Supporting Information

Redox switchable ferrocene decorated n-heterocyclic carbene (NHC) palladium catalyst for cross coupling of arylboronic acid and acetic anhydride in phosphine, base and additive free conditions

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Experimental

The stepwise synthesis of the ligand and metal complex was carried out in oven dried glass wares in Schlenk line under Argon atmosphere. All the chemicals purchased from commercial suppliers (Avra, Alfa Aesar and Sigma-Aldrich) were used as received. Purifications of each step in the ligand synthesis were carried out by column chromatography using silica gel (100-200 mesh). Analytical thin-layer chromatography was performed using silica gel 60F254 plates and visualized under UV light. NMR (^{1}H, ^{13}C, ^{31}P, ^{19}F) spectra were recorded on a Brucker Avance 500 & 400 MHz spectrometer at room temperature using TMS as an external standard. All chemical shifts (δ) are reported in parts-per-million (ppm, δ) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet etc. HRMS were recorded on a Q-TOF spectrometer (Xevo XS QTof mass spectrometer) in electrospray ionization mode. Absorption spectra were recorded using SPECORD® 210 PLUS spectrophotometer (SPECORD® 210 PLUS, Analytik Jena, Germany). UV-Vis NIR, Agilent Technologies). The voltammetric analysis was carried out using conventional three electrode system (Working electrode: Platinum disk; Counter electrode: Platinum wire; Reference electrode: Ag/AgCl) by using BASI electrochemical analyzer (Epsilon EClipse™, USA). Melting points were recorded using M-560, BUCHI Laborites AGCH-9230 Flawil 1, Switzerland. FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer with KBr pellet as well as U-ATR in the frequency range of 4000-400 cm^{-1}. XPS spectra were recorded by an X-ray photo electron Spectrometer (ESCALAB Xi+, Thermo Fisher Scientific Pvt. Ltd., UK). The Elemental analyses were conducted on a CHN analyzer PE-2400 (Perkin Elmer, USA).

1. Synthesis and characterization of 2-(3-Ethyl-(1H-imidazol-3-ium-1-yl))-5-ferrocenylpyridine hexafluorophosphate ligand (L1)

1.1 Synthesis of 2-(1H-imidazol-1-yl)-5-ferrocenylpyridine:

Imidazole (3.6 mmol, 0.245 g), KO^{t}Bu (4.2 mmol, 0.471 g), 2-bromo-4-ferrocenylpyridine (3 mmol, 1.02 g) and CuI (0.3 mmol, 0.057 g) were taken in a two necked RB and 10 mL DMF was added and heated at 120 °C for 24 h. The reaction mixture was cooled to room temperature, quenched with distilled water and then extracted using EtOAc (3x30 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane/ethyl acetate) to obtain the final product, (**1**). Yield: 0.781 g (78.96 %), ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm: 8.58 (d, 1H), 8.34 (s, 1H), 7.86 (dd, J = 8.4, 2.4 Hz, 1H), 7.64 (t, J = 1.3 Hz, 1H), 7.28 (dd, J = 8.4, 0.8 Hz, 1H), 7.21 (s, 1H), 4.68 (t, J = 5 Hz, 2H), 4.41 (t, J = 5 Hz, 2H), 4.08 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.2, 135.9, 134.8, 134.4, 130.5, 116.1, 112.0, 80.6, 69.7, 66.4. HRMS (ESI-TOF-Q) calculated for $C_{18}H_{15}FeN_3$ $[M]^+$: 330.0615, found: 330.0761; Mp: 210-212 °C; Anal. Calcd for Chemical Formula: $C_{18}H_{15}FeN_3$: C, 65.68; H, 4.59; N, 12.77, found: C, 65.70; H, 4.57; N, 12.79.

1.2 Characterization of 2-(1H-imidazol-1-yl)-5-ferrocenylpyridine

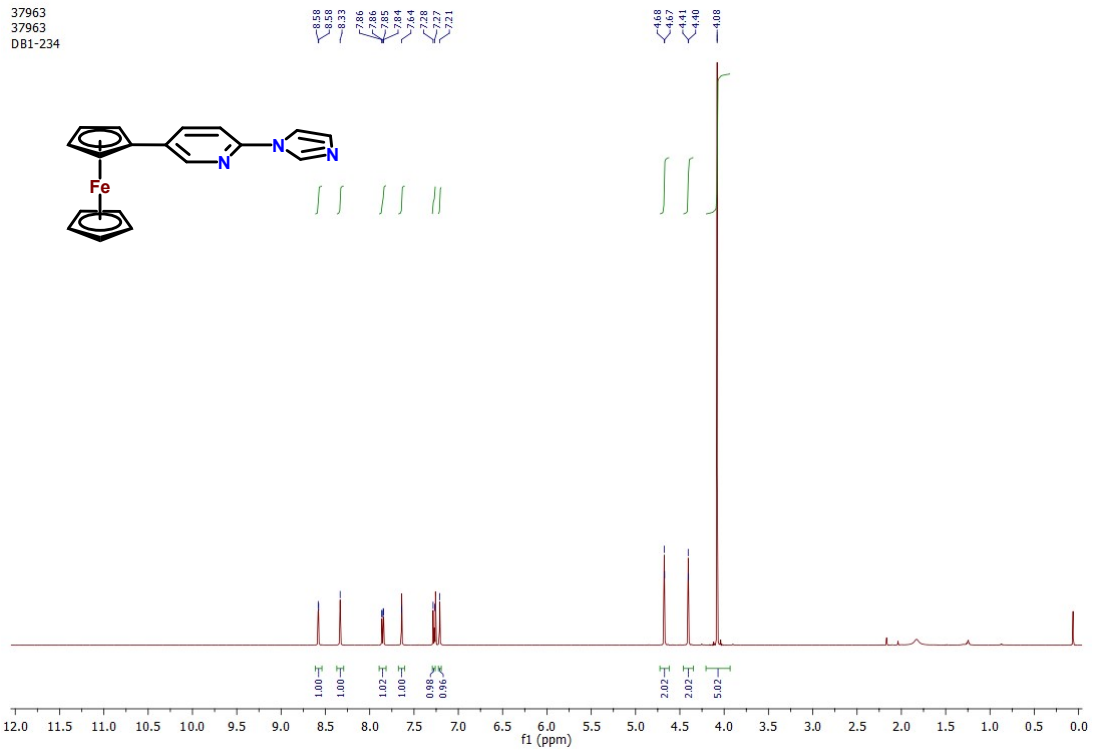


Figure S1 ^{1}H NMR spectrum of 2-(1H-imidazol-1-yl)-5-ferrocenylpyridine

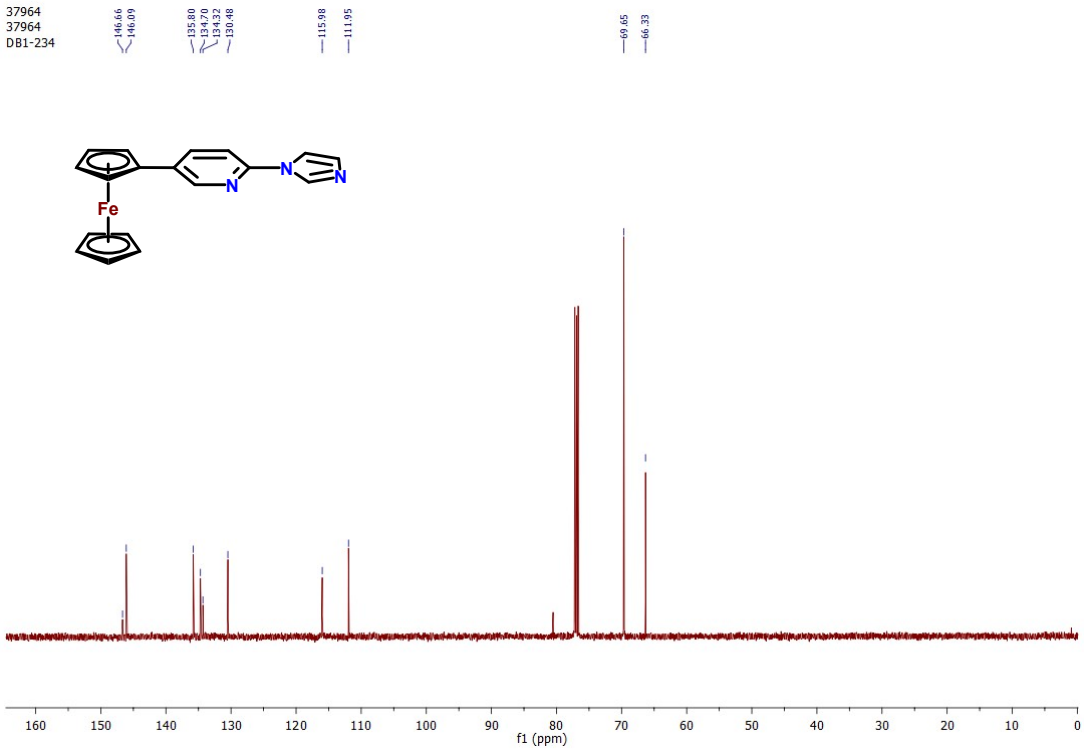


Figure S2 ^{13}C NMR spectrum of 2-(1H-imidazol-1-yl)-5-ferrocenylpyridine

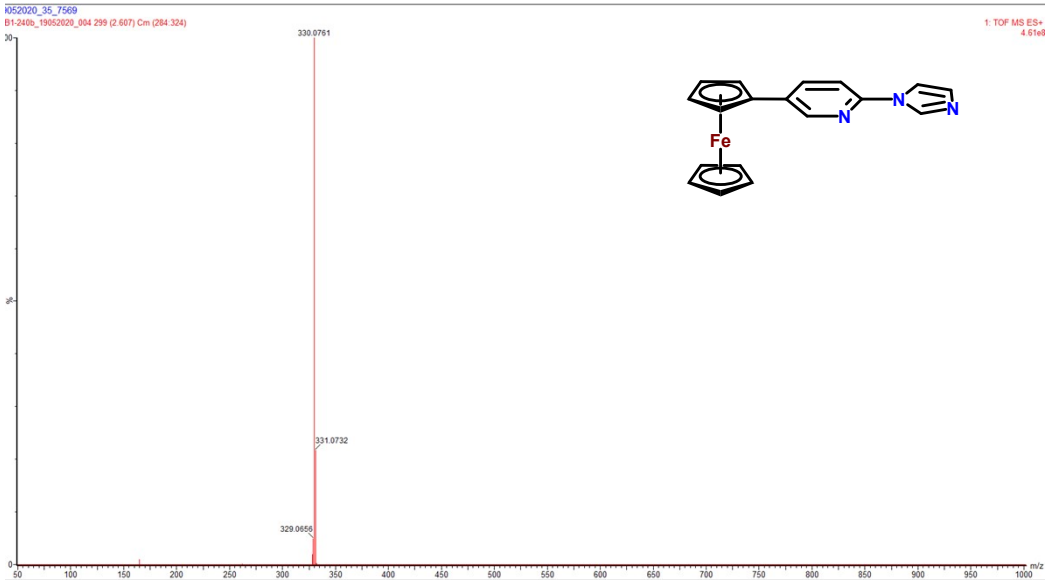


Figure S3 HRMS spectrum of 2-(1H-imidazol-1-yl)-5-ferrocenylpyridine

1.3 Synthesis of 2-(3-ethyl-(1H-imidazol-3-ium-1-yl))-5-ferrocenylpyridine hexafluorophosphate (L1):

2-(1H-imidazol-1-yl)-5-ferrocenylpyridine (1 mmol, 0.329 g) was taken in a round bottom flask and dissolved in dry acetonitrile (10 mL) by heating the mixture at 70 °C for 30 min. Then iodoethane (5 mmol, 0.4 mL) was added into it and refluxed with continuous stirring under N_2 atmosphere for 48 h. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and then diethyl ether was added under vigorous stirring for precipitation. Orange precipitate was obtained immediately after the addition of ether. The supernatant solution was decanted off after sometime. Washed several times with ether and the precipitate was finally dried under vacuo. Aqueous NH_4PF_6 solution was added and the orange compound was extracted in dry dichloromethane to finally obtain the desired ligand **L1**. Yield: 0.447 g (89%); ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 10.04 (t, *J* = 1.6 Hz, 1H), 8.80 (d, *J* = 2.0 Hz, 1H), 8.52 (t, *J* = 2.0 Hz, 1H), 8.33 (dd, *J* = 8.6, 2.3 Hz, 1H), 8.07 (t, *J* = 1.9 Hz, 1H), 7.92 (dd, *J* = 8.5, 0.7 Hz, 1H), 5.06 (t, *J* = 1.9 Hz, 2H), 4.50 (t, *J* = 1.9 Hz, 2H), 4.32 (q, *J* = 7.3 Hz, 2H), 4.08 (s, 5H), 1.51 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 145.6, 143.9, 137.4, 136.5, 134.3, 123.1, 119.1, 113.9, 79.2, 70.0, 69.6, 66.8, 44.9, 14.9. HRMS (ESI, m/z) calculated for $C_{20}H_{20}FeN_3$ $[M]^+$: 358.1006, found: 358.1161. FT-IR (KBr pellet, cm^{-1}): 3160.82, 1504.12, 1216.49, 831.95, 560.82; Mp: 238−240 °C; Anal. Calcd for Chemical Formula: $C_{20}H_{20}PF_6FeN_3$: C, 47.74; H, 4.01; N, 8.35; found: C, 47.76; H, 4.02; N, 8.37.

1.4 Characterization of 2-(3-Ethyl-(1H-imidazol-3-ium-1-yl))-5-ferrocenylpyridine hexafluorophosphate ligand (L1)

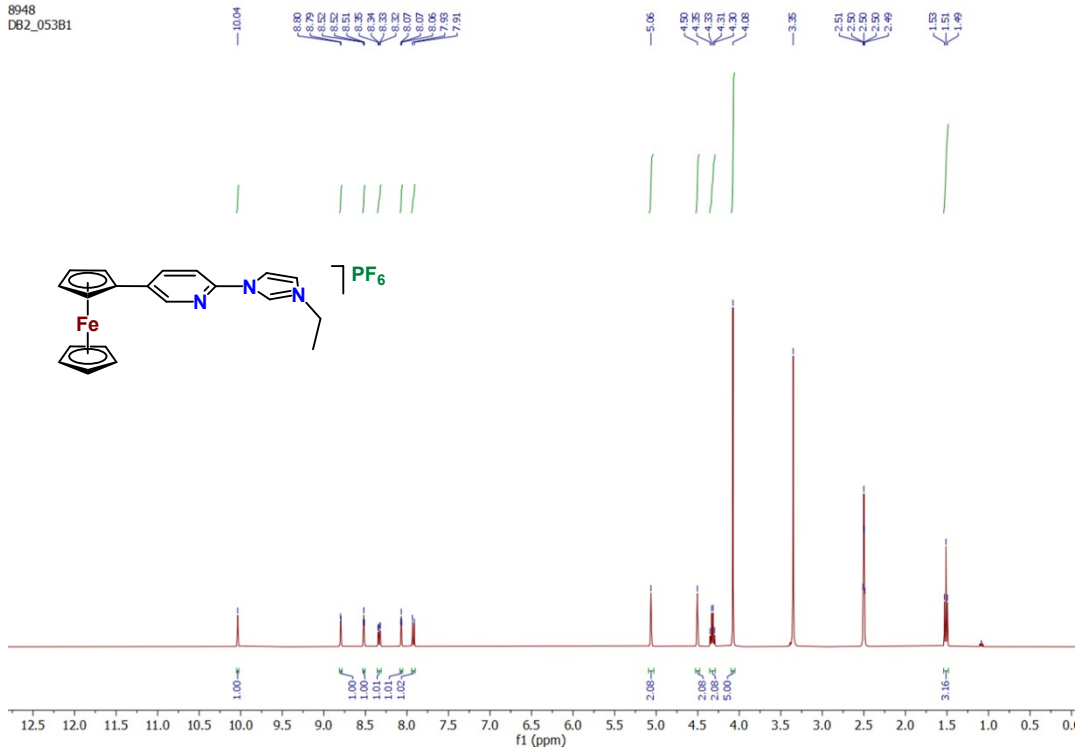


Figure S4 ^{1}H NMR spectrum of **L1**

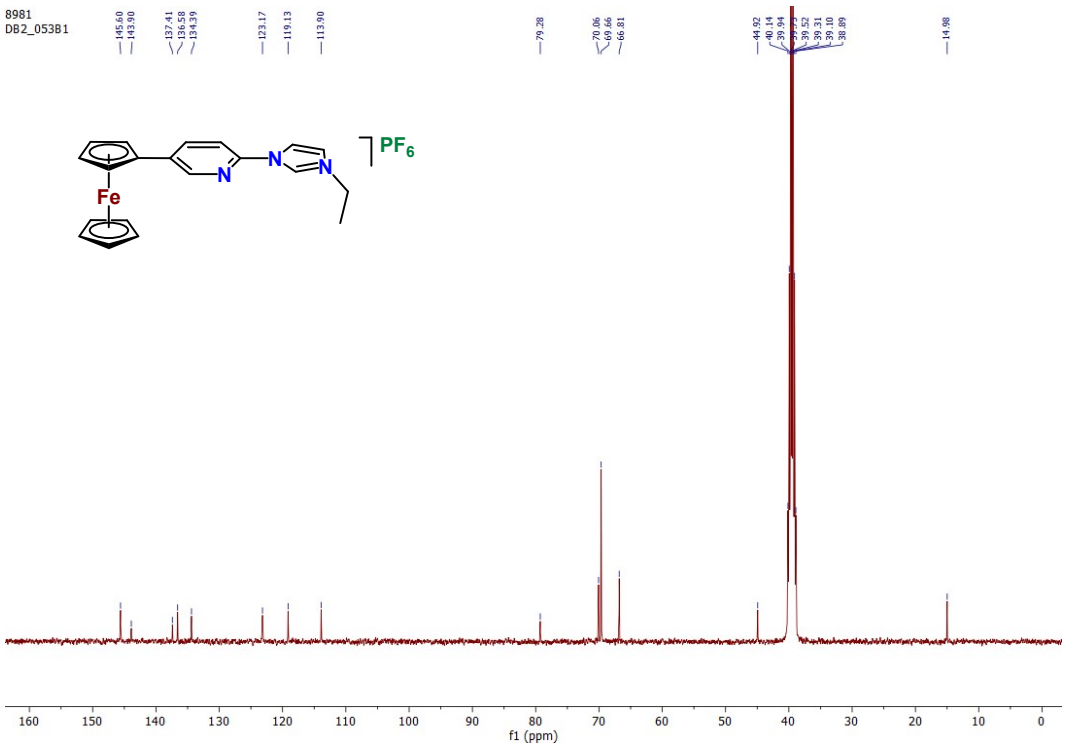
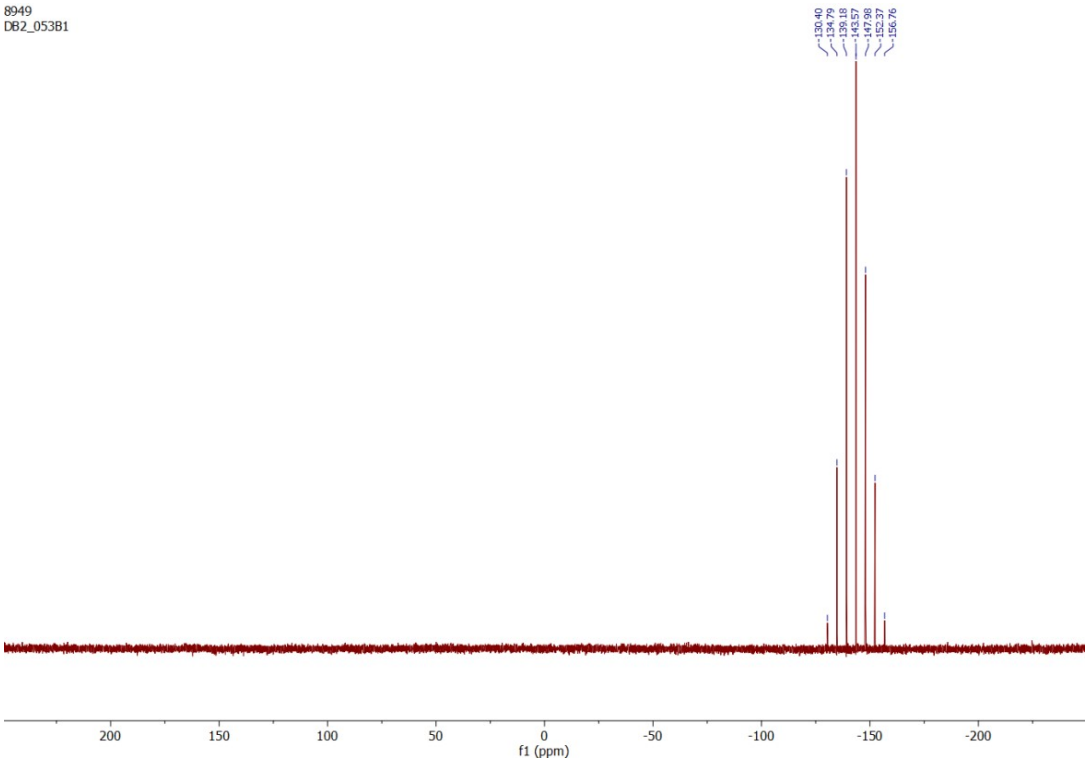


Figure S5 ^{13}C NMR spectrum of **L1**



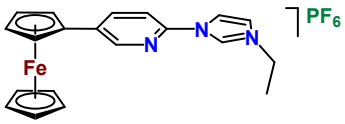
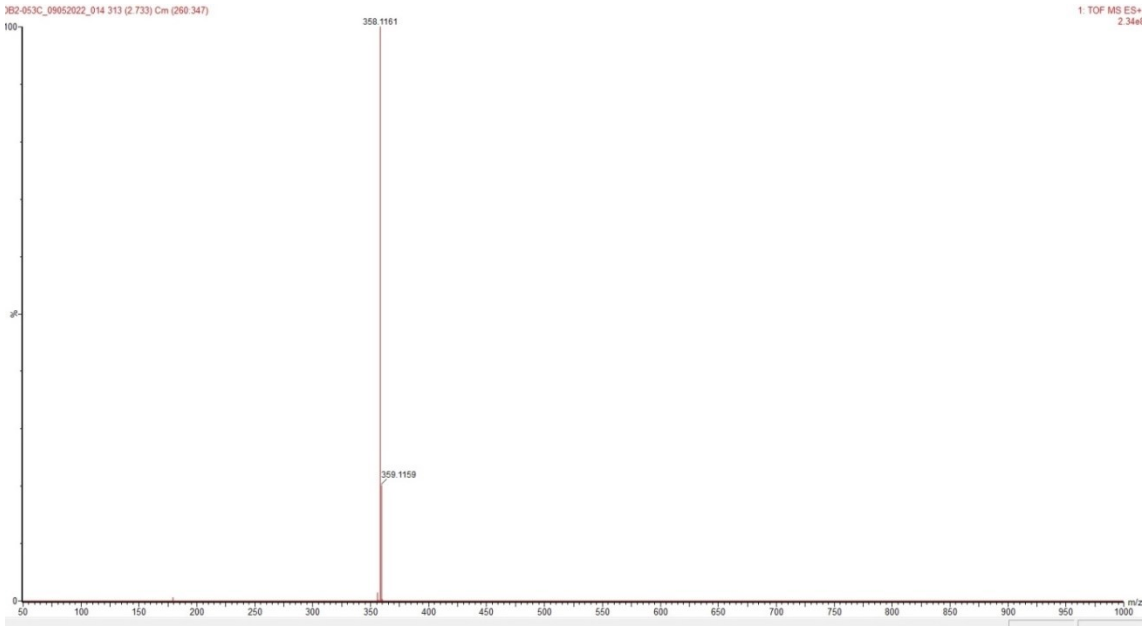


Figure S6 ^{31}P NMR spectrum of **L1**



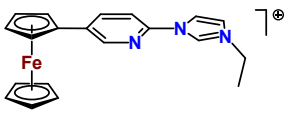


Figure S7 HRMS spectrum of **L1**

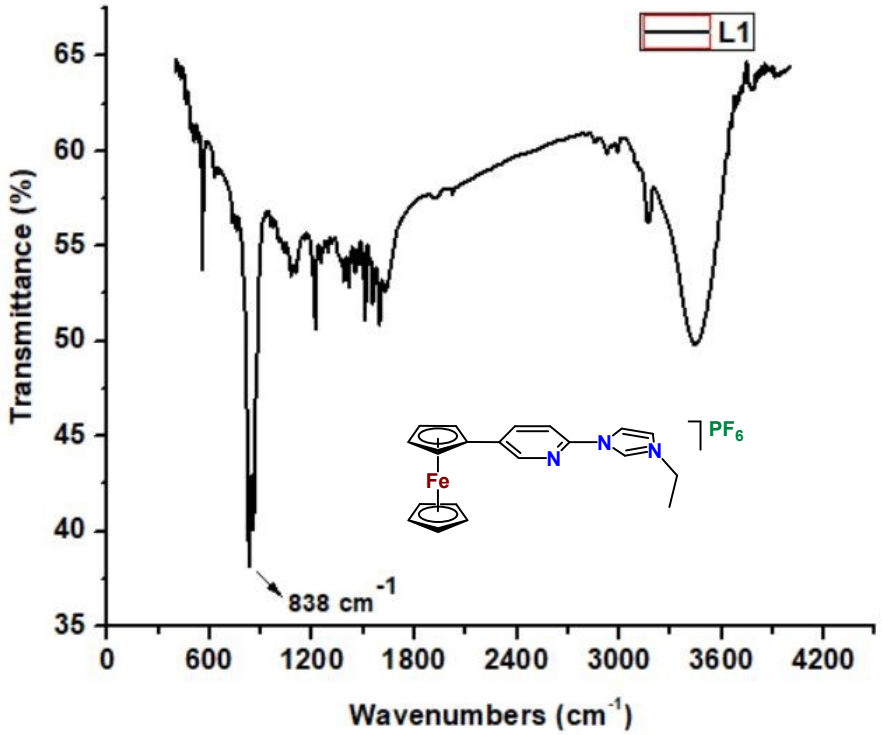


Figure S8 FT-IR spectrum of **L1**

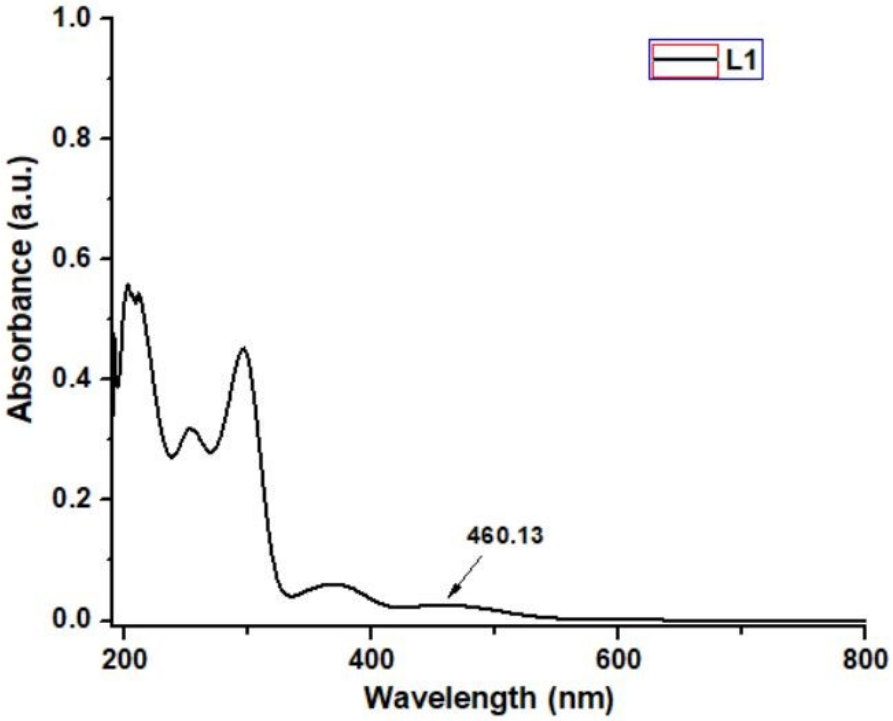


Figure S9 UV-Vis spectrum of **L1**

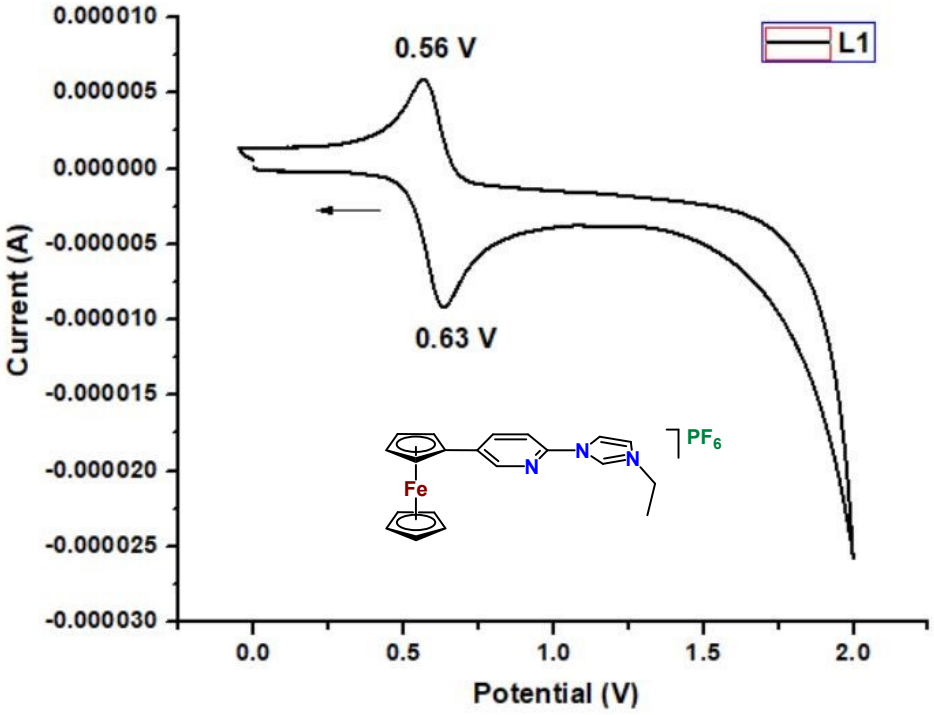


Figure S10 Full scan cyclic voltammogram from 0 to 2 V for **L1.** Working electrode: Platinum disc; Counter electrode: Platinum Wire; Reference electrode: Ag/AgCl. Solvent: acetonitrile; Electrolyte: 0.1 M tetrabutylammonim hexafluorophosphate; [**L1**] = 0.001 M; Scan rate: 100 mVs^{-1}; RT

2. Synthesis of [(L1)Pd(acac)](PF_6) complex (1)

0.100 g (0.2 mmol) of ligand (**L1**) was added to a flame dried Schlenk RB and dissolved in 10 mL of dry acetonitrile. Then 0.060 g (0.2 mmol) of $Pd(acac)_2$ was added followed by 0.026 g (0.24 mmol) of KO^{t}Bu and refluxed for 5 h. Then reaction mixture was allowed to cool to room temperature and the solvent was evaporated under reduced pressure. Dry dichloromethane was added and the mixture solution passed through a bed of celite and the bed was washed further with dry DCM to obtain a red coloured filtrate. The filtrate was concentrated to 1 mL and dry hexane (10 mL) was added for precipitation. The peach red precipitate obtained was washed two to three times with dry hexane and cannula filtration was performed to decant the supernatant liquid. Finally, the precipitate was dried well under vacuo. Yield: 0.102 g (72.8 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 9.01 (s, 1H), 8.89 (d, *J* = 8.6 Hz, 2H), 8.61 (d, *J* = 2.1 Hz, 1H), 8.29 (dd, *J* = 8.6, 2.2 Hz, 1H), 5.63 (s, 1H), 4.68 (t, *J* = 1.9 Hz, 2H), 4.49 – 4.48 (m, 2H), 4.46 (d, *J* = 7.3 Hz, 2H), 4.10 (s, 5H), 2.07 (s, 3H), 1.50 (t, *J* = 7.3 Hz, 3H), 1.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 142.5, 140.3, 137.2, 135.8, 123.3, 119.6, 114.9, 101.8, 101.7, 78.8, 70.8, 70.2, 67.1, 48.4, 44.2, 25.6, 16.8. HRMS (ESI, m/z): calculated for $C_{25}H_{26}FeN_3O_2Pd$: $[M\text{-}PF_6]^+$: 562.0409, found: 562.0765; FT-IR (KBr pellet, cm^{-1}): 3429, 3088, 2927, 1511, 1104, 838; Mp: 250−252 °C; Anal. Calcd for Chemical Formula: $C_{25}H_{26}F_6FeN_3O_2PPd$: C, 42.43; H, 3.70; N, 5.94; found: C, 42.45; H, 3.72; N, 5.92.

3. Characterization of [(L1)Pd(acac)](PF$_6$) complex (1)

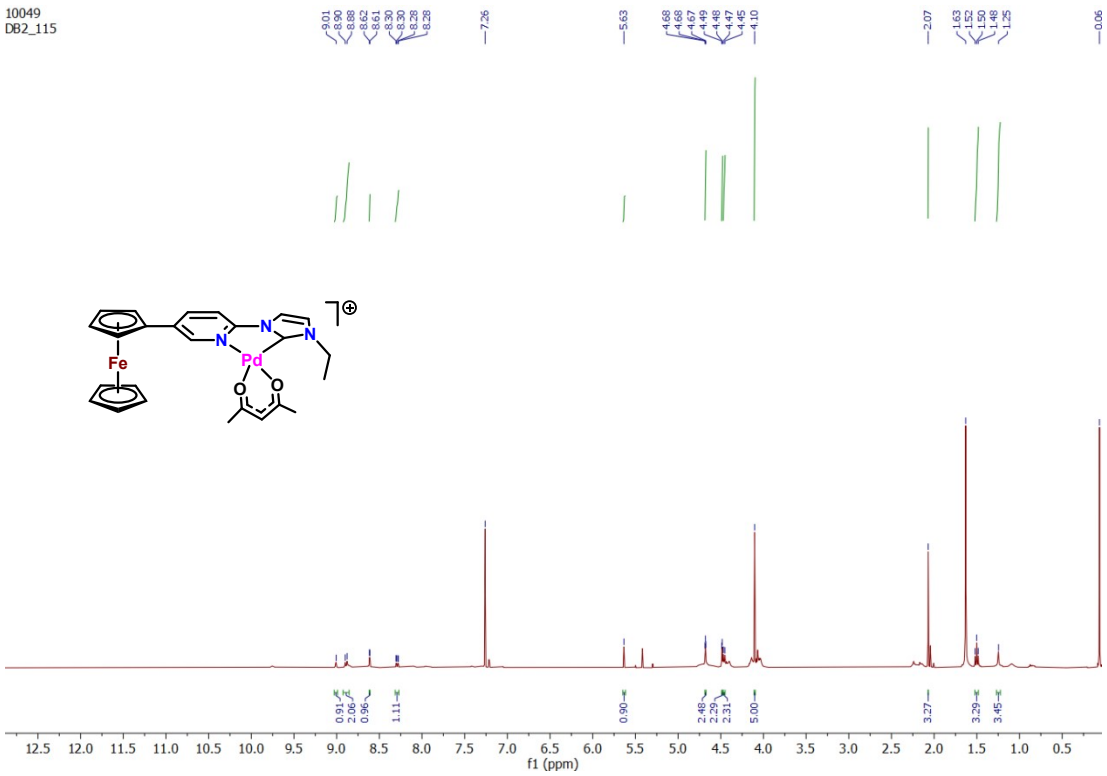


Figure S11 ^{1}H NMR spectrum of **1**

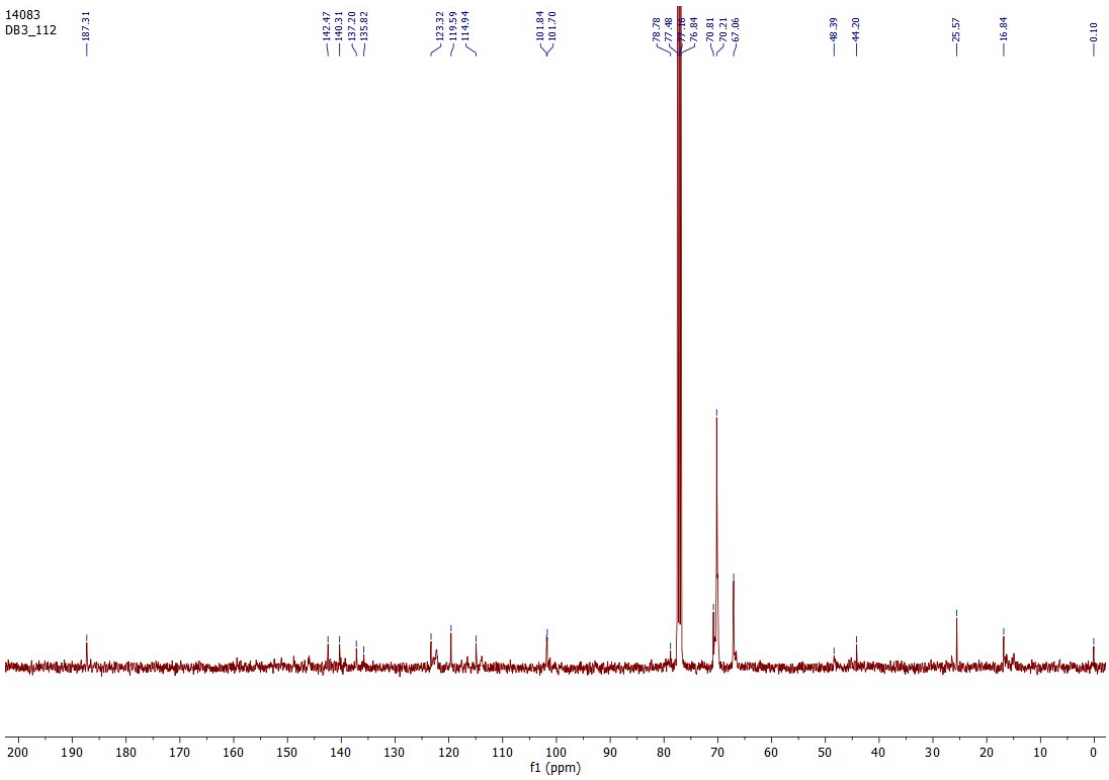


Figure S12 ^{13}C NMR spectrum of **1**

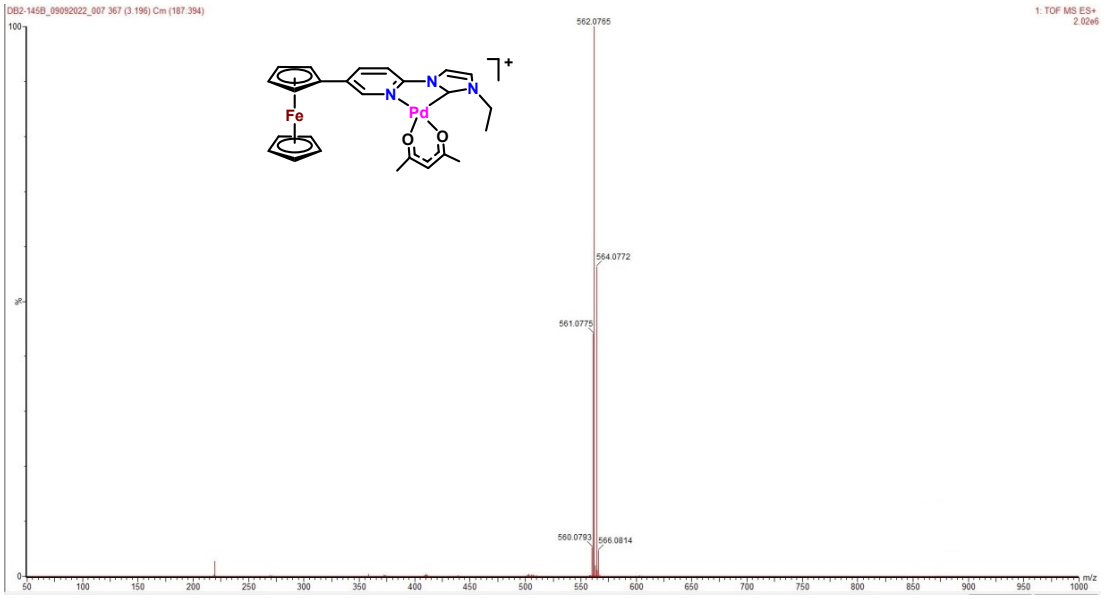


Figure S13 HRMS spectrum of **1**

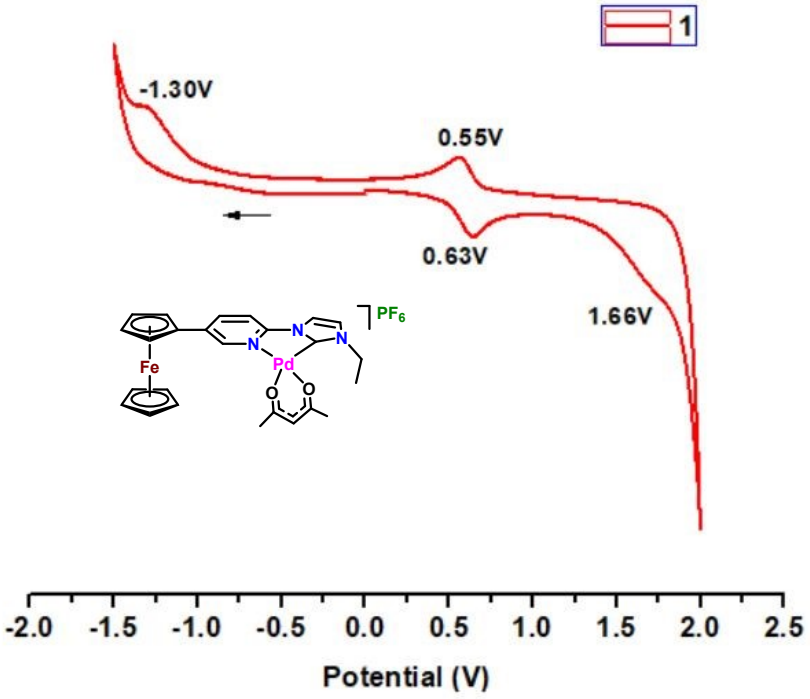


Figure S14 Full scan cyclic voltammogram from 2 to -1.5 V for **1.** Working electrode: Platinum disc; Counter electrode: Platinum Wire; Reference electrode: Ag/AgCl. Solvent: acetonitrile; Electrolyte: 0.1 M tetrabutylammonim hexafluorophosphate; [**1**] = 0.001 M; Scan rate: 100 mVs^{-1}; RT

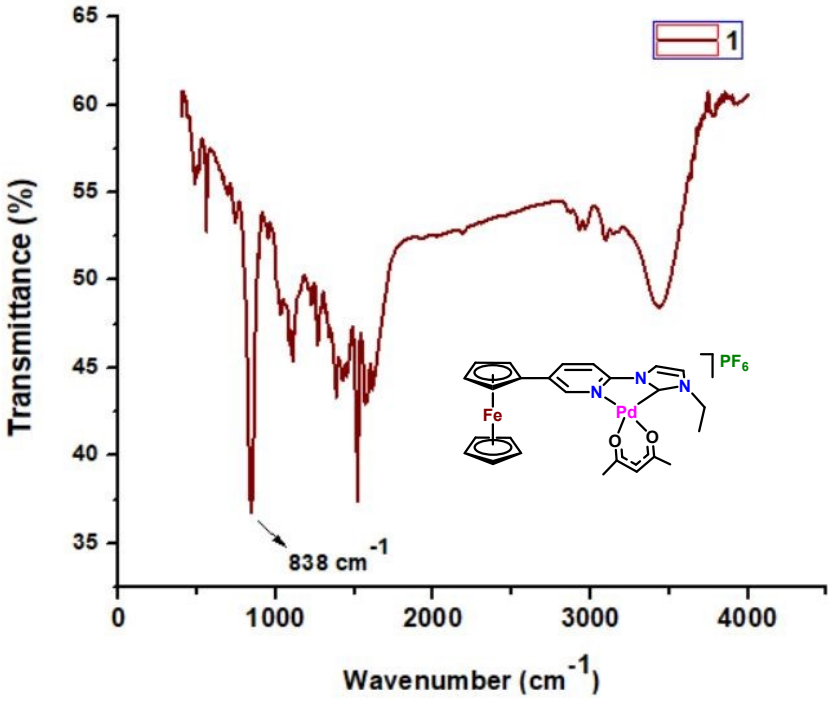


Figure S15 FT-IR Spectrum of **1**

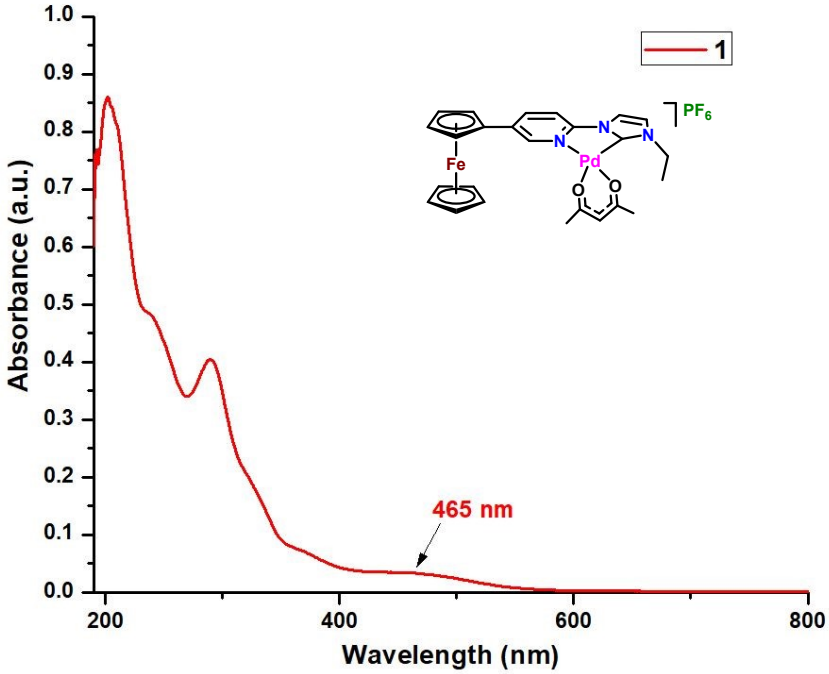


Figure S16 UV-Vis Spectrum of **1**

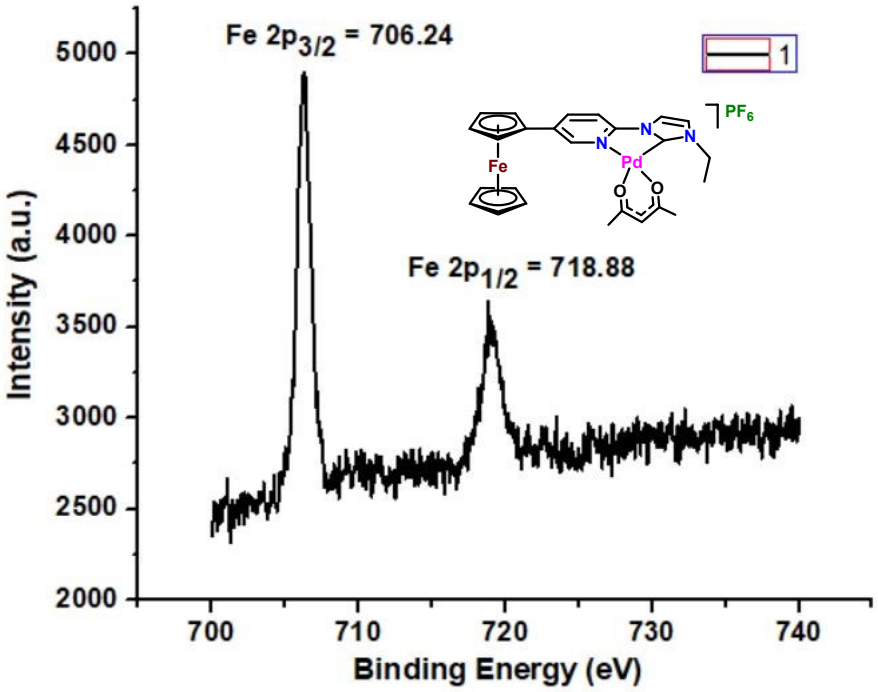


Figure S17 XPS spectra of Fe in **1**

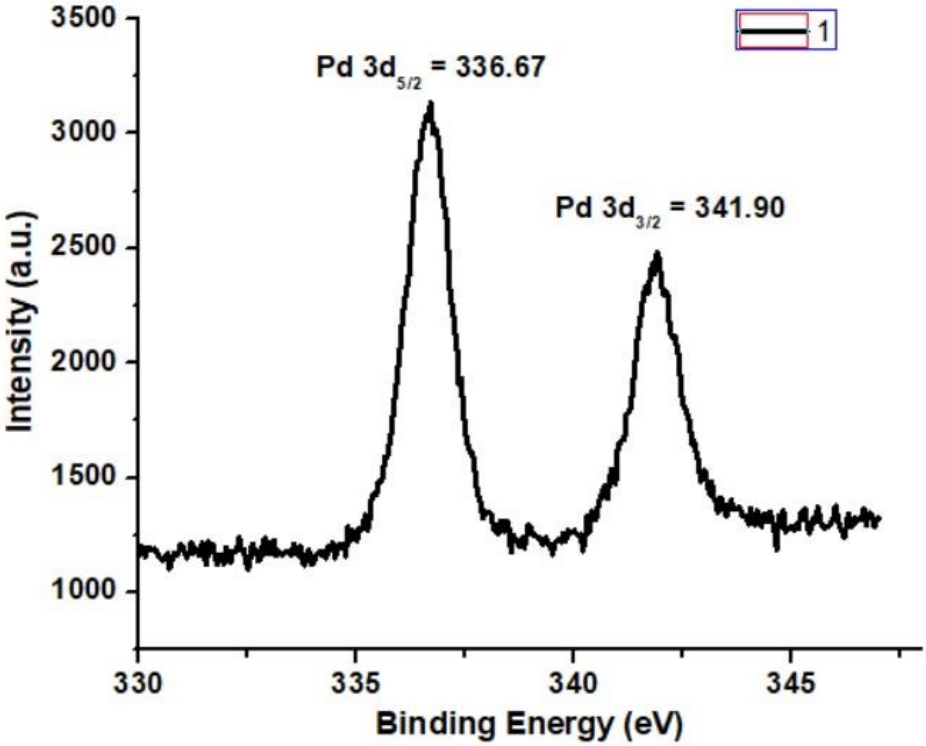


Figure S18 XPS spectra of Pd in **1**

4. Crystallographic Data:

Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low-temperature attachment. All the data were collected at 100(2) K using graphite-monochromated MoK_α radiation (λ_α = 0.71073 Å). The frames were indexed, integrated, and scaled by using the SMART and SAINT software packages[1] and the data were corrected for absorption by using the SADABS program.[2] The structures were solved and refined with the SHELX suite of programs.[3] All the hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. Structure solution and refinement details for compound **1** is provided in the ESI.‡ Pertinent crystallographic data for compound **1** is summarized in Table S1 in the ESI.‡ The crystallographic figures used in this manuscript were generated using Diamond 3.1e software.[4] CCDC-2291666 http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (**1**), contain the supplementary crystallographic data for this paper.

Table S1. Crystallographic Data and Pertinent Refinement Parameters for **1**.

	1
Empirical formula	C_{25} H_{26} Fe N_3 O_2 Pd, F_6 P
Formula Weight	707.71
Crystal System	triclinic
Space Group	*P* -1
a (Å)	9.5977(2)
b (Å)	11.8495(3)
c (Å)	12.2334(3)
α (deg)	110.729(2)
β (deg)	101.751(2)
γ (deg)	93.823(2)
V (Å^3)	1259.23(5)
Z	2
ρ_{calcd} (g cm^{-3})	1.866
μ (mm^{-1})	11.667

F(000)	708
Reflections	
Collected	21859
Independent	4578
Observed [I >2σ(I)]	4342
No. of variables	355
GooF	1.067
R_{int}	0.0526
Final R indices [I > 2σ(I)][a]	R1 = 0.0315 wR2 = 0.0804
R indices (all data)[a]	R1 = 0.0330 wR2 = 0.0814

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]^{1/2}$

Table S2. Comparison of bond distance and angle of **1**.

Bond Distance (Å)	
Pd1-C1	1.962(3)
Pd1-N3	2.028(3)
Pd1-O2	2.002(2)
Pd1-O1	2.032(2)
C1-N1	1.334(4)
C1-N2	1.370(4)
N2-C2	1.388(4)
N3-C6	1.348(4)
C6-N2	1.400(4)
C6-C7	1.378(4)
N3-C10	1.347(4)
N1-C4	1.473(4)
C4-C5	1.513(5)
C2-C3	1.346(5)
C9-C10	1.393(4)
C9-C11	1.465(4)
C11-Fe1	2.055(3)
Fe1-C16	2.053(4)
O1-C21	1.282(4)
O2-C23	1.284(4)
C21-C22	1.401(5)
C22-C23	1.387(5)
C21-C24	1.502(4)
P1-F1	1.602(2)
P1-F6	1.591(2)
C16-C20	1.420(5)
Bond Angle (º)	
Pd1-N3-C6	115.4 (2)
Pd1-C1-N2	113.3 (2)
Pd1-O1-C21	123.7 (2)
Pd1-O2-C23	123.5 (2)
Pd1-C1-N1	141.1 (2)
Pd1-N3-C10	125.7 (2)

N3-Pd1-C1	79.99 (11)
O1-Pd1-O2	93.09 (8)
C10-N3-C6	118.9 (3)
C1-N1-C3	110.1 (3)
C1-N2-C2	110.7 (3)
C1-N2-C6	118.5 (3)
C6-N2-C2	130.8(3)
N1-C4-C5	112.3 (3)
N3-C6-C7	122.7 (3)
N2-C6-C7	124.9 (3)
C21-C22-C23	126.6 (3)
C22-C21-C24	119.0 (3)
O1-C21-C22	125.8 (3)
C1-N1-C4	125.2 (3)
C8-C9-C10	116.8 (3)
C8-C9-C11	122.2 (3)
C9-C11-C15	126.9 (3)
C11-Fe1-C15	41.03 (12)
C11-Fe1-C16	141.88 (14)
C16-Fe1-C20	40.55 (14)
Fe1-C11-C15	69.51 (17)
Fe1-C16-C20	69.4 (2)
F1-P1-F2	90.23 (15)
F1-P1-F6	179.24 (14)
F1-P1-F3	89.92 (12)

5. Experimental procedure for the synthesis of 1^{ox}

70.7 mg (0.1 mmol) of **1** was taken in a flame dried Schlenk RB and dissolved in dry dichloromethane. $NOBF_4$ (11.6 mg, 0.1 mmol) was measured in a glove box filled with Argon atmosphere and added to the Schlenk flask containing **1**. The reaction mixture was stirred for 2 h at room temperature inside the glove box. Dark green coloured precipitate was observed after two hours. The supernatant liquid was decanted off and the precipitate was washed two to three times with dry DCM. Finally, the precipitate was dried under vacuo (Yield = 59.4 mg, 84 %). NMR of this compound could not be recorded as the compound is paramagnetic. HRMS (ESI, m/z): calculated for $C_{25}H_{26}FeN_3O_2Pd$: $[M-(PF_6)-(BF_4)]^{2+}$: 281.0204, found: 281.0636; FT-IR (UATR, cm^{-1}): 1785, 1619, 1507, 1032, 839; Mp: 255−258 °C; Anal. Calcd for Chemical Formula: $C_{25}H_{26}F_{10}BFeN_3O_2PPd$: C, 37.79; H, 3.30; N, 5.29; found: C, 37.80; H, 3.32; N, 5.30.

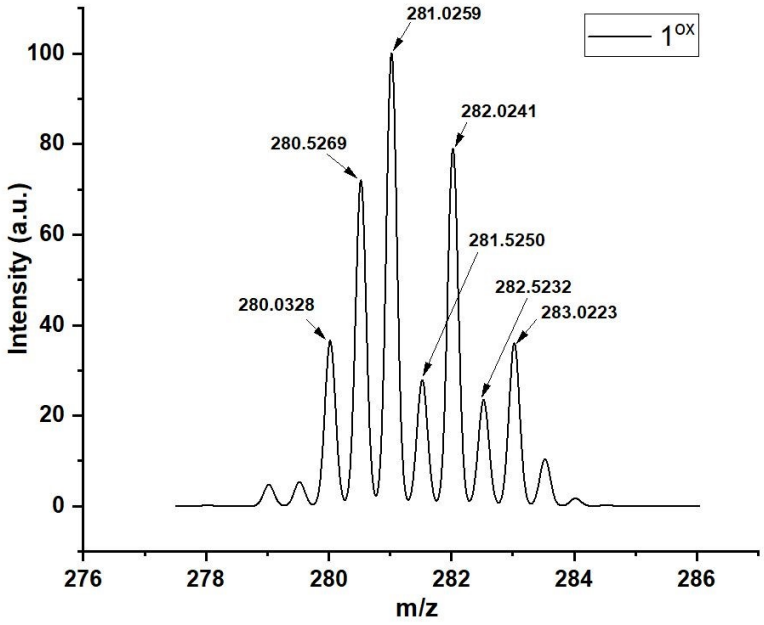


Figure S24A Experimental HRMS spectra of $\mathbf{1^{ox}}$

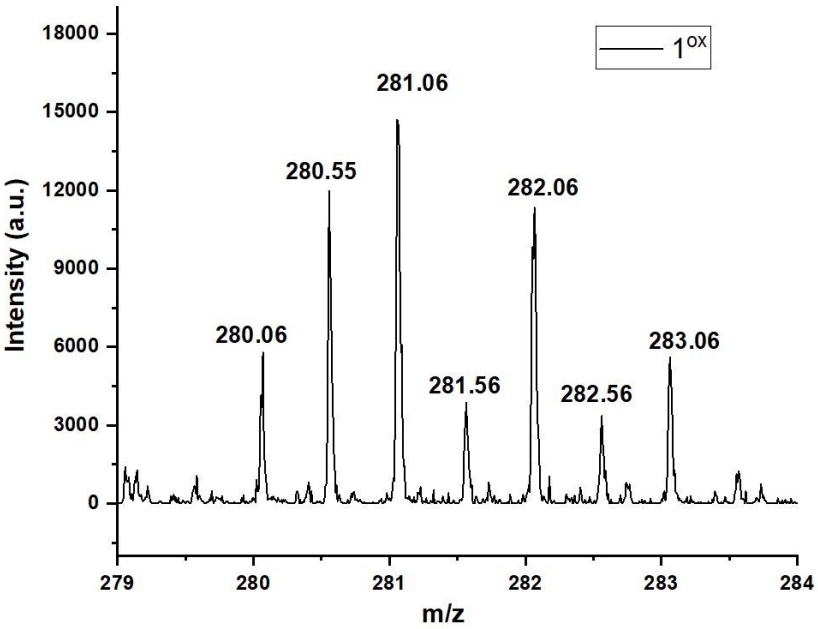


Figure S24B Theoretical HRMS spectra of **1ox**

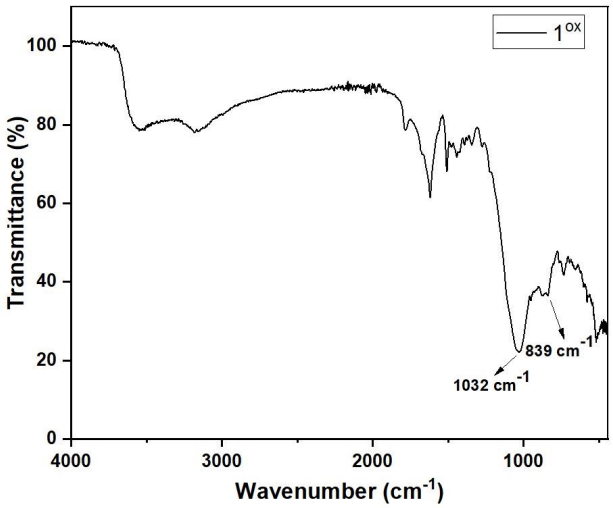


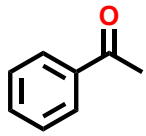
Figure S25 FT-IR spectrum of complex **1ox**

6. General procedure for the acylative coupling of arylboronic acid with acetic anhydride by 1.

Arylboronic acid (0.5 mmol, 0.0619 g) and acetic anhydride (0.5 mmol, 47.2 µL) were subjected to a flame dried RB containing 0.007 g of catalyst (2 mol %, 0.01 mmol) dissolved in 2 mL solvent (acetonitrile: water (1:1)). The mixture was heated to 80 °C for 12 h under Argon atmosphere with continuous stirring. The reaction mixture was allowed to cool to room temperature and then extracted with ethyl acetate (3x10 mL) and brine washed. The organic layer was separated and dried to obtain the crude product. The desired product was further purified by column chromatographic technique.

7. Characterization of substituted aromatic ketones (NMR Data)

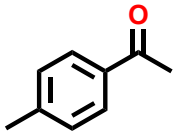
Acetophenone (3a)



Colourless liquid (58.8 mg, 98% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 137.2, 133.2, 128.7, 128.4, 26.7 ppm.

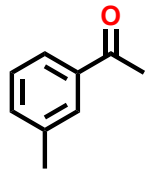
4-methylacetophenone (3b)



Colourless liquid (54.3 mg, 81 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 144.0, 134.8, 129.3, 128.5, 26.6, 21.7 ppm.

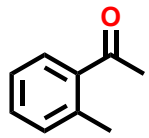
3-methylacetophenone (3c)



Light yellow liquid (64.4 mg, 96 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 13.5 Hz, 2H), 7.40 – 7.32 (m, 2H), 2.59 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 138.5, 137.3, 133.9, 128.9, 128.6, 125.7, 26.8, 21.4 ppm.

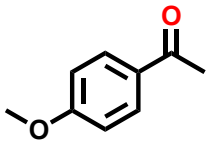
2-methylacetophenone (3d)



Colourless Liquid (67 mg, 100 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 6.8 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 2.58 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 138.5, 137.7, 132.2, 131.6, 129.5, 125.8, 29.7, 21.7 ppm.

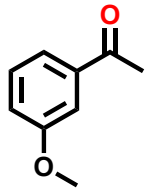
4-methoxyacetophenone (3e)



White crystalline solid (65.3 mg, 87 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 1H), 6.92 (d, *J* = 8.9 Hz, 1H), 3.86 (s, 2H), 2.54 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 163.6, 130.7, 130.4, 113.8, 55.6, 26.5 ppm.

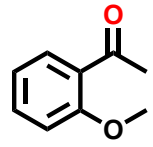
3-methoxyacetophenone (3f)



Colourless liquid (43.5 mg, 58 % yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.11 (dd, *J* = 9.2, 2.7 Hz, 1H), 3.86 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 159.9, 138.6, 129.7, 121.3, 119.8, 112.4, 55.6, 26.9 ppm.

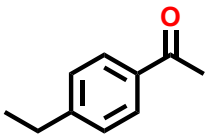
2-methoxyacetophenone (3g)



Light yellow liquid (70.5 mg, 94 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 9.6 Hz, 1H), 7.47 (t, *J* = 8.8 Hz, 1H), 7.03 – 6.95 (m, 2H), 3.92 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 159.1, 133.8, 130.5, 128.4, 120.7, 111.7, 55.6, 31.9 ppm.

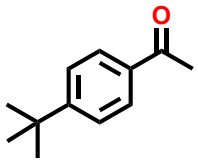
4-ethylacetophenone (3h)



Clear colourless liquid (65.2 mg, 88 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.18 (m, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 2.52 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 150.2, 135.1, 128.7, 128.2, 29.1, 26.7, 15.4 ppm.

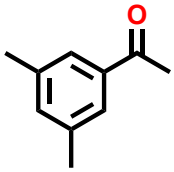
4-tertbutylacetophenone (3i)



Colourless liquid (76.6 mg, 87 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 2.59 (s, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 157.0, 134.7, 128.4, 125.7, 35.2, 31.2, 26.7 ppm.

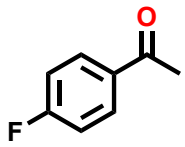
3,5-dimethylacetophenone (3j)



Colourless liquid (65.2 mg, 88% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.20 (s, 1H), 2.58 (s, 3H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 138.3, 137.4, 134.9, 126.3, 26.9, 21.7 ppm.

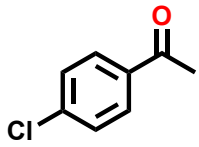
4-fluoroacetophenone (3k)



Clear yellow liquid (62.8 mg, 91 % yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 167.2, 164.6, 133.7, 131.1 (d, *J* = 9.2 Hz), 115.8 (d, *J* = 22.2 Hz), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.25 ppm.

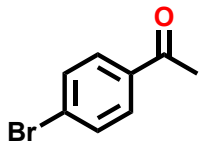
4-chloroacetophenone (3l)



Colourless liquid (62.6 mg, 81% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 139.7, 135.5, 129.8, 128.9, 26.7 ppm.

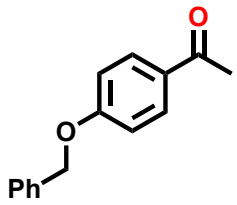
4-bromoacetophenone (3m)



White crystalline solid (64.6 mg, 65% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 135.9, 132.1, 129.9, 128.4, 26.7 ppm.

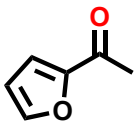
4-benzyloxyacetophenone (3n)



White solid (53 mg, 47 % yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.91 (m, 2H), 7.46 – 7.32 (m, 5H), 7.04 – 6.97 (m, 2H), 5.13 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 162.7, 136.3, 130.7, 130.6, 128.8, 128.4, 127.6, 114.7, 70.3, 26.5 ppm.

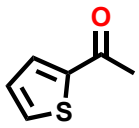
2-acetylfuran (3o)



Yellowish liquid (41 mg, 74% yield)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.15 (d, J = 3.5 Hz, 1H), 6.51–6.50 (m, 1H), 2.45 (dd, J = 1.7, 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 152.9, 146.5, 117.7, 112.3, 26.1 ppm.

2-acetylthiophene (3p)

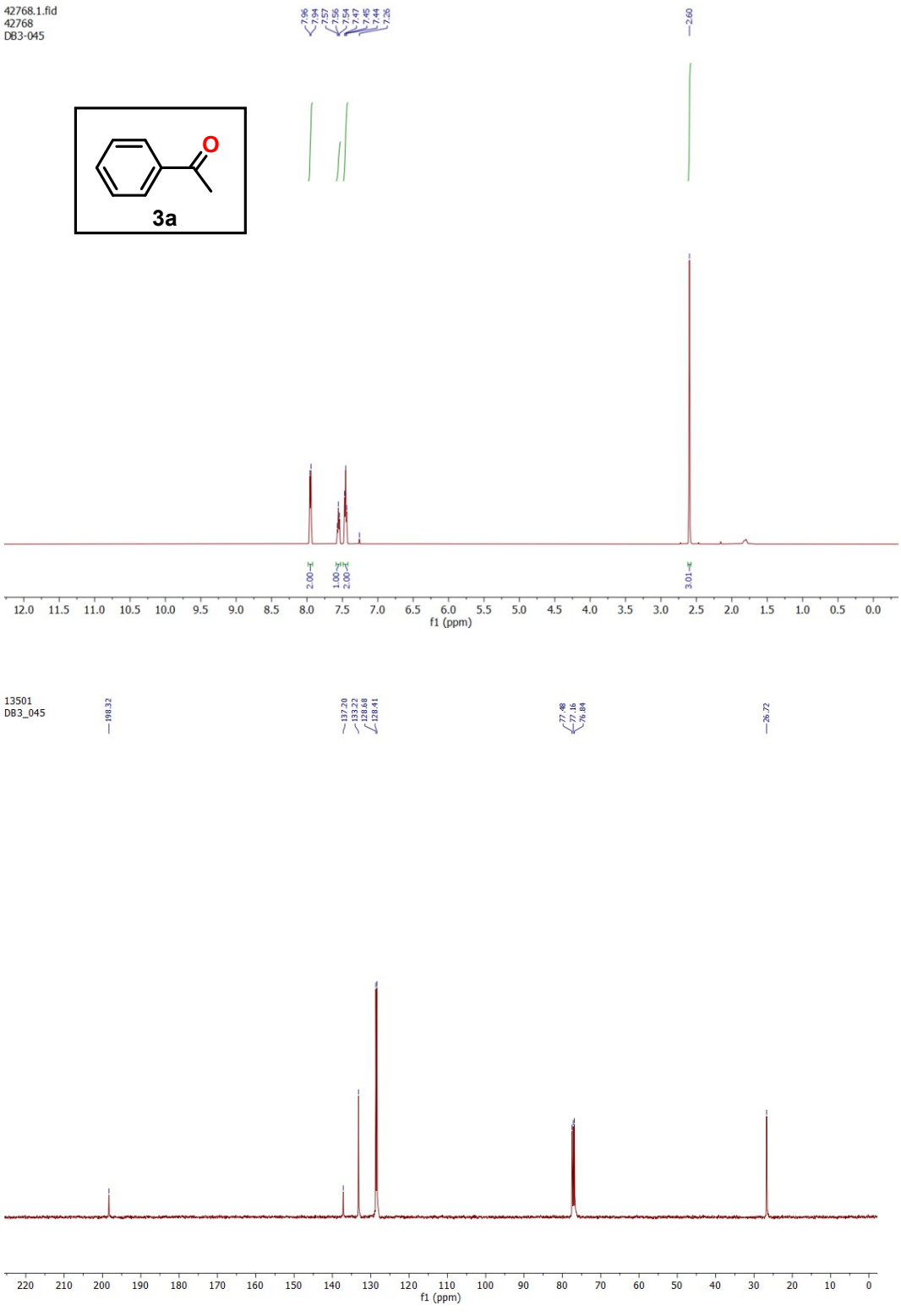


Yellowish liquid (38.4 mg, 61% yield)

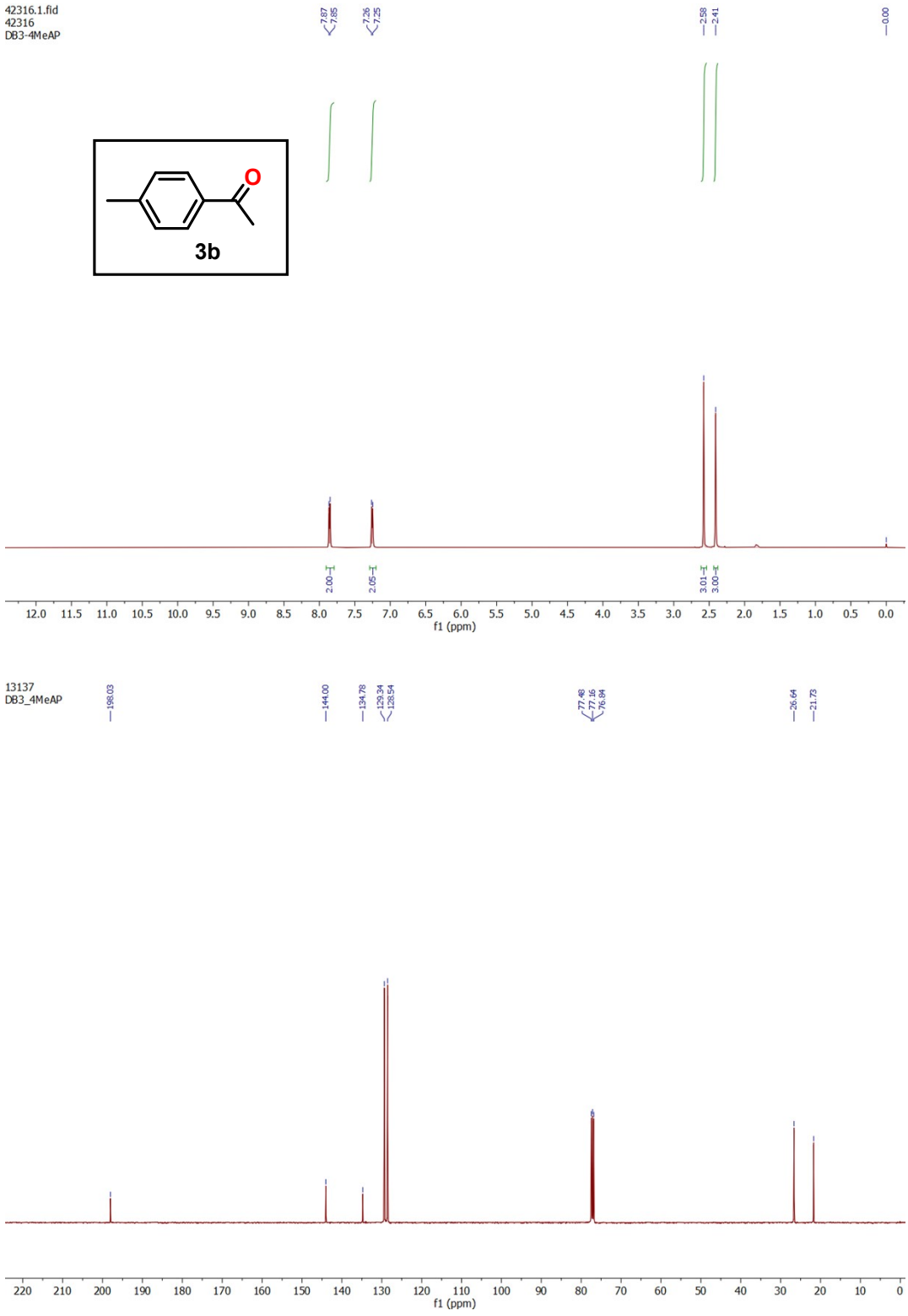
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 (dd, J = 5.0, 1.3 Hz, 1H), 7.11 (dd, J = 5.0, 3.7 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 144.7, 133.9, 132.6, 128.2, 27.0 ppm.

NMR Spectra of the substituted aromatic ketones

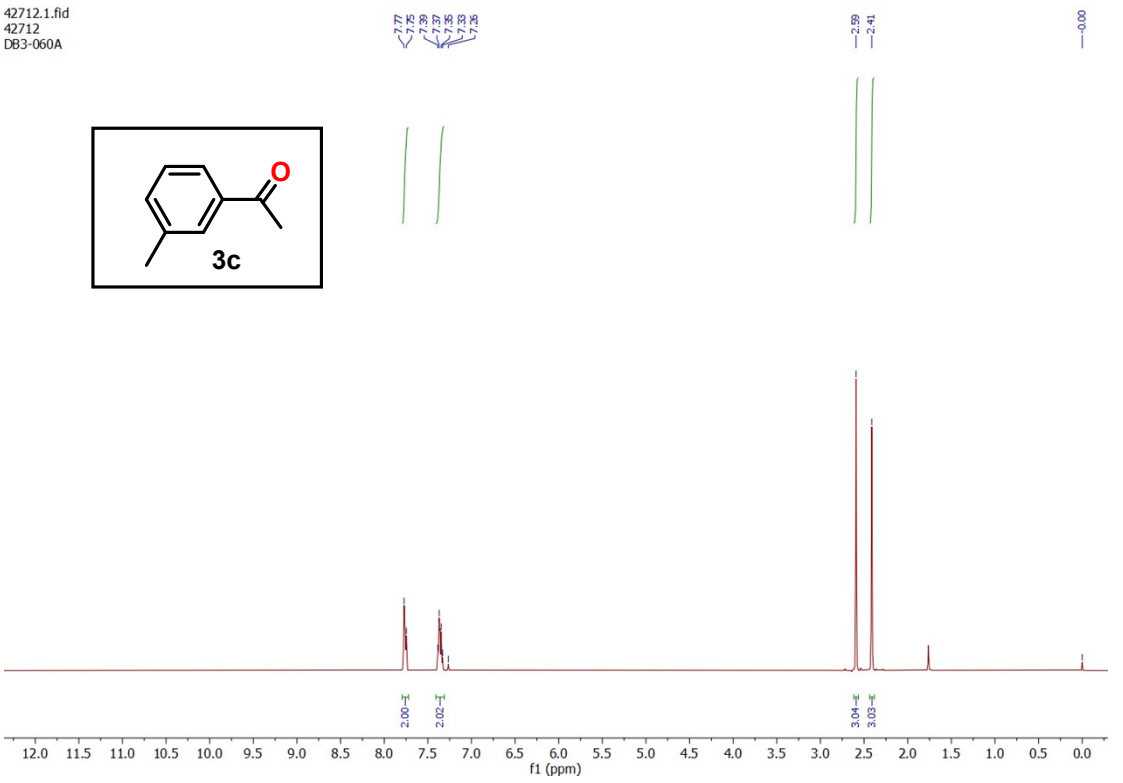
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of acetophenone (3a)

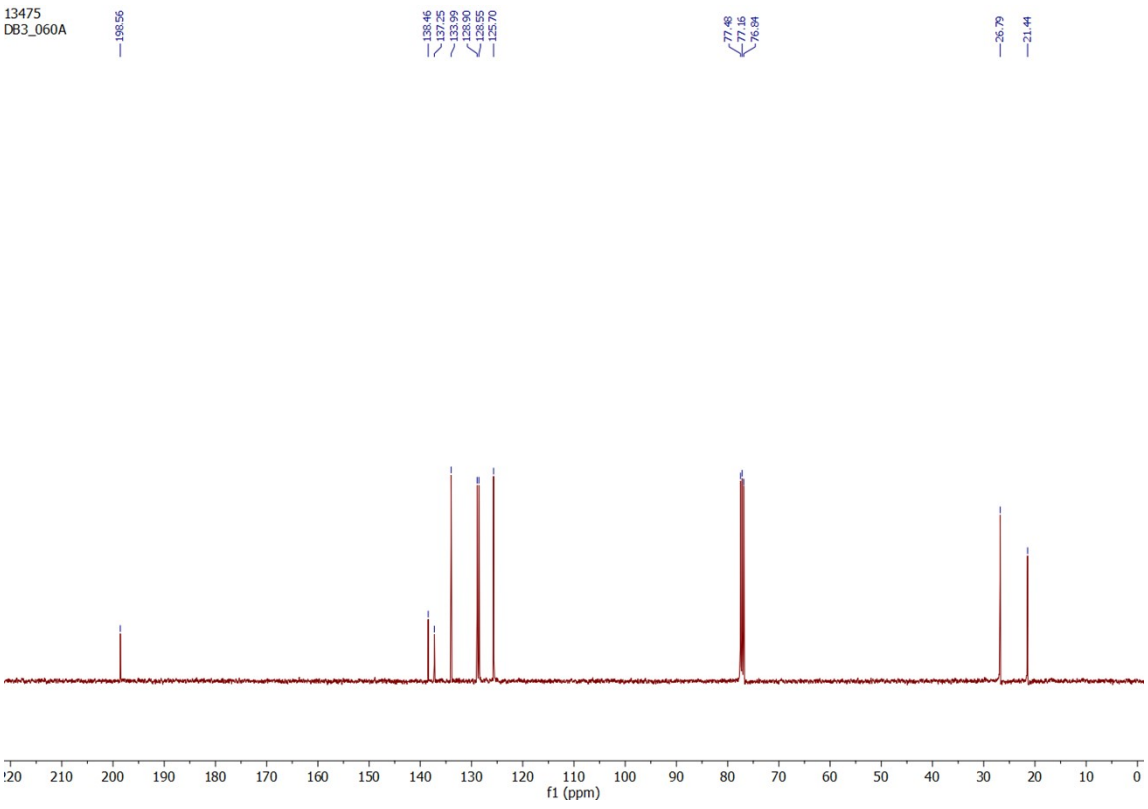


^{1}H NMR $CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 4-methylacetophenone (3b)

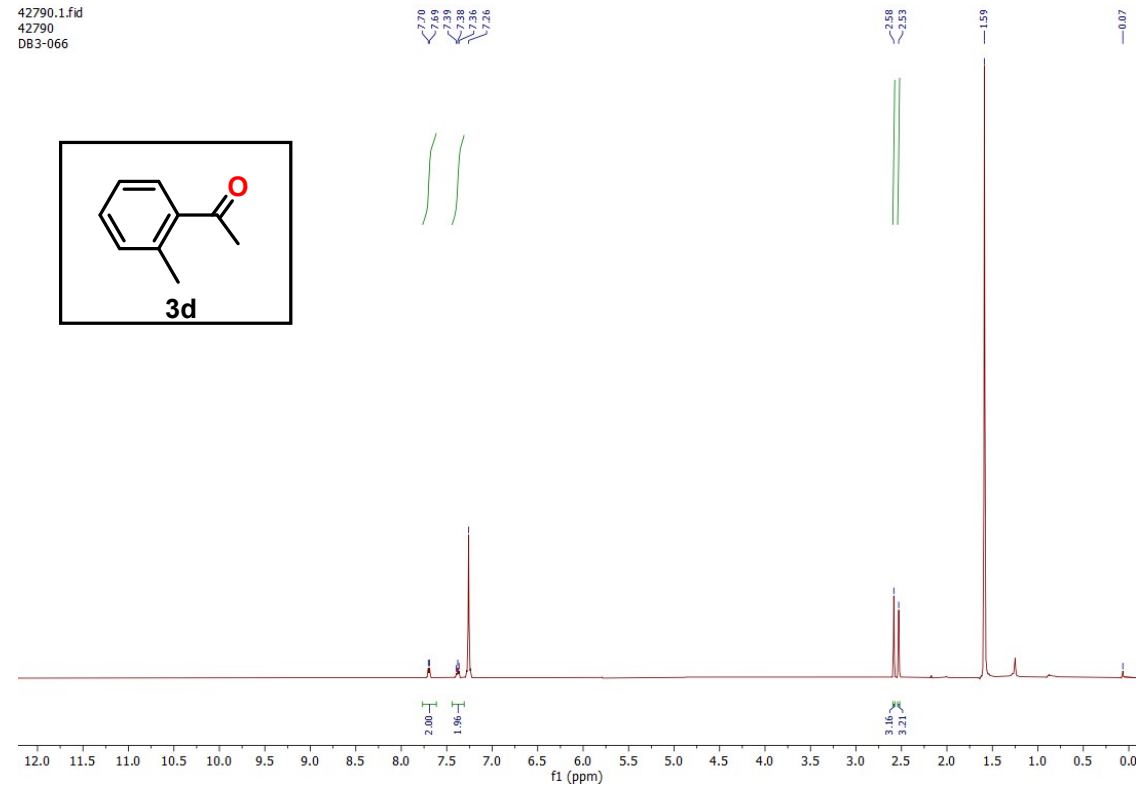


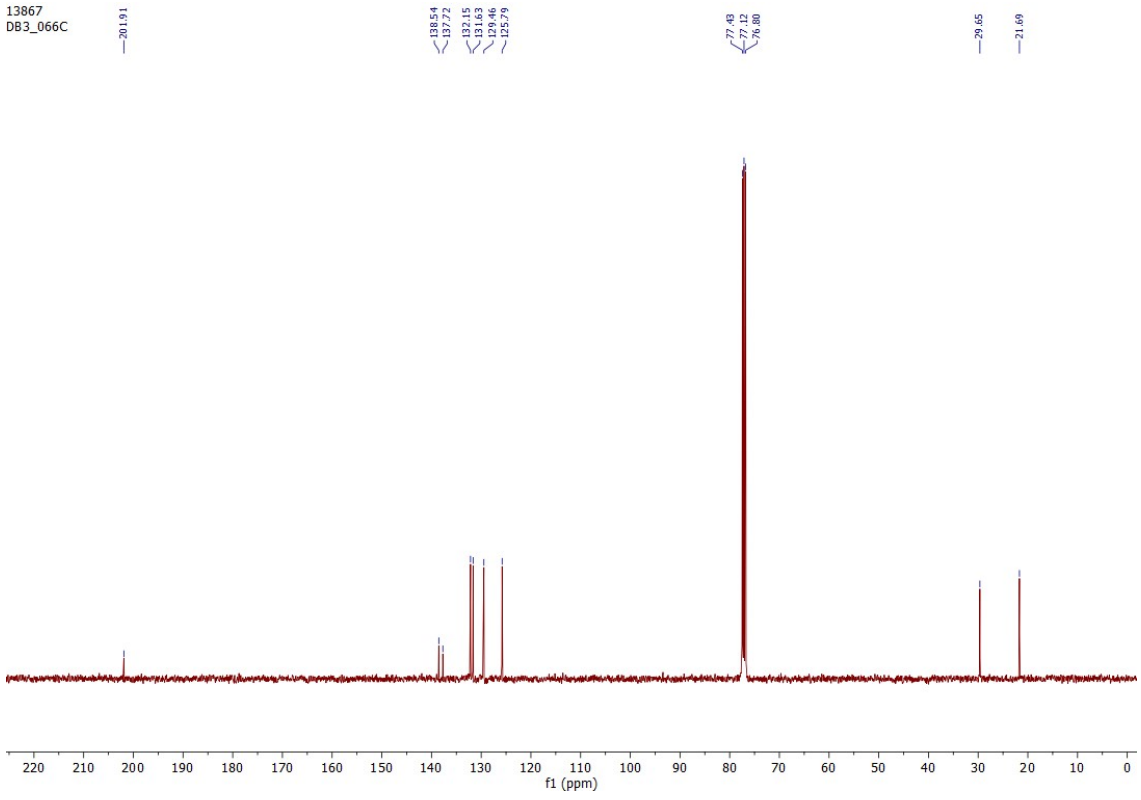
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 3-methylbenzaldehyde (3c)



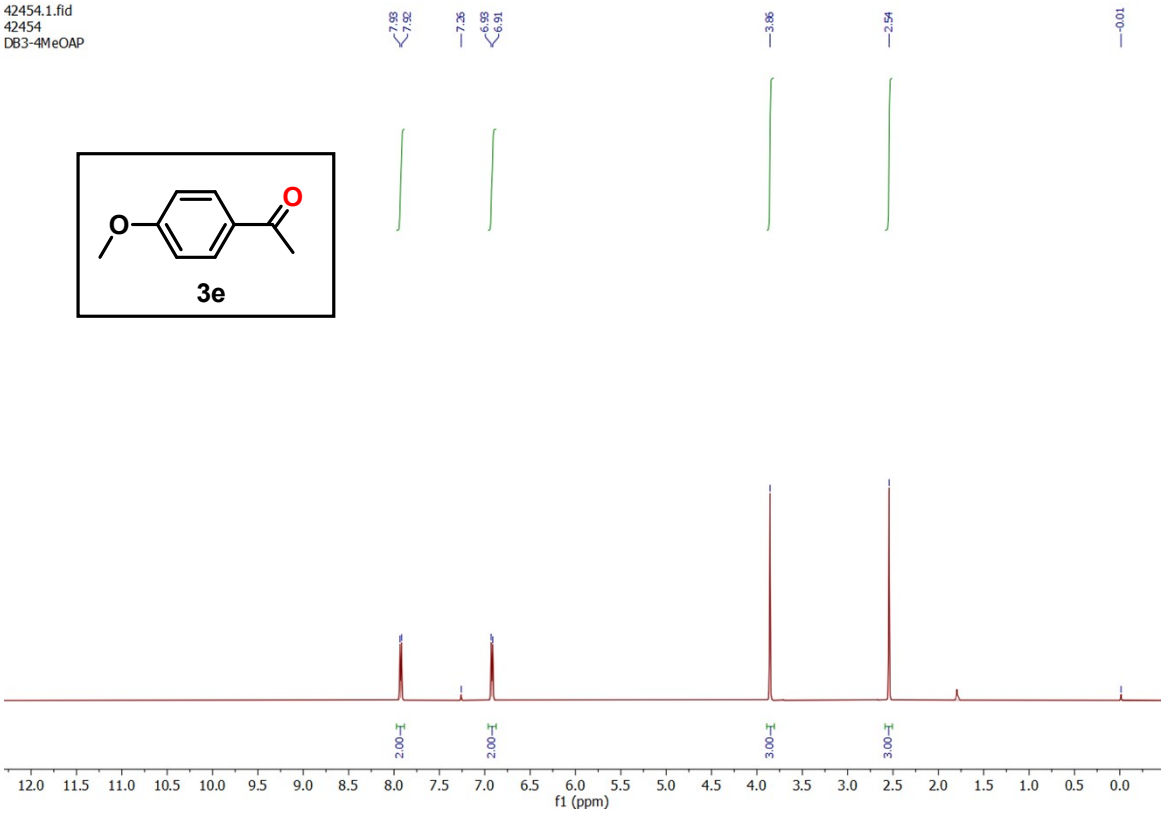


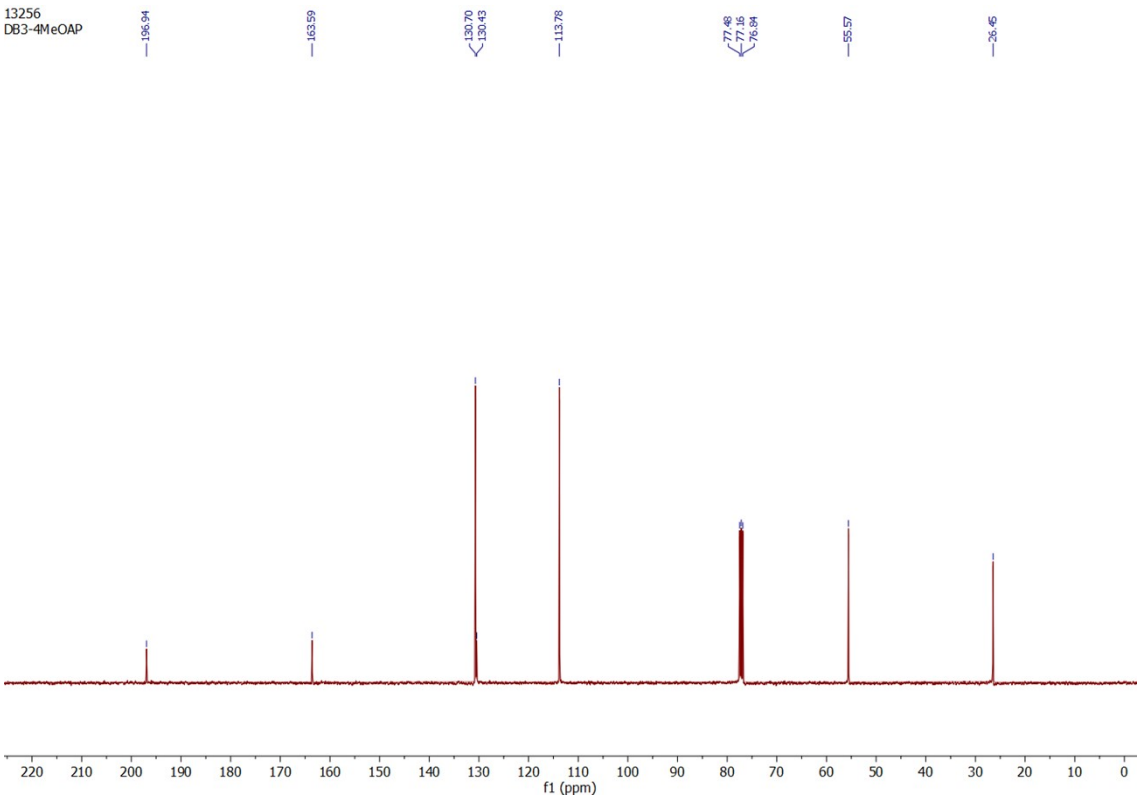
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 2-methylbenzaldehyde (3d)



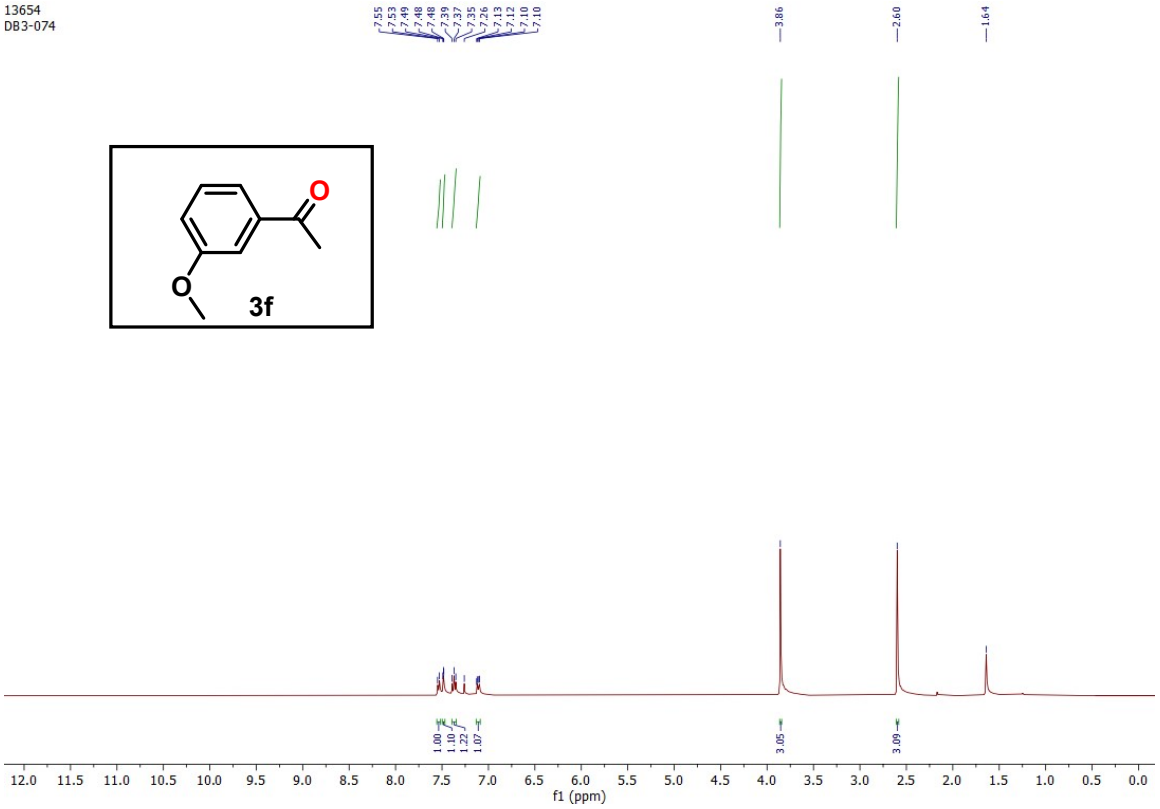


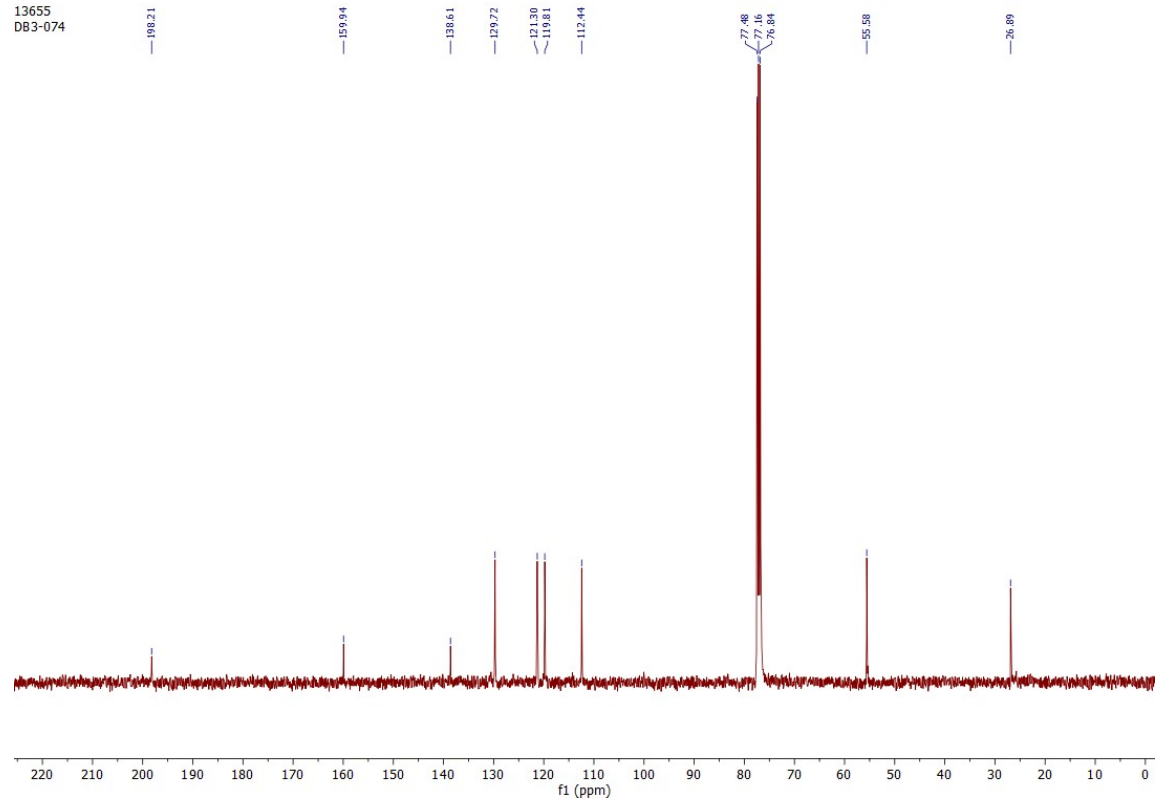
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 4-methoxyacetophenone (3e)



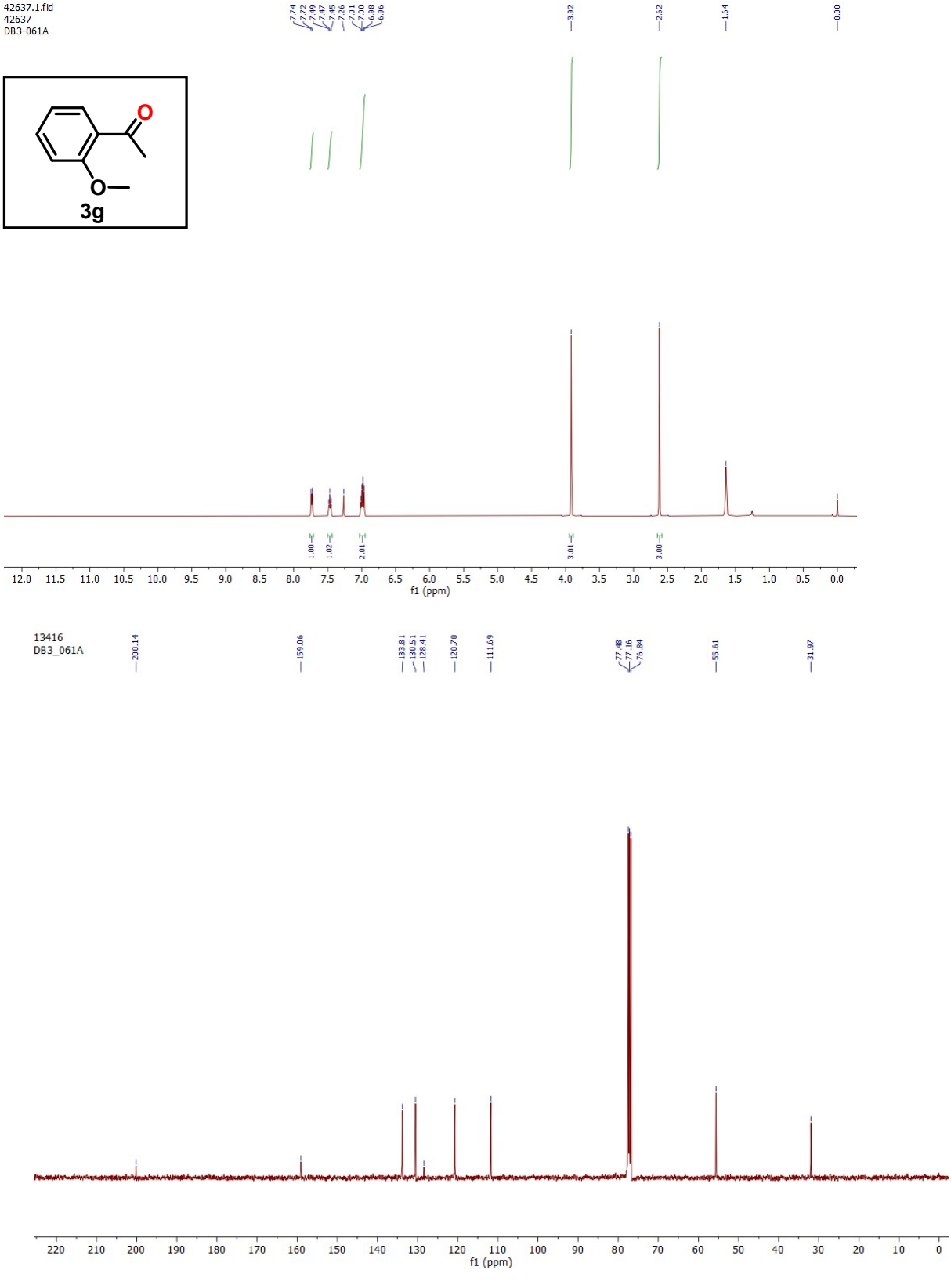


^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 3-methoxyacetophenone (3f)

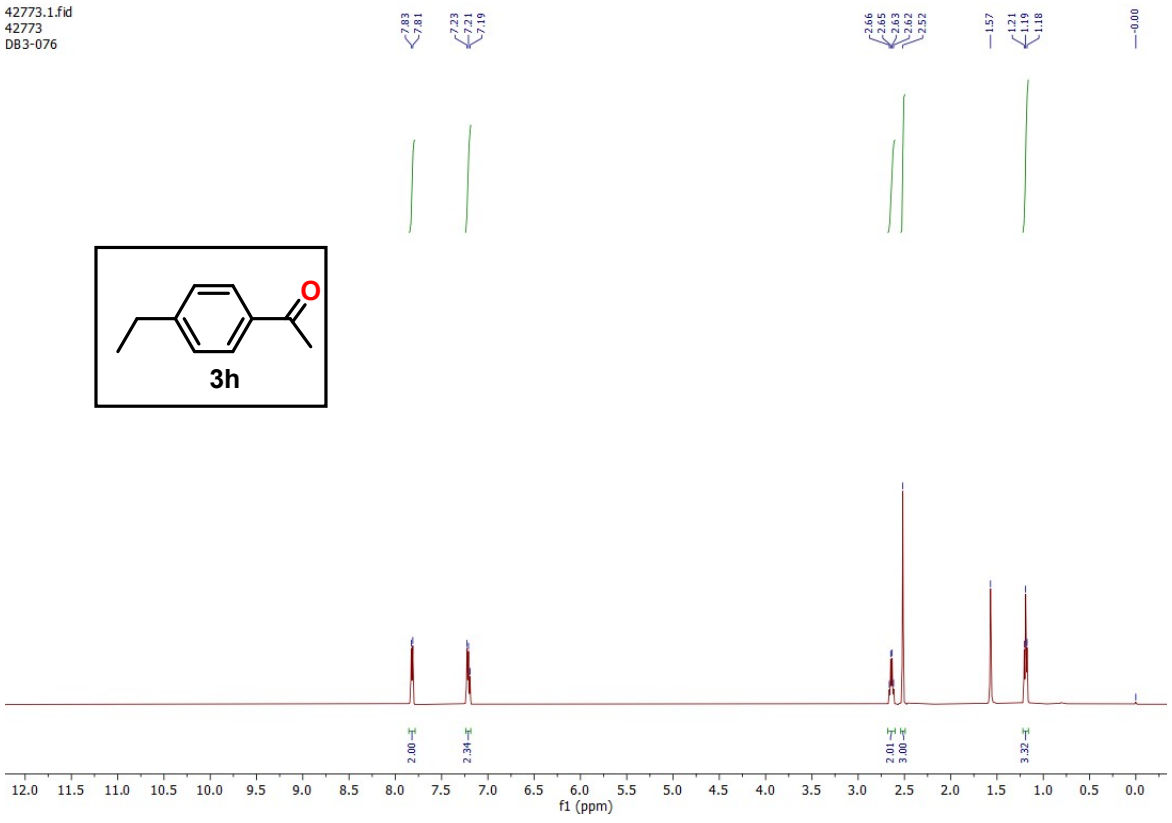


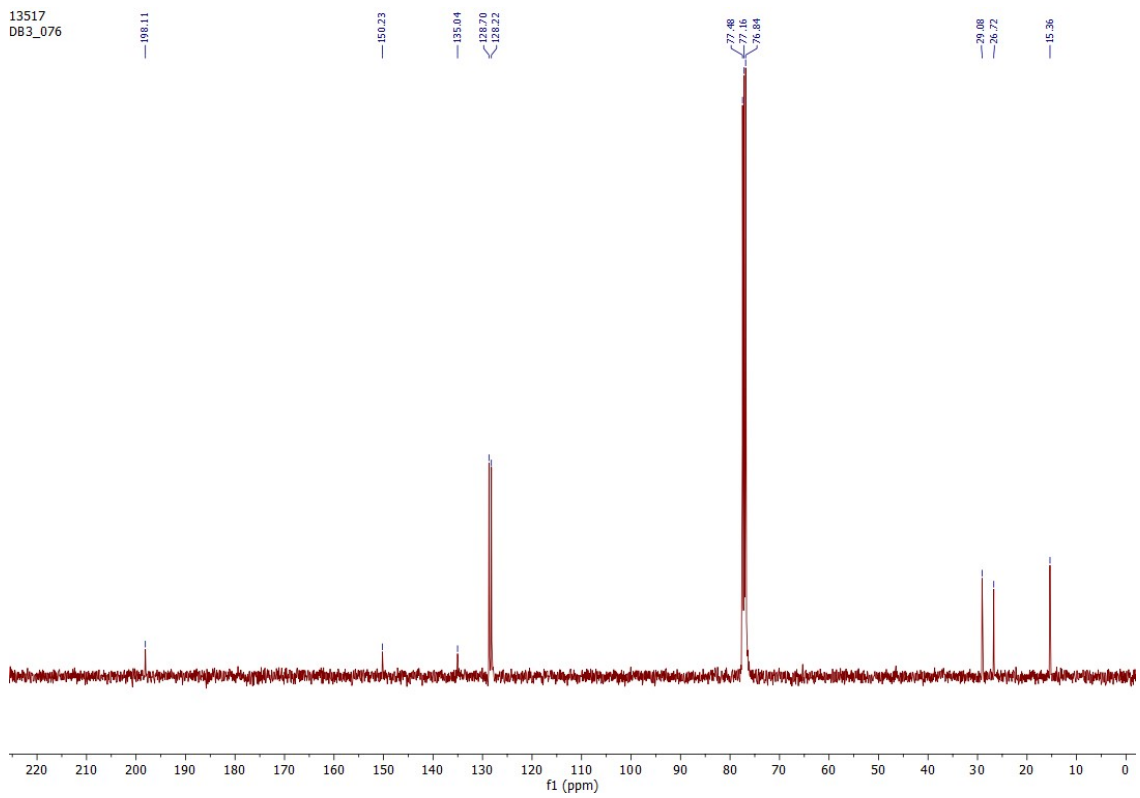


^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 2-methoxyacetophenone (3g)

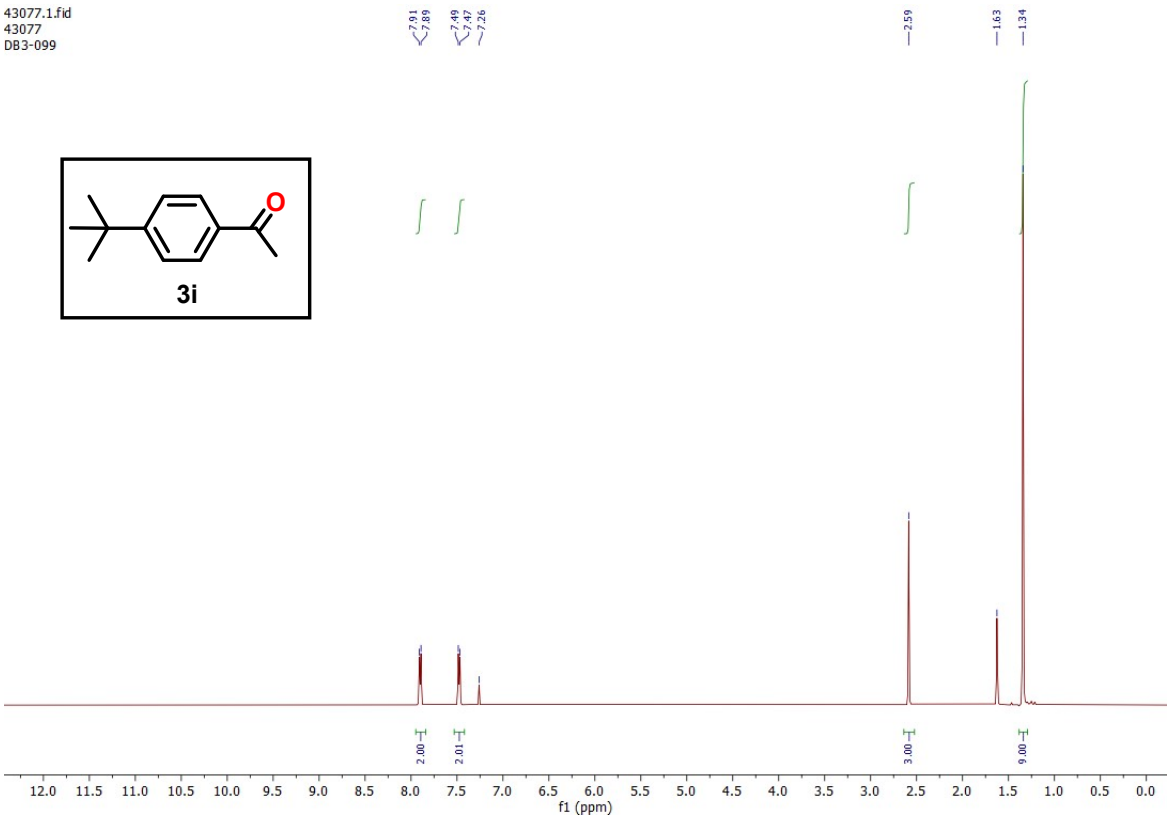


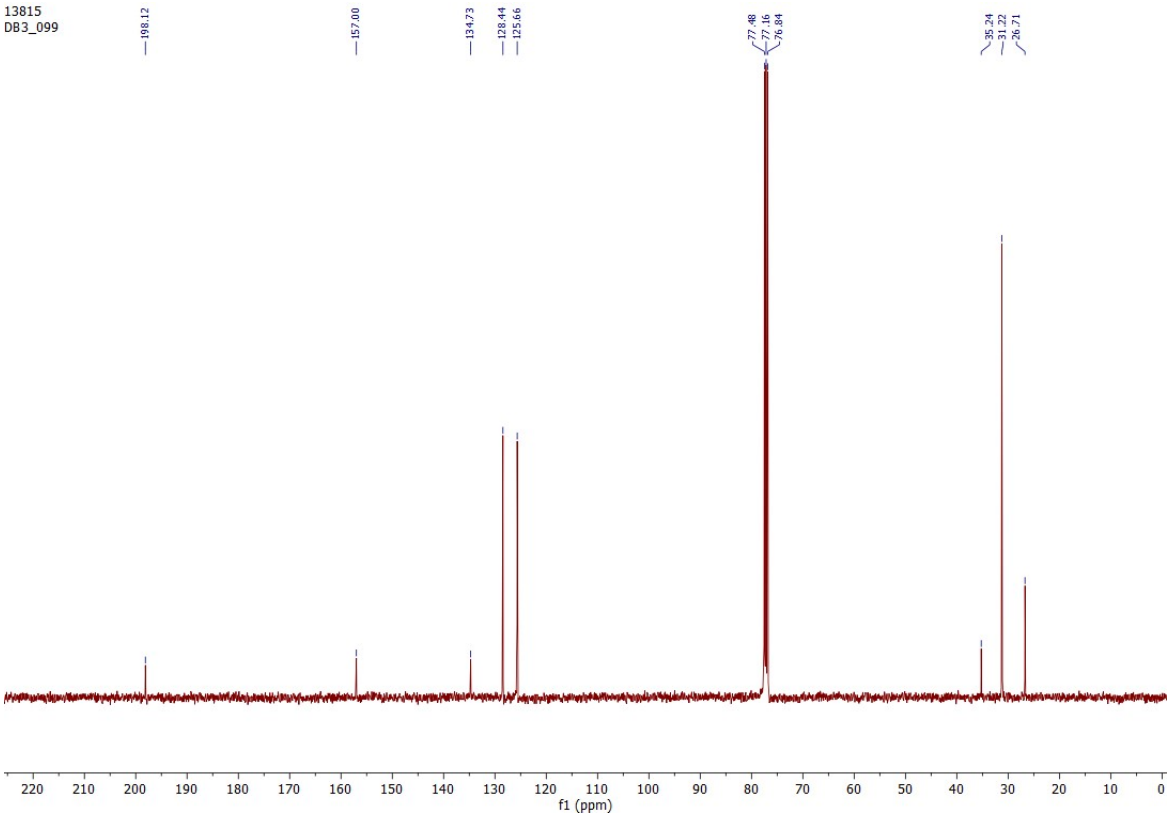
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 4-ethylacetophenone (3h)



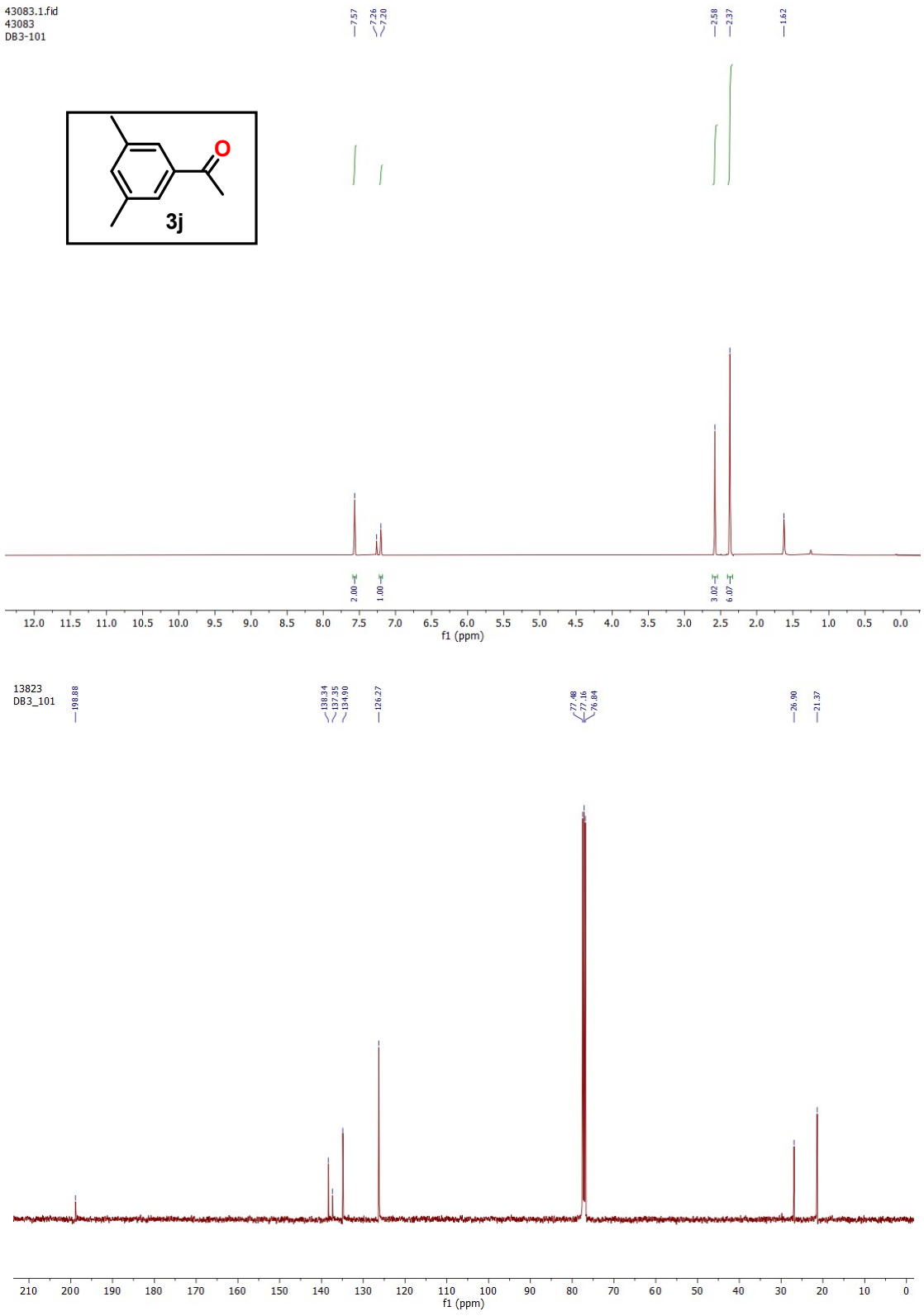


^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 4-tertbutylacetophenone (3i)

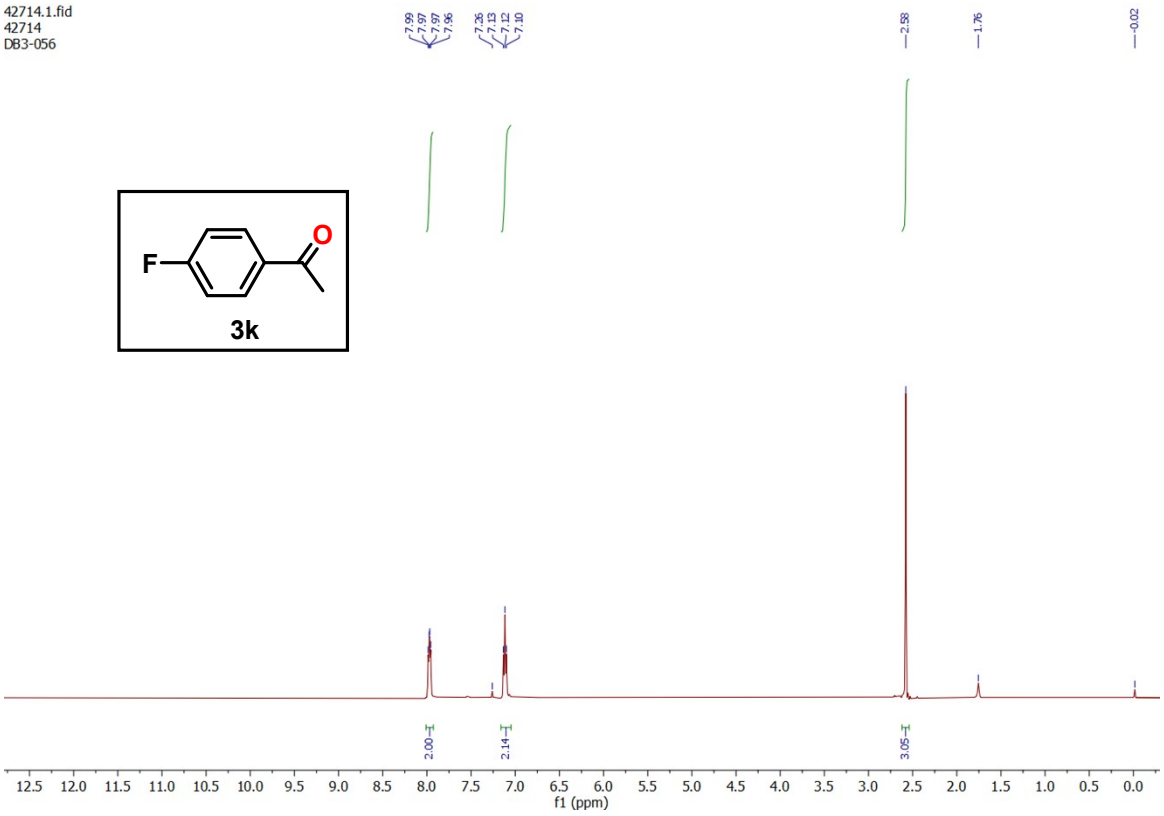


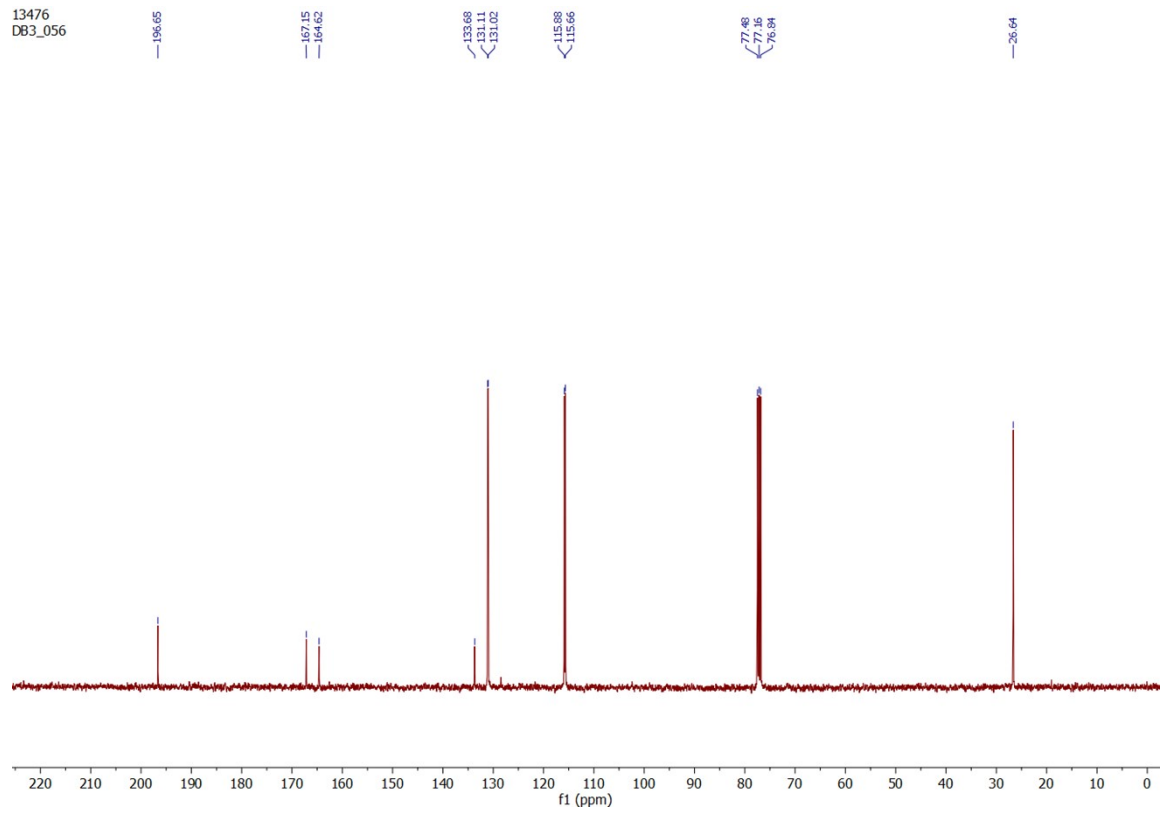


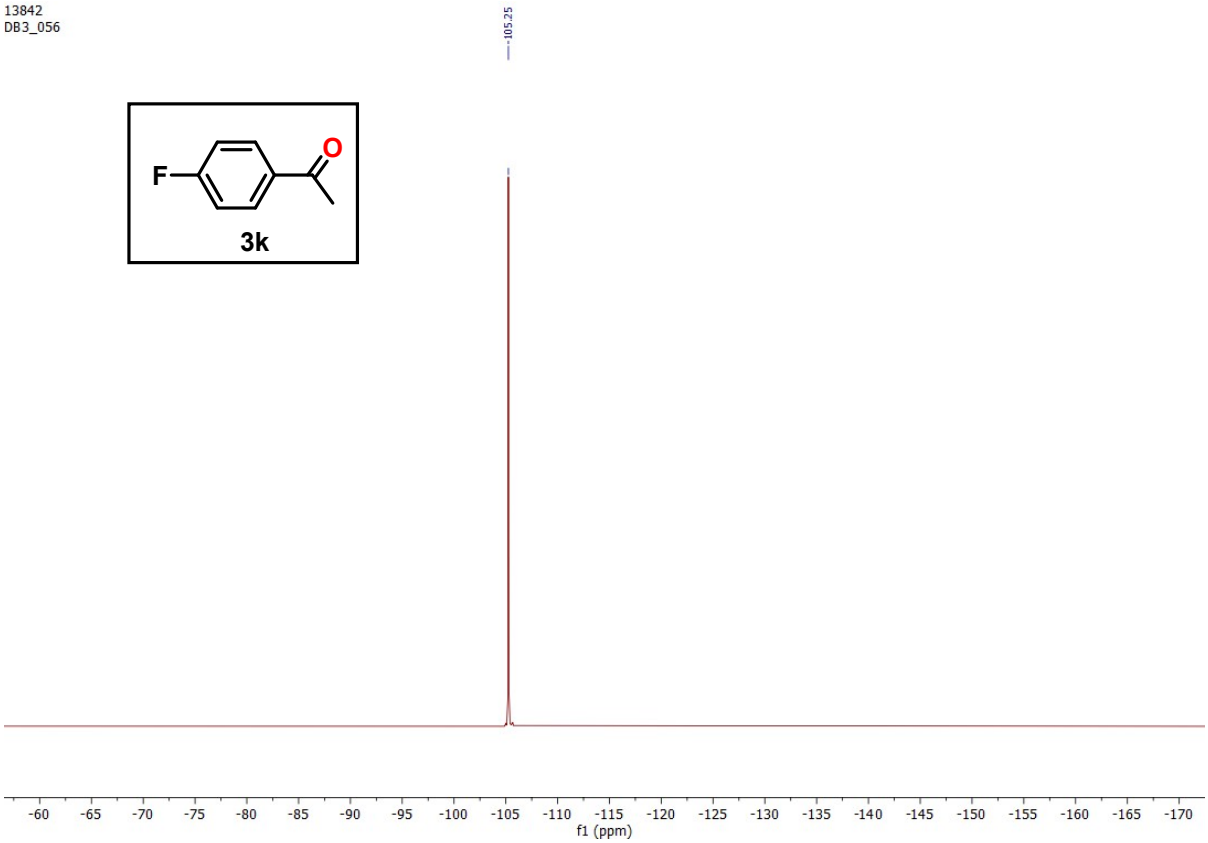
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 3,5-dimethylacetophenone (3j)



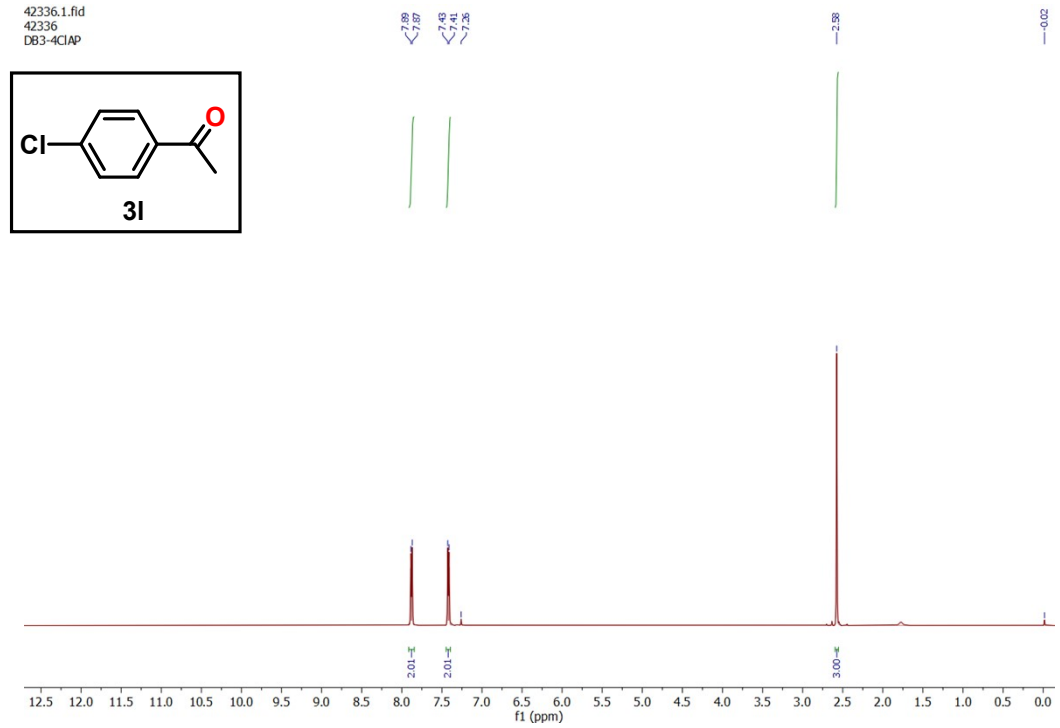
^{1}H NMR ($CDCl_3$, 500 MHz), ^{13}C NMR ($CDCl_3$, 100 MHz) and ^{19}F NMR ($CDCl_3$, 376 MHz) spectra of 4-fluoroacetophenone (3k)

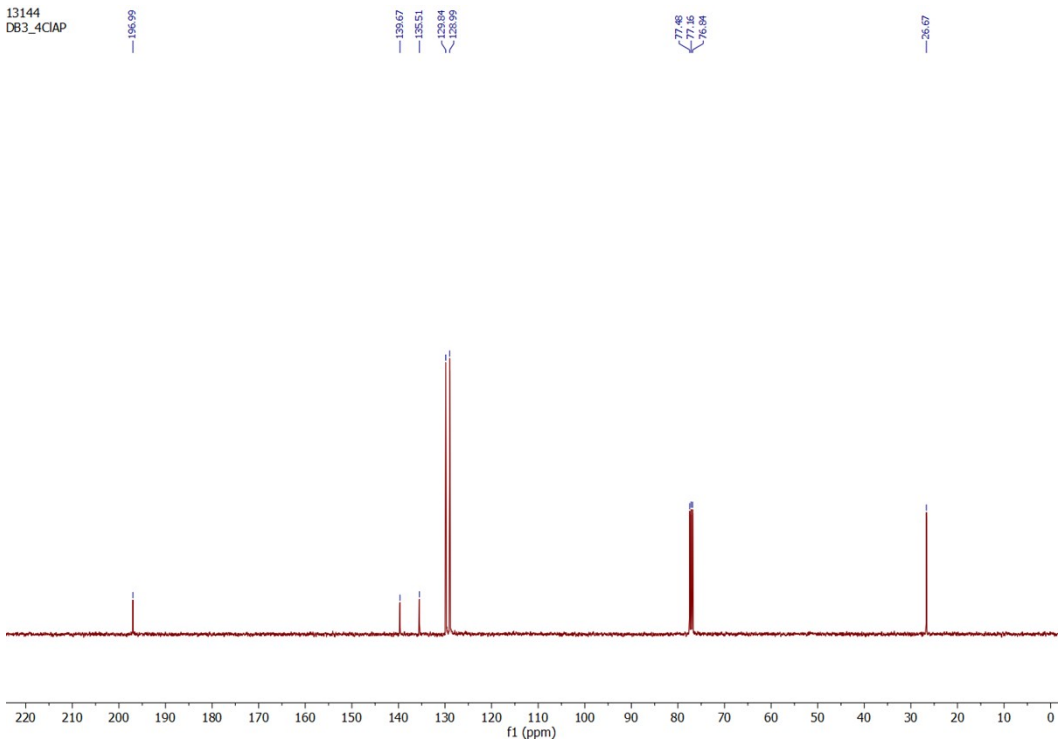




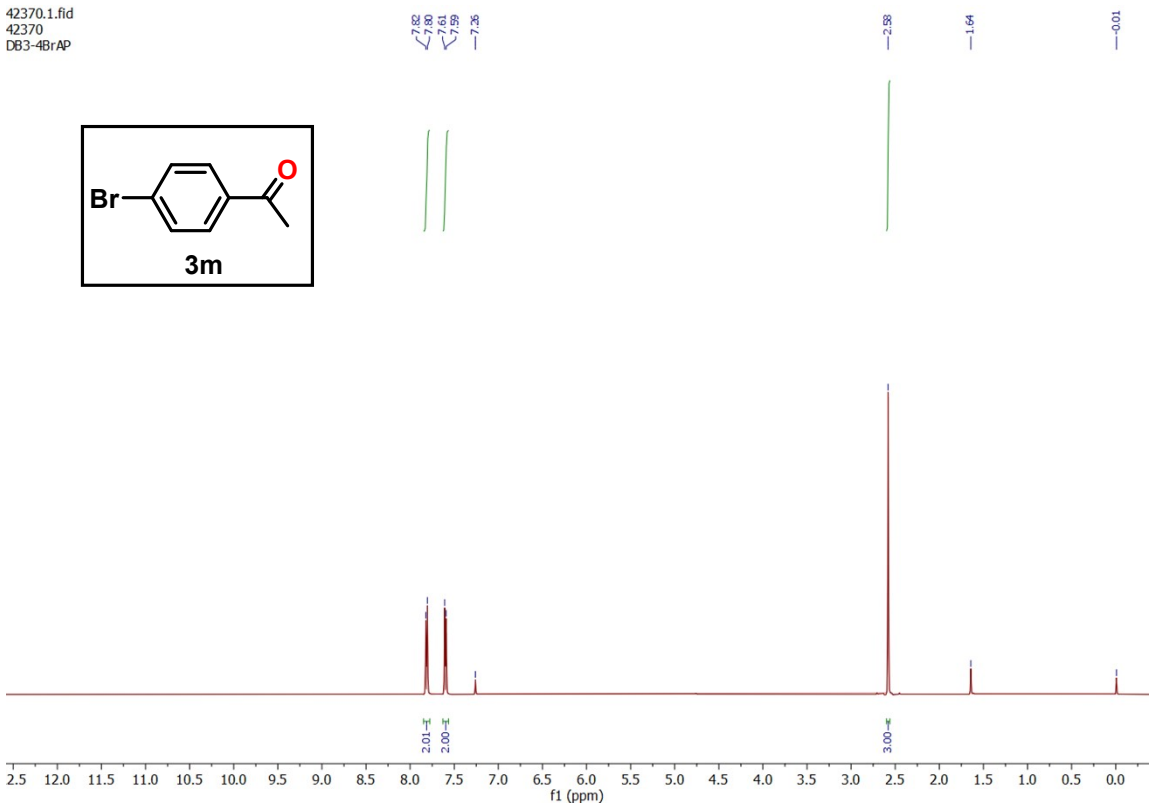

13842
DB3_056
-105.25
F
O
3k
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
f1 (ppm)

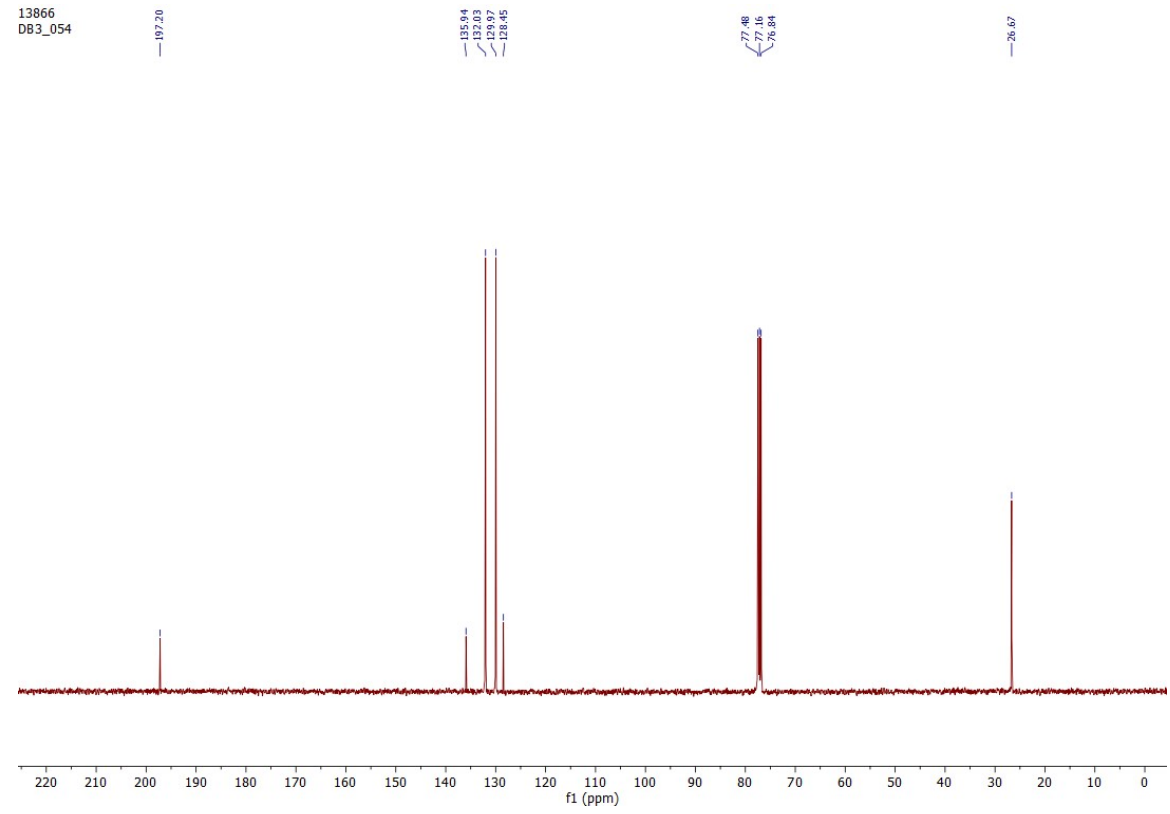
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 4-chloroacetophenone (3l)



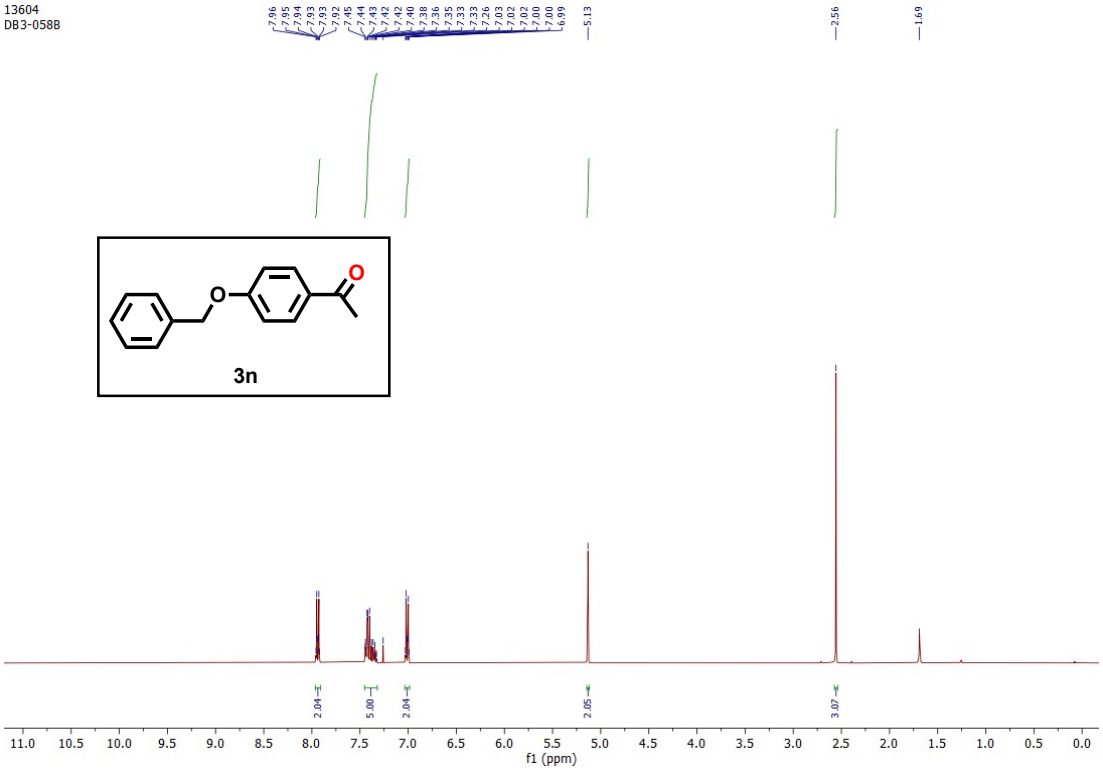


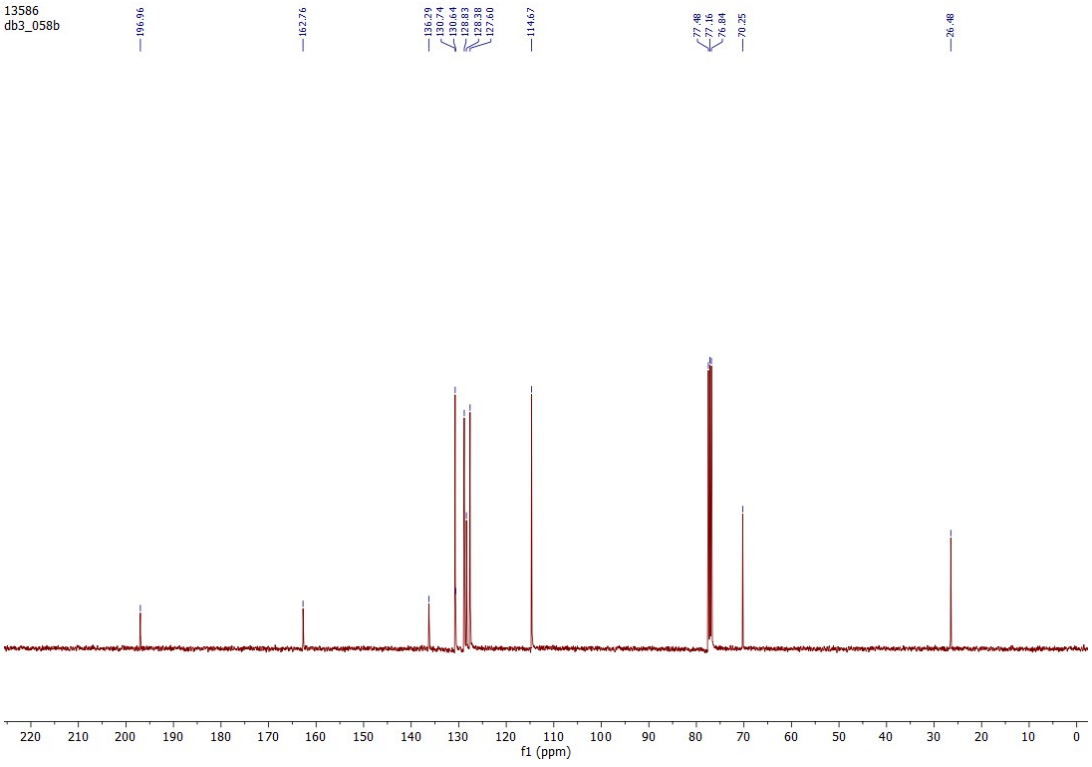
^{1}H NMR ($CDCl_3$, 500 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 4-bromoacetophenone (3m)



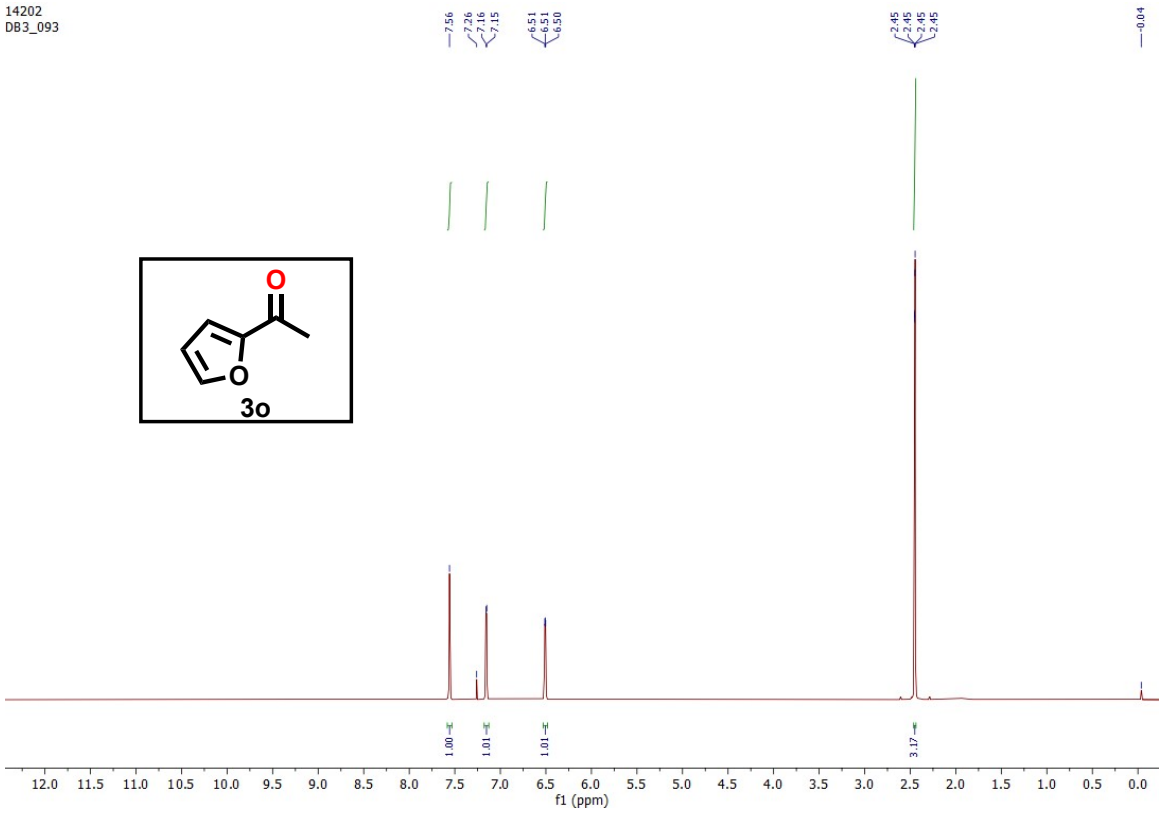


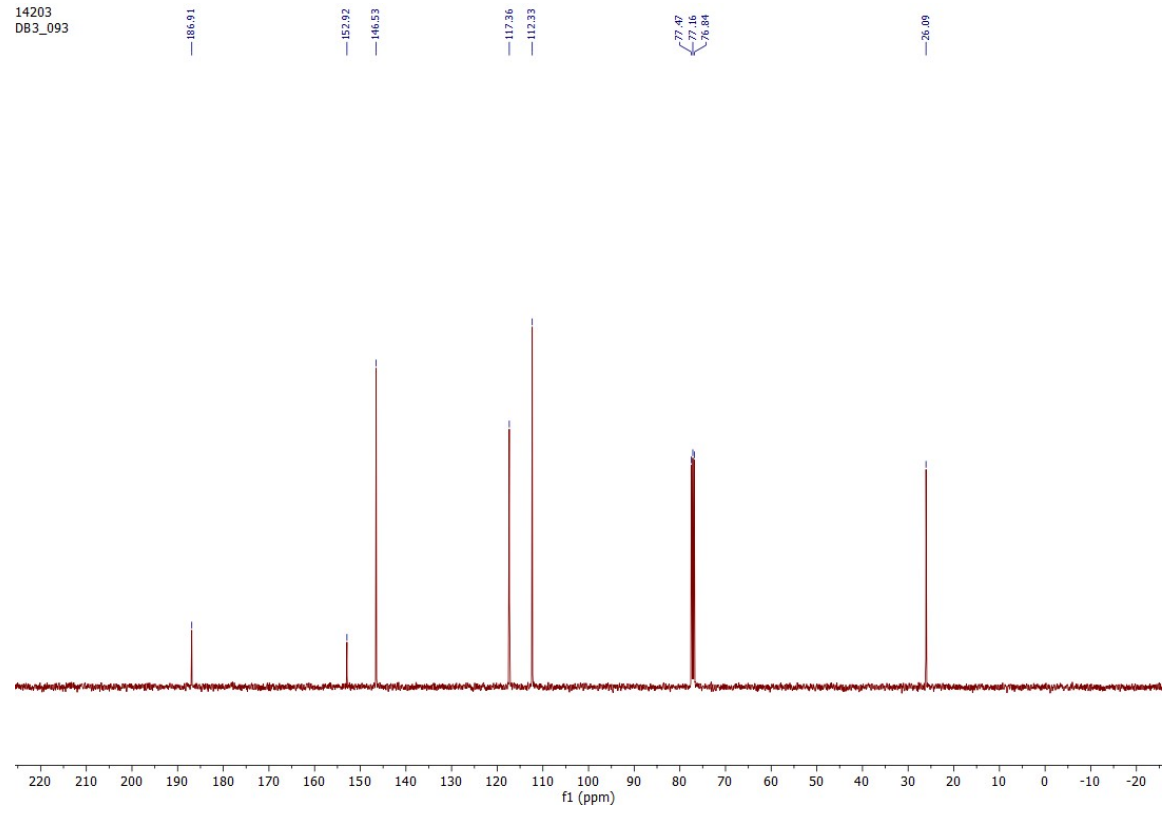
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 4-benzyloxyacetophenone (3n)



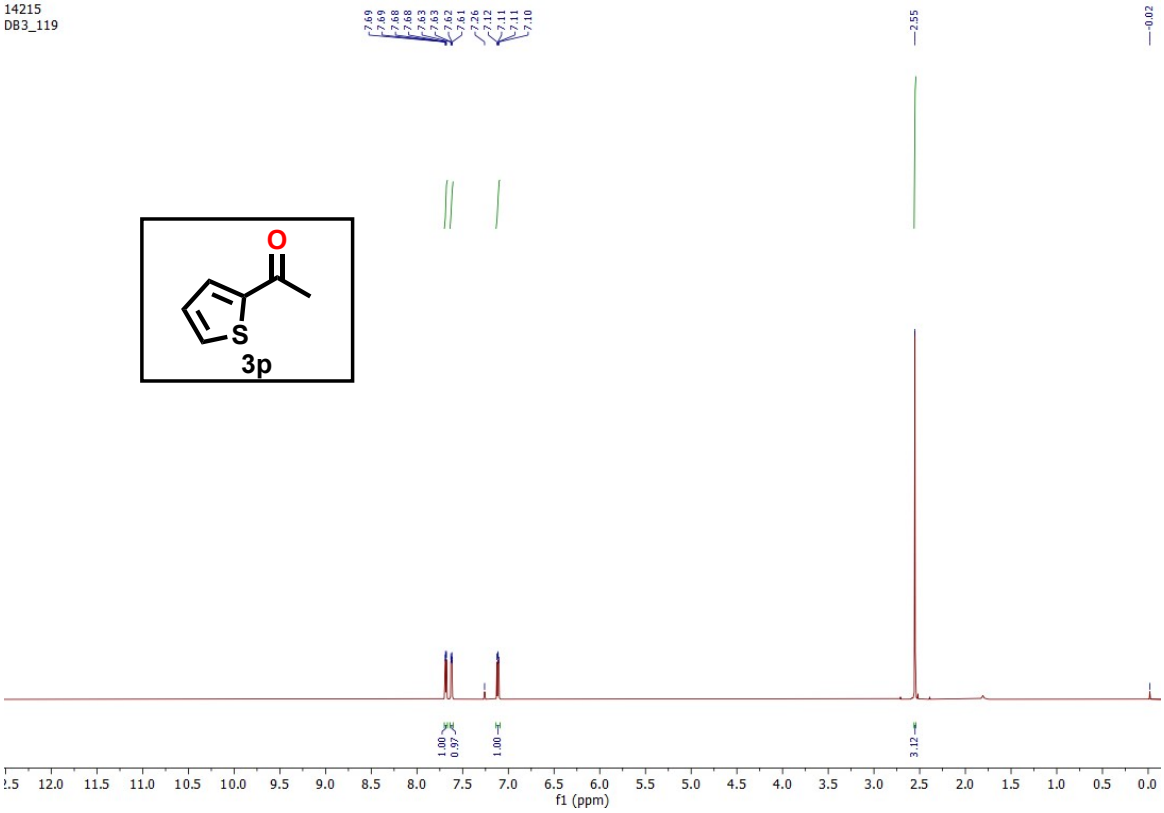


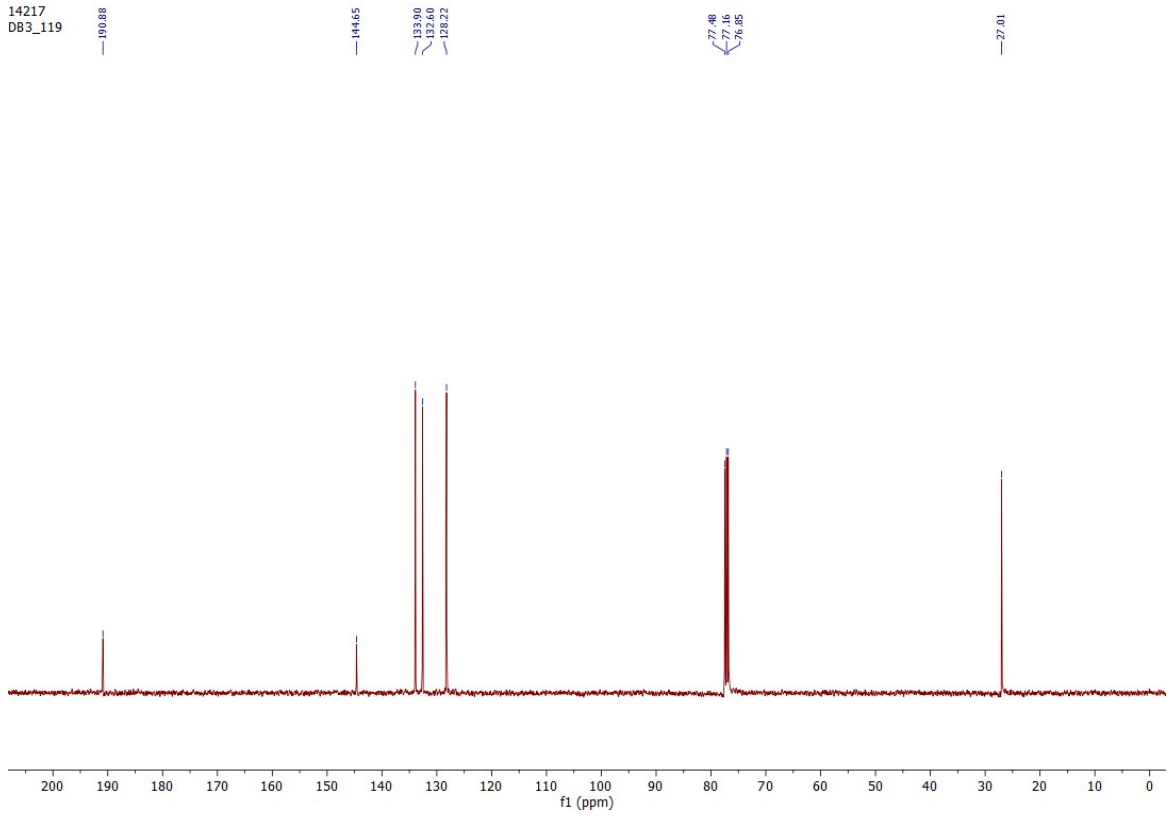
^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 2-acetylfuran (3o)





^{1}H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) spectra of 2-acetylthiophene (3p)





[1]*SAINT+software for CCD diffractometers*, Bruker AXS, Madison, WI, 2000.

[2]G. M. Sheldrick, SADABS *Program for Correction of Area Detector Data*, University of Göttingen, Göttingen (Germany), 1999.

[3]*SHELXTL Package v. 6.10*, Bruker AXS, Madison, WI, 2000; G. M. Sheldrick, *SHELXS-86 and SHELXL-97*, University of Göttingen, Göttingen (Germany), 1997.

[4]K. Brandenburg, *Diamond, v3.1e*, Crystal Impact GbR, Bonn, Germany, 2005.