ELECTRONIC SUPPLEMENTARY INFORMATION

Microwave assisted batch and continuous flow Suzuki-Miyaura reaction in GVL using Pd/PiNe biowaste-derived heterogeneous catalyst

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1. General Remarks

Unless otherwise stated, all chemicals were purchased and used without any further purification. Reactions were performed in a CEM Discover SP microwave oven equipped with 10 mL tubes for batch protocols and used in open vessel configuration for the continuous-flow process. GLC analyses were performed by using Hewlett-Packard HP 5890 SERIES II equipped with a capillary column DB-5MS (30 m, 0.32 mm), a FID detector, and helium as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 mass selective detector equipped with an electron impact ionizer at 70 eV. Melting points were measured on a Büchi 510 apparatus. NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz (^{1}H at 400 MHz, ^{13}C at 100.6 MHz and ^{19}F at 376.4 MHz) in $CDCl_3$ and DMSO-d_6. Chemical shifts are reported in ppm (δ), coupling constant (J) in hertz and multiplicity are reported as follows: *s* = singlet, *bs* = broad singlet, *d* = doublet, *dd* = double doublet, *td* = double triplet, *t* = triplet, *m* = multiplet. Products purification was performed using 230-400 mesh silica gel. Elemental Analysis (EA) were conducted on Elementar UNICUBE® elemental analyser. Metal loading was measured using MP-AES 4210 instrument.

Pd/PiNe[1] and 4-(4-bromophenyl)-4-oxobutanoic acid[2] (**1l**) were synthesized as reported in the literature.

Characterization data, copies of ^{1}H and ^{13}C NMR spectra are reported below.

2. General procedures

Typical procedure for Suzuki reaction in batch (extraction work up).

In a 10 mL microwave vial equipped with a magnetic stirrer, aryl halide **1** (0.5 mmol), aryl boronic acid **2** (1.1 eq), KOPiv (1.2 eq), **Pd/PiNe** (8 wt%, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, µλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was recovered by extraction with heptane (1 mL) washed with 1 M Na_2CO_3 (2 mL) solution.

Typical procedure for Suzuki reaction in batch (precipitation work up).

In a 10 mL microwave vial equipped with a magnetic stirrer, aryl halide **1** (0.5 mmol), aryl boronic acid **2** (1.1 eq), KOPiv (1.2 eq), **Pd/PiNe** (8 wt%, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, µλ: 50 W, 40 cycles). After removing the catalyst by filtration, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration.

Pd/PiNe recycle.

After the reaction completion the catalyst was recovered by centrifugation, washed with EtOH and water and dried at 80 °c for 1 h. The dried catalyst was reused under the optimized conditions.

General procedure for leaching determination

The crude reaction mixture, after separation from the catalyst was dried under vacuum, dissolved in 2 mL of aqua regia, and stirred for 1h at room temperature. The mixture was transferred in a 10 mL graduated flask and Milli-Q water was added to reach the final volume. If present, residual solid was filtered off and the sample was analysed by MP-AES 4210 instrument.

General procedure for Suzuki reaction under continuous flow conditions.

A PTFE tube (50 cm length, 2 mm width) was packed with 100 mg of Pd/PiNe (8 wt%) dispersed in 2 g of quartz powder. The coil reactor was endfitted with a back pressure regulator (45 psi) and placed in a 35 mL vessel collocated in the MW oven. The mixture of aryl halide, boronic acid (1.1 eq) and KOPiv (1.2 eq) in GVL:H_2O (9:1) was pumped through the reactor using a SHIMADZU LC-40D HPLC pump at a flow rate of 0.1 mL/min (measured at the coil outlet). The microwave irradiation was set at fixed power (50 W) allowing a temperature range between 100 and 120 °C at the steady state. The mixture collected was evaporated to remove water and then the GVL was recovered by distillation under vacuum (96 %). The solid residue was washed with water affording the pure product.

References:

1. a) F. Valentini, F. Ferlin, S. Lilli, A. Marrocchi, L. Ping, Y. Gu and L. Vaccaro, *Green Chem*., 2021, **23**, 5887–5895; b) F. Ferlin, F. Valentini, D. Sciosci, M. Calamante, E. Petricci, and L. Vaccaro, *ACS Sustainable Chem. Eng*. 2021, **9**, 12196−12204

2. G. Xiao, G. Xiao, C. Xie, Q. Guo, G. Zi, G. Hou, and Y. Huang, *Org. Lett.* 2022, **24**, 2722–2727

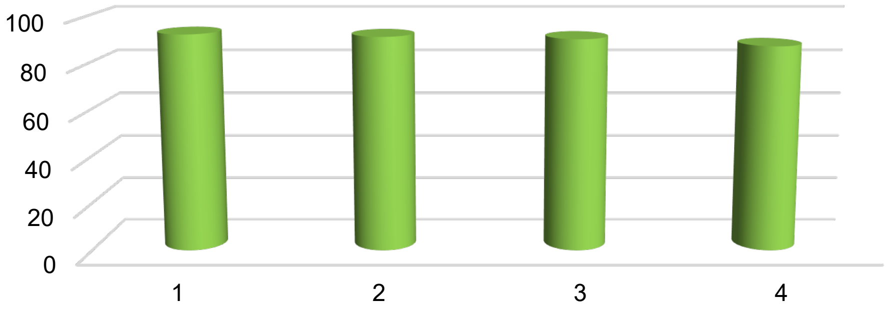


Figure ESI-1. Pd/PiNe recycle and Pd leaching under batch conditions and MW-irradiations at not full conversion. Reaction conditions: **1a** (0.5 mmol), **2a** (1.1 eq), Pd/PiNe (0.5 mol%), KOPiv (1.2 eq), 0.5 mL GVL:H_2O (9:1), 90-120°C, MW fixed power (t_{MW} = 2 min; t_{cool} = 1 min), 30 cycles.

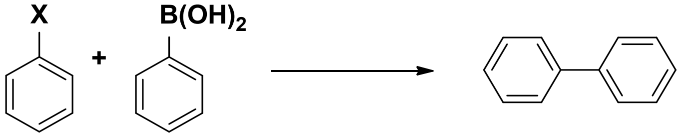
3. E-factor calculation

SM coupling partner	**Without H_2O recovery**	**with H_2O recovery**
SM coupling batch between **1a** and **2a**	E-factor = ((93.4 mg (**1a**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 87 mg (**3a**)) / 87 mg (**3a**)) = **14.6**	E-factor = ((93.4 mg (**1a**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 87 mg (**3a**)) / 87 mg (**3a**)) = **4.3**
SM coupling flow between **1a** and **2a**		E-factor = ((186 mg (**1a**) + 136 mg (**2a**) + 170 mg (KOPiv) + 1890 mg (GVL) + 200 mg (H_2O) + 1000 mg (H_2O) – 1815 mg (GVL recovered) – 900 mg (H_2O recovered) – 176 mg (**3a**)) / 176 mg (**3a**)) = **3.9**
SM coupling batch between **1b** and **2a**	E-factor = ((102 mg (**1b**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 97 mg (**3b**)) / 97 mg (**3b**)) = **13.1**	E-factor ((102 mg (**1b**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 97 mg (**3b**)) / 97 mg (**3b**)) = **3.8**
SM coupling batch between **1c** and **2a**	E-factor = ((101 mg (**1b**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 88 mg (**3c**)) / 88 mg (**3c**)) = **14.5**	E-factor ((101 mg (**1c**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 88 mg (**3c**)) / 88 mg (**3c**)) = **4.3**
SM coupling batch between **1d** and **2a**	E-factor = ((115.7 mg (**1d**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 113 mg (**3d**)) / 113 mg (**3d**)) = **11.2**	E-factor ((115.7 mg (**1d**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 113 mg (**3d**)) / 113 mg (**3d**)) = **3.2**
SM coupling batch between **1e** and **2a**	E-factor = ((97.6 mg (**1e**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 90 mg (**3e**)) / 90 mg (**3e**)) = **14.2**	E-factor ((97.6 mg (**1e**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 90 mg (**3e**)) / 90 mg (**3e**)) = **4.2**

SM coupling batch between **1f** and **2a**	E-factor = ((107 mg (**1e**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 82 mg (**3e**)) / 82 mg (**3e**)) = **15.8**	E-factor ((107 mg (**1f**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 82 mg (**3f**)) / 82 mg (**3f**)) = **4.8**
SM coupling batch between **1g** and **2a**	E-factor = ((110 mg (**1g**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 945 mg (GVL) + 100 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 1382 mg (GVL recovered) – 66 mg (**3g**)) / 66 mg (**3g**)) = **21.0**	E-factor = ((110 mg (**1g**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 945 mg (GVL) + 100 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 1382 mg (GVL recovered) – 900 mg (H_2O recovered) – 66 mg (**3e**)) / 66 mg (**3e**)) = **7.4**
SM coupling batch between **1h** and **2a**	E-factor = ((119 mg (**1h**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 68 mg (**3h**)) / 68 mg (**3h**)) = **19.4**	E-factor ((119 mg (**1h**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 68 mg (**3h**)) / 68 mg (**3h**)) = **6.1**
SM coupling batch between **1i** and **2a**	E-factor = ((104 mg (**1i**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 66 mg (**3i**)) / 66 mg (**3i**)) = **19.8**	E-factor ((104 mg (**1i**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 82 mg (**3i**)) / 82 mg (**3i**)) = **6.1**
SM coupling batch between **1j** and **2a**	E-factor = ((80.6 mg (**1j**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 2000 mg (Na_2CO_3aq) + 684 mg (heptane) – 937.7 mg (GVL recovered) – 616 (heptane recovered) – 69 mg (**3j**)) / 69 mg (**3j**)) = **34.0**	E-factor ((80.6 mg (**1j**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 2000 mg (Na_2CO_3aq) + 684 mg (heptane) – 937.7 mg (GVL recovered) – 616 (heptane recovered) – 1800 mg (H_2O recovered) – 69 mg (**3j**)) / 69 mg (**3j**)) = **7.9**
SM coupling batch between **1k** and **2a**	E-factor = ((102.5 mg (**1k**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 99 mg (**3k**)) / 99 mg (**3k**)) = **12.8**	E-factor ((102.5 mg (**1k**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 99 mg (**3k**)) / 99 mg (**3k**)) = **3.7**

SM coupling batch between **1i** and **2b**	E-factor = ((104 mg (**1i**) + 86.8 mg (**2b**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 75 mg (**3a**)) / 75 mg (**3a**)) = **17.5**	E-factor ((104 mg (**1i**) + 86.8 mg (**2b**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 75 mg (**3a**)) / 75 mg (**3a**)) = **5.5**
SM coupling batch between **1i** and **2c**	E-factor = ((104 mg (**1i**) + 90.5 mg (**2c**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 51 mg (**3e**)) / 51 mg (**3e**)) = **26.3**	E-factor ((104 mg (**1i**) + 90.5 mg (**2c**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 51 mg (**3e**)) / 51 mg (**3e**)) = **8.7**
SM coupling batch between **1i** and **2d**	E-factor = ((104 mg (**1i**) + 105 mg (**2d**) + 88.5 mg (KOPiv) + 945 mg (GVL) + 100 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 99 mg (**3l**)) / 99 mg (**3l**)) = **18.5**	E-factor ((104 mg (**1i**) + 105 mg (**2d**) + 88.5 mg (KOPiv) + 945 mg (GVL) + 100 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 99 mg (**3l**)) / 99 mg (**3l**)) = **9.4**
SM coupling batch between **1a** and **2e**	E-factor = ((93.4 mg (**1a**) + 86 mg (**2e**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 98 mg (**3m**)) / 98 mg (**3m**)) = **13.1**	E-factor ((93.4 mg (**1a**) + 86 mg (**2e**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 98 mg (**3m**)) / 98 mg (**3m**)) = **3.9**
SM coupling batch between **1a** and **2f**	E-factor = ((93.4 mg (**1a**) + 76.3 mg (**2f**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 82 mg (**3n**)) / 82 mg (**3n**)) = **15.7**	E-factor ((93.4 mg (**1a**) + 76.3 mg (**2f**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 82 mg (**3n**)) / 82 mg (**3n**)) = **4.7**
SM coupling batch between **1l** and **2a**	E-factor = ((128 mg (**1l**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 126 mg (**3o**)) / 126 mg (**3o**)) = **10.1**	E-factor ((128 mg (**1l**) + 68.5 mg (**2a**) + 88.5 mg (KOPiv) + 472.5 mg (GVL) + 50 mg (H_2O) + 525 mg (GVL washing) + 1000 mg (H_2O) – 937.7 mg (GVL recovered) – 900 mg (H_2O recovered) – 126 mg (**3o**)) / 126 mg (**3o**)) = **2.9**

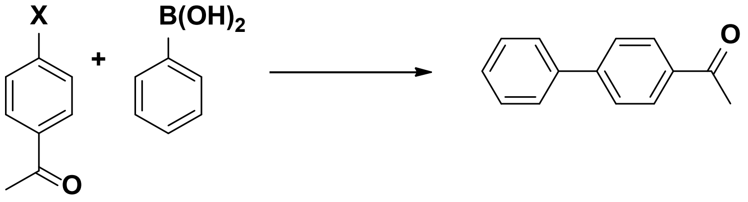
3.1 E-factor comparison:



E-factor = 6.1 (*this work - batch*)

Ref main text	**General procedure**	**E-factor**
16a	Preparation of stock solution of the SM catalyst: To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, palladium pre-catalyst $Pd(ACN)_2Cl_2$ (0.04 mmol, 10.4 mg) and ligand sSPhos, (0.12 mmol, 61.6 mg) were dissolved in 4 mL of HEP/water(40%) solution. The mixture was stirred for 5 min at room temperature. To an oven-dried 10 mL Schlenk purged under N_2 atmosphere, 50 µL of the stock solution (0.05 mol% of palladium catalyst) was added along with the amount of HEP/water (40%) solution needed to achieve the desired concentration. The other reagents were then added in the following order:base (1.1 mmol, 1.1 equiv), aryl chloride (1.0 mmol, 1.0 equiv) and boronic acid (1.05 mmol, 1.05 equiv). The reaction mixture was heated to the desired temperature with an oil bath and maintained at this temperature under stirring; the conversion was evaluated through HPLC-UV analysis at 210 nm considering the appropriate RRF (see Chapter 9 for RRF calculation). At reaction completion, the mixture was extracted with an appropriate organic solvent (3x1 mL). The collected organic phases were concentrated under reduced pressure. The product was isolated without need of purification. The reaction mixture, containing HEP/water, conjugated base (K_2CO_3 or Cs_2CO_3 acid and the catalyst complex, was treated with sodium formate (0.1 mmol, 10.0 mg) for 1h at 60°C in order to generate palladium black. At reaction completion, the mixture was filtered out with the aid of charcoal (60 mg) and the palladium metal was recovered. The filtrate was distilled under reduced pressure to recover HEP in 95% yield	E-factor = (1.1 g (chlorobenzene) + 1.2 g (phenylboronic acid) + 3.57 g (Cs_2CO_3) + 0.007 g (sSPhos) + 0.0001 g ($Pd(CAN)_2Cl_2$ not recovered) + 0.34 g (HEP not recovered) + 4 g (H_2O) + 0.01 g (HCOONa) + 0.06 g (charcoal) + 1.16 g (cyclohexane not recovered) – 1.47 (product)) /1.47 g (product) = **6.8**
16c	A stirring bar and a cubic sample of Pd@PDA@PUF of *ca.* 8 cm^3, whose mass was adjusted in relation to its Pd content established by ICP-AES to reach a Pd loading of 7 µmol, were introduced in a tube in a similar fashion to the hydrogenation experiments. Ethanol/water (1 : 1)	**0.5 mmol scale** E-factor = (3.144 g (EtOH) + 4.000 g (H_2O) + 0.0785 g (bromobenzene) + 0.0731 g (phenylboronic) + 0.1365 g (K_2CO_3)+ 2.000 g (H_2O) +

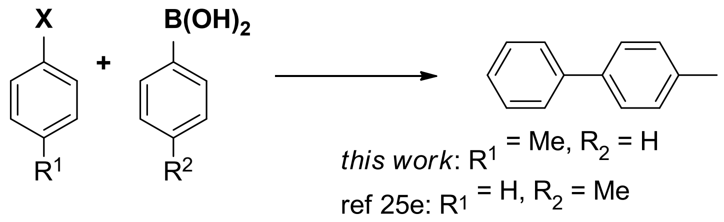
	(8 mL) was then added to immerse the foam. This was followed by the addition of phenylboronic acid (0.6 or 3.6 mmol), K_2CO_3 (0.75 or 4.5 mmol), and aryl bromide (0.5 or 3 mmol) (Pd content: 1.4 or 0.23 mol% *vs.* aryl bromide). The reaction mixture was then heated under stirring (625 rpm) by putting the tube in an oil bath at 65 °C. After 4 h, the reaction medium was poured into water (2 mL) and the product was extracted with ethyl acetate (2 × 10 mL). The combined extracts were then washed with brine (10 mL) and dried over anhydrous $MgSO_4$. At this point, an aliquot was removed by syringe to determine the conversion of aryl bromide by GC analysis, and the solvent was removed under reduced pressure. The crude material was then purified by column chromatography over silica with petroleum ether/ethyl acetate (20 : 1) as eluent to give the desired product, whose identity was confirmed by ^{1}H and ^{13}C NMR in $CDCl_3$	18.040 g (EtOAc) + 12.000 g (brine) – 0.07556 g (product)) / 0.07556 g (product) = 521.4 **Column chromatography was not included in the calculation** **3 mmol scale:** E-factor = (3.144 g (EtOH) + 4.000 g (H_2O) + 0.471 g (bromobenzene) + 0.4389 g (phenylboronic) + 0.6219 g (K_2CO_3) + 2.000 g (H_2O) + 18.040 g (EtOAc) + 12.000 (brine) – 0.45337 g (product))/ 0.45337 g (product) = **88.8** **Column chromatography was not included in the calculation**
25d	An exactly weighed quantity of bromoarenes (100 mg), Pd/CNS catalyst (10 mol%), boronic acid (1.5 equivalents), Na_2CO_3 (3.0 equivalents), and solvent (5 mL) was taken in a reaction vessel. The reaction mixture was heated at 150 °C under microwave irradiation for 40–60 min. After cooling, the reaction mixture was filtered and dried; column chromatography was performed on silica gel (60–120 mesh) or neutral alumina using hexane and ethyl acetate as eluents to isolate the product.	E-factor = (0.100 g (bromobenzene) + 0.1165 g (phenyl boronic acid) + 0.2025 g (Na_2CO_3) + 3.960 g (MeOH) – 0.09134 g (93 % product)) / 0.09134 g (93 % product) = **46.9** **Column chromatography was not included in the calculation**



E-factor = 4.3 (*this work - batch*)

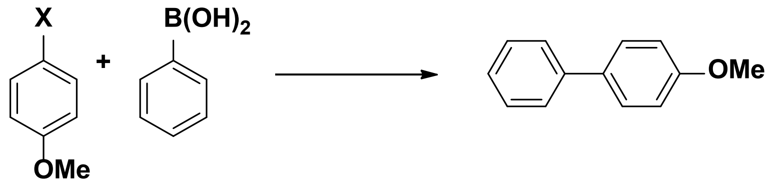
16h	HNT-Pd catalyst (1% or 0.1 mol%), phenylboronic acid (65 mg,0.547 mmol), K_2CO_3 (84 mg, 0.615 mmol), aryl bromide (0.55mmol), ethanol (0.6 ml) and water (0.6 ml) were placed in a micro-wave test tube provided with a cap. The mixture was inserted into microwave apparatus at a temperature of 120 °C and 14 W power, under constant stirring for 10 min; the solvent was then removed under reduced pressure and the residue was checked by ^{1}H-NMR to calculate conversion.	E-factor = 65 mg (phenylboronicacid) + 84 mg (K_2CO_3) + 109.47 mg (4-bromoacetophenone) + 473 mg (EtOH) + 600 mg (H_2O) - 106.27 (99% product) / 106.27 (99% product) = **11.5** **Calculated on conversion without work-up and purification**
25a	The microwave reaction vessel was lunshed with a mixture containing 1 mmol of 4′-bromoacetophenone (6) (199 mg), 1.2 mmol of phenylboronic acid (5a) (146 mg),	E-factor = 0.199 g (4’-bromoacetophenone) + 0.146 g (phenylboronic acid) + 0.194

	0.6 mmol of TBAB (194 mg) (in case of using water as a solvent), 1 mmol of the approperiate base, 0.75 mol% of Pd-complex 4a and 10–15 mL of the approperiate solvent. The microwaves irradiation parameters was adjusted in such away that the vessel temperature always kept near the boiling point of the approperiate solvent with low rate stirring (to avoid the pressure irregularities inside the reaction vessel). The reaction monitoring and working up have been done as in the conventional method to give 4-acetyl-1,1′-biphenyl as a white solid (Reaction workup was achieved by extraction the reaction product using ethyl acetate (3 × 20 mL), then drying the axtracts using unhydrous sodium sulphate. The organic layer was evporated under vaccum to give 4-acetyl-1,1′-biphenyl as a white solid).	g (TBAB) + 0.138 g (K_2CO_3) + 10.00 g (H_2O) + 54.120 g (EtOAc) – 0.196 g (100% product)) / 0.196 g (100% product) = **331.6**
26f	Batch: General Procedure for the Microwave Assisted Suzuki Coupling in Batch (Method A). The aryl halide (0.5 mmol) and boronic acid (0.5 mmol) were dissolved in ethanol (6 mL, 95%) in a microwave vial. Tetra-butylammonium acetate (1 mmol) was added in ethanol (1 mL) followed by Pd EnCat-30™ (63 mg, 5 mol%). The reaction was irradiated in a microwave apparatus at 120 °C for 10 min. After cooling to ambient temperature in the microwave cavity the reaction mixture was purified on an SCXII cartridge using DCM (10 mL) as eluent and evaporated to dryness.	E-factor: (0.0995 g (4’-bromoacetophenone) + 0.0610 g (phenyl boronic acid) + 4.724 g (EtOH) + 0.3015 g (TBAAc) + 0.789 g (EtOH) + 13.3 g (DCM) – 0.0863 g (88 % product)) / 0.0863 g (88 % product) = **222**
26f	Flow: The flow reactor was packed with Pd EnCat-30™ (170 – 190 mg, 0.06 – 0.07 mmol) and sand used as an inert packing material at the outer (non microwaved) regions of the flow reactor. Ethanol was pumped through the cell at a flow rate of 0.1 mL/min for 10 min to purge the system using a Gilson 402 syringe pump. Stock solutions of the aryl halide (0.5 mmol), boronic acid (0.5 mmol) and tetra-butylammonium acetate (1.0 mmol) in ethanol (**0.01**, 0.07 or **0.2**M) were fed into the reactor at a flow rate of 0.1 mL/min for the required time (pumping controlled by Gilson 402 syringe pumps). During this period the flow reactor was irradiated in a microwave apparatus at 50W with compressed air cooling (4 bar, 22 ºC temperature). The 4 product was diverted through a scavenging column containing Amberlyst 15 resin (4 g) before collection and evaporated to dryness. Following the reaction ethanol was pumped into the reactor at a rate of 0.1 mL/min in order to flush the system before passing in the next components.	E-factor = (99.5 mg (4-bromoacetophenone) + 60.9 mg (phenylboronic acid) + 301.5 mg (TBAAc) + 1970 mg (EtOH **0.2** M) – 88.3 (90% product)) / 88.3 (90% product) = **26.5** E-factor = (99.5 mg (4-bromoacetophenone) + 60.9 mg (phenylboronic acid) + 301.5 mg (TBAAc) + 39450 mg (EtOH **0.01** M) – 88.3 (90% product)) / 88.3 (90% product) = **451.0** **Calculated without considering Amberlyst 15 resin.**



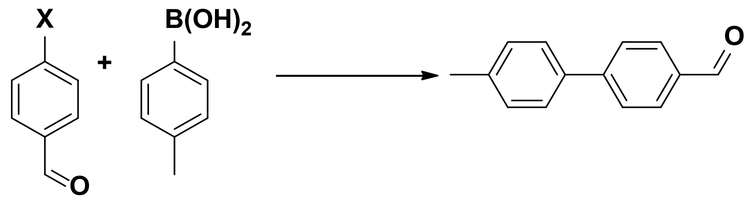
E-factor = 7.4 (*this work - batch*)

25e	The synthesis of 4-methylbiphenyl is representative of the general reaction protocol: PEG 400 (2 g), palladium chloride (0.050 g, 0.282 mmol), *p*-methylphenylboronic acid (0.150 g, 1.10 mmol) and bromobenzene (0.156 g, 1 mmol) were placed in a 25 ml round bottomed flask and mixed well on a Fisher Scientific touch mixer (Model 231). Potassium fluoride (0.390 g) was added to the reaction mixture, mixed well and the contents were then heated in an unmodified household microwave oven (Panasonic NN-S740WA, 1200 W)11at 240 W for 50 s. The reaction mixture turned from red to brown–black and the bulk temperature was found to be between 100 and 105 °C. After cooling, the product was extracted into diethyl ether (2 mL 33) by vortexing and was purified by flash chromatography to afford 4-methylbiphenyl (84%)	E-factor = (0.150 g (*p*-methylphenylboronic acid) + 0.156 g (bromobenzene) + 0.390 g (KF) + 4.338 g (Et_2O) – 0.1413 (84% product)) / 0.1413 (84% product) = **34.6** **PEG 400 and Pd catalyst were recovered and thus excluded from calculation.** **Column chromatography was not included in the calculation.**



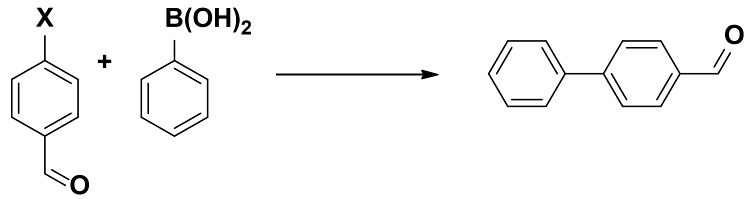
E-factor = 6.1 (*this work - batch*)

16e	DaPdNPs were added to a 15 mL Hungate tube containing aryl halide (25 mM), phenyl boronic acid (30 mM), K_2CO_3 (30 mM) and TPGS1000/TPGS-750-M (2% w/v) in H_2O (5 mL). The tubes were sealed with butyl rubber septa and screw-caps and incubated at 37 ˚C (200 rpm) for 20 h in a New Brunswick Innova 44 incubator shaker (Eppendorf). After this time, the reactions were cooled to room temperature, extracted with methyl *tert*-butyl ether (MTBE, 3 x 1.7 mL) and concentrated under reduced pressure. The crude residue was dissolved in 1 mL $CDCl_3$ containing 10 mM TMB and analysed by 1H NMR spectroscopy.	E-factor = 23.4 mg (4-bromoanisole) + 18.3 mg (phenylboronic acid) + 20.7 mg (K_2CO_3) + 5010 mg (TPG in H_2O) +3774 mg (MTBE) – 22.8 mg (99 % product) / 22.8 mg (99 % product) = **387.0** **Calculated on conversion**



E-factor = 4.7 (*this work - batch*)

26b	A solution of aryl bromide (0.1 M), aryl boronic acid (1.5 equiv), DBU (1.5 equiv) and Pd(dppf)Cl_2 (2 %) in DMF:water (95:5) was prepared and then pumped at a flow rate of 1 mL/min through the 200 mm x 3 mm Øi SiC reactor at a temperature of 180-240 °C. The crude reaction mixture was concentrated and loaded upon silica and thereafter subjected to flash column silica gel chromatography using a *i*-hexanes:ethyl acetate gradient to yield the desired product.	1 mmol scale E-factor = (0.185 g (4-bromobenzaldehyde) + 0.204 mg (phenyl boronic acid) + 0.228 g (DBU) + 0.500 g (H_2O) + 8.968 g (DMF) – 0.161 g (82 % product)) / 0.161 g (82 % product) = **63.7** **Column chromatography was not included in the calculation.**

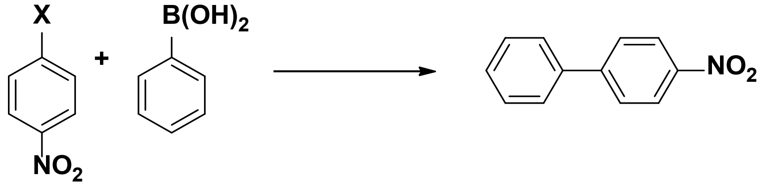


E-factor = 4.3 (*this work - batch*)

E-factor = 3.9 (*this work - flow*)

26d	A reactant solution containing an aryl halide (0.1 M), arylboronic acid (0.12 M), K_2CO_3 (0.3 M) in DMF/H_2O (3:1) solvent was pumped through the reactor with an HPLC pump, and a backpressure valve (45–75 psi) was used to minimize the formation of gas bubbles (see Supporting Information File 1, Figure S6). The residence times of the reactants within the catalytic monoliths were determined based on the known monolith and pore volume and from the different flow rates. Product samples were collected at defined flow periods during a reaction run, weighed and a known amount of dodecane was added to the individual samples as an internal standard. Samples were treated with 1 M aqueous NaOH to remove unreacted arylboronic acid and extracted with DCM. The remaining organic material was then washed three times with distilled water, collected and dried over $MgSO_4$.	**1mmol scale** E-factor = (0.185 g (4-bromobenzaldehyde) + 0.146 g (phenyl boronic acid) + 0.415 g (K_2CO_3) + 7.080 g (DMF) + 2.500 (H_2O) – 0.173 (95 % product)) / 0.173 (95 % product) = 58.6 **Calculated without work-up and purification.**
26e	A stock solution containing the aryl halide (0.6 mmol, 1 equiv), arylboronic acid (1.2 equiv), base (2 M KOH, 0.9 mL, 3 equiv) in DMF (2 mL) was prepared.	E-factor = (0.111 g (4-bromobenzaldehyde) + 0.0878 g (phenylboronic acid) + 0.900 g (H_2O) + 0.101 g (KOH) +

		1.888 g (DMF) – 0.0962 (88% product)) / 0.0962 (88% product). **Calculated on conversion without work-up and purification.**

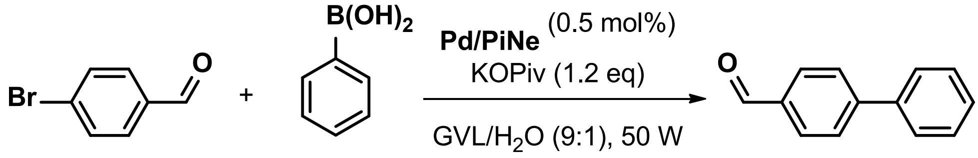


E-factor = 3.8 (*this work - batch*)

26g	The catalyst particles (355–420 µm, selected by sieving) were loaded in the U-tube and prevented from moving along the tube by insertion of a glass rod (outer radius 300 mm) at the end of the catalyst bed. Reactant solution, containing an aryl halide (0.1 M), phenylboronic acid (0.12 M), base (0.25 M) in a solvent mixture consisting of 75 vol.% dimethylformamide (DMF) in water, was pumped through the reactor using the syringe pump. Samples were treated with 1 M aqueous NaOH to remove unreacted PBA, the remaining organic material was then extracted, washed three times with distilled water, collected and dried over $MgSO_4$.	**1mmol scale** E-factor = (0.202 g (4-bromonitrobenzene) + 0.146 g (phenylboronic acid) + 0.3455 g (K_2CO_3) + 7.080 g (DMF) + 2.500 g (H_2O) – 0.1554 g (74 % product)) / 0.1554 g (74 % product) = **65.1** **Work-up and purification are excluded from this calculation.**

4. Characterization data

Chem.Name	[1,1'-biphenyl]-4-carbaldehyde (**3a**)
Lit.Ref	Bivona, L.A., Giacalone, F., Vaccaro, L., Aprile, C. and Gruttadauria, M., *ChemCatChem*, **2015**, *7*, 2526-2533



1a **2a** **3a**

MW: 182,22 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 4-bromobenzaldehyde **1a** (0.5 mmol, 93.4 mg, 99 % purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, μλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3a** was obtained as white solid (87 mg, 95 % yield).

Mol Formula	$C_{13}H_{10}O$	**m.p.**	58-60 °C

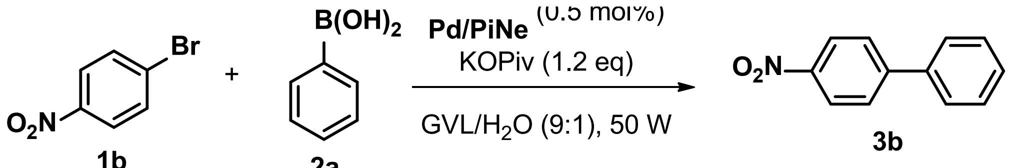
Elemental Analysis: calc: C, 85.69; H, 5.53; found: C, 85.64; H, 5.61

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	10.06	1	*s*	
	7.96	2	*d*	8.2
	7.76	2	*d*	8.2
	7.64	2	*d*	7.3
	7.53-7.46	2	*m*	
	7.45-7.39	1	*m*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 192.1, 147.4, 139.9, 135.3, 130.4, 129.2, 128.6, 127.8, 127.5

GC-EIMS (m/z, %): 182 (M^+, 100), 181 (79), 154 (14), 153 (39), 152 (84), 151 (29), 150 (12), 127 (13), 74 (21), 63 (12), 51 (15), 50 (15)

Chem.Name	4-nitro-1,1'-biphenyl (**3b**)
Lit.Ref	E. Ismalaj, G. Strappaveccia, E. Ballerini, F. Elisei, O. Piermatti, D. Gelman, L. Vaccaro *ACS Sustainable Chem. Eng.*, **2014,** 2, 2461-2464



MW: 199,21 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 1-bromo-4-nitrobenzene **1b** (0.5 mmol, 102 mg, 99% purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, μλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3b** was obtained as withe solid (97 mg, 97 % yield).

Mol Formula	$C_{12}H_9NO_2$	**m.p.**	116-117°C

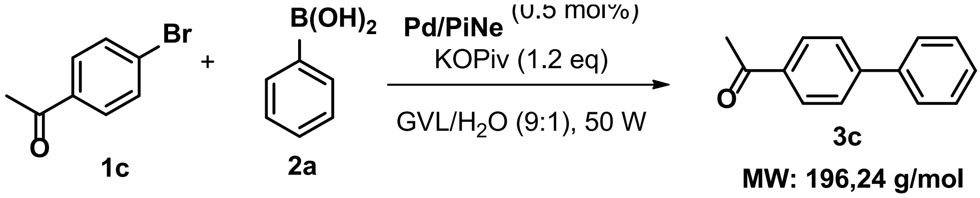
Elemental Analysis: Calc.: C: 72.35; H: 4.55; N: 7.03. found: C, 72.41; H: 4.57; N: 7.11

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	8.31	2	*d*	8.7
	7.74	2	*d*	8.7
	7.63	2	*d*	7.2
	7.52-7.43	3	*m*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 147.8, 147.2, 138.9, 129.3, 129.1, 128.0, 127.5, 124.3.

GC-EIMS (m/z, %): 199 (M^+, 100), 169 (37), 153 (23), 152 (77), 141 (26), 115 (12)

Chem.Name	1-([1,1'-biphenyl]-4-yl)ethanone (**3c**)
Lit.Ref	E. Ismalaj, G. Strappaveccia, E. Ballerini, F. Elisei, O. Piermatti, D. Gelman, L. Vaccaro *ACS Sustainable Chem. Eng.*, **2014,** 2, 2461-2464



MW: 196,24 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 1-(4-bromophenyl)ethanone **1c** (0.5 mmol, 101 mg, 98 % purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, µλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3c** was obtained as withe solid (88 mg, 90 % yield).

Mol Formula	$C_{14}H_{12}O$	**m.p.**	115-117 °C

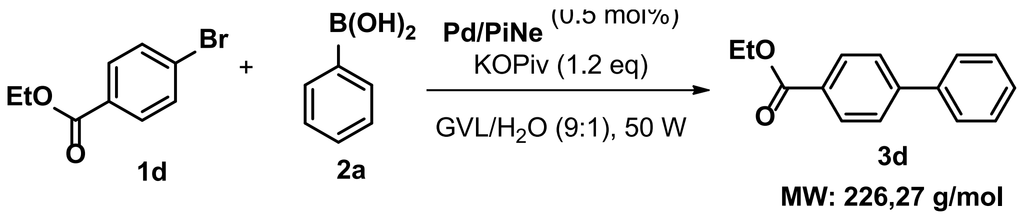
Elemental Analysis: Calc.: C: 85.68; H: 6.16. found: C: 85.74; H: 6.20

^{1}H NMR (400 MHz, $CDCl_3$)	δ value:	No. H	Mult	J value/Hz
	8.03	2	*d*	8.3
	7.69	2	*d*	8.3
	7.63	2	*d*	7.5
	7.48	2	*t*	7.2
	7.42-7.38	1	*m*	
	2.64	3	*s*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 197.9, 145.9, 140.0, 136.0, 129.1, 129.1, 128.4, 127.4, 127.4, 26.8

GC-EIMS (m/z, %): 196 (M^+, 14), 195 (88), 180 (100), 153 (53), 152 (79), 151 (22), 76 (22)

Chem.Name	ethyl [1,1'-biphenyl]-4-carboxylate (**3d**)
Lit.Ref	Q. Cao, J. L. Howard, E. Wheatley, D. L. Browne, *Angew. Chem. Int. Ed.,* 2018, **57**, 11339 -11343



Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, ethyl 4-bromobenzoate **1d** (0.5 mmol, 82.5 µL, 99% purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, µλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3d** was obtained as pale-yellow solid (113 mg, 99 % yield).

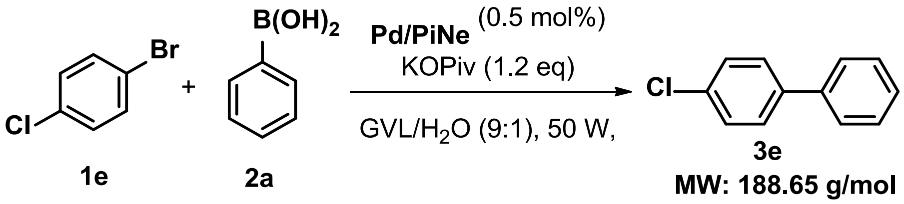
Mol Formula	$C_{15}H_{14}O_2$	**m.p.**	92-94°C

Elemental Analysis: C: 79.62; H: 6.24; found: C: 79.59; H: 6.26

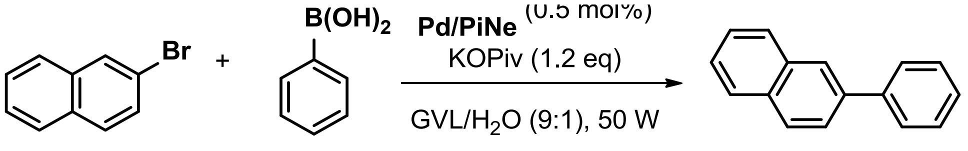
	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	8.13	2	*d*	8.4
	7.70-7.60	4	*m*	
	7.47	2	*t*	7.2
	7.41-7.38	1	*m*	
	4.41	2	*q*	7.1
	1.42	3	*t*	7.1

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 166.7, 145.7, 140.2, 130.2, 129.4, 129.1, 128.3 ,127.4, 127.2, 61.1, 14.5

GC-EIMS (m/z, %): 227 (M^+ + 1, 42), 226 (M+, 100), 199 (17), 198 (100), 182 (68), 181 (100), 153 (100), 152 (100), 151 (48), 150 (14), 127 (17), 126 (15), 90 (17), 77 (14), 76 (36), 75 (12)

<table>
<tr><td>Chem.Name</td><td colspan="4">4-chloro-1,1'-biphenyl (3e)</td></tr>
<tr><td>Lit.Ref</td><td colspan="4">E. Shirakawa, K.-i. Itoh, T. Higashino, T. Hayashi, <i>J. Am. Chem. Soc.</i> 2010, 132, 15537–15539</td></tr>
<tr><td colspan="5">
</td></tr>
<tr><td colspan="5">Method:
In a 10 mL microwave vial equipped with a magnetic stirrer, 1-bromo-4-chlorobenzene 1e (0.5 mmol, 97.6 mg, 98% purity), phenylboronic acid 2a (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), Pd/PiNe (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, μλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product 3e was obtained as withe solid (90 mg, 95 % yield).</td></tr>
<tr><td>Mol Formula</td><td>$C_{11}H_9N$</td><td>m.p.</td><td colspan="2">77-79 °C</td></tr>
<tr><td colspan="5">Elemental Analysis: calc: C, 76.40; H, 4.81; found: C, 76.37; H, 4.87.</td></tr>
<tr><td rowspan="3">^{1}H NMR
(400 MHz, CDCl$_3$)</td><td>δ value:</td><td>No. H</td><td>Mult</td><td>J value/Hz</td></tr>
<tr><td>7.59-7.50</td><td>4</td><td><i>m</i></td><td></td></tr>
<tr><td>7.49-7.36</td><td>5</td><td><i>m</i></td><td></td></tr>
<tr><td colspan="5">^{13}C NMR (100.6 Hz, CDCl$_3$) δ: 140.1, 139.8, 133.5, 129.0, 128.5, 127.7, 127.1</td></tr>
<tr><td colspan="5">GC-EIMS (m/z, %): 190 (34), 188 (M^+, 100), 153 (26), 152 (41)</td></tr>
</table>

Chem.Name	2-phenylnaphthalene (**3f**)
Lit.Ref	C. Savarin, L. S. Liebeskind, *Org. Lett.* 2001, **3**, 2149-2152



1f **2a** **3f**

MW: 204.27 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 2-bromonaphthalene **1f** (0.5 mmol, 107 mg, 97% purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95% purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, μλ: 50 W, 60 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3f** was obtained as withe solid (82 mg, 80 % yield).

Mol Formula	$C_{16}H_{12}$	**m.p.**	104-105 °C

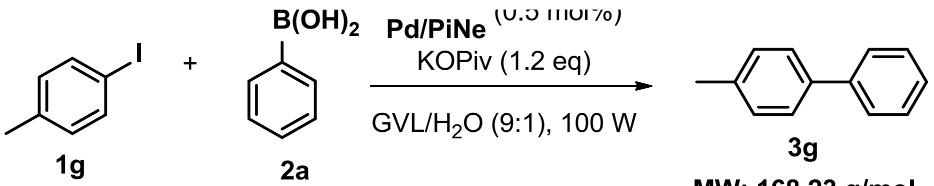
Elemental Analysis: calc: C, 94.08; H, 5.92; found: C, 94.13; H, 5.90

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	8.06	1	*s*	
	7.96-7.84	3	*m*	
	7.79-7.70	3	*m*	
	7.55-7.46	4	*m*	
	7.39	1	*t*	7.4

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 141.3, 138.7, 133.8, 132.8, 129.0, 128.6, 128.3, 127.8, 127.6, 127.5, 126.4, 126.1, 125.9, 125.7.

GC-EIMS (m/z, %): 205 (M^++1, 37), 204 (100), 203 (50), 202 (67), 200 (12), 102 (14), 101 (26)

Chem.Name	4-methyl-1,1'-biphenyl (**3g**)
Lit.Ref	E. Ismalaj, G. Strappaveccia, E. Ballerini, F. Elisei, O. Piermatti, D. Gelman, L. Vaccaro *ACS Sustainable Chem. Eng.*, **2014,** 2, 2461-2464



1g + **2a** → **3g**

MW: 168,23 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 4-iodo toluene **1g** (0.5 mmol, 110 mg, 99 % purity) phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95% purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 1.0 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 100 °C, T_{max}: 150 °C, μλ: 100 W, 80 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product (**3g**) was obtained as withe solid (66 mg, 79 % yield).

Mol Formula	$C_{13}H_{12}$	**m.p.**	45-47 °C

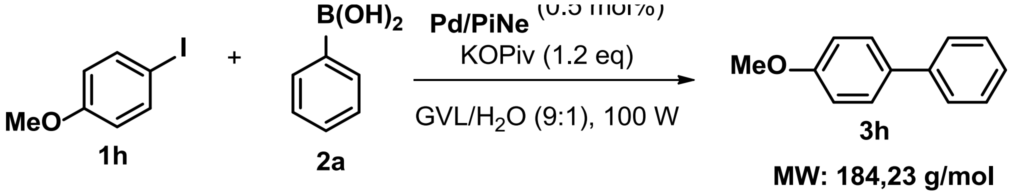
Elemental Analysis: Calc.: C: 92.81; H: 7.19. found: C, 92.74; H: 7.22

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	7.61	2	*d*	7.4
	7.52	2	*d*	8.0
	7.45	2	*t*	7.7
	7.36	1	*t*	7.2
	7.29-7.27	2	*m*	
	2.43	3	*s*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 141.3, 138.5, 137.2, 129.6, 128.9, 127.1, 127.1, 127.1, 21.2

GC-EIMS (m/z, %): 169 (M^+ +1, 36), 168 (M^+, 100), 167 (100), 166 (16), 165 (55), 153 (35), 152 (47), 139 (11), 115 (19), 91 (11), 83 (13), 82 (14), 63 (11)

Chem.Name	4-methoxy-1,1'-biphenyl (**3h**)
Lit.Ref	E. Ismalaj, G. Strappaveccia, E. Ballerini, F. Elisei, O. Piermatti, D. Gelman, L. Vaccaro *ACS Sustainable Chem. Eng.***, 2014,** 2, 2461-2464



MW: 184,23 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 4-iodo anisole **1h** (0.5 mmol, 119 mg, 98% purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95% purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 100 °C, T_{max}: 150 °C, µλ: 100 W, 80 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3h** was obtained as yellow solid (68 mg, 74 % yield).

Mol Formula	$C_{13}H_{12}O$	**m.p.**	87-89 °C

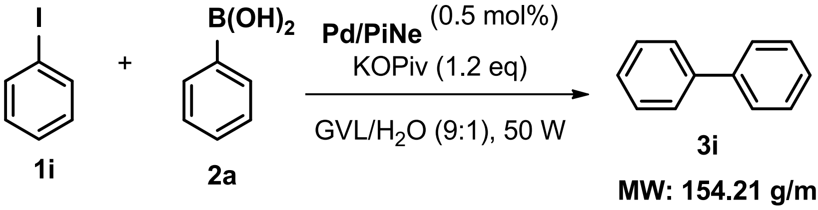
Elemental Analysis: Calc.: C: 84.75; H: 6.57. found: C: 84.78; H: 6.60

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	7.55	4	*t*	7.8
	7.42	2	*t*	7.4
	7.31	1	*t*	7.2
	6.98	2	*d*	8.2
	3.86	3	*s*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5

GC-EIMS (m/z, %): 185 (15), 184 (M^+, 100), 169 (48), 141 (43), 115 (30)

Chem.Name	1,1'-biphenyl (**3i**)
Lit.Ref	E. Ismalaj, G. Strappaveccia, E. Ballerini, F. Elisei, O. Piermatti, D. Gelman, L. Vaccaro *ACS Sustainable Chem. Eng.*, **2014,** 2, 2461-2464



MW: 154.21 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, iodobenzene **1i** (0.5 mmol, 57 µL, 98% purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95% purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 100 °C, T_{max}: 150 °C, µλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3i** was obtained as withe solid (66 mg, 86 % yield).

Mol Formula	$C_{12}H_{10}$	**m.p.**	70-71 °C

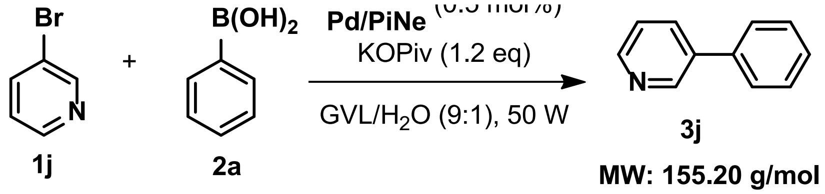
Elemental Analysis: calc: C, 93.46; H, 6.54; found: C, 93.39; H, 6.59

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	7.60	4	*d*	7.4
	7.45	4	*t*	7.4
	7.35	2	*t*	7.3

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 141.4, 128.9, 127.4, 127.3

GC-EIMS (m/z, %): 155 (M^+ +1, 13), 154 (M^+, 100), 153 (37), 152 (25), 76 (13)

Chem.Name	3-phenylpyridine (**3j**)
Lit.Ref	E. Shirakawa, K.-i. Itoh, T. Higashino, T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 15537–15539



Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 3-bromopyridine **1j** (0.5 mmol, 49 µL, 98% purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95% purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 100 °C, T_{max}: 150 °C, µλ: 50 W, 45 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was extracted with heptane (1 mL) and 1 M Na_2CO_3 (2 mL) solution. The product **3j** was obtained as pale-yellow oil (69 mg, 88 % yield).

Mol Formula	$C_{11}H_9N$	**m.p.**	oil

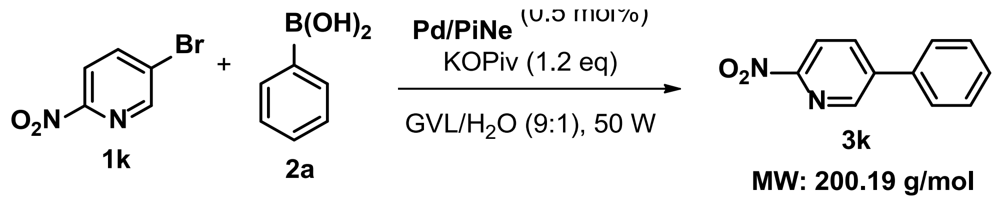
Elemental Analysis: calc: C, 85.13; H, 5.85; N, 9.03; found: C, 85.03; H, 5.90; N, 8.99

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	8.85	1	*s*	
	8.59	1	*d*	3.8
	7.87	1	*d*	7.6
	7.58	2	*d*	7.4
	7.48	2	*t*	7.4
	7.44-7.33	2	*m*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 148.6, 148.4, 137.9, 136.7, 134.4, 129.2, 128.2, 127.3, 123.6

GC-EIMS (m/z, %): 156 (M^+ +1, 12), 155 (M^+, 100), 154 (51), 128 (12), 127 (17), 102 (16), 51 (17)

Chem.Name	2-nitro-4-phenylpyridine (**3k**)
Lit.Ref	M.L.N. Rao, R.J. Dhanorkar, *Eur. J. Org. Chem.*, 2014: 5214-5228



MW: 200.19 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 5-bromo-2-nitropyridine **1k** (0.5 mmol, 102.5 mg, 99% purity), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95% purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, μλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3k** was obtained as withe solid (99 mg, 99 % yield).

Mol Formula	$C_{11}H_8N_2O_2$	**m.p.**	115-117 °C

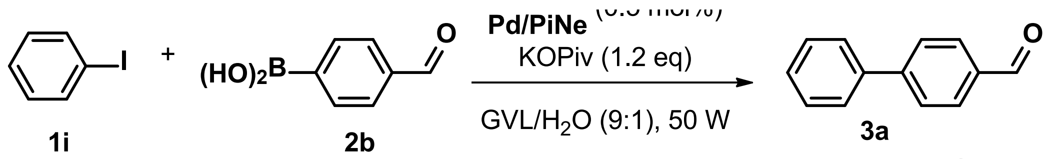
Elemental Analysis: calc C, 66.00; H, 4.03; N, 13.99; found: C, 65.90; H, 4.07; N, 14.02

	δ value:	No. H	Mult	J value/Hz
^1H NMR (400 MHz, $CDCl_3$)	8.85	1	*d*	1.8
	8.35	1	*d*	8.5
	8.19	1	*dd*	8.4, 2.0
	7.64	2	*d*	6.8
	7.59-7.49	3	*m*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 147.4, 142.6, 137.9, 135.5, 129.9, 129.7, 127.7, 118.3

GC-EIMS (m/z, %): 200 (M^+, 38), 155 (13), 152 (100), 128 (22), 127 (50), 77 (13)

Chem.Name	[1,1'-biphenyl]-4-carbaldehyde (**3a**)
Lit.Ref	Bivona, L.A., Giacalone, F., Vaccaro, L., Aprile, C. and Gruttadauria, M., *ChemCatChem*, **2015**, *7*, 2526-2533



MW: 182,22 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, iodobenzene **1i** (0.5 mmol, 57 μL, 98% purity), (4-formylphenyl)boronic acid **2b** (1.1 eq, 86.8 mg, 95% purity), KOPiv (1.2 eq), **Pd/PiNe** (0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 100 °C, T_{max}: 150 °C, μλ: 50 W, 60 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3a** was obtained as withe solid (75 mg, 82 % yield).

Mol Formula	$C_{13}H_{10}O$	**m.p.**	58-60 °C

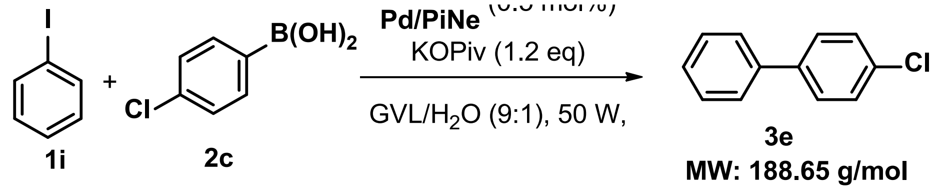
Elemental Analysis: calc: C, 85.69; H, 5.53; found: C, 85.64; H, 5.61

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	10.06	1	*s*	
	7.96	2	*d*	8.2
	7.76	2	*d*	8.2
	7.64	2	*d*	7.3
	7.53-7.46	2	*m*	
	7.45-7.39	1	*m*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 192.1, 147.4, 139.9, 135.3, 130.4, 129.2, 128.6, 127.8, 127.5

GC-EIMS (m/z, %): 182 (M^+, 100), 181 (79), 154 (14), 153 (39), 152 (84), 151 (29), 150 (12), 127 (13), 74 (21), 63 (12), 51 (15), 50 (15)

Chem.Name	4-chloro-1,1'-biphenyl (**3e**)
Lit.Ref	E. Shirakawa, K.-i. Itoh, T. Higashino, T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 15537–15539



Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, iodobenzene **1i** (0.5 mmol, 57 µL, 98% purity), 4-chloro phenylboronic acid **2c** (1.1 eq, 90.5 mg, 95% purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 100 °C, T_{max}: 150 °C, µλ: 50 W, 60 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3e** was obtained as withe solid (51 mg, 54 % yield).

Mol Formula	$C_{11}H_9N$	**m.p.**	77-79 °C

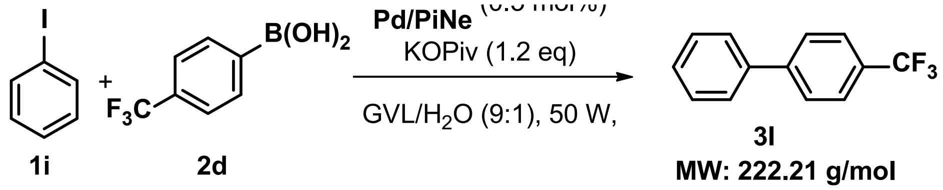
Elemental Analysis: calc: C, 76.40; H, 4.81; found: C, 76.37; H, 4.87.

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	7.59-7.50	4	*m*	
	7.49-7.36	5	*m*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 140.1, 139.8, 133.5, 129.0, 128.5, 127.7, 127.1

GC-EIMS (m/z, %): 190 (34), 188 (M^+, 100), 153 (26), 152 (41)

Chem.Name	4-(trifluoromethyl)-1,1'-biphenyl (**3l**)
Lit.Ref	E. Shirakawa, K.-i. Itoh, T. Higashino, T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 15537–15539



Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, iodobenzene **1i** (0.5 mmol, 57 µL, 98% purity), (4-(trifluoromethyl)phenyl)boronic acid **2d** (1.1 eq, 105 mg, 99% purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 1 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 100 °C, T_{max}: 150 °C, µλ: 50 W, 80 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3l** was obtained as withe solid (99 mg, 89 % yield).

Mol Formula	$C_{13}H_9F_3$	**m.p.**	70-72 °C

Elemental Analysis: calc: C, 70.27; H, 4.08; found: C, 70.31; H, 4.10;

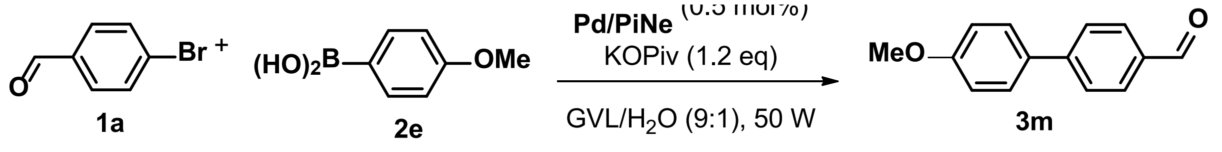
	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	7.60	4	*m*	
	7.60	2	*d*	7.2
	7.53-7.44	2	*m*	
	7.44-7.36	1	*m*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 144.7, 139.8, 129.3 ($J_{C–F}$: 32 Hz), 129.0, 128.2, 127.4, 127.3, 125.6 ($J_{C–F}$: 3.8 Hz), 122.9

^{19}F NMR (376.4 Hz, $CDCl_3$) δ: - 62.4

GC-EIMS (m/z, %): 223 (M^++1, 65), 222 (M^+, 100), 203 (44), 201 (47), 172 (19), 170 (11), 153 (71), 151 (32), 111 (14), 101 (10), 86 (25), 85 (14), 76 (17), 75 (16), 74 (10), 63 (12), 51 (15)

Chem.Name	4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (**3m**)
Lit.Ref	S.-L. Mao, Y. Sun, G.-A. Yu, C. Zhao, Z.-J. Han, J. Yuan, X. Zhu, Q. Yangand, S.-H. Liu *Org. Biomol. Chem.*, 2012,**10**, 9410-9417



MW: 212.24 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 4-bromobenzaldehyde **1a** (0.5 mmol, 93.4 mg, 99 % purity), (4-methoxyphenyl)boronic acid **2e** (1.1 eq, 86 mg, 97% purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt %, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, µλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3m** was obtained as pale-yellow solid (98 mg, 93 % yield).

Mol Formula	$C_{14}H_{12}O_2$	**m.p.**	100-102 °C

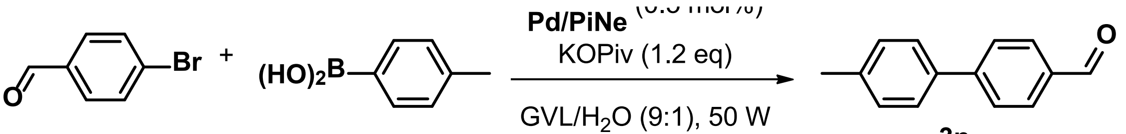
Elemental Analysis: calc: C, 79.22; H, 5.70; found: C, 79.16; H, 5.74

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	10.04	1	*s*	
	7.93	2	*d*	8.2
	7.72	2	*d*	8.2
	7.60	2	*d*	8.8
	7.01	2	*d*	8.7
	3.87	3	*s*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 192.1, 160.3, 147.0, 134.8, 132.2, 130.5, 128.7, 127.2, 114.6, 55.6

GC-EIMS (m/z, %): 213 (M^++1, 15), 212 (M^+, 100), 211 (37), 197 (11), 141 (16), 139 (21), 115 (13)

Chem.Name	4'-methyl-[1,1'-biphenyl]-4-carbaldehyde (**3n**)
Lit.Ref	X. Chen, H. Ke, G. Zou *ACS Catal.* 2014, **4**, 379–385



1a **2f** **3n**

MW: 196,24 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 4-bromobenzaldehyde **1a** (0.5 mmol, 93.4 mg, 99 % purity), p-tolylboronic acid **2f** (1.1 eq, 76.3 mg, 98% purity), KOPiv (1.2 eq, 88.5 mg, 95 % purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, μλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3n** was obtained as pale-yellow solid (82 mg, 84 % yield).

Mol Formula	$C_{14}H_{12}O$	**m.p.**	105-107 °C

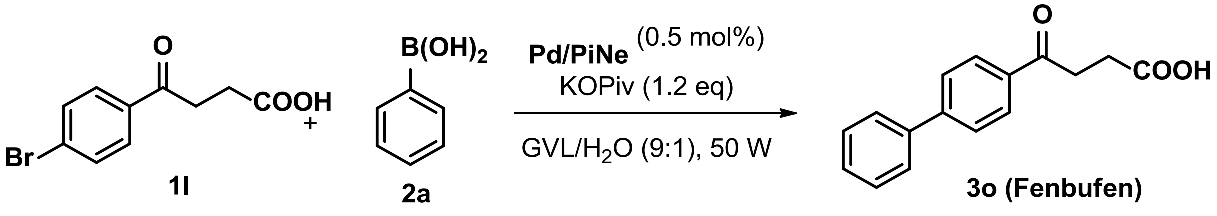
Elemental Analysis: calc: C, 85.68; H, 6.16; found: C, 85.61; H, 6.19;

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, $CDCl_3$)	10.05	1	*s*	
	7.94	2	*d*	8.0
	7.74	2	*d*	8.0
	7.55	2	*d*	7.8
	7.29	2	*d*	7.8
	2.42	3	*s*	

^{13}C NMR (100.6 Hz, $CDCl_3$) δ: 192.1, 147.3, 138.7, 137.0, 135.1, 130.4, 129.9, 127.6, 127.4, 21.3

GC-EIMS (m/z, %): 197 (M^++1, 40), 196 (M^+, 100), 195 (100), 168 (15), 167 (59), 166 (29), 155 (88), 153 (18), 152 (100), 151 (17), 139 (16), 115 (24), 97 (13), 84 (13), 83 (22), 82 (25), 63 (17), 51 (12)

Chem.Name	4-([1,1'-biphenyl]-4-yl)-4-oxobutanoic acid (**3o**)
Lit.Ref	A. Ohno, T. Sato, T. Mase, Y. Uozumi, Y. M. A. Yamada, *Adv. Synth. Catal.* 2020, **362**, 4687.



MW: 254.28 g/mol

Method:

In a 10 mL microwave vial equipped with a magnetic stirrer, 4-(4-bromophenyl)-4-oxobutanoic acid **1l** (0.5 mmol, 128 mg), phenylboronic acid **2a** (1.1 eq, 68.5 mg, 98 % purity), KOPiv (1.2 eq, 88.5 mg, 95% purity), **Pd/PiNe** (8 wt%, 3.3 mg, 0.5 mol%), and GVL:H_2O (9:1, 0.5 mL) were consecutively added. The reaction was performed in MW cyclic mode (T_{min}: 90 °C, T_{max}: 120 °C, µλ: 50 W, 40 cycles). After removing the catalyst by filtration and washing with 0.5 mL of GVL, the water was evaporated and the remaining GVL was recovered (94%) by distillation. The product was precipitated with 1 mL of water at 0°C and recovered by filtration. The product **3o** (Fenbufen) was obtained as white solid (126 mg, 99 % yield).

Mol Formula	$C_{16}H_{14}O_3$	**m.p.**	184-186 °C

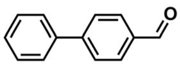
Elemental Analysis: calc: C, 75.57; H, 5.55; found: C, 75.62; H, 5.50

	δ value:	No. H	Mult	J value/Hz
^{1}H NMR (400 MHz, DMSO-d$_6$)	12.15	1	*s*	
	8.07	2	*d*	8.2
	7.84	2	*d*	8.2
	7.75	2	*d*	7.3
	7.53-7.49	2	*m*	
	7.45-7.42	1	*m*	
	3.29	2	*d*	6.5
	2.60	2	*d*	6.5

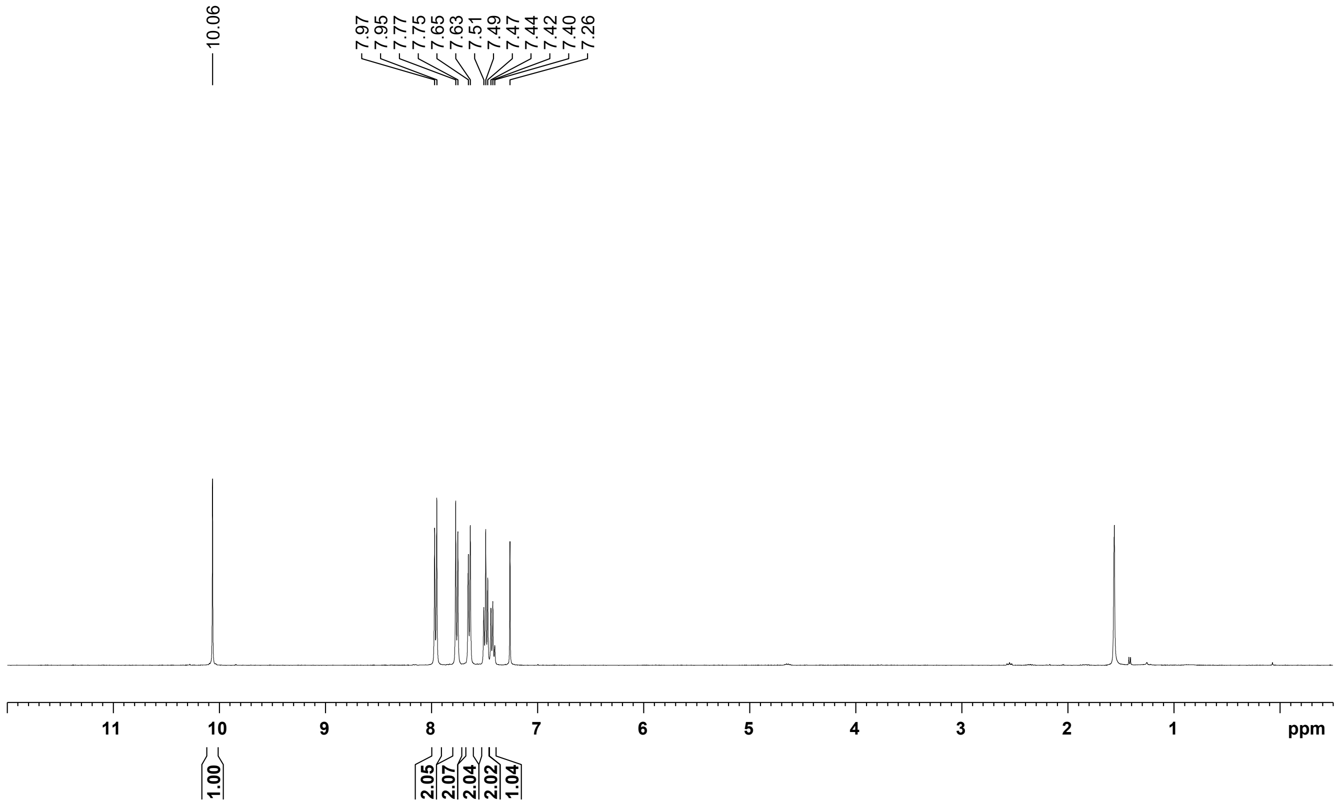
^{13}C NMR (100.6 Hz, DMSO-d$_6$) δ: 198.0, 173.8, 144.5, 138.9, 135.3, 129.1, 128.6, 128.4, 127.0, 126.9, 33.1, 27.9

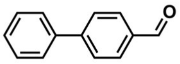
GC-EIMS (m/z, %): 237 (10), 182 (15), 181 (100), 153 (23), 152 (43), 151 (12)

5. ^{1}H ^{13}C and ^{19}F NMR spectra

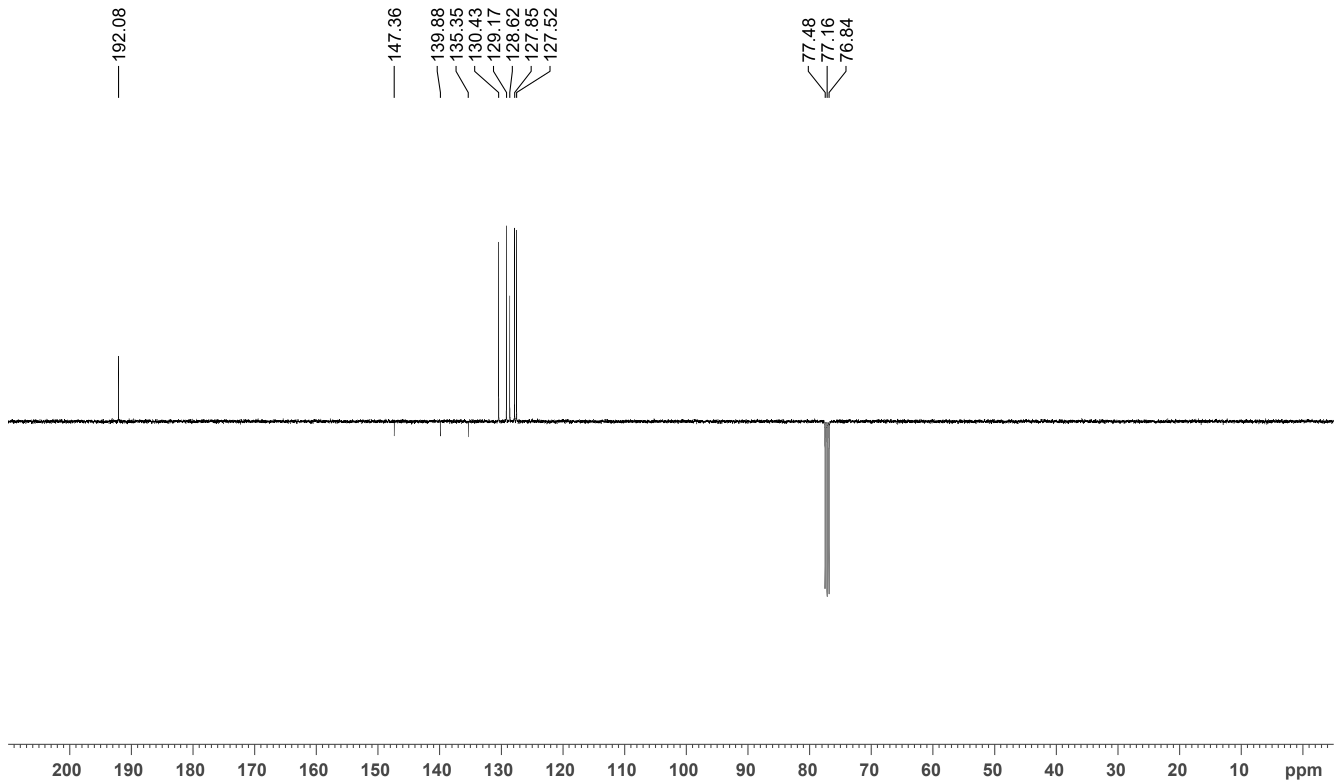


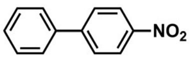
[1,1'-biphenyl]-4-carbaldehyde (**3a**)



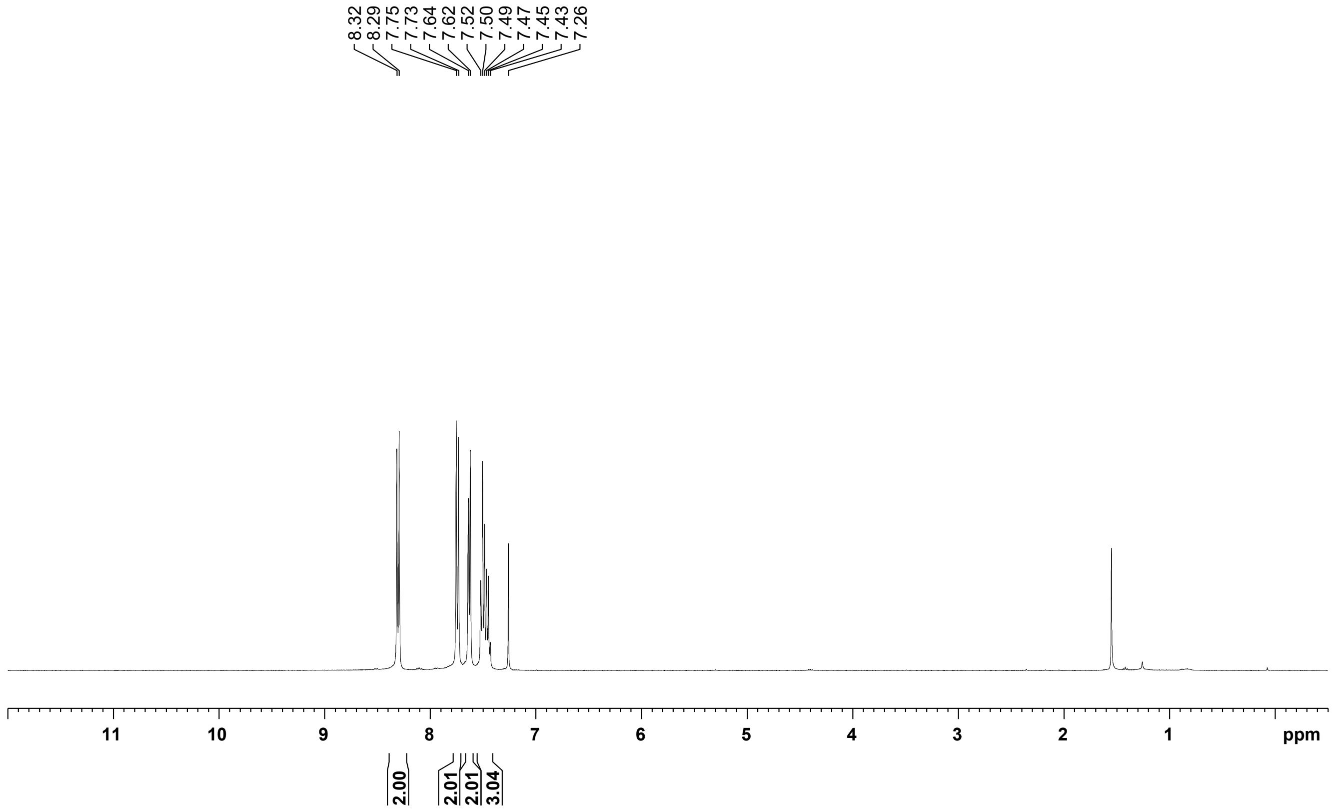


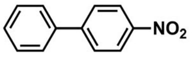
[1,1'-biphenyl]-4-carbaldehyde (**3a**)



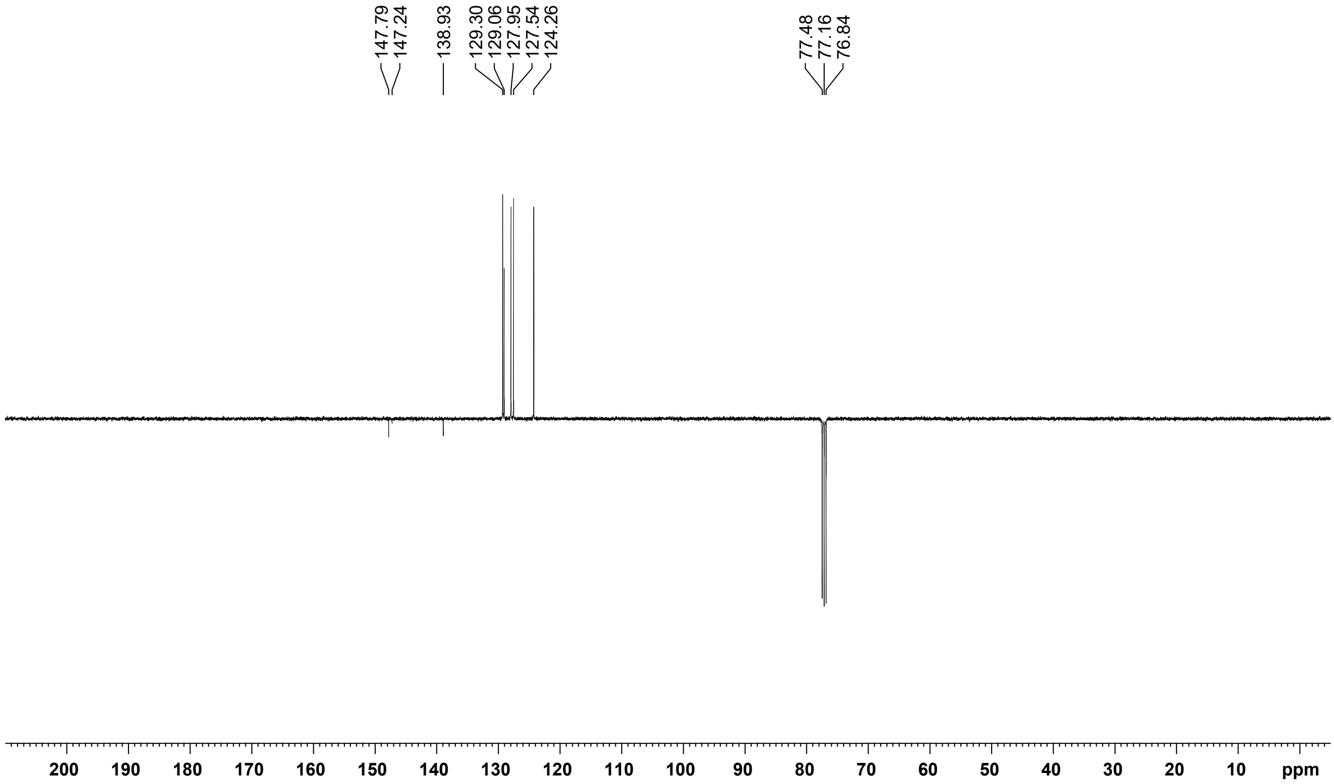


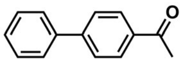
4-nitro-1,1'-biphenyl (**3b**)



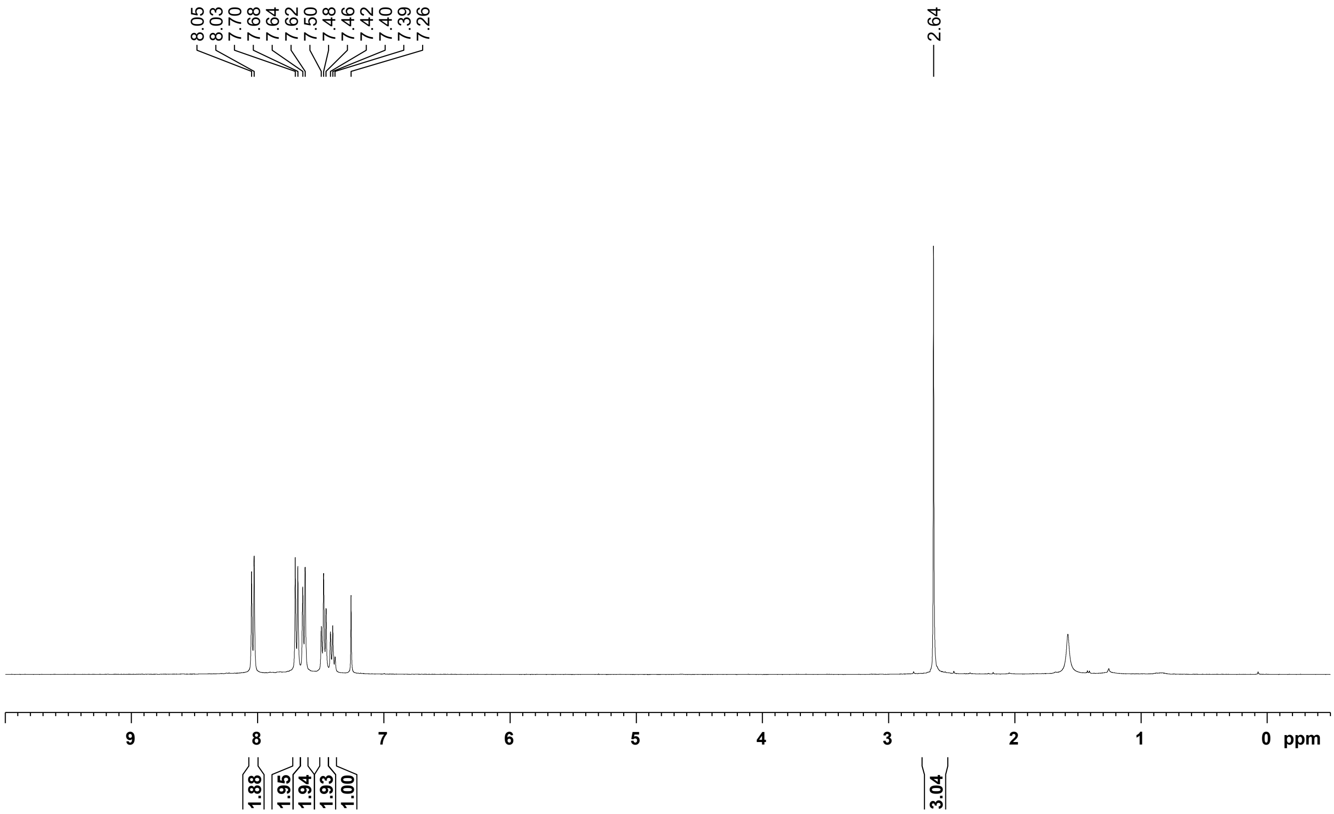


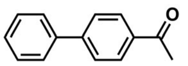
4-nitro-1,1'-biphenyl (**3b**)



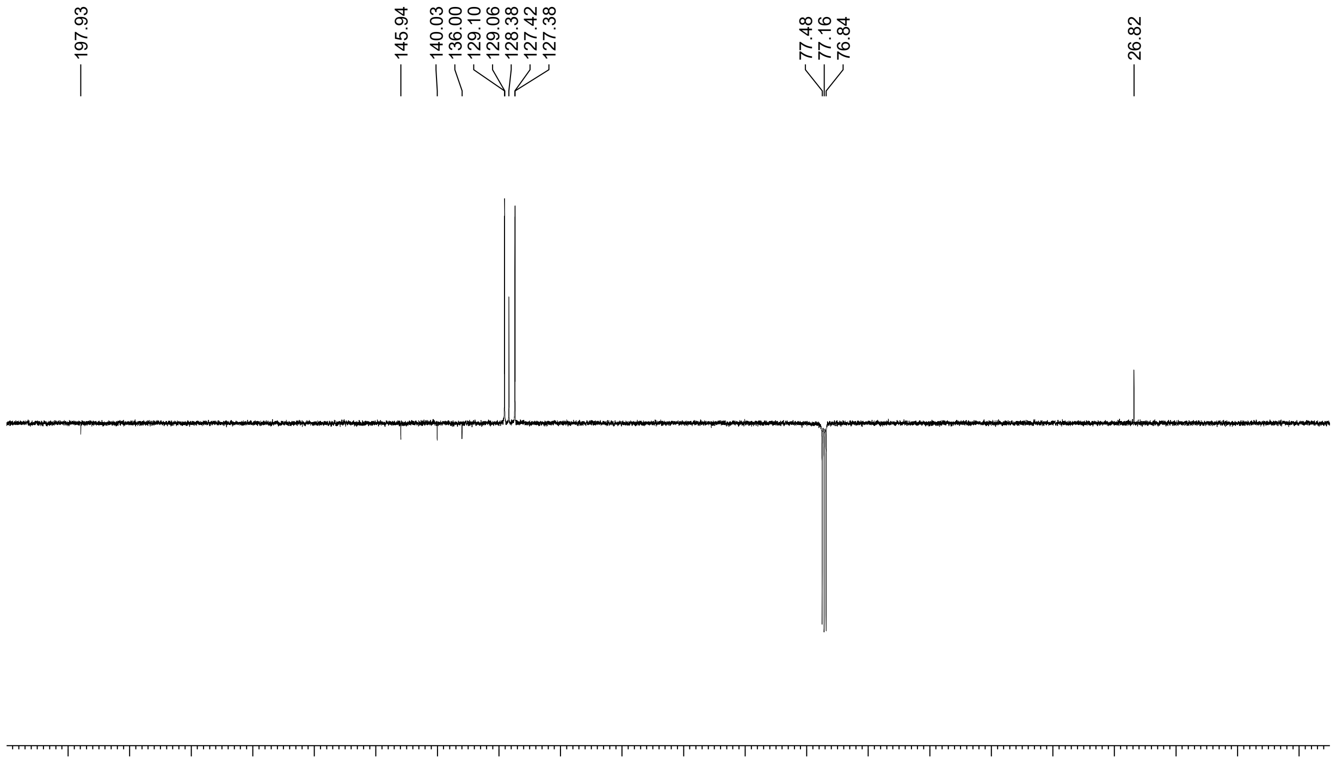


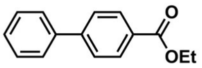
1-([1,1'-biphenyl]-4-yl)ethanone (**3c**)



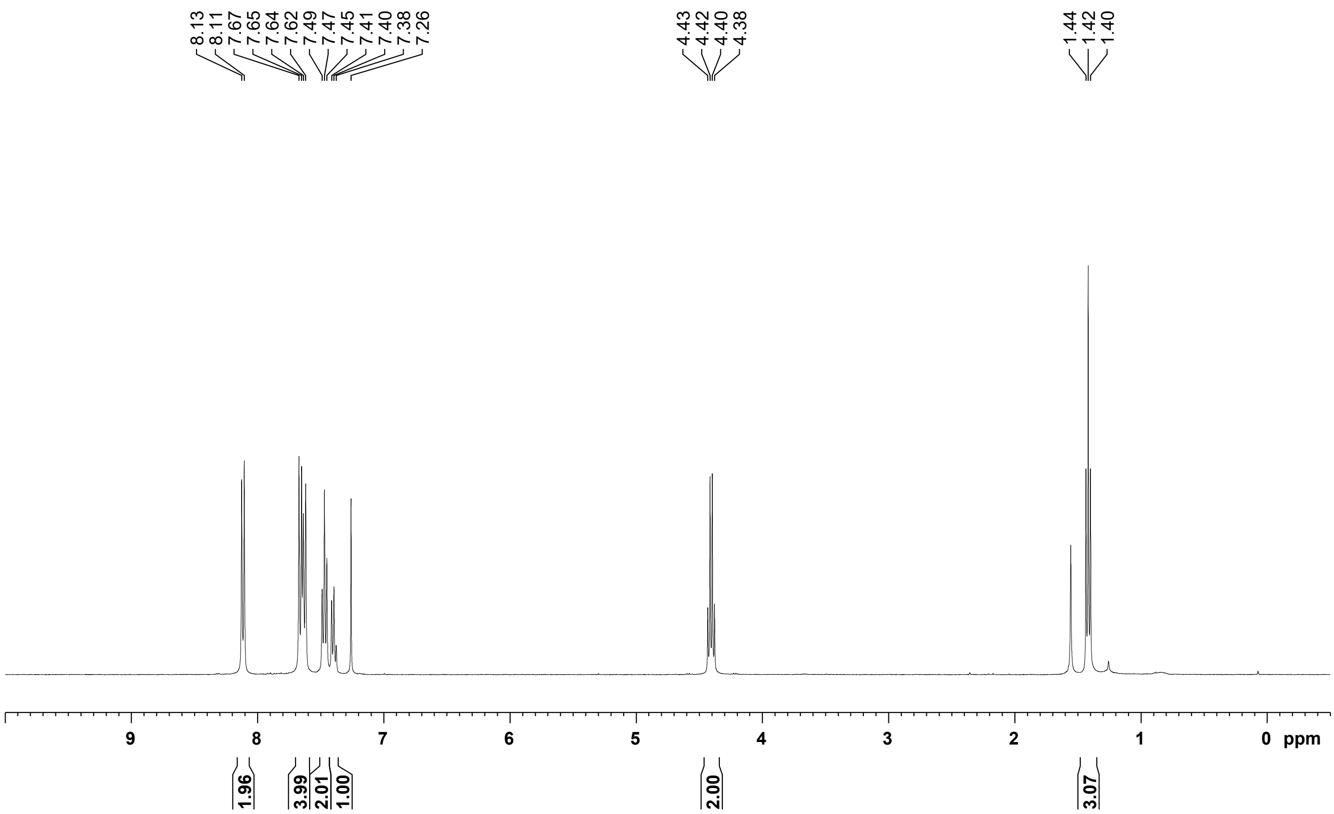


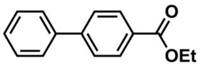
1-([1,1'-biphenyl]-4-yl)ethanone (**3c**)



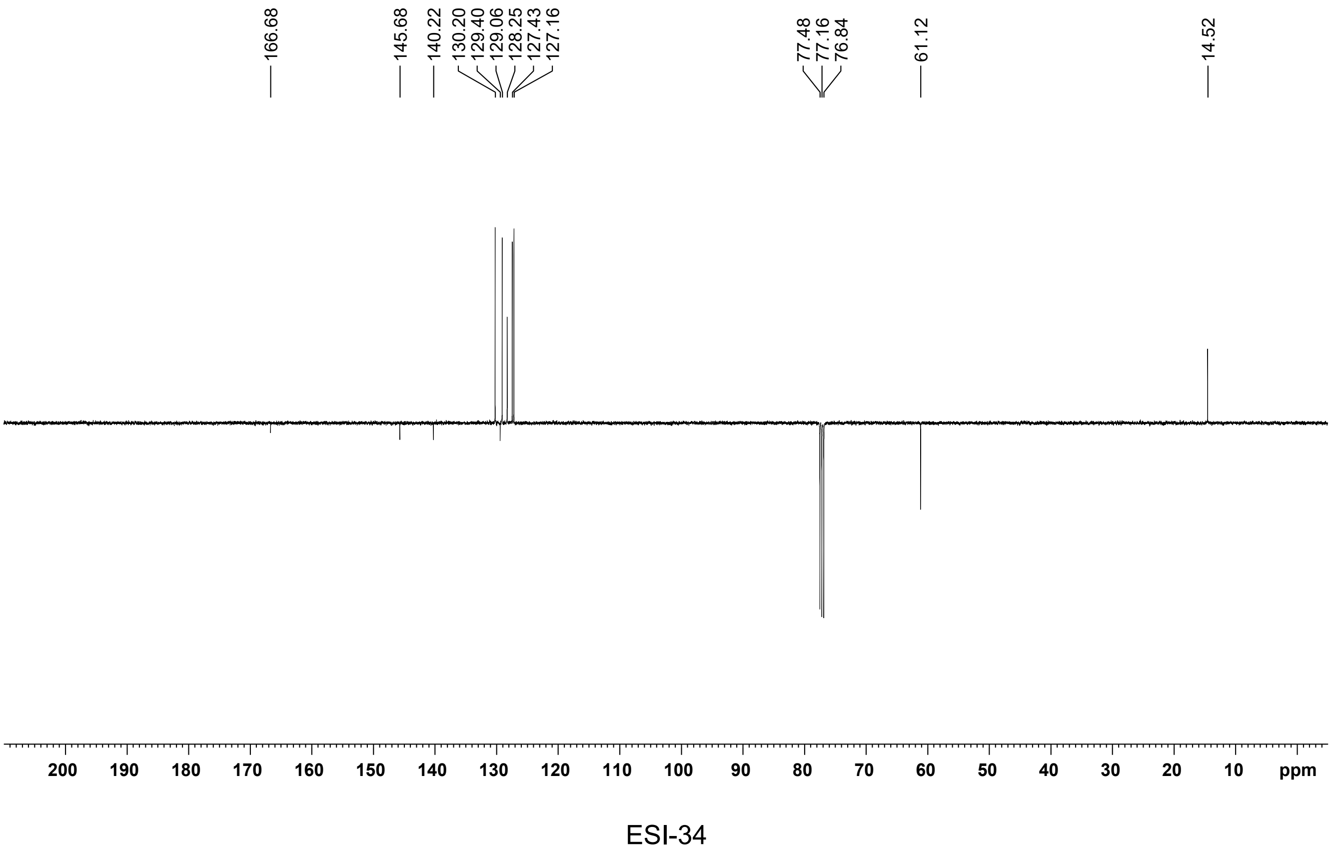


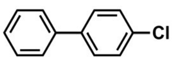
ethyl [1,1'-biphenyl]-4-carboxylate (**3d**)



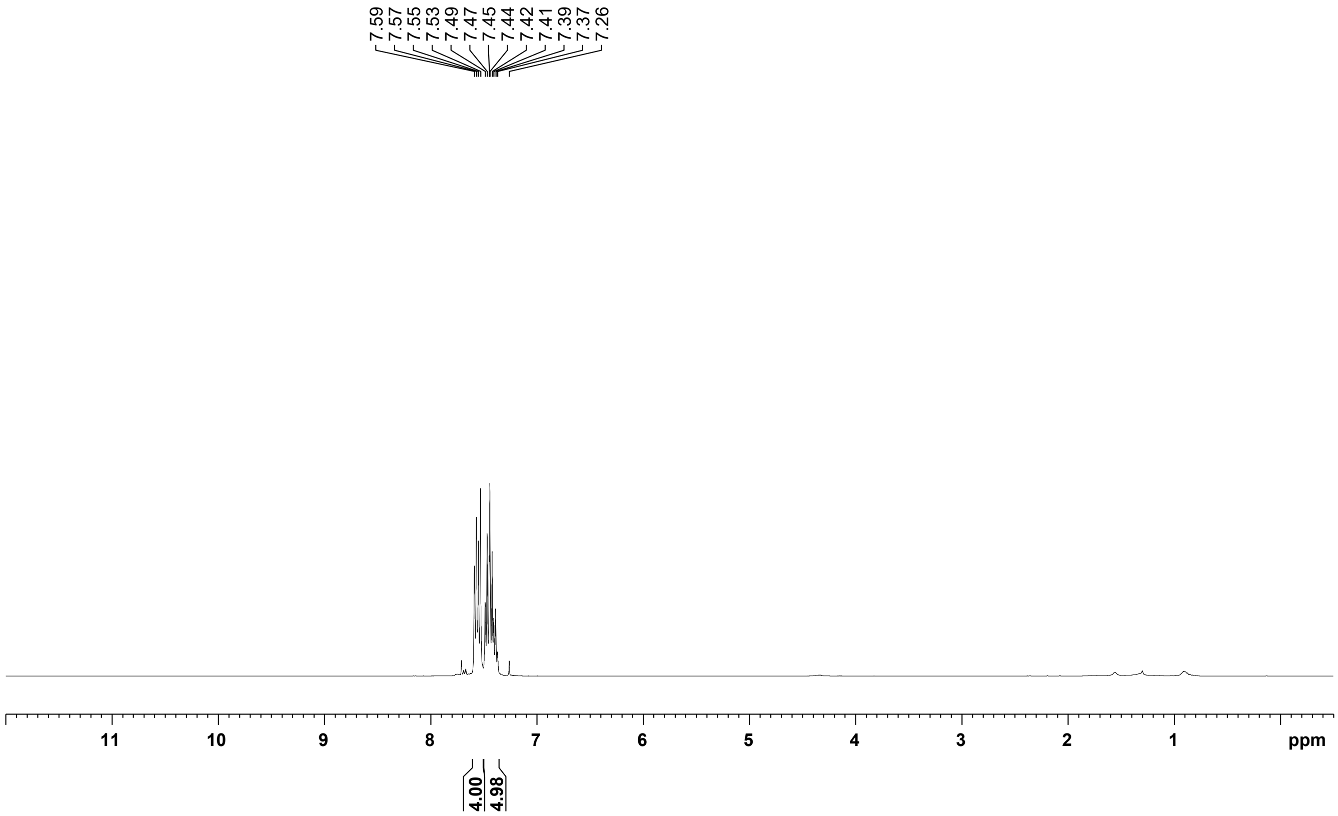


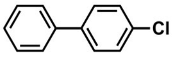
ethyl [1,1'-biphenyl]-4-carboxylate (**3d**)



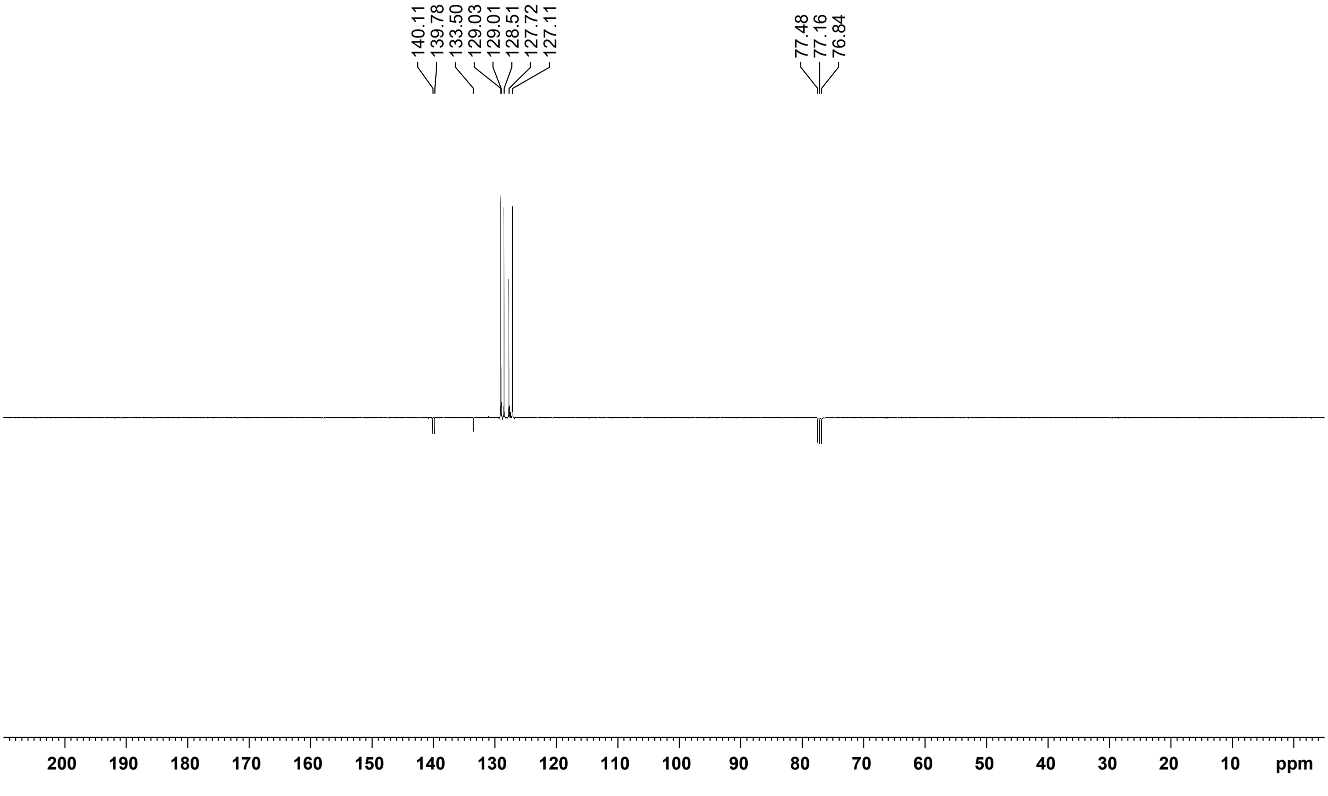


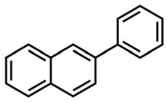
4-chloro-1,1'-biphenyl (**3e**)



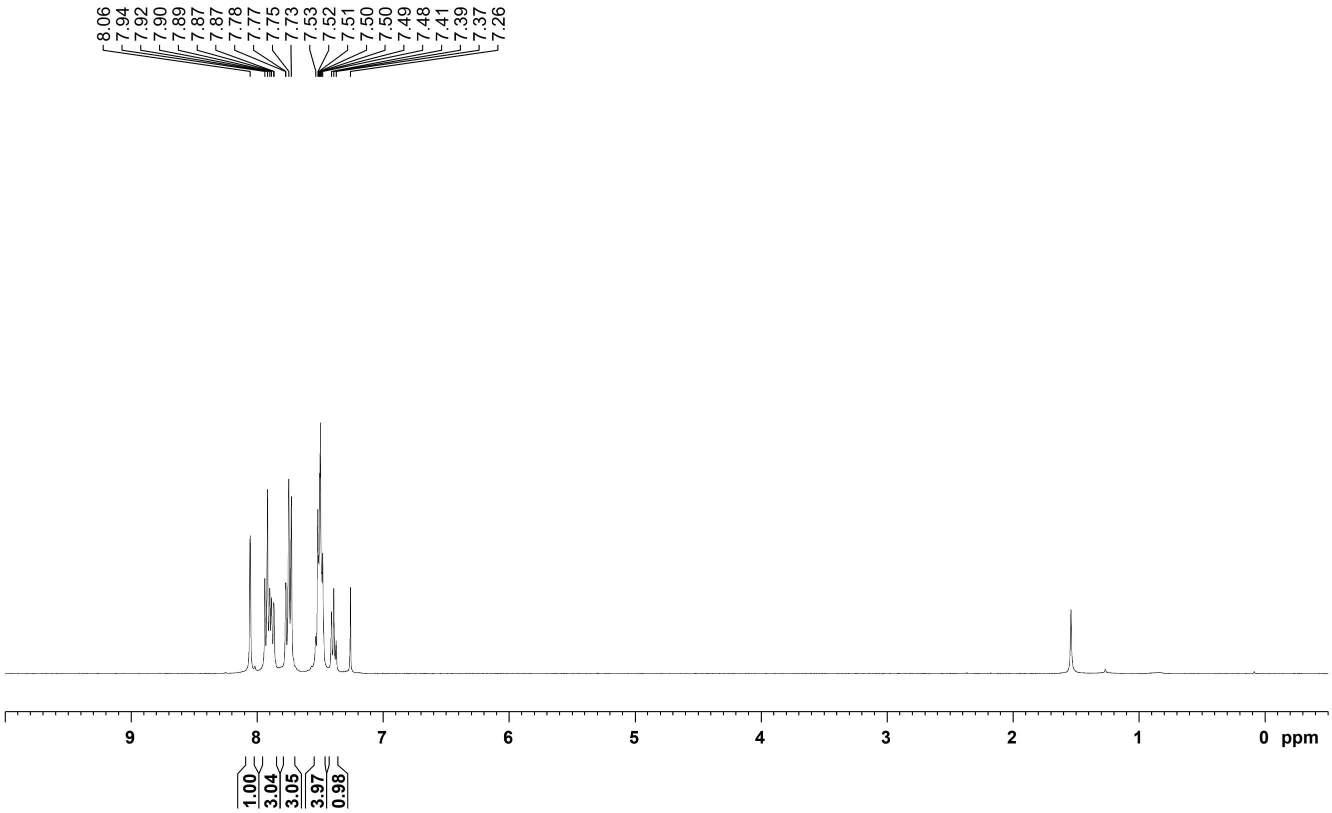


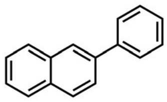
4-chloro-1,1'-biphenyl (**3e**)



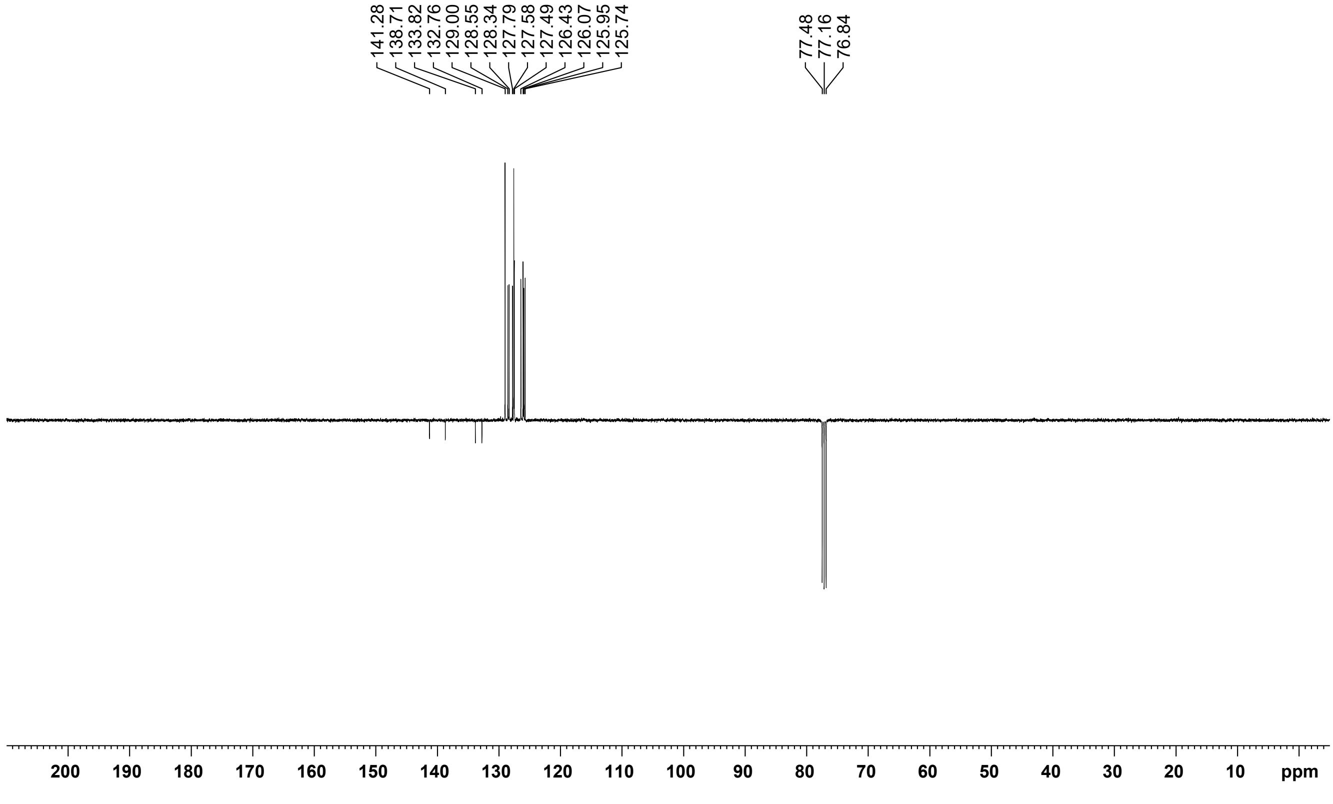


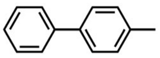
2-phenylnaphthalene (**3f**)



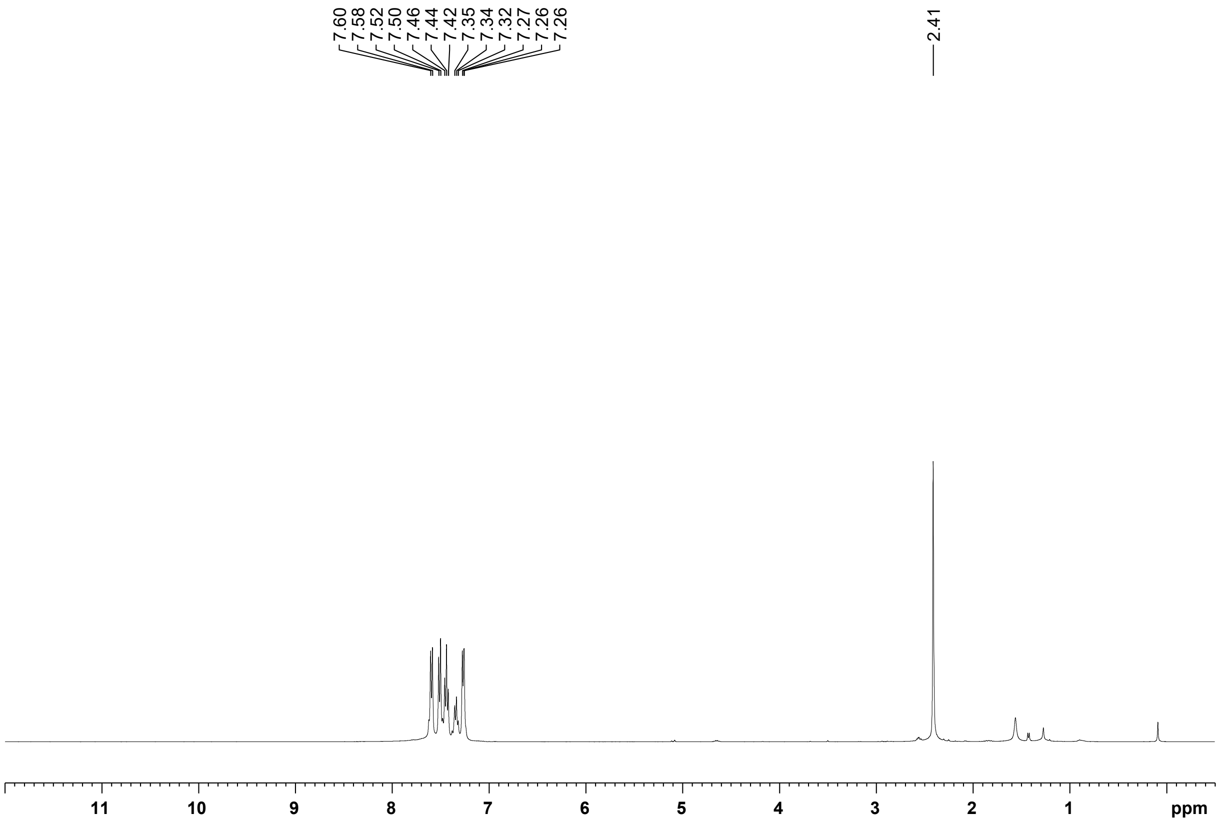


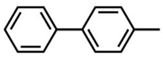
2-phenylnaphthalene (**3f**)





4-methyl-1,1'-biphenyl (**3g**)





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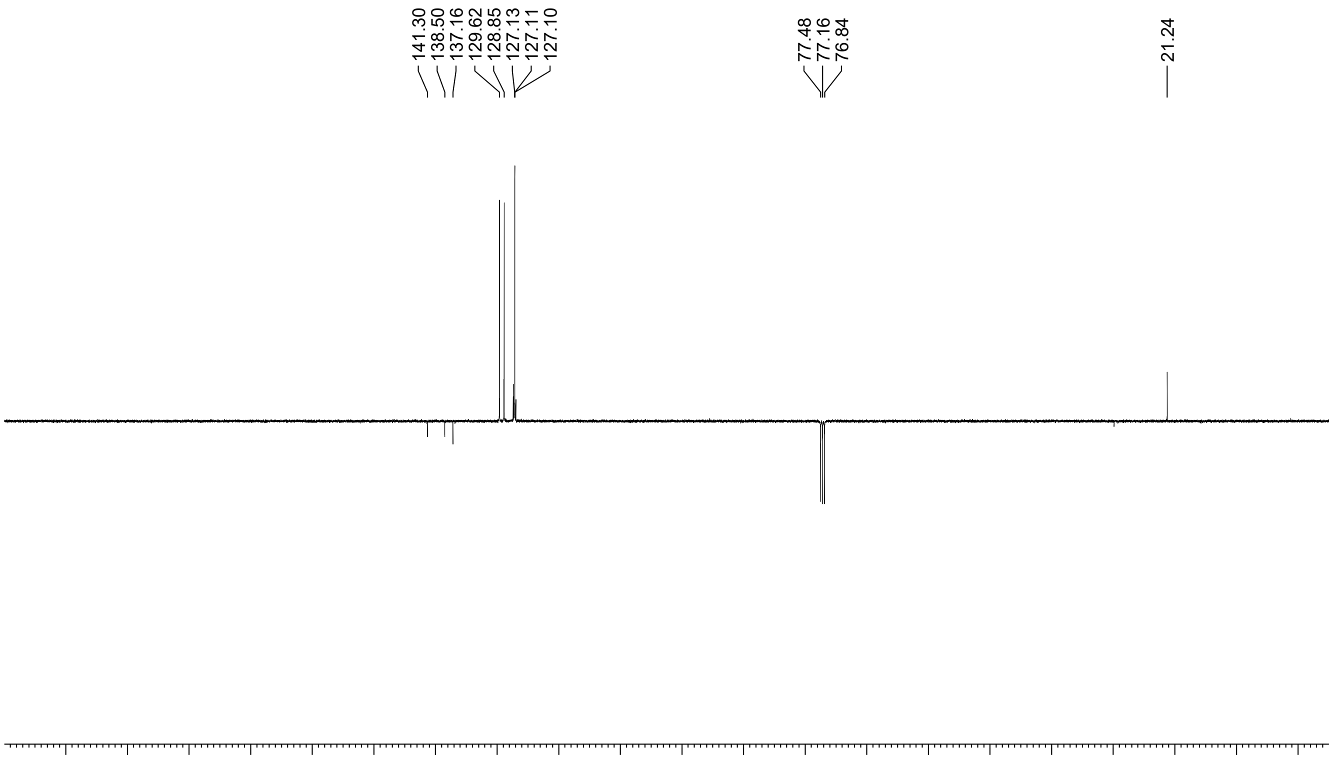
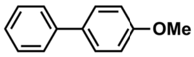
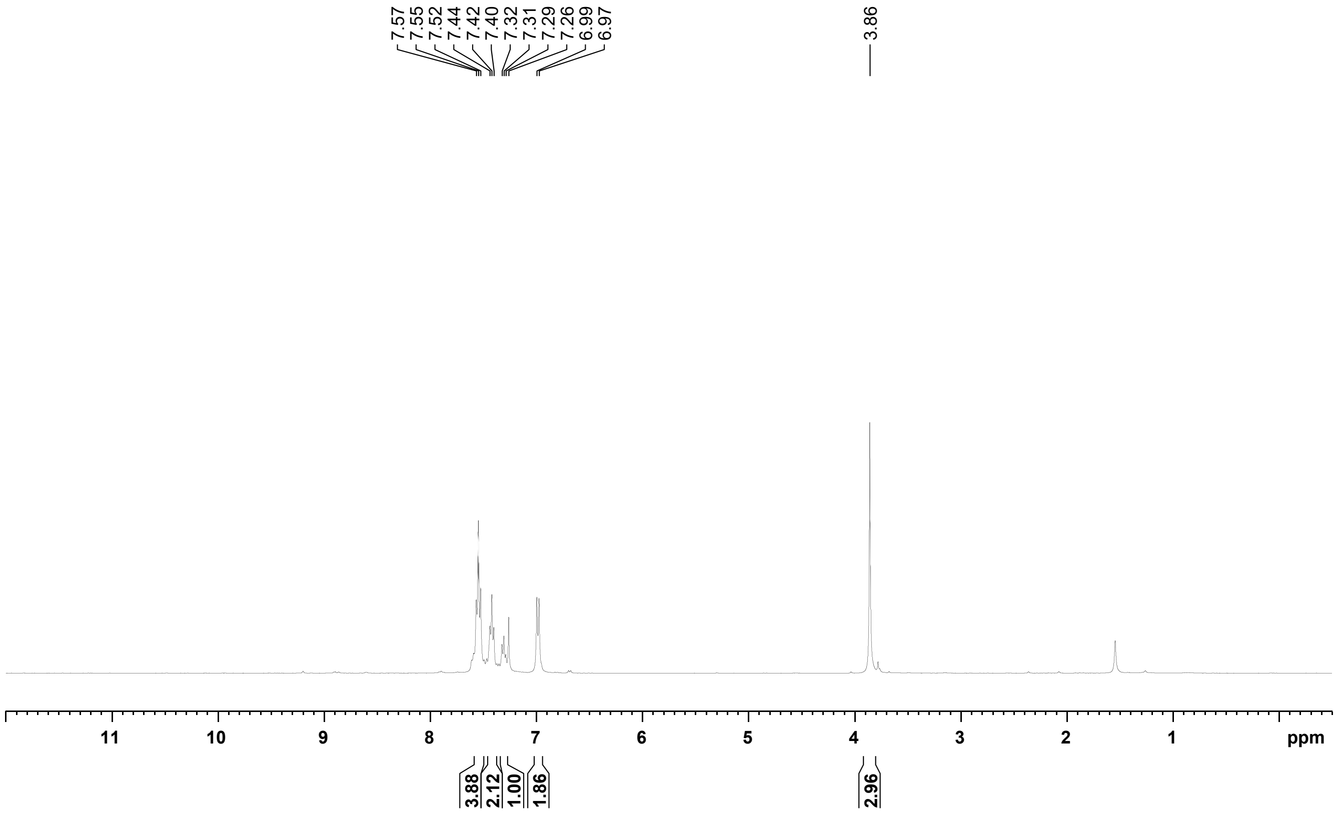
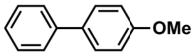


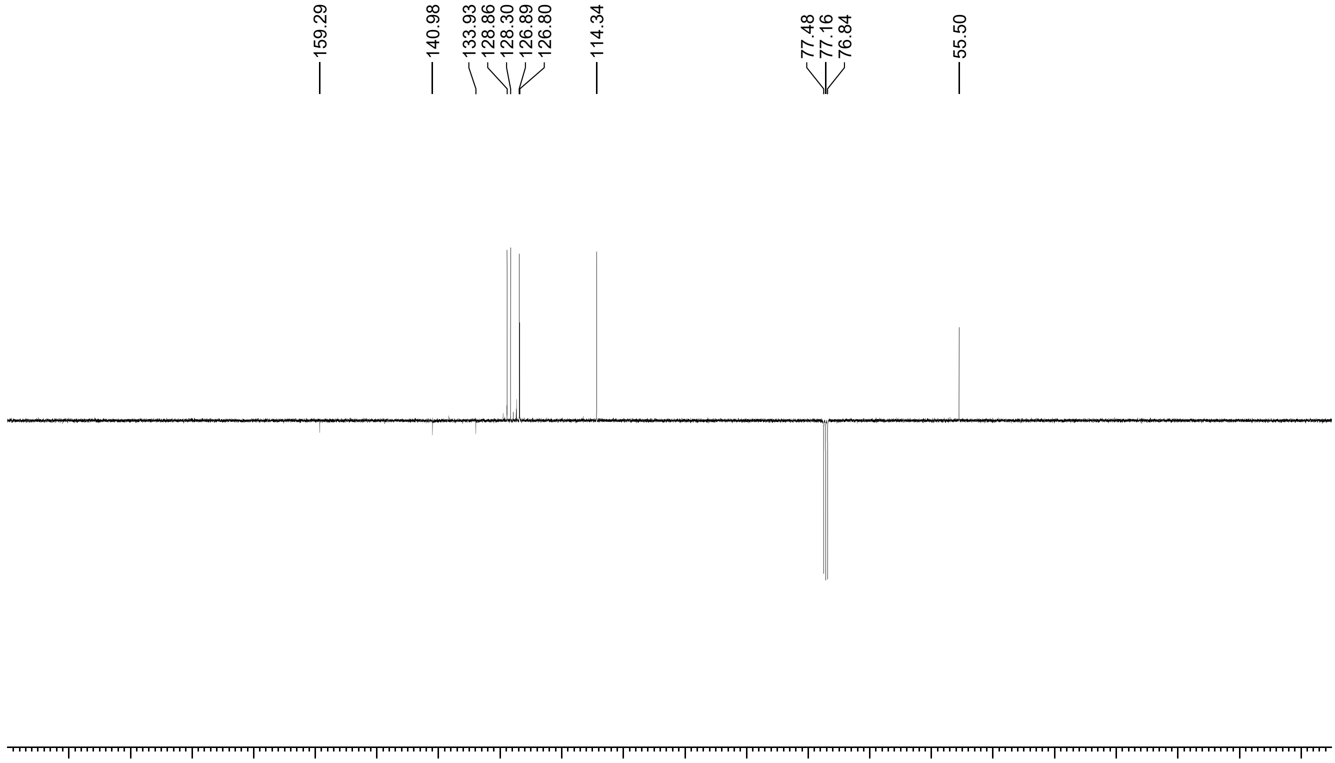


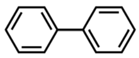
4-methoxy-1,1'-biphenyl (**3h**)



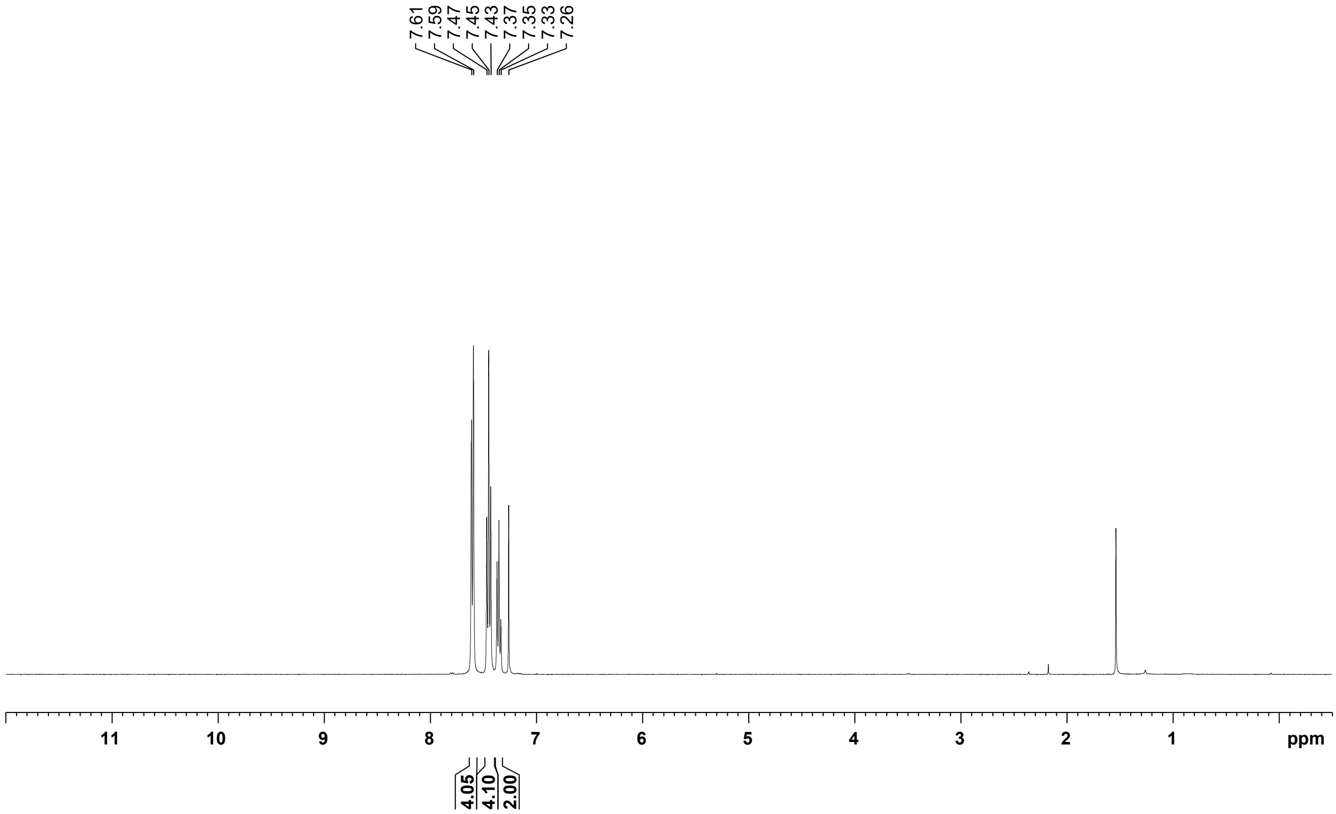


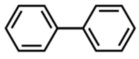
4-methoxy-1,1'-biphenyl (**3h**)



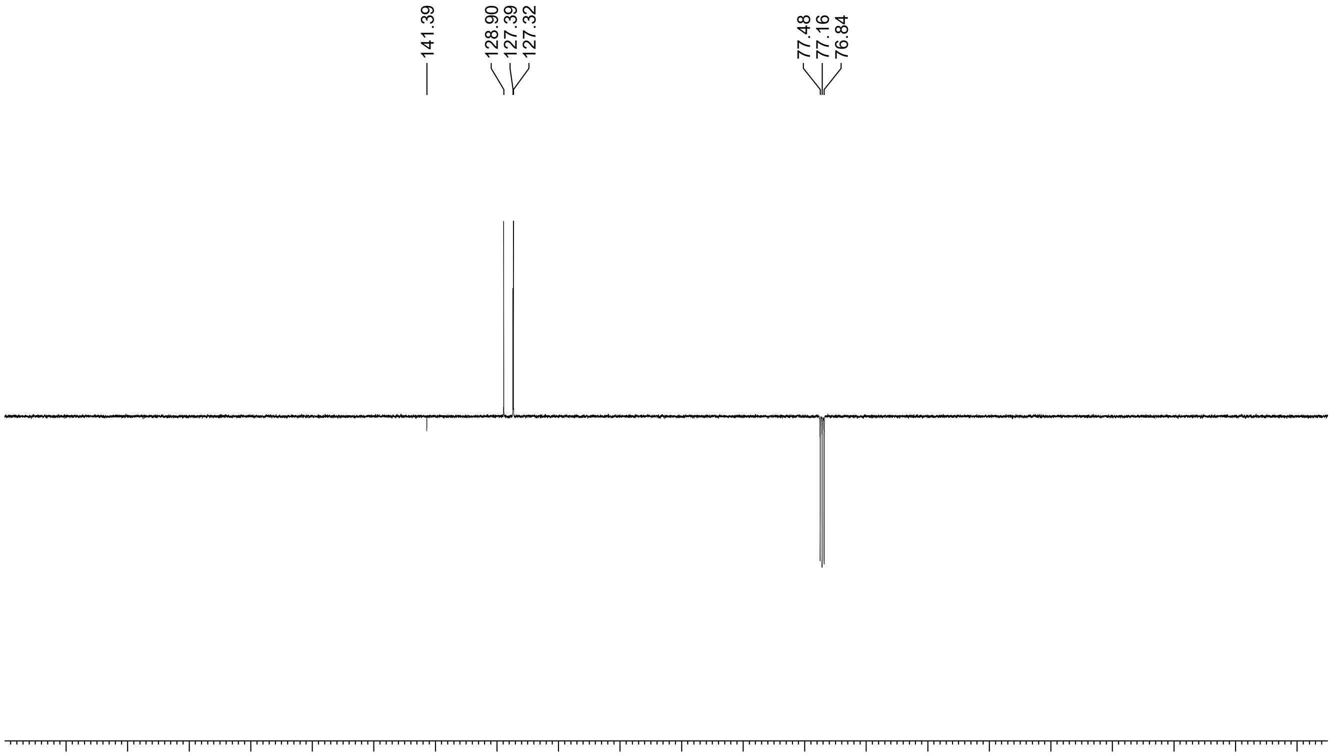


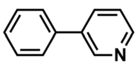
1,1'-biphenyl (**3i**)



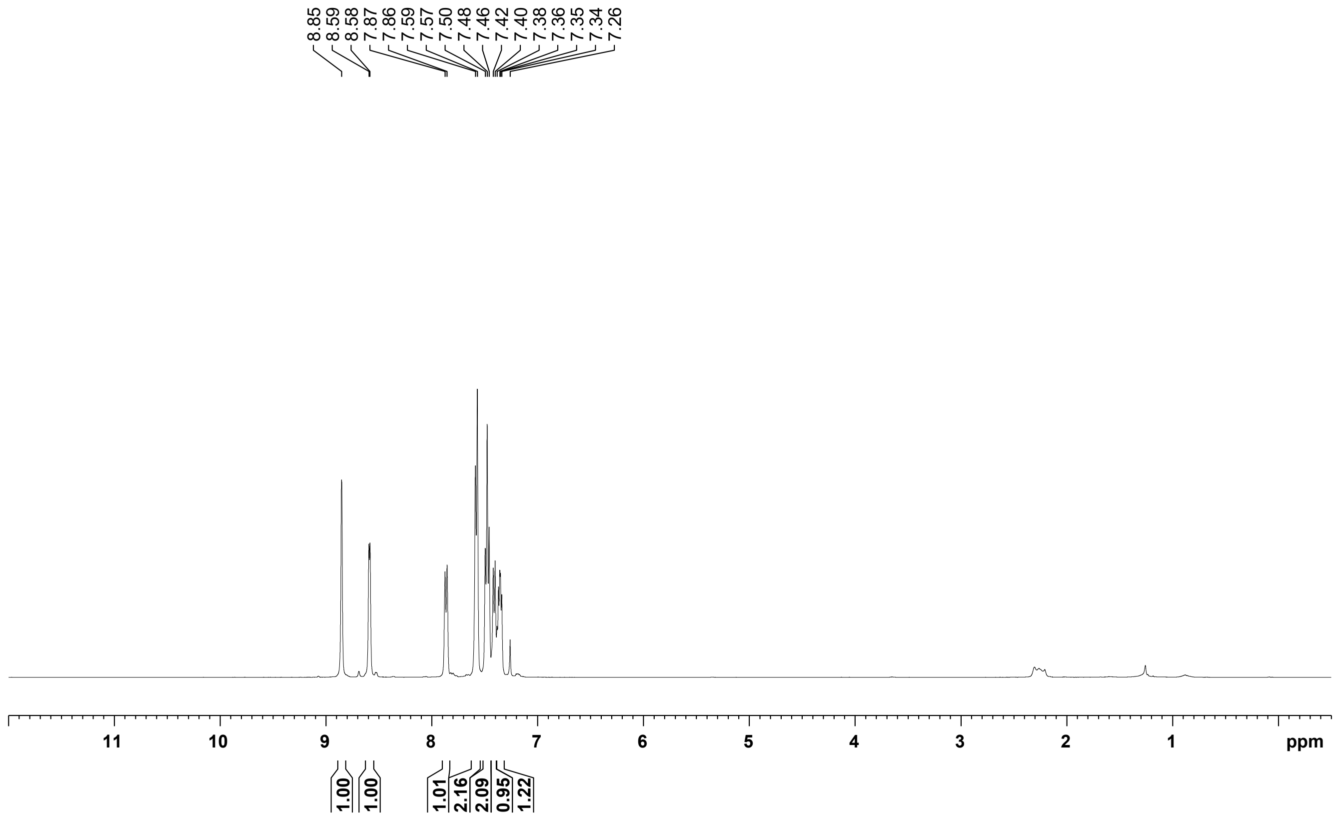


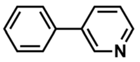
1,1'-biphenyl (**3i**)



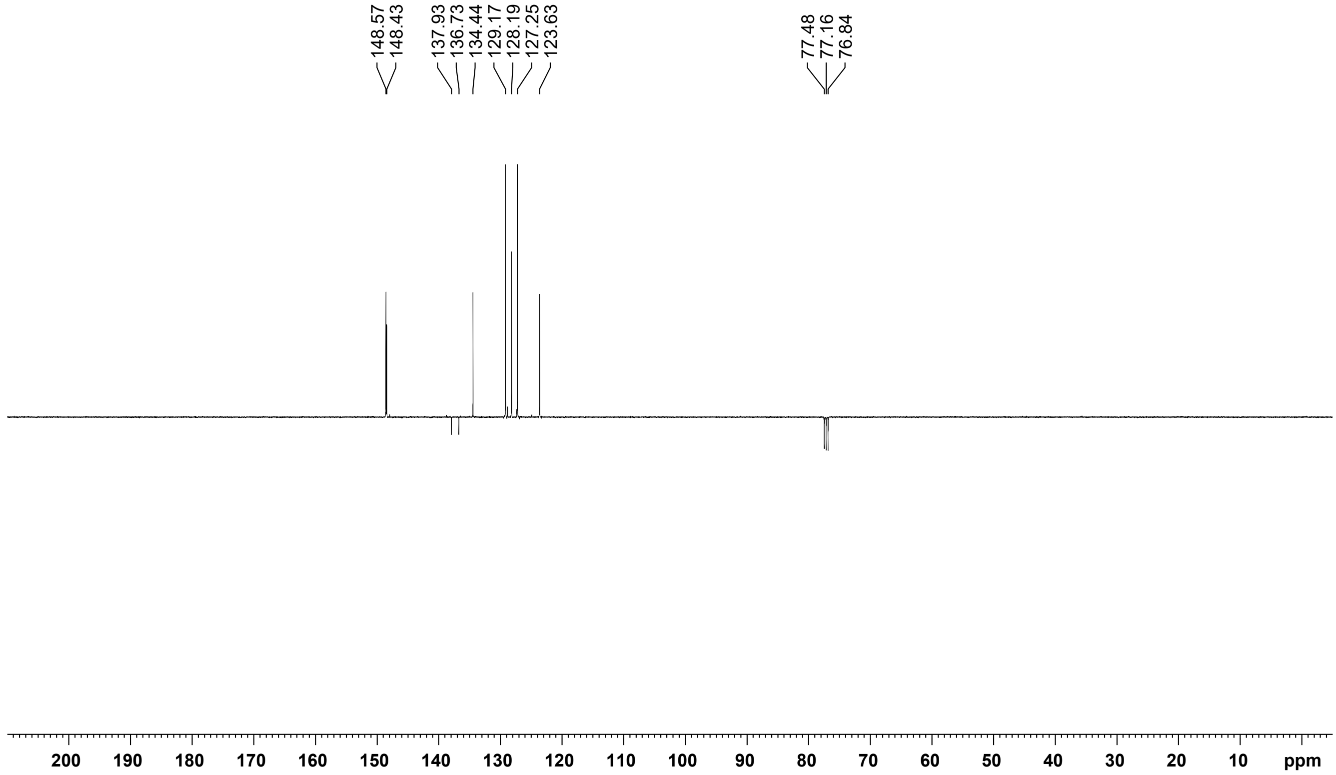


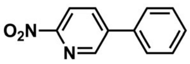
3-phenylpyridine (**3j**)



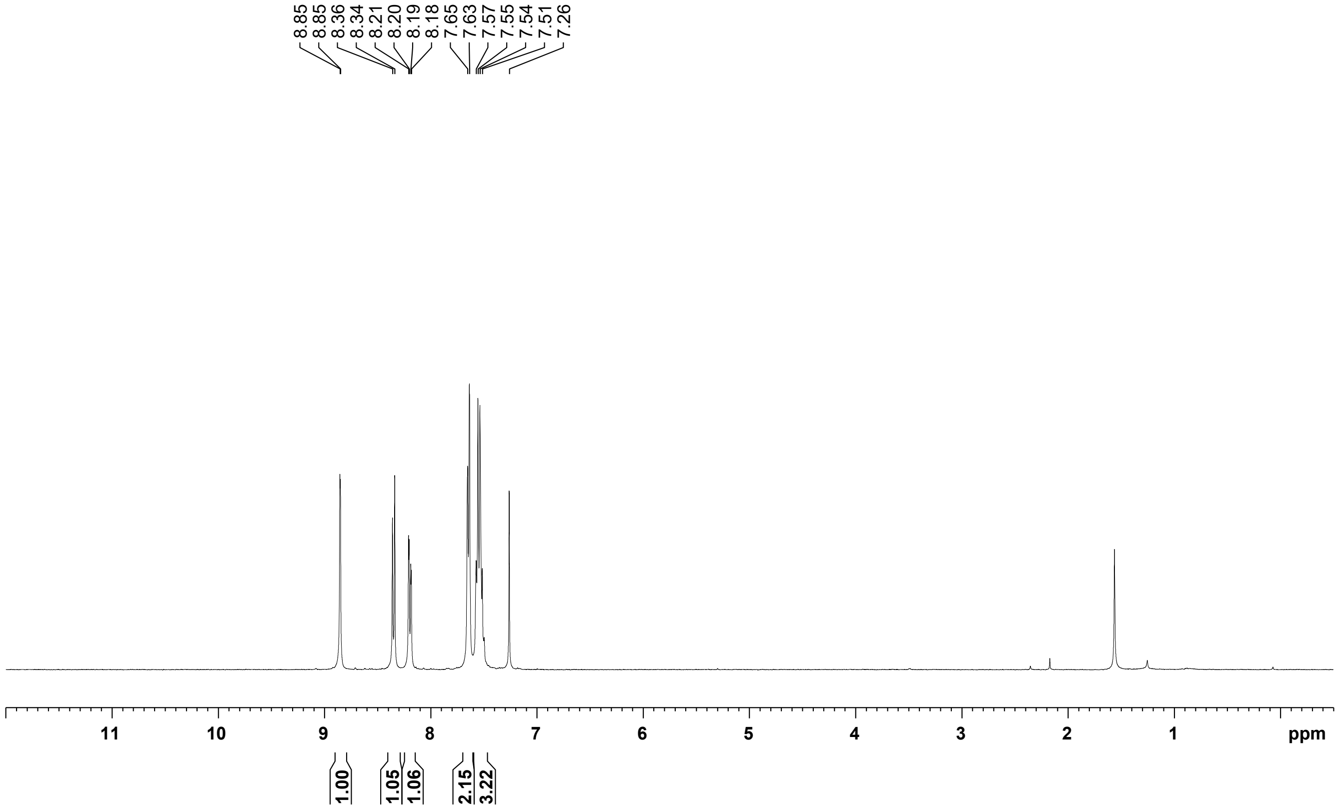


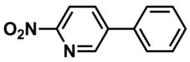
3-phenylpyridine (**3j**)



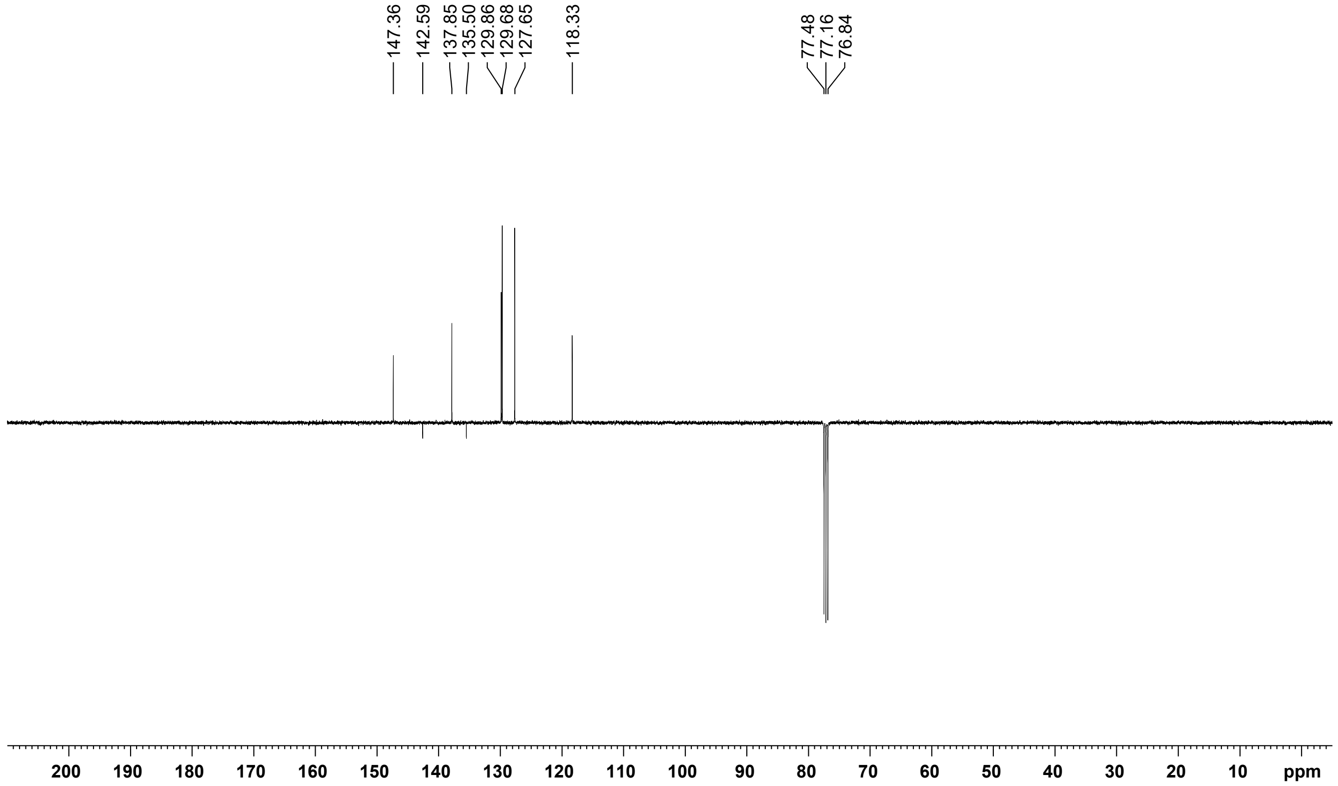


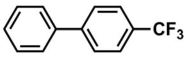
2-nitro-4-phenylpyridine (**3k**)



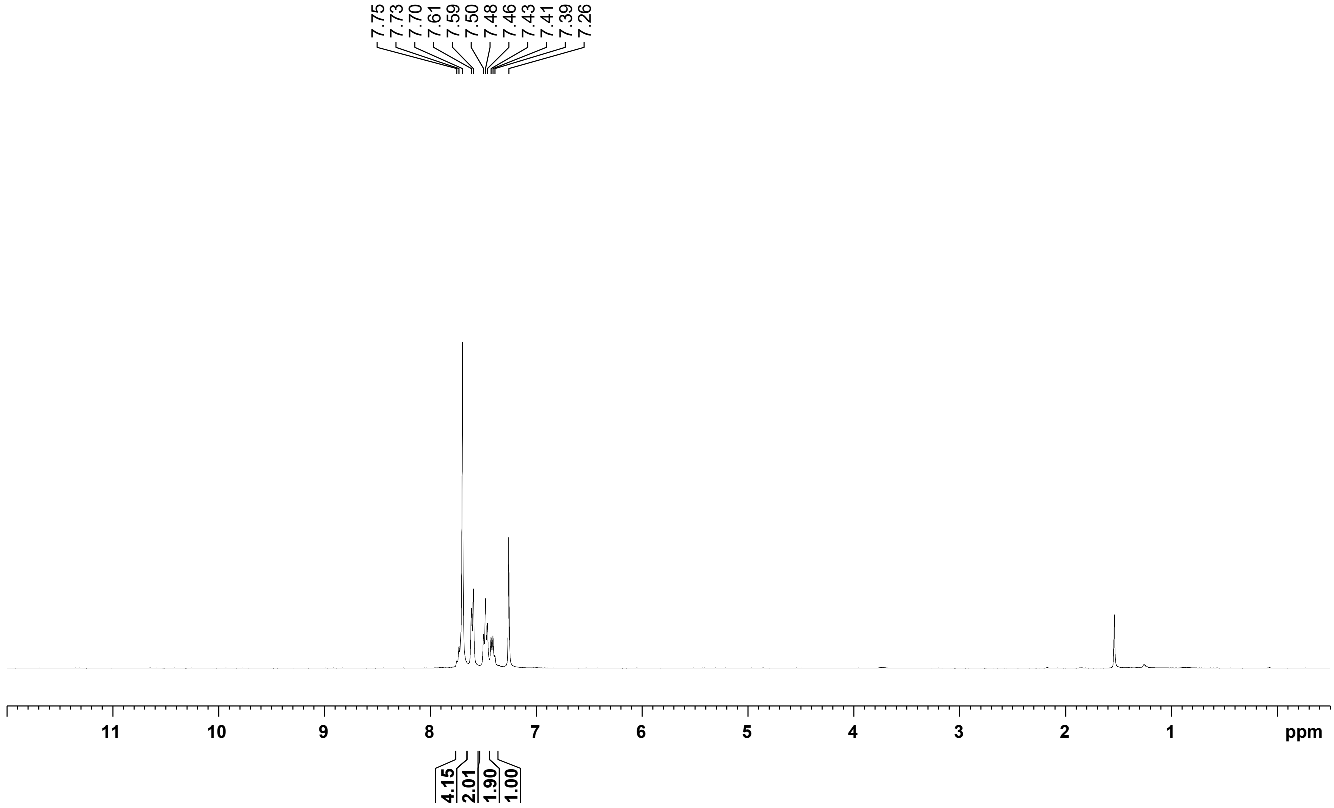


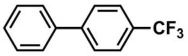
2-nitro-4-phenylpyridine (**3k**)



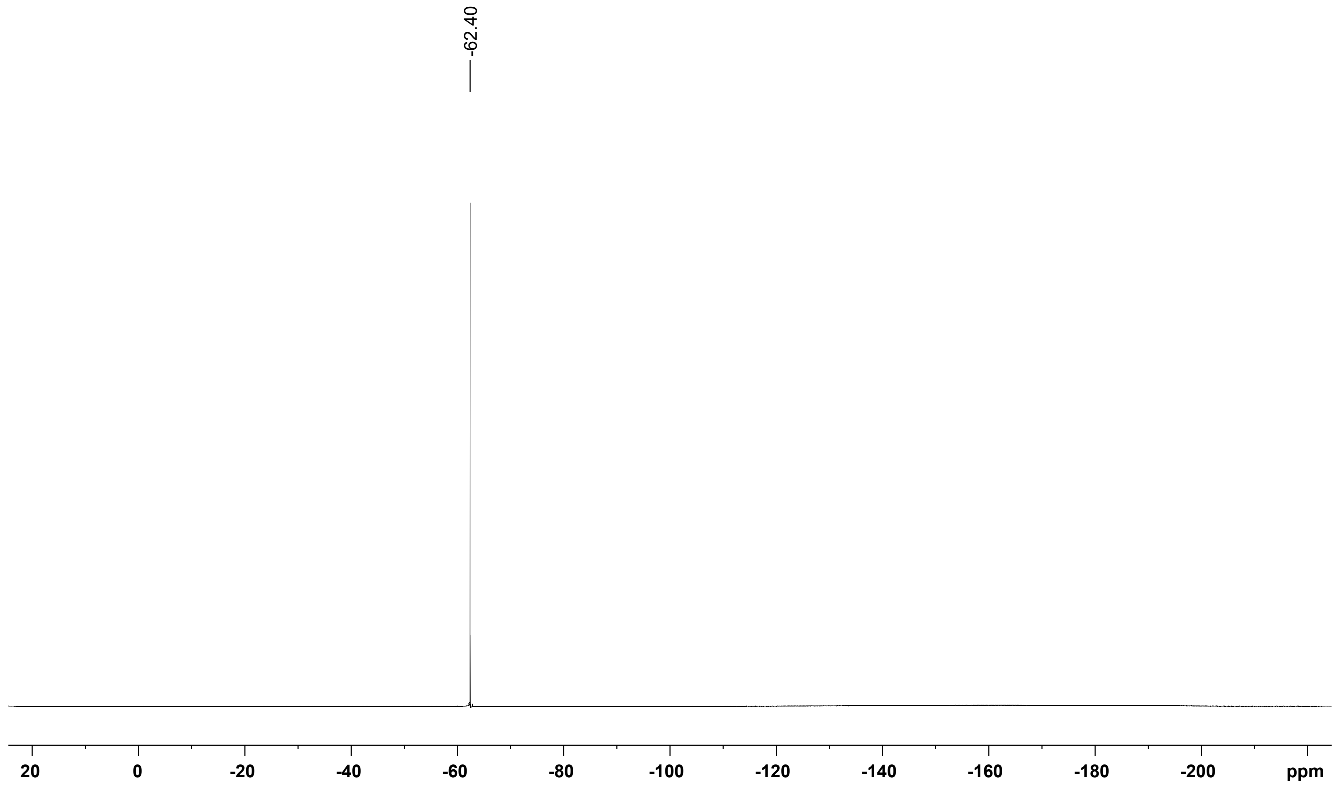


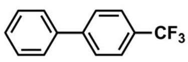
4-(trifluoromethyl)-1,1'-biphenyl (**3l**)



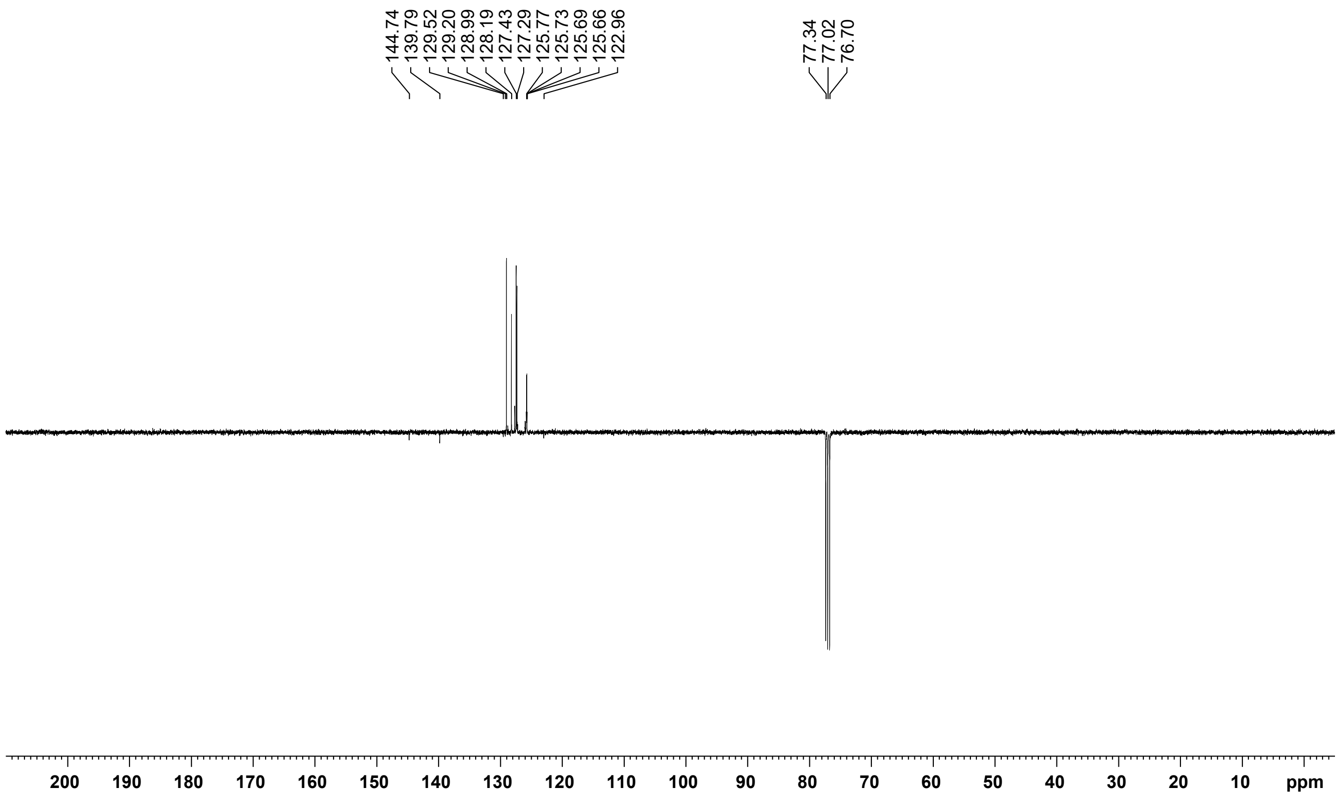


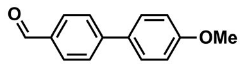
4-(trifluoromethyl)-1,1'-biphenyl (**3l**)



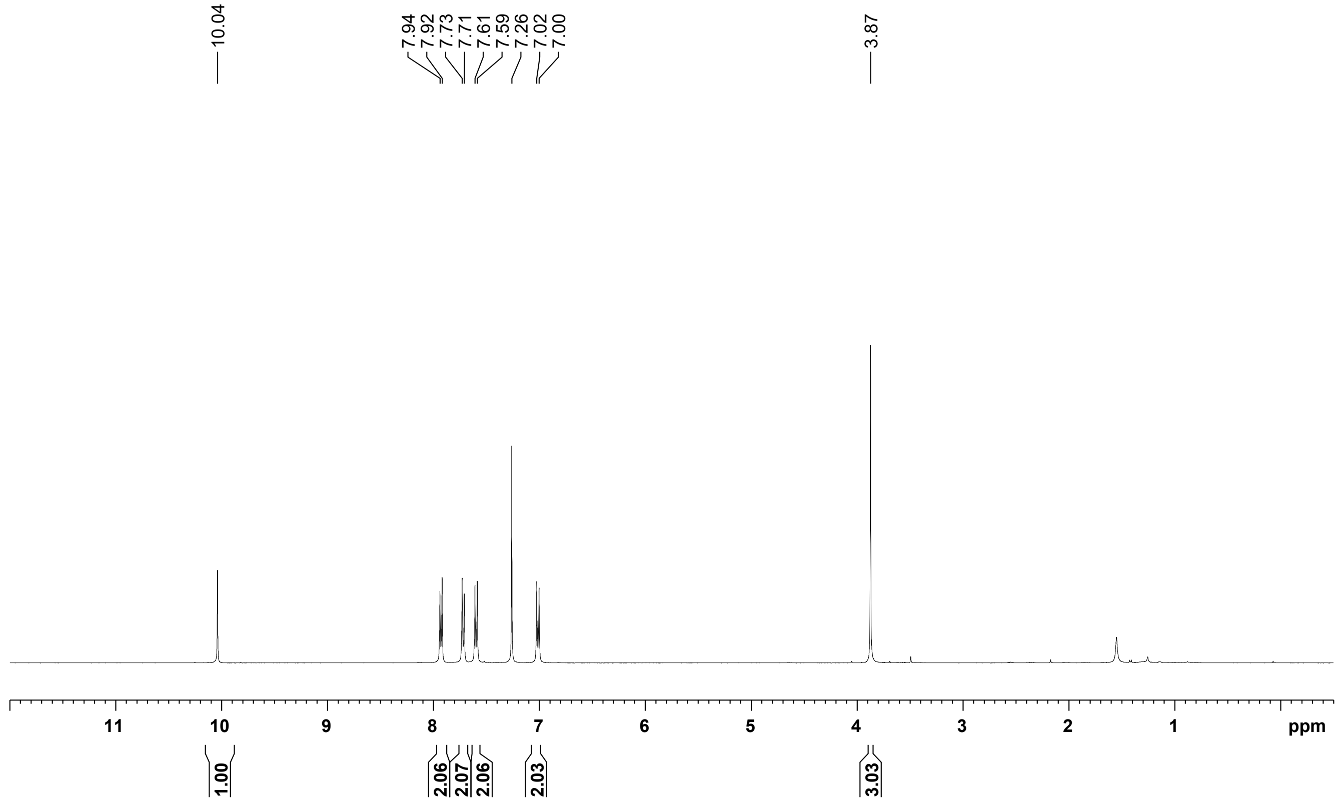


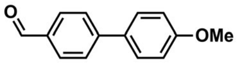
4-(trifluoromethyl)-1,1'-biphenyl (**3l**)



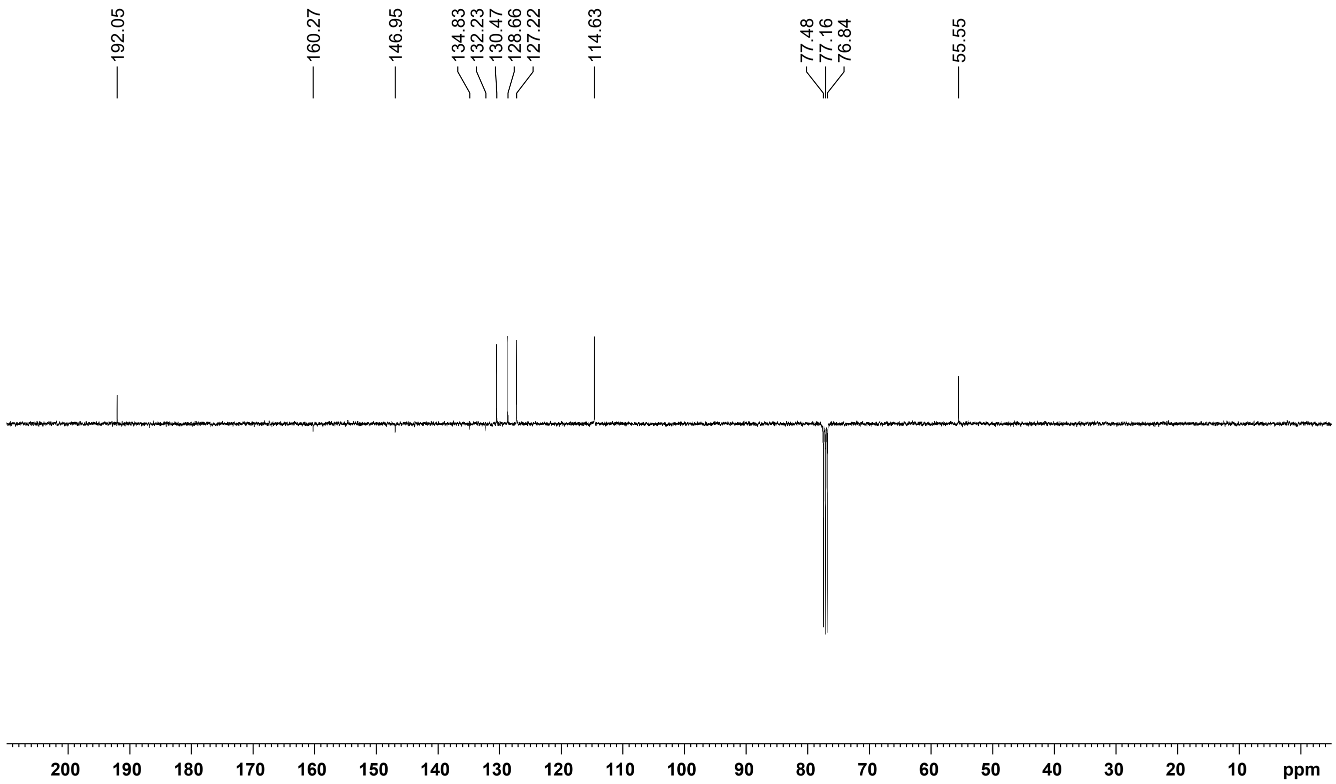


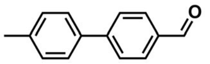
4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (**3m**)



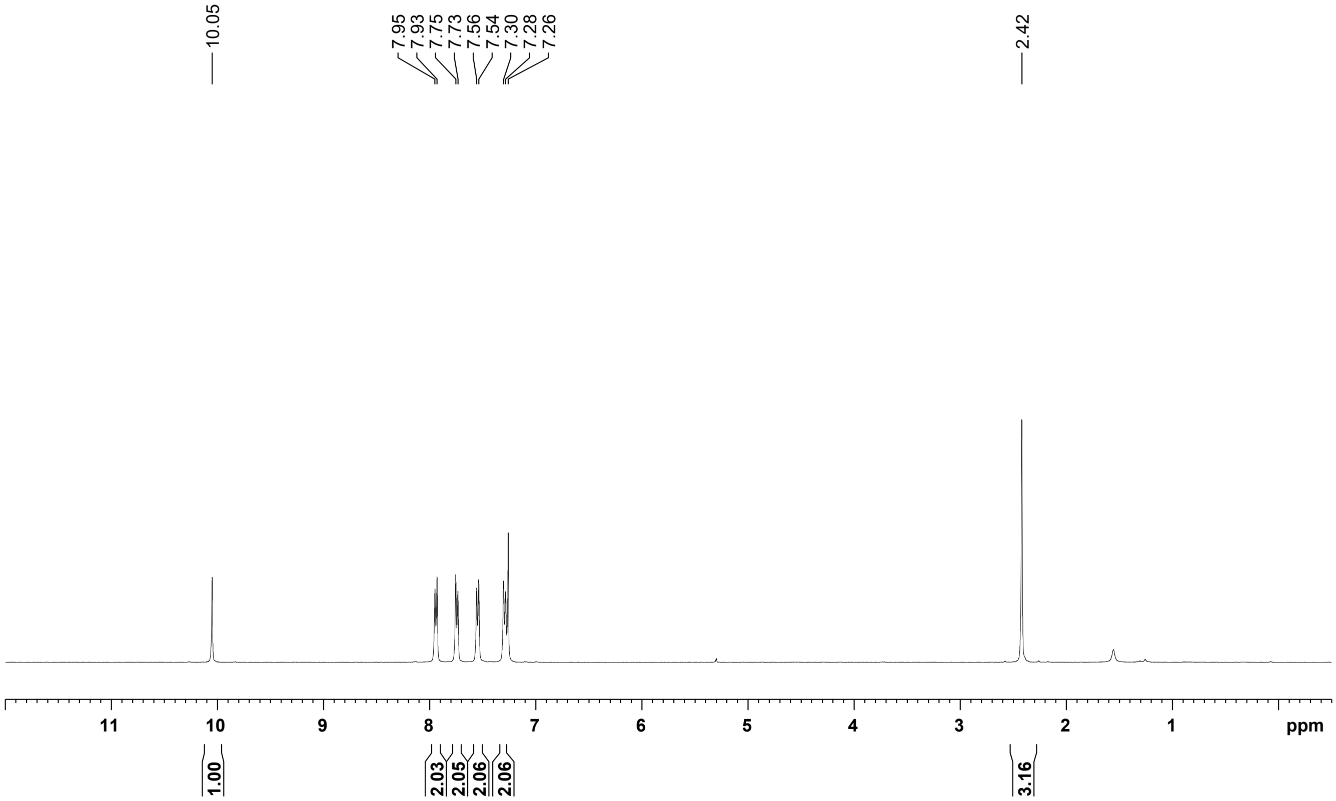


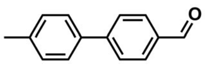
4'-methoxy-[1,1'-biphenyl]-4-carbaldehyde (**3m**)



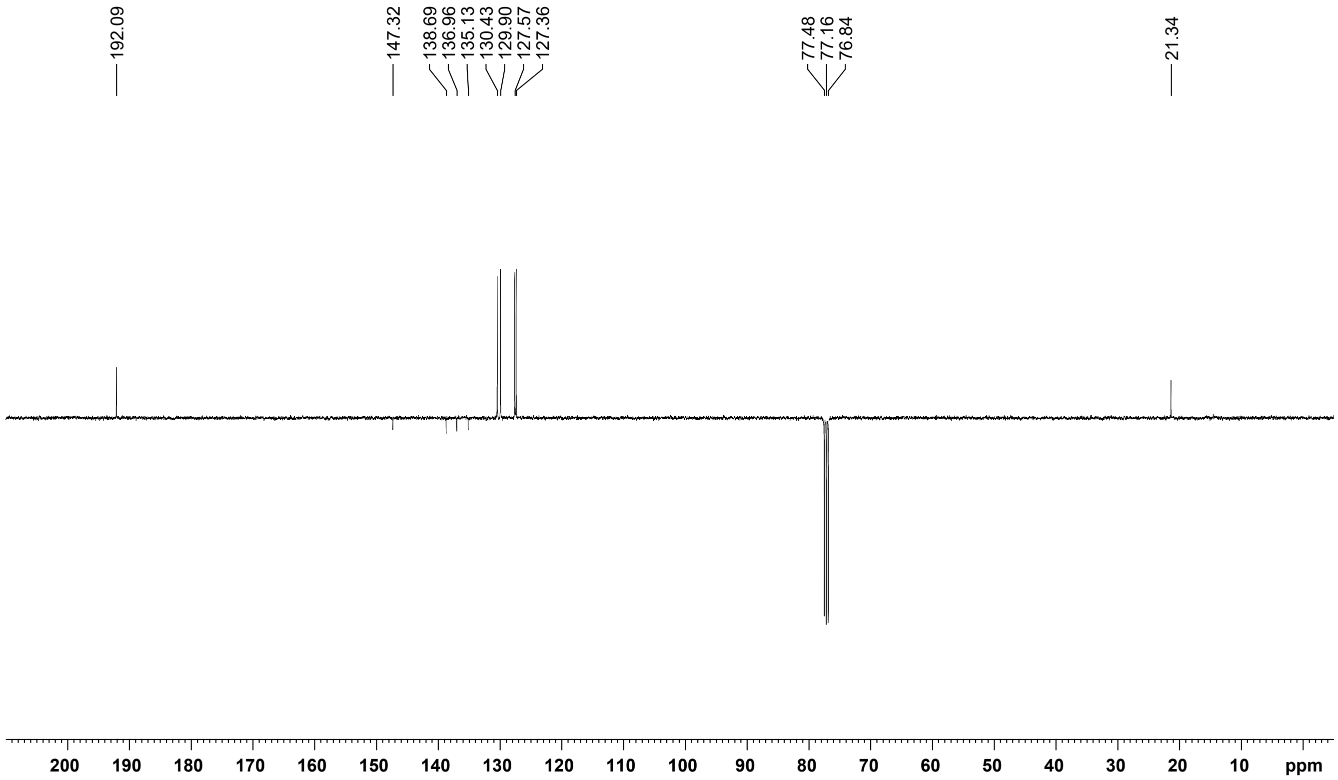


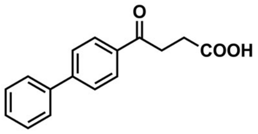
4'-methyl-[1,1'-biphenyl]-4-carbaldehyde (**3n**)



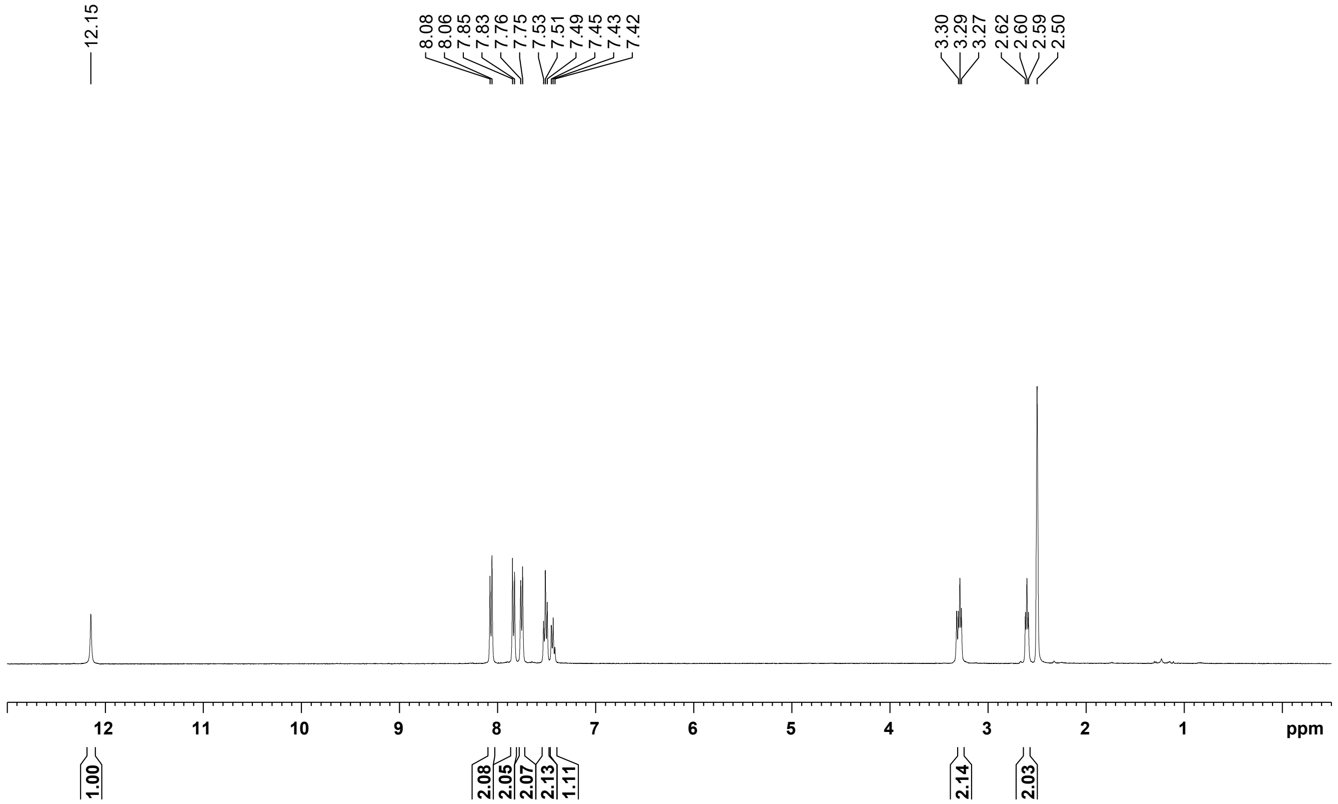


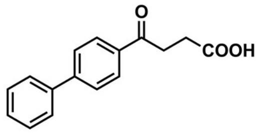
4'-methyl-[1,1'-biphenyl]-4-carbaldehyde (**3n**)





4-([1,1'-biphenyl]-4-yl)-4-oxobutanoic acid (**3o**)





4-([1,1'-biphenyl]-4-yl)-4-oxobutanoic acid (**3o**)