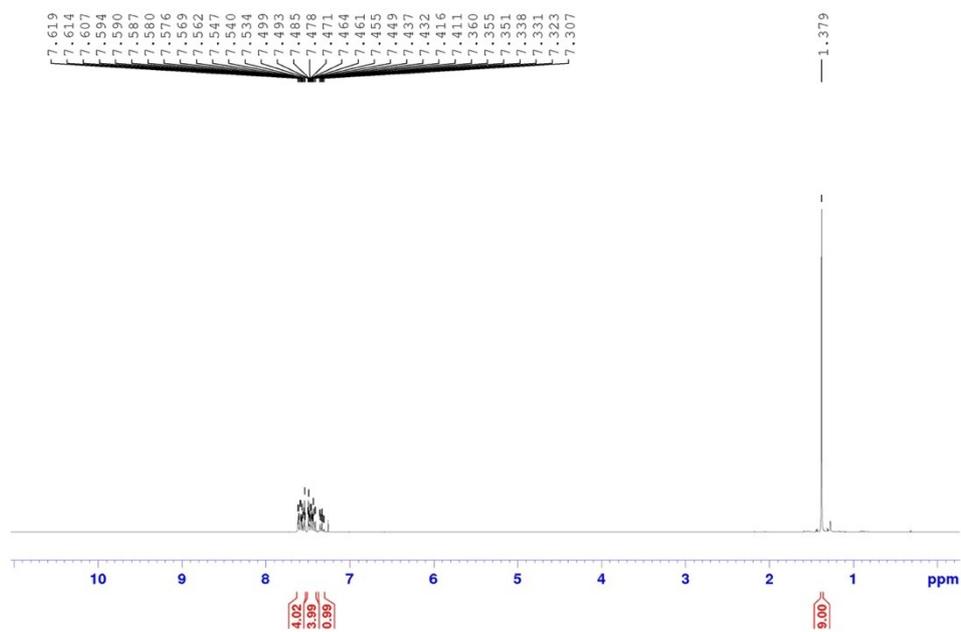
### $^1\text{H}$ NMR spectra of 5a



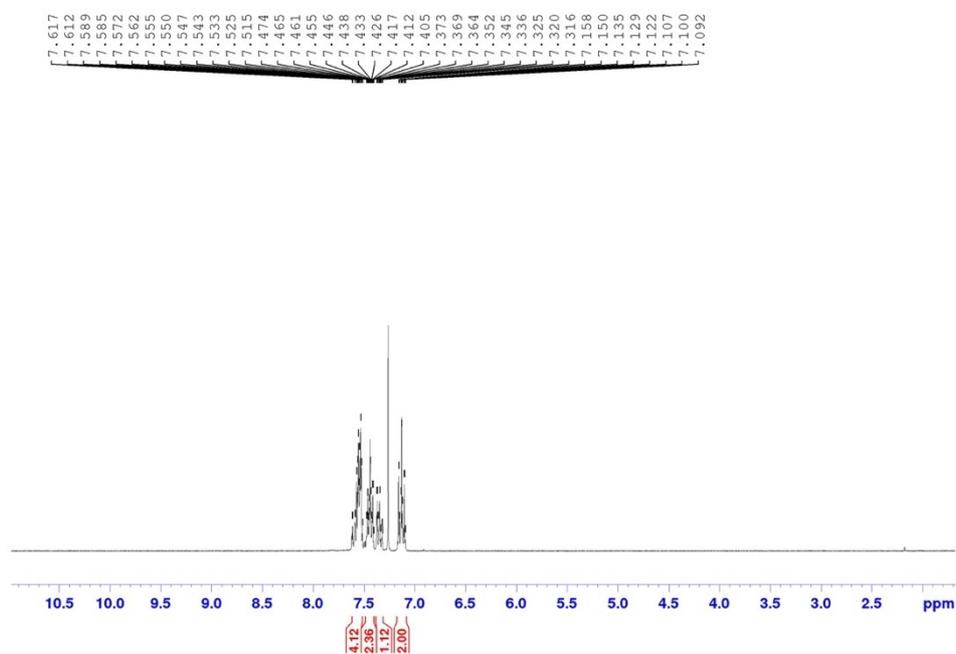
### $^1\text{H}$ NMR spectra of 5b



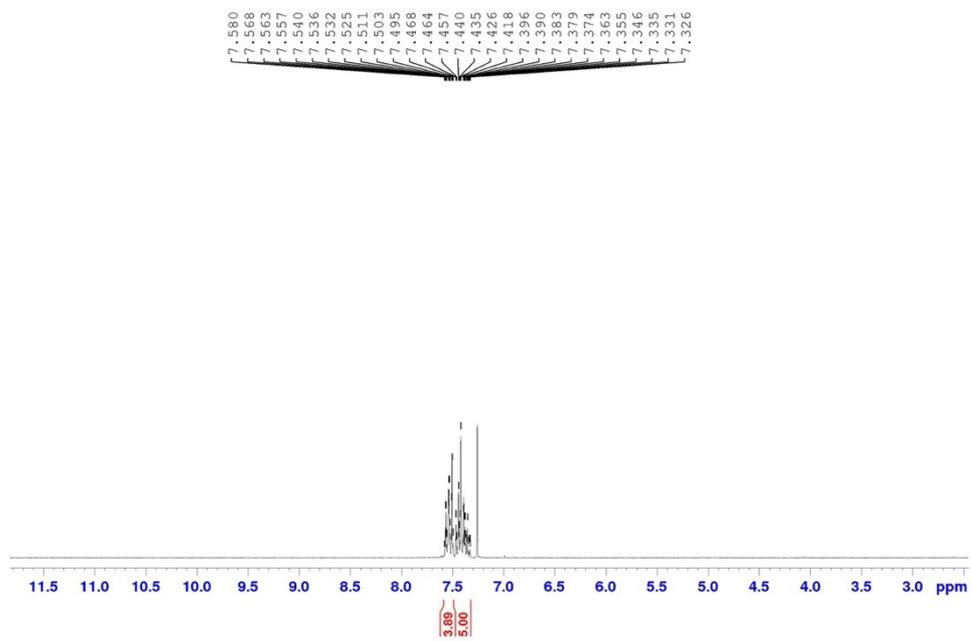
### <sup>1</sup>H NMR spectra of 5c



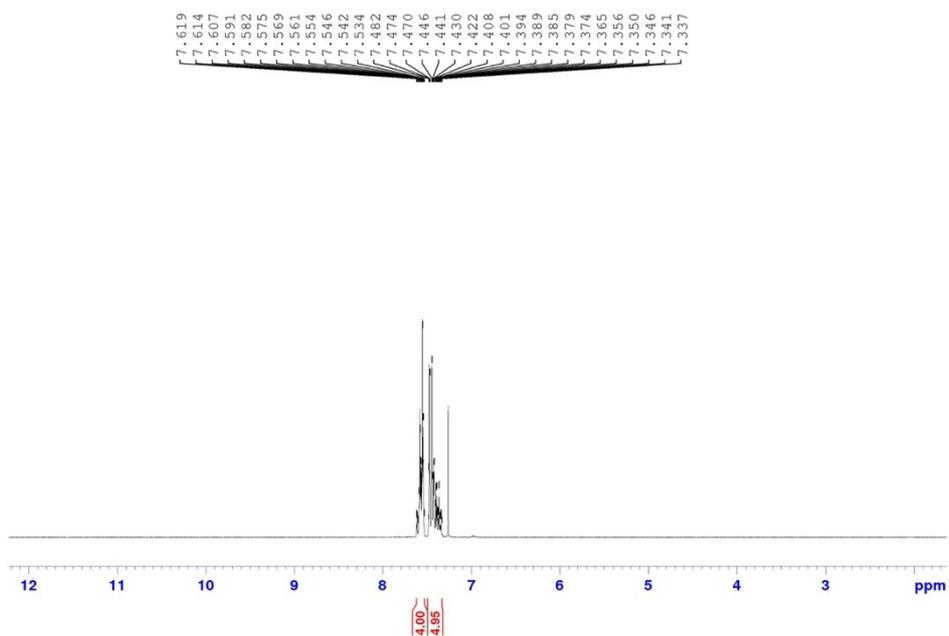
### <sup>1</sup>H NMR spectra of 5d



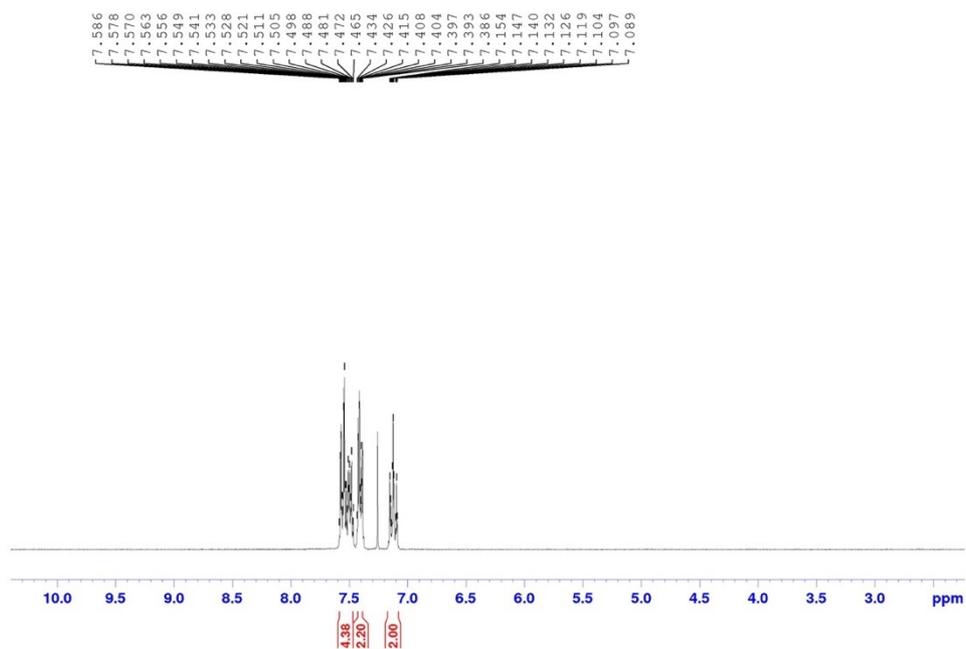
### <sup>1</sup>H NMR spectra of 5e



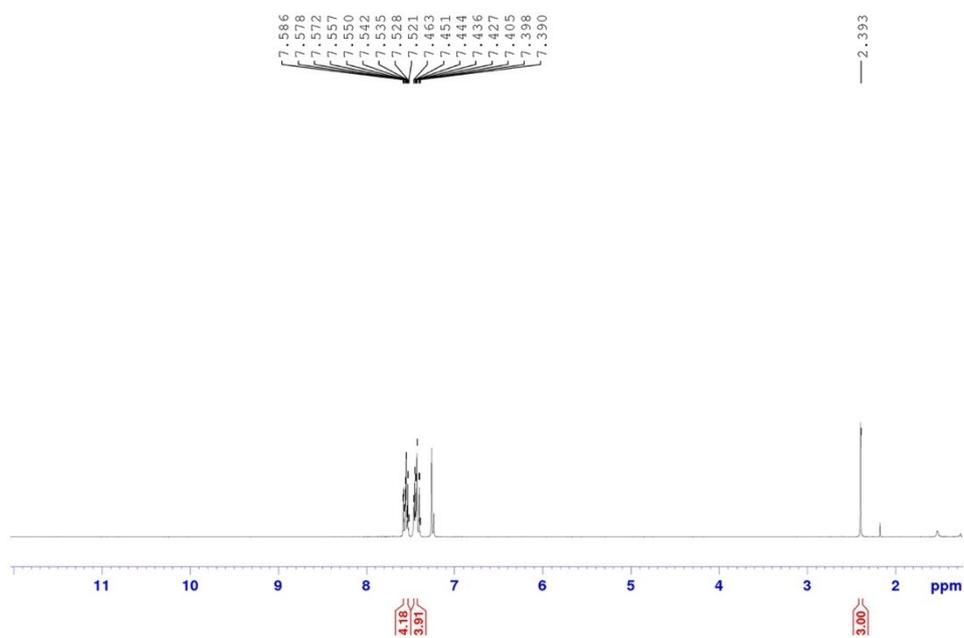
### <sup>1</sup>H NMR spectra of 5f



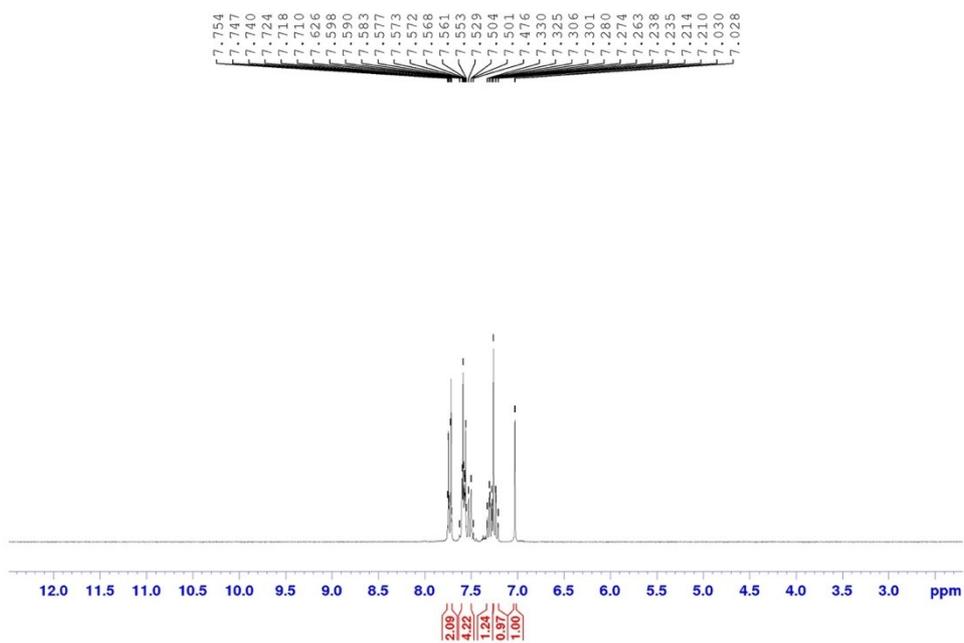
### <sup>1</sup>H NMR spectra of 5g



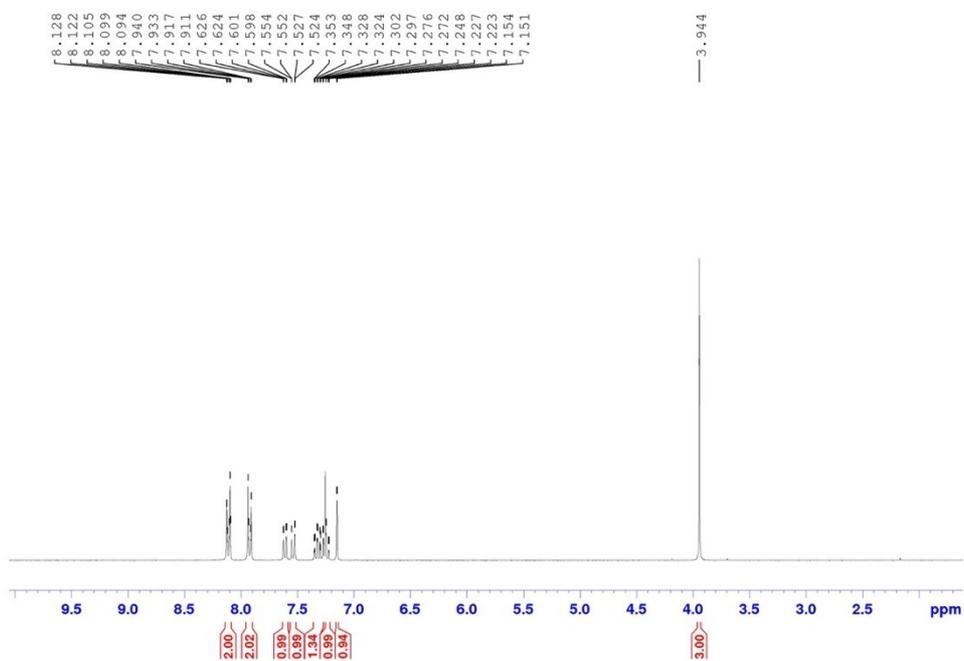
### <sup>1</sup>H NMR spectra of 5h



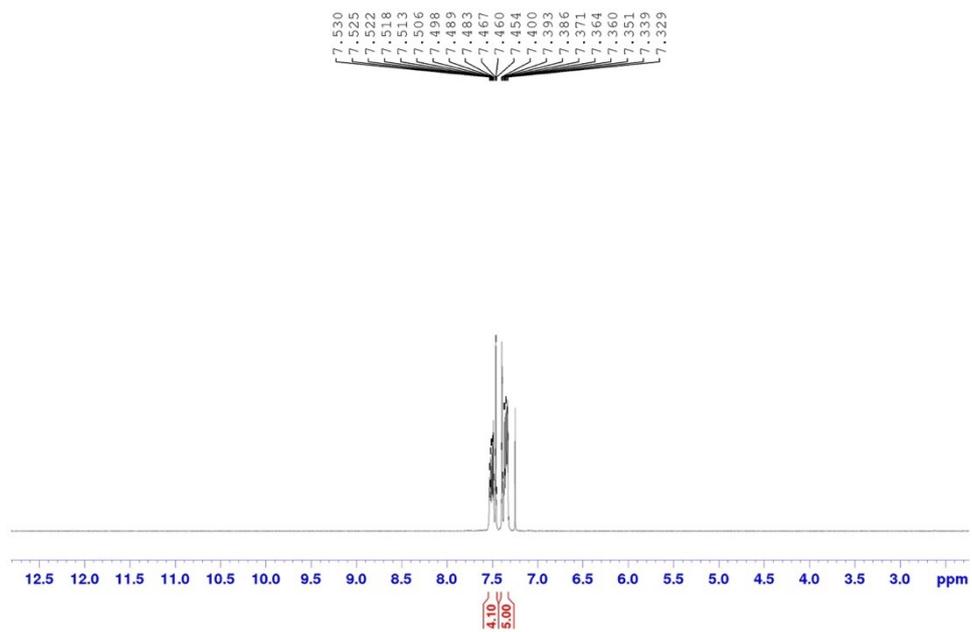
### <sup>1</sup>H NMR spectra of 5i



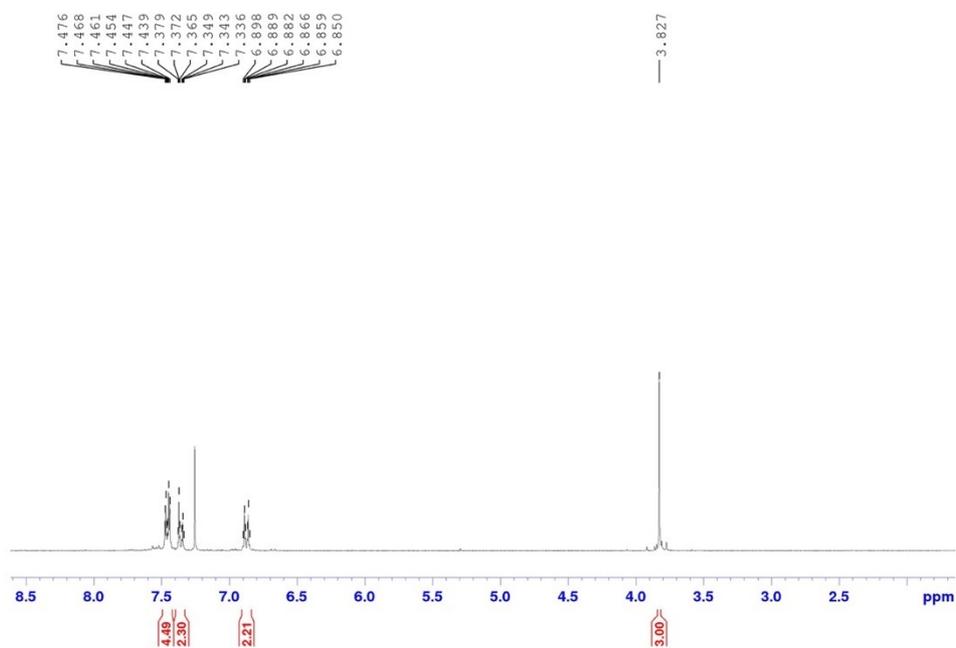
### <sup>1</sup>H NMR spectra of 5j



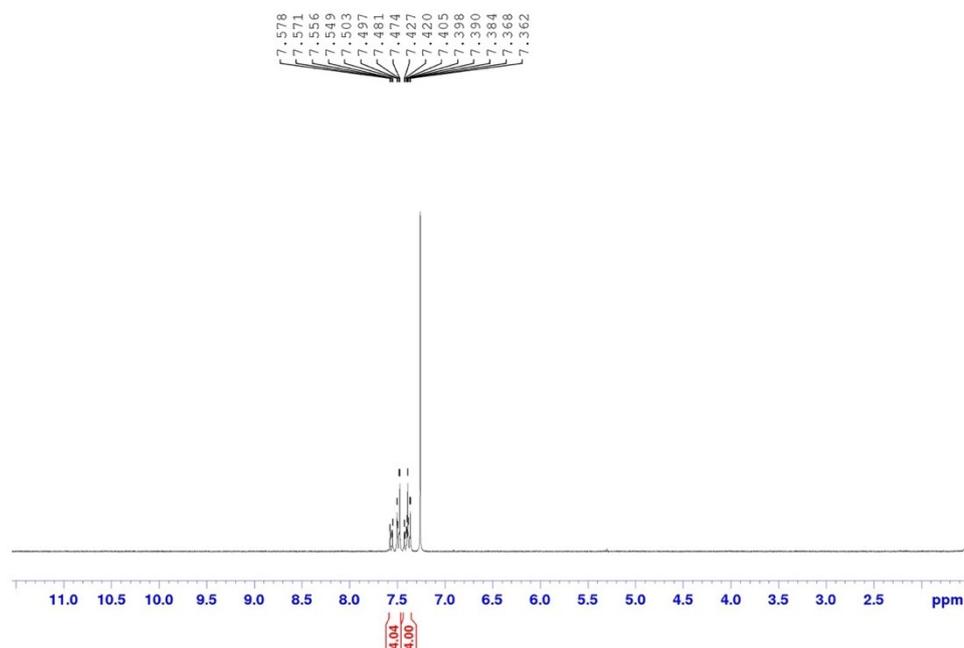
### <sup>1</sup>H NMR spectra of 7a



### <sup>1</sup>H NMR spectra of 7b



## <sup>1</sup>H NMR spectra of 7c



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