Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

for

Synthesis of Polyisobutylene-Tagged *fac*-Ir(ppy)$_3$ Complexes and their Application as Recyclable Visible-Light Photocatalysts in a Continuous Flow Process

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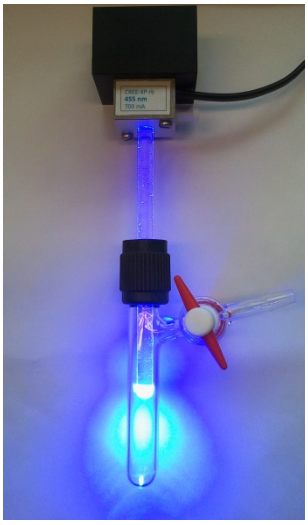
Experimental details, characterization data and spectra

1. General information

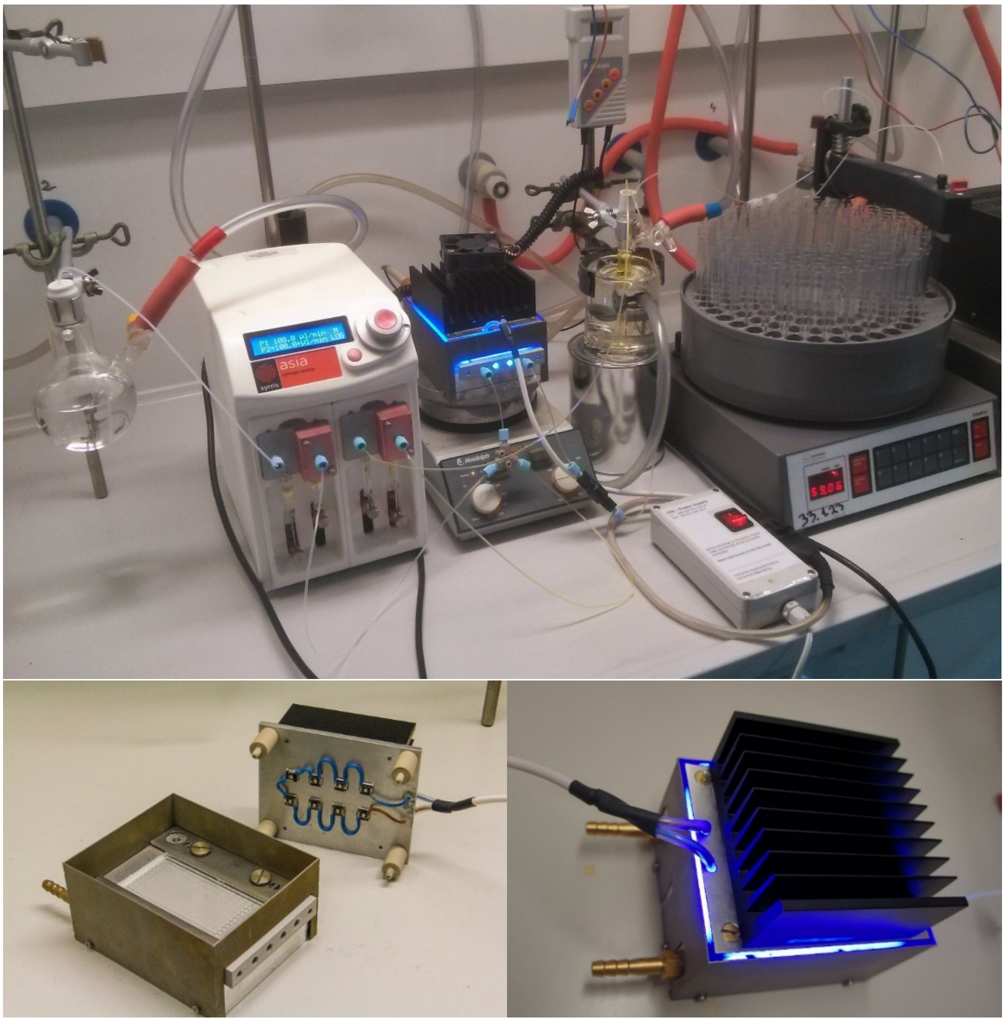
All chemicals were used as received or purified according to Purification of Common Laboratory Chemicals if necessary.[1] Glassware was dried in an oven at 110 °C or flame dried and cooled under a dry atmosphere prior to use. All reactions were performed using Schlenk techniques. The blue light irradiation in batch processes was performed using a CREE XLamp XP-E D5-15 LED (λ = 450-465 nm). In micro reactor processes 8 OSRAM OSLON Black Series LD H9GP LEDs (λ = 455±10 nm) were employed. Analytical thin layer chromatography was performed on Merck TLC aluminium sheets silica gel 60 F 254. Reactions were monitored by TLC and visualized by a short wave UV lamp and stained with a solution of potassium permanganate, p-anisaldehyde, or Seebach's stain. Flash column chromatography was performed using Merck flash silica gel 60 (0.040-0.063 mm). The melting points were measured on a Büchi SMP-20 apparatus in a silicon oil bath. Values thus obtained were not corrected. ATR-IR spectroscopy was carried out on a Biorad Excalibur FTS 3000 spectrometer, equipped with a Specac Golden Gate Diamond Single Reflection ATR-System. NMR spectra were recorded on Bruker Avance 300 and Bruker Avance 400 spectrometers. Chemical shifts for ^{1}H NMR were reported as δ, parts per million, relative to the signal of $CHCl_3$ at 7.26 ppm. Chemical shifts for ^{13}C NMR were reported as δ, parts per million, relative to the center line signal of the $CDCl_3$ triplet at 77 ppm. Coupling constants *J* are given in Hertz (Hz). The following notations indicate the multiplicity of the signals: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, and m = multiplet. Mass spectra were recorded at the Central Analytical Laboratory at the Department of Chemistry of the University of Regensburg on a Varian MAT 311A, Finnigan MAT 95, Thermoquest Finnigan TSQ 7000 or Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS. Gas chromatographic analyses were performed on a Fisons Instuments gas chromatograph equipped with a capillary column (30 m × 250 µm × 0.25 µm) and a flame ionisation detector. The yields reported are referred to the isolated compounds unless otherwise stated.

2. Setup

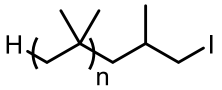
a. Setup for batch reactions



b. Microreactor

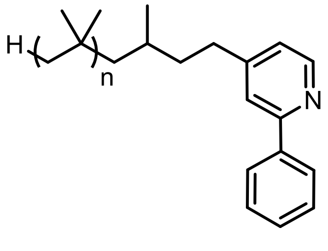


3. Synthesis of complexes



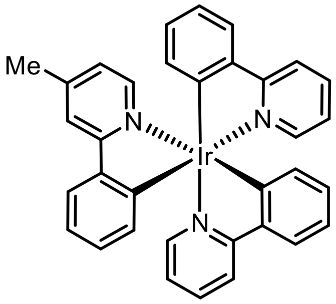
Polyisobutylene iodide (6).

In a 2 L Schlenk flask polyisobutylene hydroxide[2] (**5**, 102 g, 100 mmol, 1.00 equiv) was dissolved in 1.00 L DCM and the mixture was cooled to 0 °C. Et_3N (46.0 mL, 33.4 g, 330 mmol, 3.30 equiv) followed by $MeSO_2Cl$ (23.2 mL, 33.4 g, 300 mmol, 3.00 equiv) were added dropwise over 15 min each. The reaction mixture was stirred for 6 h at room temperature after which the solvent was evaporated under reduced pressure and the residue was redissolved in mixture of 750 mL hexanes and 750 mL acetone. LiI (134 g, 1.00 mol, 10.0 equiv) was added and the suspension was refluxed for 7 d. After cooling, reaction mixture was transferred to a separatory flask with the help of 1.5 L of hexanes, the lower acetone phase was discarded and the upper hexanes phase was washed with 1.0 L water, 2x 200 mL DMF, 2x 500 mL water, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give 86.0 g (76.2 mmol, 76.2%) of polyisobutylene iodide (**6**) as a viscous, colorless oil. IR (neat): 2949, 2893, 1470, 1389, 1365, 1230, 952, 921 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 3.21 (dd, *J* = 9.4, 4.3 Hz, 1H), 3.07 (dd, J = 9.4, 6.7 Hz, 1H), 1.45 – 0.90 (m, PIB, 190H); ^{13}C NMR (75 MHz, $CDCl_3$): 60 – 56 (multiple PIB peaks), 52.66 (PIB-$\mathit{C}H_2CH(CH_3)CH_2$-I), 39 – 29 (multiple PIB peaks), 23.93 (PIB-$CH_2CH(\mathit{C}H_3)CH_2$-I), 20.97 (PIB-$CH_2CH(CH_3)$ $\mathit{C}H_2$-I).



4-(methylpolyisobutyl)-2-phenylpyridine (PIB-ppy, 8).

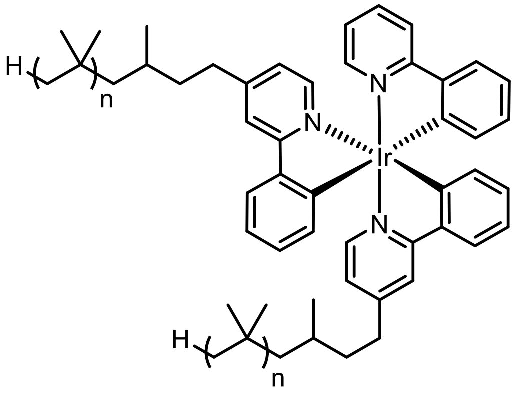
A Schlenk flask was charged with 4-methyl-2-phenylpyridine[3] (355 mg, 2.10 mmol, 1.05 equiv), 10 mL THF and cooled to -78 °C. A solution of LDA, prepared *in situ* by treating a solution of $^iPr_2NH$ (336 µL, 243 mg, 2.40 mmol, 1.20 equiv) in 5 mL THF with ^nBuLi (1.6 M in hexanes, 1.10 mL, 2.20 mmol, 1.10 equiv), was added dropwise. The solution was stirred for 30 min at -78 °C during which it turned intense red. A solution of polyisobutylene iodide (**6**, 2.26 g, 2.00 mmol, 1.00 equiv) in 10 mL hexanes was added dropwise and the reaction mixture was allowed to reach room temperature over night. After evaporation of the solvents under reduced pressure, purification was achieved by flash silica gel chromatography (hexanes / EtOAc, 10:1 to 5:1 with 2% Et_3N) to give 1.96 g (1.66 mmol, 83.0%) of PIB-ppy (**8**) as a viscous slightly yellow oil. R_f (hexanes / EtOAc, 6:1 with 2% Et_3N) = 0.60; IR (neat): 2950, 2896, 1741, 1600, 1558, 1471, 1389, 1366, 1231, 951, 923, 933, 774, 693, 637 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 8.60 (d, *J* = 5.2 Hz, 1H), 8.04 – 7.96 (m, 2H), 7.58 (s, 1H), 7.53 – 7.40 (m, 3H), 7.14 (d, *J* = 5.1 Hz), 2.80 – 2.58 (m, 2H), 1.80 – 0.70 (m, 200H); ^{13}C NMR (75 MHz, $CDCl_3$): 156.71, 148.38, 129.37, 128.88, 127.18, 122.65, 121.33, 60 – 53 (multiple PIB peaks), 41 – 20 (multiple PIB peaks).



Ir(ppy)$_2$(4-Me-ppy) (10).[4]

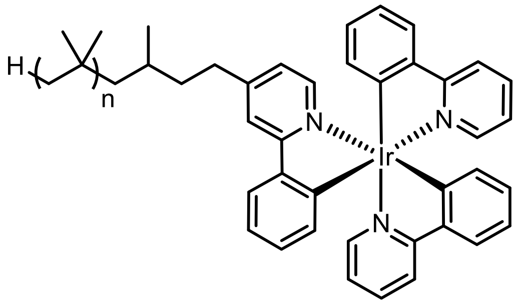
To a solution of [Ir(ppy)$_2$Cl]$_2$ (793 mg, 740 µmol, 1.00 equiv) in 74 mL DCM a solution of AgOTf (399 mg, 1.55 mmol, 2.09 equiv) in 37 mL MeOH was dropwise added. The mixture was stirred at room temperature over night in the dark and subsequently filter through a short plug of Celite® with the help of 100 mL DCM. The solvent was evaporated under reduced pressure to give 1.06 g (1.48 mmol, 100%) of [Ir(ppy)$_2$(MeOH)$_2$](OTf) (**7**)as a green solid which was used without further purification.

A Schlenk flask was charged with [Ir(ppy)$_2$(MeOH)$_2$](OTf) (1.06 g, 1.48 mmol, 1.00 equiv), 4-methyl-2-phenylpyridine[3] (751 mg, 4.44 mmol, 3.00 equiv), 30 mL EtOH, and 30 mL MeOH. The mixture was degassed by N_2 sparging for 5 min and subsequently refluxed for 24 h after which 6 g of Celite® was added to reaction mixture stirred for another 5 min. This suspension was filtered through a plug of Celite®, which was then washed with 100 mL MeOH and 100 mL hexanes. The filtrates were discarded and the complex was eluted with 200 mL DCM. Evaporation under reduced pressure and drying of the residue *in vacuo* gave 563 mg (842 µmol, 56.9% over two steps) of Ir(ppy)$_2$(4-Me-ppy) (**10**) as a bright yellow powder. R_f (hexanes / EtOAc, 1:1) = 0.23; IR (neat): 3034, 1613, 1598, 1578, 1469, 1411, 1299, 1261, 1157, 1058, 1026, 876, 816, 752, 730 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2): 7.92 (dd, J = 8.4, 2.9 Hz, 2H), 7.75 (s, 1H), 7.70 – 7.62 (m, 5H), 7.60 (d, J = 5.6 Hz, 1H), 7.57 (d, J = 5.3 Hz, 1H), 7.41 (d, J = 5.8 Hz, 1H), 6.96 – 6.85 (m, 5H), 6.82 – 6.70 (m, 7H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2): 166.92, 166.30, 161.76, 161.71, 161.33, 148.36, 147.62, 147.60, 169.99, 144.35, 144.31, 144.27, 137.24, 137.21, 137.07, 136.58, 136.56, 130.04, 129.89, 124.43, 124.19, 123.70, 122.48, 120.23, 120.17, 120.02, 119.24, 21.50; HRMS (ESI) m/z calculated for $C_{34}H_{27}IrN_3$ ([M+H]$^+$) 670.1830, found 670.1811.



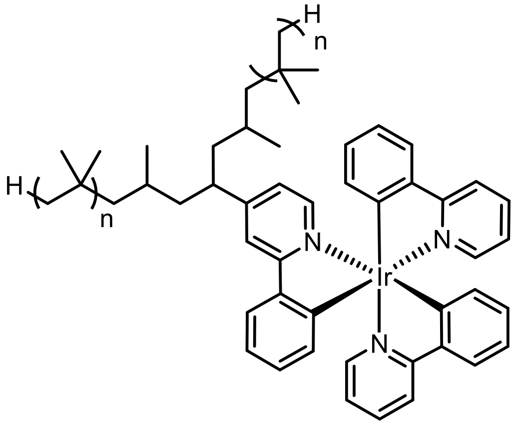
Ir(ppy)(PIB-ppy)$_2$ (S1).

A Schlenk flask was charged with [Ir(ppy)$_2$(MeOH)$_2$](OTf) (429 mg, 600 µmol, 1.00 equiv), PIB-pyy (**6**, 707 mg, 600 µmol, 1.00 equiv), and 18 mL dioxane. The mixture was degassed by N_2 sparging for 5 min and subsequently refluxed for 7 d after which the reaction mixture was transferred to a separatory funnel with 100 mL Et$_2$O. The mixture was washed twice with 50 mL water each, back washed twice with 50 mL Et$_2$O each, dried over Na$_2$SO$_4$ and evaporated under reduced pressure. The remaining brow oil was purified by flash chromatography (hexanes / Et$_2$O, 10:1 to 1:1) on basic Al$_2$O$_3$. Fractions containing mixtures of the complex and the free ligand were united, evaporated under reduced pressure, redissolved in 20 mL heptane, washed with a solution of 1 mL AcOH in 20 mL MeCN, and again evaporated under reduced pressure to give 54.9 mg (20.3 µmol, 6.8%) of Ir(ppy)(PIB-ppy)$_2$ as a yellow oil. R$_f$ (Al$_2$O$_3$, hexanes / Et$_2$O, 5:1) = 0.86; IR (neat): 2951, 2897, 1600, 1580, 1556, 1471, 1389, 1366, 1261, 1231, 1158, 1093, 1058, 1026, 952, 923, 800, 776, 753, 733, 693, 638 cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): 8.55 (d, J = 5.1 Hz, 1H), 8.02 (d, J = 7.4 Hz, 2H), 7.92 (dd, J = 8.1, 3.1, 1H), 7.76 (s, 1H), 7.72 – 7.56 (m, 5H), 7.53 – 7.39 (m, 4H), 7.11 (d, J = 4.7 Hz, 1H), 6.96 – 6.86 (m, 3H), 6.83 – 6.72 (m, 5H), 2.79 – 2.60 (m, 4H), 1.75 – 0.75 (m, 320H); ^{13}C NMR (101 MHz, CD$_2$Cl$_2$): 166.96, 166.45, 161.76, 161.61, 149.55, 147.61, 147.56, 147.07, 144.41, 144.29, 137.25, 137.15, 136.56, 130.08, 129.87, 129.28, 129.05, 127.32, 124.44, 124.20, 122.94, 122.45, 121.13, 120.24, 120.19, 120.13, 119.22, 59 – 57 (multiple PIB peaks), 41 – 22 (multiple PIB peaks).



Ir(ppy)$_2$(PIB-ppy) (3).

A Schlenk flask was charged with Ir(ppy)$_2$(4-Me-ppy) (**10**, 268 mg, 400 µmol, 1.00 equiv), 8 mL THF and cooled to -78 °C. A solution of LDA, prepared *in situ* by treating a solution of ^{i}Pr$_2$NH (79 µL, 57 mg, 0.56 mmol, 1.4 equiv) in 6 mL THF with ^{n}BuLi (1.6 M in hexanes, 0.33 mL, 0.52 mmol, 1.3 equiv), was added dropwise. The solution was stirred for 15 min at -78 °C during which it turned dark red / brown. A solution of polyisobutylene iodide (**6**, 0.63 g, 0.56 mmol, 1.4 equiv) in 6 mL hexanes was added dropwise and the reaction mixture was allowed to reach room temperature over night. After evaporation of the solvents under reduced pressure, purification was achieved by flash silica gel chromatography (hexanes / DCM, 1:0 to 1:1) to give 363 mg (216 µmol, 54.0%) of Ir(ppy)$_2$(PIB-ppy) (**3**) as a bright yellow solid. R$_f$ (hexanes / DCM, 2:1) = 0.50; mp: >190 °C; IR (neat): 2948, 1891, 1600, 1570, 1469, 1411, 1388, 1364, 1261, 1227, 1156, 1056, 1027, 950, 831, 779, 752, 732, 649 cm^{-1}; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): 7.94 – 7.88 (m, 2H), 7.55 (s, 1H), 7.70 – 7.60 (m, 5H), 7.57 (t, *J* = 5.1 Hz, 2H), 7.42 (d, *J* = 5.8 Hz, 1H), 6.95 – 6.85 (m, 5H), 6.82 – 6.71 (m, 7H), 2.78 – 2.58 (m, 2H), 1.75 – 0.70 (m, 150H); ^{13}C NMR (101 MHz, CDCl$_3$): 165.76, 165.20, 151.11, 151.08, 146.05, 145.53, 142.79, 142.69, 142.63, 136.14, 136.10, 136.01, 134.78, 128.80, 128.63, 122.82, 122.60, 121.28, 120.76, 118.66, 118.63, 117.66, 59 – 52 (multiple PIB peaks), 40 – 20 (multiple PIB peaks); LRMS (ESI) m/z calculated for $C_{106}H_{170}IrN_3$ ($[M+H]^+$) 1679.3, found 1679.7.

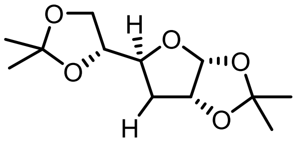


Ir(ppy)$_2$(PIB$_2$-ppy) (9).

A Schlenk flask was charged with Ir(ppy)$_2$(4-Me-ppy) (**10**, 27 mg, 39 µmol, 1.0 equiv), 1 mL THF and cooled to -78 °C. A solution of LDA, prepared *in situ* by treating a solution of $^{i}Pr_2NH$ (79 µL, 57 mg, 0.56 mmol, 14 equiv) in 6 mL THF with ^{n}BuLi (1.6 M in hexanes, 0.33 mL, 0.52 mmol, 13 equiv), was added dropwise. The solution was stirred for 15 min at -78 °C during which it turned dark red / brown. A solution of polyisobutylene iodide (**6**, 0.63 g, 0.56 mmol, 14 equiv) in 6 mL hexanes was added dropwise and the reaction mixture was allowed to reach room temperature over night. After evaporation of the solvents under reduced pressure, purification was achieved by flash silica gel chromatography (hexanes / DCM, 1:0 to 1:1) to give 89 mg (33 µmol, 84%) of Ir(ppy)$_2$(PIB$_2$-ppy) (**9**) as a yellow oil. R_f (hexanes / DCM, 2:1) = 0.71; IR (neat): 2950, 2895, 1601, 1580, 1471, 1389, 1366, 1261, 1230, 1158, 1058, 1025, 952, 923, 753, 734, 666, 630 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.91 – 7.82 (m, 2H), 7.70 – 7.60 (m, 4H), 7.69 – 7.35 (m, 5H), 6.95 – 6.32 (m, 12H), 2.77 – 2.63 (m, 1H), 1.60 – 0.70 (m, 360H); ^{13}C NMR (101 MHz, CD_2Cl_2): 167.03, 166.53, 166.49, 161.84, 161.63, 161.26, 157.57, 157.02, 147.62, 147.32, 147.17, 144.46, 144.27, 144.15, 137.27, 136.55, 130.13, 129.92, 124.46, 124.34, 124.22, 122.59, 122.43, 122.35, 120.24, 119.24, 118.94, 118.43, 60 – 52 (multiple PIB peaks), 42 – 22 (multiple PIB peaks).

4. Photoreactions in a batch setup

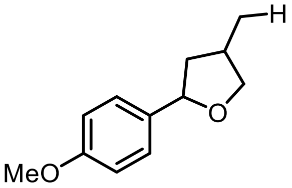
Literature conditions



(*3aR,5S,6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (12).[5]

A Schlenk tube was charged with (3aR,5R,6R,6aS)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-iodo-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole[6] (**11**, 368 mg, 1.00 mmol, 1.00 equiv) and *fac*-Ir(ppy)$_3$ (6.6 mg, 10 µmol, 1.0 mol%), Hantzsch ester (507 mg, 2.00 mmol, 2.00 equiv) sealed with a screw-cap, evacuated and backfilled with N_2 (three cycles), and 10 mL MeCN and Bu_3N (0.48 mL, 0.37 g, 2.0 mmol, 2.0 equiv) were added. The reaction was degassed by N_2 sparging for 10 min and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED took place from above while the reaction was magnetically stirred below. After 16 h of irradiation the LED was switched off, the reaction mixture was evaporated under reduced pressure, and the obtained residue was redissolved in 25 mL EtOAc. After washing with 25 mL 1 M HCl (aq), back extraction with 25 ml EtOAc (twice), washing with 25 mL sat $NaHCO_3$ (aq) and 25 ml brine, the organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash silica gel chromatography (hexanes / EtOAc, 6:1) to give 145 mg (598 µmol, 59.8%) of (*3aR,5S,6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (**12**) as white solid. ^{1}H NMR (300 MHz, $CDCl_3$): 5.74 (d, *J* = 3.6 Hz, 1H), 4.69 (t, *J* = 4.2 Hz, 1H), 4.14 – 3.98 (m, 3H), 3.81 – 3.69 (m, 1H), 2.11 (dd, *J* = 12.9, 3.3 Hz, 1H), 1.76 – 1.62 (m, 1H), 1.44 (s, 3H), 1.35 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H).

The reaction was repeated as above on a 0.3 mmol scale at 85 °C with 3 mL of heptane as co-solvent and an irradiation time of 3 h after which all starting material was consumed as judged by TLC control. The reaction mixture was transferred to a separatory funnel with the help of 3 mL MeCN and 3 mL heptane and phases were separated. Diphenylmethane was added to the MeCN and an aliquot was analyzed by GC-FID showing full starting material conversion and 73% yield of (*3aR,5S,6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (**12**) in the MeCN phase.

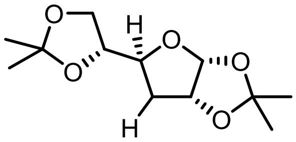


2-(4-methoxyphenyl)-4-methyltetrahydrofuran (14).[5]

A Schlenk tube was charged with 1-(1-(allyloxy)-2-iodoethyl)-4-methoxybenzene[7] (**13**, 318 mg, 1.00 mmol, 1.00 equiv) and *fac*-Ir(ppy)$_3$ (16 mg, 25 µmol, 2.5 mol%), sealed with a screw-cap, evacuated and backfilled with N_2 (three cycles), and 10 mL MeCN, Bu_3N (2.38 mL, 1.85 g, 10.0 mmol, 10.0 equiv), and HCOOH (377 µL, 460 mg, 10.0 mmol, 10.0 equiv) were added. The reaction was degassed by N_2 sparging for 10 min and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED took place from above while the reaction was magnetically stirred below. After 16 h of irradiation the LED was switched off, the reaction mixture was evaporated under reduced pressure, and the obtained residue was redissolved in 25 mL EtOAc. After washing with 25 mL 1 M HCl (aq), back extraction with 25 ml EtOAc (twice), washing with 25 mL sat $NaHCO_3$ (aq) and 25 ml brine, the organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash silica gel chromatography (hexanes / EtOAc, 50:1 to 6:1) to give 110 mg (573 µmol, 57.3%) of 2-(4-methoxyphenyl)-4-methyltetrahydrofuran (**14**, dr = 5.3:1) as a slightly yellow oil. ^{1}H NMR (major diastereomer, 300 MHz, $CDCl_3$): 7.31 – 7.21 (m, 2H), 6.92 – 6.82 (m, 2H), 4.98 (t, *J* = 7.0 Hz, 1H), 4.21 (dd, *J* = 8.2, 6.9 Hz, 1H), 3.79 (s, 3H), 3.46 (dd, *J* = 8.2, 7.0 Hz, 1H), 2.56 – 2.35 (m, 1H), 2.07 – 1.85 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 3H).

The reaction was repeated as above on a 0.3 mmol scale at 85 °C with 3 mL of heptane as co-solvent and an irradiation time of 3 h after which all starting material was consumed as judged by TLC control. The reaction mixture was transferred to a separatory funnel with the help of 3 mL MeCN and 3 mL heptane and phases were separated. Diphenylmethane was added to the MeCN phase and an aliquot was analyzed by GC-FID showing full starting material conversion and 37% yield of 2-(4-methoxyphenyl)-4-methyltetrahydrofuran (**13**) in the MeCN phase.

Recycling conditions



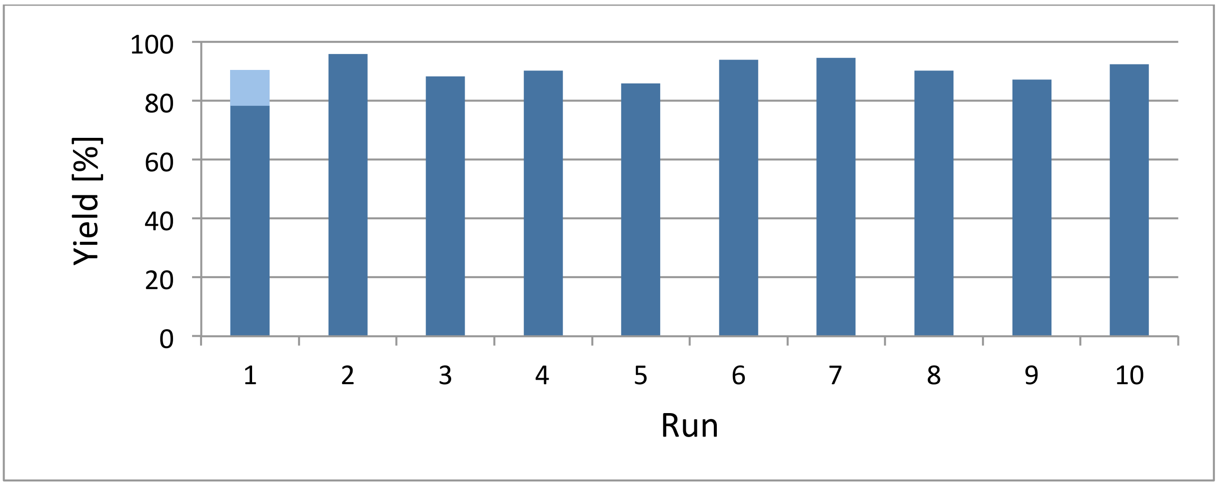
(*3aR,5S,6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (12).[5]

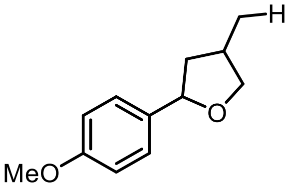
A Schlenk tube was charged with Hantzsch ester (152 mg, 0.60 mmol, 2.0 equiv), (3aR,5R,6R,6aS)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-6-iodo-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole[6] (**11**, 0.10 M solution in MeCN, 3.0 mL, 0.30 mmol, 1.0 equiv) and Ir(ppy)$_2$(PIB-ppy) (**3**, 5.0 mg, 3.0 µmol, 1.0 mol%), sealed with a screw-cap, and Bu$_3$N (143 µL, 111 mg, 0.60 mmol, 2.0 equiv) was added. The reaction was degassed by N$_2$ sparging for 10 min and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED took place from above while the reaction was magnetically stirred and heated in an aluminum block below. After 3 h of irradiation at 85 °C the LED was switched off, the reaction mixture was washed into a separatory flask with the help of 3 mL MeCN and 3 mL heptane, and the phases were separated. Diphenylmethane was added to the MeCN phase and an aliquot was analyzed by GC-FID to determine the yield of (*3aR,5S,6aR*)-5-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxole (**12**). The heptane phase was evaporated under reduced pressure and the residue used as catalyst in the next run.

All following catalyst runs were set up equally to the first run using all of the yellow, oily, heptane phase residue of the previous run instead of Ir(ppy)$_2$(PIB-ppy) (**3**). All reaction parameters were kept constant for the following runs.

Entry	Catalyst	Conditions	Run	Yield [%][a]
1	Ir(ppy)$_3$	Original[5]	-	60[b]
2	Ir(ppy)$_3$	MeCN/heptane at UCST	-	73
3	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	1	78+12[c]
4	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	2	96
5	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	3	88
6	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	4	90
7	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	5	86
8	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	6	94
9	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	7	94
10	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	8	90
11	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	9	87
12	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	10	92

[a]Determined by GC-FID with diphenylmethane as internal standard. [b]Isolated yield. [c]Additional amount of product extracted from heptane phase after all catalysis runs.


100
80
60
40
20
0
Yield [%]
1
2
3
4
5
6
7
8
9
10
Run



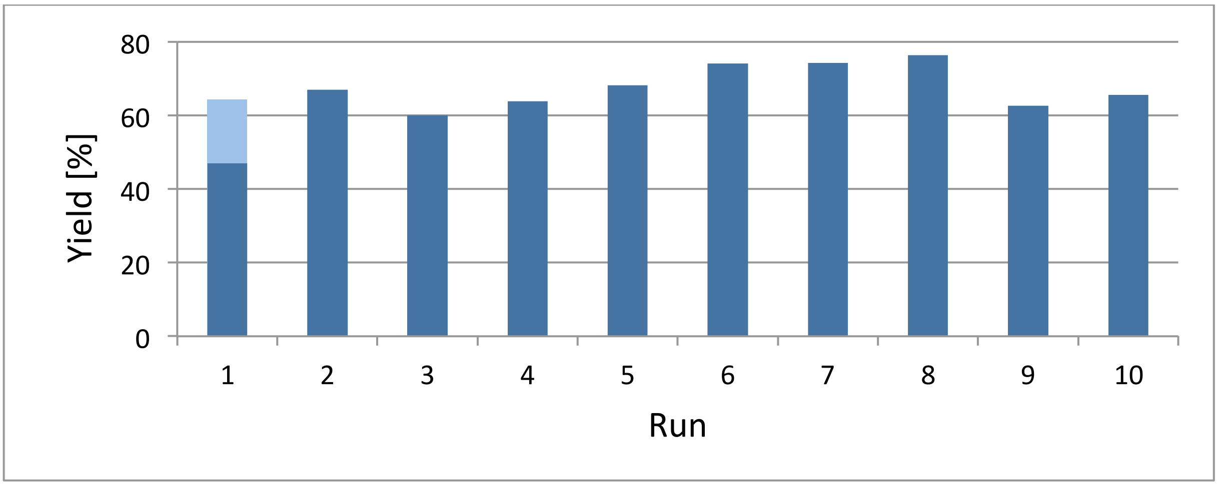
2-(4-methoxyphenyl)-4-methyltetrahydrofuran (14).[5]

A Schlenk tube was charged with 1-(1-(allyloxy)-2-iodoethyl)-4-methoxybenzene[7] (**13**, 0.10 M solution in MeCN, 3.0 mL, 0.30 mmol, 1.0 equiv) and Ir(ppy)$_2$(PIB-ppy) (**3**, 12.6 mg, 7.5 µmol, 2.5 mol%), sealed with a screw-cap, and Bu$_3$N (0.71 mL, 0.56 g, 3.0 mmol, 10 equiv) and HCOOH (113 µL, 138 mg, 10.0 mmol, 10.0 equiv) were added. The reaction was degassed by N$_2$ sparging for 10 min and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED took place from above while the reaction was magnetically stirred and heated in an aluminum block below. After 3 h of irradiation at 85 °C the LED was switched off, the reaction mixture was washed into a separatory flask with the help of 3 mL MeCN and 3 mL heptane, and the phases were separated. Diphenylmethane was added to the MeCN phase and an aliquot was analyzed by GC-FID to determine the yield of 2-(4-methoxyphenyl)-4-methyltetrahydrofuran (**14**). The heptane phase was evaporated under reduced pressure and residue used as catalyst in the next run.

All following catalyst runs were set up equally to the first run using all of the yellow, oily, heptane phase residue of the previous run instead of Ir(ppy)$_2$(PIB-ppy) (**3**). All reaction parameters were kept constant for the following runs.

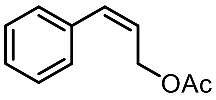
Entry	Catalyst	Conditions	Run	Yield [%][a]
1	Ir(ppy)$_3$	Original[5]	-	57[b]
2	Ir(ppy)$_3$	MeCN/heptane at UCST	-	37
3	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	1	47+17[c]
4	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	2	67
5	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	3	60
6	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	4	64
7	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	5	68
8	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	6	74
9	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	7	74
10	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	8	76
11	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	9	63
12	Ir(ppy)$_2$(PIB-ppy) (**3**)	MeCN/heptane at UCST	10	66

[a]Determined by GC-FID with diphenylmethane as internal standard. [b]Isolated yield. [c]Additional amount of product extracted from heptane phase after all catalysis runs.


80
60
40
20
0
Yield [%]
1
2
3
4
5
6
7
8
9
10
Run

5. Photoreactions in continuous flow

Literature conditions



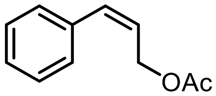
(*Z*)-3-phenylallyl acetate (16).

A Schlenk tube was charged with (*E*)-3-phenylallyl acetate (**15**, 176 mg, 1.00 mmol, 1.00 equiv), *fac*-Ir(ppy)$_3$ (4.6 mg, 7.0 µmol, 0.7 mol%), 5 mL MeCN, and ^{i}Pr$_2$NEt (17 µL, 13 mg, 0.10 mmol, 0.10 equiv), and sealed with a screw-cap. The reaction was degassed by N_2 sparging for 10 min and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED took place from above while the reaction was magnetically stirred below. After 4 h of irradiation the LED was switched off, the reaction mixture was analyzed by GC-FID and ^{1}H-NMR showing a *Z*:*E* ratio of 82:18 with both analysis techniques. ^{1}H NMR (*Z* isomer, 300 MHz, CDCl$_3$): 7.24 – 6.98 (m, 5H), 6.47 (d, J = 11.7 Hz, 1H), 5.66 – 5.55 (m, 1H), 4.65 – 4.58 (m, 2H), 1.85 (s, 3H).

The reaction was repeated as above at 90 °C. GC-FID of the reaction mixture again showed a *Z*:*E* ratio of 82:18.

The reaction was repeated as above at 90 °C with with 2.5 mL MeCN as solvent and 2.5 mL heptane as co-solvent. Ir(ppy)$_2$(PIB-ppy) (**3**, 11.8 mg, 7.0 µmol, 0.7 mol%) was used instead of *fac*-Ir(ppy)$_3$. Phases were separated after the reaction. GC-FID of the MeCN phase again showed a *Z*:*E* ratio of 82:18.

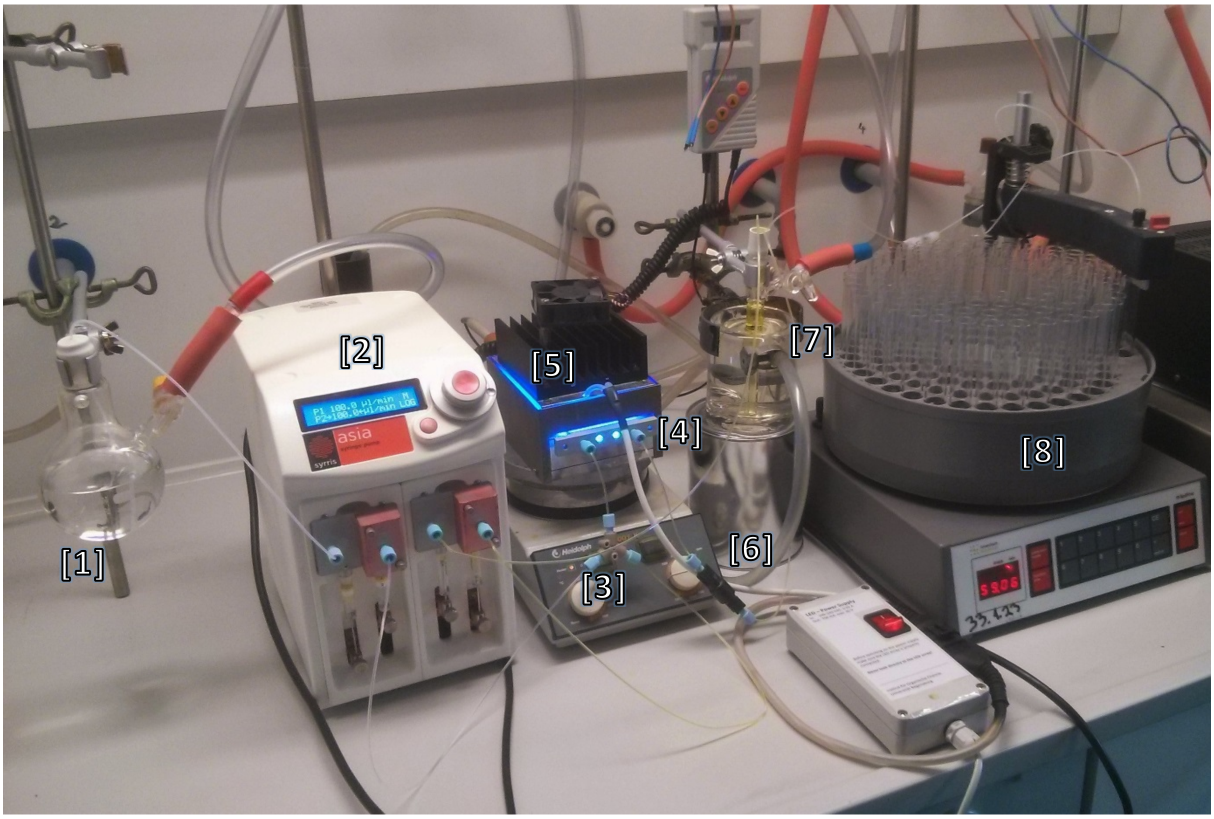
Recycling conditions



(*Z*)-3-phenylallyl acetate (16).

Note: Numbers in brackets represent the corresponding device in the picture.

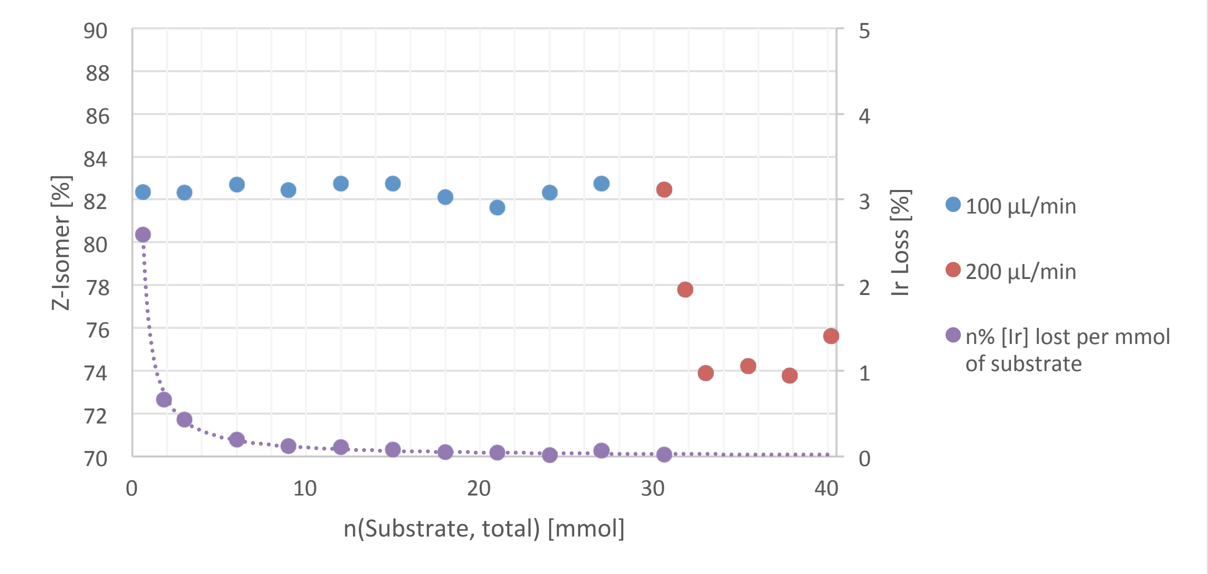
A Schlenk flask [1] was charged with (*E*)-3-phenylallyl acetate (**15**, 7.04 g, 40.0 mmol, 1.00 equiv), 190 mL MeCN (heptane saturated)*, 10 mL heptane**, and $^{i}Pr_2NEt$ (0.70 mL, 0.52 g, 4.0 mmol, 0.10 equiv). The reaction was degassed by N_2 sparging for 15 min. A Schlenk tube was charged with $Ir(ppy)_2(PIB\text{-}ppy)$ (**3**, 11.8 mg, 7.0 µmol, 0.018 mol%) and 5 mL heptane and the mixture was degassed by N_2 sparging for 5 min. The complete microreactor setup was purged with N_2 for 15 min.



The substrate solution [1] was connected to the Asia dual syringe pump system [2] and the photocatalyst solution was transferred to the phase separator unit [7]. The heptane syringe pump was started (100 µL/min) and thus the microreactor unit [4] was filled with catalyst solution. The microreactor unit [4] was heated and once it reached 90 °C, the LED array [5] and the MeCN syringe pump were turned on (100 µL/min), heptane and MeCN stream mixed [3] and were subsequently pumped through the hot microreactor unit [4]. In there, the hepatane / MeCN reached the upper critical solution temperature (UCST) and thus the mixture became homogeneous. To avoid boiling of the solvent mixture a 60 psi pressure valve [6] was connected to the output of the microreactor unit. After about 3 mL of product-containing MeCN were collected in the phase separator unit [7], the N_2

valve of the phase separator unit was closed which triggered collection of the product-containing MeCN phase in the fraction collector [8]. The collected fractions (pooling rate 30 min, 3.0 mL MeCN, 0.60 mmol product) were analyzed by GC-FID to determine the *Z*:*E* ratio and afterwards by ICP-OES to determine the iridium content.

For the ICP-OES analysis (*properly working fume hood, full protection gear!*) the solvent of each sample was evaporated in a stream of N_2 and the residue was treated with 2 mL conc HNO_3 (aq), boiled for about 1 min till the evolution of nitrous gases stopped. Afterwards the sample was treated with 2 mL conc H_2SO_4 and again boiled till the evolution of nitrous gases stopped (about 1 min). The sample was then treated with another 2 mL conc HNO_3 (aq) and boiled until it was a fully homogeneous yellow to orange liquid (about 2 min). After cooling to room temperature, the sample was diluted with water to a total volume of 8.0 mL, filtered through a 0.2 µm syringe filter, and measured in the ICP-OES apparatus.

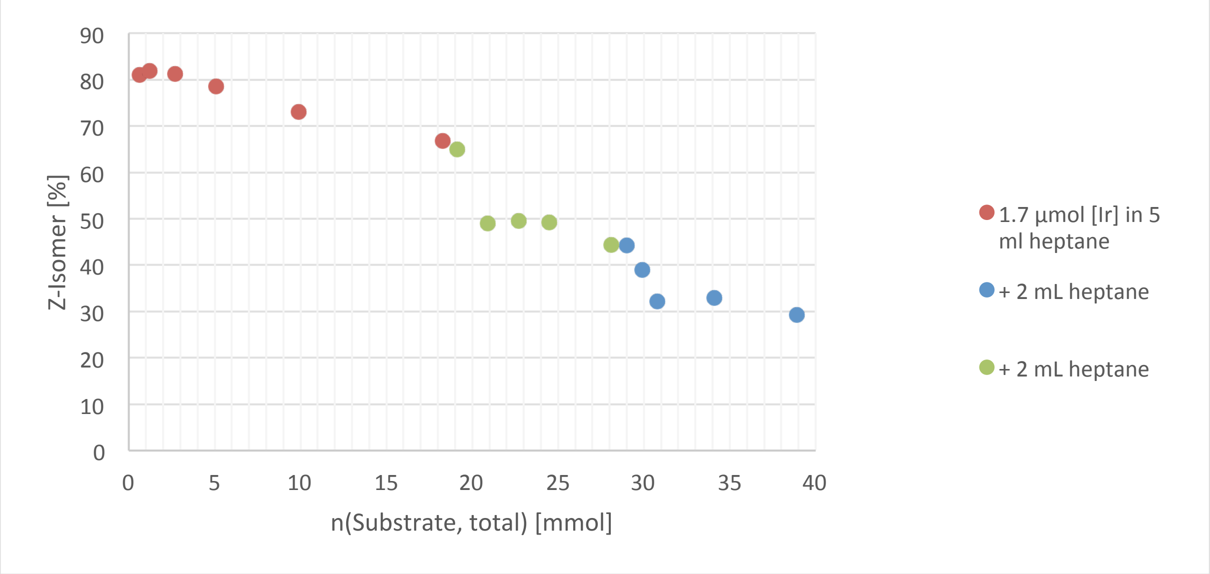


*Heptane saturated MeCN has to be used in order to avoid unnecessary leaching of heptane into the collected MeCN fractions, caused by minimal solubility of heptane in MeCN.

Additionally, the addition of (*E*)-3-phenylallyl acetate (15**, 0.2 M) and $^{i}Pr_2NEt$ (0.02 M) to already heptane saturated MeCN leads to an increased solubility of heptane which has to be addressed by the addition of further quantities of heptane to the substrate solution before starting the reaction.

When the reaction setup was run as above with only 2.9 mg Ir(ppy)$_2$(PIB-ppy) (**3**, 1.7 µmol) instead of with 11.8 mg Ir(ppy)$_2$(PIB-ppy) (**3**, 7.0 µmol), a relative severe decline of the *Z*:*E* ratio can be observed after already 3 mmol of converted substrate.

Also, in this experiment the increased solubility of heptane in the reaction solution was not addressed. The lost heptane had to be replaced two times during the experiments with 2 mL heptane each. The so-caused dilution of the catalyst solution lead to two erratic drops in *Z*:*E* ratio.



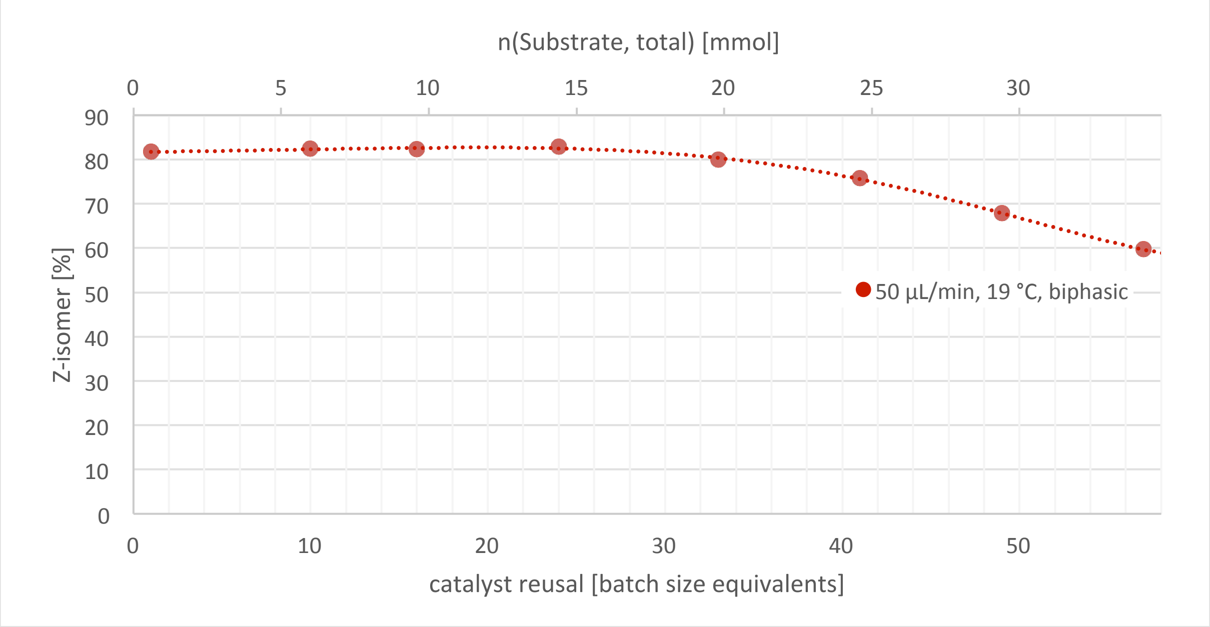
The photoisomerization of (*E*)-3-phenylallyl acetate (**15**) could also be performed at ambient temperatures. The microreactor system was set up as above. Instead of heating to 90 °C, the microreactor was hold at a constant temperature of 19 °C through a water cooling system. The flowrate of substrate solution and catalyst solution was set to 50 µL/min.

Chemicals used:

Substrate solution: (*E*)-3-phenylallyl acetate (**15**, 7.04 g, 40.0 mmol, 1.00 equiv), 190 mL MeCN (heptane saturated), 10 mL heptane, and ^{i}Pr$_2$NEt (0.70 mL, 0.52 g, 4.0 mmol, 0.10 equiv).

Catalyst solution: Ir(ppy)$_2$(PIB-ppy) (**3**, 7.0 mg, 4.17 µmol, 0.0104 mol%) and 3 mL heptane.

In the following chart the (*Z*) isomer percentage is depicted relative to the amount of collected substrate and relative to the number of catalyst reusals as compared to the literature reported batch conditions.



6. References

(1) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 6th ed.; Butterworth-Heinemann: Oxford, 2009.

(2) Li, J.; Sung, S.; Tian, J.; Bergbreiter, D. E. *Tetrahedron* **2005**, *61* (51), 12081.

(3) Rao, X.; Liu, C.; Qiu, J.; Jin, Z. *Org. Biomol. Chem.* **2012**, *10* (39), 7875.

(4) Kottas, G.; Ansari, N.; Elshenawy, Z.; Deangelis, A.; Xia, C. Heteroleptic Irdidium Complexes as Dopants. EP2551933A1, 2013.

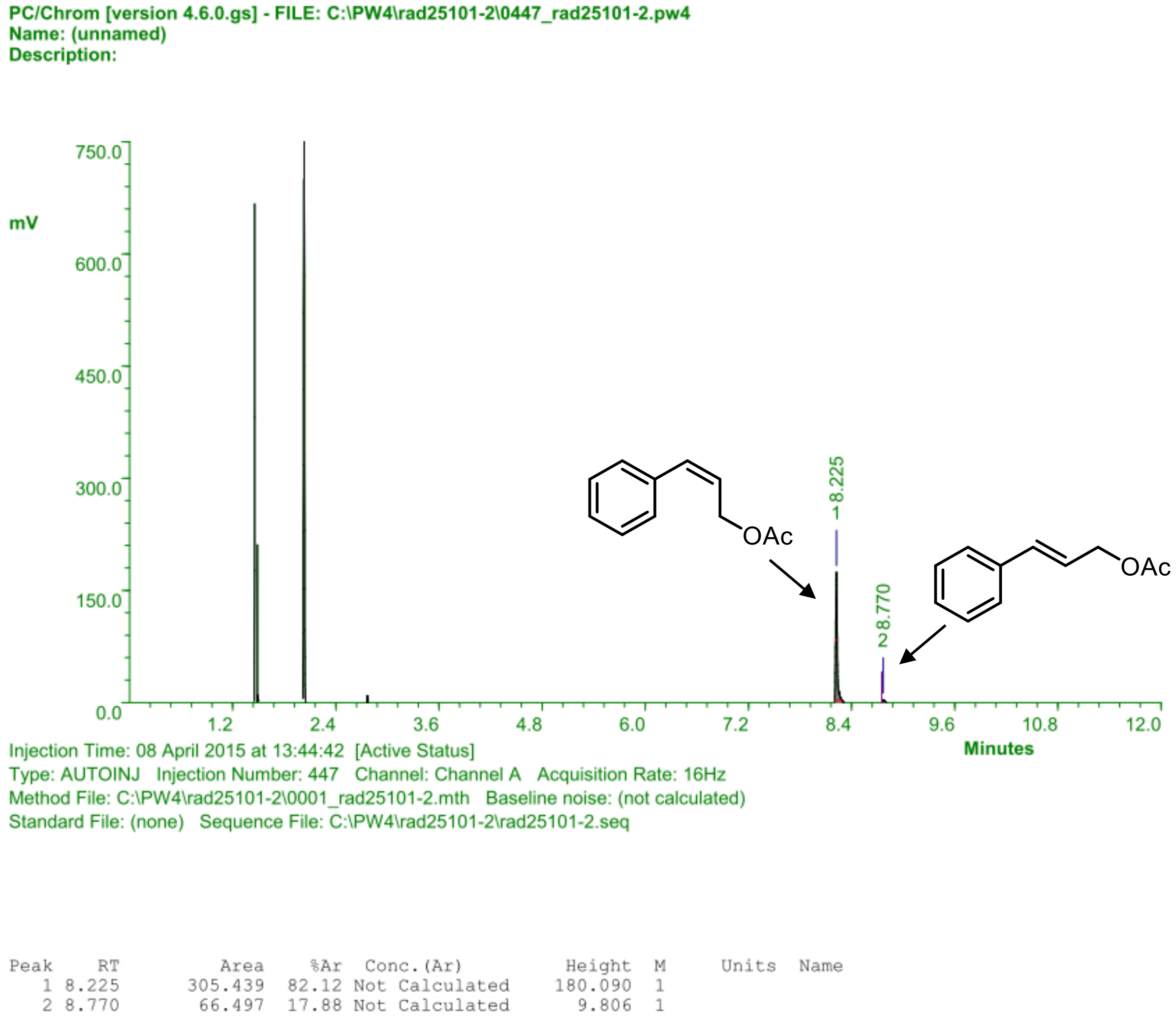
(5) Nguyen, J. D.; D'Amato, E. M.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2012**, *4* (10), 854.

(6) Ueng, S.-H.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. *Org. Biomol. Chem.* **2011**, *9*, 3415.

(7) Murphy, J. A.; Khan, T. A.; Zhou, S.-Z.; Thomson, D. W.; Mahesh, M. *Angew. Chem. Int. Ed.* **2005**, *44* (9), 1356.

7. GC-FID analysis

An example GC-FID spectrum of the reaction mixture of the photochemical *E*/*Z* isomerization of (*Z*)-3-phenylallyl acetate (**16**) is depicted below.



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Description:
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Type: AUTOINJ   Injection Number: 447   Channel: Channel A   Acquisition Rate: 16Hz
Method File: C:\PW4\rad25101-2\0001_rad25101-2.mth   Baseline noise: (not calculated)
Standard File: (none)   Sequence File: C:\PW4\rad25101-2\rad25101-2.seq
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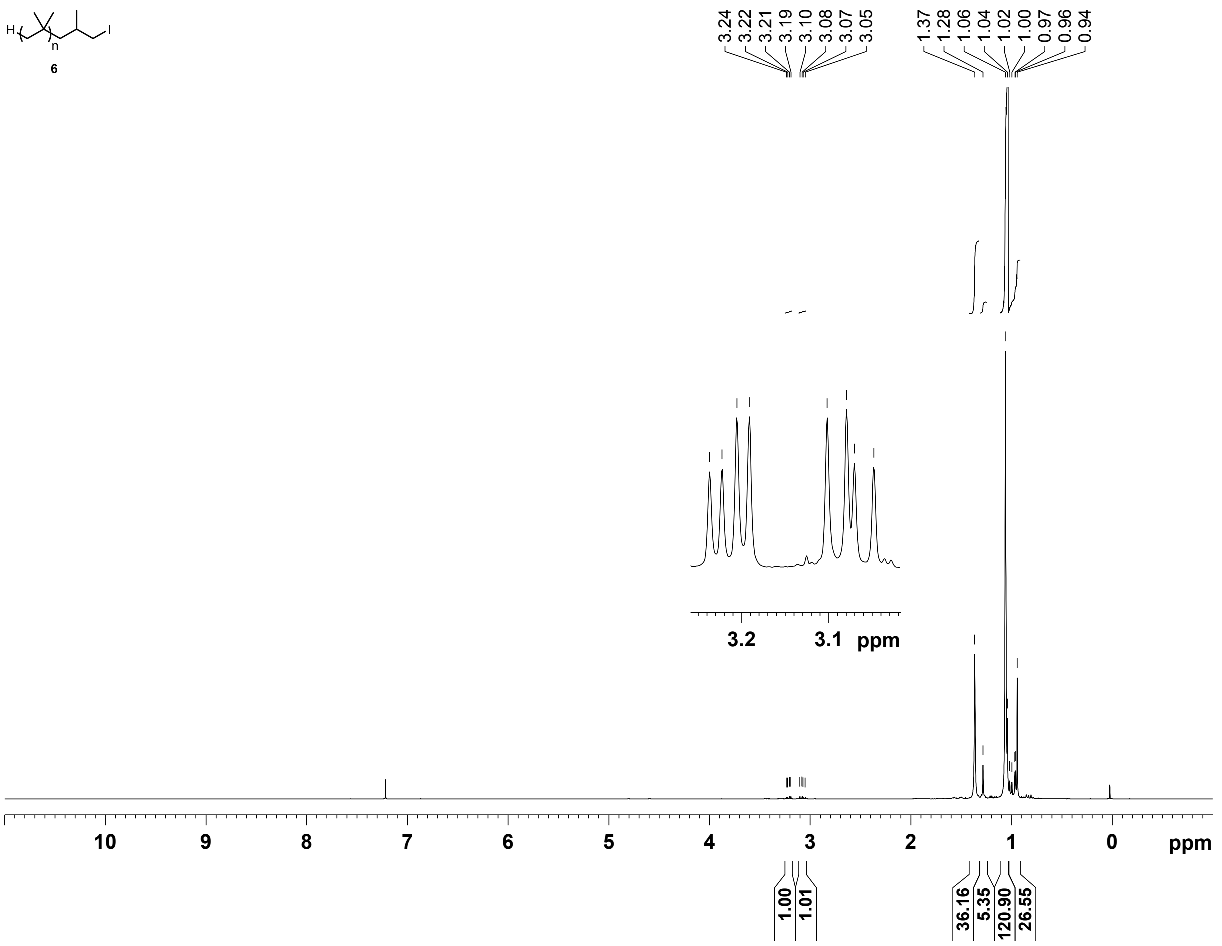
   2 8.770       66.497   17.88 Not Calculated      9.806  1
```

Analysis were carried out using following temperature program:

Starting temperature:	75 °C
Hold:	1 min
Heating rate:	15 °C/min
End temperature:	240 °C

8. NMR spectra of new compounds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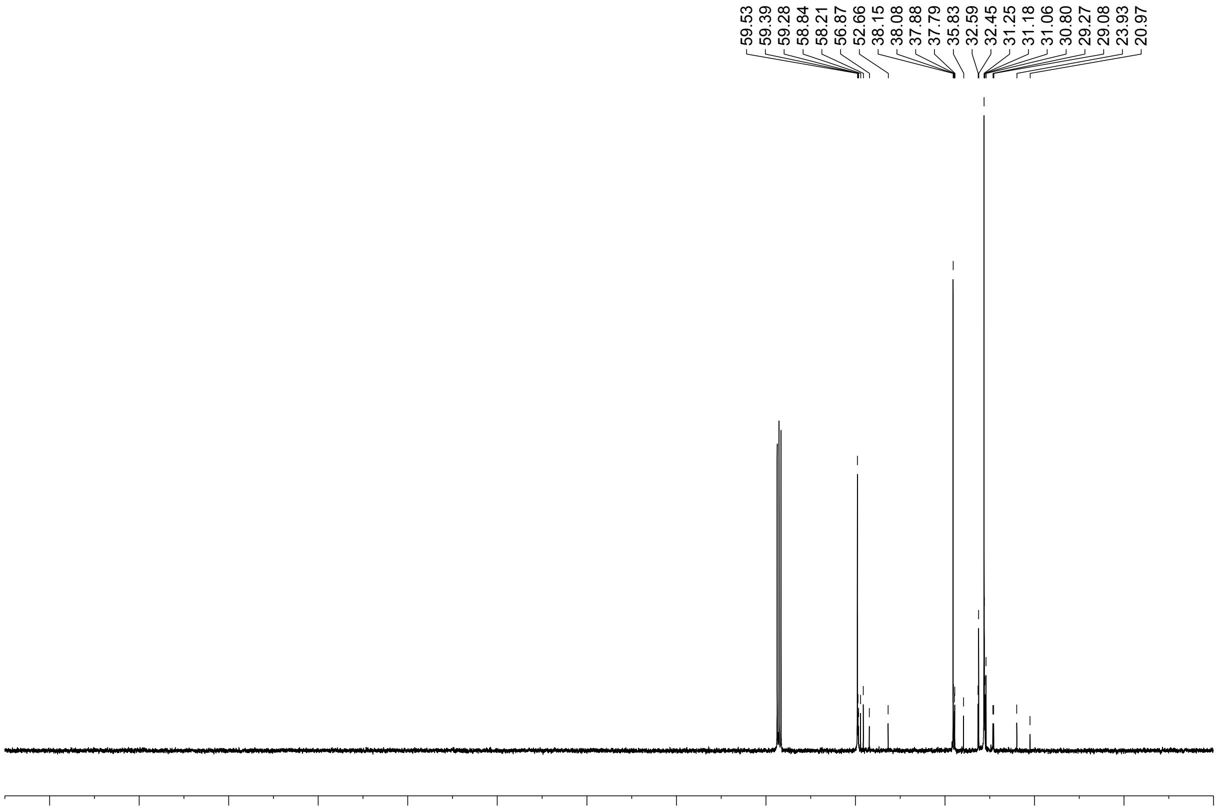
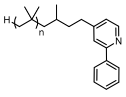
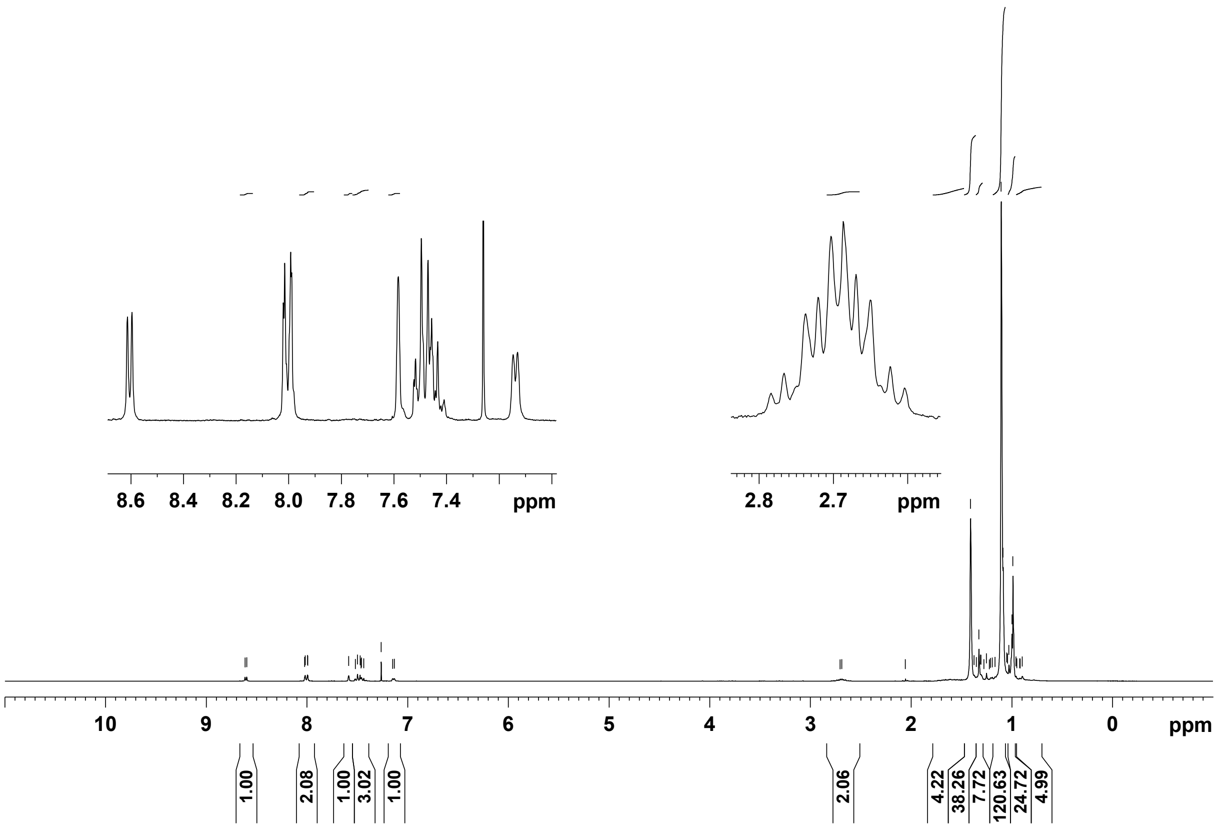



H
n
N

6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7.15
7.13
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2.69
2.06
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1.37
1.35
1.33
1.31
1.30
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1.21
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1.05
1.04
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ppm
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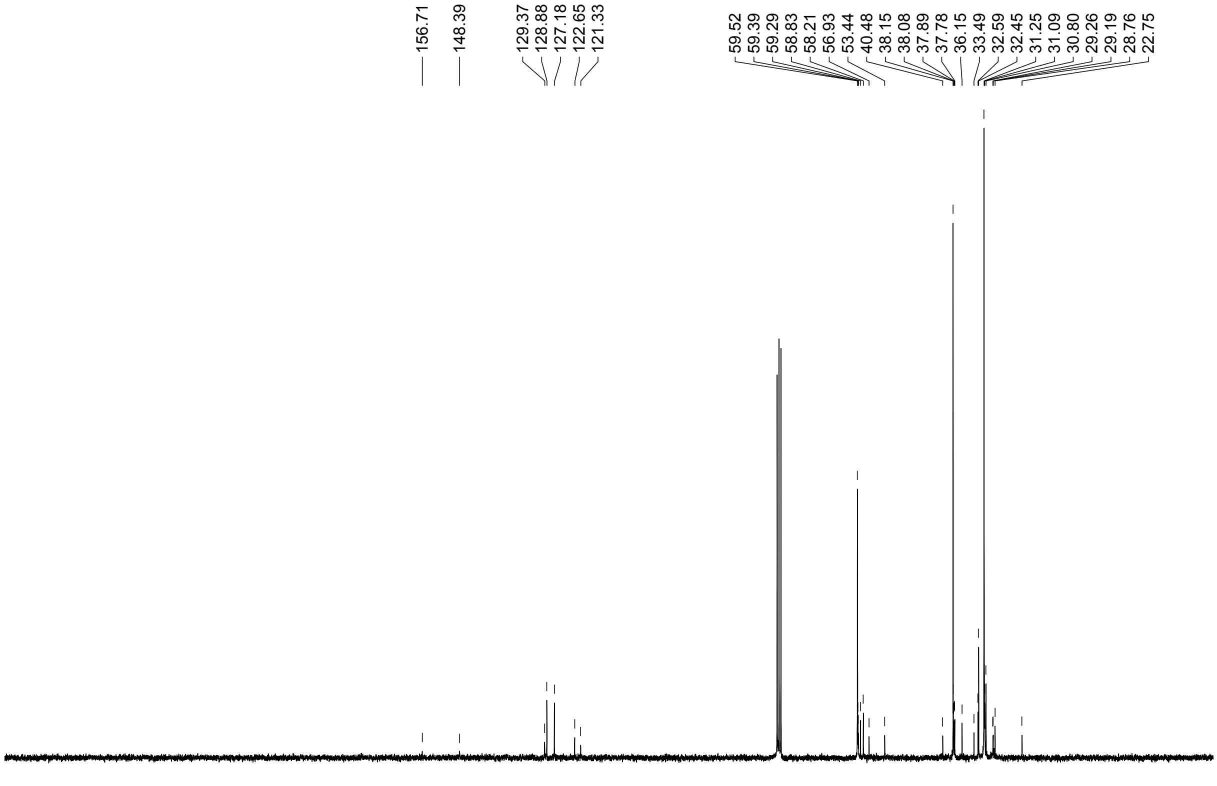
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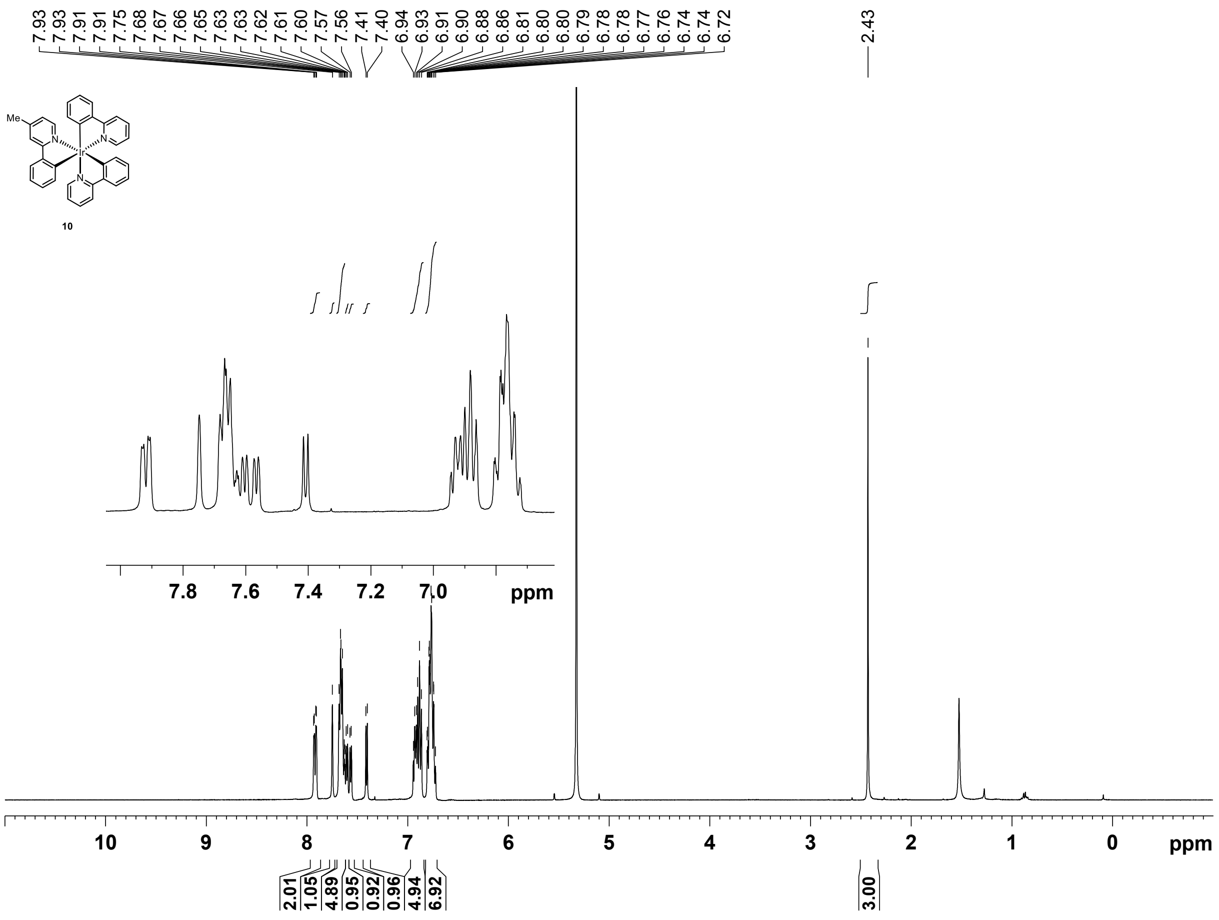
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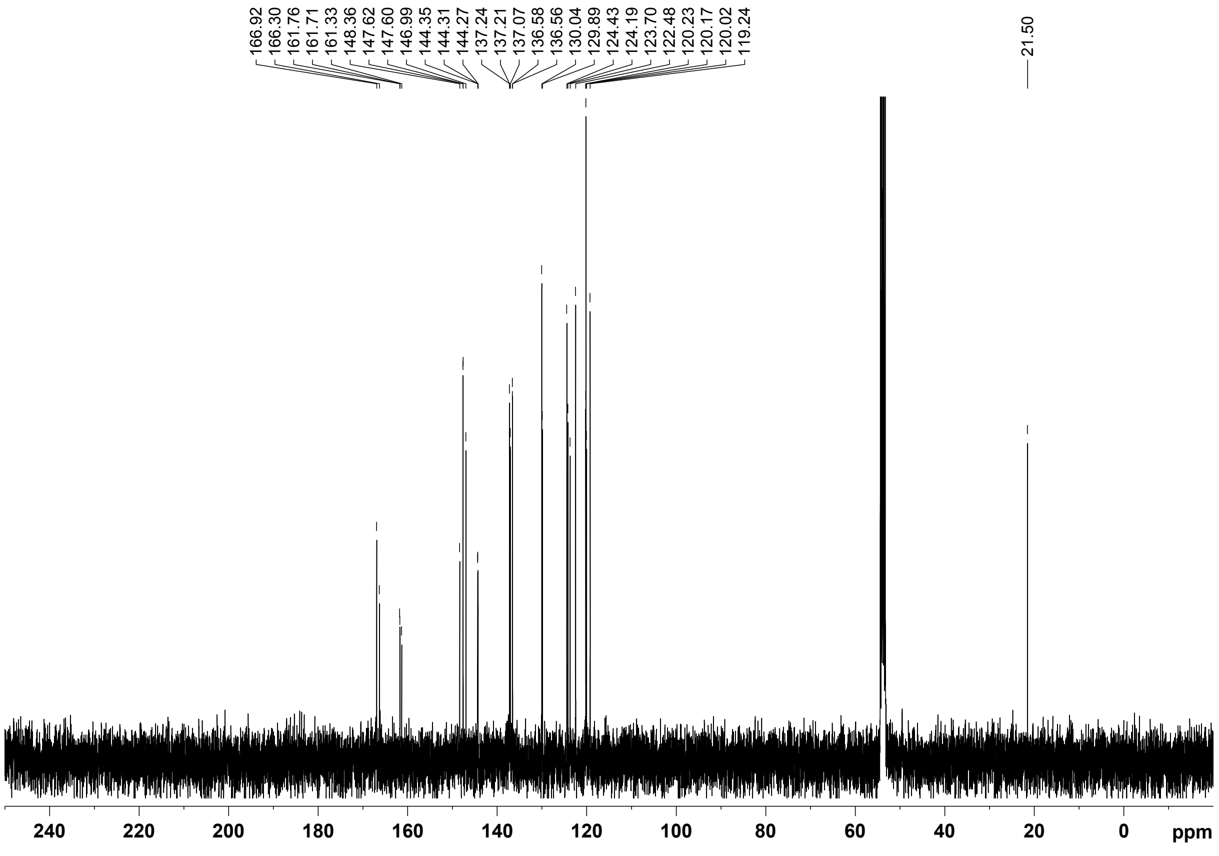
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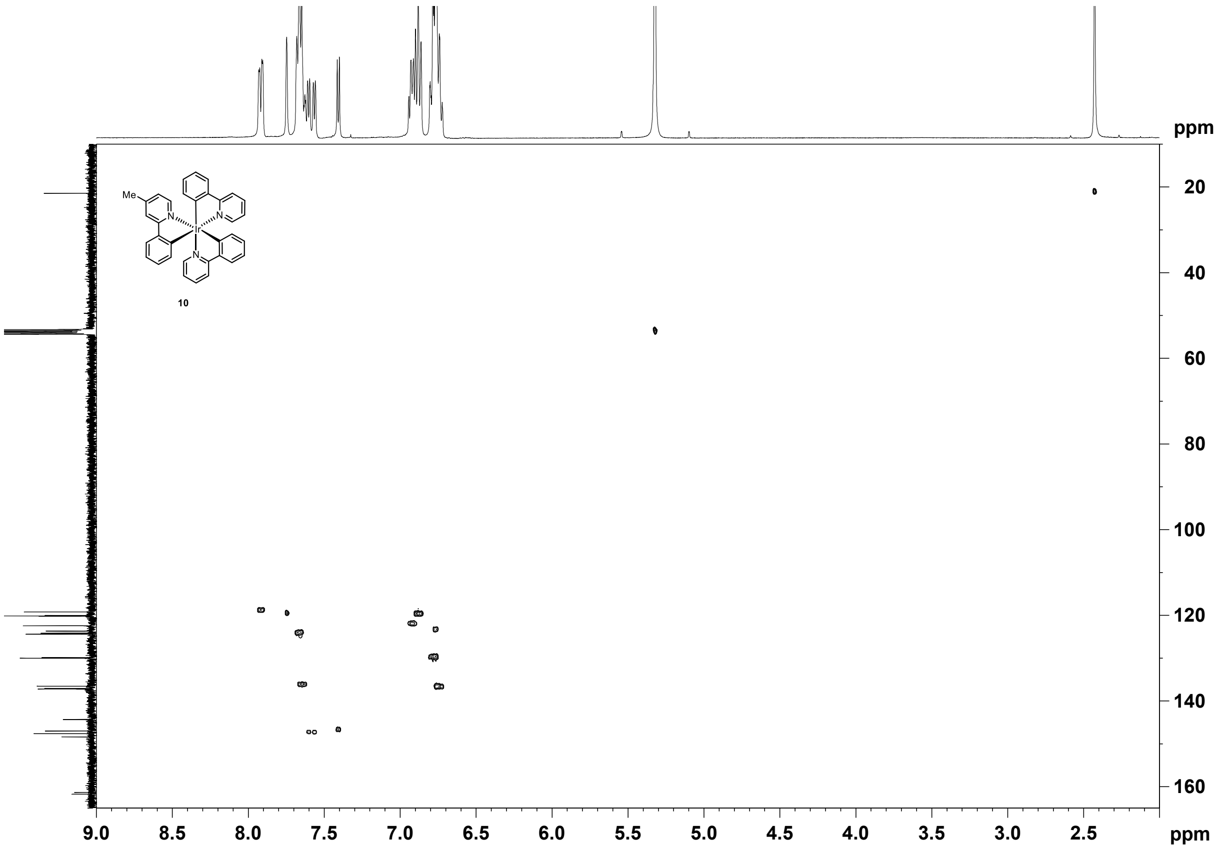
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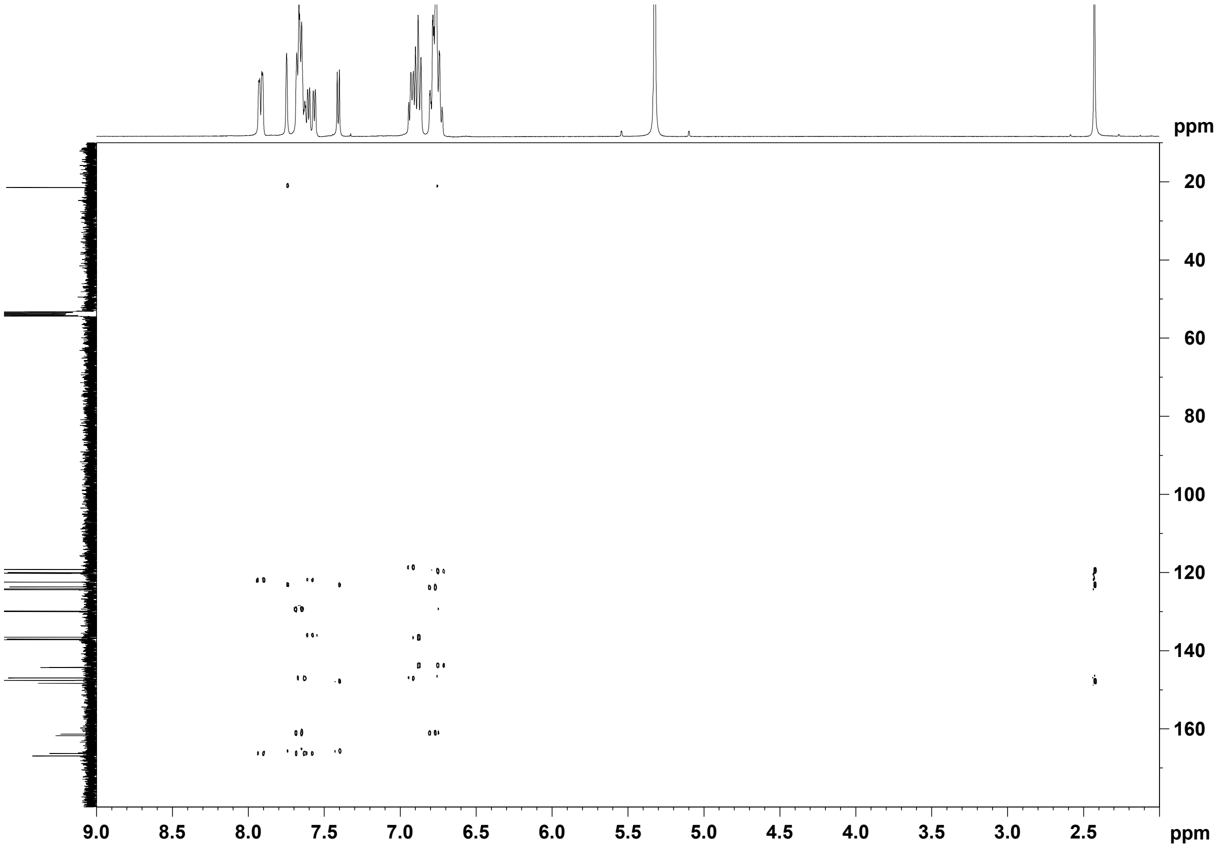
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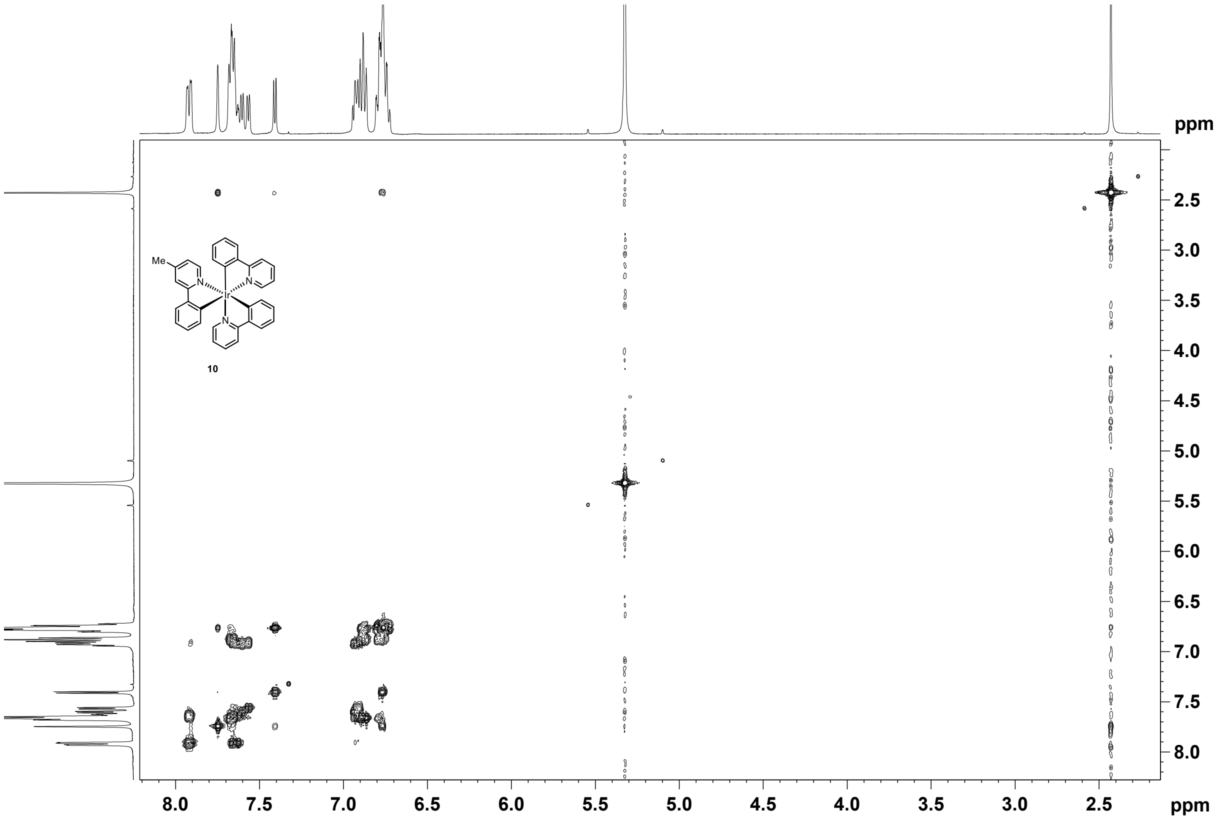
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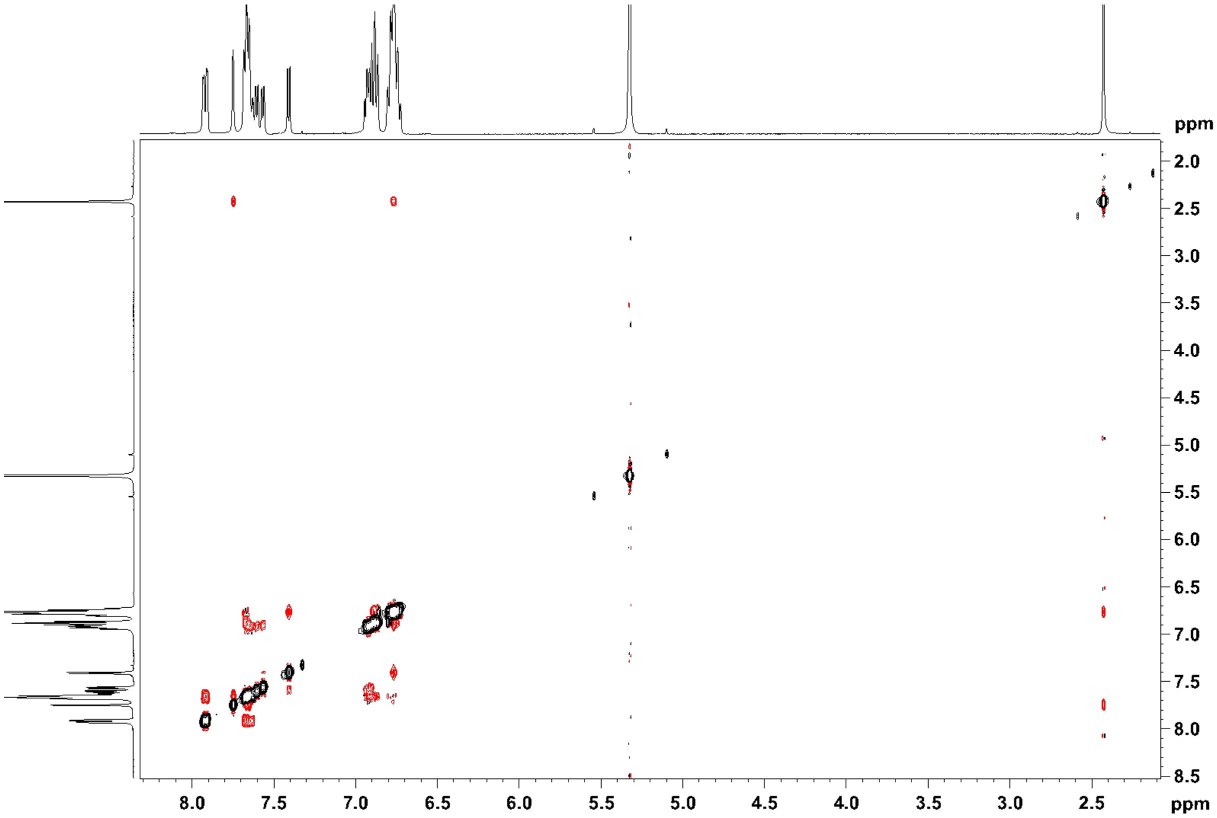
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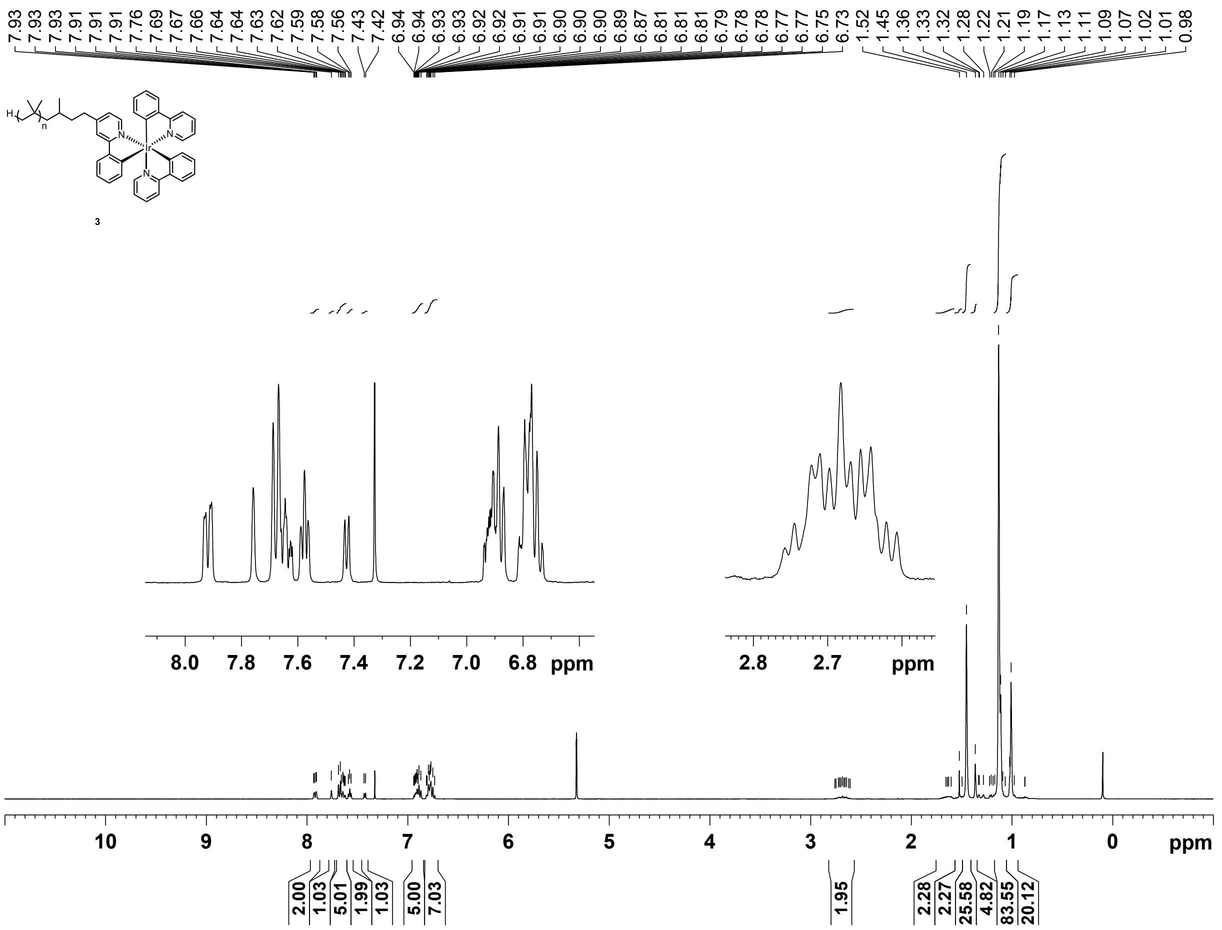
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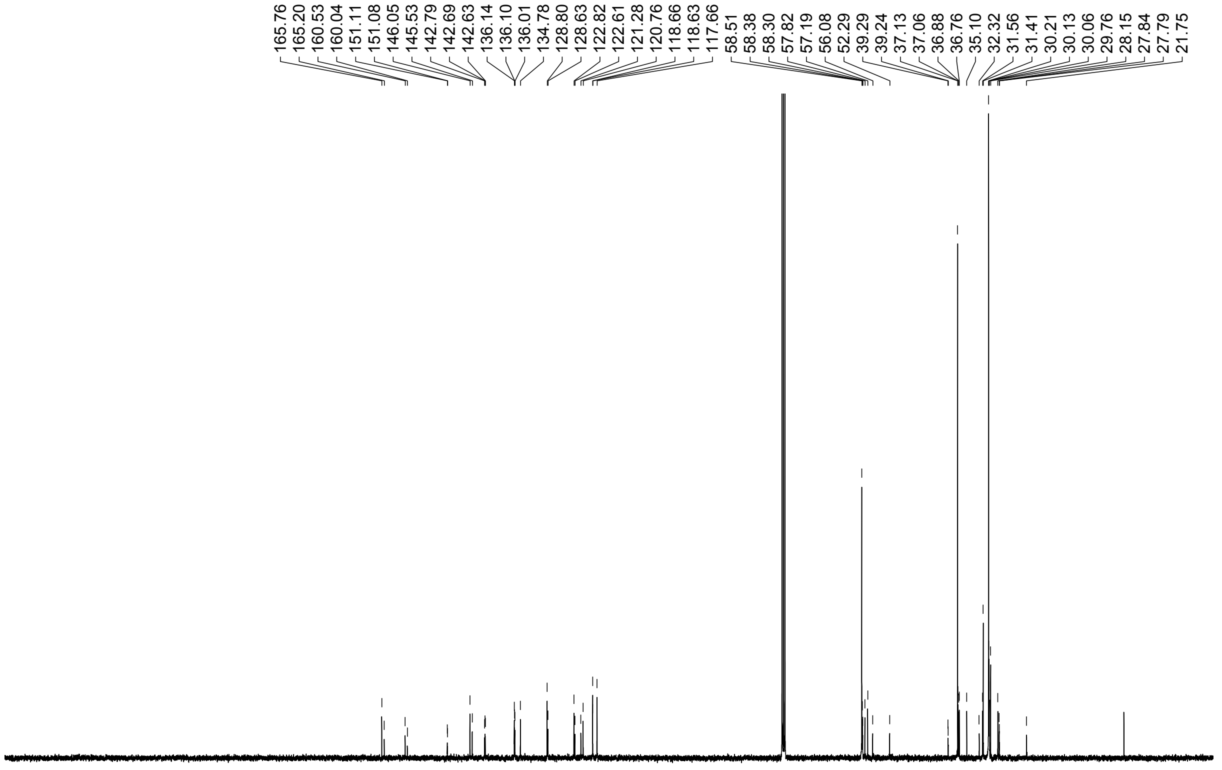
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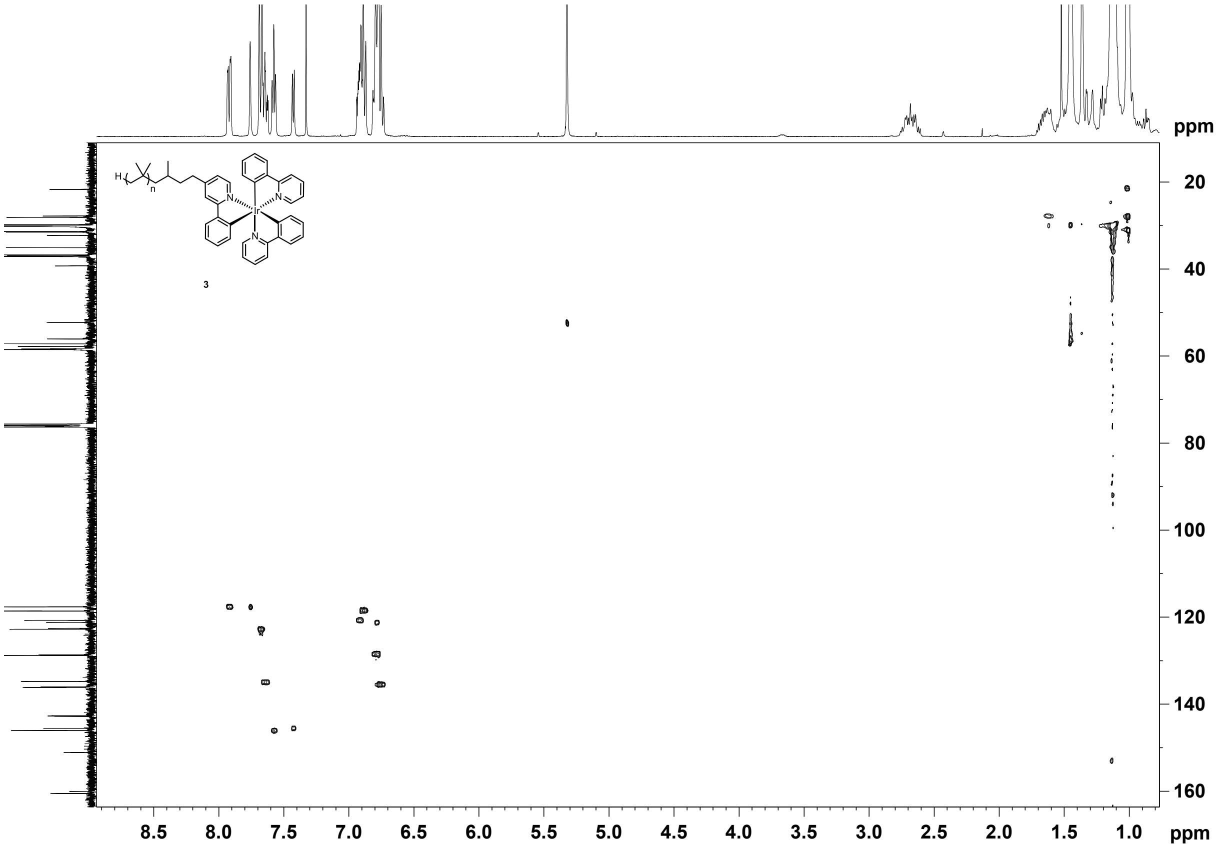

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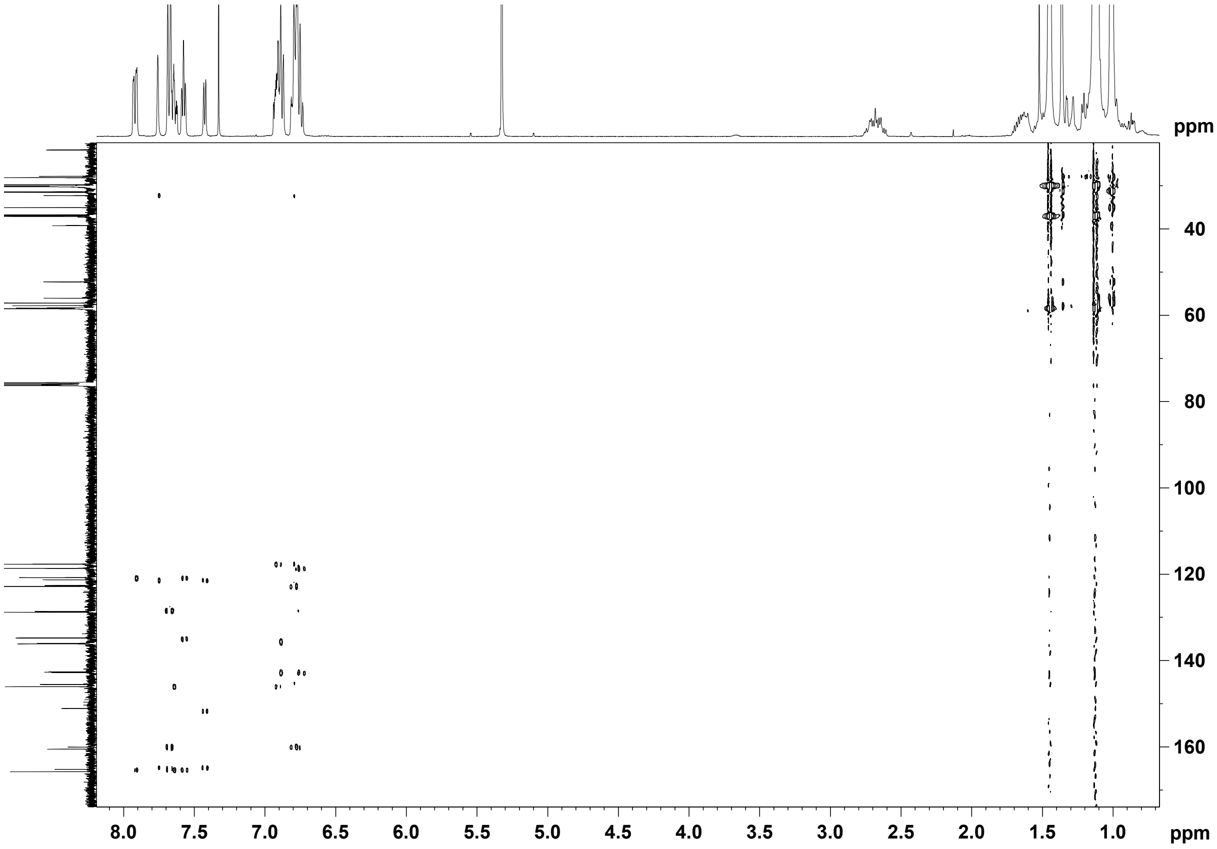
ppm



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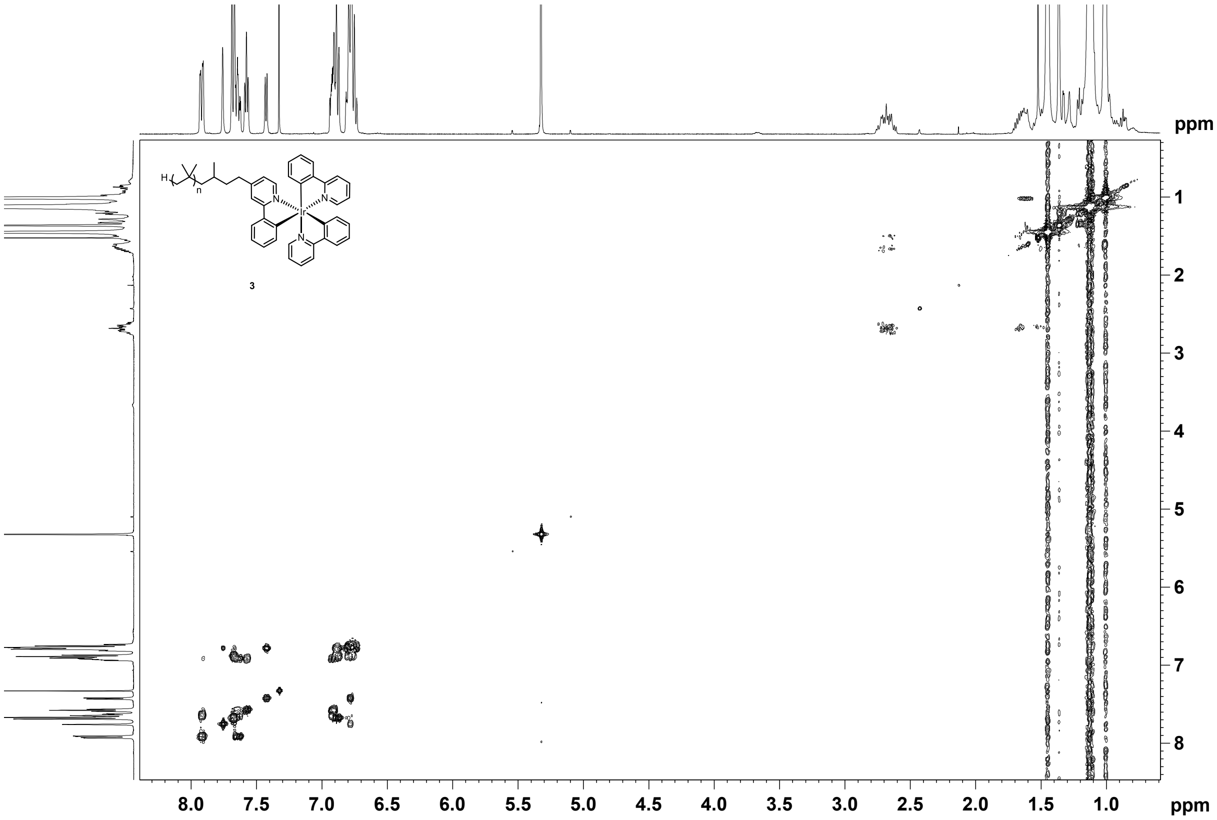
ppm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Ir
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1.0
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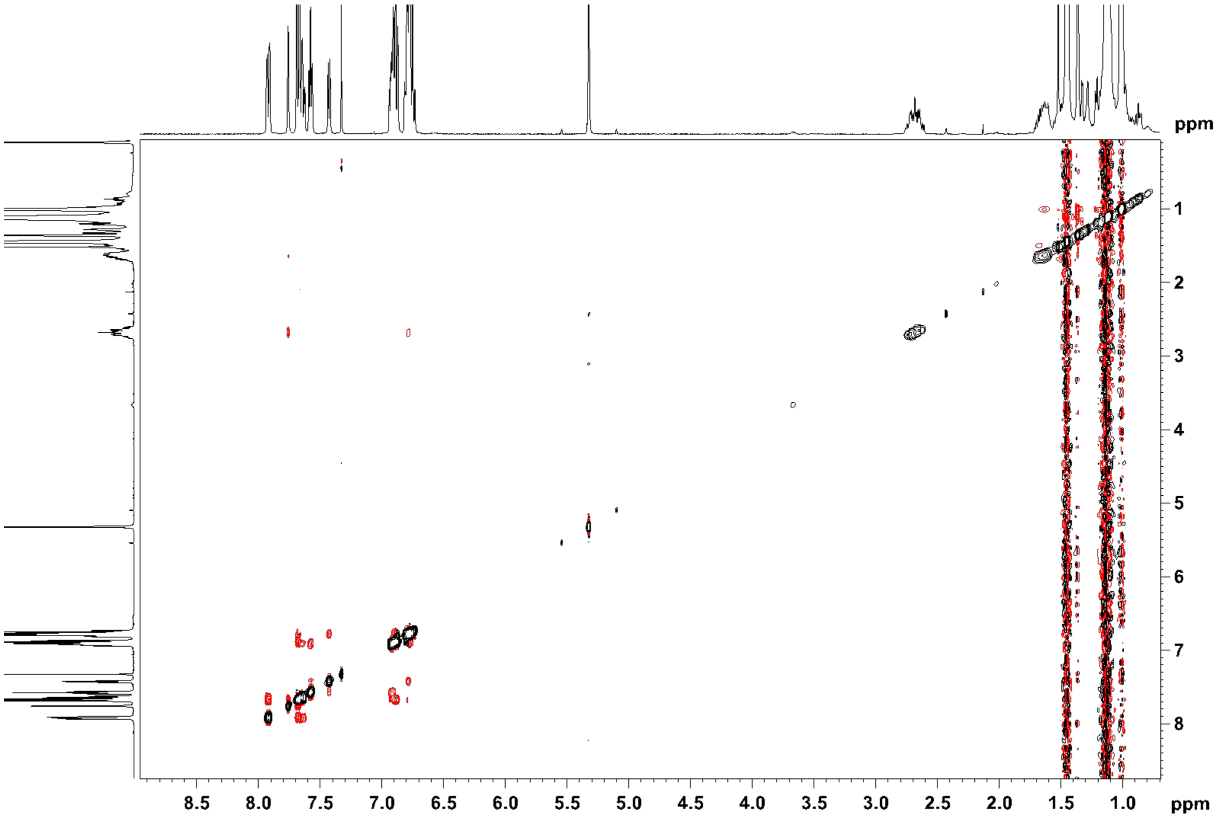
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5.0
4.5
4.0
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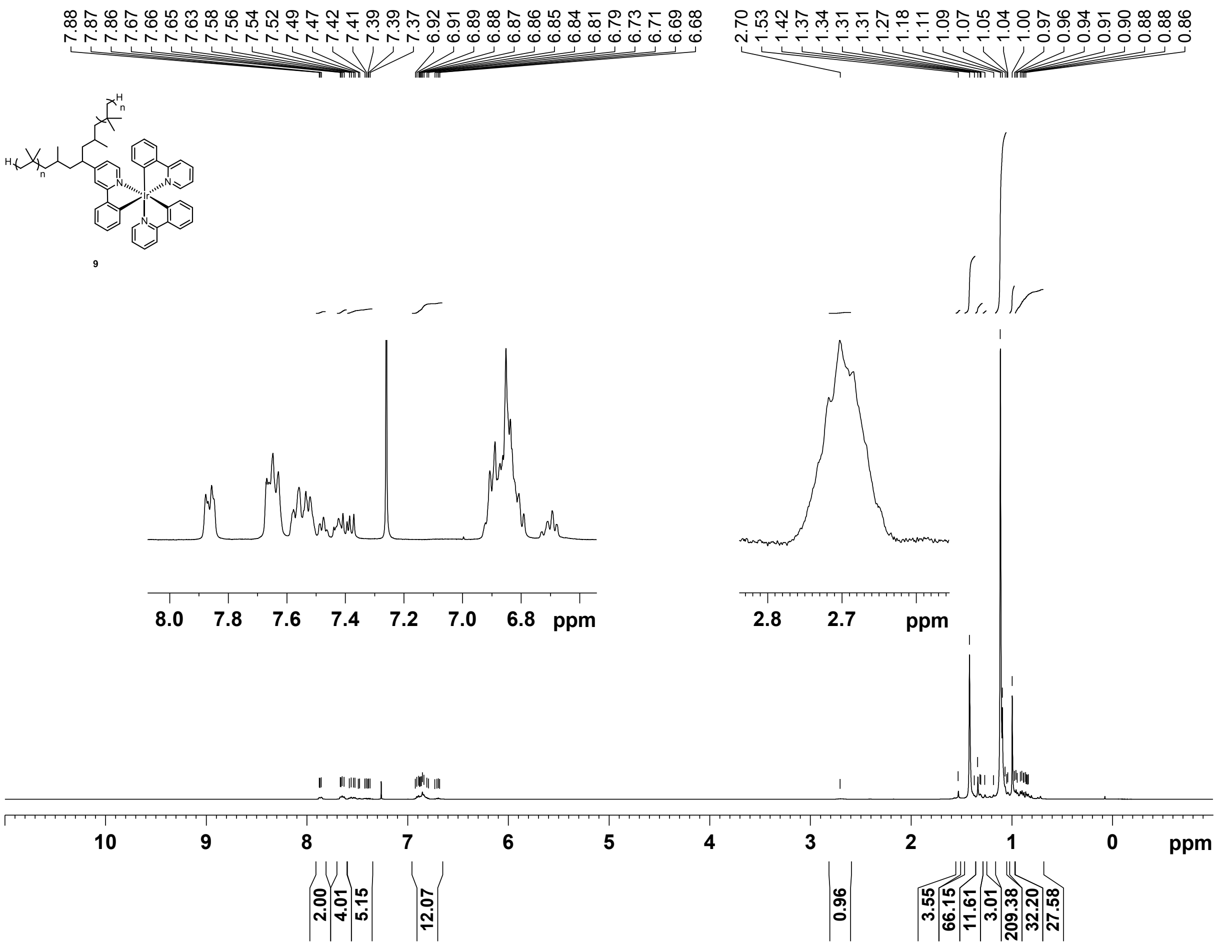
2.0
1.5
1.0
ppm

H
n
N
Ir
N
N
H
n

9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7.42
7.41
7.39
7.39
7.37
6.92
6.91
6.89
6.88
6.87
6.86
6.85
6.84
6.81
6.79
6.73
6.71
6.69
6.68
2.70
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1.42
1.37
1.34
1.31
1.31
1.27
1.18
1.11
1.09
1.07
1.05
1.04
1.00
0.97
0.96
0.94
0.91
0.90
0.88
0.88
0.86
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7.4
7.2
7.0
6.8
ppm
2.8
2.7
ppm
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9
8
7
6
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3
2
1
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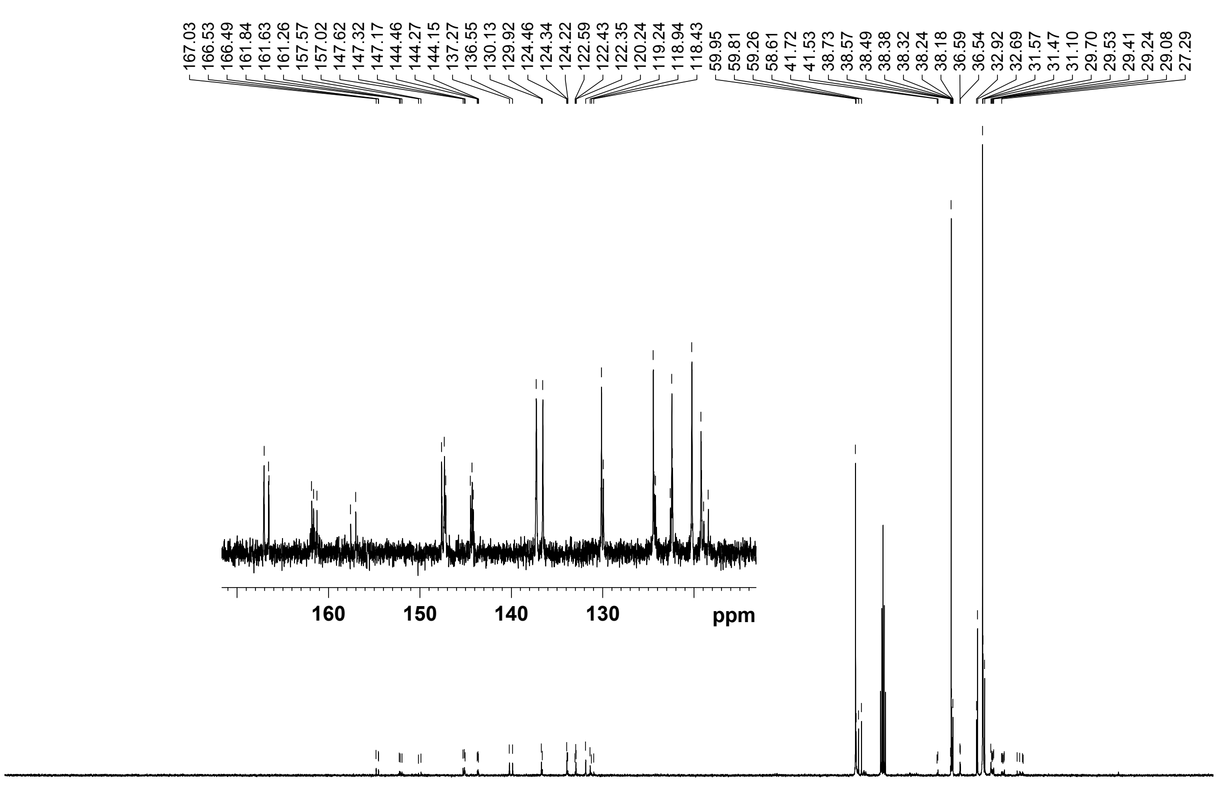
27.58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124.34
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58.61
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38.24
38.18
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36.54
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31.57
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31.10
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29.53
29.41
29.24
29.08
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ppm
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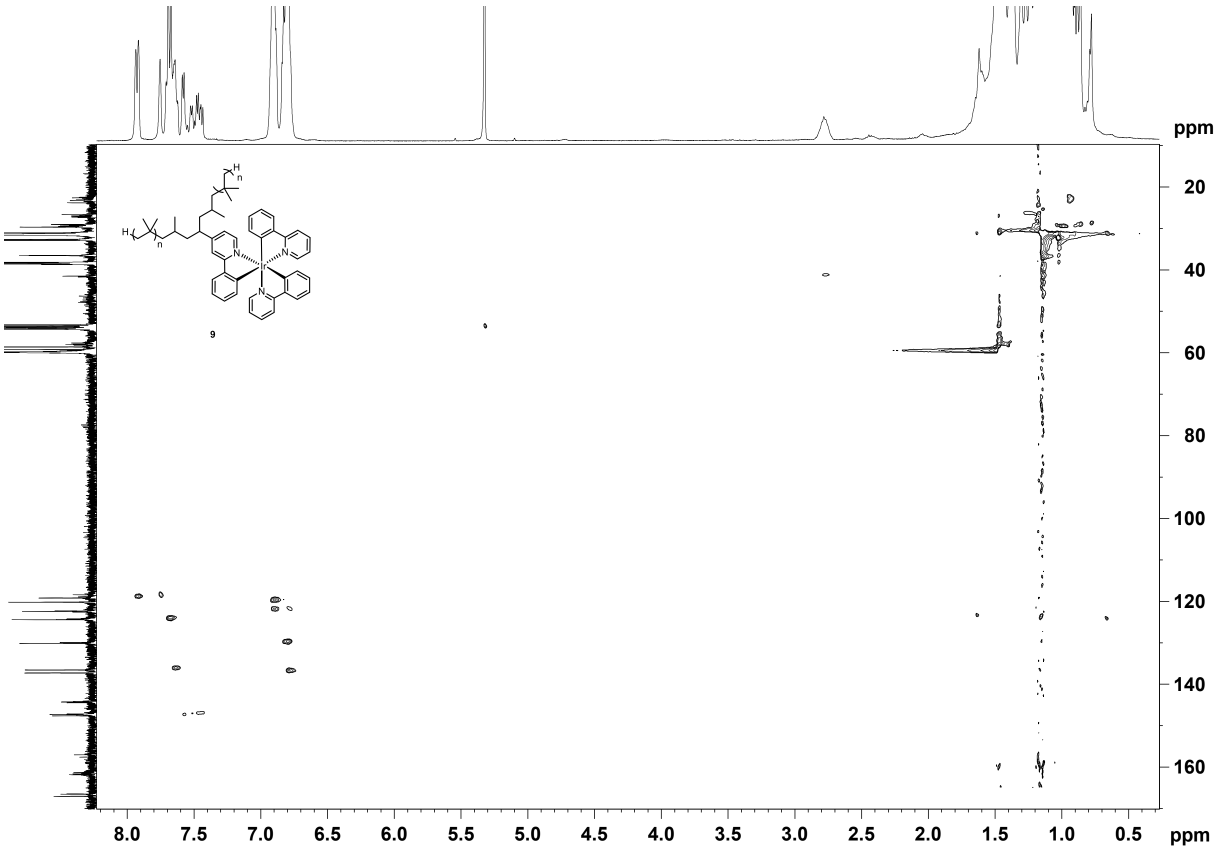
9
ppm
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1.0
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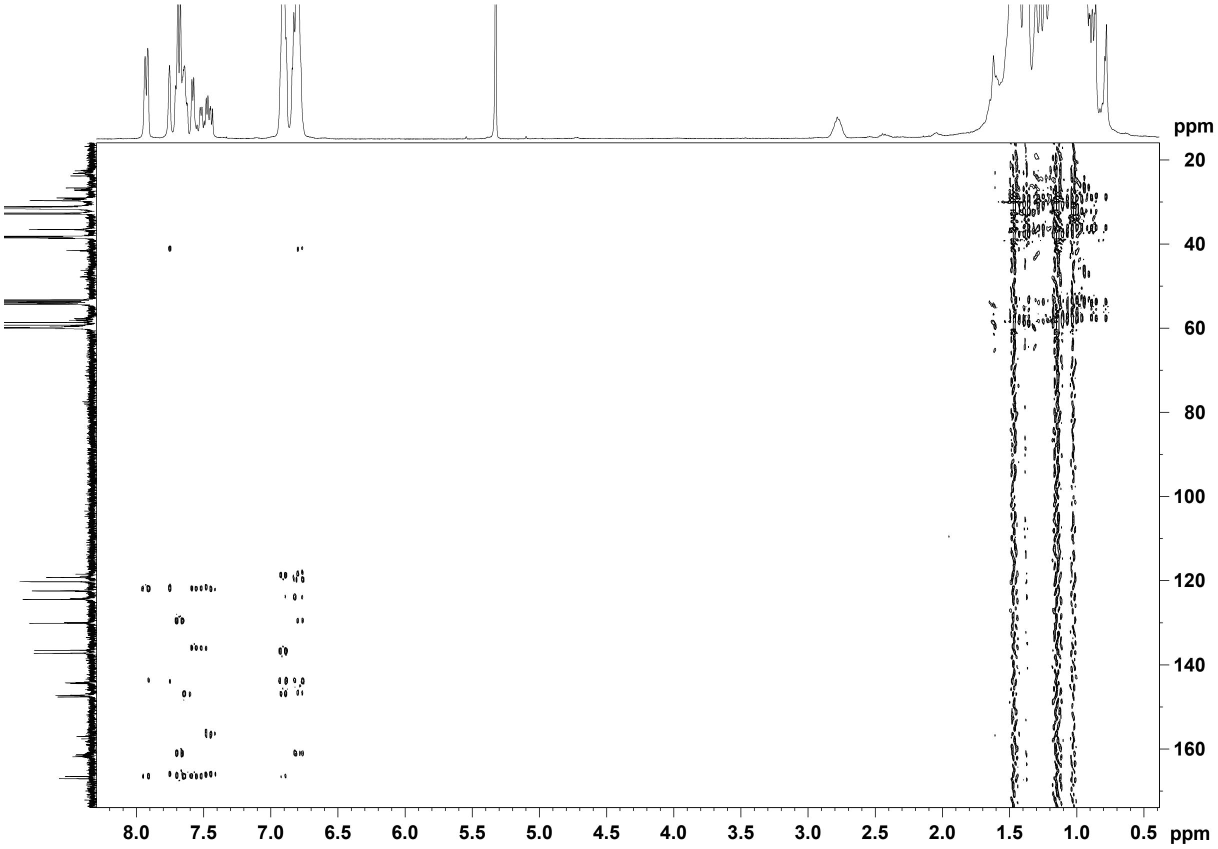
ppm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4.5
4.0
3.5
3.0
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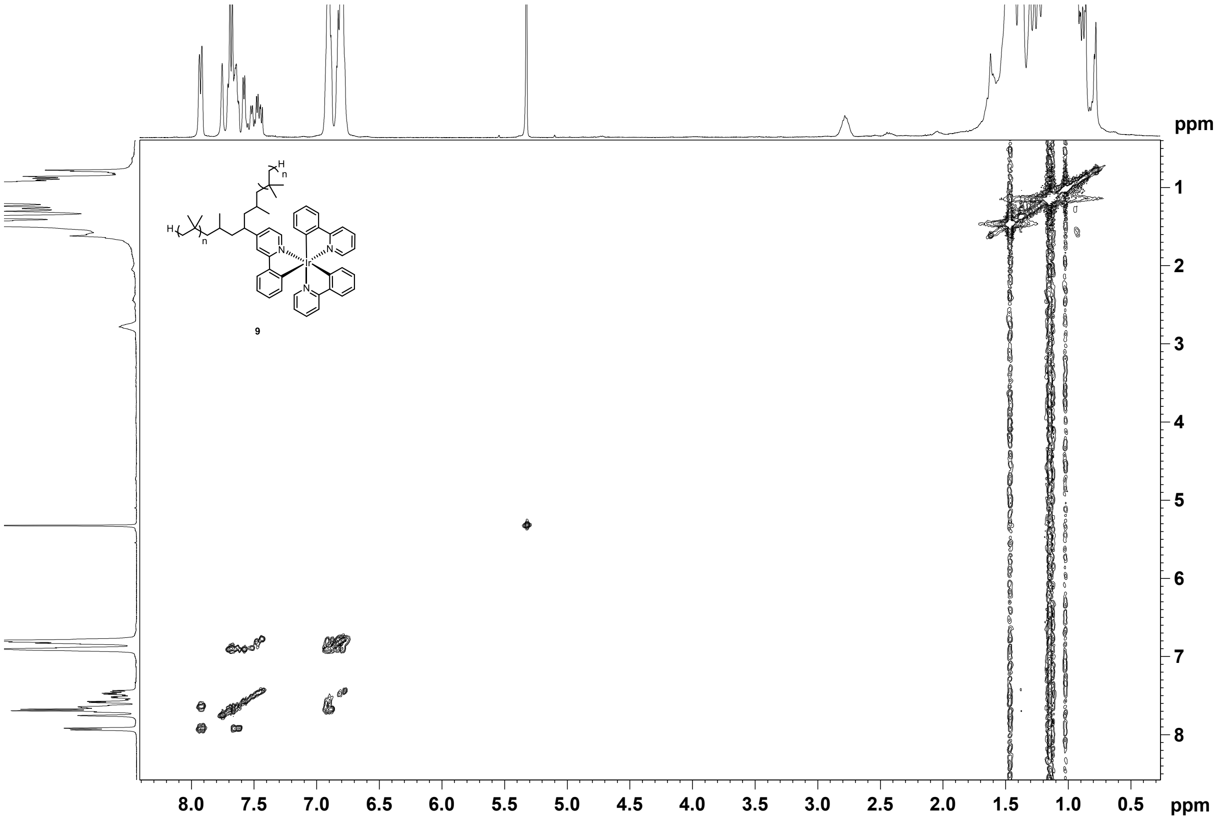
2.0
1.5
1.0
0.5
ppm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8
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7.0
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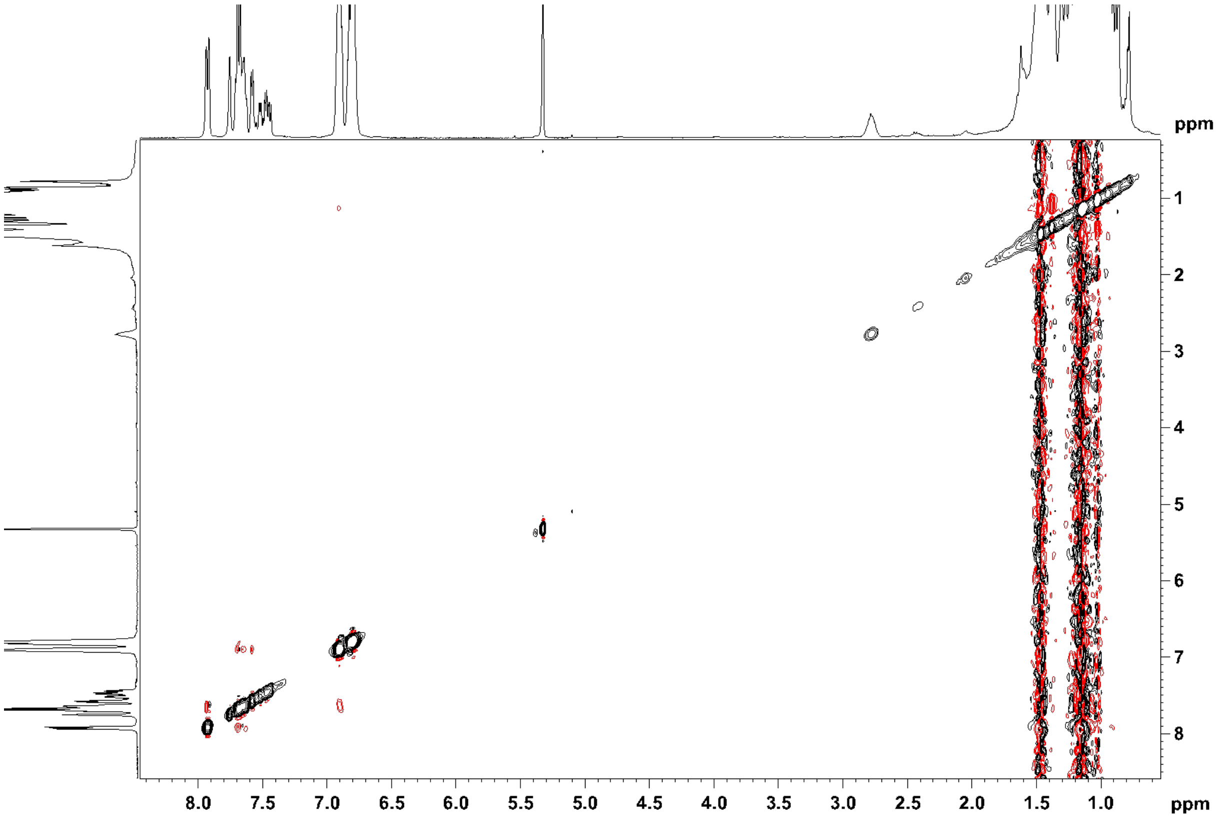
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
H
n
H
n
N
N
N
9


ppm
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7.0
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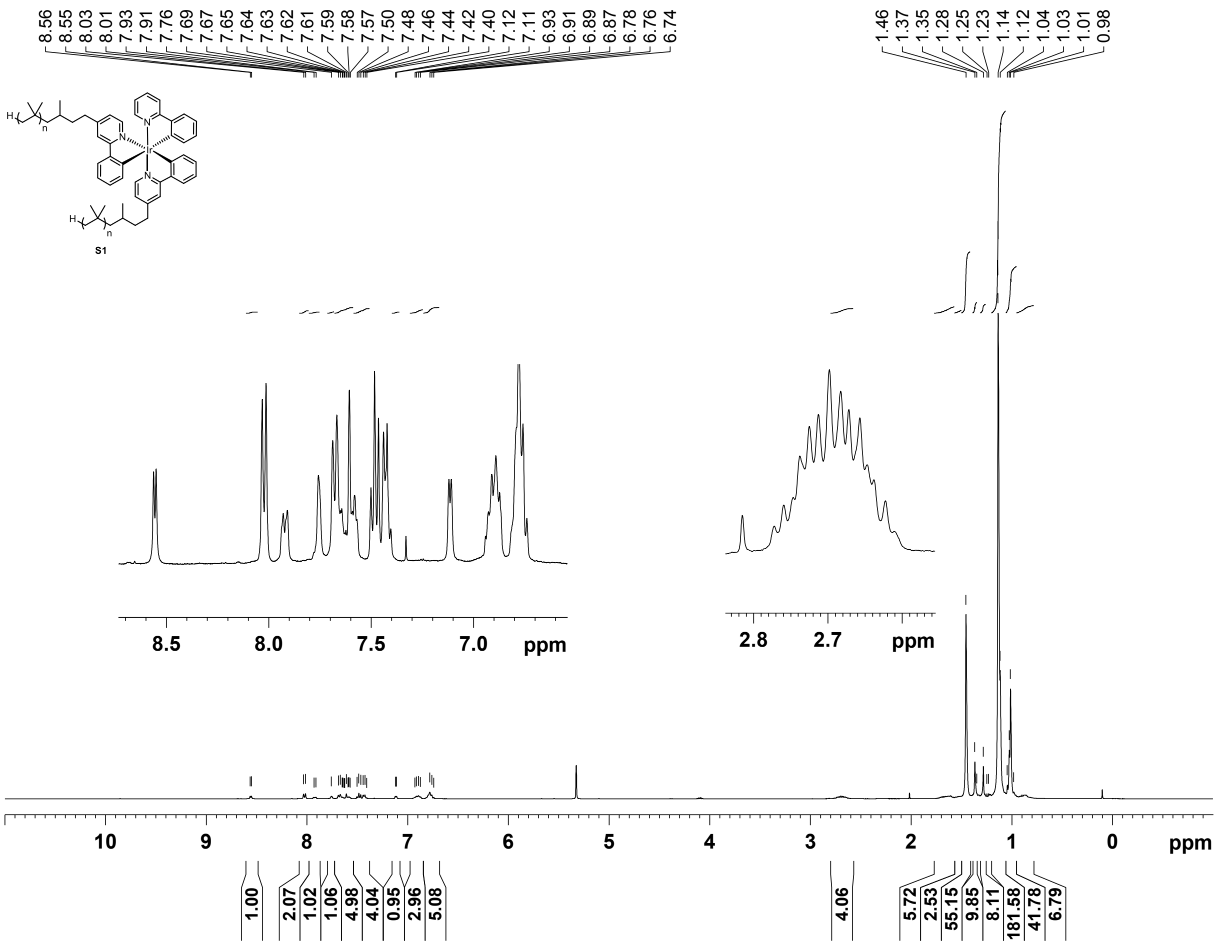
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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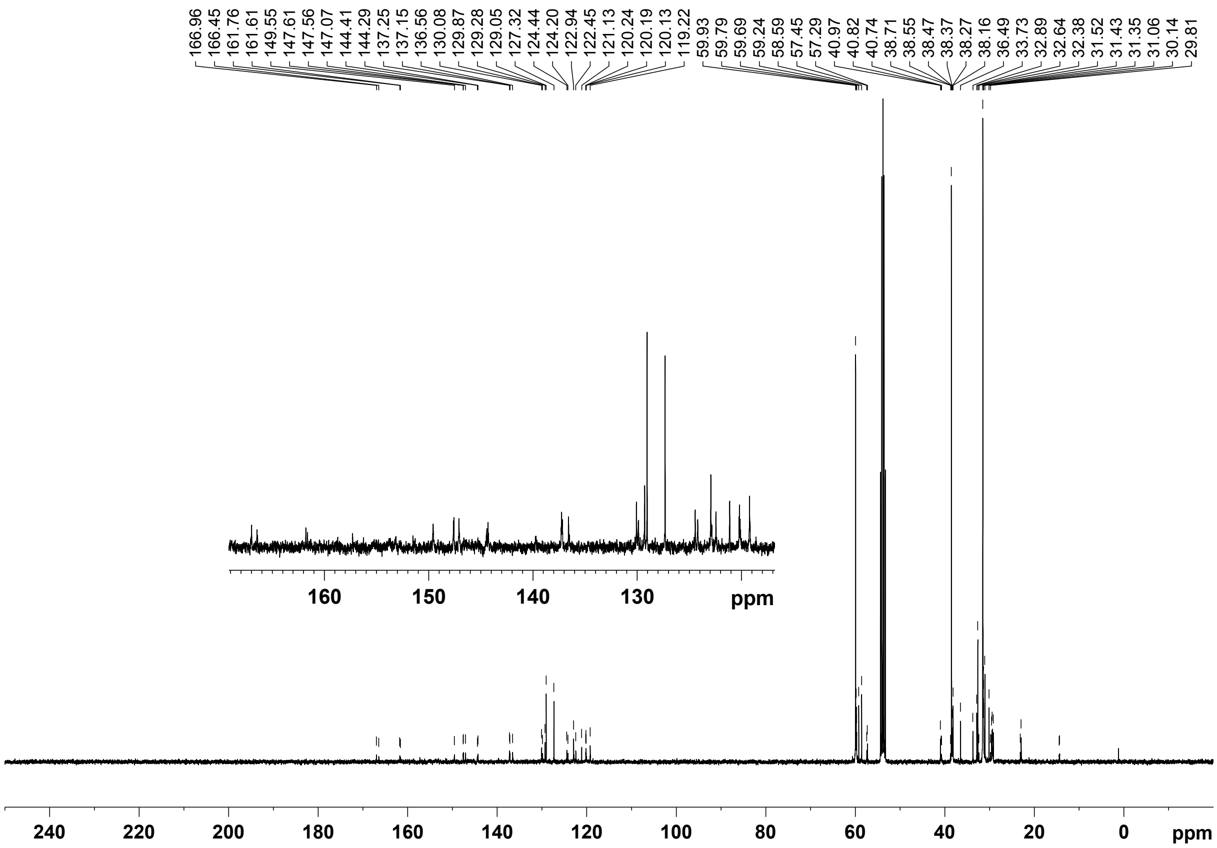
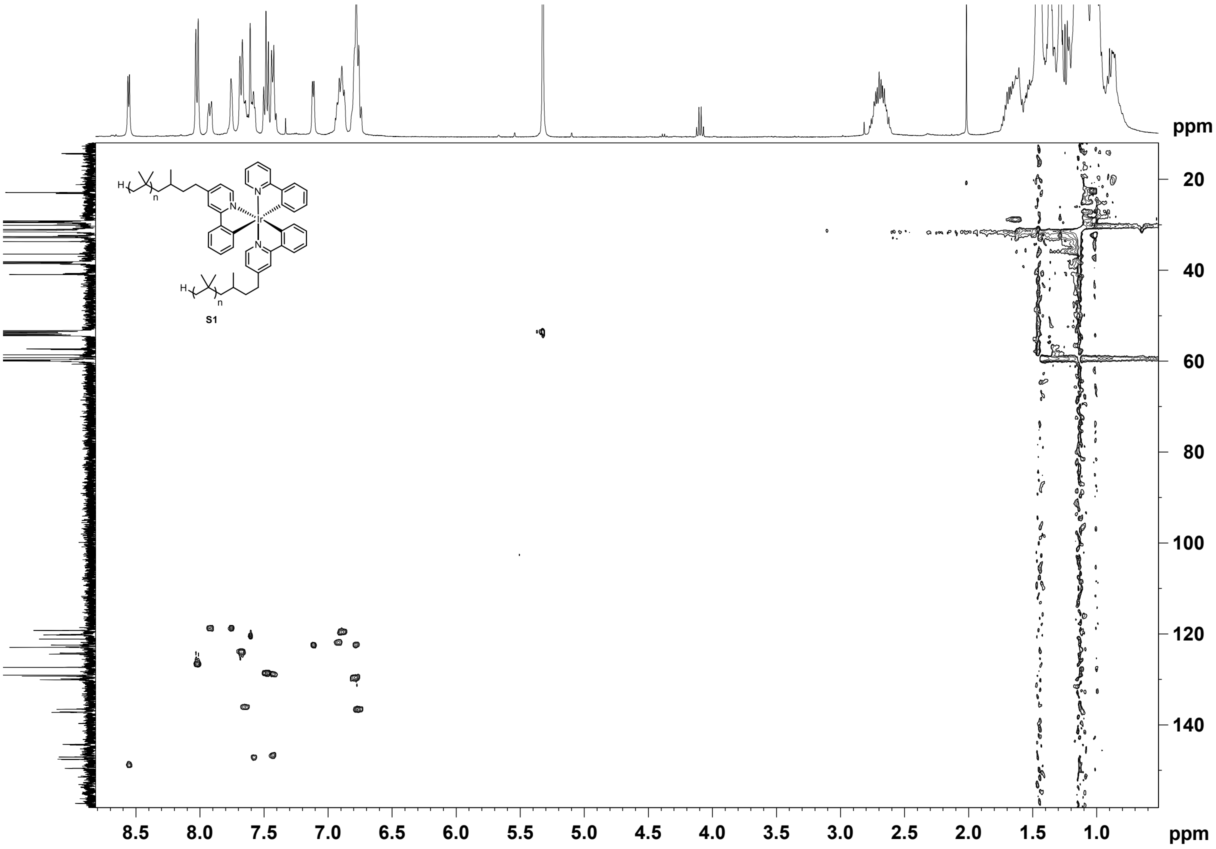
1.46 1.37 1.35 1.28 1.25 1.23 1.14 1.12 1.04 1.03 1.01 0.98
H
n
N
Ir
S1
8.5 8.0 7.5 7.0 ppm
2.8 2.7 ppm
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00 2.07 1.02 1.06 4.98 4.04 0.95 2.96 5.08
4.06
5.72 2.53 55.15 9.85 8.11 181.58 41.78 6.79


166.96 166.45 161.76 161.61 149.55 147.61 147.56 147.07 144.41 144.29 137.25 137.15 136.56 130.08 129.87 129.28 129.05 127.32 124.44 124.20 122.94 122.45 121.13 120.24 120.19 120.13 119.22
59.93 59.79 59.69 59.24 58.59 57.45 57.29 40.97 40.82 40.74 38.71 38.55 38.47 38.37 38.27 38.16 36.49 33.73 32.89 32.64 32.38 31.52 31.43 31.35 31.06 30.14 29.81
160 150 140 130 ppm
240 220 200 180 160 140 120 100 80 60 40 20 0 ppm


H
n
N
Ir
N
N
H
n
S1
ppm
20
40
60
80
100
120
140
8.5
8.0
7.5
7.0
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5.0
4.5
4.0
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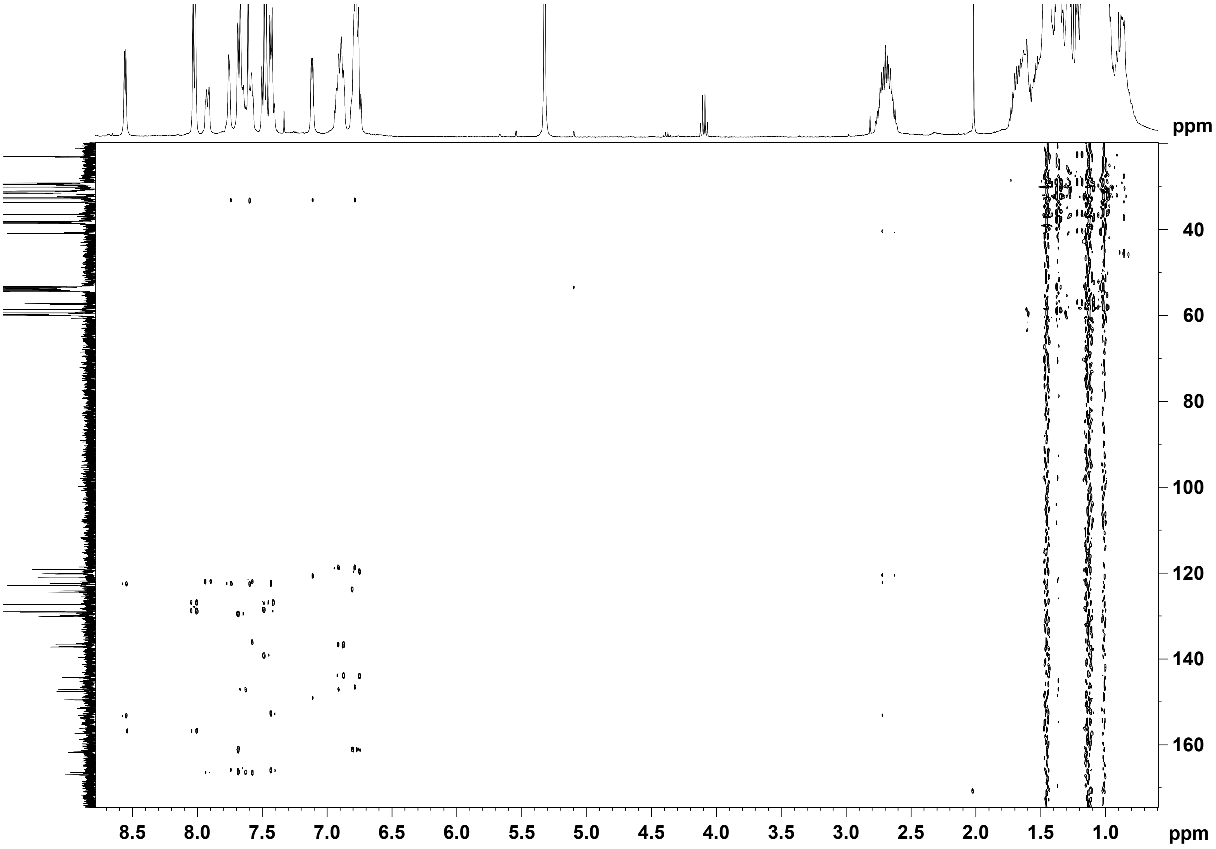
ppm


ppm
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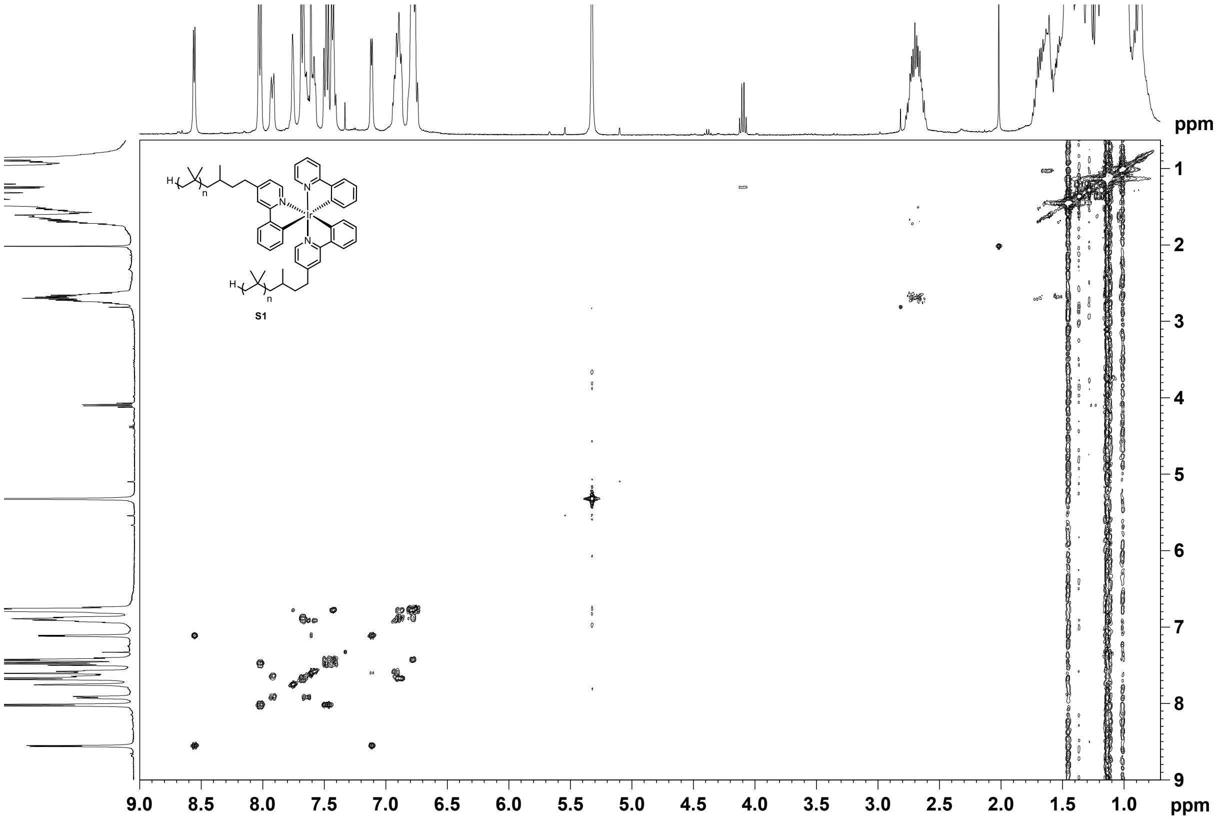
ppm


S1
ppm
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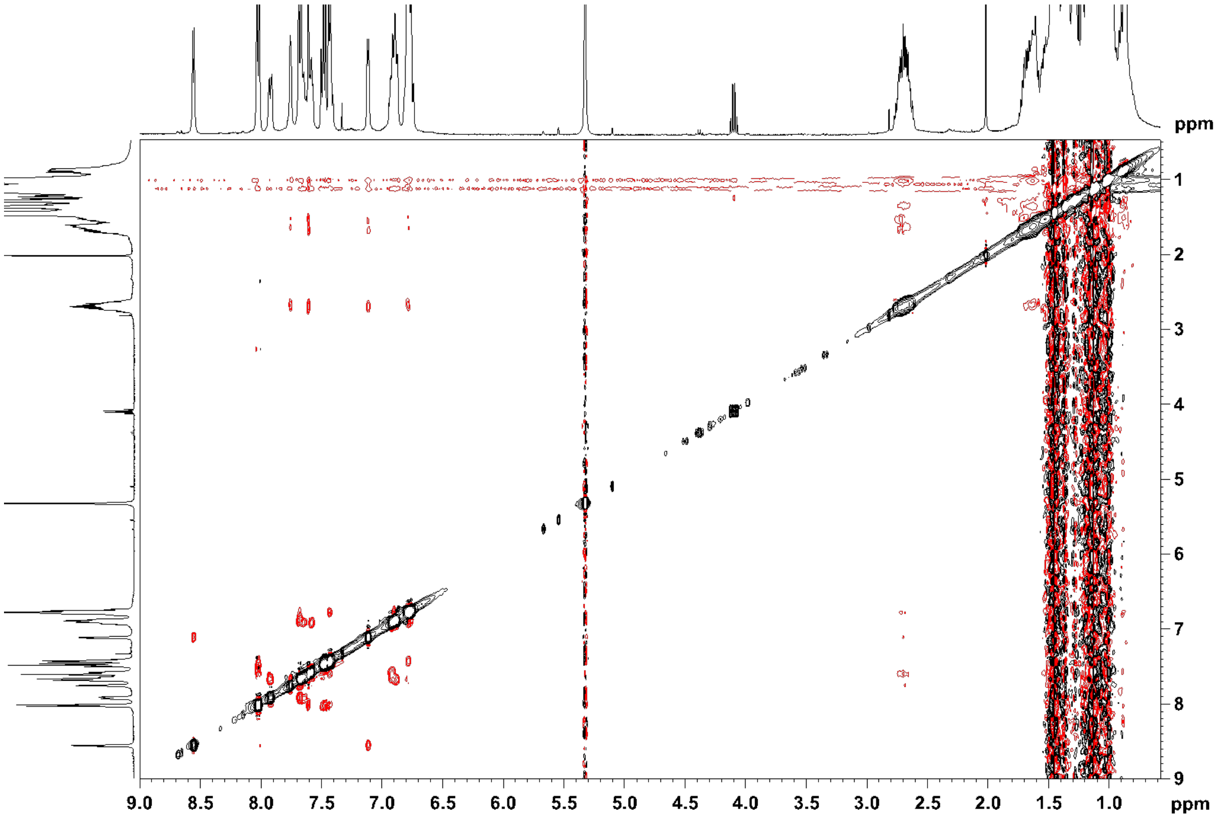
ppm


ppm
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5.0
4.5
4.0
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3.0
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2.0
1.5
1.0
ppm