Supplementary Information

PNNP-iridium: A prototypical catalyst framework tailored for diverse hydrogenative depolymerization of polyesters

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1. General Information

All experiments were performed under an inert gas atmosphere unless otherwise stated. Reagents were used as received without further purification. Solvents for metal complex synthesis were degassed by bubbling with inert gas before use, whereas solvents for polymerization reactions were distilled over calcium hydride. Products were purified by flash column chromatography on neutral silica gel (40–100 μm, Kanto Chemical Co.). Further information on reagents and solvents employed is provided below.

Gases: Hydrogen (H_2, 99.99%, Air Water Green Design Co., Ltd.; filled to 7 m^3 at 35 °C, 14.7 MPa), deuterium (D_2, >99.5%, Sumitomo Seika Chemicals Co., Ltd.; volume 10 L, filled to 500 L at 35 °C), and argon (Ar, 99.9999%, Taiyo Nippon Sanso Corporation; filled to 14.7 MPa at 35 °C) were used for depolymerization reactions. All gases were used as received.

Solvents: Hexane (FUJIFILM Wako Pure Chemical Corporation), 1,4-dioxane, super dehydrated (FUJIFILM Wako Pure Chemical Corporation), methanol, dehydrated (Kanto Chemical Co., Inc.), dichloromethane (Kanto Chemical Co., Inc.), ethyl acetate (Kanto Chemical Co., Inc.), diethyl ether (Kanto Chemical Co., Inc.), acetonitrile, dehydrated (Kanto Chemical Co., Inc.), tetrahydrofuran, stabilizer-free, dehydrated (Kanto Chemical Co., Inc.), $CDCl_3$ (Cambridge Isotope Laboratories), CD_3OD (Tokyo Chemical Industry Co., Ltd.), and DMSO-d_6 (FUJIFILM Wako Pure Chemical Corporation or Aldrich). All solvents were purified by standard procedures (distillation, dehydration, or degassing) when required.

Reagents for ligand and iridium complex synthesis: $NaSO_4$ (FUJIFILM Wako Pure Chemical Corporation), Celite 545 (Celite Co.), NaH, dispersion in paraffin liquid, purity >55% (Kanto Chemical Co., Inc.), ^{n}BuLi (~15% in *n*-hexane, ~1.6 M, Tokyo Chemical Industry Co., Ltd.), chlorodicyclohexylphosphine (Tokyo Chemical Industry Co., Ltd.), morpholine (Tokyo Chemical Industry Co., Ltd.), chloro(1,5-cyclooctadiene)iridium(I) dimer (FURUYA METAL Co., Ltd.), borane–tetrahydrofuran complex solution (1.0 M in THF, Sigma-Aldrich Co.), and lithium tetraphenylborate tris(1,2-dimethoxyethane) (Thermo Fisher Scientific Inc.). All reagents were used as received unless otherwise noted.

NMR spectroscopy: JEOL ECA-600. Chemical shifts (δ, ppm) are referenced to internal TMS (0 ppm) or residual solvent signals: CD_3OD (3.31 ppm for ^1H, 49.00 ppm for ^{13}C), DMSO-d_6 (2.50 ppm for ^1H, 39.52 ppm for ^{13}C), and $CDCl_3$ (77.16 ppm for ^{13}C). ^{31}P and ^{19}F NMR spectra were referenced to external phosphoric acid (85 wt% in H_2O, 0 ppm) and trifluoroacetic acid (–76.55 ppm), respectively.

Mass spectrometry: Bruker compact (ESI-QTOF).

Gel permeation chromatography (GPC): For PVL, PCL, PHL, PLA, PEA, PBA, PEAz: A JASCO system (pump: PU-4180 RHPLC, column oven: CO-4060 (40 °C), detectors: UV (UV-4070) and RI (RI-4030), columns: TSKgel α-3000 and α-M) 0.1 M LiCl in DMF was used as the eluent (flow rate 1.0 mL/min), and calibration was performed with PMMA standards (M_w = 202–273600 g/mol). **For PET and PBT:** A JASCO system (pump: PU-4185 RHPLC, column oven: CO-4060 (40 °C), detectors: UV (UV-4075) and RI (RI-4035), columns: Shodex HK-405 and HK-404L) 5 mM CF_3COONa in HFIP was used as the eluent (flow rate 0.20 mL/min) and calibration was performed with PMMA standards (M_w = 202–320000 g/mol).

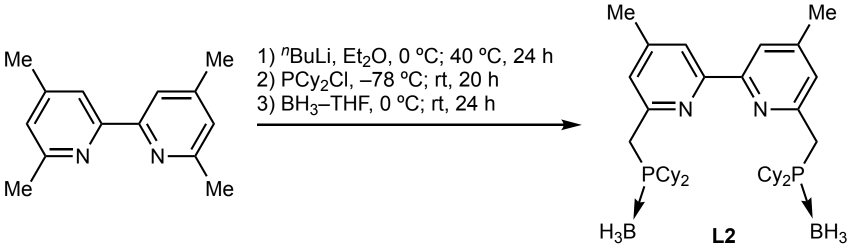
Autoclaves: Stainless steel autoclaves (30 mL, Taiatsu Techno Co., Ltd.) were used for high-pressure reactions.

2. Preparation of Ir Complexes

Ligands (**L1**–**L7**) and iridium complexes (**Ir1**–**Ir7**) were synthesized according to previously reported methods: **L1** and **Ir1**[1]; 4,4’,6,6’-tetramethyl-2,2’-bipyridine[2]; 3-cyano-6-methyl-4-trifluoromethyl-2-pyridone, 6-methyl-4-trifluoromethyl-2-pyridone, and 2-bromo-6-methyl-4-trifluoromethylpyridine[3]; 6,6’-dimethyl-4,4’-bis(trifluoromethyl)-2,2’-bipyridine[4]*; **L4** and **Ir4**[5]; **L5** and **Ir5**[6]; **L6** and **Ir6**[7]; and **L7** and **Ir7**[1].

*The synthesis of 6,6’-dimethyl-4,4’-bis(trifluoromethyl)-2,2’-bipyridine was carried out by adapting the procedure reported in ref. [4] for 4,4’-bis(trifluoromethyl)-2,2’-bipyridine, and its structure was confirmed using the NMR data reported in ref. [3].

2.1. Synthesis of L2



To a flame-dried 100 mL two-necked flask, 4,4’,6,6’-tetramethyl-2,2’-bipyridine (1.06 g, 5.01 mmol) was added along with diethyl ether (25 mL) under an inert atmosphere. The solution was cooled to 0 ºC, and ^{n}BuLi (1.6 M, 6.40 mL, 10 mmol) was added dropwise. The reaction mixture was then warmed to 40 ºC and stirred for 24 hours. After that, the reaction mixture was cooled to –78 ºC, and chlorodicyclohexylphosphine (2.20 mL, 1.06 g/mL, 10.0 mmol) was added dropwise. The mixture was allowed to warm gradually to room temperature and stirred for 20 hours. BH_3–THF (1.0 M, 25.0 mL, 25 mmol) was then added at 0 ºC, and the reaction mixture was stirred at room temperature for 24 hours. The reaction was quenched at 0 ºC with water (25 mL). THF was removed under reduced pressure using a rotary evaporator. The residue was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure using a rotary evaporator. The resulting residue was filtered, and the solid was washed with a small amount of ethyl acetate. The crude material was then purified by flash column chromatography (hexane/ethyl acetate = 4:1 → CH_2Cl_2 → CH_2Cl_2/ethyl acetate = 4:1), affording the desired product as a white solid (298 mg, 0.470 mmol, 9%).

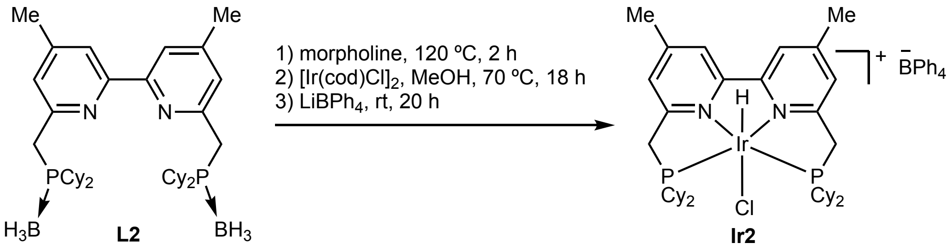
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (s, 2H), 7.11 (s, 2H), 3.25 (d, J = 10.8 Hz, 4H), 2.40 (s, 6H), 1.92–1.78 (20H), 1.68–1.67 (4H), 1.43–1.33 (8H), 1.24–1.13 (12H), 0.44–0.28 (br, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 155.3, 154.41, 154.36, 148.4, 125.98, 125.96, 119.9, 31.7, 31.5, 30.5, 30.3, 27.2, 27.11, 27.07, 27.0, 26.9, 26.8, 26.1, 21.4 (observed complexity due to P–C splitting; definitive assignments have not been made).

^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 28.5.

HRMS (ESI-QTOF): *m*/*z*: calculated for $[C_{38}H_{64}B_2N_2P_2+H]^+$: 633.4816; Found: 633.4816.

2.2. Synthesis of Ir2



A flame-dried Schlenk flask was charged with 6,6'-bis((dicyclohexylphosphino)methyl)-4,4'-dimethyl-2,2'-bipyridine–diborane complex (**L2**, 304 mg, 0.480 mmol) and degassed morpholine (12.5 mL), and the mixture was stirred at 120 ºC for 2 hours. The morpholine was then removed under reduced pressure on a Schlenk line without exposing the reaction mixture to air. Degassed methanol (15 mL) was added to the residue, followed by chloro(1,5-cyclooctadiene)iridium(I) dimer (167 mg, 0.249 mmol). The mixture was stirred at 70 ºC for 18 hours and filtered through a Celite pad under an argon atmosphere. In a separate flame-dried Schlenk flask, lithium tetraphenylborate tris(1,2-dimethoxyethane) (357 mg, 0.599 mmol) was dissolved in methanol (5 mL). This solution was added to the iridium-complex solution, and the combined mixture was stirred at room temperature for 20 hours. The mixture was then filtered and washed with methanol and diethyl ether to afford the product as a yellow solid (416 mg, 0.361 mmol, 75% yield).

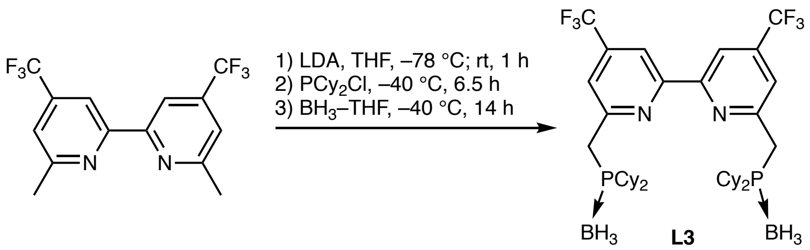
^{1}H NMR (600 MHz, DMSO-d_6): δ 8.30 (s, 2H), 7.76 (s, 2H), 7.184–7.181 (8H), 6.92 (t, J = 7.2 Hz, 8H), 6.78 (t, J = 6.6 Hz, 4H), 4.08–3.83 (m, 4H), 2.53 (s, 6H), 2.45–2.38 (2H), 2.25–2.21 (2H), 2.03–1.55 (22H), 1.44–1.40 (2H), 1.32–1.16 (12H), 1.06–0.96 (4H), –21.4 (t, J = 17.4 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 163.8, 163.5, 163.2, 162.9, 160.7, 155.4, 151.3, 135.5, 125.2, 124.5, 123.3, 121.5, 38.0, 37.7, 34.9, 34.7, 34.5, 27.85, 27.82, 27.3, 26.7, 26.6, 26.54, 26.51, 25.9, 25.81, 25.77, 25.6, 21.1 (observed complexity due to P–C splitting; definitive assignments have not been made).

^{31}P{^{1}H} NMR (243 Hz, DMSO-d_6): δ 19.3.

HRMS (ESI-QTOF): m/z: calculated for $[C_{38}H_{59}ClIrN_2P_2]^+$: 833.3459; Found: 833.3462.

2.3. Synthesis of L3



In a flame-dried 300 mL two-necked flask, 6,6'-dimethyl-4,4'-bis(trifluoromethyl)-2,2'-bipyridine (1.44 g, 4.50 mmol) was dissolved in THF (45 mL) and cooled to –78 ºC. Separately, to prepare diisopropylamide (LDA), diisopropylamine (1.26 mL, 0.72 g/mL, 9.0 mmol) was added to THF (4.5 mL) and then ^{n}BuLi (1.6 M, 5.63 mL, 9.0 mmol) was added dropwise at 0 ºC in a flame-dried 100 mL two-necked flask. The mixture was stirred for 10 minutes at 0 ºC. The freshly prepared LDA solution was then added dropwise to the solution of 6,6'-dimethyl-4,4'-bis(trifluoromethyl)-2,2'-bipyridine at –78 ºC. The reaction mixture was then allowed to warm gradually to room temperature and stirred for 1 hour. Chlorodicyclohexylphosphine (2.20 mL, 1.06 g/mL, 10.0 mmol) was added dropwise at –40 ºC and the mixture was stirred for 6.5 hours. BH_3–THF (1.0 M, 45.0 mL, 45 mmol) was added at –40 ºC and the mixture was stirred for additional 14 hours. After the reaction, the mixture was cooled to 0 ºC and quenched with water (50 mL). THF was removed under reduced pressure using a rotary evaporator. The residue was extracted with CH_2Cl_2 (3 × 40 mL), the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (CH_2Cl_2/hexane = 1:1), followed by washing with ethyl acetate, yielded the product as a white solid (1.33 g, 1.80 mmol, 40%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (s, 2H), 7.59 (s, 2H), 3.40 (d, J = 11.4 Hz, 4H), 1.98–1.82 (20H), 1.71–1.70 (4H), 1.47–1.31 (8H), 1.25–1.14 (12H), 0.41–0.23 (br, 6H).

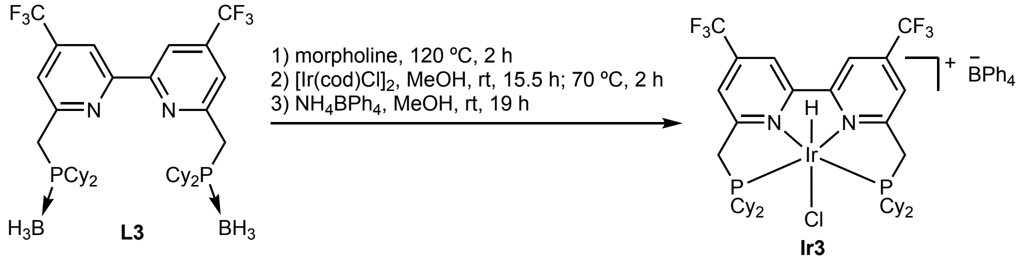
^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ 156.93, 156.89, 155.3, 140.0 (q, J = 34.7 Hz), 122.9 (q, J = 273.3 Hz), 121.7, 114.9, 32.1, 31.9, 30.6, 30.4, 27.05, 27.01, 26.95, 26.92, 26.87, 26.0 (observed complexity due to P–C splitting; definitive assignments have not been made).

^{19}F NMR (565 MHz, $CDCl_3$): δ –65.2.

^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 30.0.

HRMS (ESI-QTOF): *m*/*z* calculated for $[C_{38}H_{58}B_2F_6N_2P_2+Na]^+$: 763.4070. Found: 763.4090.

2.4. Synthesis of Ir3



In a flame-dried Schlenk flask, 6,6'-bis((dicyclohexylphosphino)methyl)-4,4'-bis(trifluoromethyl)-2,2'-bipyridine–diborane complex ligand (**L3**, 371 mg, 0.501 mmol) was dissolved in degassed morpholine (12.5 mL). The mixture was stirred at 120 ºC for 2 hours, after which morpholine was removed under reduced pressure while maintaining an inert atmosphere to prevent air exposure. $[Ir(cod)Cl]_2$ (168 mg, 0.250 mmol) and degassed methanol (25 mL) were then added. The mixture was stirred at room temperature for 15.5 hours, then heated to 70 ºC, and stirred for 2 hours. The mixture was filtered through a Celite pad under argon, and the pad was washed with degassed methanol (3 × 12.5 mL). Ammonium tetraphenylborate (202 mg, 0.600 mmol) was added to the filtrate, and the resulting solution was stirred at room temperature for 19 hours, during which a green solid precipitated. The solid was collected by filtration and washed with methanol to afford the desired product as a greenish-yellow solid (502 mg, 0.398 mmol, 80%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (s, 2H), 7.55 (8H), 7.41 (2H),7.00 (t, *J* = 7.2 Hz, 8H), 6.82 (t, *J* = 7.2 Hz, 4H), 3.41–3.07 (m, 4H), 2.39–2.38 (2H), 2.11–2.10 (2H), 1.91–0.89 (40H), –20.5 (t, *J* = 17.4 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 165.1, 164.8, 164.4, 164.2, 164.1, 156.0, 140.5 (q, *J* = 36.2 Hz), 136.2, 125.9, 122.1, 122.0, 121.7 (q, *J* = 274.6 Hz), 118.2, 39.3, 39.1, 36.0, 35.8, 35.7, 35.6, 28.7, 28.4, 28.1, 27.6, 27.1, 27.0, 26.40, 26.37, 26.3, 26.2, 26.14, 26.11, 25.89. 25.87 (observed complexity due to P–C splitting; definitive assignments have not been made).

^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) 20.2.

^{19}F NMR (564 MHz, $CDCl_3$): δ –64.7.

HRMS (ESI-QTOF): *m*/*z* calculated for $[C_{38}H_{53}ClF_6IrN_2P_2]^+$: 941.2894; Found: 941.2894.

3. Preparation of Polyesters

3.1. Commercially available polymer substrates

Commercially available polymers were used as substrates and were employed as received unless otherwise noted. Their molecular characteristics, determined by GPC (SEC), are summarized in Table S1.

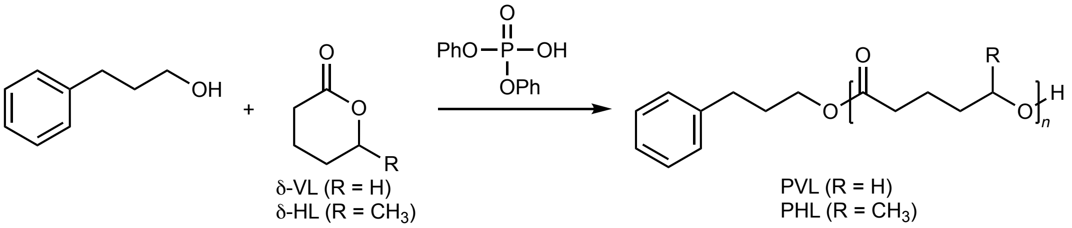
Table S1. Commercially available polymer substrates and molecular characteristics

Polymer	Supplier	Catalog No.	CAS No.	Lot No.	GPC Eluent	M_w	M_n	$Đ$
PCL-a	Sigma-Aldrich	440752	24980-41-4	MKCQ9376	DMF	23,000	13,000	1.72
PCL-b	Sigma-Aldrich	440744	24980-41-4	MKCS9213	DMF	150,000	100,000	1.48
PLA	Sigma-Aldrich	38534	26100-51-6	BCCL0106	DMF	65,000	32,100	2.10
PEA	Sigma-Aldrich	181919	24938-37-2	MKCT2723	DMF	9,400	4,700	2.02
PBA	Sigma-Aldrich	181501	25103-87-1	MKCS0688	DMF	10,000	4,900	2.06
PEAz	Scientific Polymer Products	842	26760-99-6	901119002	DMF	18,000	8,700	2.05
PET	Polysciences	04301-250	25038-59-9	46418	HFIP	25,000	10,000	2.44
PBT	Sigma-Aldrich	190942	30965-26-5	00203JN	HFIP	25,000	11,000	2.32

3.2. Synthesized polyesters

Poly(δ-valerolactone)[8] (PVL-a: M_w = 12000, M_n = 11000, $Đ$ = 1.09; PVL-b: M_w = 64000, M_n = 48000, $Đ$ = 1.34) and poly(δ-hexanolactone)[9] (PHL: M_w = 15000, M_n = 14000, $Đ$ = 1.08) were synthesized following the reported procedures.

General procedure for ring-opening polymerization



Note: δ-Valerolactone (δ-VL) and δ-hexanolactone (δ-HL) were distilled over CaH_2 under reduced pressure. Similarly, 3-phenyl-1-propanol (PPA) was distilled over CaH_2 under an argon atmosphere to maintain an inert environment.

In a flame-dried Schlenk flask, 3-phenyl-1-propanol and the monomer (δ-VL or δ-HL) were combined inside a glove box. Polymerization was initiated by adding a 1 M CH_2Cl_2 solution of diphenyl phosphate (DPP) to the monomer solution under an inert atmosphere at the reaction temperature specified in Table S2. After the designated reaction time (Table S2), the mixture was quenched with triethylamine (1 equiv. relative to DPP). The mixture was washed with deionized water (3 × 20 mL), and the organic solvents were removed under reduced pressure. The residue was dissolved in a minimal volume of CH_2Cl_2 and reprecipitated by dropwise addition into a cold hexane/methanol mixed solvent (4:1), affording the purified polymer.

Table S2. Synthesis of poly(δ-valerolactone) and poly(δ-hexanolactone)

Polyester	Monomer	Temp. [ºC]	$[M]_0$[a] [mol/L]	$[PPA]_0/[M]_0/[DPP]_0$	Time [h]	$M_{n,\text{ theor}}$	$M_{n,\text{ NMR}}$	$M_{n,\text{ SEC}}$	M_w/M_n
PVL-a	δ-VL	30	3.0	1/100/1	2	10000	9700	11000	1.09
PVL-b	δ-VL	40	3.5	1/600/1	24	69000	-	48000	1.34
PHL	δ-HL	rt	5.7	1/107/1	24	12000	11000	14000	1.08

[a] $[M]_0$ represents the concentration of the monomer (either δ-VL or δ-HL)

3.3. Commodity PET Products

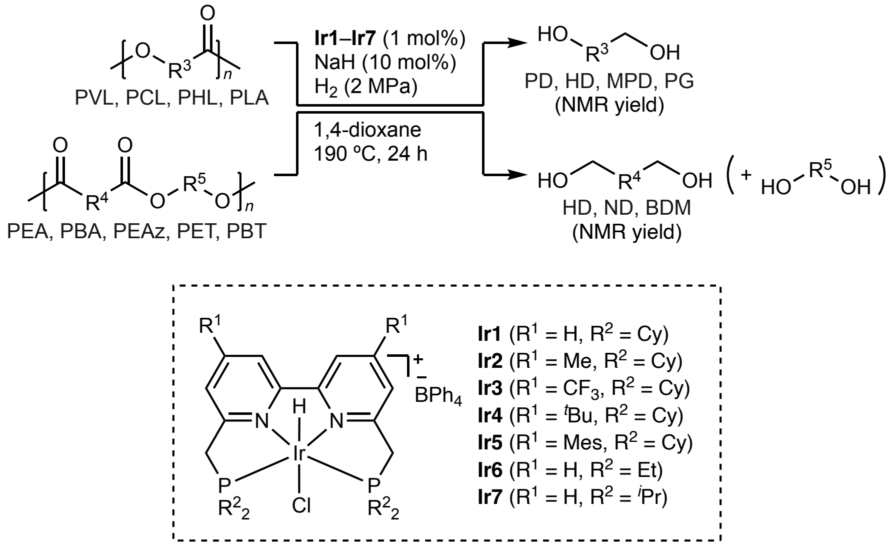
Commodity PET products were used as polyester substrates. Beverage bottles were washed with deionized water and air-dried at room temperature before use, whereas no treatment was performed on the T-shirts. All samples were cut into small pieces before use. The substrates employed in this study included: a colorless Coca-Cola beverage bottle, a colored Pellegrino beverage bottle, a white DX Dry T-Shirt L White 001 (Artec Co., Ltd.), and a black DX Dry T-Shirt L Black 005 (Artec Co., Ltd.).

Colorless bottle Colored bottle White T-shirt Black T-shirt

Figure S1. Commodity PET products used in the reactions.

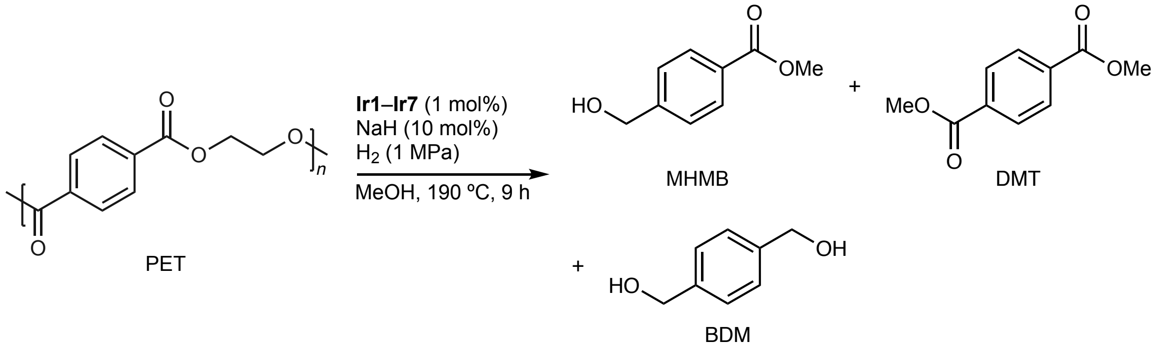
4. Experimental Procedures for Hydrogenation Reactions

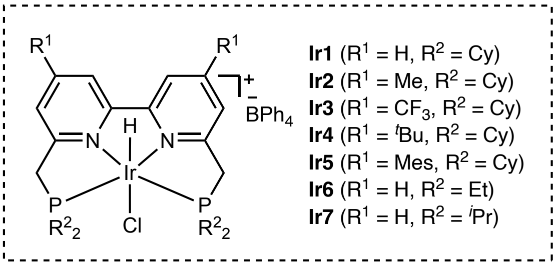
4.1. General procedure for full hydrogenation of polyesters



A flame-dried glass tube equipped with a magnetic stirrer bar was prepared. To this tube, an iridium complex (10.0 μmol), sodium hydride (NaH, 4.36 mg, 0.100 mmol, 55% dispersion in mineral oil), and a polyester substrate (corresponding to 1.00 mmol of repeating units) were added. The tube was then transferred to an autoclave, which was tightly sealed, evacuated, and backfilled with argon three times. Subsequently, 1,4-dioxane (3 mL) was added under a flow of argon, and the autoclave was resealed. The autoclave was flushed with hydrogen gas (~1 MPa) ten times and then pressurized to 2 MPa. The sealed autoclave was placed in a preheated heating block at 190 ºC and stirred at 500 rpm for 24 hours. After completion, the autoclave was cooled in an ice bath. Once the reaction mixture reached room temperature, it was dissolved in CH_2Cl_2 (for PD, 1,6-HD, 1,5-HD, PG, or ND) or methanol (for BDM) and transferred to a 50 mL round-bottom flask. The solvents were removed under reduced pressure (40 ºC, ~40 mmHg), and mesitylene (ca. 46.0 μL, 0.865 g/mL, 0.333 mmol) was added as an internal standard. The residue was dissolved in 1.5 mL of deuterated solvent: $CDCl_3$ for PD, 1,6-HD, 1,5-HD, PG, or ND, and CD_3OD for BDM.

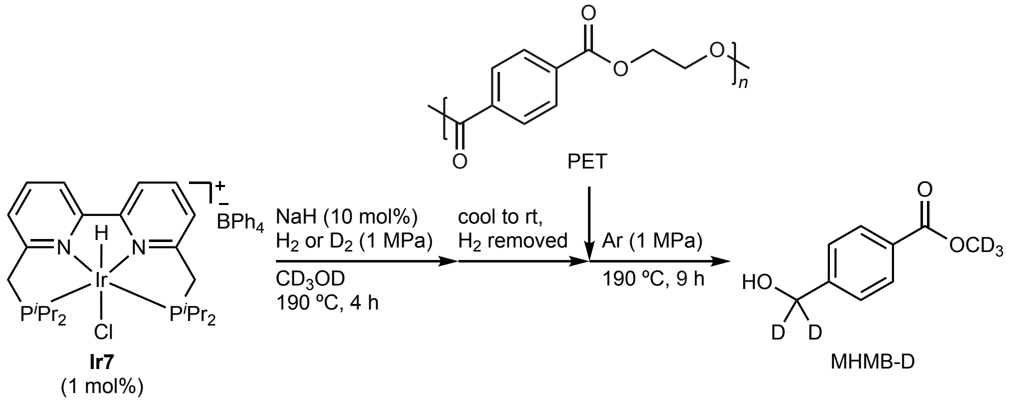
4.2. General procedure for semi-hydrogenation of PET





A flame-dried glass tube equipped with a magnetic stirrer bar was prepared. An iridium complex (10.0 μmol), sodium hydride (NaH, 4.36 mg, 0.100 mmol, 55% dispersion in mineral oil), and a polyester substrate (corresponding to 1.00 mmol of repeating units) were added. The tube was then transferred to an autoclave, which was sealed, evacuated, and backfilled with argon three times. Methanol (5 mL) was added under a flow of argon, and the autoclave was resealed. The autoclave was flushed with hydrogen gas (~1 MPa) ten times and then pressurized to 1 MPa. It was placed in a preheated heat block at 190 ºC and stirred at 500 rpm for 9 hours. After completion, the autoclave was cooled in an ice bath. Once the mixture reached room temperature, it was dissolved in CH_2Cl_2 or methanol, selecting whichever solvent more effectively dissolved the crude mixture, and transferred to a 50 mL round-bottom flask. The solvents were removed under reduced pressure (40 ºC, ~40 mmHg), and mesitylene (ca. 46.0 μL, 0.865 g/mL, 0.333 mmol) was added as an internal standard. The residue was dissolved in 1.5 mL of deuterated solvent for ^1H NMR analysis. $CDCl_3$ was used when DMT was expected as the major side product, whereas CD_3OD was used when BDM was expected to predominate, based on relative solubilities. The main product, MHMB, is soluble in both solvents.

4.3. General procedure for hydrogenation with pre-activation of Ir7



A flame-dried glass tube equipped with a magnetic stirrer bar was prepared. **Ir7** (9.64 mg, 10.0 μmol), and NaH (4.36 mg, 0.100 mmol, 55% dispersion in mineral oil) were added, and the tube was then transferred to an autoclave. The autoclave was sealed, evacuated, and backfilled with argon three times. Methanol (5 mL) was then added under a flow of argon, and the autoclave was resealed. For the pre-activation step, the autoclave was flushed with hydrogen gas ten times and then pressurized to 1 MPa with hydrogen. It was placed in a preheated heating block at 190 ºC and stirred at 500 rpm for 4 hours. After pre-activation, the autoclave was cooled in an ice bath. Once it reached room temperature, the hydrogen gas was carefully vented, and the autoclave was backfilled with argon. Under a flow of argon, polyethylene terephthalate (PET, amount corresponding to 1.00 mmol of repeating units; 192 mg) was added. The autoclave was sealed, pressurized to 1 MPa with argon, and placed in a preheated heating block at 190 ºC, where it was stirred at 500 rpm for 9 hours. After the reaction, the autoclave was cooled in an ice bath. After cooling to room temperature, the mixture was dissolved in CH_2Cl_2 and methanol, and transferred to a 50 mL round-bottom flask. The solvents were removed under reduced pressure (40 ºC, ~40 mmHg), and mesitylene (ca. 46.0 μL, 0.865 g/mL, 0.333 mmol) was added as an internal standard. The residue was dissolved in 1.5 mL of CD_3OD.

4.4. Hydrogenation of Commodity PET Materials

Hydrogenation reactions of commodity PET materials were carried out following the general procedures described above (full-hydrogenation: Section 4.1; semi-hydrogenation: Section 4.2). For each reaction using a single PET source, the sample weight was adjusted to correspond to 1.00 mmol of PET repeating units (192 mg), assuming the material consisted entirely of PET. When using a mixture of four PET sources, each was weighed to provide 0.250 mmol of repeating units (48.0 mg), giving a total of 1.00 mmol per reaction.

Although the T-shirts were labeled as “100% polyester” and the bottles as “PET,” these materials may contain other polyesters, processing additives, dyes, or minor components. As a result, the actual PET content may be slightly lower than the nominal mass, which could lead to a slight underestimation of the actual yield of BDM or MHMB. Nevertheless, under the optimized conditions, either BDM or MHMB was consistently obtained as the major product, indicating that PET is the predominant reactive component. Therefore, treating these samples as primarily PET for yield calculations is reasonable.

5. Compound Data

5.1. Compound data identified from the literature

The following compounds were identified by comparison with the reported data and our experimental results. The corresponding literature values are provided for reference.

1,5-Pentanediol (PD)

^{1}H NMR (400 MHz, $CDCl_3$)[10]: δ 3.61 (t, *J* = 6.4 Hz, 4H), 2.22 (br, 2H), 1.53–1.60 (m, 4H), 1.42–1.44 (m, 2H).

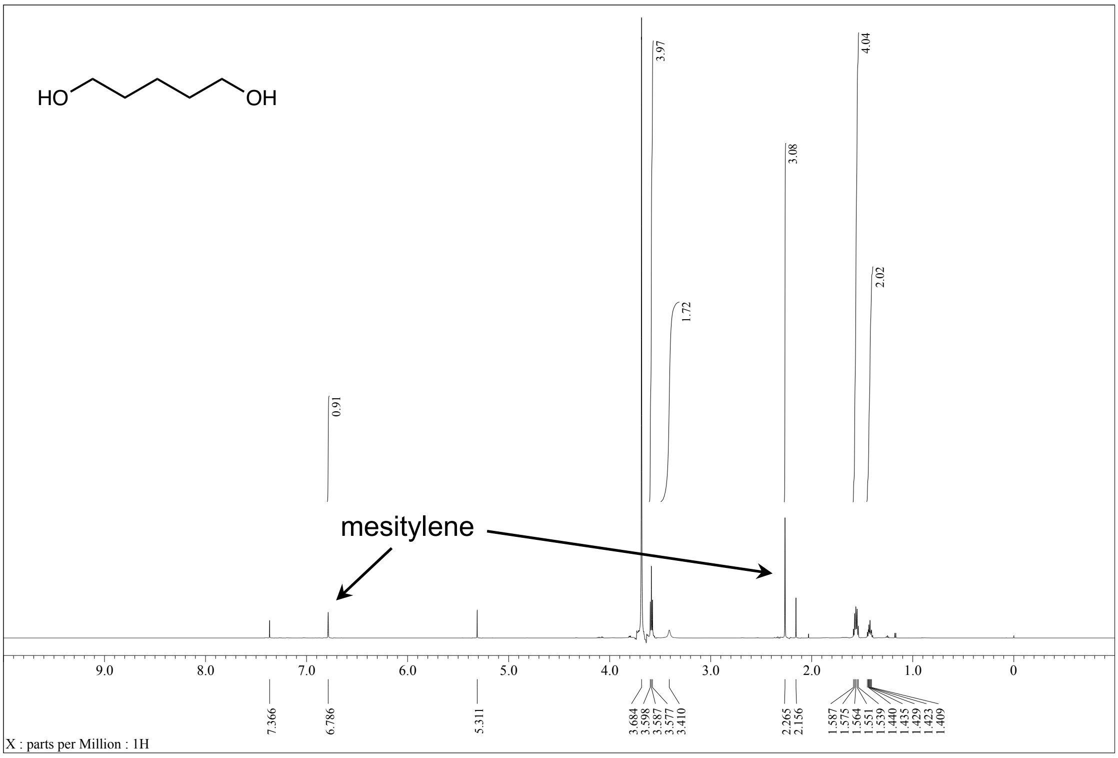


Figure S2. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of PD in the reaction mixture obtained from full hydrogenation of PVL-a with **Ir3**. The peak at 3.61 ppm was used for NMR yield calculation. As the major solvent-derived impurities, dichloromethane (5.31 ppm) and 1,4-dioxane (3.68 ppm) were detected.

1,6-Hexanediol (1,6-HD)

^{1}H NMR (400 MHz, $CDCl_3$)[10]: δ 3.61 (t, *J* = 6 Hz, 4H), 1.94 (br, 2H), 1.53–1.57 (m, 4H), 1.34–1.38 (m, 4H).

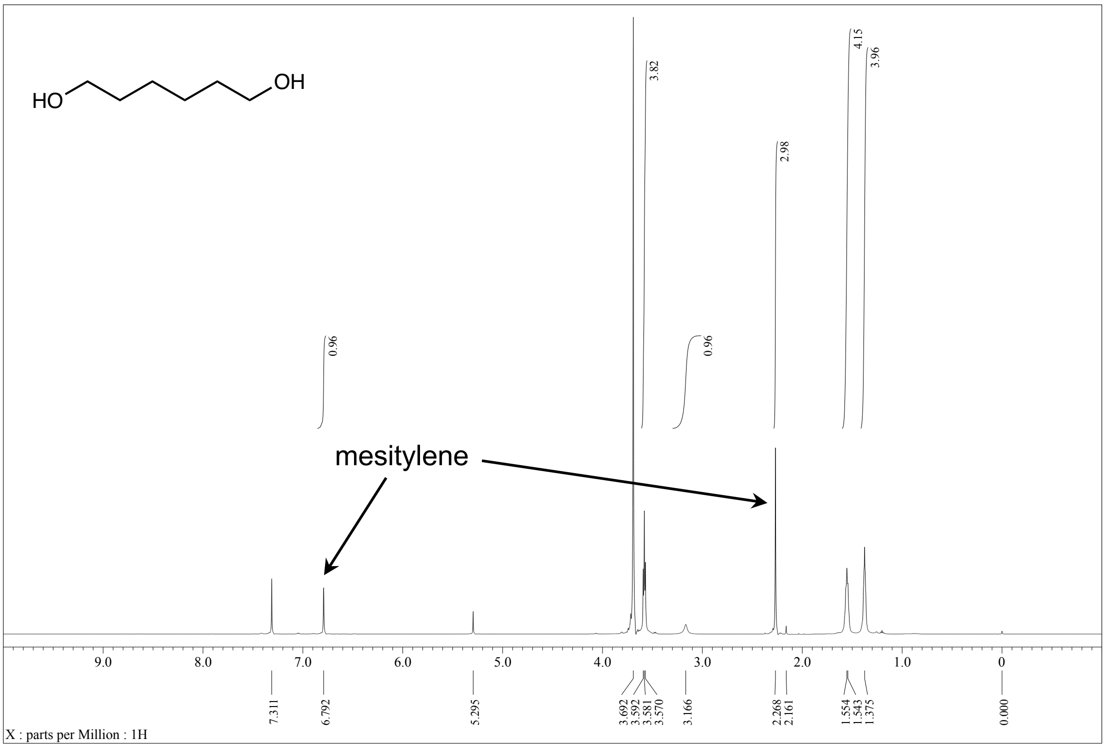


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of 1,6-HD in the reaction mixture obtained from full hydrogenation of PCL-a with **Ir3**. As the major solvent-derived impurities, dichloromethane (5.30 ppm) and 1,4-dioxane (3.69 ppm) were detected.

1,5-Hexanediol (1,5-HD)

^{1}H NMR (600 MHz, $CDCl_3$)[11]: δ 3.86–3.78 (m, 1H), 3.66 (t, *J* = 6.5 Hz, 2H), 1.67–1.56 (br, 2H), 1.55–1.35 (m, 6H), 1.20 (d, *J* = 6.1 Hz, 3H).

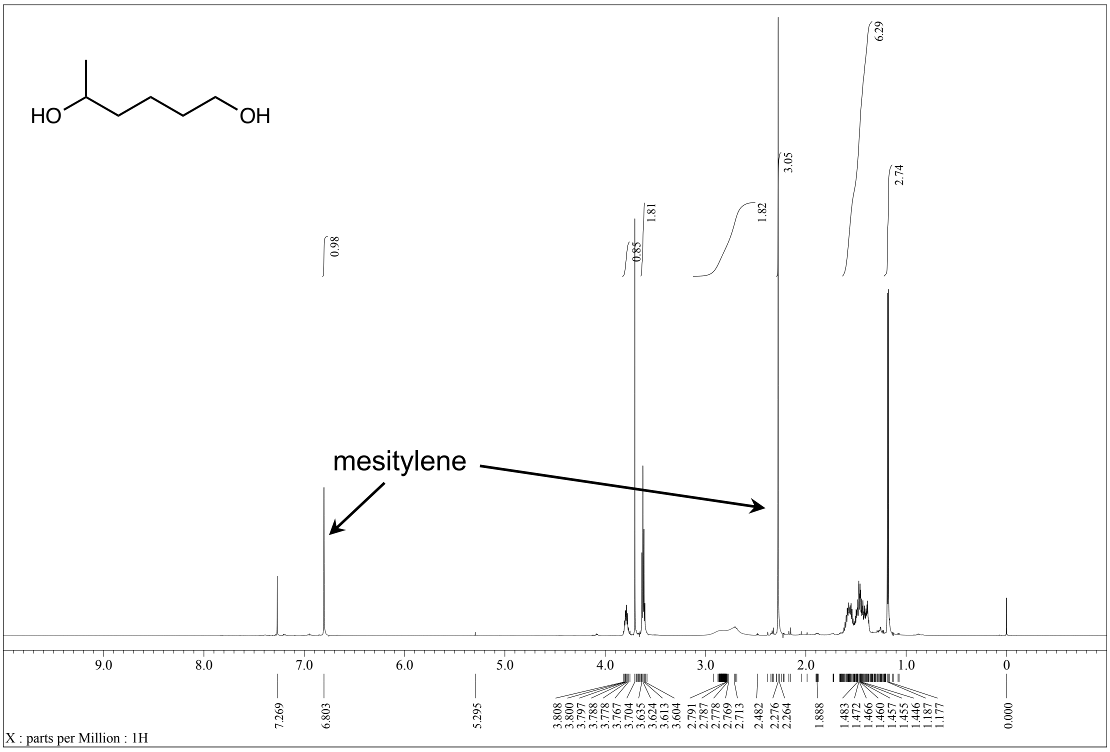


Figure S4. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of 1,5-HD in the reaction mixture obtained from full hydrogenation of PHL with **Ir5**. The peak at 3.66 ppm was used for NMR yield calculation. As the major solvent-derived impurity, 1,4-dioxane (3.70 ppm) was detected.

Propylene glycol (PG)

^{1}H NMR (300 MHz, $CDCl_3$)[12]: δ 3.91 (m, 1H), 3.62 (d, *J* = 10.8 Hz, 1H), 3.39 (dd, *J* = 11.0, 8.0 Hz, 1H), 3.07 (br, 2H), 1.16 (d, *J* = 6.3 Hz, 3H).

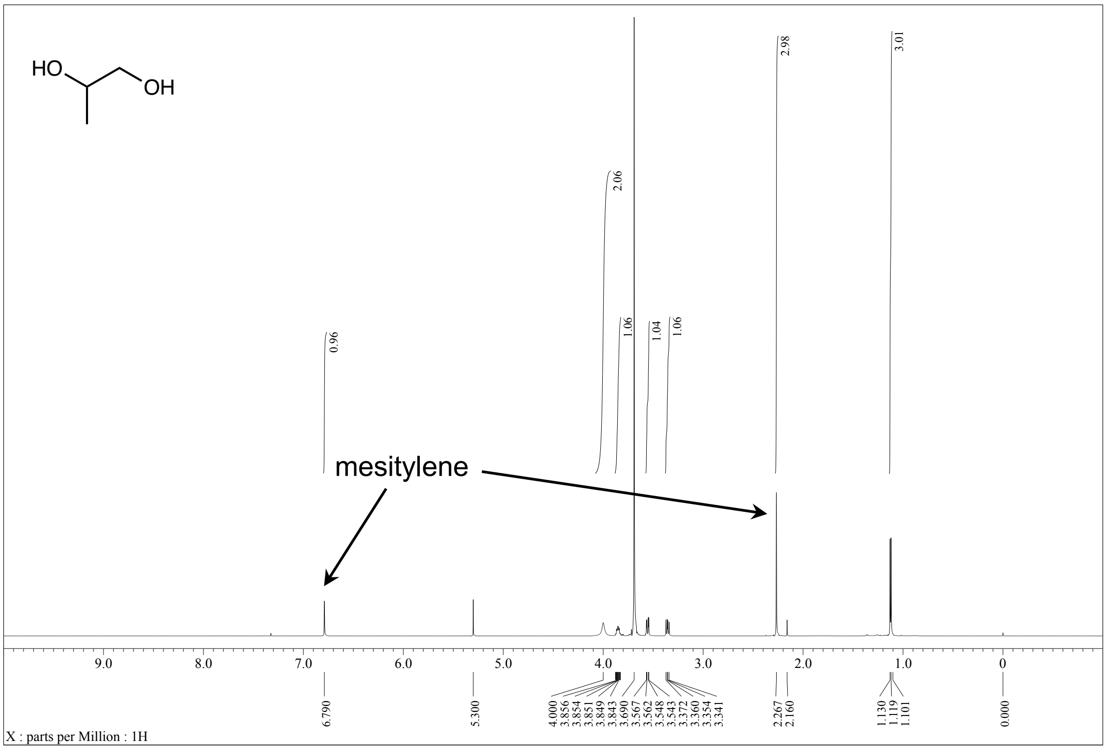


Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of PG in the reaction mixture obtained from full hydrogenation of PLA with **Ir3**. The peak at 3.62 ppm was used for NMR yield calculation. As the major solvent-derived impurities, dichloromethane (5.30 ppm) and 1,4-dioxane (3.69 ppm) were detected.

1,9-Nonanediol (ND)

^{1}H NMR (500 MHz, $CDCl_3$)[13]: δ 3.61–3.58 (m, 4H), 1.55–1.51 (m, 4H), 1.29 (m, 10H).

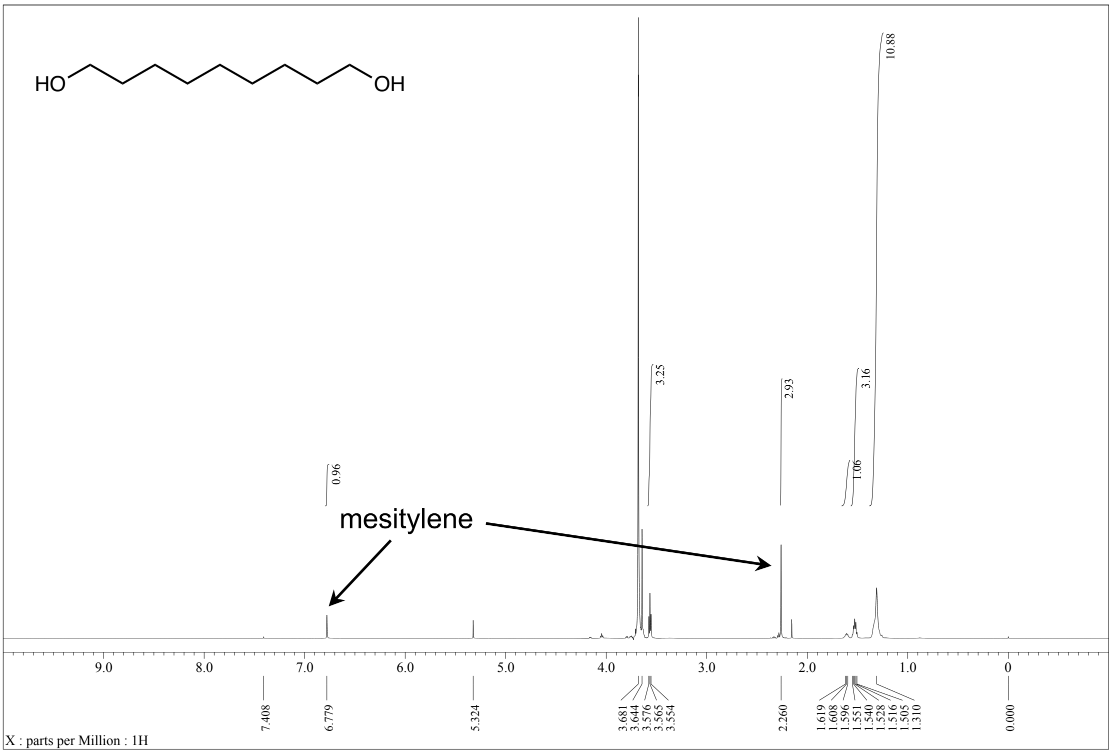


Figure S6. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of ND in the reaction mixture obtained from full hydrogenation of PEAz with **Ir3**. The peak at 3.58–3.61 ppm was used for calculating the NMR yield. As the major solvent-derived impurities, dichloromethane (5.32 ppm) and 1,4-dioxane (3.68 ppm) were detected.

1,4-Benzenedimethanol (BDM)

BDM was isolated and characterized in this study. For NMR yield calculation, the following ^{1}H NMR information was used:

^{1}H NMR (600 MHz, CD_3OD): δ 7.33 (s, 4H), 4.87 (s, 2H), 4.59 (s, 4H)[14].

Detailed spectroscopic data for the isolated compound are provided in Section 5.2, where DMSO-d_6 was used for the NMR analysis.

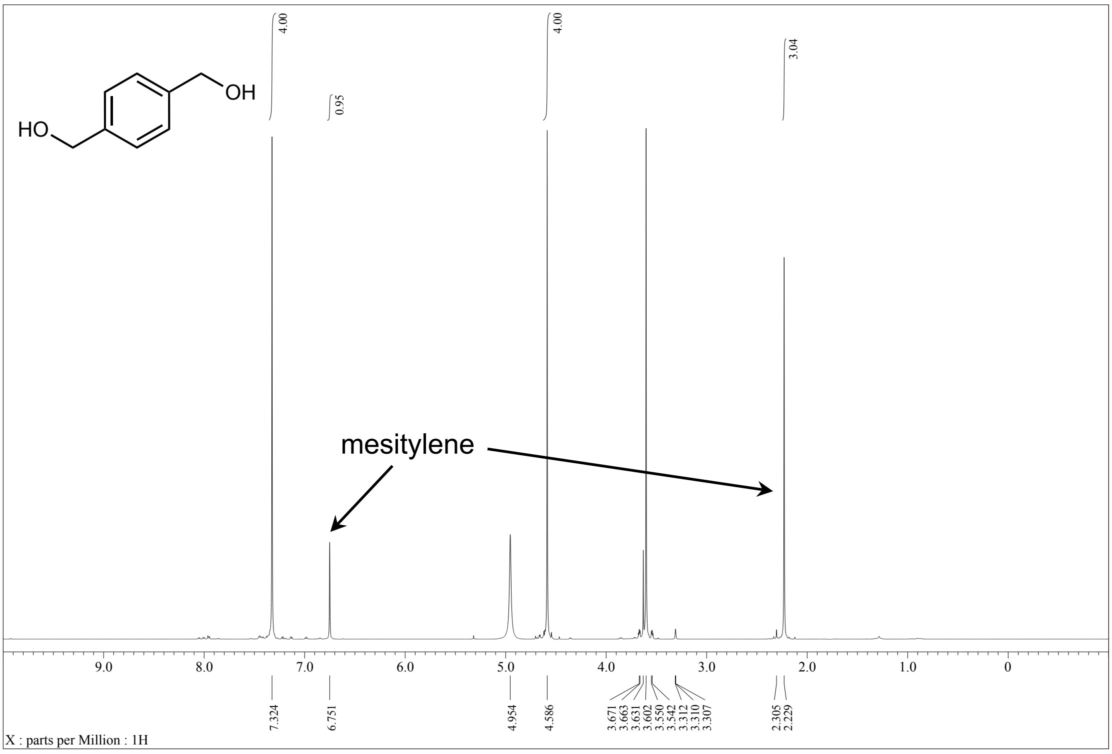


Figure S7. ^{1}H NMR spectrum (600 MHz, CD_3OD, rt) of BDM in the reaction mixture obtained from full hydrogenation of PET with **Ir3**. The peak at 7.33 ppm was used for NMR yield calculation.

NMR spectra for PD, 1,6-HD, and BDM in reaction mixtures obtained using other polyesters in full hydrogenation

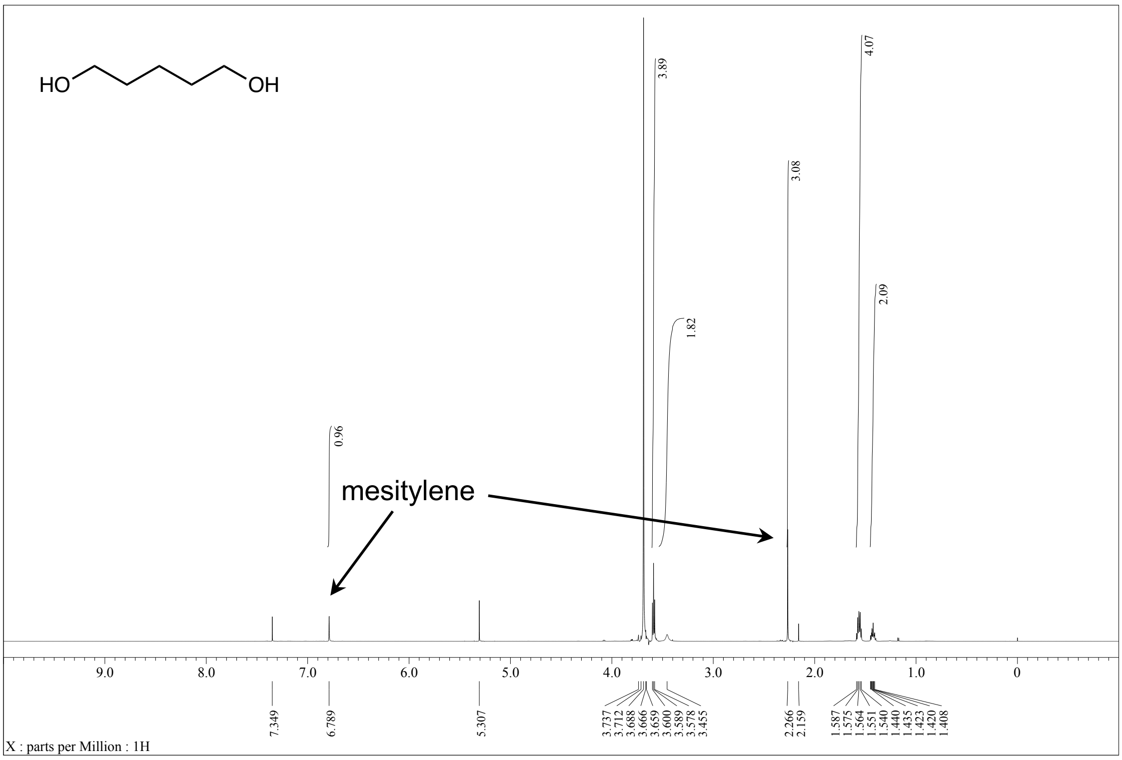


Figure S8. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of PD in the reaction mixture obtained from full hydrogenation of PVL-b with **Ir3**. The peak at 3.61 ppm was used for NMR yield calculation. As the major solvent-derived impurities, dichloromethane (5.31 ppm) and 1,4-dioxane (3.69 ppm) were detected.

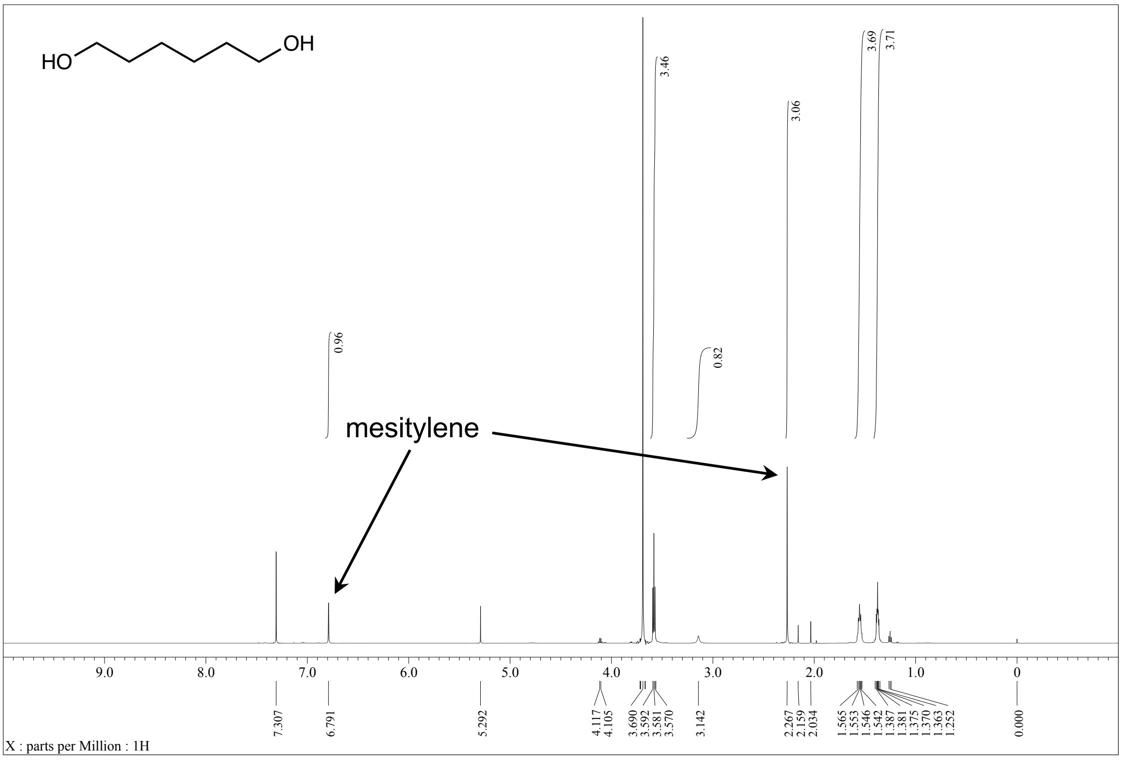


Figure S9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of 1,6-HD in the reaction mixture obtained from full hydrogenation of PCL-b with **Ir3**. The peak at 3.61 ppm was used for NMR yield calculation. As the major solvent-derived impurities, dichloromethane (5.29 ppm) and 1,4-dioxane (3.69 ppm) were detected.

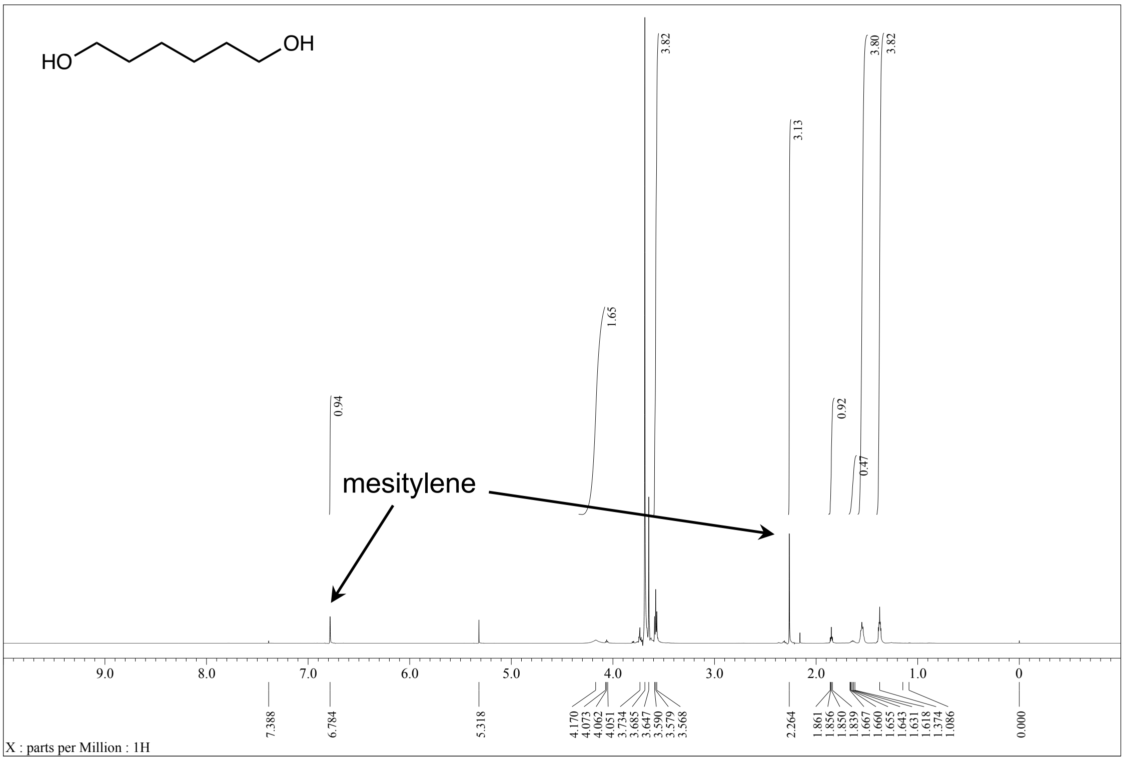


Figure S10. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of 1,6-HD in the reaction mixture obtained from full hydrogenation of PEA with **Ir3**. The peak at 3.61 ppm was used for NMR yield calculation; in cases where overlap with other peaks occurred, such as when using a different iridium complex, the peak at 1.34–1.38 ppm was used instead. As the major solvent-derived impurities, dichloromethane (5.32 ppm) and 1,4-dioxane (3.69 ppm) were detected.

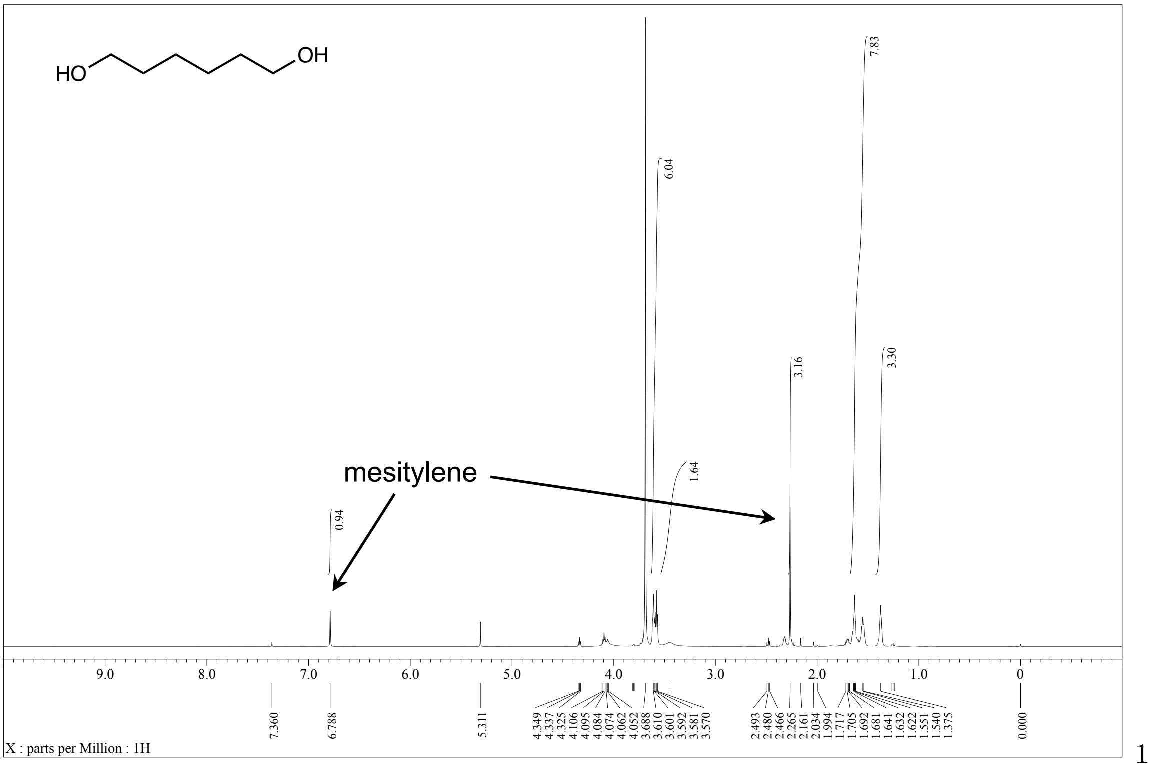


Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, rt) of 1,6-HD in the reaction mixture obtained from full hydrogenation of PBA with **Ir6**. The peak at 3.61 ppm was normally used for NMR yield determination; in this case, due to overlap with other peaks, the peak at 1.34–1.38 ppm was used instead. As the major solvent-derived impurities, dichloromethane (5.31 ppm) and 1,4-dioxane (3.69 ppm) were detected.

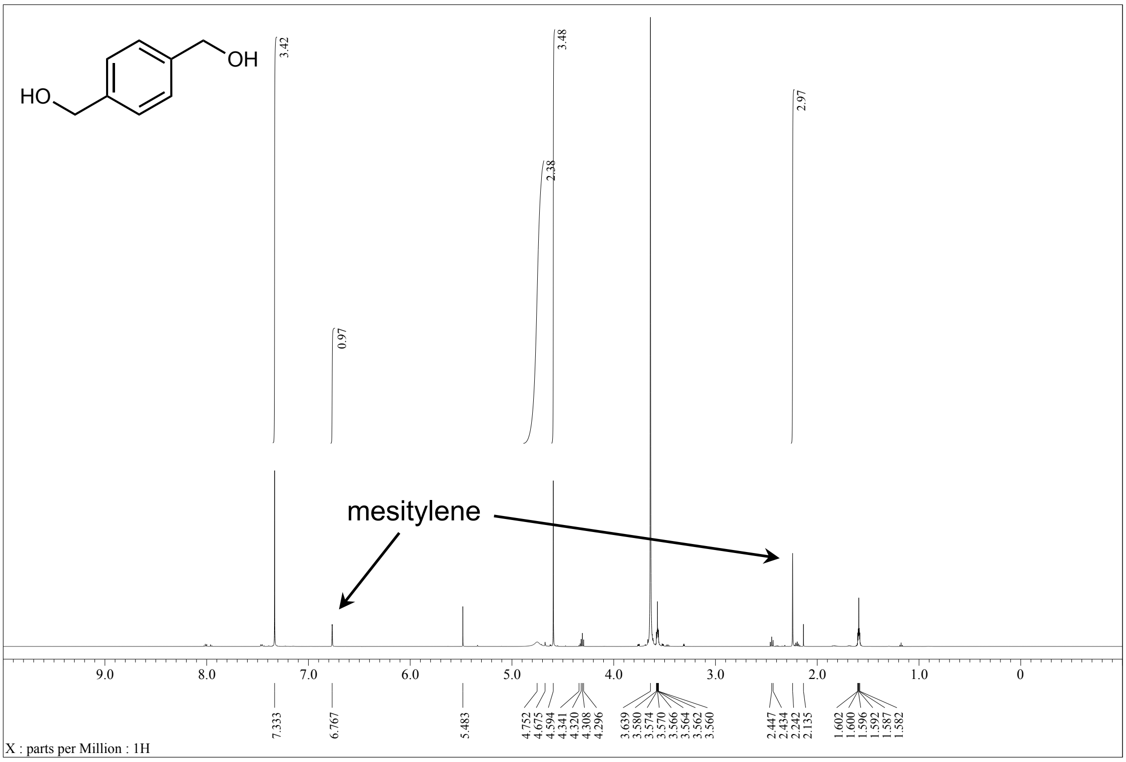
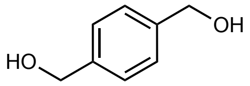


Figure S12. ^{1}H NMR spectrum (600 MHz, CD$_3$OD, rt) of BDM in the reaction mixture obtained from full hydrogenation of PBT with **Ir6**. The peak at 7.33 ppm was used for NMR yield calculation. As the major solvent-derived impurities, dichloromethane (5.48 ppm) and 1,4-dioxane (3.64 ppm) were detected.

5.2. Compounds isolated in this work

1,4-Benzenedimethanol (BDM)



After completion of the hydrogenation reaction, the autoclave was cooled to room temperature and opened. The reaction mixture was filtered to remove insoluble residues, and the residues were washed with methanol, The combined filtrates were concentrated under reduced pressure using a rotary evaporator. The residue was dissolved in hot water, and any remaining insoluble solid was removed by filtration. The clear aqueous solution was concentrated under reduced pressure to obtain a crude solid, which was suspended in CH_2Cl_2 and filtered to remove orange-colored impurities. Then, the desired BDM was obtained as a white solid (128 mg, 0.929 mmol, 93%)

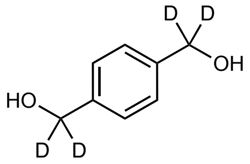
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.25 (s, 4H), 5.12 (t, *J* = 6.0 Hz, 2H), 4.47 (d, *J* = 5.4 Hz, 4H).

^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 140.9, 126.2, 62.8.

HRMS (ESI-QTOF): *m*/*z* calculated for $[C_8H_{10}O_2+Na]^+$: 161.0573; found: 161.0582.

The analytical data are consistent with literature values.[15]

1,4-Benzenedi(methan-d_2-ol) (BDM-D)



BDM-D was prepared following the same hydrogenation and workup procedure as BDM. The resulting white solid was collected and dried under vacuum to give BDM-D as a white solid (122 mg, 0.860 mmol, 86% yield, 96% D).

^{1}H NMR (600 MHz, CD_3OD): δ 7.32 (s, 4H). Hydroxyl protons were not observed.

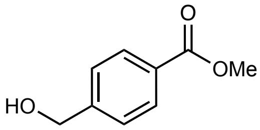
^{2}H NMR (91 MHz, MeOH): δ 4.89 (minor, OD), 4.57 (benzylic CD_2).

^{13}C{^{1}H} NMR (151 MHz, CD_3OD): δ 141.6, 128.1, 64.8–64.1.

HRMS (ESI-QTOF): *m*/*z* calculated for $[C_8H_6D_4O_2+Na]^+$: 165.0824; found: 165.0834.

The analytical data are consistent with literature values.[16]

Methyl 4-(hydroxymethyl)benzoate (MHMB)



After completion of the hydrogenation reaction and solvent removal under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt/Et_3N = 100:50:1 → 3:2:0) to give MHMB as a white solid (97.5 mg, 0.587 mmol, 59%).

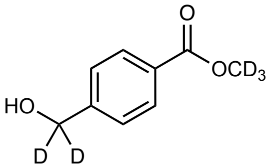
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 4.77 (d, *J* = 5.4 Hz, 2H), 3.92 (s, 3H), 1.86 (t, *J* = 6.0 Hz, 1H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.2, 146.2, 129.9, 129.3, 126.6, 64.7, 52.2.

HRMS (ESI-QTOF): *m*/*z* calculated for $[C_9H_{10}O_3+Na]^+$: 189.0522; found: 189.0528.

The analytical data are consistent with literature values.[17]

Methyl-*d*$_3$ 4-(hydroxymethyl-*d*$_2$)benzoate (MHMB-D)



MHMB-D was obtained following the same hydrogenation and workup procedure as MHMB. The residue was purified by flash column chromatography on silica gel (hexane/AcOEt/Et_3N = 100:50:1 → 3:2:0) to give MHMB as a white solid (90.7 mg, 0.530 mmol, 53% yield, >99% D for the benzylic position and 98% D for OCD_3).

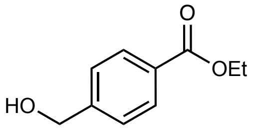
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 1.75 (s, 1H).

^{2}H NMR (91 MHz, $CHCl_3$): δ 4.75, 3.90.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 167.2, 146.1, 129.9, 129.4, 126.6, 64.3–63.7, 51.8–51.3.

HRMS (ESI-QTOF): *m*/*z* calculated for $[C_9H_5D_5O_3+Na]^+$: 194.0836; found: 194.0833.

Ethyl 4-(hydroxymethyl)benzoate (EHMB)



After completion of the hydrogenation reaction and solvent removal under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt/Et_3N = 100:50:1 → 3:2:0) to give EHMB as a colorless oil (101 mg, 0.560 mmol, 56%).

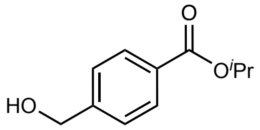
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 4.76 (s, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.95 (s, 1H), 1.40 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 166.7, 146.1, 129.9, 129.7, 126.5, 64.7, 61.1, 14.4.

HRMS (ESI-QTOF): m/z calculated for $[C_{10}H_{12}O_3+Na]^+$: 203.0679; found: 203.0679.

The analytical data are consistent with literature values.[18]

Isopropyl 4-(hydroxymethyl)benzoate (IHMB)



After completion of the hydrogenation reaction and solvent removal under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane/AcOEt/Et_3N = 100:50:1 → 3:2:0) to give IHMB as a colorless oil (99.3 mg, 0.514 mmol, 51%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 5.25 (m, 1H), 4.77 (d, *J* = 3.6 Hz, 2H), 1.83 (m, 1H), 1.37 (t, *J* = 6.6 Hz, 6H).

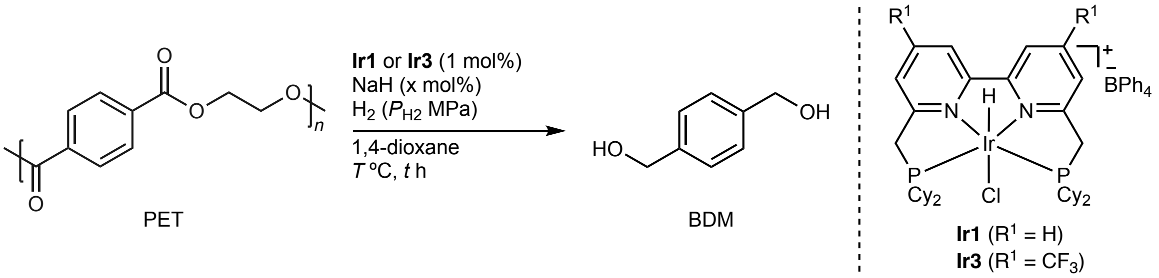
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 166.2, 146.0, 130.1, 129.9, 126.5, 68.5, 64.8, 22.0.

HRMS (ESI-QTOF): m/z calculated for: $[C_{11}H_{14}O_3+Na]^+$: 217.0837; found: 217.0835.

The analytical data are consistent with literature values.[19]

6. Supplementary Tables for Investigation into Various Reaction Conditions

Table S3. Optimization of reaction conditions for full hydrogenation



Entry	Ir complex	NaH (x mol%)	P_{H2} (MPa)	*T* (ºC)	*t* (h)	BDM (%)[a]
1	**Ir1**	10	2	190	24	88
2	**Ir1**	10	1	190	24	40
3	**Ir1**	10	2	160	24	46
4	**Ir1**	10	2	190	12	62
5	**Ir1**	5	2	190	24	73
6	**Ir1**	-[b]	2	190	24	3
7	-[c]	10	2	190	24	n.d.
8[d]	**Ir1**	10	2	190	24	61
9[e]	**Ir1**	10	2	190	24	4
10	**Ir3**	10	2	190	24	>99
11	**Ir3**	10	P_{Ar} = 2 MPa [f]	190	24	n.d.

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

[b] No base added.

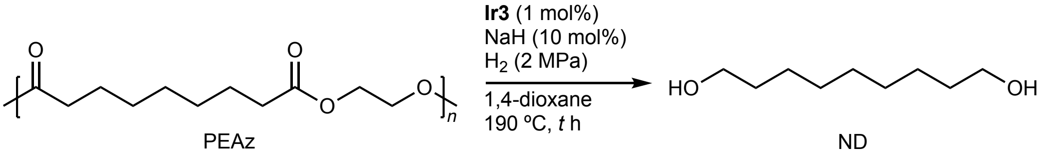
[c] No iridium complex added.

[d] Toluene used as the solvent instead of 1,4-dioxane.

[e] α,α,α-Trifluorotoluene used as the solvent instead of 1,4-dioxane.

[f] Reaction under an argon atmosphere.

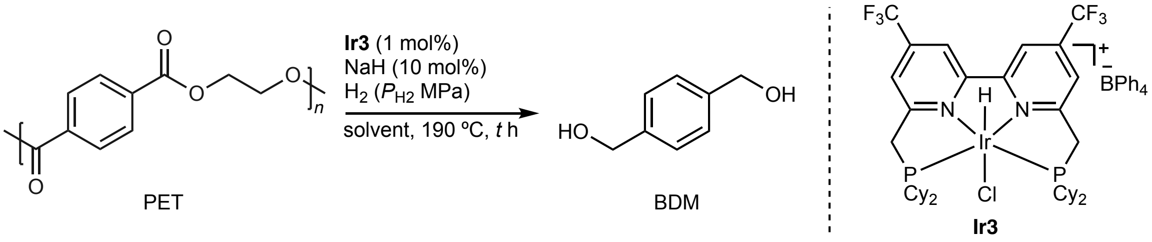
Table S4. Effect of reaction time on the depolymerization of PEAz using **Ir3**



Entry	*t* (h)	ND (%)[a]
1	24	81
2	48	79

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

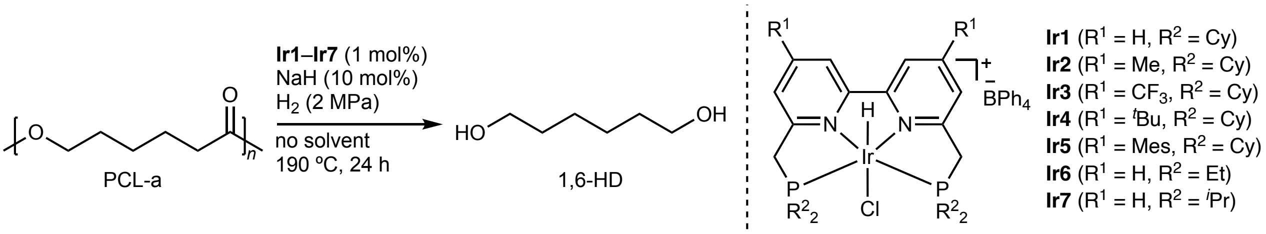
Table S5. Effect of hydrogen pressure and solvent on the depolymerization of PET



Entry	P_{H2} (MPa)	solvent	*t* (h)	BDM (%)[a]
1	2	1,4-dioxane (3 mL)	24	>99%
2	1	1,4-dioxane (3 mL)	48	81
3	2	no solvent	24	<1

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

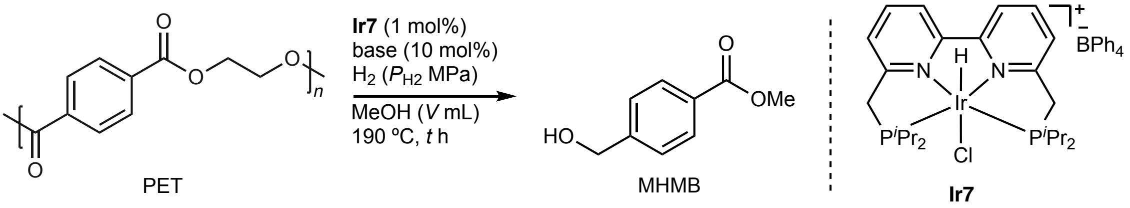
Table S6. Screening of Ir complexes for solvent-free depolymerization of PCL-a



Entry	Ir complex	1,6-HD (%)[a]
1	**Ir1**	83
2	**Ir2**	43
3	**Ir3**	52
4	**Ir4**	86
5	**Ir5**	56
6	**Ir6**	36
7	**Ir7**	24

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

Table S7. Optimization of reaction conditions for semi-hydrogenation of PET



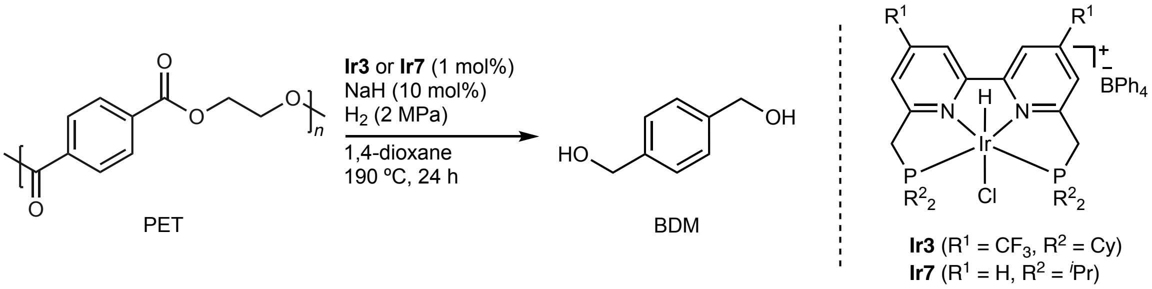
Entry	base	P_{H2} (MPa)	*V* (mL)	*t* (h)	MHMB (%)[a]
1	NaOMe	5	5.0	12	68
2	NaOMe	1	5.0	9	67
3	NaOMe	1	5.0	6	59
4	NaOMe	1	3.0	6	60
5	KO*t*Bu	1	5.0	9	67
6	NaO*t*Bu	1	5.0	9	69
7	NaH	1	5.0	9	72 (59)
8	–[b]	1	5.0	9	n.d.
9[c]	NaH	1	5.0	9	n.d.

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard. The value in parentheses for entry 7 refers to the isolated yield.

[b] No base added.

[c] No iridium complex added.

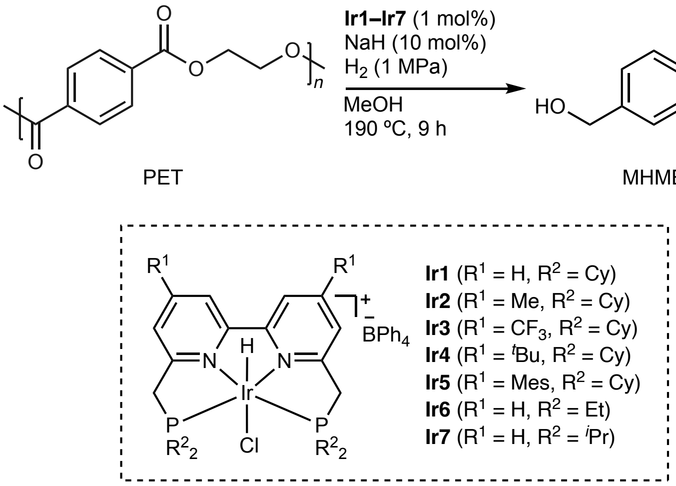
Table S8. Comparison of the catalytic activities of **Ir3** and **Ir7** in full hydrogenation of PET to BDM



Entry	Ir complex	BDM (%)[a]
1	**Ir3**	>99
2	**Ir7**	27

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

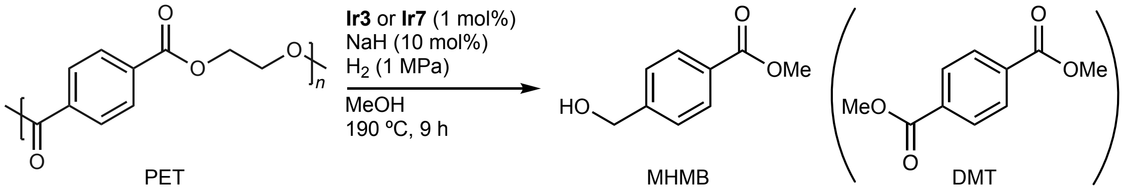
Table S9. Catalytic activities of **Ir1**–**Ir7** in semi-hydrogenation of PET



Entry	Ir complex	MHMB (%)[a]
1	**Ir1**	64
2	**Ir2**	1
3	**Ir3**	2
4	**Ir4**	n.d.
5	**Ir5**	n.d.
6	**Ir6**	30
7	**Ir7**	72 (59)

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard. The value in parentheses for entry 7 refers to the isolated yield.

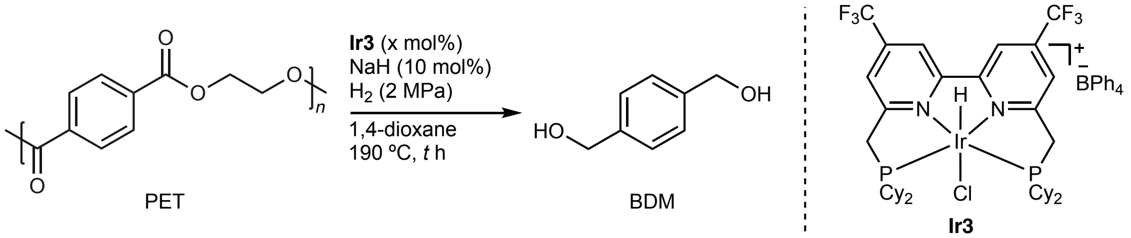
Table S10. Comparison of the catalytic activities of **Ir3** and **Ir7** in semi-hydrogenation of PET



Entry	Ir complex	MHMB (%)[a]	DMT (%)[a]
1	**Ir3**	2	96
2	**Ir7**	72 (59)	11

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard. The value in parentheses for entry 2 refers to the isolated yield.

Table S11. Screening of reaction conditions for the hydrogenation of commodity PET products using **Ir3**



Colorless bottle

Colored bottle

White T-shirt

Black T-shirt

Entry	material	**Ir3** (mol%)	*t* (h)	BDM (%)[a]
1	colorless bottle	1	24	>99
2	colored bottle	1	24	50
3	colored bottle	1	48	88
4	white T-shirt	1	24	81
5	white T-shirt	1	48	94
6	black T-shirt	1	24	53
7	black T-shirt	2	24	95

[a] Determined by ^1H NMR analysis using mesitylene as an internal standard.

7. Supplementary References

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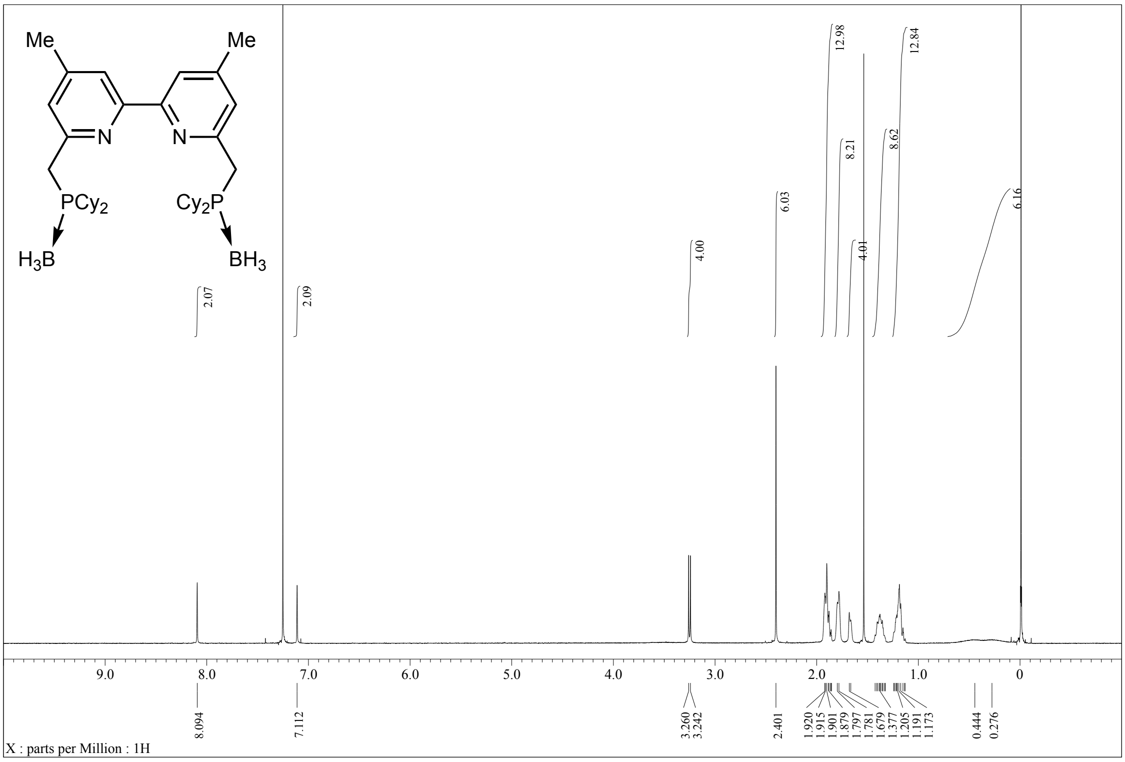
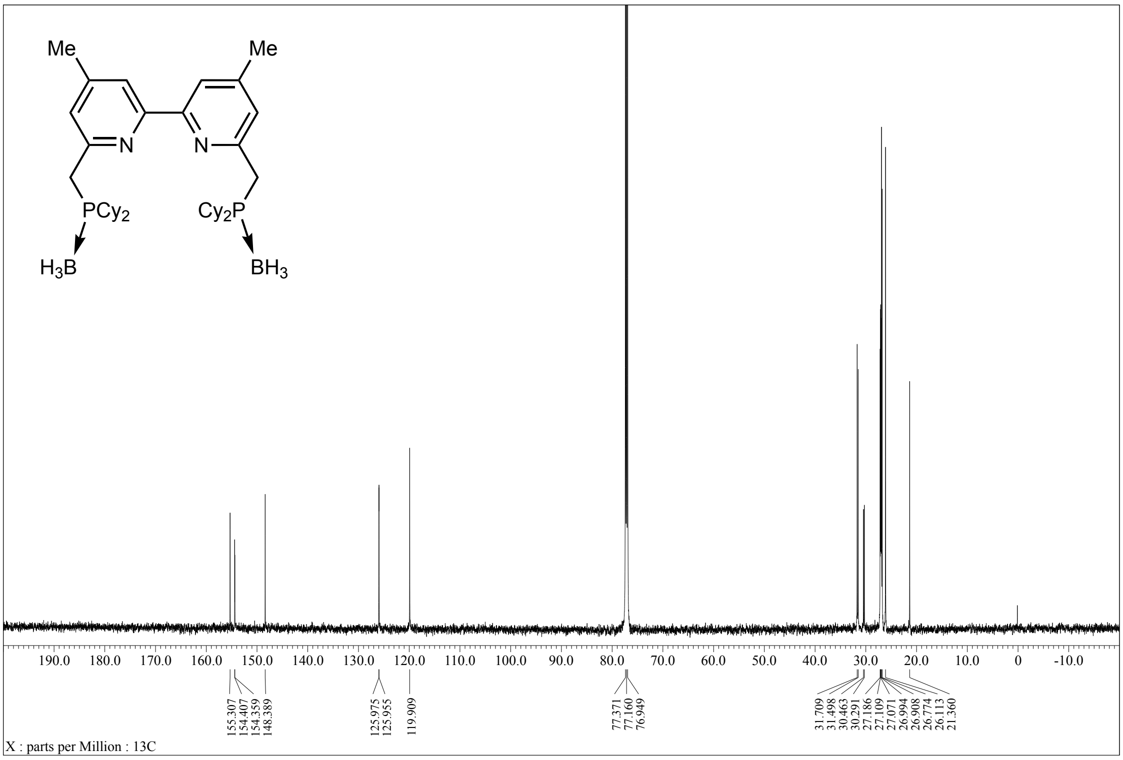
8. NMR Spectra

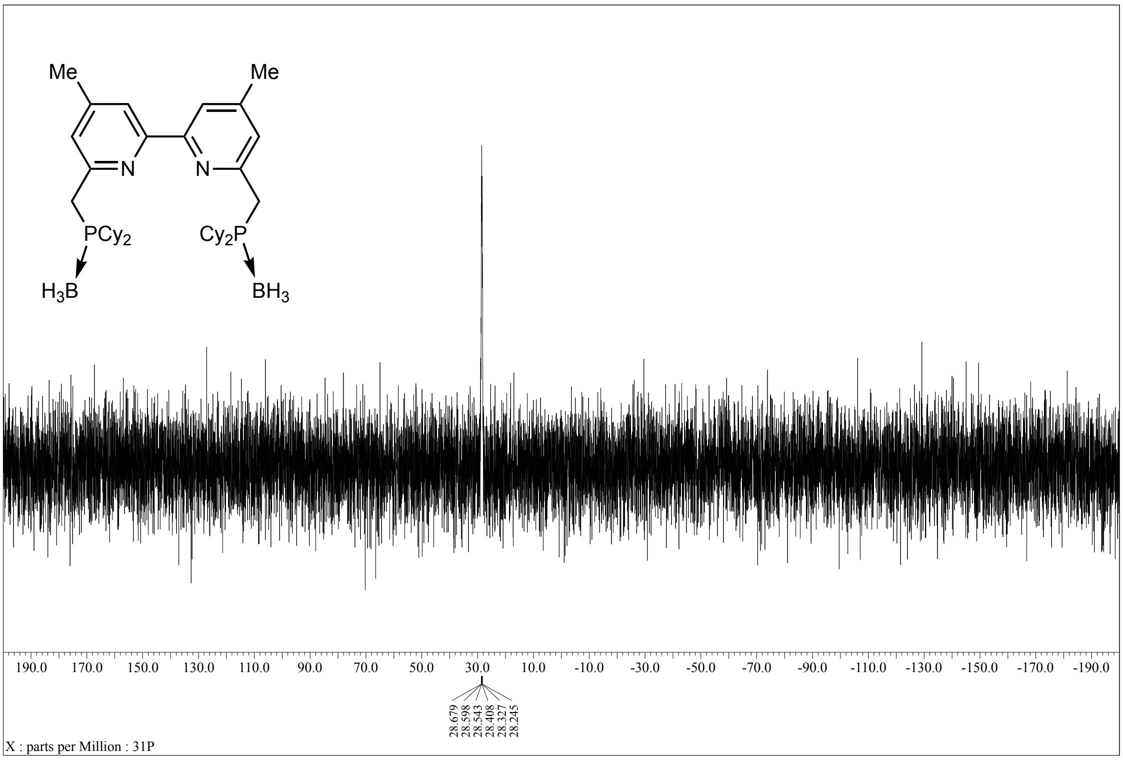
L2, ^{1}H NMR (600 MHz, $CDCl_3$, rt)



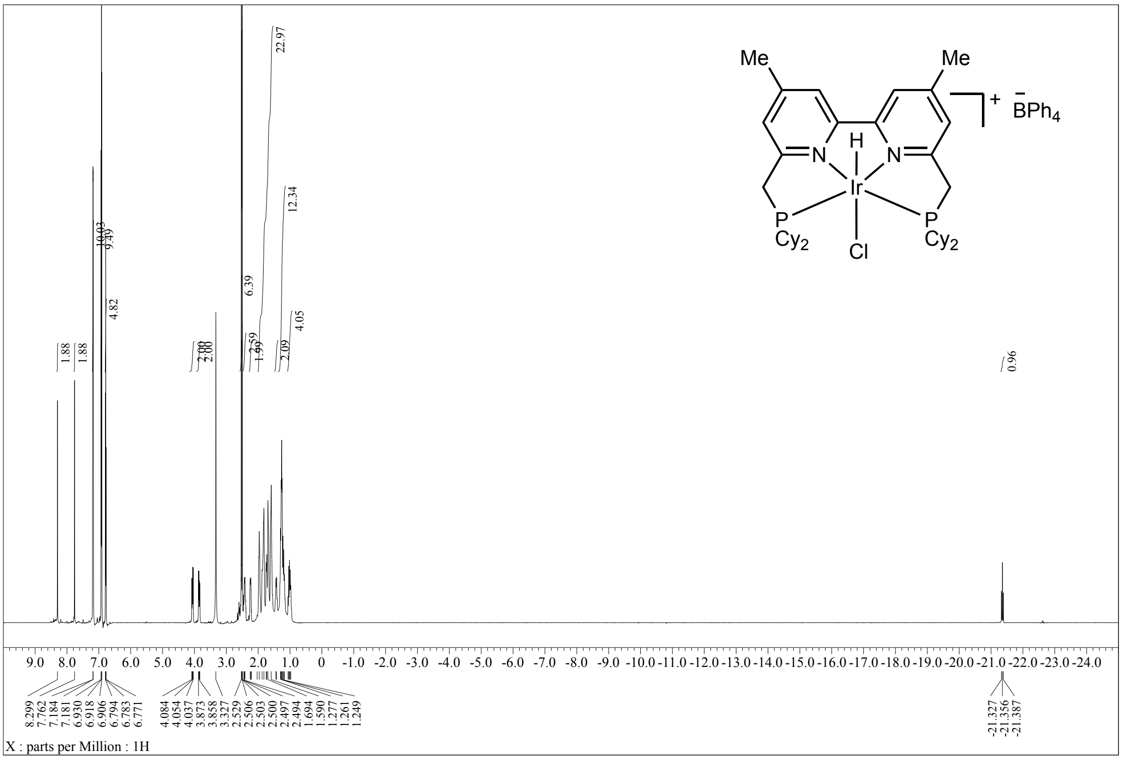
L2, $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, rt)



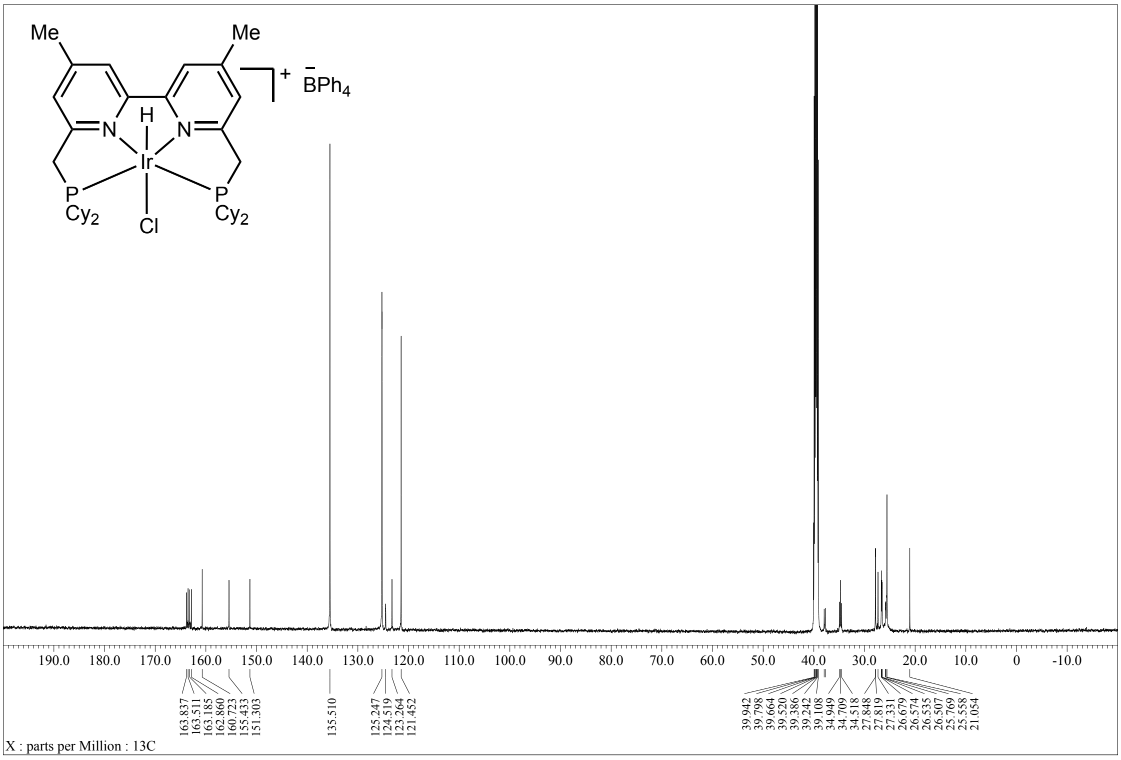
L2, $^{31}P\{^1H\}$ NMR (243 MHz, CDCl$_3$, rt)



Ir2, ^1H NMR (600 MHz, DMSO-d_6, rt)



Ir2, ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6, rt)



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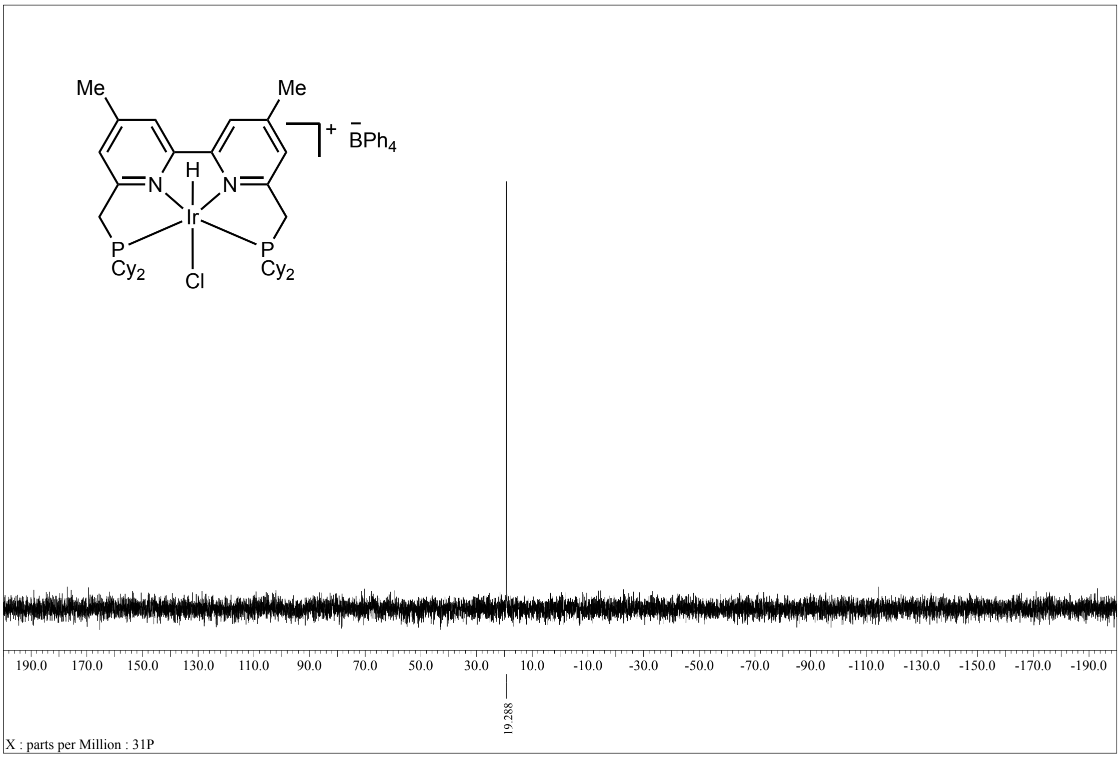
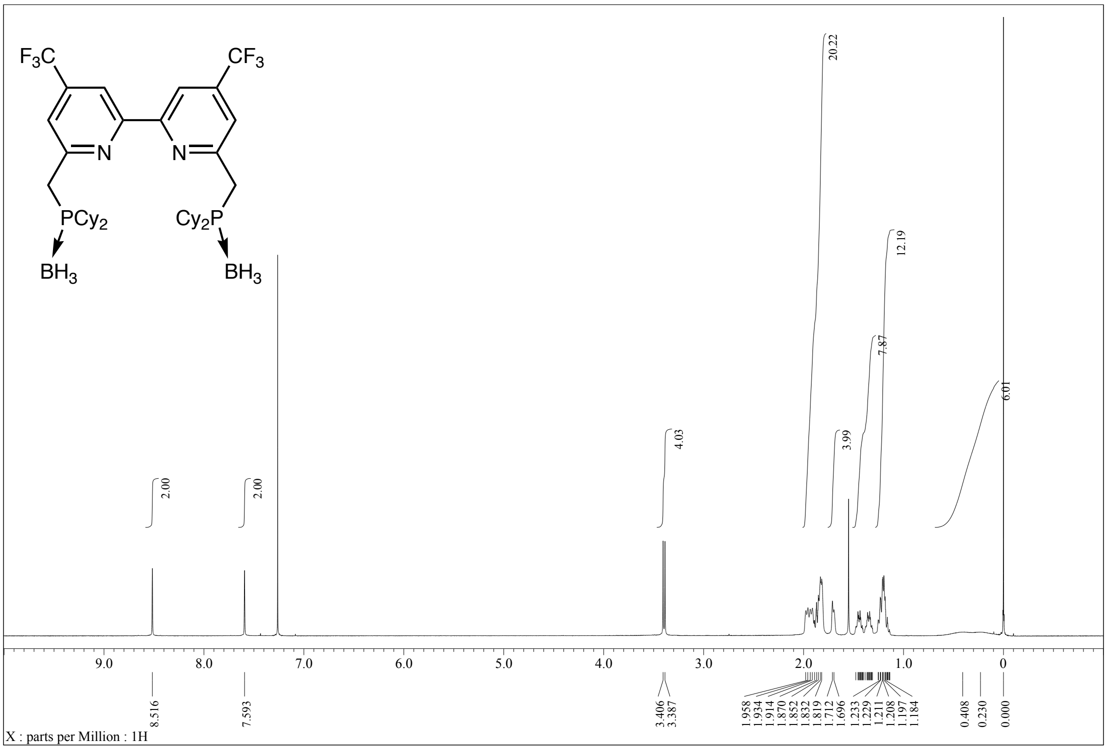
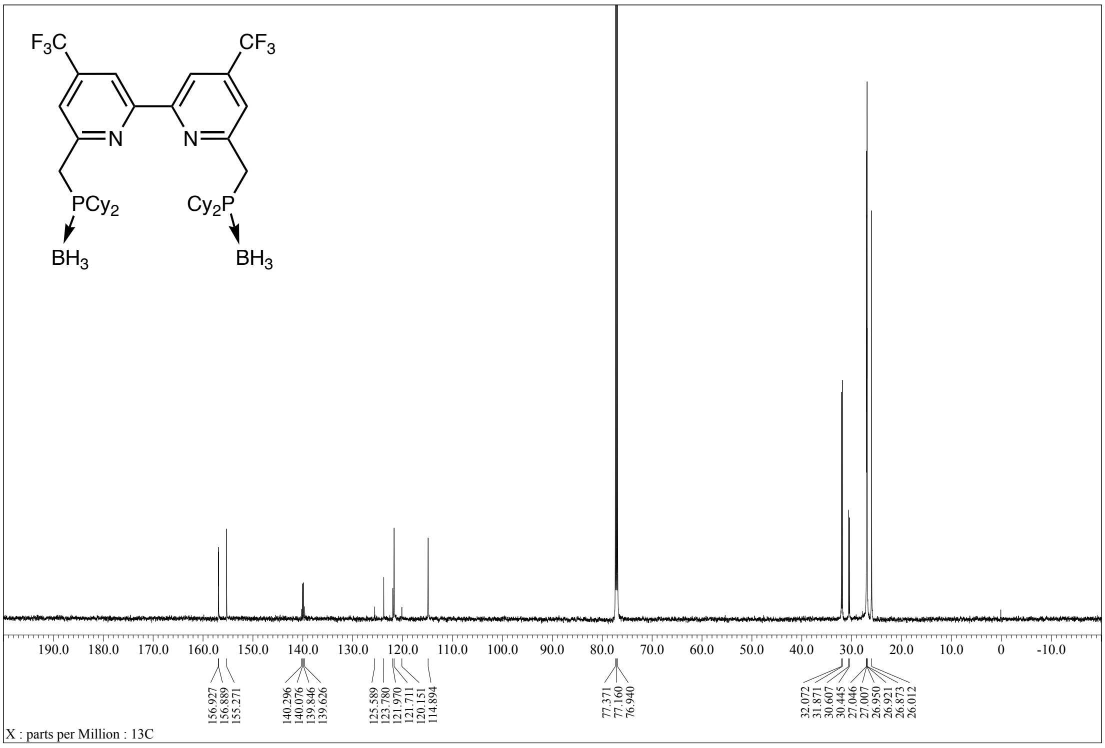


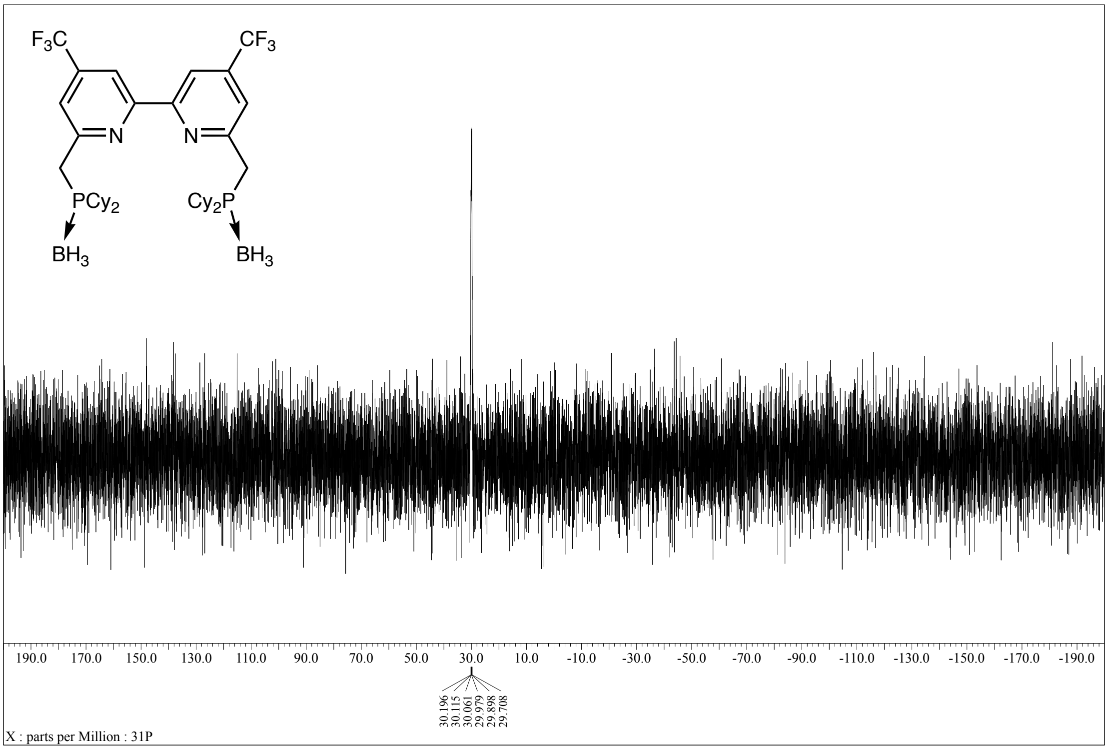
L3, ^{1}H NMR (600 MHz, $CDCl_3$, rt)



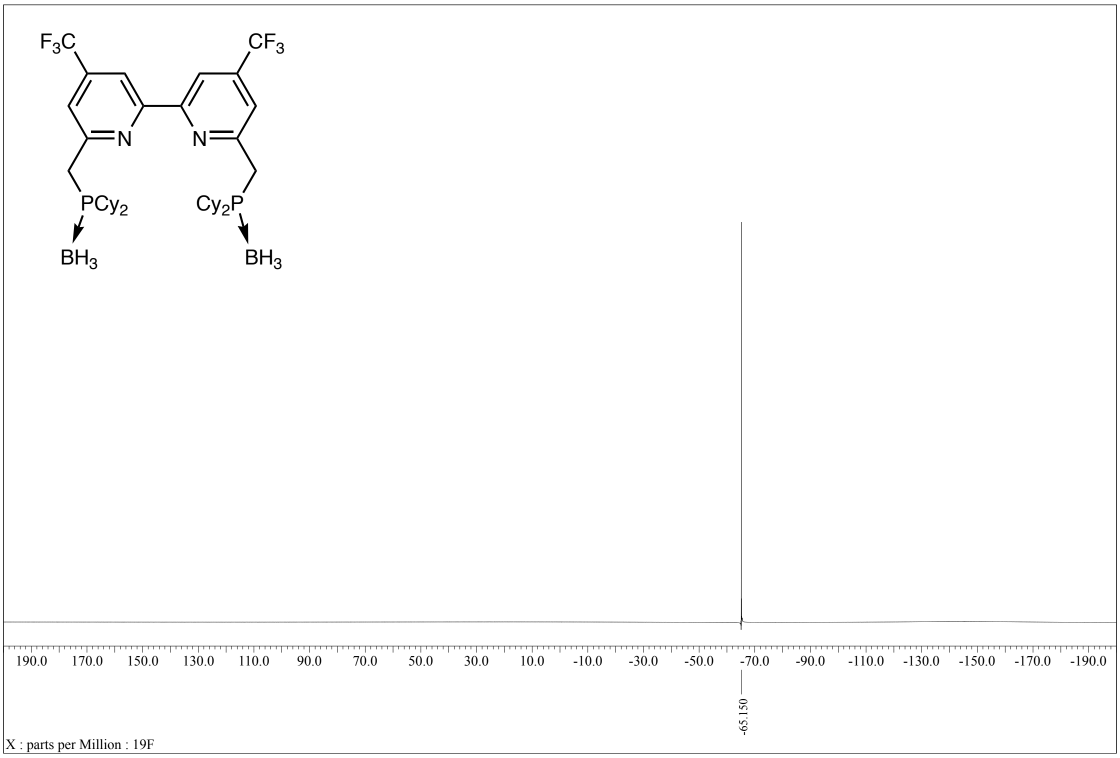
L3, ^{13}C NMR (151 MHz, $CDCl_3$, rt)



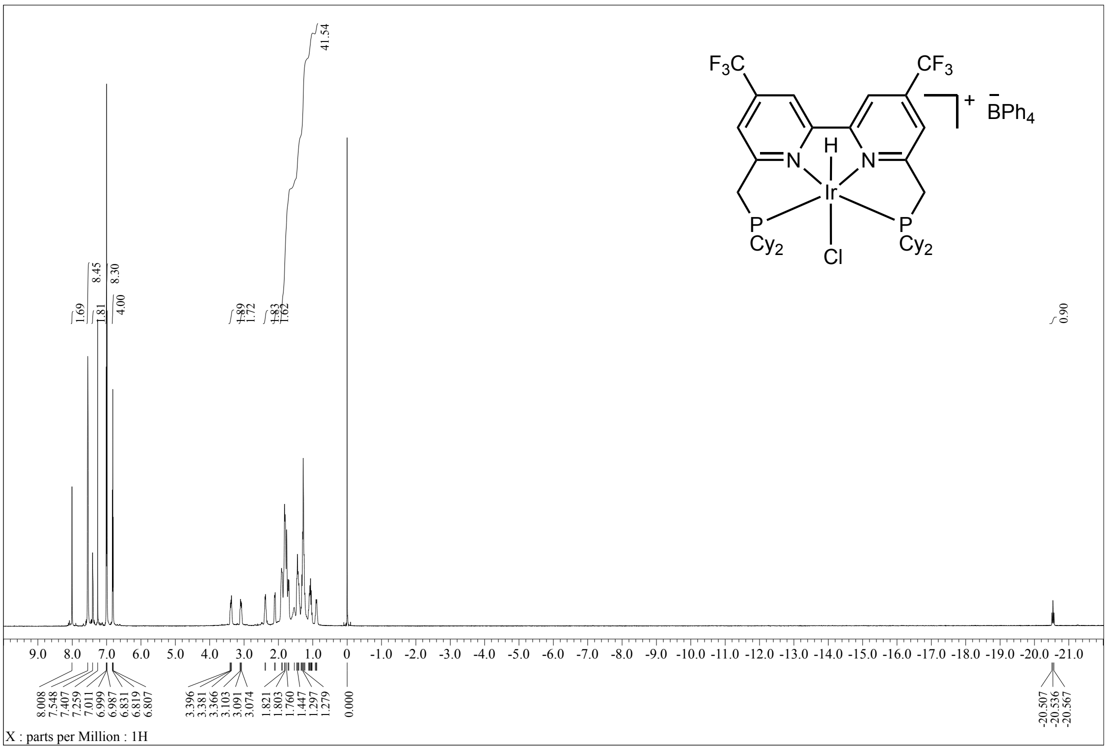
L3, ^{31}P NMR (243 MHz, CDCl$_3$, rt)



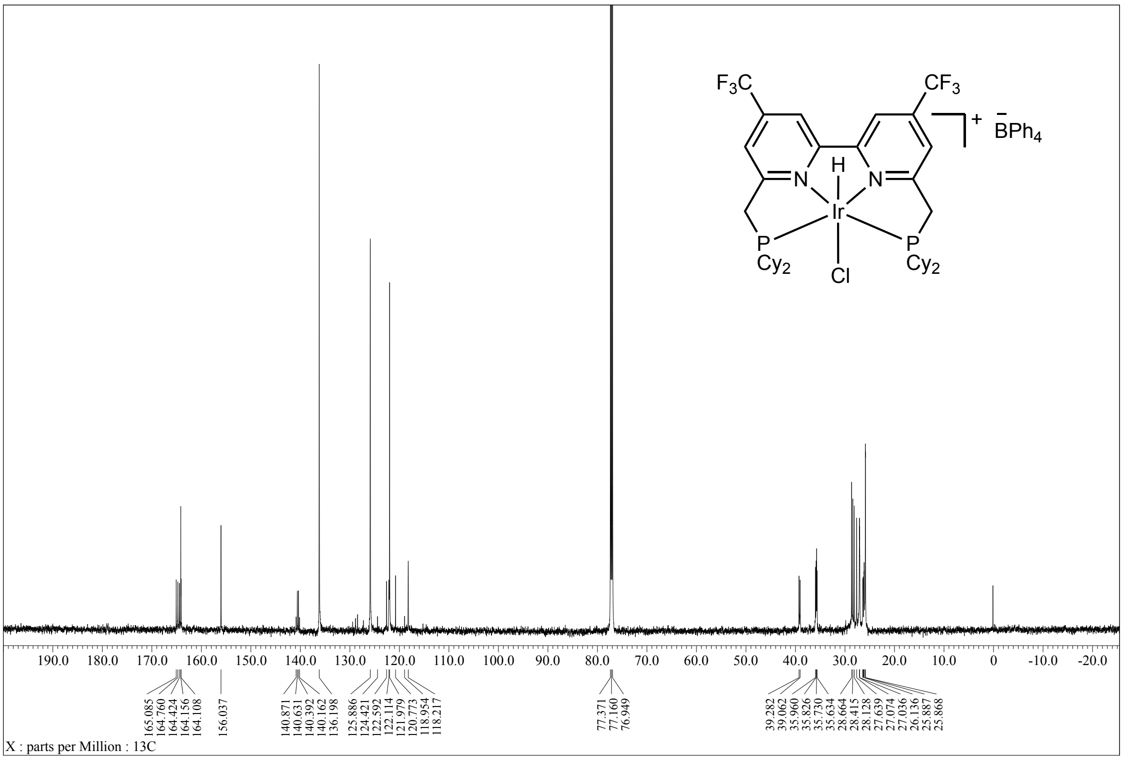
L3, ^{19}F NMR (565 MHz, CDCl$_3$, rt)



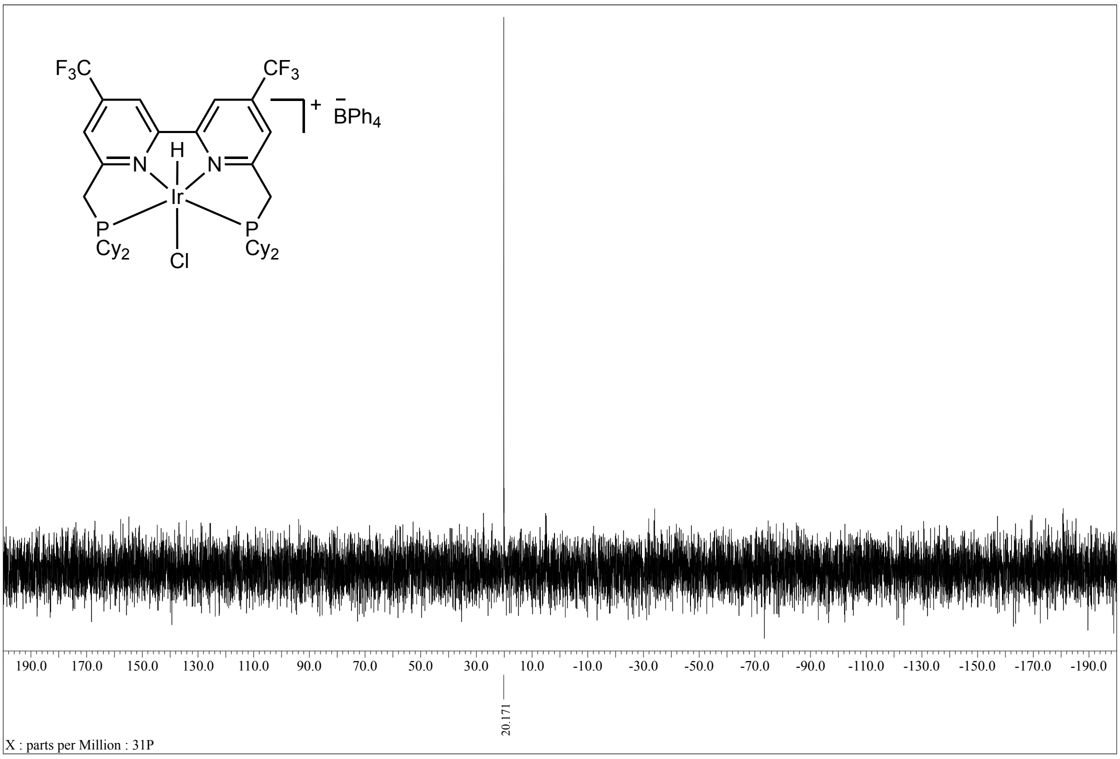
Ir3, ^{1}H NMR (600 MHz, CDCl$_3$, rt)



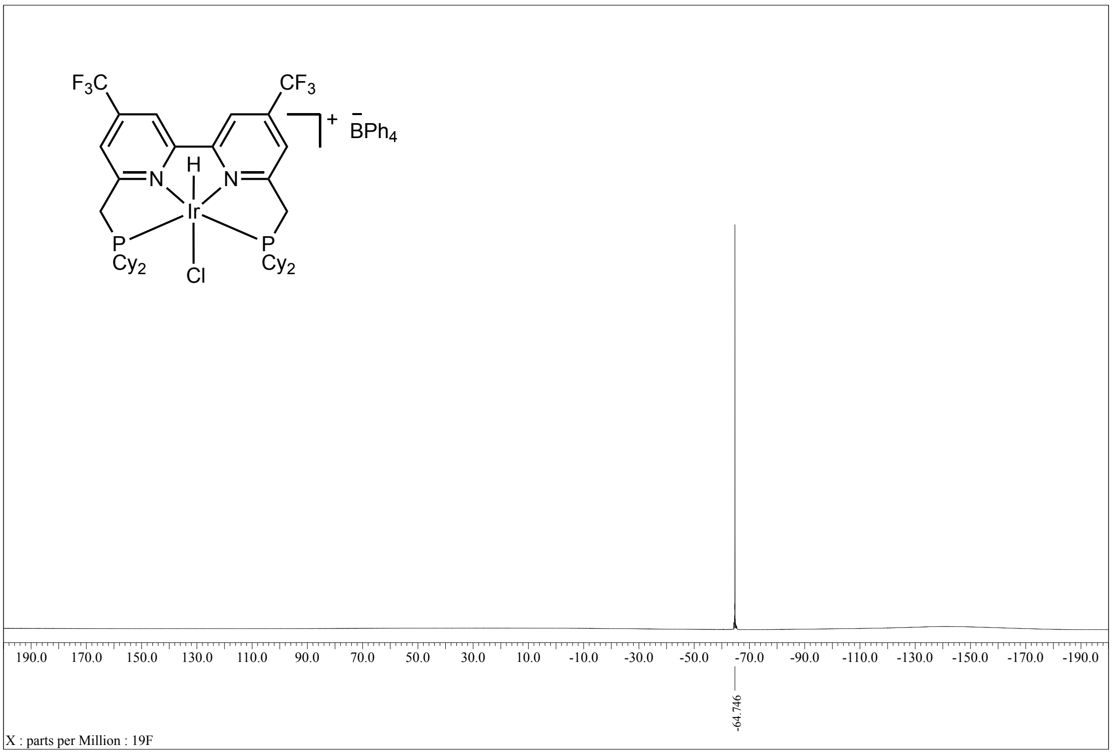
Ir3, ^{13}C NMR (151 MHz, CDCl$_3$, rt)



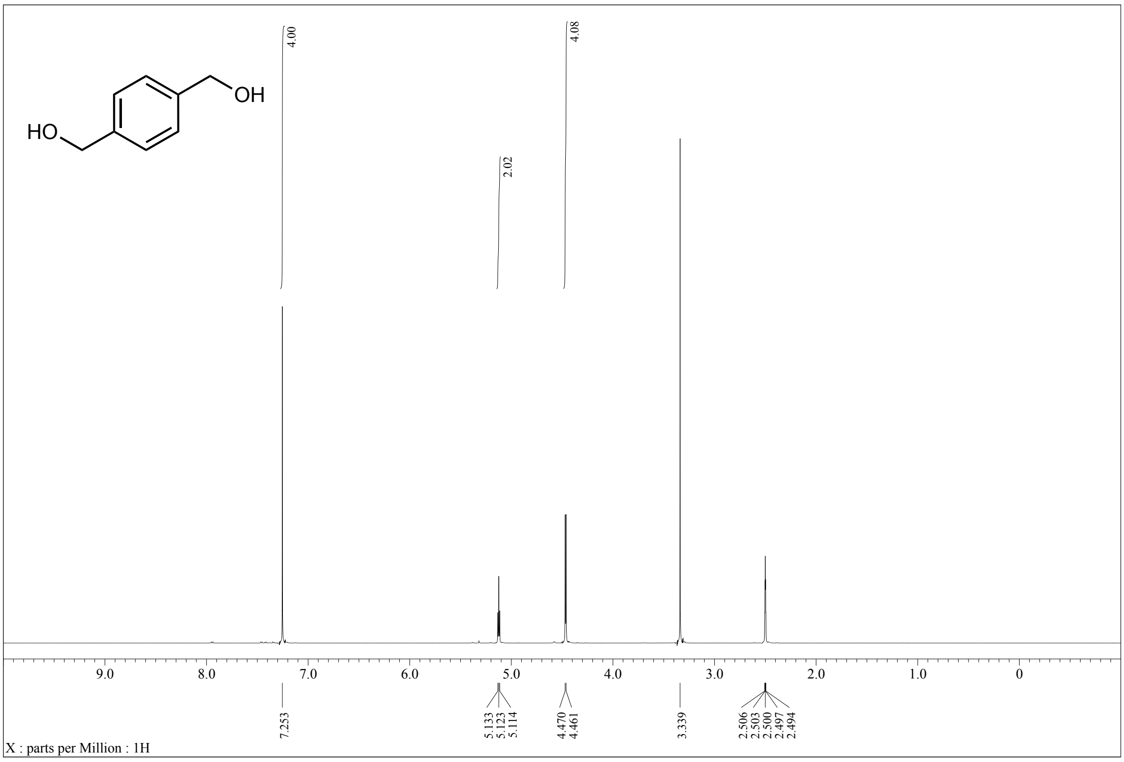
Ir3, ^{31}P NMR (243 MHz, $CDCl_3$, rt)



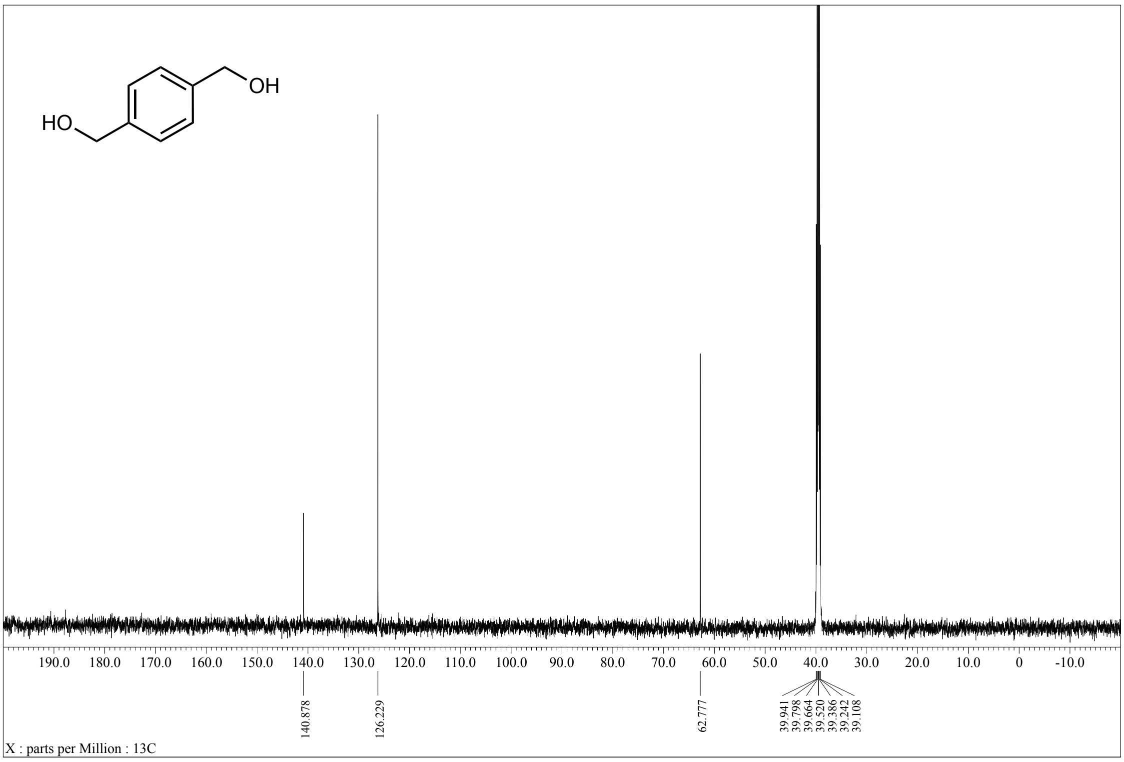
Ir3, ^{19}F NMR (564 MHz, $CDCl_3$, rt)



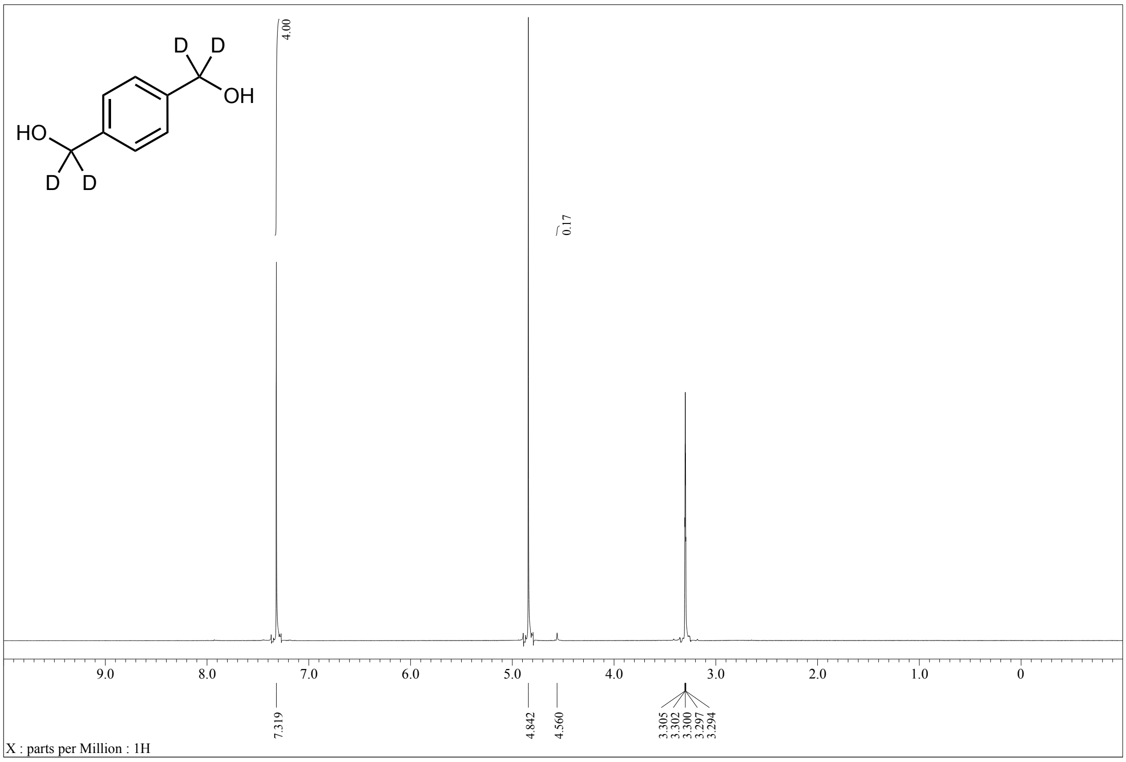
BDM, ^{1}H NMR (600 MHz, DMSO-d_6, rt)



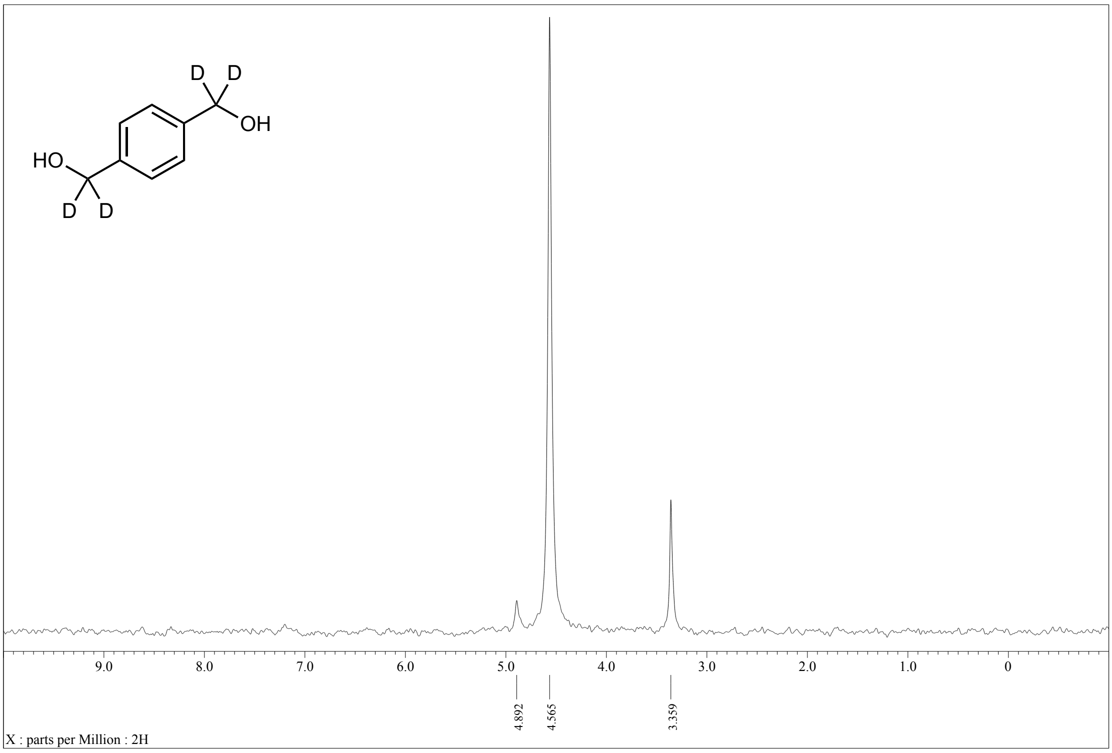
BDM, ^{13}C NMR (151 MHz, DMSO-d_6, rt)



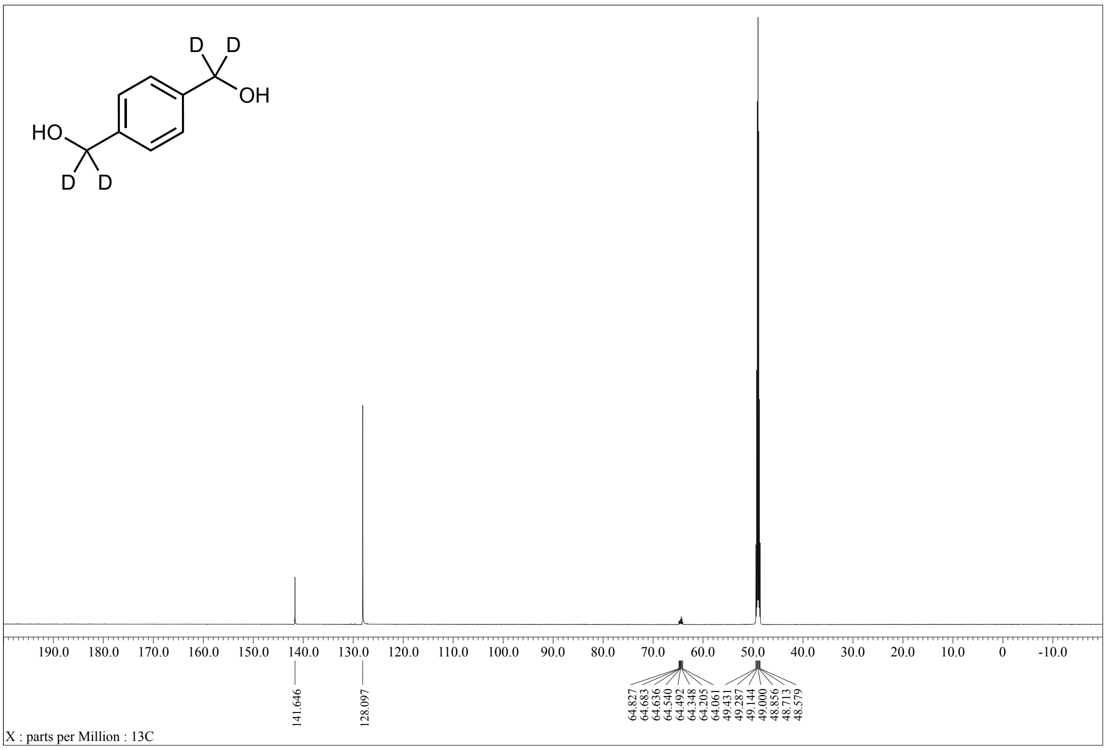
BDM-D, ^{1}H NMR (600 MHz, CD_3OD, rt)



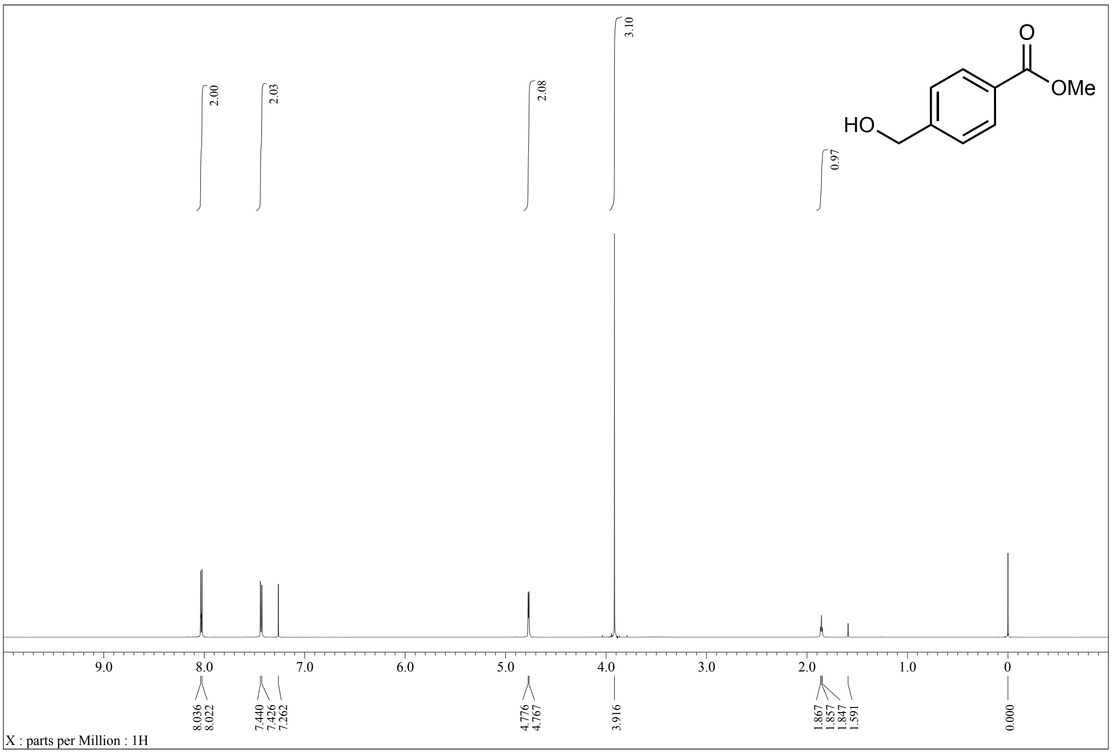
BDM-D, ^{2}H NMR (91 MHz, MeOH, rt)



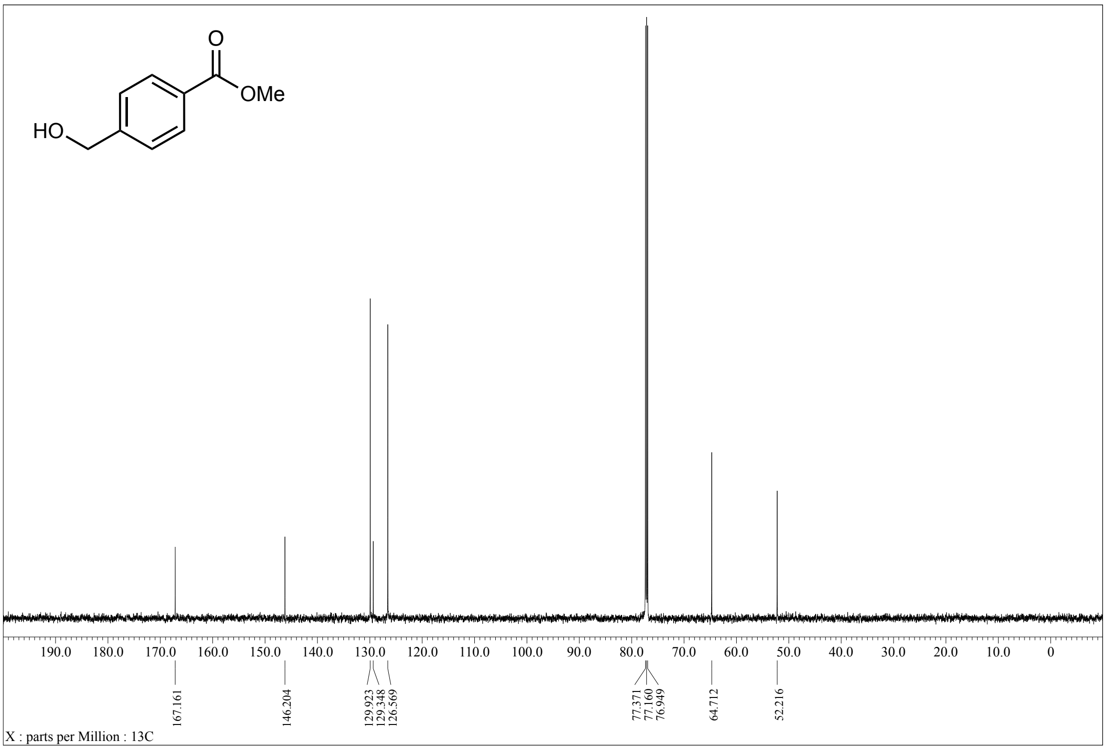
BDM-D, ^{13}C NMR (151 MHz, CD_3OD, rt)



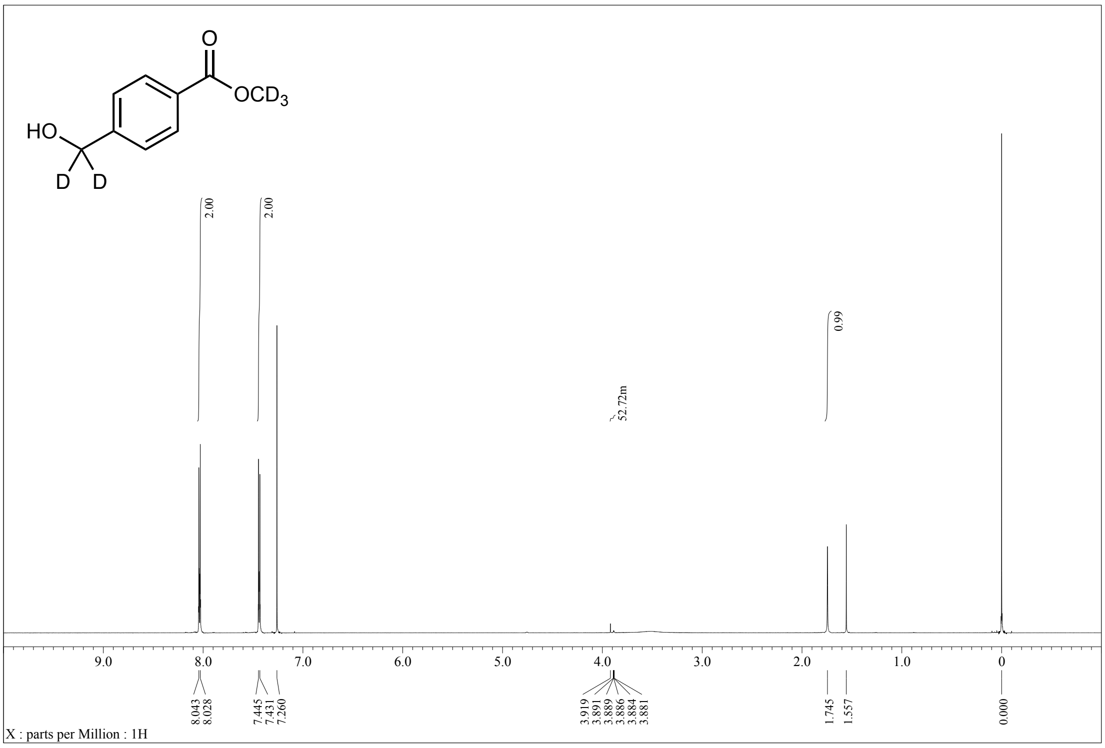
MHMB, ^{1}H NMR (600 MHz, $CDCl_3$, rt)



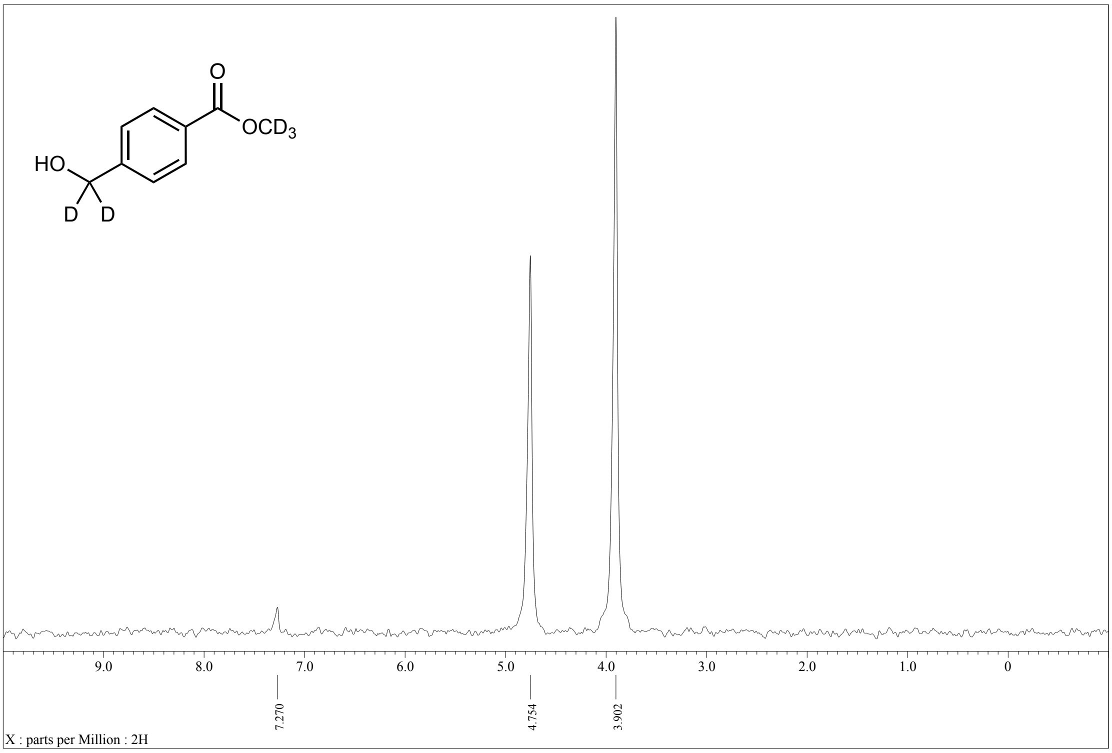
MHMB, ^{13}C NMR (151 MHz, $CDCl_3$, rt)



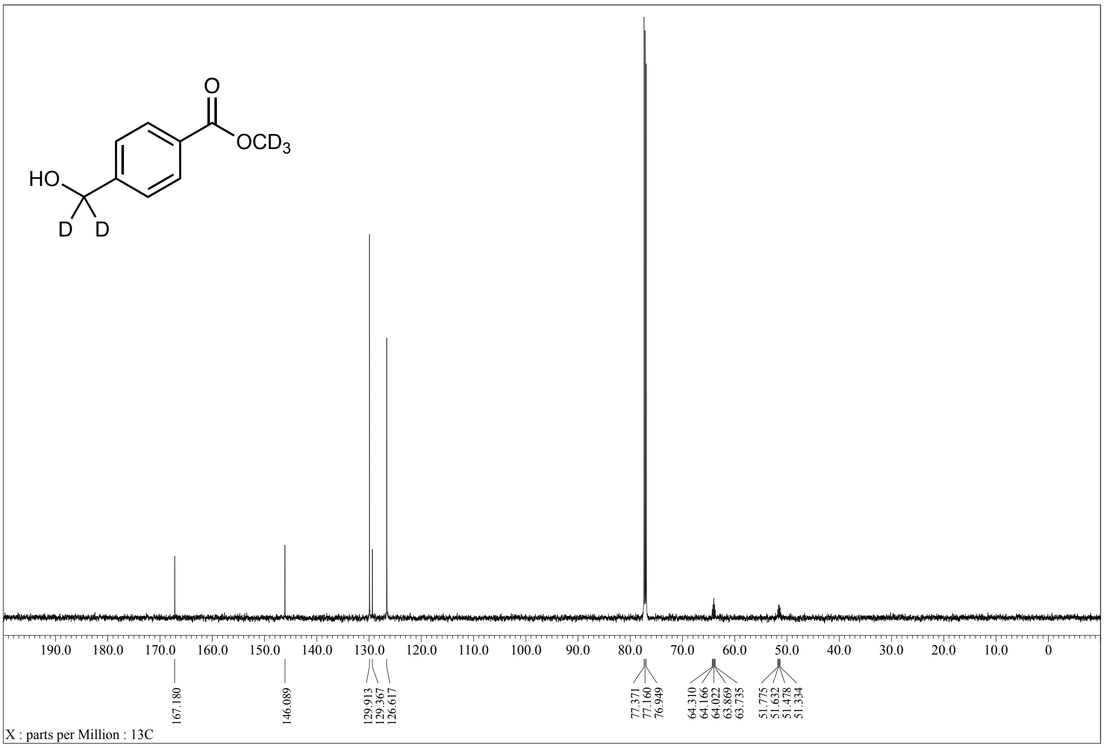
MHMB-D, ^{1}H NMR (600 MHz, $CDCl_3$, rt)



MHMB-D, ^{2}H NMR (91 MHz, $CHCl_3$, rt)

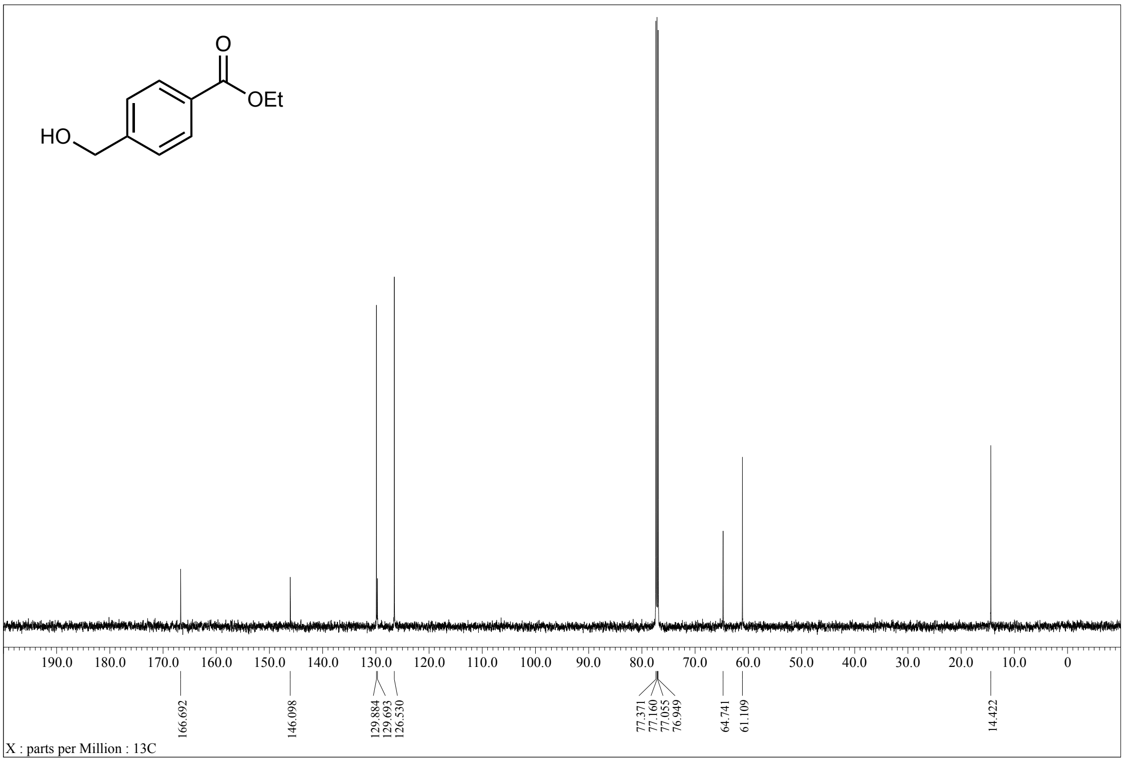


MHMB-D, ^{13}C NMR (151 MHz, $CDCl_3$, rt)



EHMB, ^{1}H NMR (600 MHz, $CDCl_3$, rt)

EHMB, ^{13}C NMR (151 MHz, $CDCl_3$, rt)



IHMB, ^{1}H NMR (600 MHz, $CDCl_3$, rt)

IHMB, ^{13}C NMR (151 MHz, $CDCl_3$, rt)