Supporting information:

Recyclable Pd/$CuFe_2O_4$ nanowires: Highly active catalyst for C–C couplings and Synthesis of Benzofuran derivatives

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Experimental:

General Considerations

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CHCl_3$ (δH = 7.25 ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CHCl_3$ [δC = 77.00 ppm (central line of triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD and DEPT spectra. All small-scale dry reactions were carried out using the standard syringe-septum technique. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 40 to 60 °C was used. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material). It is worth noting that these sort of general procedures have already been published elsewhere.

Reference: B. Lakshminarayana, L. Mahendar, P. Ghosal, B. Sreedhar, G. Satyanarayana, Ch Subrahmanyam. *New J. Chem.* 2018, **42**, 1646-1654.

Synthesis of $CuFe_2O_4$:

To a crystalline dish containing $Cu(NO_3)_2$•$3H_2O$ (1.208 g, 5 mmol), were added $Fe(NO_3)_3$•$9H_2O$ (4.04 g, 10 mmol) and urea (2.0 g, 33.3 mmol) simultaneously, and dissolved with milli-Q water (5 mL). The resultant solution was kept in a muffle furnace at 400 °C. Initially, the solution boiled with froth and foam followed by ignition after complete dehydration and finally burned with flame yielding solid product within 2 min. This solid material was further subjected to calcined at 400 °C, for 15 min.

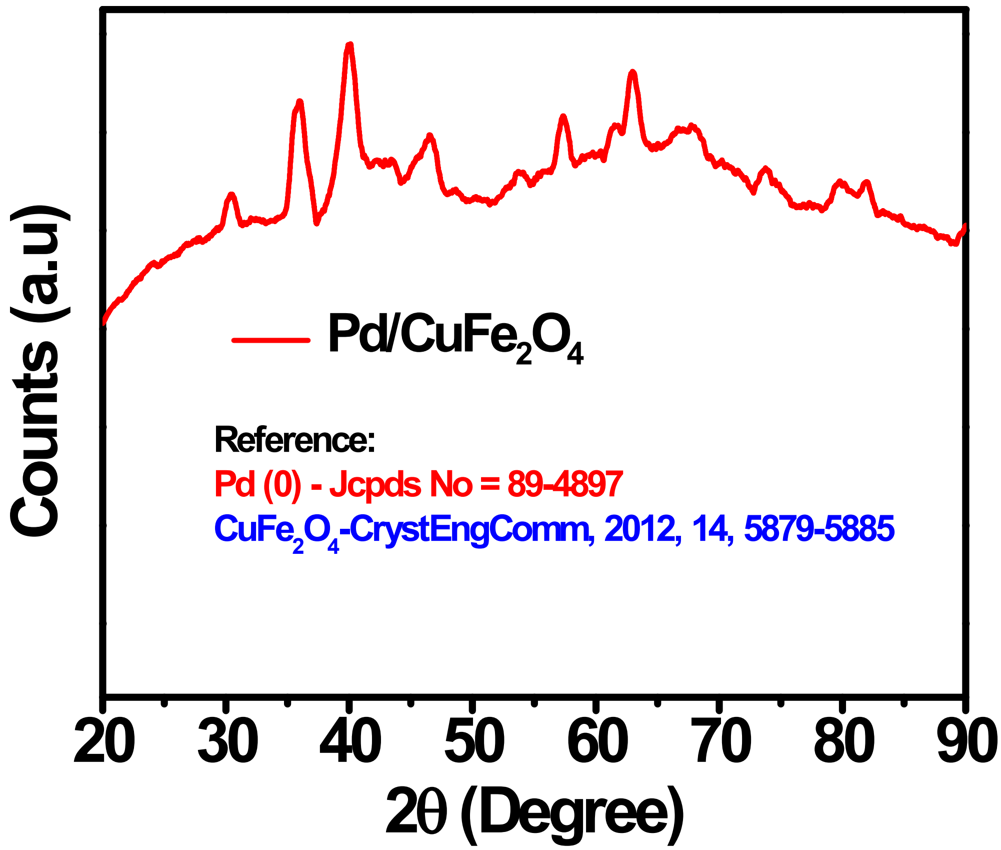
Synthesis of Pd/$CuFe_2O_4$ nanowires:

To a 250 mL beaker, were added $CuFe_2O_4$ (200mg, 0.42 mmol), $PdCl_2$(100 mg, 0.28 mmol) and ethanol (25 mL). The reaction mixture was ultra-sonicated at room temperature for 30 minutes. Then, aqueous $NaBH_4$ (0.47 g, 25 mL, 0.5M) was added dropwise. The resultant solution was stirred for 2h at room temperature. The solution was washed and centrifuged with ethanol (14 mL) and water (14 mL) and the solvent was decanted. Finally, the solid material was centrifuged with acetone (14 mL) and dried overnight in a hot air oven at 60 °C. The resultant catalyst was grained and utilized for further examination.

XRD:

For the examination of crystalline stage and immaculateness of the synthesized $CuFe_2O_4$ and Pd/$CuFe_2O_4$, powder X-Ray diffraction (XRD) measurements were carried out. XRD measurement of exposed Pd/$CuFe_2O_4$ in Figure 1. Crystallographic countenances of magnetite and Bragg's reflections related to Pd/$CuFe_2O_4$ at 2θ:30.57°, 35.78°, 36.67°, 40.15°(Pd), 46.63°(Pd), 57.36°, 61.56°, 63.08°, 68.48°(Pd), 73.70°, 79.89°, 82.21°(Pd) which relate to the planes (220), (311), (222), (111), (200), (511), (224), (400), (220), (533), (444),(311). These outcomes were observed to be reliable with the standard XRD information of the Joint Committee on Powder Diffraction Standards (JCPDS) card number 25-0283 ($CuFe_2O_4$), 89-4897 (Pd).

Figure S1: PXRD diffraction of Pd/$CuFe_2O_4$ nanowires

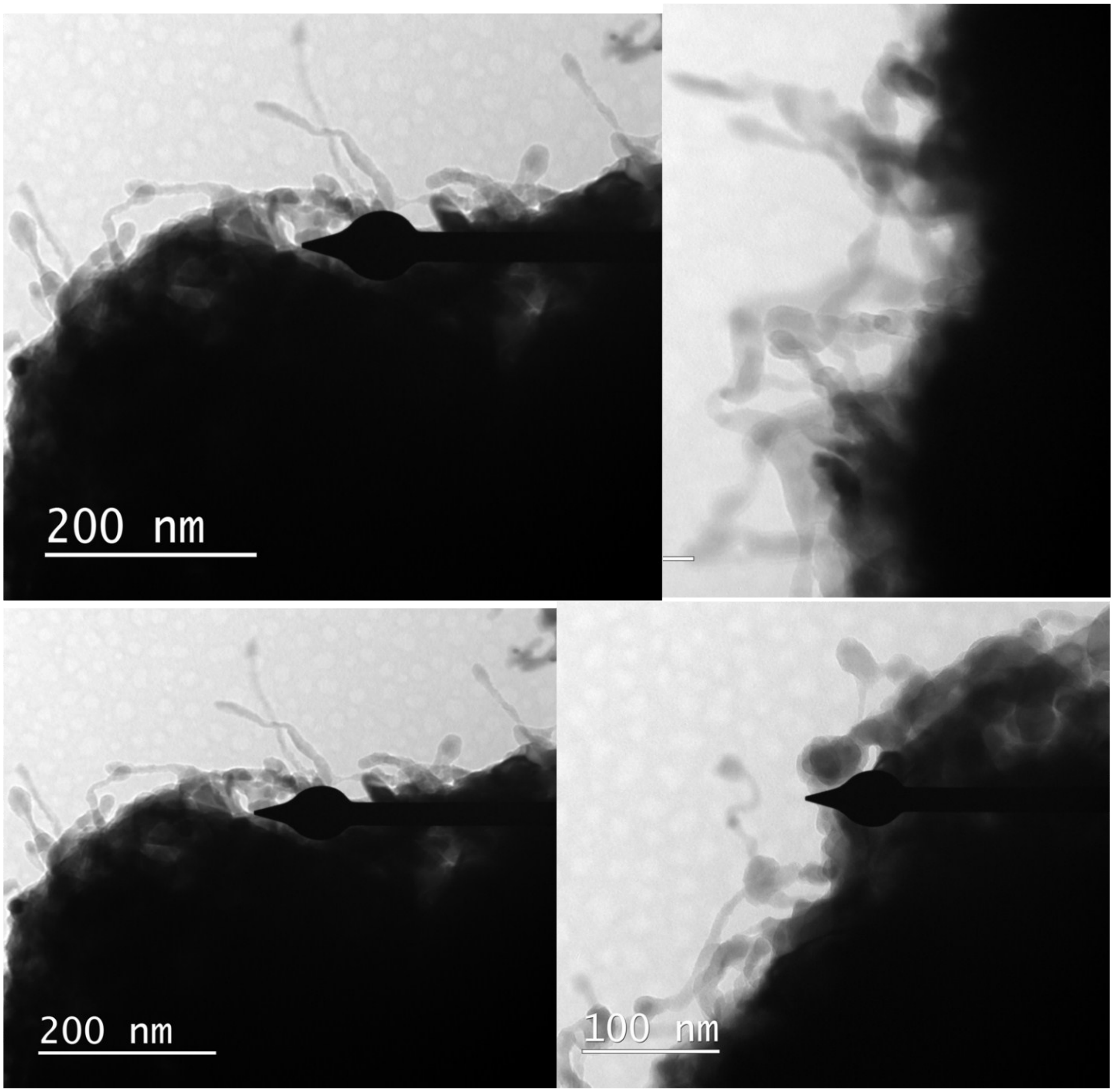


Reference: B. Lakshminarayana, L. Mahendar, P. Ghosal, B. Sreedhar, G. Satyanarayana, Ch Subrahmanyam. *New J. Chem.* 2018, **42**, 1646-1654.

TEM:

As shown in Figure 2, We have effectively built up an easy and proficient synthetic procedure to manufacture Pd/$CuFe_2O_4$ nanowires. From the low-magnification TEM image, one can see high quality intertwining nanowires with normal width of around 14 nm, and there is no detection of any nanoparticles all through the whole image

Figure S2: TEM image of the catalyst Pd/$CuFe_2O_4$ nanowires



Reference: B. Lakshminarayana, L. Mahendar, P. Ghosal, B. Sreedhar, G. Satyanarayana, Ch Subrahmanyam. *New J. Chem.* 2018, **42**, 1646-1654.

XRF analysis:

The elemental composition of the material by X-ray fluorescence (XRF) analysis, as-prepared Pd/$CuFe_2O_4$ was analysed with XRF spectrometry. The results showed in Table S1, the percentages of Pd, Cu and Fe are 22.5%, 27.4% and 48% respectively.

Table S1: The elemental composition of Pd/$CuFe_2O_4$

Catalyst	Pd	Cu	Fe
Pd/$CuFe_2O_4$	22.5 %	27.4 %	48 %

Reference: B. Lakshminarayana, L. Mahendar, P. Ghosal, B. Sreedhar, G. Satyanarayana, Ch Subrahmanyam. *New J. Chem.* 2018, **42**, 1646-1654.

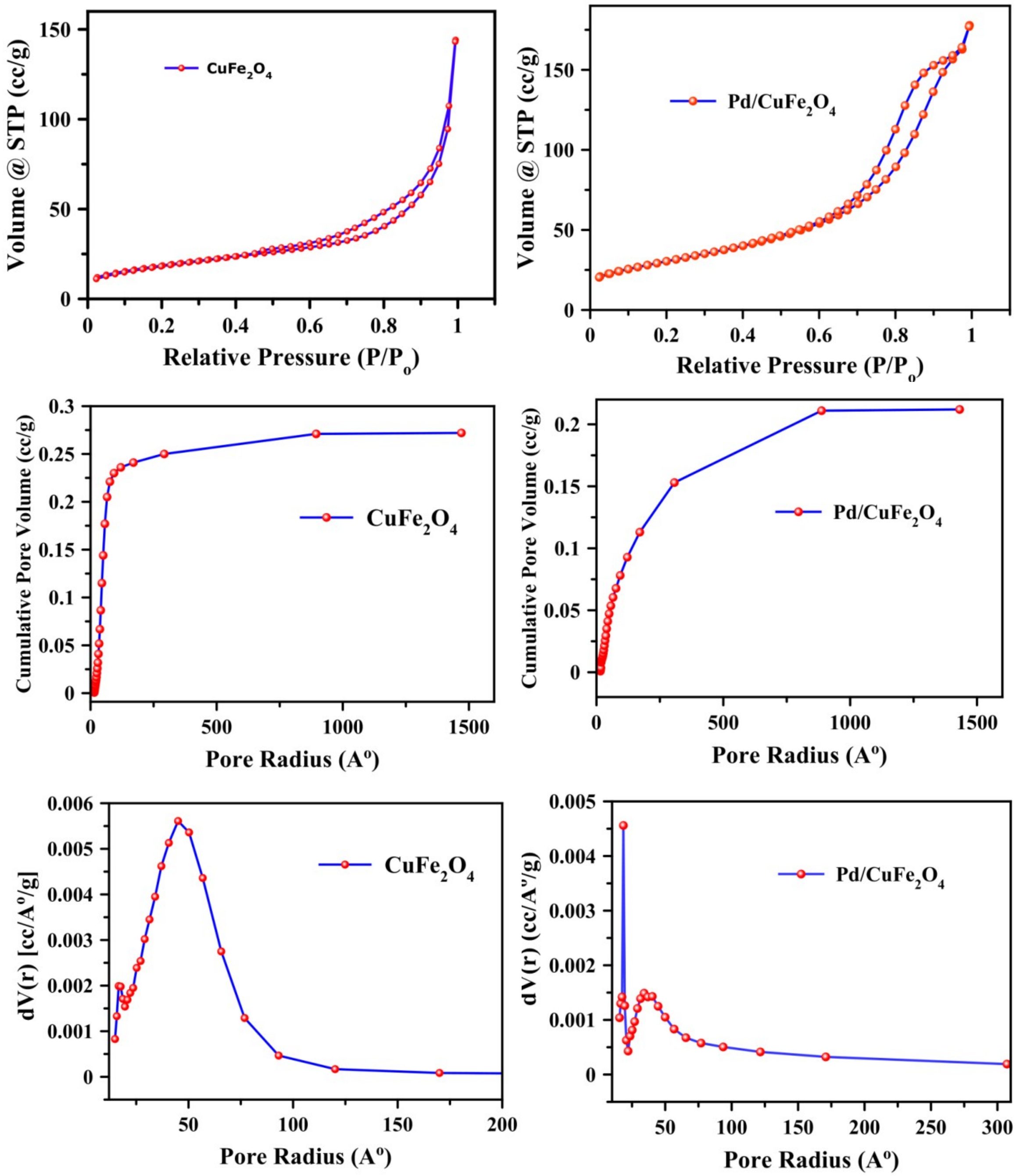
BET Analysis:

As shown Table S1 When Pd nanowires incorporated on $CuFe_2O_4$, the growth of surface area of $CuFe_2O_4$ increased from 66.87 m^2/g to 109.96 m^2/g. When Pd nanowires impregnated on $CuFe_2O_4$ the pore radius and total pore volume decreases. It the direct indication of the $CuFe_2O_4$ is wrapped by Pd nanowires. Figure S3 shows the isotherm, pore-size distribution of $CuFe_2O_4$ ad Pd/$CuFe_2O_4$.

Table S1. BET analysis data of $CuFe_2O_4$ and Pd/$CuFe_2O_4$

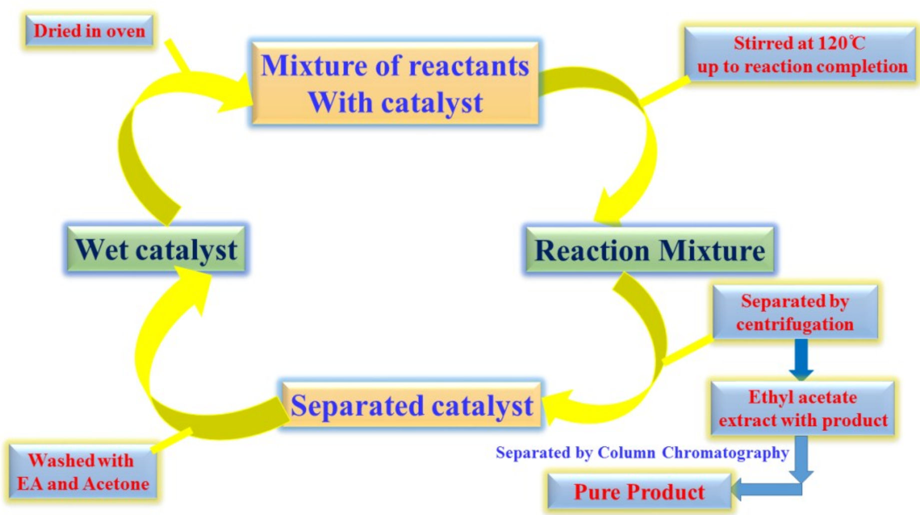
Catalyst	**Surface Area (m^2/g)**	**Pore Radius Dv(r) (Å)**	**Total Pore Volume (cc/g)**
$CuFe_2O_4$	66.87	45.02	0.275
Pd/$CuFe_2O_4$	109.96	18.51	0.223

Figure S3. BET isotherm and pore size distributions of $CuFe_2O_4$ and Pd/$CuFe_2O_4$ nanowires



Recyclability of the catalyst: This recyclability of $Pd/CuFe_2O_4$ nanowires has been studied on the coupling of 4-methoxy iodobenzene with simple boronic acid. After the first run, the catalyst was recovered using centrifugation method. The catalyst present in the centrifuge tube was washed with a 1:1 mixture of ethyl acetate and acetone (5 × 10 mL) and dried in an oven. The recovered $Pd/CuFe_2O_4$ catalyst was reused for the next run, as depicted in Figure S3.

Figure S4: The process of recyclability of the catalyst $Pd/CuFe_2O_4$ nanowires.



General Procedure 1 (Synthesis of Biphenyls 3):

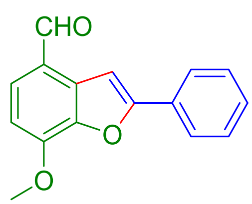
In an oven-dried Schlenk tube, were added iodoarene **1** (0.25 mmol), arylboroic acid **2** (0.5 mmol), $Pd/CuFe_2O_4$ nanowires catalyst (5 mg, 4 mol%), K_2CO_3 (138 mg, 0.5 mmol) and solvent DMSO (1 mL). The resulting reaction mixture was stirred at 120 °C for 10 min to 12 h. The progress of the reaction was monitored by TLC. Then the reaction mixture was allowed to cool to room temperature, diluted with aqueous NH_4Cl (10 mL) solution followed by extracted with ethyl acetate (3 × 10 mL). The organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent, furnished the biphenyls **3**.

General Procedure 2 (Synthesis of Diphenyl Acetylenes 5):

In an oven-dried Schlenk tube, were added iodoarenes **1** (0.5 mmol), terminal alkynes **4** (1 mmol), Pd/$CuFe_2O_4$ nanowires catalyst (5 mg, 4 mol%), K_2CO_3 (138 mg, 1 mmol) and solvent (DMSO) (1 mL) were added. The resulting reaction mixture was stirred at 120 °C for 12 h. The progress of the reaction was monitored by TLC. Then the reaction mixture was allowed to cool to room temperature, diluted with aqueous NH_4Cl (10 mL) solution followed by extracted with ethyl acetate (3 × 10 mL). The organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent, furnished the diphenyl acetylene **5**.

General Procedure 3 (Synthesis of Benzofurans 7):

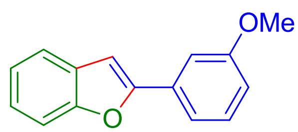
In an oven-dried Schlenk tube 2-iodophenol **1** (0.5 mmol), terminal alkyne **4** (0.5 mmol), Pd/$CuFe_2O_4$ (5 mg, 4 mol%), K_2CO_3 (138 mg, 1 mmol) and solvent (DMSO) (1 mL) were added. The resulting reaction mixture was stirred at 120 °C for 5 to 30 min. The progress of the reaction was monitored by TLC. Then the reaction mixture was allowed to cool to room temperature, diluted with aqueous NH_4Cl (10 mL) solution followed by extracted with ethyl acetate (3 × 10 mL). The organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent, furnished the benzofuran **7**.



7ra

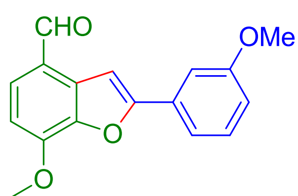
This compound was prepared according to the GP and isolated as colorless liquid 96% yield (107 mg):[TLC (petroleum ether/ethyl acetate 9:1, R_f(**1r**)=0.50, R_f(**4a**)=0.60, UV detection]. ^{1}H NMR

(CDCl$_3$, 400 MHz) δ = 10.06 (s, 1 H), 7.95 (d, *J* = 7.8 Hz, 2 H), 7.80 (s, 1 H), 7.67 (d, *J* = 8.3 Hz, 1 H), 7.51 - 7.43 (m, 2 H), 7.43 - 7.35 (m, 1 H), 6.90 (d, *J* = 8.3 Hz, 1 H), 4.14 (s, 3 H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 190.8 (CH), 159.0 (Cq), 149.8 (Cq), 144.1 (Cq), 132.1 (CH), 129.9 (Cq), 129.7 (Cq), 129.3 (CH), 128.9 (CH), 125.4 (CH), 123.0 (Cq), 106.1 (CH), 102.0 (CH), 56.5 (CH$_3$). HR-MS (ESI$^+$) m/z calculated for $[C_{16}H_{13}O_3]^+$=[M+H]$^+$: 253.0859; found: 253.0863.



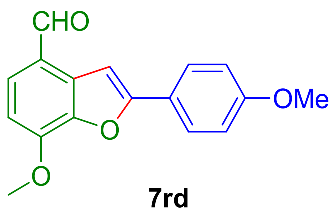
7nc

This compound was prepared according to the GP and isolated as colorless liquid 93% yield (105 mg):[TLC (petroleum ether/ethyl acetate 9:1, R_f(**1n**)=0.50, R_f(**4c**)=0.60, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ*=7.59 (d, *J*=7.3 Hz, 1H), 7.53 (d, *J*=7.3 Hz, 1H), 7.46 (d, *J*=8.8 Hz, 1H), 7.42 (s, 1H), 7.36 (dd, *J*=7.8 and 7.8 Hz, 1H), 7.29 (dd, *J*=8.3 and 7.3 Hz, 1H), 7.23 (d, *J*=7.3 Hz, 1H), 7.03 (s, 1H), 6.91 (dd, *J*=7.3 and 2.0 Hz, 1H), 3.89 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=159.9 (C$_q$), 155.7 (C$_q$), 154.8 (C$_q$), 131.7 (C$_q$), 129.8 (CH), 129.1 (C$_q$), 124.3 (CH), 122.9 (CH), 120.9 (CH), 117.5 (CH), 114.4 (CH), 111.2 (CH), 110.1 (CH), 101.6 (CH), 55.3 (CH$_3$) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{15}H_{13}O_2]^+$=[M+H]$^+$: 225.0910; found: 225.0895.



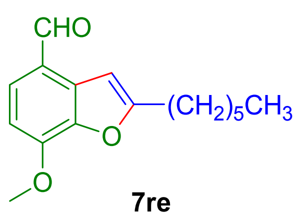
7rc

This compound was prepared according to the GP and isolated as pale yellow color viscous liquid 92% yield (128 mg):[TLC (petroleum ether/ethyl acetate 8:2, R_f(**1r**)=0.50, R_f(**4c**)=0.60, UV detection]. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ*=10.03 (s, 1H), 7.78 (s, 1H),7.65 (d, *J*=8.3 Hz, 1H), 7.53 (d, *J*=7.8 Hz, 1H), 7.44 (dd, *J*=2.4 and 2.0 Hz, 1H), 7.36 (dd, *J*=8.3 and 7.8 Hz, 1H), 6.93 (dd, *J*=8.8 and 3.2 Hz, 1H), 6.88 (d, *J*=8.3 Hz, 1H), 4.11 (s, 3H), 3.88 (s, 3H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=190.8 (C$_q$), 159.9 (C$_q$), 158.8 (C$_q$), 149.8 (C$_q$),144.0 (C$_q$), 132.1 (CH), 130.9 (C$_q$), 129.9 (CH), 129.8 (C$_q$), 122.9 (C$_q$), 118.0 (CH), 115.5 (CH), 110.3 (CH), 106.1 (CH), 102.2 (CH), 56.4 (CH_3), 55.4 (CH_3) ppm. HR-MS (ESI^+) m/z calculated for $[C_{17}H_{15}O_4]^+$=$[M+H]^+$: 283.0965; found: 283.0973.



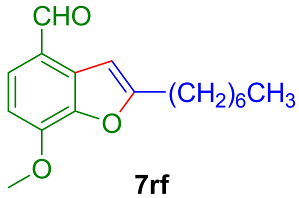
7rd

This compound was prepared according to the GP and isolated as brown color solid 89% yield (127 mg):mp 80-82°C;[TLC (petroleum ether/ethyl acetate 8:2, R_f(**1r**)=0.40, R_f(**4d**)=0.50, UV detection]. ^1H NMR ($CDCl_3$, 400 MHz): δ=10.04 (s, 1H), 7.87 (d, J=8.8 Hz, 1H), 7.65 (s, 1H), 7.63 (d, J=8.3 Hz, 1H), 6.97 (d, J=8.8 Hz, 1H), 6.85 (d, J=8.3 Hz, 1H), 4.12 (s, 3H), 3.86 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=190.8 (C_q), 160.6 (C_q), 159.3 (C_q), 149.6 (C_q), 143.8 (C_q), 131.8 (CH), 130.4 (C_q), 127.0 (CH), 122.7 (C_q), 122.5 (C_q), 114.3 (CH), 105.8 (CH), 100.4 (CH), 56.4 (CH_3), 55.4 (CH_3) ppm. HR-MS (ESI^+) m/z calculated for $[C_{17}H_{15}O_4]^+$=$[M+H]^+$: 283.0965; found: 283.0971.



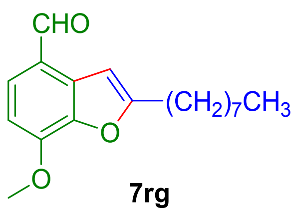
7re

This compound was prepared according to the GP and isolated as brown color viscous liquid 85% yield (114 mg):[TLC (petroleum ether/ethyl acetate 8:2, R_f(**1r**)=0.50, R_f(**4e**)=0.60, UV detection]. ^1H NMR ($CDCl_3$, 400 MHz): δ=10.01 (s, 1H), 7.62 (d, J=8.3 Hz, 1H), 7.14 (s, 1H), 6.82 (d, J=8.3 Hz, 1H), 4.08 (s, 3H), 2.81 (t, J=7.3 Hz, 2H), 1.85-1.70 (m, 2H),1.45-1.15 (m, 6H), 0.87 (t, J=7.3 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.6 (C_q), 131.3 (CH), 129.8 (C_q), 122.6 (C_q), 105.0 (CH), 102.6 (CH), 56.3 (CH_3), 31.5 (CH_2), 28.9 (CH_2), 28.5 (CH_2), 27.6 (CH_2), 22.5 (CH_2), 14.0 (CH_3) ppm. HR-MS (ESI^+) m/z calculated for $[C_{16}H_{20}NaO_3]^+$ = $[M+Na]^+$: 283.1305; found: 283.1308.



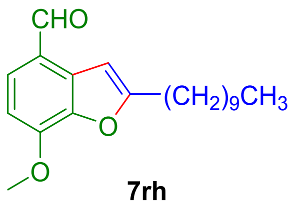
7rf

This compound was prepared according to the GP and isolated as brown color viscous liquid 87% yield (119 mg):[TLC (petroleum ether/ethyl acetate 9:1, R_f(**1r**)=0.40, R_f(**4f**)=0.70, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=10.02 (s, 1H), 7.63 (d, J=8.3 Hz, 1H), 7.15 (s, 1H), 6.84 (d, J=8.3 Hz, 1H), 4.09 (s, 3H), 2.83 (t, J=7.8 Hz, 2H), 1.85-1.70 (m, 2H), 1.45-1.15 (m, 8H), 0.88 (t, J=7.8 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.7 (C_q), 131.3 (CH), 129.9 (C_q), 122.6 (C_q), 105.0 (CH), 102.6 (CH), 56.3 (CH_3), 31.7 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.5 (CH_2), 27.6 (CH_2), 22.6 (CH_2), 14.0 (CH_3) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{17}H_{22}NaO_3]^+$=$[M+Na]^+$: 297.1461; found: 297.1465.



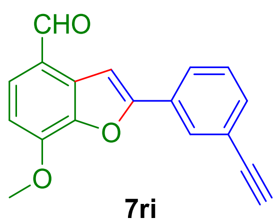
7rg

This compound was prepared according to the GP and isolated as brown color viscous liquid 92% yield (130 mg):[TLC (petroleum ether/ethyl acetate 8:2, R_f(**1r**)=0.50, R_f(**4g**)=0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=10.01 (s, 1H), 7.62 (d, J=8.3 Hz, 1H), 7.14 (s, 1H), 6.83 (d, J=8.3 Hz, 1H), 4.08 (s, 3H), 2.81 (t, J=7.3 Hz, 2H), 1.85-1.70 (m, 2H),1.45-1.15 (m, 10H), 0.87 (t, J=7.3 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.7 (C_q), 131.3 (CH), 129.9 (C_q), 122.6 (C_q), 105.1 (CH), 102.6 (CH), 56.3 (CH_3), 31.8 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 27.6 (CH_2), 22.6 (CH_2), 14.1 (CH_3) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{18}H_{26}O_3]^+$=$[M+H]^+$: 289.1798; found: 289.1801.



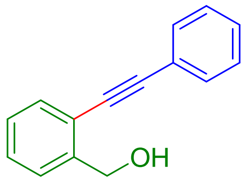
7rh

This compound was prepared according to the GP and isolated as pale yellow color liquid 94% yield (144 mg):[TLC (petroleum ether/ethyl acetate 8:2, R_f(**1r**)=0.50, R_f(**4h**)=0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz): *δ*=10.01 (s, 1H), 7.62 (d, *J*=7.8 Hz, 1H), 7.14 (s, 1H), 6.83 (d, *J*=8.3 Hz, 1H), 4.08 (s, 3H), 2.82 (t, *J*=7.3 Hz, 2H), 1.85-1.70 (m, 2H), 1.45-1.15 (m, 14H), 0.87 (t, *J*=7.3 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): *δ*=190.8 (C_q), 163.4 (C_q), 149.4 (C_q), 143.7 (C_q), 131.3 (CH), 129.9 (C_q), 122.6 (C_q), 105.1 (CH), 102.6 (CH), 56.3 (CH_3), 31.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (2C, CH_2), 29.2 (CH_2), 28.5 (CH_2), 27.6 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. HR-MS (ESI$^+$) m/z calculated for $[C_{20}H_{28}NaO_3]^+$=$[M+Na]^+$: 339.1931; found: 339.1930.



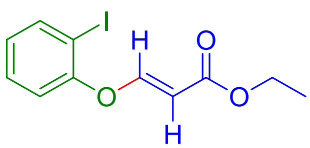
7ri

This compound was prepared according to the GP and isolated as a block color solid compound with 76% yield (105 mg):[TLC (petroleum ether/ethyl acetate 8:2, R_f(**1r**)=0.50, R_f(**4i**)=0.60, UV detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 10.00 (s, 1 H), 8.03 (s, 1 H), 7.85 (d, *J* = 7.8 Hz, 1 H), 7.76 (s, 1 H), 7.61 (d, *J* = 8.3 Hz, 1 H), 7.47 (td, *J* = 1.3, 7.6 Hz, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 6.84 (d, *J* = 7.8 Hz, 1 H), 4.08 (s, 3 H), 3.15 (s, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 190.6 (CH), 157.7 (Cq), 149.8 (Cq), 144.1 (Cq), 132.6 (CH), 132.1 (CH), 129.9 (Cq), 129.5 (Cq), 128.9 (CH), 128.8 (CH), 125.6 (CH), 122.9 (Cq), 122.9 (Cq), 106.2 (CH), 102.6 (CH), 83.0 (Cq), 78.0 (Cq), 56.4 (CH_3). HR-MS (ESI$^+$) m/z calculated for $[C_{18}H_{13}O_3]^+$=$[M+H]^+$: 277.0859; found: 277.0870.



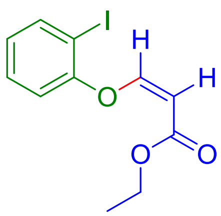
5qa

This compound was prepared according to the GP and isolated as a block color solid compound with 86% yield (45 mg):[TLC (petroleum ether/ethyl acetate 8:2, R_f(**1q**)=0.50, R_f(**4a**)=0.60, UV detection]. ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.57 - 7.50 (m, 3 H), 7.50 - 7.45 (m, 1 H), 7.38 - 7.32 (m, 5 H), 4.91 (s, 2 H), 2.19 (br. s., 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 142.6 (Cq), 132.2 (CH), 131.6 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 127.5 (CH), 127.3 (CH), 122.9 (Cq), 121.3 (Cq), 94.2 (Cq), 86.7 (Cq), 64.0 (CH_2). HR-MS (ESI^+) m/z calculated for $[C_{15}H_{16}NO]^+$=$[M+NH_4]^+$: 226.1226; found: 226.1228.



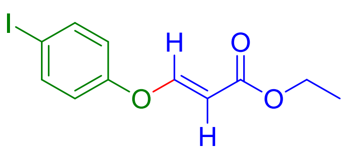
E isomer, 6nb

This compound was prepared according to the GP and isolated as a block color solid compound with 57% yield (45 mg):[TLC (petroleum ether/ethyl acetate 10:0, R_f(**1n**)=0.50, R_f(**4b**)=0.80, UV& I_2 detection]. ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.84 (dd, J = 1.5, 7.8 Hz, 1 H), 7.70 (d, J = 12.2 Hz, 1 H), 7.41 - 7.32 (m, 1 H), 7.07 (dd, J = 1.2, 8.1 Hz, 1 H), 6.95 (dt, J = 1.5, 7.6 Hz, 1 H), 5.50 (d, J = 12.2 Hz, 1 H), 4.19 (q, J = 6.8 Hz, 2 H), 1.33 - 1.22 (t, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.0 (Cq), 158.8 (CH), 155.1 (Cq), 140.0 (CH), 130.0 (CH), 127.0 (CH), 119.1 (CH), 102.7 (CH), 87.9 (Cq), 60.2 (CH_2), 14.3 (CH_3). HR-MS (ESI^+) m/z calculated for $[C_{11}H_{11}NaIO_3]^+$=$[M+Na]^+$: 340.9645; found: 340.9658.



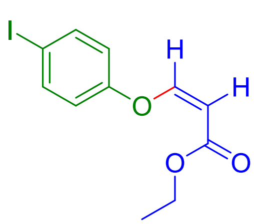
Z isomer, 6nb'

This compound was prepared according to the GP and isolated as a block color solid compound with 39% yield (31 mg):[TLC (petroleum ether/ethyl acetate 10:0, R_f(**1n**)=0.50, R_f(**4b**)=0.80, UVUV& I_2 detection].^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.84 (dd, *J* = 1.5, 7.8 Hz, 1 H), 7.40 - 7.31 (m, 1 H), 7.03 (dd, *J* = 1.5, 8.3 Hz, 1 H), 6.96 - 6.88 (m, 1 H), 6.75 (d, *J* = 6.8 Hz, 1 H), 5.22 (d, *J* = 7.3 Hz, 1 H), 4.25 (q, *J* = 7.3 Hz, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 164.5 (Cq), 156.6 (Cq), 153.1 (CH), 140.0 (CH), 129.8 (CH), 126.4 (CH), 117.5 (CH), 101.3 (CH), 87.4 (Cq), 60.1 (CH_2), 14.4 (CH_3).



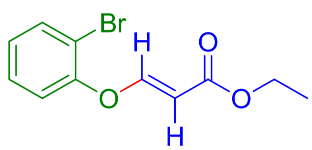
E isomer, 6ob

This compound was prepared according to the GP and isolated as a block color solid compound with 51% yield (43 mg):[TLC (petroleum ether/ethyl acetate 10:0, R_f(**1o**)=0.50, R_f(**4b**)=0.80, UV& I_2 detection].^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.73 (d, *J* = 12.2 Hz, 1 H), 7.70 - 7.65 (m, 2 H), 6.87 - 6.82 (m, 2 H), 5.57 (d, *J* = 12.2 Hz, 1 H), 4.20 (q, 2 H), 1.29 (t, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.0 (Cq), 158.1 (CH), 155.7 (Cq), 139.0 (CH), 120.2 (CH), 103.0 (CH), 88.3 (Cq), 60.2 (CH_2), 14.3 (CH_3). HR-MS (ESI$^+$) m/z calculated for $[C_{11}H_{12}IO_3]^+$=$[M+H]^+$: 318.9826; found: 318.9830.



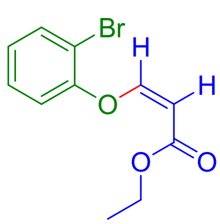
Z isomer, 6ob'

This compound was prepared according to the GP and isolated as a block color solid compound with 49% yield (40 mg):[TLC (petroleum ether/ethyl acetate 10:0, R_f(**1o**)=0.50, R_f(**4b**)=0.80, UV& I_2 detection].^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.66 (d, *J* = 8.8 Hz, 2 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.80 (d, *J* = 6.8 Hz, 1 H), 5.20 (d, *J* = 6.8 Hz, 1 H), 4.21 (q, 2 H), 1.30 (t, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 164.5 (Cq), 156.9 (Cq), 153.1 (CH), 138.8 (CH), 119.8 (CH), 101.0 (CH), 87.9 (Cq), 60.1 (CH_2), 14.3 (CH_3).



E-isomer, 6pb

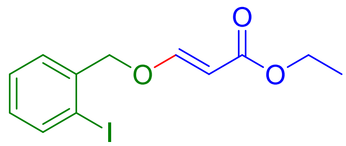
This compound was prepared according to the GP and isolated as a block color solid compound with 50% yield (68 mg):[TLC (petroleum ether/ethyl acetate 10:0, R_f(**1p**)=0.30, R_f(**4b**)=0.80, UV& I_2 detection].^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.71 (d, *J* = 12.2 Hz, 1 H), 7.61 (d, *J* = 7.8 Hz, 1 H), 7.37 - 7.30 (m, 1 H), 7.14 - 7.06 (m, 2 H), 5.46 (d, *J* = 12.2 Hz, 1 H), 4.19 (q, *J* = 7.3 Hz, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 166.9 (Cq), 158.9 (CH), 152.3 (Cq), 134.0 (CH), 128.9 (CH), 126.7 (CH), 120.3 (CH), 114.2 (Cq), 102.5 (CH), 60.2 (CH_2), 14.3 (CH_3). HR-MS (ESI^+) m/z calculated for $[C_{11}H_{12}BrO_3]^+$=$[M+H]^+$: 270.9964; found: 270.9974.



Z-isomer, 6pb'

This compound was prepared according to the GP and isolated as a block color solid compound with 49% yield (66 mg):[TLC (petroleum ether/ethyl acetate 10:0, R_f(**1p**)=0.50, R_f(**4b**)=0.80, UV& I_2 detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.60 (dd, *J* = 1.5, 7.8 Hz, 1 H), 7.34 - 7.29 (m, 1 H), 7.12 - 7.03 (m, 2 H), 6.76 (d, *J* = 6.8 Hz, 1 H), 5.21 (d, *J* = 6.8 Hz, 1 H), 4.24 (q, *J* =

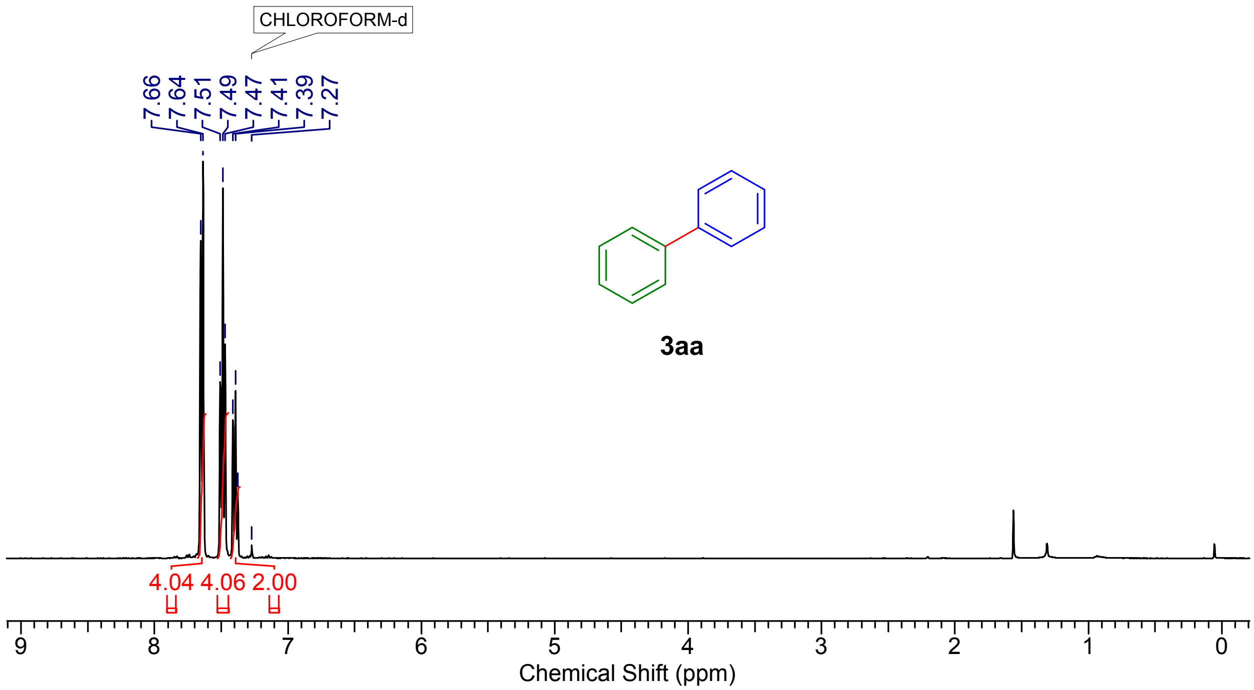
7.3 Hz, 2 H), 1.32 (t, J = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 164.5 (Cq), 154.0 (Cq), 153.4 (CH), 133.9 (CH), 128.8 (CH), 126.1 (CH), 118.7 (CH), 113.8 (Cq), 101.1 (CH), 60.1 (CH_2), 14.3 (CH_3).



6qb

This compound was prepared according to the GP and isolated as a block color solid compound with 72% yield (120 mg):[TLC (petroleum ether/ethyl acetate 10:0, R_f(**1p**)=0.40, R_f(**4b**)=0.80, UV& I_2 detection]. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.86 (d, J = 7.8 Hz, 1 H), 7.71 (d, J = 12.7 Hz, 1 H), 7.39 (d, J = 4.4 Hz, 2 H), 7.08 - 7.01 (m, 1 H), 5.35 (d, J = 12.7 Hz, 1 H), 4.89 (s, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 1.29 (t, J = 7.1 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 167.6 (Cq), 161.6 (CH), 139.5(CH), 137.6 (Cq), 130.0 (CH), 128.8 (CH), 128.5 (CH), 97.8 (CH), 97.4 (Cq), 76.3 (CH_2), 60.0 (CH_2), 14.4 (CH_3). HR-MS (ESI^+) m/z calculated for $[C_{12}H_{14}IO_3]^+$=$[M+H]^+$: 232.9982; found: 232.9990.

Figure S5: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3aa** in $CDCl_3$



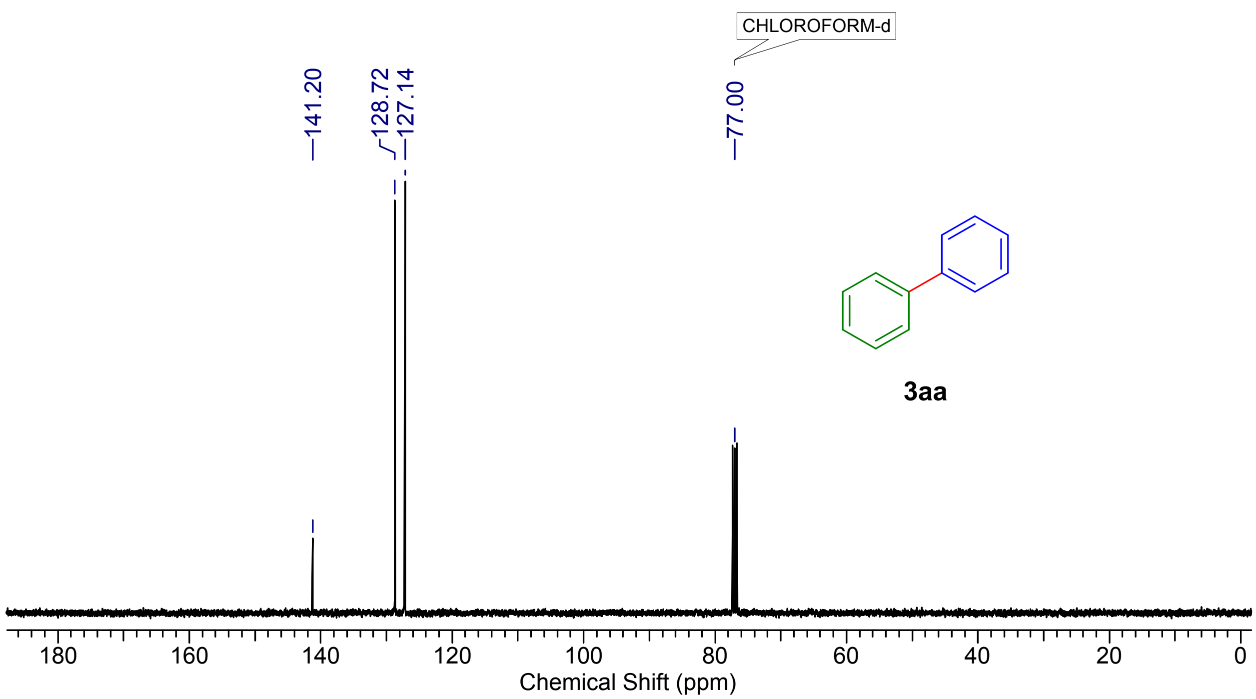
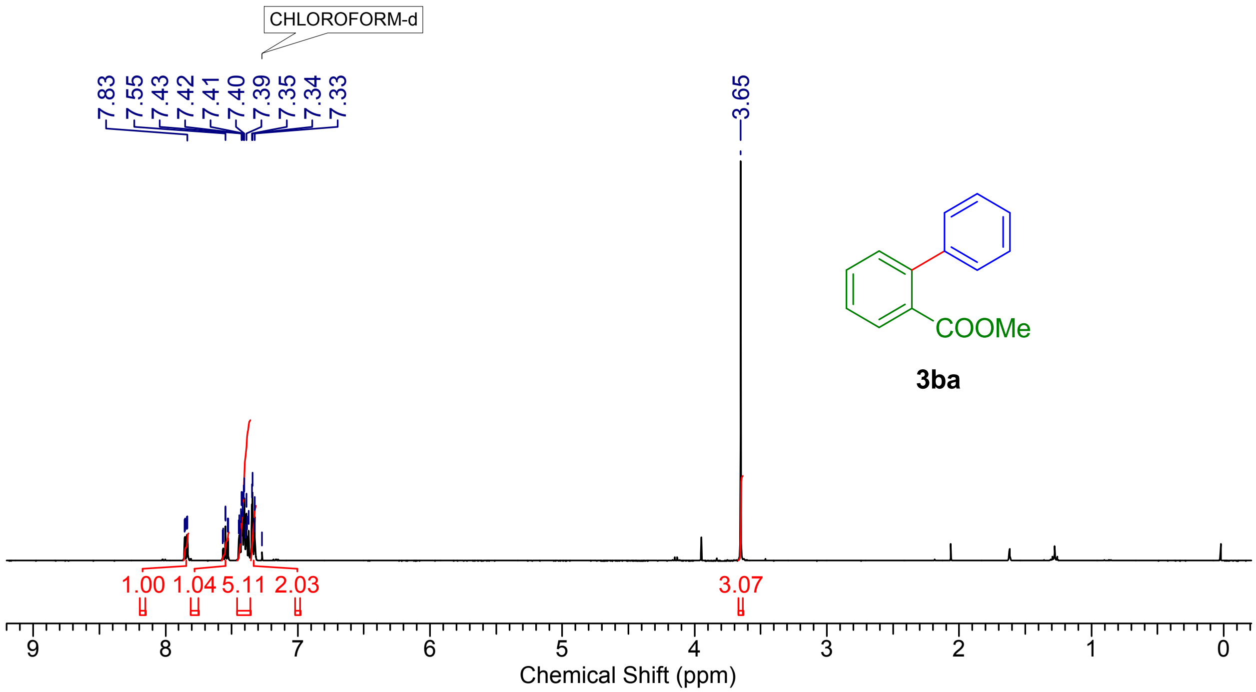


Figure S6: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3ba** in $CDCl_3$



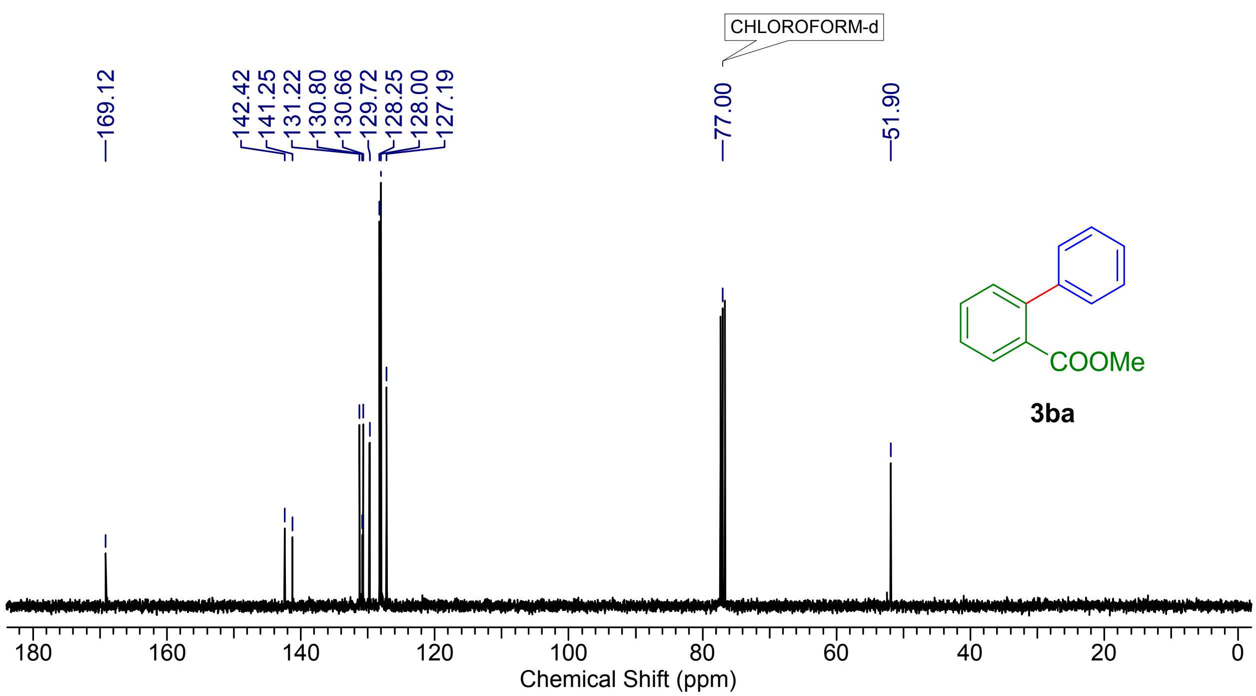
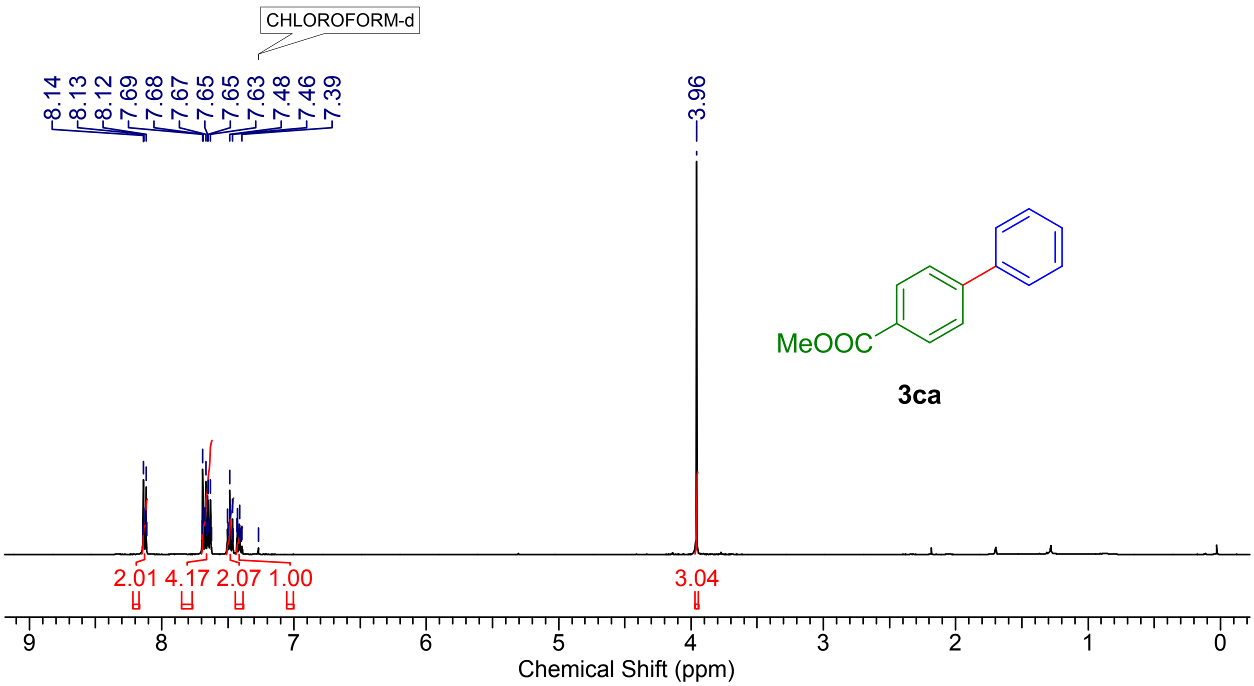


Figure S7: [1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **3ca** in $CDCl_3$



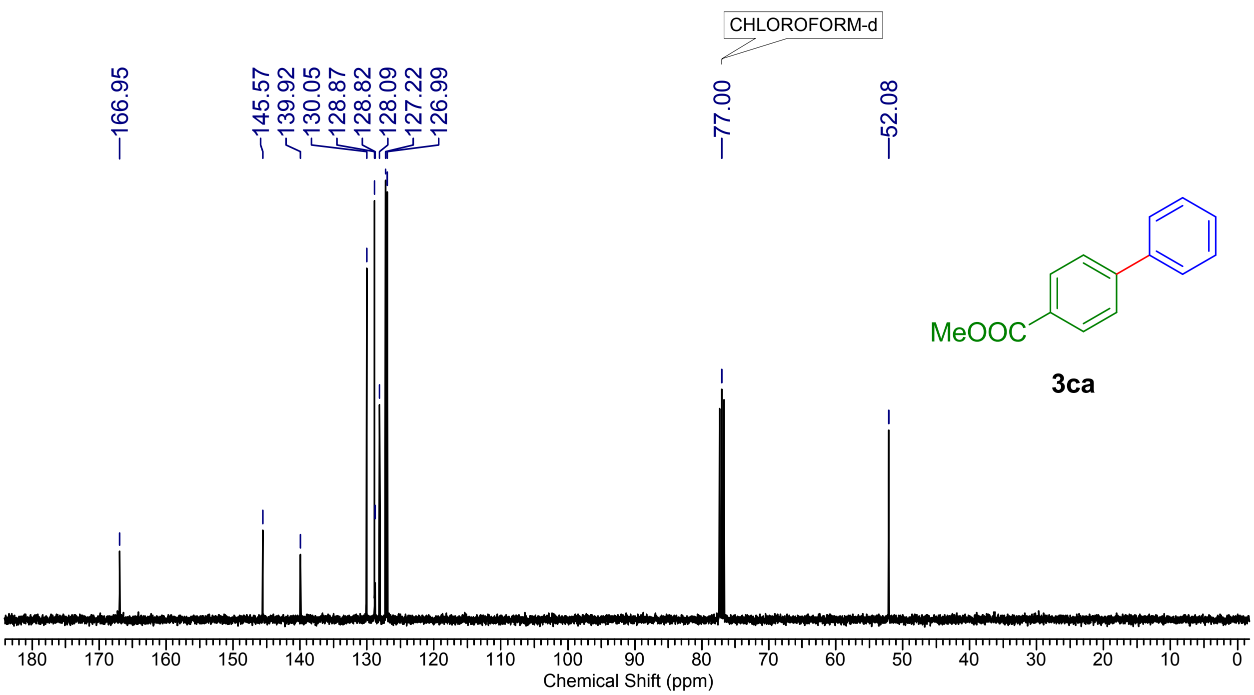
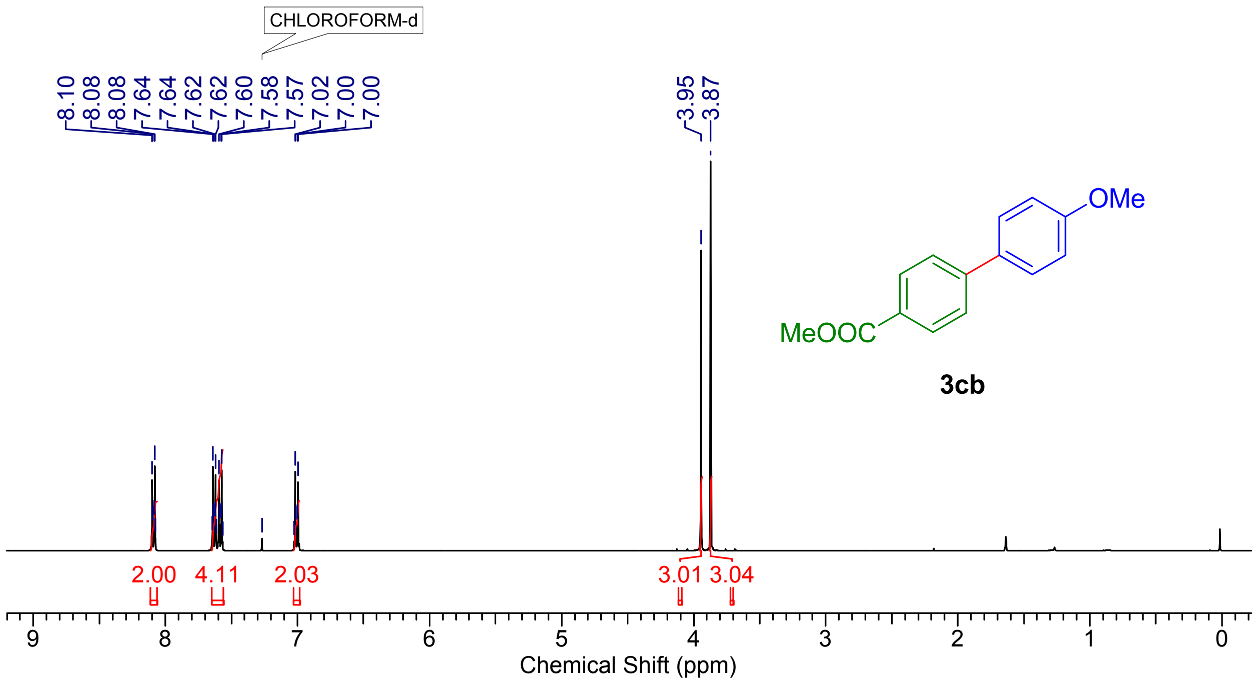


Figure S8: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3cb** in $CDCl_3$



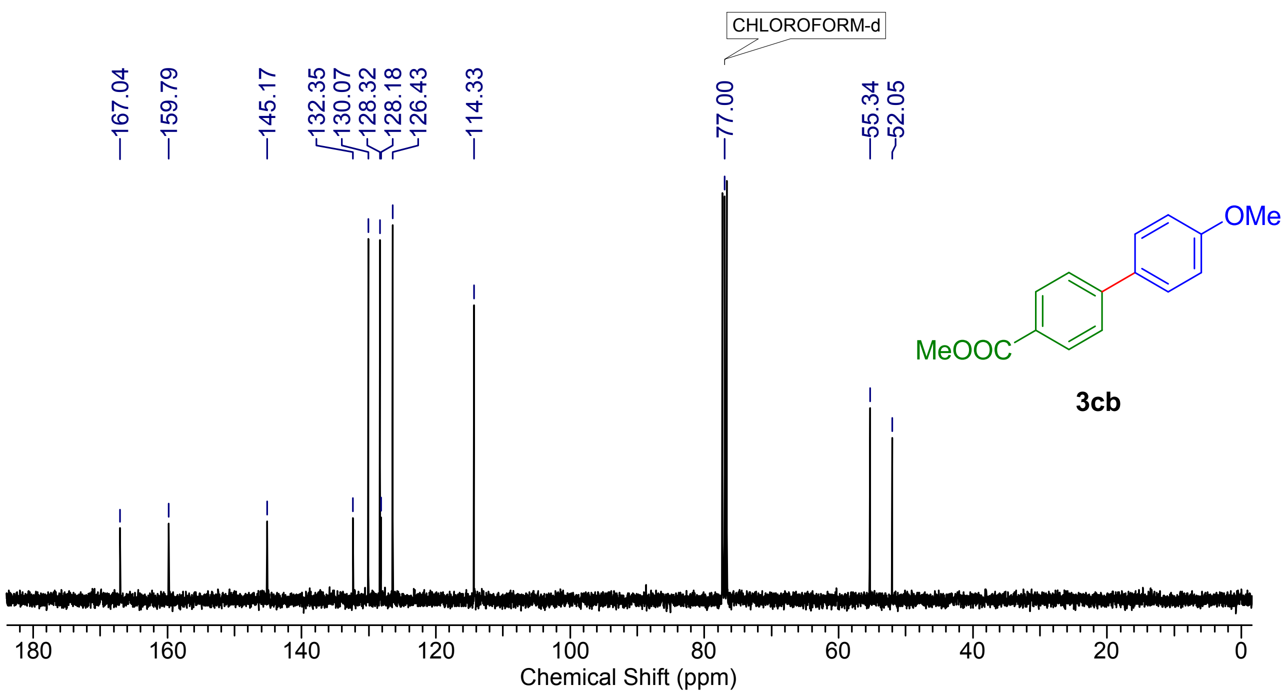
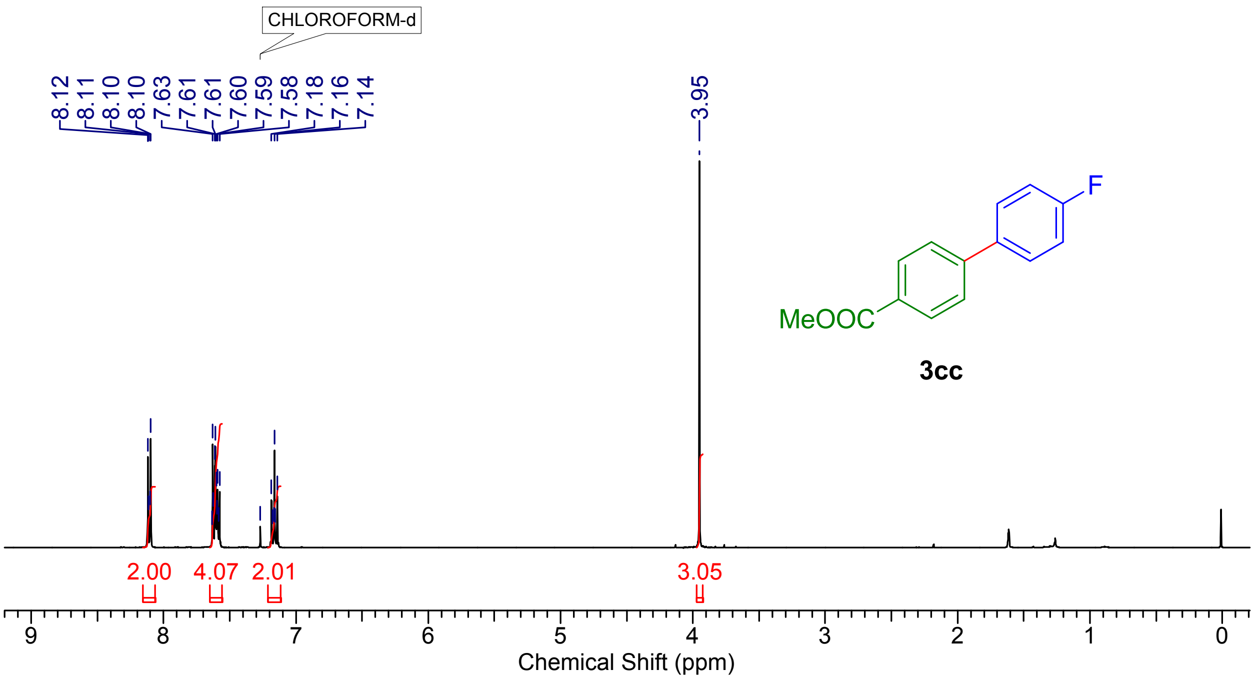


Figure S9: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3cc** in $CDCl_3$



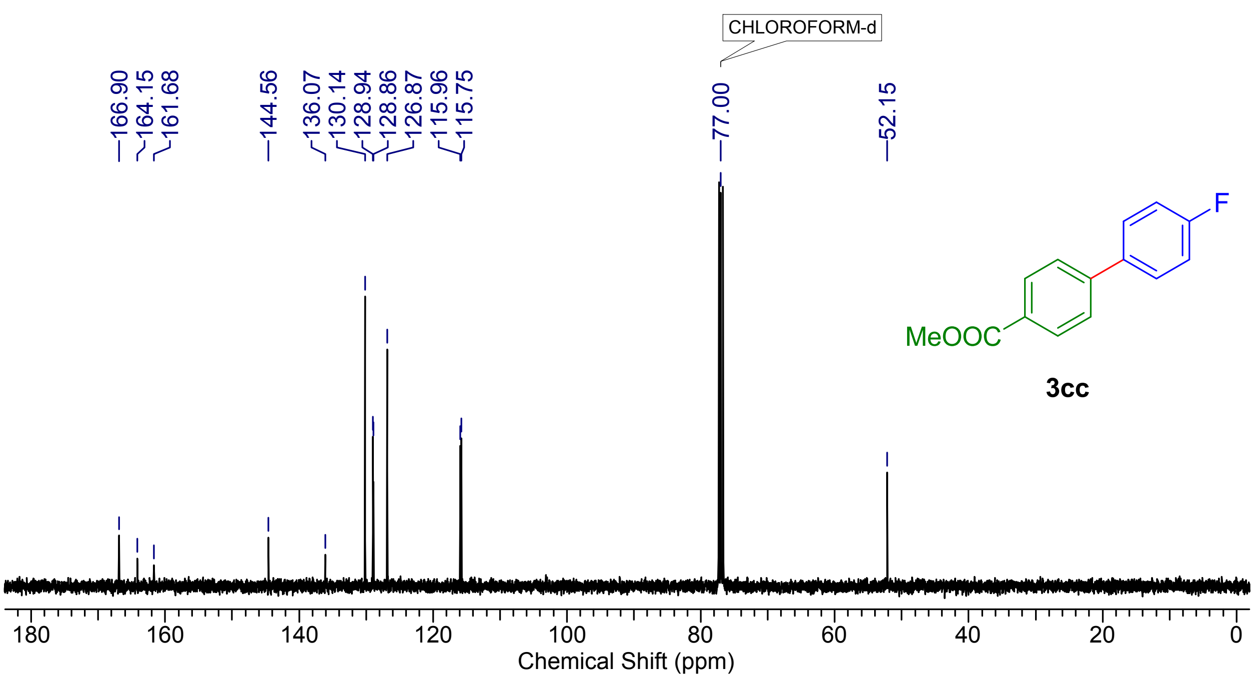
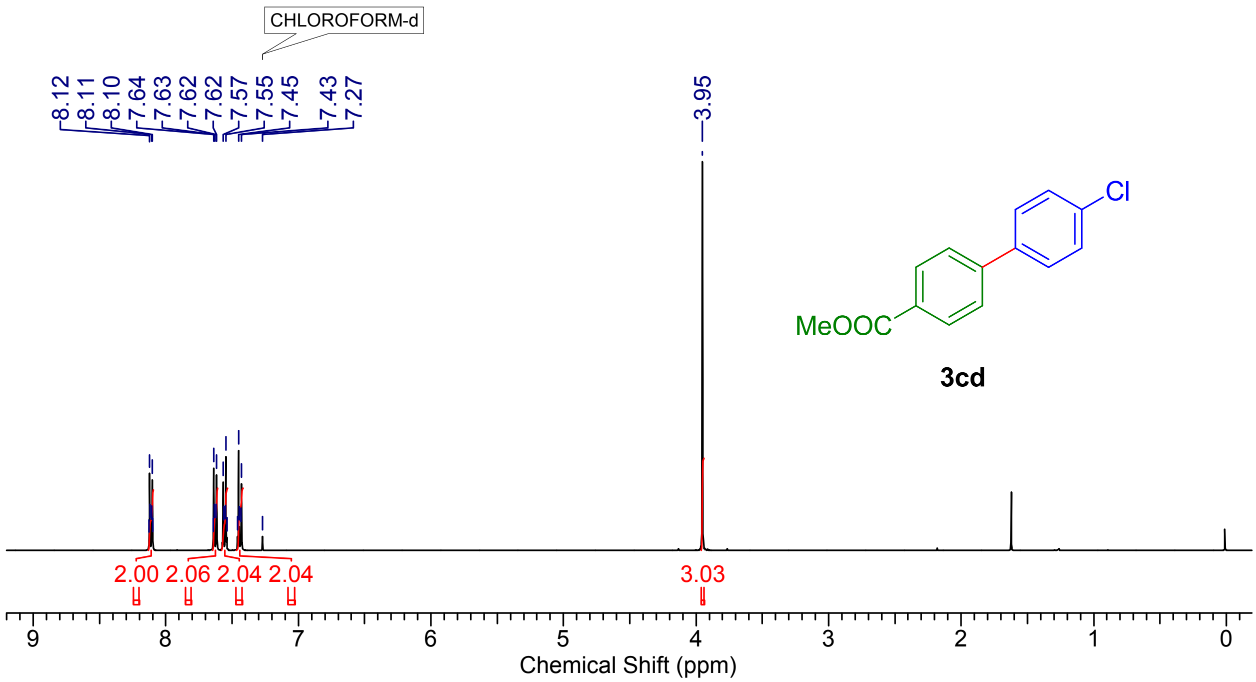


Figure S10:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **3cd** in $CDCl_3$



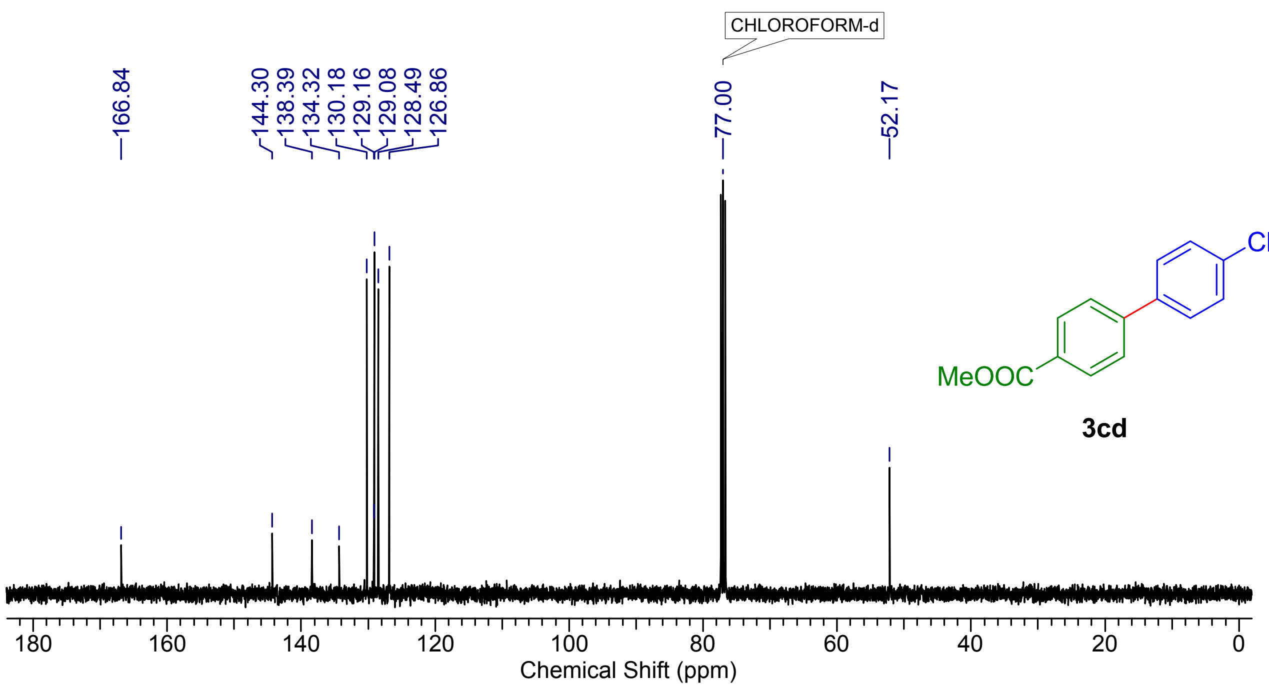
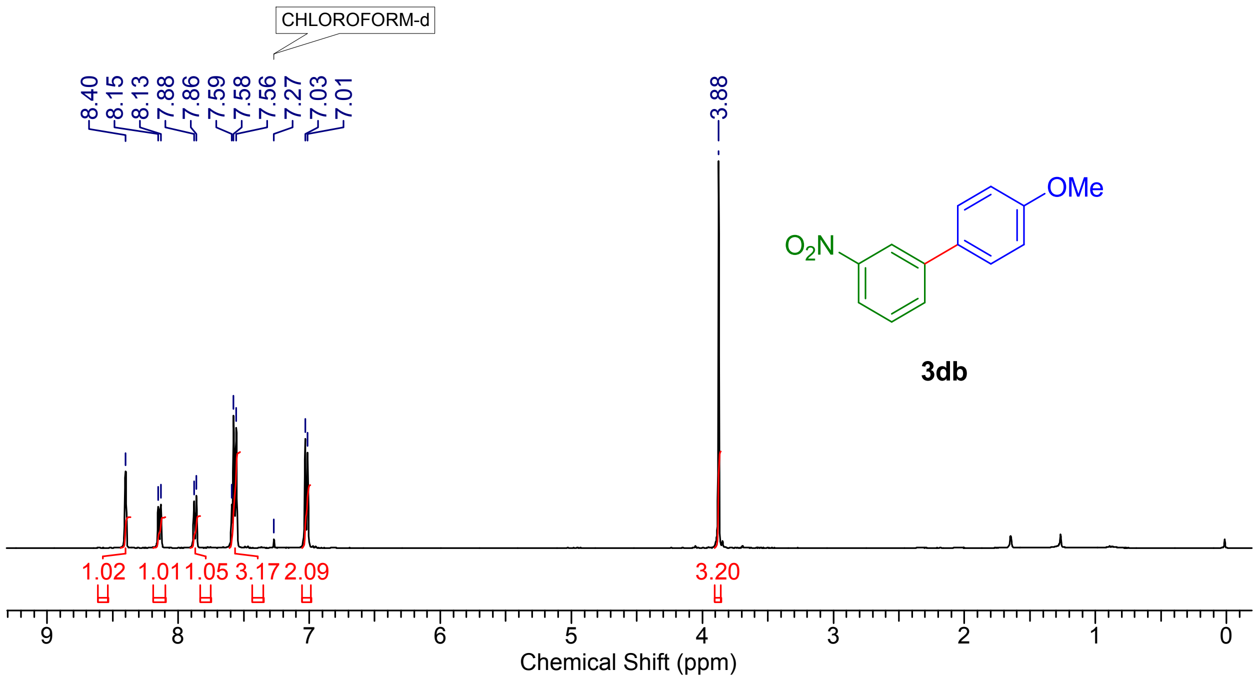


Figure S11:^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3db** in $CDCl_3$



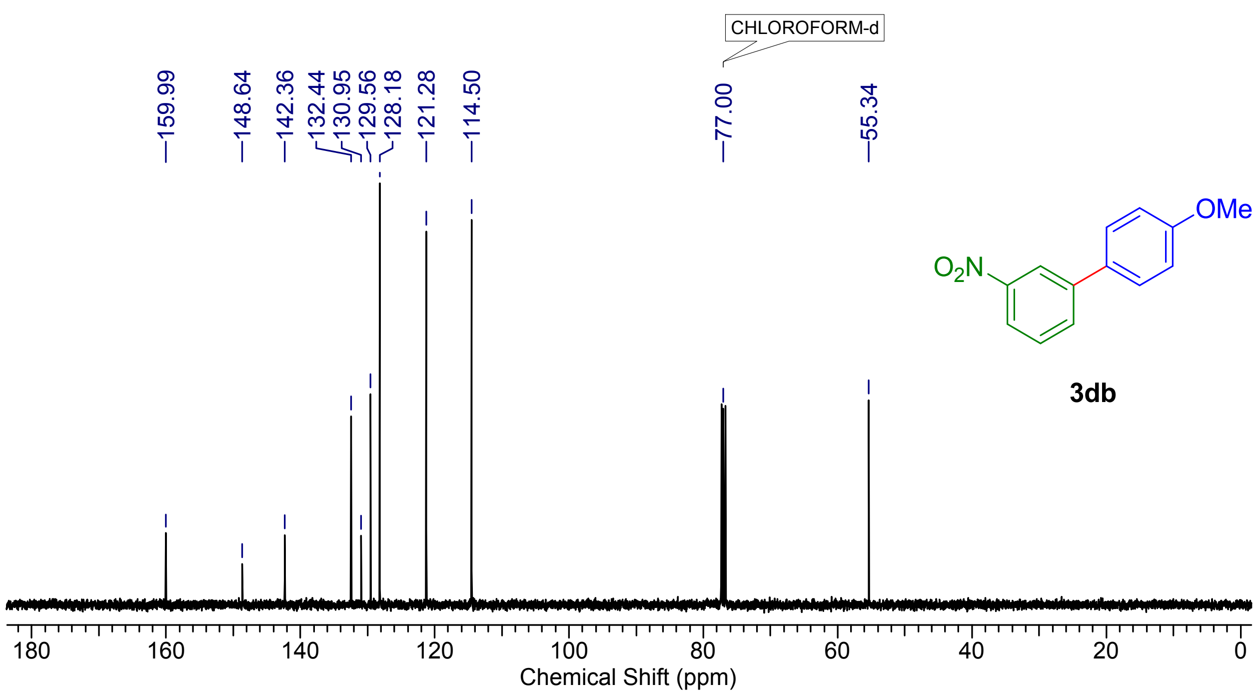
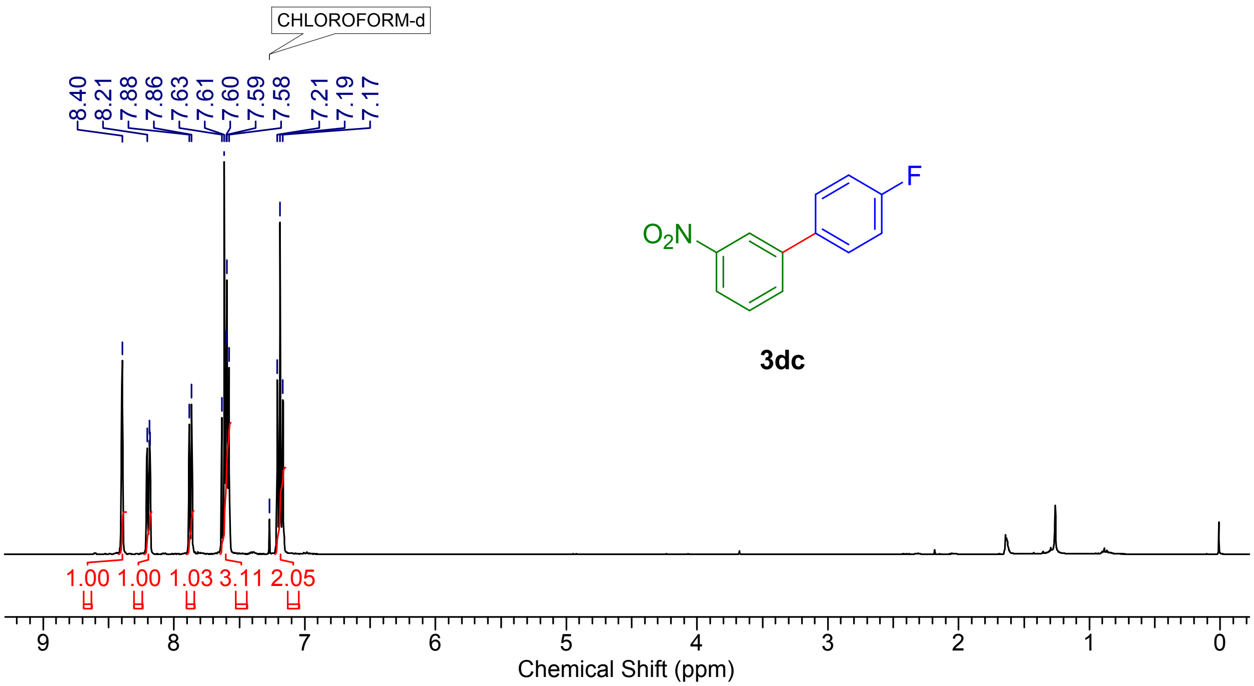


Figure S12: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3dc** in $CDCl_3$



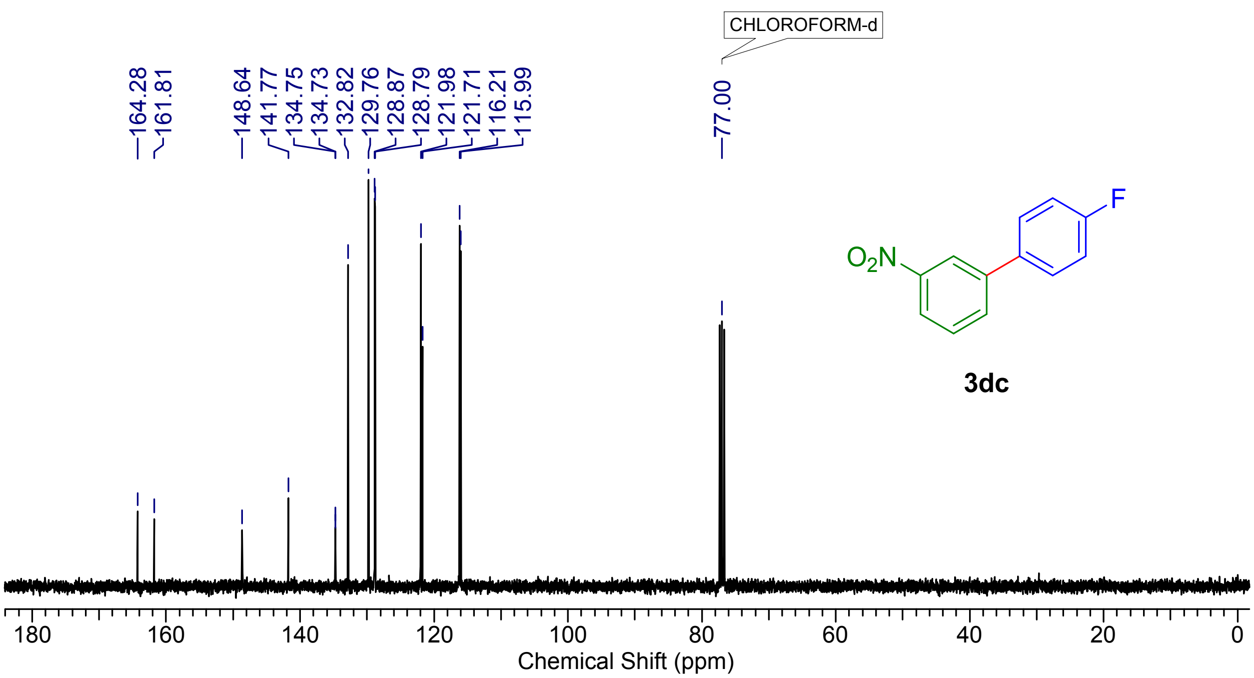
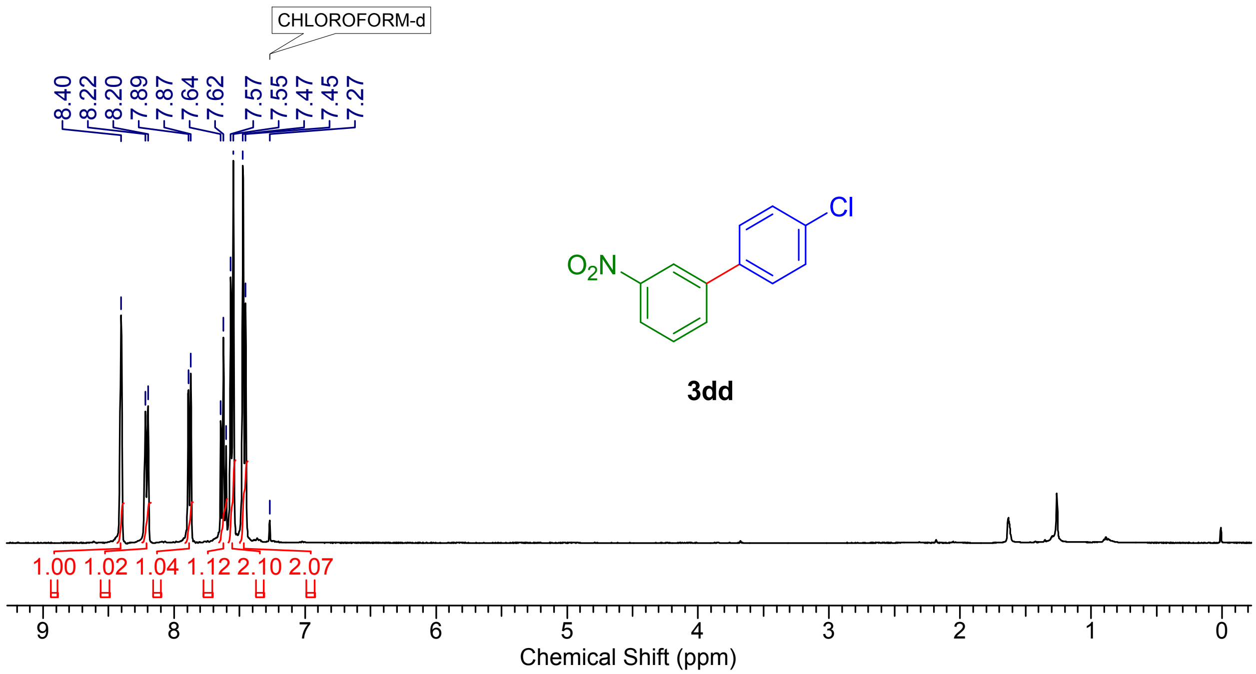


Figure S13: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3dd** in $CDCl_3$



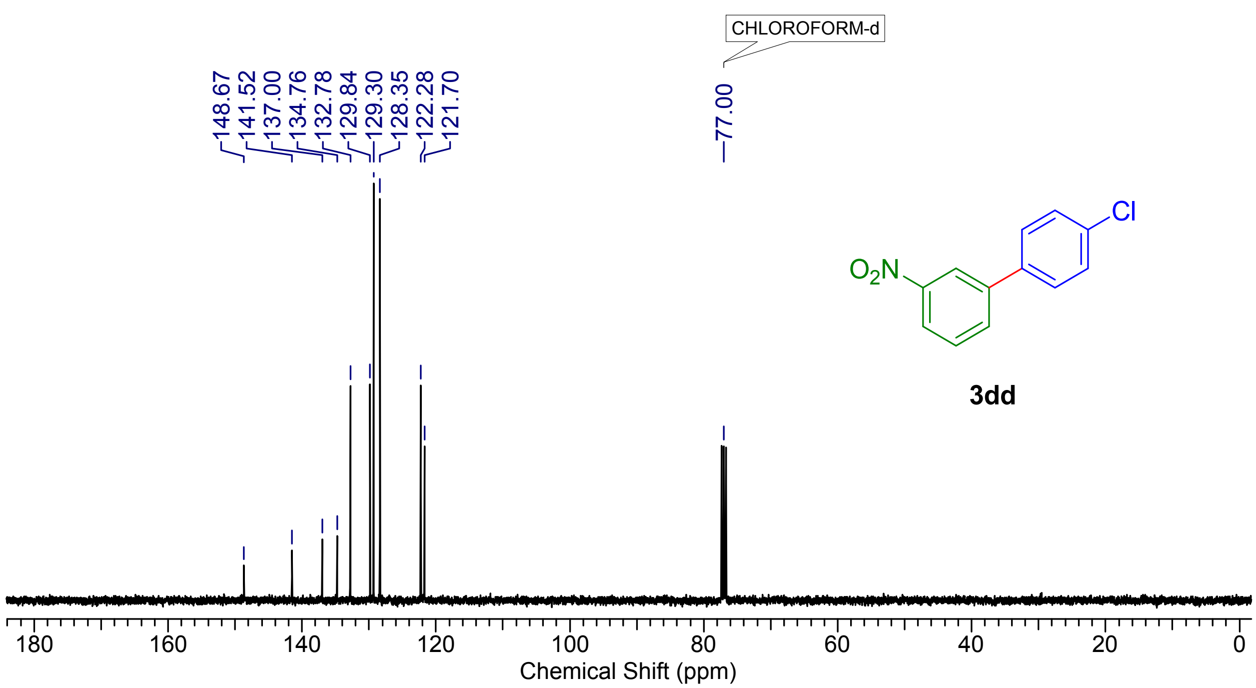
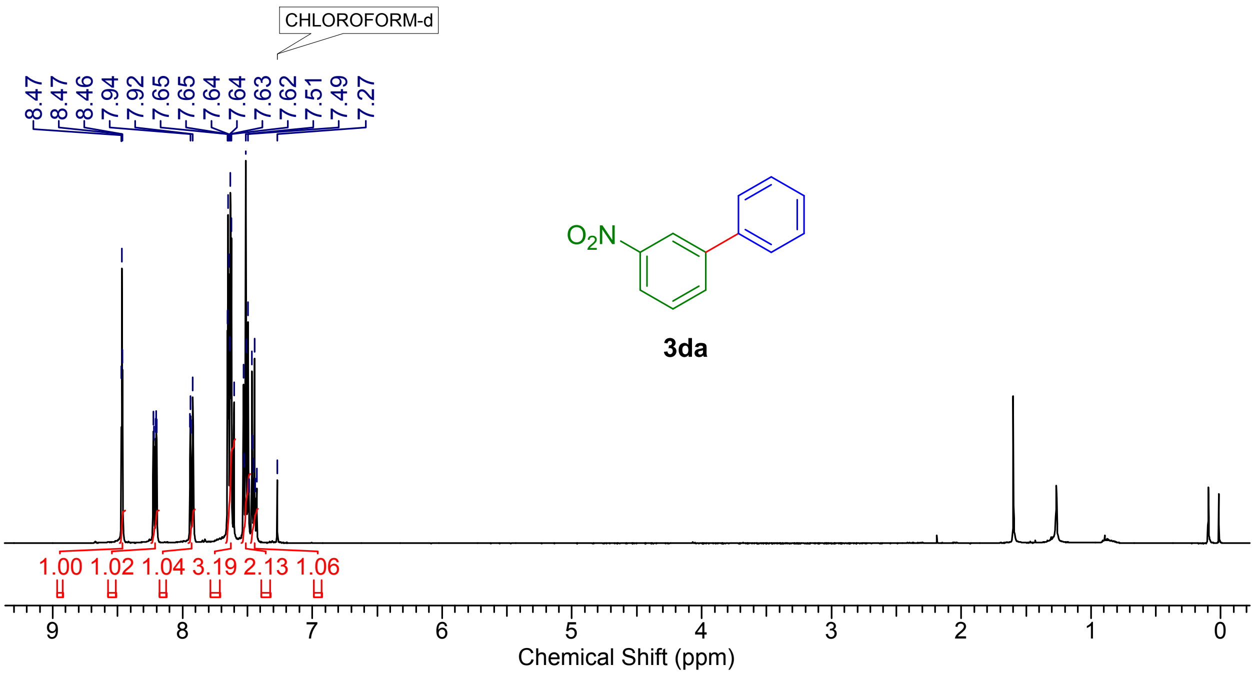


Figure S14: [1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **3ea** in $CDCl_3$



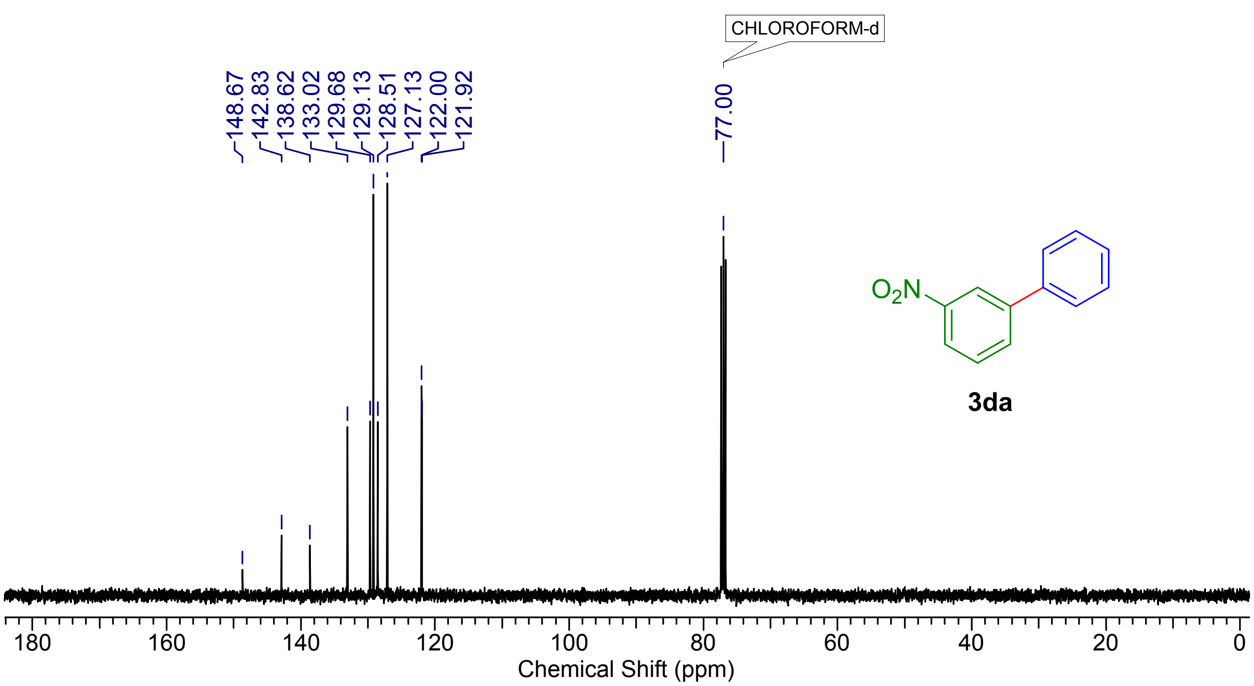
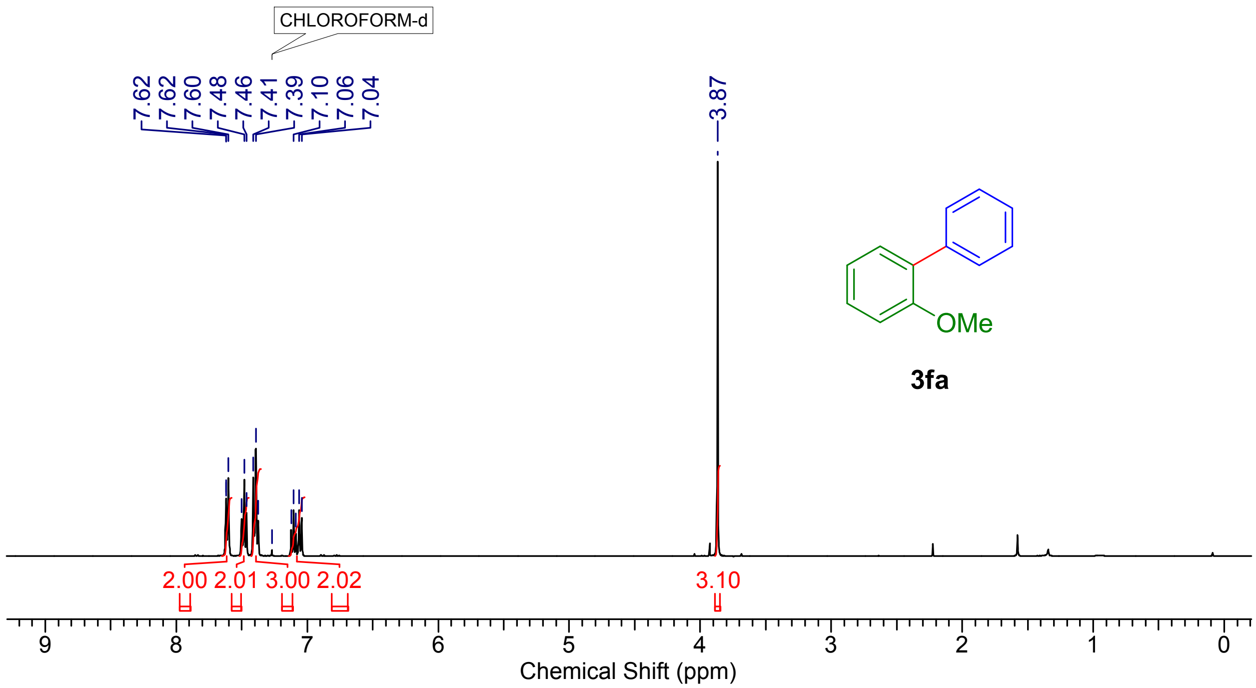


Figure S15: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3fa** in $CDCl_3$



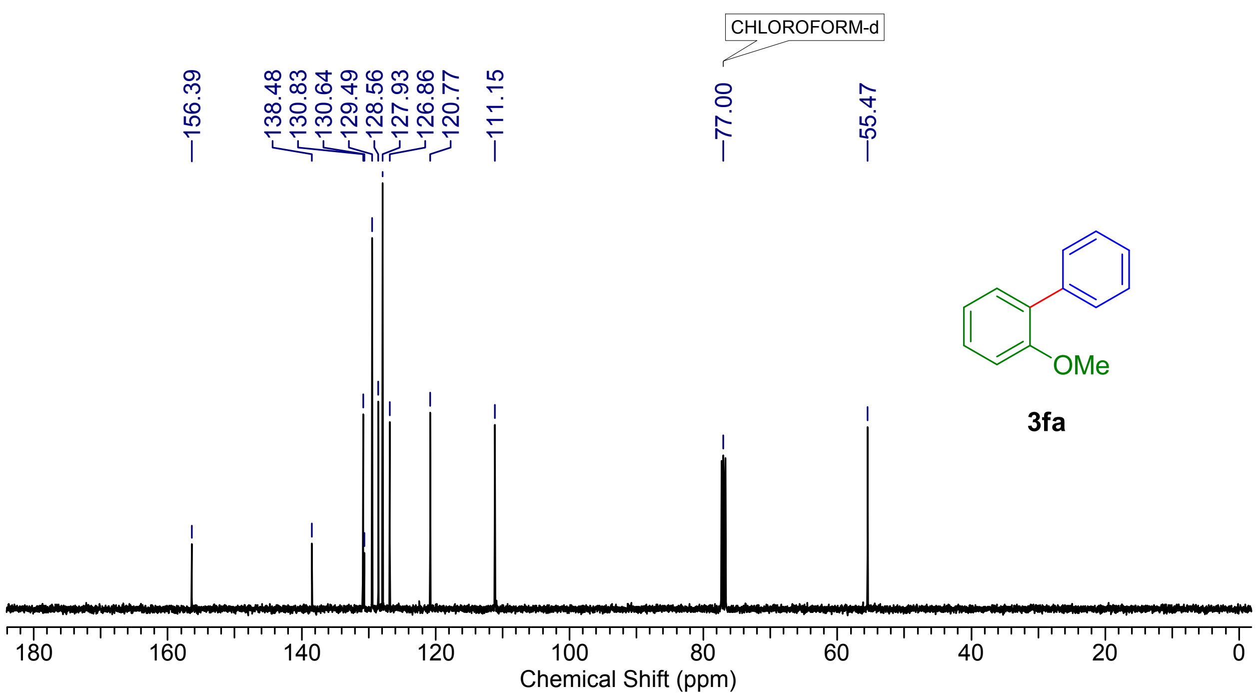
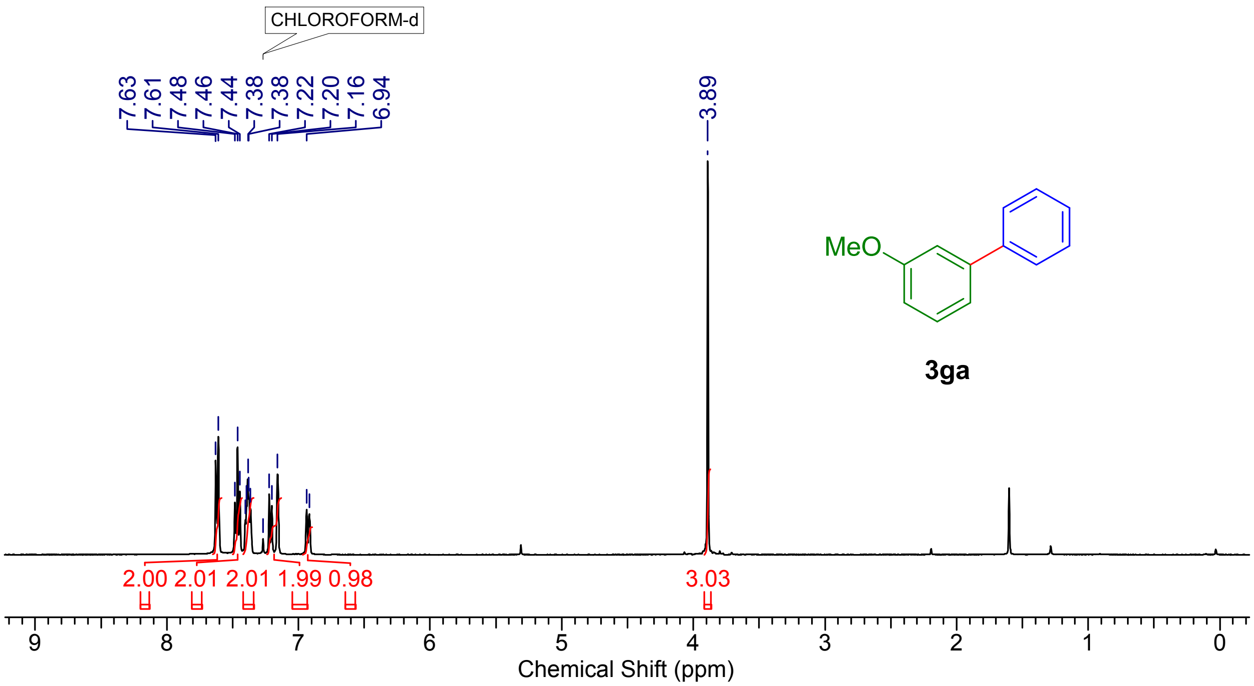


Figure S16:^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3ga** in $CDCl_3$



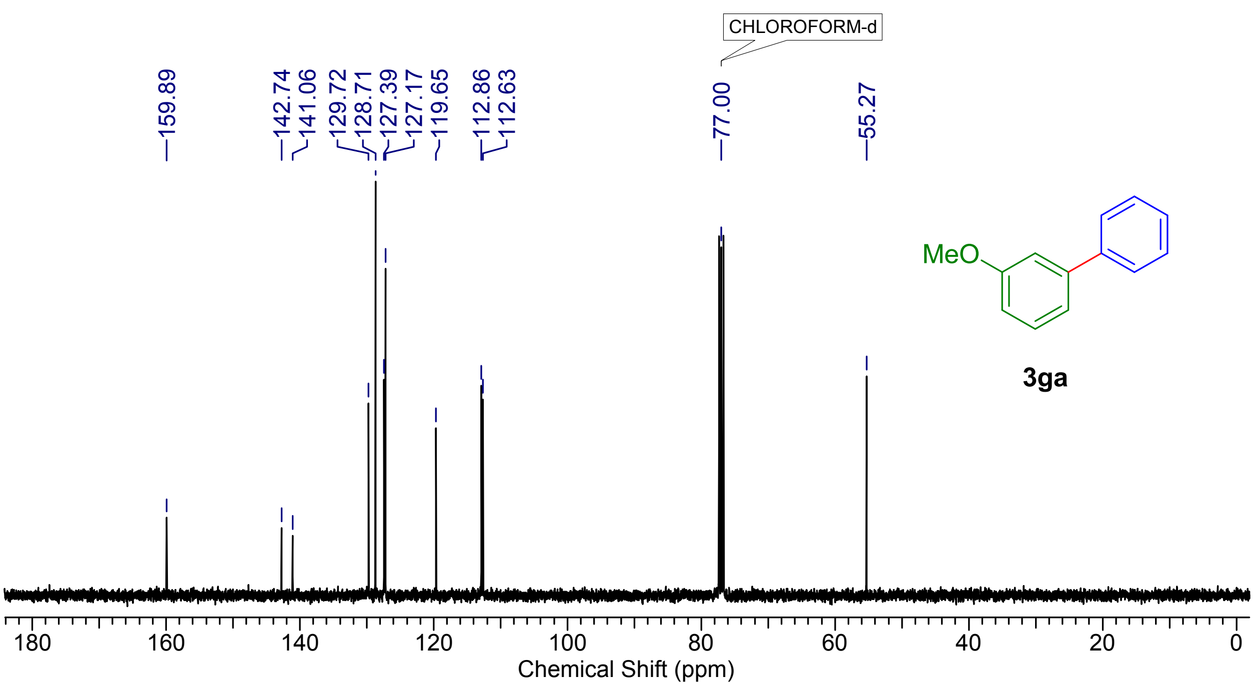
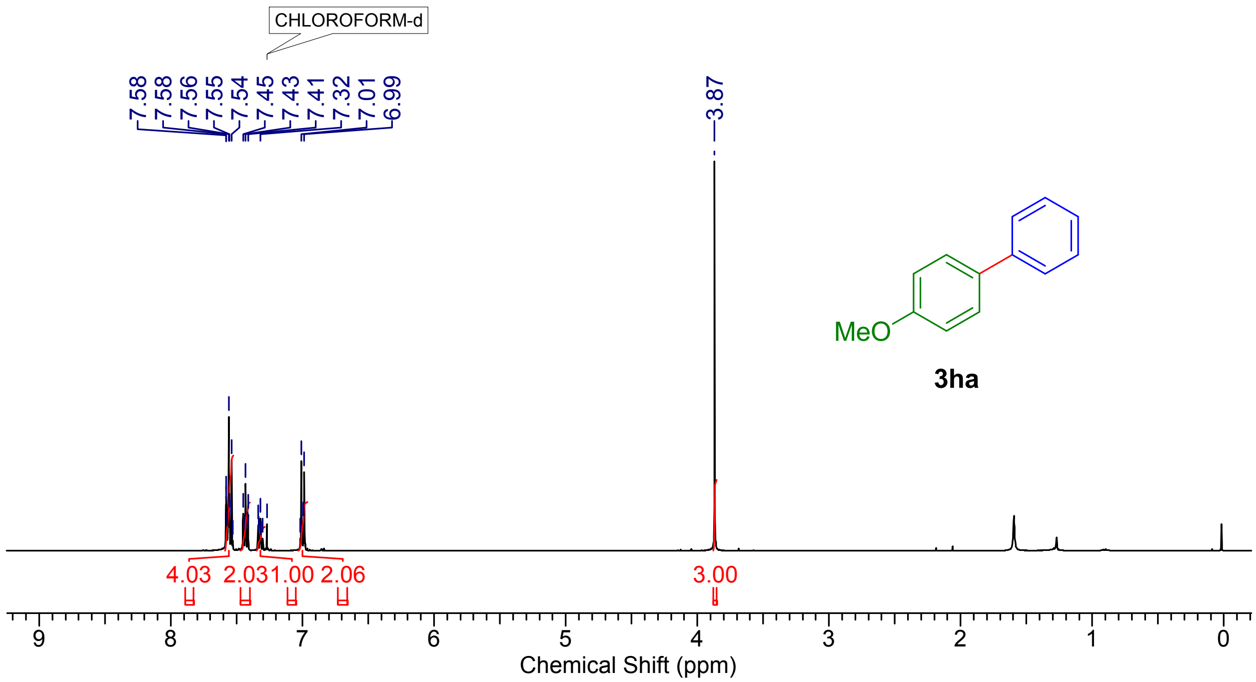


Figure S17: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3ha** in $CDCl_3$



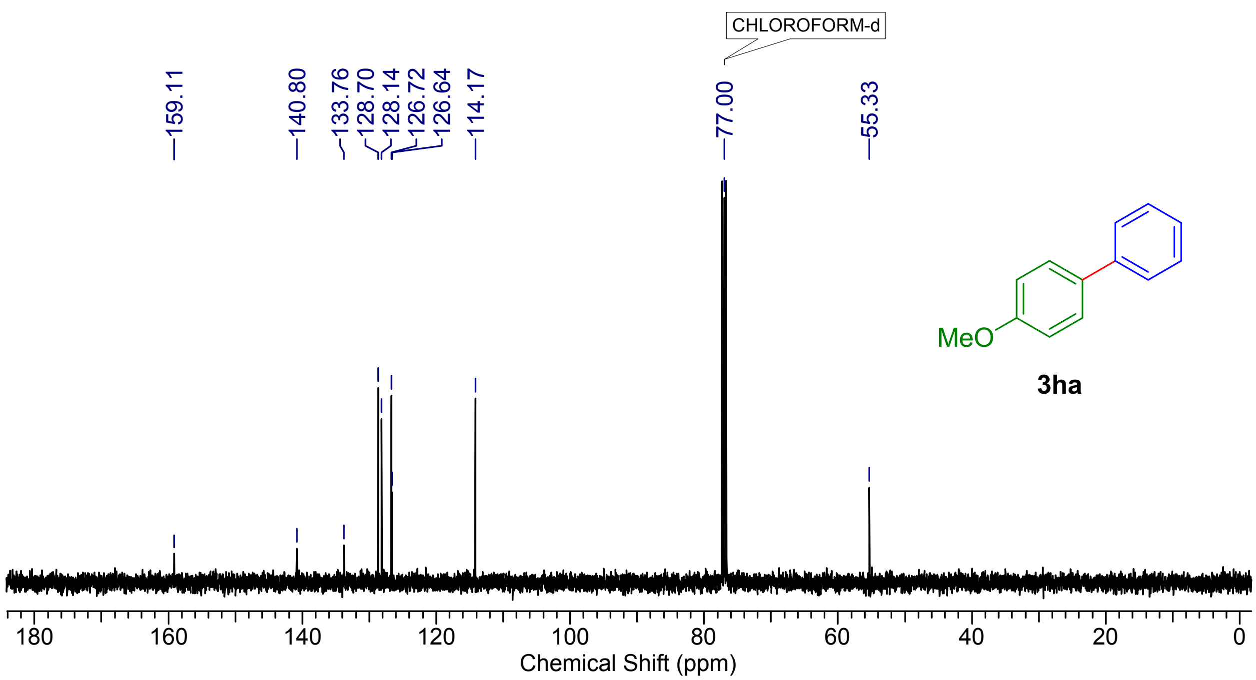
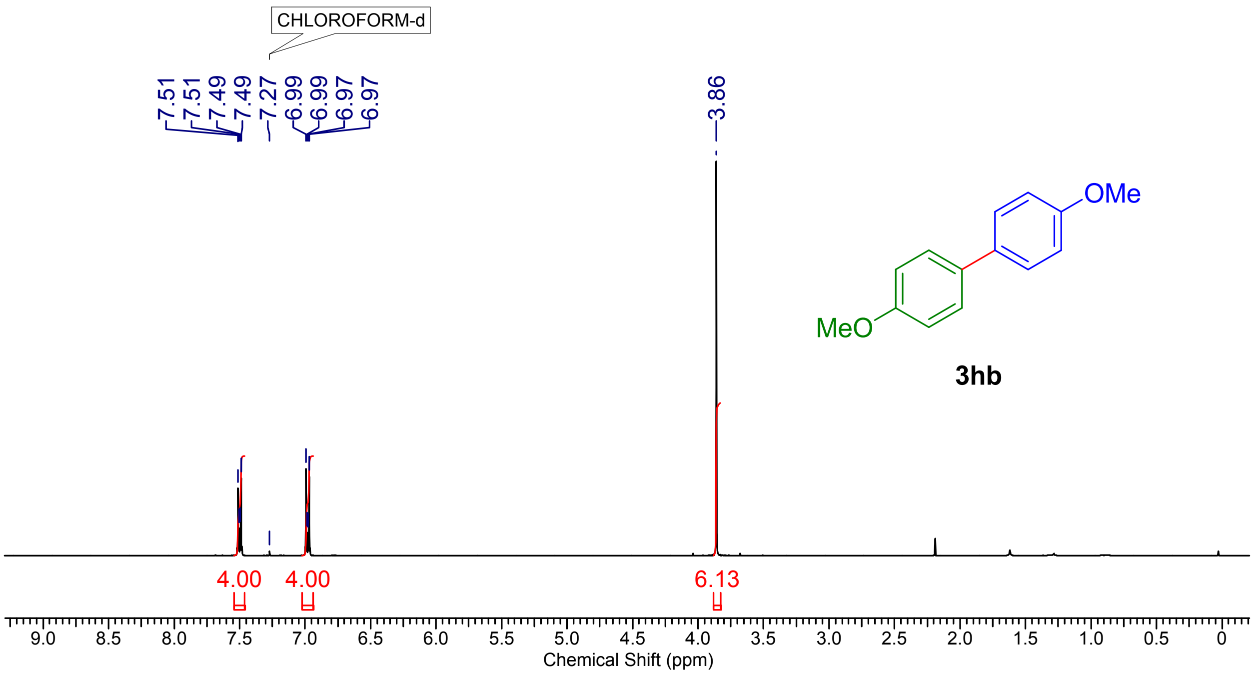


Figure S18:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **3hb** in $CDCl_3$



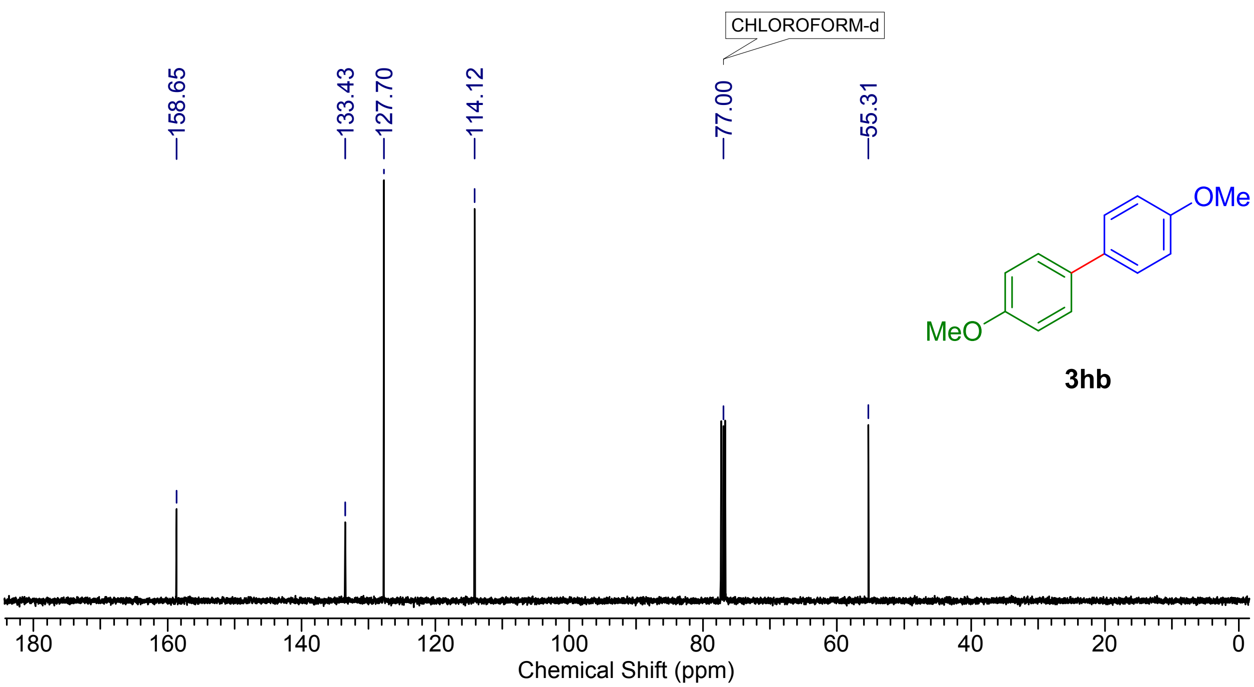
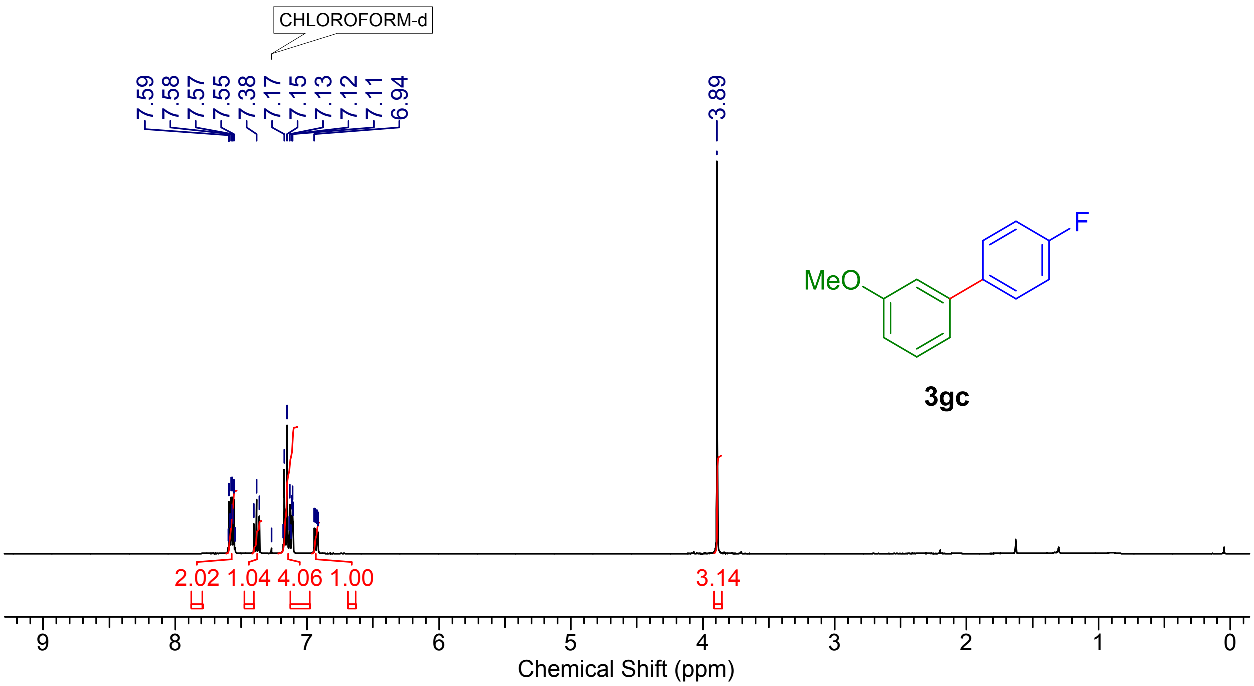


Figure S19: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3gc** in $CDCl_3$



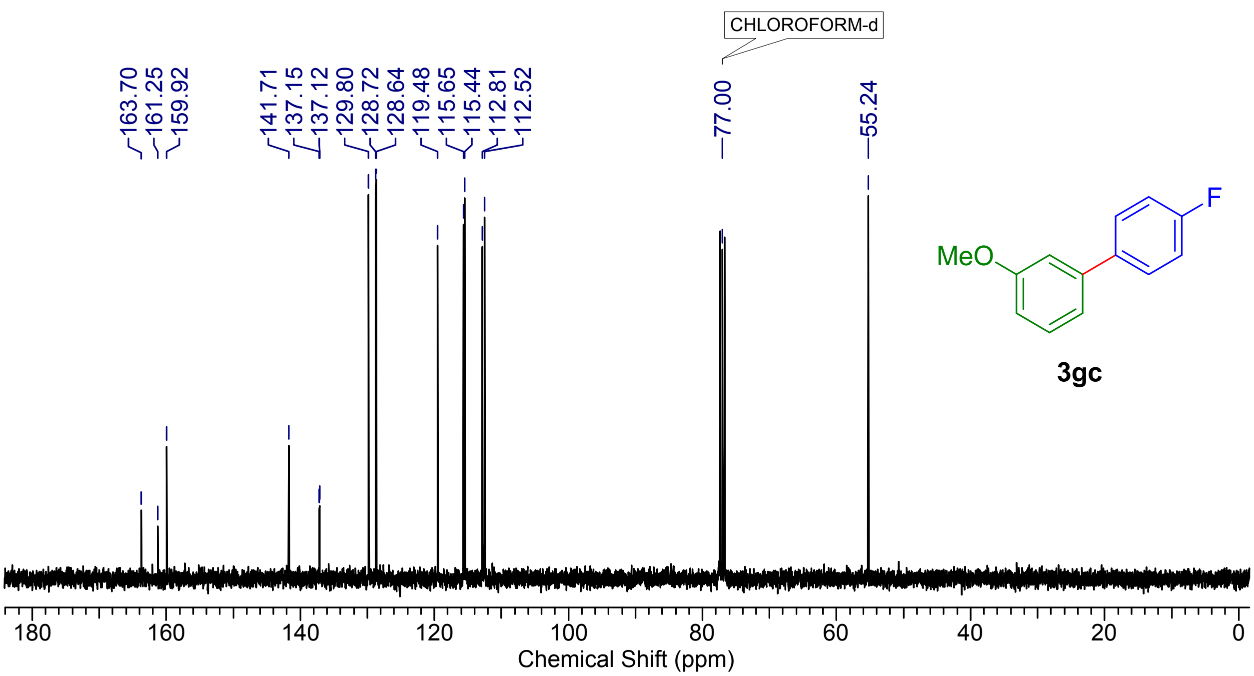
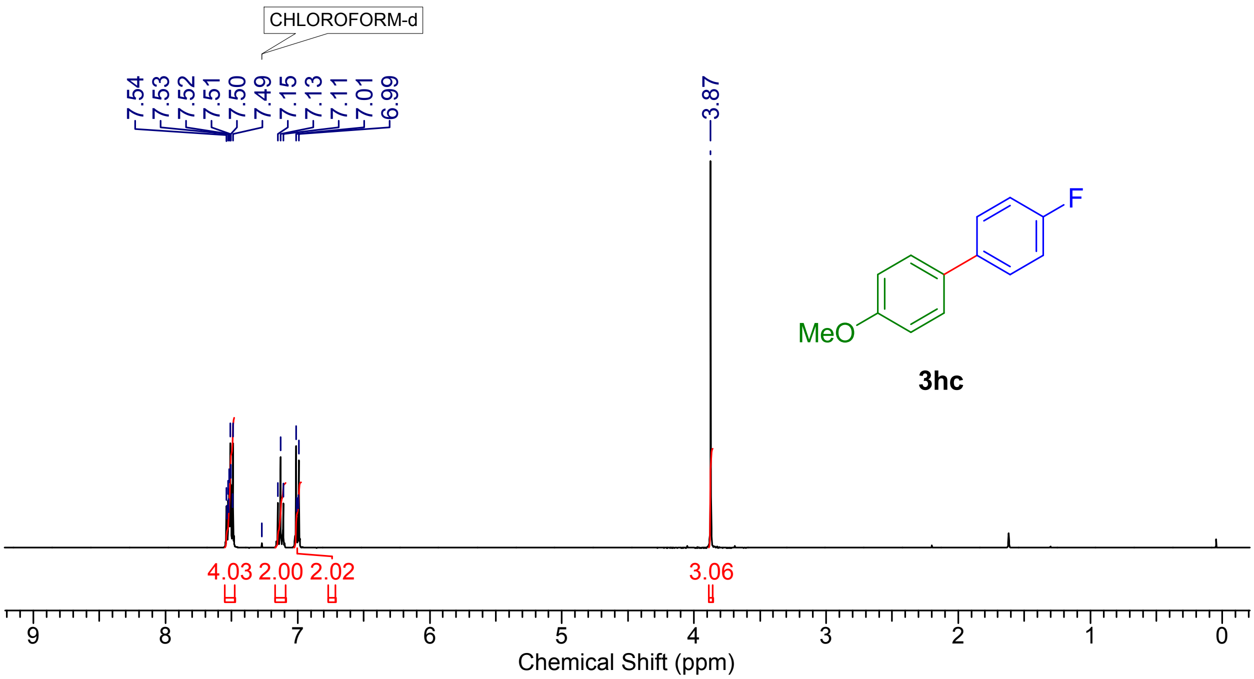


Figure S20:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **3hc** in $CDCl_3$



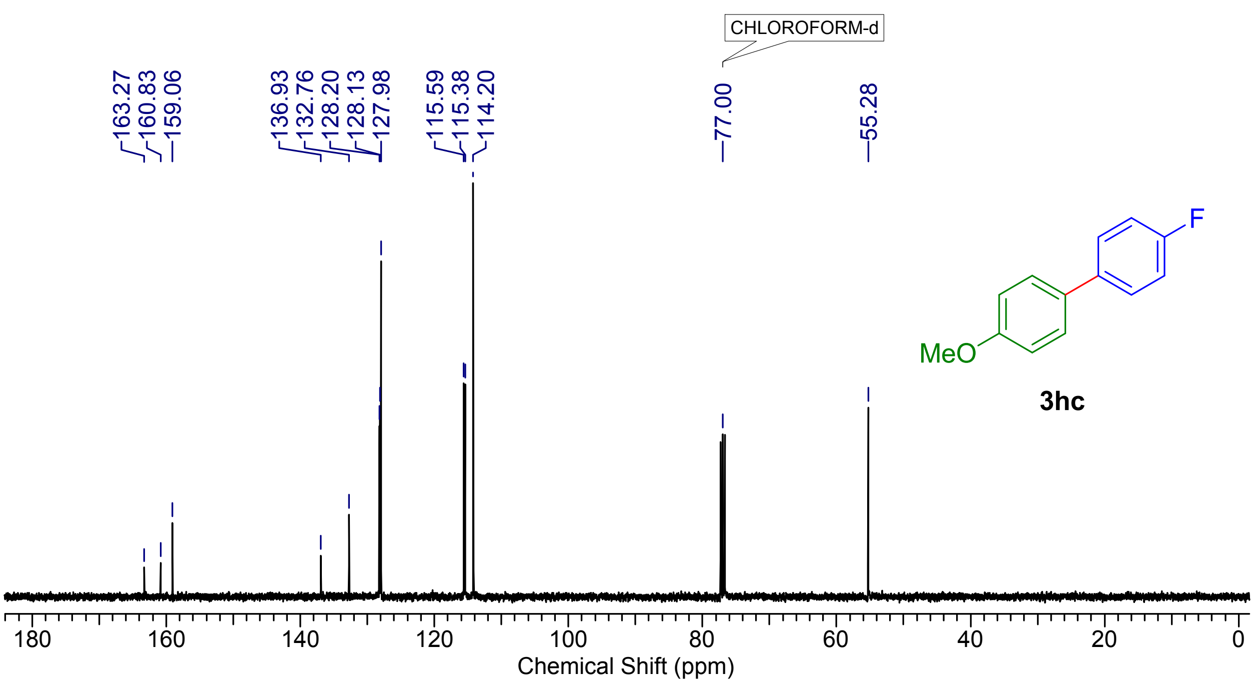
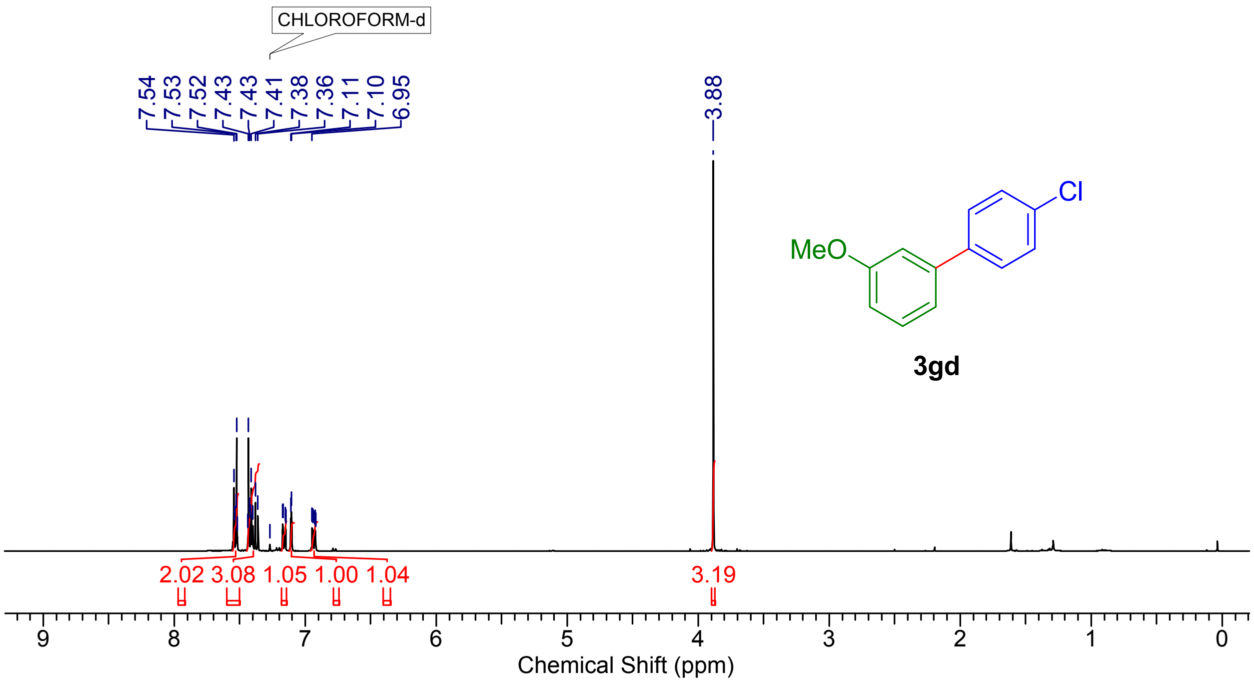


Figure S21: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3gd** in $CDCl_3$



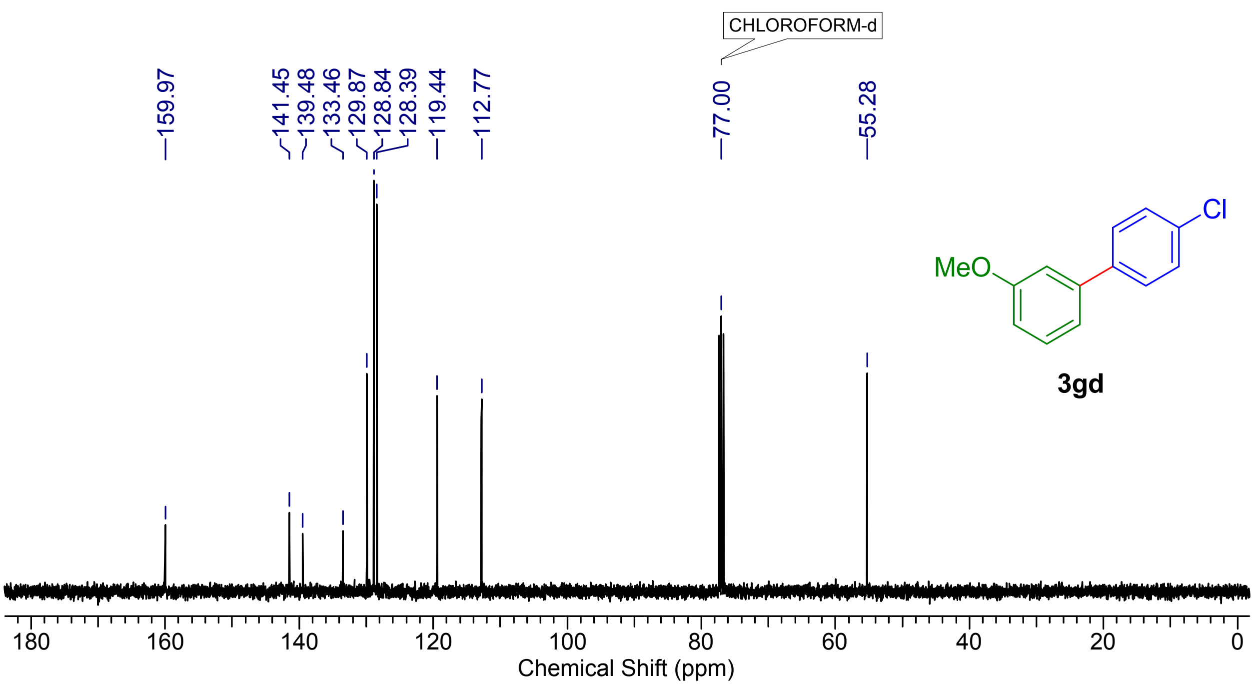
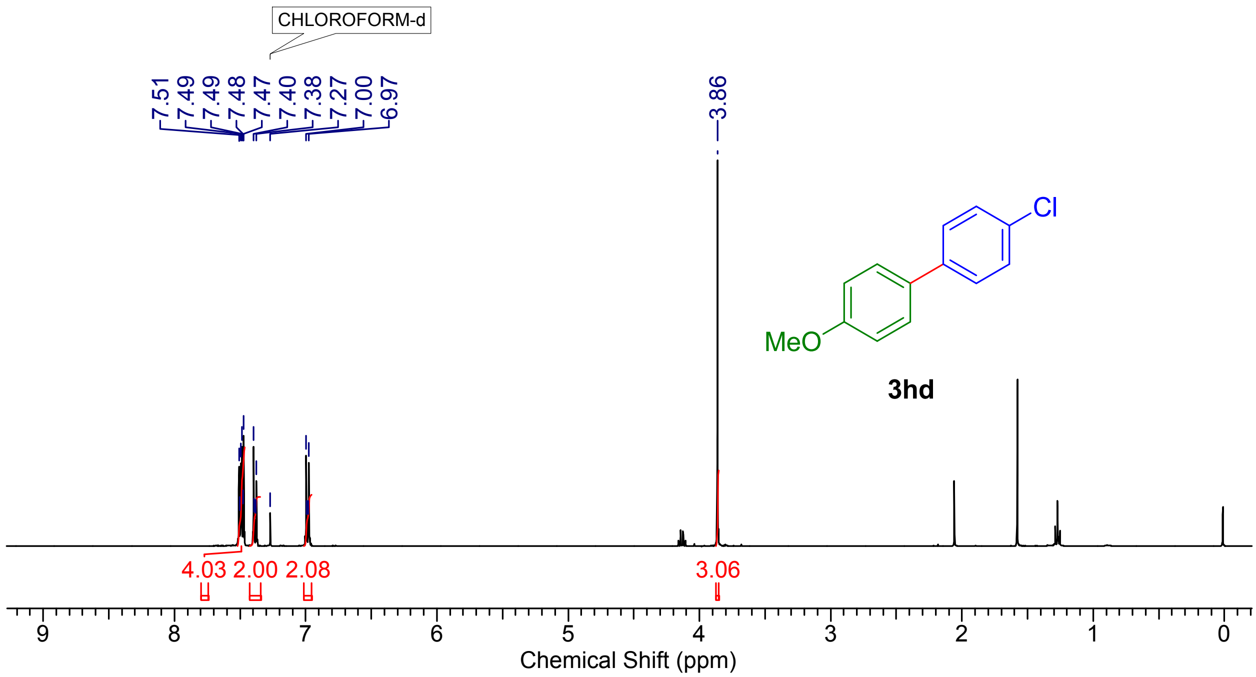


Figure S22:^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3hd** in $CDCl_3$



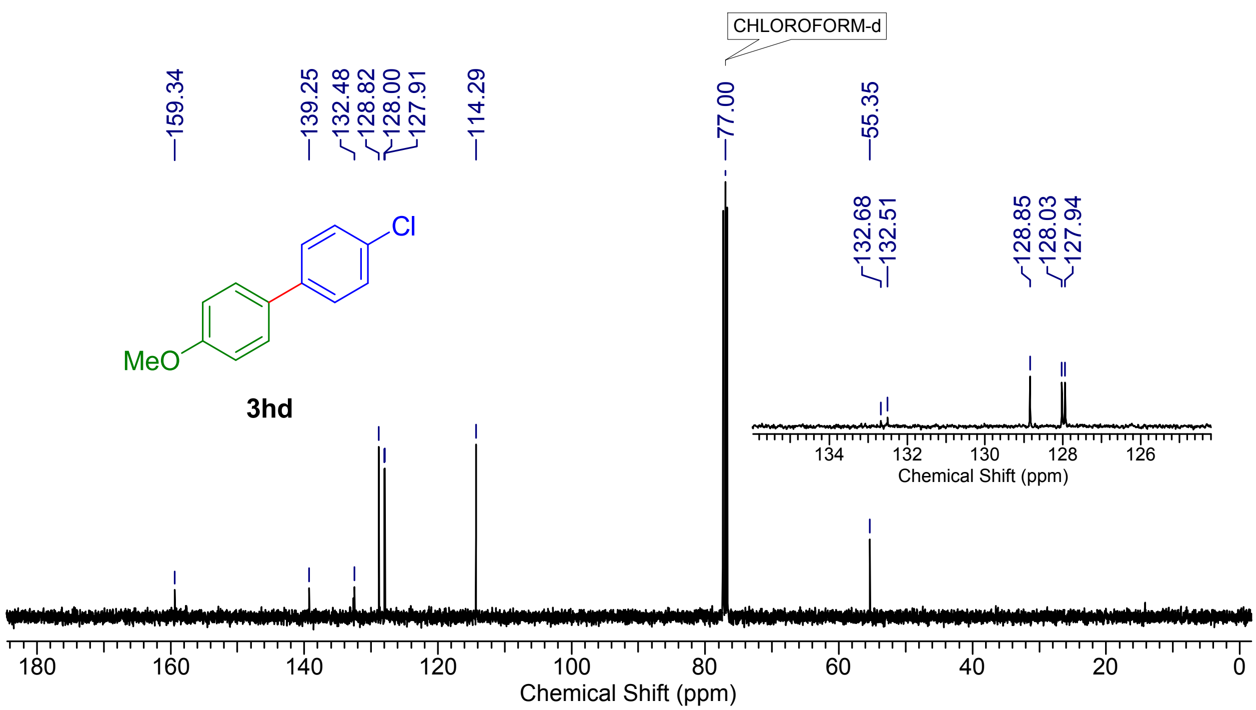
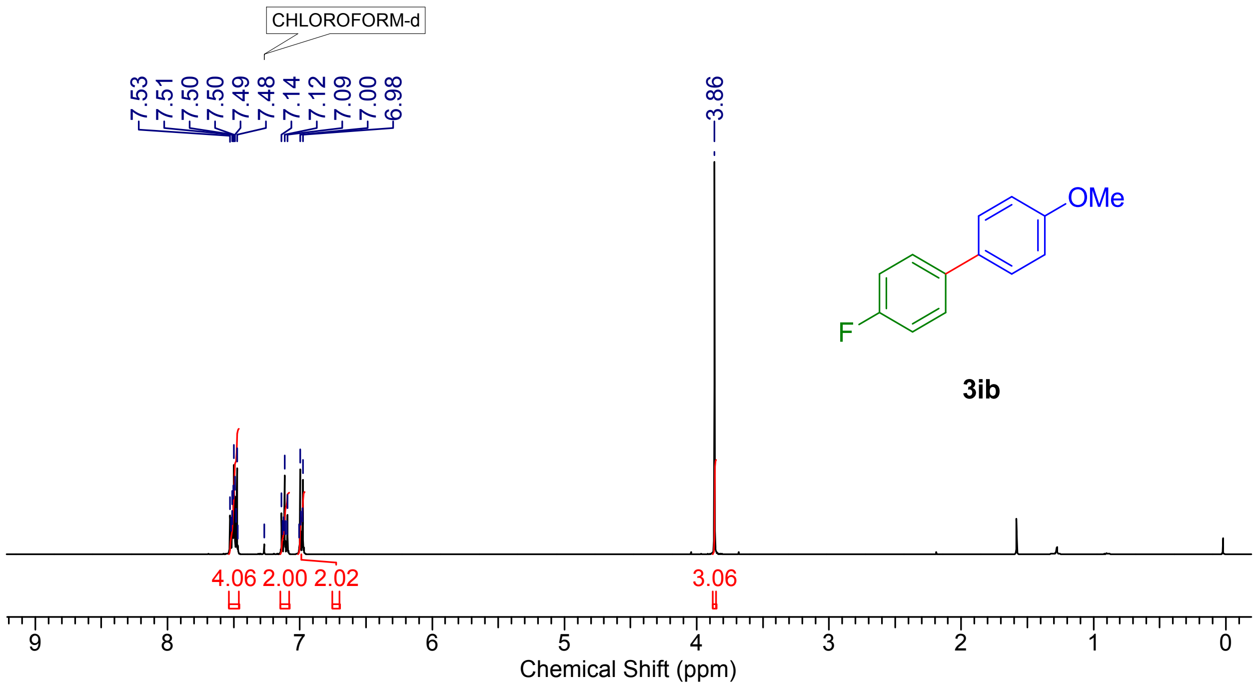


Figure S23: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3ib** in $CDCl_3$



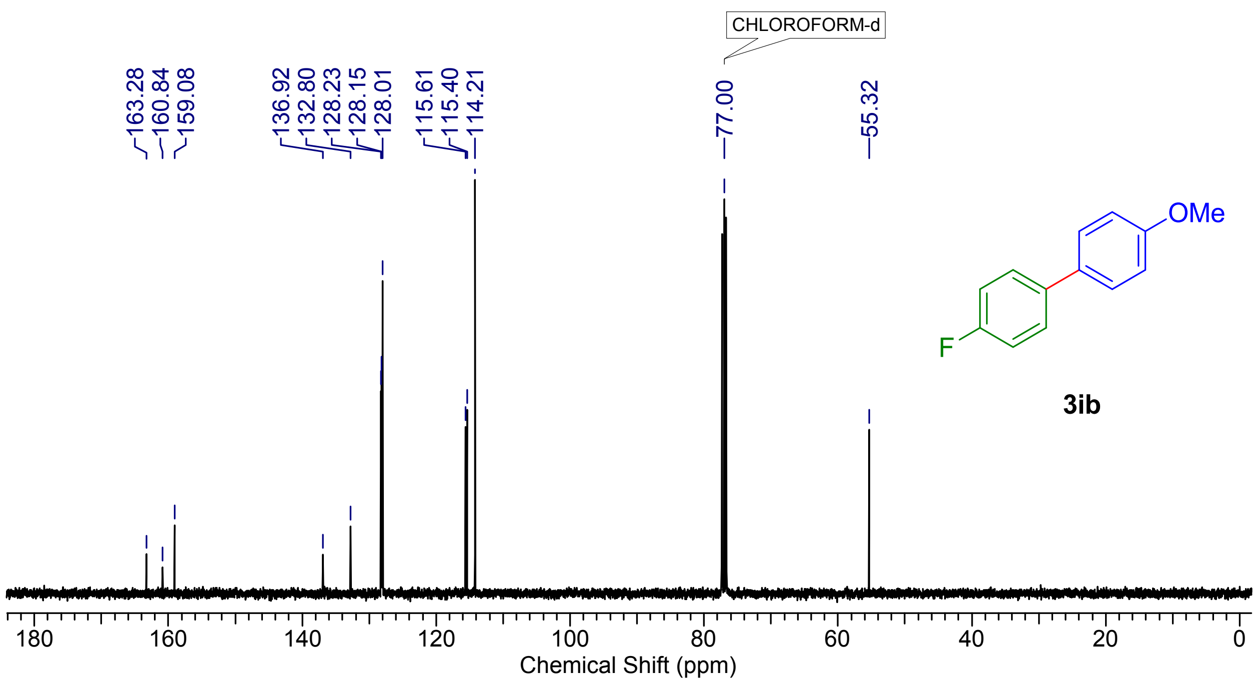
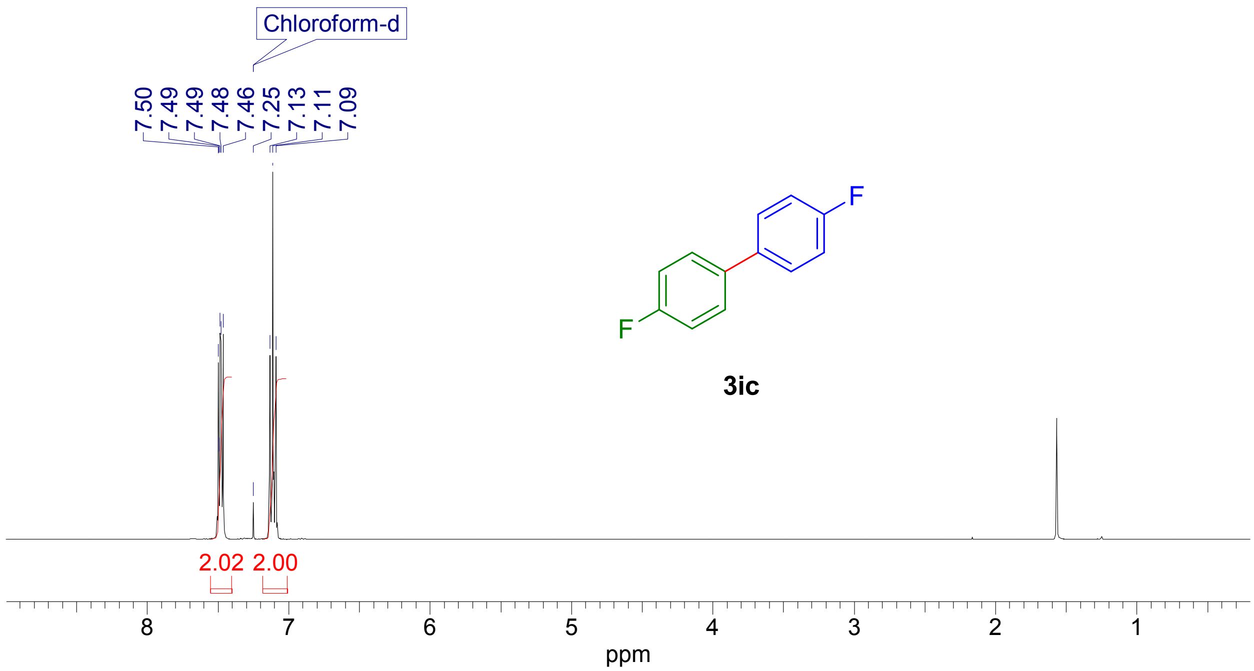


Figure S24: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3ic** in $CDCl_3$



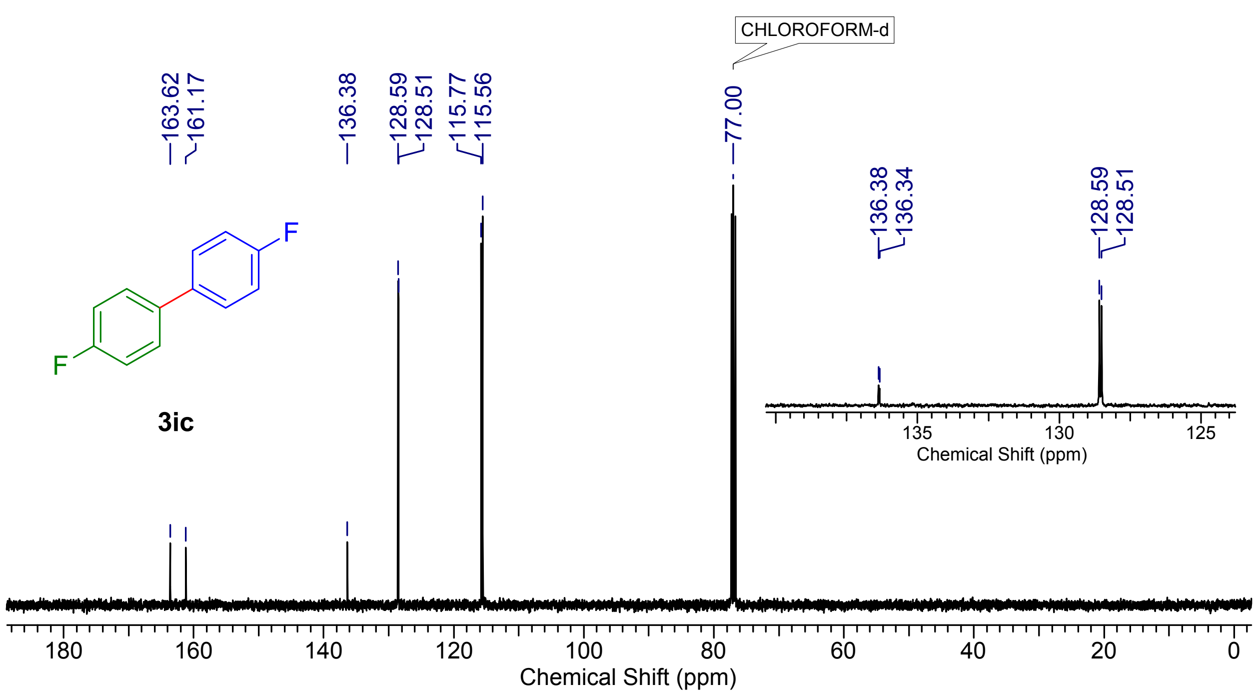


Figure S25: ^1H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3jd** in $CDCl_3$

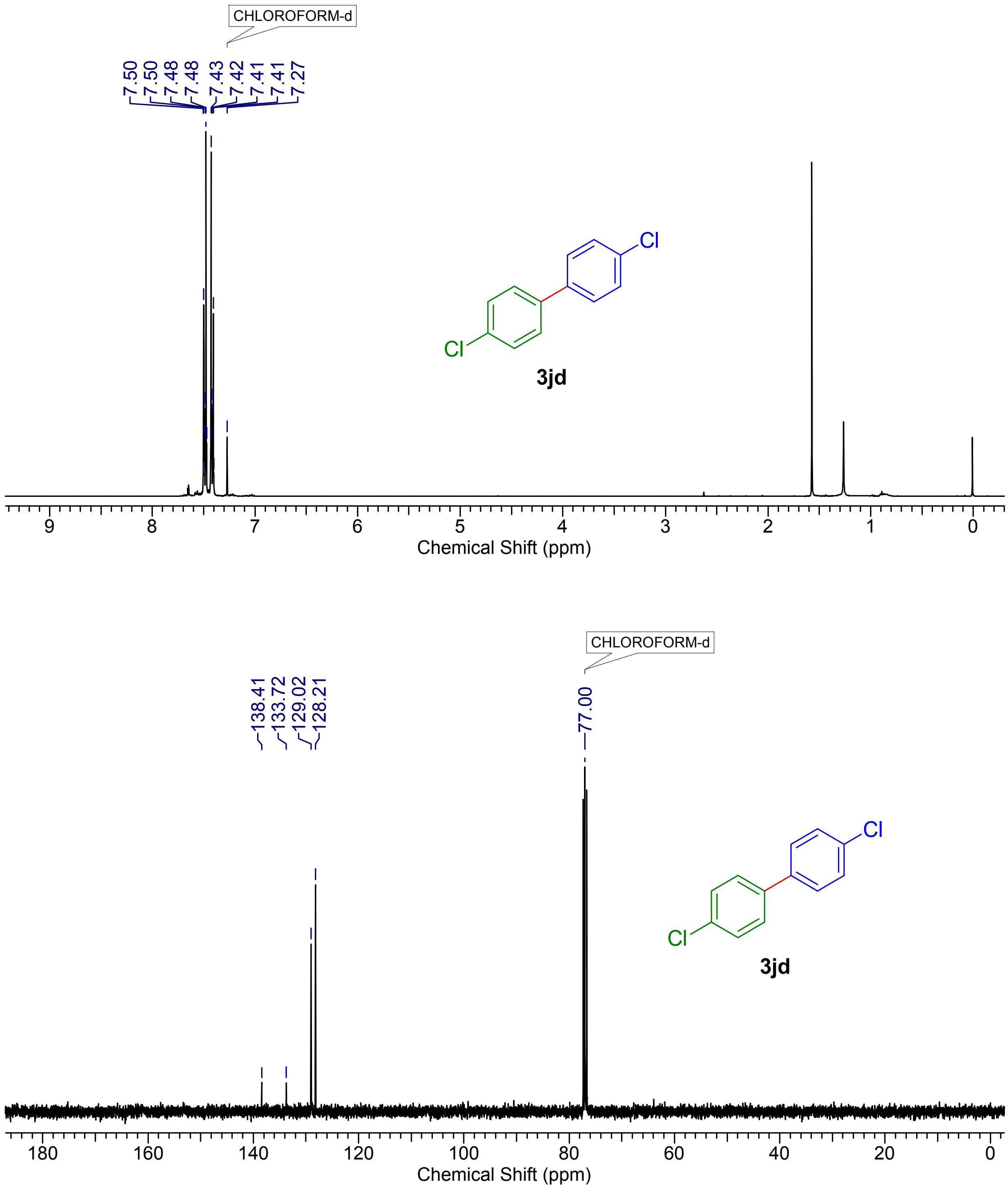
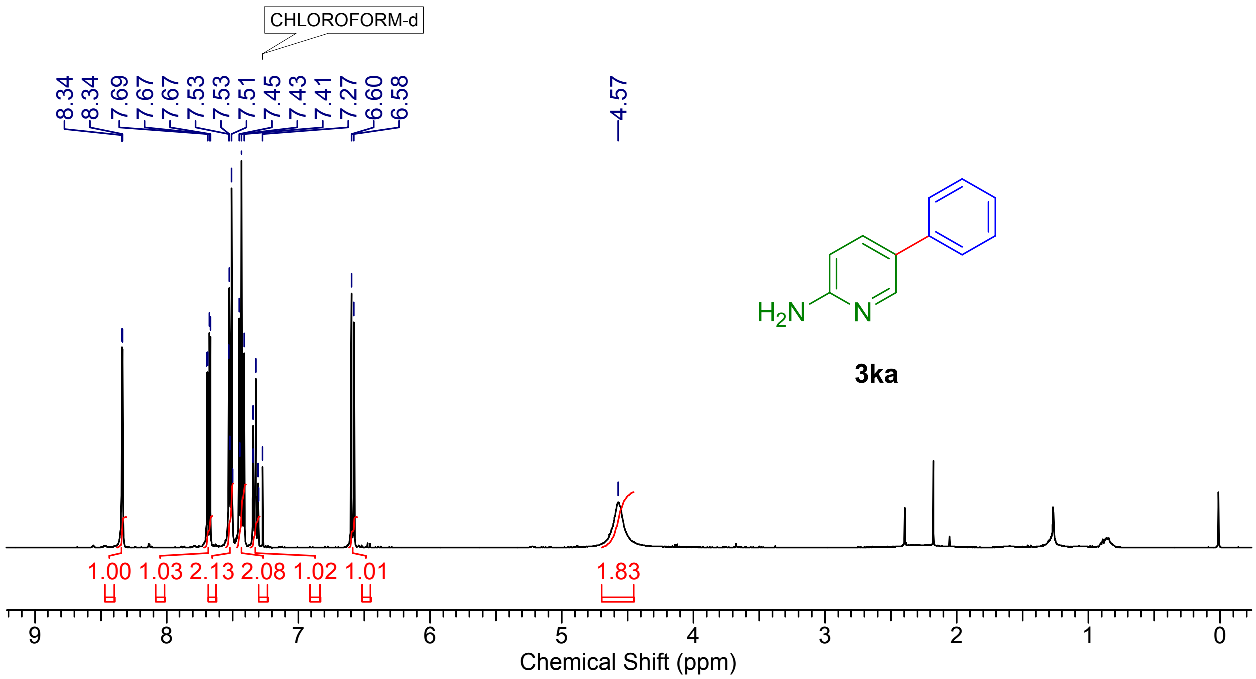


Figure S26: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3ka** in $CDCl_3$



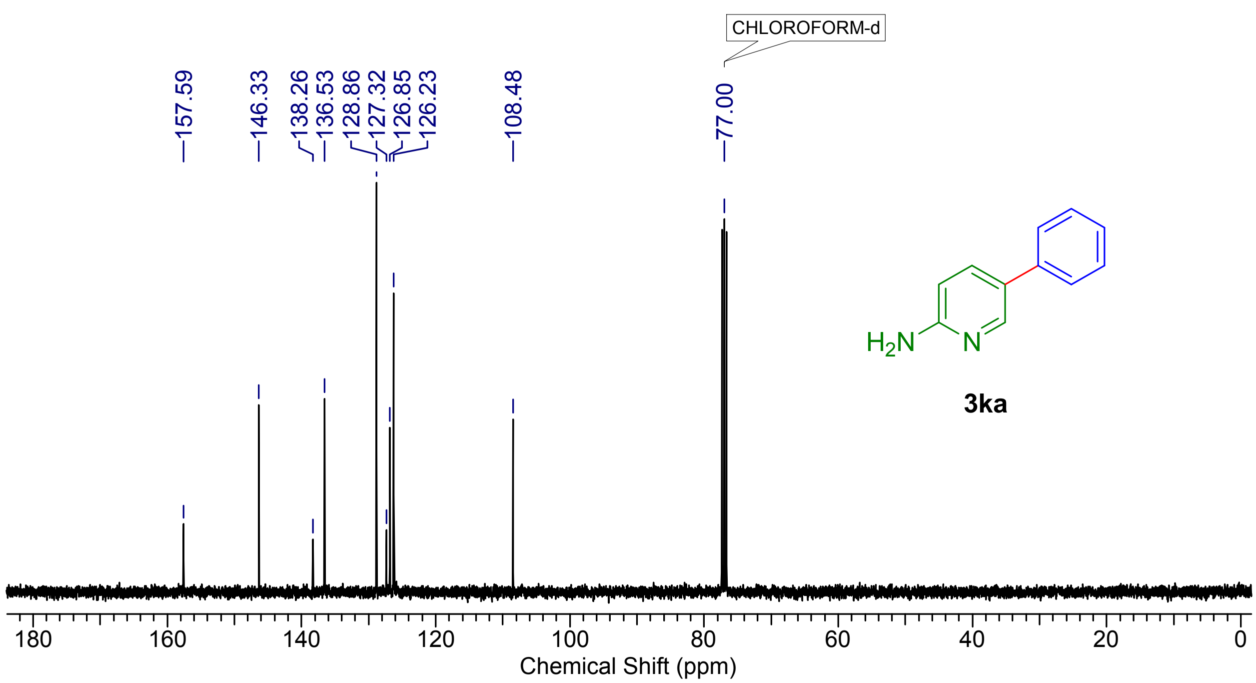
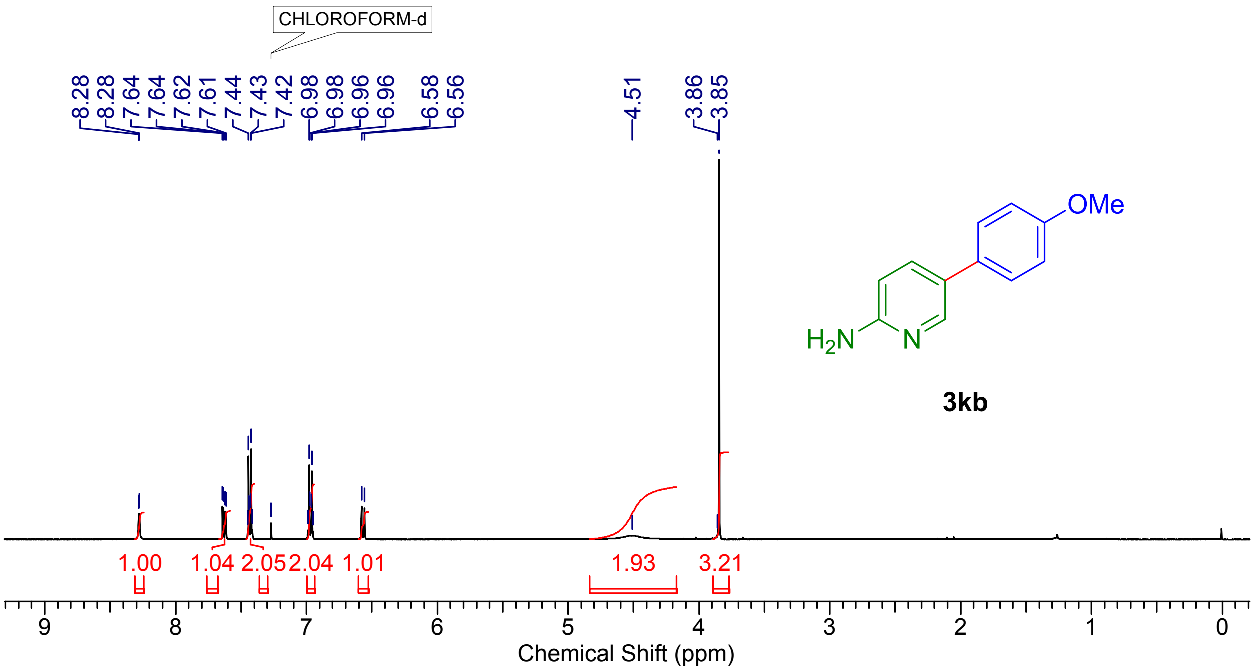


Figure S27: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3kb** in $CDCl_3$



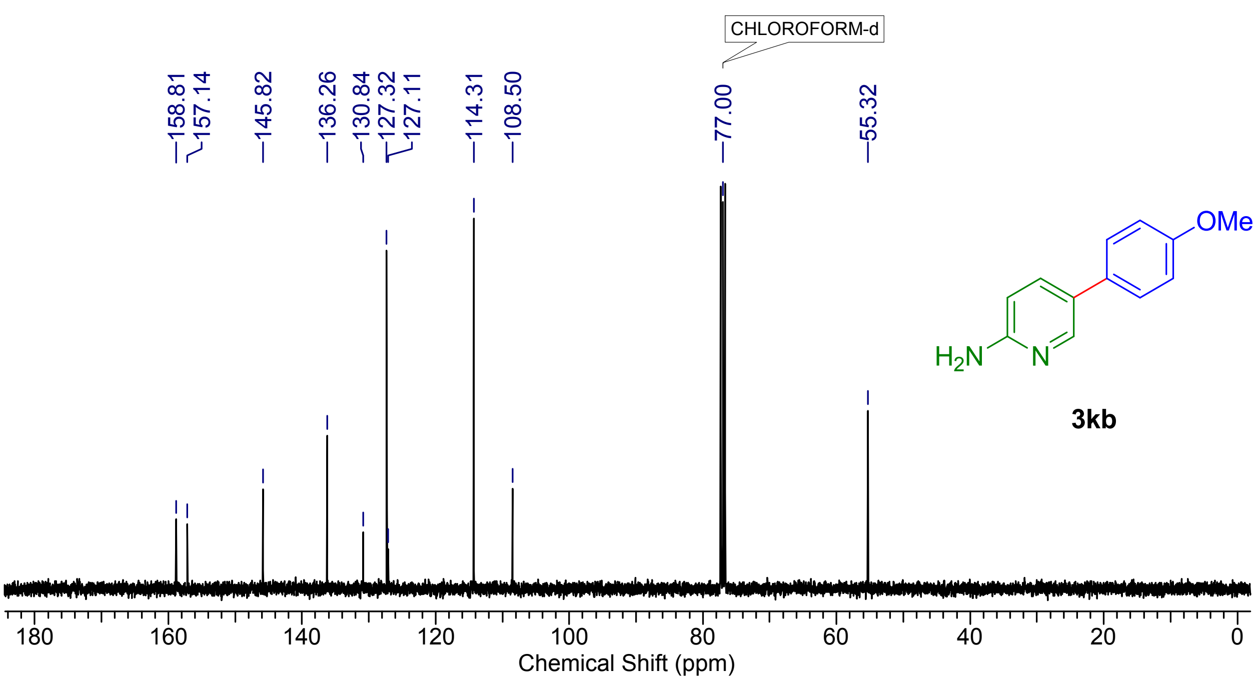
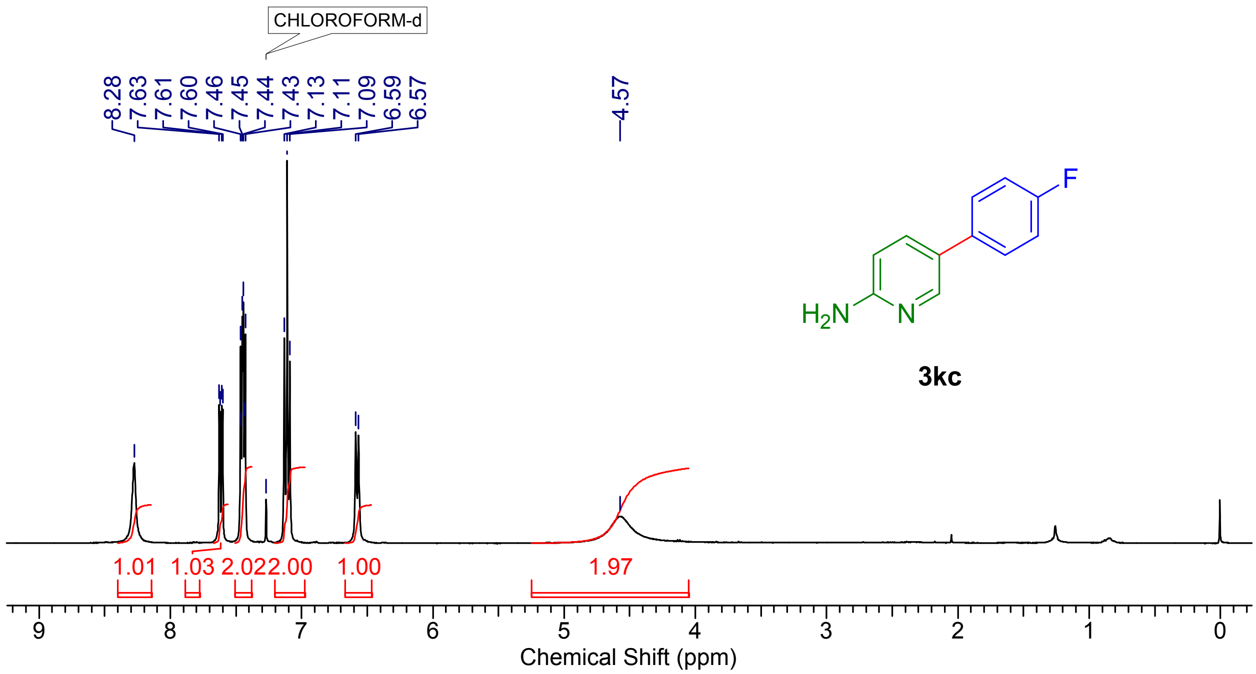


Figure S28: [1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **3kc** in $CDCl_3$



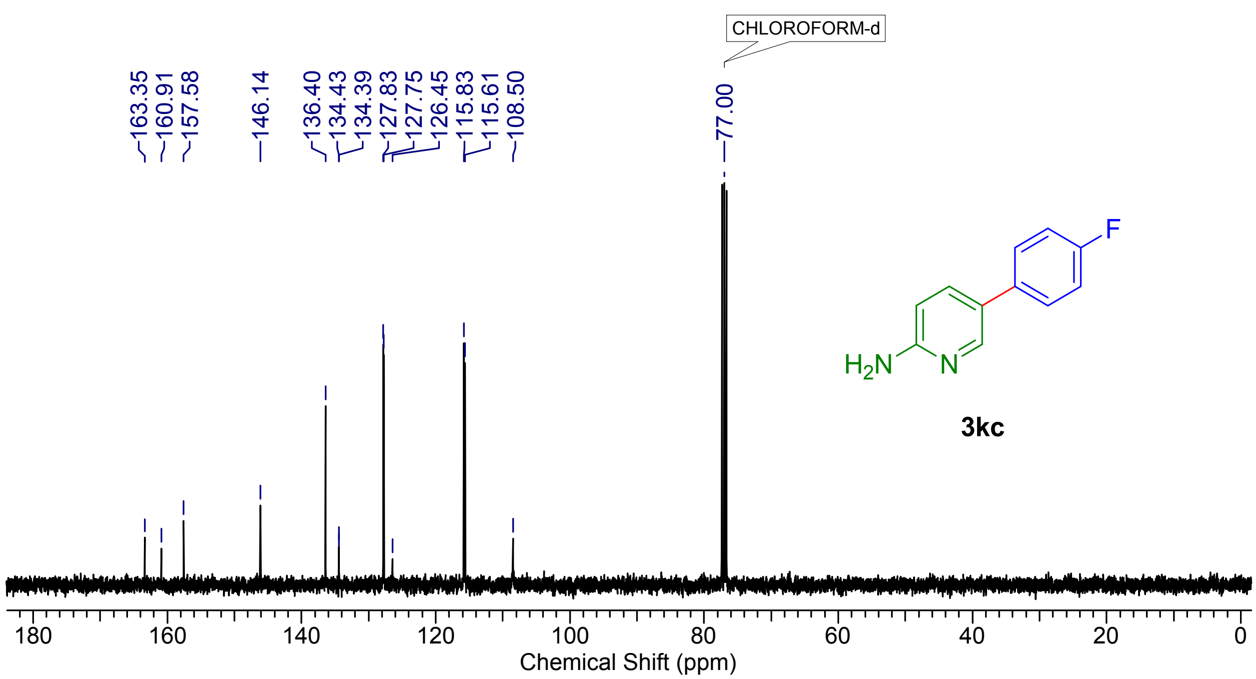
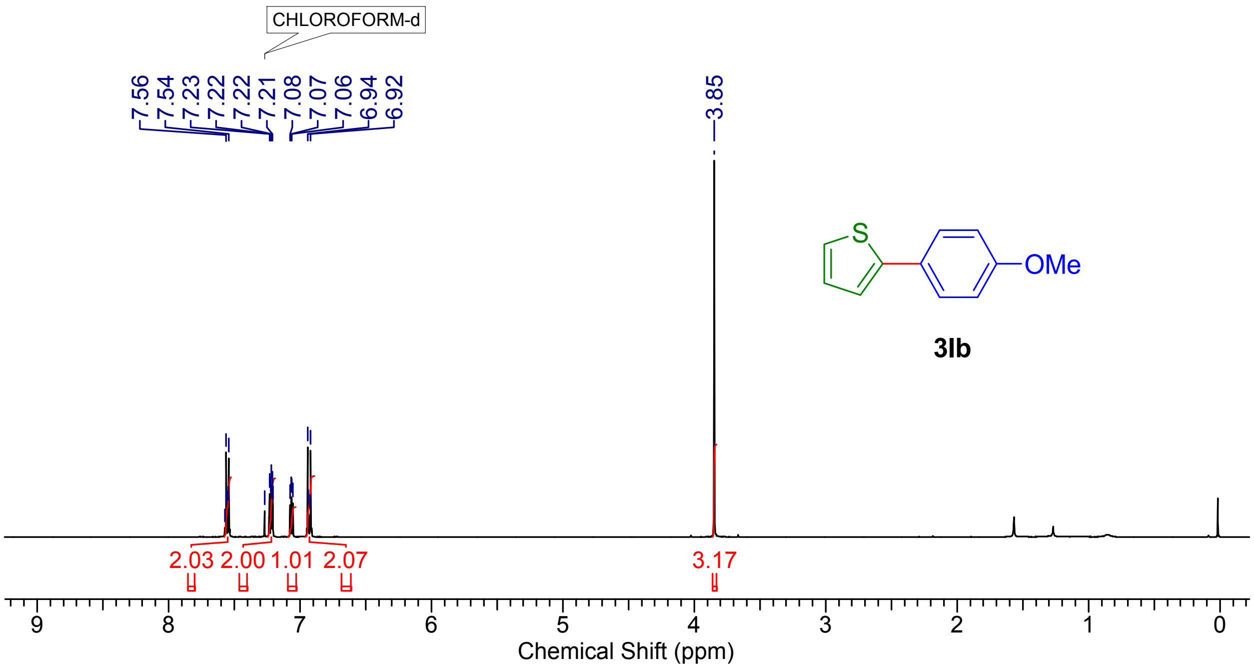


Figure S29: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3lb** in $CDCl_3$



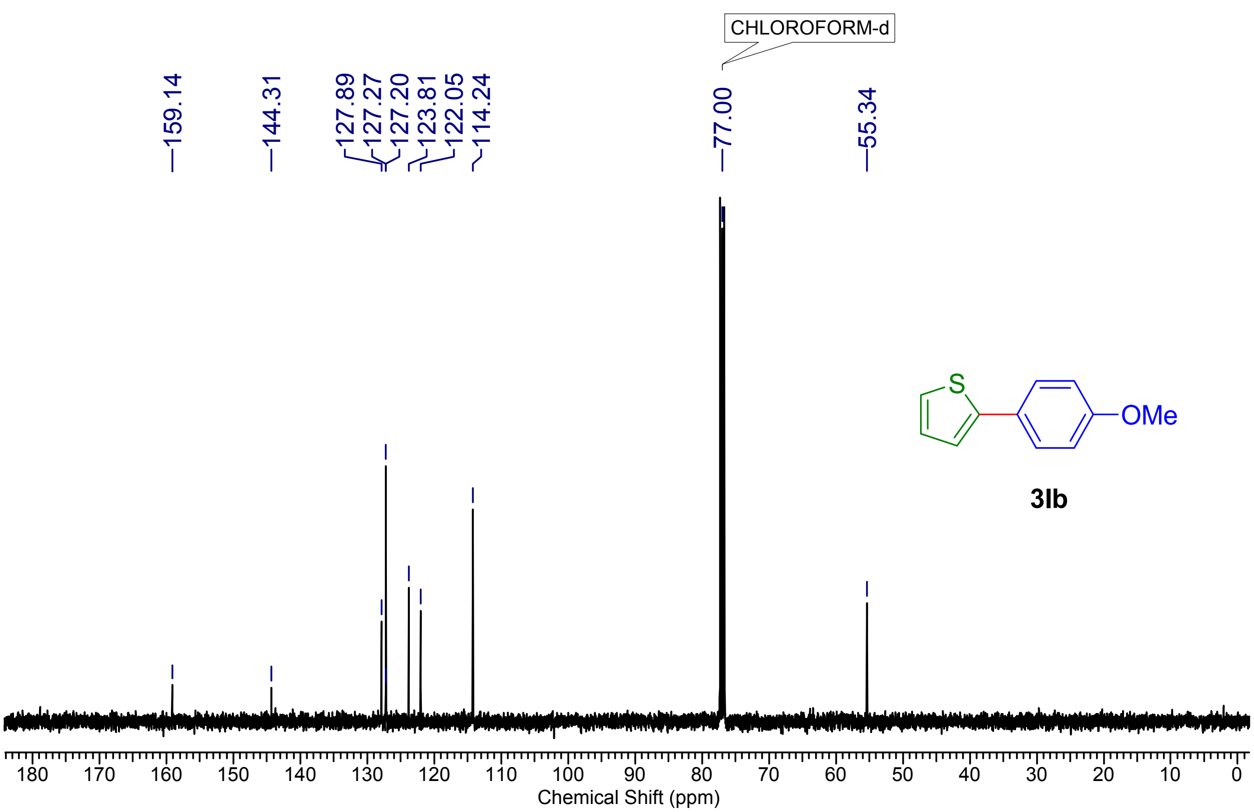
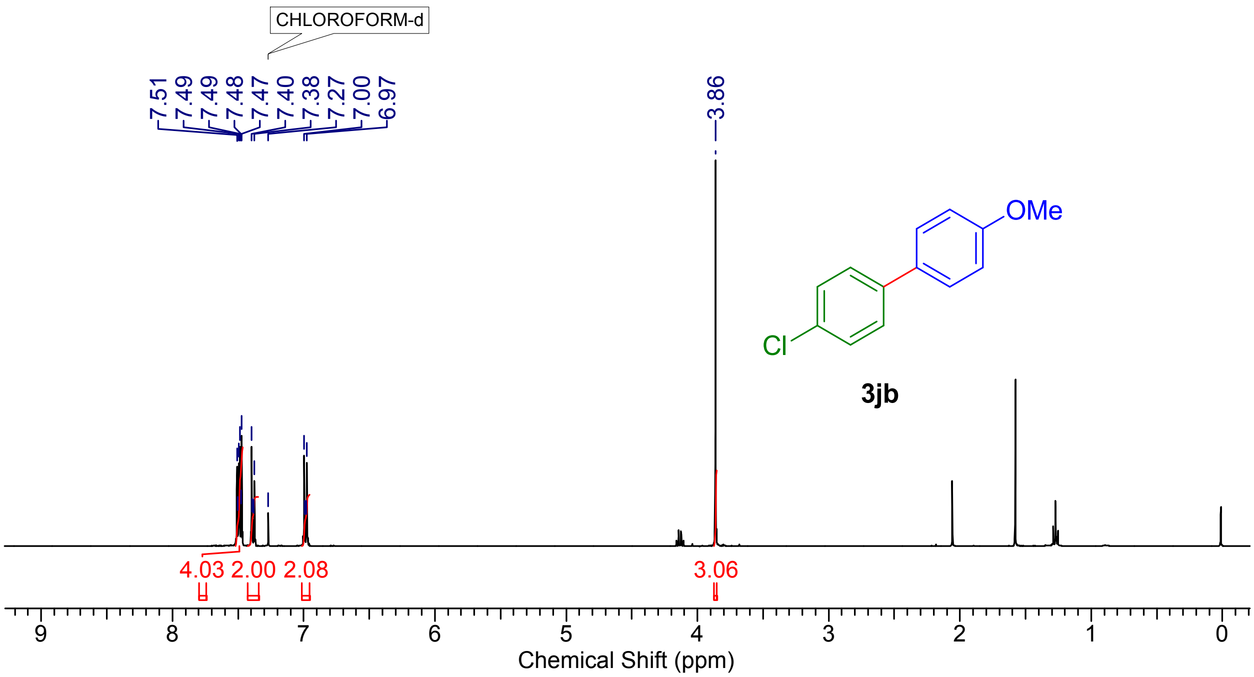


Figure S30: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **3jb** in $CDCl_3$



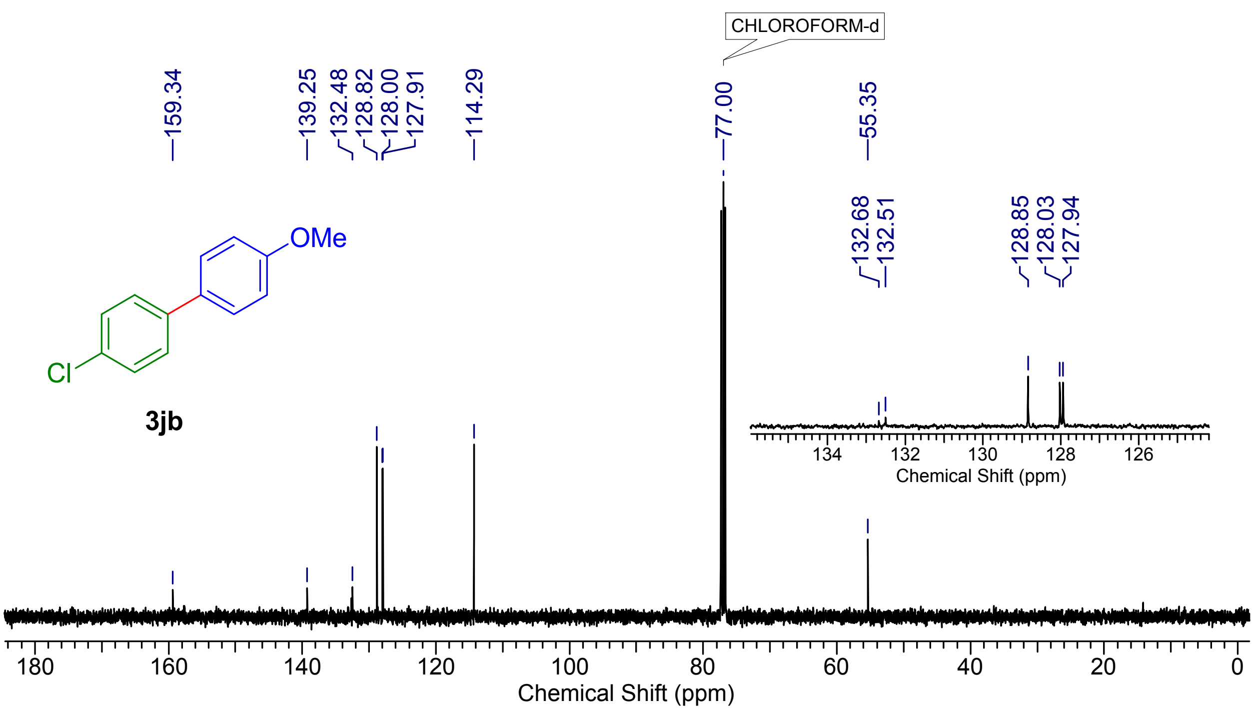
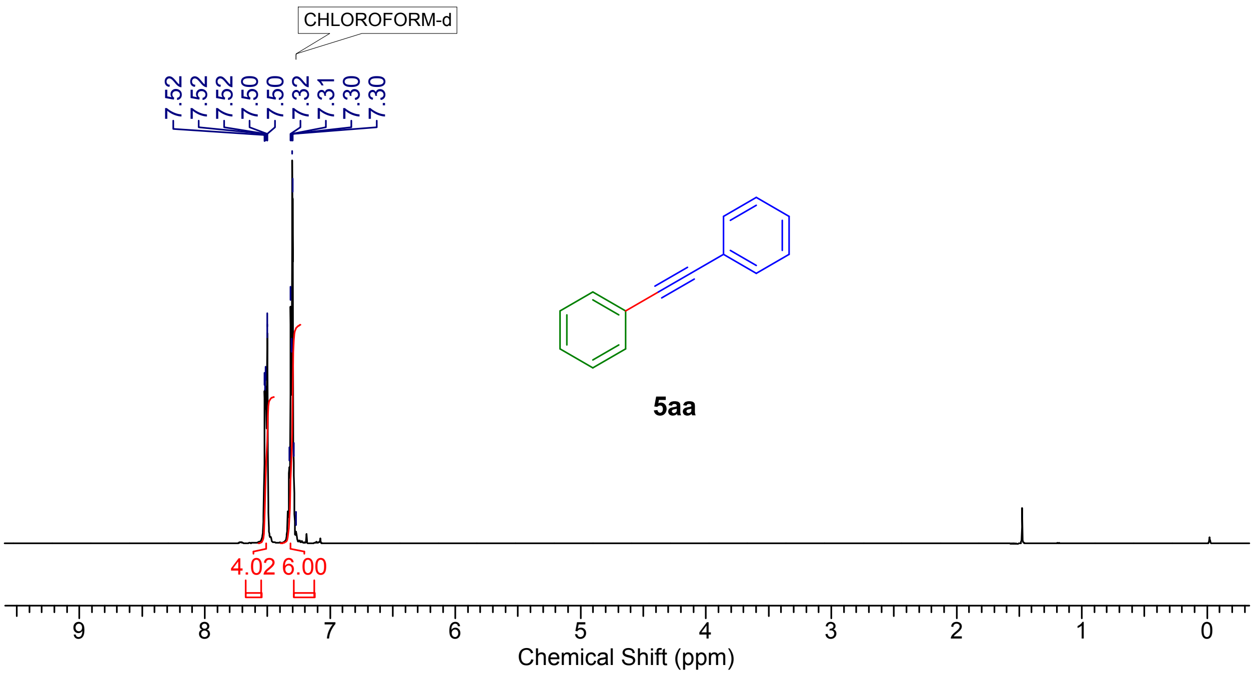


Figure S31: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5aa** in $CDCl_3$



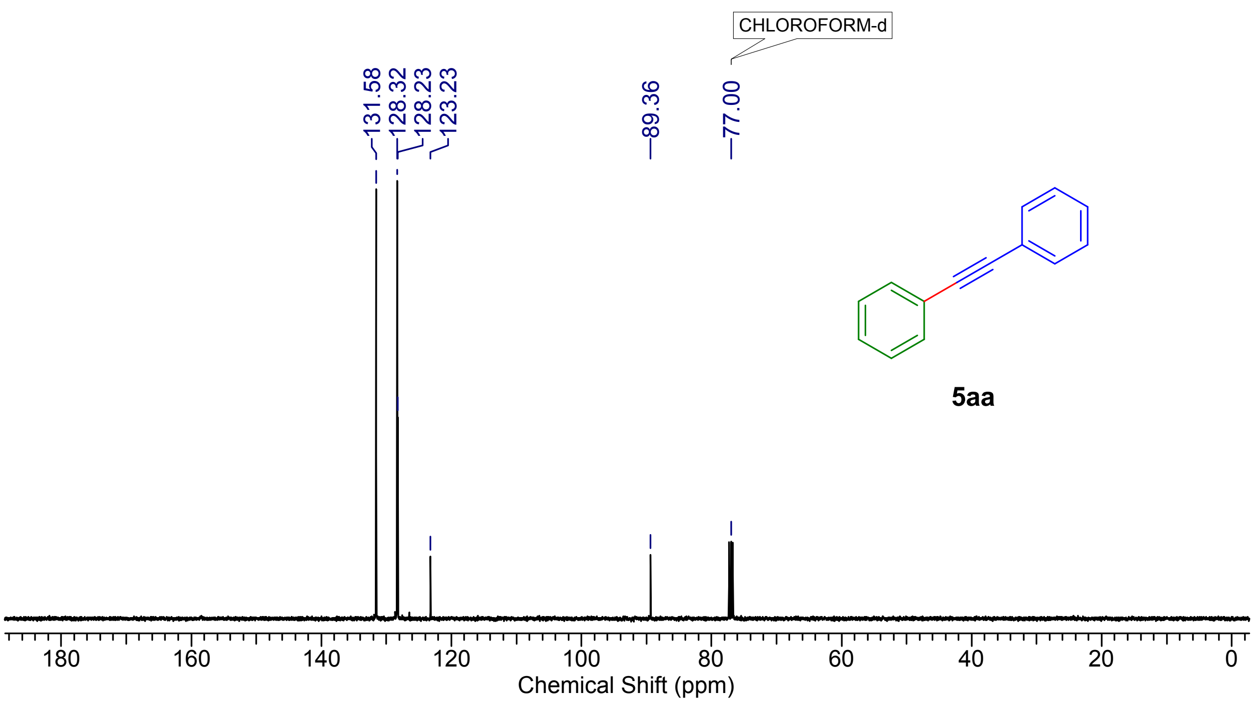
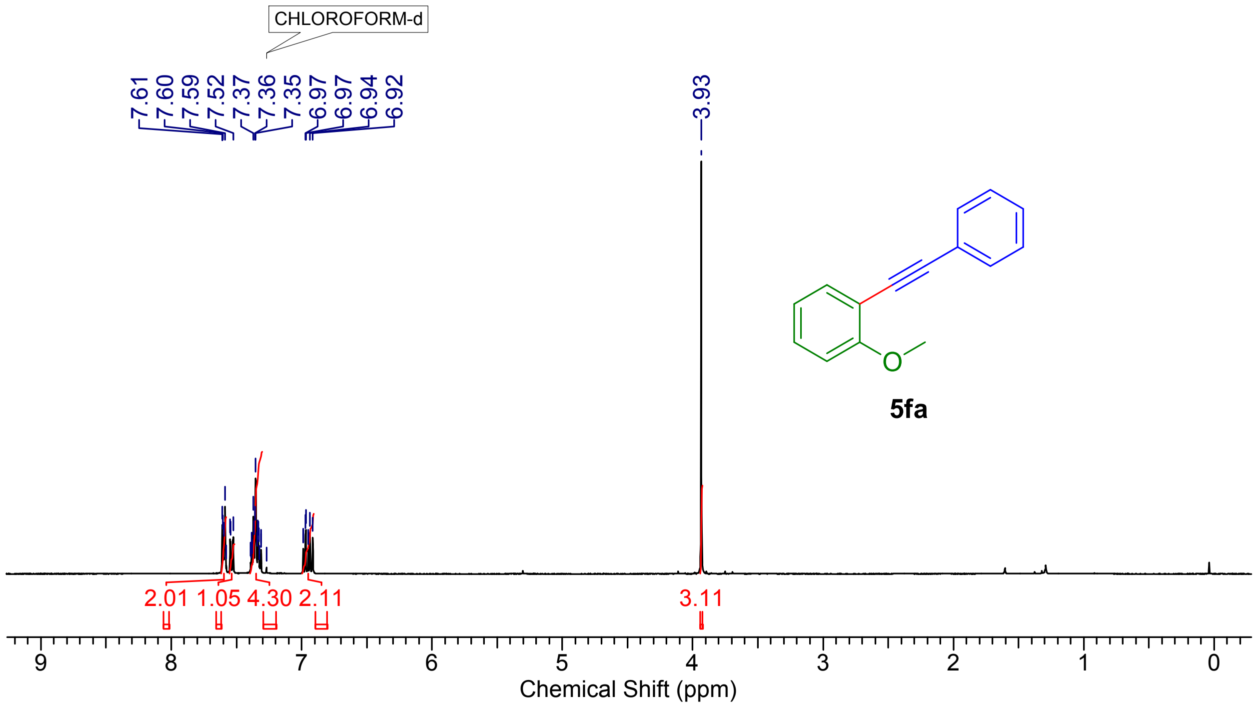


Figure S32: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5fa** in $CDCl_3$



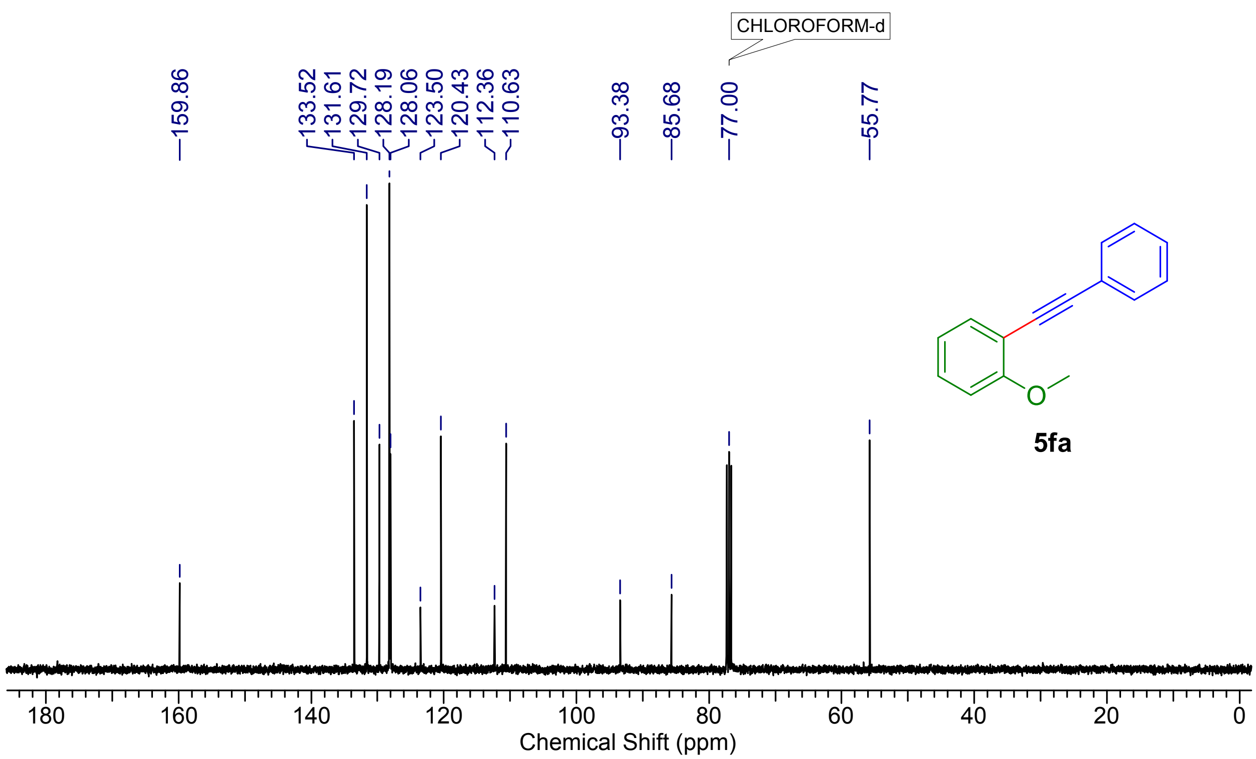
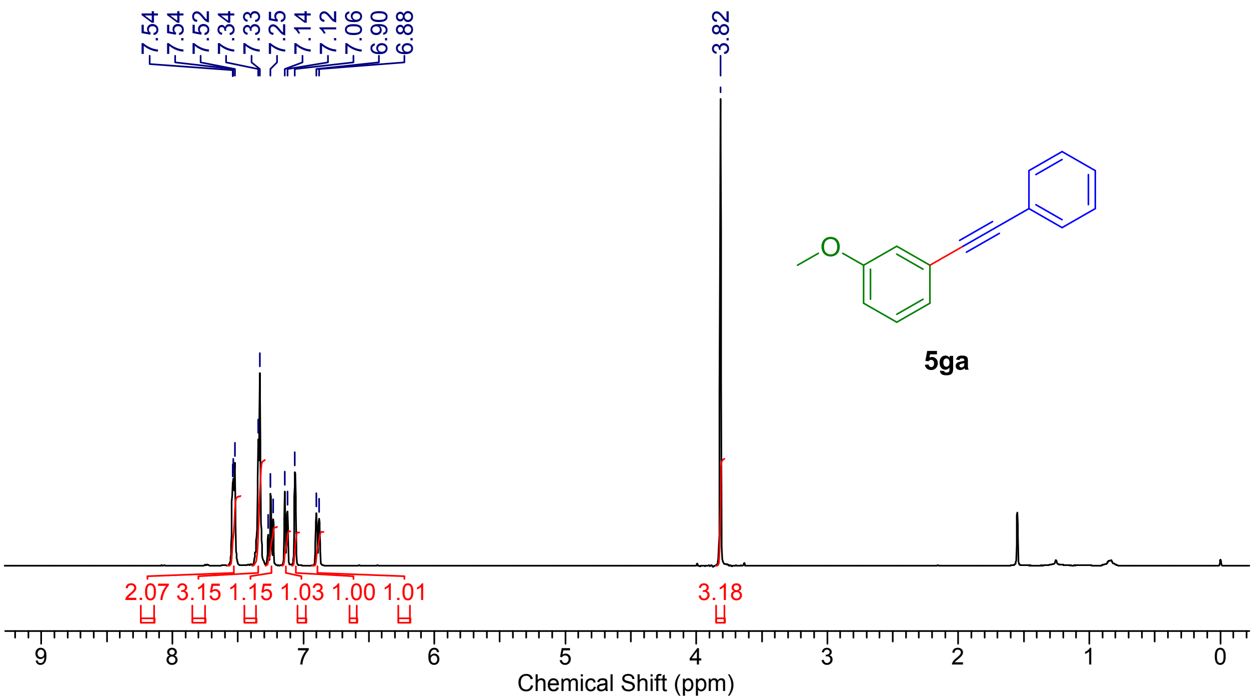


Figure S33:^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5ga** in $CDCl_3$



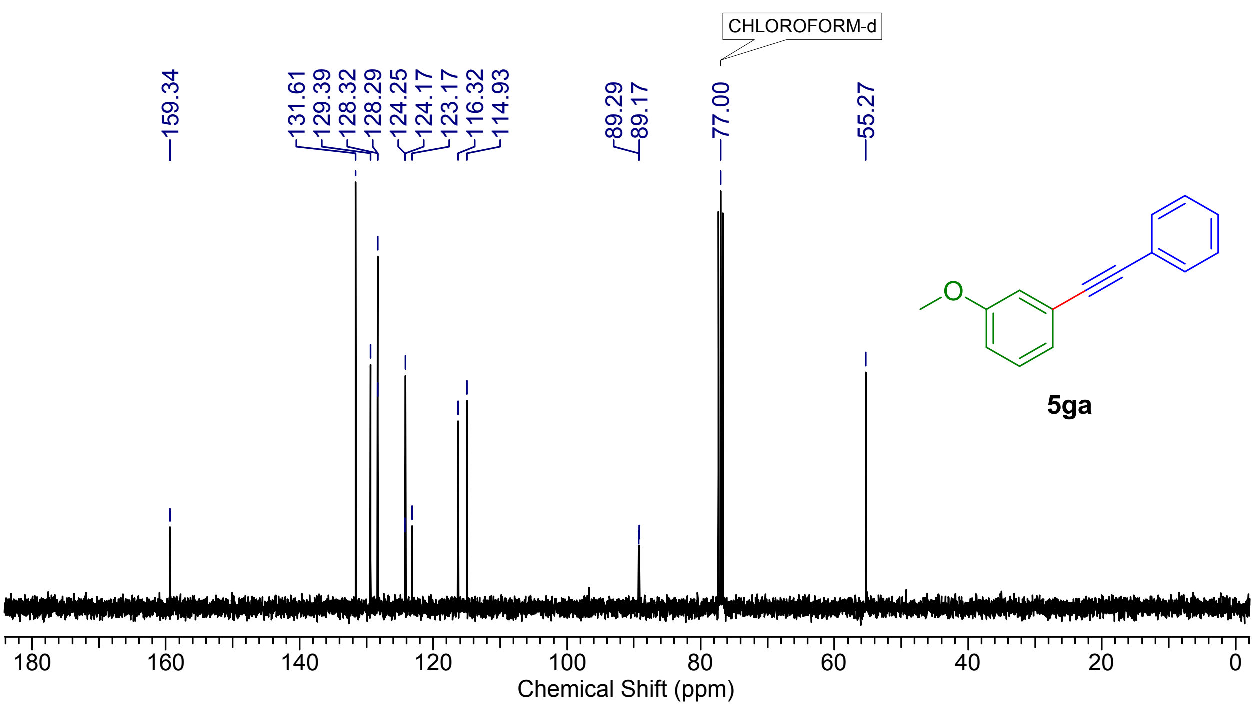
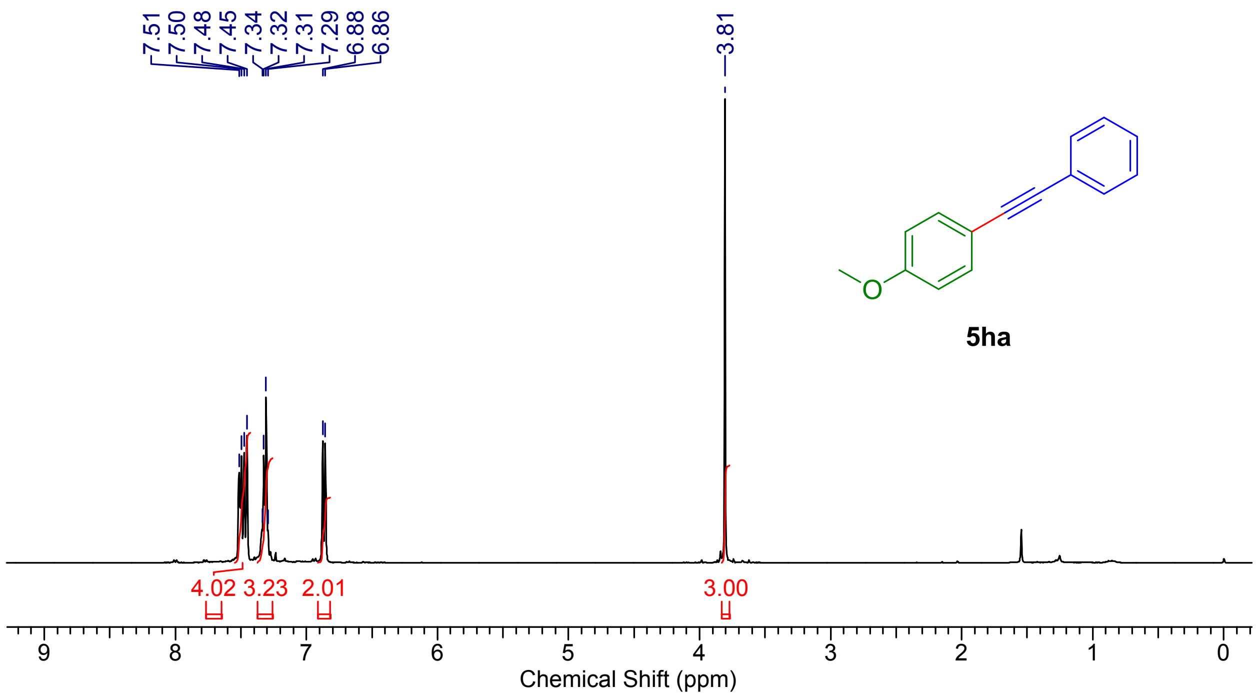


Figure S34: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5ha** in $CDCl_3$



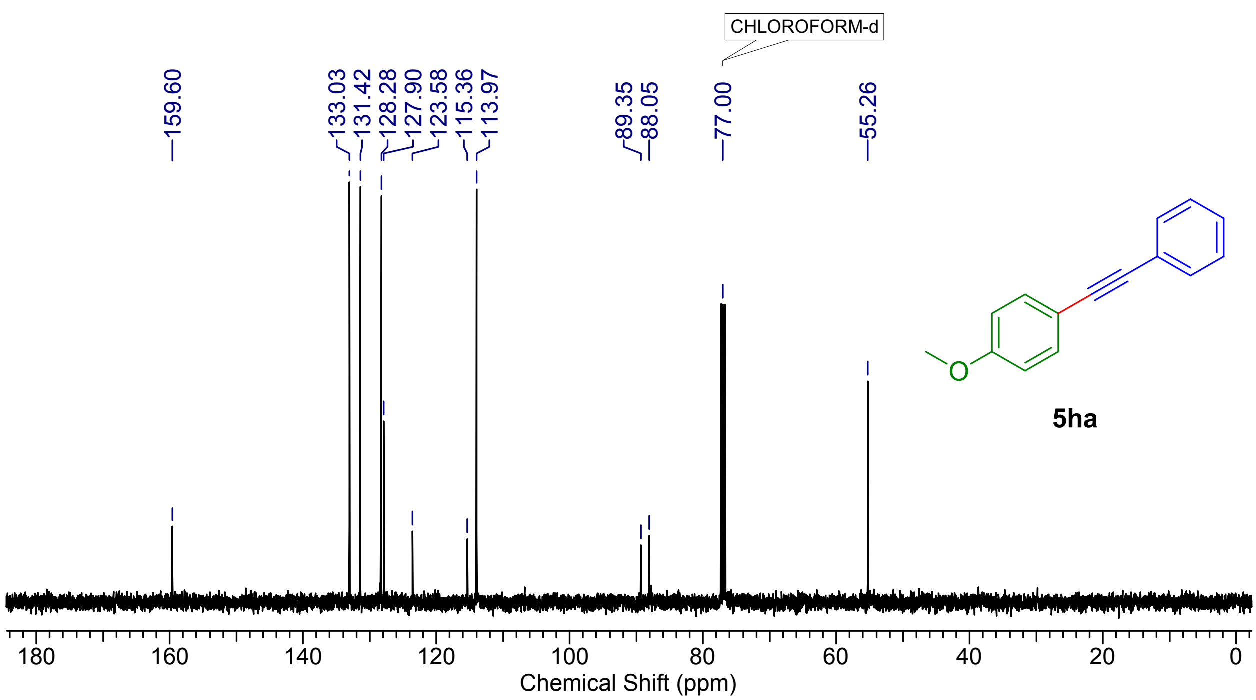
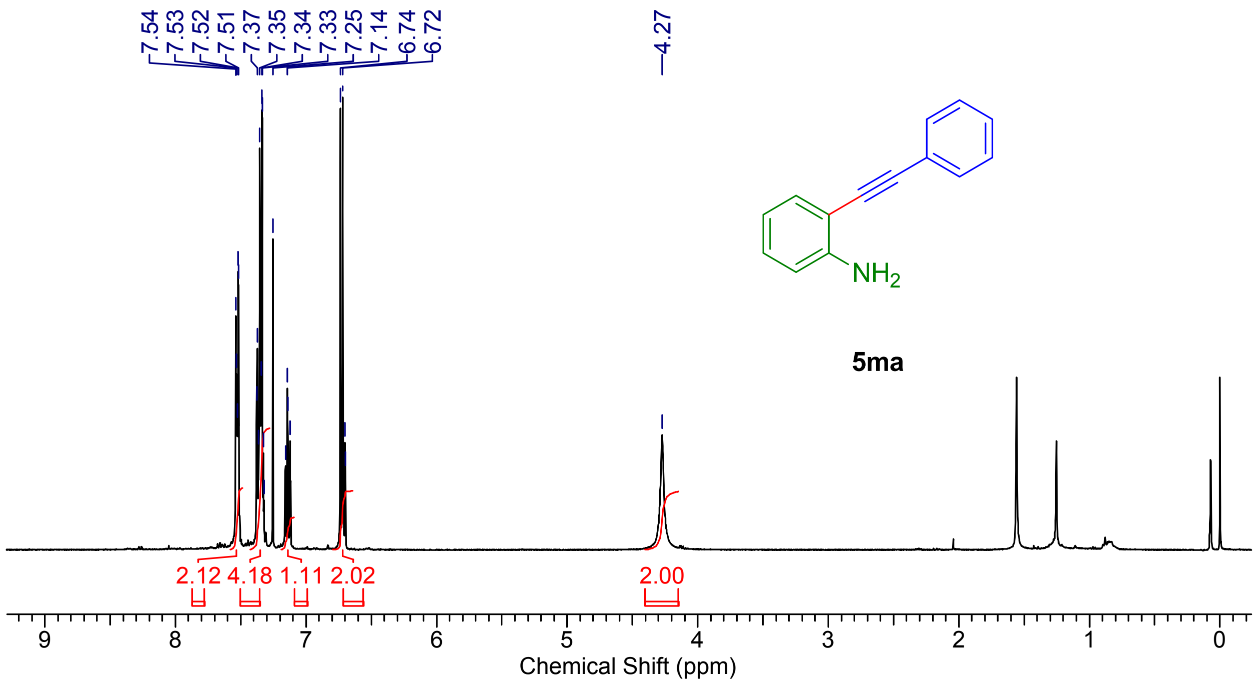


Figure S35: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5ma** in $CDCl_3$



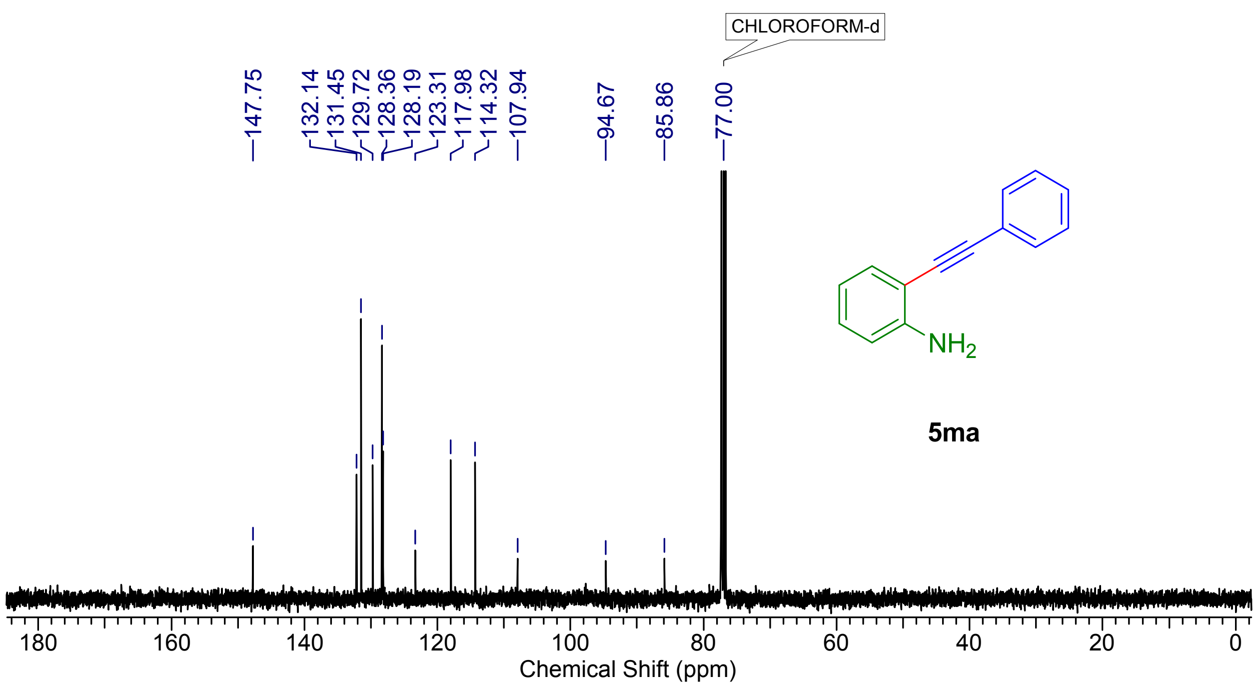
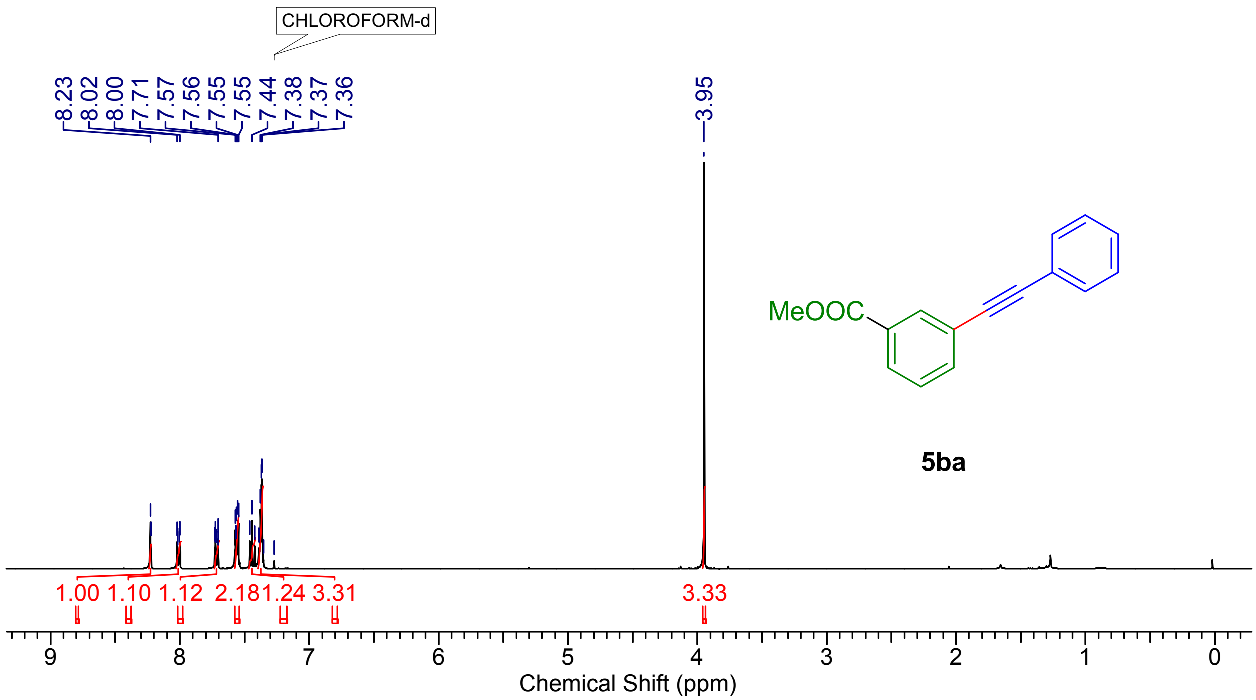


Figure S36: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5ba** in $CDCl_3$



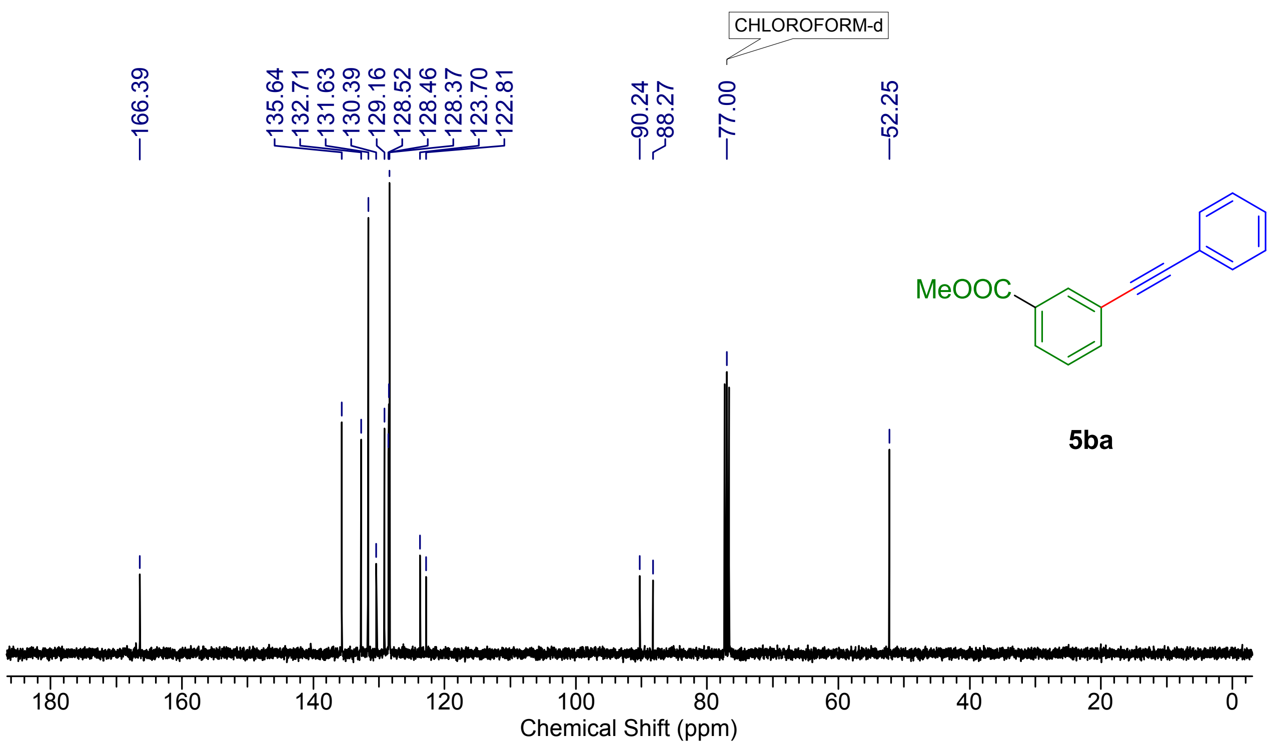
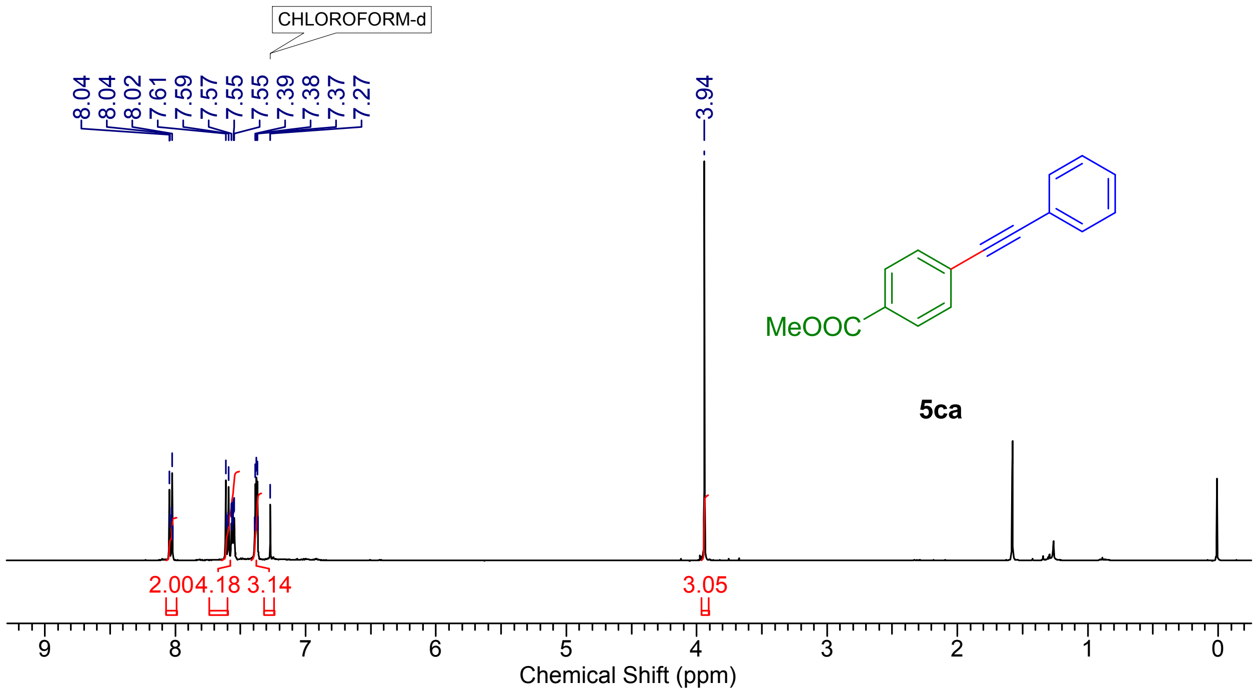


Figure S37:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **5ca** in $CDCl_3$



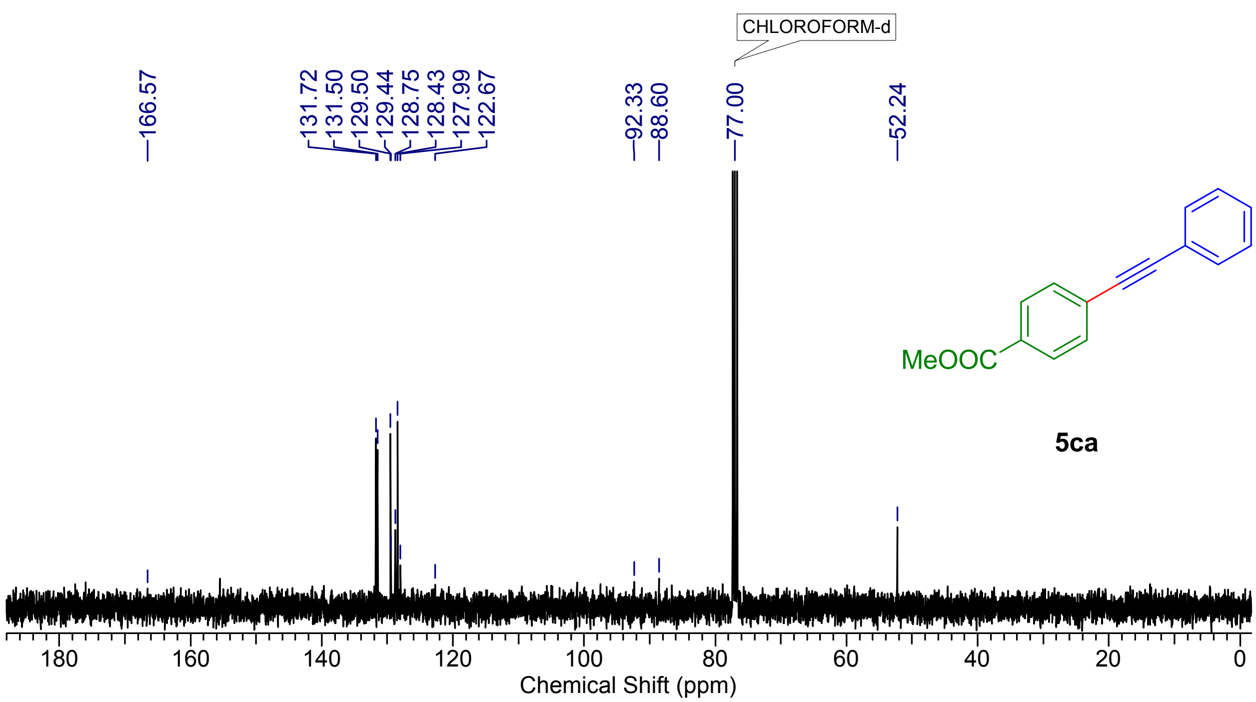
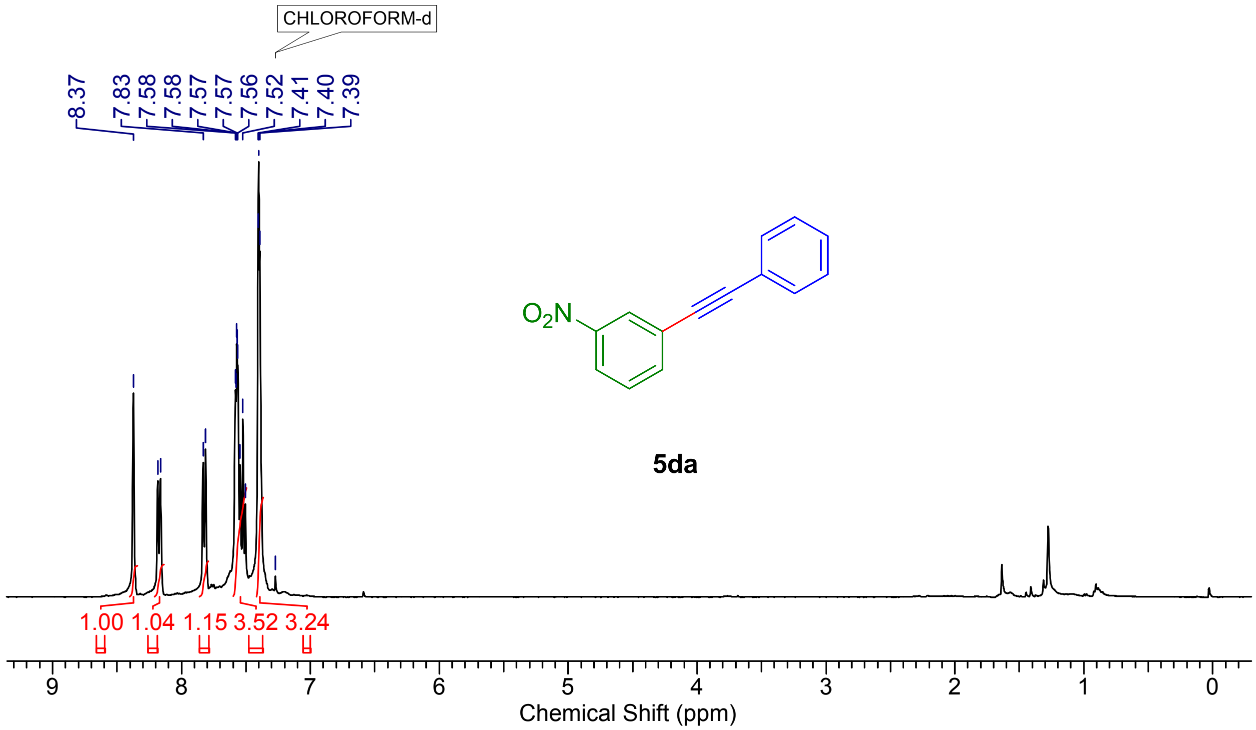


Figure S38: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5da** in $CDCl_3$



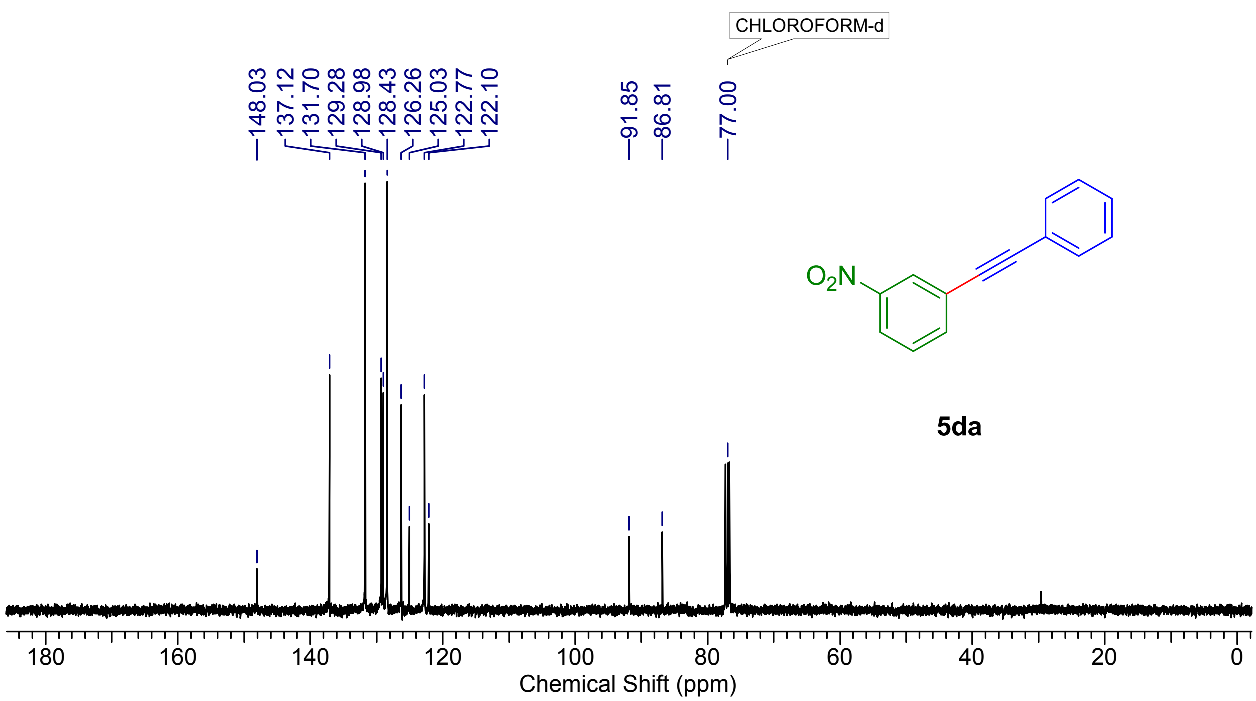
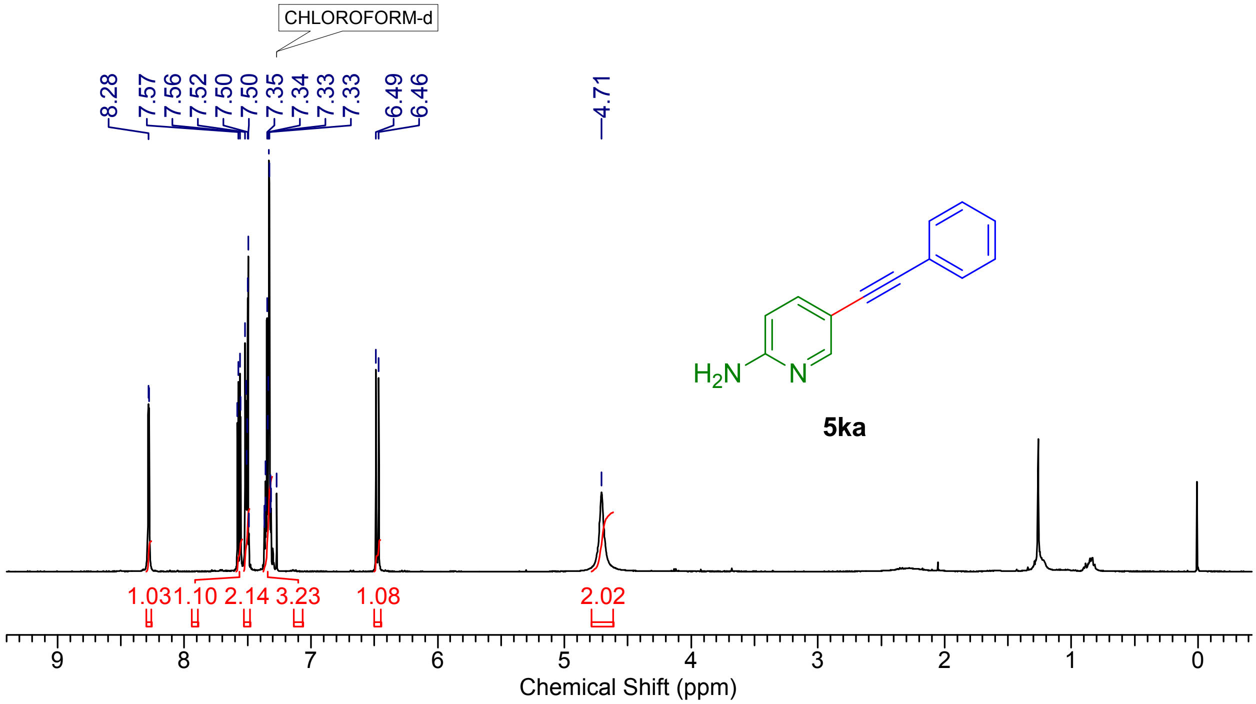
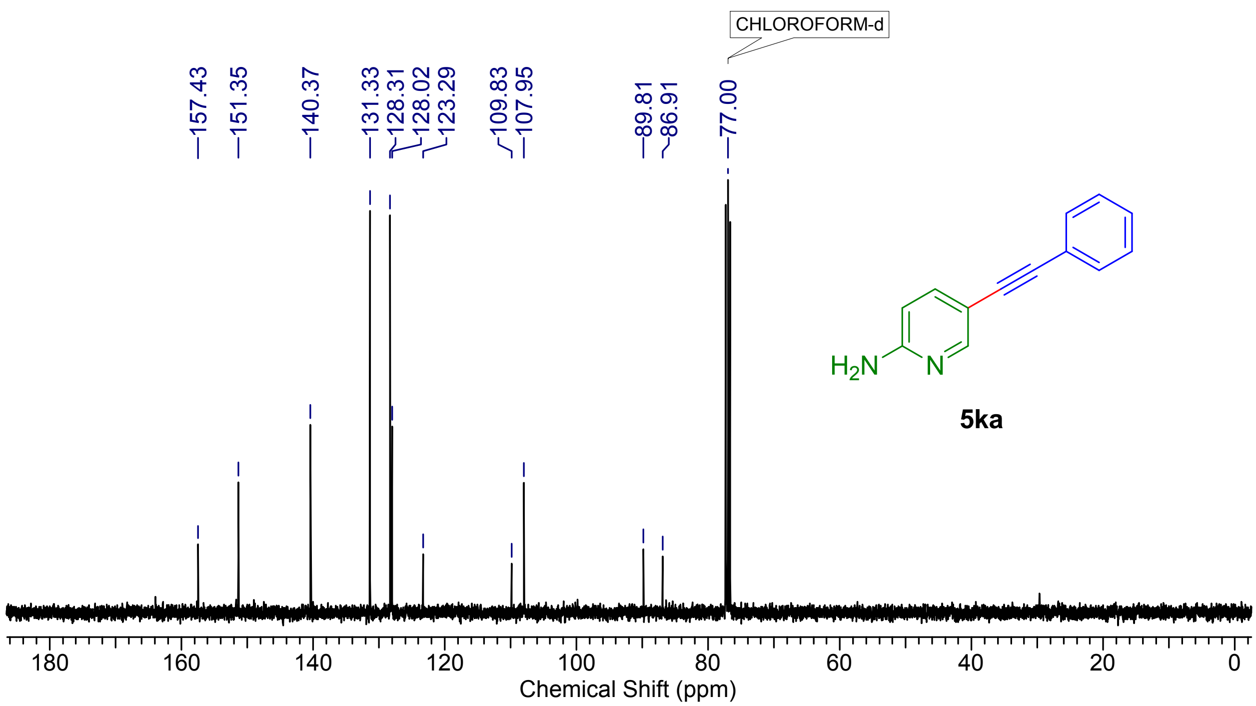


Figure S39: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5ka** in $CDCl_3$

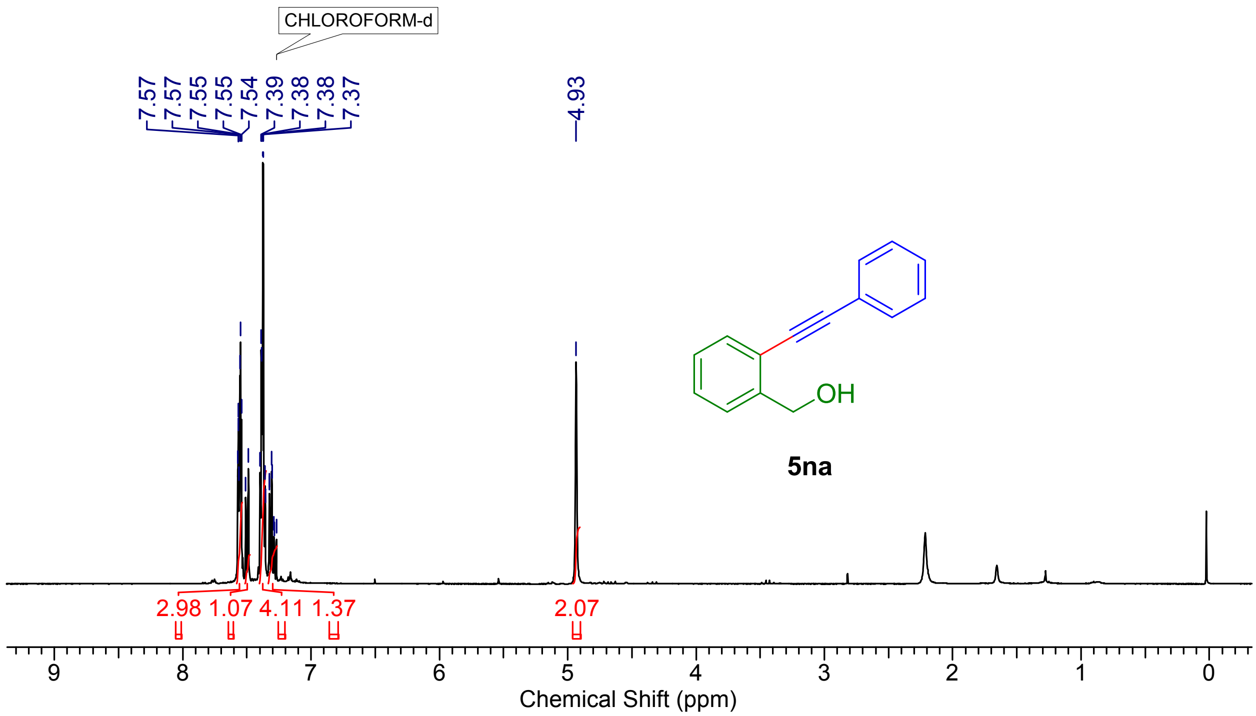


5ka



5ka

Figure S40:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **5na** in $CDCl_3$



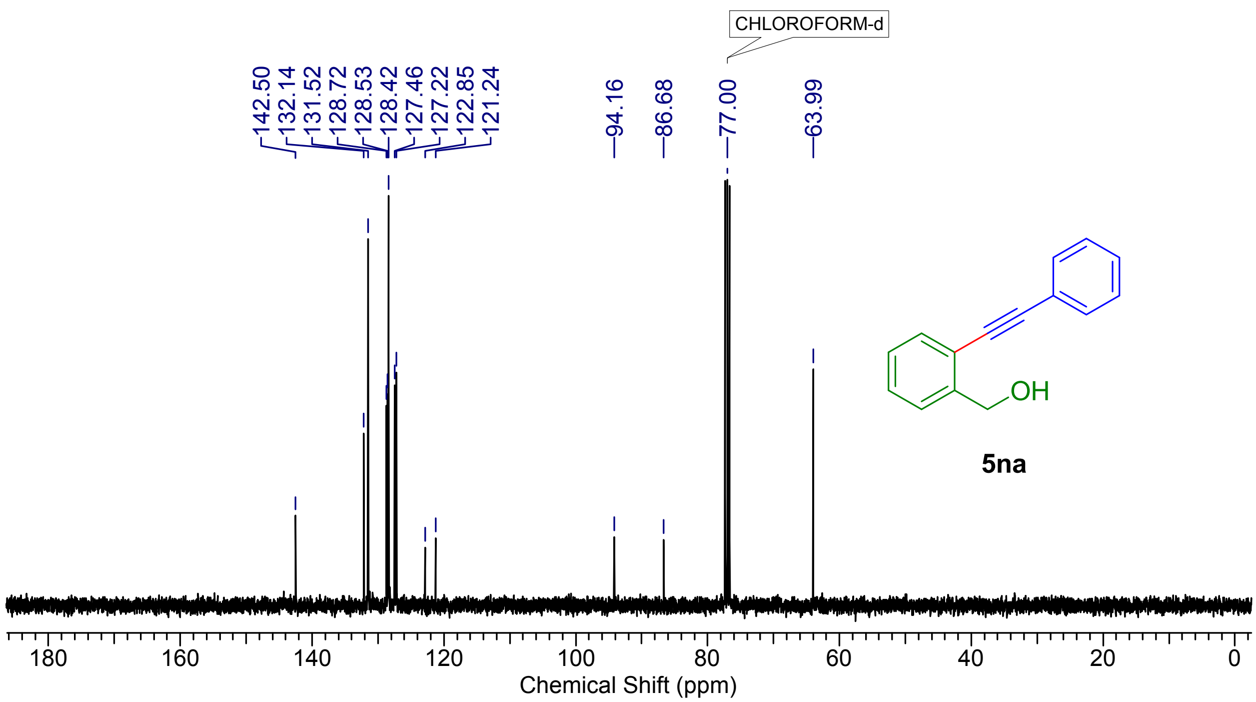
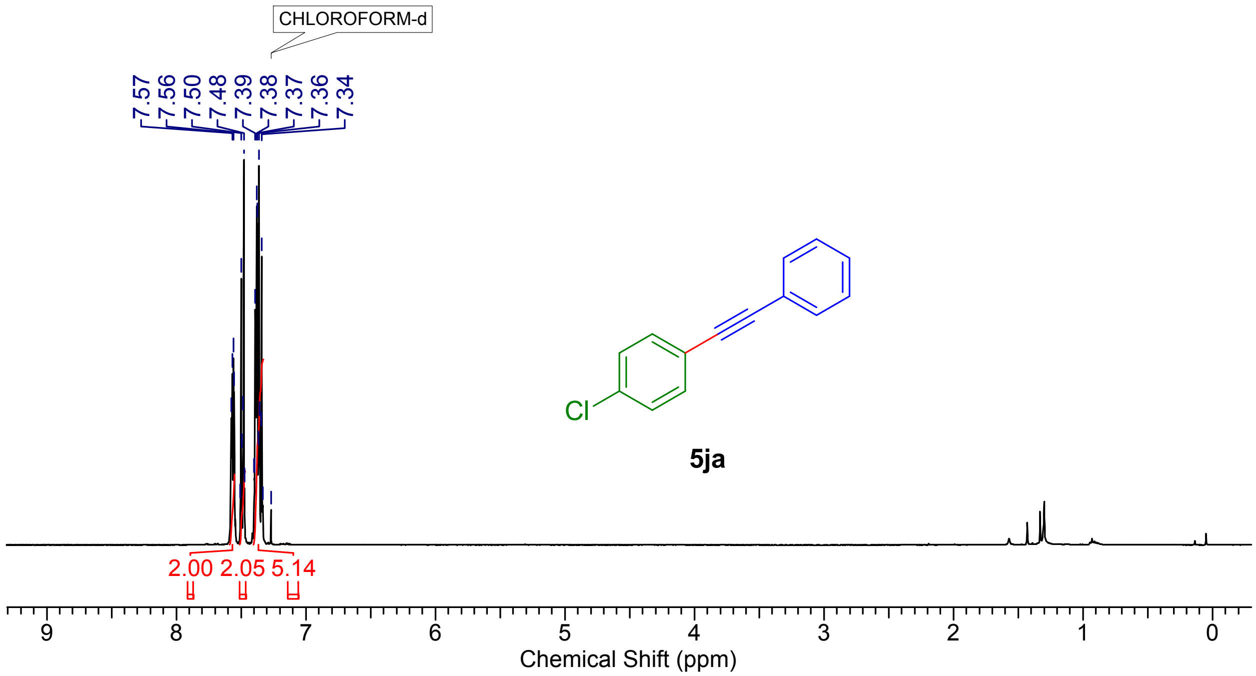


Figure S41: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **5ja** in $CDCl_3$



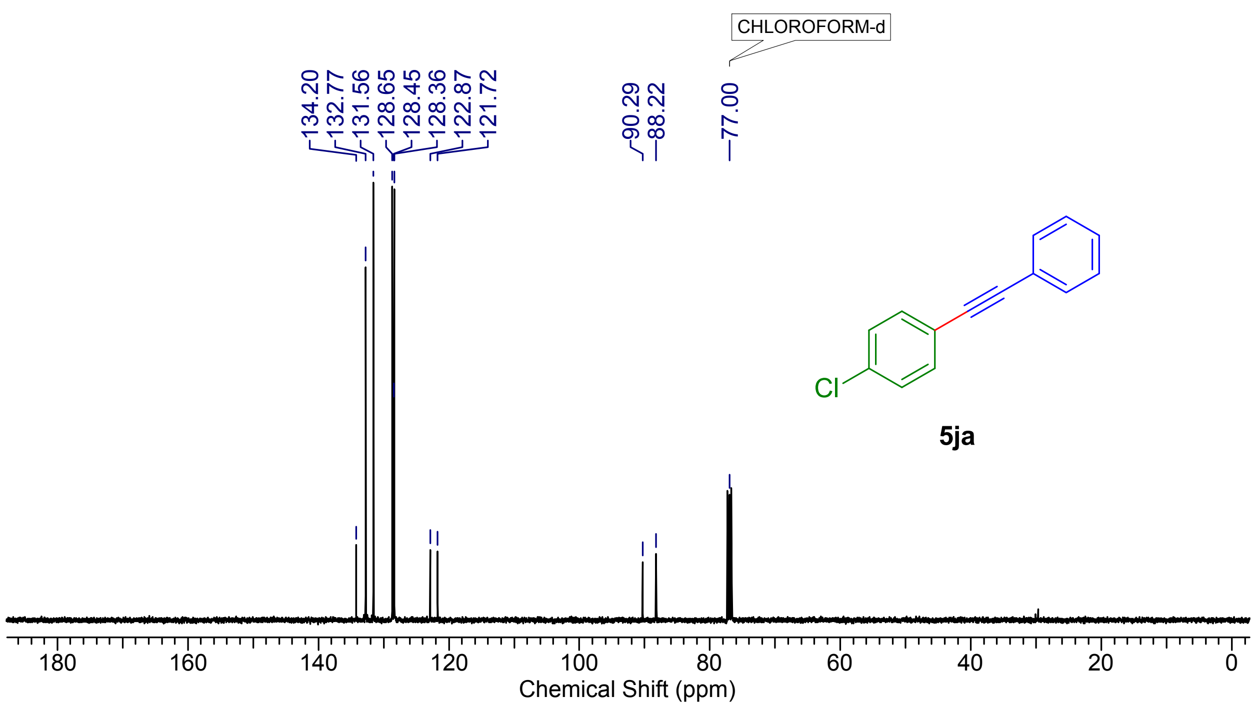
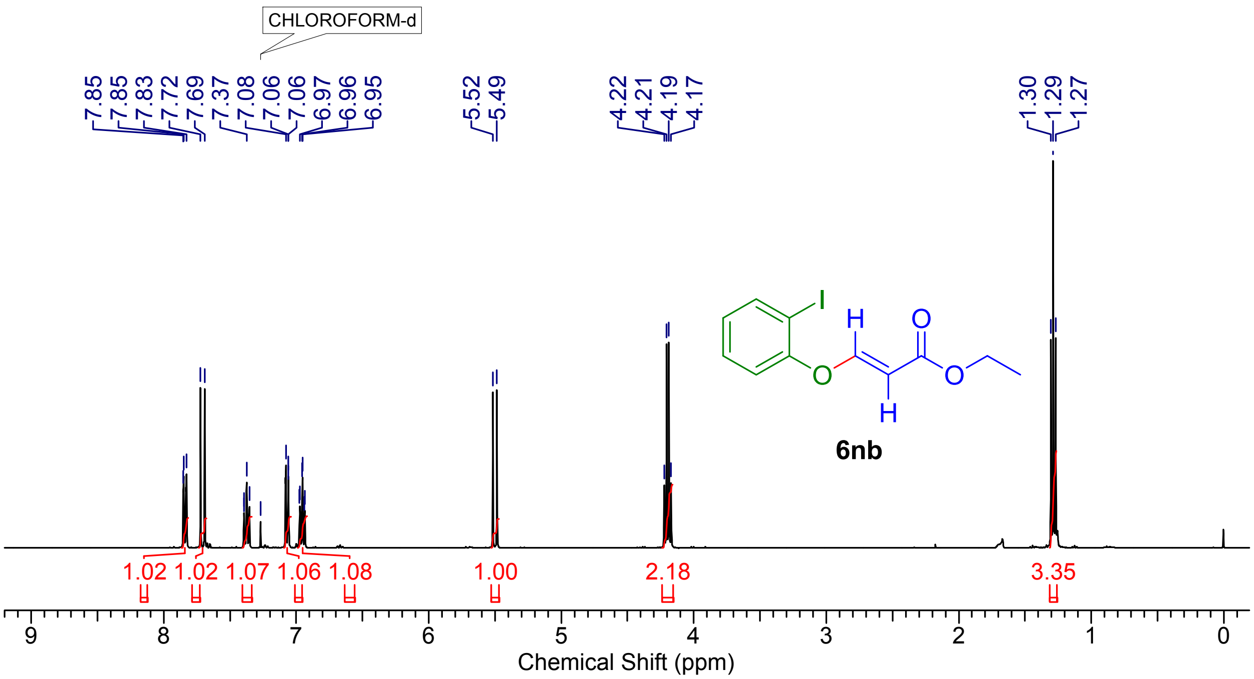


Figure S42: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **6nb-T** in $CDCl_3$



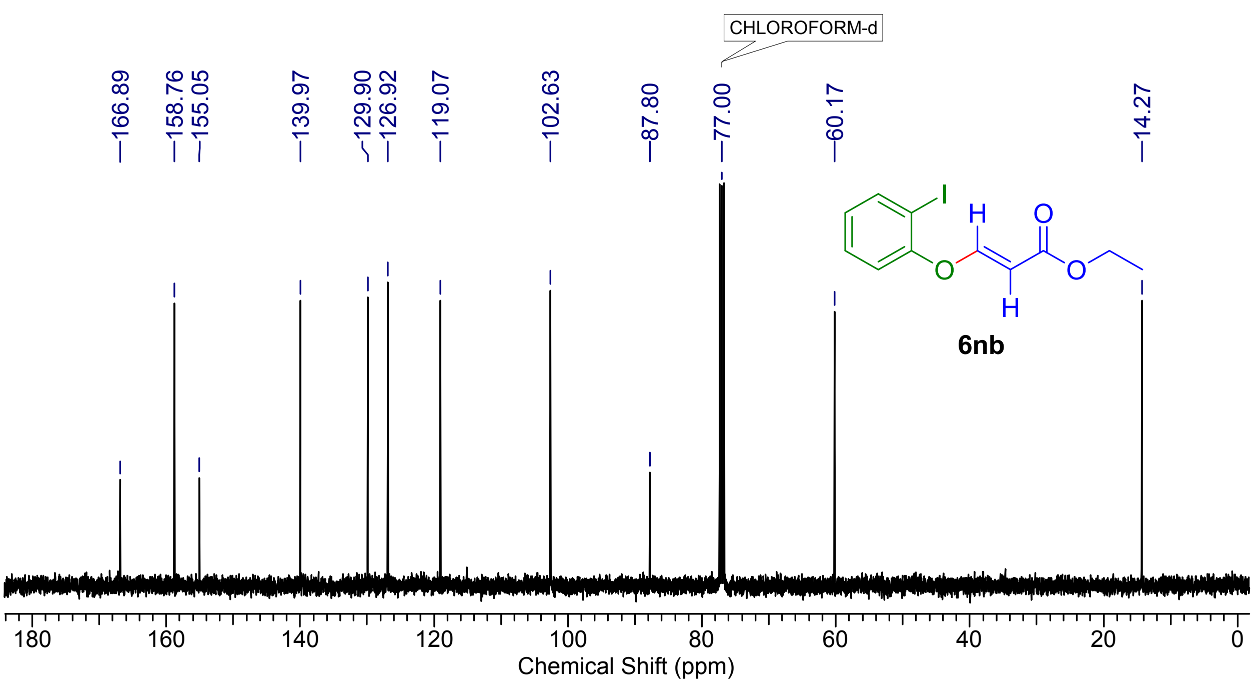
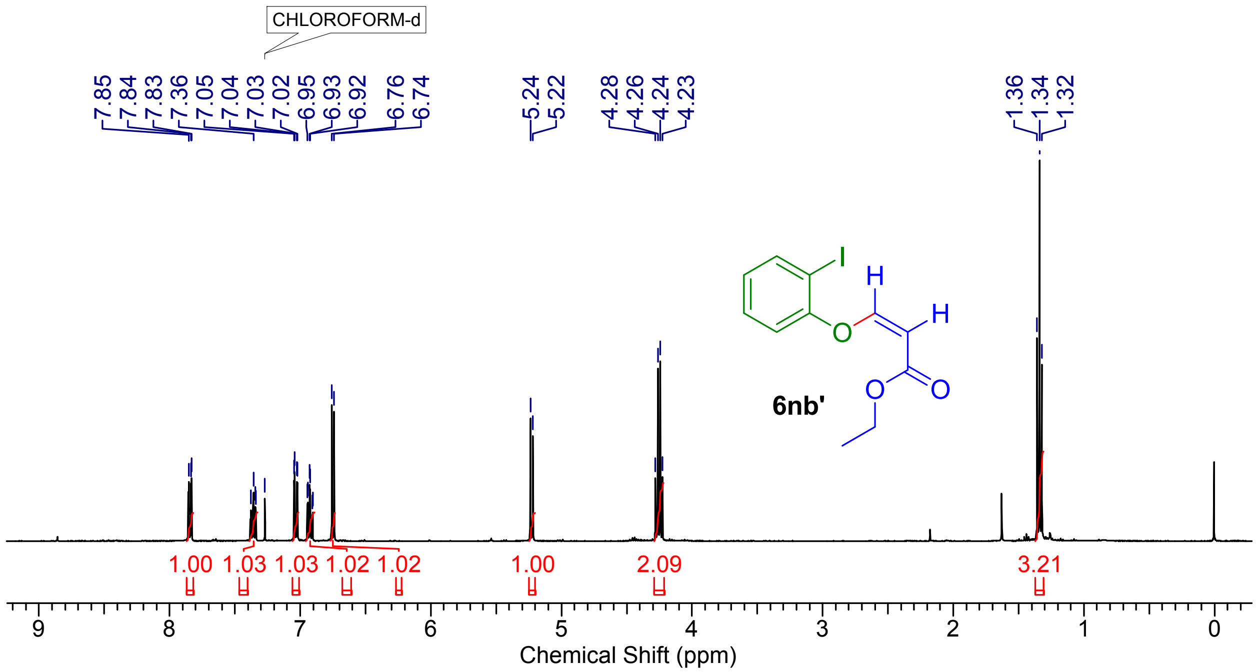


Figure S43:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **6nb-C** in $CDCl_3$



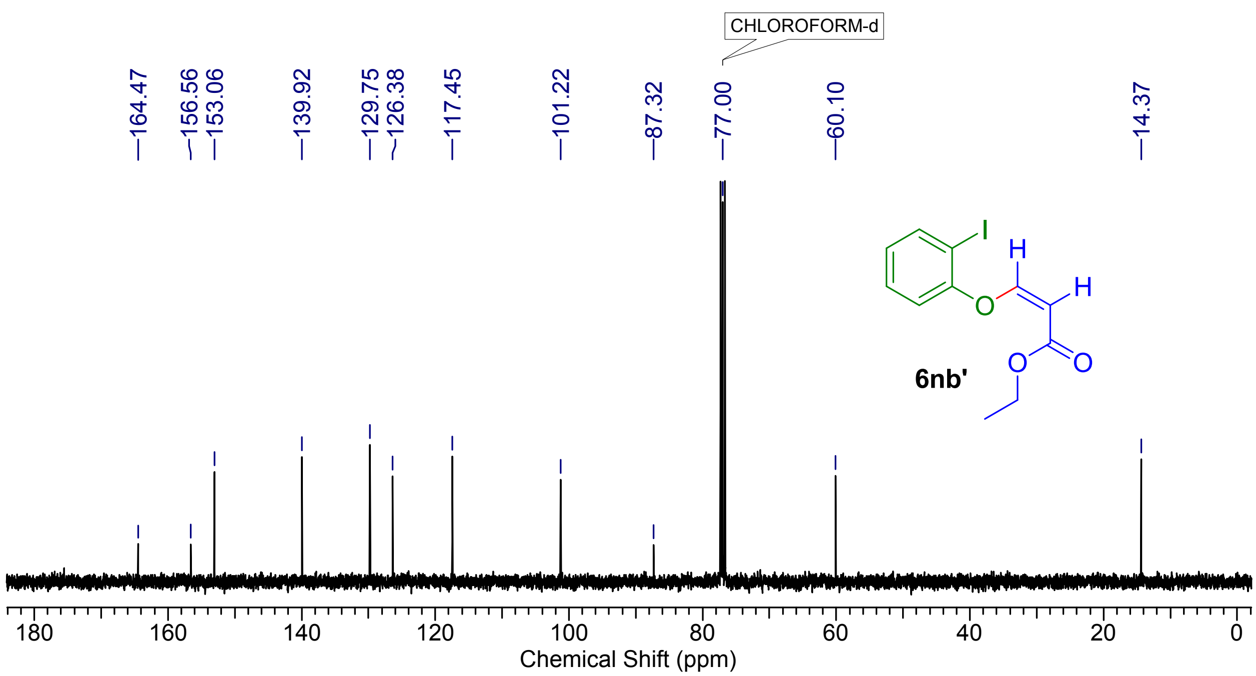
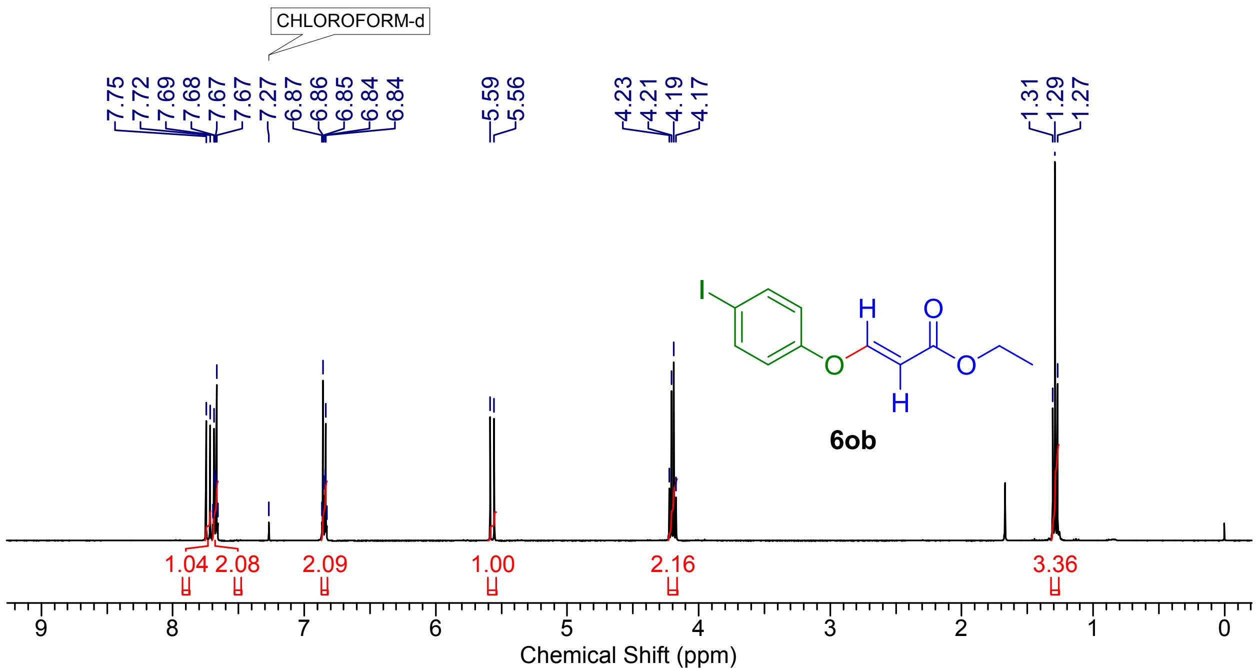


Figure S44: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **6ob-T** in $CDCl_3$



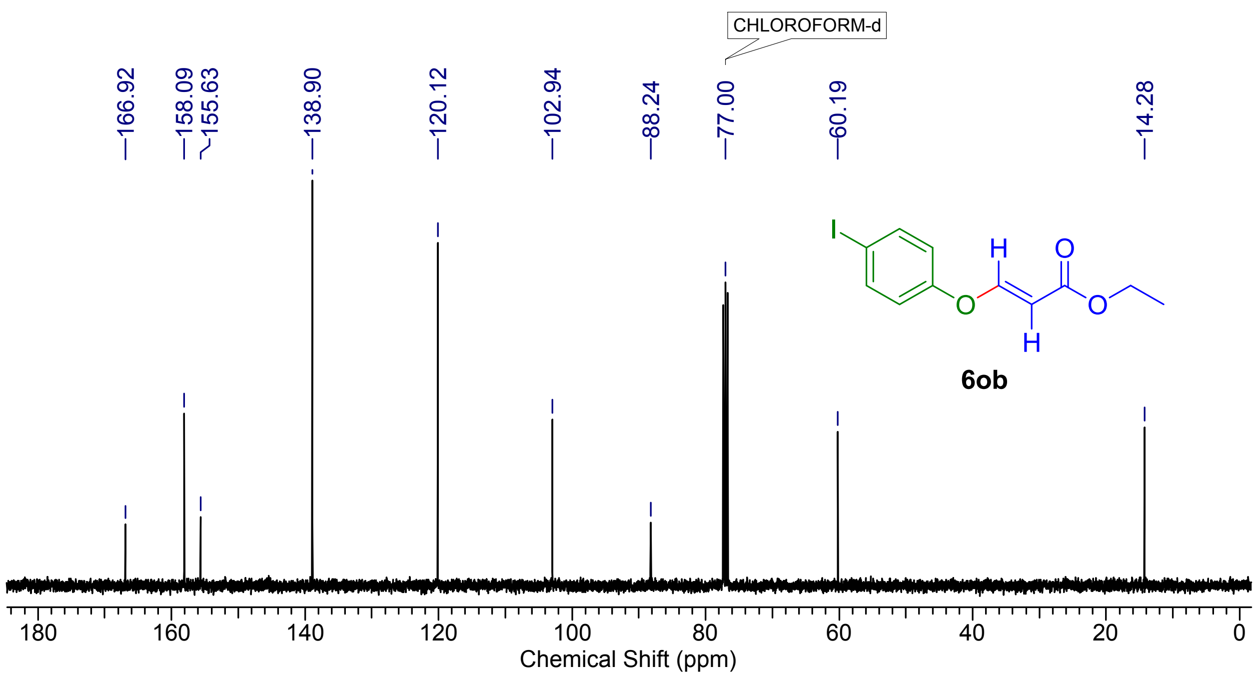
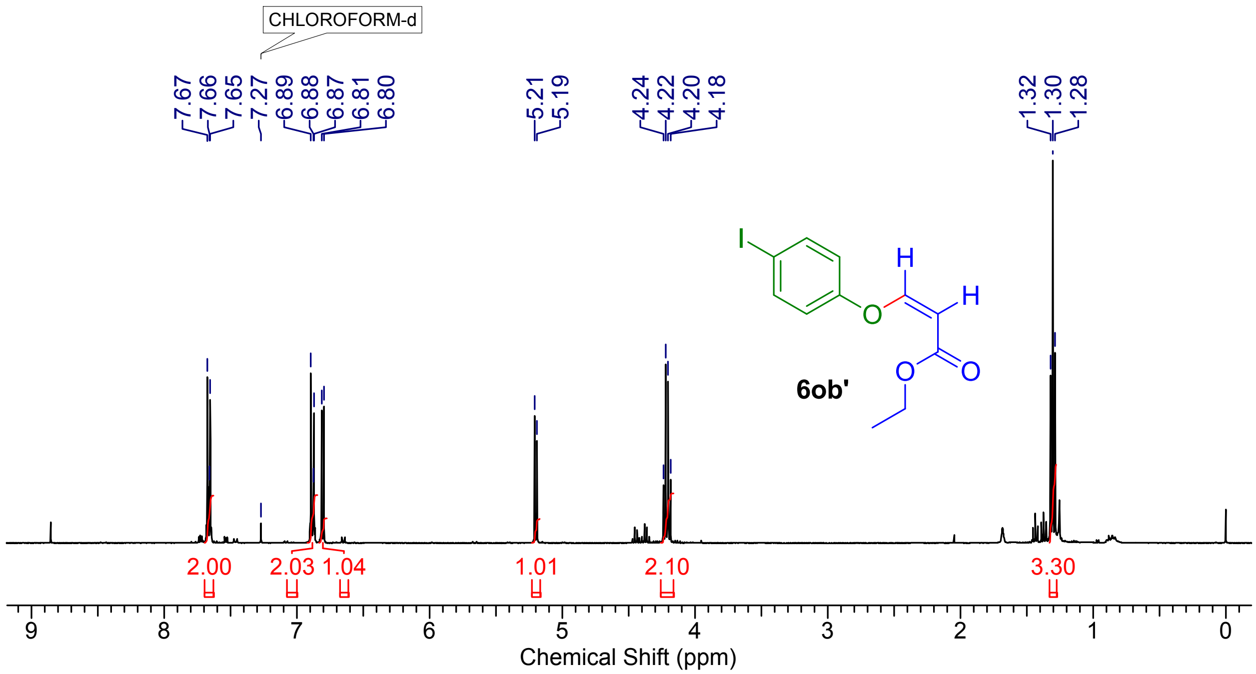


Figure S45: [1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **6ob-C** in $CDCl_3$



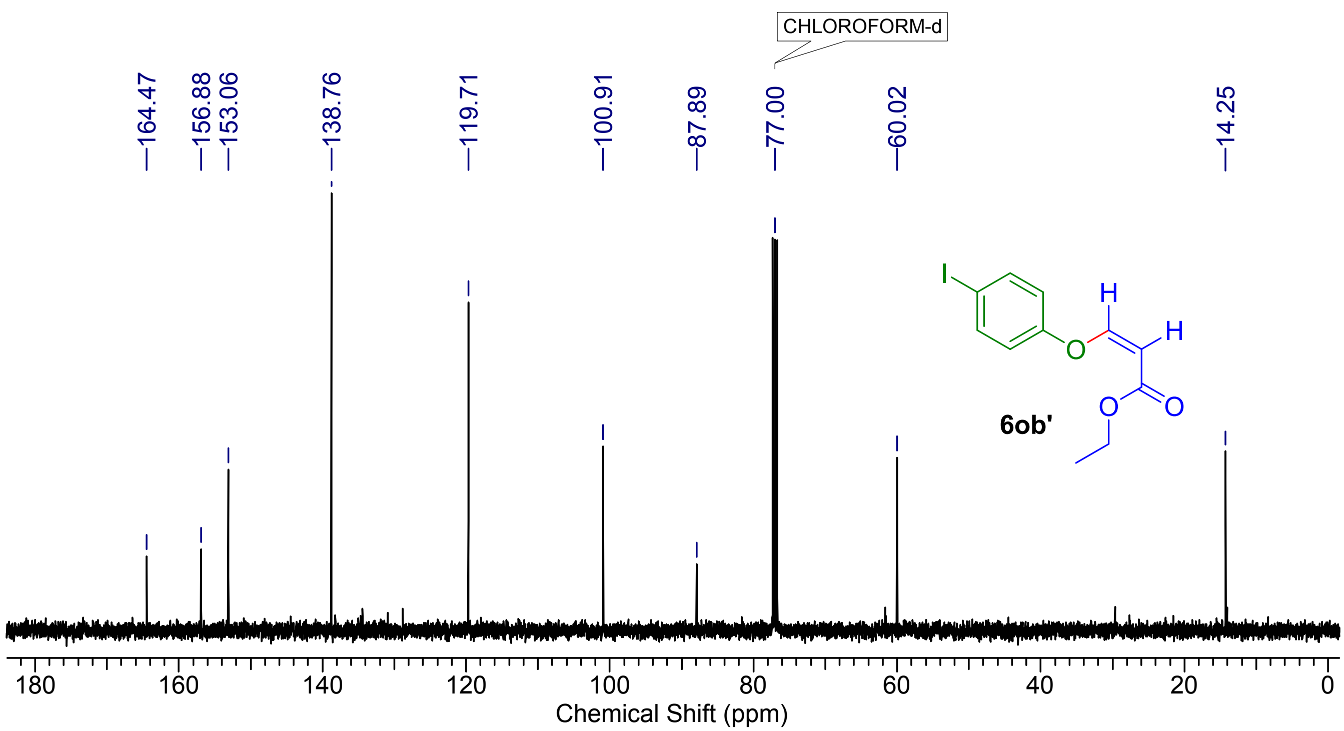
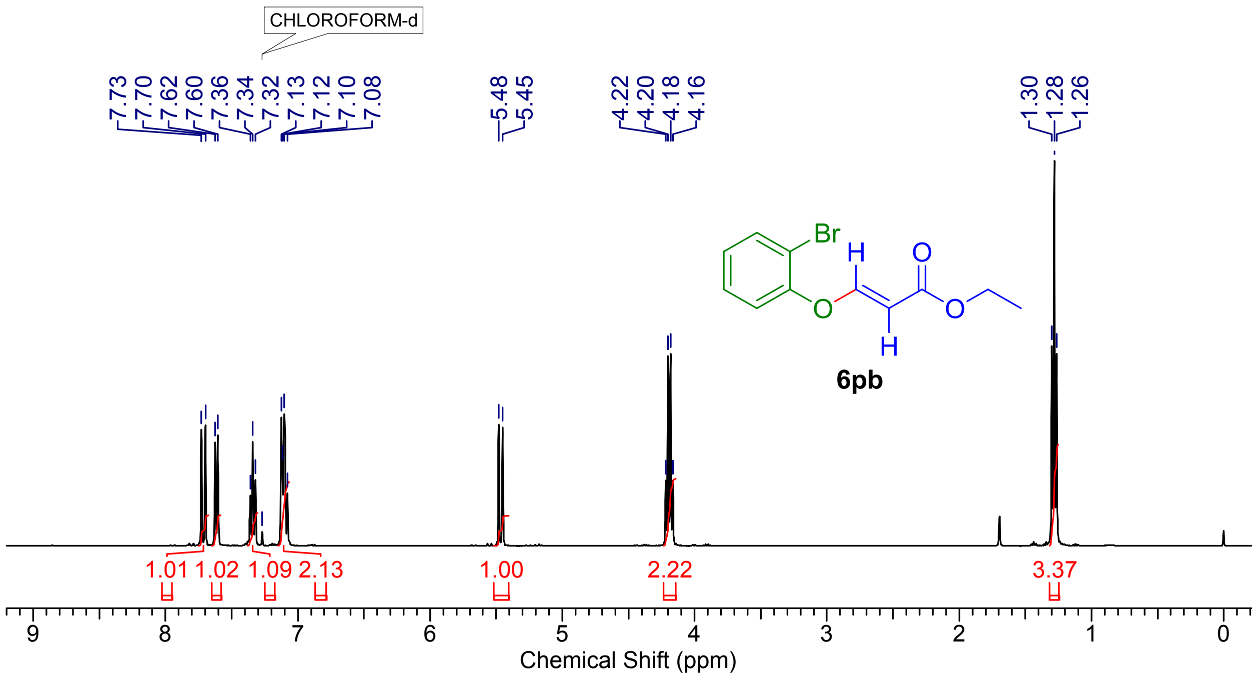


Figure S46: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **6pb-T** in $CDCl_3$



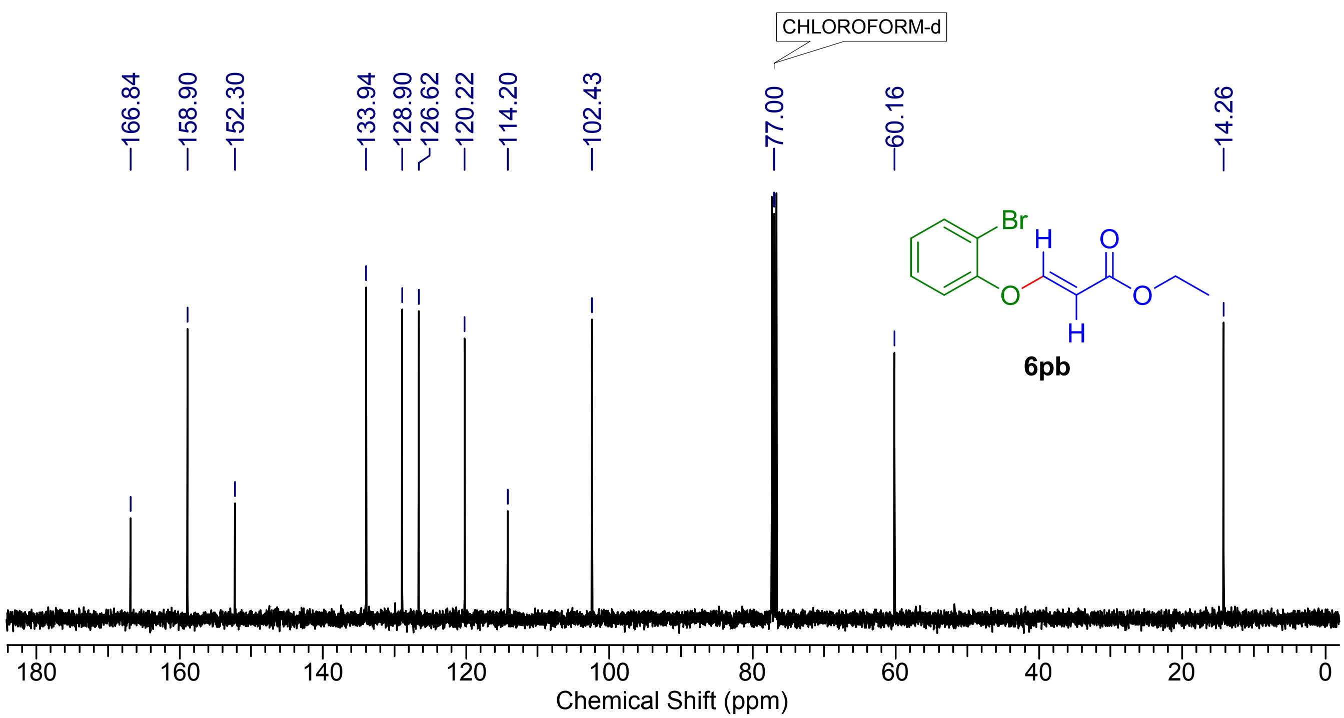
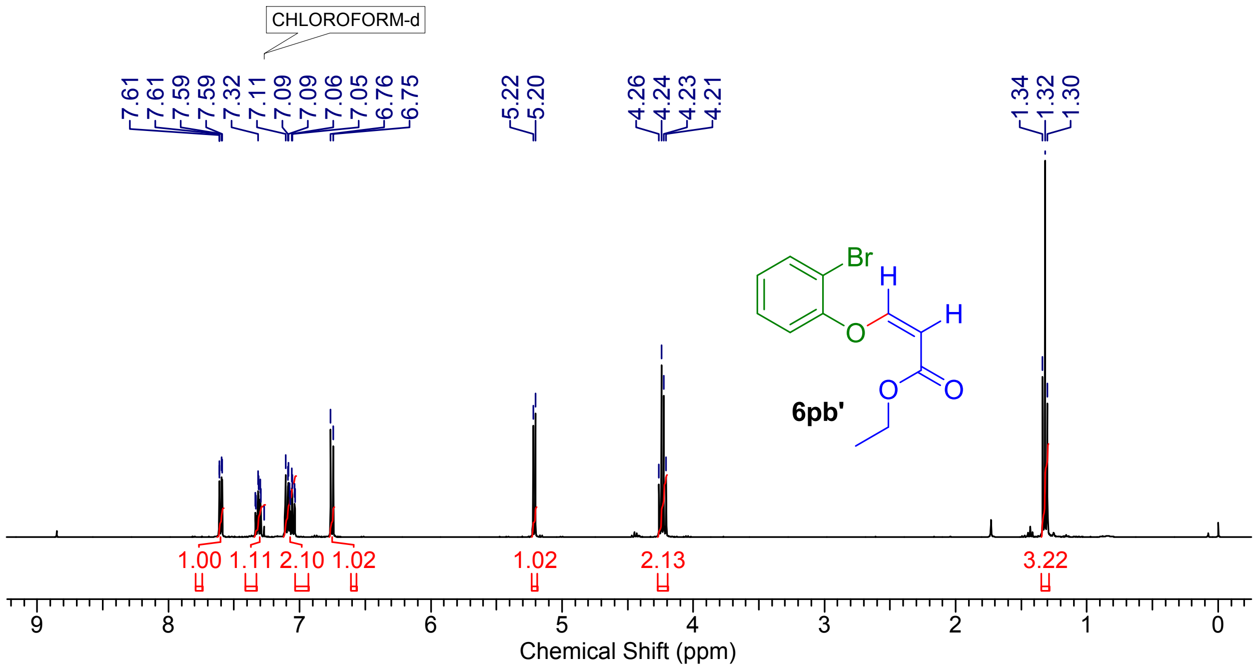


Figure S47: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **6pb-C** in $CDCl_3$



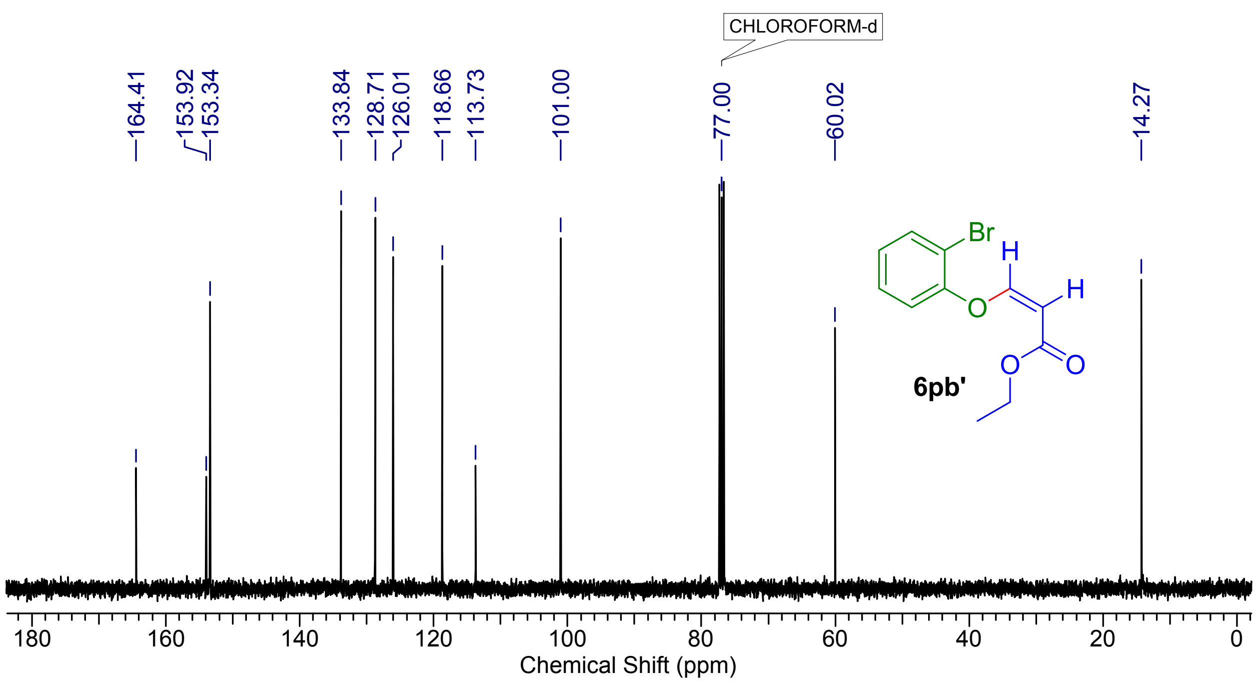
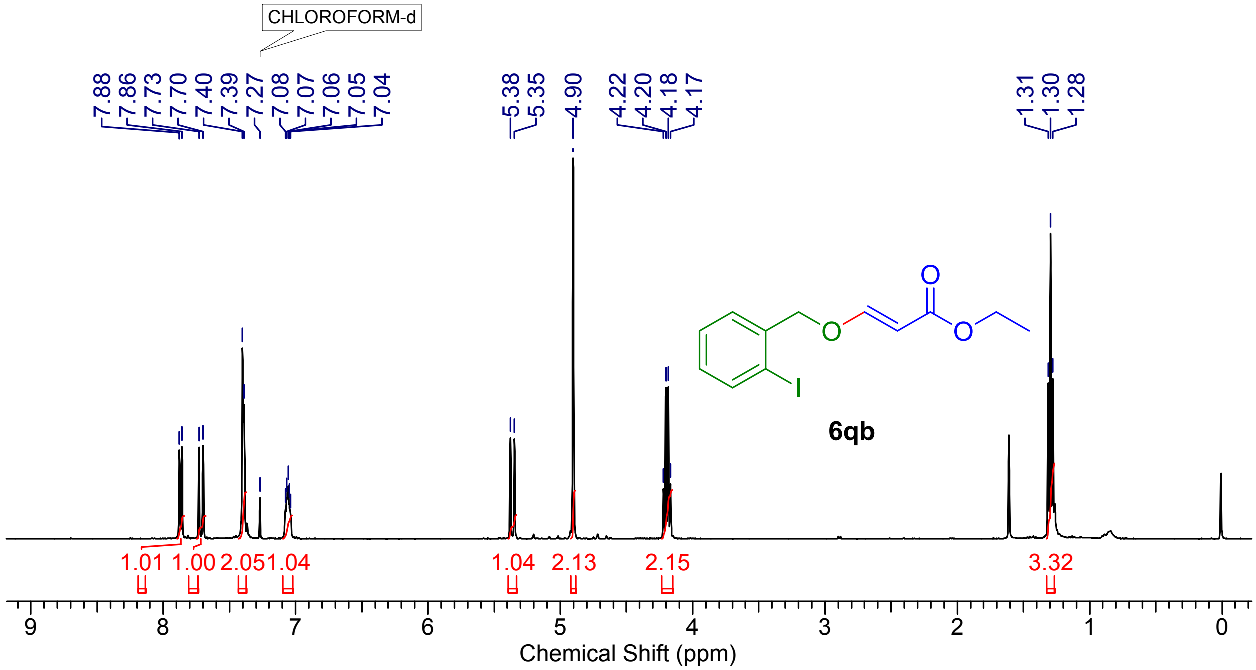


Figure S48: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **6qb-T** in $CDCl_3$



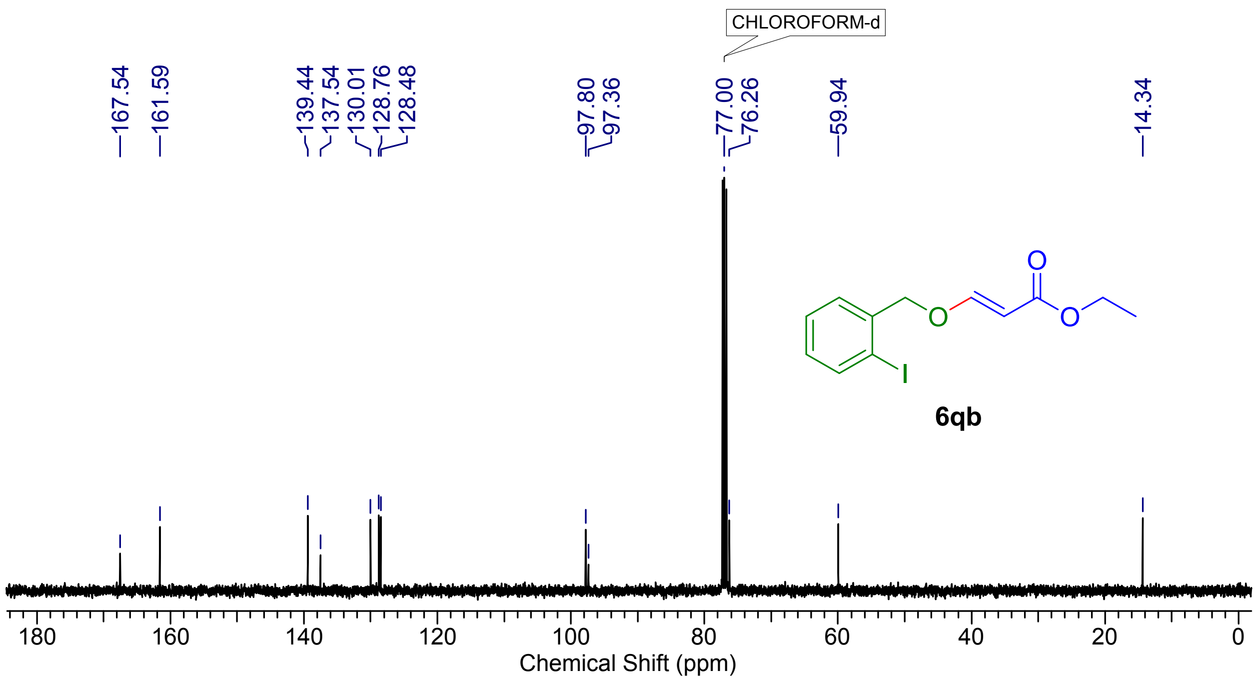
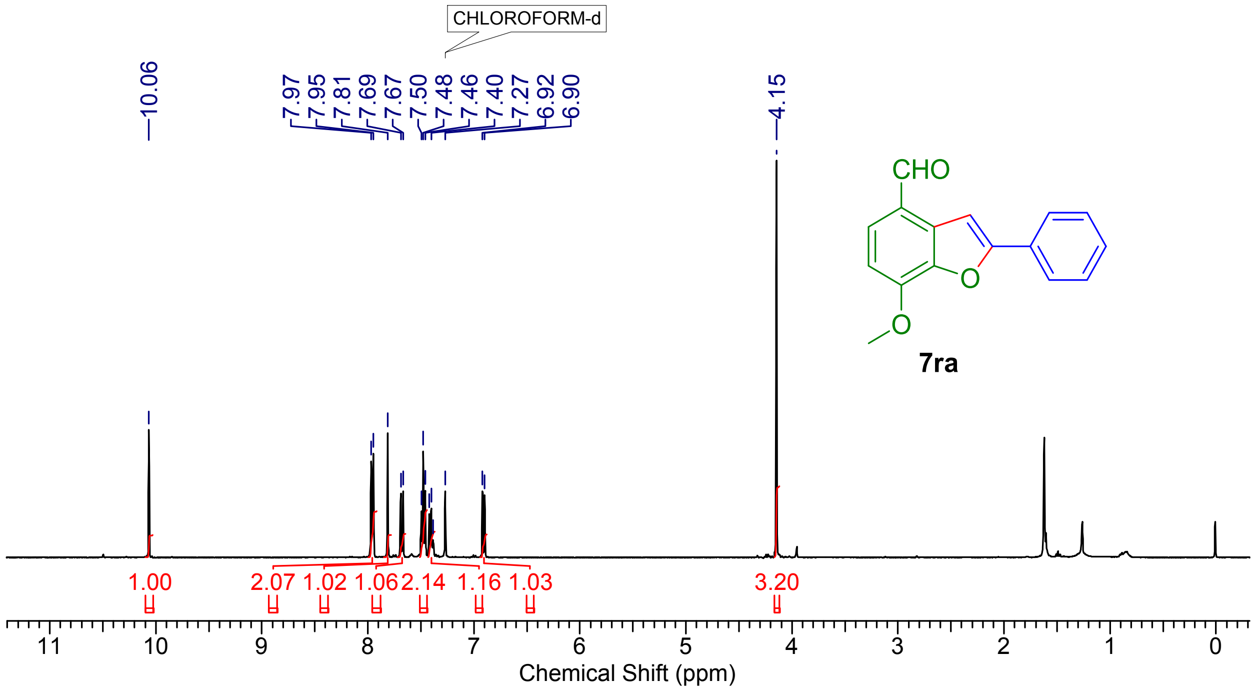


Figure S49: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **7ra** in $CDCl_3$



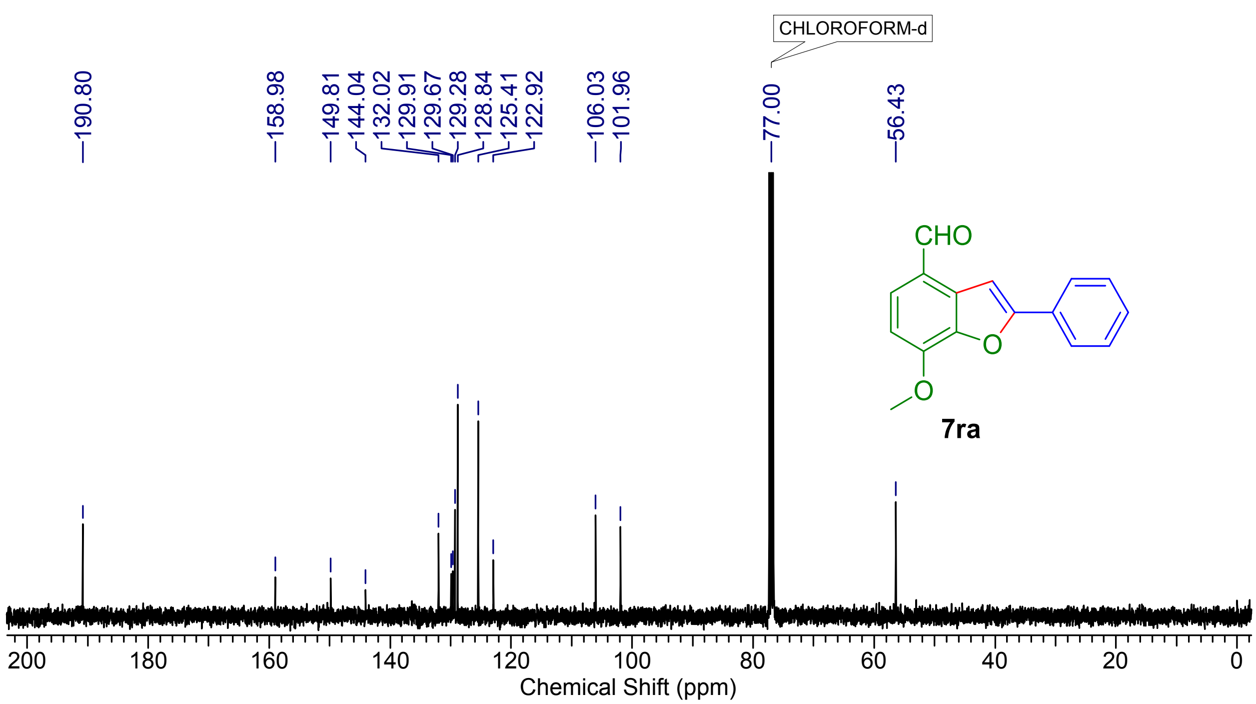
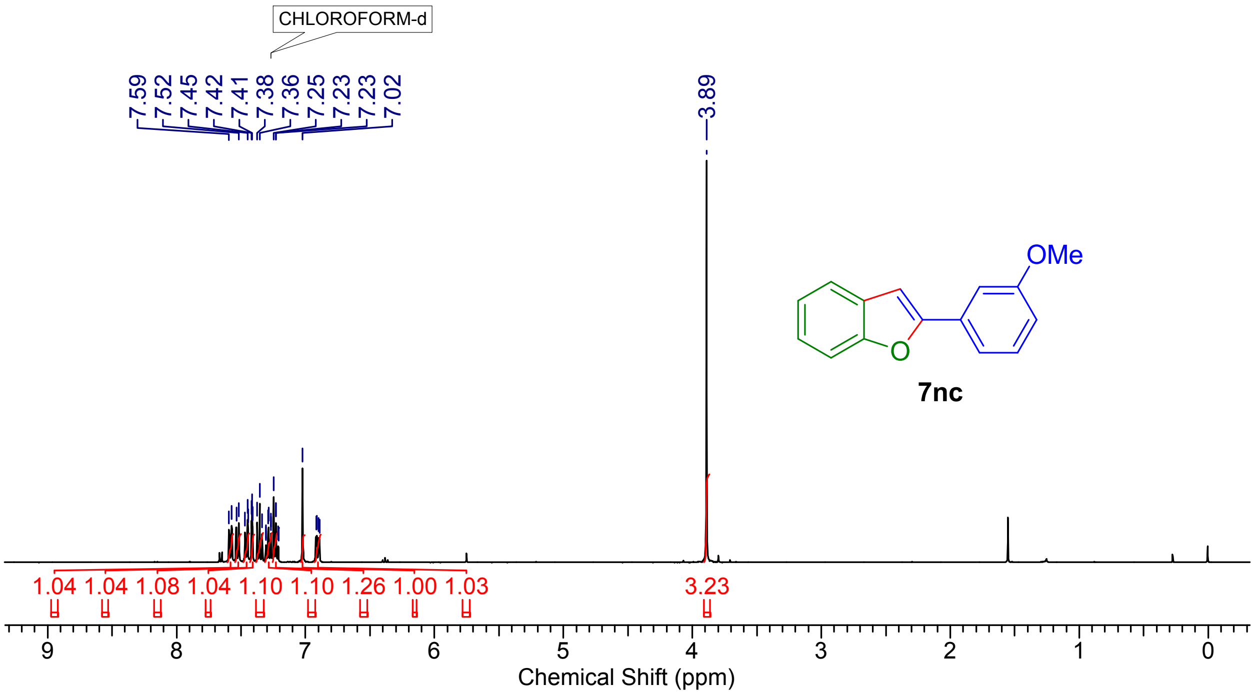


Figure S50: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **7nc** in $CDCl_3$



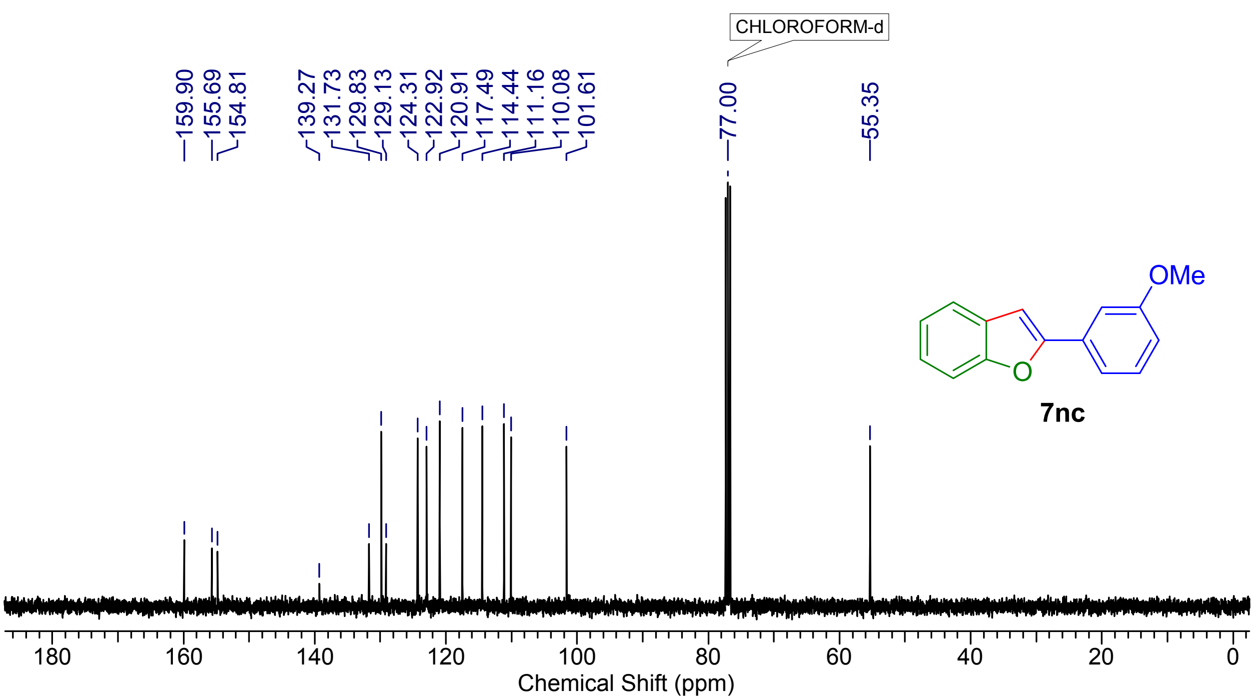
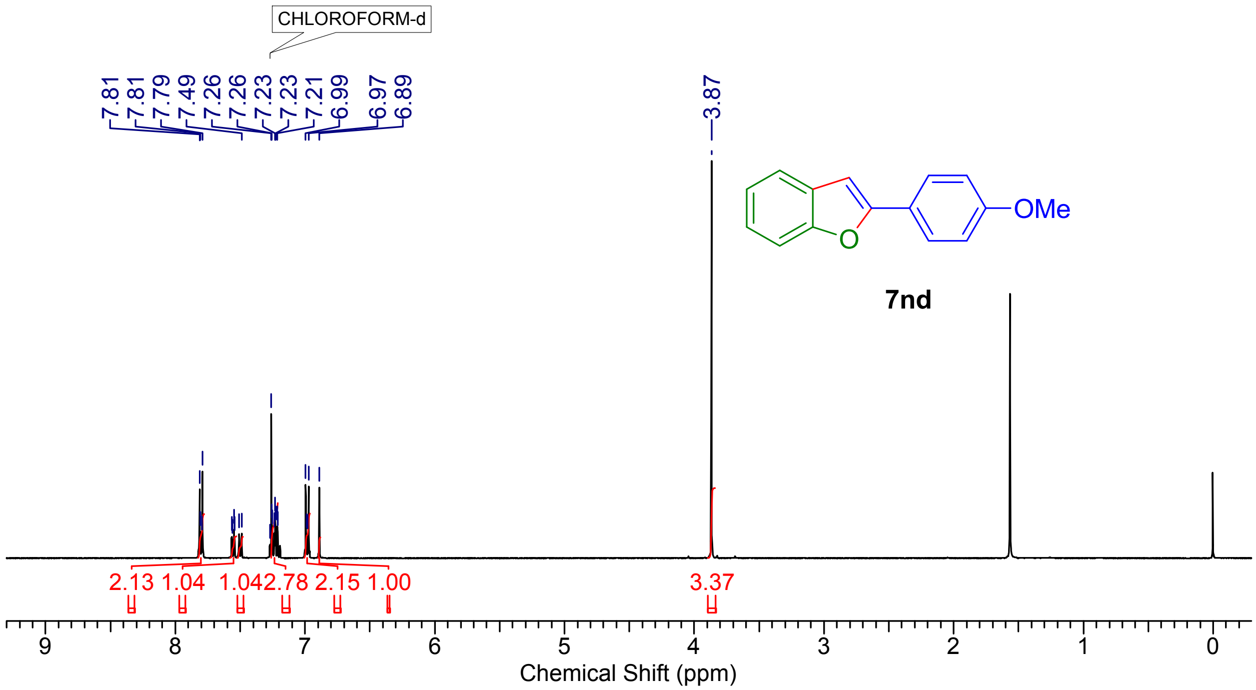


Figure S51: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **7nd** in $CDCl_3$



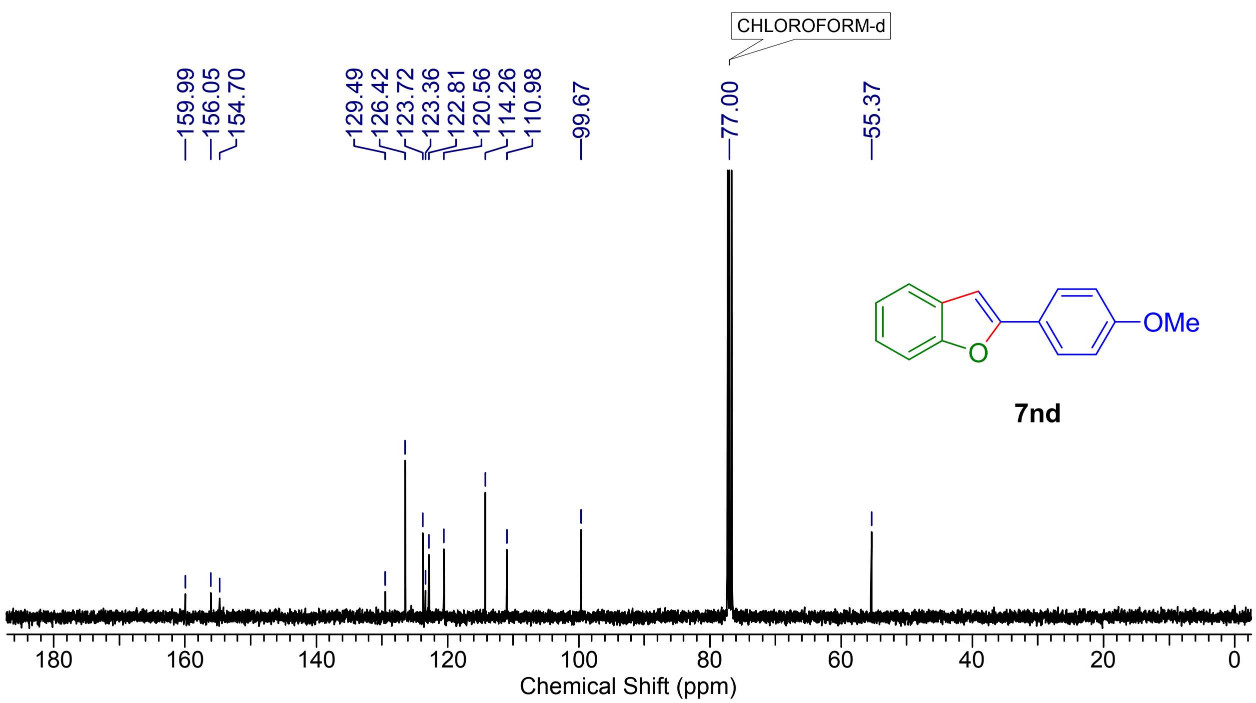
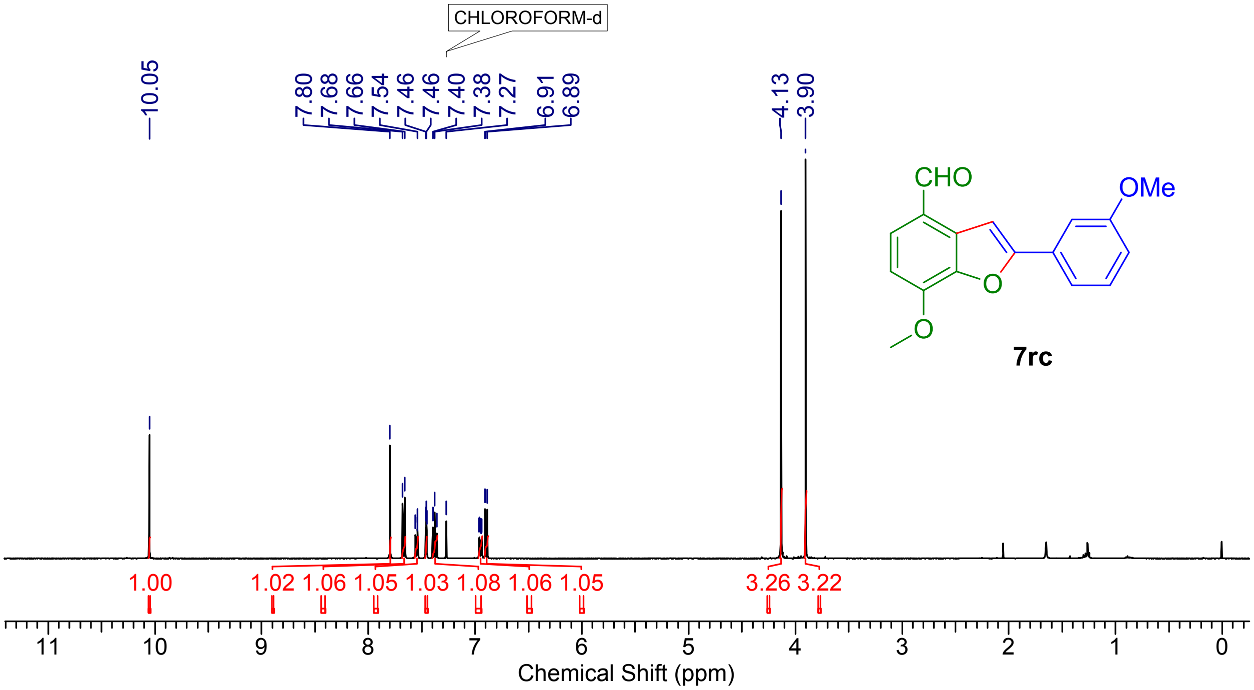


Figure S52: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **7rc** in $CDCl_3$



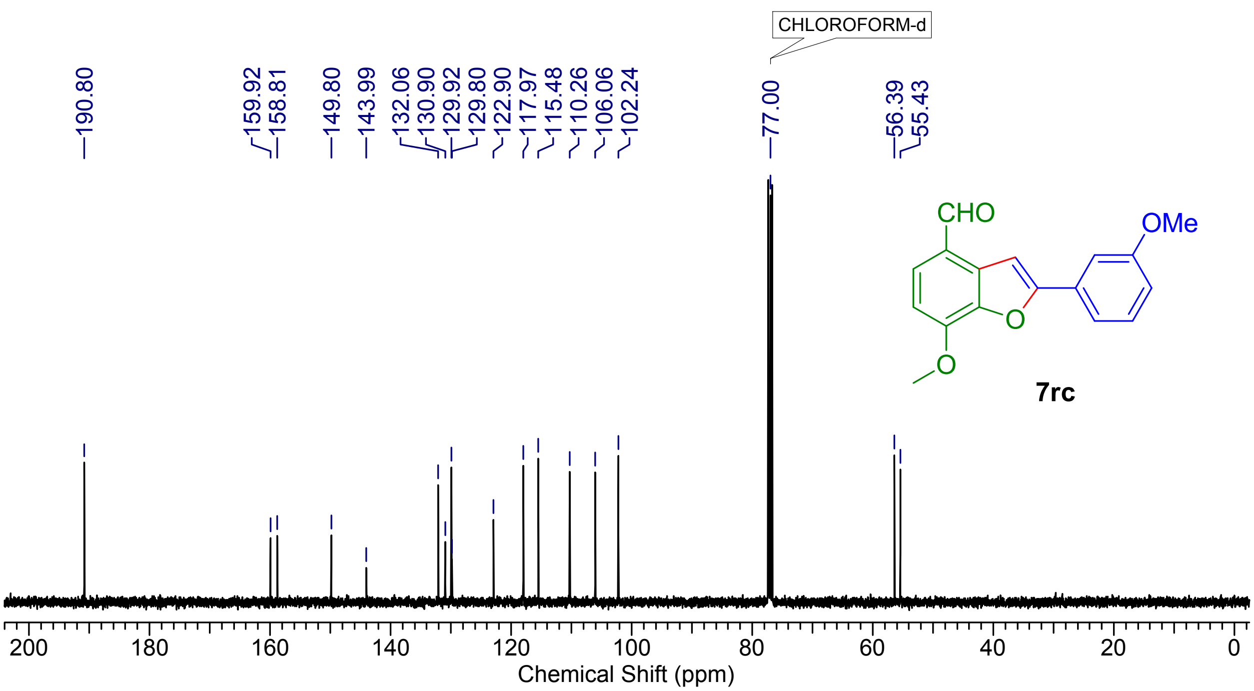
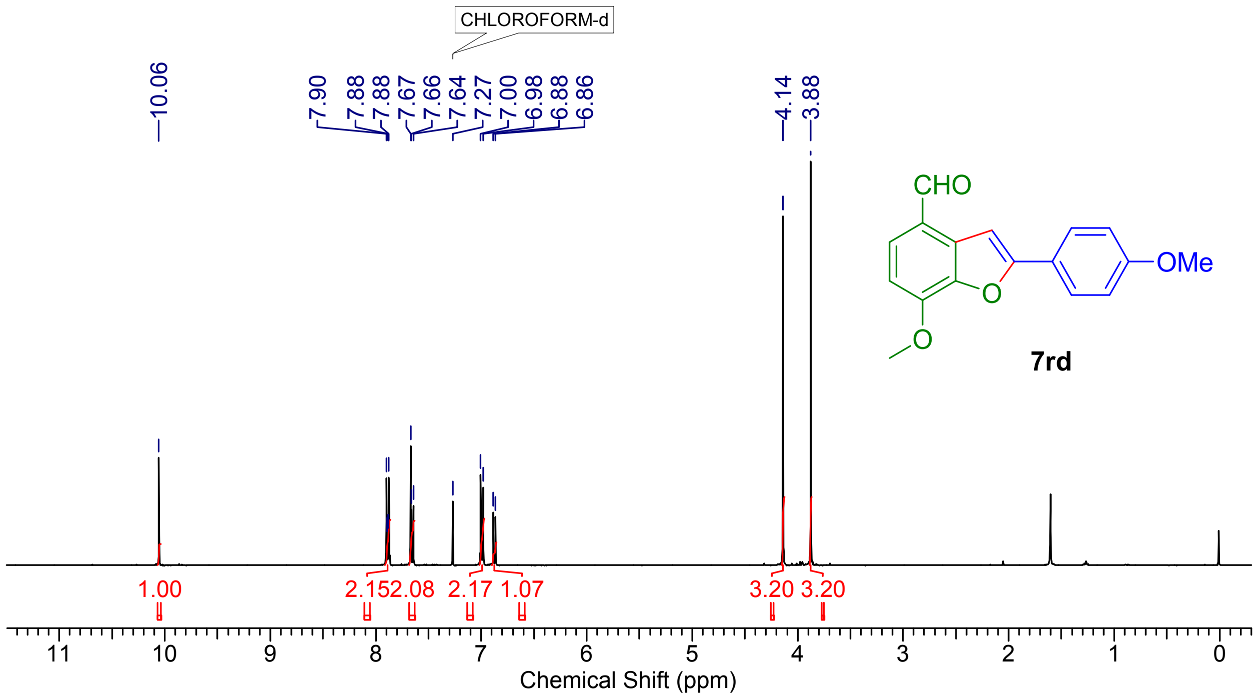


Figure S53: [1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **7rd** in $CDCl_3$



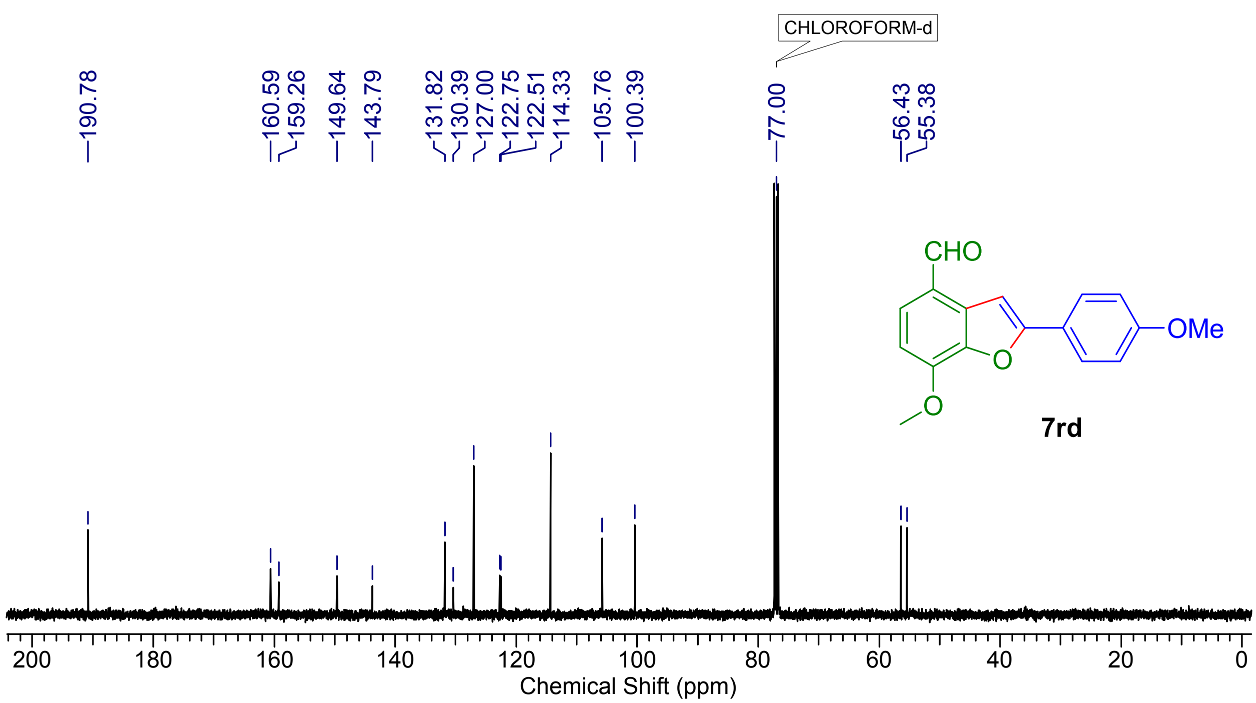
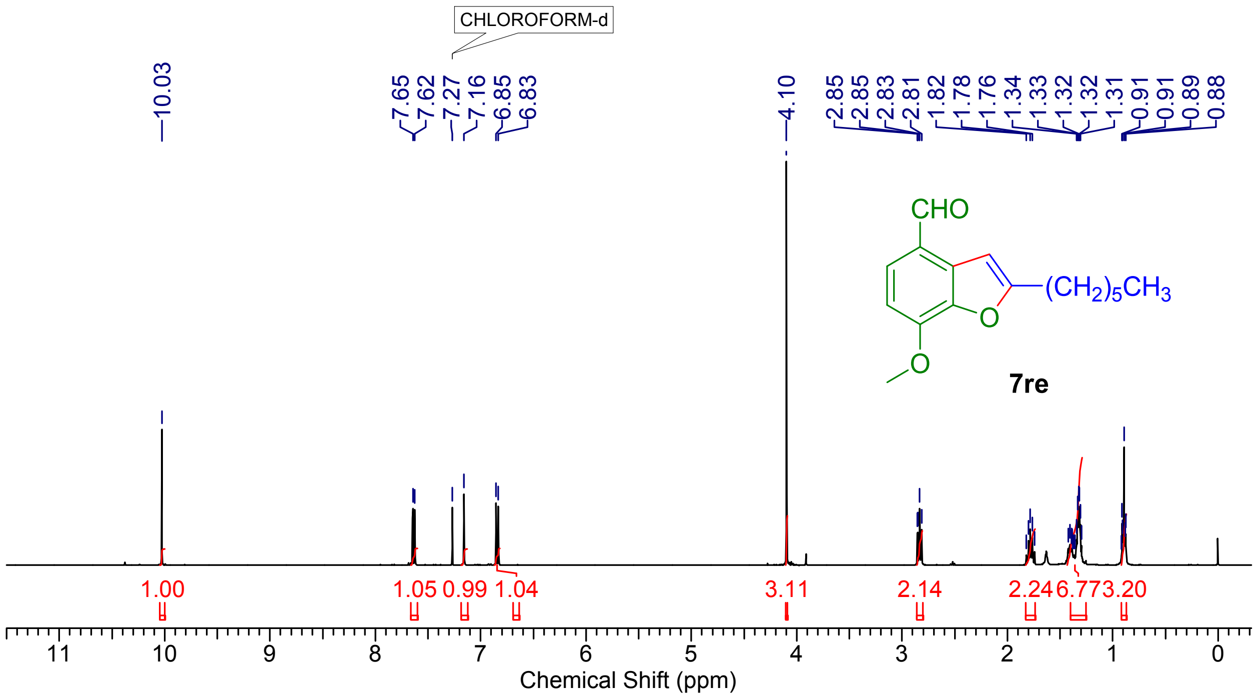


Figure S54:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **7re** in $CDCl_3$



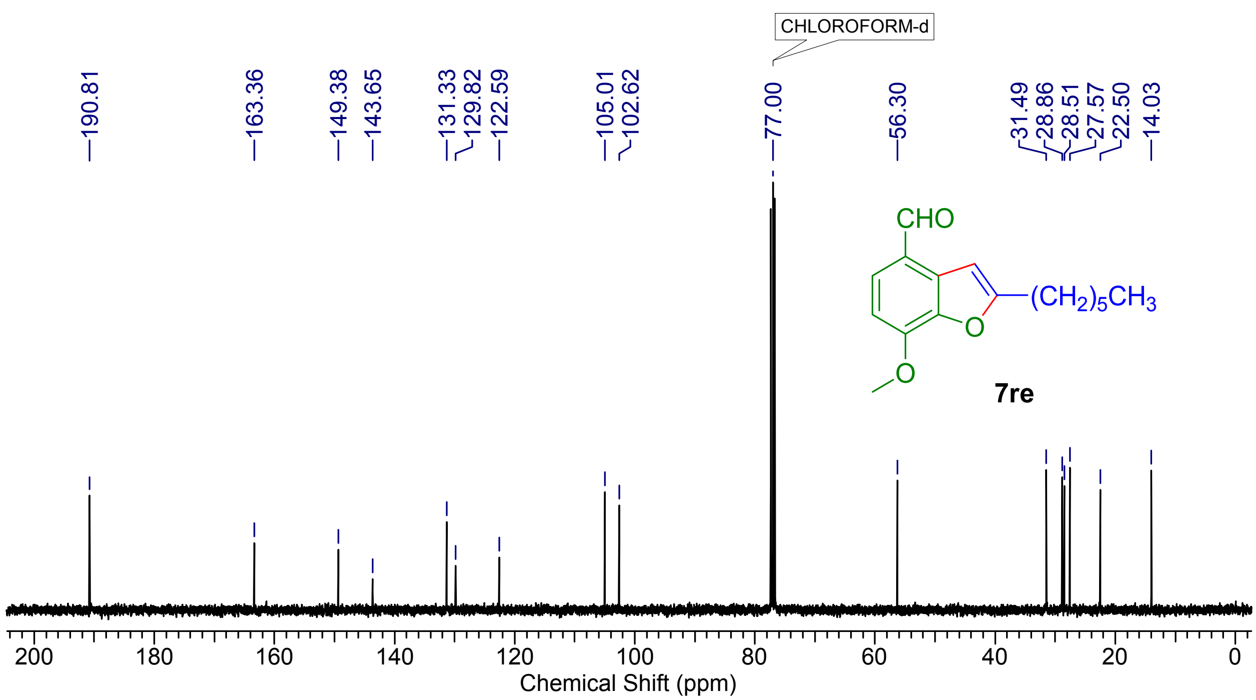
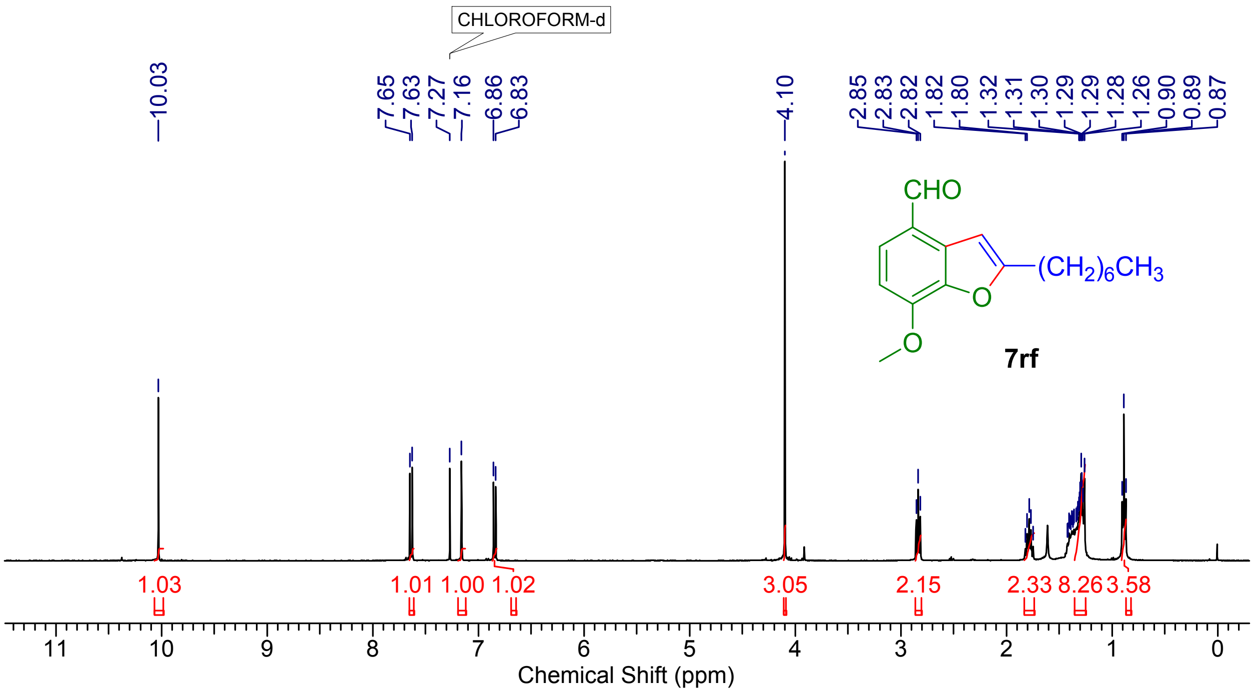


Figure S55: [1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **7rf** in $CDCl_3$



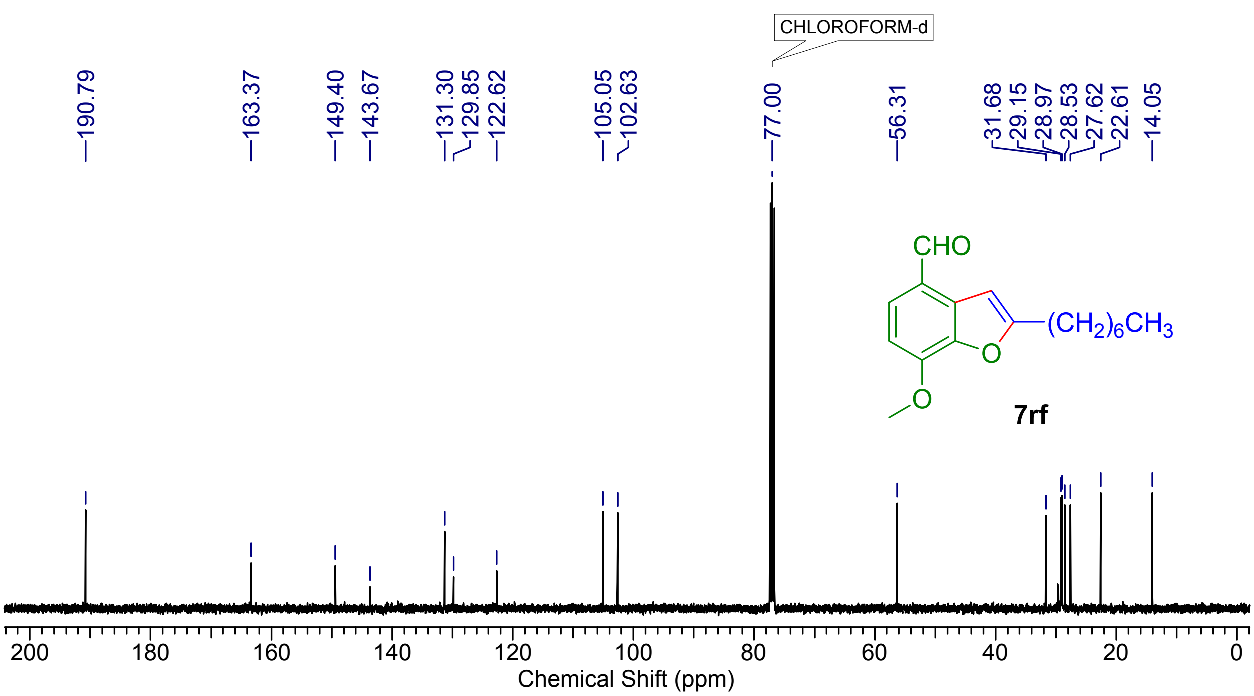
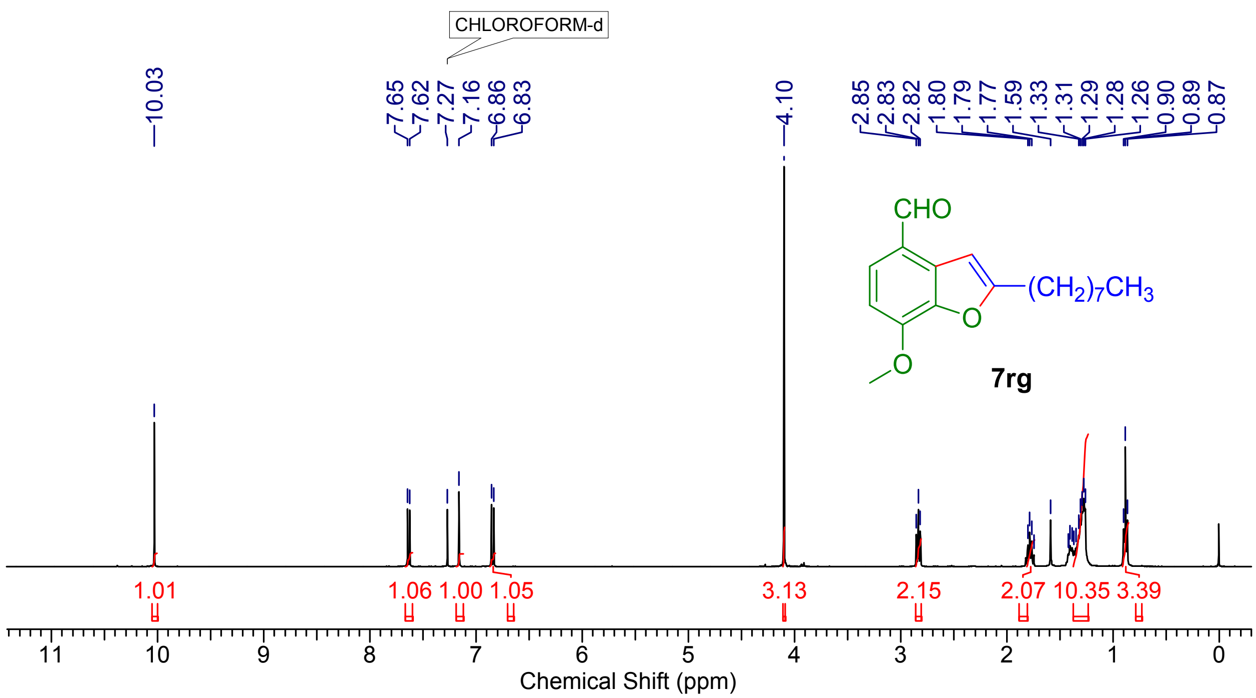


Figure S56:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **7rg** in $CDCl_3$



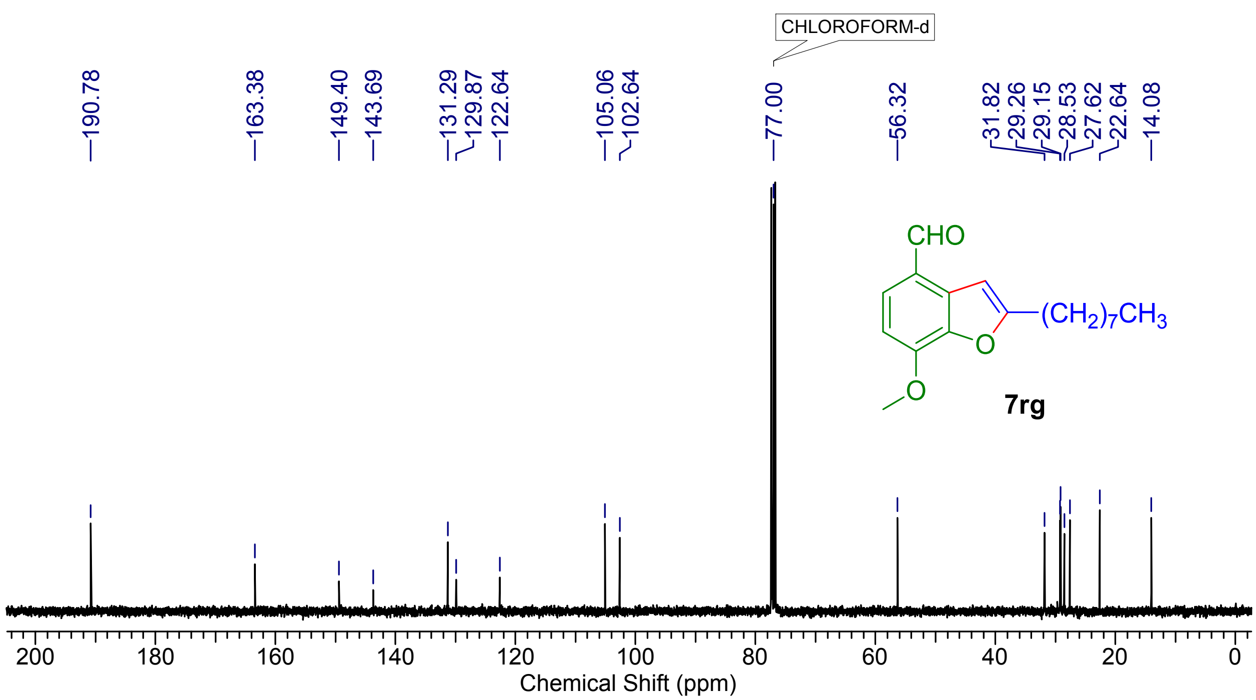
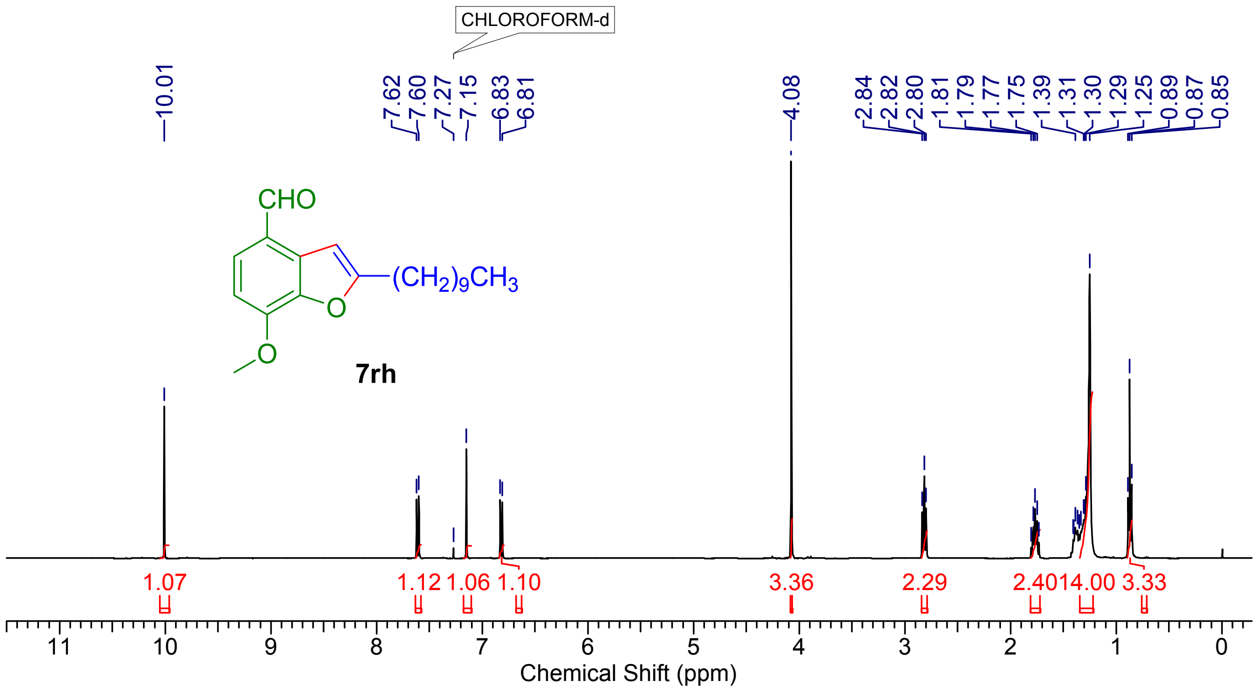


Figure S57: ^{1}H NMR (400 MHz) spectrum (upper) and ^{13}C NMR (100 MHz) spectrum (down) of **7rh** in $CDCl_3$



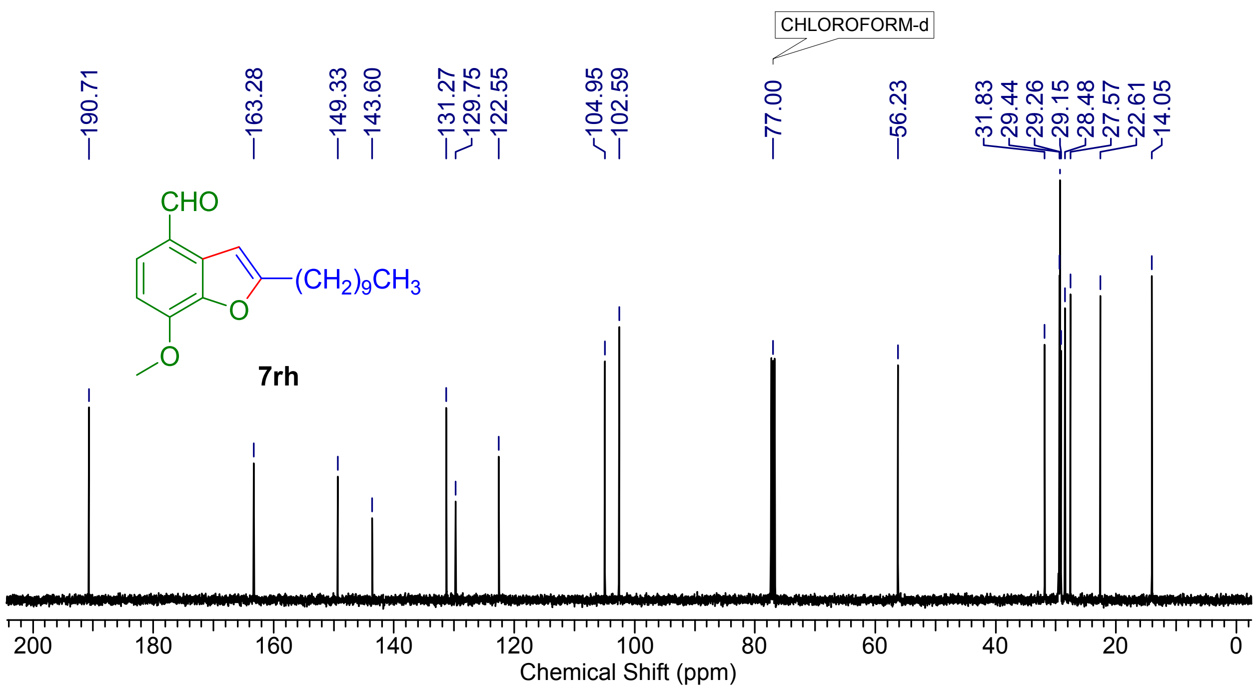


Figure S58:[1]H NMR (400 MHz) spectrum (upper) and [13]C NMR (100 MHz) spectrum (down) of **7rh** in $CDCl_3$