Electronic Supplementary Material

A Facile Synthesis of Mesoporous Graphitic Carbon Nitride Supported Palladium Nanoparticles as Highly Effective and Reusable Catalysts for the Stille Coupling Reactions under Mild Conditions

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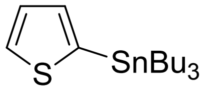
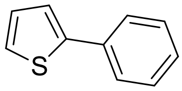
Tributyl(thiophen-2-yl)stannane [1]



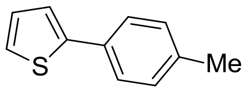
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 – 7.66 (m, 1H), 7.30 – 7.28 (m, 1H), 7.22 (dd, *J* = 3.3, 0.8 Hz, 1H), 1.65 – 1.56 (m, 6H), 1.37 (sext, *J* = 7.3 Hz, 6H), 1.18 – 1.10 (m, 6H), 0.93 (t, *J* = 7.3 Hz, 9H).

2-phenylthiophene [2]



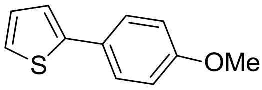
Light beige crystals; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.3, 1.2 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32-7.26 (m, 3H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H),

2-(*p*-tolyl)thiophene [3]



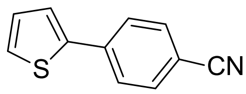
White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.29-7.26 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 2.39 (s, 3H).

2-(4-methoxyphenyl)thiophene [4]



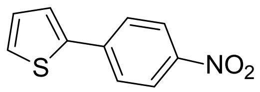
Colorless solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.9 Hz, 2H), 7.23-7.21 (m, 2H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.94-6.92 (m, 2H), 3.85 (s, 3H).

4-(thiophen-2-yl)benzonitrile [5]



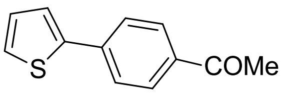
White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71-7.65 (m, 4H), 7.43 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.41 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.14 (dd, *J* = 5.1, 3.7 Hz, 1H).

2-(4-nitrophenyl)thiophene [6]



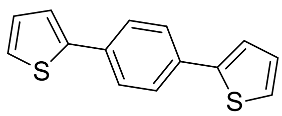
Yellow solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.24 (d, J = 8.9 Hz, 2H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.48 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.44 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.15 (dd, *J* = 5.1, 3.7 Hz, 1H).

1-(4-(thiophen-2-yl)phenyl)ethanone [6]



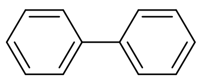
White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.44 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.38 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.13 (dd, J = 5.1, 3.7 Hz, 1H), 2.62 (s, 3H).

1,4-di(thiophen-2-yl)benzene [7]



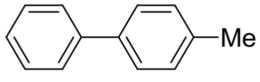
Shiny yellow spangles; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (s, 4H), 7.35 (dd, *J* = 3.6, 1.0 Hz, 2H), 7.30 (dd, *J* = 5.1, 1.0 Hz, 2H), 7.11 (dd, *J* = 5.1, 3.6 Hz, 2H).

1,1'-biphenyl [4]



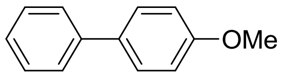
White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65-7.64 (m, 4H), 7.50-7.47 (m, Hz, 4H), 7.38 (m, 2H).

4-methyl-1,1'-biphenyl [8]



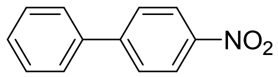
White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (td, *J* = 8.7, 8.1, 1.2 Hz, 2 H), 7.53-7.50 (m, 2 H), 7.47-7.42 (m, 2 H), 7.35-7.32 (m, 1 H), 7.28 (d, *J* = 8.5 Hz, 2 H), 2.43 (s, 3H).

4-methoxy-1,1'-biphenyl [9]



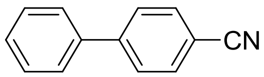
White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58-7.54 (m, 4H), 7.45-7.41 (m, 2H), 7.34-7.30 (m, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H).

4-nitro-1,1'-biphenyl [10]



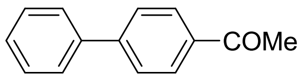
Yellow solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.31 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.66-7.62 (m, 2H), 7.53-7.50 (m, 2H), 7.48-7.45 (m, 1H).

[1,1'-biphenyl]-4-carbonitrile [10]

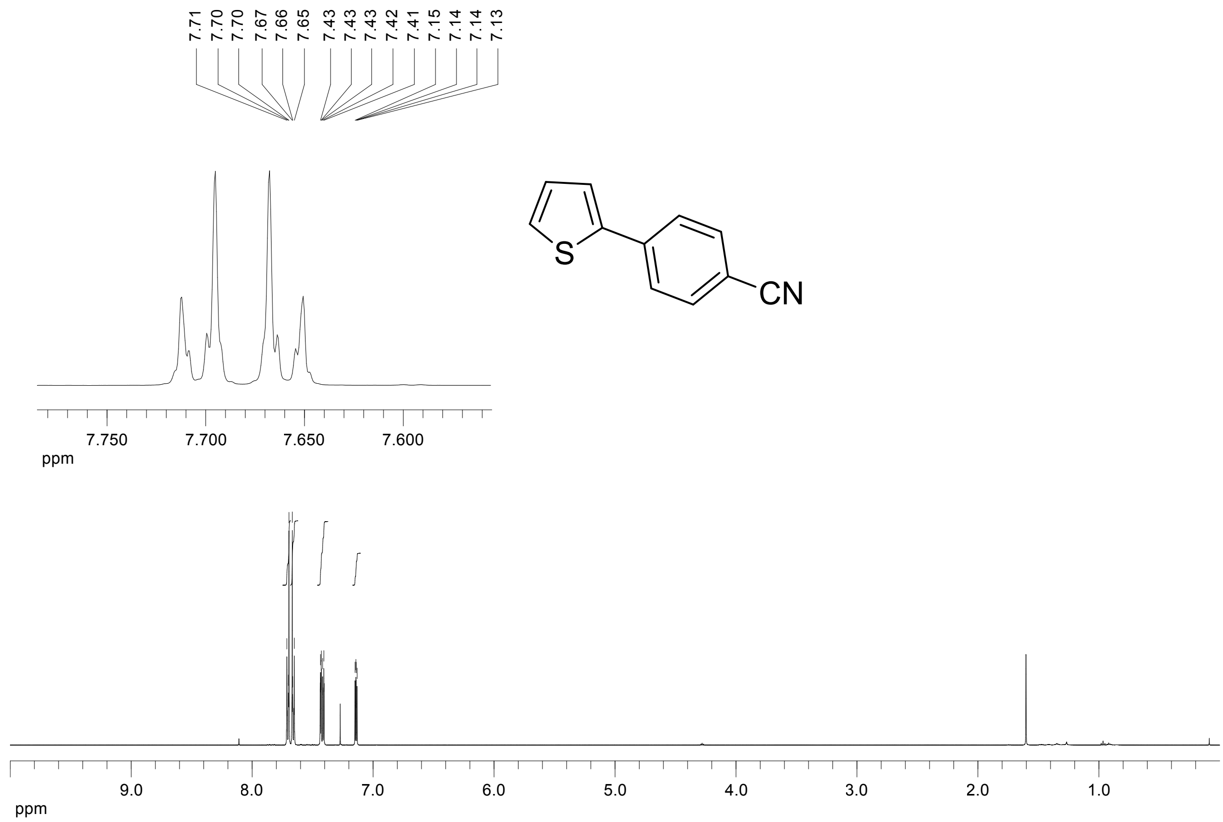


White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74-7.68 (m, 4H), 7.61-7.60 (m, 2H), 7.50 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.46-7.42 (m, 1H).

1-([1,1'-biphenyl]-4-yl)ethanone [9]



White solid; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H,), 7.66-7.62 (m, *J* = 8.4 Hz, 2H), 7.51-7.46 (m, 2H), 7.44-7.39 (m, 1H), 2.65 (s, 3H).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CN
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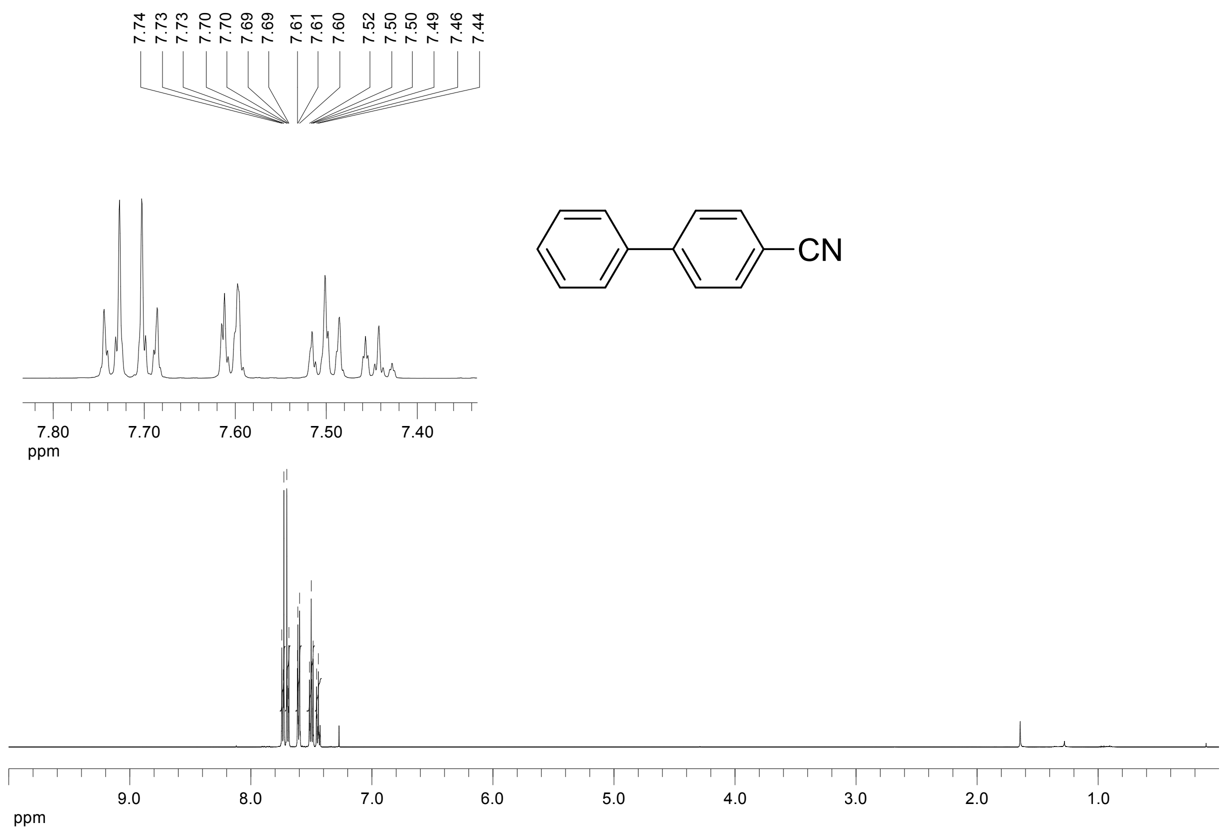
ppm
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm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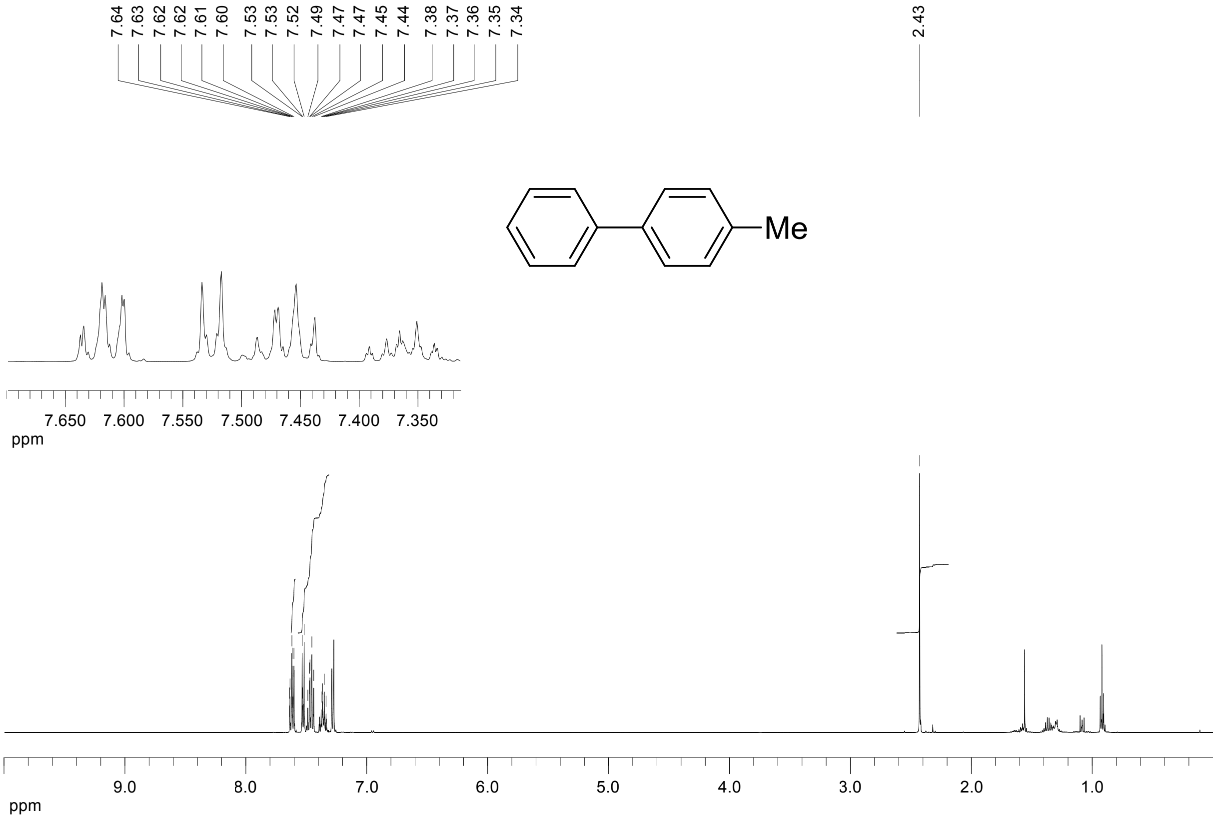
ppm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2.43
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ppm
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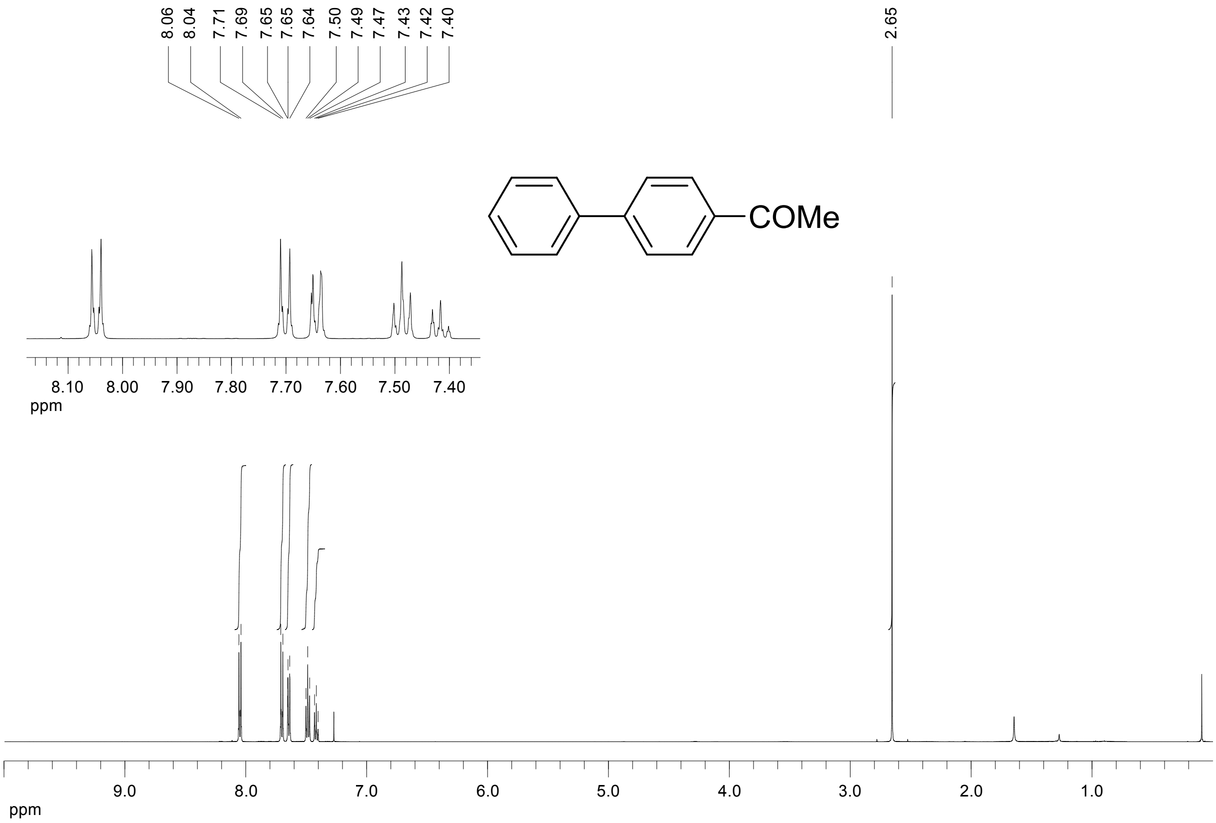
ppm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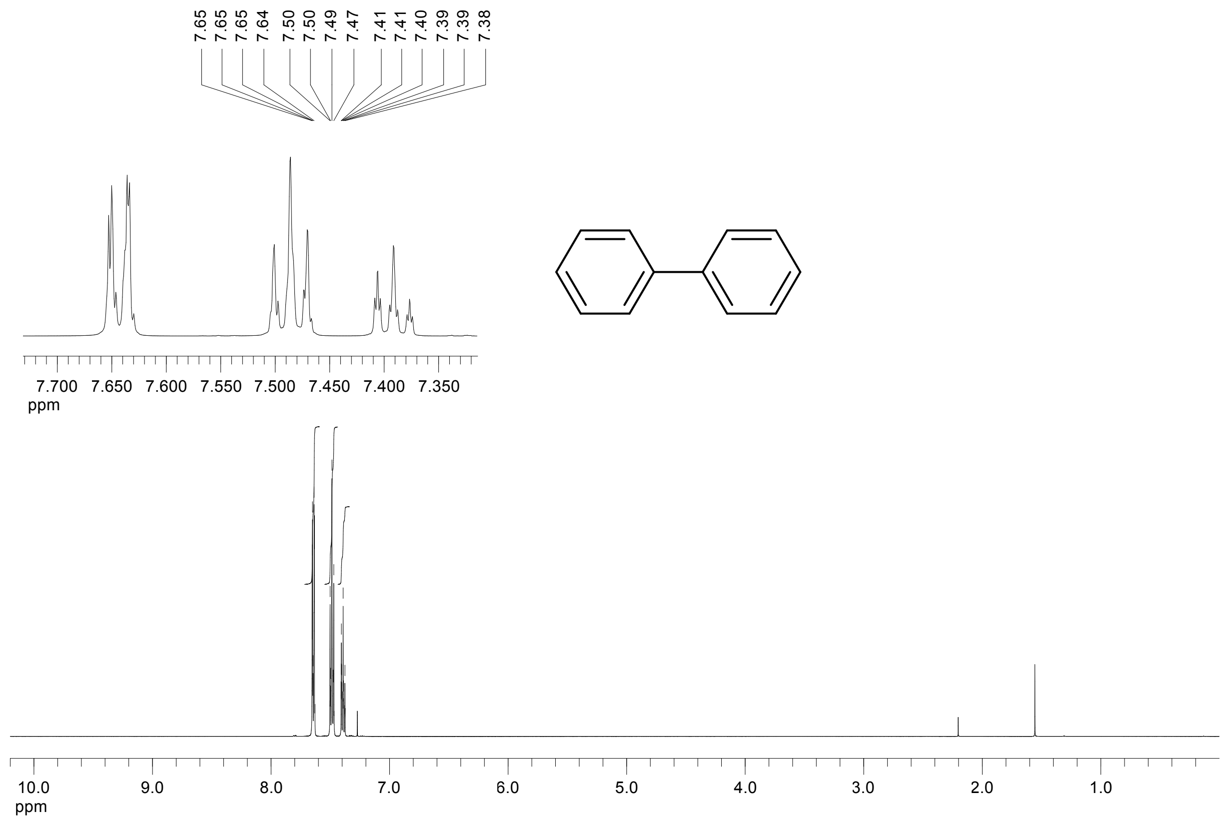
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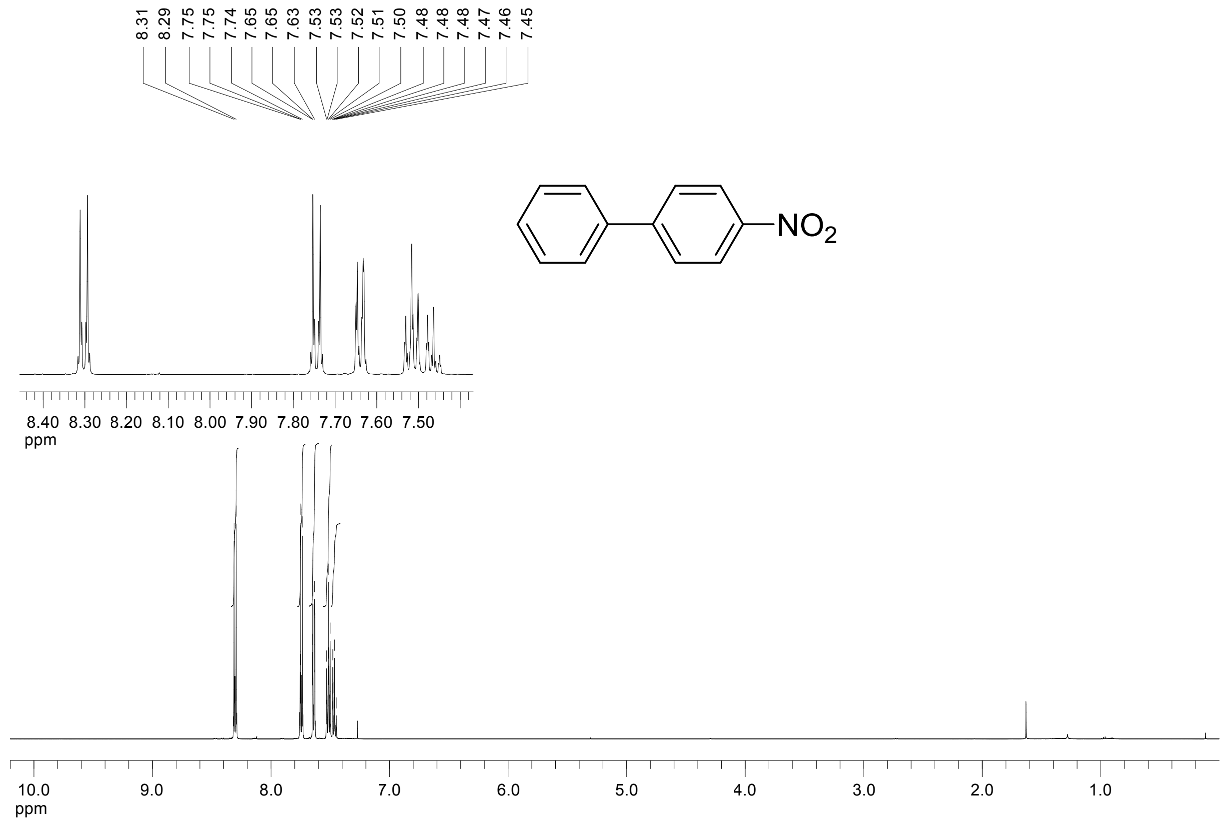
ppm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NO2
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ppm
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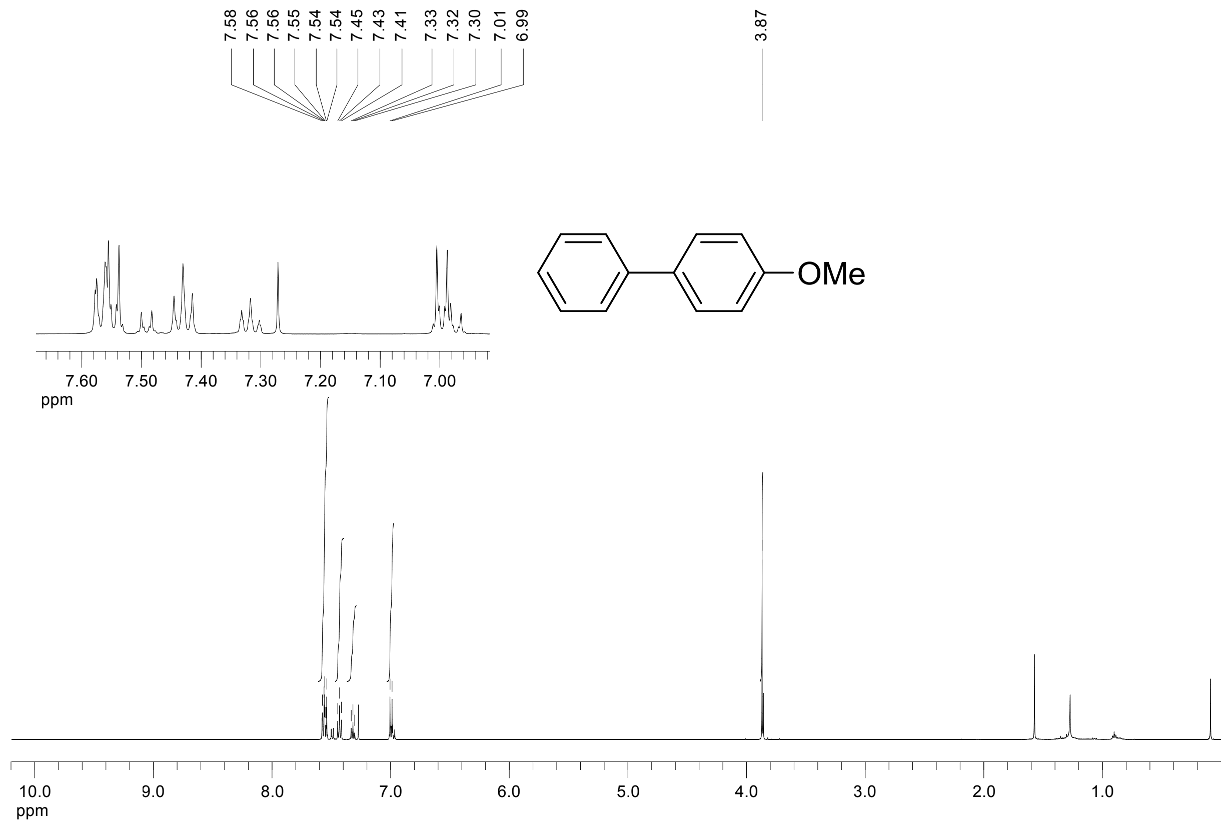
ppm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3.87
OMe
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ppm
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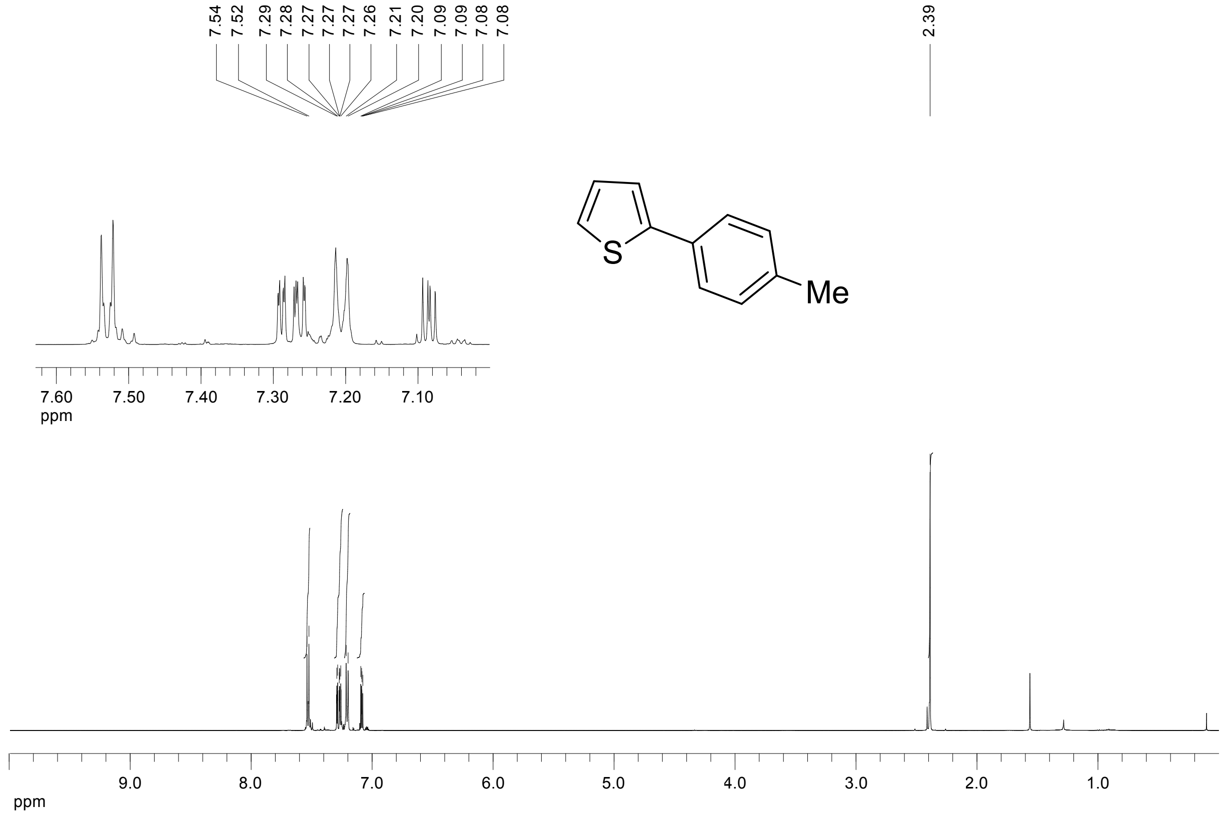
ppm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2.39
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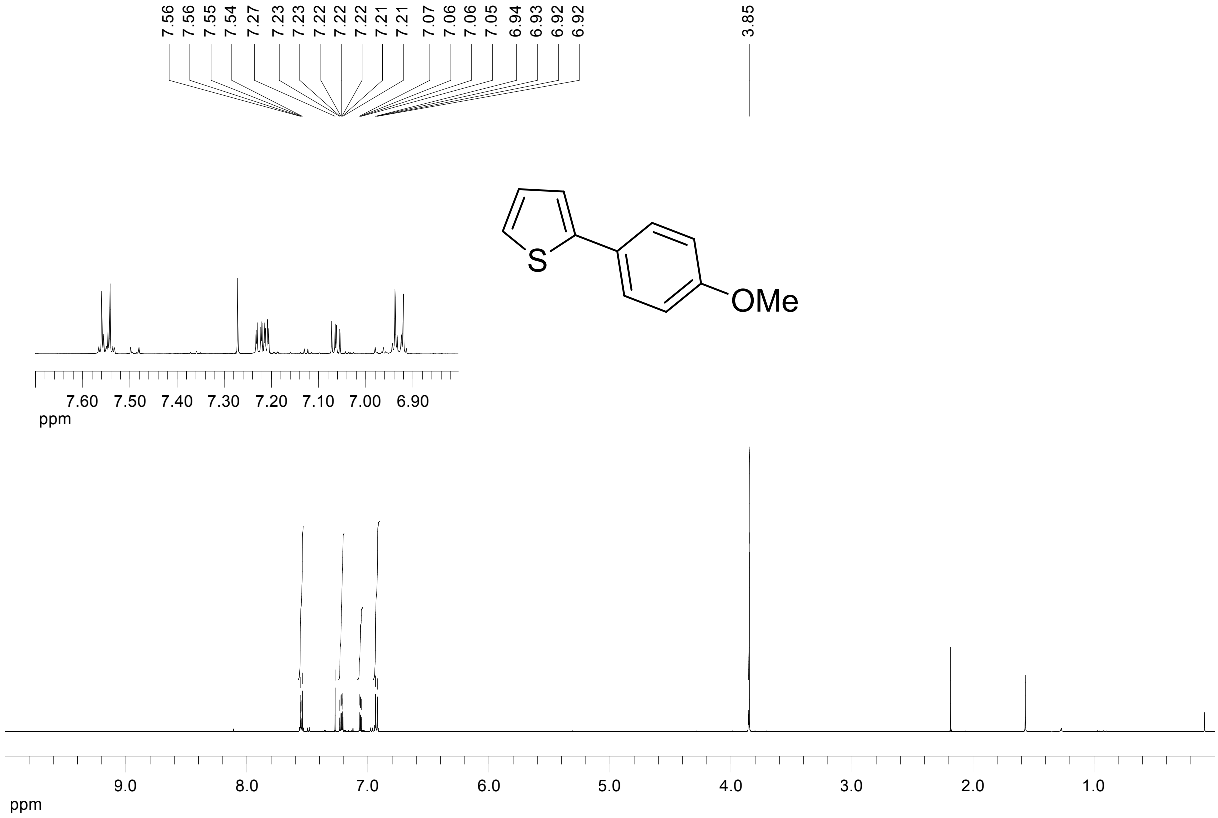
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7.06
7.06
7.05
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6.93
6.92
6.92
3.85
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ppm
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm


7.63
7.63
7.62
7.61
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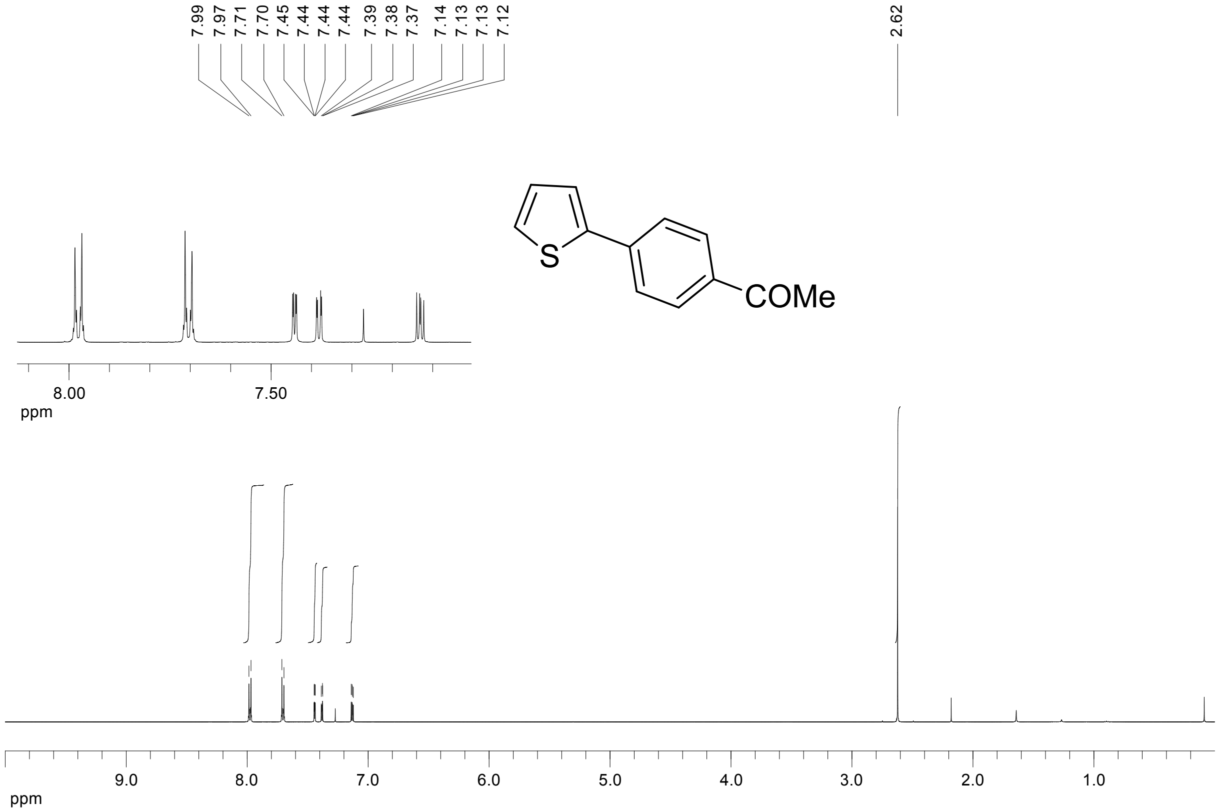
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1.0
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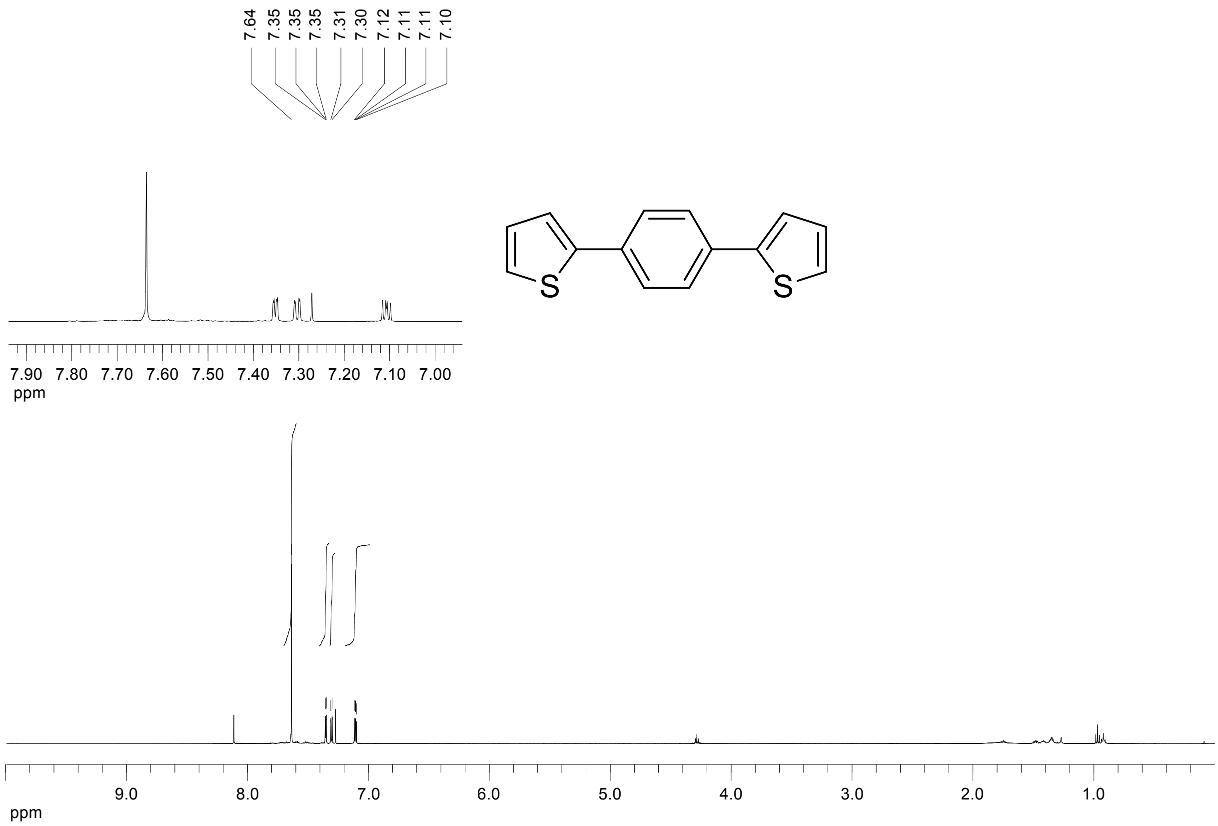
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S
S
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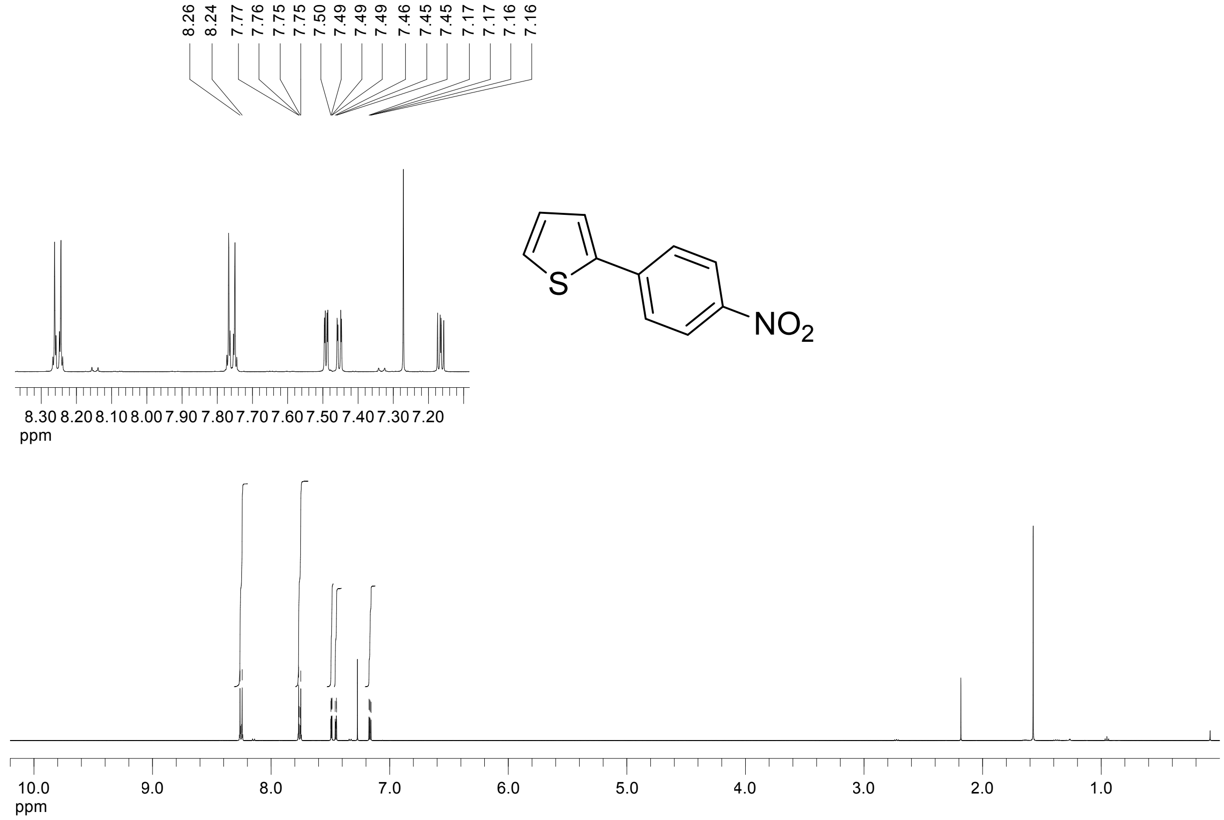
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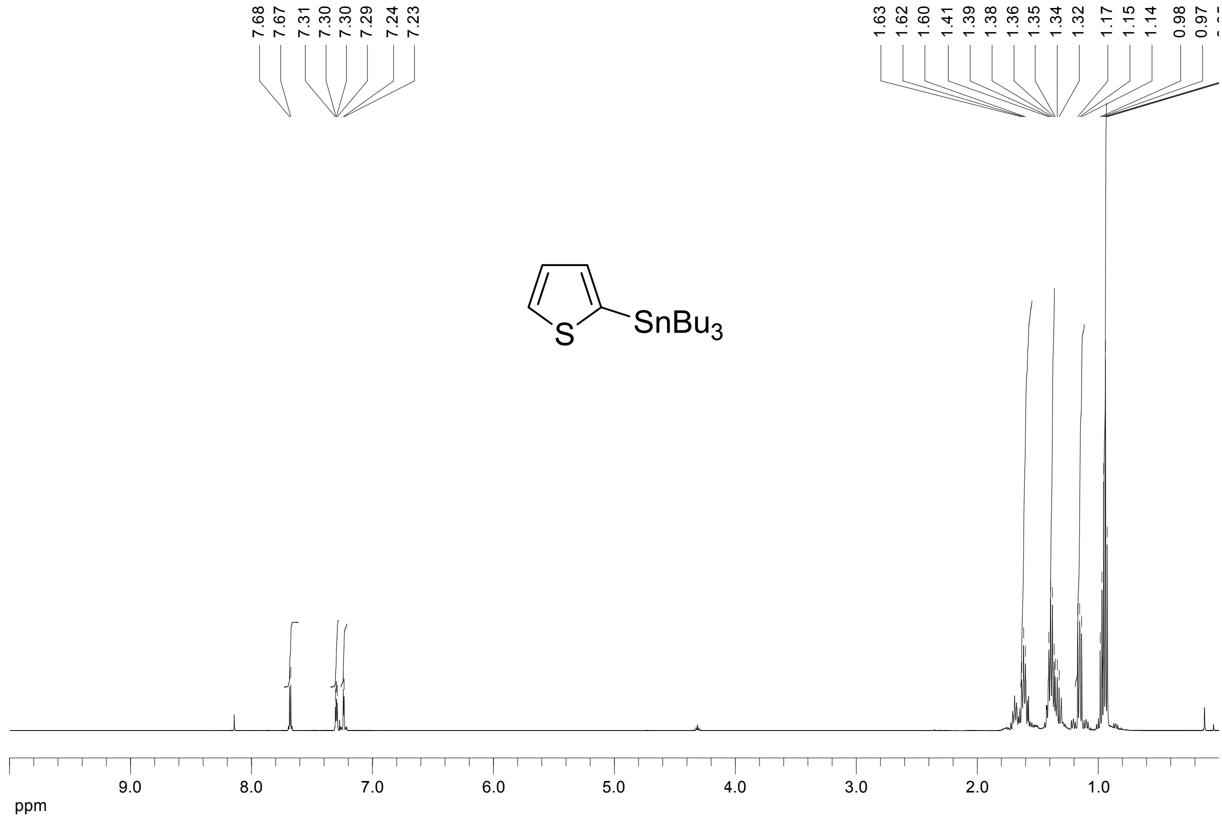
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1.36
1.35
1.34
1.32
1.17
1.15
1.14
0.98
0.97
S
SnBu3
ppm

Table S1. Heterogeneous Pd-based catalysts that have been tested in Stille cross-coupling reactions.

No	Catalyst	Mol (%)	Base	Solvent	Temp (°C)	Time (h)	Yield (%)			Recycles	Ref.
							PhI	PhBr	PhCl		
1	Pd_{np-2}	1.0	K_2CO_3	DMF	110	7-16	-	80-94	-	6	[10]
2	NAP-Mg-Pd	1-3	NaOAc	NMP	100	2-18	90-95	88	70-92	4	[11]
3	Pd-EGCG-CF.	1-2.5	-	DMF	60-80	5-24	84-88	-	-	5	[12]
4	Fe_3O_4/SiO_2-PAP-Pd	0.75	Na_2CO_3	PEG	80	0.5-4	40-96	89-98	51	5	[13]
5	MCM-41-2P-Pd	0.5-2	-	DMF	25-100	4-24	4-23	-	-	10	[14]
6	PdNPs@H_2P-CMP	0.5	-	H_2O	80	5	-	-	88-96	10	[15]
7	PS-dpp-Pd(0)	1.0	-	DMF	65-120	7-14	83-88	-	71-75	5	[16]
8	Pd/$CaCO_3$	0.5-5	K_2CO_3	EtOH/ H_2O	80	24	75-93	66-98	60	3	[17]
9	Fe_3O_4@PTA–Pd	5	DMAP	PEG	100	0.5-2.5	78-97	93-98	79	2	[18]
10	PdcNPs/C@Fe_3O_4	0.73-1.5	K_2CO_3	DMF	100	12-24	82-99	45-99	68-82	5	[8]
11	Pd(0)-SMT-MCM-41	1.2	K_2CO_3	PEG	80	20-165min	95-97	94-97	95-96	-	[19]
12	SBA-15-EDTA-Pd	0.87	-	DMSO	120	4-20	80-94	85-90	76	-	[20]
13	SBA-Pd	0.157	Na_2CO_3	PEG	80	10-360min	85-96	68-95	71	6	[21]
14	Boehmite@tryptophan-Pd	0.075	Na_2CO_3	EtOH	70	50-210min	87-96	77-94	78	5	[22]
15	Pd(0)-guanidine@MCM41		KOH	DMSO	80	20-185min	65-97	65-93	-	10	[23]
16	Fe_3O_4@MCM-41@Pd-SPATB	0.94	K_2CO_3	PEG	80	40-140min	88-94	84-93	-	5	[24]

References

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