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Supporting Information

Ester Hydrogenolysis *via* β-C–O Bond Cleavage Catalyzed by a Phenanthroline-Based PNNP-Cobalt(I) Complex

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General. All experiments were performed under a nitrogen atmosphere using Schlenk techniques or a glove box unless otherwise noted. ^{1}H, $^{31}P\{^{1}H\}$, $^{19}F\{^{1}H\}$ spectra (^{1}H, 600 MHz; ^{31}P, 243 MHz, ^{19}F, 565 MHz) were recorded on a Bruker 600 Ultrashield NMR. Electrochemical measurements were performed by a P/G analyzer (EC Frontier, ECstat-301). ESR spectra were recorded on a Bruker EMXplus. Column chromatography was performed with silica gel (Kanto Chemical Co., INC. Silica gel 60N, 100-210 μm). GC analyses were performed on Shimadzu GC-2014 with DB-WAXetr122-7332 column or Shimadzu GC-2014S with GL Sciences 1010-11142 column. GC-MS analyses were performed on a QP2010 gas chromatography-mass spectrometry (GC-MS) spectrometer (Shimadzu) (He carrier, a capillary column [TC-1, GL Sciences]).

Chemicals. *n*-Hexane (KANTO Chemical CO. Inc.), THF (KANTO Chemical Co. Inc.), benzene (KANTO Chemical Co. Inc.), and dichloromethane (FUJIFILM Wako Pure Chemical Co.) were purified by a solvent purification system (MBraun SPS-800). Potassium tert-butoxide (KO*t*Bu), sodium tert-butoxide (NaO*t*Bu), benzyl benzoate (**BnBz**), benzyl acetate (**BnAc**), 1,3,5-trimethylbenzene (mesitylene) 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), 4-(trifluoromethyl)benzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol, benzoyl chloride, 4-(trifluoromethyl)benzoic acid, p-toluic acid, p-anisic acid, benzyl chloride, benzhydrol, trityl chloride, sodium benzoate, 2-naphthalenemethanol, 4-nitrotoluene, 2,2,6,6-tetramethylpiperidine 1-oxyl free radical (TEMPO) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were purchased from Tokyo Chemical Industries (TCI) Co. Ltd. 1,3,5-trimethylbenzene was dried over 3A molecular sieve (FUJIFILM Wako Pure Chemical Co.). 4-nitrobenzyl alcohol, p-nitrobenzoic acid, DMSO (Super dehydrated), acetonitrile (Super dehydrated) 4-dimethylaminopyridine (DMAP), K_2CO_3 were purchased from FUJIFILM Wako Pure Chemical Co. Triethylamine was purchased from Sigma-Aldrich Co. C_6D_6, DMSO-d_6, and $CDCl_3$, and 2-propanol (dehydrated) were purchased from KANTO Chemical Co. Inc. C_6D_6 was dried over sodium benzophenone ketyl and distilled. DMSO-d_6 was dried over calcium hydride and distilled. H_2 gas (99.9%) was purified by a clean column (CG-X, NIKKA SEIKO CO., LTD.). Other chemicals are used without further purification.

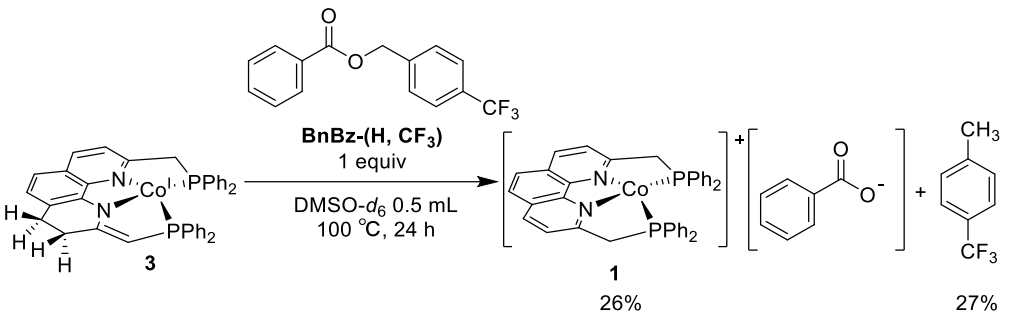
Synthesis of [CoCl(PNNP)] (1). Synthesis of PNNP (2,9-bis((diphenylphosphanyl)methyl)-1,10-phenanthroline) ligand[S1] and **1**[S2] were conducted according to the reported literature.

Synthesis of [Co(PNNP')] (2). A 20 mL vial was charged with a benzene (10 mL) solution of [CoCl(PNNP)] (1) (34 mg, 0.050 mmol) and potassium tert-butoxide (KO*t*Bu) (8.0 mg 0.071 mmol). The solution was stirred at room temperature overnight. Then the solution was filtered with a PTFE syringe filter (0.22 μm) and evaporated. Complex **2** as a yellow-green solid (22 mg, 0.034 mmol, 69%) was obtained. Complex **2** was identified by comparing the ^{1}H and $^{31}P\{^{1}H\}$ spectra with those reported in the literature.[S2]

Synthesis of [Co(PNNP'')] (3). A 20 ml vial was charged with a benzene (10 mL) solution of [Co(PNNP')] (**2**) (22 mg 0.034 mmol). 2-propanol (1 mL) was added to the solution, and the solution was stirred overnight. The solution was once frozen at −20 ℃ and dried under the reduced pressure to give **3** as an aerogel-like red-brown powder (21 mg, 0.033 mmol, 95%). Complex **3** was identified by comparing the ^{1}H and $^{31}P\{^{1}H\}$ spectra with those reported in the literature.[S2]

Caution: If the solution is dried without freezing, **3** becomes a sticky red-brown solid, which is difficult to handle.

Reaction of 3 with 1 equiv BnBz-(H, CF_3) in DMSO-d_6



Scheme S1. Reaction of **3** with 1 equiv **BnBz-(H, CF_3)** in DMSO-d_6.

In a J-Young NMR tube, complex **3** (6.4 mg, 0.010 mmol) was dissolved in DMSO-d_6 (0.50 mL). To the solution, was added 1 equivalent **BnBz-(H, CF_3)** (1.9 μL, 0.010 mmol). The solution was kept at 100 °C for 24 hours. Mesitylene (1.4 μL, 0.010 mmol) and triphenyl phosphate (6.5 mg, 0.020 mmol) were added to the solution as internal standards. The reaction was followed by ^{1}H (Figure S1), ^{19}F{^{1}H} (Figure S2), and ^{31}P{^{1}H} (Figure S3) NMR spectroscopy, showing the formation of $\mathbf{1}^{+}$ (yield: 26%) and of 4-trifluoromethyltoluene (yield: 27%). Conversion of **3** could not be determined due to the severe broadening of the signals.

$\mathbf{1}^{+}$: ^{1}H NMR (600 MHz DMSO-d_6, 25 °C) δ 8.68 (br, 2H, Phen-*H*), 8.02 (br, 4H, Phen-*H*), 7.36 (br, 4H, P*Ph*$_2$), 7.16 (br, 16H, P*Ph*$_2$), 4.83 (s, 4H, C*H*$_2$PPh$_2$). ^{31}P{^{1}H} NMR (243 MHz DMSO-d_6, 25 °C) δ 65.1 (s).
4-trifluoromethyltoluene: ^{1}H NMR (600 MHz DMSO-d_6, 25 °C) δ 7.58 (d, 2H), 7.38 (d, 2H), 7.36 (br, 4H), 2.37 (s, 3H). ^{19}F{^{1}H} NMR (243 MHz DMSO-d_6, 25 °C) δ –60.7 (s).

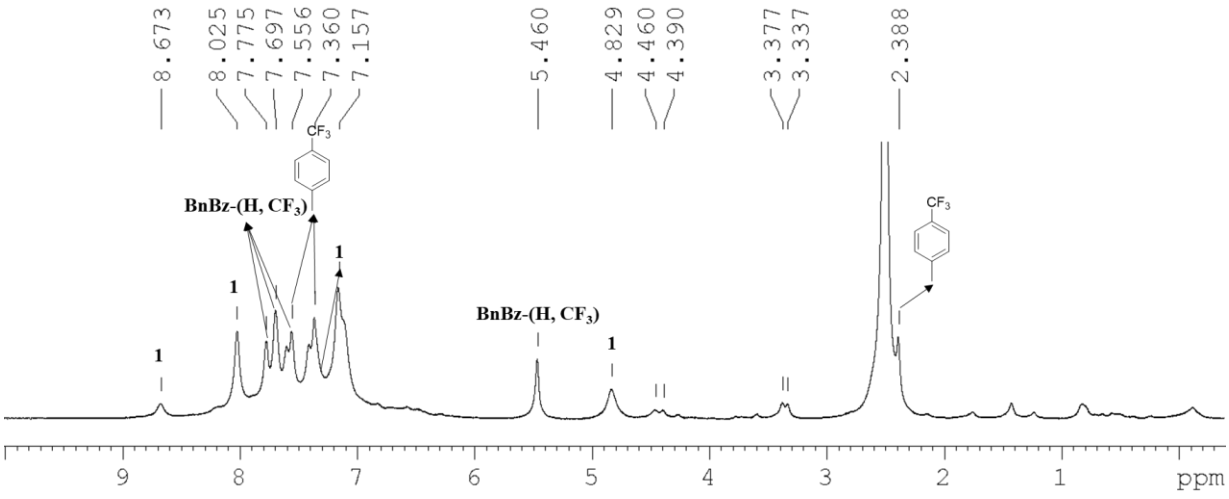


Figure S1. ^{1}H NMR (DMSO-d_6) spectrum of the reaction solution.

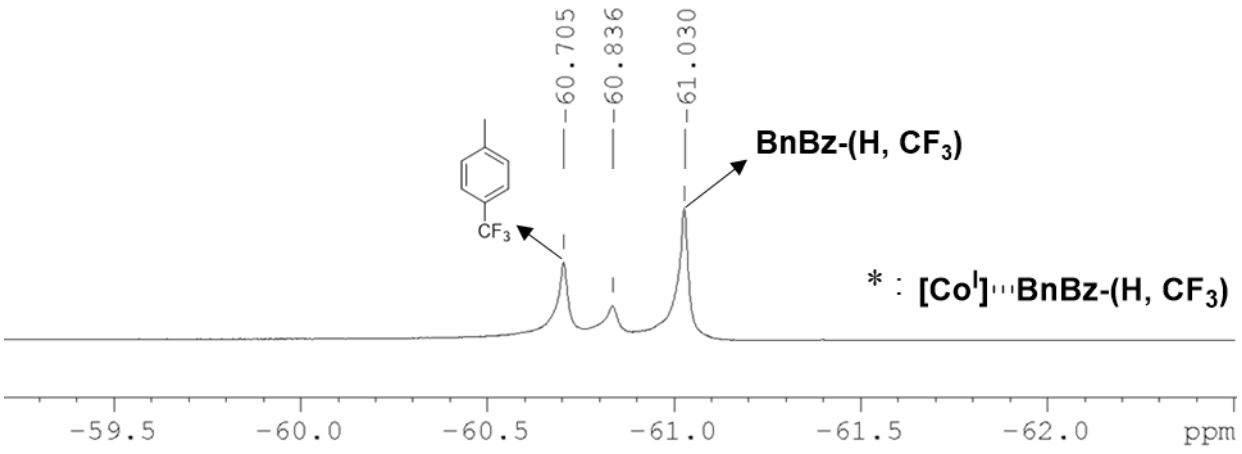


Figure S2. $^{19}F\{^{1}H\}$ NMR (DMSO-d_6) spectrum of stoichiometric reaction solution.

*: The signal at –60.8 ppm is based on unidentified compounds, which might be the adduct intermediate of **BnBz-(H,CF$_3$)** and **3**.

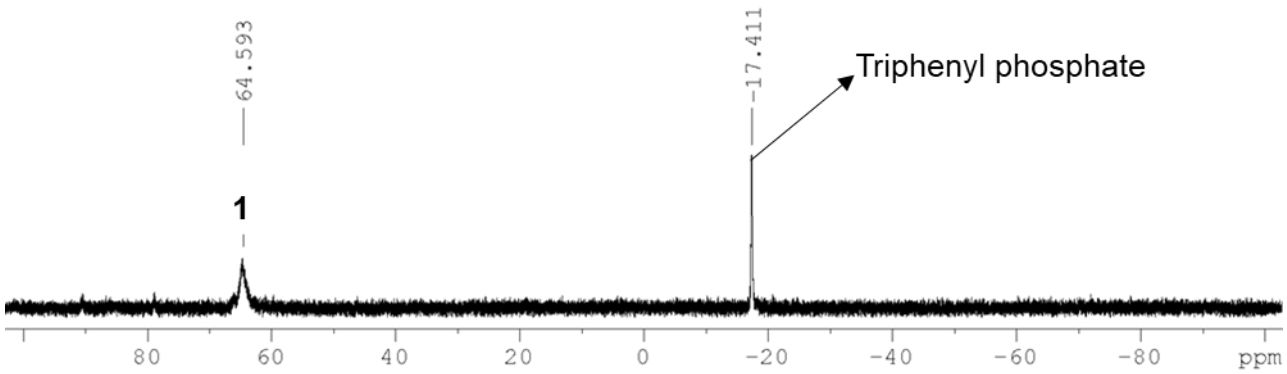


Figure S3. $^{31}P\{^{1}H\}$ NMR (DMSO-d_6) spectrum of stoichiometric reaction solution.

General Procedure for Catalytic Hydrogenolysis of Esters (Tables 1 and S1).

The procedure for Table 1, entry 1 serves as typical procedure for catalytic hydrogenolysis of esters. Modification was made to this typical procedure to fulfill each subsequent experiment (Tables 1 and S1).

Table S1, entry 1 A DMSO solution (0.12 mL) containing **1** (6.7 mg, 0.010 mmol), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) (60 μL, 0.40 mmol), and **BnBz** (38 μL, 0.20 mmol) were charged in a 10 mL Schlenk tube equipped with a Teflon valve. After one freeze-pump-thaw cycle, H_2 gas (1 atm) was introduced into the flask. The solution was kept at 100 °C for 15 h with stirring. The color of the solution turned brown. Mesitylene (28 μL, 0.20 mmol) as an internal standard was added to the solution for quantification in ^{1}H NMR measurements. Then, the solution was analyzed by NMR and GC-MS. Identification of products was performed by comparing their NMR spectra and GC-MS profiles with those of the authentic samples. Conversion yield of **BnBz**, the product yields of benzoic acid and toluene were determined to be 80%, 80%, and 65%, respectively.

Large Scale Catalytic Hydrogenolysis of 2-Naphthalenylmethyl Benzoate (NMBz) (Table 1, Entry 11).

A DMSO solution (1.2 mL) containing **1** (67.2 mg, 0.10 mmol), DBU (609 mg, 4.0 mmol), and **NMBz** (526 mg, 2.0 mmol) were charged in a 10 mL Schlenk tube equipped with a Teflon valve. After one freeze-pump-thaw cycle, H_2 gas (1 atm) was introduced into the flask. The solution was kept at 100 °C for 15 h with stirring. 1,3,5-Trimethoxybenzene (168 mg, 1.0 mmol) as an internal standard was added to the solution for quantification in ^{1}H NMR measurements. Then, the solution was analyzed by NMR, revealing the NMR yields of benzoic acid (>95%) and 2-methylnaphthalene (>95%). The reaction mixture was transferred to a 50 mL round flask, and the volatiles were transferred to a different flask using a trap to trap method under vacuum. The separated liquid part, which contained mainly DMSO and 2-methylnaphthalene, was purified by silica column chromatography (eluent: hexane:AcOEt = 1:9 v/v). Analytically pure 2-methylnaphthalene (224 mg, 1.58 mmol, 78%) was isolated. After the trap-to trap distillation, the brown solid residue was obtained. To this, was added HCl_{aq} (1 M, 6 mL) to transfer benzoate DBU salt to PhCOOH, which was extracted with Et_2O (10 ml ×3). The extract was purified by silica column chromatography (eluent: hexane:AcOEt = 1:9 v/v, then AcOEt only) to give benzoic acid (213 mg, 1.74 mmol, 87%).

Benzoic Acid

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, 2H), 7.62 (t, 1H), 7.48 (m, 2H).

2-Methylnaphthalene

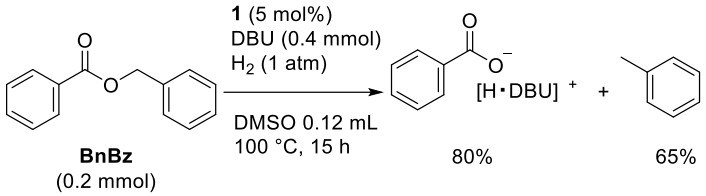
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.73 (m, 3H), 7.61 (t, 1H), 7.46-7.38 (m, 2H), 7.32 (d, 1H), 2.52 (s, 3H).

Table S1. Optimization of the Reaction Conditions

entry	deviation from standard conditions [a]	toluene yield [b]
1	None	65%
2	0.12 mL toluene	13% [c]
3	0.12 mL THF	12%
4	0.12 mL acetonitrile	9%
5	0.60 mL DMSO	trace
6	80 ℃	trace
7	0.01 mmol DBU	trace
8	0.01 mmol NaO*t*Bu	trace
9	without **1**	ND
10	without H_2	ND

[a] Standard conditions: **BnBz** (0.2 mmol), **1** (5 mol%), DBU (0.4 mmol), H_2 (1 atm), DMSO (0.12 mL), 100 °C, 15 h; [b] Yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [c] Yield of benzoic acid.

GC-MS Chart of the Reaction Mixture of Catalytic Hydrogenolysis of BnBz.



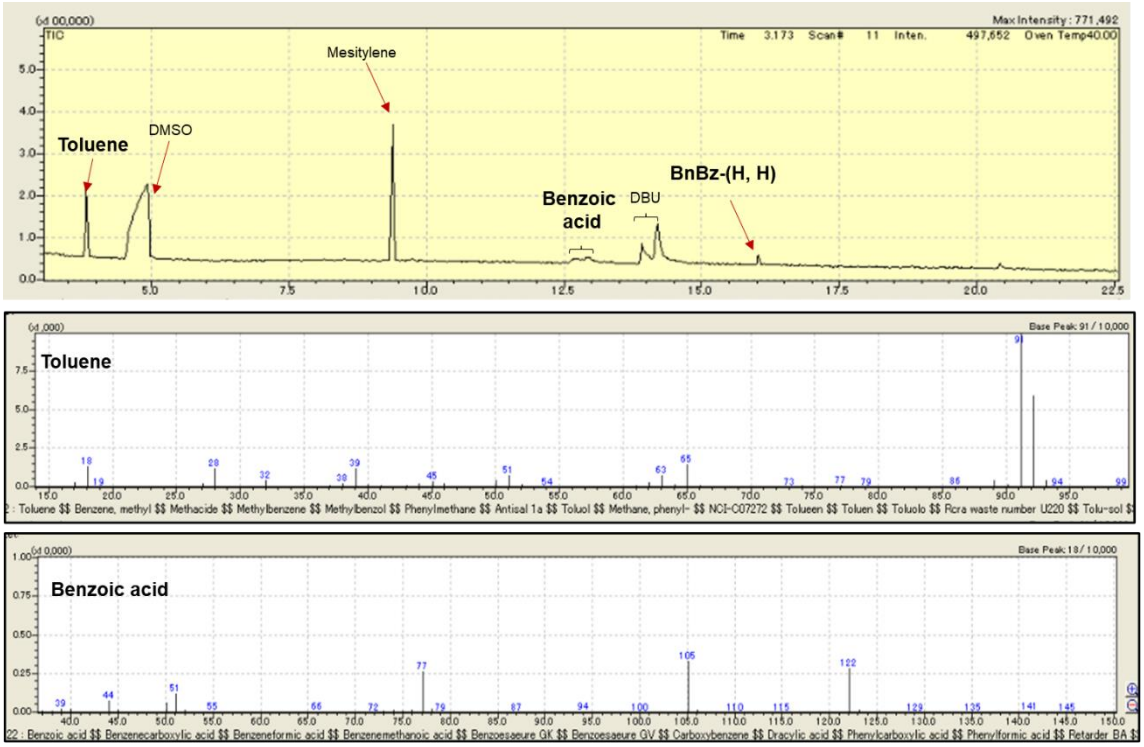
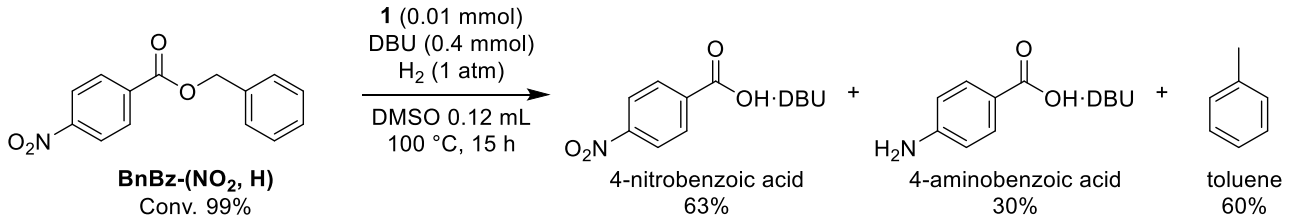


Figure S4. A GC-MS chart (top) and corresponding MS spectra (bottom, at 3.72 min for toluene and 12.71 min for benzoic acid) of the reaction mixture of catalytic hydrogenolysis of **BnBz**.

Procedure for Catalytic Hydrogenolysis of Benzyl 4-Nitrobenzoate (BnBz-(NO_2, H) (Table 2, entry 4)



Scheme S2. Hydrogenolysis of **BnBz-(NO_2, H)** by PNNP-Co system.

A DMSO solution (0.12 mL) containing **1** (6.7 mg, 0.010 mmol), DBU (60 μL, 0.40 mmol), and **BnBz-(NO_2, H)** (51.5 mg, 0.20 mmol) was charged in a 30 mL Schlenk equipped with a Teflon valve. After one freeze-pump-thaw cycle, H_2 gas (1 atm) was introduced into the flask. The solution was kept at 100 °C for 15 h with stirring. Mesitylene (28 μL, 0.20 mmol) as an internal standard was added to the solution. Then, the solution was analyzed by ^{1}H NMR measurements. The obtained ^{1}H NMR spectrum is shown in Figure S5. Identification of products was performed by comparing their NMR spectra with those of the authentic samples. The yields of the products 63% for 4-nitrobenzoic acid and 30% for 4-aminobenzoic acid and 30% for toluene and conversion of **BnBz-(NO_2, H)** (99%) were determined by ^{1}H NMR analysis using mesitylene as an internal standard.

4-Nitrobenzoic acid: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 8.17 (m, 4H).

4-Aminobenzoic acid: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 7.84 (d, 2H), 6.62 (d, 2H), 3.73 (s, 2H).

Toluene: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 7.32-7.27 (overlapped, 5H), 2.47 (s, 3H).

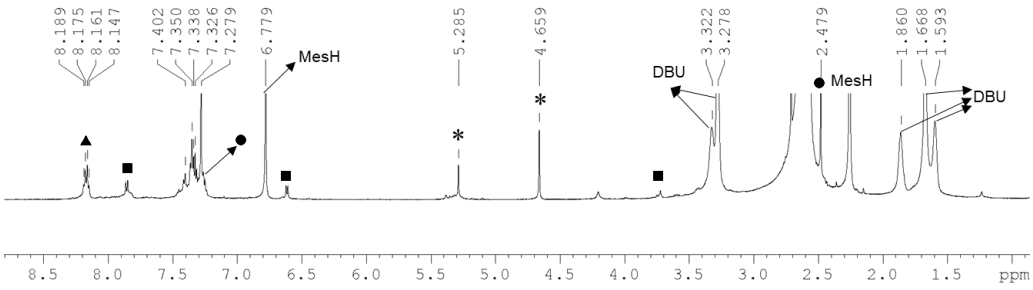
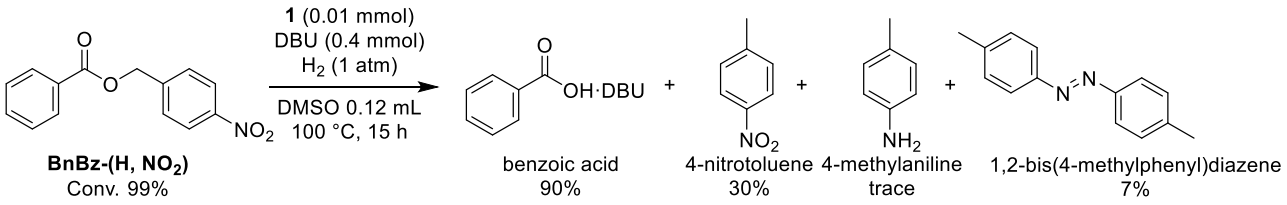


Figure S5. ^{1}H NMR spectrum of the reaction mixture obtained from hydrogenolysis of **BnBz-(NO_2, H)** catalyzed by **1**. ▲: 4-nitrobenzoic acid; ■: 4-Aminobenzoic acid; ●: Toluene. *: Signals at 5.28 ppm and 4.57 ppm are unidentified compounds.

Procedure for Catalytic Hydrogenolysis of 4-Nitrobenzyl Benzoate (BnBz-(H, NO_2) (Table 2, entry 8)



Scheme S3. Hydrogenolysis of **BnBz-(H, NO_2)** by PNNP-Co system.

A DMSO solution (0.12 mL) containing **1** (6.7 mg, 0.010 mmol), DBU (60 μL, 0.40 mmol), and **BnBz-(H, NO_2)** (27 mg, 0.20 mmol) was charged in a 30 mL Schlenk equipped with a Teflon valve. After one freeze-pump-thaw cycle, H_2 gas (1 atm) was introduced into the flask. The solution was kept at 100 °C for 15 h with stirring. Mesitylene (28 μL, 0.20 mmol) as an internal standard was added to the solution. Then, the solution was analyzed by NMR. The obtained ^{1}H NMR spectrum is shown in Figure S6. Identification of products was performed by comparing their NMR spectra with those of the authentic samples. The yields of the products 90% for benzoic acid, 30% for 4-nitrotoluene, trace amount of 4-methylaniline, and 7% for 1,2-bis(4-methylphenyl)diazene) and conversion of **BnBz-(H, NO_2)** (99%) were determined by ^{1}H NMR using mesitylene as an internal standard.

benzoic acid: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 8.04 (d, 2H), 7.53 (t, 1H), 7.41 (t, 2H).

4-nitrotoluene: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 8.10 (d, 2H), 7.31 (d, 2H), 2.45 (s, 3H).

4-methylaniline: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 6.91 (d, 2H), 6.64 (d, 2H).

1,2-bis(4-methylphenyl)diazene : ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 7.83 (d, 4H), 7.30 (d, 4H), 2.54 (overlapped, 6H).

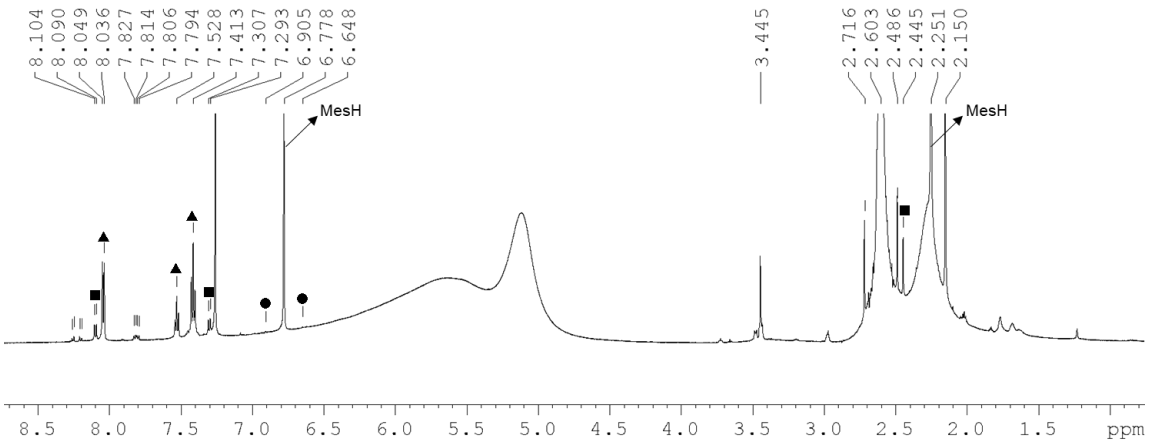
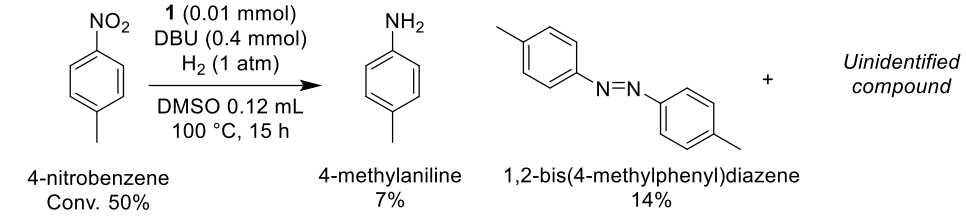


Figure S6. ^{1}H NMR spectrum of the reaction mixture obtained from hydrogenolysis of **BnBz-(H, NO_2)** catalyzed by **1**. ▲: benzoic acid; ■: 4-nitrotoluene; ●: 4-methylaniline. ♦ 1,2-bis(4-methylphenyl)diazene.

Reaction of 4-Nitrotoluene with H_2 (1 atm) Catalyzed by 1



Scheme S4. Reduction of 4-nitrotoluene by PNNP-Co system.

A DMSO solution (0.12 mL) containing **1** (6.7 mg, 0.010 mmol), DBU (60 μL, 0.40 mmol), and 4-nitrotolune (27 mg, 0.20 mmol) was charged in a 30 mL Schlenk equipped with a Teflon valve. After one freeze-pump-thaw cycle, H_2 gas (1 atm) was introduced into the flask. The solution was kept at 100 °C for 15 h with stirring. Mesitylene (28 μL, 0.20 mmol) as an internal standard was added to the solution. Then, the solution was analyzed by NMR. The obtained ^{1}H NMR spectrum is shown in Figure S7. Identification of products was performed by comparing their NMR spectra with those of the authentic samples. The yields of the products (7% for 4-methylaniline and 14% for 1,2-bis(4-methylphenyl)diazene) and conversion of 4-nitrotoluene (50%) were determined by ^{1}H NMR using mesitylene as an internal standard.

4-nitrotoluene: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 8.10 (d, 2H), 7.31 (d, 2H), 2.45 (s, 3H).
4-methylaniline: ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 6.93 (d, 2H), 6.57 (d, 2H), 3.42 (br, 2H), 2.21(s, 3H).
1,2-bis(4-methylphenyl)diazene : ^{1}H NMR (600 MHz $CDCl_3$, 25 °C) δ 7.83 (d, 4H), 7.32 (overlapped, 4H), 2.54 (overlapped, 6H).

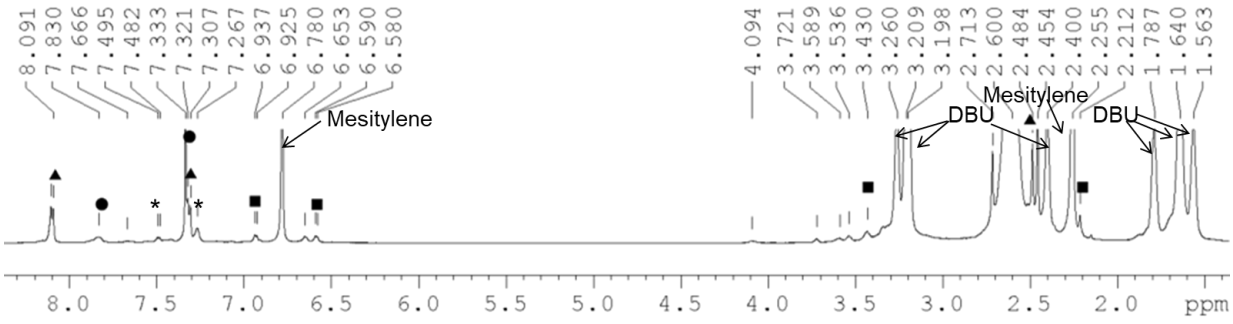


Figure S7. ^{1}H NMR spectrum of the reaction mixture obtained from hydrogenation of 4-nitrotoluene with H_2 catalyzed by **1**.
▲: 4-nitrotoluene; ■: 4-methylaniline; ●: 1,2-bis(4-methylphenyl)diazene. *: Signals at 6.85 ppm and 7.40 ppm are unidentified compounds.

Compound Characterization Data

Benzoic acid, 4-methylbenzoic acid, 4-methoxybenzoic acid, 4-nitrobenzoic acid, 4-trifluoromethylbenzoic acid, 4-trifluoromehyltoluene, and 4-nitrotoluene were characterized by the comparison with the commercially available chemicals by NMR spectroscopy. Toluene[S3], xylene[S4], 4-methoxytoluene[S5], 4-aminotoluene[S6], and 1,2-di-*p*-tolydiazeneare[S7] are also identified by literature reports.

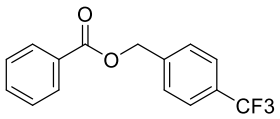
Typical Procedure for Synthesis of Benzyl Substituted Esters (BnBz-(H, Y)).

The modified procedure[S8] for synthesis of **BnBz-(H, CF_3)** (Table 1, entry 7) serves as typical procedure for synthesis of benzyl substituted esters. Modification was made to this typical procedure to synthesis each benzyl substituted esters (Table 1 entries 5–8).

A 50 mL Schlenk was charged with a CH_2Cl_2 (12 mL) solution of 4-trifluoromethylbenzyl alcohol (0.92 g 6.0 mmol), triethylamine (1.2 mL 9.0 mmol), and *N*,*N*-dimethyl-4-aminopyridine (DMAP) (0.037 g, 0.30 mmol). benzoyl chloride (0.70 mL, 6.0 mmol) was added to the solution. The solution was stirred at room temperature for 1 hour, then quenched with an excess amount of HCl (1 M, 10 mL) at room temperature. The solution was extracted with Et_2O (20 mL) three times. The product was purified by column chromatography (Hex:AcOEt, 5:1, v/v), **BnBz-(H, CF_3)** was obtained as a colorless oil (0.69 g, 2.7 mmol, 44%)

The procedure for synthesizing the other esters mentioned in Table 1, entries 1–4, followed the same procedure above. The primary difference in the procedure was the utilization of the substituted benzyl alcohol corresponding to each specific ester.

4-Trifluoromethylbenzyl Benzoate (BnBz-(H, CF_3))

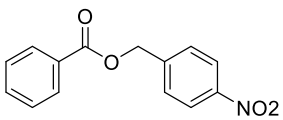


A colorless oil (0.92 g, 1.2 mmol, 56%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, 2H), 7.65 (d, 2H), 7.60-7.56 (m, 3H), 7.46 (t, 2H), 5.42 (s, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.62.

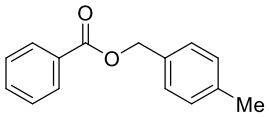
4-Nitrobenzyl Benzoate (BnBz-(H, NO_2))



A white crystalline solid (0.68 g, 2.2 mmol, 44%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, 2H), 8.09 (d, 2H), 7.60 (t, 3H), 7.48 (t, 2H), 5.46 (s, 2H).

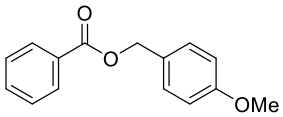
4-Methylbenzyl Benzoate (BnBz-(H, Me))



A colorless oil (0.60 g, 2.7 mmol, 53%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, 2H), 7.56 (t, 1H), 7.44 (t, 2H), 7.36 (d, 2H), 7.21 (d, 2H), 5.34 (s, 2H), 2.38 (s, 3H).

4-Methoxybenzyl Benzoate (**BnBz-(H, OMe)**)



A colorless oil (0.84 g, 3.5 mmol, 58%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, 2H), 7.55 (t, 1H), 7.43 (t, 2H), 7.40 (d, 2H), 6.92 (d, 2H), 5.31 (s, 2H), 3.82 (s, 3H).

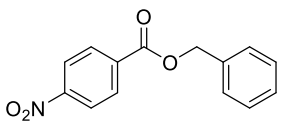
Typical Procedure for Synthesis of Benzoate Substituted Esters (BnBz-(X, H)).

The modified procedure[S9] for synthesis of **BnBz-(NO_2, H)** (Table 1, entry 4) serves as typical procedure for synthesis of benzyl substituted esters. Modification was made to this typical procedure to synthesis benzoate substituted esters (Table 1 entries 1–4).

A 100 mL Schlenk was charged with acetonitrile (30 mL) solution of 4-nitrolbenzoic acid (1.7 g 10 mmol), and K_2CO_3 (1.5 g, 12 mmol). benzyl chloride (1.3 g, 10 mmol) was added to the solution. The solution was stirred at 60 ℃ overnight. Then the solution was extracted with Et_2O (20 mL) three times. The product was purified by column chromatography (Hex:AcOEt, 5:1, v/v) and **BnBz-(NO_2, H)** was obtained as a colorless crystalline solid (1.2 g, 4.7 mmol, 47%).

The procedure for synthesizing the other esters mentioned in Table 1, entries 5–8, followed the same procedure above. The primary difference in the procedure was the utilization of the substituted benzoic acid corresponding to each specific ester.

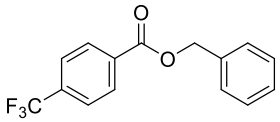
Benzyl 4-Nitrobenzoate (BnBz-(NO_2, H))



A white crystalline solid (1.2 g, 4.7 mmol, 47%)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, 2H), 8.23 (d, 2H), 7.45–7.35 (m, 5H), 5.40 (s, 2H).

Benzyl 4-Trifloromethylbenzoate (BnBz-(CF_3, H))

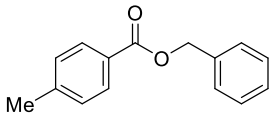


A Colorless oil (0.92 g, 3.3 mmol, 33%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, 2H), 8.20 (d, 2H), 7.46-7.35 (m, 5H), 5.40 (s, 2H).

^{19}F NMR (565 MHz, $CDCl_3$) δ -63.15.

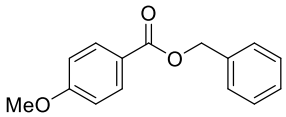
Benzyl 4-Methylbenzoate (BnBz-(Me, H))



A colorless oil (0.89 g, 3.9 mmol, 39%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, 2H), 7.46 (d, 2H), 7.40 (t, 2H), 7.35 (t, 1H), 7.24 (d, 2H), 5.36 (s, 1H), 2.41 (s, 3H).

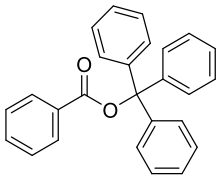
Benzyl 4-Methoxybenzoate (BnBz-(OMe, H))



A colorless oil (0.80 g, 3.3 mmol, 33%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, 2H), 7.45 (d, 2H), 7.39 (t, 2H), 7.34 (t, 1H), 6.92 (d, 2H), 5.34 (s, 1H), 3.86 (s, 3H).

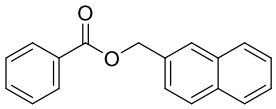
Procedure for Synthesis of Trityl Benzoate (TrBz)



The trityl benzoate was synthesized by following the reported literature.[S10] A 250 mL 3-neck flask was charged with an acetone (40 mL) solution of trityl chloride (2.0 g 7.2 mmol), and sodium benzoate (1.1 g, 7.4 mmol) was added to the solution. The solution was refluxed at 60 ℃ for 12 hours, then the solution was filtrated and evaporated. The product was purified by column chromatography (Hex:AcOEt, 5:1, v/v) and **TrBz** was obtained as a colorless powdery solid (1.8 g, 4.9 mmol, 69%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, 2H), 7.47 (t, 1H), 7.37-7.35 (m, 8H), 7.21 (t, 6H), 7.15 (t, 3H).

Procedure for Synthesis of 2-Naphthalenylmethyl Benzoate (NMBz)



A 50 mL Schlenk was charged with a THF (10 mL) solution of 2-naphthalenemethanol (0.79 g 5.0 mmol), triethylamine (1.0 mL 7.5 mmol), and DMAP (0.061 g, 0.50 mmol). Benzoyl chloride (0.70 g, 1.0 mmol) was added to the solution. The solution was stirred at 60 ℃ for 20 hours, then quenched with an excess amount of HCl (1 M, 10 mL) at room temperature. The solution was extracted with Et_2O (10 mL) three times. The product was purified by column chromatography (Hex:AcOEt, 5:1, v/v) (Rf = 0.6), and **NMBz** was obtained as a colorless crystalline solid (1.0 g, 3.9 mmol, 78%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, 2H), 7.92 (s, 1H), 7.88-7.85 (m, 3H), 7.56 (t, 2H), 7.51-7.49 (m, 2H), 7.45 (t, 2H) 5.53 (s, 2H).

Determination of Initial Rates from the Reaction of BnBz with H_2

Six individual 20 mL Schlenk tubes equipped with a Teflon valve were charged with a DMSO solution (0.12 mL) of **1** (6.7 mg, 0.010 mmol), DBU (60 μL, 0.40 mmol), and **BnBz** (0.20 mmol) in each tube. After one freeze-pump-thaw cycle, H_2 gas (1 atm) was introduced into the flask. The reaction solution was kept at 100 °C with stirring. The reaction was terminated after appropriate reaction time, and mesitylene (28 μL, 0.20 mmol) was added to the solution. The solution was analyzed by ^{1}H NMR to determine the product yields. The concentration of toluene was calculated by its yield, [Toluene] = (0.2 × Y) / (0.12 + 0.060 + 0.018) (Y = yield of toluene). The initial rates (v_0) were similarly determined at different substrate concentrations (Table S1). The data was used for Michaelis-Menten-type analysis.

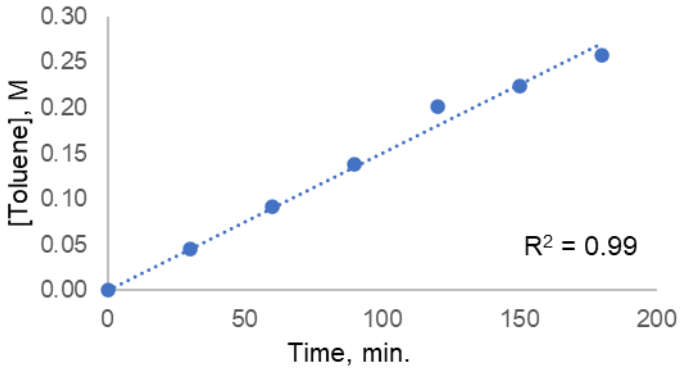


Figure S8. Plots of Concentration of Toluene against Time (min). Slope: 1.5×10^{-3} (M/min).

Table S2. Initial Rates for Hydrogenolysis of **BnBz** at Different Initial Substrate Concentration

[**BnBz**]$_0$, M	v_0, M/min
0.11	0.24×10^{-3}
0.21	0.60×10^{-3}
0.35	0.79×10^{-3}
0.50	1.18×10^{-3}
0.92	1.52×10^{-3}
1.27	1.90×10^{-3}

Michaelis-Menten equation:

$$v_0 = \frac{V_{max}[S]}{K_M + [S]} \quad \text{(eq. 1)}$$

Based on the curve-fitting analysis:

V_{max} = 3.6×10^{-3} M/min

K_M (Michaelis constant) = 1.1 M

Determination of Initial Rates for Hydrogenolysis of BnBz derivatives

Two individual 20 mL Schlenk tubes equipped with a Teflon valve were charged with a DMSO solution (0.12 mL) of **1** (6.7 mg, 0.010 mmol), DBU (60 μL, 0.40 mmol), and **BnBz** derivatives (0.20 mmol) in each tube. After one freeze-pump-thaw cycle, H_2 gas (1 atm) was introduced into the flask. The reaction solution was kept at 100 °C with stirring. The reaction was terminated after the appropriate reaction time, and mesitylene (28 μL, 0.20 mmol) was added to the solution. The product yields were determined by ^{1}H NMR analysis. The concentration of both corresponding toluene and carboxylic acids were determined by using mesitylene as an internal standard.

[Toluene] = (0.20 × Y1) / (0.12 + 0.060 + *V*)

(Y1 = yield of toluene product, *V* = the volume of esters substrate, if the substrate is solid, *V* = 0)

[Acid] = (0.20 × Y2) / (0.12 + 0.060 + *V*)

(Y2 = yield of carboxylic acid product, *V* = the volume of esters substrate, if the substrate is solid, *V* = 0)

Table S3. Initial Rates of Toluene Formation

substrate	v_0, M/min	substrate	v_0, M/min
BnBz-(H, NO_2)	1.1×10^{-2}	**BnBz-(NO_2, H)**	1.0×10^{-2}
BnBz-(H, CF_3)	4.1×10^{-3}	**BnBz-(CF_3, H)**	8.7×10^{-3}
BnBz-(H, Me)	1.2×10^{-3}	**BnBz-(Me, H)**	0.7×10^{-3}
BnBz-(H, OMe)	1.8×10^{-3}	**BnBz-(OMe, H)**	0.9×10^{-3}

Table S4. Initial Rates of Carboxylic Acid Formation

substrate	v_0, M/min	substrate	v_0, M/min
BnBz-(H, NO_2)	1.8×10^{-2}	**BnBz-(NO_2, H)**	1.0×10^{-2}
BnBz-(H, CF_3)	4.9×10^{-3}	**BnBz-(CF_3, H)**	1.1×10^{-2}
BnBz-(H, Me)	2.2×10^{-3}	**BnBz-(Me, H)**	0.7×10^{-3}
BnBz-(H, OMe)	1.9×10^{-3}	**BnBz-(OMe, H)**	0.8×10^{-3}

Table S5. Hammett Parameters and $\log_{10}(v_0X/v_0H)$ Determined by Initial Rates of Toluene Formation.

substrate	Hammett parameters (σ_p)[S11]	$\log_{10}(v_0X/v_0H)$
BnBz-(H, NO_2)	+0.71	0.84
BnBz-(NO_2, H)	+0.71	0.82
BnBz-(H, CF_3)	+0.54	0.43
BnBz-(CF_3, H)	+0.54	0.76
BnBz-(H, H)	0	0.0
BnBz-(H, Me)	–0.17	–0.10
BnBz-(Me, H)	–0.17	–0.36
BnBz-(OMe, H)	–0.27	0.07
BnBz-(H, OMe)	–0.27	–0.23

Cyclic Voltammograms (CV) and Differential Pulse Voltammograms (DPV) of Substrates

Substrates (0.010 mmol, 0.10 mM) was dissolved in a DMSO solution of tetrabutylammonium hexafluorophosphate ([N(*n*-Bu)$_4$]PF$_6$) (10 mL, 0.10 M). A glassy carbon electrode, a platinum wire, and a Ag/AgNO$_3$ were used as a working, a counter, and a reference electrode, respectively. After 30 minutes of nitrogen gas bubbling, the cyclic voltammetry was carried in a 100 mV/s scan rate at room temperature. The 1st cathodic potentials ($E_{p,c}$) are determined from the CV measurements.

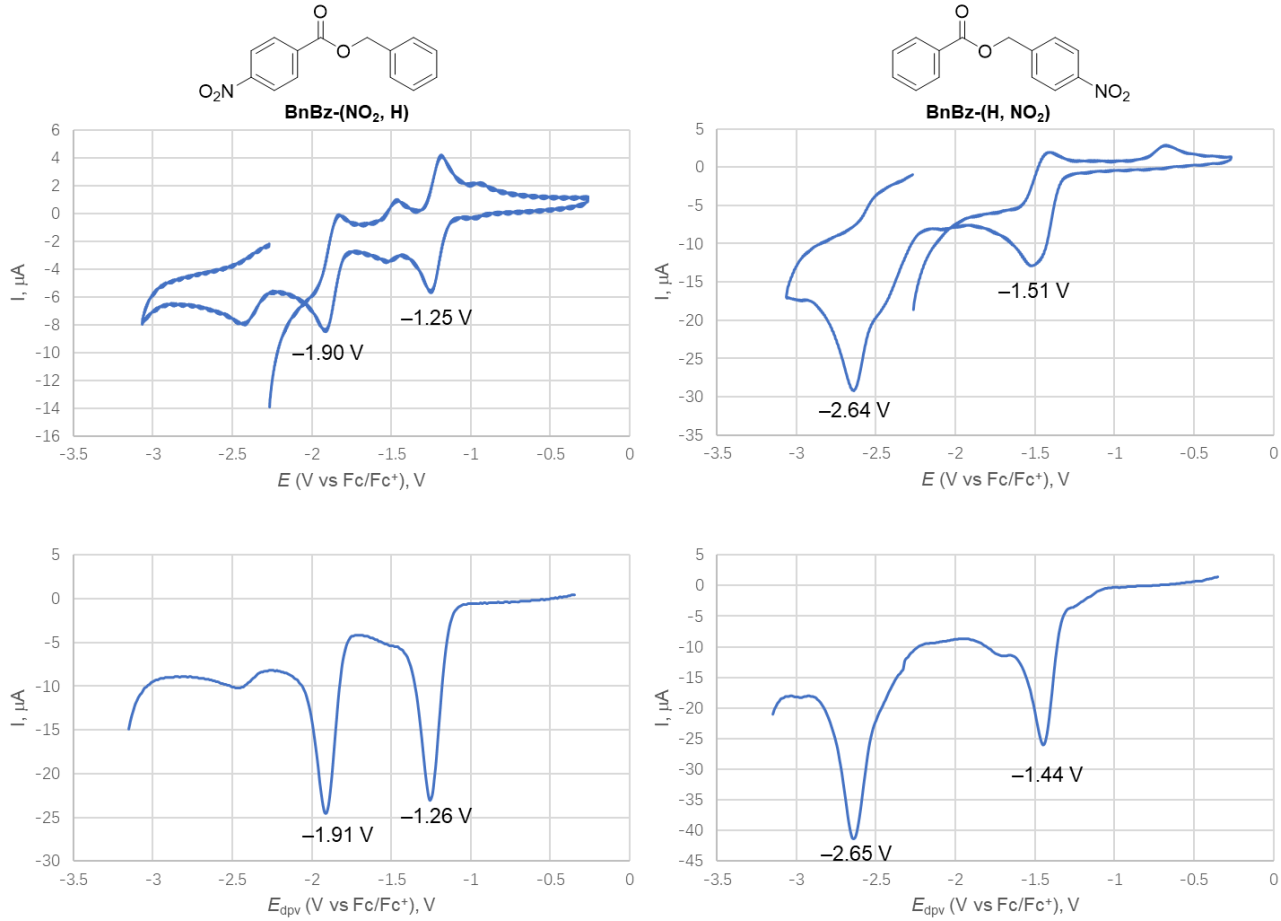


Figure S9. CV (top) and DPV (bottom) of **BnBz-(NO$_2$, H)** and **BnBz-(H, NO$_2$).**

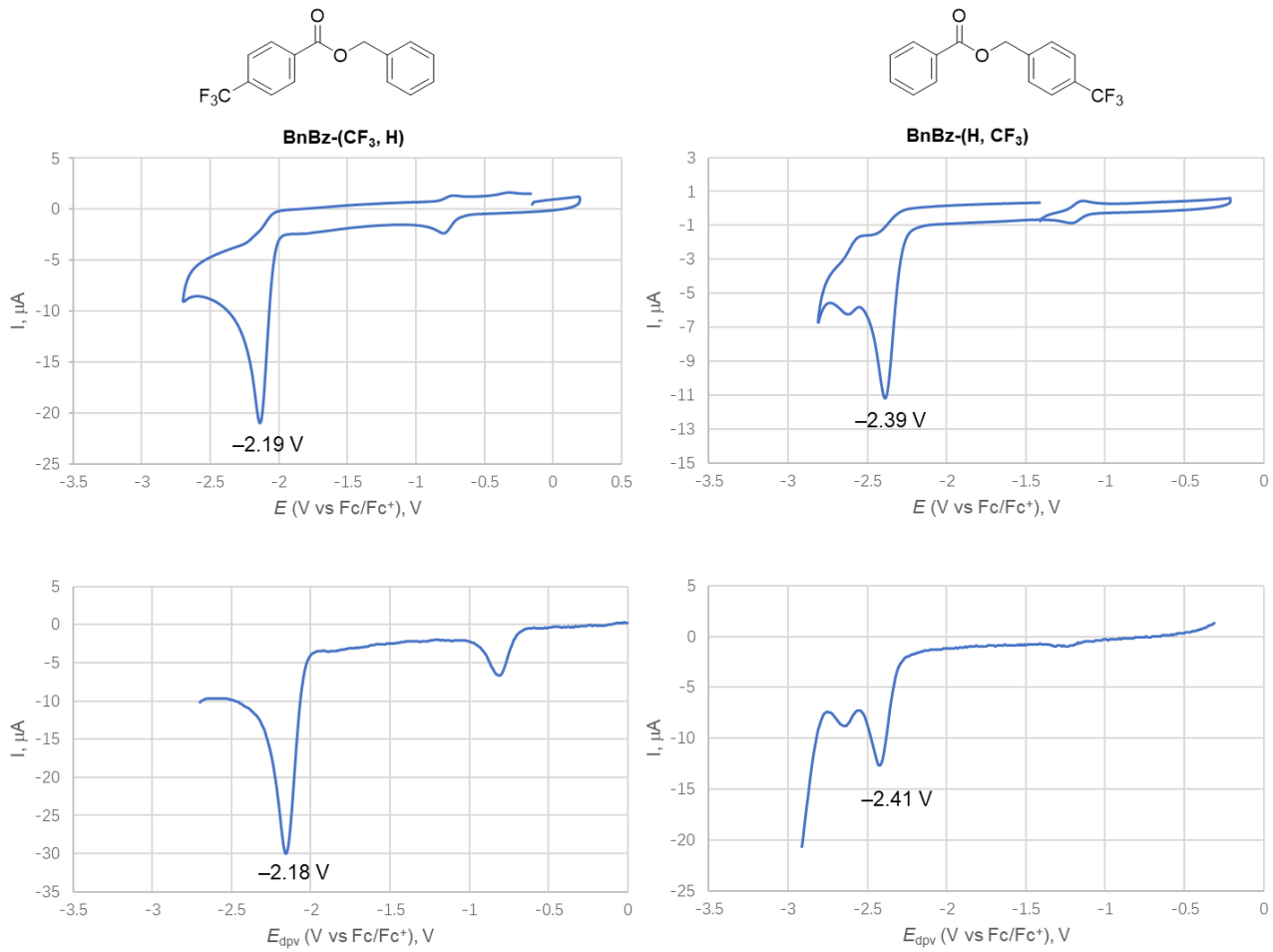


Figure S10 CV (top) and DPV (bottom) of **BnBz-(CF_3, H)** and **BnBz-(H, CF_3).**

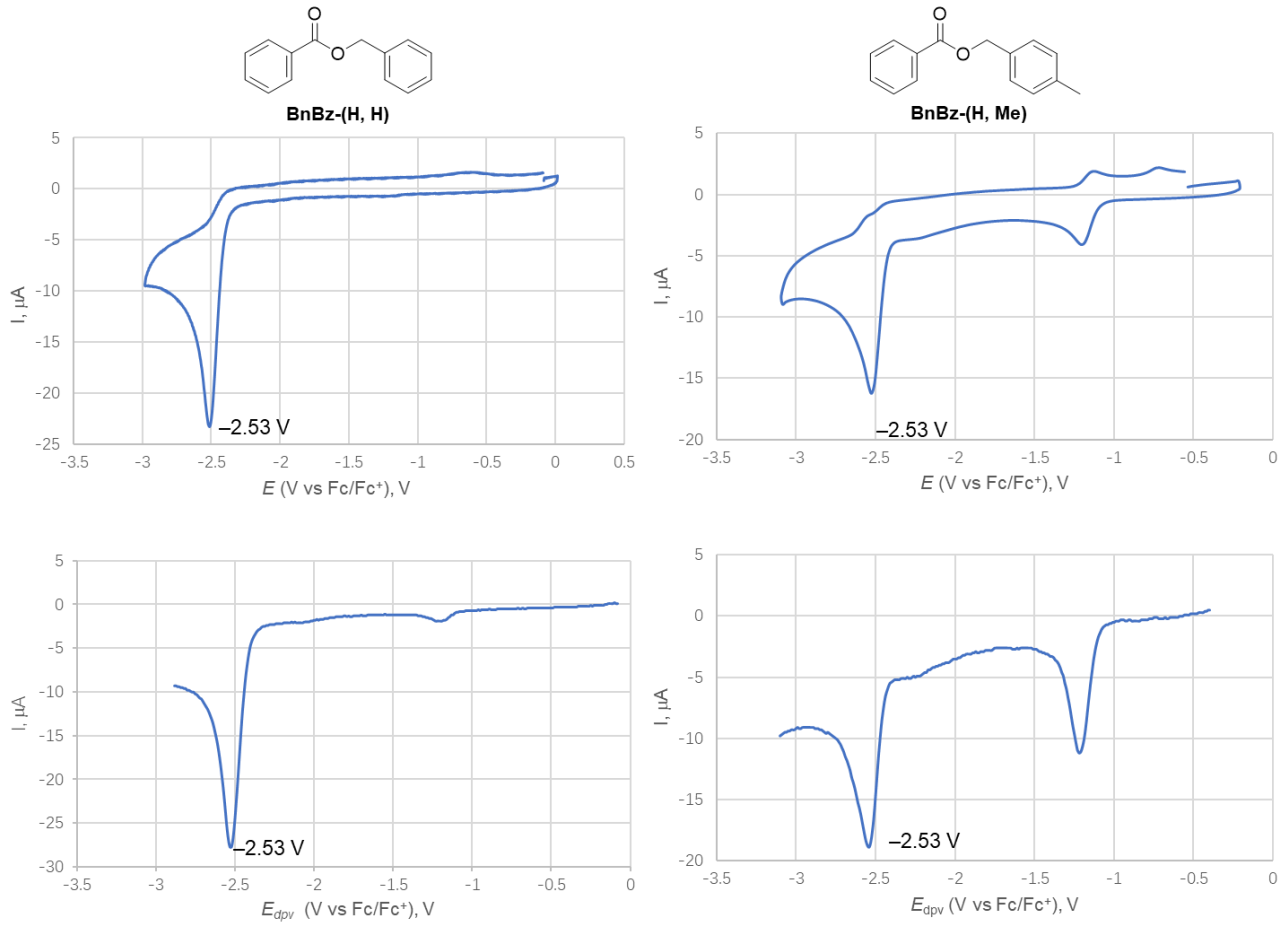


Figure S11 CV (top) and DPV (bottom) of **BnBz-(H, H)** and **BnBz-(H, Me).**

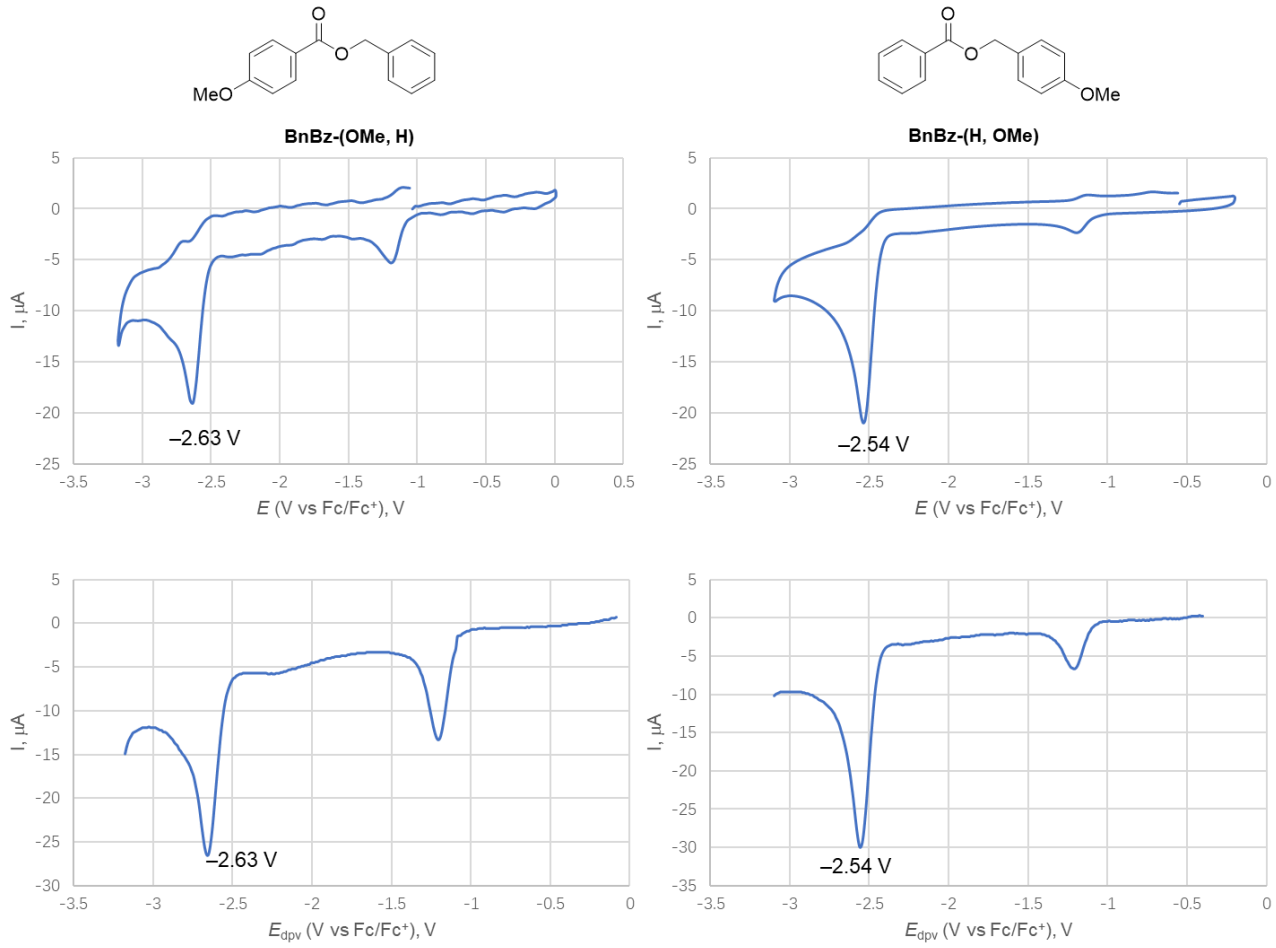


Figure S12 CV (top) and DPV (bottom) of **BnBz-(OMe, H)** and **BnBz-(H, OMe).**

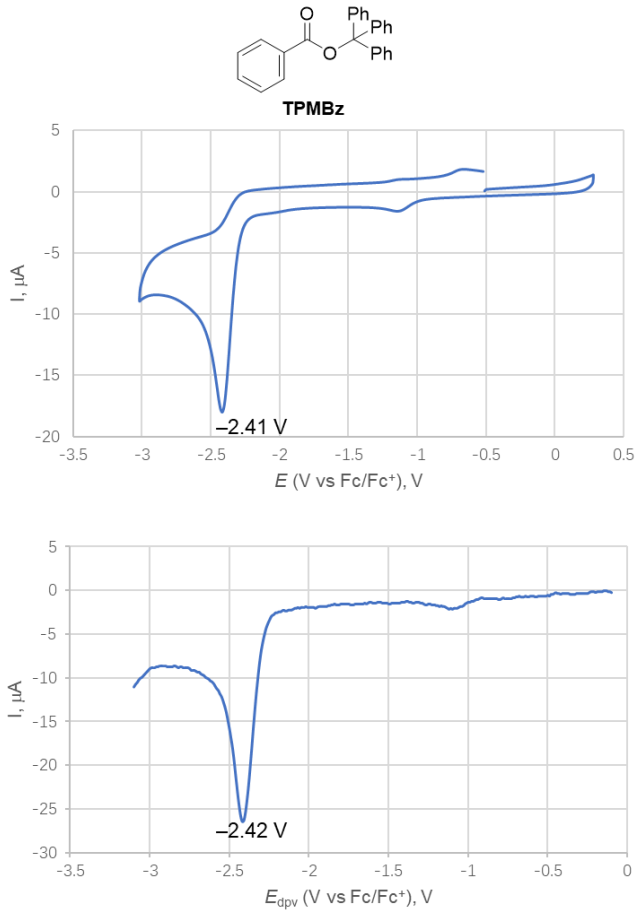


Figure S13 CV (top) and DPV (bottom) of **TPMBz.**

Table S6. The Summary for $E_{p,c}$ (V/vs Fc/Fc$^+$) of Substrates.

substrate	$E_{p,c}$, V	substrate	$E_{p,c}$,V
BnBz-(H, NO_2)	–1.51	**BnBz-(NO_2, H)**	–1.25
BnBz-(H, CF_3)	–2.39	**BnBz-(CF_3, H)**	–2.19
BnBz-(H, Me)	–2.53	**BnBz-(H, H)**	–2.53
BnBz-(H, OMe)	–2.54	**BnBz-(OMe, H)**	–2.63
TrBz	–2.41	**BnAc**	n.d.

n.d.: not detected within the potential window.

The correlation between $\log_{10}(v_0X/v_0H)$ and 1st cathodic potential ($E_{p,c}$) of benzyl benzoate and its derivatives was studied.

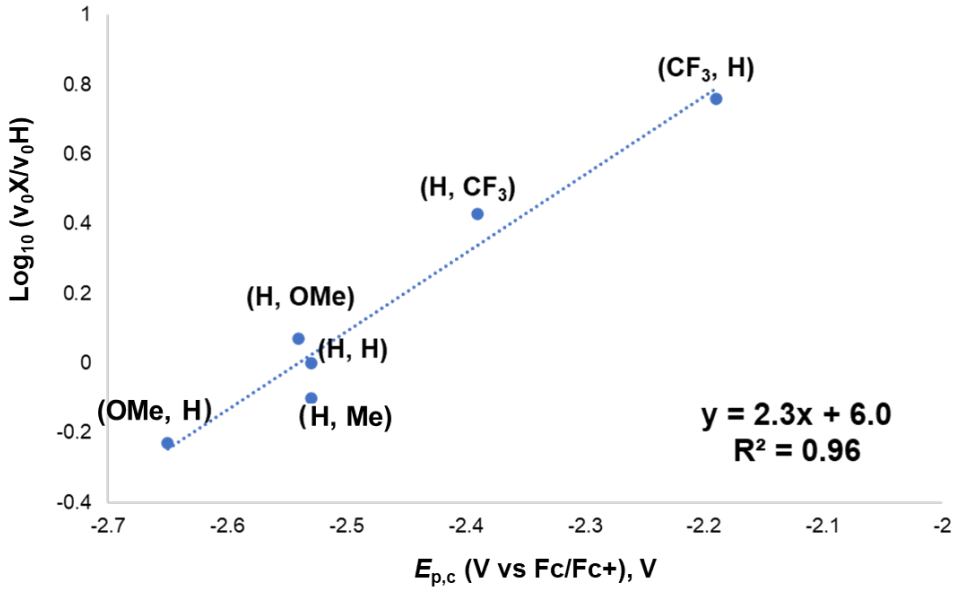


Figure S14. The correlation diagram between $\log_{10}(v_0$ X / v_0 H) and 1st cathodic potential ($E_{p,c}$) of substrates except for NO_2-containing substrates.

^{1}H NMR Spectra

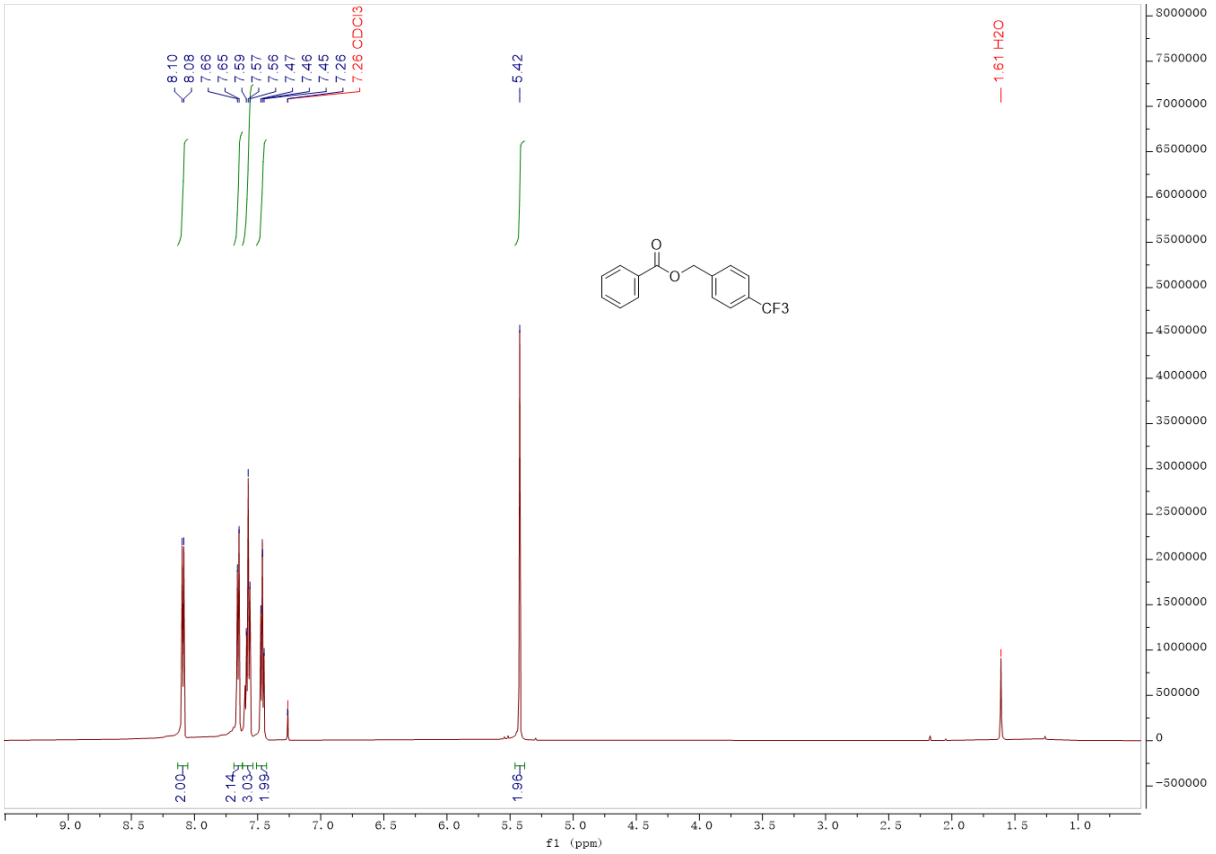


Figure S15. ^{1}H NMR Spectrum of **BnBz-(H, CF_3)**.

Figure S16. ^{19}F{^{1}H} NMR Spectrum of **BnBz-(H, CF_3)**.

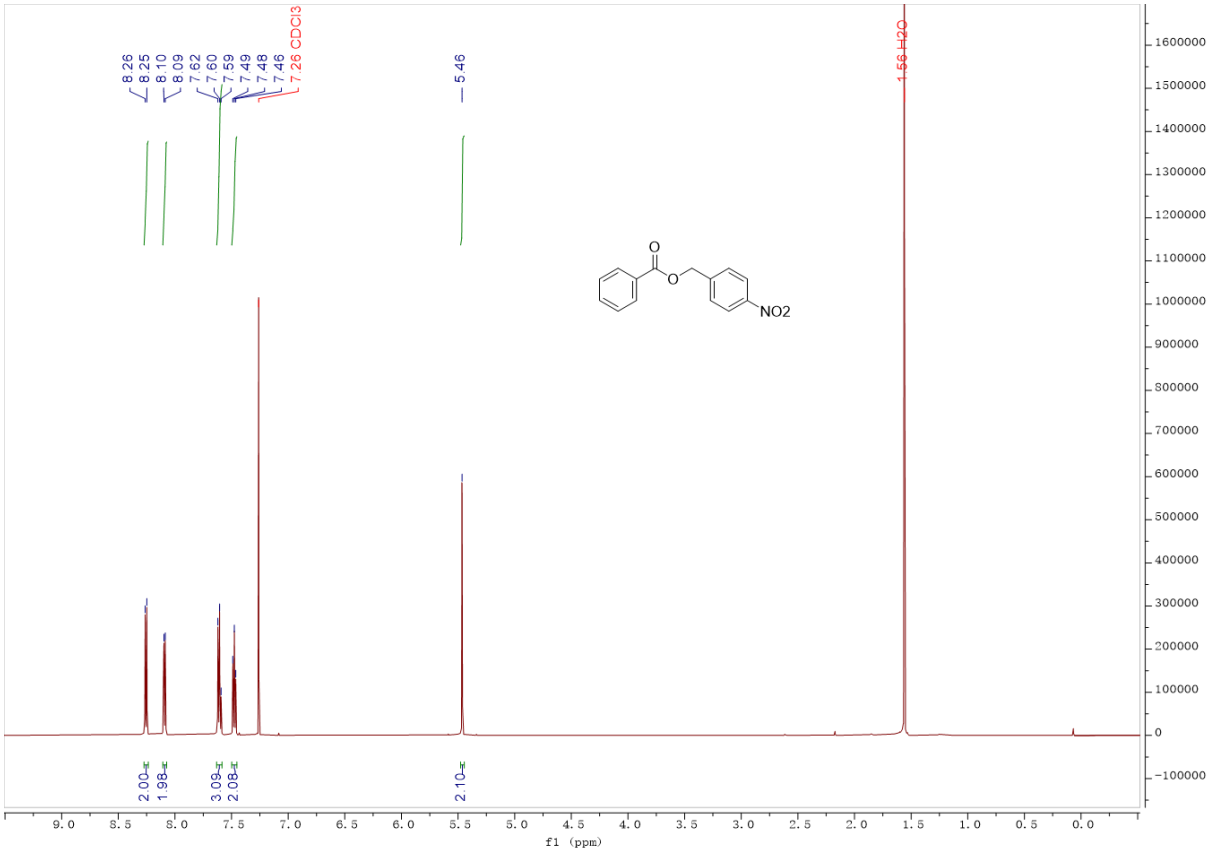


Figure S17. ^{1}H NMR Spectrum of **BnBz-(H, NO_2)**.

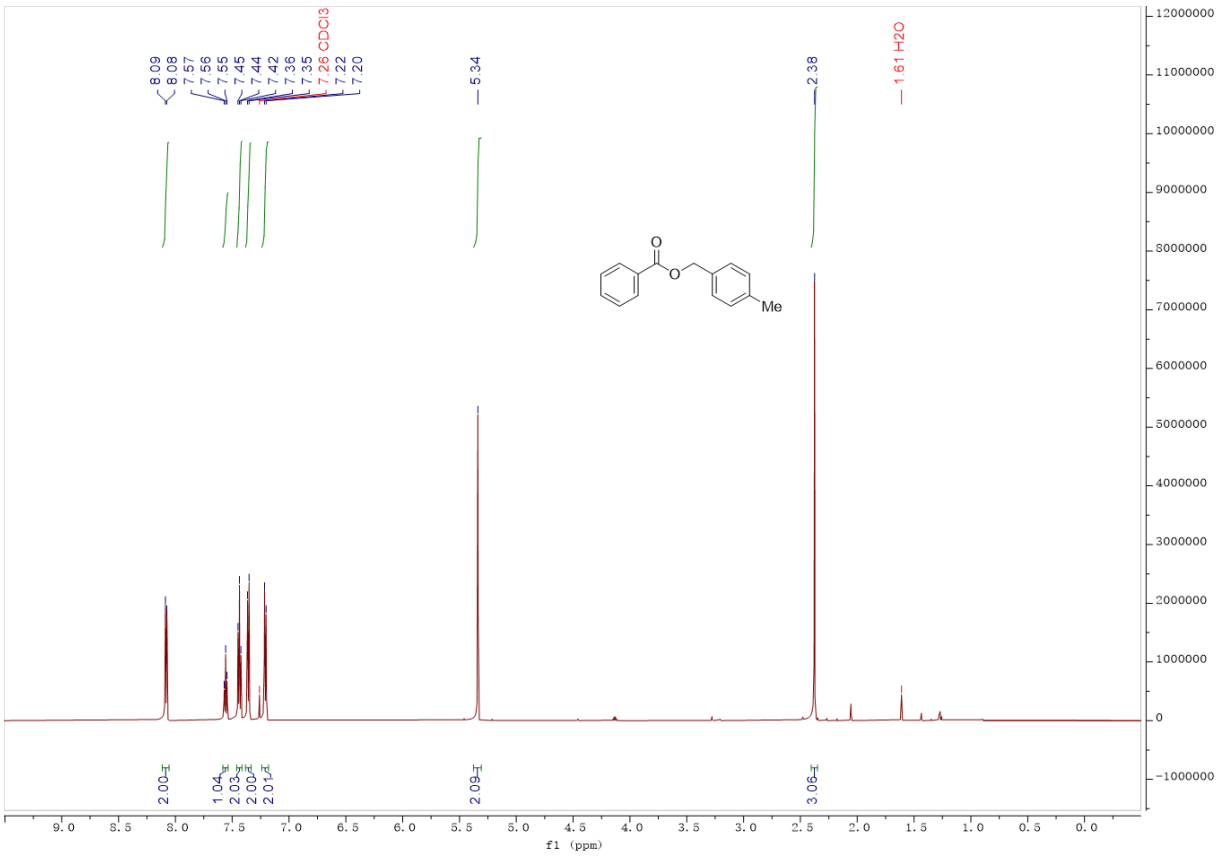


Figure S18. ^{1}H NMR Spectrum of **BnBz-(H, Me)**.

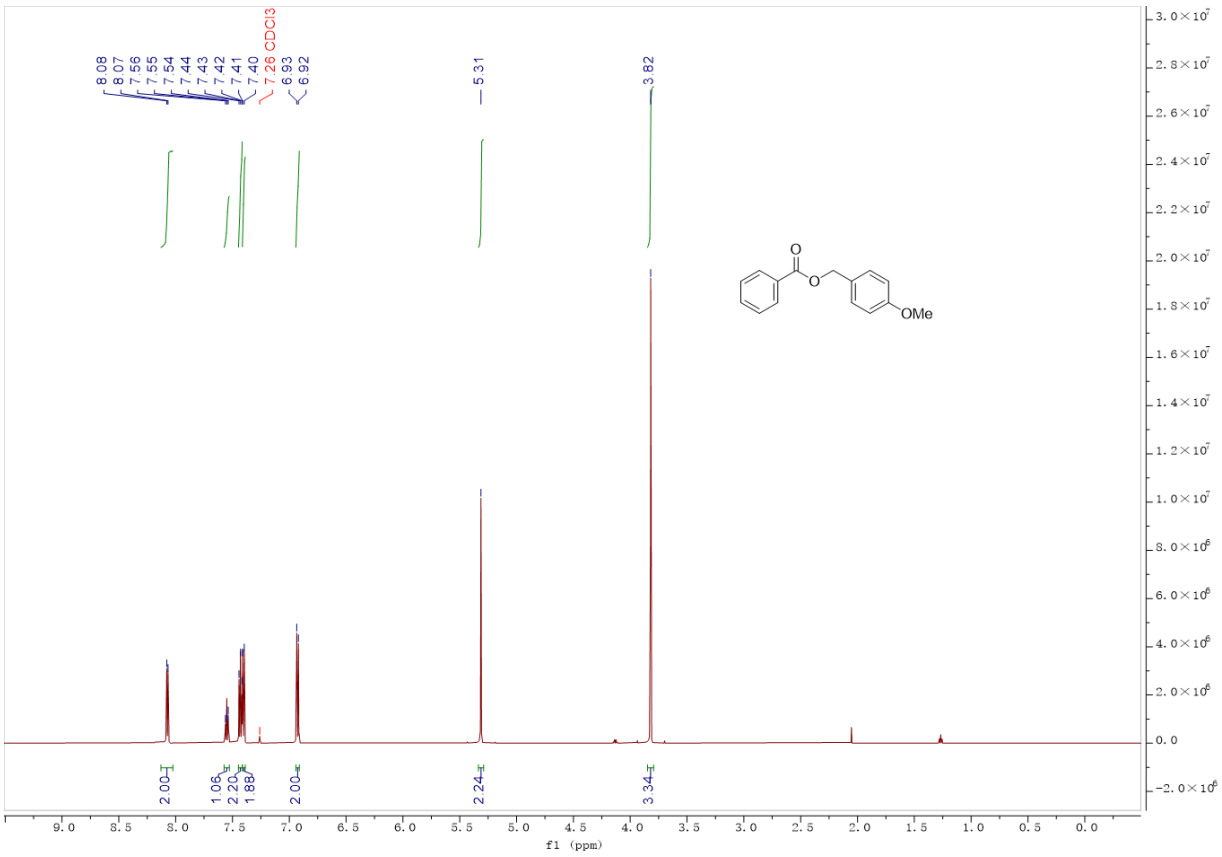


Figure S19. ^{1}H NMR Spectrum of **BnBz-(H, OMe)**.

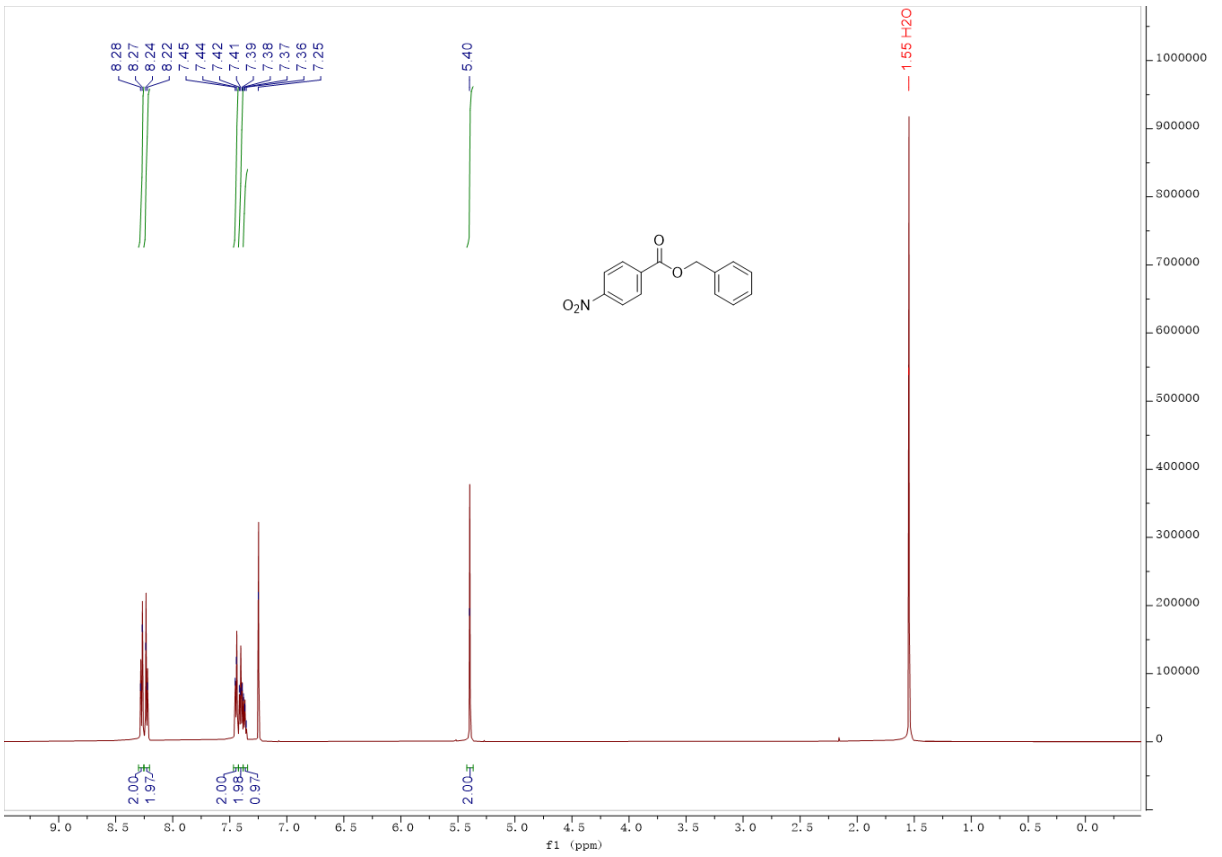


Figure S20. ^{1}H NMR Spectrum of **BnBz-(NO_2, H)**.

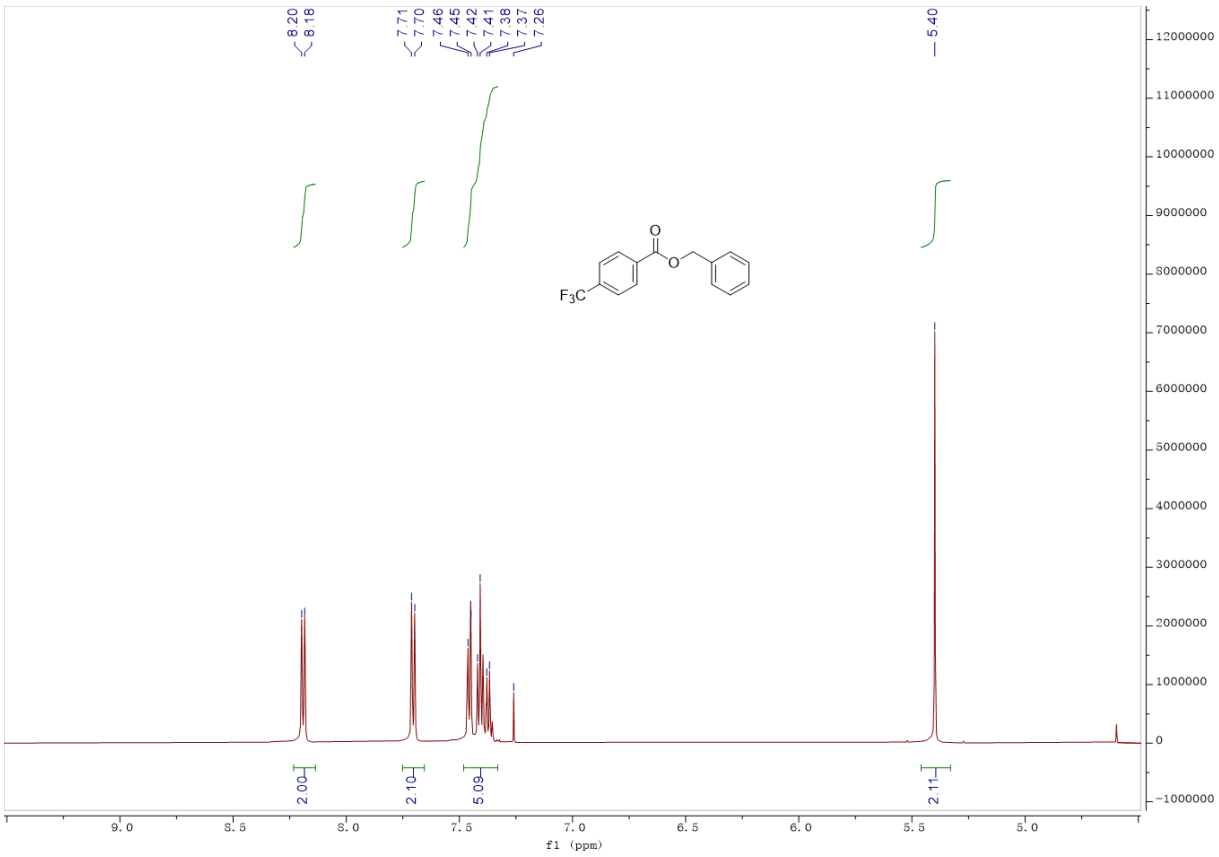


Figure S21. ^{1}H NMR Spectrum of **BnBz-(CF_3, H)**.

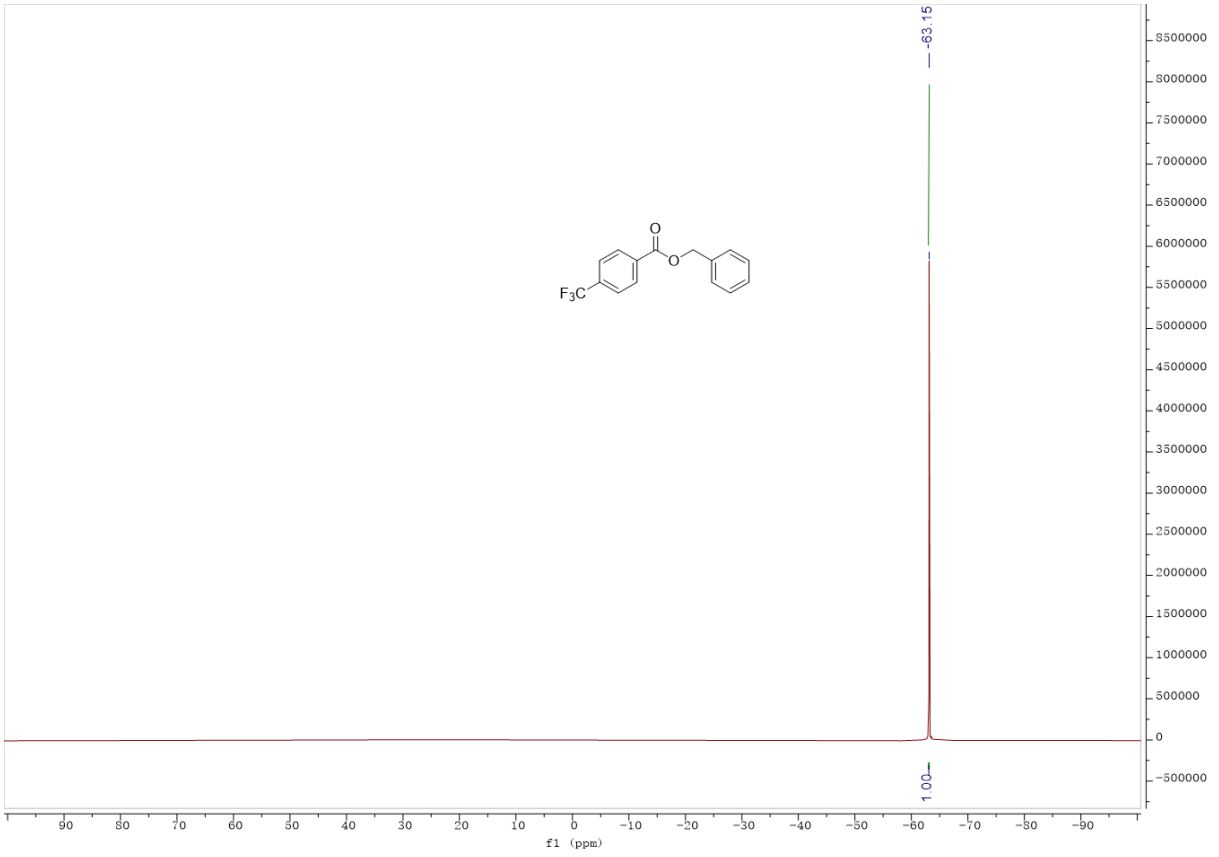


Figure S22. ^{19}F{^{1}H} NMR Spectrum of **BnBz-(CF_3, H)**.

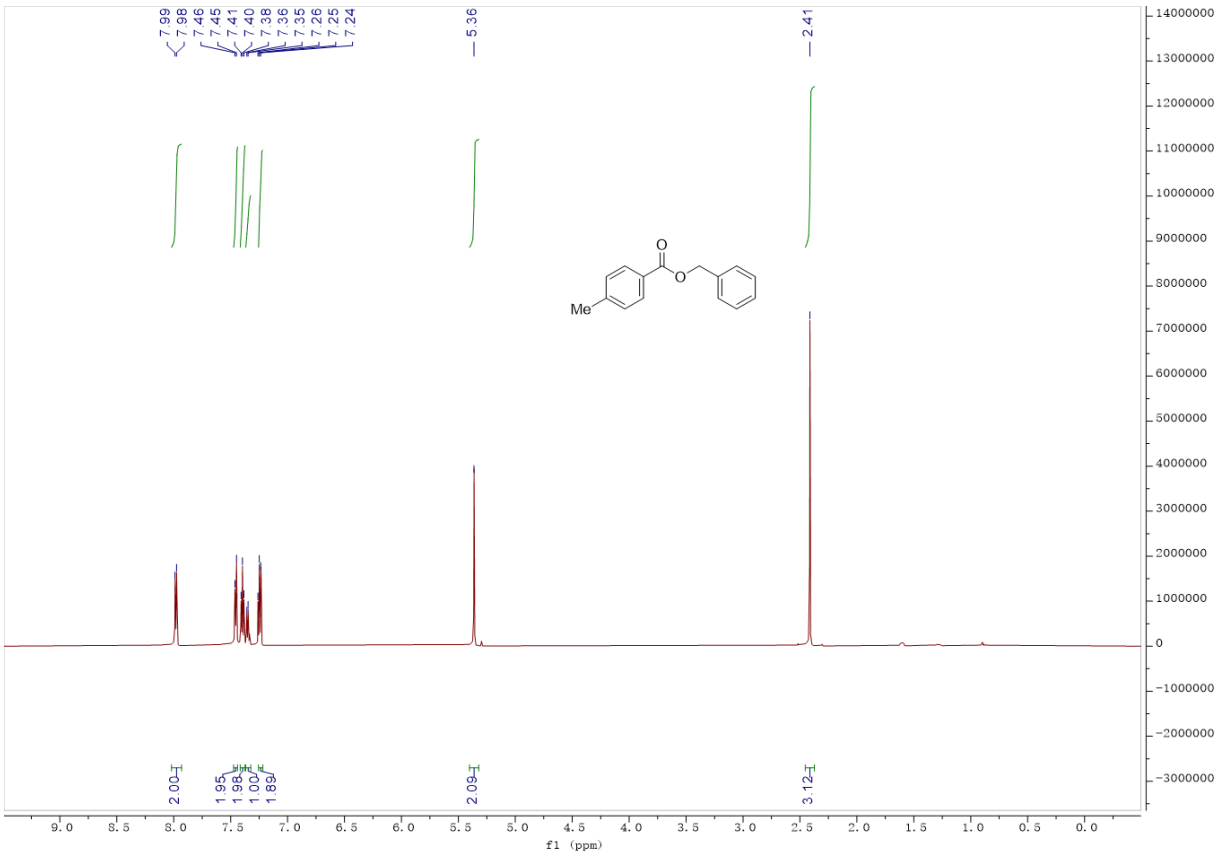


Figure S23. ^{1}H NMR Spectrum of **BnBz-(Me, H)**.

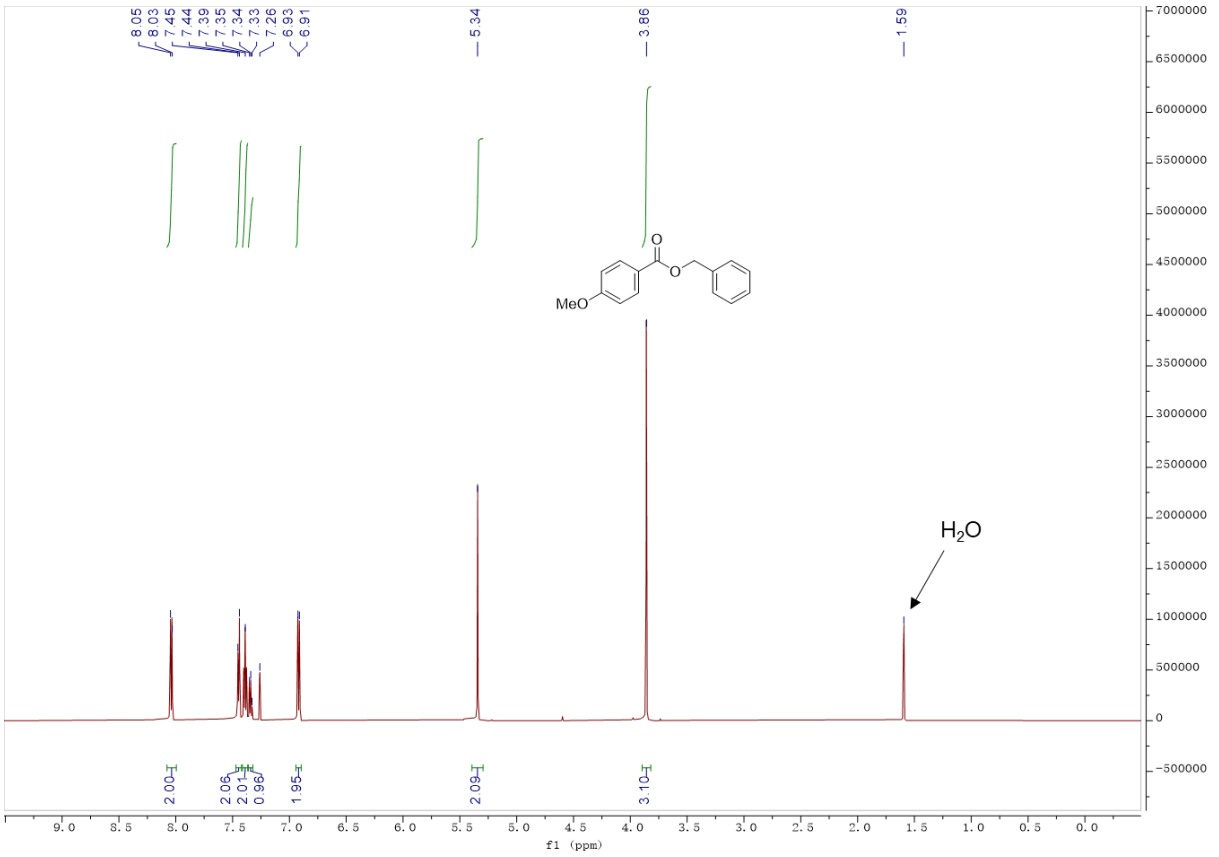


Figure S24. ^{1}H NMR Spectrum of **BnBz-(OMe, H)**.

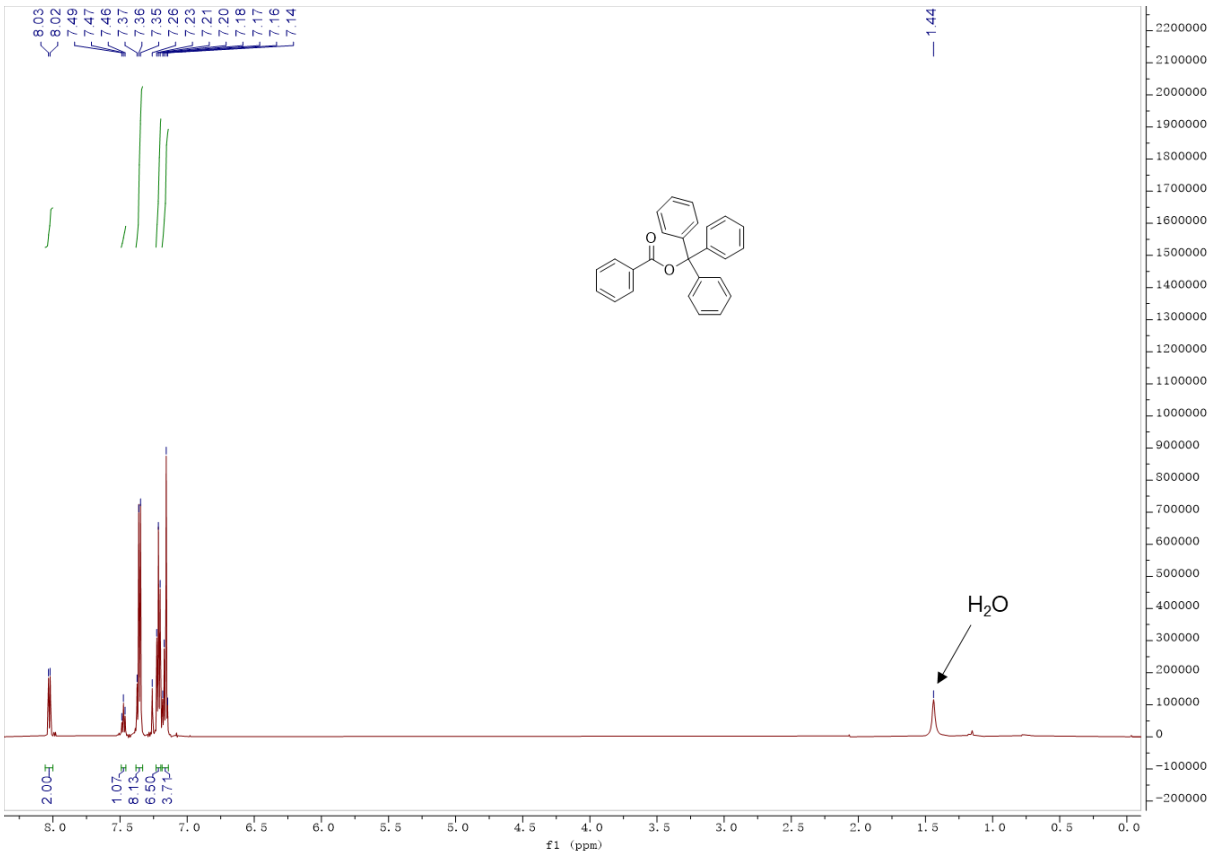


Figure S25. ^{1}H NMR Spectrum of **TrBz**.

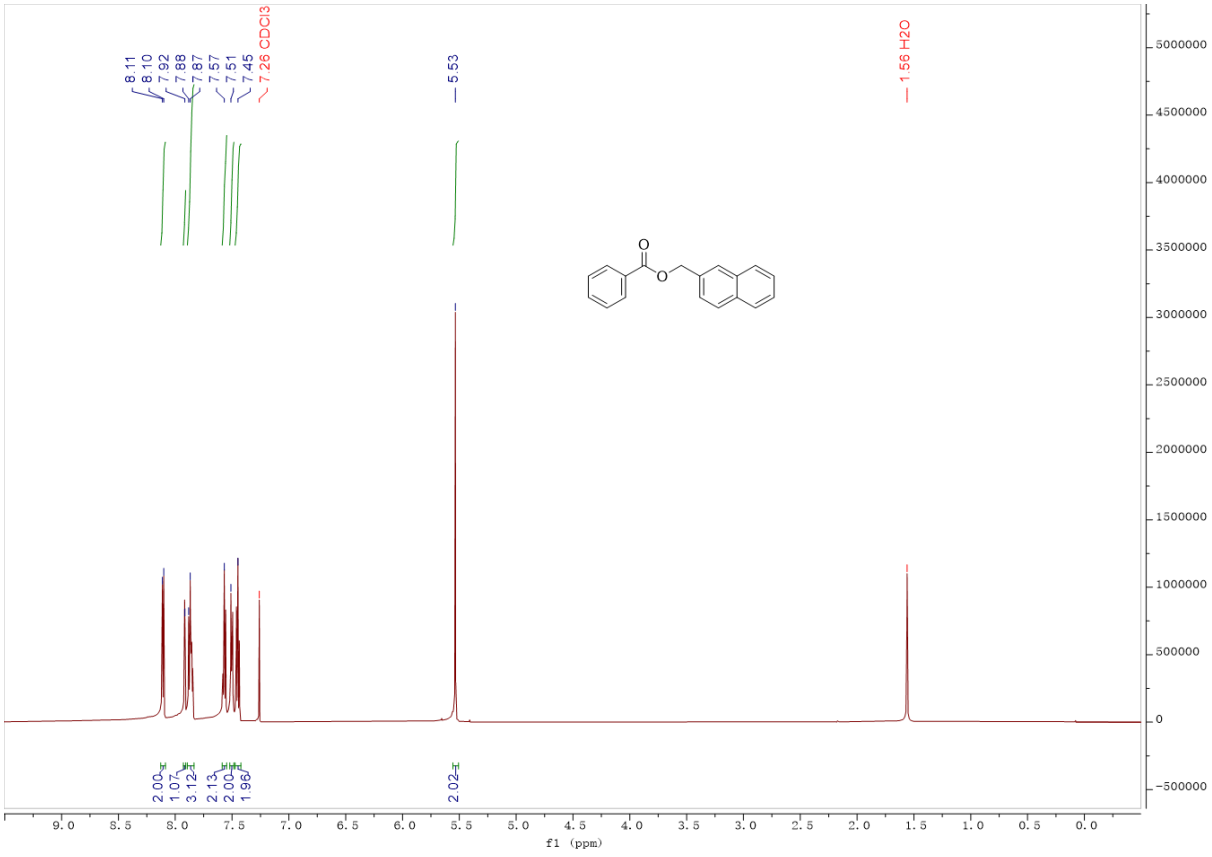


Figure S26. ^{1}H NMR Spectrum of **NMBz**.

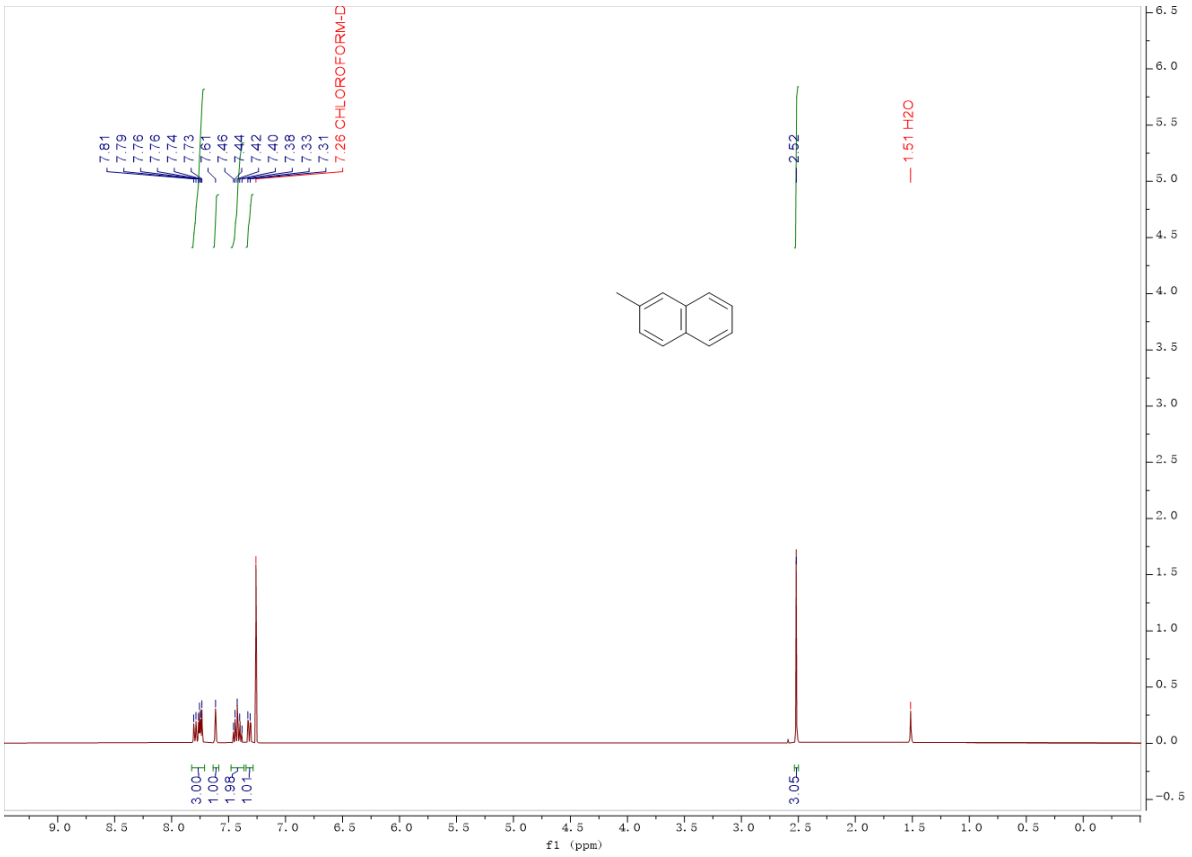


Figure S27. [1]H NMR Spectrum of 2-methylnaphthalene.

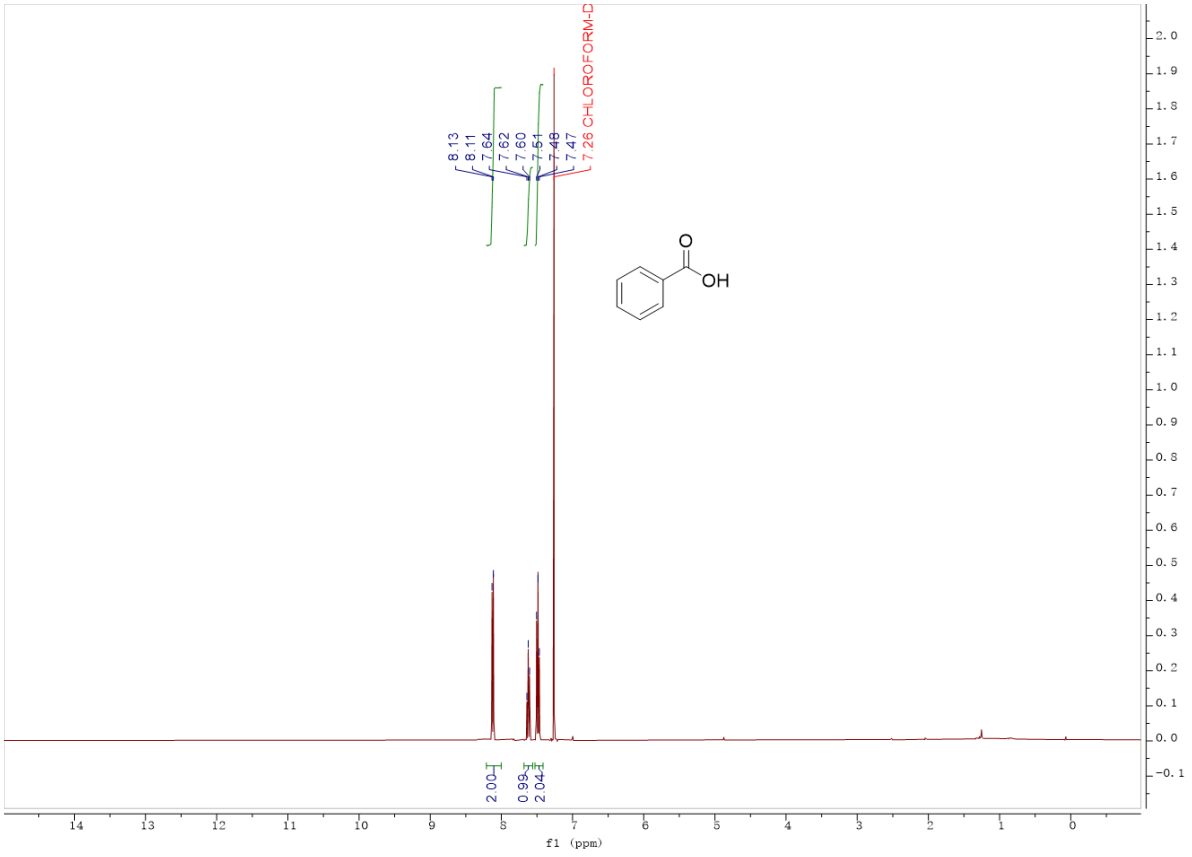


Figure S28. [1]H NMR Spectrum of benzoic acid.

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