Electronic Supplementary Information

Cationic Palladium(II) Complexes as Catalysts for the Oxidation of Terminal Olefins to Methyl Ketones using Hydrogen Peroxide

Qun Cao, David S. Bailie, Runzhong Fu and Mark J. Muldoon*

School of Chemistry and Chemical Engineering, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast, UK, BT9 5AG

m.j.muldoon@qub.ac.uk

1. General Considerations

Unless otherwise stated, all reagents were purchased from Sigma-Aldrich and used without further purification. Thin layer chromatography (TLC) was carried out using Merck TLC silica gel 60 sheets, and visualized with ultraviolet light or potassium permanganate stain. Flash column chromatography (FCC) was performed with Fluorochem silica gel 60 Å as the stationary phase and solvents employed were analytical grade. ^{1}H NMR spectra were recorded on a Bruker AVX400 (400 MHz) spectrometer at ambient temperature. ^{13}C NMR spectra were recorded on a Bruker AVX400 (100 MHz) spectrometer at ambient temperature. The (PBO)Pd(MeCN)$_2$(OTf)$_2$ complex in CD_3CN was analysed using an Agilent ProPulse NMR system ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz). Elemental Analysis data was obtained using a Perkin Elmer PE2400 CHNS Elemental Analyzer. Mass spectra （ESI or EI) data were analyzed using Waters LCT Premier TOF and Waters GCT Premier – TOF Mass spectrometer, respectively.

Gas chromatography analysis was carried out using Agilent 7820A series gas chromatograph. An Agilent 19091J-413HP-5 column (30.0 m × 320 μm × 0.25 μm nominal) was employed for all the separations using the following conditions: initial column temperature, 40 °C; initial hold time, 1 min; next temperature, 100 °C; hold time, 5 min; rate of temperature ramp 1, 4 °C/min, final temperature 320 °C; hold time, 5 min; rate of temperature ramp 2, 30 °C/min; injection temperature, 250 °C; injection volume 1 μL; detection temperature, 300 °C, split mode. The effluent was combusted in an H_2/Air flame and detected using FID (flame ionization detector).

The GC yield of products and conversion of substrates were determined by using the internal standard method. The response factor (RF) of analytes was determined by analysing known quantities of internal standard against known quantities of substrate and product:

$$RF = \frac{Area_{internal\ standard} \times Moles_{analyte}}{Area_{analyte} \times Moles_{internal\ standard}}$$

The quantity of an analyte was then calculated according to the following equation:

$$Moles_{analyte} = \frac{RF \times Moles_{internal\ standard} \times Area_{analyte}}{Area_{internal\ standard}}$$

2. Catalytic Reactions

General procedure for catalyst testing of $Pd(OAc)_2$ for the oxidation of styrene in acetic acid:

Into a 30 mL glass vial were added $Pd(OAc)_2$ (0.01 g, 1 mol%, 0.0445 mmol) and ligand (1 mol%) and benzophenone (0.04 g) as an internal standard. A magnetic stirrer bar was added to the vial along with acetic acid (8 mL). Once the catalyst was dissolved, then 5 or 10 equiv. of H_2O_2 was added followed by styrene (0.46 g, 4.4167 mmol). After adding the substrate, the vial was capped (the cap had small hole pierced in the top) and was then transferred to a water bath at 27 °C (on a hot plate stirrer) and stirred (600 rpm) for 6 hours. The reaction was analysed by GC by taking an aliquot (~ 50 µL) and passing it through a pipette containing a small plug of silica gel using diethyl ether as the eluent. The conversion and product yield were calculated relative to benzophenone (internal standard).

General procedure for testing ligand and cationic catalysts prepared *in situ* with silver salts (for both styrene and 1-octene):

Silver salt stock solutions (0.0552 mmol/mL) were freshly prepared by dissolving the appropriate Ag salt in either acetonitrile (for styrene) or acetone (for 1-octene) into a sample vial covered with aluminium foil. Into another glass vial (30 mL) (this was also covered with aluminium foil and the cap had a small hole pierced in the top) was added Pd(II) salt (1 mol%, 0.0224 mmol), ligand (1 mol% unless specified) and biphenyl (internal standard) (0.02 g) Then 3 mL of acetonitrile (in case of styrene) or 3 mL acetone (in case of 1-octene) was added into the sample vial and the mixture was sonicated at room temperature for 1 min and then stirred at room temperature for 10 min. To the solution of Pd complex, the silver salt stock solution (1 mL, 0.0552 mmol, 2.5 mol%) was added. The vial was then sonicated at room temperature for 1 min and stirred for another 10 min at room temperature to generate the catalyst *in situ*. In the case of 1-octene, an additional 6 mL of acetone was then added (*i.e.* a total of 10 mL of acetone in the reaction). The vial was cooled in an ice bath for 5 min to reach 0 °C, then H_2O_2 (50 wt%, 1.29 mL, 10 equiv.) was added, followed by substrate (2.2 mmol). After adding the substrate, the reaction sample was transferred to a water bath (on a

hot plate stirrer) which was maintained at 27 °C and stirred for the required amount of time. GC samples were taken and filtered through a short silica plug using diethyl ether as the eluent.

Comment on side products for styrene substrates:

When acetic acid was used as a solvent, it was clear from the mass balance that we produced a significant quantity of side products, not all of which are accounted for on the GC trace. Some of these side products are thought to be due to styrene oxide being produced *via* oxidation of styrene with peracetic acid. Styrene oxide can potentially produce a large number of side products. Control experiments showed that exposing styrene oxide to the reaction conditions produced a number of products including benzaldehyde and 2-oxo-phenylethyl acetate. Both these products were also produced when styrene was used as the starting material (see Figure S1) and the reaction carried out in acetic acid. In the case of 2-oxo-phenylethyl acetate this was suggested by GC-MS software library, however we also saw the analogous product when 4-*tert*-butylstyrene was used as the starting material. For this electron donating substrate, a larger quantity is produced (Figure S2), furthermore because it is less volatile it could be readily isolated *via* column chromatography and the ^{1}H and ^{13}C NMR spectra (Figures S3 and S4) supported the structure that was suggested by the GC-MS library. An example GC trace is also shown for the optimised catalyst in acetonitrile (Figure S5).

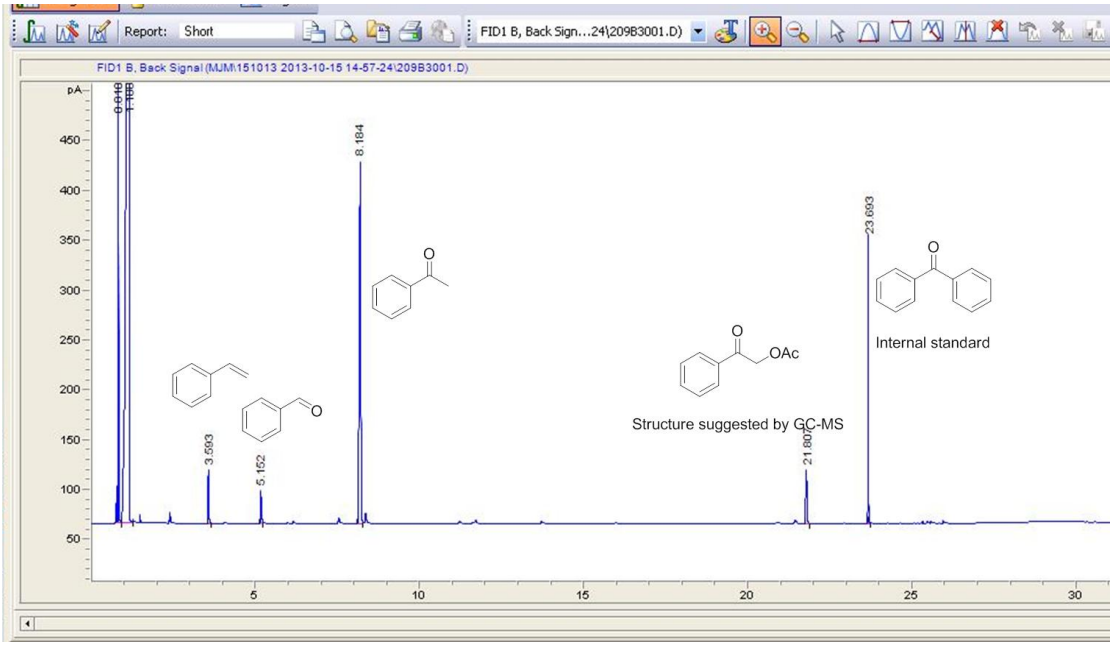


Figure S1. GC trace after 6 hours from the oxidation of styrene in acetic acid using $Pd(OAc)_2$ and PBO ligand

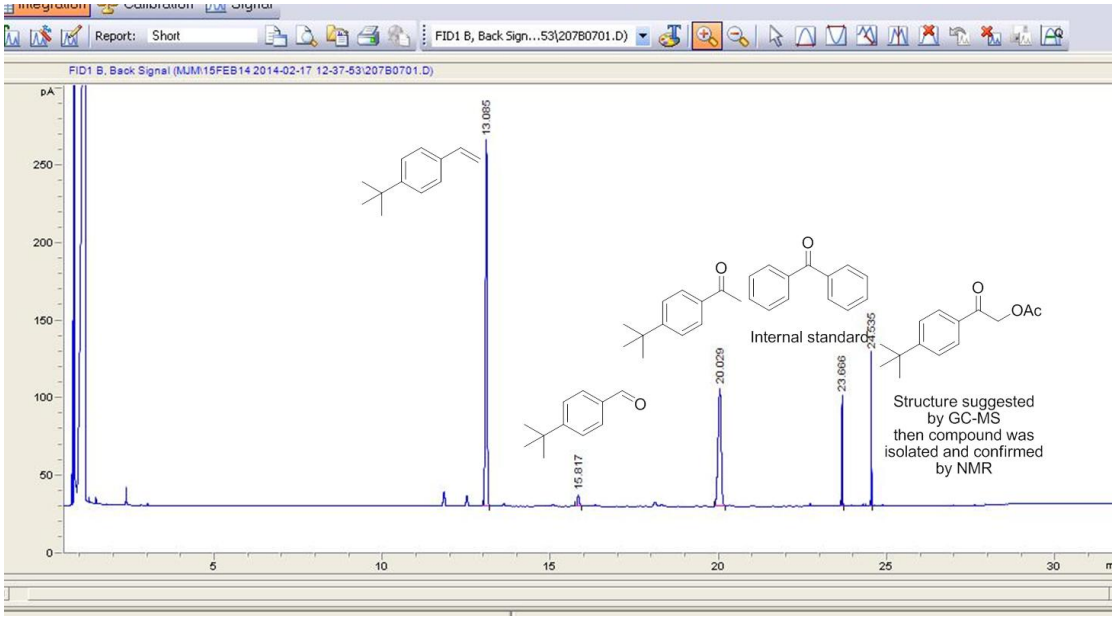


Figure S2. GC trace of 4-*tert*-butylstyrene after 1 hour in acetic acid using $Pd(OAc)_2$ and PBO ligand

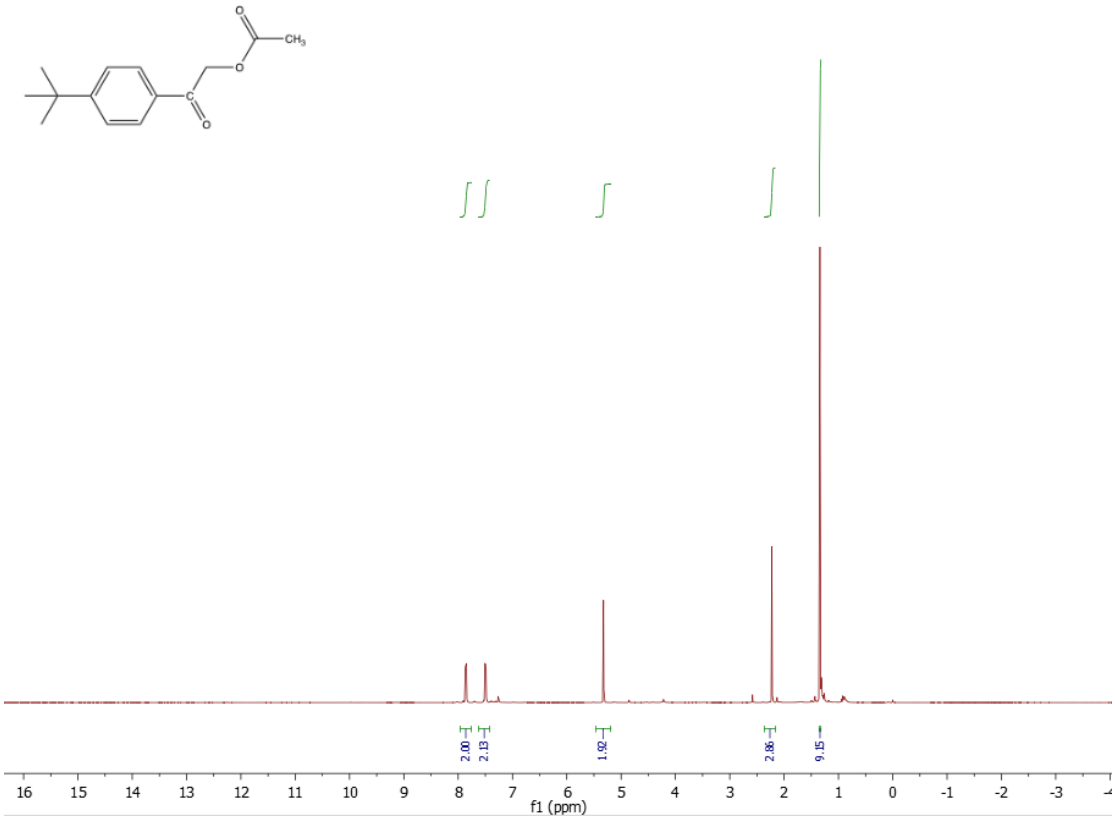


Figure S3

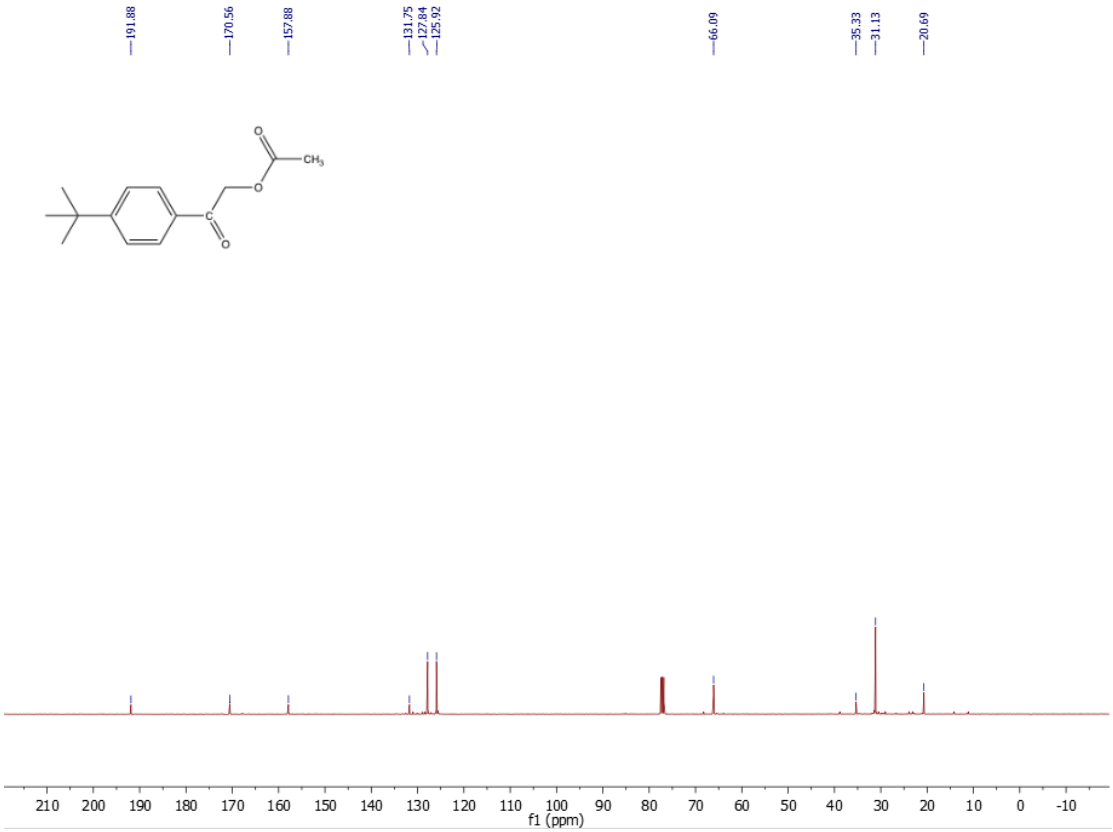


Figure S4

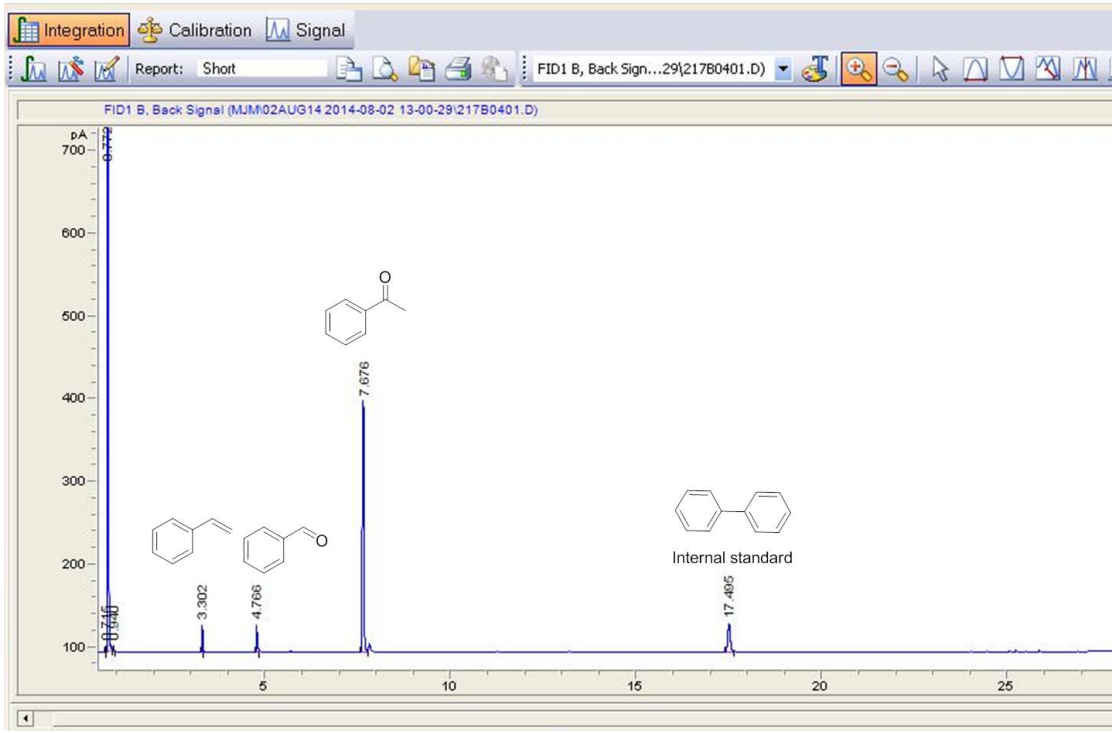
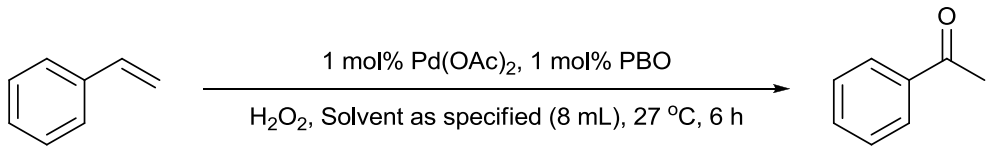


Figure S5 GC trace of styrene in acetonitrile (PBO)Pd(MeCN)$_2$(OTf)$_2$ after 24 hours (*i.e.* optimised conditions)

Table S1 Effect of solvent, H_2O_2 concentration and ligand (PBO) on $Pd(OAc)_2$ catalysed oxidation of styrene



Entry	Solvent	Time [h]	Conversion [%][a]	Yield [%][a]
1[b]	*tert*-butanol	6	36	6
2[c]	DMA	6	10	0
3[c]	DMF	6	6	0
4[d]	acetonirile	6	8	3
5[d]	propionic acid	6	87	58
6[b]	acetic acid	6	95	65
7[b][e]	acetic acid	6	98	29
8[c]	acetic acid	6	100	70

Procedure as described in general procedure above for $Pd(OAc)_2$ in acetic acid.

[a] Yield and conversion were determined by GC using benzophenone as an internal standard.

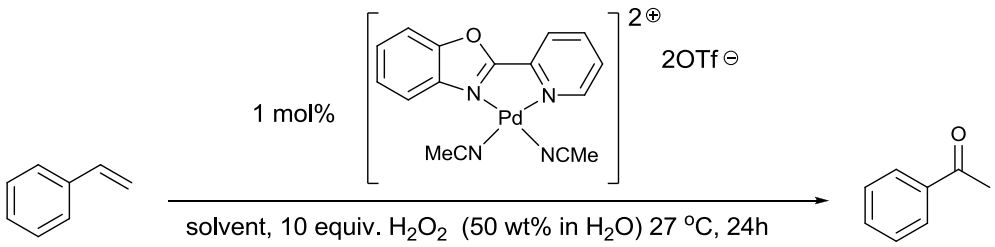
[b] 5 equivalents of H_2O_2 (30 wt% in H_2O)

[c] 5 equivalents of H_2O_2 (50 wt% in H_2O)

[d] 10 equivalents of H_2O_2 (50 wt% in H_2O)

[e] Without adding PBO ligand.

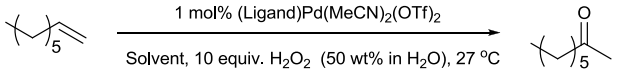
Table S2 Influence of solvent for the (PBO)Pd(MeCN)$_2$(OTf)$_2$ / H_2O_2 oxidation of styrene



Entry	Solvent	Time	Conv. [%]	Yield[%]
1	Acetone	6 h	100	56
2	*t*BuOH	3 h	98	58
3	MeOH	3 h	100	55
4	EtOAc	24 h	99	47
5	DMA	24 h	58	21
6	MeCN	24 h	99	74
7[a]	MeCN	24 h	27	8
8[b]	MeCN	24 h	64	44
9[c]	MeCN	24 h	81	72
10[d]	MeCN	24 h	34	25
11[e]	**MeCN**	**24 h**	**92**	**80**
12[f]	MeCN	6 h	100	75
13[g]	MeCN	24 h	88	71
14[h]	MeCN	24 h	91	71

Procedure: Pre-prepared (PBO)Pd(MeCN)$_2$(OTf)$_2$ (1 mol%, 0.0150 g, 0.0221 mmol) and biphenyl (~0.02 g) were weighed into a 30 mL glass vial (containing a micro-stir bar). Solvent (4 mL) was added and the solution was stirred until the catalyst dissolved. The solution was then cooled to 0 °C and then 10 equiv. H_2O_2 (50 wt% in H_2O)(1.29 mL) and styrene (0.23 g, 2.208 mmol) were added. The vial was then capped (cap had a small hole in the top) and transferred to a water bath (on a hot plate stirrer) at either 27 °C or 50 °C and the solution was stirred at 600 rpm. Aliquots (~ 50 µL) of the reaction mixture were taken periodically, and analyzed by GC. The conversions and products yields were calculated relative to the biphenyl internal standard. [a] $PdCl_2(MeCN)_2$ (1 mol% 0.0058 g, 0.0221 mmol), AgOTf (2.5 mol%, 0.0142 g, 0.0553 mmol), no ligand was added. [b] $PdCl_2(MeCN)_2$ (1 mol% 0.0058 g, 0.0221 mmol), AgOTf (2.5 mol%, 0.0142 g, 0.0553 mmol), 2-(2-pyridiyl)benzoxzole (1 mol%, 0.0044 g, 0.0221 mmol). [c] 8 mL MeCN [d] 0.645 mL H_2O was added instead of H_2O_2 [e] 5 equiv. 50 wt% H_2O_2 [f] 5 equiv. 50 wt% H_2O_2, 50 °C [g] 5 equiv. 30 wt% H_2O_2 [h] 2 equiv. 50 wt% H_2O_2

Table S3 Influence of solvent and ligand on Pd(II) / H_2O_2 oxidation of 1-octene



Entry	Ligand	Solvent	Time	Conversion[a] [%]	Yield[a] [%]	Isomer[a][%]
1	PBO	MeCN	1 h	99	7	85
2[b]	PBO	MeCN	1 h	99	9	77
3[c]	PBO	MeCN	1 h	> 99	9	80
4	PBO	DMA	3 h	15	1	6
5	PBO	EtOH	3 h	31	1	5
6	PBO	*t*Butanol	24 h	100	18	24
7	PBO	EtOAc	1 h	69	27	21
			6 h	96	38	17
8	PBO	MeOH	24 h	93	7	41
9	PBO	Acetone	1 h	97	25	61
10[d]	PBO	MeCN/DCM	24 h	> 99	11	76
11[e]	PBO	MeCN/EtOAc	24 h	100	11	81
12[f]	PBO	MeCN/DMA	24	37	3	24
13[g]	PBO	MeCN/DMA	24 h	82	12	44
14	Phen	MeCN	24 h	89	25	55
15[h]	Phen	MeCN	24 h	96	29	46
16	Phen	EtOAc	24 h	12	12	0
17[i]	Phen	EtOAc	24 h	14	11	0
18[i]	Phen	*t*Butanol	24 h	80	23	5
19	Phen	MeOH	24 h	93	8	2
20[h]	Phen	EtOAc	6 h	94	57	< 1
21[j]	no ligand	Acetone	24 h	2	0	< 1
22	Phen	Acetone	24 h	> 99	67	< 1
23	Bphen	Acetone	24 h	> 99	80	< 1
24[k]	Bphen	Acetone	24 h	> 99	74	< 1
25	Bphen	2-Butanone	24 h	89	74	2
26[k]	Bphen	2-Butanone	24 h	91	70	< 1

Procedure: Pre-prepared complex (Ligand)Pd(MeCN)$_2$(OTf)$_2$ (1 mol%, 0.0221 mmol) and biphenyl (~0.02 g) were weighed into a 30 mL glass vial (containing a micro-stir bar). Solvent (10 mL) was added and the solution was stirred until the catalyst dissolved. The solution was then cooled to 0 °C and then 10 equiv. H_2O_2 (50 wt% in H_2O) (1.29 mL) and 1-octene (0.23 g, 2.208 mmol) were added. The vial was capped (cap had a small hole in the top) and transferred to a water bath (on a hot plate stirrer) at 27 ^oC and the solution was stirred at 600 rpm. Aliquots (~ 50 µL) of the reaction mixture were taken periodically, and analyzed by GC. The conversions and product yields were calculated relative to the biphenyl internal standard. [a] Conversion, yield, and degree of isomerisation were determined by GC using biphenyl as an internal standard [b] 10 mol% benzoquinone was added. [c] 50 mol% phenol was added a [d] MeCN: DCM = 8.5: 1.5 [e] MeCN: EtOAc = 8.5: 1.5 [f] MeCN: DMA = 5: 5 [g] MeCN: DMA = 9:1 [h] 50 ^oC [i] 2 mol% Pd complex used [j] No Pd salt was added.

[k] 1-decene (0.3097 g, 2.208 mmol) was used as the substrate**.**

Note: although no problems occurred during these studies, as noted in the main manuscript acetone peroxide and 2-butanone peroxide could be formed and can be dangerous.[3]

GC analysis for 1-octene:

As shown in Table S3 a significant amount of internal isomers were produced in some cases. These were quantified by GC and GC-MS was used to confirm the GC peaks corresponded to the internal isomers. Example GC traces are shown below (Figures S6 and S7). The quantity of remaining 1-octene and internal isomers was obtained by using the internal standard. We determined the response factor for 1-octene and assumed that the internal isomers had the same response factor as the 1-octene.

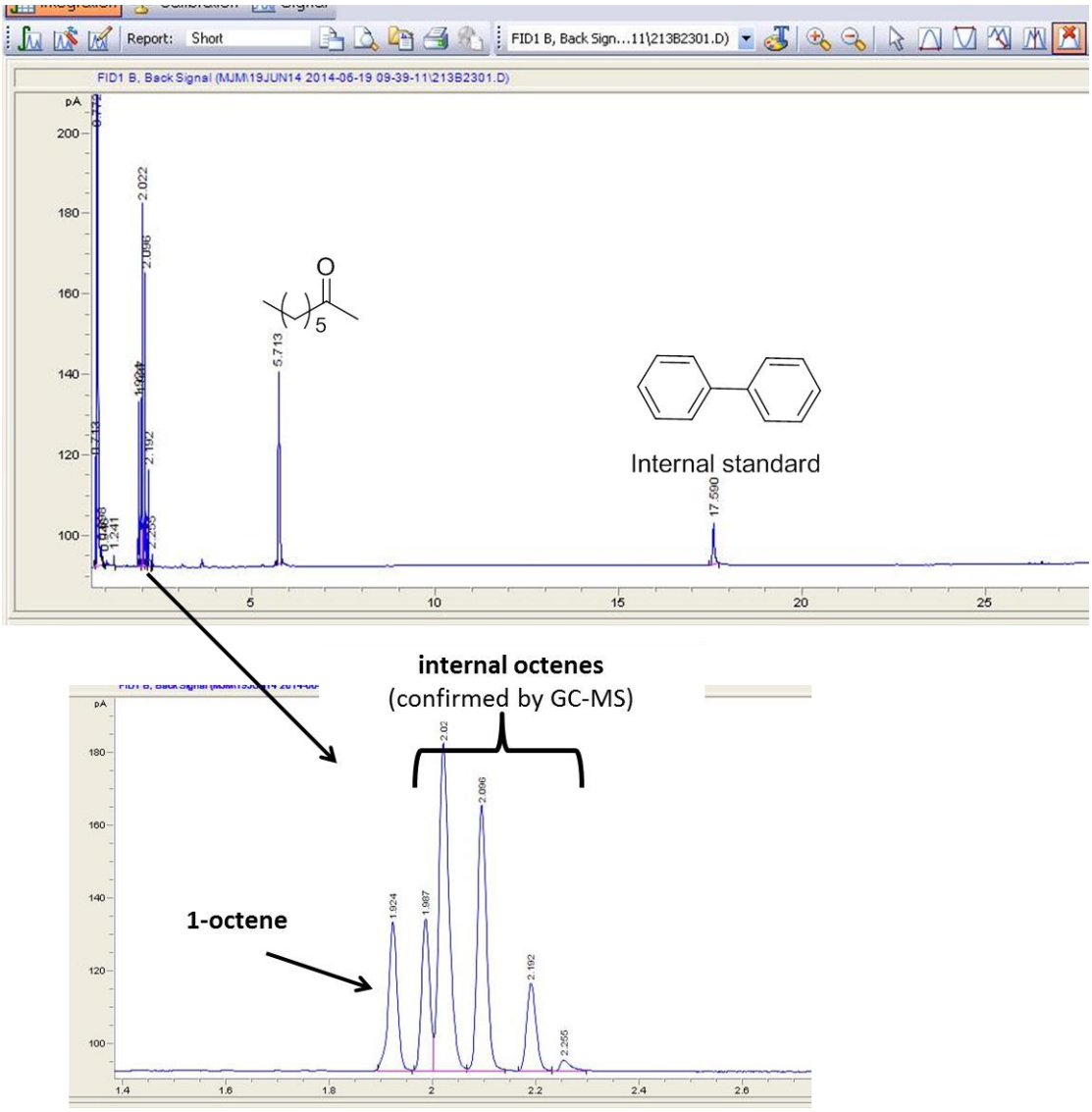


Figure S6 GC trace for the oxidation of 1-octene in acetonitrile using (Phen)Pd(MeCN)$_2$(OTf)$_2$ after 3 hours.

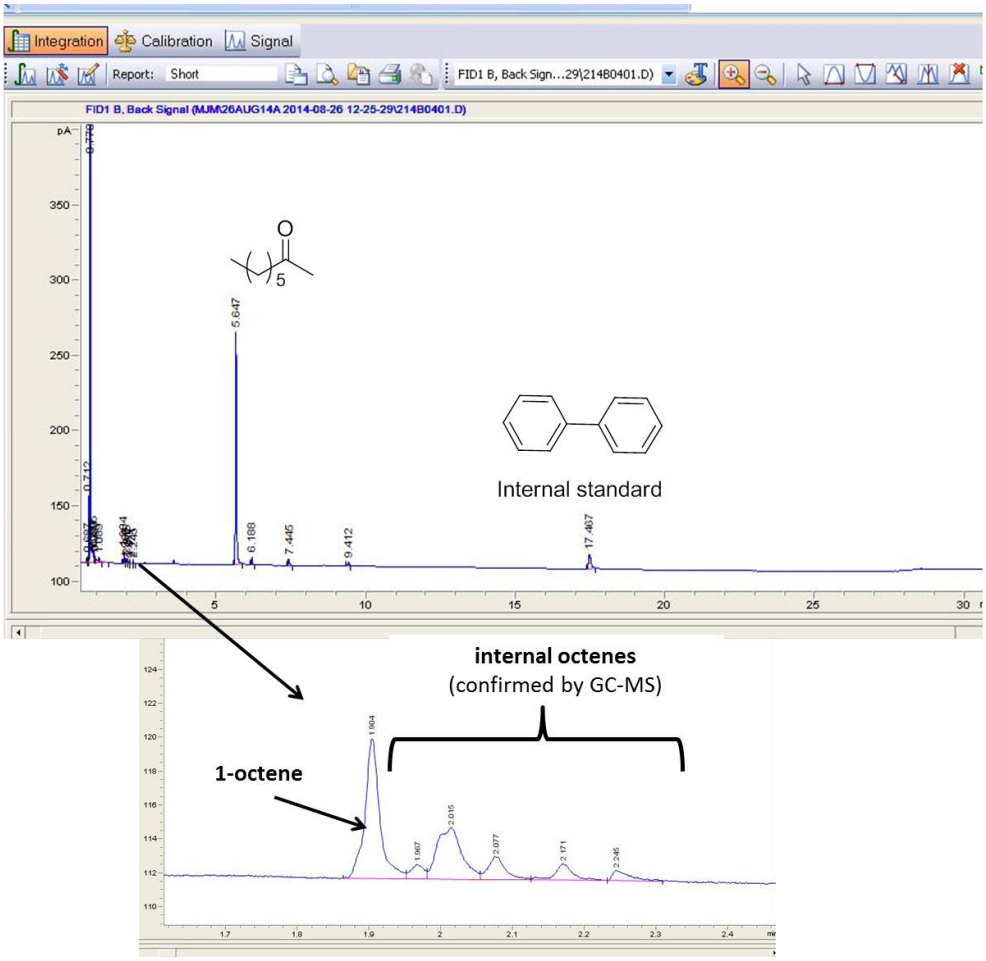
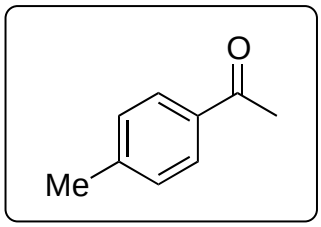


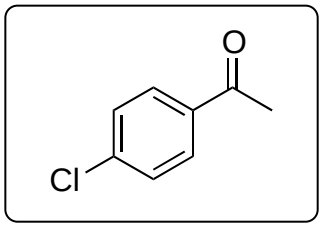
Figure S7 GC trace for the oxidation of 1-octene in acetone using (Bphen)Pd(MeCN)$_2$(OTf)$_2$ after 3 hours.

Isolated Yields for Styrene Products:

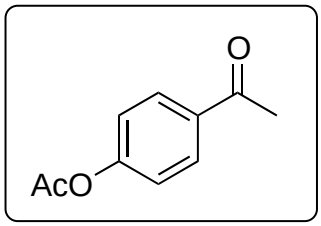
Analysis was mainly carried out with GC using an internal standard; however we also isolated some of the less volatile styrene products to further validate the GC method. In these cases, reactions were carried out using the following conditions: Pre-prepared (PBO)Pd(MeCN)$_2$(OTf)$_2$ (1 mol%, 0.0150 g, 0.0221 mmol) was weighed into a 30 mL glass vial (containing a micro-stir bar). Acetonitrile (4 mL), was added and the solution was stirred until the catalyst dissolved. The solution was then cooled to 0 °C and then 5 equiv. H_2O_2 (50 wt% in H_2O) (0.645 mL) and styrene (2.208 mmol) were added. The vial was then capped (cap had a small hole in the top) and transferred to a water bath (on a hot plate stirrer) at 27 ^oC and the solution was stirred at 600 rpm. When the reactions were finished, the reaction was quenched with a saturated aqueous solution of Na_2SO_3 (30 mL) to consume excess peroxide. The mixture was transferred to a separating funnel and diluted with diethyl ether (50 mL). The aqueous layer was separated and back extracted with diethyl ether (25 mL) twice. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was then purified by silica gel flash chromatography (diethyl ether: petroleum ether 1:10); the product containing fractions were combined and concentrated under reduced pressure.



The 1-*p*-tolyethanone was prepared from 4-methyl styrene (0.2610 g, 2.208 mmol) to afford 1-*p*-tolyethanone (0.2665 g, 90%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.40 (s, 3H), 2.57 (s, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.8, 26.7, 128.6, 129.4, 134.9, 144.0, 198.0. NMR data is consistent with literature values.[1]



1-(4-chlorophenyl)ethanone was prepared from 4-chloro styrene (0.3747 g, 2.208 mmol) to afford 1-(4-chlorophenyl)ethanone (0.2619 g, 77%) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.54 (s, 3H), 7.38 (d, *J* = 8.0 Hz), 7.84 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 26.7, 129.0, 129.8, 135.6, 139.7, 196.9. NMR data is consistent with literature values.[1]



The 4-acetylphenyl acetate was prepared from 4-acetoxystyrene (0.3579 g, 2.208 mmol) to afford 4-acetylphenyl acetate (0.2935 g, 82%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.31 (3H, s), 2.59 (3H, s), 7.19 (2H, d, *J* = 8.8 Hz), 7.99 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.3, 26.7, 121.9, 130.1, 134.9, 154.5, 169.0, 197.0. NMR data is consistent with literature values.[2]

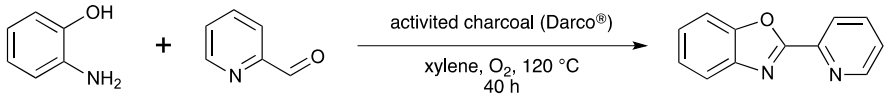
3. Synthesis of ligands and Pd(II) complexes

Synthesis of Bis(acetonitrile)dichloropalladium

Bis(acetonitrile)dichloropalladium was prepared according to the literature.[4]

Elemental Analysis: Predicted: C, 18.52; H, 2.33; N, 10.80; Found: C, 18.67; H, 2.34; N, 11.09.

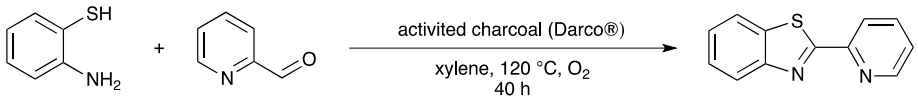
Synthesis of 2-(2-pyridyl)benzoxazole



The 2-(2-pyridyl)benzoxazole was prepared using the method developed by Hayashi and coworkers.[5,6] A mixture of 2-aminophenol (1 g, 9.1633 mmol), 2-pyridylaldehyde (1.15 g, 10.74 mmol), activated charcoal (Darco®, −100 mesh particle size, powder, 1 g) and xylene (20 mL) were placed in a 100 mL round bottom flask. The flask was connected to a water cooled condenser, which had rubber septum and a 1 L balloon filled with O_2 on the top. The reaction mixture was heated to 120 °C for 40 hours (note that it has previously been discussed by Hayashi and coworkers[5,6] that shorter reaction times are possible depending on the type of activated carbon used). The mixture was filtered using Celite and washed with methanol. The filtrate was concentrated and then purified by flash chromatography twice (ethyl acetate: hexane = 1:2, and then ethyl acetate: dichloromethane = 1:20). The product is a light yellow crystalline solid (Yield: 1.2738 g, 71%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 7.45-7.53 (m, 2H), 7.65 (dd, *J* =7.2, 4.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.2 Hz,

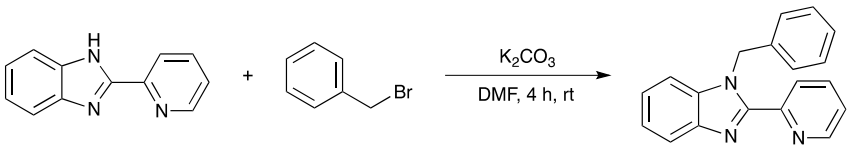
1H), 8.08 (ddd, *J* = 9.0, 6.8, 1.6, 1H), 8.36 (d, *J* = 8.0 Hz,1H), 8.81 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 111.3, 120.3,123.6, 125.1, 126.2, 137.7, 141.2, 145.2, 150.2, 150.4, 161.3. NMR Data is consistent with literature values.[5,6] Elemental Analysis: Predicted: C, 73.46; H, 4.11; N, 14.28; Found: C, 73.31; H, 4.42; N, 13.95.

Synthesis of 2-(2-pyridyl)benzothiazole



The 2-(2-pyridyl)benzothiazole was prepared using the method developed by Hayashi and coworkers.[5,6] A mixture of 2-aminobenzenethiol (1 g, 7.99 mmol), 2-pyridylaldehyde (1.07 g, 10 mmol), activated charcoal (Darco®, −100 mesh particle size, powder, 1 g, 50 wt%)and xylene (20 mL) were placed in a 100 mL round bottom flask. The flask was connected to a water cooled condenser, which had rubber septum and a 1 L balloon filled with O_2 on the top. The reaction mixture was then heated to 120 °C for 40 hours (note that it has previously been discussed by Hayashi and coworkers[5,6] that shorter reaction times are possible depending on the type of activated carbon used). The mixture was then filtered using Celite and washed with methanol. The filtrate was concentrated and then purified by Flash chromatography (ethyl acetate: hexane = 3:1. The product is light yellow crystalline solid (Yield: 1.3486 g, 79.5%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 7.51 (ddd, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.56-7.63 (m, 2H), 8.05 (ddd, *J* = 8.0, 8.0, 2.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 7.2 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 8.70 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 120.3, 122.5, 123.3, 125.9, 126.3, 126.6, 135.4, 137.7, 149.9, 150.3, 153.3, 169.0. NMR data is consistent with literature values.[4,5,7] Elemental Analysis: Predicted: C, 67.90; H, 3.80; N, 13.20; S, 15.11; Found: C, 68.10; H, 3.61; N, 13.23; S, 14.82.

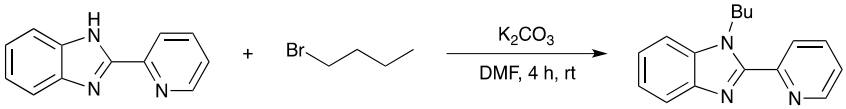
Synthesis of 1-benzyl-2-(2-pyridyl)benzoimidazole



The 1-benzyl-2-(2-pyridyl)benzoimidazole was prepared using the method developed by Diau and coworkers.[7] 2-(2-pyridyl)benzimidazole (0.4375 g, 2.24 mmol) and K_2CO_3 (0.4960 g, 3.6 mmol) were dissolved in DMF (5 mL) and stirred for 30 min; (bromomethyl)benzene (0.5011 g, 3 mmol) was added to the reaction mixture that was then stirred at room temperature for 4 h. After evaporation of the solvent under reduced pressure, H_2O (25 mL) and ethyl acetate (30

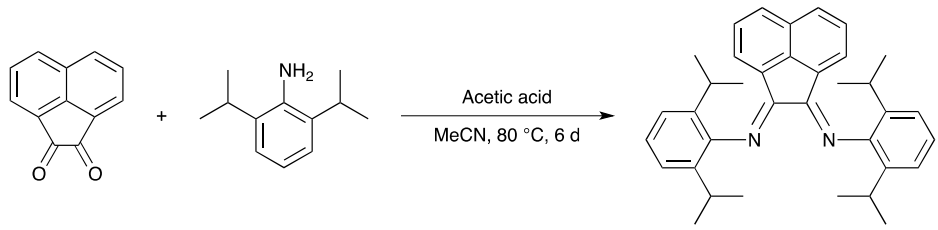
mL) were added. The organic layer was separated and the aqueous phase extracted further with ethyl acetate (30 mL) twice. The organic layers were combined and dried over $MgSO_4$. The crude product was purified using column chromatography with ethyl acetate and hexane (1:3) as the eluent. The product is a light purple crystalline solid (0.5912 g, 92.4%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 6.23 (s, 2H), 7.13-7.29 (m, 7H), 7.51 (m, 1H), 7.56 (m, 1H), 7.75 (m, 1H), 8.01 (ddd, *J* = 8.0, 8.0, 1.6 Hz, 1H), 8.38 (d, *J* = 7.6 Hz, 1H), 8.70 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 47.9, 111.3, 119.6, 122.6, 123.4, 124.4, 126.7, 127.2, 128.5, 136.5, 137.50, 137.7, 142.2, 148.8, 149.2, 150.0. NMR data is consistent with literature values.[7] Elemental Analysis: Predicted: C, 79.98; H, 5.30; N, 14.73; Found: C, 79.85; H, 5.42; N, 14.39.

Synthesis of 1-butyl-2-(2-pyridyl)benzoimidazole



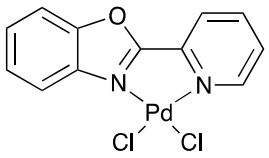
The 1-butyl-2-(2-pyridyl)benzoimidazole was prepared using the method developed by Diau and coworkers.[7] 2-(2-pyridyl)benzimidazole (0.4374 g, 2.24 mmol) and K_2CO_3 (0.4960 g, 3.6 mmol) were dissolved in DMF (5 mL) and stirred for 30 min; 1-bromobutane (0.4111 g, 3 mmol) was added to the reaction mixture that was then stirred at room temperature for 4 h. After evaporation of the solvent under reduced pressure, H_2O (25 mL) and ethyl acetate (30 mL) were added. The organic layer was separated and the aqueous phase was extracted by ethyl acetate (30 mL) twice. The organic layers were combined and dried over $MgSO_4$. The crude product was purified using column chromatography with ethyl acetate and hexane (1:3) as the eluent. The product is a light yellow coloured liquid (0.1969 g, 35.0%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 0.80 (t, 3H), 1.24 (m, 2H), 1.73 (m, 2H), 4.87 (t, 2H), 7.24-7.32(m, 2H), 7.50 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.8 Hz 1H), 7.99 (ddd, *J* = 7.8, 7.8, 1.6 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.73 (d, *J* = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 13.5, 19.4, 31.9, 44.4, 110.9, 119.5, 122.3, 123.1, 124.2, 124.3, 136.4, 137.4, 142.1, 148.8, 149.3, 150.2. Elemental Analysis: Predicted: C, 76.46; H, 6.82; N, 16.72; Found: C, 76.05; H, 7.08; N, 15.96.

Synthesis of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN)



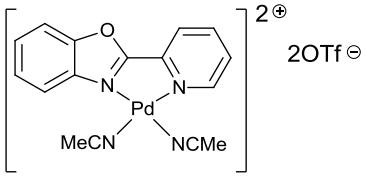
In an oven dried round bottomed flask, with a magnetic stirrer bar, acenaphthenequinone (0.551 g, 3.02 mmol) and 2,6-diisopropylaniline (1.354 g, 7.64 mmol) were mixed in dry acetonitrile (40 mL) and glacial acetic acid (2 mL). The mixture was heated to 80 °C and stirred under reflux for 6 days. The solution was then cooled, filtered under vacuum and the retentate washed with *n*-hexane, before drying overnight *in vacuo* to yield a yellow powder. (Yield = 1.315 g, 87%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88 (d, 2H, *J* = 8.4 Hz), 7.37 (t, 2H, *J* = 7.7 Hz), 7.27 (s, 6H), 6.64 (d, 2H, *J* = 7.1 Hz), 3.15 – 2.93 (m, 4H), 1.24 (d, 12H, J=6.9 Hz), 0.98 (d, 12H, *J* = 6.9 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 161.1, 147.6, 141.0, 135.6, 131.3, 129.7, 129.0, 128.0, 124.4, 123.6, 123.5, 28.8, 23.6, 23.3. NMR analysis is in agreement with literature data.[8] Elemental Analysis: Predicted: C, 86.35; H, 8.05; N, 5.59. Found: C, 86.43; H, 8.26; N, 5.62.

Synthesis of (2-(2-pyridyl)benzoxazole)$PdCl_2$



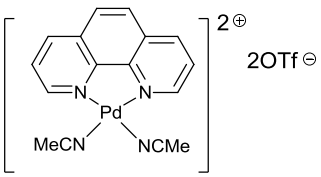
Bis(acetonitrile)dichloropalladium (0.0754 g, 0.291 mmol) was dissolved in dichloromethane (16 mL). Then a solution of 2-pyridyl-benzoxazole (0.0570 g, 0.291 mmol) in dichloromethane (2 mL) was added dropwise into the $PdCl_2(MeCN)_2$ solution with stirring. The reaction mixture was then stirred at room temperature for 16 hours. The yellow precipitate was then filtered, washed with 100 mL of diethyl ether and then dried under reduced pressure. The product was a yellow solid (0.0942 g, 87%). ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 7.62 (ddd, *J* = 7.7, 7.4, 1.2 Hz, 1H), 7.69 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 7.97 (ddd, *J* = 7.5, 5.8, 1.6 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.37 (d, *J* = 6.8 Hz, 1H), 8.44 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 9.10 (d, *J* = 4.8 Hz, 1H). ^{1}H NMR analysis in agreement with literature data.[5] Elemental Analysis: Predicted: C, 38.59; H, 2.16; N, 7.50; Found: C, 38.03; H, 2.01; N, 7.32.

Synthesis of (2-(2-pyridyl)benzoxazole)Pd(MeCN)$_2$(OTf)$_2$



(2-(2-pyridyl)benzoxazole) (0.0600 g, 0.3058 mmol) and Pd(OAc)$_2$ (0.0687 g, 0.3060 mmol) were weighed into an sample vial and were dissolved in acetonitrile (4 mL). The reaction mixture was stirred at room temperature for 1 hour, with a yellow precipitate forming after this time. Then a solution of triflic acid (0.1147g) in acetonitrile (2 mL) was added dropwise to the reaction mixture resulting in a light yellow solution. The solution was then stirred for 16 hours. Then 20 mL of diethyl ether was added into the sample vial resulting in a light yellow precipitate. The solid was then filtered using a Buchner funnel and washed with 100 mL of diethyl ether. It was then dried under high vacuum overnight. The Pd(2-pyridyl benzoxzole)(MeCN)$_2$(OTf)$_2$ was isolated (0.1750 g, 83.8% yield) as a light yellow powder. ESI-MS: $[M+H^+-2OTf]^+$: $C_{16}H_{15}N_4OPd$, calcd m/z 385.03, found 385.04 $[OTf]^-$: $CF_3SO_3^-$, calcd m/z 148.95, found 148.96 ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 2.04 (s, 6H), 7.62 – 7.72 (m, 1H), 7.72 - 7.81 (m, 1H), 7.90 (d, *J* = 7.9 Hz 1H), 7.92 – 7.99 (m, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.56 – 8.39 (m, 3H). ^{1}H-NMR (600 MHz, CD_3CN): δ (ppm) 1.97 (s, 6H), 7.75-7.78 (m, 2H), 7.80-7.84 (m, 1H), 7.93-7.98 (m, 2H), 8.36 (dd, *J* = 1.6, 7.8 Hz) 8.53 (ddd, *J* = 1.3, 7.2, 7.8 Hz) 8.68 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (150 MHz,CD_3CN): δ (ppm) 1.7, 114.1, 118.8, 122.05 (q, *J* = 320.1 Hz, $CF_3SO_3^-$), 127.5, 129.7, 131.01, 131.6, 135.4, 144.4, 145.4, 149.9, 154.9, 165.9.Elemental Analysis: Predicted: C, 31.63; H, 2.05; N, 8.20; S, 9.37; Found: C, 31.34; H, 1.75; N, 8.08; S, 9.28.

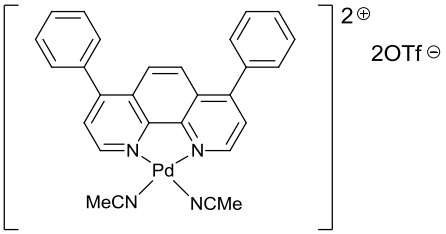
Synthesis of (1,10-phenanthroline)Pd(MeCN)$_2$(OTf)$_2$



(1,10-Phenanthroline)Pd(OAc)$_2$ was synthesised using the method reported by Sheldon and coworkers.[9] A solution of 1,10-phenanthroline (0.2292 g, 1.272 mmol) in dichloromethane (4 mL) was added to a solution of Pd(OAc)$_2$ (0.1373 g, 1.223 mmol) in toluene (25 mL) at room temperature under N_2. The reaction mixture was stirred overnight, and then HPLC grade hexane was added to precipitate the complex. Then the yellow solid was filtered off and washed with diethyl ether and dried under vaccum. Yield: 0.4528 g, 92%. (1,10-phenanthroline)Pd(MeCN)$_2$(OTf)$_2$ was synthesized by using the method modified from the literature.[10] To a slurry of (1,10-phenanthroline)Pd(OAc)$_2$ (0.2361 g, 0.5892 mmol) in

acetonitrile (1 mL) was added a solution of triflic acid in acetonitrile (0.33 M, 4 mL, 2.5 equiv). The solution was stirred for 1 hour at room temperature and then precipitated by the addition of diethyl ether to give a yellow solid. The crude product was filtered and then re-dissolved in acetonitrile (1 mL) and a solution of triflic acid in acetonitrile (0.33 M, 4 mL 2.5 equiv) was added again. After stirring for 1 hour, diethyl ether was once again used to precipitate the complex. The light yellow solid was filtered, washed with diethyl ether (80 mL) and dried under vaccum. Yield: 0.3377 g, 86%. ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 2.03 (s, 6H), 8.10 (dd, *J* = 8.2, 5.4 Hz 2H), 8.31 (s, 2H), 8.66 (d, *J* = 4.8 Hz, 2H), 9.03 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 1.1, 120.7 (q, *J* = 320.1Hz, $CF_3SO_3^-$), 126.1, 127.8, 130.5, 141.3, 146.6, 149.7. Elemental Analysis: Predicted: C, 32.39; H, 2.10; N, 8.40; S, 9.60; Found: C, 32.18; H, 2.02; N, 7.98; S, 9.17. ESI-MS: $[M\text{-}MeCN\text{ -}OTf]^+$: $C_{15}H_{11}F_3O_3N_3PdS$, calcd m/z 475.96, found 475.97; $[M\text{-}2MeCN\text{-}OTf]^+$: $C_{13}H_8F_3N_2O_3PdS$, calcd m/z 434.93, found 434.94; $[OTf]^-$:$CF_3SO_3^-$, calcd m/z 148.95, found 148.96.

Synthesis of (bathophenanthroline)Pd(MeCN)$_2$(OTf)$_2$



This complex was prepared using a method modified from the literature.[10] First (bathophenanthroline)Pd(OAc)$_2$ was synthesised using similar methods reported by Sheldon and coworkers.[9] A solution of bathophenanthroline (0.1015 g, 0.3023 mmol) in dichloromethane (2 mL) was added to a solution of Pd(OAc)$_2$ (0.0656 g, 0.2922 mmol) in toluene (12 mL) and stirred at room temperature under a N_2 atmosphere overnight. HPLC grade hexane was then added to precipitate the complex. The yellow solid was filtered and washed with diethyl ether and dried under vacuum. Yield: 0.1514 g, 93%. To a slurry of (bathophenanthroline)-Pd(OAc)$_2$ (0.1373 g, 0.2469 mmol) in acetonitrile (1 mL) was added a solution of triflic acid (0.1096 g, 2.5 equiv) in acetonitrile (1mL). The solution was stirred for 1 hour at room temperature then precipitated with diethyl ether to give a yellow solid. The crude product was then re-dissolved in acetonitrile (1 mL) a solution of triflic acid (0.1096 g, 2.5 equiv) in acetonitrile (1 mL) was added again. After stirring for 1 hour, diethyl ether was added to precipitate the complex. The yellow crystalline solid was filtered off and washed with diethyl ether (80 mL) and dried under vacuum. Yield: 0.1393 g, 69%. ^{1}H-NMR (400 MHz, DMSO-d_6): δ (ppm) 2.07 (s, 6H), 7.76-7.77 (m, 10H), 8.09 (d, 5.7 Hz 2H), 8.15 (s, 2H), 8.76 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 1.1, 118.0, 120.7 (q, *J* = 320.1 Hz, $CF_3SO_3^-$), 125.9, 126.2, 128.2, 129.3, 129.8, 130.4, 134.5, 147.07, 149.3, 152.4. ESI-MS: $[M+H^+\text{-}2OTf]^+$: $C_{28}H_{22}N_4Pd$, calcd m/z 521.10, found 521.07; $[M\text{-}2MeCN\text{-}OTf]^+$:

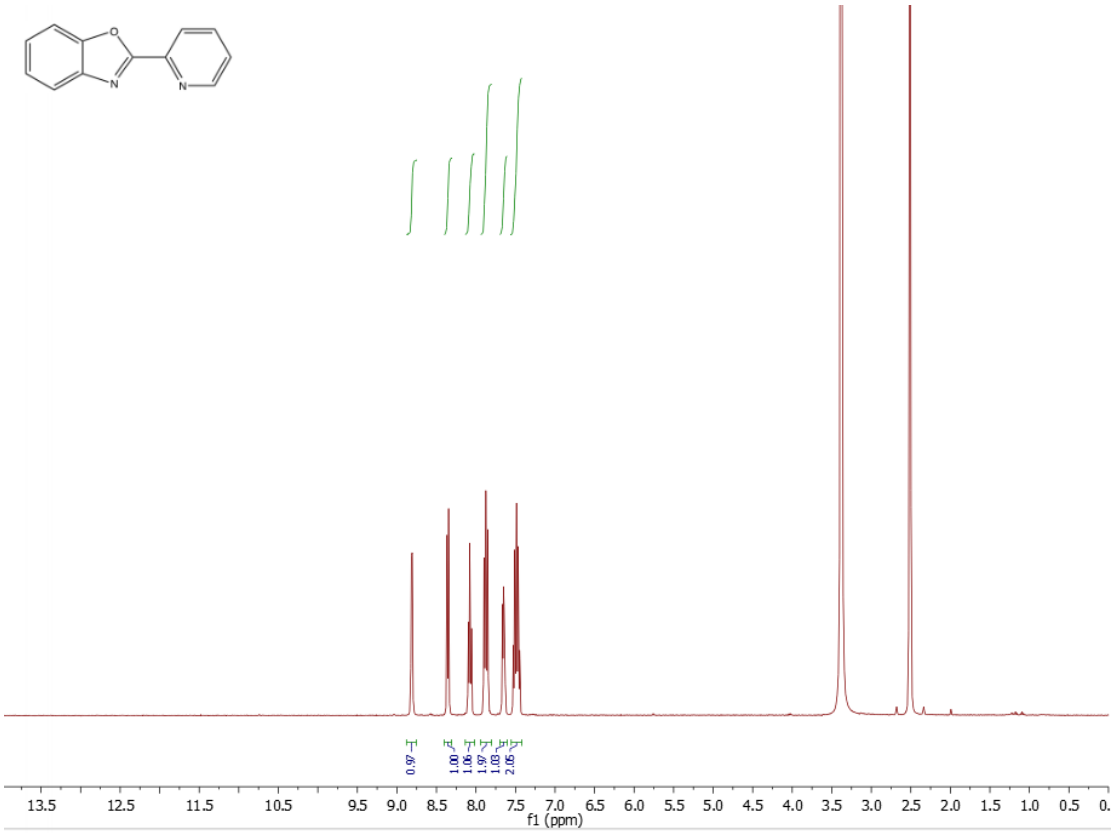
$C_{25}H_{16}F_3N_2O_3PdS$, calcd m/z 586.99, found 587.00; $[OTf]^-$:$CF_3SO_3^-$, calcd m/z 148.95, found 148.96 Elemental Analysis: Predicted: C, 43.95; H, 2.69; N, 6.84; S, 7.81; Found: C, 42.95; H, 2.58; N, 6.44; S, 7.17.

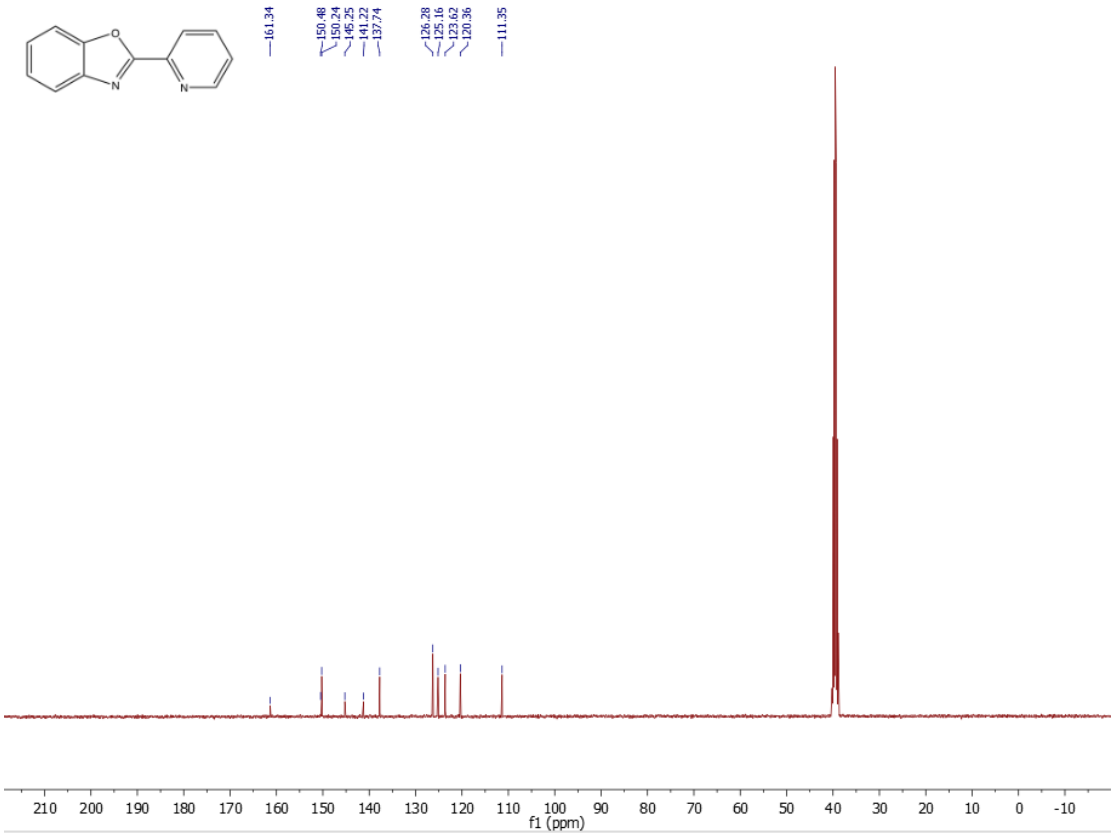
4. References

1. Y.-F. Wang, Y.-R. Gao, S. Mao, Y.-L. Zhang, D.-D. Guo, Z.-L. Yan, S.-H. Guo and Y.-Q. Wang, *Org. Lett.*, 2014, **16**, 1610.
2. K. J. Ratnam, R. S. Reddy, N. S. Sekhar, M. L. Kantam and F. Figueras, *J. Mol. Catal. A: Chem.*, 2007, **276**, 230.
3. a) J. C. Oxley, J. L. Smith, P. R. Bowden and R. C. Rettinger, *Propellants Explos. Pyrotech*. 2013, **38**, 244. (b) J. C. Oxley, J. L. Smith, L. Steinkamp and G. Zhang, *Propellants Explos. Pyrotech*. 2013, **38**, 841. (c) J. -H. Chia, S.-H. Wub and C.-M. Shu, *J. Hazard Mater*., 2009, **171**, 1145.
4. C. J. Mathews, P. J. Smith and T. Welton, *J. Mol. Catal. A: Chem.*, 2004, **214**, 27.
5. S. Haneda, Z. Gan, K. Eda and M. Hayashi, *Organometallics*, 2007, **26**, 6551.
6. Y. Kawashita, N. Nakamichi, H. Kawabata and M. Hayashi, *Org. Lett.*, 2003, **5**, 3713.
7. W.-K. Huang, C.-W. Cheng, S.-M. Chang, Y.-P. Lee and E. W.-G. Diau, *Chem. Commun.*, 2010, **46**, 8992.
8. T. Tu, Z. Sun, W. Fang, M. Xu and Y. Zhou, *Org. Lett.*, 2012, **14**, 4250.
9. G.-J. T. Brink, I. W. C. E. Arends, M. Hoogenraad, G. Verspui and R. A. Sheldon, *Adv. Synth. Catal.*, 2003, **345**, 1341.
10. N. R. Conley, L. A. Labios, D. M. Pearson, C. C. L. McCrory and R. M. Waymouth, *Organometallics*, 2007, **26**, 5447.

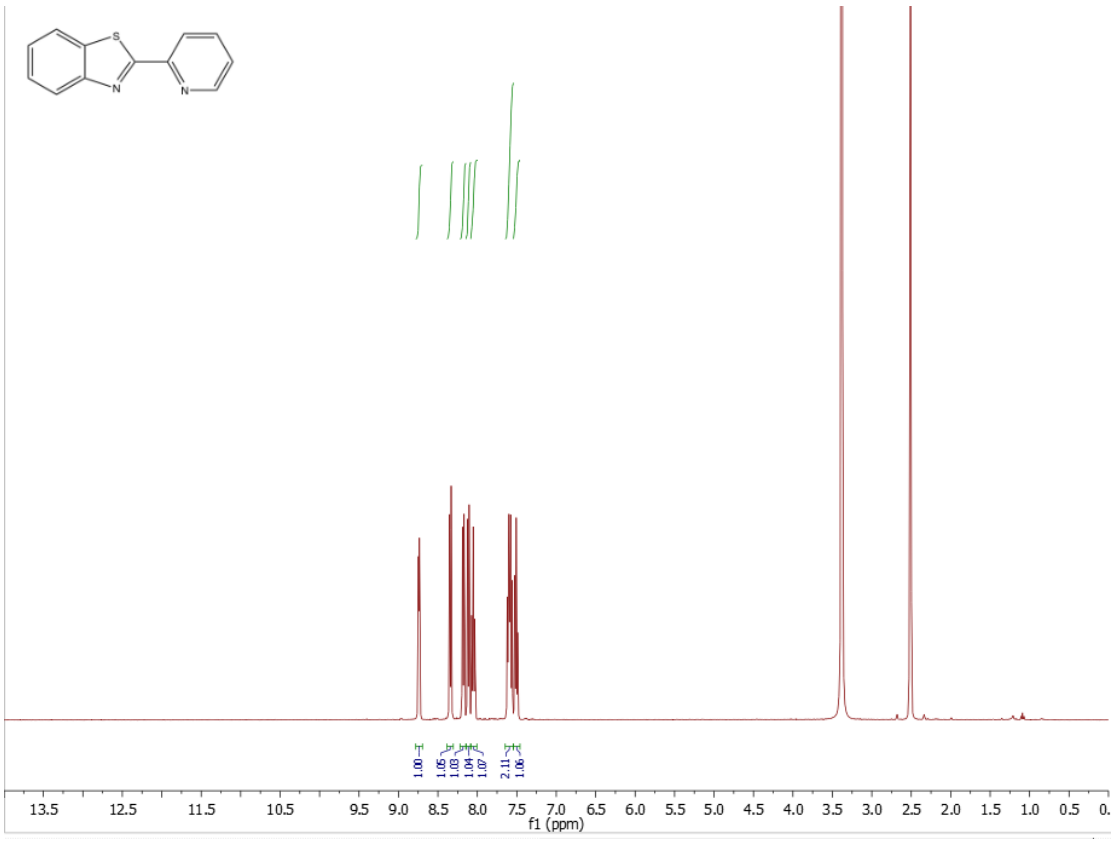
5. NMR Spectra

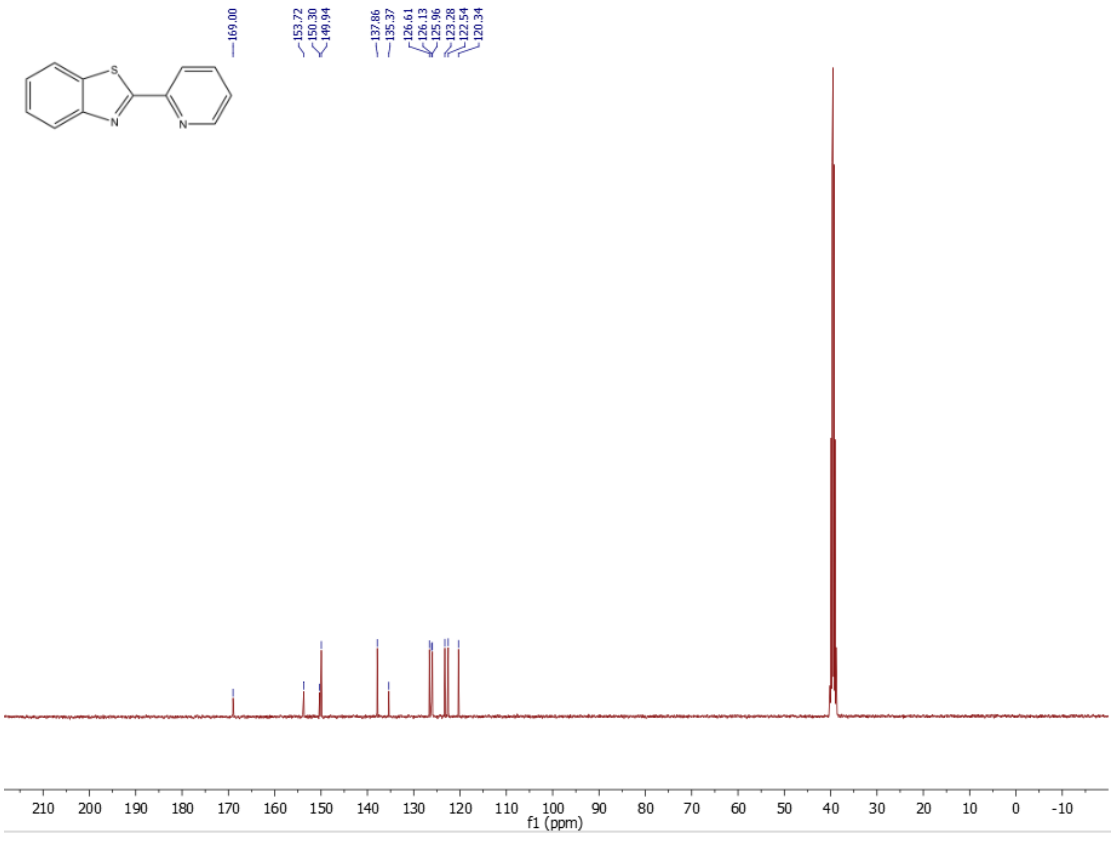
2-(2-Pyridyl)benzoxazole: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in d^{6}-DMSO



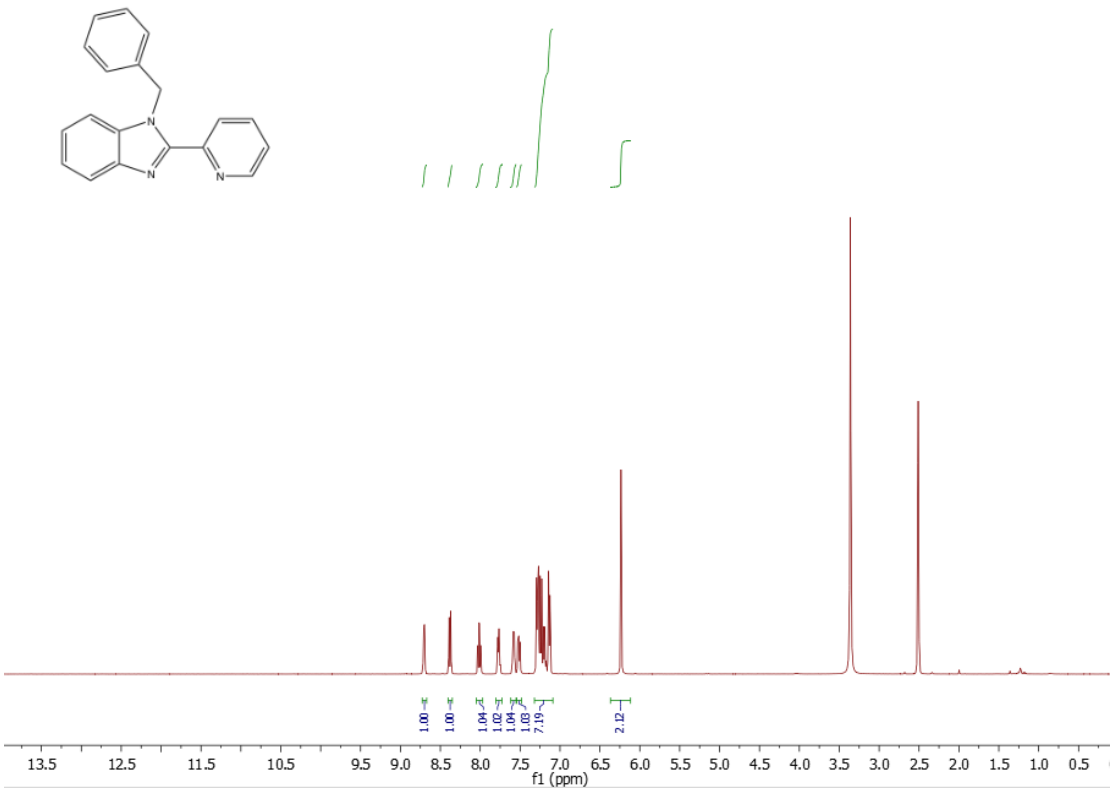


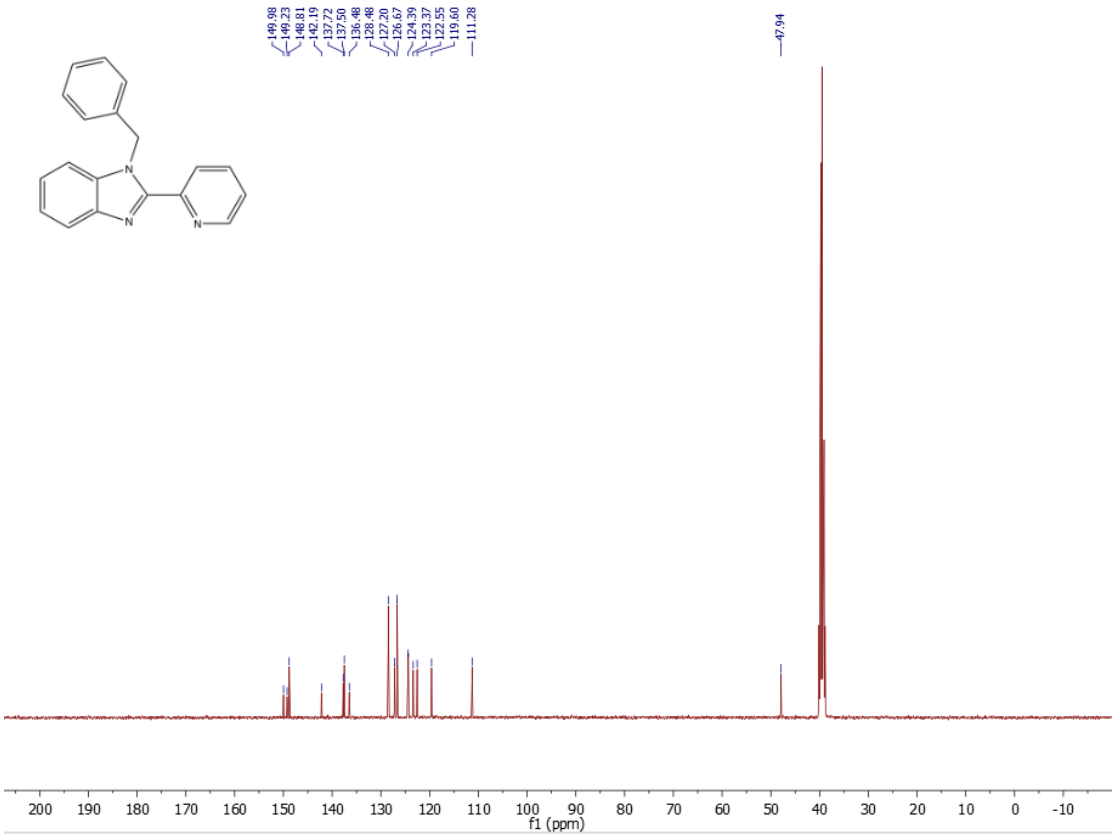
2-(2-Pyridiyl)benzothiazole: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in d^{6}-DMSO



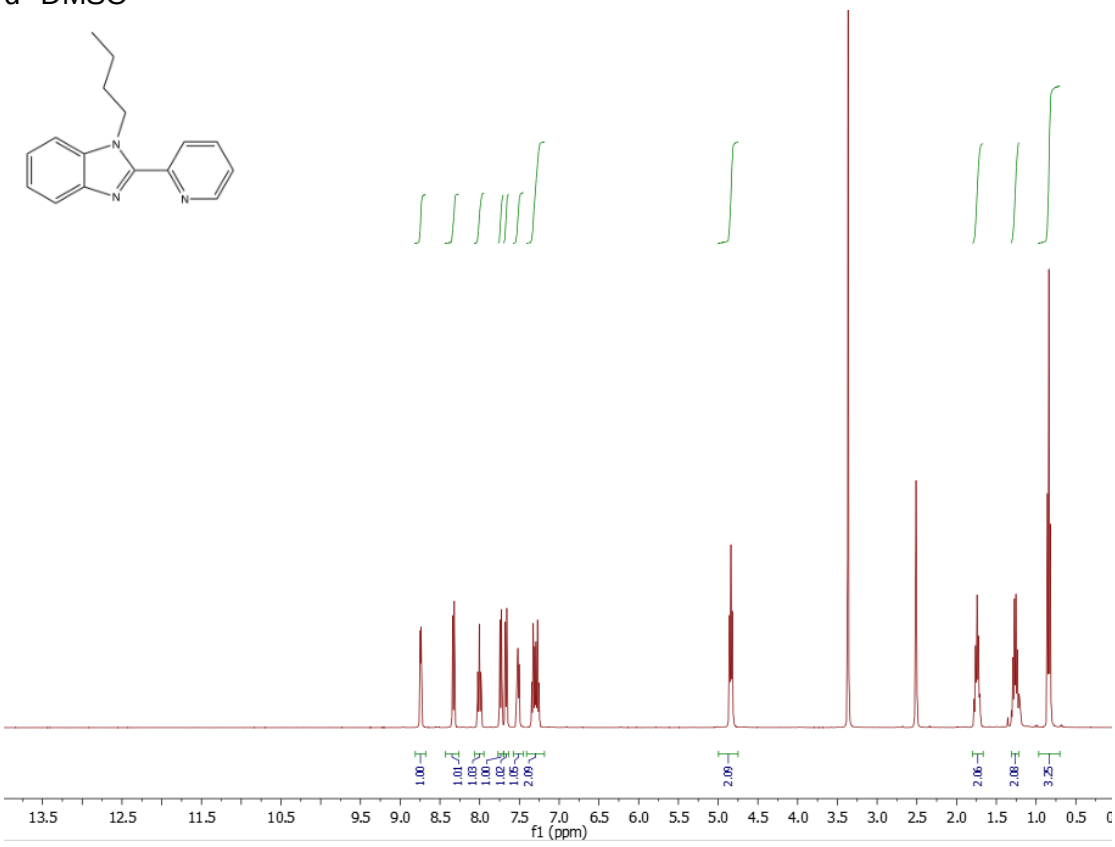


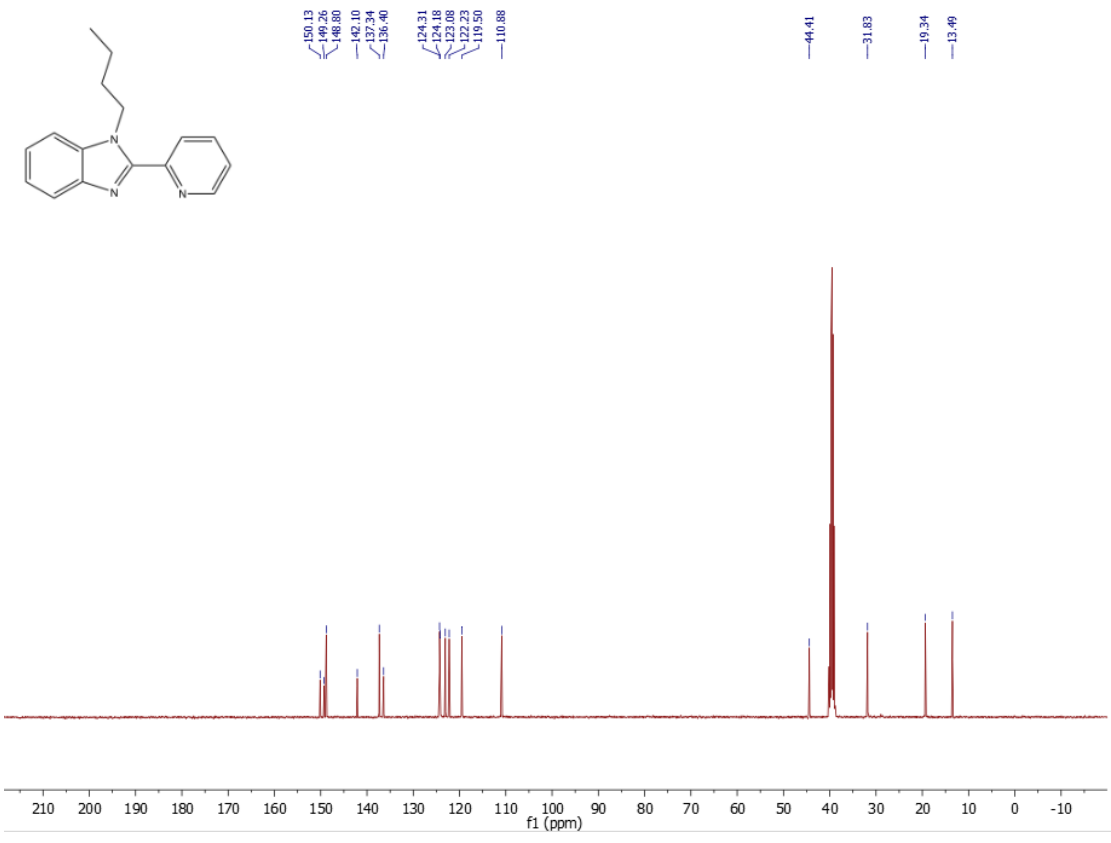
1-Benzyl-2-(2-pyridinyl)benzimidazole: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in d^{6}-DMSO



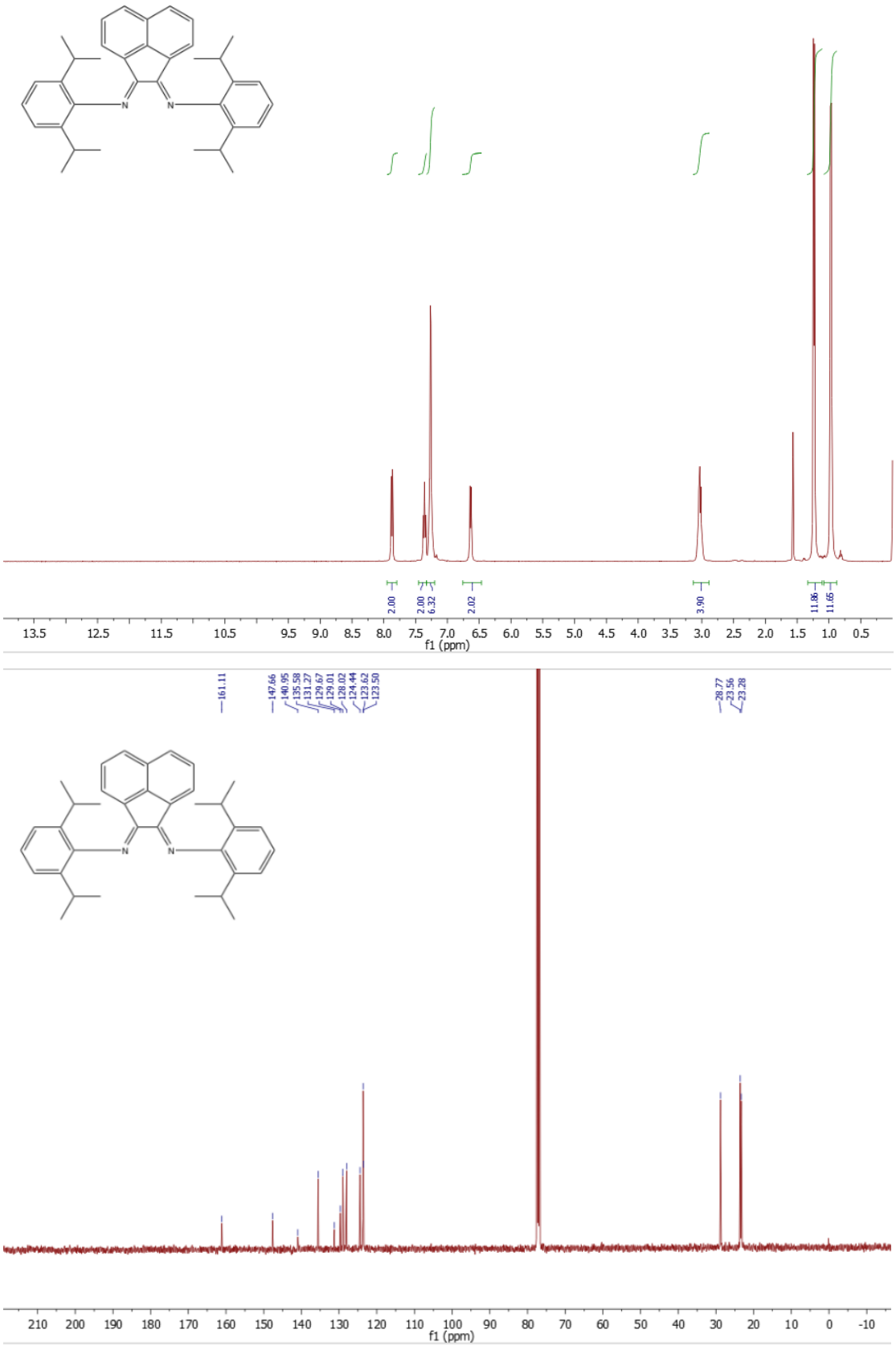


1-Butyl-2-(2-pyridiyl)benzimidazole: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in d^{6}-DMSO

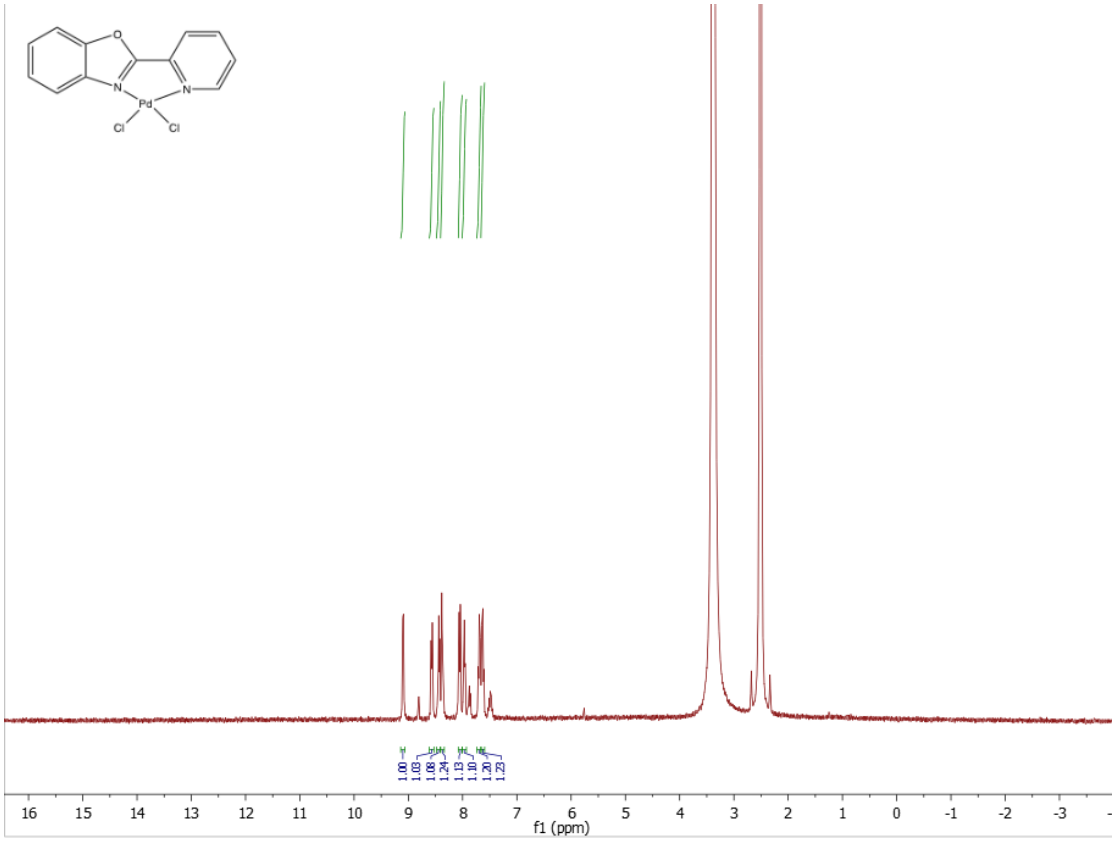




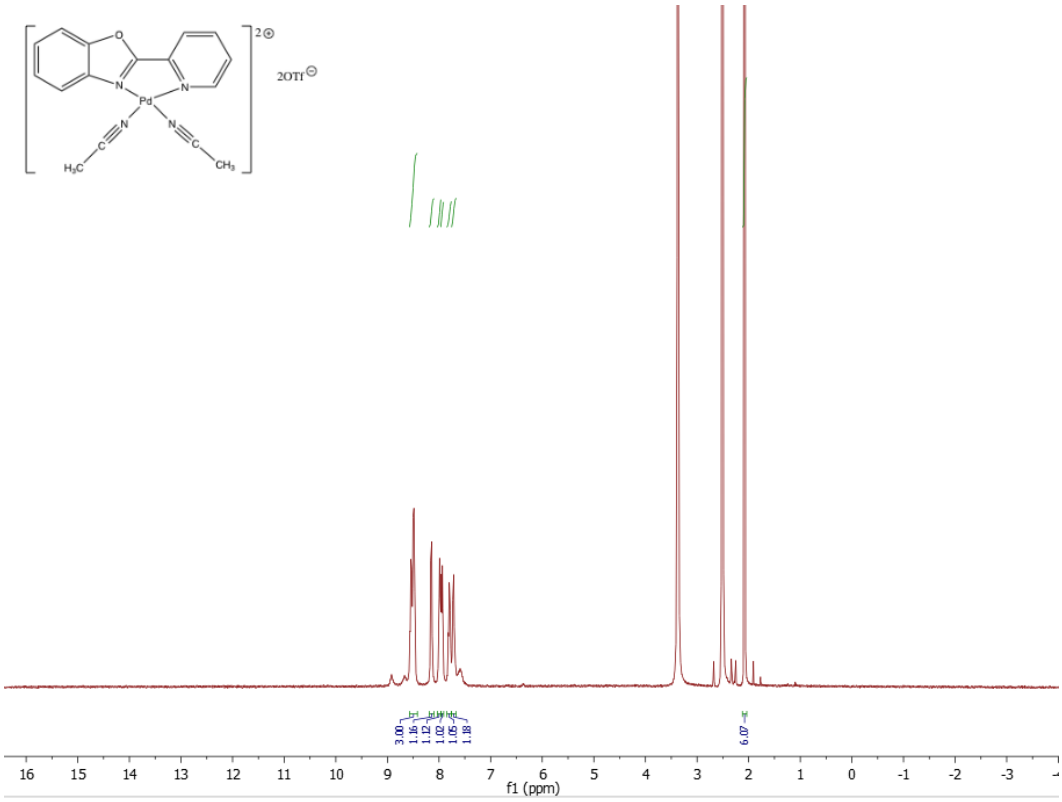
1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN): ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in $CDCl_3$



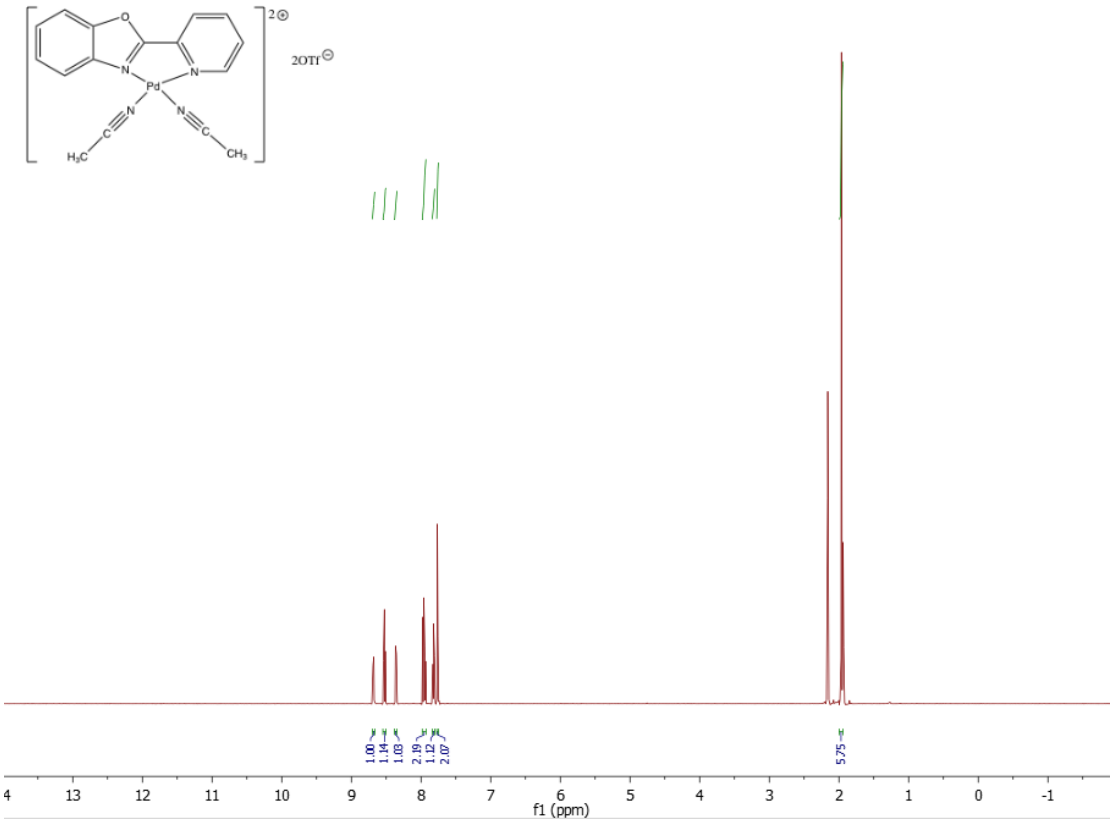
Dichloro(2-(2-pyridyl)benzoxazole)palladium(II): ^{1}H NMR (400 MHz) in d^{6}-DMSO

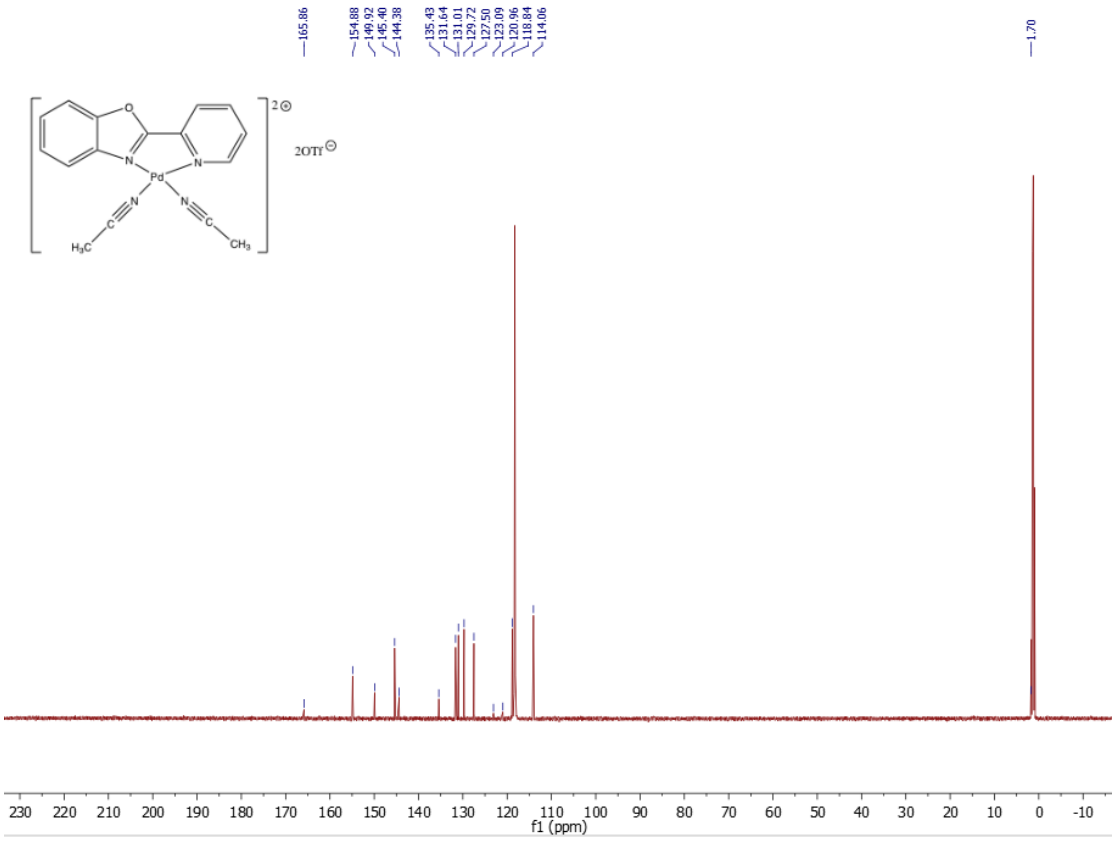


(2-(2-Pyridyl)benzoxazole)Pd(MeCN)$_2$(OTf)$_2$: ^{1}H NMR (400 MHz) in d^6-DMSO

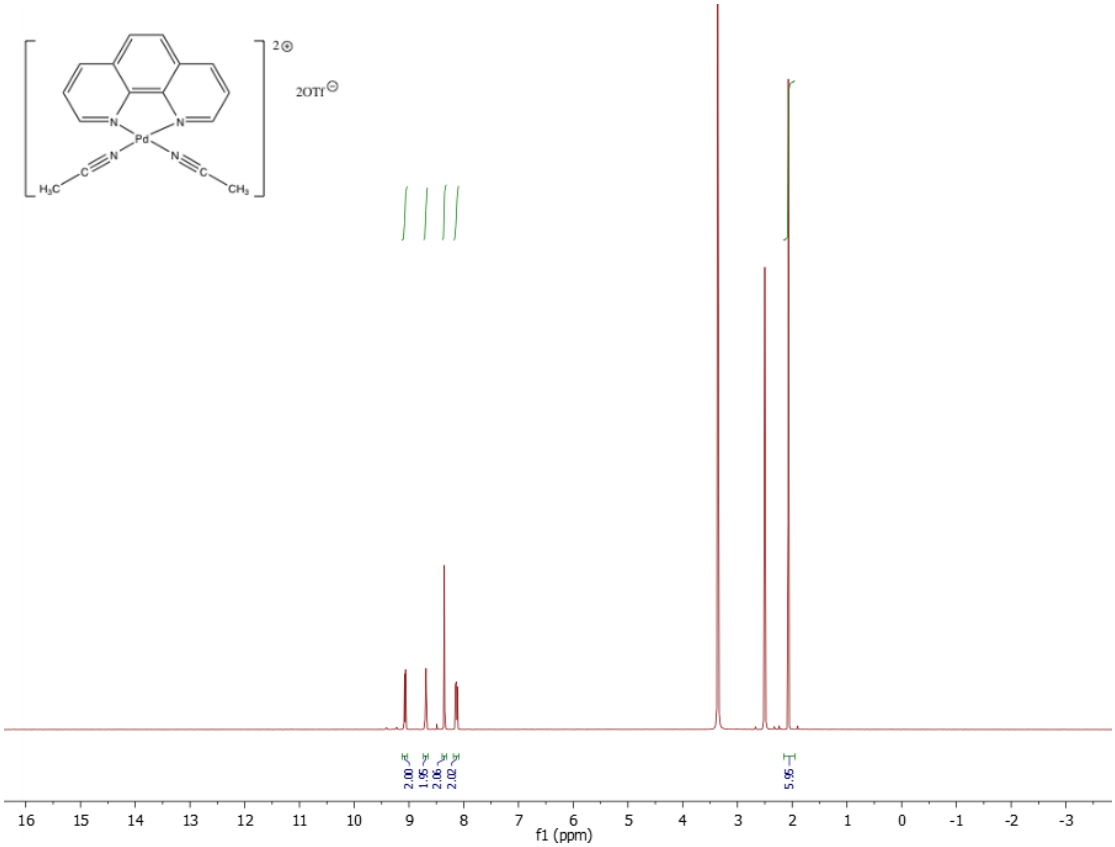


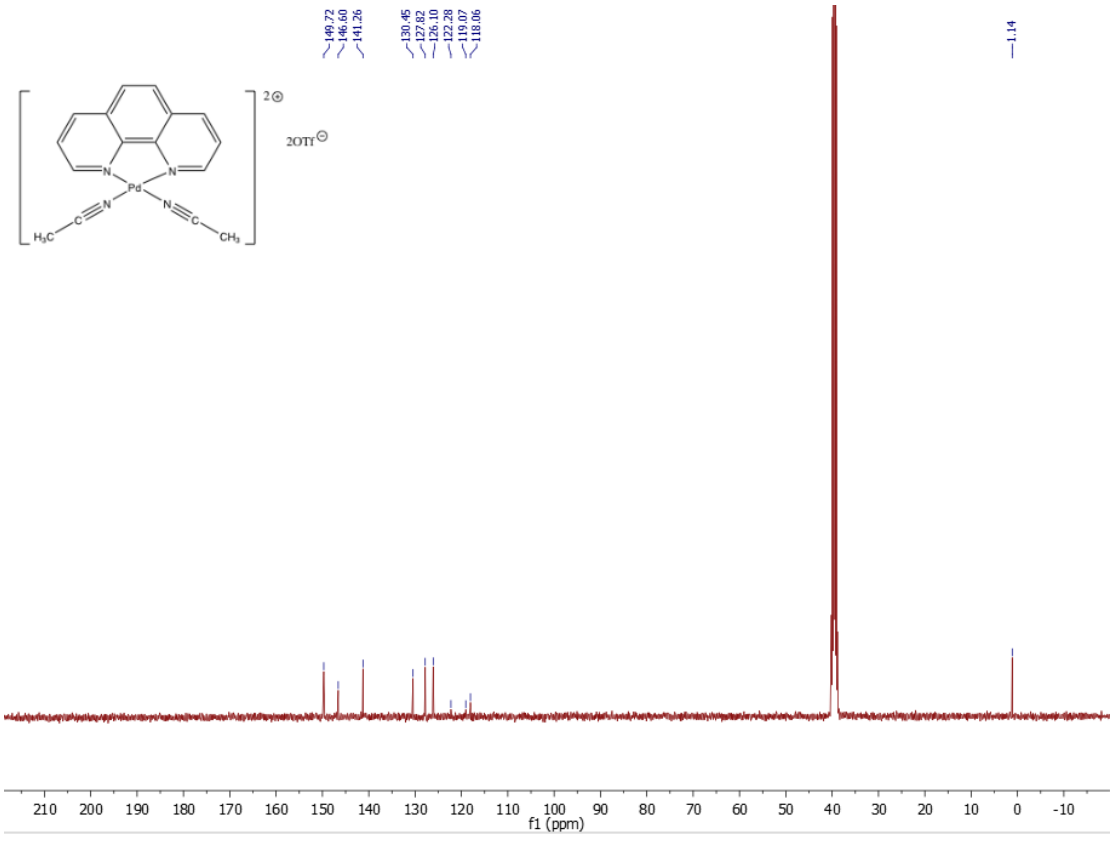
(2-(2-Pyridyl)benzoxazole)Pd(MeCN)$_2$(OTf)$_2$: ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) in CD_3CN



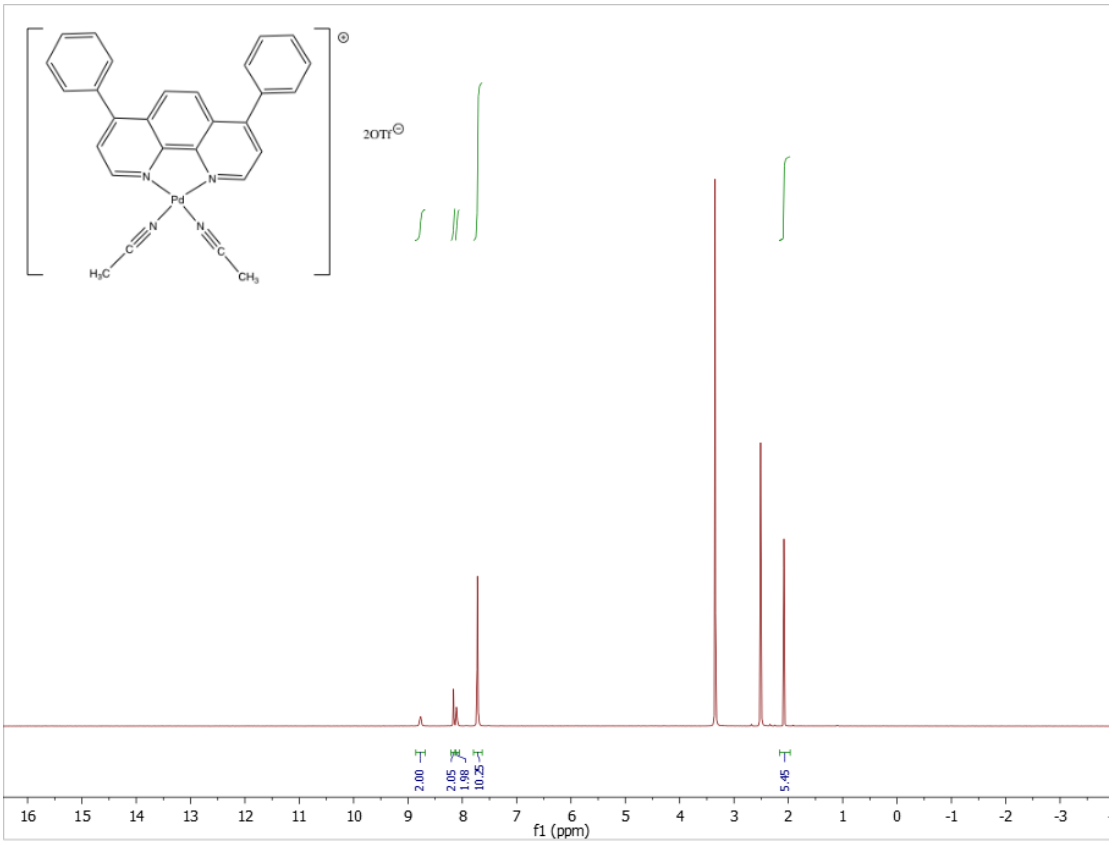


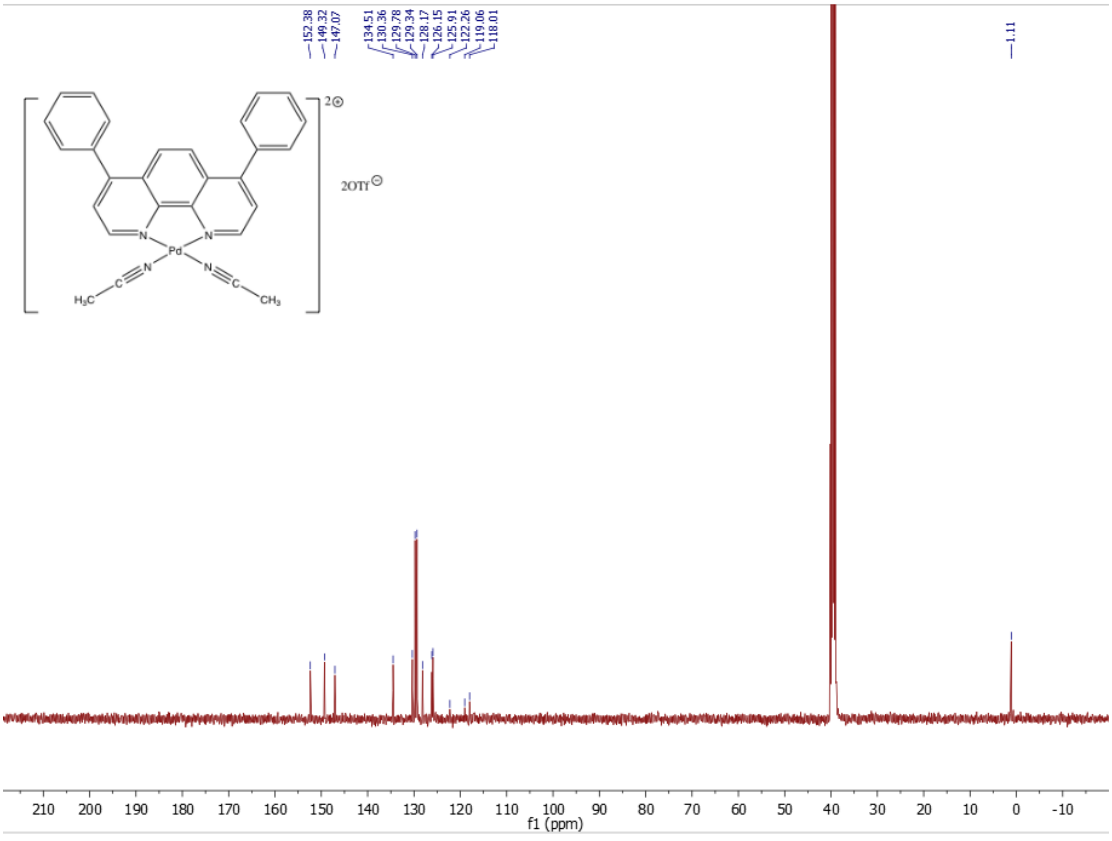
(Phenanthroline)Pd(MeCN)$_2$(OTf)$_2$: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in d_6-DMSO



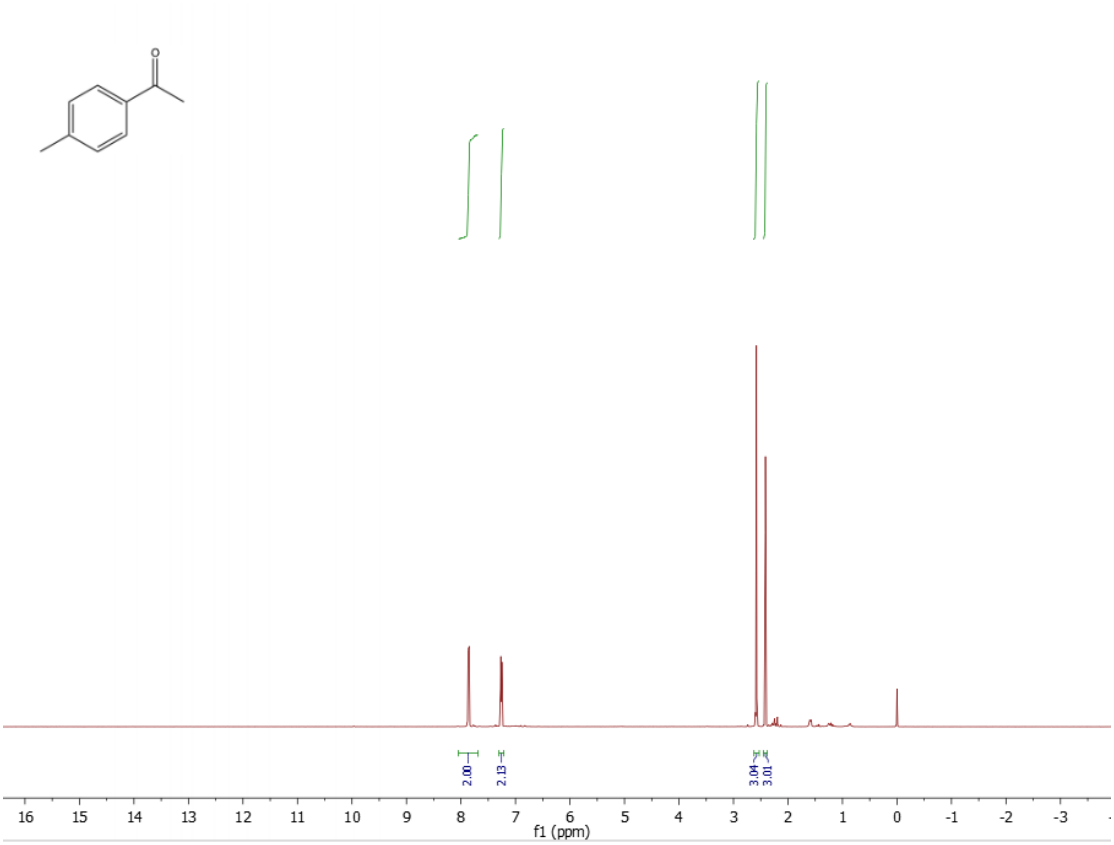


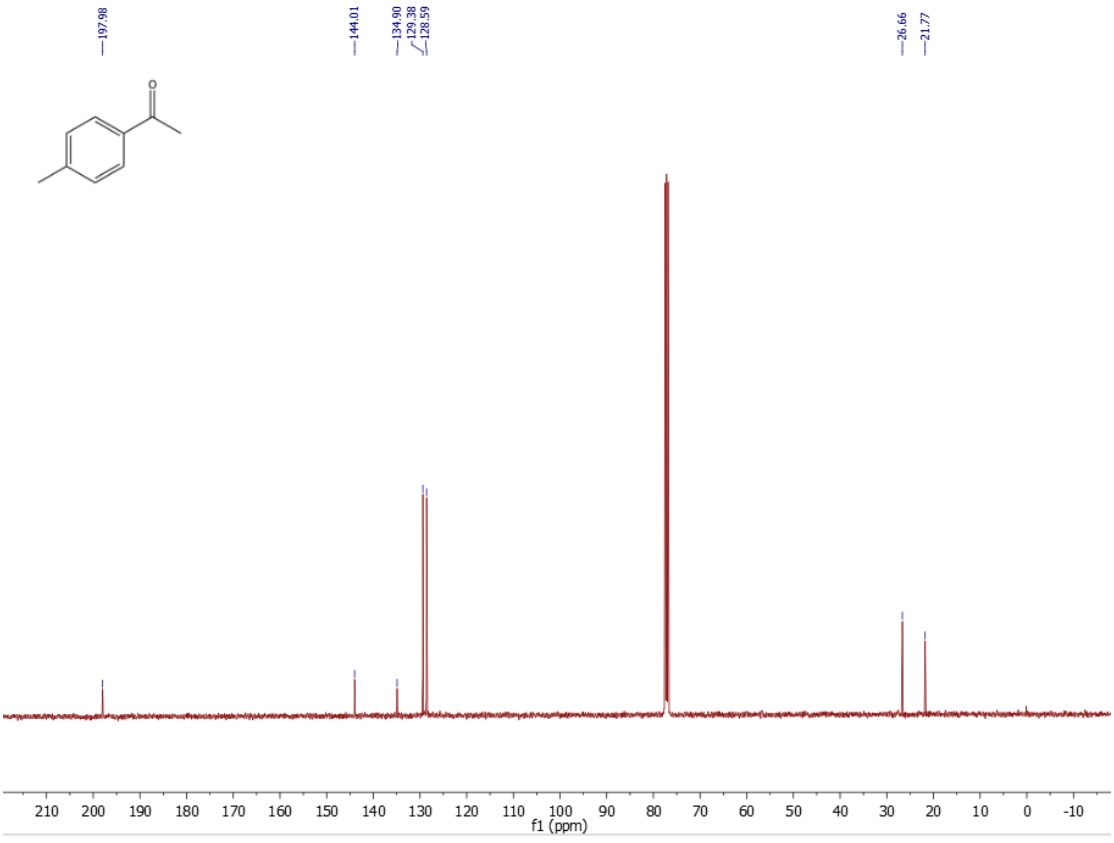
(Bathophenanthroline)Pd(MeCN)$_2$(OTf)$_2$: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in d$_6$-DMSO



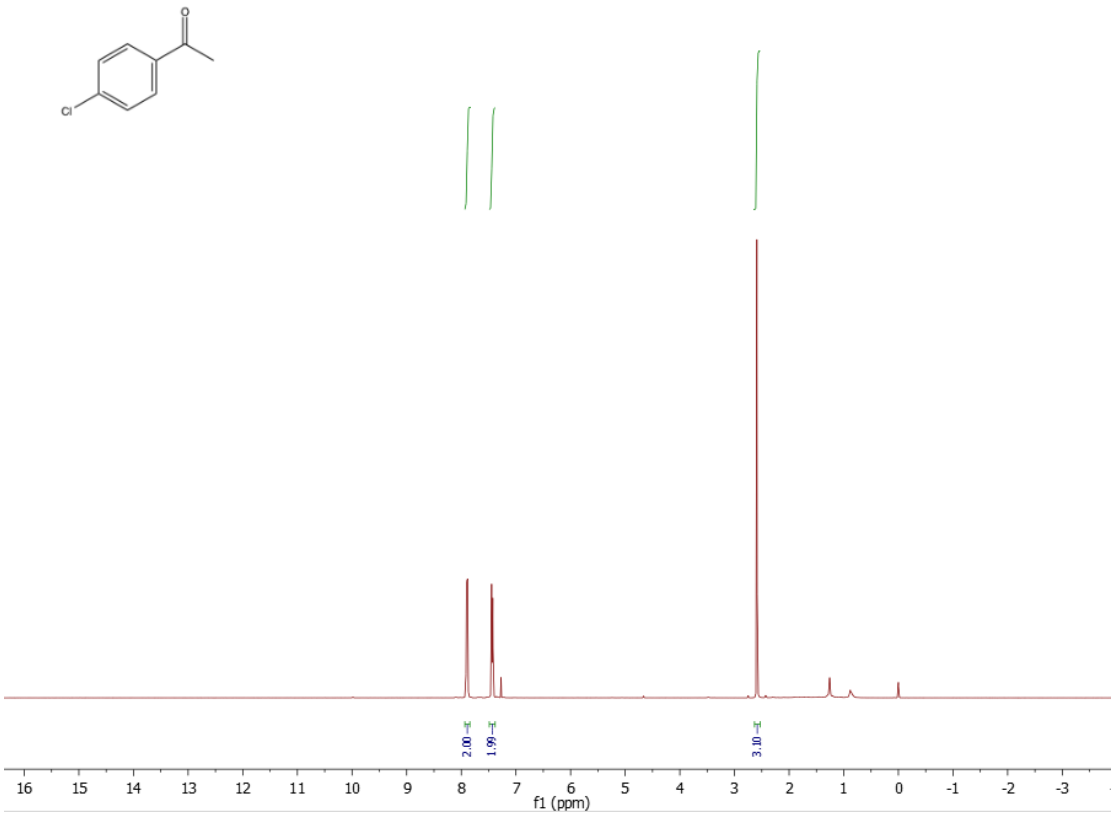


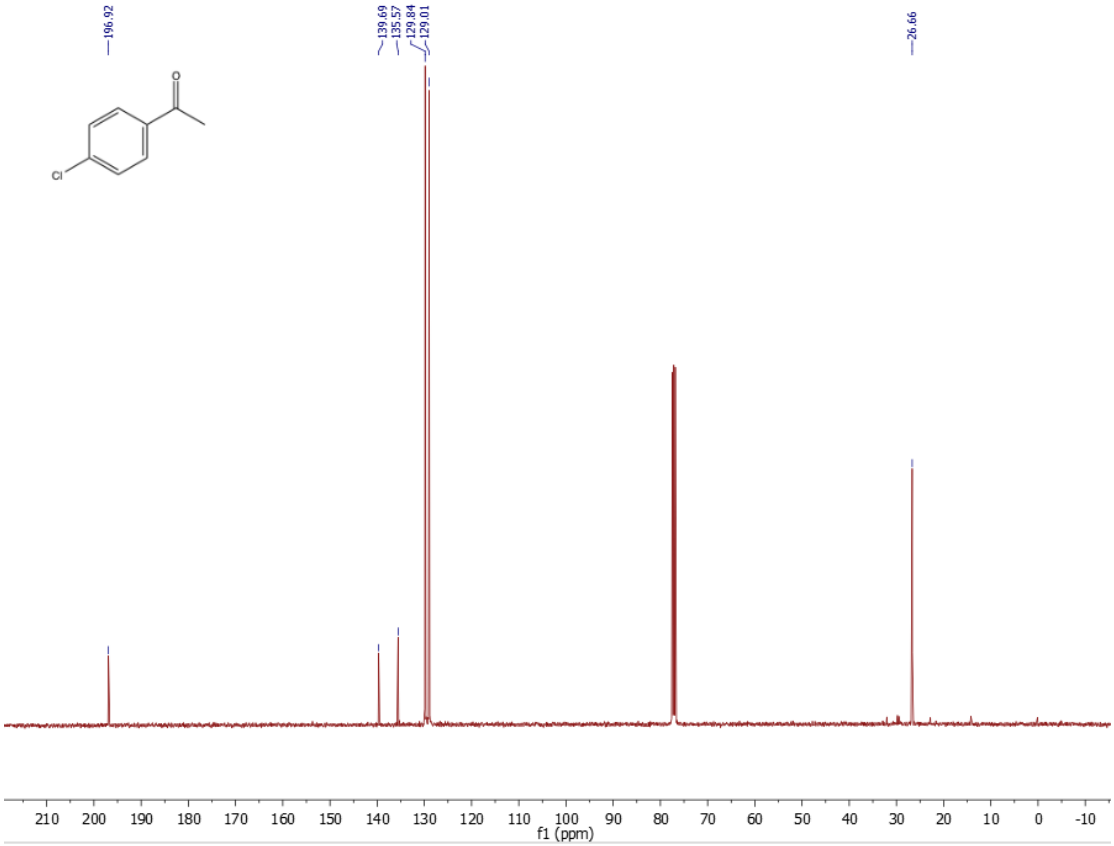
1-*p*-Tolyethanone: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in $CDCl_3$





1-(4-Chlorophenyl)ethanone: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in $CDCl_3$





4-Acetylphenyl acetate: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) in $CDCl_3$