Supporting Information

Highly active $[Pd(\mu\text{-}Cl)(Cl)(NHC)]_2$ (NHC = *N*-Heterocyclic Carbene) in the Cross Coupling of Grignard Reagents with Aryl Chlorides

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General

All manipulations were performed under an inert atmosphere of argon using standard Schlenk technique, a MBraun glove-box containing less than 1 ppm Oxygen and water and using dried solvents and glassware. The dimeric complexes $[Pd(\mu\text{-}Cl)(Cl)(SIPr)]_2$ (**1**), $[Pd(\mu\text{-}Cl)(Cl)(IPr)]_2$ (**2**), $[Pd(\mu\text{-}Cl)(Cl)(SIMes)]_2$ (**3**) and $[Pd(\mu\text{-}Cl)(Cl)(IMes)]_2$ (**4**) were prepared according to the literature.[1,2]

Reagents for the cross coupling reaction were purchased and used as received. The LiCl-activated Grignard reagent was synthesized according to literature.[3] All reported yields are average of minimum two runs. Flash column chromatography was performed on silica gel 60 (230-400 mesh). Gas Chromatography analyses were performed on an Agilent 6890 apparatus equipped with a flame ionization detector and a silicon column (30 m, 320 µm, film thickness: 0.25 µm). NMR spectra were recorded on a Bruker Avance 400 ULTRASHIELD spectrometer at 25 ºC. IR spectra were recorded on a FTIR spectrometer Bruker Tensor 27. High resolution mass spectra (HRMS) were recorded on an ESI-TOF waters LCT Premier instrument.

General procedure for the cross coupling reaction.

In a glovebox, a 5 mL screwcap-vial fitted with a septum and equipped with a magnetic stirring bar was charged with a 0.005 M solution of $[Pd(\mu\text{-}Cl)(Cl)(NHC)]_2$ in THF and 1.5 mL of dry THF. Outside the glove box, the aryl halide (0.50 mmol) and the Grignard reagent (0.55 mmol) were added simultaneously. Alternatively, if the aryl halide was solid at room temperature, it was weighed and added to the catalyst solution in the glove box. The reaction mixture was then allowed to stir at rt/60 ºC and the conversion was monitored by gas chromatography. When the reaction reached completion, or no further conversion was observed by gas chromatography, the solvent was removed under *vacuum*. The product was then purified by flash chromatography.

Catalysts

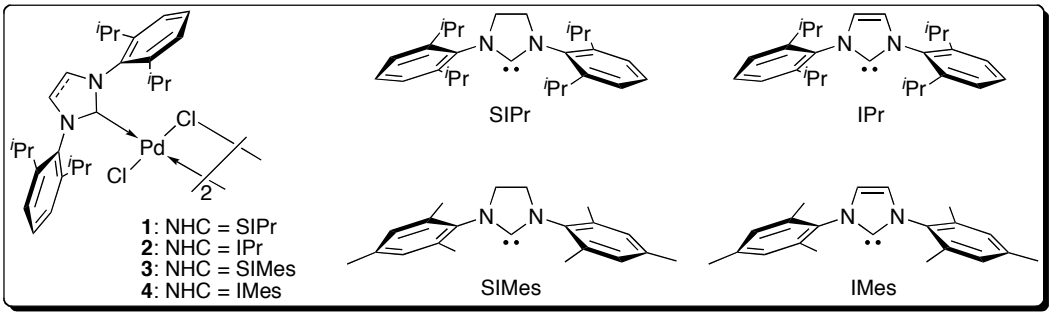
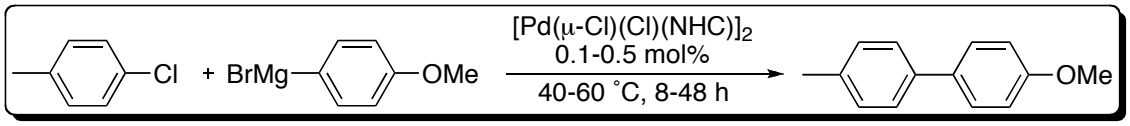


Table S1. Catalytic optimization studies.[a]



entry	Catalyst (mol%)	No. equiv. ArMgBr	solvent	T (°C)	t (h)	Conv. (%)[b]
1	**1** (0.5)	3	THF	60	24	93
2	**1** (0.5)	3	THF/toluene 1:1	60	24	78
3	**1** (0.5)	3	THF/1,4-dioxane 1:1	60	24	70
4	**1** (0.5)	3	THF/DMI 1:1	60	24	40
5	**1** (0.5)	3	THF/DME 1:1	60	24	9
6	**1** (0.5)	3	THF	60	24	70[c]
7	**1** (0.5)	3	THF/DME 1:1	60	24	74[c]
8	**1** (0.5)	3	THF	60	8	51
9	**1** (0.5)	3	THF	60	8	56[d]
10	**1** (0.5)	1.5	THF	60	20	96
11	**1** (0.5)	1.1	THF	60	16	96
12	**1** (0.5)	1.1	THF	50	16	68
13	**1** (0.5)	1.1	THF	40	16	62
14	**1** (0.2)	**1.1**	**THF**	**60**	**16**	**99**
15	**1** (0.1)	1.1	THF	60	48	84
16	**2** (0.2)	1.1	THF	60	16	57
17	**3** (0.2)	1.1	THF	60	16	25
18	**4** (0.2)	1.1	THF	60	16	<5

[a]Reaction conditions: 4-chlorotoluene (0.5 mmol), 4-methoxy-phenylmagnesium bromide (0.55-1.5 mmol), 0.1-0.5 mol% $[Pd(\mu\text{-}Cl)(Cl)(NHC)]_2$, Solvent (2.05-3.0 mL). [b]Conversion to coupling product, based on 4-chlorotoluene, determined by GC (average of two runs). [c]LiCl added (1.0 mmol) [d]Using TurboGrignard reagent ArMgBr·LiCl.

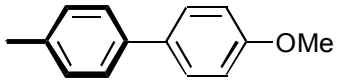
As shown in Table S1, solvent optimization was performed at 60 °C, for 24 h, for the coupling of 4-chlorotoluene with 4-methoxyphenylmagnesium bromide as a model reaction. Because the Grignard reagent is commercially available as a THF-solution, the solvent screening was performed in solvent mixtures. As can be seen in Table S1, optimum results were obtained when the reaction was carried out in neat THF (Table S1, entries 1-5). Grignard reagents can be activated *in situ* by lithium salts, we thus tested this strategy with our system.[4] In THF, the presence of LiCl was deleterious to catalyst activity (Table S1, entries 1 vs 6), while in THF/DME mixture, the conversion was drastically improved when LiCl was used (Table S1, entries 5 vs 7). However, this result was still not superior to the one obtained in THF without additive. Following the procedure developed by Knochel,[5] the reagent ArMgBr·LiCl was synthesized and used as coupling partner. This system did not lead to a sufficient improvement in catalyst efficiency to make its use advantageous (Table S1, entries 8 vs 9). Subsequent reactions were thus carried out in neat THF, using ArMgX reagents in the absence of additives.

The necessity of using an excess of Grignard reagent was then assessed. As can be seen (Table S1, entries 1, 10 and 11), reducing the amount of ArMgBr increases the efficiency of the catalytic process. This is also interesting from an economic and environmental perspective as less Grignard reagent is used, less waste is generated, and purification is therefore facilitated.

In order to further optimize the reaction conditions, the reaction temperature was decreased, resulting in diminished catalyst efficiency (Table S1, entries 12 and 13). It was then of interest to lower the catalyst loading. To our delight, at 0.2 mol% catalyst loading the reaction reached completion within 16 hours (Table S1, entry 14). Decreasing further the catalyst loading to 0.1 mol% showed complex **1** to be slower but still highly efficient for the coupling of 4-chlorotoluene with 4-methoxyphenylmagnesium bromide (Table S1, entry 15). Finally, the catalytic efficiency of four dimers of the $[Pd(\mu\text{-}Cl)(Cl)(NHC)]_2$ type (NHC = IPr, SIPr, IMes, SIMes) was compared (Table S1, entries 14, 16-18). $[Pd(\mu\text{-}Cl)(Cl)(SIPr)]_2$ (**1**) led to the best result with a quantitative conversion to the biaryl product.

Cross coupling products

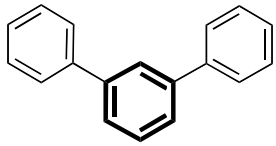
4-methoxy-4´-methylbiphenyl (Table S1).[6]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 20:1), 98 mg (99%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.50 (d, $^{3}J_{HH}$ = 8.6 Hz, 2 H, CH), 7.43 (d, $^{3}J_{HH}$ = 8.2 Hz, 2 H, CH), 7.22 (d, $^{3}J_{HH}$ = 8.2 Hz, 2 H, CH), 6.96 (d, $^{3}J_{HH}$ = 8.6 Hz, 2 H, CH), 3.84 (s, 3 H, OMe), 2.38 (s, 3 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 158.9, 138.0, 136.4, 133.8, 129.5, 128.0, 126.6, 114.2, 55.4, 21.1.

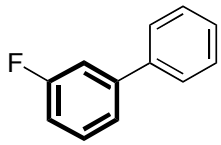
1,3-diphenylbenzene (Table 1, entry 1).[7]



The procedure afforded, after flash chromatography on silica gel (hexane), 92 mg (80%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.80 (s, 1 H, CH), 7.64 (d, $^{3}J_{HH}$ = 7.7 Hz, 4 H, CH), 7.58-7.56 (m, 2 H, CH), 7.50 (dd, $^{3}J_{HH}$ = 6.8 Hz, 1 H, CH), 7.46 (dd, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.7 Hz, 4 H, CH), 7.36 (pseudo-triplet, $^{3}J_{HH}$ = 7.5 Hz, 2 H, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 141.8, 141.2, 129.2, 128.8, 127.4, 127.3, 126.19, 126.15.

3-fluorobiphenyl (Table 1, entry 2).[8]

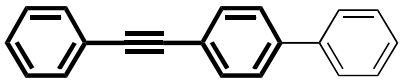


The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 60:1), 75 mg (81%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.58-7.56 (m, 2 H, CH), 7.46-7.42 (m, 2 H, CH), 7.40-7.35 (m, 3 H, CH), 7.30-7.27 (m, 1 H, CH), 7.06-7.01 (m, 1 H, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 163.2 (d, $^{1}J_{CF}$ = 245.7 Hz), 143.5 (d, $^{3}J_{CF}$ = 7.3 Hz), 140.0 (d, $^{4}J_{CF}$ = 2.3 Hz), 130.2 (d, $^{3}J_{CF}$ = 7.3 Hz), 128.9 (s), 127.9 (s),

127.1 (s), 122.8 (d, $^{4}J_{CF}$ = 2.9 Hz), 114.04 (d, $^{2}J_{CF}$ = 21.2 Hz), 114.03 (d, $^{2}J_{CF}$ = 21.2 Hz). ^{19}F-{^{1}H} NMR ($CDCl_3$, 376 MHz) δ (ppm) = -113.3 (s).

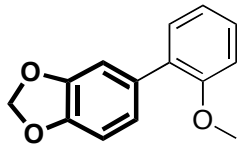
4-(phenylethynyl)-1,1'-biphenyl (Table 1, entry 3).[9]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 60:1), 93 mg (73%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.62-7.57 (m, 6 H, CH), 7.55-7.54 (m, 2 H, CH), 7.45 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 7.9 Hz, 2 H, CH), 7.38-7.34 (m, 4 H, CH). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 141.0, 140.4, 132.0, 131.6, 128.9, 128.4, 128.3, 127.7, 127.0, 123.3, 122.2, 90.1, 89.3.

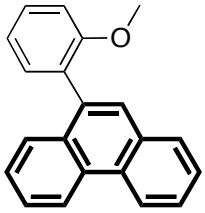
2'-methoxy-3,4-(methylenedioxy)biphenyl (Table 1, entry 4).[10]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 60:1), 64 mg (56%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.30-7.28 (m, 2 H, CH), 7.05 (s, 1 H, CH), 7.01-6.94 (m, 3 H, CH), 6.85 (d, $^{3}J_{HH}$ = 8.0 Hz, 1 H, CH), 5.95 (s, 2 H, CH_2), 3.79 (s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 156.4, 147.2, 146.6, 132.5, 130.8, 130.4, 128.4, 122.9, 120.9, 111.2, 110.3, 108.1, 101.0, 55.6.

9-(2-methoxyphenyl)phenantrene (Table 1, entry 5).[11]

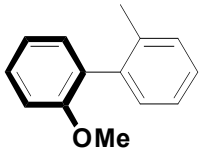


The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 40:1), 116 mg (91%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.73 (d, $^{3}J_{HH}$ = 8.3 Hz, 1 H, CH), 8.69 (d, $^{3}J_{HH}$ = 8.3 Hz, 1 H, CH), 7.86 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ =1.3 Hz, 1 H, CH), 7.66 (s, 1 H, CH), 7.65-7.55 (m, 4 H, CH), 7.49-7.41 (m, 2 H, CH), 7.34 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ =1.7 Hz, 1 H, CH), 7.11-7.07 (m, 1 H, CH), 7.03 (d, $^{3}J_{HH}$ = 8.3 Hz, 1 H, CH), 3.65

(s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 157.6, 135.9, 131.9, 131.8, 131.5, 130.3, 130.2, 129.7, 129.2, 128.7, 127.9, 127.2, 126.7, 126.5, 126.32, 126.28, 122.8, 122.6, 120.8, 111.0, 55.6.

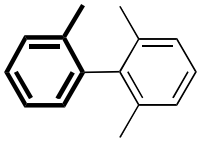
2-methyl-2'-methoxybiphenyl (Table 1, entry 6).[12]



The procedure afforded, after flash chromatography on silica gel (hexane, then hexane/ethyl acetate 98:2), 76 mg (77%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.32 (ddd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1 H, CH), 7.25-7.16 (m, 4 H, CH), 7.14 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 1.7 Hz, 1 H, CH), 6.99 (d, $^{3}J_{HH}$ = 7.4 Hz, 1 H, CH), 6.94 (d, $^{3}J_{HH}$ = 8.2 Hz, 1 H, CH), 3.73 (s, 3 H, OMe), 2.13 (s, 3 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 156.7, 138.7, 136.9, 131.1, 131.0, 130.1, 129.7, 128.6, 127.4, 125.5, 120.5, 110.8, 55.4, 20.0.

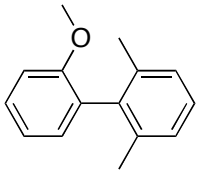
2,2',6'-trimethylbiphenyl (Table 2, entry 1).[13]



The procedure afforded, after flash chromatography on silica gel (hexane), 94 mg (95%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.29-7.23 (m, 3 H, CH), 7.16 (dd, $^{3}J_{HH}$ = 6.2 Hz, 1 H, CH), 7.10 (d, $^{3}J_{HH}$ = 7.5 Hz, 2 H, CH), 7.02-7.00 (m, 1 H, CH), 1.96 (s, 3 H, Me), 1.94 (s, 6 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 141.1, 140.6, 135.9, 135.6, 130.0, 128.9, 127.2, 127.0, 126.9, 126.1, 29.4, 19.4.

2-Methoxy-2',6'-dimethylbiphenyl (Table 2, entries 2 and 3).[14]

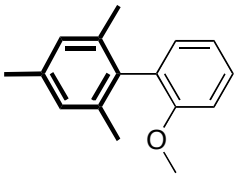


The procedure (Table 3, entry 2) afforded, after flash chromatography on silica gel (hexane, then hexane/ethyl acetate 40:1), 103 mg (97%) of the title compound.

The procedure (Table 3, Entry 3) afforded, after flash chromatography on silica gel (hexane, then hexane/ethyl acetate 40:1), 76 mg (72%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.32-7.27 (m, 1 H, CH), 7.16 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 8.4 Hz, 1 H, CH), 7.10 (d, $^{3}J_{HH}$ = 7.5 Hz, 2 H, CH), 7.04-7.01 (m, 2 H, CH), 6.98 (d, $^{3}J_{HH}$ = 8.4 Hz, 1 H, CH), 3.73 (s, 3 H, OMe), 2.01 (s, 6 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 156.6, 138.3, 136.6, 130.7, 129.6, 128.4, 127.09, 127.05, 120.7, 110.9, 55.5, 20.5.

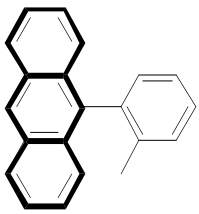
2-Methoxy-2',4',6'-trimethylbiphenyl (Table 2, entry 4).[15]



The procedure afforded, after flash chromatography on silica gel (hexane, then hexane/ethyl acetate 98:2), 43 mg (42%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.32 (ddd, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 2.3 Hz, 1 H, CH), 7.03-6.97 (m, 3 H, CH), 6.93 (s, 2 H, CH), 3.72 (s, 3 H, OMe), 2.32 (s, 3 H, Me), 1.98 (s, 6 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 156.8, 136.55, 136.51, 135.3, 131.0, 129.6, 128.3, 128.0, 120.7, 110.9, 55.5, 21.2, 20.4.

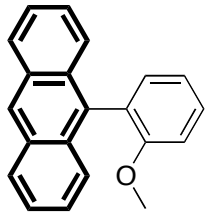
9-(2-methylphenyl)anthracene (Table 2, entry 5).[16]



The procedure afforded, after flash chromatography on silica gel (hexane), 134 mg (>99%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.48 (s, 1 H, CH), 8.04 (d, $^{3}J_{HH}$ = 8.2 Hz, 2 H, CH), 7.51-7.42 (m, 6 H, CH), 7.39-7.30 (m, 3 H, CH), 7.25 (d, $^{3}J_{HH}$ = 7.2 Hz, 1 H, CH), 1.86 (s, 1 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 138.2, 137.8, 136.4, 131.5, 131.2, 130.1, 130.0, 128.5, 127.9, 126.5, 126.4, 125.9, 125.5, 125.2, 19.8.

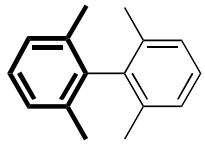
9-(2-methoxyphenyl)anthracene (Table 2, entry 6).[16]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 60:1), 127 mg (90%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.42 (s, 1 H, CH), 7.97 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, CH), 7.59 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, CH), 7.47 (ddd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, CH), 7.39 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, CH), 7.29 (ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.3 Hz, 2 H, CH), 7.24 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, CH), 7.11 (ddd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 0.9 Hz, 1 H, CH), 7.07 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 0.9 Hz, 1 H, CH), 3.52 (s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 158.1, 133.9, 133.0, 131.6, 130.5, 129.4, 128.5, 127.4, 126.9, 126.7, 125.3, 125.1, 120.8, 111.4, 55.7.

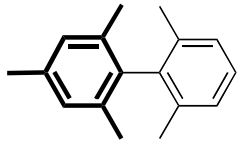
2,2'-6,6'-tetramethylbiphenyl (Table 2, entry 7).[17]



The procedure afforded, after flash chromatography on silica gel (hexane), 72 mg (69%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.16 (d, $^3J_{HH}$ = 8.9 Hz, 2 H, CH) 7.19-7.10 (m, 4 H, CH), 1.99 (s, 12 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 140.0, 135.5, 127.5, 126.9, 19.9.

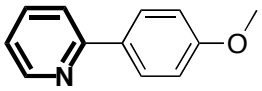
2,2',4,6,6'-pentamethylbiphenyl (Table 2, entry 8).[18]



The procedure afforded, after flash chromatography on silica gel (hexane), 39 mg (35%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.14-7.09 (m, 3 H, CH), 6.94 (s, 2 H, CH), 2.33 (s, 3 H, Me), 1.90 (s, 6 H, Me), 1.86 (s, 6 H, Me). ^{13}C -{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 140.1, 137.0, 136.2, 135.8, 135.3, 128.3, 127.4, 126.7, 21.2, 19.9, 19.8.

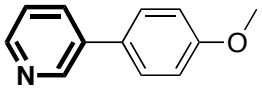
2-(4-methoxyphenyl)pyridine (Table 3, entry 1).[19]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 20:1), 92 mg (99%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.65 (d, $^{3}J_{HH}$ = 4.8 Hz, 1 H, CH), 7.95 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, CH), 7.73-7.65 (m, 2 H, CH), 7.18-7.17 (m, 1 H, CH), 7.00 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, CH), 3.86 (s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 160.5, 157.2, 149.6, 136.6, 132.1, 128.2, 121.4, 119.8, 114.1, 55.4.

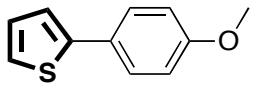
3-(4-methoxyphenyl)pyridine (Table 3, entry 2).[20]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 20:1, then 1:1), 92 mg (99%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.82 (bs, 1 H, CH), 8.55 (d, $^{3}J_{HH}$ = 4.0 Hz, 1 H, CH), 7.83 (ddd, $^{3}J_{HH}$ = 8.0 Hz, $^{4}J_{HH}$ = 1.9 Hz, $^{4}J_{HH}$ = 1.9 Hz, 1 H, CH), 7.52 (d, $^{3}J_{HH}$ = 8.7 Hz, 2 H, CH), 7.35-7.31 (m, 1 H, CH), 7.01 (d, $^{3}J_{HH}$ = 8.7 Hz, 2 H, CH), 3.86 (s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 159.8, 148.0, 147.9, 136.3, 133.8, 130.3, 128.2, 123.5, 114.6, 55.4.

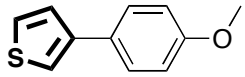
2-(4-methoxyphenyl)thiophene (Table 3, entry 3).[21]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 20:1), 84 mg (89%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.54 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, CH), 7.22-7.19 (m, 2 H, CH), 7.05 (dd, $^{3}J_{HH}$ = 5.0 Hz, $^{3}J_{HH}$ = 3.7 Hz, 1 H, CH), 6.91 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, CH), 3.83 (s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 159.2, 144.3, 127.9, 127.3, 127.2, 123.8, 122.1, 114.3, 55.4.

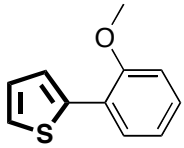
3-(4-methoxyphenyl)thiophene (Table 3, entry 4).[22]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 40:1), 51 mg (54%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.53 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, CH), 7.38-7.34 (m, 3 H, CH), 6.94 (d, $^{3}J_{HH}$ = 8.8 Hz, 2 H, CH), 3.84 (s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 159.0, 128.8, 127.6, 126.3, 126.1, 118.9, 114.2, 55.3

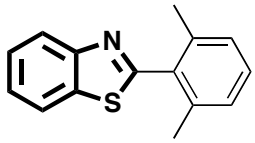
2-(2-methoxyphenyl)thiophene (Table 3, entry 5).[23]



The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 40:1), 92 mg (97%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.64 (dd, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1 H, CH), 7.49 (dd, $^{3}J_{HH}$ = 3.7 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1 H, CH), 7.31 (dd, $^{3}J_{HH}$ = 5.1 Hz, $^{4}J_{HH}$ = 1.1 Hz, 1 H, CH), 7.25 (ddd, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 1.6 Hz, 1 H, CH), 7.08 (dd, $^{3}J_{HH}$ = 5.1 Hz, $^{3}J_{HH}$ = 3.7 Hz, 1 H, CH), 7.01-6.96 (m, 2 H, CH), 3.91 (s, 3 H, OMe). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 155.6, 139.5, 128.6, 128.4, 126.8, 125.44, 125.37, 123.4, 121.0, 111.7, 55.6.

2-(2,6-Dimethylphenyl)benzothiazole (Table 3, entry 6).

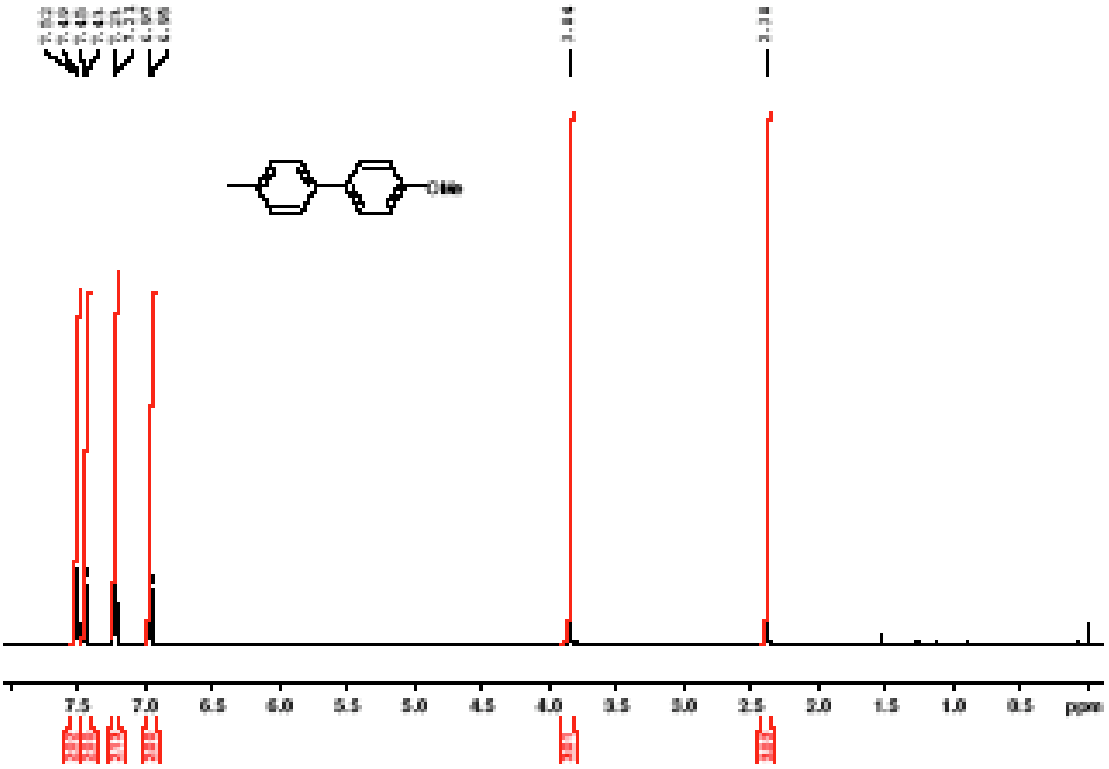


The procedure afforded, after flash chromatography on silica gel (hexane/ethyl acetate 60:1), 109 mg (90%) of the title compound.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 8.12 (d, $^{3}J_{HH}$ = 7.6 Hz, 1 H, CH), 7.95 (d, $^{3}J_{HH}$ = 8.0 Hz, 1 H, CH), 7.55-7.51 (m, 1 H, CH), 7.46-7.42 (m, 1 H, CH), 7.29-7.27 (m, 1 H, CH), 7.14 (d, $^{3}J_{HH}$ = 7.6 Hz, 2 H, CH), 2.21 (s, 6 H, Me). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 167.5, 153.5, 137.4, 136.3, 133.6, 129.6, 127.6, 126.0, 125.2, 123.5, 121.6, 20.2. IR (neat, cm^{-1}): ν 3057, 2917, 2852, 1514, 1456, 1434, 1210, 956, 786, 765, 733. HRMS (ESI) calcd for $C_{15}H_{13}NS$: 240.0857; found: 240.0847.

NMR Spectra of cross coupling products

Table S1



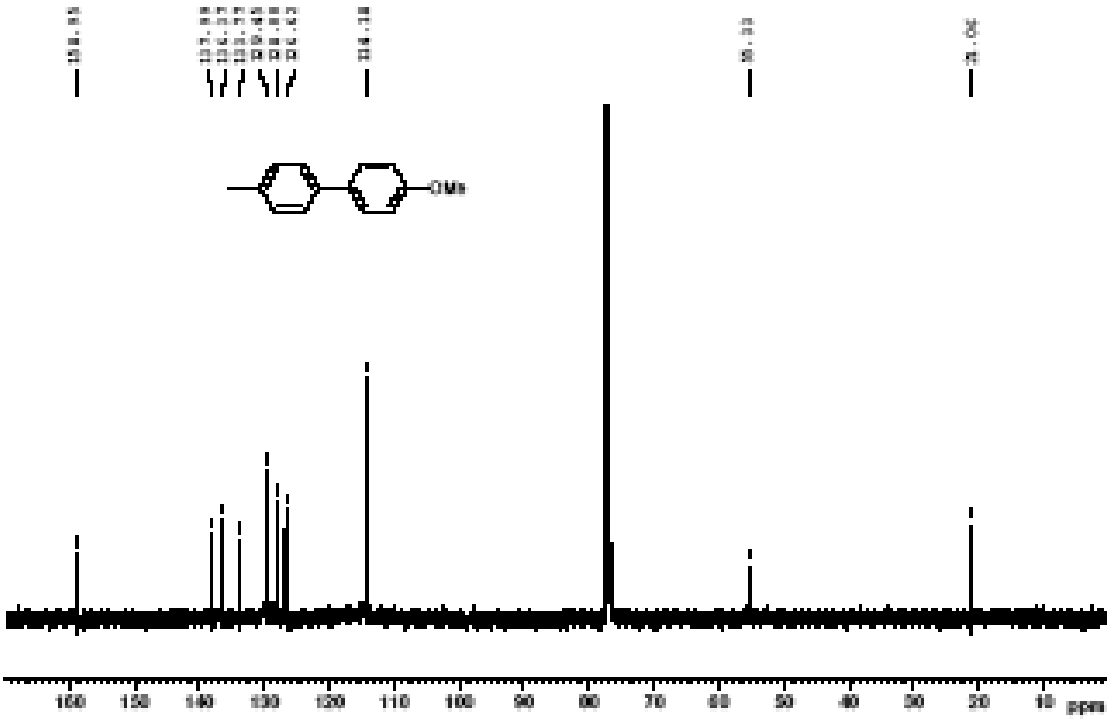
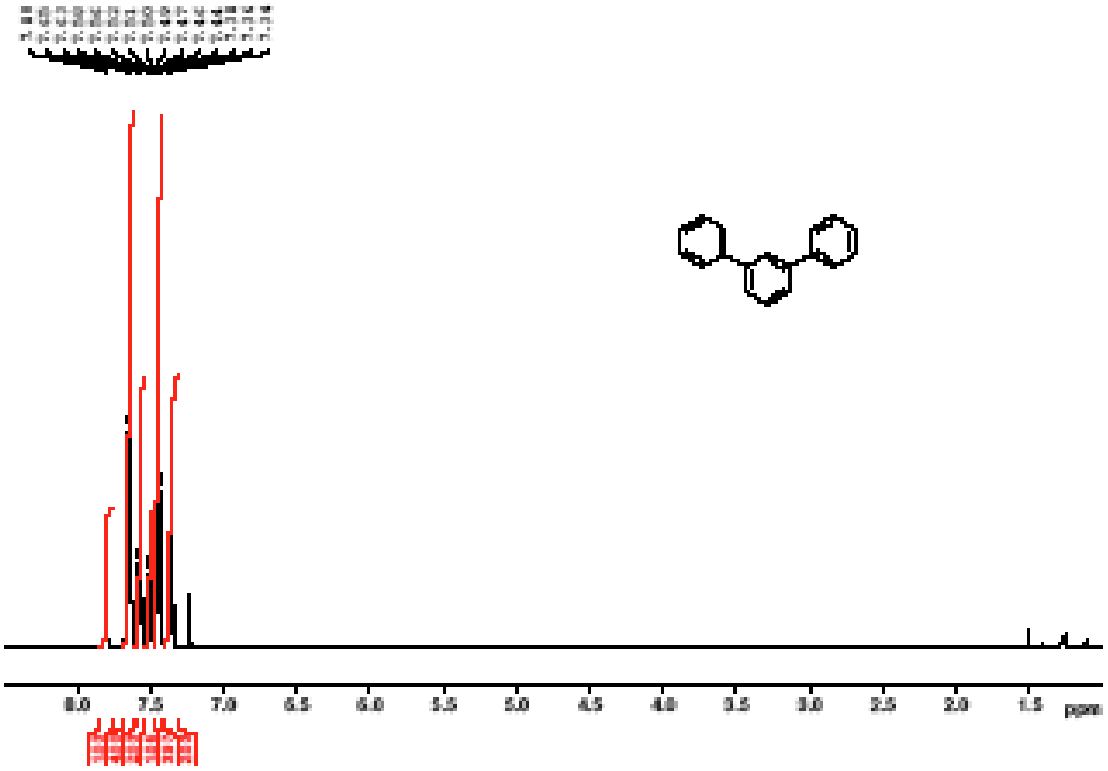


Table 1, entry 1



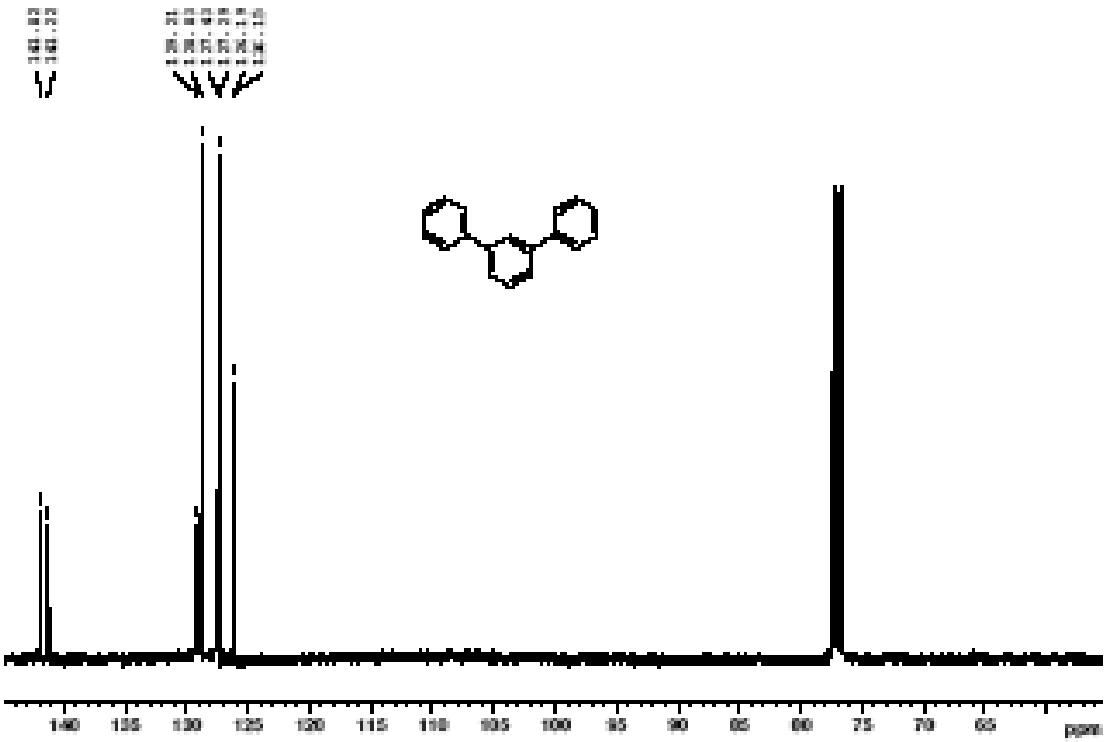
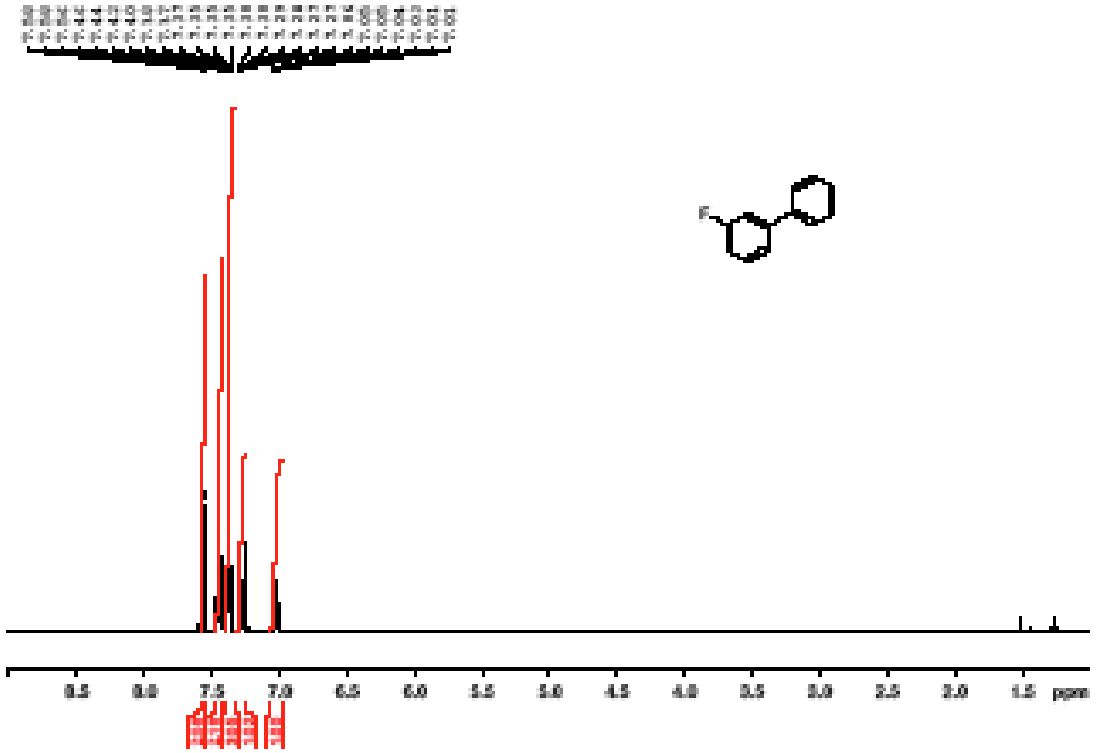
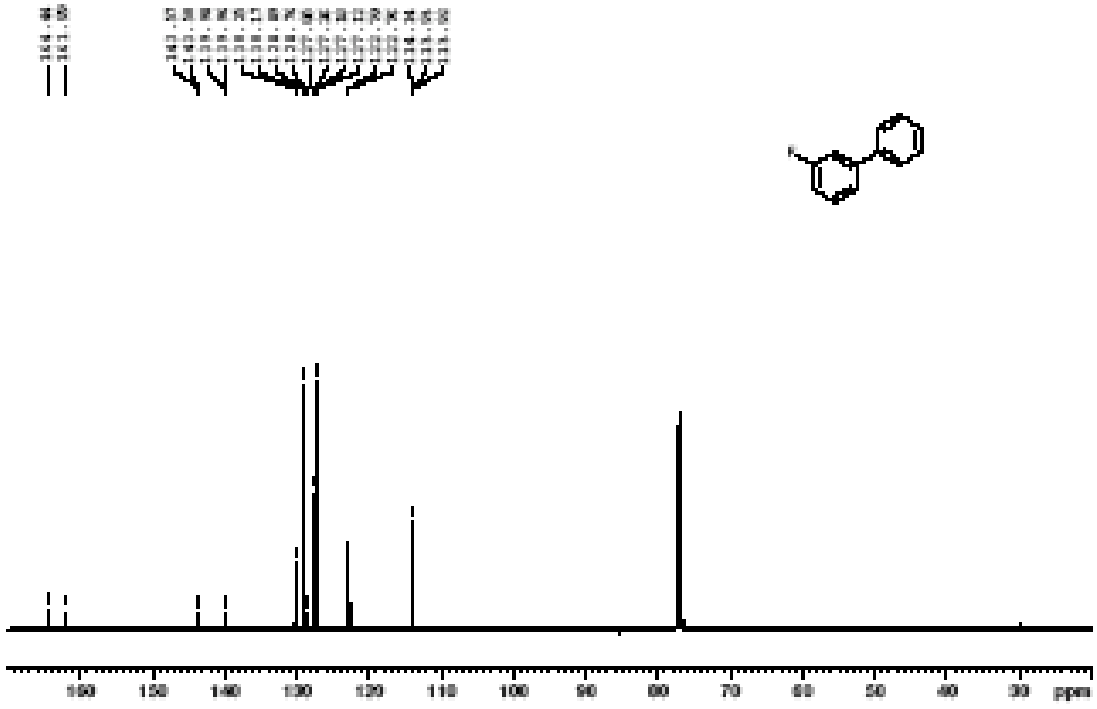


Table 1, entry 2





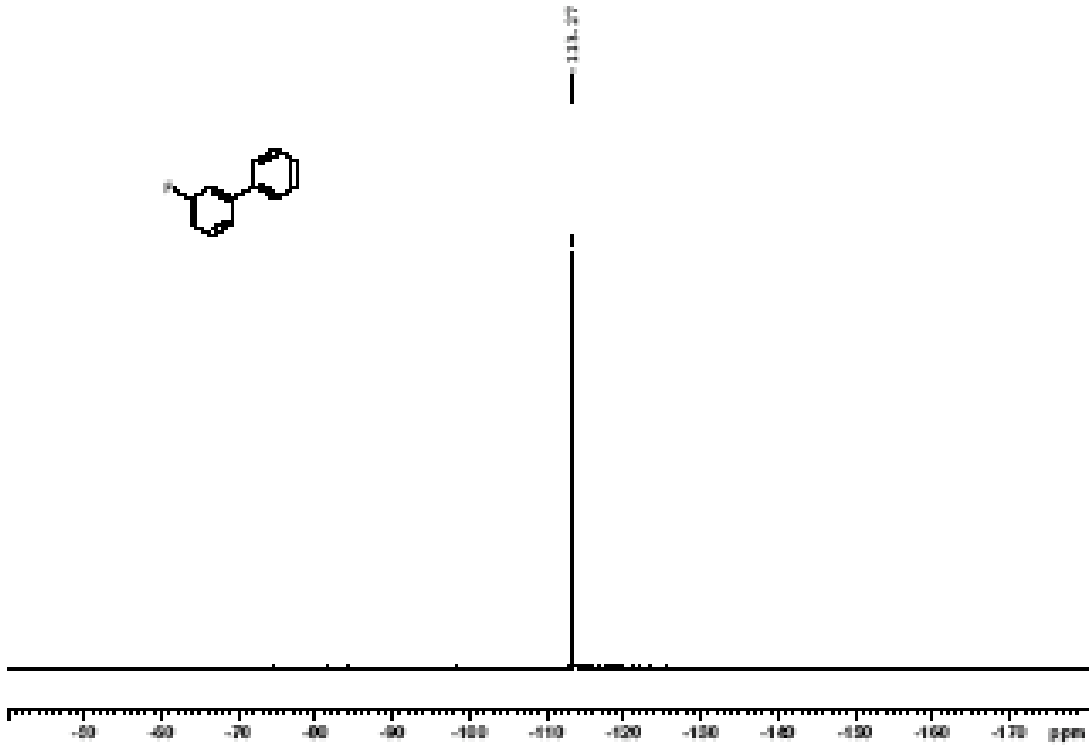
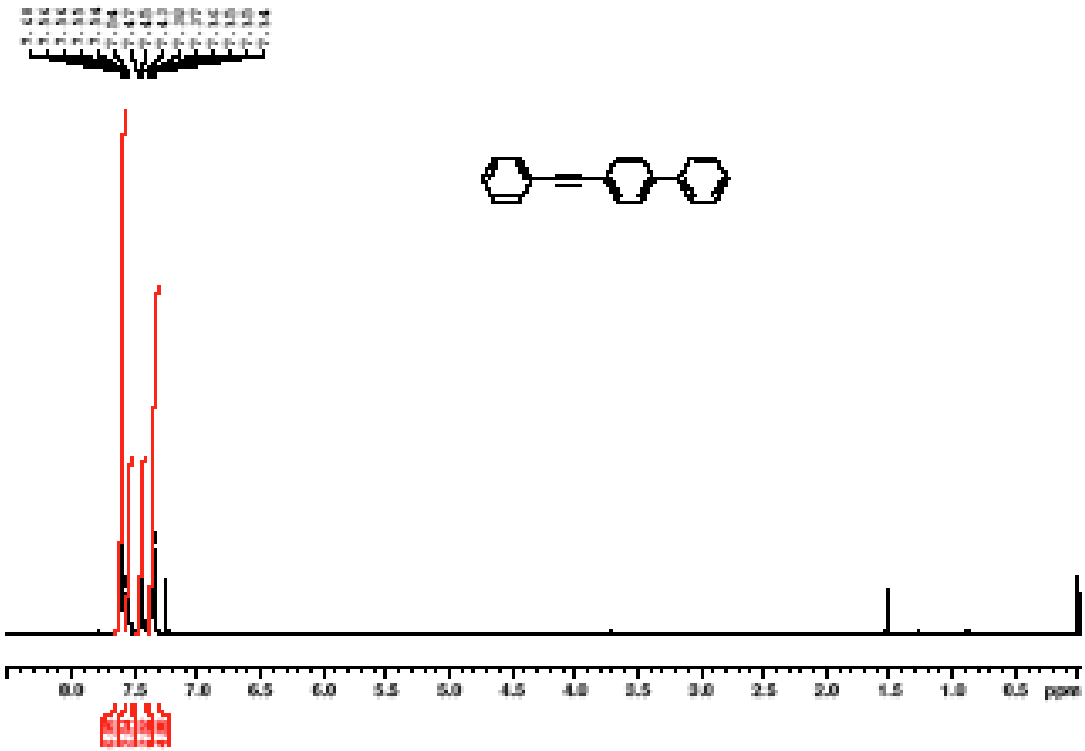

-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
ppm

Table 1, entry 3



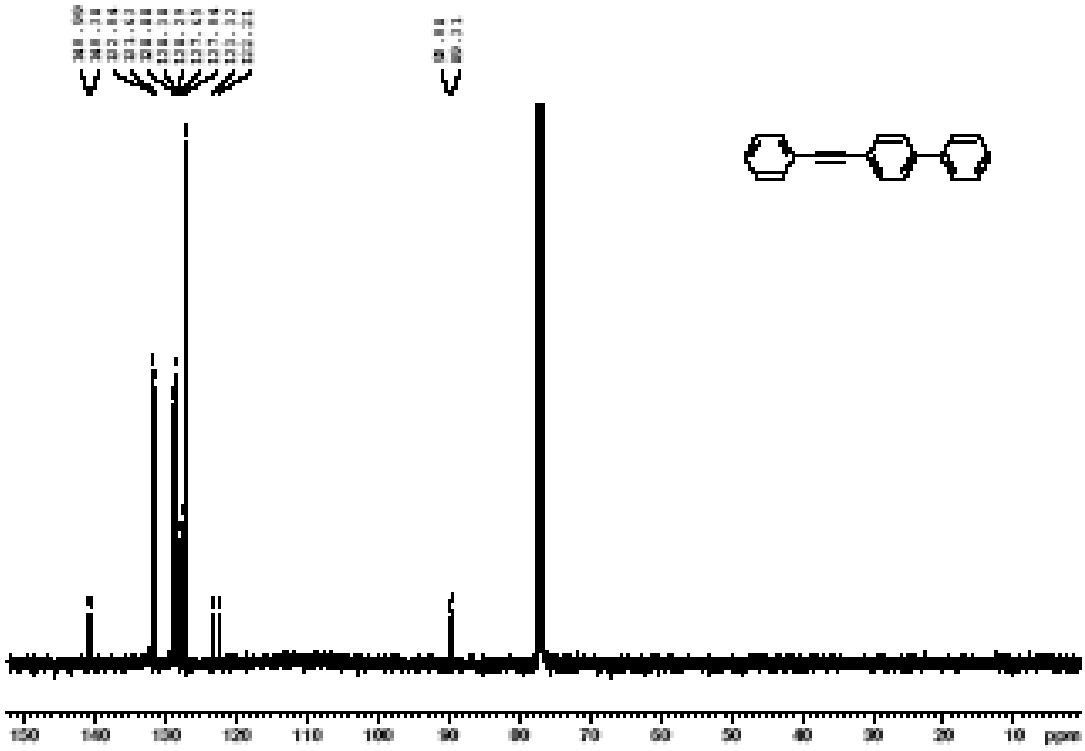
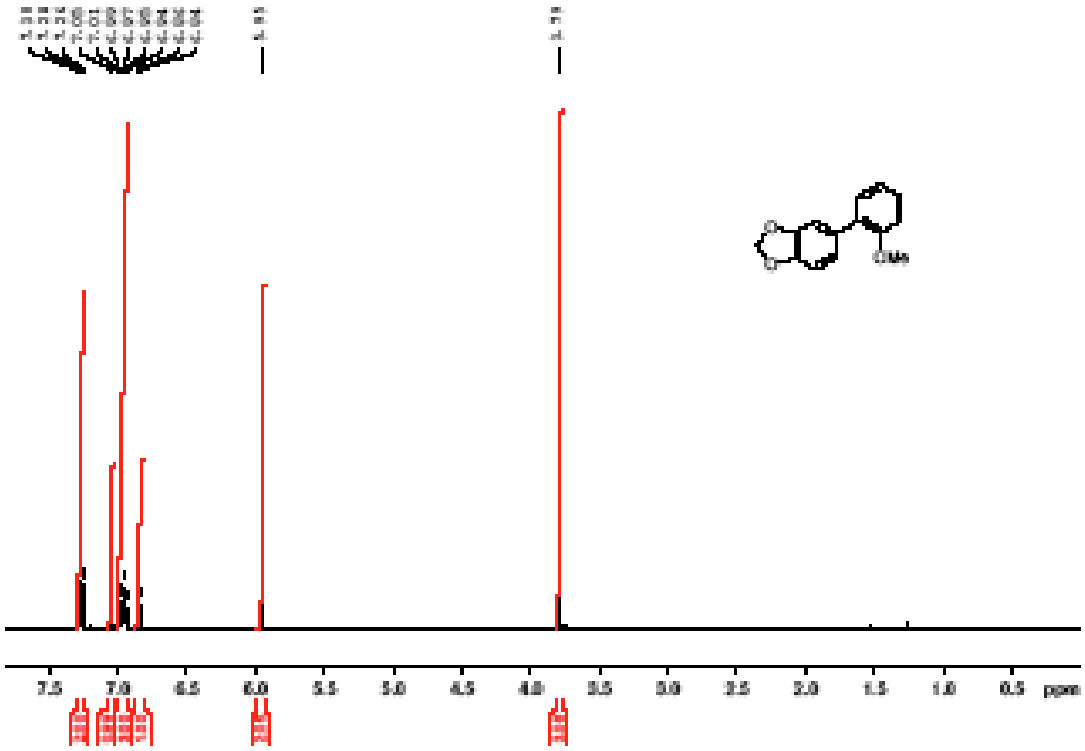
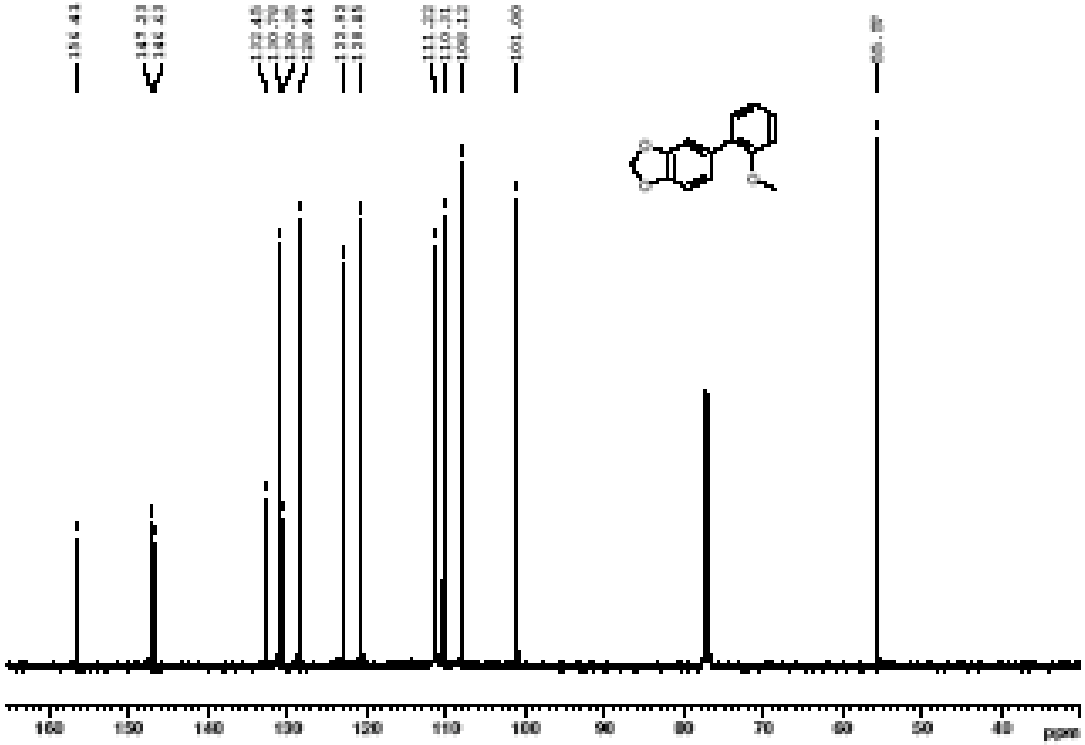


Table 1, entry 4





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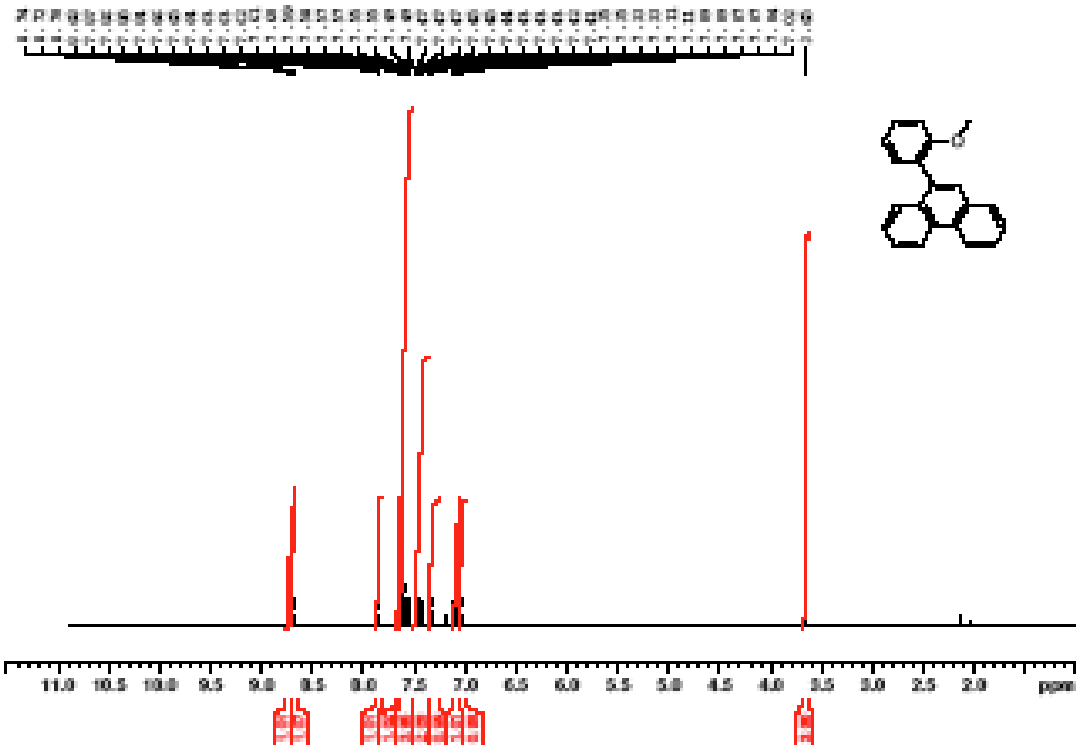


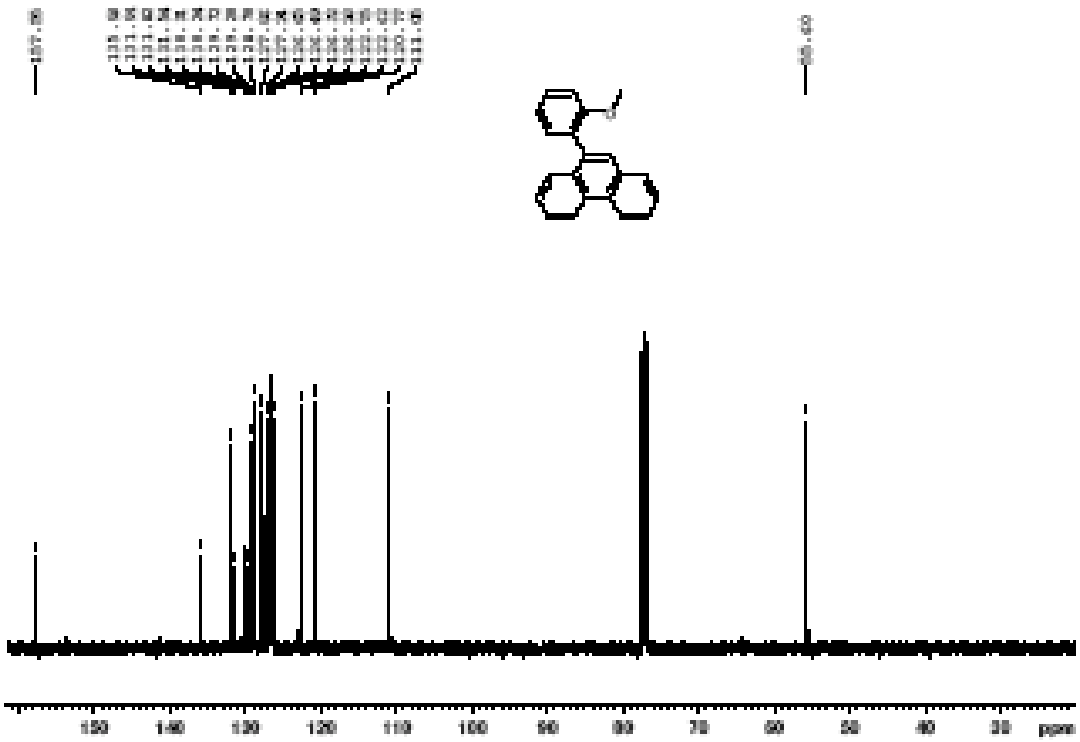
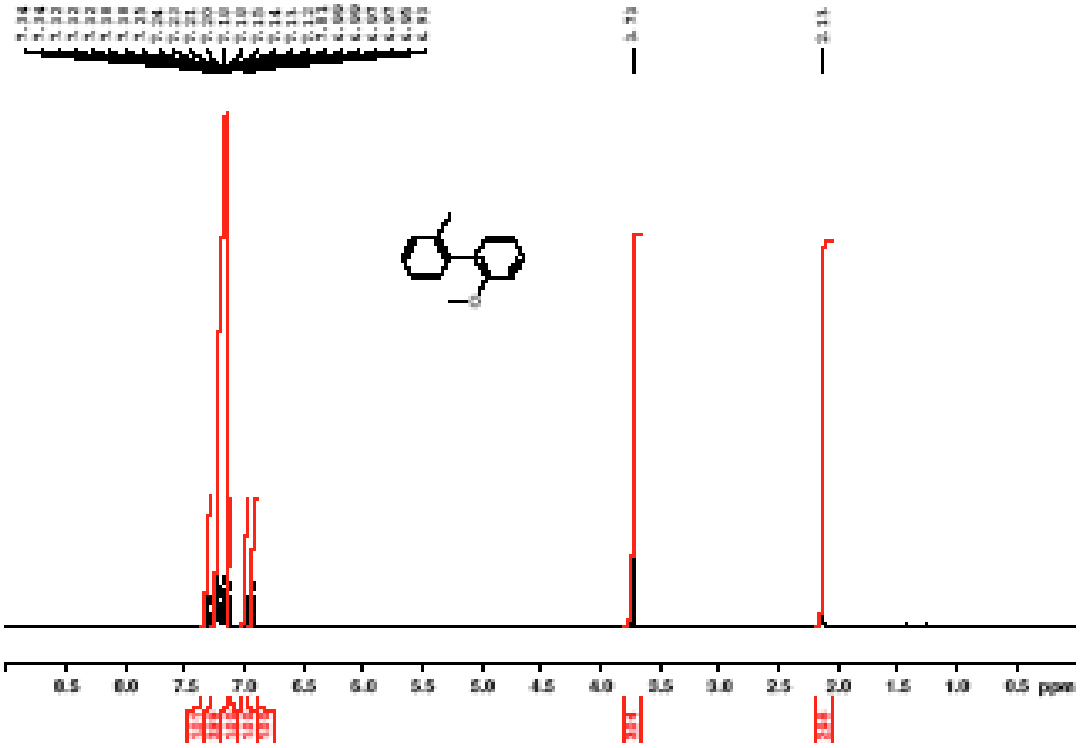


Table 1, entry 6



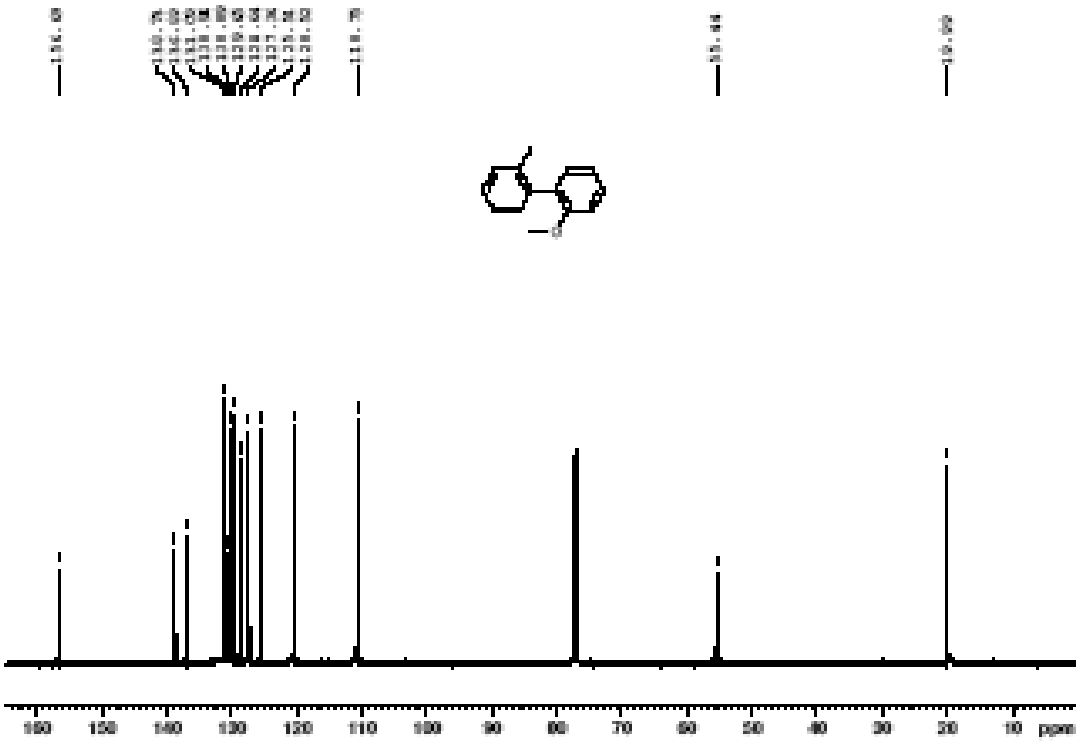
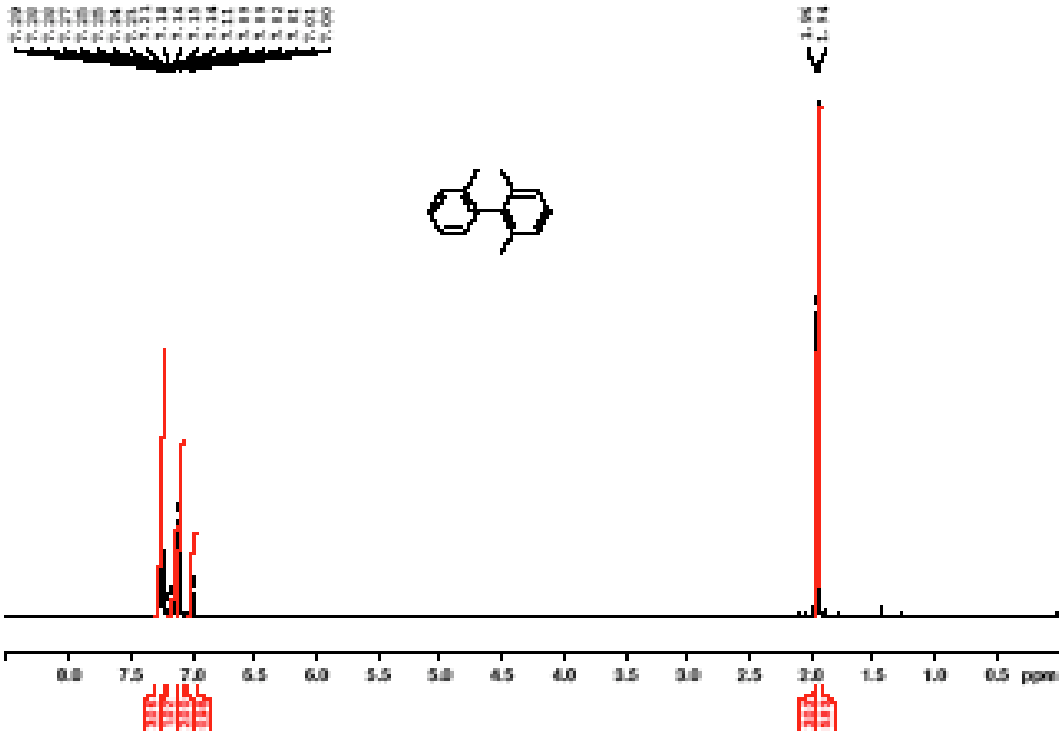


Table 2, entry 1



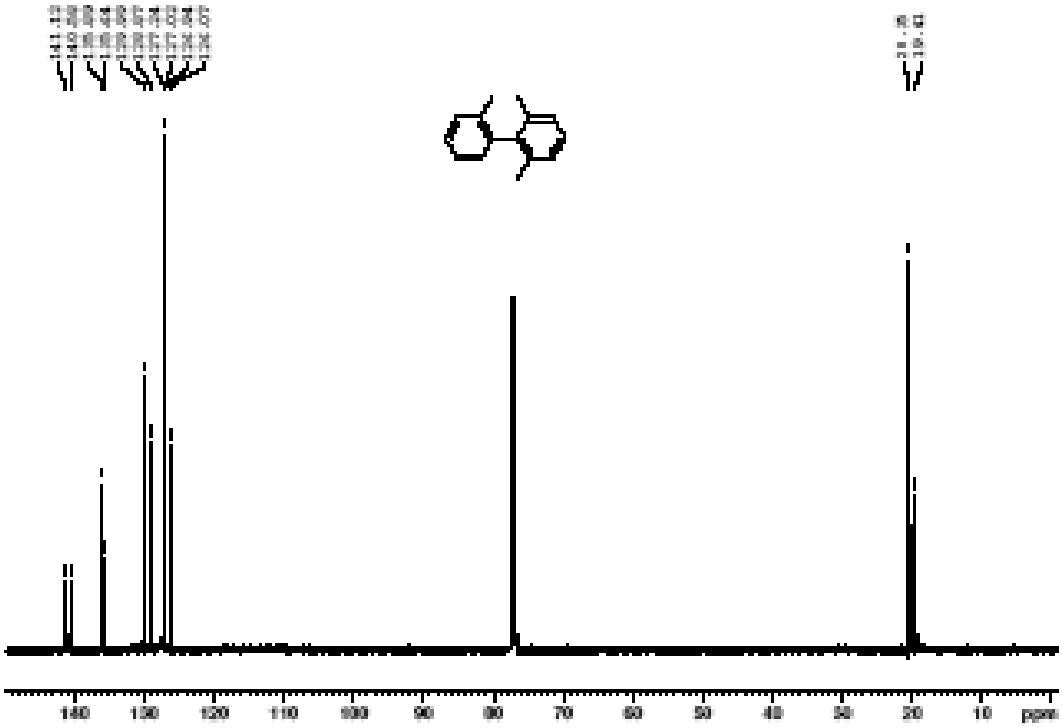
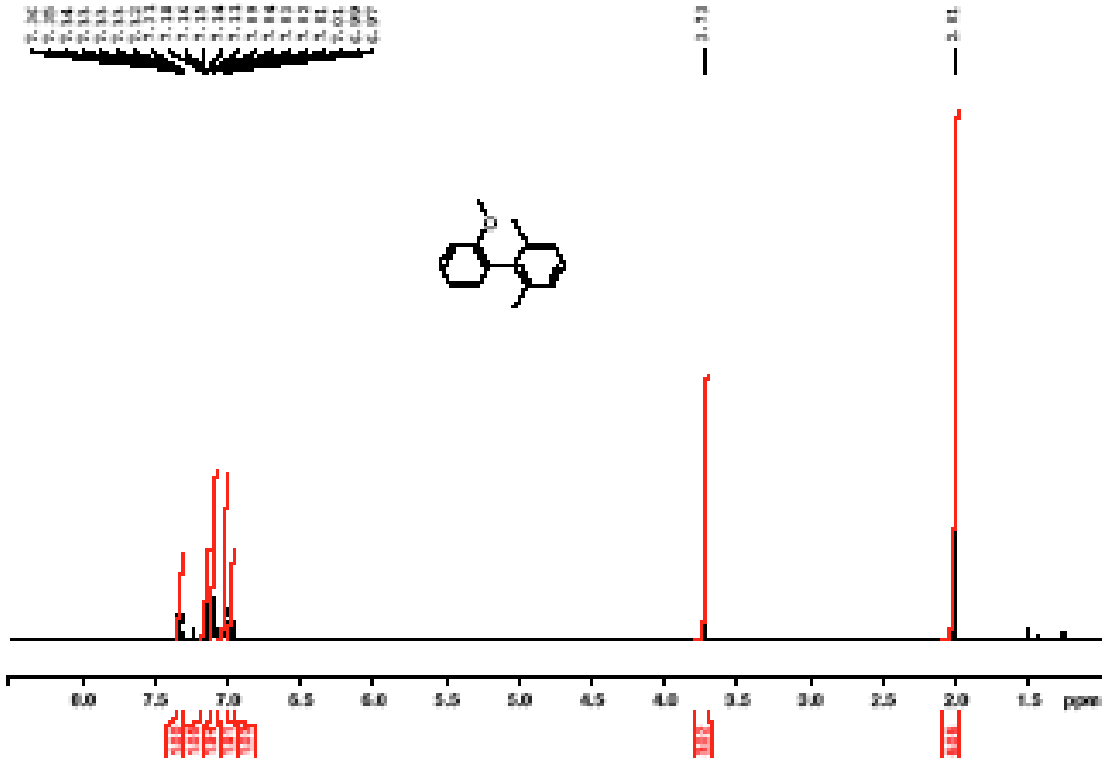
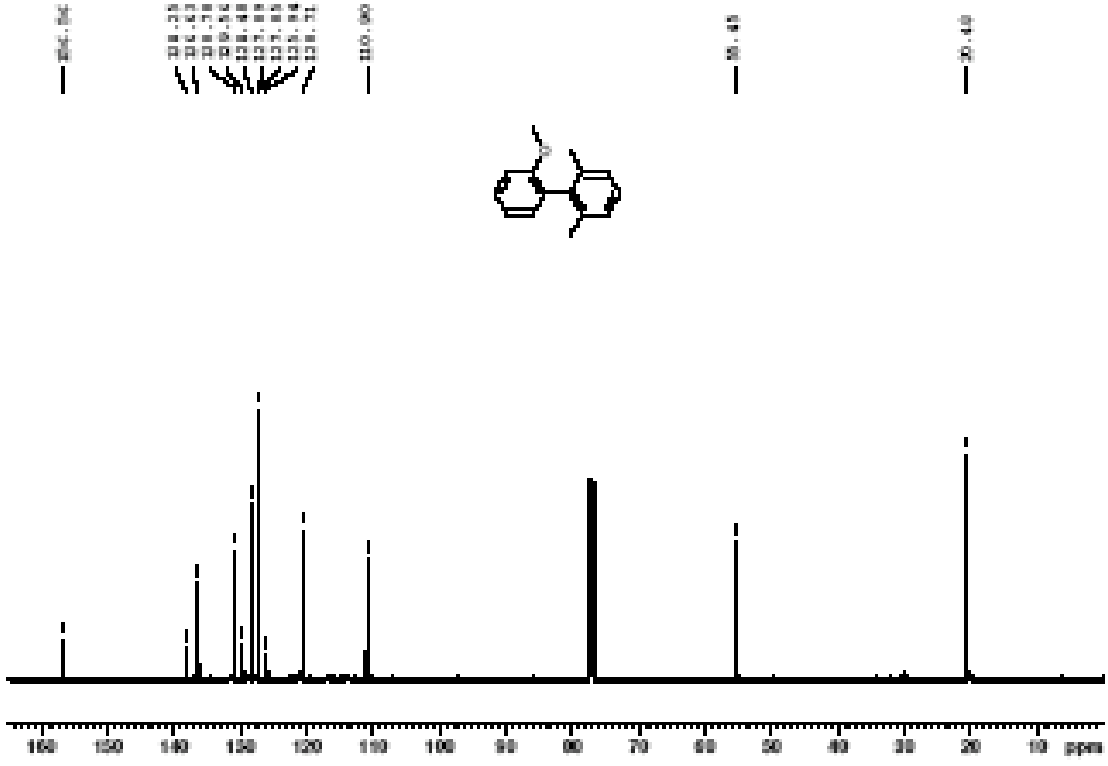


Table 2, entries 2 and 3





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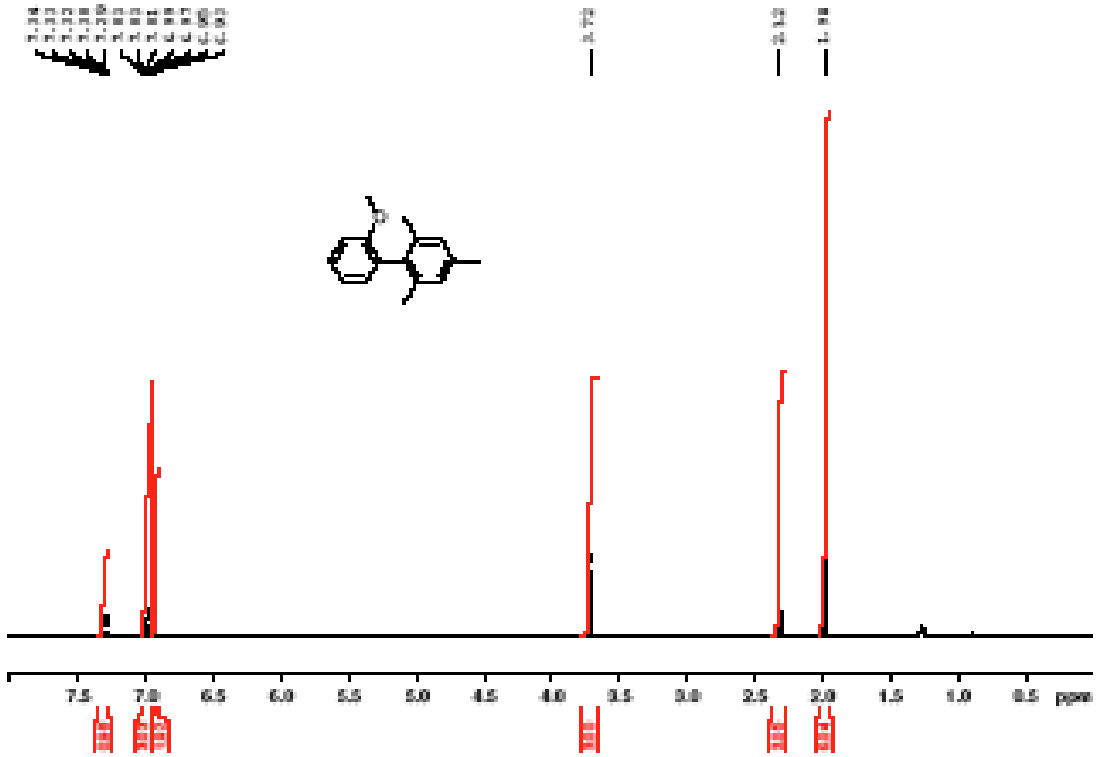


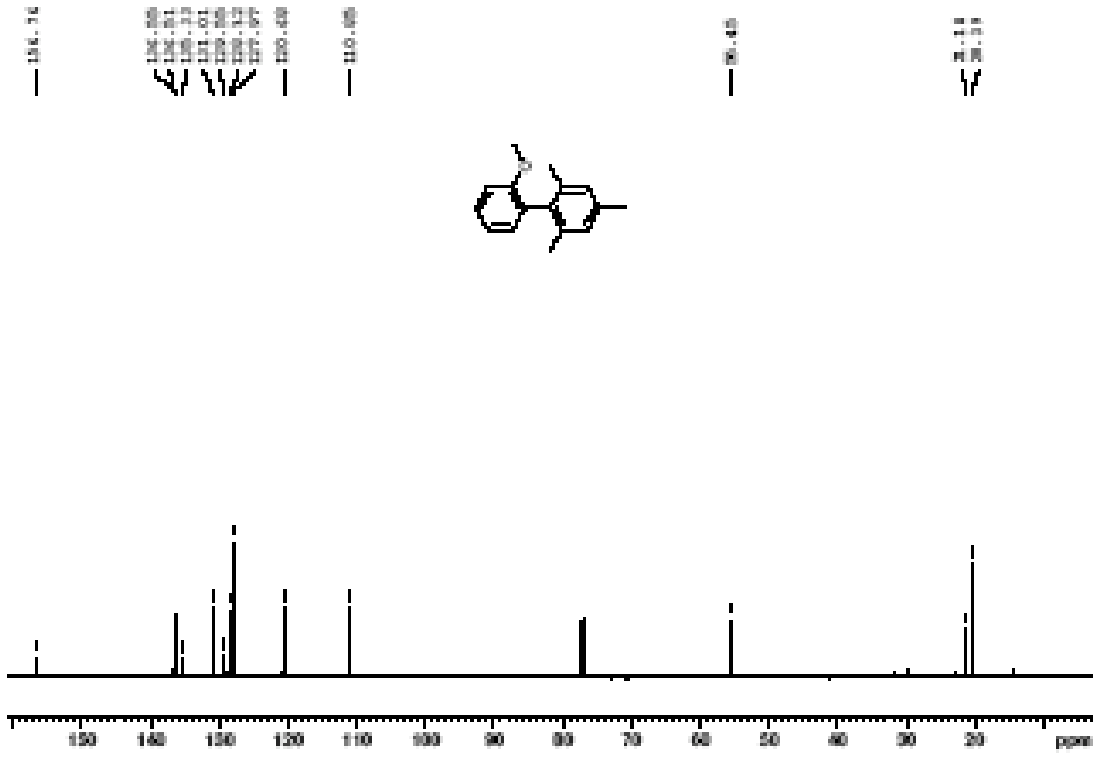
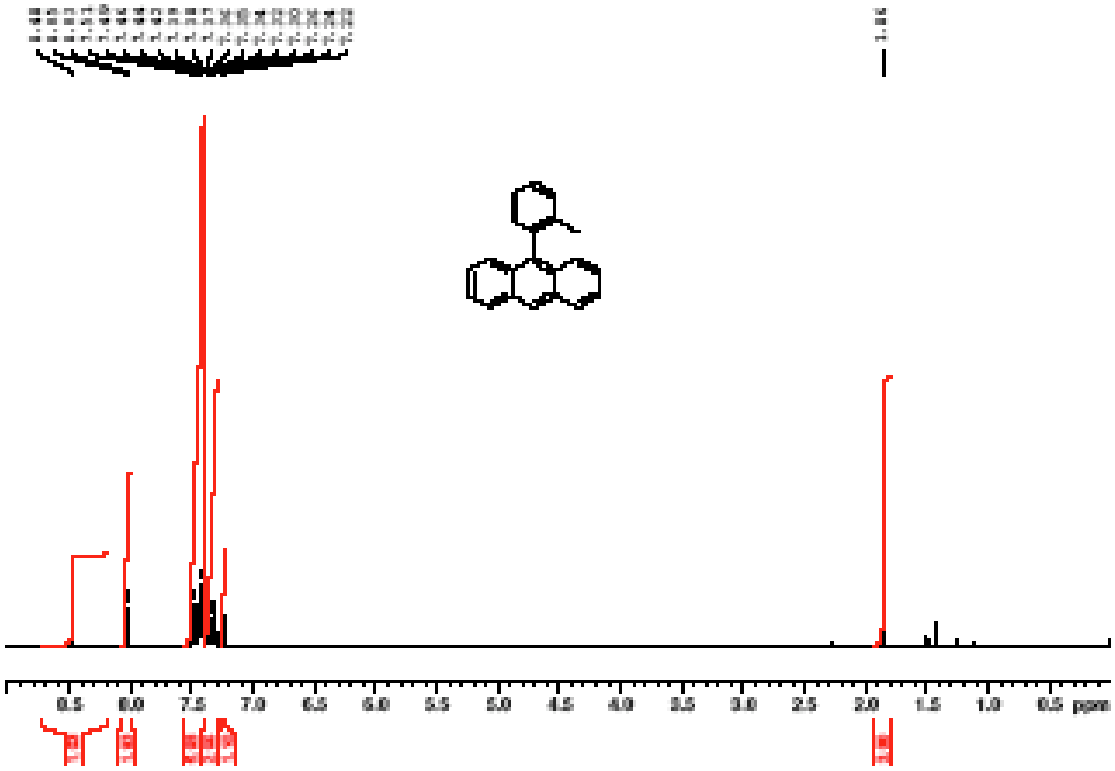


Table 2, entry 5



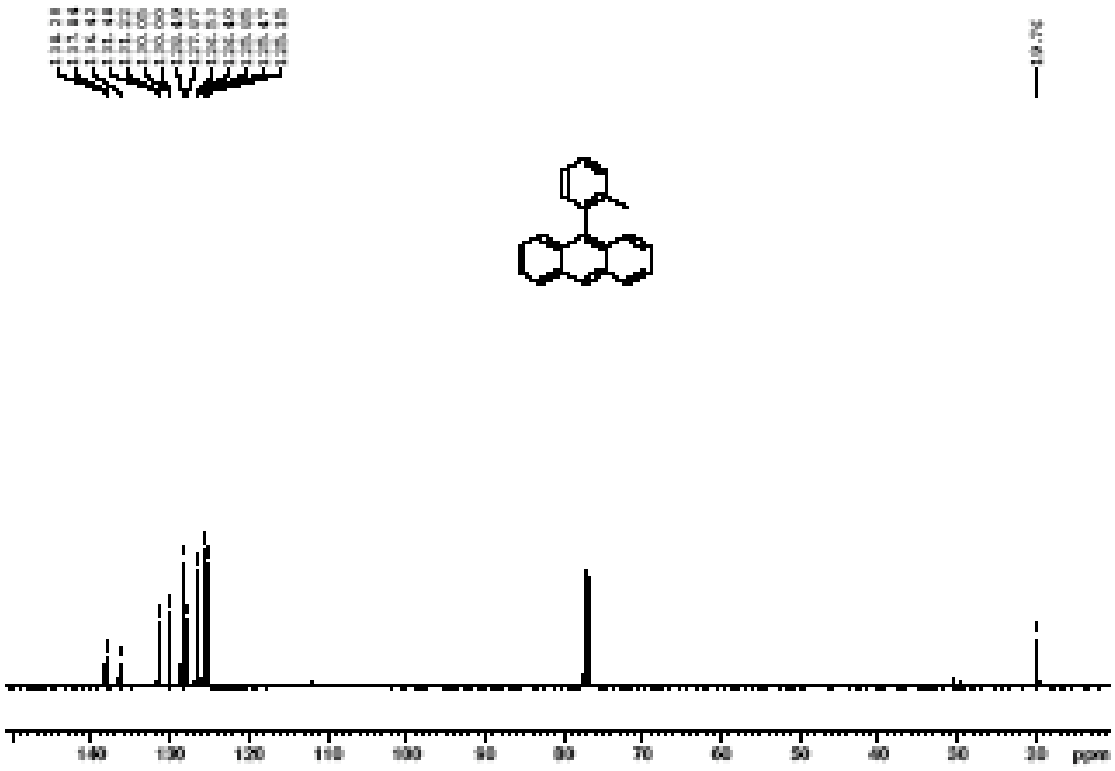
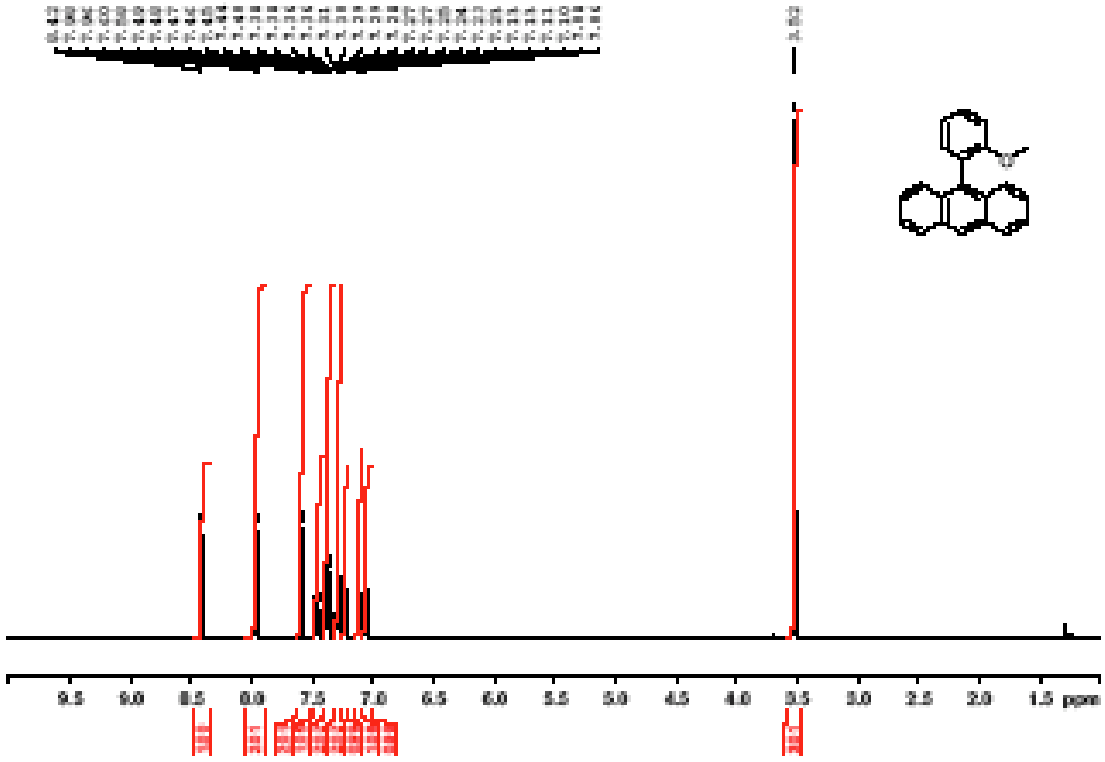
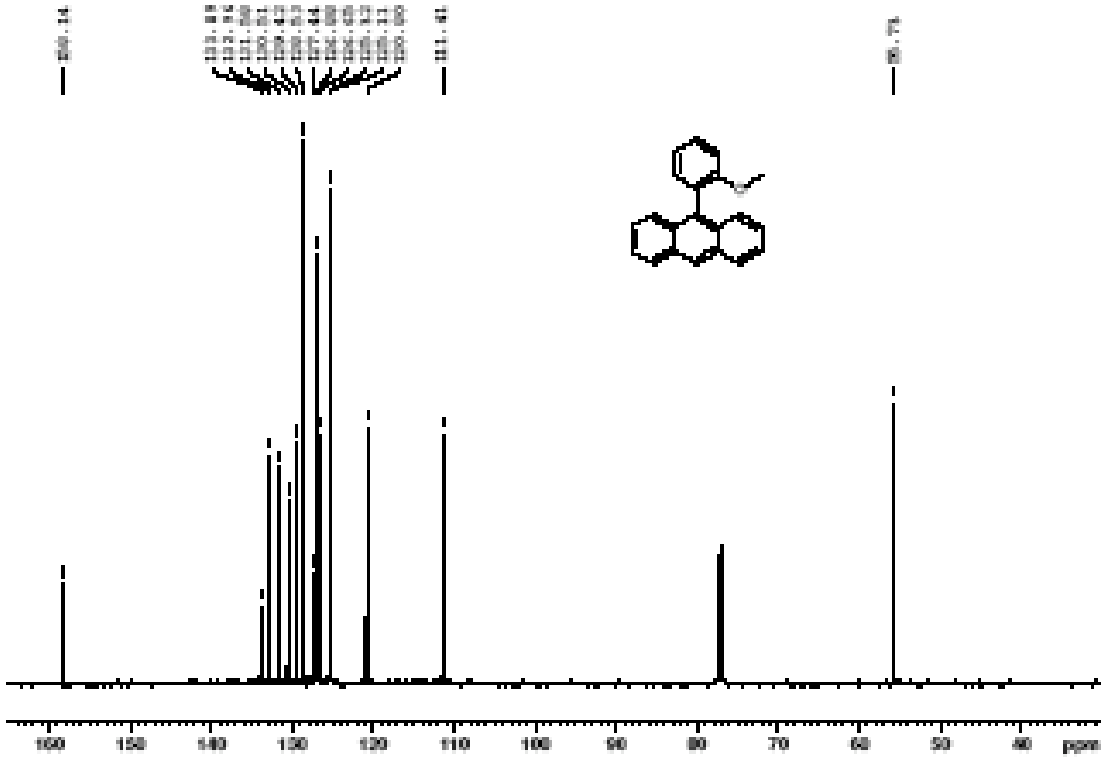


Table 2, entry 6





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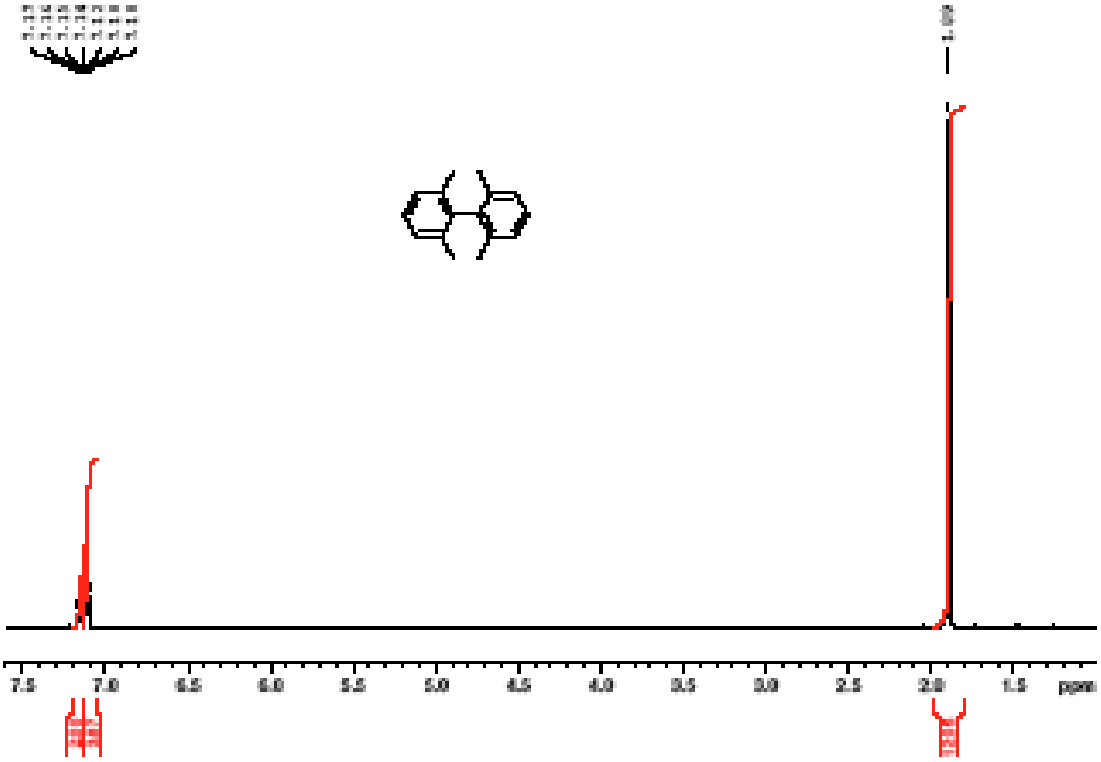

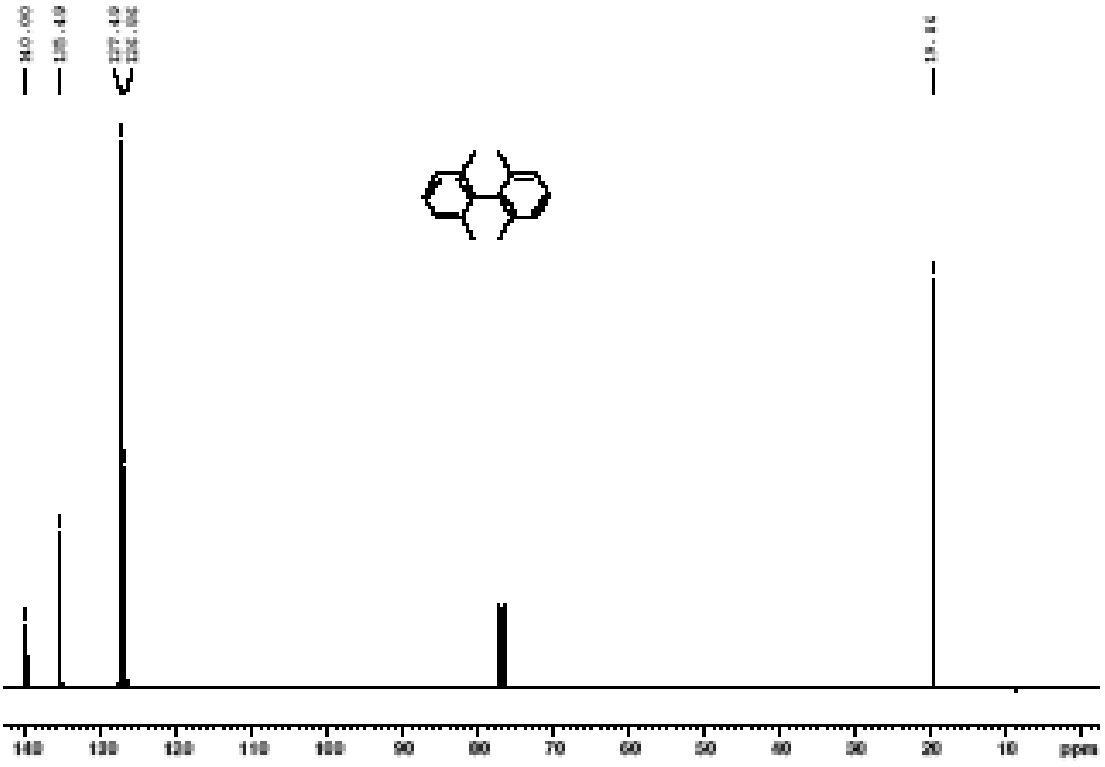

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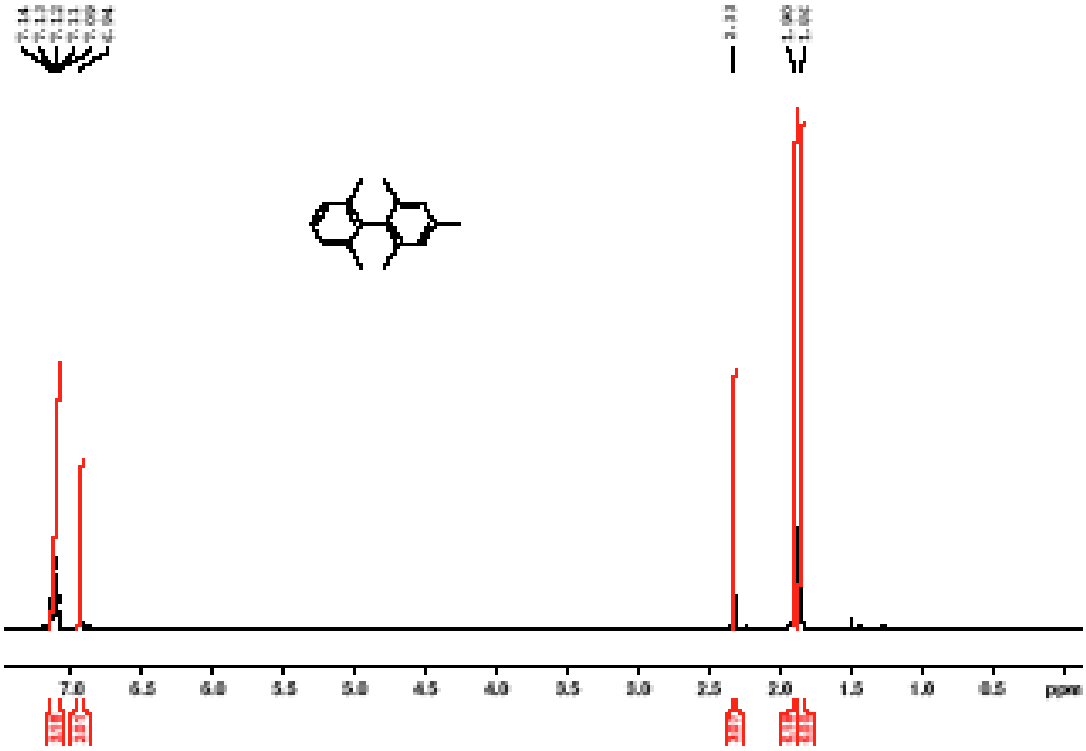


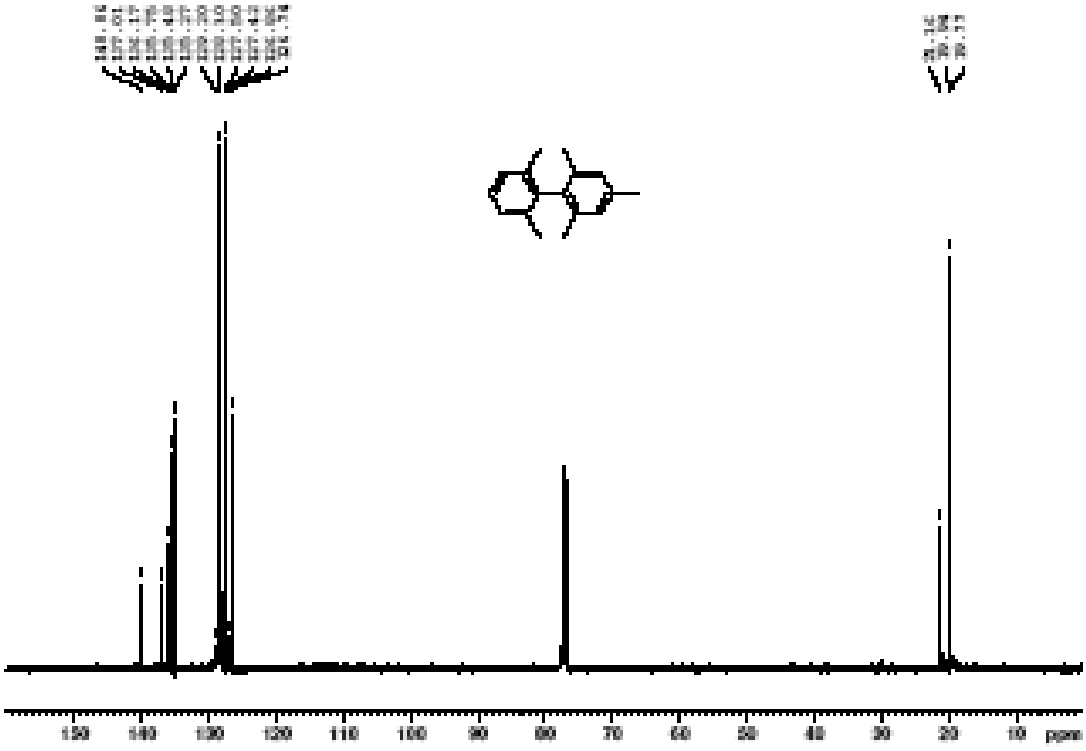


Table 3, entry 1

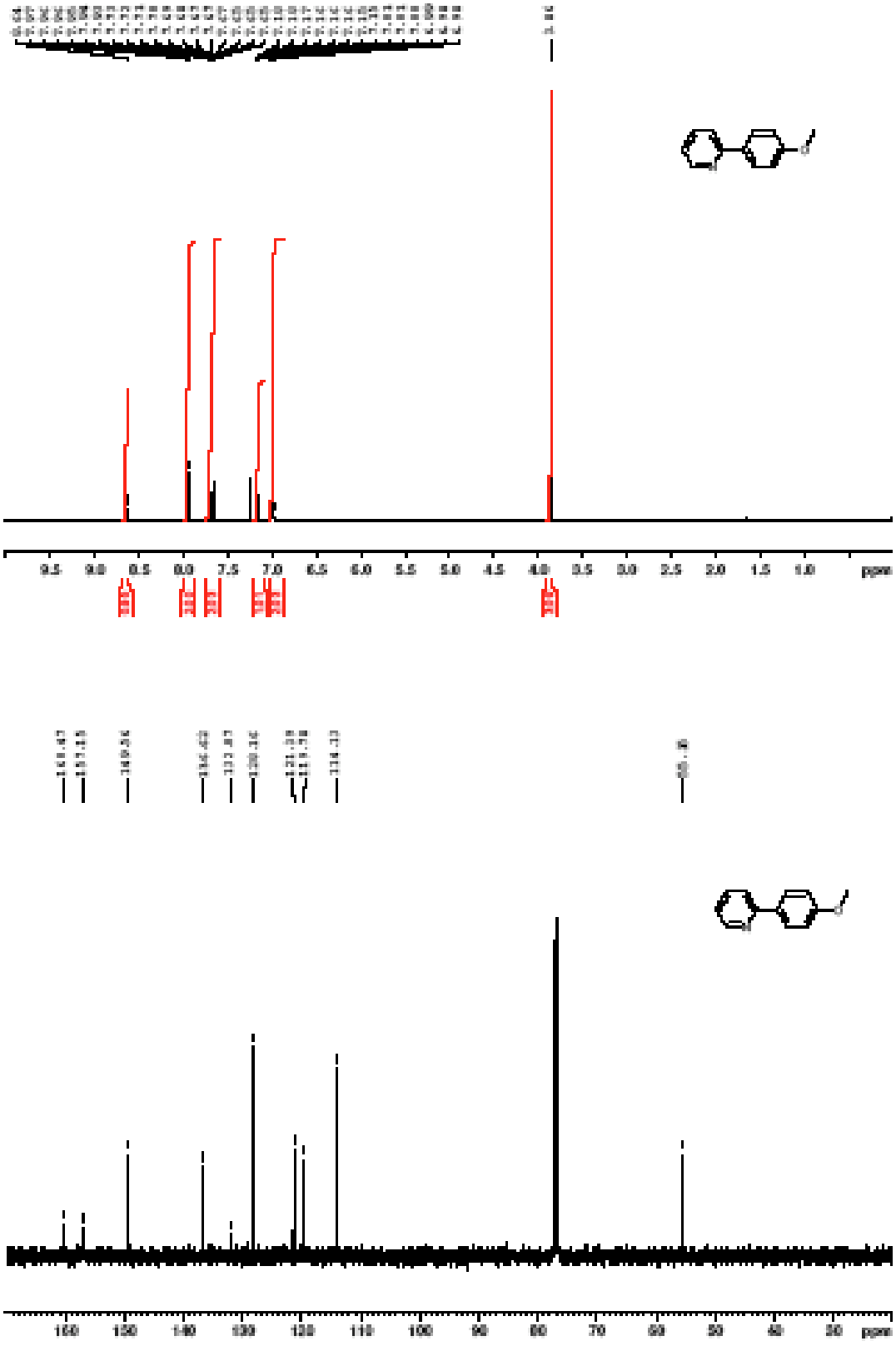
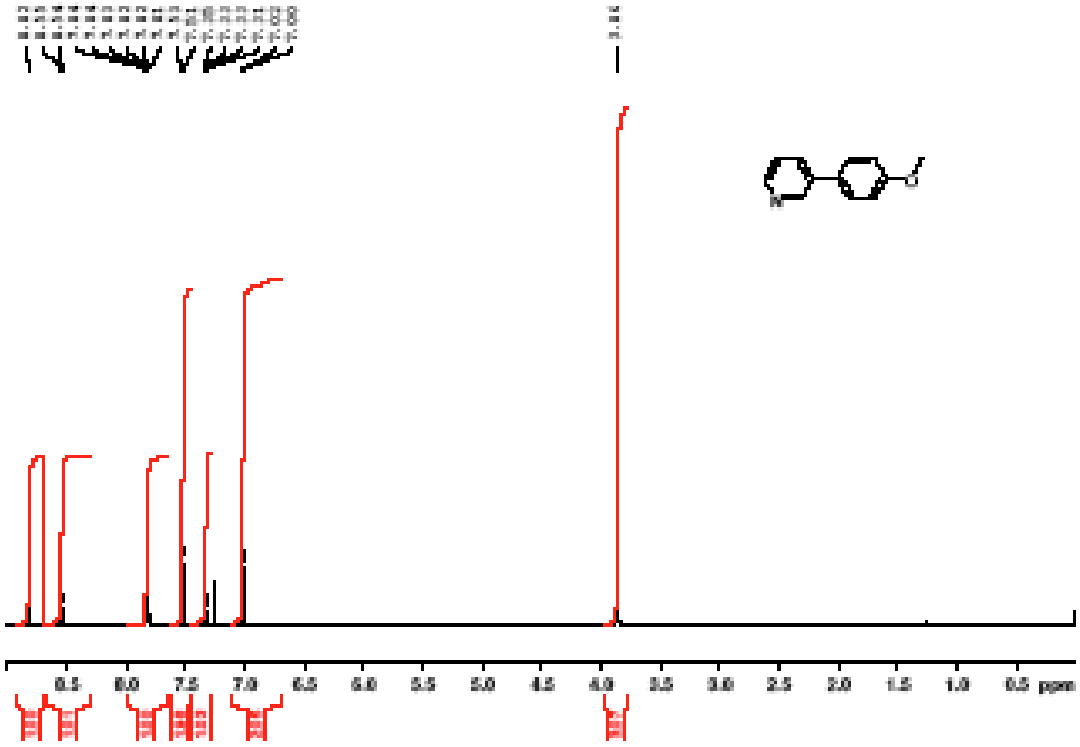


Table 3, entry 2



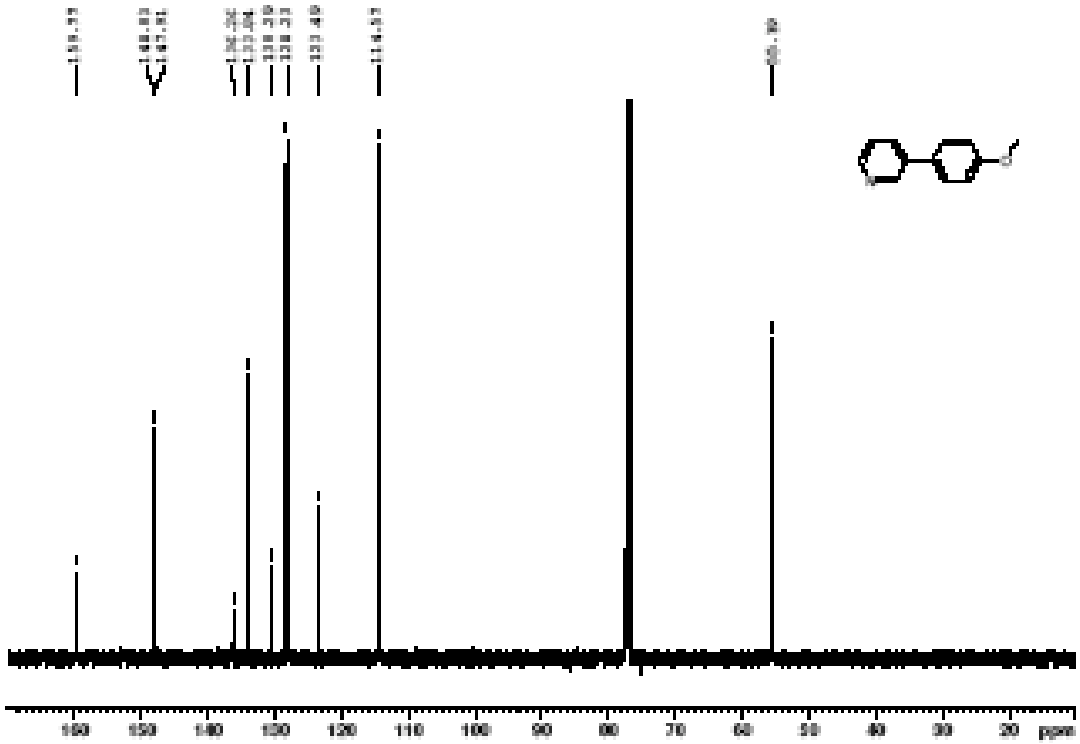
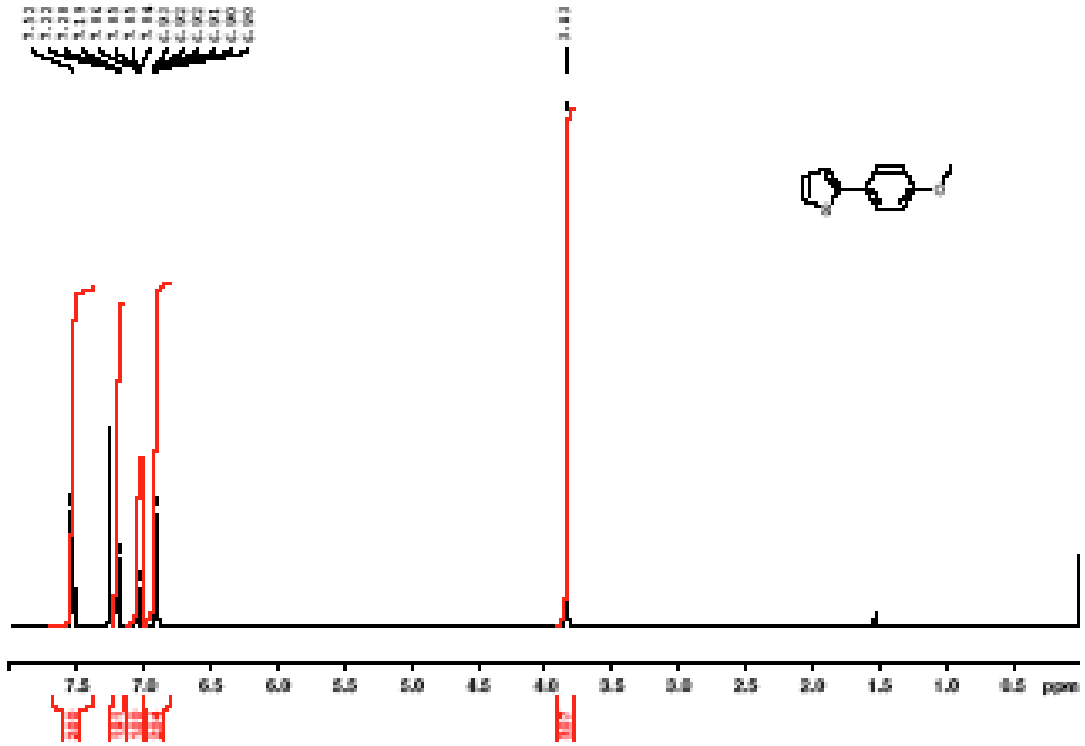
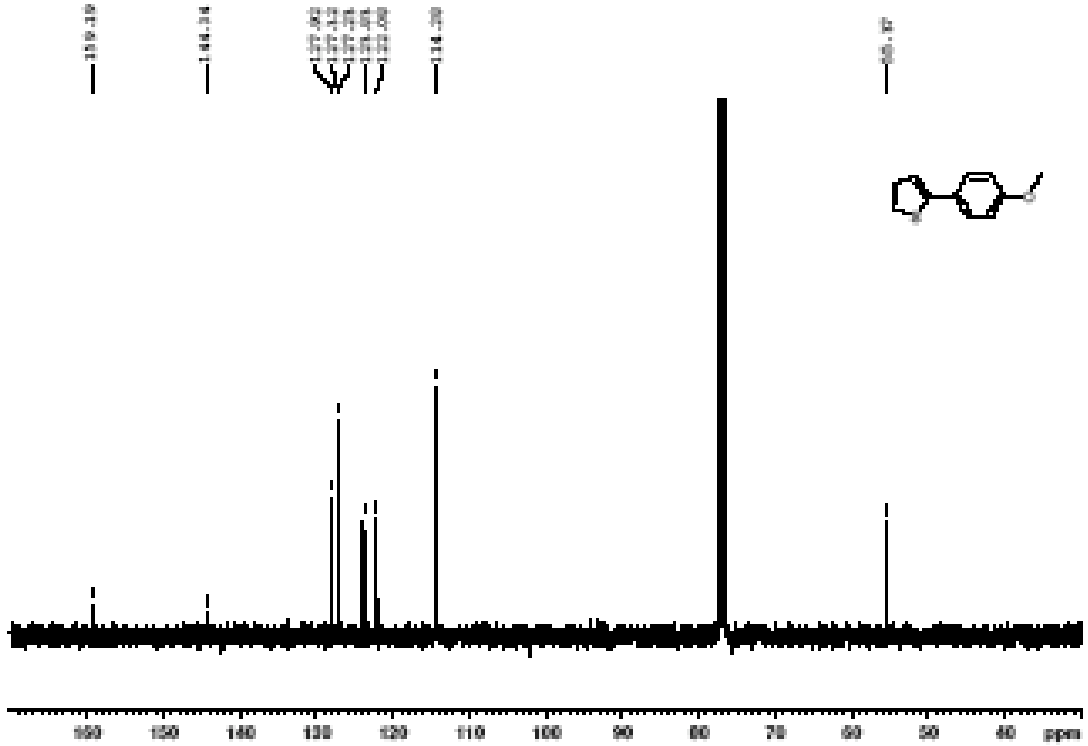


Table 3, entry 3





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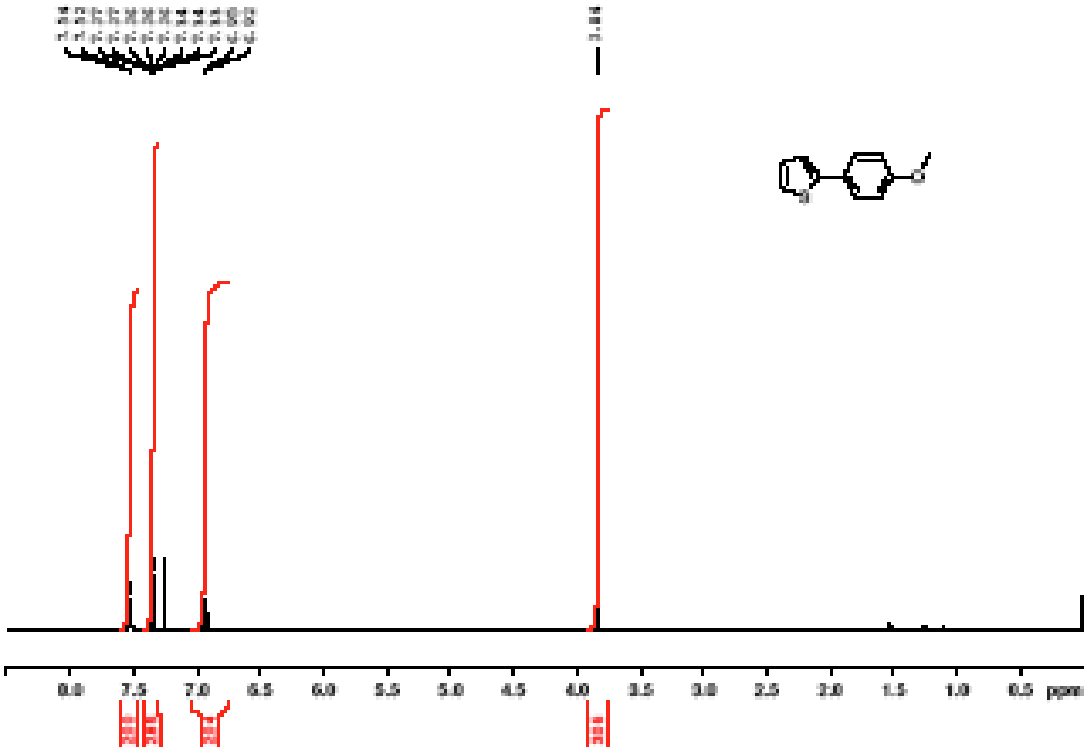


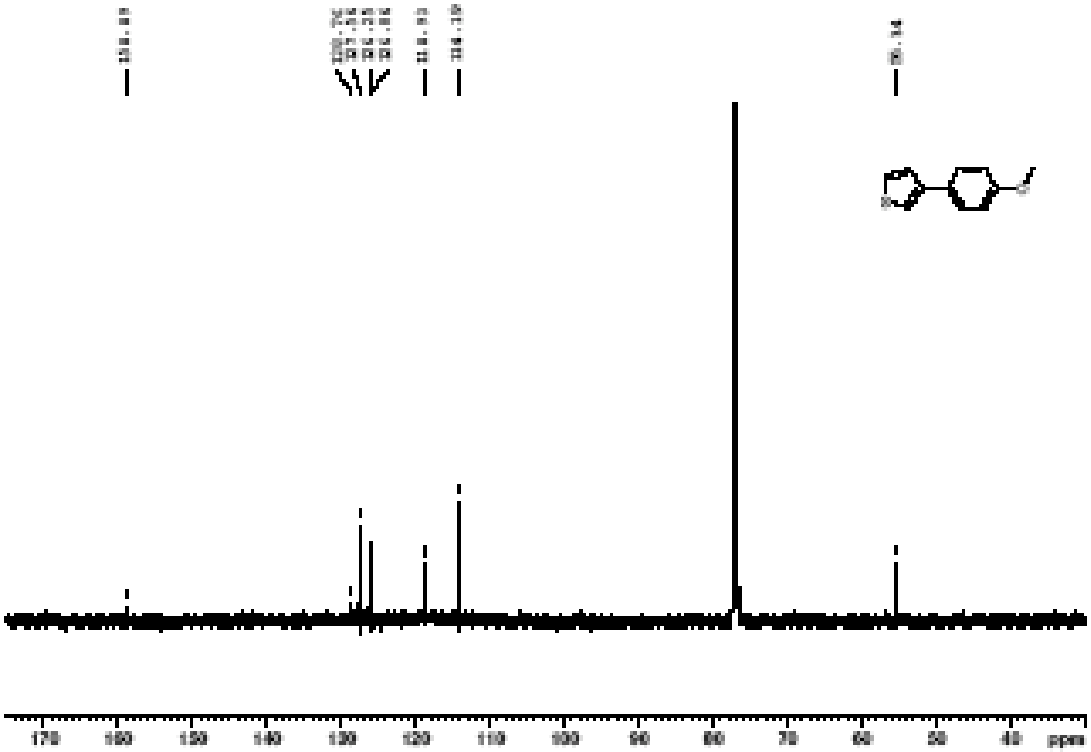
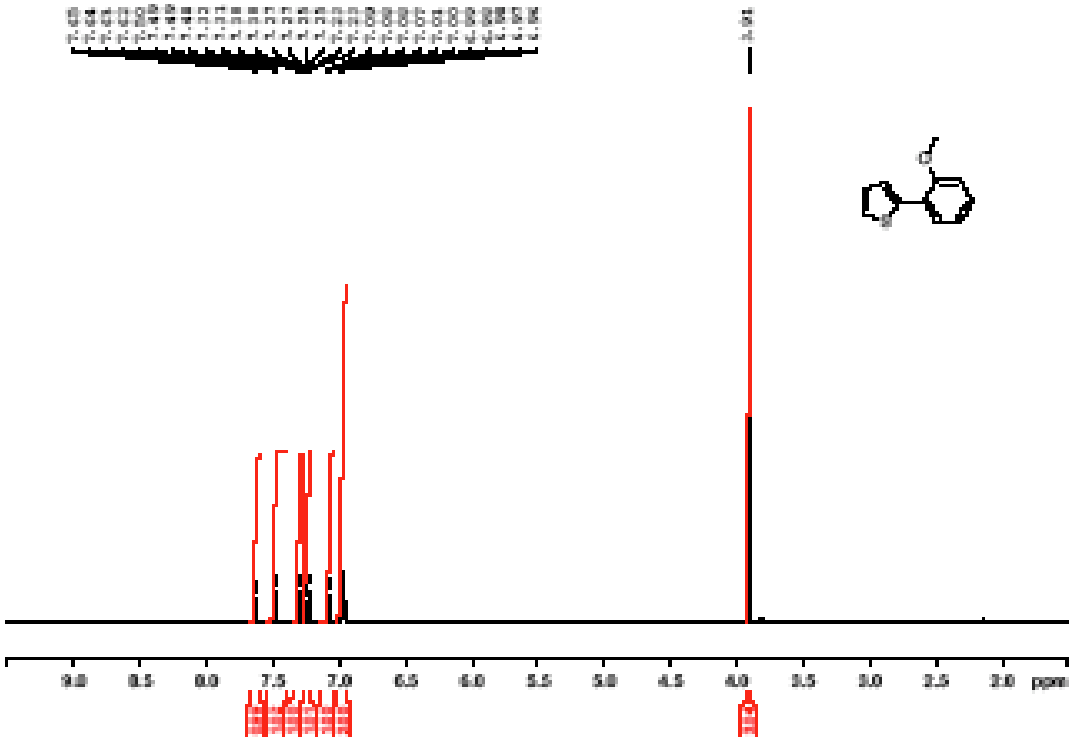


Table 3, entry 5



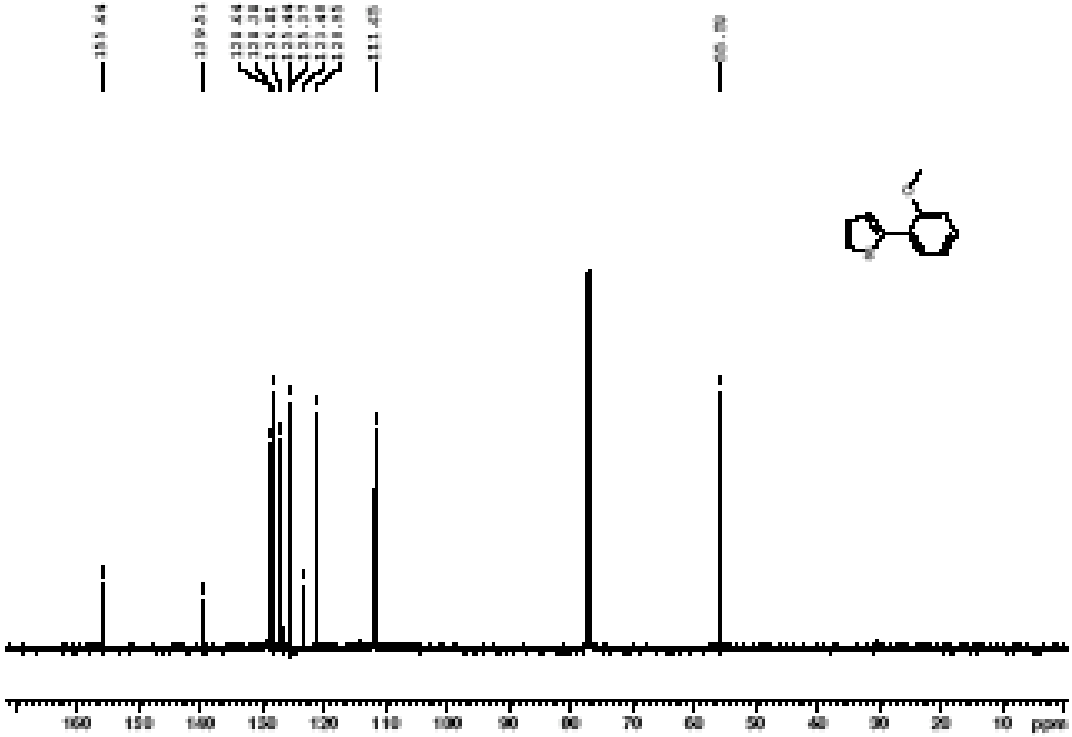
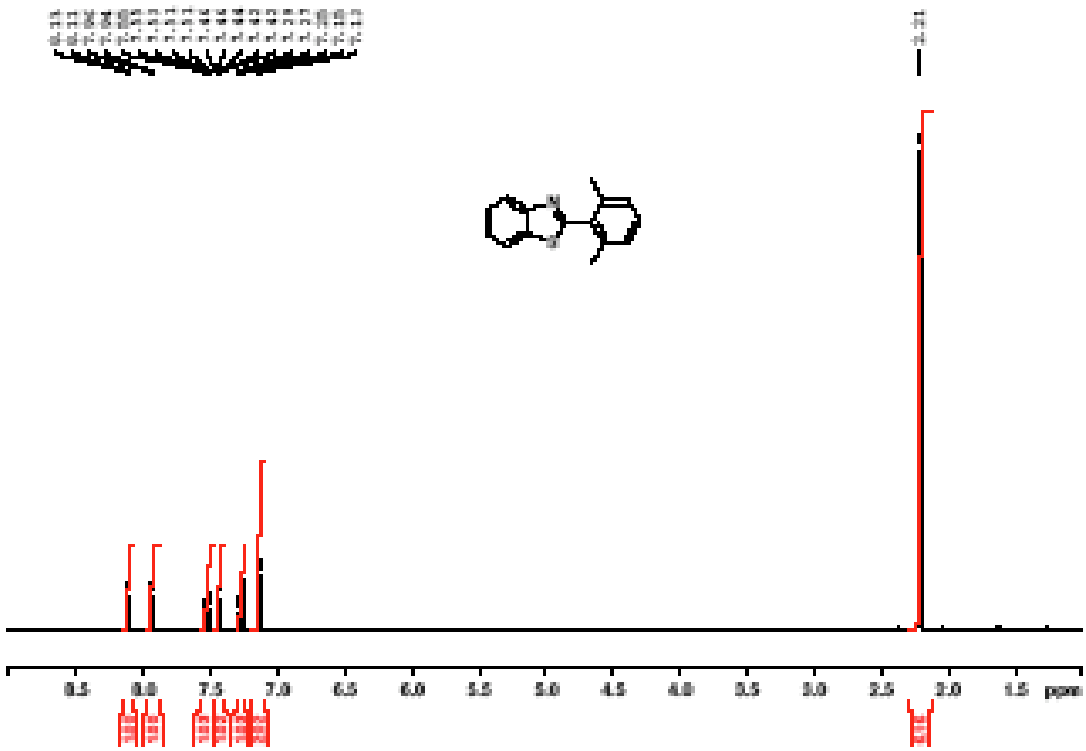


Table 3, entry 6



References

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