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In the version of this file originally posted online, there were several compound numbering errors. On page S3, isomerized product **2r** should have been **2x**. A similar change was made to the column heading of Table S1 on page S4. In Table S3, compound **3u** should have been **4u**. On page S10 **2a**–**2x** should have been **2a**–**2z**; on page S17, **5a**–**5r** should have been **5a**–**5s**; On page S62, **3o** should have been **5o**. In the section describing 'Preparation of organolithium reagents' on page S9: 4-methoxy-phenyllithium was added to section B. These errors have been corrected in this file 17 June 2013.

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SUPPLEMENTARY INFORMATION

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Direct Catalytic Cross-Coupling of Organolithium Compounds

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General methods:

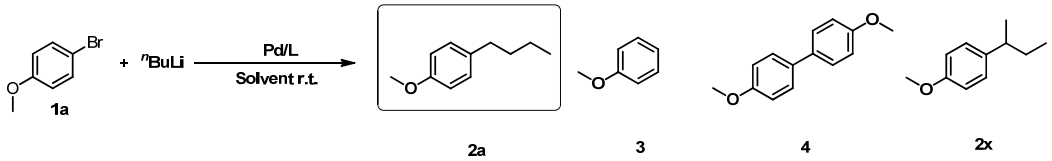
Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and cerium/molybdenum or potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ^{1}H- and ^{13}C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Carbon assignments are based on APT ^{13}C-NMR experiments. Melting points were measured using a Büchi Melting Point B-545.
All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. Dichloromethane was dried and distilled over calcium hydride; THF, Et_2O and toluene were dried and distilled over sodium. $Pd[P(^{t}Bu)_3]_2$, was purchased from strem, $Pd_2(dba)_3$, SPhos, XPhos, DavePhos and $P(^{t}Bu)_3$ were purchased from Aldrich and used without further purification. ^{n}BuLi (1.6 M solution in hexane) and PhLi (2.0 M solution in dibutylether) were purchased from Acros. ^{sec}BuLi (1.4 M in cyclohexane), MeLi (1.6 M in diethylether), $TMSCH_2Li$ (1.0 M in pentane), HexLi (2.3 M in hexane), thienylLi (1.0 M in THF/hexane), ^{tert}BuLi (1.7 M in pentane) and the compounds used as precursor for the preparation of lithium reagents, namely furan, 1-bromo-2,6-dimethyl-benzene and 1-bromobenzene-3-trifluoromethyl-benzene were purchased from Aldrich. All the bromides were commercially available and were purchased from Aldrich with the exception of 2-bromo-5-phenylthiophene (Maybridge) and 2-(4-bromophenyl)-1,3-dioxolane (Acros). Organolithium other than the aforementioned were prepared according to described procedures (see below).

Optimization Study: Additional Data

A. Cross-coupling with alkyllithium reagents

After preliminary results obtained by using XPhos as ligand (Table S1, entry 1), the amount of lithium reagent used was lowered (to 1.2 equiv) without loss in terms of conversion (entry 2). Changing Pd salt (entry 3), reducing the catalyst loading (entry 4) and varying the Pd/ligand ratio (1:3, entry 5) alkyllithium reagent did not affect the reaction at all regarding conversion and selectivity. The use of hexane as solvent, in order to minimize the halogen-metal exchange, resulted in no conversion at all. When SPhos was used in place of XPhos better selectivity was observed as well as complete suppression of the isomerized product **2x** (entry 7). With longer addition time no improvements were observed (entry 8). The use of a hybrid catalytic system with palladium and copper (in order to first form in situ the cuprate from the lithium reagent) was detrimental for the selectivity (entry 9). The addition time could be shortened down to 1h without any negative effect on the reaction (entry 10). The use of a double amount of catalyst or changing the Pd source did not increase the selectivity (entries 11 and 13) and when hexane was added as cosolvent again no reaction was observed (entry 12). The use of DavePhos resulted in lower selectivity imparted to the reaction (entries 14 and 15). Finally the use of the hindered trialkylphosphine $P(^{t}Bu)_3$ led to comparable results to those obtained with SPhos(entry 16). When the reaction was performed in THF without Pd catalyst at room temperature full conversion was not achieved and a mixture was obtained in which the product was present as well as a complex mixture of side products dominated by dehalogenated product **3** (entry 18).

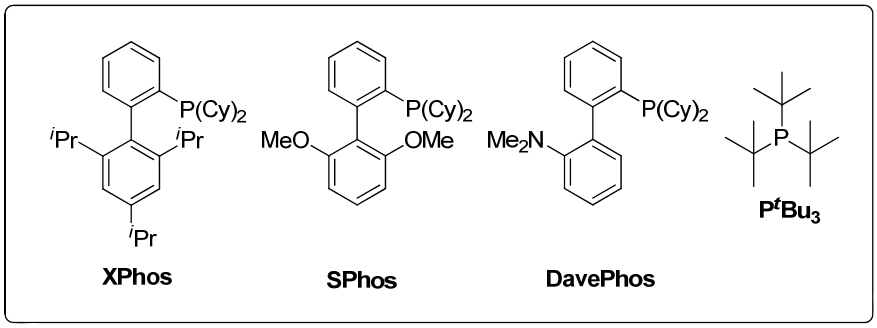
Table S1.



Entry[a]	L mol%	Pd mol%	nBuLi	Reaction time	Solvent	Conversion	2a/3/4/2x
1	**XPhos 10%**	$Pd_2(dba)_3$ 5%	1.5 equiv	3h	toluene	Full	80/5/10/5
2	**XPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	3h	toluene	Full	80/5/10/5
3	**XPhos 10%**	$Pd(OAc)_2$ 5%	1.2 equiv	3h	toluene	Full	80/5/10/5
4	**XPhos 5%**	$Pd_2(dba)_3$ 1.75%	1.2 equiv	3h	toluene	Full	80/5/10/5
5	**XPhos 15%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	3h	toluene	Full	80/5/10/5
6	**XPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	3h	hexane	No conversion	-
7	**SPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	3h	toluene	Full	89/5/6/-
8	**SPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	6h	toluene	Full	88/6/6/-
9	**SPhos 10%**	$Pd_2(dba)_3$ 1.25% %CuBr·SMe_2 2.5%	1.2 equiv	3h	toluene	Full	82/5/13/-
10	**SPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	1h	toluene	Full	89/5/6/-
11	**SPhos 20%**	$Pd_2(dba)_3$ 5%	1.2 equiv	1h	toluene	Full	89/5/6/-
12	**SPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	1h	toluene/hexane 3:1	No conversion	-
13	**SPhos 10%**	$Pd(OAc)_2$ 5%	1.2 equiv	1h	toluene	Full	88/6/6/-
14	**DavePhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	1h	toluene	Full	80/10/10/-
15	**DavePhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	3h	toluene	Full	82/7/11/-
16	**$P(^tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv	1h	toluene	Full	90/6/4/-
17	**-**	$Pd[P(^tBu)_3]_2$ 5%	1.2 equiv	1h	toluene	Full	96/4/-/-
18	**-**	-	1.2 equiv	2h	THF	86%	Complex mixture

[a]Conditions: ^{n}BuLi (1.6 M solution in hexane diluted in toluene to a final concentration of 0.36 M) with 4-methoxy-bromobenzene. (**1a** 0.3 mmol, solvent 2mL)

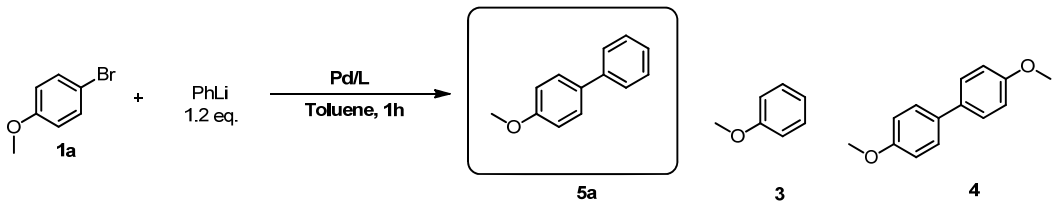
Figure S1.
Ligands screened during optimization studies.



B. Cross-coupling with aryllithium reagents

The use of XPhos as ligand for the Pd catalyze cross coupling of PhLi with 4-methoxy-bromobenzene gave rise mainly to the desired coupling product with the presence of 11% of homocoupled side product **4** (Table S2, entry 1). Addition time (3 h to 1h) and catalyst loading ($Pd_2(dba)_3$ 5mol% to 2.5 mol%) could be both lowered without detectable decrease in selectivity (entry 2, 3). The use of SPhos led to identical results to the ones observed with XPhos (entry 4) while instead $P(^{t}Bu)_3$ gave rise to significant improvement of the selectivity (entry 7). As incomplete conversion was obtained with the use of the preformed catalyst $Pd[P(^{t}Bu)_3]_2$ (see Table 2), a mixture of the aforementioned preformed catalyst and $Pd_2(dba)_3$ was tested but still full conversion could not be achieved (entry 6). Diluting PhLi in THF instead of toluene (entry 7) gave better results but traces of dehalogenated product **3** arose (probably the increasing amount of THF accumulated during the addition slightly increased the rate of halogen-metal exchange). When THF was used also as solvent for the reaction very low selectivity was observed (entry 8). Using Et_2O instead of THF for the dilution (entry 9) as well as the solvent of the reaction (entry 10) resulted in lower selectivity. In order to suppress the formation of **3** a lower amount of THF was used in the dilution of PhLi obtaining a more selective reaction (entry 11). To exclude that the beneficial effect was due only to the higher concentration of the lithium reagent the same dilution (0.6 M) was used with toluene leading to poorer results (entry 12). As diluting PhLi with THF was shown to give better results we then observed that by using slightly different ratio ligand/Pd (1.5:1) we could obtain a highly selective reaction (entry 13).

Table S2.



Entry[a]	L mol%	Pd mol%	PhLi dilution	Reaction time	Solvent	Conversion	5a/3/4
1	**XPhos 10%**	$Pd_2(dba)_3$ 5%	1.5 equiv 0.45 M toluene	3h	toluene	Full	89/-/11
2	**XPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M toluene	3h	toluene	Full	89/-/11
3	**XPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M toluene	1h	toluene	Full	89/-/11
4	**SPhos 10%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M toluene	1h	toluene	Full	89/-/11
5	**$P(tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M toluene	1h	toluene	Full	94/-/6
6	-	$Pd_2(dba)_3$ 1.25% $Pd[P(tBu)_3]_2$ 2.5%	1.2 equiv 0.36 M toluene	1h	toluene	70%	90/-/10
7	**$P(tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M THF	1h	toluene	Full	96/1/4
8	**$P(tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M THF	1h	THF	Full	75/15/10
9	**$P(tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M Et_2O	1h	toluene	Full	89/-/11
10	**$P(tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.36 M Et_2O	1h	Et_2O	Full	88/-/12
11	**$P(tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.60 M THF	1h	toluene	Full	97/-/3
12	**$P(tBu)_3$ 6%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.60 M toluene	1h	toluene	Full	94/-/6
13	**$P(tBu)_3$ 7.5%**	$Pd_2(dba)_3$ 2.5%	1.2 equiv 0.60 M THF	1h	toluene	Full	98/-/2

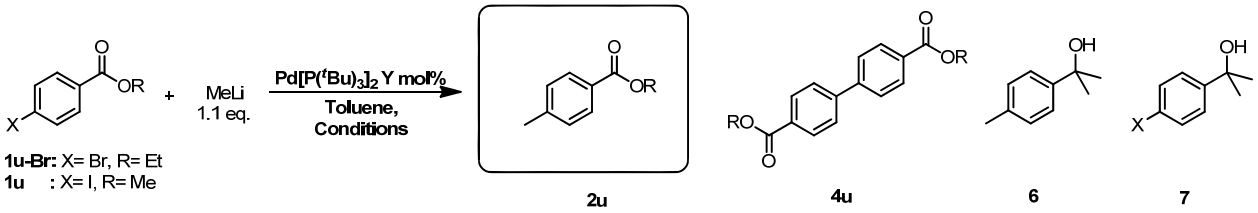
[a]Conditions PhLi (2.0 M solution in dibutyl ether diluted as specified in this table) with 4-methoxy-bromobenzene (**1a** 0.3 mmol, solvent 2mL).

C. Cross-coupling of methyllithium with ester containing substrates.

The coupling of aryl halides containing ester moieties was explored starting by using ethyl 4-bromobenzoate **1u-Br** in combination with MeLi providing a mixture including the desired product (entry 1) but due to low selectivity 1,2-addition products **6** and **7** were observed as well as a consistent amount of starting material. Lowering the temperature to 0 °C didn't improve the selectivity (entry 2). Suspecting that the oxidative addition of Pd was too slow to compete with the fast 1,2-addition of the lithium reagent to the carbonyl

moiety this reaction was tested on the more reactive aryl iodide **1u**. In this case the reaction seems to proceed with higher selectivity but still full conversion was not achieved (entry 3). When the addition rate of the lithium reagent was decreased (entry 4) the conversion and selectivity dropped while using 10 mol% of Pd catalyst (entry 5) the selectivity improved leading nearly to full conversion. A screening (entries 6, 7 and 8) of the temperature pointed out that lowering the temperature to -10 °C (entry 7) could reduce the amount of 1,2-addition product allowing also the total consumption of the starting material. Finally performing the reaction at -10 °C using 7.5 mol% of catalyst (entry 9) we could obtain a remarkable selectivity of 74% and only 9% of the final mixture is represented by the side product **6** arising from 1,2 addition.

Table S3.



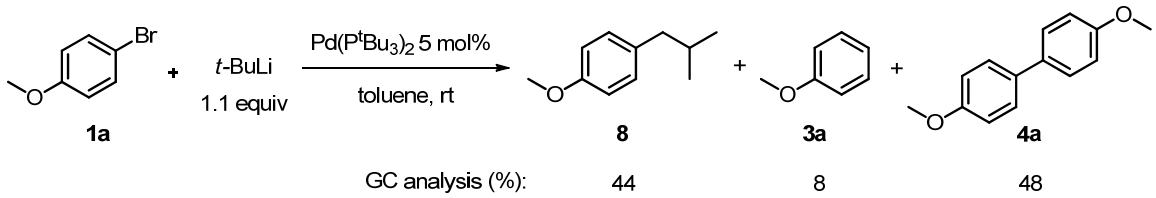
Entry	R	X	Y	Temperature	Reaction time	1u/2u/4u/6/7
1	Et	Br	5	r.t.	1h	37/23/-/28/12
2	Et	Br	5	0 °C	1h	31/28/-/26/15
3	Me	I	5	r.t.	1h	45/36/8/4/7
4	Me	I	5	r.t.	3h	52/28/-/17/3
5	Me	I	10	r.t.	1h	8/60/16/-/16
6	Me	I	5	0 °C	1h	-/59/24/9/-
7	Me	I	5	-10 °C	1h	-/61/21/7/-
8	Me	I	5	-20 °C	1h	-/54/33/14/-
9	Me	I	7.5	-10 °C	1h	-/74/17/9/-

D. Cross-coupling of *tert*-buthyllithium with 4-bromoanisole 1a.

When cross-coupling of 4-bromoanisole **1a** with ^{t}BuLi in presence of 5 mol% of Pd[P(^{t}Bu)$_3$]$_2$ was attempted the only coupled product that was observed was the isomerized 4-*iso*-buthylanisole **8** (Scheme S1). This isomerization is in accordance with

the previous reports on the use of *tert*-buthyl organometallics reagents in cross-coupling reactions. [1]

Scheme S1.



General Procedures for the Cross-Coupling of Organolithium Reagents

Method A: General procedure for the cross-coupling with alkyllithium reagents.

In a dry Schlenk flask $Pd[P(^tBu)_3]_2$ (5 mol%, 0.015 mmol, 7.66 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene. The corresponding lithium reagent (1.2 equiv) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 1h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH_4Cl was added and the mixture was extracted three times with ether. The organic phases were collected and evaporation under reduced pressure afforded the crude product that was then purified by column chromatography.

Method B: General procedure for the cross-coupling with aryllithium reagents.

In a dry Schlenk flask $Pd_2(dba)_3$ (2.5 mol%, 0.0075 mmol, 6.87 mg) and $P(^tBu)_3$ (7.5 mol%, 0.0225 mmol, 4.55 mg) were dissolved in toluene and the substrate (0.3 mmol) was added. The corresponding lithium reagent (1.5 equiv) was diluted with THF to reach the concentration of 0.6 M (unless otherwise specified); this solution was slowly added over 1h by the use of a syringe pump. After the addition was completed a saturated solution of aqueous NH_4Cl was added and the mixture was extracted 3 times with ether. The organic phases were collected and the solvent evaporation under reduced pressure afforded the crude product that was then purified by column chromatography.

Method C: General procedure for the cross-coupling with thienyllithium.

In a dry Schlenk flask $Pd_2(dba)_3$ (2.5 mol%, 0.0075 mmol, 6.87 mg) and $P(^tBu)_3$ were dissolved in toluene and the substrate (0.3 mmol) was added and the solution was warmed up to 40 °C. Thienyllithium (1.5 equiv) was diluted with toluene to reach the concentration of 0.6 M and TMEDA (1.5 equiv) was added to it; this soluition was slowly added over 1h by the use of a syringe pump. After the addition was completed a saturated solution of NH_4Cl was added and the mixture was extracted 3 times with ether. The organic phases were collected and evaporation under reduced pressure afforded the crude mixture that was then purified by column chromatography.

[1] A. Lei and co., *Org. Lett.* **9**, 4571 (2007).

Method D: General procedure for the cross-coupling of methyllithium with an ester containing substrate.

In a dry Schlenk flask $Pd[P(^tBu)_3]_2$ (7.5 mol%, 0.0225 mmol, 11.49 mg) and the substrate (0.3 mmol) were dissolved in 2 mL of dry toluene. Methyllithium (1.1 equiv) was diluted with toluene to reach the concentration of 0.36 M; this solution was slowly added over 1h by the use of a syringe pump. After the addition was completed a saturated aqueous solution of NH_4Cl was added and the mixture was extracted three times with ether. The organic phases were collected and evaporation under reduced pressure afforded the crude product that was then purified by column chromatography.

Preparation of organolithium reagents:

A. Hexadecyllithium

Hexadecyllithium was prepared in accordance with a previously reported procedure.[2]

B. 3-Trifluoromethyl-phenyllithium and 4-methoxy-phenyllithium

In a dry Schlenk flask the corresponding bromide (1.8 mmol) was dissolved in dry THF (0.9 mL) and the solution was cooled down to -78 ºC. ^{t}BuLi (2 equiv) was added slowly and the solution was stirred for 1h. Then the solution was allowed to reach room temperature.

C. 2,6-Dimethyl-phenyllithium

In a dry Schlenk flask 1-bromo-2,6-dimethyl-benzene (1.8 mmol, 333 mg) was dissolved in dry THF (0.9 mL) and the solution was cooled down to -78 ºC. ^{t}BuLi (2 equiv) was added slowly and the solution was stirred for 1h. Then the solution was allowed to reach room temperature.

D. Furyllithium

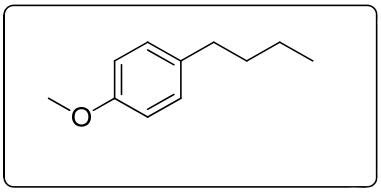
According to a literature procedure[3] furane (9.0 mmol, 612.6 mg, 654.5 µl) was dissolved in THF (4.5 mL) and the solution was cooled down to -40 ºC. ^{n}BuLi (8.5 mmol.) was added slowly. Then the solution was allowed to reach room temperature and stirred for 3h.

E. 2-Methoxymethoxy-phenyllithium

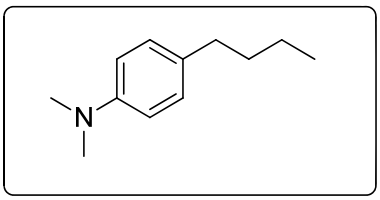
In a dry Schlenk flask (methoxymethoxy)benzene[4] (1.0 mmol, 138 mg) was dissolved in dry THF (3 mL) and the solution was cooled down to -78 ºC. ^{t}BuLi (1 equiv) was added slowly and the solution was stirred for 1 h. Then the solution was allowed to reach room temperature.

[2] H. Merten, H. Gilman, *J. Am. Chem. Soc.* **76**, 5798 (1954).
[3] J. Raczko, A. Golebiowski, J. W. Krajewski, P. Gluzinski, J. Jurczak, *Tetrahedron Lett.* **31**, 3797 (1990).
[4] C. T. Vo, T. A. Mitchell, J. W. Bode, *J. Am. Chem. Soc.* **133**, 14082 (2011).

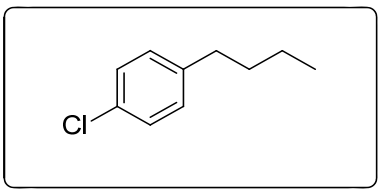
Spectral data of compounds 2a-2z:



1-Butyl-4-methoxybenzene (2a): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [80% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.68 – 1.51 (m, 2H), 1.37 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 135.0, 129.2, 113.6, 55.2, 34.7, 33.9, 22.3, 14.0. The physical data were identical in all respects to those previously reported.[5]

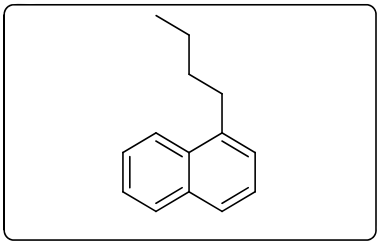


4-Butyl-*N*,*N*-dimethylaniline (2b): Synthesized according to **Method A**. Transparent semisolid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:3), [88% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 2.93 (s, 6H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.52 (m, 2H), 1.43–1.32 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 131.3, 129.0, 113.0, 41.0, 34.6, 34.0, 22.4, 14.0. The physical data were identical in all respects to those previously reported.[6]

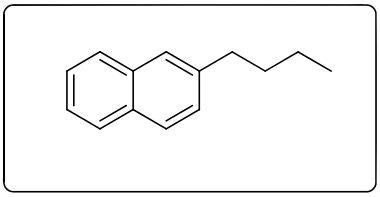


1-Butyl-4-chlorobenzene (2c): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane), [84% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.63-1.52 (m, 2H), 1.40-1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 131.2, 129.7, 128.3, 35.0, 33.5, 22.2, 13.9. The physical data were identical in all respects to those previously reported.[7]

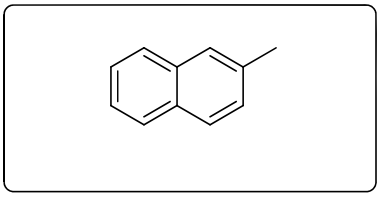
[5] L. Ackermann, A. R. Kapdi, C. Schulzke, *Org*. *Lett*. **12**, 2298 (2010).
[6] B. K. Lee, M. R. Biscoe, S. L. Buchwald, *Tetrahedron Lett*. **50**, 3672 (2009).
[7] Y. Nakao, M. Takeda, T. Matsumoto, T. Hiyama, *Angew*. *Chem*. *Int*. *Ed*. **49**, 4447 (2010).



1-Butylnaphthalene (2d): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane), [91% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 6.1, 1.6 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.42 (t, *J* = 8.7 Hz, 1H), 7.34 (d, *J* = 6.9 Hz, 1H), 3.10 (t *J* = 7.9 Hz, 2H), 1.82 – 1.71 (m, 2H), 1.56 – 1.41 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 133.9, 131.9, 128.7, 126.4, 125.8, 125.6, 125.5, 125.3, 123.9, 33.0, 32.8, 22.9, 14.0. The physical data were identical in all respects to those previously reported.[8]

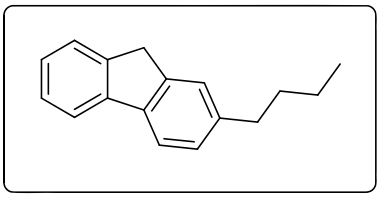


2-Butylnaphthalene (2e): Synthesized according to **Method A**.Colorless oil obtained after column chromatography (SiO_2, *n*-pentane), [87% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 3H), 7.65 (s, 1H), 7.51 – 7.41 (m, 2H), 7.37 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.81 (t, *J* = 7.7 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.50 – 1.38 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 133.6, 131.9, 127.7, 127.6, 127.5, 127.4, 126.3, 125.8, 125.0, 35.8, 33.5, 22.4, 14.0. The physical data were identical in all respects to those previously reported.[9]

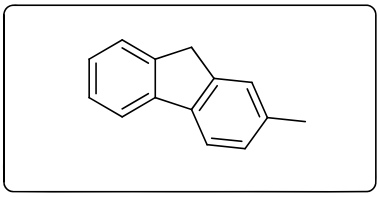


2-Methylnaphthalene (2f): Synthesized according to **Method A**. White solid obtained after column chromatography (SiO_2, *n*-pentane), [83% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 1H), 7.80 – 7.76 (m, 2H), 7.64 (s, 1H), 7.50 – 7.40 (m, 2H), 7.35 (dd, *J* = 8.4, 1.4 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 133.7, 131.7, 128.1, 127.7, 127.6, 127.2, 126.8, 125.9, 124.9, 21.7. The physical data were identical in all respects to those previously reported.[10]

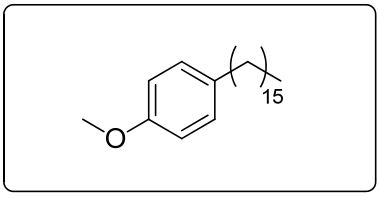
[8] C. Zhu, N. Yukimura, M. Yamane, *Organometallics*, **29**, 2098 (2010).
[9] M. E. Limmert, A. H. Roy, J. F. Hartwig, *J. Org. Chem.* **70**, 9364 (2005).
[10] B. Guan *et al*. *Chem. Comm*. 1437 (2008).



2-Butyl-9*H*-fluorene (2g): Synthesized according to **Method A**. (The reaction was carried out with a commercially available mixture of 2-bromo-9*H*-fluorene/2,7-dibromo-9*H*-fluorene ≅ 95/5) White solid obtained as a mixture 2-butyl-9*H*-fluorene/2,7-dibutyl-9*H*-fluorene/fluorene 95/5) after column cromatography (SiO_2, *n*-pentane), [88% yield with respect to the 2-bromo-9*H*-fluorene in the starting material]. NMR spectra of major product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H) 3.87 (s, 2H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.74 – 1.61 (m, 2H), 1.46 – 1.31 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 143.1, 141.8, 141.7, 139.3, 127.0, 126.6, 126.1, 125.1, 124.9, 119.56, 119.54, 36.8, 35.9, 34.0, 22.4, 14.0. The physical data were identical in all respects to those previously reported.[11]



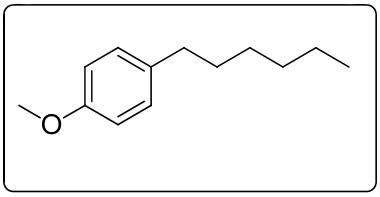
2-Methyl-9*H*-fluorene (2h): Synthesized according to **Method A**. (The reaction was carried out with a commercially available mixture of 2-bromo-9*H*-fluorene/2,7-dibromo-9*H*-fluorene ≅ 95/5) White solid obtained as a mixture 2-methyl-9*H*-fluorene/2,7-dimethyl-9*H*-fluorene/fluorene 96/4) after column cromatography (SiO_2, *n*-pentane), [90% yield with respect to the 2-bromo-9*H*-fluorene in the starting material]. NMR spectra of major product: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.28 (dt, *J* = 7.4, 1.1 Hz, 1H), 7.20 (dd, *J* = 7.4, 0.6 Hz, 1H), 3.86 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.0, 141.8, 139.1, 136.5, 127.5, 126.6, 126.2, 125.7, 124.9, 119.6, 119.5, 36.8, 21.6. The physical data were identical in all respects to those previously reported.[12]



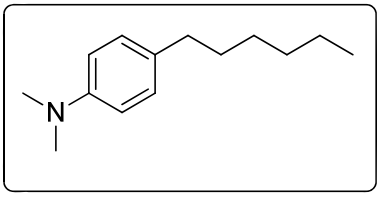
1-Hexadecyl-4-methoxybenzene (2i): Synthesized according to **Method A**. [78% yield] White solid obtained after column chromatography (SiO_2, *n*-pentane). Mp: 44-46 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 3.80 (s, 3H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.53 (m, 2H), 1.32 – 1.24 (m, 26H), 0.90 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 135.3, 129.4, 113.9, 55.4, 35.3, 32.2,

[11] C. Hsiao, Y. Lin, C. Liu, T. Wu, Y. Wu, *Adv. Synth. Catal.* **352**, 3267 (2010).
[12] K. Fuchibe, T. Akiyama, *J. Am. Chem. Soc.* **128**, 1434 (2006).

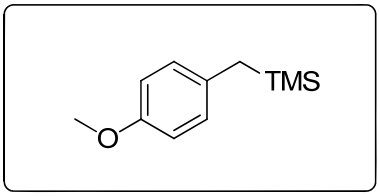
32.0, 29.9 (7C), 29.8, 29.8, 29.6, 29.5, 22.9, 14.3. HRMS (APCI+, *m/z*): calcd for $C_{23}H_{41}O_1$ $[M+H]^+$: 333.31519; found: 333.31467.



1-Hexyl-4-methoxybenzene (2j): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [94% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.56 (t, *J* = 7.8 Hz, 2H), 1.64-1.54 (m, 2H), 1.39-1.25 (m, 6H), 0.90 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 135.0, 129.2, 113.6, 55.2, 35.0, 31.7, 31.7, 28.9, 22.6, 14.1. The physical data were identical in all respects to those previously reported.[4]

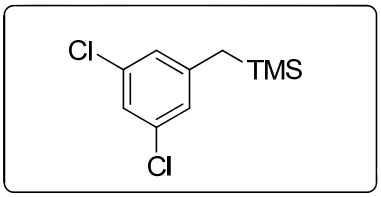


4-Hexyl-*N*,*N*-dimethylaniline (2k): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:3), [95% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 2.93 (s, 6H), 2.54 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.39 – 1.26 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 131.3, 129.0, 113.0, 112.6, 41.0, 34.9, 31.8, 29.1, 22.7, 14.1. The physical data were identical in all respects to those previously reported.[13]

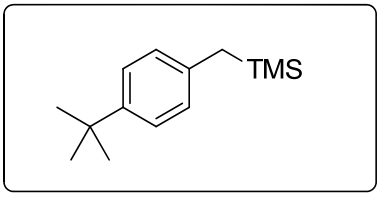


(4-Methoxybenzyl)trimethylsilane (2l): Synthesized according to **Method A**. Colorless liquid obtained after column cromatography (SiO_2, *n*-pentane/EtOAc 100:0.5), [93% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.3 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 2.02 (s, 2H), 0.1 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 132.6, 129.1, 113.9, 55.5, 26.0, -1.6. The physical data were identical in all respects to those previously reported.[14]

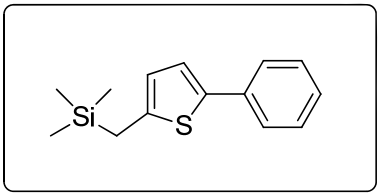
[13] C. Yang, Z. Zhang, Y. Liu, L. Liu, *Angew. Chem. Int. Ed.* **50**, 3904 (2011).
[14] M. Tobisu, Y. Kita, Y. Ano, N. Chatani, *J. Am. Chem. Soc.* **130**, 15982 (2008).



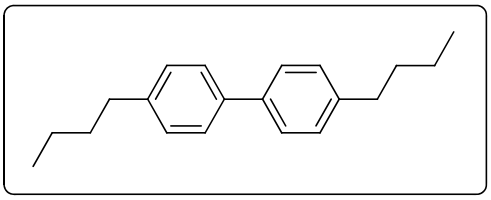
(3,5-Dichlorobenzyl)trimethylsilane (2m): Synthesized according to **Method A**. Transparent oil obtained after column cromatography (SiO_2, *n*-pentane), [97% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 1H), 6.87 (d, *J* = 1.4 Hz, 2H), 2.02 (s, 2H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 134.6, 126.3, 124.3, 27.2, -1.9.



(4-(*tert*-Butyl)benzyl)trimethylsilane (2n): Synthesized according to **Method A**. Transparent oil obtained after column cromatography (SiO_2, *n*-pentane), [93% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 2.03 (s, 2H), 1.29 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.0, 129.5, 126.8, 36.0, 33.3, 28.2, 0.0. HRMS (APCI+, *m/z*): calculated for $C_{14}H_{25}Si$ [M+H$^+$]: 221.17200; found: 221.17171.

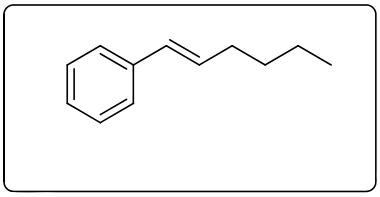


Trimethyl((5-phenylthiophen-2-yl)methyl)silane (2o): Synthesized according to **Method A**. Transparent oil obtained after column cromatography (SiO_2, *n*-pentane), [87% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.58 (d, *J* = 3.3 Hz, 1H), 2.31 (s, 2H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 140.2, 135.0, 129.0, 126.8, 125.4, 124.4, 123.2, 21.2, -1.6. HRMS (APCI+, *m/z*): calculated for $C_{14}H_{19}SSi$ [M+H$^+$]: 247.09712; found: 247.09715.

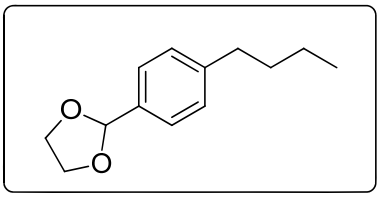


4,4'-Dibutyl-1,1'-biphenyl (2p): Synthesized according to **Method A**. [91% yield] White solid obtained after column chromatography (SiO_2, *n*-pentane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.1 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 4H), 2.75 – 2.60 (m, 4H), 1.78 – 1.60 (m, 4H), 1.51 – 1.35 (m, 4H), 0.99 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (75 MHz,

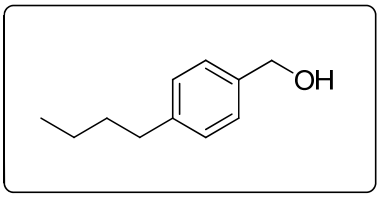
$CDCl_3$) δ 141.9, 138.8, 129.0, 127.0, 35.5, 33.9, 22.7, 14.2. The physical data were identical in all respects to those previously reported.[15]



(*E*)-Hex-1-enylbenzene (2q): (The reaction was carried out on commercially available mixture *cis*/*trans* 84/16) Colorless oil obtained as pure *E* isomer from a 84/16 *E*/*Z* crude mixture after column chromatography (SiO_2, *n*-pentane), [89% yield with respect to the *E* isomer in the starting material]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 5H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.8 Hz, 1H), 2.27 – 2.18 (m, 2H), 1.59 – 1.29 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 131.2, 129.7, 128.4, 126.7, 125.9, 32.7, 31.5, 22.3, 14.0. The physical data were identical in all respects to those previously reported.[16]

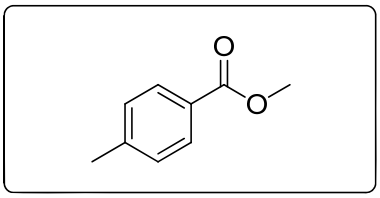


2-(4-Butylphenyl)-1,3-dioxolane (2s): Synthesized according to **Method A**. Transparent liquid obtained after column cromatography (SiO_2, *n*-pentane/EtOAc 7:1), [92% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) 7.40 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 2H), 5.80 (s, 1H), 4.16 – 4.11 (m, 2H), 4.05 – 4.00 (m, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.54 (m, 2H), 1.41 – 1.29 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 135.1, 128.4, 126.3, 103.8, 65.3, 35.4, 33.6, 22.3, 14.00. HRMS (APCI+, *m*/*z*): calculated for $C_{13}H_{19}O_2$ [$M+H^+$]: 207.13796; found: 207.13784.

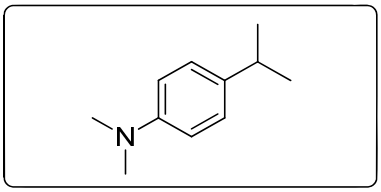


4-Butylbenzyl alcohol (2t): Synthesized according to **Method A**. [61% yield] Light yellow oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.65 (s, 2H), 2.61 (t, J = 7.3 Hz, 2H), 1.75 (bs, 1H), 1.65 – 1.54 (m, 2H), 1.42 – 1.30 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.9, 128.6, 127.1, 65.3, 35.3, 33.7, 22.3, 13.9.

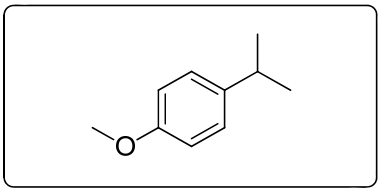
[15] K. L. Billingley, T. E. Barder, S. L. Buchwald, *Angew*. *Chem*. *Int*. *Ed*. **46**, 5359 (2007).
[16] A. Herve, A. L. Rodriguez, E. Fouquet, *J*. *Org*. *Chem*. **70**, 1953 (2005).



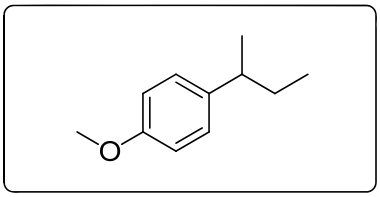
Methyl 4-methylbenzoate (2u): Synthesized according to **Method D**. [34% yield] White solid obtained after column chromatography (SiO_2, *n*-pentane/DCM 7:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 143.5, 129.6, 129.0, 127.4, 51.9, 21.6. The physical data were identical in all respects to those previously reported.[17]



1-Isopropyl-4-methoxybenzene (2v): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 35:1), [75% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, J = 8.8, 2.1 Hz, 2H), 6.76 (dd, J = 9.0, 2.4 Hz, 2H), 2.94 (s, 6H), 2.86 (septet, J = 6.9 Hz, 1H) 1.26 (d, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 137.2, 126.9, 113.0, 41.0, 33.1, 24.2. The physical data were identical in all respects to those previously reported.[18]

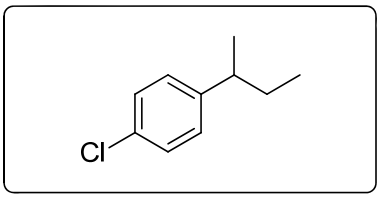


1-Isopropyl-4-methoxybenzene (2w): Synthesized according to **Method A**. Colorless oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [78% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J = 9.1, 2.0 Hz, 2H), 6.86 (dd, J = 8.6, 2.0 Hz, 2H), 3.82 (s, 3H), 2.89 (septet, J = 6.9 Hz, 1H), 1.25 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 141.0, 127.2, 113.7, 55.2, 33.3, 24.2. The physical data were identical in all respects to those previously reported.[19]

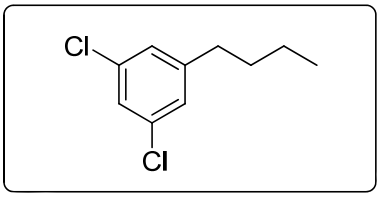


[17] S. Kanemura, A. Kondoh, H. Yorimitsu, K. Oshima, *Tetrahedron*, **63**, 12720 (2007).
[18] S. Kanemura, A. Kondoh, H. Yorimitsu, K. Oshima, *Synthesis*, 2659 (2008).
[19] S. D. Dreher, P. G. Dormer, D. L. Sandrock, G. A. Molander, *J. Am. Chem. Soc.* **130**, 9257 (2008).

1-(*sec*-Butyl)-4-methoxybenzene (2x): Synthesized according to **Method A**. [73% yield] Colorless oil obtained after column chromatography (SiO_2, *n*-pentane/Et_2O 20:1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.56 (h, *J* = 7.0 Hz, 1H), 1.65 – 1.49 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 139.8, 127.8, 113.6, 55.2, 40.8, 31.3, 22.0, 12.2. The physical data were identical in all respects to those previously reported.[20]

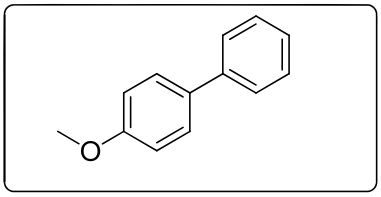


1-(*sec*-Butyl)-4-chlorobenzene (2y): Synthesized according to **Method A**. [78% yield] Colorless oil obtained after column chromatography (SiO_2, *n*-pentane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 2.58 (h, *J* = 7.0 Hz, 1H), 1.66 – 1.49 (m, 2H), 1.22 (d, *J* = 6.9 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.3, 131.5, 128.6, 128.5, 41.4, 31.3, 22.0, 12.3. The physical data were identical in all respects to those previously reported.[21]



1-Butyl-3,5-dichlorobenzene (2z): Synthesized according to **Method A**. Colorless liquid obtained after column chromatography (SiO_2, *n*-pentane), [86% yield]. ^1H NMR (400 MHz, $CDCl_3$) 7.18 (t, *J* = 1.8 Hz, 1H), 7.06 (d, *J* = 1.8, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.63-1.53(m, 2H), 1.41-1.28 (m, 2H), 0.93 (t, *J* = 7.3, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 134.5, 126.9, 125.8, 35.1, 33.1, 22.2, 13.8.

Spectral data of compounds 5a-5s:

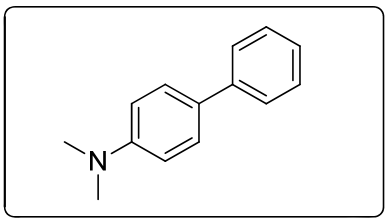


4-Methoxybiphenyl (5a): Synthesized according to **Method B**. White solid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [84% yield]. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 4H), 7.47 – 7.39 (m, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1,

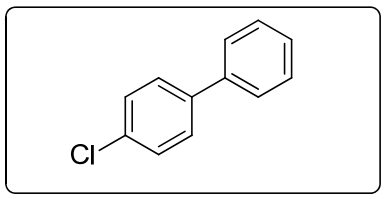
[20] S. McIntyre, E. Hoermann, F. Menges, S. P. Smidt, A. Pfaltz, *Adv. Synth. Catal.* **347**, 282 (2005).
[21] B. Guan, Y. Wang, B. Li, D. Yu, Z. Shi, *J. Am. Chem. Soc.* **130**, 14468 (2008).

140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3. The physical data were identical in all respects to those previously reported.[22]

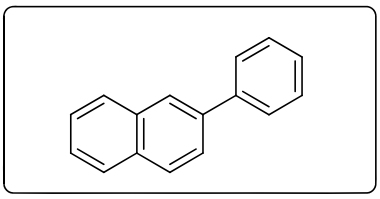
The reaction performed with 5.5 mmol (1.029 g) of substrate in the presence of 1 mol% of Pd_2dba_3 and 3 mol% of P^tBu_3 afforded the product in 93% yields.



***N*,*N*-Dimethyl-[1,1'-biphenyl]-4-amine (5b):** Synthesized according to **Method B**. [80% yield] White solid obtained after column chromatography (SiO_2, *n*-pentane/ Et_2O 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.57 – 7.51 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 141.2, 129.3, 128.7, 127.7, 126.3, 126.0, 112.8, 40.6. The physical data were identical in all respects to those previously reported.[20]

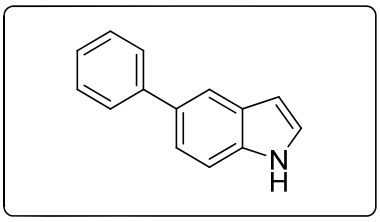


4-Chloro-1,1'-biphenyl (5c): Synthesized according to **Method B**. [85% yield] White solid obtained after column chromatography (SiO_2, *n*-pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.33 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.7, 133.4, 128.9, 128.9, 128.4, 127.6, 127.0. The physical data were identical in all respects to those previously reported.[14]

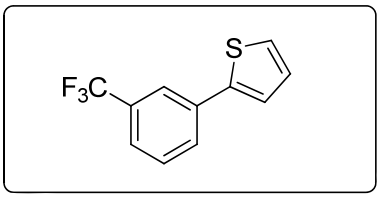


2-Phenylnaphthalene (5d): Synthesized according to **Method B**. White solid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [83% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.95 – 7.85 (m, 3H), 7.81 – 7.72 (m, 3H), 7.56 – 7.47 (m, 4H), 7.41 (dt, *J* = 7.5, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.6, 133.7, 132.6, 128.9, 128.4, 128.2, 127.6, 127.4, 127.4, 126.3, 125.9, 125.8, 125.6. The physical data were identical in all respects to those previously reported.[19]

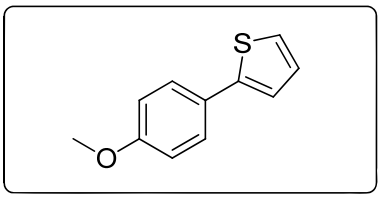
[22] N. Yoshikai, H. Mashima, E. Nakamura, *J. Am. Chem. Soc.* **127**, 17978 (2005).



5-Phenyl-1H-indole (5e): Synthesized according to **Method B** using 3 equiv of PhLi. [95% conv.; 89% yield] White solid obtained after column chromatography (SiO_2, *n*-pentane/ EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.87 (s, 1H), 7.69 – 7.62 (m, 2H), 7.50 – 7.39 (m, 4H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.65 – 6.57 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 135.3, 133.4, 128.6, 128.4, 127.4, 126.3, 124.8, 121.9, 119.2, 111.2, 103.0. The physical data were identical in all respects to those previously reported.[23]

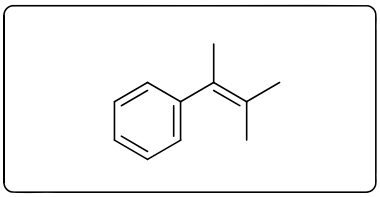


2-(3-Trifluoromethylphenyl)thiophene (5f): Synthesized according to **Method C**. Transparent oil obtained after column chromatography (SiO_2, *n*-pentane), [81% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.78 (d, *J* = 7.5 Hz, 1H), 7.57 – 7.46 (m, 2H), 7.38 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.35 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 135.2, 131.3 (q, *J* = 32.3 Hz), 129.4, 129.0, 128.2, 125.8, 124.1, 124.0 (q, *J* = 3.8 Hz), 122.5 (q, *J* = 3.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63. The physical data were identical in all respects to those previously reported.[24]

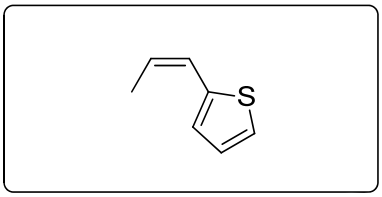


2-(4-Methoxyphenyl)thiophene (5g): Synthesized according to **Method C**. White solid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:2), [88% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.9 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.2 128.0, 127.3, 127.2, 123.8, 122.1, 114.2, 55.34. The physical data were identical in all respects to those previously reported.[25]

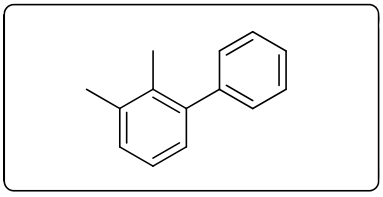
[23] G. Manolikakes, C. M. Hernandez, M. A. Schade, A. Metzger, P. Knochel, *J. Org. Chem.* **73**, 8422 (2008).
[24] A. Yokooji, T. Satoh, M. Miura, M. Nomura, *Tetrahedron*, **60**, 6757 (2004).
[25] H. A. Stefani *et al*., *Tetrahedron Lett*. **52**, 4398 (2011).



α,β,β-Trimethylstyrene (5h): Synthesized according to **Method B** and performed on a 1.5 mmol scale. Transparent oil obtained after column chromatography (SiO_2, *n*-pentane), [81% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.20 (dt, *J* = 7.3, 1.3 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.3 Hz, 2H), 1.97 (s, 3H), 1.82 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 130.0, 128.4, 128.0, 127.2, 125.7, 22.1, 20.8, 20.5. The physical data were identical in all respects to those previously reported.[26]

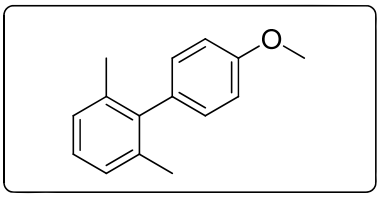


(*Z*)-2-(Prop-1-en-1-yl)thiophene (5i): Synthesized according to **Method C**. [99% (GC yield)]. Single product isolated yield could not be accurately determined because toluene could not be completely removed due to volatility issues. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 6.63 (dq, *J* = 11.4, 1.7 Hz, 1H), 5.76 (dq, *J* = 11.4, 7.3 Hz, 1H), 2.03 (dd, *J* = 7.3, 1.7 Hz, 3H).

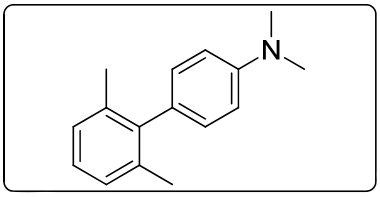


2,3-Dimethylbiphenyl (5j): Synthesized according to **Method B**. White solid obtained after column chromatography (SiO_2, *n*-pentane), [84% yield] (8% of biphenyl contaminant present in the commercial PhLi could not be separated from the final product) . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.32 (m, 5H), 7.21 – 7.10 (m, 3H), 2.38 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 142.3, 137.2, 134.0, 129.4, 128.9, 128.0, 127.7, 126.6, 125.2, 20.7, 17.0. The physical data were identical in all respects to those previously reported.[27]

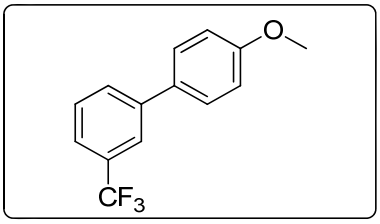
[26] J. Waser, E. M. Carreira, *Angew. Chem. Int. Ed.* **43**, 4099 (2004).
[27] S. Vuoti, J. Autio, M. Laitila, M. Haukka, J. Pursiainen, *Eur. J. Inorg. Chem.* 397 (2008).



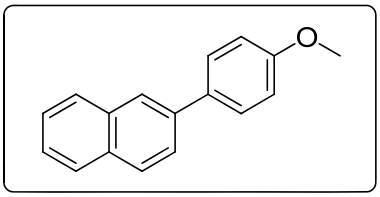
4'-Methoxy-2,6-dimethyl-1,1'-biphenyl (5k): Synthesized according to **Method B**. White solid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [90% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.04 (m, 5H), 7.03 – 6.95 (m, 2H), 3.88 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 141.5, 136.5, 133.3, 130.1, 127.2, 126.9, 113.8, 55.2, 20.9. The physical data were identical in all respects to those previously reported.[28]



(2',6'-Dimethylbiphenyl-4yl)dimethylamine (5l): Synthesized according to **Method B**. White solid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [75% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.09 (m, 3H), 7.04 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 3.02 (s, 6H), 2.10 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 142.0, 136.8, 129.7, 129.1, 127.2, 126.6, 112.4, 40.6, 21.0. The physical data were identical in all respects to those previously reported.[29]

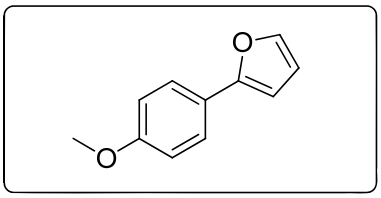


4'-Methoxy-3-(trifluoromethyl)1,1'-biphenyl (5m): Synthesized according to **Method B**. Transparent liquid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [71% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.73 (d, J = 7.3 Hz, 1H), 7.63 – 7.48 (m, 4H), 7.01 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 141.5, 132.2, 131.2 (d, J = 32.2 Hz) 129.9, 129.1, 128.2, 123.4 (q, J = 3.8 Hz), 123.2 (q, J = 3.8 Hz), 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6. The physical data were identical in all respects to those previously reported.[19]

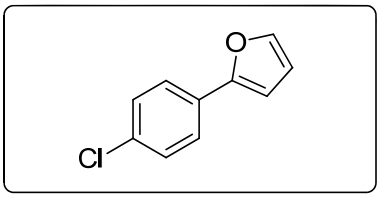


[28] T. M. Razler *et al*., *J*. *Org*. *Chem*. **74**, 1381 (2009).
[29] B. Dhudshia, A. N. Thadani, *Chem*. *Comm*. 668 (2006).

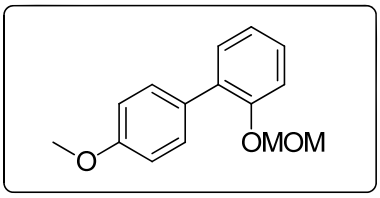
2-(4-Methoxyphenyl)naphthalene (5n): White solid obtained after column chromatography (6% of 4,4'-dimethoxhy-1,1'-biphenyl, coming from the homocoupling of the lithium reagent, was present after purification) (SiO_2, *n*-pentane/EtOAc 100:1), [80% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.93– 7.82 (m, 3H), 7.73 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.56 – 7.43 (m, 2H), 7.09 – 6.93 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 138.1, 133.7, 133.6, 132.3, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 114.15, 55.4. The physical data were identical in all respects to those previously reported.[30]



2-(4-Methoxyphenyl)furan (5o): Synthesized according to **Method B**. White solid obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:2), [84% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.9 Hz, 2H), 7.44 (dd, *J* = 1.7, 0.6 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.52 (dd, *J* = 3.3, 0.6 Hz, 1H), 6.45 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 154.0, 141.4, 125.2, 124.0, 114.1, 111.5, 103.3, 55.3. The physical data were identical in all respects to those previously reported.[31]



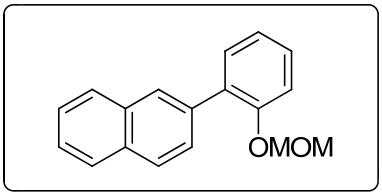
2-(4-Chlorophenyl)furan (5p): Synthesized according to **Method B**. [88% yield] Yellow solid obtained after column chromatography (SiO_2, *n*-pentane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 1.3 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 3.3 Hz, 1H), 6.48 (dd, *J* = 3.3, 1.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 142.5, 133.2, 129.6, 129.1, 125.2, 112.0, 105.6. The physical data were identical in all respects to those previously reported.[32]



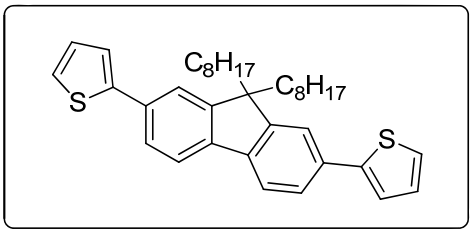
4'-Methoxy-2-(methoxymethoxy)-1,1'-biphenyl (5q): Synthesized according to **Method B**. Transparent oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [86% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz 2H), 7.36 (dt, *J* = 7.4, 1.5 Hz, 1H), 7.31 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.25 (dd, *J* = 8.2, 1.0

[30] H. Shen, S. Pal, J. Lian, R. Liu, *J. Am. Chem. Soc.* **125**, 15762 (2003).
[31] S. E. Denmark, J. D. Baird, *Org. Lett.* **8**, 793 (2006).
[32] A. R. Katritzky, J. Li, M. F. Gordeev, *J. Org. Chem.* **58**, 3038 (1993).

Hz, 1H), 7.12 (td, J = 7.4, 1.2 Hz, 1H), 7.01 (d, J = 8.7 Hz, 2H), 5.17 (s, 2H), 3.90 (s, 3H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 154.2, 131.5, 131.0, 130.8, 130.6, 128.2, 122.3, 115.8, 113.5, 95.1, 56.1, 55.3. HRMS (ESI+, *m/z*): calculated for $C_{15}H_{16}O_3Na$ [M+Na$^+$]: 267.09917; found: 267.09933.



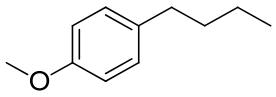
2-(2-(Methoxymethoxy)phenyl)naphthalene (5r): Synthesized according to **Method B**. Transparent viscous oil obtained after column chromatography (SiO_2, *n*-pentane/EtOAc 100:1), [82% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.85 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 8.4 Hz, 8H), 7.54 – 7.38 (m, 3H), 7.32 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 7.4 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 5.11 (s, 2H), 3.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 136.2, 133.3, 132.4, 131.8, 131.2, 128.7, 128.1, 128.0, 127.6, 127.1, 125.9, 125.8, 122.3, 115.7, 95.1, 56.1. HRMS (APCI+, *m/z*): calculated for $C_{18}H_{17}O_2$ [M+H$^+$]: 265.12231; found: 265.12227.



2,7-Dithienyl-9,9-dioctylfluorene (5s): Synthesized according to **Method C**. Transparent oil obtained after column chromatography (SiO_2, *n*-pentane/AcOEt 100:1), [86% yield]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.9 Hz, 2H), 7.62 (dd, J = 7.9, 1.6 Hz, 2H), 7.58 (d, J = 1.2 Hz, 2H), 7.39 (dd, J = 3.6, 1.1 Hz, 2H), 7.30 (dd, J = 5.1, 1.0 Hz, 2H), 7.12 (dd, J = 5.1, 3.6 Hz, 2H), 2.10 – 1.95 (m, 4H), 1.26 – 0.97 (m, 20H), 0.80 (t, J = 7.3 Hz, 6H), 0.75 – 0.61 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 145.1, 140.19, 133.2, 128.0, 124.9, 124.5, 122.9, 120.14, 120.06, 55.3, 40.4, 31.8, 30.0, 29.2, 29.16, 23.7, 22.6, 14.0. The physical data were identical in all respects to those previously reported.[33]

[33] L. Liu *et al*. *Adv*. *Funct*. *Mater*. **18**, 2824 (2008).

^{1}H and ^{13}C NMR of isolated compounds



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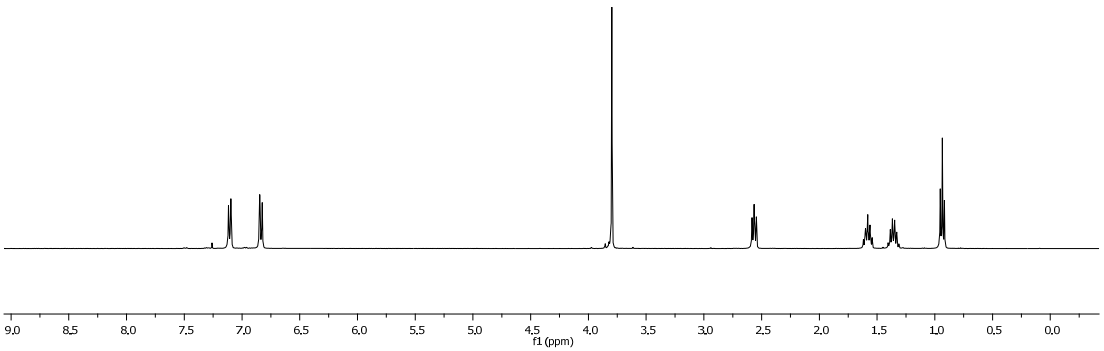

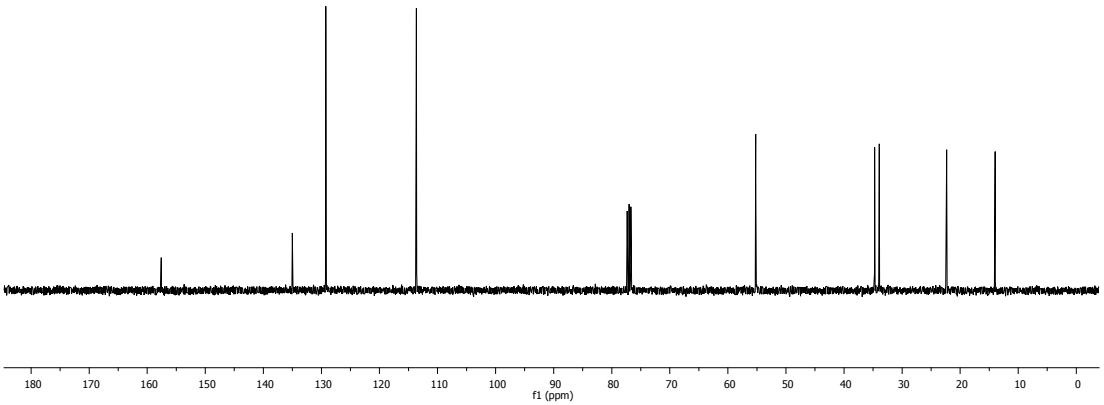

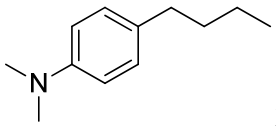

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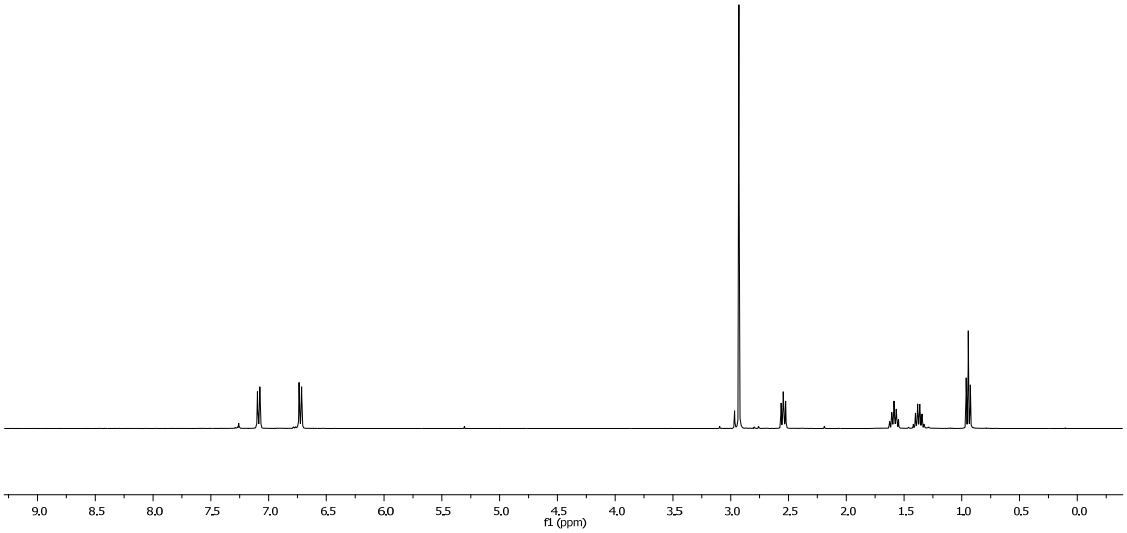

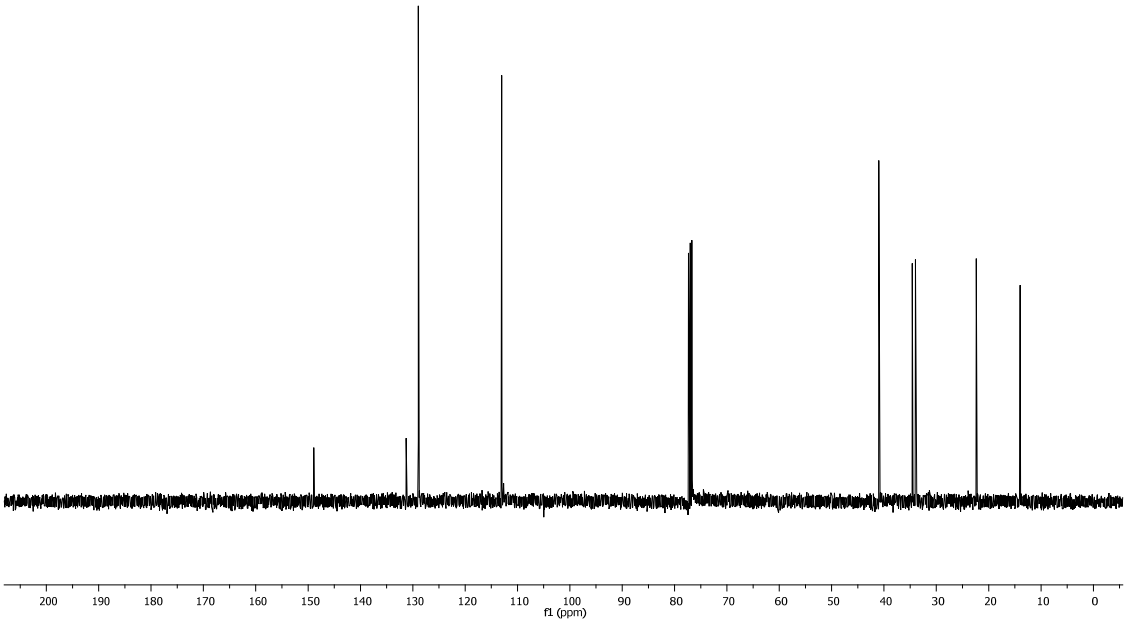

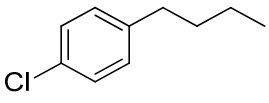

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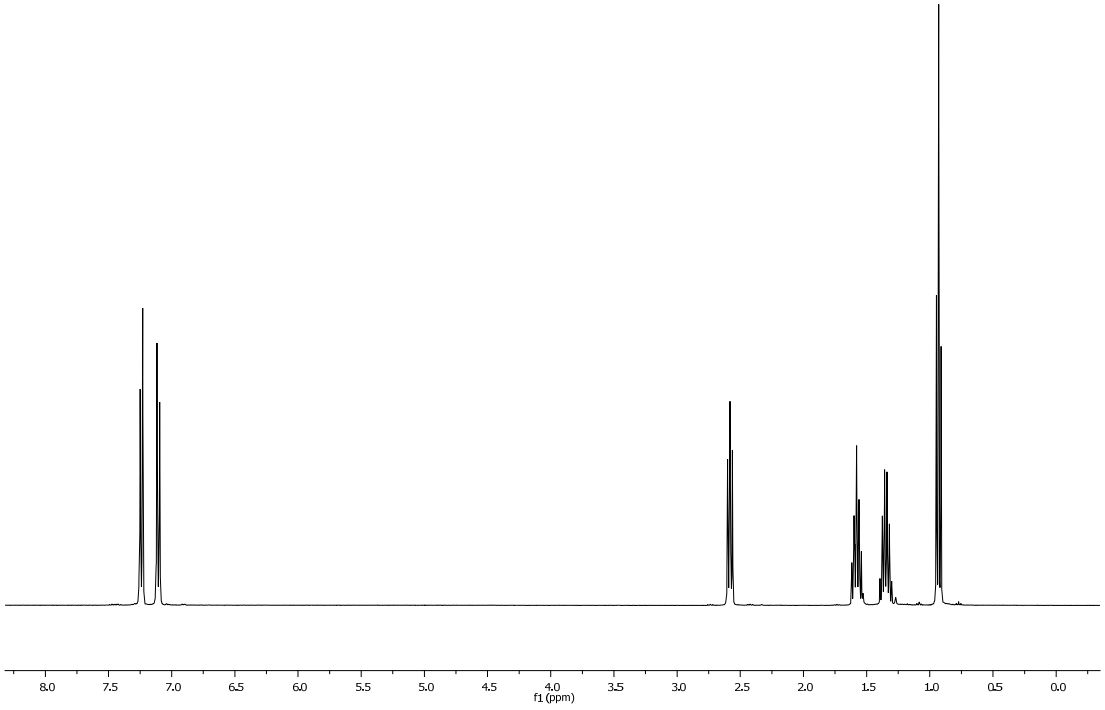

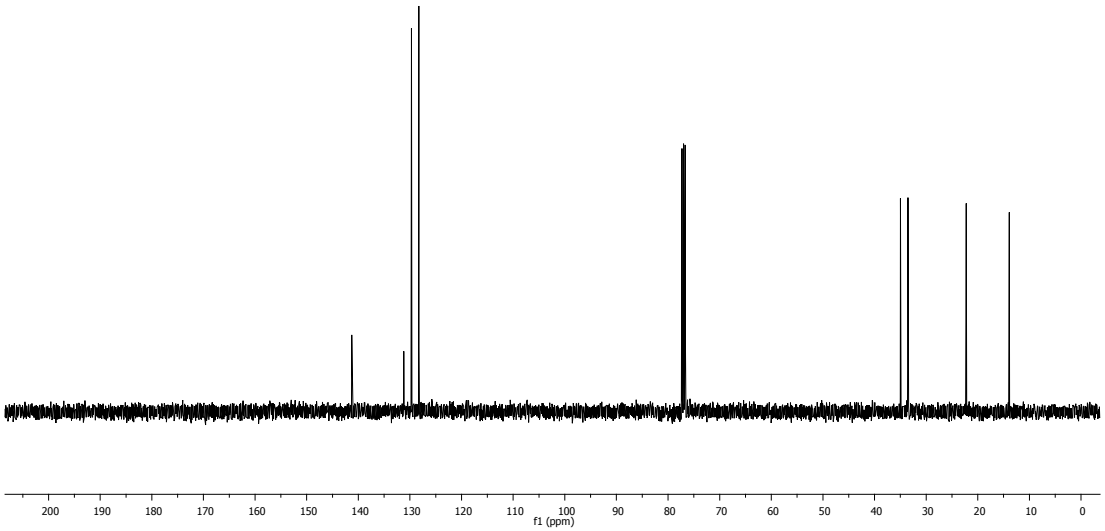

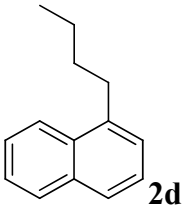

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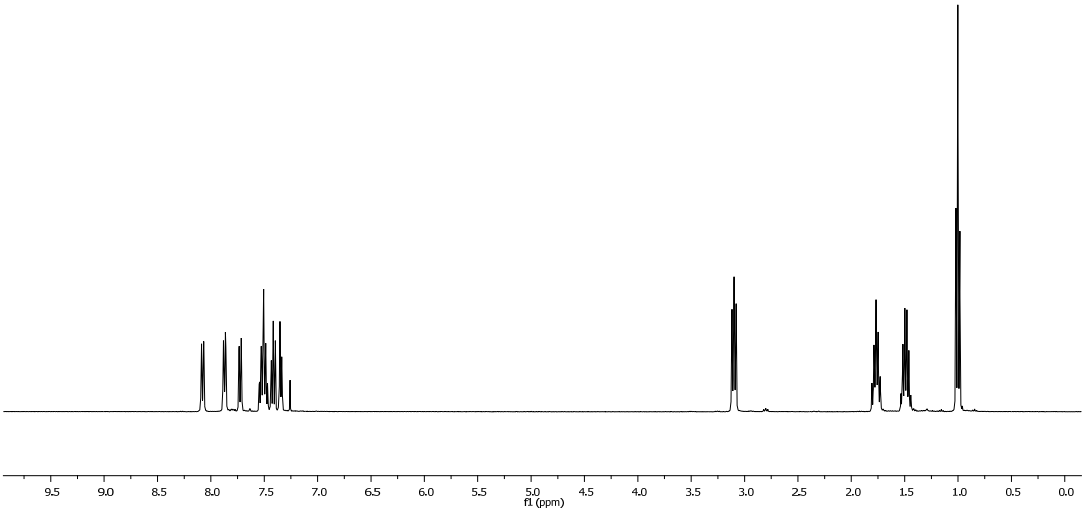

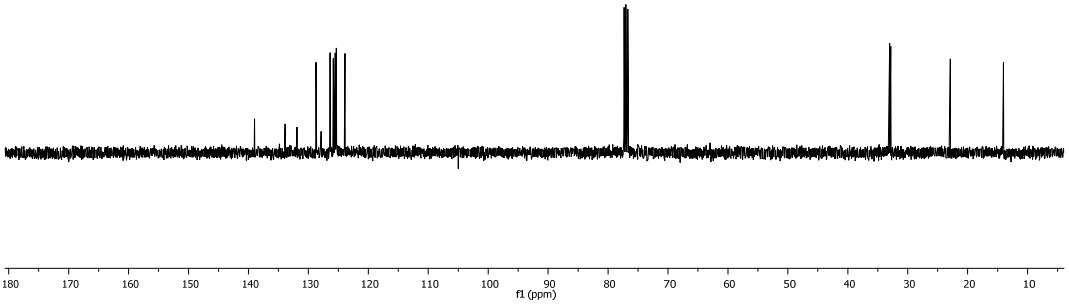

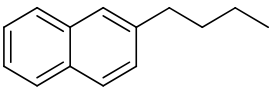

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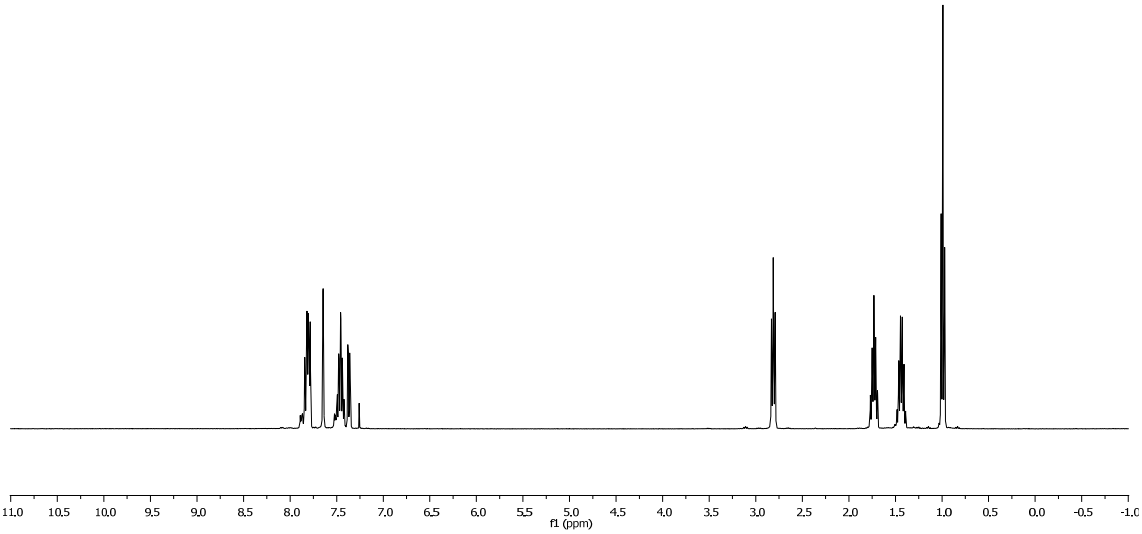

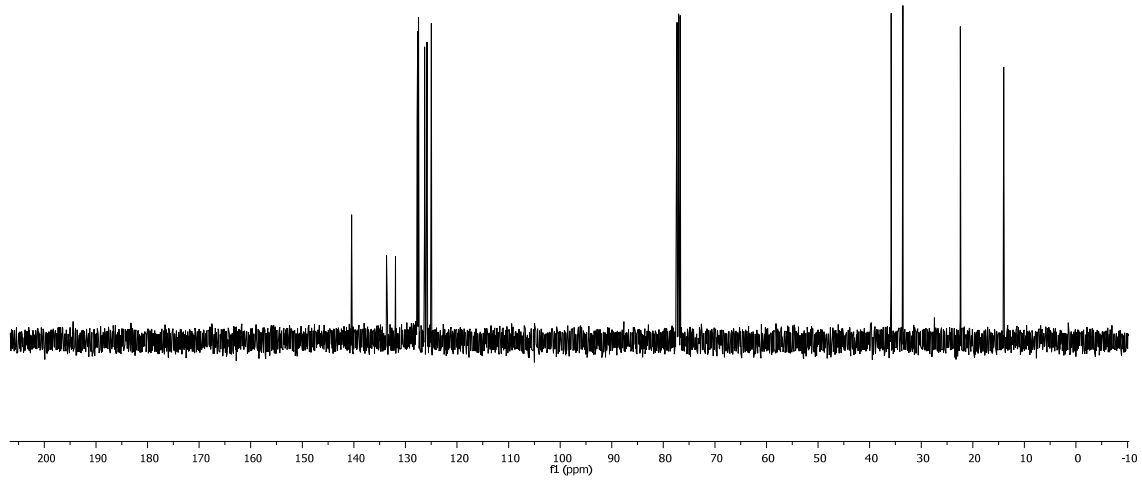

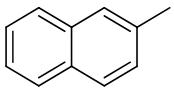

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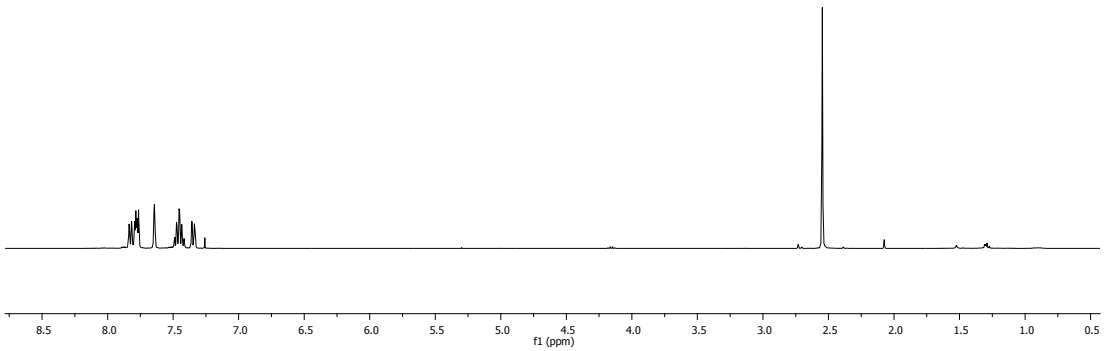

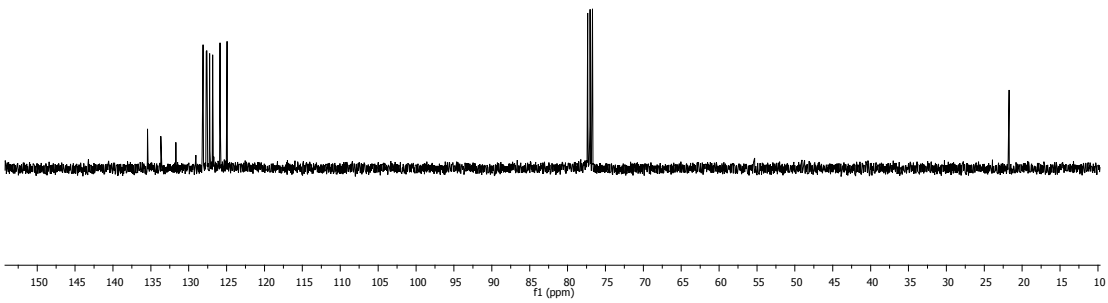

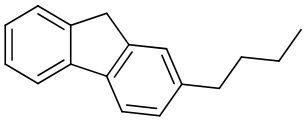

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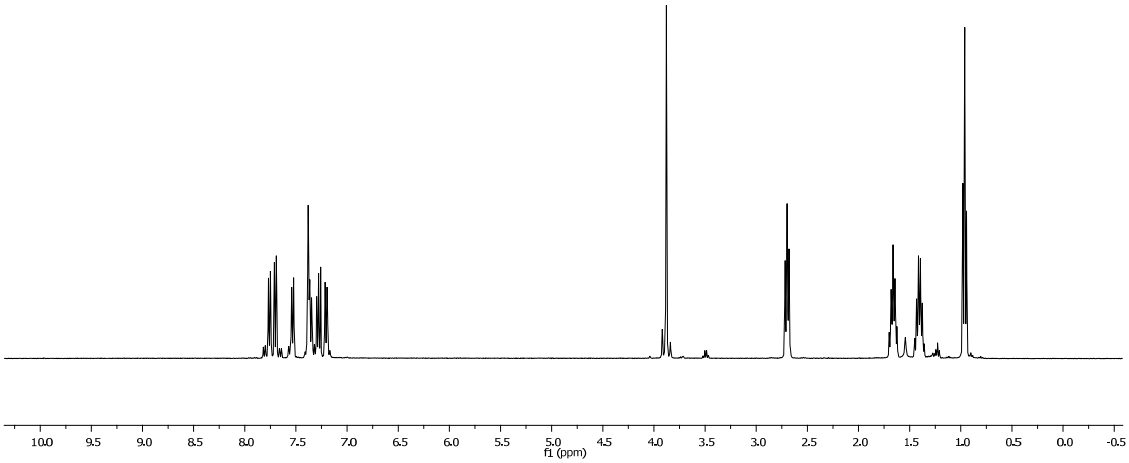

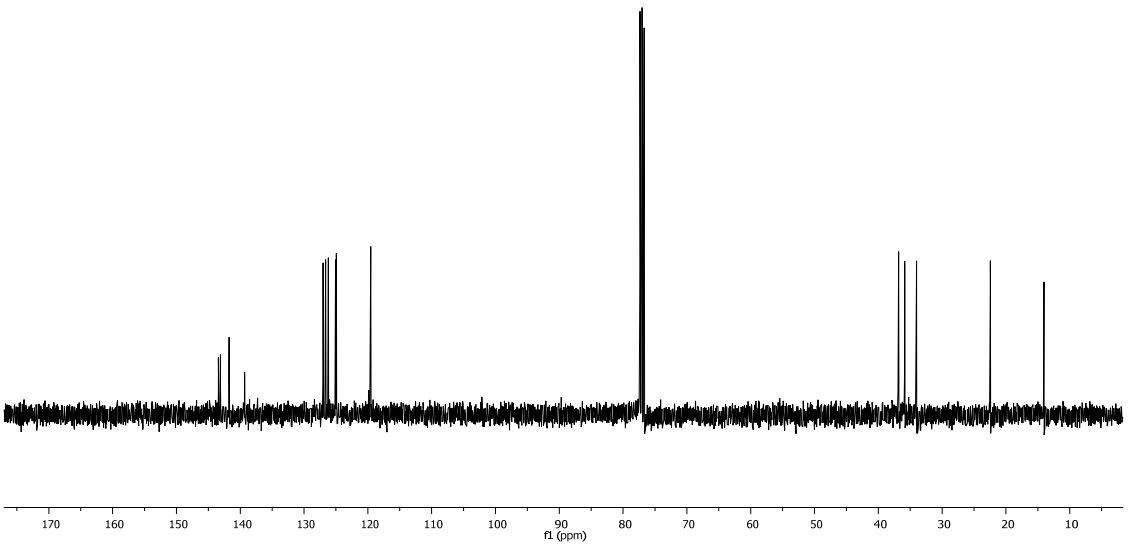

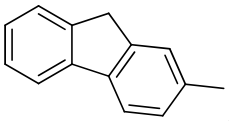

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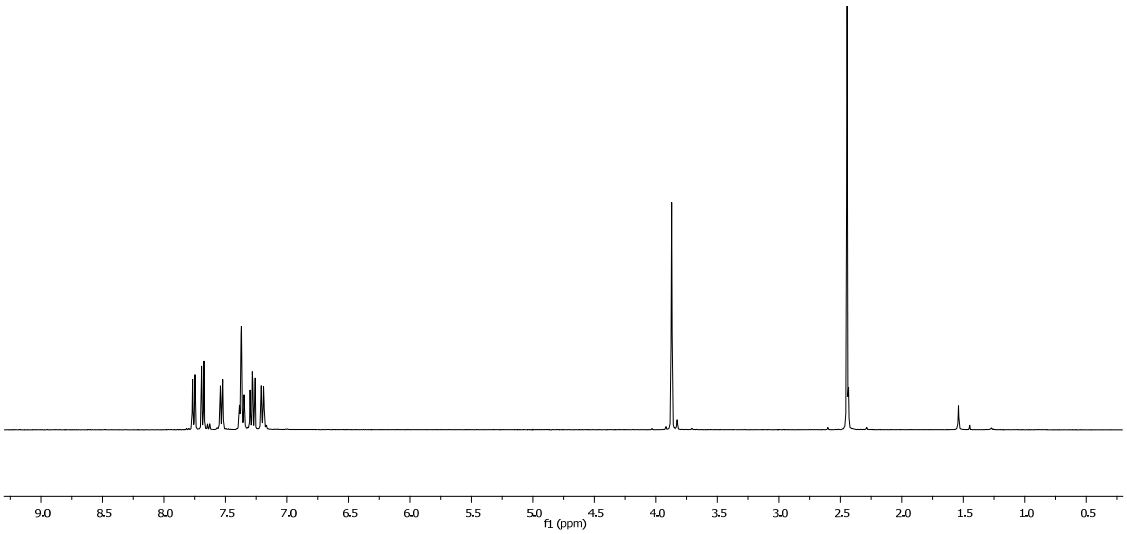

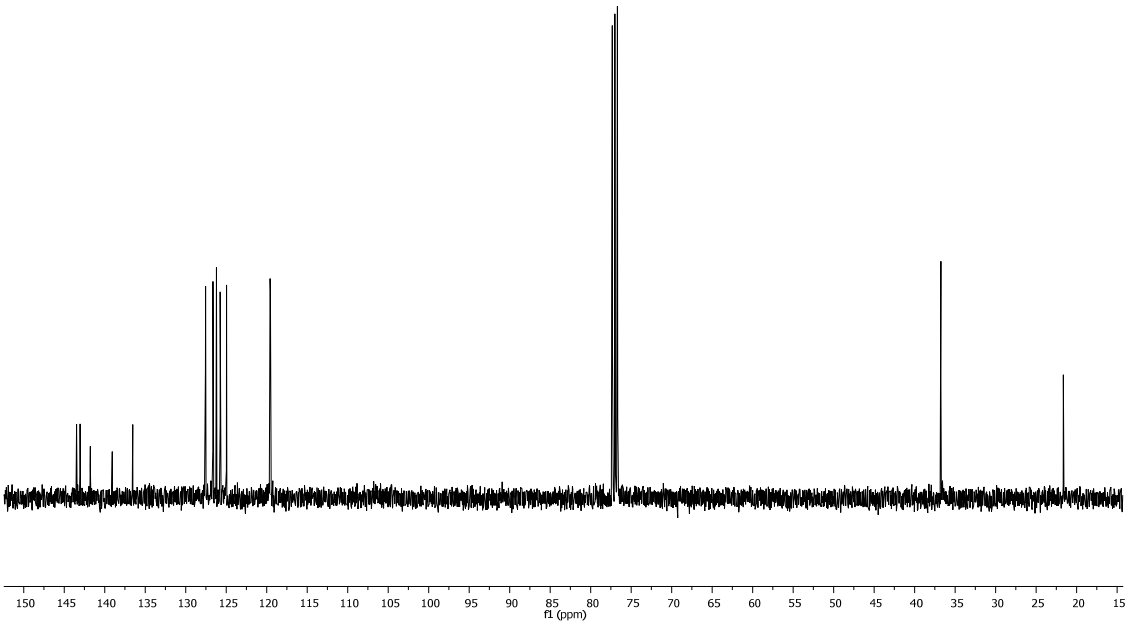

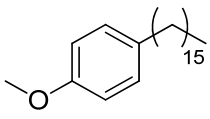

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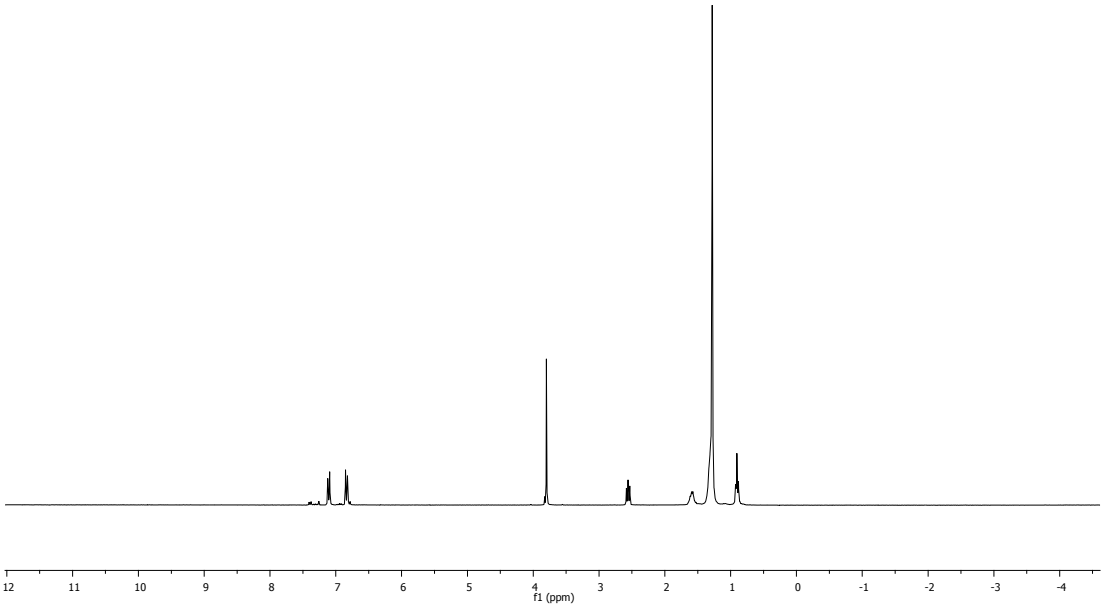

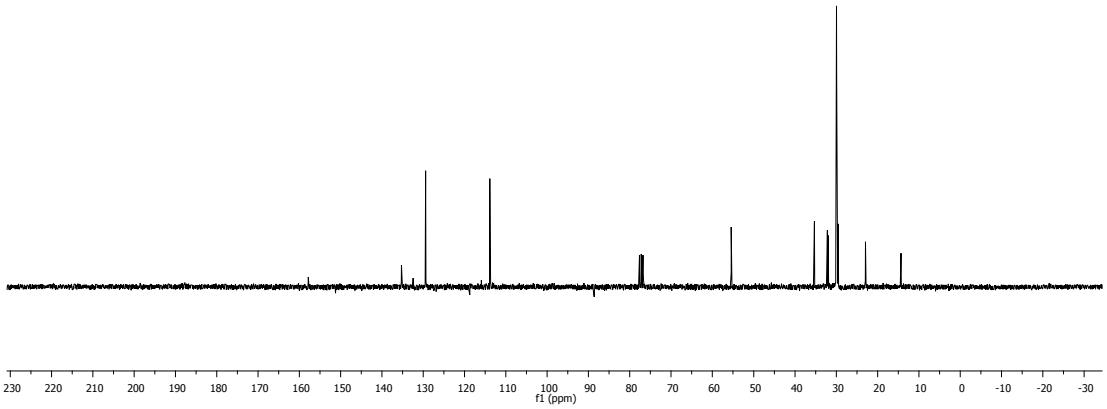

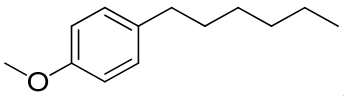

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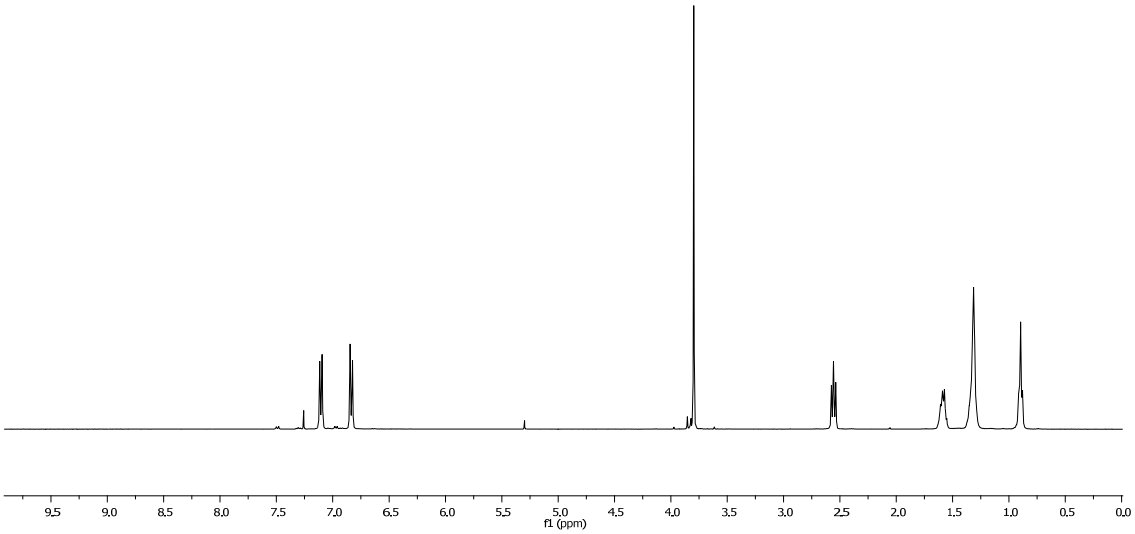

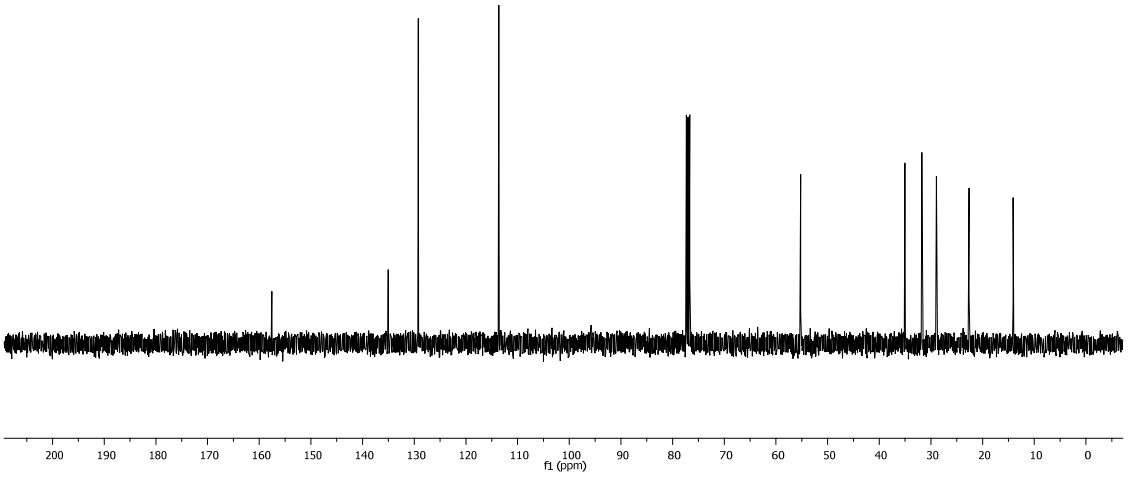

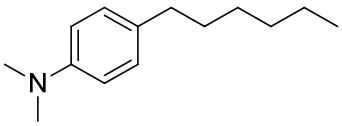

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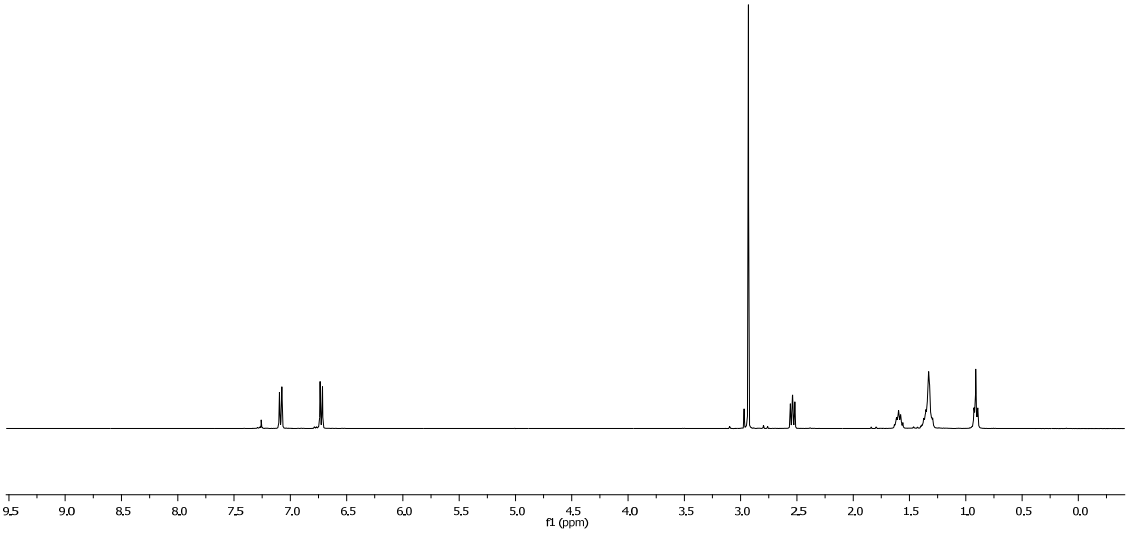

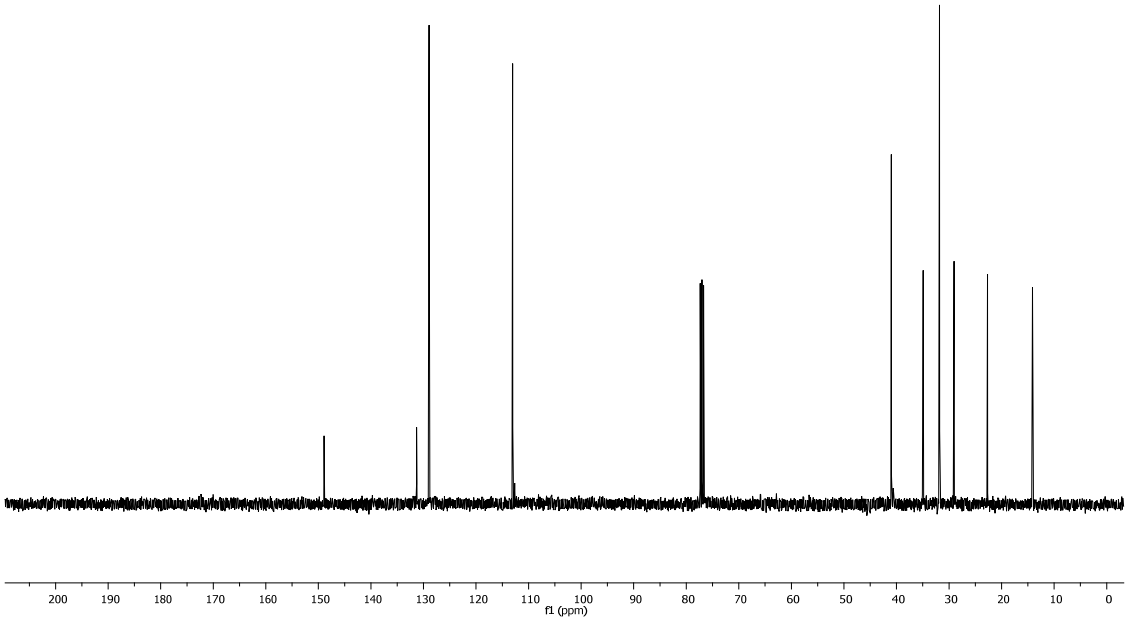

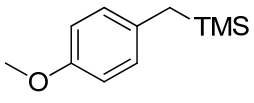

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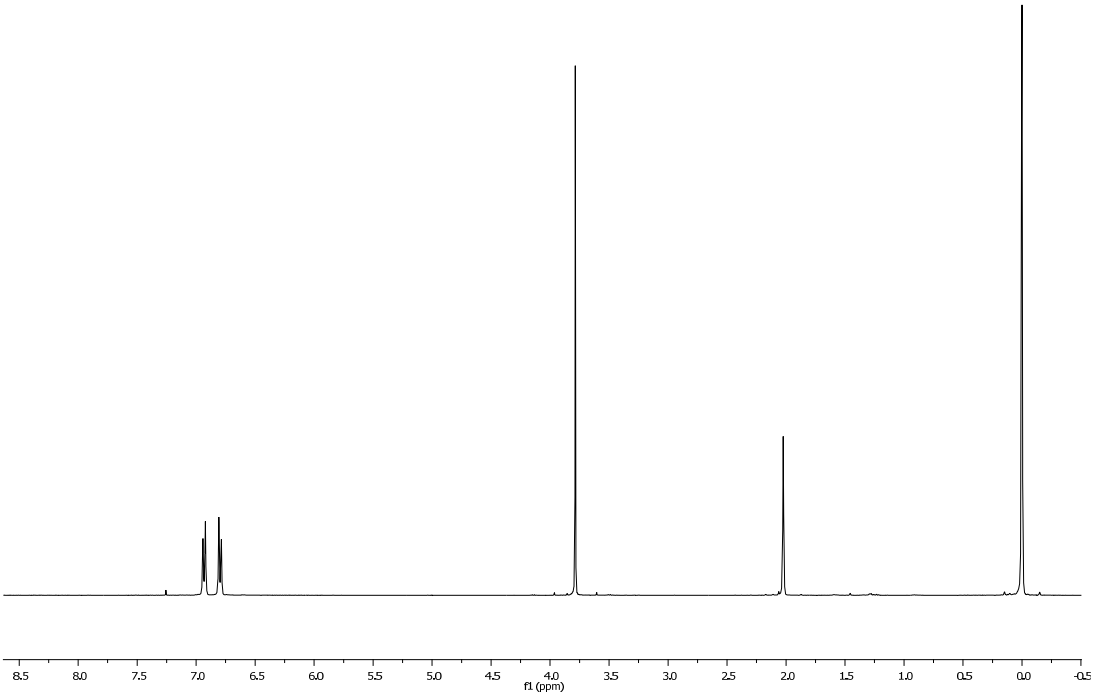

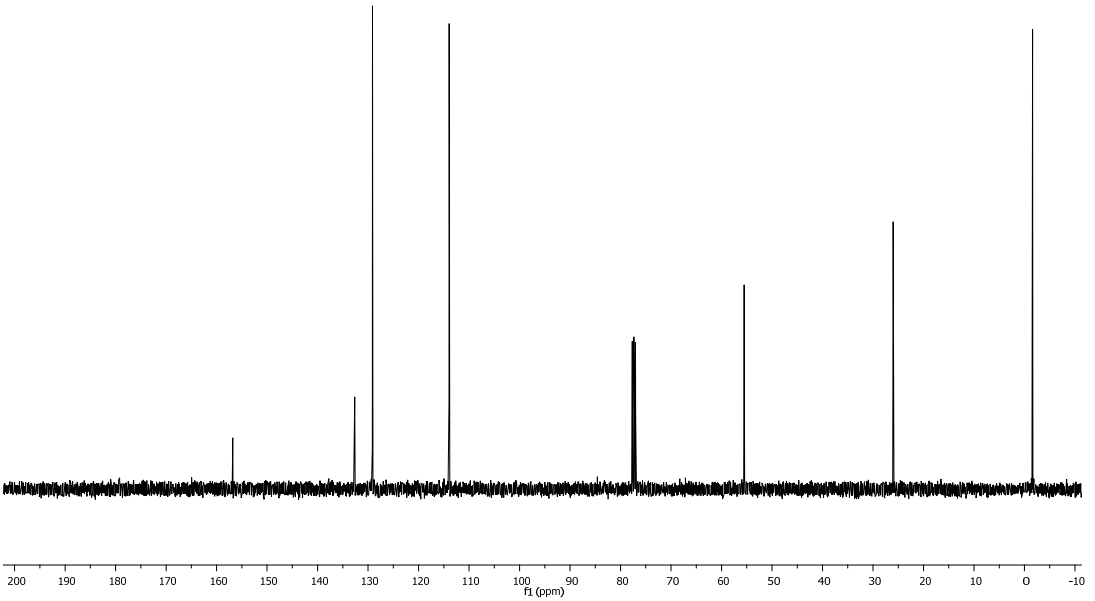

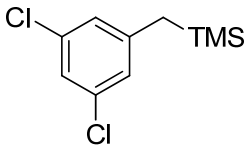

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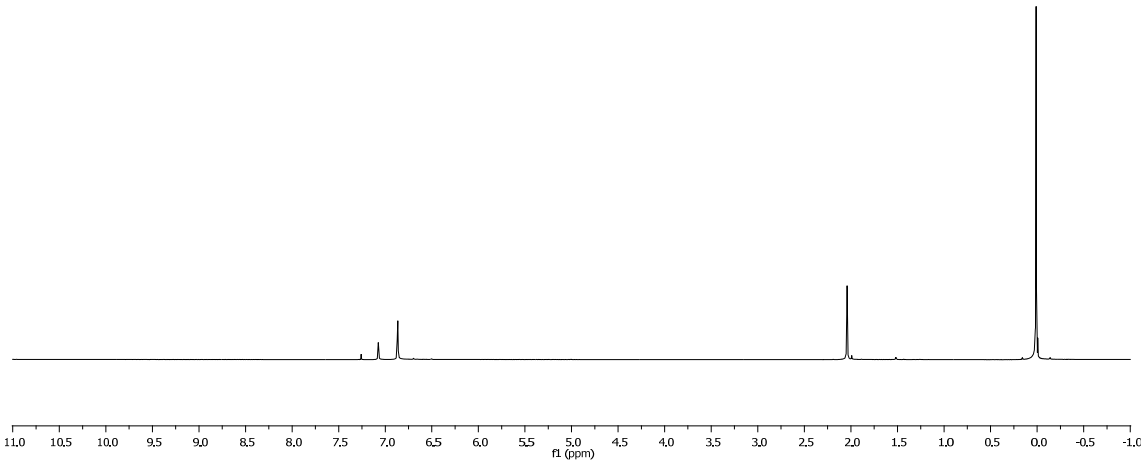

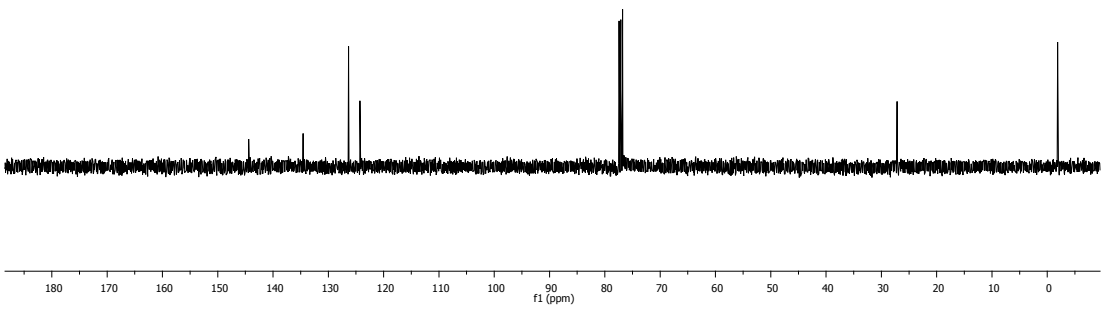

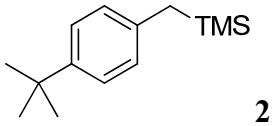

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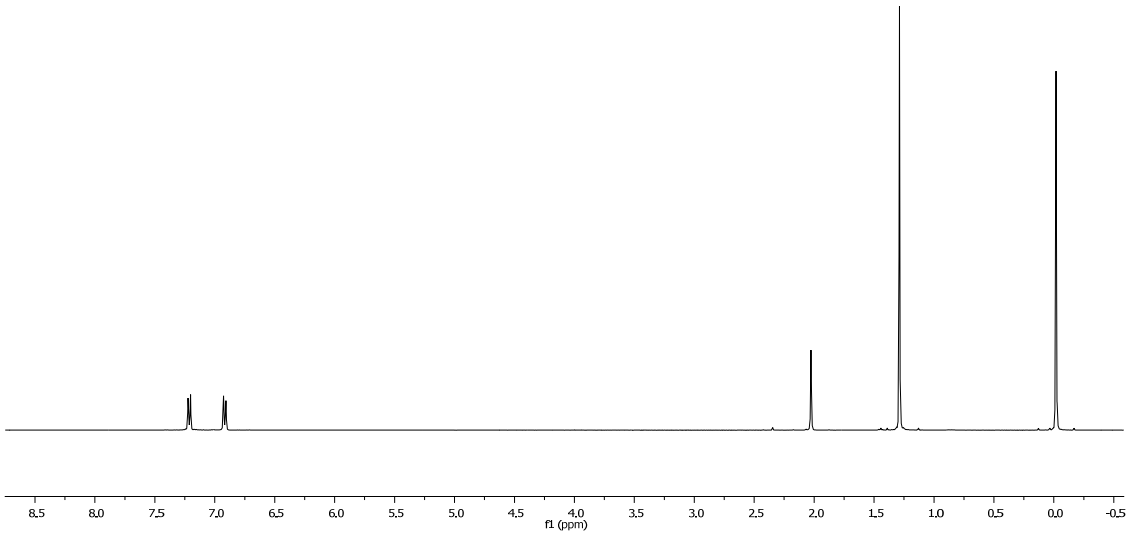

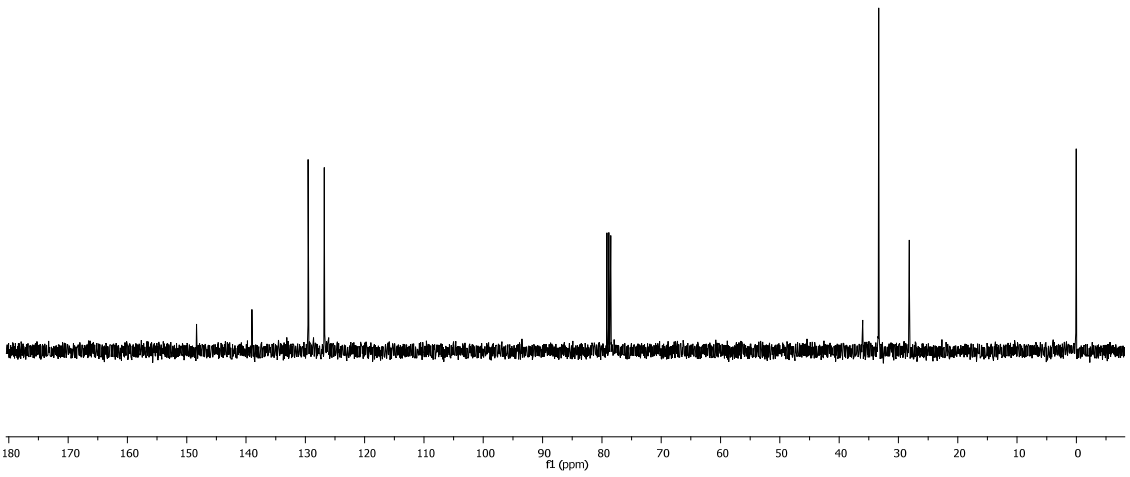

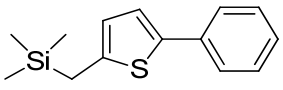

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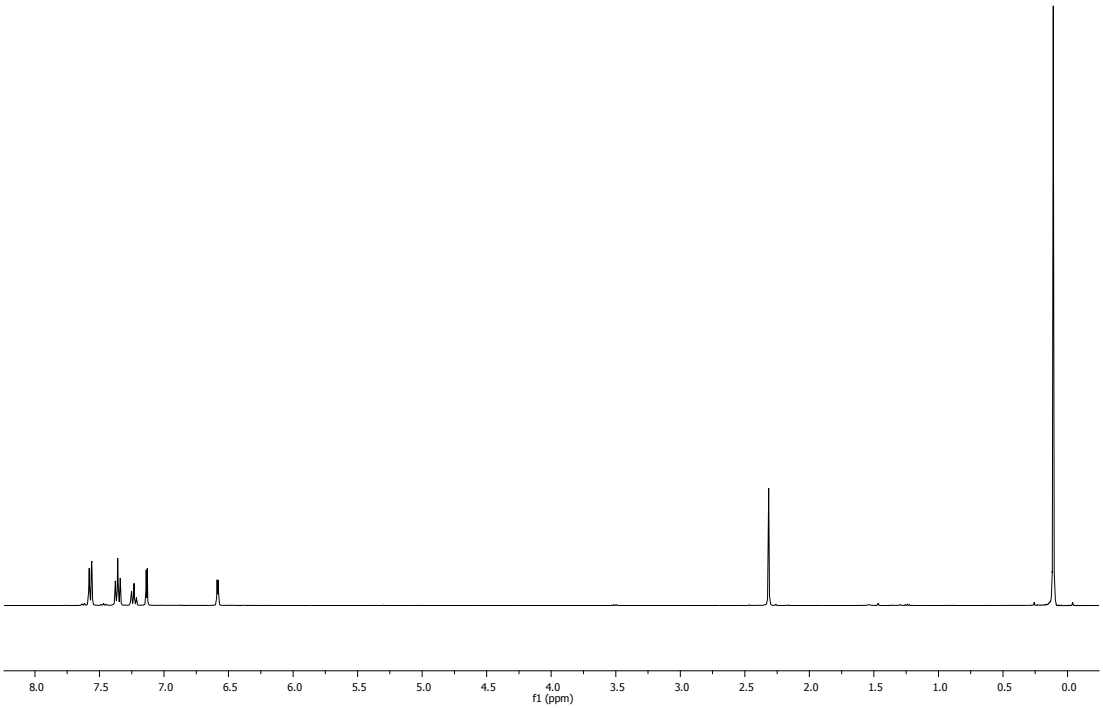

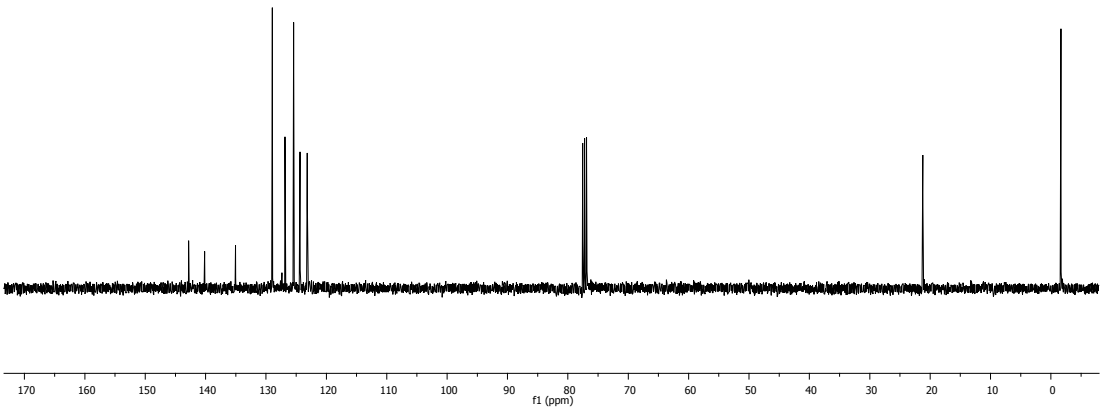

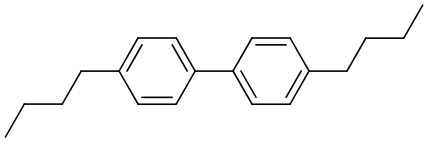

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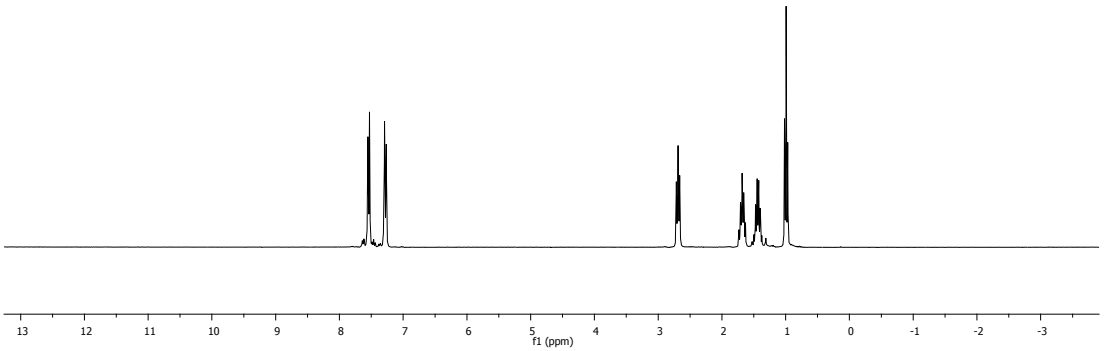

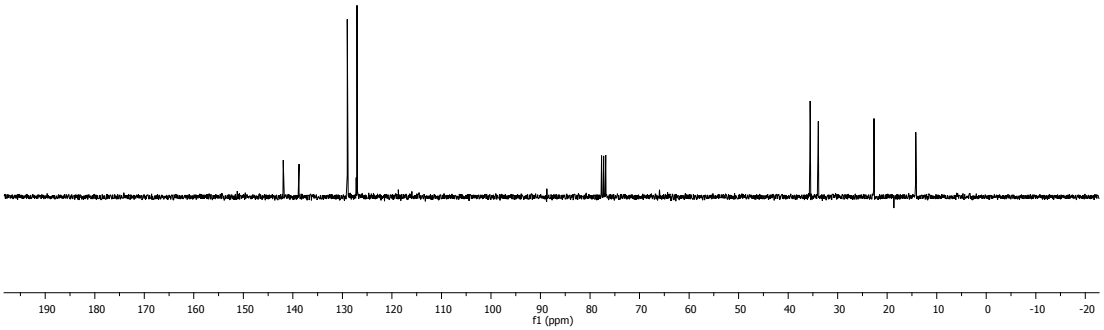

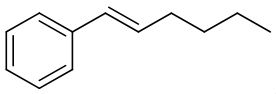

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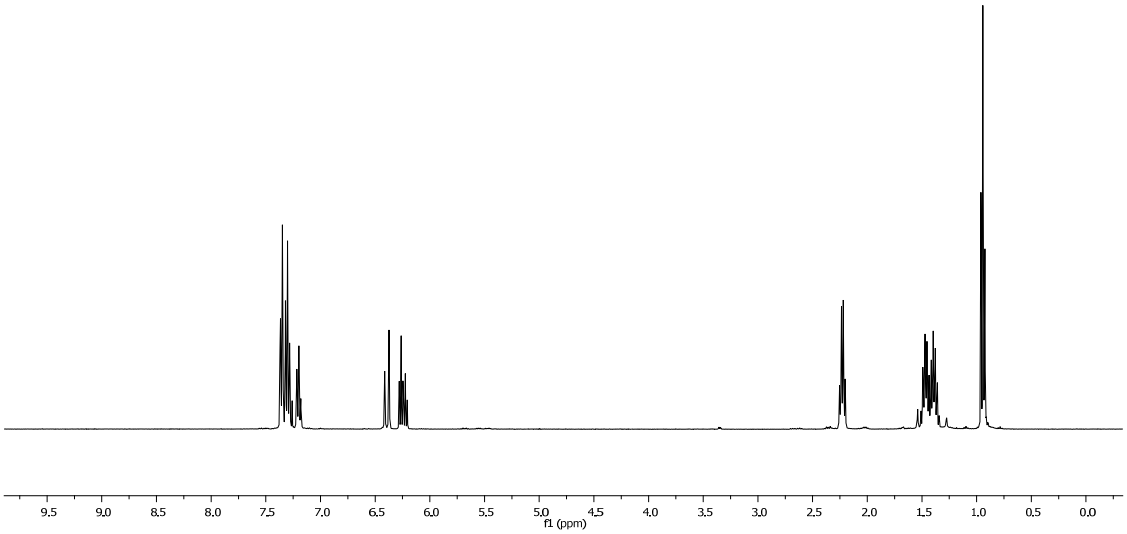

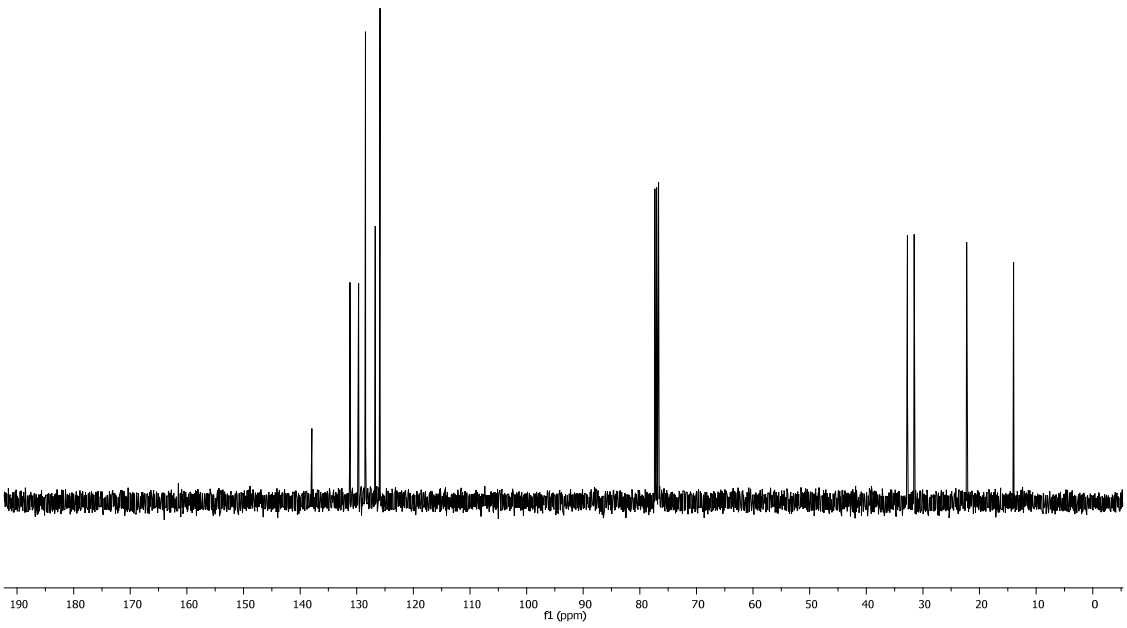

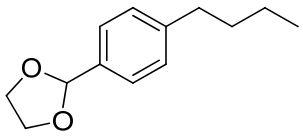

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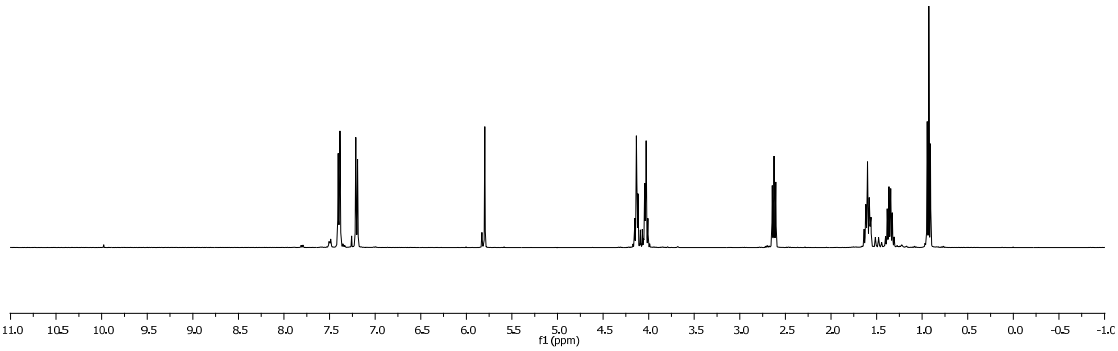

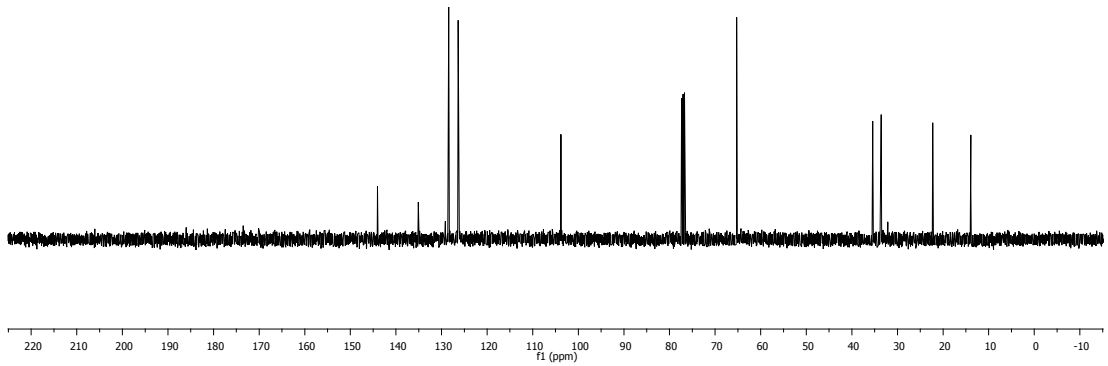

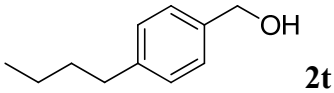

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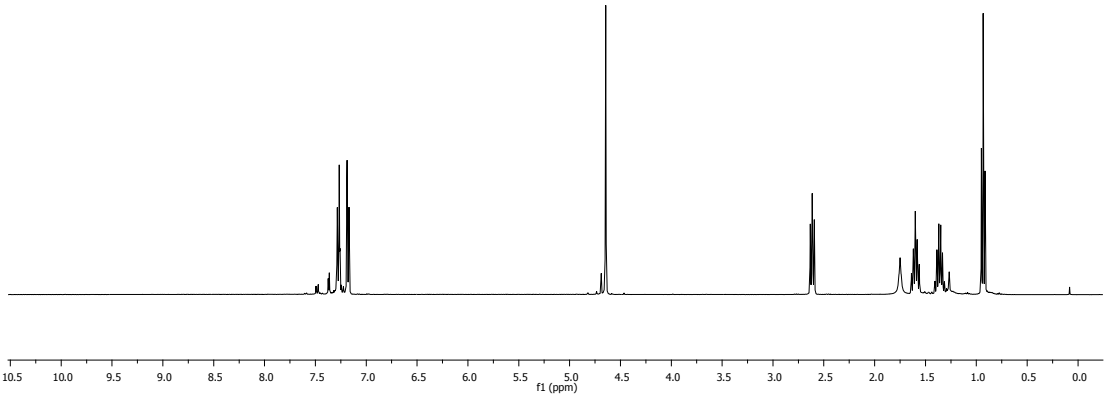

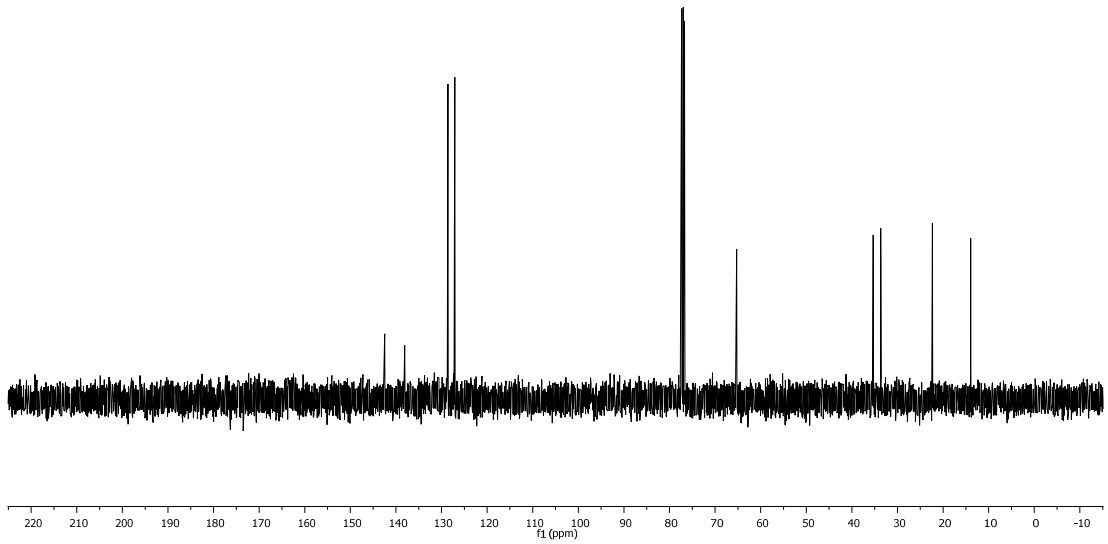

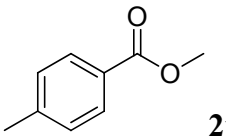

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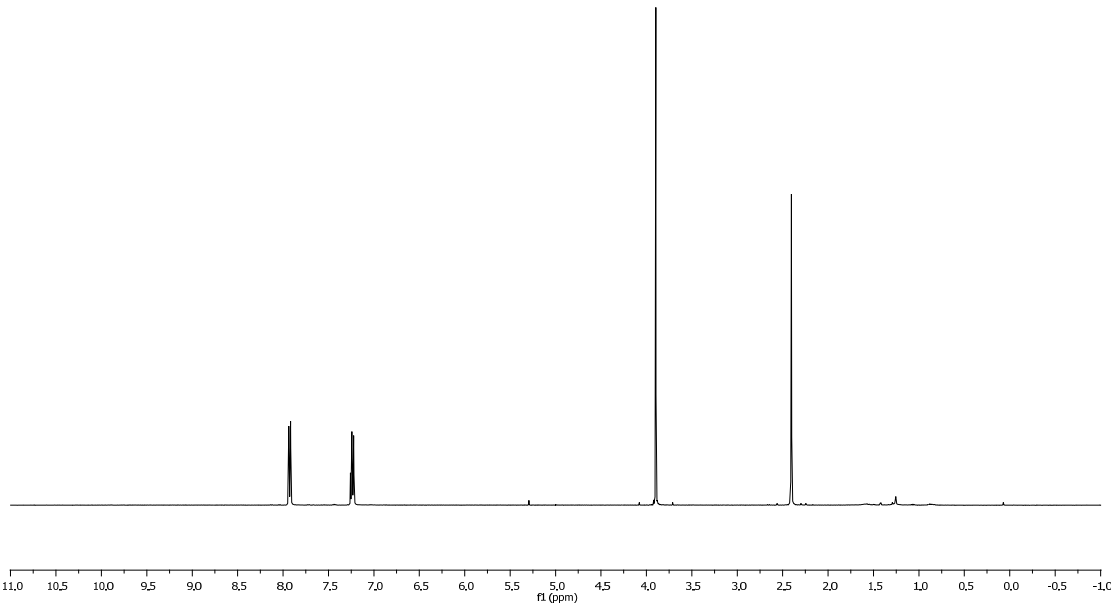

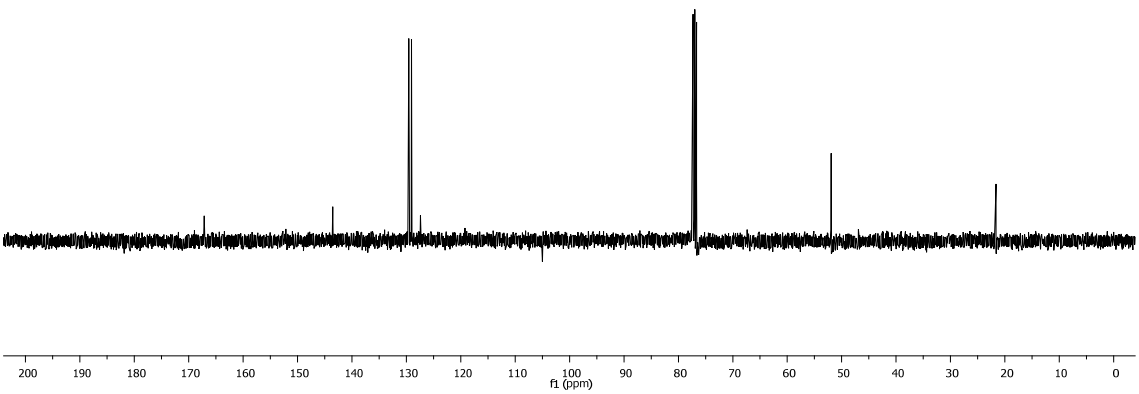

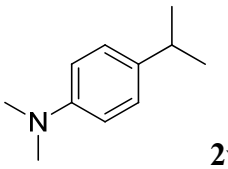

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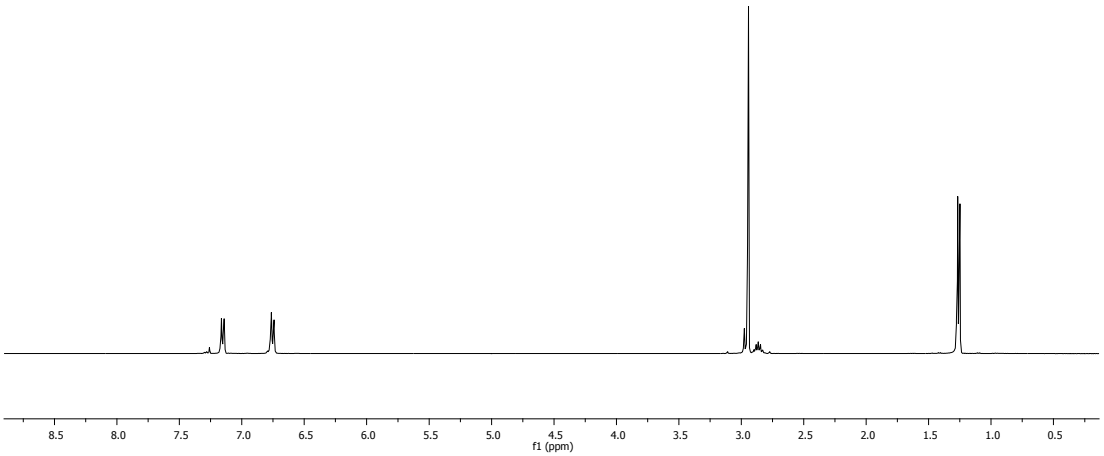

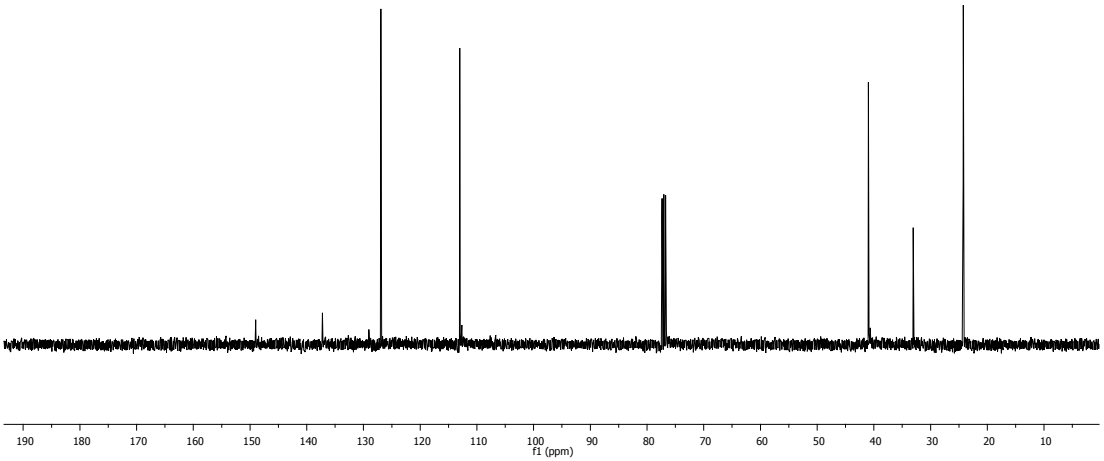

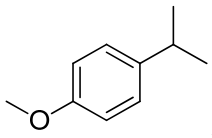

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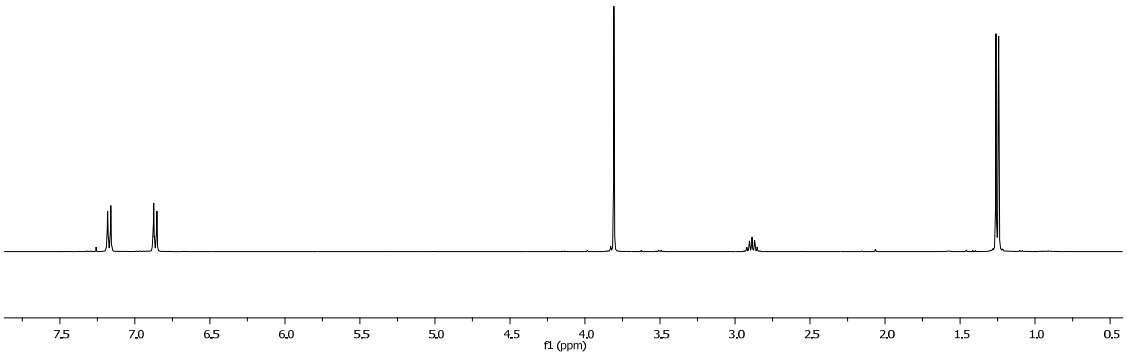

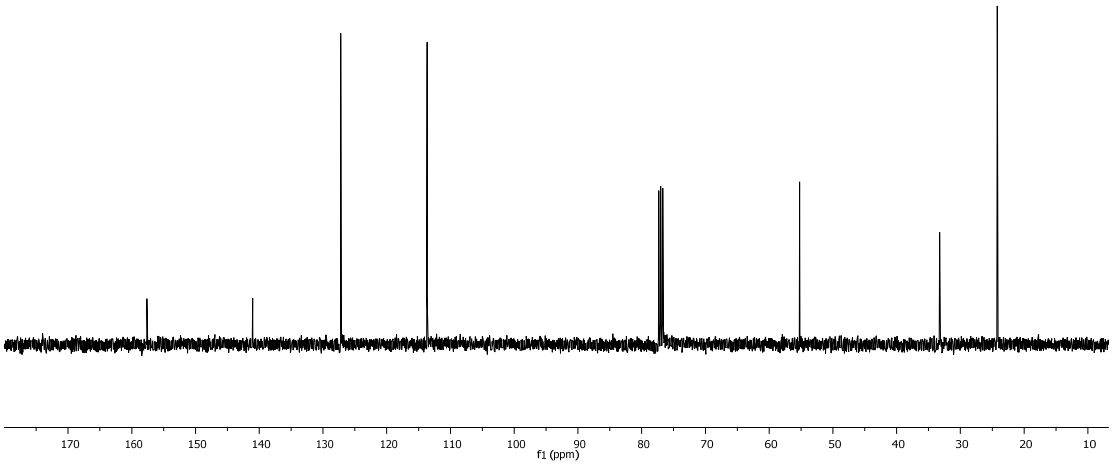

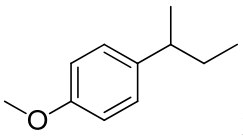

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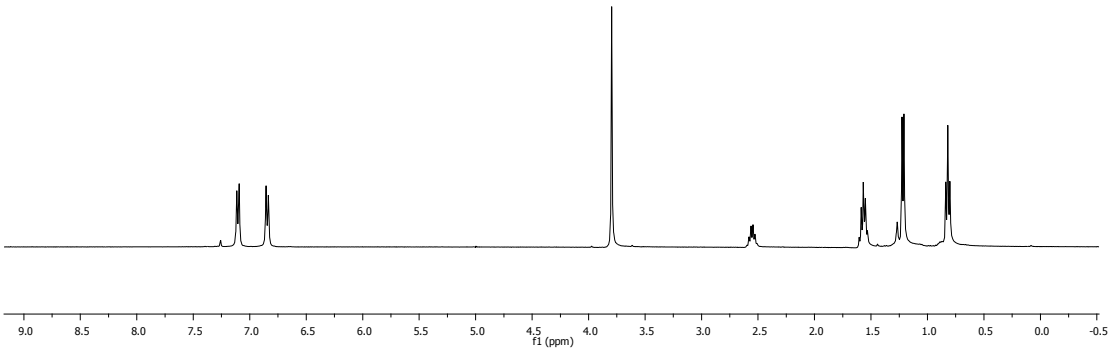

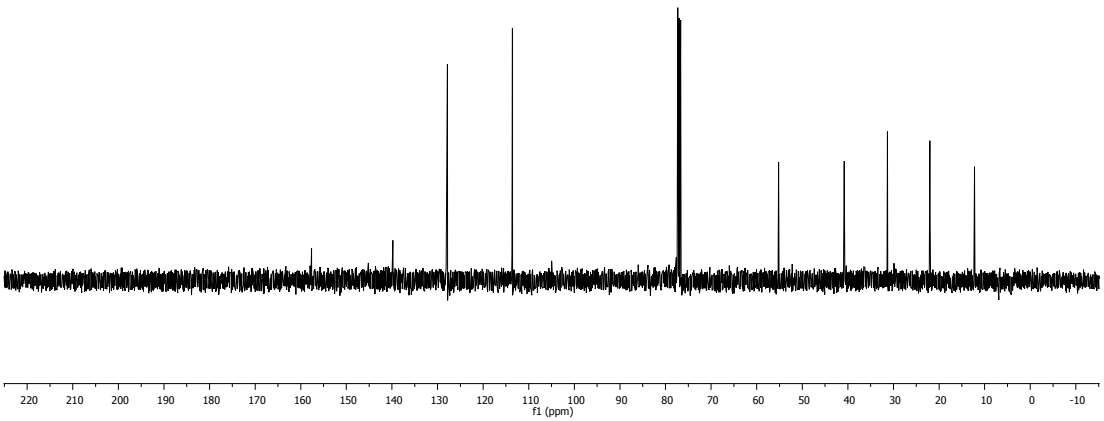

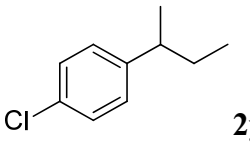

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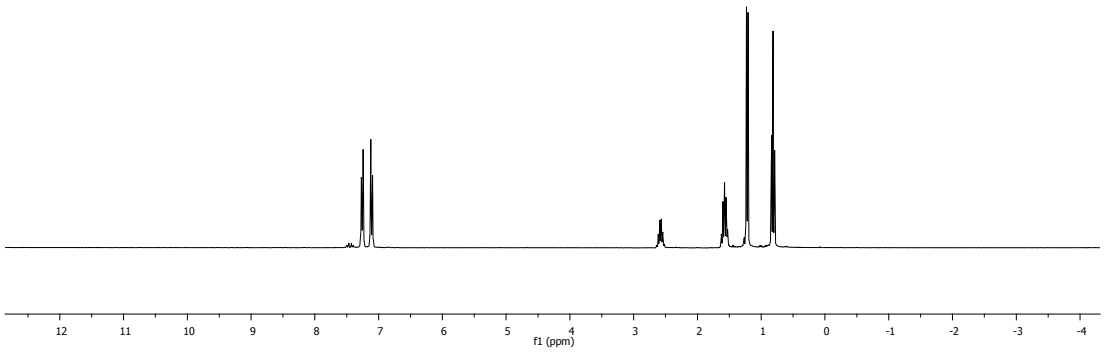

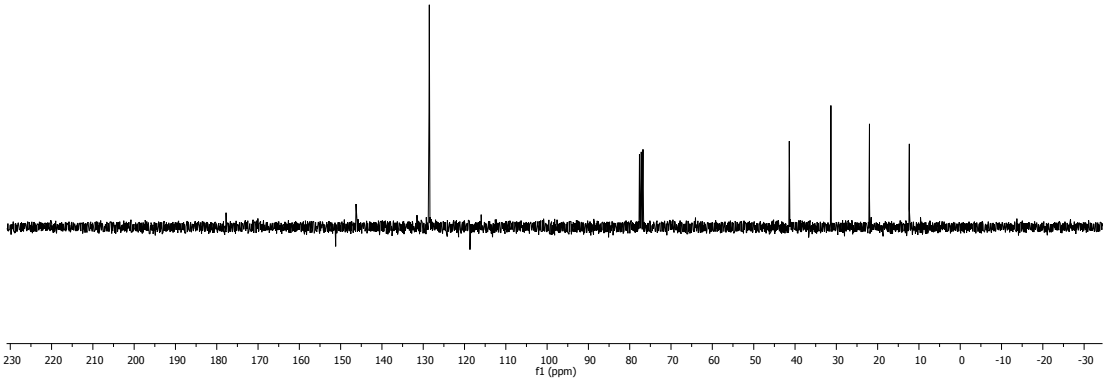

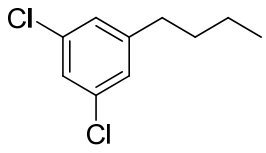

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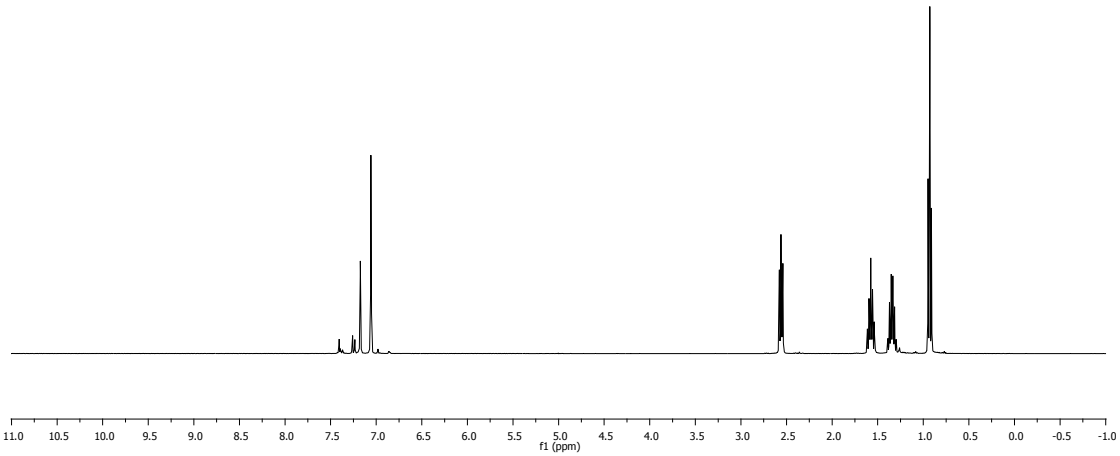

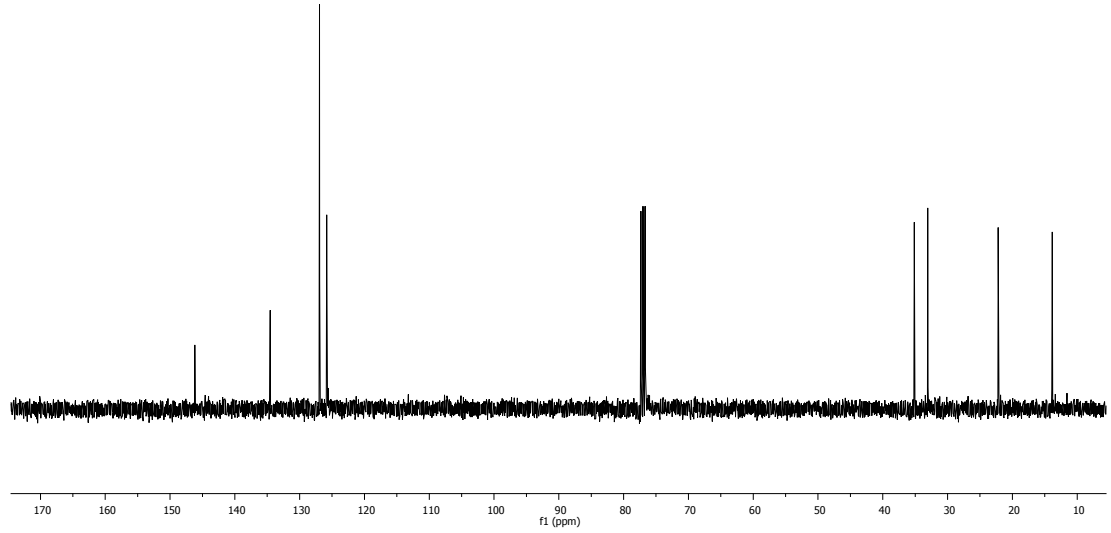

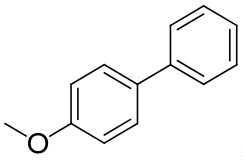

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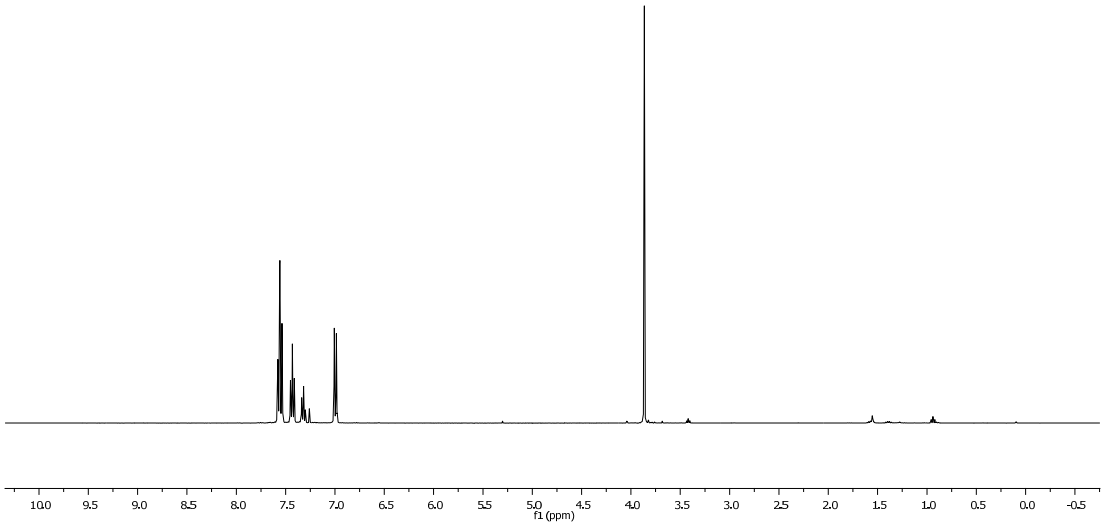

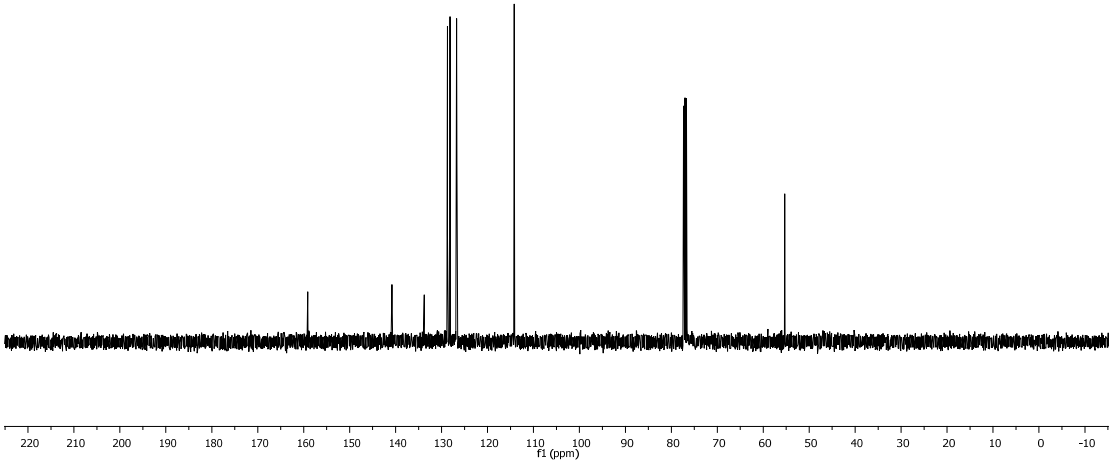

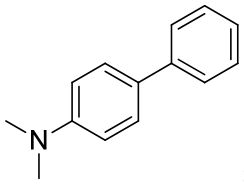

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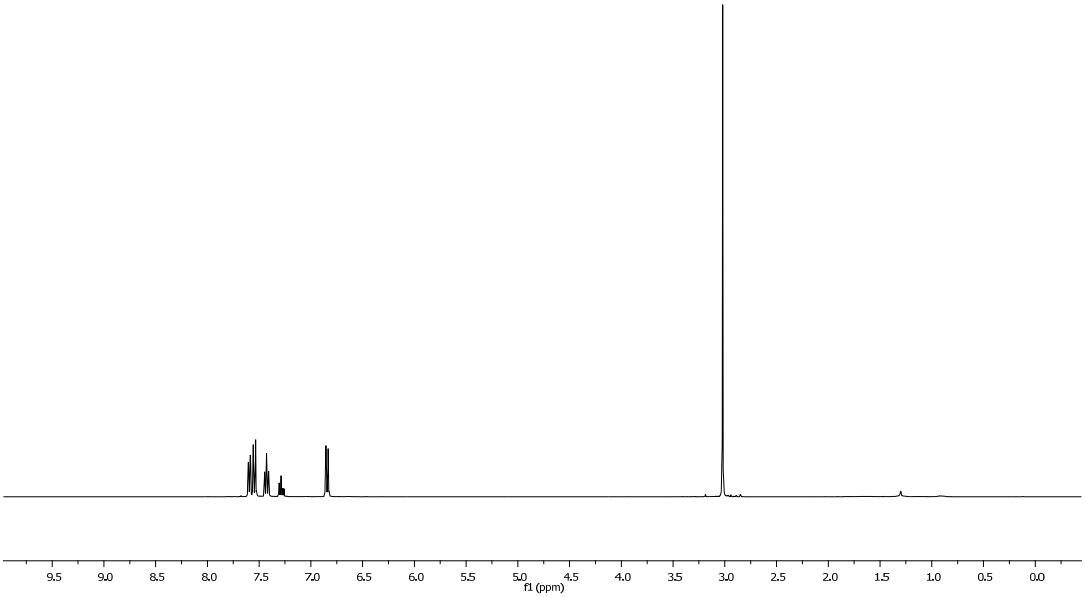

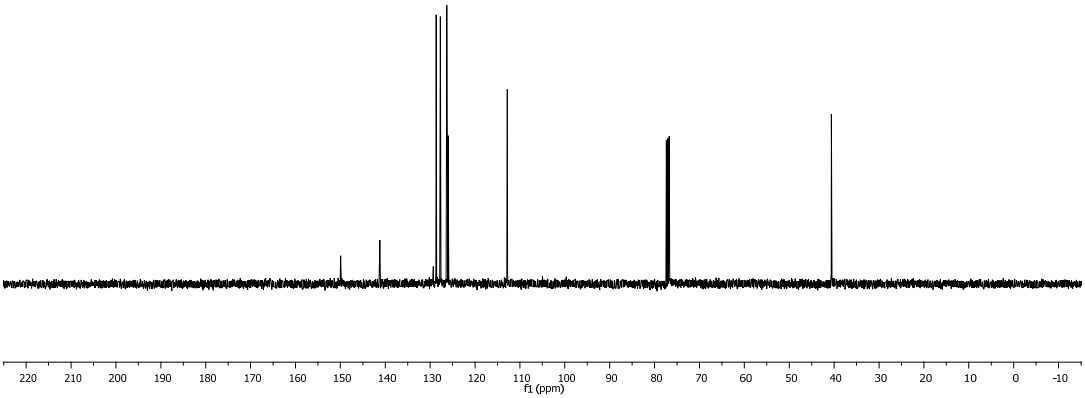

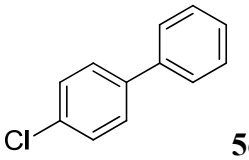

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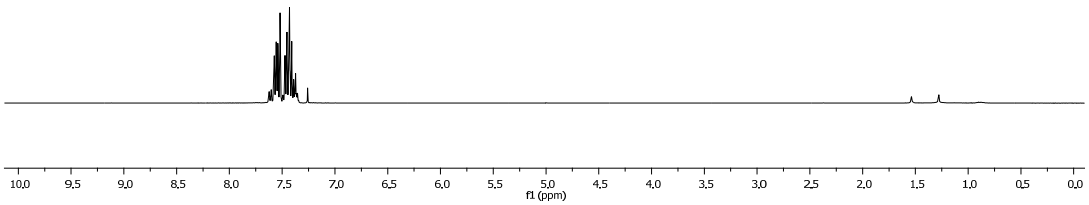

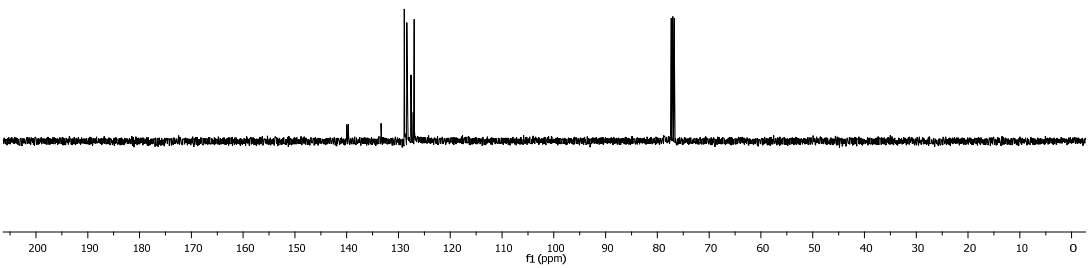

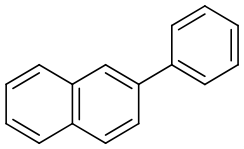

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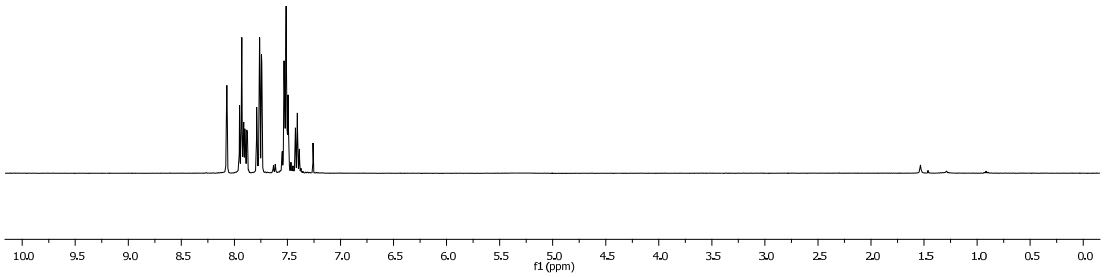

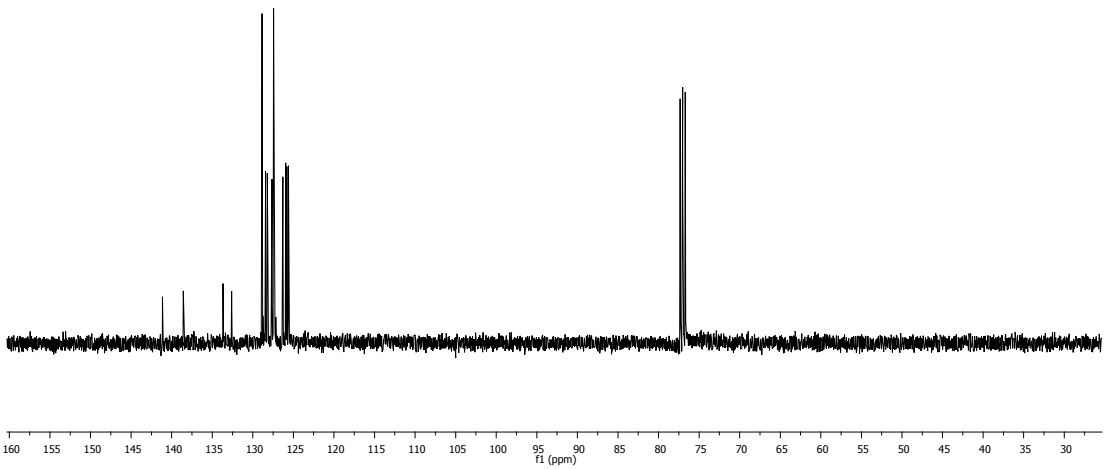

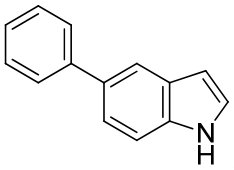

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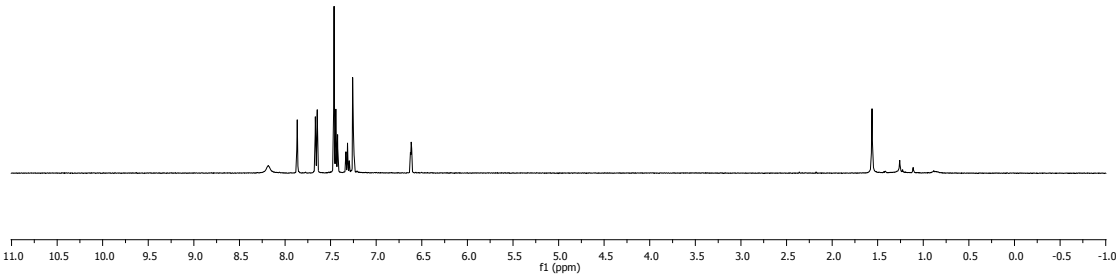

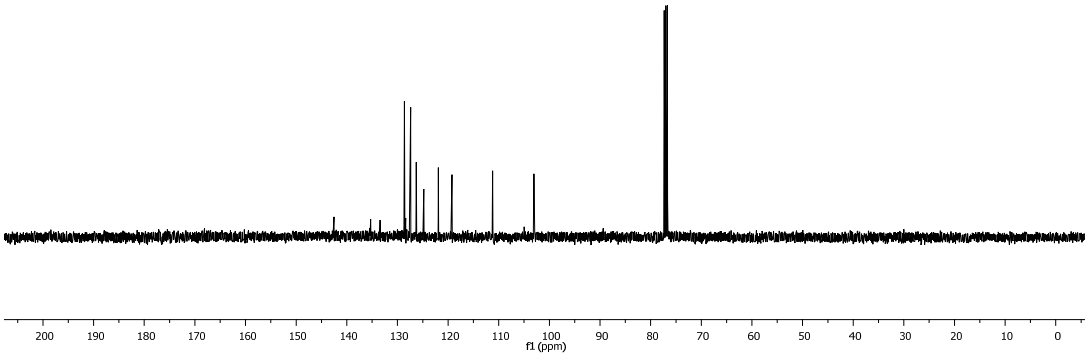

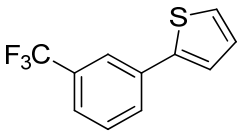

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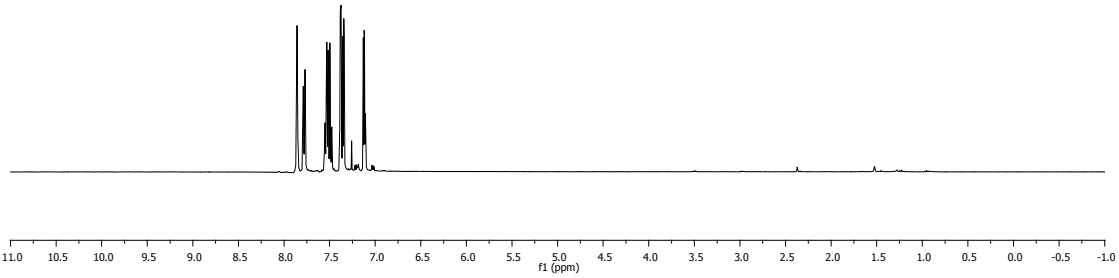

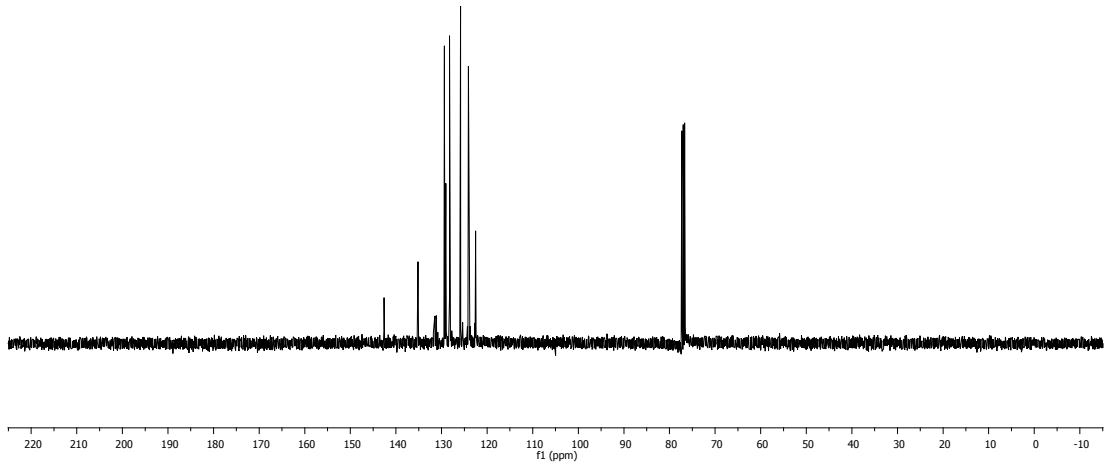

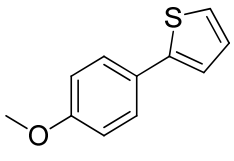

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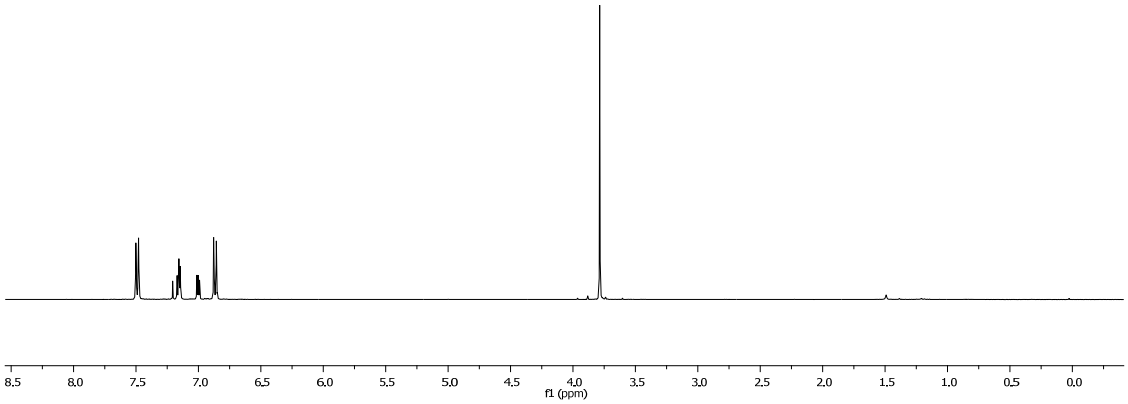

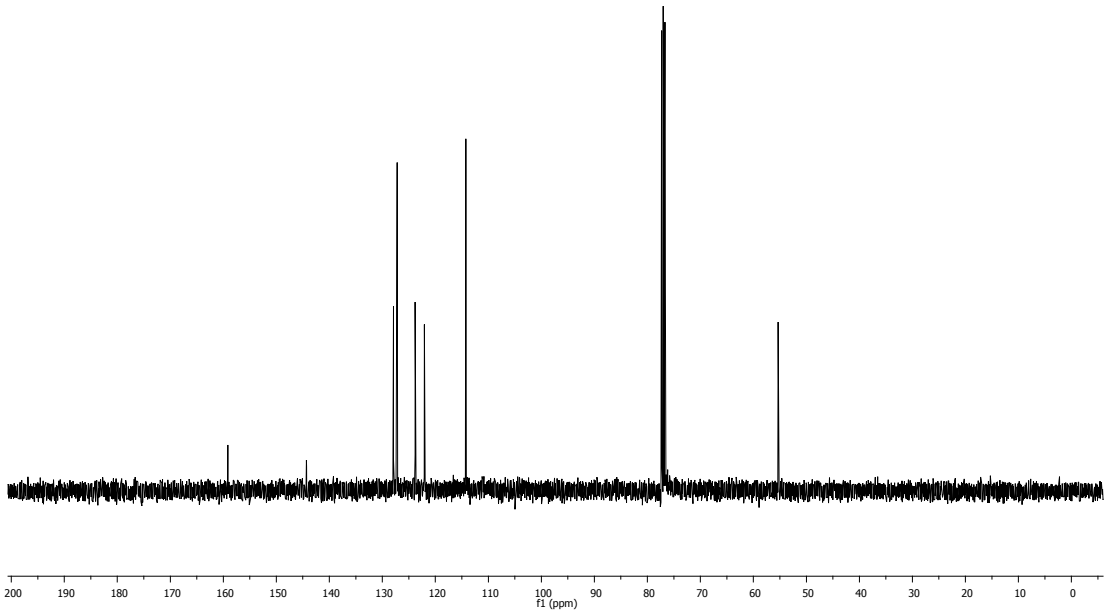

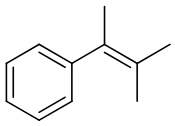

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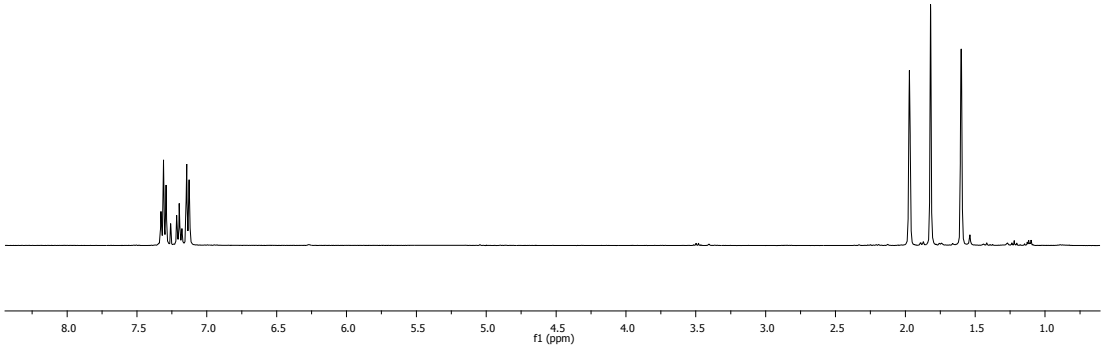

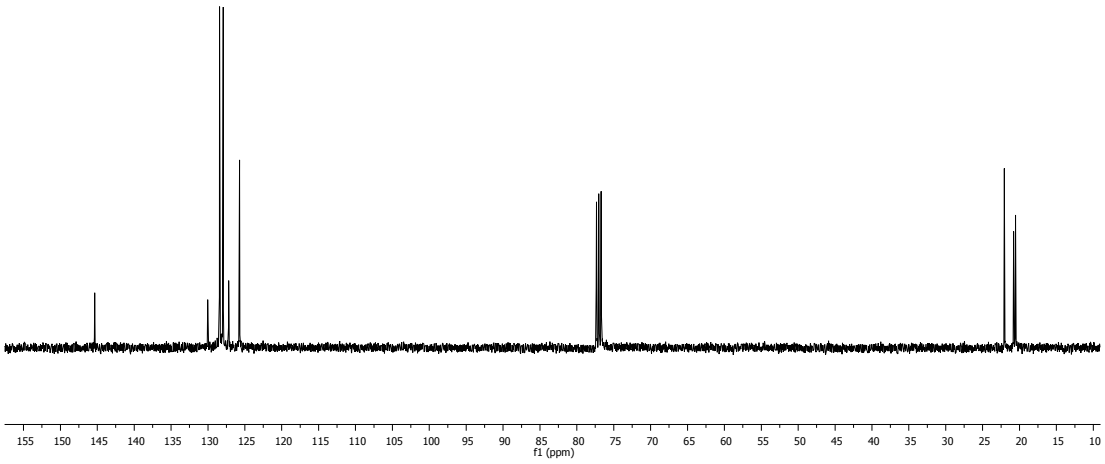

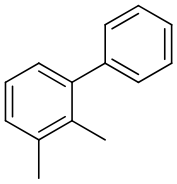

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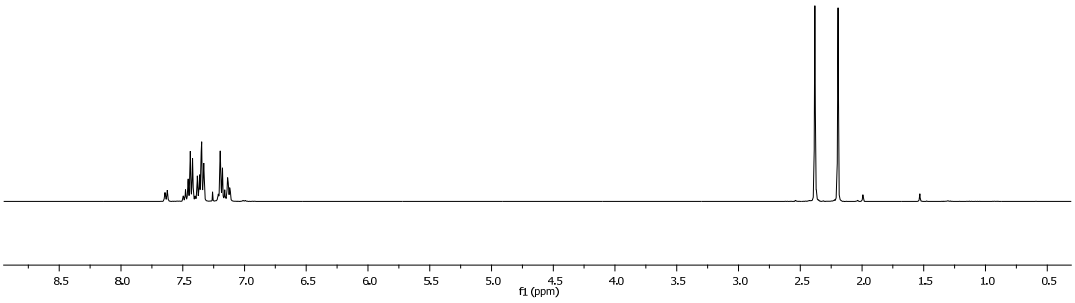

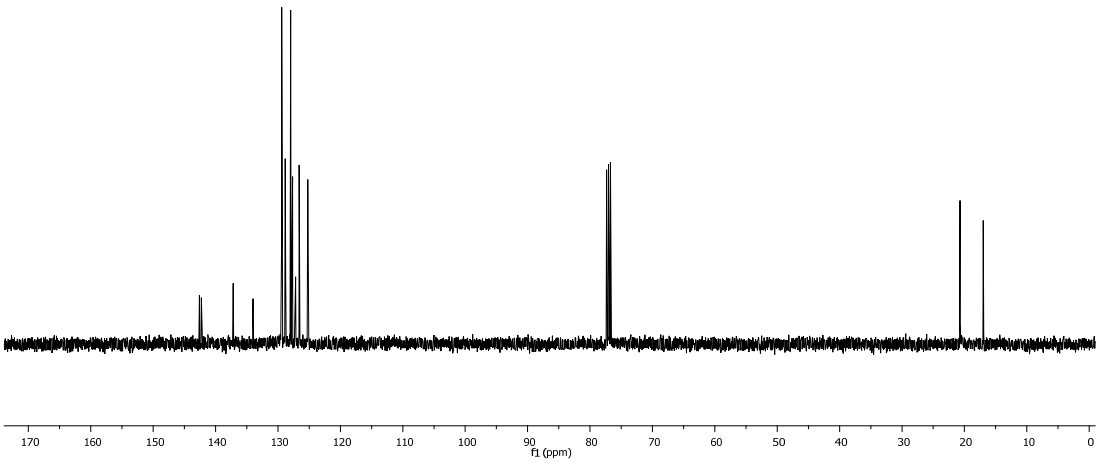

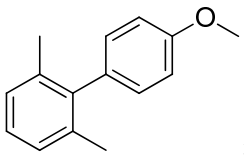

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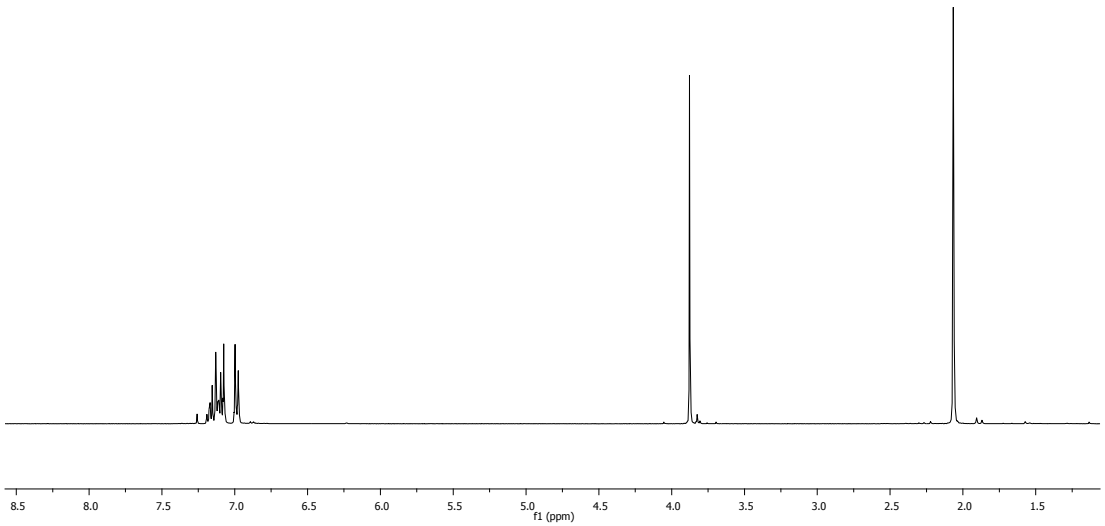

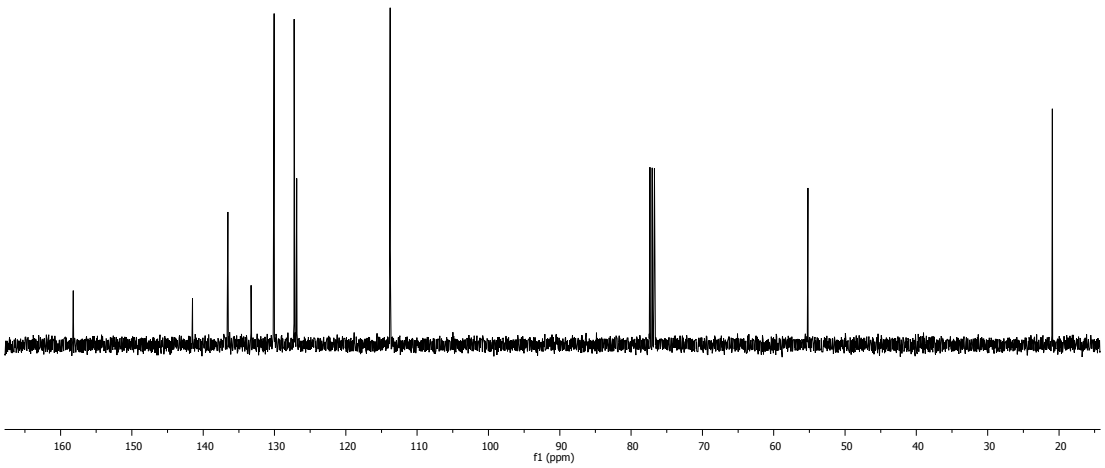

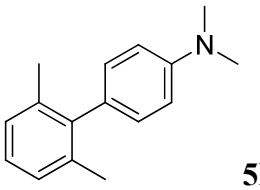

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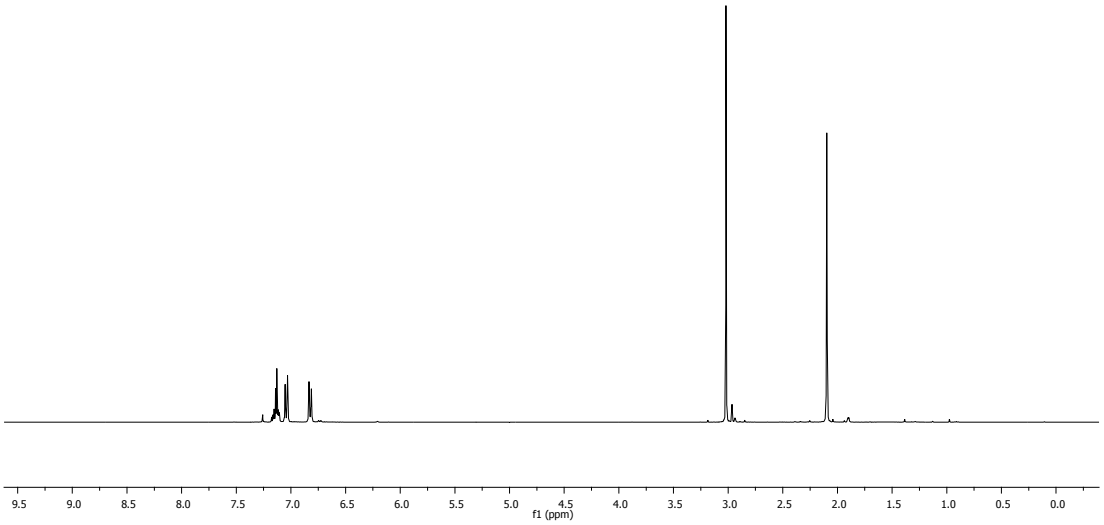

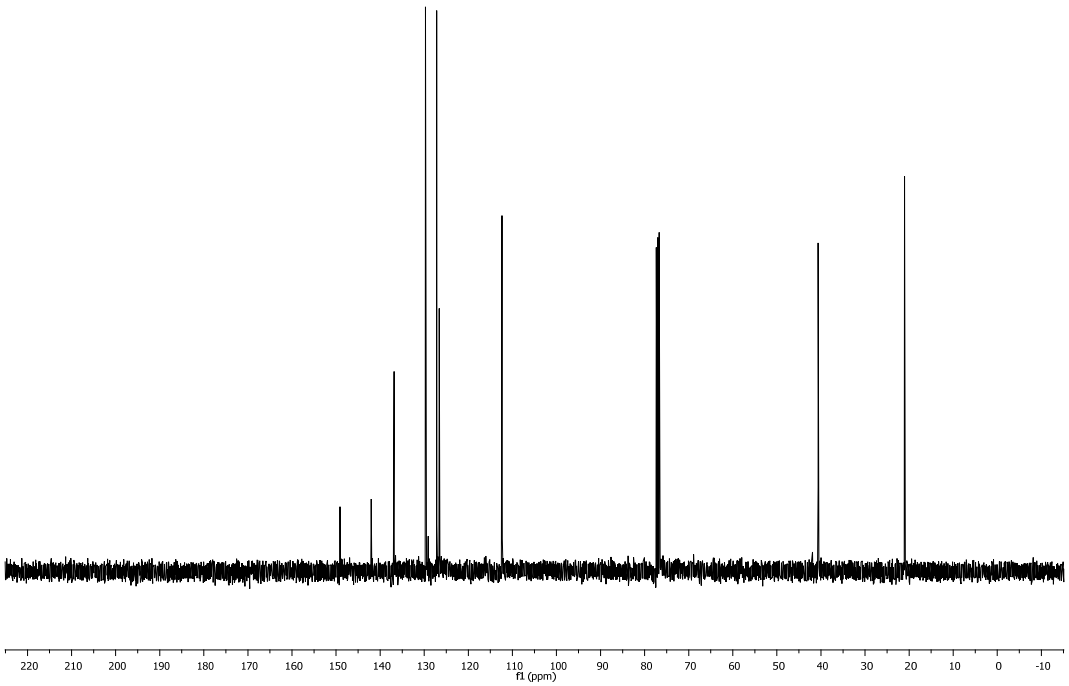

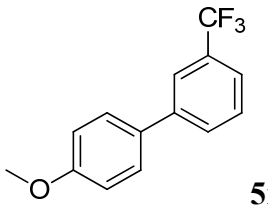

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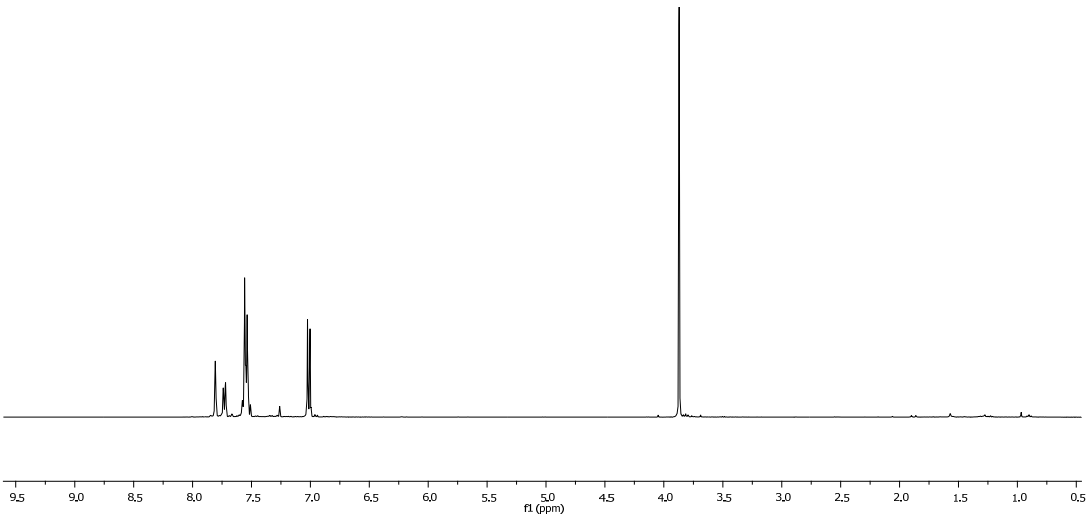

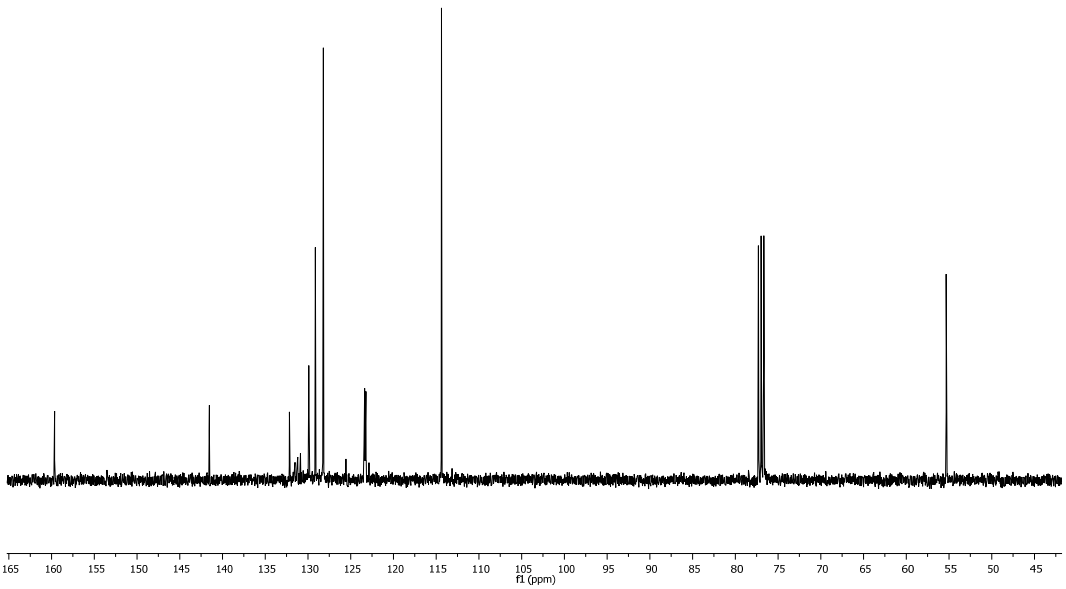

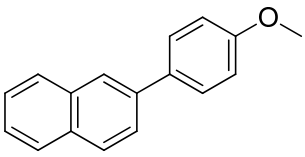

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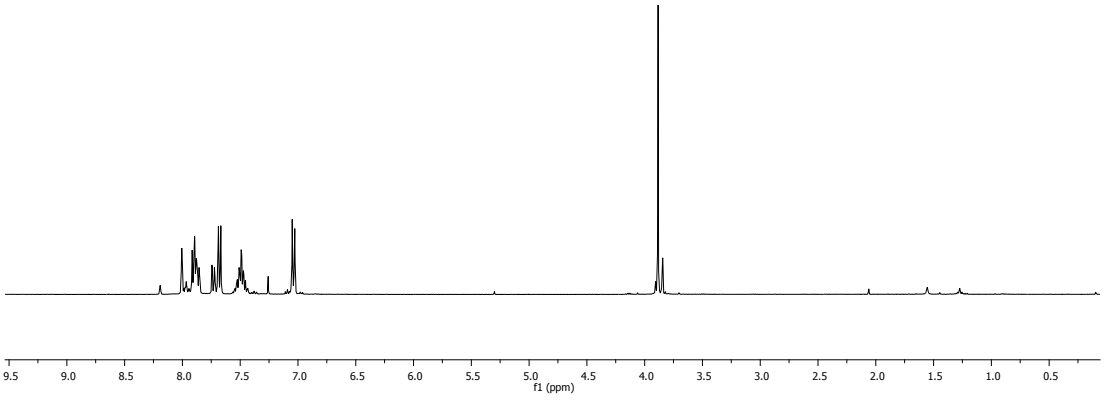

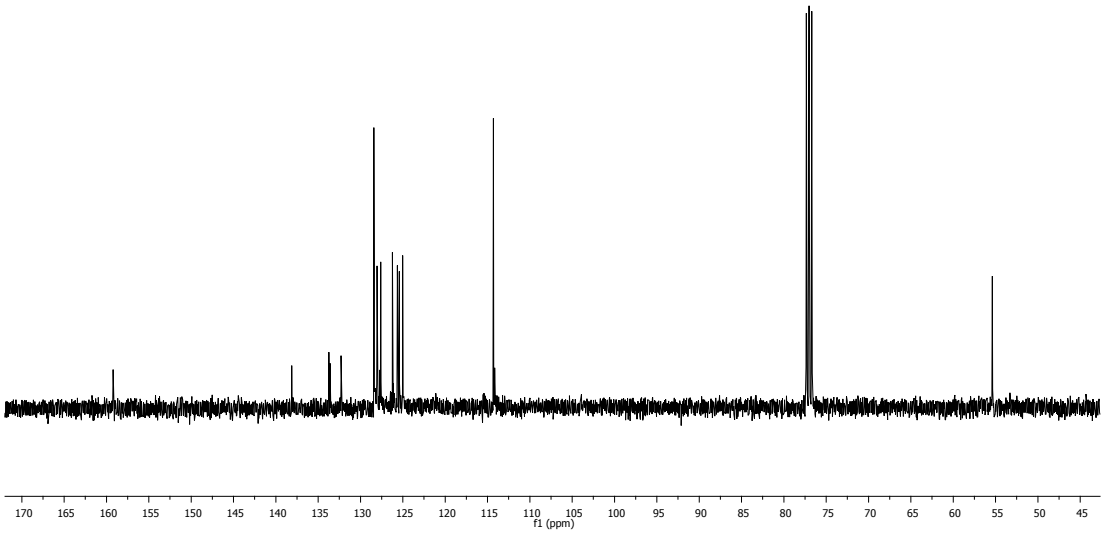

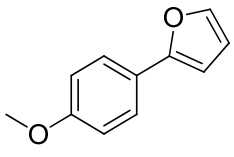

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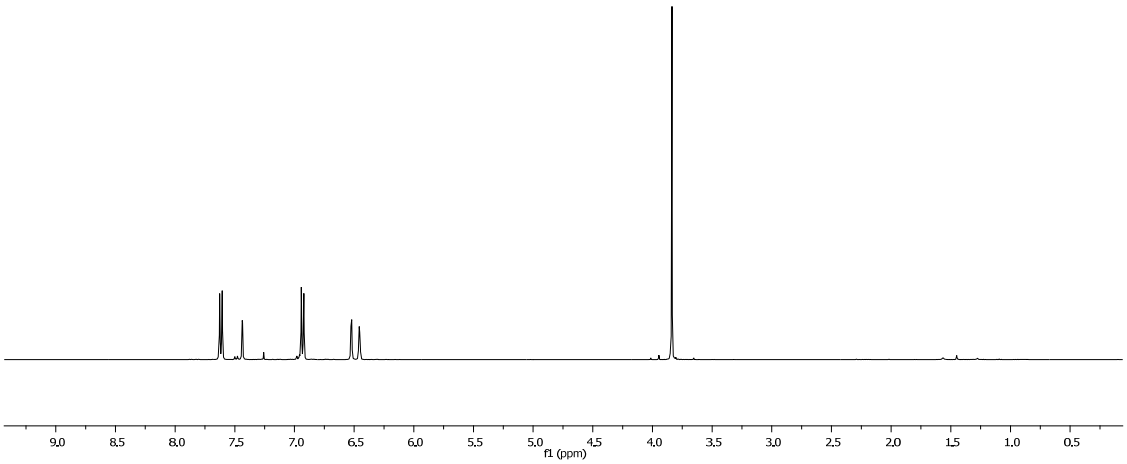

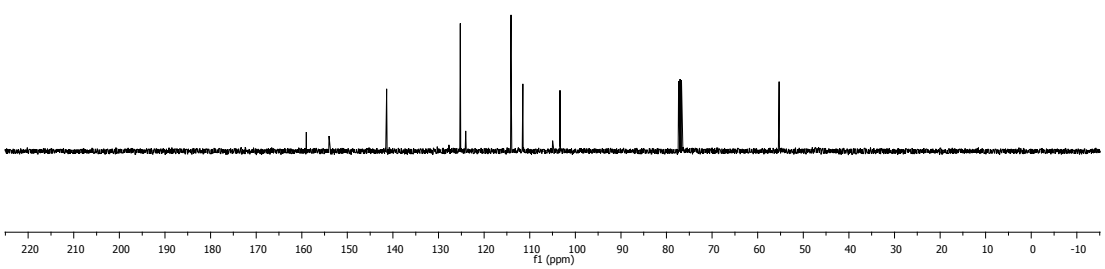

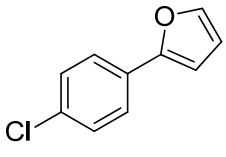

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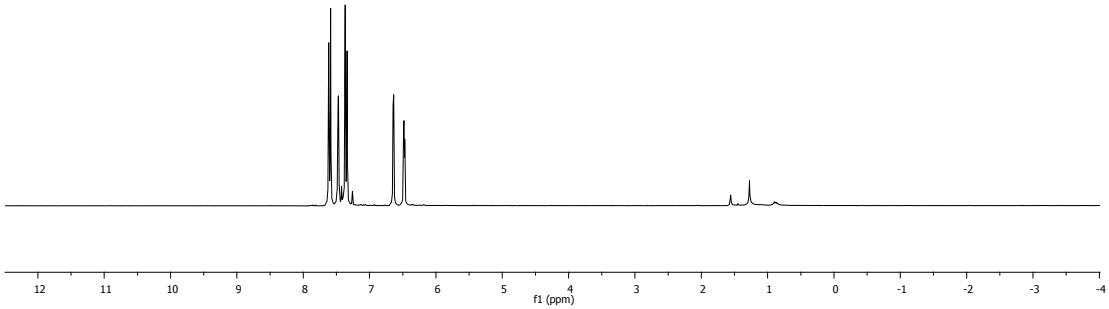

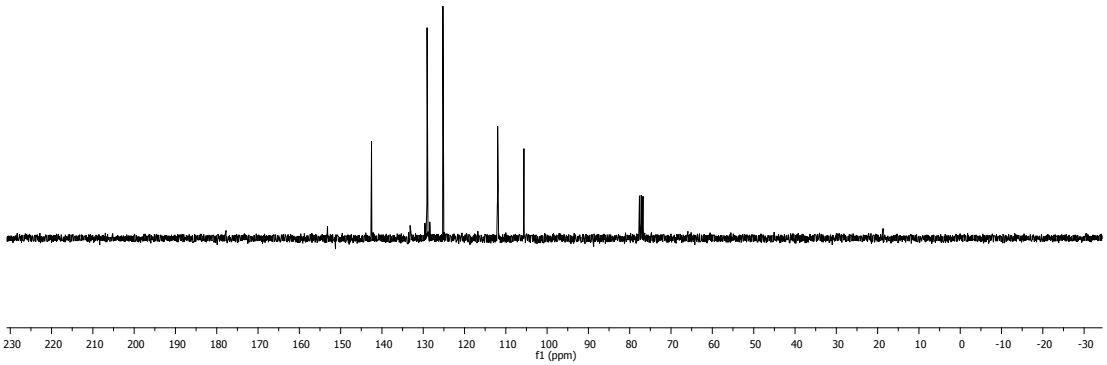

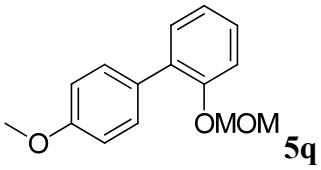

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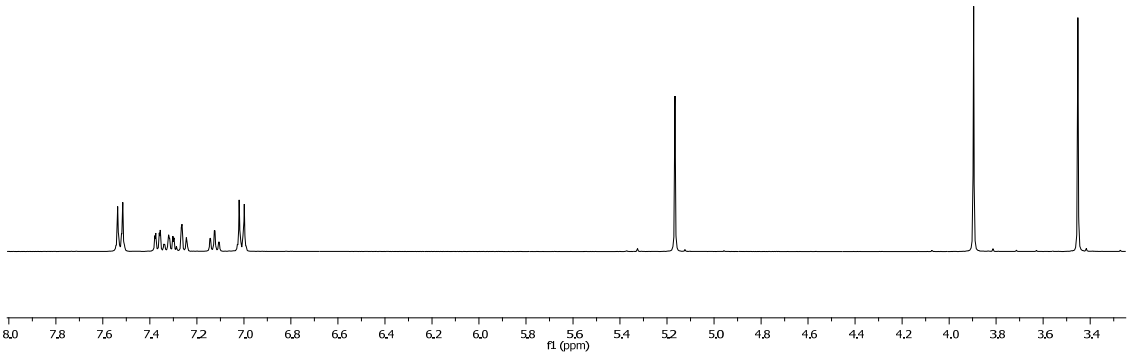

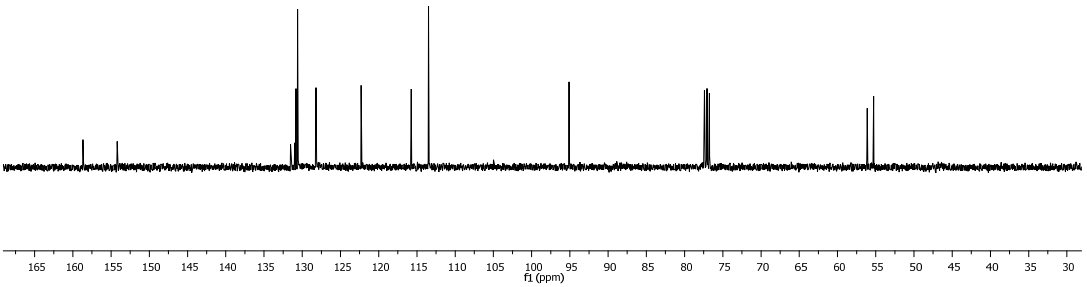

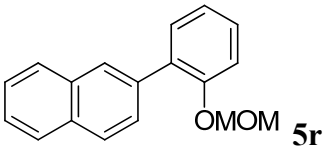

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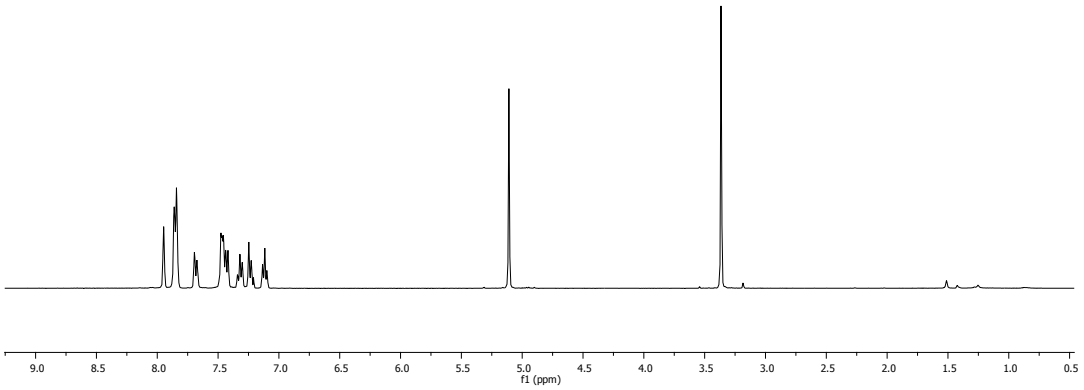

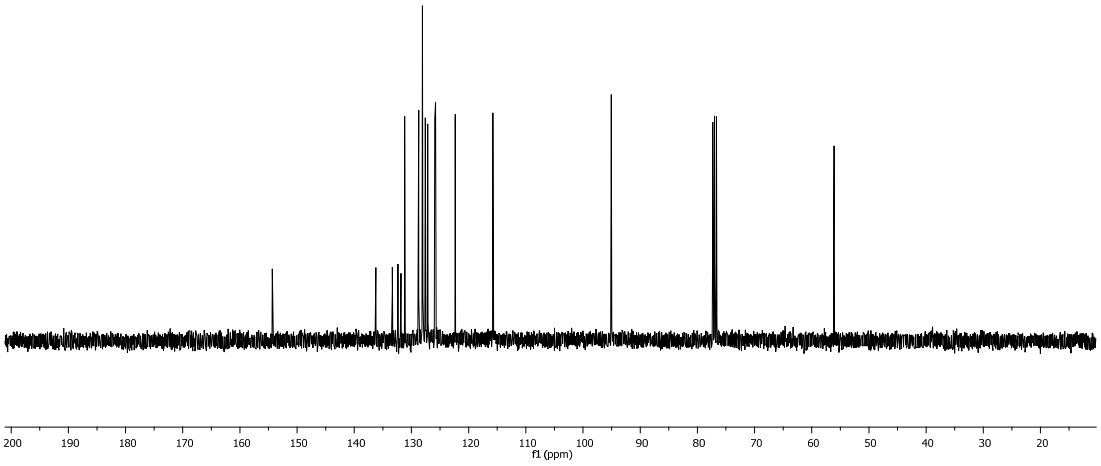

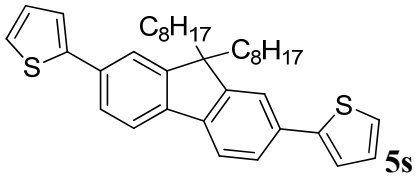

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