Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information

Suitably fabricated ternary nanocomposite (Cu-CuO@rGO-SiO_2) as sustainable and common heterogeneous catalyst for C–S, C–O & C–N coupling reactions

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S1. General information

All reagents were purchased from Sigma Aldrich and used directly without further purification. Tetraethyl orthosilicate (TEOS) was procured from Sigma Aldrich and used as received. The solvents were purchased from commercial suppliers and used after distillation. All the products were purified by column chromatography on 60–120 mesh silica gel (SRL, India). For TLC, Merck plates coated with silica gel 60, F_{254} were used. FT-IR spectra were recorded in FT–IR 8300 SHIMADZU spectrophotometer. The NMR spectra were recorded on Bruker Ascend 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) and Bruker AV 300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$. Splitting patterns of protons were described as s (singlet), d (doublet), t (triplet), dd (doublet of doublet) and m (multiplet). Chemical shifts (δ) were reported in parts per million (ppm) relative to TMS as internal standard. *J* values (coupling constant) were reported in Hz (Hertz). ^{13}C NMR spectra were recorded with complete proton decoupling ($CDCl_3$: δ 77.0 ppm). Centrifugation was done in REMI R-8C DX centrifuge. The X-ray diffraction studies (PXRD) were done by the Rigaku SmartLab (9 kW) diffractometer using CuKα radiation. Raman spectra of the samples were obtained with Renishaw InVia micro Raman spectroscopy with 514 nm laser source. Scanning Electron Microscopy (SEM) and Electron Dispersive X-ray Spectroscopy (EDS) were performed using JEOL JSM-IT 100 electron microscope. Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2100F electron microscope. X-ray photoelectron spectroscopic (XPS) measurements were done on a PHI 5000 Versaprobe II XPS system with an Al Kα source and a charge neutralizer at room temperature. BET surface areas and pore size were measured by determining the N_2 adsorption isotherms and using the Brunauer, Emmett, and Teller (BET) method with the Nova Touch LX2 gas sorption analyzer from Quantachrome Instruments. Copper content in the nanocomposite was measured by single quadrupole inductively coupled plasma mass spectrometry (ICP-MS) with Agilent ICP-MS (model: 7700) instrument.

S2. General procedure for the preparation of catalyst

S2.I. Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared according to the Tour's method.[1] In this method a 9:1 (v/v) mixture of H_2SO_4 / H_3PO_4 (180:20 mL) was added to a mixture of graphite powder (1.5 g) and $KMnO_4$ (9.0 g). The mixture was then stirred at 50 °C for 12 h. After cooling the mixture to room temperature, it was gradually poured into crushed ice (200 g), which was followed by the slow addition H_2O_2 (30 %, 1.5 mL). The solution was then centrifuged (5000

rpm) and the supernatant was discarded. The residual solid material was successively washed with deionised water (100 mL) and then with 30% HCl (100 mL). The solid material was then repeatedly washed with water and centrifuged. Finally, the solid brown material was collected and dried at 60 °C under vacuum to obtain solid graphene oxide.

S2.II. Preparation of GO-SiO_2 hybrid nanocomposite

GO-SiO_2 hybrid nanocomposite was prepared by following a previously reported method.[2] For this purpose, the well-known hydrolysis of tetraethyl orthosilicate (TEOS) was employed. Initially graphene oxide (300 mg) prepared and TEOS (5.0 g) were dispersed separately in ethanol (30.0 g). The two suspensions were then mixed together and placed into a preheated oil bath at 40 °C for 10 minutes. This was followed by the addition of hydrous ammonia ($NH_3 \cdot H_2O$, 0.76 g) into the suspension of GO and TEOS. The entire contents were stirred for 15 h at 40 °C before cooling to room temperature. The solid material was filtered and washed of de-ionized water (3 x 20 mL) and ethanol (3 x 20 mL), and finally dried under vacuum at 60 °C for 48 h.

S2.III. Preparation of Cu-CuO@rGO-SiO_2 nanocomposite

GO-SiO_2 hybrid nanocomposite (1.0 g) was taken in a teflon-capped sealed tube. To it $Cu(OAc)_2 \cdot H_2O$ (1.0 mmol, 200 mg) and $NaBH_4$ (5.26 mmol, 200 mg) was added followed by the addition of distilled water (5 mL). It was then placed in a pre-heated oil bath at 100 °C and gently stirred for 3 h. The mixture was then cooled to room temperature and centrifuged at 5000 rpm. The supernatant was discarded and the residue was washed with de-ionized water (3 x 20 mL) and finally with acetone (2 x 20 mL). The solid mass was then dried under vacuum for 48 h to obtain powdered Cu-CuO@rGO-SiO_2 nanocomposite. This nanocompsite was used for all cross-coupling reactions.

S3. General procedure for cross-coupling reactions

S3.I. C–S cross-coupling reaction

A teflon-capped sealed tube equipped with a small magnetic stir bar, aryl halides (1.0 mmol), thiols (1.0 mmol), Cu-CuO@rGO-SiO_2 (25 mg), K_2CO_3 (2.0 mmol), TBAB (10 mol%) and H_2O (2 mL) were added. The resulting reaction mixture was stirred at 90 °C for 8 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The catalyst was then recovered through simple filtration. The reaction mixture was diluted with water and extracted with ethyl acetate (3 x 5 mL). Finally, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

The residue obtained was then purified by column chromatography on silica gel using the light petroleum ether and ethyl acetate as eluent to afford the desired thioethers (**3a**-**3i**). All the products were characterized by ^{1}H and ^{13}C NMR spectroscopy.

S3.II. C–O cross-coupling reaction

In a teflon-capped sealed tube equipped with a magnetic stir bar, aryl halides (1.0 mmol), phenols (1.0 mmol), Cu-CuO@rGO-SiO_2 (25 mg), K_3PO_4 (2 mmol), 2,2′-bipyridine (10 mol%) and DMF (2 mL) were added. The resulting reaction mixture was stirred at 110 °C for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and diluted with H_2O. The catalyst was then recovered through simple filtration and the reaction mixture was extracted with ethyl acetate (3 x 5 mL). Finally, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel using the light petroleum ether and ethyl acetate as eluent to afford the desired products (**5a**-**5f**). All the compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy.

S3.III. C–N cross-coupling reaction

A teflon-capped sealed tube equipped with a magnetic stir bar, aryl halides (1.0 mmol), imidazoles (1.0 mmol), Cu-CuO@rGO-SiO_2 (25 mg), KOH (2 mmol) and MeCN (2 mL) were added. The resulting reaction mixture was placed in an oil bath and stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The catalyst was then recovered through simple filtration. The reaction mixture was diluted with water and extracted by ethyl acetate (3 x 5 mL). Finally, the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel using the light petroleum ether and ethyl acetate as eluent to afford the desired products (**7a**-**7i**). All the products were characterized by ^{1}H and ^{13}C NMR spectroscopy.

S4. Characterization of the catalyst after the reaction

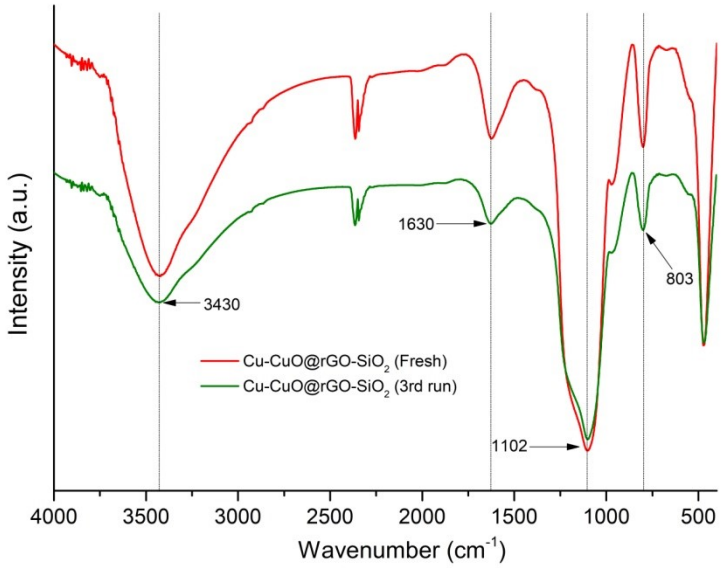


Figure S4.I. FT-IR spectra of the catalyst; fresh and after the third run

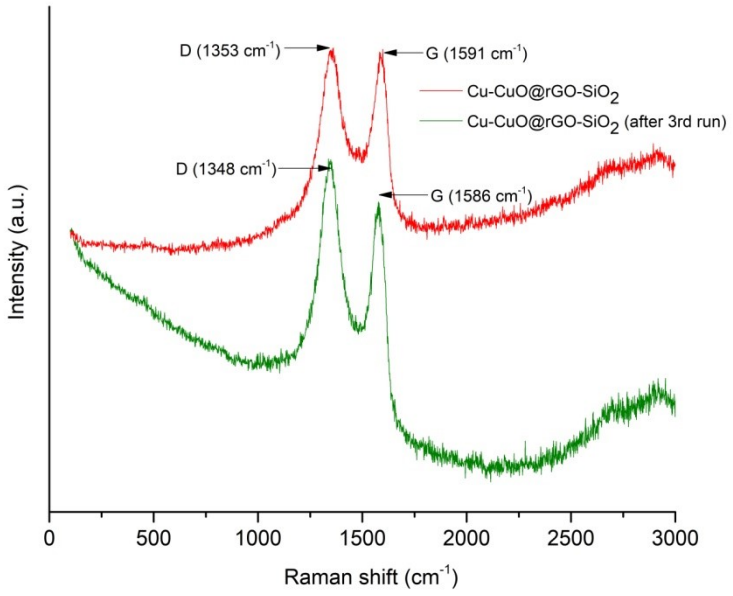


Figure S4.II. Raman spectra of the catalyst; fresh and after the third run

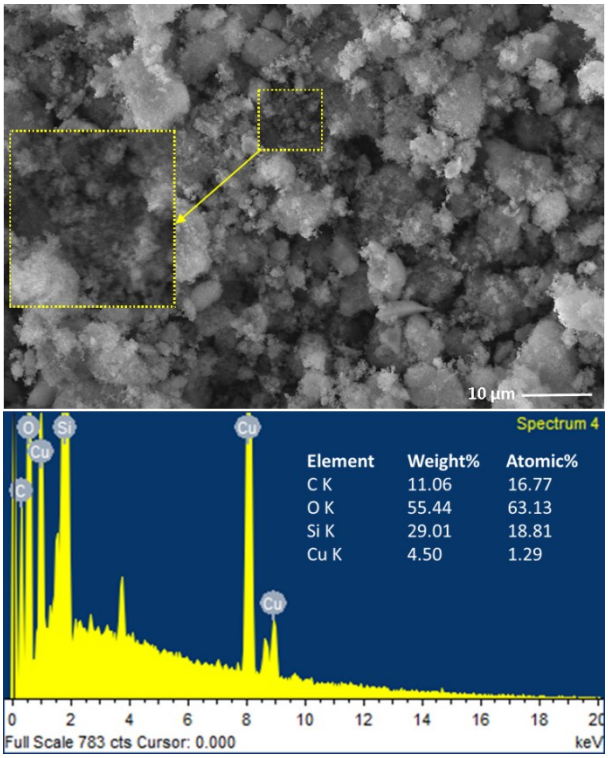


Figure S4.III. SEM and SEM-EDS image of the catalyst after the third run

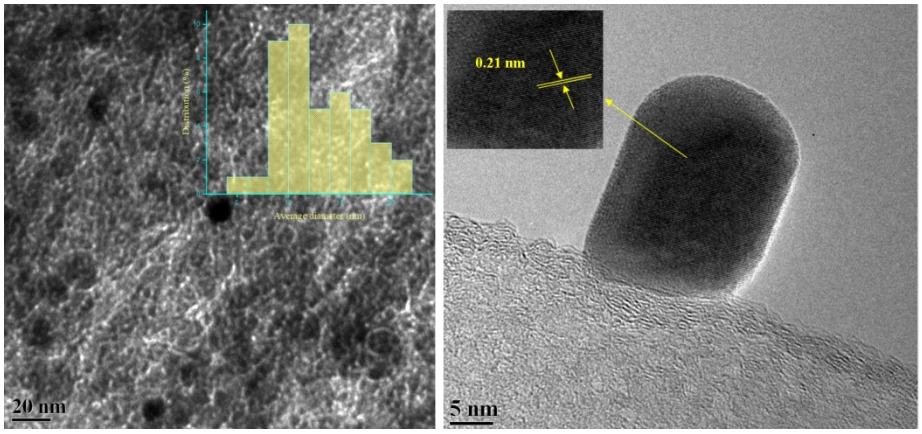


Figure S4.IV. HRTEM images of the catalyst after the third run

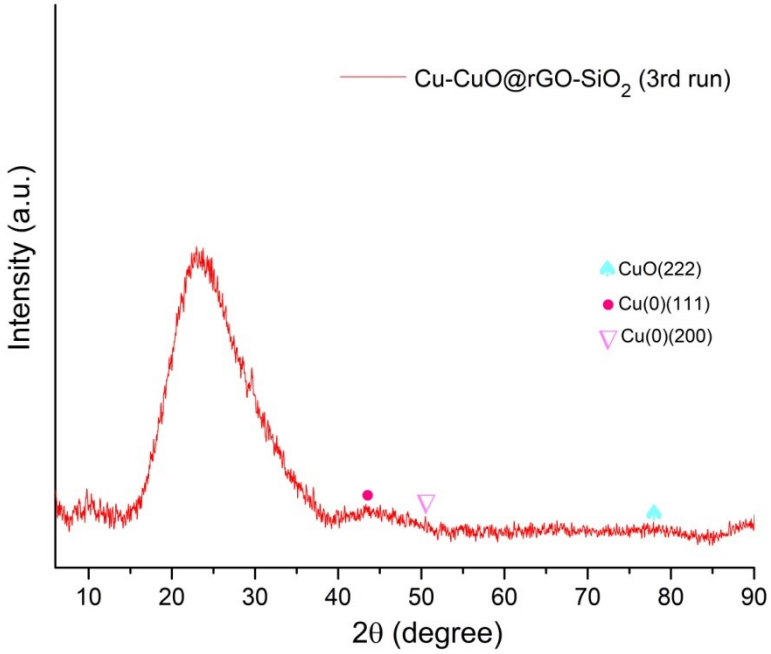


Figure S4.V. PXRD of the catalyst after the third run

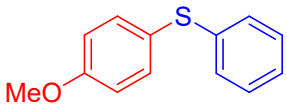
S5. Comparison of catalytic performances of various copper catalysts in C–S, C–N and C–O cross-coupling reactions

Entry	Catalyst	Reaction conditions	Yield (%)	References
1	Dual Responsive Sustainable Cu_2O/ Cu Nanocatalyst	**Chan-Lam Cross-Coupling:** Phenylboronic acid, imidazole, Cu-463K (20 wt%), MeOH, 60 °C, 7 h.	41-90	3
2	GO–PN–CuO	**C–O Coupling reaction**: 4-bromobenzaldehyde, ArOH, catalyst (20 mg), 110 °C, 12 h.	10-94	4
3	DS/GO	**C–S cross coupling reaction:** Iodobenzene, 3,5-dimethylthio phenol, catalyst (25 mg), Cs_2CO_3, DMSO, 110 °C, 4 h. **C–N cross coupling reaction:** Iodobenzene, methylamine, catalyst (25 mg), Cs_2CO_3, DMF/water, 110 °C, 24 h.	>90 (conversion) >90 (conversion)	5
4	Cu–Cu_2O/C and CuO–Cu_2O/C catalysts	**C–N cross coupling reactions:** Iodobenzene, imidazole, KOH, catalyst (15 mg), DMSO, 80 °C, 24 h.	40.1-96.2	6
5	CuONPs	**For C–N coupling reaction**:	25-90	7

		Benzamide, iodobenzene, K_2CO_3, CuONPs (6 mg), DMF, 110-120 °C, 12 h.		
6	CuO NPs	**C–S cross coupling reaction:** RSH, ArI, base, $[CuSPh]_n$ (1 mol%), DMSO, 110 °C, 21 h, Ar atmosphere.	57-98	8
7	Cu-Fe hydrotalcite	**C–S cross coupling reaction**: Aryl halide, thiol, catalyst (30 mg), K_2CO_3, DMF, 120 °C.	25-90	9
8	CuO on mesoporous silica	**C–S cross coupling reaction:** Aryl iodide, alkyl thiol, catalyst (1 mol%), Cs_2CO_3, DMSO, 110 ^oC, 21 h.	66-96	10
9	Cu-CuO@rGO-SiO_2	**C–S cross coupling reaction:** Iodobenzene, thiophenol, catalyst (25 mg), K_2CO_3, water, TBAB (10 mol%), 90 ^oC, 8 h. **C–O cross coupling reaction:** Iodobenzene, phenol, catalyst (25 mg), K_3PO_4, 2,2′-bipyridine, DMF, 110 ^oC, 24 h. **C–N cross coupling reaction:** Iodobenzene, imidazole, catalyst (25 mg), KOH, MeCN, 80 ^oC, 24 h.	80-93 79-93 81-89	**This work**

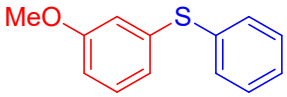
S6. Characterization data for various cross-coupled products

(4-Methoxyphenyl)(phenyl)sulfane (3a)[11]



^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.94 (dd, *J* = 4, 12 Hz, 2H), 7.15-7.22 (m, 3H), 7.25-7.29 (m, 2H), 7.45 (dd, *J* = 4, 8 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 55.3, 114.9, 124.2, 125.7, 128.1, 128.8, 135.3, 138.5, 159.7.

(3-Methoxyphenyl)(phenyl)sulfane (3b)[11]

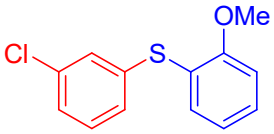


^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 3H), 6.77-6.80 (m, 1H), 6.87-6.88 (m, 1H), 6.90-6.93 (m, 1H), 7.21 (t, *J* = 8 Hz, 1H), 7.26-7.28 (m, 1H), 7.30-7.34 (m, 2H), 7.36-7.39 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 55.2, 112.7, 115.8, 122.9, 127.2, 129.2, 129.9, 131.4, 135.2, 137.2, 160.0.

(2-Methoxyphenyl)(*p*-tolyl)sulfane (3c)[12]

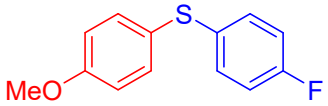
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 1H), 3.89 (s, 1H), 6.81-6.85 (m, 1H), 6.87-6.89 (m, 1H), 6.93 (dd, *J* = 8, 2 Hz, 1H), 7.14-7.19 (m, 3H), 7.31-7.33 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 21.1, 55.8, 110.6, 121.1, 125.6, 127.3, 129.8, 130.0, 132.9, 137.7, 156.5.

(3-Chlorophenyl)(2-methoxyphenyl)sulfane (3d)



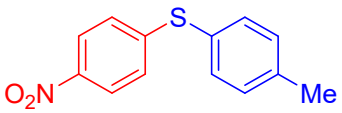
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.91-6.95 (m, 2H), 7.12-7.19 (m, 3H), 7.21-7.22 (m, 1H), 7.25-7.27 (m, 1H), 7.30-7.35 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 55.9, 111.2, 121.3, 121.6, 126.5, 127.7, 129.2, 129.7, 129.9, 133.7, 134.7, 137.9, 158.2.

(4-Fluorophenyl)(4-methoxyphenyl)sulfane (3e)[13]



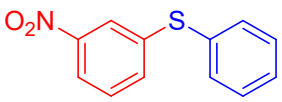
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 6.86-6.90 (m, 2H), 6.93-6.97 (m, 2H), 7.18-7.22 (m, 2H), 7.34-7.38 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 55.3, 114.9, 116.0 (d, *J* = 22 Hz), 125.2, 131.0 (d, *J* = 8 Hz), 133.1 (d, *J* = 4 Hz), 134.4, 159.6, 160.3, 162.8.

(4-Nitrophenyl)(*p*-tolyl)sulfane (3f)[13]



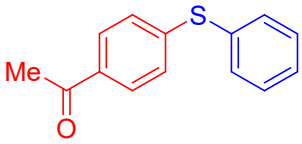
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 1H), 7.16 (s, 2H), 7.30 (s, 2H), 7.45 (s, 2H), 8.06 (s, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 21.2, 123.9, 126.2, 126.6, 130.8, 134.9, 140.1, 145.2, 149.2.

(3-Nitrophenyl)(phenyl)sulfane (3g)[11]



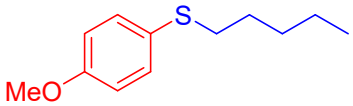
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.43 (m, 4H), 7.47-7.51 (m, 3H), 7.98-8.01 (m, 1H), 8.03 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 120.9, 123.1, 128.9, 129.6, 129.8, 132.1, 133.4, 134.2, 140.5, 148.7.

1-(4-(Phenylthio)phenyl)ethanone (3h)[11]



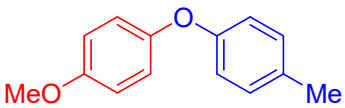
^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 3H), 7.18-7.21 (m, 2H), 7.37-7.40 (m, 3H), 7.47-7.49 (m, 2H), 7.78-7.82 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 26.3, 127.3, 128.6, 128.7, 129.5, 131.9, 133.7, 134.3, 144.7, 196.9.

(4-Methoxyphenyl)(pentyl)sulfane (3i)[14]



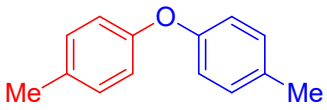
^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 8 Hz, 3H), 1.25-1.41 (m, 6H), 1.58 (t, *J* = 8 Hz, 2H), 3.79 (s, 3H), 6.83 (dd, *J* = 8.4, 2.2 Hz, 2H), 7.32 (dd, *J* = 8.8, 2.4 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 13.9, 22.2, 29.0, 30.8, 35.7, 55.3, 114.4, 126.9, 132.9, 158.7.

1-Methoxy-4-(*p*-tolyloxy)benzene (5a)[15]



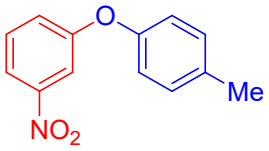
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H), 3.77 (s, 3H), 6.79-6.86 (m, 4H), 6.88-6.97 (m, 2H), 7.02-7.11 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 20.6, 55.6, 114.8, 117.8, 120.3, 130.1, 132.0, 150.7, 155.6, 156.1.

4,4'-Oxybis(methylbenzene) (5b)[15]



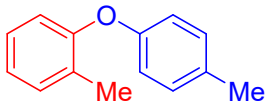
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 6H), 6.88 (d, *J* = 8.1 Hz, 4H), 7.11 (d, *J* = 7.8 Hz, 4H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 20.7, 118.6, 130.1, 132.4, 155.3.

1-Nitro-3-(*p*-tolyloxy)benzene (5c)[16]



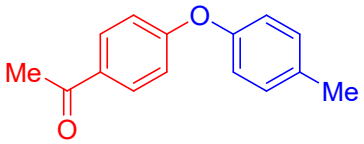
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.28 (dd, *J* = 10.5, 2.4 Hz, 1H), 7.43 (t, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 2.2 Hz, 1H), 7.85-7.89 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 20.8, 112.2, 117.2, 119.9, 123.7, 130.2, 130.7, 134.6, 149.2, 153.0, 159.0.

1-Methyl-2-(*p*-tolyloxy)benzene (5d)[15]



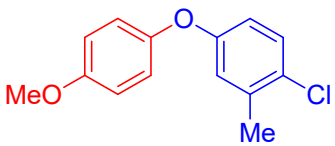
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.30 (s, 3H), 6.79-6.87 (m, 3H), 7.00-7.15 (m, 4H), 7.21-7.24 (m, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 16.2, 20.6, 117.5, 119.2, 123.6, 127.0, 129.7, 130.1, 131.3, 131.9, 155.0, 155.5.

1-(4-(*p*-Tolyloxy)phenyl)ethanone (5e)[17]



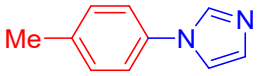
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H), 2.56 (s, 3H), 6.94-6.99 (m, 4H), δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.90-7.94 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 20.8, 26.4, 116.8, 120.2, 130.5, 130.6, 131.5, 134.4, 153.0, 162.5, 196.9.

1-Chloro-4-(4-methoxyphenoxy)-2-methylbenzene (5f)



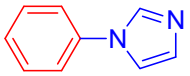
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H), 3.79 (s, 3H), 6.70 (dd, *J* = 11.7, 2.8 Hz, 1H), 6.81 (d, *J* = 2.8 Hz, 1H), 6.85-6.89 (m, 2H), 6.92-6.96 (m, 2H), 7.22 (d, *J* = 8.6 Hz, 1H), **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 20.2, 55.6, 114.9, 116.2, 119.9, 120.7, 127.6, 129.8, 137.3, 149.9, 156.0, 157.0.

1-(*p*-Tolyl)-1*H*-imidazole (7a)[18]



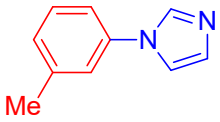
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 7.18 (s, 1H), 7.23-7.28 (m, 5H), 7.81 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 20.9, 118.3, 121.4, 130.1, 130.3, 134.9, 135.6, 137.4.

1-Phenyl-1*H*-imidazole (7b)[18]



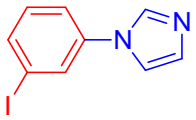
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24-7.28 (m, 2H), 7.35-7.40 (m, 3H), 7.46-7.51 (m, 2H), 7.90 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 118.7, 121.9, 127.7, 128.0, 130.1, 130.2, 133.9, 135.7.

1-(*m*-Tolyl)-1*H*-imidazole (7c)[19]



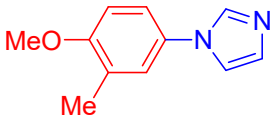
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 6.92-7.38 (m, 5H), 7.85 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 21.3, 118.2, 118.5, 122.1, 128.2, 129.6, 130.2, 135.6, 137.3, 140.0.

1-(3-Iodophenyl)-1*H*-imidazole (7d)[20]



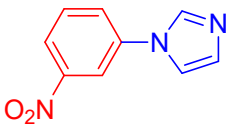
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.07-7.12 (m, 2H), 7.16-7.17 (m, 1H), 7.26-7.28 (m, 1H), 7.57-7.65 (m, 2H), 7.75 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 94.7, 117.9, 120.5, 130.1, 130.7, 131.2, 135.4, 136.4, 138.2.

1-(4-Methoxy-3-methylphenyl)-1*H*-imidazole (7e)



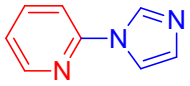
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.26 (s, 3H), 3.87 (s, 3H), 6.85-6.89 (m, 1H), 7.14-7.18 (m, 4H), 7.78 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 16.3, 55.6, 110.2, 110.4, 120.2, 124.4, 125.6, 128.3, 129.7, 130.2, 157.1.

1-(3-Nitrophenyl)-1*H*-imidazole (7f)[21]



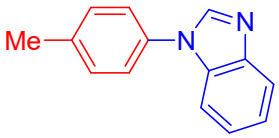
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (s, 1H), 7.40 (s, 1H), 7.70-7.81 (m, 2H), 7.99 (s, 1H), 8.23-8.26 (m, 1H), 8.30 (t, *J* = 2.1 Hz, 1 H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 116.2, 117.9, 122.0, 126.8, 131.1, 131.3, 135.4, 138.1, 149.0.

2-(1*H*-imidazol-1-yl)pyridine (7g)[21]



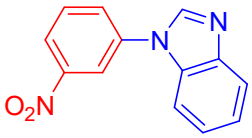
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (s, 1H), 7.17-7.21 (m, 1H), 7.31 (d, *J* = 12 Hz, 1H), 7.60 (t, *J* = 1.6 Hz, 1H), 7.75-7.79 (m, 1H), 8.32 (s, 1H), 8.41-8.43 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 112.2, 116.0, 121.9, 130.3, 134.8, 138.9, 149.0, 164.95.

1-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole (7h)[22]



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.30-7.40 (m, 6H), 7.48-7.52 (m, 1H), 7.84-7.88 (m, 1H), 8.09 (s, 1H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 21.1, 110.5, 120.4, 122.7, 123.6, 124.0, 130.6, 133.7, 138.1, 142.3, 143.7.

1-(3-Nitrophenyl)-1*H*-benzo[*d*]imidazole (7i)[22]



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.42 (m, 2H), 7.55-7.58 (m, 1H), 7.77-7.83 (m, 1H), 7.88-7.94 (m, 2H), 8.1 (s, 1H), 8.31-8.34 (m, 2H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ: 110.0, 118.7, 121.0, 122.5, 123.5, 124.5, 129.4, 131.2, 133.0, 137.4, 141.7, 144.1, 149.2.

S7. References

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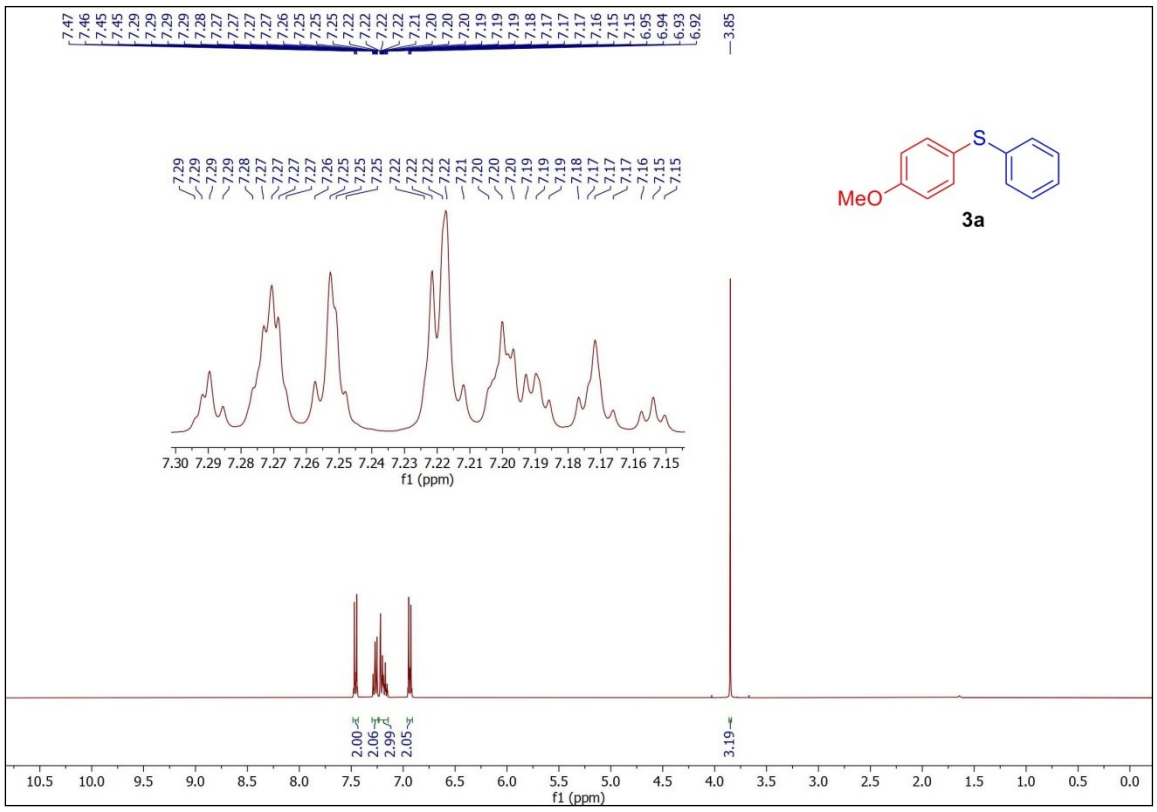
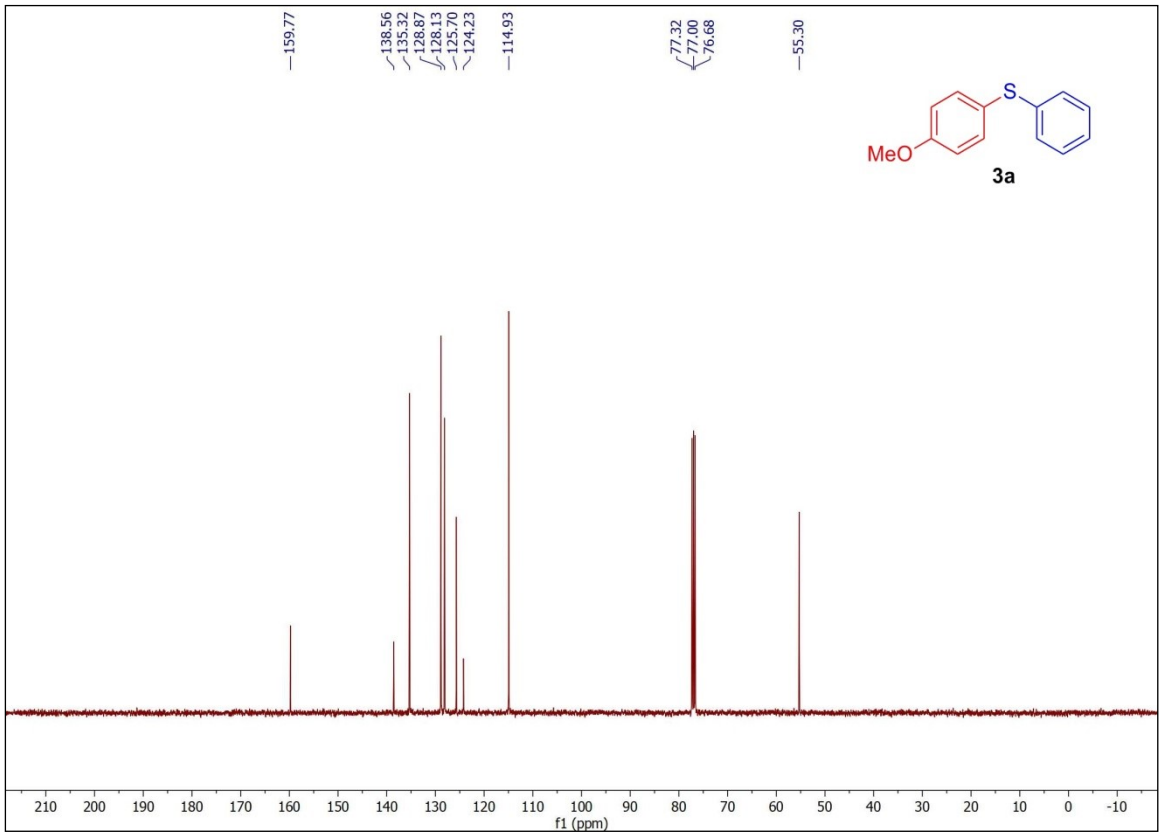
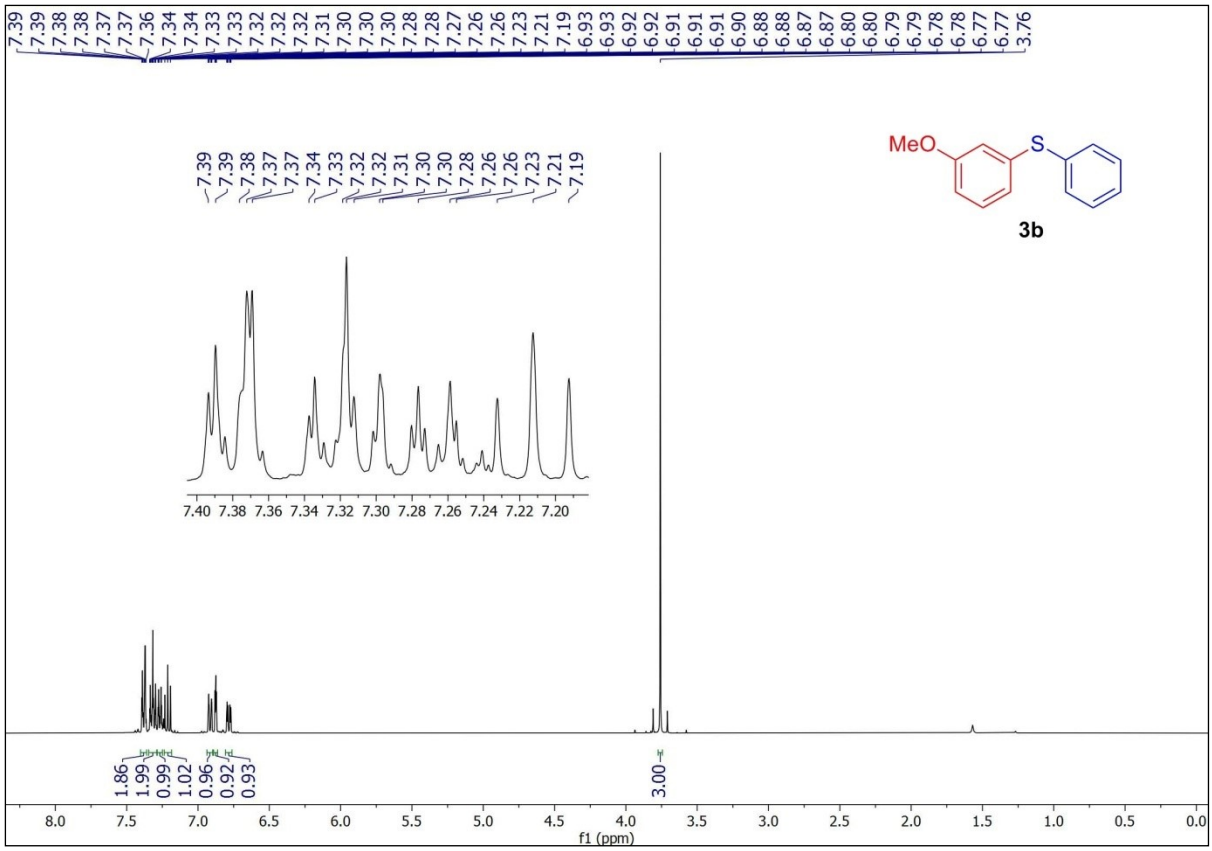
S8. Copies of ^{1}H and ^{13}C NMR spectra of various cross-coupled products



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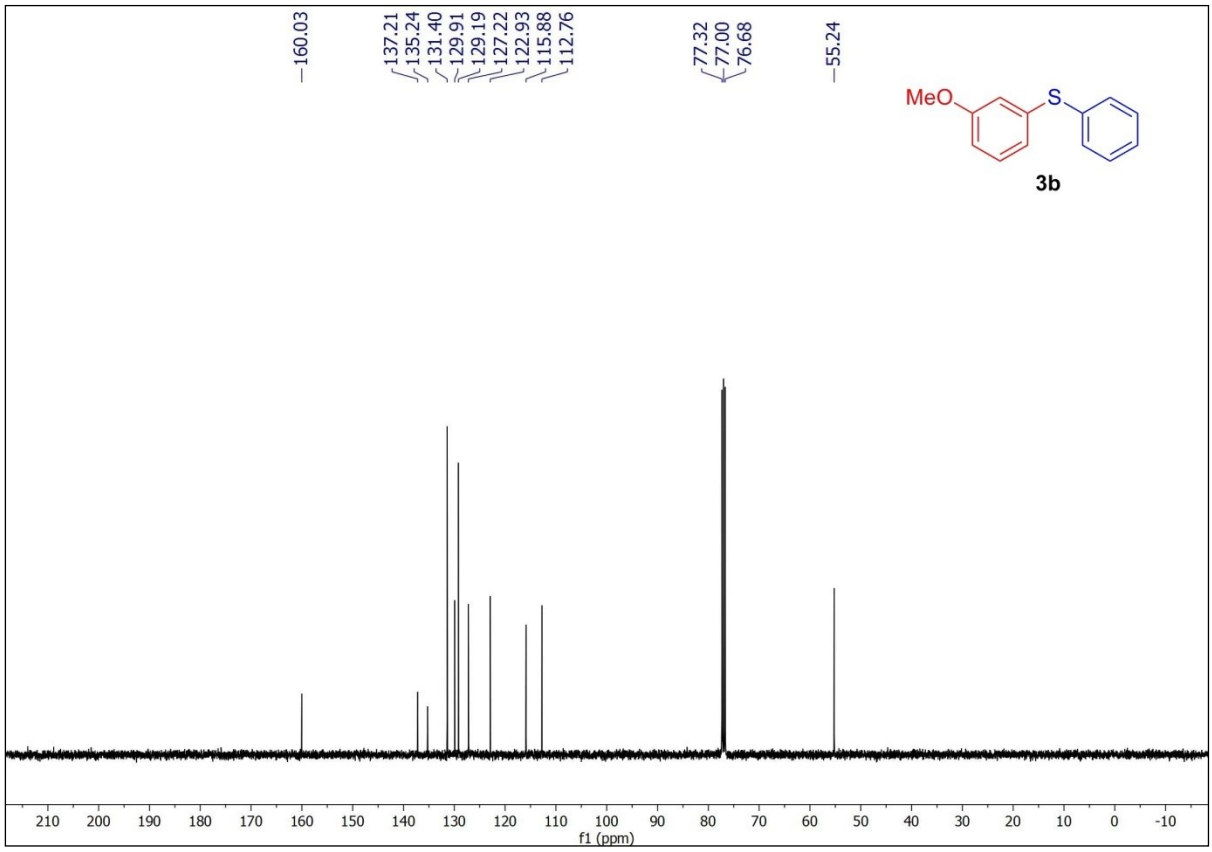
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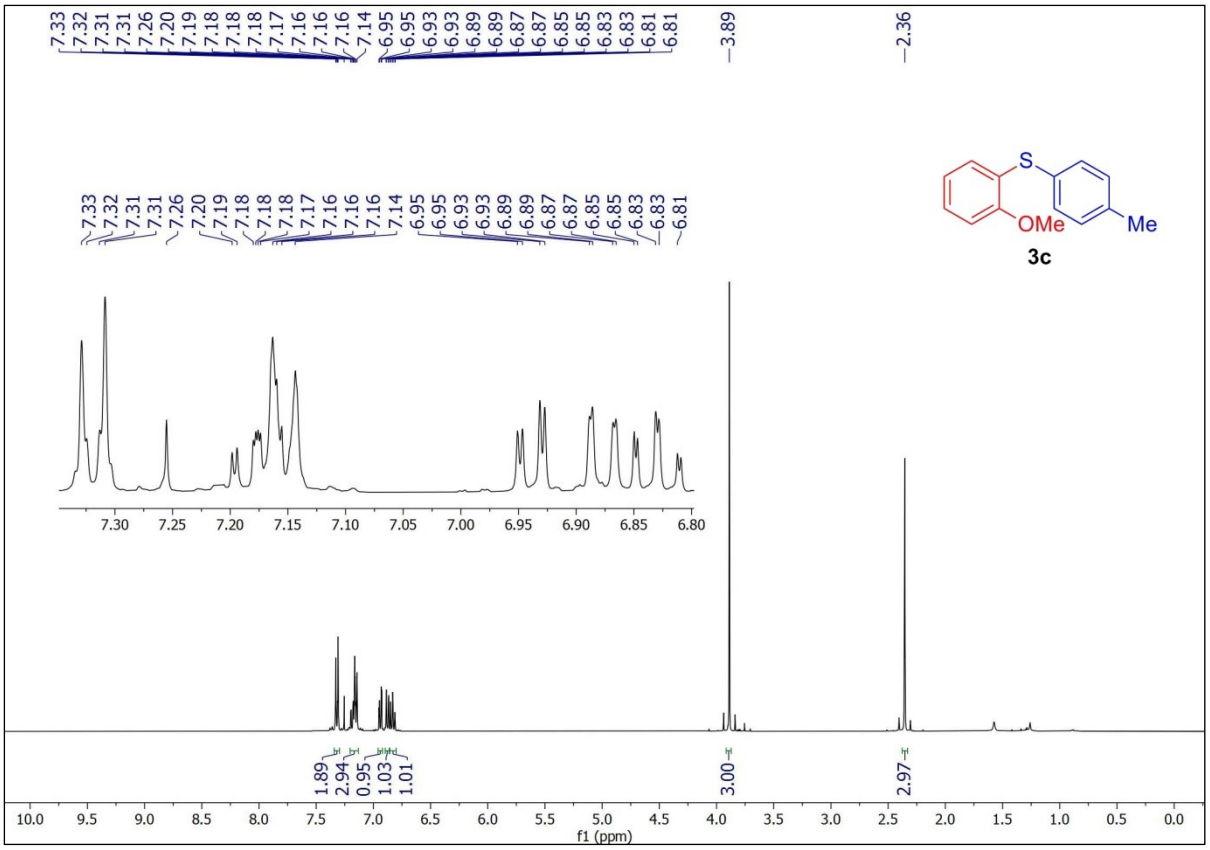
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6.81
3.89
2.36
S
OMe
Me
3c
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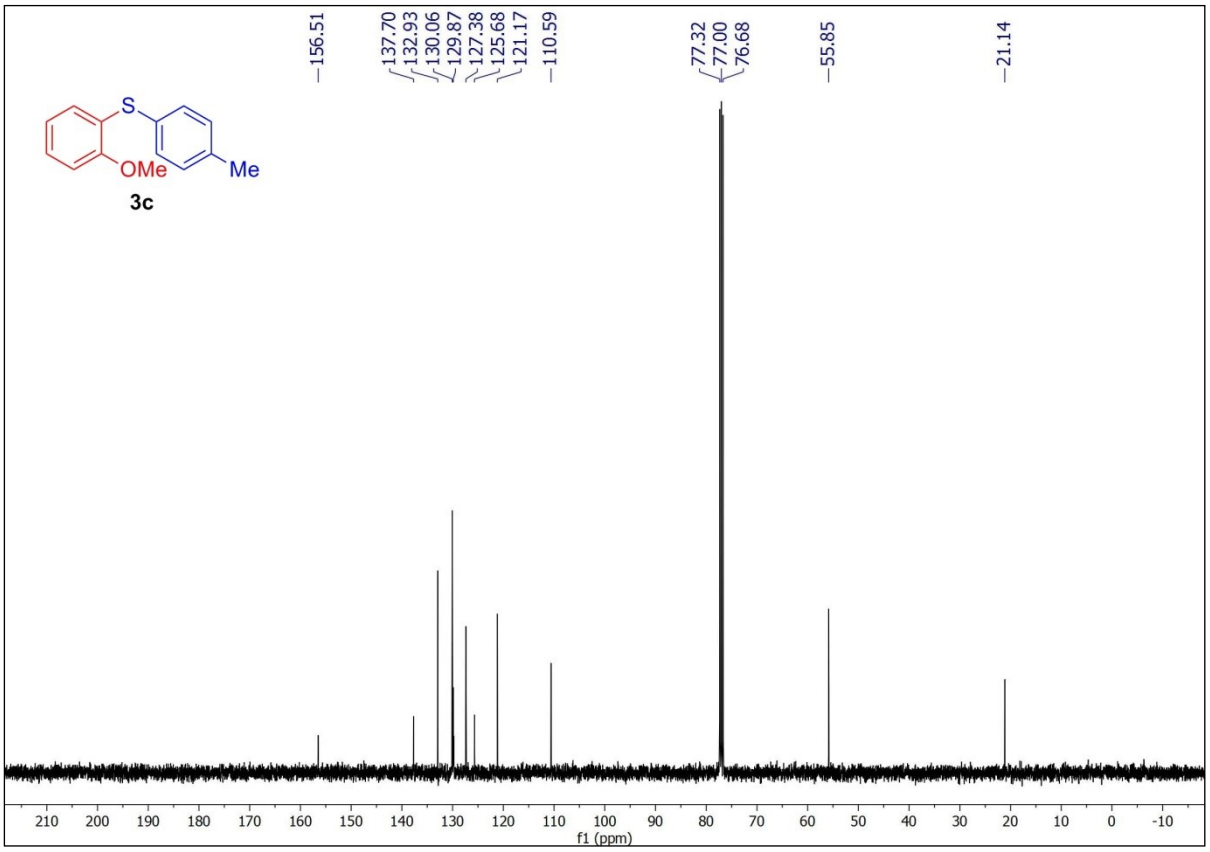
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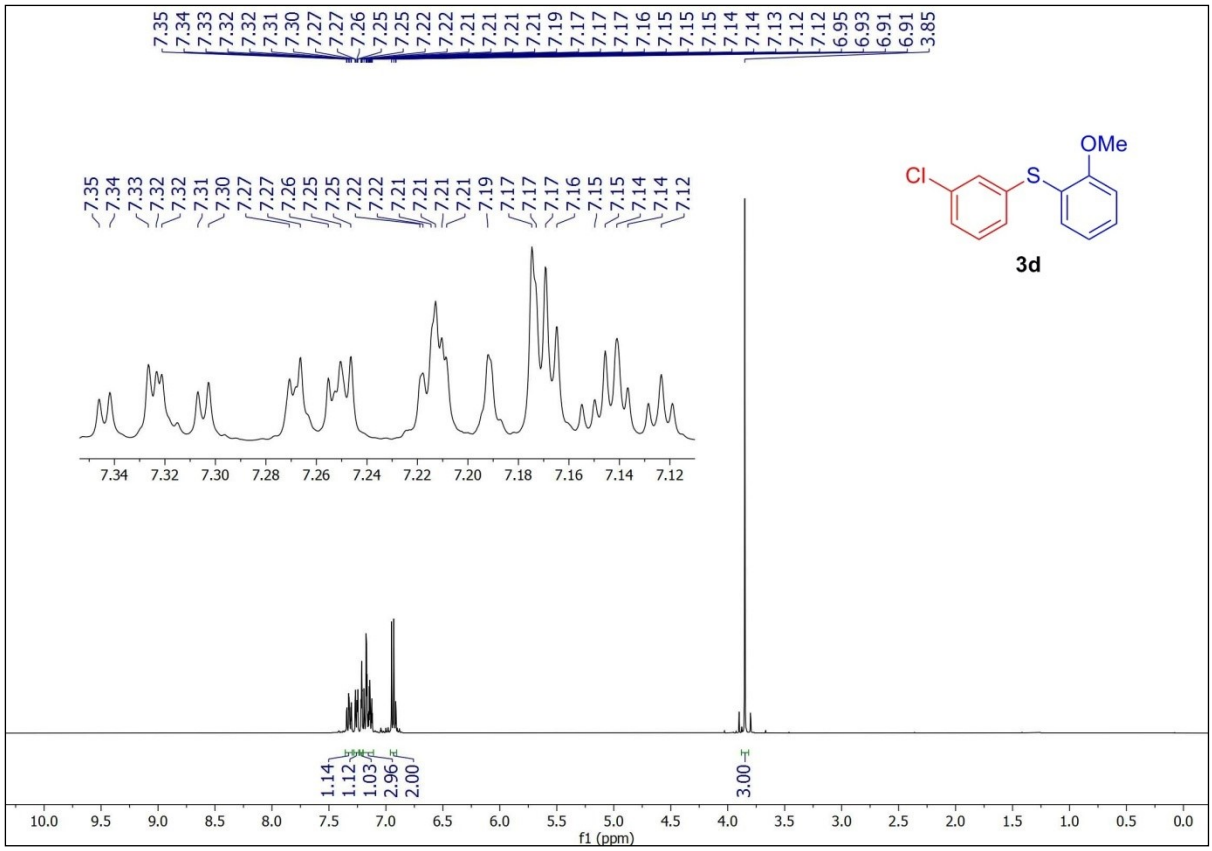
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Cl
S
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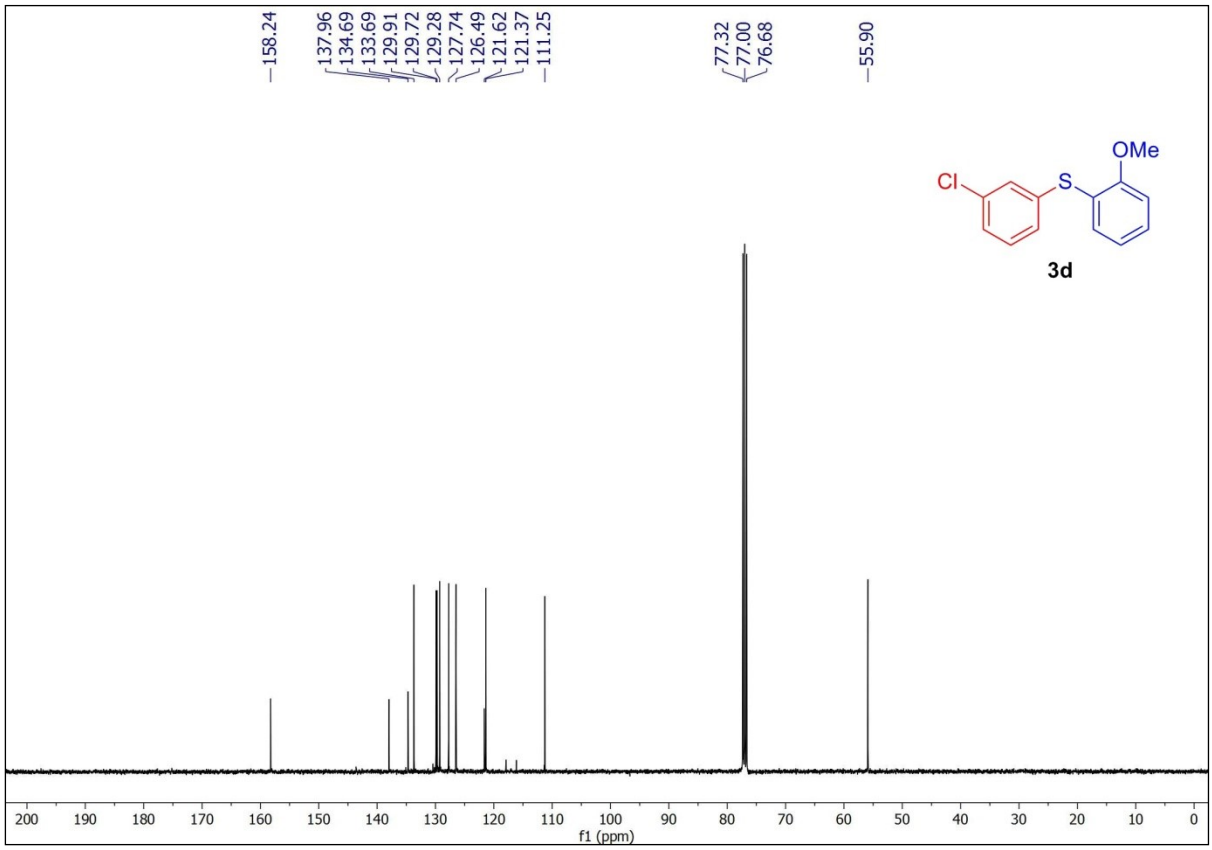
3.00
f1 (ppm)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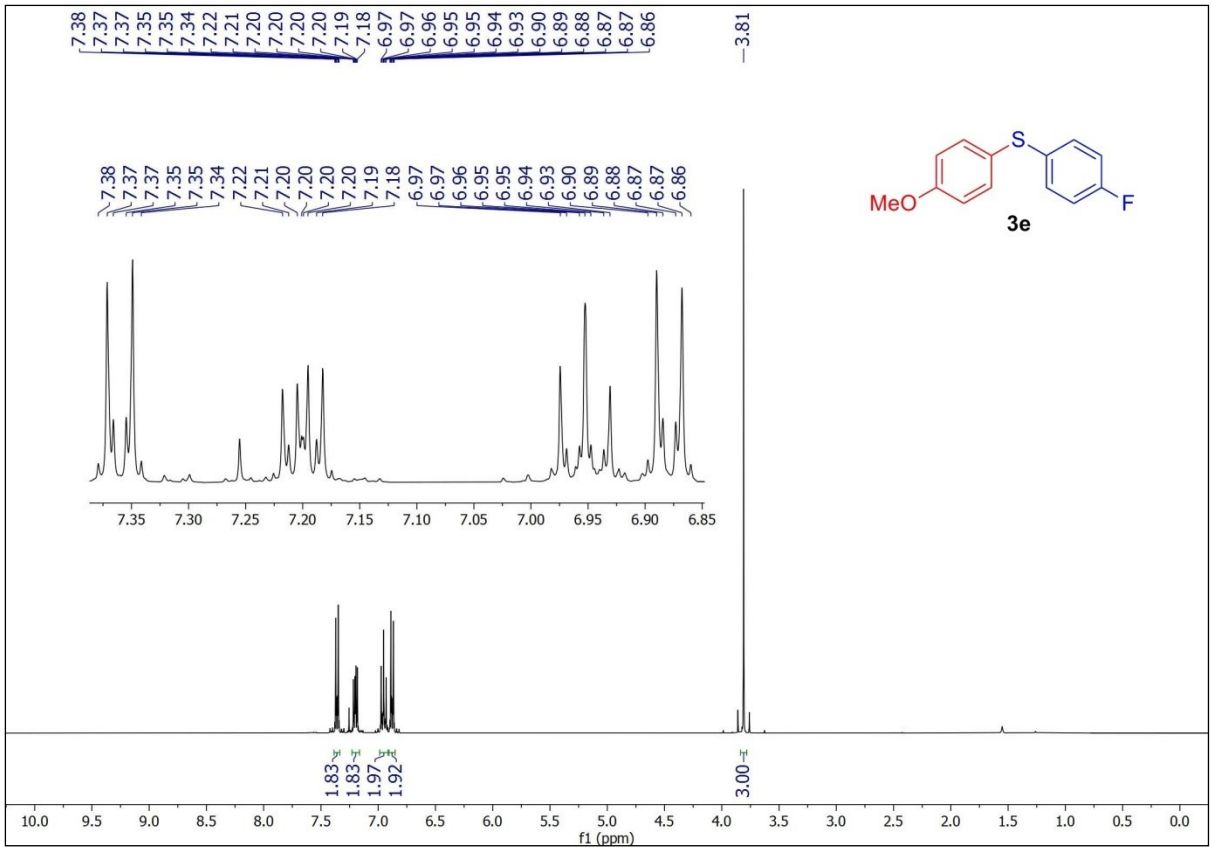
Cl
S
3d
f1 (ppm)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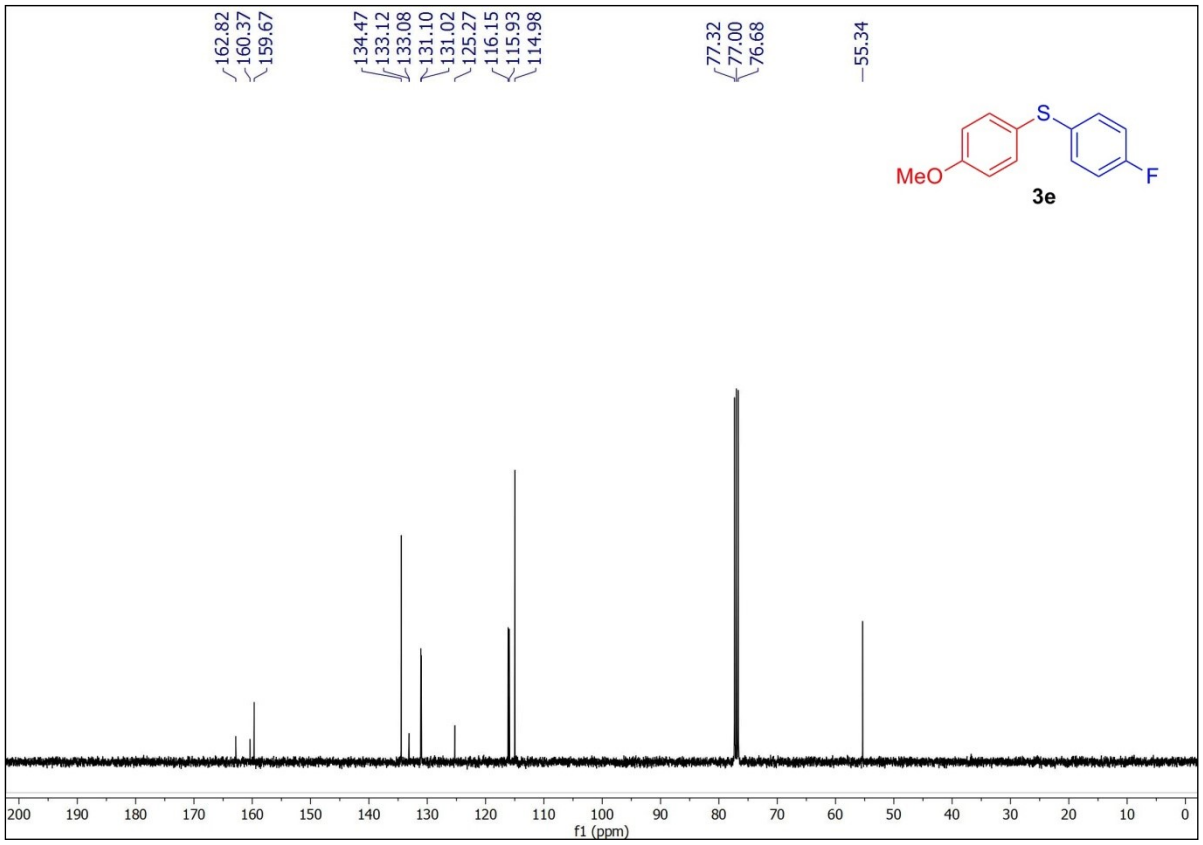
f1 (ppm)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MeO
S
F
3e
f1 (ppm)


S
O2N
Me
3f
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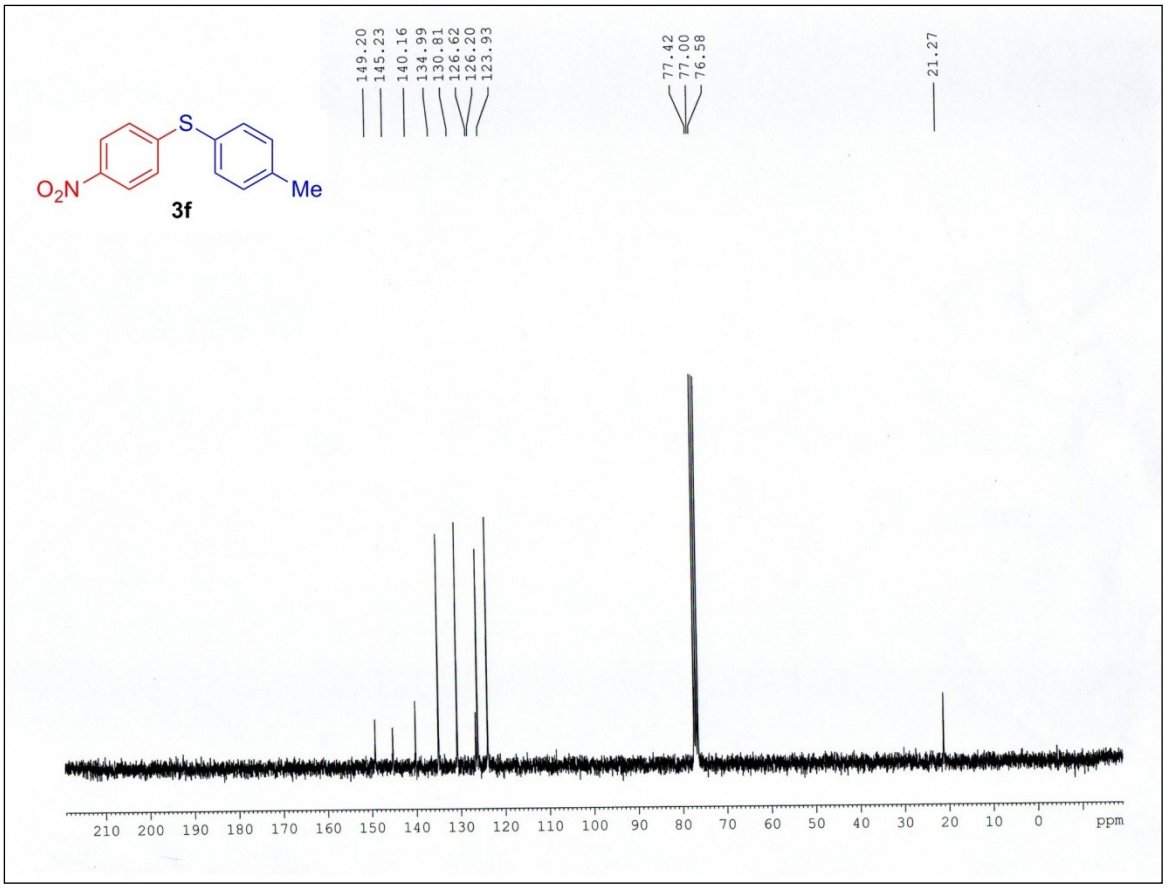
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O_2N
Me
3f
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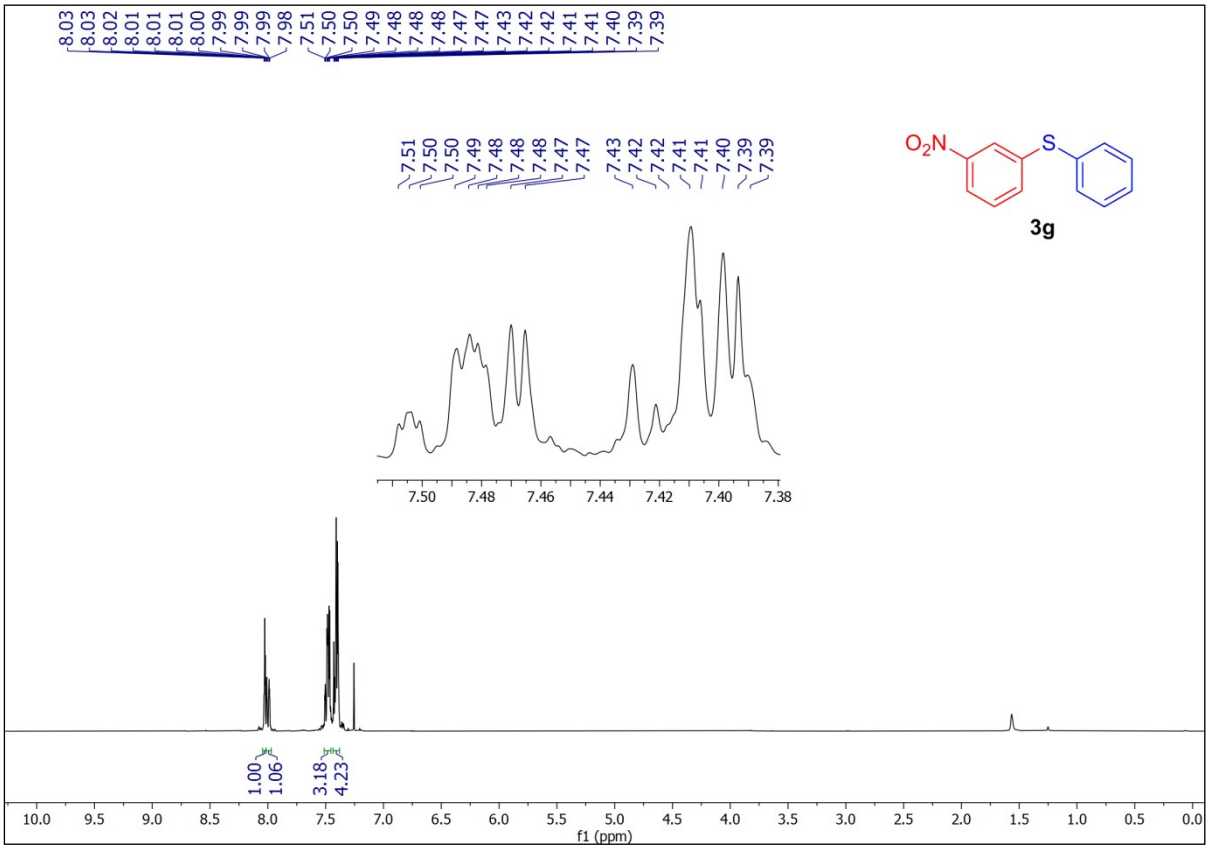
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O_2N
S
3g
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1.00 1.06 3.18 4.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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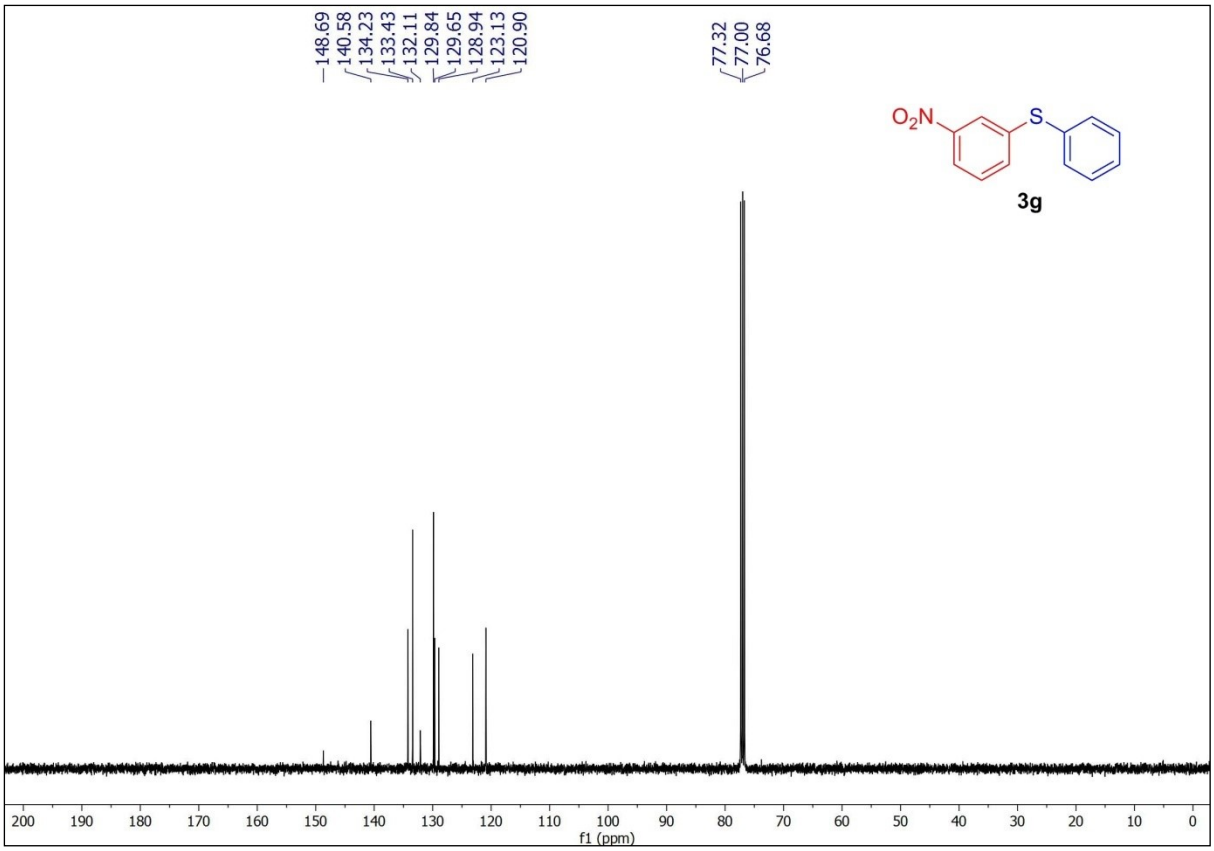
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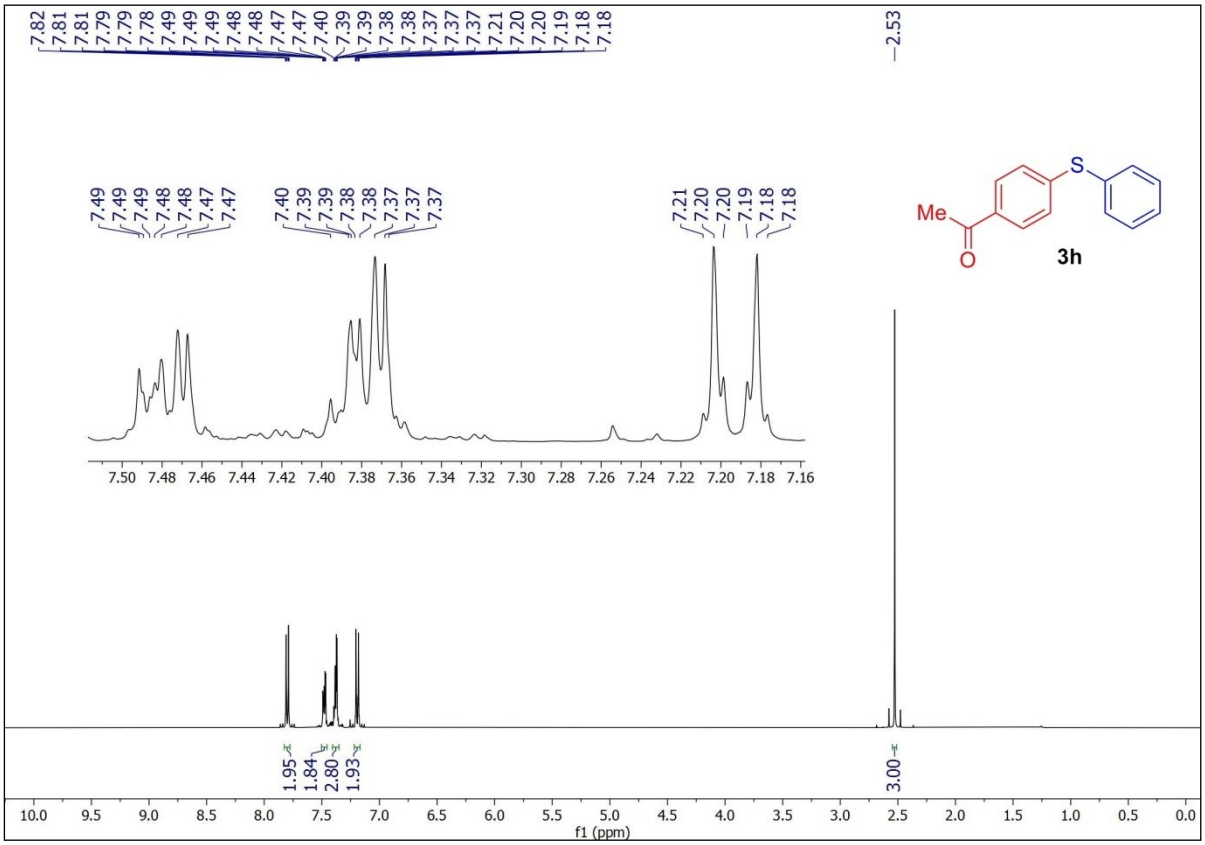
S
3g
f1 (ppm)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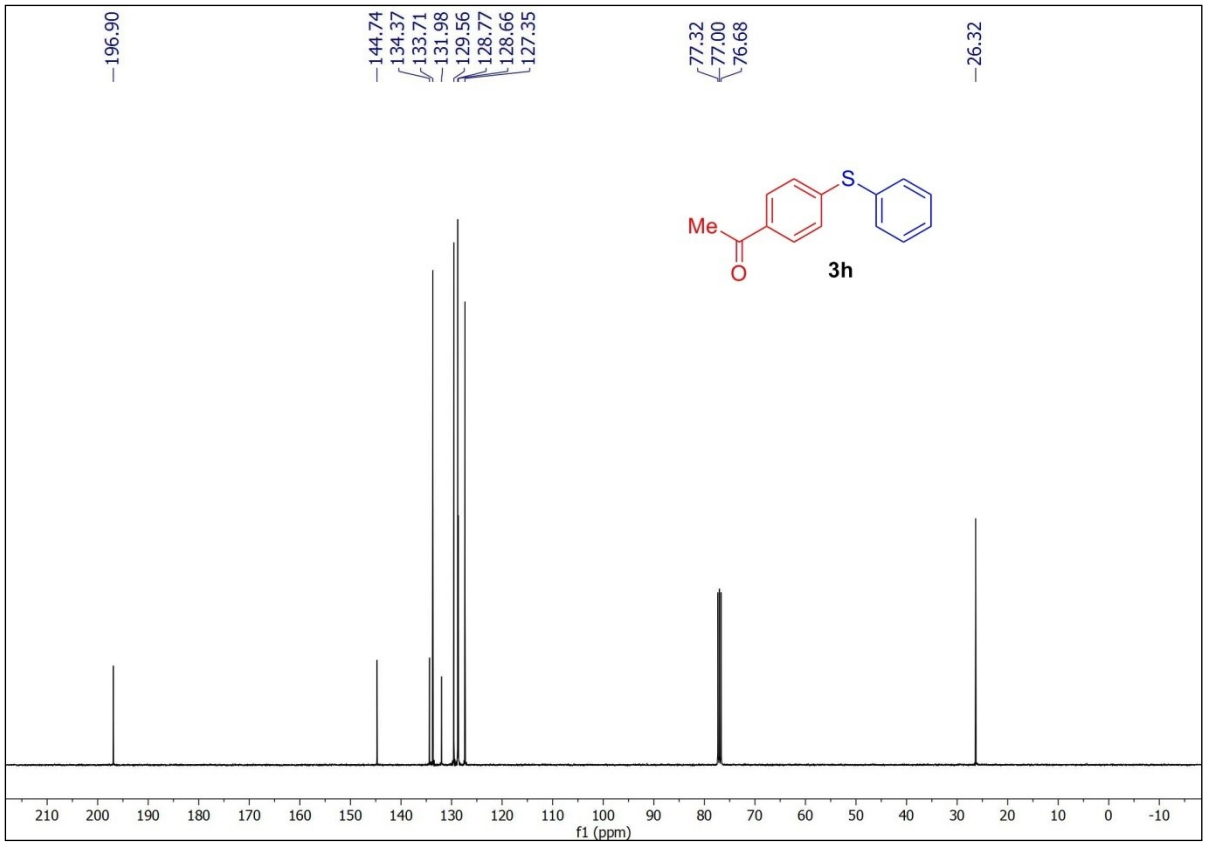
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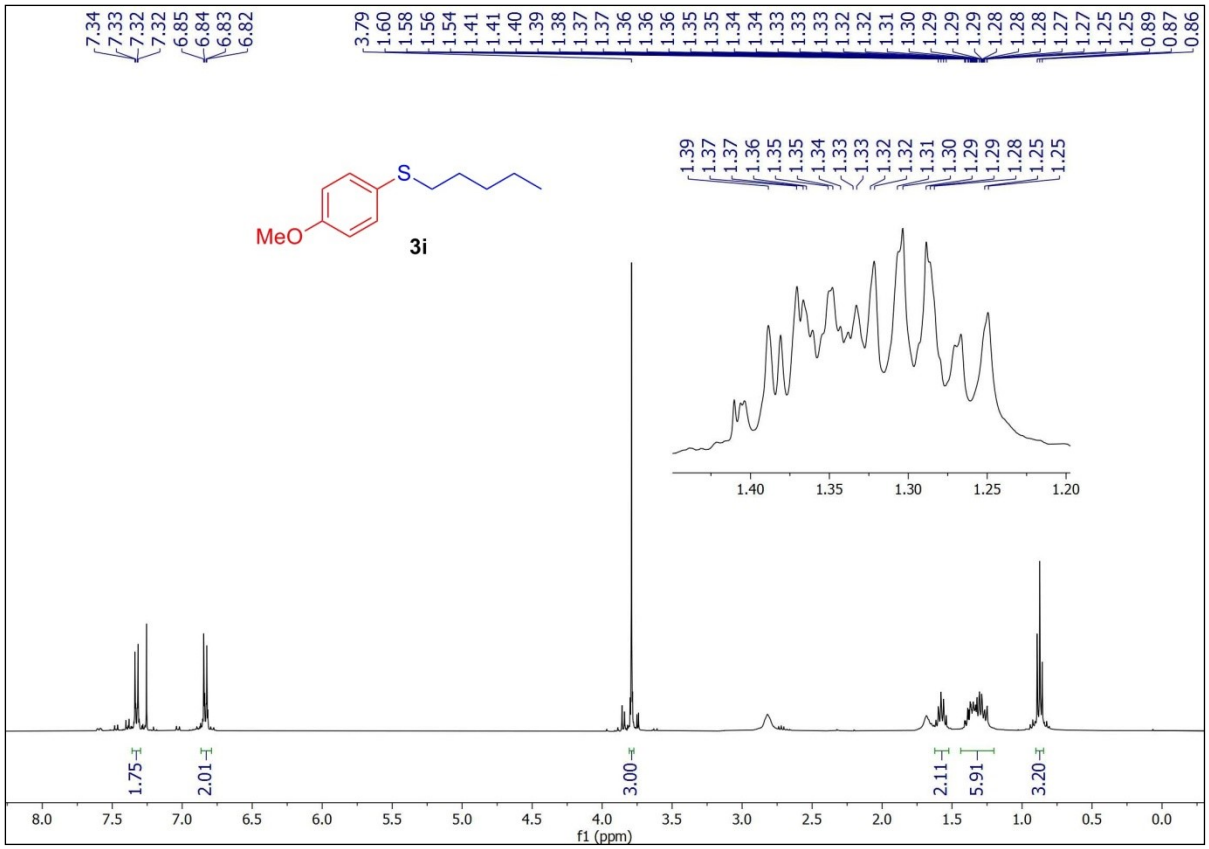
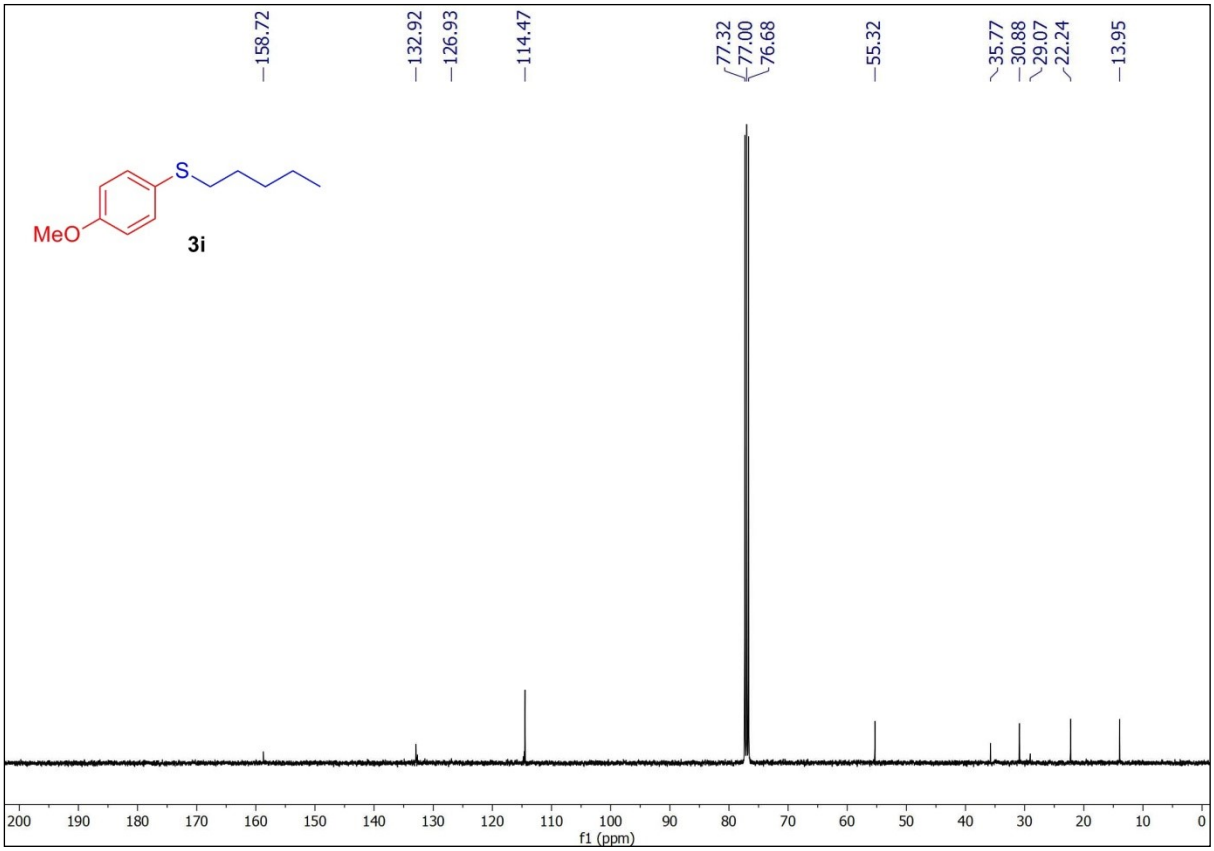
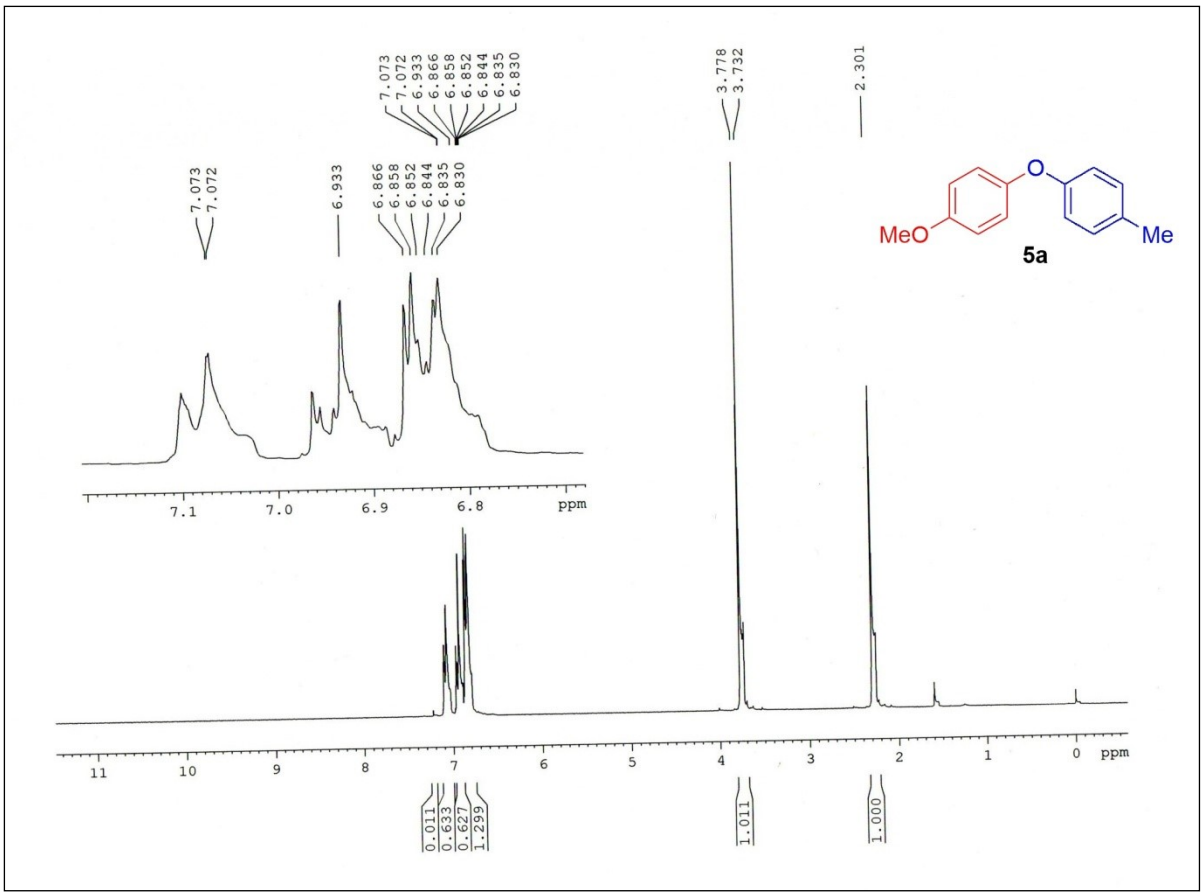
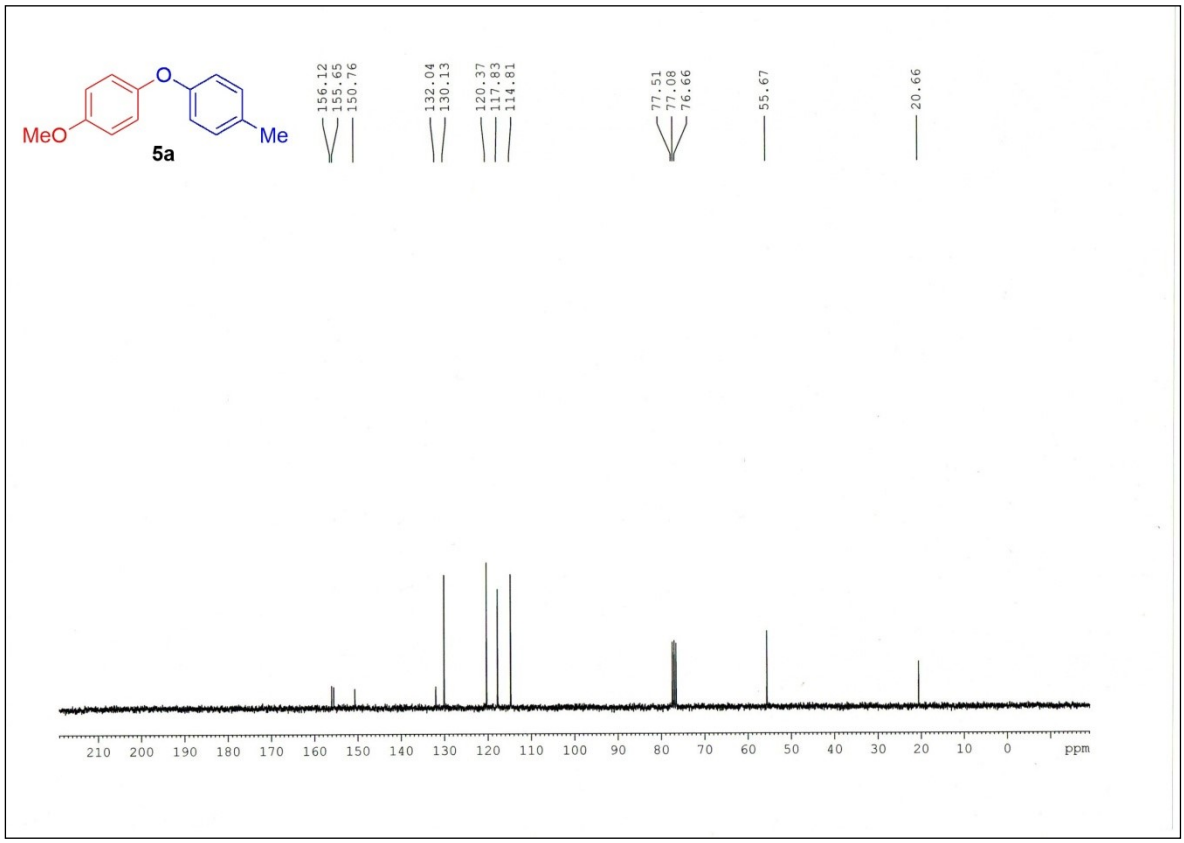
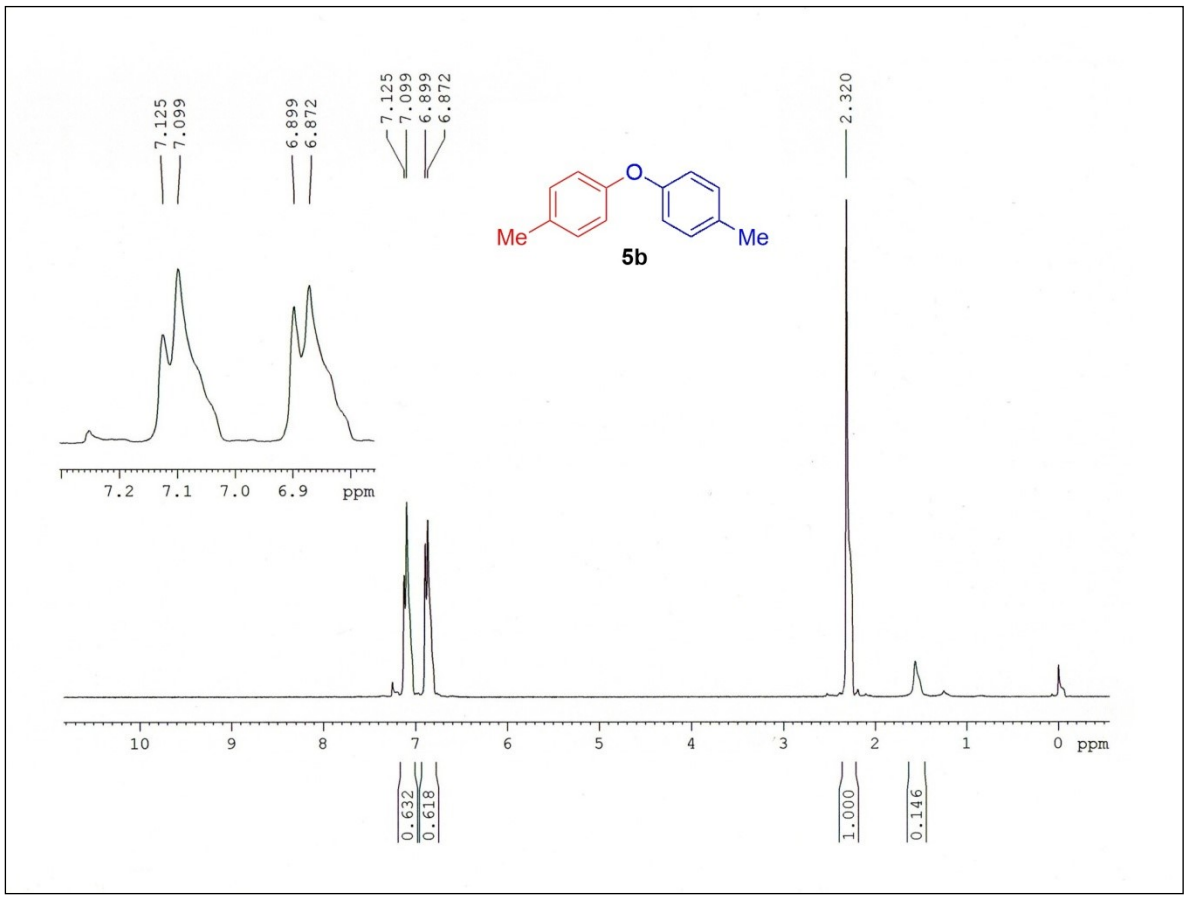
S
Me
O
3h
f1 (ppm)

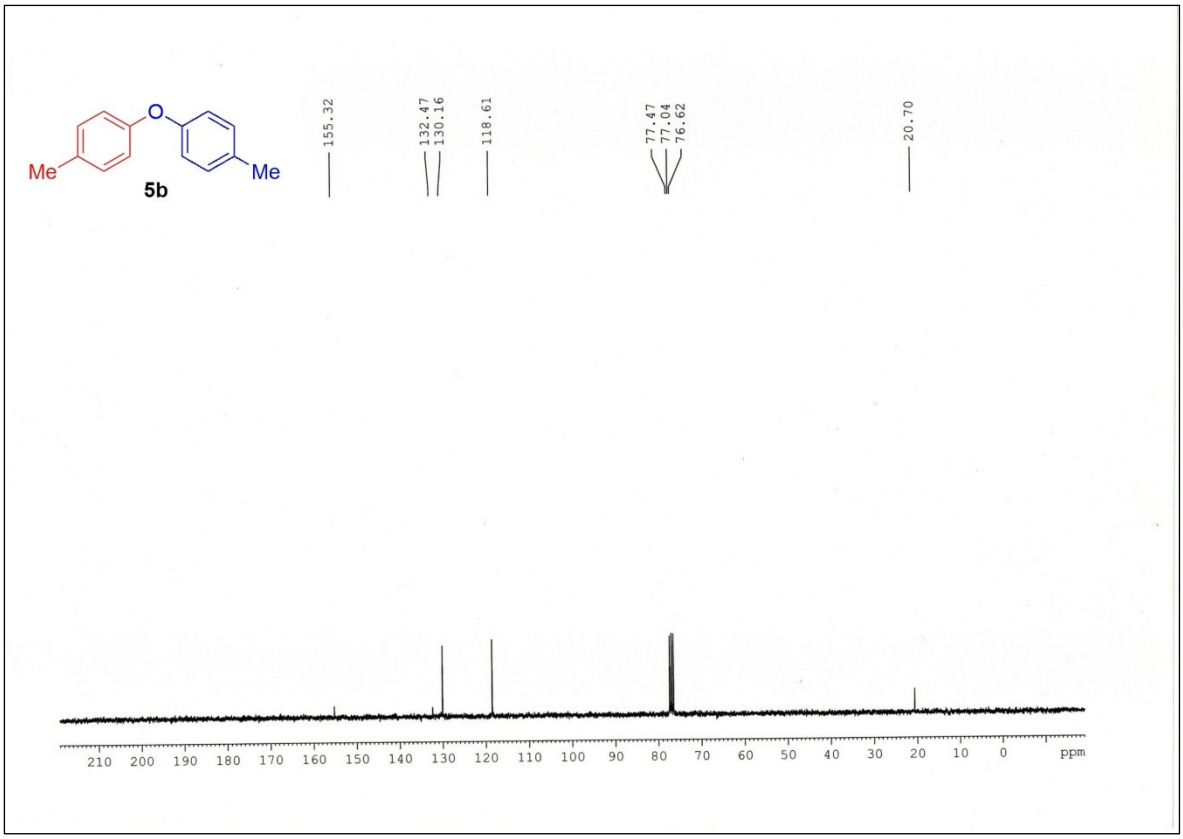

7.34
7.33
7.32
7.32
6.85
6.84
6.83
6.82
3.79
1.60
1.58
1.56
1.54
1.41
1.41
1.40
1.39
1.38
1.37
1.37
1.36
1.36
1.36
1.35
1.35
1.34
1.34
1.33
1.33
1.33
1.32
1.32
1.31
1.30
1.29
1.29
1.29
1.28
1.28
1.28
1.27
1.27
1.25
1.25
0.89
0.87
0.86
S
MeO
3i
1.75
2.01
3.00
2.11
5.91
3.20
f1 (ppm)

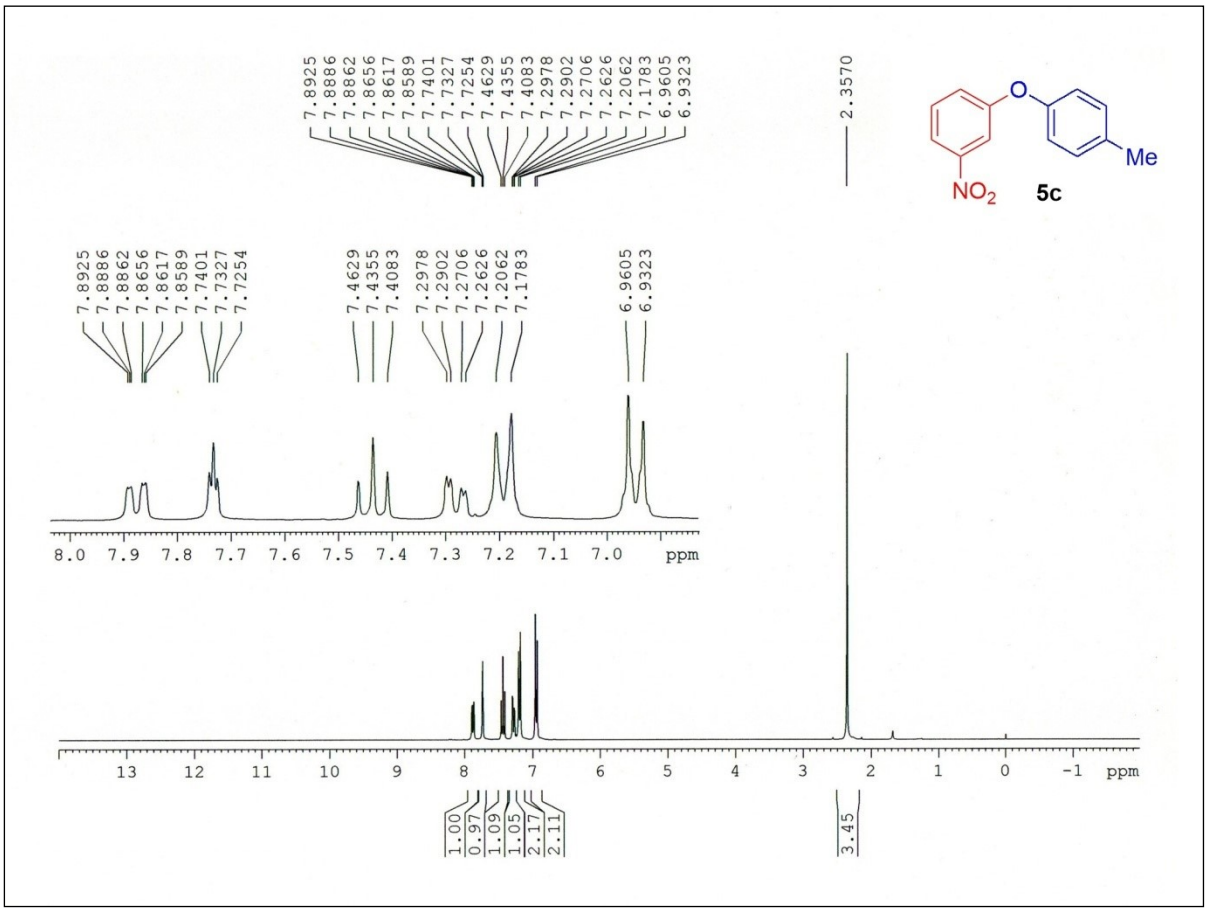

158.72
132.92
126.93
114.47
77.32
77.00
76.68
55.32
35.77
30.88
29.07
22.24
13.95
S
MeO
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

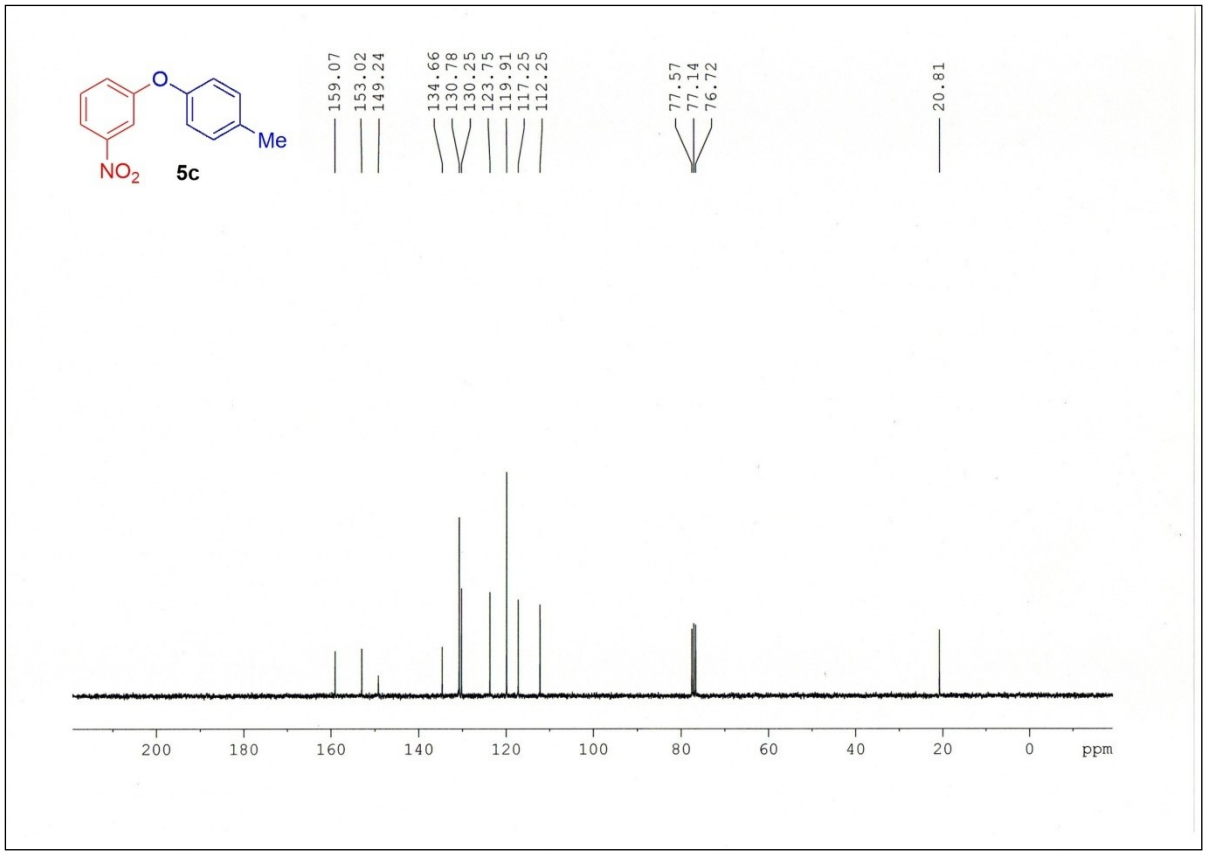

7.073
7.072
6.933
6.866
6.858
6.852
6.844
6.835
6.830
3.778
3.732
2.301
O
MeO
Me
5a
7.1 7.0 6.9 6.8 ppm
11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.011
0.633
0.627
1.299
1.011
1.000

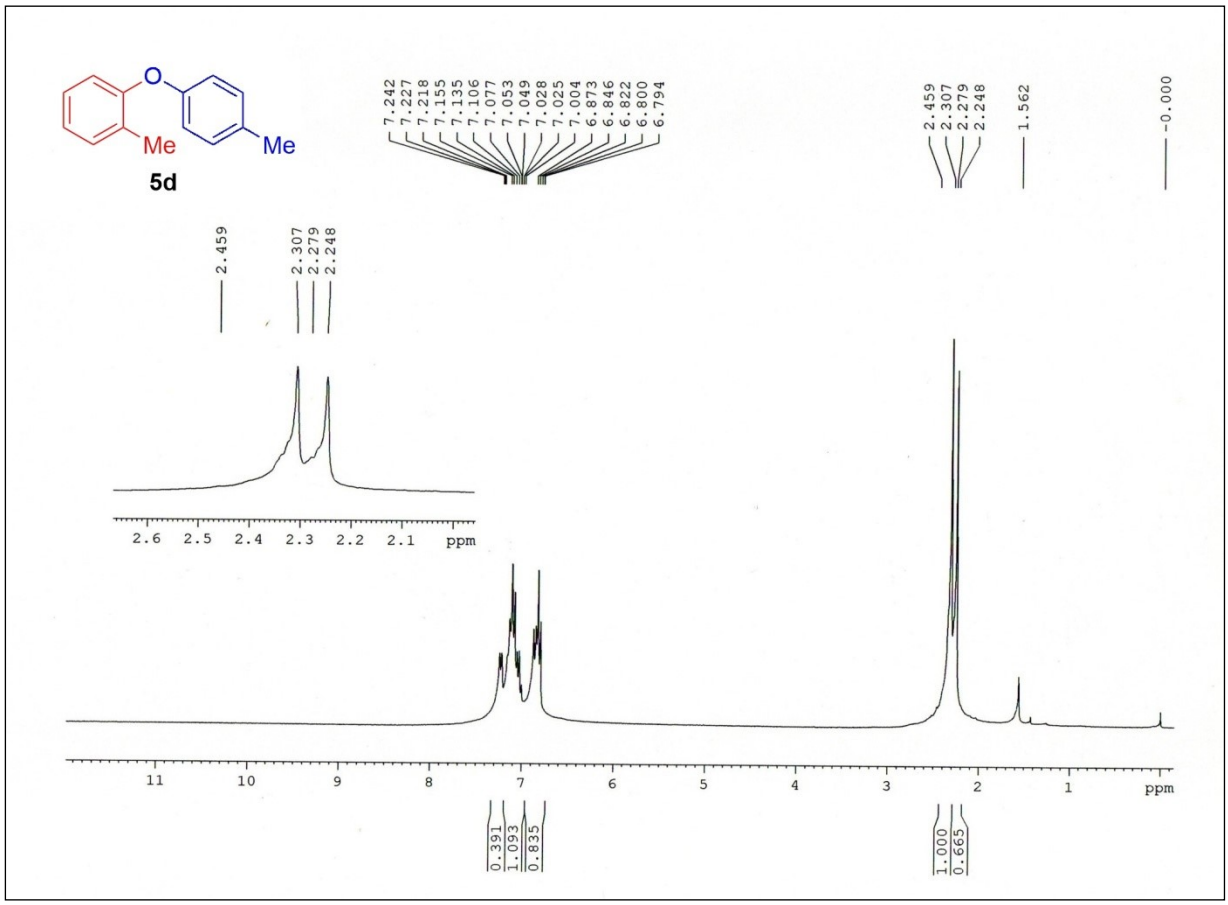

MeO
Me
O
5a
156.12
155.65
150.76
132.04
130.13
120.37
117.83
114.81
77.51
77.08
76.66
55.67
20.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

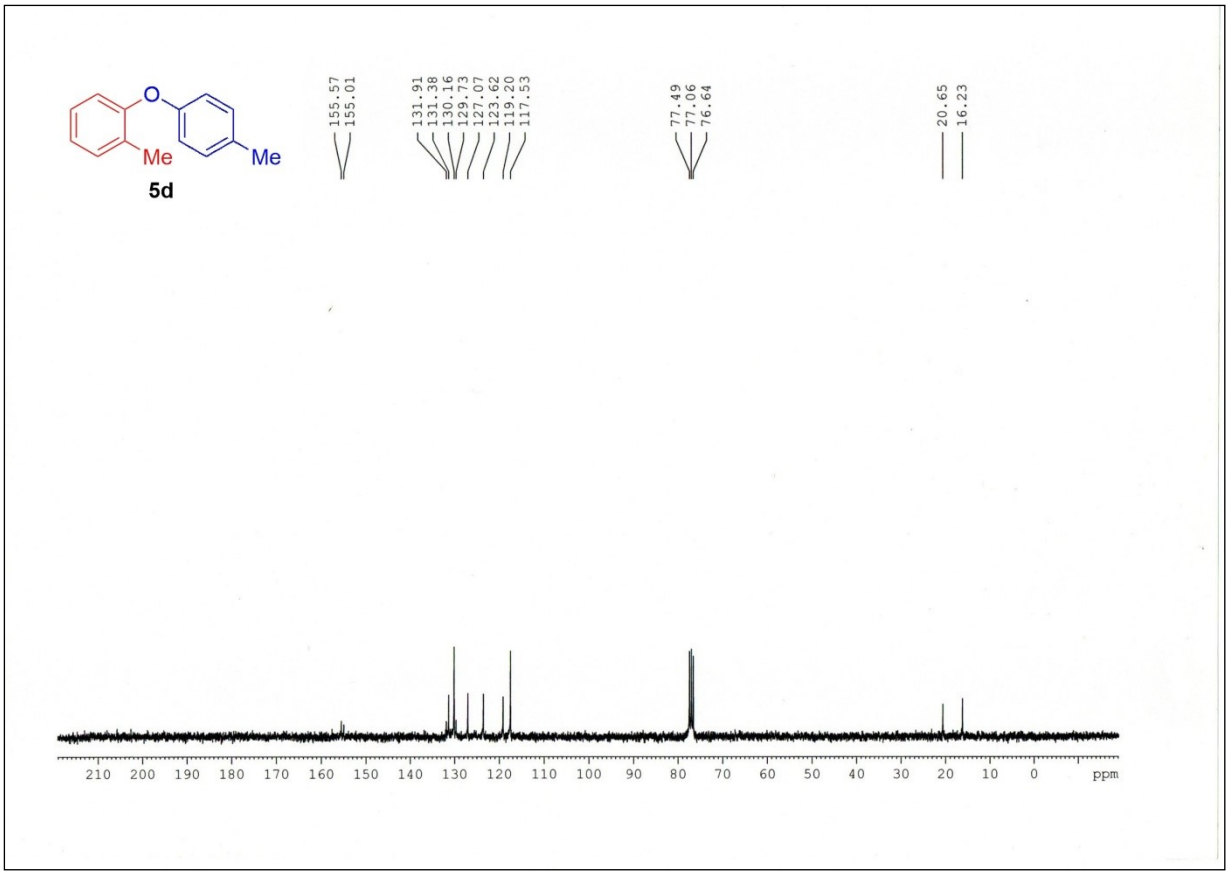

7.125
7.099
6.899
6.872
7.125
7.099
6.899
6.872
2.320
Me
Me
O
5b
7.2 7.1 7.0 6.9 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
0.632
0.618
1.000
0.146

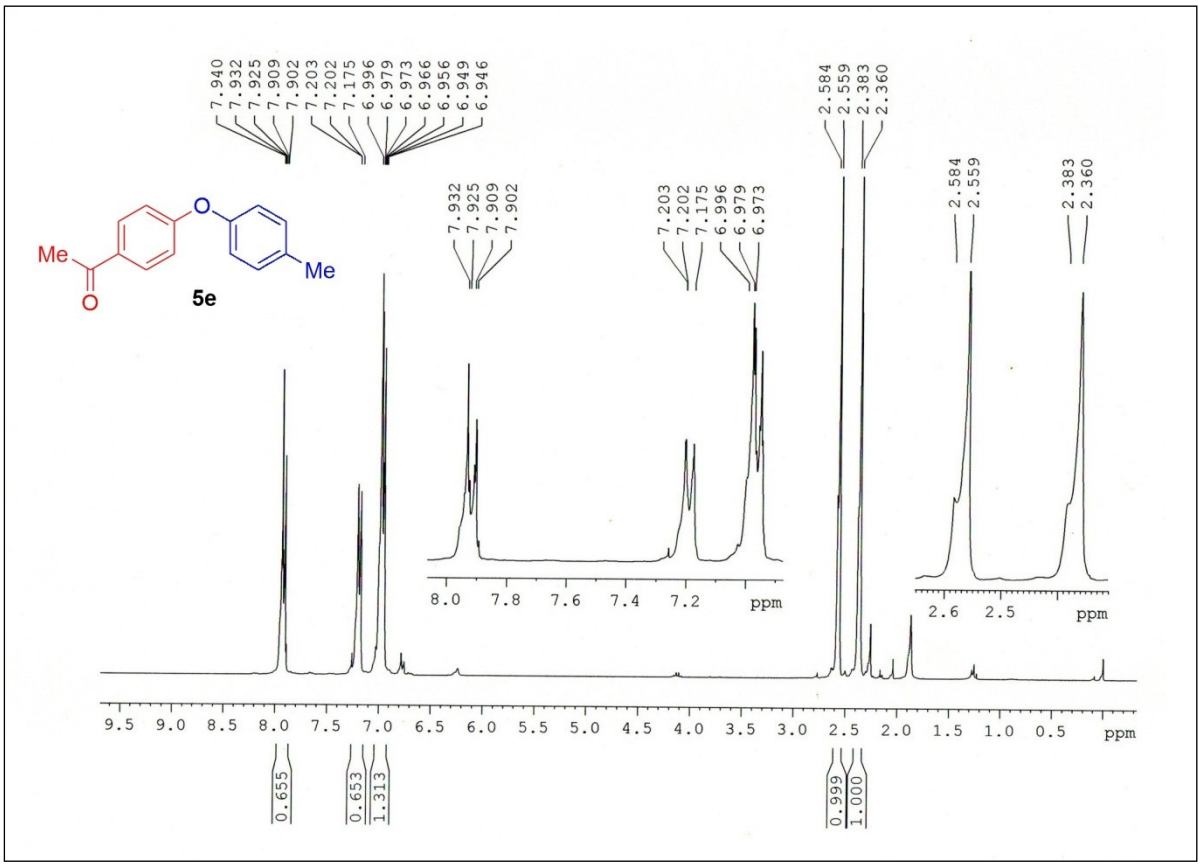

Me
O
Me
5b
155.32
132.47
130.16
118.61
77.47
77.04
76.62
20.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

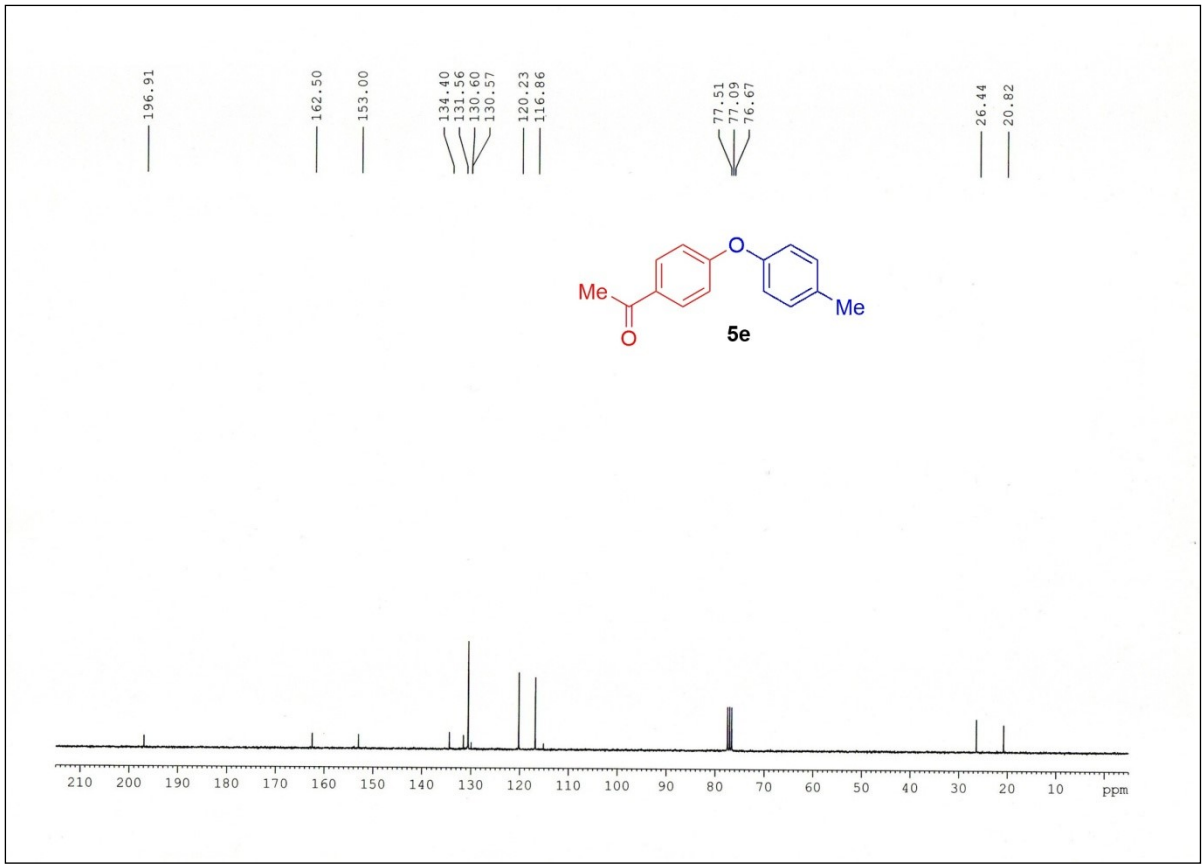

7.8925
7.8886
7.8862
7.8656
7.8617
7.8589
7.7401
7.7327
7.7254
7.4629
7.4355
7.4083
7.2978
7.2902
7.2706
7.2626
7.2062
7.1783
6.9605
6.9323
2.3570
O
Me
NO2
5c
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 ppm
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
1.00
0.97
1.09
1.05
2.17
2.11
3.45

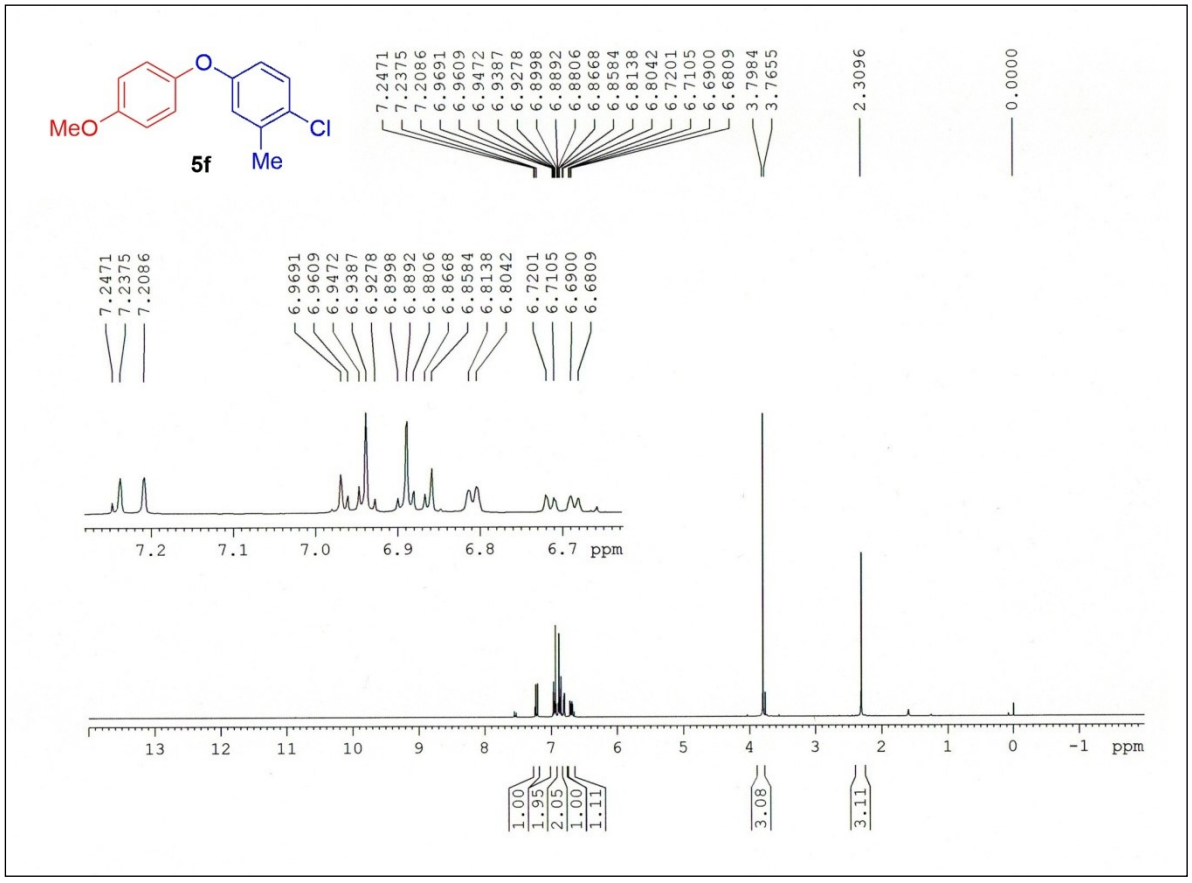

O
Me
NO2
5c
159.07
153.02
149.24
134.66
130.78
130.25
123.75
119.91
117.25
112.25
77.57
77.14
76.72
20.81
200
180
160
140
120
100
80
60
40
20
0
ppm

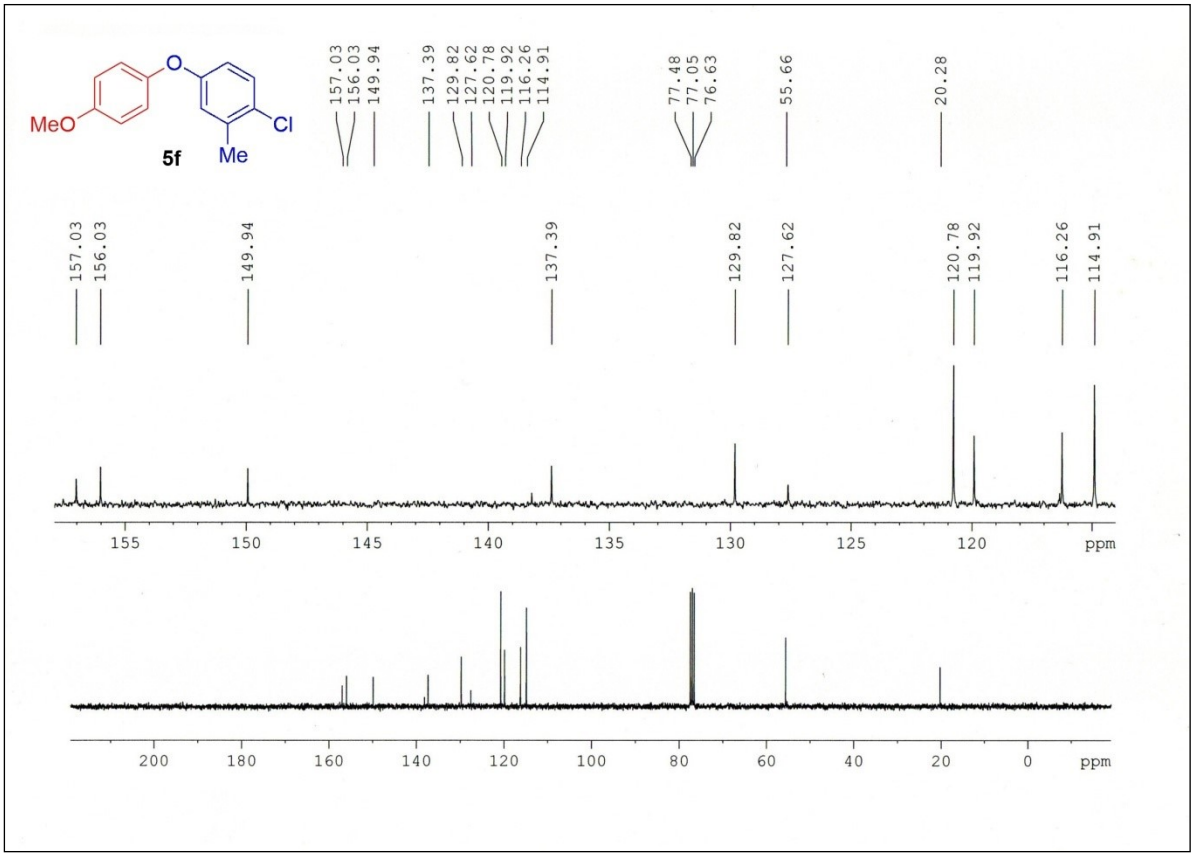

O
Me
Me
5d
7.242
7.227
7.218
7.155
7.135
7.106
7.077
7.053
7.049
7.028
7.025
7.004
6.873
6.846
6.822
6.800
6.794
2.459
2.307
2.279
2.248
1.562
-0.000
2.6
2.5
2.4
2.3
2.2
2.1
ppm
11
10
9
8
7
6
5
4
3
2
1
ppm
0.391
1.093
0.835
1.000
0.665

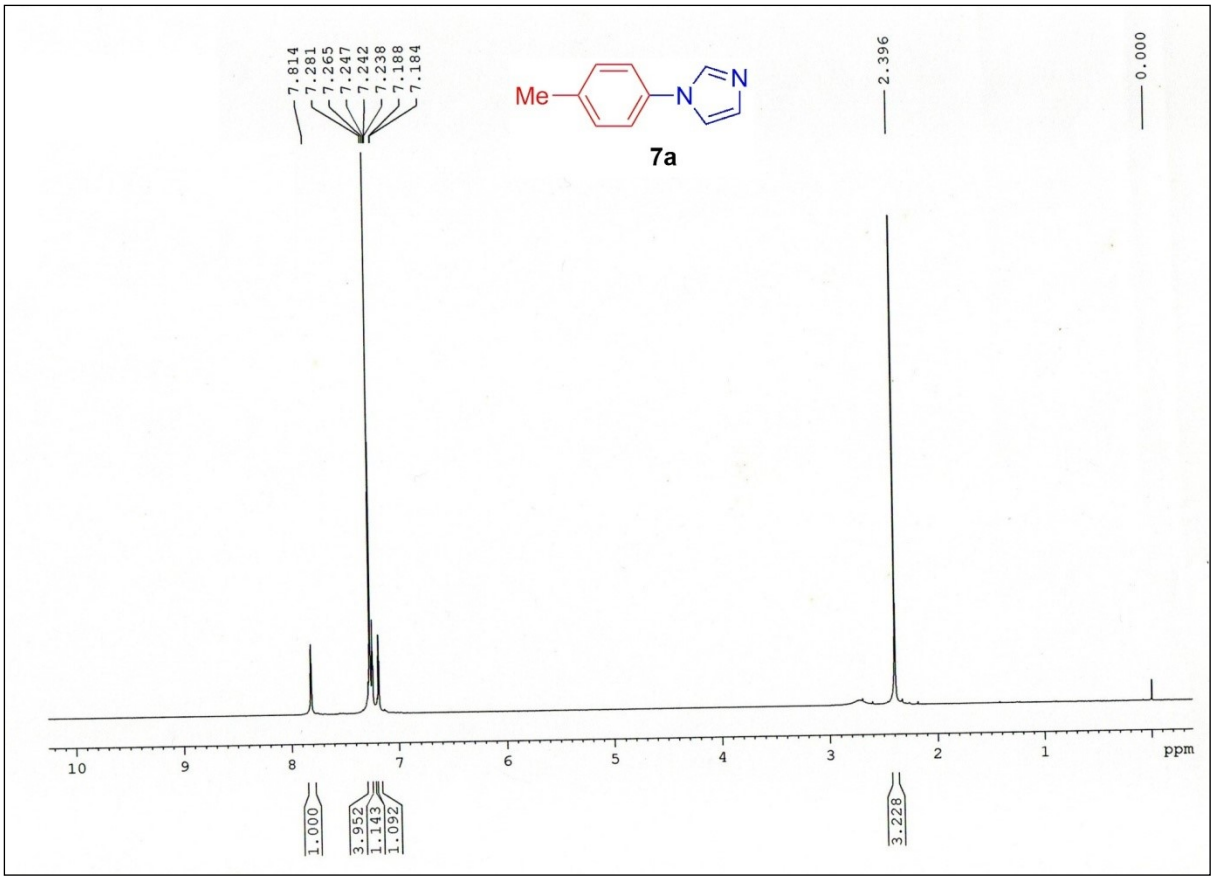

Me
Me
5d
155.57
155.01
131.91
131.38
130.16
129.73
127.07
123.62
119.20
117.53
77.49
77.06
76.64
20.65
16.23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

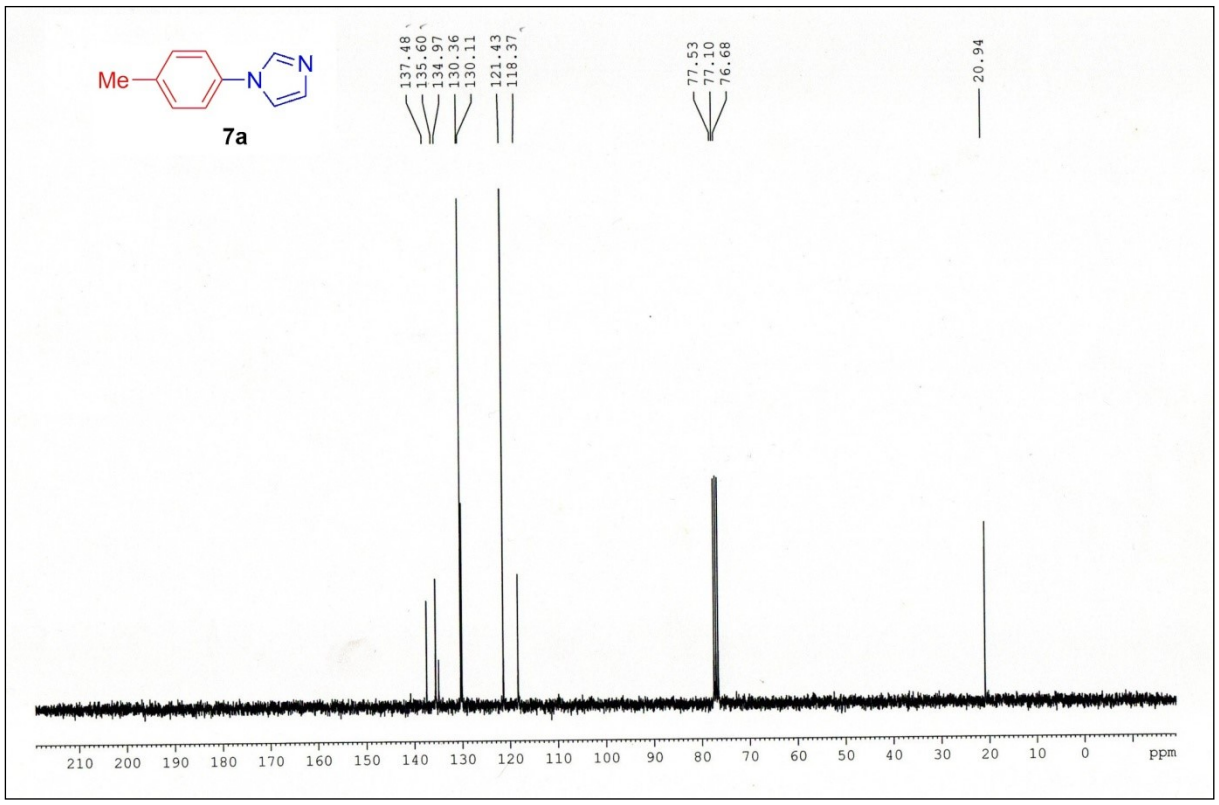

7.940
7.932
7.925
7.909
7.902
7.203
7.202
7.175
6.996
6.979
6.973
6.966
6.956
6.949
6.946
2.584
2.559
2.383
2.360
Me
Me
O
5e
8.0 7.8 7.6 7.4 7.2 ppm
2.6 2.5 ppm
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.655
0.653
1.313
0.999
1.000

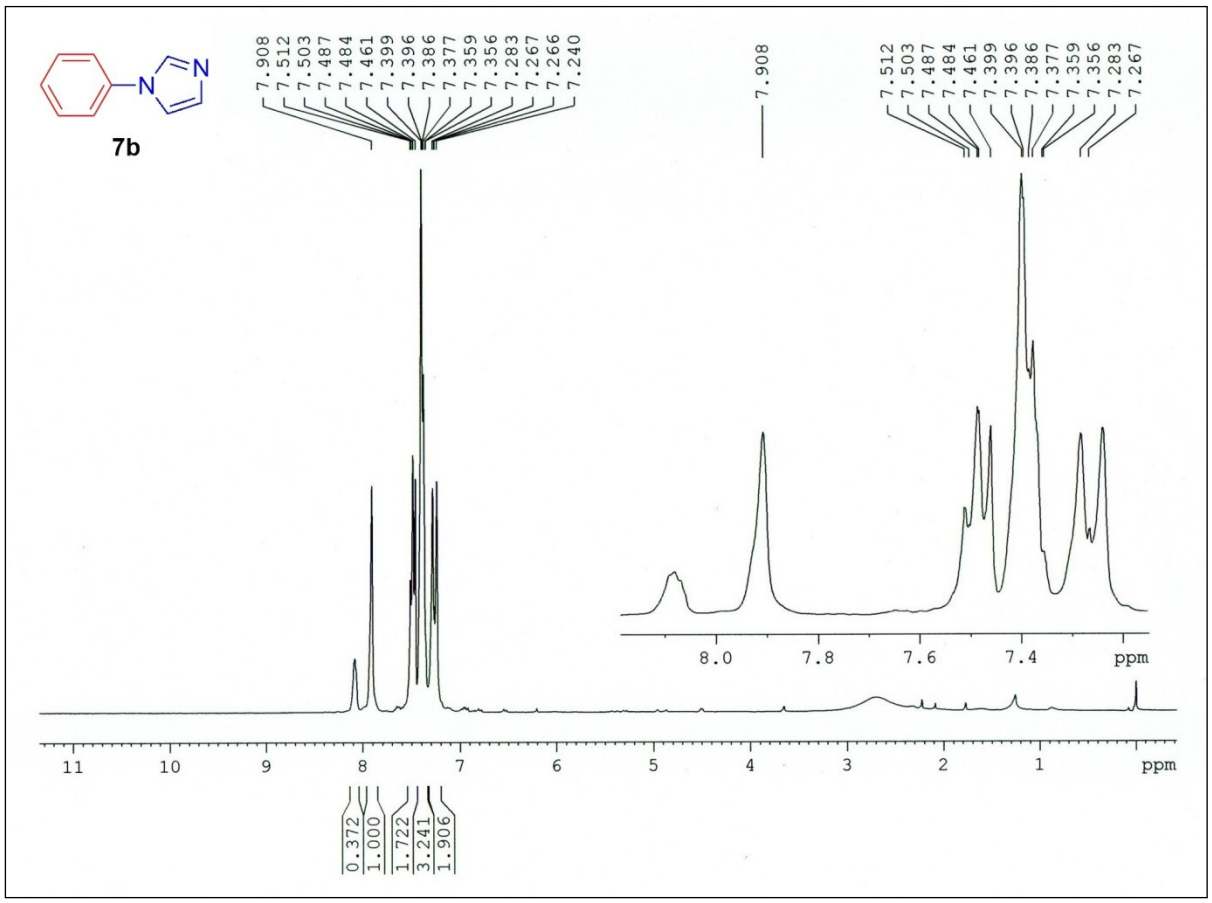

196.91
162.50
153.00
134.40
131.56
130.60
130.57
120.23
116.86
77.51
77.09
76.67
26.44
20.82
Me
O
O
Me
5e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

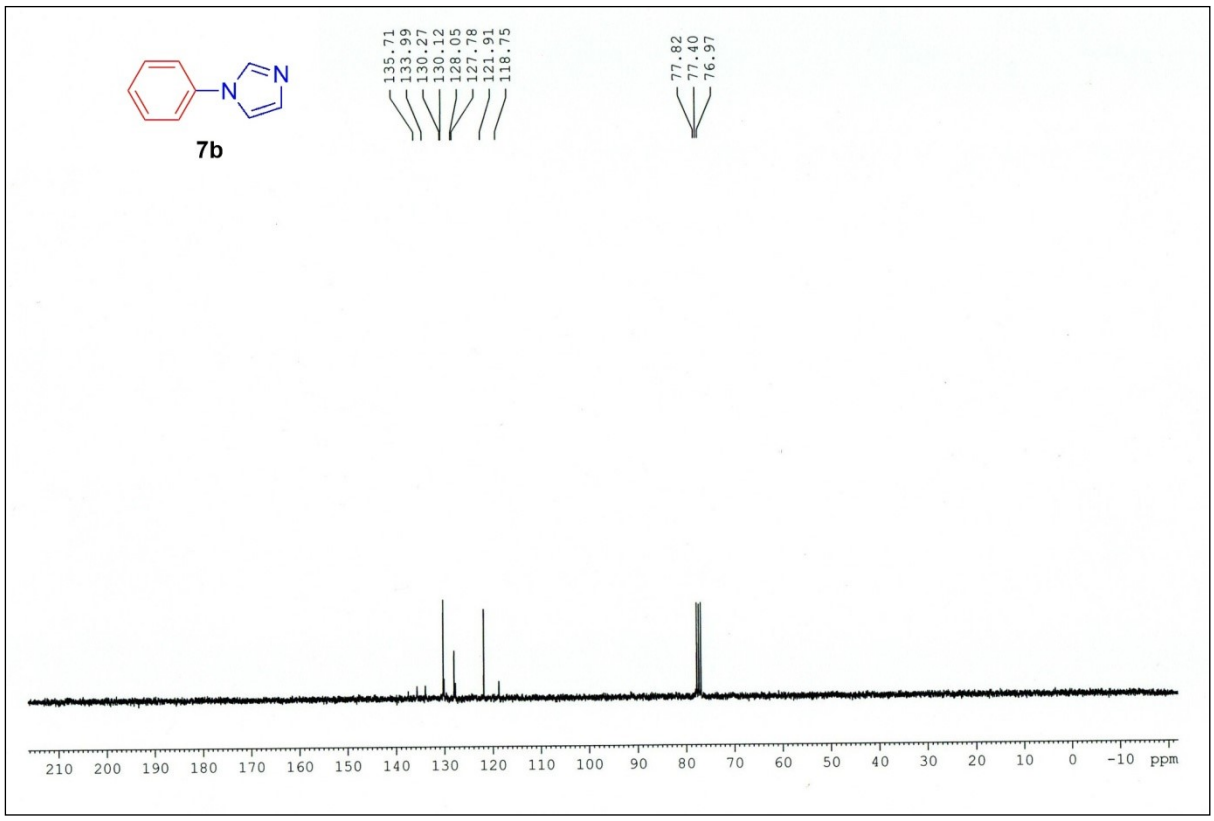

MeO
O
Cl
Me
5f
7.2471
7.2375
7.2086
6.9691
6.9609
6.9472
6.9387
6.9278
6.8998
6.8892
6.8806
6.8668
6.8584
6.8138
6.8042
6.7201
6.7105
6.6900
6.6809
3.7984
3.7655
2.3096
0.0000
7.2 7.1 7.0 6.9 6.8 6.7 ppm
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
1.00
1.95
2.05
1.00
1.11
3.08
3.11

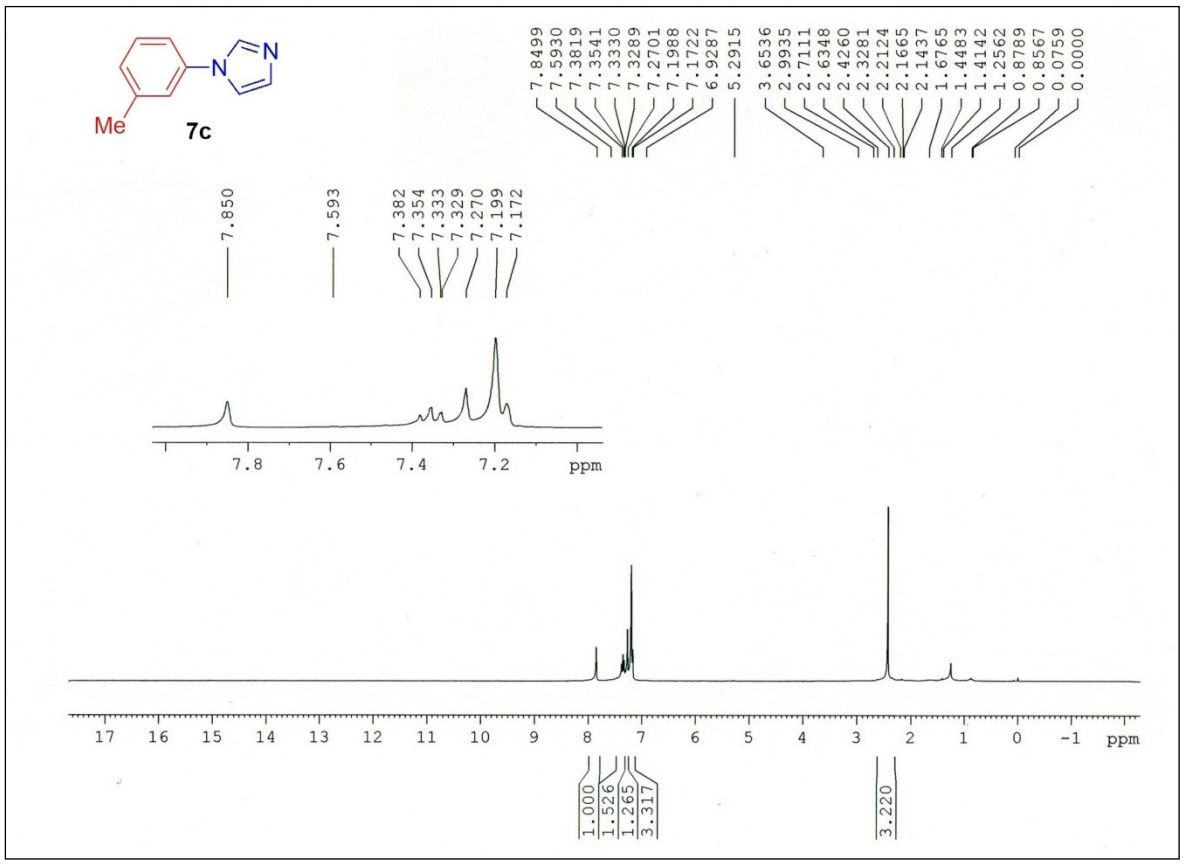

MeO
O
Cl
Me
5f
157.03
156.03
149.94
137.39
129.82
127.62
120.78
119.92
116.26
114.91
77.48
77.05
76.63
55.66
20.28
155
150
145
140
135
130
125
120
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

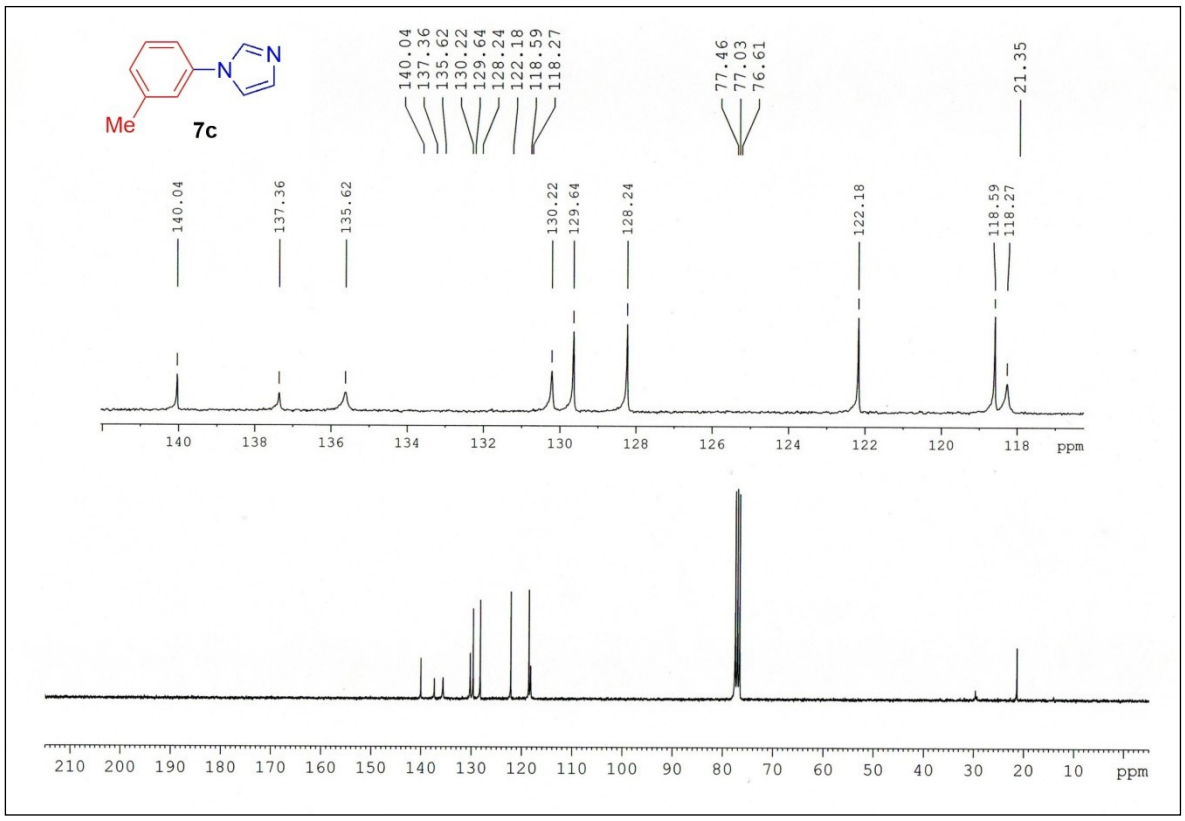

7.814
7.281
7.265
7.247
7.242
7.238
7.188
7.184
Me
N
N
7a
2.396
0.000
10
9
8
7
6
5
4
3
2
1
ppm
1.000
3.952
1.143
1.092
3.228

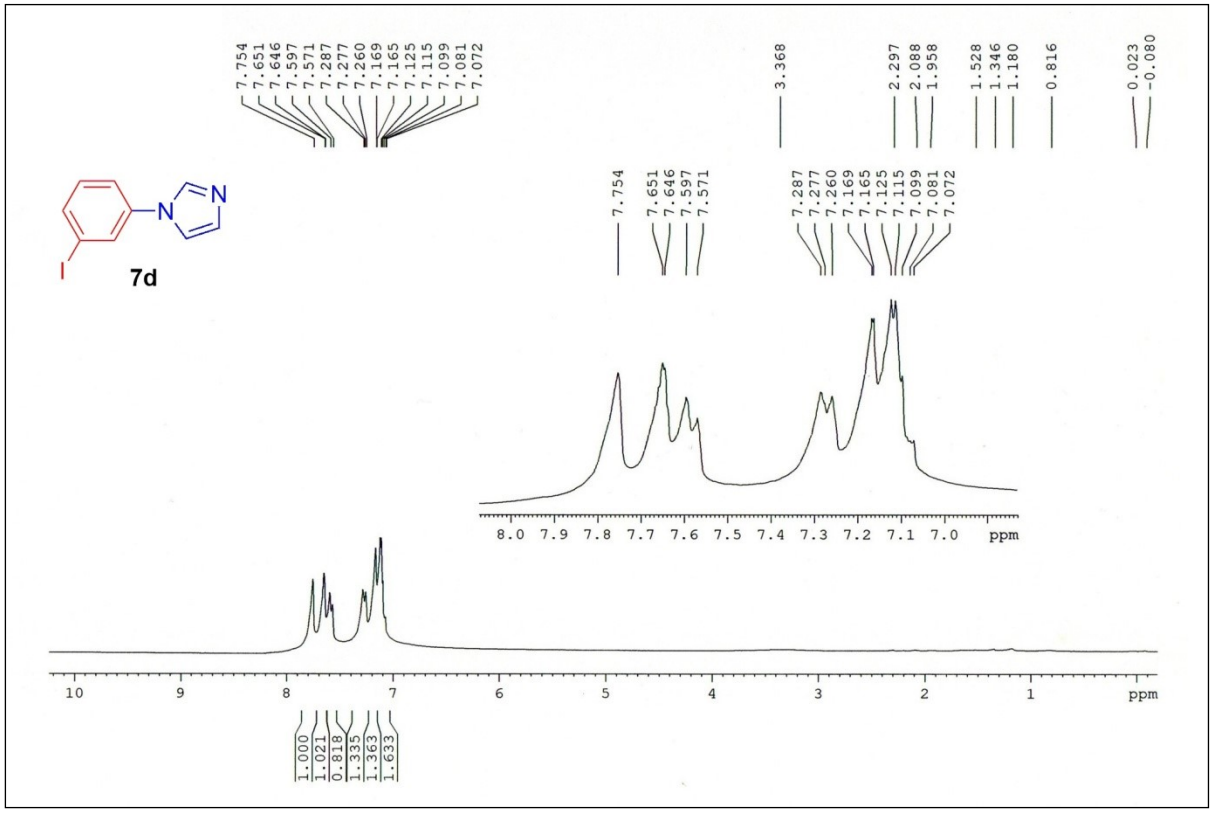

Me
N
N
7a
137.48
135.60
134.97
130.36
130.11
121.43
118.37
77.53
77.10
76.68
20.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

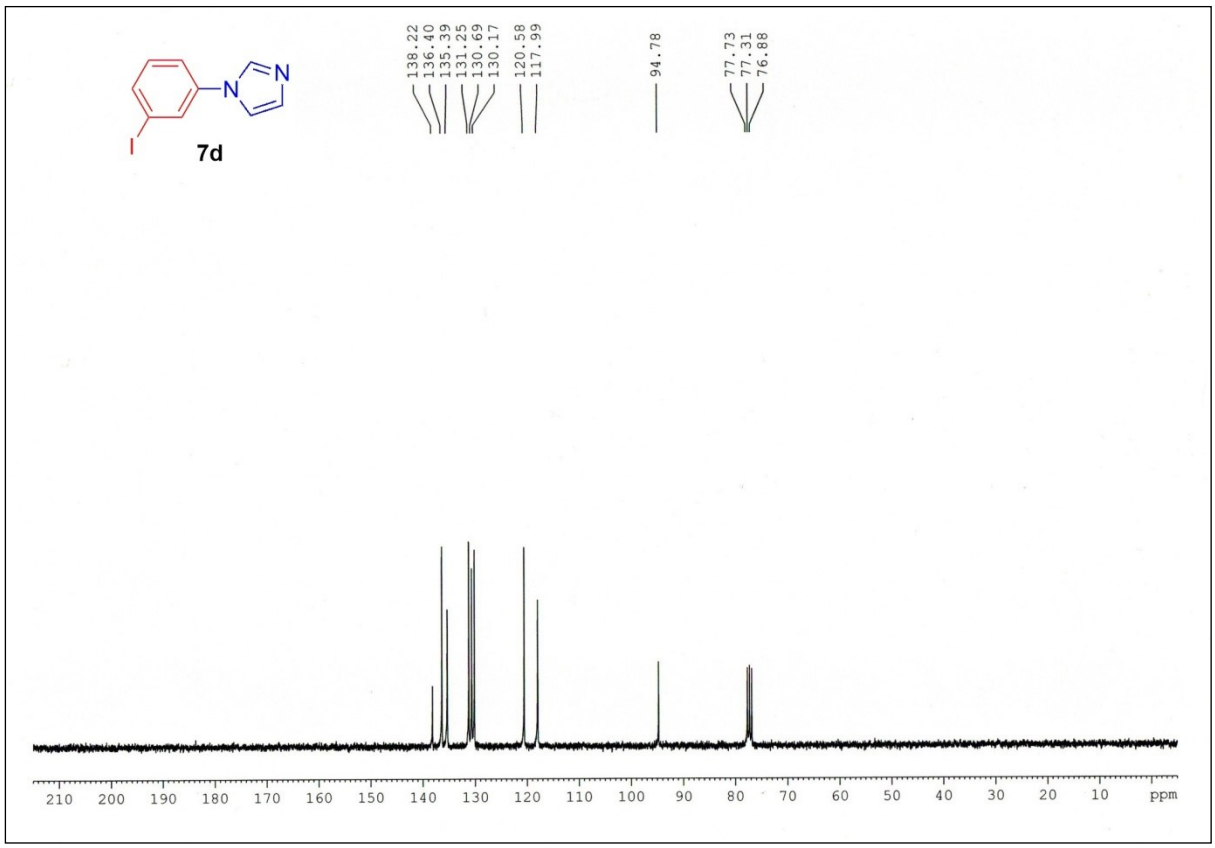

N
N
7b
7.908
7.512
7.503
7.487
7.484
7.461
7.399
7.396
7.386
7.377
7.359
7.356
7.283
7.267
7.266
7.240
8.0 7.8 7.6 7.4 ppm
11 10 9 8 7 6 5 4 3 2 1 ppm
0.372
1.000
1.722
3.241
1.906

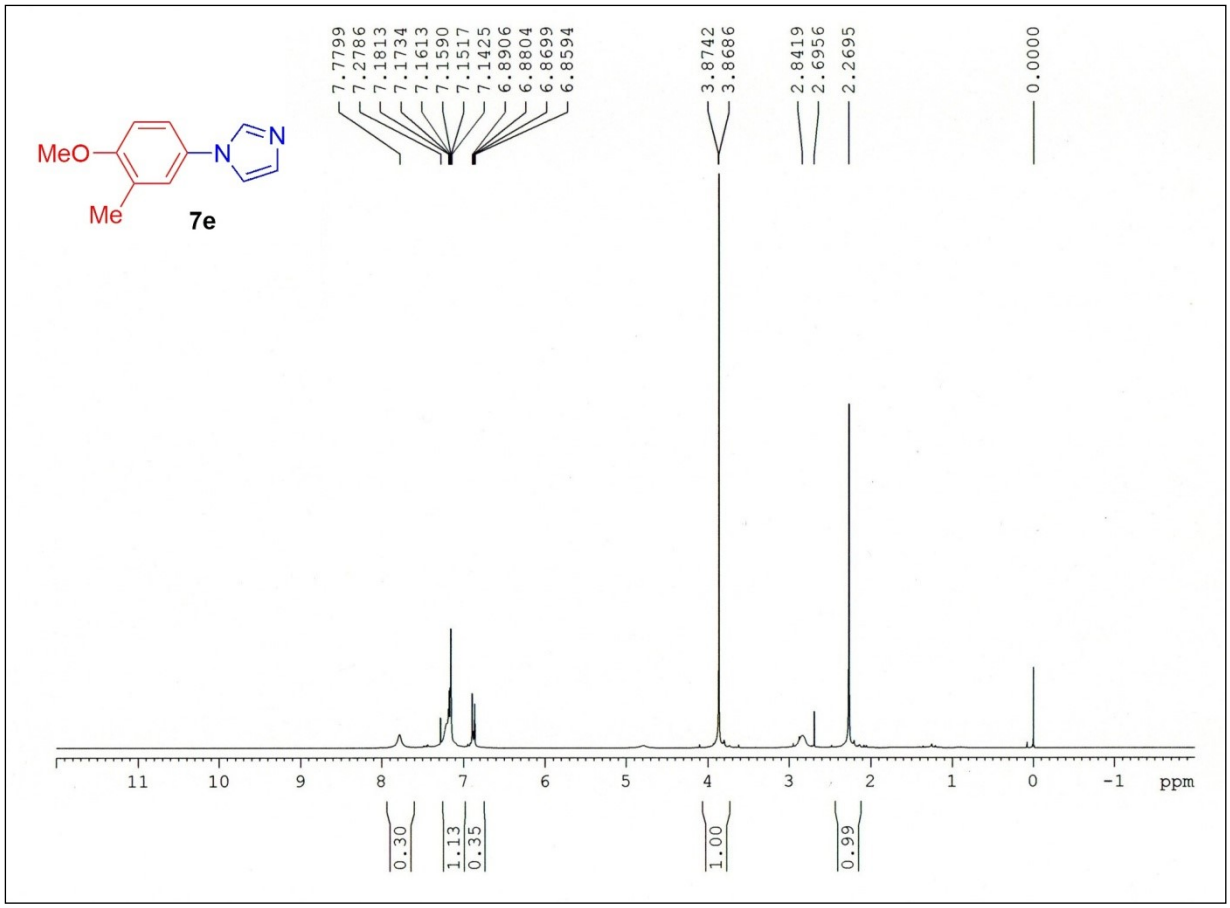

7b
135.71
133.99
130.27
130.12
128.05
127.78
121.91
118.75
77.82
77.40
76.97
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

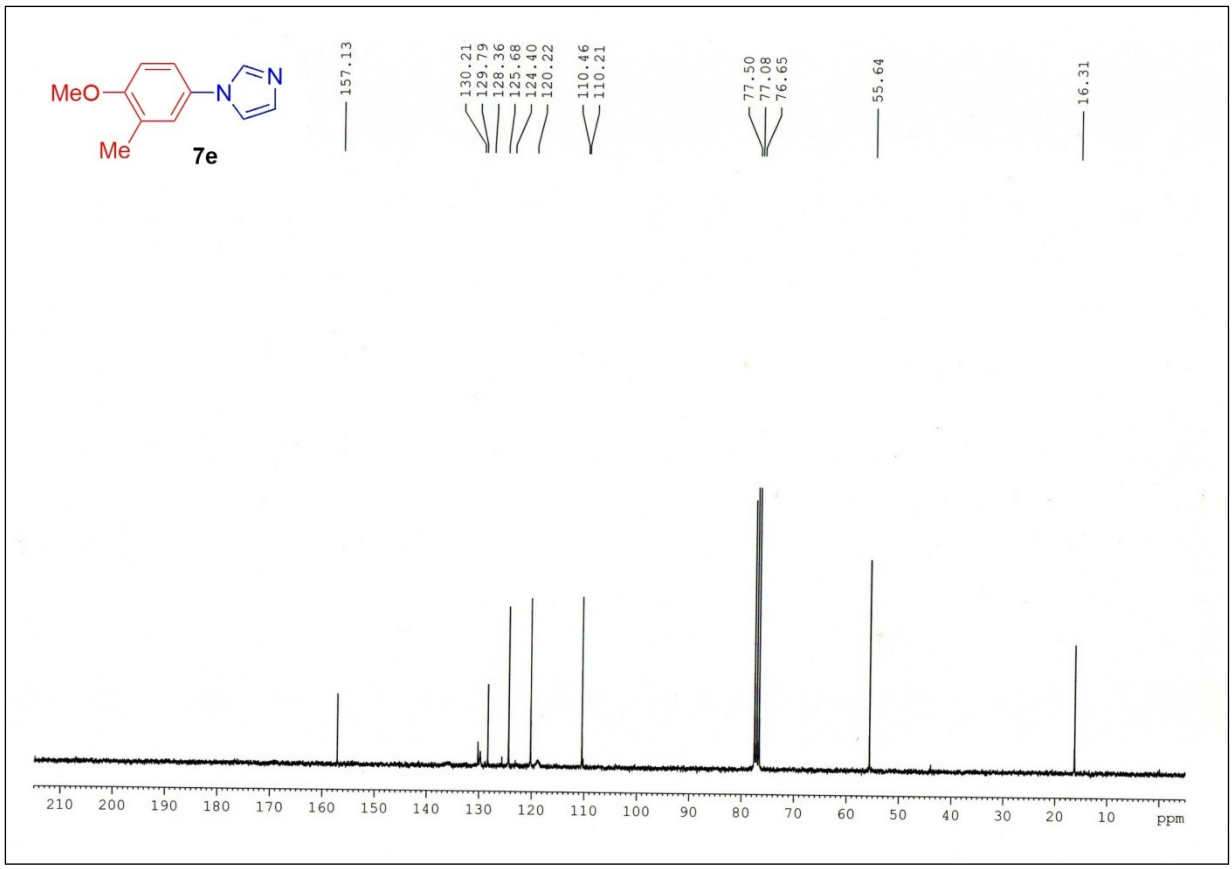

Me
7c
7.8499
7.5930
7.3819
7.3541
7.3330
7.3289
7.2701
7.1988
7.1722
6.9287
5.2915
3.6536
2.9935
2.7111
2.6348
2.4260
2.3281
2.2124
2.1665
2.1437
1.6765
1.4483
1.4142
1.2562
0.8789
0.8567
0.0759
0.0000
7.850
7.593
7.382
7.354
7.333
7.329
7.270
7.199
7.172
7.8 7.6 7.4 7.2 ppm
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
1.000
1.526
1.265
3.317
3.220

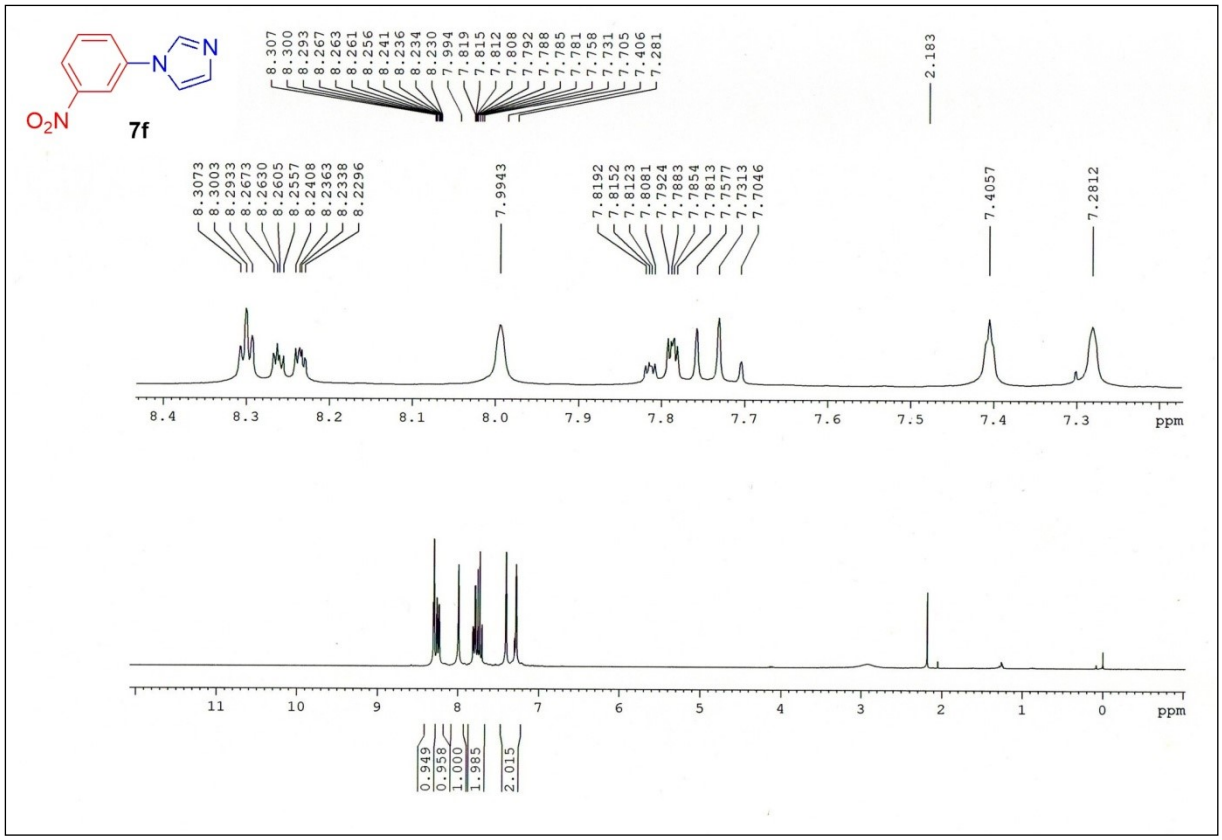

Me
7c
140.04
137.36
135.62
130.22
129.64
128.24
122.18
118.59
118.27
77.46
77.03
76.61
21.35
ppm

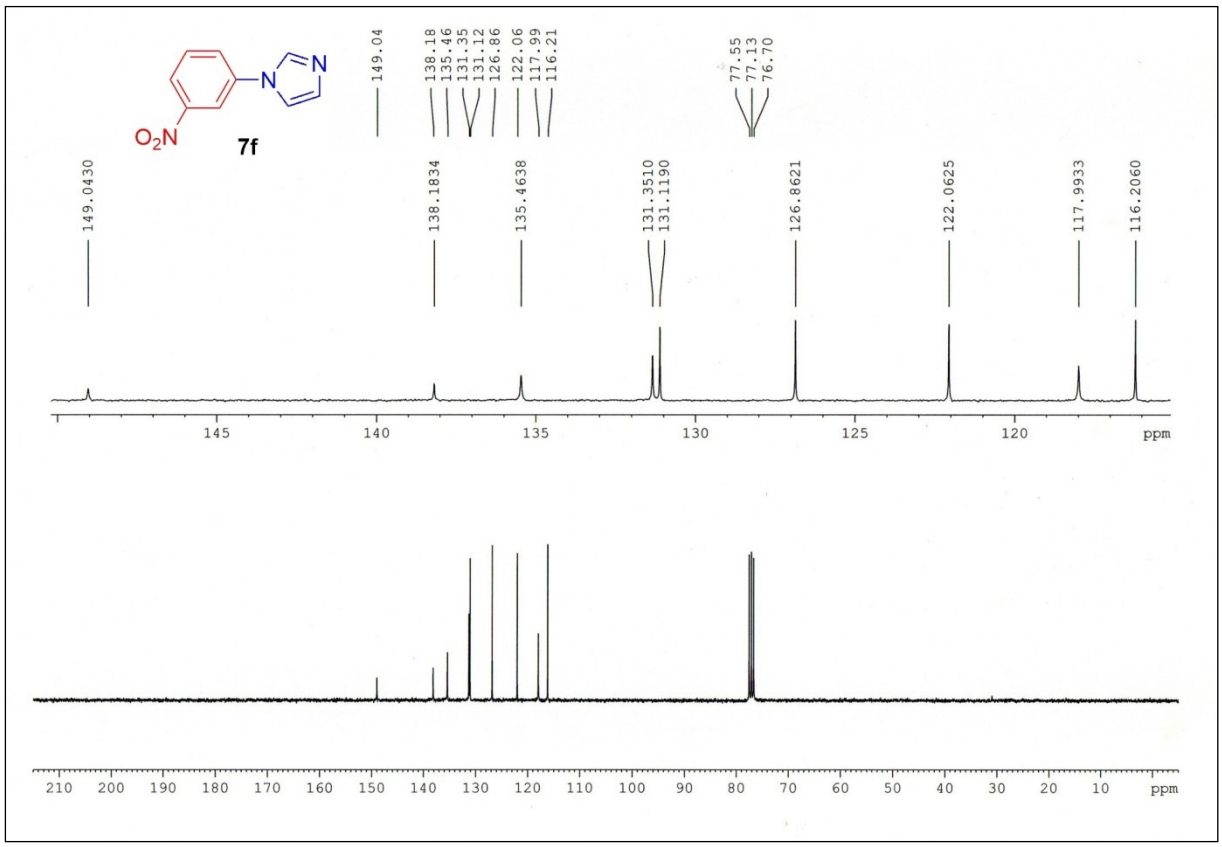

7d
7.754
7.651
7.646
7.597
7.571
7.287
7.277
7.260
7.169
7.165
7.125
7.115
7.099
7.081
7.072
3.368
2.297
2.088
1.958
1.528
1.346
1.180
0.816
0.023
-0.080
1.000
1.021
0.818
1.335
1.363
1.633
ppm

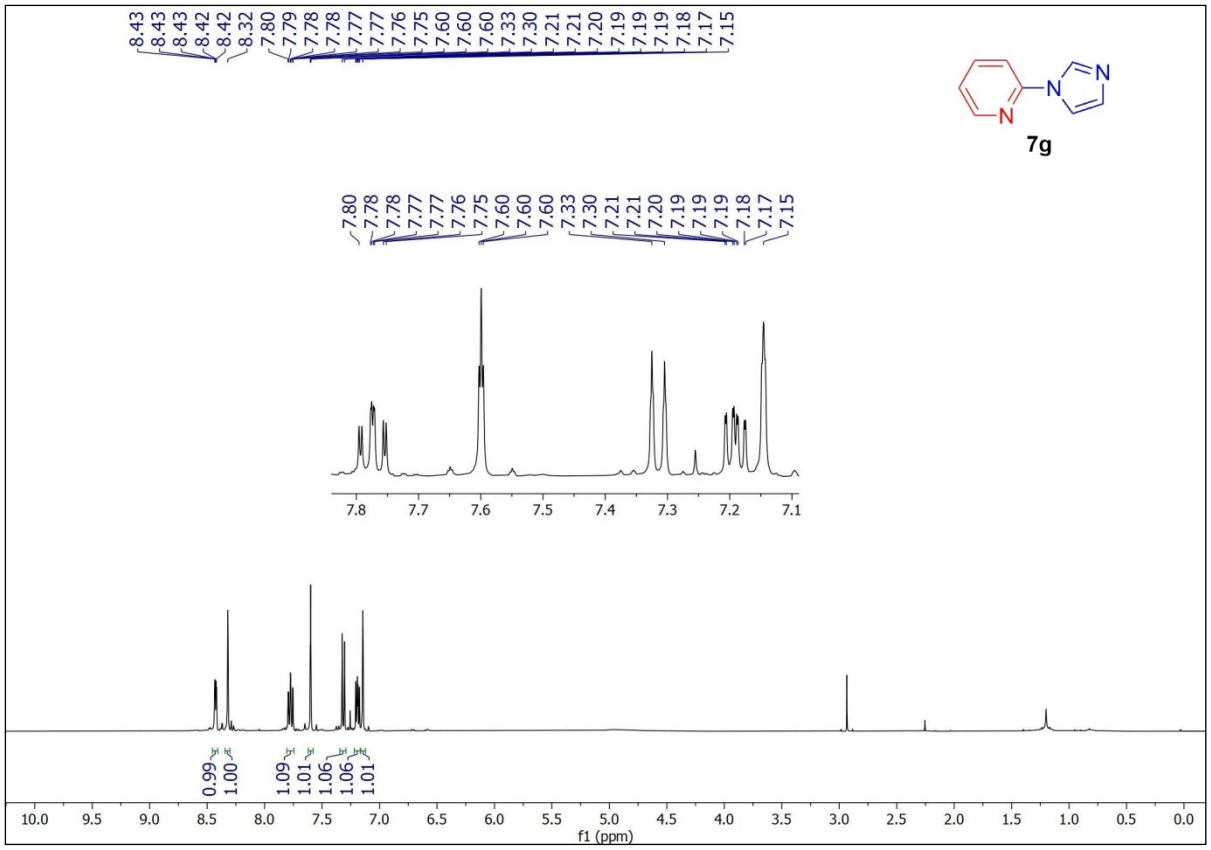

7d
138.22
136.40
135.39
131.25
130.69
130.17
120.58
117.99
94.78
77.73
77.31
76.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

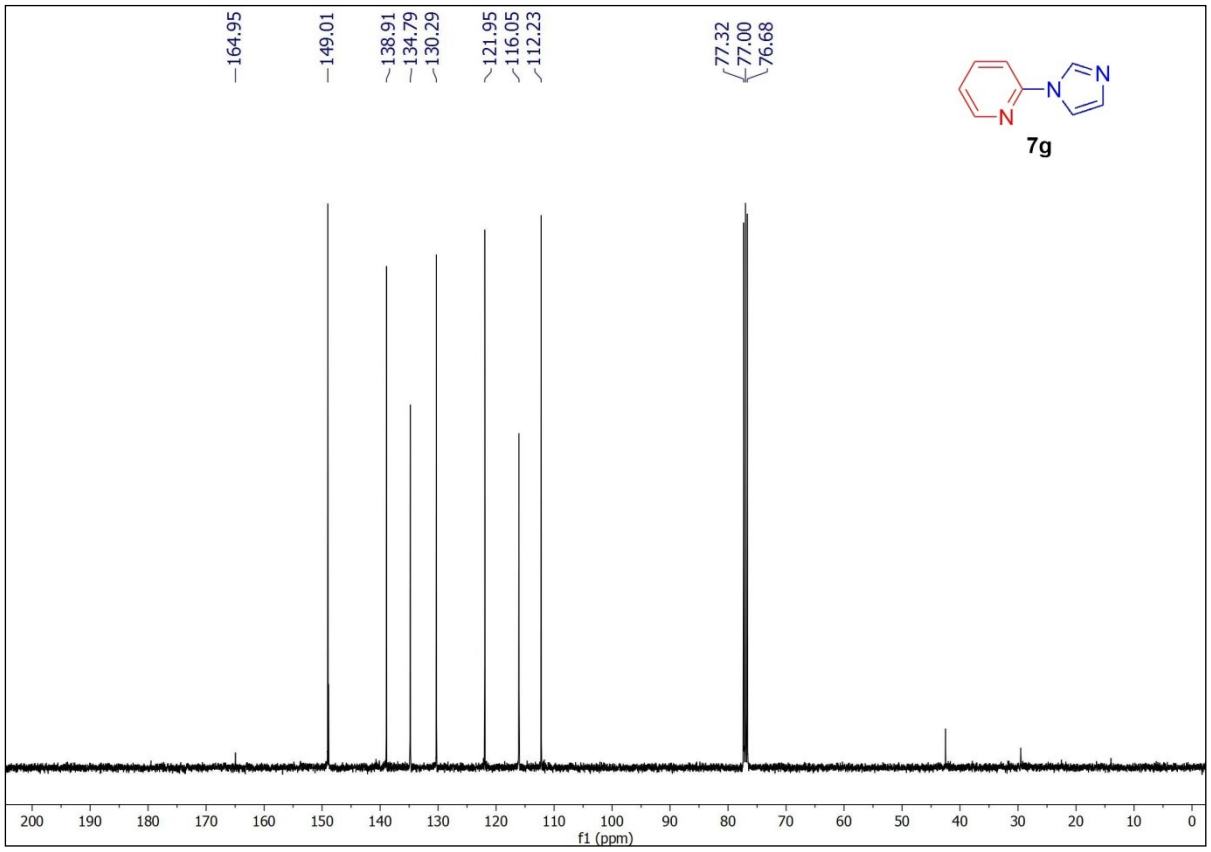

MeO
Me
N
N
7e
7.7799
7.2786
7.1813
7.1734
7.1613
7.1590
7.1517
7.1425
6.8906
6.8804
6.8699
6.8594
3.8742
3.8686
2.8419
2.6956
2.2695
0.0000
11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm
0.30
1.13
0.35
1.00
0.99

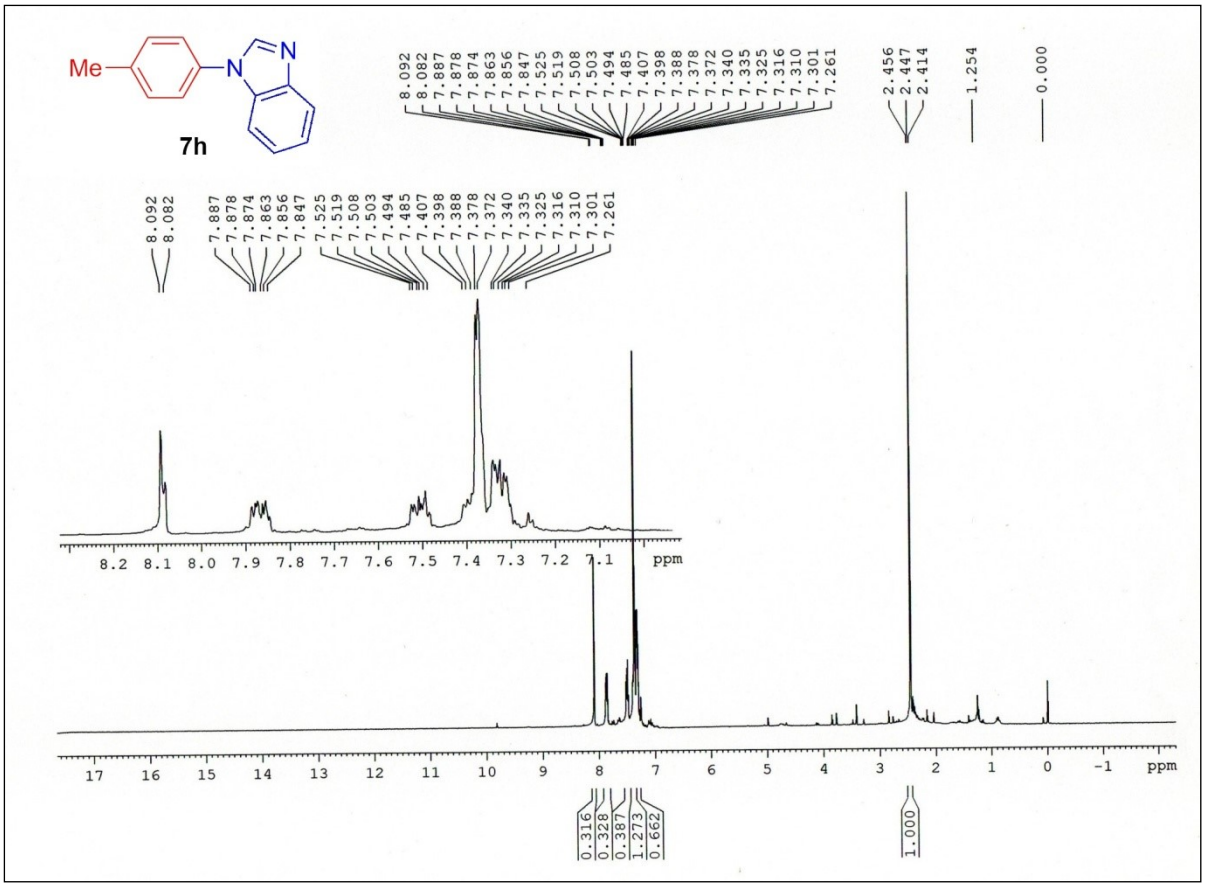

MeO
Me
N
N
7e
157.13
130.21
129.79
128.36
125.68
124.40
120.22
110.46
110.21
77.50
77.08
76.65
55.64
16.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7f
8.307
8.300
8.293
8.267
8.263
8.261
8.256
8.241
8.236
8.234
8.230
7.994
7.819
7.815
7.812
7.808
7.792
7.788
7.785
7.781
7.758
7.731
7.705
7.406
7.281
2.183
8.3073
8.3003
8.2933
8.2673
8.2630
8.2605
8.2557
8.2408
8.2363
8.2338
8.2296
7.9943
7.8192
7.8152
7.8123
7.8081
7.7924
7.7883
7.7854
7.7813
7.7577
7.7313
7.7046
7.4057
7.2812
ppm
0.949
0.958
1.000
1.985
2.015


7f
149.04
138.18
135.46
131.35
131.12
126.86
122.06
117.99
116.21
77.55
77.13
76.70
149.0430
138.1834
135.4638
131.3510
131.1190
126.8621
122.0625
117.9933
116.2060
ppm


8.43 8.43 8.43 8.42 8.42 8.32 7.80 7.79 7.78 7.78 7.77 7.77 7.76 7.75 7.60 7.60 7.60 7.33 7.30 7.21 7.21 7.20 7.19 7.19 7.19 7.18 7.17 7.15
7g
7.80 7.78 7.78 7.77 7.77 7.76 7.75 7.60 7.60 7.60 7.33 7.30 7.21 7.21 7.20 7.19 7.19 7.19 7.18 7.17 7.15
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1
0.99 1.00 1.09 1.01 1.06 1.06 1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.95 149.01 138.91 134.79 130.29 121.95 116.05 112.23 77.32 77.00 76.68
7g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
N
N
7h
8.092
8.082
7.887
7.878
7.874
7.863
7.856
7.847
7.525
7.519
7.508
7.503
7.494
7.485
7.407
7.398
7.388
7.378
7.372
7.340
7.335
7.325
7.316
7.310
7.301
7.261
2.456
2.447
2.414
1.254
0.000
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 ppm
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0.316
0.328
0.387
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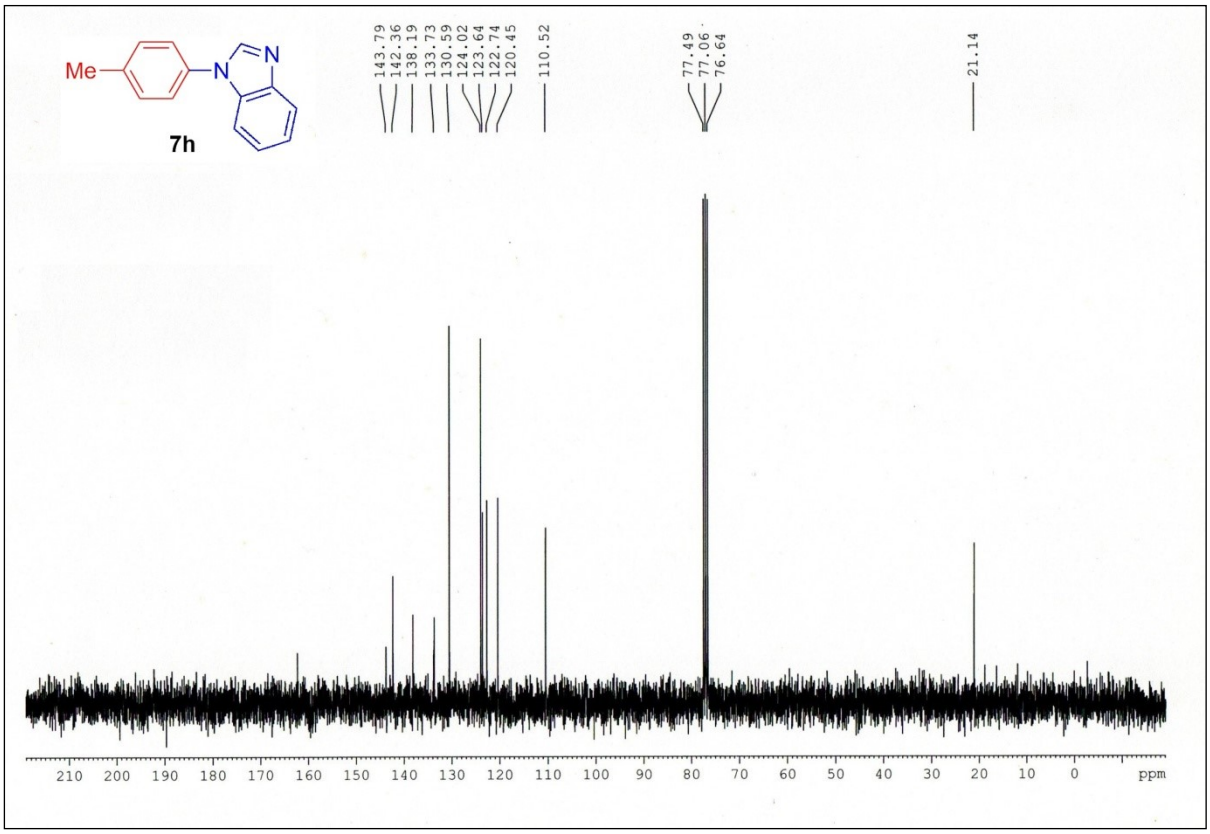
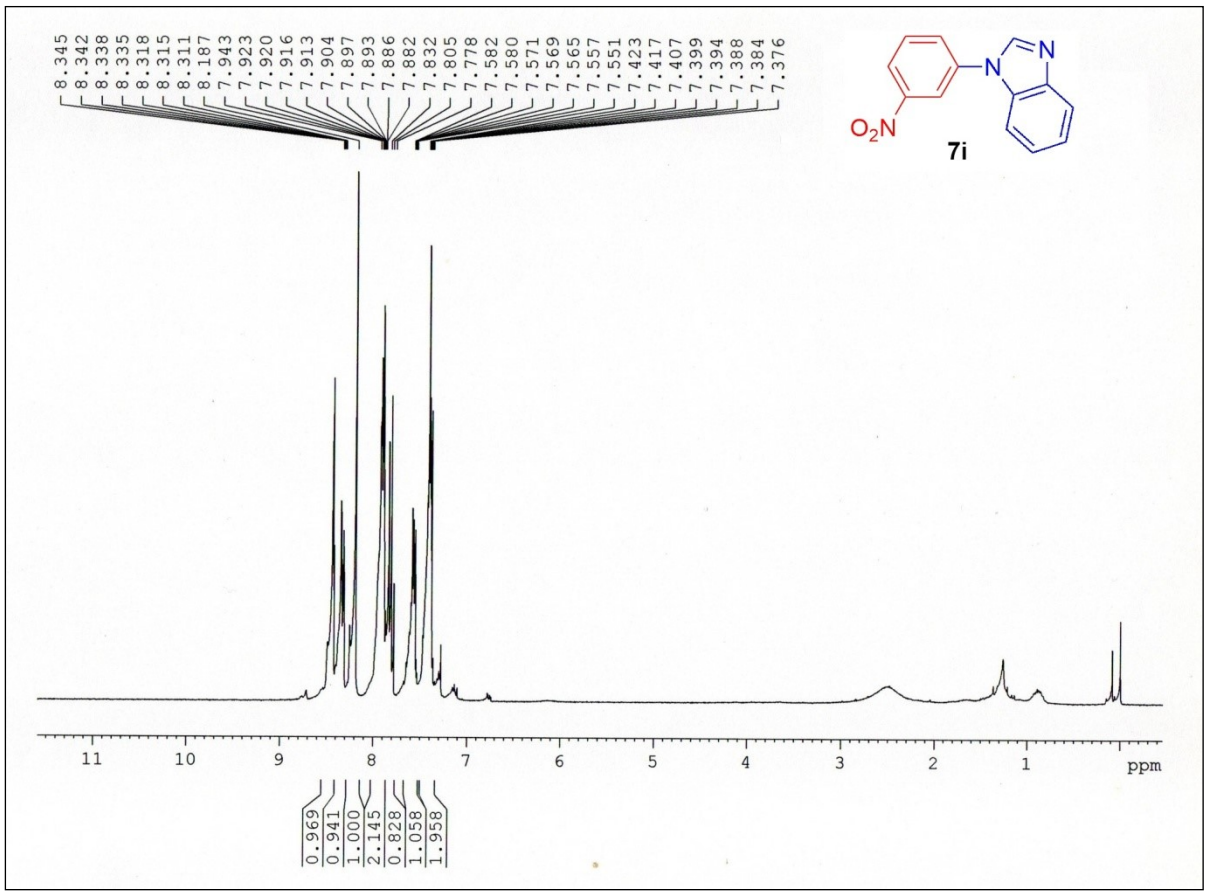
0.662
1.000


Me
N
N
7h
143.79
142.36
138.19
133.73
130.59
124.02
123.64
122.74
120.45
110.52
77.49
77.06
76.64
21.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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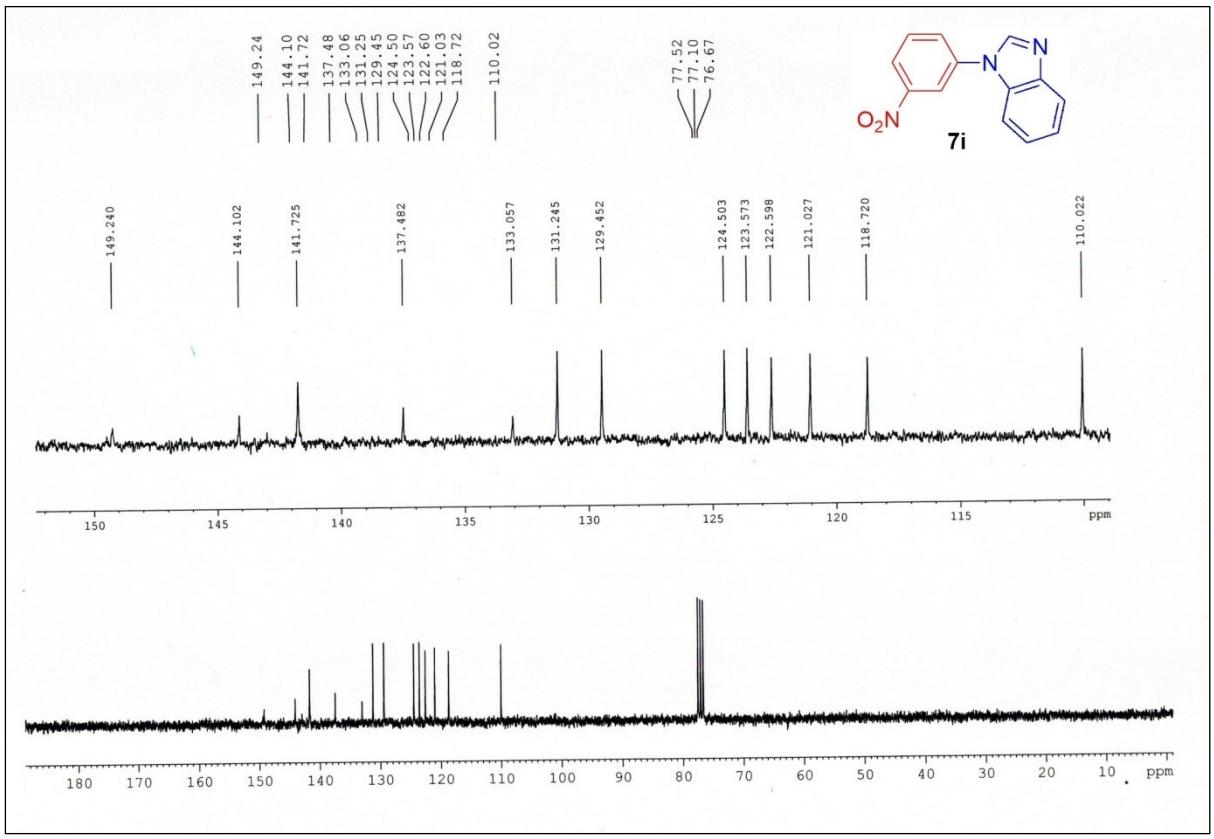
8.342
8.338
8.335
8.318
8.315
8.311
8.187
7.943
7.923
7.920
7.916
7.913
7.904
7.897
7.893
7.886
7.882
7.832
7.805
7.778
7.582
7.580
7.571
7.569
7.565
7.557
7.551
7.423
7.417
7.407
7.399
7.394
7.388
7.384
7.376
O2N
N
N
7i
11
10
9
8
7
6
5
4
3
2
1
ppm
0.969
0.941
1.000
2.145
0.828
1.058
1.958


149.24
144.10
141.72
137.48
133.06
131.25
129.45
124.50
123.57
122.60
121.03
118.72
110.02
77.52
77.10
76.67
O2N
N
N
7i
149.240
144.102
141.725
137.482
133.057
131.245
129.452
124.503
123.573
122.598
121.027
118.720
110.022
150
145
140
135
130
125
120
115
ppm
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm