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Unimolecular Cooperative Metallaphotocatalysis with Conjugately Bridged Ir-Ni Complexes and its applications in organic coupling reactions

Mahesh Bhagwan Thoke,[a,b] Gui-Jun Sun,[a] Rahul Anil Borse,[a,b] Ping lin[a] and Shao-Xia Lin*[,a]

[a]State Key Laboratory of Structural Chemistry, Center for Excellence in Molecular Synthesis, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 155 Yangqiao Road West, Fuzhou, 350002, P. R. of China

[b]University of Chinese Academy of Sciences, Beijing, 100049, P. R. of China

Supporting Information

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I. General Information

All non-aqueous reactions were performed in oven-dried glassware and standard Schlenk tubes under an atmosphere of nitrogen. Solvents were dried by Vigor VSPS-5 Solvent Purification System and stored under nitrogen over 4 Å molecular sieves. All other reagents were used as received unless otherwise noted. Thin layer chromatography was performed using silica gel 60 F-254 precoated plates (0.2~0.3 mm) and visualized by short-wave UV (254 nm) irradiation, $KMnO_4$, or iodine stain. Column chromatography was performed with silica gel (200-300 mesh, Yantai Jiangyou Silica Gel Development Co., Ltd). The NMR spectra were obtained in $CDCl_3$, using Bruker Avance III spectrometer at 400 and 100 MHz for ^1H and ^{13}C NMR, respectively. Chemical shifts (δ) for ^1H NMR spectra are recorded in parts per million from tetramethylsilane with solvent resonance as the internal standard (chloroform, δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet), coupling constant in Hz, and integration. Chemical shifts for ^{13}C NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (δ 77.23 ppm) as the internal standard. The infrared spectra were recorded on VERTEX 70 IR spectrometer as KBr pellets, with absorption reported in cm^{-1}. HRMS data were obtained on a thermo Fisher Scientific LTQ FT Ultrasystem. The UV-Visible absorption experiments were performed on Perkin Elmer Lambda 950 UV/VIS/NIR spectroscopy, Borken, Germany in the wavelength range 200 nm to 700 nm. Fluorescence spectra, emission quantum yield and photoluminescence decay were measured on a FLS1000 photoluminescence spectrometer (Edinburgh Instruments, Livingston, UK).

II. Synthesis and Characterization of Catalysts

L1,[1-2] **L2**,[3] **L3**,[4] **L4**,[5] **L5**[6] and $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$[7] were prepared according to reported procedure.

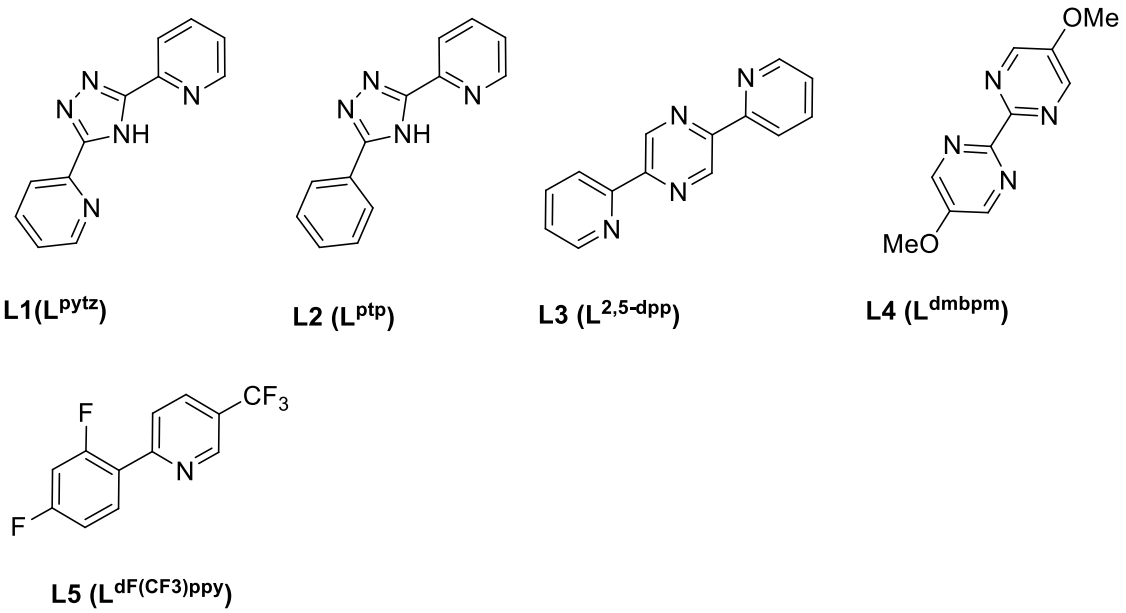
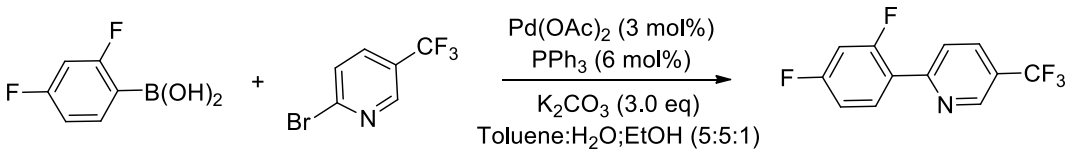


Fig. S1: Ligands

1. Synthesis of $[Ir(dF(CF_3)ppy)_2(L^{pytz})]$ (PC1):

2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyridine

The titled compound was synthesized according to a literature report and the characterisation data are consistent with reported literature.[6]

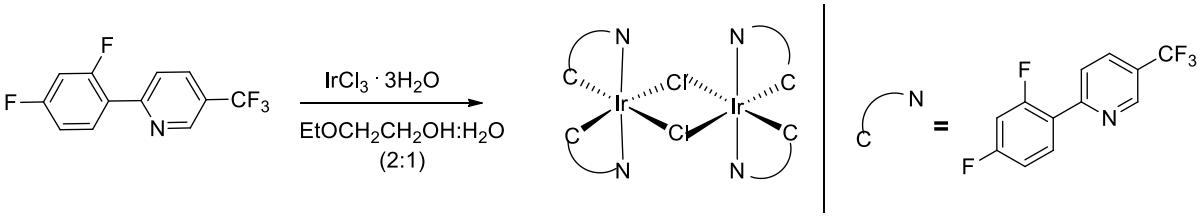


A flame-dried 250 two-necked round bottom flask charged with a magnetic stir bar was added *2-bromo-5-(trifluoromethyl)pyridine* (6.78 g, 30 mmol, 1.0 equiv.), *(2,4-difluorophenyl)boronic acid* (5.68 g, 36 mmol, 1.2 equiv.), $Pd(OAc)_2$ (202 mg, 0.90 mmol, 3 mol%), PPh_3 (472 mg, 1.80 mmol, 6 mol%), K_2CO_3 (12.44 g, 90 mmol, 3.0 equiv.). The flask

was evacuated and backfilled with nitrogen three times. Ethanol (8 mL), Toluene (40 mL) and water (40 mL) were added and reaction was heated up to reflux under stirring overnight. The reaction was cooled to room temperature and 100 mL water was added to quench the reaction. Separate the organic phase in separatory funnel and organic phase washed with 40 mL ether three times. The combined organic phase was washed with brine for three times. Collect the organic phase, dried over Na_2SO_4, filtered and concentrated. Product was purified by silica gel flash chromatography to afford a light-yellow solid (6.99 g, 90%).

[Ir(dF(CF$_3$)ppy)$_2$Cl]-dimer

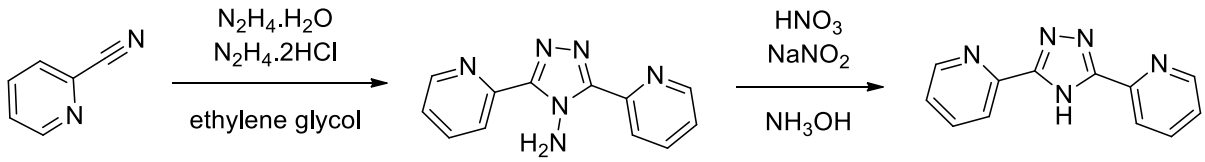
Ir-dimer complex synthesized according to literature report with little modification.[6]



To a Flame dried 500 mL two necked bottom flask with reflux condenser charged with an stir bar was added $IrCl_3{\cdot}H_2O$ (3.17 g, 10 mmol, 1.0 equiv.) and *2-(2,4-difluorophenyl)-4-(trifluoromethyl)pyridine* (5.7 g, 22 mmol, 2.2 equiv.). The flask was evacuated and backfilled with nitrogen three times. 2-ethoxyethanol (134 mL) and water (67 mL) was added. The reaction was heated to reflux for overnight. Let the reaction cool to room temperature and a lot of precipitate formed at the bottom. Filter the crystal and washed the solid with 100 mL water for three times and with few drops of MeOH. Final step carried on yellow crude.

L^{pytz} (L1)

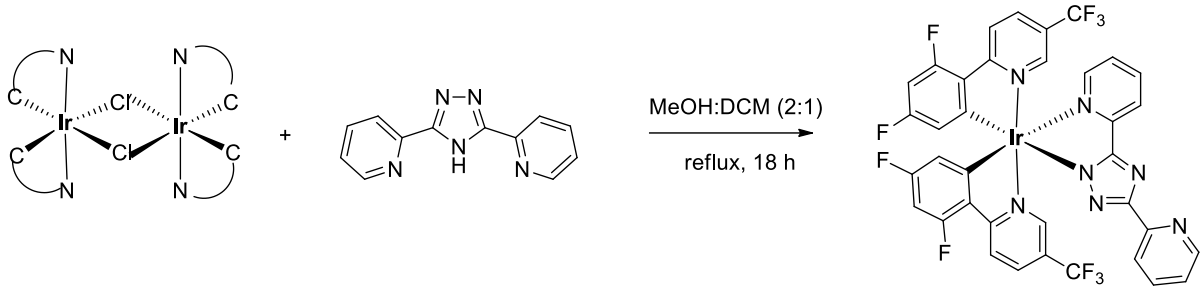
L1 was synthesized according to literature reports and all and the characterisation data are consistent with reported literature.[1-2]



A mixture of 2-cyanopyridine (10.4 g, 100 mmol), hydrazine hydrochloride (10.5 g, 100 mmol) and hydrazine hydrate (15 g, 300 mmol) in ethylene glycol were heated at 130 ^oC for 6 hr. After cooling the reaction mixture was diluted with water (200 mL). The precipitate thus

obtained was filtered, washed with water, dried and recrystalized from ethanol as a white powder (9.8 g, 82%), used as it is for further process. A 250 mL round bottom flask was charged with above product (2 g 8.4 mmol), $HNO_{3(aq)}$ (20 mL, 5 M) and the mixture was stirred at 40 ^oC for 30 min. The solution was cooled to 0 ^oC and $NaNO_2$ (4 g in 20 mL of H_2O) was added drop wise. The mixture was maintained at 0 ^oC and stirred for further 30 min. NH_3OH (3 M) was then added dropwise until the mixture was alkaline and white precipitate formed. The precipitate was filter and dried to afford white solid of L^{pytz} (1.6 g, 86%).

[Ir(dF(CF$_3$)ppy)$_2$(L^{pytz})] (PC1)



Catalyst [Ir(dF(CF$_3$)ppy)$_2$(L^{pytz})] was synthesized using modified procedure from literature report.[2]

A oven dried two-necked 250 mL round bottom flask was flushed with nitrogen and charged it with L^{pytz} (0.49 g, 2.17 mmol, 3.1 equiv.) and [Ir(dF(CF$_3$)ppy)$_2$Cl]-dimer (1.04 g, 0.7 mmol, 1 equiv.). To this MeOH (150 mL) and CH_2Cl_2 (75 mL) was added. The flask covered with aluminium foil and heated to reflux for 18 hr under nitrogen. Let the reaction cool to room temperature and the concentrated in vacuo. The crude was purified on basic alumina using CH_2Cl_2 and later CH_2Cl_2: MeOH (99:1) as an eluent, to afford yellow crystal. (910 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.3 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.35 (td, *J* = 8.3, 2.9 Hz, 2H), 8.17 – 8.06 (m, 2H), 7.98 – 7.90 (m, 2H), 7.87 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.72 – 7.61 (m, 2H), 7.58 (s, 1H), 7.22 (ddd, *J* = 7.2, 5.5, 1.4 Hz, 1H), 7.21 – 7.13 (m, 1H), 6.56 (ddd, *J* = 11.8, 9.0, 2.3 Hz, 1H), 6.47 (ddd, *J* = 11.8, 9.1, 2.3 Hz, 1H), 5.78 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.70 (dd, *J* = 8.5, 2.3 Hz, 1H).

^{19}FNMR (376 MHz, $CDCl_3$) δ -62.55, -62.81, -103.32 (q, *J* = 8.6 Hz), -104.16 (q, *J* = 8.8 Hz), -107.15 (t, *J* = 12.3 Hz), -108.16 (t, *J* = 12.1 Hz).

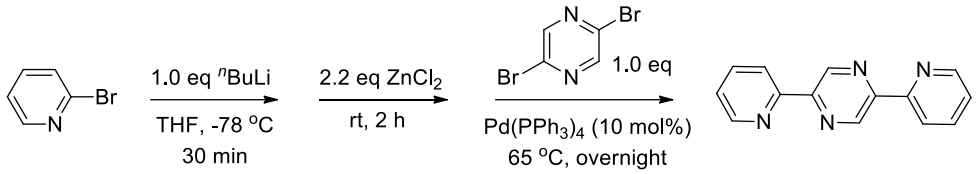
IR (KBr): *v*(cm^{-1}) 1602, 1571, 1490, 1384, 1330, 1294,1164, 1139, 1105, 1089, 991, 844, 829, 723

HRMS (ESI, m/z) calculated for $C_{36}H_{18}F_{10}IrN_7Na^+[M+Na]^+$ 954.0991, found 954.0985

2. Synthesis of [Ir(dF(CF$_3$)ppy)$_2$(L$^{2,5\text{-dpp}}$)] (PC2):

2,5-Di(pyridine-2-yl)pyrazine (L$^{2,5\text{-dpp}}$)

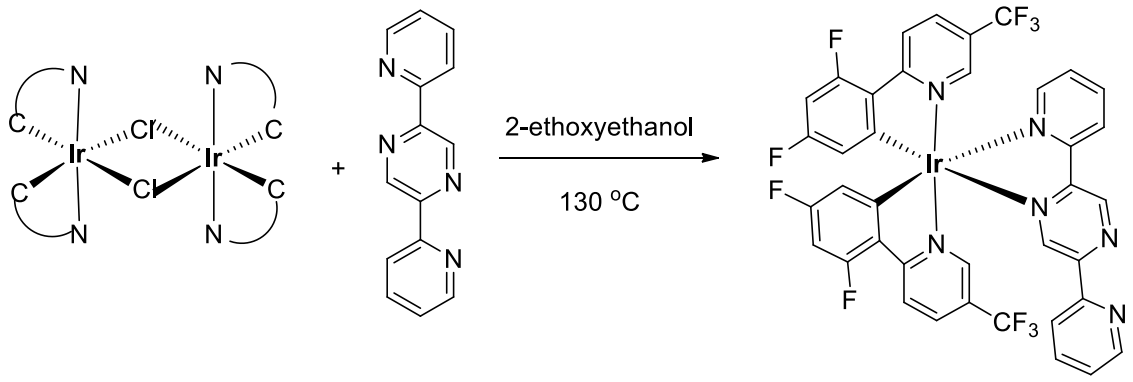
The titled compound was synthesized according to a literature report and the characterisation data are consistent with reported literature.[4]



To a suspension of 2-bromopyridine (9.25 mmol, 880 µL, 2.2 equiv.) in 30 mL of dry THF under a nitrogen atmosphere at -78 °C was added dropwise over 30 min n-BuLi (9.25 mmol, 5.8 mL, 2.2 equiv.). The reaction was stirred for 30 min, and mixture of $ZnCl_2$ (1.25 h, 9.25 mmol, 2.2 equiv.) in 30 mL of dry THF was added. The mixture was then stirred 2 h at room temperature and then added via cannula to a mixture of 2,5-dibromopyrazine (1 g, 4.20 mmol, 1 equiv.) and $Pd(PPh_3)_4$ (485 mg, 10 mol%) in 40 mL of dry THF at room temperature. The reaction mixture was stirred overnight at 65 °C under nitrogen. The solid was filtered, washed several times with diethyl ether and dissolved in 100 mL of saturated aqueous EDTA and 50 mL of saturated aqueous Na_2CO_3. The mixture was stirred for 1 hour and the solid was filtered, washed several times with water and dried over reduced pressure to obtained desired solid product (490 mg, 50%).

[Ir(dF(CF$_3$)ppy)$_2$(L$^{2,5\text{-dpp}}$)] (PC2)

Catalyst [Ir(dF(CF$_3$)ppy)$_2$(L$^{2,5\text{-dpp}}$)] was synthesize using modified procedure from literature.[4]



A oven dried two-neck 100 mL round bottom flask was flushed with nitrogen and charged it with [Ir(dF(CF$_3$)ppy)$_2$Cl]-dimer (378 mg, 0.3 mmol, 1 equiv.). To this was added L$^{2,5\text{-dpp}}$ (173

mg, 0.75 mmol, 2.5 equiv.) and 2-ethoxyethanol (7.5 mL). The flask was evacuated and backfilled with nitrogen three times. The suspension was heated at 130 °C for 24 h. The reaction mixture was cooled to room temperature and diluted with water. The aqueous suspension was washed several times with Et_2O. The aqueous layer was heated at 70 °C for 30 min and cooled to RT. A solution of NH_4PF_6 (10 equiv., 0.5 g/5 mL) was added to the aqueous phase, which cause the precipitation of red solid. The suspension was cooled to 0 °C for 1 h, filtered and resulting solid washed with water. The crude solid was purified by flash chromatography on silica gel to afford brownish solid (452 mg, 69%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 1H), 9.12 (d, *J* = 8.1 Hz, 1H), 8.80 (s, 1H), 8.63 (d, *J* = 3.4 Hz, 1H), 8.54 – 8.34 (m, 6H), 8.11 – 7.99 (m, 3H), 7.81 (t, *J* = 6.7 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.21 – 6.98 (m, 2H), 5.93 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.65 (dd, *J* = 8.3, 2.4 Hz, 1H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -60.88, -61.63, -69.20, -71.09, -103.15 – -103.26 (m), -103.28 – -103.39 (m), -106.61 (t, *J* = 12.2 Hz), -106.89 (t, *J* = 12.4 Hz).

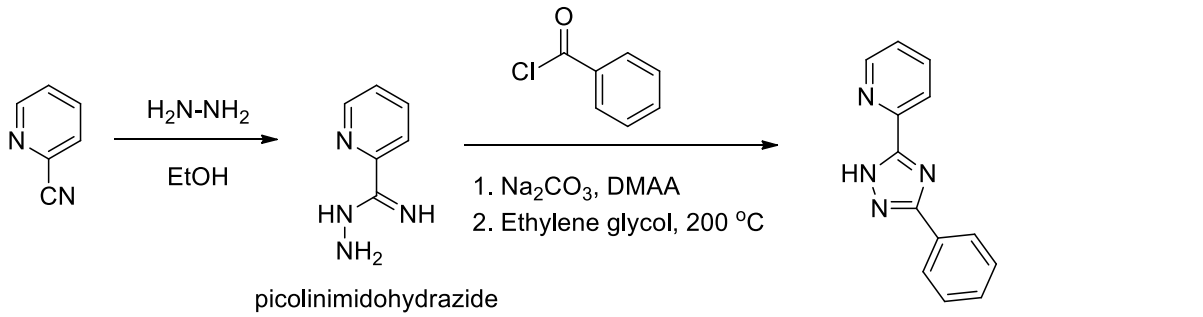
IR (KBr): *v*(cm^{-1}) 1600, 1579, 1458, 1382, 1330, 1298, 1184, 1141, 1109, 1091, 991, 839, 783, 721, 557

HRMS (ESI, m/z) calculated for $C_{38}H_{21}F_{10}IrN_6^+[M+H]^+$ 944.1297, found 944.1241

3. Synthesis of [Ir(dF(CF$_3$)ppy)$_2$(L^{ptp})] (PC3):

2-(3-phenyl-1H-1,2,4-triazol-5-yl)pyridine (L^{ptp})

The titled compound was synthesized according to a literature report and the characterisation data are consistent with reported literature.[3]



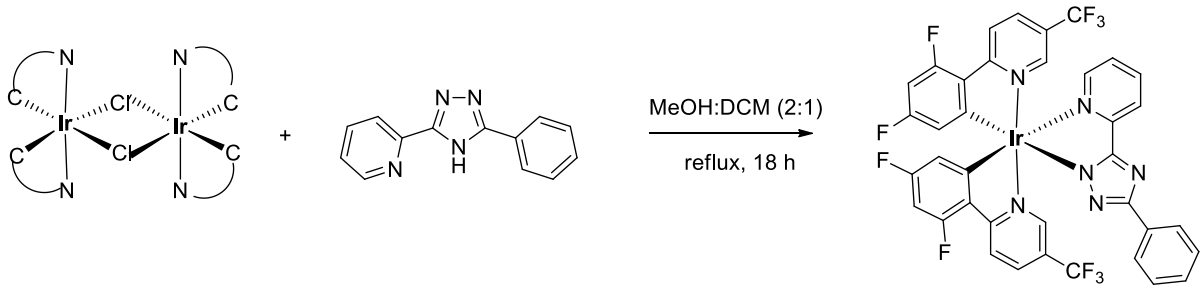
Picolinimidohydrazide: After melting 5.2 g (50 mmol) of 2-cyanopyridine with gentle heating, 2.65 mL (2.75 g, 55 mmol) of hydrazine monohydrate was added, yielding a cloudy mixture. Ethanol (2.5 mL) was added until the mixture became clear, and the resulting

solution was stirred overnight at room temperature, gel like product to formed. All solvent were removed under reduced pressure, and the solid was suspended in petroleum ether (25 mL), cooled in an ice bath, and filtered, washing with cold petroleum ether, yielding 5.2 g (77 %) of amidrazone which used without further purification.

2-(3-phenyl-1H-1,2,4-triazol-5-yl)pyridine (L^{ptp}):

In a flame dried, nitrogen purged 30 mL Schlenk tube were placed Picolinimidohydrazide (2.0 g, 15 mmol) and Na_2CO_3 (1.6 g, 15 mmol). The flask was evacuated and gently heated. After cooling, the flask was purged with nitrogen. Next, 15 mL of dry dimethylacetamide and 5 mL of dry THF were added, yielding a pale-yellow suspension that was cooled to 0 ^oC. In a separate, dry 10 mL Schlenk flask, (1.8 mL, 15 mmol) of the benzoyl chloride was dissolved in 5 mL of DMAA. This solution was then added to precooled amidrazone mixture dropwise, which caused it to turn bright yellow. The mixture was slowly warmed to room temperature and stirred for additional 5 h, yielding a thick yellow mixture. The contents were filtered. The solid was washed with water and ethanol and then resulting pale yellow solid allowed to air dry. The solid was suspended in 20 mL of ethylene glycol and heated to 190 ^oC for 1.5 h. Upon cooling to room temperature, a white solid formed, collected and washed with water. The solid (L^{ptp}) was dried under vacuum (1.99 g, 60%) and used without further purification.

[Ir(dF(CF_3)ppy)$_2$(L^{ptp})] (PC3)



A oven dried two-neck 250 mL round bottom flask was flushed with nitrogen and charged it with L^{ptp} (276 mg, 1.24 mmol, 3.1 equiv.) and [Ir(dF(CF_3)ppy)$_2$Cl]-dimer (486 mg, 0.4 mmol, 1 equiv.). To this MeOH (85 mL) and CH_2Cl_2 (42 mL) was added. The flask covered with Aluminium foil and heated to reflux for 18 hr under nitrogen. Let the reaction cool to room temperature and the concentrated in vacuo. The crude was purified on basic alumina using CH_2Cl_2 as an eluent, to afford yellow solid. (380 g, 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.32 (m, 3H), 8.14 – 8.04 (m, 3H), 7.99-7.86 (m, 3H), 7.73 (d, *J* = 5.5 Hz, 1H), 7.64 (s, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.65 – 6.45 (m, 2H), 5.80 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.72 (dd, *J* = 8.5, 2.3 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.66, -62.75, -103.42 (q, *J* = 8.5 Hz), -104.15 (dt, *J* = 9.0 Hz), -107.25 (t, *J* = 11.9 Hz), -108.17 (t, *J* = 12.2 Hz).

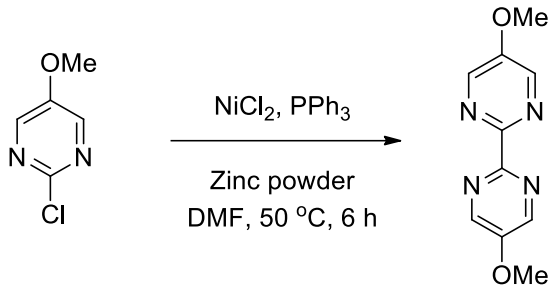
IR (KBr): *ν*(cm^{-1}) 3068, 1606, 1571, 1492, 1461, 1421, 1384, 1330, 1294, 1251, 1137, 1107, 1089, 991, 844, 829, 721, 696

HRMS (ESI, m/z) calculated for $C_{37}H_{19}F_{10}IrN_6Na^+$[M+Na]$^+$ 953.1039, found 953.1033

4. Synthesis of [Ir(dF(CF$_3$)ppy)$_2$(L^{dmbpm})] (PC4):

5,5'-dimethoxy-2,2'-bipyrimidine (L^{dmbpm})

5,5'-dimethoxy-2,2'-bipyrimidine was synthesize using modified procedure from literature.[5]



In a flame dried, nitrogen purged two-necked round bottom flask added triphenylphosphine (10.5 g, 40 mmol), $NiCl_2$ (1.3 g, 10 mmol), zinc powder (1.3 g, 20 mmol) and put under vacuum for 20 mins and then added dry DMF (40 mL). After vigorous stirring at room temperature for an hour, 2-chloro-5-methoxypyrimidine (1.4 g, 10 mmol, 1 equiv.) was added. Vigorously stirred for 1 hr further at room temperature and then heated to 50 °C for 6 h. After checking the TLC, stopped the reaction and allow cool down to room temperature. Reaction filter through Celite bed, washed with chloroform several times, this chloroform mixture added to NH_3OH solution. The aqueous layer was extracted with chloroform, dried over Na_2SO_4 and concentrated. Product was purified by silica gel flash chromatography to afford a white solid (0.815 g, 75%).

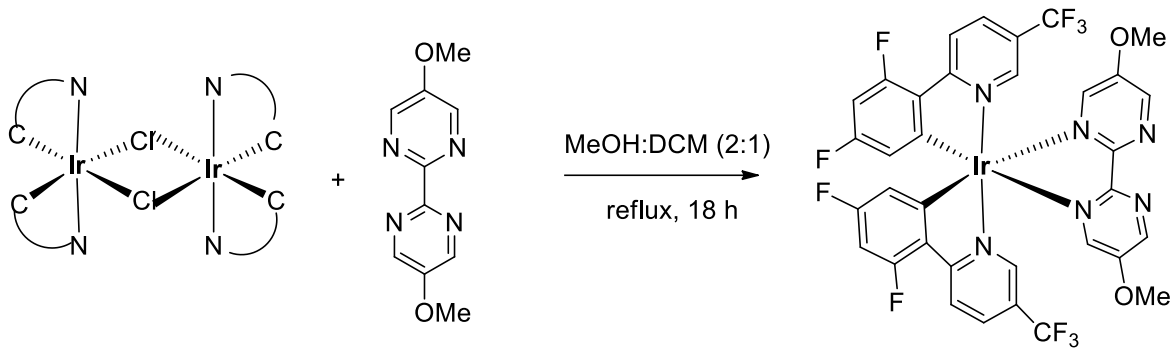
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 4H), 3.98 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.27, 153.36, 144.05, 56.32.

IR (KBr): ν(cm^{-1}) 1635, 1573, 1543, 1427, 1384, 1278, 1172, 1002, 918, 763, 642, 580

HRMS (ESI, m/z) calculated for $C_{10}H_{10}N_4O_2Na^+$[M+Na]$^+$ 241.0702, found 241.0696

[Ir(dF(CF$_3$)ppy)$_2$(L^{dmbpm})] (PC4)



A oven dried two-neck 250 mL round bottom flask was flushed with nitrogen and charged it with L^{dmbpm} (229 mg, 1.05 mmol, 2.1 equiv) and [Ir(dF(CF$_3$)ppy)$_2$Cl]-dimer (608 mg, 0.5 mmol, 1 equiv.). To this MeOH (107 mL) and CH_2Cl_2 (54 mL) was added. The flask covered with aluminium foil and heated to reflux for 18 hr under nitrogen. The mixture was cooled to room temperature, concentrated in vacuo. The crude was purified on basic alumina using CH_2Cl_2/MeOH (70:30) as an eluent, to afford yellow solid. (290 mg, 31%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.12 (d, J = 3.2 Hz, 2H), 8.46 (s, 4H), 7.97 (s, 2H), 7.63 (d, J = 3.2 Hz, 2H), 7.08 (ddd, J = 12.2, 9.4, 2.4 Hz, 2H), 5.76 (d, J = 2.3 Hz, 1H), 5.73 (d, J = 2.3 Hz, 1H), 3.95 (s, 6H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -60.94, -103.71 (q, J = 9.0 Hz), -106.79 (t, J = 12.2 Hz).

^{13}C NMR (100 MHz, DMSO-d_6) δ 166.33 (d, J = 6.5 Hz), 164.00 (dd, J = 203.3, 73.3 Hz), 162.16 (d, J = 13.2 Hz), 160.16 (d, J = 13.0 Hz), 154.51, 153.06, 150.83 (dd, J = 563.8, 186.8 Hz), 145.28 (d, J = 2.8 Hz), 137.80, 126.78, 124.62 (d, J = 35.0 Hz), 123.61 (d, J = 20.8 Hz), 122.03 (d, J = 272.5 Hz), 120.67, 114.63 (d, J = 18.2 Hz), 99.85 (t, J = 26.8 Hz), 57.08.

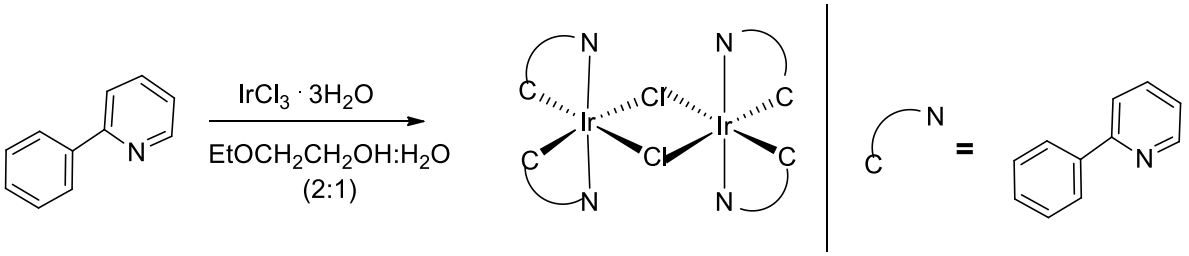
IR (KBr): ν(cm^{-1}) 2918, 2850, 1652, 1597, 1541, 1382, 1328, 1286, 1168, 1132, 1109, 1087, 993, 721

HRMS (ESI, m/z) calculated for $C_{34}H_{21}F_{10}IrN_6O_2^+$[M+H]$^+$ 928.1196, found 928.1133

5. Synthesis of [Ir(ppy)$_2$(L^{pytz})] (PC5):

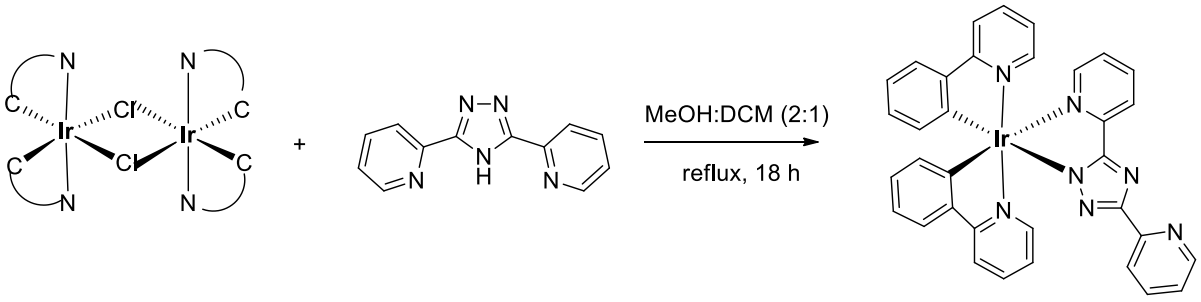
[Ir(ppy)$_2$Cl]-dimer

Ir-dimer synthesized according to a literature report.[7]



To a flame dried 250 mL two necked bottom flask with reflux condenser charged with an stir bar was added $IrCl_3 \cdot H_2O$ (0.389 g, 1.31 mmol) and 2-phenylpyridine (0.76 g, 4.9 mmol). The flask was evacuated and backfilled with nitrogen three times. 2-ethoxyethanol (30 mL) and water (10 mL) was added and refluxed for 24 h. Let the reaction cool to room temperature and the yellow precipitate formed at the bottom. Filter the precipitate and was washed with ethanol (60 mL) and acetone (60 mL), then dissolved in dichloromethane (75 mL) and filtered. Toluene (25 mL) and hexanes (10 mL) were added to the filtrate, which was then reduced in volume by evaporation to 50 mL and cooled to give crystals of $[Ir(ppy)_2Cl]_2$ (408 mg).

$[Ir(ppy)_2(L^{pytz})]$ (PC5)



A oven dried two-neck 250 mL round bottom flask was flushed with nitrogen and charged it with Lpytz (347 mg, 1.55 mmol, 3.1 equiv.) and $[Ir(ppy)_2Cl]$-dimer (536 g, 0.5 mmol, 1 equiv.). To this MeOH (107 mL) and CH_2Cl_2 (54 mL) was added. The flask covered with aluminium foil and heated to reflux for 18 hr under nitrogen. The mixture was cooled to room temperature and the concentrated in vacuo. The crude was purified on basic alumina using CH_2Cl_2 and then CH_2Cl_2/CH_3CN (90:10) as an eluent, to give yellow solid. (475 mg, 66 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 3.3 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 5.7 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.73 (d, *J* = 5.4 Hz, 1H), 7.69 –

7.57 (m, 5H), 7.53 (d, *J* = 5.8 Hz, 1H), 7.16 (dd, *J* = 7.5, 4.9 Hz, 1H), 7.09 (t, *J* = 6.0 Hz, 1H), 6.97 (td, *J* = 7.5, 3.2 Hz, 2H), 6.92 – 6.79 (m, 4H), 6.38 (dd, *J* = 7.5, 2.7 Hz, 2H).

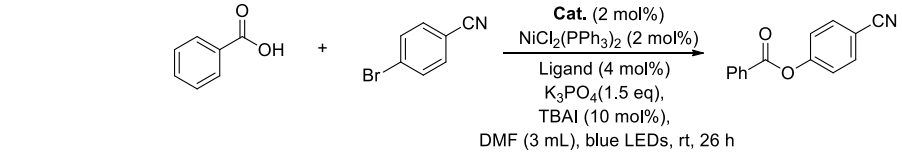
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.58, 168.13, 164.46, 163.57, 153.69, 151.71, 150.85, 150.54, 149.72, 149.62, 149.42, 148.56, 144.66, 144.08, 138.50, 137.30, 136.94, 136.84, 132.34, 132.31, 130.44, 129.91, 124.74, 124.53, 124.46, 122.99, 122.86, 122.37, 122.24, 122.05, 121.85, 121.63, 119.37, 118.91.

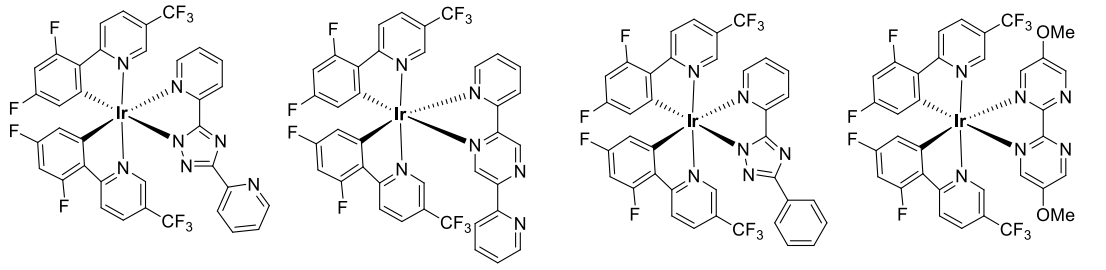
IR (KBr): ν(cm^{-1}) 3039, 1606, 1585, 1475, 1419, 1384, 1269, 1159, 1028, 800, 757, 729

HRMS (ESI, m/z) calculated for $C_{34}H_{24}IrN_7Na^+$[M+Na]$^+$ 746.1620, found 746.1616

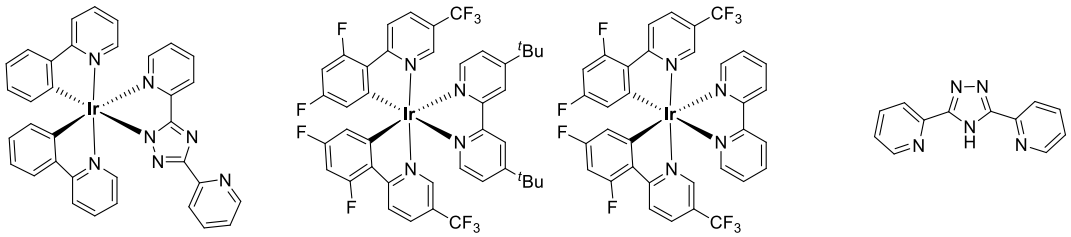
III. Reaction Optimization and Control Experiments

Table S1. Screening of Heteroleptic Ir (III) Photocatalysts.





PC1 PC2 PC3 PC4

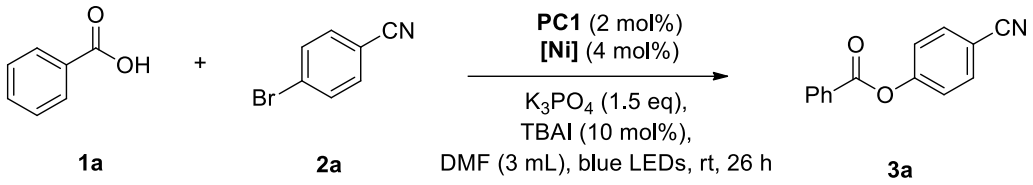


PC5 $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ L^{ptyz}

entry	Cat.	Ligand	yield[a,b]
1	**PC1**	-	86%
2	**PC2**	-	NR
3	**PC3**	-	6%
4	**PC4**	-	NR
5	**PC5**	-	81%
6	**$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$**	**dtbbpy**	10%
7	**$[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$**	**dtbbpy**	6%
8	**$[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$**	**L^{pytz}**	NR
9	**-**	**L^{pytz}**	NR

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **cat.** (2 mol%), $NiCl_2(PPh_3)_2$ (2 mol%), Ligand (4 mol%), K_3PO_4 (1.5 equiv.), TBAI (10 mol%), DMF (3 mL), 24W blue LEDs. [b] NMR yields using CH_2Br_2 as internal standard

Table S2. Screening Nickel Catalysts

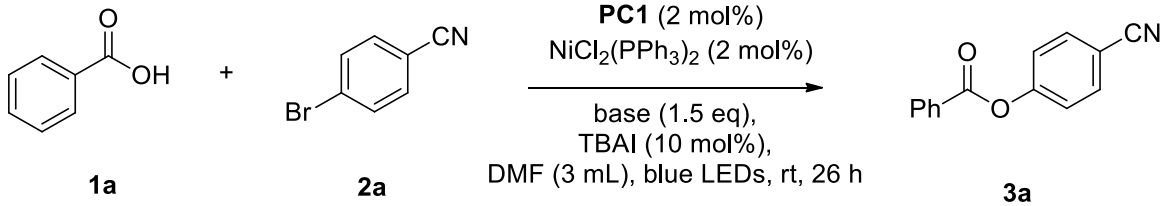


1a **2a** **3a**

entry	Nickel catalyst	yield[a,b]
1	$NiCl_2$•$6H_2O$	16%
2	$Ni(COD)_2$	25%
3	$NiCl_2$•glyme	17%
4	$Ni(acac)_2$	51%
5	$NiCl_2(PPh_3)_2$	87%
6	$NiCl_2$(dppe)	11%
7	$NiCl_2$(dppp)	10%
8	$NiCl_2(PCy_3)_2$	76%
9	NiF_2	0
10	$NiCl_2$	0
11	$NiBr_2$	0
12[c]	$NiCl_2(PPh_3)_2$	86%

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **cat.1** (2 mol%), [Ni] (4 mol%), K_3PO_4 (1.5 equiv.), TBAI: tetrabutylammonium iodide (10 mol%), DMF (3 mL), 24W blue LEDs. [b] NMR yields using CH_2Br_2 as internal standard. [c] **cat.1** (2 mol%), $NiCl_2(PPh_3)_2$ (2 mol%)

Table S3. Screening Base

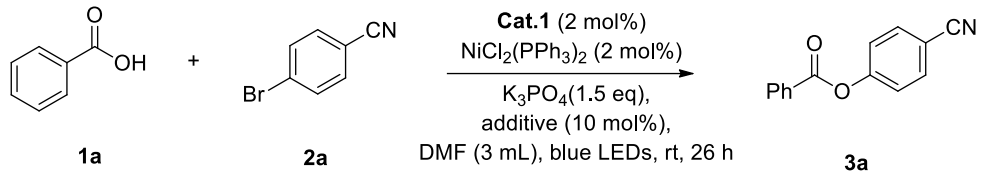


1a **2a** **3a**

entry	base	yield[a,b]
1	K_3PO_4	86%
2	Cs_2CO_3	55%
3	DBU	15%
4	$^{i}Pr_2NH$	72%
5	2,6-Lutidine	trace
6	Na_2CO_3	84%

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **cat.1** (2 mol%), $NiCl_2(PPh_3)_2$ (2 mol%), Base (1.5 equiv.), TBAI (10 mol%), DMF (3 mL), 24W blue LEDs. [b] NMR yields using CH_2Br_2 as internal standard

Table S4. Screening Additives

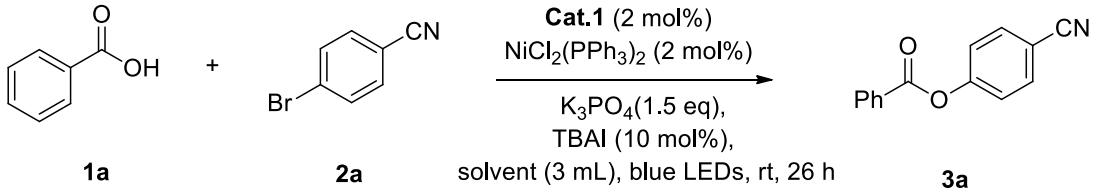


1a **2a** **3a**

entry	Additives (10 mol%)	yield[a,b]
1	TBAI	86%
2	-	80%
3	TBACl	75%
4	TBABr	61%
5	LiI	54%

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **cat.1** (2 mol%), $NiCl_2(PPh_3)_2$ (2 mol%), K_3PO_4 (1.5 equiv.), additive (10 mol%), DMF (3 mL), 24W blue LEDs. [b] NMR yields using CH_2Br_2 as internal standard

Table S5. Screening Solvents

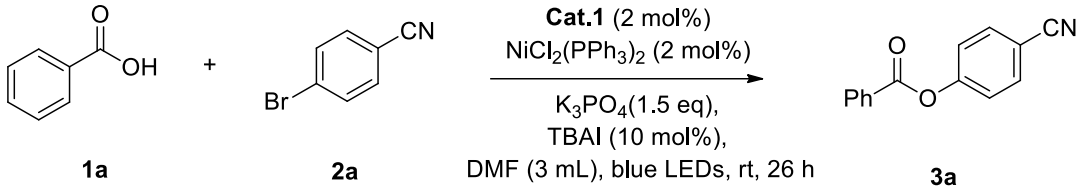


1a **2a** **3a**

entry	solvents	yield[a,b]
1	DMF	86%
2	**DMSO**	**90% (93%)[c]**
3	MeCN	10%
4	DCE	trace
5	Toluene	17%
6	DME	13%

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **cat.1** (2 mol%), $NiCl_2(PPh_3)_2$ (2 mol%), K_3PO_4 (1.5 equiv.), TBAI (10 mol%), solvent (3 mL), 24W blue LEDs. [b] NMR yields using CH_2Br_2 as internal standard. [c] Isolated yield.

Table S6. Control Experiments

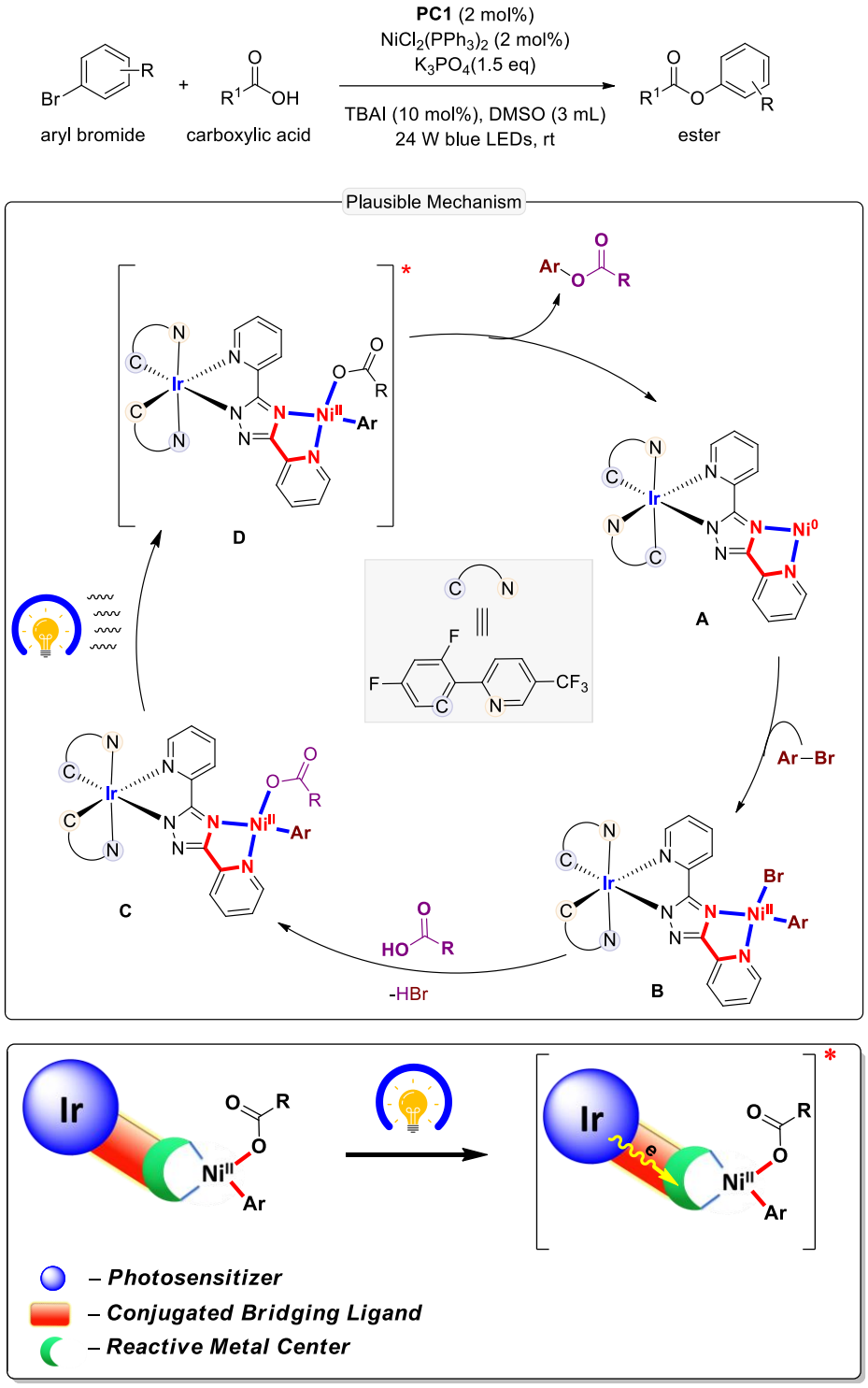


1a **2a** **3a**

entry	Light	**Cat.1**	$NiCl_2(PPh_3)_2$	yield[a,b]
1	√	√	√	86%
2	×	√	√	NR
3	√	×	√	NR
4	√	√	×	NR

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **cat.1** (2 mol%), $NiCl_2(PPh_3)_2$ (2 mol%), K_3PO_4 (1.5 equiv.), TBAI (10 mol%), DMF (3 mL), 24W blue LEDs. [b] NMR yields using CH_2Br_2 as internal standard

IV. Plausible Reaction Mechanism



Scheme S1. A plausible reaction mechanism for unimolecular bimetallic cooperative metallaphotocatalysis with conjugated bridging ligand.

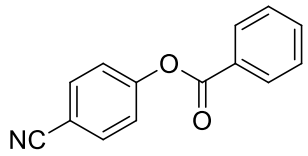
V. Synthesis and Characterization of Products

General Procedure for Esterification of Aryl and Vinyl Bromides via Cooperative Metallaphotocatalysis with an Ir–Ni Bimetallic Complex.

To the oven dried Schlenk tube equipped with a rubber septum and magnetic stir bar were added Aryl halide **1** (0.2 mmol, 1 equiv.), Acid **2** (0.4 mmol, 2 equiv.), TBAI (0.02 mmol, 0.10 equiv.). Schlenk tube brought into glove box and charged with PC1 (2 mol%), $NiCl_2(PPh_3)_2$ (2 mol%), and K_3PO_4 (1.5 equiv.). The Schlenk tube was placed under an atmosphere of nitrogen, then the DMSO (3 mL) was added. The reaction mixture then was cooled to -78 ^oC and degassed with vacuum evacuation (5 min), backfilled with nitrogen and then warmed to room temperature. This process repeated three times, then Schlenk tube was sealed with glass stopper and parafilm, placed 1-2 cm away from 24 W blue LED strips, and irradiated allowing temperature to rise due to the proximity of lights. After 24 hrs, reaction poured into ice-cold water and extracted three times with ethyl acetate. Dried over Na_2SO_4 and concentrated *in vacuo*. The product was purified by flash column chromatography.

Note: Although PC1, $NiCl_2(PPh_3)_2$ are air stable, we always used glove box for addition to assure reproducibility and to get consistent results. In case of liquid Vinyl bromides, we added them at last, after degassing.

4-cyanophenyl benzoate (1)



White solid. Yield 90%. M.P. = 90-94 ^oC.

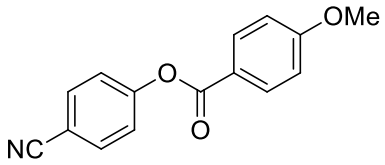
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.53, 154.47, 134.38, 133.95, 130.51, 128.97, 128.85, 123.14, 118.48, 110.05.

IR (KBr film): *v* (cm^{-1}) 2363, 2229, 1734, 1599, 1502, 1450, 1262, 1215, 1171, 1078, 1064, 1022, 883, 702

HRMS (ESI, *m/z*) calculated for $C_{14}H_9NO_2Na^+[M+Na]^+$ 246.0531, found 246.0525

4-cyanophenyl 4-methoxybenzoate (2)



White solid. Yield 95%. M.P. = 107-109 °C.

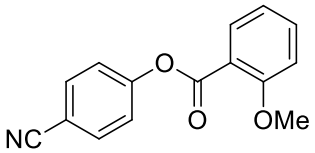
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.53, 164.19, 154.61, 133.85, 132.67, 123.17, 121.01, 118.54, 114.23, 109.75, 55.77.

IR (KBr film): *v* (cm^{-1}) 2228, 1730, 1612, 1516, 1279, 1215, 1171, 1068, 1014, 868, 842, 760, 670, 544

HRMS (ESI, *m/z*) calculated for $C_{15}H_{11}NO_3Na^+$[M+Na]$^+$ 276.0637, found 276.0631

4-cyanophenyl 2-methoxybenzoate (3)



White solid. Yield 89%. M.P. = 92-94 °C.

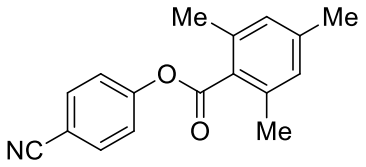
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.58 (ddd, *J* = 8.8, 7.4, 1.8 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.09 – 7.02 (m, 2H), 3.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.44, 160.33, 154.50, 135.18, 133.76, 132.48, 123.20, 120.44, 118.54, 118.04, 112.43, 109.65, 56.19.

IR (KBr film): *v* (cm^{-1}) 2228, 1751, 1599, 1493, 1460, 1435, 1290, 1260, 1234, 1209, 1165, 1016, 877, 754, 696, 656, 552

HRMS (ESI, *m/z*) calculated for $C_{15}H_{11}NO_3Na^+$[M+Na]$^+$ 276.0637, found 276.0631

4-cyanophenyl 2,4,6-trimethylbenzoate (4)



White solid. Yield 90%. M.P. = 110-112 ºC.

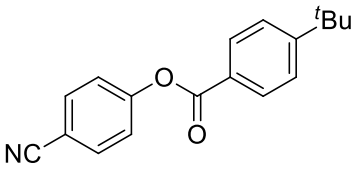
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.95 (s, 2H), 2.45 (s, 6H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.51, 154.17, 140.81, 136.10, 133.95, 129.04, 129.02, 122.91, 118.38, 110.02, 21.36, 20.29.

IR (KBr film): *v* (cm^{-1}) 2232, 1753, 1602, 1502, 1425, 1244, 1203, 1161, 1040, 875, 854, 810, 603, 549

HRMS (ESI, *m/z*) calculated for $C_{17}H_{15}NO_2Na^+$[M+Na]$^+$ 288.1000, found 288.0995

4-cyanophenyl 4-(*tert*-butyl)benzoate (5)



White solid. Yield 95%. M.P. = 102-104 ºC.

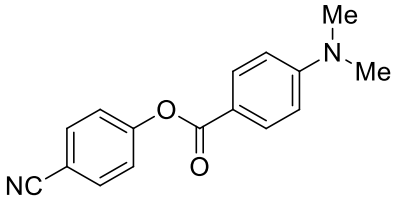
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.47, 158.30, 154.53, 133.85, 130.38, 125.96, 125.93, 123.13, 118.48, 109.83, 35.44, 31.23.

IR (KBr film): *v* (cm^{-1}) 2229, 1738, 1600, 1496, 1463, 1406, 1363, 1272, 1068, 870, 821, 770, 702, 545

HRMS (ESI, *m/z*) calculated for $C_{18}H_{17}NO_2Na^+$[M+Na]$^+$ 302.1157, found 302.1151

4-cyanophenyl 4-(dimethylamino)benzoate (6)



White solid. Yield 64%. M.P. = 151-153 ^{o}C.

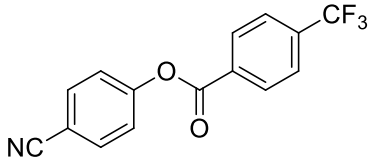
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 9 Hz, 2H), 7.70 (d, *J* = 8.7, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 9.1 Hz, 2H), 3.09 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.74, 155.07, 154.20, 133.74, 132.38, 123.28, 118.74, 114.89, 111.00, 109.26, 40.24.

IR (KBr film): *v* (cm^{-1}) 2914, 2228, 1720, 1605, 1527, 1497, 1445, 1367, 1273, 1219, 1167, 1051, 876, 824, 760, 690, 552

HRMS (ESI, *m/z*) calculated for $C_{16}H_{14}N_2O_2Na^+$[M+Na]$^+$ 289.0953, found 289.0947.

4-cyanophenyl 4-(trifluoromethyl)benzoate (7)



White solid. Yield 75%. M.P. =124-126 ^{o}C.

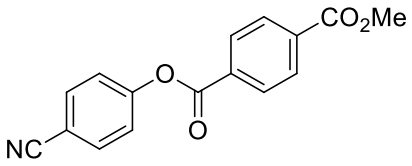
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.34, 154.02, 135.68 (q, *J* = 33.0 Hz), 134.01, 132.09, 130.88, 125.98 (q, *J* = 4.1 Hz), 123.61 (q, *J* = 272.8 Hz), 122.98, 118.29, 110.41.

IR (KBr film): *v* (cm^{-1}) 2231, 1730, 1601, 1502, 1395, 1335, 1275, 1197, 1040, 887, 850, 790, 768, 680

HRMS (ESI, *m/z*) calculated for $C_{15}H_8F_3NO_2Na^+$[M+Na]$^+$ 314.0405, found 314.0395

4-cyanophenyl methyl terephthalate (8)



White solid. Yield 67%. M.P. = 172-174 °C.

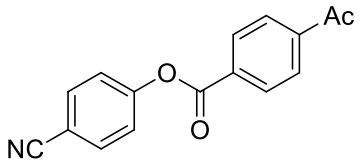
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 3.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.15, 163.72, 154.14, 135.16, 133.98, 132.53, 130.42, 130.02, 123.00, 118.32, 110.29, 52.78.

IR (KBr film): *v* (cm^{-1}) 2231, 1730, 1654, 1500, 1407, 1385, 1275, 1175, 1109, 1080, 1016, 880, 813, 719, 549

HRMS (ESI, *m/z*) calculated for $C_{16}H_{11}NO_4Na^+$[M+Na]$^+$ 304.0586, found 304.0580

4-cyanophenyl 4-acetylbenzoate (9)



White solid. Yield 40%. M.P. = 158-160 °C.

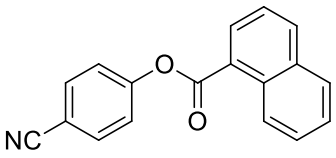
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 2.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.48, 163.70, 154.15, 141.33, 134.02, 132.53, 130.76, 128.68, 123.02, 118.35, 110.37, 27.15.

IR (KBr film): *v* (cm^{-1}) 2233, 1736, 1686, 1500, 1402, 1263, 1219, 1169, 1087, 880, 815, 756, 686, 548

HRMS (ESI, *m/z*) calculated for $C_{16}H_{11}NO_3Na^+$[M+Na]$^+$ 288.0637, found 288.0631

4-cyanophenyl 1-naphthoate (10)



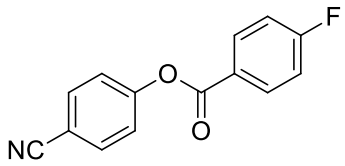
White solid. Yield 68%. M.P. = 99-101 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 8.6 Hz, 1H), 8.48 (dd, *J* = 7.4, 1.3 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.95 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.67 (ddd, *J* = 8.5, 6.8, 1.4 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.88, 154.49, 135.25, 134.13, 133.94, 131.90, 131.82, 129.04, 128.71, 126.82, 125.65, 124.87, 124.68, 123.30, 118.50, 109.99.

IR (KBr film): *v* (cm^{-1}) 2231, 1737, 1598, 1500, 1273, 1236, 1211, 1184, 1110, 982, 880, 780, 548, 505

HRMS (ESI, *m/z*) calculated for $C_{18}H_{11}NO_2Na^+$[M+Na]$^+$ 296.0687, found 296.0682

4-cyanophenyl 4-fluorobenzoate (11)



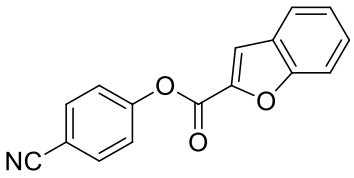
White solid. Yield 91%. M.P. = 97-100 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.20 (t, *J* = 8.6 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.64 (d, *J* = 256.3 Hz), 163.52, 154.27, 133.95, 133.17 (d, *J* = 9.6 Hz), 125.08 (d, *J* = 3.0 Hz), 123.07, 118.40, 116.24 (d, *J* = 22.1 Hz), 110.14.

IR (KBr film): *v* (cm^{-1}) 2235, 1730, 1597, 1506, 1413, 1275, 1207, 887, 852, 794, 758, 681, 550

HRMS (ESI, *m/z*) calculated for $C_{14}H_8FNO_2Na^+$[M+Na]$^+$ 264.0437, found 264.0431

4-cyanophenyl benzofuran-2-carboxylate (12)



White solid. Yield 32%. M.P. = 162-164 ^{o}C.

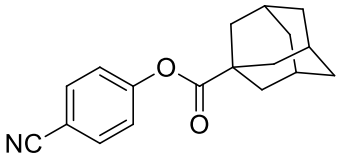
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 4H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.53 (td, *J* = 8.5, 1.3 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.37 (td, *J* = 8.0, 1.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.10, 156.46, 153.64, 144.06, 134.04, 128.82, 126.91, 124.46, 123.40, 122.93, 118.33, 116.61, 112.73, 110.42.

IR (KBr film): *v* (cm^{-1}) 2229, 1743, 1562, 1504, 1300, 1213, 1170, 1142, 1078, 740, 550

HRMS (ESI, *m/z*) calculated for $C_{16}H_9NO_3Na^+$[M+Na]$^+$ 286.0480, found 286.0475

(3*r*,5*r*,7*r*)-4-cyanophenyl adamantane-1-carboxylate (13)



White solid. Yield 67%. M.P. = 108 – 110 ^{o}C.

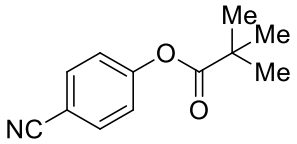
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 2.10 – 2.03 (m, 3H), 2.01 (d, *J* = 2.9 Hz, 6H), 1.79 – 1.69 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.47, 154.71, 133.74, 122.95, 118.51, 109.58, 41.37, 38.81, 36.50, 27.96.

IR (KBr film): *v* (cm^{-1}) 2910, 2852, 2231, 1751, 1604, 1506, 1454, 1205, 1169, 1038, 901, 862, 791, 547

HRMS (ESI, *m/z*) calculated for $C_{18}H_{19}NO_2Na^+$[M+Na]$^+$ 304.1313, found 304.1308

4-cyanophenyl pivalate (14)



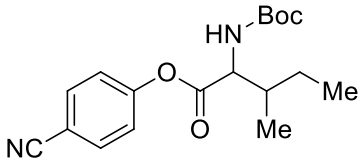
Colourless liquid. Yield 86%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 1.35 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.39, 153.63, 132.76, 121.88, 117.46, 108.67, 38.41, 26.16.

IR (KBr film): *v* (cm^{-1}) 2972, 2233, 1761, 1600, 1500, 1479, 1276, 1211, 1168, 1109, 1031, 897, 852, 550

HRMS (ESI, *m/z*) calculated for $C_{12}H_{13}NO_2Na^+$[M+Na]$^+$ 226.0844, found 226.0838

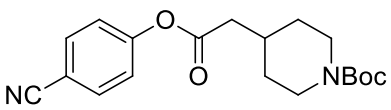
4-cyanophenyl 2-((*tert*-butoxycarbonyl)amino)-3-methylpentanoate (15)



Yellowish liquid. Yield 87%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.8 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 5.08 (d, *J* = 8.6 Hz, 1H), 4.63 – 4.18 (m, 1H), 2.00 (s, 1H), 1.57 – 1.49 (m, 1H), 1.44 (s, 9H), 1.32 – 1.25 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.57, 155.76, 153.83, 133.85, 122.76, 118.23, 110.13, 80.37, 58.33, 37.88, 28.41, 25.35, 15.83, 11.71.
IR (KBr film): *v* (cm^{-1}) 2972, 2929, 2231, 1766, 1714, 1602, 1498, 1369, 1207, 1165, 1120, 1014, 864, 551
HRMS (ESI, *m/z*) calculated for $C_{18}H_{24}N_2O_4Na^+$[M+Na]$^+$ 355.1634, found 355.1628

***tert*-butyl 4-(2-(4-cyanophenoxy)-2-oxoethyl)piperidine-1-carboxylate (16)**



White solid. Yield 77%. M.P. = 104-106 °C.

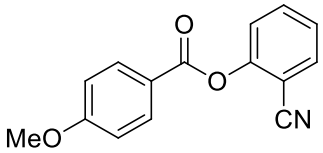
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 4.11 (s, 2H), 2.74 (t, *J* = 13.1 Hz, 2H), 2.51 (d, *J* = 7.0 Hz, 2H), 2.11 – 1.95 (m, 1H), 1.81 – 1.73 (m, 2H), 1.44 (s, 9H), 1.30 – 1.21 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.14, 154.92, 153.97, 133.84, 122.86, 118.35, 109.95, 79.68, 41.10, 33.23, 31.91, 28.60.

IR (KBr film): *v* (cm^{-1}) 2978, 2928, 2231, 1765, 1690, 1602, 1498, 1425, 1365, 1284, 1245, 1211, 1169, 1136, 972, 852, 771, 548

HRMS (ESI, *m/z*) calculated for $C_{19}H_{24}N_2O_4Na^+$[M+Na]$^+$ 367.1634, found 367.1628

2-cyanophenyl 4-methoxybenzoate (17)



White solid. Yield 81%. M.P. = 124-126 °C.

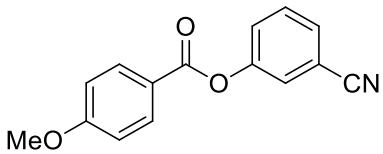
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 2H), 7.72 – 7.60 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.52, 163.72, 152.83, 134.12, 133.35, 132.77, 126.15, 123.45, 120.55, 115.43, 114.18, 107.05, 55.66.

IR (KBr film): *v* (cm^{-1}) 2231, 1730, 1608, 1508, 1189, 1383, 1257, 1175, 1020, 839, 756, 690, 638, 507

HRMS (ESI, *m/z*) calculated for $C_{15}H_{11}NO_3Na^+$[M+Na]$^+$ 276.0637, found 276.0631

3-cyanophenyl 4-methoxybenzoate (18)



White solid. Yield 93%. M.P. = 99-102 °C.

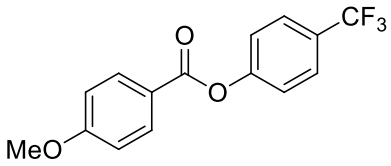
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.57 – 7.42 (m, 4H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.36, 164.28, 151.25, 132.50, 130.45, 129.48, 126.97, 125.68, 120.84, 118.01, 114.10, 113.43, 55.64.

IR (KBr film): *v* (cm^{-1}) 2237, 1718, 1606, 1510, 1383, 1363, 1232, 1168, 1064, 1028, 910, 842, 785, 757, 686, 636

HRMS (ESI, *m/z*) calculated for $C_{15}H_{11}NO_3Na^+$[M+Na]$^+$ 276.0637, found 276.0631

4-(trifluoromethyl)phenyl 4-methoxybenzoate (19)



White solid. Yield 90%. M.P. = 97-100 °C.

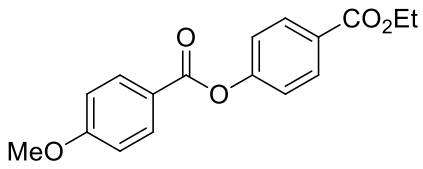
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.53, 164.38, 153.81 (d, *J* = 1.6 Hz), 132.58, 128.09 (q, *J* = 32.7 Hz), 126.93 (q, *J* = 3.7 Hz), 124.14 (q, *J* = 271.9 Hz), 122.51, 121.33, 114.14, 55.66.

IR (KBr film): *v* (cm^{-1}) 1732, 1635, 1510, 1384, 1338, 1263, 1211, 1164, 1118, 1055, 879, 846, 817, 760, 688, 592

HRMS (ESI, *m/z*) calculated for $C_{15}H_{11}F_3O_3Na^+$[M+Na]$^+$ 319.0558, found 319.0552

4-(ethoxycarbonyl)phenyl 4-methoxybenzoate (20)



White solid. Yield 97%. M.P. = 96-98 °C.

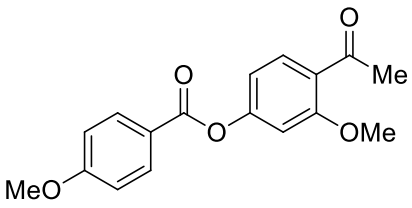
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, *J* = 8.6 Hz, 4H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.94, 164.39, 164.18, 154.78, 132.44, 131.17, 127.97, 121.85, 121.39, 114.00, 61.12, 55.58, 14.40.

IR (KBr film): *v* (cm^{-1}) 1732, 1708, 1602, 1510, 1385, 1261, 1203, 1159, 1110, 1060, 1024, 889, 846, 758, 690, 603, 511

HRMS (ESI, *m/z*) calculated for $C_{17}H_{16}O_5Na^+$[M+Na]$^+$ 323.0895, found 323.0890

4-acetyl-3-methoxyphenyl 4-methoxybenzoate (21)



White solid. Yield 71%. M.P. = 141-143 ºC.

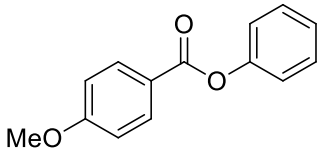
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.9 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 6.88 – 6.80 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.59 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.48, 164.42, 164.23, 160.17, 155.54, 132.45, 131.77, 125.55, 121.32, 114.05, 114.03, 105.85, 55.83, 55.63, 31.92.

IR (KBr film): *v* (cm^{-1}) 1741, 1726, 1662, 1606, 1579, 1454, 1419, 1385, 1257, 1190, 1159, 1122, 1074, 1055, 1028, 877, 842, 810, 761, 692, 624

HRMS (ESI, *m/z*) calculated for $C_{17}H_{16}O_5Na^+$[M+Na]$^+$ 323.0895, found 323.0889

phenyl 4-methoxybenzoate (22)



White solid. Yield 79%. M.P. = 70-73 ºC.

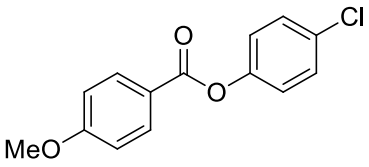
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 2H), 7.11 (dd, *J* = 19.5, 7.8 Hz, 3H), 6.84 (d, *J* = 8.7 Hz, 2H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.98, 163.98, 151.17, 132.35, 129.51, 125.80, 121.90, 113.93, 55.54.

IR (KBr film): *v* (cm^{-1}) 1728, 1639, 1612, 1508, 1454, 1384, 1319, 1276, 1197, 1166, 1080, 1024, 846, 762, 744, 690, 516

HRMS (ESI, *m/z*) calculated for $C_{14}H_{12}O_3Na^+$[M+Na]$^+$ 251.0684, found 251.0679

4-chlorophenyl 4-methoxybenzoate (23)



White solid. Yield 75%. M.P. = 90-93 ^{o}C.

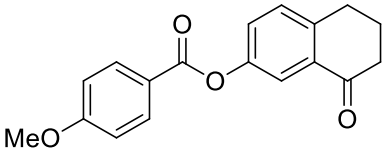
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 5.9 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.73, 164.15, 149.66, 132.43, 131.13, 129.56, 123.32, 121.51, 114.01, 55.60.

IR (KBr film): *v* (cm^{-1}) 1730, 1635, 1490, 1384, 1276, 1205, 1166, 1072, 1020, 842, 804, 761, 694, 607, 503

HRMS (ESI, *m/z*) calculated for $C_{14}H_{11}ClO_3Na^+$[M+Na]$^+$ 285.0294, found 285.0289

8-oxo-5,6,7,8-tetrahydronaphthalen-2-yl 4-methoxybenzoate (24)



Faint brown. Yield 36%. M.P. = 85-90 ^{o}C.

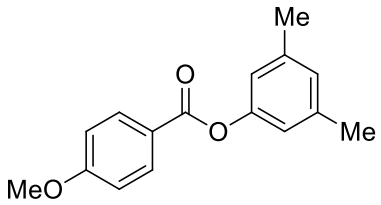
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.1 Hz, 2H), 7.83 (s, 1H), 7.32 (s, 2H), 6.98 (d, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 2.98 (t, *J* = 6.1 Hz, 2H), 2.66 (t, *J* = 6.2 Hz 2H), 2.16 (p, *J* = 6.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.70, 165.06, 164.18, 149.90, 142.06, 133.88, 132.52, 130.19, 127.36, 121.67, 120.13, 114.06, 55.71, 39.01, 29.36, 23.38.

IR (KBr film): *v* (cm^{-1}) 1730, 1686, 1606, 1510, 1488, 1419, 1384, 1249, 1222, 1205, 1165, 1066, 1024, 848, 763, 690, 617

HRMS (ESI, *m/z*) calculated for $C_{18}H_{16}O_4Na^+$[M+Na]$^+$ 319.0946, found 319.0941

3,5-dimethylphenyl 4-methoxybenzoate (25)



White Solid. Yield 90%. M.P. =60-62 ºC.

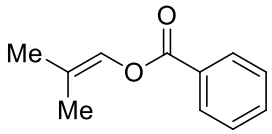
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.92 (s, 1H), 6.86 (s, 2H), 3.88 (s, 3H), 2.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.18, 163.90, 151.07, 139.31, 132.29, 127.54, 122.09, 119.47, 113.88, 55.51, 21.32.

IR (KBr film): *v* (cm^{-1}) 1730, 1604, 1508, 1460, 1384, 1249, 1168, 1139, 1076, 1026, 842, 763, 688, 586

HRMS (ESI, *m/z*) calculated for $C_{16}H_{16}O_3Na^+$[M+Na]$^+$ 279.0997, found 279.0992

2-methylprop-1-en-1-yl benzoate (26)



Colourless liquid. Yield 95%.

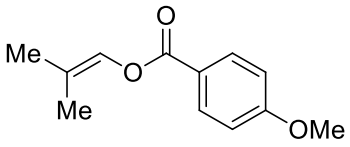
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 7.5, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.02 (s, 1H), 1.72 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.83, 133.37, 130.13, 129.91, 129.82, 128.60, 118.96, 19.87, 15.98.

IR (KBr film): *v* (cm^{-1}) 1732, 1637, 1384, 1263, 1132, 798, 709

HRMS (ESI, *m/z*) calculated for $C_{11}H_{12}O_2Na^+$[M+Na]$^+$ 199.0735, found 199.0730

2-methylprop-1-en-1-yl 4-methoxybenzoate (27)



White solid. Yield 97%. M.P. = 38-42 ºC.

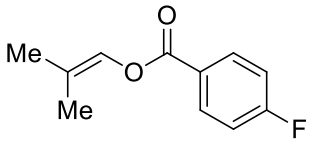
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.98 (s, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 3H), 1.69 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.70, 163.48, 131.87, 130.09, 122.03, 118.28, 113.80, 55.44, 19.77, 15.85.

IR (KBr film): *v* (cm^{-1}) 1722, 1608, 1510, 1385, 1259, 1168, 1132, 1029, 844, 765, 613

HRMS (ESI, *m/z*) calculated for $C_{12}H_{14}O_3Na^+$[M+Na]$^+$ 229.0841, found 229.0836

2-methylprop-1-en-1-yl 4-fluorobenzoate (28)



Colourless liquid. Yield 90%

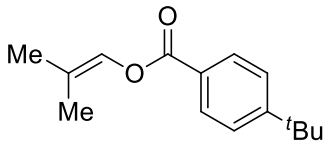
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.17 – 7.04 (m, 3H), 1.79 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.10 (d, *J* = 254.5 Hz), 162.89, 132.49 (d, *J* = 9.4 Hz), 130.08, 126.10 (d, *J* = 3.0 Hz), 119.14, 115.82 (d, *J* = 22.1 Hz), 19.86, 15.98.

IR (KBr film): *v* (cm^{-1}) 1732, 1637, 1508, 1384, 1265, 1130, 808, 763, 611

HRMS (ESI, *m/z*) calculated for $C_{11}H_{11}FO_2Na^+$[M+Na]$^+$ 217.0641, found 217.1052

2-methylprop-1-en-1-yl 4-(*tert*-butyl)benzoate (29)



Colourless liquid. Yield 92%

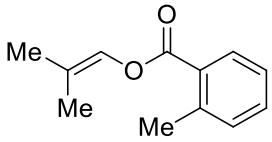
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 1H), 1.82 (s, 3H), 1.72 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.94, 157.11, 130.19, 129.85, 127.04, 125.63, 118.78, 35.28, 31.27, 19.93, 16.00.

IR (KBr film): *v* (cm^{-1}) 2960, 1732, 1608, 1384, 1267, 1135, 1012, 769, 702

HRMS (ESI, *m/z*) calculated for $C_{15}H_{20}O_2Na^+$[M+Na]$^+$ 255.1361, found 255.1356

2-methylprop-1-en-1-yl 2-methylbenzoate (30)



Colourless liquid. Yield 81%

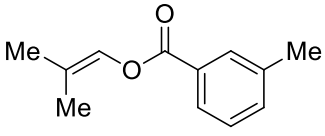
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.22 (m, 1H), 7.18 – 7.07 (m, 2H), 6.99 (s, 1H), 2.52 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.58, 140.84, 132.38, 131.92, 130.91, 130.19, 128.99, 125.88, 118.52, 21.98, 19.85, 16.05.

IR (KBr film): *v* (cm^{-1}) 2970, 1732, 1384, 1244, 1139, 1112, 800, 738

HRMS (ESI, *m/z*) calculated for $C_{12}H_{14}O_2Na^+$[M+Na]$^+$ 213.0891, found 213.0886

2-methylprop-1-en-1-yl 3-methylbenzoate (31)



Colourless liquid. Yield 74%

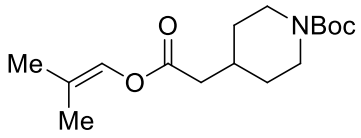
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.3 Hz, 2H), 7.32 – 7.19 (m, 2H), 7.00 (s, 1H), 2.30 (s, 3H), 1.72 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.01, 138.39, 134.14, 130.44, 130.20, 129.75, 128.48, 127.05, 118.85, 21.40, 19.86, 15.99.

IR (KBr film): *v* (cm^{-1}) 2918, 1726, 1383, 1275, 1192, 1128, 739

HRMS (ESI, *m/z*) calculated for $C_{12}H_{14}O_2Na^+$[M+Na]$^+$ 213.0891, found 213.0886

tert-butyl 4-(2-((2-methylprop-1-en-1-yl)oxy)-2-oxoethyl)piperidine-1-carboxylate (32)



Colourless liquid. Yield 76%

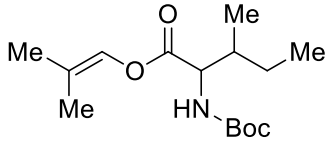
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 4.07 (s, 2H), 2.70 (t, *J* = 12.9 Hz, 2H), 2.31 (d, *J* = 7.4 Hz, 2H), 2.00 – 1.88 (m, 1H), 1.73 – 1.59 (m, 8H), 1.43 (s, 9H), 1.22 – 1.09 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.86, 154.98, 129.89, 118.57, 79.58, 41.04, 43.87, 33.22, 31.95, 28.62, 19.80, 15.85.

IR (KBr film): *v* (cm^{-1}) 2977, 2922, 1745, 1693, 1419, 1284, 1153, 972

HRMS (ESI, *m/z*) calculated for $C_{16}H_{27}NO_4Na^+$[M+Na]$^+$ 320.1838, found 320.1832

2-methylprop-1-en-1-yl 2-((_tert_-butoxycarbonyl)amino)-3-methylpentanoate (33)



Colourless liquid. Yield 71%

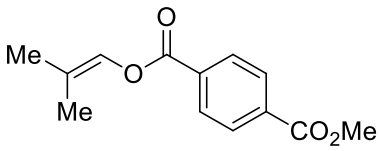
^{1}H NMR (400 MHz, $CDCl_3$) δ .84 (s, 1H), 5.05 (d, *J* = 9.0 Hz, 1H), 4.34 (dd, *J* = 9.0, 4.7 Hz, 1H), 1.89 (s, 1H), 1.73 (s, 1H), 1.66 (d, *J* = 12.6 Hz, 6H), 1.44 (s, 9H), 1.26 – 1.15 (m, 1H), 0.89 – 0.94 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 155.73, 129.74, 119.45, 80.06, 57.92, 38.29, 28.52, 25.31, 19.78, 15.94, 15.71, 11.86.

IR (KBr film): *v* (cm^{-1}) 2966, 2929, 1749, 1716, 1508, 1382, 1247, 1155, 1095

HRMS (ESI, *m/z*) calculated for $C_{15}H_{27}NO_4Na^+$[M+Na]$^+$ 308.1838, found 308.1832

methyl (2-methylprop-1-en-1-yl) terephthalate (34)



White solid. Yield 60%. M.P. = 78-81 ^{o}C.

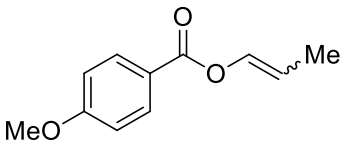
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (q, *J* = 8.4 Hz, 4H), 7.07 (s, 1H), 3.91 (s, 3H), 1.79 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.27, 162.92, 134.25, 133.56, 130.01, 129.81, 129.74, 119.56, 52.56, 19.82, 16.00.

IR (KBr film): *v* (cm^{-1}) 1730, 1702, 1630, 1504, 1382, 1262, 1128, 760

HRMS (ESI, *m/z*) calculated for $C_{13}H_{14}O_4Na^+$[M+Na]$^+$ 257.0790, found 257.0785

prop-1-en-1-yl 4-methoxybenzoate (35)



Colourless liquid. Yield 94%

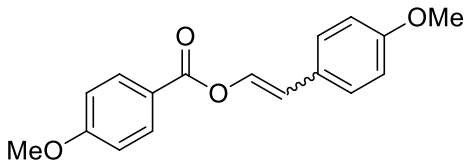
^{1}H NMR (400 MHz, $CDCl_3$, *E/Z* 1: 3) δ 8.02 – 7.86 (m, 2.73H), 7.24 – 7.12 (m, 1.34H), 6.90 – 6.76 (m, 2.76H), 5.53 – 5.41 (m, 0.33H), 4.93 (p, *J* = 6.8 Hz 1H), 3.76 (s, 4H), 3.75 (s, 1H), 1.70 (dd, *J* = 6.9, 1.8 Hz, 3H), 1.60 (dd, *J* = 7.0, 1.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.90, 163.84, 163.71, 163.43, 136.36, 135.19, 132.09, 121.86, 121.70, 113.92, 113.86, 109.97, 108.80, 55.57, 55.55, 12.59, 10.14.

IR (KBr film): *v* (cm^{-1}) 2935, 2844, 1722, 1606, 1510, 1261, 1168, 1103, 1031, 844, 765, 694, 611

HRMS (ESI, *m/z*) calculated for $C_{11}H_{12}O_3Na^+$[M+Na]$^+$ 215.0684, found 215.0679

4-methoxystyryl 4-methoxybenzoate (36)



White solid. Yield 87%. M.P. = 70-74 ^{o}C.

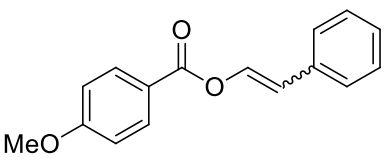
^{1}H NMR (400 MHz, $CDCl_3$, *E/Z* 1:2) δ 8.16 – 8.05 (m, 3H), 7.99 (d, *J* = 12.7 Hz, 0.5H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.03 – 6.91 (m, 5H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.52 (d, *J* = 12.7 Hz, 0.5H), 5.77 (d, *J* = 7.2 Hz, 1H), 3.89 – 3.80 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.10, 164.02, 163.56, 163.35, 159.18, 158.84, 135.33, 133.06, 132.34, 132.22, 130.57, 127.53, 127.13, 126.94, 121.41, 121.39, 115.11, 114.34, 114.17, 114.04, 113.98, 111.88, 55.64, 55.61, 55.41, 55.39.

IR (KBr film): *v* (cm^{-1}) 2837, 1724, 1604, 1510, 1384, 1258, 1164, 1097, 1028, 839, 759, 613

HRMS (ESI, *m/z*) calculated for $C_{17}H_{16}O_4Na^+$[M+Na]$^+$ 307.0946, found 307.0941

styryl 4-methoxybenzoate (37)



Yellowish white solid. Yield 83%. M.P. = 92-95 ^{o}C.

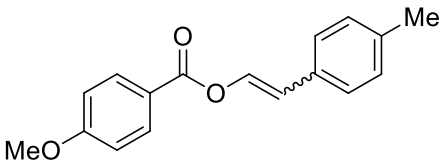
^{1}H NMR (400 MHz, $CDCl_3$, E/Z 1:2.77) δ 8.04 – 7.94 (m, 3H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.32 – 7.24 (m, 2.86H), 7.24 – 7.09 (m, 2.36H), 6.90 – 6.79 (m, 2.83H), 6.43 (d, *J* = 12.7 Hz, 0.36H), 5.70 (d, *J* = 7.2 Hz, 1H), 3.74 (s, 4.19H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.16, 164.09, 163.45, 163.24, 136.73, 134.49, 134.47, 134.42, 132.41, 132.28, 129.28, 128.86, 128.61, 127.47, 127.36, 126.36, 121.24, 115.46, 114.19, 114.01, 112.24, 55.63, 55.60.

IR (KBr film): *v* (cm^{-1}) 2839, 1726, 1606, 1510, 1384, 1257, 1166, 1093, 1029, 842, 761, 690, 611

HRMS (ESI, *m/z*) calculated for $C_{16}H_{14}O_3Na^+$[M+Na]$^+$ 277.0841, found 277.0835

4-methylstyryl 4-methoxybenzoate (38)



Yellowish white solid. Yield 91%. M.P. = 65-70 ^{o}C.

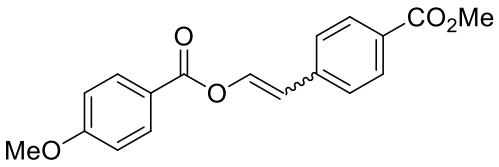
^{1}H NMR (400 MHz, $CDCl_3$, *E/Z* 1: 2.38) δ 8.02 – 7.90 (m, 3.30H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 0.89H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 0.89H), 6.89 – 6.77 (m, 2.96H), 6.39 (d, *J* = 12.7 Hz, 0.42H), 5.66 (d, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 1.31H), 2.24 (s, 3H), 2.21 (s, 1.30H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.09, 164.02, 163.47, 163.25, 137.25, 137.15, 136.07, 133.82, 132.35, 132.21, 131.54, 131.51, 129.54, 129.30, 129.19, 126.24, 121.32, 121.30, 115.38, 114.13, 113.96, 112.18, 55.57, 55.55, 21.37, 21.30.

IR (KBr film): *v* (cm^{-1}) 2920, 1720, 1606, 1510, 1384, 1255, 1166, 1085, 761, 611

HRMS (ESI, *m/z*) calculated for $C_{17}H_{16}O_3Na^+$[M+Na]$^+$ 291.0997, found 291.0992

4-(methoxycarbonyl)styryl 4-methoxybenzoate (39)



White solid. Yield 42%. M.P. = 75-80 ^{o}C.

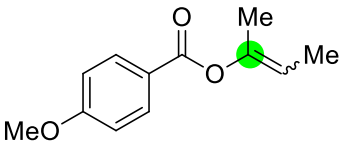
^{1}H NMR (400 MHz, $CDCl_3$ *E/Z* 1:1.22) δ 8.17 (d, *J* = 12.9 Hz, 1.24H), 8.13 – 8.02 (m, 6.28H), 7.98 (d, *J* = 8.1 Hz, 1.83H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1.71H), 7.03 – 6.91 (m, 3.92H), 6.54 (d, *J* = 12.8 Hz, 0.82H), 5.84 (d, *J* = 7.2 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 2.36H), 3.88 (s, 3H), 3.86 (s, 2.45H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 166.95, 164.36, 164.28, 163.26, 162.99, 139.40, 139.06, 138.51, 136.21, 132.49, 132.40, 130.21, 129.90, 129.09, 128.90, 128.63, 126.15, 120.92, 120.90, 114.56, 114.31, 114.10, 111.24, 55.70, 55.67, 52.26, 52.22.

IR (KBr film): *v* (cm^{-1}) 2949, 1720, 1606, 1508, 1384, 1280, 1255, 1166, 1112, 1083, 759, 696

HRMS (ESI, *m/z*) calculated for $C_{18}H_{16}O_5Na^+$[M+Na]$^+$ 335.0895, found 335.0890

but-2-en-2-yl 4-methoxybenzoate (40)



Colourless liquid. Yield 68%.

^{1}H NMR (400 MHz, $CDCl_3$. E/Z 1: 2) δ 8.08 – 7.97 (m, 3H), 6.96 – 6.87 (m, 3H), 5.26 (q, *J* = 7.0 Hz, 0.48H), 5.13 (q, *J* = 6.7, 1H), 3.84 (s, 4.72H), 1.95 (s, 4.48H), 1.67 (d, *J* = 7.1 Hz, 1.51H), 1.52 (dd, *J* = 6.8, 1.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.12, 164.11, 163.69, 163.60, 146.08, 145.83, 132.00, 131.94, 122.48, 122.19, 113.75, 113.68, 111.98, 111.44, 55.43, 55.41, 19.66, 15.03, 11.88, 10.73.

IR (KBr film): ν (cm^{-1}) 2925, 2841, 1722, 1604, 1510, 1259, 1168, 1103, 1080, 1028, 844, 767, 694, 615

HRMS (ESI, *m/z*) calculated for $C_{12}H_{14}O_3Na^+[M+Na]^+$ 229.0841, found 229.0835

VI. Photophysical Properties of photocatalysts

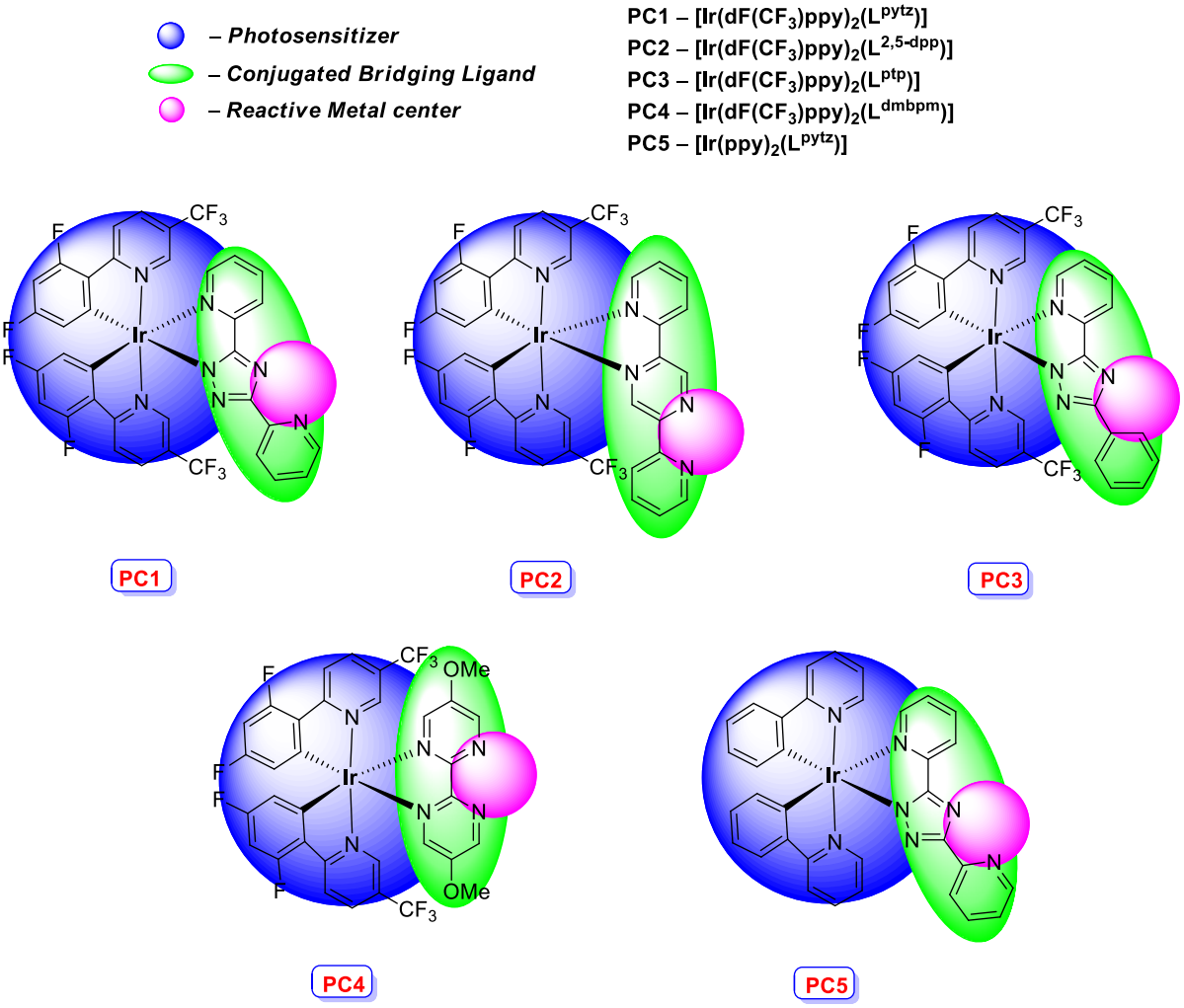


Fig. S2: Heteroleptic Ir(III) photocatalysts

Table S7: absorption and emission data of PC1 to PC4 at room temperature

photo-complex	absorbance λ (nm)	emission λ (nm)	τ (ns)	Φ
PC1	267, 291, 380, 436	479, 504	239	13.24
PC2	268, 307, 324, 351, 406, 464	572	821	18.27
PC3	267, 313, 383, 440	479, 504	196	12.34
PC4	279, 324, 391	490, 525, 565	94, 1002	4.66
PC5	266, 293, 353, 392	487, 516	82	4

VII. Absorption and Fluorescence Spectra

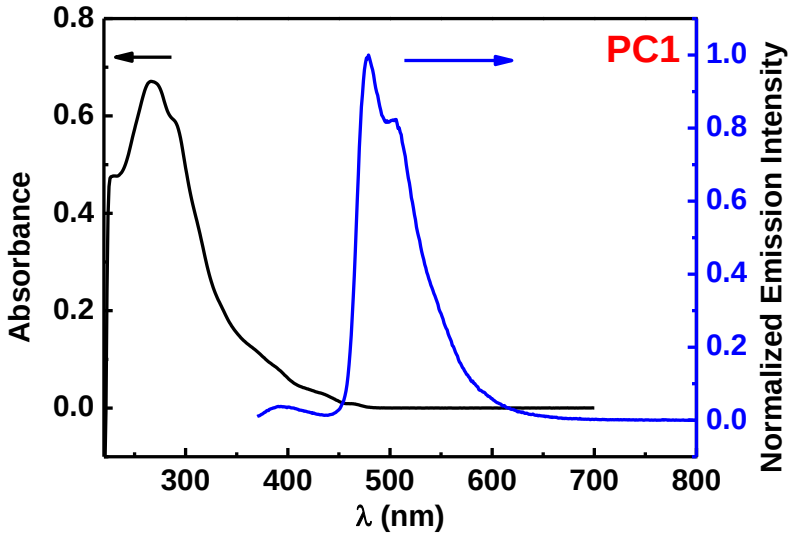


Fig. S3: UV-Visible absorption and emission spectrum of PC1 in DCM.

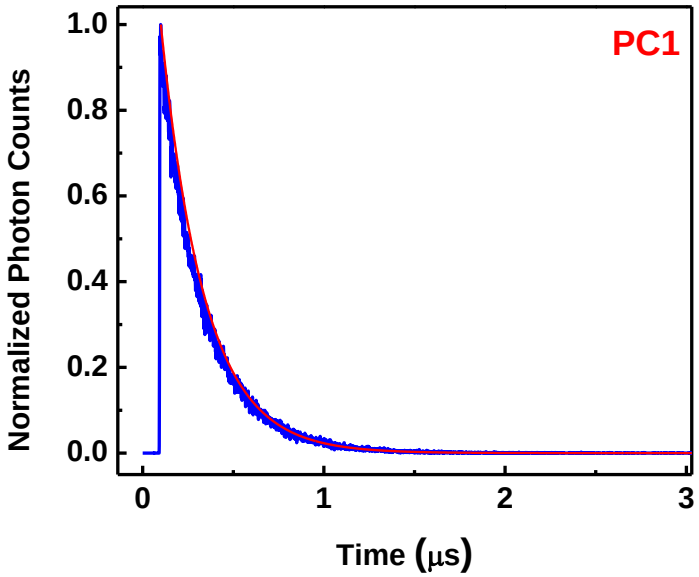


Fig. S4: Fluorescence decay curve of PC1 in DCM (10 μM). Samples are photoexcited at 375 nm.

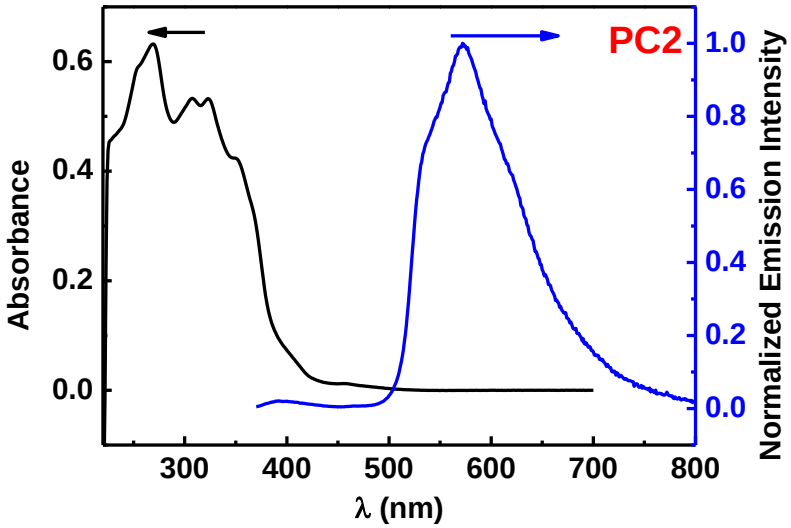


Fig. S5: UV-Visible absorption and emission spectrum of PC2 in DCM.

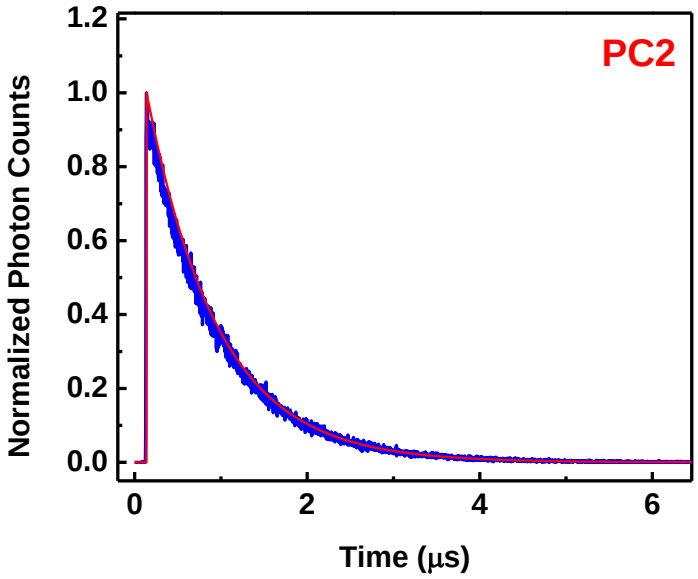


Fig. S6: Fluorescence decay curve of PC2 in DCM (10 μM). Samples are photoexcited at 375 nm.

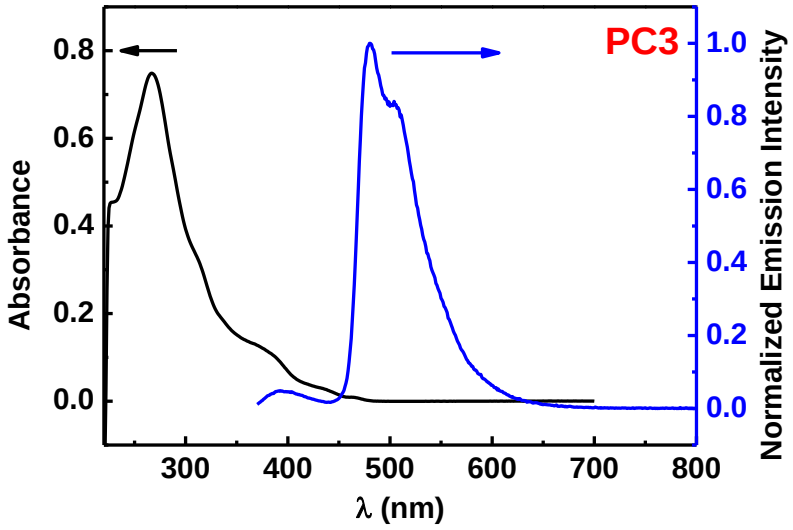


Fig. S7: UV-Visible absorption and emission spectrum of PC3 in DCM.

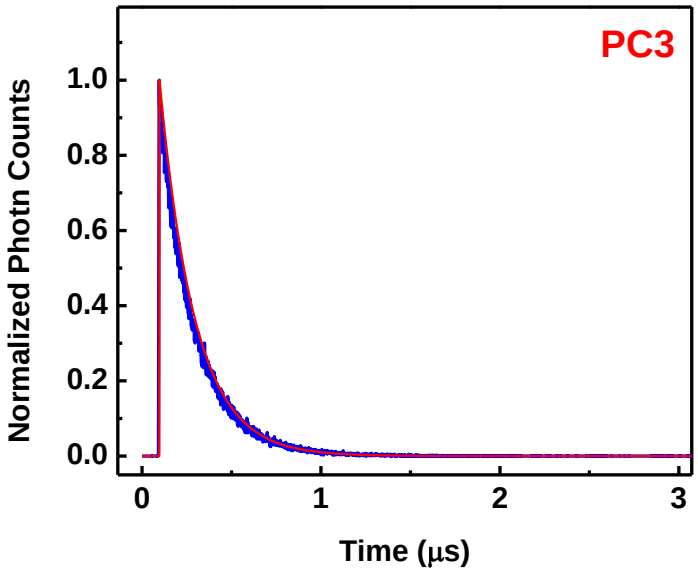


Fig. S8: Fluorescence decay curve of PC3 in DCM (10 μM). Samples are photoexcited at 375 nm.

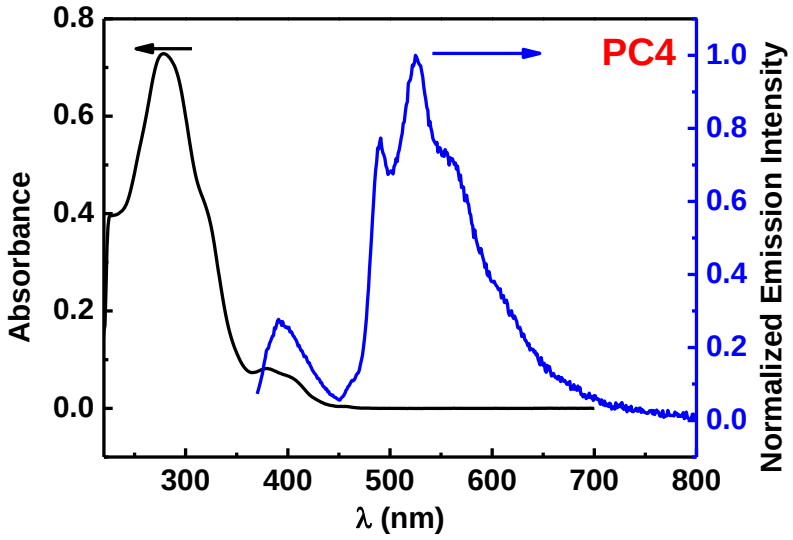


Fig. S9: UV-Visible absorption and emission spectrum of PC4 in DCM.

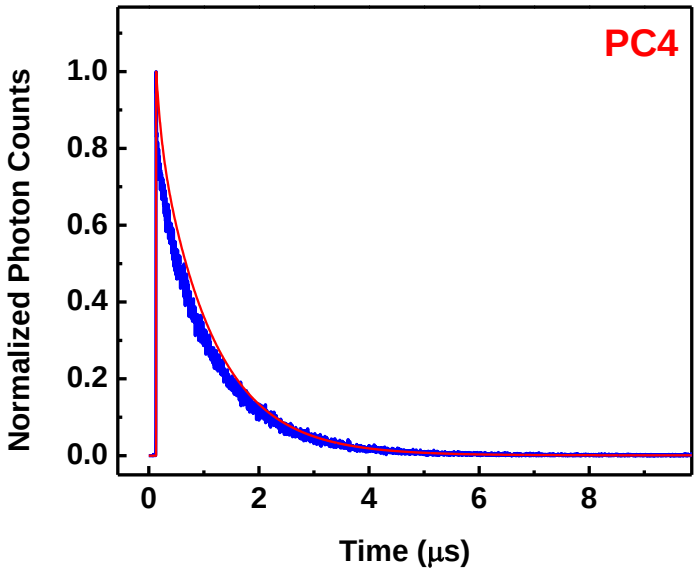


Fig. S10: Fluorescence decay curve of PC4 in DCM (10 μM). Samples are photoexcited at 375 nm.

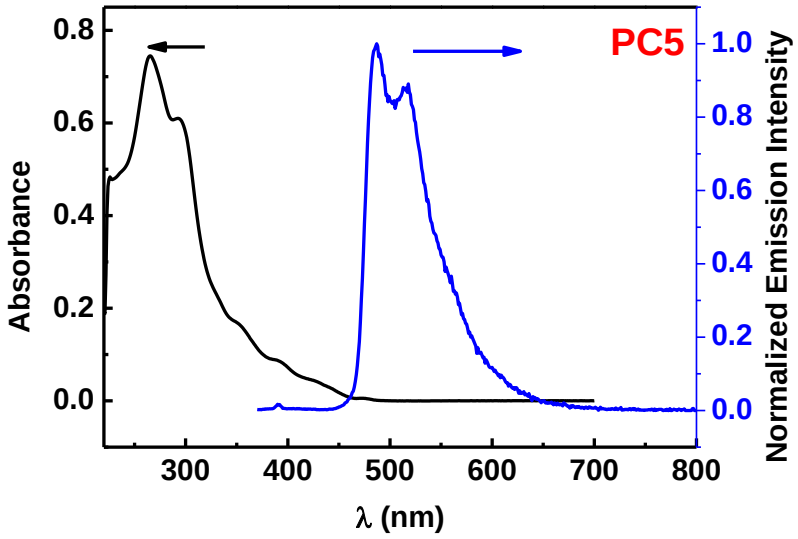


Fig. S11: UV-Visible absorption and emission spectrum of PC5 in DCM.

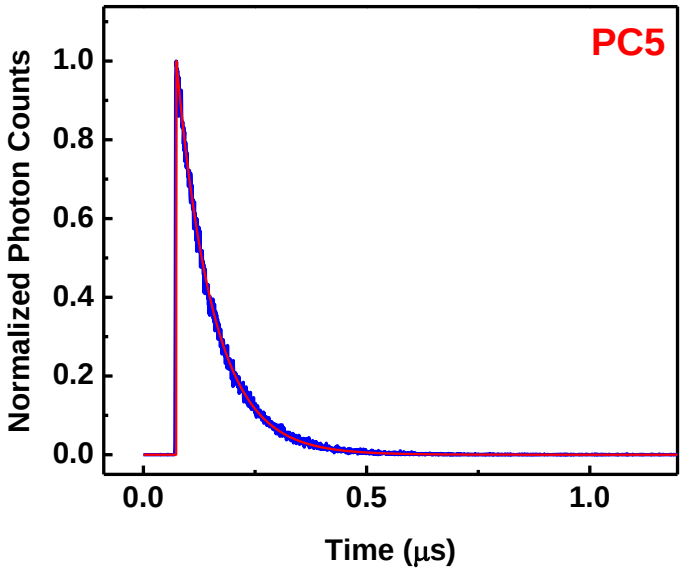


Fig. S12: Fluorescence decay curve of PC5 in DCM (10 μM). Samples are photoexcited at 375 nm.

VIII. Absorption and Fluorescence Overlays

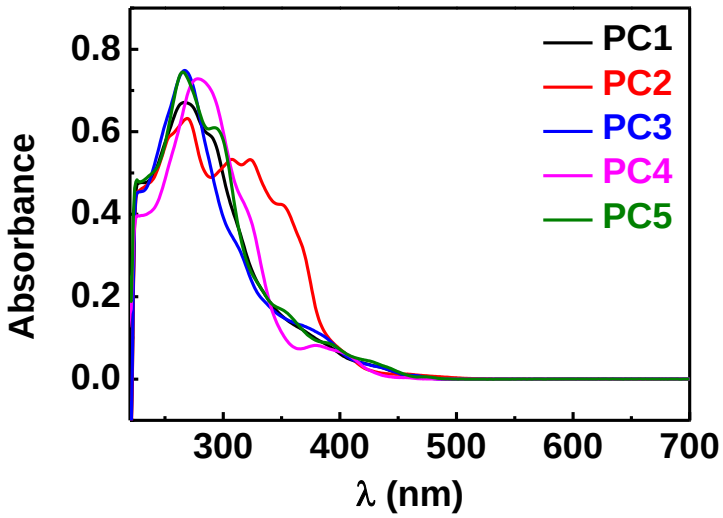


Fig. S13: UV-Visible absorption spectra overlay of PC1 to PC5 in DCM.

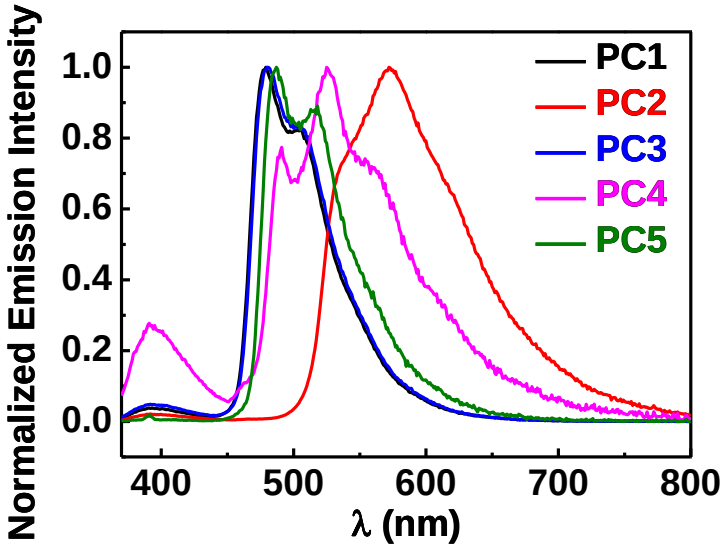


Fig. S14: Emission spectra overlay of PC1 to PC5 (10 μM in DCM).

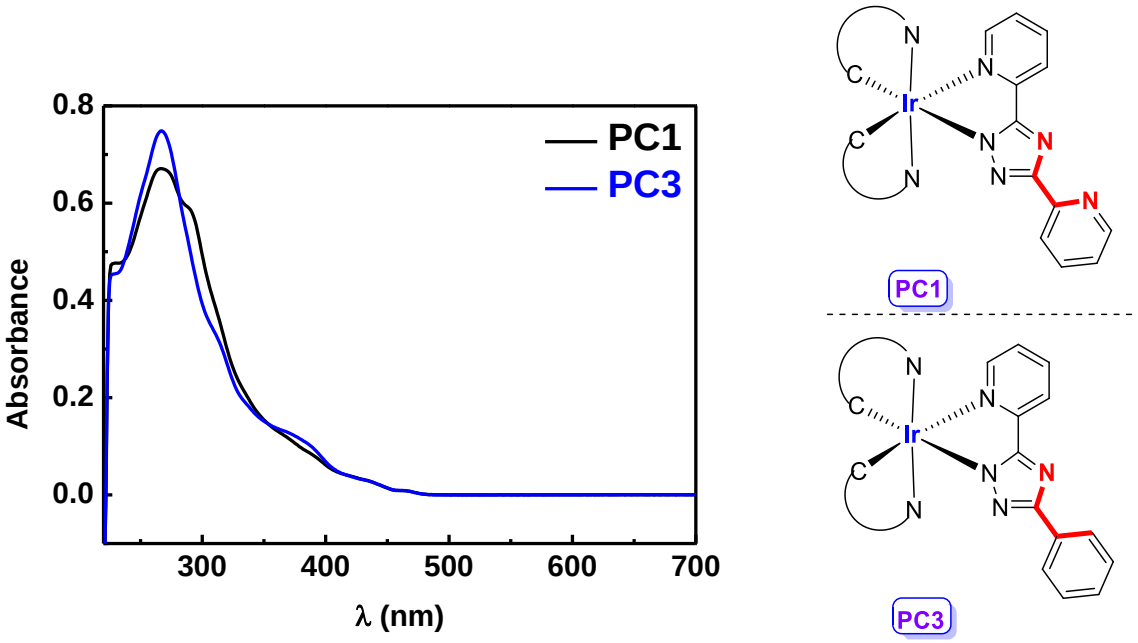


Fig. S15: UV-Visible absorption spectra overlay of PC1 (black) and PC3 (blue) in DCM.

IX. Comparative Study of Component Absorption Spectra

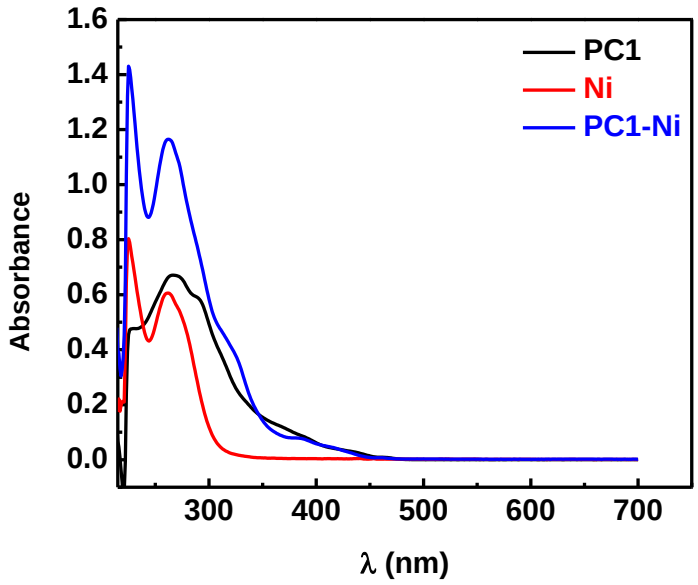


Fig. S16: Comparison of component UV-Visible absorption spectra; PC1 (black), $NiCl_2PPh_3$ (red) and PC1- $NiCl_2PPh_3$ (blue) in DCM.

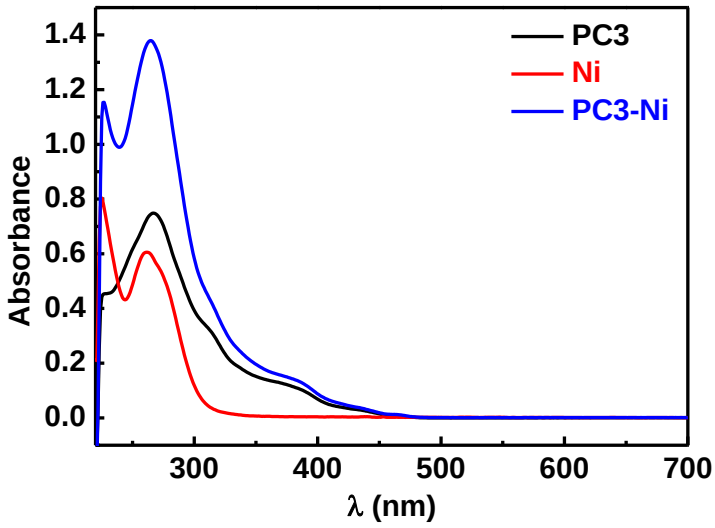


Fig. S17: Comparison of component UV-Visible absorption spectra; PC3 (black), $NiCl_2PPh_3$ (red) and PC3- $NiCl_2PPh_3$ (blue) in DCM.

X. Emission Quenching Experiment

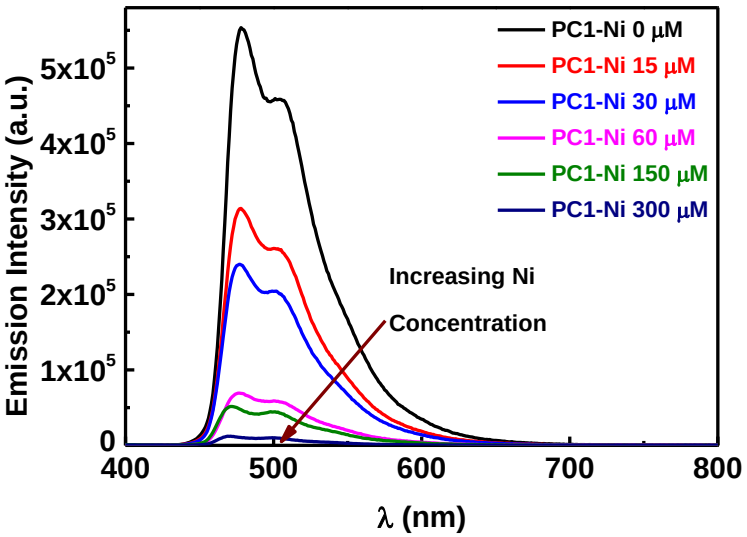


Fig. S18: Emission spectra of PC1 (10 μM) with $NiCl_2PPh_3$ (0-300 μM) in DCM. Excitation wavelength at 350 nm. Progressive quenching of Ir based emission observed as $NiCl_2PPh_3$ concentration increased.

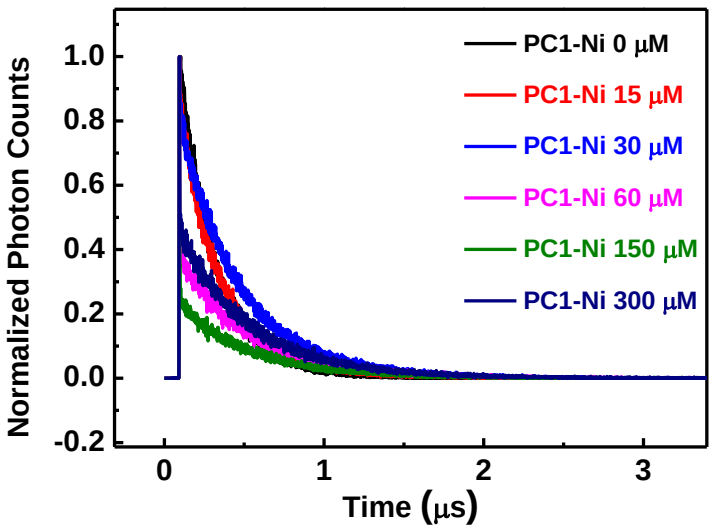


Fig. S19: Time-resolved luminescence decay of PC1 (10 μM) with $NiCl_2PPh_3$ (0-300 μM) in DCM. Samples are photoexcited at 375 nm, with emission monitored at 479 nm.

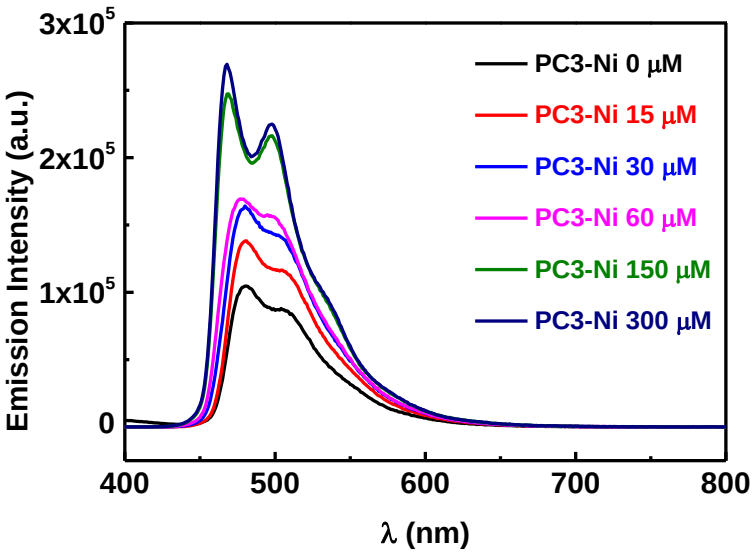


Fig. S20: Emission spectra of PC3 (10 μM) with $NiCl_2PPh_3$ (0-300 μM) in DCM. Excitation wavelength at 350 nm. No significant quenching observed in case of PC3 upon increasing concentration of $NiCl_2PPh_3$.

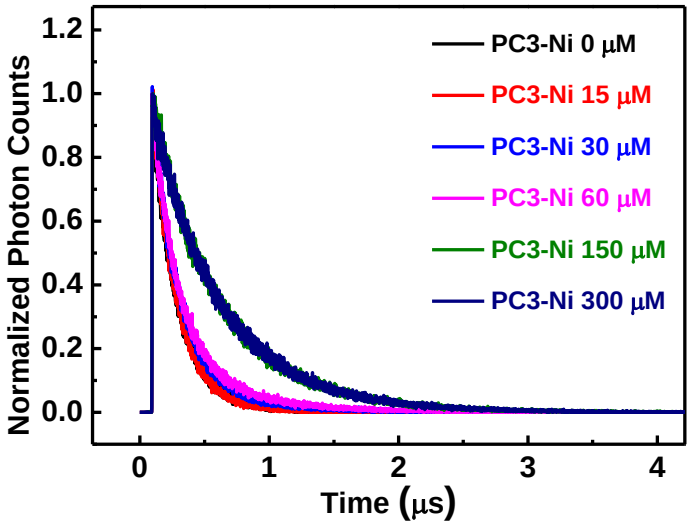


Fig. S21: Time-resolved luminescence decay of PC3 (10 μM) with $NiCl_2PPh_3$ (0-300 μM) in DCM. Samples are photoexcited at 375 nm.

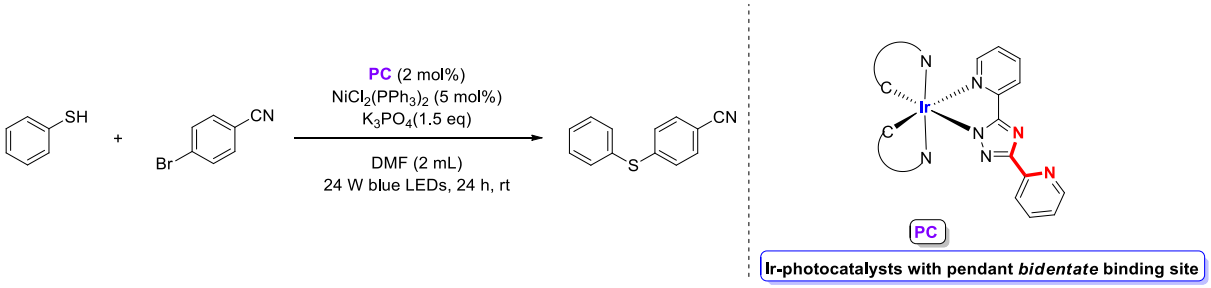
Table S8: PC1 and PC3 PL decay on Ni addition

Sr. No.	PC1 (10 μM) + Ni	$\tau_1 + \tau_2$ (ns)	PC3 (10 μM) + Ni	$\tau_1 + \tau_2$ (ns)
1	PC1 + Ni (0 μM)	230	PC3 + Ni (0 μM)	196
2	PC1 + Ni (15 μM)	184 + 346	PC3 + Ni (15 μM)	194
3	PC1 + Ni (30 μM)	146 + 397	PC3 + Ni (30 μM)	191 + 468
4	PC1 + Ni (60 μM)	3 + 428	PC3 + Ni (60 μM)	179 + 497
5	PC1 + Ni (150 μM)	2 + 432	PC3 + Ni (150 μM)	174 + 553
6	PC1 + Ni (300 μM)	2 +437	PC3 + Ni (300 μM)	161 + 553

XI. Application of Ir-Ni Dinuclear complexes in Organic reactions

Aryl Bromide and Thiophenol Coupling

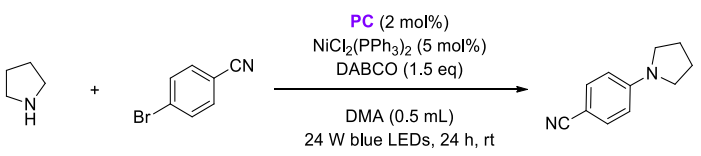
General procedure for thioetherification of aryl bromides via cooperative metallaphotocatalysis with an Ir–Ni bimetallic complex.

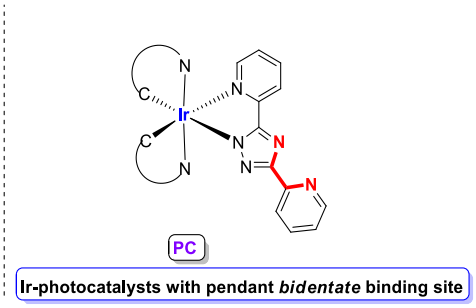


To the oven dried Schlenk tube equipped with a rubber septum and magnetic stir bar were added 4-bromobenzonitrile (0.2 mmol, 1 equiv.). Schlenk tube brought into glove box and charged with PC (2 mol%), $NiCl_2(PPh_3)_2$ (5 mol%), and K_3PO_4 (1.5 equiv.). The Schlenk tube was placed under an atmosphere of nitrogen, added thiophenol (0.3 mmol, 1.5 equiv.) fallowed by the DMF (2 mL). The reaction mixture then was cooled to -78 ^oC and degassed with vacuum evacuation (5 min), backfilled with nitrogen and then warmed to room temperature. This process repeated three times, then Schlenk tube was sealed with glass stopper and parafilm, placed 1-2 cm away from 24 W blue LED strips, and irradiated allowing temperature to rise due to the proximity of lights. After 24 hrs, the resulting reaction mixture was concentrated in vacuo, ^1H NMR spectrum recorded. Yields were referenced to the internal standard.

Aryl Bromide and Amine Coupling.

General procedure for aryl amination via cooperative metallaphotocatalysis with an Ir–Ni bimetallic complex.





To the oven dried Schlenk tube equipped with a rubber septum and magnetic stir bar were added 4-bromobenzonitrile (0.2 mmol, 1 equiv.) and pyrrolidine (0.3 mmol, 1.5 equiv.). Schlenk tube brought into glove box and charged with PC (2 mol%), $NiCl_2(PPh_3)_2$ (5 mol%), and DABCO (1.8 equiv.). The Schlenk tube was placed under an atmosphere of nitrogen, then the DMA (0.5 mL) was added. The reaction mixture then was cooled to -78 ^oC and degassed with vacuum evacuation (5 min), backfilled with nitrogen and then warmed to room temperature. This process repeated three times, then Schlenk tube was sealed with glass stopper and parafilm, placed 1-2 cm away from 24 W blue LED strips, and irradiated allowing temperature to rise due to the proximity of lights. After 24 hrs, the resulting reaction mixture was concentrated in vacuo, ^1H NMR spectrum recorded. Yields were referenced to the internal standard.

XII. References

1. W.-J. Wang, C.-H. Lin, J.-S. Wang and S.-W. Tang, Synthesis and Characterization of Copper(I) Complexes with Triazole Derivative Ligands Containing an α-Diimine Moiety, *Mol. Cryst. Liq. Cryst.*, 2006, **456**, 209-219.
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XIII. NMR Spectra

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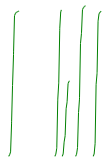

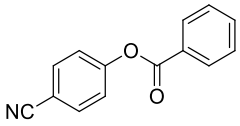

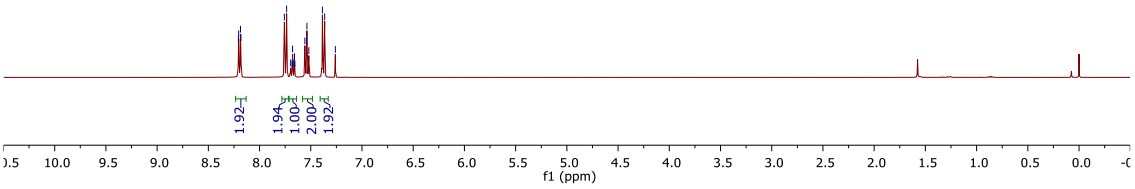

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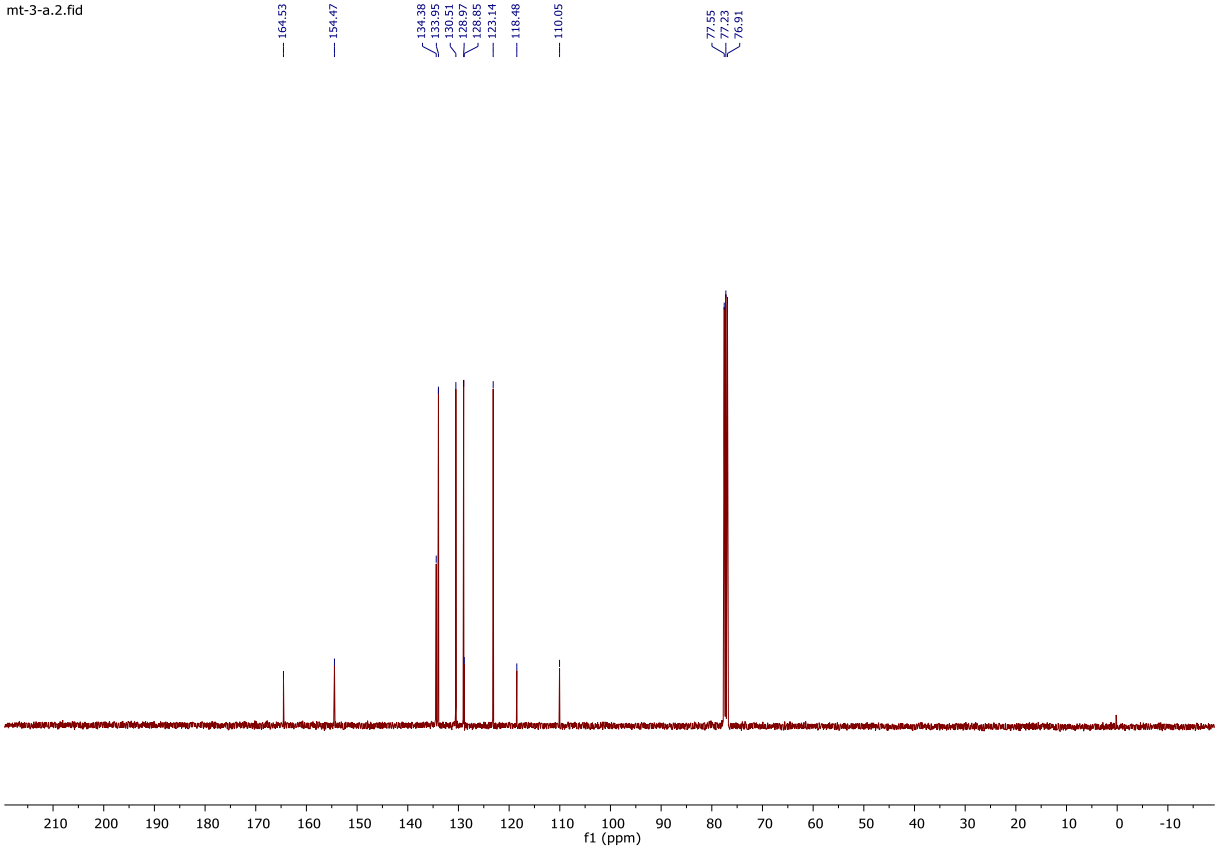

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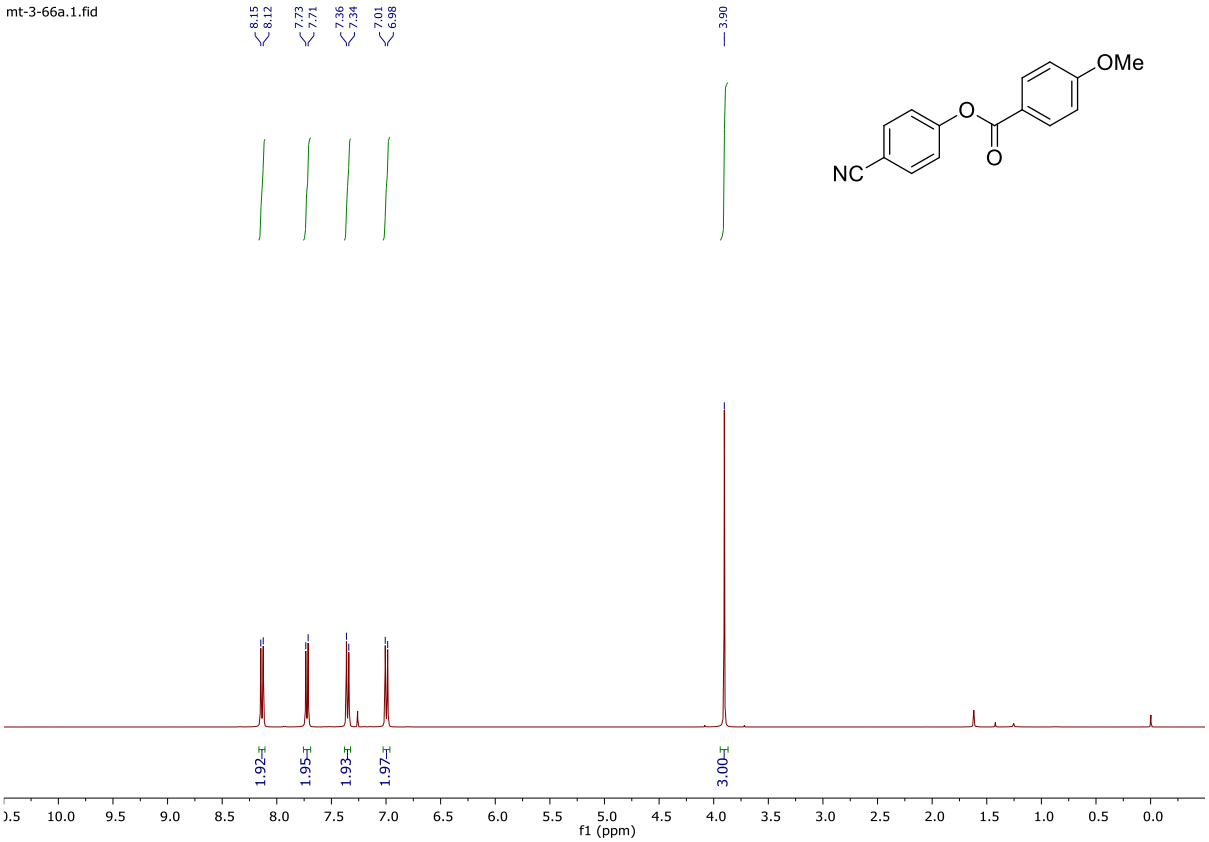

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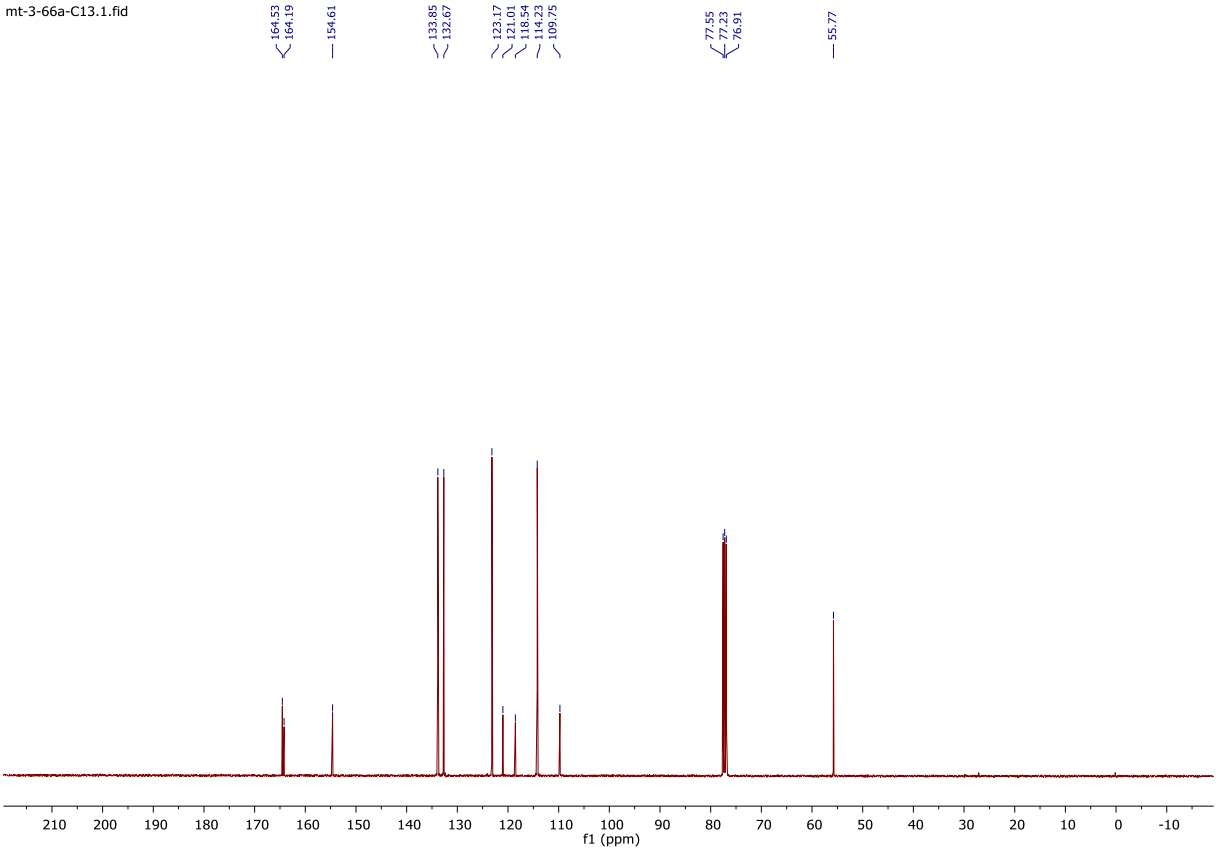

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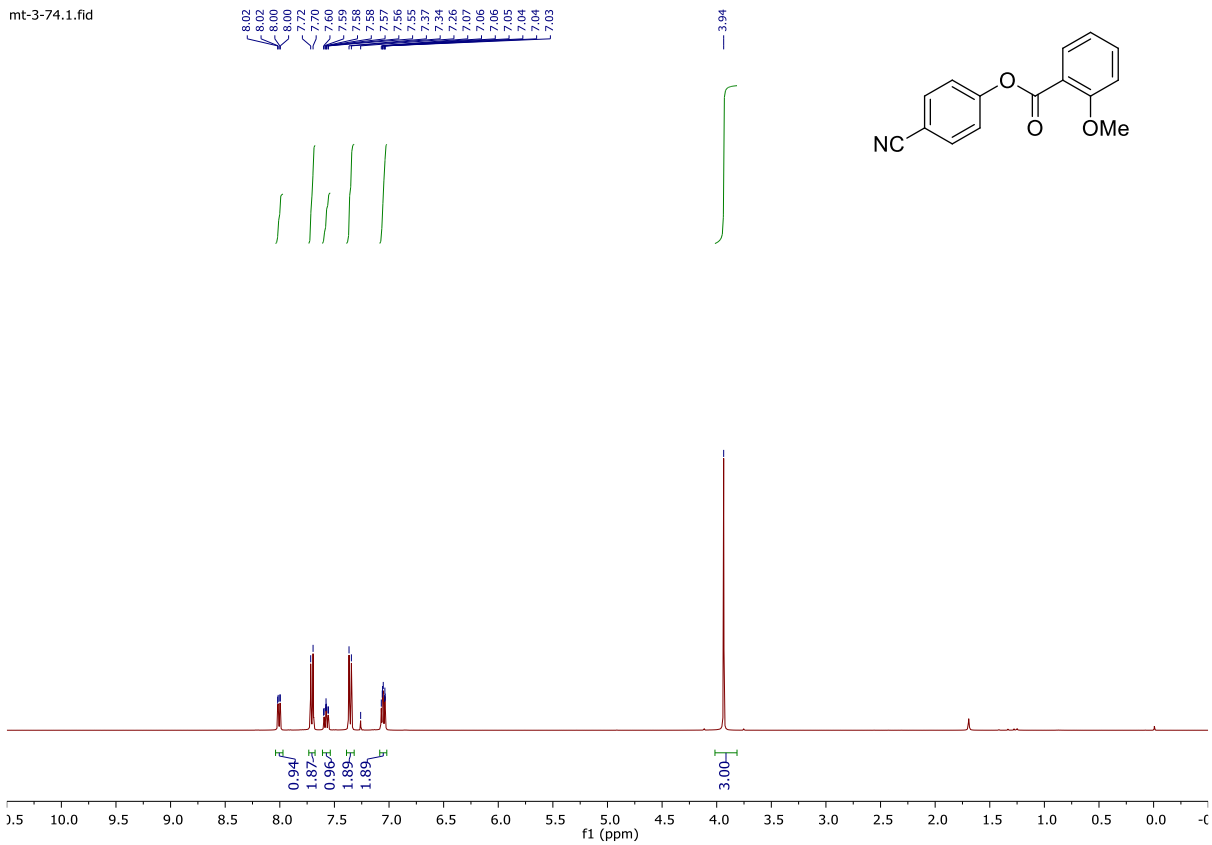

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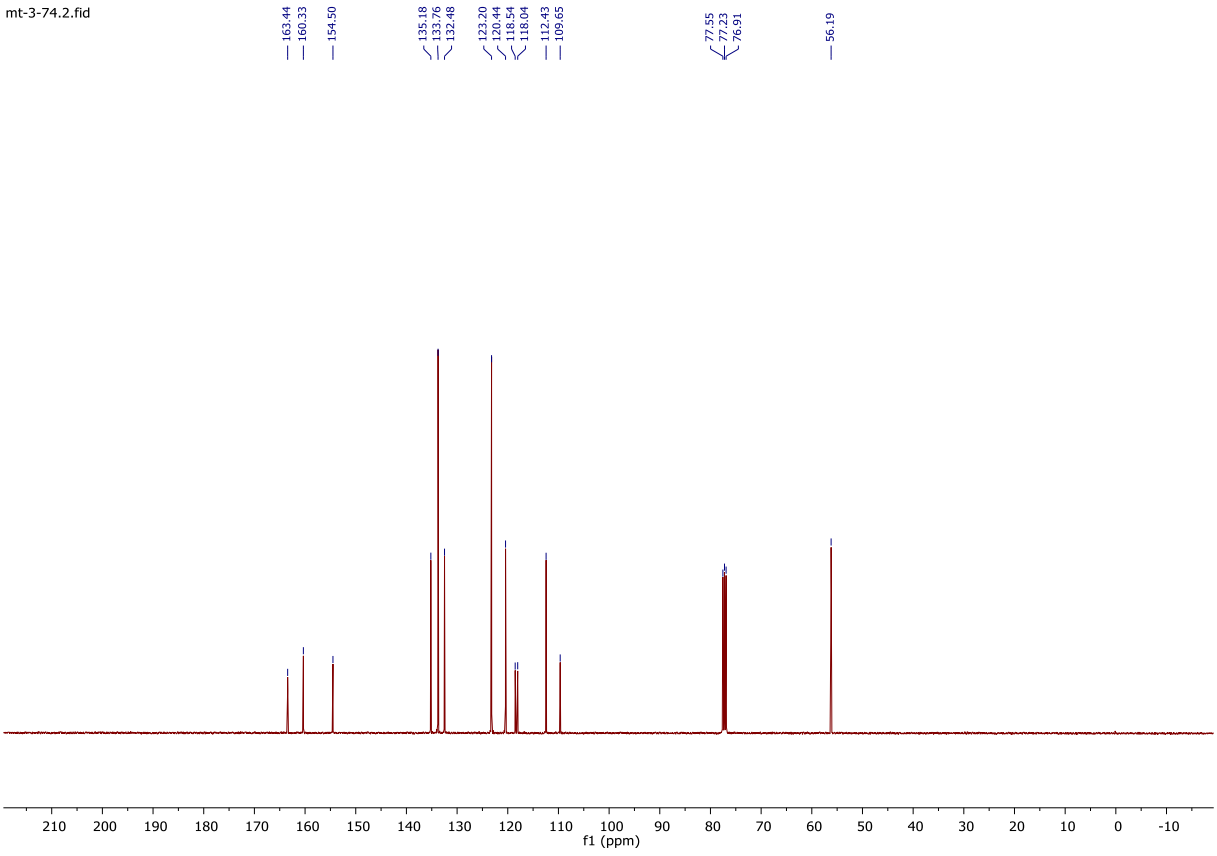

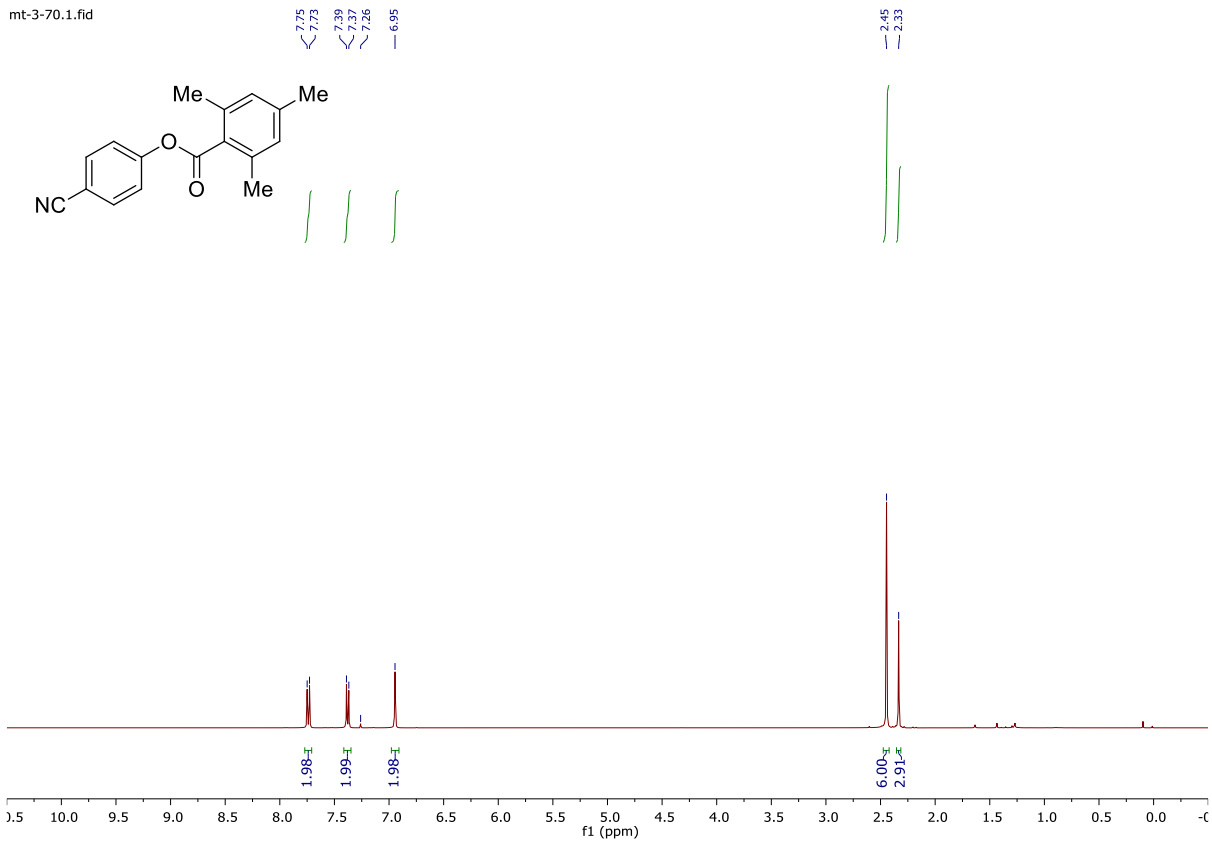
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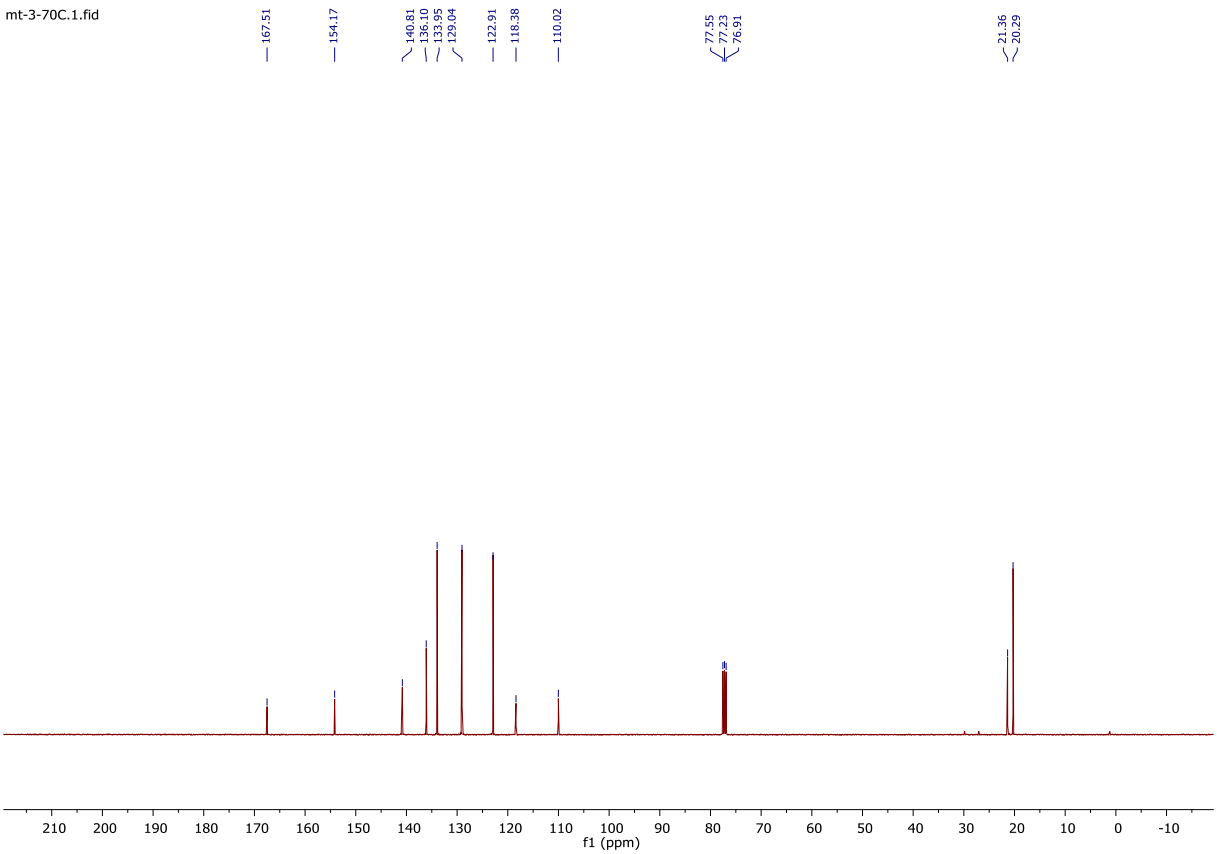
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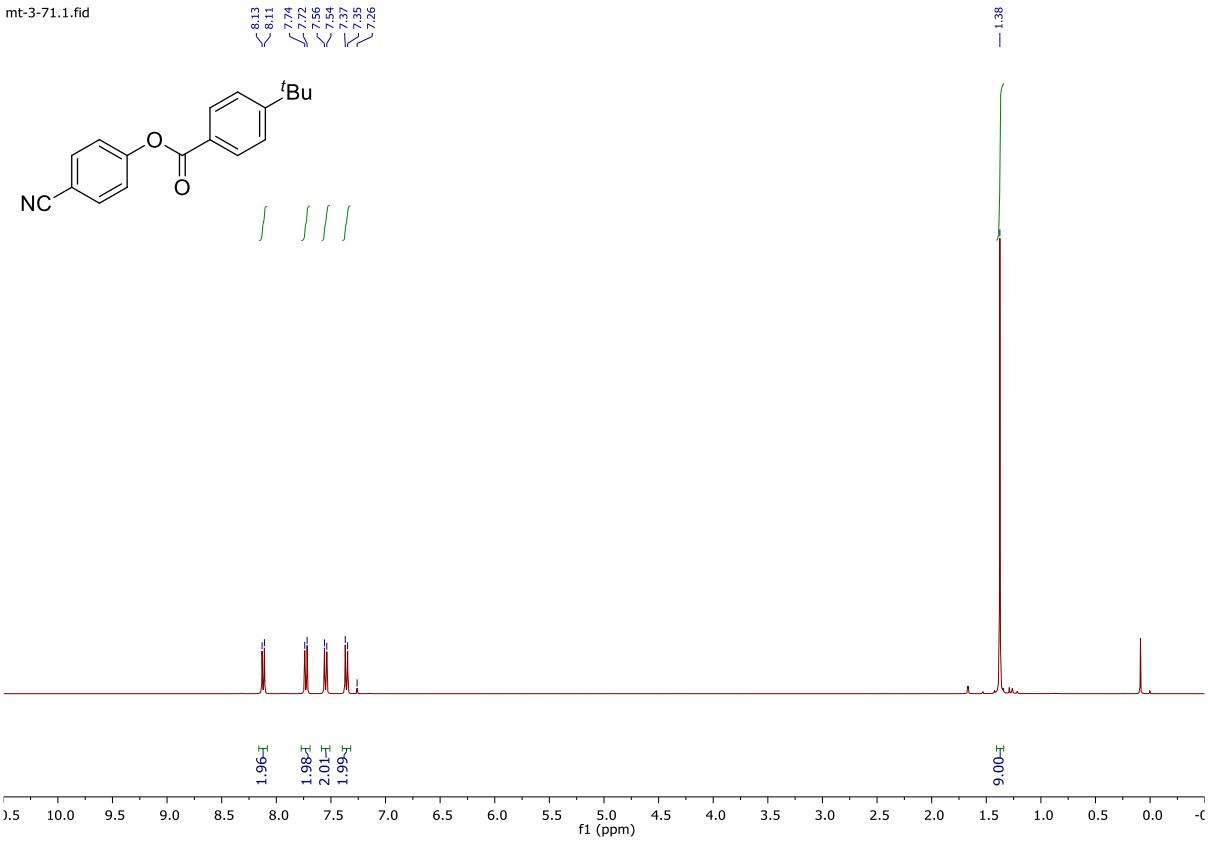
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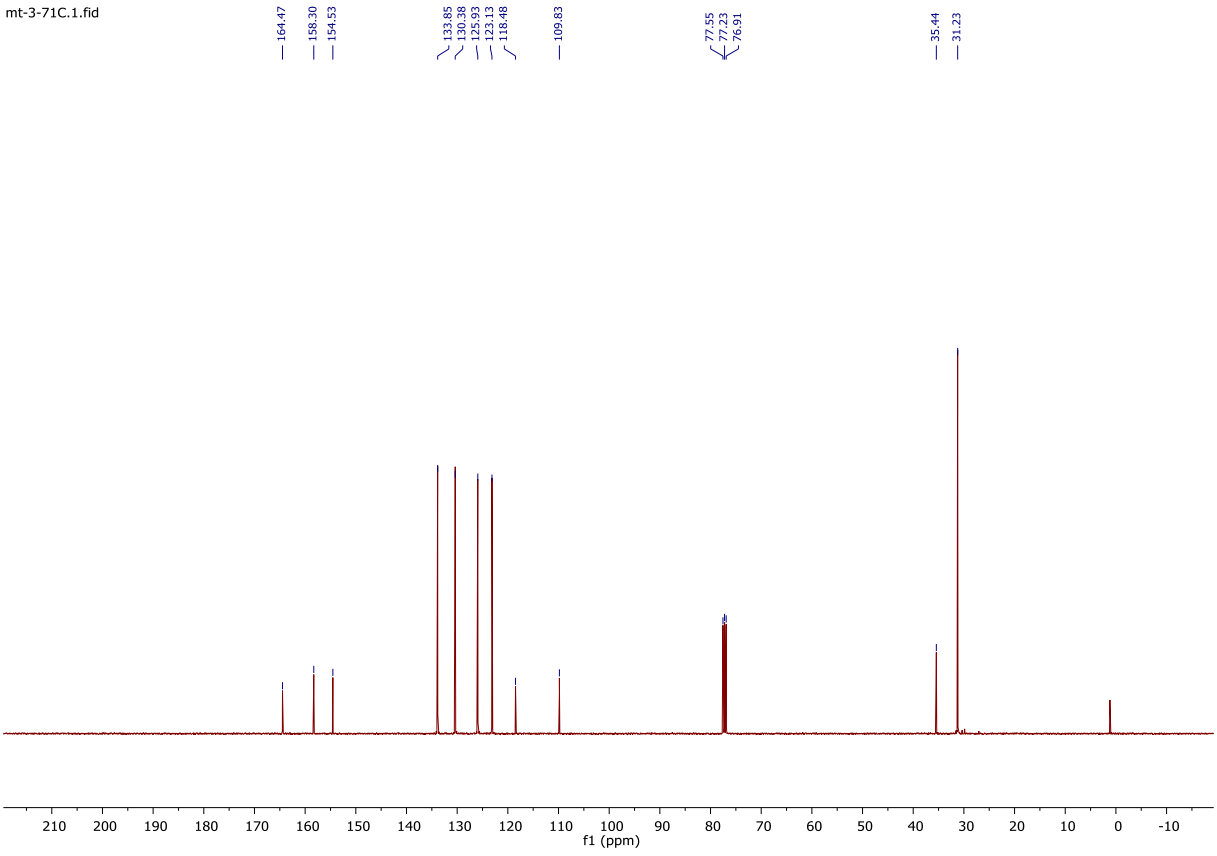
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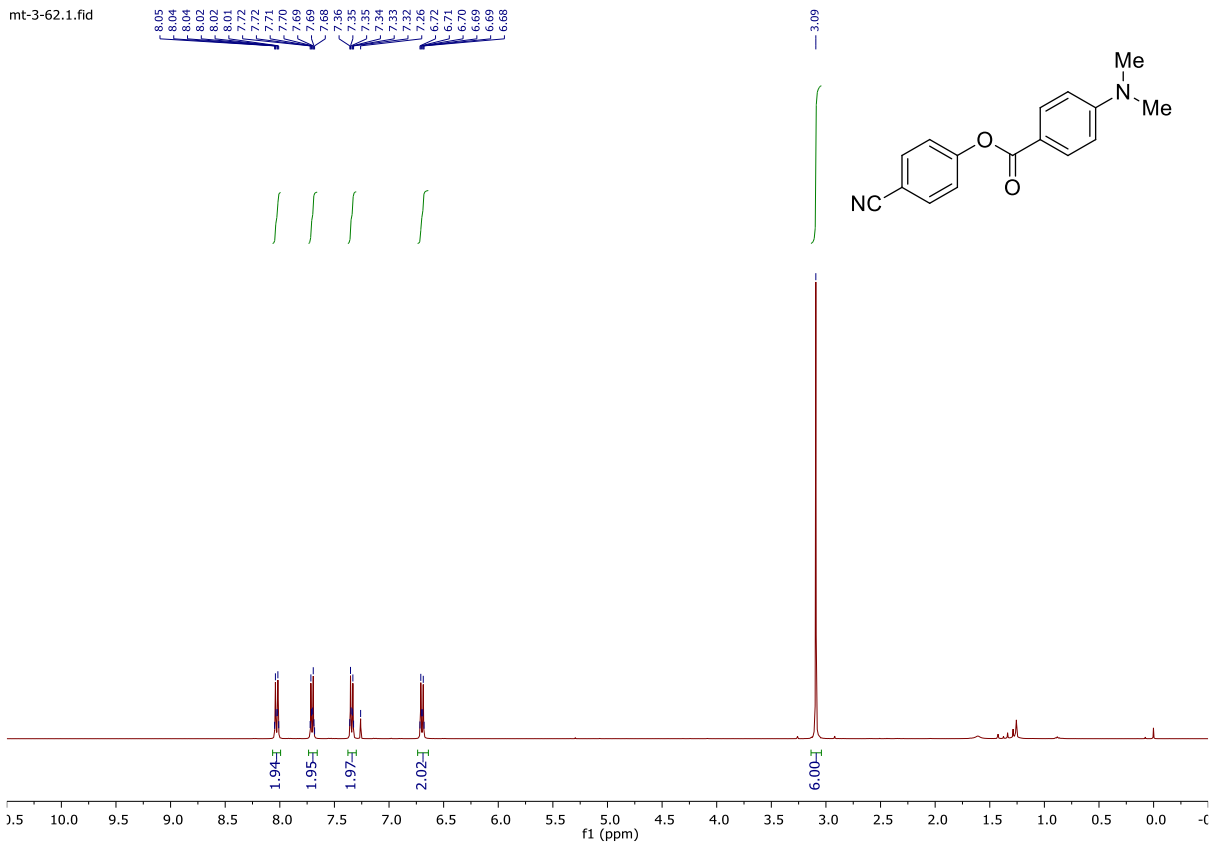
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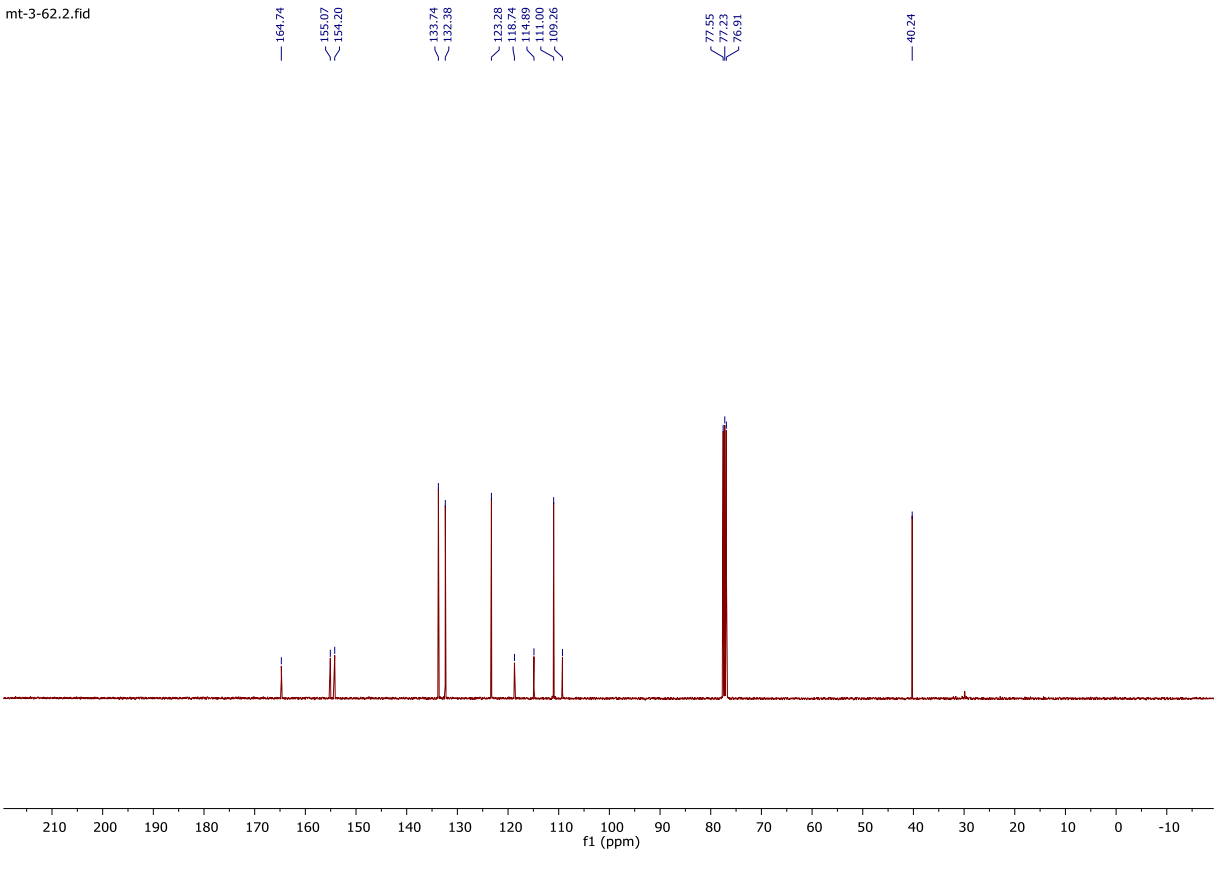
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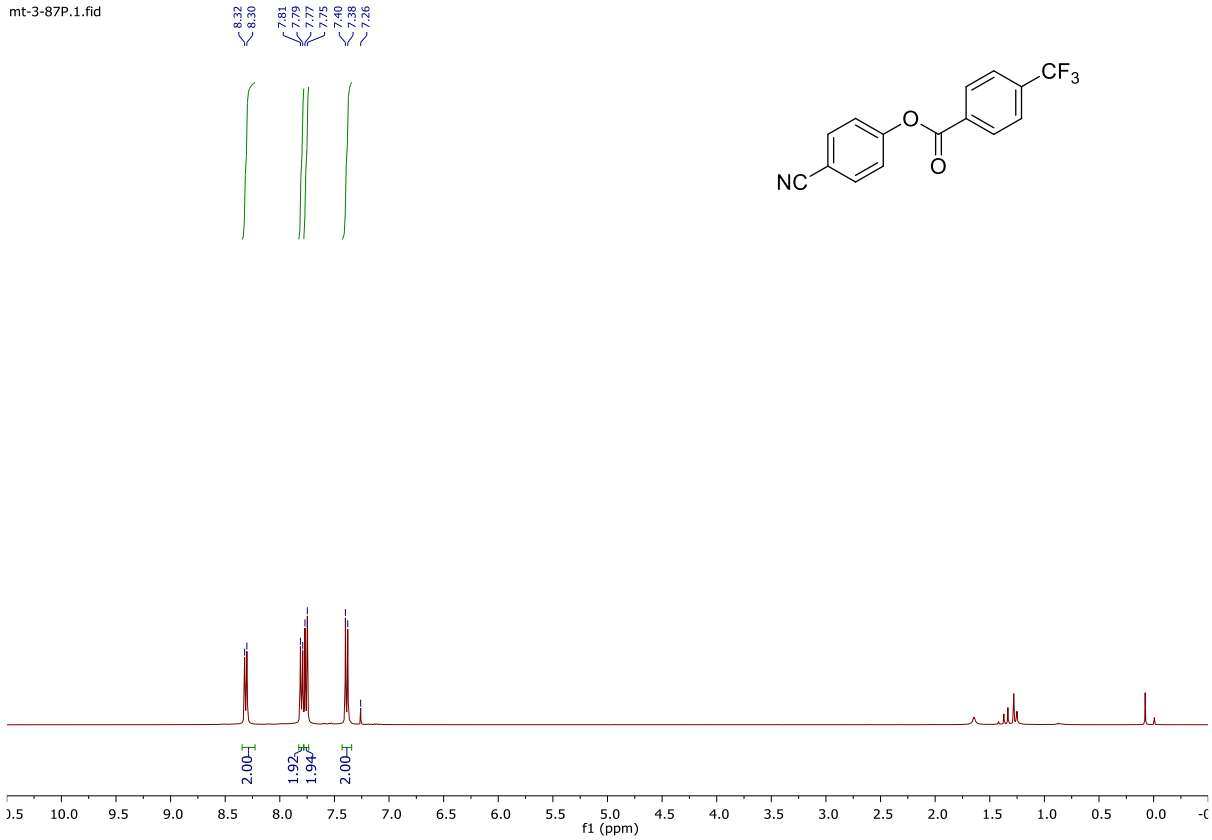
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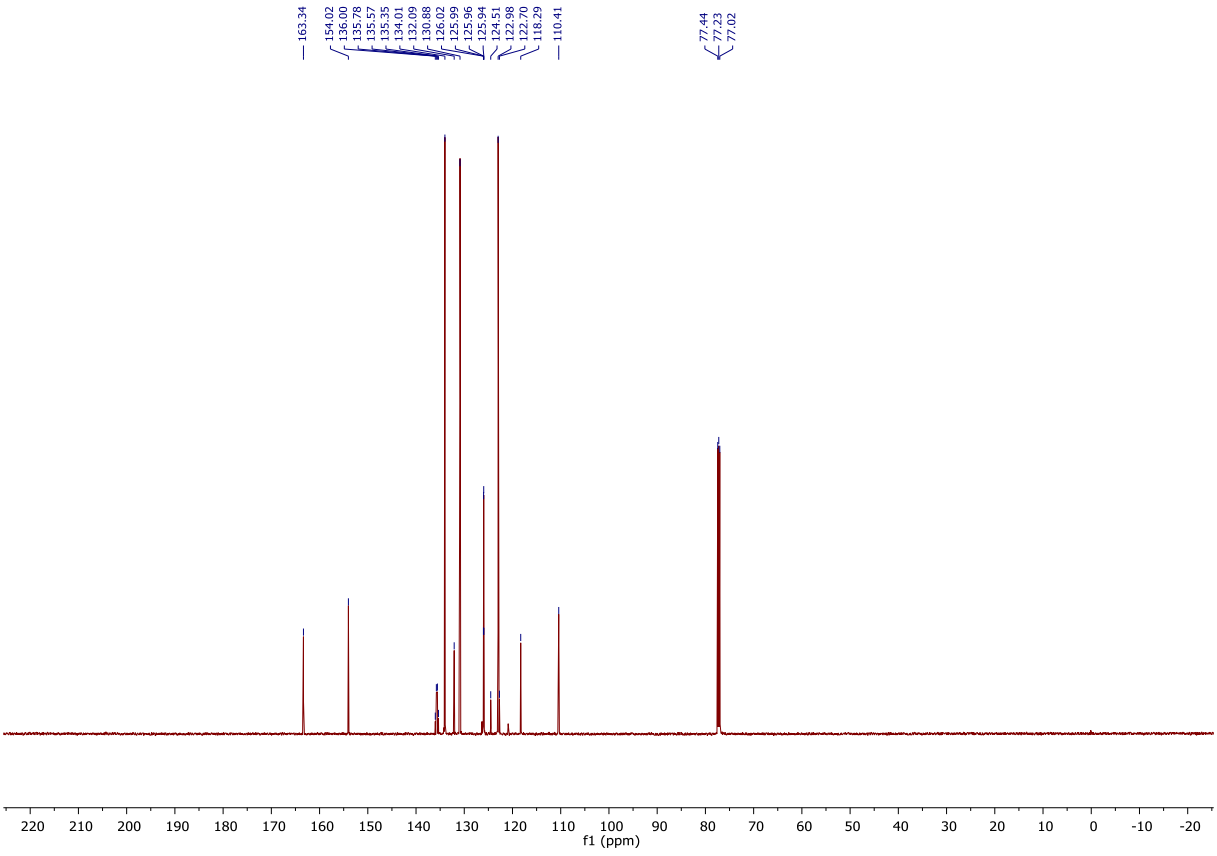
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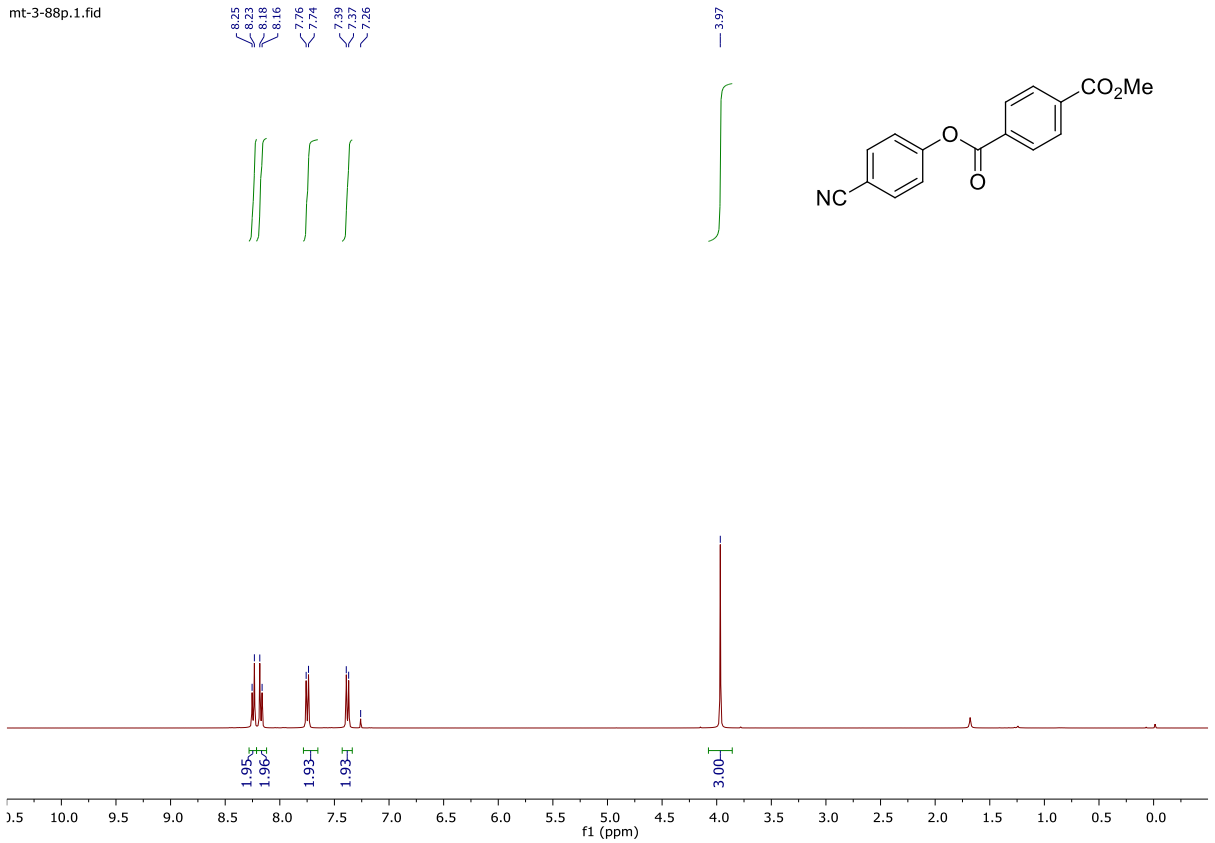
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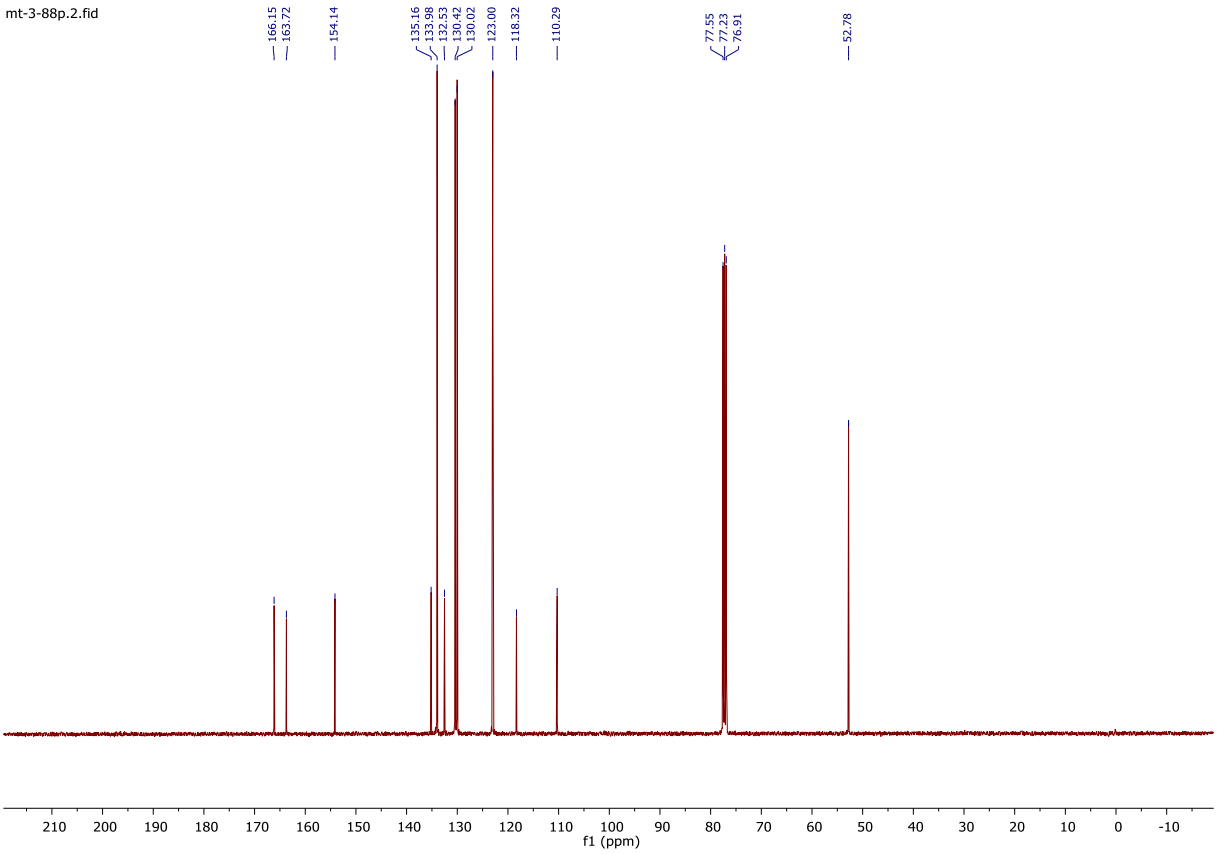
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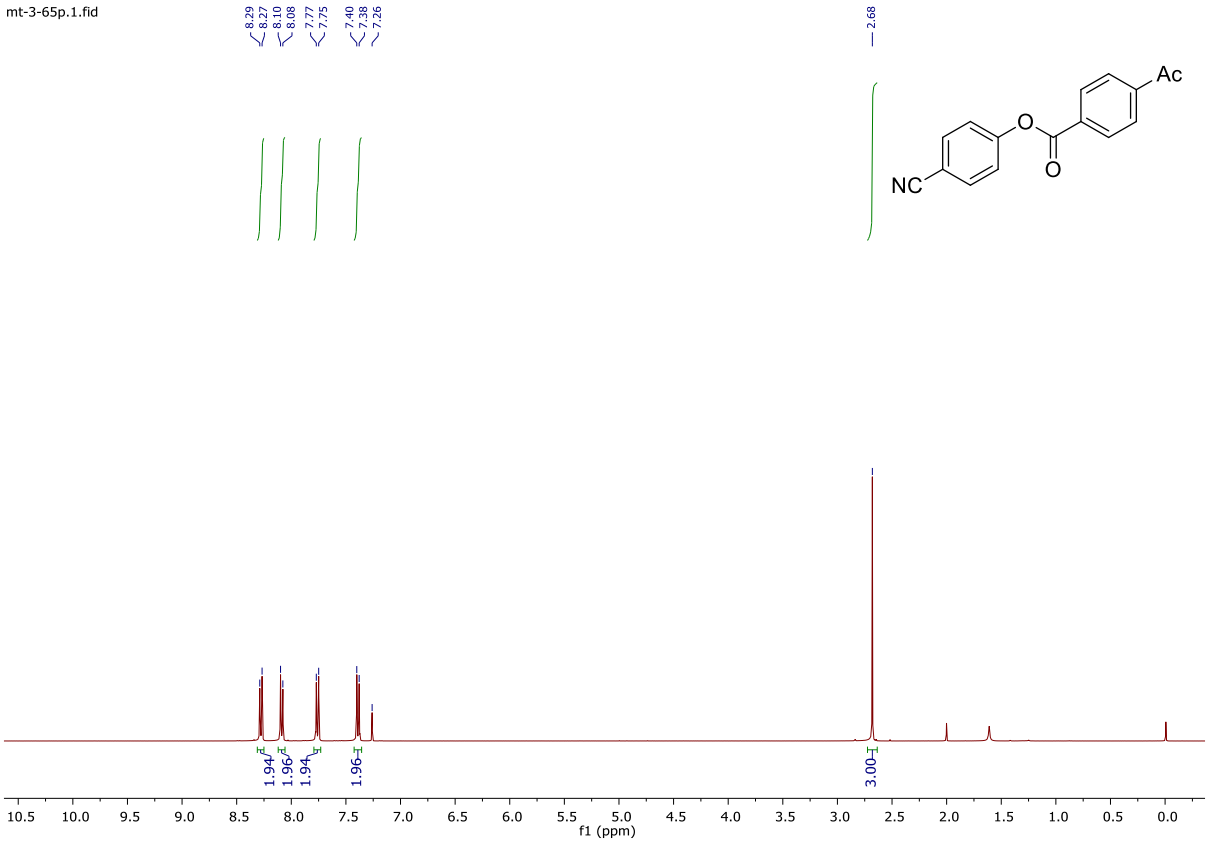

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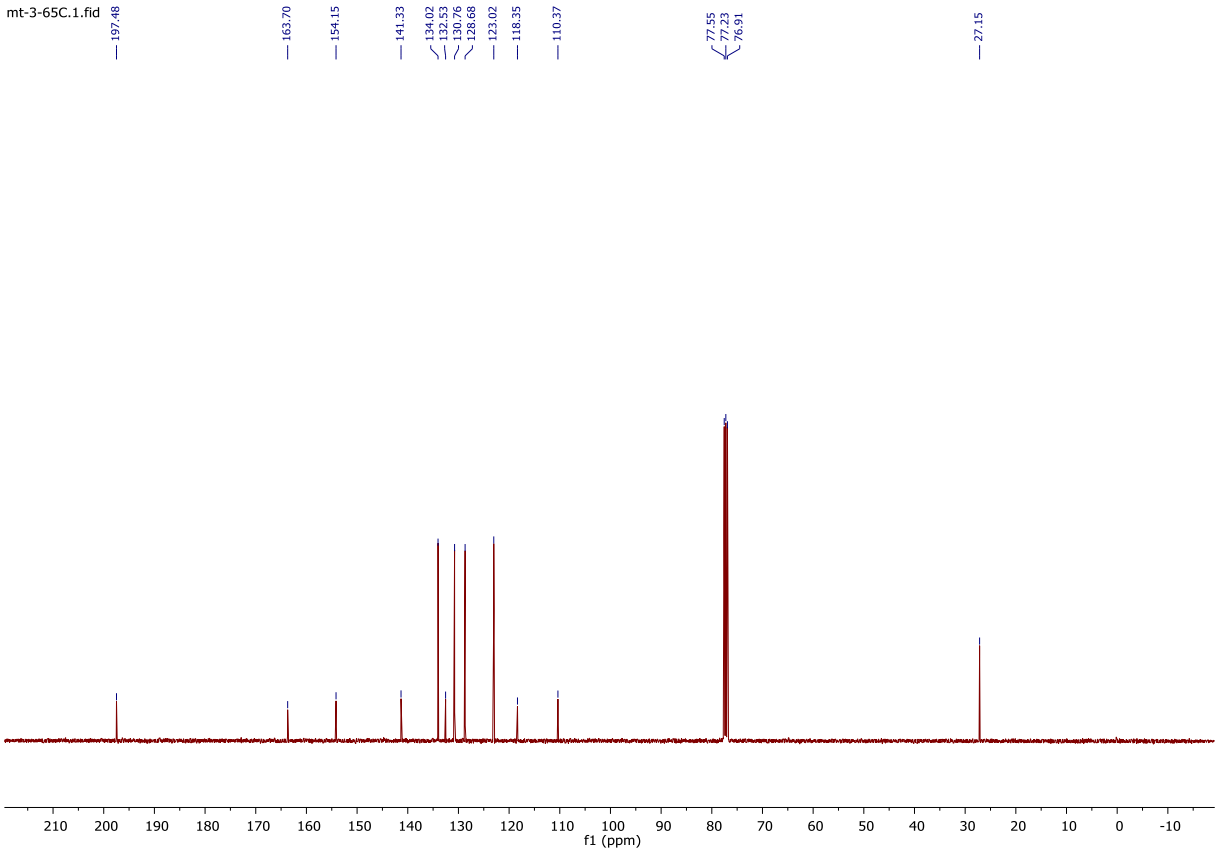

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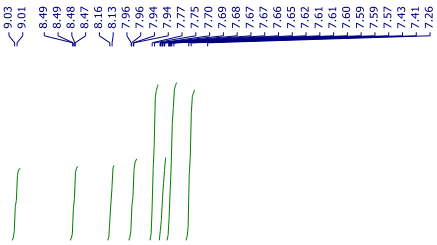

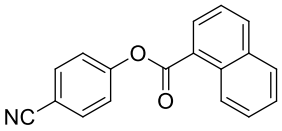

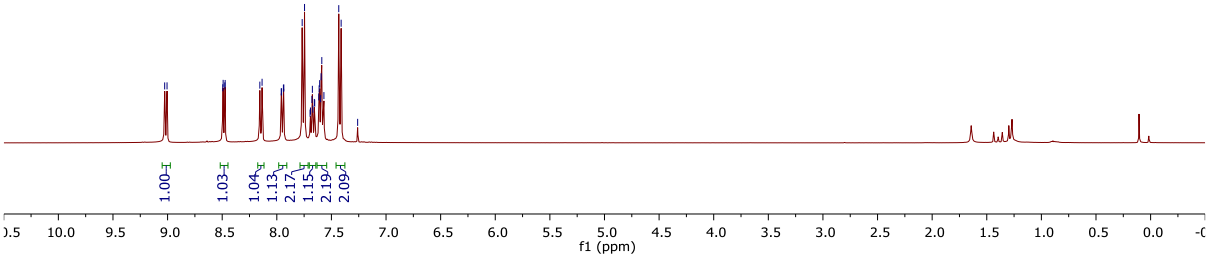

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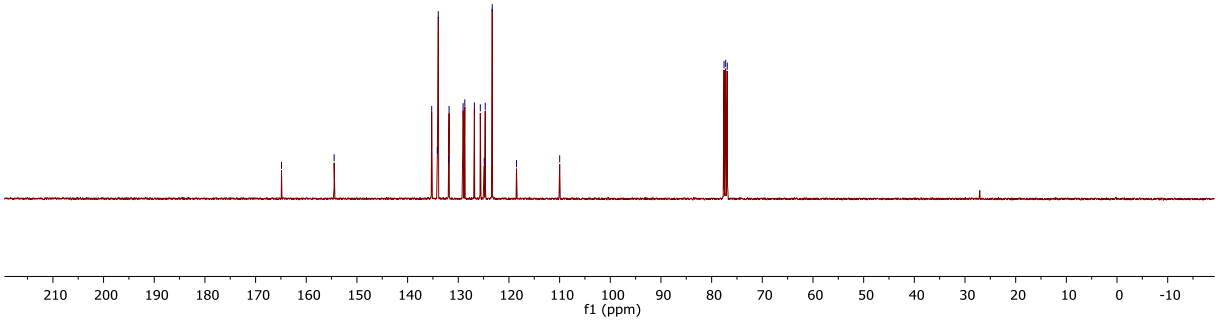

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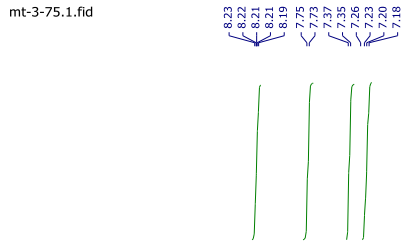
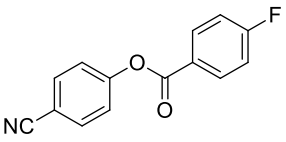
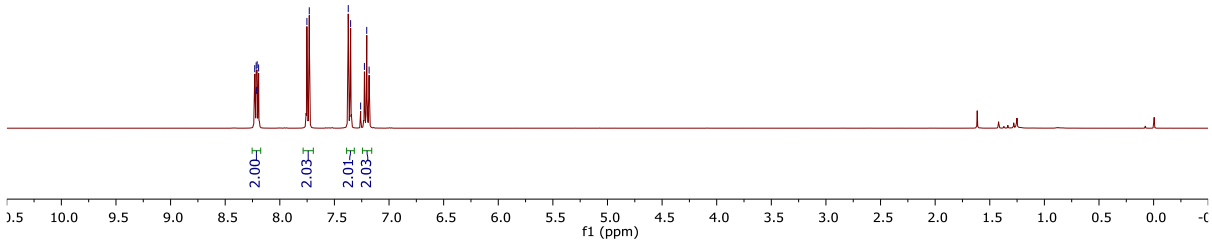
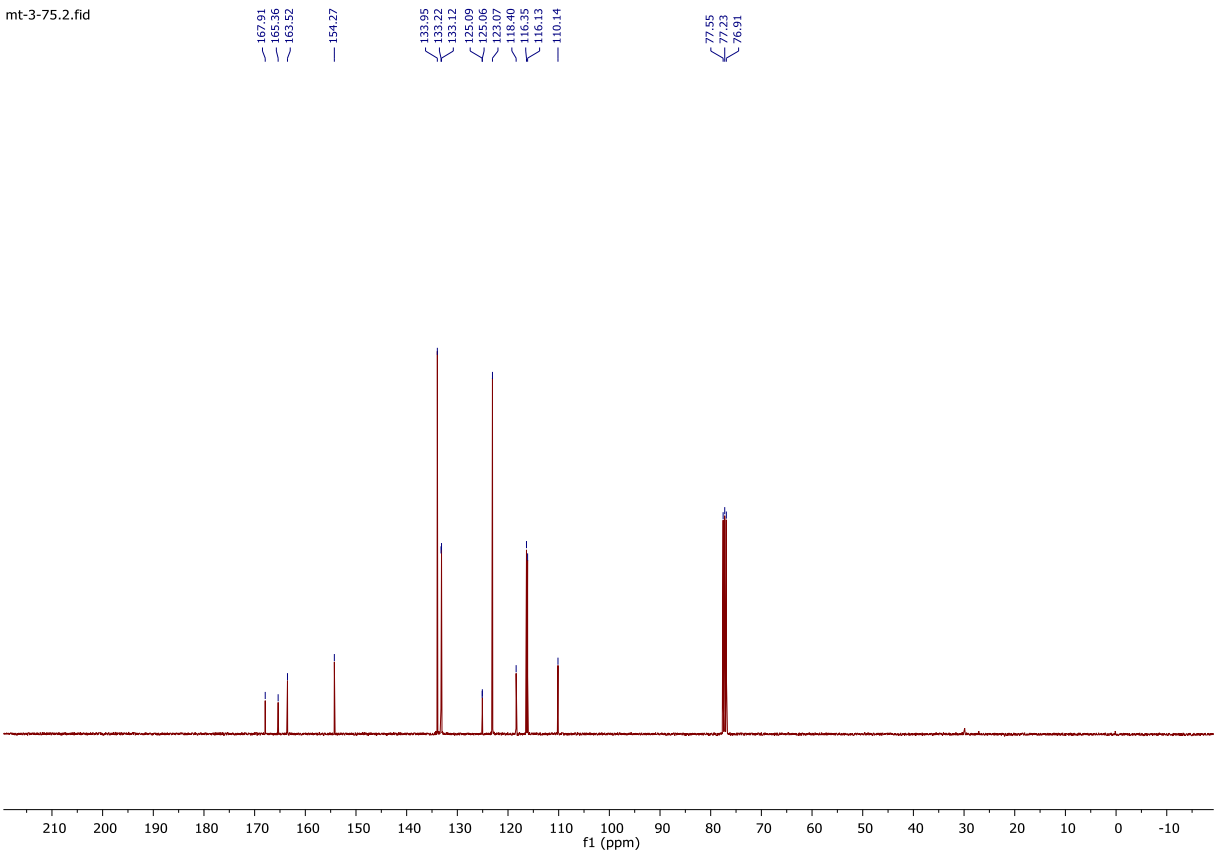


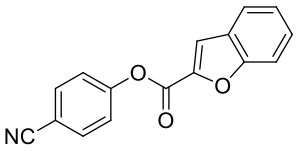


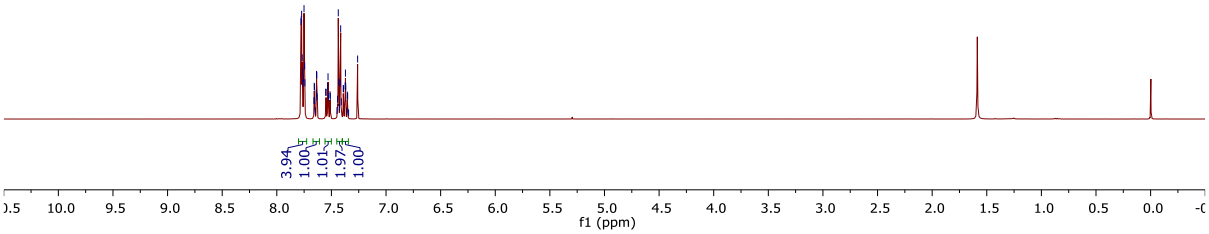


mt-3-75.2.fid

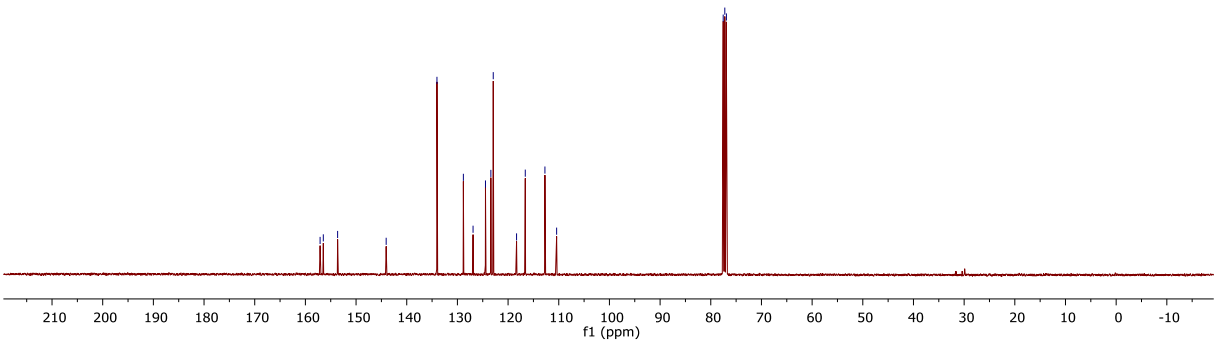


mt-3-64pp1.fid

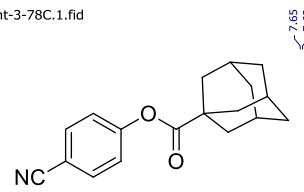




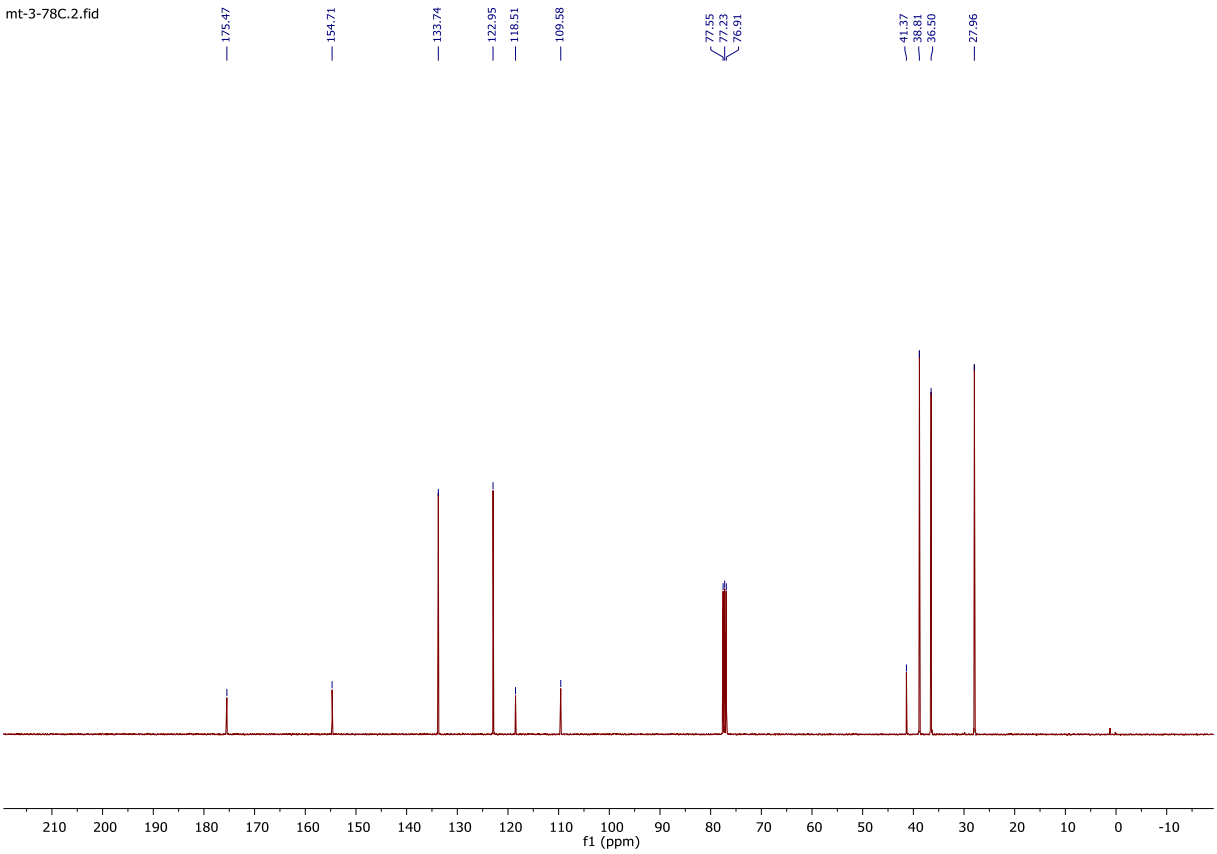
mt-3-64.2.fid

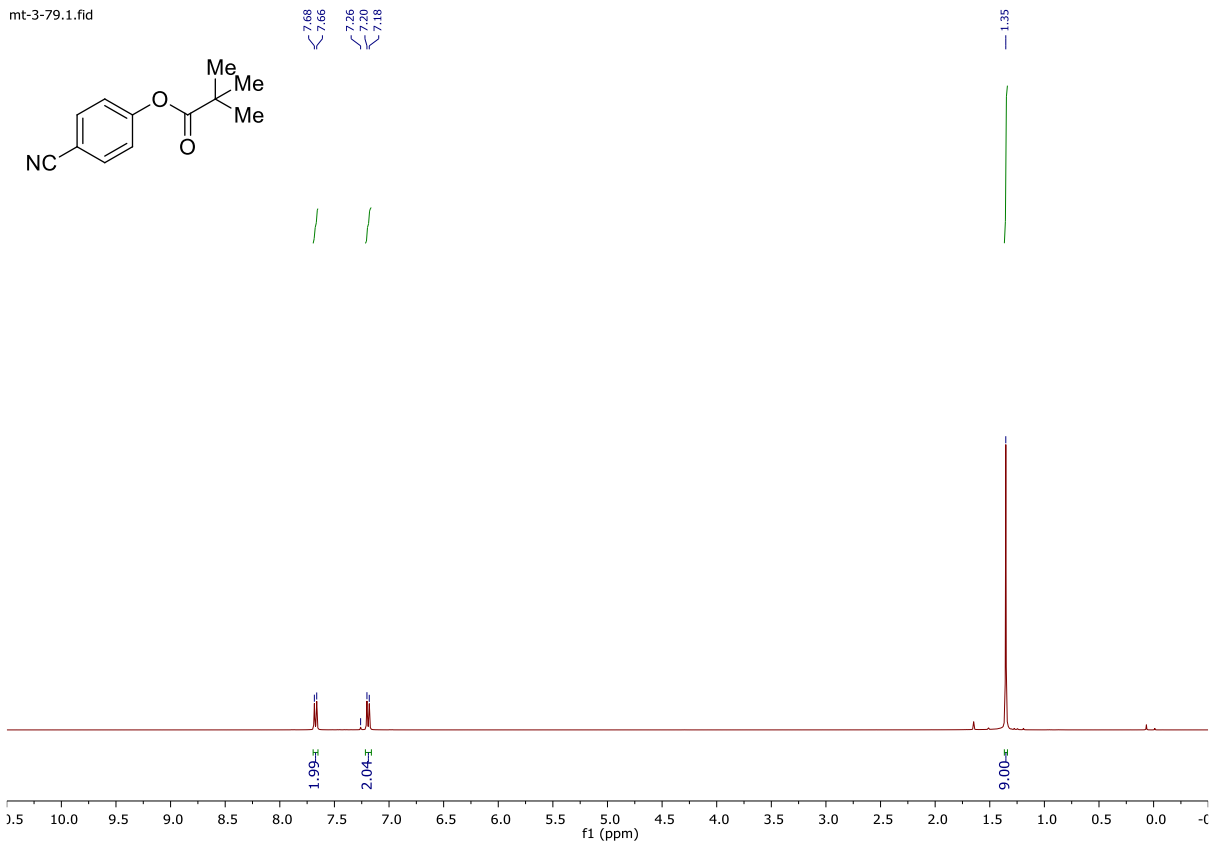


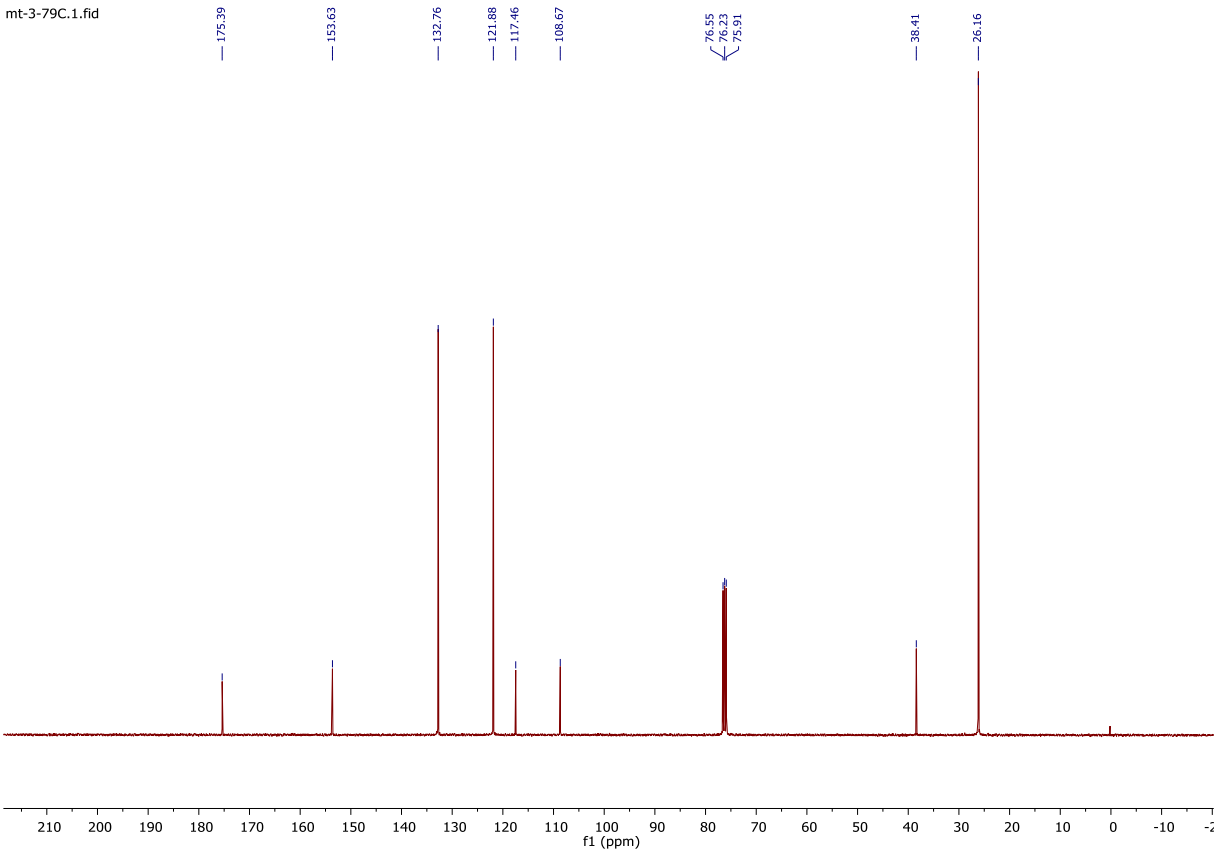
mt-3-78C.1.fid



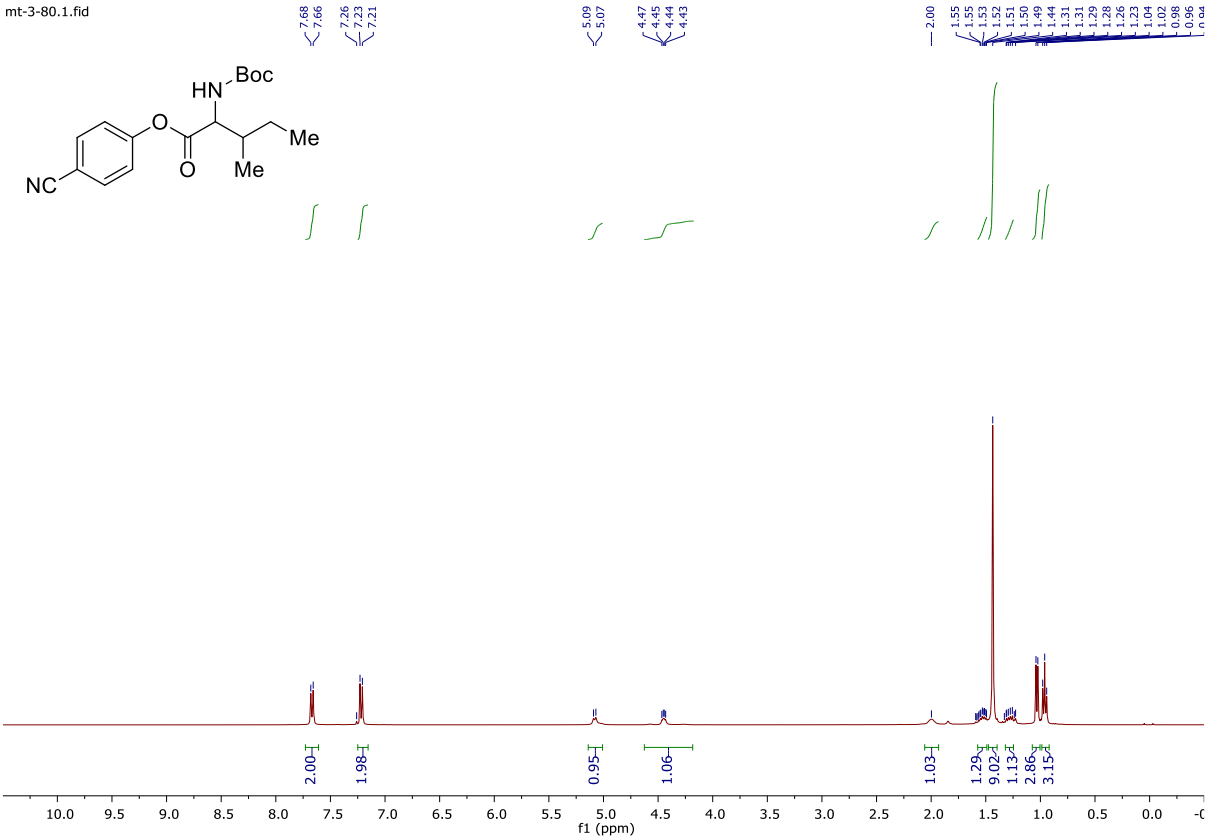
mt-3-78C.2.fid



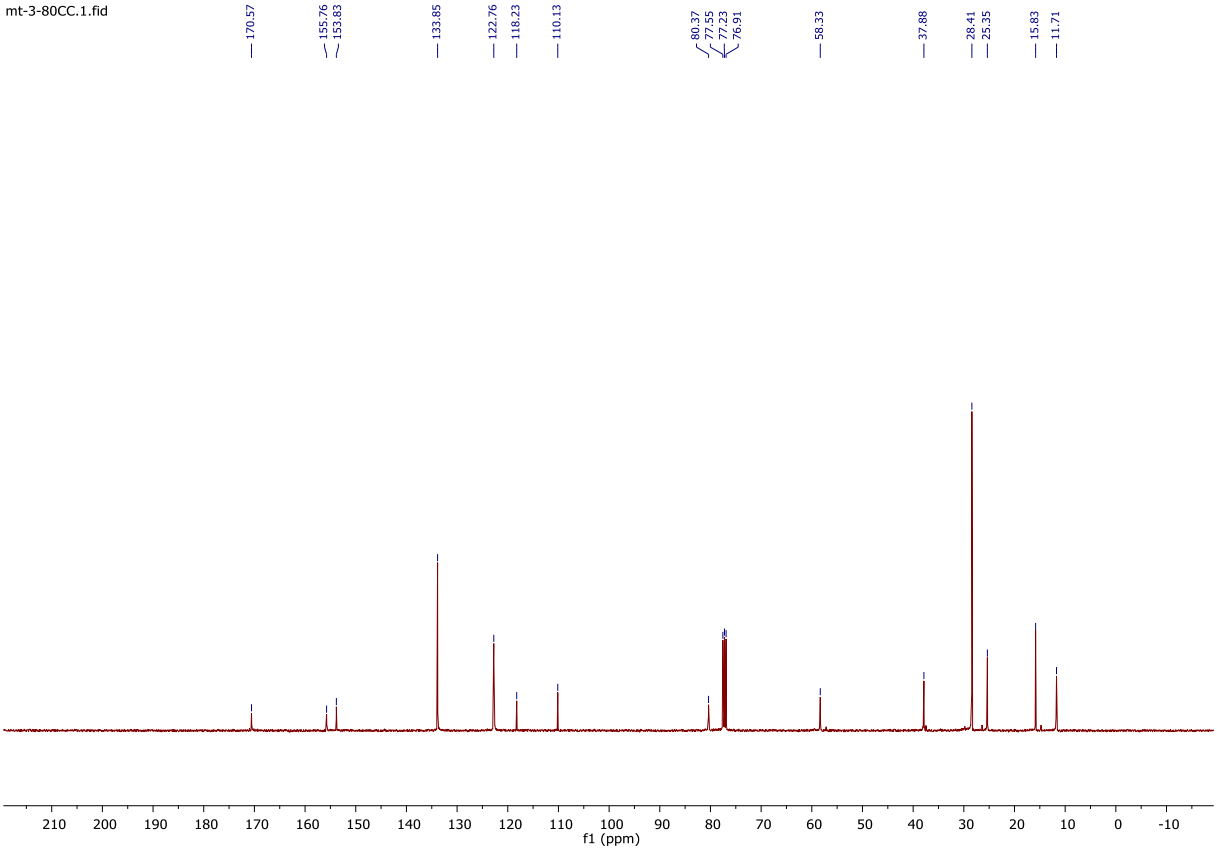

mt-3-79.1.fid
7.68
7.66
7.26
7.20
7.18
1.35
Me
Me
Me
O
O
NC
1.99
2.04
9.00
f1 (ppm)

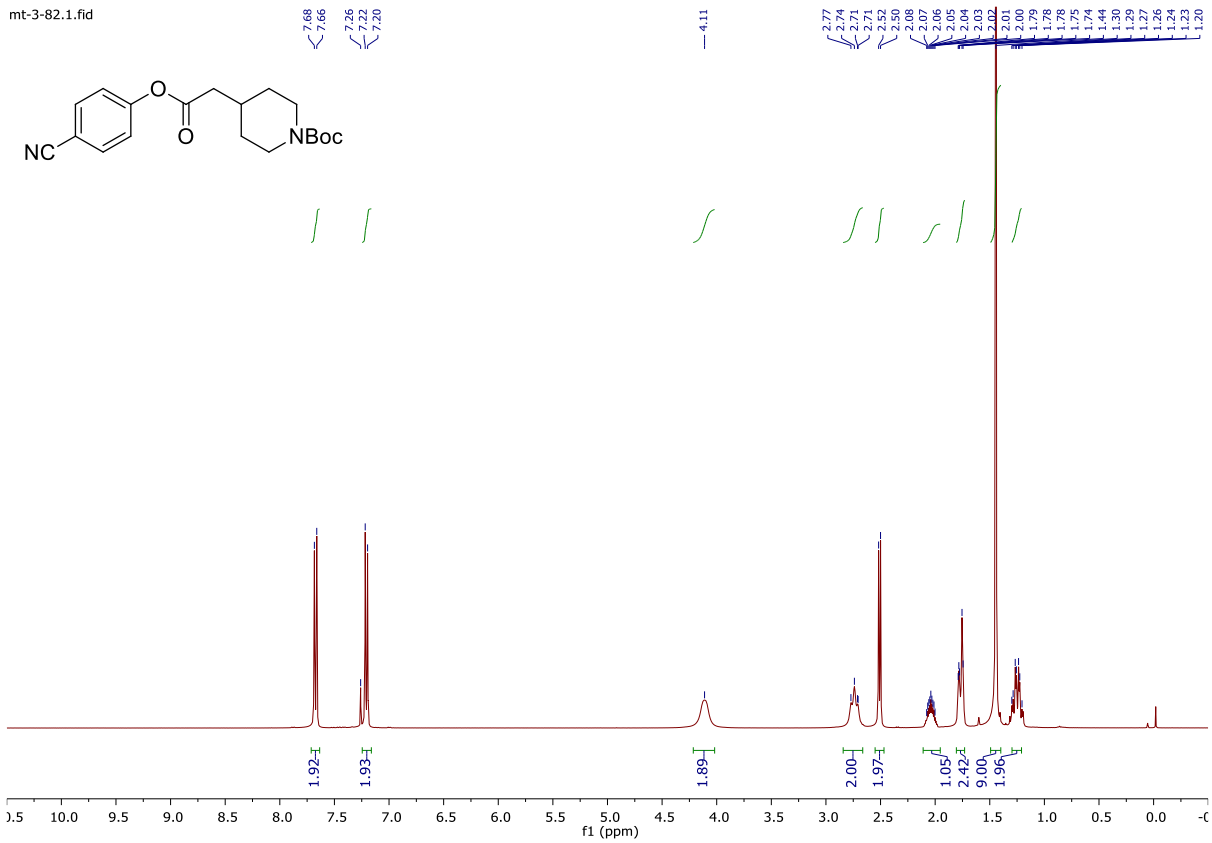

mt-3-79C.1.fid
175.39
153.63
132.76
121.88
117.46
108.67
76.55
76.23
75.91
38.41
26.16
f1 (ppm)

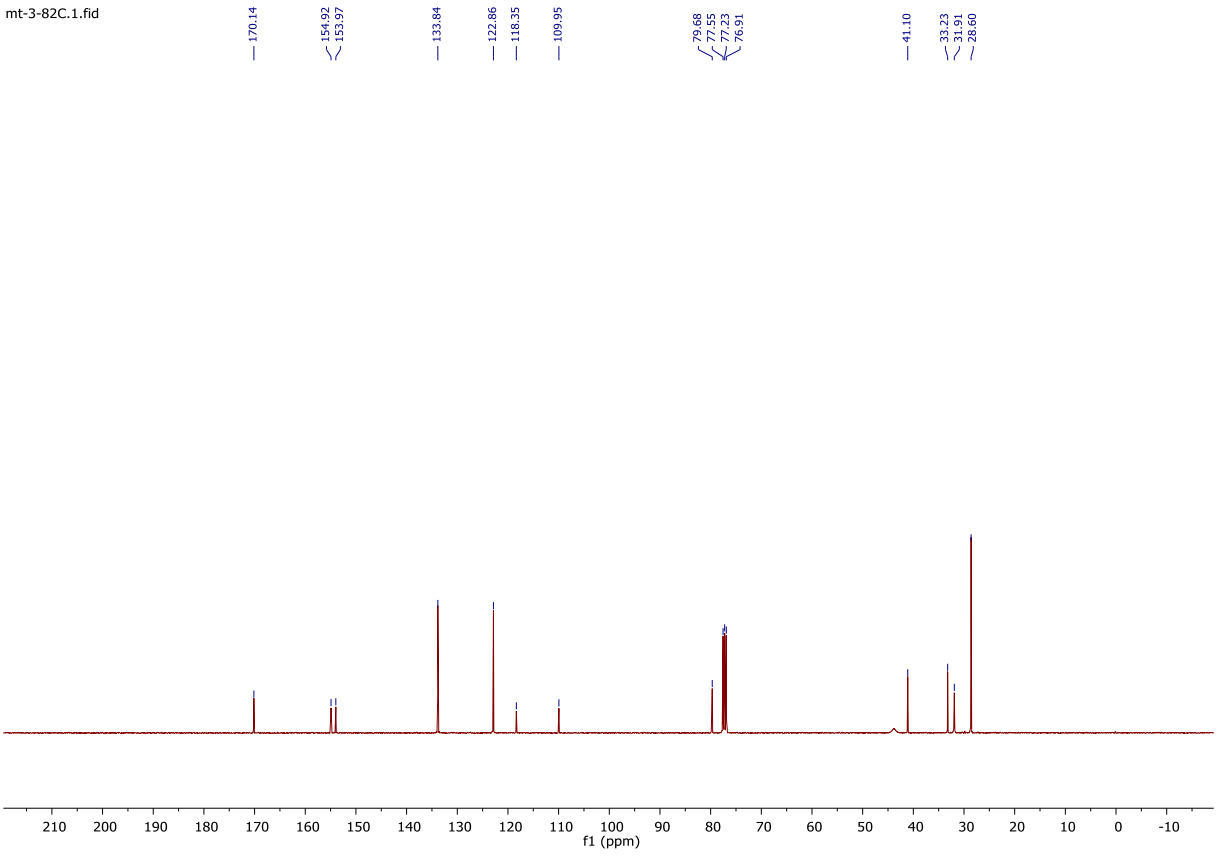
mt-3-80.1.fid

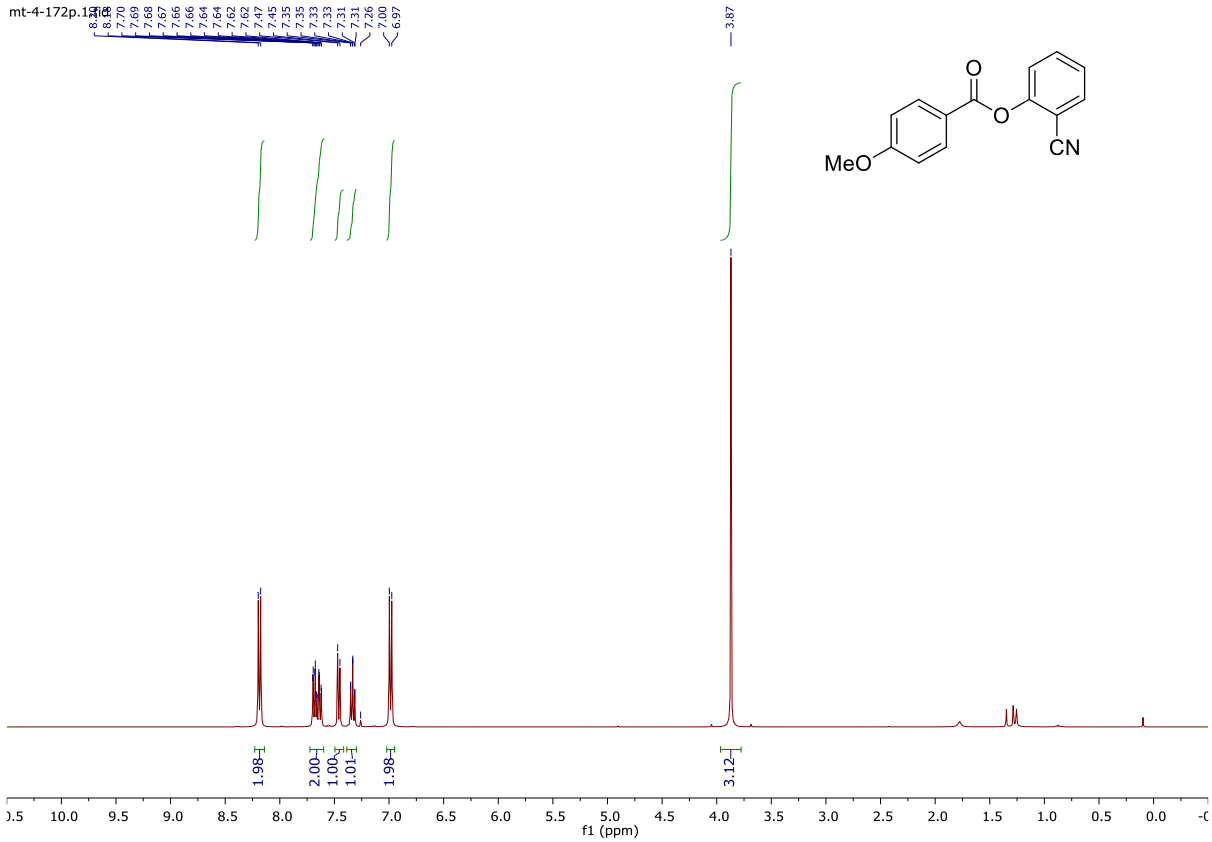


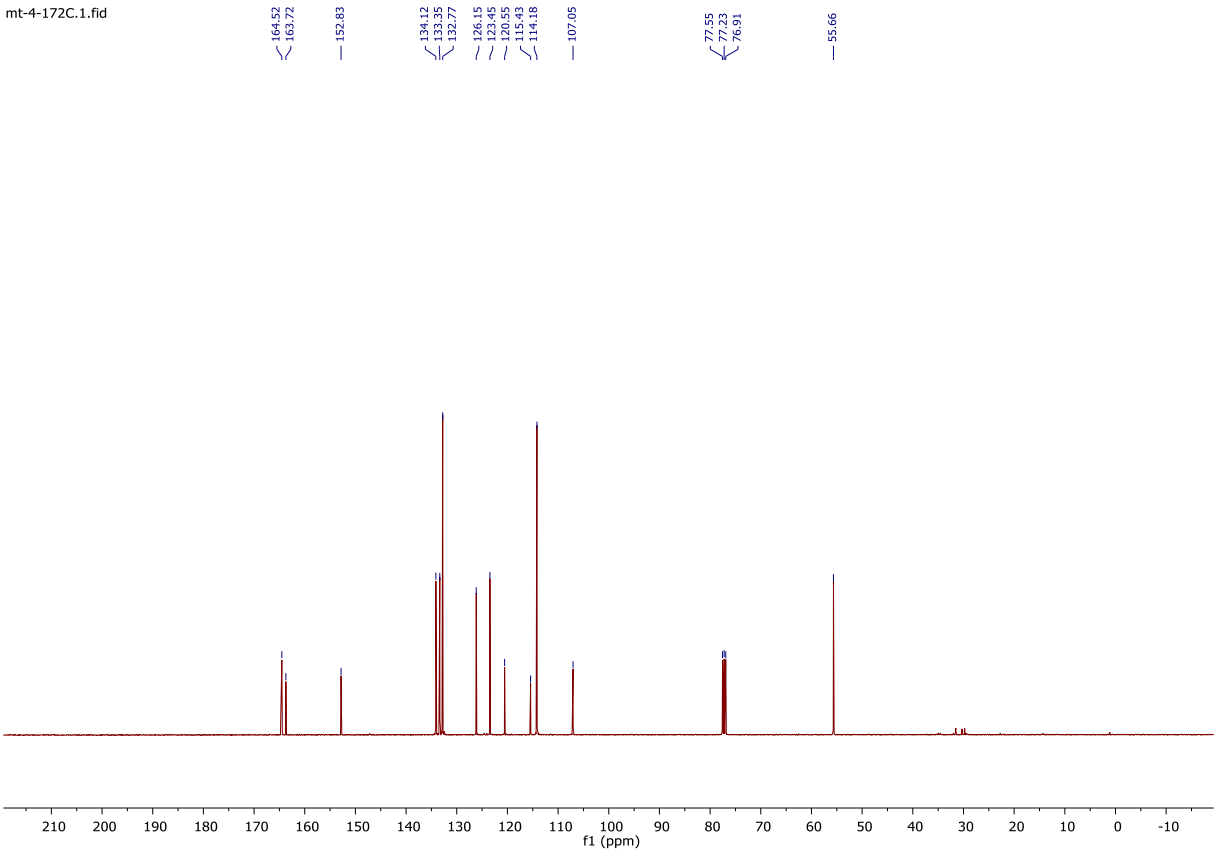
mt-3-80CC.1.fid

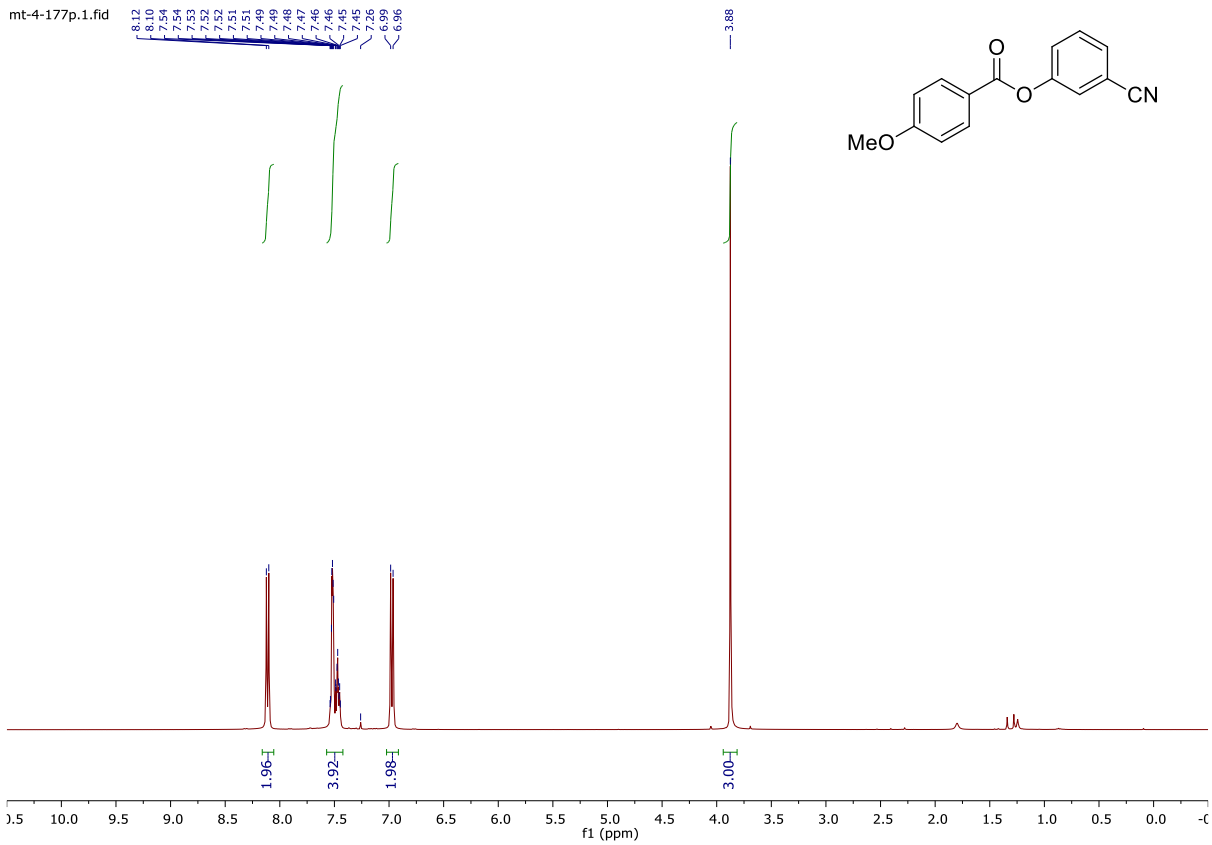


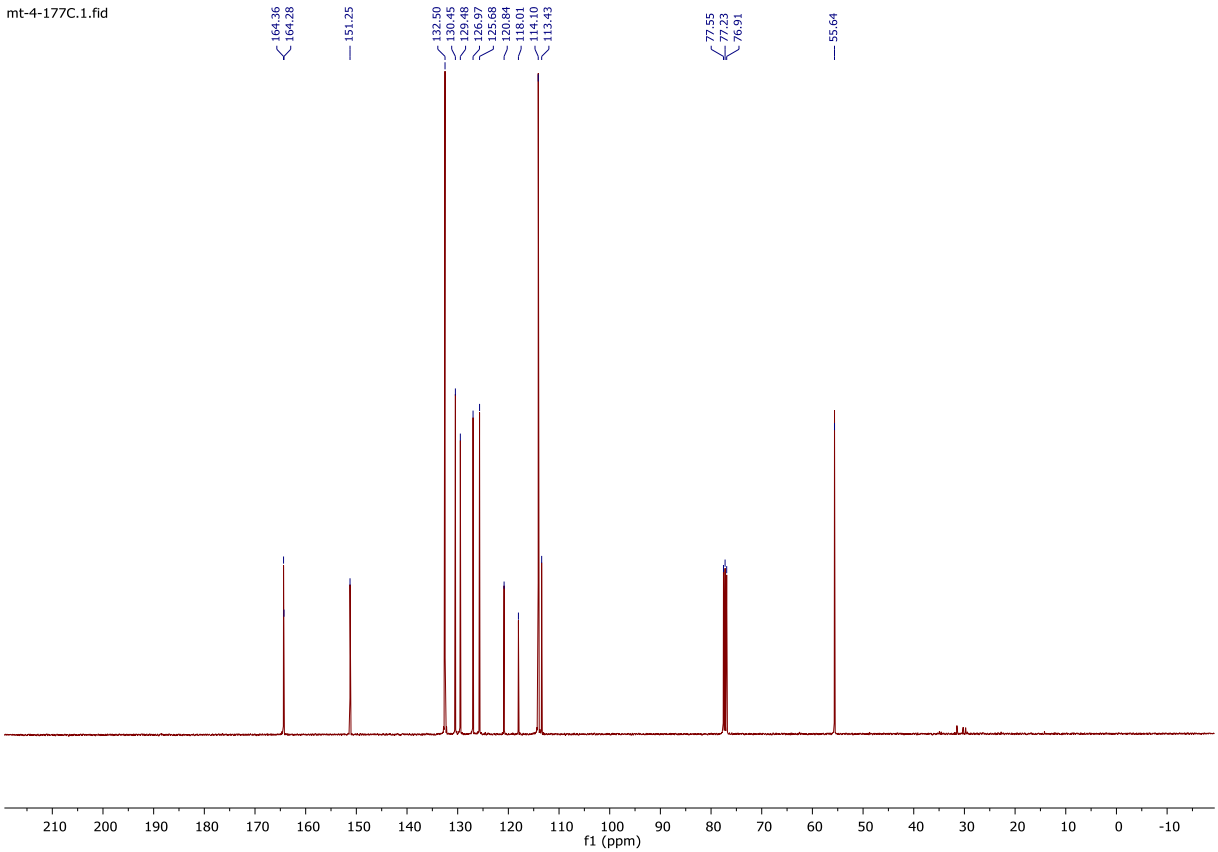

mt-3-82.1.fid
NC
O
O
NBoc
f1 (ppm)


mt-3-82C.1.fid
f1 (ppm)

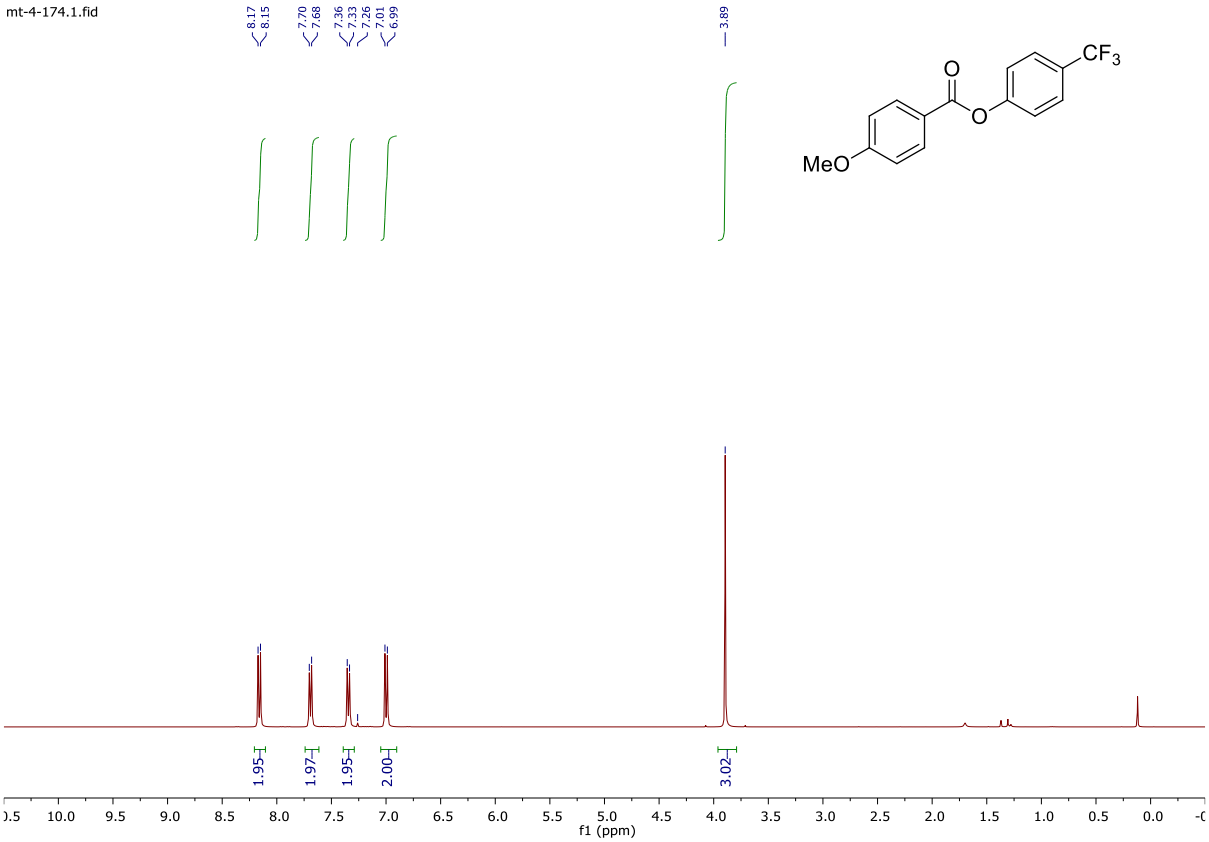

mt-4-172p.1.fid
8.18
8.18
7.70
7.69
7.68
7.67
7.66
7.66
7.64
7.64
7.62
7.62
7.47
7.45
7.35
7.35
7.33
7.33
7.31
7.31
7.26
7.00
6.97
3.87
O
O
MeO
CN
1.98
2.00
1.00
1.01
1.98
3.12
f1 (ppm)


mt-4-172C.1.fid
164.52
163.72
152.83
134.12
133.35
132.77
126.15
123.45
120.55
115.43
114.18
107.05
77.55
77.23
76.91
55.66
f1 (ppm)

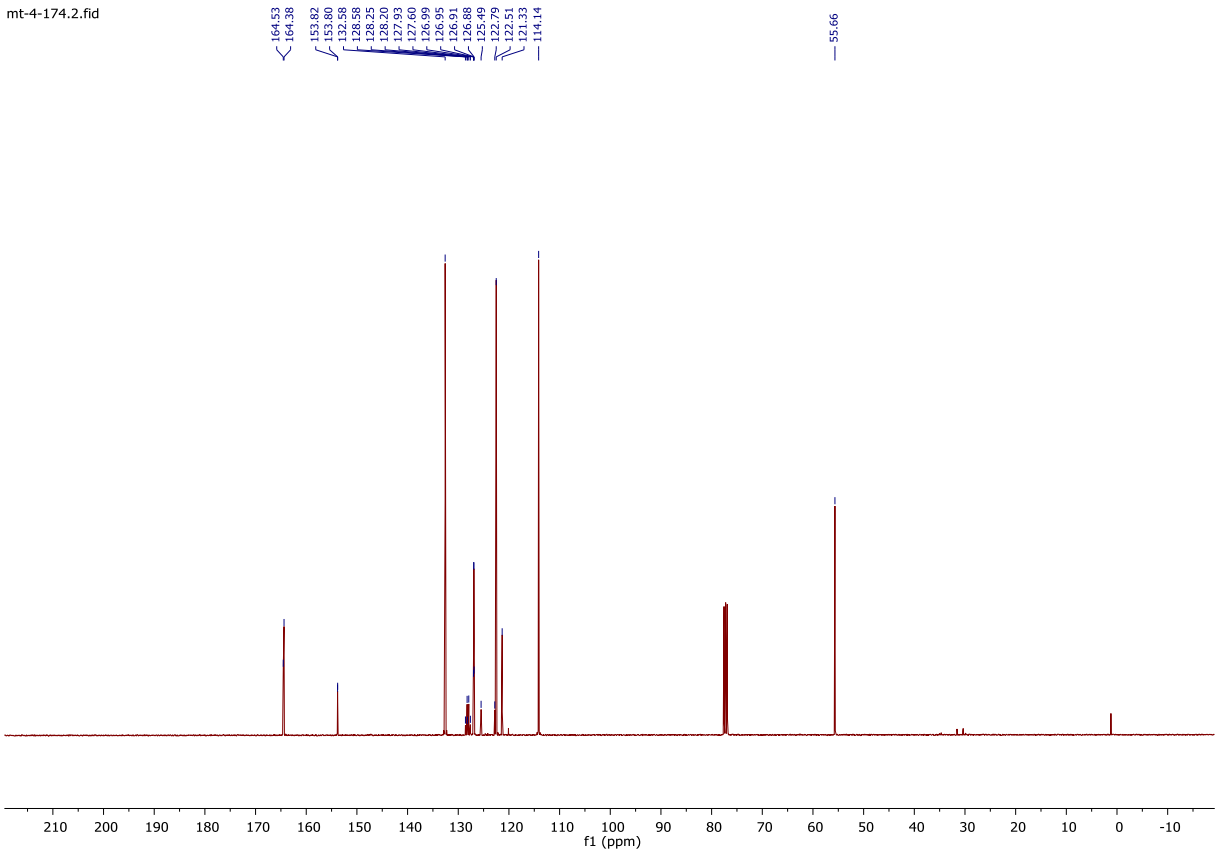

mt-4-177p.1.fid
8.12
8.10
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.49
7.49
7.48
7.47
7.46
7.46
7.45
7.45
7.26
6.99
6.96
3.88
O
O
CN
MeO
1.96
3.92
1.98
3.00
f1 (ppm)

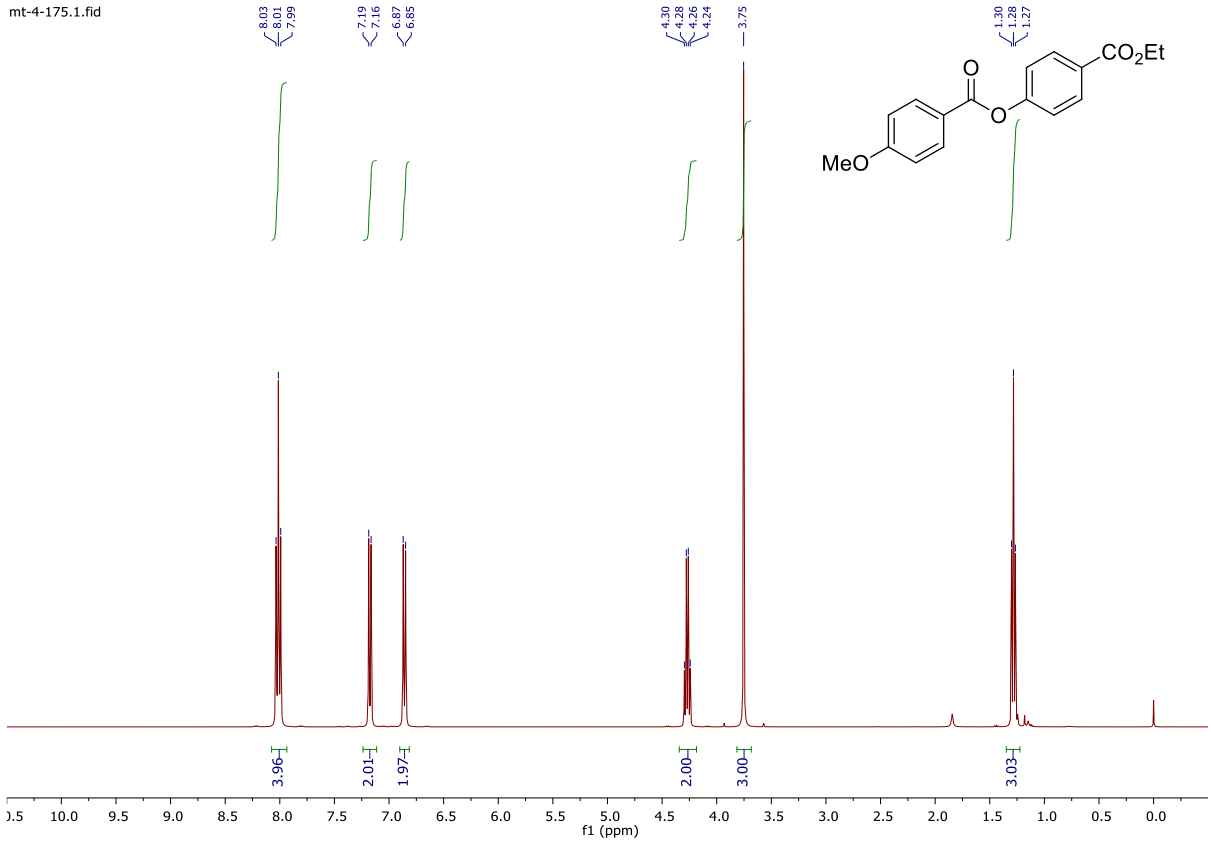

mt-4-177C.1.fid
164.36
164.28
151.25
132.50
130.45
129.48
126.97
125.68
120.84
118.01
114.10
113.43
77.55
77.23
76.91
55.64
f1 (ppm)

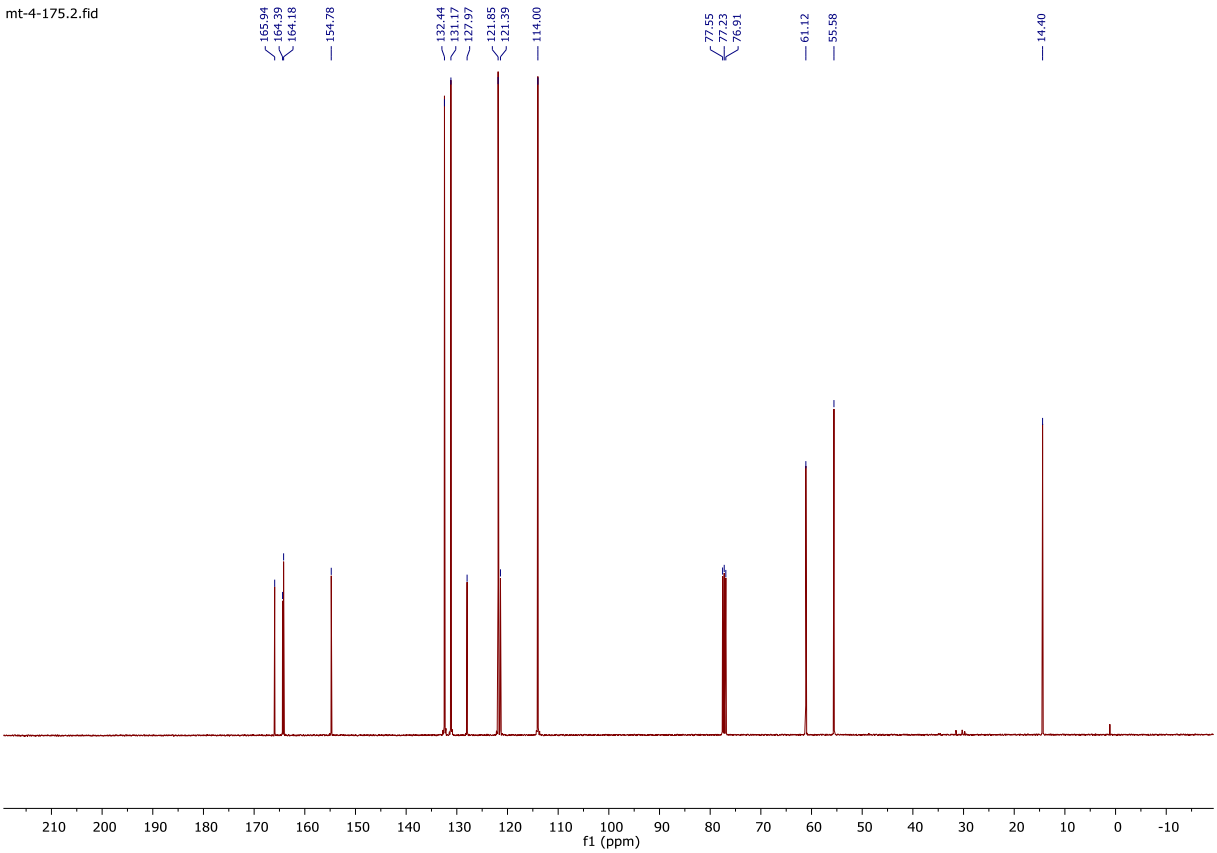
mt-4-174.1.fid

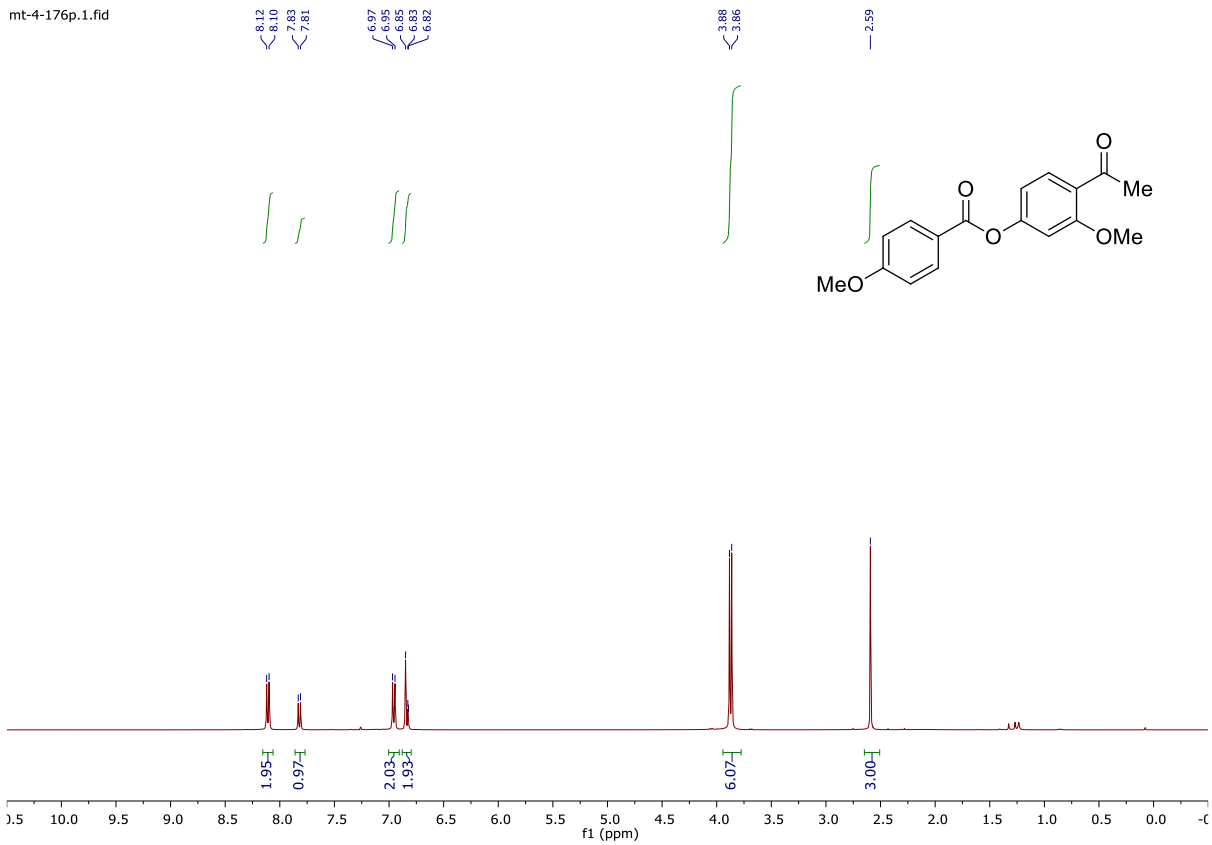


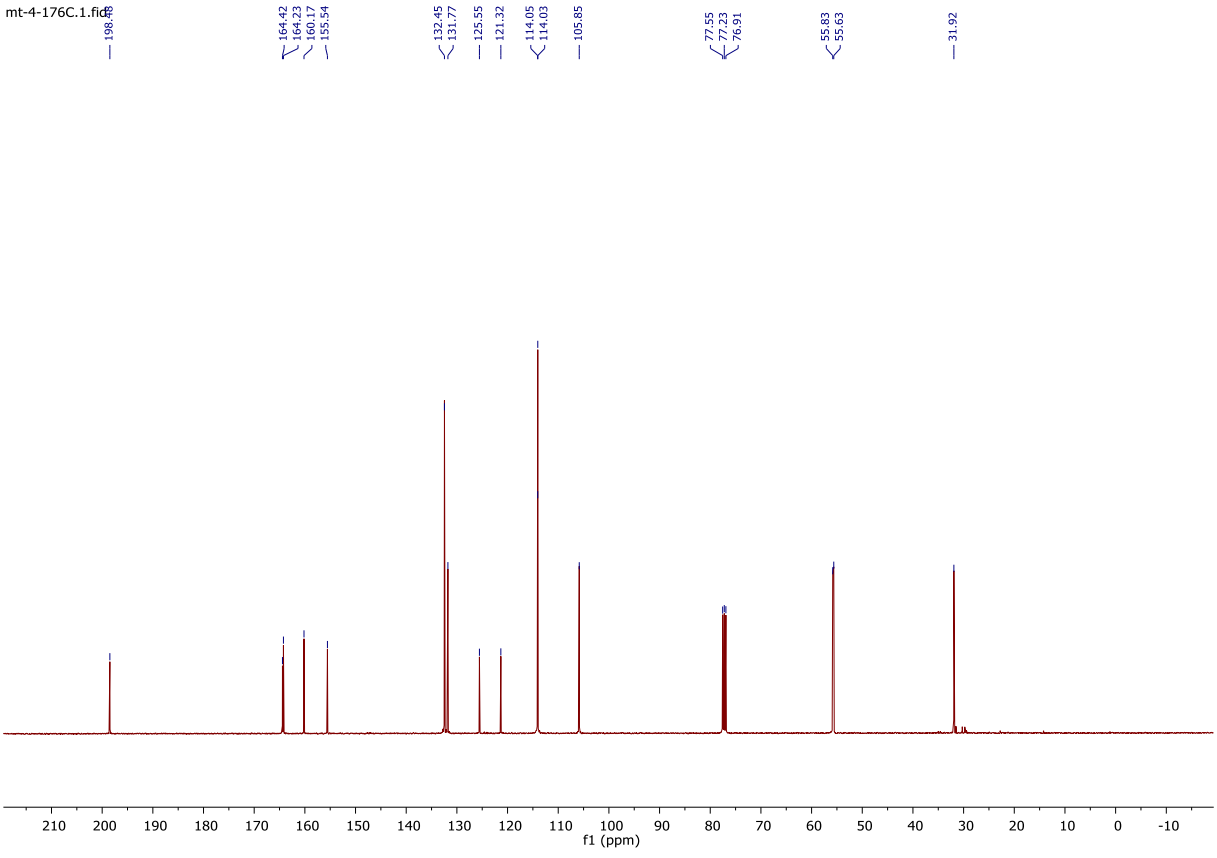
mt-4-174.2.fid



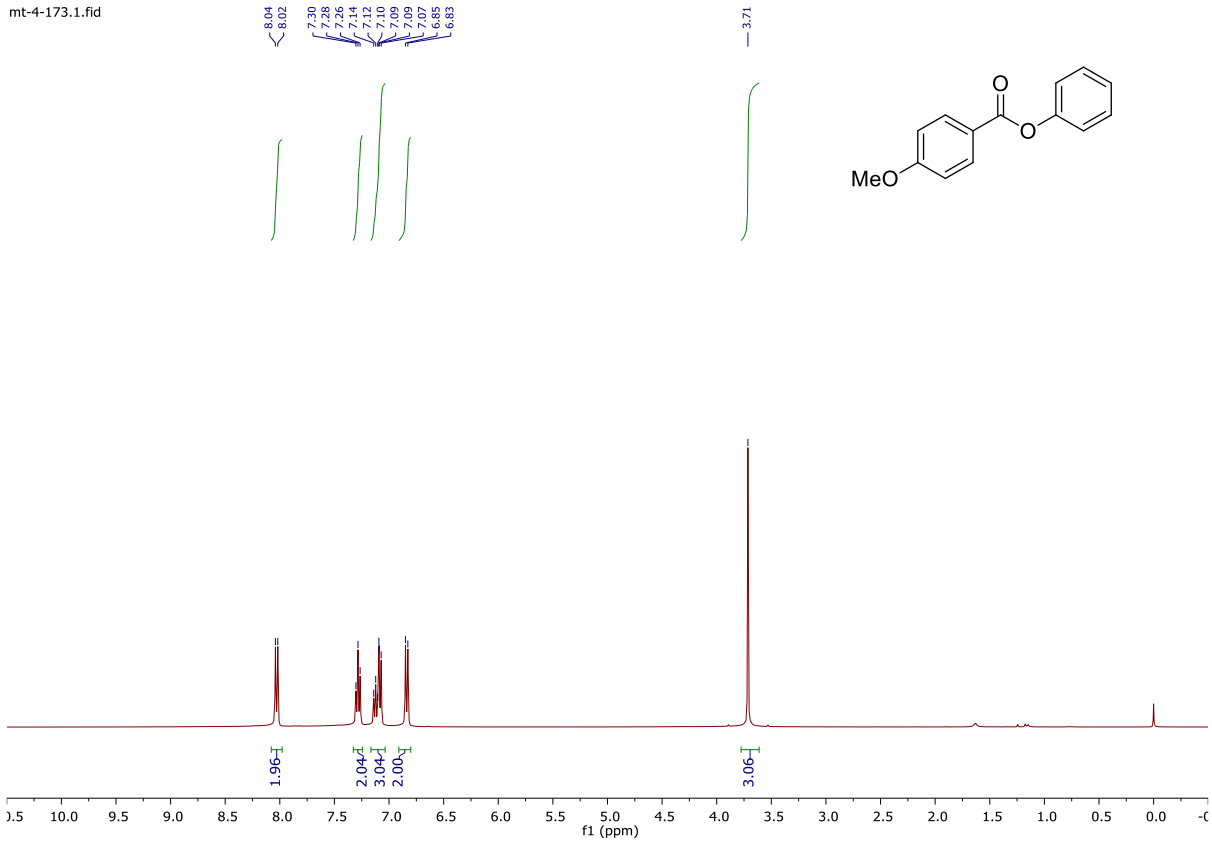

mt-4-175.1.fid
8.03
8.01
7.99
7.19
7.16
6.87
6.85
4.30
4.28
4.26
4.24
3.75
1.30
1.28
1.27
CO2Et
O
O
MeO
3.96
2.01
1.97
2.00
3.00
3.03
f1 (ppm)


mt-4-175.2.fid
165.94
164.39
164.18
154.78
132.44
131.17
127.97
121.85
121.39
114.00
77.55
77.23
76.91
61.12
55.58
14.40
f1 (ppm)

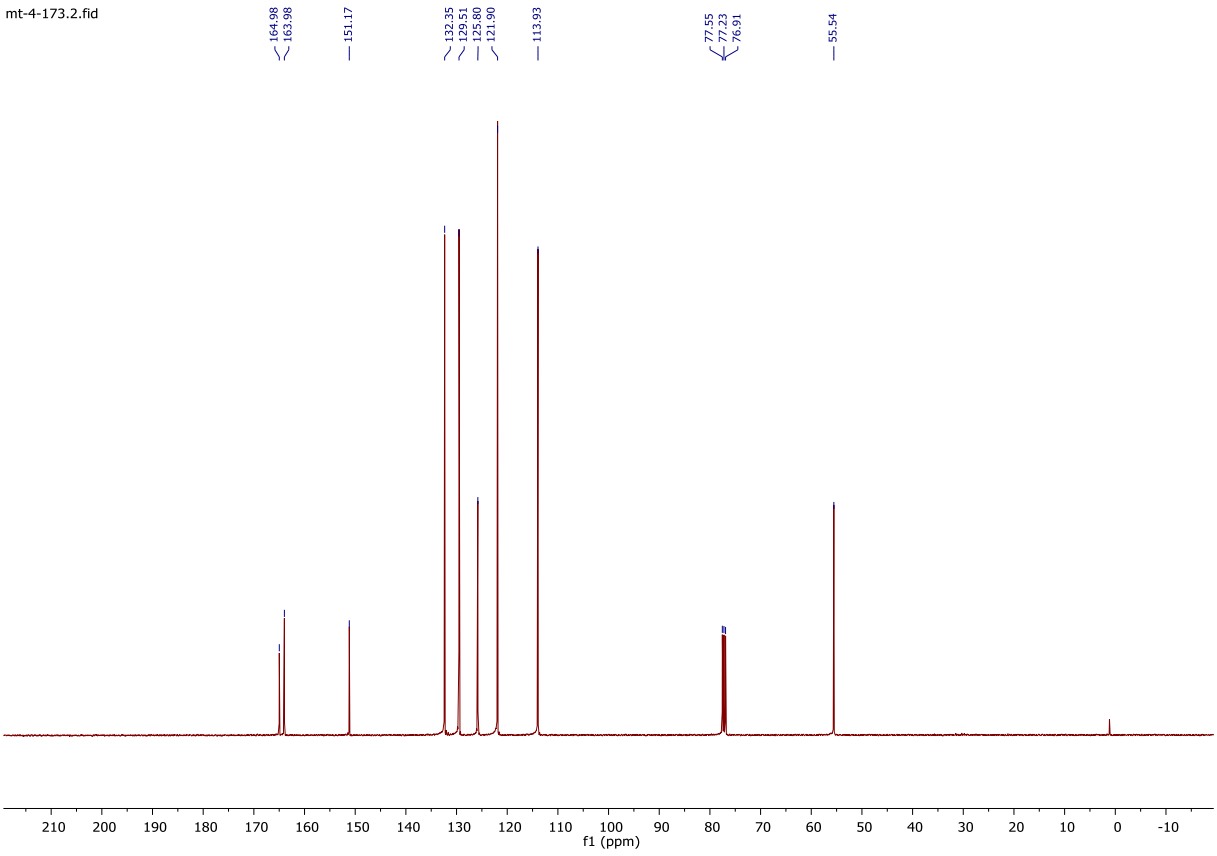

mt-4-176p.1.fid
8.12
8.10
7.83
7.81
6.97
6.95
6.85
6.83
6.82
3.88
3.86
2.59
O
Me
O
O
OMe
MeO
1.95
0.97
2.03
1.93
6.07
3.00
f1 (ppm)


mt-4-176C.1.fid
198.48
164.42
164.23
160.17
155.54
132.45
131.77
125.55
121.32
114.05
114.03
105.85
77.55
77.23
76.91
55.83
55.63
31.92
f1 (ppm)

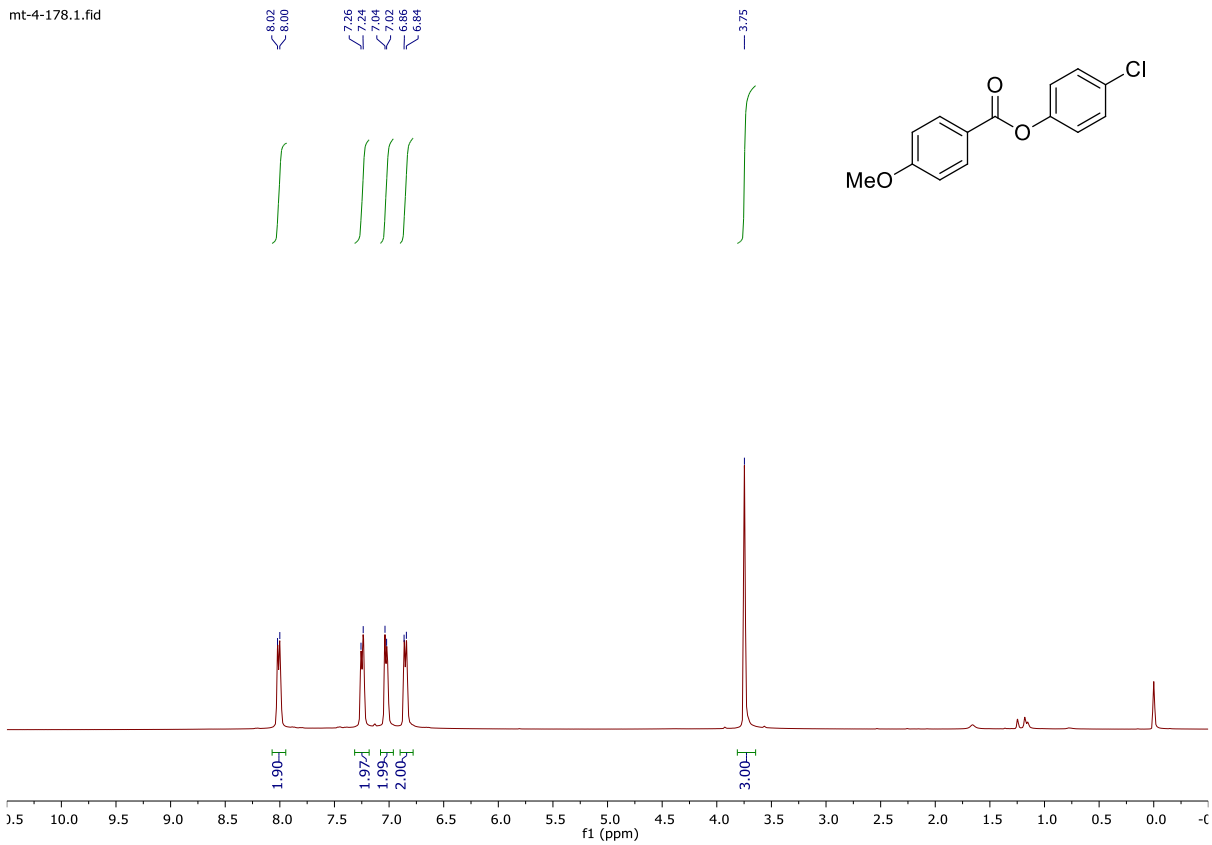
mt-4-173.1.fid



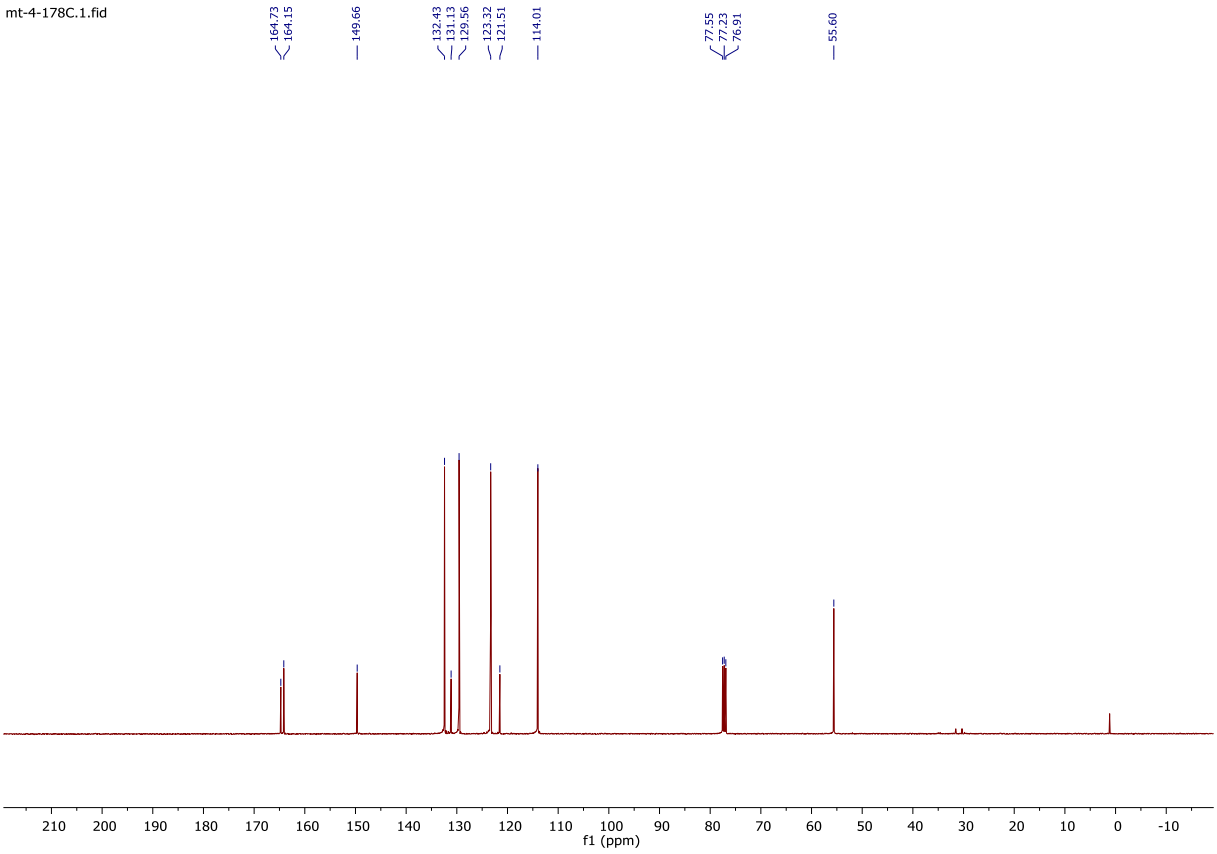
mt-4-173.2.fid

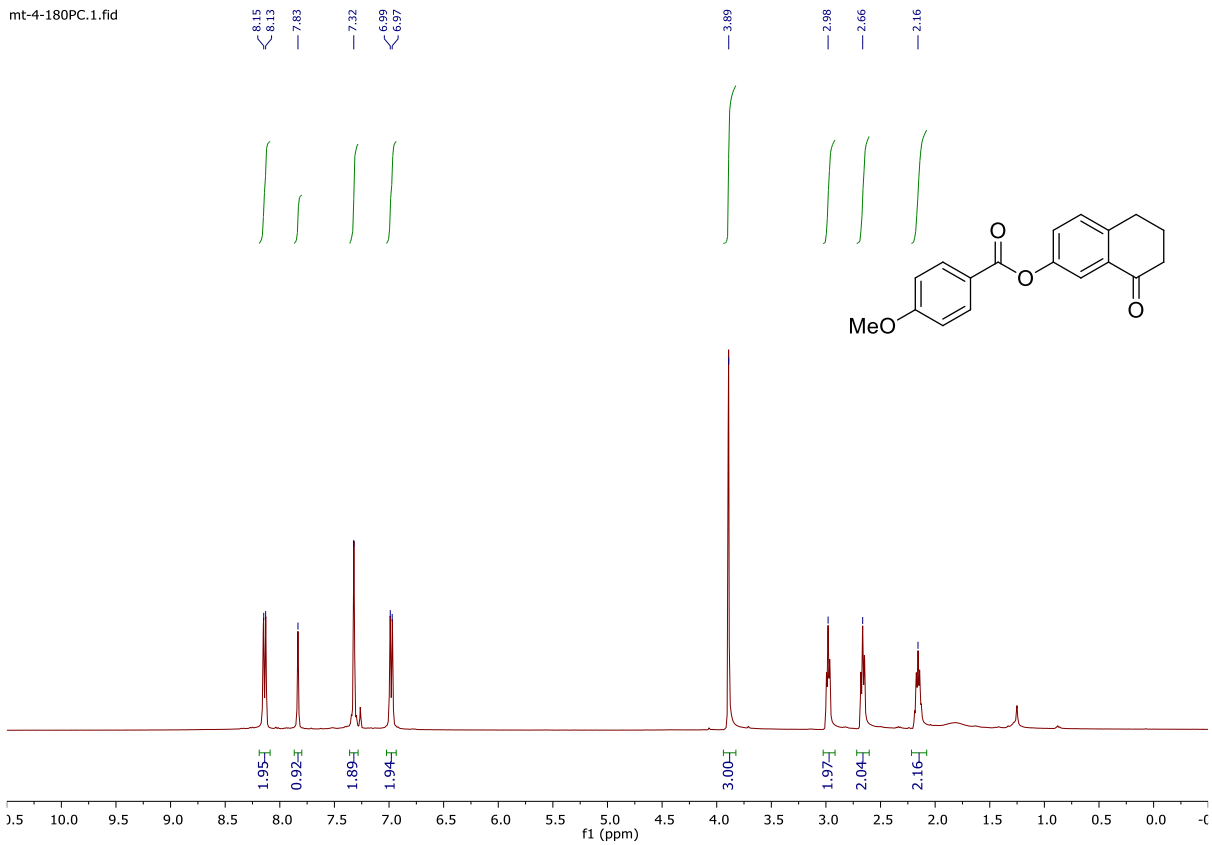


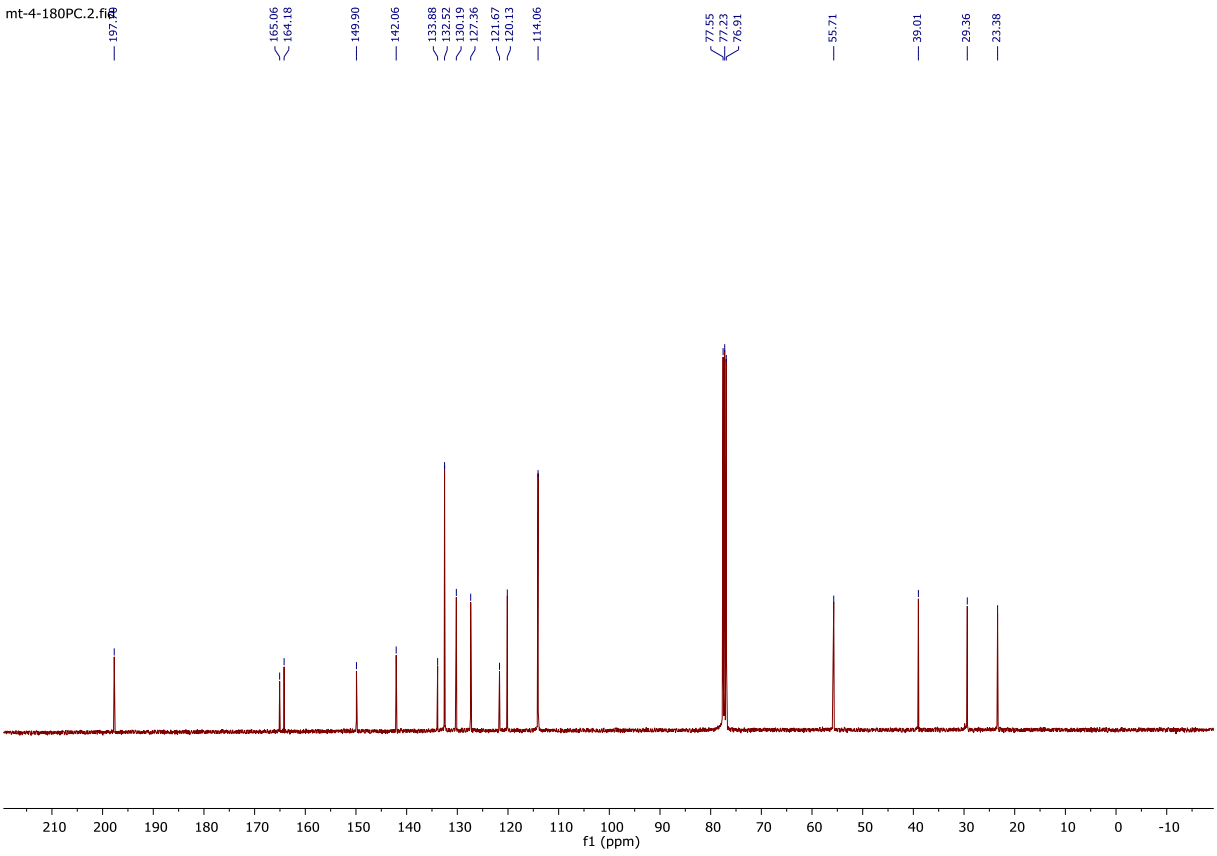
mt-4-178.1.fid

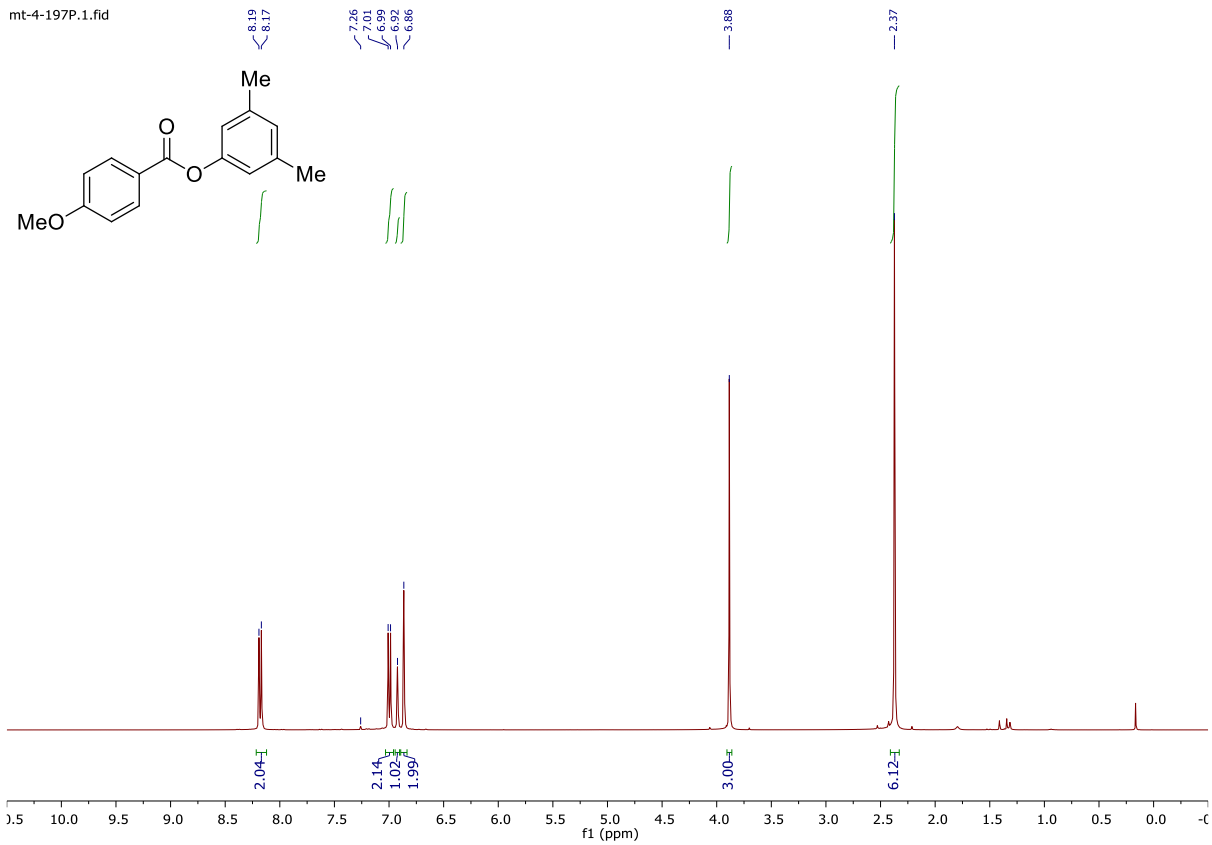


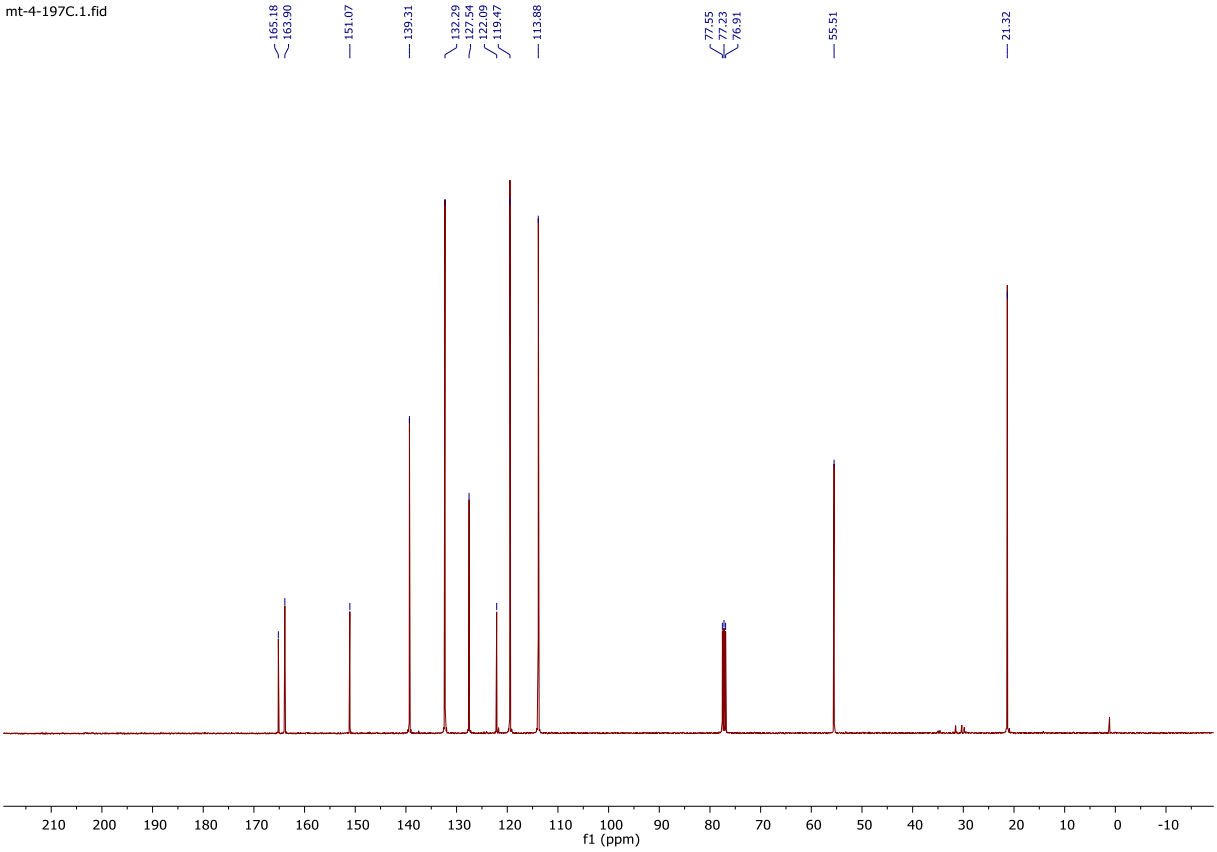
mt-4-178C.1.fid



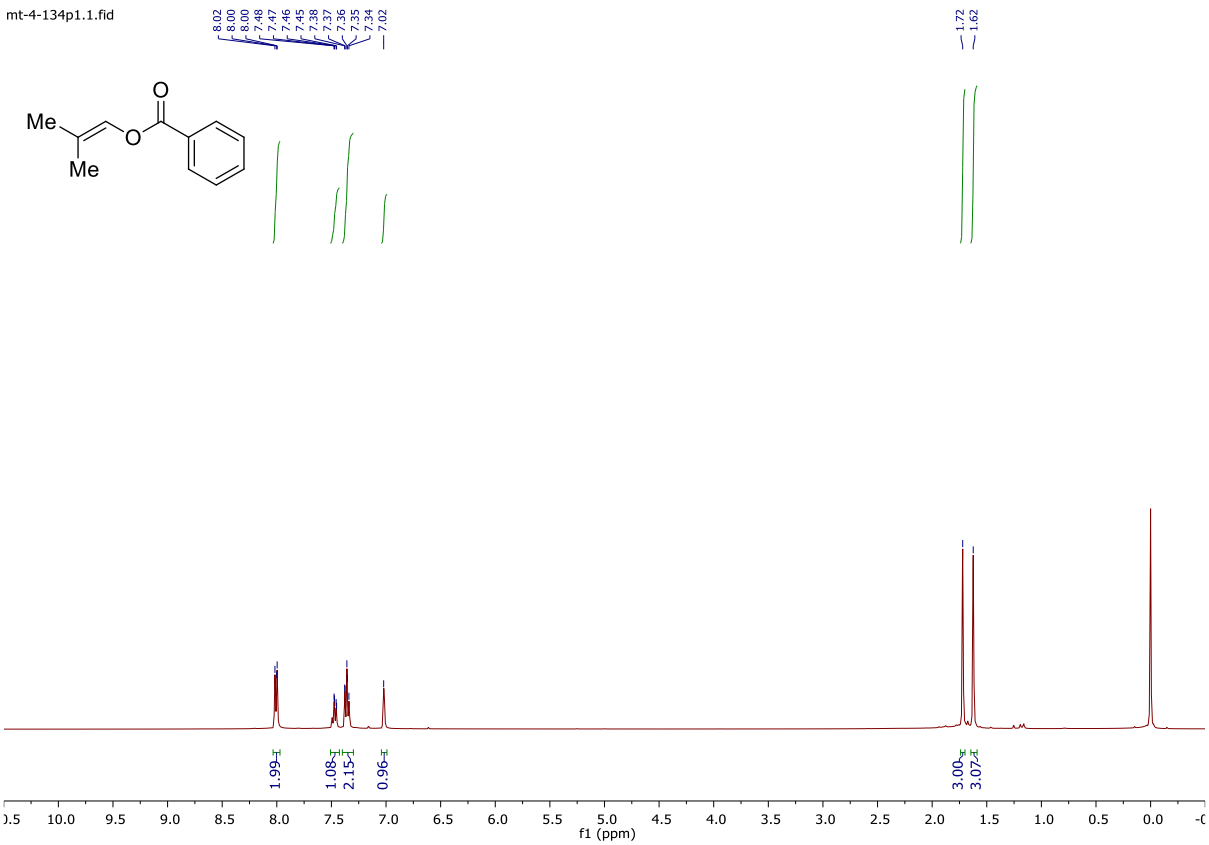

mt-4-180PC.1.fid
8.15
8.13
7.83
7.32
6.99
6.97
3.89
2.98
2.66
2.16
O
O
O
MeO
1.95
0.92
1.89
1.94
3.00
1.97
2.04
2.16
f1 (ppm)


mt-4-180PC.2.fid
197.82
165.06
164.18
149.90
142.06
133.88
132.52
130.19
127.36
121.67
120.13
114.06
77.55
77.23
76.91
55.71
39.01
29.36
23.38
f1 (ppm)

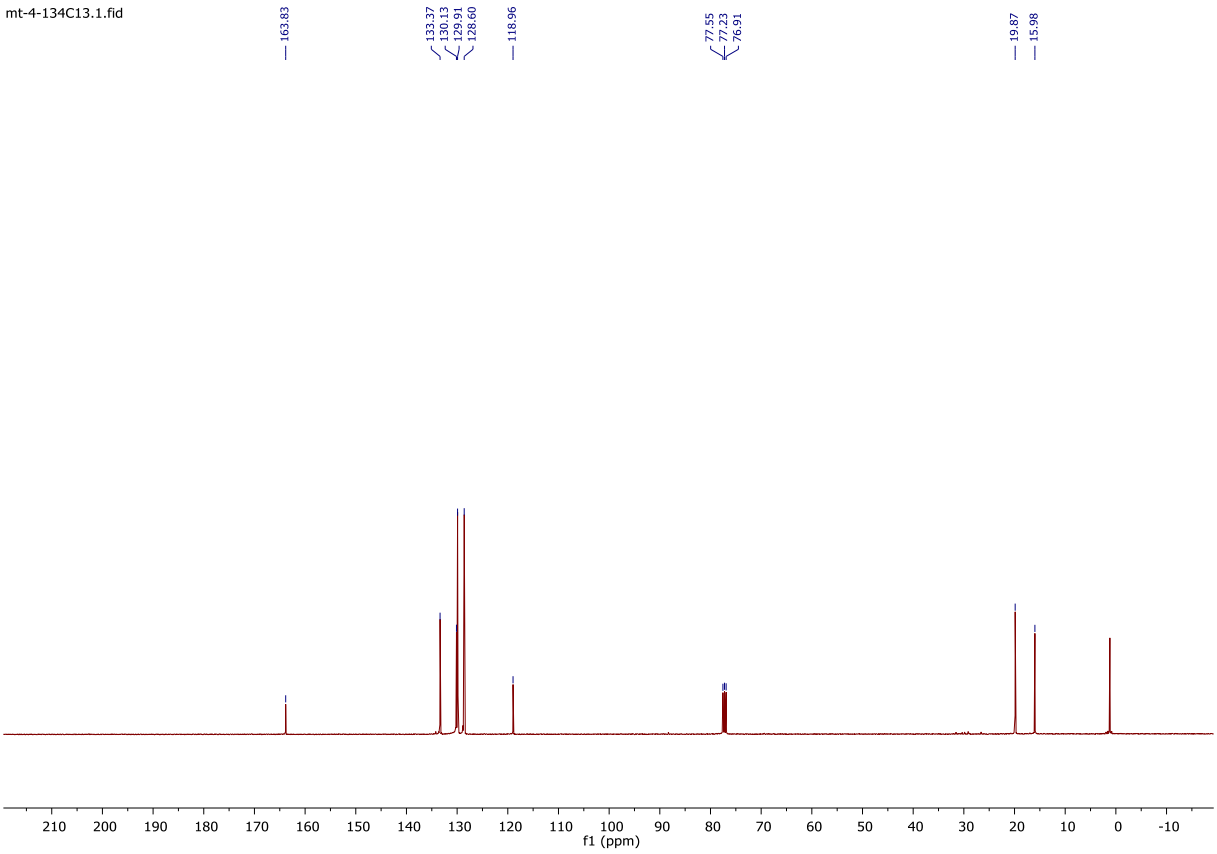

mt-4-197P.1.fid
8.19
8.17
7.26
7.01
6.99
6.92
6.86
3.88
2.37
Me
O
O
Me
MeO
2.04
2.14
1.02
1.99
3.00
6.12
f1 (ppm)

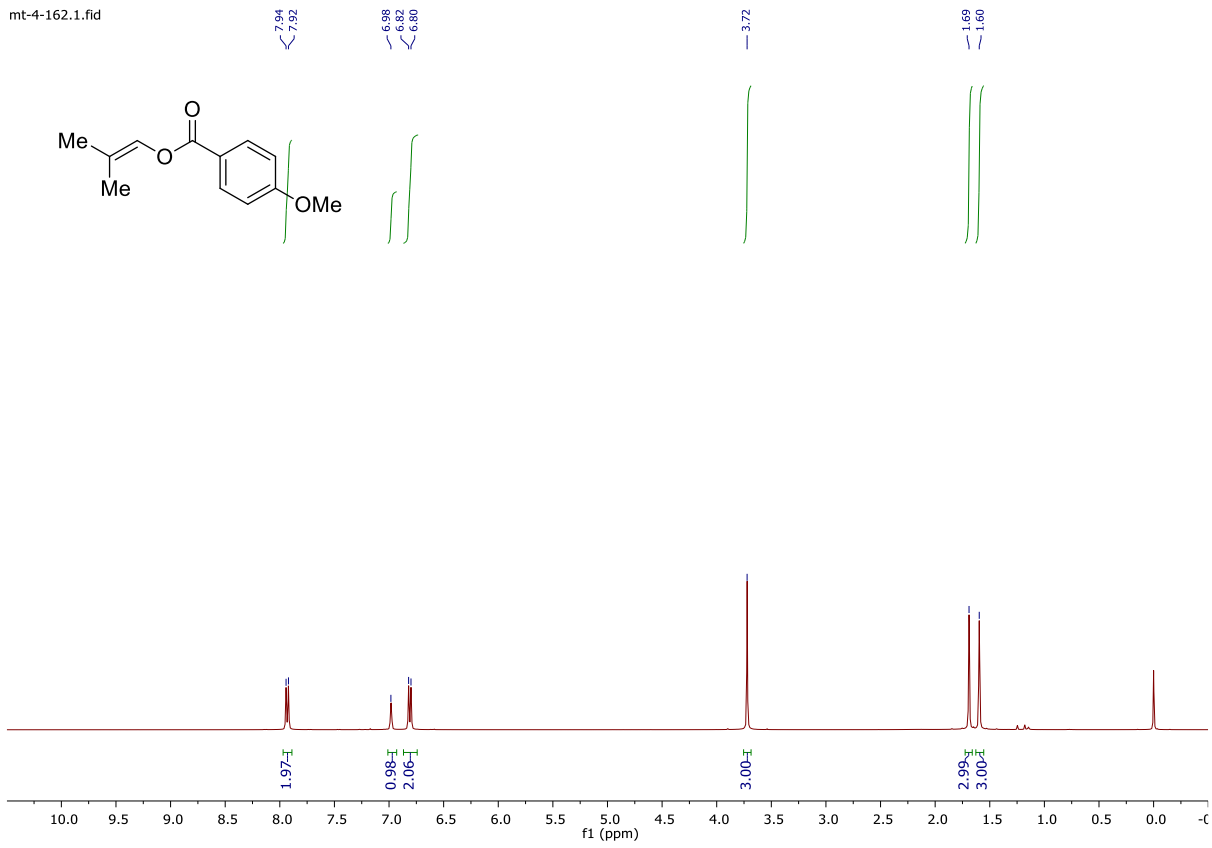

mt-4-197C.1.fid
165.18
163.90
151.07
139.31
132.29
127.54
122.09
119.47
113.88
77.55
77.23
76.91
55.51
21.32
f1 (ppm)

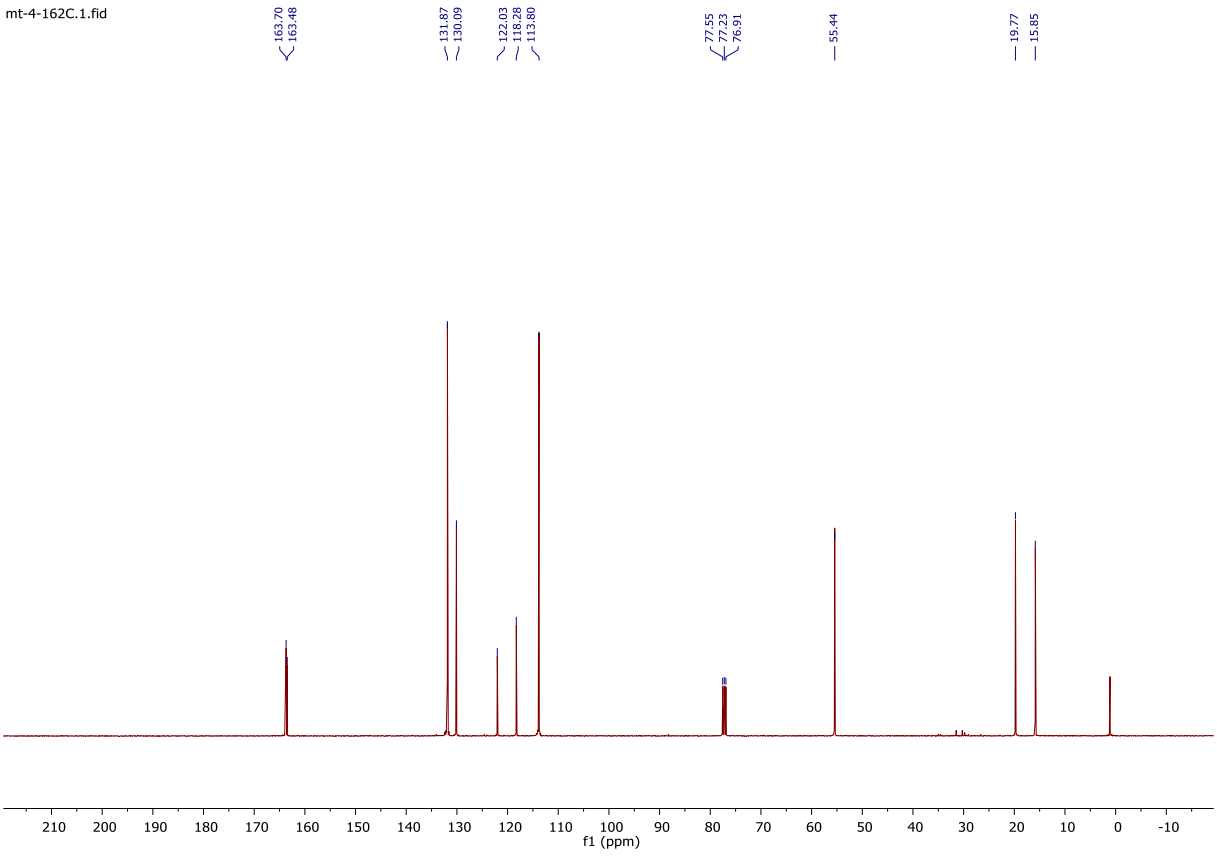
mt-4-134p1.1.fid



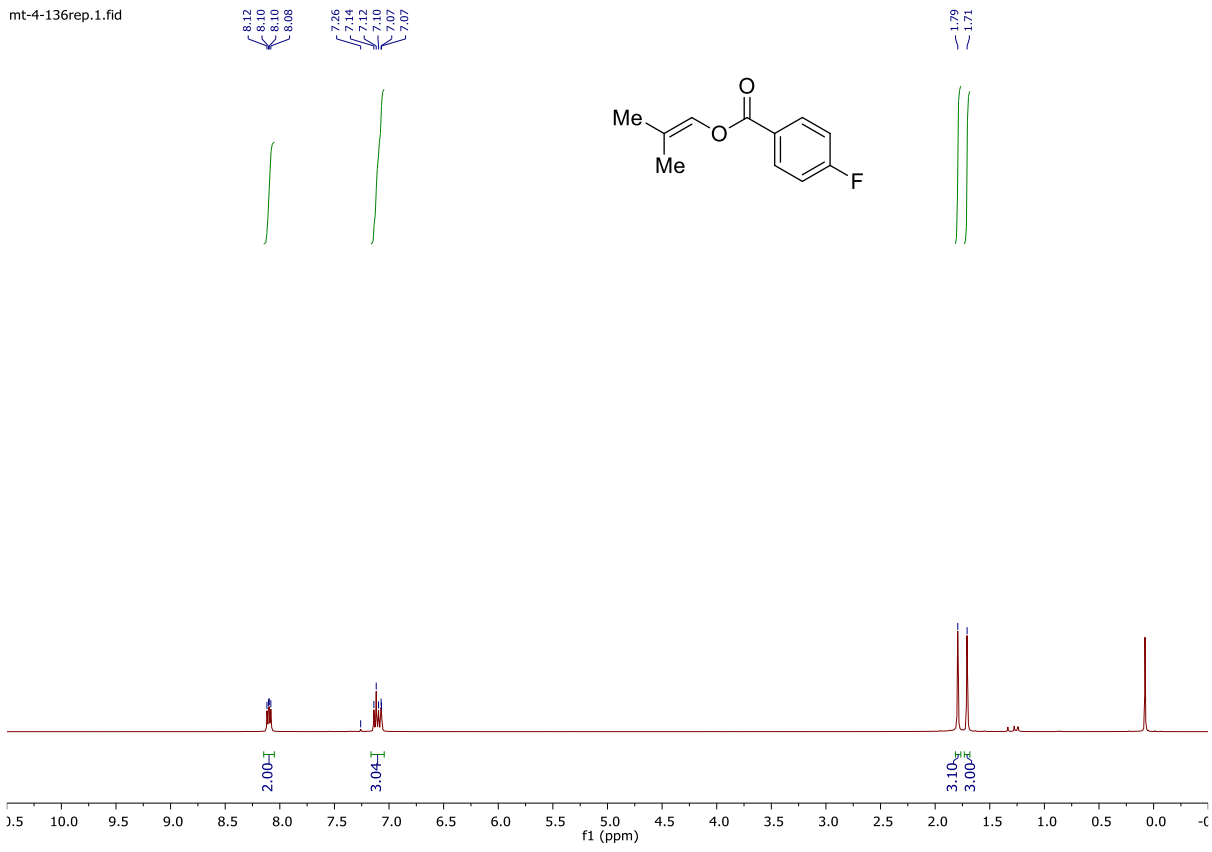
mt-4-134C13.1.fid



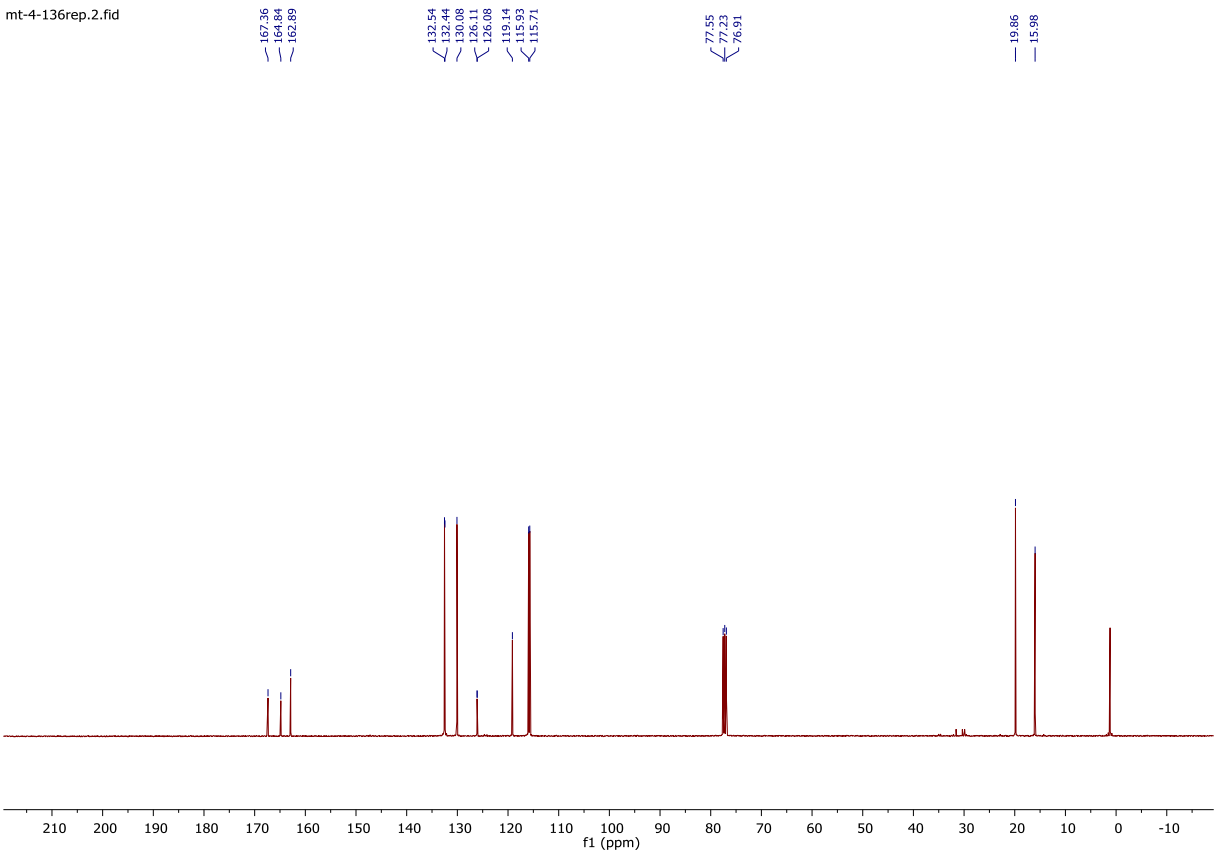

mt-4-162.1.fid
7.94
7.92
6.98
6.82
6.80
3.72
1.69
1.60
O
Me
O
Me
OMe
1.97
0.98
2.06
3.00
2.99
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


mt-4-162C.1.fid
163.70
163.48
131.87
130.09
122.03
118.28
113.80
77.55
77.23
76.91
55.44
19.77
15.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

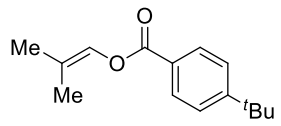
mt-4-136rep.1.fid



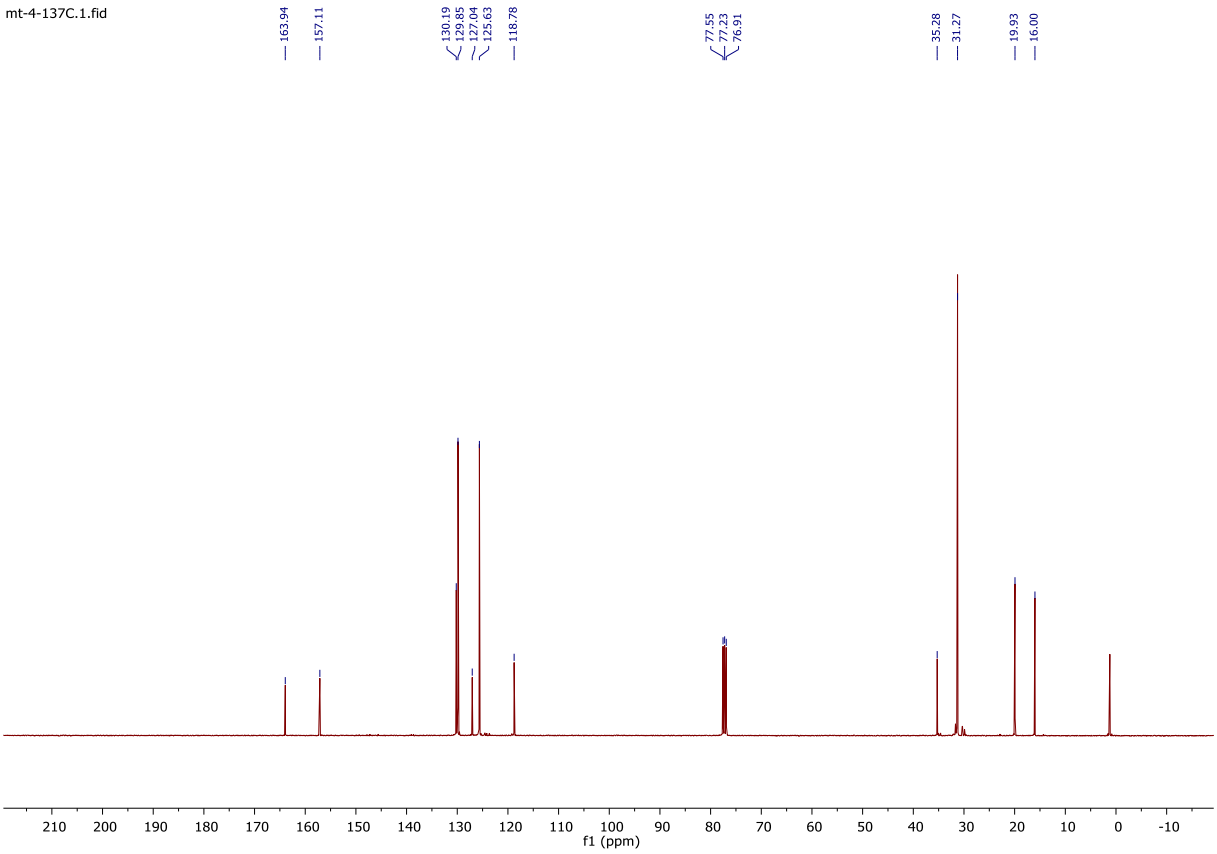
mt-4-136rep.2.fid

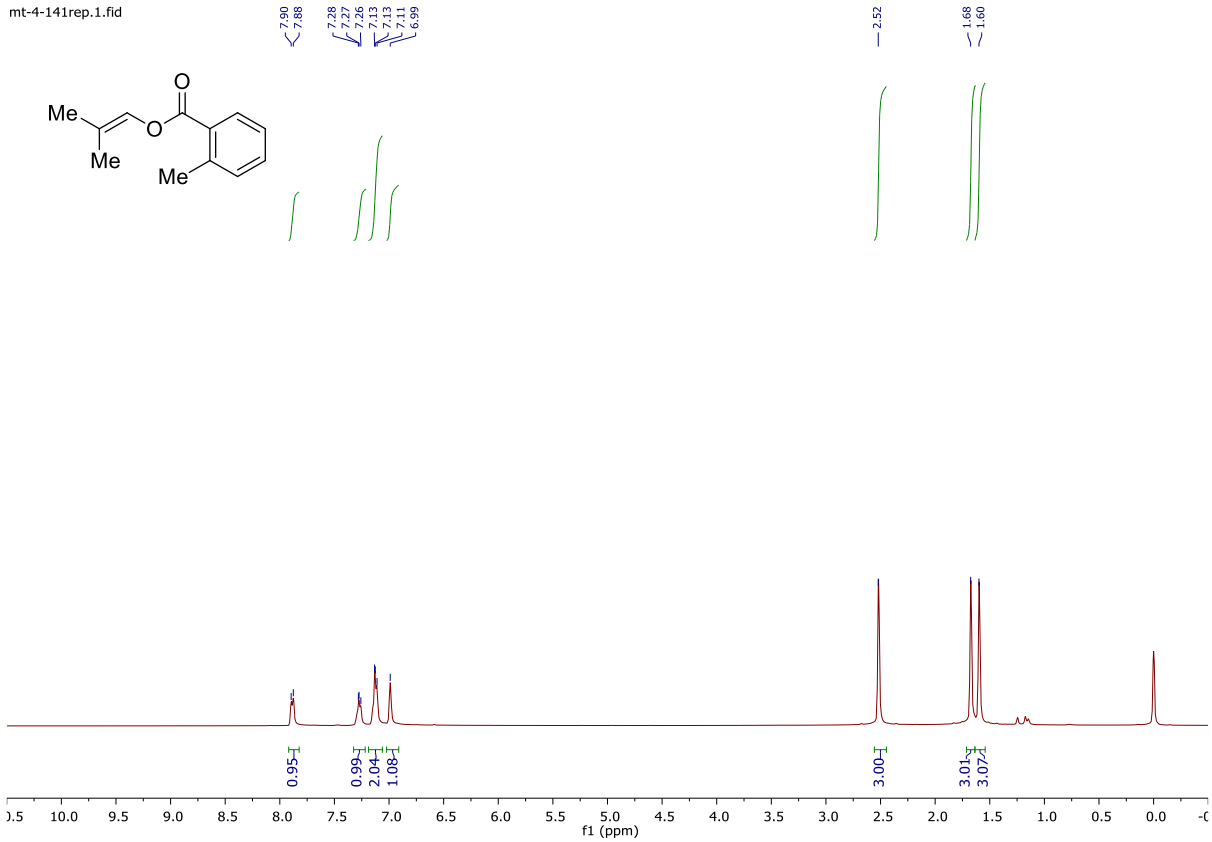


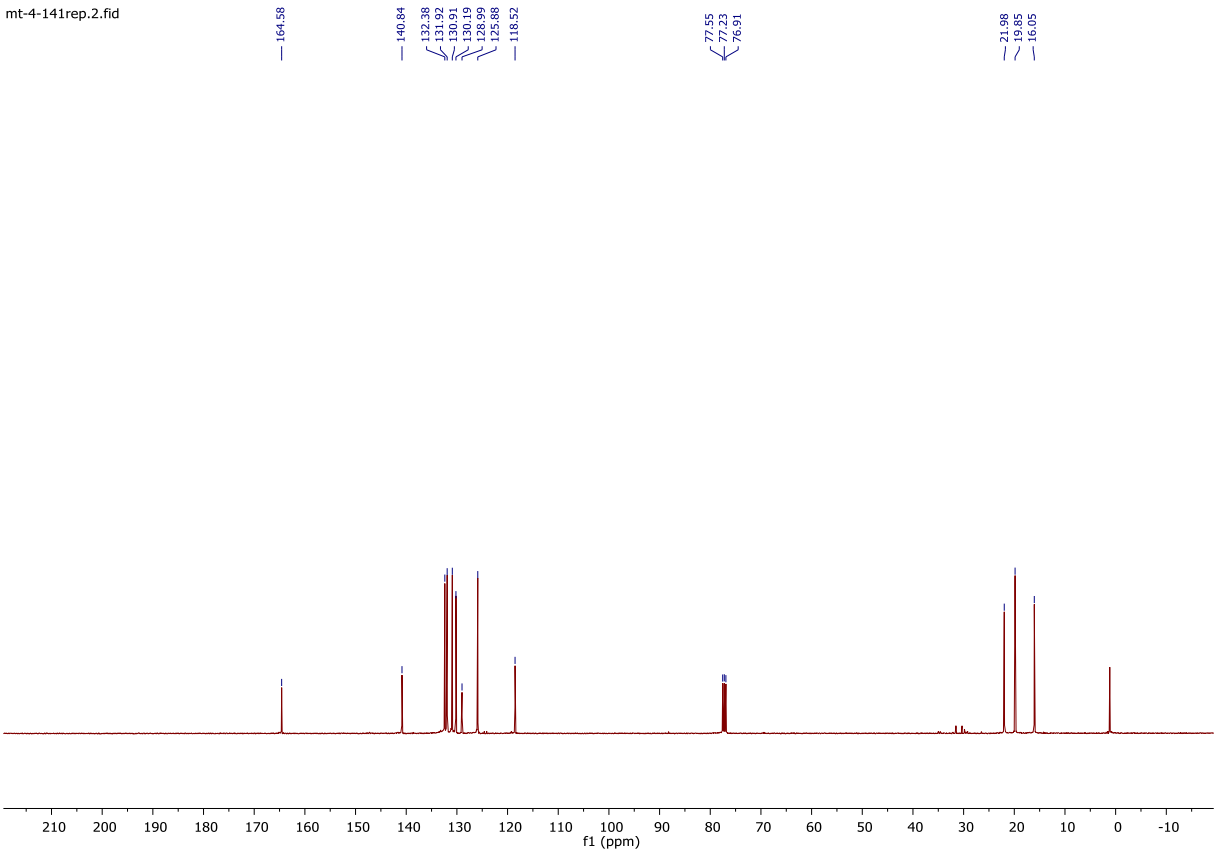
mt-4-137p.1.fid



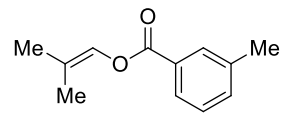
mt-4-137C.1.fid



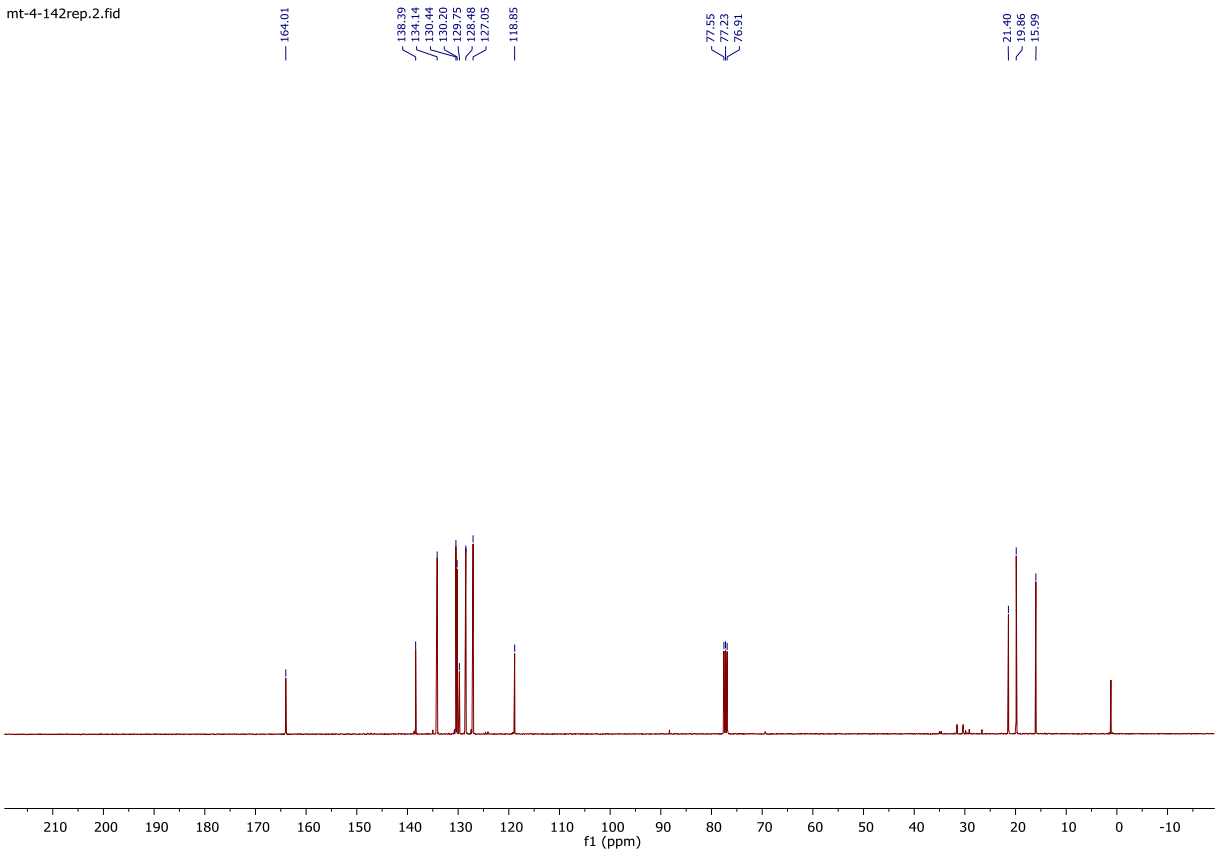

mt-4-141rep.1.fid
7.90
7.88
7.28
7.27
7.26
7.13
7.13
7.11
6.99
2.52
1.68
1.60
Me
O
O
Me
Me
0.95
0.99
2.04
1.08
3.00
3.01
3.07
f1 (ppm)

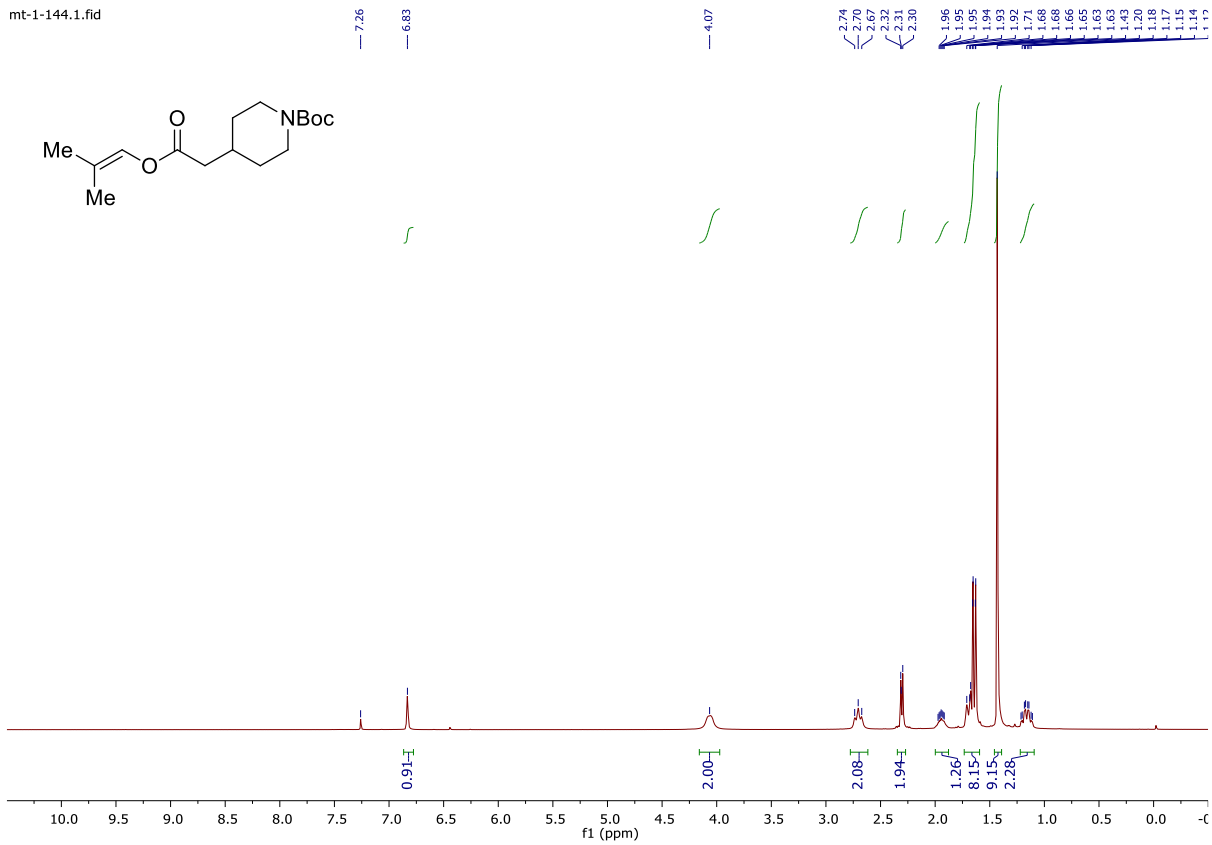

mt-4-141rep.2.fid
164.58
140.84
132.38
131.92
130.91
130.19
128.99
125.88
118.52
77.55
77.23
76.91
21.98
19.85
16.05
f1 (ppm)

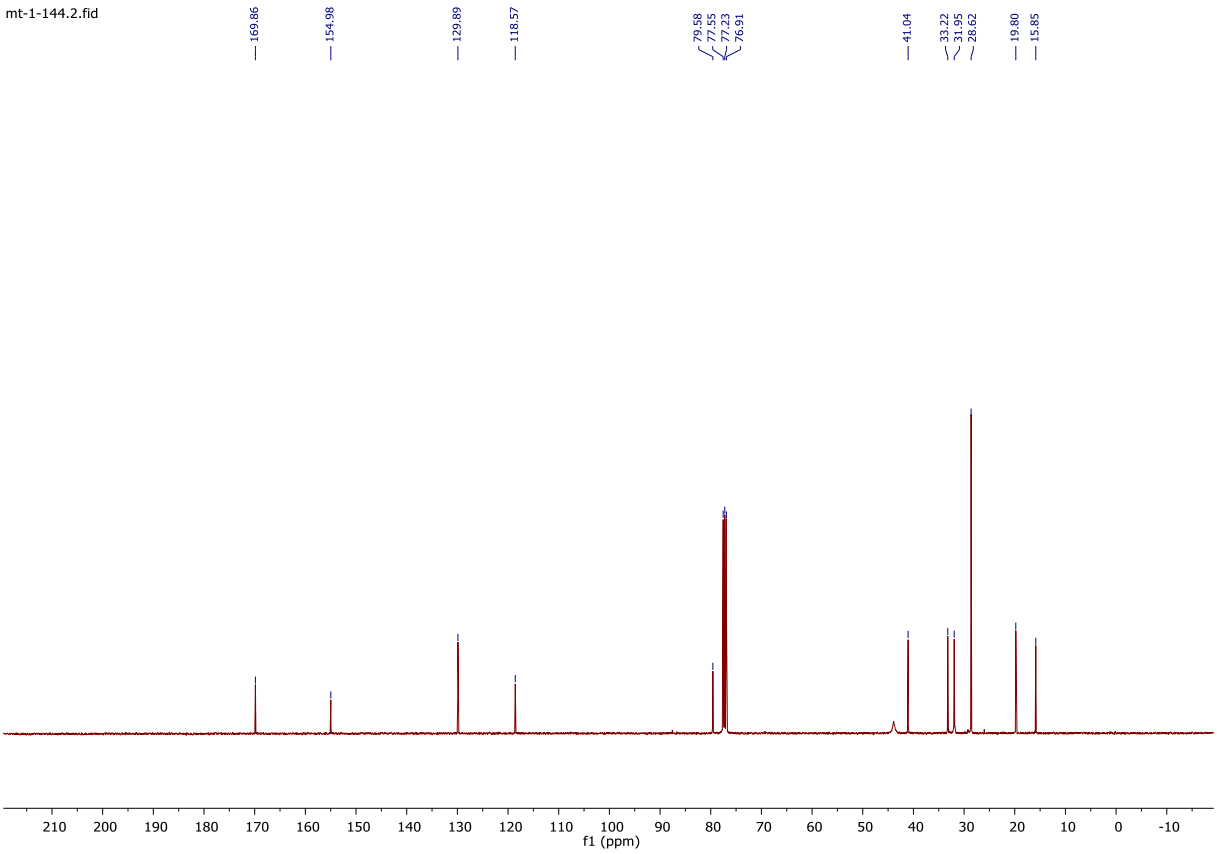
mt-4-142rep.1.fid



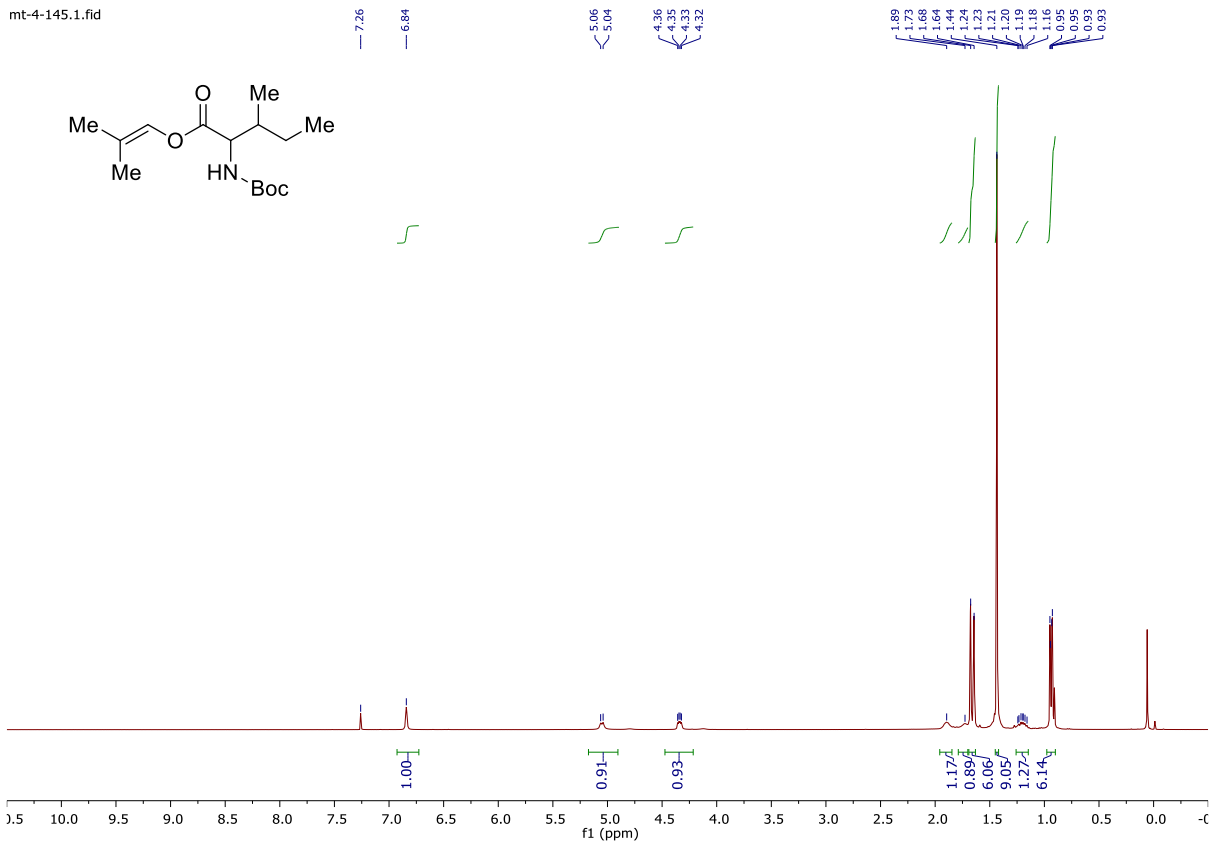
mt-4-142rep.2.fid



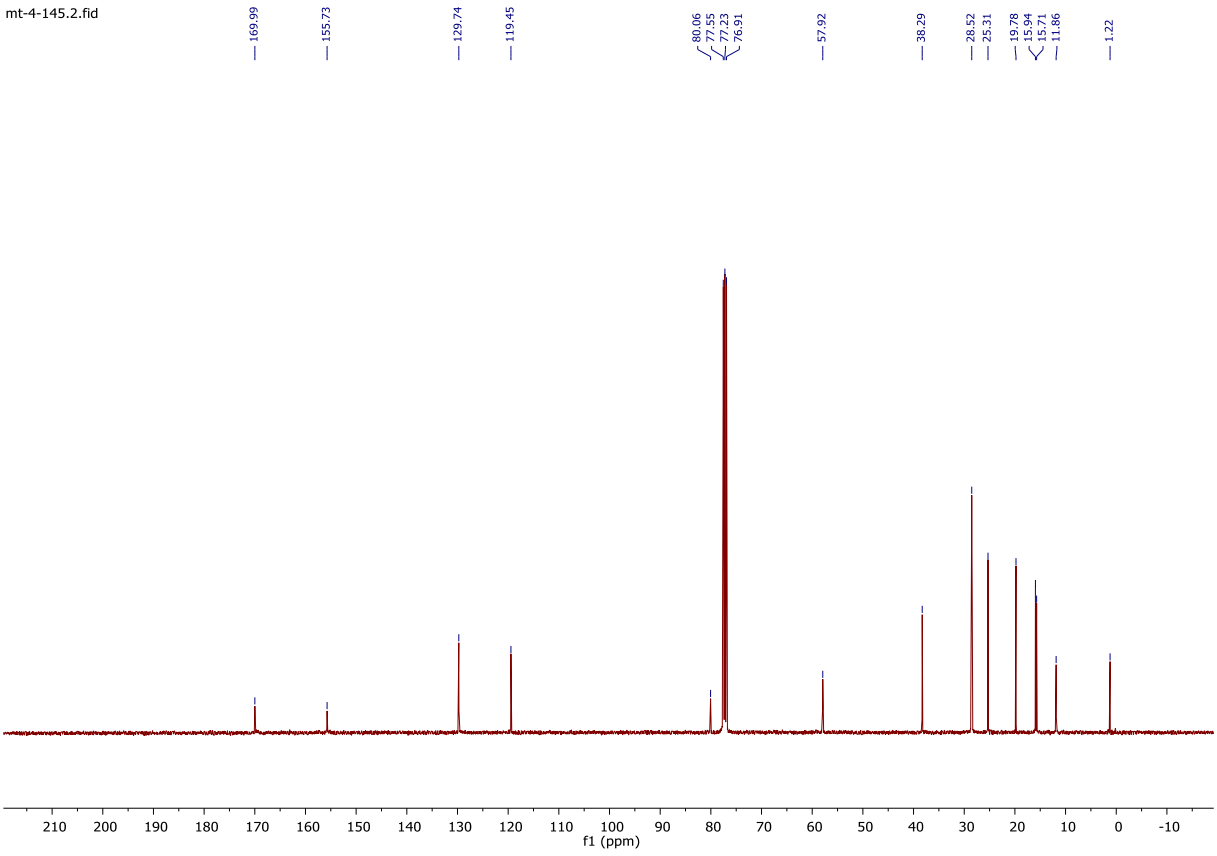

mt-1-144.1.fid
7.26
6.83
4.07
2.74
2.70
2.67
2.32
2.31
2.30
1.96
1.95
1.95
1.94
1.93
1.92
1.71
1.68
1.68
1.66
1.65
1.63
1.63
1.43
1.20
1.18
1.17
1.15
1.14
O
NBoc
Me
O
Me
0.91
2.00
2.08
1.94
1.26
8.15
9.15
2.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


mt-1-144.2.fid
169.86
154.98
129.89
118.57
79.58
77.55
77.23
76.91
41.04
33.22
31.95
28.62
19.80
15.85
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

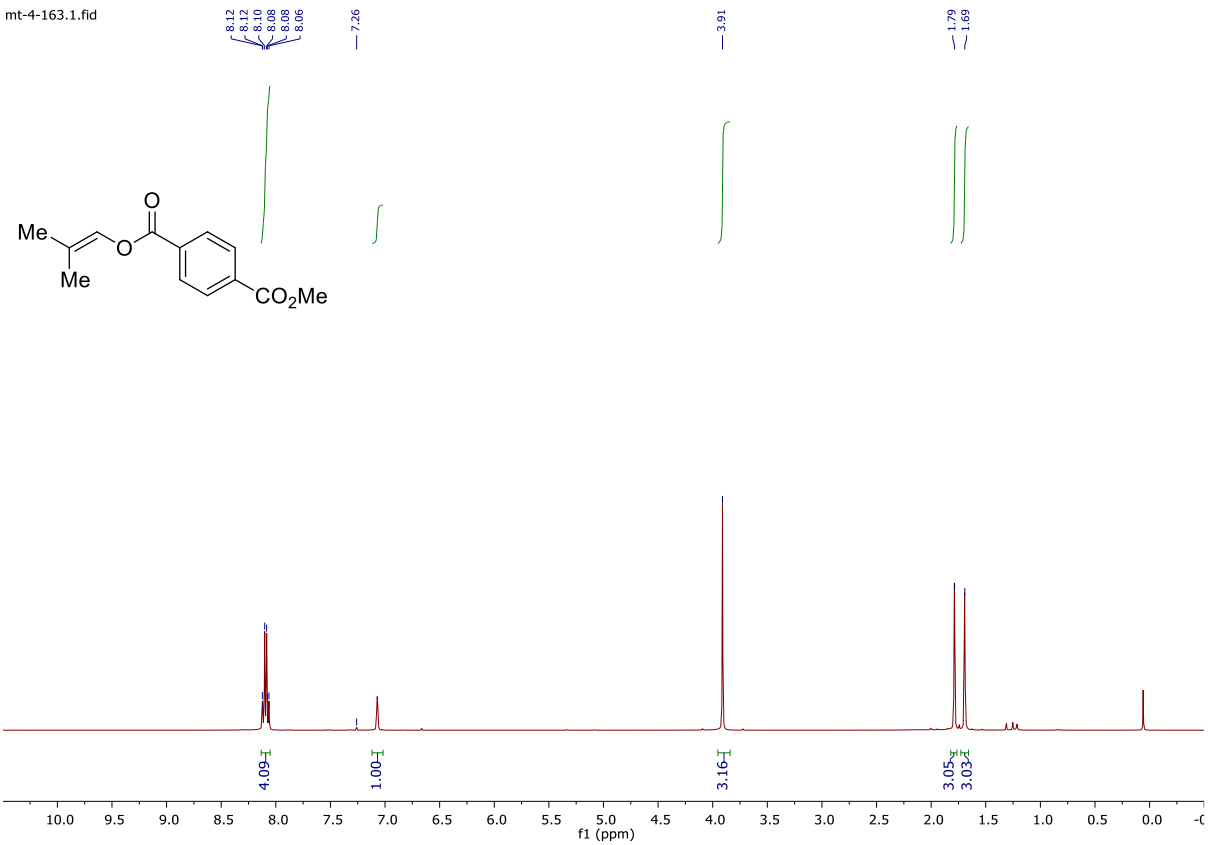
mt-4-145.1.fid



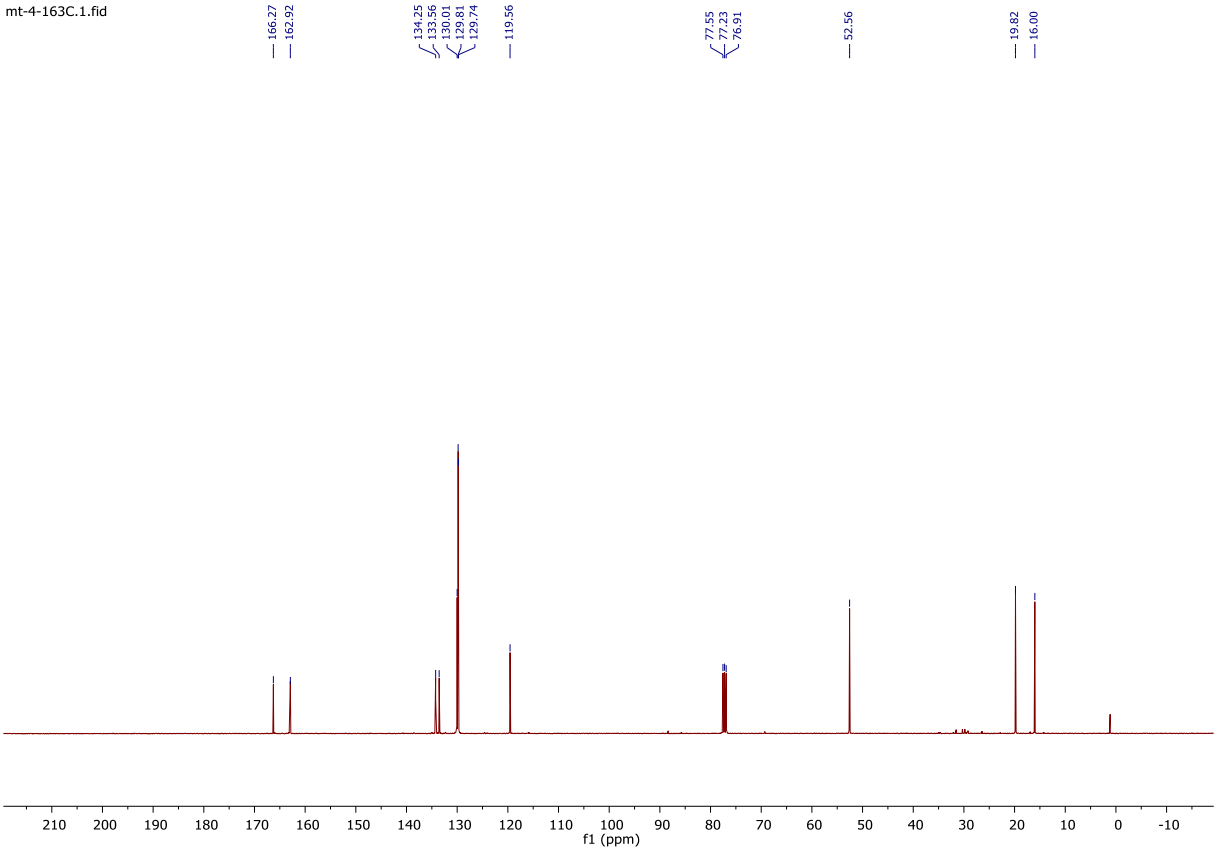
mt-4-145.2.fid

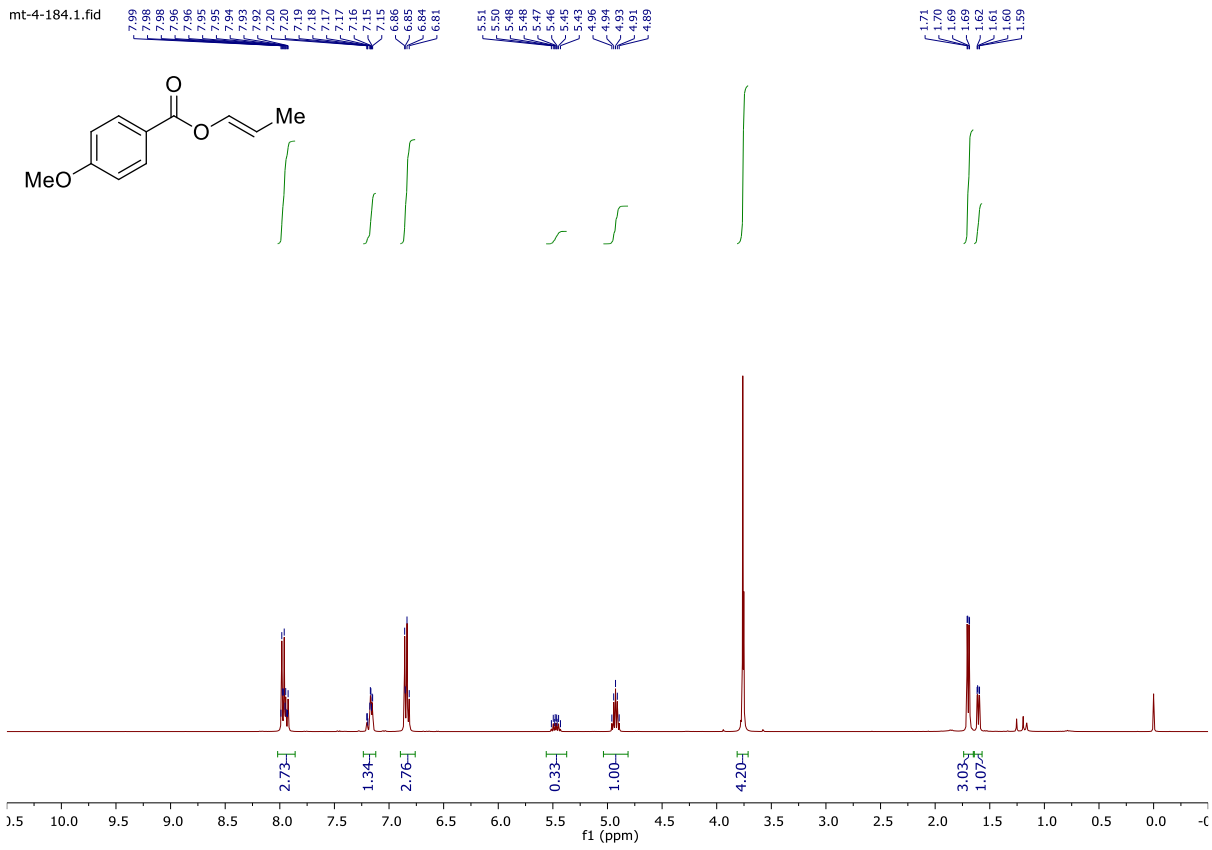


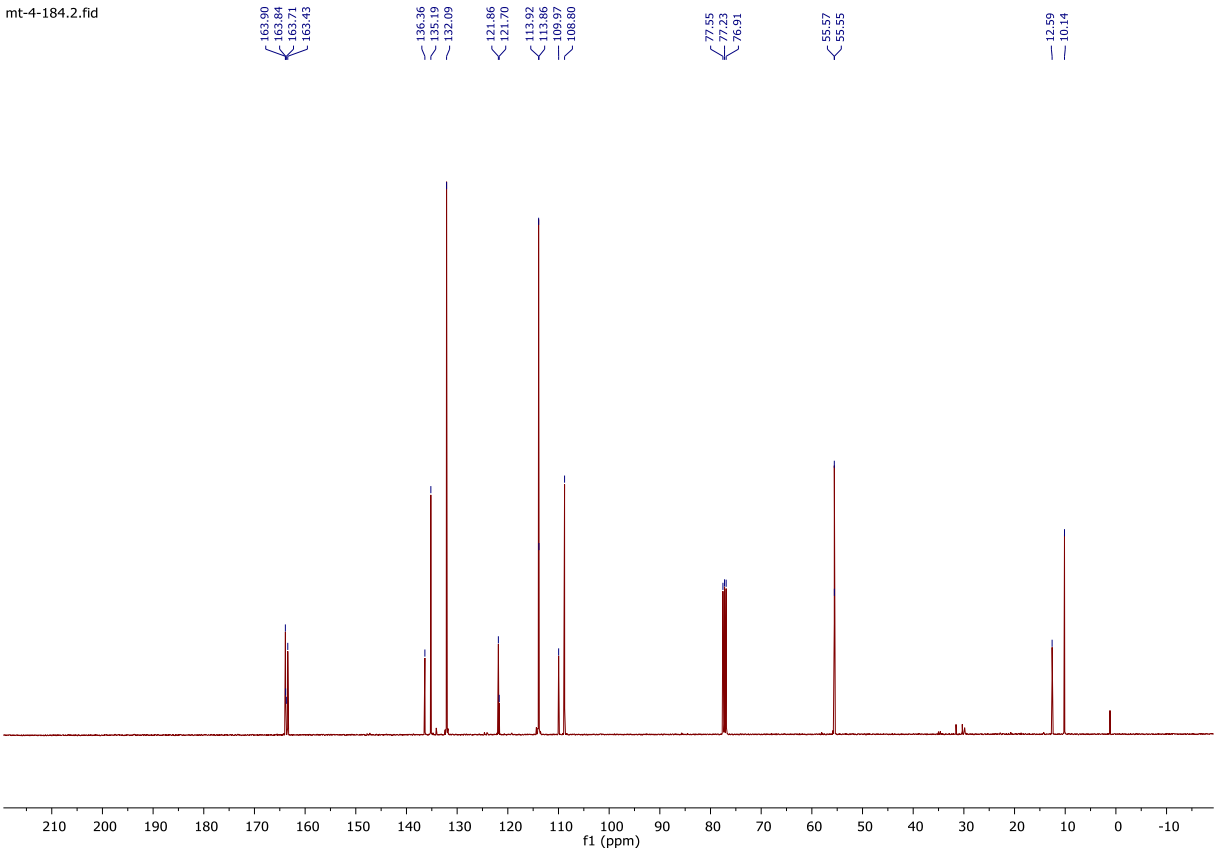
mt-4-163.1.fid



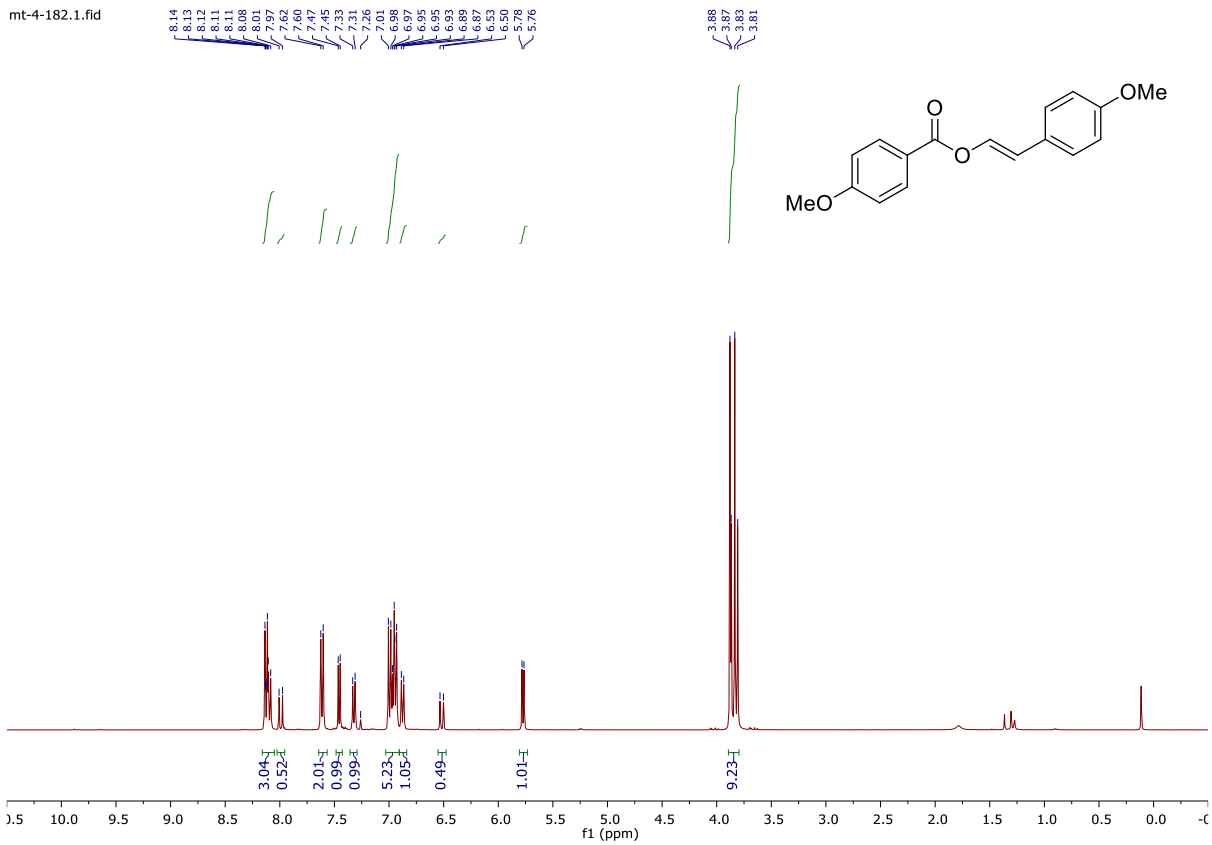
mt-4-163C.1.fid



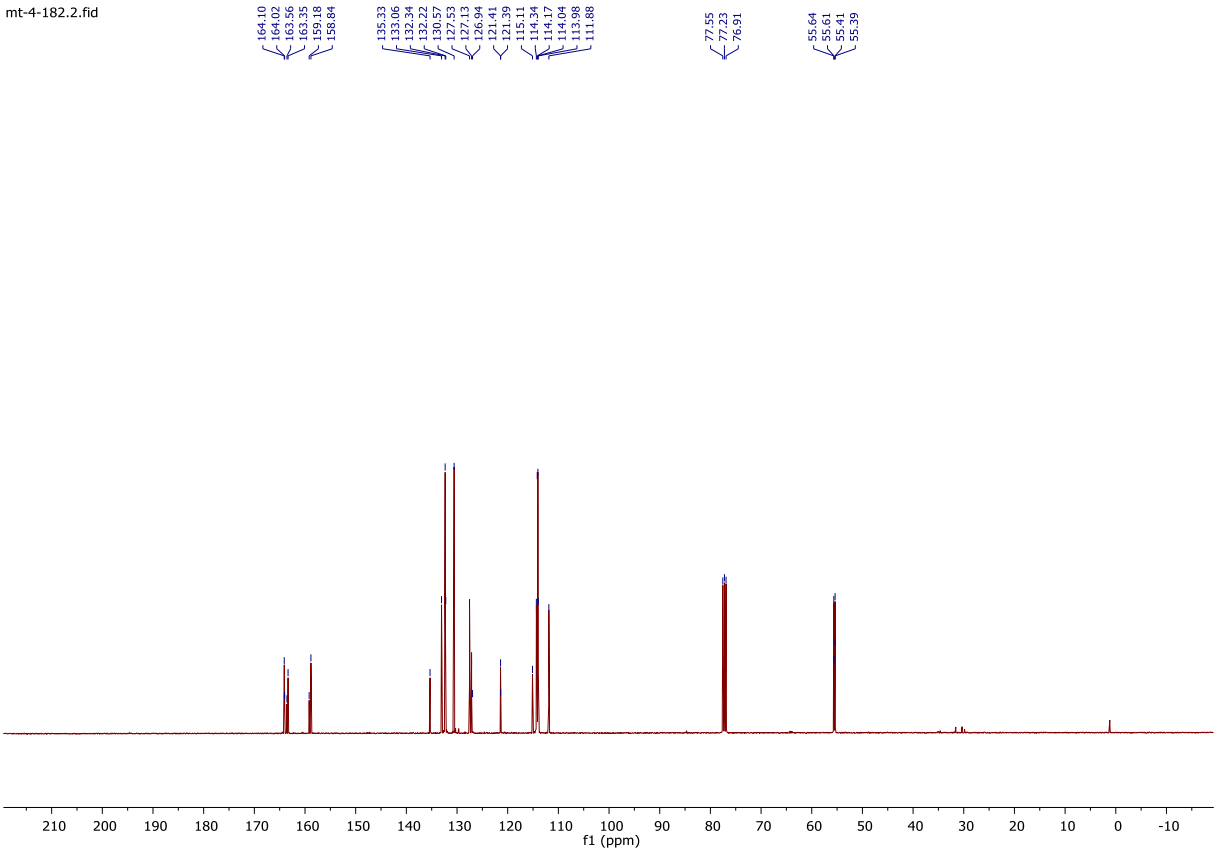

mt-4-184.1.fid
7.99
7.98
7.98
7.96
7.96
7.95
7.95
7.94
7.93
7.92
7.20
7.19
7.18
7.17
7.17
7.16
7.15
7.15
6.86
6.85
6.84
6.81
5.51
5.50
5.48
5.48
5.47
5.46
5.45
5.43
4.96
4.94
4.93
4.91
4.89
1.71
1.70
1.69
1.69
1.62
1.61
1.60
1.59
O
O
Me
MeO
2.73
1.34
2.76
0.33
1.00
4.20
3.03
1.07
f1 (ppm)

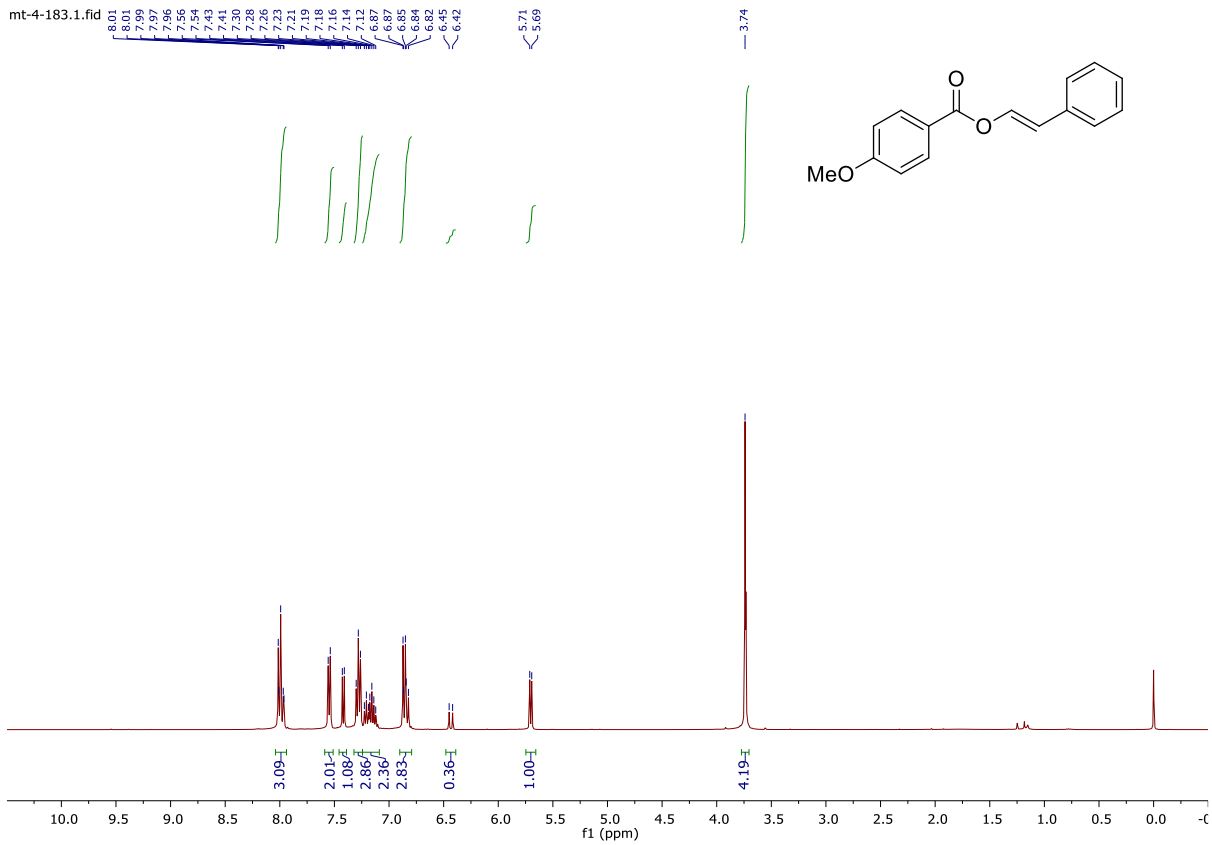

mt-4-184.2.fid
163.90
163.84
163.71
163.43
136.36
135.19
132.09
121.86
121.70
113.92
113.86
109.97
108.80
77.55
77.23
76.91
55.57
55.55
12.59
10.14
f1 (ppm)

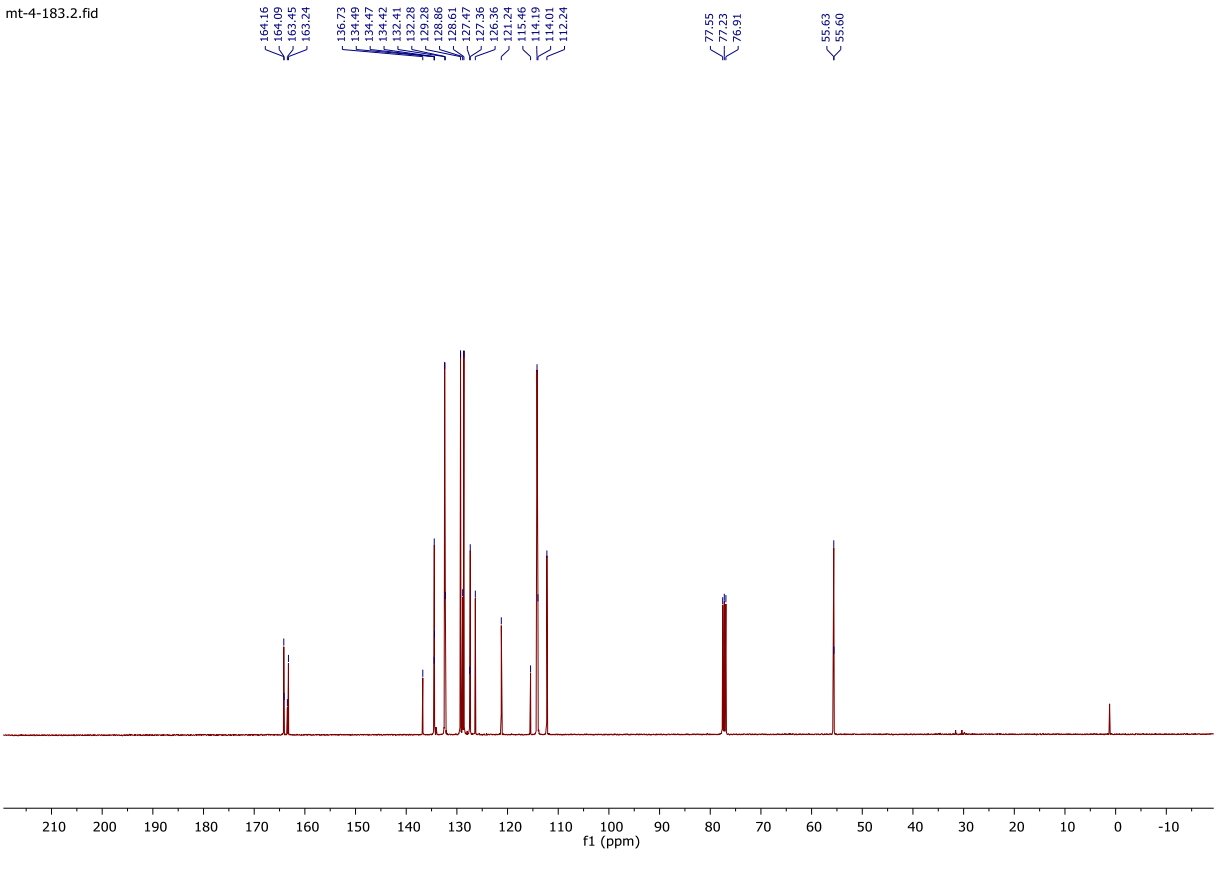
mt-4-182.1.fid

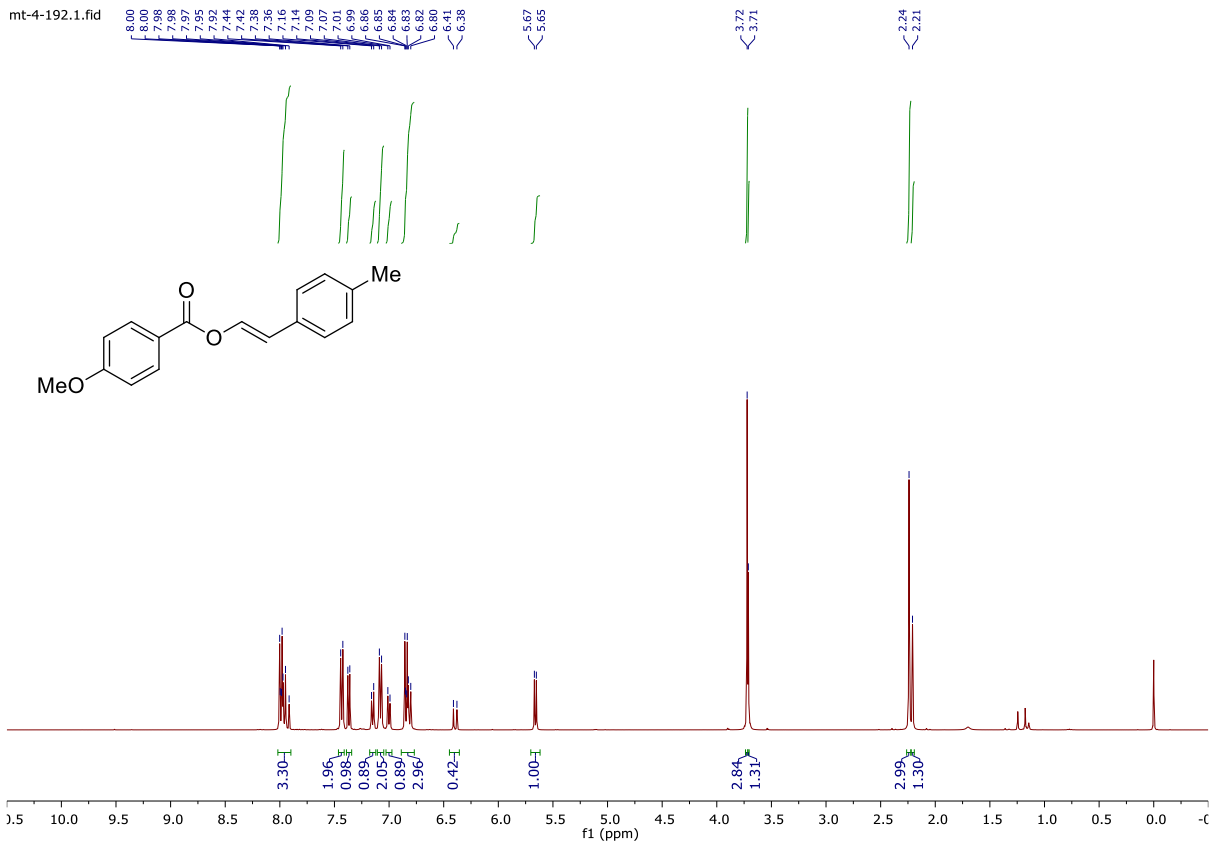


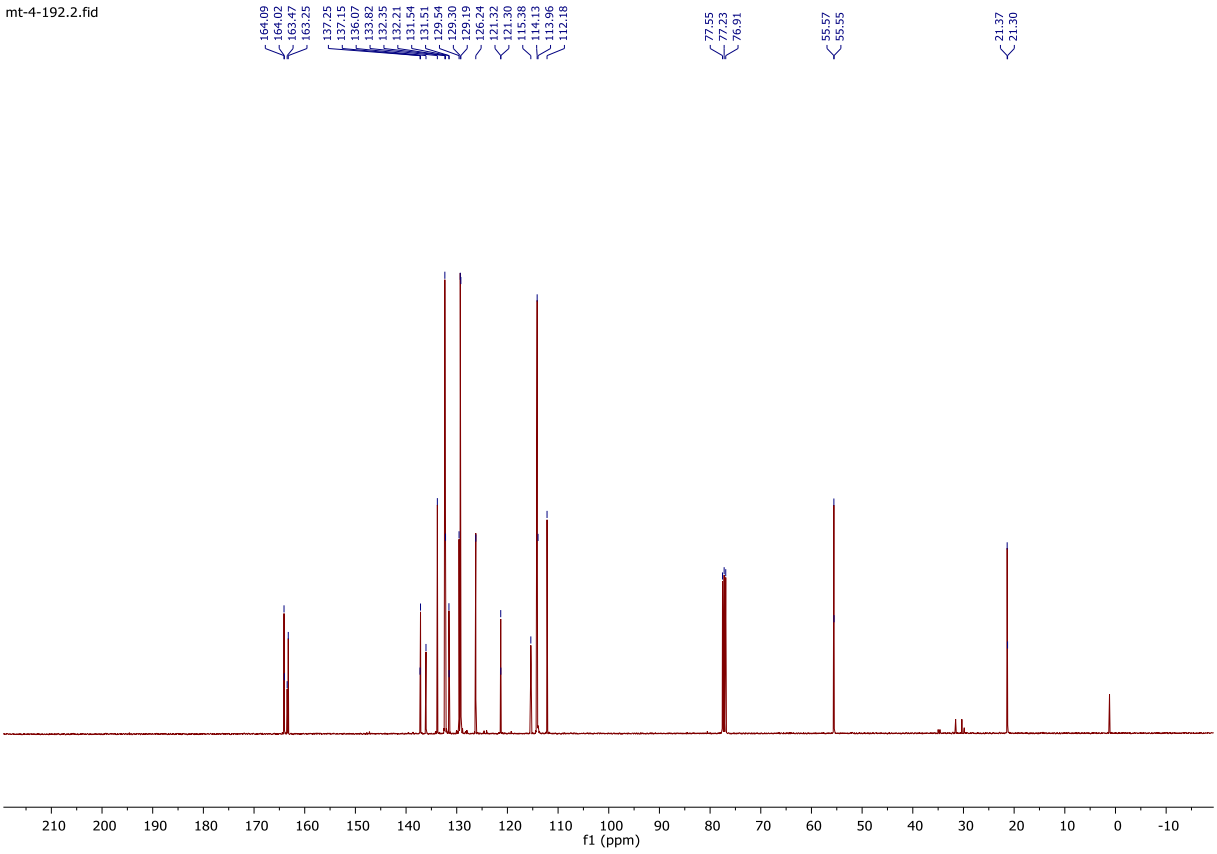
mt-4-182.2.fid

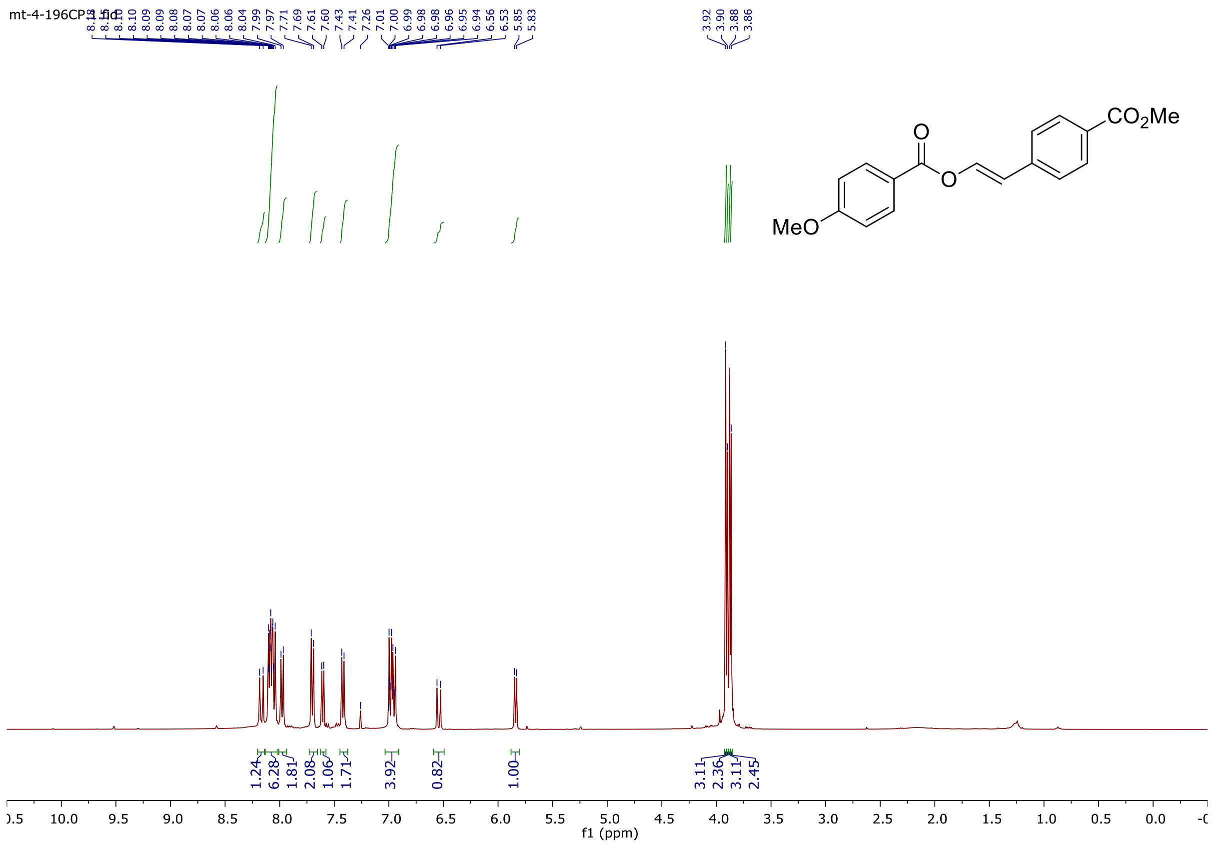


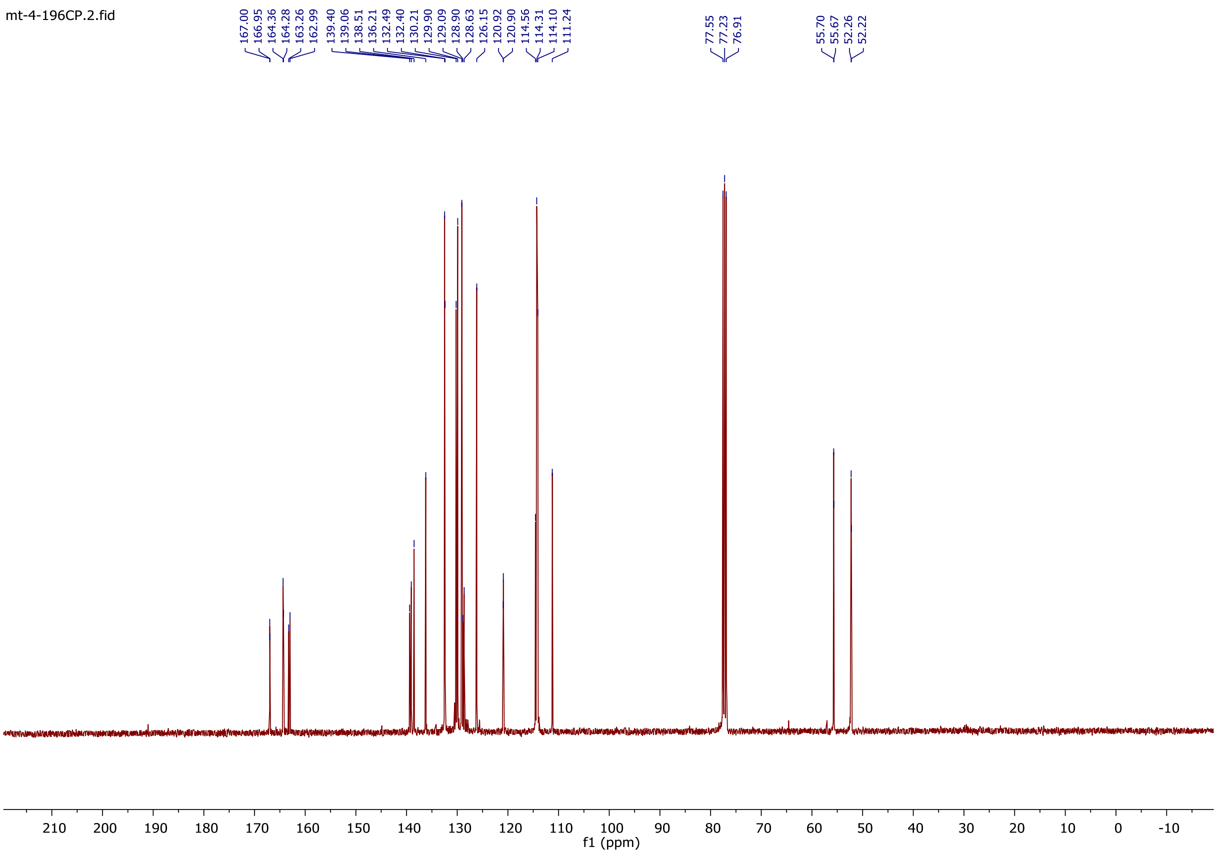

mt-4-183.1.fid
8.01
8.01
7.99
7.97
7.96
7.56
7.54
7.43
7.41
7.30
7.28
7.26
7.23
7.21
7.19
7.18
7.16
7.14
7.12
6.87
6.87
6.85
6.84
6.82
6.45
6.42
5.71
5.69
3.74
O
O
MeO
3.09
2.01
1.08
2.86
2.36
2.83
0.36
1.00
4.19
f1 (ppm)

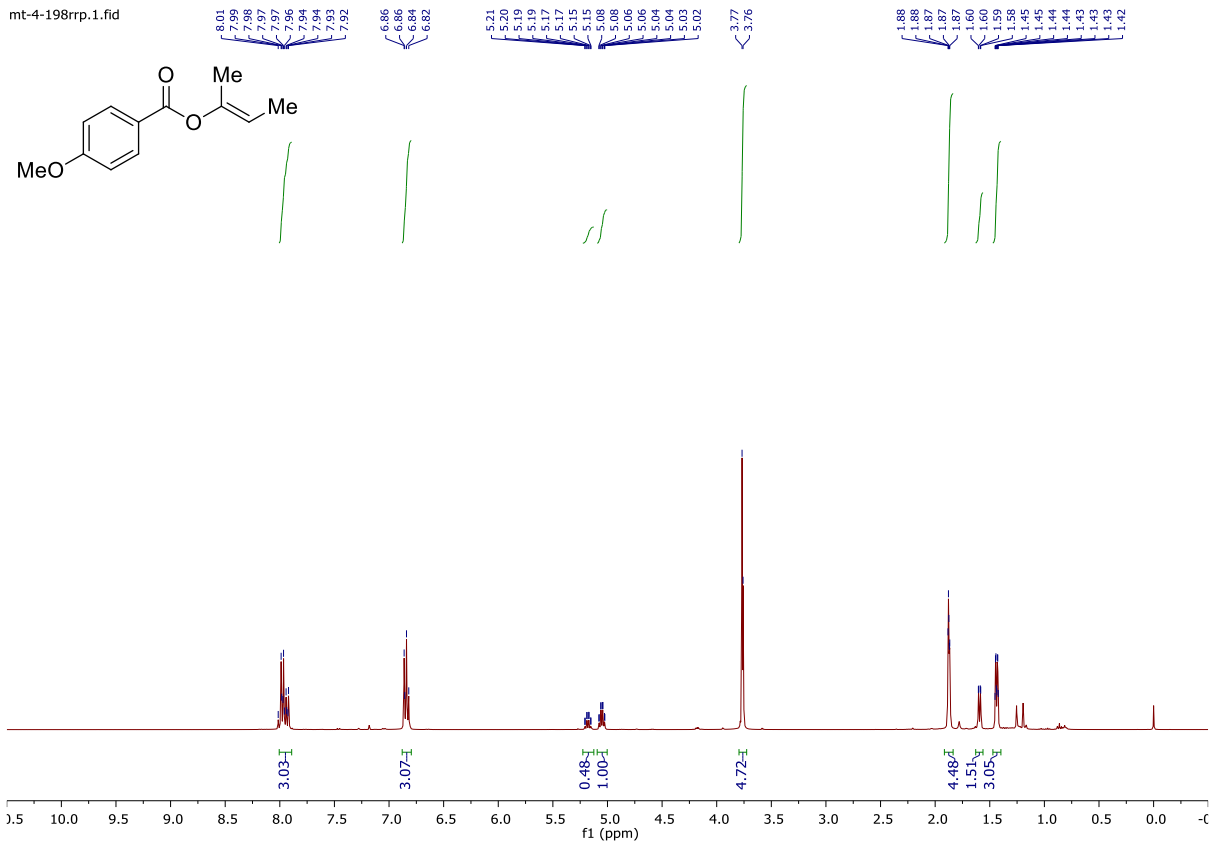

mt-4-183.2.fid
164.16
164.09
163.45
163.24
136.73
134.49
134.47
134.42
132.41
132.28
129.28
128.86
128.61
127.47
127.36
126.36
121.24
115.46
114.19
114.01
112.24
77.55
77.23
76.91
55.63
55.60
f1 (ppm)

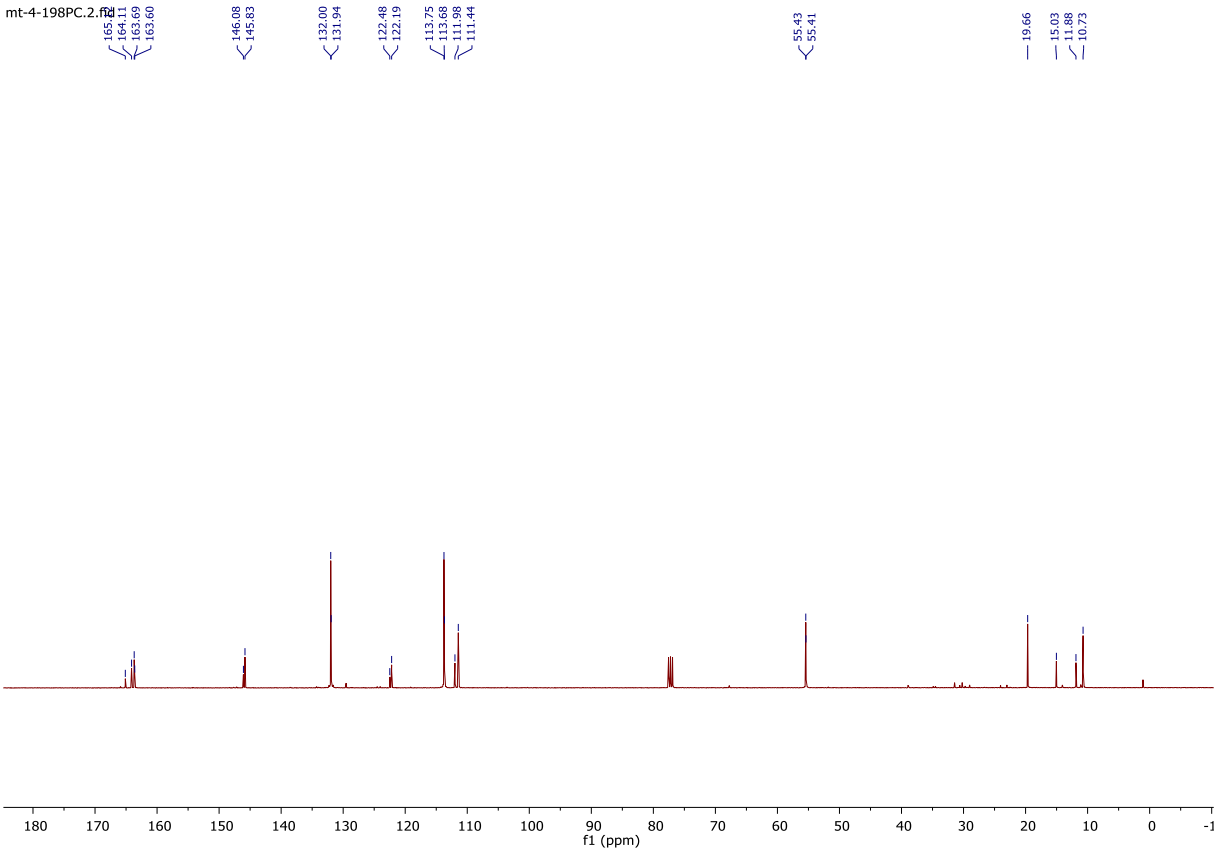

mt-4-192.1.fid
8.00
8.00
7.98
7.98
7.97
7.95
7.92
7.44
7.42
7.38
7.36
7.16
7.14
7.09
7.07
7.01
6.99
6.86
6.85
6.84
6.83
6.82
6.80
6.41
6.38
5.67
5.65
3.72
3.71
2.24
2.21
Me
O
O
MeO
3.30
1.96
0.98
0.89
2.05
0.89
2.96
0.42
1.00
2.84
1.31
2.99
1.30
f1 (ppm)

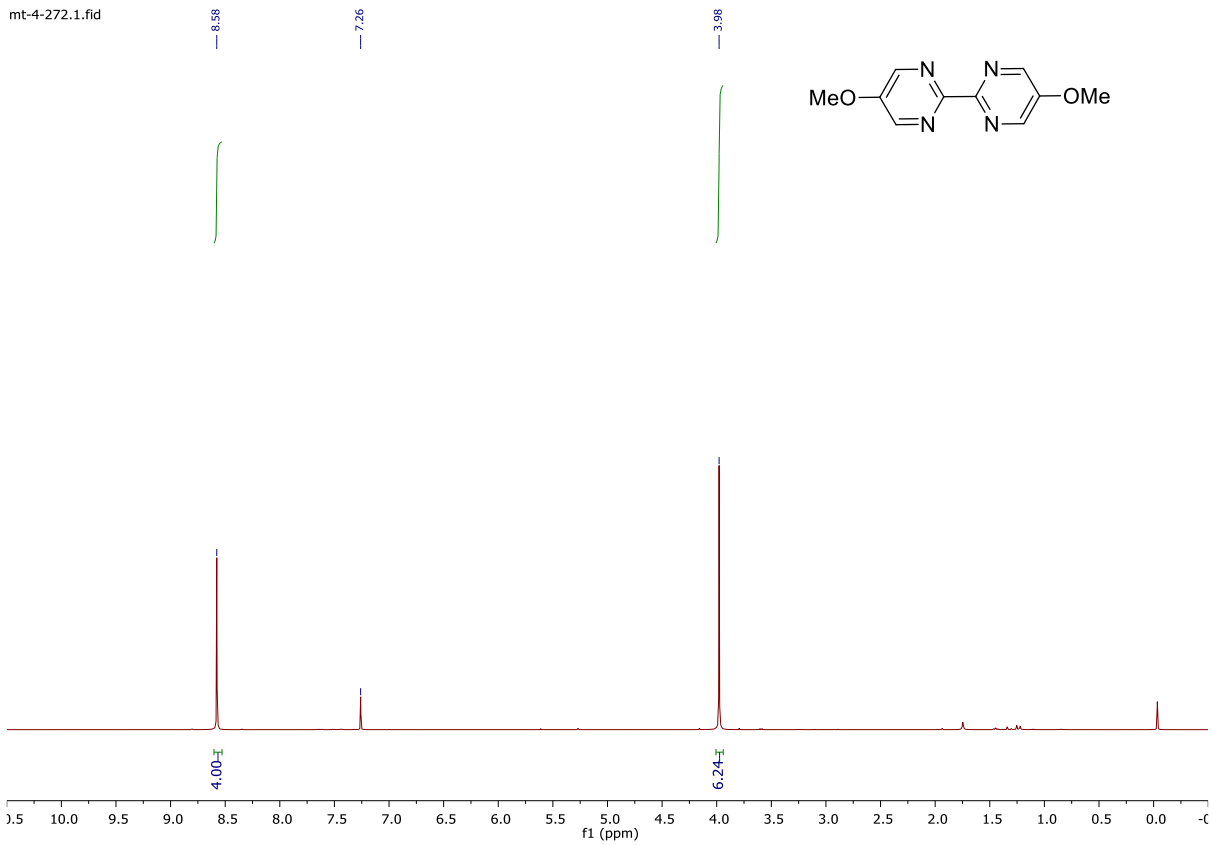

mt-4-192.2.fid
164.09
164.02
163.47
163.25
137.25
137.15
136.07
133.82
132.35
132.21
131.54
131.51
129.54
129.30
129.19
126.24
121.32
121.30
115.38
114.13
113.96
112.18
77.55
77.23
76.91
55.57
55.55
21.37
21.30
f1 (ppm)

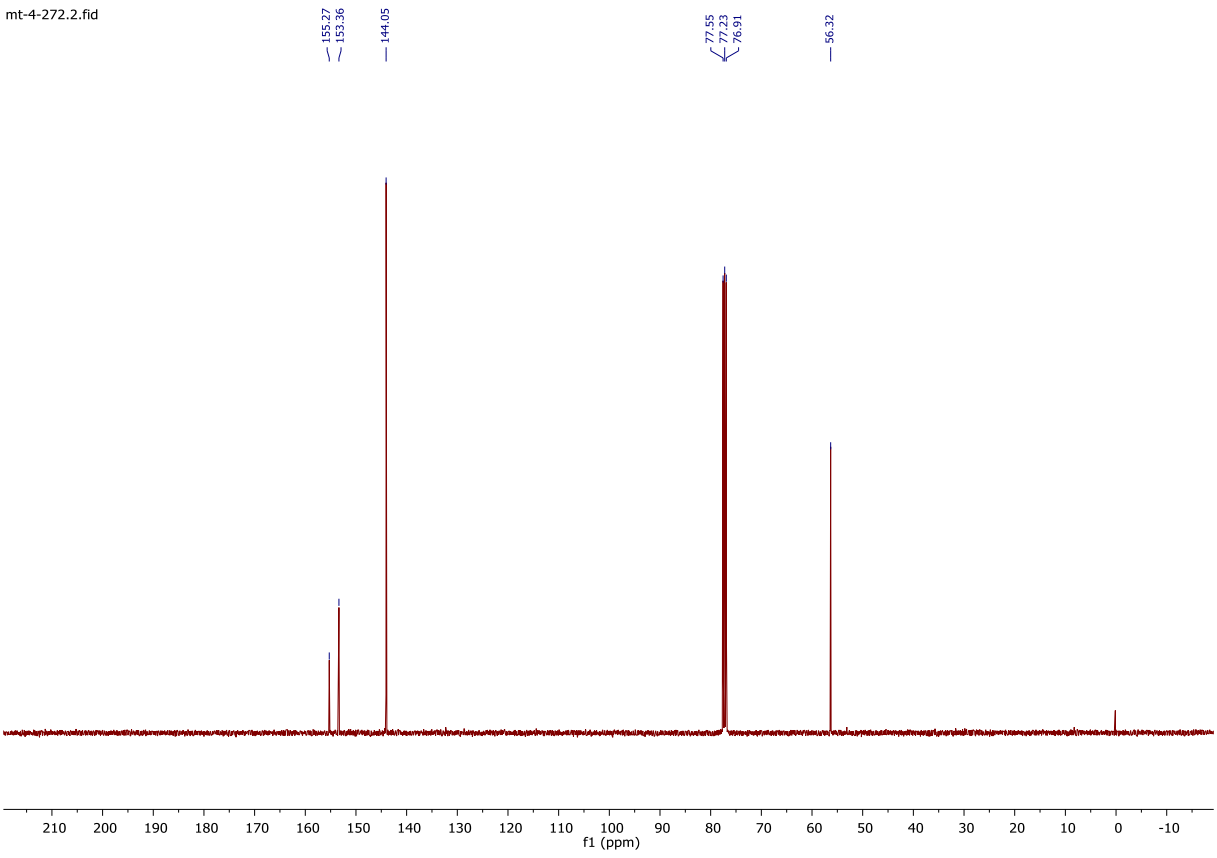

mt-4-196CP.1.fid
8.12 8.12 8.10 8.09 8.09 8.08 8.07 8.07 8.06 8.06 8.04 7.99 7.97 7.71 7.69 7.61 7.60 7.43 7.41 7.26 7.01 7.00 6.99 6.98 6.98 6.96 6.95 6.95 6.94 6.56 6.53 5.85 5.83
3.92 3.90 3.88 3.86
O
O
CO$_2$Me
MeO
1.24 6.28 1.81 2.08 1.06 1.71 3.92 0.82 1.00 3.11 2.36 3.11 2.45
f1 (ppm)


mt-4-196CP.2.fid
167.00 166.95 164.36 164.28 163.26 162.99 139.40 139.06 138.51 136.21 132.49 132.40 130.21 129.90 129.09 128.90 128.63 126.15 120.92 120.90 114.56 114.31 114.10 111.24
77.55 77.23 76.91
55.70 55.67 52.26 52.22
f1 (ppm)

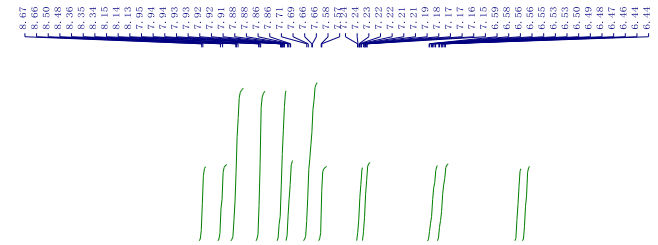

mt-4-198rrp.1.fid
8.01 7.99 7.98 7.97 7.97 7.96 7.94 7.94 7.93 7.92
6.86 6.86 6.84 6.82
5.21 5.20 5.19 5.19 5.17 5.17 5.15 5.15 5.08 5.08 5.06 5.06 5.04 5.04 5.03 5.02
3.77 3.76
1.88 1.88 1.87 1.87 1.87 1.60 1.60 1.59 1.58 1.45 1.45 1.44 1.44 1.43 1.43 1.43 1.42
O
Me
Me
O
MeO
3.03 3.07 0.48 1.00 4.72 4.48 1.51 3.05
f1 (ppm)

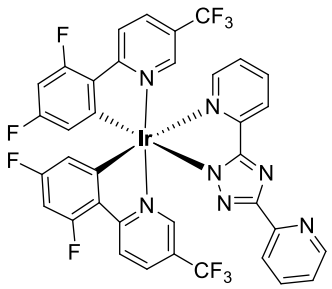

mt-4-198PC.2.fid
165.42 164.11 163.69 163.60
146.08 145.83
132.00 131.94
122.48 122.19
113.75 113.68 111.98 111.44
55.43 55.41
19.66
15.03 11.88 10.73
f1 (ppm)

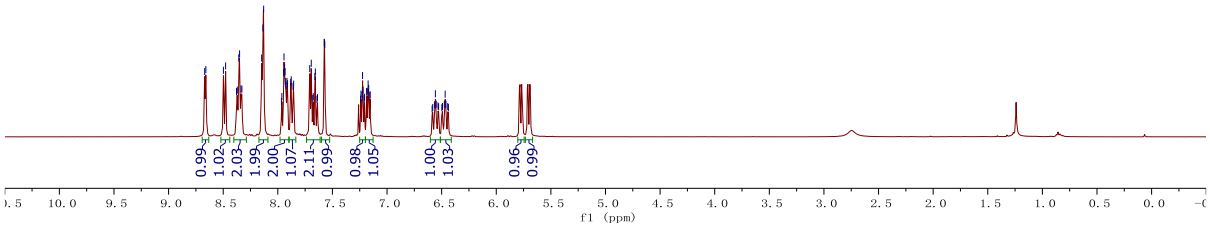

mt-4-272.1.fid
8.58
7.26
3.98
MeO
OMe
N
N
N
N
4.00
6.24
f1 (ppm)

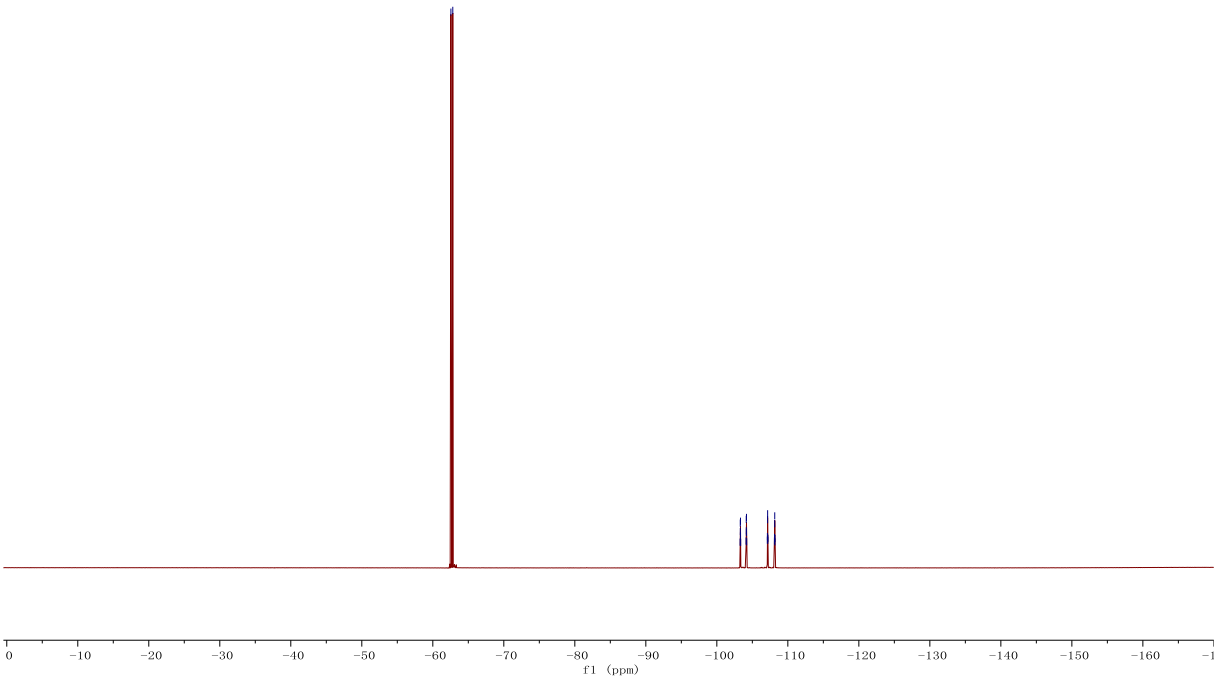

mt-4-272.2.fid
155.27
153.36
144.05
77.55
77.23
76.91
56.32
f1 (ppm)

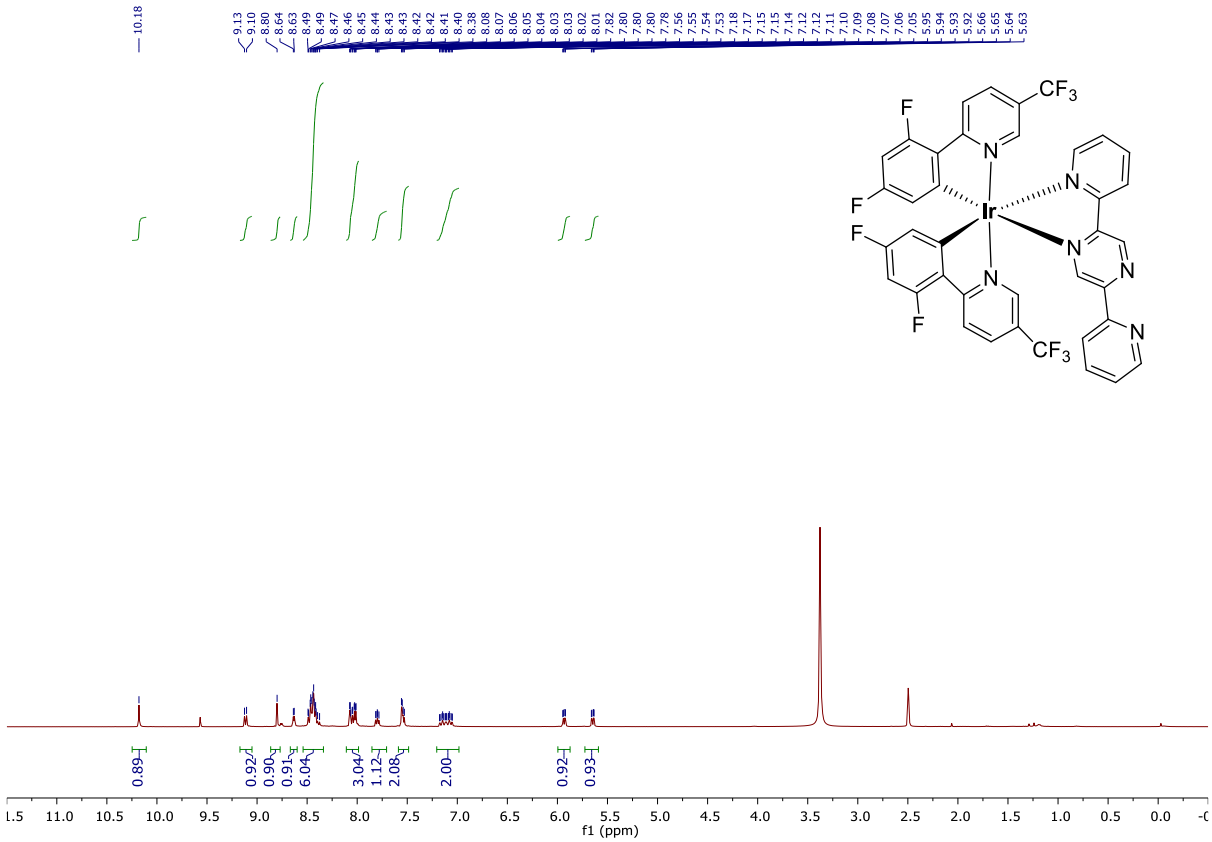
NMR Spectra of New Photocatalysts



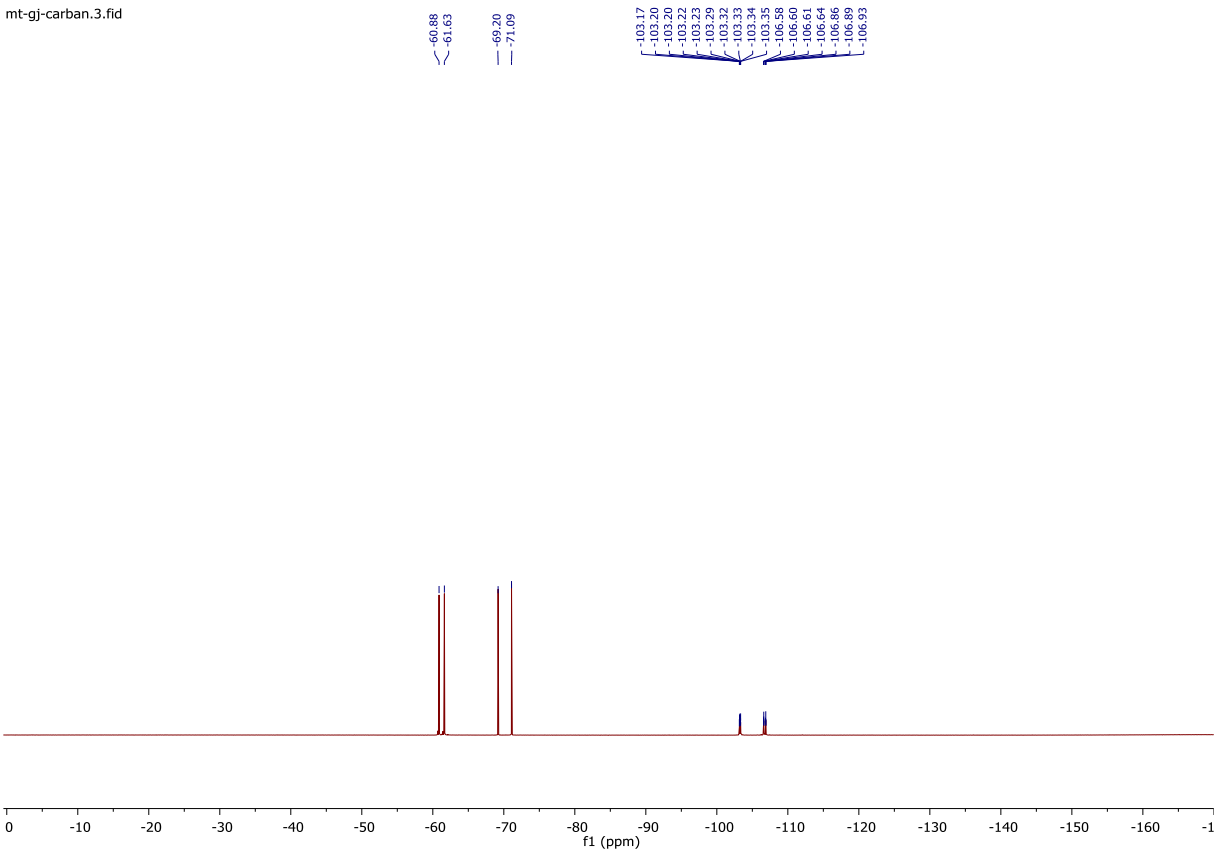


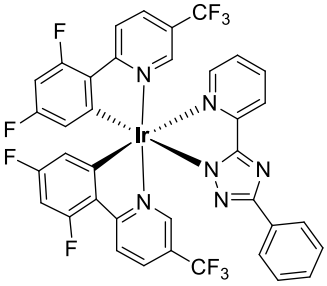


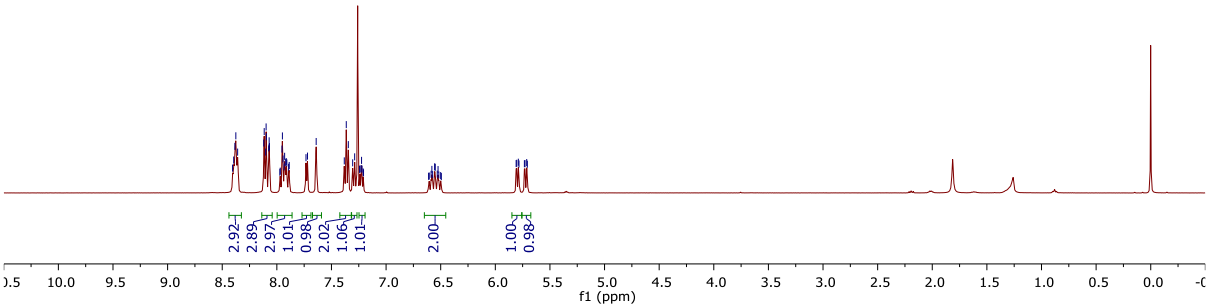




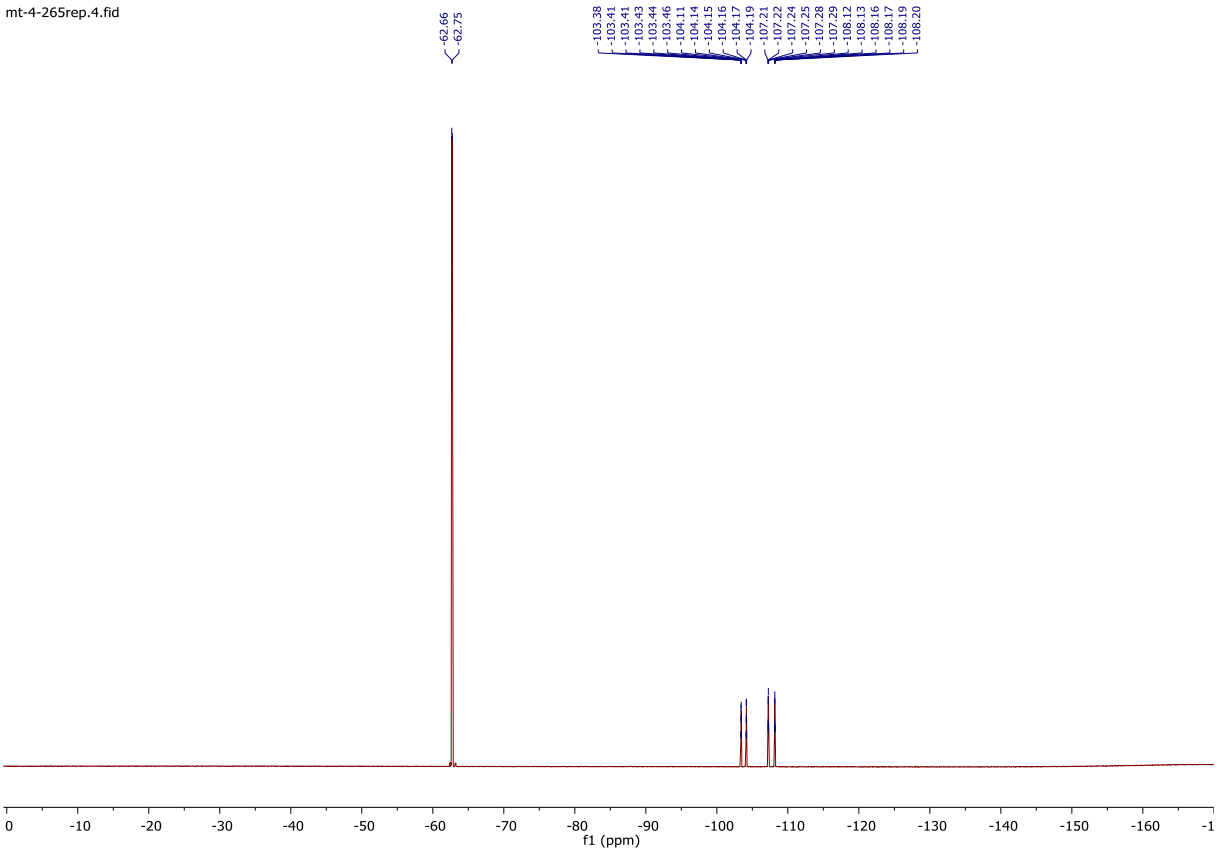
mt-gj-carban.3.fid

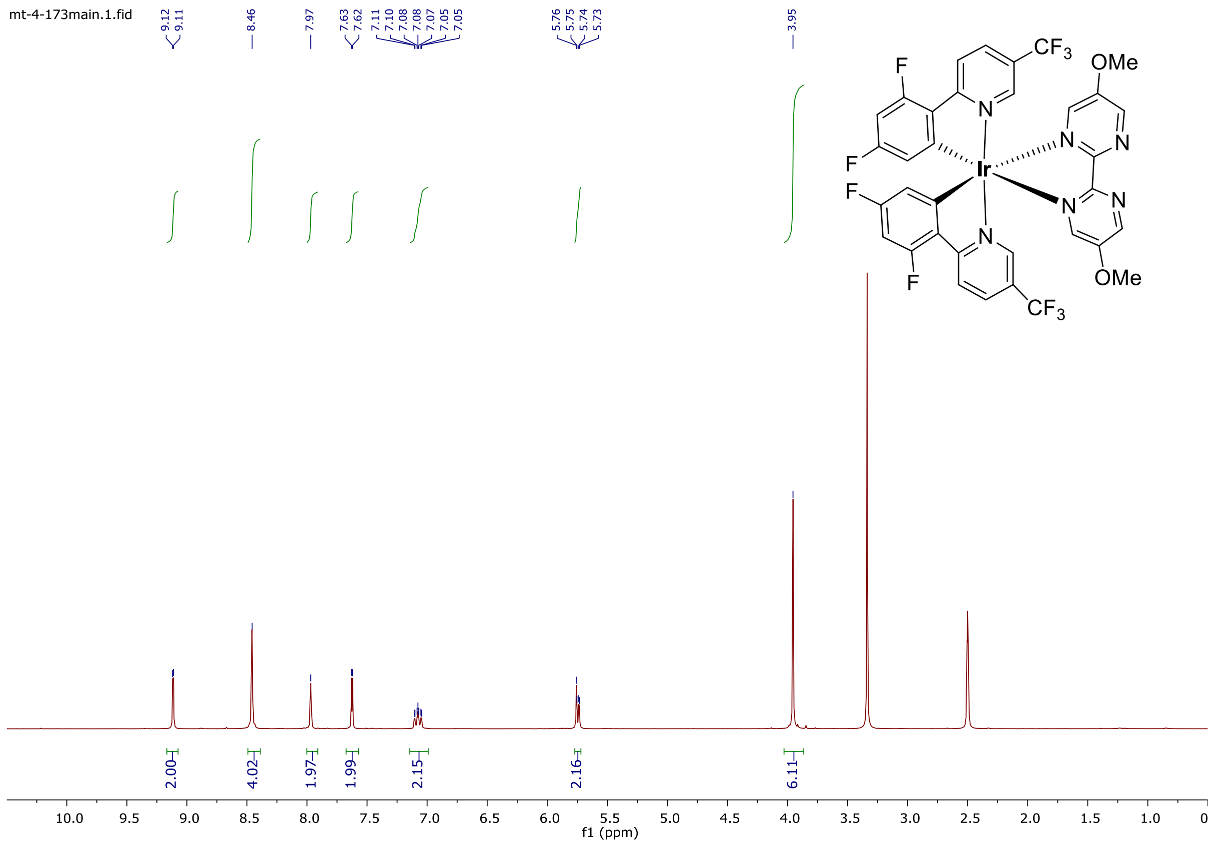


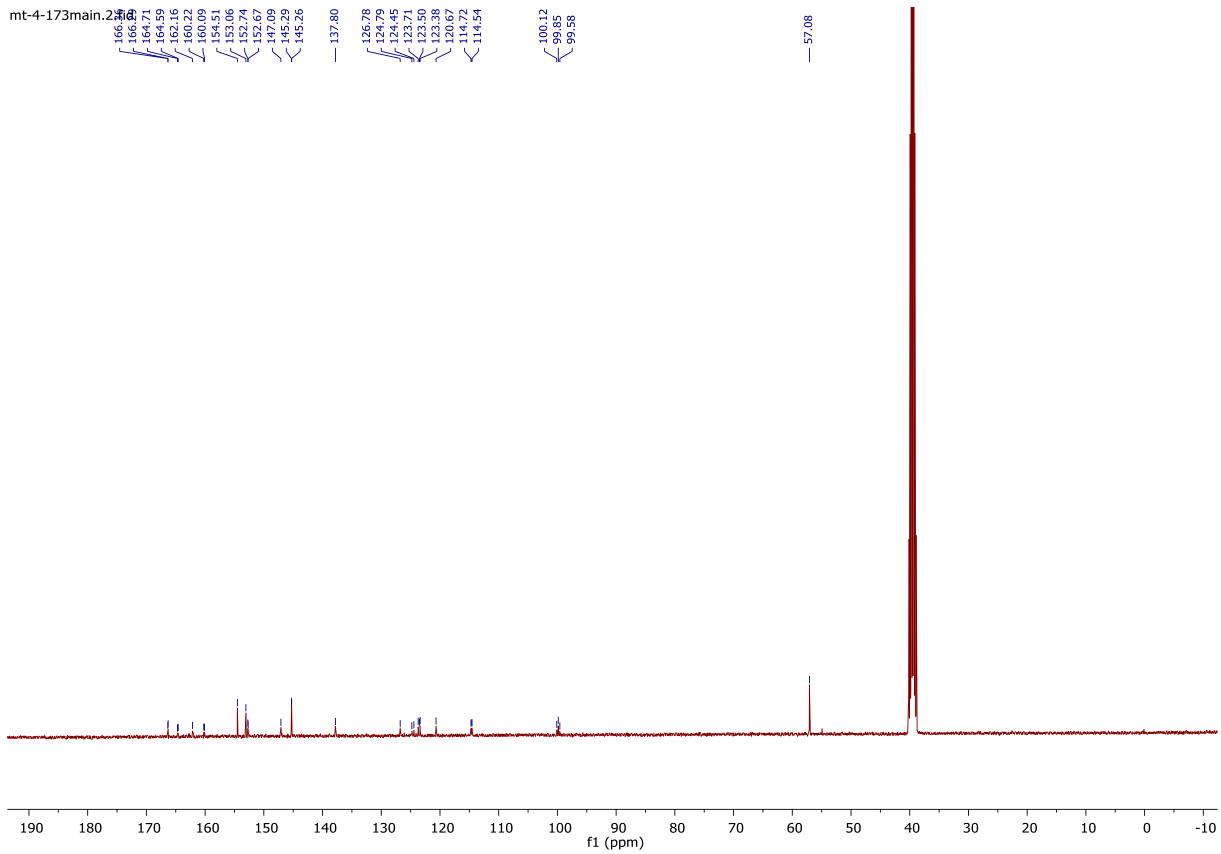




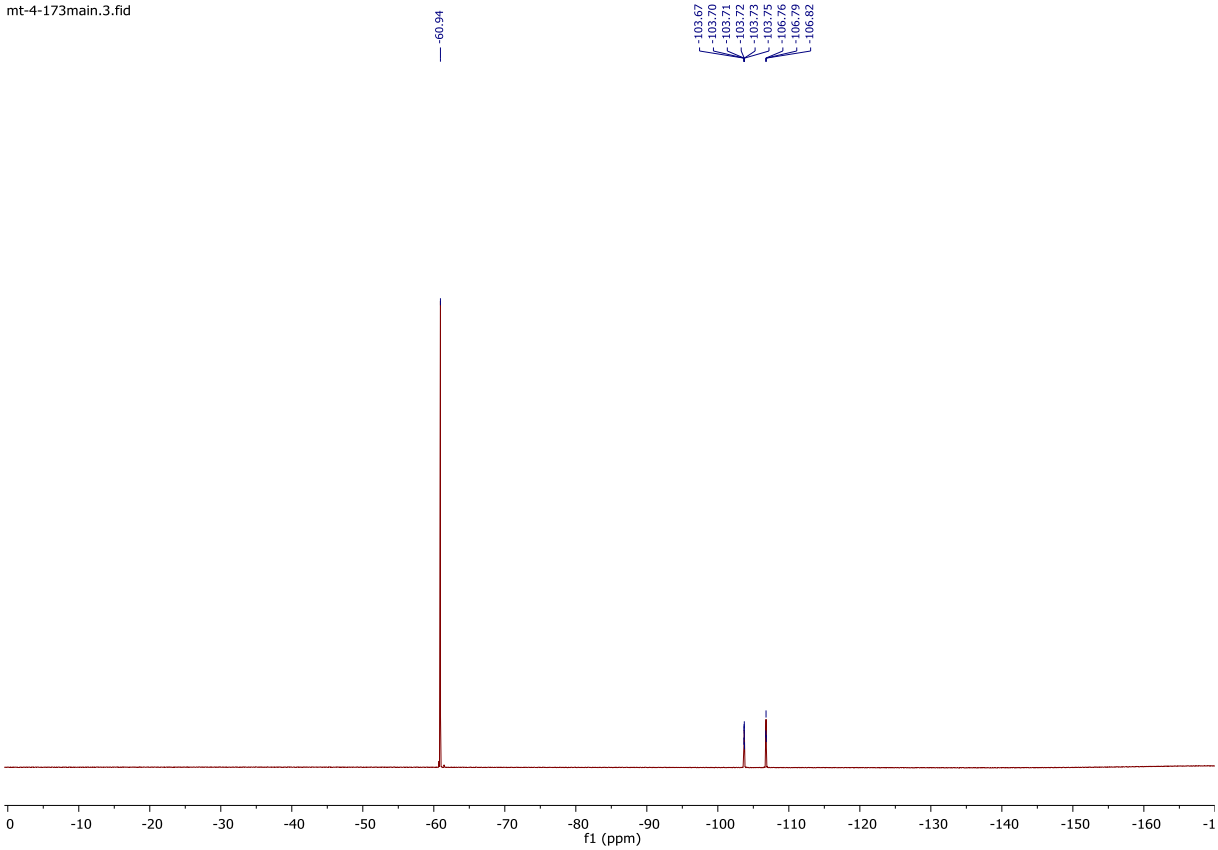
mt-4-265rep.4.fid



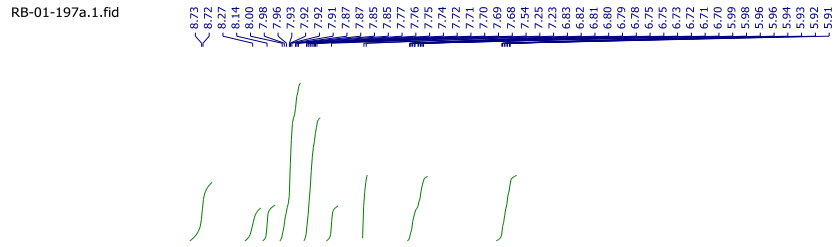

mt-4-173main.1.fid
9.12 9.11 8.46 7.97 7.63 7.62 7.11 7.10 7.08 7.08 7.07 7.05 7.05 5.76 5.75 5.74 5.73 3.95
2.00 4.02 1.97 1.99 2.15 2.16 6.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0
f1 (ppm)
F
F
F
F
CF_3
CF_3
OMe
OMe
N
Ir

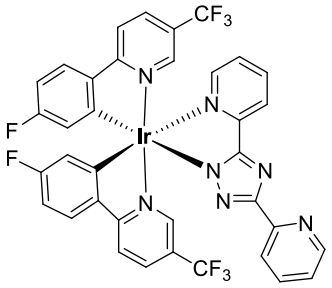

164.71 164.59 162.16 160.22 160.09 154.51 153.06 152.74 152.67 147.09 145.29 145.26 137.80 126.78 124.79 124.45 123.71 123.50 123.38 120.67 114.72 114.54 100.12 99.85 99.58 57.08
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

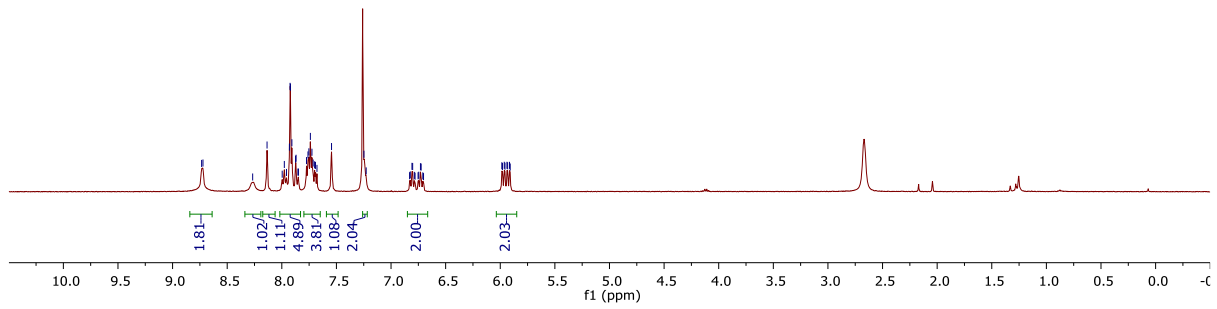
mt-4-173main.3.fid



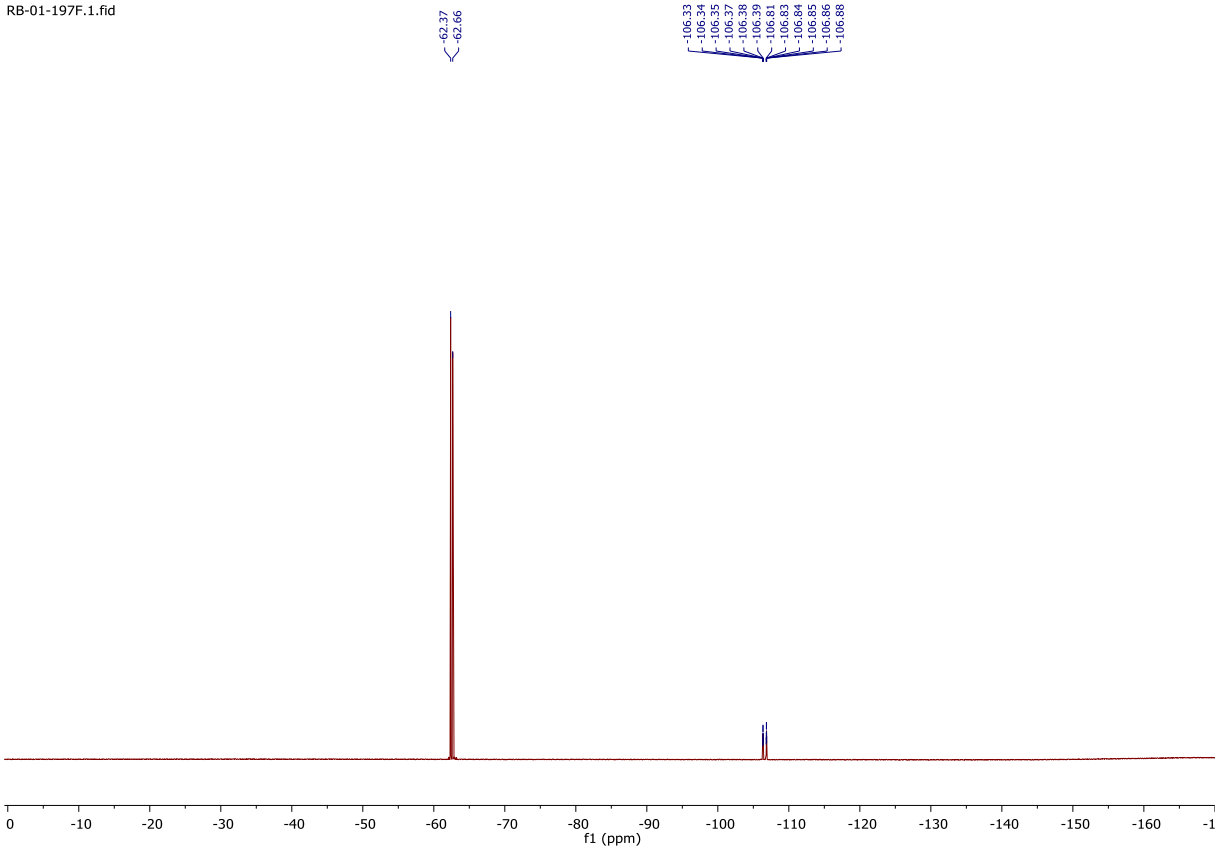
RB-01-197a.1.fid



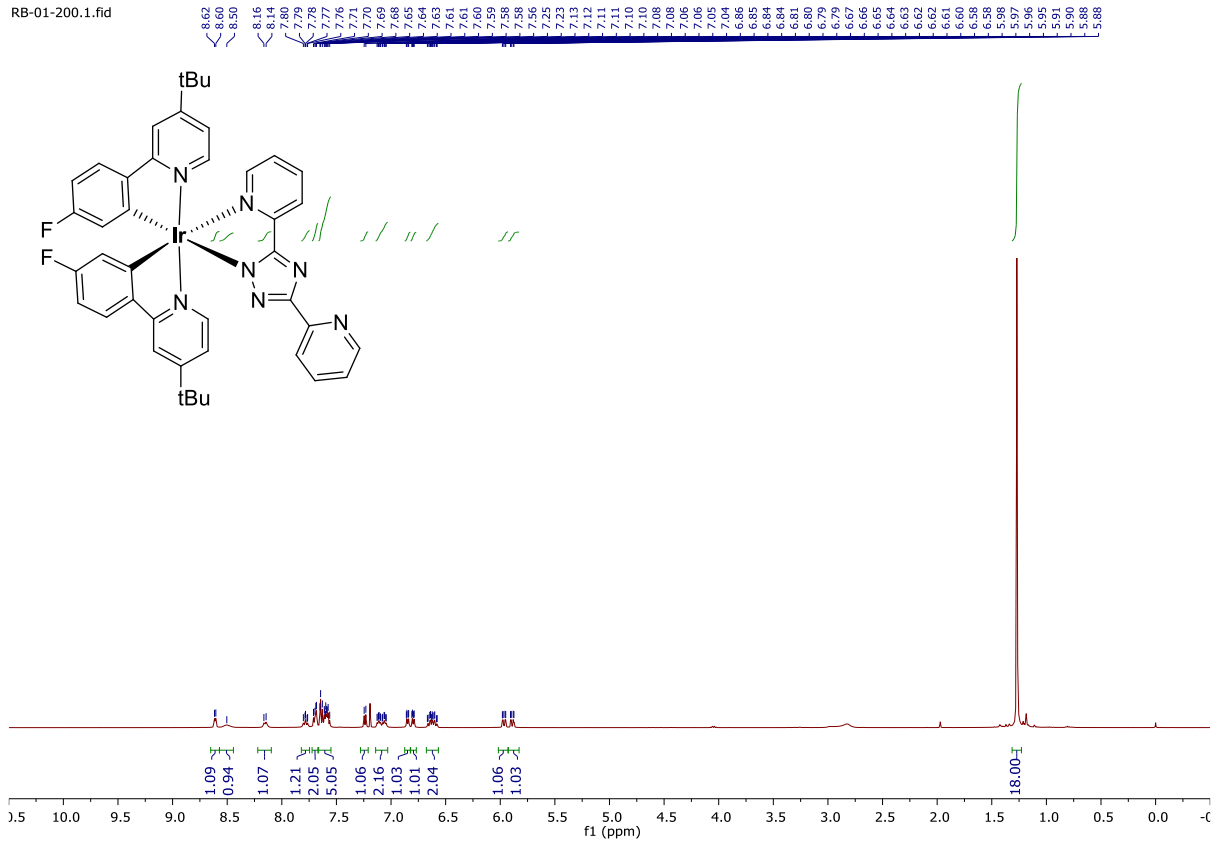




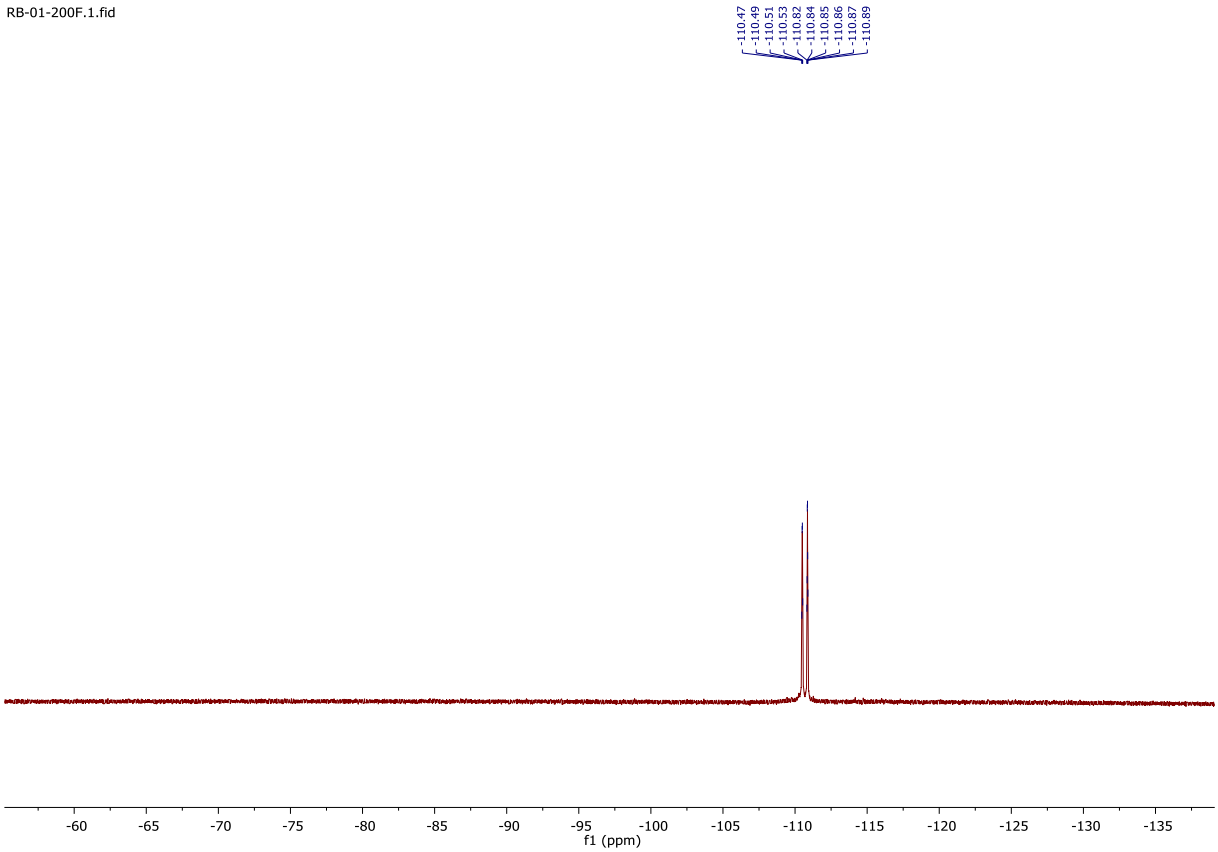
RB-01-197F.1.fid



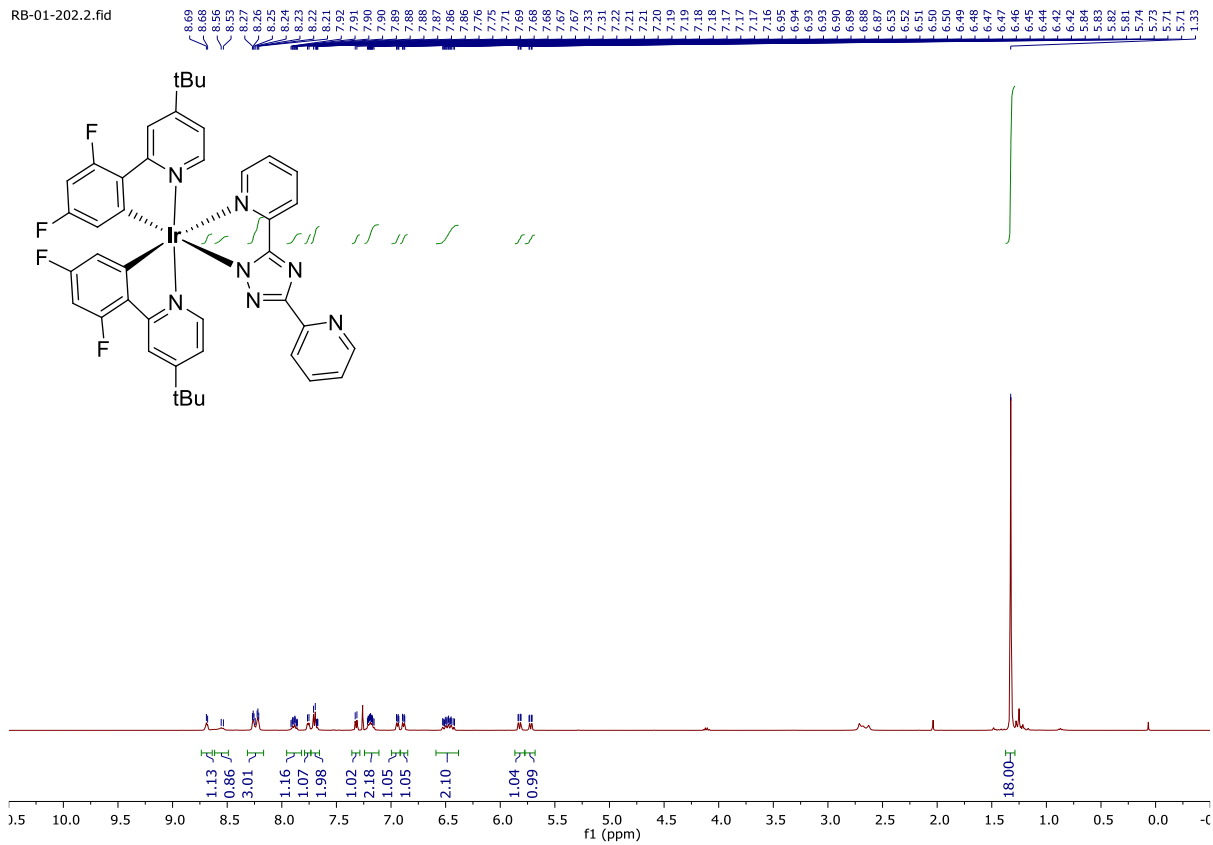
RB-01-200.1.fid



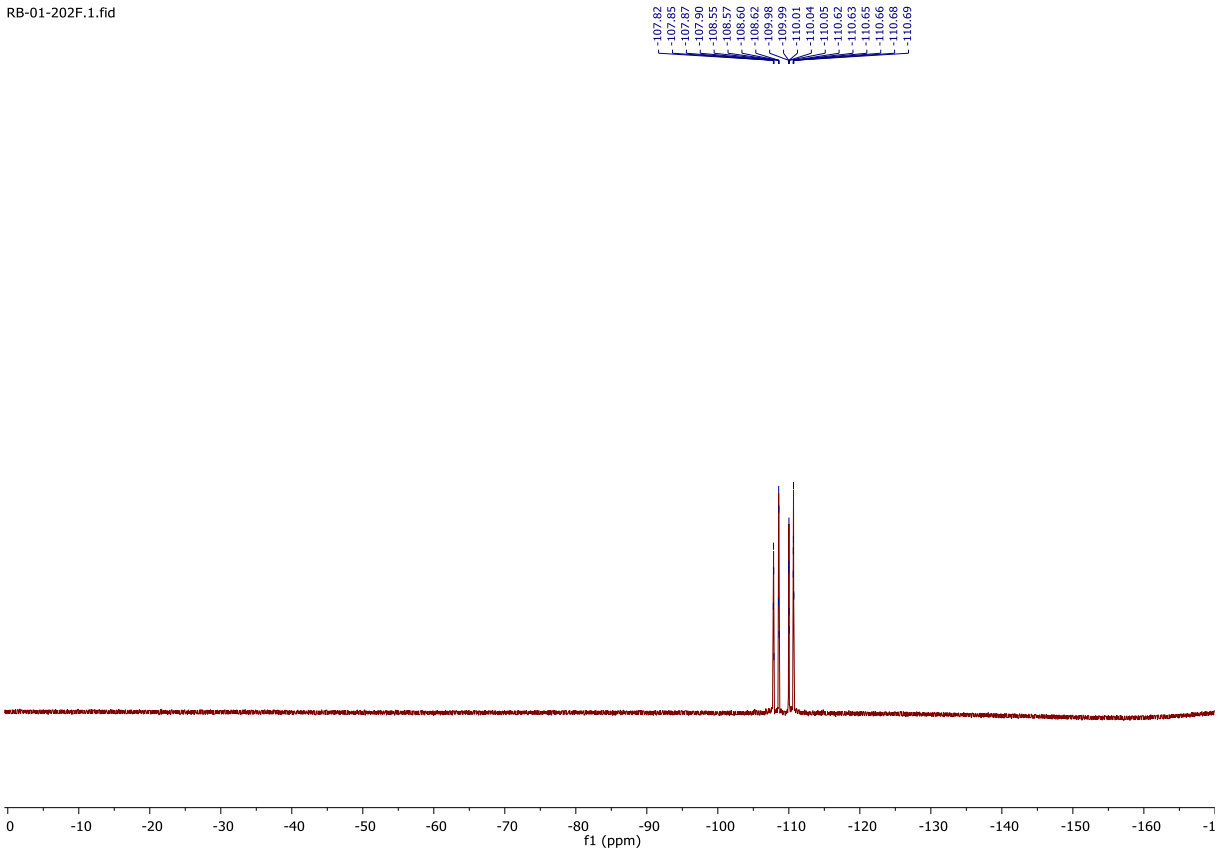
RB-01-200F.1.fid



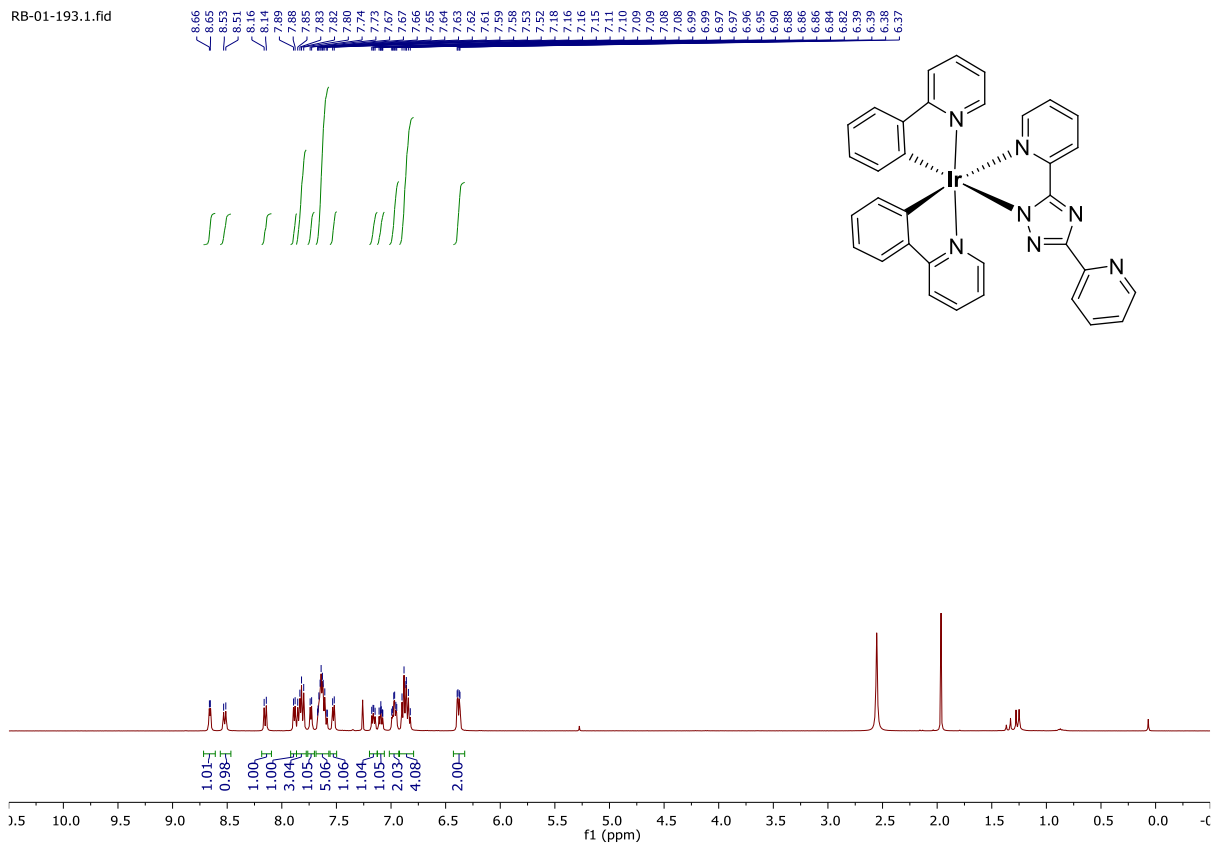
RB-01-202.2.fid

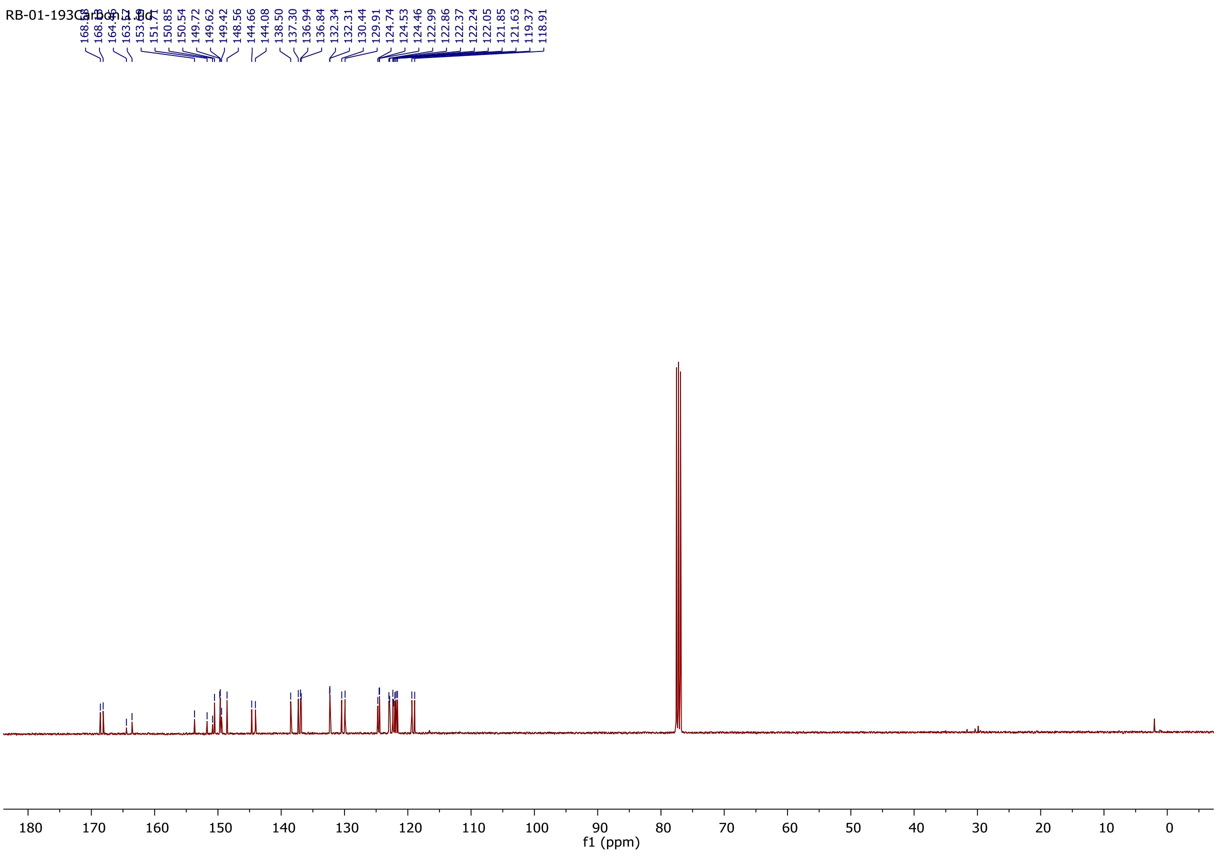


RB-01-202F.1.fid



RB-01-193.1.fid




RB-01-193Carbon.1.fid
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150.85
150.54
149.72
149.62
149.42
148.56
144.66
144.08
138.50
137.30
136.94
136.84
132.34
132.31
130.44
129.91
124.74
124.53
124.46
122.99
122.86
122.37
122.24
122.05
121.85
121.63
119.37
118.91
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)