Supporting Information

Efficient C-2 Arylation of Azoles *via* [κ²N] N-bound Triazolylpyridine Pd-Complexes Enabled by Silver in HFIP

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Contents	Page #

1. Experimental Section

General information

All of the laboratory glassware was oven-dried and then used for the general experimental procedures. The melting point of solid compound was recorded in an open capillary on a Sisco melting point instrument and thereafter presented uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer at 400 MHz for ^{1}H proton NMR and 100 MHz for ^{13}C proton NMR, and $CDCl_3$ and DMSO-d_6 were used as the solvents to prepare the samples. Both tetramethylsilane (TMS) (δ 0.00) and $CDCl_3$ were applied as the internal standards while recording the ^{1}H proton NMR (δ 7.246) and ^{13}C (δ 77.0) NMR spectral data. The patterns of the chemical shifts in proton NMR are presented in parts per million. The peak splitting patterns are defined as singlet (s), broad singlet (brs), doublet (d), doublet of doublets (dd), triplet (t), and multiplet (m). All coupling constant (*J*) values are presented in hertz. High-resolution electron impact mass spectra (HR-EIMS) were analyzed on a Xevo G2-Q-Tof instrument (Agilent) that was compatible with ACQUITY UPLC and nano ACQUITY UPLC systems. The mass spectra were also recorded on a Agilent Q-Tof-Micro Micromass instrument. Column chromatography was performed using normal (particle size, 100–200 mesh) and flash (particle size, 230–400 mesh) silica gels, which were obtained from Qualigens, Spectrochem, and Rankem. TLC plates coated with silica gel (Kiesel 60-F254, Merck) were used to track the progress of the chemical reactions. The visualizing agent that was utilized for TLC was UV light. To dry and concentrate all of the solvents, a D-LAB Rotavapor RE-100S was used. All of the supplied solvents such as MeOH, EtOAc, Hexane and HFIP were of analytical grade, and they were used without any prior purification. The chemicals and reagents used for the chemical reactions were purchased from Sigma-Aldrich Chemical Co., TCI Pvt. Ltd., Merck, Spectrochem, etc., and used without any purification prior to use.

2. General procedure

Synthesis of di(prop-2-yn-1-yl)phthalate [dpp] (1)

Phthalic acid (3 g, 1.80 mmol) and K_2CO_3 (9.98 g, 7.22 mmol) were combined in a 100 mL round bottom flask and 5-7 mL of dry CH_3CN was added to the reaction mixture. The reaction mixture was refluxed for one hour and propargyl bromide (8.59 g, 7.22 mmol) was added to the solution. The reaction mixture was continued to reflux and the progress of the reaction was monitored by TLC at regular intervals. On completion of the reaction (4 hours), acetonitrile was removed under a low pressure and 50 mL of water was added to the dried reaction mixture. The targeted compound was extracted from the reaction mixture using $CHCl_3$ and was dried over anhydrous Na_2SO_4. Evaporation of $CHCl_3$ gave the crude product, which was later purified by column chromatography using 3% ethyl acetate in hexane. An analytically pure brown viscous liquid was obtained as the final product.[1]

Synthesis of bis((1-(pyridin-2-ylmethyl)-1H-1,2,3-triazol-4-yl)methyl) phthalate [bpmtmp] (2a)

A 1:2 mixture of [dpp] (1) (0.242 g, 1.0 mmol) and 2-(azido methyl)pyridine (0.268 g, 2.0 mmol) in 5 mL of methanol was stirred at room temperature in the presence of 2 mol% $Cu(OAc)_2$. The progress of the reaction was followed using TLC. In 10 hours, the reaction was completed as observed in TLC. Methanol was removed from the reaction mixture under reduced pressure and the formed compound was purified by column chromatography using chloroform to get an analytically pure pale yellow viscous liquid. Yield : 0.311 g (61%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48-8.46 (m, 2H), 8.27 (s, 2H), 7.78-7.74 (m, 2H), 7.69 – 7.62 (m, 4H), 7.30 – 7.25 (m, 4H), 5.69 (s, 4H), 5.26 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.1, 155.4, 149.9, 141.9, 137.9, 132.4, 131.6, 129.4, 126.5, 123.8, 122.8, 59.1, 54.9. IR max υ (cm^{-1}): 3071 (w, N-N stretch.), 2958 (w, C_{sp}^3-H stretch.), 1718 (s, C=O stretch.), 1589 (m, C=C_{sp}^2 stretch.), 1438 (m, C_{sp}^3-H bend.), 1267 (s, C-N stretch.), 1119 (m, C-C_{sp}^3 stretch.), 755 (s, C=C_{sp}^2 bend.) HRMS (ES) m/z calcd for $C_{26}H_{22}N_8O_4$: 510.1764; found 510.7000.

Synthesis of bis((1-(pyridin-2-yl)-1H-1,2,3-triazol-5yl)methyl)phthalate [bptmp] (2b)

2-Azidopyridine (0.252 g, 2.1 mmol) and [dpp] (0.242 g, 1.0 mmol) were mixed in a 100 mL round bottom flask and the reaction mixture was charged under a nitrogen atmosphere. 5 mL of dry $CHCl_3$ was added to the reaction mixture to obtain a heterogeneous solution. The reaction mixture was allowed to stir for 10 minutes, and then CuBr (0.029 g, 0.2 mmol) and DIPEA (0.259 g, 2.0 mmol) were added to the reaction mixture under a nitrogen flow. Additionally, the reaction mixture was refluxed for 16 hours under a nitrogen atmosphere. The solvent was removed under reduced pressure and the formed compound was purified by column chromatography using 5% MeOH in $CHCl_3$ to get an analytically pure off-white solid.[1]

Synthesis of [$PdCl_2$(bpmtmp)] (3a)

Solid [bpmtmp] (2a) (0.510 g, 1.0 mmol) was mixed with solid [$PdCl_2(CH_3CN)_2$] (0.259 g, 1.0 mmol) in a 10 mL round bottom flask and 2 mL of dry $CHCl_3$ was added to the reaction mixture at reflux. In 30 minutes, the reaction mixture solution turned into a turbid pale-yellow solution. The reaction mixture was allowed to stir for additional 10 hours at reflux. On completion of the reaction, the yellowish solid was separated using Whatman's filter paper and was washed with chloroform to remove the excess ligand from the product. A pale-yellow solid was obtained as an analytically pure compound. Dichloromethane was allowed to diffuse into a saturated solution of complex 3a in dimethyl-sulfoxide. Single crystals suitable for X-ray diffraction were obtained within 10 days. Yield : 0.487 g (71%). Mp: 342-345 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.52 – 8.51 (m, 2H), 8.32 (s, 2H), 7.82-7.78 (m, 2H), 7.74 – 7.71 (m, 2H), 7.68 – 7.66 (m, 2H), 7.34 – 7.29 (m, 4H), 5.74 (s, 4H), 5.31 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.0, 154.2, 148.5, 142.0, 140.0, 132.4, 131.6, 129.4, 126.6, 124.6, 123.7, 59.0, 53.9. IR max υ(cm^{-1}): 3077 (w, N-N stretch.), 1719 (s, C=O stretch.), 1606 (m, C=C_{sp}^2 stretch.), 1442 (m, C_{sp}^3-H bend.), 1273 (s, C-N stretch.), 1119 (m, C-C_{sp}^3 stretch.), 767 (s, C=C_{sp}^2 bend.) HR-MS (ESI) m/z calcd for $C_{26}H_{22}Cl_2N_8O_4Pd + H^+$ $[M+H]^+$ 688.8413, found 688.6000. Anal. calcd for $C_{26}H_{22}Cl_2N_8O_4Pd$: C, 45.40; H, 3.22; N, 16.29. Found: C, 44.98; H, 3.10; N, 15.92.

Synthesis of [$PdCl_2$(bptmp)] (3b)

Solid [bptmp] (2b) (0.482 g, 1.0 mmol) was mixed with solid [$PdCl_2(CH_3CN)_2$] (0.259 g, 1.0 mmol) in a 10 mL round bottom flask and 2 mL of dry $CHCl_3$ was added to the reaction mixture at room temperature to get a clear red-wine solution. In 30 minutes, the clear red-wine solution turned into a turbid pale-yellow solution. The reaction mixture was allowed to stir for additional 10 hours at room temperature. On completion of the reaction, the yellowish solid was separated

using Whatman's filter paper and was washed with chloroform to remove the excess ligand from the product. A pale-yellow solid was obtained as an analytically pure compound. Dichloromethane was allowed to diffuse into a saturated solution of complex 3b in dimethyl-sulfoxide. Single crystals suitable for X-ray diffraction were obtained in 1 day.[1]

3. X-ray structure determination

A crystal was mounted on the goniometer. Data for complex **3a** were collected from a single crystal in n/a hours at 296(2) K on a Bruker APEX-II CCD diffractometer. The diffractometer used MoK_α radiation (λ = 0.71073 Å). All data were integrated with, yielding 51325 reflections of which 7540 where independent and 85.4% were greater than 2σ(F^2). A multi-scan absorption correction using was applied. The structure was solved with SHELXT 2018/2 and refined by full-matrix least-squares methods against F^2 using SHELXL-2019/2.[2,3] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[4]
CCDC : 2477385, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using Final Cif of complex **3a** (https://dkratzert.de/finalcif.html).

4. Structural data for complex 3a

4.1 Table S1. Crystal data and structure refinement for complex 3a

CCDC number	2477385
Empirical formula	$C_{28}H_{23}Cl_2N_9O_4Pd$
Formula weight	726.85
Temperature [K]	296(2)
Crystal system	monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	8.1522(2)
b [Å]	23.0108(6)
c [Å]	16.0988(4)
α [°]	90
β [°]	91.1220(10)
γ [°]	90
Volume [Å^3]	3019.37(13)
Z	4
ρ_{calc} [gcm^{-3}]	1.599
μ [mm^{-1}]	0.842
F(000)	1464

Crystal size [mm^3]	0.22×0.08×0.08
Crystal colour	brown
Crystal shape	needle
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.35 to 56.72 (0.75 Å)
Index ranges	−10 ≤ h ≤ 10 −30 ≤ k ≤ 30 −19 ≤ l ≤ 21
Reflections collected	51325
Independent reflections	7540 R_{int} = 0.0538 R_{sigma} = 0.0354
Completeness to θ = 25.242°	99.9
Data / Restraints / Parameters	7540 / 552 / 516
Goodness-of-fit on F^2	1.074
Final R indexes [I≥2σ(I)]	R_1 = 0.0398 wR_2 = 0.0887
Final R indexes [all data]	R_1 = 0.0498 wR_2 = 0.0932
Largest peak/hole [eÅ^{-3}]	0.95/−0.80

4.2 Table S2. Bond lengths and angles (Å) for complex **3a**

Atom–Atom	**Length [Å]**
Pd1–N4	2.007(2)
Pd1–N3	2.022(2)
Pd1–Cl1	2.2857(8)
Pd1–Cl2	2.2882(8)
O1–C13	1.348(3)
O1–C12	1.453(3)
O2–C28	1.348(3)
O2–C27	1.457(3)
O3–C28	1.197(3)
O4–C13	1.199(4)
N1–N2	1.342(3)

N1–C9	1.350(4)
N1–C6	1.427(12)
N1–C6'	1.532(12)
N2–N3	1.310(3)
N3–C8	1.361(3)
N4–N5	1.321(3)
N4–C11	1.360(3)
N5–N6	1.336(3)
N6–C10	1.341(4)
N6–C20	1.467(4)
N7–C30	1.136(5)
N9–C5	1.312(16)
N9–C1	1.341(15)
C1–C2	1.391(11)
C1–C6	1.516(12)
C2–C3	1.382(9)
C3–C4	1.380(9)
C4–C5	1.422(17)
N9'–C1'	1.386(12)
N9'–C3'	1.401(9)
C1'–C2'	1.30(2)
C1'–C6'	1.505(13)
C2'–C5'	1.309(19)
C3'–C4'	1.353(11)
C4'–C5'	1.327(19)
C8–C9	1.370(4)
C8–C12	1.484(4)
C10–C11	1.371(4)
C11–C27	1.488(4)

C13–C14	1.491(4)
C14–C19	1.391(4)
C14–C15	1.403(4)
C15–C16	1.387(4)
C15–C28	1.500(4)
C16–C17	1.392(4)
C17–C18	1.381(4)
C18–C19	1.387(4)
C20–C21	1.48(3)
C20–C21'	1.56(4)
N8–C21	1.32(4)
N8–C23	1.392(9)
C21–C25	1.46(3)
C22–C25	1.345(8)
C22–C24	1.547(19)
C23–C24	1.151(18)
N8'–C21'	1.20(5)
N8'–C22'	1.325(9)
C21'–C25'	1.44(5)
C22'–C24'	1.31(3)
C23'–C25'	1.400(10)
C23'–C24'	1.53(2)
C29–C30	1.445(5)
Atom–Atom–Atom	**Angle [°]**
N4–Pd1–N3	176.08(9)
N4–Pd1–Cl1	88.58(7)
N3–Pd1–Cl1	89.77(7)
N4–Pd1–Cl2	89.78(7)

N3–Pd1–Cl2	91.93(7)
Cl1–Pd1–Cl2	178.09(3)
C13–O1–C12	115.1(2)
C28–O2–C27	116.7(2)
N2–N1–C9	111.9(2)
N2–N1–C6	123.3(5)
C9–N1–C6	124.7(5)
N2–N1–C6'	116.6(5)
C9–N1–C6'	130.2(5)
N3–N2–N1	105.3(2)
N2–N3–C8	111.2(2)
N2–N3–Pd1	119.17(18)
C8–N3–Pd1	129.54(19)
N5–N4–C11	111.2(2)
N5–N4–Pd1	116.92(18)
C11–N4–Pd1	131.78(19)
N4–N5–N6	104.9(2)
N5–N6–C10	112.3(2)
N5–N6–C20	118.6(2)
C10–N6–C20	129.0(2)
C5–N9–C1	118.9(10)
N9–C1–C2	122.2(8)
N9–C1–C6	116.6(8)
C2–C1–C6	120.7(8)
C3–C2–C1	119.3(6)
C4–C3–C2	118.5(6)
C3–C4–C5	118.6(8)
N9–C5–C4	122.3(13)
N1–C6–C1	109.1(8)

C1'–N9'–C3'	116.5(7)
C2'–C1'–N9'	121.0(9)
C2'–C1'–C6'	118.6(10)
N9'–C1'–C6'	120.3(8)
C1'–C2'–C5'	120.2(13)
C4'–C3'–N9'	120.6(7)
C5'–C4'–C3'	117.6(10)
C2'–C5'–C4'	124.0(16)
C1'–C6'–N1	112.9(9)
N3–C8–C9	106.7(2)
N3–C8–C12	123.4(2)
C9–C8–C12	129.9(3)
N1–C9–C8	104.9(2)
N6–C10–C11	105.4(2)
N4–C11–C10	106.2(2)
N4–C11–C27	124.1(2)
C10–C11–C27	129.7(3)
O1–C12–C8	107.9(2)
O4–C13–O1	124.3(3)
O4–C13–C14	123.3(3)
O1–C13–C14	112.5(2)
C19–C14–C15	119.8(3)
C19–C14–C13	121.2(3)
C15–C14–C13	118.8(3)
C16–C15–C14	119.6(3)
C16–C15–C28	119.2(2)
C14–C15–C28	121.1(2)
C15–C16–C17	119.8(3)
C18–C17–C16	120.8(3)

C17–C18–C19	119.6(3)
C18–C19–C14	120.3(3)
N6–C20–C21	113.6(15)
N6–C20–C21'	109.7(17)
C21–N8–C23	123.4(14)
N8–C21–C25	117(2)
N8–C21–C20	125(2)
C25–C21–C20	117(3)
C25–C22–C24	117.6(9)
C24–C23–N8	122.8(12)
C23–C24–C22	120.6(18)
C22–C25–C21	118.0(15)
C21'–N8'–C22'	117(2)
N8'–C21'–C25'	128(3)
N8'–C21'–C20	121(4)
C25'–C21'–C20	111(3)
C24'–C22'–N8'	129.0(13)
C25'–C23'–C24'	117.8(11)
C22'–C24'–C23'	112.1(17)
C23'–C25'–C21'	113.5(17)
O2–C27–C11	106.8(2)
O3–C28–O2	125.1(3)
O3–C28–C15	125.9(3)
O2–C28–C15	109.0(2)
N7–C30–C29	179.1(4)

4.3 Table S3. Atomic coordinates and Ueq [Å^2] for complex **3a**

Atom	***x***	***y***	***z***	U_{eq}
Pd1	0.23108(2)	0.62107(2)	0.44552(2)	0.01227(6)

Cl1	0.34725(9)	0.62809(5)	0.31784(5)	0.0339(2)
Cl2	0.12196(9)	0.61577(4)	0.57517(5)	0.02676(17)
O1	−0.0177(2)	0.74513(9)	0.40605(13)	0.0202(4)
O2	0.4161(2)	0.75022(8)	0.50092(12)	0.0160(4)
O3	0.5304(3)	0.83923(9)	0.48909(13)	0.0209(4)
O4	0.2157(3)	0.78941(9)	0.36824(13)	0.0246(5)
N1	−0.2084(3)	0.57217(11)	0.34729(15)	0.0174(5)
N2	−0.0705(3)	0.56430(11)	0.39282(16)	0.0191(5)
N3	0.0071(3)	0.61411(10)	0.39019(15)	0.0148(5)
N4	0.4573(3)	0.62277(10)	0.49684(14)	0.0146(4)
N5	0.5092(3)	0.57476(10)	0.53386(15)	0.0166(5)
N6	0.6635(3)	0.58624(11)	0.55802(15)	0.0167(5)
N7	0.6483(5)	0.77294(18)	0.6876(2)	0.0537(10)
N9	−0.3613(18)	0.5469(5)	0.1895(8)	0.0110(17)
C1	−0.3358(10)	0.5070(4)	0.2492(6)	0.0163(15)
C2	−0.3314(8)	0.4478(2)	0.2322(4)	0.0230(12)
H2	−0.321971	0.420976	0.275280	0.028
C3	−0.3411(9)	0.4292(3)	0.1506(4)	0.0298(13)
H3	−0.337243	0.389826	0.137776	0.036
C4	−0.3565(10)	0.4704(3)	0.0887(4)	0.0261(13)
H4	−0.359694	0.459460	0.033038	0.031
C5	−0.368(2)	0.5299(8)	0.1117(10)	0.019(2)
H5	−0.379622	0.557780	0.070175	0.023
C6	−0.3329(14)	0.5289(5)	0.3380(7)	0.0150(18)
H6A	−0.438830	0.545354	0.351288	0.018
H6B	−0.310708	0.496947	0.375868	0.018
N9'	−0.2191(9)	0.4504(3)	0.2107(4)	0.0340(13)
C1'	−0.2951(12)	0.5016(5)	0.2340(6)	0.0153(16)
C2'	−0.351(3)	0.5383(7)	0.1784(11)	0.015(2)
H2'	−0.392236	0.574006	0.194999	0.019
C3'	−0.2128(10)	0.4394(3)	0.1253(4)	0.0293(14)
H3'	−0.161708	0.405843	0.106464	0.035
C4'	−0.2804(11)	0.4770(3)	0.0698(5)	0.0259(14)
H4'	−0.279575	0.469501	0.013092	0.031
C5'	−0.348(2)	0.5250(9)	0.0994(10)	0.020(2)
H5'	−0.396233	0.550764	0.061767	0.024
C6'	−0.3065(15)	0.5175(5)	0.3245(8)	0.0131(19)
H6'A	−0.266367	0.485252	0.357956	0.016
H6'B	−0.420775	0.523675	0.337671	0.016
C8	−0.0786(3)	0.65379(12)	0.34412(17)	0.0136(5)
C9	−0.2189(3)	0.62664(12)	0.31643(17)	0.0156(5)
H9	−0.302951	0.642292	0.283567	0.019
C10	0.7088(3)	0.64051(13)	0.53871(17)	0.0164(5)
H10	0.809235	0.658190	0.550353	0.020
C11	0.5757(3)	0.66443(12)	0.49817(16)	0.0140(5)
C12	−0.0187(4)	0.71352(12)	0.32790(18)	0.0187(6)
H12A	0.091100	0.712162	0.305817	0.022
H12B	−0.090193	0.732722	0.287608	0.022
C13	0.1108(4)	0.78122(12)	0.41810(18)	0.0173(6)
C14	0.1063(3)	0.81144(12)	0.49996(18)	0.0158(5)

C15	0.2548(3)	0.82885(11)	0.53785(17)	0.0138(5)
C16	0.2524(4)	0.86266(13)	0.60917(18)	0.0188(6)
H16	0.350302	0.875008	0.634024	0.023
C17	0.1031(4)	0.87806(14)	0.64340(19)	0.0222(6)
H17	0.101888	0.900603	0.691330	0.027
C18	−0.0434(4)	0.86027(13)	0.60708(19)	0.0217(6)
H18	−0.142505	0.870538	0.630655	0.026
C19	−0.0418(4)	0.82700(13)	0.5352(2)	0.0213(6)
H19	−0.140167	0.815041	0.510542	0.026
C20	0.7549(4)	0.54190(13)	0.60525(19)	0.0204(6)
H20A	0.864853	0.539166	0.583671	0.031
H20B	0.701907	0.504566	0.596763	0.031
N8	0.7741(8)	0.5140(3)	0.7541(4)	0.0363(12)
C21	0.766(6)	0.5539(14)	0.695(2)	0.020(2)
C22	0.7522(9)	0.6258(3)	0.8032(4)	0.0307(13)
H22	0.743669	0.663606	0.822884	0.037
C23	0.7808(10)	0.5270(3)	0.8385(4)	0.0328(13)
H23	0.793197	0.496704	0.876292	0.039
C24	0.772(3)	0.5738(6)	0.8635(14)	0.030(2)
H24	0.775863	0.580307	0.920519	0.036
C25	0.7482(7)	0.6143(2)	0.7213(3)	0.0193(11)
H25	0.734330	0.643882	0.682472	0.023
N8'	0.6337(7)	0.5805(3)	0.7287(3)	0.0264(12)
C21'	0.750(6)	0.5564(16)	0.700(2)	0.021(2)
C22'	0.6392(10)	0.5911(3)	0.8096(4)	0.0310(14)
H22'	0.543122	0.605716	0.831752	0.037
C23'	0.8924(10)	0.5434(4)	0.8292(4)	0.0319(14)
H23'	0.971183	0.526805	0.864421	0.038
C24'	0.761(3)	0.5840(7)	0.8626(16)	0.029(2)
H24'	0.767448	0.601587	0.914611	0.035
C25'	0.8902(9)	0.5319(3)	0.7438(4)	0.0255(13)
H25'	0.971232	0.510547	0.717648	0.031
C27	0.5554(3)	0.72319(12)	0.46074(19)	0.0174(6)
C28	0.4164(3)	0.80873(12)	0.50539(17)	0.0152(5)
C29	0.3976(5)	0.70466(17)	0.6930(2)	0.0365(8)
H29A	0.343162	0.709404	0.744953	0.055
H29B	0.433710	0.665154	0.687710	0.055
H29C	0.322890	0.713895	0.648129	0.055
C30	0.5375(5)	0.74309(16)	0.6906(2)	0.0325(8)

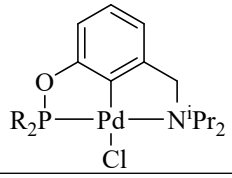
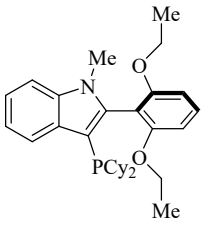
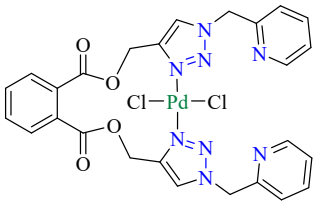
4.4 Table S4. Anisotropic displacement parameters (Å^2) for complex **3a**. The anisotropic displacement factor exponent takes the form:
$-2\pi^2[\, h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\,]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	0.00985(10)	0.01361(10)	0.01327(10)	0.00015(8)	−0.00187(7)	−0.00003(8)
Cl1	0.0145(3)	0.0725(6)	0.0148(3)	−0.0044(4)	0.0002(3)	−0.0004(4)
Cl2	0.0135(3)	0.0496(5)	0.0171(3)	0.0066(3)	−0.0008(3)	−0.0048(3)
O1	0.0160(10)	0.0196(10)	0.0250(11)	−0.0097(8)	−0.0029(8)	−0.0024(8)
O2	0.0124(9)	0.0148(9)	0.0208(10)	−0.0014(8)	0.0042(8)	0.0001(7)

O3	0.0179(10)	0.0197(10)	0.0251(11)	−0.0029(9)	0.0025(9)	−0.0062(8)
O4	0.0329(12)	0.0246(11)	0.0162(10)	−0.0034(8)	0.0008(9)	−0.0121(10)
N1	0.0151(11)	0.0222(12)	0.0146(12)	0.0021(9)	−0.0042(9)	−0.0065(10)
N2	0.0192(12)	0.0190(12)	0.0188(12)	0.0034(10)	−0.0057(10)	−0.0040(10)
N3	0.0119(11)	0.0163(11)	0.0162(11)	−0.0020(9)	−0.0014(9)	−0.0002(9)
N4	0.0110(10)	0.0179(11)	0.0150(11)	0.0007(9)	0.0001(9)	0.0012(9)
N5	0.0130(11)	0.0201(12)	0.0166(12)	0.0010(9)	−0.0014(9)	0.0037(9)
N6	0.0117(11)	0.0239(13)	0.0146(11)	0.0011(9)	0.0001(9)	0.0039(9)
N7	0.049(2)	0.060(2)	0.051(2)	−0.0077(19)	−0.0174(18)	−0.0188(19)
N9	0.017(2)	0.006(3)	0.010(3)	−0.003(2)	0.003(2)	0.005(2)
C1	0.019(3)	0.013(3)	0.017(3)	−0.004(2)	−0.002(2)	−0.002(2)
C2	0.028(3)	0.017(2)	0.024(3)	−0.002(2)	−0.004(2)	0.000(2)
C3	0.041(3)	0.019(2)	0.029(3)	−0.006(2)	−0.012(2)	0.002(2)
C4	0.033(3)	0.026(3)	0.019(3)	−0.009(2)	−0.004(2)	0.002(3)
C5	0.023(3)	0.016(3)	0.020(4)	−0.003(3)	0.004(3)	0.003(3)
C6	0.019(4)	0.013(4)	0.013(4)	−0.003(3)	0.001(3)	−0.005(3)
N9'	0.040(3)	0.028(3)	0.034(3)	−0.003(2)	−0.007(3)	0.001(2)
C1'	0.020(3)	0.012(3)	0.013(3)	−0.004(2)	0.000(3)	−0.003(3)
C2'	0.024(3)	0.009(4)	0.014(4)	−0.004(3)	0.006(3)	0.003(3)
C3'	0.042(3)	0.019(3)	0.027(3)	−0.009(2)	−0.004(3)	0.009(3)
C4'	0.032(3)	0.025(3)	0.021(3)	−0.007(2)	0.001(3)	−0.003(3)
C5'	0.028(4)	0.020(4)	0.012(4)	−0.005(3)	0.000(3)	0.000(3)
C6'	0.014(4)	0.010(4)	0.016(4)	−0.004(3)	0.001(3)	−0.004(3)
C8	0.0112(12)	0.0152(13)	0.0143(13)	−0.0024(10)	0.0000(10)	0.0013(10)
C9	0.0139(13)	0.0191(14)	0.0137(13)	−0.0013(10)	−0.0002(10)	0.0014(11)
C10	0.0100(12)	0.0239(14)	0.0152(13)	−0.0017(11)	0.0017(10)	0.0017(11)
C11	0.0106(12)	0.0202(13)	0.0111(12)	−0.0028(10)	0.0008(10)	0.0010(10)
C12	0.0240(15)	0.0166(13)	0.0152(14)	−0.0019(11)	−0.0076(11)	−0.0019(11)
C13	0.0194(14)	0.0112(12)	0.0211(15)	−0.0012(10)	−0.0051(12)	0.0007(10)
C14	0.0184(14)	0.0118(12)	0.0170(13)	−0.0005(10)	−0.0021(11)	−0.0009(10)
C15	0.0160(13)	0.0117(12)	0.0137(13)	0.0010(9)	−0.0007(10)	−0.0012(10)
C16	0.0183(14)	0.0215(14)	0.0164(13)	−0.0020(11)	−0.0035(11)	−0.0014(11)
C17	0.0269(16)	0.0240(15)	0.0156(14)	−0.0038(12)	−0.0001(12)	0.0053(13)
C18	0.0195(14)	0.0223(14)	0.0236(15)	0.0001(12)	0.0041(12)	0.0047(12)
C19	0.0146(13)	0.0186(14)	0.0307(17)	−0.0046(12)	−0.0032(12)	0.0021(11)
C20	0.0167(14)	0.0257(15)	0.0188(14)	0.0033(12)	−0.0010(11)	0.0063(12)
N8	0.043(3)	0.036(3)	0.030(2)	0.001(2)	−0.001(2)	0.006(2)
C21	0.018(3)	0.024(4)	0.018(4)	0.001(3)	0.000(3)	0.004(3)
C22	0.042(3)	0.026(3)	0.024(3)	−0.004(2)	−0.001(2)	0.004(2)
C23	0.044(3)	0.031(3)	0.023(2)	0.006(2)	−0.003(2)	0.007(2)
C24	0.038(4)	0.034(4)	0.018(3)	0.002(4)	−0.004(3)	0.005(4)
C25	0.029(2)	0.015(2)	0.013(2)	0.0009(18)	−0.001(2)	0.002(2)
N8'	0.026(2)	0.037(3)	0.016(2)	−0.004(2)	0.000(2)	0.011(2)
C21'	0.019(3)	0.027(4)	0.016(4)	0.002(3)	0.002(3)	0.003(4)
C22'	0.033(3)	0.037(3)	0.022(3)	−0.003(2)	0.000(2)	0.005(3)
C23'	0.033(3)	0.041(3)	0.021(3)	0.000(2)	−0.012(3)	0.011(3)
C24'	0.035(4)	0.031(4)	0.020(3)	−0.004(4)	−0.001(3)	0.008(4)
C25'	0.021(3)	0.035(3)	0.020(3)	−0.001(2)	0.000(2)	0.011(2)
C27	0.0118(12)	0.0191(14)	0.0214(14)	−0.0003(11)	0.0050(11)	0.0031(10)
C28	0.0163(13)	0.0163(13)	0.0128(13)	−0.0003(10)	−0.0020(10)	−0.0018(10)
C29	0.042(2)	0.041(2)	0.0272(18)	0.0007(15)	0.0094(16)	−0.0078(17)
C30	0.038(2)	0.038(2)	0.0214(17)	−0.0087(14)	−0.0055(14)	−0.0005(16)

5. Comparison table with previous work

Table S5:

Catalyst	Reaction conditions	References
$Ni(OAc)_2$ 2,2́-bipyridine	[catalyst: $Ni(OAc)_2$ (10 mol%), bipy (10 mol%), base: LiO^tBu, solvent: 1,4-dioxane, time: 36 h, 85 °C]	5
	[catalyst: 0.5 mol%, base: Cs_2CO_3, solvent: DMF, additive: CuI (5 mol%), time: 16 h, 120 °C]	6
$Pd(OAc)_2$	[catalyst: $Pd(OAc)_2$ (1.0 mol%), Ag_2O (1.0 equiv.), base: NaOAc, solvent: HFIP, time: 12 h, N_2 atmosphere, rt]	7
$Pd_2(dba)_3$ $Phen.H_2O$	[catalyst: $Pd_2(dba)_3$ (2.5 mol%), $Phen.H_2O$, PPh_3 base: K_3PO_4, solvent: DMF, time: 4 h, N_2 atmosphere, 100-140 °C]	8
2,4,6-tris(5-formyl-2-pyridinoxy)-1,3,5-triazine (TFPT) benzidine (BZ) co-valent organic frame-work (COF)/Pd	[catalyst: TFPT-BZ COF/Pd (40 mg), base: K_2CO_3, solvent: 2-Me THF, time: 5-6 h, reflux]	9
$Pd(OAc)_2$  (PCy_2-Man-phos)	[catalyst: $Pd(OAc)_2$ (2.0 mol%), PCy_2-Man-phos (8.0 mol%), base: LiO^tBu , solvent: THF, time: 24 h, 110 °C]	10
	• New Pd(II)-complex of N-bound triazolyl-pyridine ligand • Low catalyst loading (0.25 mol%) • No, phosphorus-based additive • Lower reaction time • Room temperature	Our work

6. **Spectral data for ligand and complexes**

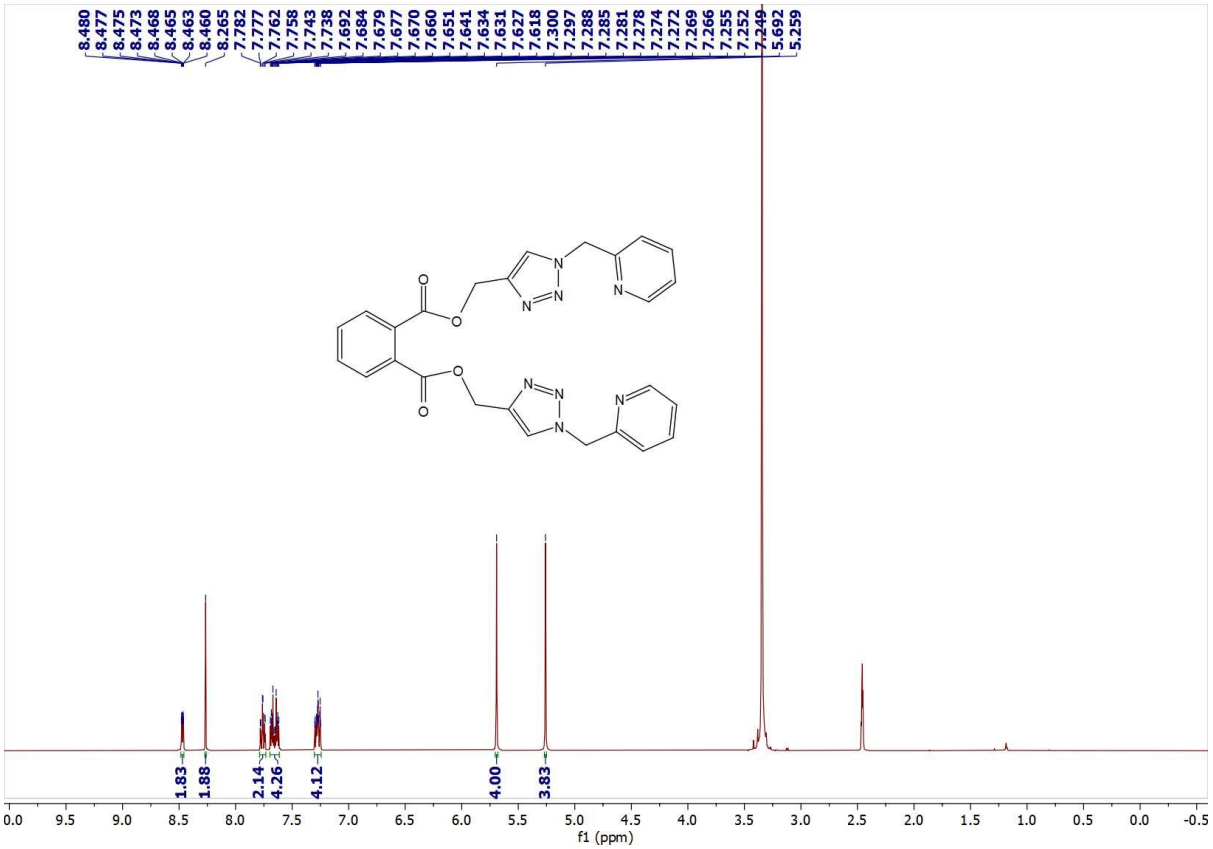


Fig. S1 ^{1}H-NMR Spectrum of [bpmtmp] **2a**

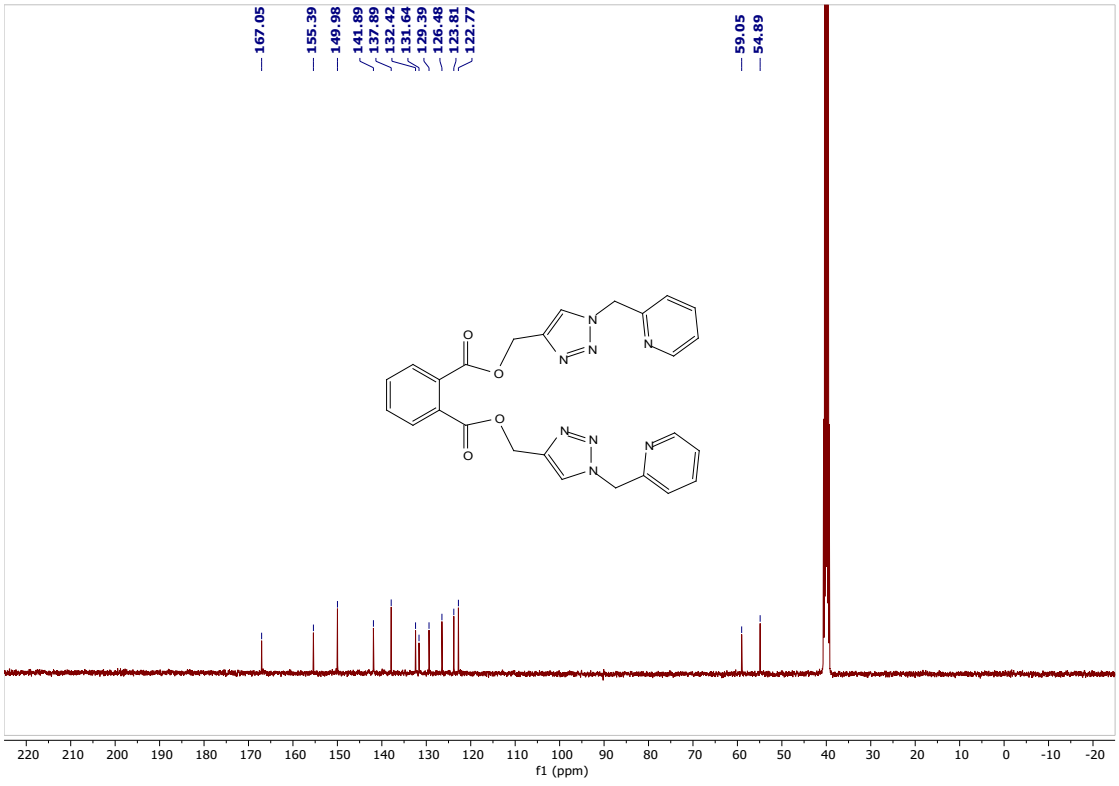


Fig. S2 ^{13}C-NMR Spectrum of [bpmtmp] **2a**

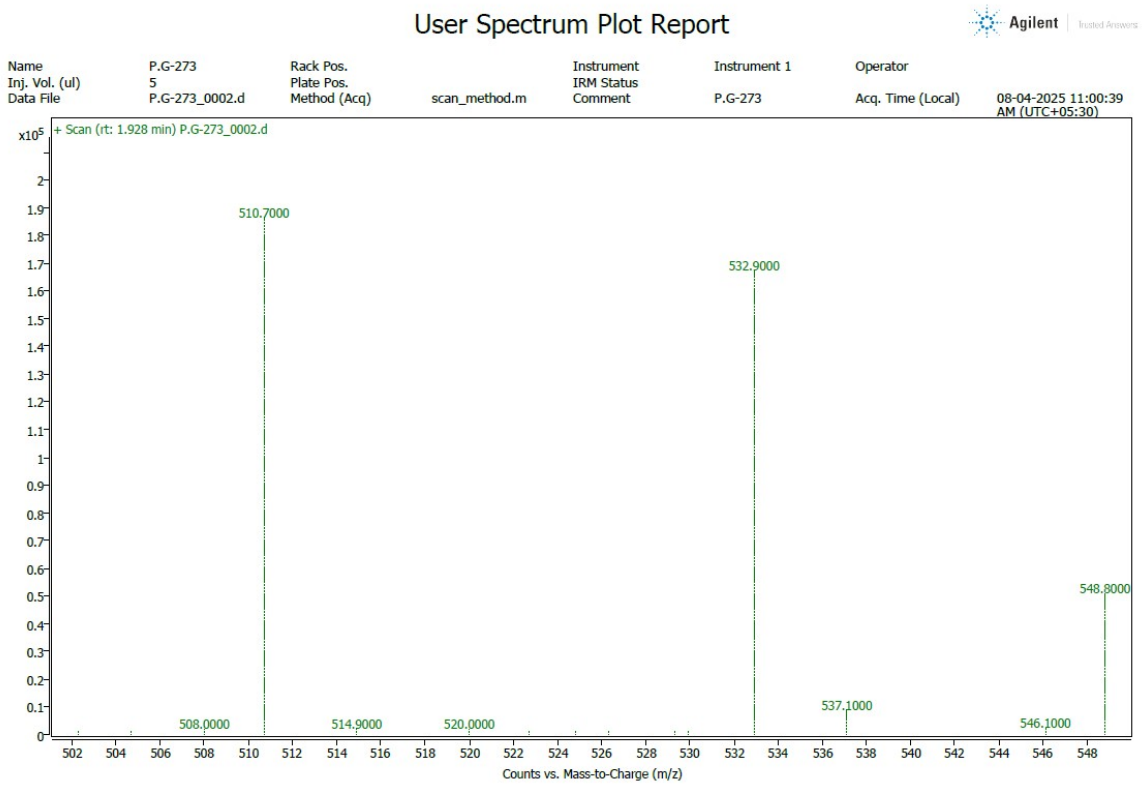


Fig. S3 ESI-MS spectra of [bpmtmp] **2a**

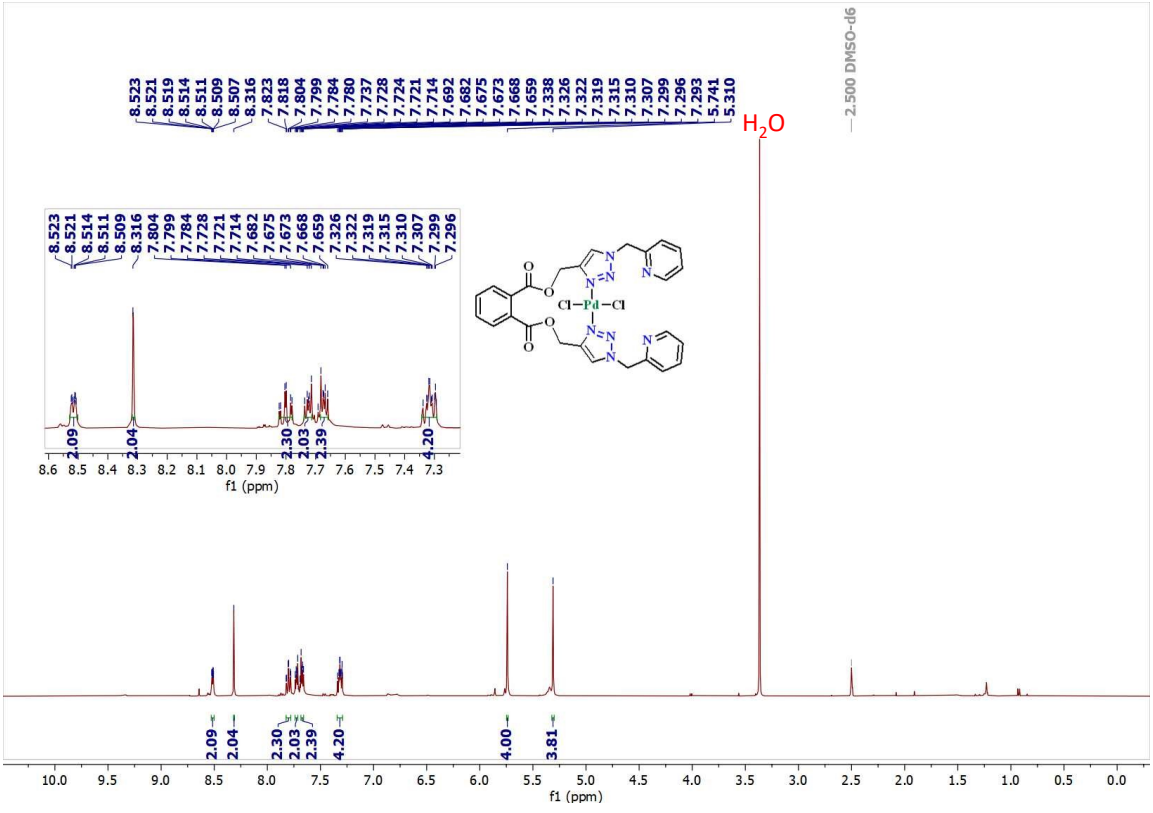


Fig. S4 ^{1}H-NMR Spectrum of [$PdCl_2$(bpmtmp)] **3a**

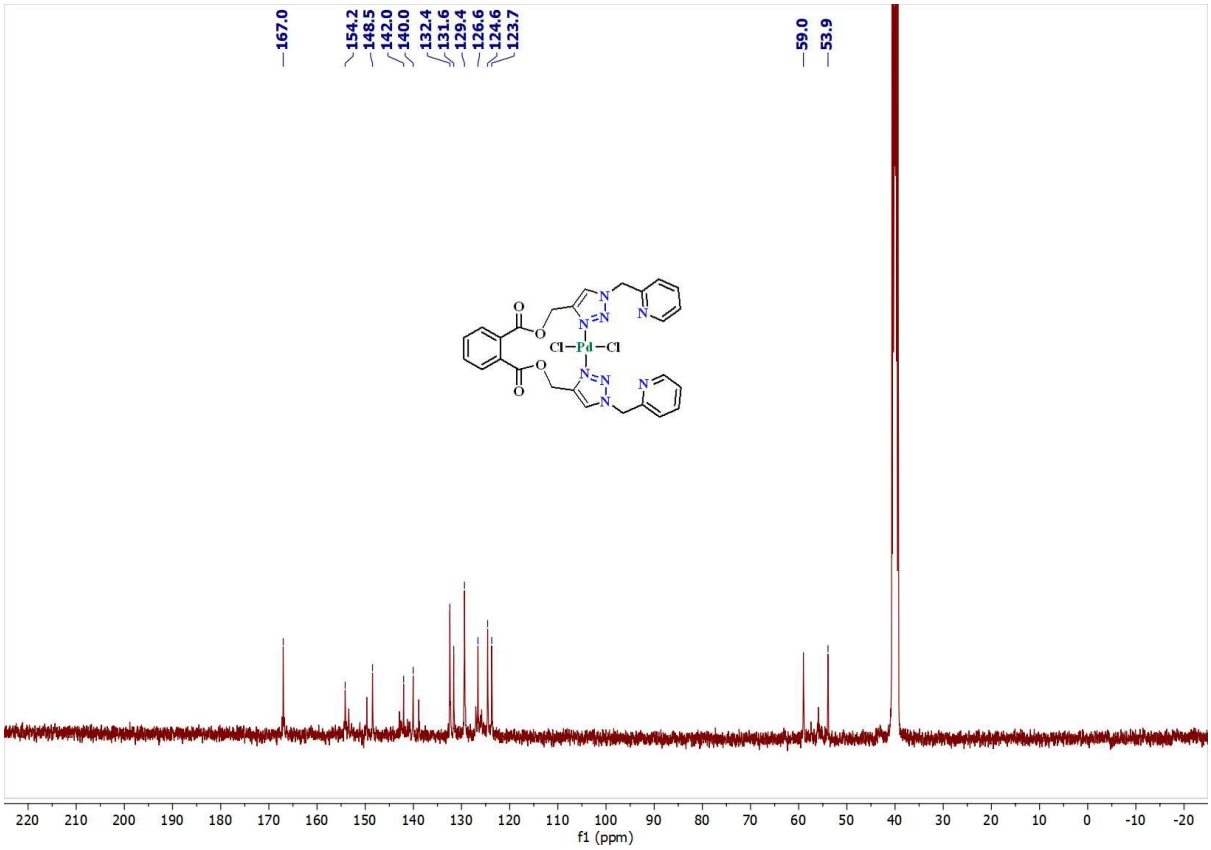


Fig. S5 ^{13}C-NMR Spectrum of [$PdCl_2$(bpmtmp)] **3a**

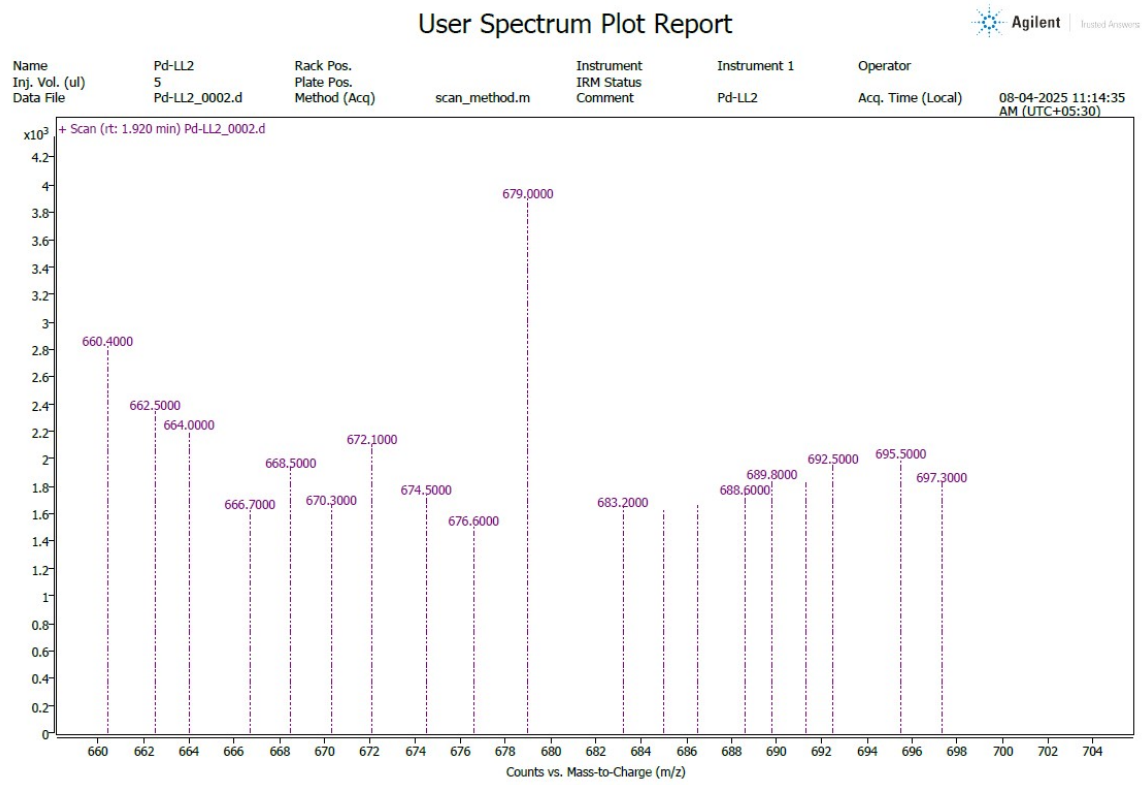


Fig. S6 ESI-MS spectra of [$PdCl_2$(bpmtmp)] **3a**

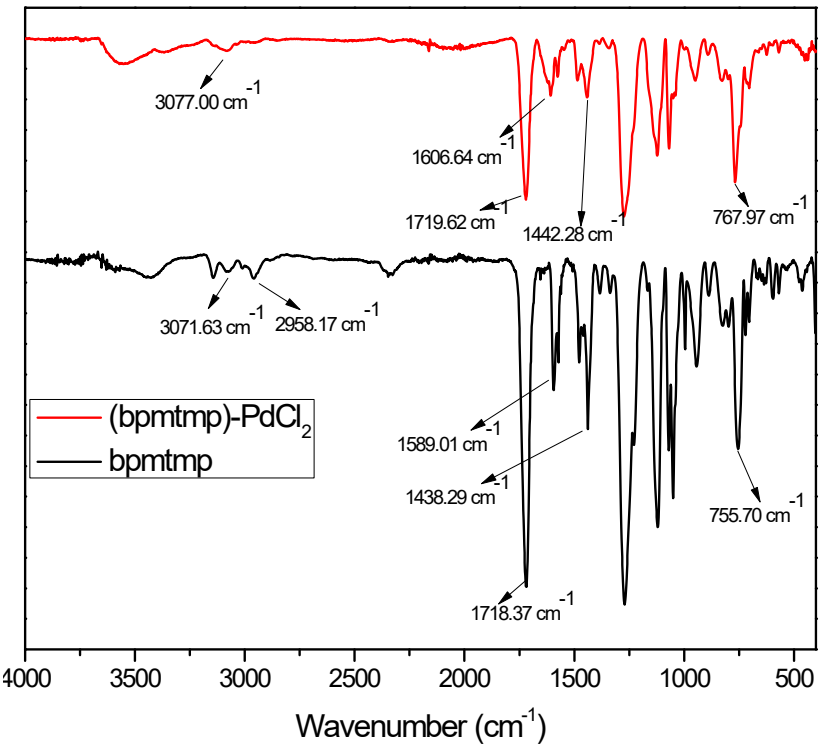


Fig. S7 FT-IR spectra of [$PdCl_2$(bpmtmp)] **3a** and bpmtmp **(2a)**

Graphic report

	ht [mg]	Name	N [%]	C [%]	H [%]	S [%]	Date Time
25	1.9590	PdCl2	15.92	44.98	3.108	0.000	30.04.2025 15:16

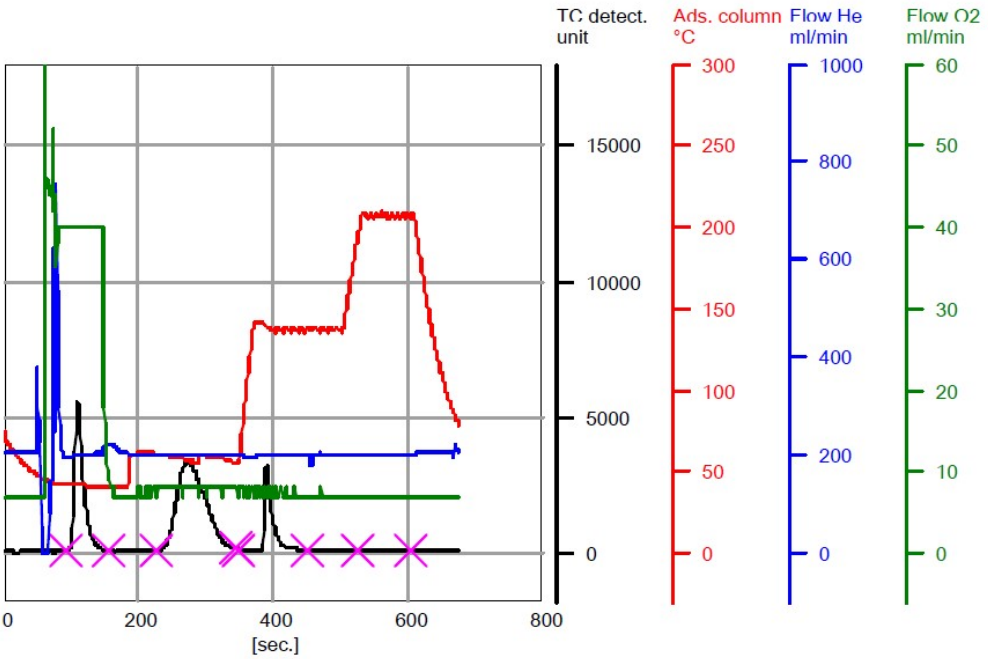


Fig. S8 Elemental analysis of [$PdCl_2$(bpmtmp)] **3a**

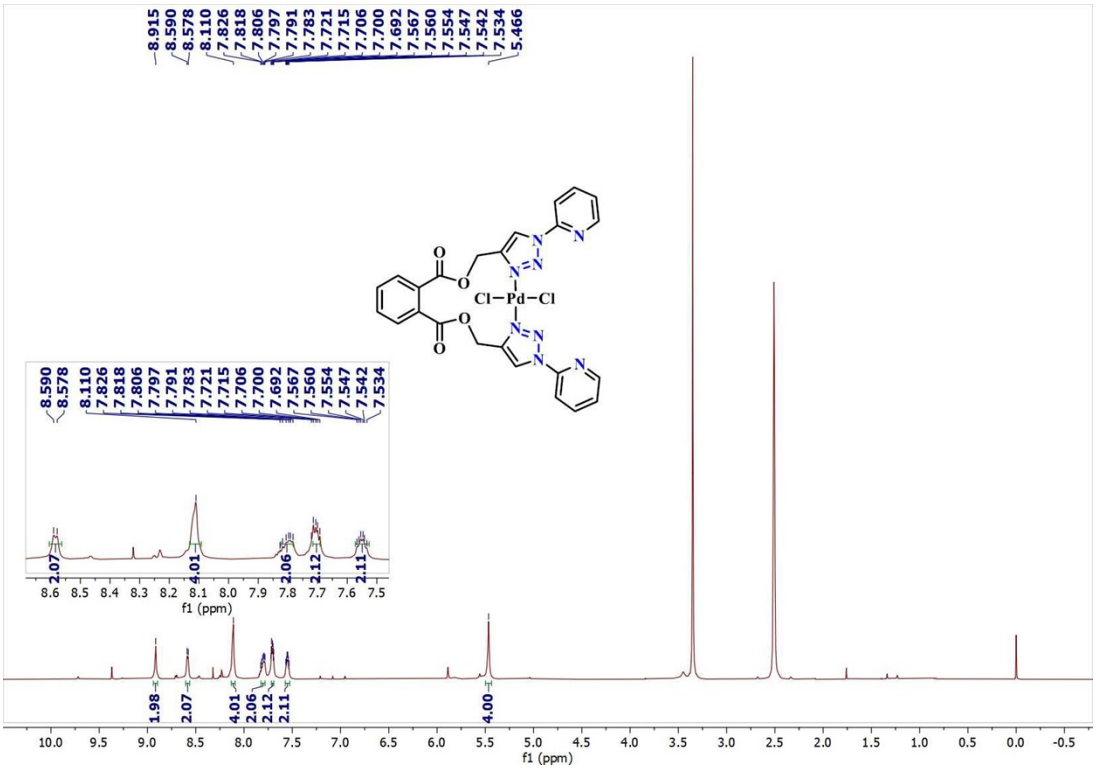


Fig. S9 ^{1}H-NMR Spectrum of [$PdCl_2$(bptmp)] **3b**

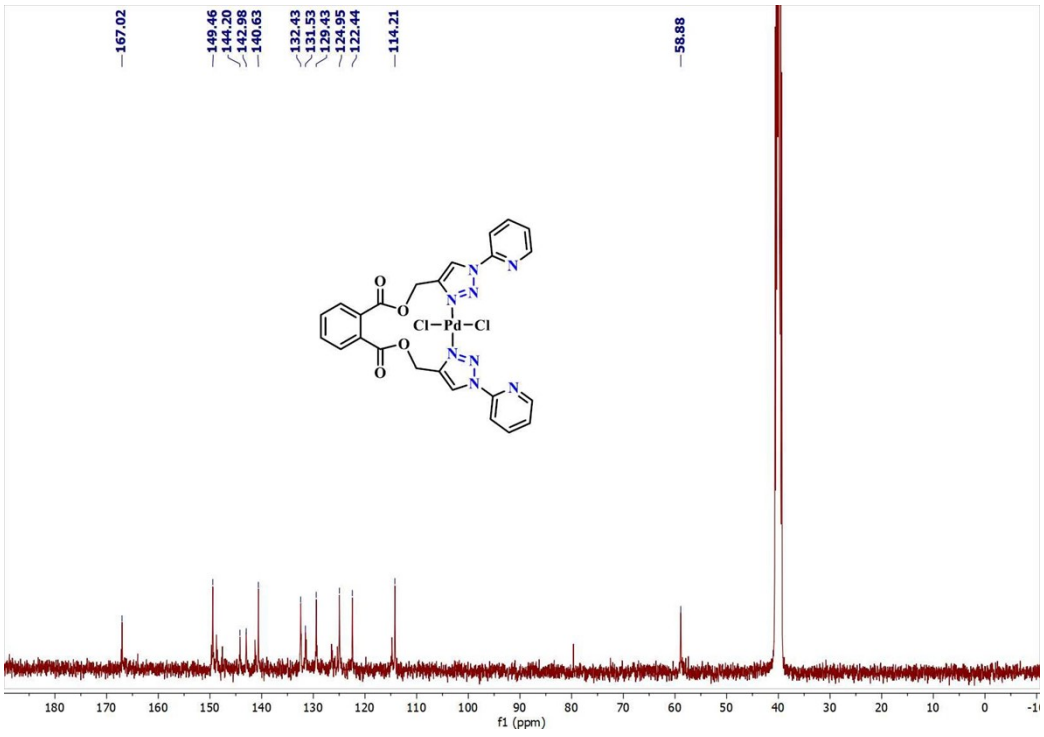


Fig. S10 ^{13}C-NMR Spectrum of [$PdCl_2$(bptmp)] **3b**

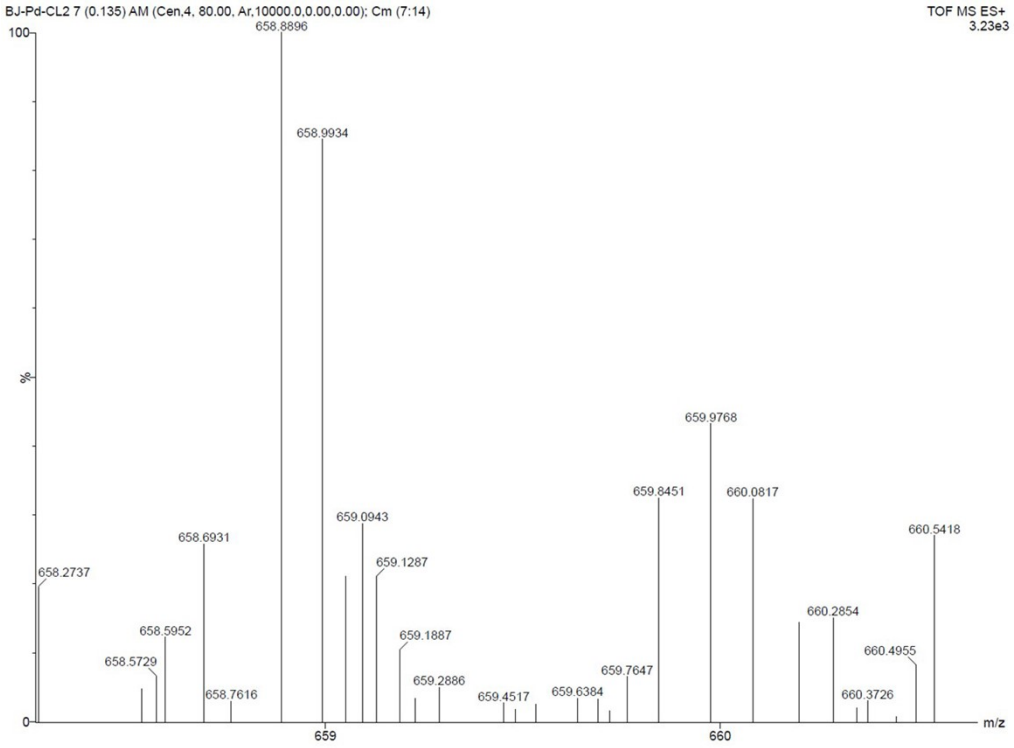


Fig. S11 ESI-MS spectra of $[PdCl_2(bptmp)]$ **3b**

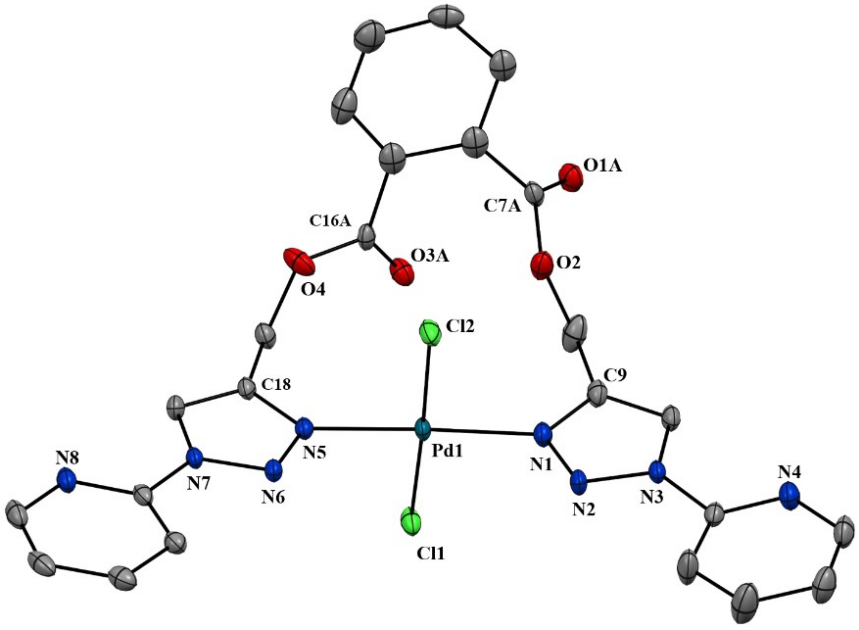


Fig. S12 Molecular structure and atom numbering scheme of compound **3b**. The thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]:

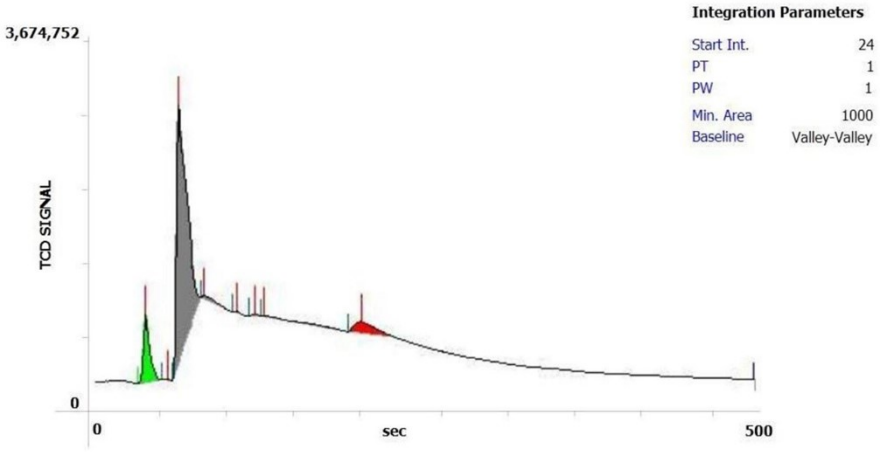
EuroEA Elemental Analyser

AutoRun Name	:	2022-43 (189)
Date of Analysis	:	17 Dec 2022
Time of Analysis	:	15:13:38
Analysed By	:	EVR
Signed By	:	EVR
Operator Group	:	GRP1
Configuration	:	CHNS
Sample Name	:	PdCl2(bptmp) B
Sample Position #	:	11
Type	:	Smp
Sample Weight	:	1.668 (mg)
Calibration type	:	Linear

Instrument Parameters

Carrier (kPa)	Purge (ml/min)	Oxygen (ml)	Delta P O2 (kPa)	Sampling Delay (s)	Run Time (s)	Front (°C)	Rear (°C)	Oven (°C)
100	80	15	35	8	500	980	Off	100

Chromatogram



Results

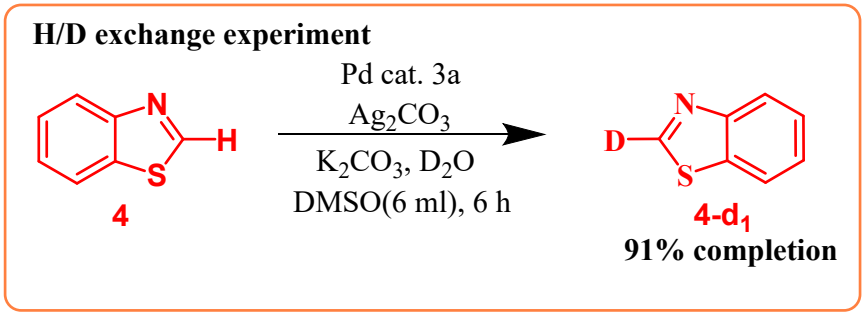
Element	RT (s)	Area	Area %	Element %
Nitrogen	39	467,862	13.020	15.680
Carbon	83	2,814,660	78.330	43.653
Hydrogen	201	310,811	8.650	2.224
Sulphur	-	-	-	-

Fig. S13 C,H,N analysis of [$PdCl_2$(bptmp)] **3b**

7. Kinetics experiment

Synthesis of 4-d_1-benzothiazole

2-*d*-benzothiazole was synthesized using a modified procedure of Huang et al., benzothiazole (0.210 g, 1.5 mmol) was added to a vigorously stirred solution of silver cabonate (0.124 g, 0.45 mmol), Pd cat. 3a (0.031 g, 0.045 mmol) and potassium carbonate (0.207 g, 1.5 mmol) in dimethyl sulfoxide (3.0 mL) in the air. D_2O (0.600 g) was added to it. The reaction mixture was stirred at 80 °C for 6 h. Then the reaction was quenched with saturated NH_4Cl solution. The product was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of solvents under vacuum, the crude product was purified via column chromatography.



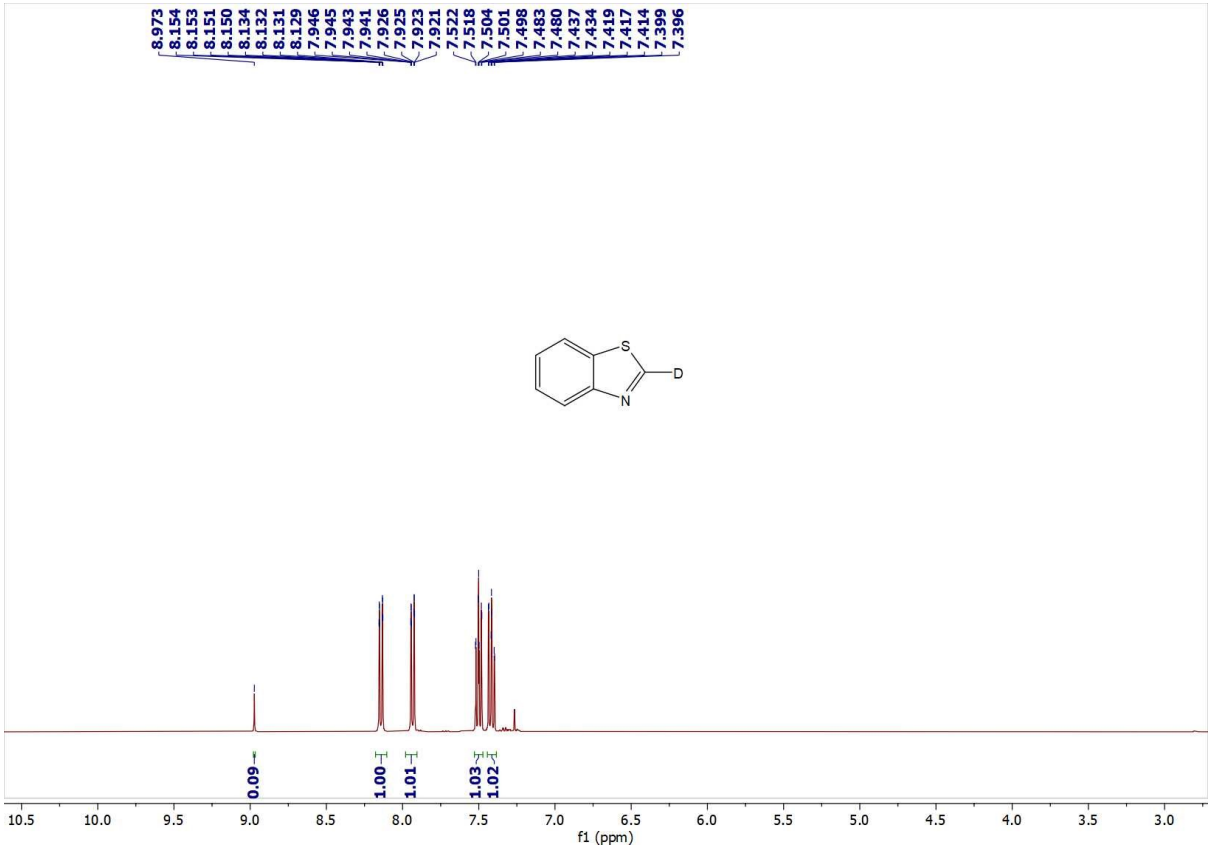


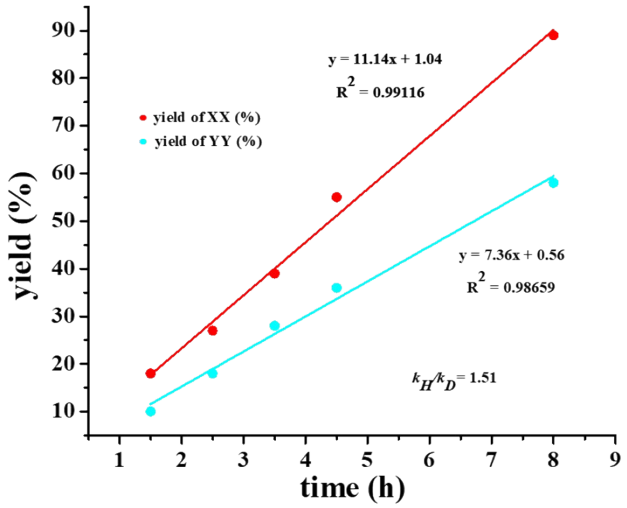
Fig. S14 ^{1}H-NMR Spectrum of **4-d_1**

Determination of kinetic isotope effect [KIEs]

Kinetic investigations were conducted in oven-dried and sealed with Teflon caps. Each tube maintained a consistent concentration of both the substrate and catalyst. A time frame of 1 and a half hour was used to record the data. Final results are the average values that were derived from five independent experimental runs. The KIE value (K_H/K_D = 1.51) was observed when the parallel reactions were performed. These experiments conclude that the cleavage of C-H bond of azoles may not be the rate determining step.

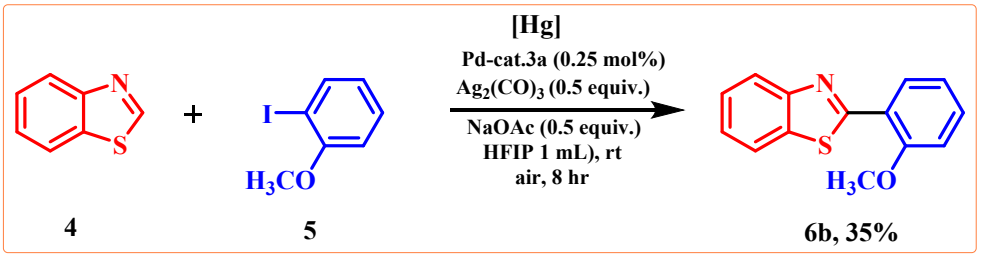
t/h / %yield	1.5	2.5	3.5	4.5	8
4	18	27	39	55	89

4-d_1	12	21	30	42	63



8. **Mercury drop experiment**

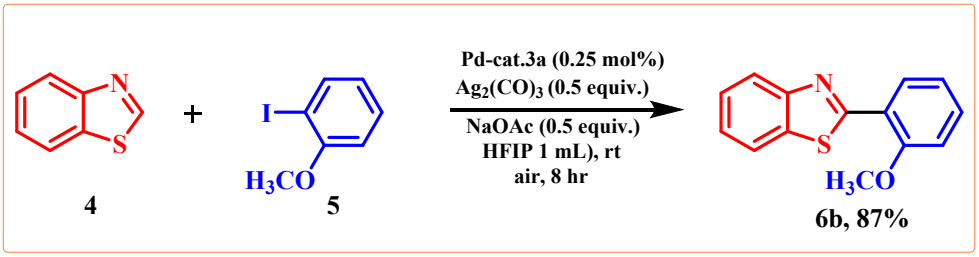
To determine whether catalyst 3a operates via a heterogeneous or homogeneous pathway in the C-2 arylation of azoles, a mercury drop experiment was performed. In this test, a reaction mixture with (0.100 g, 0.74 mmol) benzothiazole (**4**), (0.173 g, 0.74 mmol) 2-iodoanisole (**5**), (0.030g, 0.37 mmol) NaOAc, (0.101 g, 0.37 mmol) Ag_2CO_3 and 0.25 mol% of catalyst 3a was prepared in a 1 ml of HFIP. A drop of mercury was introduced into the reaction, and the mixture was stirred at room temperature for 8 hours. The presence of mercury resulted in an approximately 52% reduction in the yield of the C-2 arylated product of **6b**, indicating that catalyst 3a predominantly functions through a heterogeneous mechanism.



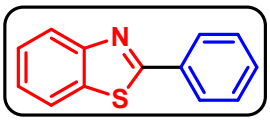
9. **Representative procedure for C-2 arylation of azoles: synthesis of 2-(2-methoxyphenyl)benzo[d]thiazole (6b)**

An oven dried reaction tube was charged with (0.100 g, 0.74 mmol) benzothiazole (**4**), (0.173 g, 0.74 mmol) 2-iodoanisole (**5**), (0.030g, 0.37 mmol) NaOAc, (0.101 g, 0.37 mmol) Ag_2CO_3 and 0.25 mol% of catalyst 3a in a 1 ml of HFIP. The reaction mixture was stirred at room temperature for 8 hours. The completion of the reaction was monitored by TLC at one and a half time intervals. After completion of the reaction, water (20 mL) was added to the reaction mixture, which was then extracted three times with ethyl acetate ($CH_3COOC_2H_5$, 25 mL each). The combined organic extracts were dried over anhydrous Na_2SO_4, and the solvent was

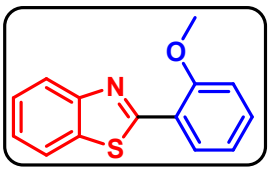
removed under reduced pressure. The resulting residue was purified by silica gel column chromatography using a gradient of n-hexane-ethyl acetate (30:1 to 20:1), affording compound **6b** as an off-white solid (0.155 g, 87% yield).



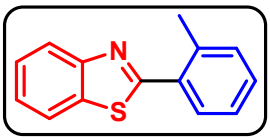
10. **Characterization data for C-2 arylated azoles**



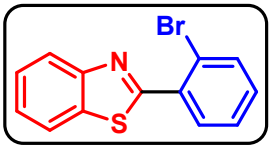
2-phenylbenzo[d]thiazole (6a): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and iodo/bromo-benzene **5** (0.150 g for I and 0.116 g for Br, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane) yielded **6a** (0.145 g, I = 93%,0.136 g, Br = 87%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03- 8.00 (m, 3H), 7.85- 7.82 (m, 1H), 7.44 – 7.40 (m, 4H), 7.34- 7.29 (m, 1H). This compound is further confirmed by ref.[6]



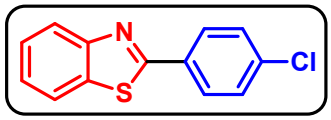
2-(2-methoxyphenyl)benzo[d]thiazole (6b): Yielded **6b** as an off-white solid (0.155 g, I = 87%, 0.128 g, Br = 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47- 8.44 (m, 1H), 8.02- 8.00 (m, 1H), 7.86 – 7.84 (m, 1H), 7.44- 7.37 (m, 2H), 7.32 – 7.28 (m, 1H), 7.08- 7.04 (m, 1H), 7.01- 6.99 (m, 1H), 3.99 (s, 3H). This compound is further confirmed by ref.[7]



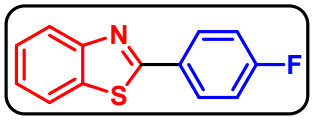
2-(o-tolyl)benzo[d]thiazole (6c): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 2-iodo/bromo-toluene **5** (0.161 g for I and 0.126 g for Br, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 25/1) yielded **6c** (0.135 g, I = 81%,0.106 g, Br = 64%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04- 8.02 (m, 1H), 7.87- 8.85 (m, 1H), 7.70- 7.67 (m, 1H), 7.46- 7.42 (m, 1H), 7.36 – 7.22 (m, 4H), 2.59 (s, 3H). This compound is further confirmed by ref.[7]



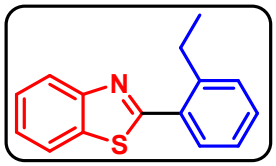
2-(o-tolyl)benzo[d]thiazole (6d): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 1-bromo-2-iodobenzene/1,2-di-bromobenzene **5** (0.209 g for I and 0.174 g for Br, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded **6d** (0.178 g, I = 83%,0.109 g, Br = 51%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.13 (m, 1H), 8.00 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.97-7.94 (m, 1H), 7.75 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.56-7.52 (m, 1H), 7.48-7.43 (m, 2H), 7.36-7.32 (m, 1H). This compound is further confirmed by ref.[7]



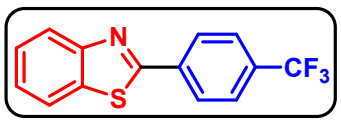
2-(4-chlorophenyl)benzo[d]thiazole (6f): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 4-chloro-iodobenzene **5** (0.176 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 30/1) yielded **6f** (0.154 g, I = 85%) as an off white solid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.00- 7.98 (m, 1H), 7.97 – 7.94 (m, 2H), 7.84-7.82 (m, 1H), 7.45 – 7.38 (m, 3H), 7.35- 7.31 (m, 1H). This compound is further confirmed by ref.[6]



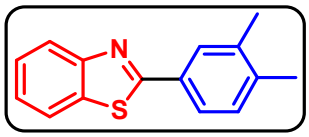
2-(4-fluorophenyl)benzo[d]thiazole (6g): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 4-fluoro-iodobenzene **5** (0.164 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded **6g** (0.133 g, I = 79%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.04 (m, 3H), 7.90 – 7.87 (m, 1H), 7.51-7.47 (m, 1H), 7.40-7.36(m, 1H), 7.20 – 7.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (s), 164.7 (s), 162.2 (s), 153.1 (s), 134.0 (s), 128.9 (s), 128.9 (s), 128.5 (s), 128.5 (s), 125.4 (s), 124.2 (s), 122.2 (s), 120.6 (s), 115.3 (s), 115.0 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.79. This compound is further confirmed by ref.[6]



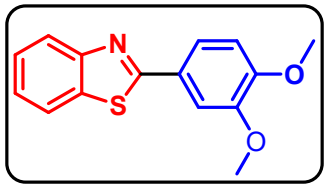
2-(2-ethylphenyl)benzo[d]thiazole (6h): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 2-ethyl-iodobenzene **5** (0.171 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 30/1) yielded **6h** (0.134 g, I = 76%) as pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.59- 7.56 (m, 1H), 7.44 – 7.40 (m, 1H), 7.35- 7.27 (m, 3H), 7.23- 7.19 (m, 1H), 2.95 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8 (s), 152.8 (s), 142.4 (s), 134.7 (s), 131.7 (s), 129.7 (s), 129.2 (s), 128.8 (s), 125.1 (s), 124.9 (s), 124.0 (s), 122.4 (s), 120.3 (s), 25.7 (s), 14.6 (s). This compound is further confirmed by ref.[11]



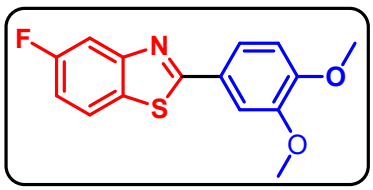
2-(4-(trifluoromethyl)phenyl)benzo[d]thiazole (6i): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 4-(trifluoromethyl)-iodobenzene/-bromobenzene **5** (0.201 g for I and 0.166 g for Br, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 30/1) yielded **6i** (0.169 g, I = 82%, 0.101 g, Br = 49%) as a white solid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.15- 8.07(m, 3H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.51- 7.39 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0 (s), 153.0 (s), 135.8 (s), 134.2 (s), 131.6 (s), 131.3 (s), 126.7 (s), 125.8 (s), 125.6 (s), 125.1 (s), 125.0 (s), 124.9 (s), 124.9 (s), 124.8 (s), 124.2 (s), 123.1 (s), 122.6 (s), 121.4 (s), 121.0 (s), 120.7 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.73. This compound is further confirmed by ref.[8]



2-(3,4-dimethylphenyl)benzo[d]thiazole (6j): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 3,4-dimethyl-iodobenzene **5** (0.171 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded **6j** (0.148 g, I = 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.72- 7.69 (m, 1H), 7.41 – 7.36 (m, 1H), 7.29- 7.25 (m, 1H), 7.16-7.14 (m, 1H), 2.27 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4 (s), 153.1 (s), 139.1 (s), 136.4 (s), 133.9 (s), 130.2 (s), 129.2 (s), 127.4 (s), 125.2 (s), 124.1 (s), 123.9 (s), 121.9 (s), 120.5 (s), 18.8 (s), 18.7 (s). This compound is further confirmed by ref.[12]

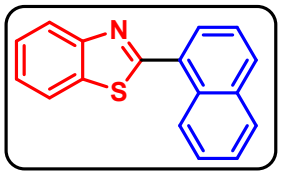


2-(3,4-dimethoxyphenyl)benzo[d]thiazole (6l): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 3,4-dimethoxy-iodobenzene **5** (0.195 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded **6l** (0.162 g, I = 81%) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05- 8.02 (m, 1H), 7.89-7.86 (m, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.61- 7.58 (m, 1H), 7.50- 7.45 (m, 1H), 7.38- 7.34 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 3.95 (s, 3H).This compound is further confirmed by ref.[7]

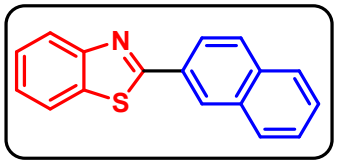


2-(3,4-dimethoxyphenyl)-5-fluorobenzo[d]thiazole (6m): The representative procedure was followed, using **4** (5-fluorobenzothiazole) (0.100 g, 0.74 mmol) and 3,4-dimethoxy-iodobenzene **5** (0.172 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded **6m** (0.149 g, I = 79%) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81- 7.77 (m, 1H), 7.72 – 7.69 (m, 2H), 7.60 – 7.57 (m, 1H), 7.16- 7.10 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4

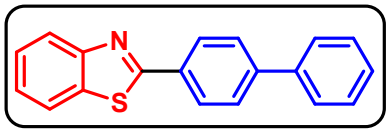
(s), 163.1 (s), 160.7 (s), 155.1 (s), 154.9 (s), 151.8 (s), 149.3 (s), 126.3 (s), 122.2 (s), 122.1 (s), 121.2 (s), 113.6 (s), 113.3 (s), 110.9 (s), 109.8 (s), 109.1 (s), 108.9 (s), 56.1 (s), 56.1 (s). This compound is further confirmed by ref.[7]



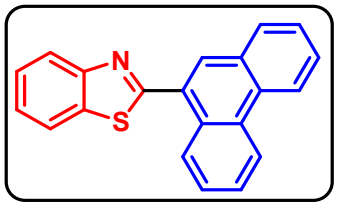
2-(naphthalen-1-yl)benzo[d]thiazole (6n): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 1-iodonephthalene **5** (0.187 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 30/1) yielded **6s** (0.156 g, I = 81%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 – 8.90 (m, 1H), 8.20- 8.18 (m, 1H), 8.00 – 7.91 (m, 4H), 7.64 – 7.52 (m, 4H), 7.47- 7.43 (m, 1H). This compound is further confirmed by ref.[7]



2-(naphthalen-2-yl)benzo[d]thiazole (6o): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 2-iodonephthalene **5** (0.187 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 30/1) yielded **6t** (0.152 g, I = 79%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.88- 7.86 (m, 1H), 7.80 – 7.78 (m, 1H), 7.63 – 7.52 (m, 4H), 7.23 – 7.16 (m, 3H), 7.08- 7.04 (m, 1H). This compound is further confirmed by ref.[7]

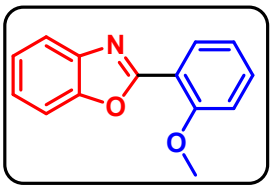


2-([1,1'-biphenyl]-4-yl)benzo[d]thiazole (6p): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 4-iodobiphenyl **5** (0.206 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded **6u** (0.178 g, I = 84%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 2H), 8.10- 8.08 (m, 1H), 7.93 – 7.90 (m, 1H), 7.74 – 7.71 (m, 2H), 7.67 – 7.65 (m, 2H), 7.53 – 7.46 (m, 3H), 7.42 – 7.37 (m, 2H). This compound is further confirmed by ref.[7]

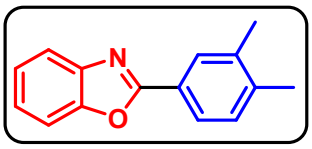


2-(phenanthren-9-yl)benzo[d]thiazole (6q): The representative procedure was followed, using **4** (0.100 g, 0.74 mmol) and 9-iodophenanthrene **5** (0.224 g, 0.74 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 30/1) yielded **6v** (0.172 g, I = 75%) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 – 8.90 (m, 1H), 8.80 – 8.76 (m,

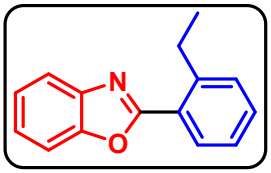
1H), 8.74 – 8.71 (m, 1H), 8.22 – 8.20 (m, 2H), 8.00 – 7.96 (m, 2H), 7.75 – 7.63 (m, 4H), 7.59-7.55 (m, 1H), 7.49- 7.45 (m, 1H). This compound is further confirmed by ref.[7]



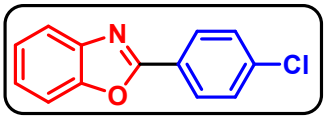
2-(2-methoxyphenyl)benzo[d]oxazole (6r): The representative procedure was followed, using **4** (0.100 g, 0.84 mmol) and 2-methoxy-iodobenzene **5** (0.196 g, 0.84 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 25/1) yielded **6n** (0.117 g, I = 62%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.77- 7.73 (m, 1H), 7.54 – 7.50 (m, 1H), 7.46 – 7.41 (m, 1H), 7.30- 7.25 (m, 2H), 7.05- 7.01 (m, 2H), 3.95 (s, 3H). This compound is further confirmed by ref.[13]



2-(3,4-dimethylphenyl)benzo[d]oxazole (6s): The representative procedure was followed, using **4** (0.100 g, 0.84 mmol) and 1-iodo-3,4-dimethylbenzene **5** (0.195 g, 0.84 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 25/1) yielded **6o** (0.121 g, I = 65%) as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.78-7.76 (m, 1H), 7.59 – 7.54 (m, 1H), 7.37 – 7.33 (m, 1H), 7.16 – 7.10 (m, 2H), 7.07- 7.05 (m, 1H), 2.15 (s, 3H), 2.12 (s, 3H). This compound is further confirmed by ref.[14]

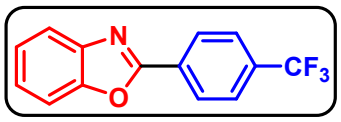


2-(2-ethylphenyl)benzo[d]oxazole (6t): The representative procedure was followed, using **4** (0.100 g, 0.84 mmol) and 2-ethyl-iodobenzene **5** (0.194 g, 0.84 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 20/1) yielded **6p** (0.110 g, I = 59%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13- 8.10 (m, 1H), 7.81 – 7.77 (m, 1H), 7.60 – 7.57 (m, 1H), 7.47- 7.43 (m, 1H), 7.39 – 7.32 (m, 4H), 3.23 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (s), 150.2 (s), 144.8 (s), 141.9 (s), 130.9 (s), 130.1 (s), 129.9 (s), 125.8 (s), 125.5 (s), 124.8 (s), 124.1 (s), 119.9 (s), 110.3 (s), 27.3 (s), 15.3 (s).



2-(4-chlorophenyl)benzo[d]oxazole (6u): The representative procedure was followed, using **4** (0.100 g, 0.84 mmol) and 4-chloro-iodo/bromo-benzene **5** (0.200 g for I, 0.160 g for Br, 0.84

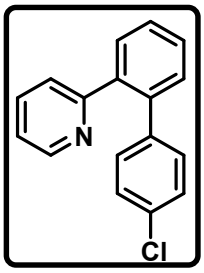
mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 25/1) yielded **6q** (0.129 g, I = 63%, 0.38 g, I = 20%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.17 (m, 2H), 7.80 – 7.75 (m, 1H), 7.59 – 7.56 (m, 1H), 7.52 – 7.49 (m, 2H), 7.39 – 7.34 (m, 2H).This compound is further confirmed by ref.[15]



2-(4-(trifluoromethyl)phenyl)benzo[d]oxazole (6v): The representative procedure was followed, using **4** (0.100 g, 0.84 mmol) and 4-(trifluoromethyl)-iodobenzene **5** (0.228 g, 0.84 mmol). Purification by column chromatography on silica gel (n-hexane/EtOAc: 25/1) yielded **6o** (0.149 g, I = 63%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.33 (m, 2H), 7.80 – 7.75 (m, 3H), 7.60 – 7.56 (m, 1H), 7.40 – 7.35 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (s), 149.8 (s), 140.9 (s), 129.4 (s), 126.8 (s), 124.9 (s), 124.9 (s), 124.9 (s), 124.8 (s), 123.9 (s), 119.4 (s), 109.8 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.07. This compound is further confirmed by ref.[16]

11. **Application in C-arylation of bi-phenyl pyridine**

2-(4'-methyl-[1,1'-biphenyl]-2-yl)pyridine (9) : The representative procedure was also utilised in the other application of C-2 arylation of 2-(2-iodophenyl)pyridine. Purification by column chromatography on silica gel (n-hexane/EtOAc: 25/1) yielded **9** (0.158 g, I = 83%) as a light brown liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63- 8.61 (m, 1H), 7.68 – 7.66 (m, 1H), 7.49 – 7.40 (m, 4H), 7.22 – 7.19 (m, 2H), 7.15- 7.12 (m, 1H), 7.10 – 7.06 (m, 2H), 6.93- 6.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6 (s), 149.1 (s), 139.4 (s), 139.1 (s), 138.9 (s), 135.1 (s), 132.4 (s), 130.6 (s), 130.2 (s), 129.9 (s), 128.3 (s), 127.9 (s), 127.6 (s), 124.9 (s), 121.1 (s). This compound is further confirmed by ref.[17]

12. **NMR-data for C-2 arylated products**

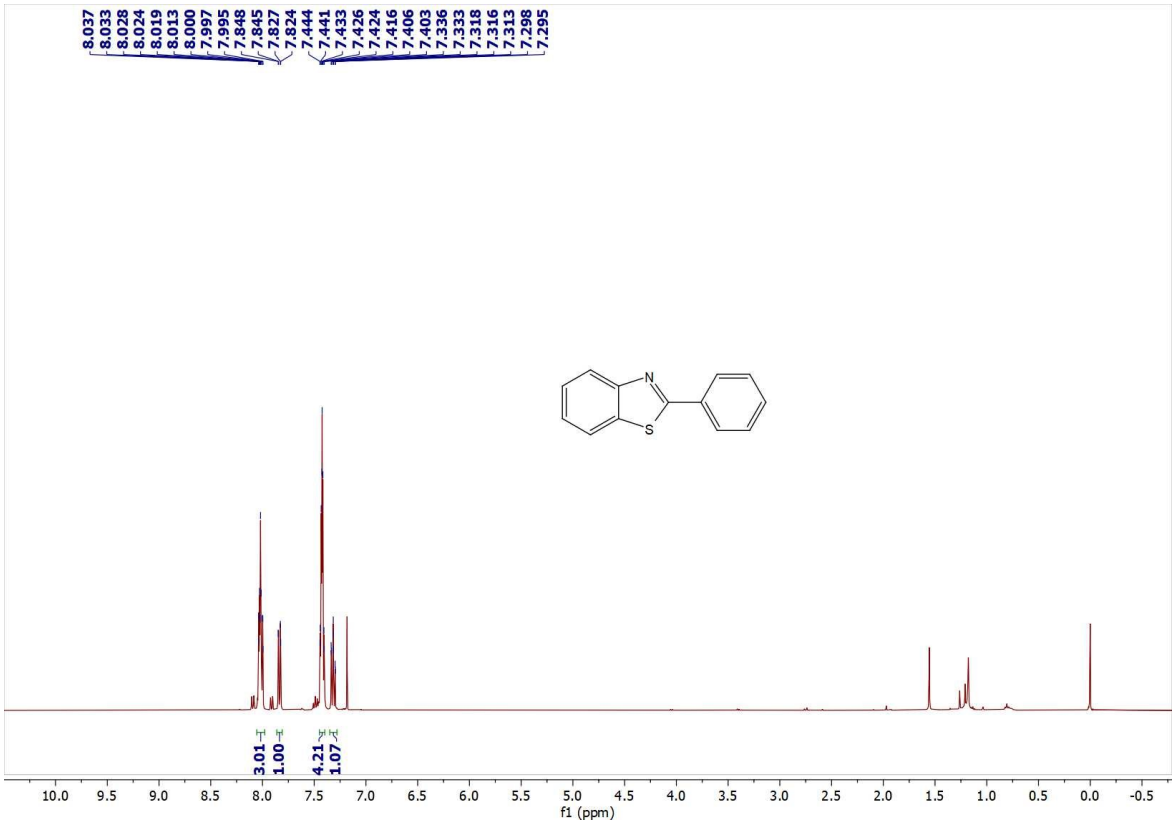


Fig. S15 [1]H-NMR Spectrum of **6a**

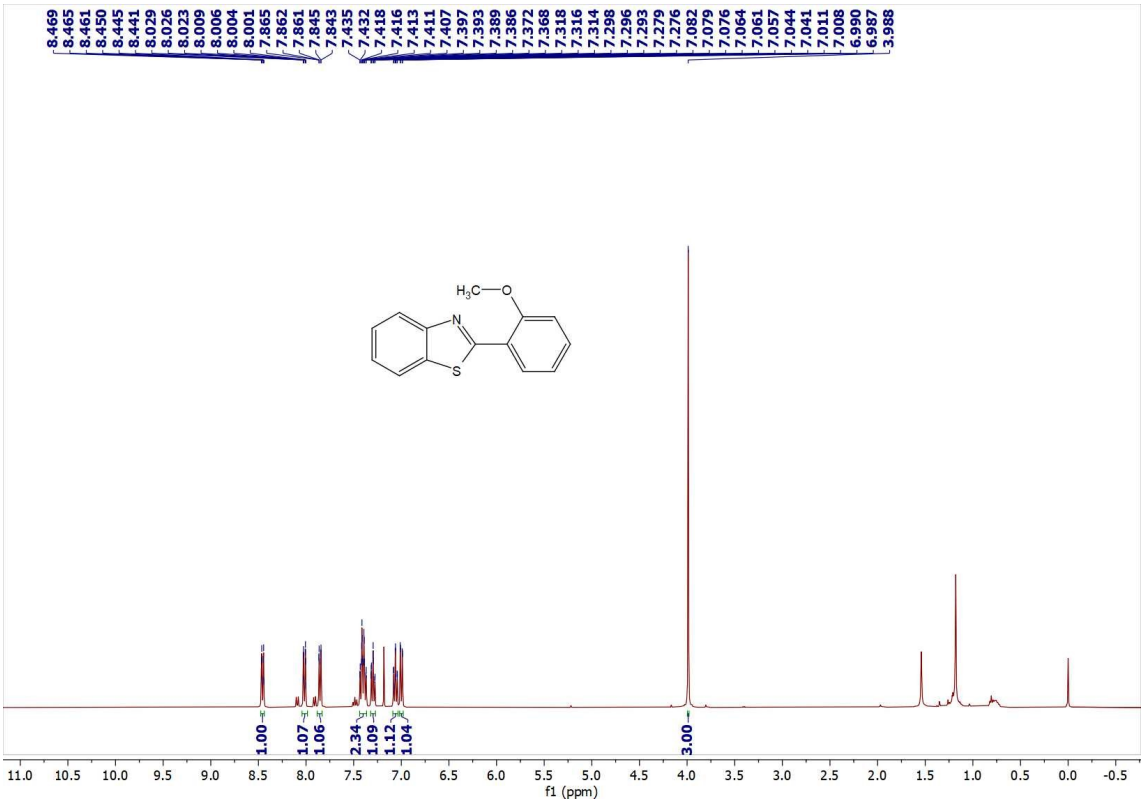


Fig. S16 [1]H-NMR Spectrum of **6b**

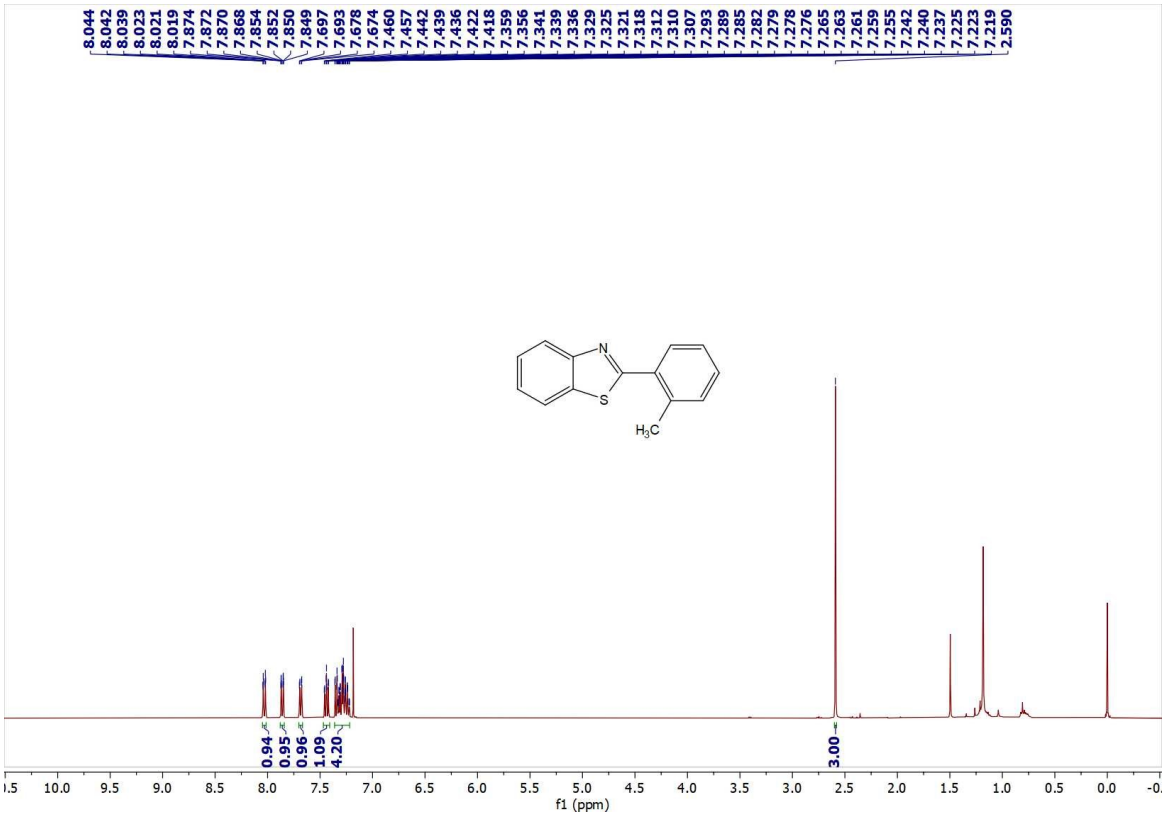


Fig. S17 ^{1}H-NMR Spectrum of **6c**

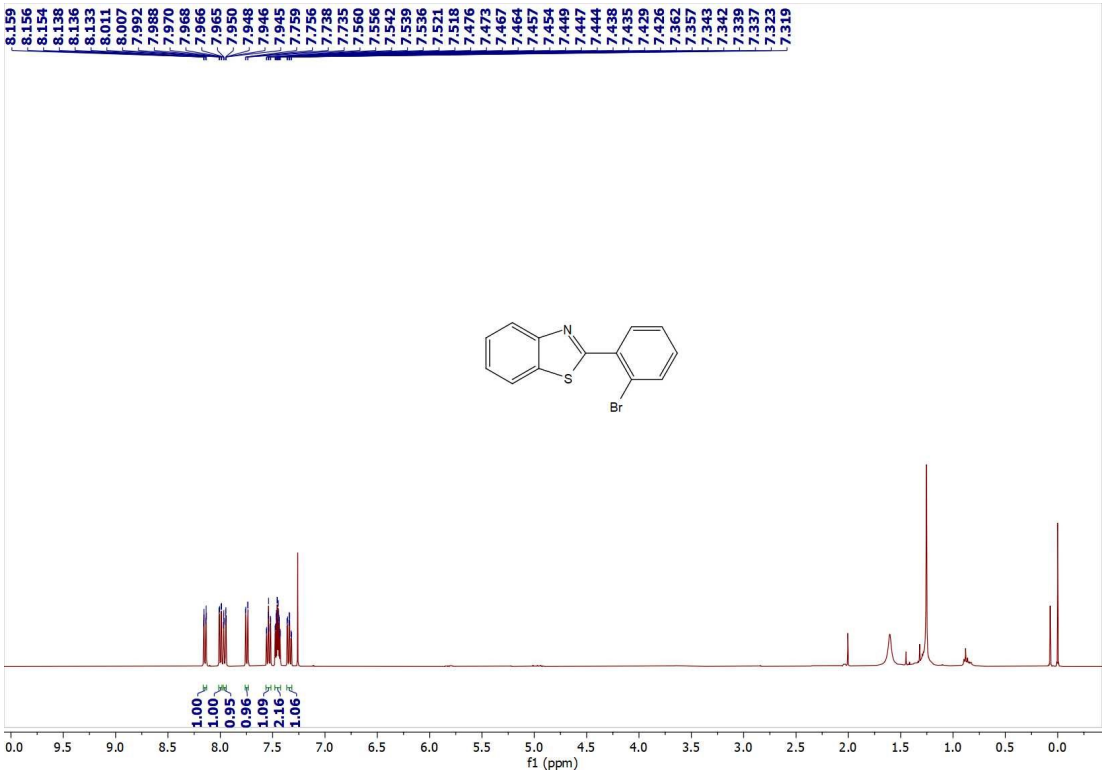


Fig. S18 ^{1}H-NMR Spectrum of **6d**

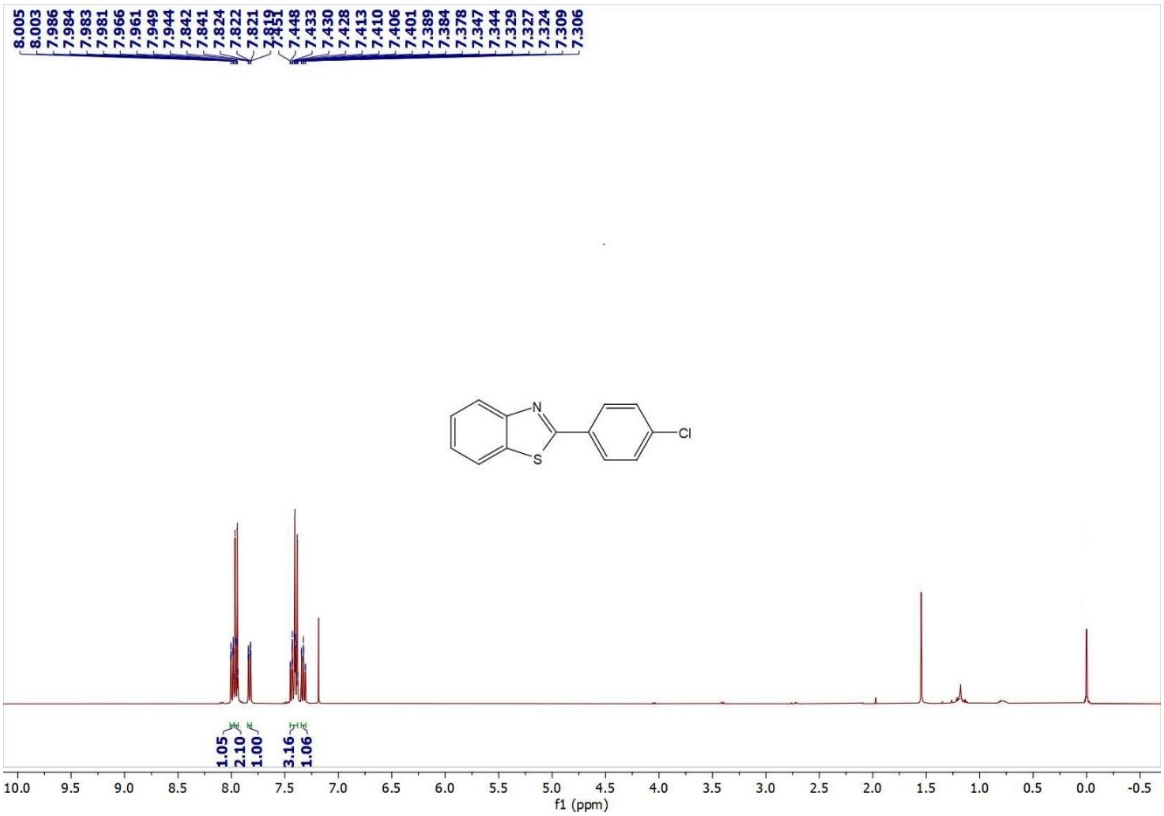


Fig. S19 [1]H-NMR Spectrum of **6f**

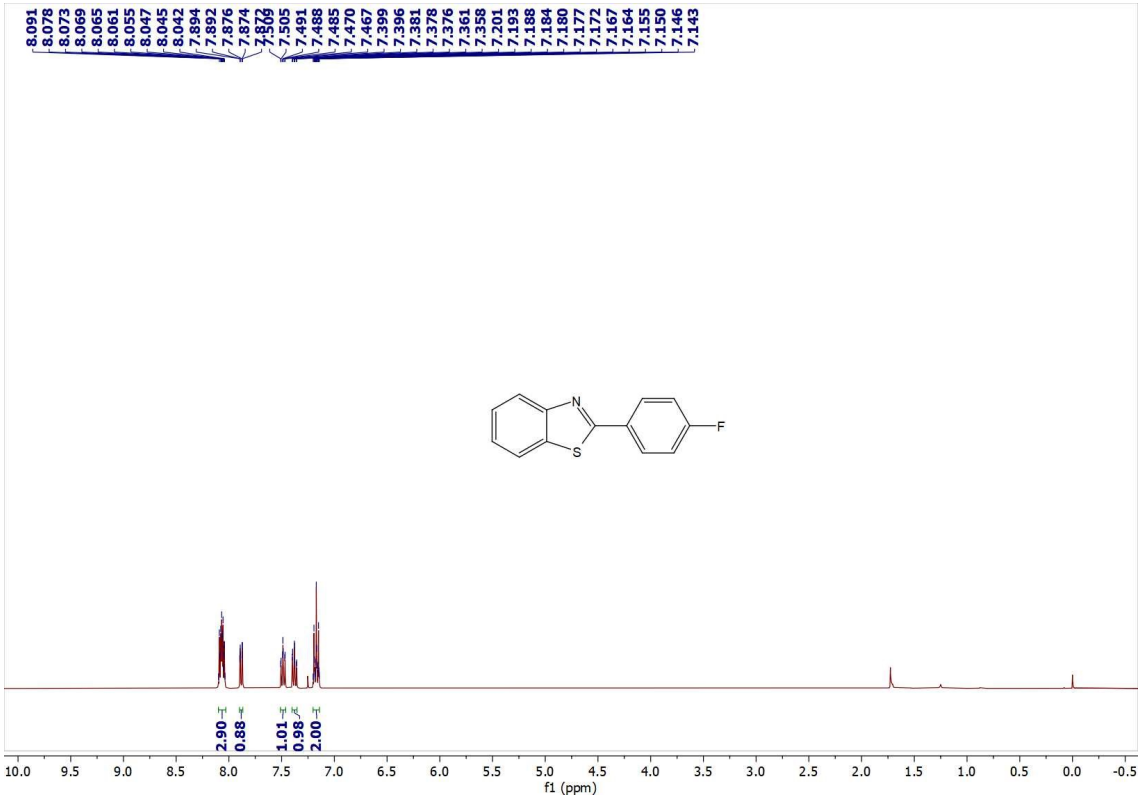


Fig. S20 [1]H-NMR Spectrum of **6g**

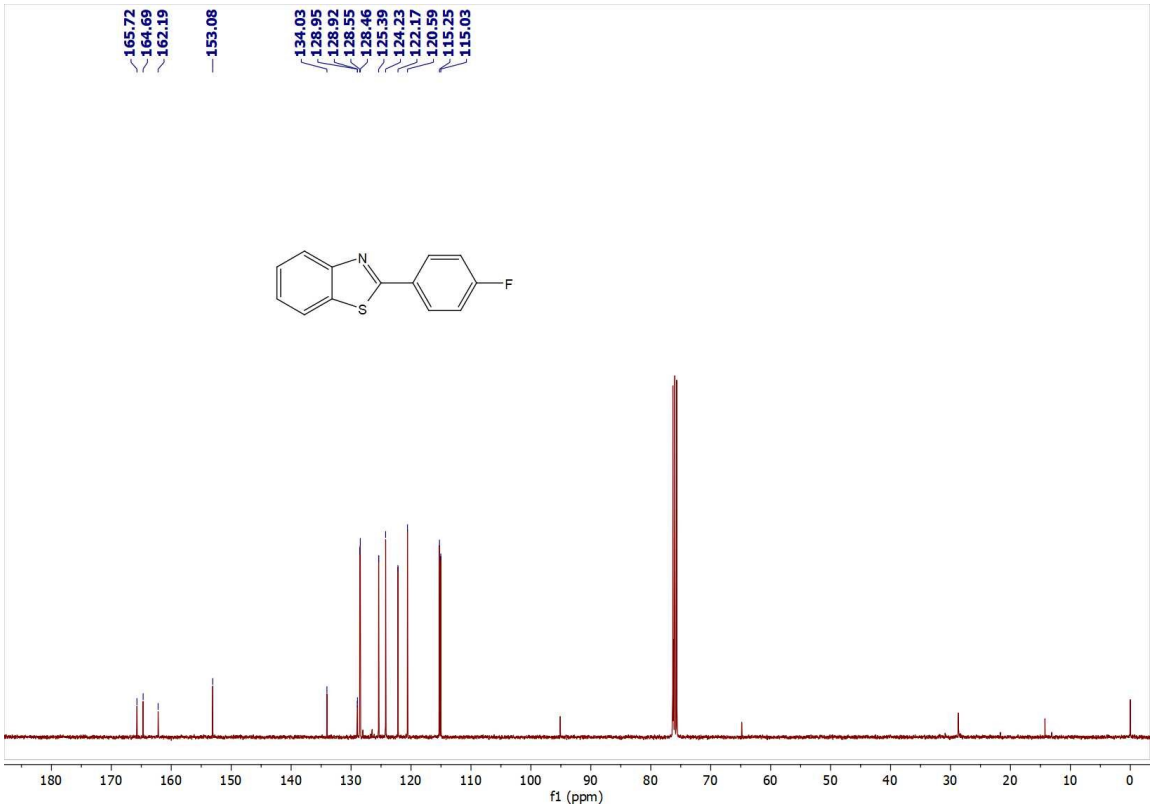


Fig. S21 $^{13}C\{^{1}H\}$-NMR Spectrum of **6g**

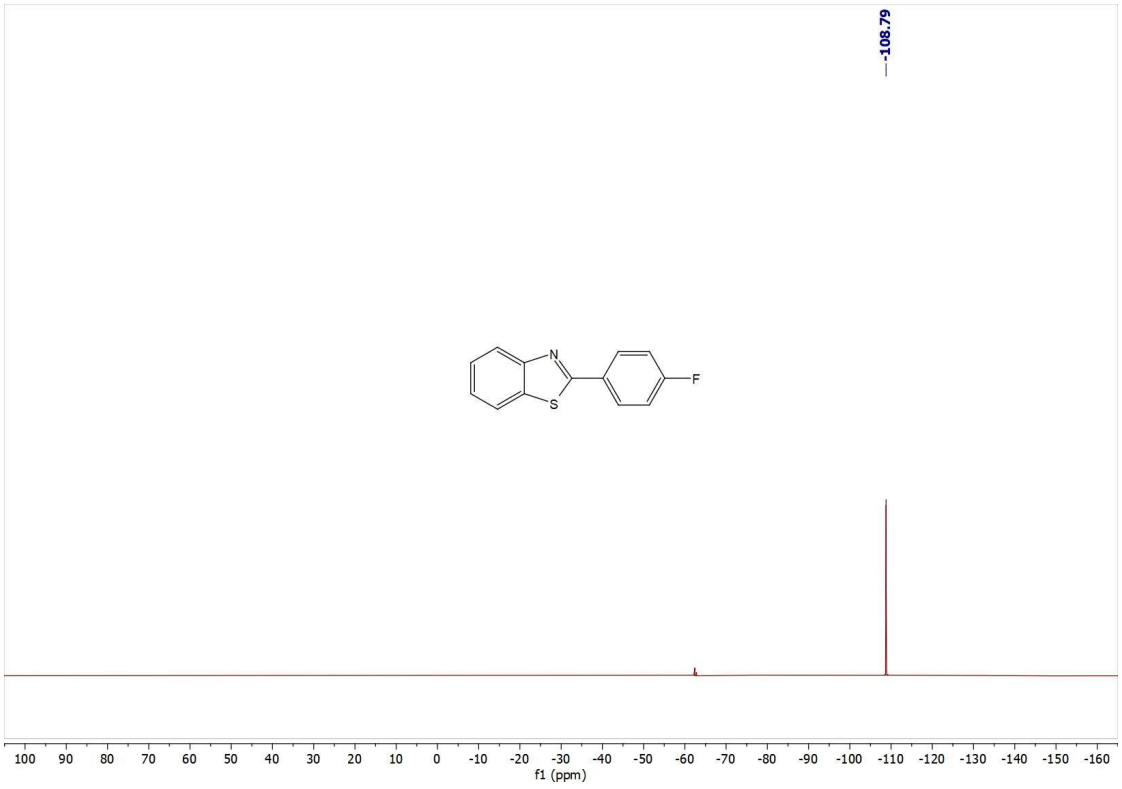


Fig. S22 ^{19}F-NMR Spectrum of **6g**

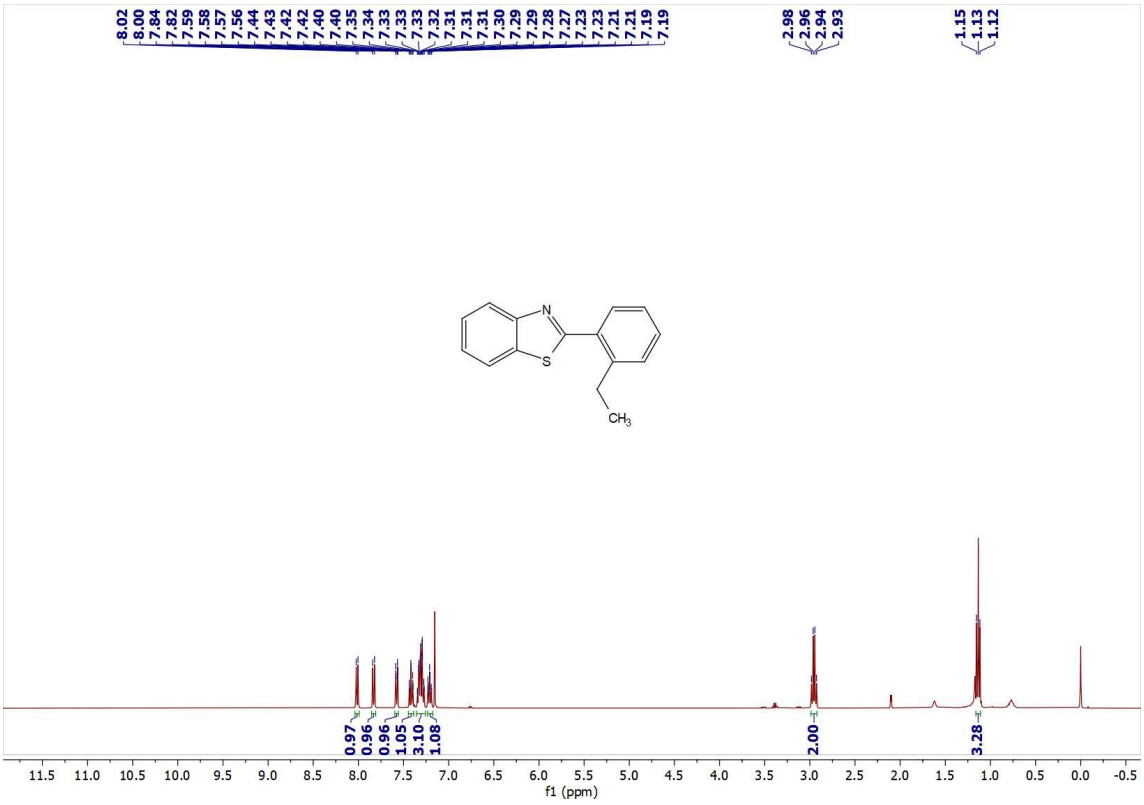


Fig. S23 ^{1}H-NMR Spectrum of **6h**

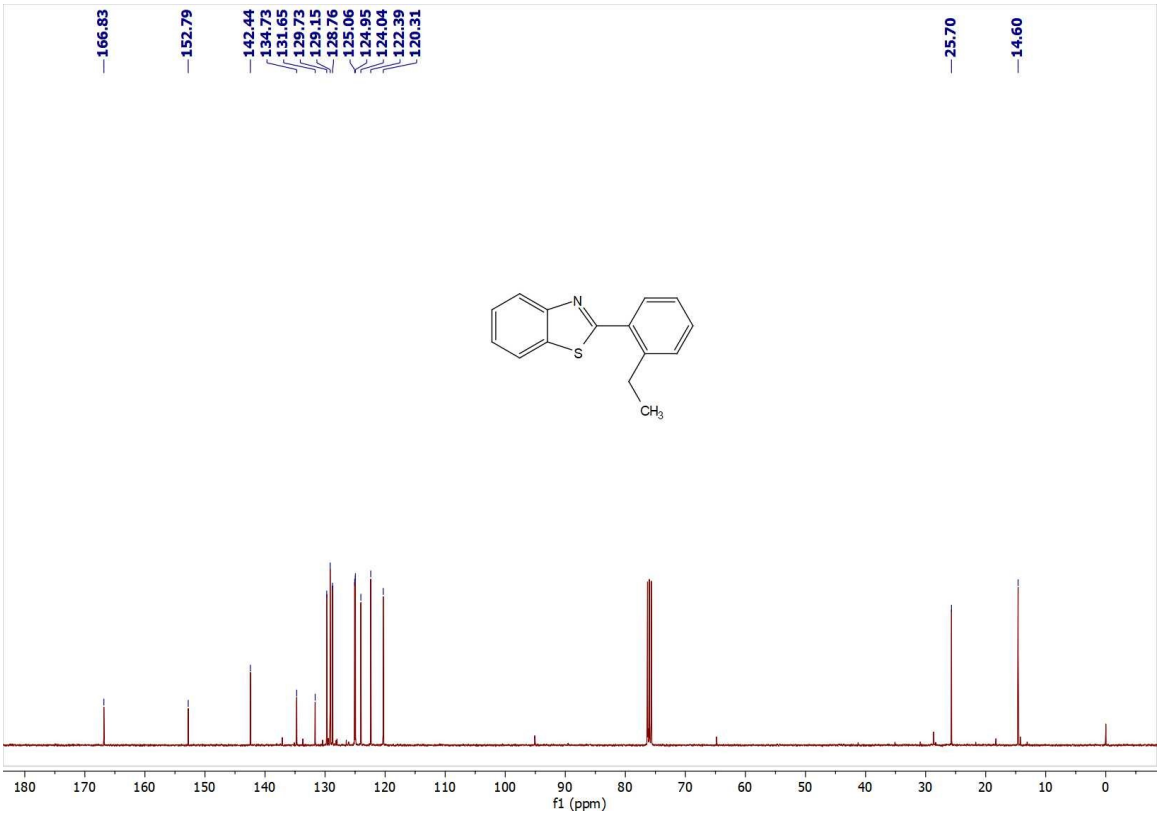


Fig. S24 ^{13}C{^{1}H}-NMR Spectrum of **6h**

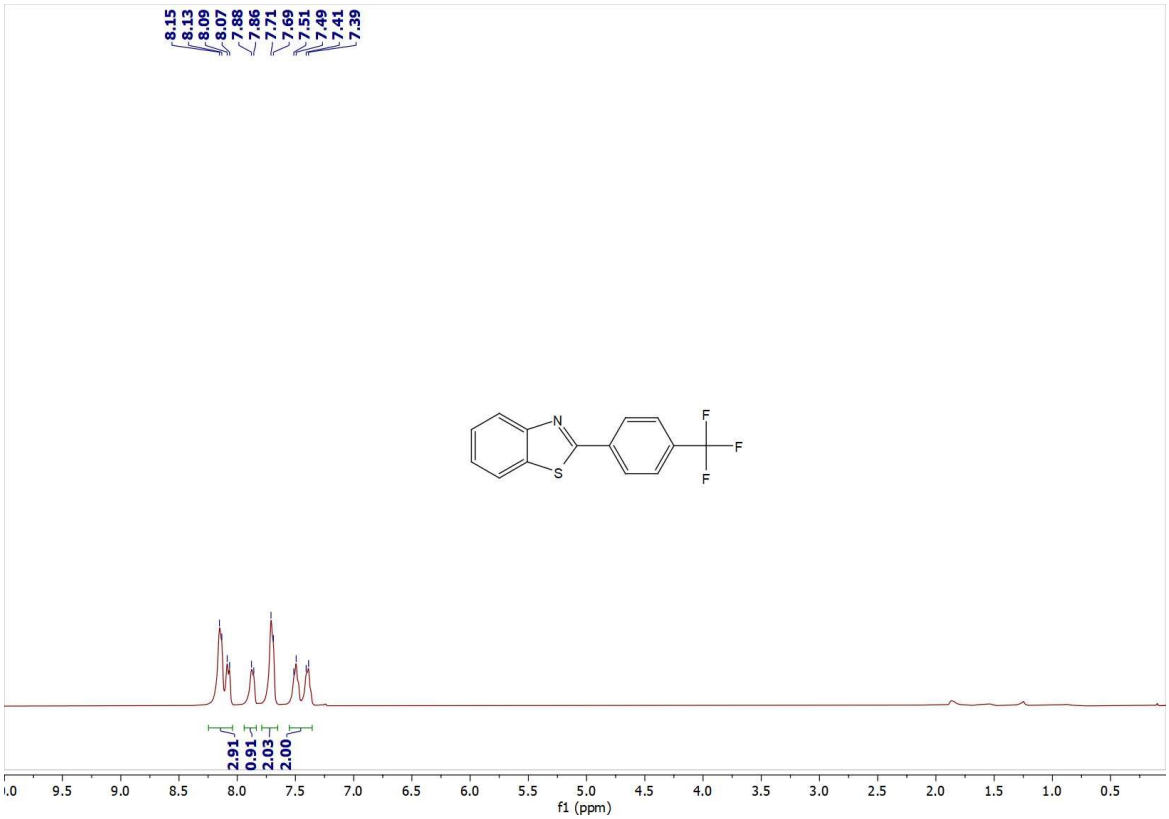


Fig. S25 ^{1}H-NMR Spectrum of **6i**

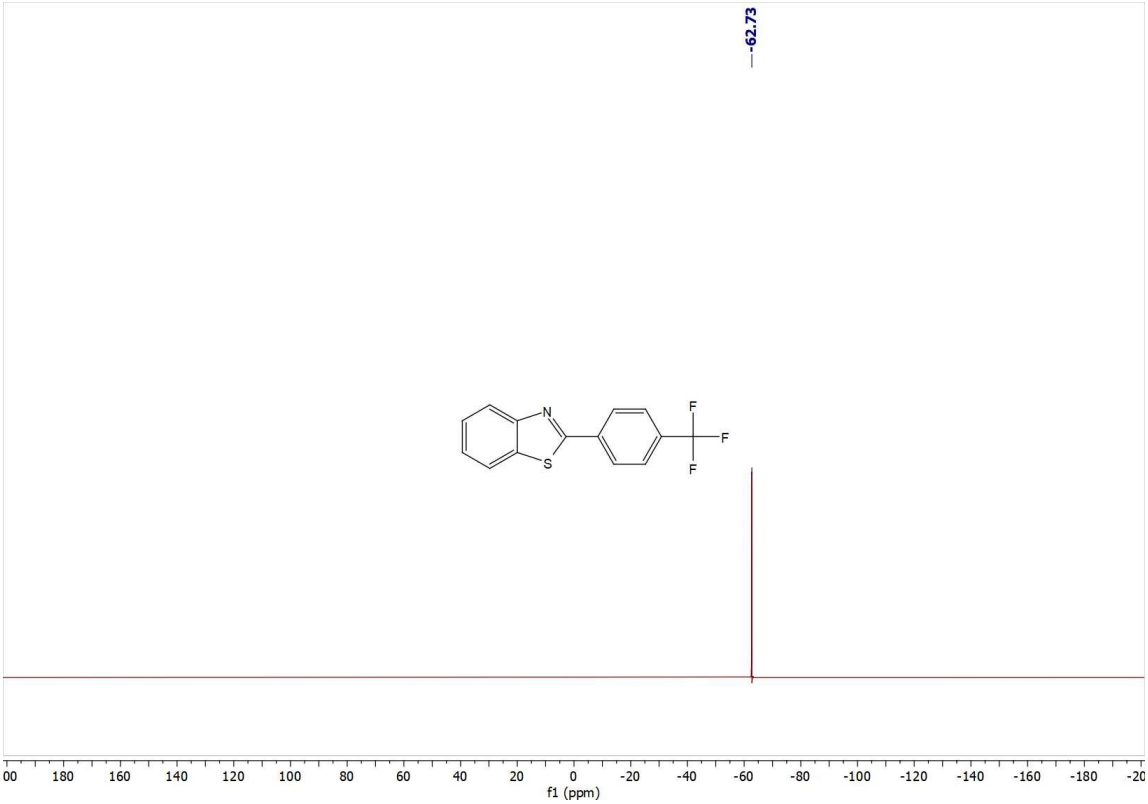


Fig. S26 ^{19}F-NMR Spectrum of **6i**

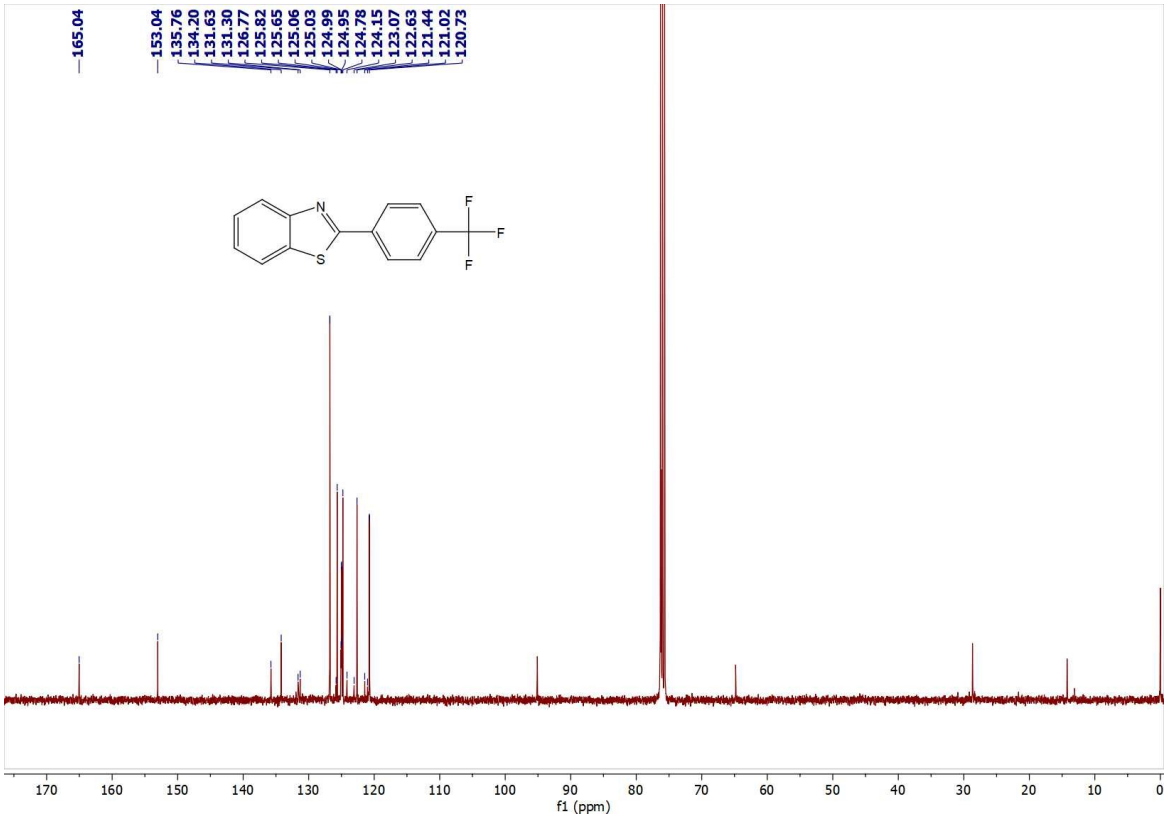


Fig. S27 $^{13}C\{^{1}H\}$-NMR Spectrum of **6i**

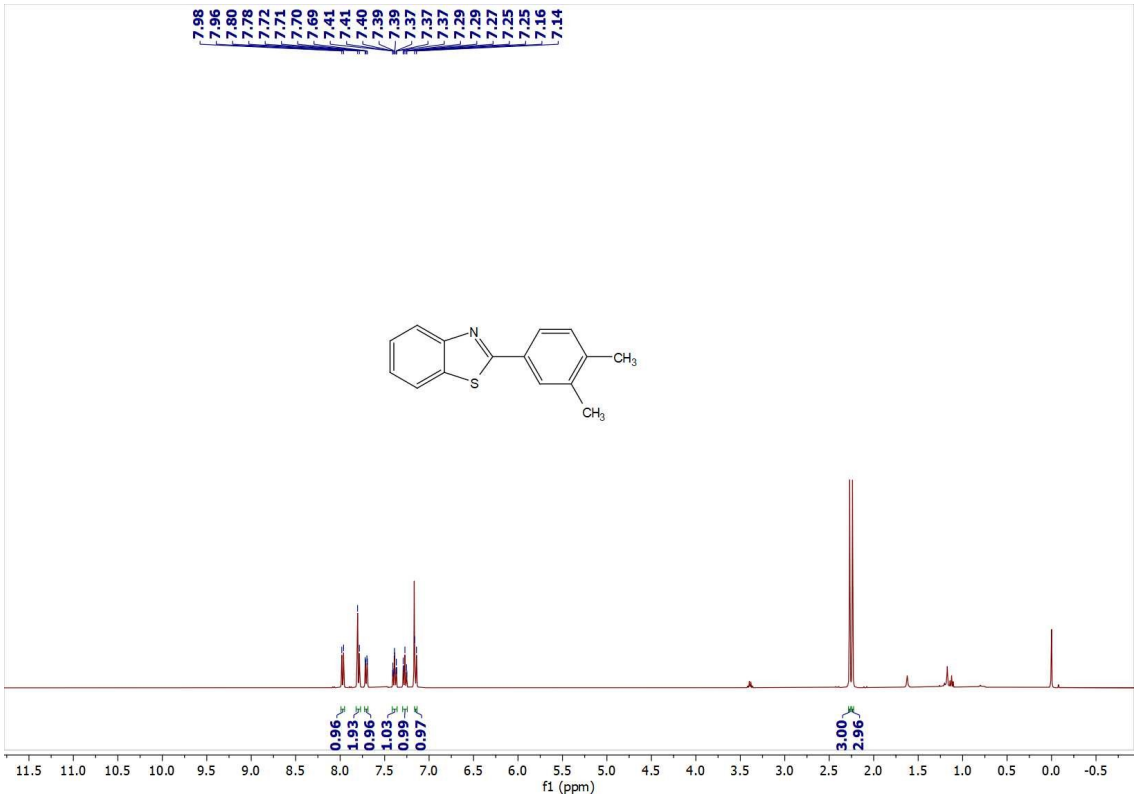


Fig. S28 ^{1}H-NMR Spectrum of **6j**

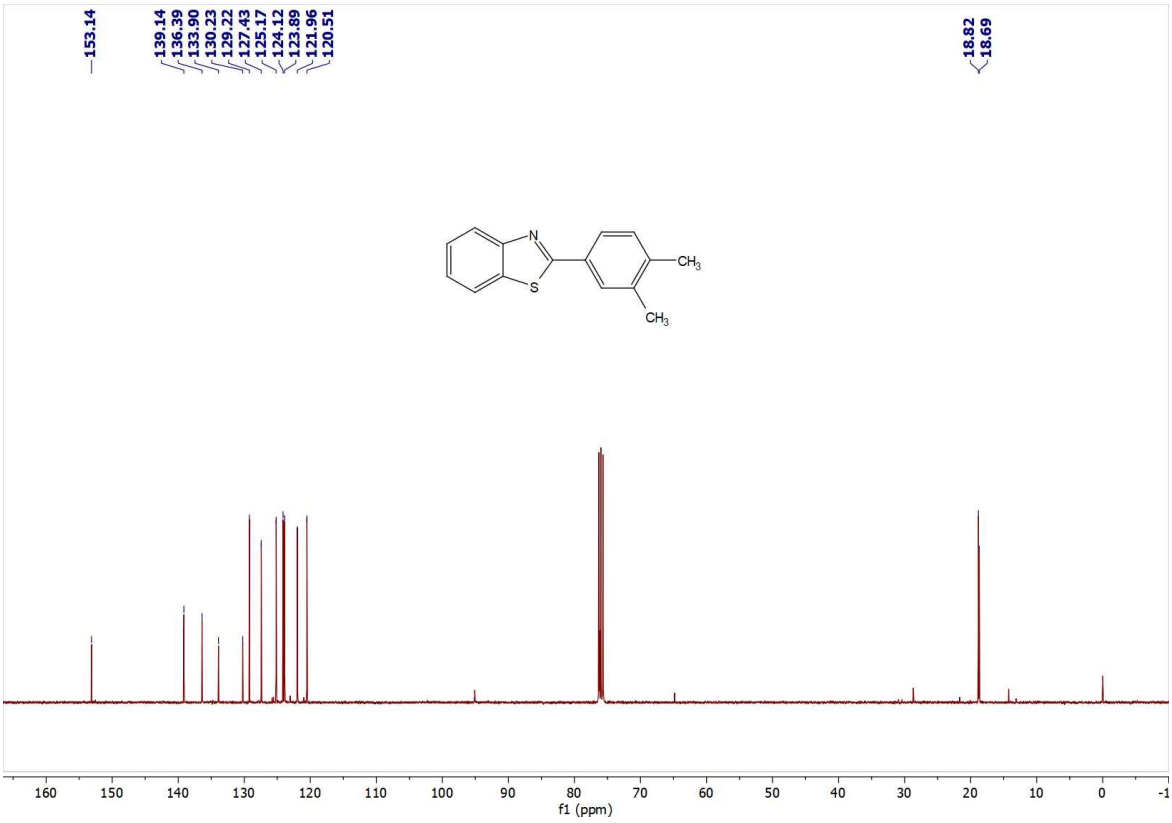


Fig. S29 $^{13}C\{^{1}H\}$-NMR Spectrum of **6j**

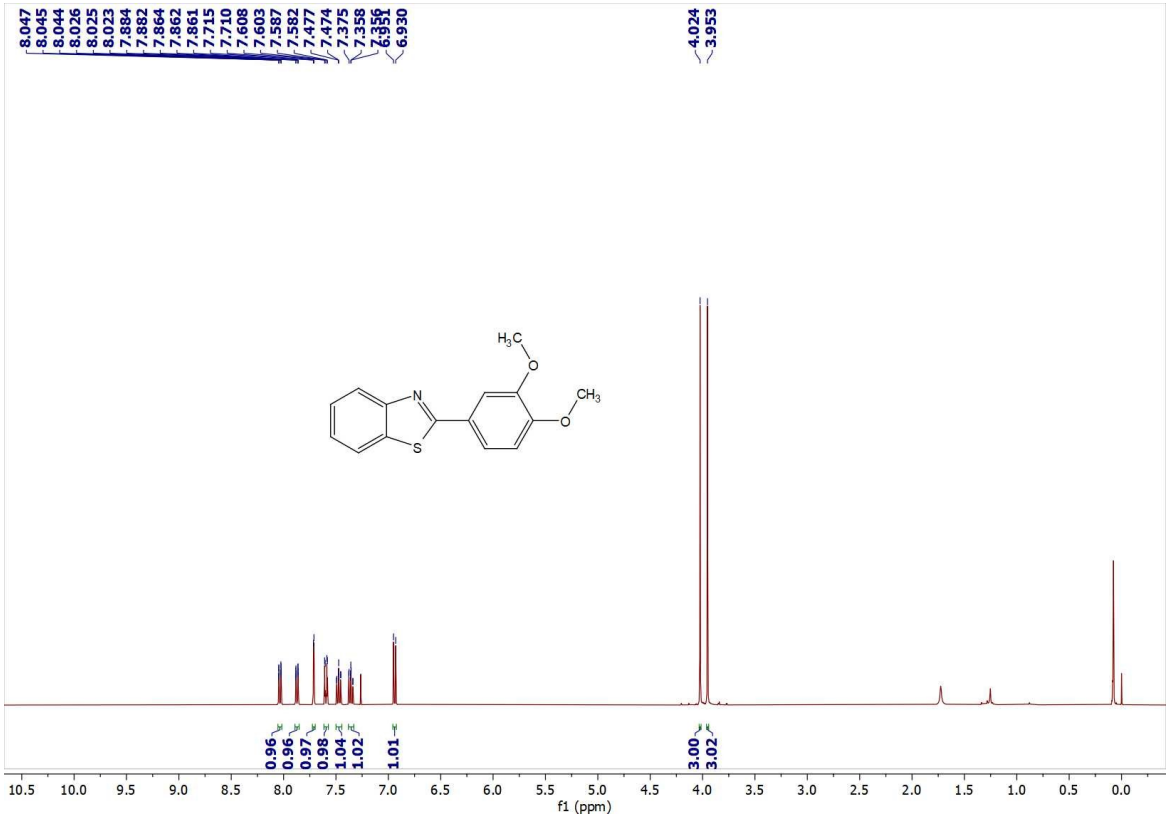


Fig. S30 ^{1}H-NMR Spectrum of **6l**

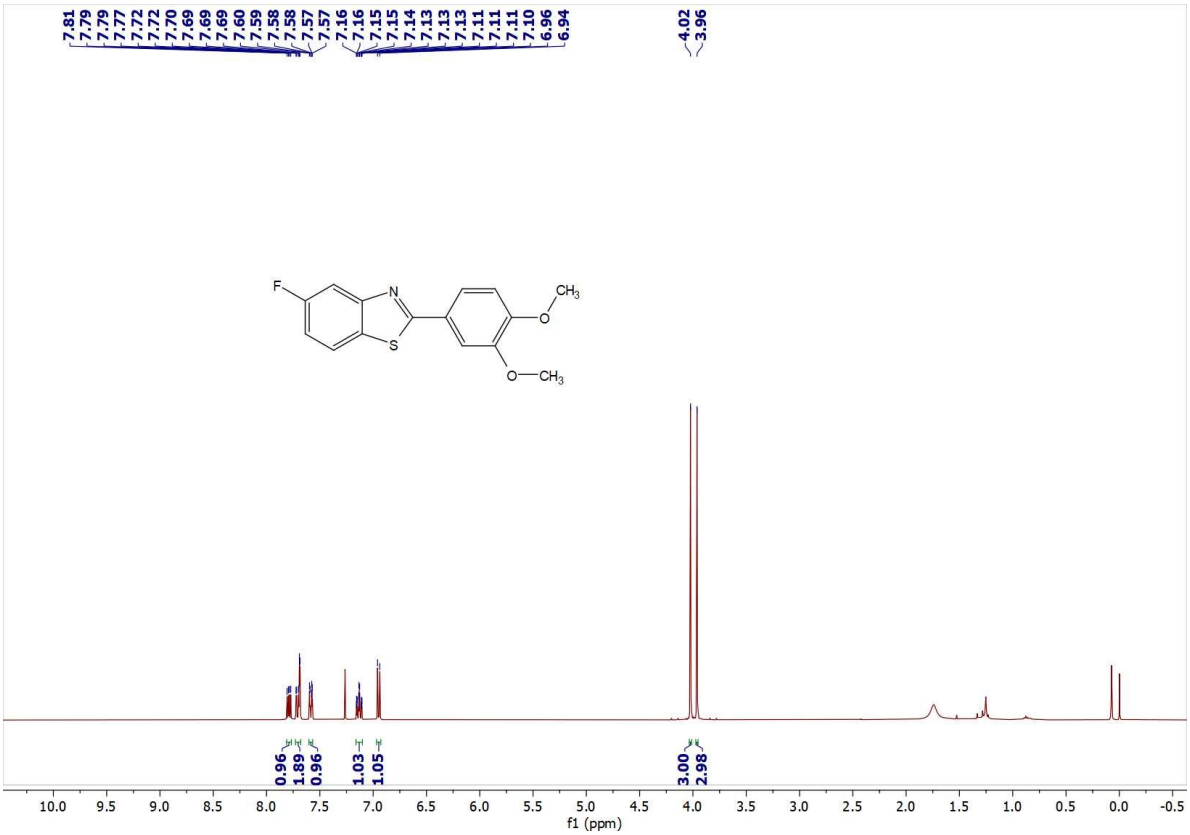


Fig. S31 [1]H-NMR Spectrum of **6m**

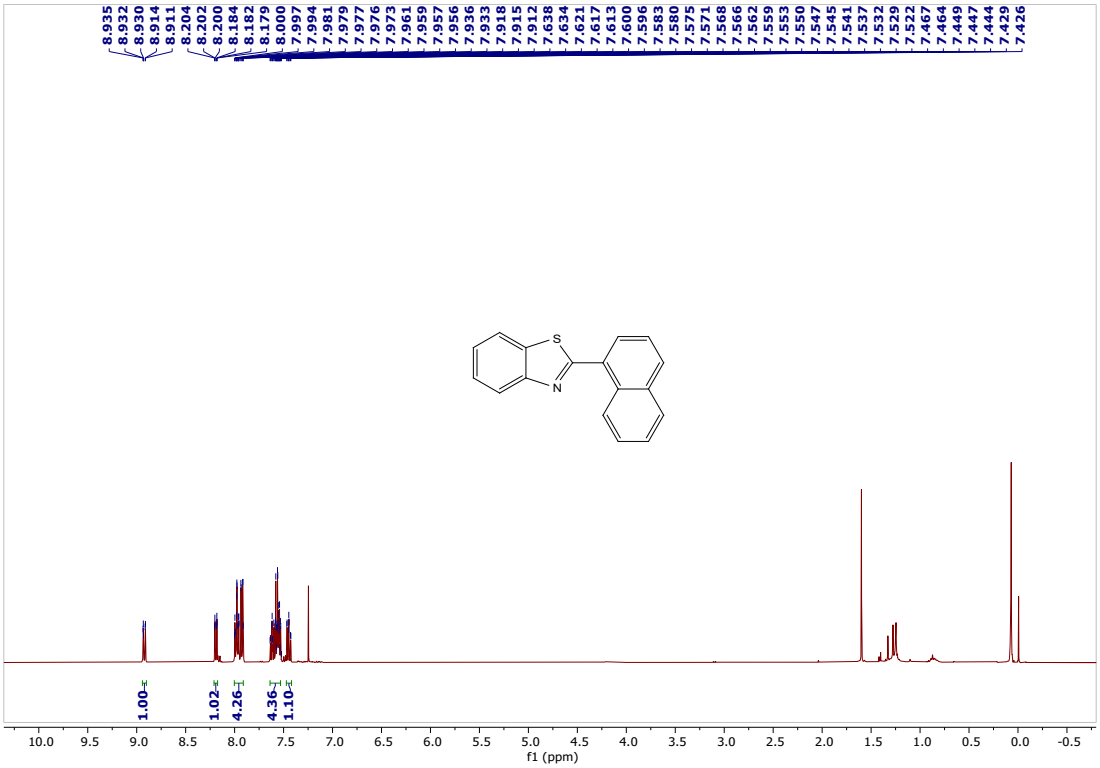


Fig. S32 [1]H-NMR Spectrum of **6n**

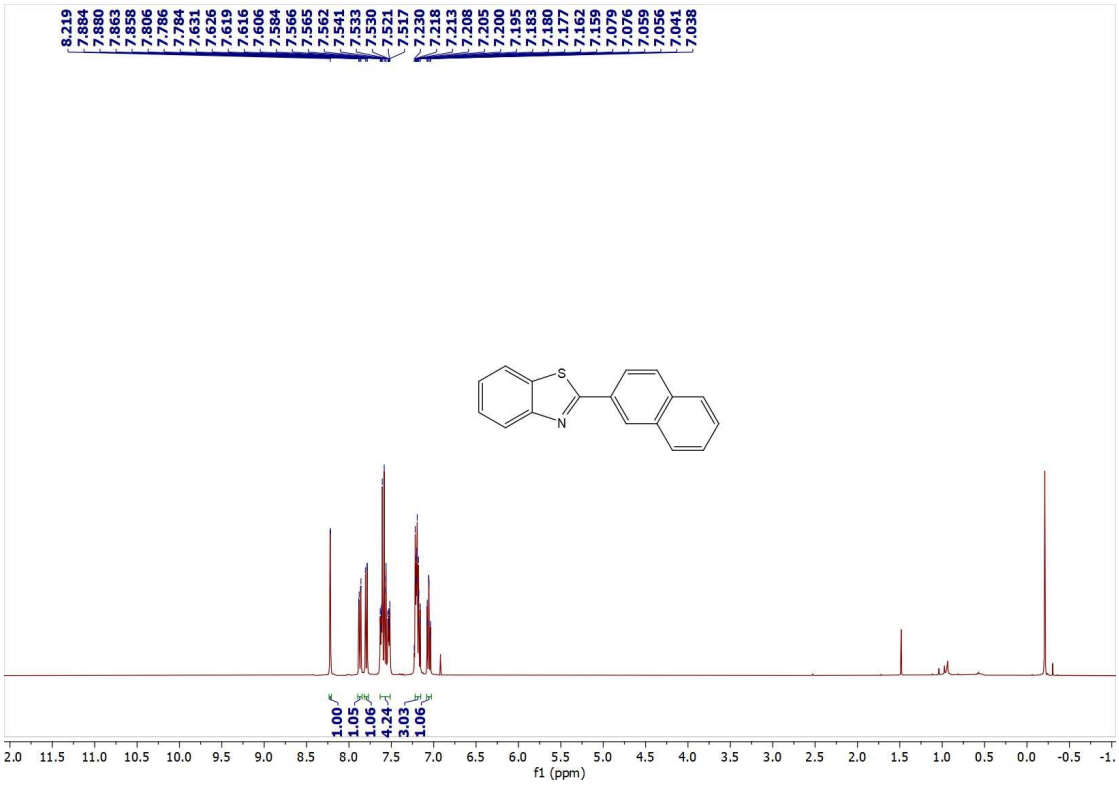


Fig. S33 ^{1}H-NMR Spectrum of **6o**

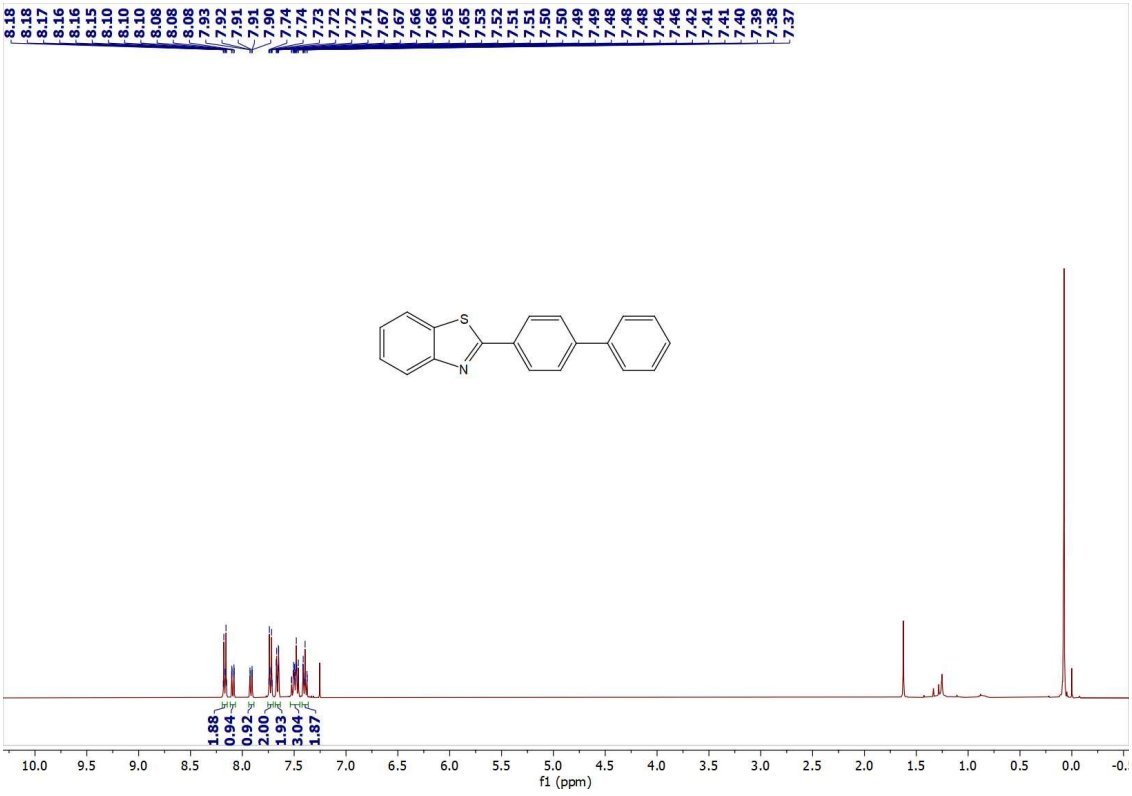


Fig. S34 ^{1}H-NMR Spectrum of **6p**

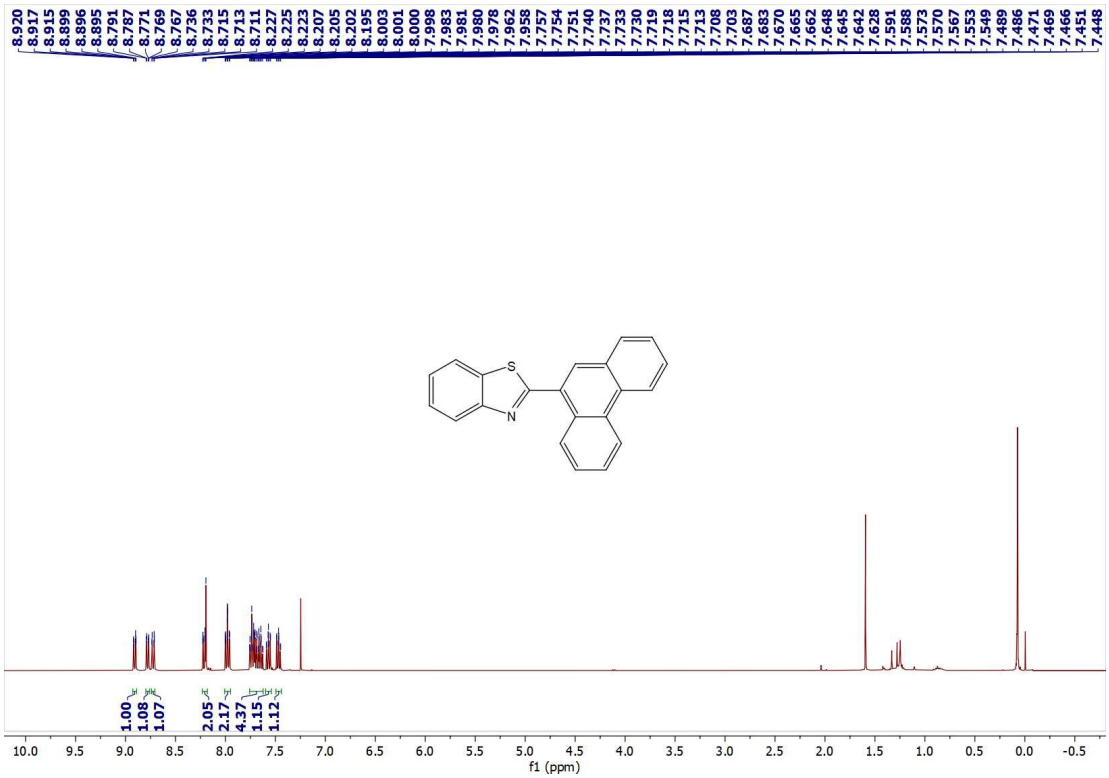


Fig. S35 ^{1}H-NMR Spectrum of **6q**

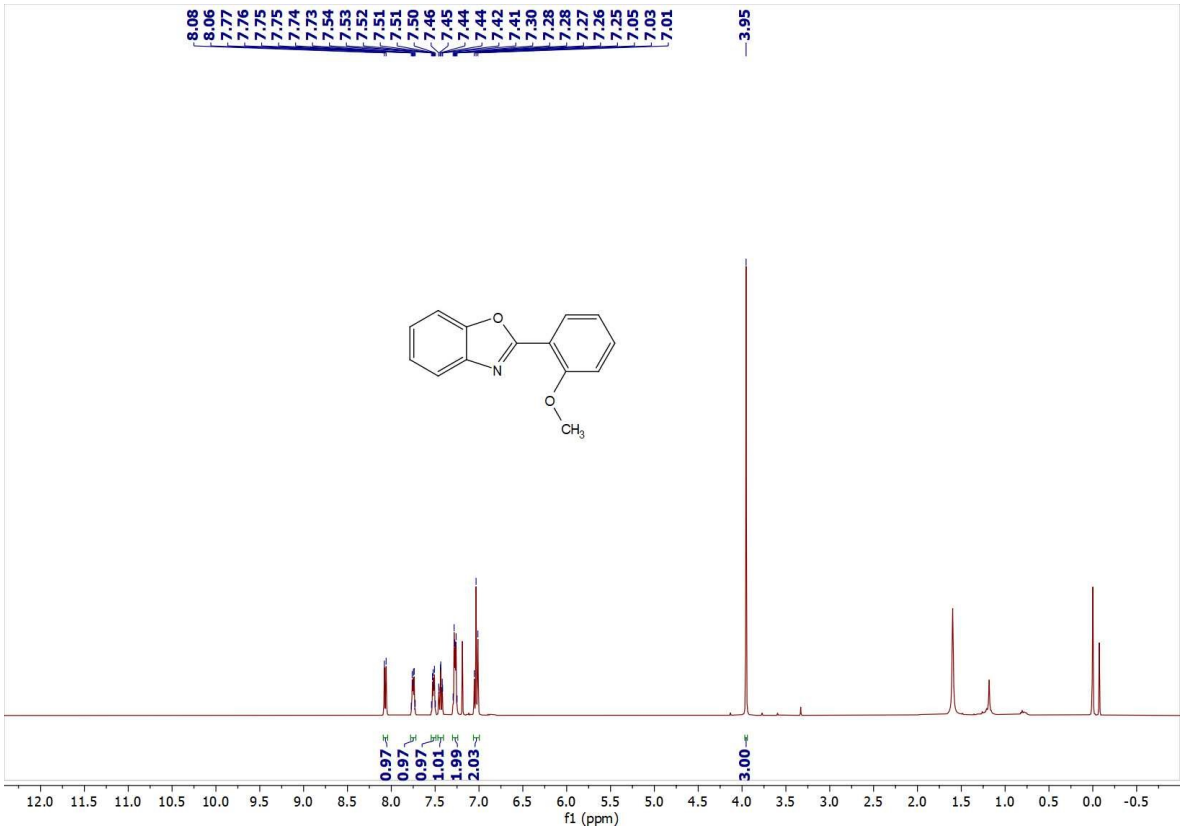


Fig. S36 ^{1}H-NMR Spectrum of **6r**

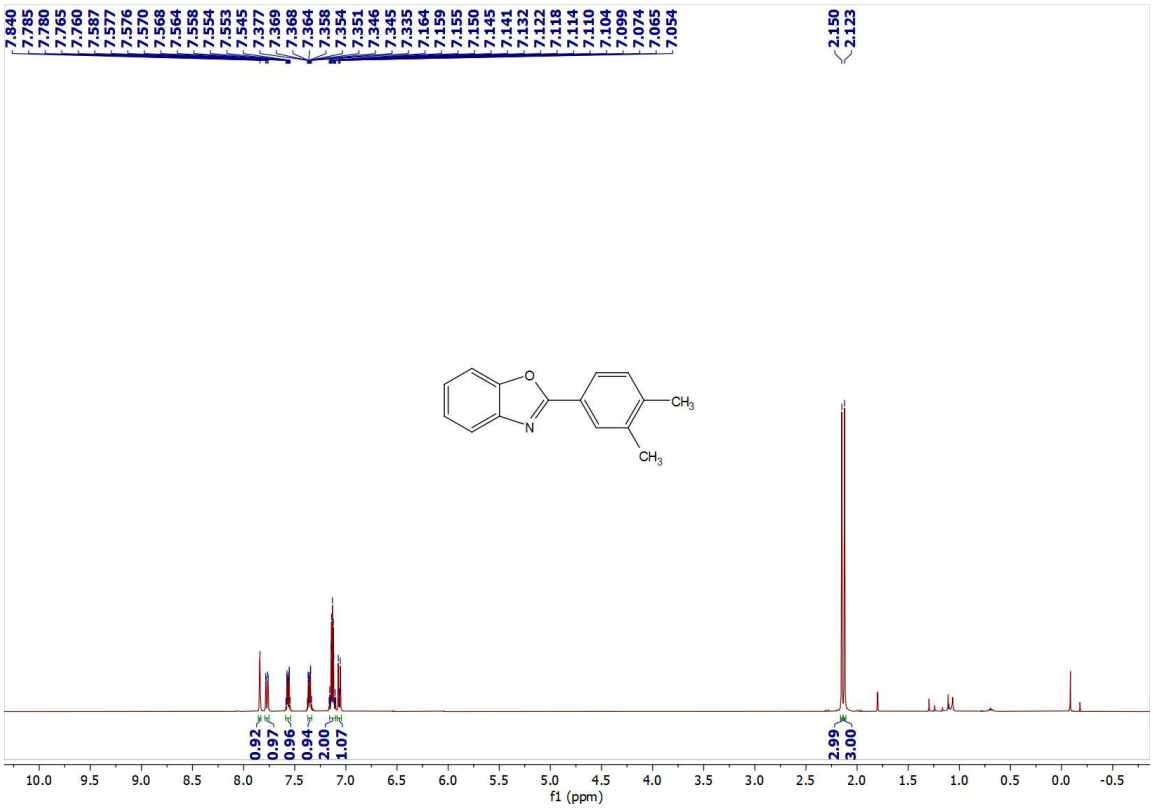


Fig. S37 ^{1}H-NMR Spectrum of **6s**

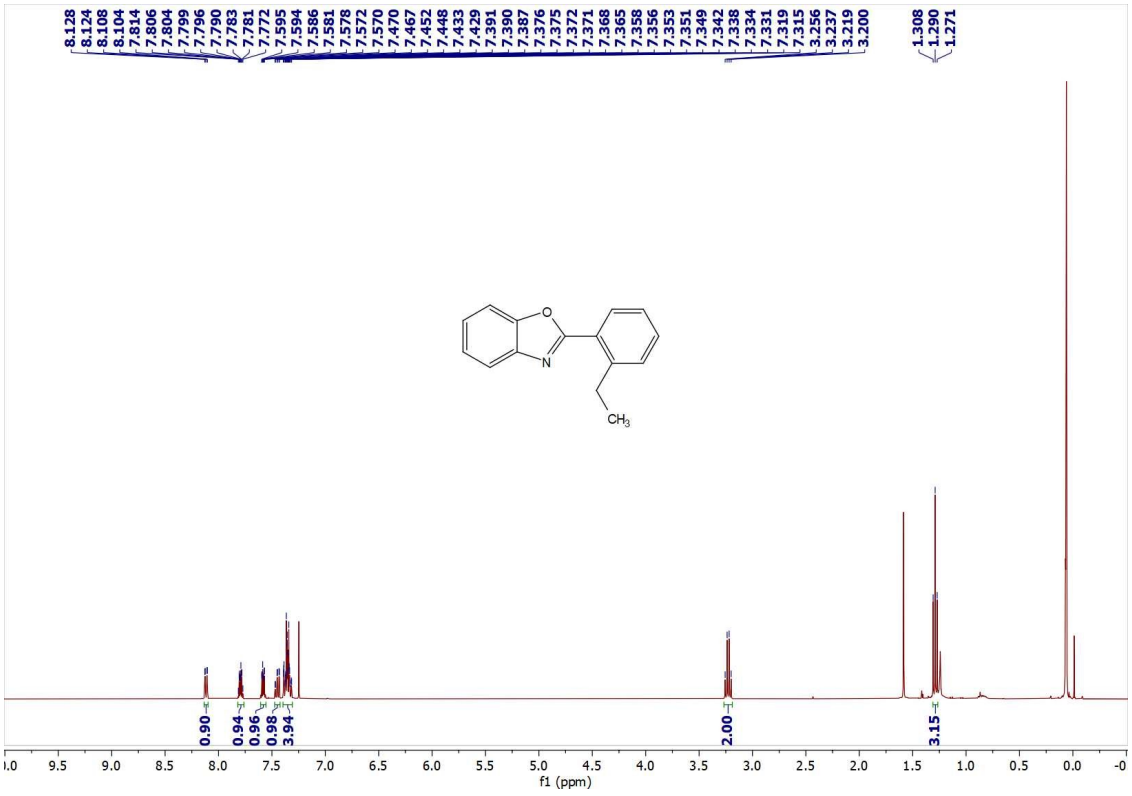


Fig. S38 ^{1}H-NMR Spectrum of **6t**

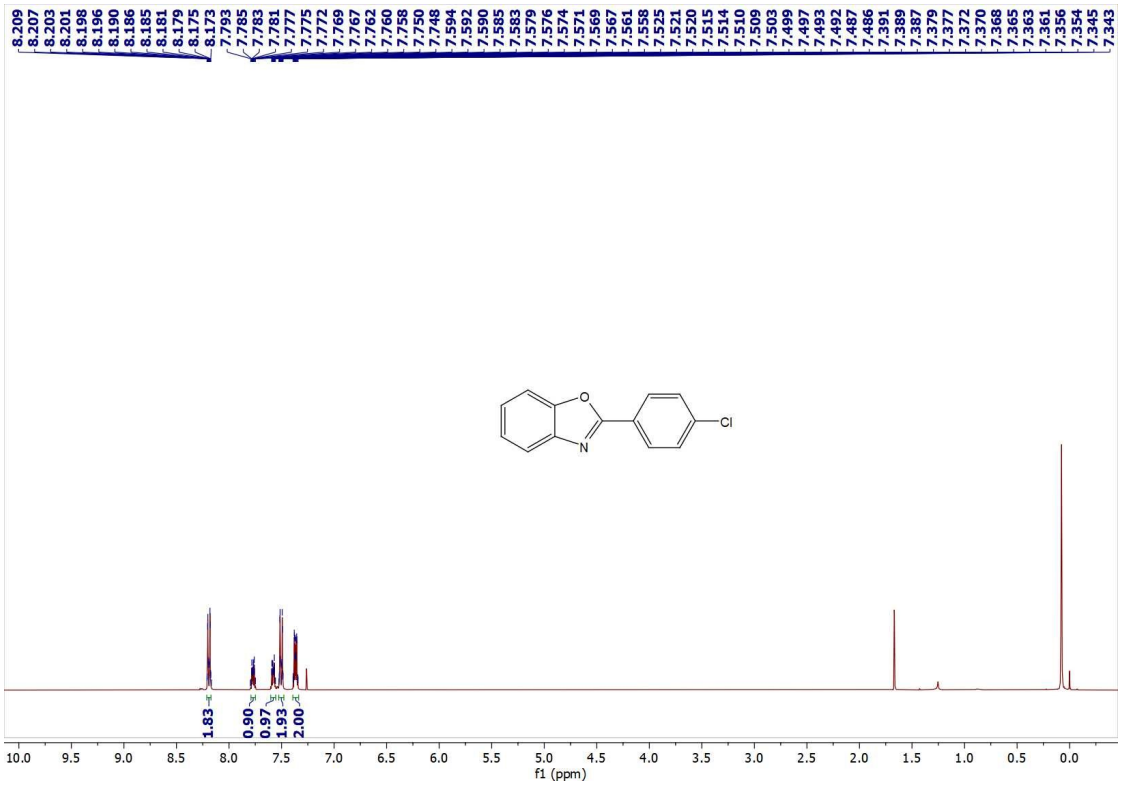


Fig. S39 ^{1}H-NMR Spectrum of **6u**

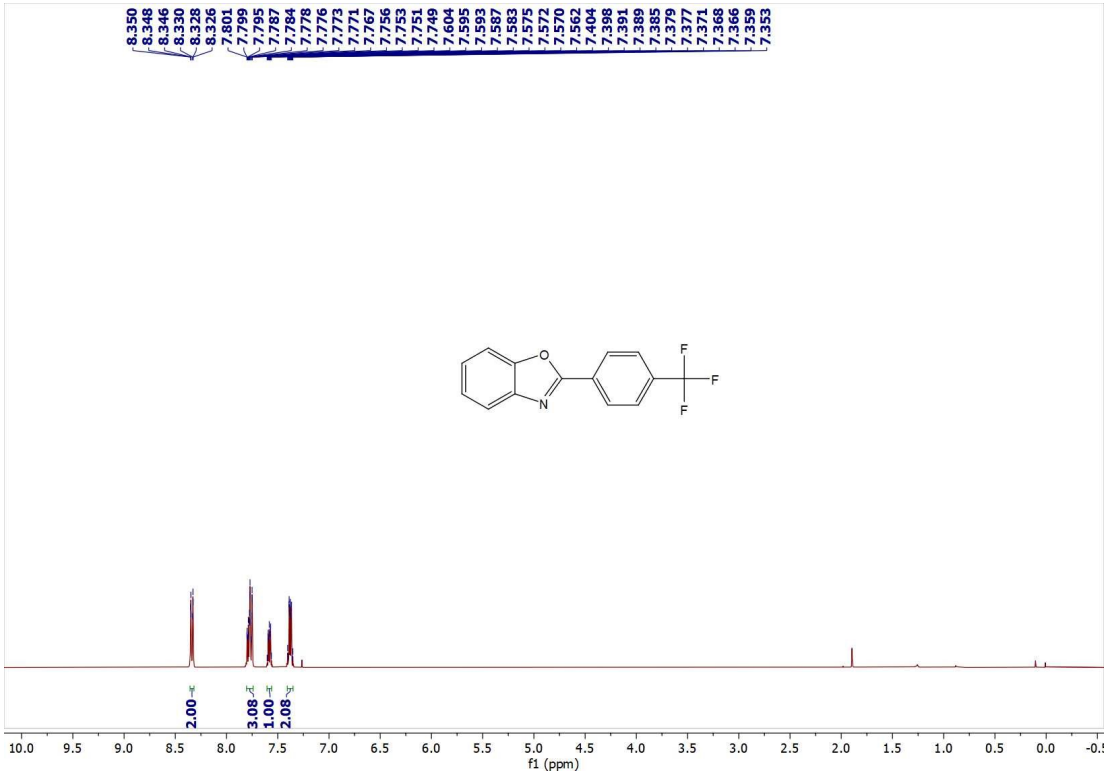


Fig. S40 ^{1}H-NMR Spectrum of **6v**

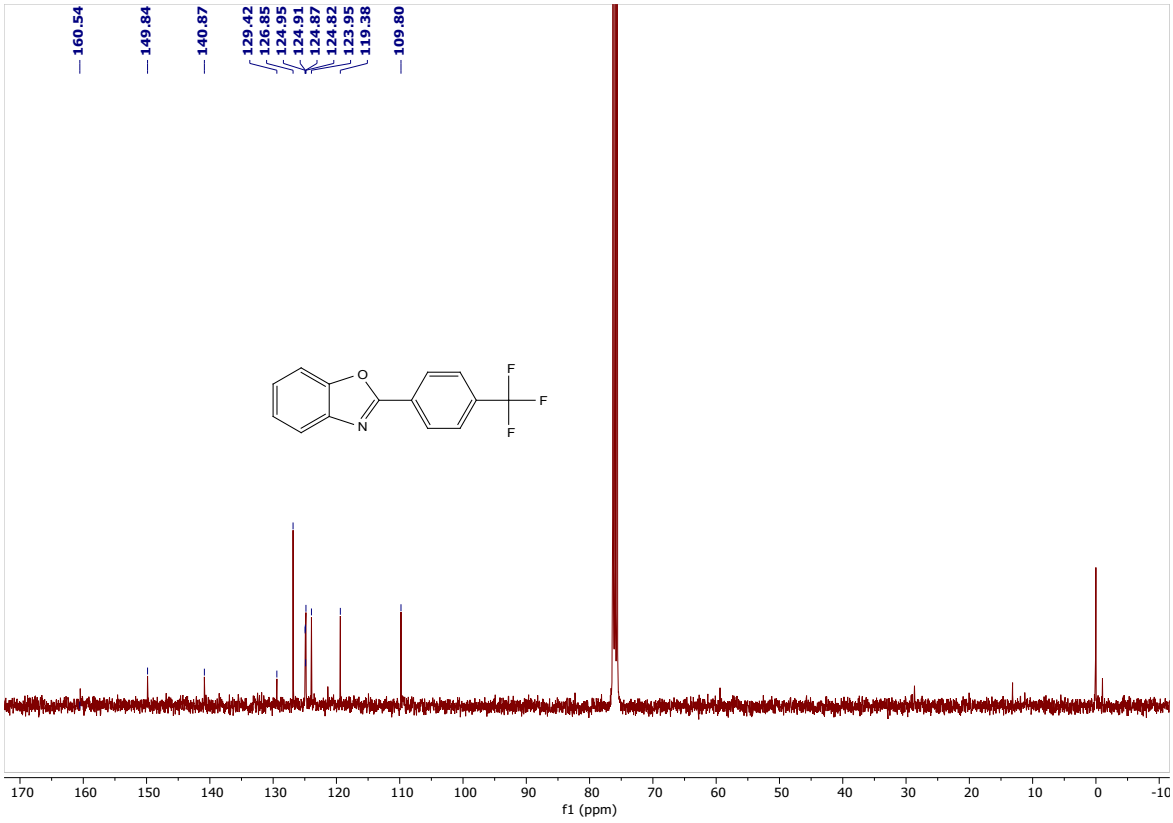


Fig. S41 $^{13}C\{^{1}H\}$-NMR Spectrum of **6v**

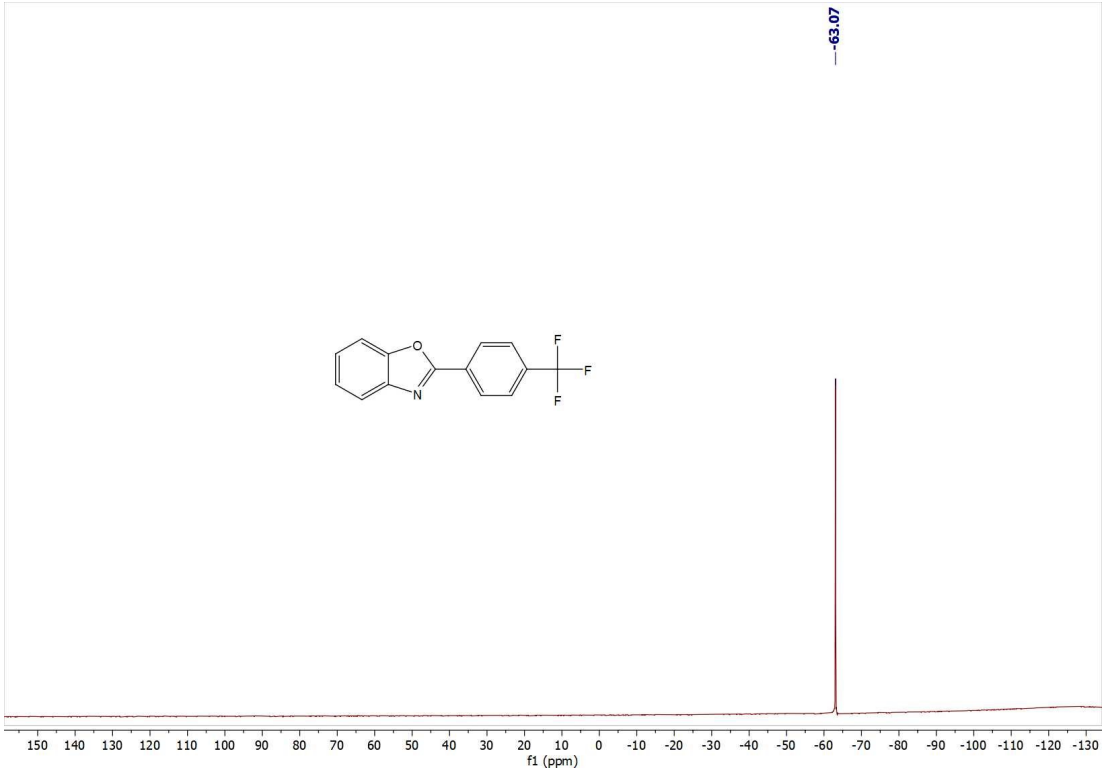


Fig. S42 ^{19}F-NMR Spectrum of **6v**

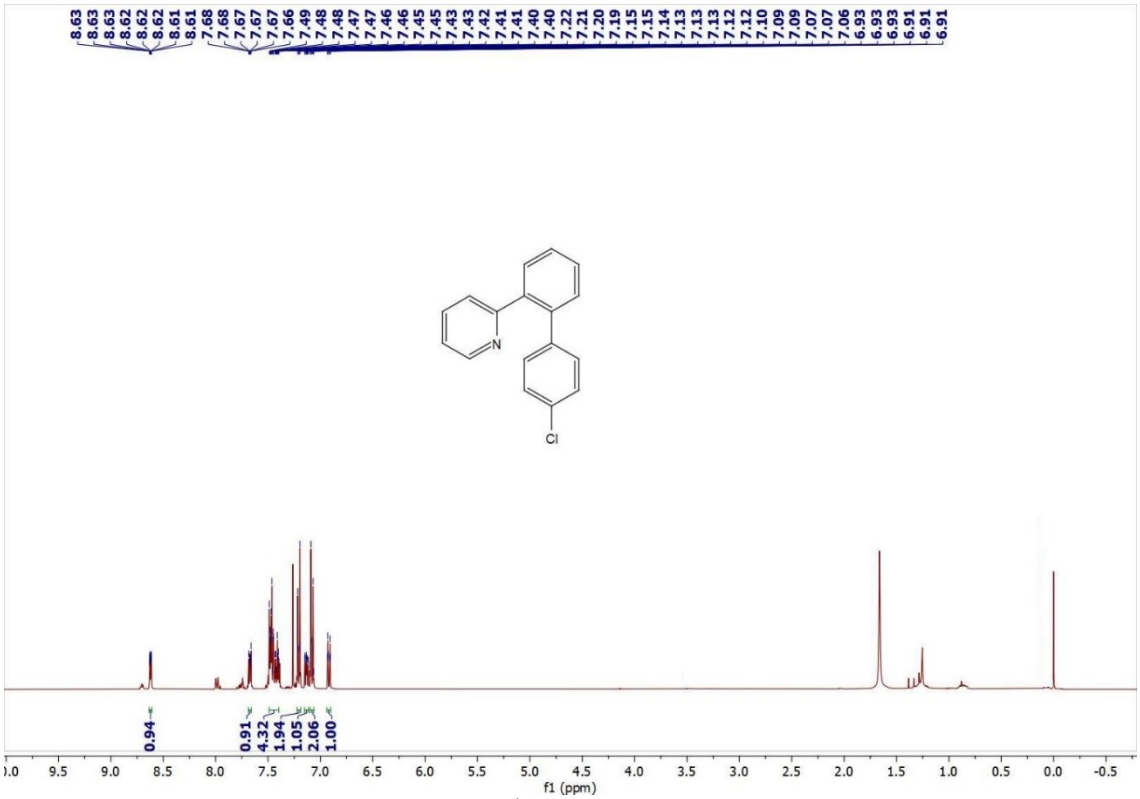


Fig. S43 ^{1}H-NMR Spectrum of **9**

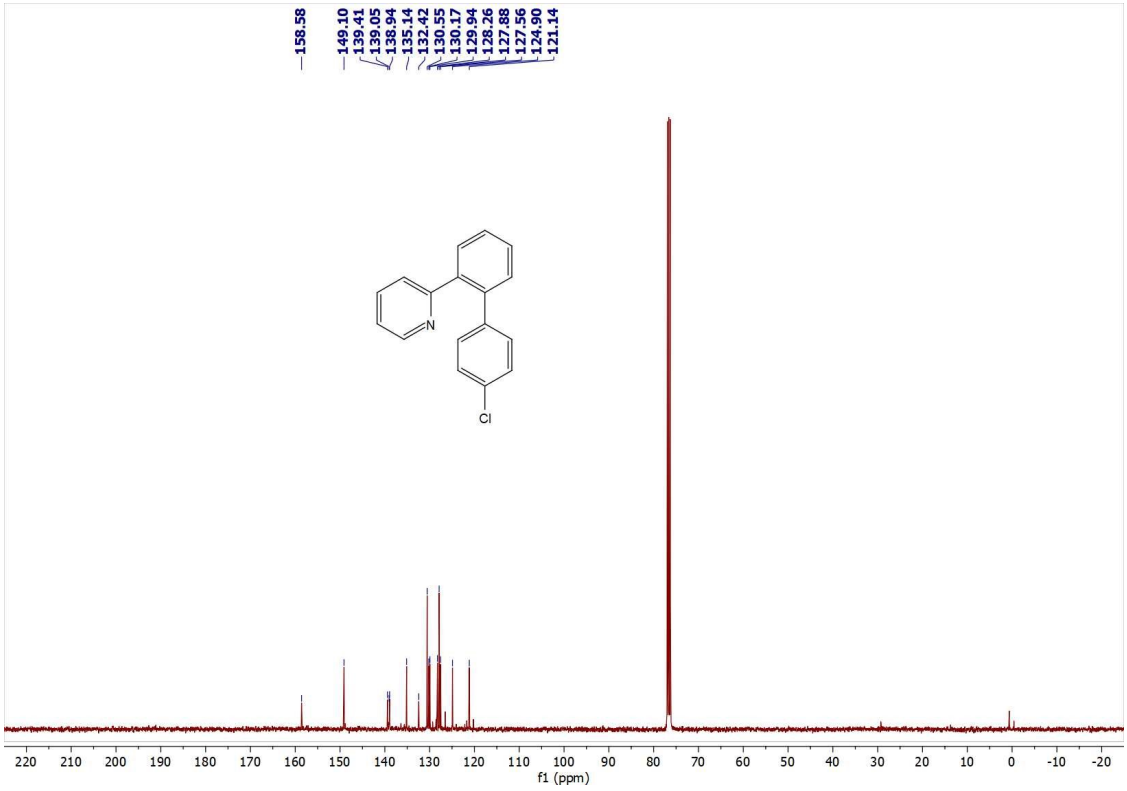


Fig. S44 ^{13}C-NMR Spectrum of **9**

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