Supporting information for

Iron carbonyl cluster-incorporated Cu(I) NHC complexes in homocoupling of arylboronic acids: an effective $[TeFe_3(CO)_9]^{2-}$ ligand

Chien-Nan Lin,[a] Chung-Yi Huang,[a] Chia-Chi Yu,[a] Yen-Ming Chen,[a] Wei-Ming Ke,[a] Guan-Jung Wang,[a] Gon-Ann Lee*[b] and Minghuey Shieh*[a]

Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan, Republic of China

Department of Chemistry, Fu Jen Catholic University, Xinzhuang, New Taipei 24205, Taiwan, Republic of China

Contents

Experimental Section

All reactions were performed under an atmosphere of pure nitrogen using standard Schlenk techniques.[1] Solvents were purified, dried, and distilled under nitrogen prior to use. KO^{t}Bu, 3-nitrophenylboronic acid, 4-methoxylphenylboronic acid (all ACROS), 2-bromophenylboronic acid (AK Scientific), 3-bromophenylboronic acid (AK Scientific), 4-bromophenylboronic acid (Lancaster), and 4-nitrophenylboronic acid (Lancaster) were used as received. $[Et_4N]_2[TeFe_3(CO)_9]$,[2] $[Cu(MeCN)_4][BF_4]$,[3] $[TeFe_3(CO)_9Cu_2(MeCN)_2]$,[4] $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$,[5] and the imidazolium salts, 1,3-dimethylimidazolium iodide ($Me_2Im{\cdot}HI$),[6a] 1,1'-dimethyl-3,3'-methylene-diimidazolium diiodide ($MeImCH_2ImMe{\cdot}H_2I_2$),[6b] 1,1'-dimethyl-3,3'-ethylene-diimidazolium dibromide ($MeIm(CH_2)_2ImMe{\cdot}H_2Br_2$),[6a] and 1,1'-dimethyl-3,3'-propylene-diimidazolium diiodide ($MeIm(CH_2)_3ImMe{\cdot}H_2I_2$)[6c] were prepared according to the published methods. Chromatographic purification of compounds was achieved with Merck 60 silica gel (40─63 μm). Analytical thin layer chromatography (TLC) was performed on Silica Gel 60 F254 precoated plates. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 IR spectrometer. The NMR spectra were obtained on a Bruker AV 400 at 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C or on a Bruker AV 500 at 500.13 MHz for ^{1}H and 125.76 MHz for ^{13}C. ^{1}H and ^{13}C chemical shifts are reported in parts per million and were calibrated relative to DMSO-d_6 (^{1}H: 2.49 ppm, ^{13}C: 39.51 ppm) as the internal standard. Elemental analyses for

C, H, and N were performed on a Perkin-Elmer 2400 analyzer at the MOST Regional Instrumental Center at National Taiwan University, Taipei, Taiwan.

Synthesis of [$TeFe_3(CO)_9Cu_2(Me_2Im)_2$] (1). A THF solution (20 mL) of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] (0.30 g, 0.40 mmol), Me_2Im • HI (0.18 g, 0.80 mmol), and KO^{t}Bu (0.090 g, 0.80 mmol) was stirred at ambient temperature overnight. The resultant solution was filtered, and the solvent was evaporated under vacuum. The residue was washed with deionized water and hexanes several times and then extracted with CH_2Cl_2 to give a purplish-brown solution, which was recrystallized with hexanes/MeOH/CH_2Cl_2 to give [$TeFe_3(CO)_9Cu_2(Me_2Im)_2$] (**1**) (yield 0.19 g, 0.22 mmol, 55 % based on [$TeFe_3(CO)_9Cu_2(MeCN)_2$]). IR (ν_{CO}, CH_2Cl_2): 2031 (m), 1972 (vs), 1918 (w) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6, 300 K, ppm): δ 7.30 (s, 4H, NC*H*), 3.77 (s, 12H, NCH_3). ^{13}C NMR (125 MHz, DMSO-d_6, 300 K, ppm): δ 218.90 (Fe-*C*O), 178.20 ($C_{carbene}$), 122.00 (N*C*H), 37.18 (N*C*H_3). Anal. Calcd for $C_{19}H_{16}Cu_2Fe_3N_4O_9Te$: C, 26.33; H, 1.86; N, 6.47. Found: C, 26.10; H, 2.12; N,6.48. Mp: 166 ^{o}C dec. Crystals of [$TeFe_3(CO)_9Cu_2(Me_2Im)_2$] (**1**) suitable for X-ray diffraction were grown from hexanes/MeOH/CH_2Cl_2.

Synthesis of [$TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)$] (2). *Method 1.* A THF solution (20 mL) of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] (0.60 g, 0.79 mmol), $MeImCH_2ImMe{\cdot}H_2I_2$ (0.34 g, 0.79 mmol), and KO^{t}Bu (0.18 g, 1.60 mmol) was stirred at 40 ^{o}C overnight. The resultant reddish-brown solution was filtered, and the solvent was evaporated under vacuum. The

residue was extracted with Et_2O to give a purplish-brown solution and evaporated under vacuum again. The solid was washed with deionized water and hexanes several times and then extracted with CH_2Cl_2 to give a purplish-brown solution, which was recrystallized with hexanes/MeOH/CH_2Cl_2 to give [$TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)$] (**2**) (yield 0.14 g, 0.16 mmol, 20% based on [$TeFe_3(CO)_9Cu_2(MeCN)_2$]). IR (ν_{CO}, CH_2Cl_2): 2033 (m), 2023 (w), 1987 (vs), 1974 (s), 1934 (w), 1892 (m) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 300 K, ppm): δ 7.70 (s, 2H, NC*H*), 7.39 (s, 2H, NC*H*), 6.54 (br, 1H, NCH_2N), 6.40 (br, 1H, NCH_2N), 3.77 (s, 6H, NCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, 300 K, ppm): δ 218.27 (Fe-*C*O), 177.18 ($C_{carbene}$), 123.40, 120.99 (N*C*H), 62.10 (NCH_2N), 37.63 (NCH_3). Anal. Calcd for $C_{18}H_{12}Cu_2Fe_3N_4O_9Te$: C, 25.42; H, 1.42; N, 6.59. Found: C, 25.53; H, 1.65; N, 6.67. Mp: 166 ^oC dec. Crystals of [$TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)$] (**2**) suitable for X-ray diffraction were grown from hexanes/MeOH/CH_2Cl_2.

Method 2. Freshly dried THF (10 mL) was added to a mixture of $MeImCH_2ImMe{\cdot}H_2I_2$ (0.173 g, 0.40 mmol) and KO^{t}Bu (0.090 g, 0.80 mmol), and the mixture was stirred in an ice-water bath for 2 h. The resultant solution was filtered, and the pale yellow filtrate was then transferred to a THF solution (10 mL) of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] (0.30 g, 0.40 mmol), which was stirred for another 30 min. The resultant solution was filtered, and the solvent was removed under vacuum. The residue was washed with deionized water and hexanes several times and then extracted with CH_2Cl_2 to give a purplish-brown solution, which was

recrystallized with hexanes/MeOH/CH_2Cl_2 to give [$TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)$] (**2**) (yield 0.14 g, 0.16 mmol, 40% based on [$TeFe_3(CO)_9Cu_2(MeCN)_2$]).

Synthesis of [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)$] (3). *Method 1.* A THF solution (20 mL) of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] (0.33 g, 0.44 mmol), $MeIm(CH_2)_2ImMe{\cdot}H_2Br_2$ (0.16 g, 0.45 mmol), and KO^tBu (0.099 g, 0.88 mmol) was stirred at ambient temperature for 5 h. The resultant solution was filtered, and the solvent was evaporated under vacuum. The residue was extracted with Et_2O to give a purplish-brown solution and evaporated under vacuum again. The solid was washed with deionized water and hexanes several times and then extracted with CH_2Cl_2 to give a purplish-brown solution, which was recrystallized with hexanes/MeOH/CH_2Cl_2 to give [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)$] (**3**) (yield 0.079 g, 0.091 mmol, 21 % based on [$TeFe_3(CO)_9Cu_2(MeCN)_2$]). IR (ν_{CO}, CH_2Cl_2): 2032 (m), 1985 (vs), 1967 (m), 1955 (m) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, 300 K, ppm): δ 7.31 (s, 2H, NC*H*), 7.22 (s, 2H, NC*H*), 4.58 (s, 4H, NCH_2CH_2N), 3.74 (s, 6H, NCH_3). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K, ppm): δ 218.44 (Fe-*C*O), 176.60 ($C_{carbene}$), 122.34, 121.32 (N*C*H), 50.58 (NCH_2CH_2N), 37.48 (NCH_3). Anal. Calcd for $C_{19}H_{14}Cu_2Fe_3N_4O_9Te$: C, 26.40; H, 1.63; N, 6.48. Found: C, 26.62; H, 1.79; N, 6.81. Mp: 171 ^oC dec. Crystals of [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)$] (**3**) suitable for X-ray diffraction were grown from hexanes/MeOH/CH_2Cl_2.

Method 2. Freshly dried THF (15 mL) was added to a mixture of $MeIm(CH_2)_2ImMe{\cdot}H_2Br_2$

(0.19 g, 0.54 mmol) and KO^{t}Bu (0.12 g, 1.07 mmol), and the mixture was stirred in an ice-water bath for 3 h. The resultant solution was filtered, and the pale yellow filtrate was then transferred to a THF solution (10 mL) of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] (0.40 g, 0.53 mmol), which was stirred for another 1.5 h. The resultant solution was filtered, and the solvent was removed under vacuum. The residue was extracted with CH_2Cl_2 to give a purplish-brown solution and evaporated under vacuum again. The solid was washed with deionized water and hexanes several times and then extracted with THF to give a purplish-brown solution, which was recrystallized with hexanes/MeOH/THF to give [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)$] (**3**) (yield 0.23 g, 0.27 mmol, 51% based on [$TeFe_3(CO)_9Cu_2(MeCN)_2$].

Synthesis of [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)$] (4). *Method 1.* A THF solution (20 mL) of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] (0.35 g, 0.46 mmol), $MeIm(CH_2)_3ImMe{\cdot}H_2I_2$ (0.21 g, 0.46 mmol), and KO^{t}Bu (0.103 g, 0.92 mmol) was stirred at ambient temperature for 9 h. The resultant solution was filtered, and the solvent was evaporated under vacuum. The residue was washed with deionized water and hexanes several times and then extracted with CH_2Cl_2 to give a purplish-brown solution, which was recrystallized with hexanes/MeOH/CH_2Cl_2 to give [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)$] (**4**) (yield 0.043 g, 0.049 mmol, 11 % based on [$TeFe_3(CO)_9Cu_2(MeCN)_2$]). IR (ν_{CO}, CH_2Cl_2): 2032 (m), 1984 (vs), 1968 (m), 1956 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6, 300 K, ppm): δ 7.60 (br, 2H, NC*H*), 7.50 (br, 2H, NC*H*), 4.06 (s, 4H, NCH_2CH$_2$CH_2N), 3.41 (br, 6H, NCH_3), 2.43 (s, 2H, NCH$_2$CH_2CH$_2$N). ^{13}C NMR

(125 MHz, DMSO-d_6, 300 K, ppm): δ 218.94 (Fe-*C*O), 175.58 ($C_{carbene}$), 123.75, 120.71 (N*C*H), 46.13 (N*C*$H_2$$CH_2$*C*$H_2$N), 36.63 (N*C*$H_3$), 29.65 (N$CH_2$*C*$H_2$$CH_2$N). Anal. Calcd for $C_{20}H_{16}Cu_2Fe_3N_4O_9Te$: C, 27.34; H, 1.84; N, 6.38. Found: C, 27.68; H, 1.91; N, 6.38. Mp: 166 ^oC dec. Crystals of [$TeFe_3(CO)_9Cu_2$(MeIm$(CH_2)_3$ImMe)] (**4**) suitable for X-ray diffraction were grown from hexanes/MeOH/CH_2Cl_2.

Method 2. Freshly dried THF (10 mL) was added to a mixture of MeIm$(CH_2)_3$ImMe·H_2I_2 (0.184 g, 0.40 mmol) and KO^{t}Bu (0.090 g, 0.80 mmol), and the mixture was stirred in an ice-water bath for 2 h. The resultant solution was filtered, and the pale yellow filtrate was then transferred to a THF solution (10 mL) of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] (0.30 g, 0.40 mmol), which was stirred for another 30 min. The resultant solution was filtered, and the solvent was removed under vacuum. The residue was washed with deionized water and hexanes several times and then extracted with CH_2Cl_2 to give a purplish-brown solution, which was recrystallized with hexanes/MeOH/CH_2Cl_2 to give [$TeFe_3(CO)_9Cu_2$(MeIm$(CH_2)_3$ImMe)] (**4**) (yield 0.17 g, 0.19 mmol, 48% based on [$TeFe_3(CO)_9Cu_2(MeCN)_2$]).

The General Procedure for the Homocoupling of 2-, 3-, or 4-Bromophenylboronic Acids Leading to Biaryls. A solution of catalyst **1** (0.0050 mmol) and 2-, 3-, or 4-bromophenylboronic acids (1.00 mmol) in MeOH (3 mL) was stirred at 25 ^oC. The resultant reaction mixture was evaporated under vacuum. The residue was purified by flash chromatography on silica gel eluted with *n*-hexane to afford biaryls. To compare the

productivities of the catalysts, all the homocoupling reactions mentioned herein were carried out repeatedly and carefully to ensure accuracy.

The General Procedure for the Homocoupling of 3-Nitro- or 4-Methoxyphenylboronic Acids Leading to Biaryls. A solution of catalyst **1** (0.0050 mmol) and 3-nitro- or 4-methoxyphenylboronic acids (1.00 mmol) in MeOH (3 mL) was stirred at 25 ^{o}C. The resultant reaction mixture was evaporated under vacuum. The residue was purified by flash chromatography on a silica gel column (petroleum ether/ethyl acetate, 5: 1) to afford biaryls. To compare the productivities of the catalysts, all the homocoupling reactions mentioned herein were carried out repeatedly and carefully to ensure accuracy.

The General Procedure for the Homocoupling of 4-Nitrophenylboronic Acids Leading to Biaryls. A solution of catalyst **1** (0.0050 mmol) and 4-nitrophenylboronic acid (1.00 mmol) in MeOH (3 mL) was stirred at 25 ^{o}C. The resultant reaction mixture was evaporated under vacuum. The residue was purified by flash chromatography on a silica gel column (petroleum ether/ethyl acetate, 5: 1) to afford 4,4'-dinitrobiphenyl (0.39 mmol, 78 %) and 4-nitrophenol (0.21 mmol, 21 %). To compare the productivities of the catalysts, the homocoupling reaction mentioned herein was carried out repeatedly and carefully to ensure accuracy.

Optimization of [$TeFe_3(CO)_9Cu_2(MeCN)_2$]- and 1−4-Catalyzed Homocoupling of 4-Bromophenylboronic Acid under Different Reaction Conditions. In order to explore the behavior of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] and **1**−**4** in catalyzing Suzuki homocoupling reactions, complex **1** was chosen as the model catalyst and 4-bromophenylboronic acid was chosen as the model substrate to optimize catalytic conditions (Table S1). We found that complex **1** (2.0 mol% of Cu loading) exhibited good catalytic performances in the homocoupling of 4-bromophenylboronic acid in MeOH at room temperature in air, without any additives such as a base or a ligand, affording the 4,4'-dibromobiphenyl product in an 84% yield (Table S1, Entry 1), which indicated that a catalytic cycle was operating under the current conditions. In the absence of catalyst **1** or under N_2, this homocoupling reaction did not occur (Entries 2-4). Moreover, when 3 mol% of Fe loading of catalyst $[Et_4N]_2[TeFe_3(CO)_9]$ was used, no biaryl products were observed, indicating that Cu was essential for the catalytic performance (Entry 5). We next examined the effect of the polar protic or aprotic solvents (Entries 6-9); however, the protic methanol was still the best choice (Entry 1). The reaction temperature had great influence on this reaction. When the temperature was increased to the refluxing MeOH temperature, the product was formed in a lower yield (27%) (Entry 10), indicating the thermal instability of catalyst **1**. Notably, when O_2 was introduced into the system, the time required for the completion of the reaction reduced to 1 h and the yield maintained at a good yield (85 %) (Entry 11), suggesting that sufficient O_2 was necessary. On the other hand, the

influence of the amount of complex **1** on the reaction was also examined. The results showed that a Cu loading (1.0 mol%) of catalyst **1** gave the best reaction condition with 88% yield (Entry 12), however, the lower Cu loading (0.5 mol%) required the longer reaction time (12 h) for completion of the reaction (Entry 13). Other catalysts like **2—4** and $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ were also used to catalyze the homocoupling of 4-bromophenylboronic acid under conditions that included 1.0 mol% of Cu loading, methanol as the solvent, room temperature, an atmosphere of O_2, and without any additives such as bases, ligands, or other oxidants (Entries 14-17).

Electrochemical Measurements. The electrochemical measurements were performed at room temperature under a nitrogen atmosphere and recorded using a CHI 621D electrochemical potentiostat. A glassy carbon working electrode, a platinum wire auxiliary electrode, and a non-aqueous Ag/Ag^+ electrode were used in a three-electrode configuration. Tetra-*n*-butylammonium perchlorate (TBAP) was used as the supporting electrolyte, and the solute concentration was ~10^{-3} M. The redox potentials were calibrated with a ferrocenium/ferrocene (Fc^+/Fc) couple in the working solution and were referenced to SCE.

To explore the effect of the incorporation of the mono- or bidentate NHC ligands into the $TeFe_3(CO)_9Cu_2$ cluster core, the electrochemical behaviors of $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1**−**4** were investigated by differential pulse voltammetry (DPV). For comparison, the DPVs of $[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$ and $[Cu(MeCN)_4][BF_4]$ were performed as well.

Because of the irreversible desorption of Cu (−0.198 to −0.489 V),[7] the DPV profiles were only disscussed between 1.004 and −0.20 V. The DPV data are summarized in Table S4.

For the DPV analysis, the measurement of the peak width at the half height ($W_{1/2}$) determined the electron stoichiometry.[8a] [$TeFe_3(CO)_9Cu_2(MeCN)_2$] and **1**−**4** exhibited similar redox behaviors and each showed two one-electron quasi-reversible oxidations (0.015 ~ 0.134 V and 0.232 ~ 0.286 V) and a one-electron quasi-reversible reduction (−0.085 ~ −0.143 V) (Table S4). The widths of the DPV peaks at the half-height ($W_{1/2}$) of these complexes were a bit greater or lower than the value ($W_{1/2}$ = 90 mV) expected for the one-electeron reversible redox couples, indicating that these DPV responses were quasi-reversible.[8]

X-ray Structural Characterization of 1—4. Selected crystallographical data for **1—4** are given in Table S5. All crystals were mounted on glass fibers with epoxy cement. Data collections for **1**, **2**, and **4** were carried out on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation at 200(2) K in the 2θ range of 2.0—50.0°. Data collection for **3** were carried out on a Bruker-Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation at 200(2) K employing the θ—2θ scan mode. An empirical absorption correction by the multi-scan method was applied to the data using SADABS.[9] The structures of **1—4** were solved by direct methods and refined with SHELXL-97.[10] Each of **3** and **4** contained two independent but chemically similar asymmetric structures in the unit cell where their bond distances and angles were similar and

only one structure was described for further comparison. For complex **4**, in order to obtain reasonable thermal parameters, the N7 and C36 atoms were restrained by using SIMU and DELU commands and the C34 and C35 atoms were restrained by using DELU command during the least-squares refinement. The non-hydrogen atoms for all structures were refined with anisotropic temperature factors. The selected distances and angles for **1**─**4** are listed in Table S6. These Cu─C distances are within the van der Waals interaction (2.245(5)─2.863(6) Å, **1**; 2.268(5)─2.803(5) Å, **2**; 2.307(6)─2.597(6) Å, **3**; 2.296(4)─2.787(5) Å, **4**), and the corresponding Fe─C─O angles are slightly bent from 180° (166.3(5)─174.2(6)^{o}, **1**; 160.2(5)─179.3(4)^{o}, **2**; 167.3(5)─174.8(6)^{o}, **3**; 166.0(4)─173.3(4)^{o}, **4**) (Fig. 1 and S2─S4).

Explanation for the Checkcif Alert for 4:

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Explanation: The crystal selected for data collection was of poor quality which resulted in very weak diffraction intensity at high theta angles.

Computational Details. All calculations reported in the present study were performed via density functional theory (DFT) using the Gaussian 03 series of packages.[11] Attempts at optimization of clusters [$TeFe_3(CO)_9Cu_2(MeCN)_2$] and **1** led to the elongation of the Cu─Fe and Cu─Cu bonds, respectively, by more than 0.2 Å. Thus, to precisely calculate the natural charges[12] and Wiberg bond indices,[13] the single-point calculations of [$TeFe_3(CO)_9Cu_2(MeCN)_2$] and **1**−**4** with a PBE1PBE (PBE0)[14] hybrid functional and the large basis set Def2-TZVP[15] were carried out by using the Weinhold NBO method[16] based on their single-crystal diffraction data. Graphical representations of the molecular orbitals were obtained using GaussView 5.0 software. For orbital contributions, the molecular orbital compositions were analyzed using the AOMix program.[17]

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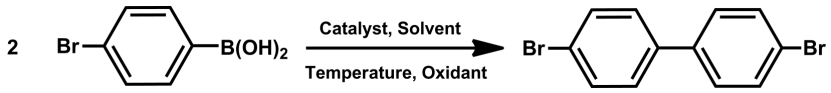
Table S1 $[TeFe_3(CO)_9Cu_2(MeCN)_2]$- and **1**−**4**-catalyzed homocoupling of 4-bromophenylboronic acid: the optimization of the reaction conditions.[a]



Entry	Catalyst	Solvent	Cu (mol%)	Temp. (^oC)	Time (h)	Oxidant	Yield (%)[b,c]
1	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	MeOH	2.0	25	2	Air	84
2	–	MeOH	0	25	20	Air	0
3	–	MeOH	0	25	20	O_2[e]	0
4	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	MeOH	2.0	25	8	—[f]	0
5	$[Et_4N]_2[TeFe_3(CO)_9]$	MeOH	0[d]	25	12	O_2[e]	0
6	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	EtOH	2.0	25	24	Air	26
7	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	*i*PrOH	2.0	25	24	Air	Trace[g]
8	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	THF	2.0	25	24	Air	Trace[g]
9	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	DMF	2.0	25	24	Air	60
10	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	MeOH	2.0	64	8	Air	27
11	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	MeOH	2.0	25	1	O_2[e]	85
12	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	MeOH	1.0	25	2	O_2[e]	88
13	$[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**)	MeOH	0.5	25	12	O_2[e]	82
14	$[TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)]$ (**2**)	MeOH	1.0	25	2	O_2[e]	87
15	$[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)]$ (**3**)	MeOH	1.0	25	2	O_2[e]	88
16	$[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)]$ (**4**)	MeOH	1.0	25	2	O_2[e]	88
17	$[TeFe_3(CO)_9Cu_2(MeCN)_2]$	MeOH	1.0	25	3	O_2[e]	85
18	$[TeFe_3(CO)_9Cu_2(MeCN)_2]$	MeOH	0.5	25	17	O_2[e]	78

[a] Reaction conditions: 4-bromophenylboronic acid (1.0 mmol), solvent (3.0 mL). [b] Isolated yield as an average of three runs. [c] All reactions were monitored by TLC. [d] 3.0 mol% of Fe loading. [e] O_2 (1 atm, balloon). [f] N_2 atmosphere. [g] Detected by ^1H NMR.

Table S2 The reported catalytic systems for homocoupling of 4-bromophenylboronic acid, in which higher temperature (Entries 1-8), additional base (Entries 1, 3, 5, 6, and 8-10), external additives (Entries 7-10), longer reaction time (Entries 5-14), and higher loading of the catalyst (Entries 2 and 8-14) are required compared to our system.

Entry	Catalyst	Additive	Base	Solvent	Oxidant	Temp. (^{o}C)	Time (h)	Yield (%)	Reference
1	Nano-FGT[a]	—	0.1 N NaOH	H_2O	—	120-130 (Microwave irradiation)	0.75-1	> 99	18
2	$Cu(OAc)_2$ (50.0 mol%)	—	—	DMF	O_2	100	1	93	19
3	Nano-ferrite glutathione	—	0.1 M NaOH	H_2O	—	120-130 (Microwave irradiation)	0.75	> 99	20
4	CuNP-rGO (25 mg mL^{-1})	—	—	DMF	—	Microwave irradiation (360 W)	0.25	92	21
5	Au-(MCM-41)	—	K_2CO_3 (2 eq.)	Xylene	—	130	24	95	22
6	Au(I) PS-*co*-PMAA	—	Cs_2CO_3	1-methyl-pyrrolidin-2-one /H_2O	—	110	43	99	23
7	Pd_{np}/Te-Dps (0.05 mol%)	1 M Tris-HCl Buffer at PH 8.9	—	H_2O	Air	100	24	78	24
8	$Pd(OAc)_2$ (5.0 mol%)	PPh_3	K_2CO_3 (2 eq.)	DMF	Air	90	4	12	25
9	$PdCl_2$ (3.0 mol%)	*p*-Toluenesulfonyl chloride	Na_2CO_3 (2 eq.)	EtOH/H_2O	—[b]	r.t.	12	96	26
10	$PdCl_2$ (3.0 mol%)	*p*-Toluenesulfonyl chloride	Na_2CO_3 (2 eq.)	EtOH/H_2O	Air	—	12	93	27
11	Cu(BDC) MOF (19.4 mol%)	—	—	DMF	Air	r.t.	16	93	28
12	$[\{(phen)Cu(\mu\text{-}OH)\}_2Cl_2]$ • $3H_2O$ (2.0 mol%)	—	—	IPA	Air	28	12	92	29
13	$[Pd(Phbz)(OAc)(PPh_3)]$ (5.0 mol%)	—	—	THF	Air	20	24	82	30
14	CuCl (2.0 mol%)	—	—	MeOH	Air	25	4	74	31

[a] Glutathione-functionalized nano-Fe_3O_4. [b] Under N_2.

Table S3 Results of natural bond order of $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1**−**4** at the level of PBE0/Def2-TZVP.

Complex	Wiberg bond index					
	Te─Fe	Fe─Fe	Cu─Fe	Cu─X[a]	Cu─Cu	Te─Cu
$[TeFe_3(CO)_9Cu_2(MeCN)_2]$	0.616	0.160	0.079	0.200	0.028	
1	0.625	0.157	0.065	0.363	0.035	0.174
2	0.628	0.161	0.078	0.336	0.030	
3	0.626	0.158	0.066	0.366	0.034	0.208
4	0.626	0.159	0.068	0.354	0.029	0.182

[a] X = N or C atom.

Table S4 Differential pulse voltammetry of $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1**−**4**.

Complex	Oxidation process		Reduction process	
	E_p^{red}/V[a] ($W_{1/2}$/mV[c])	E_p^{ox}/V[b] ($W_{1/2}$/mV[c])	E_p^{red}/V[a] ($W_{1/2}$/mV[c])	E_p^{ox}/V[b] ($W_{1/2}$/mV[c])
$[TeFe_3(CO)_9Cu_2(MeCN)_2]$	0.054 (109)	—[d] (br)	−0.124 (105)	—[d] (br)
	0.232 (118)	0.220 (95)	−0.464 (84)	−0.198 (98)[e]
1	0.015 (113)	—[d] (br)	−0.085 (113)	—[d] (br)
	0.277 (117)	0.263 (111)	−0.449 (97)	−0.337 (134)[e]
2	0.134 (108)	—[d] (br)	−0.130 (105)	−0.174 (83)
	0.286 (101)	0.274 (119)	−0.430 (111)	−0.398 (72)[e]
3	0.097 (111)	0.083 (89)	−0.143 (99)	−0.193 (120)
	0.265 (82)	0.255 (82)	−0.475 (115)	−0.489 (170)[e]
4	0.060 (101)	—[d] (br)	−0.140 (103)	−0.148 (96)
	0.242 (97)	0.232 (85)	−0.496 (104)	−0.380 (124)[e]
$[Cu_2(MeIm(CH_2)_2ImMe)_2][PF_6]_2$	0.399 (125)	0.363 (br)	−0.529 (50)	
	0.517 (128)	—[d] (br)		−0.317 (166)[e]
$[Cu(MeCN)_4][BF_4]$	1.004 (119)	1.016 (132)	−0.600 (48)	
				−0.280 (106)[e]

[a] E_p^{red} = reductive peak potential. [b] E_p^{ox} = oxidative peak potential. [c] $W_{1/2}$ = width at half-height. [d] Difficult to determine due to the Cu desorption. [e] The Cu desorption peak.

Table S5 Crystallographic data for $[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**), $[TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)]$ (**2**), $[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)]$ (**3**), and $[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)]$ (**4**).

	1	**2**	**3**	**4**
Empirical formula	$C_{19}H_{16}Cu_2Fe_3N_4O_9Te$	$C_{18}H_{12}Cu_2Fe_3N_4O_9Te$	$C_{19}H_{14}Cu_2Fe_3N_4O_9Te$	$C_{20}H_{16}Cu_2Fe_3N_4O_9Te$
Fw	866.59	850.55	864.57	878.60
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic
Space group	*C2/c*	*Pnma*	$P\bar{1}$	$P\bar{1}$
Crystal dimens, mm	0.44 x 0.32 x 0.20	0.38 x 0.21 x 0.10	0.27 x 0.17 x 0.03	0.38 x 0.24 x 0.12
a, Å	32.1115(6)	16.6462(5)	9.9886(1)	10.1041(4)
b, Å	8.6471(2)	16.1627(5)	13.5547(2)	13.6572(5)
c, Å	21.3640(5)	9.3673(3)	20.5089(3)	20.2351(8)
α, deg			75.7093(7)	76.356(2)
β, deg	116.247(1)		81.2285(6)	82.953(2)
γ, deg			77.5563(7)	79.062(2)
V, $Å^3$	5320.5(2)	2520.3(1)	2613.10(6)	2655.3(2)
Z	8	4	4	4
D (calcd), g cm^{-3}	2.164	2.242	2.198	2.198
μ, mm^{-1}	4.299	4.535	4.376	4.308
Color, habit	black, prism	black, prism	black, prism	black, prism
Diffractometer	Apex II CCD	Apex II CCD	Nonius (Kappa CCD)	Apex II CCD
Radiation (λ), Å	0.71073	0.71073	0.71073	0.71073
Temperature, K	200(2)	200(2)	200(2)	200(2)
θ range for data collection, deg	1.96－25.02	2.45－25.02	2.06－25.02	1.56－25.07
T_{min}/T_{max}	0.25/0.48	0.28/0.66	0.42/0.64	0.29/0.63
No. of indep. reflns ($I > 2\sigma(I)$)	4123 (R_{int} = 0.027)	1998 (R_{int} = 0.026)	7628 (R_{int} = 0.054)	7888 (R_{int} = 0.024)
No. of parameters	337	175	685	703
Goodness of fit	1.192	1.333	1.094	1.042
$R_1{}^a/wR_2{}^a$ ($I > 2\sigma(I)$)	0.032/0.096	0.020/0.066	0.035/0.098	0.030/0.074
$R_1{}^a/wR_2{}^a$ (all data)	0.042/0.117	0.034/0.101	0.051/0.116	0.036/0.077

[a] The functions minimized during least-squares cycles were $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S6 Selected bond distances (Å) and bond angles (deg) for [$TeFe_3(CO)_9Cu_2(Me_2Im)_2$] (**1**), [$TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)$] (**2**), [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)$] (**3**), and [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)$] (**4**).

		1	
Te(1)─Fe(1)	2.5073(8)	Fe(2)─Cu(1)	2.5418(8)
Te(1)─Fe(2)	2.5118(8)	Fe(2)─Cu(2)	2.6348(9)
Te(1)─Fe(3)	2.4984(8)	Fe(1)─Fe(2)	2.7492(9)
Te(1)─Cu(2)	2.7818(7)	Fe(1)─Fe(3)	2.6409(9)
Cu(1)─Cu(2)	2.5949(9)	Fe(2)─Fe(3)	2.6498(9)
Fe(1)─Cu(1)	2.5434(8)	Cu(2)─C(15)	1.936(5)
Fe(1)─Cu(2)	2.5004(9)	Cu(1)─C(10)	1.929(5)
Te(1)─Fe(1)─Fe(2)	56.87(2)	Fe(1)─Fe(2)─Fe(3)	58.54(2)
Te(1)─Fe(1)─Fe(3)	57.99(2)	Fe(1)─Fe(3)─Fe(2)	62.61(2)
Te(1)─Fe(2)─Fe(1)	56.71(2)	Fe(2)─Fe(1)─Fe(3)	58.85(2)
Te(1)─Fe(2)─Fe(3)	57.82(2)	Fe(1)─Cu(1)─Cu(2)	58.23(2)
Te(1)─Cu(2)─Cu(1)	100.67(2)	Fe(1)─Cu(2)─Cu(1)	59.86(2)
Te(1)─Fe(3)─Fe(1)	58.32(2)	Fe(2)─Cu(1)─Cu(2)	61.71(2)
Te(1)─Fe(3)─Fe(2)	58.32(2)	Fe(2)─Cu(2)─Cu(1)	58.15(2)
Te(1)─Fe(1)─Cu(1)	110.13(3)	Fe(1)─Cu(1)─Fe(2)	65.45(3)
Te(1)─Fe(2)─Cu(1)	110.04(3)	Fe(1)─Cu(2)─Fe(2)	64.68(3)
Te(1)─Fe(1)─Cu(2)	67.49(2)	Cu(1)─Fe(1)─Cu(2)	61.92(3)
Te(1)─Fe(2)─Cu(2)	65.39(2)	Cu(1)─Fe(2)─Cu(2)	60.14(2)
Te(1)─Cu(2)─Fe(1)	56.37(2)	Fe(3)─Fe(1)─Cu(1)	103.17(3)
Te(1)─Cu(2)─Fe(2)	55.18(2)	Fe(2)─Fe(1)─Cu(1)	57.25(2)
Fe(2)─Cu(1)─Cu(2)	58.15(2)	Fe(3)─Fe(2)─Cu(1)	102.96(3)
Fe(1)─Te(1)─Cu(2)	56.14(2)	Fe(3)─Fe(2)─Cu(2)	108.47(3)
Fe(2)─Te(1)─Cu(2)	59.44(2)	Fe(1)─Fe(2)─Cu(2)	55.30(2)
Fe(3)─Te(1)─Cu(2)	108.48(2)	Fe(1)─Fe(2)─Cu(1)	57.30(2)
Fe(1)─Te(1)─Fe(2)	66.43(2)	Fe(2)─Fe(1)─Cu(2)	60.03(3)
Fe(1)─Te(1)─Fe(3)	63.69(2)	Fe(3)─Fe(1)─Cu(2)	113.00(3)
Fe(2)─Te(1)─Fe(3)	63.86(2)		
		2	
Te(1)─Fe(1)	2.4651(6)	Te(1)─Fe(2)	2.4762(7)
Fe(1)─Cu(1)	2.4660(7)	Fe(2)─Cu(1)	2.5292(8)
Fe(1)─Fe(1a)	2.668(1)	Cu(1)─Cu(1a)	2.548(1)
Fe(1)─Fe(2)	2.7391(8)	Cu(1)─C(9)	1.939(4)

Te(1)─Fe(1)─Cu(1)	114.31(2)	Cu(1a)─Fe(2)─Fe(1)	85.77(3)
Te(1)─Fe(1)─Fe(1a)	57.24(1)	Te(1)─Fe(2)─Fe(1a)	56.14(2)
Cu(1)─Fe(1)─Fe(1a)	88.62(2)	Cu(1)─Fe(2)─Fe(1a)	85.77(3)
Te(1)─Fe(1)─Fe(2)	56.53(2)	Cu(1a)─Fe(2)─Fe(1a)	55.65(2)
Cu(1)─Fe(1)─Fe(2)	57.86(2)	Fe(1)─Fe(2)─Fe(1a)	58.28(3)
Fe(1a)─Fe(1)─Fe(2)	60.86(1)	Fe(1)─Cu(1)─Fe(2)	66.49(2)
Te(1)─Fe(2)─Cu(1)	111.71(3)	Fe(1)─Cu(1)─Cu(1a)	91.39(2)
Te(1)─Fe(2)─Cu(1a)	111.71(3)	Fe(2)─Cu(1)─Cu(1a)	59.75(1)
Cu(1)─Fe(2)─Cu(1a)	60.50(3)	Fe(1)─Te(1)─Fe(1a)	65.51(3)
Te(1)─Fe(2)─Fe(1)	56.14(2)	Fe(1)─Te(1)─Fe(2)	67.33(2)
Cu(1)─Fe(2)─Fe(1)	55.65(2)	Fe(1a)─Te(1)─Fe(2)	67.33(2)

3

Te(1)─Fe(1)	2.4853(9)	Fe(3)─Cu(2)	2.521(1)
Te(1)─Fe(3)	2.5124(8)	Fe(2)─Cu(2)	2.588(1)
Te(1)─Fe(2)	2.5263(8)	Fe(1)─Fe(2)	2.644(1)
Te(1)─Cu(1)	2.6755(8)	Fe(1)─Fe(3)	2.660(1)
Fe(3)─Cu(1)	2.537(1)	Fe(2)─Fe(3)	2.751(1)
Fe(2)─Cu(1)	2.571(1)	Cu(1)─C(19)	1.928(5)
Cu(1)─Cu(2)	2.620(1)	Cu(2)─C(28)	1.939(6)
Fe(1)─Te(1)─Fe(3)	64.31(3)	Te(1)─Fe(1)─Fe(3)	58.34(2)
Fe(1)─Te(1)─Fe(2)	63.67(3)	Fe(2)─Fe(1)─Fe(3)	62.49(3)
Fe(3)─Te(1)─Fe(2)	66.19(3)	Te(1)─Fe(2)─Cu(1)	63.31(2)
Fe(1)─Te(1)─Cu(1)	110.25(3)	Te(1)─Fe(2)─Cu(2)	108.19(3)
Fe(3)─Te(1)─Cu(1)	58.45(2)	Cu(1)─Fe(2)─Cu(2)	61.03(3)
Fe(2)─Te(1)─Cu(1)	59.16(2)	Te(1)─Fe(2)─Fe(1)	57.41(3)
Fe(3)─Cu(1)─Fe(2)	65.18(3)	Cu(1)─Fe(2)─Fe(1)	108.61(3)
Fe(3)─Cu(1)─Cu(2)	58.50(3)	Cu(2)─Fe(2)─Fe(1)	104.21(4)
Fe(2)─Cu(1)─Cu(2)	59.81(3)	Te(1)─Fe(2)─Fe(3)	56.67(2)
Fe(3)─Cu(1)─Te(1)	57.56(2)	Cu(1)─Fe(2)─Fe(3)	56.81(3)
Fe(2)─Cu(1)─Te(1)	57.53(2)	Cu(2)─Fe(2)─Fe(3)	56.24(3)
Cu(2)─Cu(1)─Te(1)	102.95(3)	Fe(1)─Fe(2)─Fe(3)	59.04(3)
Fe(3)─Cu(2)─Fe(2)	65.15(3)	Te(1)─Fe(3)─Cu(2)	110.79(3)
Fe(3)─Cu(2)─Cu(1)	59.10(3)	Te(1)─Fe(3)─Cu(1)	63.99(3)
Fe(2)─Cu(2)─Cu(1)	59.16(3)	Fe(1)─Fe(3)─Fe(2)	58.46(3)
Te(1)─Fe(1)─Fe(2)	58.92(2)	Te(1)─Fe(3)─Fe(1)	57.35(3)
Te(1)─Fe(3)─Fe(2)	57.15(2)	Cu(1)─Fe(3)─Fe(1)	109.15(4)
Cu(1)─Fe(3)─Fe(2)	58.01(3)	Cu(2)─Fe(3)─Fe(2)	58.61(3)

Cu(2)─Fe(3)─Fe(1)	105.65(4)		
	4		
Te(1)─Fe(1)	2.5151(6)	Fe(3)─Cu(2)	2.5325(8)
Te(1)─Fe(2)	2.4874(6)	Cu(1)─Cu(2)	2.5817(7)
Te(1)─Fe(3)	2.4999(6)	Fe(1)─Fe(2)	2.6350(7)
Te(1)─Cu(1)	2.7929(5)	Fe(1)─Fe(3)	2.7865(8)
Fe(1)─Cu(1)	2.5165(7)	Fe(2)─Fe(3)	2.6451(8)
Fe(1)─Cu(2)	2.5797(8)	Cu(1)─C(19)	1.925(4)
Fe(3)─Cu(1)	2.5550(7)	Cu(2)─C(29)	1.944(4)
Te(1)─Fe(1)─Cu(1)	67.43(2)	Te(1)─Fe(3)─Fe(1)	56.51(2)
Te(1)─Fe(1)─Cu(2)	109.02(2)	Cu(2)─Fe(3)─Fe(1)	57.79(2)
Cu(1)─Fe(1)─Cu(2)	60.86(2)	Cu(1)─Fe(3)─Fe(1)	56.01 (2)
Te(1)─Fe(1)─Fe(2)	57.70(2)	Fe(2)─Fe(3)─Fe(1)	57.97(2)
Cu(1)─Fe(1)─Fe(2)	110.90(3)	Fe(1)─Cu(1)─Fe(3)	66.65(2)
Cu(2)─Fe(1)─Fe(2)	100.48(3)	Fe(1)─Cu(1)─Cu(2)	60.78(2)
Te(1)─Fe(1)─Fe(3)	55.99(2)	Fe(3)─Cu(1)─Cu(2)	59.08(2)
Cu(1)─Fe(1)─Fe(3)	57.34(2)	Fe(1)─Cu(1)─Te(1)	56.26 (2)
Cu(2)─Fe(1)─Fe(3)	56.16(2)	Fe(3)─Cu(1)─Te(1)	55.52(2)
Fe(2)─Fe(1)─Fe(3)	58.33(2)	Cu(2)─Cu(1)─Te(1)	100.97(2)
Te(1)─Fe(2)─Fe(1)	58.73(2)	Fe(3)─Cu(2)─Fe(1)	66.05(2)
Te(1)─Fe(2)─Fe(3)	58.20(2)	Fe(3)─Cu(2)─Cu(1)	59.94(2)
Fe(1)─Fe(2)─Fe(3)	63.71(2)	Fe(1)─Cu(2)─Cu(1)	58.36(2)
Te(1)─Fe(3)─Cu(2)	111.04(2)	Fe(2)─Te(1)─Fe(3)	64.06(2)
Te(1)─Fe(3)─Cu(1)	67.07(2)	Fe(2)─Te(1)─Fe(1)	63.57(2)
Cu(2)─Fe(3)─Cu(1)	60.99(2)	Fe(3)─Te(1)─Fe(1)	67.51(2)
Te(1)─Fe(3)─Fe(2)	57.74 (2)	Fe(2)─Te(1)─Cu(1)	106.82(2)
Cu(2)─Fe(3)─Fe(2)	101.45(3)	Fe(3)─Te(1)─Cu(1)	57.41(2)
Cu(1)─Fe(3)─Fe(2)	109.37(3)	Fe(1)─Te(1)─Cu(1)	56.31(2)

Table S7 Electronic energy and cartesian coordinates of $[TeFe_3(CO)_9Cu_2(Me_2Im)_2]$ (**1**) (PBE0/Def2-TZVP) (in gas).

E = −11297.7735507 a.u.

atomic symbol	x	y	z
C	-0.702010	4.435960	5.669820
C	1.824220	4.593340	5.704310
C	0.316500	5.497830	3.539090
C	2.198720	9.139990	5.049000
C	1.619510	9.246340	7.513140
C	3.210100	7.274810	6.794590
C	0.312800	7.296420	9.329630
C	1.828060	5.380230	8.425220
C	-0.844930	5.120810	8.421380
C	4.304020	6.174030	3.429870
C	3.745060	3.919730	2.544620
H	4.098980	3.325680	1.852900
H	2.814050	4.143690	2.335760
H	3.784950	3.470080	3.414540
C	5.620130	5.392330	1.789660
H	5.966490	4.820760	1.113270
C	6.098720	6.589950	2.134570
H	6.853590	7.032690	1.762840
C	5.441640	8.347050	3.786270
H	6.216920	8.810530	3.399210
H	5.588050	8.214750	4.746250
H	4.636240	8.885760	3.648310
C	0.740910	8.748270	2.234210
C	2.278630	7.390680	0.829680
H	2.751770	7.513470	-0.019160
H	1.680050	6.619360	0.760700
H	2.930360	7.235030	1.546320
C	1.449650	9.683890	0.312330
H	1.899210	9.798890	-0.517350
C	0.646790	10.558970	0.902500
H	0.418290	11.424550	0.584420
C	-0.700020	10.593560	3.021730
H	-0.952310	11.484210	2.699820

H	-0.251370	10.673980	3.889740
H	-1.501880	10.040150	3.117540
N	4.535790	5.138110	2.592520
N	5.279310	7.055170	3.138620
N	1.508280	8.577920	1.128600
N	0.207520	9.970970	2.065590
O	-1.400000	3.530610	5.880600
O	2.599770	3.772730	5.976400
O	0.175050	5.119080	2.460310
O	2.647260	9.979620	4.412840
O	1.644680	10.087710	8.289170
O	4.237330	6.922870	7.191230
O	0.236240	7.922470	10.278110
O	2.740520	4.799140	8.841020
O	-1.640520	4.391860	8.800780
Fe	0.480530	5.673710	5.318410
Fe	1.653130	7.965970	6.281840
Fe	0.412820	6.265430	7.891380
Cu	2.801570	6.434050	4.609820
Cu	0.661910	7.693500	3.855830
Te	-0.833080	7.618700	6.200510

Table S8 Electronic energy and cartesian coordinates of [$TeFe_3(CO)_9Cu_2(MeImCH_2ImMe)$] (**2**) (PBE0/Def2-TZVP) (in gas).

E = −11257.0567454 a.u.

atomic symbol	x	y	z
C	15.728990	2.597350	4.075710
C	18.194300	2.340360	4.758590
C	16.416480	1.121690	6.331360
C	15.459330	5.383800	8.758430
C	13.591620	4.040680	7.590320
C	11.988590	0.339420	6.513080
H	11.257820	-0.307090	6.603950
H	12.078480	0.850160	7.344900
H	12.824230	-0.137380	6.331360
C	10.535380	1.213820	4.670540
H	9.816260	0.601250	4.772640
C	10.613620	2.204590	3.785330
H	9.962750	2.434100	3.130550
C	12.501300	2.243380	5.029300
C	12.261590	4.040680	3.337570
H	13.250380	4.040680	3.292610
H	11.917020	4.040680	2.409270
N	11.699280	1.247760	5.414300
N	11.821470	2.838170	4.002650
O	15.317830	2.459960	3.010650
O	19.168770	2.091450	4.198420
O	16.258340	0.087280	6.813770
O	15.474970	6.238800	9.514370
O	12.507950	4.040680	7.970640
Fe	16.679490	2.706930	5.586280
Fe	15.393240	4.040680	7.603530
Cu	14.220350	2.766570	5.760050
Te	17.850400	4.040680	7.297130
Cu	14.220350	5.314780	5.760050
N	11.821470	5.243180	4.002650
Fe	16.679490	5.374420	5.586280
C	15.459330	2.697550	8.758430
C	15.728990	5.484000	4.075710

C	16.416480	6.959660	6.331360
C	12.501300	5.837970	5.029300
C	10.613620	5.876760	3.785330
C	18.194300	5.740990	4.758590
O	15.474970	1.842550	9.514370
O	15.317830	5.621390	3.010650
O	16.258340	7.994070	6.813770
N	11.699280	6.833590	5.414300
C	10.535380	6.867530	4.670540
H	9.962750	5.647250	3.130550
O	19.168770	5.989900	4.198420
C	11.988590	7.741930	6.513080
H	9.816260	7.480100	4.772640
H	11.257820	8.388440	6.603950
H	12.078480	7.231190	7.344900
H	12.824230	8.218730	6.331360

Table S9 Electronic energy and cartesian coordinates of [$TeFe_3(CO)_9Cu_2(MeIm(CH_2)_2ImMe)$] (**3**) (PBE0/Def2-TZVP) (in gas).

E = −11296.7983211 a.u.

atomic symbol	x	y	z
Te	1.208800	9.157380	4.009490
Cu	2.834050	8.137230	5.873820
Cu	5.049800	7.701050	4.545840
Fe	2.369050	9.248390	1.813590
Fe	2.743630	7.224090	3.472230
Fe	3.649720	9.747070	4.091060
O	0.028320	8.483210	0.233220
O	2.346360	12.023240	0.923000
O	4.496500	8.311620	0.031620
O	4.978310	5.905530	2.110850
O	0.894340	5.781330	1.739280
O	2.208480	5.165990	5.488610
O	4.867110	10.204790	6.704130
O	3.156710	12.633820	3.986510
O	6.079980	9.775070	2.462660
N	1.801050	7.907540	8.645010
N	3.528350	6.701760	8.336680
N	6.850070	6.676680	6.654720
N	7.758410	6.486480	4.735580
C	0.955120	8.758410	0.843950
C	2.347870	10.942540	1.304460
C	3.662770	8.646860	0.755000
C	4.148170	6.493910	2.701810
C	1.620830	6.392930	2.397440
C	2.474210	6.056120	4.798830
C	4.319770	9.895410	5.727760
C	3.327110	11.501340	4.012200
C	5.118660	9.701780	3.089200
C	2.703830	7.579380	7.714100
C	0.717510	8.839790	8.425620
H	0.184660	8.920410	9.245850
H	0.148270	8.512920	7.698280
H	1.082780	9.715910	8.186470

C	2.040900	7.240120	9.842740
H	1.530940	7.303880	10.641220
C	3.141700	6.482620	9.643110
H	3.565080	5.914320	10.275580
C	4.679330	6.101670	7.688400
H	4.446150	5.879380	6.751560
H	4.911670	5.257790	8.150890
C	5.892600	7.028680	7.696310
H	5.591830	7.963040	7.561910
H	6.337190	6.976760	8.579780
C	8.083540	6.077890	6.850390
H	8.451880	5.805150	7.682470
C	8.653020	5.959150	5.670440
H	9.507850	5.585580	5.488610
C	8.037490	6.579790	3.300680
H	8.917440	6.190750	3.114890
H	8.030650	7.519750	3.027930
H	7.350040	6.089300	2.802610
C	6.639960	6.922250	5.336420

Table S10 Electronic energy and cartesian coordinates of $[TeFe_3(CO)_9Cu_2(MeIm(CH_2)_3ImMe)]$ (**4**) (PBE0/Def2-TZVP) (in gas).
E = −11335.9868279 a.u.

atomic symbol	x	y	z
C	9.144640	9.829650	5.803080
C	8.103300	11.401990	4.031390
C	9.907040	9.712710	3.174940
C	7.226340	10.711440	1.236660
C	5.886620	8.511310	0.872130
C	8.599730	8.396500	0.958360
C	6.344430	6.226400	2.665380
C	8.850070	6.283990	2.880960
C	7.232720	6.026960	5.077940
C	7.355670	7.698200	7.862870
C	4.888710	7.966590	7.815830
H	4.149120	7.831020	8.444940
H	4.747690	7.413240	7.020140
H	4.927270	8.911310	7.555170
C	6.237230	7.126580	9.744310
H	5.519400	6.983060	10.349900
C	7.514660	6.924410	9.973610
H	7.895120	6.599420	10.781070
C	9.626640	7.264330	8.729120
H	10.017020	6.927550	9.573810
H	9.949390	8.190190	8.588010
C	10.109900	6.336100	7.504220
H	9.906090	5.386770	7.696280
H	9.641300	6.596840	6.673250
C	11.525360	6.516470	7.351350
H	12.002920	5.964590	8.019660
H	11.756530	7.464660	7.514020
C	13.107580	5.409930	5.820720
H	13.575580	4.907720	6.477260
C	13.436040	5.546600	4.548780
H	14.179460	5.148520	4.111740
C	12.593920	6.886800	2.614420
H	13.359540	6.473590	2.163660

H	12.714020	7.858860	2.637940
H	11.771760	6.670420	2.126420
C	11.551130	6.743540	4.858440
N	6.148930	7.586790	8.456110
N	8.204980	7.267990	8.829460
N	11.957110	6.132300	6.004940
N	12.498760	6.376060	3.976510
O	9.743680	10.109030	6.764770
O	7.913820	12.531840	3.951030
O	10.860140	9.892270	2.544650
O	7.238120	11.755130	0.764920
O	5.001900	8.184100	0.230280
O	9.476400	8.000600	0.333170
O	5.617850	5.581950	2.049990
O	9.575360	5.627860	2.267340
O	7.012770	5.180340	5.807390
Fe	8.446490	9.673650	4.169750
Fe	7.236560	9.064290	1.889870
Fe	7.482700	7.119270	3.661370
Cu	7.677570	8.152260	6.012190
Cu	9.892100	7.669300	4.470980
Te	6.001700	9.113280	4.042280

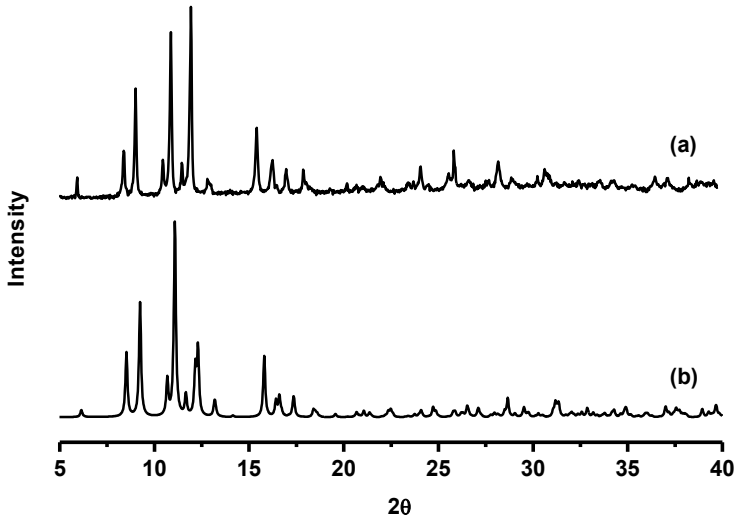


Fig. S1 Powder X-ray diffraction (PXRD) patterns for (a) Crystals of **1** exposure to air for 10 days; (b) Calculated pattern for **1**.

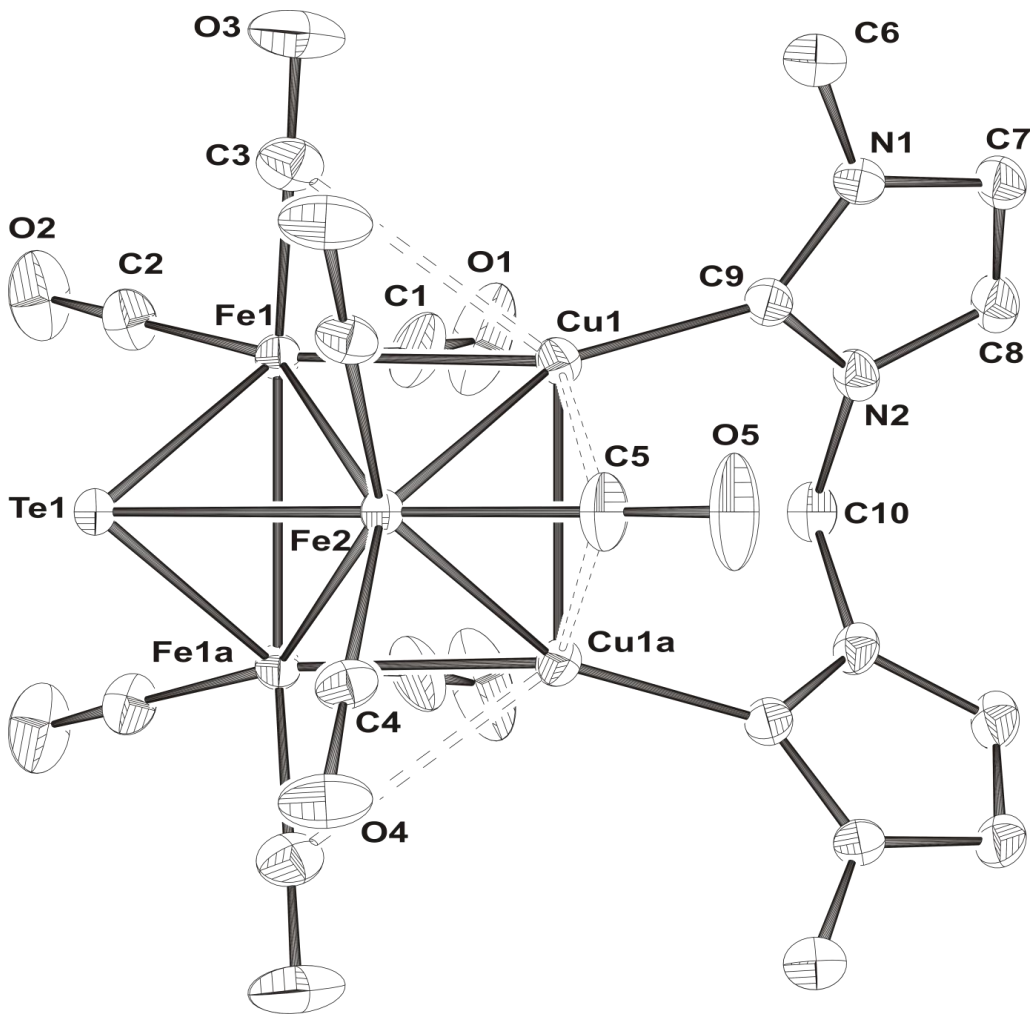


Fig. S2 ORTEP of **2** at 30% probability and hydrogen atoms are omitted for clarity. The atoms with an additional label (a) are at the equivalent position (x, $1/2 - y$, z).

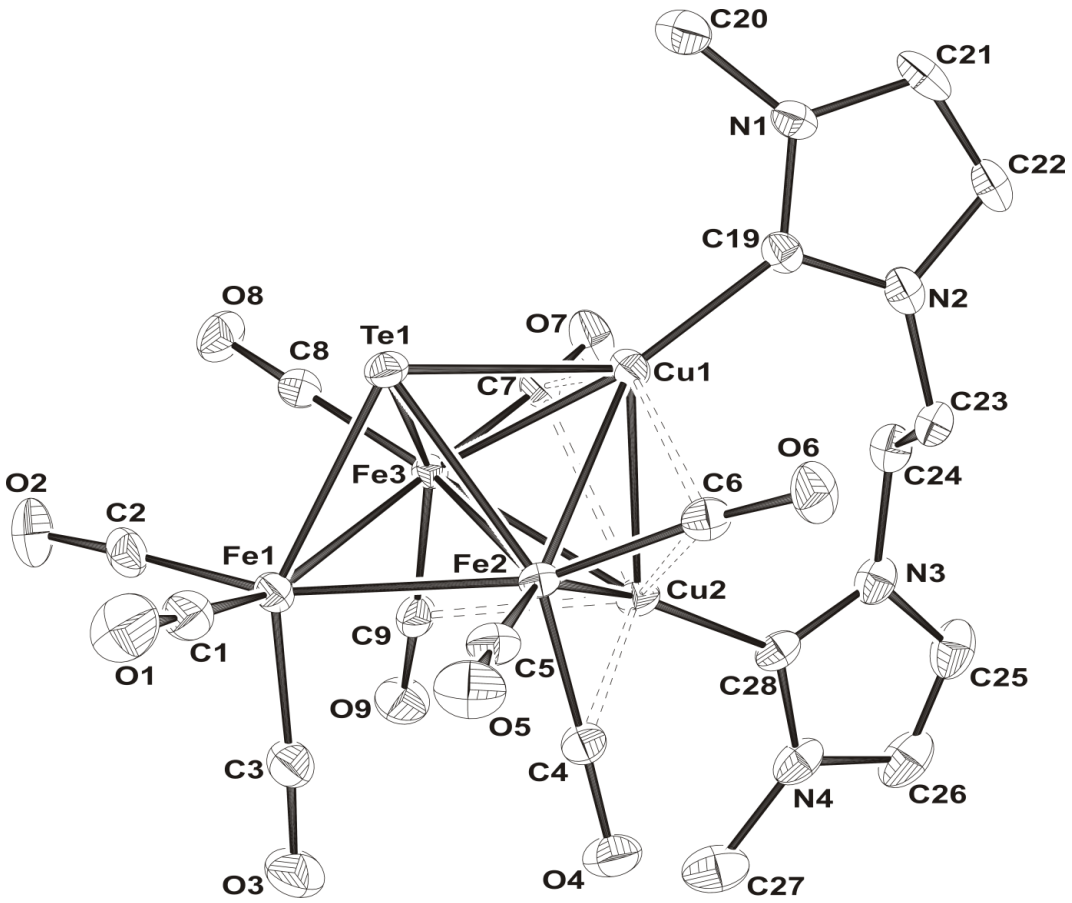


Fig. S3 ORTEP of **3** at 30% probability and hydrogen atoms are omitted for clarity.

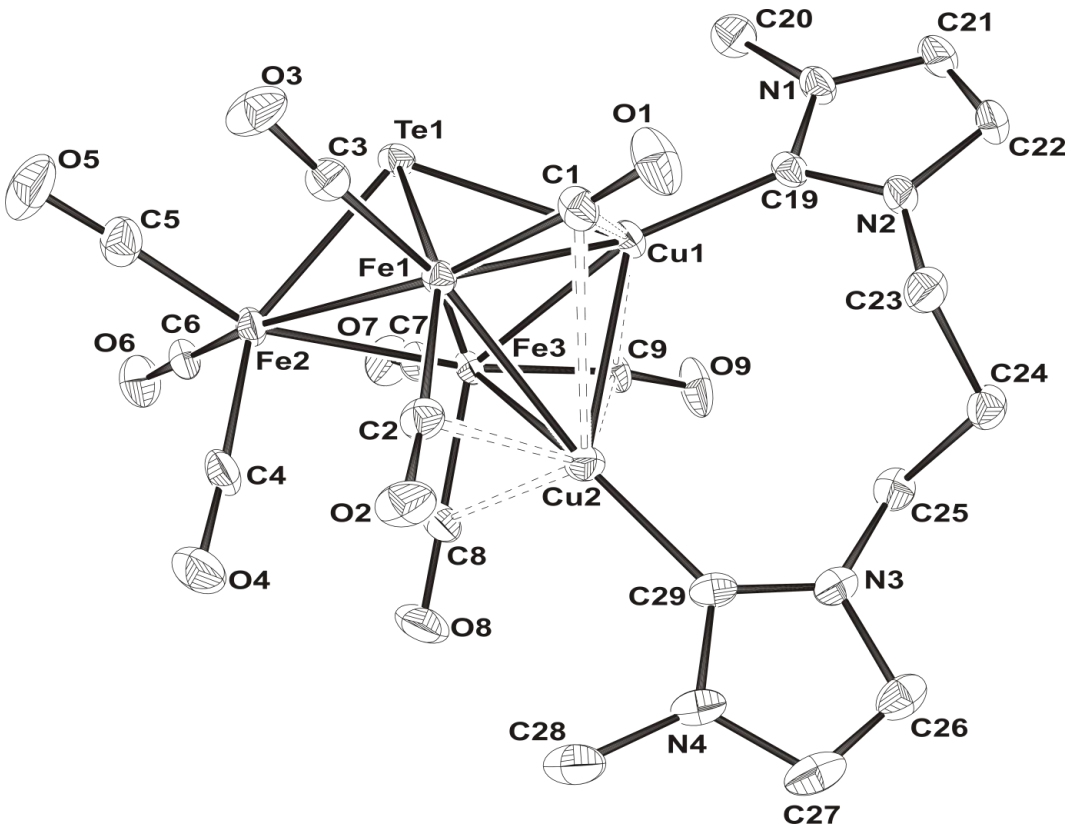


Fig. S4 ORTEP of **4** at 30% probability and hydrogen atoms are omitted for clarity.

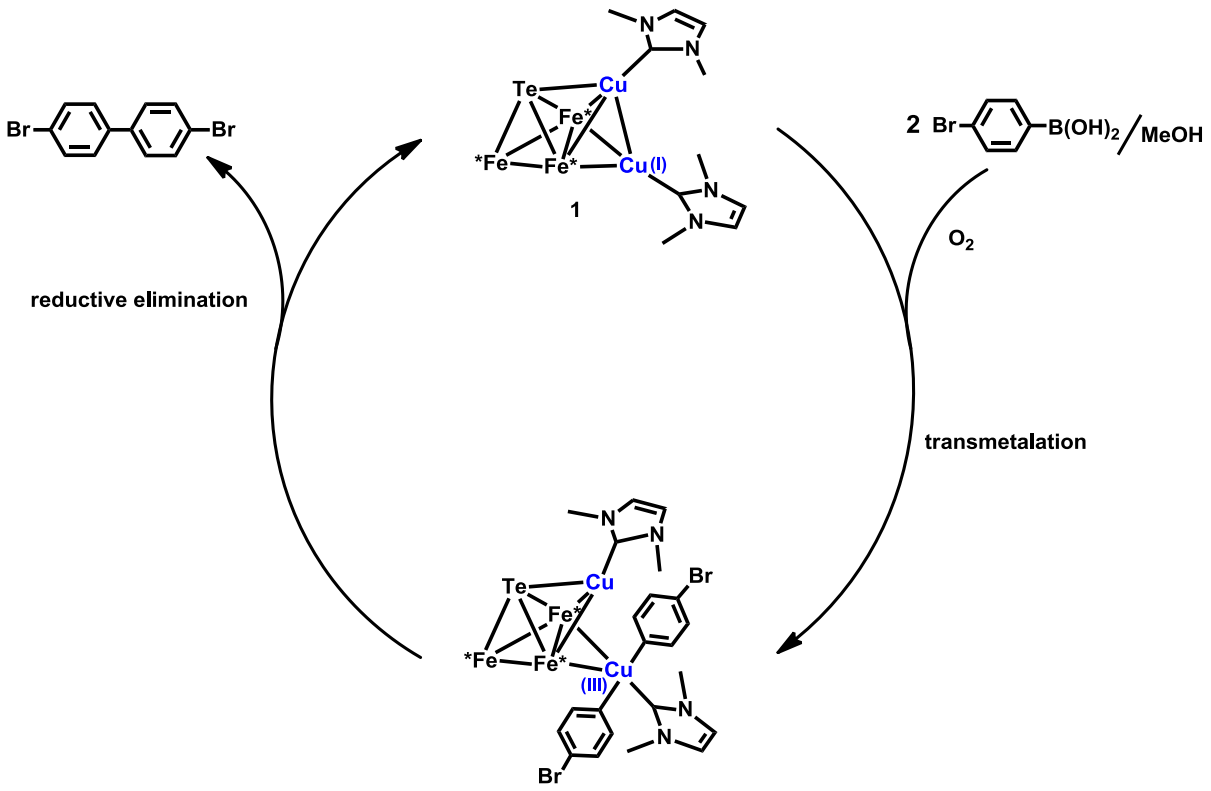


Fig. S5 The proposed mechanism using the model complex **1** as the catalyst for the homocoupling of 4-bromophenylboronic acid to 4,4'-dibromobiphenyl.[19,28]

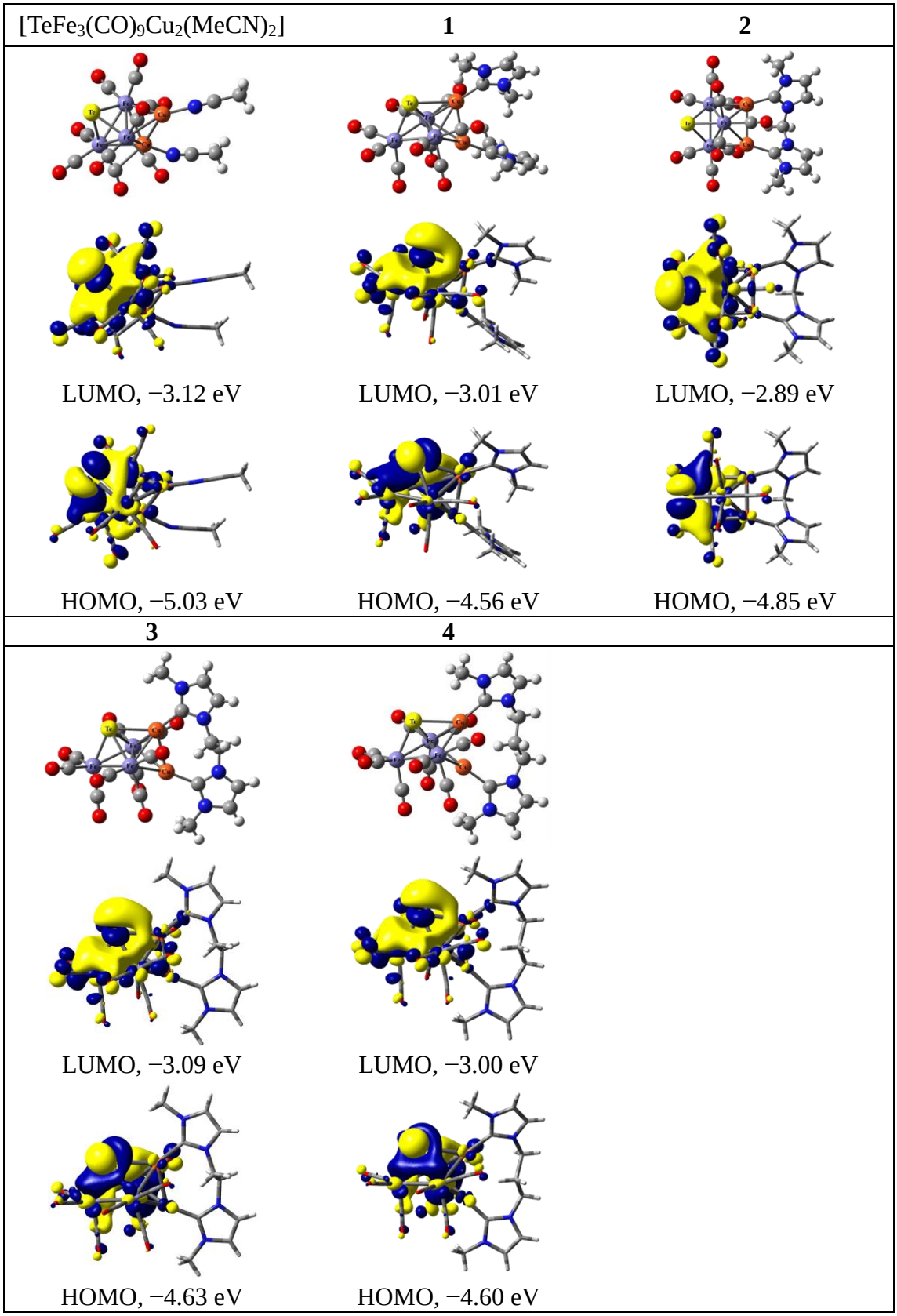


Fig. S6 Spatial graphs (isovalue = 0.03) of the selected frontier molecular orbitals and their associated energies of $[TeFe_3(CO)_9Cu_2(MeCN)_2]$ and **1**−**4**.

ArX[a]	Yield (%)	Product ratio	K_{Ar}/K_{ArBr}	log (K_{ArX}/K_{ArBr})
p-BrC_6H_4	88	88/88	1	0
p-$OMeC_6H_4$	70	70/88	0.795	−0.100
p-$NO_2C_6H_4$	99[b]	99/88	1.125	0.051
m-BrC_6H_4	68	68/68	1	0
m-$NO_2C_6H_4$	97	97/68	1.426	0.154

[a] X = substituents. [b] 78%/79% (based on 78% yield of 4,4'-dinitrobiphenyl and 21% yield of 4-nitrophenol).

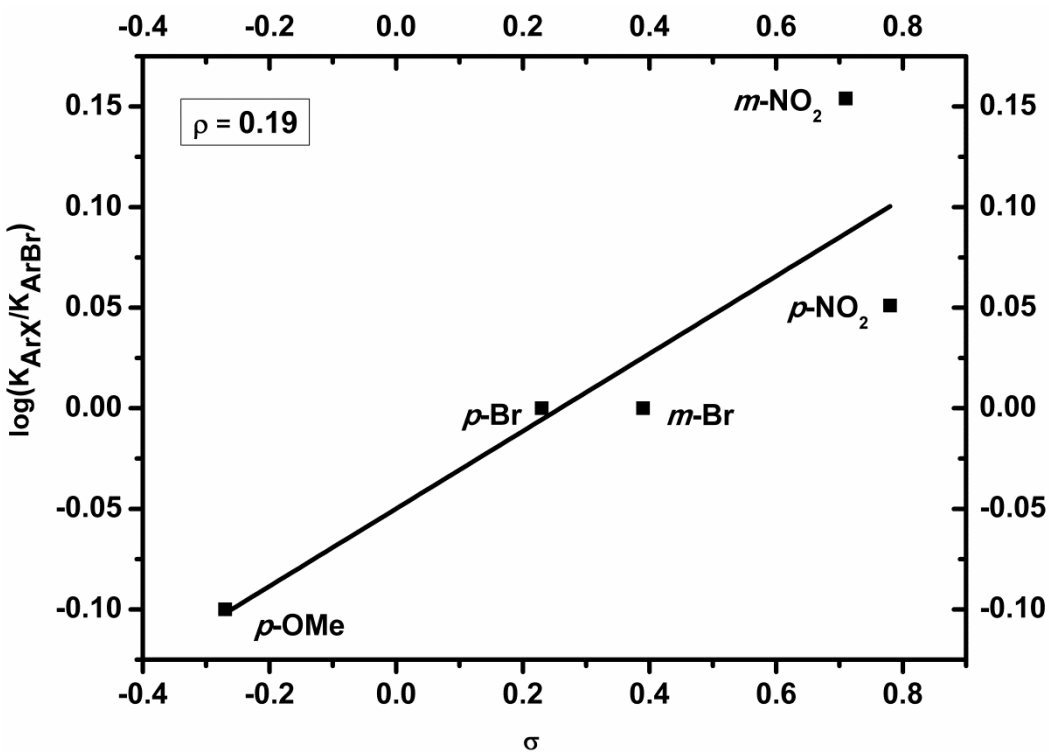
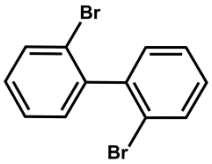


Fig. S7 Correlation of product ratios with the Hammett equation. y = 0.19 x − 0.05; R^2 = 0.70.

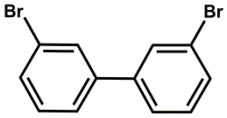
Spectroscopic data of products

2,2'-dibromobiphenyl



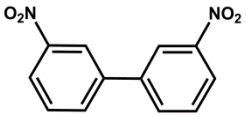
^{1}H NMR (400 MHz, DMSO, ppm): δ 7.72 (dd, 2H, *J* = 7.6, 1.4 Hz), 7.46 (td, 2H, *J* = 7.6, 1.4 Hz), 7.35 (td, 2H, *J* = 7.6, 1.4 Hz), 7.28 (dd, 2H, *J* = 7.6, 1.4 Hz); ^{13}C NMR (100 MHz, DMSO, ppm): δ 141.95, 132.81, 131.52, 130.42, 128.15, 123.21

3,3'-dibromobiphenyl



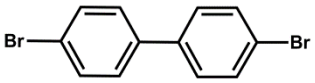
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.71 (t, 2H, *J* = 1.8 Hz), 7.53─7.48 (m, 4H), 7.32 (t, 2H, *J* = 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 141.82, 130.83, 130.39, 130.19, 125.75, 123.00

3,3'-dinitrobiphenyl



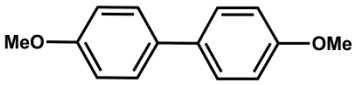
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.50 (t, 2H, *J* = 1.8 Hz), 8.30 (m, 2H), 7.97 (m, 2H), 7.70 (t, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.90, 140.35, 133.07, 130.31, 123.31, 122.12

4,4'-dibromobiphenyl



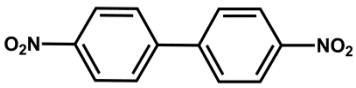
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.56 (dd, 4H, *J* = 8.4 Hz), 7.41 (dd, 4H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.93, 132.03, 128.52, 121.96

4,4'-dimethoxybiphenyl



^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49 (dd, 4H, *J* = 8.6 Hz), 6.97 (dd, 4H, *J* = 8.6 Hz), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.71, 133.51, 127.73, 114.17, 55.35

4,4'-dinitrobiphenyl

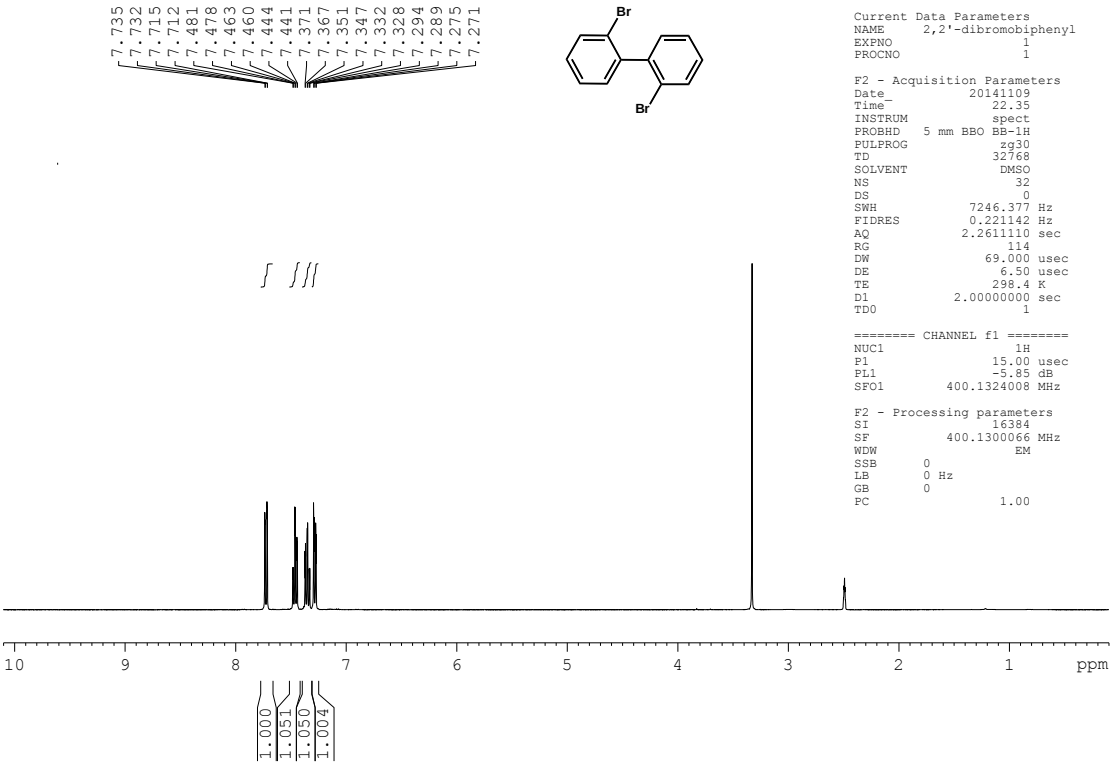


^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.38 (dd, 4H, *J* = 8.8 Hz), 7.80 (dd, 4H, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.10, 144.99, 128.33, 124.39

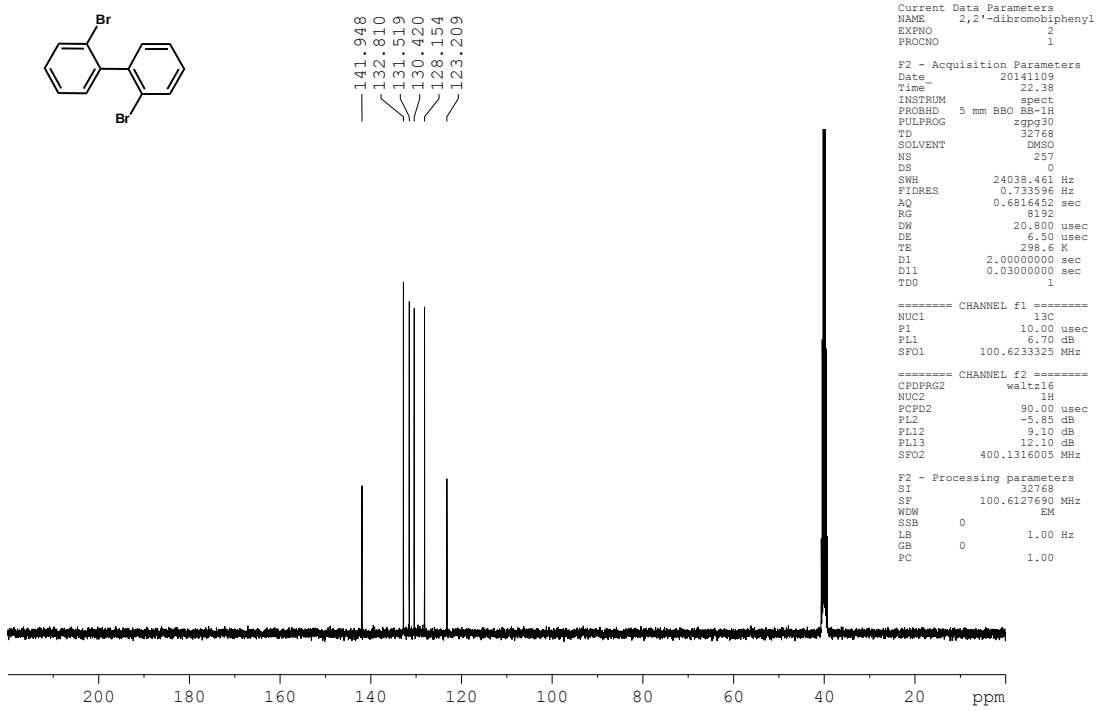
4-nitrophenol

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.17 (dd, 2H, *J* = 9.2 Hz), 6.90 (dd, 2H, *J* = 9.2 Hz), 5.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.82, 141.39, 126.38, 115.83

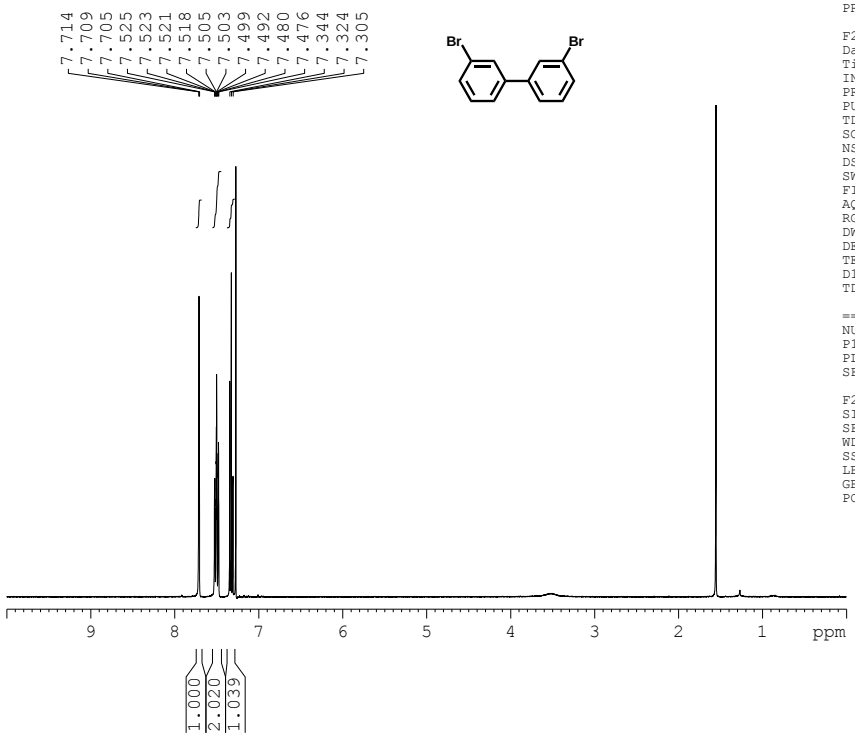
^{1}H NMR (400 MHz, DMSO, 25 °C)



^{13}C{^{1}H} NMR (100 MHz, DMSO, 25 °C)

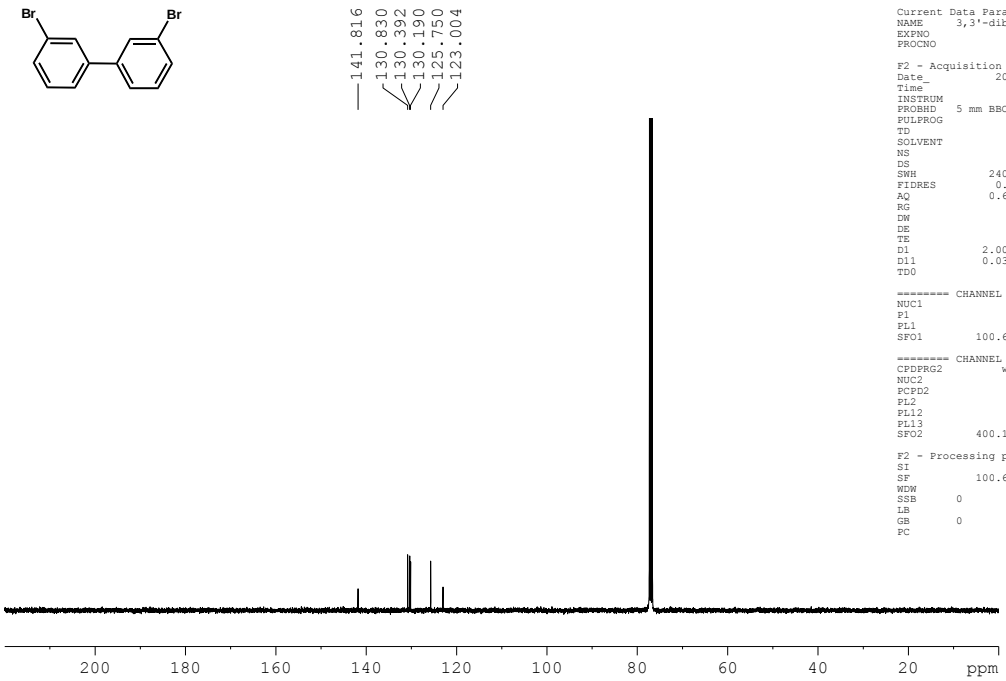


^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C)



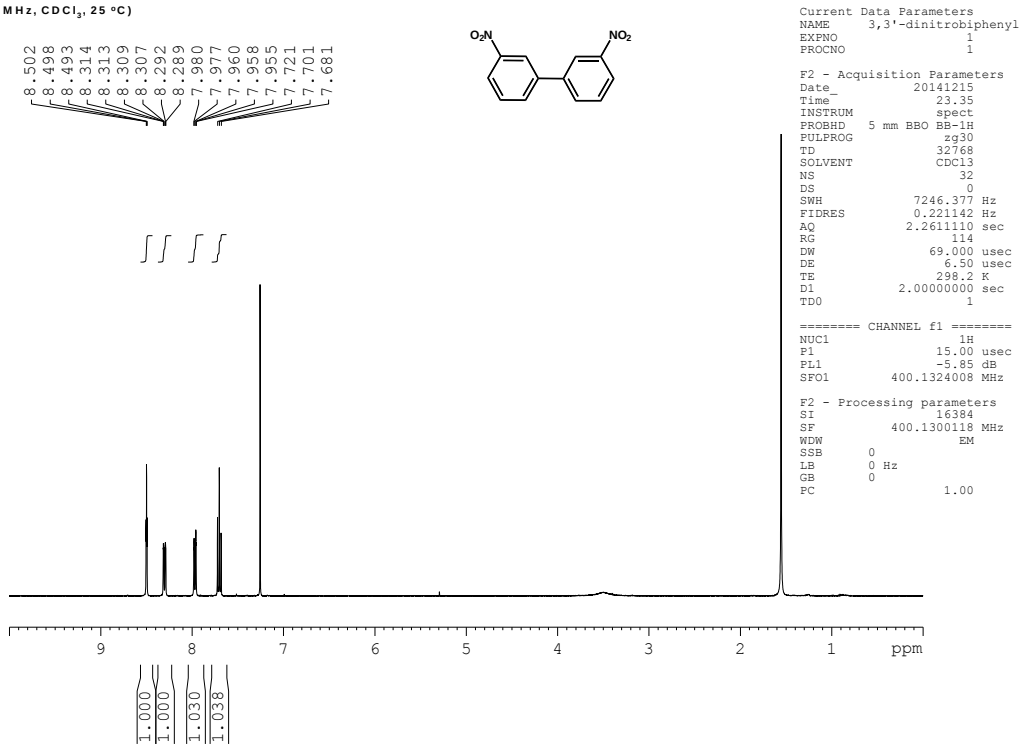

```
Current Data Parameters
NAME      3,3'-dibromobiphenyl
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_            20141109
Time                 20.29
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      32
DS                       0
SWH              7246.377 Hz
FIDRES           0.221142 Hz
AQ              2.2611110 sec
RG                     114
DW                  69.000 usec
DE                    6.50 usec
TE                   298.4 K
D1             2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PL1                  -5.85 dB
SFO1          400.1324008 MHz

F2 - Processing parameters
SI                   16384
SF            400.1300052 MHz
WDW                     EM
SSB       0
LB        0 Hz
GB        0
PC                    1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C)

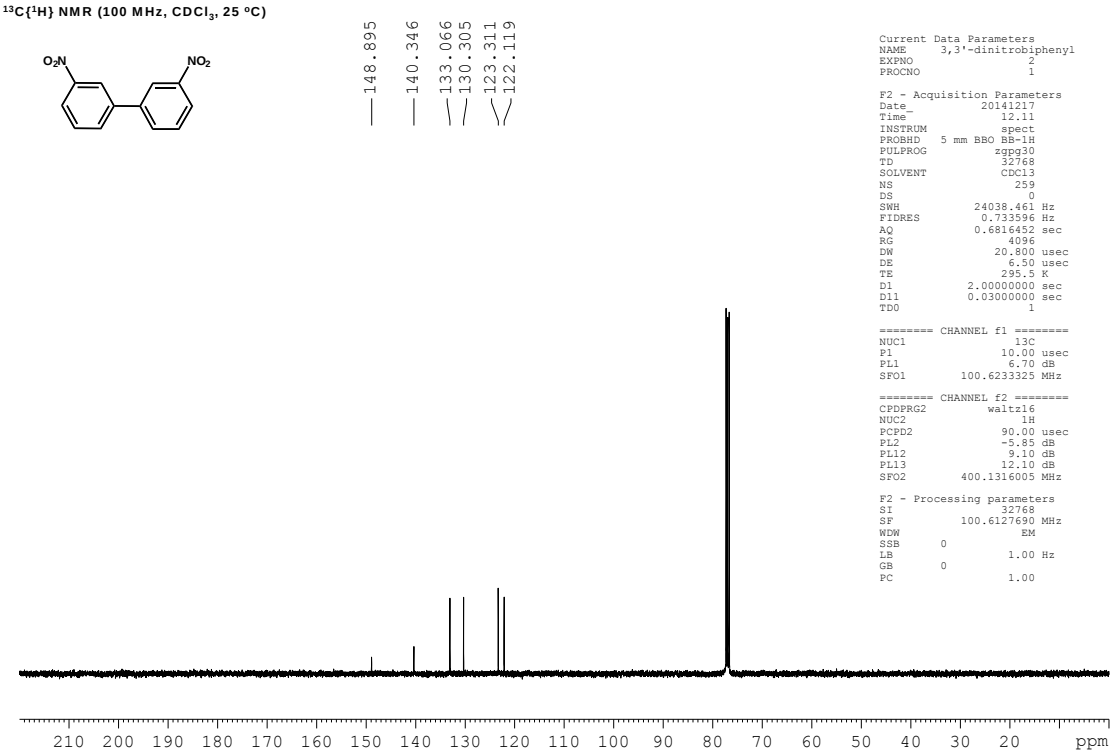



```
Current Data Parameters
NAME      3,3'-dibromobiphenyl
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_            20141109
Time                 21.14
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg30
TD                   32768
SOLVENT              CDCl3
NS                     973
DS                       0
SWH             24038.461 Hz
FIDRES           0.733596 Hz
AQ              0.6816452 sec
RG                    4096
DW                  20.800 usec
DE                    6.50 usec
TE                   299.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PL1                   6.70 dB
SFO1          100.6233325 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -5.85 dB
PL12                  9.10 dB
PL13                 12.10 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127690 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.00
```

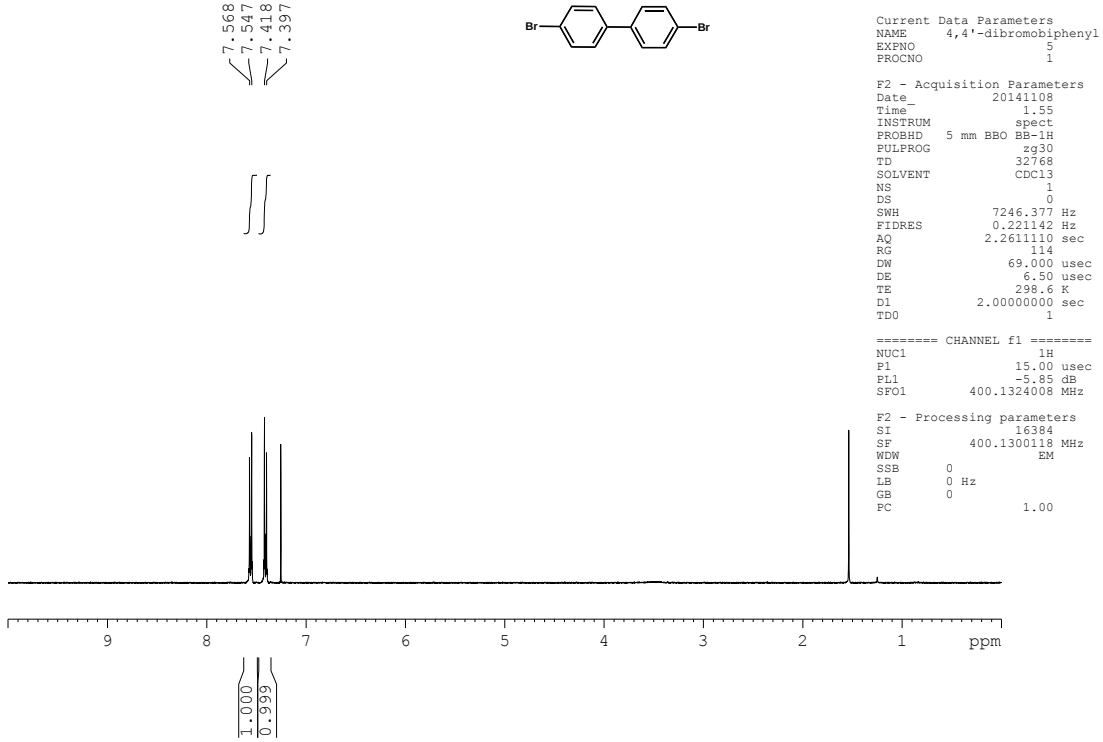
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)



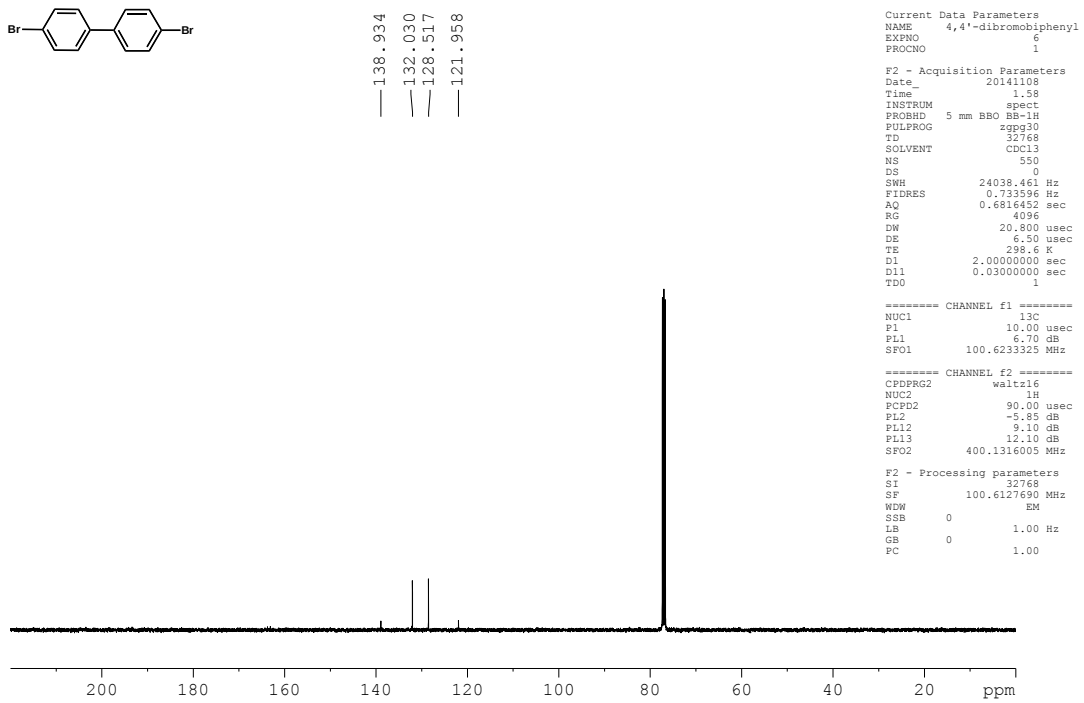
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C)



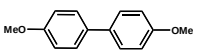
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

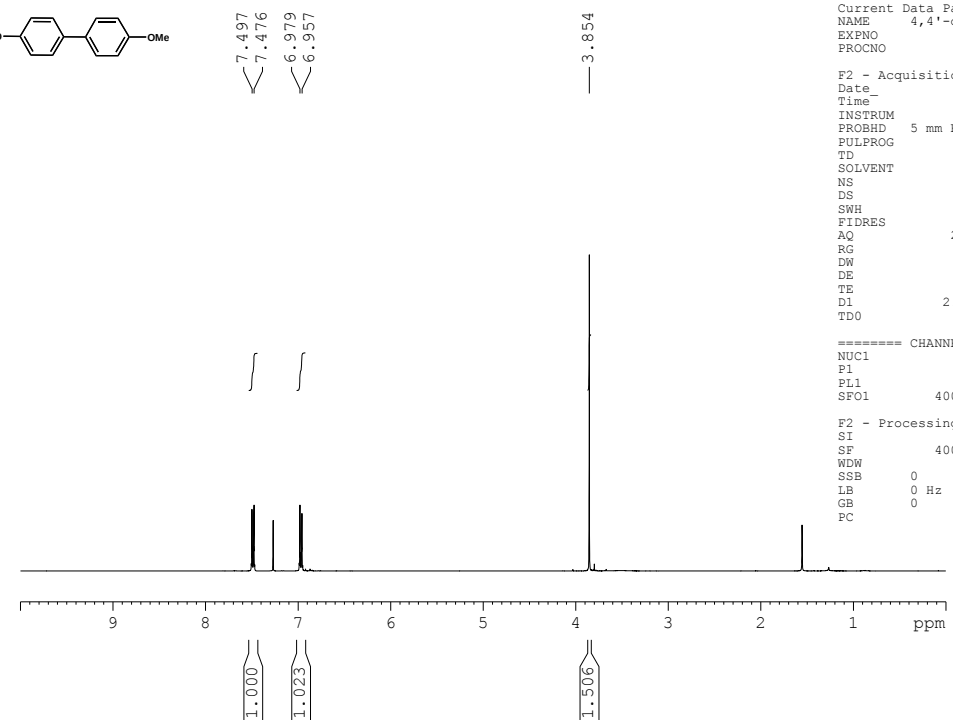


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C)



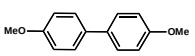
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)

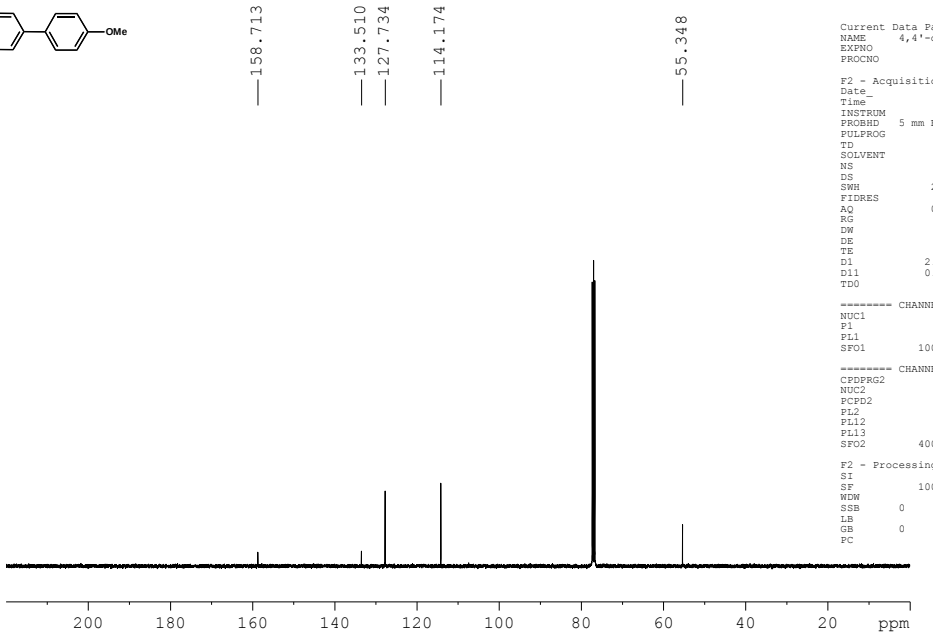





```
Current Data Parameters
NAME      4,4'-dimethoxybiphenyl
EXPNO                          2
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20141107
Time                       22.39
INSTRUM                    spect
PROBHD   5 mm BBO BB-1H
PULPROG                     zg30
TD                         32768
SOLVENT                    CDCl3
NS                            32
DS                             0
SWH                    7246.377 Hz
FIDRES                 0.221142 Hz
AQ                    2.2611110 sec
RG                          114
DW                       69.000 usec
DE                         6.50 usec
TE                        298.1 K
D1                   2.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                        15.00 usec
PL1                        -5.85 dB
SFO1                400.1324008 MHz

F2 - Processing parameters
SI                         16384
SF                  400.1300058 MHz
WDW                            EM
SSB       0
LB        0 Hz
GB        0
PC                          1.00
```

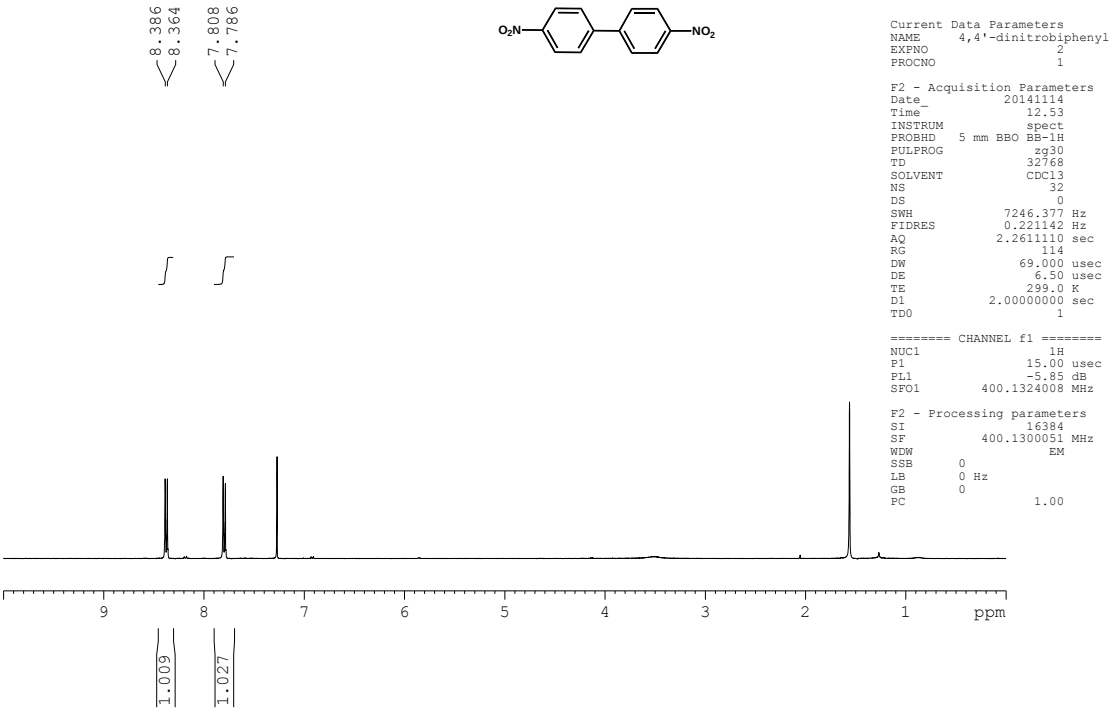
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C)





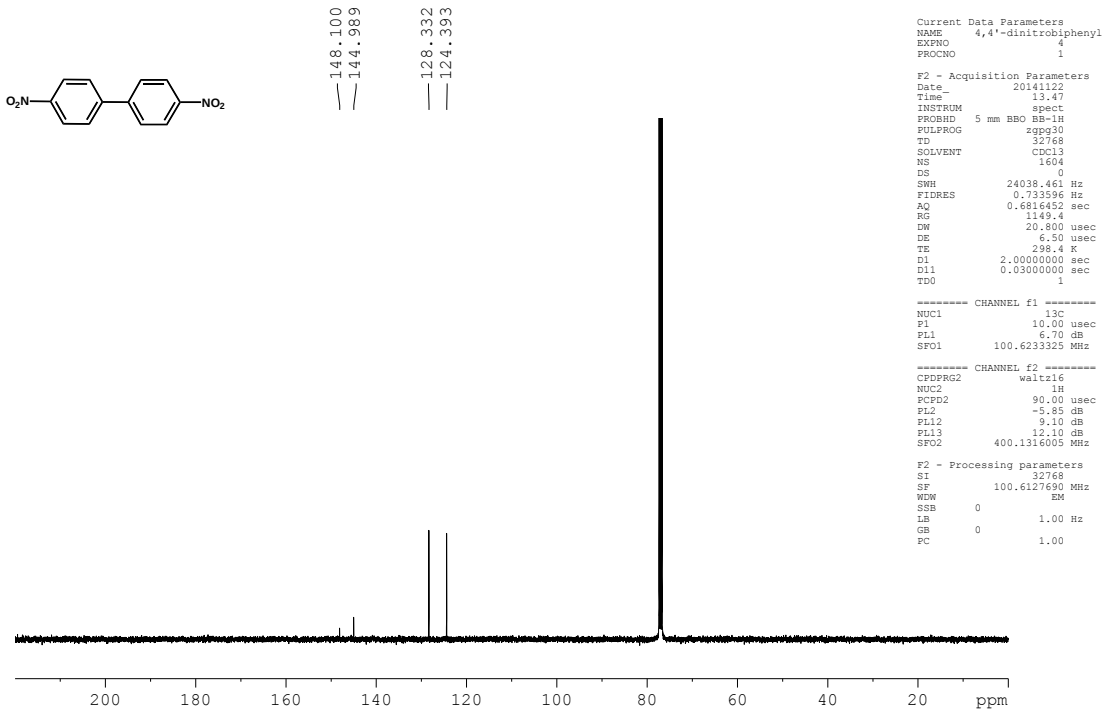

```
Current Data Parameters
NAME      4,4'-dimethoxybiphenyl
EXPNO                          3
PROCNO                         1

F2 - Acquisition Parameters
Date_                   20141107
Time                       22.49
INSTRUM                    spect
PROBHD   5 mm BBO BB-1H
PULPROG                   zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                           748
DS                             0
SWH                   24038.461 Hz
FIDRES                 0.733596 Hz
AQ                    0.6816452 sec
RG                          4096
DW                       20.800 usec
DE                         6.50 usec
TE                        298.9 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          13C
P1                        10.00 usec
PL1                        6.70 dB
SFO1               100.6233325 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                     90.00 usec
PL2                       -5.85 dB
PL12                       9.10 dB
PL13                      12.10 dB
SFO2               400.1316005 MHz

F2 - Processing parameters
SI                         32768
SF                 100.6127690 MHz
WDW                            EM
SSB       0
LB                         1.00 Hz
GB        0
PC                          1.00
```

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)



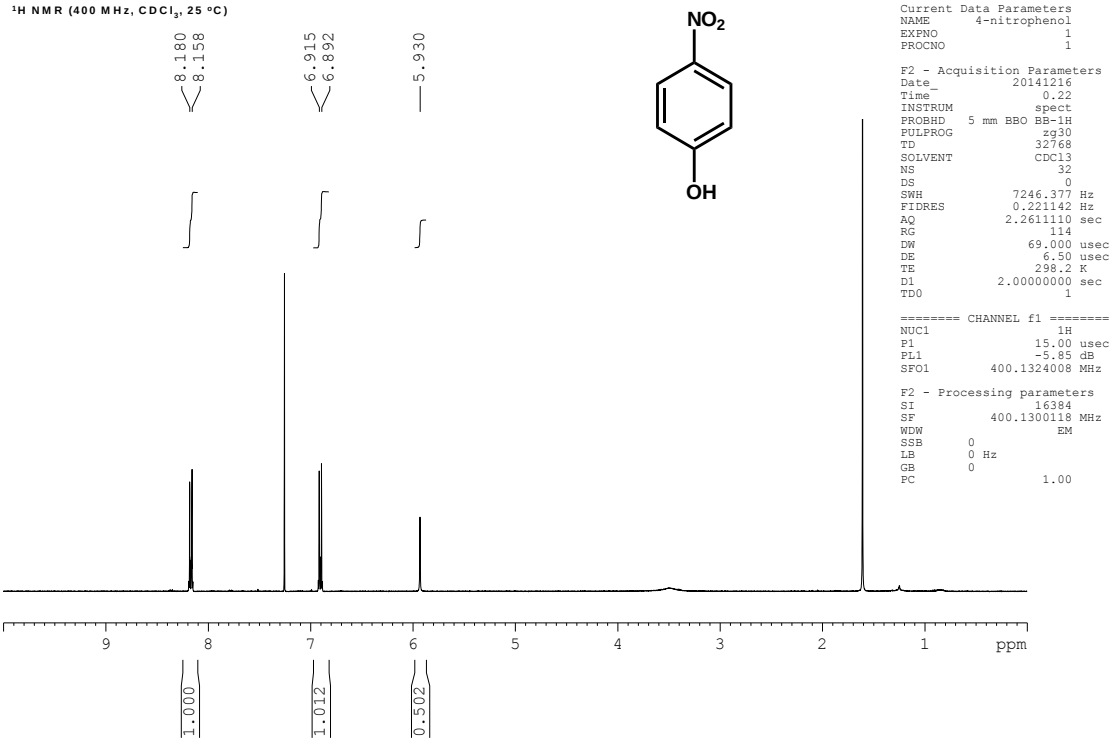

```
Current Data Parameters
NAME      4,4'-dinitrobiphenyl
EXPNO                        2
PROCNO                       1

F2 - Acquisition Parameters
Date_            20141114
Time                12.53
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             7246.377 Hz
FIDRES          0.221142 Hz
AQ             2.2611110 sec
RG                   114
DW                69.000 usec
DE                  6.50 usec
TE                 299.0 K
D1             2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                15.00 usec
PL1               -5.85 dB
SFO1         400.1324008 MHz

F2 - Processing parameters
SI                 16384
SF           400.1300051 MHz
WDW                   EM
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C)



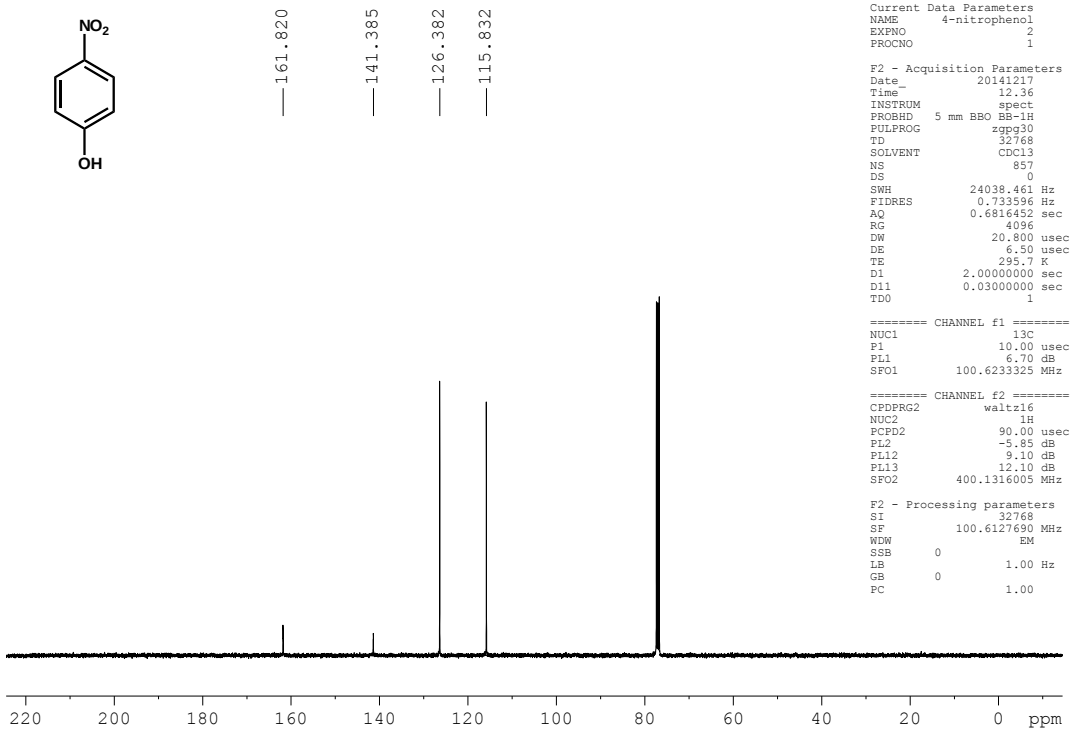

```
Current Data Parameters
NAME      4,4'-dinitrobiphenyl
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_            20141122
Time                13.47
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                  1604
DS                     0
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ             0.6816452 sec
RG                1149.4
DW                20.800 usec
DE                  6.50 usec
TE                 298.4 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PL1                6.70 dB
SFO1         100.6233325 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             90.00 usec
PL2               -5.85 dB
PL12               9.10 dB
PL13              12.10 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.00
```

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)




```
Current Data Parameters
NAME      4-nitrophenol
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20141216
Time               0.22
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    0
SWH            7246.377 Hz
FIDRES         0.221142 Hz
AQ            2.2611110 sec
RG                  114
DW               69.000 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PL1               -5.85 dB
SFO1        400.1324008 MHz

F2 - Processing parameters
SI                16384
SF          400.1300118 MHz
WDW                  EM
SSB      0
LB       0 Hz
GB       0
PC                 1.00
```

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C)




```
Current Data Parameters
NAME      4-nitrophenol
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20141217
Time               12.36
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  857
DS                    0
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            0.6816452 sec
RG                 4096
DW               20.800 usec
DE                 6.50 usec
TE                295.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1                6.70 dB
SFO1        100.6233325 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -5.85 dB
PL12               9.10 dB
PL13              12.10 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB      0
LB                1.00 Hz
GB       0
PC                 1.00
```