Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Less hindered ligands give improved catalysts for the nickel-catalysed Grignard cross-coupling of aromatic ethers

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1. General Information

All catalytic reactions were carried out under an argon atmosphere using standard vacuum line techniques. Unless otherwise stated, all glassware used was flame dried and cooled under vacuum before use. Unless otherwise stated, all solvents were thoroughly degassed before use by either freeze-pump-thaw or rigorous purging with nitrogen. 2-MeTHF (anhydrous ≥99%, inhibitor free, Sigma-Aldrich) was degassed by freeze-pump-thaw before use.

Unless stated chemicals were purchased from Acros-UK, Alfa Aeasar, Apollo Scientific, Fluorochem, Sigma-Aldrich, or TCI Strem and used without further purification. All Grignard reagents were used as supplied (Aldrich and Acros) and titrated before use. Conditions were obtained using an oil bath equipped with a contact thermometer. *In vacuo* refers to the use of a Heidolph Laborota 4001 rotary evaporator with a vacuum controller. Analytical thin layer chromatography (TLC) was performed on pre-coated aluminium plates (Kieselgel 60 F254 silica). TLC visualisation was carried out with ultraviolet light (254 nm), followed by staining with a 1% aqueous $KMnO_4$ solution or vanillin stain. Flash silica chromatography was performed on Kieselgel 60 silica in the solvent system stated.

^1H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz, ^1H, 75 MHz ^{13}C and 282 MHz ^{19}F), a Bruker Avance II 400 (400 MHz, ^1H, 100 MHz ^{13}C and 376 MHz ^{19}F), Bruker Ultrashield 500 (500 MHz, ^1H, 125 MHz ^{13}C and 470 MHz ^{19}F) or a Bruker Ultrashield 700 (700 MHz, ^1H, 125 MHz ^{13}C and 470 MHz ^{19}F) spectrometer at ambient temperature in the deuterated solvent stated. All chemical shifts are quoted in parts per million (ppm) relative to the residual solvent as the internal standard. All coupling constants, *J*, are quoted in Hz and reported high to low. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet), The abbreviation app is used to denote apparent.

Infrared spectra (νmax) were recorded on a Shimadzu IRAffinity-1 using a Pike attenuated total reflectance (ATR) accessory. Only characteristic absorbances are quoted.

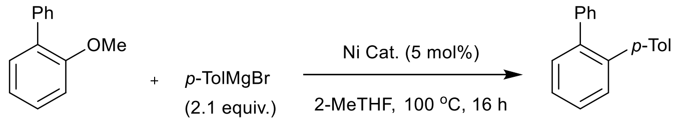
Melting points were recorded on a Stuart SMP30 melting point apparatus and are uncorrected.

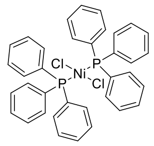
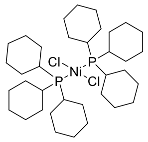
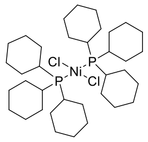
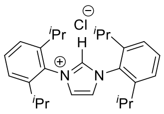
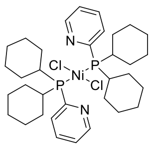
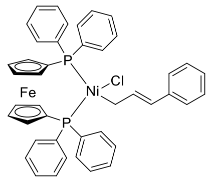
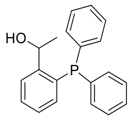
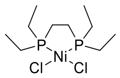
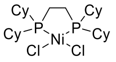
Mass spectrometric (m/z) data were acquired by electrospray ionisation (ESI), electron impact (EI) or chemical ionisation (CI) (atmospheric solids analysis probe (ASAP)) either at the University of St Andrews Mass Spectrometry facility ([A] quoted) or at the EPSRC National Mass Spectrometry Service Centre, Swansea ([A]+ or [A]- quoted). At the University of St Andrews, high resolution ESI was carried out on a Micromass LCT spectrometer and high resolution EI and CI were carried out on a Micromass GCT spectrometer. At the EPSRC National Mass Spectrometry Service Centre, high resolution CI was carried out on a Waters Xevo G2-S spectrometer with ASAP probe. Values are quoted as a ratio of mass to charge in Daltons.

2. Nickel-catalysed Grignard cross-coupling of aromatic ethers

2.a) Initial investigation into the effect of catalyst on the nickel-catalysed cross-coupling of 2-methoxybiphenyl with *p*-TolMgBr.

Table S-1: Initial test reactions of a range of Ni catalytic systems for the Grignard cross-coupling of 2-methoxybiphenyl with *p*-TolMgBr.

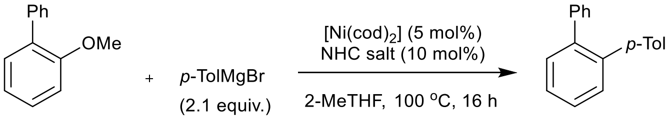


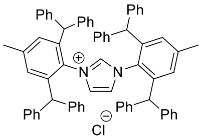
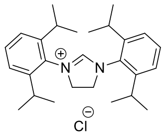
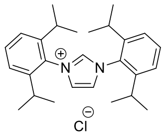
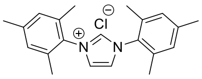
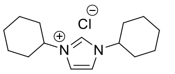
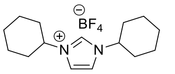
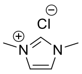
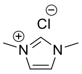
Entry[a]	**Catalyst**	**Catalyst Loading (mol%)**	**Ligand (mol%)**	**Conversion (%)**[b]	**Product (%)**[b]
1	Ni(cod)$_2$	5	-	17	0
2		5	-	8	1
3	Ni(cod)$_2$	5	PCy$_3$ (10.5)	28	8
4		5	-	36	15
5		5	PCy$_3$ (10)	37	30
6	Ni(cod)$_2$	5	 IPr.HCl (10)	79	42
7		5	-	10	3
8[c]		5	-	4	3
9[c]	Ni(acac)$_2$	5	 (5.5)	9	1
10[d]		5	-	12	4
11		5	-	10	3

[a] Reactions were carried out on the scale of 2-methoxybiphenyl (0.50 mmol), *p*-TolMgBr (1.05 mmol in Et$_2$O, 0.5 M), Ni cat. (0.025 mmol), 2-MeTHF (2.25 mL) in sealed vessels unless otherwise noted. [b] Conversions and yields were determined by ^{1}H NMR using 1-methylnaphthalene as an internal standard. [c] Reaction time 45 h. [d] 1.5 equiv. Grignard added.

2.b) Further investigation of Ni / NHC catalyst systems as a function of ligand steric effects, as measured by % buried volume, %V_{bur},[1] (in order of decreasing ligand size).

Table S-2: Effect of %V_{bur} of NHC on the Grignard cross-coupling of 2-methoxybiphenyl with *p*-TolMgBr.

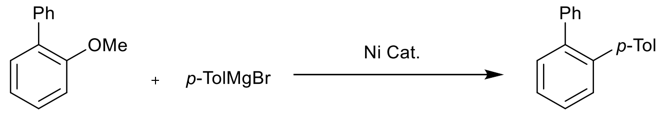


Entry[a]	NHC Salt	NHC Salt Structure	% V_{bur} [b] for M-NHC length at:		Conversion (%)[c]	Product (%)[c]
			2.00 Å	**2.28 Å**		
1	IPr*.HCl		50.4 [d]	-	20	8
2	SIPr.HCl		47.0	41.5	41	10
3	IPr.HCl		44.5	39.0	79	42
4	IMes.HCl		36.5	31.2	> 99	64
5	ICy.HCl		27.4	23.5	> 99	79
6	ICy.HBF₄		27.4	23.5	> 99	72
7	IDM.HCl		26.3	22.7	80	50
8[e]	IDM.HCl		26.3	22.7	78	43

[a] Reactions were carried out on the scale of 2-methoxybiphenyl (0.50 mmol), *p*-TolMgBr (1.05 mmol in Et_2O, 0.5 M), Ni cat. (0.025 mmol), 2-MeTHF (2.25 mL) in sealed vessels unless otherwise noted. [b] %V_{bur} for NHC in [(NHC)AuCl] complexes.[1] [c] Conversions and yields were determined by ^{1}H NMR using 1-methylnaphthalene as an internal standard. [d] %V_{bur} value obtained from reference 2. [e] [$NiCl_2(PCy_3)_2$] (5 mol%) as Ni precursor and NHC.HCl (5 mol%).

2.c) Optimisation for nickel-catalysed cross-coupling of 2-methoxybiphenyl with *p*-TolMgBr.

Table S-3: Grignard cross-coupling of 2-methoxybiphenyl with *p*-TolMgBr under a range of conditions.

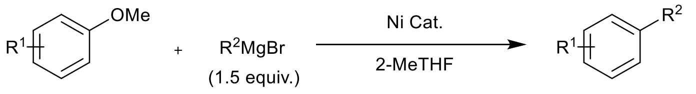


Entry[a]	**Catalyst (mol%)**	**Grig. Equiv.**	**Solvent**	**Temp (°C)**	**Time (h)**	**Conversion (%)**[b]	**Product (%)**[b]
1	**1** (5)	2.1	^{t}AmOMe	100	19	25	10
2[c]	**1** (5) / L (10)	2.1	^{t}AmOMe	100	19	27	21
3[c]	**1** (5) / L (10)	2.1	^{t}AmOMe	100	45	33	22
4[cd]	**1** (5) / L (10)	2.1	^{t}AmOMe	100	42	44	23 [13]
5[c]	**1** (5) / L (10)	3.0	^{t}AmOMe	100	42	30	8
6	**5** (5)	2.1	^{t}AmOMe	100	45	70	52
7	**1** (5)	2.1	PhMe	100	16	13	10
8	**5** (5)	2.1	PhMe	100	16	65	49
9	**1** (5)	2.1	2-MeTHF	100	16	36	15
10[c]	**1** (5) / L (10)	2.1	2-MeTHF	100	16	37	30
11	**1** (5)	2.1	2-MeTHF	100	45	22	10
12[c]	**1** (5) / L (10)	2.1	2-MeTHF	100	45	45	26
13	**5** (5)	2.1	2-MeTHF	100	16	88	78
14	**5** (5)	2.1	2-MeTHF	125	16	88	77
15	**5** (5)	2.1	2-MeTHF	100	45	96	80
16[e]	**5** (5)/ L (10)	2.1	2-MeTHF	100	45	98	84 [84]
17	**2** (5)	2.1	2-MeTHF	100	16	23	21
18	**3** (5)	2.1	2-MeTHF	100	16	59	51
19	**4** (5)	2.1	2-MeTHF	100	16	61	47
20	**6** (5)	2.1	2-MeTHF	100	16	20	7
21	**6** (5)	1.5	2-MeTHF	100	16	25	12
22	$Ni(cod)_2$ (5) / P^nBu_3 (10.5)	2.1	2-MeTHF	100	16	81	63
23	**5** (5)	4.2	2-MeTHF	100	16	70	67
24	**5** (5)	1.5	2-MeTHF	100	16	85	79
25[f]	**1** (5)	1.5	2-MeTHF	80	16	29	19
26[f]	**5** (5)	1.5	2-MeTHF	80	16	54	43
27	**5** (5)	1.5	2-MeTHF	80	16	53	38

[a] Reactions were carried out on the scale of aryl ether (0.50 mmol), Grignard reagent (Et_2O, 0.5 M), solvent (2.25 mL) in sealed vessels unless otherwise noted. [b] Conversions and yields were determined by ^{1}H NMR using 1-methylnaphthalene as an internal standard [yield of isolated product in square brackets]. [c] L = PCy_3. [d] Grignard reagent (0.5 M in ^{t}AmOMe). [e] L = P^nBu_3. [f] Reaction performed in a Schlenk flask.

2.d) Table of results for nickel-catalysed cross-coupling of aryl ethers.

Table S-4: Grignard cross-coupling of challenging aryl methyl ethers.

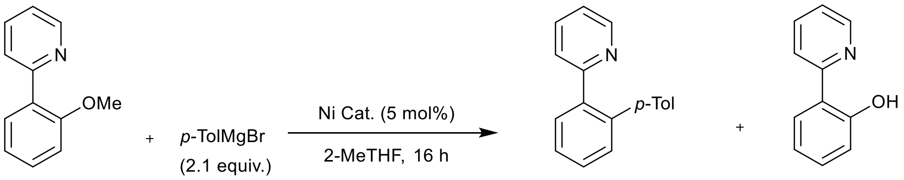


Entry[a]	R^1	R^2 (M)[b]	Catalyst (mol%)	Temp (°C)	Time (h)	Conversion (%)[c]	Product (%)[c]
1	**2-Ph**	*o*-Tol (2.0)	**1** (5)	100	16	23	8
2	**2-Ph**	*o*-Tol (2.0)	**5** (5)	100	16	25	21 [21]
3	**2-Ph**	*o*-Tol	**5** (5)	100	16	30	26
4	**2-Ph**	Ph (1.7)	**5** (5)	100	16	97	96 [86]
5[ef]	**2-Ph**	Me (2.4)	**1** (5)	100	16	9	3
6[ef]	**2-Ph**	Me (2.4)	**5** (5)	100	16	48	46 [27][g]
7	**2-(4-$NMe_2C_6H_4$)**	*p*-Tol	**5** (5)	100	40	79	55 [40]
8[e]	**2-Me**	*p*-Tol	**1** (10)	100	64	18	1
9[e]	**2-Me**	*p*-Tol	**5** (10)	100	64	76	56 [40][h]
10	**4-Ph**	*p*-Tol	**1** (5)	100	16	59	34
11	**4-Ph**	*p*-Tol	**5** (5)	100	16	84	70 [65]
12	**4-Ph**	*o*-Tol (2.0)	**5** (5)	100	16	51	49 [43]
13[d]	**2-Phnap[j]**	*p*-Tol	**1** (1)	80	16	82	70
14	**2-Phnap[j]**	*p*-Tol	**1** (1)	100	16	70	60
15[d]	**2-Phnap[j]**	*p*-Tol	**5** (1)	80	16	54	41
16	**2-Phnap[j]**	*p*-Tol	**5** (1)	100	16	91	85 [83]
17[d]	**2-Phnap[j]**	*o*-Tol (2.0)	**1** (1)	80	16	48	27
18	**2-Phnap[j]**	*o*-Tol (2.0)	**1** (1)	100	16	59	40
19[d]	**2-Phnap[j]**	*o*-Tol (2.0)	**5** (1)	80	16	31	15
20	**2-Phnap[j]**	*o*-Tol (2.0)	**5** (1)	100	16	76	61 [59]
21[de]	**H-nap[k]**	*p*-Tol	**1** (5)	80	64	> 99	96 [89]
22	**H-nap[k]**	*p*-Tol	**1** (1)	80	16	84	71
23[d]	**H-nap[k]**	*p*-Tol	**1** (1)	80	16	91	81
24[f]	**H-nap[k]**	*p*-Tol	**1** (1)	80	16	75	51
25[df]	**H-nap[k]**	*p*-Tol	**1** (1)	80	16	64	57
26	**H-nap[k]**	*p*-Tol	**1** (1)	20	70	27	17
27	**H-nap[k]**	*p*-Tol	**1** (0.5)	80	16	39	38
28[d]	**H-nap[k]**	*p*-Tol	**1** (0.5)	80	16	85	73
29	**H-nap[k]**	*p*-Tol	**1** (0.5)	100	16	75	59
30	**H-nap[k]**	*p*-Tol	**5** (1)	80	16	48	37
31[d]	**H-nap[k]**	*p*-Tol	**5** (1)	80	16	88	81
32[f]	**H-nap[k]**	*p*-Tol	**5** (1)	80	16	5	5
33[df]	**H-nap[k]**	*p*-Tol	**5** (1)	80	16	64	48
34	**H-nap[k]**	*p*-Tol	**5** (1)	20	70	5	5
35	**H-nap[k]**	*p*-Tol	**5** (0.5)	80	16	17	16
36[d]	**H-nap[k]**	*p*-Tol	**5** (0.5)	80	16	68	54
37	**H-nap[k]**	*p*-Tol	**5** (0.5)	100	16	93	89
38	**H-nap[k]**	*p*-Tol	**5** (0.25)	100	16	83	71
39	**H-nap[k]**	*p*-Tol	**5** (0.10)	100	69	62	56
40[d]	**H-nap[k]**	*o*-Tol (2.0)	**1** (1)	80	16	> 99	95
41[d]	**H-nap[k]**	*o*-Tol (2.0)	**5** (1)	80	16	> 99	97 [82]

[a] Reactions were carried out on the scale of aryl ether (0.50 mmol), Grignard reagent (0.75 mmol in Et_2O, 0.5 M), 2-MeTHF (2.25 mL) in sealed vessels unless otherwise noted. [b] Grignard molarity in brackets. [c] Conversions and yields were determined by ^1H NMR using 1-methylnaphthalene as an internal standard [yield of isolated product in square brackets]. [d] Reaction performed in a Schlenk flask. [e] 2.1 equiv. Grignard added. [f] PhMe as reaction solvent. [g] 27 % yield isolated with 1-methylnaphthalene impurity; total product obtained = 24 %. [h] 40 % yield isolated with 1-methylnaphthalene impurity; total product obtained = 38 %. [j] 2-Phnap = 1-phenyl-2-methoxynaphthalane. [k] H-nap = 2-methoxynaphthalane.

2.e) Table of results for nickel-catalysed cross-coupling of 2-(2-methoxyphenyl)pyridine.

Table S-5: Investigation of the effect of Ni catalysts in the reaction of *p*-TolMgBr with 2-(2-methoxyphenyl)pyridine.

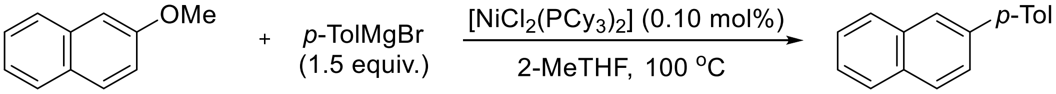


Entry[a]	**Catalyst (mol%)**	**Temp (°C)**	**Conversion (%)**[b]	**Product (%)**[b]	**-OH**[b]
1[c]	-	80	96	83 [71]	13
2	-	80	> 99	88	7
3	**1**	80	79	7	6
4	**5**	80	88	15	6
5	-	20	< 5	0	0
6	**1**	20	85	21	17
7	**5**	20	85	42	15

[a] Reactions were carried out on the scale of aryl ether (0.50 mmol), *p*-TolMgBr (1.05 mmol in Et_2O, 0.5 M), 2-MeTHF (2.25 mL). [b] Conversions and yields were determined by ^1H NMR using 1-methylnaphthalene as an internal standard [yield of isolated product in square brackets]. [c] Reaction carried out with no internal standard (therefore values are of relative ratios in ^1H NMR), in THF in a sealed microwave vial with crimp cap, with 2.4 equiv. Grignard for 67 h.

2.f) Time profile analysis of the nickel-catalysed Grignard cross-coupling of 2-methoxynaphthalene with *p*-TolMgBr.

Table S6 – Time profile analysis for the reaction of 2-methoxynaphthalene with *p*-TolMgBr using 0.10 mol% of $[NiCl_2(PCy_3)_2]$.



Entry[a]	MgI_2 (equiv.)	Catalyst	t (h)	Conversion (%)	Product (%)
1	**0**	**$[NiCl_2(PCy_3)_2]$**	**4**	**3**	**0**
			16	**3**	**0**
			28	**10**	**1**
			69	**46**	**30**
			90	**68**	**43**
2[c]	0	$[NiCl_2(PCy_3)_2]$	16	3	0
			28	13	2
			69	56	34
			90	67	43
3	0	$[NiCl_2(PCy_3)_2]$	28	11	1
			69	66	40
			90	80	52
4	0	$[NiCl_2(PCy_3)_2]$	69	49	32
			90	68	42

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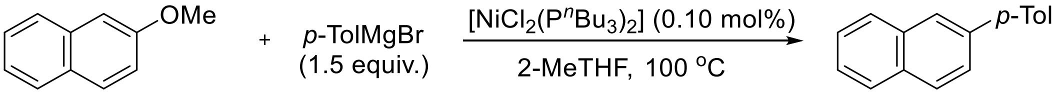
[a] Reactions were carried out on the scale of 2-methoxynaphthalene (0.50 mmol), *p*-TolMgBr (0.75 mmol in Et_2O, 0.5 M), Ni catalyst (0.0005 mmol), 2-MeTHF (2.25 mL) in sealed microwave vials with crimp cap unless otherwise noted. Data in **bold** used to produce Figure 4.9 in Section 4.2.3.5. [b] Conversions and yields were determined by ^1H NMR using 1-methylnaphthalene as an internal standard. [c] Reaction spiked with P^nBu_3 (0.033 mol%, in 25 µL) after 49 h.

Table S7 – Time profile analysis for the reaction of 2-methoxynaphthalene with *p*-TolMgBr using 0.10 mol% of $[NiCl_2(P^nBu_3)_2]$.



Entry[a]	Additive (equiv.)	Catalyst	t (h)	Conversion (%)	Product (%)
1	-	$[NiCl_2(P^nBu_3)_2]$	2	0	0
			4	0	0
			16	11	5
			28	19	15
			69	64	56
2	**-**	**$[NiCl_2(P^nBu_3)_2]$**	**4**	**0**	**0**
			16	**11**	**4**
			28	**19**	**12**
			69	**64**	**50**
3	-	$[NiCl_2(P^nBu_3)_2]$	16	0	0
			28	5	5
			69	34	33
4	-	$[NiCl_2(P^nBu_3)_2]$	28	15	12
			69	65	58
5[c]	**MgI_2 (1.5)**	**$[NiCl_2(P^nBu_3)_2]$**	**11**	**25**	**22**
			45	**83**	**70**
			59	**85**	**72**
			90	**85**	**72**
6[c]	MgI_2 (1.5)	$[NiCl_2(P^nBu_3)_2]$	11	23	21
			45	86	71
			59	88	73
			90	88	73
7[d]	**MeOH (0.3)**	**$[NiCl_2(P^nBu_3)_2]$**	**4**	**9**	**7**
			16	**39**	**36**
			28	**65**	**59**
			69	**83**	**72**
			90	**84**	**72**
8[e]	**BrMg(OMe) (0.3)**	**$[NiCl_2(P^nBu_3)_2]$**	**4**	**0**	**0**
			16	**12**	**10**
			28	**28**	**24**
			69	**81**	**72**
			90	**81**	**72**
9[f]	MgI_2 (1.5)	-	45	0	0
			90	0	0

[a] Reactions were carried out on the scale of 2-methoxynaphthalene (0.50 mmol), *p*-TolMgBr (0.75 mmol in Et_2O, 0.5 M), Ni catalyst (0.0005 mmol), 2-MeTHF (2.25 mL) in sealed microwave vials with crimp cap unless otherwise noted. Data in **bold** used to produce Figure 1. [b] Conversions and yields were determined by ^1H NMR using 1-methylnaphthalene as an internal standard. [c] MgI_2 (0.75 mmol) added prior to the start of the reaction. [d] MeOH (0.15 mmol) added to the solution containing catalyst and substrate, prior to addition of Grignard reagent (0.90 mmol). [e] MeOH (0.15 mmol) added to the Grignard reagent (0.90 mmol) prior to the addition of catalyst and substrate. [f] No nickel catalyst.

3. Experimental and NMR details of all products for Grignard cross-coupling of aromatic ethers

3.a) Synthesis of nickel complexes **2-4**

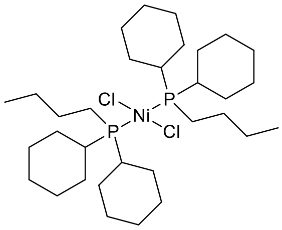
4-(diethylphosphino)-*N*,*N*-dimethylaniline is commercially available and was purchased from Sigma Aldrich. dicyclohexyl^{n}butylphosphine and cyclohexyldi^{n}butylphosphine were prepared by modification of a literature procedure[3], reacting excess ^{n}butylmagnesium chloride with chlorodicyclohexylphosphine and cyclohexyldichlorophosphine respectively.

$[NiCl_2(PCy_3)_2]$, **1**, is commercially available and was purchased from Strem Chemicals, Inc. $[NiCl_2(P^nBu_3)_2]$, **5**, is commercially available and was purchased from Sigma Aldrich. $[NiCl_2(PMe_3)_2]$, **6**, is commercially available and was purchased from Sigma Aldrich. $Ni(cod)_2$, **9**, is commercially available and was purchased from Strem Chemicals, Inc. (dppf)Ni(cinnamyl)Cl, **10**, was commercially available and was purchased from Sigma Aldrich. $Ni(acac)_2$ is commercially available and was purchased from Sigma Aldrich. $NiCl_2$(depe), **12**, is commercially available was purchased from Sigma Aldrich.

1-(2-diphenylphosphinophenyl)ethanol (PO) was prepared following a literature procedure with spectroscopic data in agreement.[4]

Nickel complexes **2** – **4** were prepared by adapting a literature procedure.[5] As is normal with nickel (II) complexes, some broadness appears in the NMR spectra due to paramagnetic effects (either traces or not idealised square planar geometries).

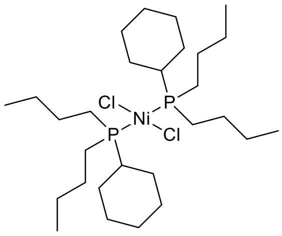
$[NiCl_2(PCy_2{}^nBu)_2]$, **2**



$NiCl_2{\cdot}6H_2O$ (94.0 mg, 0.40 mmol), ethanol (1 mL) and a magnetic stir bar were added to a flame dried Schlenk flask. The solution was sparged with nitrogen for 15 minutes and a solution of dicylcohexyl^{n}butylphosphine (210.6 mg, 0.83 mmol) in ethanol (2 mL) was added in one portion. The reaction mixture was stirred overnight at 80 °C and then cooled to room temperature. Once cool, the flask was chilled to 0 °C for 10 minutes, after which the solid was collected by canula filtration, washed twice with ethanol (2 x 5 mL) and twice with diethyl ether (2 x 5 mL). Drying under vacuum yielded **2** (208.5 mg, 83 %) as a fine, red powder.

mp 140-142 °C; ν_{max} (ATR) 2914 (s), 2845 (m), 1458 (w), 1441 (m), 1206 (w), 1171 (w), 1049 (w), 1003 (m), 907 (w), 887 (w), 847 (m), 752 (m); δ_H (500 MHz, $CDCl_3$) 2.70-2.45 (4H, m, C*H₂*), 2.02-1.40 (40H, m, CH_2, C*H*), 1.36-1.16 (12H, m, CH_2), 0.99 (6H, m, CH_3); δ_P (202 MHz, $CDCl_3$) 9.5; δ_C (125 MHz, $CDCl_3$) 33.4 (*C*H), 30.1 (*C*H₂), 29.5 (*C*H₂), 28.2 (*C*H₂), 28.0 (*C*H₂), 27.7 (*C*H₂), 26.9 (*C*H₂), 25.7 (*C*H₂), 18.8 (*C*H₂), 14.2 (*C*H₃); *m/z* HRMS (APCI$^+$) $C_{32}H_{62}ClNiP_2^+$ ($[M\text{-}Cl]^+$) requires 601.3369; found 601.3363 (-1.0 ppm); Anal. Calcd for $C_{32}H_{62}Cl_2NiP_2$: C, 60.21; H, 9.79; Found: C, 60.32; H, 9.90.

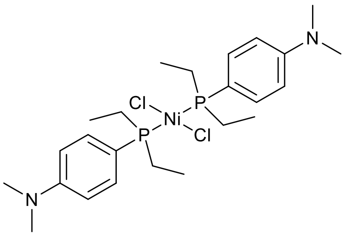
$[NiCl_2(PCy^nBu_2)_2]$, **3**



$NiCl_2{\cdot}6H_2O$ (349.8 mg, 1.47 mmol), ethanol (4 mL) and a magnetic stir bar were added to a flame dried Schlenk flask. The solution was sparged with nitrogen for 15 minutes and a solution of cylcohexyldi^{n}butylphosphine (705.9 mg, 3.09 mmol) in ethanol (2 mL) was added in one portion. The reaction mixture was stirred overnight at 80 °C and then cooled to room temperature. Once cool, the flask was chilled to 0 °C for 10 minutes, after which the solid was collected by canula filtration, washed twice with ethanol (2 x 10 mL) and twice with diethyl ether (2 x 10 mL). Drying under vacuum yielded **3** (569.9 mg, 66 %) as a fine, red powder.

mp 68-69 °C; ν_{max} (ATR) 2953 (m), 2918 (s), 2849 (m), 1449 (m), 1092 (w), 1061 (m), 1045 (w), 1001 (w), 907 (m), 891 (w), 777 (s); δ_H (500 MHz, $CDCl_3$) 2.30 (4H, app d, *J* 12.4, C*H*$_2$), 2.10-1.97 (6H, m, C*H*$_2$, C*H*), 1.83-1.67 (16H, m, C*H*$_2$), 1.65-1.58 (2H, m, C*H*$_2$), 1.52-1.39 (12H, m, C*H*$_2$), 1.28-1.16 (6H, m, C*H*$_2$), 0.96 (12H, t, *J* 7.3, C*H*$_3$); δ_P (202 MHz, $CDCl_3$) 5.9; δ_C (125 MHz, $CDCl_3$) 34.7 (*C*H), 29.3 (*C*H$_2$), 27.6 (*C*H$_2$), 27.4 (*C*H$_2$), 26.8 (*C*H$_2$), 25.3 (*C*H$_2$), 19.9 (*C*H$_2$), 14.1 (*C*H$_3$); *m/z* HRMS (APCI$^+$) $C_{28}H_{58}ClNiP_2^+$ ($[M-Cl]^+$) requires 549.3056; found 549.3056 (±0.0 ppm); Anal. Calcd for $C_{28}H_{58}Cl_2NiP_2$: C, 57.36; H, 9.97; Found: C, 57.47; H, 9.89.

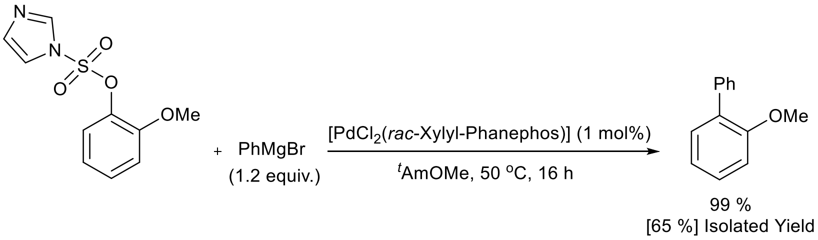
[$NiCl_2(PEt_2Ar)_2$], Ar = 4-(NMe_2)C_6H_4, **4**



$NiCl_2·6H_2O$ (134.7 mg, 0.57 mmol), ethanol (3 mL) and a magnetic stir bar were added to a flame dried Schlenk flask. The solution was sparged with nitrogen for 15 minutes and diethyl[4-(*N*,*N*-dimethylamino)phenyl]phosphine (244 µL, 1.19 mmol) was added in one portion. The reaction mixture was stirred overnight at 80 °C and then cooled to room temperature. Once cool, the flask was chilled to 0 °C for 10 minutes, after which the solid was collected by canula filtration, washed twice with ethanol (2 x 5 mL) and twice with diethyl ether (2 x 5 mL). Drying under vacuum yielded **4** (291.5 mg, 94 %) as a fine, dark red powder.

mp 108-110 °C; ν_{max} (ATR) 2880 (w), 1595 (m), 1508 (m), 1447 (w), 1362 (m), 1227 (w), 1206 (m), 1105 (m), 1072 (w), 1036 (m), 1024 (m), 980 (w), 943 (w), 808 (s), 758 (m); δ_H (500 MHz, $CDCl_3$) 7.75 (4H, br d, *J* 8.2, C_{Ar}*H*), 6.57 (4H, br d, *J* 8.2, C_{Ar}*H*), 3.41-2.64 (8H, m, C*H*$_2$), 2.48 (12H, s, NC*H*$_3$), 1.27 (12H, br t, C*H*$_3$); δ_C (125 MHz, $CDCl_3$) 151.8 (*C*$_{Ar}$H), 135.7 (*C*$_{Ar}$H), 120.3 (*C*$_{Ar}$H), 112.2 (*C*$_{Ar}$H), 39.6 (N*C*H$_3$), 18.1 (*C*H$_2$), 10.2 (*C*H$_3$); Anal. Calcd for $C_{24}H_{40}Cl_2N_2NiP_2$: C, 52.59; H, 7.36; N, 5.11; Found: C, 52.72; H, 7.44; N, 5.14.

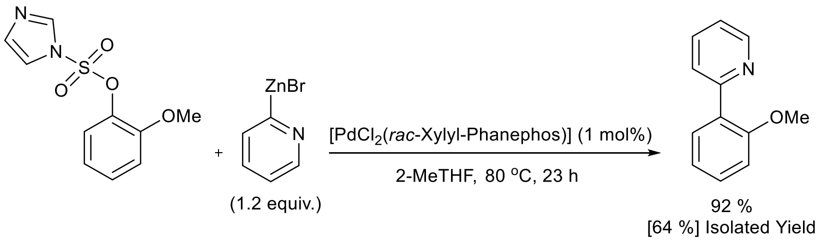
3.b) Palladium-catalysed cross-coupling of guaiacol-derived 2-methoxyphenyl-1*H*-imidazole-1-sulfonate



Nickel catalytic systems tested include: [NiCl$_2$*(PCy*$_3$*)*$_2$*], [NiCl*$_2$*(P*^{n}*Bu*$_3$*)*$_2$*], [Ni(acac)*$_2$*]/ICy·HBF*$_4$*, [Ni(acac)*$_2$*]/IPr*·HCl, [Ni(acac)*$_2$*]/IPr·HCl, [Ni(cod)*$_2$*], [Ni(cod)*$_2$*]/PO and [Ni(acac)*$_2$*]/PO. However, these did not catalyse the reaction well with product yields ranging from 5-63 %, with significant amounts of 2-methoxyphenol (guaiacol) being formed.*

2-Methoxyphenyl-1*H*-imidazole-1-sulfonate (127.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 µL, 0.21 mmol) were dissolved in degassed *tert*-amyl methyl ether (1.0 mL). A t_0 sample (approximately 10 µL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to [PdCl$_2$(*rac*-Xylyl-Phanephos)] (4.3 mg, 0.005 mmol). Phenylmagnesium bromide (350 µL, 0.60 mmol, 1.7 M in Et$_2$O) was added dropwise over 30 minutes. The reaction mixture was stirred at 50 °C for 16 hours. Upon cooling to rt, approximately 20 µL of the crude reaction mixture was analysed by ^{1}H NMR to assess the ratio between SM and desired product. Saturated aqueous ammonium chloride (5.0 mL) was added to the reaction mixture and the aqueous phase was extracted three times with ethyl acetate (3 x 5.0 mL), dried over sodium sulfate and concentrated under reduced pressure. Purification *via* column chromatography on silica gel (eluent petrol:EtOAc, 100:0 to 98:2) gave 2-methoxybiphenyl as a colourless oil (59.5 mg, 65 %), with spectroscopic data in accordance with the literature.[6]

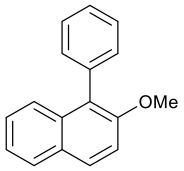
δ_H (500 MHz, CDCl$_3$) 7.57–7.52 (2H, m, $C_{Ar}H$), 7.45–7.40 (2H, m, $C_{Ar}H$), 7.36–7.31 (3H, m, $C_{Ar}H$), 7.04 (1H, td, *J* 7.5, 1.1, $C_{Ar}H$), 7.00 (1H, dd, *J* 8.7, 1.1, $OC_{Ar}C_{Ar}H$), 3.82 (3H, s, OCH_3); δ_C (125 MHz, CDCl$_3$) 156.6 ($C_{Ar}O$), 138.7 ($C_{Ar}C_{Ar}$), 131.0 ($C_{Ar}H$), 130.8 ($C_{Ar}C_{Ar}$), 129.7 (2C, $C_{Ar}H$) , 128.7 ($C_{Ar}H$), 128.1 (2C, $C_{Ar}C_{Ar}H$), 127.1 ($C_{Ar}H$), 120.9 ($C_{Ar}H$), 111.3 ($OC_{Ar}C_{Ar}H$), 55.7 (OCH_3); *m/z* HRMS (EI$^+$) $C_{13}H_{12}O^+$ ([M]$^+$) requires 184.0888; found 184.0884 (–2.2 ppm).



2-Methoxyphenyl-1*H*-imidazole-1-sulfonate (63.6 mg, 0.25 mmol) and 1-methylnaphthalene (30 µL, 0.11 mmol) were dissolved in degassed 2-MeTHF (500 µL). A t_0 sample (approximately 10 µL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to [PdCl$_2$(*rac*-Xylyl-Phanephos)] (2.2 mg, 0.0025 mmol). 2-Pyridylzinc bromide (600 µL, 0.30 mmol, 0.5 M in THF) was added dropwise over 30 minutes. The reaction mixture was stirred at 80 °C for 23 hours. Upon cooling to rt, approximately 20 µL of the crude reaction mixture was analysed by ^{1}H NMR to assess the ratio between SM and desired product. Saturated aqueous ammonium chloride (5.0 mL) was added to the reaction mixture and the aqueous phase was extracted three times with ethyl acetate (3 x 5.0 mL), dried over sodium sulfate and concentrated under reduced pressure. Purification *via* column chromatography on silica gel (eluent hexane:EtOAc, 80:20) gave 2-(2-methoxyphenyl)pyridine as a pale yellow oil (29.6 mg, 64 %), with spectroscopic data in accordance with the literature.[7]

δ_H (500 MHz, CDCl$_3$) 8.70 (1H, ddd, *J* 4.9, 1.9, 1.0, NC$_{py}$*H*)*, 7.81 (1H, dt, *J* 8.0, 1.0, NC$_{py}$C$_{py}$*H*)*, 7.76 (1H, dd, *J* 7.4, 1.8, C$_{Ar}$C$_{Ar}$*H*), 7.70 (1H, ddd, *J* 8.0, 7.5, 1.9, C$_{py}$*H*), 7.38 (1H, ddd, *J* 8.3, 7.4, 1.8, C$_{Ar}$*H*), 7.21 (1H, ddd, *J* 7.5, 4.9, 1.0, NC$_{py}$HC$_{py}$*H*), 7.08 (1H, td, *J* 7.4, 1.0, C$_{Ar}$*H*), 7.01 (1H, dd, *J* 8.3, 1.0, OC$_{Ar}$C$_{Ar}$*H*), 3.89 (OC*H*$_3$); δ_C (125 MHz, CDCl$_3$) 157.0 (*C*$_{Ar}$O), 156.2 (N*C*$_{py}$), 149.5 (N*C*$_{py}$H), 135.7 (*C*$_{py}$H), 131.2 (C$_{Ar}$*C*$_{Ar}$H), 130.0 (*C*$_{Ar}$H), 129.2 (*C*$_{Ar}$), 125.2 (NC$_{py}$*C*$_{py}$H), 121.7 (NC$_{py}$H*C*$_{py}$H), 121.1 (*C*$_{Ar}$H), 111.4 (OC$_{Ar}$*C*$_{Ar}$H), 55.7 (O*C*H$_3$); *m/z* HRMS (ESI$^+$) $C_{12}H_{12}NO^+$ ([M+H]$^+$) requires 186.0913; found 186.0911 (-1.1 ppm).

3.c) Synthesis of substrate 1-phenyl-2-methoxynaphthalene



1-bromo-2-methoxynaphthalene (2.0 g, 8.44 mmol) and [$PdCl_2$(dppf)] (61.5 mg, 0.084 mmol) were added to a flame dried Schlenk flask equipped with a stirrer bar. Degassed 2-MeTHF (10 mL) was added and the solution was stirred. Phenylmagnesium bromide (15.7 mL, 1.71 M in Et_2O, 26.88 mmol) was added dropwise to the solution over 15 minutes. The reaction mixture was stirred overnight at 80 ^{o}C. The reaction mixture was allowed to cool to ambient temperature and saturated aqueous ammonium chloride solution (10 mL) was added and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organics were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting oil was purified by column chromatography on silica gel (eluent petroleum ether:EtOAc, 100:0 to 95:5) to give 1-phenyl-2-methoxynaphthalene (1.59 g, 81 %) as a white solid, with spectroscopic data in accordance with the literature.[8]

mp 50-52 °C {lit[9] 50-51 °C}; δ_H (500 MHz, $CDCl_3$) 7.89 (1H, d, *J* 9.0, $C_{Ar}H$), 7.86-7.81 (1H, m, $C_{Ar}H$), 7.53-7.47 (3H, m, $C_{Ar}H$), 7.46-7.41 (1H, m, $C_{Ar}H$), 7.40-7.36 (3H, m, $C_{Ar}H$), 7.36-7.31 (2H, m, $C_{Ar}H$), 3.85 (3H, s, $C_{Ar}OCH_3$); δ_C (125 MHz, $CDCl_3$) 153.8 (C_{Ar}), 136.5 (C_{Ar}), 133.7 (C_{Ar}), 131.1 (2C, $C_{Ar}H$), 129.2 ($C_{Ar}H$), 129.1 (C_{Ar}), 128.3 (2C, $C_{Ar}H$), 128.0 ($C_{Ar}H$), 127.2 ($C_{Ar}H$), 126.4 ($C_{Ar}H$), 125.5 (C_{Ar}), 125.4 ($C_{Ar}H$), 123.6 ($C_{Ar}H$), 113.9 ($C_{Ar}H$), 56.9 ($C_{Ar}OCH_3$) ; *m/z* HRMS (EI^+) $C_{17}H_{14}O^+$ ($[M]^+$) requires 234.1045; found 234.1046 (+0.4 ppm).

3.d) Experimental and NMR details of all products for Grignard cross-coupling of aromatic ethers

General procedure for the Grignard cross-coupling of aromatic ethers

To an oven dried microwave vial equipped with a stirrer bar was added the desired nickel catalyst. The vial was sealed with a crimp cap and flushed with argon for 30 minutes. Aryl ether (0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a flame dried Schlenk flask under an inert atmosphere. Degassed solvent (2.25 mL) was then added to the Schlenk flask to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to the nickel catalyst *via* syringe. The requisite Grignard solution was added dropwise over 15 minutes. The reaction mixture was stirred vigorously in an oil bath at a specific temperature for the required period of time. *Time profiling samples (where applicable) were obtained by carefully inserting an argon-flushed needle and syringe into the reaction vials, and then transferring approximately 20 μL of the reaction mixture into sample vials. Samples were then quenched with $CDCl_3$, filtered through a small cotton wool plug and analysed by ^{1}H NMR.* Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with $CDCl_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^{1}H NMR was run to assess the ratio between SM and desired product. Saturated aqueous ammonium chloride (5 mL) was added to the reaction mixture and the aqueous phase was extracted three times with ethyl acetate (3 x 5 mL), dried over sodium sulfate and concentrated under reduced pressure. Purification *via* either column chromatography on silica gel or trituration yielded product. The initial crude ^{1}H NMR was then spiked with product to verify product peaks.

All entries were performed using ***general procedure*** *unless noted otherwise. Below are examples of any entries deviating from* ***general procedure*** *as well as all isolated runs.*

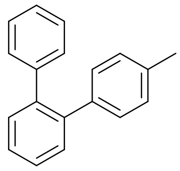


Table **S-3**, Entry 16:

Prepared following **general procedure** at 100 °C for 16 hours with 2-methoxybiphenyl (92.1 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (13.4 mg, 0.025 mmol) and *p*-tolylmagnesium bromide (1.50 mL, 0.75 mmol, 0.5 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 4-methyl-1,1′:2′,1″-terphenyl (102.7 mg, 84 %) as a white crystalline solid with spectroscopic data in accordance with the literature.[10]

mp 70-73 °C {lit[11] 60-62 °C}; δ_H (500 MHz, $CDCl_3$); 7.45-7.39 (4H, m, $C_{Ar}H$), 7.26-7.20 (3H, m, $C_{Ar}H$), 7.19-7.15 (2H, m, $C_{Ar}H$), 7.06-7.01 (4H, m, $C_{Ar}H$), 2.32 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 141.8 (C_{Ar}), 140.6 (2C, C_{Ar}), 138.7 (C_{Ar}), 136.2 (C_{Ar}), 130.8 (2C, C_{Ar}H), 130.0 (2C, C_{Ar}H), 129.9 (2C, C_{Ar}H), 128.8 (2C, C_{Ar}H), 128.0 (2C, C_{Ar}H), 127.6 (C_{Ar}H), 127.4 (C_{Ar}H), 126.5 (C_{Ar}H), 21.3 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{19}H_{16}^+$ ($[M]^+$) requires 244.1252; found 244.1250 (-0.8 ppm).

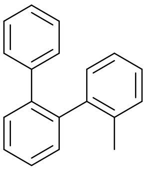


Table **S-4**, Entry 2:

Prepared following **general procedure** at 100 °C for 16 hours with 2-methoxybiphenyl (92.1 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (13.4 mg, 0.025 mmol) and *o*-tolylmagnesium bromide (375 µL, 0.75 mmol, 2.0 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 2-methyl-1,1':2',1"-terphenyl (25.6 mg, 21 %) as a colourless oil with spectroscopic data in accordance with the literature.[12]

δ_H (500 MHz, $CDCl_3$); 7.49-7.38 (3H, m, $C_{Ar}H$), 7.31 (1H, dd, *J* 7.4, 1.7, $C_{Ar}H$), 7.24-7.11 (8H, m, $C_{Ar}H$), 7.08 (1H, d, *J* 7.8, $C_{Ar}H$), 1.92 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 141.5 (C_{Ar}), 141.4 (C_{Ar}), 141.1 (C_{Ar}), 140.4 (C_{Ar}), 135.9 (C_{Ar}), 130.8 (C_{Ar}H), 130.7 (C_{Ar}H), 130.1 (C_{Ar}H), 129.9 (C_{Ar}H), 129.5 (2C, C_{Ar}H), 127.8 (2C, C_{Ar}H), 127.6 (C_{Ar}H), 127.2 (C_{Ar}H), 127.1 (C_{Ar}H), 126.6 (C_{Ar}H), 125.4 (C_{Ar}H), 20.2 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{19}H_{16}^+$ ($[M]^+$) requires 244.1252; found 244.1250 (-0.8 ppm).

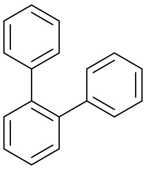


Table **S-4**, Entry 4:

Prepared following **general procedure** at 100 °C for 16 hours with 2-methoxybiphenyl (92.1 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (13.4 mg, 0.025 mmol) and phenylmagnesium bromide (439 µL, 0.75 mmol, 1.7 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 1,1':2',1"-terphenyl (98.6 mg, 86 %) as a colourless oil with spectroscopic data in accordance with the literature.[13]

δ_H (500 MHz, $CDCl_3$); 7.49-7.42 (4H, m, $C_{Ar}H$), 7.26-7.20 (6H, m, $C_{Ar}H$), 7.19-7.14 (4H, m, $C_{Ar}H$); δ_C (125 MHz, $CDCl_3$) 141.6 (2C, C_{Ar}), 140.7 (2C, C_{Ar}), 130.7 (2C, C_{Ar}H), 130.0 (4C, C_{Ar}H), 128.0 (4C, C_{Ar}H), 127.6 (2C, C_{Ar}H), 126.6 (2C, C_{Ar}H); *m/z* HRMS (EI^+) $C_{18}H_{14}^+$ ($[M]^+$) requires 230.1096; found 230.1092 (-1.7 ppm).

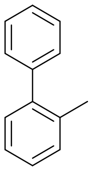


Table **S-4**, Entry 6:

Prepared following **general procedure** at 100 °C for 16 hours with 2-methoxybiphenyl (92.1 mg, 0.50 mmol), PhMe (2.25 mL), $NiCl_2(P^nBu_3)_2$ (13.4 mg, 0.025 mmol) and methylmagnesium bromide (434 µL, 1.05 mmol, 2.4 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave a mixture of 2-methylbiphenyl and 1-methylnaphthalene (88:12 ^{1}H NMR) (22.9 mg) [total product = 24 %] as a colourless oil with spectroscopic data in accordance with the literature.[14]

δ_H (500 MHz, $CDCl_3$); 7.48-7.41 (2H, m, $C_{Ar}H$), 7.39-7.34 (3H, m, $C_{Ar}H$), 7.32-7.24 (4H, m, $C_{Ar}H$), 2.31 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 142.1 (C_{Ar}), 142.1 (C_{Ar}), 135.5 (C_{Ar}), 130.4 (C_{Ar}H), 129.9 (C_{Ar}H), 129.3 (2C, C_{Ar}H), 128.2 (2C, C_{Ar}H), 127.4 (C_{Ar}H), 126.9 (C_{Ar}H), 125.9 (C_{Ar}H), 20.6 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{13}H_{12}^+$ ($[M]^+$) requires 168.0939; found 168.0938 (-0.6 ppm).

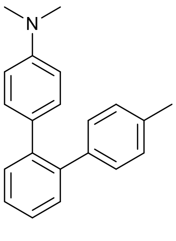


Table **S-4**, Entry 7:

Prepared following **general procedure** at 100 °C for 16 hours with 2-methoxybiphenyl (113.7 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (13.4 mg, 0.025 mmol) and *p*-tolylmagnesium bromide (1.50 mL, 0.75 mmol, 0.5 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether:EtOAc, 100:0 to 99:1) gave 2-(4-*N*,*N*-dimethylaniline)-4'-dimethyl-1,1'-biphenyl (56.9 mg, 40 %) as a light yellow oil.

ν_{max} (ATR) 2920 (w), 2245 (w), 1713 (w), 1611 (m), 1524 (m), 1477 (m), 1441 (w), 1352 (m), 1221 (w), 1196 (w), 907 (s), 818 (s), 758 (s); δ_H (500 MHz, $CDCl_3$) 7.46-7.34 (4H, m, $C_{Ar}H$), 7.13-7.09 (2H, m, $C_{Ar}H$), 7.09-7.04 (4H, m, $C_{Ar}H$), 6.67-6.61 (2H, m, $C_{Ar}H$), 2.95 (6H, s, NCH_3), 2.35 (3H, s, CH_3); δ_C (125 MHz, $CDCl_3$) 149.1 ($C_{Ar}NCH_3$), 140.6 (C_{Ar}), 140.3 (2C, C_{Ar}), 139.2 (C_{Ar}), 135.9 (C_{Ar}), 130.8 ($C_{Ar}H$), 130.7 (2C, $C_{Ar}H$), 130.6 ($C_{Ar}H$), 129.8 (2C, $C_{Ar}H$), 128.8 (2C, $C_{Ar}H$), 127.4 ($C_{Ar}H$), 126.7 ($C_{Ar}H$), 112.9 (2C, $C_{Ar}H$), 40.7 (2C, NCH_3), 21.3 ($C_{Ar}CH_3$); *m/z* HRMS (ESI$^+$) $C_{21}H_{22}N^+$ ($[M+H]^+$) requires 288.1747; found 288.1741 (-2.1ppm).

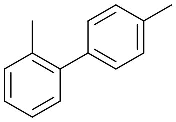


Table **S-4**, Entry 9:

Prepared following **general procedure** at 100 °C for 64 hours with 2-methylanisole (61.1 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (26.7 mg, 0.05 mmol) and *p*-tolylmagnesium bromide (2.10 mL, 1.05 mmol, 0.5 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave a mixture of 2,4'-dimethyl-1,1'-biphenyl and 1-methylnaphthalene (93:7 ^{1}H NMR) (36.8 mg) [total product = 38 %] as a colourless oil with spectroscopic data in accordance with the literature.[15]

δ_H (500 MHz, $CDCl_3$); 7.29-7.22 (8H, m, $C_{Ar}H$), 2.42 (3H, s, $C_{Ar}CH_3$), 2.30 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 142.0 (C_{Ar}), 139.1 (C_{Ar}), 136.5 (C_{Ar}), 135.5 (C_{Ar}), 130.4 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 129.2 (2C, $C_{Ar}H$), 128.9 (2C, $C_{Ar}H$), 127.2 ($C_{Ar}H$), 125.9 ($C_{Ar}H$), 21.3 ($C_{Ar}CH_3$), 20.7 ($C_{Ar}CH_3$); *m/z* HRMS (EI$^+$) $C_{14}H_{14}^+$ ($[M]^+$) requires 182.1096; found 182.1098 (+1.1 ppm).

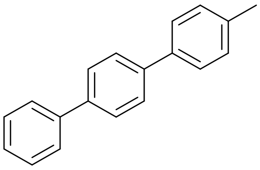


Table **S-4**, Entry 11:

Prepared following **general procedure** at 100 °C for 16 hours with 4-methoxybiphenyl (92.1 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (13.4 mg, 0.025 mmol) and *p*-tolylmagnesium bromide (1.50 mL, 0.75 mmol, 0.5 M in Et_2O). Purification *via* filtration through a small plug of silica gel (eluent EtOAc), concentration under reduced pressure and trituration with petroleum ether (3 x 10 mL) gave 4-methyl-1,1':4',1"-terphenyl (79.0 mg, 65 %) as a white solid with spectroscopic data in accordance with the literature.[16]

mp 210-213 °C {lit[17] 214 °C}; δ_H (500 MHz, $CDCl_3$); 7.67 (4H, s, C_{Ar}*H*), 7.65 (2H, d, *J* 7.5, C_{Ar}*H*), 7.55 (2H, d, *J* 7.9, C_{Ar}*H*), 7.46 (2H, t, *J* 7.6, C_{Ar}*H*), 7.36 (1H, t, *J* 7.4, C_{Ar}*H*), 7.28 (2H, d, *J* 7.8, C_{Ar}*H*), 2.42 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 140.9 (*C*$_{Ar}$), 140.2 (*C*$_{Ar}$), 139.9 (*C*$_{Ar}$), 137.9 (*C*$_{Ar}$), 137.3 (*C*$_{Ar}$), 129.7 (2C, *C*$_{Ar}$H), 128.9 (2C, *C*$_{Ar}$H), 127.6 (2C, *C*$_{Ar}$H), 127.4 (3C, *C*$_{Ar}$H), 127.2 (2C, *C*$_{Ar}$H), 127.0 (2C, *C*$_{Ar}$H), 21.3 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{19}H_{16}^+$ ($[M]^+$) requires 244.1252; found 244.1253 (+0.4 ppm).

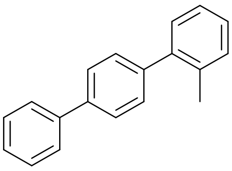


Table **S-4**, Entry 12:

Prepared following **general procedure** at 100 °C for 16 hours with 4-methoxybiphenyl (92.1 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (13.4 mg, 0.025 mmol) and *o*-tolylmagnesium bromide (375 µL, 0.75 mmol, 2.0 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 2-methyl-1,1':4',1"-terphenyl (52.2 mg, 43 %) as a white solid with spectroscopic data in accordance with the literature.[18]

mp 87-88 °C {lit[19] 88-89 °C}; δ_H (500 MHz, $CDCl_3$); 7.70-7.64 (4H, m, C_{Ar}*H*), 7.51-7.45 (2H, m, C_{Ar}*H*), 7.45-7.41 (2H, m, C_{Ar}*H*), 7.41-7.36 (1H, m, C_{Ar}*H*), 7.33-7.27 (4H, m, C_{Ar}*H*), 2.35 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 141.6 (*C*$_{Ar}$), 141.1 (*C*$_{Ar}$), 141.0 (*C*$_{Ar}$), 139.7 (*C*$_{Ar}$), 135.5 (*C*$_{Ar}$), 130.5 (*C*$_{Ar}$H), 130.0 (*C*$_{Ar}$H), 129.8 (2C, *C*$_{Ar}$H), 128.9 (2C, *C*$_{Ar}$H), 127.5 (*C*$_{Ar}$H), 127.4 (*C*$_{Ar}$H), 127.2 (2C, *C*$_{Ar}$H), 126.9 (2C, *C*$_{Ar}$H), 126.0 (*C*$_{Ar}$H), 20.7 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{19}H_{16}^+$ ($[M]^+$) requires 244.1252; found 244.1250 (-0.8 ppm).

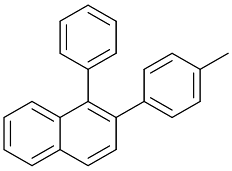


Table **S-4**, Entry 16:

Prepared following **general procedure** at 100 °C for 16 hours with 1-phenyl-2-methoxynaphthalene (117.2 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (2.7 mg, 0.005 mmol) and *p*-tolylmagnesium bromide (1.50 mL, 0.75 mmol, 0.5 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 1-phenyl-2-(*p*-tolyl)naphthalene (122.2 mg, 83 %) as a white crystalline solid.

mp 92-93 °C; ν_{max} (ATR) 2920 (w), 1503 (w), 1441 (w), 1373 (w), 1024 (w), 957 (w), 829 (w), 806 (s), 789 (m), 758 (m); δ_H (500 MHz, $CDCl_3$) 7.97-7.91 (2H, m, $C_{Ar}H$), 7.68 (1H, d, *J* 8.6, $C_{Ar}H$), 7.63-7.59 (1H, m, $C_{Ar}H$), 7.53-7.48 (1H, m, $C_{Ar}H$), 7.45-7.40 (1H, m, $C_{Ar}H$), 7.37-7.29 (3H, m, $C_{Ar}H$), 7.26-7.22 (2H, m, $C_{Ar}H$), 7.08 (2H, d, *J* 8.0, $C_{Ar}H$), 7.02 (2H, d, *J* 8.0, $C_{Ar}H$), 2.31 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 139.3 (C_{Ar}), 139.1 (C_{Ar}), 138.3 (C_{Ar}), 137.6 (C_{Ar}), 135.9 (C_{Ar}), 132.8 (C_{Ar}), 132.8 (C_{Ar}), 131.6 (2C, $C_{Ar}H$), 130.1 (2C, $C_{Ar}H$), 128.6 ($C_{Ar}H$), 128.5 (2C, $C_{Ar}H$), 128.0 (2C, $C_{Ar}H$), 128.0 ($C_{Ar}H$), 127.7 ($C_{Ar}H$), 126.9 ($C_{Ar}H$), 126.8 ($C_{Ar}H$), 126.3 ($C_{Ar}H$), 125.7 ($C_{Ar}H$), 21.2 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{23}H_{18}^+$ ($[M]^+$) requires 294.1409; found 294.1413 (+1.4 ppm).

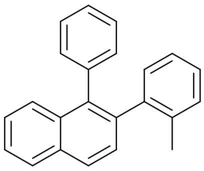


Table **S-4**, Entry 20:

Prepared following **general procedure** at 100 °C for 16 hours with 1-phenyl-2-methoxynaphthalene (117.2 mg, 0.50 mmol), 2-MeTHF (2.25 mL), $NiCl_2(P^nBu_3)_2$ (2.7 mg, 0.005 mmol) and *o*-tolylmagnesium bromide (375 µL, 0.75 mmol, 2.0 M in Et_2O). Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 1-phenyl-2-(*o*-tolyl)naphthalene (87.5 mg, 59 %) as a white crystalline solid.

mp 120-121 °C; ν_{max} (ATR) 1489 (w), 1375 (w), 870 (w), 820 (m), 760 (m); δ_H (500 MHz, $CDCl_3$) 7.96 (1H, d, *J* 8.1, $C_{Ar}H$), 7.93 (1H, d, *J* 8.5, $C_{Ar}H$), 7.69 (1H, d, *J* 8.5, $C_{Ar}H$), 7.55-7.50 (1H, m, $C_{Ar}H$), 7.47-7.40 (2H, m, $C_{Ar}H$), 7.31-7.22 (4H, m, $C_{Ar}H$), 7.16-7.12 (1H, m, $C_{Ar}H$), 7.12-7.09 (2H, m, $C_{Ar}H$), 7.06-7.01 (2H, m, $C_{Ar}H$), 2.09 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 141.6 (C_{Ar}), 138.9 (C_{Ar}), 138.5 (C_{Ar}), 138.1 (C_{Ar}), 135.8 (C_{Ar}), 133.0 (C_{Ar}), 132.8 (C_{Ar}), 131.6 ($C_{Ar}H$), 130.8 ($C_{Ar}H$), 130.2 ($C_{Ar}H$), 129.6 ($C_{Ar}H$), 128.3 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 127.8 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 127.3 ($C_{Ar}H$), 126.9 ($C_{Ar}H$), 126.9 ($C_{Ar}H$), 126.8 ($C_{Ar}H$), 126.3 ($C_{Ar}H$), 125.7 ($C_{Ar}H$), 124.9 ($C_{Ar}H$), 20.6 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{23}H_{18}^+$ ($[M]^+$) requires 294.1409; found 294.1409 (±0.0 ppm).

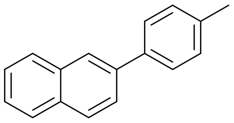


Table **S-4**, Entry 21:

$NiCl_2(PCy_3)_2$ (17.3 mg, 0.025 mmol) was added to a flame dried Schlenk flask under an inert atmosphere, equipped with a stirrer bar. 2-methoxynaphthalene (79.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a separate flame dried Schlenk flask under an inert atmosphere. 2-MeTHF (2.25 mL) was then added to the Schlenk flask containing 2-methoxynaphthalene and internal standard to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution was added to the nickel catalyst *via* syringe. *p*-tolylmagnesium bromide (2.10 mL, 1.05 mmol, 0.5 M in Et_2O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 80 °C for 16 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with $CDCl_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^{1}H NMR was run to assess the ratio between SM and desired product. Saturated aqueous ammonium chloride (5 mL) was added to the reaction mixture and the aqueous phase was extracted three times with ethyl acetate (3 x 5 mL), dried over sodium sulfate and concentrated under reduced pressure. Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 2-(*p*-tolyl)naphthalene (97.4 mg, 89 %) as a white crystalline solid with spectroscopic data in accordance with the literature.[16]

mp 93-94 °C {lit[20] 92-94 °C}; δ_H (500 MHz, $CDCl_3$); 8.07 (1H, s, $C_{Ar}H$), 7.96-7.87 (3H, m, $C_{Ar}H$), 7.79 (1H, dd, *J* 8.5, 1.9, $C_{Ar}H$), 7.67 (2H, d, *J* 7.9, $C_{Ar}H$), 7.57-7.48 (2H, m, $C_{Ar}H$), 7.34 (2H, d, *J* 7.9, $C_{Ar}H$), 2.47 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 138.6 (C_{Ar}), 138.3 (C_{Ar}), 137.3 (C_{Ar}), 133.8 (C_{Ar}), 132.6 (C_{Ar}), 129.7 (2C, C_{Ar}H), 128.5 (C_{Ar}H), 128.3 (C_{Ar}H), 127.8 (C_{Ar}H), 127.4 (2C, C_{Ar}H), 126.4 (C_{Ar}H), 125.9 (C_{Ar}H), 125.7 (C_{Ar}H), 125.6 (C_{Ar}H), 21.3 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{17}H_{14}^+$ ($[M]^+$) requires 218.1096; found 218.1094 (-0.9 ppm).

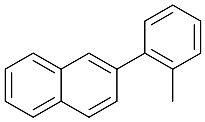


Table **S-4**, Entry 41:

$NiCl_2(P^nBu_3)_2$ (2.7 mg, 0.005 mmol) was added to a flame dried Schlenk flask under an inert atmosphere, equipped with a stirrer bar. 2-methoxynaphthalene (79.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a separate flame dried Schlenk flask under an inert atmosphere. 2-MeTHF (2.25 mL) was then added to the Schlenk flask containing 2-methoxynaphthalene and internal standard to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^1H NMR (to calibrate the ratio of internal standard to starting material). The solution was added to the nickel catalyst *via* syringe. *o*-tolylmagnesium bromide (375 μL, 0.75 mmol, 2.0 M in Et_2O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 80 °C for 16 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with $CDCl_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^1H NMR was run to assess the ratio between SM and desired product. Saturated aqueous ammonium chloride (5 mL) was added to the reaction mixture and the aqueous phase was extracted three times with ethyl acetate (3 x 5 mL), dried over sodium sulfate and concentrated under reduced pressure. Purification *via* column chromatography on silica gel (eluent petroleum ether) gave 2-(*o*-tolyl)naphthalene (89.8 mg, 82 %) as a colourless oil with spectroscopic data in accordance with the literature.[21]

δ_H (500 MHz, $CDCl_3$); 7.95-7.89 (3H, m, $C_{Ar}H$), 7.83 (1H, s, $C_{Ar}H$), 7.58-7.51 (3H, m, $C_{Ar}H$), 7.40-7.31 (4H, m, $C_{Ar}H$), 2.37 (3H, s, $C_{Ar}CH_3$); δ_C (125 MHz, $CDCl_3$) 142.0 (C_{Ar}), 139.6 (C_{Ar}), 135.7 (C_{Ar}), 133.4 (C_{Ar}), 132.4 (C_{Ar}), 130.5 ($C_{Ar}H$), 130.1 ($C_{Ar}H$), 128.1 ($C_{Ar}H$), 127.9 ($C_{Ar}H$), 127.9 ($C_{Ar}H$), 127.8 ($C_{Ar}H$), 127.6 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 126.3 ($C_{Ar}H$), 126.0 ($C_{Ar}H$), 126.0 ($C_{Ar}H$), 20.7 ($C_{Ar}CH_3$); *m/z* HRMS (EI^+) $C_{17}H_{14}^+$ ($[M]^+$) requires 218.1096; found 218.1094 (-0.9 ppm).

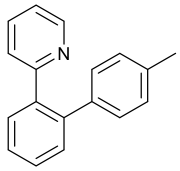
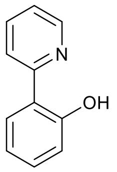


Table **S-5**, Entry 1:

To an oven dried microwave vial equipped with a stirrer bar was added 2-(2-methoxyphenyl)pyridine (46.31 mg, 0.25 mmol). The vial was sealed with a crimp cap and flushed with argon for 30 minutes. THF (1.13 mL) was then added to the vial to make a solution. *p*-tolylmagnesium bromide (1.2 mL, 0.60 mmol, 0.5 M in Et_2O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 80 °C for 67 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with $CDCl_3$. A ^1H NMR was run to assess the ratio between SM and desired product. The reaction mixture was then quenched with MeOH (3 mL) and concentrated under reduced pressure. Saturated aqueous ammonium chloride (3 mL) was added to the reaction mixture and the aqueous phase was extracted three times with ethyl acetate (3 x 3 mL), dried over sodium sulfate and concentrated under reduced pressure. Purification *via* column chromatography on silica gel (eluent EtOAc:petroleum ether, 20:80) gave 2-(4'-methyl-[1,1'-biphenyl]-2-yl)pyridine (43.3 mg, 71 %) as a light yellow oil with spectroscopic data in accordance with the literature.[22]

δ_H (500 MHz, $CDCl_3$); 8.66-8.63 (1H, m, $C_{Ar}H$), 7.71-7.66 (1H, m, $C_{Ar}H$), 7.48-7.42 (3H, m, $C_{Ar}H$), 7.40 (1H, td, *J* 7.6, 1.5, $C_{Ar}H$), 7.11 (1H, ddd, *J* 7.6, 4.9, 1.5, $C_{Ar}H$), 7.05 (4H, s, $C_{Ar}H$), 6.91 (1H, dt, *J* 7.6, 1.5, $C_{Ar}H$), 2.32 (3H, s, $C_{Ar}CH_3$); δ_C (100 MHz, $CDCl_3$) 159.5 ($C_{Ar}N$), 149.5 ($NC_{Ar}H$), 140.7 (C_{Ar}), 139.4 (C_{Ar}), 138.4 (C_{Ar}), 136.5 (C_{Ar}), 135.4 ($C_{Ar}H$), 130.6 ($C_{Ar}H$), 130.6 ($C_{Ar}H$), 129.7 (2C, $C_{Ar}H$), 128.9 (2C, $C_{Ar}H$), 128.6 ($C_{Ar}H$), 127.5 ($C_{Ar}H$), 125.6 ($C_{Ar}H$), 121.4 ($C_{Ar}H$), 21.2 ($C_{Ar}CH_3$); *m/z* HRMS (ESI^+) $C_{18}H_{16}N^+$ ($[M+H]^+$) requires 246.1277; found 246.1272 (-2.0 ppm).



2-(pyridine-2-yl)phenol as a light yellow oil with spectroscopic data in accordance with the literature.[23]

δ_H (500 MHz, $CDCl_3$); 14.38 (1H, br s, $C_{Ar}OH$), 8.52-8.50 (1H, m, $C_{Ar}H$), 7.92 (1H, d, *J* 8.2, $NC_{Ar}H$), 7.86-7.78 (2H, m, $C_{Ar}H$), 7.31 (1H, ddd, *J* 8.3, 7.2, 1.4, $C_{Ar}H$), 7.27-7.22 (1H, m, $C_{Ar}H$), 7.04 (1H, dd, *J* 8.3, 1.4, $C_{Ar}H$), 6.91 (1H, ddd, *J* 8.3, 7.2, 1.4, $C_{Ar}H$); δ_C (125 MHz, $CDCl_3$) 160.1 ($C_{Ar}OH$), 158.0 ($C_{Ar}N$), 145.9 ($NC_{Ar}H$), 137.9 ($C_{Ar}H$), 131.6 ($C_{Ar}H$), 126.2 ($C_{Ar}H$), 121.6 ($C_{Ar}H$), 119.2 ($C_{Ar}H$), 118.9 ($C_{Ar}H$), 118.7 ($C_{Ar}H$); *m/z* HRMS (ESI^+) $C_{11}H_{10}NO^+$ ($[M+H]^+$) requires 172.0757; found 172.0751 (-3.4 ppm).

Modifications of ***general procedure***

Table **S-1**, Entry 1:

In a glovebox $Ni(cod)_2$ (6.9 mg, 0.025 mmol) was added to an oven dried microwave vial equipped with a stirrer bar. The vial was sealed with a crimp cap and removed from the glovebox. 2-methoxybiphenyl (92.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a flame dried Schlenk flask under an inert atmosphere. 2-MeTHF (2.25 mL) was then added to the Schlenk flask to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^1H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to the microwave vial containing $Ni(cod)_2$. *p*-tolylmagnesium bromide (2.10 mL, 1.05 mmol, 0.5 M in Et_2O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 100 °C for 16 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with $CDCl_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^1H NMR was run to assess the ratio between SM and desired product. The reaction was not worked-up.

Table **S-1**, Entry 3:

In a glovebox Ni(cod)$_2$ (6.9mg, 0.025 mmol) was added to an oven dried microwave vial equipped with a stirrer bar. The vial was sealed with a crimp cap and removed from the glovebox. 2-methoxybiphenyl (92.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a flame dried Schlenk flask under an inert atmosphere. 2-MeTHF (2.25 mL) was then added to the Schlenk flask to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to another Schlenk flask under an inert atmosphere containing tricyclohexylphopshine (15.4 mg, 0.055 mmol) and this subsequent solution was added to the microwave vial containing Ni(cod)$_2$. *p*-tolylmagnesium bromide (2.10 mL, 1.05 mmol, 0.5 M in Et$_2$O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 100 °C for 16 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with CDCl$_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^{1}H NMR was run to assess the ratio between SM and desired product. The reaction was not worked-up.

Table **S-3**, Entry 22:

In a glovebox Ni(cod)$_2$ (6.9 mg, 0.025 mmol) was added to an oven dried microwave vial equipped with a stirrer bar. The vial was sealed with a crimp cap and removed from the glovebox. 2-methoxybiphenyl (92.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a flame dried Schlenk flask under an inert atmosphere. 2-MeTHF (2.25 mL) was then added to the Schlenk flask to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to another Schlenk flask under an inert atmosphere containing tri^{n}butylphopshine (13.7 μL, 0.055 mmol) and this subsequent solution was added to the microwave vial containing Ni(cod)$_2$. *p*-tolylmagnesium bromide (2.10 mL, 1.05 mmol, 0.5 M in Et$_2$O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 100 °C for 16 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with CDCl$_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^{1}H NMR was run to assess the ratio between SM and desired product. The reaction was not worked-up.

Table **S-4**, Entry 38:

An oven dried microwave vial equipped with a stirrer bar was sealed with a crimp cap and flushed with argon for 30 minutes. In a flame dried Schlenk under an inert atmosphere, a stock solution containing 0.67 mgml^{-1} of $NiCl_2(P^nBu_3)_2$ in 2-MeTHF was created. An aliquot (1 mL) of this solution was then added to the microwave vial. 2-methoxynaphthalene (79.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a separate flame dried Schlenk flask under an inert atmosphere. 2-MeTHF (1.25 mL) was then added to the Schlenk flask to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to the microwave vial containing the nickel catalyst. *p*-tolylmagnesium bromide (1.5 mL, 0.75 mmol, 0.5 M in Et_2O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 100 °C for 16 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with $CDCl_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^{1}H NMR was run to assess the ratio between SM and desired product. The reaction was not worked-up.

Table **S-1**, Entry 6 and Table **S-2**, Entries 1-7:

NHC salt (10 mol%) was added to an oven dried microwave vial equipped with a stirrer bar and then sealed with a crimp cap and flushed with argon for 30 minutes. Under an inert atmosphere, a stock solution containing 6.88 mgml^{-1} of $Ni(cod)_2$ in 2-MeTHF was created. An aliquot (1 mL) of this solution was then added to the microwave vial. 2-methoxybiphenyl (92.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol, internal standard) were added to a separate flame dried Schlenk flask under an inert atmosphere. 2-MeTHF (1.25 mL) was then added to the Schlenk flask to make a solution. A t_0 sample (approximately 10 μL) was taken and analysed by ^{1}H NMR (to calibrate the ratio of internal standard to starting material). The solution containing the electrophile and internal standard was added to the microwave vial containing the nickel catalyst and NHC salt. *p*-tolylmagnesium bromide (2.10 mL, 1.05 mmol, 0.5 M in Et_2O) was added dropwise over 15 minutes and the reaction mixture was stirred vigorously in an oil bath at 100 °C for 16 hours. Upon cooling to rt, approximately 20 μL of the crude reaction mixture was added to a vial and quenched with $CDCl_3$. The resulting mixture was then filtered through a small cotton wool plug into an NMR tube and a ^1H NMR was run to assess the ratio between SM and desired product. The reaction was not worked-up.

4. An example of an ^{1}H NMR showing how conversion and yield were calculated in the Grignard cross-coupling of aromatic ethers

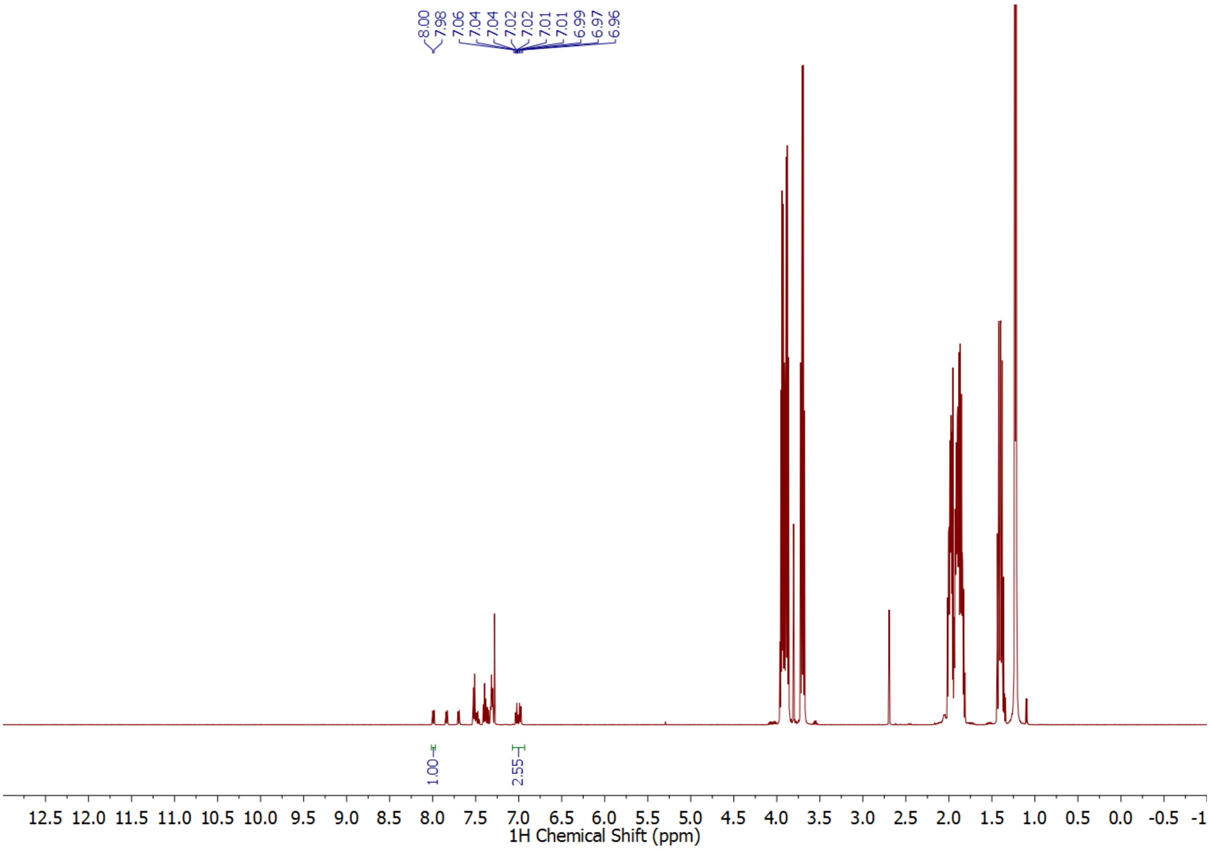


Figure S-1 - An ^{1}H NMR spectrum of a t_0 (Table **S-3**, Entry 13) showing the ratio between the doublet of 1-methylnaphthalene, the internal standard at 7.99 ppm and the multiplet of 2-methoxybiphenyl, the substrate at 7.06-6.96 ppm.

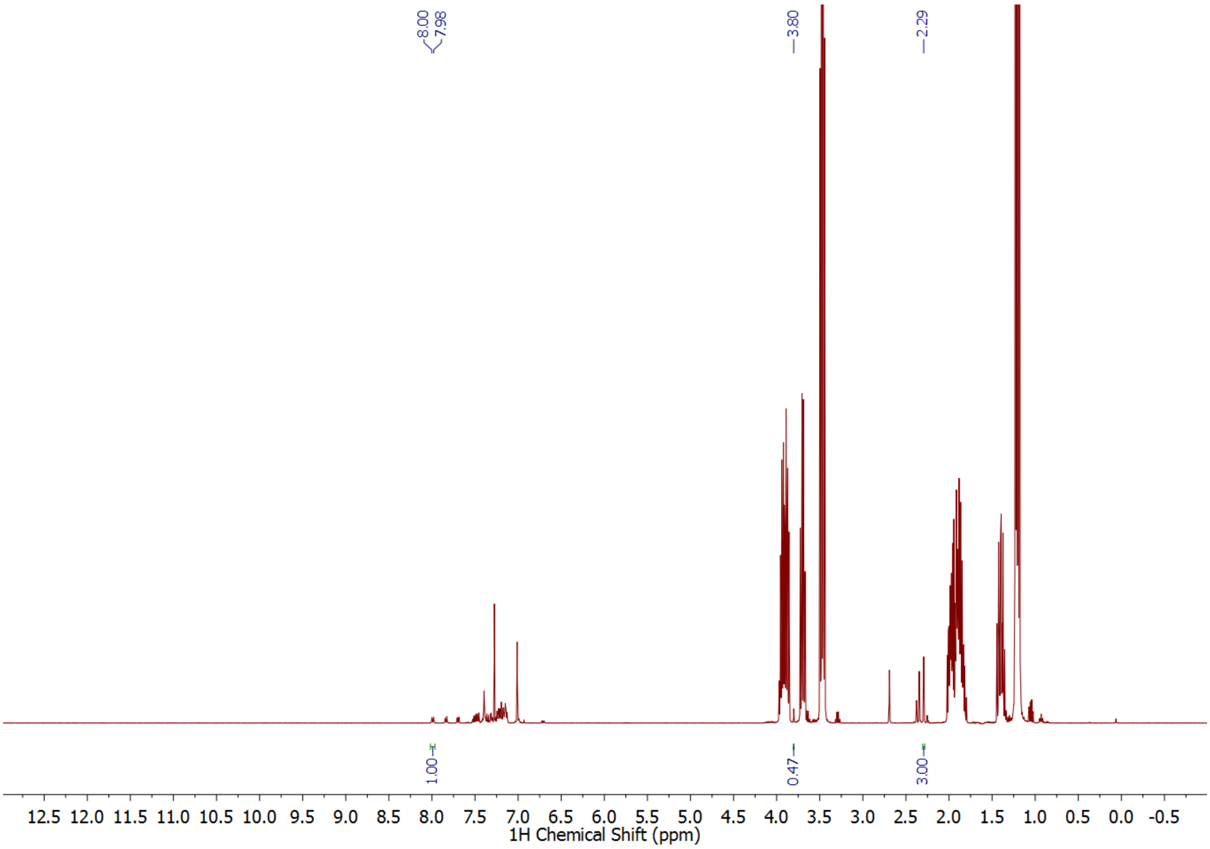


Figure S-2 - An ^{1}H NMR spectrum of a t_{final} (Table **S-3**, Entry 13) showing the ratio between the doublet of 1-methylnaphthalene, the internal standard at 7.99 ppm, the singlet of 2-methoxybiphenyl, the substrate at 3.80 ppm and the singlet of 4-methyl-1,1′:2′,1″-terphenyl, the product at 2.29 ppm.

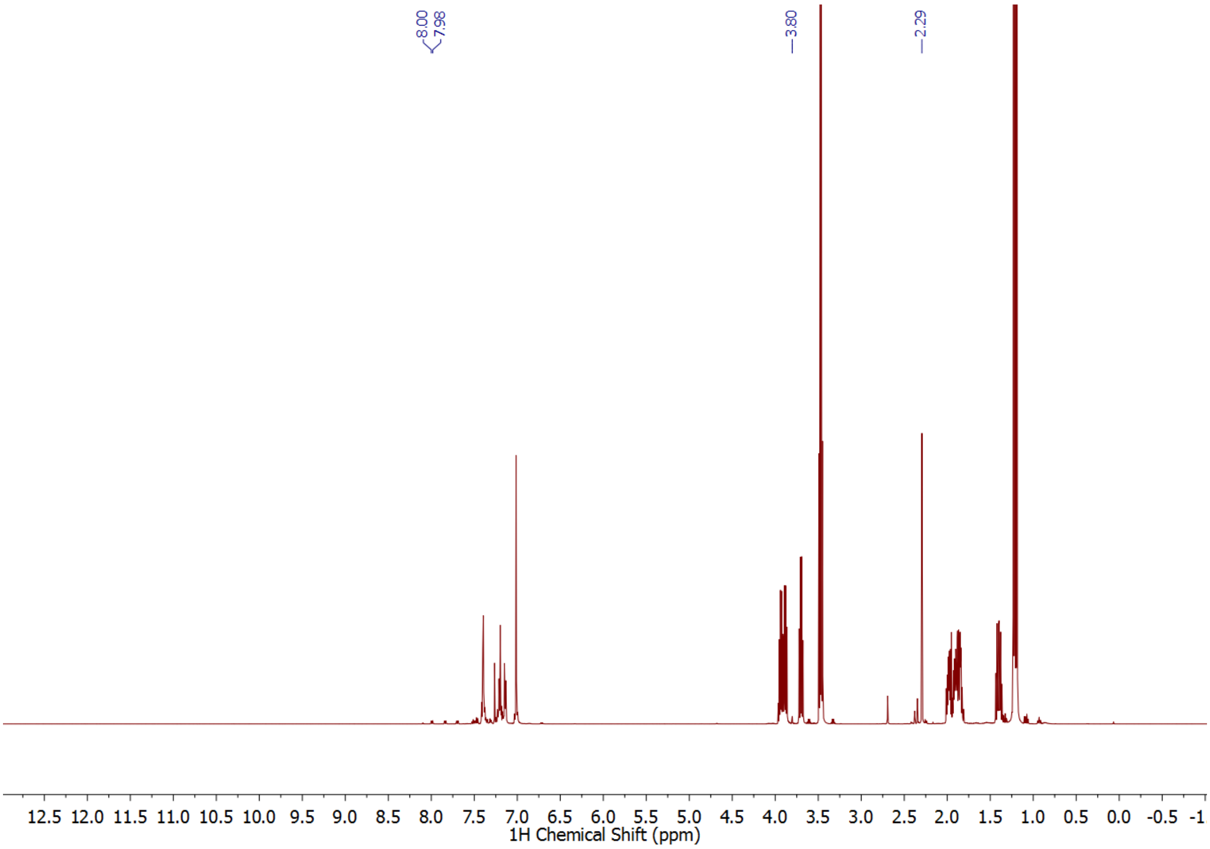
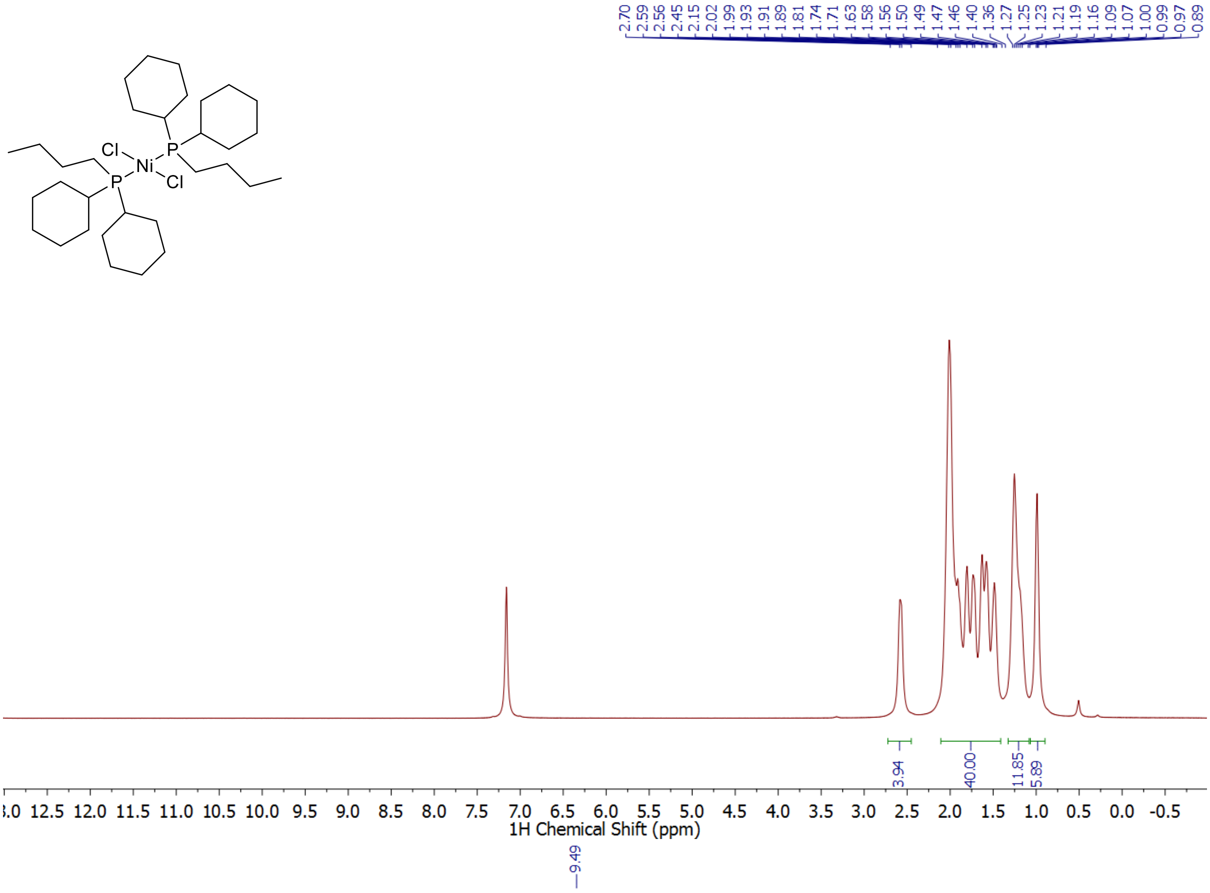
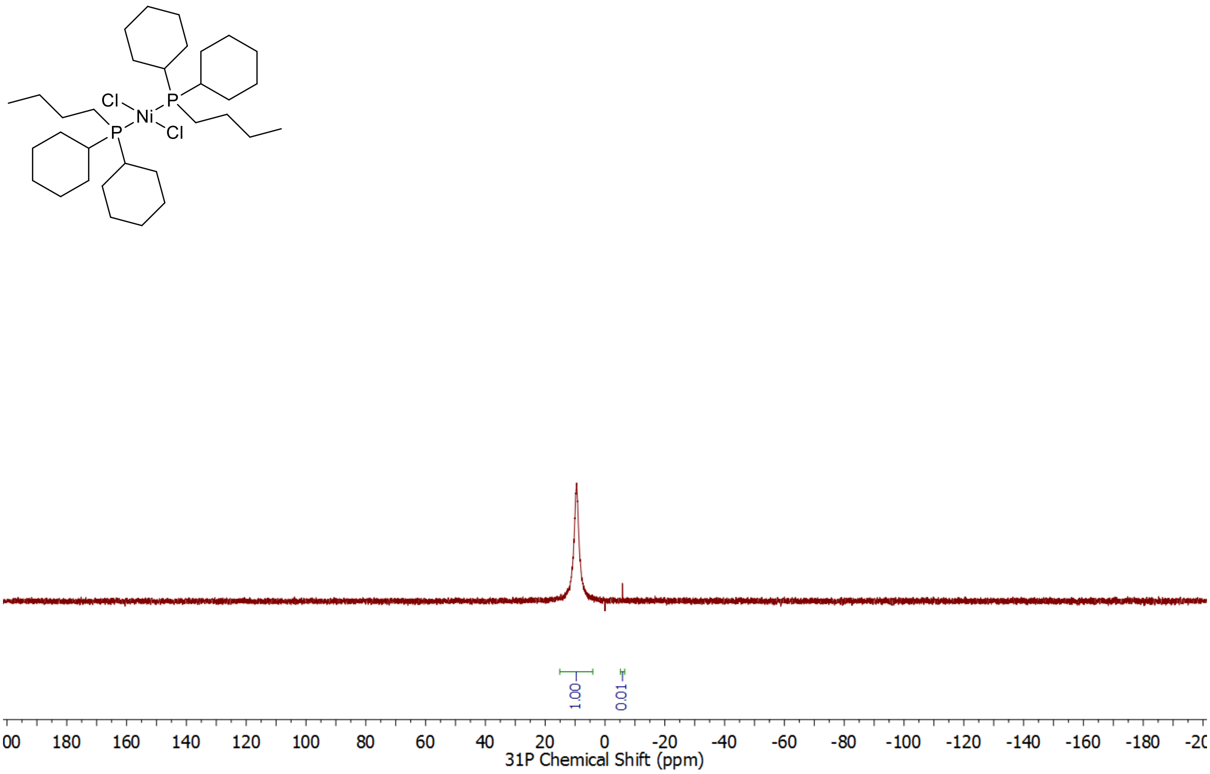


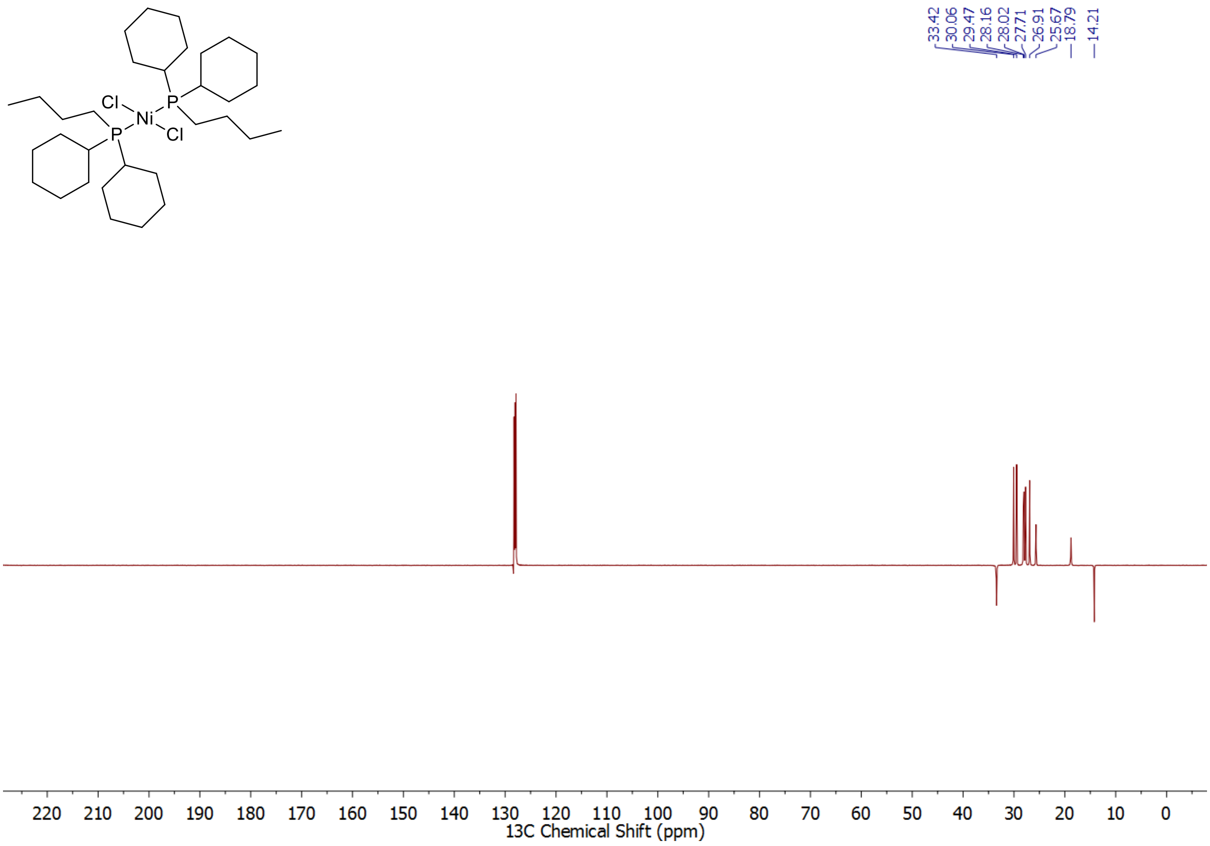
Figure S-3 - An ^{1}H NMR spectrum of a t_{final} (Table **S-3**, Entry 13) spiked with isolated product showing the increase in intensity of the singlet of 4-methyl-1,1′:2′,1″-terphenyl, the product at 2.29 ppm.

5. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra of all products

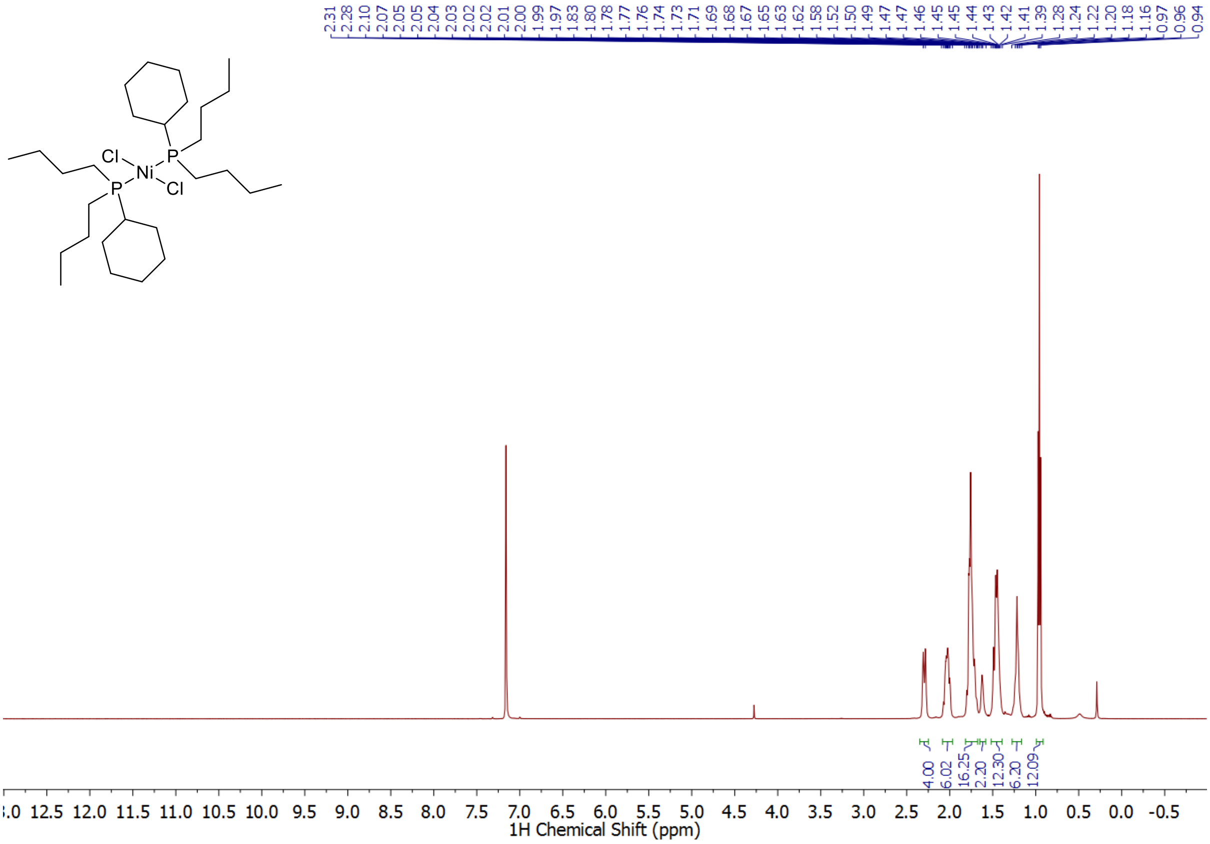
[$NiCl_2(PCy_2{}^nBu)_2$], **2**:

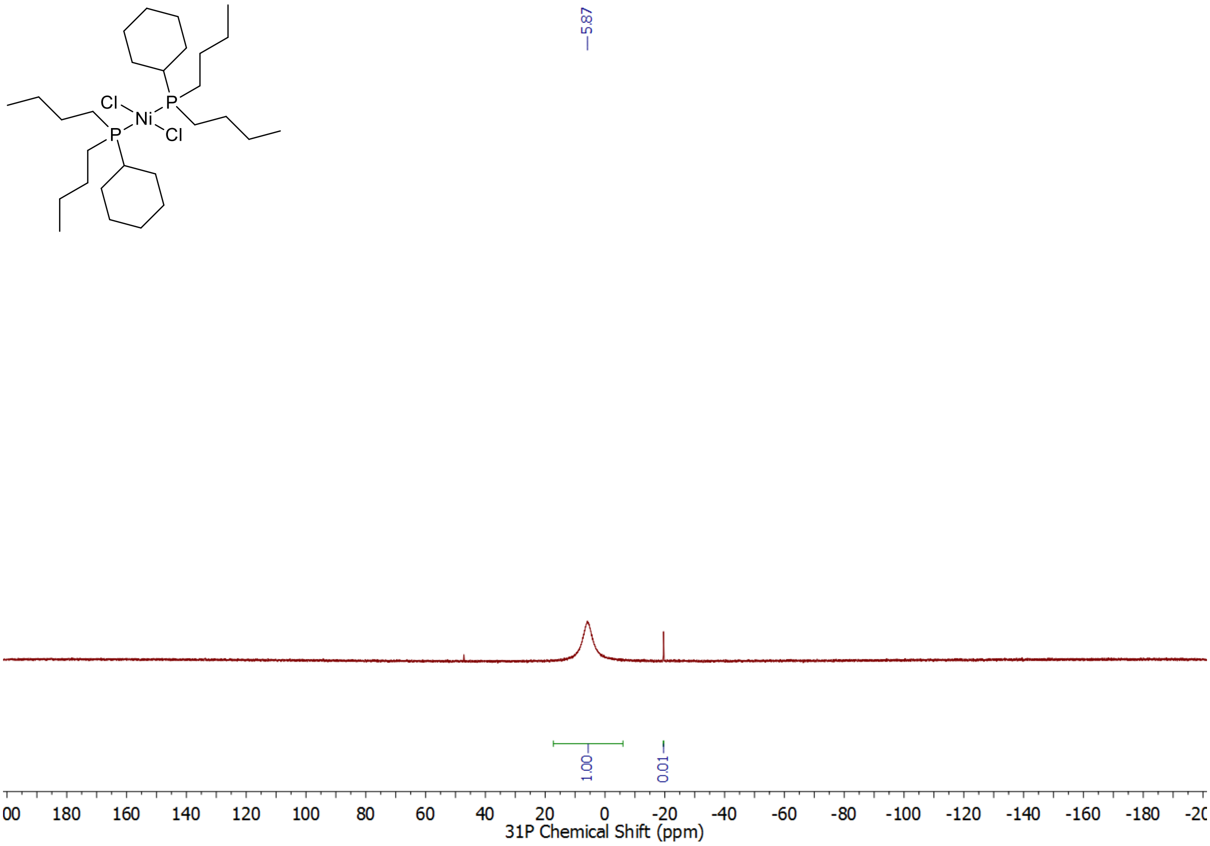






[NiCl$_2$(PCy^{n}Bu$_2$)$_2$], **3**:





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Cl
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0.01
00
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140
120
100
80
60
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20
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-20
-40
-60
-80
-100
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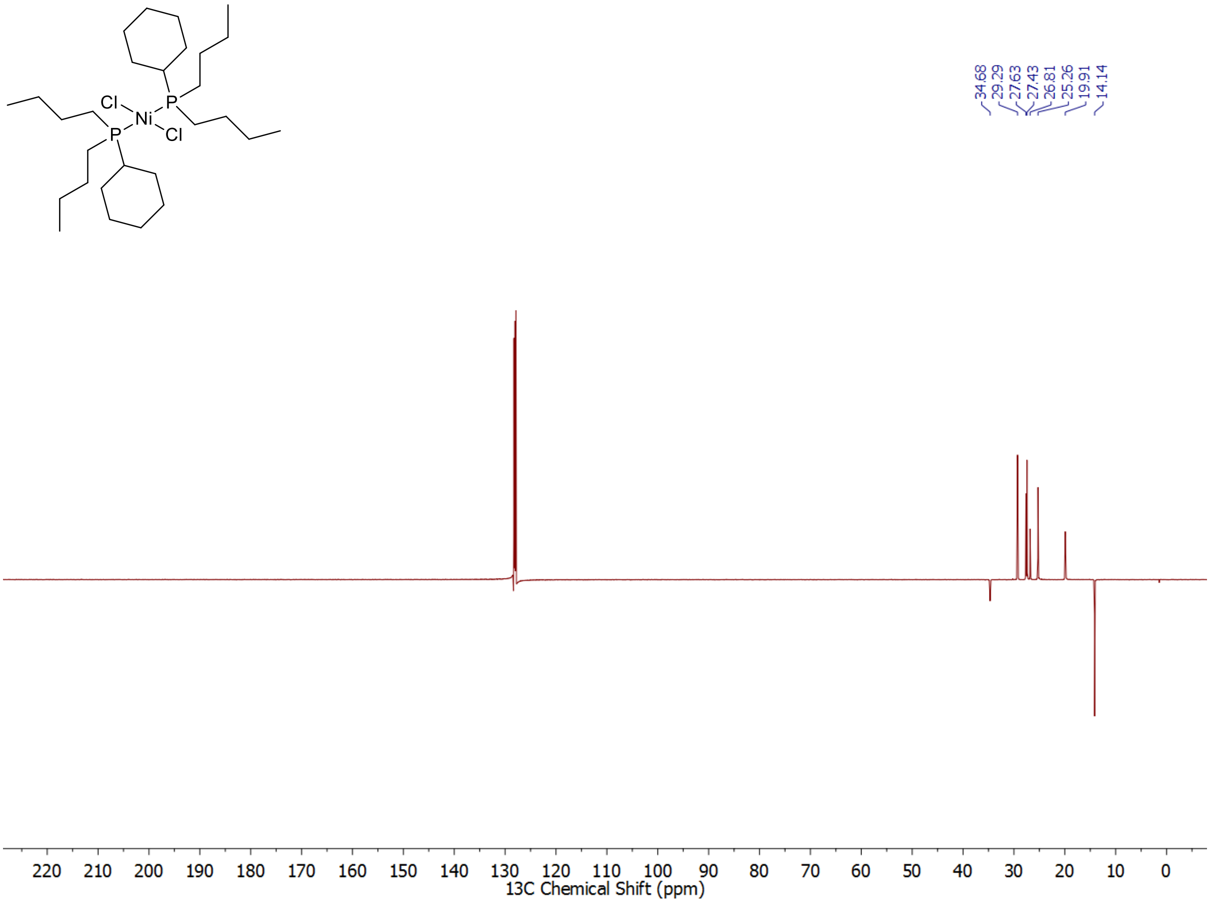
-140
-160
-180
-2C
31P Chemical Shift (ppm)



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Cl
P
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26.81
25.26
19.91
14.14
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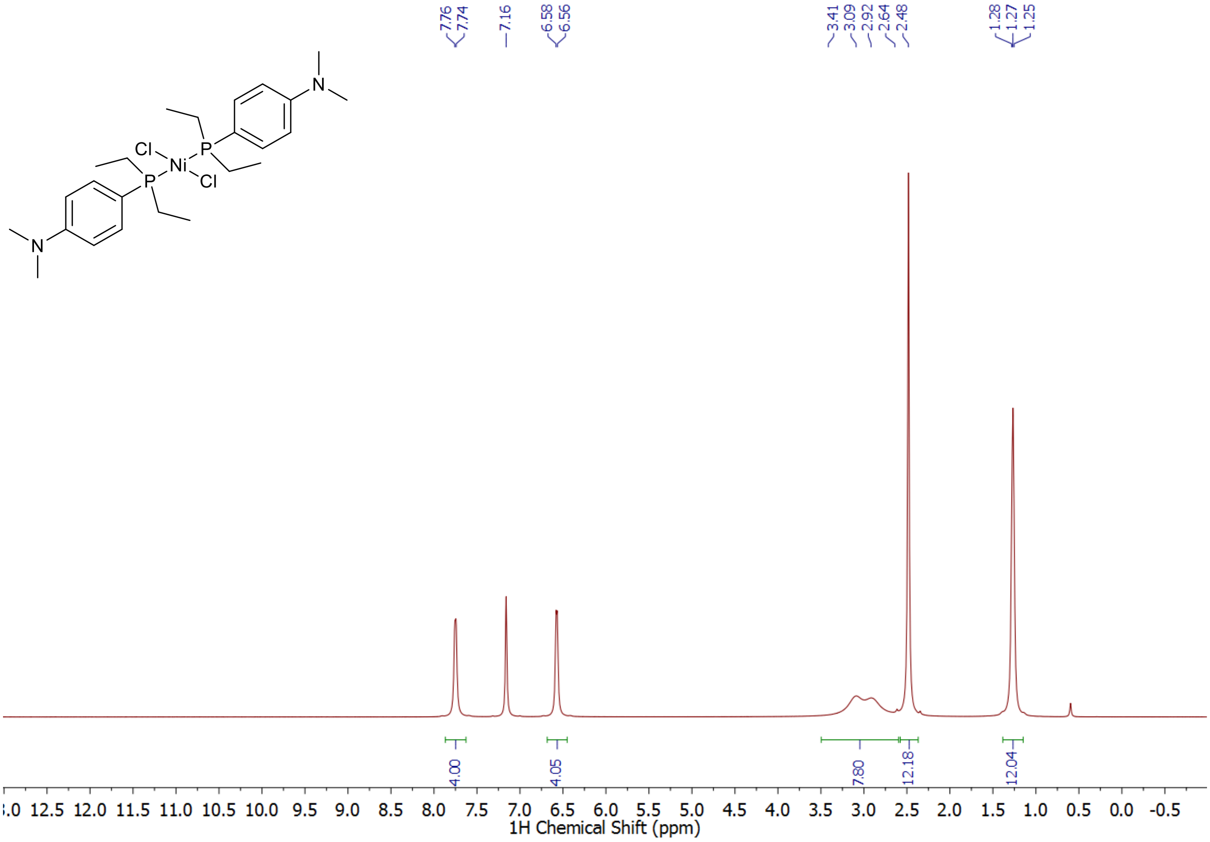
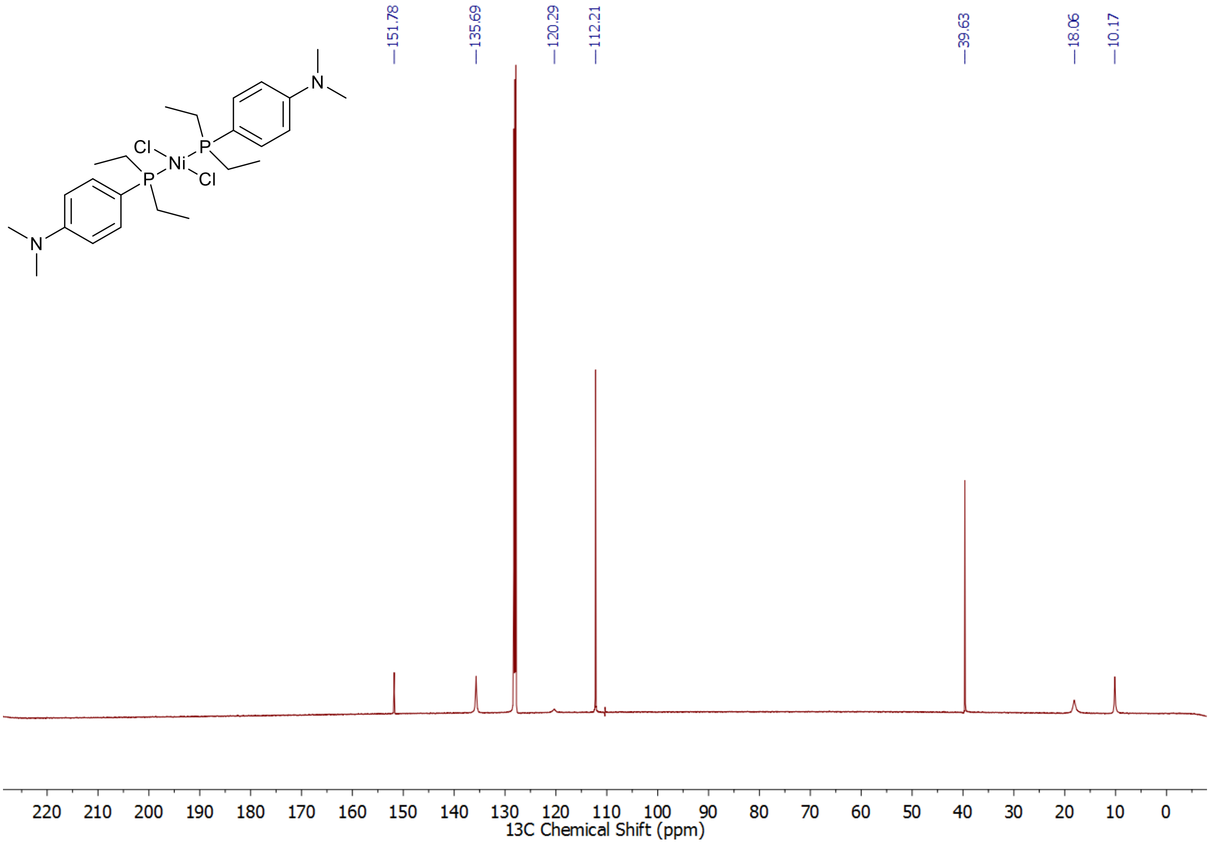
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
13C Chemical Shift (ppm)

[$NiCl_2(PEt_2Ar)_2$], Ar = 4-(NMe_2)C_6H_4, **4**:





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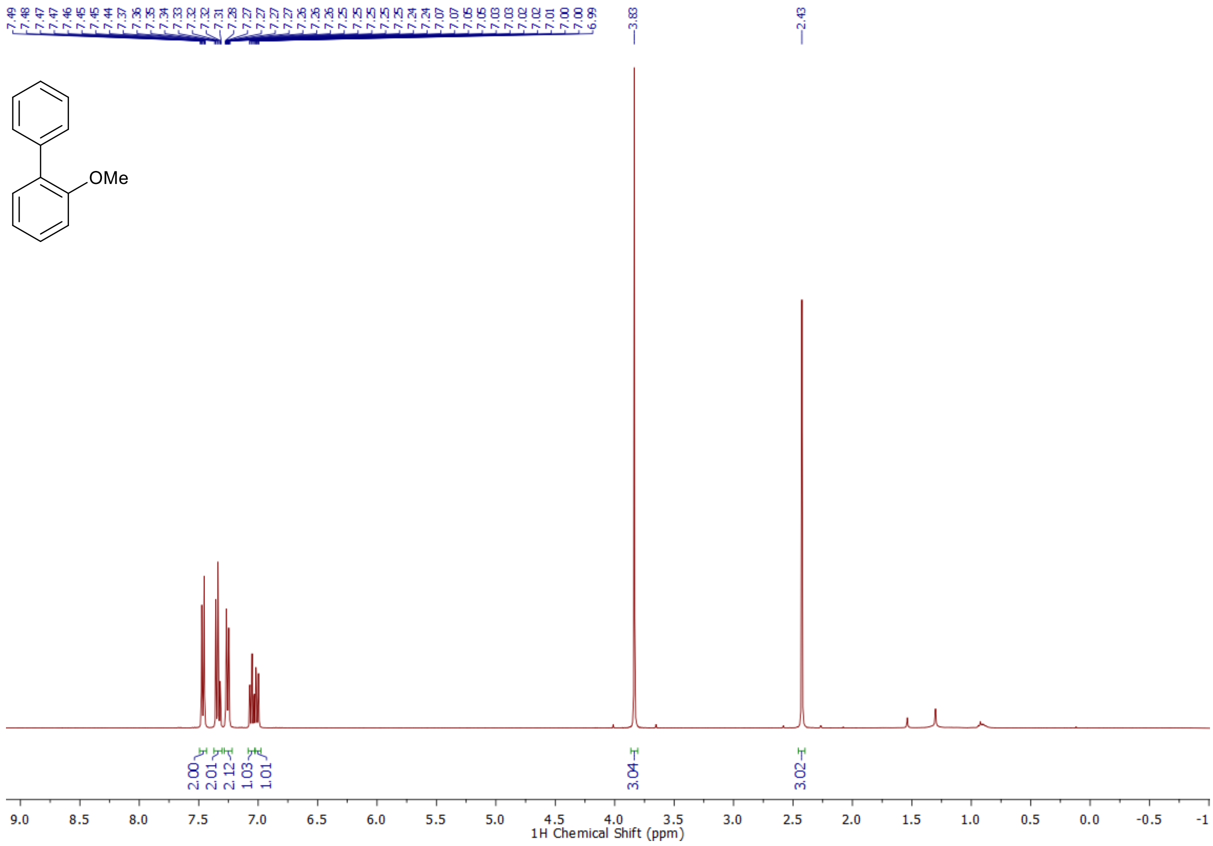

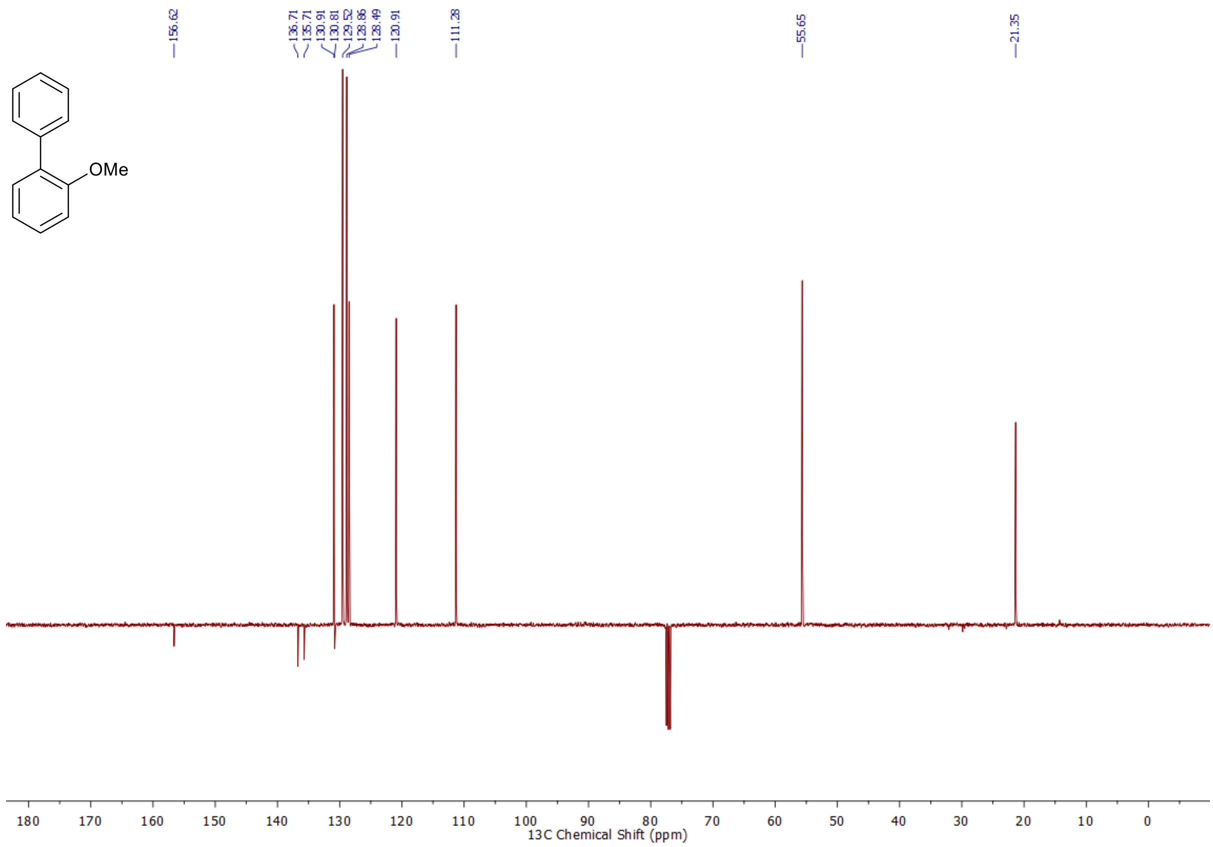

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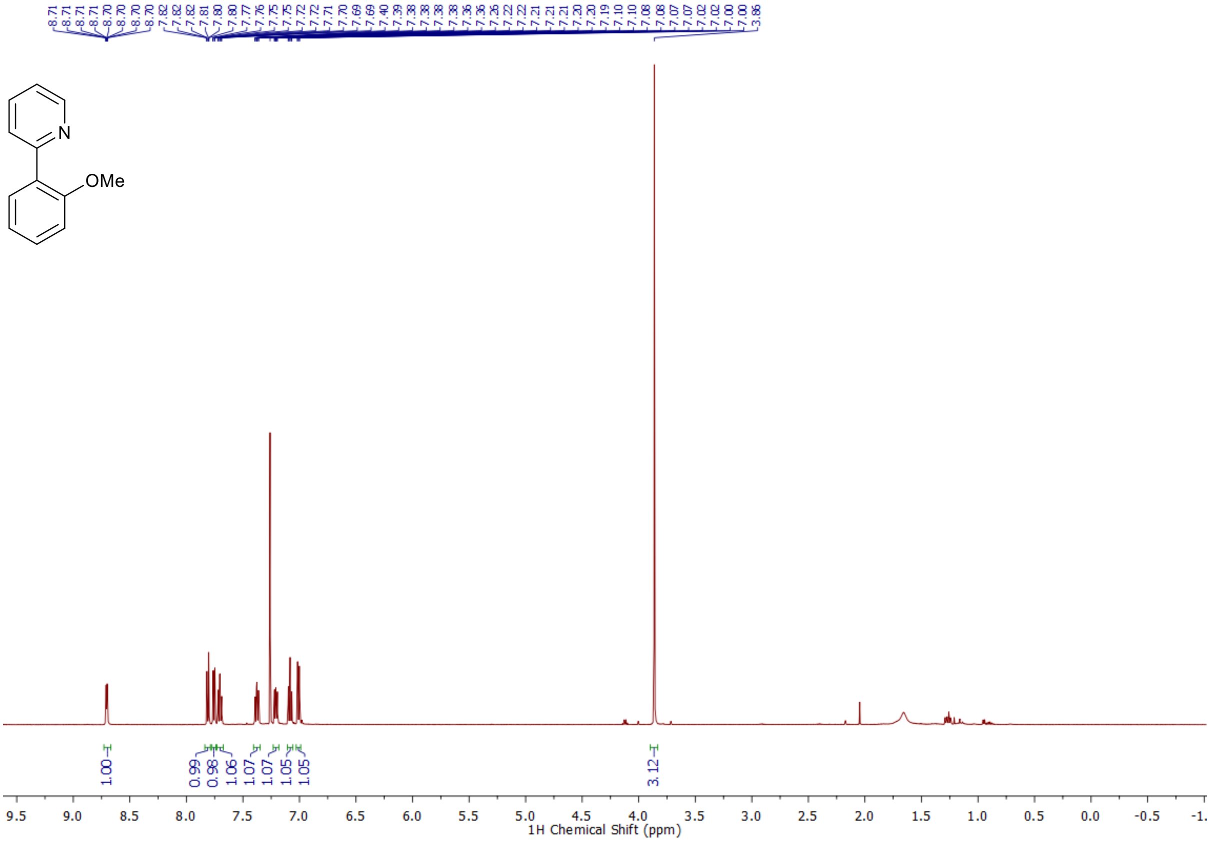

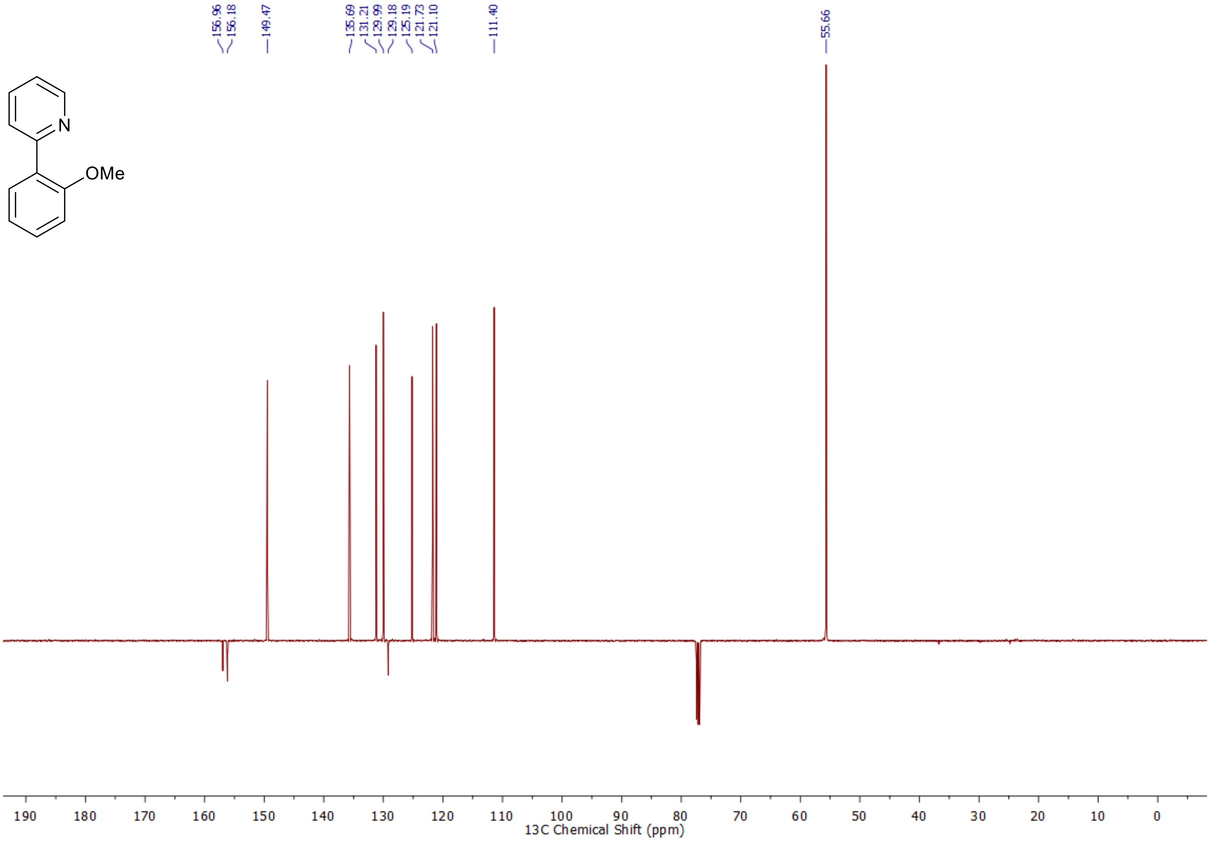

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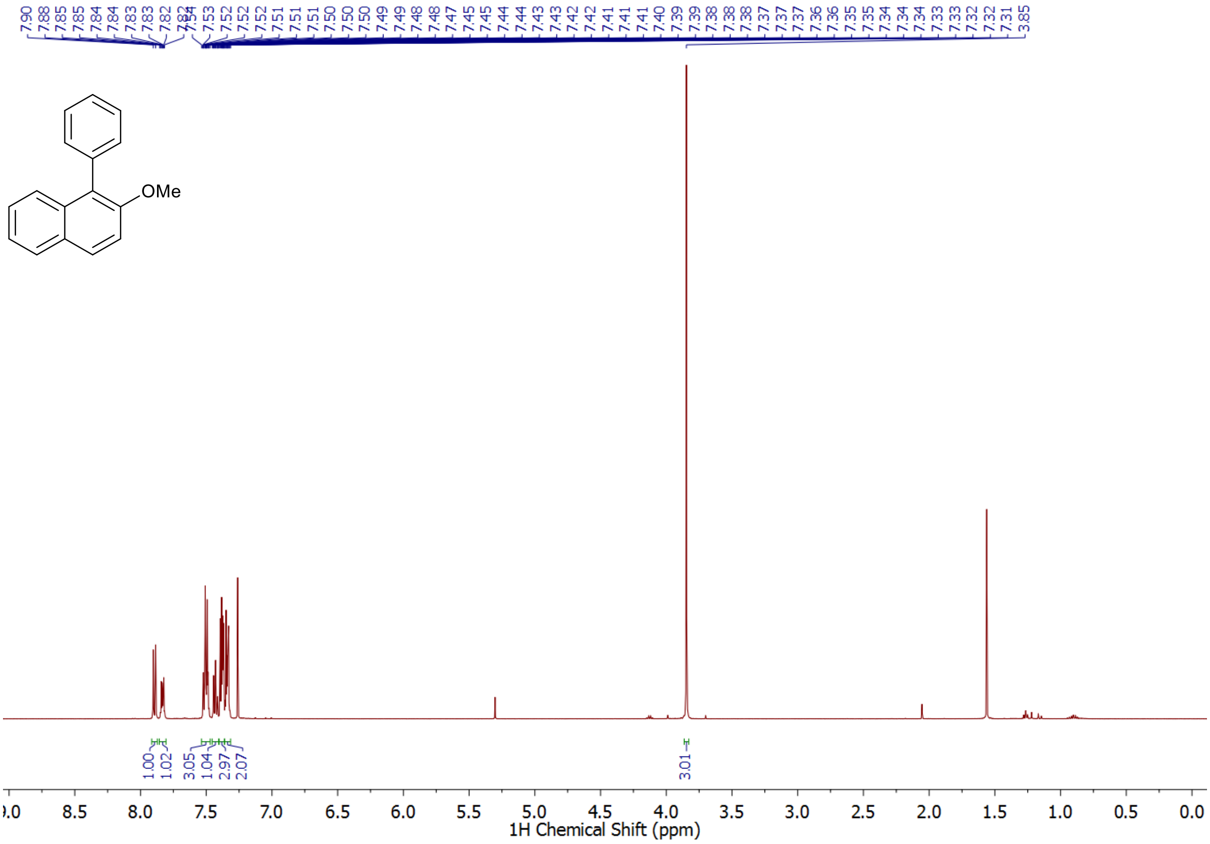

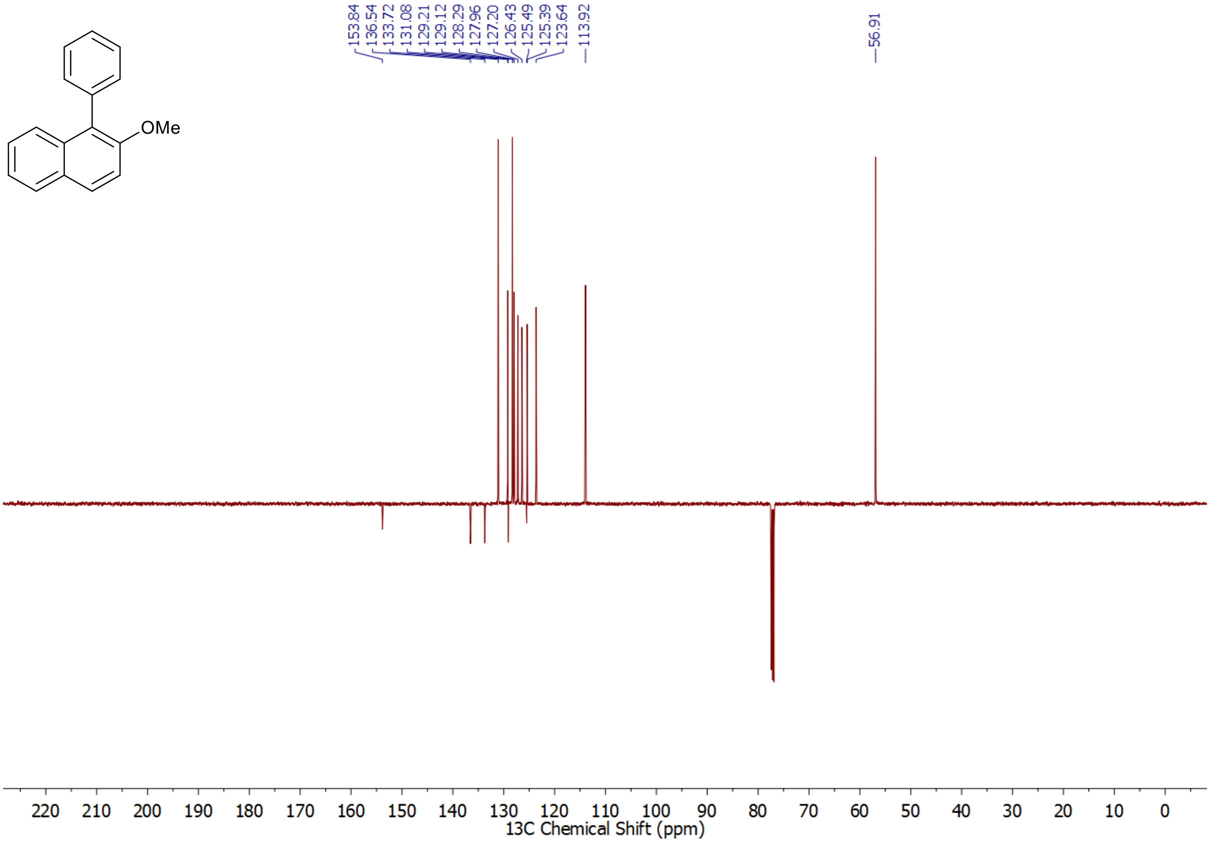

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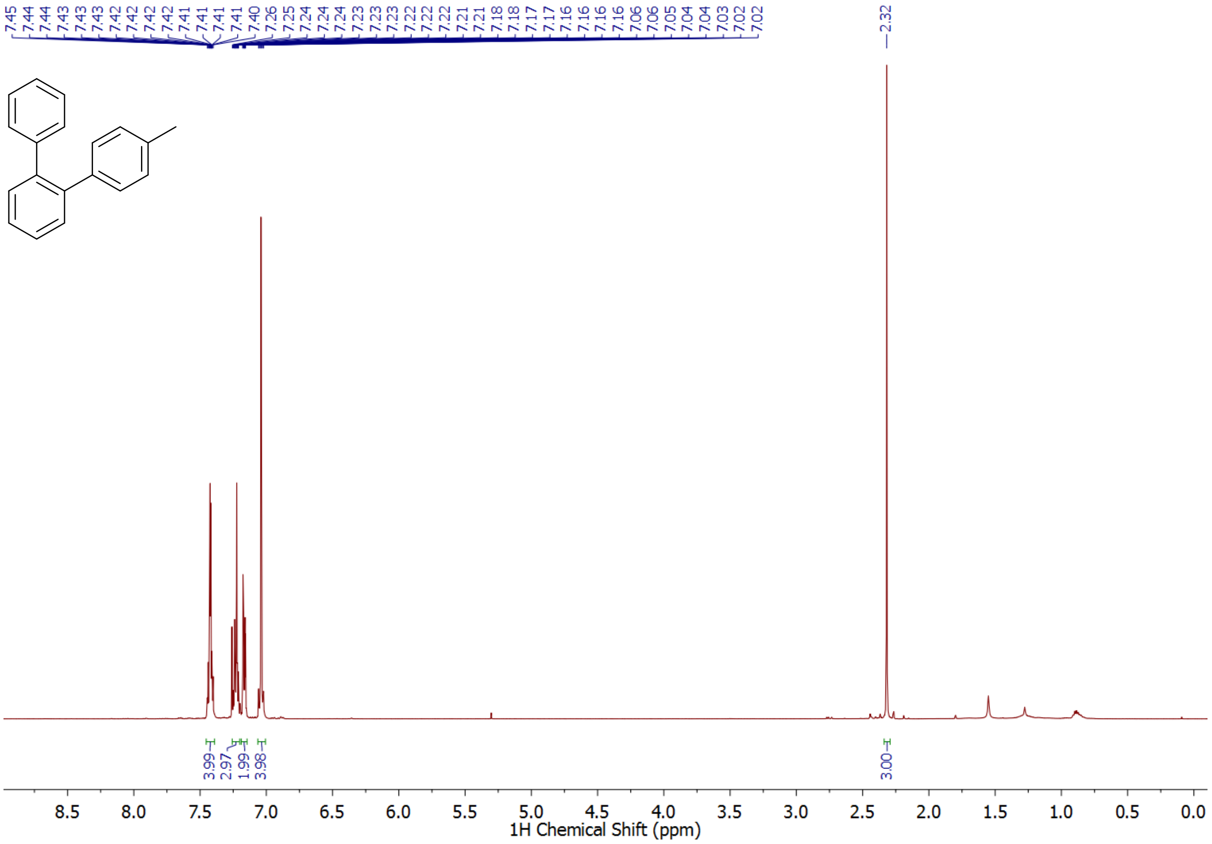
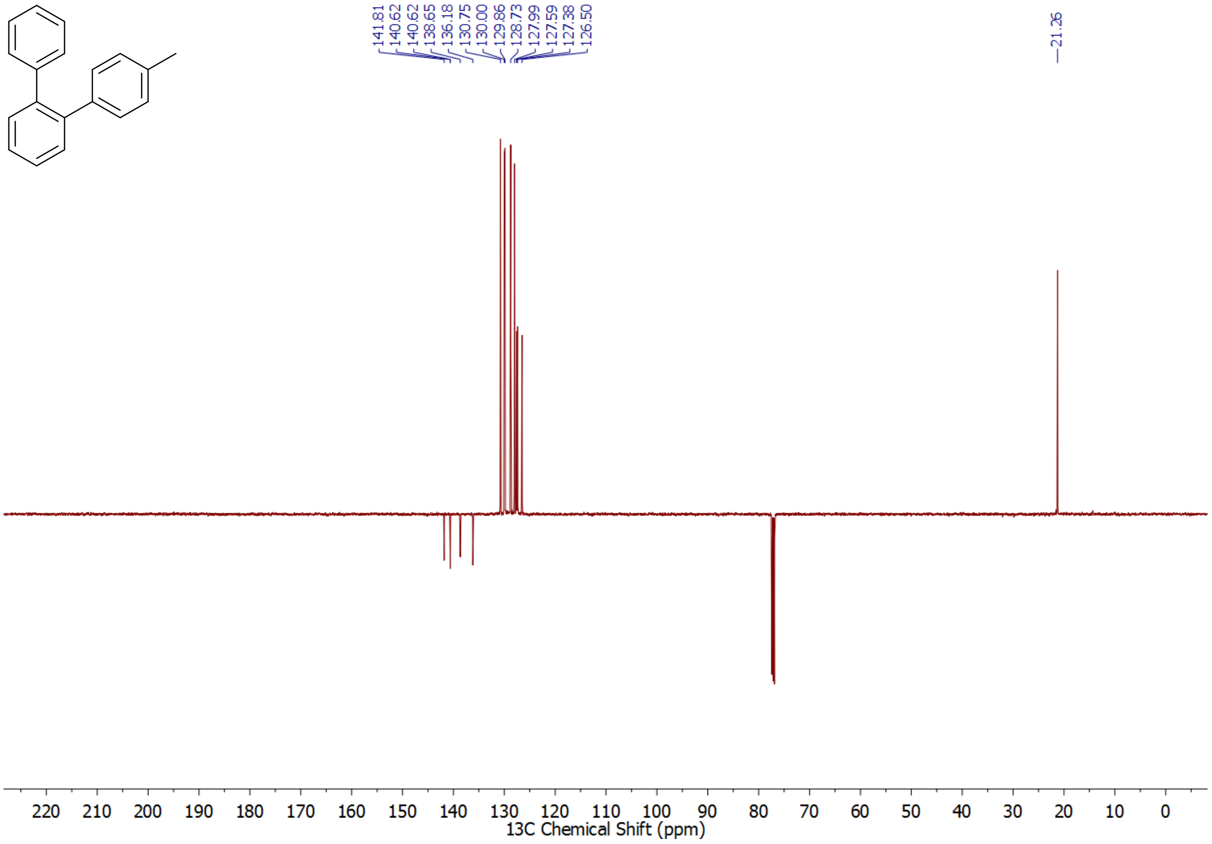
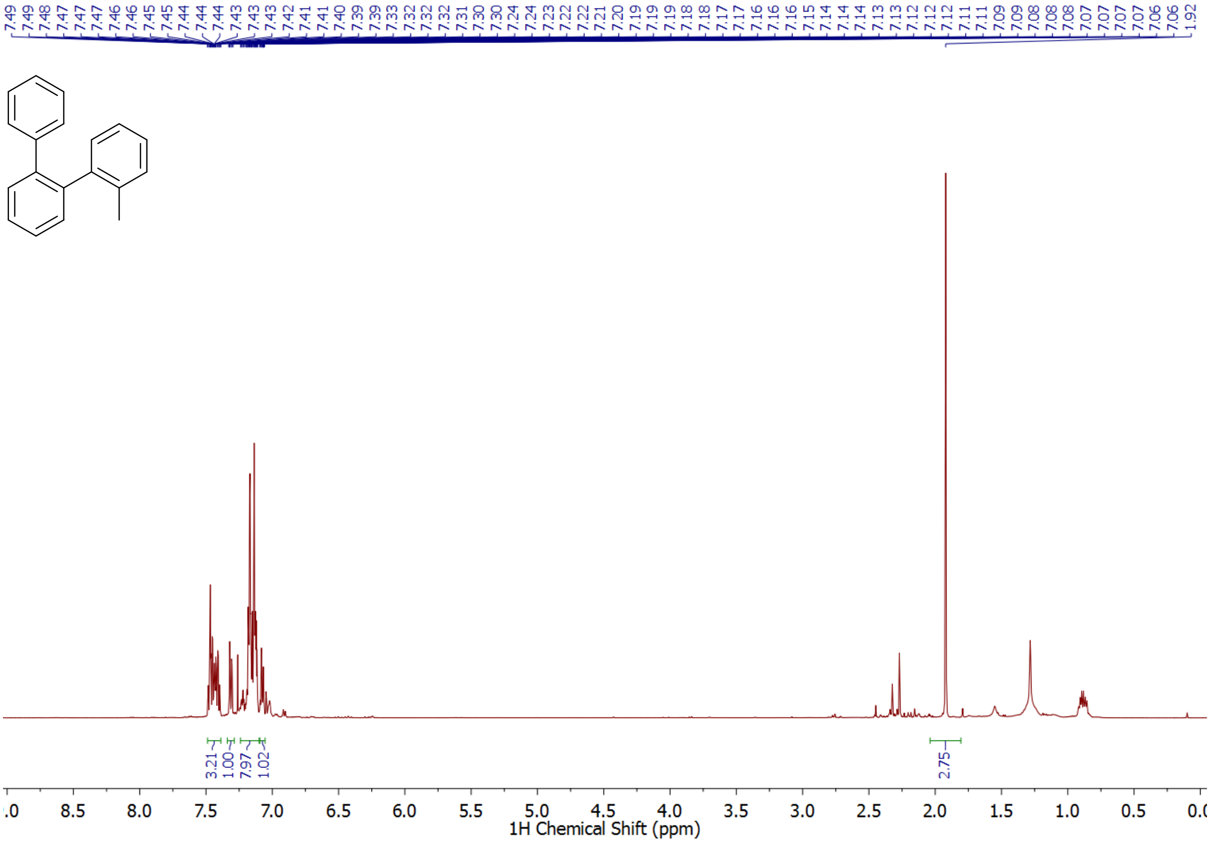
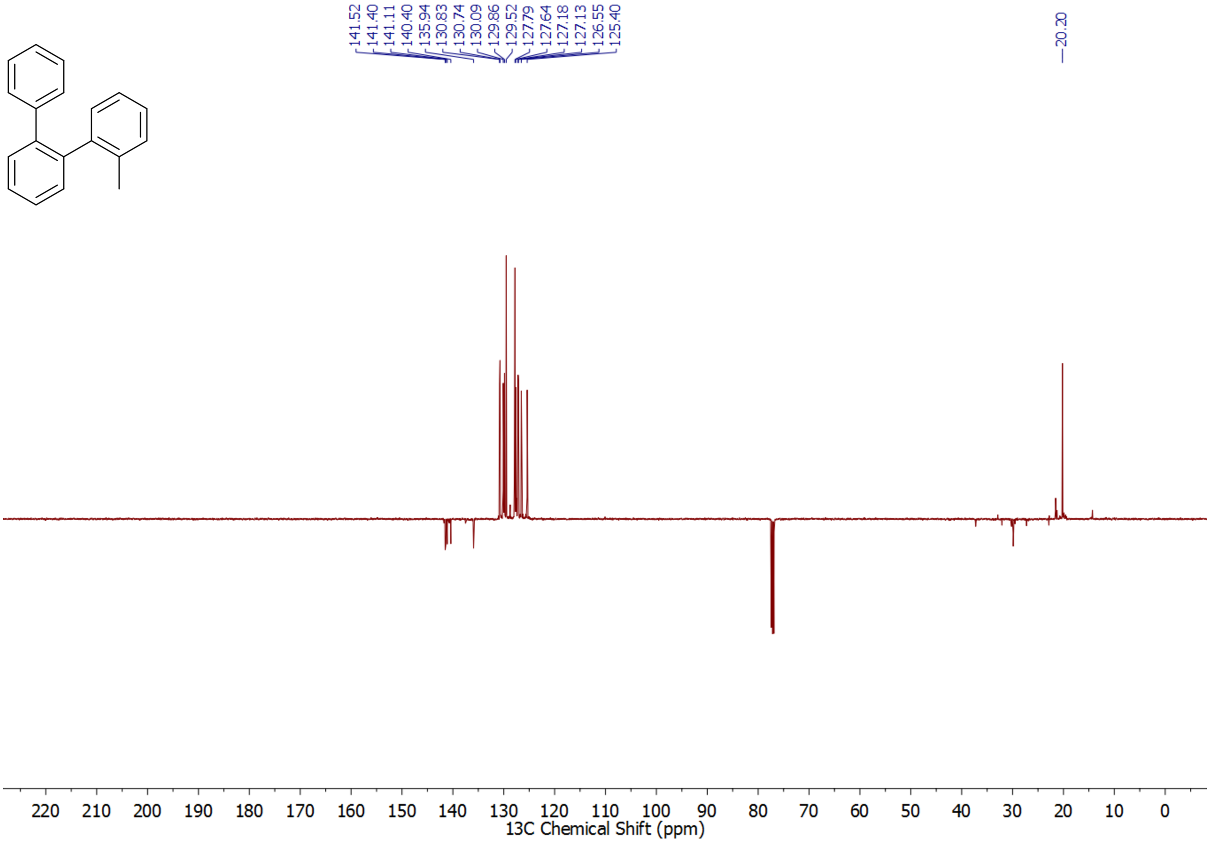


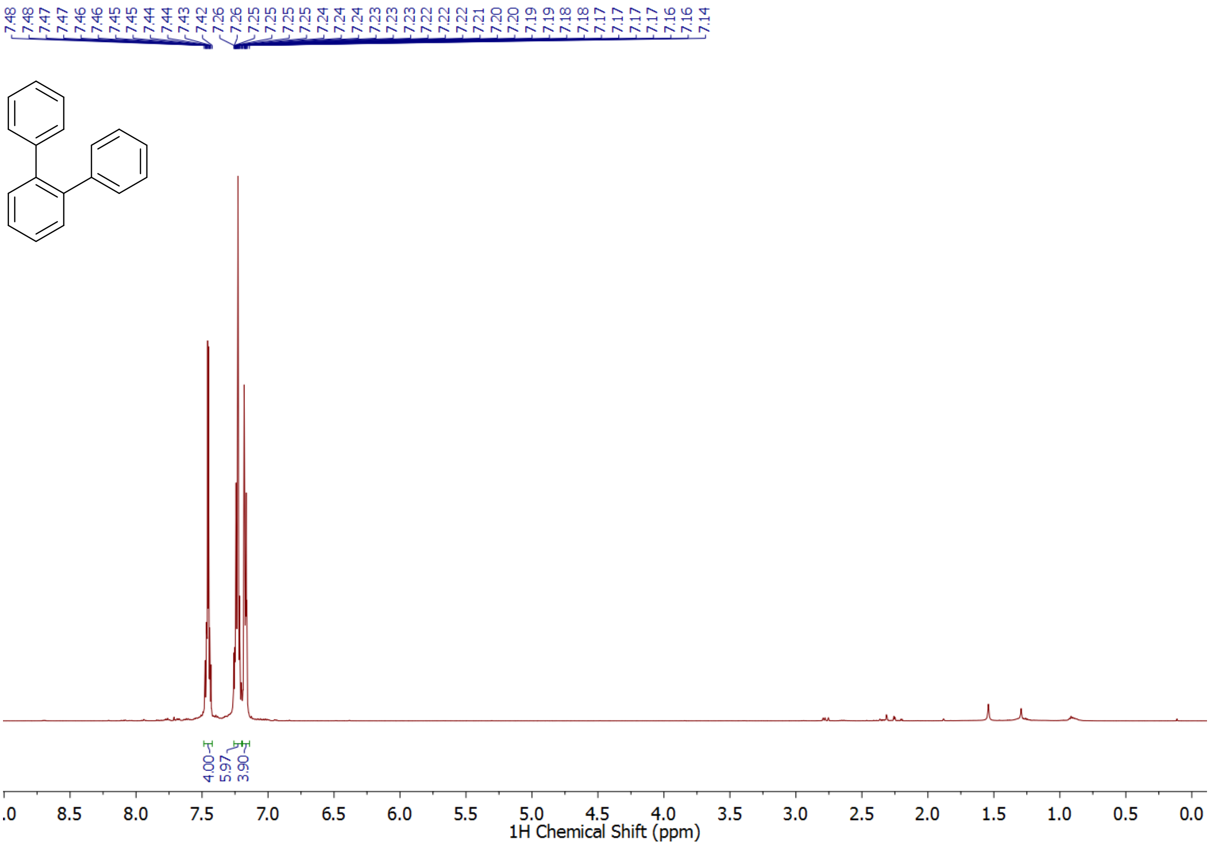


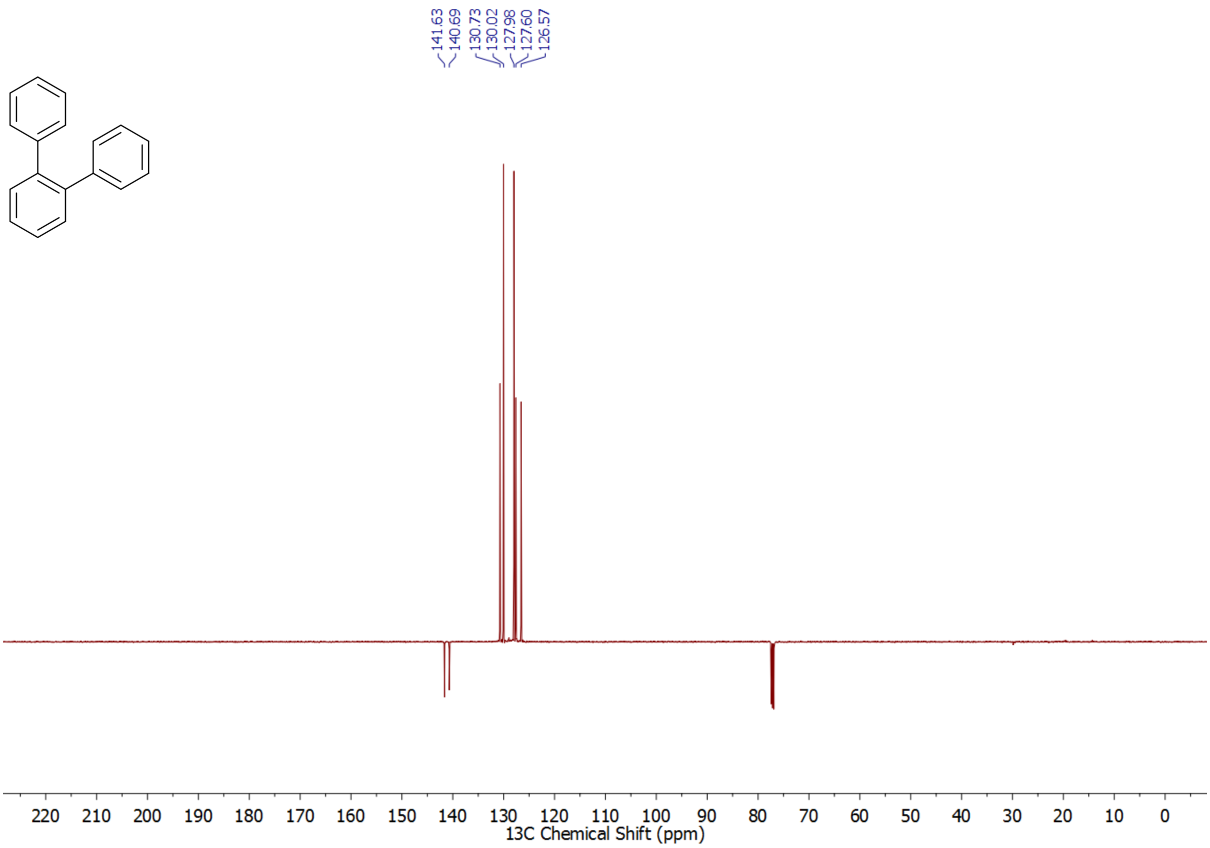
2-methyl-1,1':2',1"-terphenyl:





1,1':2',1''-terphenyl:





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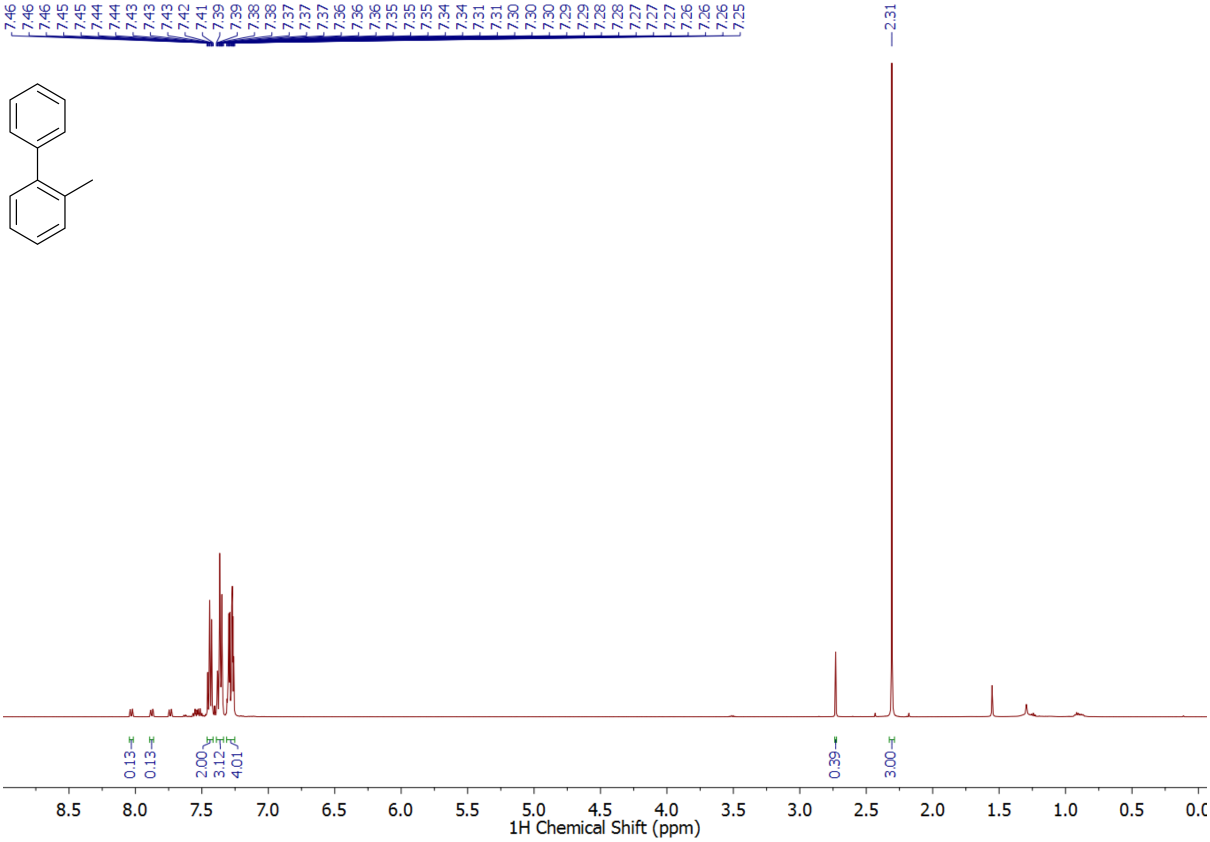
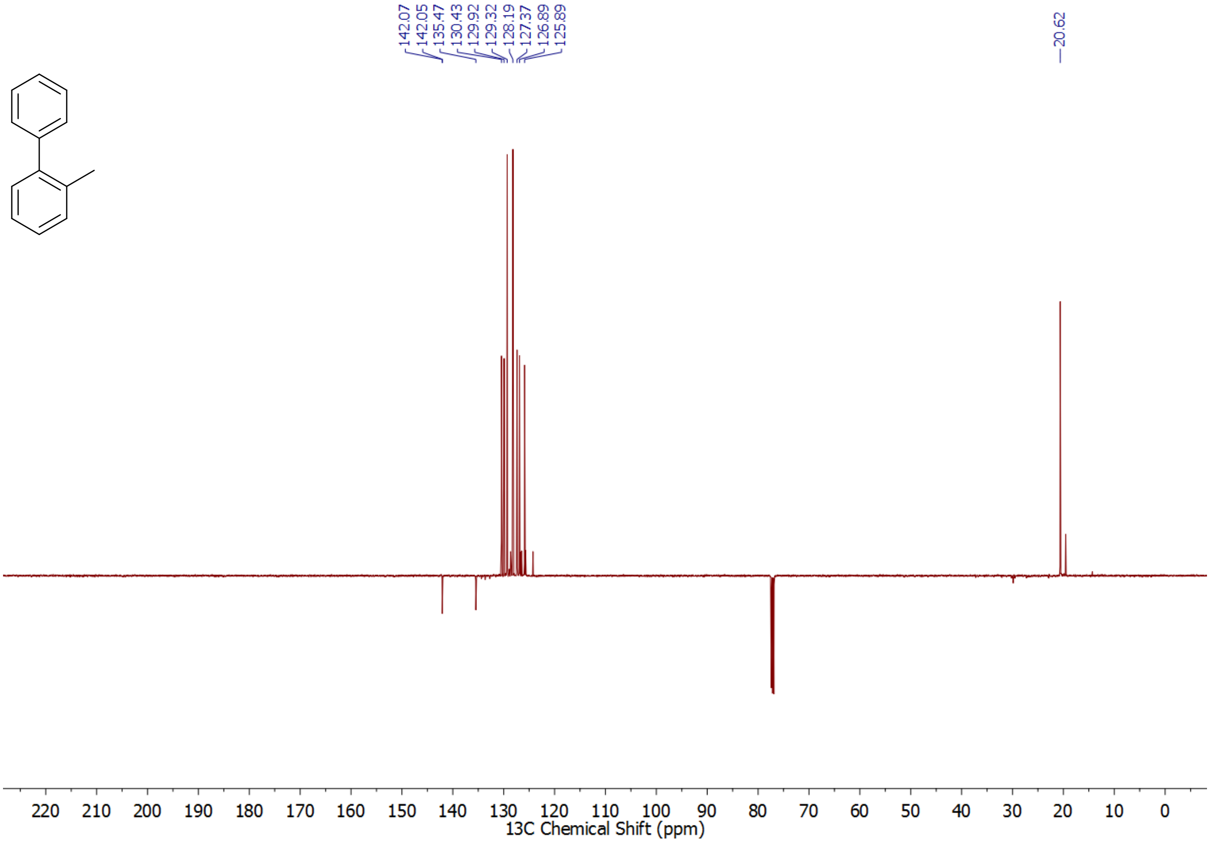
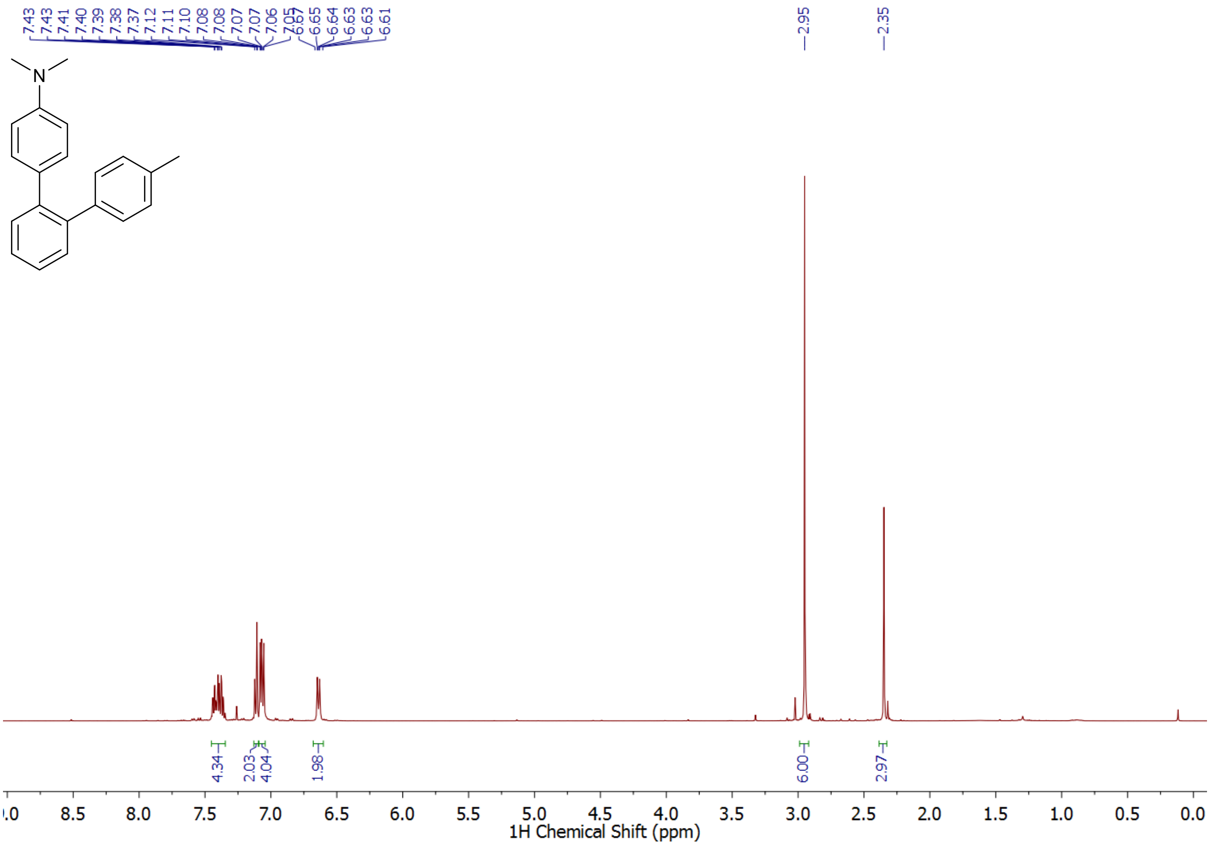
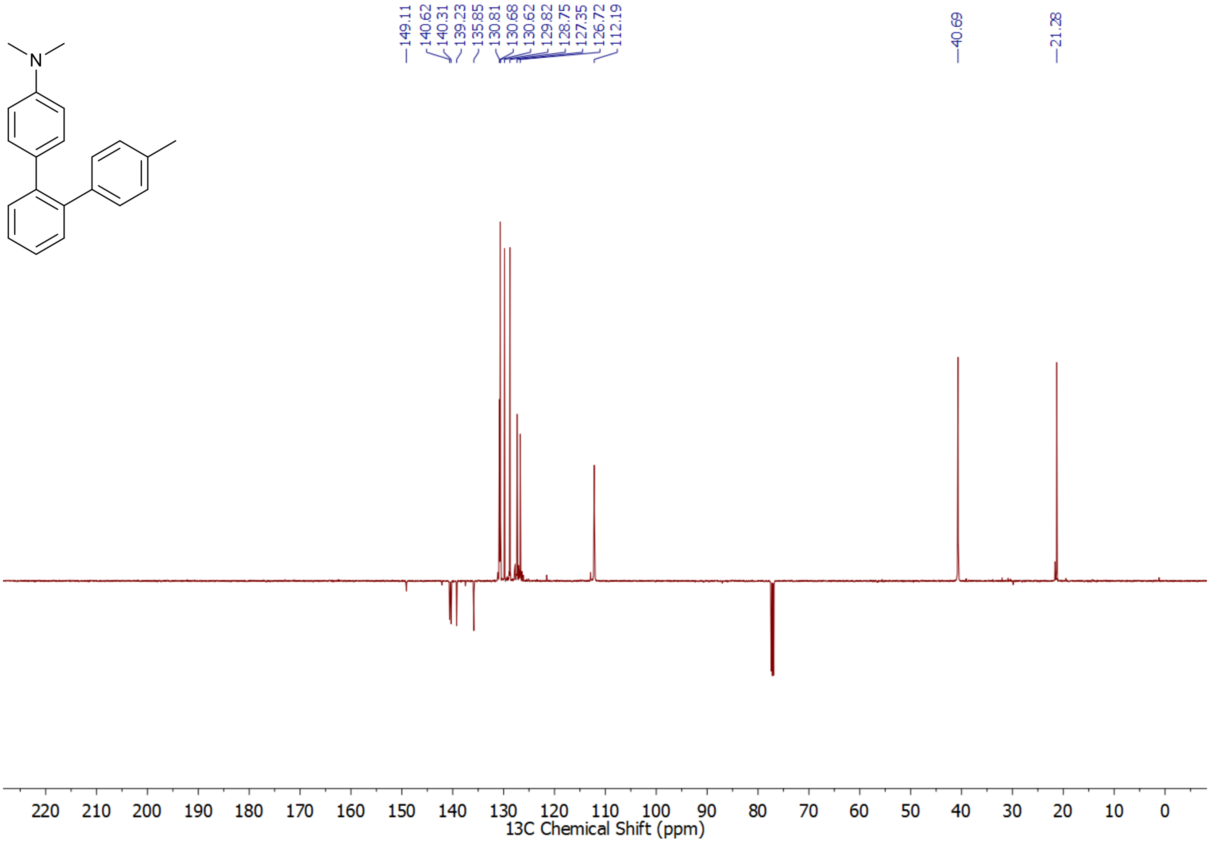




2-(4-*N*,*N*-dimethylaniline)-4'-dimethyl-1,1'-biphenyl:





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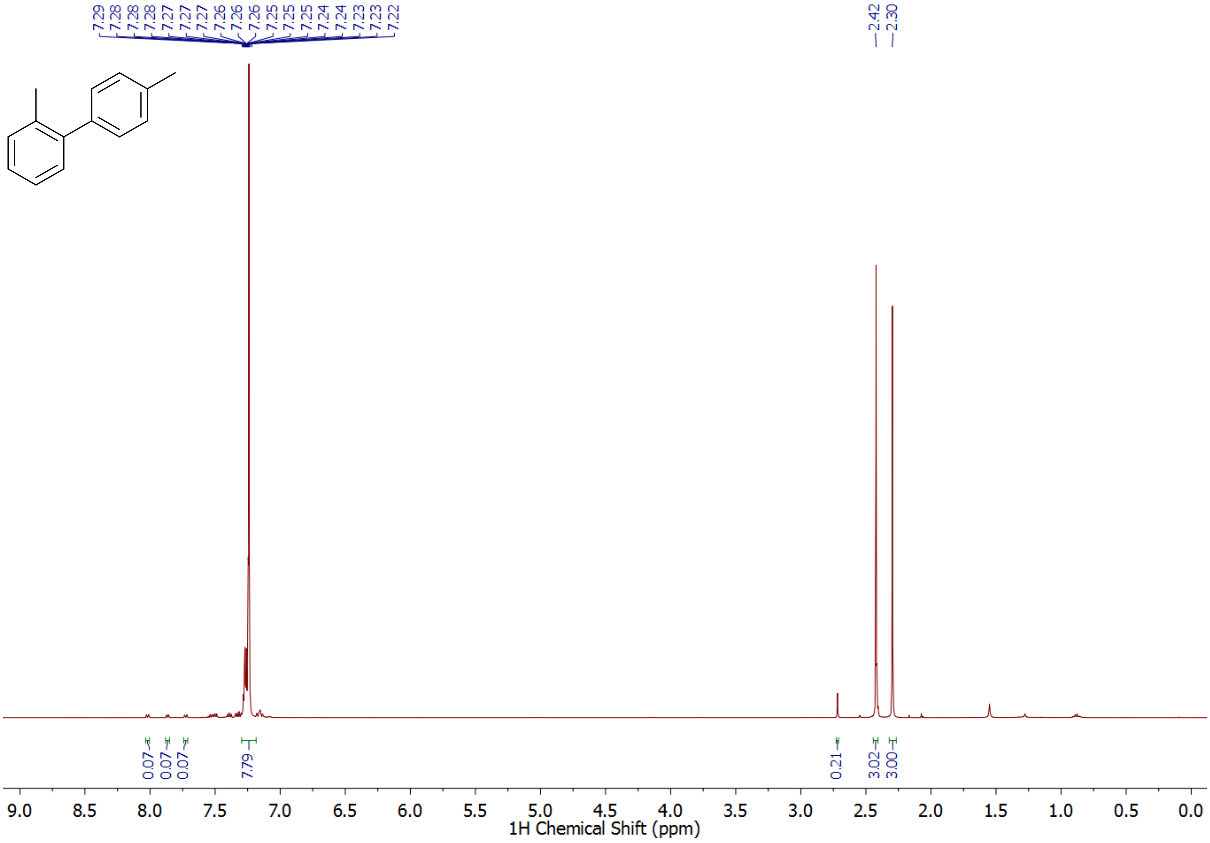

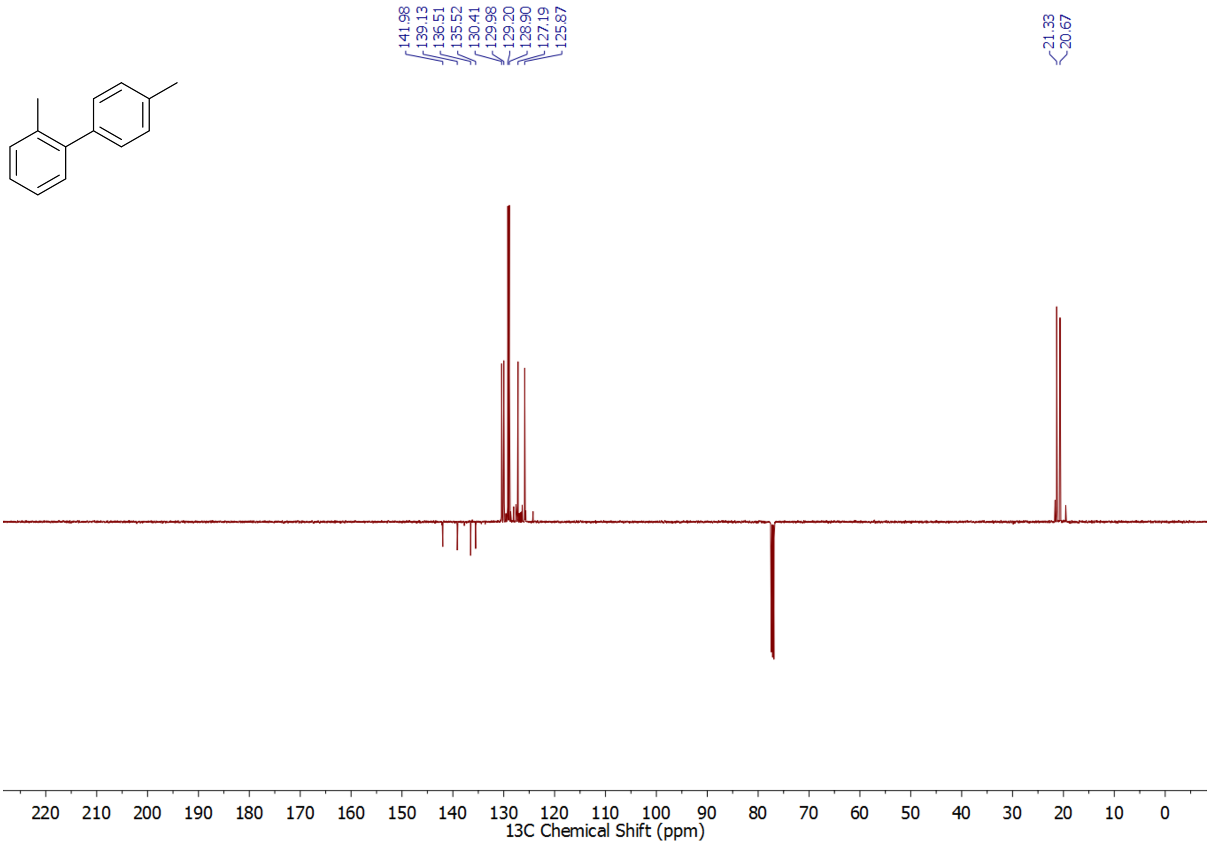

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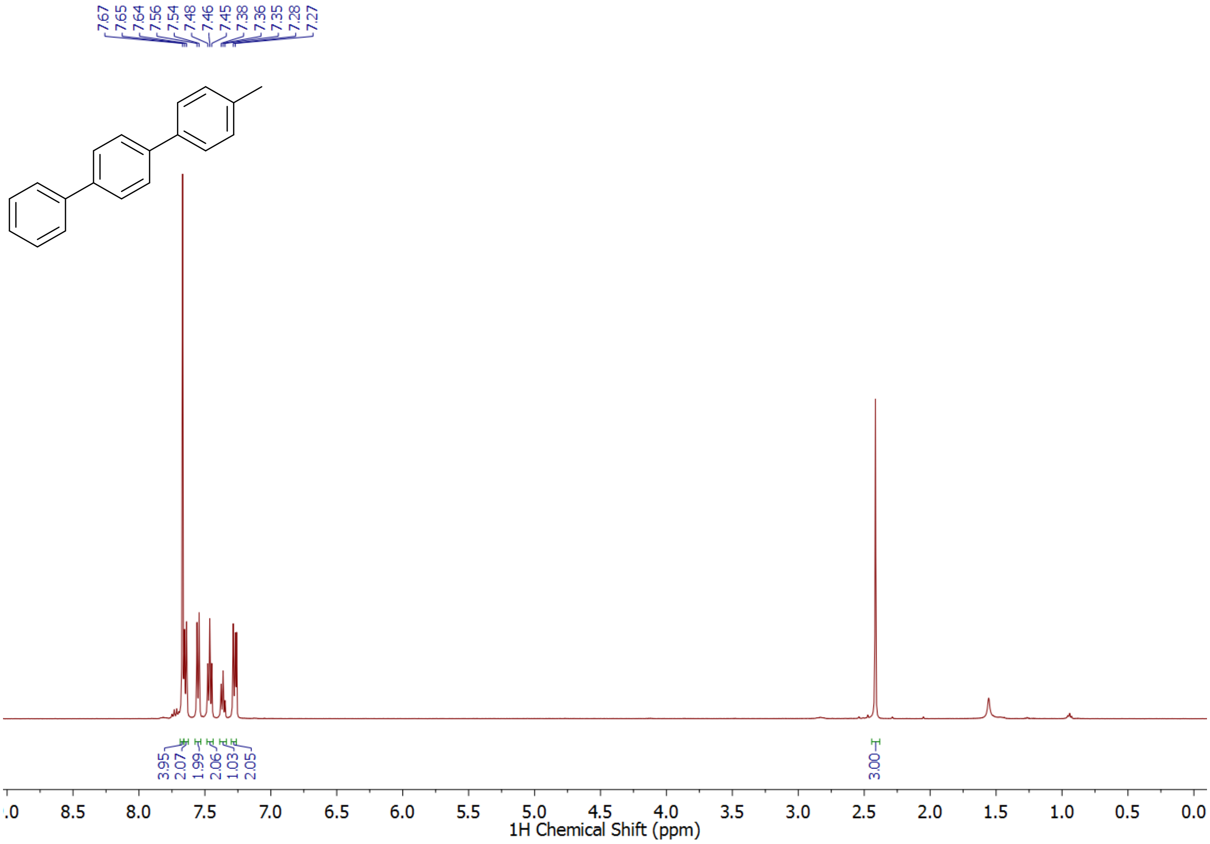

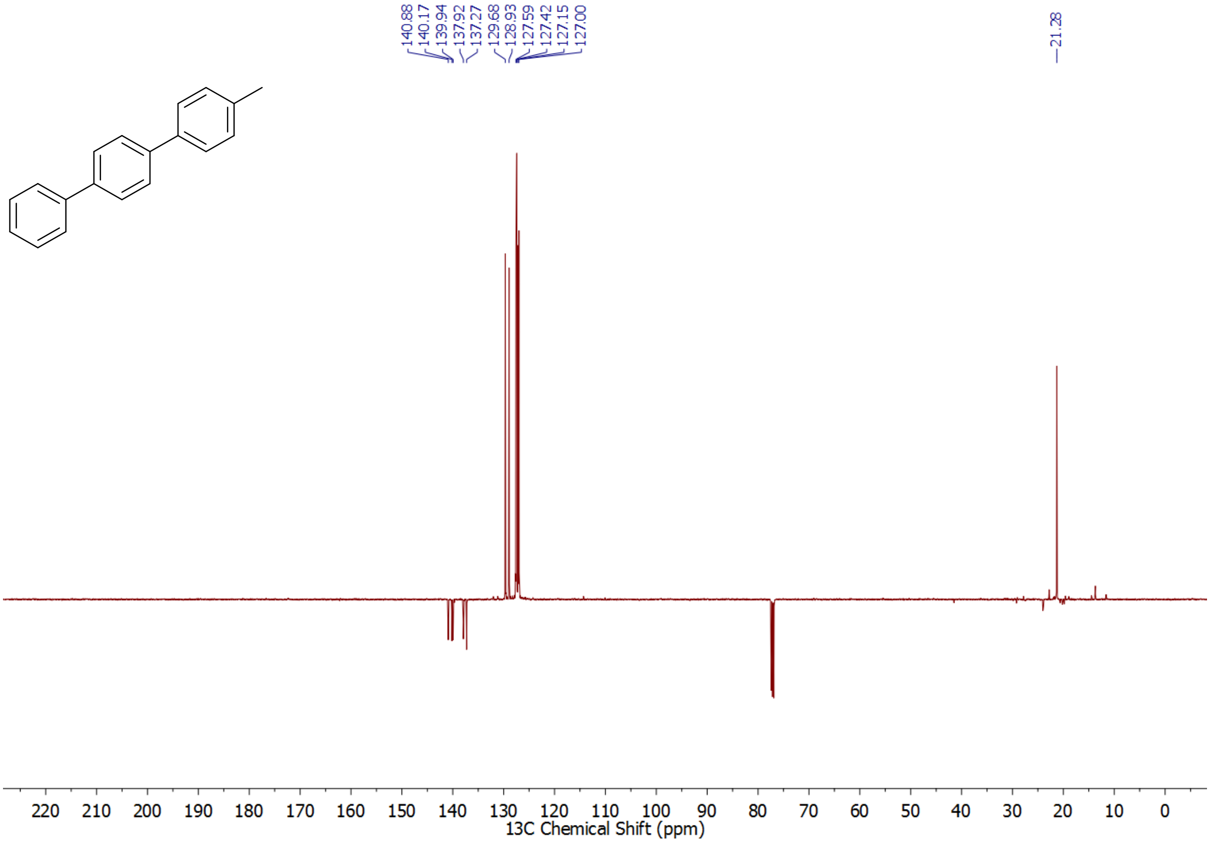

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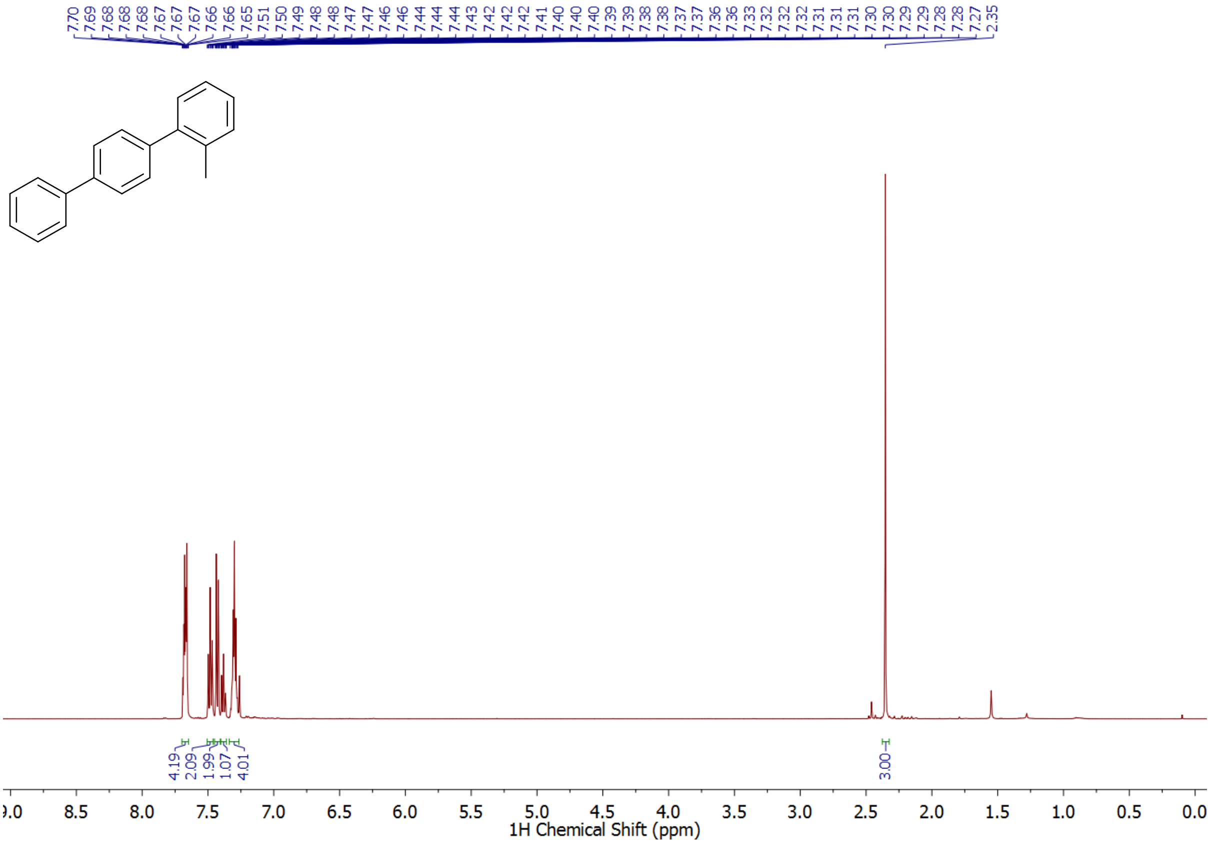

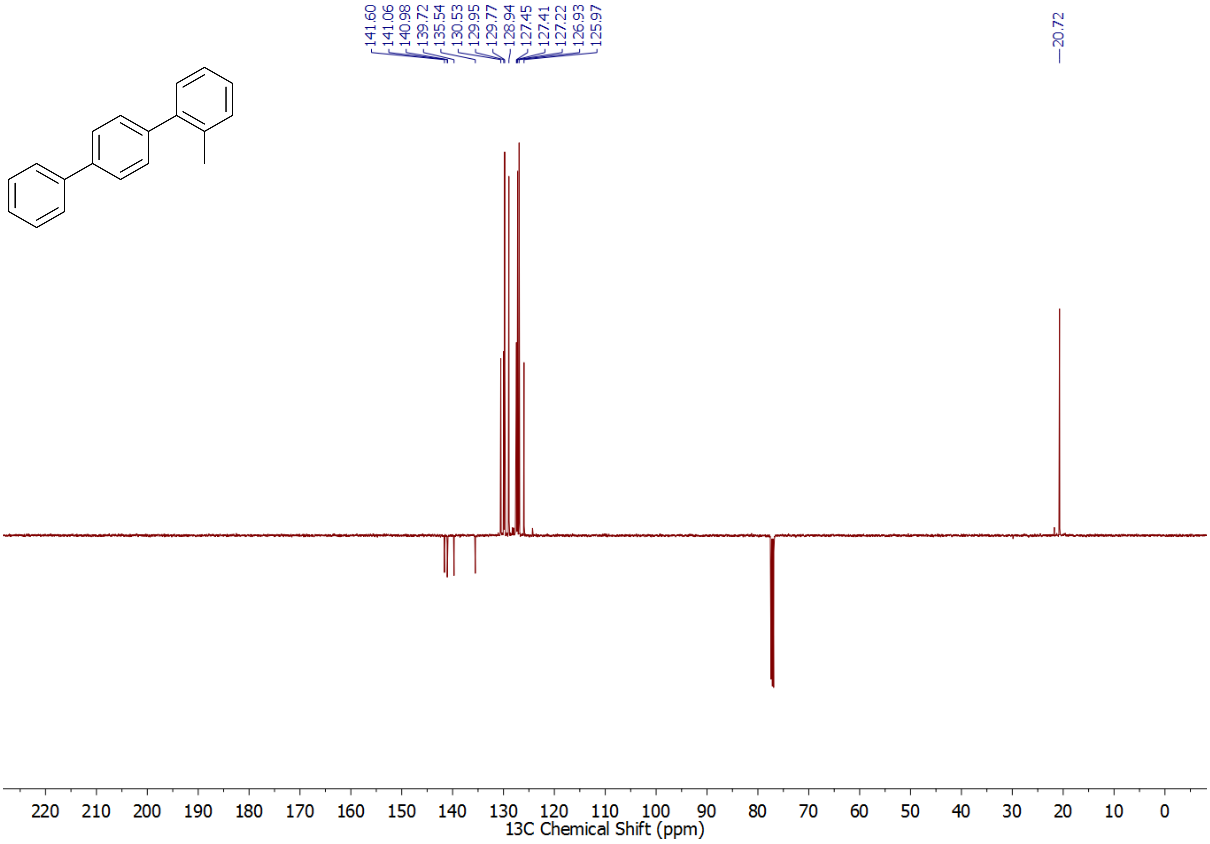

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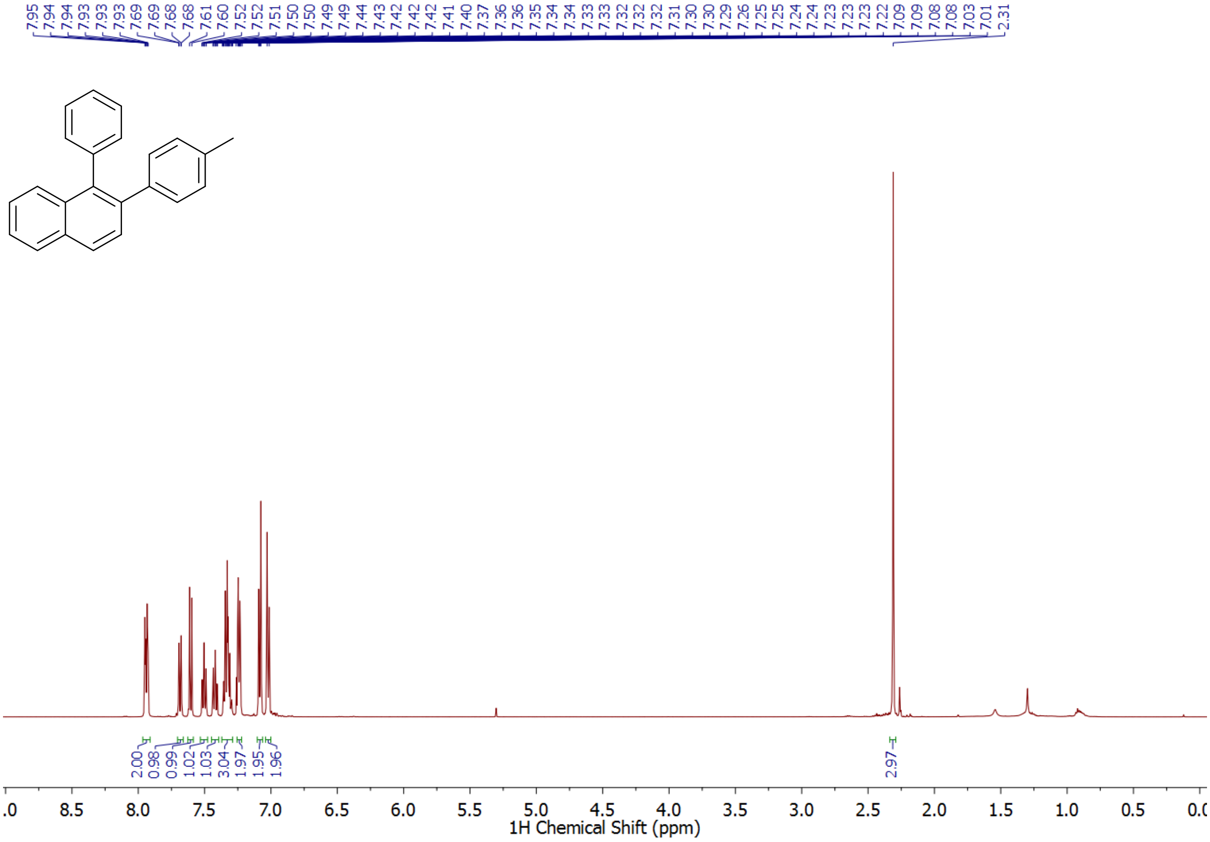

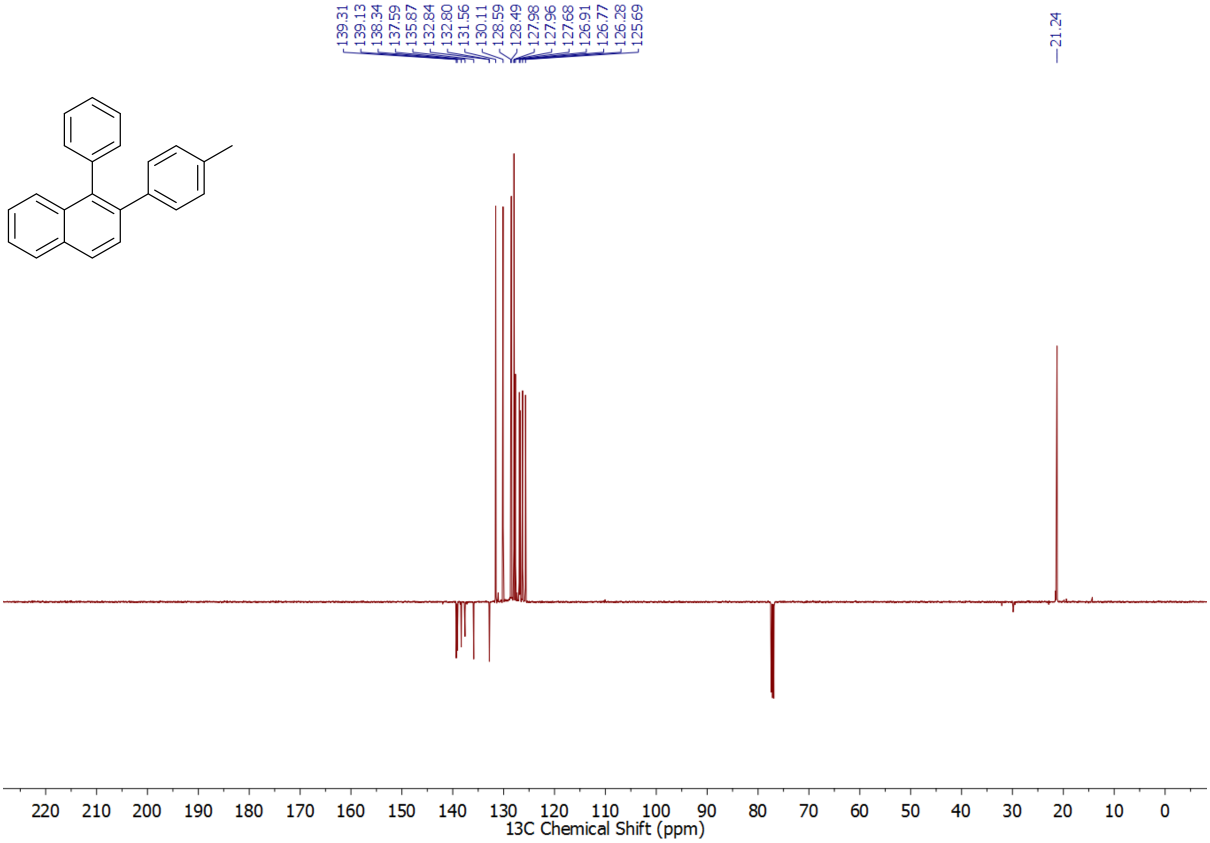

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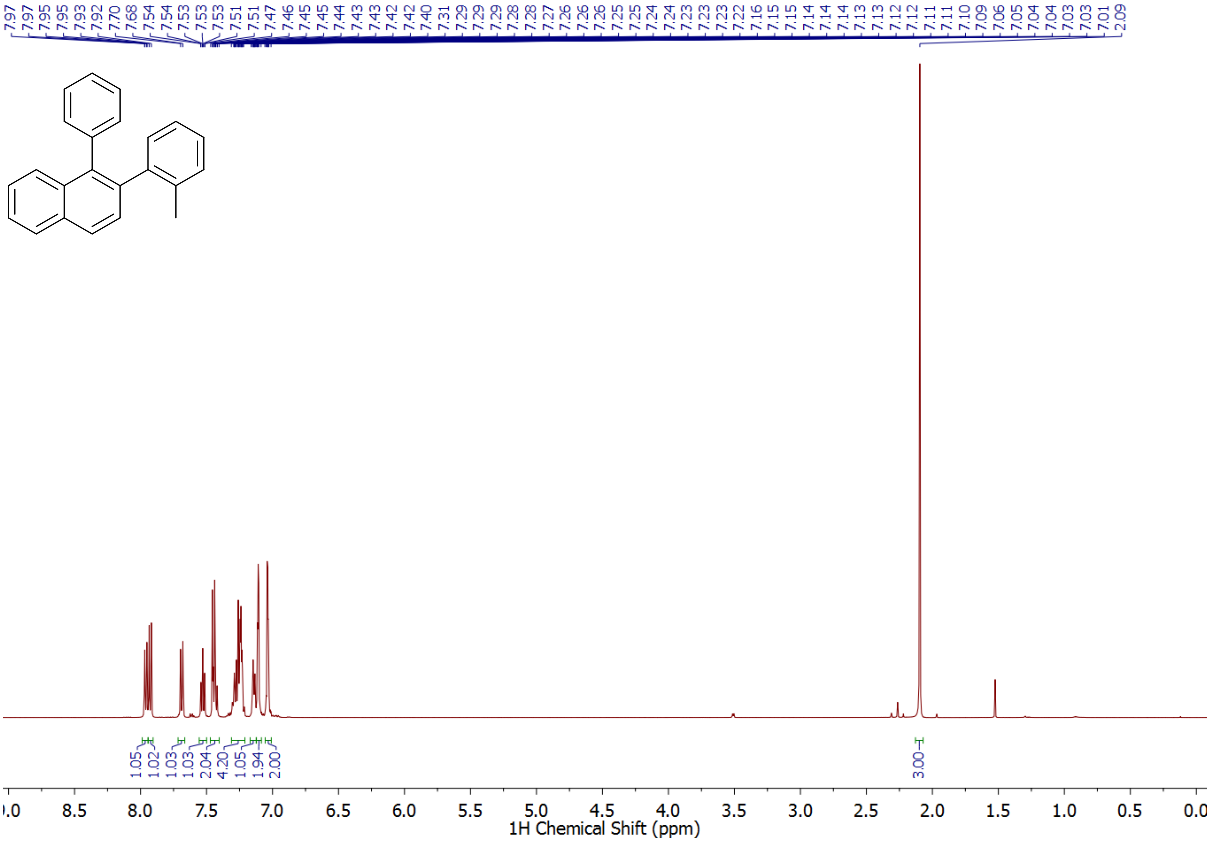
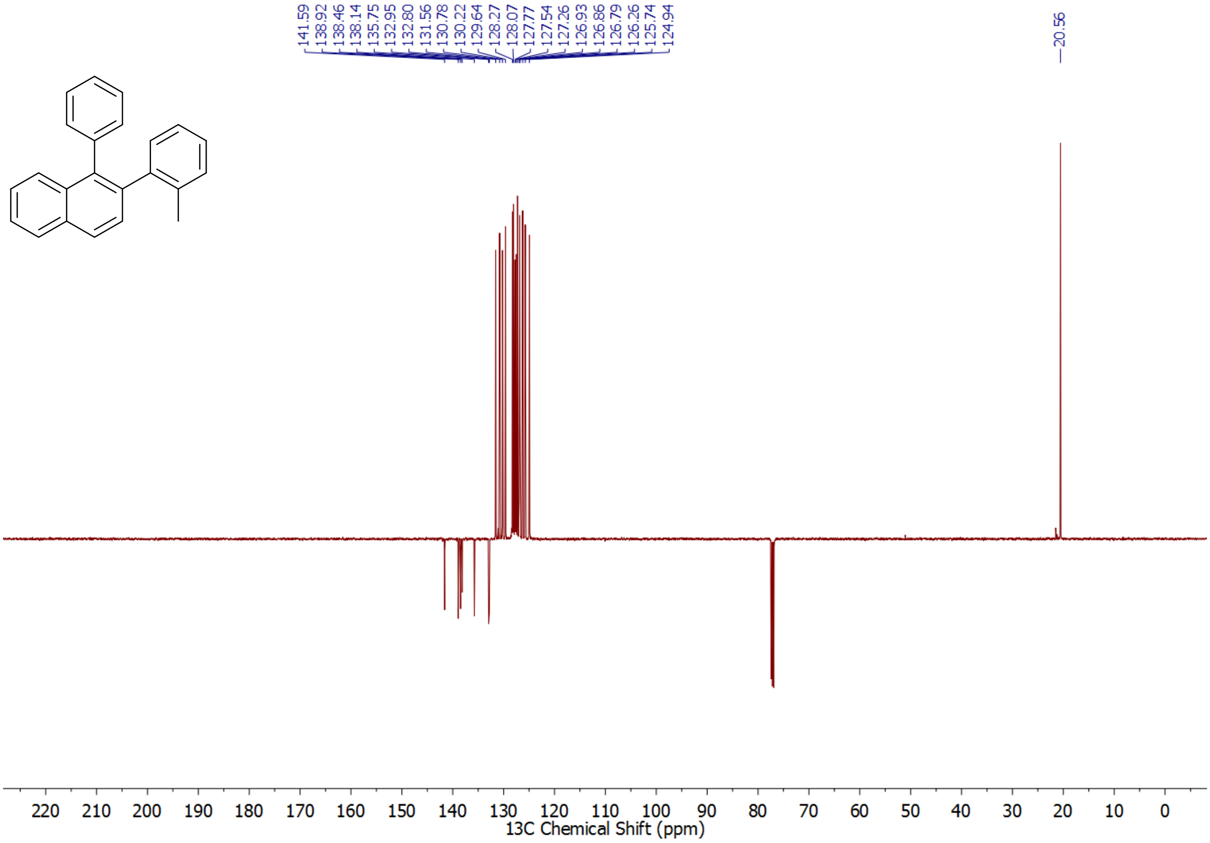
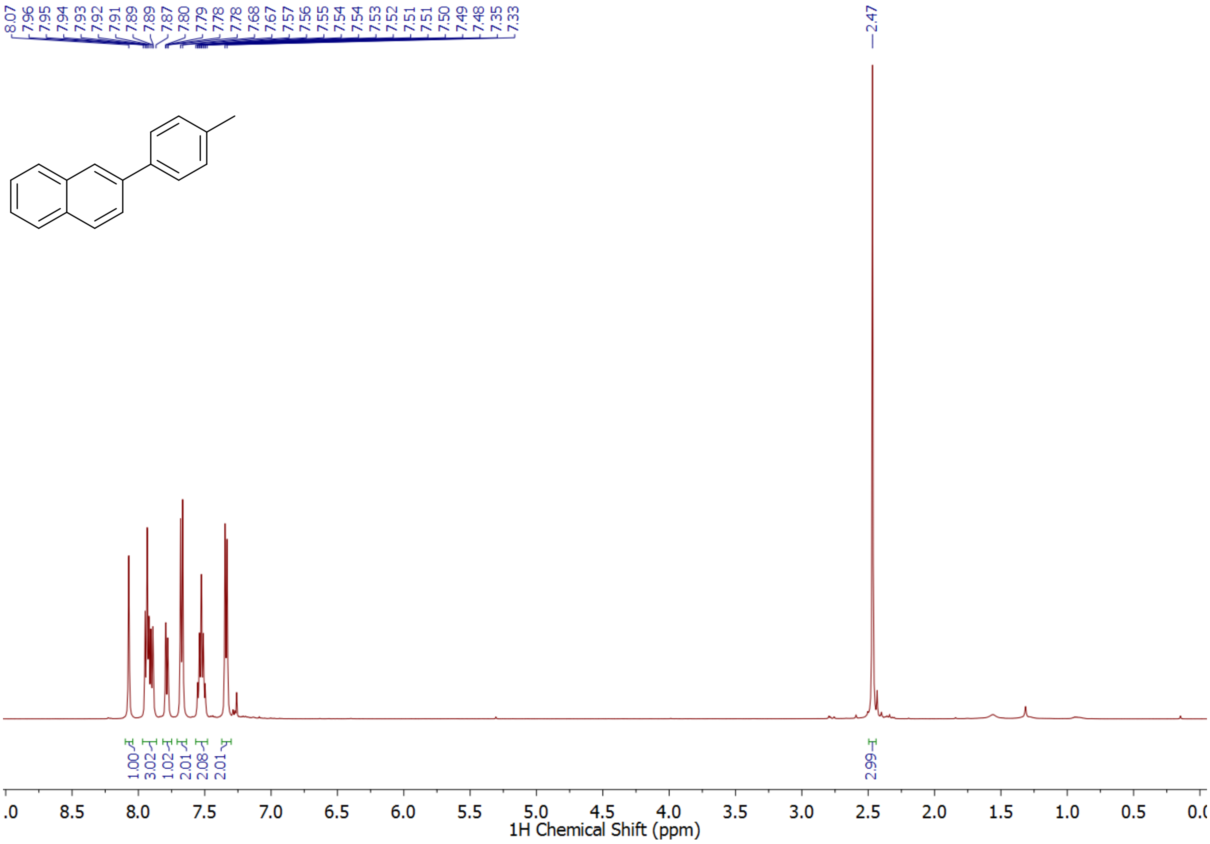
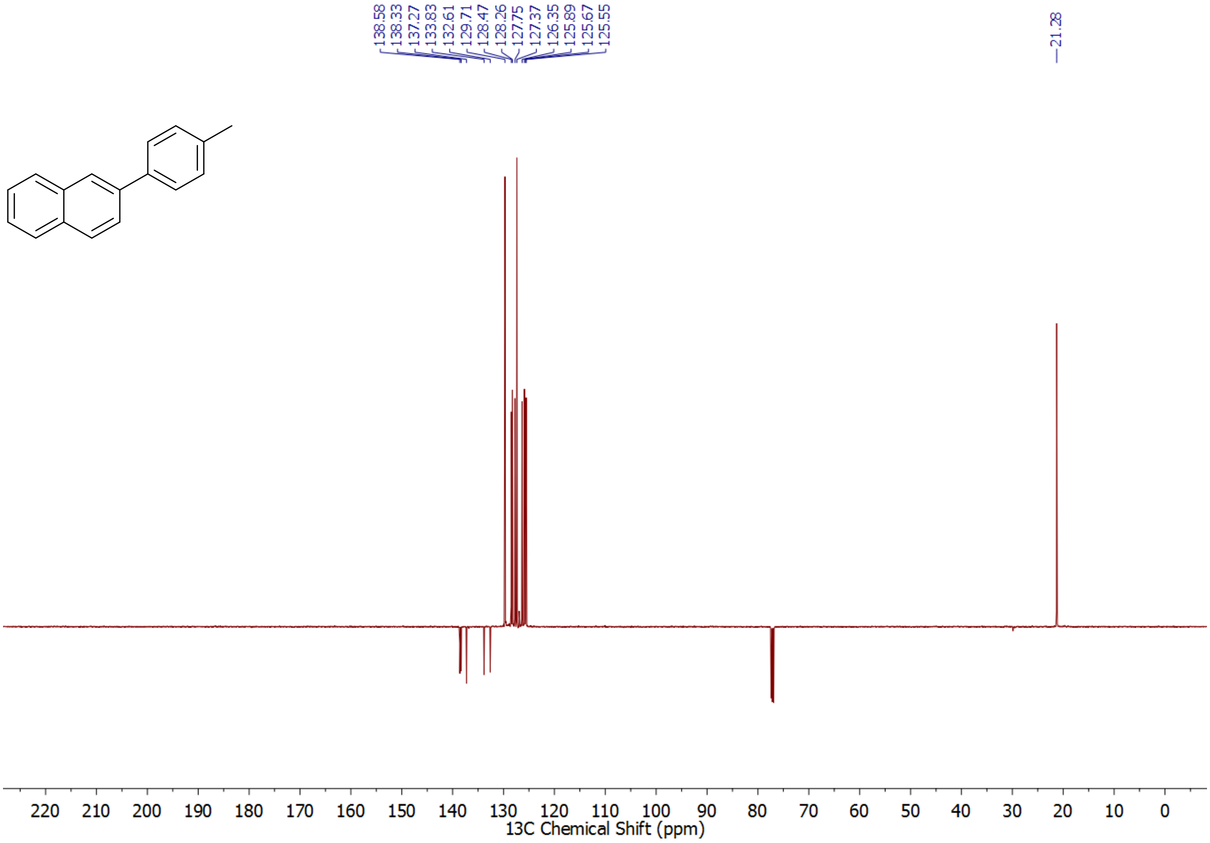


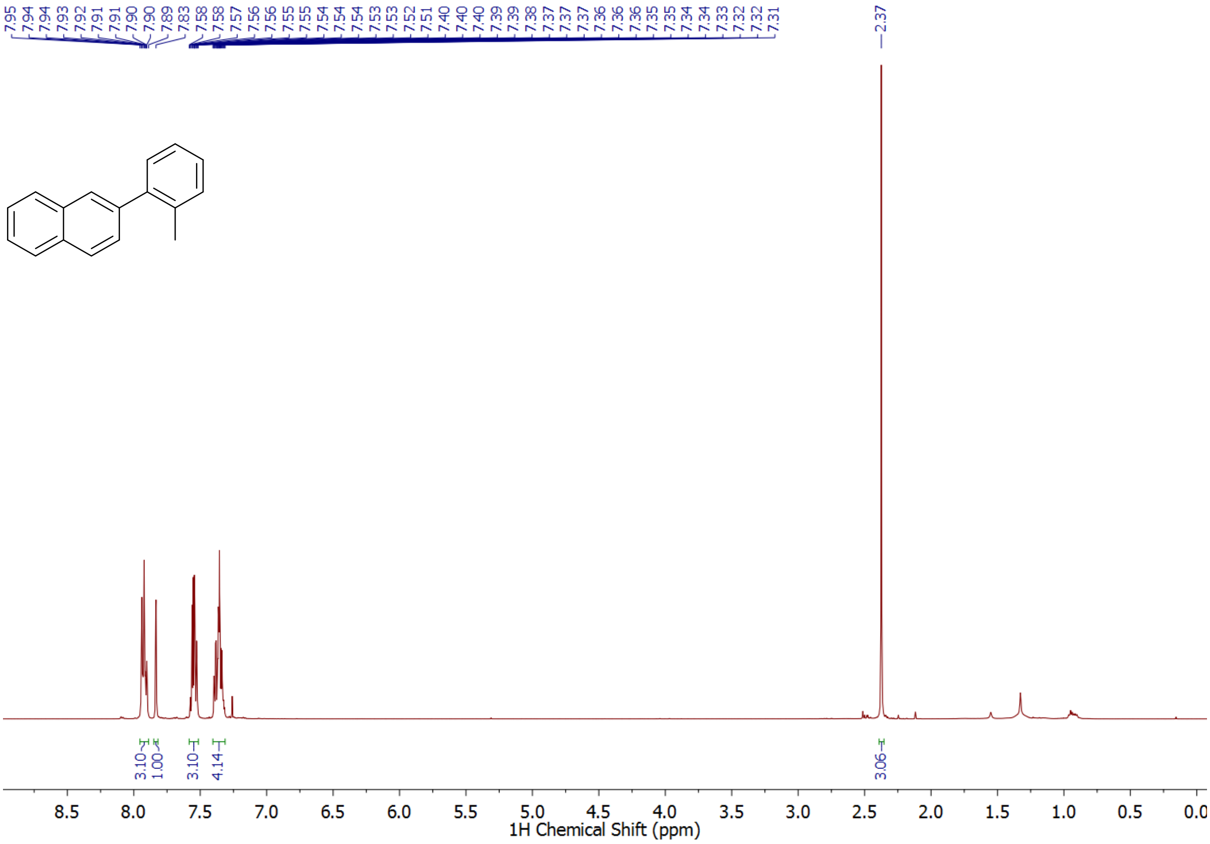


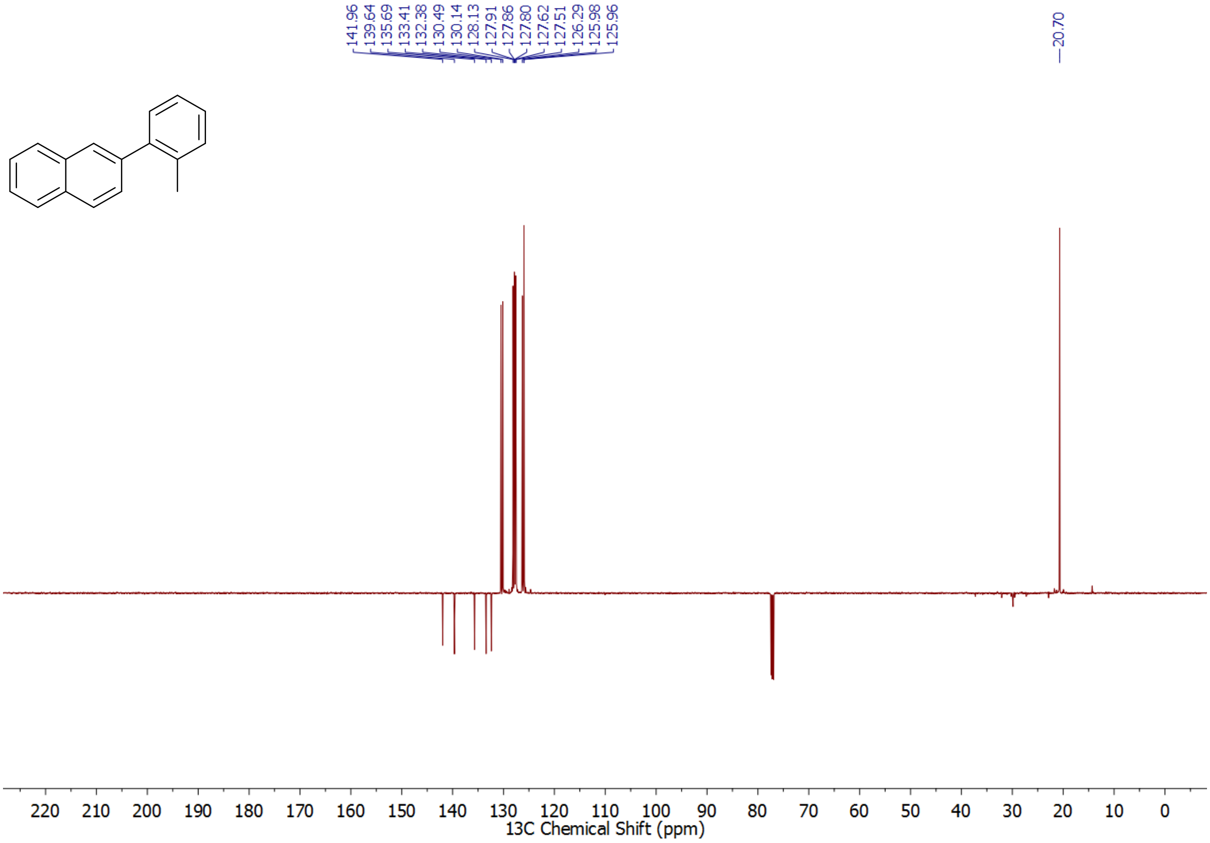
2-(*p*-tolyl)naphthalene:



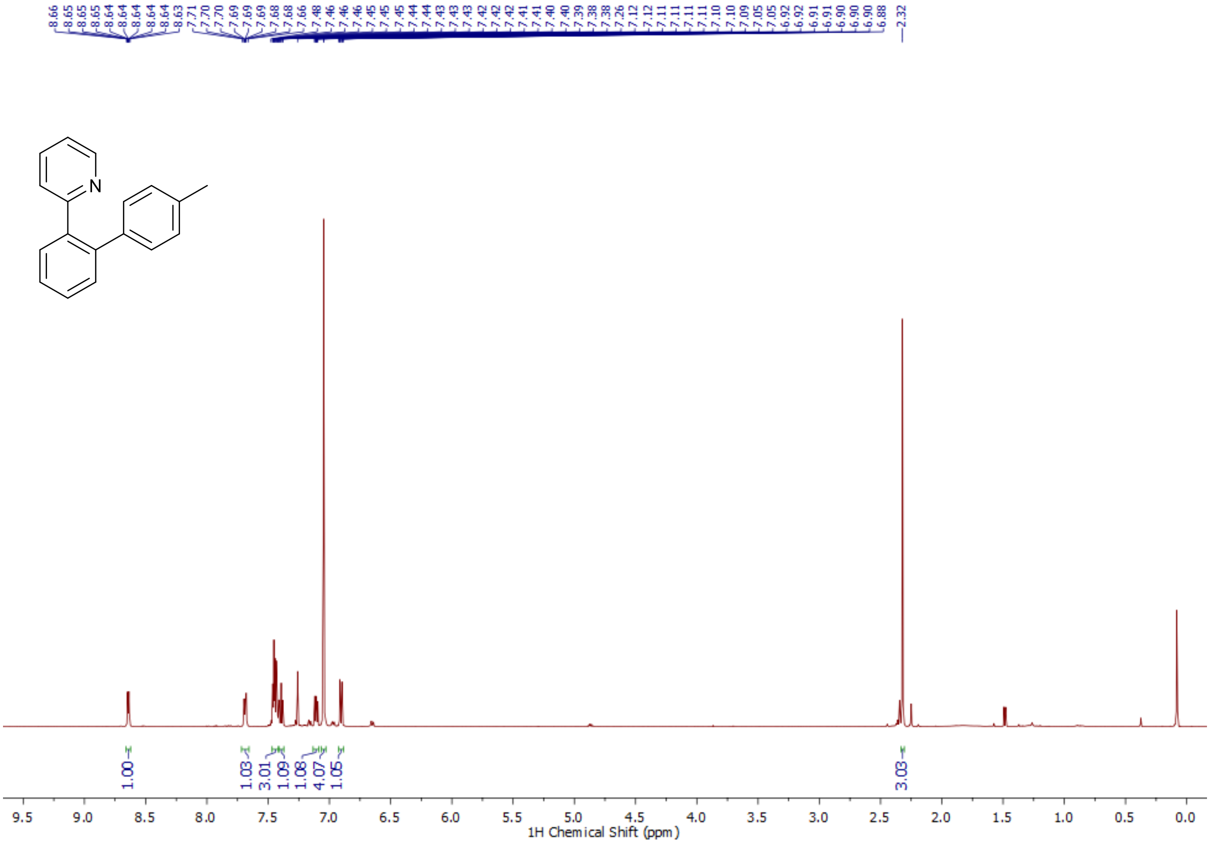


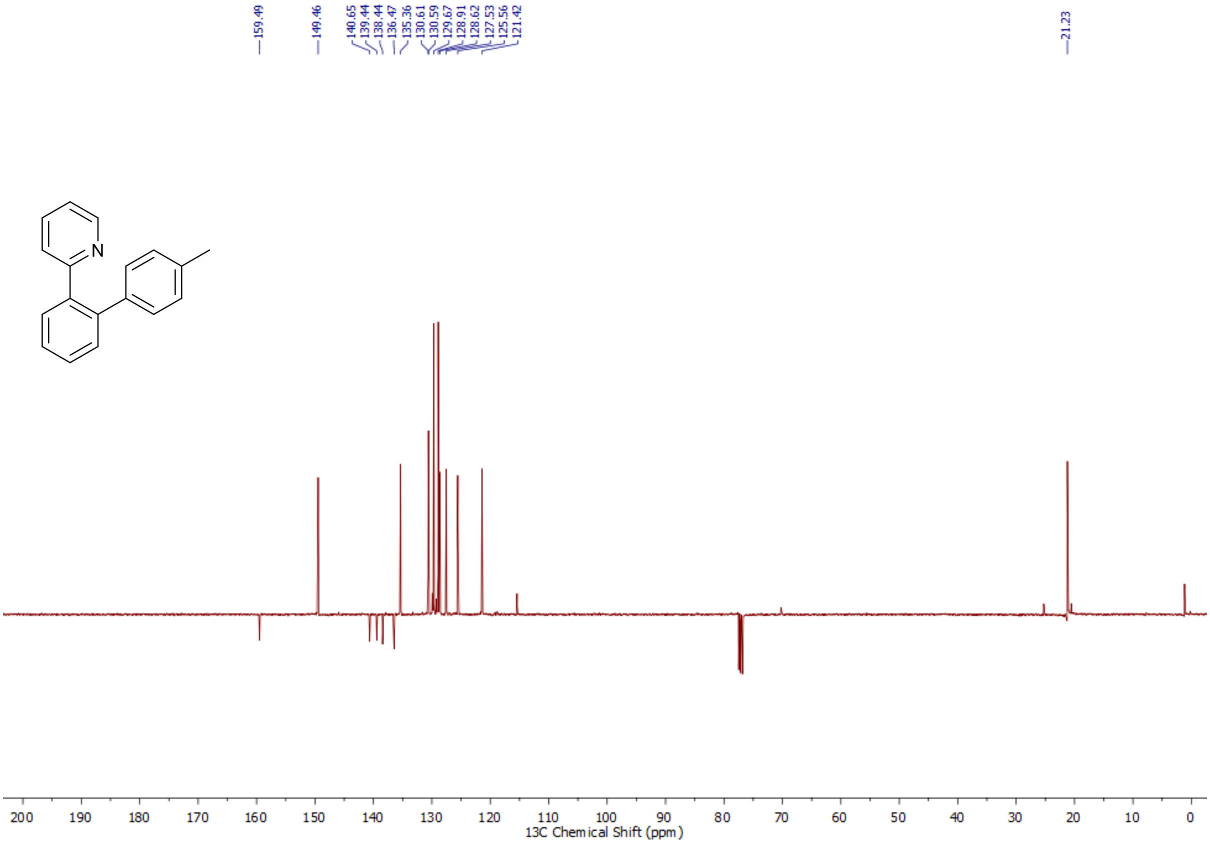
2-(*o*-tolyl)naphthalene:



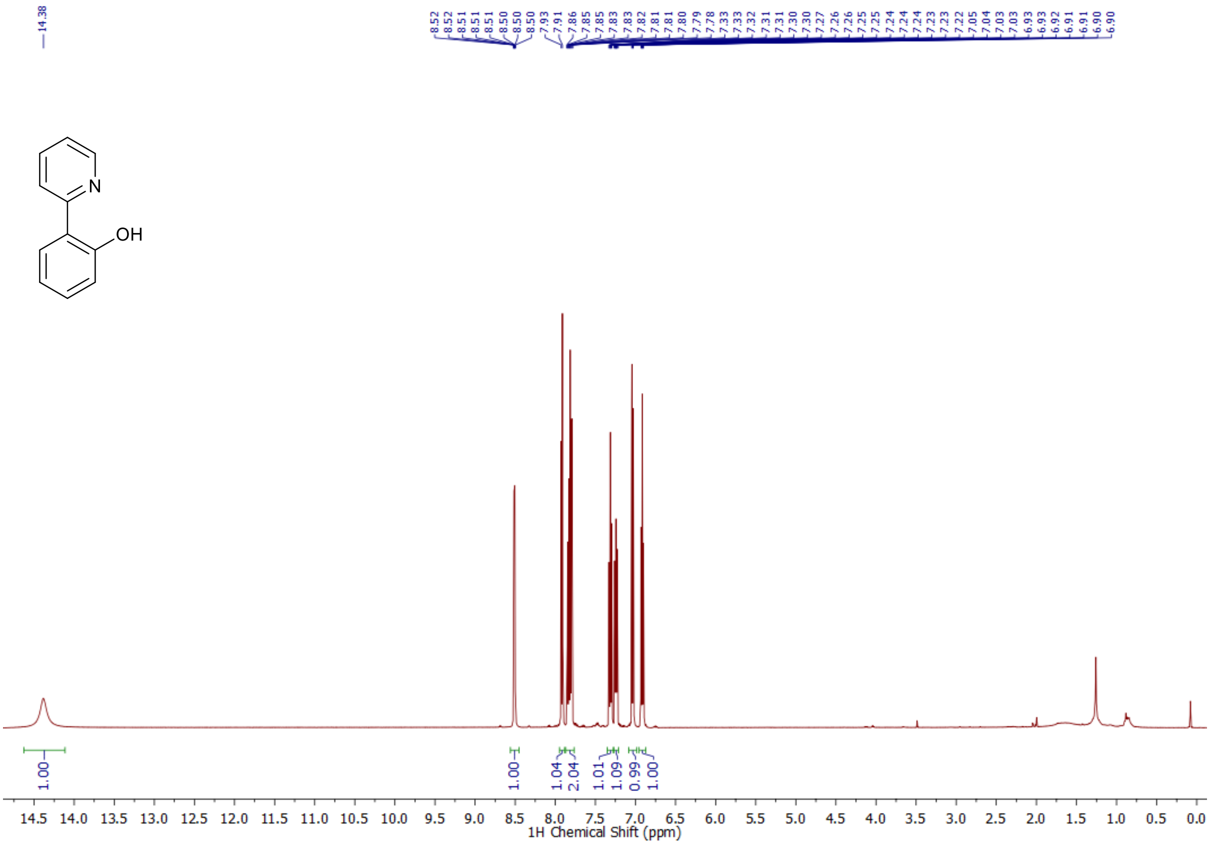


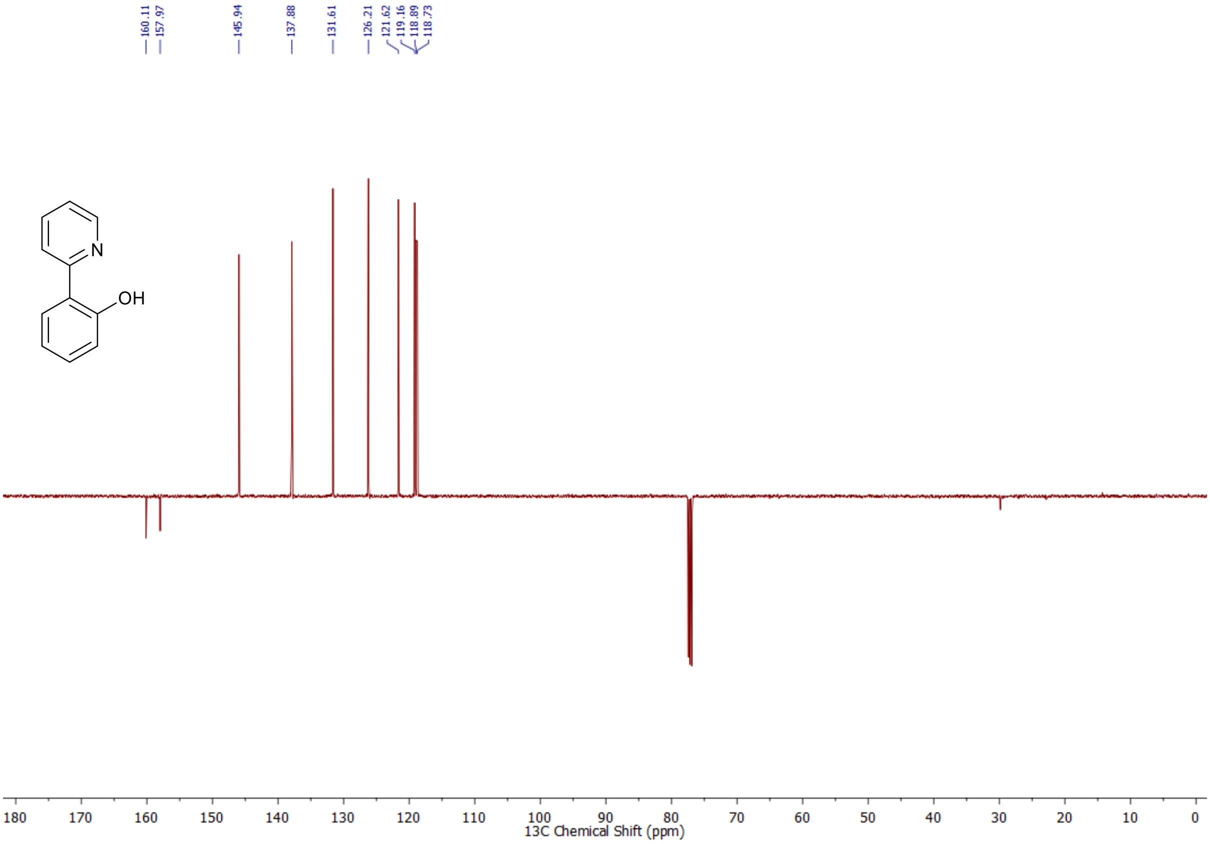
2-(4'-methyl-[1,1'-biphenyl]-2-yl)pyridine:





2-(pyridine-2-yl)phenol:





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