Electronic Supplementary Information for:

Formal Base-Free Homolytic Aromatic Substitutions via Photoredox Catalysis

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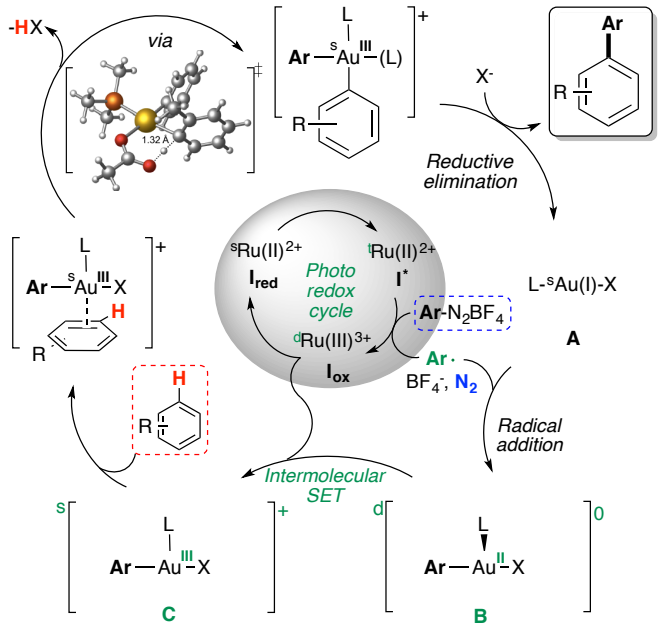
Contents

1. General Remarks

Unless those presented hereafter all reagents, $Ru(bpy)_3Cl_2.6H_2O$ and $Ru(bpy)_3(PF_6)_2$ were obtained from commercial sources and used as received. $Ru(bpy)_3(SbF_6)_2$ was synthesized through a suitable modification of a procedure reported in the iterature.[1] 2-(methoxycarbonyl)benzenediazonium tetrafluoroborate, 2-bromo-4-fluorobenzenediazonium tetrafluoroborate and 2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate were prepared according to reported procedures.[2] Acetonitrile was dried using microwave activated molecular sieves (3 Å), degassed by bubbling argon for at least 30 minutes and stored under an inert atmosphere. Arenes used for coupling were similarly degassed immediately prior to use. Reactions were carried out under argon using standard Schlenk technique. *Longer reaction times and less reproducible results were obtained performing reactions under air on in the presence of moisture.* Flash column chromatographies were performed on Merck Geduran SI 60 A silica gel (40−63 µm) and thin-layer chromatography on Merck 60F254 plates. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, $(CD_3)_2CO$ and CD_3CN on a Bruker 300 AVANCE spectrometer fitted with a QNP probehead using the solvent as internal standard (7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR for $CDCl_3$, 2.05 ppm for ^{1}H NMR and 29.84 ppm for ^{13}C NMR for $(CD_3)_2CO$ and 1.94 ppm for ^{1}H NMR and 118.26 ppm for ^{13}C NMR for CD_3CN). IR spectra were recorded with a Perkin Elmer Spectrum BX FT-IR system. Reported assignments are based on decoupling, COSY, NOESY, HSQC and HMBC correlation experiments. The terms m, s, d, t and q represent multiplet, singlet, doublet, triplet and quadruplet respectively, and the term br means a broad signal. Exact masses were recorded on Waters LCT Premier XE mass spectrometer equipped with an electrospray ionization source and a time of flight analyzer. CCDC 1015490 contains the supplementary crystallographic data for complex $Ru(bpy)_3(SbF_6)_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

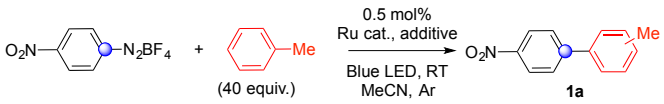
2. Additional Experimental Details

As mentioned in the manuscript, we begun present project on homolytic aromatic substitutions pivoting on our previous computational results that suggested the relative easiness of the addition of aryl radicals on suitable metal complexes to provide corresponding, stable, open-shell organometallic derivatives. Reasoning on the feasibility of Ru/Pd dual catalytic cascades, we wondered whether it would have been possible to develop an alternative access to biaryls via Ru/Au joint catalysis (Scheme 2). Reasoning on redox potentials, the photocatalyst ($\mathbf{I}^*$) should transfer an electron to a diazonium salt upon excitation and the resulting radical should then collapse into an aryl radical and a nitrogen molecule. The former might add on Au(I) complex **A** to form open shell intermediate **B** that could be oxidized to Au(III) complex **C** by Ru(III) complex $\mathbf{I_{ox}}$.[6c] Preliminary DFT modelling suggested the feasibility of an intramolecular base-assisted C-H activation by Au(III) and sequential Au(III)/Au(I) C-C forming reductive elimination.



Scheme S1. Originally envisaged strategy to biaryls.

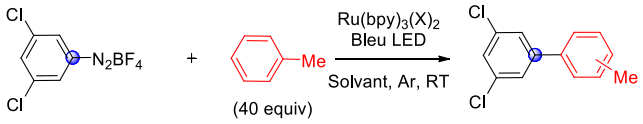
Table S1: Effects of air and/or moisture on conversion of diazonium reagent and yield of 1a



Entry	Catalyst, *mol %*	Time (h)	Remarks	Yield (%)
1	$Ru(bpy)_3(SbF_6)_2$, *0.5*	6	--	79
2	$Ru(bpy)_3(SbF_6)_2$, *0.5*	24	Under air	63
3	$Ru(bpy)_3(SbF_6)_2$, *0.5*	1	With 0.2 mL water	63

Reaction conditions: as Table 2, ArN_2BF_4 0.45 mmol. Conversion of substrate proved slower in the presence of air (entry 2, 24 vs 6 hours) and the yield of **1a** dropped to 63%. Addition of 0.2 mL of water via syringe allowed to observed reproducible results in these reactions, provided full conversion of the substrate in one hour but did not allow to achieve a yield comparable to our best result (entry 3, 63%). The regioselectivity did not change significantly among these different experiments, ranging from 4:1.3:1 (o:m:p, entry 1) to 3.8:1.4.1 (entry 3).

Table S2: Screening of different solvents

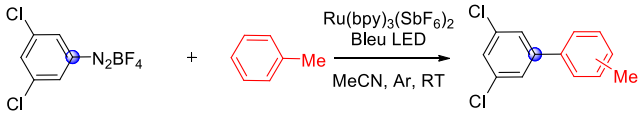


Entry	Catalyst, *mol %*	Solvent	Yield (%)	Time (h)
1	$Ru(bpy)_3(SbF_6)_2$, *0.5*	MeCN	84	4
2	$Ru(bpy)_3(SbF_6)_2$, *0.5*	DMF	50	1
3	$Ru(bpy)_3(SbF_6)_2$, *0.5*	DMSO	62	1
4	$Ru(bpy)_3Cl_2$, *0.5*	DMF	58	1
5	$Ru(bpy)_3Cl_2$, *0.5*	DMSO	64	1

Reaction conditions: as Table 2, ArN_2BF_4 0.45 mmol, 0.225 M.

We tested various polar solvents on a model reaction. Once again, conversion of the substrate proved faster, but selectivity towards desired product dropped. Both DMF and DMSO provided full conversion of diazonium reagent in one hour, with both Ru photocatalysts. The yield of biaryl roducts ranged from 50 to 64%, remaining significantly lower than that isolated when reactions are performed using MeCN. Furthermore, removal of the latter during work-up is much more practical. Less polar solvents do not favor solubilization of the reagent and were thus ignored to avoid incomparable results. in more polar Despite of shorter reaction time with DMF or DMSO, MeCN is the best solvent for this reaction

Table S3: Molar excess of the arene acceptor

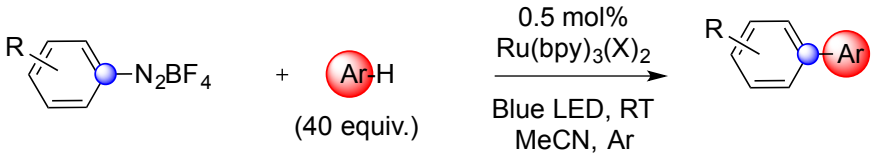


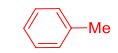
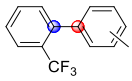
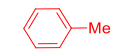
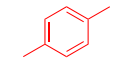
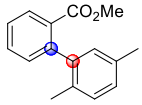
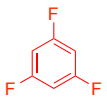
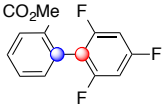
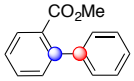
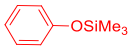
Entry	Catalyst, *mol %*	equiv. Toluene	yield (%)	Time (h)
1	$Ru(bpy)_3(SbF_6)_2$, *0.5*	40	84	4
2	$Ru(bpy)_3(SbF_6)_2$, *0.5*	20	70	23
3	$Ru(bpy)_3(SbF_6)_2$, *0.5*	10	59	48

Reaction conditions: as Table 2, ArN_2BF_4 0.45 mmol.

Reduction of the molar excess of the arene acceptor provided both lower yields of biaryl and slower conversion of the starting material. Reaction with 20 equiv. of toluene delivered 70% of product and full conversion was attained after 23 hours. Further reduction of the arene acceptor to 10 equiv. resulted in full conversion after two days and provided 59% of biaryl product.

Table S4: Limitations of the scope



Entry	Ar-H	Time (h)	product	yield (%)	regio selectivity
1		18		10	n. d.
2		23		30	3:1.7:1
3		15		10	--
4		20		18	--
5		24		22	--
6		1	--	0	--

Reaction conditions: as Table 2, ArN_2BF_4 0.45 mmol.

Low yields were observed performing reactions with *ortho*-substituted diazonium salts. Their steric hindrance most likely favors the direct reduction of the initially generated aryl radical rather than addition of the latter on an arene molecule. The reaction of a reagent with an ortho trifluoromethyl group showed full conversion in 18 hours but just 10% of desired product as a mixture of its regioisomers. Because of purification issues, we were unable to fully characterize these biaryls. Low yields were similarly obtained employing other ortho-substituted reagents, bearing both electron donating (entry 2, 30%, 23 hours for full conversion) and withdrawing substituents (entries 3-5, 10-22%). The presence of acid sensitive groups as trimethylsilyl ethers is similarly not tolerated. Full conversion was observed in one hour but no traces of either desired product or its deprotected peer were detected (entry 6).

3. Experimental procedures

Synthesis of complex $Ru(bpy)_3(SbF_6)_2$

The complex was synthesized from $RuCl_3.H_2O$ (137 mg, 0.66 mmol) according the procedure reported in the literature for $Ru(bpy)_3(PF_6)_2$,[1] replacing KPF_6 with $KSbF_6$ (363 mg, 1.32 mmol). Upon simple filtration, the complex was retrieved as a red solid in 32% yield (0.21 mmol, 220 mg). Crystals suitable for X-ray diffraction were obtained by slow evaporation from a MeOH/acetone mixture (see section 5 for details).

Synthesis of diazonium salts

2-(methoxycarbonyl)benzenediazonium tetrafluoroborate, **2-bromo-4-fluorobenzenediazonium tetrafluoroborate** and **2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate**

To a round-bottom flask were added the desired aniline (1 equiv.), 50% aqueous fluoroboric acid (3 equiv.) and EtOH. The mixture was cooled to 0°C (-30°C for 2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate) and isoamyl nitrite (1.25 equiv.) was then added dropwise. Cooling was removed and the reaction mixture was then stirred for one hour in order to come back to room temperature. Addition of diethylether allowed the precipitation of products that could be then recovered by simple filtration. Their spectroscopic data corresponded to those described in the literature.[2]

Photocatalytic synthesis of biaryls 1a-2k

To a Schlenk-type flask was added under argon $Ru(bpy)_3(SbF_6)_2$ (2.3 mg, 0.00225 mmol, 0.005 equiv.). At least three vacuum/argon cycles were made before adding under argon the diazonium salt (0.45 mmol, 1 equiv.). MeCN (2 mL) and the desired arene (18 mmol, 40 equiv.) were then added via syringes in the dark. The resulting mixture was then irradiated by a blue LED and kept under stirring at room temperature until complete conversion of the diazonium salt. The solvent was removed under reduced pressure and the crude mixture was analyzed by ^1H NMR spectroscopy. Products were isolated by flash column chromatography on silica gel with a mixture of petroleum ether (PE) and methyl terbutyl ether (MTBE) as eluents.

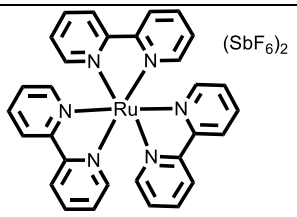
Aryl radical quench by TEMPO

Synthesis of **2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine**[3]

To a schlenk-type flask was added under argon $Ru(bpy)_3(SbF_6)_2$ (2.4 mg, 0.0023 mmol, 0.005 equiv.), 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol, 1 equiv.) and TEMPO (140 mg, 0.9 mmol, 2 equiv.). Three vacuum/argon cycles were made before adding MeCN (0.5 mL) and toluene (0.5 mL, 4.5 mmol, 10 equiv.) via syringe in dark before switching on the blue LED. The mixture was then stirred with a magnetic bar at room temperature until complete conversion of the diazonium salt (two hours). The solvent was removed under reduced pressure and the crude mixture was analyzed by ^1H NMR spectroscopy. 2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine (50 mg, 0.18 mmol, 40%) was isolated by flash column chromatography. Spectroscopic data corresponded to those described in the literature.[3]

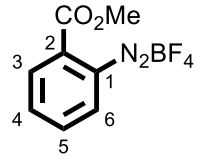
4. Spectroscopic data

▶ **$Ru(bpy)_3(SbF_6)_2$**

 $(SbF_6)_2$ $C_{30}H_{24}F_{12}N_6RuSb_2$ MW 1041,12 g/mol	Purification : filtration Red solid Yield: 32% (220 mg) **^{1}H NMR** (300 MHz, CD_3CN) δ 8.49 (d, *J* = 8.1 Hz, 6H), 8.05 (td, *J* = 7.9 Hz, 1.5 Hz, 6H), 7.72 (d, *J* = 5.6 Hz, 6H), 7.39 (ddd, *J* = 7.5 Hz, 5.6 Hz, 1.3 Hz, 6H); **^{13}C NMR** (75 MHz, CD_3CN) δ 152.6, 138.7, 128.5, 125.2; **IR (cm^{-1})** 2924, 1605, 1464, 1447 1162, 759, 730, 651, 511, 501; **HRMS** calculated for $C_{30}H_{24}F_6N_6RuSb^+$: 805.0048, found: 805.0048.

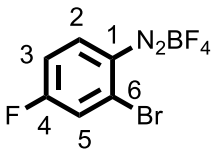
▶ **2-(methoxycarbonyl)benzenediazonium tetrafluoroborate**

According to the general procedure described above, 2-(methoxycarbonyl)benzenediazonium tetrafluoroborate has been synthesized from methyl 2-aminobenzoate (1.4 mL, 10.6 mmol), 50% aqueous fluoroboric acid (2 mL, 31.8 mmol, 3 equiv.) and isoamyl nitrite (1.8 mL, 13.25 mmol, 1.25 equiv.) in EtOH (3 mL). Reaction time: 1h. Spectroscopic data correspond to the literature.[4]

 $C_8H_7BF_4N_2O_2$ MW 249,96 g/mol	Purification : filtration (Et_2O) White solid Yield: 99% (2.64 g) **^{1}H NMR** (300 MHz, $(CD_3)_2CO$) δ 9.02 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.53 (dtd, *J* = 9.0, 7.9, 1.3 Hz, 2H), 8.32 (ddd, *J* = 8.3, 7.5, 1.6 Hz, 1H), 4.12 (s, 3H); **^{13}C NMR** (75 MHz, $(CD_3)_2CO$) δ 162.5 (C(O)), 142.3 (C4), 136.8 (C6), 136.2 (C5), 133.8 (C3), 132.1 (C2), 116.2 (C1), 54.7 (COO*Me*); **^{19}F NMR** (120 MHz, $(CD_3)_2CO$) δ 26.35, 26.30 (BF_4); **IR (cm^{-1})** 3111, 2280, 1725, 1298, 1020, 764.

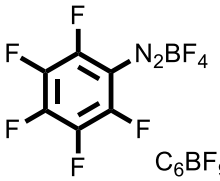
▶ **2-bromo-4-fluorobenzenediazonium tetrafluoroborate**

According to the general procedure described above, 2-bromo-4-fluorobenzenediazonium tetrafluoroborate has been synthesized from 2-bromo-4-fluoroaniline (1 g, 5.3 mmol), 50% aqueous fluoroboric acid (2 mL, 16.1 mmol, 3 equiv.) and isoamyl nitrite (0.773 g, 6.6 mmol, 1.25 equiv.) in EtOH (3 mL). Reaction time: 1h.

 $C_6H_3BBrF_5N_2$ MW 288,81 g/mol	Purification : filtration (Et_2O) White solid Yield: 94% (1.43 g) **^{1}H NMR** (300 MHz, $(CD_3)_2CO$) δ 9.05 (dd, *J* = 9.4 , 4.7 Hz, 1H, H5), 8.29 (dd, *J* = 8.0 , 2.5 Hz, 1H, H2), 7.92 (ddd, *J* = 9.4 Hz, 7.8 Hz, 2.5 Hz, 1H, H3); **^{13}C NMR** (75 MHz, $(CD_3)_2CO$) δ 169.0 (d, *J* = 273.7 Hz, C4), 138.9 (d, *J* = 13.5 Hz, C5), 127.9 (d, *J* = 12.9 Hz, C6), 124.0 (d, *J* = 29.2 Hz, C2), 119.0 (d, *J* = 25.2, C3), 114.14 (s, C1); **^{19}F NMR** (120 MHz, $(CD_3)_2CO$) δ 93.27 (q, *J* = 5.4 Hz F4), 26.63, 26.57 (BF_4); **IR (cm^{-1})** 2918, 2285, 1477, 1260, 1048, 801.

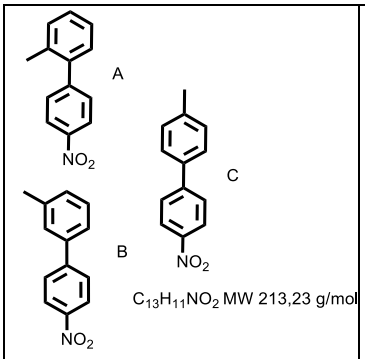
▶2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate

According to the general procedure described above, 2-bromo-4-fluorobenzenediazonium tetrafluoroborate has been synthesized from 2-bromo-4-fluoroaniline (1 g, 5.3 mmol), 50% aqueous fluoroboric acid (2 mL, 16.1 mmol, 3 equiv.) and isoamyl nitrite (0.773 g, 6.6 mmol, 1.25 equiv.) in EtOH (3 mL). Reaction time: 1h. Spectroscopic data correspond to the literature.[5]

 $C_6BF_9N_2$ MW 281,87 g/mol	Purification : filtration (Et_2O) White solid Yield: 43% (642 mg) **^{13}C NMR** (75 MHz, $(CD_3)_2CO$) δ 154.6-152.7 (dm), 149.5-147.5 (dm), 140.2-138.3 (dm) **^{19}F NMR** (120 MHz, CD_3CN) δ -119.9 (m, 1F), -123.7 (m, 2F), -152.1 (s, 4F), -152.8 (m, 2F); **IR (cm^{-1})** 2158, 2128, 1603, 1309, 988.

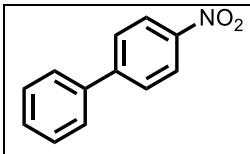
▶ **4-nitro-1,1'-biphenyl / 3-methyl-4'-nitro-1,1'-biphenyl / 4-methyl-4'-nitro-1,1'-biphenyl (1a)**

According to the general procedure described above, **1a** has been synthesized from 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol) and toluene (2 mL, 18 mmol, 40 equiv.). Reaction time: 3h. Spectroscopic data of regioisomers A, B and C correspond to the literature.[6] Ratio of regioisomeres were determinated by ^{1}H RMN.

 $C_{13}H_{11}NO_2$ MW 213,23 g/mol	Purification : (PE/ MTBE 95:5) White solid Yield: 81% (82 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.30-8.29 (m, 2H + 2H +2H, ABC), 7.76-7.73 (m, 2H + 2H, BC), 7.59-7.55 (m, 2H + 2H, AC), 7.52-7.51 (m, 2H + 2H, AC), 7.47-7.41 (m, 3H, B), 7.36-7.24 (m, 4H + 1H + 2H, ABC), 2.48 (s, 3H, B), 2.45 (s, 3H, C), 2.31 (s, 3H, A); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 148.7 (A), 147.7 (B), 147.4 (C), 146.8 (BC), 146.7 (A), 139.5 (A), 138.9 (C), 138.7 (B), 138.5 (B), 135.6 (C), 134.9 (A), 130.6 (A), 129.9 (A), 129. 8 (C), 129.5 (B), 129.3 (A), 128.9 (B), 128.3 (A), 127.9 (B), 127.6 (B), 127.3 (C), 127.0 (C), 126.0 (A), 124.4 (B), 123.9 (C), 123.3 (A), 21.4 (B), 21.1 (C), 20.2 (A); **IR (cm^{-1})** 2920, 1596, 1514, 1344, 1258, 1100, 1007, 854, 789, 748, 699; **HRMS** calculated for $C_{13}H_{11}NO_2^+$ 213.0790, found 213.0786.

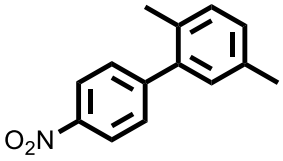
▶ **4-Nitro-biphenyl (1b)**

According to the general procedure described above, **1b** has been synthesized from 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol) and benzene (1.7 mL, 18 mmol, 40 equiv.). Reaction time: 8h.
Spectroscopic data correspond to the literature.[7]

 $C_{12}H_9NO_2$ MW 199,20 g/mol	Purification : (PE) White solid Yield: 79% (71 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.58–7.40 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.7, 147.1, 138.8, 129.2, 129.0, 127.9, 127.5, 124.2; **IR (cm^{-1})** 1594, 1575, 1506, 1478, 1449, 1338, 1103; **HRMS** calculated for $C_{12}H_9NO_2^+$ 199.0633, found 199.0625.

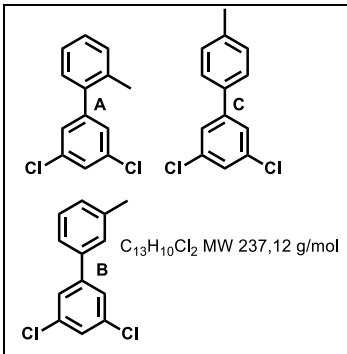
▶ 2,5-dimethyl-4'-nitro-1,1'-biphenyl (1c)

According to the general procedure described above, **1c** has been synthesized from 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol)and *p*-xylene (2 mL, 18 mmol, 40 equiv.). Reaction time: 7h.
Spectroscopic data correspond to the literature.[8]

 $C_{14}H_{13}NO_2$ MW= 227,26 g/mol	Purification : PE White solid Yield: 69% (70 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.32–8.24 (m, 2H), 7.55–7.46 (m, 2H), 7.23-7.14 (m, 2H), 7.06 (s, 1H), 2.39 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 148.9, 146.7, 139.4, 135.6, 131.8, 130.6, 130.0, 129.1, 123.3, 20.8, 19.8; **IR (cm^{-1})** 1595, 1510, 1350, 850; **HRMS** calculated for $C_{14}H_{13}NO_2^+$ 227.0946, found 227.0936.

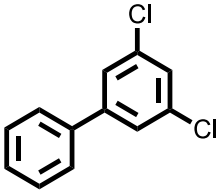
▶ 3',5'-dichloro-2-methyl-1,1'-biphenyl / 3,5-dichloro-3'-methyl-1,1'-biphenyl / 3,5-dichloro-4'-methyl-1,1'-biphenyl (1d)

According to the general procedure described above, **1d** has been synthesized from 3,5-dichlorobenzenediazonium tetrafluoroborate (117.3 mg, 0.45 mmol) and toluene (2 mL, 18 mmol, 40 equiv.). Reaction time: 4h.
Spectroscopic data of regioisomer C correspond to the literature.[9,10] Ratio of regioisomeres were determinated by ^{1}H RMN.

 $C_{13}H_{10}Cl_2$ MW 237,12 g/mol	Purification : (PE) White solid Yield: 84% (85 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 – 7.17 (m, 7H, H Ar, ABC), 2.44 (s, CH_3, B), 2.42 (s, CH_3, C), 2.28 (s, CH_3, A) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.8 (A), 144.3 (B), 144.1 (C), 139.2 (A), 138.7 (B), 138.5 (C), 138.4(B), 135.6 (C), 135.1 (A+C), 134.5 (A), 130.5 (A), 129.7 (C), 129.4 (A), 129.1 (B), 128.8 (B), 128.3 (B), 128.1 (A), 127.7 (B), 127.6 (A), 126.98 (B), 126.9 (A), 126.8 (C), 126.7 (C), 125.9 (A), 125.6 (B), 125.3 (C), 124.1 (B), 21.4 (B), 21.1 (C), 20.2 (A) **IR** (cm^{-1}) 3074, 3024, 2956, 2923, 1586, 1556, 1428, 1408, 1381, 1123, 1096, 856, 750, 690 **HRMS** calculated for $C_{13}H_{10}Cl_2^+$ 236.0160, found 236.0148

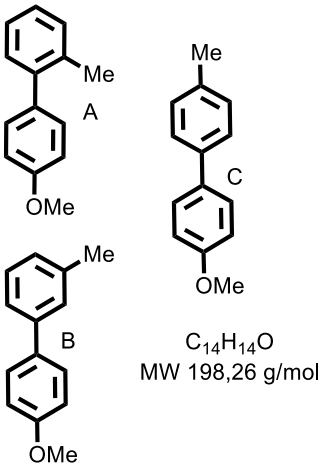
▶3,5-dichloro-1,1'-biphenyl (1e)

According to the general procedure described above, **1e** has been synthesized from 3,5-dichlorobenzenediazonium tetrafluoroborate (117.3 mg, 0.45 mmol) and benzene (1.7 mL, 18 mmol, 40 equiv.). Reaction time: 24h.
Spectroscopic data correspond to the literature.[10]

 $C_{12}H_8Cl_2$ MW 223,10 g/mol	Purification : PE/MTBE 9:1 White solid Yield: 91% (91 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55-7.41 (m, 7H), 7.35 (t, 1H, *J* = 1.9 Hz); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.1, 138.4, 135.2, 128.9, 128.4, 127.0, 126.9, 125.6; **IR (cm^{-1})** 3066, 1739, 1585, 1557 1430, 1407, 1280, 1123, 1097, 856, 801, 710, 695; **HRMS** calculated for $C_{12}H_8Cl_2^+$: 222.0003, found 221.9994.

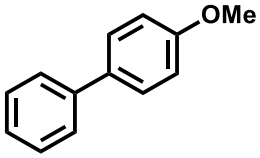
▶4'-methoxy-2-methyl-1,1'-biphenyl/4'-methoxy-3-methyl-1,1'-biphenyl/4-methoxy-4'-methyl-1,1'-biphenyl (1f)

According to the general procedure described above, **1f** has been synthesized from 4-methoxybenzenediazonium tetrafluoroborate (100 mg, 0.45 mmol) and toluene (2 mL, 18 mmol, 40 equiv.). Reaction time: 48h.
Spectroscopic data of regioisomers A, B and C correspond to the literature.[11] Ratio of regioisomeres were determinated by ^{1}H RMN.

 $C_{14}H_{14}O$ MW 198,26 g/mol	Purification : PE/MTBE 9:1 White solid Yield: 32% (29 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, 2H, *J* = 8.8 Hz, B), 7.53 (d, 2H, *J* = 8.8 Hz, C), 7.47 (d, 2H, *J* = 8.2 Hz, C), 7.39-7.33 (m, 3H, B), 7.29-7.24 (m, 2H + 2H, AC), 7.14 (d, 1H, *J* = 7.5 Hz, B), 7.00-6.96 (m, 2H + 2H + 2H, ABC), 3.87 (s, 3H + 3H + 3H , ABC), 2.43 (s, 3H, B), 2.40 (s, 3H, C), 2.30 (s, 3H, A); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.4 (A), 141.5 (A), 135.4 (A), 134.3 (A), 130.3 (A), 130.2 (A), 129.9 (A), 126.9 (A), 125.7 (A), 113.4 (A), 55.2 (A), 20.5 (A); **IR (cm^{-1})** 3020, 2954, 2835, 2058, 1612, 1515, 1483, 1210, 1177, 1038, 833, 761; **HRMS** calculated for $C_{14}H_{14}O^+$: 198.1045, found 198.1034.

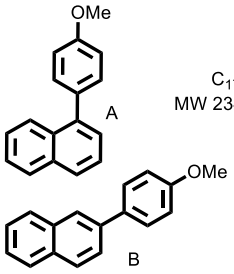
▶ **4-methoxy-1,1'-biphenyl (1g)**

According to the general procedure C described above, **1g** has been synthesized 4-methoxybenzenediazonium tetrafluoroborate (100 mg, 0.45 mmol) and benzene (1.7 mL, 18 mmol, 40 equiv.). Reaction time: 96h.
Spectroscopic data correspond to the literature.[11]

 $C_{13}H_{12}O$ MW 184,23	Purification : PE White solid Yield: 37% (29 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58–7.54 (m, 4H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.3, 141.0, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5; **IR (cm^{-1})** 2920, 2852, 1611, 1454, 1258, 833, 760, 685; **HRMS** calculated for $C_{13}H_{12}O^{+}$ 184.0888, found 184.0875.

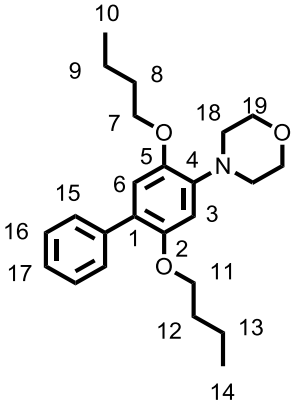
▶ **1-(4-methoxyphenyl)naphthalene / 2-(4-methoxyphenyl)naphthalene (1h)**

According to the general procedure described above, **1h** has been synthesized from 4-methoxybenzenediazonium tetrafluoroborate (100 mg, 0.45 mmol) and naphtalene (2.4 g, 18 mmol, 40 equiv.). Reaction time: 24h.
Spectroscopic data of regioisomers A and B correspond to the literature.[12, 13] Ratio of regioisomeres were determinated by ^{1}H RMN.

 $C_{17}H_{14}O$ MW 234,29 g/mol	Purification : PE/ MTBE 9:1 White solid Yield: 86% (91 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08-7.91 (m, 3H + 3H, AB), 7.82-7.73 (m, 3H, B), 7.61-7.48 (m, 6H + 2H, AB), 7.14-7.08 (m, 2H + 2H, AB), 3.95 (s, 3H, A), 3.92 (s, 3H, B); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.1 (B), 158.8 (A), 139.8 (A), 138.0 (B), 133.8 (A), 133.7 (B), 133.5 (B), 133.0 (A), 132.2 (B), 131.7 (A), 131.0 (A), 128.3 (B), 128.29 (B), 128.20 (A), 127.9 (B), 127.5 (B), 127.2 (A), 126.8 (A), 126.1 (B), 126.0 (A), 125.8 (A), 125.6 (A), 125.5 (B), 125.3 (AB), 124.9 (B), 114.2 (B), 113.6 (A), 55.2 (AB); **IR (cm^{-1})** 2834, 1608, 1503, 1241, 1175, 1033, 799, 775; **HRMS** calculated for $C_{17}H_{14}O^{+}$: 234.1045, found 234.1036.

▶ 4-(2,5-dibutoxy-[1,1'-biphenyl]-4-yl)morpholine (1i)

According to the general procedure described above, **1i** has been synthesized from 2,5-dibutoxy-4-morpholinobenzenediazonium tetrafluoroborate (190 mg, 0.45 mmol) and benzene (1.7 mL, 18 mmol, 40 equiv.). Reaction time: 48h.

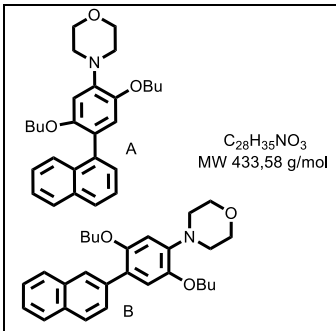


$C_{24}H_{33}NO_3$
MW: 383,52 g/mol

Purification : PE/ MTBE 9:1
Brown solid
Yield: 35% (60 mg)
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.54 (m, 2H, H16), 7.42-7.37 (m, 2H, H15), 7.32-7.27 (m, 1H, H17), 6.89 (s, 1H, H6), 6.61 (s, 1H, H3), 4.01 (t, 2H, *J* = 6.4 Hz, CH_2(C7)), 3.96-3.86 (m, 4H, CH_2(C19)), 3,88 (t, 2H, *J* = 6.3 Hz, CH_2(C11)), 3.18-3.15 (m, 4H, CH_2(C18)), 1.86-1.76 (m, 2H, CH_2(C8)), 1.71-1.61 (m, 2H, CH_2(C12)), 1.57-1.45 (m, 2H, CH_2(C9)), 1.45-1.34 (m, 2H, CH_2(C13)), 1.00 (t, 3H, *J* = 7.4 Hz, CH_3(C10)), 0.91 (t, 3H, *J* = 7.4 Hz, CH_3(C14));
^{13}C NMR (75 MHz, $CDCl_3$) δ 150.3 (C2), 146.0 (C5), 141.2 (C4), 138.5 (C1a), 129.3 (C16), 127.8 (C15), 126.3 (C17), 124.8 (C1), 115.7 (C6), 105.3 (C3), 69.6 (C11), 68.5 (C7), 67.1 (C19), 51.0(C18), 31.5 (C8), 31.4 (C12), 19.3 (CH_2(C9)), 19.2 (CH_2(C13)), 13.8 (CH_3(C10)), 13.7 (CH_3(C14))
IR (cm^{-1}) 2957, 2933, 2871, 1608, 1514, 1489, 1207, 1118, 1158, 902;
HRMS calculated for $C_{24}H_{34}NO_3^+$: 384.2533, found 384.2580.

▶ 4-(2,5-dibutoxy-4-(naphthalen-1-yl)phenyl)morpholine / 4-(2,5-dibutoxy-4-(naphthalen-2-yl)phenyl)morpholine (1j)

According to the general procedure described above, **1j** has been synthesized from 2,5-dibutoxy-4-morpholinobenzenediazonium tetrafluoroborate (190 mg, 0.45 mmol) and naphtalene (2.4 g, 18 mmol, 40 equiv.). Reaction time: 24h. Ratio of regioisomeres were determinated by ^{1}H RMN.

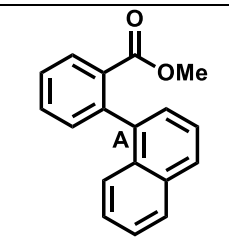
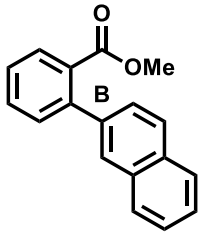


$C_{28}H_{35}NO_3$
MW 433,58 g/mol

Purification : PE/ MTBE 9:1
Brown oil
Yield: 50% (98 mg)
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H, B), 7.90-7.84 (m, 2H + 3H, AB), 7.78 (d, 1H, *J* = 1.6 Hz, B), 7.73 (d, 1H, *J* = 8.2 Hz, A), 7.55-7.39 (m, 4H + 2H, AB), 7.04 (s, 1H, B), 6.87 (s, 1H, A), 6.71 (s, 1H, A), 6.68 (s, 1H, B), 4.07 (t, 2H, *J* = 6.5 Hz, B), 3.99-3.89 (m, 4H + 4H, AB), 3.78 (t, 2H, *J* = 6.4 Hz, A), 3.31-3.18 (m, 4H + 4H, AB), 1.87-0.88 (m, 11H + 14H, AB), 0.67 (t, 3H, *J* = 7.4 Hz, A);
^{13}C NMR (75 MHz, $CDCl_3$) δ 150.9 (A), 150.6 (B), 146.1 (B), 145.7 (A), 141.4 (B), 141.3 (A), 136.9 (A), 136.1 (B), 133.4 (A), 133.3 (B), 132.2 (A), 132.1 (B), 128.05 (B), 127.8 (A), 127.6 (B), 127.4 (B), 127.3 (A), 127.2 (A), 126.9 (B), 126.6 (A), 125.7 (B), 125.4 (B), 125.39 (A), 125.36 (A), 125.1 (A), 123.9 (B), 116.6 (A), 115.9 (B), 105.5 (A), 105.3 (B), 69.7 (A), 69.5 (B), 68.5 (B), 68.3 (A), 67.2 (A), 67.1(B), 51.0 (A), 31.5 (A), 31.2 (A), 19.3 (A), 19.2 (B), 18.7 (A), 13.8 (A), 13.7 (B), 13.4 (A);
IR (cm^{-1}) 2956, 2933, 2870, 1511, 1504, 1201, 1118, 778;
HRMS calculated for $C_{28}H_{36}NO_3^+$: 434.2690, found 434.2706.

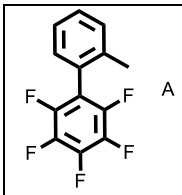
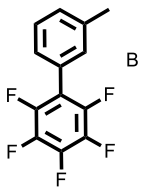
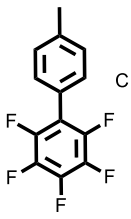
▶ **Methyl 2-(naphthalen-1-yl)-benzoate / Methyl 2-(naphthalen-2-yl)-benzoate (1k)**

According to the general procedure described above, **1k** has been synthesized from 2-(methoxycarbonyl)benzenediazonium tetrafluoroborate (112.4 mg, 0.45 mmol) and naphtalene (2.4 g, 18 mmol, 40 equiv.). Reaction time: 36h.
Spectroscopic data of regioisomers A and B correspond to the literature.[14,15] Ratio of regioisomeres were determinated by ^{1}H RMN.

 $C_{18}H_{14}O_2$ MW 262,30 g/mol 	Purification : PE White solid Yield: 54% (64 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.7, 1.0 Hz, 1H, A), 7.95 – 7.85 (m, 2H + 5H, AB), 7.63 (td, *J* = 7.5, 1.5 Hz, 1H, A), 7.58-7.35 (m, 7H + 6H, AB), 3.64 (s, 3H, B), 3.41 (s, 3H, A); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 169.0 (B), 167.8 (A), 142.4 (B), 141.3 (A), 139.5 (A), 138.9 (B), 133.20 (B), 133.15 (A), 132.4 (B), 131.9 (B), 131.9 (A), 131.8 (A), 131.5 (A), 131.3 (A), 131.0 (B), 130.8 (B), 130.0 (A), 129.9 (B), 128.1 (A), 128.0 (B), 127.8 (B), 127.6 (B), 127.5 (A), 127.3 (A), 127.2 (B), 126.9 (B), 126.7 (B), 126.1 (B), 125.9 (A), 125.8 (A), 125.7 (B), 125.5 (A), 125.4 (A), 125.0 (A), 51.9 (B), 51.7 (A); **IR (cm^{-1})** 3058, 2948, 1726, 1716, 1285, 1245, 1120, 1080; **HRMS** calculated for $C_{18}H_{15}O_2^+$: 262.0994, found 262.1056.

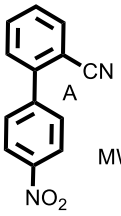
▶ **2,3,4,5,6-pentafluoro-2'-methyl-1,1'-biphenyl/ 2,3,4,5,6-pentafluoro-3'-methyl-1,1'-biphenyl/ 2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl (1l)**

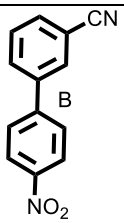
According to the general procedure described above, **1l** has been synthesized from 2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate (126.8 mg, 0.45 mmol) and toluene (2.0 mL, 18 mmol, 40 equiv.). Reaction time: 12h.
Spectroscopic data of regioisomers A, B and C correspond to the literature.[16] Ratio of regioisomeres were determinated by ^{19}F RMN.

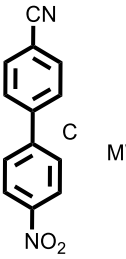
   $C_{13}H_7F_5$ MW 258,19 g/mol	Purification : PE/ MTBE 9:1 White solid Yield: 71% (82 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.42-7.19 (m, 12H), 2.44 (s, 6H), 2.21 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.8-145.6 (m, ABC), 142.6-141.7 (m, AB), 139.4 (C), 138.5 (B), 137.3-135.9 (m, ABC), 130.7 (B), 130.6 (A), 130.5 (A), 130.0 (B), 129.9 (C), 129.6 (A), 129.4 (C), 128.6 (B), 127.2 (B), 126.3 (B), 125.9 (A), 125.8 (A), 123.4 (C), 115.9-115.7 (m, ABC), 21.36 (B), 21.30 (C), 19.6 (A); **^{19}F NMR** (120 MHz, $CDCl_3$) δ -140.62 (dd, *J* = 22.9, 8.1 Hz, 2F, A), -143.16 (dd, *J* = 22.8, 8.0 Hz, 2F, B), -143.44 (dd, *J* = 22.8, 8.0 Hz, 2F, C), -155.55 (t, *J* = 20.8 Hz, 1F, A), -156.05 (t, *J* = 20.8 Hz, 1F, B), -156.31 (t, *J* = 20.8 Hz, 1F, C), -162.30-162.70 (m, 6F, ABC); **IR** (cm^{-1}) 2928, 1652, 1607, 1510, 1522, 1489, 1063, 984; **HRMS** calculated for $C_{13}H_7F_5^+$: 258.0468, found 258.0469.

▶4'-nitro-[1,1'-biphenyl]-2-carbonitrile/4'-nitro-[1,1'-biphenyl]-3-carbonitrile/4'-nitro-[1,1'-biphenyl]-4-carbonitrile (2a)

According to the general procedure described above, **2a** has been synthesized from 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol) and benzonitrile (1.9 mL, 18 mmol, 40 equiv.) A 3.5:1:1.4 mixture of regioisomers denoted as **A**, **B** and **C**, 67% combined yield. Ratio was determined after separation of regioisomeres by SFC, performed with a Viridis Silica-2-EthylPyridine column 250*10mm, 5 µm (15% EtOAc as cosolvent, 12 ml/min, at 150 bars, 25°C; concentration of sample: 10mg/mL and 90 µL volume of injection). Reaction time: 5h.
Spectroscopic data of regioisomers A and C correspond to the literature.[17,18]

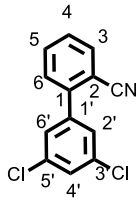
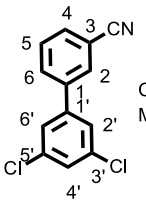
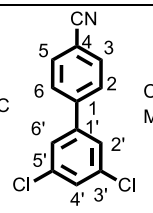
 $C_{13}H_8N_2O_2$ MW 224,21 g/mol	Purification : (PE/ MTBE 7:3) then SFC White solid Yield: 39% (40 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ ^{1}H NMR ($CDCl_3$, 300 K): δ 8.37-8.34 (m, 2H), 7.83 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.75-7.70 (m, 3H), 7.58-7.53 (m, 2H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.9, 144.3, 142.9, 133.9, 133.2, 129.9, 129.8, 128.9, 123.9, 117.9, 111.3 **IR** (cm^{-1}) 2901, 2017, 1518, 1066, 858 **HRMS** calculated for $C_{13}H_8N_2O_2$: 224.0586, found 224.0577

 $C_{13}H_8N_2O_2$ MW 224,21 g/mol	Purification : (PE/ MTBE 7:3) then SFC White solid Yield: 11% (12 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ ^{1}H NMR ($CDCl_3$, 300 K): δ 8.37-8.34 (m, 2H), 7.91-7.84 (m, 2H), 7.78 – 7.70 (m, 1H), 7.63 (t, *J* = 7.7 Hz, 1H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.8, 145.0, 140.1, 132.2, 131.6, 130.9, 130.1, 128.0, 124.4, 118.2, 113.6 **IR** (cm^{-1}) 2901, 2017, 1518, 1066, 858 **HRMS** calculated for $C_{13}H_8N_2O_2$: 224.0586, found 224.0577

 $C_{13}H_8N_2O_2$ MW 224,21 g/mol	Purification : (PE/ MTBE 7:3) then SFC White solid Yield: 16% (16 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ ^{1}H NMR ($CDCl_3$, 300 K): δ 8.36-8.33 (m, 2H), 7.82-7.72 (m, 6H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.8, 145.4, 143.1, 132.9, 128.14, 128.08, 124.4, 118.3, 112.7 **IR** (cm^{-1}) 2901, 2017, 1518, 1066, 858 **HRMS** calculated for $C_{13}H_8N_2O_2$: 224.0586, found 224.0577

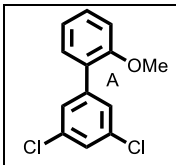
▶ **3',5'-dichloro-[1,1'-biphenyl]-4-carbonitrile, 3',5'-dichloro-[1,1'-biphenyl]-3-carbonitrile, 3',5'-dichloro-[1,1'-biphenyl]-2-carbonitrile (2b)**

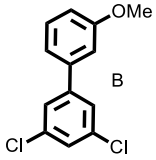
According to the general procedure described above, **2b** has been synthesized from 3,5-dichlorobenzenediazonium tetrafluoroborate (117.3 mg, 0.45 mmol) and benzonitrile (1.9 mL, 18 mmol, 40 equiv.). A 5.5: 1: 2.3 mixture of regioisomers denoted as **A**, **B** and **C**, 82% combined yield. Ratio was determined after separation of regioisomeres by SFC, performed with a Viridis Silica-2-EthylPyridine column 250*10mm, 5 µm (10% EtOAc as cosolvent, 12 ml/min, at 100 bars, 25°C; concentration of sample: 12mg/mL and 90 µL volume of injection). Reaction time: 24h.

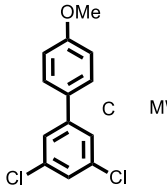
A  $C_{13}H_7Cl_2N$ MW 248,11	Purification : (PE/ MTBE 9:1) White solid Yield: 55% (62 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.68 (td, *J* = 7.7, 1.4 Hz, 1H), 7.51 (td, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.49-7.42 (m, 4H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.5 (C1), 140.9 (C1'), 135.3 (C3'+ C5'), 133.8 (C3), 133.0 (C5), 129.9 (C6), 128.8 (C5), 128.6 (C4'), 127.3 (C4'), 117.8 (CN), 111.3 (*C*-CN) **IR** (cm^{-1}) 3075, 2228, 1586, 1556, 1428, 1280, 1124, 1099, 857, 834, 799, 756, 683 **HRMS** calculated for $C_{13}H_7Cl_2N^+$: 246,9956, found 246,9953
B  $C_{13}H_7Cl_2N$ MW 248,11	Purification : (PE/ MTBE 9:1) White solid Yield: 9% (10 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.82-7.68 (m,3H), 7.61-7.55 (m, 1H), 7.44-7.41 (m, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.8 (C1), 139.8 (C1'), 135.8 (C3'+C5'), 131.8 (C6), 131.4 (C4), 130.6 (C2), 129.9 (C5), 128.3 (C4'), 125.6 (C2'+C6'), 118.3 (CN), 113.4 (*C*-CN) **IR** (cm^{-1}) 3075, 2228, 1586, 1556, 1428, 1280, 1124, 1099, 857, 834, 799, 756, 683 **HRMS** calculated for $C_{13}H_7Cl_2N^+$: 246,9956, found 246,9953
C  $C_{13}H_7Cl_2N$ MW 248,11	Purification : (PE/ MTBE 9:1) White solid Yield: 23% (25 mg) **^{1}H NMR** (300 MHz, CDCl3) δ 7.77-7.62 (m, 4H), 7.45-7.41 (m, 3H) ^{13}C NMR (75 MHz, CDCl3) δ 142.8 (C1), 142.1 (C1'), 135.7 (C3'+C5'), 132.8 (C3+C5), 128.5 (C4'), 127.8 (C2+C6), 125.7 (C4'), 118.4 (CN), 112.3 (*C*-CN) **IR** (cm^{-1}) 3075, 2228, 1586, 1556, 1428, 1280, 1124, 1099, 857, 834, 799, 756, 683 **HRMS** calculated for $C_{13}H_7Cl_2N^+$: 246,9956, found 246,9953

▶3',5'-dichloro-2-methoxy-1,1'-biphenyl / 3,5-dichloro-3'-methoxy-1,1'-biphenyl /3,5-dichloro-4'-methoxy-1,1'-biphenyl (2c)

According to the general procedure described above, **2c** has been synthesized from 3,5-dichlorobenzenediazonium tetrafluoroborate (117.3 mg, 0.45 mmol) and anisole (2.0 mL, 18 mmol, 40 equiv.). A 3.7: 1: 1.2 mixture of regioisomers denoted as **A**, **B** and **C**, 94% combined yield. Ratio was determined after separation of regioisomeres by SFC, performed with a Viridis Silica column 250*10mm, 5 µm (5% (EtOAc-Heptane 25:75) as cosolvant, 12 ml/min, at 100 bars, 25°C. Concentration of sample: 12mg/mL and 20 µL volume of injection). Reaction time: 1h.
Spectroscopic data of regioisomer C correspond to the literature.[19]

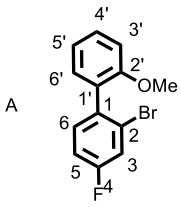
 $C_{13}H_{10}Cl_2O$ MW 253,12 g/mol	Purification : (PE/ MTBE 9:1) then SFC White solid Yield: 59% (64 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.9 Hz, 2H), 7.37 (td, *J* = 7.7, 1.7 Hz, 1H), 7.32 (t, *J* = 1.9 Hz, 1H), 7.28 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 (dd, *J* = 7.5, 0.9 Hz, 1H), 3.84 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.3, 141.4, 134.3, 130.5, 129.7, 127.99, 127,93, 126.8, 120.9, 111.4, 55.7 **IR (cm^{-1})** 3052, 1575, 1558, 1427, 1380, 858, 796; **HRMS** calculated for $C_{13}H_{11}Cl_2O^+$: 253.0182, found 253.0172.

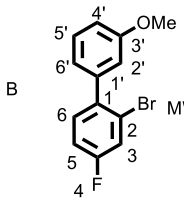
 $C_{13}H_{10}Cl_2O$ MW 253,12 g/mol	Purification : (PE/ MTBE 9:1) then SFC White solid Yield: 15% (16 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 1.9 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.11 (ddd, *J* = 7.7, 1.6, 0.9 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.94 (ddd, *J* = 8.3, 2.5, 0.8 Hz, 1H), 3.87 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.1, 144.1, 140.0, 135.2, 130.1, 127.3, 125.7, 119.5, 113.9, 112.8, 55.4 **IR (cm^{-1})** 3052, 1575, 1558, 1427, 1380, 858, 796; **HRMS** calculated for $C_{13}H_{11}Cl_2O^+$: 253.0182, found 253.0172.

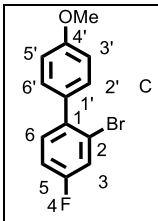
 $C_{13}H_{10}Cl_2O$ MW 253,12 g/mol	Purification : (PE/ MTBE 9:1) then SFC White solid Yield: 18% (20 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 1H), 7.28 (t, *J* = 1.9 Hz, 1H), 7.41 (d, *J* = 1.9 Hz, 1H), 7.02 – 6.94 (m, 1H), 3.86 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.0, 143.8, 135.2, 130.9, 128.2, 126.5, 125.1, 114.5, 55.4 **IR (cm^{-1})** 3052, 1575, 1558, 1427, 1380, 858, 796; **HRMS** calculated for $C_{13}H_{11}Cl_2O^+$: 253.0182, found 253.0172.

▶2-bromo-5-fluoro-2'-methoxy-1,1'-biphenyl /2-bromo-5-fluoro-3'-methoxy-1,1'-biphenyl /2-bromo-5-fluoro-4'-methoxy-1,1'-biphenyl (2d)

According to the general procedure described above, **2d** has been synthesized from 2-bromo-4-fluorobenzenediazonium tetrafluoroborate (130 mg, 0.45 mmol) and anisole (2.0 mL, 18 mmol, 40 equiv). A 3.3: 1: 1.5 mixture of regioisomers denoted as **A**, **B** and **C**, 72% combined yield. (72% starting from 500 mg of 2-bromo-4-fluorobenzenediazonium tetrafluoroborate, reaction time: 20h). Ratio was determined after separation of regioisomeres by SFC, performed with a Viridis Silica column 250*10mm, 5 µm (5% (EtOAc-Heptane 50:50) as cosolvent, 10 ml/min, at 100 bars, 40°C; concentration of sample: 12mg/mL and 25 µL volume of injection). Reaction time: 1h.

A  $C_{13}H_{10}BrFO$ MW 281,12 g/mol	Purification : (PE/ MTBE 9:1) then SFC Yellow oil Yield: 41% (52 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.2 Hz, 2.6 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.26 (dd, *J* = Hz, 8.5, 6.4 Hz, 1H), 7.15 (dd, *J* = 7.4 Hz, 1.8 Hz, 1H), 7.09 (dd, *J* = 8.4 Hz, 2.7 Hz, 1H), 7.05-6.97 (m, 2H), 3.79 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.5 (d, *J* = 249.9 Hz) (*C*-F), 156.6 (*C*-OMe), 135.9 (d, *J* = 3.2 Hz) (C1), 132.3 (d, *J* = 8.3 Hz) (C6), 130.9 (C6'), 129.5 (C4'), 129.3 (C1'), 124.3 (d, *J* = 9.5 Hz) (*C*-Br), 120.3 (C5'), 119.7 (d, *J* = 24.3 Hz) (C3), 114.2 (d, *J* = 20.9) (C5), 111.0 (C3'), 55.6 (O*Me*) **^{19}F NMR** (120 MHz, $CDCl_3$) δ -113.75 **IR** (cm^{-1}) 3052, 1575, 1558, 1427, 1380, 858, 796 **HRMS** calculated for $C_{13}H_{11}BrFO^{+}$: 280.9972, found 280.9962

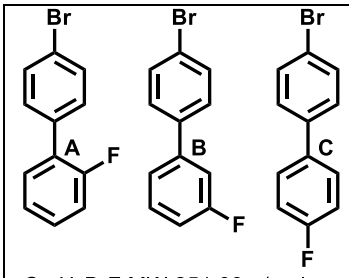
B  $C_{13}H_{10}BrFO$ MW 281,12 g/mol	Purification : (PE/ MTBE 9:1) then SFC Yellow oil Yield: 12% (16 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.34 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.3 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.07 (td, *J* = 8.1, 2.6 Hz, 1H), 6.96-6.90 (m, 3H), 3.84 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.6 (d, *J* = 250.6 Hz) (*C*-F), 159.2 (*C*-OMe), 141.5 (C1'), 138.7 (d, *J* = 3.3 Hz) (C1), 131.8 (d, *J* = 6.4 Hz) (C6), 129.1 (C5'), 122.6 (d, *J* = 9.5 Hz) (*C*-Br), 121.9 (C6'), 120.2 (d, *J* = 24.3 Hz) (C3), 115.2 (C2'), 114.5 (d, *J* = 20.8 Hz) (C5), 113.3 (C4'), 55.3 (s) (O*Me*) **^{19}F NMR** (120 MHz, $CDCl_3$) δ -113.5 **IR** (cm^{-1}) 3052, 1575, 1558, 1427, 1380, 858, 796 **HRMS** calculated for $C_{13}H_{11}BrFO^{+}$: 280.9972, found 280.9962

 C $C_{13}H_{10}BrFO$ MW 281,12 g/mol	Purification : (PE/ MTBE 9:1) then SFC Yellow oil Yield: 19% (23 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.11 – 7.02 (m, 1H), 6.99 – 6.93 (m, 2H), 3.86 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.40 (d, *J* = 250.3 Hz) (*C*-F), 159.2 (*C*-OMe), 138.3 (d, *J* = 3.3 Hz) (C1), 132.6 (C1'), 132.0 (d, *J* = 8.3 Hz) (C6), 130.6 (C2'+C6'), 122.9 (d, *J* = 9.7 Hz) (C2), 120.1 (d, *J* = 24.2 Hz)

	(C3), 114.5 (d, *J* = 20.8,) (C5), 113.5 (C3'+C5'), 55.3 (O*Me*) **^{19}F NMR** (120 MHz, $CDCl_3$) δ -114.1 **IR** (cm^{-1}) 3052, 1575, 1558, 1427, 1380, 858, 796 **HRMS** calculated for $C_{13}H_{11}BrFO^+$: 280.9972, found 280.9962

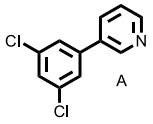
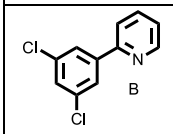
▶ 4'-bromo-2-fluoro-1,1'-biphenyl / 4'-bromo-3-fluoro-1,1'-biphenyl / 4'-bromo-4-fluoro-1,1'-biphenyl (2e)

According to the general procedure described above, **2e** has been synthesized from 4-bromobenzenediazonium tetrafluoroborate (121.8 mg, 0.45 mmol), fluorobenzene (1.7 mL, 18 mmol, 40 equiv.) and $Ru(bpy)_3(SbF_6)_2$ (2.3 mg, $2.25.10^{-3}$ mmol, 0.5 mol%) in MeCN (2 mL). Reaction time: 12h.
Spectroscopic data of regioisomer C correspond to the literature.[20] Ratio of regioisomeres were determinated by ^{19}F RMN.

 $C_{12}H_8BrF$ MW 251,09 g/mol	Purification : PE Colorless liquid Yield: 71% (80 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2H, C), 7.56 – 7.51 (m, ABC), 7.46 (d, *J* = 8.5 Hz, 2H, C), 7.41 – 7.34 (m, ABC), 7.29 – 7.09 (m, ABC); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.3 (d, *J* = 246 Hz, quat B), 162.8 (d, *J* = 247 Hz, quat A), 159.7 (d, *J* = 248 Hz, quat C), 142.2 (d, *J* = 9.5 Hz, quat B), 142.0 (quat A), 139.9 (d, *J* = 23.2 Hz, quat C), 138.8 (d, *J* = 40.7 Hz, quat A), 134.6 (quat C), 132.0 (2C), 131.9 (2A), 131.6 (2C), 130.5 (d, *J* = 3.1 Hz, 2C), 130.4 (d, *J* = 2.8 Hz, 2B), 130.3 (quat A), 129.3 (d, *J* = 8.5 Hz, 2C), 128.6 (2B), 128.5 (2A), 128.4 (quat B), 127.6 (d, *J* = 13.6 Hz, quat C), 125.5 (quat B), 124.5 (d, *J* = 3.6 Hz, B), 122.5 (d, *J* = 29.4 Hz, A), 122.1 (d, *J* = 42 Hz, B), 121.5 (A), 116.2 (d, *J* = 22.7 Hz, B), 115.8 (d, *J* = 21.5 Hz, A), 114.4 (d, *J* = 21.2 Hz, B), 113.8 (d, *J* = 22.2 Hz, A); **^{19}F NMR** (120 MHz, $CDCl_3$) δ -112.6 (B), -114.9 (A), -117.8 (C); **IR (cm^{-1})** 3066, 2926, 1588, 1477, 1451, 1390, 1211, 1073, 1005, 877, 818, 782, 735, 689; **HRMS** calculated for $C_{12}H_8BrF^+$: 249.9793, found 249.9786.

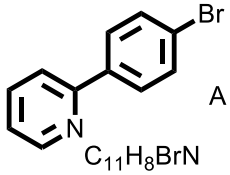
▶ 3-(3,5-dichlorophenyl)pyridine / 2-(3,5-dichlorophenyl)pyridine (2f)

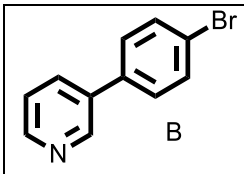
According to the general procedure described above, **2f** has been synthesized from 3,5-dichlorobenzenediazonium tetrafluoroborate (117.3 mg, 0.45 mmol) and pyridine (1.5 mL, 18 mmol, 40 equiv.) A 8: 1 mixture of regioisomers denoted as **A** and **B**, 73% combined yield. Reaction time: 1h. Spectroscopic data of regioisomer **A** correspond to the literature.[21]

 A $C_{11}H_7Cl_2N$ MW 224,09 g/mol	Purification : PE/MTBE 7:3 White solid Yield: 65% (66 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.8 (d, *J* = 1.7 Hz, 1H), 8.65 (dd, *J* = 4.9 Hz, 1.4 Hz, 1H), 7.89-7.78 (m, 1H), 7.45 (d, *J* = 1.7 Hz, 2H), 7.41-7.38 (m, 2H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 149.6, 148.0, 140.8, 135.6, 134.3, 128.0, 125.6, 123.7; **IR (cm^{-1})** 3052, 1575, 1558, 1427, 1380, 858, 796; **HRMS** calculated for $C_{11}H_7NCl_2^+$: 224.0028, found 224.0018.
 B $C_{11}H_7Cl_2N$ MW 224,09 g/mol	Purification : PE/MTBE 7:3 White solid Yield: 8% (8 mg) **^{1}H NMR** (300 MHz, CDCl3) δ 8.70 (dd, J = 4.8, 1.7 Hz, 1H), 7.90 (d, J = 1.9 Hz, 2H), 7.79 (td, J = 7.9, 1.8 Hz, 1H), 7.74 – 7.65 (m, 1H), 7.40 (t, J = 1.9 Hz, 1H), 7.30 (ddd, J = 7.4, 4.8, 1.1 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl3) δ 154.6, 149.9, 142.2, 137.0, 135.4, 128.7, 125.3, 123.1, 120.6; **IR (cm-1)** 3052, 1575, 1558, 1427, 1380, 858, 796; **HRMS** calculated for C11H7NCl2+: 224.0028, found 224.0018.

▶ 2-(4-bromophenyl)pyridine/ 3-(4-bromophenyl)pyridine (2g)

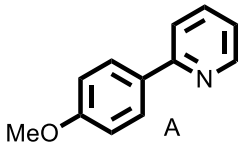
According to the general procedure described above, **2g** has been synthesized from 4-bromobenzenediazonium tetrafluoroborate (121.8 mg, 0.45 mmol) and pyridine (1.5 mL, 18.8 mmol, 40 equiv.). A 2:1 mixture of regioisomers denoted as **A** and **B** 21% combined yield. Reaction time: 1h. Spectroscopic data of regioisomer **A** and **B** correspond to the literature.[23]

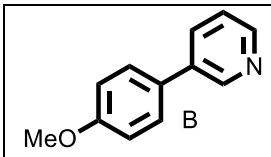
 A $C_{11}H_8BrN$ MW 234,09	Purification : (PE/ MTBE 7:3) White solid Yield: 14% (14 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.61 (ddd, *J* = 4.8, 1.7, 1.0 Hz, 1H), 7.86 – 7.76 (m, 2H), 7.86 – 7.76 (m, 2H), 7.73 – 7.59 (m, 2H), 7.57 – 7.49 (m, 2H), 7.22 – 7.14 (m, 1H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 156.2, 149.7, 138.2, 136.9, 131.9, 128.5, 123.5, 122.4, 120.3 **IR** (cm^{-1}) 2923, 1587, 1463, 1433, 1007, 772 **HRMS** calculated for $C_{11}H_{10}BrN^+$: 233,9913, found 233.9914

 $C_{11}H_8BrN$ MW 234,0919	Purification : (PE/ MTBE 7:3) Brown solid Yield: 7% (7 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.82 (d, *J* = 2.1 Hz, 1H), 8.61 (dd, *J* = 4.8, 1.3 Hz, 1H), 7.90 – 7.80 (m, 1H), 7.66 – 7.57 (m, 2H), 7.49 – 7.41 (m, 2H), 7.38 (dd, *J* = 7.9, 4.8 Hz, 1H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 148.7, 147.9, 136.7, 135.6, 134.3, 132.3, 128.7, 123.7, 122.6 **IR** (cm^{-1}) 2924, 1586, 1558, 1470, 1072, 999, 798, 710 **HRMS** calculated for $C_{11}H_{10}BrN^+$: 233.9913, found 233.9914

▶2-(4-methoxyphenyl)pyridine / 3-(4-methoxyphenyl)pyridine (2h)

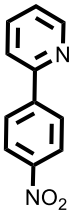
According to the general procedure described above, **2h** has been synthesized from 4-methoxybenzenediazonium tetrafluoroborate (100 mg, 0.45 mmol) and pyridine (1.5 mL, 18 mmol, 40 equiv.). A 15.6 :1 mixture of regioisomers denoted as **A** and **B**, 72% combined yield by adding 2 equiv. of K_2CO_3. Reaction time: 5h.
Spectroscopic data of regioisomers A, B and C (not observed under our conditions) correspond to the literature.[22]

 $C_{12}H_{11}NO$ MW 185,22 g/mol	Purification : (PE/ MTBE 7:3) Yellow solid Yield: 68% (56 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.66 (d, 1H, *J* = 4.9 Hz, 1H), 7.96 (dd, 2H, *J* = 6.6 Hz, 2.0 Hz, 2H), 7.73-7.66 (m, 2H), 7.18 (ddd, *J* = 6.7, 4.9, 1.4 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.5, 156.9, 149.2, 136.9, 131.6, 128.2, 121.4, 119.8, 114.1, 55.3 **IR** (cm^{-1}) 2932, 1515, 1465, 1246, 1176, 780 **HRMS** calculated for $C_{12}H_{12}NO^+$: 186,0913, found 186,0914

 $C_{12}H_{11}NO$ MW 185,22 g/mol	Purification : (PE/ MTBE 7:3) Yellow solid Yield: 4% (3 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.81 (d, *J* = 1.9 Hz, 1H), 8.54 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.83 (ddd, *J* = 7.9, 2.2, 1.7 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.34 (ddd, *J* = 7.9, 4.9, 0.6 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.7, 147.7, 147.6, 136.3, 133.9, 130.1, 128.2, 123.3, 114.5, 55.3 **IR** (cm^{-1}) 2932, 1515, 1465, 1246, 1176, 780 **HRMS** calculated for $C_{12}H_{12}NO^+$: 186,0913, found 186,0914

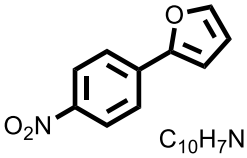
▶ 4-(4-nitrophenyl)pyridine (2i)

According to the general procedure described above, **2i** has been synthesized from 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol), pyridine (1.5 mL, 18.8 mmol, 40 equiv.) and $Ru(bpy)_3(SbF_6)_2$ (2.3 mg, $2.25.10^{-3}$ mmol, 0.5 mol%) in MeCN (2 mL). Reaction time: 2h. Spectroscopic data correspond to the literature. [24]

 $C_{11}H_8N_2O_2$ MW 200,19 g/mol	Purification : (PE/ MTBE 7:3) then SFC White solid Yield: 41% (37 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ ^{1}H NMR ($CDCl_3$, 300 K): δ 8.79 – 8.69 (m, 1H), 8.37 – 8.26 (m, 2H), 8.21 – 8.11 (m, 2H), 7.89 – 7.75 (m, 2H), 7.34 (ddd, *J* = 6.3, 4.8, 2.4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 154.8, 150.0, 148.1, 145.2, 137.1, 127.6, 123.9, 123.5, 121.2 **IR** (cm^{-1}) 3013, 1924, 1524, 1468, 1241, 1157, 858, 789 **HRMS** calculated for $C_{11}H_9N_2O_2$: 201.0659, found 201.0663

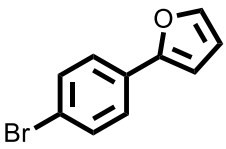
▶ **2-(4-nitrophenyl)furan (2j)**

According to the general procedure described above, **2j** has been synthesized from 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol) and furane (1.4 mL, 18 mmol, 40 equiv.). Reaction time: 1h.
Spectroscopic data correspond to the literature.[25]

 $C_{10}H_7NO_3$ MW 189,17 g/mol	Purification : PE Yellow solid Yield: 47% (40 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.49–8.01 (m, 2H), 7.89–7.68 (m, 2H), 7.56 (d, *J* = 1.3 Hz, 1H), 6.94–6.83 (m, 1H), 6.55 (dd, *J* = 3.5, 1.8 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.8, 146.5, 144.2, 136.5, 124.4, 124.0, 112.6, 109.1; **IR (cm^{-1})** 3111, 2280, 1725, 1564, 1440, 1298, 1020, 764; **HRMS** calculated for $C_{10}H_7NO_3$ 189.0426, found 189.0424.

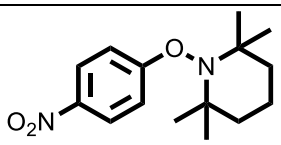
▶ **2-(4-bromophenyl)furan (2k)**

According to the general procedure described above, **2k** has been synthesized from 44-bromobenzenediazonium tetrafluoroborate (121.8 mg, 0.45 mmol) and furane (1.4 mL, 18 mmol, 40 equiv.). Reaction time: 1h.
Spectroscopic data correspond to the literature.[25]

 $C_{10}H_7BrO$ MW 223,07 g/mol	Purification : PE Orange solid Yield: 34% (34 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46–7.37 (m, 5H), 6.56 (d, *J* = 3.4 Hz, 1H), 6.38 (dd, *J* = 3.4, 1.8 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 153.1, 142.5, 131.9, 129.9, 125.4, 121.2, 111.9, 105.7; **IR (cm^{-1})** 2923, 1802, 1774, 1681, 1585, 1478, 1399, 1070, 826, 736; **HRMS** calculated for $C_{10}H_7BrO^+$: 221.9680, found 221.9679.

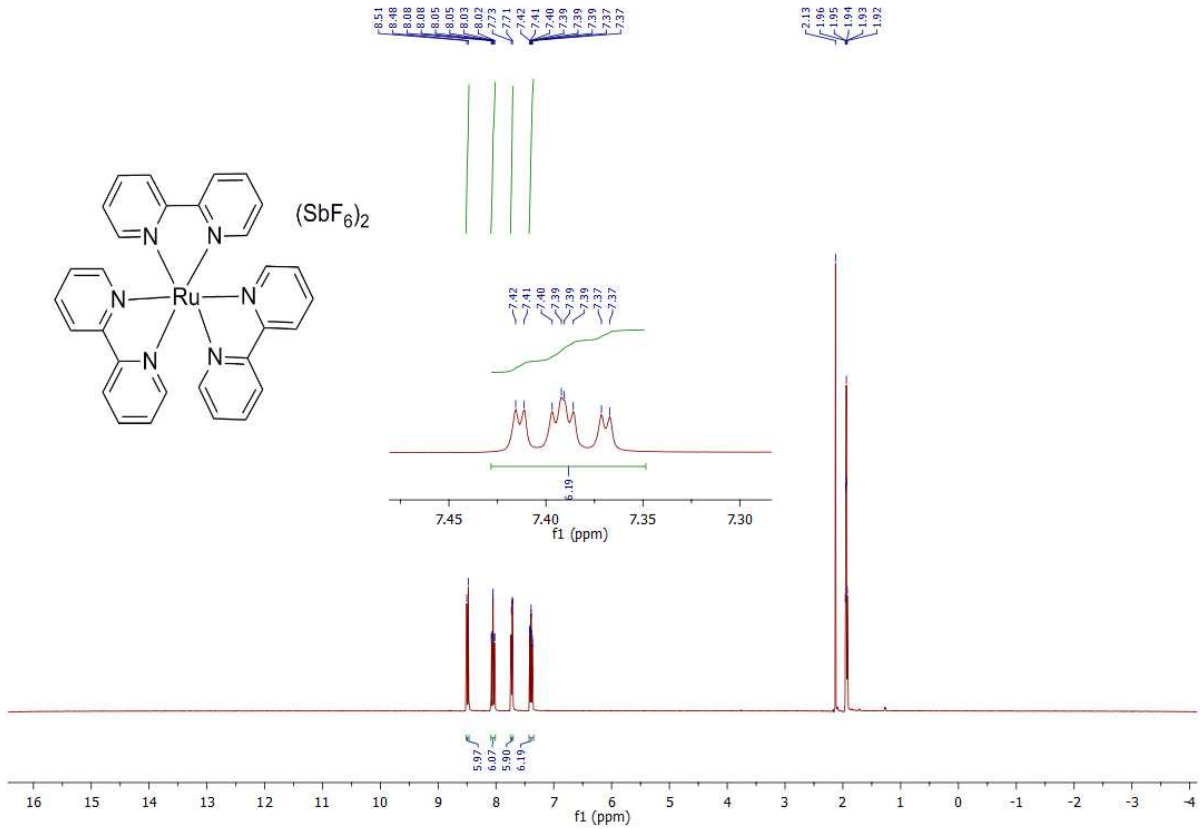
▶ 2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine

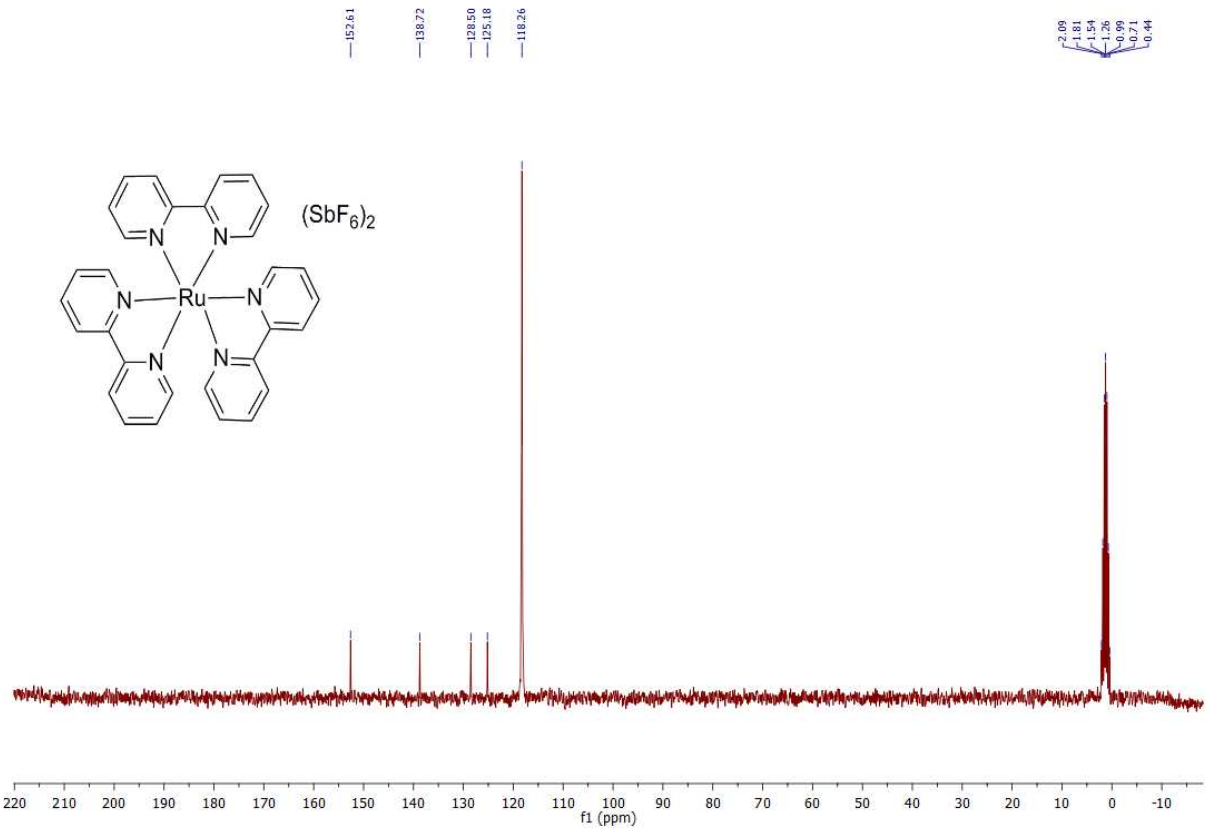
According to the procedure described above, 2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine has been synthesized from 4-nitrobenzenediazonium tetrafluoroborate (106.6 mg, 0.45 mmol), TEMPO (140 mg, 0.9 mmol, 2 equiv.), toluene (0.5 mL, 4.5 mmol, 10 equiv.) and $Ru(bpy)_3(SbF_6)_2$ (2.3 mg, $2.25.10^{-3}$ mmol, 0.5 mol%) in MeCN (2 mL). Reaction time: 2h.
Spectroscopic data correspond to the literature.[3]

 $C_{15}H_{22}N_2O_3$ MW: 278,35 g/mol	Purification : PE/MTBE 9:1 White solid Yield: 40% (50 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.16-8.12 (m, 2H), 7.35-7.15 (m, 2H), 1.66-1.59 (m, 5H), 1.45-1.42 (m, 1H), 1.24 (s, 6H), 0.98 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.6, 141.1, 125.5, 114.1, 60.9, 39.6, 32.2, 20.4, 16.9; **IR (cm^{-1})** 2975, 2933, 1588, 1512, 1486, 1337, 1253, 1110, 922, 852, 752; **HRMS** calculated for $C_{15}H_{23}N_2O_3^+$: 279.1703, found 279.1709.

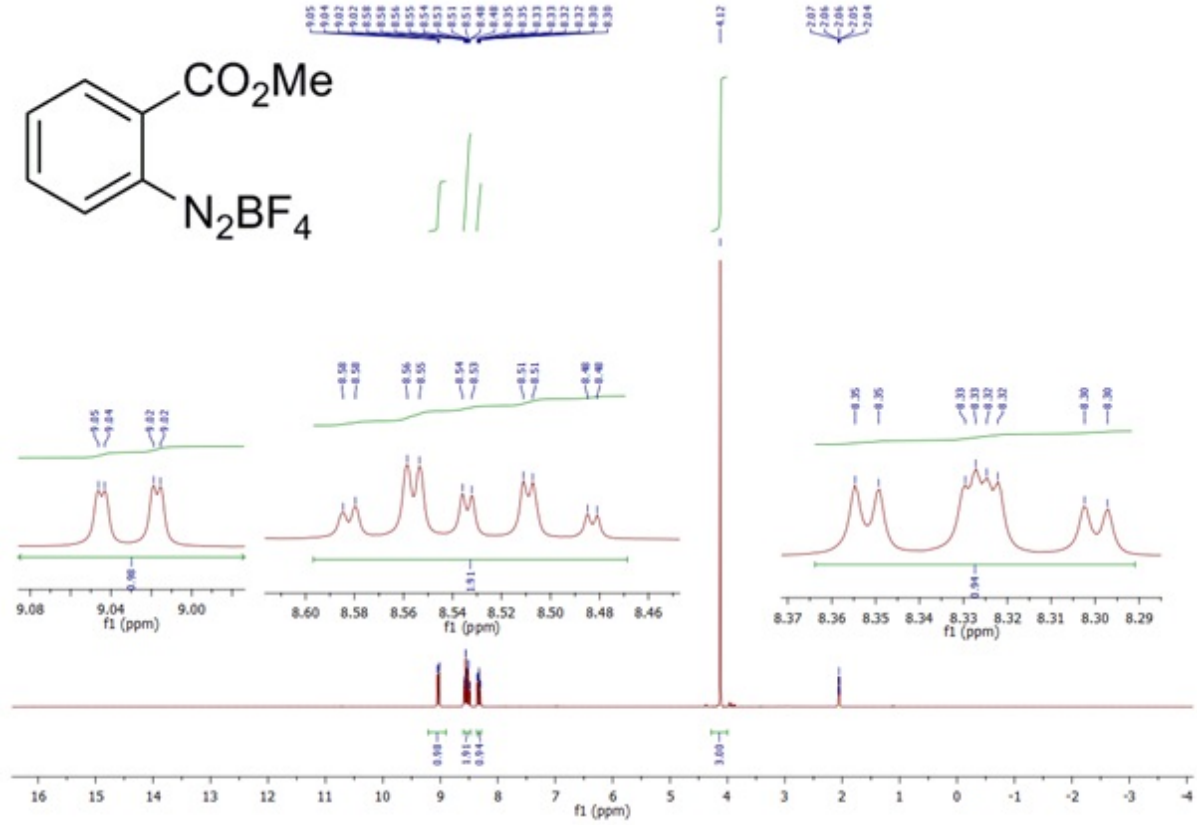
5. Copies of NMR spectra

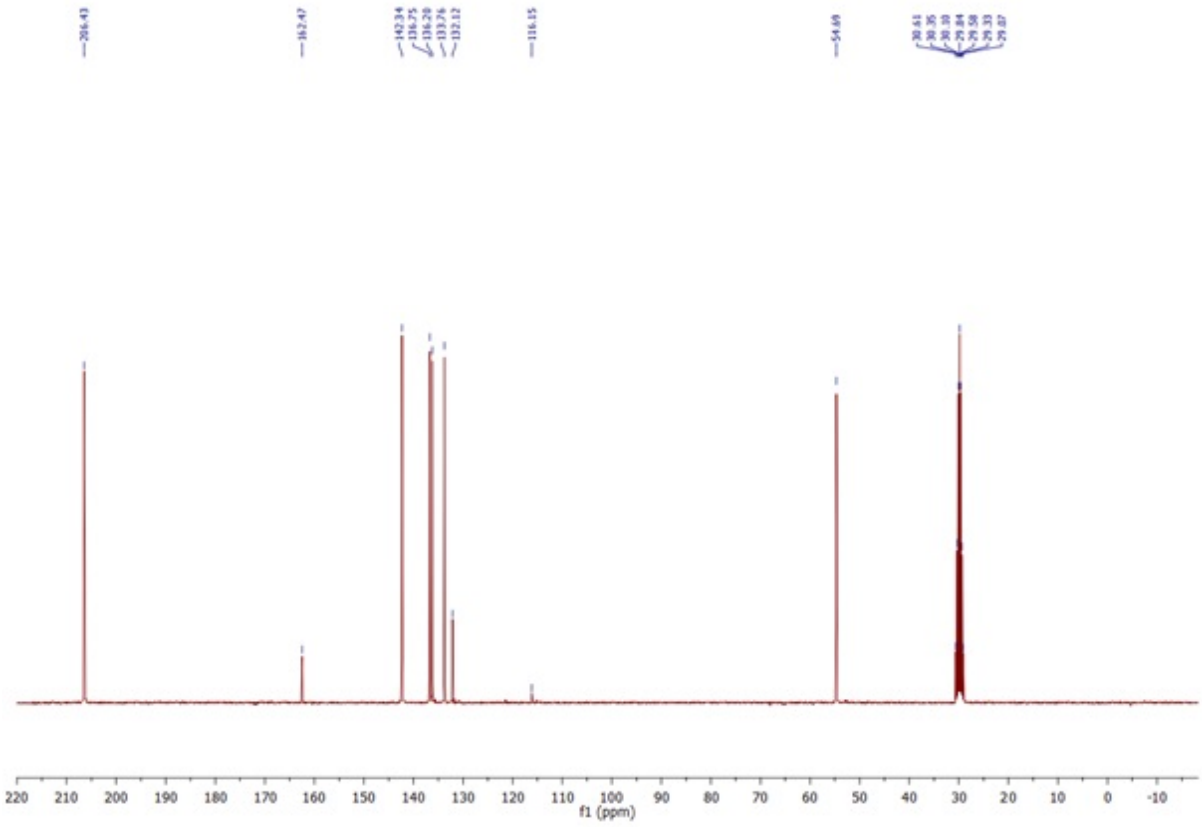
▶ $Ru(bpy)_3(SbF_6)_2$

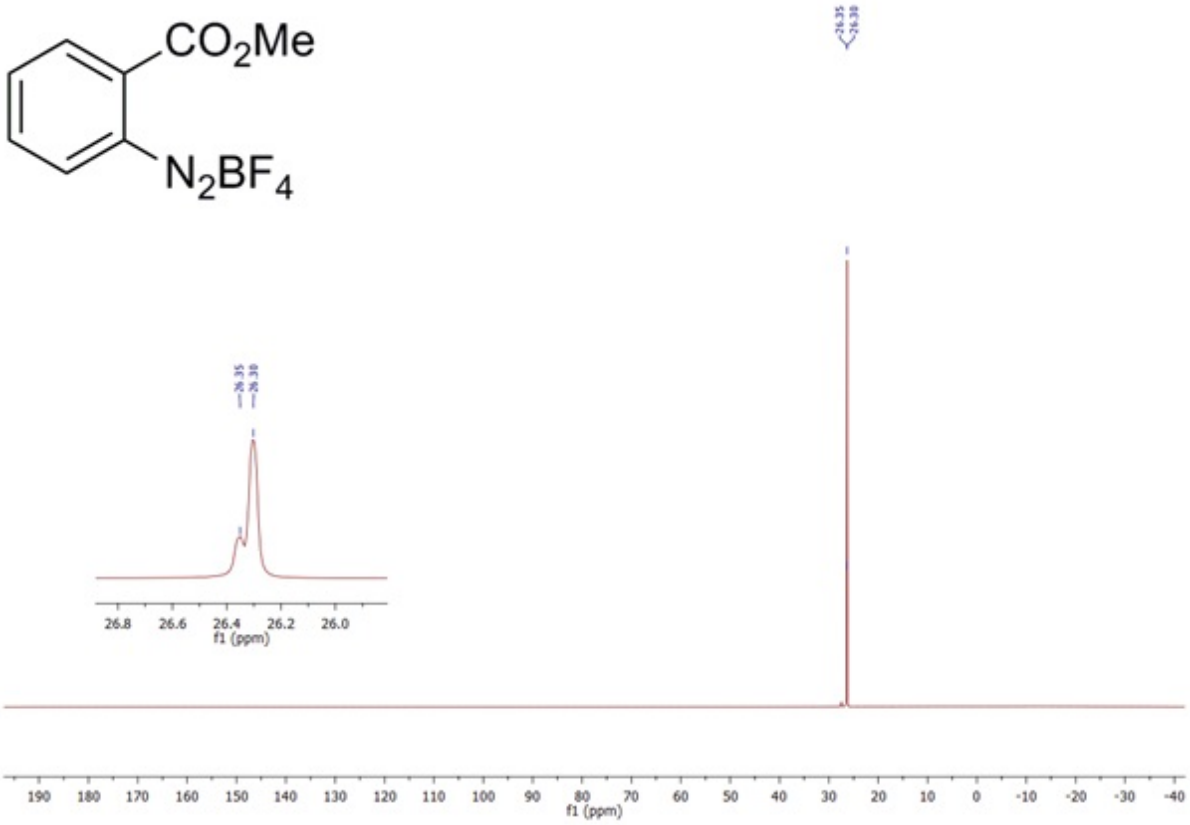




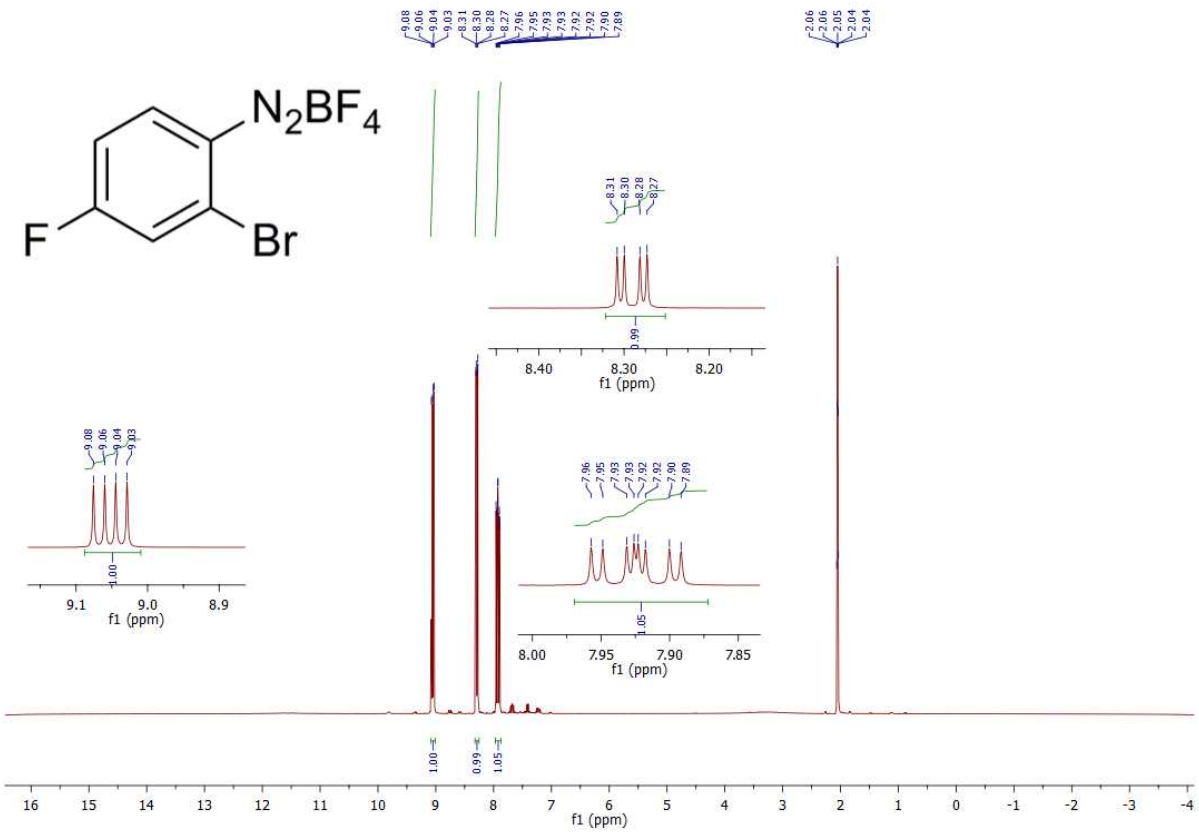
▶**2-(methoxycarbonyl)benzenediazonium tetrafluoroborate**

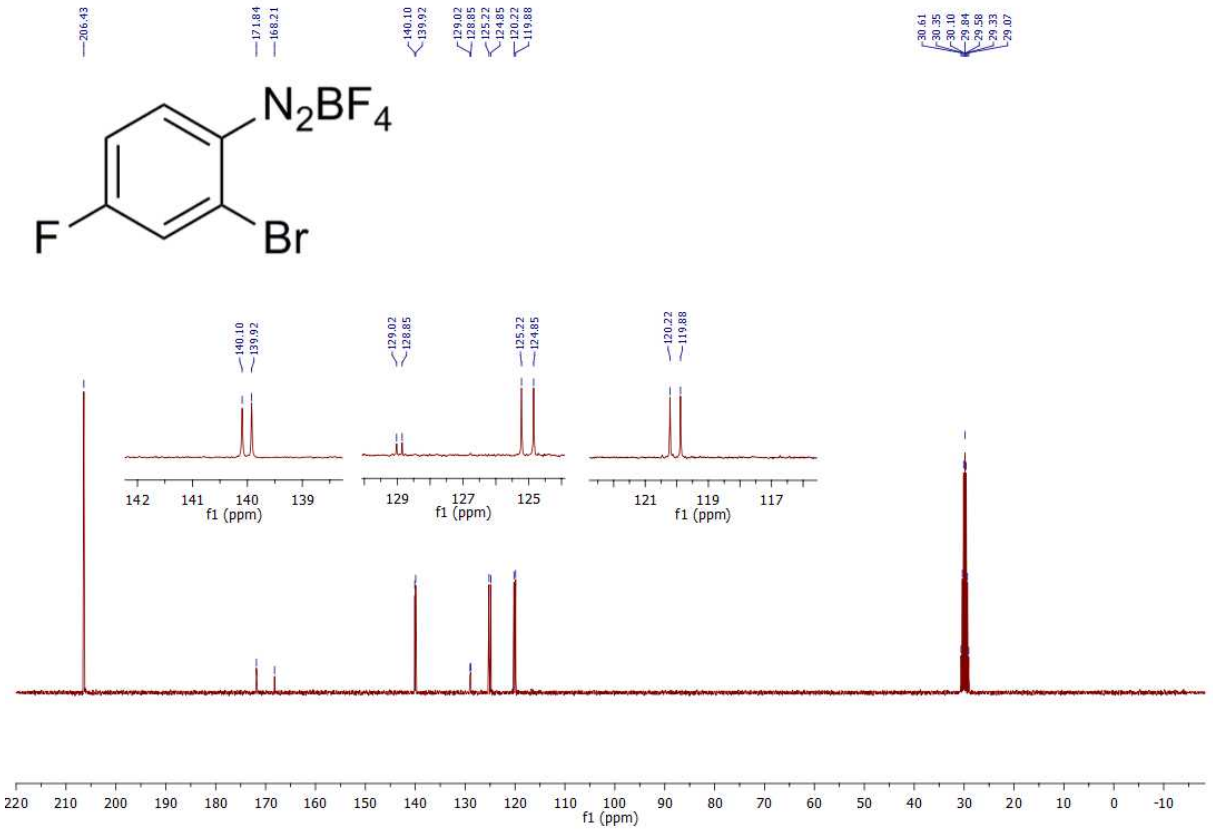






▶2-bromo-4-fluorobenzenediazonium **tetrafluoroborate**




206.43
171.84
168.21
140.10
139.92
129.02
128.85
125.22
124.85
120.22
119.88
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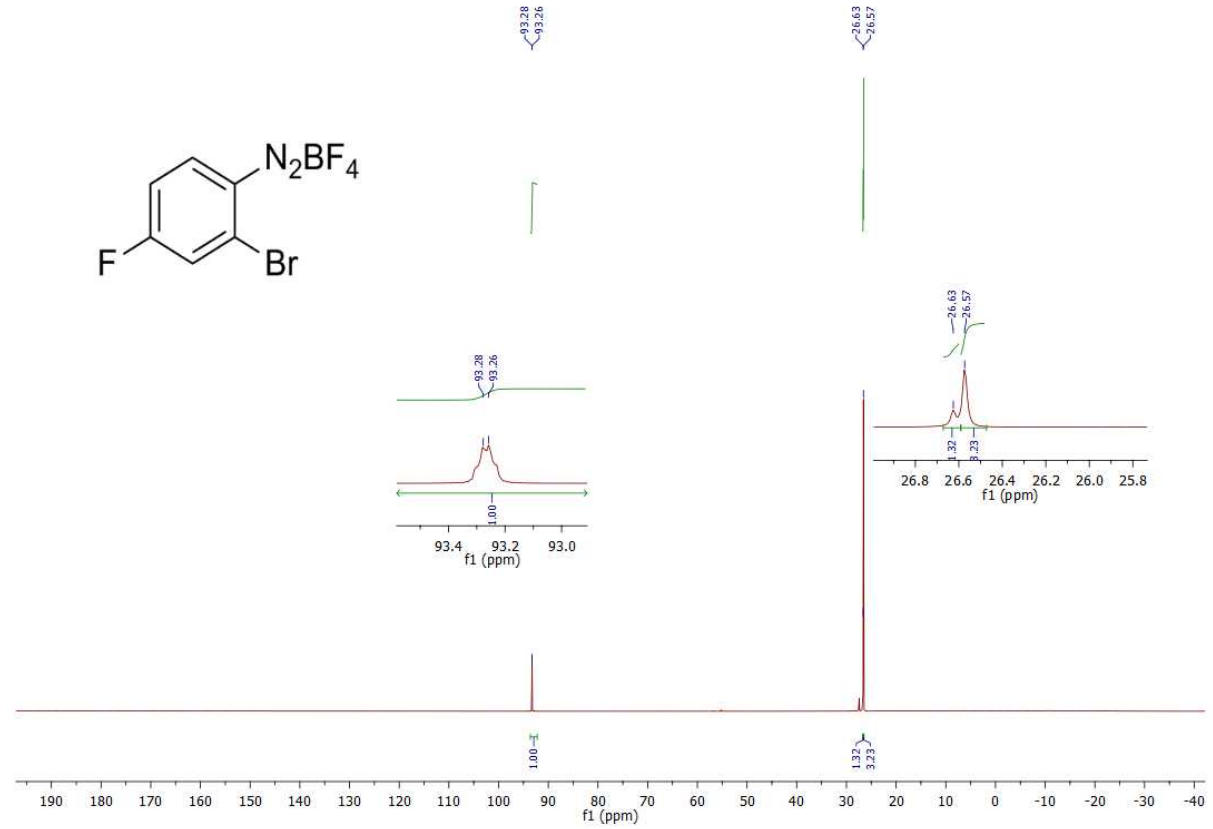
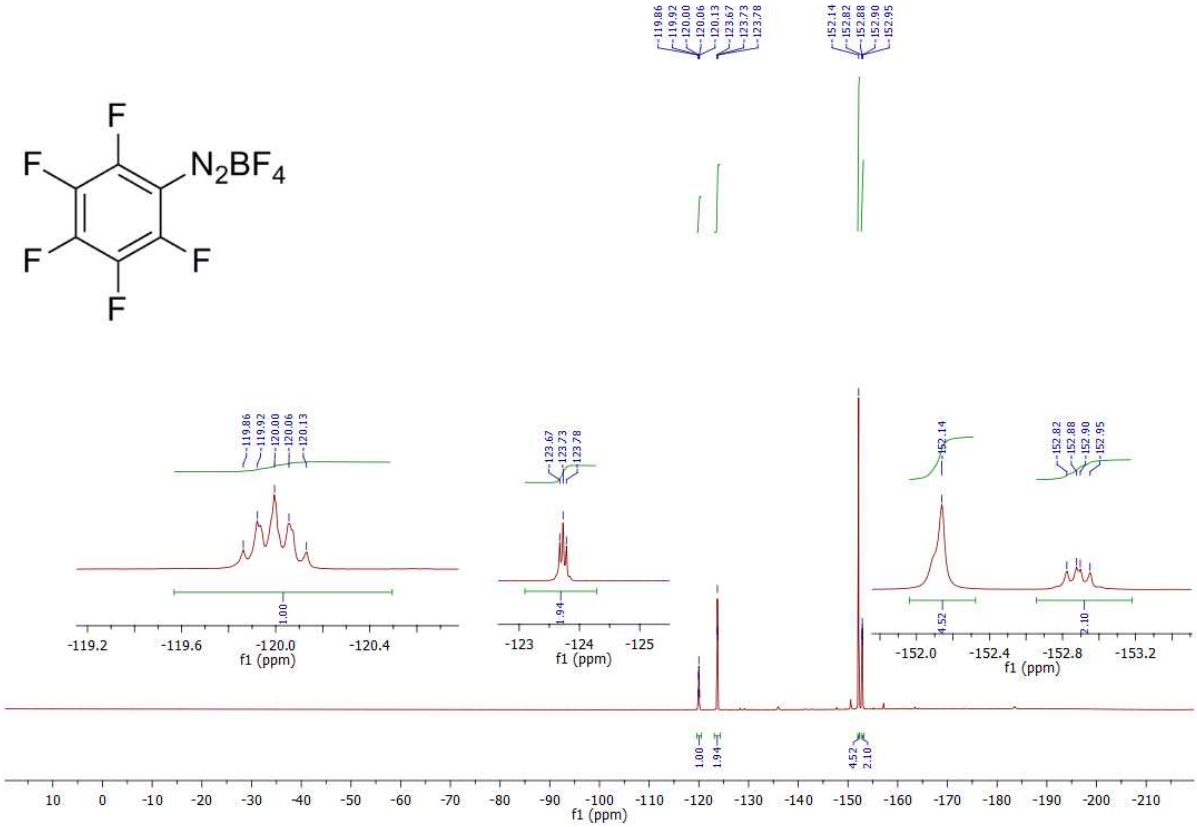
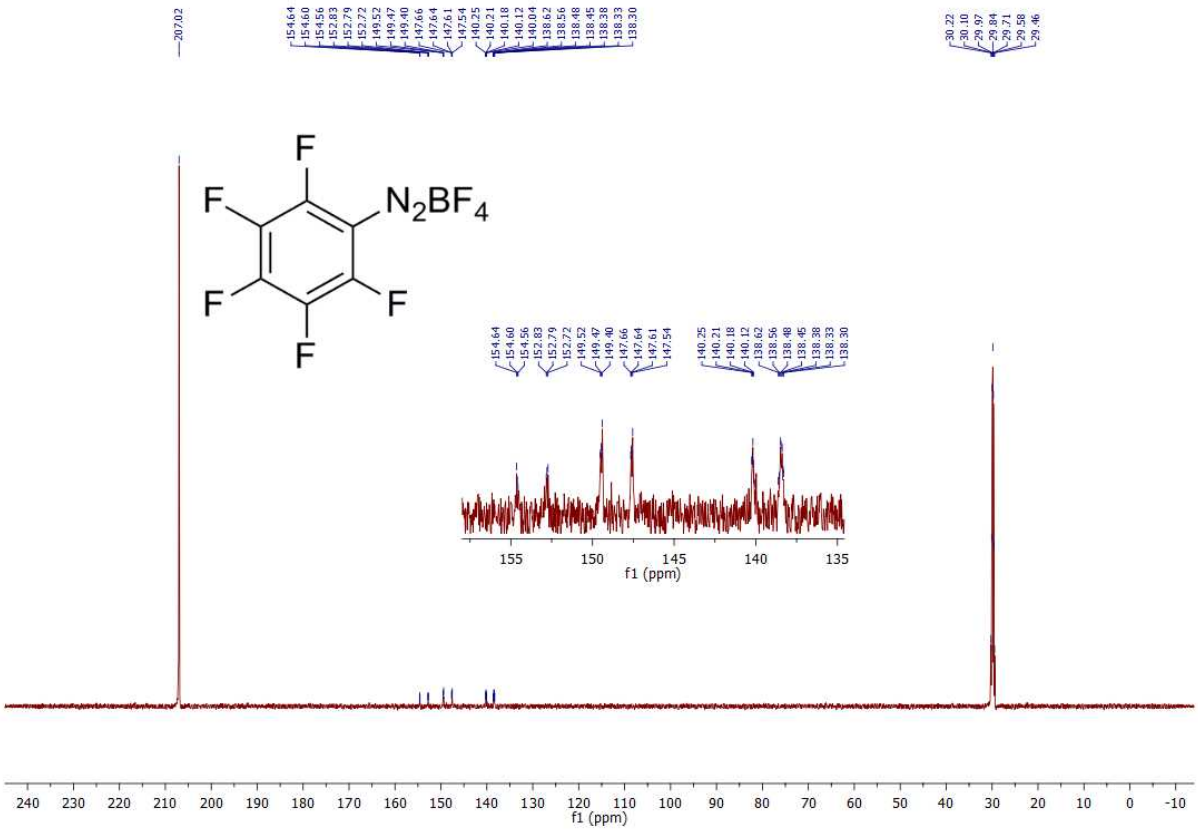
29.33
29.07
N2BF4
F
Br
f1 (ppm)

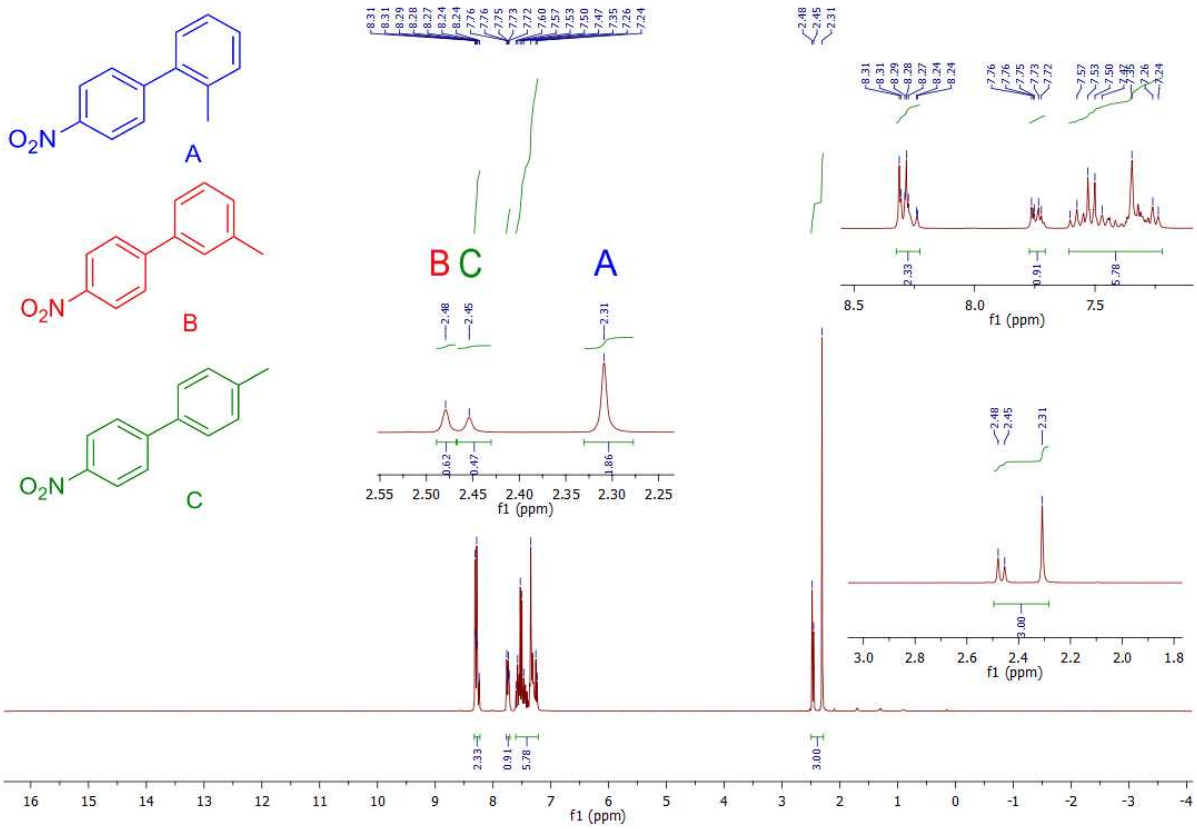

93.28
93.26
26.63
26.57
N2BF4
F
Br
1.00
1.32
3.23
f1 (ppm)

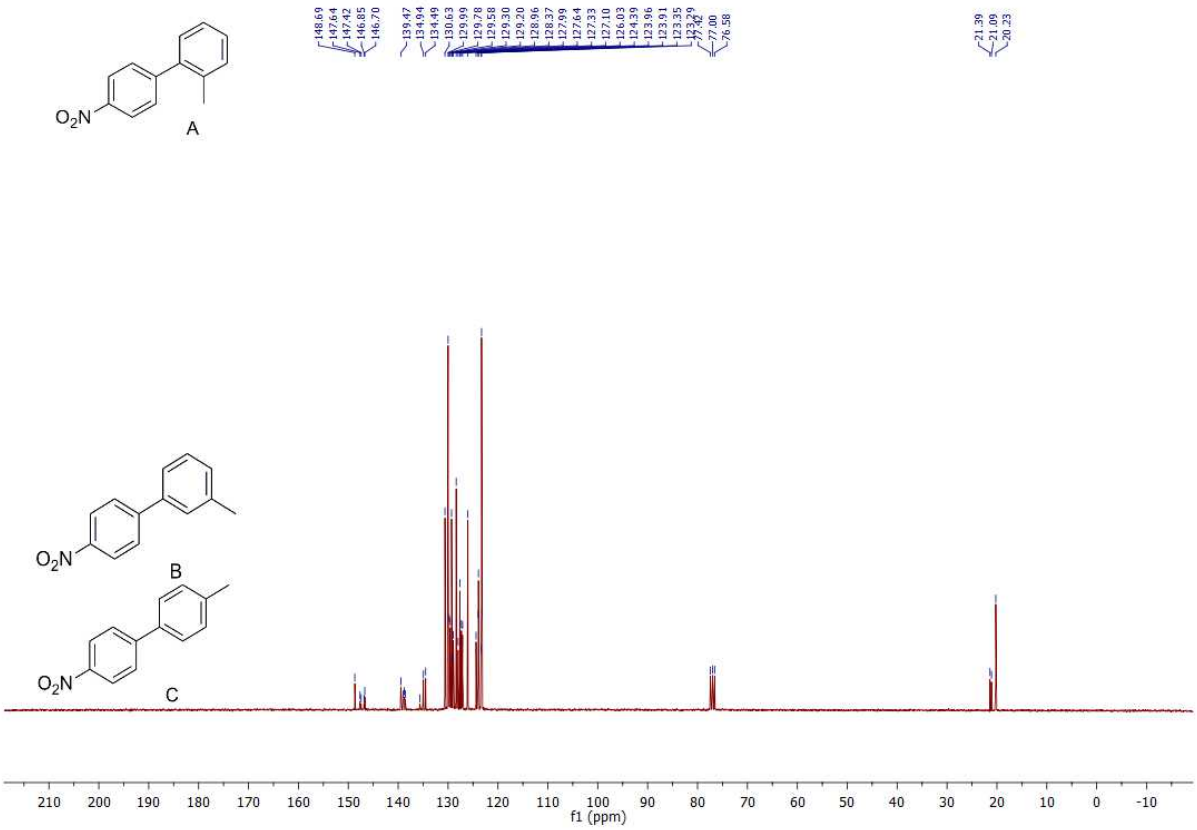
▶2,3,4,5,6-pentafluorobenzenediazonium tetrafluoroborate

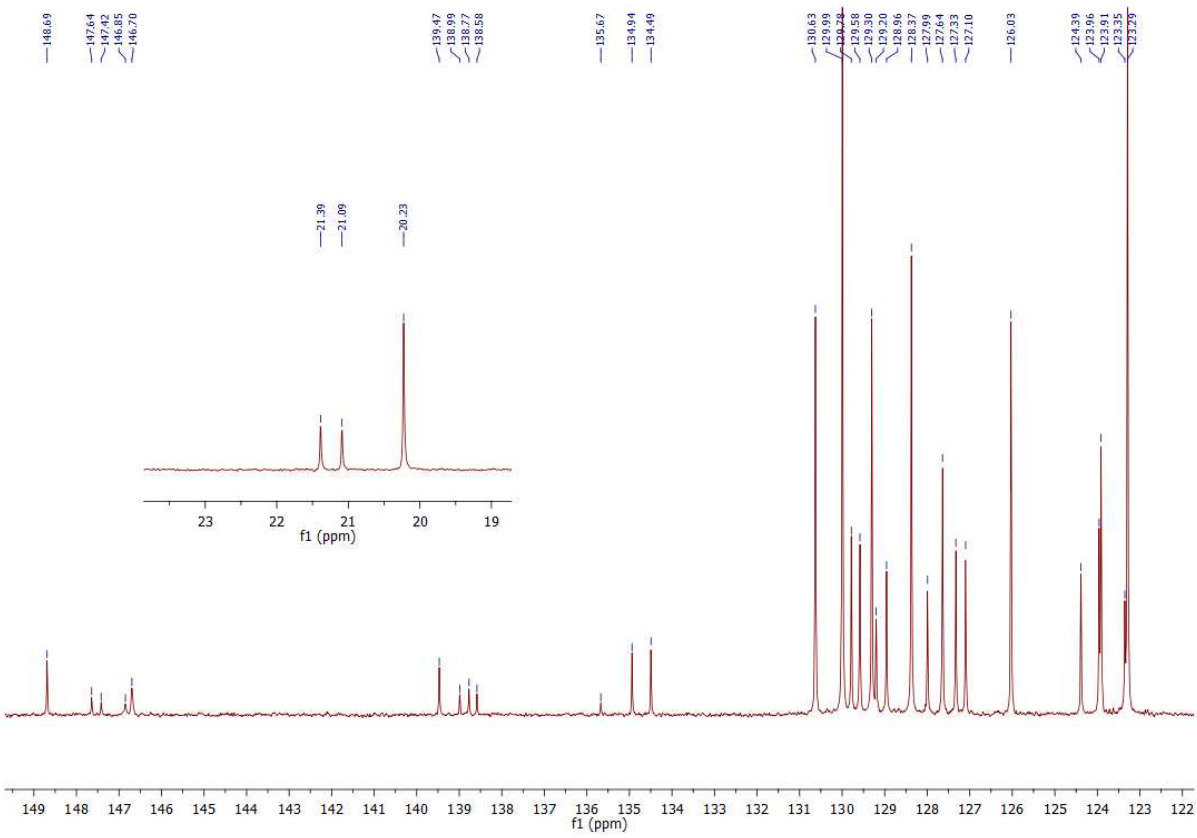




▶ **4-nitro-1,1'-biphenyl / 3-methyl-4'-nitro-1,1'-biphenyl / 4-methyl-4'-nitro-1,1'-biphenyl (1a)**



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138.77
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134.94
134.49
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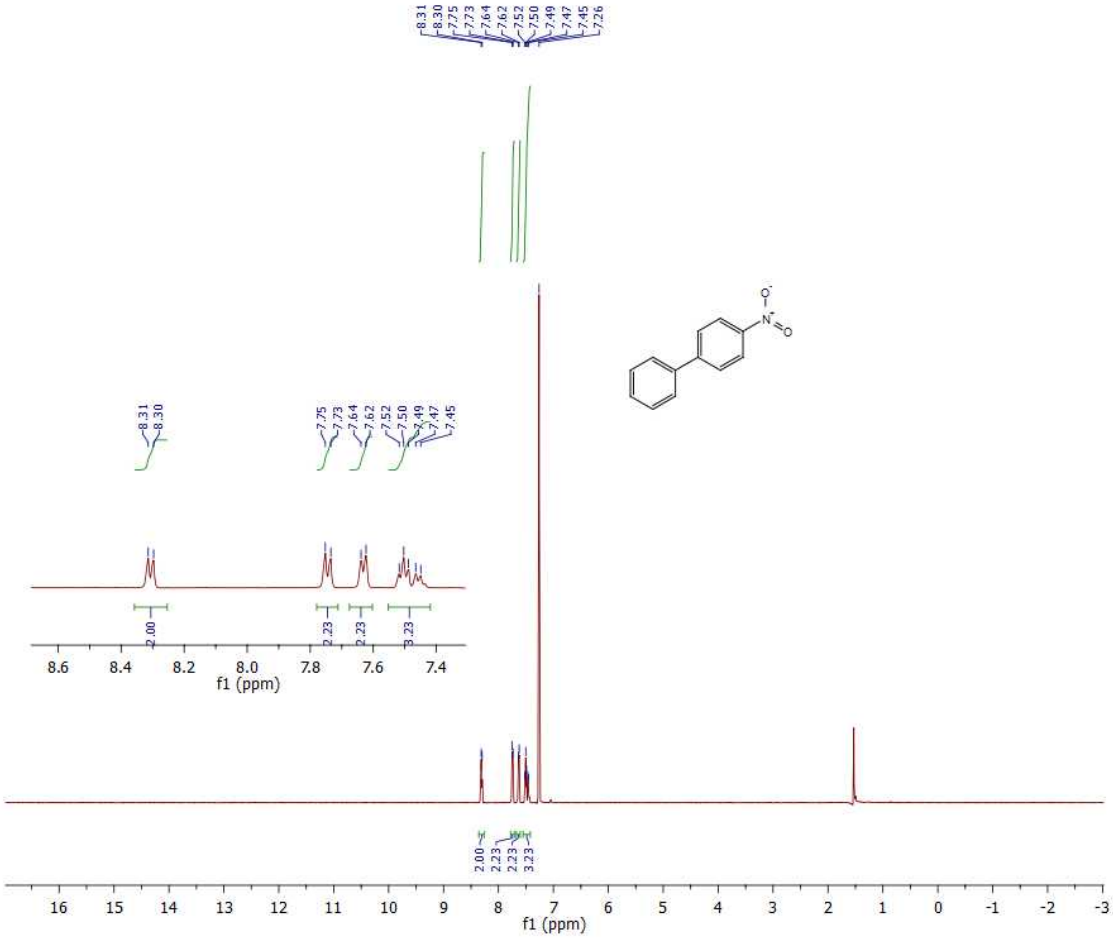
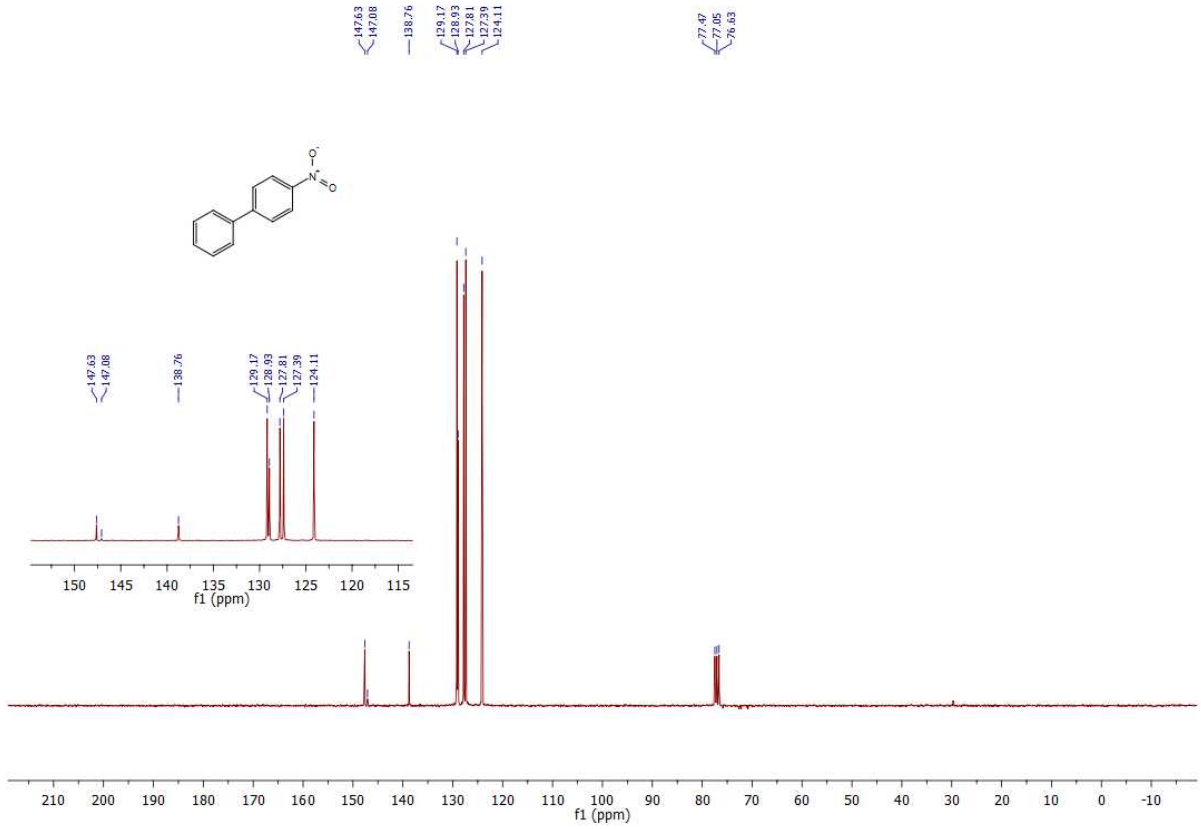
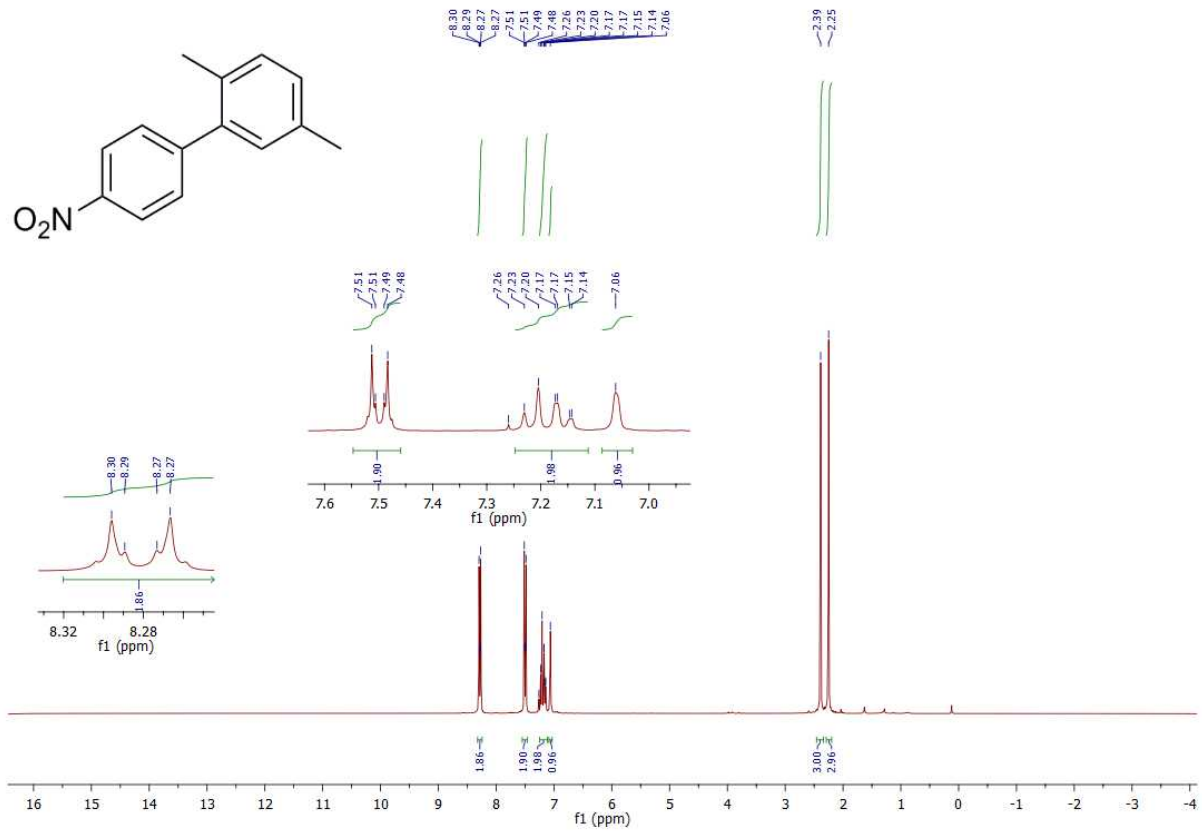
129.99
129.58
129.30
129.20
128.96
128.37
127.99
127.64
127.33
127.10
126.03
124.39
123.96
123.91
123.35
123.29
21.39
21.09
20.23
23
22
21
20
19
f1 (ppm)
149
148
147
146
145
144
143
142
141
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
f1 (ppm)

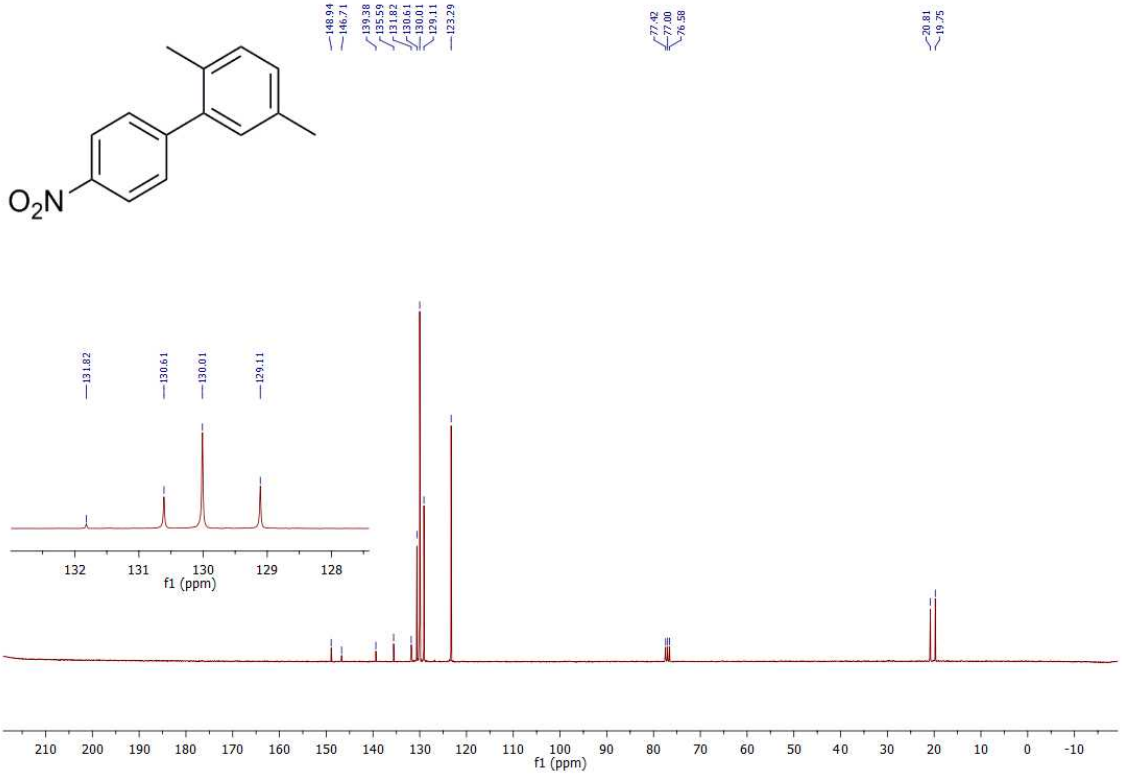
▶ **4-Nitro-biphenyl (1b)**



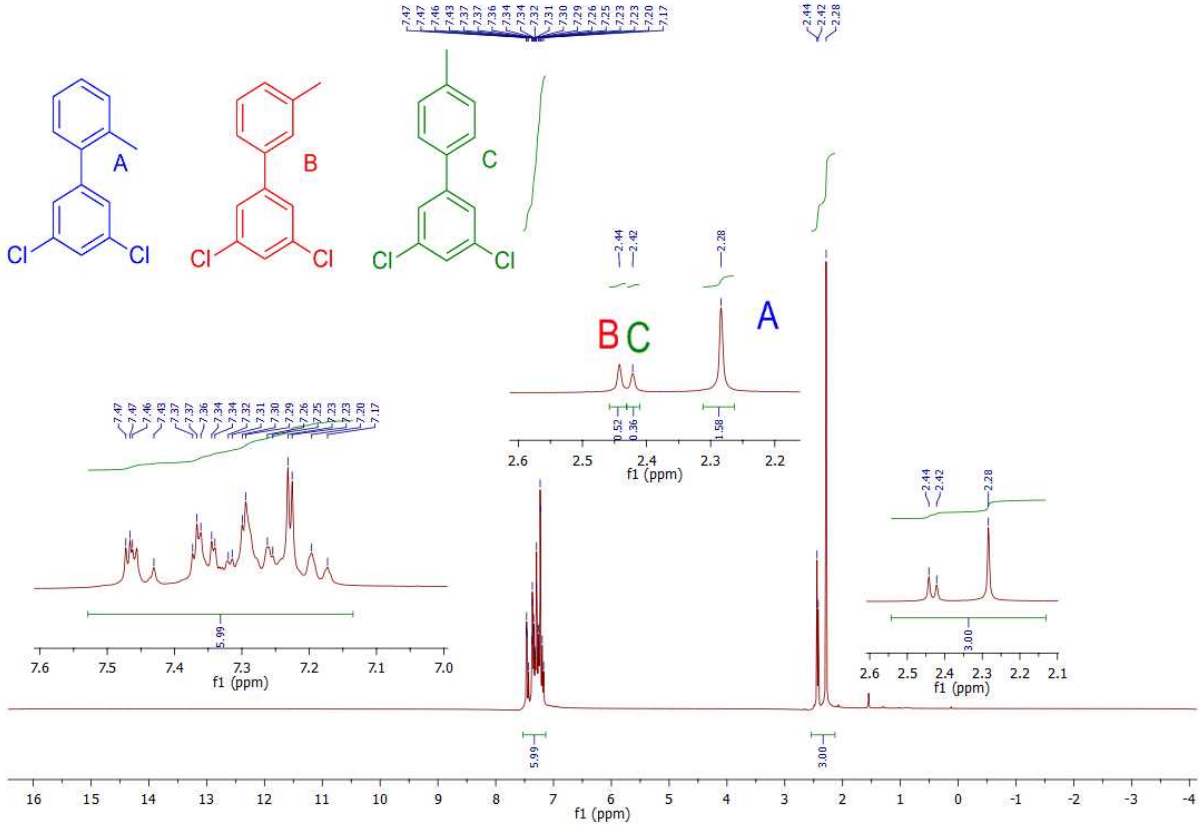


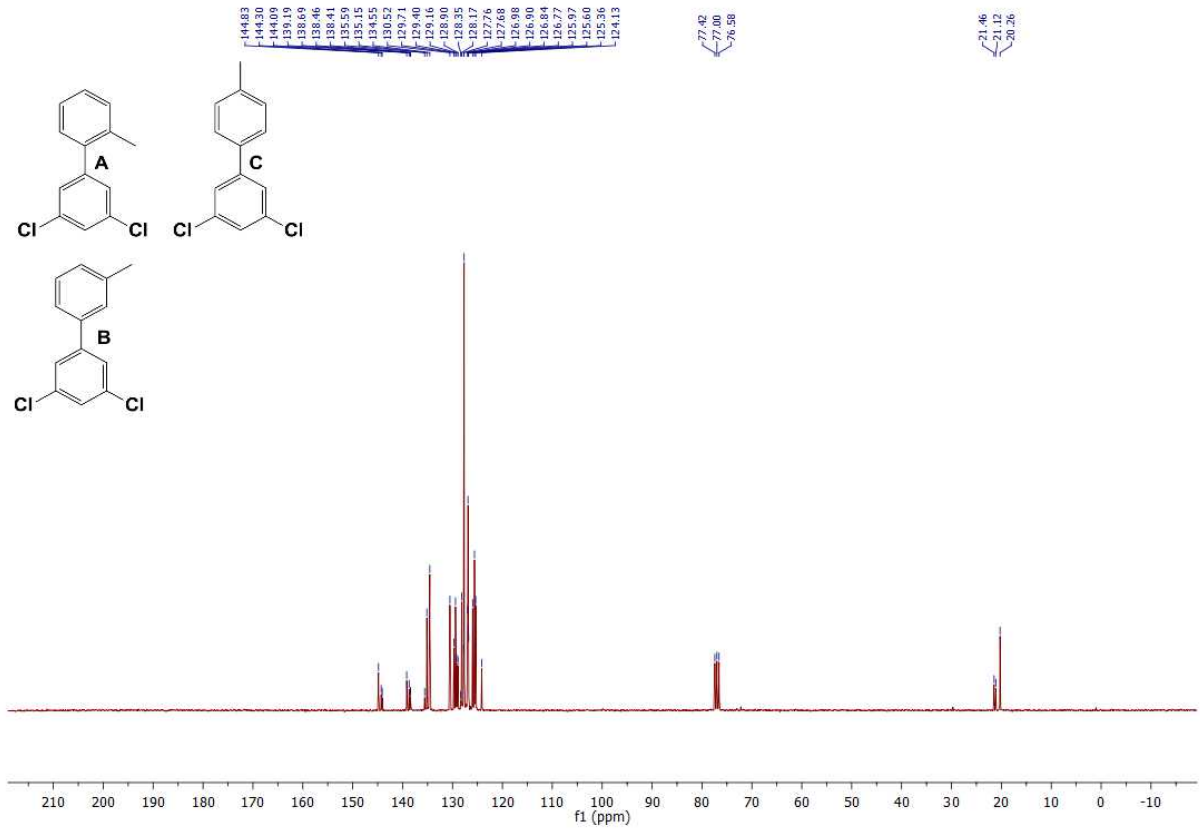
▶2,5-dimethyl-4'-nitro-1,1'-biphenyl (1c)

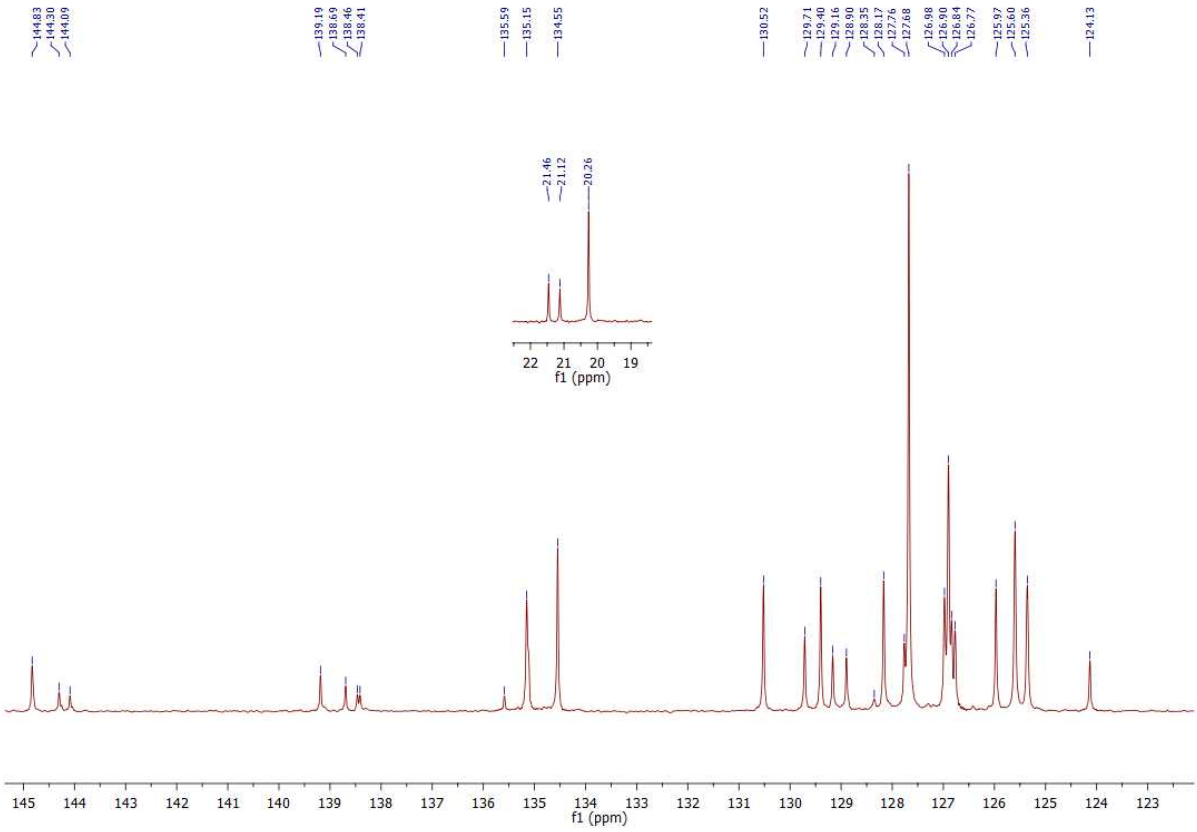




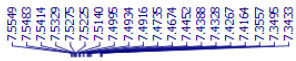
▶ 3',5'-dichloro-2-methyl-1,1'-biphenyl / 3,5-dichloro-3'-methyl-1,1'-biphenyl / 3,5-dichloro-4'-methyl-1,1'-biphenyl (1d)

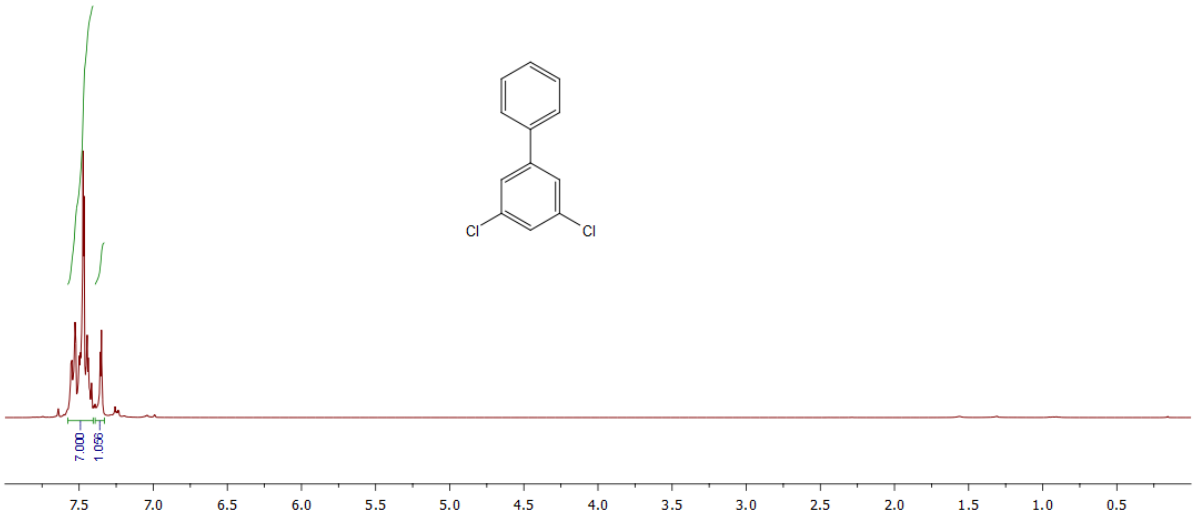


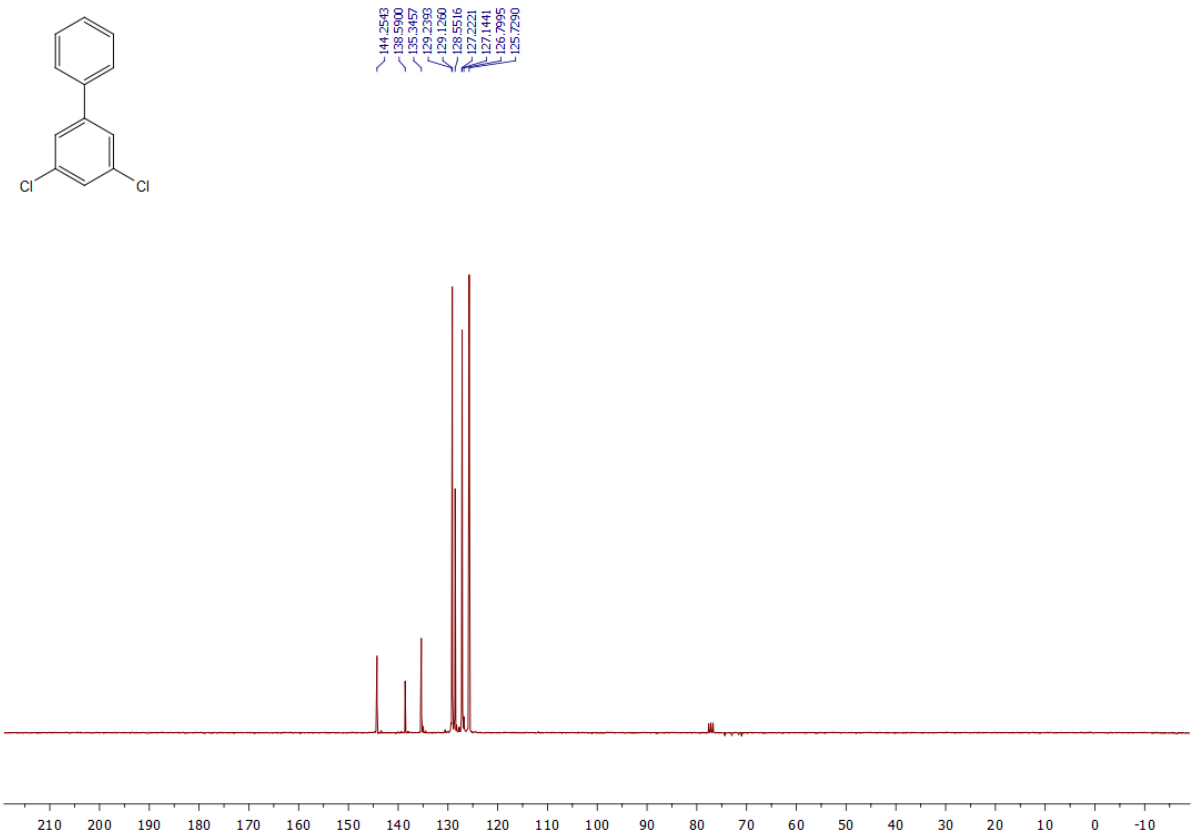




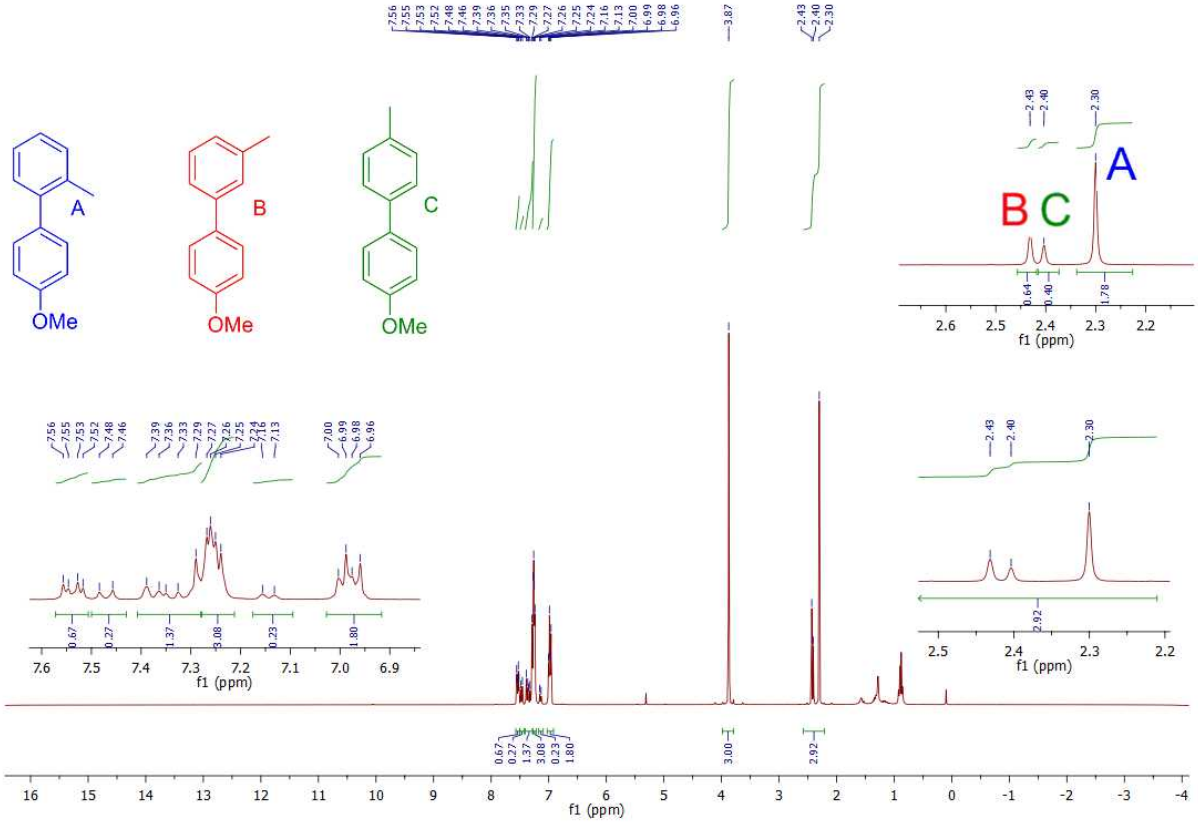
▶3,5-dichloro-1,1'-biphenyl (1e)

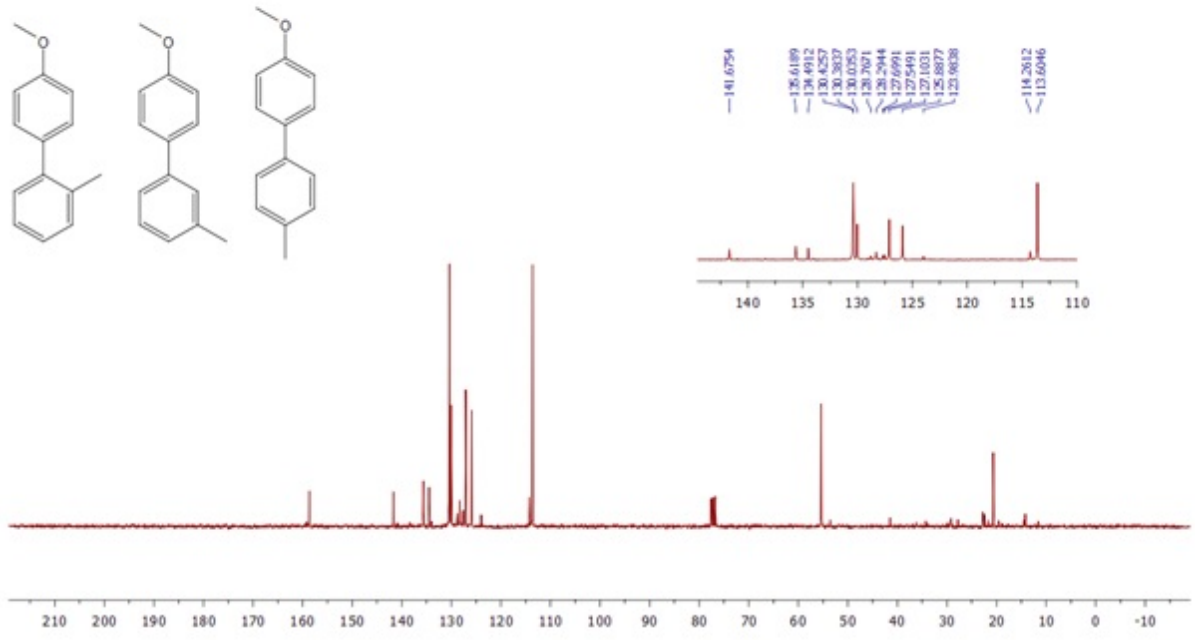




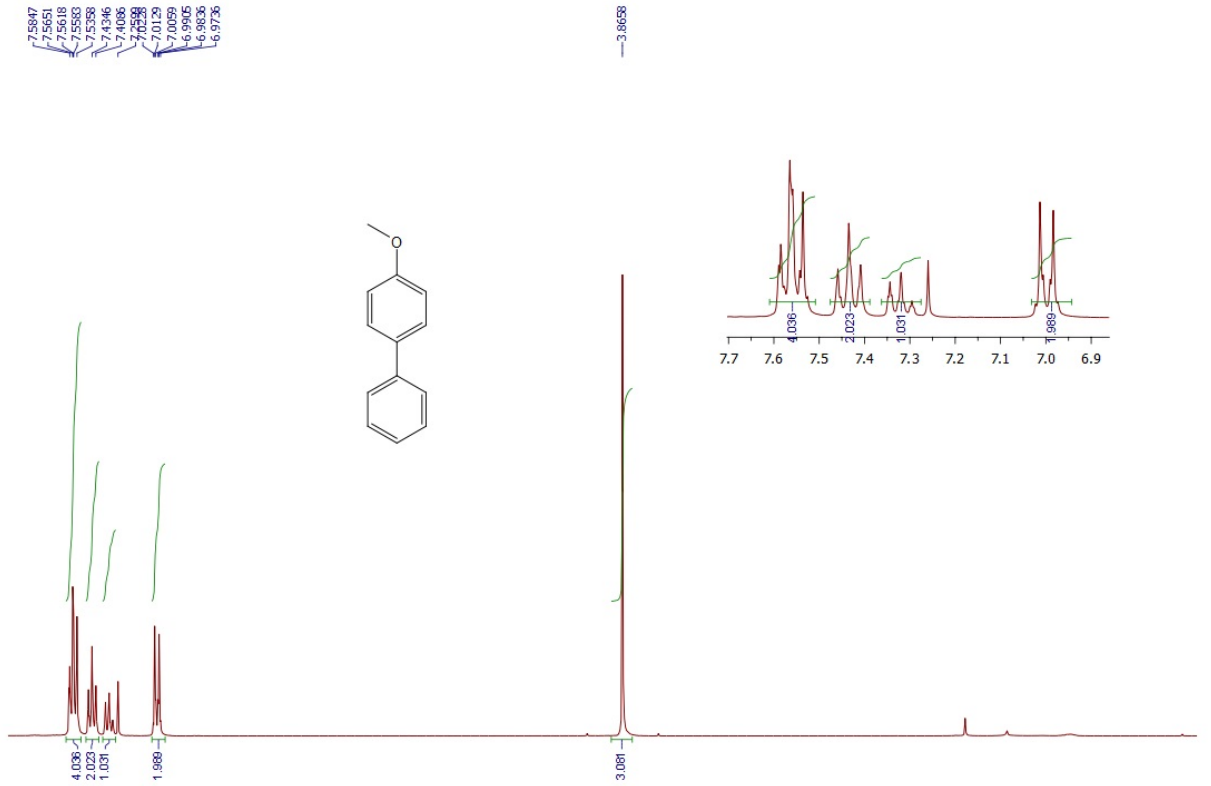

144.2543
138.5900
135.3457
129.2393
129.1260
128.5516
127.7221
127.1441
126.7995
125.7290
Cl
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

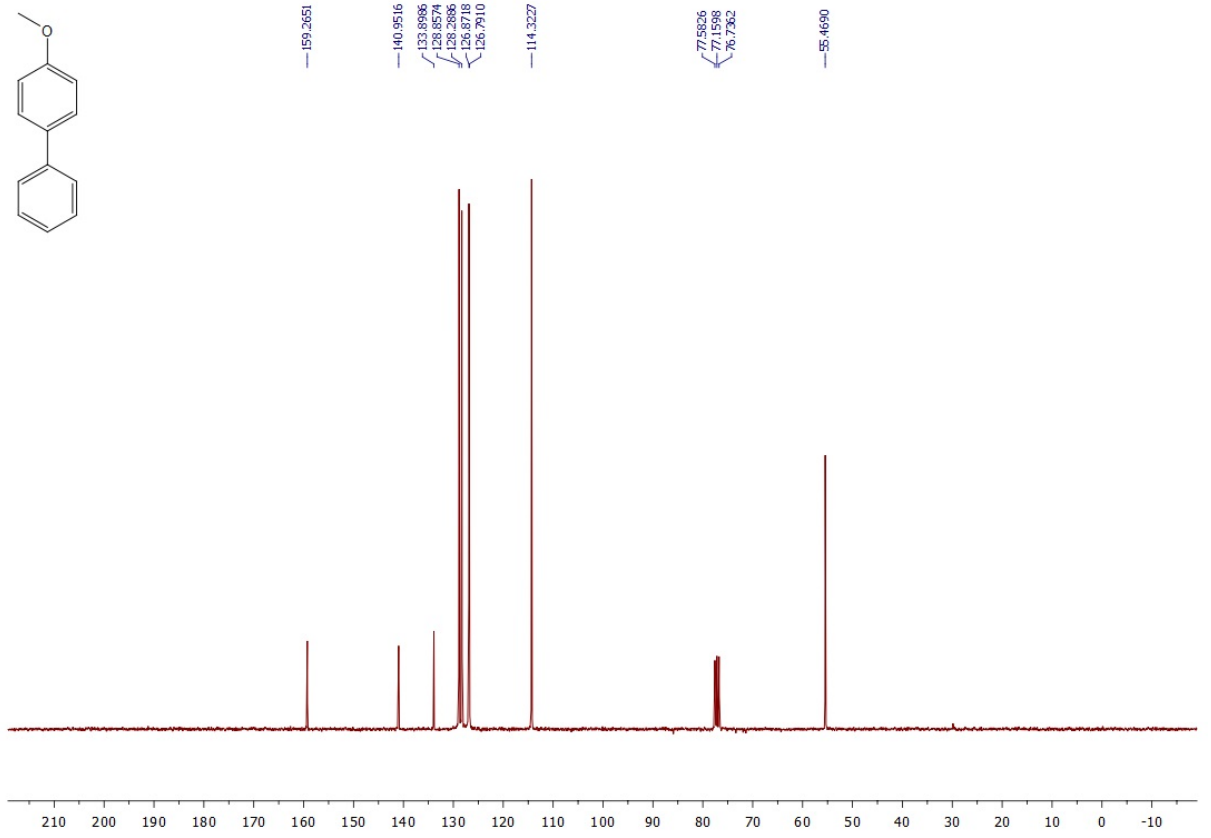
▶4'-methoxy-2-methyl-1,1'-biphenyl/4'-methoxy-3-methyl-1,1'-biphenyl/4-methoxy-4'-methyl-1,1'-biphenyl (1f)



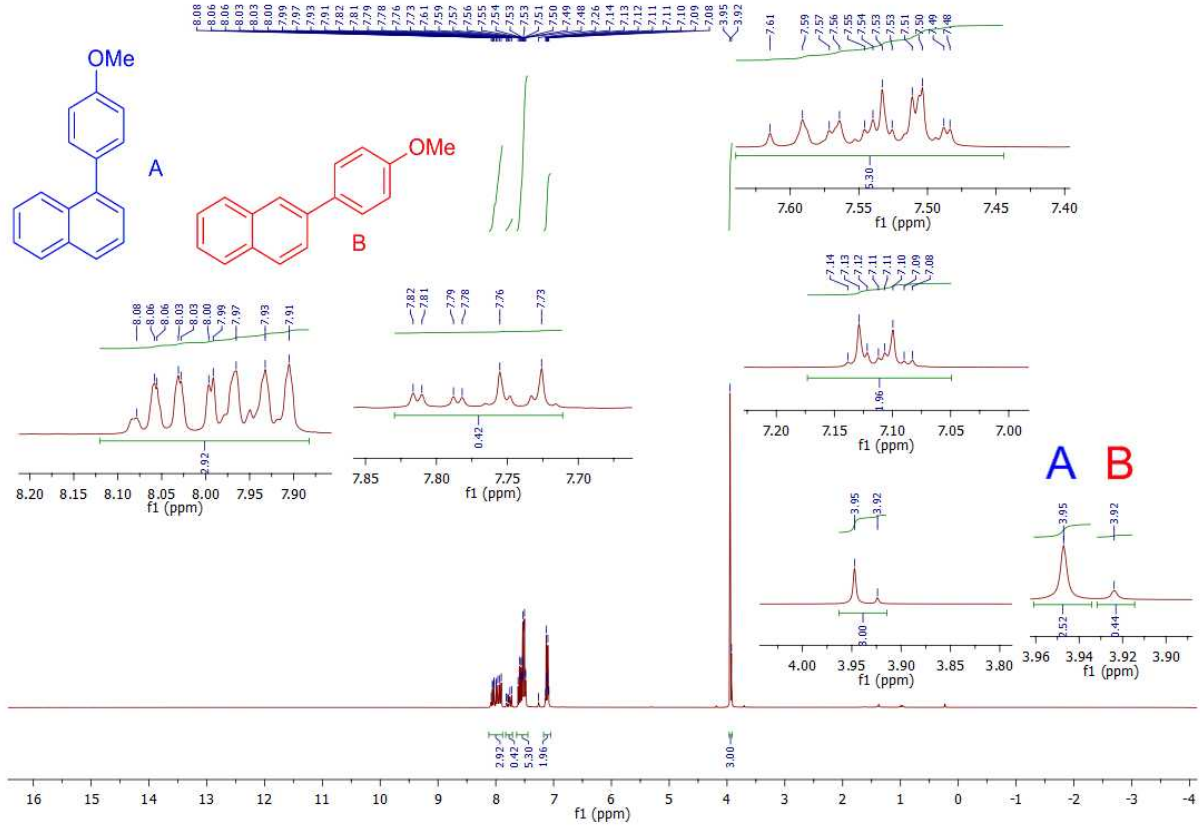


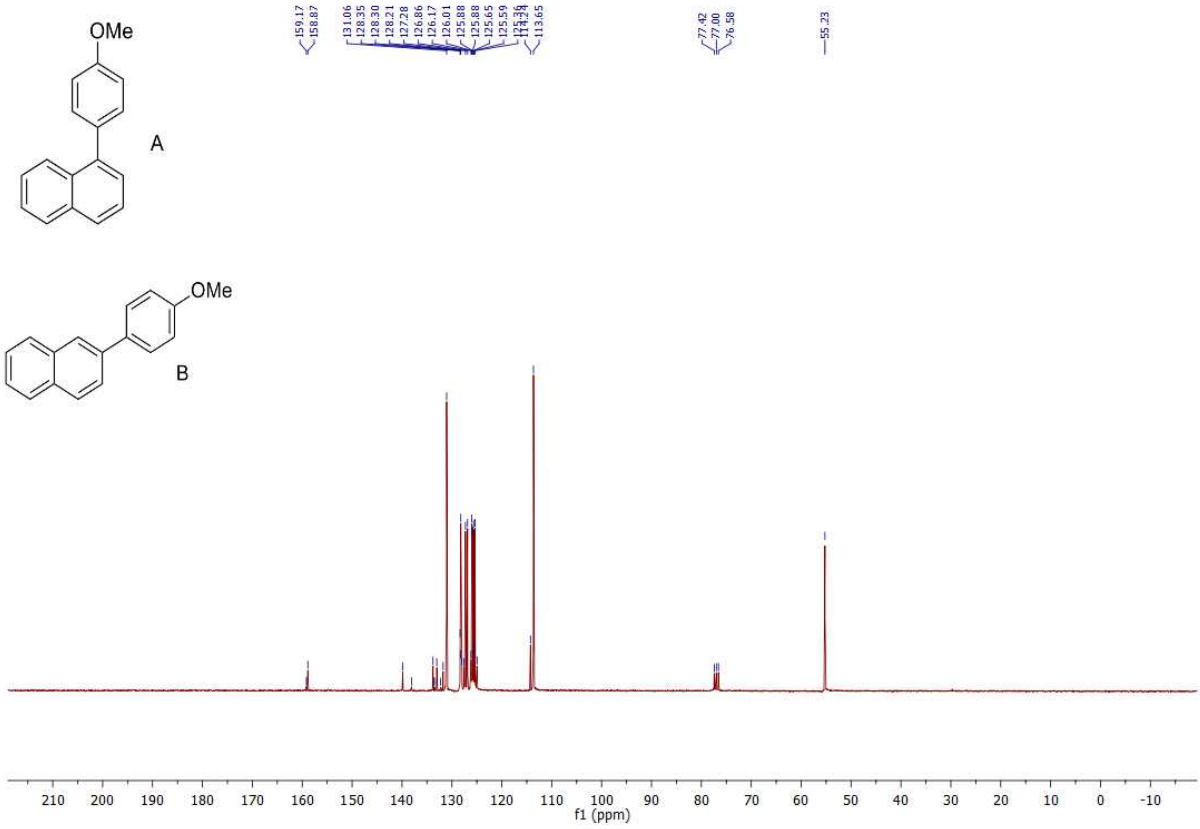
▶ 4-methoxy-1,1'-biphenyl (1g)

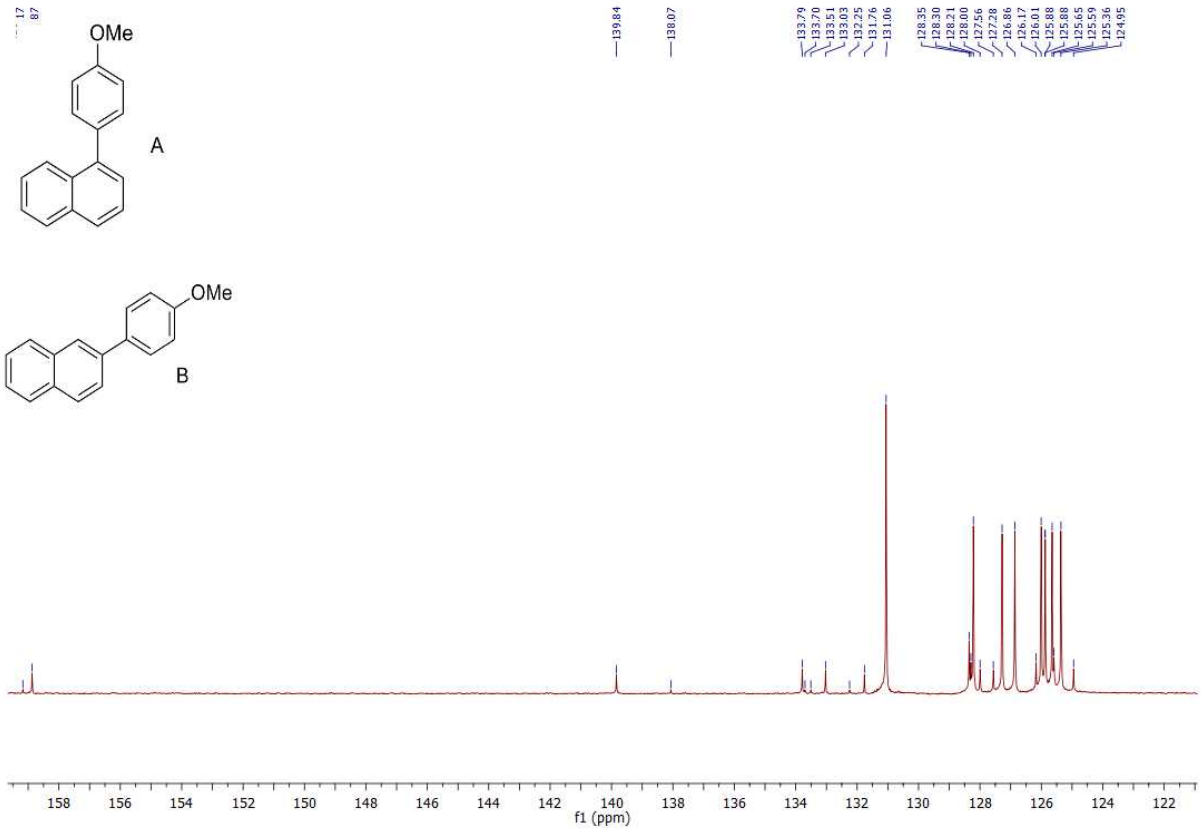




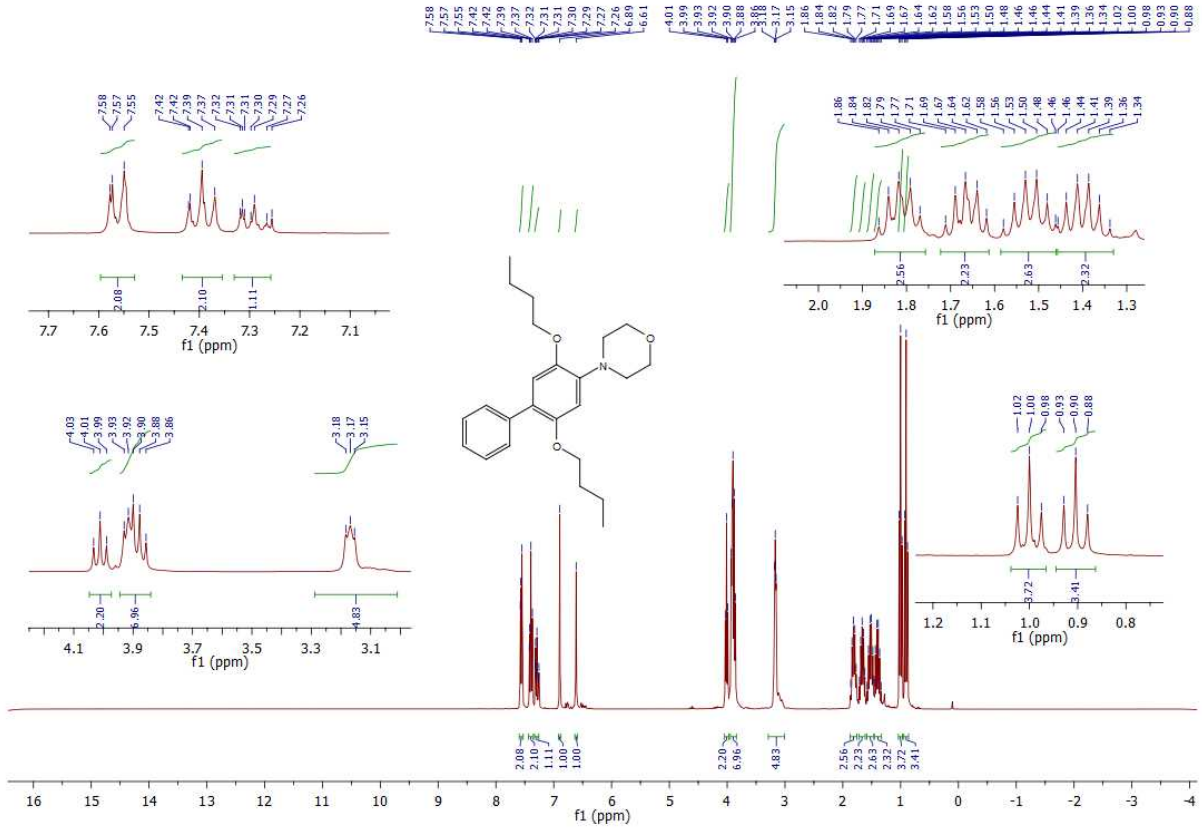
▶1-(4-methoxyphenyl)naphthalene / 2-(4-methoxyphenyl)naphthalene (1h)

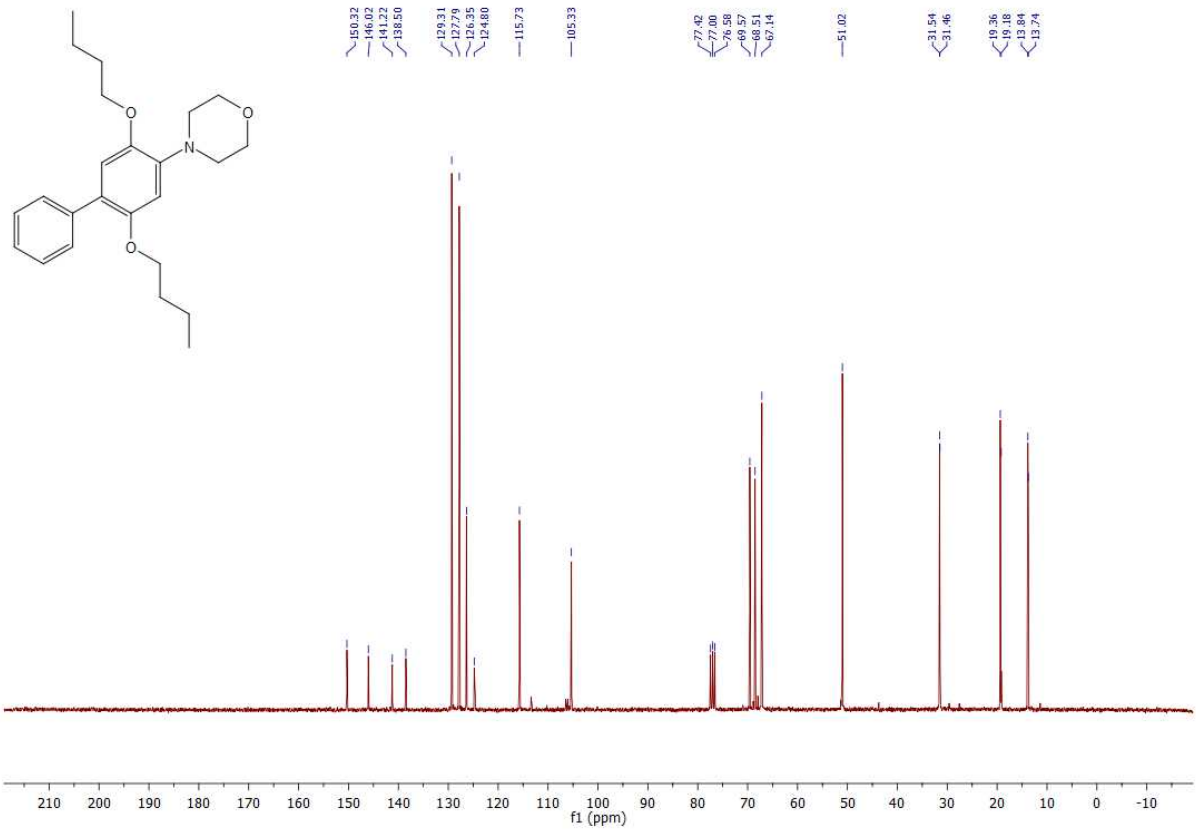




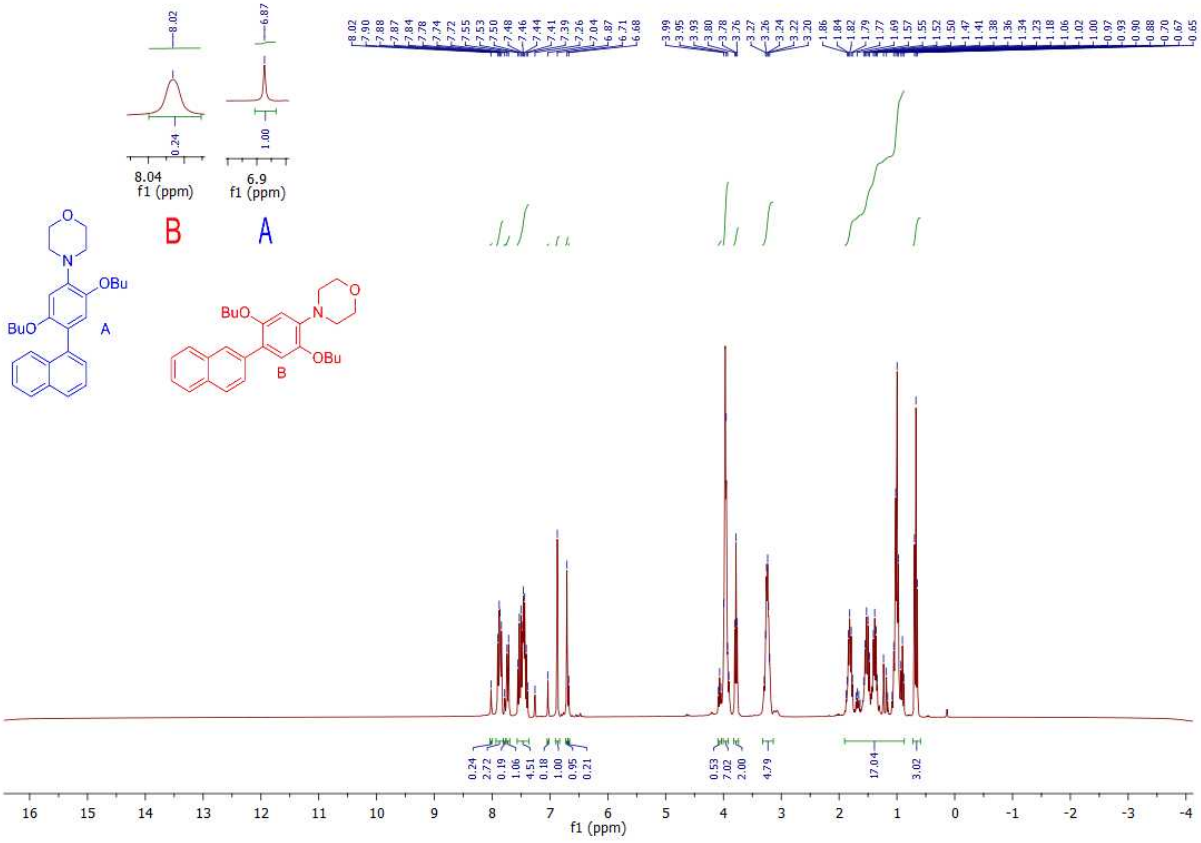


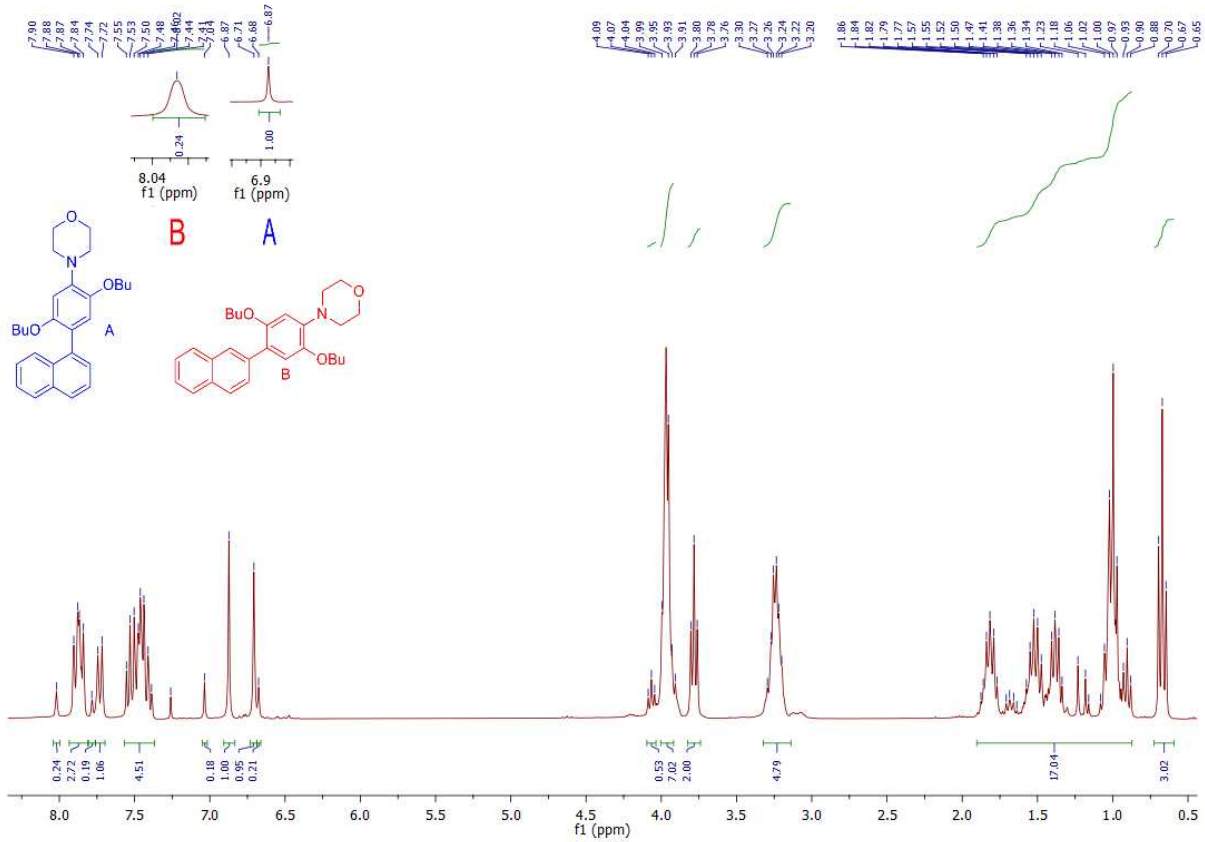
▶ 4-(2,5-dibutoxy-[1,1'-biphenyl]-4-yl)morpholine (1i)

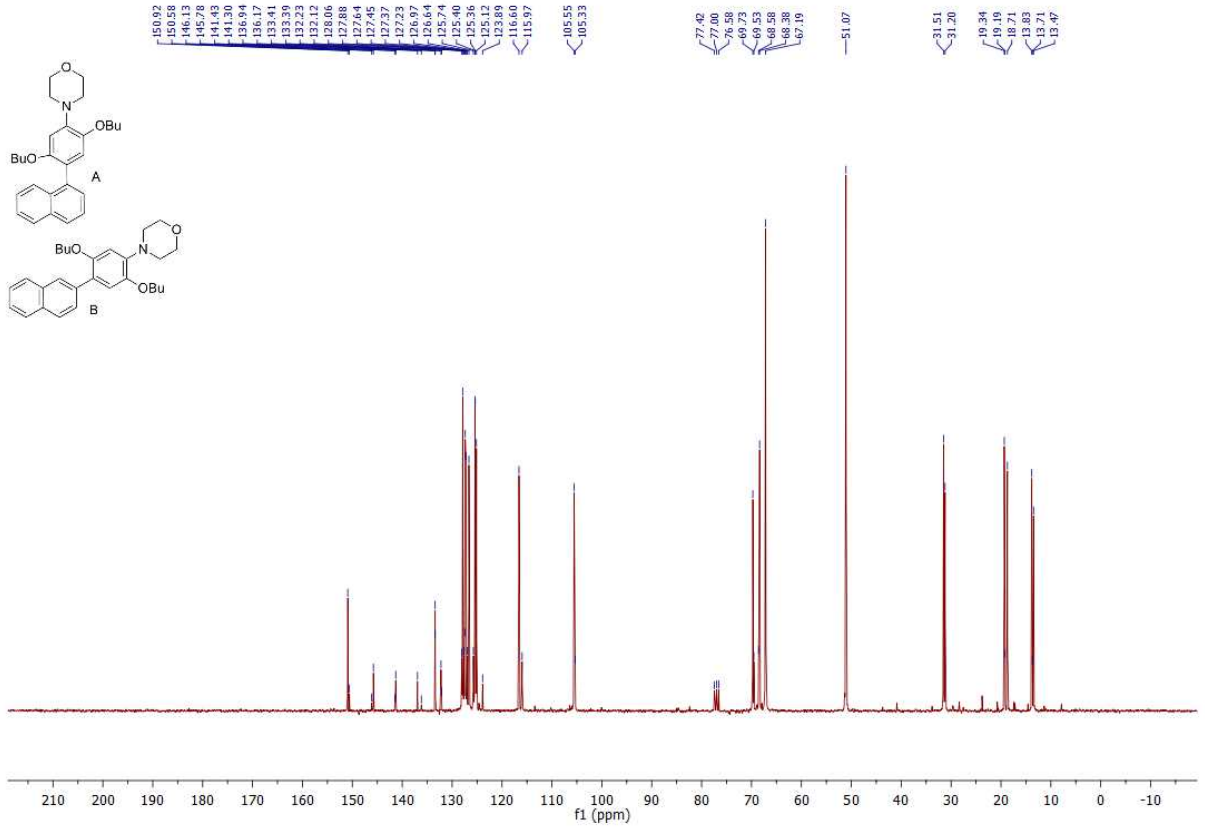


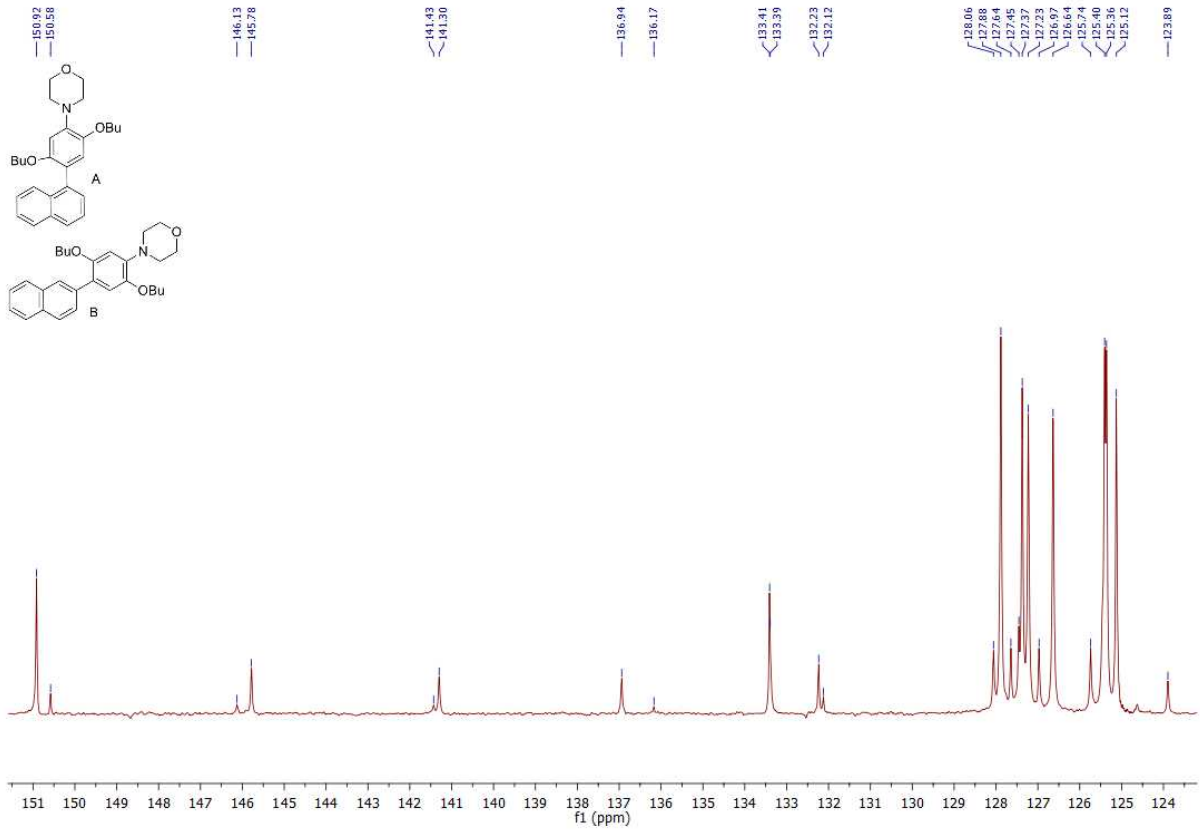


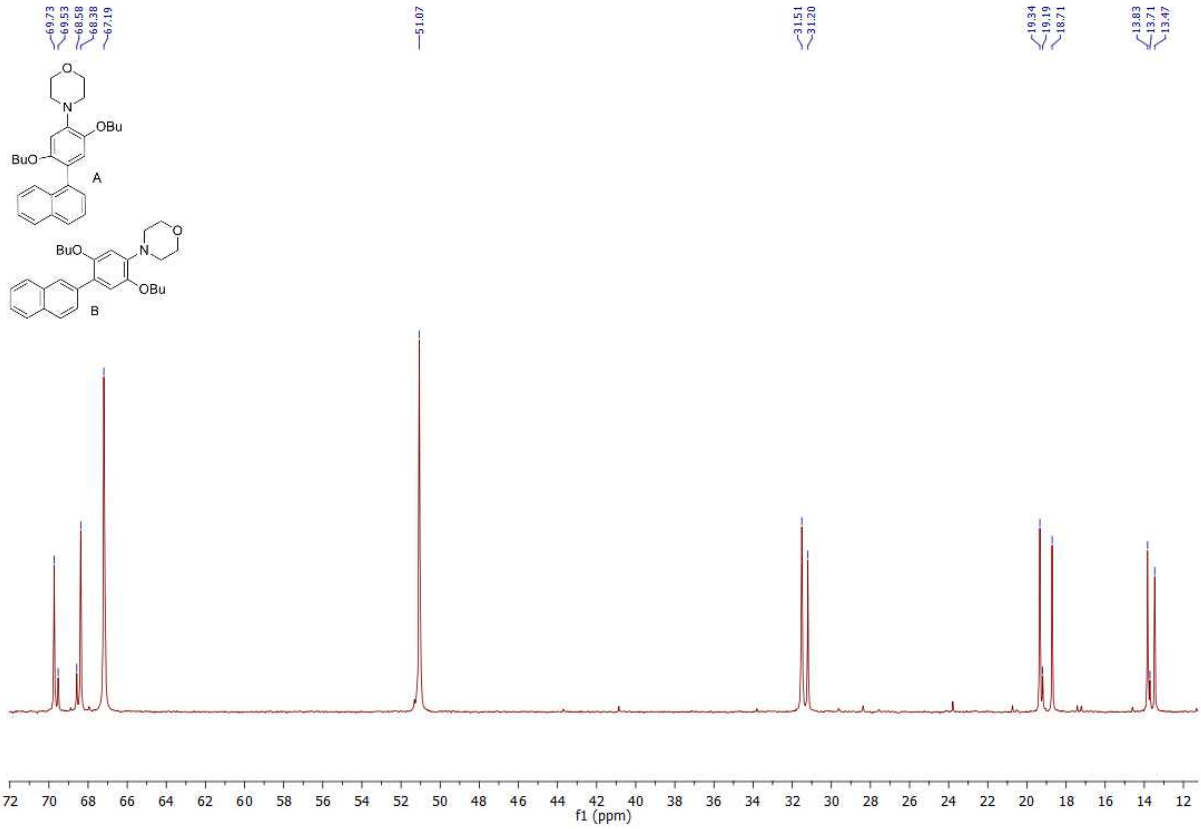
▶4-(2,5-dibutoxy-4-(naphthalen-1-yl)phenyl)morpholine / 4-(2,5-dibutoxy-4-(naphthalen-2-yl)phenyl)morpholine (1j)



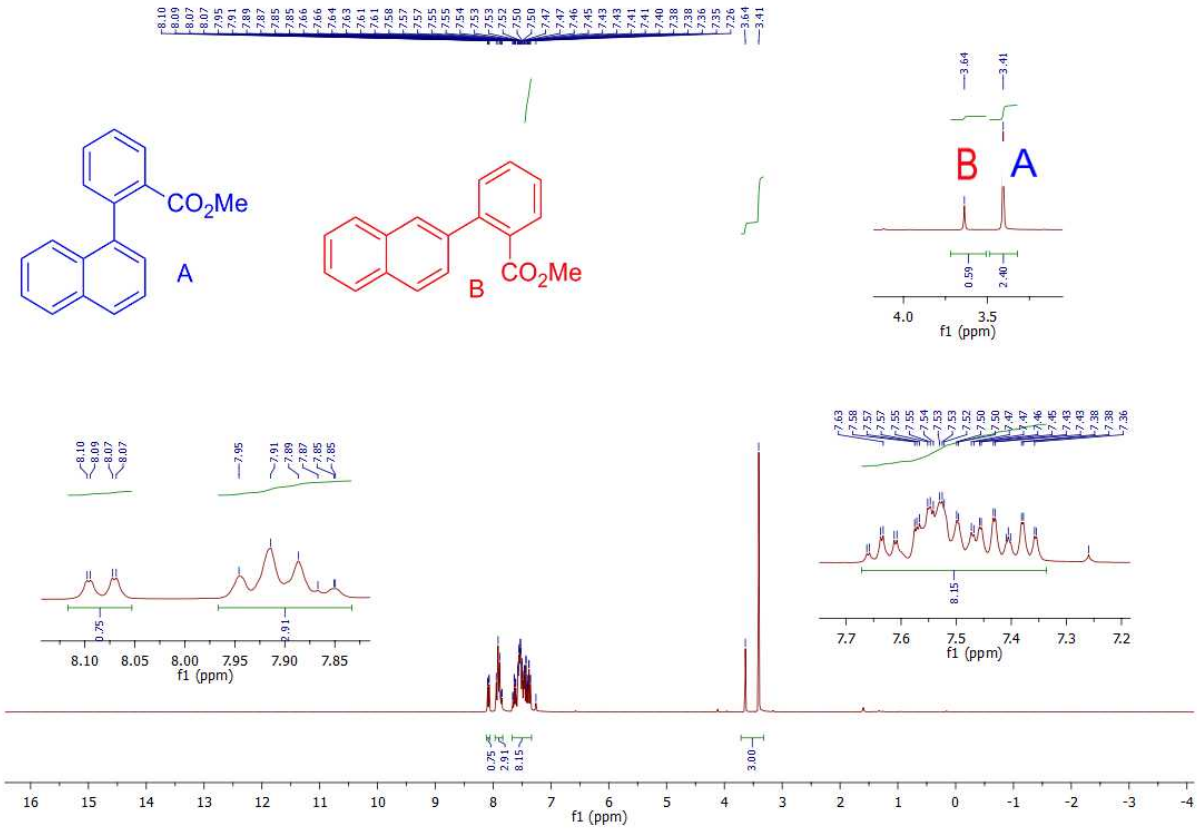

8.04
f1 (ppm)
6.9
f1 (ppm)
B
A
BuO
OBu
A
BuO
OBu
B
f1 (ppm)

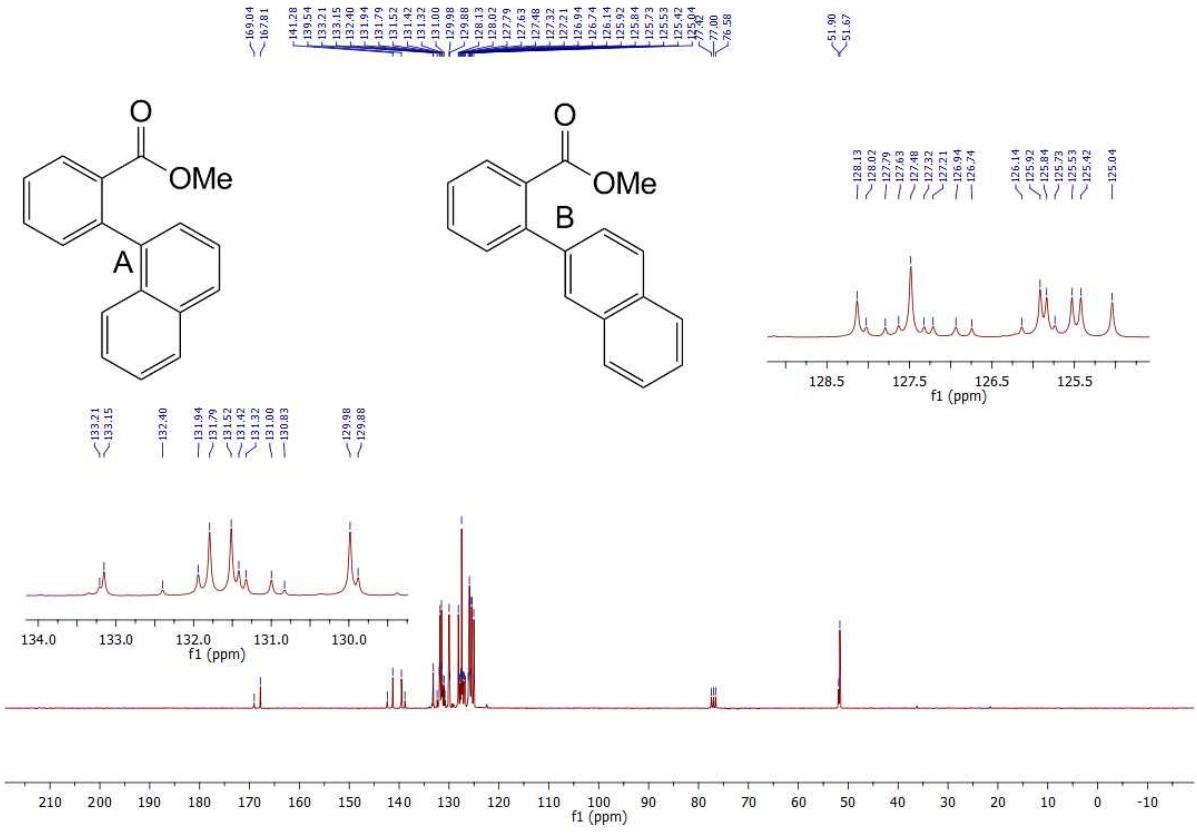

BuO
OBu
A
BuO
OBu
B
f1 (ppm)


150.92
150.58
146.13
145.78
141.43
141.30
136.94
136.17
133.41
133.39
132.23
132.12
128.06
127.88
127.64
127.45
127.37
127.23
126.97
126.64
125.74
125.40
125.36
125.12
123.89
OBu
BuO
A
BuO
OBu
B
151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)

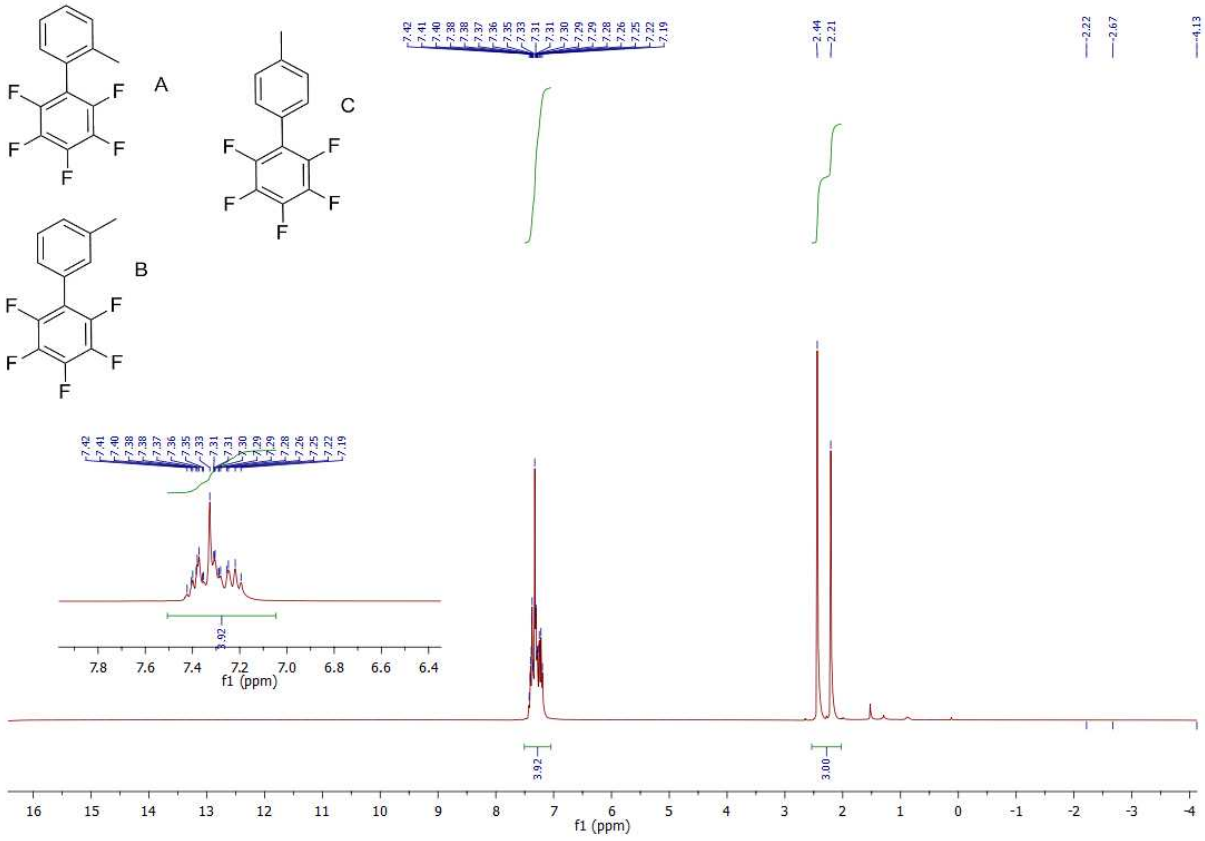

69.73
69.53
68.58
68.38
67.19
51.07
31.51
31.20
19.34
19.19
18.71
13.83
13.71
13.47
OBu
BuO
A
BuO
OBu
B
72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12
f1 (ppm)

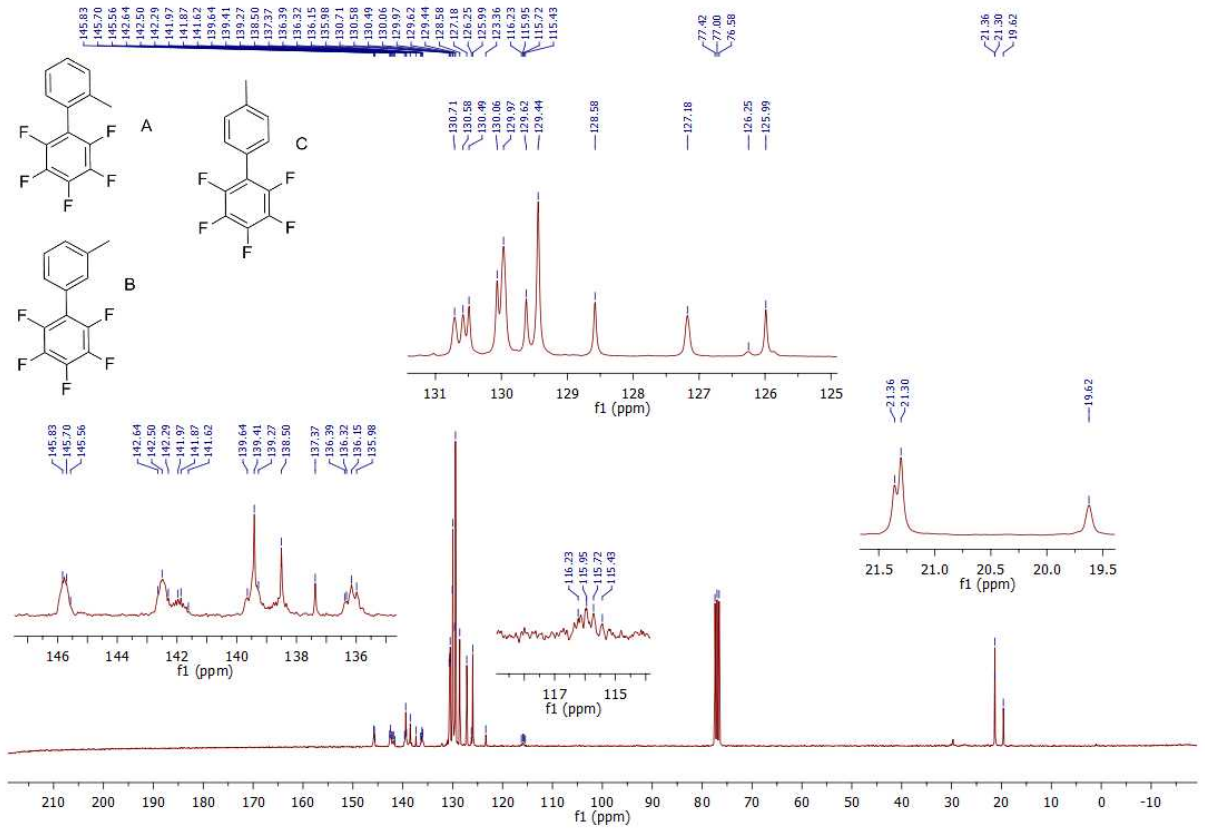
▶ Methyl 2-(naphthalen-1-yl)-benzoate / Methyl 2-(naphthalen-2-yl)-benzoate (1k)

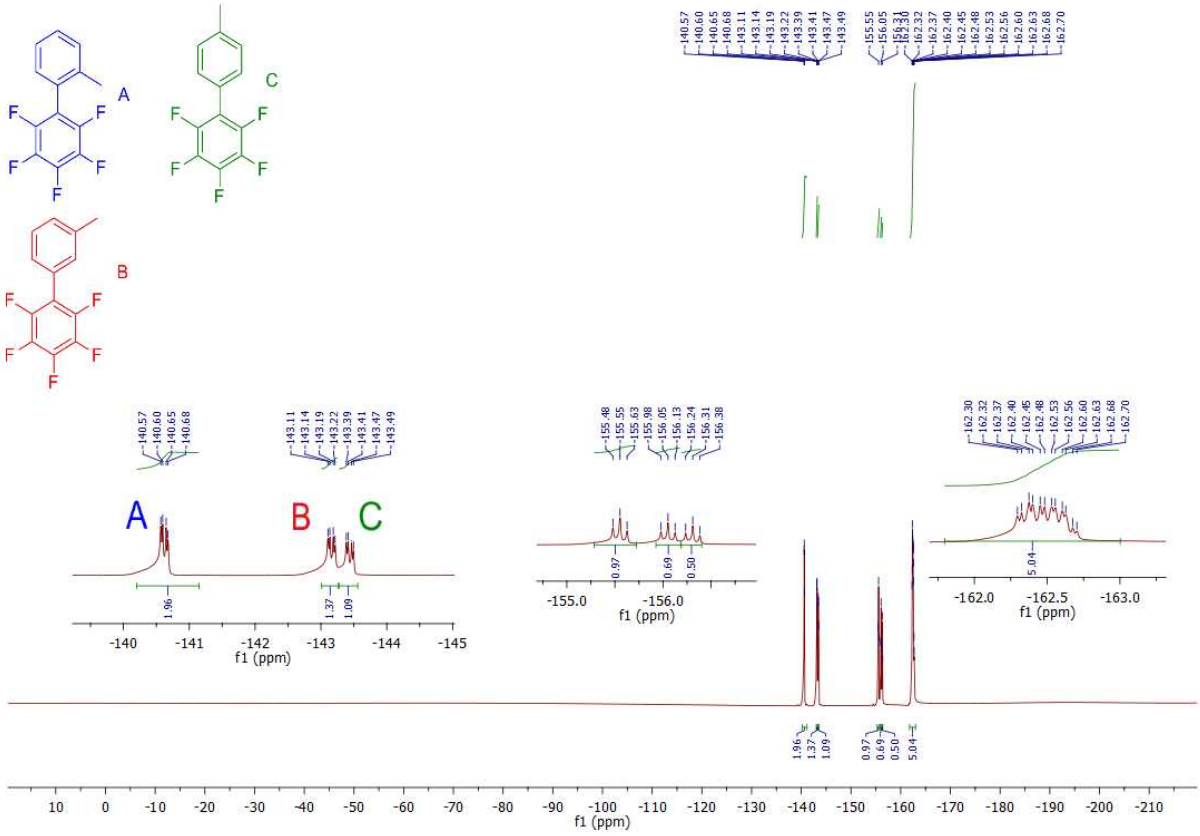




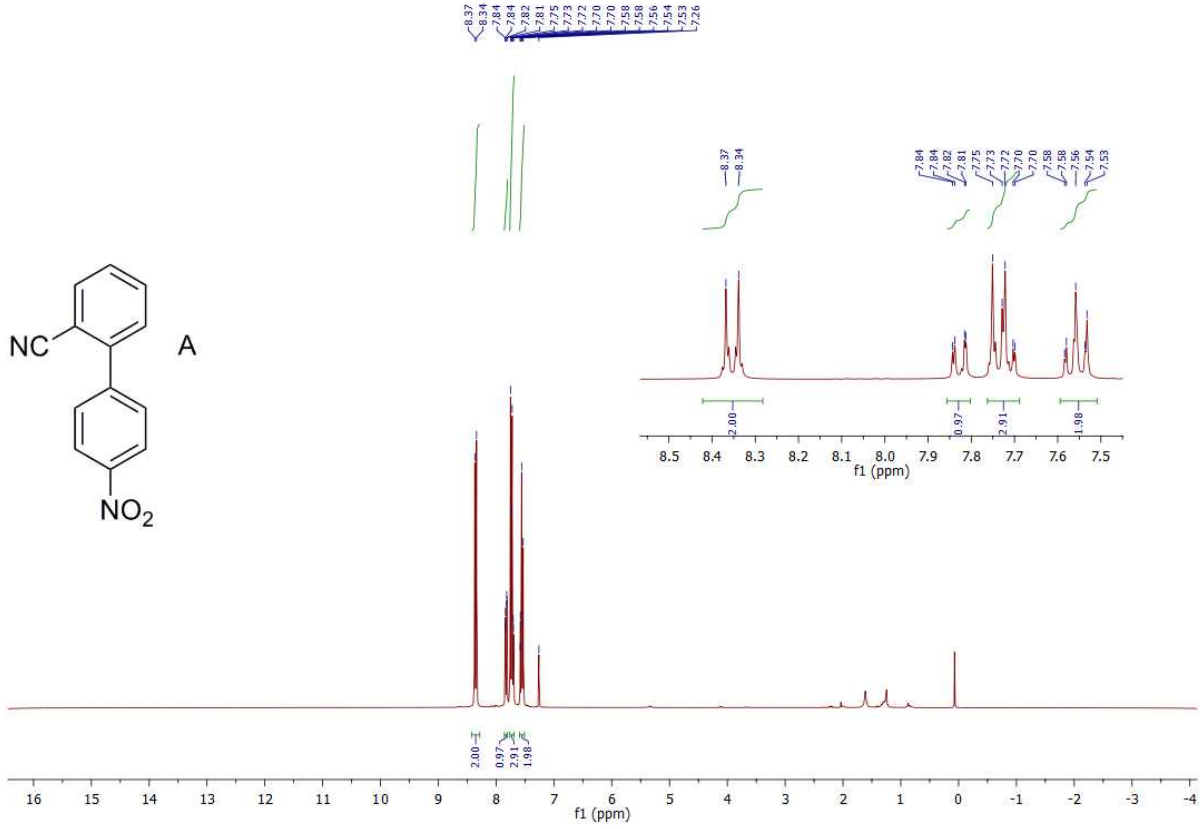
▶2,3,4,5,6-pentafluoro-2'-methyl-1,1'-biphenyl/2,3,4,5,6-pentafluoro-3'-methyl-1,1'-biphenyl/ 2,3,4,5,6-pentafluoro-4'-methyl-1,1'-biphenyl (1l)

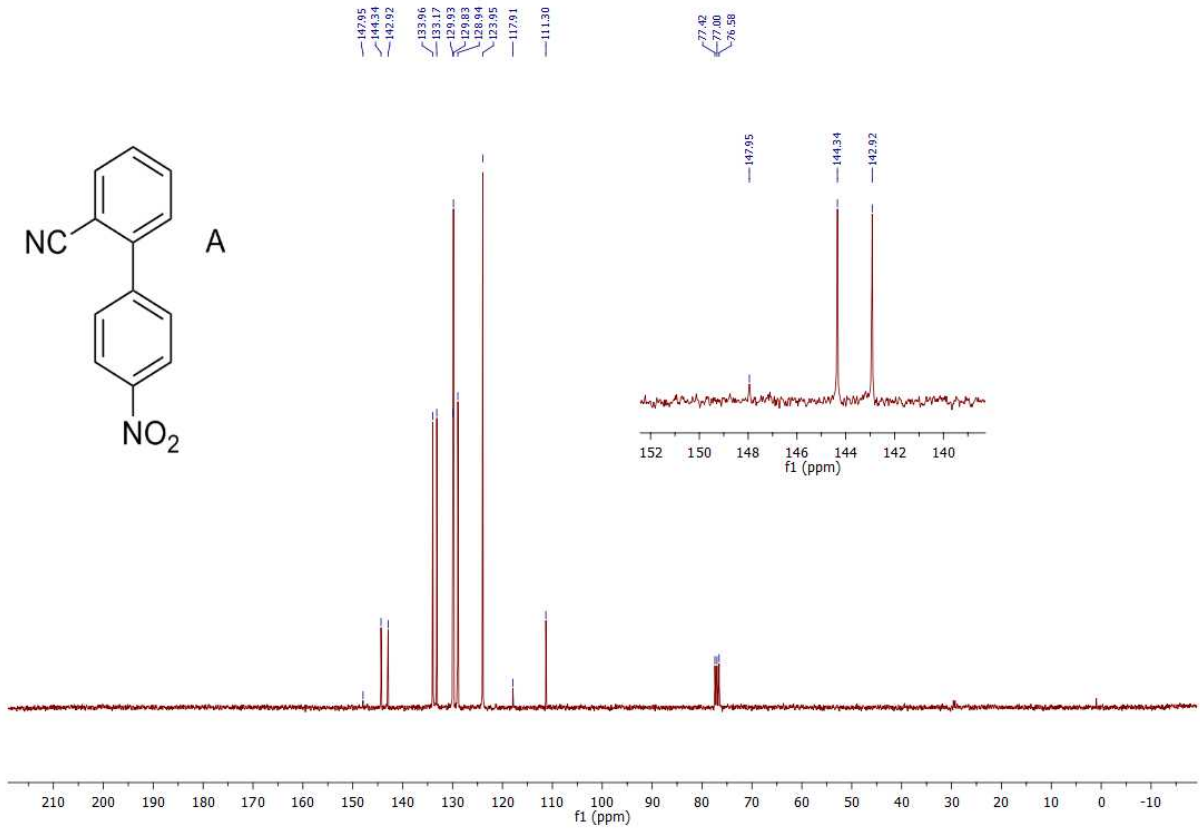


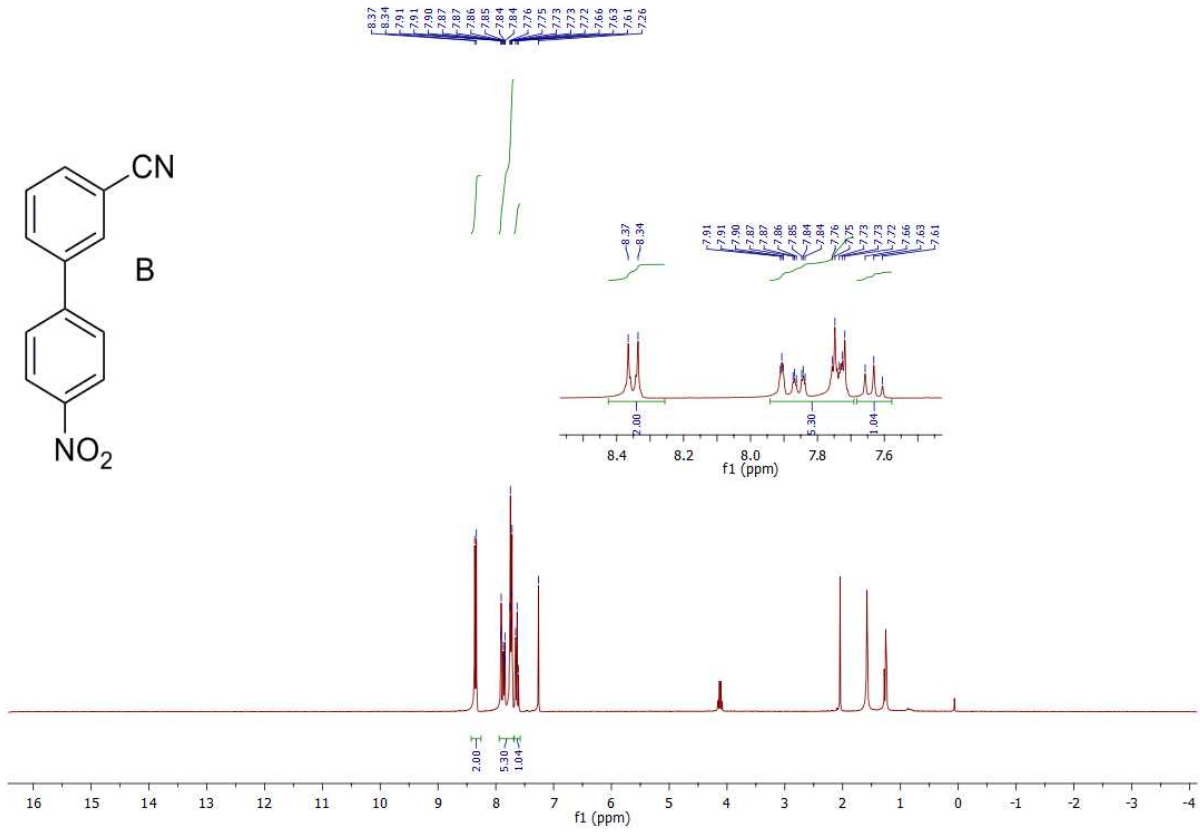


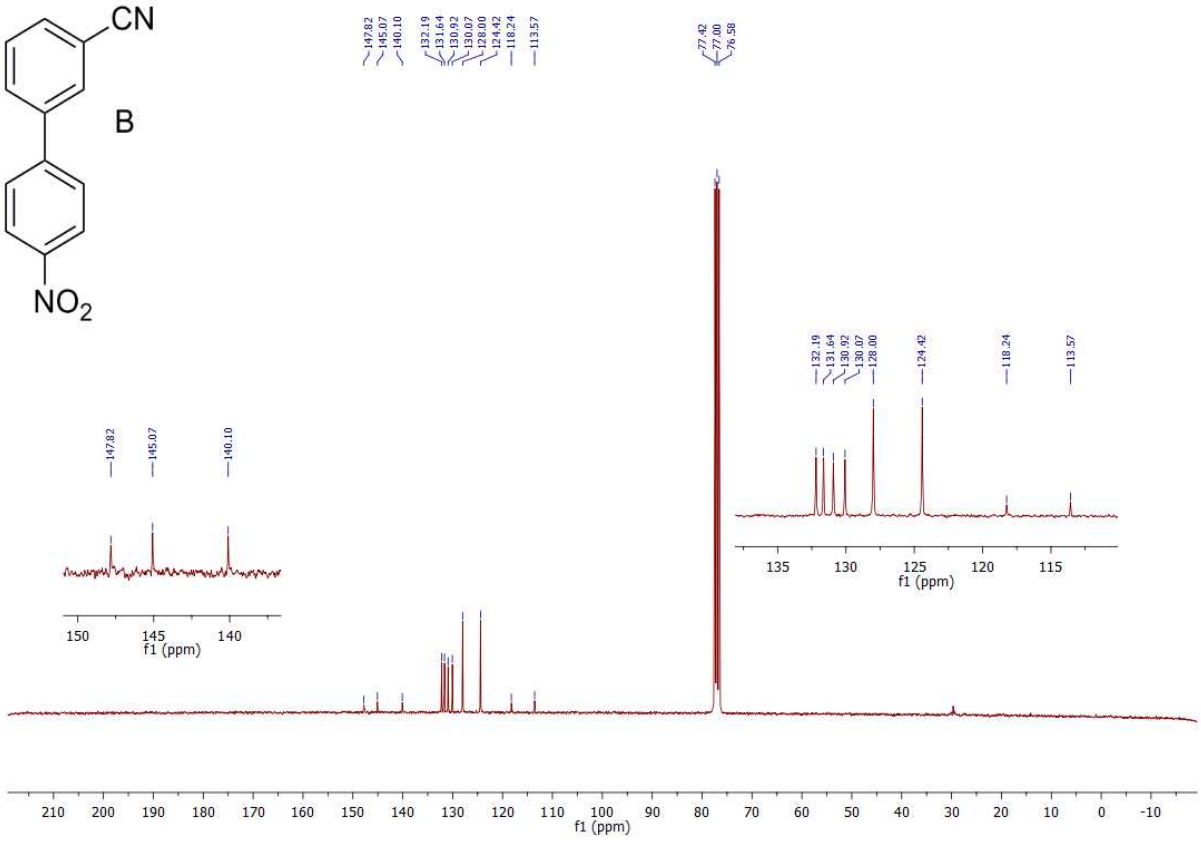

A
B
C
F
140.57
140.60
140.65
140.68
143.11
143.14
143.19
143.22
143.39
143.41
143.47
143.49
155.55
156.05
156.31
162.32
162.37
162.40
162.45
162.48
162.53
162.56
162.60
162.63
162.68
162.70
1.96
1.37
1.09
0.97
0.69
0.50
5.04
f1 (ppm)

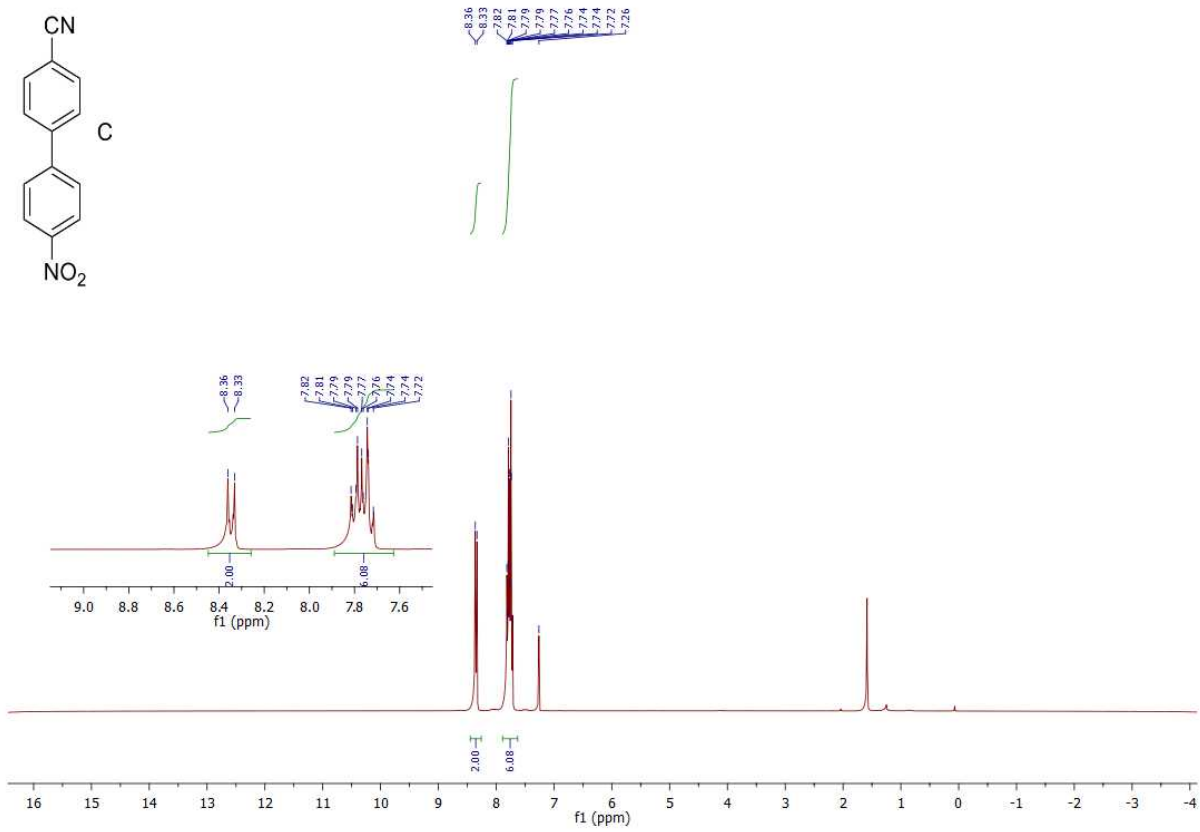
▶4'-nitro-[1,1'-biphenyl]-2-carbonitrile/4'-nitro-[1,1'-biphenyl]-3-carbonitrile/4'-nitro-[1,1'-biphenyl]-4-carbonitrile (2a)

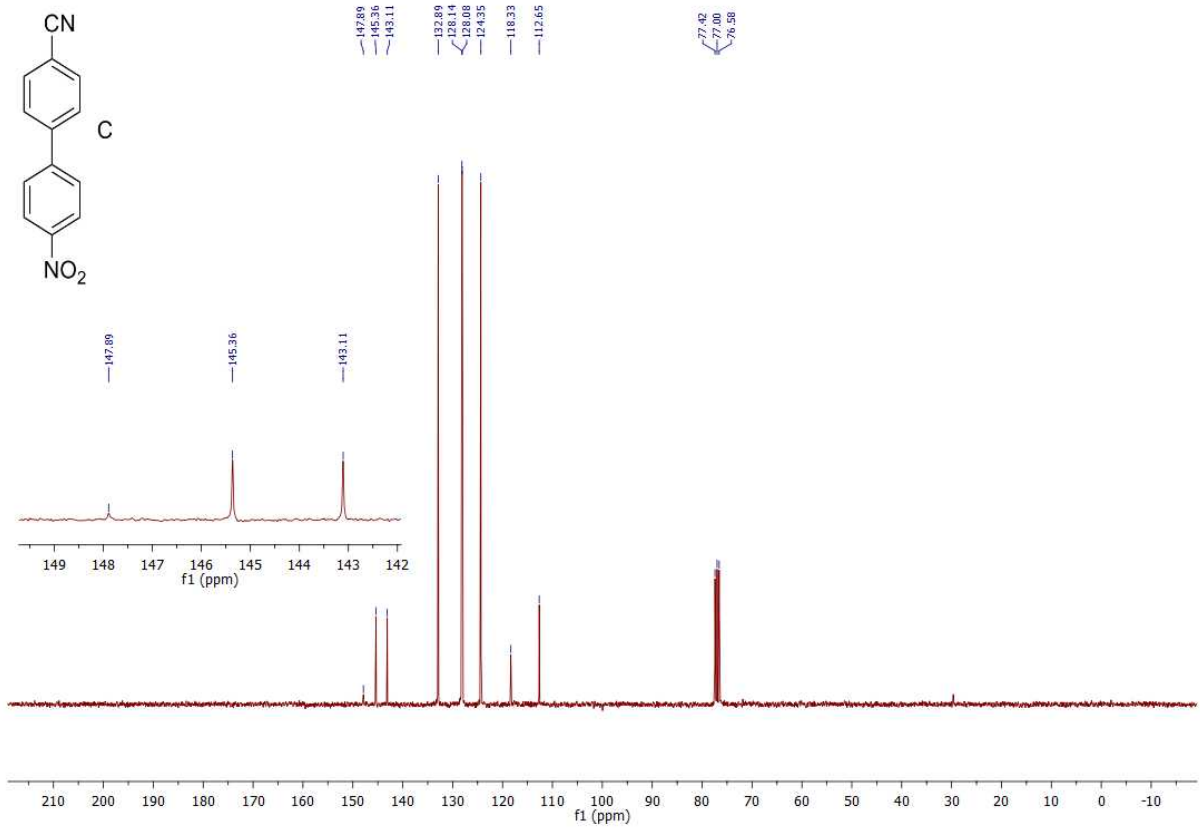




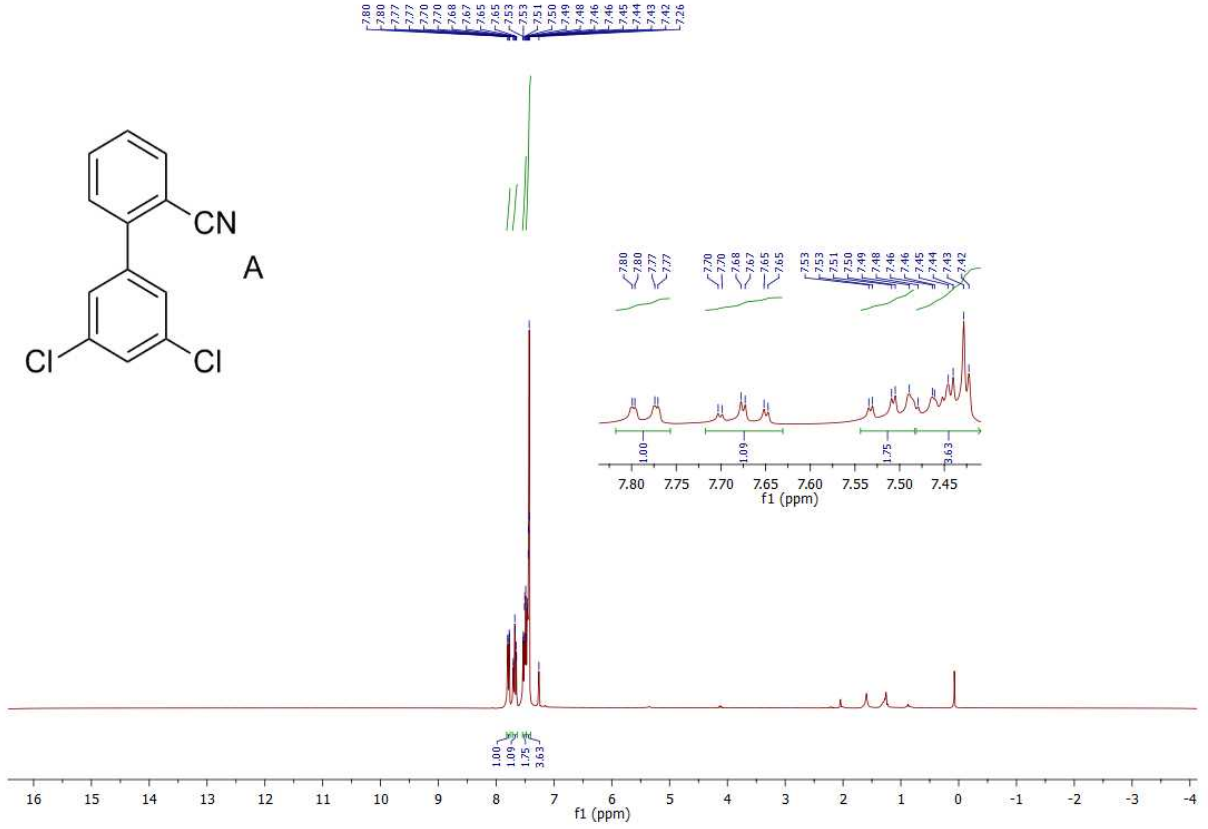

CN
B
NO2
8.37
8.34
7.91
7.90
7.87
7.86
7.85
7.84
7.76
7.75
7.73
7.72
7.66
7.63
7.61
2.00
5.30
1.04
f1 (ppm)

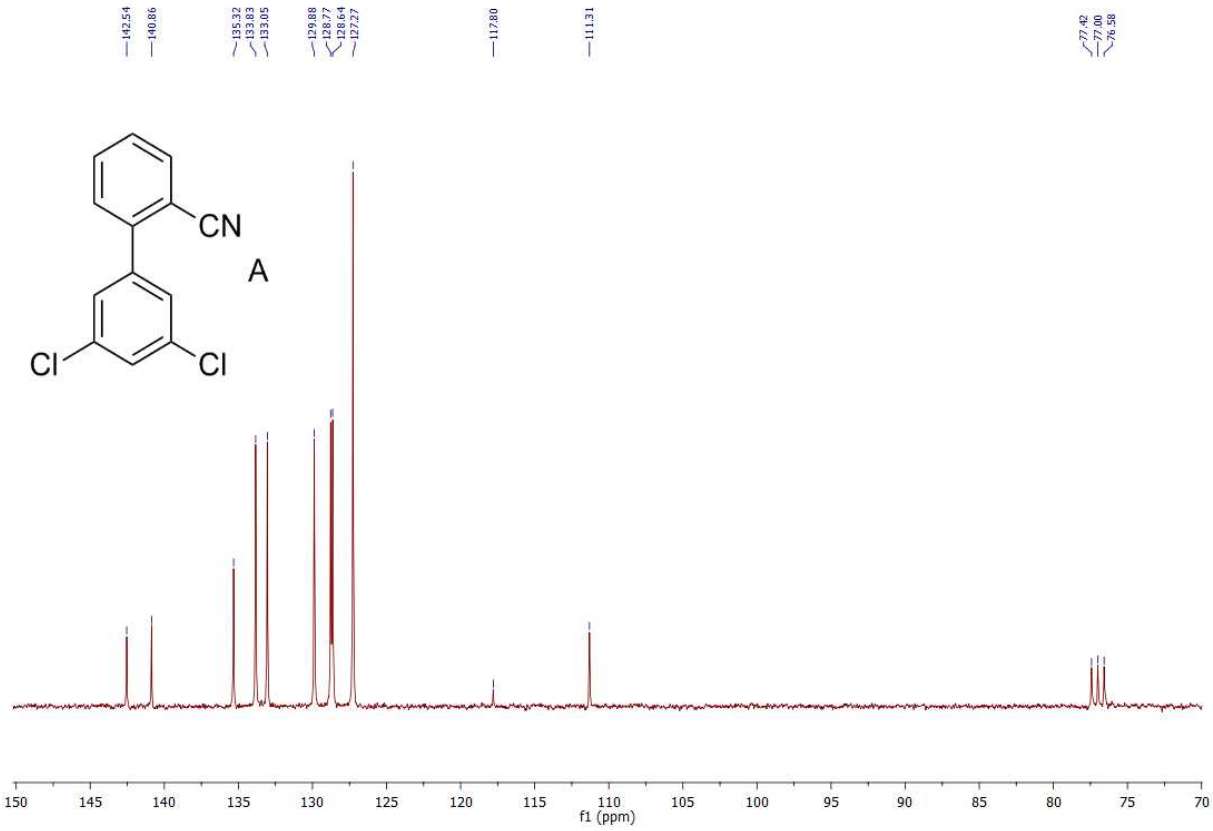

CN
B
NO2
147.82
145.07
140.10
132.19
131.64
130.92
130.07
128.00
124.42
118.24
113.57
77.42
77.00
76.58
f1 (ppm)

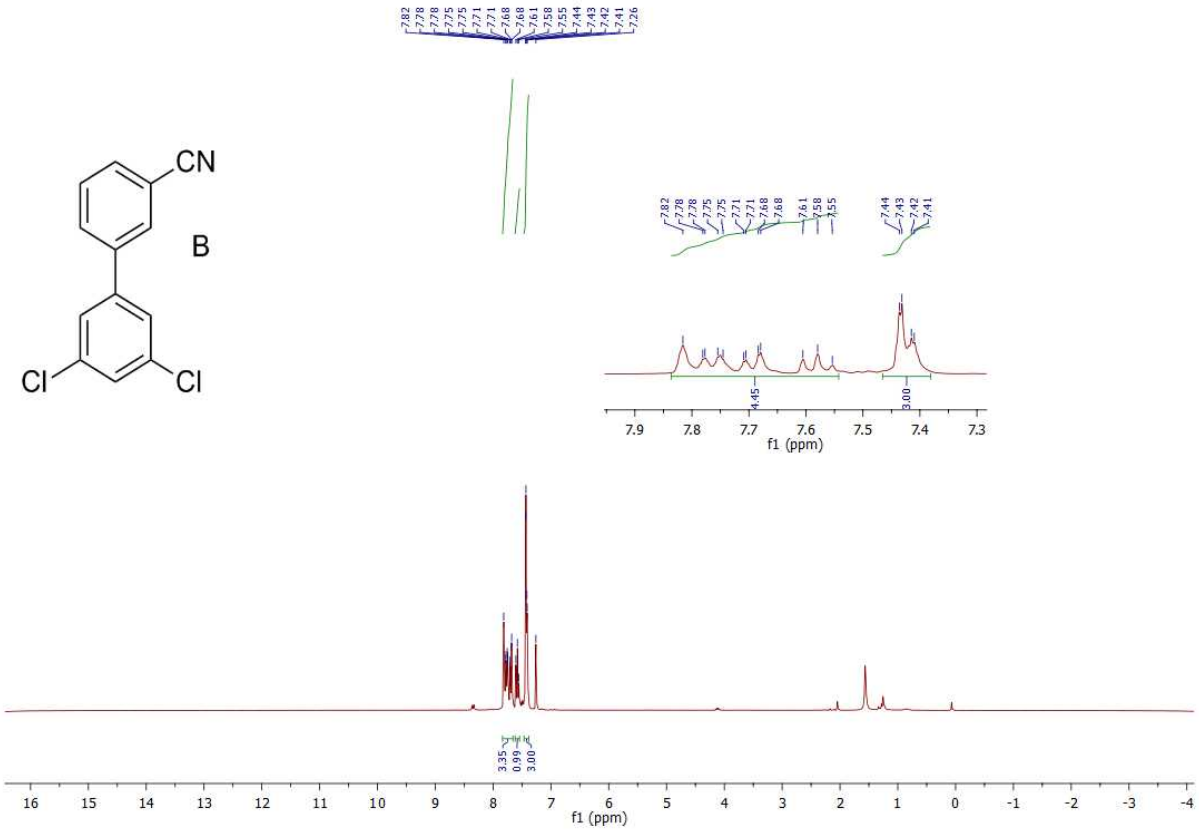

CN
C
NO2
8.36
8.33
7.82
7.81
7.79
7.79
7.77
7.77
7.76
7.74
7.74
7.72
7.72
7.26
2.00
6.08
f1 (ppm)

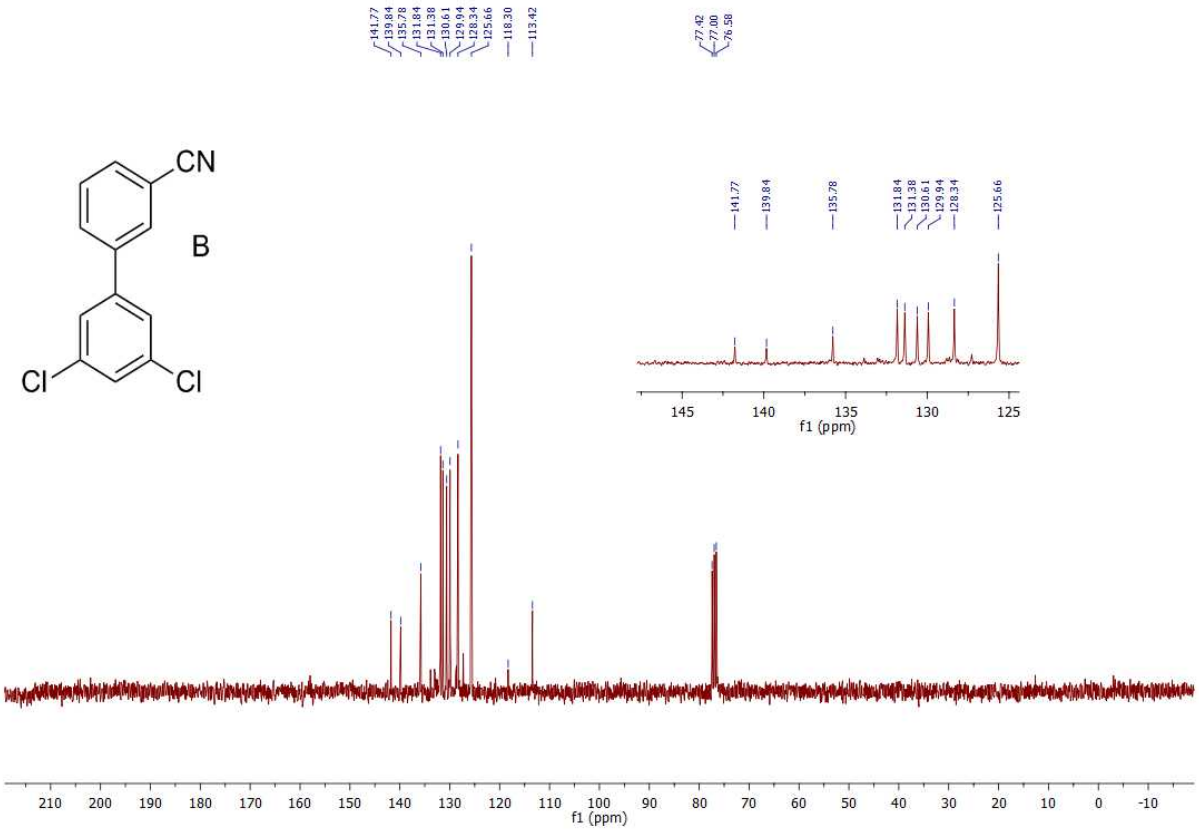

CN
C
NO2
147.89
145.36
143.11
132.89
128.14
128.08
124.35
118.33
112.65
77.42
77.00
76.58
f1 (ppm)

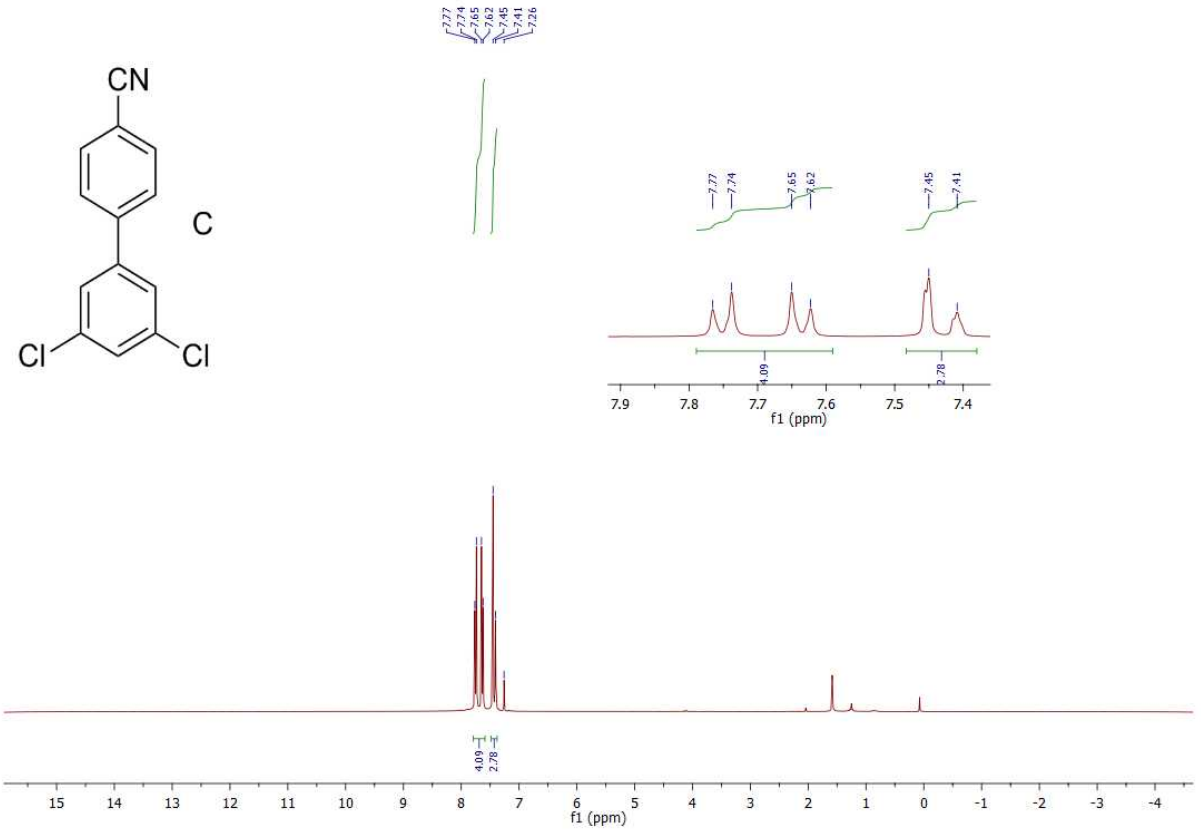
▶ 3',5'-dichloro-[1,1'-biphenyl]-4-carbonitrile, 3',5'-dichloro-[1,1'-biphenyl]-3-carbonitrile, 3',5'-dichloro-[1,1'-biphenyl]-2-carbonitrile (2b)

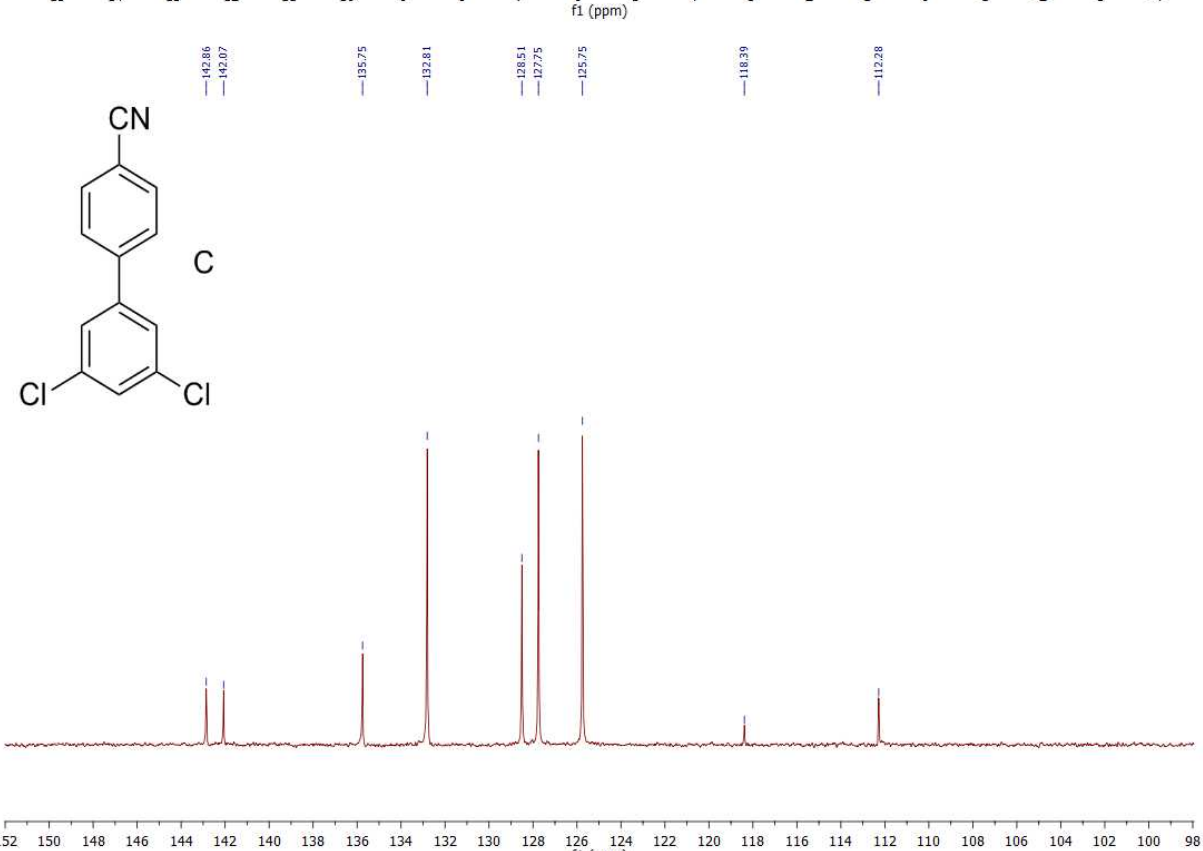




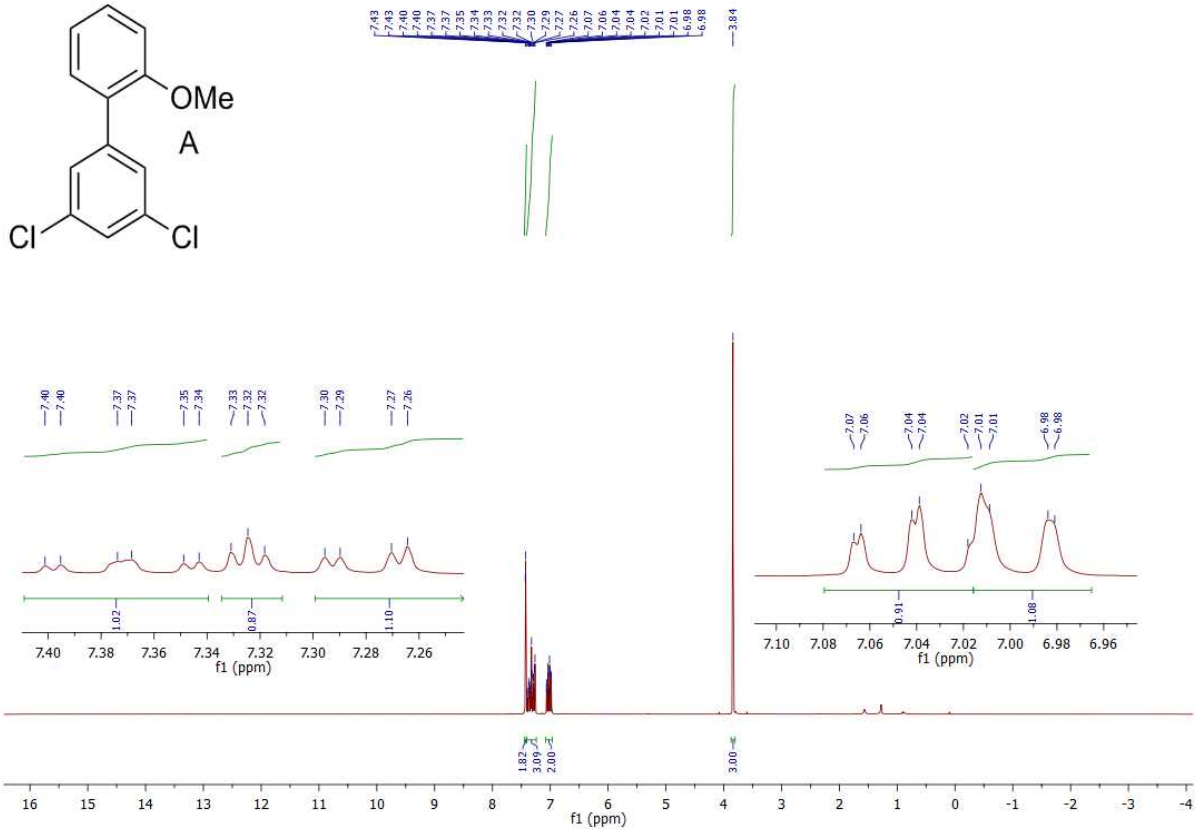

CN
B
Cl
Cl
f1 (ppm)

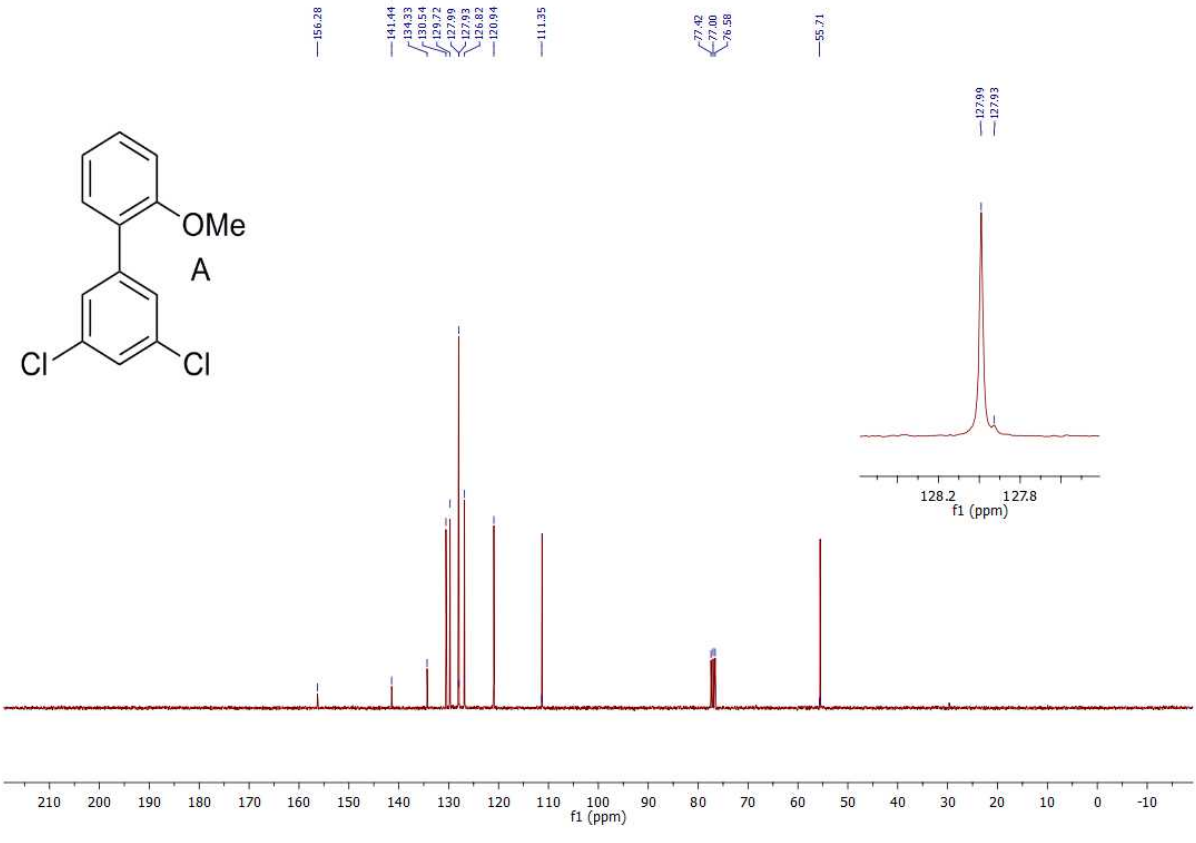

CN
B
Cl
Cl
f1 (ppm)

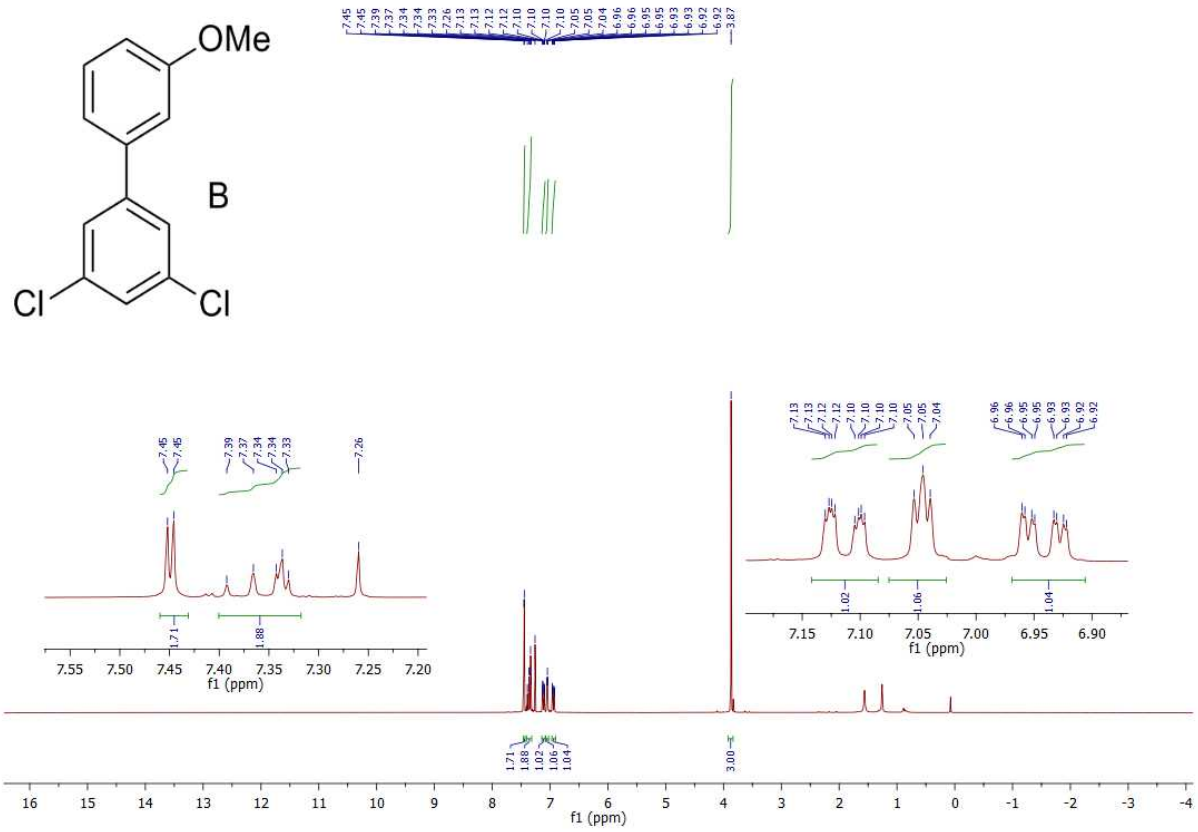

CN
C
Cl
Cl
7.77
7.74
7.65
7.62
7.45
7.41
7.26
4.09
2.78
f1 (ppm)

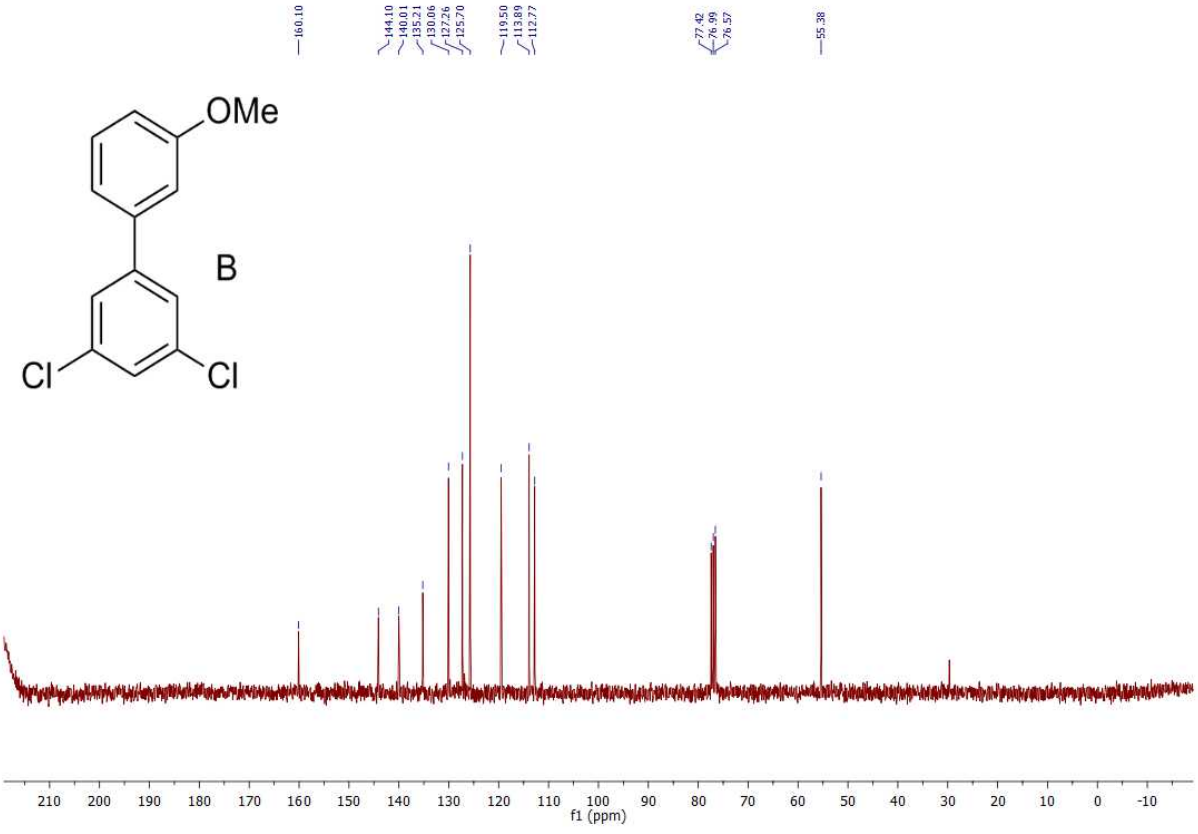

CN
C
Cl
Cl
142.86
142.07
135.75
132.81
128.51
127.75
125.75
118.39
112.28
f1 (ppm)

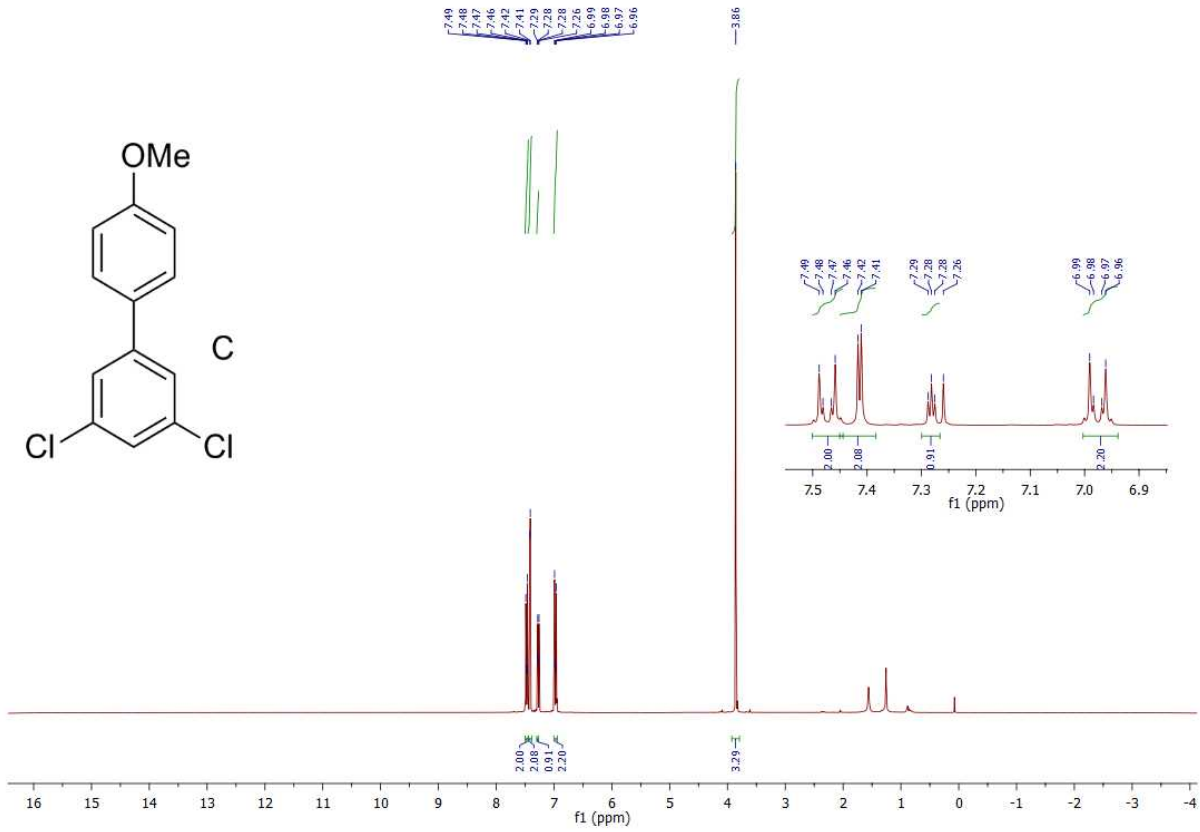
▶3',5'-dichloro-2-methoxy-1,1'-biphenyl / 3,5-dichloro-3'-methoxy-1,1'-biphenyl /3,5-dichloro-4'-methoxy-1,1'-biphenyl (2c)

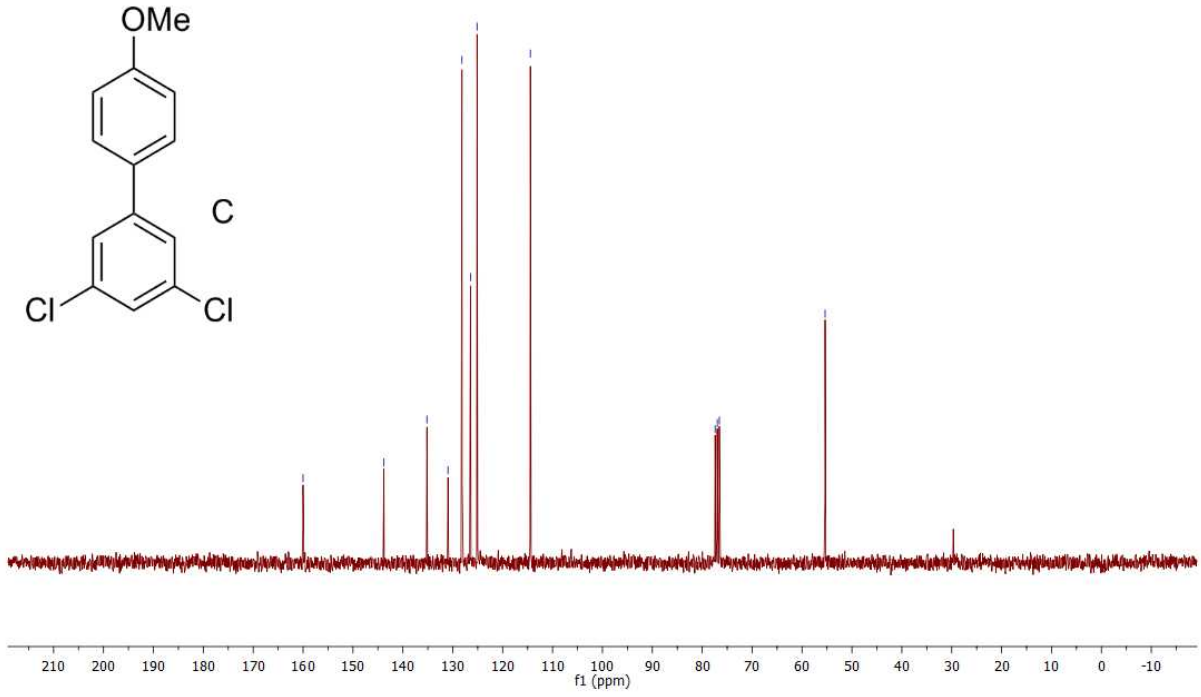




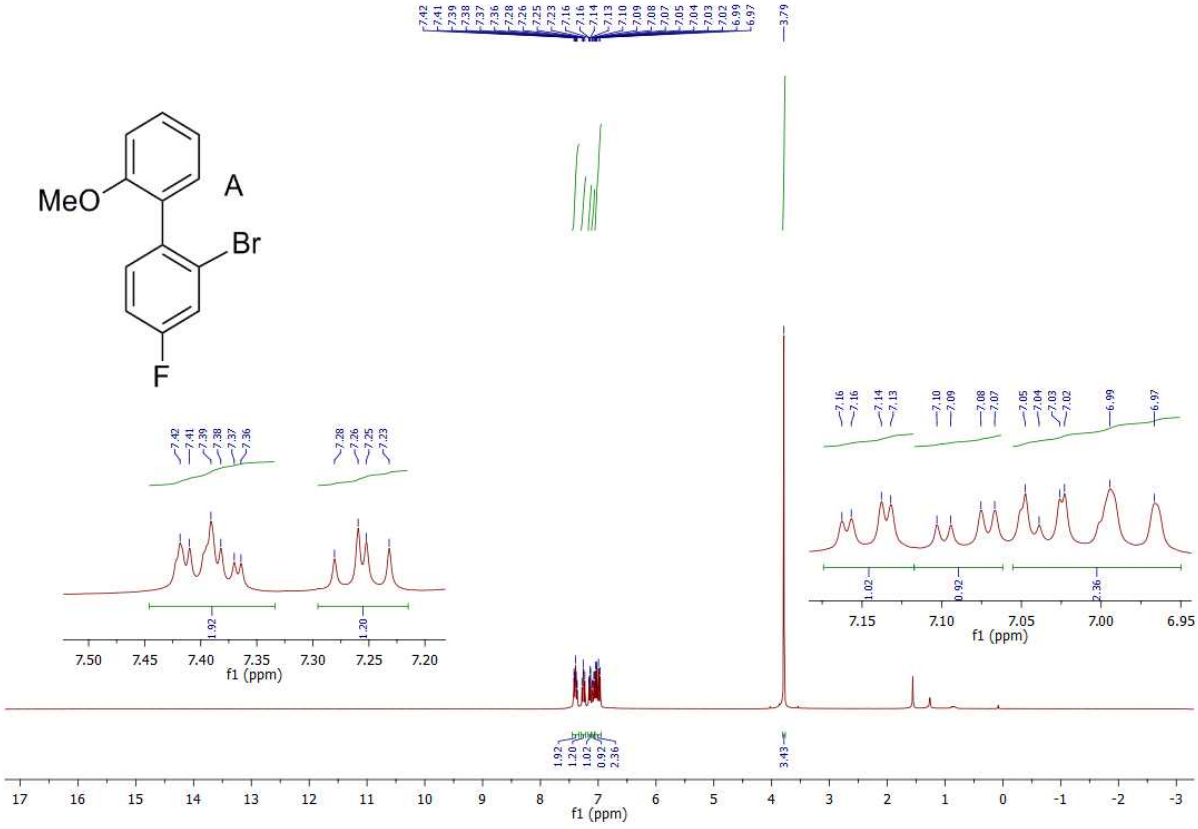

OMe
B
Cl
Cl
f1 (ppm)

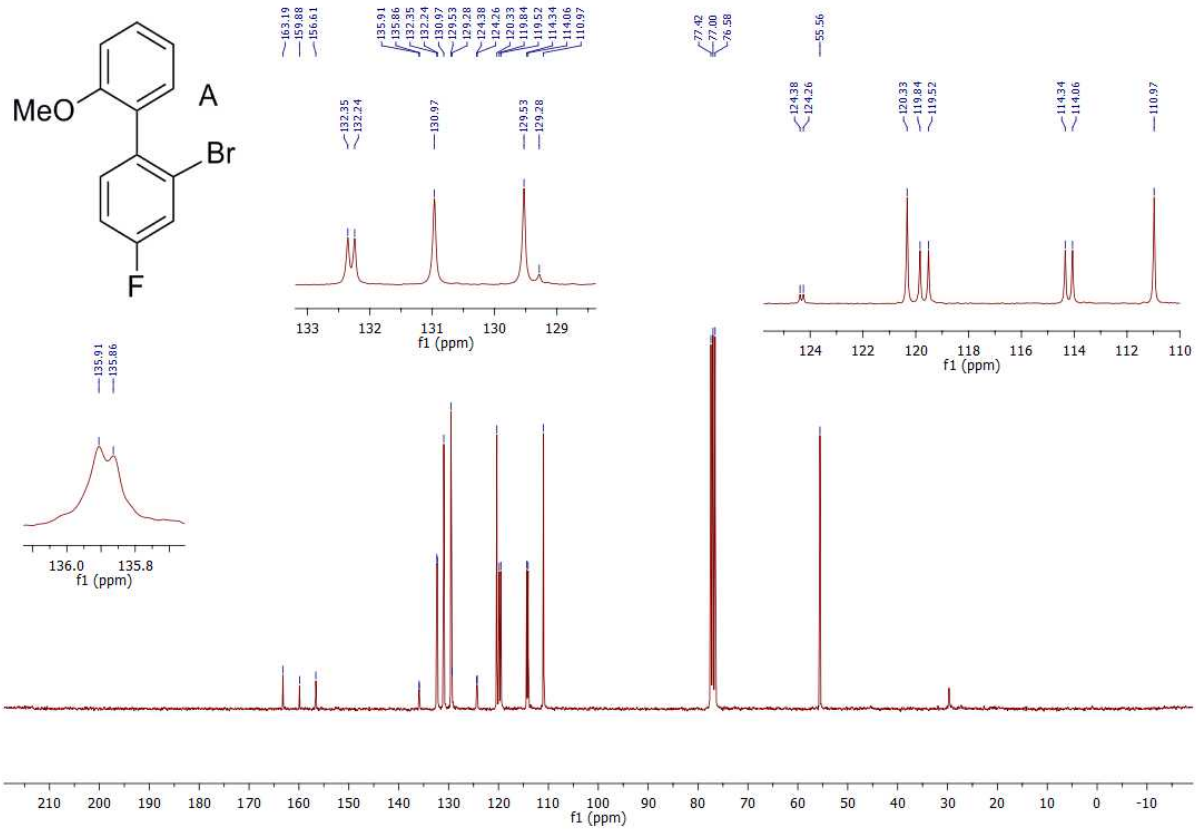

OMe
B
Cl
Cl
f1 (ppm)

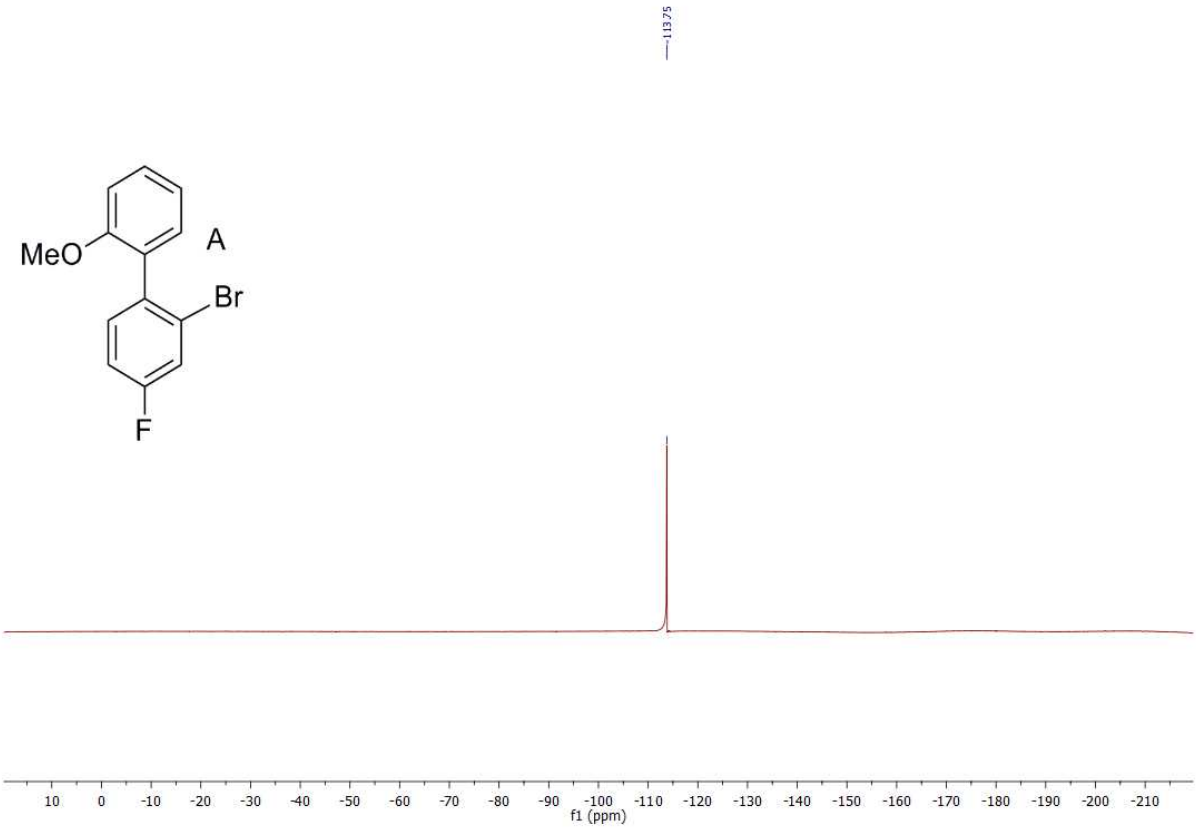

OMe
C
Cl
Cl
f1 (ppm)

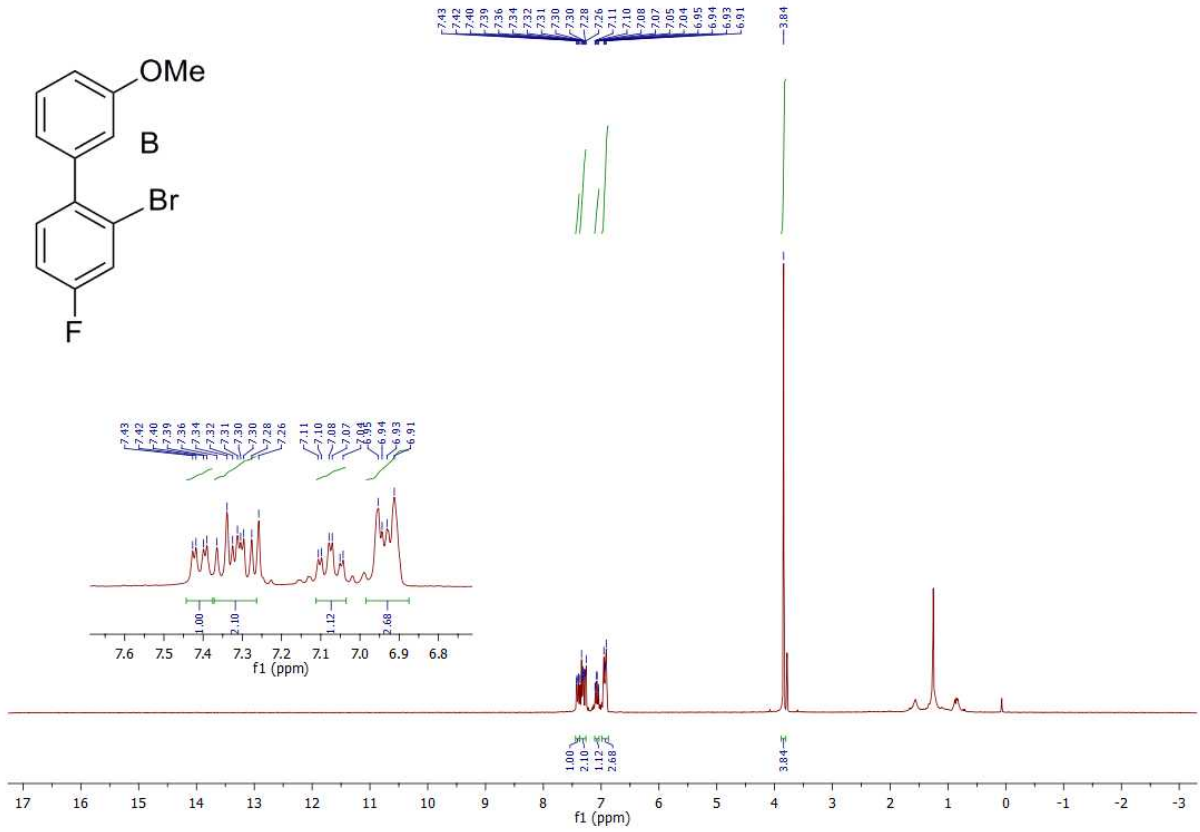

OMe
C
Cl
Cl
f1 (ppm)

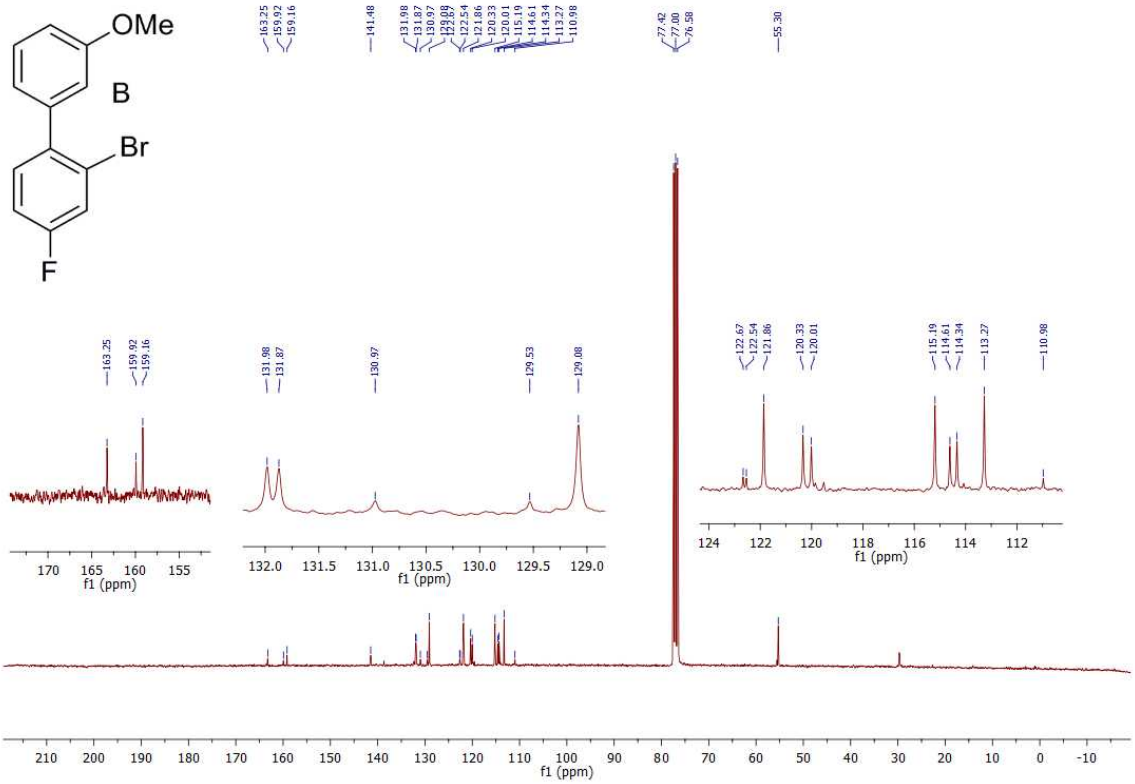
▶2-bromo-5-fluoro-2'-methoxy-1,1'-biphenyl /2-bromo-5-fluoro-3'-methoxy-1,1'-biphenyl /2-bromo-5-fluoro-4'-methoxy-1,1'-biphenyl (2d)

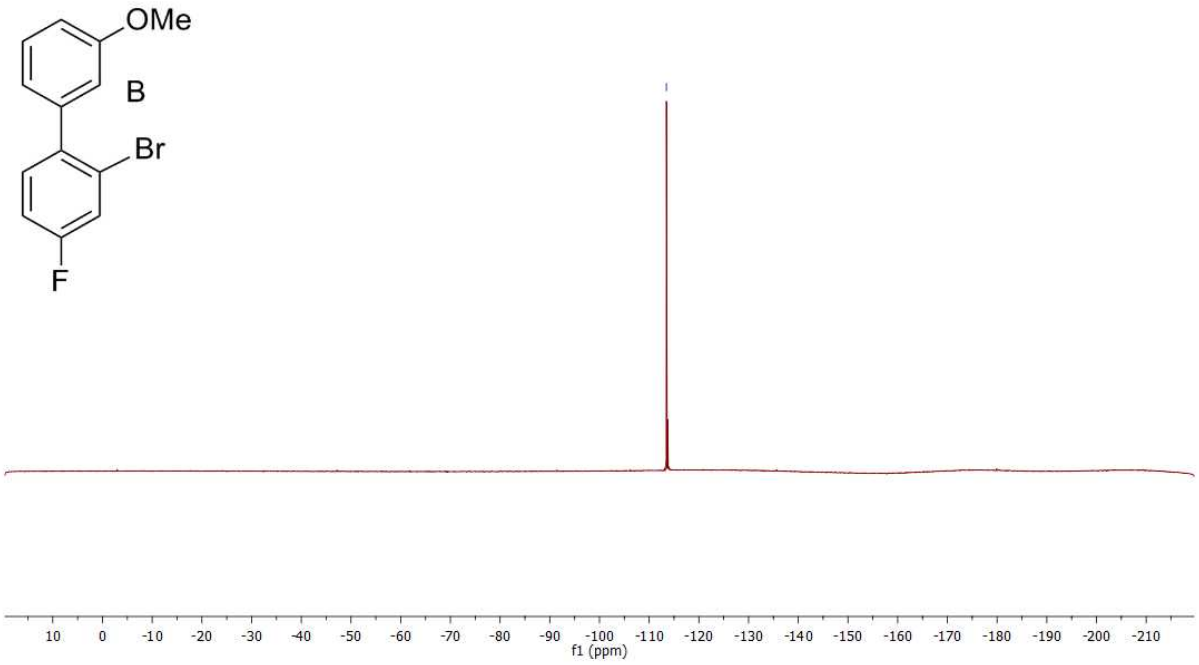


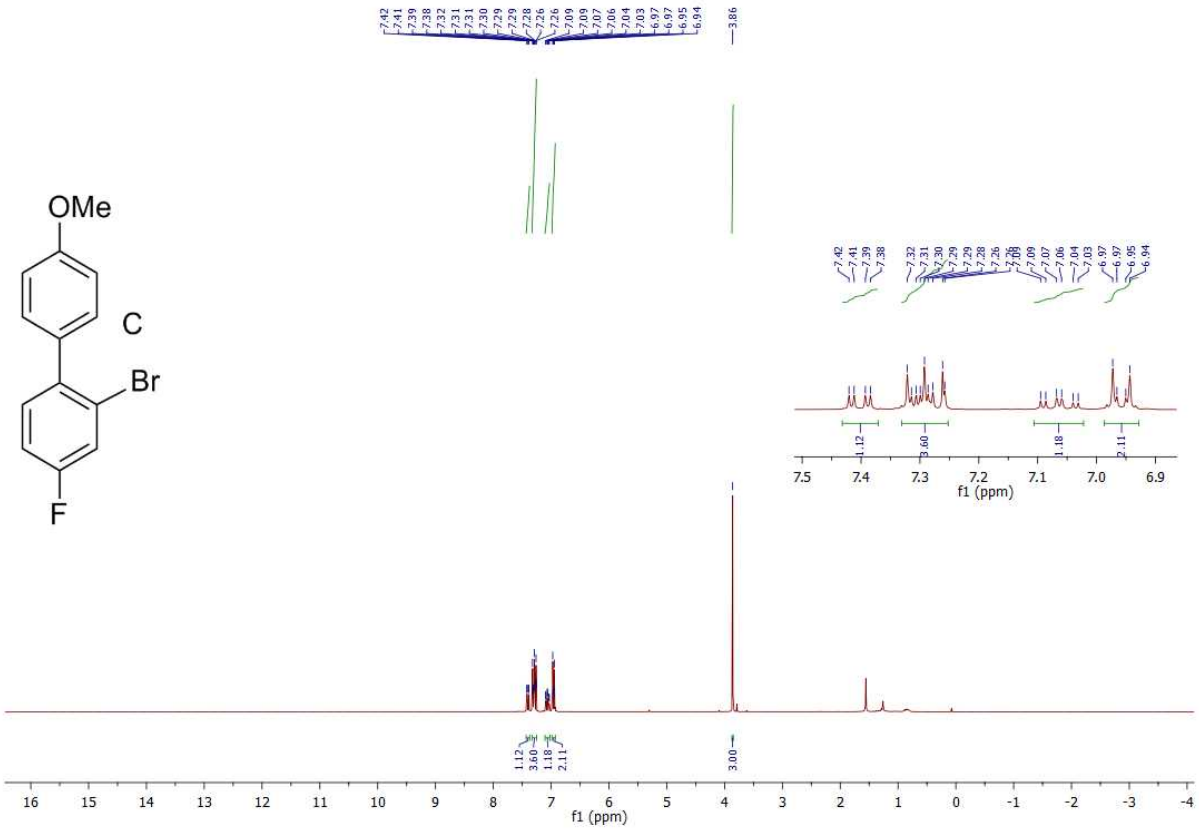

MeO
A
Br
F
163.19
159.88
156.61
135.91
135.86
132.35
132.24
130.97
129.53
129.28
124.38
124.26
120.33
119.84
119.52
114.34
114.06
110.97
77.42
77.00
76.58
55.56
f1 (ppm)

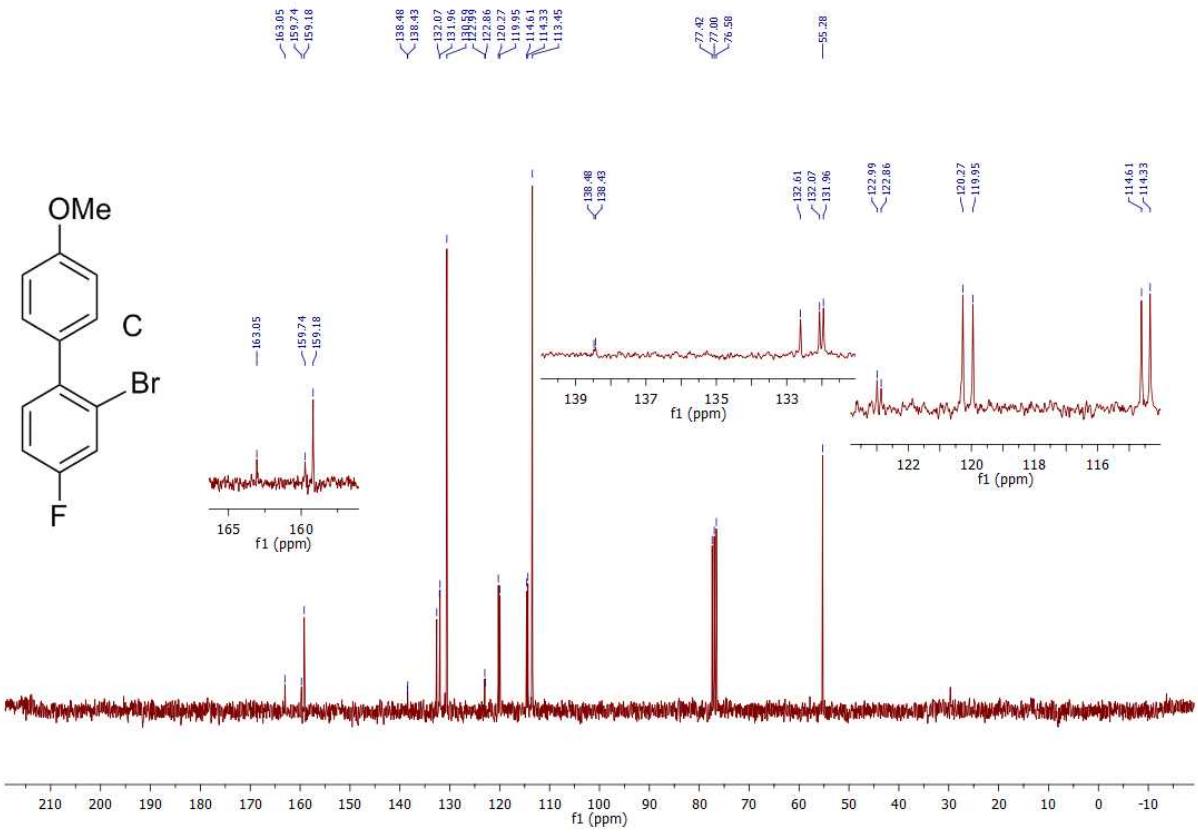

113.75
MeO
A
Br
F
f1 (ppm)

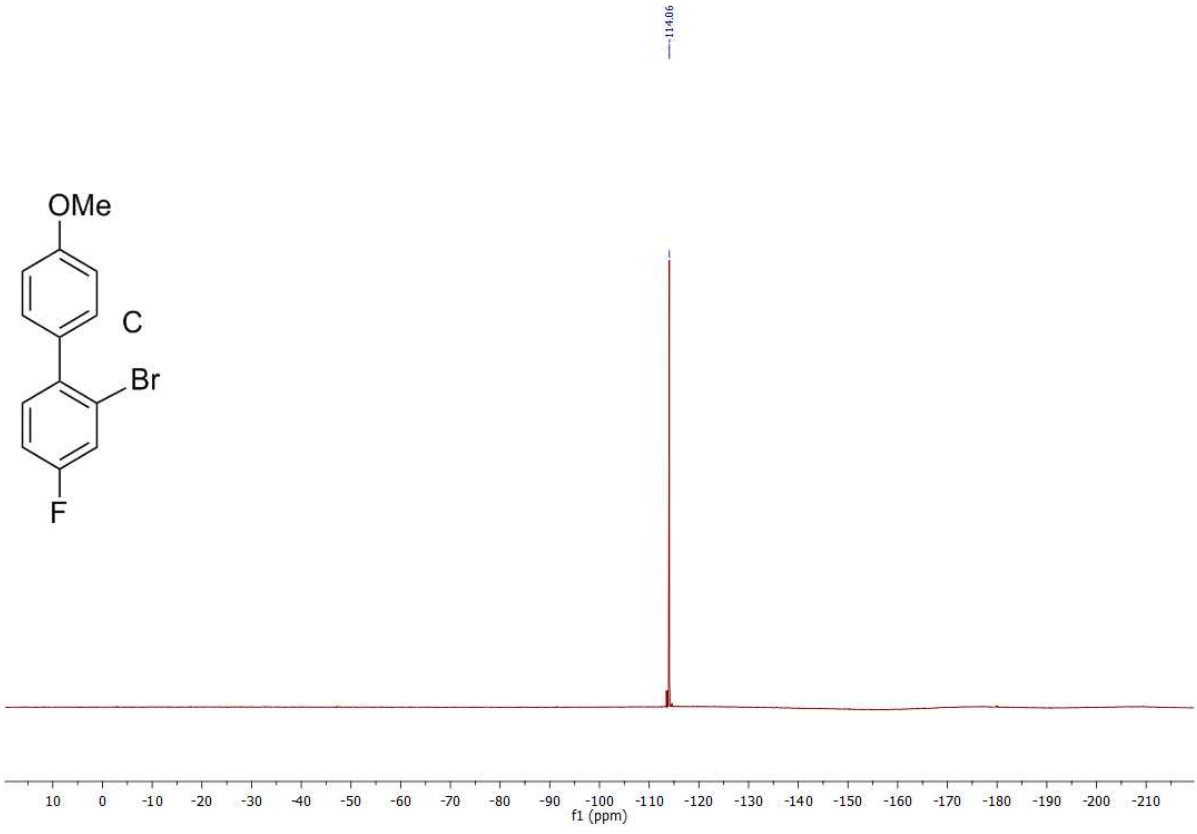

OMe
B
Br
F
f1 (ppm)


OMe
B
Br
F
f1 (ppm)

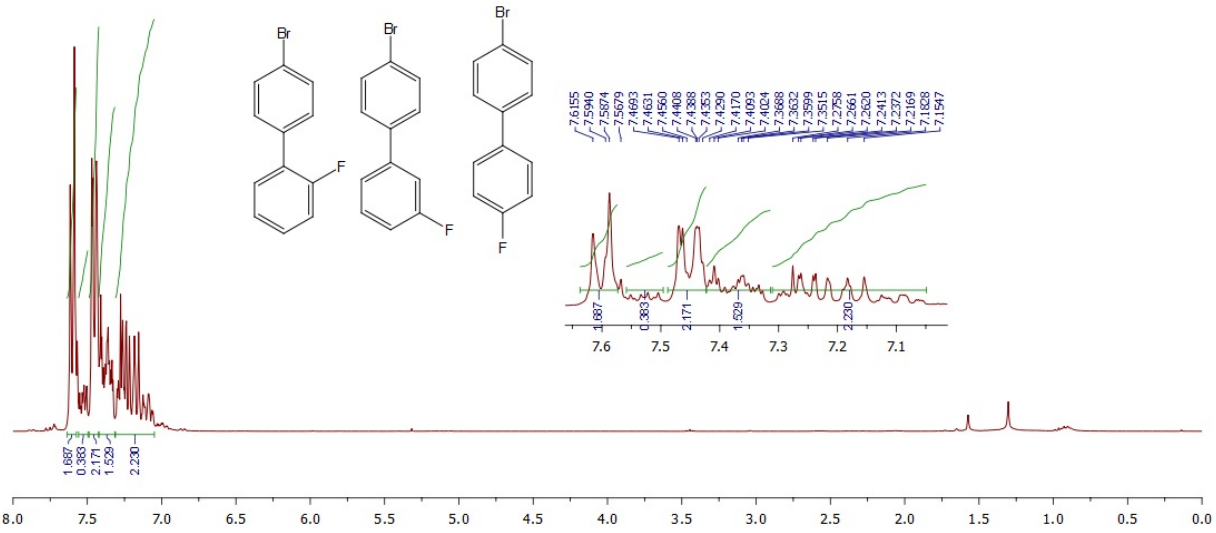

-113.47
OMe
B
Br
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

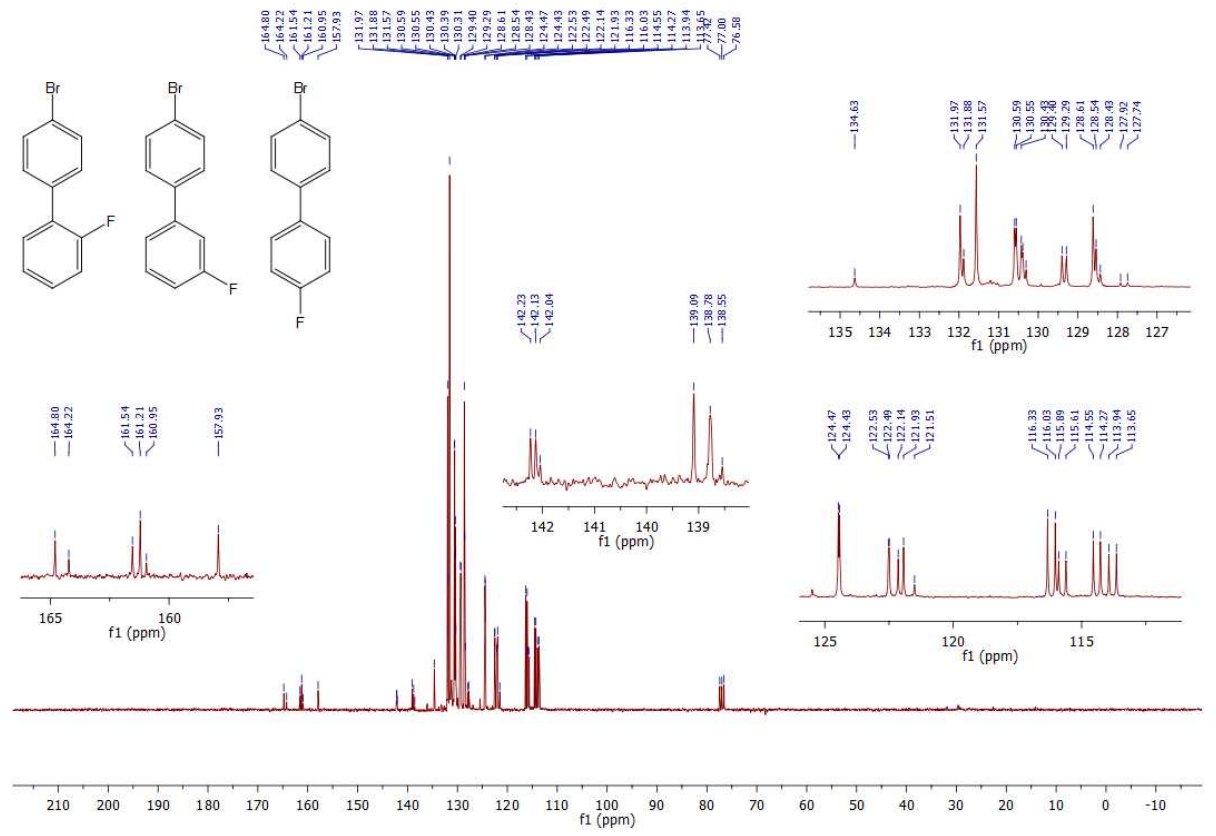

7.42
7.41
7.39
7.38
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.26
7.26
7.09
7.09
7.07
7.06
7.04
7.03
6.97
6.97
6.95
6.94
3.86
OMe
C
Br
F
1.12
3.60
1.18
2.11
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.12
3.60
1.18
2.11
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

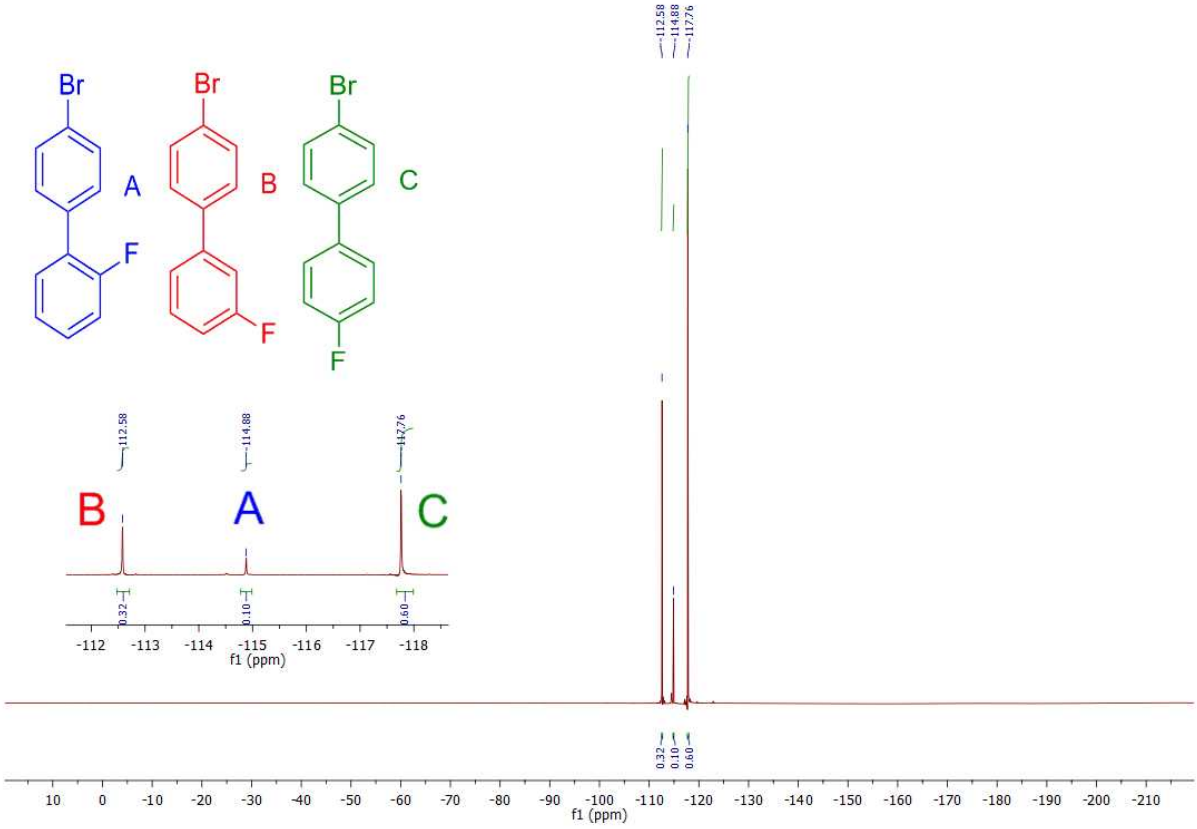

163.05
159.74
159.18
138.48
138.43
132.07
131.96
122.86
120.27
119.95
114.61
114.33
113.45
77.42
77.00
76.58
55.28
OMe
C
Br
F
f1 (ppm)


114.06
OMe
C
Br
F
f1 (ppm)

▶ 4'-bromo-2-fluoro-1,1'-biphenyl / 4'-bromo-3-fluoro-1,1'-biphenyl / 4'-bromo-4-fluoro-1,1'-biphenyl (2e)

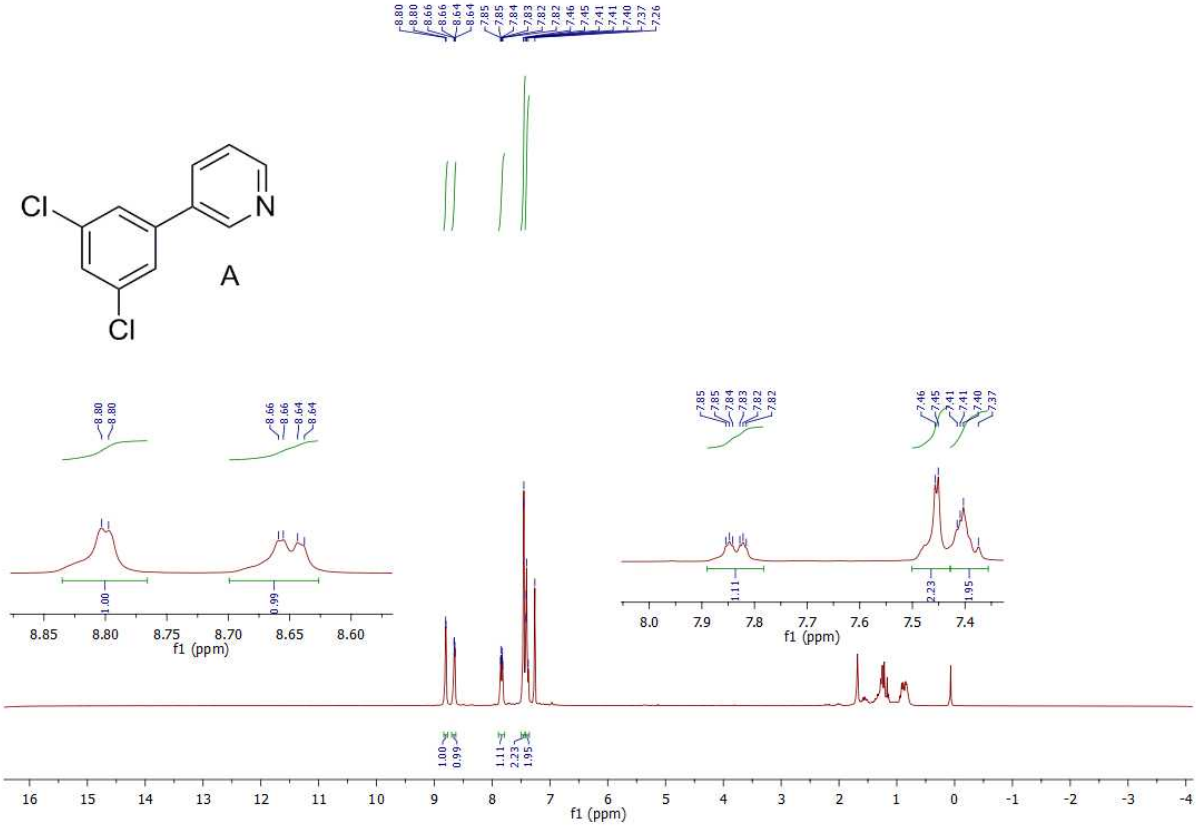


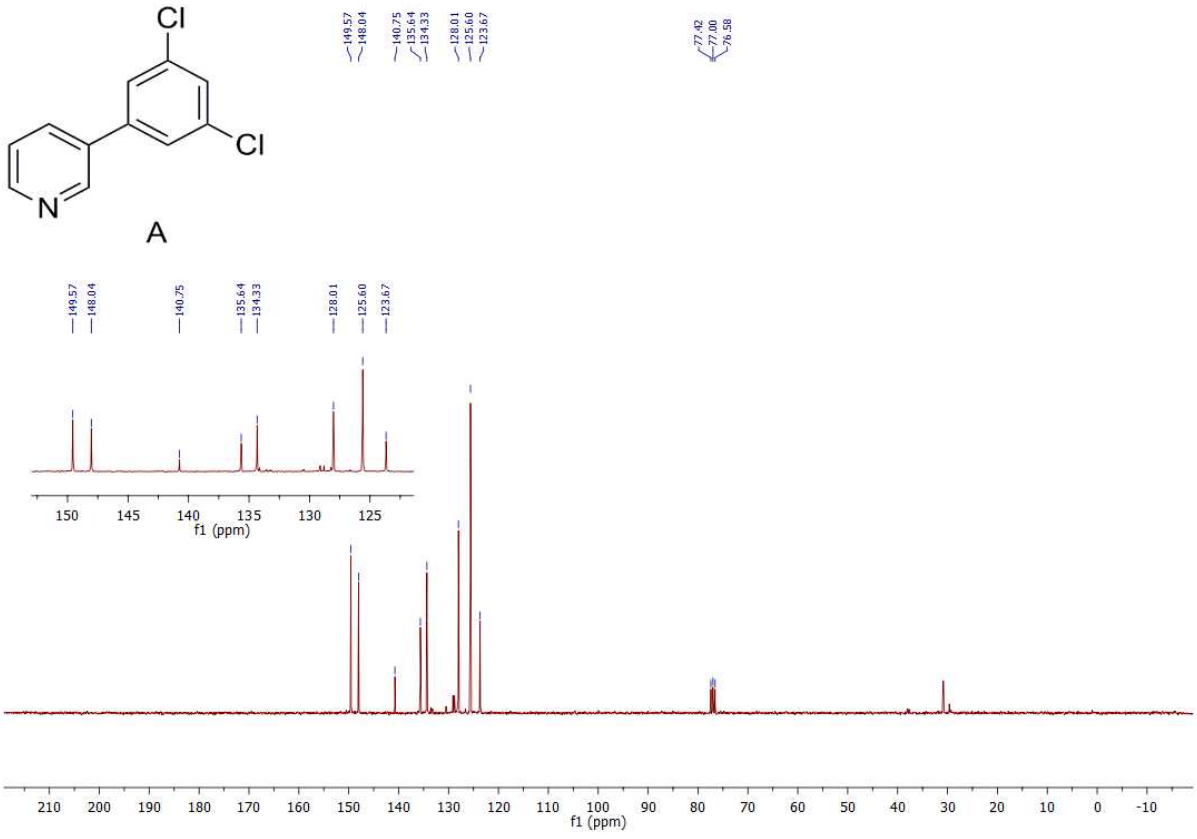



Br
A
F
Br
B
F
Br
C
F
-112.58
-114.88
-117.76
B
A
C
0.32
0.10
0.60
-112 -113 -114 -115 -116 -117 -118
f1 (ppm)
0.32
0.10
0.60
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

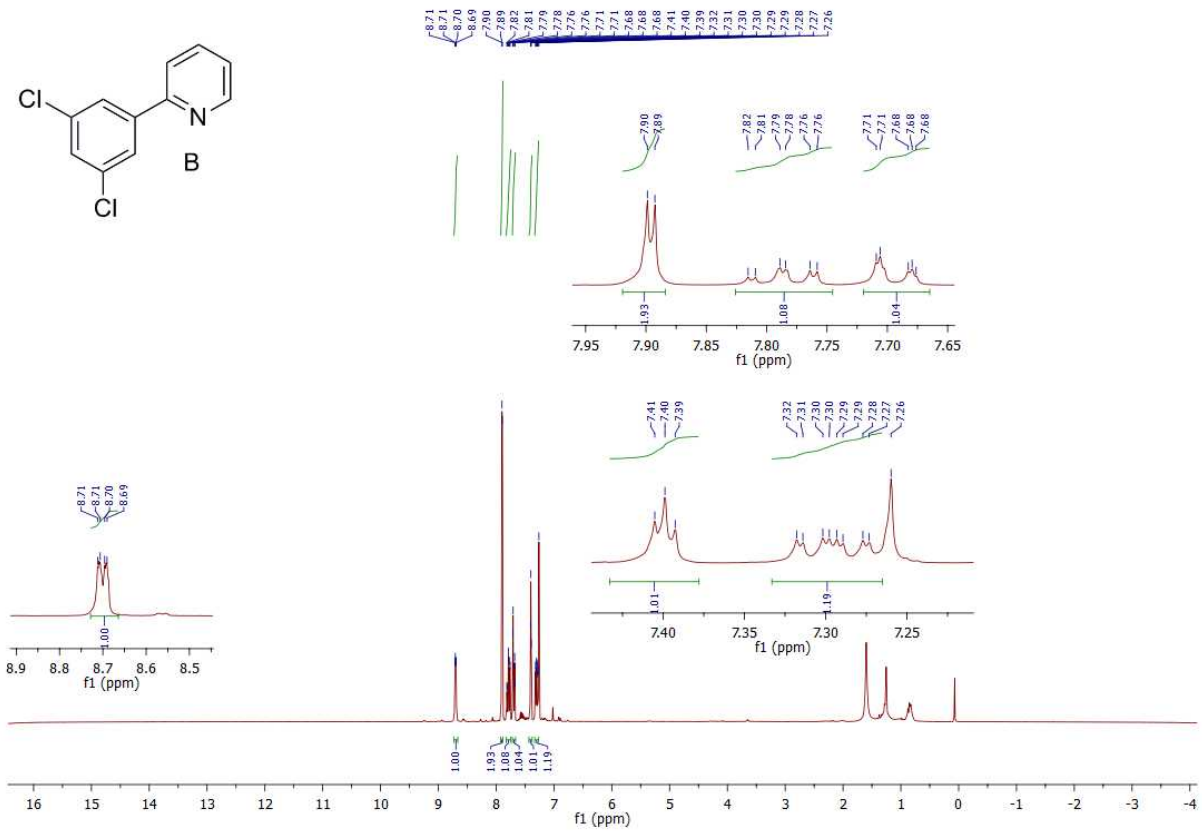
▶3-(3,5-dichlorophenyl)pyridine / 2-(3,5-dichlorophenyl)pyridine (2f)

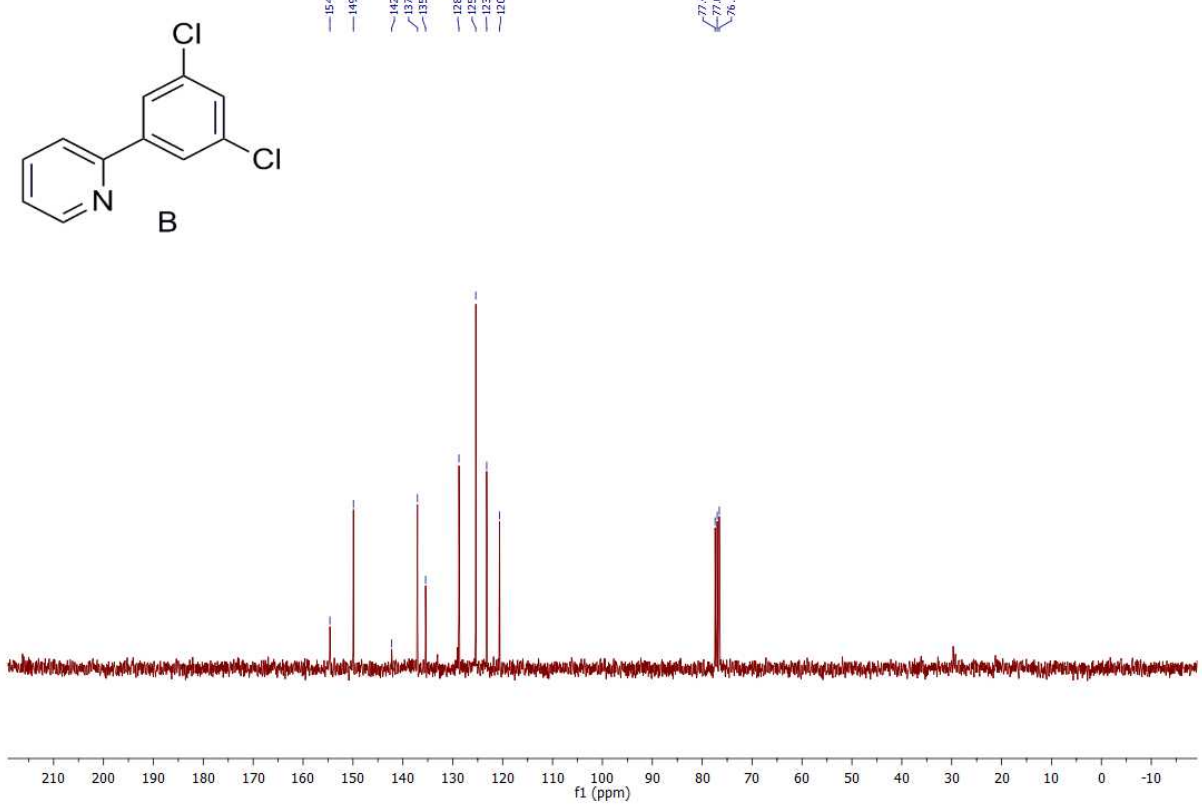
A





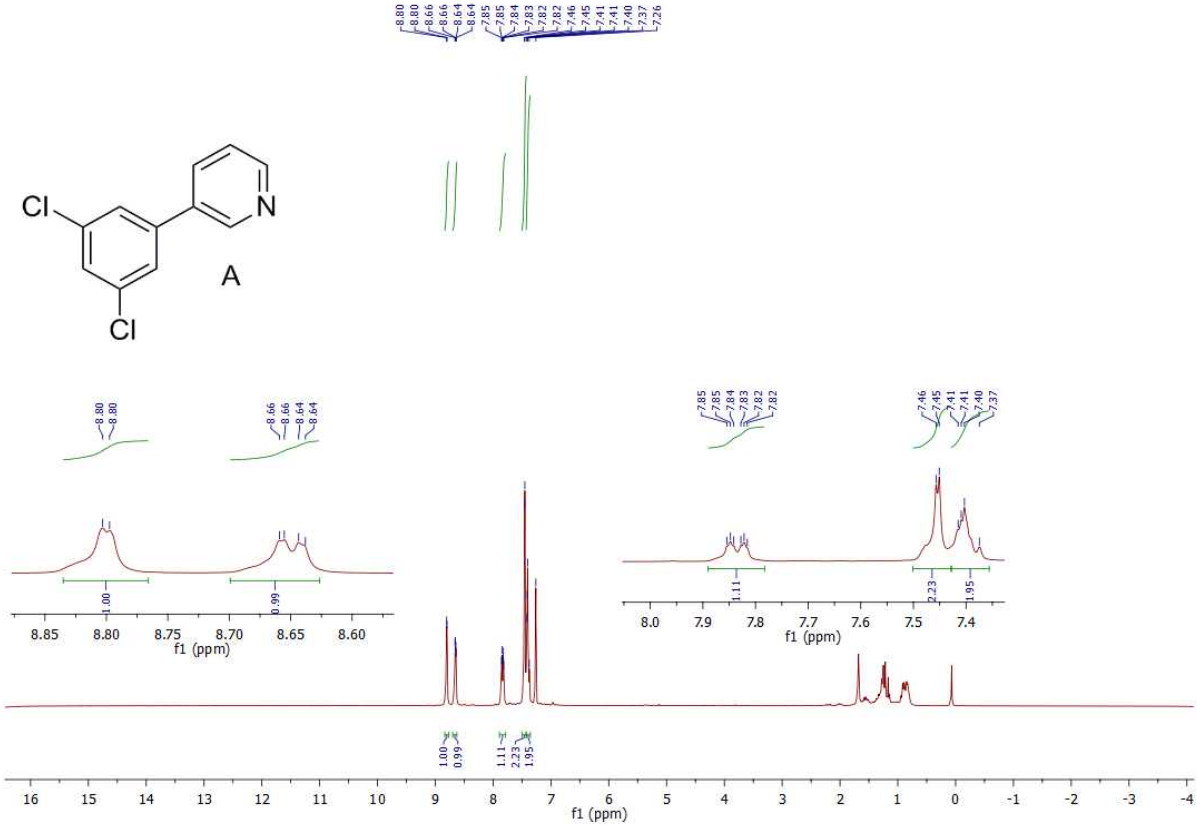
B

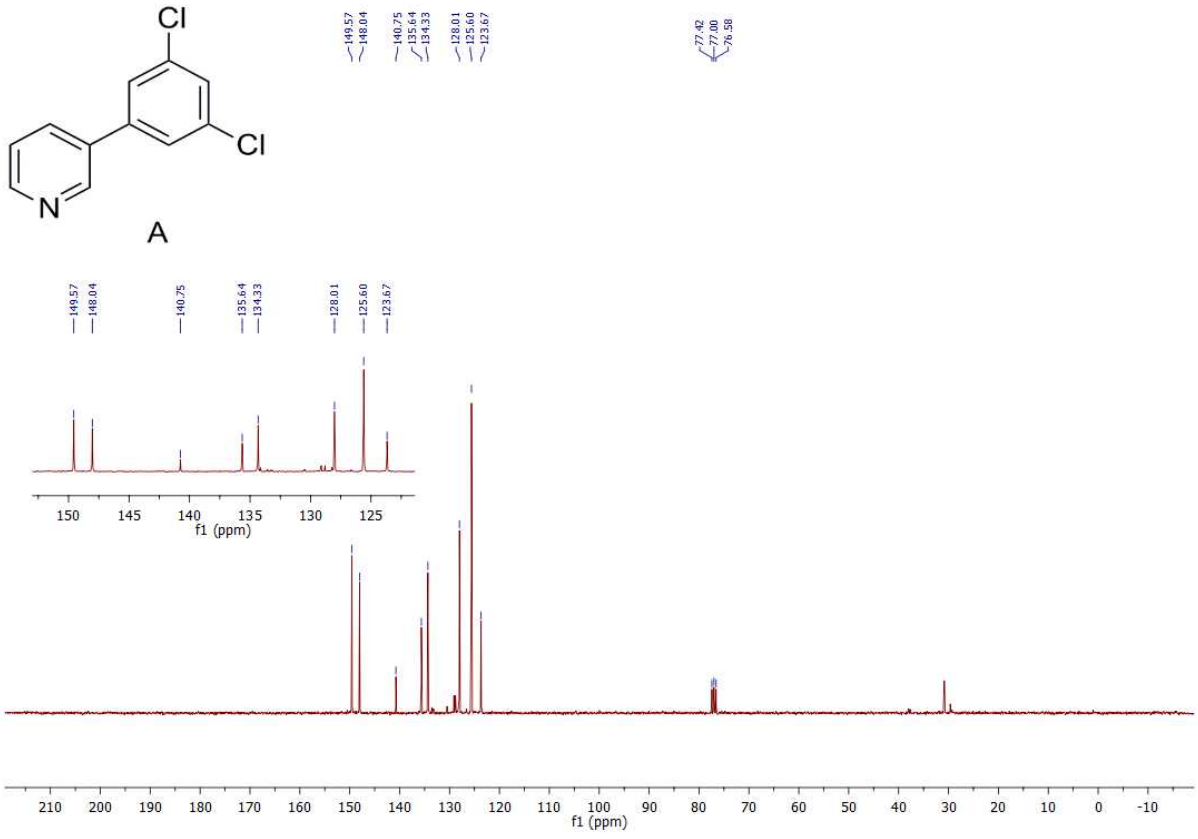




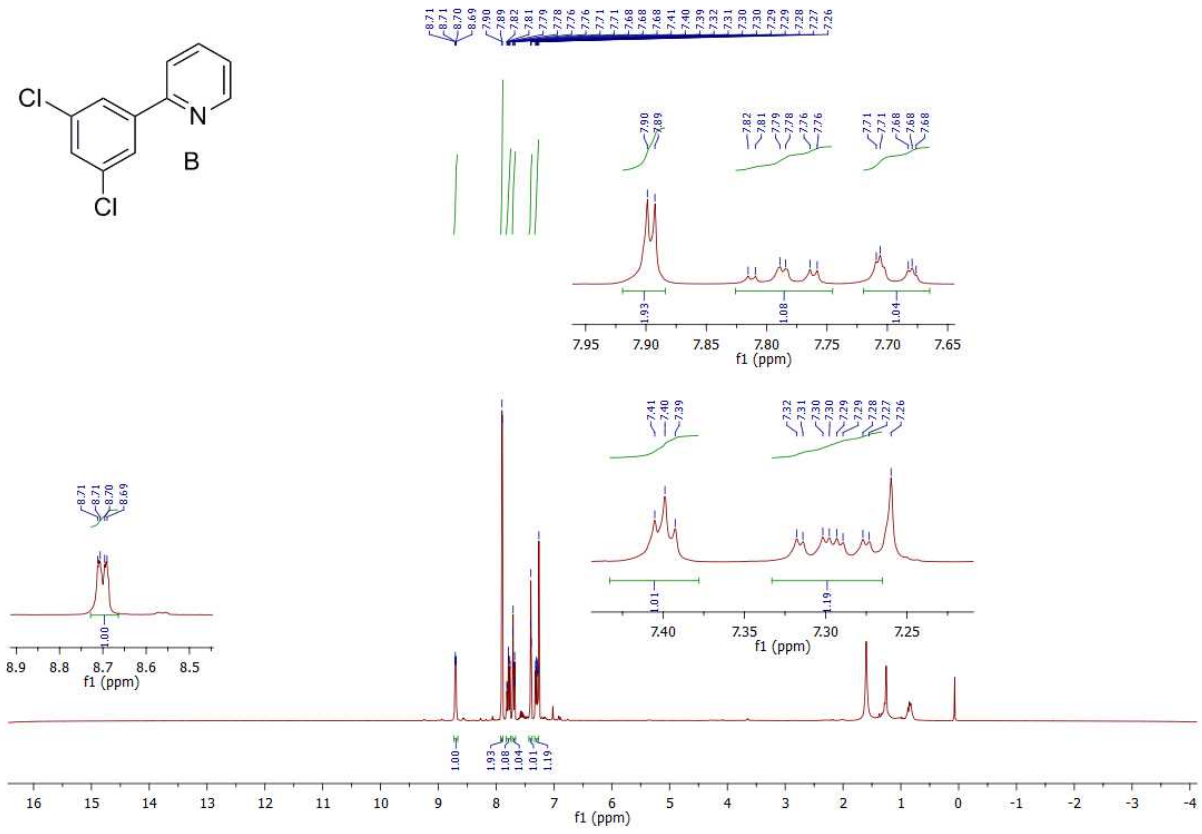
▶2-(4-methoxyphenyl)pyridine / 3-(4-methoxyphenyl)pyridine (2g)

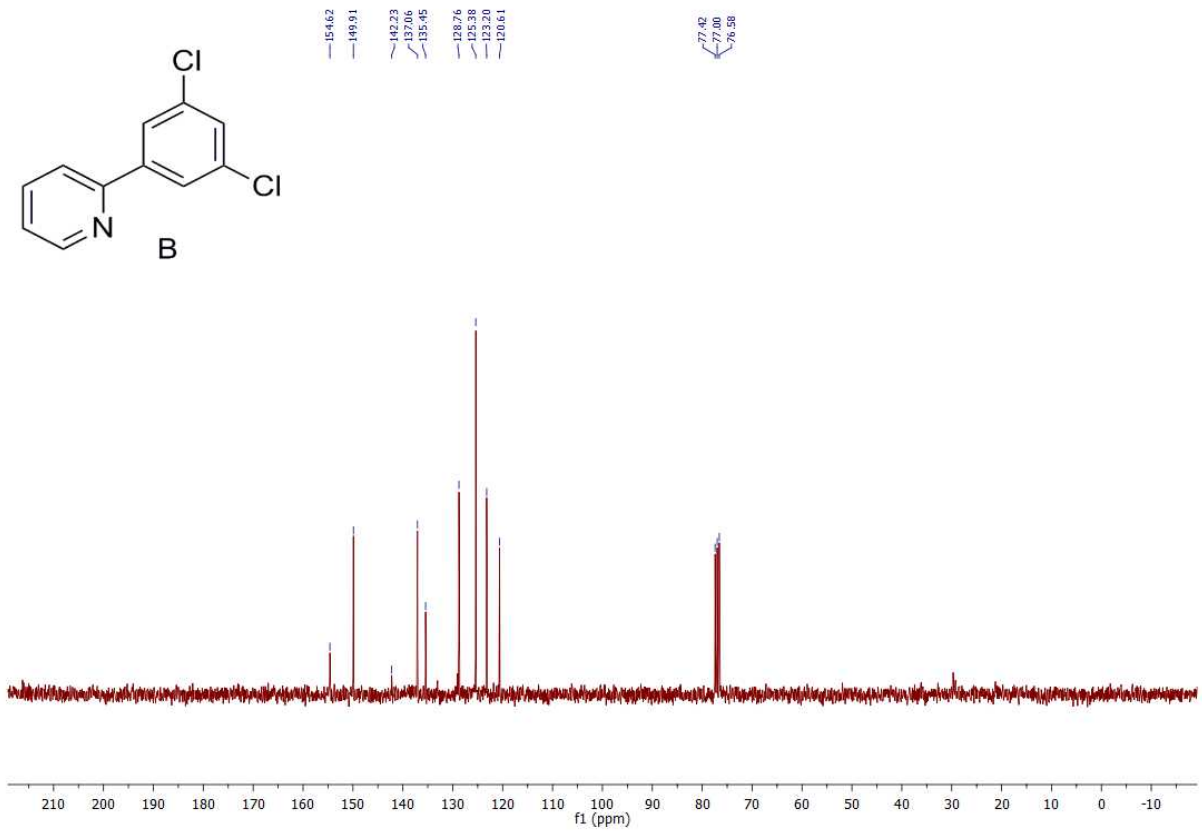
A



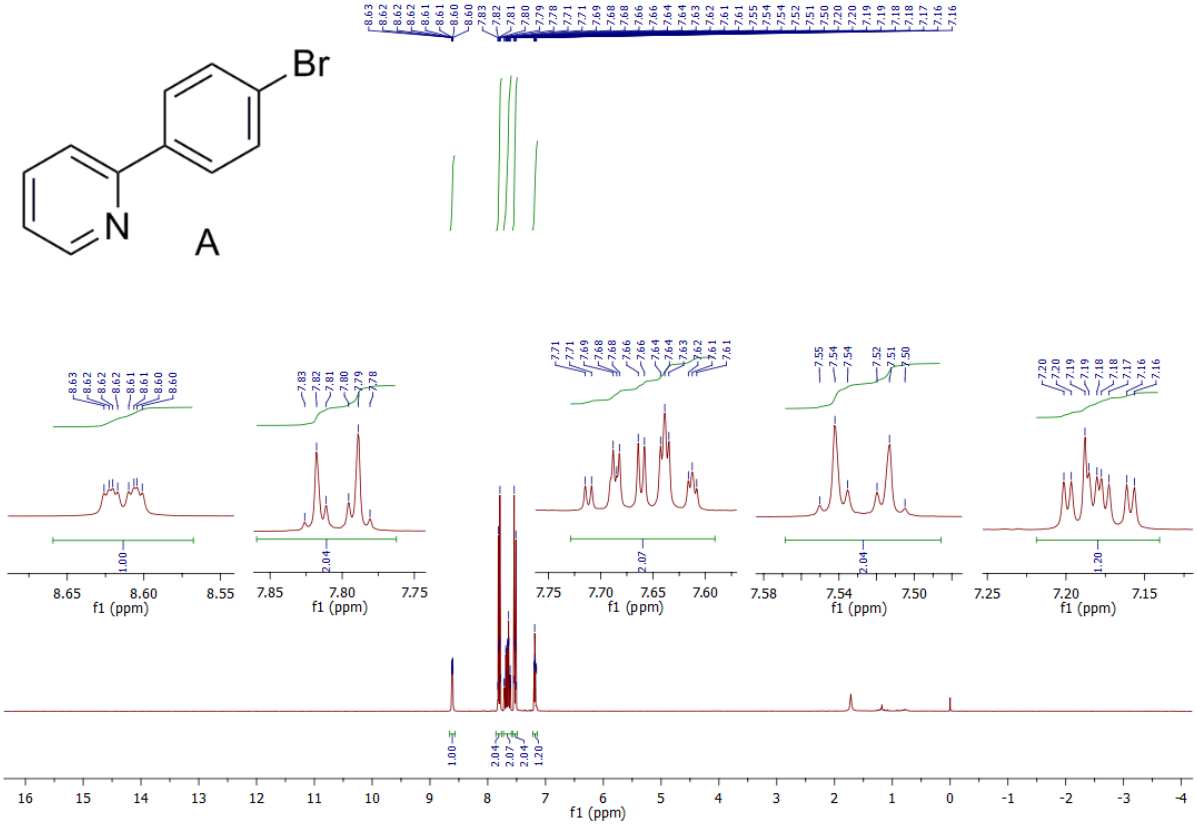


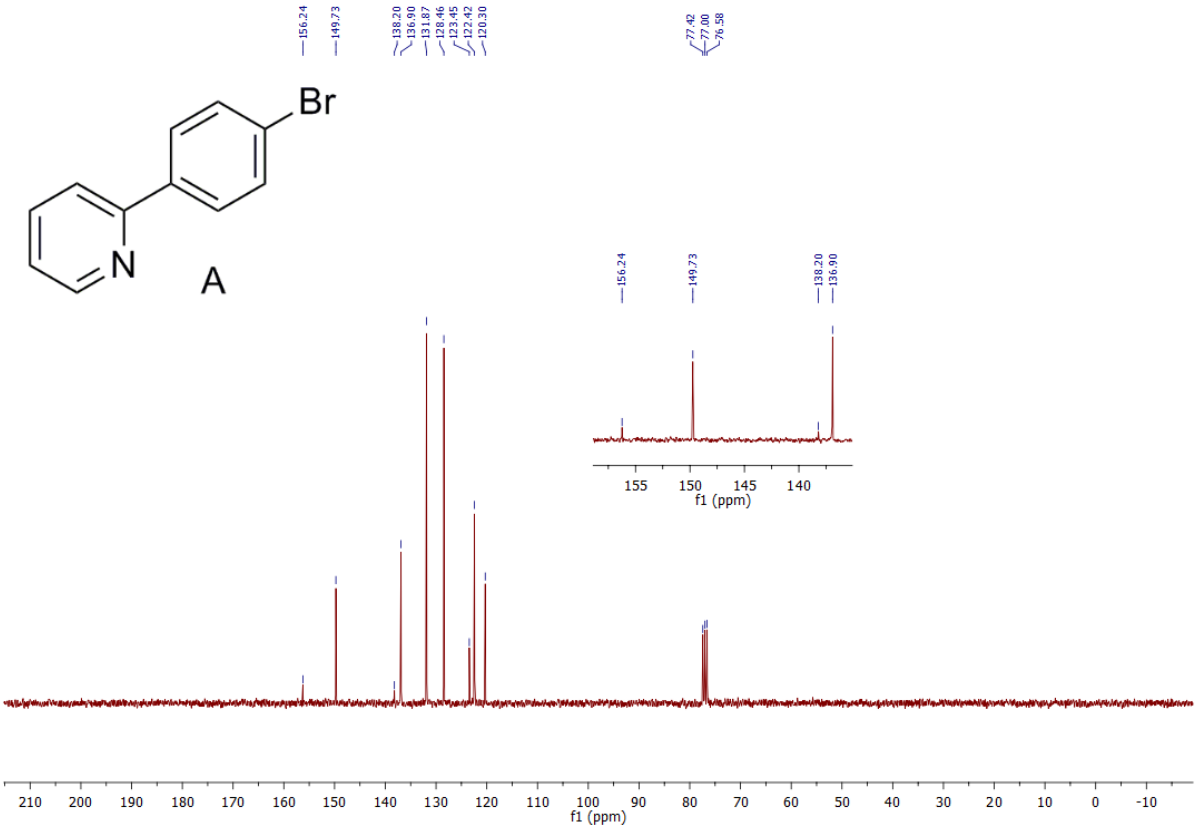
B

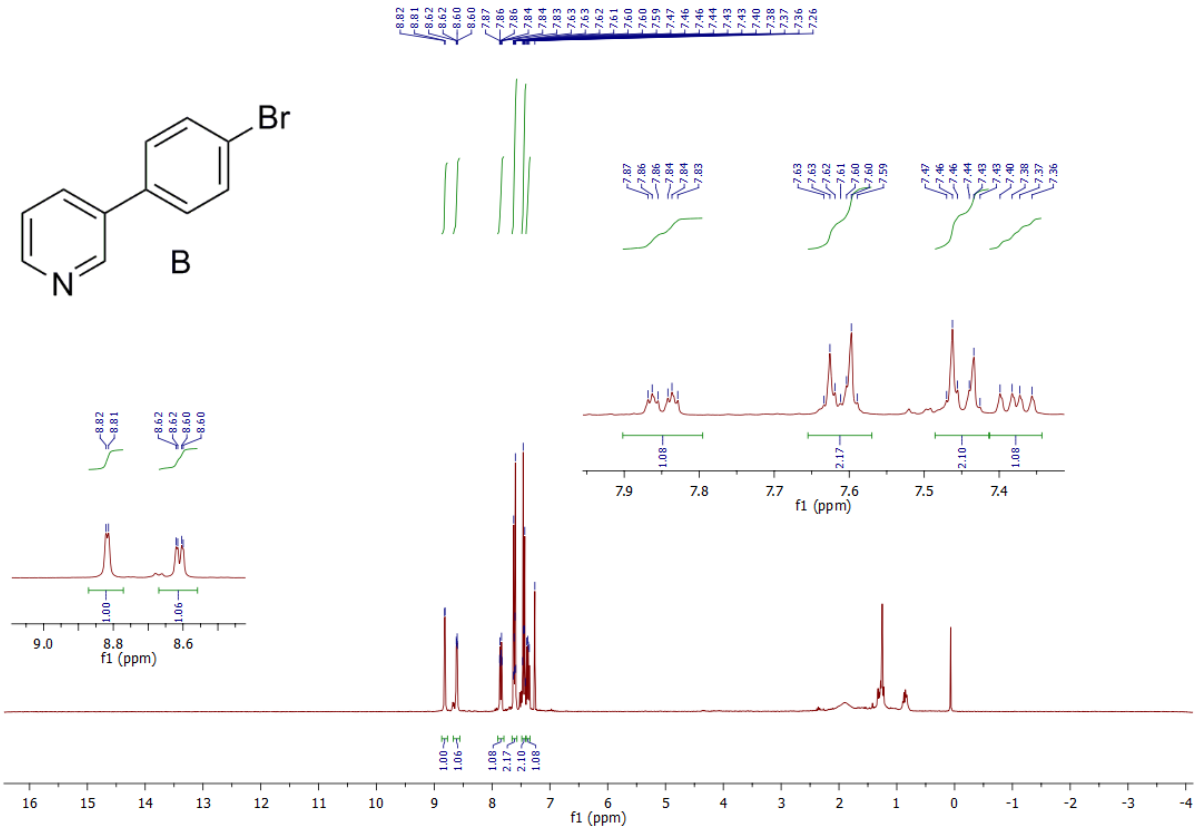


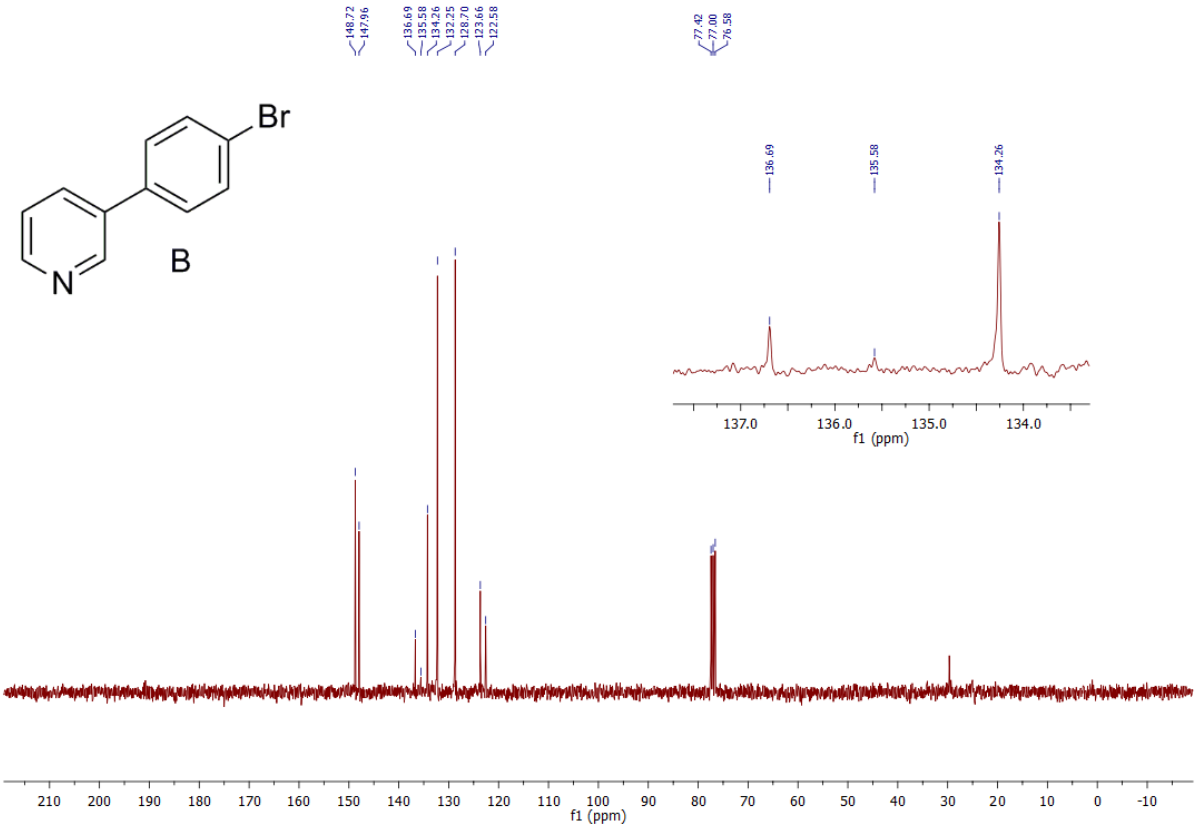


▶ **2-(4-bromophenyl)pyridine/ 3-(4-bromophenyl)pyridine (2h)**

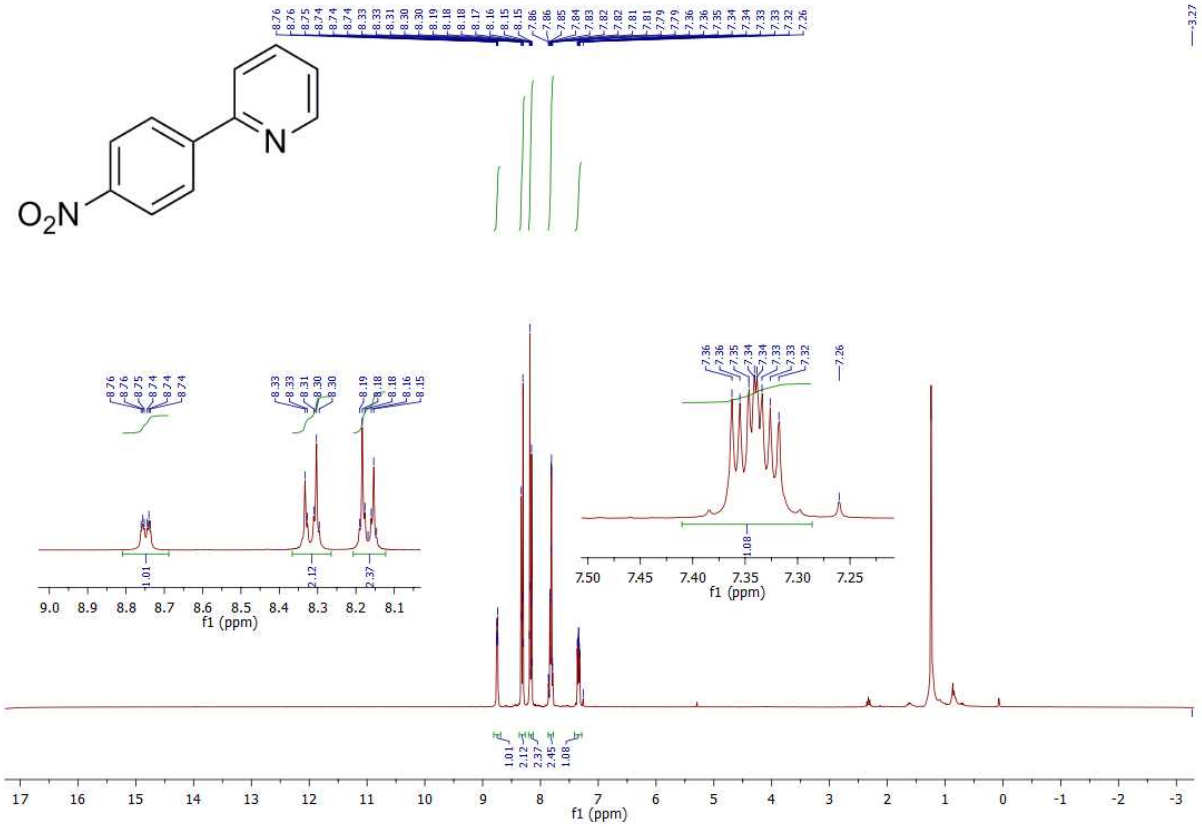


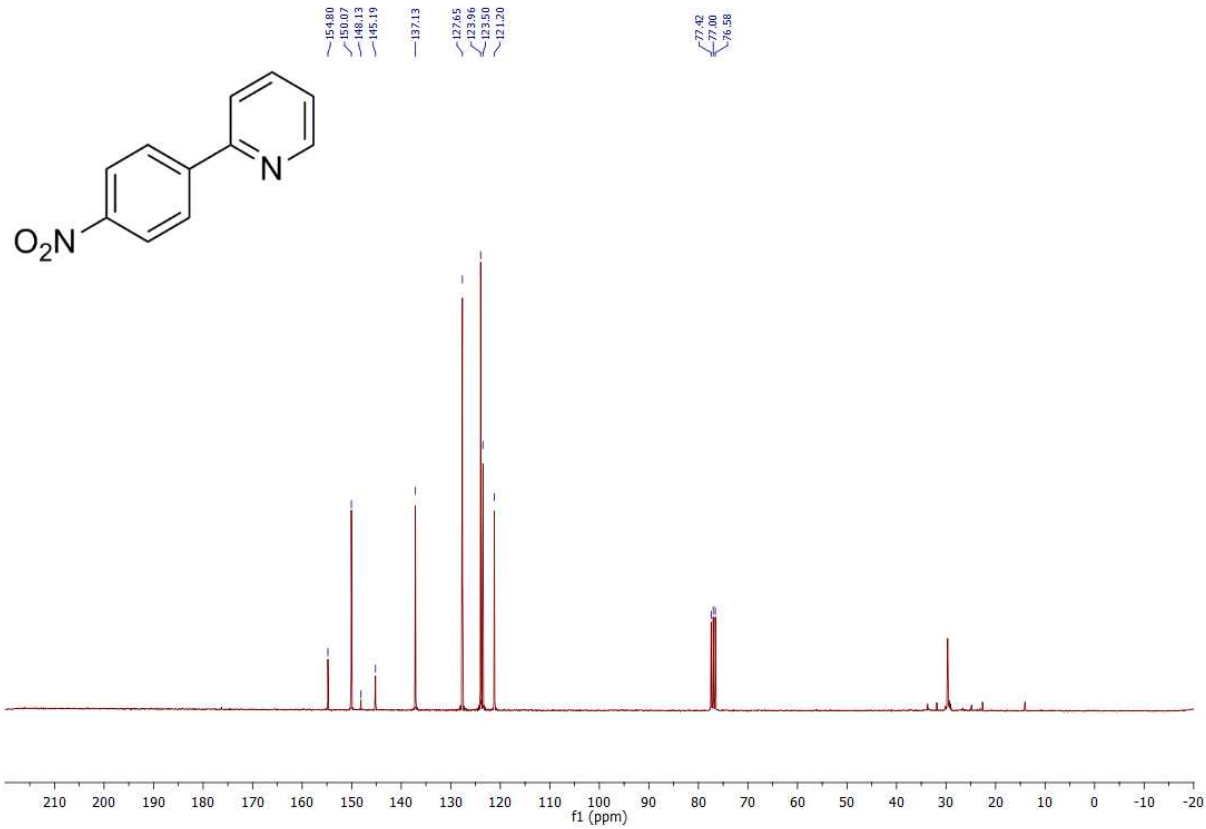



Br
N
B
f1 (ppm)

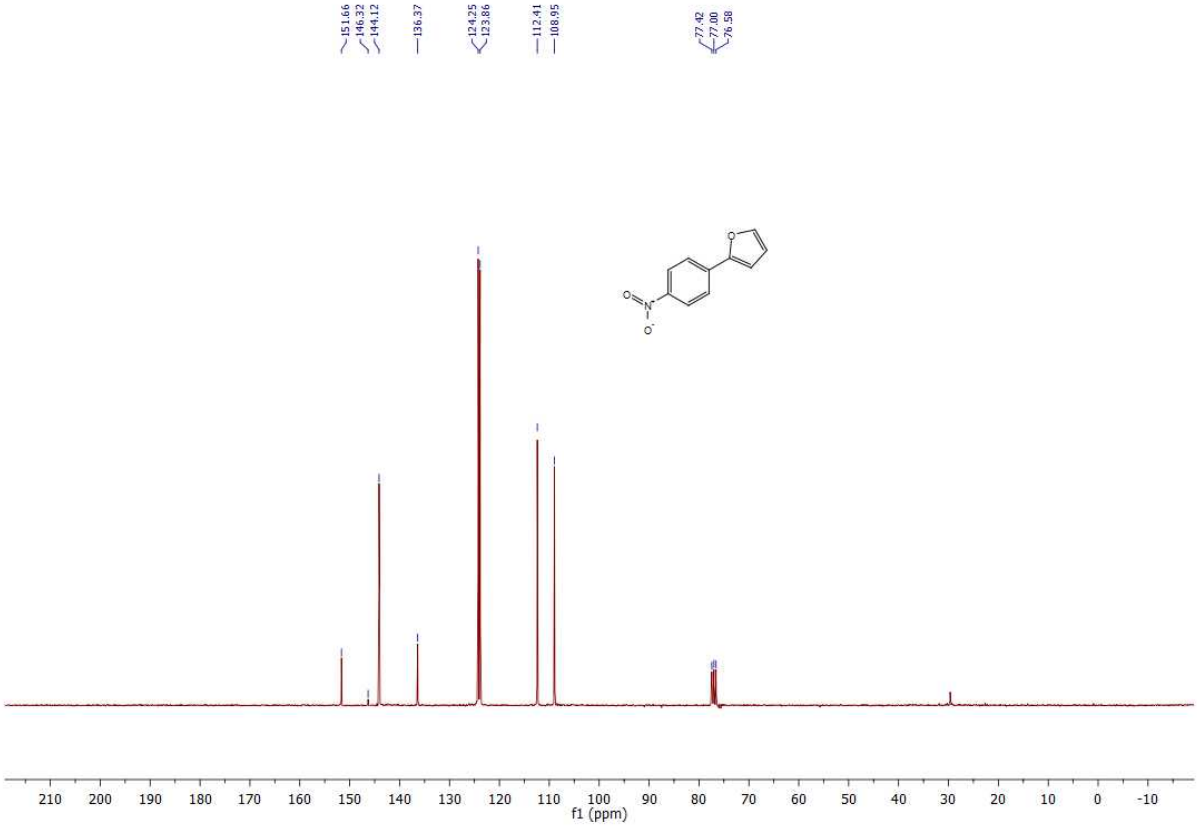

Br
N
B
f1 (ppm)

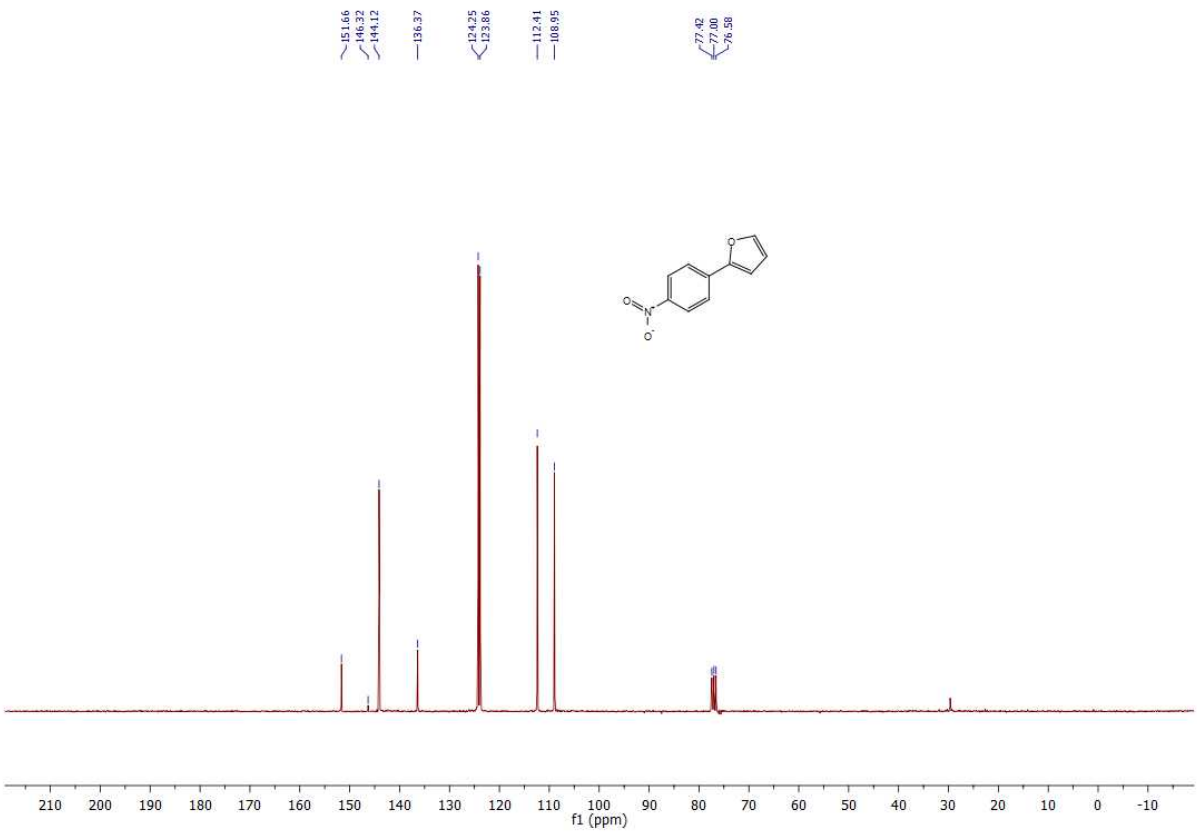
▶ **4-(4-nitrophenyl)pyridine (2i)**



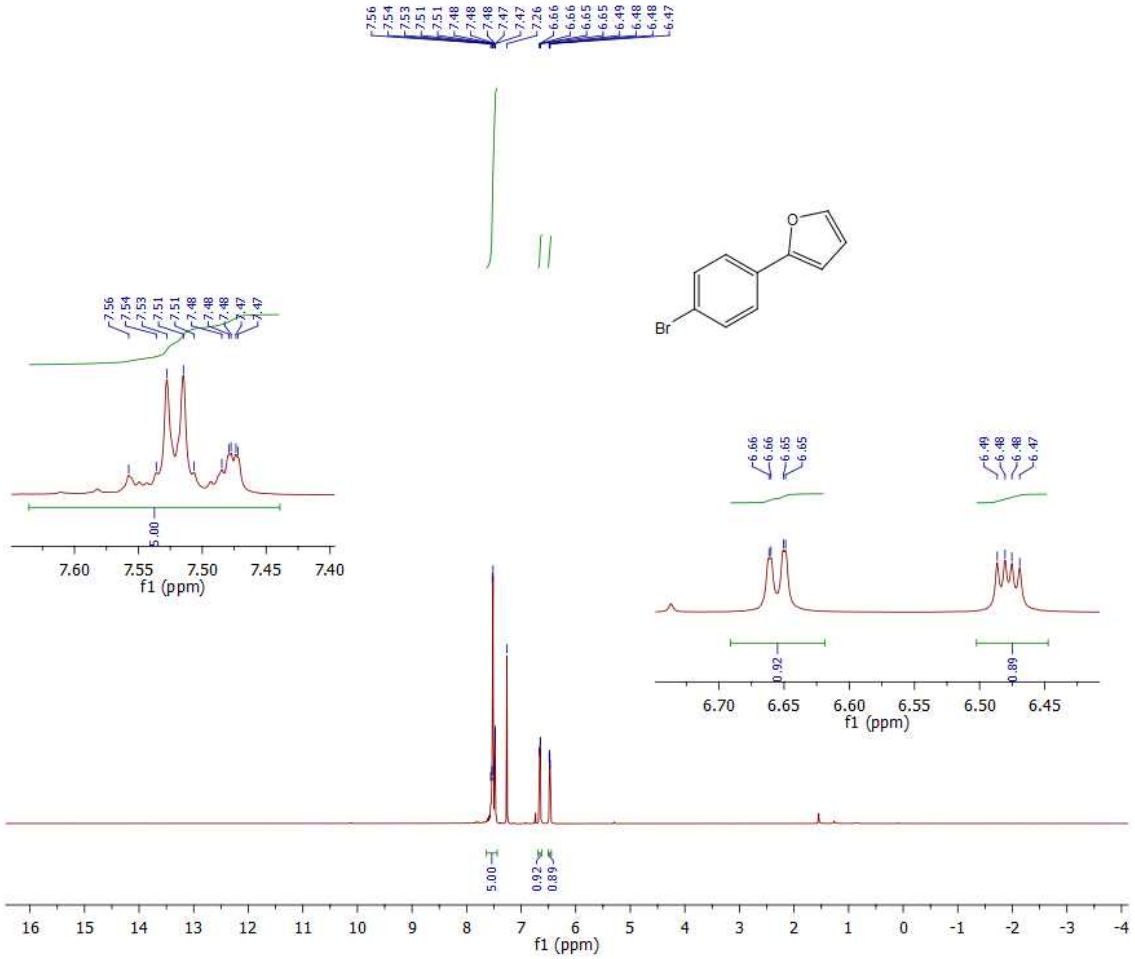


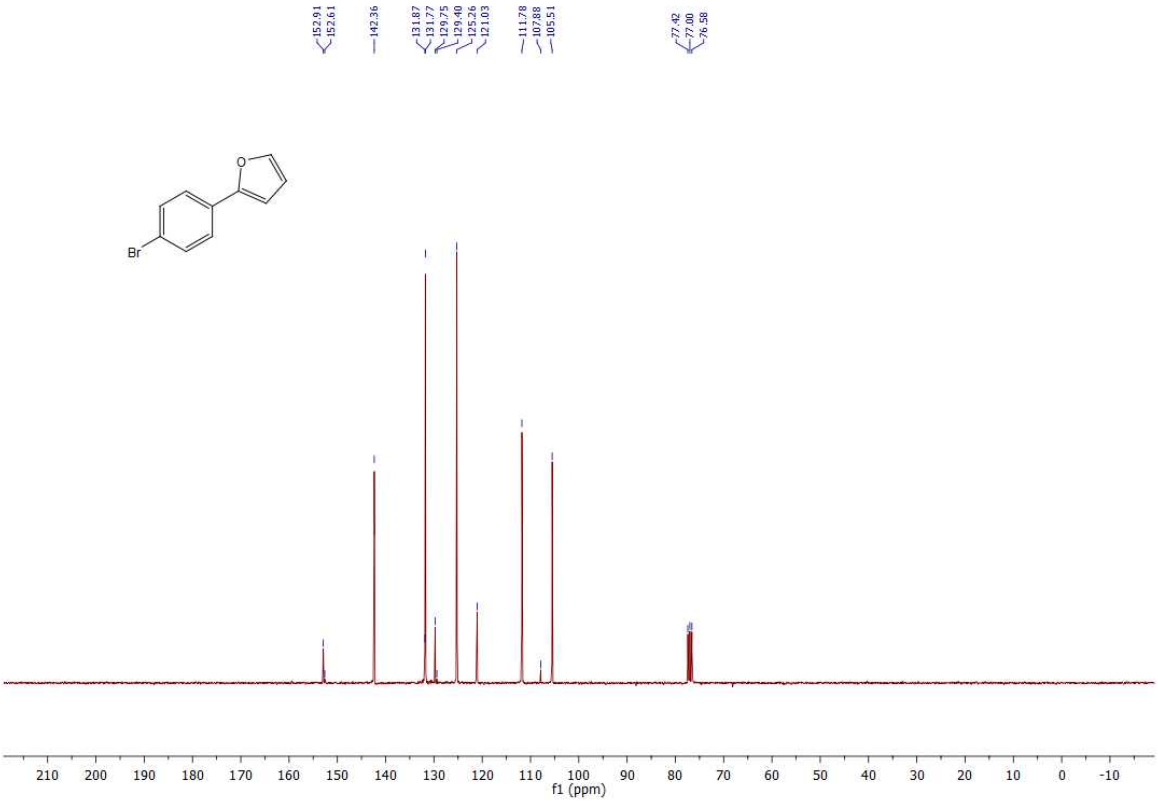
▶ **2-(4-nitrophenyl)furan (2j)**



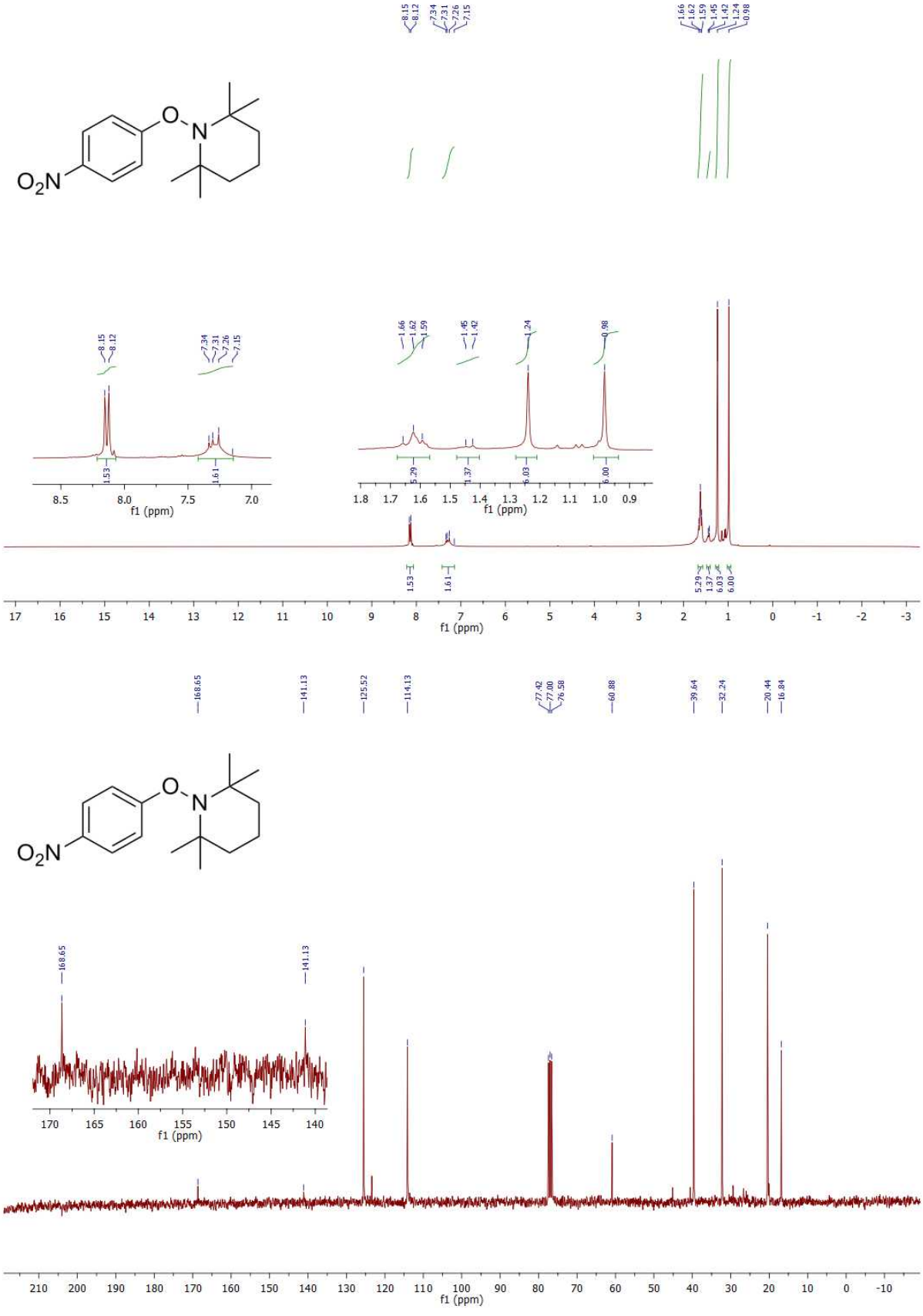


▶ **2-(4-bromophenyl)furan (2k)**





▶ **2,2,6,6-tetramethyl-1-(4-nitrophenoxy)piperidine**



6. Crystallographic data

The crystal structure presented herein was solved from a cobblestone suitable to X-ray single crystal diffraction, obtained by slow evaporation from methanol–acetone mixture. X-ray crystallographic data were collected at room temperature on an Enraf-Nonius Kappa-CCD diffractometer with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) using ϕ and ω-scans. The data analysis showed it to be a trigonal crystal with space group *P -3c1* (n°165)*. The structure was solved by direct methods with SHELXS-2013, and refined with SHELXL-2013.[26] The model was refined using full-matrix least-squares, all non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms have been added geometrically and treated as riding on their parent atoms. Molecular graphics were computed with Ortep-3.[27]

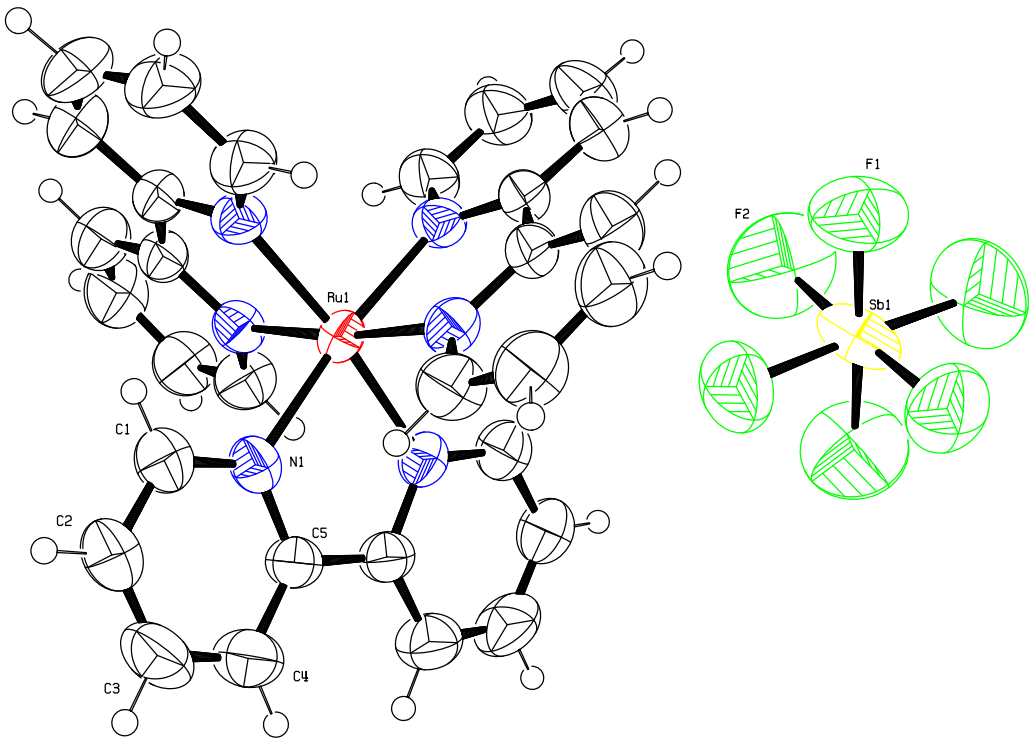


Figure 1: ORTEP-3 plot of $[Ru(bpy)_3]^{2-}$ anion and SbF_6^+ cation, showing the atom-labelling scheme on the asymmetric unit. Ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radius.

Crystal data for $Ru(bpy)_3(SbF_6)_2$: C_{30} H_{24} N_6 F_{12} Sb_2 Ru, Mr= 1041.14, crystal size 0.168 x 0.124 x 0.108 mm, trigonal, space group *P-3c1* (n°165), a = b = 10.7860(4) Å, c = 17.2860(7) Å, V= 1741.59(17) $Å^3$, Z= 2, ρ_{calcd}= 1.985 $g.cm^{-3}$, μ = 2.064 mm^{-1}, F(000)= 1000, λ = 0.71703 Å, $2\theta_{max}$= 55.0 ° (d_{min} = 0.77Å), -14 ≤ h ≤ 14, -11 ≤ k ≤ 14, -22 ≤ l ≤ 16, 3964 measured reflections, 1315 independent, R(int)= 0.032, 78 parameters were refined against 1315 reflections, R1= 0.0862, wR2= 0.1877 (using all data) based on observed *F* values, R1= 0.0515, wR2= 0.1511 (880 reflections with $I>2\sigma(I)$), $\Delta\rho_{min}$ and $\Delta\rho_{max}$= -2.11 and 0.764 $e.Å^{-3}$, GOF= 1.218 based on F^2.

CCDC-1015490 (for $Ru(bpy)_3(SbF_6)_2$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

7. DFT calculation, XYZ coord & energies in Atomic Units

Unless otherwise noted calculations were performed at the DFT level using the M06[28] functionals as implemented in Gaussian09.[29] Geometry optimization were carried out employing Def2-SVP[30] basis sets. Full optimization, without any restriction, was carried out using the CPCM.[31] Stable intermediates were characterized by the absence of any imaginary frequency in their Hessian matrix (for CPCM optimized structures, as implemented in Gaussina09, the implicit solvent effect was taken into account during optimization and thus before the frequency calculation). The same computational model proved efficient to study and describe the mechanism of redox reactions involving $Ru(bpy)^{n+}$ complexes (see ref 6c of the manuscript).

We modeled two SET reactions to compare the calculated ΔG of the two plausible mechanism presented in the main article. In both cases, biaryl Wheland type-cation **7** (R = R' = H in modeled structures) forms via oxidation of the corresponding radical intermediate **6**. In one case, the electron is formally transferred either to Ru(III) to regenerate the catalyst (**Iox** and **Ired** respectively in the article). In the alternative scenario, phenydiazonium cation is formally reduced to the corresponding phenyldiazoyl radical (**4**, R = H in calculation).

$^{d}Ru(bpy)_3^{3+}$

```
   61
scf done: -1578.555887
 C     3.001359    -0.630266    -0.404426
 N     2.506736     0.379389     0.357642
 C     3.336093     1.280308     0.903434
 C     4.706380     1.224706     0.706415
 C     5.226968     0.197507    -0.070575
 C     4.367647    -0.739587    -0.629766
Ru     0.423044     0.388860     0.621558
 H     4.762867    -1.548562    -1.236347
 C     2.001407    -1.557327    -0.944202
 N     0.715754    -1.287816    -0.599982
 N     0.853814    -0.481705     2.480699
 H     5.345212     1.976722     1.158331
 H     6.297165     0.122106    -0.242069
 H     2.881189     2.067935     1.499517
 C     2.300535    -2.645051    -1.754913
 C     1.270612    -3.458649    -2.209610
 H     3.327937    -2.859103    -2.032609
 H     1.494711    -4.313295    -2.842025
 C    -0.039958    -3.169103    -1.850335
 C    -0.279992    -2.068285    -1.044399
 H    -0.871857    -3.781082    -2.184292
 H    -1.287724    -1.800848    -0.735327
 N    -0.126115     1.348885    -1.160490
 C    -1.461360     1.492787    -1.363433
 C    -1.934722     2.133215    -2.501495
 C    -1.028995     2.627322    -3.431591
 C     0.333561     2.466750    -3.212787
 C     0.748806     1.814940    -2.062968
 C    -2.321962     0.934690    -0.314724
 H    -3.001660     2.249839    -2.664290
 H    -1.389575     3.133104    -4.323065
 H     1.071281     2.838633    -3.916721
 H     1.803551     1.665282    -1.844608
 C    -3.709958     0.987481    -0.337723
 C    -4.430339     0.428967     0.710161
 C    -3.752029    -0.173028     1.762477
 C    -2.367048    -0.192077     1.735501
```

```
 N    -1.672270     0.344009     0.721891
 H    -4.229157     1.462080    -1.164632
 H    -5.516063     0.465892     0.701854
 H    -4.278474    -0.624117     2.597592
 H    -1.790731    -0.655745     2.532559
 C     0.825937     0.355909     3.549685
 C     1.095369    -0.120477     4.826361
 C     1.395458    -1.464849     5.002352
 C     1.426616    -2.308642     3.898987
 C     1.155173    -1.777903     2.648411
 C     0.492685     1.751097     3.247151
 H     1.071306     0.548326     5.681051
 H     1.604122    -1.848935     5.997056
 H     1.657763    -3.364747     3.995043
 H     1.163107    -2.398154     1.755529
 C     0.416802     2.759071     4.200331
 C     0.081951     4.047147     3.803661
 C    -0.174883     4.304946     2.463008
 C    -0.085190     3.261025     1.556861
 N     0.247259     2.019430     1.938870
 H     0.617426     2.546533     5.245843
 H     0.019003     4.842214     4.541593
 H    -0.441641     5.297535     2.114212
 H    -0.270265     3.415006     0.496390
Zero-point correction=                           0.484178 (Hartree/Particle)
 Thermal correction to Energy=                    0.513256
 Thermal correction to Enthalpy=                  0.514200
 Thermal correction to Gibbs Free Energy=         0.423388
 Sum of electronic and zero-point Energies=          -1578.071709
 Sum of electronic and thermal Energies=             -1578.042631
 Sum of electronic and thermal Enthalpies=           -1578.041687
 Sum of electronic and thermal Free Energies=        -1578.132499

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                322.073            117.657            191.131
```

$^{S}Ru(bpy)_3^{2+}$

```
   61
scf done: -1578.767660
 C     2.993941    -0.602824    -0.422835
 N     2.490696     0.414407     0.322322
 C     3.324785     1.339923     0.818575
 C     4.692597     1.303369     0.598752
 C     5.218049     0.265617    -0.161807
 C     4.359783    -0.695585    -0.676402
Ru     0.419095     0.380723     0.629119
 H     4.755156    -1.514000    -1.270852
 C     2.001247    -1.560057    -0.930132
 N     0.719005    -1.320961    -0.553676
 N     0.792574    -0.499141     2.495146
 H     5.327101     2.077498     1.019928
 H     6.285792     0.203098    -0.354440
 H     2.866981     2.134663     1.404345
 C     2.317773    -2.647429    -1.740016
 C     1.308416    -3.497397    -2.169161
 H     3.345412    -2.831299    -2.039236
 H     1.545162    -4.349051    -2.801511
 C    -0.001134    -3.243024    -1.779316
 C    -0.252883    -2.144896    -0.972099
 H    -0.822603    -3.881140    -2.091410
 H    -1.260812    -1.907017    -0.637622
 N    -0.132989     1.391376    -1.119031
 C    -1.467567     1.498193    -1.342906
 C    -1.952756     2.156339    -2.469727
 C    -1.059770     2.709006    -3.376640
 C     0.304746     2.590753    -3.140018
 C     0.726133     1.923245    -2.000875
 C    -2.327681     0.891662    -0.318135
 H    -3.022115     2.240621    -2.639801
 H    -1.427992     3.226741    -4.258429
```

```
 H     1.038621     3.007347    -3.823588
 H     1.783349     1.809607    -1.769069
 C    -3.718885     0.907890    -0.367095
 C    -4.446053     0.304244     0.648776
 C    -3.766571    -0.305156     1.696875
 C    -2.380720    -0.287583     1.689605
 N    -1.673260     0.292302     0.709338
 H    -4.235179     1.388963    -1.192620
 H    -5.532362     0.310621     0.619883
 H    -4.294501    -0.790907     2.512215
 H    -1.804151    -0.755174     2.485148
 C     0.792223     0.348118     3.556330
 C     1.014852    -0.122896     4.847439
 C     1.242894    -1.476028     5.051775
 C     1.245787    -2.334143     3.958393
 C     1.017985    -1.805657     2.697525
 C     0.531127     1.758030     3.236113
 H     1.007744     0.559767     5.692139
 H     1.414948    -1.855850     6.055429
 H     1.419502    -3.400103     4.072258
 H     1.004901    -2.436909     1.811157
 C     0.505235     2.776597     4.185263
 C     0.255301     4.080674     3.782471
 C     0.034293     4.341898     2.435519
 C     0.075050     3.286407     1.538581
 N     0.319776     2.024532     1.922016
 H     0.682198     2.557406     5.234112
 H     0.233660     4.883074     4.515178
 H    -0.164974     5.346991     2.075824
 H    -0.084295     3.442819     0.473522
Zero-point correction=                           0.483186 (Hartree/Particle)
 Thermal correction to Energy=                    0.512128
 Thermal correction to Enthalpy=                  0.513073
 Thermal correction to Gibbs Free Energy=         0.423176
 Sum of electronic and zero-point Energies=          -1578.284474
 Sum of electronic and thermal Energies=             -1578.255532
 Sum of electronic and thermal Enthalpies=           -1578.254588
 Sum of electronic and thermal Free Energies=        -1578.344485

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                 321.365            117.702            189.204
```

Phenyldiazonium cation

```
   13
scf done:  -340.662853
 C    -0.002838    -2.558683     4.475422
 C    -0.397534    -1.761601     3.418425
 C     0.620744    -1.129550     2.687721
 C     1.991925    -1.256997     2.960614
 C     2.343202    -2.062976     4.026041
 C     1.354125    -2.706295     4.774378
 H     2.728641    -0.738853     2.354177
 H     3.391863    -2.192401     4.276810
 H     1.647148    -3.335786     5.610986
 H    -0.754003    -3.068910     5.070983
 H    -1.440763    -1.618927     3.152729
 N     0.251239    -0.332197     1.634250
 N    -0.048406     0.314471     0.779866
Zero-point correction=                           0.098993 (Hartree/Particle)
 Thermal correction to Energy=                    0.105181
 Thermal correction to Enthalpy=                  0.106125
 Thermal correction to Gibbs Free Energy=         0.068666
 Sum of electronic and zero-point Energies=           -340.563860
 Sum of electronic and thermal Energies=              -340.557672
 Sum of electronic and thermal Enthalpies=            -340.556728
 Sum of electronic and thermal Free Energies=         -340.594187

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  66.002             23.545             78.839
```

Phenyldiazoyl neutral radical (d)

```
   13
scf done:  -340.828034
 C     0.003493    -2.513360     4.419122
 C    -0.313560    -1.696251     3.343702
 C     0.722136    -1.083773     2.639550
 C     2.054439    -1.271464     2.986150
 C     2.361613    -2.092682     4.065900
 C     1.337881    -2.711450     4.778869
 H     2.828607    -0.772120     2.406751
 H     3.399700    -2.250330     4.350117
 H     1.579401    -3.353052     5.624018
 H    -0.790691    -3.000879     4.980979
 H    -1.344523    -1.523211     3.039523
 N     0.462260    -0.217371     1.503264
 N    -0.615412     0.037238     1.084457
Zero-point correction=                           0.096997 (Hartree/Particle)
 Thermal correction to Energy=                    0.103364
 Thermal correction to Enthalpy=                  0.104309
 Thermal correction to Gibbs Free Energy=         0.065761
 Sum of electronic and zero-point Energies=           -340.731037
 Sum of electronic and thermal Energies=              -340.724670
 Sum of electronic and thermal Enthalpies=            -340.723726
 Sum of electronic and thermal Free Energies=         -340.762273

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  64.862             23.936             81.129
```

N_2

```
    2
scf done:  -109.455402
 N     0.348257    -0.186478     1.453755
 N    -0.700740    -0.016431     1.151201

Zero-point correction=                           0.005622 (Hartree/Particle)
 Thermal correction to Energy=                    0.007983
 Thermal correction to Enthalpy=                  0.008927
 Thermal correction to Gibbs Free Energy=        -0.012826
 Sum of electronic and zero-point Energies=           -109.449780
 Sum of electronic and thermal Energies=              -109.447420
 Sum of electronic and thermal Enthalpies=            -109.446475
 Sum of electronic and thermal Free Energies=         -109.468229

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  5.009              4.970             45.784
```

Phenyl neutral radical (d)

```
   11
scf done:  -231.367337
 C    -0.292954    -1.672289     3.312954
 C     0.773529    -1.099138     2.661313
 C     2.098392    -1.270226     2.986503
 C     2.375035    -2.101380     4.078162
 C     1.332979    -2.709519     4.776714
 C     0.006811    -2.499569     4.401435
 H     2.902975    -0.788139     2.432693
 H     3.408095    -2.271833     4.379641
 H     1.557855    -3.353801     5.624881
 H    -0.800160    -2.980168     4.953702
 H    -1.324730    -1.499728     3.009454
Zero-point correction=                           0.087249 (Hartree/Particle)
 Thermal correction to Energy=                    0.091648
 Thermal correction to Enthalpy=                  0.092592
```

```
 Thermal correction to Gibbs Free Energy=         0.059197
 Sum of electronic and zero-point Energies=           -231.280088
 Sum of electronic and thermal Energies=              -231.275689
 Sum of electronic and thermal Enthalpies=            -231.274745
 Sum of electronic and thermal Free Energies=         -231.308140

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                   57.510             16.913             70.287
```

Phenyl cation

```
   11
scf done:  -231.151819
 C    -0.345011    -1.665752     3.301598
 C     0.822387    -1.239590     2.846175
 C     2.140680    -1.248477     2.961119
 C     2.373386    -2.102401     4.078354
 C     1.331828    -2.706561     4.772652
 C     0.008230    -2.498998     4.402459
 H     2.915948    -0.752509     2.389097
 H     3.418109    -2.247323     4.348611
 H     1.556293    -3.349213     5.618492
 H    -0.825293    -2.961744     4.928377
 H    -1.358730    -1.473222     2.970516
Zero-point correction=                           0.085068 (Hartree/Particle)
 Thermal correction to Energy=                    0.089922
 Thermal correction to Enthalpy=                  0.090866
 Thermal correction to Gibbs Free Energy=         0.057470
 Sum of electronic and zero-point Energies=           -231.066752
 Sum of electronic and thermal Energies=              -231.061897
 Sum of electronic and thermal Enthalpies=            -231.060953
 Sum of electronic and thermal Free Energies=         -231.094349

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                   56.427             18.812             70.288
```

Biphenyl neutral radical (d)

```
   23
scf done:  -463.460249
 C    -0.187778    -2.485105     3.933925
 C    -0.005219    -1.682939     2.846064
 C     1.303347    -1.011446     2.542137
 C     2.371259    -1.362661     3.537856
 C     2.140246    -2.172309     4.611017
 C     0.867981    -2.749696     4.839648
 H     3.354618    -0.918369     3.380917
 H     2.950445    -2.379678     5.310071
 H     0.702934    -3.391212     5.702616
 H    -1.165596    -2.932897     4.111411
 H    -0.829342    -1.482250     2.160866
 H     1.639852    -1.334849     1.535209
 C     1.120742     0.500361     2.450627
 C     1.325126     1.186102     1.254545
 C     1.146583     2.566591     1.189405
 C     0.761628     3.274278     2.323865
 C     0.554253     2.595435     3.524072
 C     0.732380     1.218228     3.584866
 H     1.626623     0.631946     0.364558
 H     1.309930     3.089045     0.247873
 H     0.622918     4.353035     2.274472
 H     0.253012     3.143834     4.415488
 H     0.569932     0.683734     4.522542

Zero-point correction=                           0.189488 (Hartree/Particle)
 Thermal correction to Energy=                    0.199062
 Thermal correction to Enthalpy=                  0.200006
```

```
 Thermal correction to Gibbs Free Energy=         0.152960
 Sum of electronic and zero-point Energies=           -463.270761
 Sum of electronic and thermal Energies=              -463.261188
 Sum of electronic and thermal Enthalpies=            -463.260243
 Sum of electronic and thermal Free Energies=         -463.307289

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  124.913             38.791            99.015
```

Biphenyl Wheland-type cation

```
   23
scf done:  -463.293879
 C    -0.171151    -2.557403     3.934973
 C    -0.032121    -1.653046     2.920926
 C     1.245665    -0.972344     2.659513
 C     2.347571    -1.311589     3.573606
 C     2.190657    -2.217364     4.584030
 C     0.935904    -2.828680     4.760295
 H     3.300761    -0.811696     3.409132
 H     3.010264    -2.461423     5.252962
 H     0.814990    -3.544168     5.572271
 H    -1.118179    -3.056019     4.117952
 H    -0.867488    -1.407602     2.267215
 H     1.573767    -1.358206     1.665858
 C     1.080322     0.539639     2.492285
 C     1.378039     1.169444     1.287234
 C     1.223846     2.548537     1.174312
 C     0.774841     3.293395     2.260567
 C     0.478183     2.660822     3.465538
 C     0.630801     1.284261     3.584173
 H     1.728824     0.586055     0.437000
 H     1.455716     3.040101     0.231659
 H     0.655364     4.370984     2.168277
 H     0.128060     3.240240     4.317289
 H     0.401237     0.785240     4.526981

Zero-point correction=                           0.191680 (Hartree/Particle)
 Thermal correction to Energy=                    0.201226
 Thermal correction to Enthalpy=                  0.202170
 Thermal correction to Gibbs Free Energy=         0.155732
 Sum of electronic and zero-point Energies=           -463.102199
 Sum of electronic and thermal Energies=              -463.092654
 Sum of electronic and thermal Enthalpies=            -463.091710
 Sum of electronic and thermal Free Energies=         -463.138147

                     E (Thermal)             CV                S
                      KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
 Total                  126.271             38.160            97.737
```

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