Supporting Information

Catalytic constructive deoxygenation of lignin-derived phenols: new C-C bond formation processes from imidazole-sulfonates and ether cleavage reactions.

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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 argon. 2-MeTHF (anhydrous ≥99%, Sigma-Aldrich) was degassed by freeze-pump-thaw before use in the Kumada cross-coupling and used as supplied for the Meyers reactions. Nitromethane (98+%, Alfa Aeasar) was dried over powdered 3Å molecular sieves prior to degassing by rigorous purging with argon prior to use. *tert*-Amyl methyl ether (produced by INEOS Oligomers, ≥99.0% (GC), Sigma-Aldrich) was used as supplied for the Meyers reactions and degassed by rigorous purging with argon prior to use in the Kumada cross-coupling reactions. *tert*-Butanol (ACS 99+%, Alfa-Aesar) and distilled water were degassed by rigorous purging with argon for use in the cyanation procedure.

Unless stated chemicals were purchased from Acros-UK, Alfa Aeasar, Apollo Scientific, Fluorochem, Sigma-Aldrich, or TCI and used without further purification. All Grignard reagents were used as supplied (Aldrich). Room temperature (rt) refers to 20-25 °C. Reflux 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. Flash silica chromatography was performed on Kieselgel 60 silica in the solvent system stated.

^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz ^{1}H, 75 MHz ^{13}C and 282 MHz ^{19}F), a Bruker Avance II 400 (400 MHz ^{1}H, 100 MHz ^{13}C and 376 MHz ^{19}F) or a Bruker Ultrashield 500 (500 MHz ^{1}H, 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.

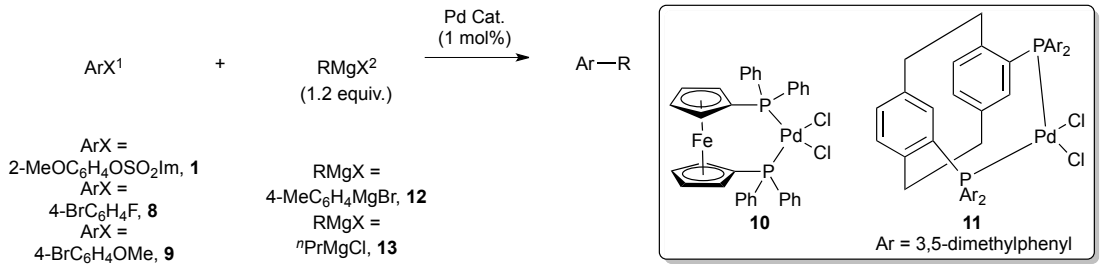
Melting points were recorded on an Gallenkamp melting point apparatus and are uncorrected. Dec refers to decomposition.

Mass spectrometric (*m/z*) data were acquired by electrospray ionisation (ESI) or chemical ionisation (CI) at the University of St Andrews Mass Spectrometry facility ([A]+ quoted). High resolution ESI was carried out on a Micromass LCT spectrometer and high resolution CI was carried out on a Micromass GCT spectrometer. Values are quoted as a ratio of mass to charge in Daltons.

2-Methoxyphenyl-1*H*-imidazole-1-sulfonate[1] and 2-(2-methoxyphenyl)benzo[*d*]oxazole[2] were prepared according to literature procedures.

2. Full table of results for Kumada cross-coupling

Table **S-1**: Comparison of Pd catalysts **10** and **11** in Kumada cross-coupling.

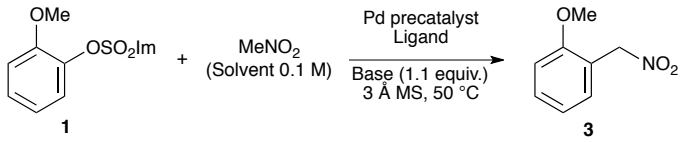


Entry	ArX	Grignard	Catalyst	Solvent	T (°C)	Conversion[1] (Time)	Product Yield[2] (Time)
1	**1**	**12**	**10**	2-MeTHF	rt	33% (4 h) 76% (23 h)	<5% (4 h) <5% (23 h)
2	**1**	**12**	**11**	2-MeTHF	rt	73% (4 h) 75% (23 h)	<5% (4 h) <5% (23 h)
3	**1**	**12**	**10**	^{t}AmOMe	50	84% (1 h) 91% (24 h)	7% (1 h) 5% (24 h)
4	**1**	**12**	**11**	^{t}AmOMe	50	>99% (17 h)	>99% (17 h) [63%]
5	**1**	**12**	**11**	^{t}AmOMe	50	>99% (1 h)	>94% (1 h)
6	**8**	**12**	**10**	2-MeTHF	rt	16% (1 h) 16% (4 h) 67% (24 h)	n.d.[3]
7	**8**	**12**	**11**	2-MeTHF	rt	66% (1 h) 95% (4 h)	n.d.[3]
8[4]	**8**	**12**	**11**	2-MeTHF	rt	n.d.[5]	[60%] (4 h)
9	**8**	**13**	**10**	2-MeTHF	rt	13% (1 h) 23% (4 h)	<5% (1 h) 5% (4 h)
10	**8**	**13**	**11**	2-MeTHF	rt	85% (1 h) 94% (4 h)	80% (1 h) 94% (4 h)
11	**8**	**13**	**11**	2-MeTHF	rt	n.d.[5]	[74%] (24 h)
12	**9**	**12**	**10**	2-MeTHF	rt	25% (18 h)	18% (18 h)
13	**9**	**12**	**11**	2-MeTHF	rt	75% (18 h)	69% (18 h)
14	**9**	**12**	**10**	2-MeTHF	40	16% (1 h) 51% (4 h) >99% (22 h)	8% (1 h) 43% (4 h) 91% (22 h)
15	**9**	**12**	**11**	2-MeTHF	40	60% (1 h) 89% (4 h) >99% (22 h)	48% (1 h) 77% (4 h) 88% (22 h)
16	**9**	**12**	**11**	2-MeTHF	40	n.d.[5]	[88%] (22 h)

[1]Conversion = %ArX consumed. [2]Product yield was determined by ^{1}H NMR analysis using either 1-methylnaphthalene (entries 1-5, 12-16) or 1-fluoronaphthalene (entries 6-11) as an internal standard against a t_0. Values in [brackets] are isolated yields of pure products after chromatography. [3]Due to the overlap of multiple signals in the ^{1}H NMR the product yield was not determined. [4]1.1 equiv. Grignard used. [5]No samples were taken on these entries as this would reduce the isolated yield.

3. Further results for nitromethylation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate

Table **S-2**. Further results for the optimisation of the nitromethylation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate, **1**.



Entry	Catalyst (mol%)	Ligand (mol%)	Base	Time (h)	Ratio 3:1 (yield)
1	Pd_2dba_3 (5 mol%)	CM-Phos (12 mol%)	Cs_2CO_3	16	<5:95
2	Pd_2dba_3 (5 mol%)	DtBPF (12 mol%)	Cs_2CO_3	16	<5:95
3	Pd_2dba_3 (5 mol%)	PCy_3 (12 mol%)	Cs_2CO_3	16	<5:95
4	$Pd(TFA)_2$ (5 mol%)	XPhos (12 mol%)	Cs_2CO_3	64	19:81
5	Pd_2dba_3 (5 mol%)	DtBPF (6 mol%)	Cs_2CO_3	23	<5:95
6	Pd_2dba_3 (5 mol%)	PPh_3 (12 mol%)	Cs_2CO_3	23	<5:95
7	Pd_2dba_3 (5 mol%)	(±)-BINAP (6 mol%)	Cs_2CO_3	23	<5:95
8	Pd_2dba_3 (5 mol%)	BrettPhos (12 mol%)	Cs_2CO_3	23	24:76
9	Pd_2dba_3 (5 mol%)	TrixiePhos (12 mol%)	Cs_2CO_3	23	74:26
10	Pd_2dba_3 (5 mol%)	TrixiePhos (12 mol%)	Cs_2CO_3	64	>95:5
11	Pd_2dba_3 (5 mol%)	DCyPF (6 mol%)	Cs_2CO_3	64	<5:95
12	Pd_2dba_3 (5 mol%)	$PhPCy_2$ (12 mol%)	Cs_2CO_3	64	<5:95
13	Pd_2dba_3 (5 mol%)	*t*-BuX-Phos (12 mol%)	Cs_2CO_3	64	33:67
14	Pd_2dba_3 (5 mol%)	JohnPhos (12 mol%)	Cs_2CO_3	64	<5:95
15	Pd_2dba_3 (5 mol%)	*t*-$BuPPh_2$ (12 mol%)	Cs_2CO_3	64	<5:95
16	Pd_2dba_3 (5 mol%)	TrixiePhos (12 mol%)	K_3PO_4	23	13:87
17	$Pd(OAc)_2$ (10 mol%)	TrixiePhos (30 mol%)	Cs_2CO_3	64	46:54
18[1]	Pd_2dba_3 (5 mol%)	TrixiePhos (12 mol%)	Cs_2CO_3	64	>95:5 (65%)

[1]Reaction was performed on a 2.5 mmol scale.

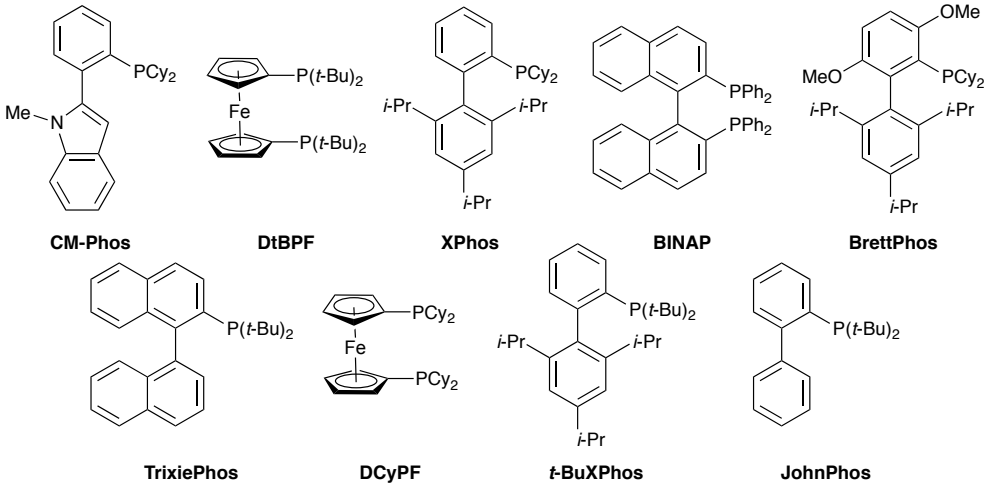
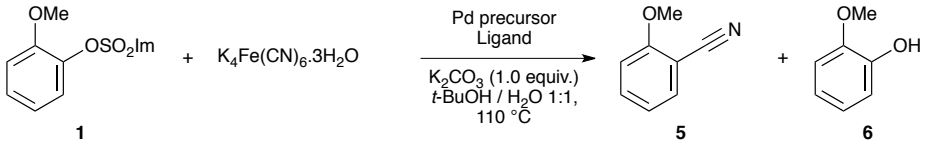


Figure **S-1**: Ligands used in the nitromethylation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate, **1**.

4. Full results for the cyanation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate

Table **S-3**: Initial results for the optimisation of the cyanation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate, **1**.

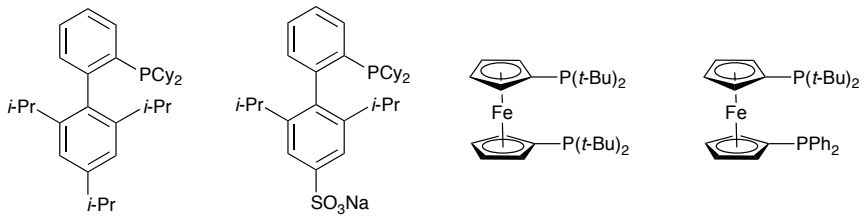


1 5 6

Entry	Catalyst (mol%)	Ligand (mol%)	$K_4Fe(CN)_6.3H_2O$ (mol%)	Time (h)	Product Ratio[1] 5:1:6 (yield)
1	$Pd(OAc)_2$ (5 mol%)	X-Phos (10 mol%)	50	24	72:24:4
2[2]	$Pd(OAc)_2$ (5 mol%)	X-Phos (10 mol%)	50	24	1:90:9
3	$Pd(OAc)_2$ (5 mol%)	X-Phos (10 mol%)	50	72	97:2:1[3]
4	$Pd(OAc)_2$ (1.5 mol%)	X-Phos (3 mol%)	50	72	5:26:69
5	None	None	50	72	0:66:44[3]
6	$Pd(OAc)_2$ (5 mol%)	X-Phos (10 mol%)	50	72	99:0:1 (50%)
7	$Pd(OAc)_2$ (5 mol%)	X-Phos (10 mol%)	50	48	98:0:2
8	$Pd(OAc)_2$ (5 mol%)	X-Phos-SO_3Na (10 mol%)	50	48	0:90:10
9	$Pd(TFA)_2$ (5 mol%)	X-Phos (10 mol%)	50	48	98:0:2
10	$Pd(TFA)_2$ (5 mol%)	X-Phos-SO_3Na (10 mol%)	50	48	0:89:11
11	$Pd(TFA)_2$ (1 mol%)	X-Phos (2 mol%)	50	48	68:25:7
12	$Pd(TFA)_2$ (5 mol%)	X-Phos (10 mol%)	21	48	88:0:11
13	$Pd(TFA)_2$ (1 mol%)	X-Phos (2 mol%)	21	48	89:0:11 (67%)
14	$Pd(TFA)_2$ (1 mol%)	X-Phos (2 mol%)	21	24	67:18:15
15	$Pd(TFA)_2$ (1 mol%)	X-Phos (3 mol%)	21	24	88:0:12
16	$Pd(TFA)_2$ (1 mol%)	PPh_3 (3 mol%)	21	24	88:8:4
17	$Pd(TFA)_2$	$P(Cy)_3$	21	24	0:83:17

	(1 mol%)	(3 mol%)			
18	$Pd(TFA)_2$ (1 mol%)	P(*o*-tolyl)$_3$ (3 mol%)	21	24	7:77:16
19	$Pd(TFA)_2$ (1 mol%)	CM-Phos (3 mol%)	21	24	77:12:11
20	$Pd(TFA)_2$ (1 mol%)	DtBPF (2 mol%)	21	24	14:66:20
21	$Pd(TFA)_2$ (1 mol%)	DtBDPPF (2 mol%)	21	24	34:50:16

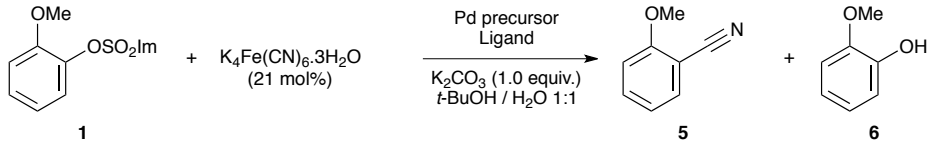
[1]As judged by ^{1}H NMR of the crude reaction mixture. [2]*t*-BuOH was used as the solvent. [3]Multiple other products were also formed.



XPhos **XPhos-SO_3Na** **DtBPF** **DtBDPPF**

Figure **S-2**: Ligands used in the cyanation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate, **1**.

Table **S-4**: Catalyst optimisation of the cyanation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate, **1**.



1 **5** **6**

Entry	Pd (mol%)	Ligand (mol%)	Temp (°C)	Time (h)	Product Ratio[1] 5:1:6 (yield)
1	$Pd(TFA)_2$ (1 mol%)	X-Phos (3 mol%)	110	24	88:0:12
2	$Pd(TFA)_2$ (1 mol%)	PPh_3 (3 mol%)	110	24	88:8:4
3	$Pd(TFA)_2$ (1 mol%)	PPh_3 (3 mol%)	100	48	95:0:5
4	$Pd(TFA)_2$ (0.5 mol%)	PPh_3 (1.5 mol%)	100	48	29:64:7
5	$Pd(TFA)_2$ (1 mol%)	PPh_3 (3 mol%)	90	48	94:5:1 (71%)
6	$Pd(TFA)_2$ (1 mol%)	PPh_3 (3 mol%)	70	48	~5%[2] **5**
7	$Pd(TFA)_2$ (1 mol%)	PPh_3 (3 mol%)	50	48	0%[2] **5**
8	$Pd(TFA)_2$ (1 mol%)	PPh_3 (3 mol%)	rt	48	0%[2] **5**
9	$Pd(TFA)_2$ (1 mol%)	$P(4\text{-}MeOPh)_3$ (3 mol%)	90	48	90:8:2
10	$Pd(TFA)_2$ (1 mol%)	$P(C_6F_5)_3$ (3 mol%)	90	48	0:97:3
11	$Pd(TFA)_2$ (1 mol%)	$Ph_2P(2\text{-pyridyl})$ (3 mol%)	90	48	18:76:6
12	$Pd(TFA)_2$ (1 mol%)	$P(3,5\text{-}CF_3Ph)_3$ (3 mol%)	90	48	0:99:9
13	$Pd(TFA)_2$ (0.5 mol%)	$P(4\text{-}MeOPh)_3$ (1.5 mol%)	90	48	2:92:6
14	$Pd(TFA)_2$ (0.5 mol%)	$P(2\text{-}MeOPh)_3$ (1.5 mol%)	90	48	0:85:15

[1]As judged by ^{1}H NMR of the crude reaction mixture. [2]Multiple other products were also formed.

5. Experimental details

Experimental details for the Kumada cross-coupling

General Procedure 1: An aryl halide or 2-methoxyphenyl-1*H*-imidazole-1-sulfonate and an internal standard were added to a flame dried Schlenk flask under an inert atmosphere. Degassed solvent was then added 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 desired palladium catalyst [L_2PdCl_2] (L_2 = diphosphine) was added to a second flame dried Schlenk flask and placed under an inert atmosphere. Solvent was then added. The solution containing the electrophile and internal standard was added to the palladium catalyst solution *via* syringe. The requisite Grignard solution was added dropwise over 30 minutes. The reaction mixture was stirred at a specific temperature for a specific time; tracking the reaction progress by ^{1}H NMR. Following reaction completion (as determined by analysis of the ^{1}H NMR), the mixture was allowed to cool to ambient temperature and either saturated aqueous ammonium chloride or dilute hydrochloric acid (1M) was added. The aqueous phase was extracted three times with ethyl acetate or diethyl ether, dried over sodium sulfate and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel.

Table **S-1**, Entry **1**: Following **General Procedure 1**, 2-methoxyphenyl-1*H*-imidazole-1-sulfonate (127.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol) were dissolved in 2-MeTHF (400 μL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed by ^{1}H NMR (to give a t_0 spectra). The remainder of this solution was added to a second Schlenk flask containing [$PdCl_2$(dppf)] (3.7 mg, 0.005 mmol). *para*-Tolylmagnesium bromide solution (1.2 mL, 0.5M in Et_2O, 0.60 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at room temperature for 4 hours. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^{1}H NMR spectrum. The reaction was incomplete therefore stirring was continued for a further 19 hours before a second sample was taken. The reaction was not worked-up.

Table **S-1**, Entry **2**: Following **General Procedure 1**, 2-methoxyphenyl-1*H*-imidazole-1-sulfonate (127.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.42 mmol) were dissolved in 2-MeTHF (400 μL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(*S*)-Xyl-Phanephos)] (4.3 mg, 0.005 mmol). *para*-Tolylmagnesium bromide solution (1.2 mL, 0.5M in Et_2O, 0.60 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at room temperature for 4 hours. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. The reaction was incomplete therefore stirring was continued for a further 19 hours before a second sample was taken. The reaction was not worked-up.

Table **S-1**, Entry **3**: Following **General Procedure 1**, 2-methoxyphenyl-1*H*-imidazole-1-sulfonate (63.6 mg, 0.25 mmol) and 1-methylnaphthalene (30 μL, 0.21 mmol) were dissolved in *tert*-amylmethyl ether (500 μL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(dppf)] (1.8 mg, 0.0025 mmol). *para*-Tolylmagnesium bromide solution (600 μL, 0.5M in Et_2O, 0.30 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at 50 °C for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. The reaction was incomplete therefore stirring was continued for a further 23 hours before a second sample was taken. The reaction was not worked-up.

2-Methoxy-4'-methyl-1,1'-biphenyl, 2

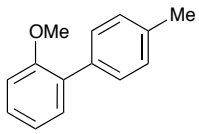


Table **S-1**, Entry **4**: Following **General Procedure 1**, 2-methoxyphenyl-1*H*-imidazole-1-sulfonate (127.1 mg, 0.50 mmol) and 1-methylnaphthalene (60 μL, 0.21 mmol) were dissolved in *tert*-amylmethyl ether (1.0 mL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(*S*)-Xyl-Phanephos)] (4.3 mg, 0.005 mmol). *para*-Tolylmagnesium bromide solution (1.2

mL, 0.5M in Et_2O, 0.60 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at 50 °C for 17 hours. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. The reaction mixture was allowed to cool to ambient temperature and saturated aqueous ammonium chloride solution (5 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 petrol:hexane, 10:90 to 100:0) to give 2-methoxy-4'-methyl-1,1'-biphenyl as a white solid (62.2 mg, 63%), with spectroscopic data in accordance with the literature;[3] δ_H (500 MHz, $CDCl_3$) 7.47 (2H, d, *J* 8.1), 7.36-7.31 (2H, m), 7.26 (2H, d, *J* 8.1), 7.08-6.99 (2H, m), 3.83 (3H, s), 2.43 (3H, s); δ_C (100 MHz, $CDCl_3$) 156.6, 136.7, 135.7, 130.9, 130.8, 129.5, 128.9, 128.5, 120.9, 111.3, 55.7, 21.3; *m/z* HRMS (ESI^+) $C_{14}H_{14}ONa^+$ ($[M+Na]^+$) requires 221.0942; found 221.0930 (–3.1 ppm).

Table **S-1**, Entry **5**: Following **General Procedure 1**, 2-methoxyphenyl-1*H*-imidazole-1-sulfonate (63.6 mg, 0.25 mmol) and 1-methylnaphthalene (30 μL, 0.21 mmol) were dissolved in *tert*-amylmethyl ether (500 μL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(*S*)-Xyl-Phanephos)] (2.2 mg, 0.0025 mmol). *para*-Tolylmagnesium bromide solution (600 μL, 0.5M in Et_2O, 0.30 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at 50 °C for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum which indicated complete conversion to 2-methoxy-4'-methyl-1,1'-biphenyl. The reaction was not worked-up.

Table **S-1**, Entry **6**: Following **General Procedure 1**, 4-bromofluorobenzene (110 μL, 1.0 mmol) and 1-fluoronaphthalene (120 μL, 0.93 mmol) were dissolved in 2-MeTHF (900 μL) and ~10 μL of the solution was diluted in 2-MeTHF and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(dppf)] (7.3 mg, 0.01 mmol). *para*-Tolylmagnesium bromide solution (2.4 mL, 0.5M in Et_2O, 1.2 mmol) was added dropwise over 30

minutes. The reaction mixture was stirred at rt for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with 2-MeTHF and obtaining a ^{1}H NMR spectrum. The reaction was incomplete therefore stirring was continued and further samples taken after 4 and 23 hours. The reaction was not worked-up.

Table **S-1**, Entry **7**: Following **General Procedure 1**, 4-bromofluorobenzene (110 μL, 1.0 mmol) and 1-fluoronaphthalene (120 μL, 0.93 mmol) were dissolved in 2-MeTHF (900 μL) and ~10 μL of the solution was diluted in 2-MeTHF and analysed using ^{1}H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(*S*)-Xyl-Phanephos)] (8.7 mg, 0.01 mmol). *para*-Tolylmagnesium bromide solution (2.4 mL, 0.5M in Et_2O, 1.2 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at rt for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with 2-MeTHF and obtaining a ^{1}H NMR spectrum. The reaction was incomplete therefore stirring was continued and a further sample was taken after 4 hours. The reaction was not worked-up.

4-Fluoro-4'-methyl-1,1'-biphenyl

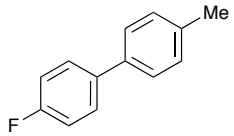


Table **S-1**, Entry **8**: Following **General Procedure 1**, 4-bromofluorobenzene (110 μL, 1.0 mmol) and [$PdCl_2$(*S*)-Xyl-Phanephos)] (8.7 mg, 0.01 mmol) were dissolved in 2-MeTHF (1.0 mL) and *para*-tolylmagnesium bromide solution (2.2 mL, 0.5M in Et_2O, 1.1 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at rt for 4 hours. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^{1}H NMR spectrum. Aqueous HCl (5 mL, 1M) was added and the aqueous phase 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 hexane) to give 4-fluoro-4'-methyl-1,1'-biphenyl as a white solid (111.7 mg, 60%) with spectroscopic data in accordance with the literature;[4] δ_H (500 MHz, $CDCl_3$) 7.57-7.53 (2H, m), 7.47 (2H, d, *J* 8.0), 7.27 (2H, d, *J* 8.0), 7.17-7.11 (2H, m), 2.42 (1H, s); δ_F (470 MHz, $CDCl_3$) –

116.3; δ_C (125 MHz, $CDCl_3$) 162.4 (d, *J* 245.5), 137.5, 137.4 (d, *J* 2.94), 137.2, 129.7, 128.6 (d, *J* 7.78), 127.0, 115.7 (d, *J* 21.5), 21.2; *m/z* HRMS (EI^+) $C_{13}H_{11}F^+$ ($[M]^+$) requires 186.0845; found 186.0839 (–3.1 ppm). Also isolated was a 66:34 mixture (as judged by ^1H NMR analysis) of 4-fluoro-4'-methyl-1,1'-biphenyl
and 4,4'-dimethylbiphenyl as a white solid (46.3 mg).

Table **S-1**, Entry **9**: Following **General Procedure 1**, 4-bromofluorobenzene (110 μL, 1.0 mmol) and 1-fluoronaphthalene (120 μL, 0.93 mmol) were dissolved in 2-MeTHF (900 μL) and ~10 μL of the solution was diluted in 2-MeTHF and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(dppf)] (7.3 mg, 0.01 mmol). *n*-Propylmagnesium chloride solution (600 μL, 2.0M in Et_2O, 1.2 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at rt for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with 2-MeTHF and obtaining a ^1H NMR spectrum. The reaction was incomplete therefore stirring was continued and a further samples taken after 4 hours. The reaction was not worked-up.

Table **S-1**, Entry **10**: Following **General Procedure 1**, 4-bromofluorobenzene (110 μL, 1.0 mmol) and 1-fluoronaphthalene (120 μL, 0.93 mmol) were dissolved in 2-MeTHF (900 μL) and ~10 μL of the solution was diluted in 2-MeTHF and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(*S*)-Xyl-Phanephos)] (8.7 mg, 0.01 mmol). *n*-Propylmagnesium chloride solution (600 μL, 2.0M in Et_2O, 1.2 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at rt for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with 2-MeTHF and obtaining a ^1H NMR spectrum. The reaction was incomplete therefore stirring was continued and a further sample taken after 4 hours. The reaction was not worked-up.

1-Fluoro-4-propylbenzene

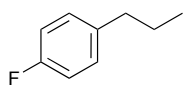


Table **S-1**, Entry **11**: Following **General Procedure 1**, 4-bromofluorobenzene (110 μL, 1.0 mmol) and [$PdCl_2$(*S*)-Xyl-Phanephos)] (8.7 mg, 0.01 mmol) were dissolved in 2-MeTHF (1.0 mL) and *n*-propylmagnesium chloride solution (600 μL, 2.0M in Et_2O,

1.2 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at rt for 24 hours. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. Aqueous HCl (5 mL, 1M) was added and the aqueous phase 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 CH_2Cl_2:hexane 70:30) to give 1-fluoro-4-propylbenzene as a pale yellow oil (102.7 mg, 74%); ν_{max} (thin film) 2959, 2928, 1508, 1499, 1223, 824; δ_H (500 MHz, $CDCl_3$) 7.16-7.10 (2H, m), 7.00-6.94 (2H, m), 2.57 (2H, t, *J* 7.6), 1.68-1.59 (2H, m), 0.94 (3H, t, *J* 7.4); δ_F (470 MHz, $CDCl_3$) –118.2; δ_C (125 MHz, $CDCl_3$) 161.3 (d, *J* 243.0), 138.3 (d, *J* 3.18), 129.8 (d, *J* 7.57), 115.0 (d, *J* 20.9), 37.3, 24.8, 13.8; *m/z* HRMS (EI^+) $C_9H_{11}F^+$ ($[M]^+$) requires 138.0845; found 138.0840 (–3.5 ppm).

Table **S-1**, Entry **12**: Following **General Procedure 1**, 4-bromoanisole (126 μL, 1.0 mmol) and 1-methylnaphthalene (120 μL, 1.0 mmol) were dissolved in 2-MeTHF (1.0 mL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(dppf)] (7.3 mg, 0.01 mmol). *para*-Tolylmagnesium bromide solution (2.4 mL, 0.5M in Et_2O, 1.2 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at rt for 18 hours. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. The reaction was not worked-up.

Table **S-1**, Entry **13**: Following **General Procedure 1**, 4-bromoanisole (126 μL, 1.0 mmol) and 1-methylnaphthalene (120 μL, 1.0 mmol) were dissolved in 2-MeTHF (1.0 mL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(*S*)-Xyl-Phanephos)] (8.7 mg, 0.01 mmol). *para*-Tolylmagnesium bromide solution (2.4 mL, 0.5M in Et_2O, 1.2 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at rt for 18 hours. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. The reaction was not worked-up.

Table **S-1**, Entry **14**: Following **General Procedure 1**, 4-bromoanisole (63 μL, 0.5 mmol) and 1-methylnaphthalene (60 μL, 0.5 mmol) were dissolved in 2-MeTHF (500 μL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(dppf)] (3.7 mg, 0.005 mmol). *para*-Tolylmagnesium bromide solution (1.2 mL, 0.5M in Et_2O, 0.6 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at 40 °C for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. The reaction was incomplete therefore stirring at 40 °C was continued and further samples taken after 4 and 22 hours. The reaction was not worked-up.

Table **S-1**, Entry **15**: Following **General Procedure 1**, 4-bromoanisole (63 μL, 0.5 mmol) and 1-methylnaphthalene (60 μL, 0.5 mmol) were dissolved in 2-MeTHF (500 μL) and ~10 μL of the solution was diluted in $CDCl_3$ and analysed using ^1H NMR (to give a t_0 spectra). The remainder of this solution was added to second Schlenk flask containing [$PdCl_2$(*S*)-Xyl-Phanephos)] (4.3 mg, 0.005 mmol). *para*-Tolylmagnesium bromide solution (1.2 mL, 0.5M in Et_2O, 0.6 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at 40 °C for 1 hour. The mixture was analysed by taking a sample (~10 μL), diluting with $CDCl_3$ and obtaining a ^1H NMR spectrum. The reaction was incomplete therefore stirring at 40 °C was continued and further samples taken after 4 and 22 hours. The reaction was not worked-up.

4-Methoxy-4'-methyl-1,1'-biphenyl

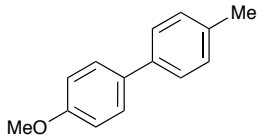


Table **S-1**, Entry **16**: Following **General Procedure 1**, 4-bromoanisole (126 μL, 1.0 mmol) and [$PdCl_2$(*S*)-Xyl-Phanephos)] (8.7 mg, 0.01 mmol) were dissolved in 2-MeTHF (1.0 mL) and *pare*-tolylmagnesium bromide solution (2.4 mL, 0.5M in Et_2O, 1.2 mmol) was added dropwise over 30 minutes. The reaction mixture was stirred at 40 °C for 22 hours. Aqueous HCl (5 mL, 1M) was added and the aqueous phase extracted with Et_2O (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 CH_2Cl_2:hexane 5:95) to give 4-methoxy-4'-methyl-1,1'-biphenyl as a white solid (173.5 mg, 88%) with spectroscopic data in accordance with the literature;[5] δ_H (500 MHz, $CDCl_3$) 7.56-7.52 (2H, m), 7.48 (2H, d, *J* 8.2), 7.26 (2H, d, *J* 8.0), 7.02-6.98 (2H, m), 3.87 (3H, s), 2.42 (3H, s); δ_C (125 MHz, $CDCl_3$) 159.0, 138.1, 136.5, 133.9, 129.6, 128.1, 126.7, 114.3, 55.5, 21.2; *m/z* HRMS (EI^+) $C_{14}H_{14}O^+$ ($[M]^+$) requires 198.1045; found 198.1043 (–0.8 ppm).

Experimental details for the nitromethylation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate, 1

General procedure: To an oven dried microwave vial was added (2-methoxyphenyl-1*H*-imidazole-1-sulfonate (127 mg, 0.50 mmol), palladium precatalyst, ligand, base (0.55 mmol) and powdered 3Å molecular sieves (100 mg). The vial was sealed with a crimp cap and flushed with argon for 5 minutes. Degassed nitromethane (5 mL) was added and the vial placed in an oil bath at 50 °C. The reaction was stirred vigorously for the required period of time. Upon cooling to rt, approximately 1 mL of the crude reaction mixture was added to an NMR tube complete with a C_6D_6 capillary and a ^1H NMR was run to assess the ratio between 2-methoxyphenyl-1*H*-imidazole-1-sulfonate **1** and 1-methoxy-2-(nitromethyl)benzene **3**.

Table **S-2**, Entry **18**: 1-methoxy-2-(nitromethyl)benzene. To a flame dried Schlenk flask under a flow of argon was added (2-methoxyphenyl-1*H*-imidazole-1-sulfonate (635 mg, 2.50 mmol), Pd_2dba_3 (114.7 mg, 0.125 mmol), TrixiePhos (120 mg, 0.300 mmol), Cs_2CO_3 (896 mg, 2.75 mmol) and powdered 3Å molecular sieves (500 mg). The Schlenk flask was sealed with a rubber septum. Degassed nitromethane (25 mL) was added and the flask placed in an oil bath at 50 °C. The reaction was stirred vigorously for 64 h. Upon cooling to rt, CH_2Cl_2 (50 mL) was added and the organics washed with sat. aqueous NH_4Cl (2 × 50 mL). The combined aqueous solutions were extracted with CH_2Cl_2 (2 × 50 mL). The combined organics were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:EtOAc 98:2 to 95:5) gave 1-methoxy-2-(nitromethyl)benzene (271 mg, 65%) as a white solid with spectroscopic data in accordance with the literature;[6] mp 59-61 °C {lit.[7] 64-65 °C}; δ_H (300 MHz, $CDCl_3$) 7.44-7.38 (1H m), 7.31-7.26 (1H, m), 7.02-6.95 (1H, m), 6.95 (1H, m), 5.46 (2H, s), 3.83 (3H, s); δ_C (75 MHz, $CDCl_3$) 158.6, 132.5, 132.2, 121.1, 118.9, 111.3, 75.1, 56.0; *m/z* HRMS (EI^+) $C_8H_9O_3N^+$ ($[M]^+$) requires 167.0582; found 167.0586 (+2.1 ppm).

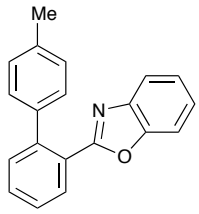
Experimental details for the cyanation of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate, 1

General procedure: To a microwave vial was added (2-methoxyphenyl-1*H*-imidazole-1-sulfonate (203 mg, 0.80 mmol), $K_4Fe(CN)_6.3H_2O$, K_2CO_3 (111 mg, 0.80 mmol), and the requisite metal precatalyst and ligand. The vial was sealed with a crimp cap and flushed with argon for 5 minutes. The selected solvent degassed by vigorous bubbling with argon before being added (4 mL) to the vial. The vial was then placed in an oil bath at the requisite temperature stirred vigorously for the required period of time. Upon cooling to rt, CH_2Cl_2 (4 mL) was added to the crude reaction mixture and the solution stirred vigorously before being allowed to settle. Approximately 1 mL of the CH_2Cl_2 layer was added to an NMR tube complete with a C_6D_6 capillary and a ^{1}H NMR was run to assess the ratio between **5**, **1** and **6**.

Table **S-4**, Entry **5**: 2-methoxybenzonitrile. To a microwave vial was added (2-methoxyphenyl-1*H*-imidazole-1-sulfonate (203 mg, 0.80 mmol), $K_4Fe(CN)_6.3H_2O$ (71.0 mg, 0.168 mmol), $Pd(TFA)_2$ (2.7 mg, 0.008 mmol), PPh_3 (6.3 mg, 0.024 mmol) and K_2CO_3 (111 mg, 0.800 mmol). The crimp cap was attached and the vial purged with argon for 5 minutes. A degassed solution of 50:50 (v:v) H_2O:^{t}BuOH (4 mL) was added and the vial placed in an oil bath at 90 °C and the reaction was stirred vigorously for 48 h. Upon cooling to rt, water (35 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL) and EtOAc (50 mL). The combined organics were dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:Et_2O 95:5 to 90:10) gave 2-methoxybenzonitrile (271 mg, 71%) as a colourless oil with spectroscopic data in accordance with the literature;[8] δ_H (300 MHz, $CDCl_3$) 7.56-7.5- (2H, m), 7.07-7.00 (2H, m), 3.92 (3H, s); δ_C (75 MHz, $CDCl_3$) 161.3, 134.5, 133.8, 120.8, 116.6, 111.4, 101.9, 56.1; *m/z* HRMS (ESI^+) $C_8H_7ONNa^+$ ($[M+Na]^+$) requires 156.0425; found 156.0414 (–0.6 ppm).

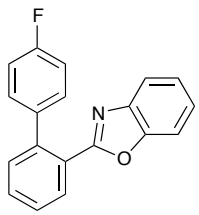
Experimental details for the Meyers reactions on 2-(2-methoxyphenyl)benzo[*d*]oxazole, 4

2-(4'-Methyl-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7a



To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in anhydrous 2-MeTHF at 40 °C was added a solution of 4-methylphenylmagnesium bromide (0.93 mL, 0.5M in Et_2O, 0.466 mmol) and the resultant mixture stirred for 16 h. Upon cooling to rt, the solution was concentrated *in vacuo* before water (25 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and EtOAc (25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:EtOAc 96:4) gave 2-(4'-methyl-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole (61.1 mg, 96%) as a white solid with spectroscopic data in accordance with the literature;[9] mp 83-85 °C {lit.[9] 88-90 °C}; ν_{max} (ATR) 2920, 1474, 1450, 1244, 1234, 1022, 742; δ_H (300 MHz, $CDCl_3$) 8.12-8.06 (1H, m), 7.77-7.71 (1H, m), 7.62-7.54 (1H, m), 7.53-7.45 (2H, m), 7.35-7.23 (3H, m), 7.22-7.10 (4H, m), 2.37 (3H, s); δ_C (75 MHz, $CDCl_3$) 164.2, 150.9, 142.5, 141.8, 138.1, 137.1, 131.3, 131.2, 131.1, 129.0, 128.8, 127.4, 126.4, 125.0, 124.4, 120.2, 110.7, 21.3; *m/z* HRMS (ESI^+) $C_{20}H_{15}ONNa^+$ ($[M+Na]^+$) requires 308.1051; found 308.1039 (–2.2 ppm).

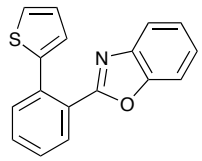
2-(4'-Fluoro-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7b



To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in *tert*-amyl methyl ether at rt was added a solution of 4-fluorophenylmagnesium bromide (0.71 mL, 1.0M in THF, 0.713 mmol) and the resultant mixture placed in an oil bath at 110 °C and stirred for 16 h. Upon cooling to rt, the solution was concentrated *in*

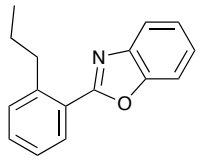
vacuo before water (25 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and EtOAc (25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:Et_2O 95:5) gave 2-(4'-fluoro-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole (50.1 mg, 78%) as a viscous oil; ν_{max} (thin film) 3059, 1605, 1508, 1473, 1450, 1221, 1029, 754; δ_H (300 MHz, $CDCl_3$) 8.19-8.12 (1H, m), 7.78-7.71 (1H, m), 7.66-7.45 (3H, m), 7.38-7.24 (5H, m), 7.09-7.01 (2H, m); δ_F (282 MHz, $CDCl_3$) –115.79; δ_C (75 MHz, $CDCl_3$) 163.7, 162.4 (d, *J* 246.3), 150.8, 141.7, 141.5, 137.1 (d, *J* 3.3), 131.2, 131.1 (d, *J* 3.3), 130.6, 130.5, 127.8, 126.4, 125.2, 124.5, 120.2, 115.2 (d, *J*, 21.5), 110.7; *m/z* HRMS (ESI^+) $C_{19}H_{12}ONFNa^+$ ($[M+Na]^+$) requires 312.0801; found 312.0788 (–2.3 ppm).

2-(2-(Thiophen-2-yl)phenyl)benzo[*d*]oxazole, 7c



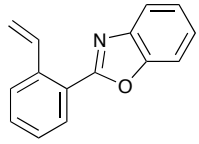
To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in *tert*-amyl methyl ether at rt was added a solution of 2-thienylmagnesium bromide (0.71 mL, 1.0M in THF, 0.713 mmol) and the resultant mixture placed in an oil bath at 110 °C and stirred for 16 h. Upon cooling to rt, the solution was concentrated *in vacuo* before water (25 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and EtOAc (25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:Et_2O 95:5) gave 2-(2-(thiophen-2-yl)phenyl)benzo[*d*]oxazole (51.7 mg, 84%) as a brown solid; mp 71-73 °C; ν_{max} (ATR) 3062, 2922, 1558, 1452, 1423, 1244, 1232, 1024, 708; δ_H (300 MHz, $CDCl_3$) 7.93 (1H, dd, *J* 7.6, 1.1), 7.76-7.68 (1H, m), 7.58-7.38 (3H, m), 7.36-7.18 (4H, m), 6.94-6.84 (2H, m); δ_C (75 MHz, $CDCl_3$) 163.4, 150.9, 141.9, 141.8, 135.0, 131.4, 131.3, 131.1, 128.0, 127.4, 126.9, 126.9, 126.2, 125.2, 124.5, 120.3, 110.8; *m/z* HRMS (ESI^+) $C_{17}H_{12}ONS^+$ ($[M+H]^+$) requires 278.0640; found 278.0624 (–3.6 ppm).

2-(2-Propylphenyl)benzo[*d*]oxazole, 7d



To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in anhydrous 2-MeTHF at 80 °C was added a solution of *n*-propylmagnesium chloride (0.37 mL, 2.0M in THF, 0.732 mmol) and the resultant mixture stirred for 16 h. Upon cooling to rt, the solution was concentrated *in vacuo* before water (25 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and EtOAc (25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:EtOAc 96:4) gave 2-(2-propylphenyl)benzo[*d*]oxazole (28.0 mg, 53%) as an off white solid; mp 77-79 °C; ν_{max} (ATR) 2959, 1454, 1379, 1273, 1161, 1107, 1068, 1030, 744; δ_H (300 MHz, $CDCl_3$) 8.16-8.11 (1H, m), 7.84-7.77 (1H, m), 7.63-7.56 (1H, m), 7.48-7.41 (1H, m), 7.40-7.31 (4H, m), 3.22-3.15 (2H, m), 1.76-1.62 (2H, m), 1.00 (3H, t, *J* 7.3); δ_C (75 MHz, $CDCl_3$) 163.5, 150.5, 143.6, 142.3, 131.1, 131.0, 130.5, 126.2, 126.1, 125.1, 124.4, 120.3, 110.6, 36.5, 24.7, 14.2; *m/z* HRMS (ESI^+) $C_{16}H_{16}ON^+$ ($[M+H]^+$) requires 238.1232; found 238.1222 (–1.9 ppm).

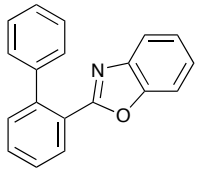
2-(2-Vinylphenyl)benzo[*d*]oxazole, 7e



To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in anhydrous 2-MeTHF (1 mL) at 20 °C was added a solution of vinylmagnesium chloride (0.29 mL, 1.6M in THF, 0.466 mmol) and the resultant mixture stirred for 4 h. The solution was concentrated *in vacuo* before aqueous saturated ammonium chloride solution (5 mL) was added. The aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organics were dried over $NaSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on Et_3N deactivated silica gel (eluent Et_3N:hexane:EtOAc 1:95:5) gave 2-(2-vinylphenyl)benzo[*d*]oxazole (36.8 mg, 75%) as an off white solid; mp 53-55 °C; ν_{max} (ATR) 3028, 2920, 1545, 1454, 1236, 1030, 918; δ_H (500 MHz, $CDCl_3$) 8.15 (1H, dd,

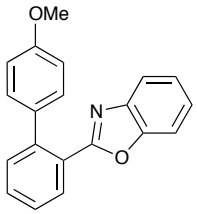
J 7.8, 1.1), 7.86-7.79 (2H, m), 7.75-7.71 (1H, m), 7.63-7.58 (1H, m), 7.53-7.49 (1H, m), 7.43 (1H, td, *J* 7.7, 1.1), 7.39-7.35 (2H, m), 5.82 (1H, dd, *J* 17.4, 1.0), 5.48 (1H, dd, *J* 11.0, 1.0); δ_C (125 MHz, $CDCl_3$) 162.8, 150.5, 142.2, 138.4, 135.9, 131.2, 130.1, 127.9, 127.3, 125.3, 125.1, 124.6, 120.4, 116.9, 110.7; *m/z* HRMS (ESI^+) $C_{15}H_{12}ON^+$ ($[M+H]^+$) requires 222.0919; found 222.0917 (–1.5 ppm).

2-([1,1'-Biphenyl]-2-yl)benzo[*d*]oxazole, 7f



To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in anhydrous 2-MeTHF at 40 °C was added a solution of phenylmagnesium bromide (0.25 mL, 3.0M in Et_2O, 0.733 mmol) and the resultant mixture stirred for 48 h. Upon cooling to rt, the solution was concentrated *in vacuo* before water (25 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and EtOAc (25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:Et_2O 95:5) gave 2-([1,1'-biphenyl]-2-yl)benzo[*d*]oxazole (57.2 mg, 95%) as a colourless sticky oil with spectroscopic data in accordance with the literature;[10] ν_{max} (thin film) 2912, 1451, 1240, 1026, 738, 696; δ_H (400 MHz, $CDCl_3$) 8.14-8.10 (1H, m), 7.72 (1H, dt, *J* 7.6, 1.1), 7.63-7.60 (1H, m), 7.55-7.47 (2H, m), 7.36-7.24 (8H, m); δ_C (100 MHz, $CDCl_3$) 164.0, 150.8, 142.6, 141.8, 141.1, 131.3, 131.1 (2 × *C*), 128.9, 128.2, 127.7, 127.4, 126.4, 125.0, 124.4, 120.2, 110.7; *m/z* HRMS (ESI^+) $C_{19}H_{14}ON^+$ ($[M+H]^+$) requires 272.1075; found 272.1067 (–1.1 ppm).

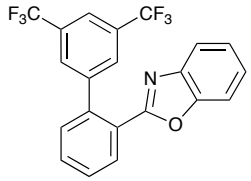
2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7g



To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in anhydrous 2-MeTHF at 40 °C was added a solution of 4-methoxyphenylmagnesium

bromide (1.86 mL, 0.5M in THF, 0.932 mmol) and the resultant mixture stirred for 48 h. Upon cooling to rt, the solution was concentrated *in vacuo* before water (25 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and EtOAc (25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:Et_2O 90:10) gave 2-(4'-methoxy-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole (32.0 mg, 48%) as a white solid; mp 105-106 °C; ν_{max} (ATR) 2938, 1610, 1508, 1456, 1435, 1229, 1177, 1016, 746; δ_H (300 MHz, $CDCl_3$) 8.09-8.06 (1H, m), 7.75-7.71 (1H, m), 7.60-7.54 (1H, m), 7.50-7.45 (2H, m), 7.35-7.19 (5H, m) 6.89-6.84 (2H, m), 3.83 (3H, s); δ_C (100 MHz, $CDCl_3$) 164.2, 159.1, 150.9, 142.2, 141.8, 133.4, 131.2, 131.2, 131.1, 130.0, 127.3, 126.3, 125.0, 124.4, 120.2, 113.7, 110.7 55.4; *m/z* HRMS (ESI^+) $C_{20}H_{16}O_2N^+$ ($[M+H]^+$) requires 302.1181; found 302.1171 (–1.5 ppm).

2-(3',5'-bis(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7h



To a solution of 2-(2-methoxyphenyl)benzo[*d*]oxazole (50.0 mg, 0.222 mmol) in *tert*-amyl methyl ether at rt was added a solution of 3,5-bis(trifluoromethyl)phenylmagnesium bromide solution (0.93 mL, 0.5M in THF, 0.466 mmol) and the resultant mixture placed in an oil bath at 110 °C and stirred for 16 h. Upon cooling to rt, the solution was concentrated *in vacuo* before water (25 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and EtOAc (25 mL). The combined organics were dried over $MgSO_4$, filtered and concentrated *in vacuo* to give the crude product. Purification *via* column chromatography on silica gel (eluent petrol:Et_2O 95:5) gave 2-(3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole (81.2 mg, 90%) as a white solid; mp 105-106 °C; ν_{max} (ATR) 2963, 1454, 1379, 1273, 1161, 1109, 1070, 898, 744; δ_H (300 MHz, $CDCl_3$) 8.33-8.27 (1H, m), 7.89 (1H, s), 7.81 (2H, s), 7.69-7.59 (3H, m), 7.40-7.44 (1H, m), 7.35-7.28 (3H, m); δ_F (282 MHz, $CDCl_3$) –63.32; δ_C (100 MHz, $CDCl_3$) 162.2, 150.6, 143.1, 141.5, 139.2, 131.4, 131.3, 131.2 (q, *J* 30.7), 130.8, 129.7 (d, *J* 2.2), 129.1, 126.1,

125.6, 124.8, 123.5 (q, *J* 272.4), 121.2 (m), 120.4, 110.5; *m/z* HRMS (ESI^+) $C_{21}H_{12}ONF_6^+$ ($[M+H]^+$) requires 408.0823; found 408.0815 (–0.6 ppm).

6. References

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7. An example of a ^{1}H NMR showing how conversion and yield were calculated in the Kumada Cross-coupling

Figure 3: An ^{1}H NMR spectrum of a t_0 showing the ratio between the doublet of 1-methylnaphthalene the internal standard at 7.99 ppm and the singlet of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate the substrate at 3.61 ppm.

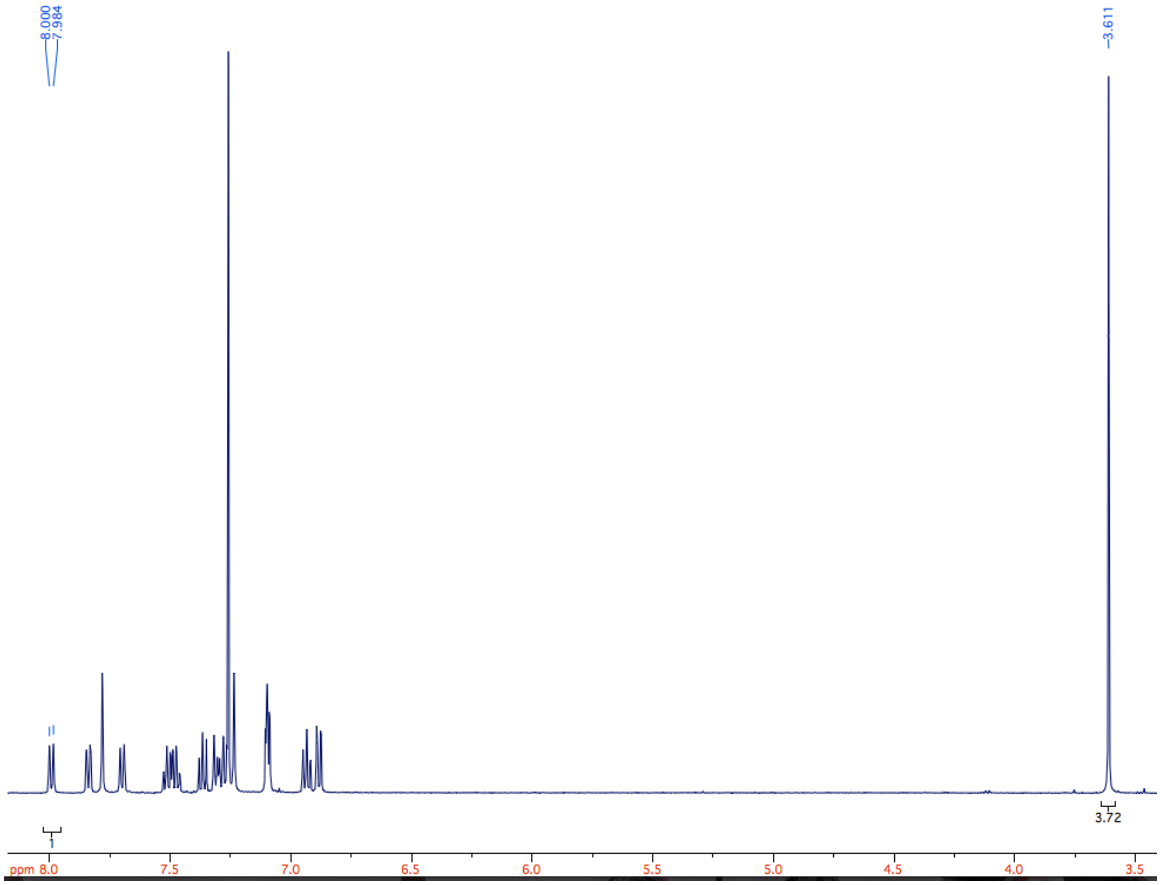


Figure 4: An ^{1}H NMR spectrum of a reaction sample with excellent conversion showing the ratio between the doublet of 1-methylnaphthalene the internal standard at 7.99 ppm and the singlet of 2-methoxy-4'-methyl-1,1'-biphenyl the product at 3.79 ppm.

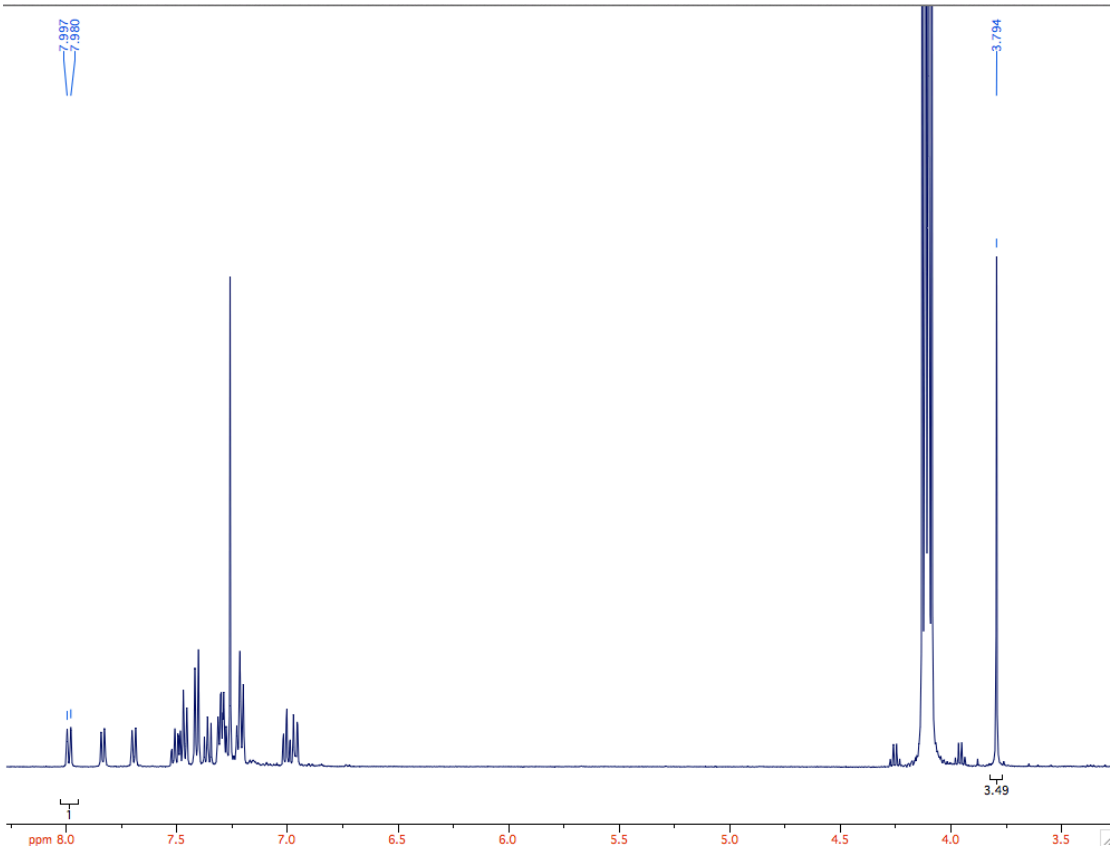
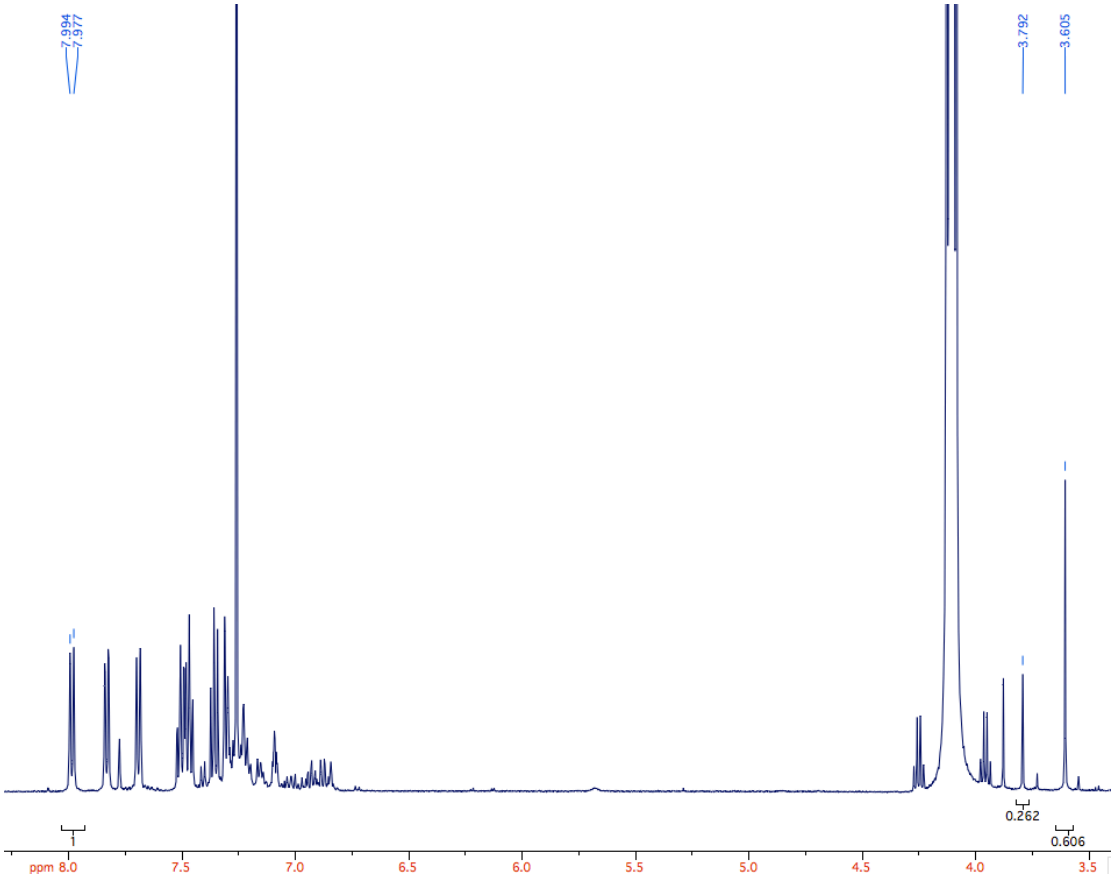
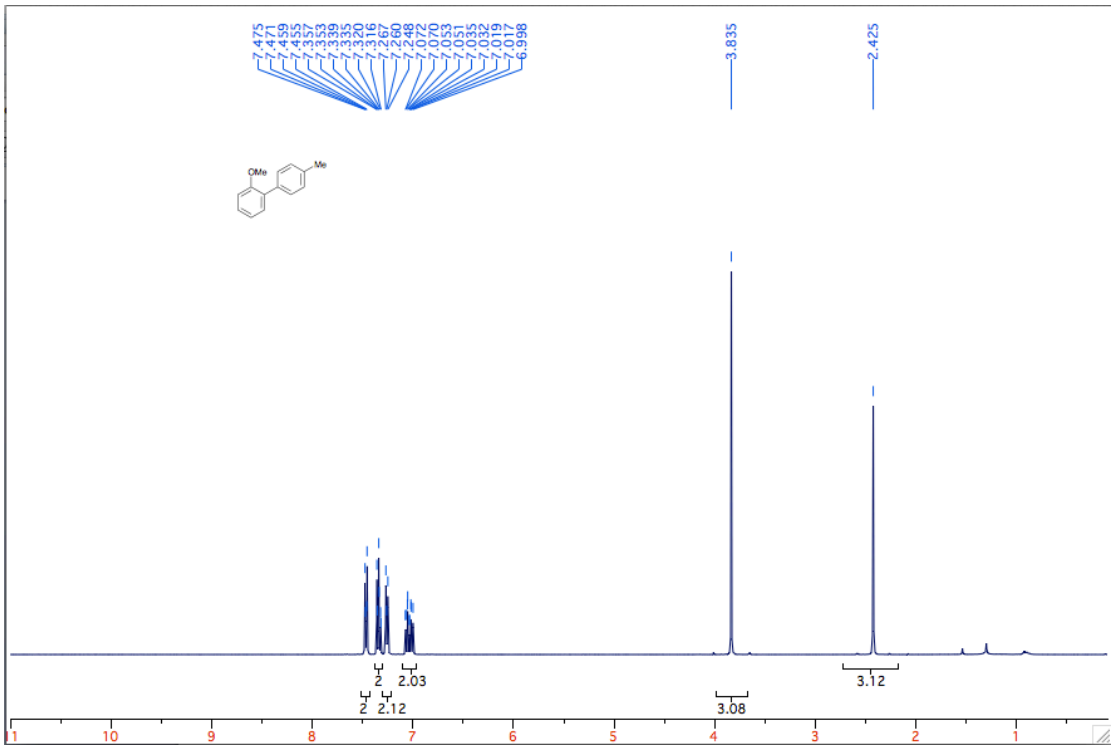


Figure 5: An ^{1}H NMR spectrum of a reaction sample with poor conversion showing the ratio between the doublet of 1-methylnaphthalene the internal standard at 7.99 ppm, the singlet of 2-methoxy-4'-methyl-1,1'-biphenyl the product at 3.79 ppm and the singlet of 2-methoxyphenyl-1*H*-imidazole-1-sulfonate the substrate at 3.61 ppm.

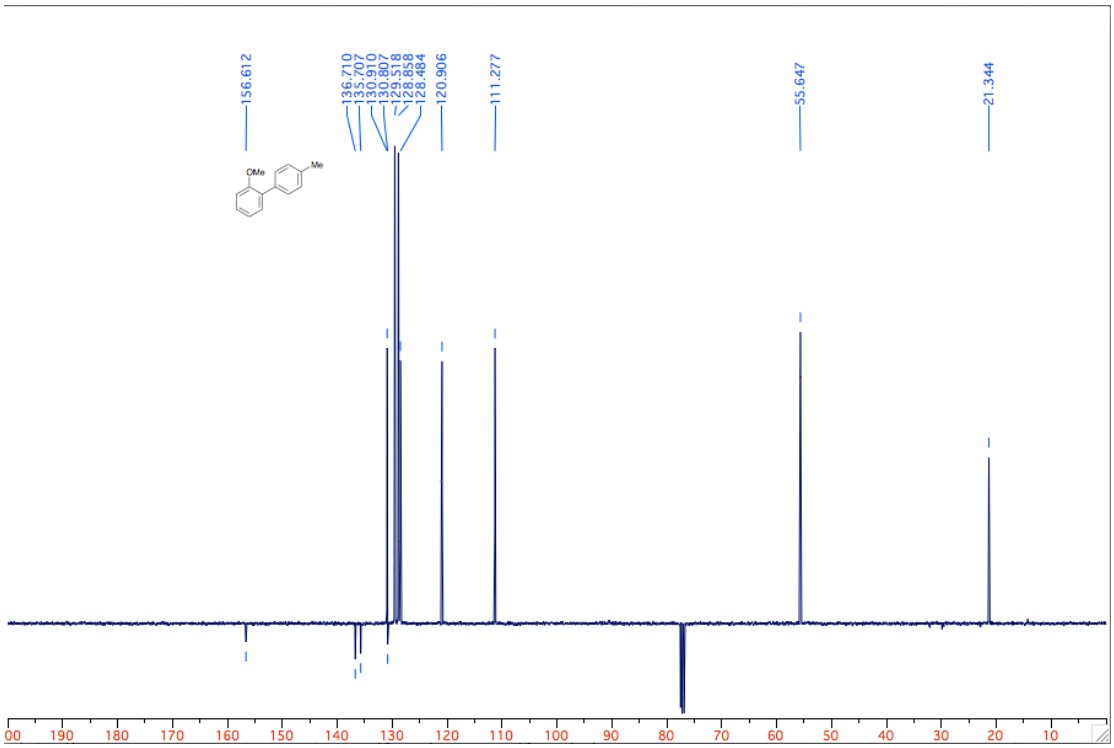


8. Copies of ^{1}H and ^{13}C NMR spectra of all products

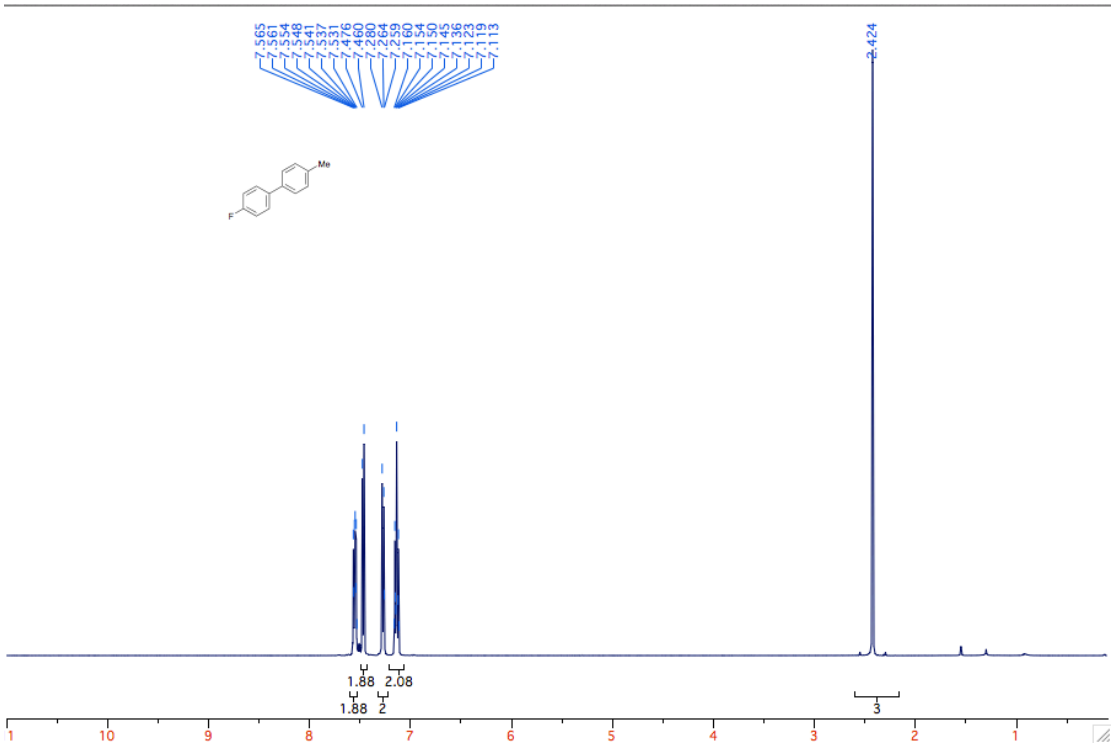
^{1}H NMR of 2-Methoxy-4'-methyl-1,1'-biphenyl, 2



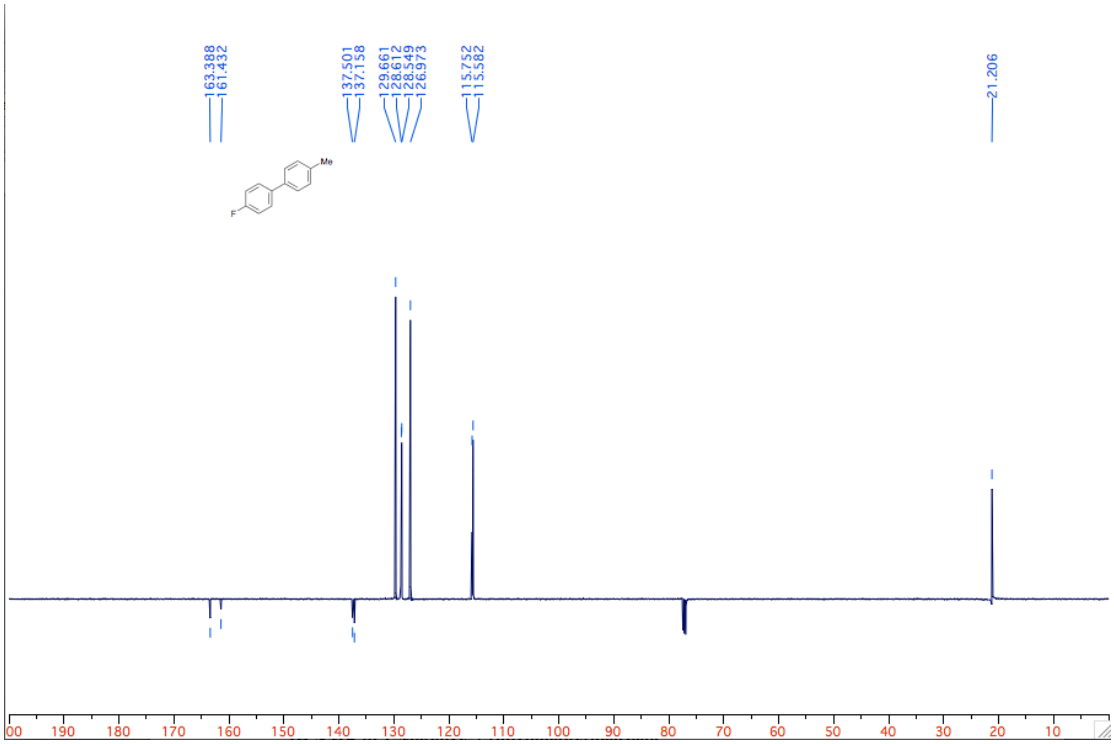
^{13}C NMR of 2-Methoxy-4'-methyl-1,1'-biphenyl, 2



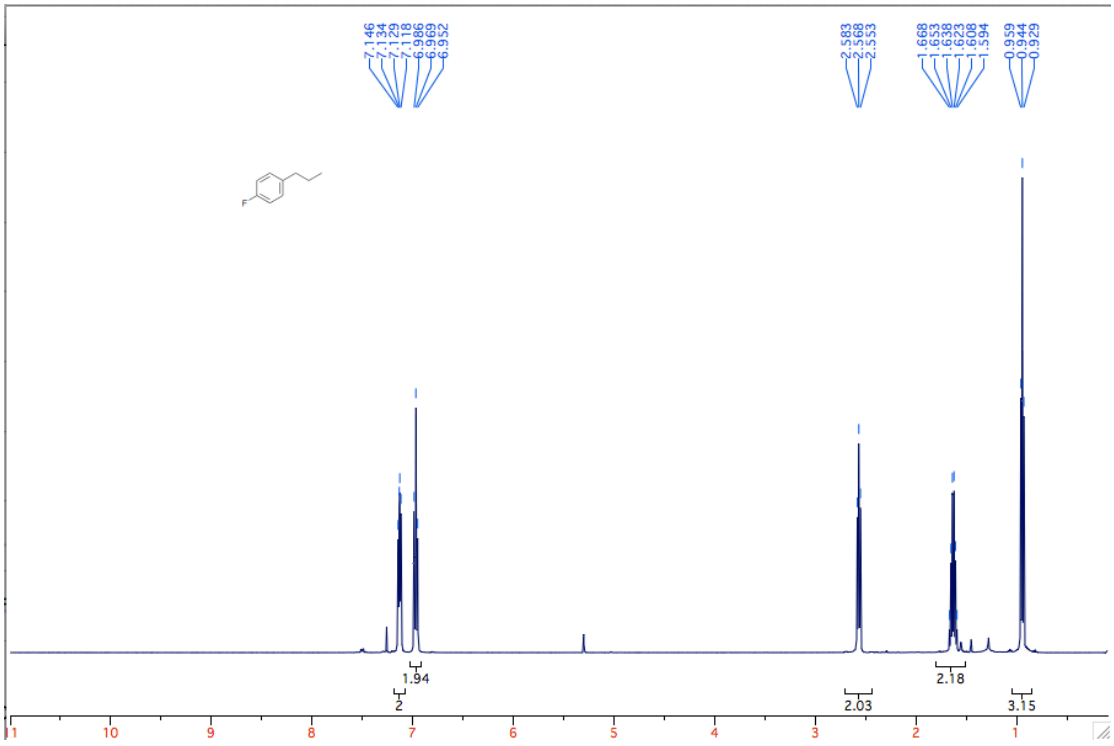
^{1}H NMR of 4-Fluoro-4'-methyl-1,1'-biphenyl



^{13}C NMR of 4-Fluoro-4'-methyl-1,1'-biphenyl



^{1}H NMR of 1-Fluoro-4-propylbenzene



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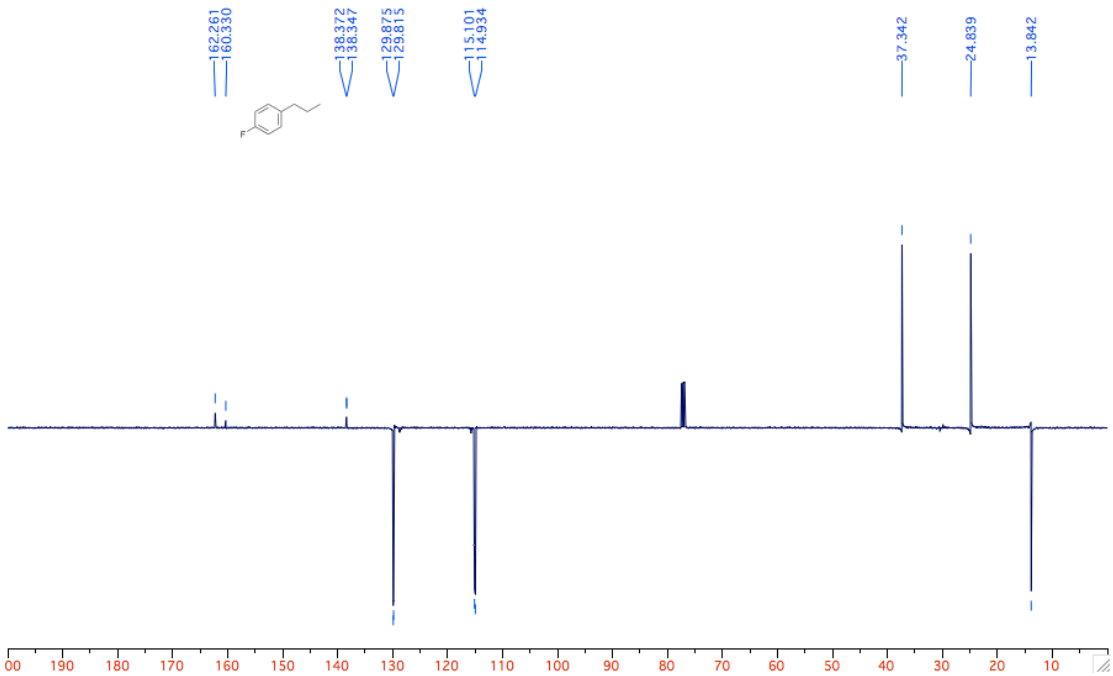
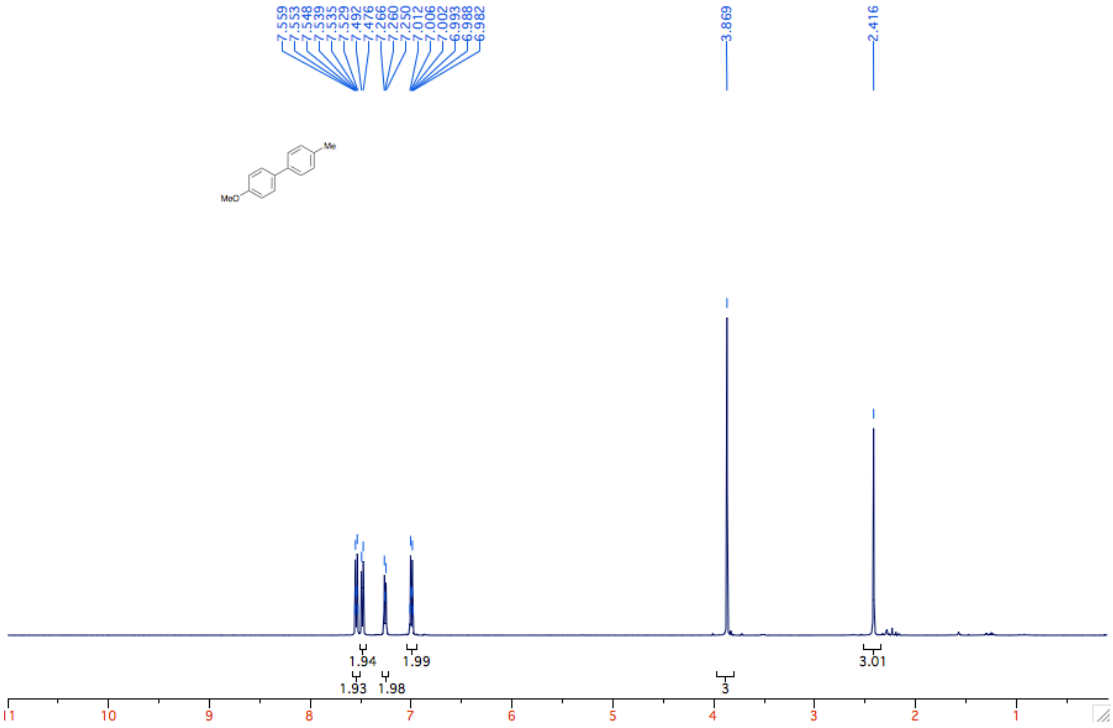
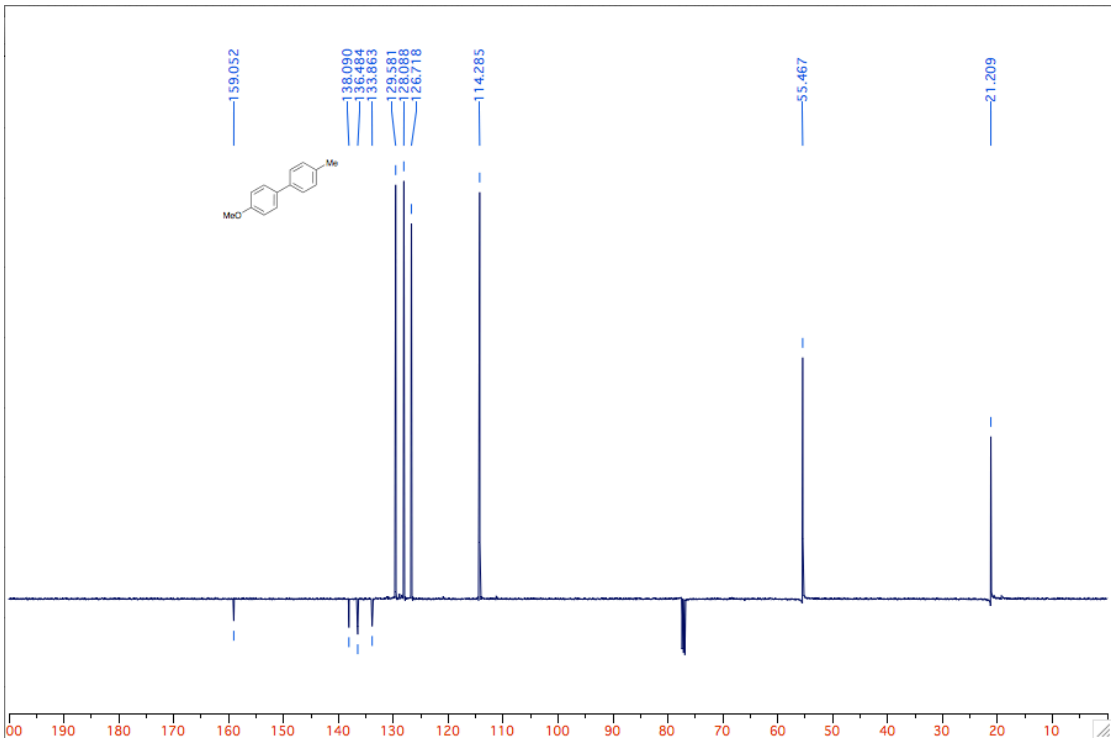


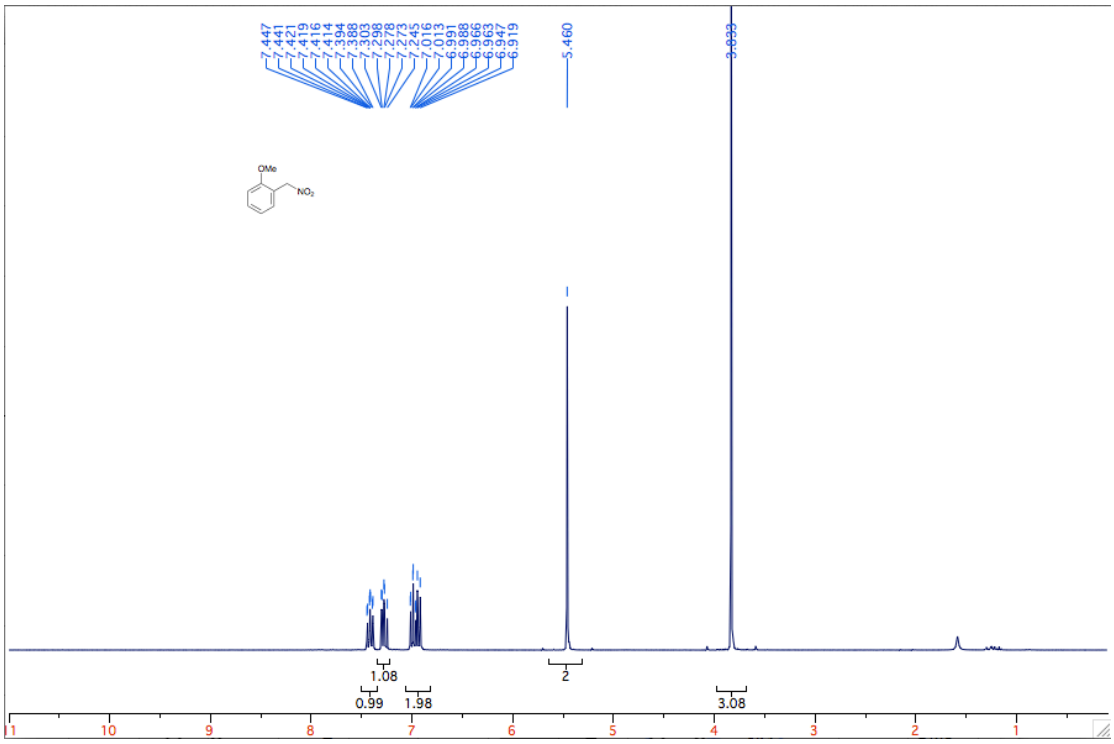
^{1}H NMR of 4-Methoxy-4'-methyl-1,1'-biphenyl



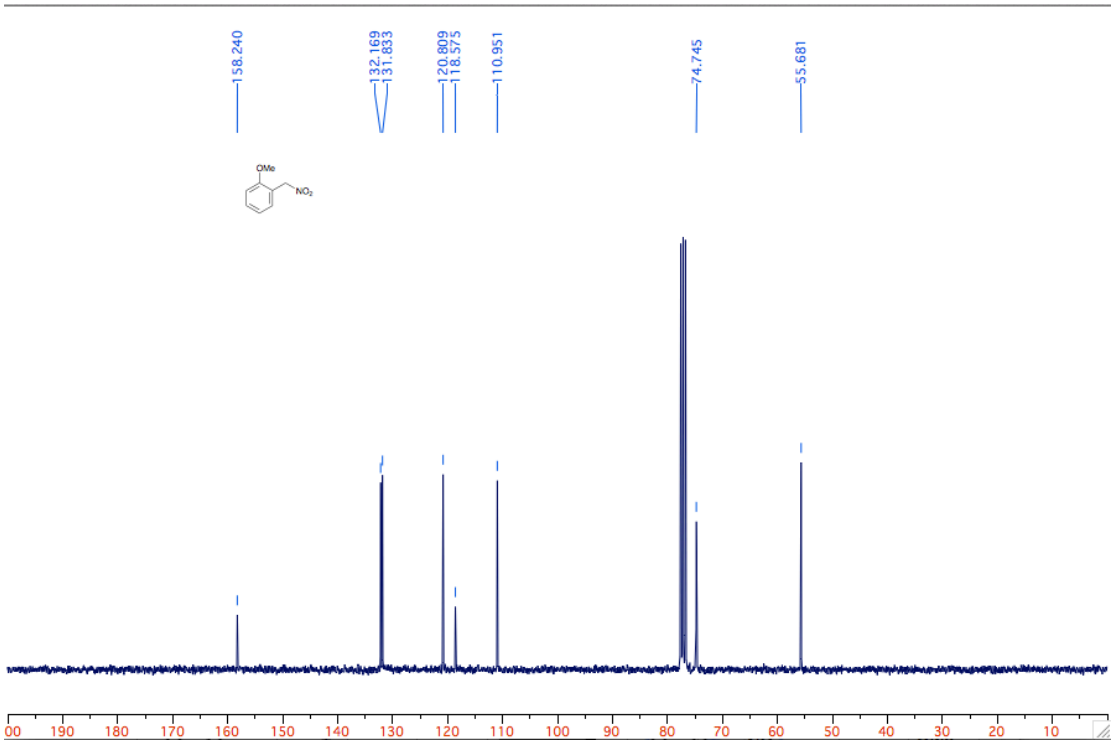
^{13}C NMR of 4-Methoxy-4'-methyl-1,1'-biphenyl



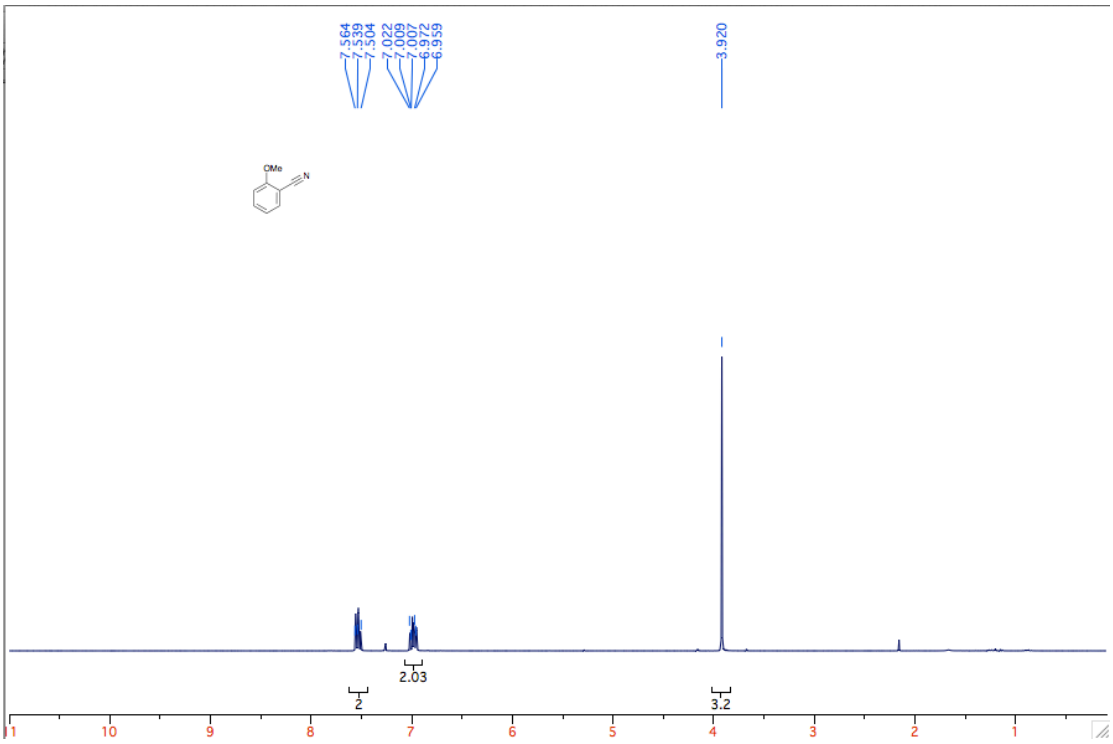
^{1}H NMR of 1-Methoxy-2-(nitromethyl)benzene, 3



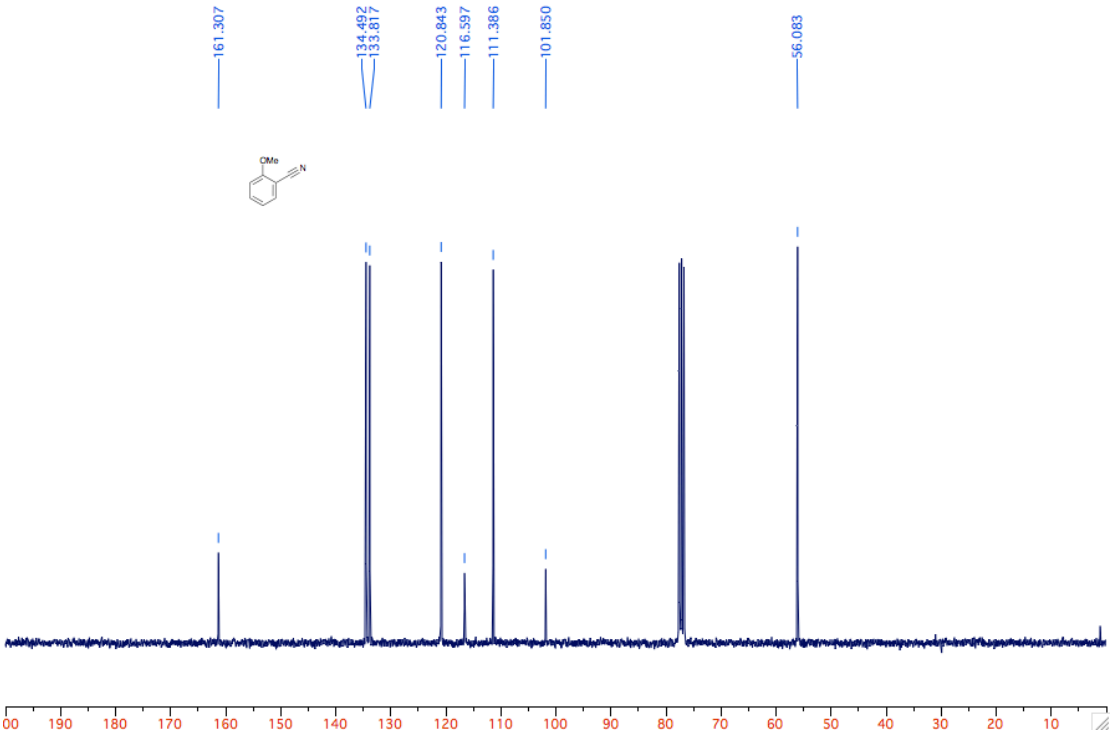
^{13}C NMR of 1-Methoxy-2-(nitromethyl)benzene, 3



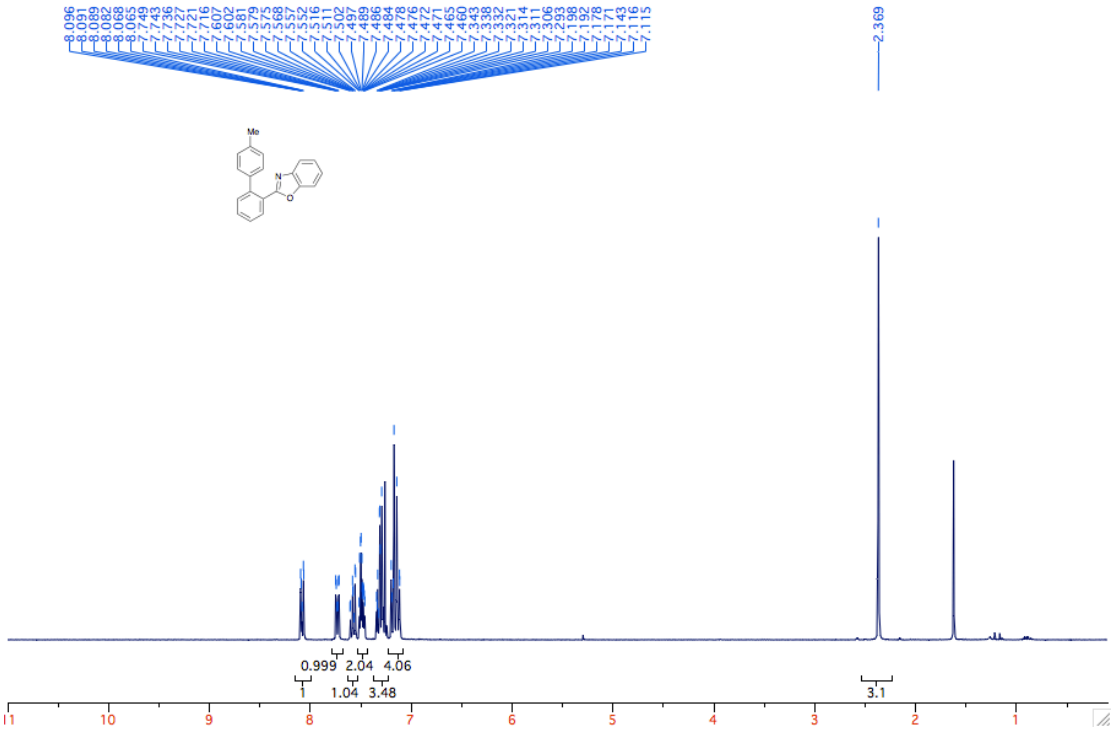
^{1}H NMR of 2-Methoxybenzonitrile, 5



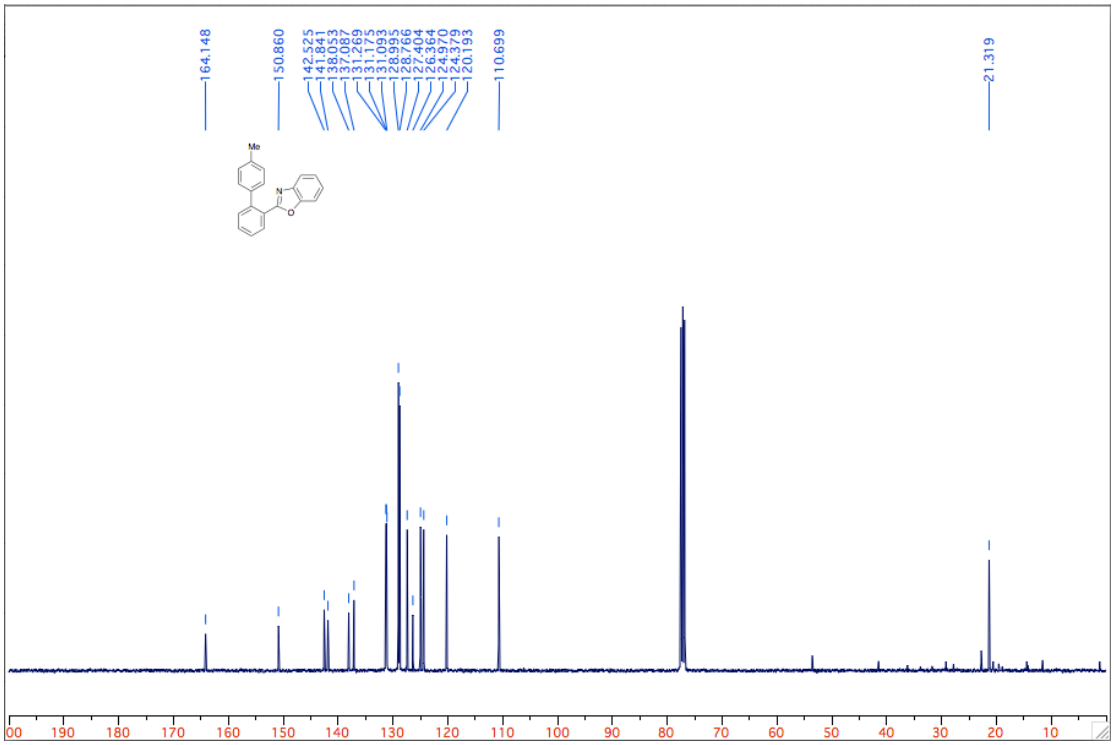
^{13}C NMR of 2-Methoxybenzonitrile, 5



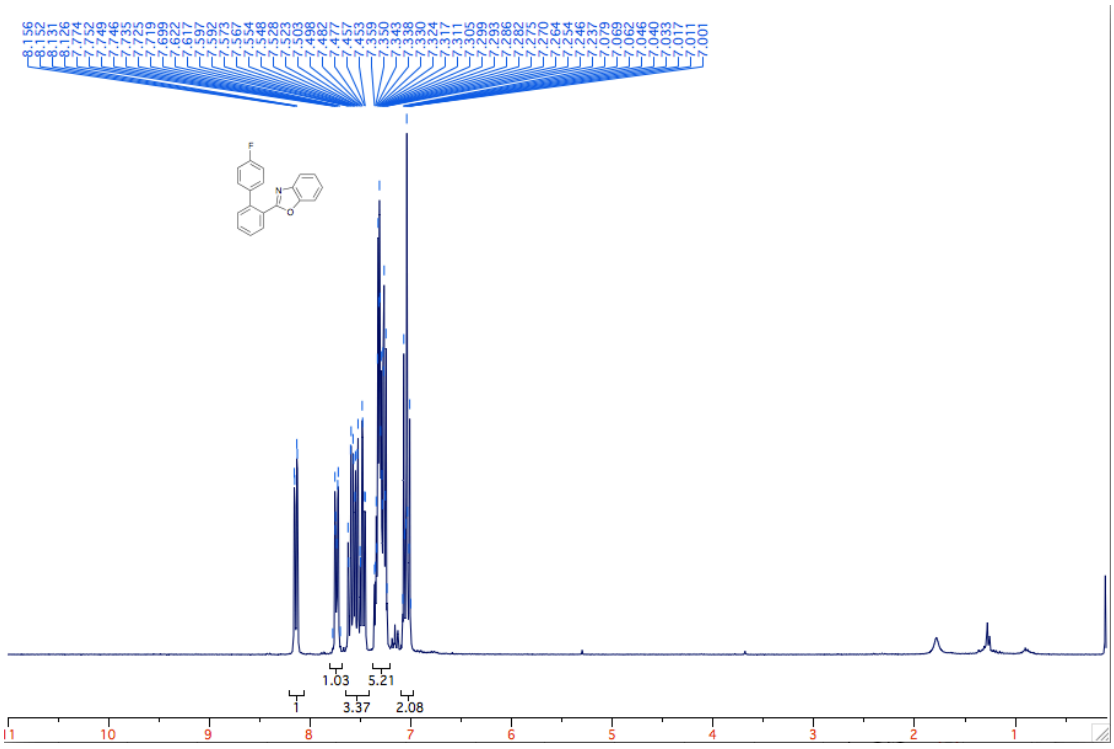
^{1}H NMR of 2-(4'-Methyl-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7a



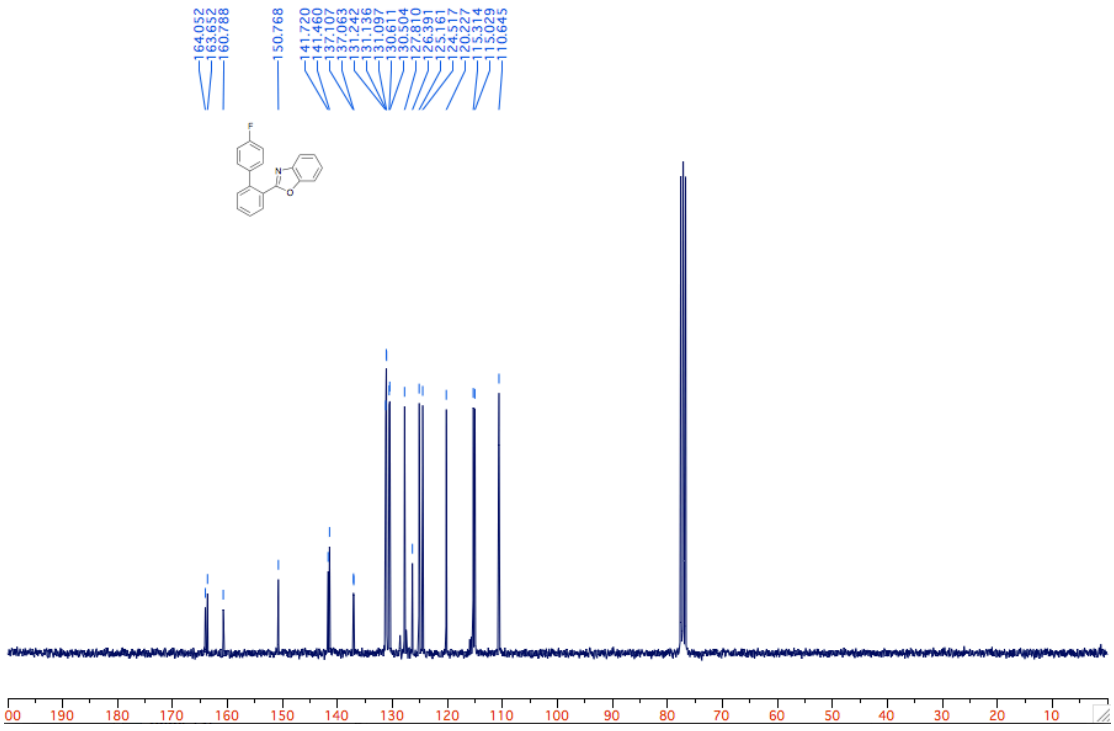
^{13}C NMR of 2-(4'-Methyl-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7a



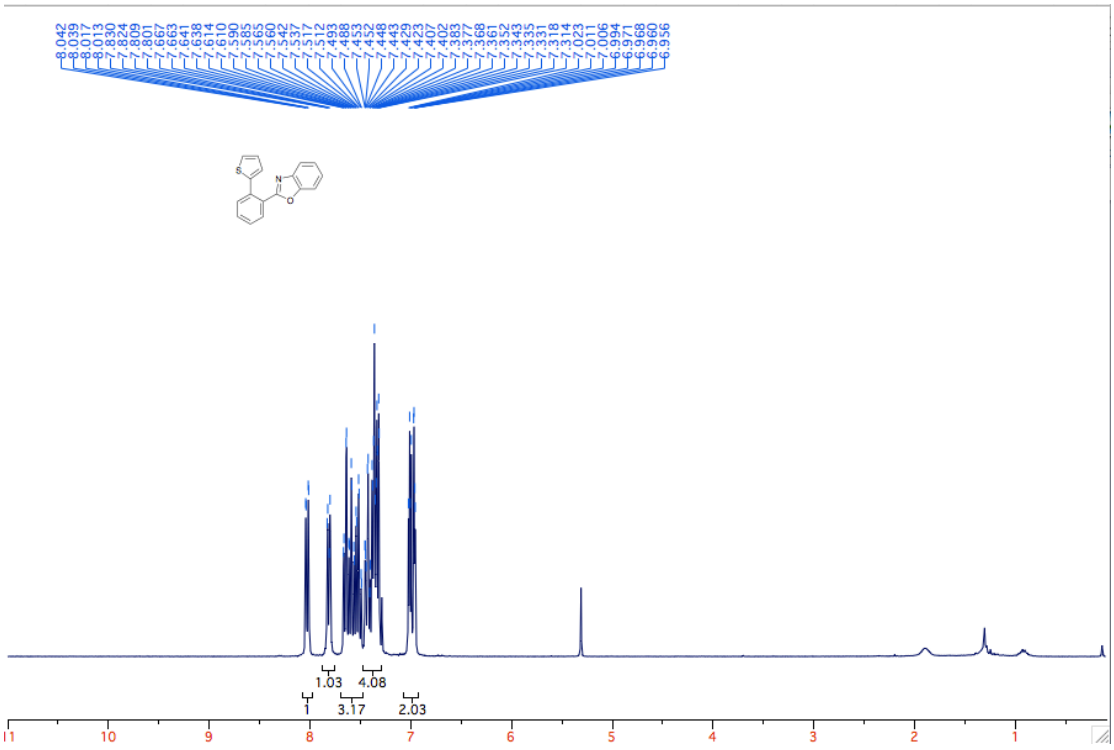
^{1}H NMR of 2-(4'-Fluoro-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7b



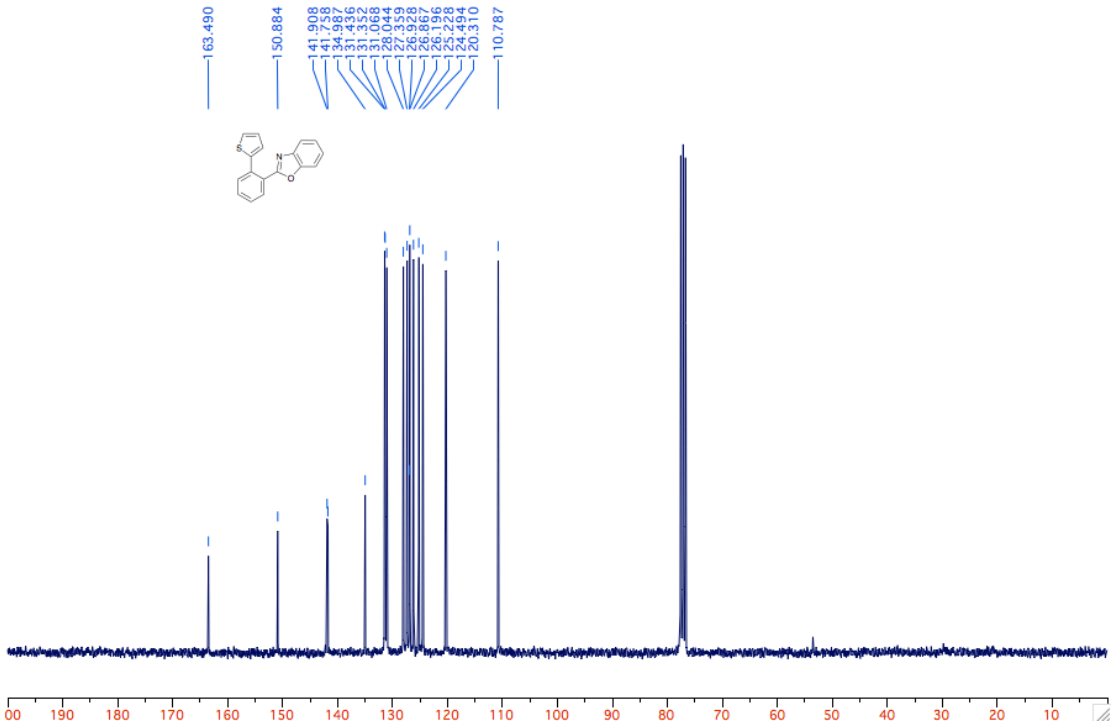
^{13}C NMR of 2-(4'-Fluoro-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7b



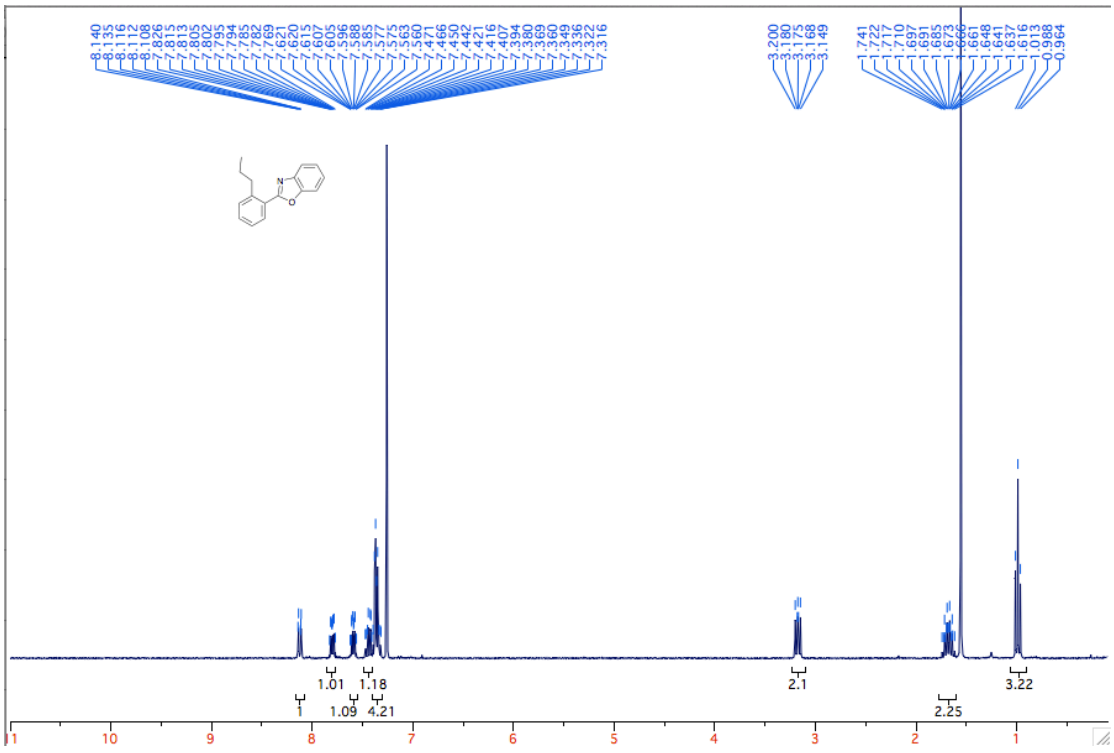
^{1}H NMR of 2-(2-(Thiophen-2-yl)phenyl)benzo[*d*]oxazole, 7c



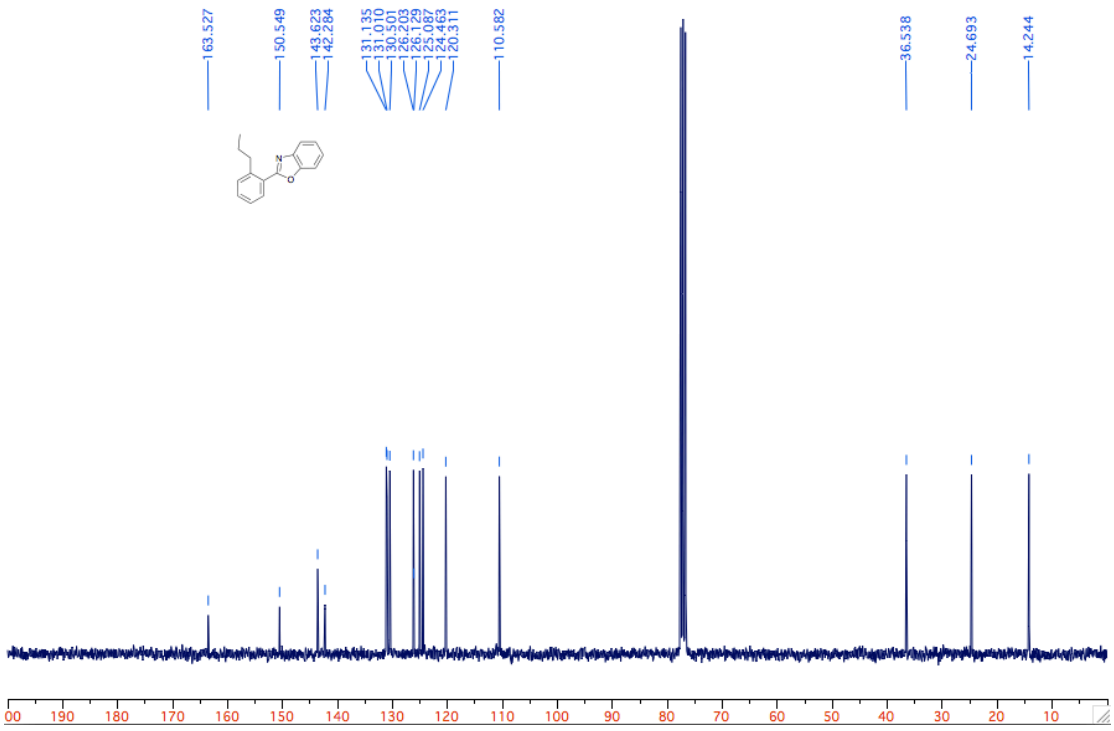
^{13}C NMR of 2-(2-(Thiophen-2-yl)phenyl)benzo[*d*]oxazole, 7c



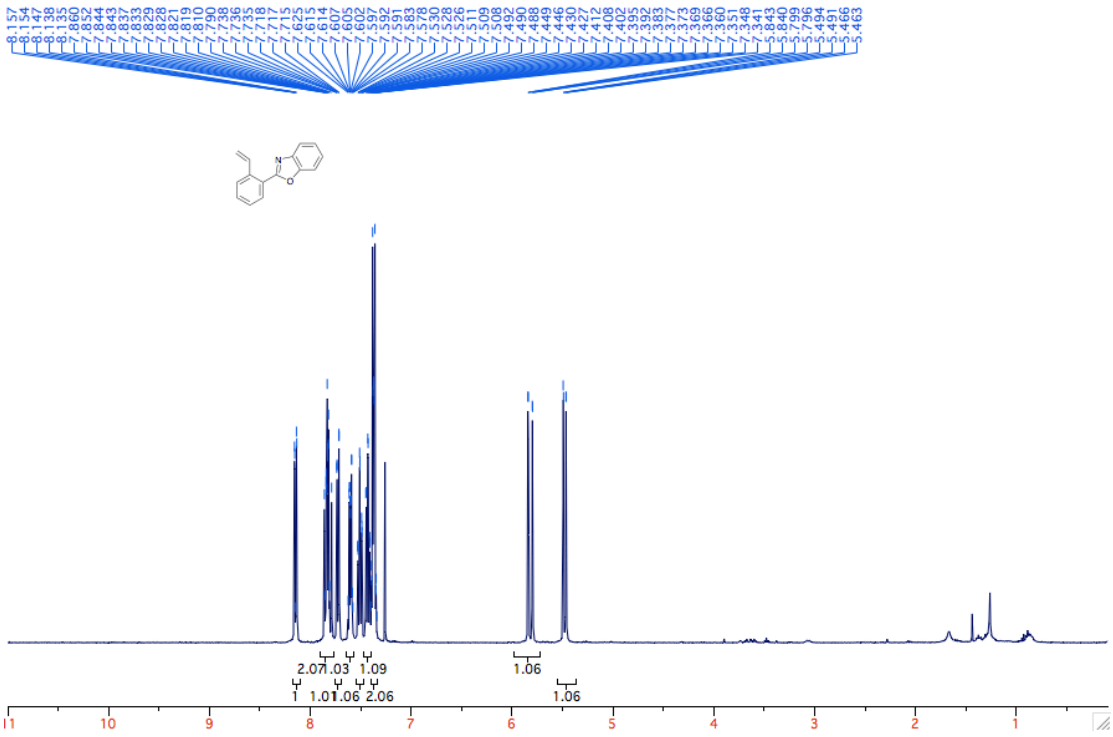
^{1}H NMR of 2-(2-Propylphenyl)benzo[*d*]oxazole, 7d



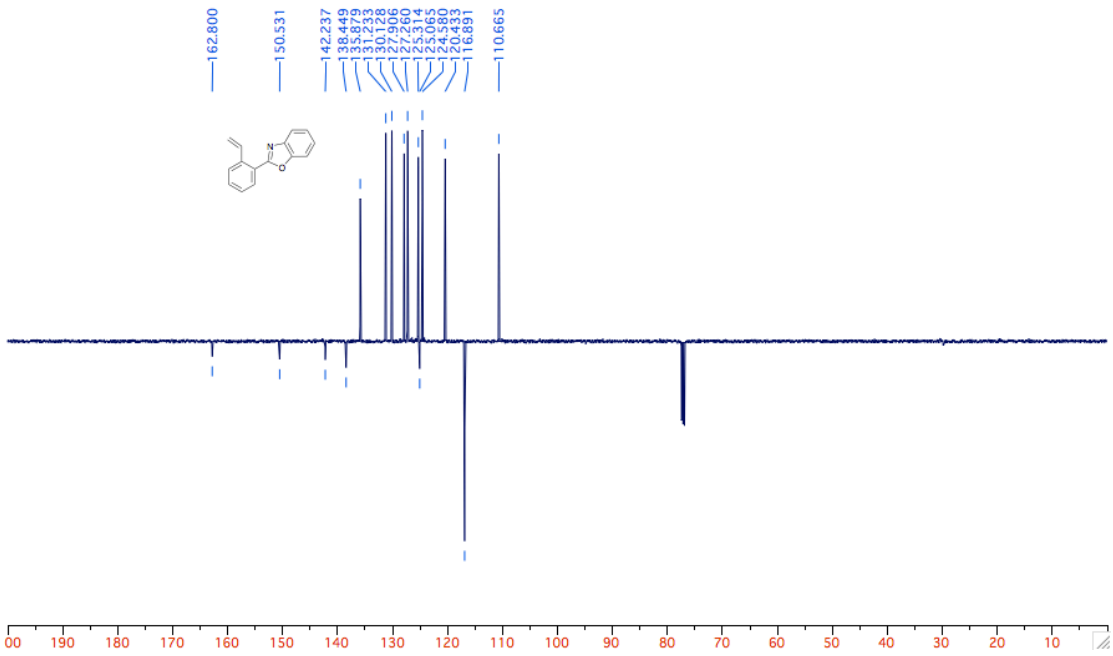
^{13}C NMR of 2-(2-Propylphenyl)benzo[*d*]oxazole, 7d



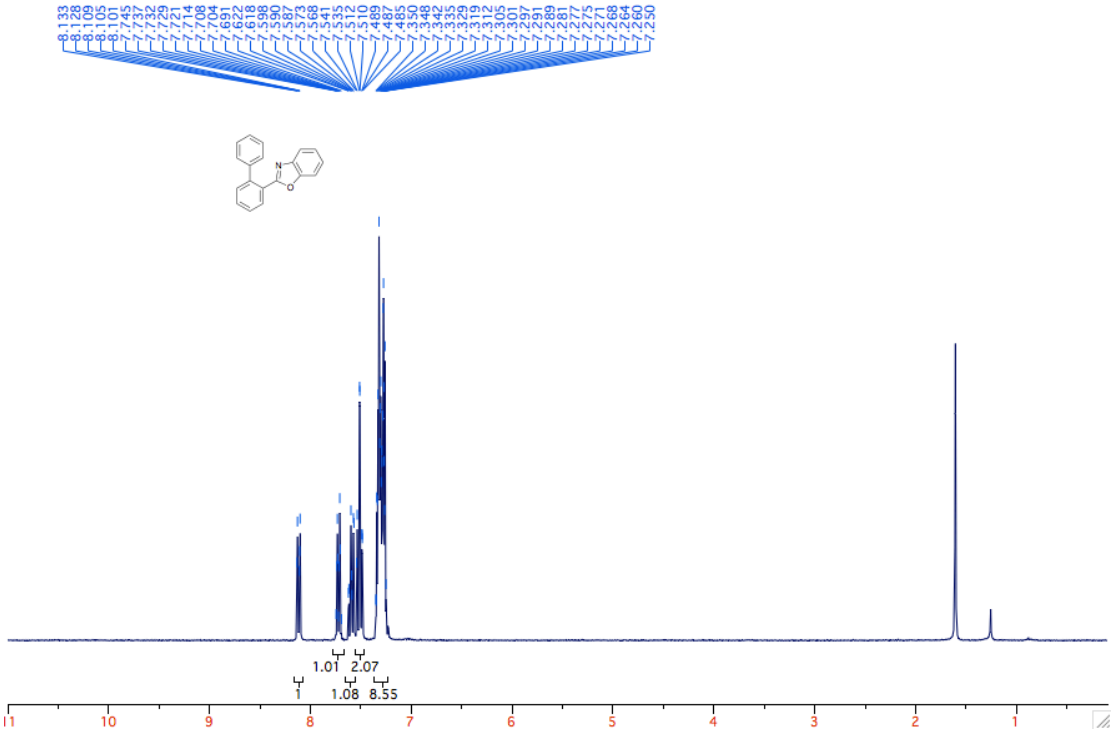
^{1}H NMR of 2-(2-Vinylphenyl)benzo[*d*]oxazole, 7e



^{13}C NMR of 2-(2-Vinylphenyl)benzo[*d*]oxazole, 7e



^{1}H NMR of 2-([1,1'-Biphenyl]-2-yl)benzo[*d*]oxazole, 7f



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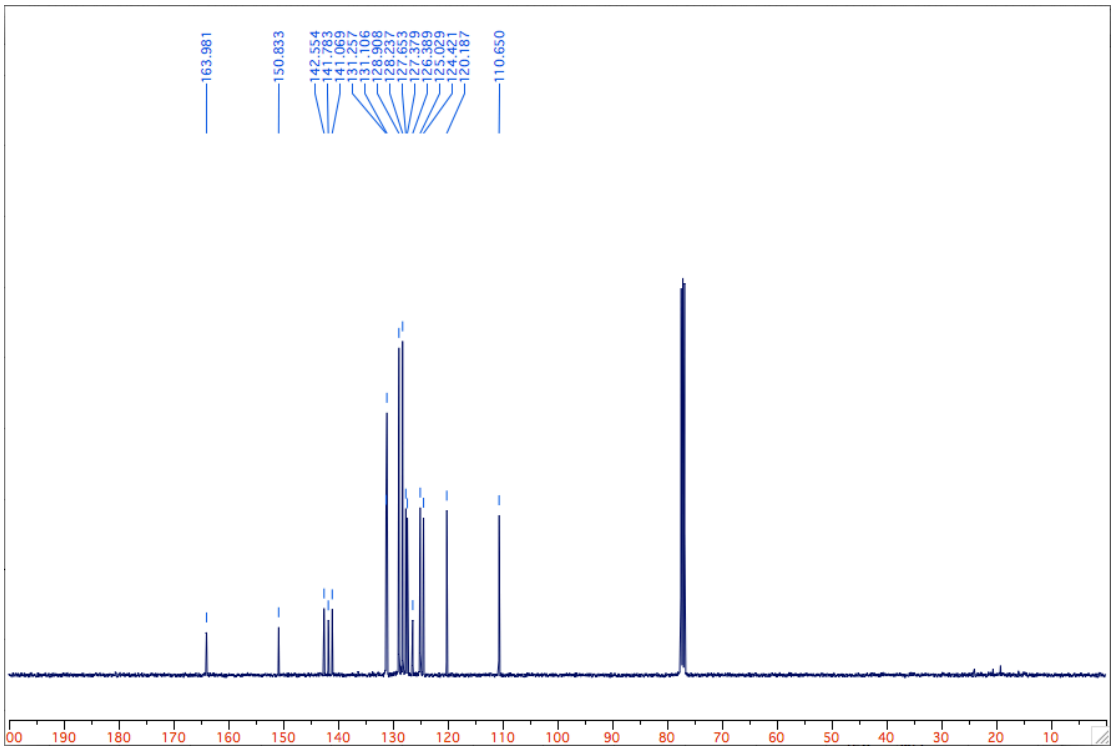
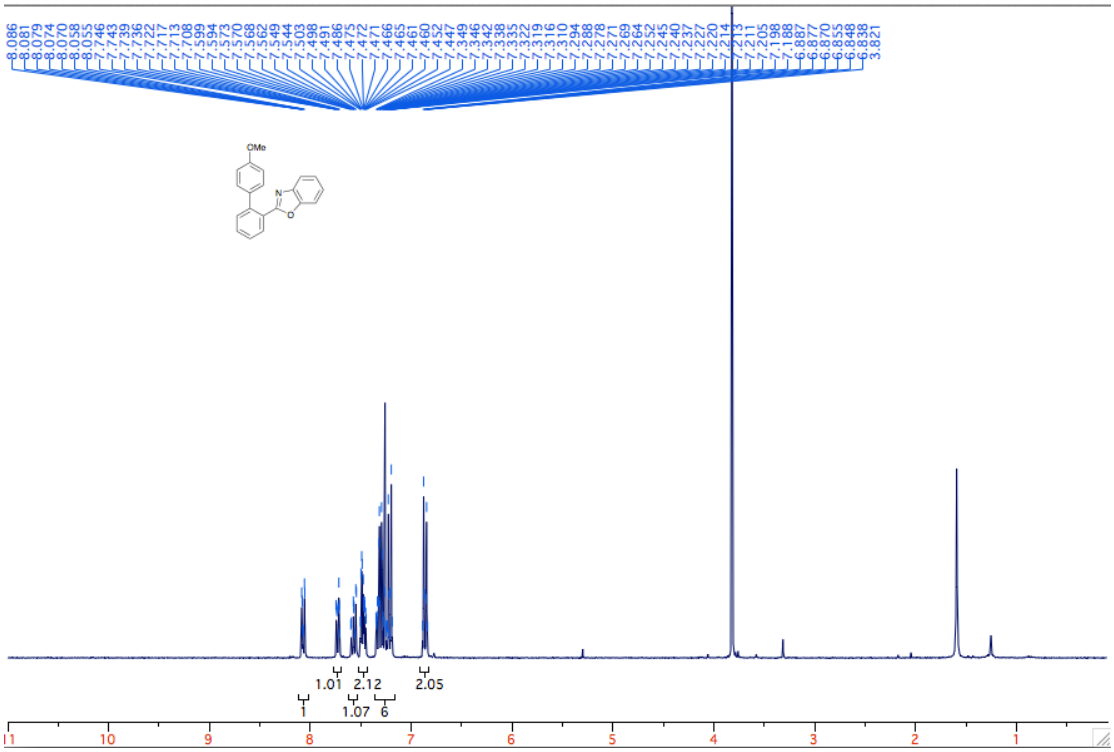
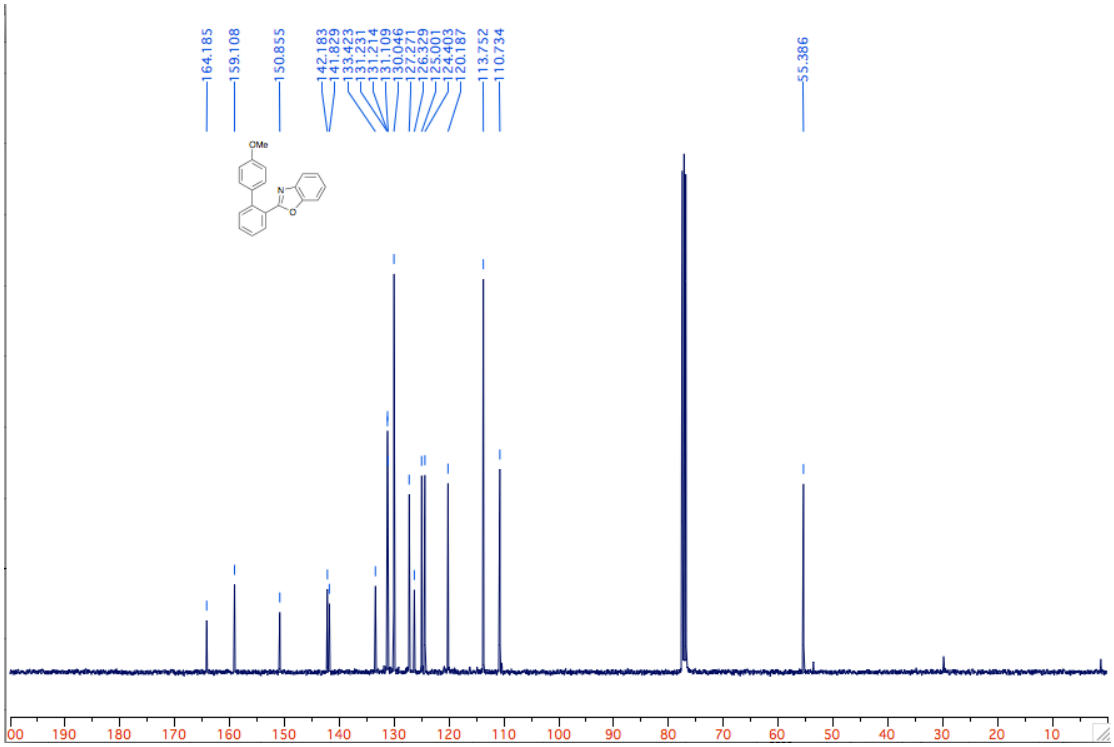


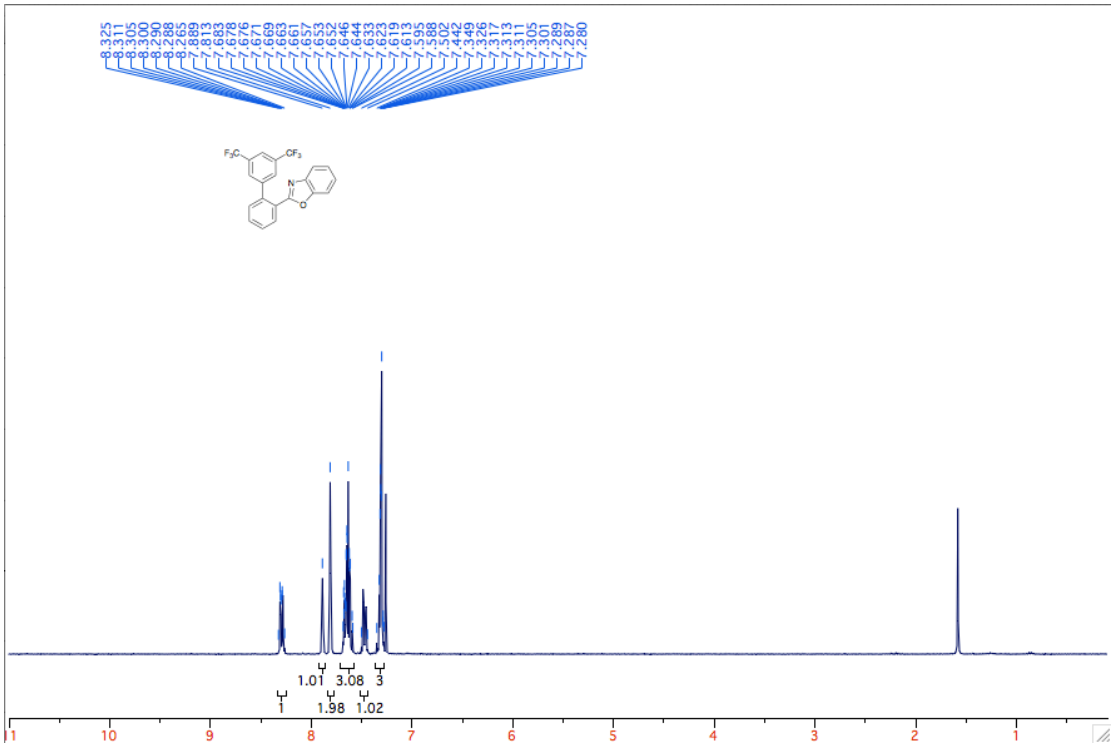
^{1}H NMR of 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7g



^{13}C NMR of 2-(4'-Methoxy-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7g



^{1}H NMR of 2-(3',5'-bis(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7h



^{13}C NMR of 2-(3',5'-bis(Trifluoromethyl)-[1,1'-biphenyl]-2-yl)benzo[*d*]oxazole, 7h