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Supporting Information

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1. Synthesis of NHC-Ag(I) catalysts

1.1 General methods

Unless otherwise noted, all the reagents and solvents were purchased from Merck, Alfa Aesar, and FluoroChem, and used without further purification. Merrifield resin HL (Novabiochem®, 100-200 mesh, 1.2 mmol g⁻¹) and chromatography grade silica gel (150 Å, 60-100 mesh, 75-250 µM, 1.15 cm³ g⁻¹ pore volume, 300 m² g⁻¹) were purchase from Merck Life Science S.r.l. (Milan, Italy). Dry solvents were obtained by distillation under nitrogen immediately prior to their use. Anhydrous reactions were conducted in flame-dried glassware under a positive pressure of nitrogen. The progress of the reactions was monitored by thin layer chromatography (TLC) (Silica gel 60 F254, Merck, Darmstadt, Germany) using the appropriate eluent system. Spots were visualized by UV detector (λ : 254 nm) and/or by staining and worming with KMnO₄. Quantitative TLCs were also used (Run length: 7 cm; Nominal conc.: 20 mg mL⁻¹; V: 10 µL each spot; Eluent: Petroleum ether/EtOAc (8:2, v/v); UV irradiation at 365 nm and 254 nm). When required, automated flash chromatography on silica gel was performed by using Biotage Isolera One. NMR spectra were recorded on a Bruker AC 400 MHz spectrometer in the indicated solvent. Chemical shifts are reported in parts per million (ppm) and are relative to CDCl₃ (7.26 ppm and 77.0 ppm), CD₃OD (3.31 ppm and 49.0 ppm) or to DMSO-d₆ (2.49 ppm and 39.7 ppm). The abbreviations used are as follows: s, singlet; brs, broad singlet; d, doublet; dd, double doublet; ddd, doublet of doublet of doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; brm, broad multiplet. The UV-Vis absorption profiles of starting materials and products were conducted in an Agilent 8453 UV-Vis spectrometer (Agilent Technologies, Germany). Scans were performed over a wavelength range of 200 to 800 nm. Standard cuvettes with optical path length of 1 cm were used and all measurements were performed in triplicate.

1.2 Synthesis of ligands (7b-e)

Ligands (**7b-e**) were synthesized according to previously reported procedures.^[1,2] Compounds characterizations were in agreement with literature data.

1-Phenyl-1H-imidazole (7b). 1.70 g (11.8 mmol, 80% yield); yellow oil. ¹H-NMR (400 MHz, CDCl₃): δ = 7.83 (s, 1H, 2-CH), 7.44 (t, J = 8.11 Hz, 2H, 2'-CH + 6'-CH), 7.35 (m, 3H, 3'-CH + 4'-CH + 5'-CH), 7.26 (s, 1 H, 5-CH), 7.18 (s, 1 H, 4-CH). ¹³C-NMR (100.6 MHz, CDCl₃): δ = 137.4, 135.6, 130.5, 130.0, 127.5, 121.5, 118.3.

2-(1'H-Imidazol-1'-yl)pyridine (7c). 1.56 g (10.8 mmol, 72% yield); pale-yellow oil. ¹H NMR (400 MHz, CDCl₃): δ= 8.43 (dd, *J*₁= 4.84 Hz, *J*₂= 0.98 Hz, 1H, 6-CH), 8.31 (s, 1H, 2'-CH), 7.75-7.77 (m, 1H, 4-CH), 7.60 (s, 1H, 5'-CH), 7.31 (d, *J*= 8.20 Hz, 1H, 3-CH), 7.19 (ddd, *J*₁= 7.42 Hz, *J*₂= 4.88 Hz, *J*₃= 0.88 Hz, 1H, 5-CH), 7.15 (s, 1H, 4'-CH imidazole). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 149.2, 149.1, 139.1, 135.1, 130.8, 122.1, 116.2, 112.4.

1-Methyl-4,5-dihydro-1H-imidazole (7e). 5.20 g (61.8 mmol, 81% yield); colourless liquid (b.p.: 178-180 °C, 765 mmHg). ¹H-NMR (400 MHz, CDCl₃): δ= 6.77 (s, 1H, 2-CH), 3.82 (t, *J*= 9.70 Hz, 2H, 4-CH), 3.17 (t, *J*= 9.70 Hz, 2H, 5-CH), 2.84 (s, 3H, N-CH₃). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 158.6, 55.4, 50.9, 34.3.

1.3 Synthesis of functionalized PS-NHC/Cl resins (8a-e)

Functionalized PS-NHC/Cl resins (**8a-e**) were prepared by *Li et al.* procedure.^[3]

PS-NHC/Cl (8a). 4.30 g of a pale resin were obtained from 4.00 g of Merrifield resin and 0.79 g of 1-benzyl-1H-imidazole (**7a**).

PS-NHC/Cl (8b). 8.50 g of a pale resin were obtained from 9.40 g of Merrifield resin and 1.70 g of 1-phenyl-1H-imidazole (**7b**).

PS-NHC/Cl (8c). 8.50 g of a pale resin were obtained from 8.60 g of Merrifield resin and 1.55 g of 2-(1'H-imidazol-1'-yl)pyridine (**7c**).

PS-NHC/Cl (8d). 9.84 g of pale resin were obtained from 10 g of Merrifield resin and 2.40 mL of 1-methyl-1H-imidazole (**7d**).

PS-NHC/Cl (8e). 14.53 g of a pale resin were obtained from 15 g of Merrifield resin and 1.60 g of 1-methyl-4,5-dihydro-1H-imidazole (**7e**).

1.4 Preparation of PS-NHC-Ag(I)/Cl catalysts (1-5)

PS-NHC-Ag(I)/Cl catalysts (**1-5**) were prepared by using *Li et al.* procedure.^[3] Ag loading was determined by ICP analysis performed in triplicate.

PS-NHC-Ag(I)/Cl (1). 7.40 g of a dark grey resin were obtained from 7.00 g of the corresponding functionalized resin (**8a**). Mean Ag loading: 8.33% wt.

PS-NHC-Ag(I)/Cl (2). 8.30 g of a dark grey resin were obtained from 8.50 g of the corresponding functionalized resin (**8b**). Mean Ag loading: 7.88% wt.

PS-NHC-Ag(I)/Cl (3). 8.00 g of a dark grey resin were obtained from 8.50 g of the corresponding functionalized resin (**8c**). Mean Ag loading: 5.36% wt.

PS-NHC-Ag(I)/Cl (4). 10.52 g of a dark grey resin were obtained from 9.64 g of the corresponding functionalized resin (**8d**). Mean Ag loading: 6.34% wt.

PS-NHC-Ag(I)/Cl (5). 14.50 g of a light grey resin were obtained from 14.35 g of the corresponding functionalized resin (**8e**). Mean Ag loading: 2.68% wt.

1.5 Preparation of Si-NHC-Ag(I)/Cl catalyst (6)

Si-NHC-Ag(I)/Cl catalyst (**6**) was prepared according to previously reported procedures.^[4,3] Ag loading was determined by ICP analysis performed in triplicate.

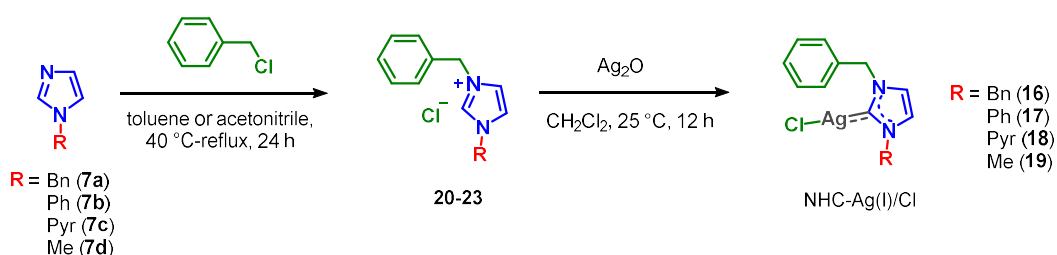
Si-NHC/Cl (10). 10.90 g as white resin were obtained from 10.00 g of commercial chromatography grade silica gel and 2.75 mL of (3-chloropropyl)-trimethoxysilane (**9**).

Si-NHC/Cl (11). 10.55 g as a white resin were obtained from 10.90 g of the corresponding functionalized resin (**10**) and 3.30 g of 1-benzyl-1*H*-imidazole (**7a**).

Si-NHC Ag(I)/Cl (6). 11.15 g of a dark grey resin were obtained from 10.55 g of the corresponding functionalized resin (**11**). Mean Ag loading: 2.83% wt.

1.6 Synthesis of NHC-Ag(I)/Cl (16-19)

Not supported Ag catalysts (**16-19**) were synthesized as previously described (Scheme S1).^[3] The spectroscopic NMR analyses of ionic liquids (**20-23**) were in agreement with literature data.^[5-9]



Scheme S1. Synthesis of homogeneous NHC-Ag(I)/Cl catalysts (**16-19**).

1,3-Dibenzyl-1*H*-imidazol-3-ium chloride (20). 10.80 g (39.5 mmol, > 98% yield); colourless liquid. ¹H-NMR (400 MHz, CDCl₃): δ= 11.15 (s, 1H, 2-CH), 7.40-7.49 (m, 4H), 7.31-7.39 (m, 6H), 7.13-7.22 (m, 2H), 5.54 (s, 4H). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 137.2, 133.2, 129.4 (x2), 129.0, 122.3, 53.3.

3-Benzyl-1-phenyl-1*H*-imidazol-3-ium chloride (21). 688 mg (2.5 mmol, 95% yield); brown oil. ¹H-NMR (400 MHz, CDCl₃): δ= 11.45 (s, 1H, 2-CH), 7.67-7.78 (m, 3H), 7.57-7.66 (m, 3H), 7.40-7.52 (m, 3H), 7.30-7.37 (m, 3H), 5.78 (s, 2H). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 135.4, 133.5, 132.2, 129.6, 129.2, 128.5, 128.4 (x2), 121.7, 120.6, 119.6, 52.6.

3-Benzyl-1-(pyridin-2-yl)-1*H*-imidazol-3-ium chloride (22). 1.54 g (5.7 mmol, > 98% yield); yellow oil. ¹H-NMR (400 MHz, CDCl₃): δ= 12.12 (s, 1H, 2-CH), 8.50-8.58 (m, 1H), 8.41-8.47 (m, 1H), 8.22-8.27 (m, 1H), 7.95-8.03 (m, 1H), 7.55-7.64 (m, 2H), 7.47-7.52 (m, 1H), 7.33-7.43 (m, 4H), 5.75 (s, 2H). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 148.9, 146.0, 140.6, 136.3, 132.9, 129.6, 129.5, 129.3, 125.1, 122.0, 118.9, 115.0, 53.9.

3-Benzyl-1-methyl-1*H*-imidazol-3-ium chloride (23). 2.80 g (13.4 mmol, > 98% yield); pale-yellow oil. ¹H-NMR (400 MHz, CDCl₃): δ= 10.83 (s, 1H, 2-CH), 7.42-7.49 (m, 2H), 7.35-7.41 (m, 3H), 7.29-7.34 (m, 1H), 7.25-7.28 (m, 1H), 7.18-7.24 (m, 1H), 5.56 (s, 2H), 4.06 (s, 3H). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 137.1, 132.1, 128.5, 128.4, 127.9, 120.7, 52.3, 35.7.

NHC-Ag(I)/Cl (16). 200 mg (0.5 mmol, > 98% yield); brownish/black oil. ¹H-NMR (400 MHz, CDCl₃): δ= 7.28-7.39 (m, 5H), 7.17-7.24 (m, 4H), 6.94-7.00 (m, 2H), 5.22 (s, 4H). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 144.5, 135.6, 129.3, 128.8, 127.9, 122.1, 55.8.

NHC-Ag(I)/Cl (17). 245 mg (0.7 mmol, 88% yield); brownish/black oil. ¹H-NMR (400 MHz, CDCl₃): δ= 7.51-7.57 (m, 2H), 7.41-7.51 (m, 3H), 7.33-7.41 (m, 3H), 7.28-7.33 (m, 2H), 7.27-7.28 (m, 1H), 7.10-7.16 (m, 1H), 5.38 (s, 2H). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 139.8, 135.2, 130.0, 129.2, 129.1, 128.9, 128.0, 124.0, 122.3, 121.7, 56.2.

NHC-Ag(I)/Cl (18). 244 mg (0.6 mmol, 84% yield); brownish/black oil. ¹H-NMR (400 MHz, CDCl₃): δ= 8.44-8.50 (d, 1H, J= 4.00), 8.06-8.13 (d, 1H, J= 4.00), 7.81-7.90 (td, 2H, J₁= 4.00, J₂= 8.00), 7.32-7.39 (m, 4H), 7.27-7.32 (m, 2H), 7.09-7.15 (d, 1H, J= 4.00), 5.42 (s, 2H). ¹³C-NMR (100.6 MHz, CDCl₃): δ= 149.7, 148.0, 138.5, 134.0, 128.2, 127.8, 126.9, 122.8, 120.7, 199.7, 114.8, 55.7.

NHC-Ag(I)/Cl (19). 247 mg of (0.8 mmol, 84% yield); brownish/black oil. ¹H-NMR (400 MHz, CDCl₃): δ= 7.23-7.31 (m, 3H), 7.14-7.18 (m, 2H), 6.92-6.96 (d, 1H, J= 4.00), 6.87-6.90 (d, 1H, J= 4.00), 5.20 (s,

2H), 3.77 (s, 3H). ^{13}C -NMR (100.6 MHz, CDCl_3): δ = 135.5, 129.1, 128.7, 127.8, 122.7, 121.2, 55.7, 38.9.

2. Characterization of NHC-Ag(I) catalysts

SEM analyses were performed using FE-SEM LEO 1525 ZEISS (Jena, DE); the acceleration potential voltage was maintained at 15 keV and measurements were carried out using AsB detector (Angle selective Backscattered detector) and In-lens detector. Samples were deposited on conductive carbon adhesive tape and metalized by sputtering with chromium (8 nm). Elemental composition and chemical mapping were determined using a Bruker Quantax EDX equipped with an annular four-channel silicon drift detector SDD XFlash 410 M and a software Esprit v. 1.9 (Bruker, Billerica, Massachusetts, USA). Inductively coupled plasma optical emission spectrometry were conducted on ICP-OES, Varian Liberty Series instrument.

3. Preliminary reaction screening

All the reactions were performed on 12.5 mg (0.12 mmol) scale of substrate. To a stirred solution of 4-cyanopyridine (**12**) (0.12 mmol, 1.0 equiv.) in the organic solvent of choice ($[\mathbf{12}] = 0.2 \text{ M}$), TFA (0.12 mmol, 1.0 equiv.) and *p*-tolylboronic acid (**13**) 0.18 mmol, 1.5 equiv.) were sequentially added. DMF (5%, *v/v*) was eventually added as the co-solvent to improve the solubility of **13**. Compound **13** in H₂O ($[\mathbf{13}] = 0.2 \text{ M}$) was then added, followed by the addition of (NH₄)₂S₂O₈ (0.36 mmol, 3.0 equiv.) and the Ag(I) catalyst **1** (40 mg, 0.04 mmol, 0.3 equiv.).^[10] After 2 h, the reaction mixture was filtered and the filtrate was washed with an aqueous solution of NaOH (2 N). The aqueous phase was extracted with the organic solvent of choice and the combined organic extracts were washed with 5% (*w/v*) aqueous solution of Na₂S₂O₃ (10 mL), H₂O (10 mL), brine (10 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude reaction mixtures were analyzed by calibrated HPLC method or purified by automated flash chromatography on silica gel.

2-(*p*-Tolyl)isonicotinonitrile (14**).**^[11] Pale yellow crystalline solid. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.81$ (d, $J = 5.0 \text{ Hz}$, 1H, 6-CH), 7.89 (s, 1H, 3-CH), 7.87 (d, $J = 8.0 \text{ Hz}$, 2H, 2'-CH + 6'-CH), 7.39 (d, $J = 5.0 \text{ Hz}$, 1H, 5-CH), 7.31 (d, $J = 8.1 \text{ Hz}$, 2H, 3'-CH + 4'-CH), 2.41 (s, 3H, CH₃). ¹³C-NMR (100.6 MHz, CDCl₃): $\delta = 158.5, 150.4, 140.4, 134.4, 129.7, 126.7, 122.7, 121.58, 120.9, 116.7, 21.2$.

3-(*p*-Tolyl)isonicotinonitrile (15**).**^[11] Pale yellow crystalline solid. ¹H-NMR (400 MHz, CDCl₃): $\delta = 8.84$ (s, 1H, 2-CH), 8.72 (d, $J = 5.0 \text{ Hz}$, 1H, 6-CH), 7.61 (d, $J = 5.0 \text{ Hz}$, 1H, 5-CH), 7.49 (d, $J = 8.1 \text{ Hz}$, 2H, 2'-CH + 6'-CH), 7.36 (d, $J = 8.0 \text{ Hz}$, 2H, 3'-CH + 5'-CH), 2.44 (s, 3H, CH₃). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 150.9, 148.3, 139.7, 138.7, 131.4, 129.8, 128.6, 126.0, 118.6, 116.5, 21.3$.

4. Kinetic study

To a solution of 4-cyanopyridine (**12**) (90 mg, 0.86 mmol) in CHCl_3 (2.5 mL), TFA (66 μL , 0.86 mmol) and *p*-tolyl boronic acid (**13**) (176 mg, 1.30 mmol) in CHCl_3 (2.5 mL) were added in a 25 mL round-bottom flask. NHC-Ag(I)-based catalyst (0.26 mmol, 0.3 equiv.)^[10] was added under dark conditions followed by the addition of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (592 mg, 2.60 mmol) in H_2O (2.5 mL). The resulting suspension was stirred for 2 h at 25 °C. Seven samples of 1 mL were collected by at time intervals: 0 min (before the addition of the oxidant), 5 min, 15 min, 30 min, 1 h, and 2 h. The mixture was filtered through a cellulose regenerated membrane filter (25 mm diameter size, 0.22 μm pore size, ClearLine, non-sterile) and washed with 0.5 mL of a $\text{CHCl}_3/\text{MeOH}$ solution (98:2, v/v). Crudes were dried under nitrogen atmosphere at 50 °C for 2 h and in a vacuum oven for 12 h at 25 °C. The crudes were analyzed by calibrated HPLC analysis.

5. Recyclability of catalyst **6**

To a solution of 4-cyanopyridine (**12**) (100 mg, 0.96 mmol) in CHCl₃ (2.5 mL), TFA (67 μL, 0.96 mmol) and *p*-tolylboronic acid (**13**) (196 mg, 1.44 mmol) in CHCl₃ (2.5 mL) were added in a 25 mL round-bottom flask. Si-NHC-Ag(I)/Cl (**6**) (900 mg, 0.29 mmol, Ag 3.50 wt%) was added followed by the addition of (NH₄)₂S₂O₈ (657 mg, 2.88 mmol) in H₂O (5 mL). The resulting suspension was stirred for 15 min at 25 °C under dark conditions. The catalyst was filtered off and washed with 5 mL of CHCl₃/MeOH 98:2 (v/v). The recovered catalyst was used for additional consecutive run without further treatment. Each run was diluted with an aqueous solution of 2 N NaOH (10 mL) and extracted with CHCl₃ (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude reaction mixtures were dissolved in CHCl₃ (5 mL), filtered through a cellulose regenerated membrane filter (25 mm diameter size, 0.22 μm pore size, ClearLine, non-sterile), dried under nitrogen atmosphere and vacuum at 40 °C for 12 h, and readily analyzed by calibrated HPLC method.

6. Reaction scope

To a 0.2 M solution of pyridine (**24a-c**) (100 mg, 1 equiv.) in CHCl₃, TFA (1 equiv.) and boronic acid (**25a-e**) (1.5 equiv.) were sequentially added into a 25 mL round bottom flask. Then, Si-NHC-Ag(I)/Cl (**6**) (0.3 equiv.) and an aqueous solution (0.2 M) of (NH₄)₂S₂O₈ (3 equiv.) were added to the organic solution. The resulting suspension was stirred for 15 min at 25 °C under dark conditions. The suspension was filtered on a Hirsh filter washing with 5 mL of CHCl₃/MeOH 98:2 (v/v). The crude was treated with an aqueous solution of 2 N NaOH (10 mL), separated, and the water layer was extracted with CHCl₃ (5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crudes were purified by automated flash chromatography using PET/EtOAc as eluting system solvent to give the desired compounds **26-32**.

2-(p-Tolyl)-4-(trifluoromethyl)pyridine (26).^[11] 140 mg (0.59 mmol). Isolated yield: 87%. Colourless oil. ¹H-NMR (CDCl₃, 400 MHz): δ= 8.84 (d, *J*= 5.1 Hz, 1H), 7.98 – 7.87 (m, 3H), 7.41 (dd, *J*= 5.1, 1.6 Hz, 1H), 7.31 (d, *J*= 8.0 Hz, 2H), 2.43 (s, 3H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ= 158.9, 150.7, 140.2, 139.0 (q, *J*= 33.9 Hz), 135.4, 129.8, 127.0, 123.1 (q, *J*= 272.6 Hz), 117.3 (q, *J*= 4.0 Hz) 115.8 (q, *J*= 4.0 Hz), 21.5. ¹⁹F-NMR (CDCl₃, 376 MHz): δ= -64.84.

2-Phenyl-4-(trifluoromethyl)pyridine (27).^[12] 100 mg (0.45 mmol). Isolated yield: 66%. Colourless oil. ¹H-NMR (CDCl₃, 400 MHz): δ= 8.87 (d, *J*= 5.1 Hz, 1H), 8.08 – 8.00 (m, 2H), 7.96 – 7.92 (m, 1H), 7.57 – 7.42 (m, 4H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ= 158.9, 150.8, 139.3 (q, *J*= 33.2 Hz), 138.2, 130.0, 129.1, 127.2, 123.1 (q, *J*= 273.6 Hz), 117.6 (q, *J*= 4.0 Hz), 116.2 (q, *J*= 3.0 Hz). ¹⁹F-NMR (CDCl₃, 376 MHz): δ= -64.83.

2-(2,3-Dimethylphenyl)-4-(trifluoromethyl)pyridine (28). 145 mg (0.58 mmol). Isolated yield: 85%. Colourless oil. ¹H-NMR (CDCl₃, 400 MHz): δ= 8.74 (d, *J*= 5.0 Hz, 1H), 7.81 (s, 1H), 7.74 (d, *J*= 2.0 Hz, 1H), 7.65 (dd, *J*= 7.8, 2.0 Hz, 1H), 7.30 (dd, *J*= 5.1, 1.6 Hz, 1H), 7.21 – 7.13 (m, 1H), 2.27 (s, 3H), 2.24 (s, 3H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ= 159.1, 150.6, 139.4 (q, *J*= 33.0 Hz), 138.9, 137.4, 135.8, 130.4, 128.3, 124.5, 123.2 (q, *J*= 273.6 Hz), 117.6 (q, *J*= 3.0 Hz), 115.8 (q, *J*= 4.0 Hz), 20.0, 19.8. ¹⁹F-NMR (CDCl₃, 376 MHz): δ= -64.83.

2-(4-Fluorophenyl)-4-(trifluoromethyl)pyridine (29). 151 mg (0.63 mmol). Isolated yield: 92%. Colourless oil. ¹H-NMR (CDCl₃, 400 MHz): δ = 8.84 (d, *J* = 5.1 Hz, 1H), 8.07 – 7.99 (m, 2H), 7.88 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.44 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.23 – 7.14 (m, 2H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ = 164.2 (d, *J* = 250.5 Hz), 157.9, 150.8, 139.4 (q, *J* = 34.2 Hz), 134.3 (d, *J* = 3.0 Hz), 129.1 (d, *J* = 9.0 Hz), 123.0 (q, *J* = 272.6 Hz), 116.2, 116.0, 115.8 (q, *J* = 4.0 Hz). ¹⁹F-NMR (CDCl₃, 376 MHz): δ = -64.86, -111.47.

2-(2-Methoxyphenyl)-4-(trifluoromethyl)pyridine (30). 139 mg (0.55 mmol). Isolated yield: 81%. Colourless oil. ¹H-NMR (CDCl₃, 400 MHz): δ = 8.86 (d, *J* = 5.1 Hz, 1H), 8.12 (dt, *J* = 1.6, 0.9 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.11 (td, *J* = 7.5, 1.1 Hz, 1H), 7.03 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.89 (s, 3H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ = 157.4, 157.2, 150.3, 138.0 (q, *J* = 33.2 Hz), 131.3, 130.9, 127.7, 123.2 (q, *J* = 272.6 Hz), 121.3, 120.9 (q, *J* = 3.0 Hz), 117.2 (q, *J* = 3.0 Hz), 111.5, 55.7. ¹⁹F-NMR (CDCl₃, 376 MHz): δ = -64.73.

Compounds **31** were obtained in 95% yield (167 mg, 0.79 mmol) and in a 1:2.7:1.5 ratio (C2:C4:C6) determined by NMR. NMR analyses were in agreement with the literature data.^[11]

1-(2-(p-Tolyl)pyridin-3-yl)ethan-1-one (C2). 32 mg (0.15 mmol). Colourless oil. ¹H-NMR (CDCl₃, 400 MHz): δ = 8.75 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.34 – 7.28 (m, 5H), 2.42 (s, 3H), 2.07 (s, 3H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ = 204.0, 157.2, 150.8, 139.6, 136.8, 136.2, 136.2, 129.5, 129.0, 121.6, 30.3, 21.3.

1-(4-(p-Tolyl)pyridin-3-yl)ethan-1-one (C4). 86 mg (0.41 mmol). White crystalline solid. ¹H-NMR (CDCl₃, 400 MHz): δ = 8.75 (s, 1H), 8.71 (d, *J* = 5.1 Hz, 1H), 7.35 – 7.27 (m, 5H), 2.45 (s, 3H), 2.10 (s, 3H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ = 202.9, 151.5, 148.8, 148.0, 139.5, 135.9, 135.0, 129.9, 128.4, 124.3, 30.6, 21.4.

1-(6-(p-Tolyl)pyridin-3-yl)ethan-1-one (C6). 49 mg (0.23 mmol). White crystalline solid. ¹H-NMR (CDCl₃, 400 MHz): δ = 9.21 (dd, *J* = 2.4, 0.9 Hz, 1H), 8.27 (dd, *J* = 8.4, 2.3 Hz, 1H), 8.01 – 7.93 (m, 2H), 7.81 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.35 – 7.28 (m, 2H), 2.65 (s, 3H), 2.42 (s, 3H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ = 196.6, 161.1, 150.3, 140.5, 136.4, 135.5, 130.6, 129.8, 127.4, 119.9, 26.8, 21.5.

Compounds **32** were obtained in 70% yield (115 mg, 0.46 mmol) in a 1:2:1.2 ratio (C2:C4:C6). C4 and C6 regioisomers could not readily be separated by silica gel chromatography, so they were

characterized from the reaction crude mixture. NMR analyses were in agreement with the literature data.^[11]

3-Bromo-2-(p-tolyl)pyridine (C2). 27 mg (0.11 mmol). White crystalline solid. ¹H-NMR (CDCl₃, 400 MHz): δ = 8.74 – 8.69 (m, 1H), 7.91 – 7.81 (m, 3H), 7.60 (dd, *J* = 8.5, 0.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H). ¹³C-NMR (CDCl₃, 100.6 MHz): δ = 156.1, 150.7, 139.6, 139.3, 135.6, 129.7, 126.8, 121.5, 119.0, 21.4.

3-Bromo-4-(p-tolyl)pyridine (C4) and 5-Bromo-2-(p-tolyl)pyridine (C6). 88 mg (0.36 mmol). Colourless oils. ¹H-NMR (CDCl₃, 400 MHz): δ 8.80 (s, 1H), 8.61 (dd, *J* = 4.6, 1.5 Hz, 1H), 8.53 (d, *J* = 4.9 Hz, 1H), 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.26 (m, 5H), 7.12 (dd, *J* = 8.0, 4.6 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H). ¹³C NMR (CDCl₃, 100.6 MHz): δ = 158.1, 152.4, 149.6, 148.2, 148.0, 141.2, 138.8, 138.6, 136.6, 135.1, 129.1, 129.0, 128.7, 128.6, 125.6, 123.0, 120.8, 119.7, 21.3, 21.3.

7. Flow reaction

7.1 Instruments

Flow experiment was performed using and a commercially available modular Syrris Asia system composed by two-channels syringe pumps (Asia blue syringes, 0.50 mL/1.0 mL), a glass tubular mesoreactors (Omnifit Labware DIBA HIT™ column, ID × L 1.6 mm x 100 mm), a T-shaped mixing elements (0.5 mm ID), back pressure regulators (BPR, 100 psi, PEEK, 1/16" OD, 1/4"-28), and a fraction collector (Gilson FC 203B fraction collector).

7.2 Flow set-up

The flow set-up consisted of two syringe pumps, a T-shaped mixer unit, a packed-bed column reactor (I.D. x L: 1.6 x 100 mm) filled with Si-supported catalyst **6**, and a BPR (100 psi). The experiment was carried out using a stock solution of 4-cyanopyridine (**12**) (0.2 M, 4.0 mmol), TFA (4.0 mmol, 1.0 equiv.), and (NH₄)₂S₂O₈ (12.0 mmol, 3.0 equiv.) in H₂O, and a solution of *p*-tolylboronic acid (**13**) (0.3 M, 6.0 mmol, 1.5 equiv.) in CHCl₃ + 5% v/v DMF (to favour the solubility of **13** and avoid clogging phenomena). The two solutions were mixed at a total flow rate of 67 μL min⁻¹ by a T-junction and entered into the tubular mesoreactor (DIBA 1.6 x 100 mm, 1 fixed and 1 adjustable endpiece, bed volume mL= 0.3421 x bed high in cm= 1 mL) filled with the supported catalyst Si-NHC-Ag(I)/Cl (**6**) (500 mg, 0.15 mmol, mean Ag loading= 3.00 wt%, h= 2.9 cm) at 25 °C (τ = 15 min). For each fraction, the outcome was collected for 15 min after the death volume for eight reaction cycles (120 min in total). The catalyst was finally washed with MeOH at reflux for 1 h. Each reaction cycle (1 mL) including the conditioning fraction were collected. The aliquots were filtered through a cellulose regenerated membrane filter (25 mm diameter size, 0.22 μm pore size, ClearLine, non-sterile) and washed with 0.5 mL of a mixture of CHCl₃/MeOH 98:2 (v/v). The crude was dried under nitrogen atmosphere at 25 °C, lyophilized, and analyzed by calibrated HPLC method.

8. HPLC analysis

All the reagents were of analytical grade. Acetonitrile (ACN) was purchased from Merck Life Science S.r.l. (Milan, Italy), while water for HPLC analysis was purified with a New Human Power I Scholar water purification system (Human Corporation, Seoul, Korea) and Milli-Q water purification system of Millipore (Milan, Italy). The HPLC study was performed on a Waters ALLIANCE 2695 Separations Module system (from Waters Corporation, Milford, MA, US), equipped with a quaternary, low-pressure mixing pump and in-line vacuum degassing, an autosampler with maximum capacity of 120 vials, and a column heater/cooler. The system is endowed with a photodiode array (PDA) detector (Waters 2996). The data management was made by a Waters® Millennium®32 Software. The column Robusta C18 (250 x 4.6 mm I.D., 5 μm , 110 Å) was purchased from SepaChrom (Rho, Italy). A water/ACN 50:50 (v/v) solution was used as the mobile phase. The column was conditioned with the selected mobile phase at a 1.0 mL min⁻¹ flow rate for at least 40 min before use. All the analyses were carried out at 25 °C column temperature and with a 1.0 mL min⁻¹ eluent flow rate. The injection volume was 20 μL , and the chromatographic analyses were followed at 254 nm for the C2 and C3 regioisomers (**14-15**), and at 220 nm for the 4-cyanopyridine (**12**). All the investigated samples were solubilized in the above hydro-organic mobile phase at a final concentration of 0.25 mg mL⁻¹. Quantitative analysis was performed by use of calibration curves in the ranges: 0.005-1.3 mM for C2 and C3 (**14-15**), and 0.009-1.2 mM. In Figure S1, an exemplary chromatogram of the complete (baseline) separation of 4-cyanopyridine (**12**, peak 1), *p*-tolylboronic acid (**13**, peak 2), 3-(*p*-tolyl)-isonicotinonitrile (**15**, peak 3, referred to as C3 isomer), and 2-(*p*-tolyl)-isonicotinonitrile (**14**, peak 4, referred to as C2 isomer), and under the optimized chromatographic conditions (see above) is shown.

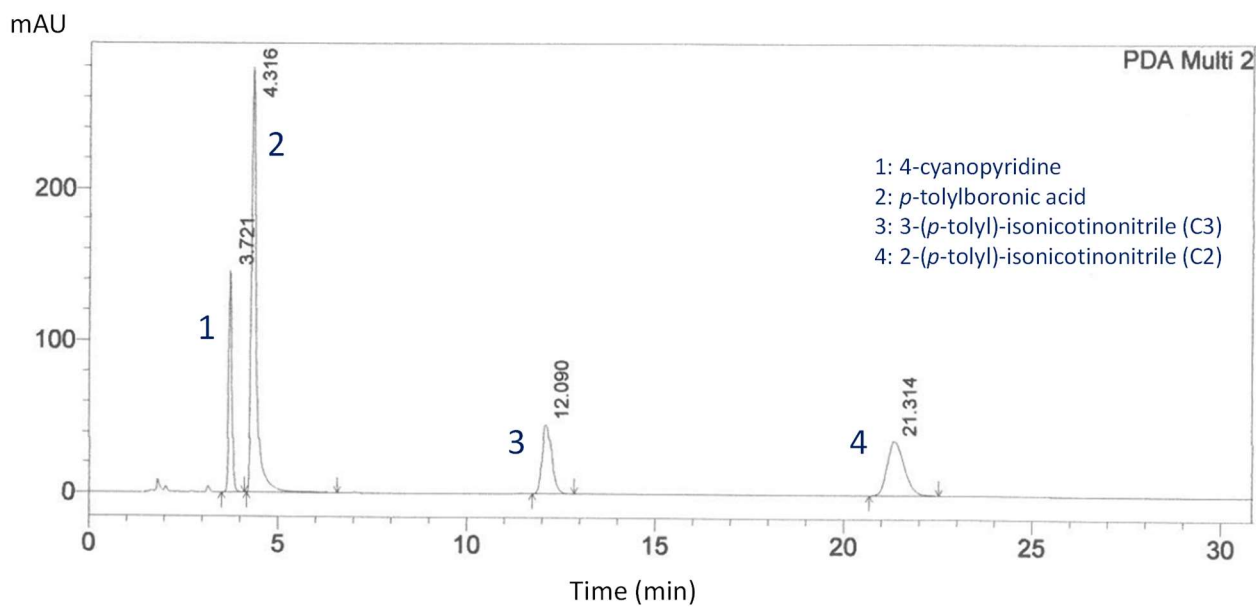


Figure S1. HPLC chromatogram of the model Borono-Minisci reaction.

9. Electrochemical measurements

Cyclic voltammetry (CV) experiments (Figure S2) were carried out in an airtight single-compartment electrochemical cell described elsewhere,^[13,14] by using glassy carbon as the working and platinum as the counter electrode and either a silver spiral as a quasi-reference electrode (QRE) or an aqueous 3 M KCl silver/silver-chloride (Ag/AgCl/KCl (3 M)) reference electrode. The drift of the quasi-reference electrode was negligible during the time required for an experiment. The cell containing the supporting electrolyte and the electroactive compound was dried under vacuum at 25 °C for about 2 h. ACN was introduced under argon (Ar) atmosphere. The solution was degassed by performing 3-times vacuum/Ar cycles and left under a blanket of Ar at 1 bar pressure. All the redox potential (E) values are referred to an aqueous Ag/AgCl/KCl (3 M) and they have been determined by adding, at the end of each experiment, ferrocene (Sigma-Aldrich) as an internal standard in the case of a quasi-reference Ag-wire was used. The $E_{1/2}$ potentials have been directly obtained from CV curves as averages of the cathodic and anodic peak potentials for one-electron peaks. The potentials thus obtained were not corrected for (i) the liquid junction potential between the organic phase and the aqueous SCE solution and (ii) the ohmic drop due to the uncompensated resistance between working and reference electrodes. Voltammograms were recorded by using a Biologic potentiostat SP300 instrument.

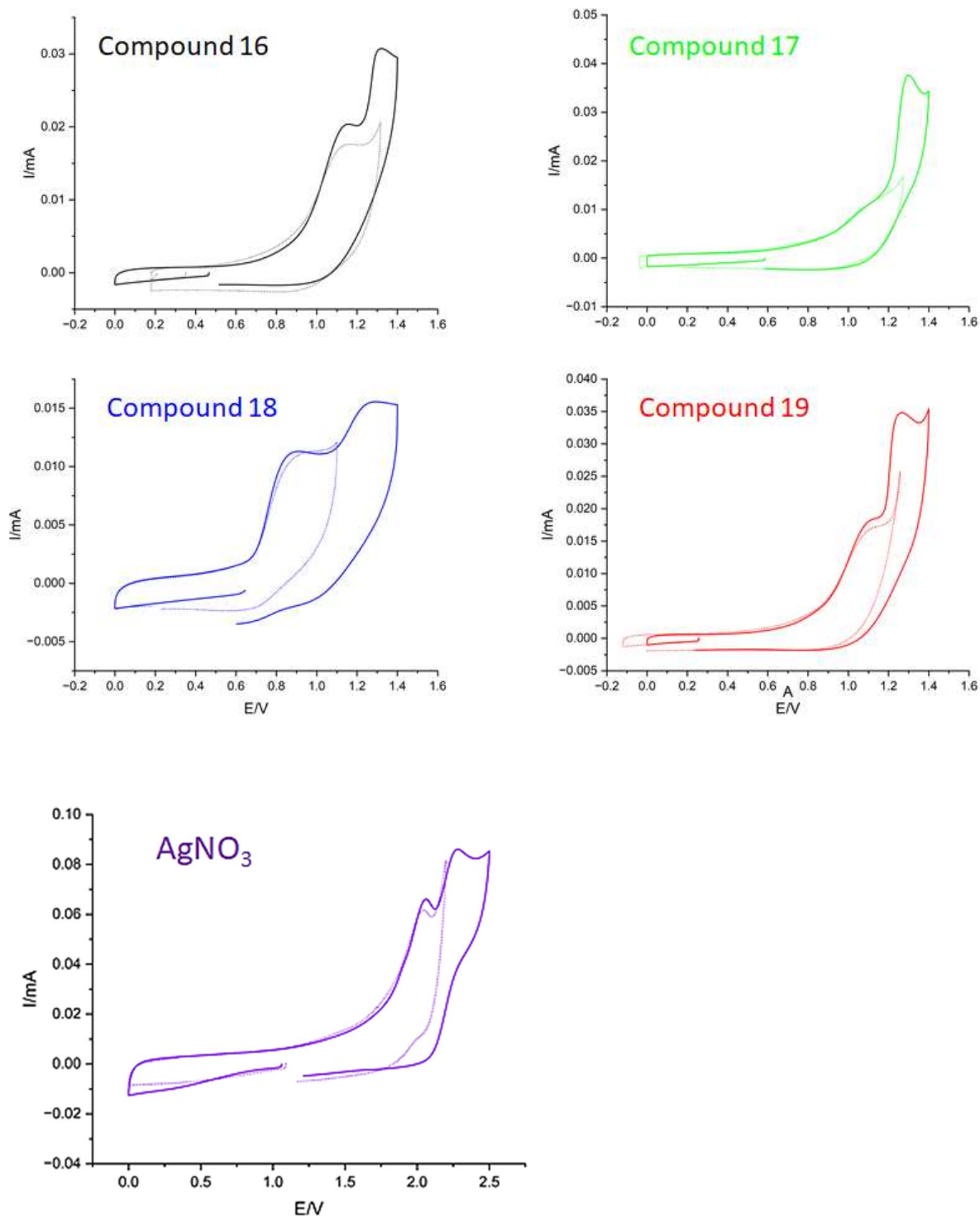
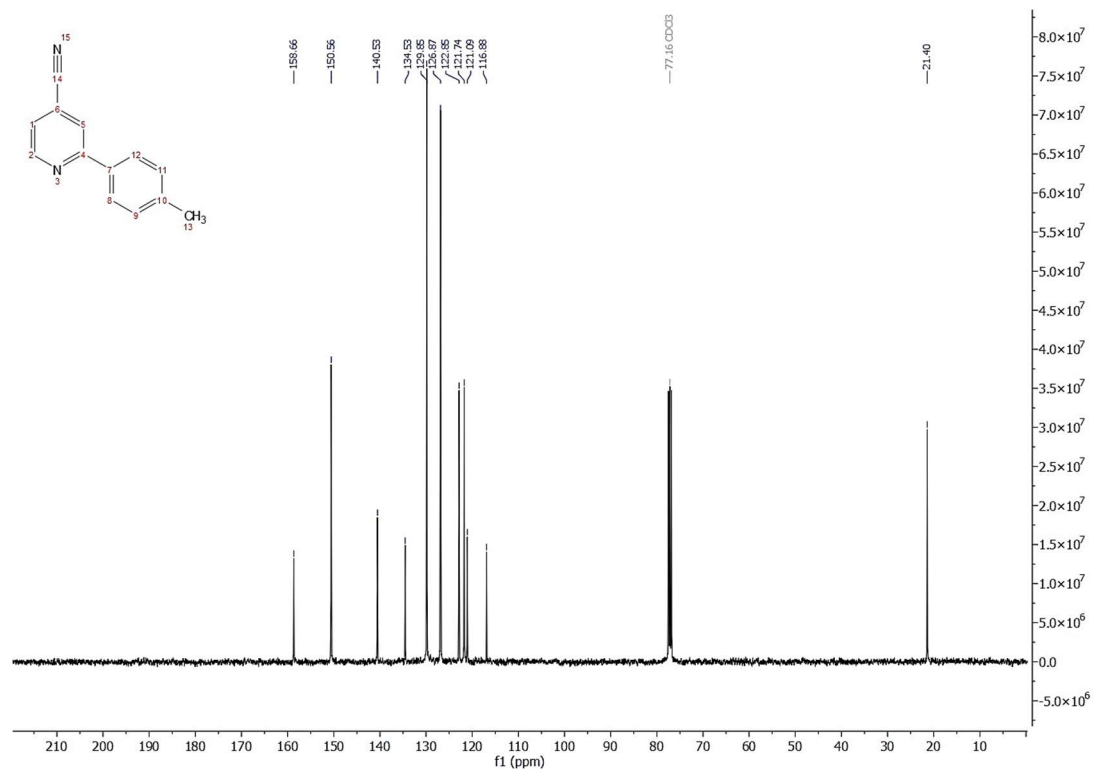
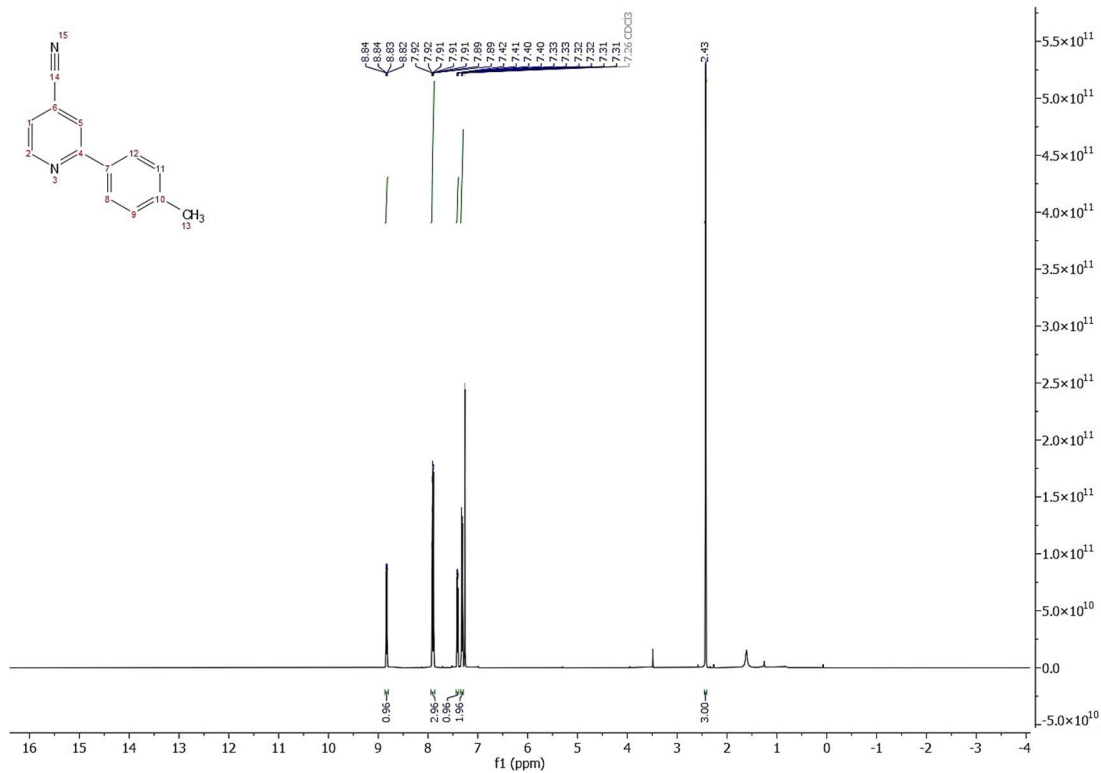


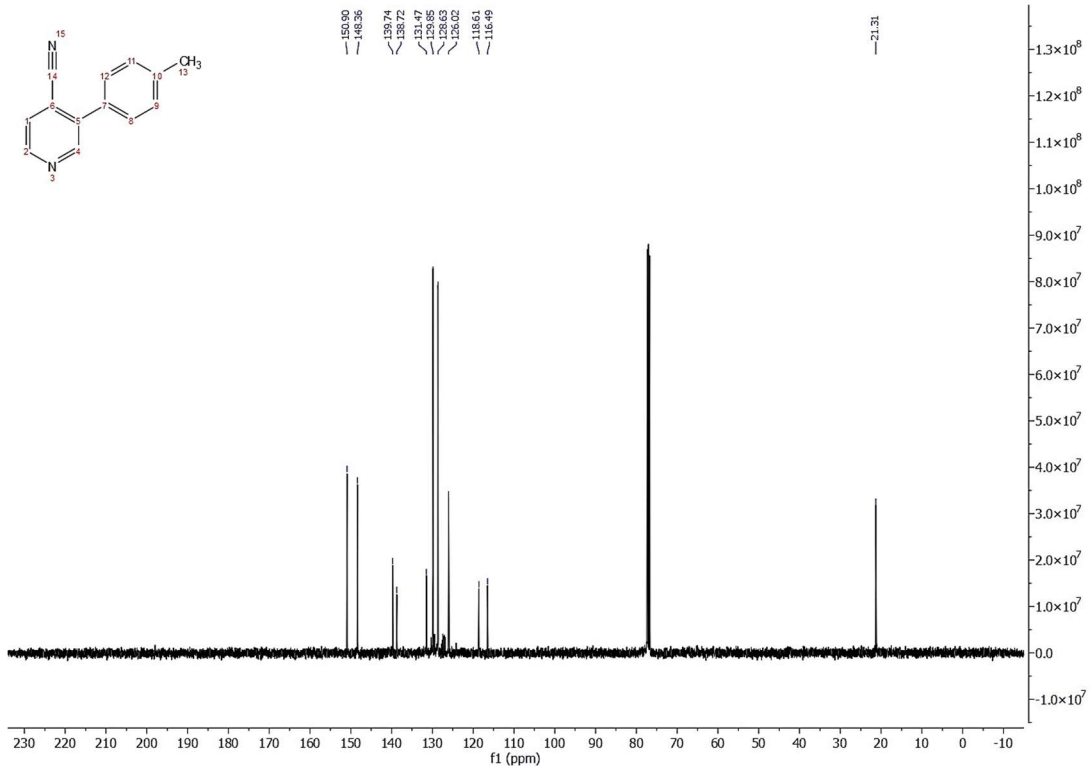
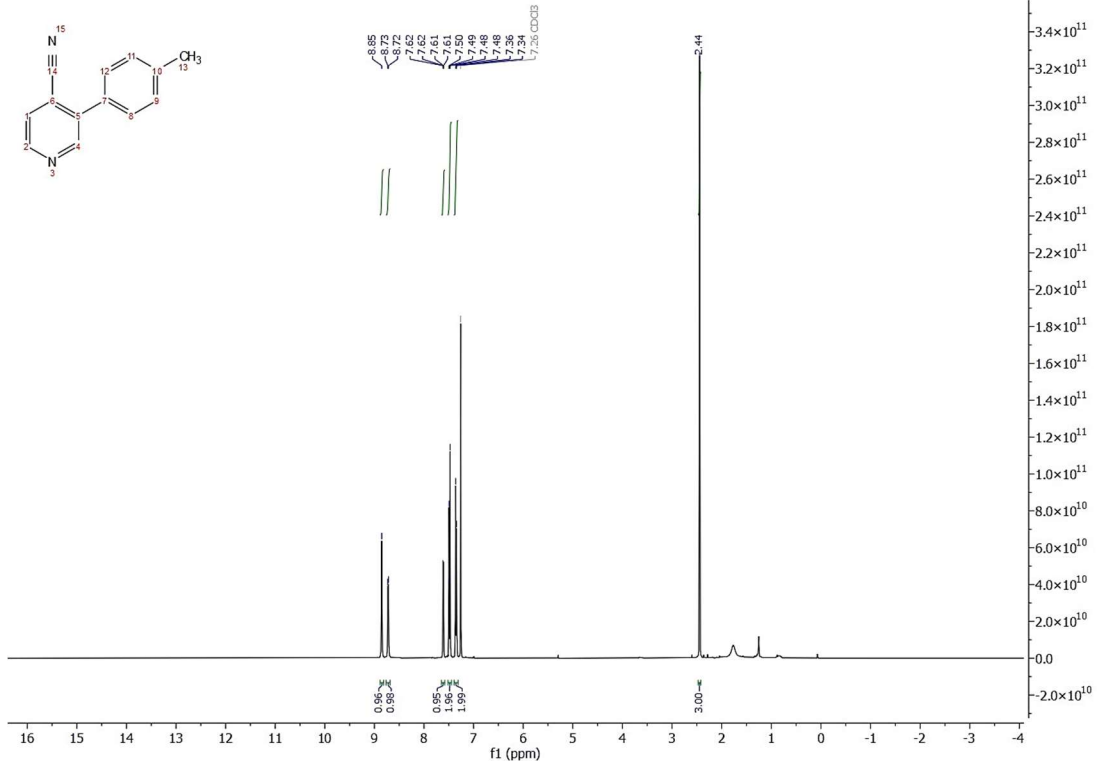
Figure S2. Cyclic voltammograms of the different Ag(I)-based catalysts (**16-19**) and AgNO_3 . Species concentration of each compound: 2 mM in 0.08 M TBAPF₆/ACN electrolyte solution. Working electrode: GC disk (3 mm, diameter); Sweep rate: 0.4 V s⁻¹; T=25°C; Reference Electrode: Ag/AgCl/KCl(3M).

10. Copies of NMR spectra

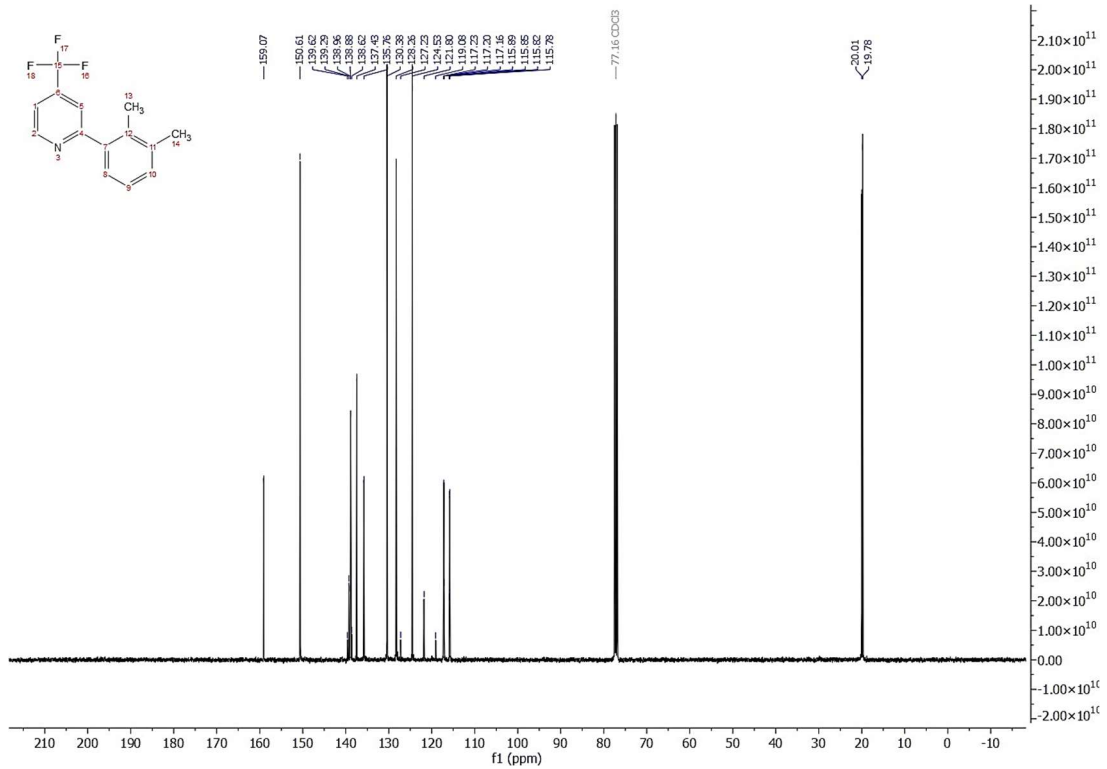
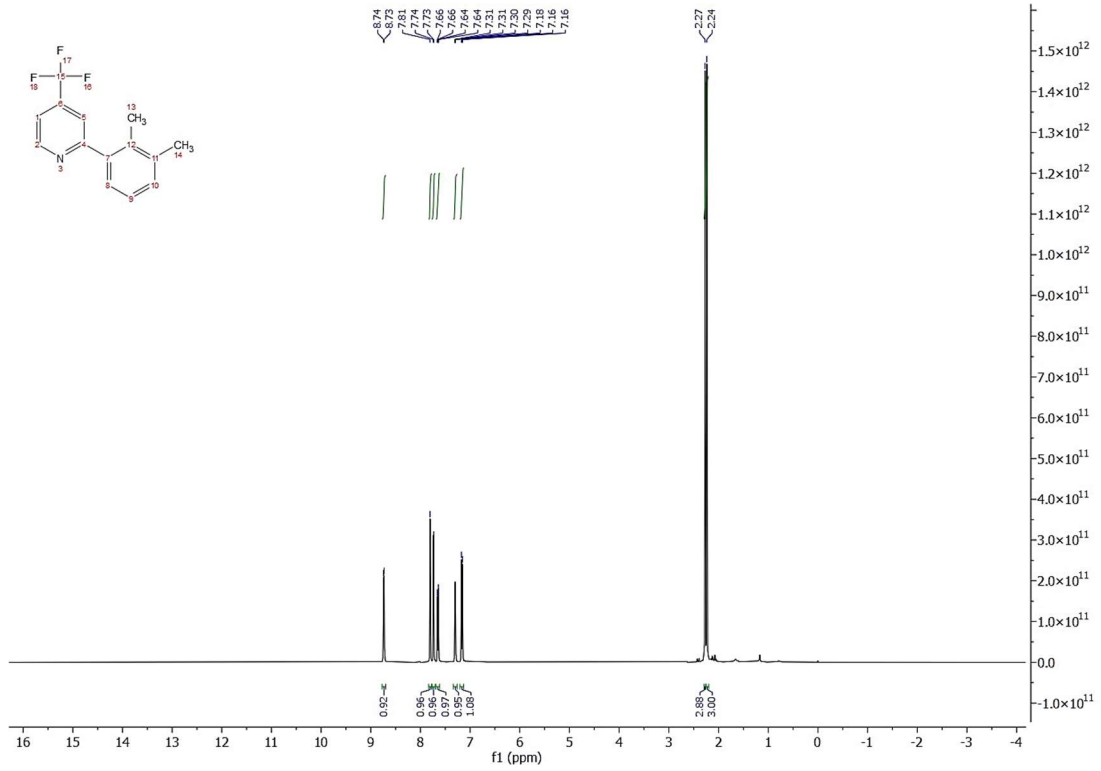
Compound 14

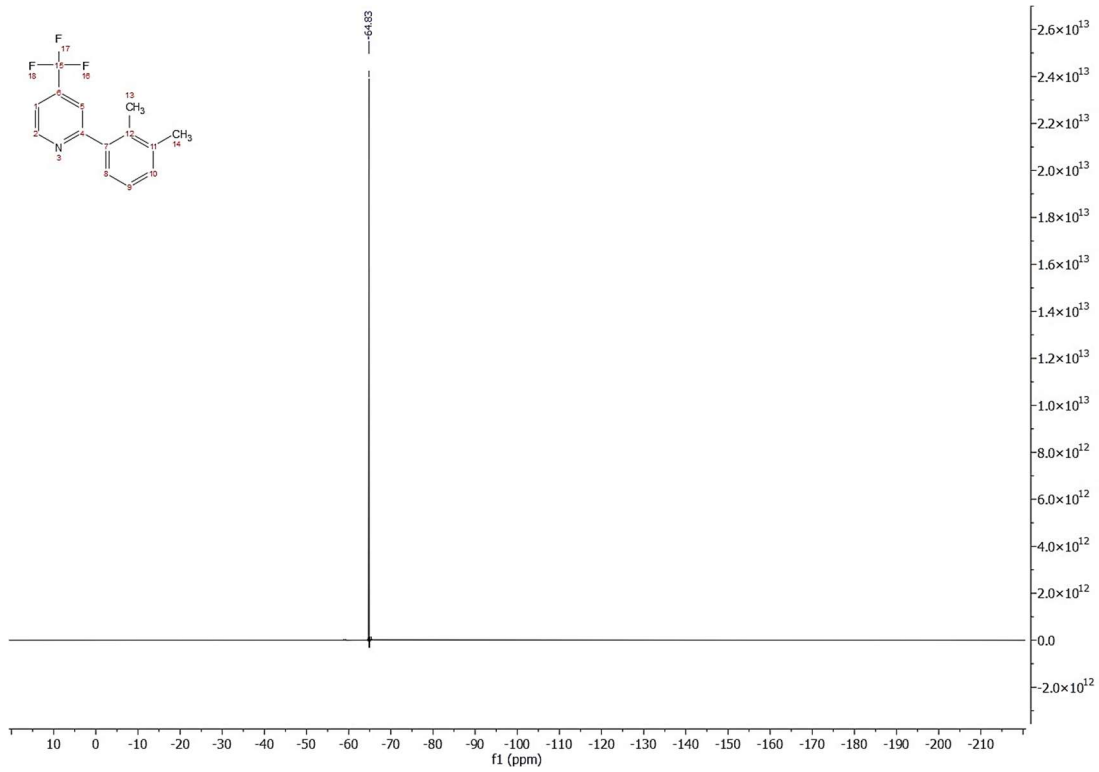


Compound 15

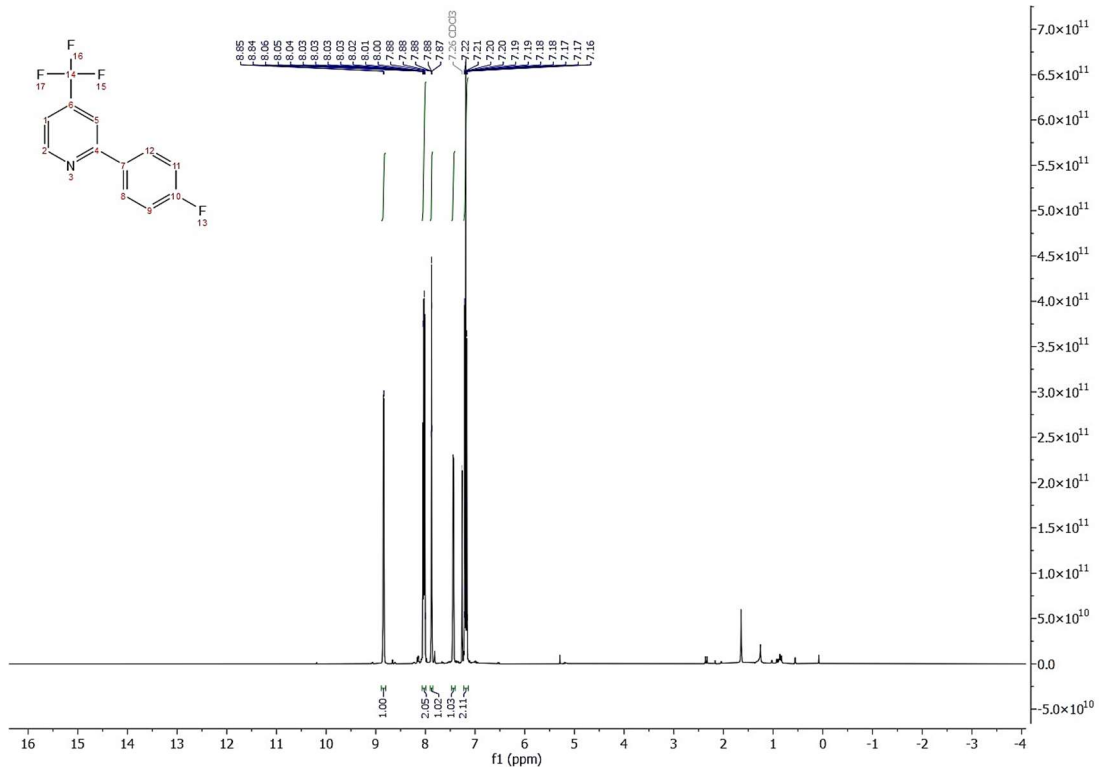


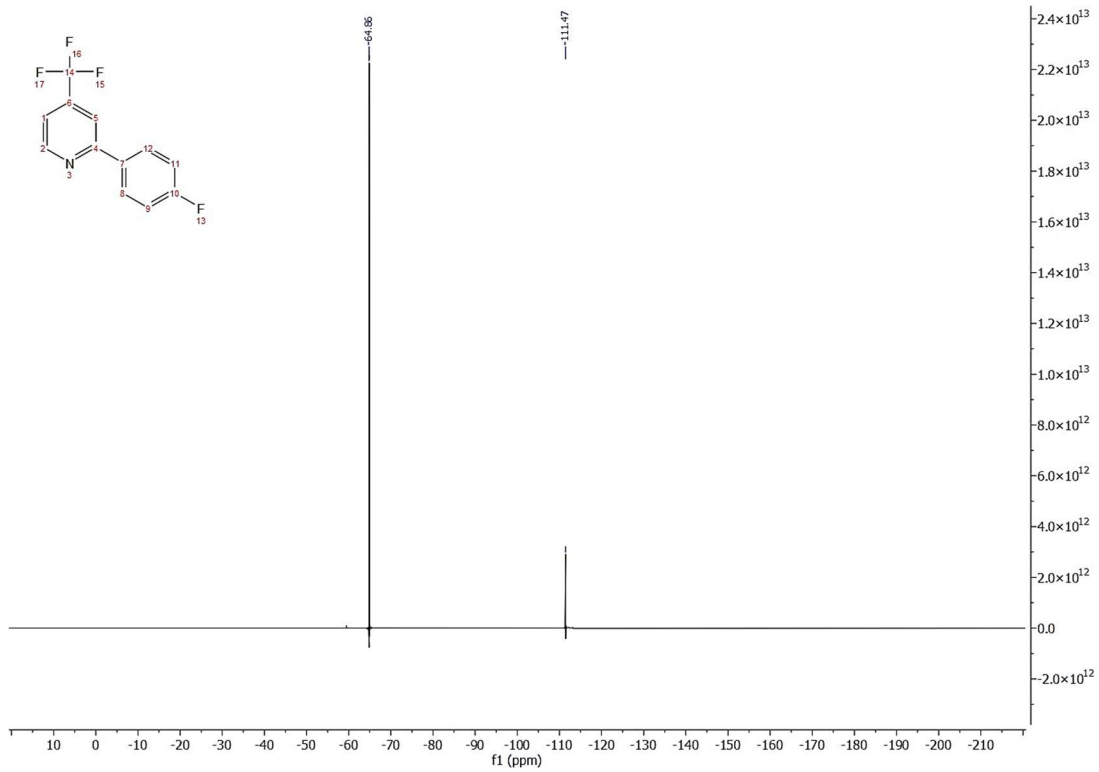
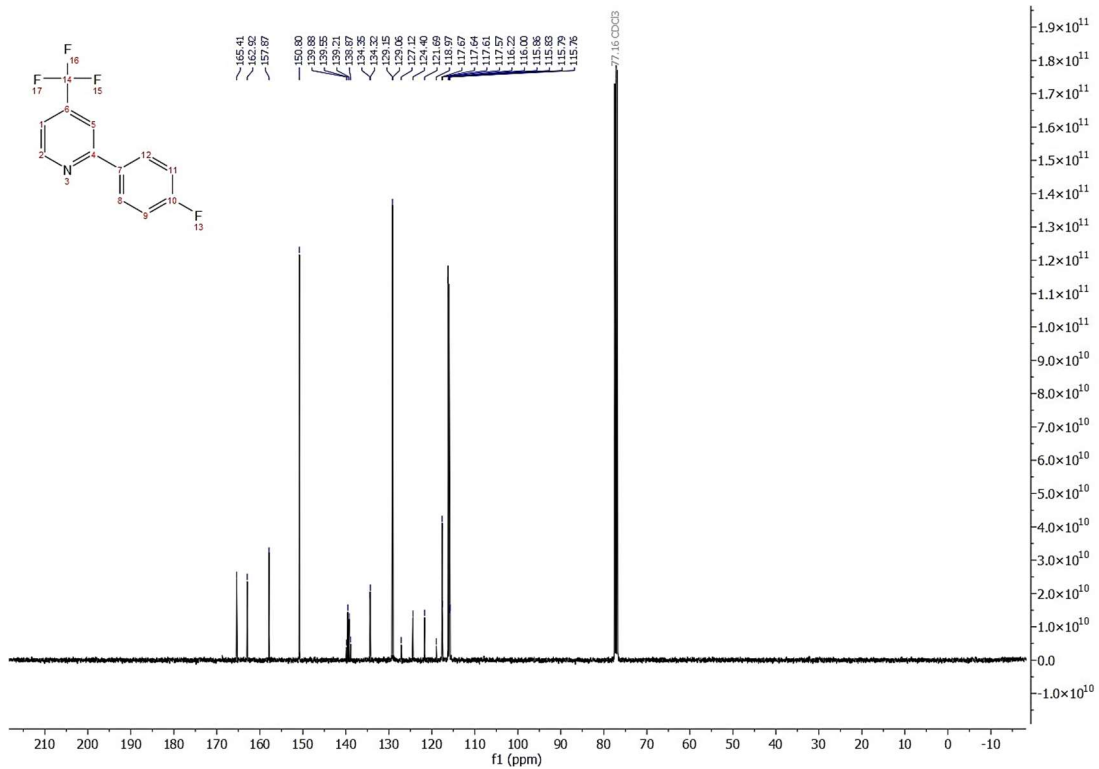
Compound 28



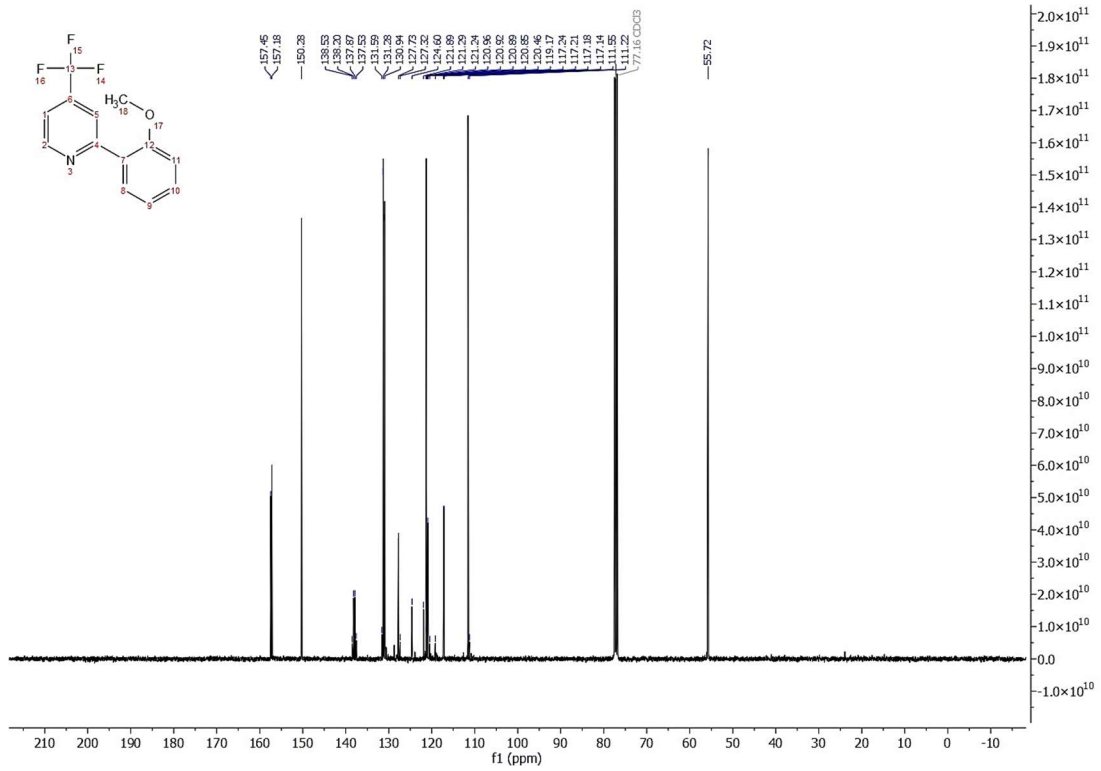
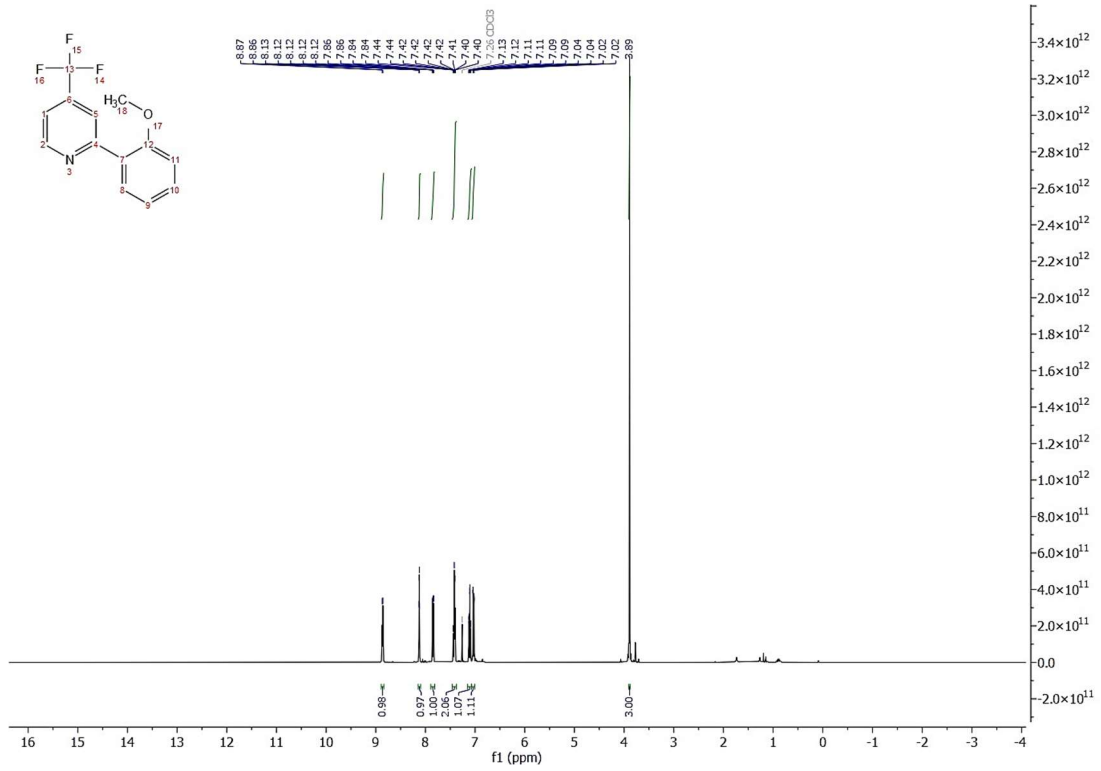


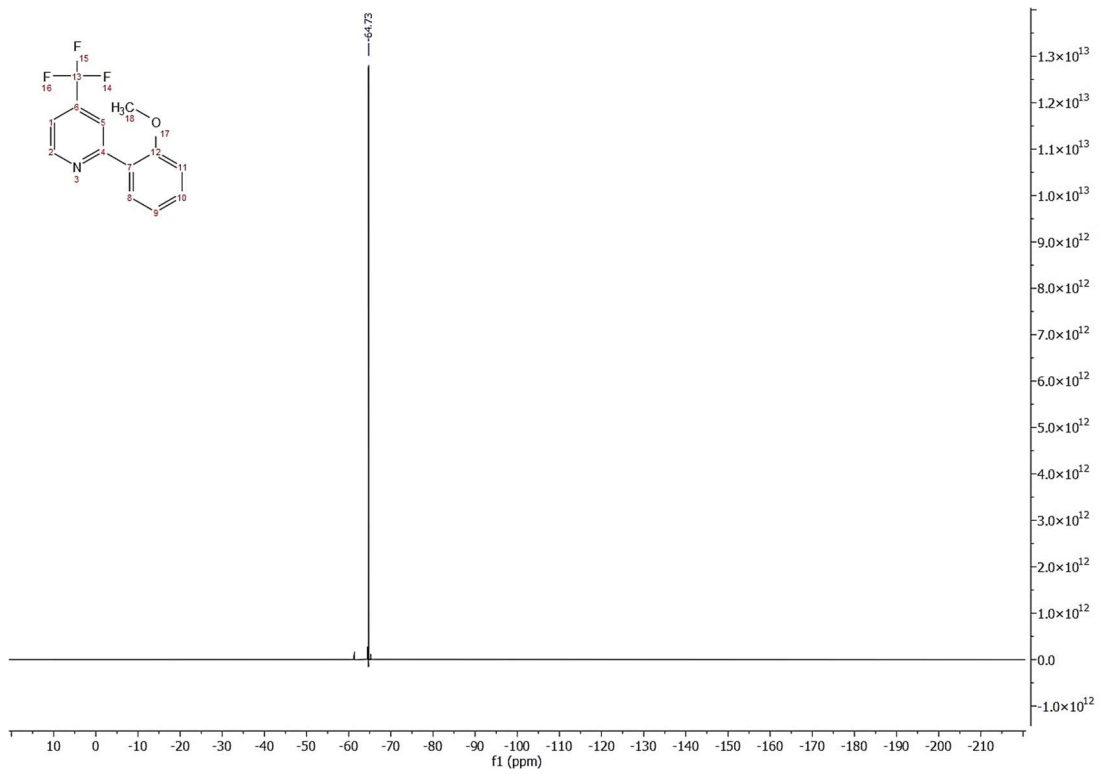
Compound 29





Compound 30





11. References and notes

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