

Electronic Supplementary Information

Cross β -arylmethylation of alcohols catalysed by recyclable Ti-Pd alloys not requiring pre-activation

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General Information

Gas chromatography (GC) was performed using a Shimadzu GC-2025 incorporating a flame ionization detector and equipped with a 0.22 mm × 25 m capillary column (BP-5). ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were acquired at 400 and 100 MHz, respectively, in CDCl₃ with TMS as an internal standard with a JEOL JNM-ECZ-400S. The products were characterized by ¹H NMR, ¹³C NMR and GC-mass spectrometry (GC-MS, EI ionization), while the **3n**, **3o**, **3q**, **5a** and **6a** specimens were also assessed by infrared spectroscopy (IR) spectroscopy and High-resolution mass spectra (HRMS). HRMS analyses of the **3n**, **3o**, **3q**, **5a** and **6a** were carried out at the Global Facility Centre, Hokkaido University. GC-MS spectra were recorded on a Shimadzu GCMS-QP2010 SE. IR spectrum were obtained on a Fourier transform (FT)-IR (Shimadzu IRAffinity-1). The product yields were estimated from the peak areas in GC chromatograms, using the internal standard technique. X-ray photoelectron spectroscopy (XPS) data were acquired with an ULVAC-PHI together with a PHI5000 VersaProbe, employing an Al K α X-ray source. Spectra were calibrated based on the Ti 2p_{3/2} peak at 459.0 eV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed using a Shimadzu ICPS-8100 instrument. The procedures used to synthesize **1a-d₁** and **2a-d₁** are described below in the Mechanistic Studies section (S3-7). All other reagents were purchased from commercial suppliers, were reagent grade or higher purity (typically >95%), and were used without further purification. Ti-Pd alloys were prepared according to a reported method.¹ The **3a**,² **3b**,² **3c**,² **3d**,² **3e**,³ **3f**,⁴ **3g**,² **3h**,⁵ **3i**,⁶ **3j**,⁴ **3k**,⁴ **3l**,² **3m**,² **3p**,² **4a**,⁷ **1a-d₁**⁸ and **2a-d₁**⁹ are known compounds and have been reported previously. **4a** was prepared using a method previously reported in the literature.¹⁰

Experimental Procedures

Typical procedure for the Ti-Pd alloy catalysed β -arylmethylation of 1a with 2a (Table 1, Entry 1): A mixture of 2-phenyl ethanol (**1a** ; 61 mg, 0.5 mmol), benzyl alcohol (**2a** ; 108 mg, 1 mmol), Ti-1.0Pd (48 mg, 1 mmol) and caesium carbonate (326 mg, 1 mmol) in toluene (2 mL) was stirred at 135 °C (bath temperature) for 48 h under air in a 15 mL pressure tube (ACE). The yield of product was determined using GC based on peak areas, employing the internal standard method with *n*-tridecane as the internal standard. The reaction was quenched by adding diisopropyl ether (8 mL). Following this, the reaction mixture was extracted with toluene (20 mL) and dried over sodium sulphate to remove small amount of water during the reaction course, with subsequent vacuum distillation in a Kugelrohr apparatus at 0.3 mmHg (pot temperature 90 °C). The product was isolated by silica gel column chromatography (*n*-hexane:ethyl acetate = 4:1) to give the pure

material as a yellow oil in a 63% yield (67 mg).

Competitive reaction of 1a with 4-methoxybenzyl alcohol/4-(trifluoromethyl)benzyl alcohol (eq 1): A mixture of 2-phenyl ethanol (**1a**; 61 mg, 0.5 mmol), 4-methoxybenzyl alcohol (138 mg, 1 mmol), 4-(trifluoromethyl)benzyl alcohol (176 mg, 1 mmol), Ti-1.0Pd (48 mg, 1 mmol) and caesium carbonate (326 mg, 1 mmol) in toluene (1 mL) was stirred at 135 °C (bath temperature) for 48 h under air in a 15 mL pressure tube (ACE). The yields of the products (**3l**, **3n**) were determined using GC based on peak areas, employing the internal standard method with *n*-decane as the internal standard.

Recycling of the Ti–Pd alloy catalyst following β -arylmethylation (Figure 1): After the reaction was performed under the optimum conditions (Table 1, Entry 1), the reaction mixture was cooled with ice and the catalyst was separated from the reaction mixture by suction filtration. The alloy was subsequently washed with methanol (20 mL), distilled water (10 mL) and methanol (50 mL) and returned to the reaction vessel, after which the residual wash solvent was removed by evaporation and the sample was ready to be used as catalyst for the next reaction cycle under the conditions of entry 1, Table 1.

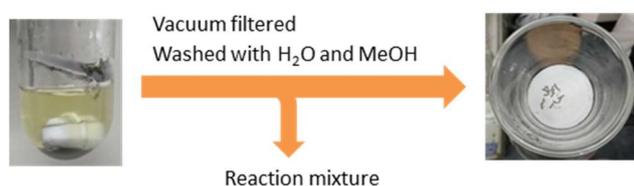


Figure S1 The procedure used to recover Ti-Pd alloy catalysts.

Typical procedures for the preparation of XPS samples (Figure 2):

Following the reaction (Table 1, entry 1), the Ti–Pd alloy catalyst for XPS sample was prepared by suction filtration from the reaction mixture and washed with 30 mL of methanol, 10 mL of distilled water, and then washed again with 50 mL of methanol. The sample was then transferred to a vial and dried for 10 min in vacuo at room temperature. The sample was stored in an Ar atmosphere. The prepared sample was fixed to the sample stand with carbon tape for XPS equipment.

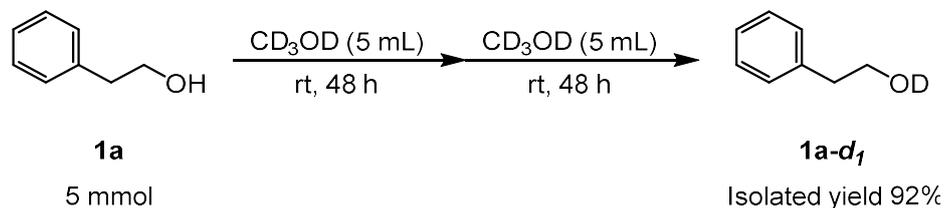
Filter experiment of the Ti-Pd alloy catalyst for during β -arylmethylation (Figure 3): A mixture of 2-phenyl ethanol (**1a**; 61 mg, 0.5 mmol), benzyl alcohol (**2a**; 108 mg, 1 mmol), Ti-1.0Pd (48 mg, 1 mmol) and caesium carbonate (326 mg, 1 mmol) in toluene (2 mL) was stirred at 135 °C for 24 h under the optimum conditions (Table 1, Entry 1). After 24

h, the reaction mixture was passed through a membrane filter (PTFE 0.22 $\mu\text{m}/\phi 13\text{ mm}$) to remove the catalyst. The filtrate was subsequently combined with caesium carbonate (326 mg, 1 mmol) and stirred at 135 °C for 24 h under air.

Typical procedure for the preparation of ICP-AES samples: Following the reaction (Table 1, Entry 1), the Ti–Pd alloy catalyst was removed from the reaction solution by passing the solution through a membrane filter. Residual solvent was then removed from the filtrate by evaporation and the filtrate was diluted with methanol (10 mL).

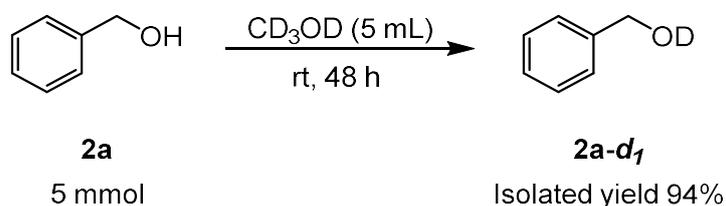
Mechanistic Studies

Preparation of 2-phenyl ethanol-*d*₁ (**1a-d**₁)



A quantity of 2-phenylethanol (611 mg, 5 mmol) was added to CD₃OD (5 mL) in a pear-shaped flask and the mixture was stirred at ambient temperature for 48 h. The reaction solution was subsequently filtered and the solvent was evaporated followed by the addition of a second portion of CD₃OD (5 mL) and a second reaction under the same conditions as the first. Following this second reaction, the reaction mixture was again filtered and the solvent evaporated. The desired product was obtained in 92% yield (567 mg) as a yellow liquid with 74% D incorporation in the OH moiety as determined by ¹H NMR.

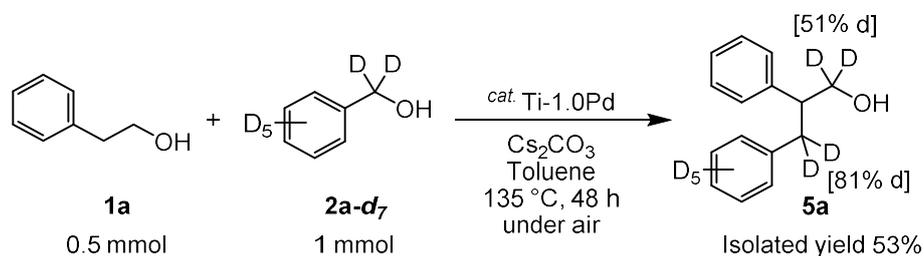
Preparation of benzyl alcohol-*d*₁ (**2a-d**₁)



Benzyl alcohol (540 mg, 5 mmol) was added to CD₃OD (5 mL) in a pear-shaped flask and the mixture was stirred at ambient temperature for 48 h, after which the reaction mixture was filtered and evaporated. The desired product was obtained in 94% yield (513 mg) as red liquid with 80% D incorporation in the OH moiety as determined by ¹H NMR.

Deuterium labelling experiments

The reaction of 2-phenyl ethanol **1a** with benzyl alcohol-*d*₇ **2a-d₇**



A mixture of 2-phenyl ethanol (**1a**; 61 mg, 0.5 mmol), benzyl alcohol-*d*₇ (**2a-d₇**; 115 mg, 1 mmol), Ti-1.0Pd (48 mg, 1 mmol) and caesium carbonate (326 mg, 1 mmol) in toluene (2 mL) was stirred at 135 °C for 48 h under air in a 15 mL pressure tube (ACE), after which the reaction was quenched by adding diisopropyl ether (8 mL). The reaction mixture was subsequently extracted with toluene (20 mL), dried over sodium sulphate to remove small amount of water generated in the reaction and vacuum distilled using a Kugelrohr apparatus at 0.3 mmHg (pot temperature 100 °C), after which the product was isolated by silica gel column chromatography (*n*-hexane:ethyl acetate = 4:1). The product **5a** was obtained in 53% yield (59 mg) as colorless oil.

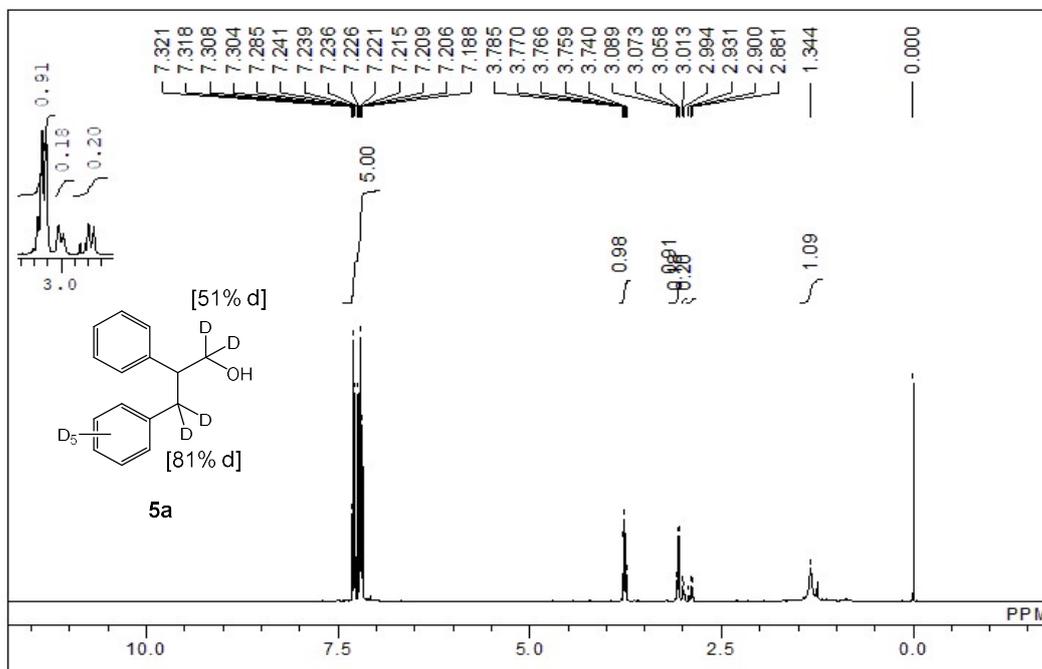


Figure S2 ¹H NMR spectra of **5a**

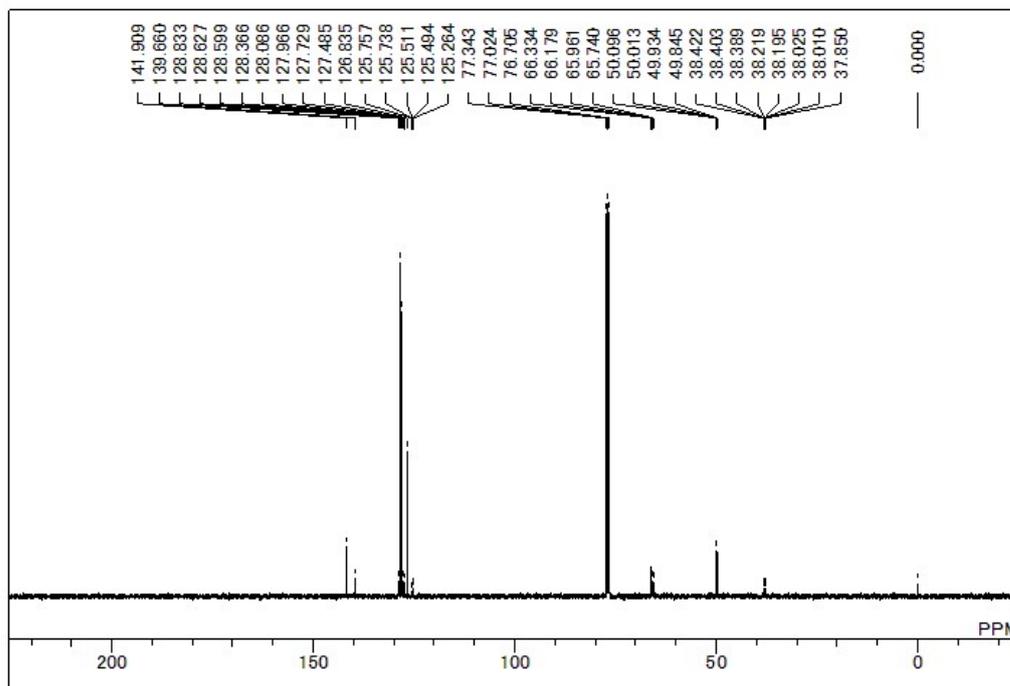
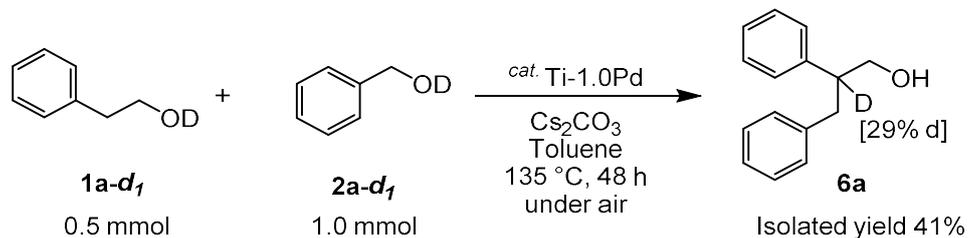


Figure S3 ^{13}C NMR spectra of **5a**

5a: yield 53% (58.7 mg) colorless oil. ^1H NMR (400 MHz; CDCl_3) δ : 7.32-7.19 (m, 5H), 3.79-3.74 (m, 2H), 3.09-3.06 (m, 1H), 3.01-2.99 (m, 1H), 2.93-2.88 (m, 1H), 1.34 (br, 1H); ^{13}C NMR (100 MHz; CDCl_3) δ : 141.9 (C), 139.7 (C), 128.6 (CH), 128.6 (t, $J = 23.4$ Hz, CD), 128.1 (CH), 127.7 (t, $J = 23.7$, CD), 126.8 (CH), 125.5 (m, CD), 66.3 (CH_2), 66.0 (t, $J = 22.1$, CD), 50.0 (q, $J = 8.4$, CD), 38.4-37.9 (m, CD); GC-MS (EI) m/z (relative intensity) 220(5) $[\text{M-H}]^+$, 122(100), 104(67), 121(66); IR (NaCl, cm^{-1}) 3335, 1494, 1452, 1061, 1030, 757, 698; HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_7\text{D}_9\text{O}$: 221.1766, found 221.1755.

The reaction of 2-phenyl ethanol- d_1 **1a-d₁ with benzyl alcohol- d_7 **2a-d₇****



A mixture of 2-phenyl ethanol- d_1 (**1a-d₁**; 62 mg, 0.5 mmol), benzyl alcohol- d_7 (**2a-d₇**; 109 mg, 1 mmol), Ti-1.0Pd (48 mg, 1 mmol) and caesium carbonate (326 mg, 1 mmol) in toluene (2 mL) was stirred at 135 °C for 48 h under air in a 15 mL pressure tube (ACE), after which the reaction was quenched by adding diisopropyl ether (8 mL). The reaction mixture was extracted with toluene (20 mL), dried over sodium sulphate to remove small amount of water generated in the reaction and vacuum distilled using a Kugelrohr apparatus at 0.3 mmHg (pot temperature 100 °C), after which the product was isolated by silica gel column chromatography (*n*-hexane:ethyl acetate = 4:1). The product **6a** was obtained in 41% yield (44 mg) as colorless oil.

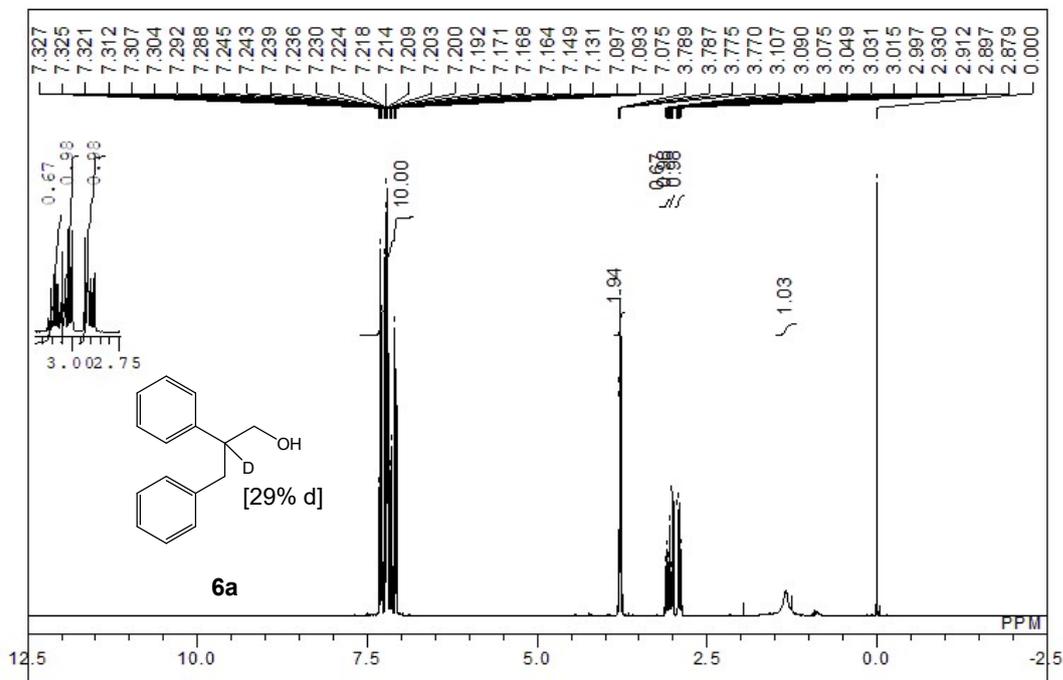


Figure S4 ¹H NMR spectra of **6a**

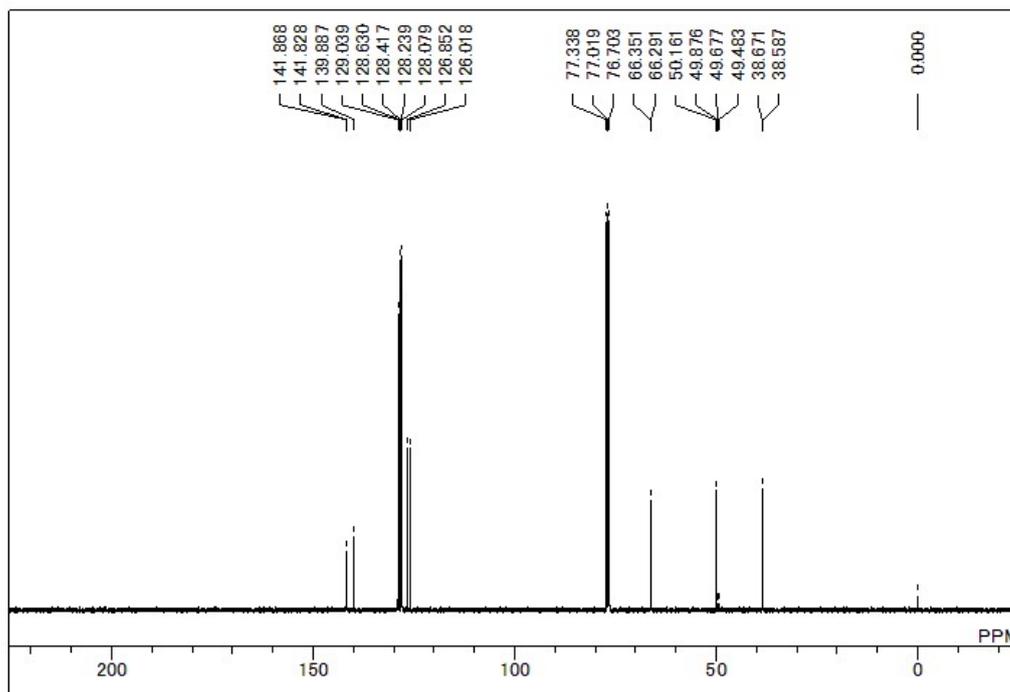
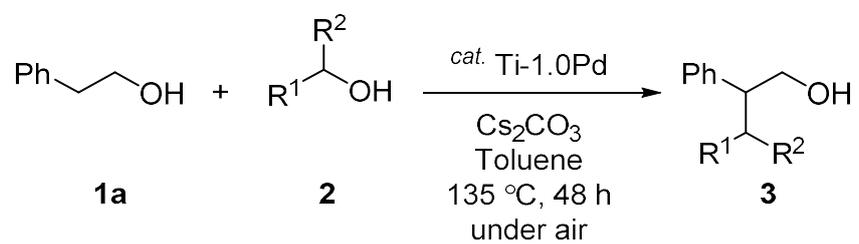


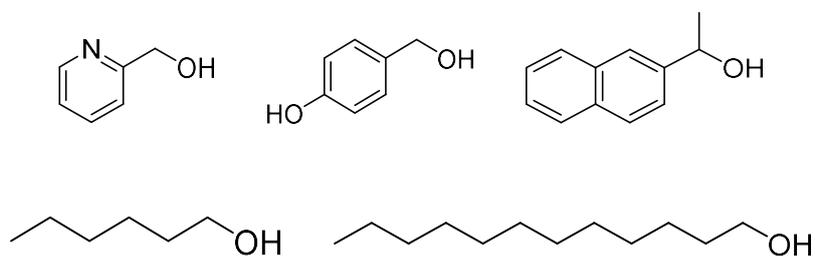
Figure S5 ^{13}C NMR spectra of **6a**

6a: yield 41% (43.7 mg), colorless oil. ^1H NMR (400 MHz; CDCl_3) δ : 7.33-7.08 (m, 10H), 3.80-3.74 (m, 2H), 3.13-3.06 (quin, $J = 6.8$ Hz, 1H), 3.02 (dd, $J = 13.3, 7.2$ Hz, 1H), 2.90 (dd, $J = 13.3, 7.2$ Hz, 1H), 1.34 (br, 1H); ^{13}C -NMR (100 MHz; CDCl_3) δ : 141.9-141.8 (m, C), 139.9 (C), 129.0 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 126.9 (CH), 126.0 (CH), 66.4-66.3 (m, CH), 50.2 (CH), 49.7 (t, $J = 19.9$, CD), 38.7-38.6 (m, CH); GC-MS (EI) m/z (relative intensity) 213(5) $[\text{M}]^+$, 121(100), 91(89), 103(81); IR (NaCl, cm^{-1}) 3338, 1453, 1383, 1068, 758, 700; HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{DO}$: 213.1264, found 213.1260.

Limitations



Unsuccessful substrates **2**



Specific surface area, crystalline size and strain (XRD) and SEM data of Ti-Pd alloys

Table S3 Specific surface area of Ti-Pd alloys ($S / \text{m}^2\text{g}^{-1}$)

Ti-1.0Pd	Ti-0.5Pd	Ti-0.2Pd	Ti
0.0233	0.0530	0.0354	0.0531

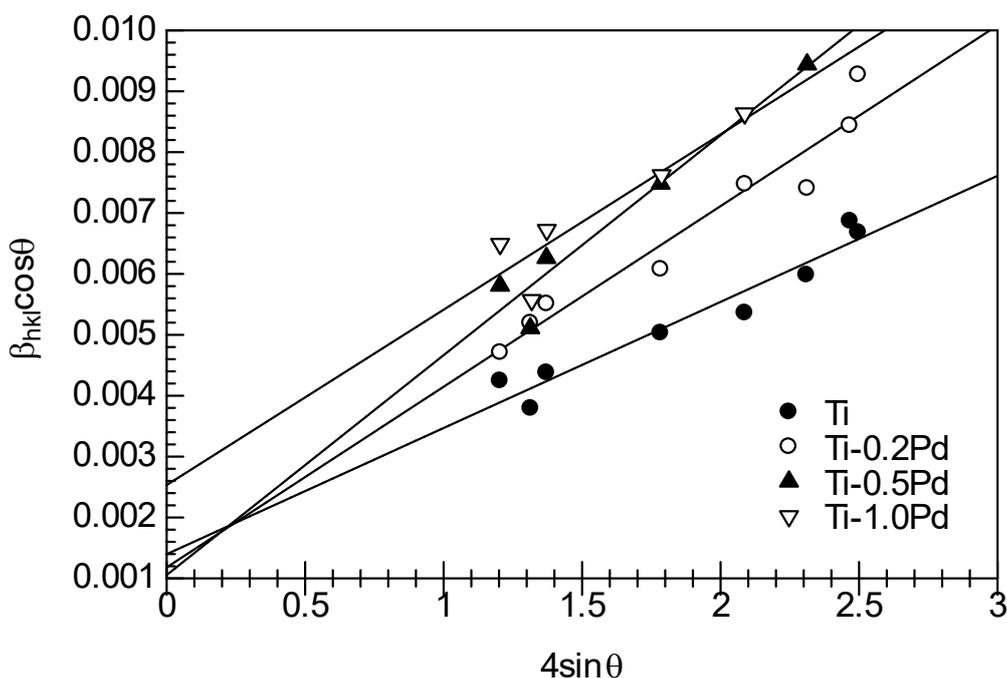


Figure S6 Williamson-Hall plots of Ti, Ti-0.2Pd, Ti-0.5Pd, and Ti-1.0Pd.

Table S4 Crystallite size and strain of Ti-Pd alloys

Samples	Crystallite size, D / nm	Strain, ε (%)
Ti-1.0Pd	54.7	0.288
Ti-0.5Pd	131.4	0.361
Ti-0.2Pd	117.4	0.297
Ti	99.2	0.207

Crystallite size and strain of Ti-Pd alloys are calculated by Williamson-Hall plots. X-ray diffraction measurement was conducted by Cu-K α radiation with tube voltage and current, 40 kV and 300 mA and parallel beam method. Peak width and positions are

correlated by Si powder of NIST standard reference material 640f. β_{hkl} means FWHM of several plane peak and θ means diffraction angel.

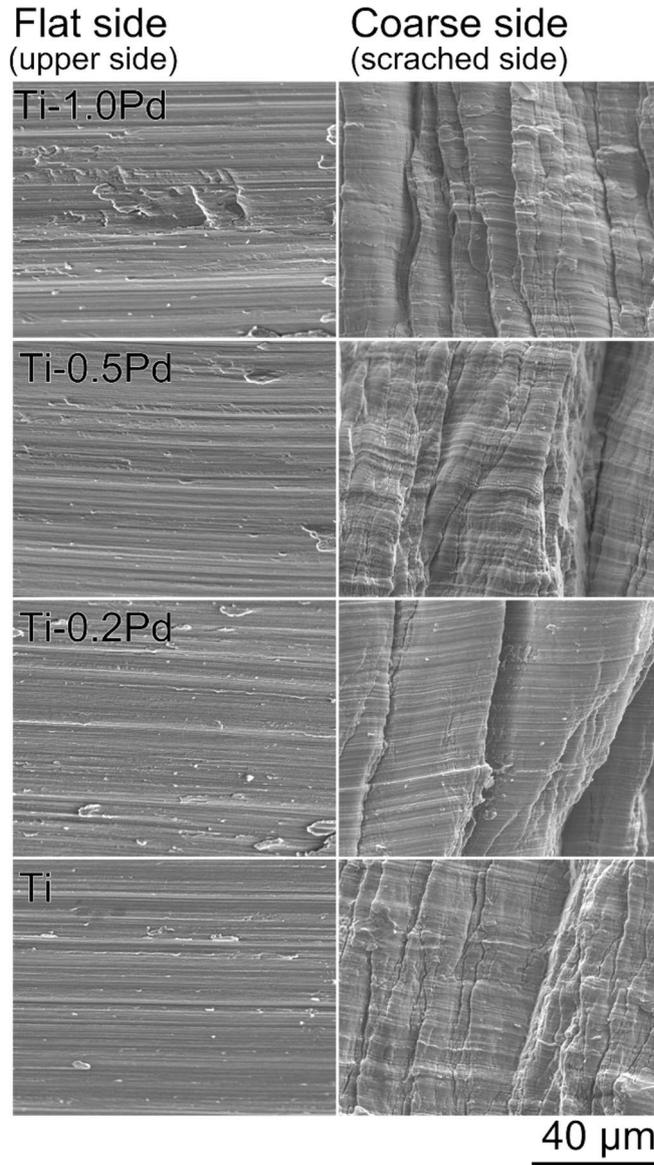


Figure S7 SEM images of turnings Ti, Ti-0.2Pd, Ti-0.5Pd, and Ti-1.0Pd. The SEM images are captured using 10 kV acceleration voltage, 11 mm working distance from turnings Ti, Ti-0.2Pd, Ti-0.5Pd, and Ti-1.0Pd. The turnings have flat side and coarse side due to machining. These figures are captured Horizontal axis of these images were correlated with the longitudinal direction of the turnings.

Results of ICP-AES Analyses

Table S5 Amounts of Ti and Pd leached after the reaction corresponding to Table 1, Entry 1, as determined by ICP-AES.

<Intensity>		
Element	Ti	Pd
Wavelength	334.941 nm	340.458 nm
First run	2.87486	0.046369
Second run	2.87398	0.046896
Third run	2.88896	0.046938
Average	2.87927	0.046734
R	0.014979	0.000569
SD	0.008404	0.000317
RSD	0.291876	0.678727

<Concentration>		
Element	Ti	Pd
Wavelength	334.941 nm	340.458 nm
Unit	ppm	ppm
First run	0.346771	0
Second run	0.346646	0
Third run	0.348759	0
Average	0.347392	0
R	0.000538	0
SD	0.00027	0
RSD	10.9621	0

The concentration of Ti in this sample was 0.347 ppm. The experimental sample had been diluted five-fold and so the actual Ti concentration in the reaction solution was 1.74 ppm. (the detection limit of Ti is 8.34×10^{-5} ppm)

Table S6 Amounts of Ti and Pd leached after the reaction corresponding to Table 1, Entry 10, as determined by ICP-AES.

<Intensity>		
Element	Ti	Pd
Wavelength	334.941 nm	340.458 nm
First run	0.431963	0.045925
Second run	0.434075	0.046152
Third run	0.435777	0.045510
Average	0.433939	0.045862
R	0.003814	0.000642
SD	0.001911	0.000326
RSD	0.440304	0.710042
<Concentration>		
Element	Ti	Pd
Wavelength	334.941 nm	340.458 nm
Unit	ppm	Ppm
First run	0.002180	0
Second run	0.002478	0
Third run	0.002718	0
Average	0.002459	0
R	0	0
SD	0	0
RSD	0	0

The concentration of Ti in this sample was 0.00246 ppm (the detection limit of Ti is 8.34×10^{-5} ppm). The experimental sample had been diluted five-fold and so the actual Ti concentration in the reaction solution was 1.23×10^{-2} ppm. (the detection limit of Ti is 8.34×10^{-5} ppm)

Figure S8 Data from the ICP-AES analyses of Ti in reaction mixtures
(orange: Table 1, Entry 1, green: Table 1, Entry 10)

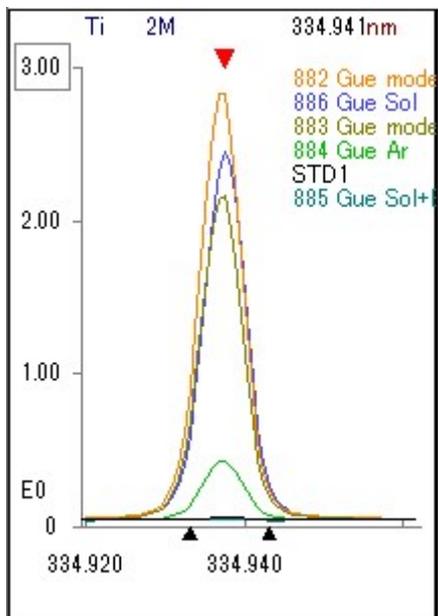
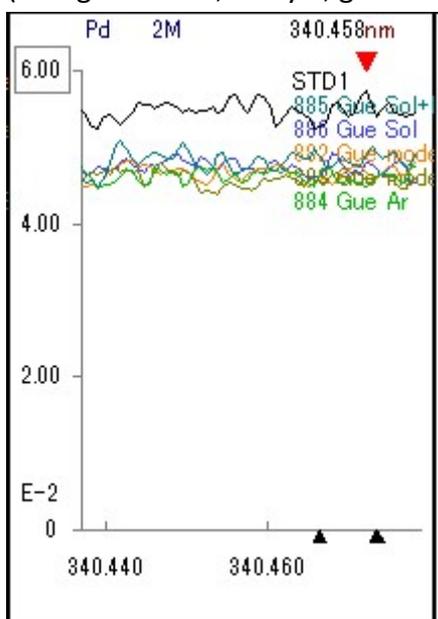


Figure S9 Data from the ICP-AES analyses of Pd in reaction mixtures
(orange: Table 1, Entry 1, green: Table 1, Entry 10)



Results of XPS Analyses

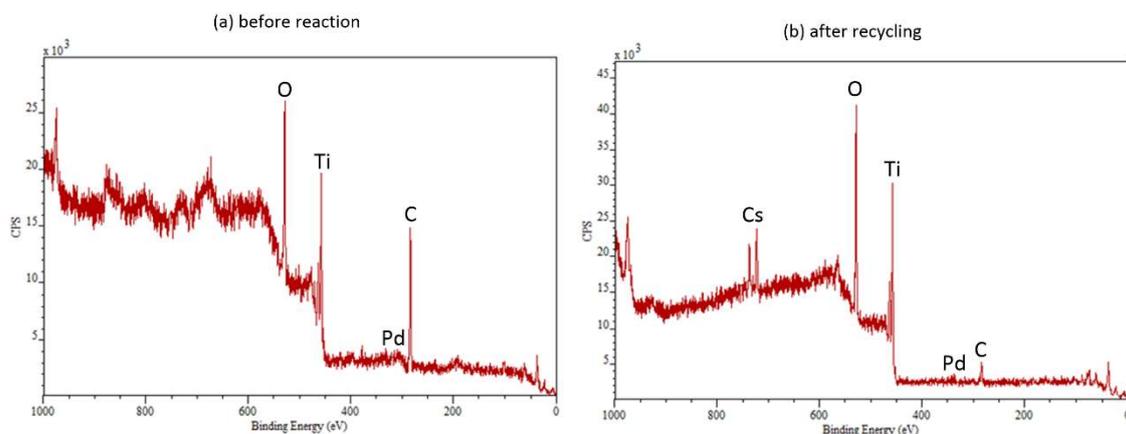


Figure S10 Wide scan XPS spectra obtained from a Ti-Pd alloy (a) before use and (b) after recycling.

Table S7 Pd XPS peak positions and full width at half maximum (FWHM) values

	Binding Energy (eV)	FWHM
Before use		
Pd 3d _{5/2}	335.8	1.2
Pd 3d _{3/2}	341.1	1.2
After recycling		
Pd 3d _{5/2}	336.1	1.2
Pd 3d _{3/2}	341.4	1.2

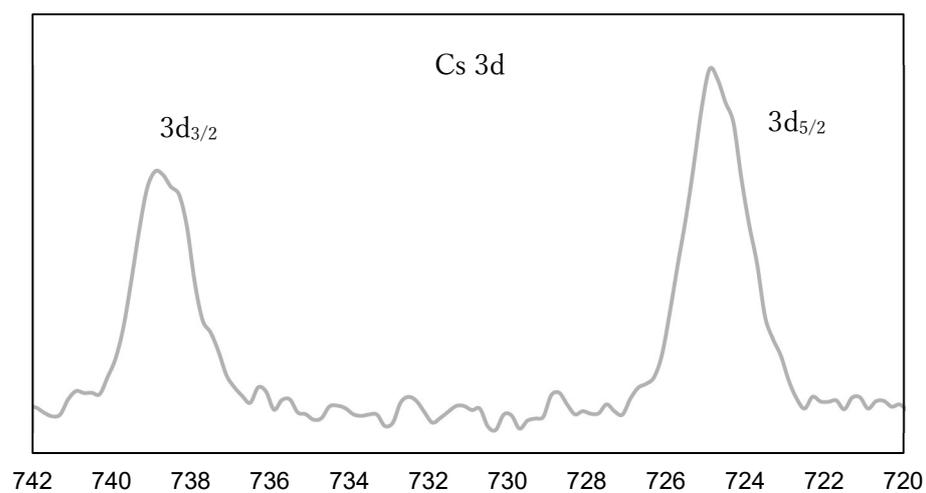


Figure S11 Cs 3d XPS spectra obtained from a Ti-Pd alloy after 5th recycling.

Spectral Data

3a²: yield 63% (66.9 mg), yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ: 7.32-7.08 (m, 10H), 3.79-3.77 (m, 2H), 3.09 (m, 1H), 3.02 (dd, *J* = 12.8, 7.2, 1H), 2.90 (dd, *J* = 13.2, 7.2, 1H), 1.32 (br, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 141.9 (C), 139.9 (C), 129.0 (CH), 128.6 (CH), 128.2 (CH), 128.1 (CH), 126.9 (CH), 126.0 (CH), 66.4 (CH₂), 50.2 (CH), 35.6 (CH₂); GC-MS (EI) *m/z* (relative intensity) 212(9) [M]⁺, 121(100), 103(93), 91(75).

3b²: yield 72% (81.5 mg), yellow oil. ¹H NMR (CDCl₃) δ: 7.15-6.99 (m, 9H), 3.65-3.63 (m, 2H), 3.65-3.63 (m, 2H), 2.98-2.88 (m, 2H), 2.79 (dd, *J* = 12.8, 7.2, 1H), 2.23 (s, 1H), 1.46 (br, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 140.0 (C), 138.7 (C), 136.3 (C), 129.3 (CH), 129.0 (C), 128.2 (CH), 127.9 (CH), 125.9 (CH), 66.4 (CH₂), 49.6 (CH), 38.7 (CH₂), 21.0 (CH₃); GC-MS (EI) *m/z* (relative intensity) 226(14) [M]⁺, 135(100), 117(49), 91(38).

3c²: yield 71% (86.0 mg), yellow oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.25-7.07 (m, 7H), 6.86-6.83 (m, 2H), 3.78-3.70 (m, 5H), 3.06-2.96 (m, 2H), 2.86 (dd, *J* = 12.8, 7.2, 1H), 1.38 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ 158.3 (C), 139.9 (C), 133.7 (C), 129.0 (CH), 128.9 (C), 128.1 (CH), 125.9 (CH), 113.9 (CH), 66.4 (CH₂), 55.1 (CH₃), 49.2 (CH), 38.8 (CH₂); GC-MS (EI) *m/z* (relative intensity) 242(11) [M]⁺, 151(100), 91(30), 121(13).

3d²: yield 48% (59.2 mg), pale yellow oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.28-7.04 (m, 9H), 3.80-3.72 (m, 2H), 3.10-3.00 (m, 2H), 2.83-2.77 (m, 1H), 1.49 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ: 140.4 (C), 139.5 (C), 132.5 (C), 129.4 (2CH), 129.0 (2CH), 128.7 (2CH), 128.3 (2CH), 126.2 (CH), 66.2 (CH₂), 49.6 (CH), 38.6 (CH₂); GC-MS (EI) *m/z* (relative intensity) 246(7) [M]⁺, 91(100), 138(27), 92(27).

3e³: yield 77% (101.0 mg), colorless oil. ¹H-NMR (CDCl₃) δ: 8.10 (d, *J* = 23.9 Hz, 1H), 7.89-7.85 (m, 1H), 7.80-7.76 (m, 1H), 7.53-7.45 (m, 4H), 7.23 (d, *J* = 19.1 Hz, 1H), 7.19-7.14 (m, 3H), 4.13-3.99 (m, 1H), 3.98-3.84 (m, 2H), 3.23 (dd, *J* = 36.1, 18.1 Hz, 1H), 3.13-3.10 (m, 1H), 1.31 (br, 1H). ¹³C-NMR (CDCl₃) δ: 140.0 (C), 137.9 (C), 134.0 (C), 132.1 (C), 129.1 (2CH), 129.0 (CH), 128.3 (2CH), 127.2 (CH), 126.1 (CH), 125.6 (CH), 125.4 (CH), 123.9 (CH), 122.9 (CH), 65.2 (CH₂), 43.4 (CH), 38.2 (CH₂). GC-MS (EI) *m/z* (relative intensity) 262(26) [M]⁺, 153(100), 128(20), 171(16)

3f⁴: yield 84% (116.2 mg), brown oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.18-6.81 (m, 8H), 3.81-3.70 (m, 5H), 3.01-2.96 (m, 2H), 2.83-2.77 (m, 1H), 1.49 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ: 158.5 (C), 138.4 (C), 133.1 (C), 131.7 (C), 130.4 (2CH), 129.0 (2CH), 128.3 (2CH),

114.1 (2CH), 66.4 (CH₂), 55.2 (CH₃), 49.3 (CH), 38.1 (CH₂); GC-MS (EI) *m/z* (relative intensity) 276(5) [M]⁺, 151(100), 91(26), 121(16).

3g²: yield 40% (45.3 mg), brown oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.33-7.17 (m, 10H), 3.48 (d, *J* = 4.9 Hz, 2H), 2.72-2.62 (m, 4H), 2.14-2.12 (m, 1H), 1.33 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ: 140.5 (2C), 129.1 (2CH), 128.4 (2CH), 126.0 (2CH), 64.0 (CH₂), 44.5 (CH), 37.4 (CH₂); GC-MS (EI) *m/z* (relative intensity) 226(6) [M]⁺, 91(100), 117(93), 92(46).

3h⁵: yield 64% (70.5 mg), colorless oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.30-7.17 (m, 5H), 3.52 (d, *J* = 5.2 Hz, 2H), 2.63 (d, *J* = 7.2 Hz, 2H), 1.82-1.76 (m, 1H), 1.37-1.26 (m, 11H), 0.87 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz; CDCl₃) δ: 140.8 (C), 129.2 (2CH), 128.3 (2CH), 125.8 (CH), 64.8 (CH₂), 42.6 (CH), 37.7 (CH₂), 31.8 (CH₂), 30.7 (CH₂), 29.6 (CH₂), 26.9 (CH₂), 22.7 (CH₂), 14.1 (CH₃); GC-MS (EI) *m/z* (relative intensity) 220(11) [M]⁺, 104(100), 91(98), 92(86).

3i⁶: yield 61% (58.7 mg), colorless oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.29-7.17 (m, 5H), 3.55-3.49 (m, 2H), 2.63 (d, *J* = 7.1 Hz, 2H), 1.80-1.77 (m, 1H), 1.38-1.29 (m, 7H), 0.88 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz; CDCl₃) δ: 140.9 (C), 129.2 (CH), 128.3 (CH), 125.8 (CH), 64.9 (CH₂), 42.6 (CH), 37.7 (CH₂), 30.5 (CH₂), 29.2 (CH₂), 23.0 (CH₂), 14.1 (CH₃); GC-MS (EI) *m/z* (relative intensity) 192(14) [M]⁺, 91(100), 92(77), 104(69).

3j⁴: yield 45% (50.9 mg), colorless oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.33-7.20 (m, 5H), 7.04-6.97 (m, 4H), 3.81-3.73 (m, 2H), 3.07 (m, 1H), 2.97 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.87 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.28 (s, 1H), 1.36 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ: 142.0 (C), 136.8 (C), 135.4 (C), 128.9 (2CH), 128.9 (2CH), 128.6 (2CH), 128.1 (2CH), 126.8 (CH), 66.4 (CH₂), 50.2 (CH), 38.2 (CH₂), 21.0 (CH₃); GC-MS (EI) *m/z* (relative intensity) 226(15) [M]⁺, 105(100), 103(29), 104(28).

3k⁴: yield 57% (76.4 mg), colorless oil. ¹H-NMR (400 MHz; CDCl₃) δ: 7.30 (d, *J* = 22.2 Hz, 2H), 7.26-7.20 (m, 5H), 7.04 (d, *J* = 8.5 Hz, 2H), 3.75-3.73 (m, 2H), 3.09-3.06 (m, 1H), 2.93 (ddd, *J* = 26.9, 13.7, 7.5 Hz, 2H), 1.30-1.26 (m, 10H); ¹³C-NMR (CDCl₃) δ: 148.8 (C), 142.2 (C), 136.8 (C), 128.6 (2CH), 128.6 (2CH), 128.0 (2CH), 126.8 (CH), 125.1 (2CH), 66.3 (CH₂, s), 49.9 (CH, s), 38.0 (CH₂, s), 34.3 (C, s), 31.3 (3CH₃); GC-MS (EI) *m/z* (relative intensity) 268(11) [M]⁺, 147(100), 120(19), 117(15)

3l²: yield 58% (70.3 mg), yellow oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.32-7.18 (m, 5H), 7.00-6.97 (m, 2H), 6.78-6.74 (m, 2H), 3.78-3.75 (m, 5H), 2.96 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.85 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.32 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ: 157.9 (C), 142.0 (C), 131.9 (C), 129.9 (2CH), 128.6 (2CH), 128.1 (2CH), 126.8 (CH), 113.6 (2CH), 66.4 (CH₂), 55.2 (CH₃), 50.4 (CH), 37.8 (CH₂); GC-MS (EI) *m/z* (relative intensity) 242(10) [M]⁺, 121(100), 122(10), 277(6).

3m²: yield 53% (65.4 mg), yellow oil; ¹H NMR (400 MHz; CDCl₃) δ: 7.32-7.14 (m, 7H), 6.98-6.96 (m, 2H), 3.76 (d, *J* = 6.0 Hz, 2H), 3.05-2.99 (m, 2H), 2.88-2.81 (m, 1H), 1.41 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ: 141.3 (C), 138.3 (C), 131.7 (C), 130.4 (2CH), 128.7 (2CH), 128.3 (2CH), 128.1 (2CH), 127.0 (CH), 66.3 (CH₂) 50.1 (CH), 37.9 (CH₂); GC-MS (EI) *m/z* (relative intensity) 246(8) [M]⁺, 121(100), 103(53), 91(18).

3n: yield 53% (69.5 mg), yellow oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.45 (d, *J* = 4.0 Hz 2H), 7.32-7.15 (m, 7H), 3.78 (*J* = 4.0 Hz, 2H), 3.15-3.04 (m, 2H), 2.93 (dd, *J* = 12.8, 7.6, 1H) 1.48 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ: 144.1 (C), 141.1 (C), 129.3 (CH), 128.7 (CH), 128.3 (q, ²*J*_{C-F}=32.4 Hz, C), 128.1 (CH), 127.1 (CH), 125.1 (q, ³*J*_{C-F}=3.9 Hz, CH), 124.3 (q, ¹*J*_{C-F}=271.5 Hz, C), 66.3 (CH₂) 50.0 (CH), 38.3 (CH₂); GC-MS (EI) *m/z* (relative intensity) 280 (2) [M]⁺, 121(100), 103(50), 91(18); IR (NaCl, cm⁻¹) 3355, 1321, 1121, 1068, 1019, 700; HRMS (EI) *m/z* calcd for C₁₅H₁₅F₃O: 280.1075, found 280.1075.

3o: yield 61% (65.1 mg), yellow oil. ¹H NMR (400 MHz; CDCl₃) δ: 8.36-8.29 (m, 2H), 7.33-7.09 (m, 7H), 3.81 (d, *J* = 6.2 Hz, 2H), 3.15-3.02 (m, 2H), 2.87 (dd, *J* = 13.1, 8.1 Hz, 1H), 2.28 (s, 1H); ¹³C NMR (100 MHz; CDCl₃) δ 150.2 (CH), 147.3 (CH), 141.0 (C), 136.6 (CH), 135.5 (C), 128.7 (CH), 128.1 (2CH), 127.1 (2CH), 123.2 (CH), 66.1 (CH₂), 50.1 (CH), 35.6 (CH₂); GC-MS (EI) *m/z* (relative intensity) 213(16) [M]⁺, 93(100), 103(32), 121(24); IR (NaCl, cm⁻¹) 3230, 1425, 1193, 1068, 1028, 701; HRMS (EI) *m/z* calcd for C₁₄H₁₅NO: 213.1154, found 213.1154.

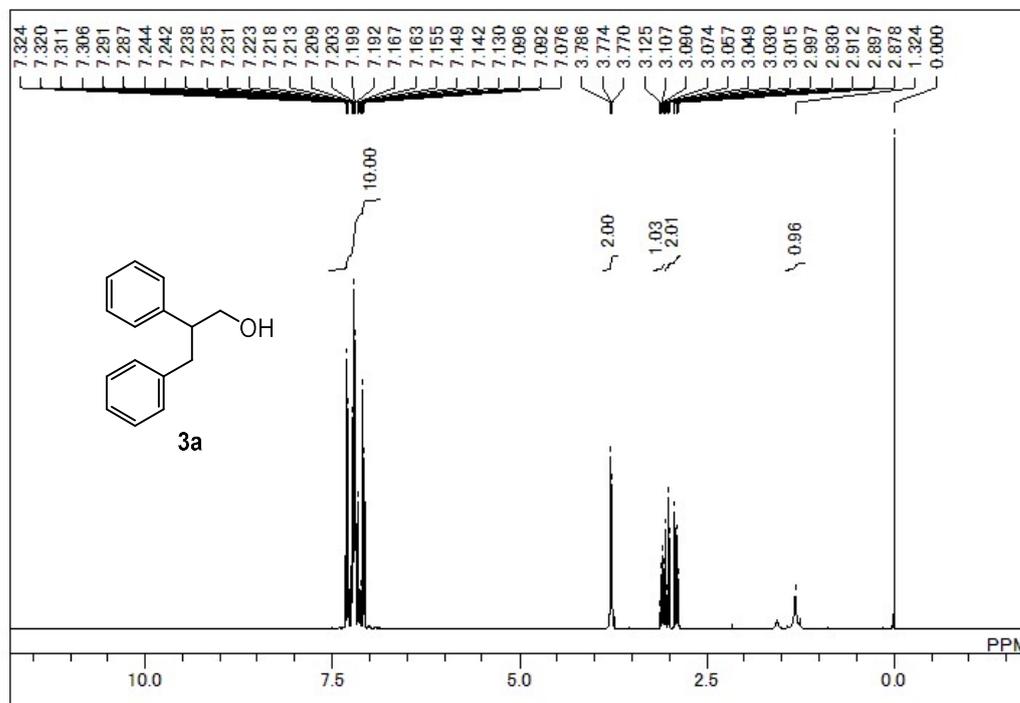
3p²: yield 56% (56.6 mg), orange oil. ¹H NMR (400 MHz; CDCl₃) δ: 7.33-7.20 (m, 6H), 6.22-6.21 (m, 1H), 5.90-5.89 (m, 1H), 3.81-3.73 (m, 2H), 3.20 (quin, *J* = 6.8 Hz, 1H), 3.10 (dd, *J* = 15.1, 7.4 Hz, 1H), 2.93 (dd, *J* = 15.1, 7.4 Hz, 2H), 1.51 (br, 1H); ¹³C NMR (100 MHz; CDCl₃) δ 153.7 (C), 141.6 (C), 141.0 (CH), 128.6 (2CH), 127.9 (2CH), 126.9 (CH), 110.2 (CH), 106.3 (CH₂), 66.4 (CH), 47.2 (CH₂), 30.7 (CH₂); GC-MS (EI) *m/z* (relative intensity) 202(24) [M]⁺, 81(100), 103(76), 121(68).

3q: yield 69% (75.3 mg), brown oil. ^1H NMR (400 MHz; CDCl_3) δ : 7.34-7.22 (m, 5H), 7.07-7.05 (m, 1H), 6.85-6.83 (m, 1H), 6.69-6.68 (m, 1H), 3.84-3.77 (m, 2H), 3.33-3.26 (m, 1H), 3.16-3.08 (m, 2H), 1.46 (br, 1H); ^{13}C NMR (100 MHz; CDCl_3) δ : 142.4 (C), 141.4 (C), 128.7 (CH), 128.1 (CH), 127.0 (CH), 126.6 (CH), 125.4 (CH), 123.5 (CH), 66.4 (CH_2) 50.4 (CH), 32.5 (CH_2); GC-MS (EI) m/z (relative intensity) 218(16) $[\text{M}]^+$, 97(100), 121(39), 103(38); IR (NaCl, cm^{-1}) 3327, 1452, 1242, 1061, 1020, 699; HRMS (EI) m/z calcd for $\text{C}_{25}\text{H}_{44}\text{O}$: 218.0765, found 218.0765.

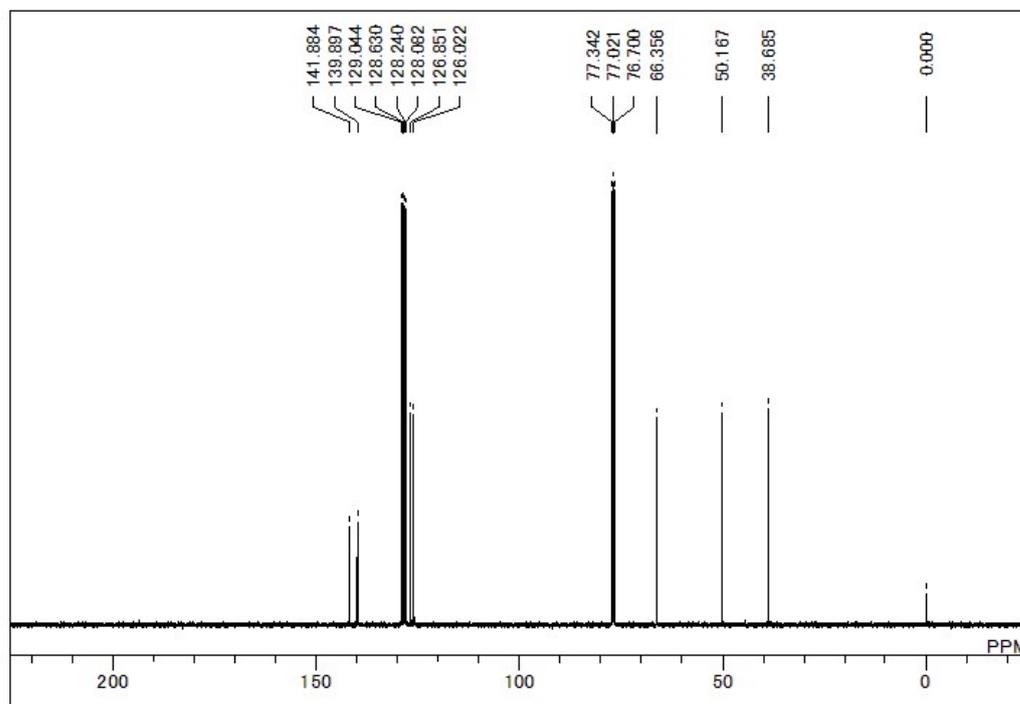
4a⁷: yield 52% (54.1 mg), white solid, m.p. 90.0-91.0 °C (lit. 94-95 °C). ^1H NMR (400 MHz; CDCl_3) δ : 9.77 (s, 1H), 7.44-7.18 (m, 11H); ^{13}C NMR (100 MHz; CDCl_3) δ : 193.9 (CH), 150.2 (CH), 141.8 (C), 134.0 (C), 133.3 (C), 130.7 (CH), 130.2 (CH), 129.3 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH); GC-MS (EI) m/z (relative intensity) 208(100) $[\text{M}]^+$, 178(78), 102(40), 165(22).

¹H and ¹³C NMR Spectra

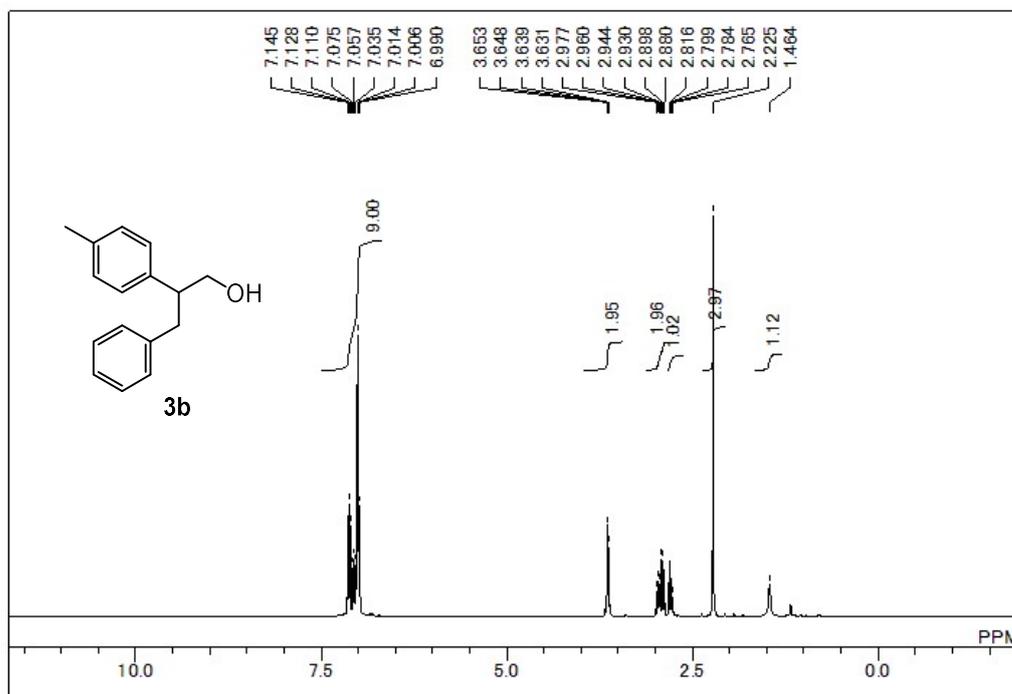
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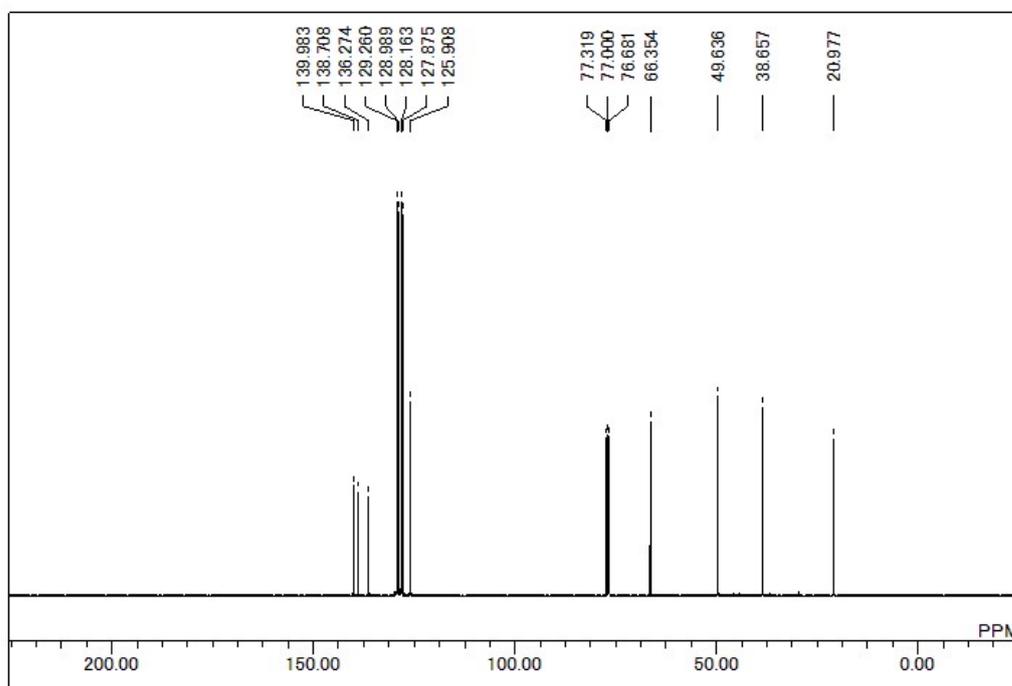
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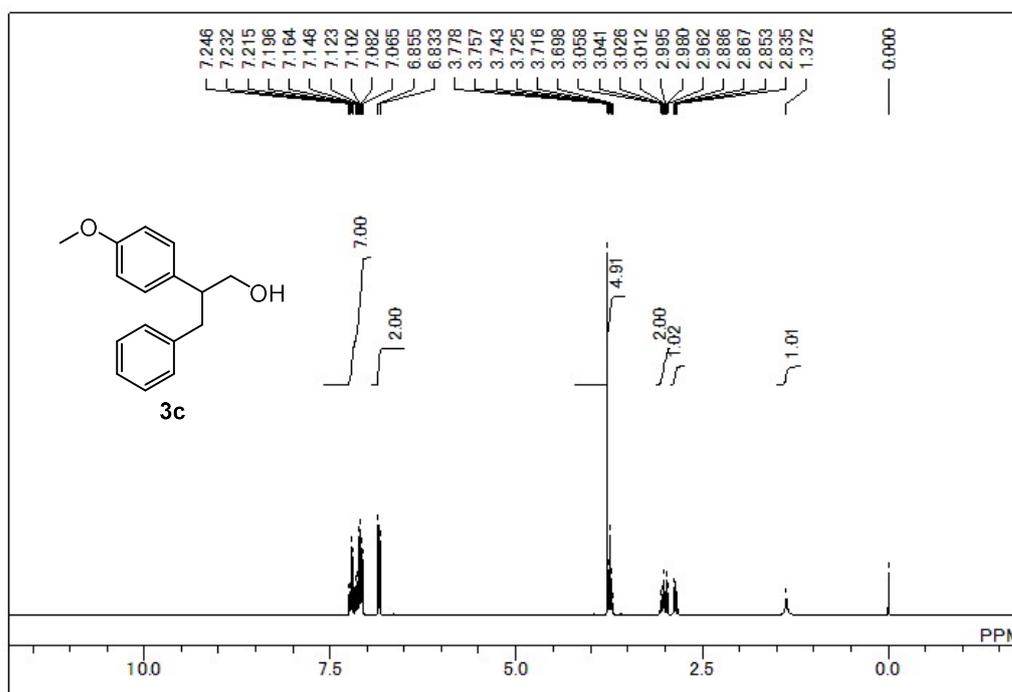
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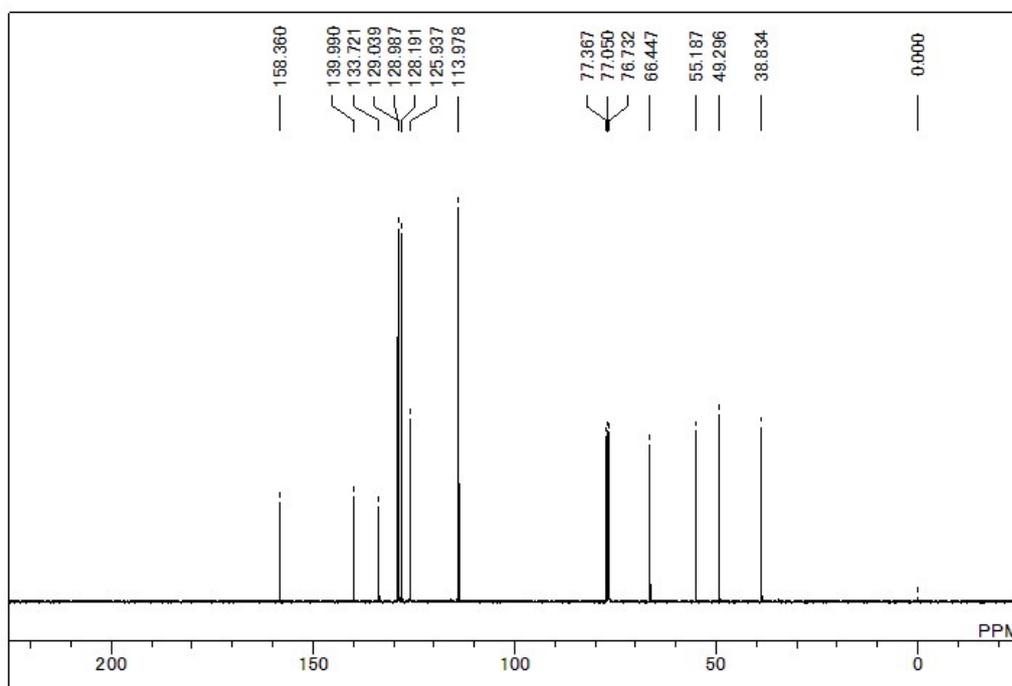
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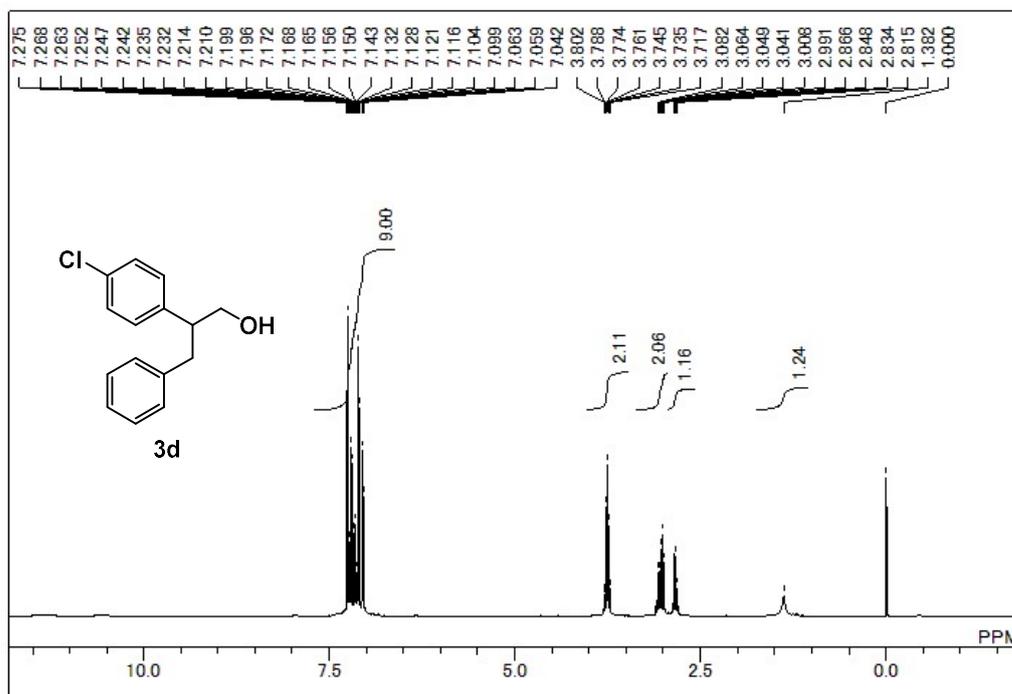
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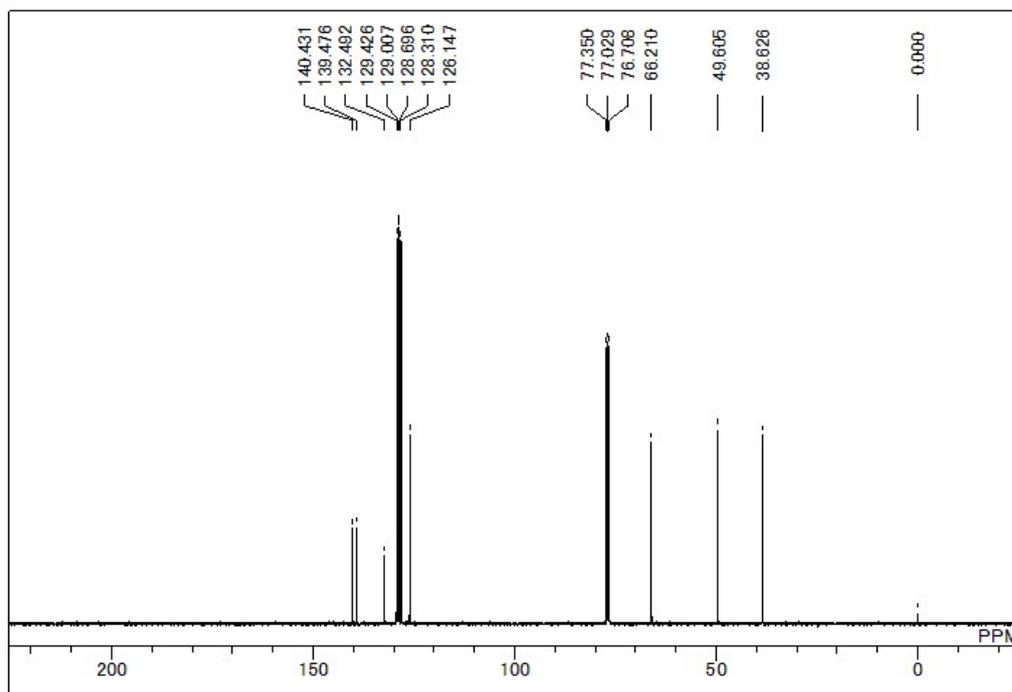
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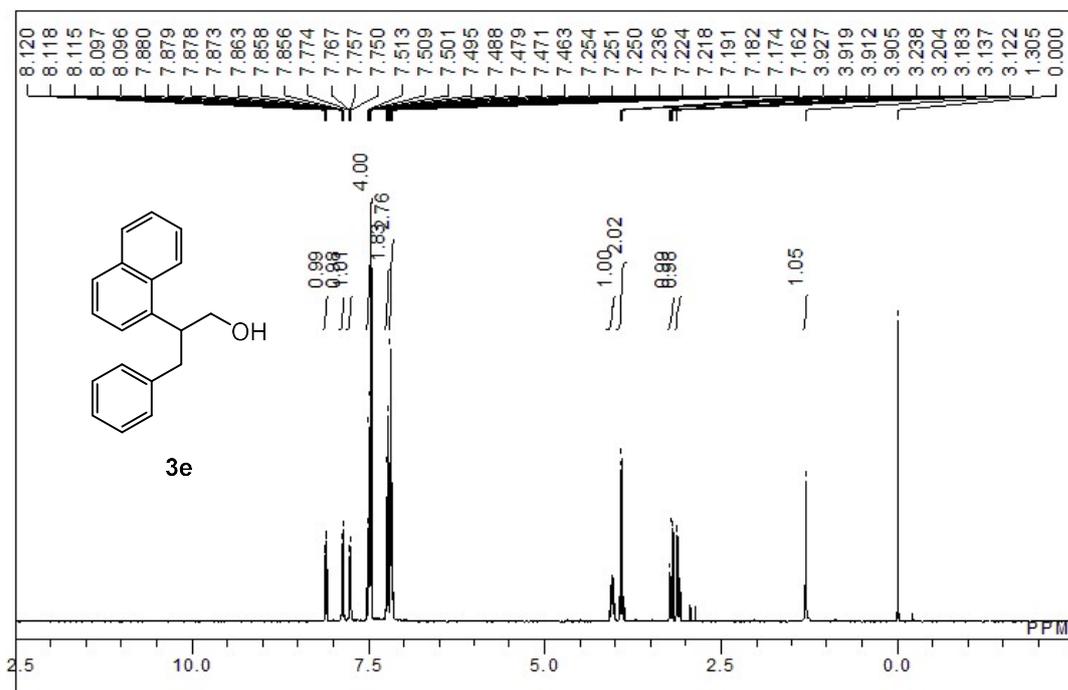
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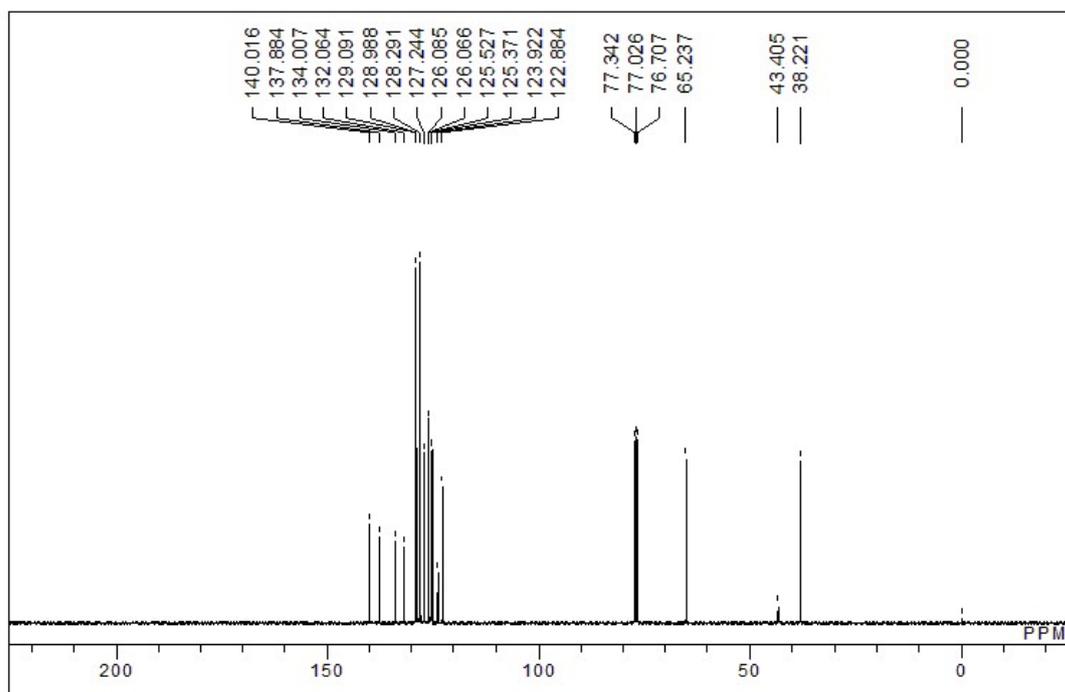
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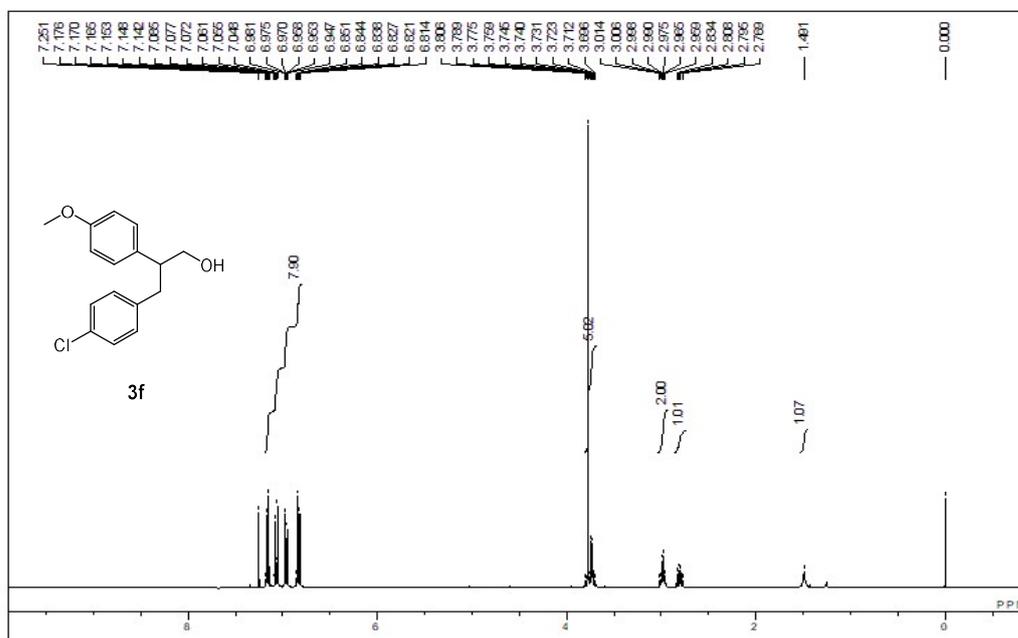
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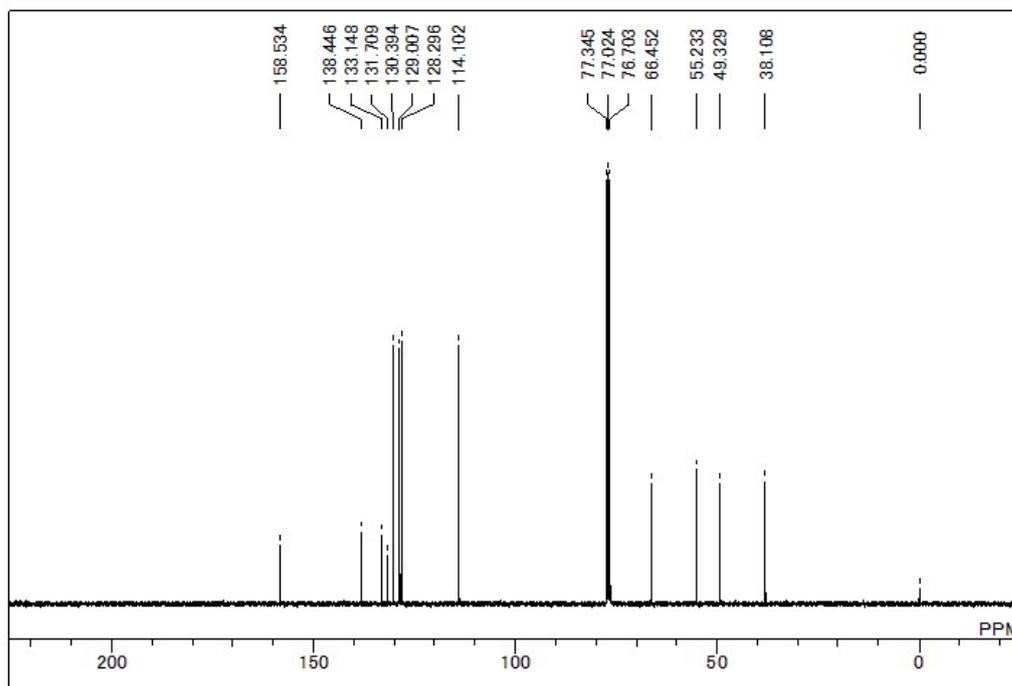
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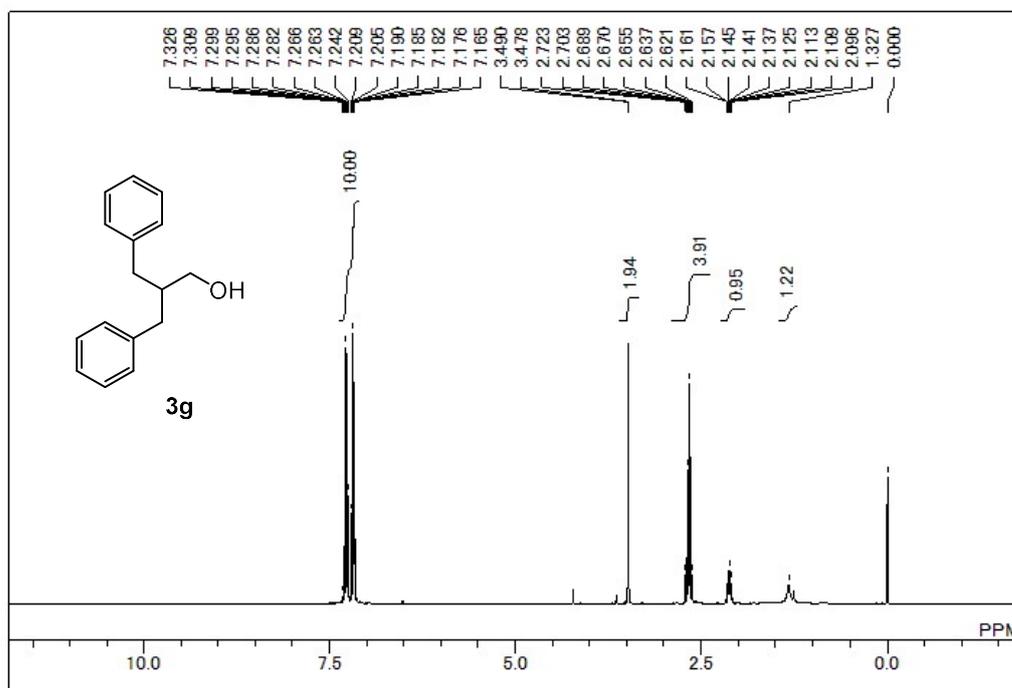
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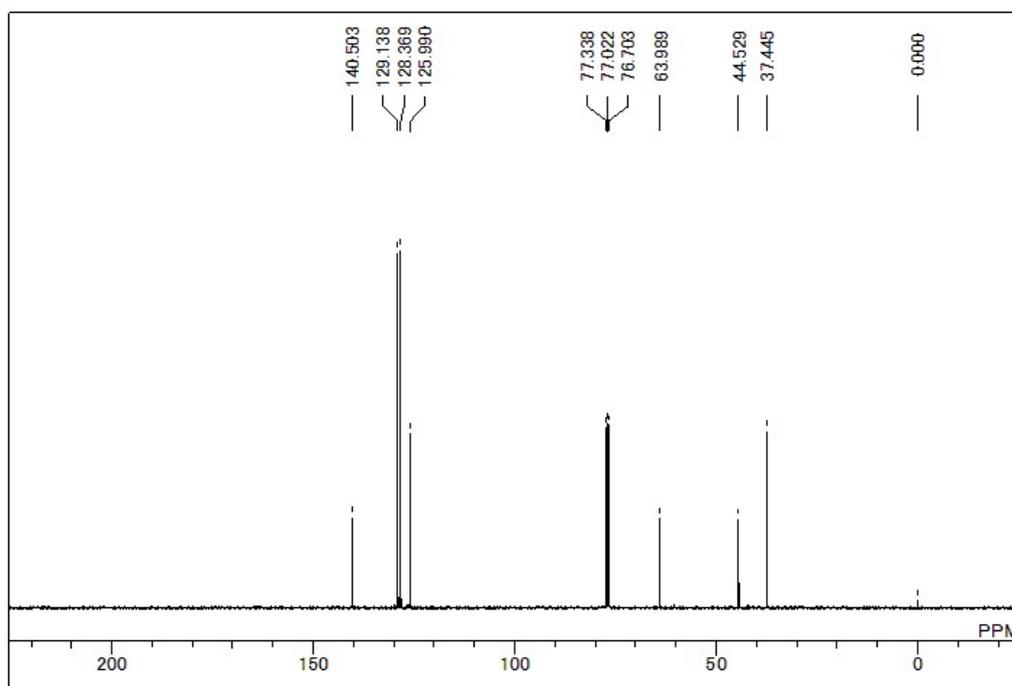
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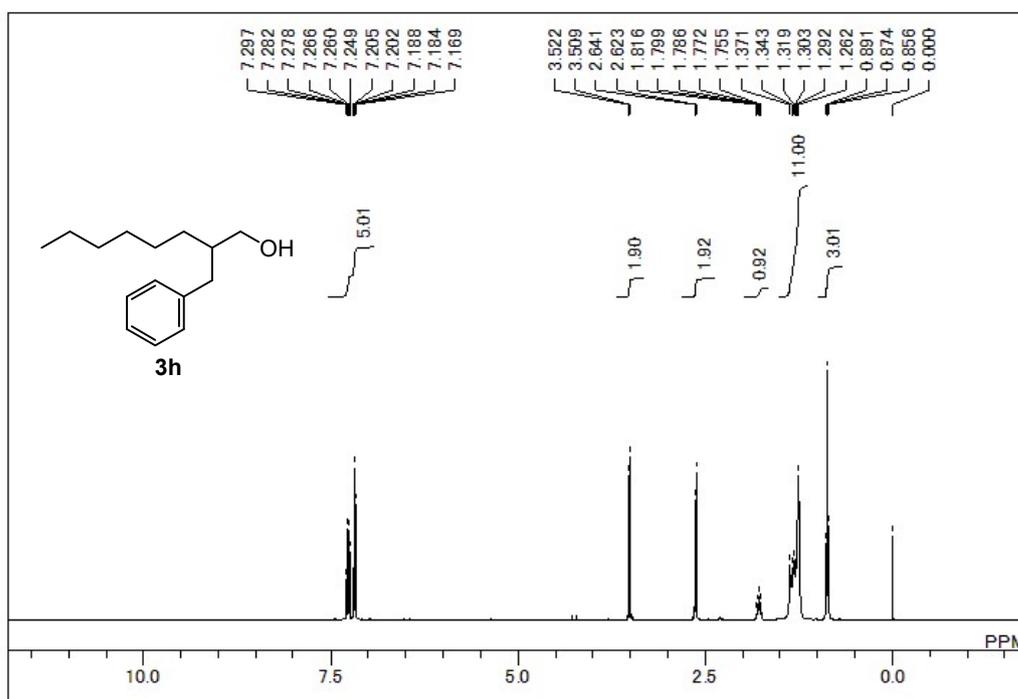
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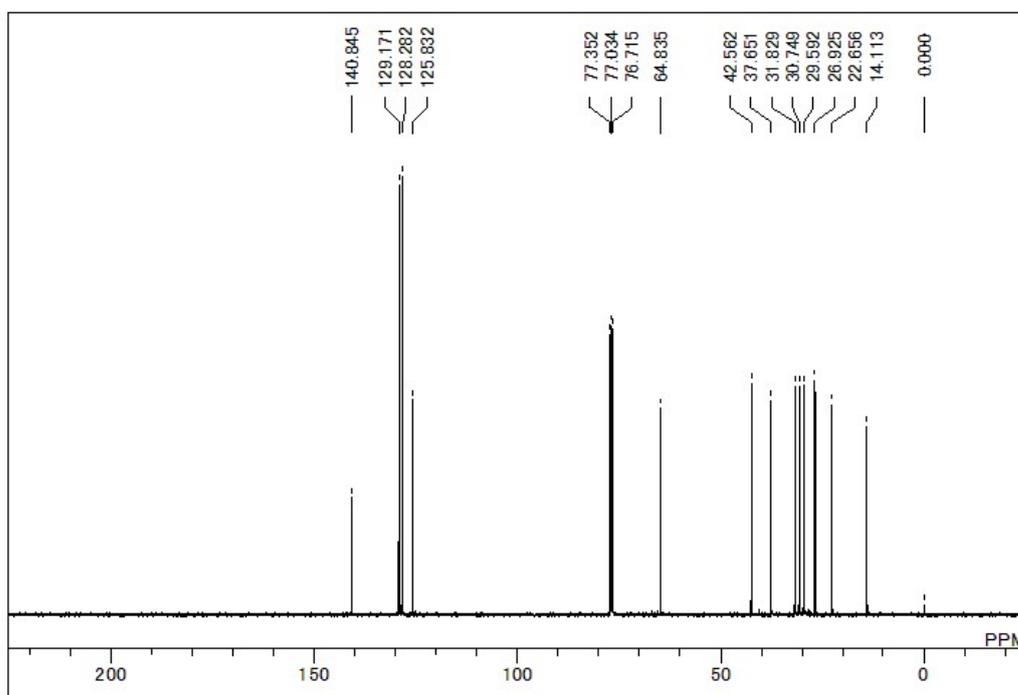
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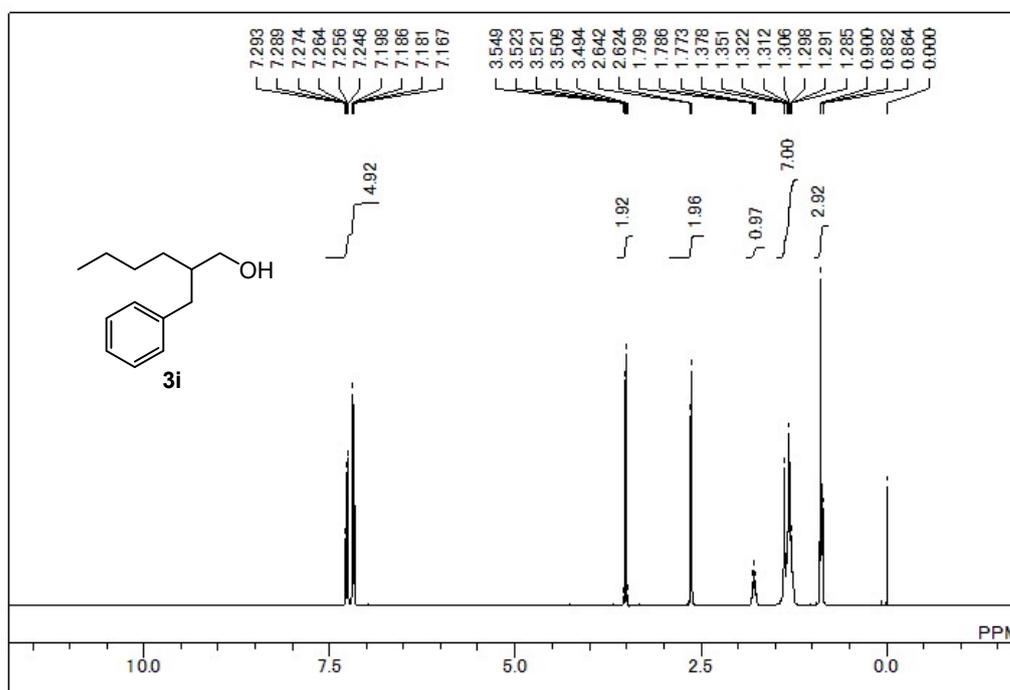
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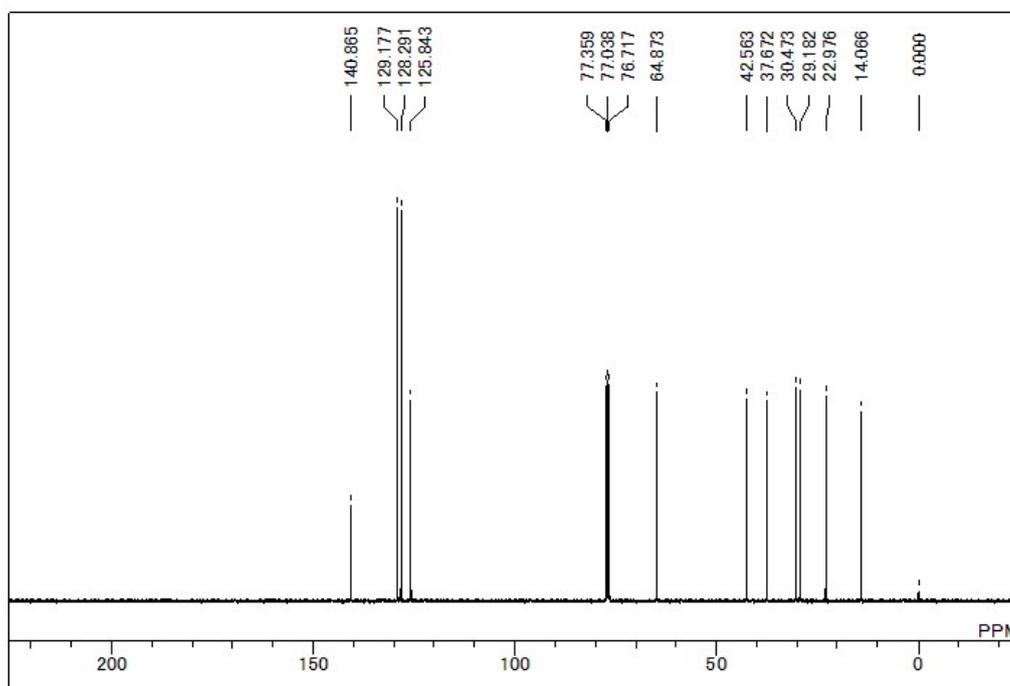
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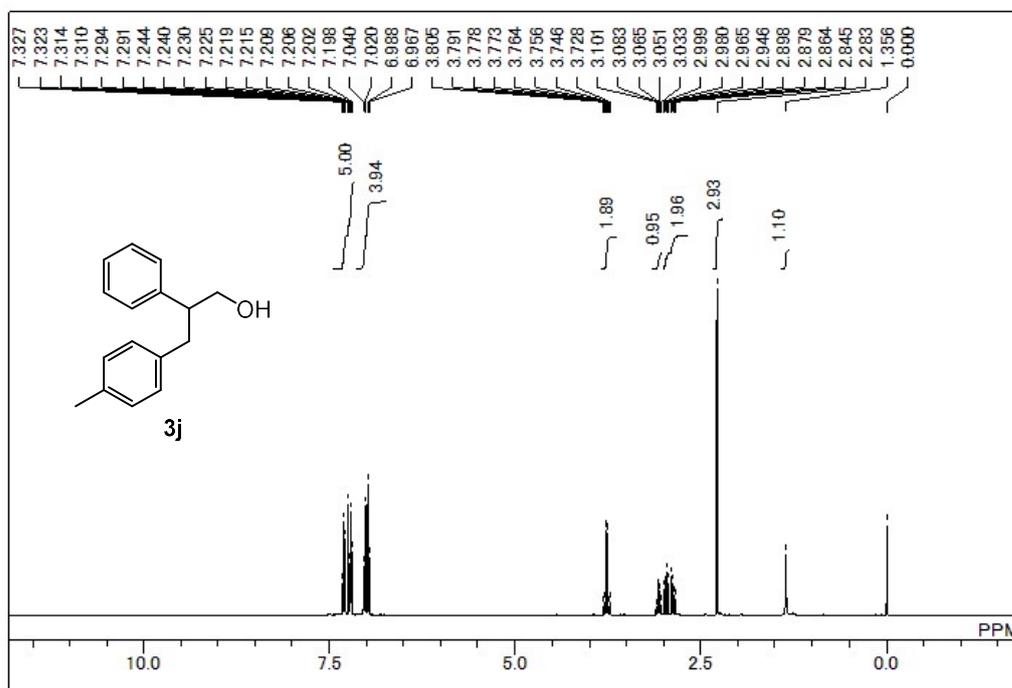
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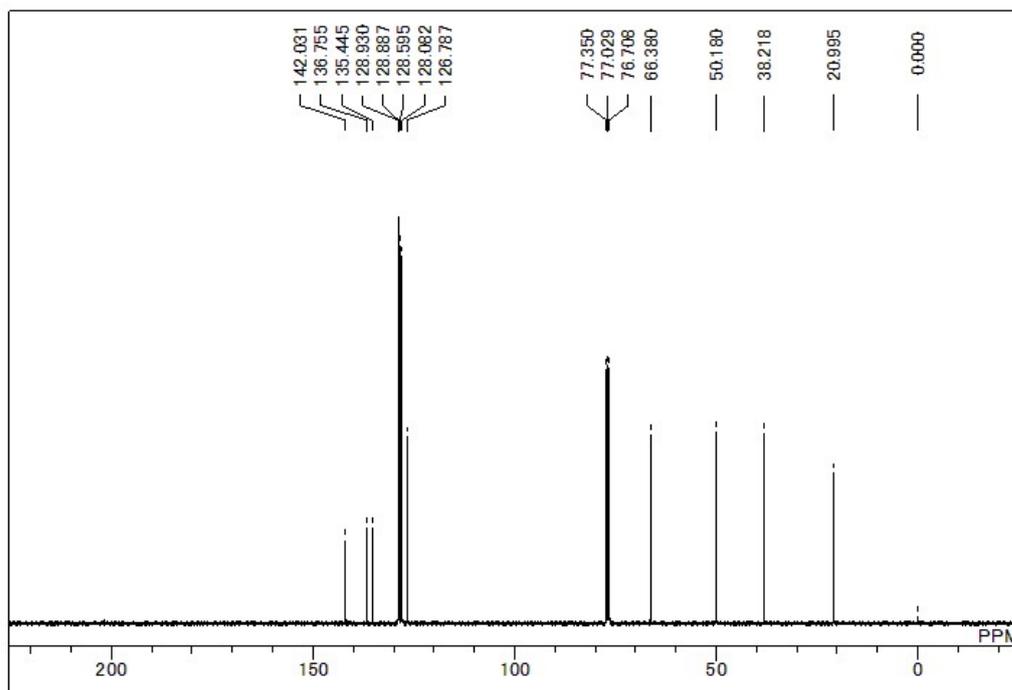
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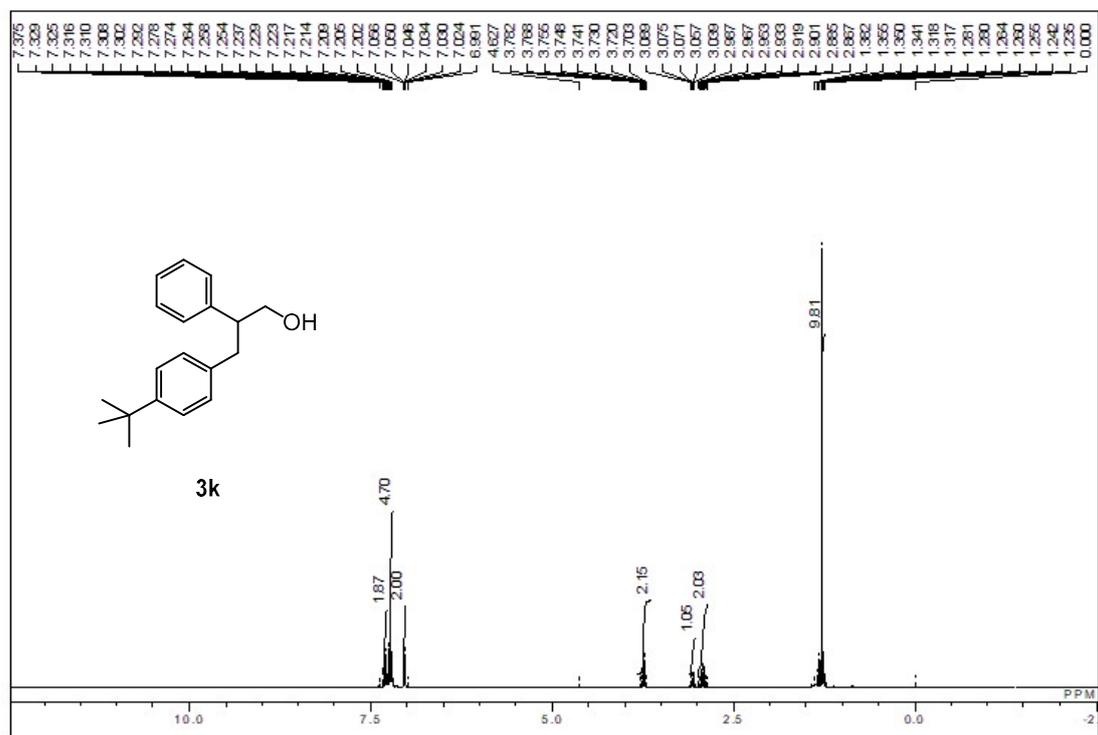
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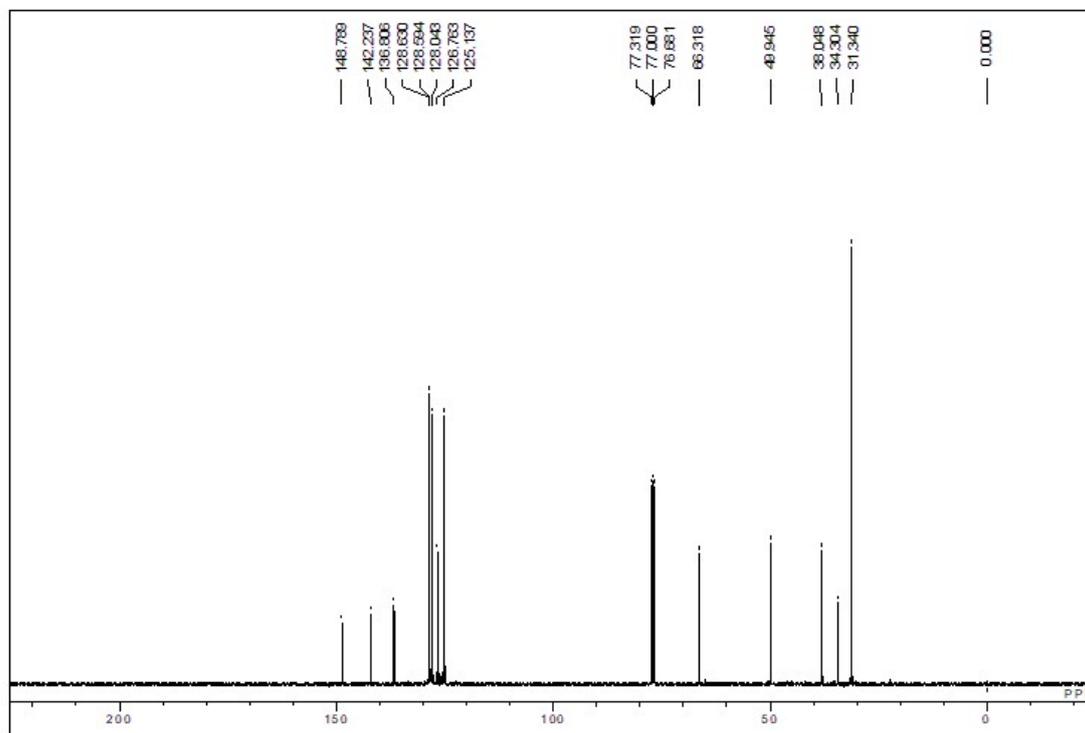
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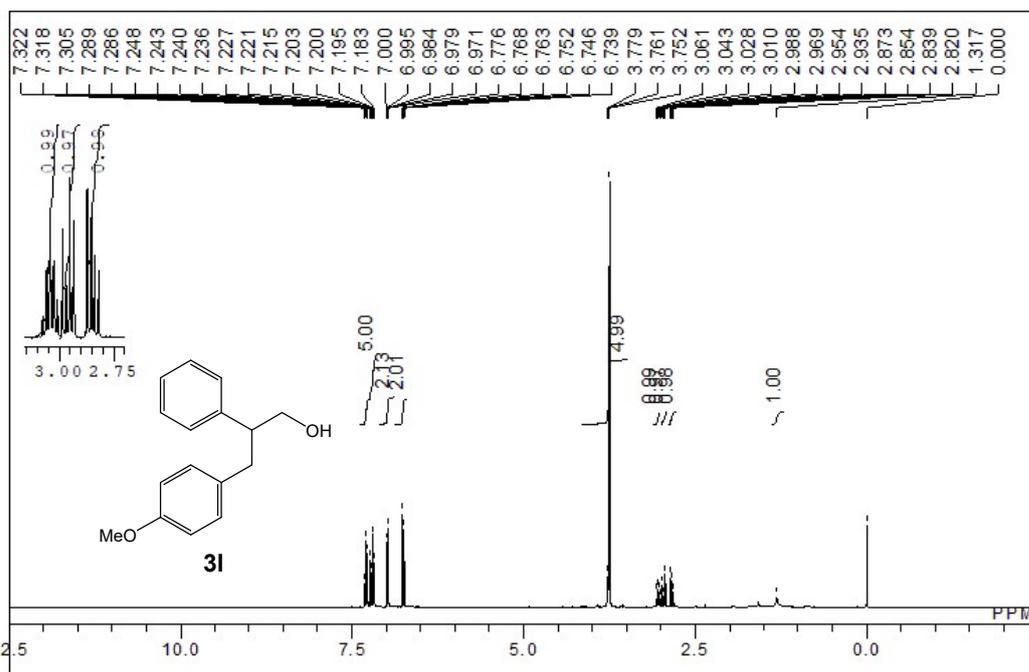
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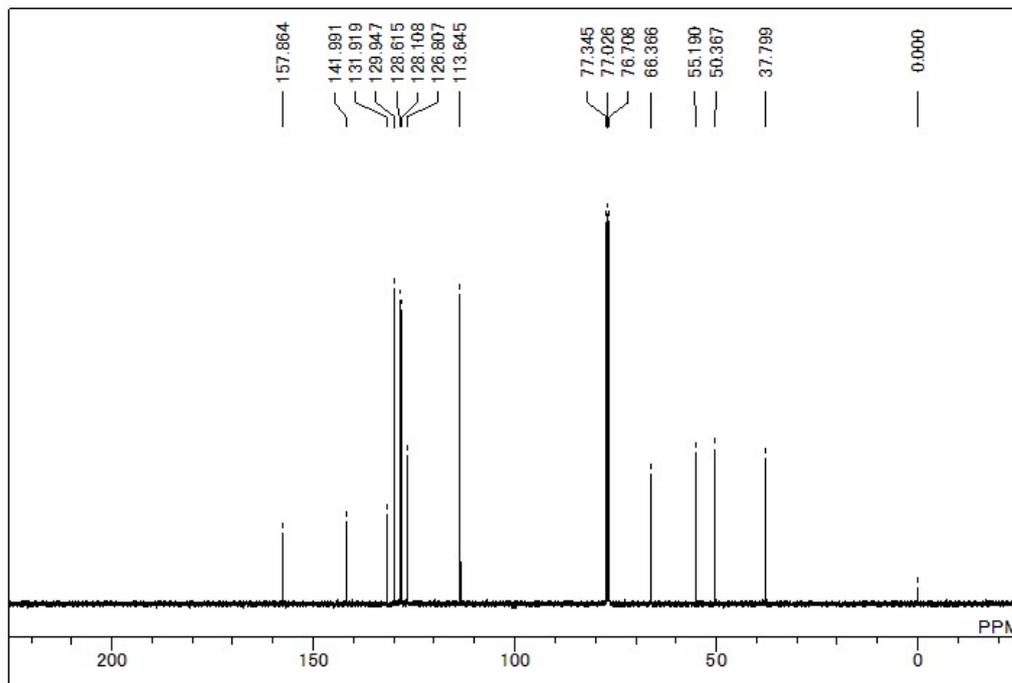
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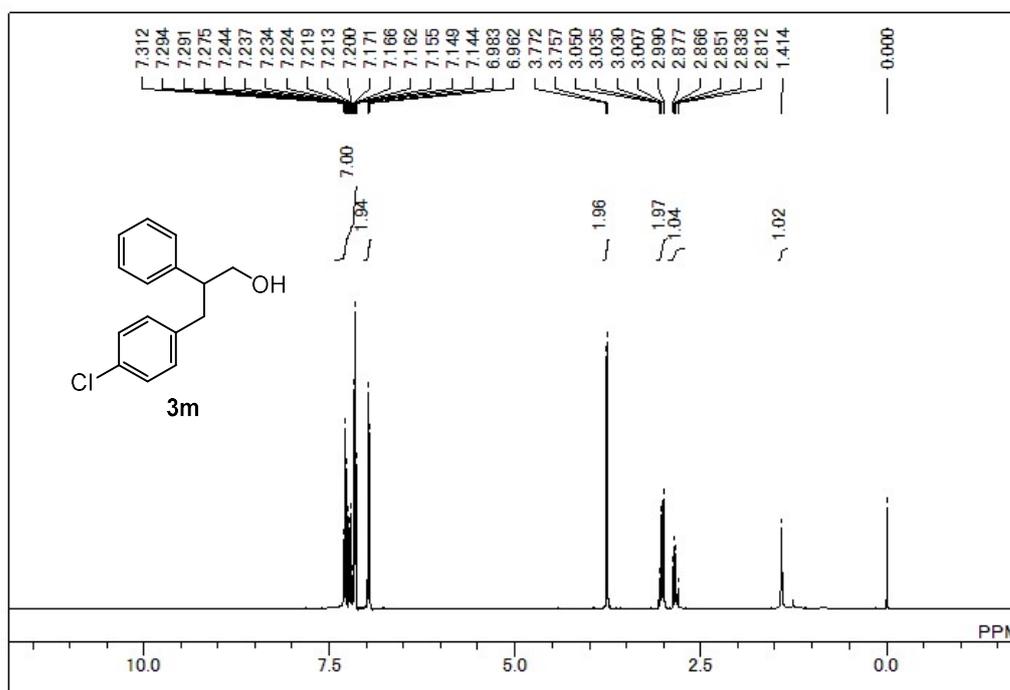
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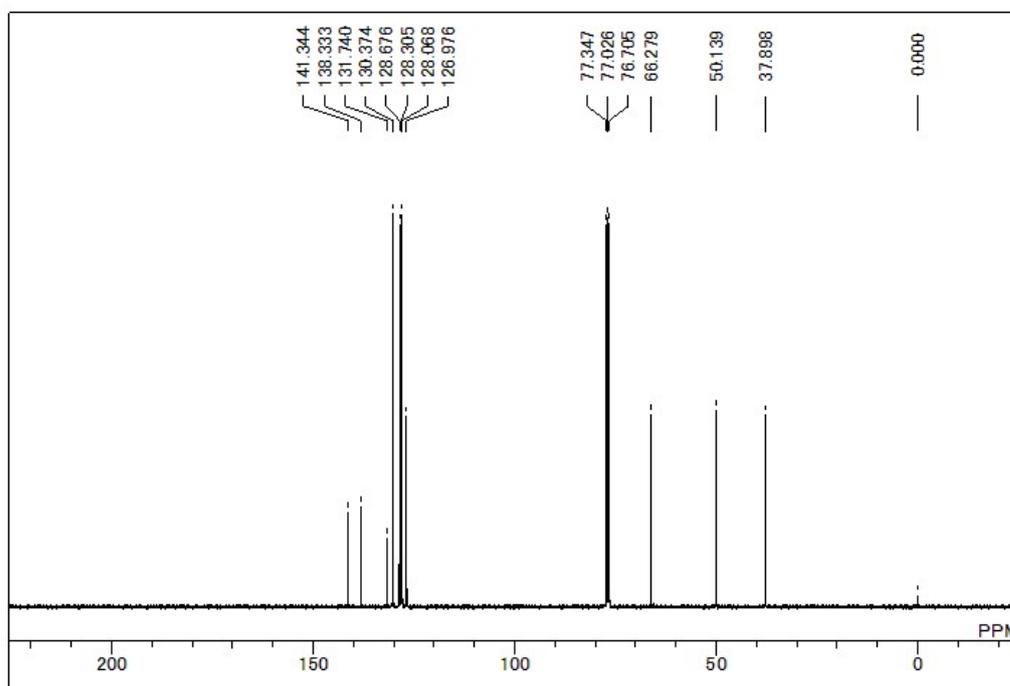
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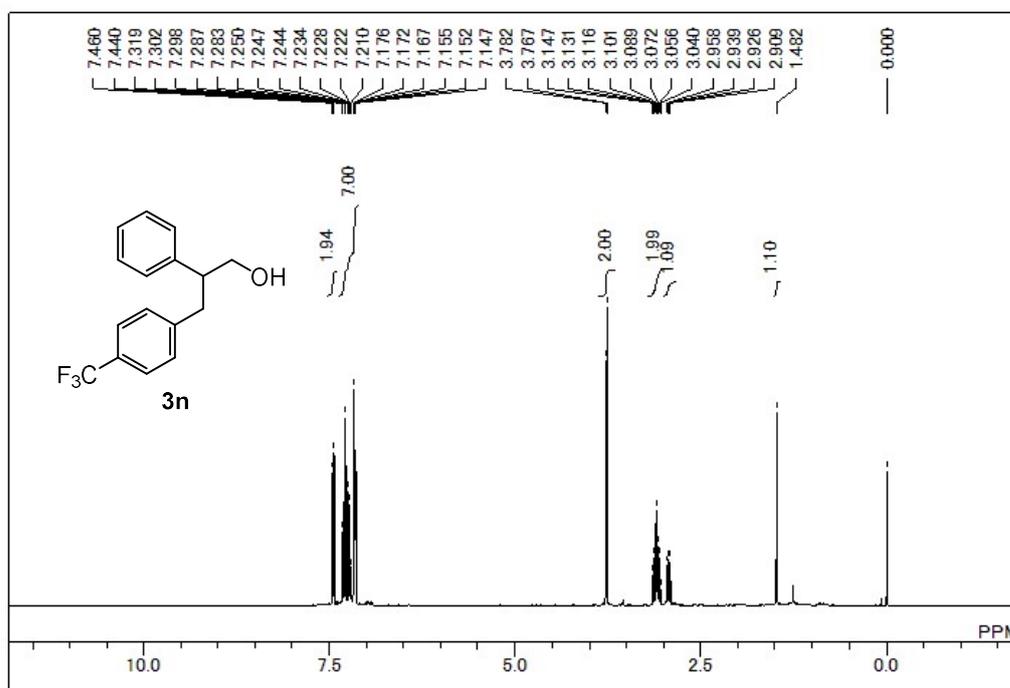
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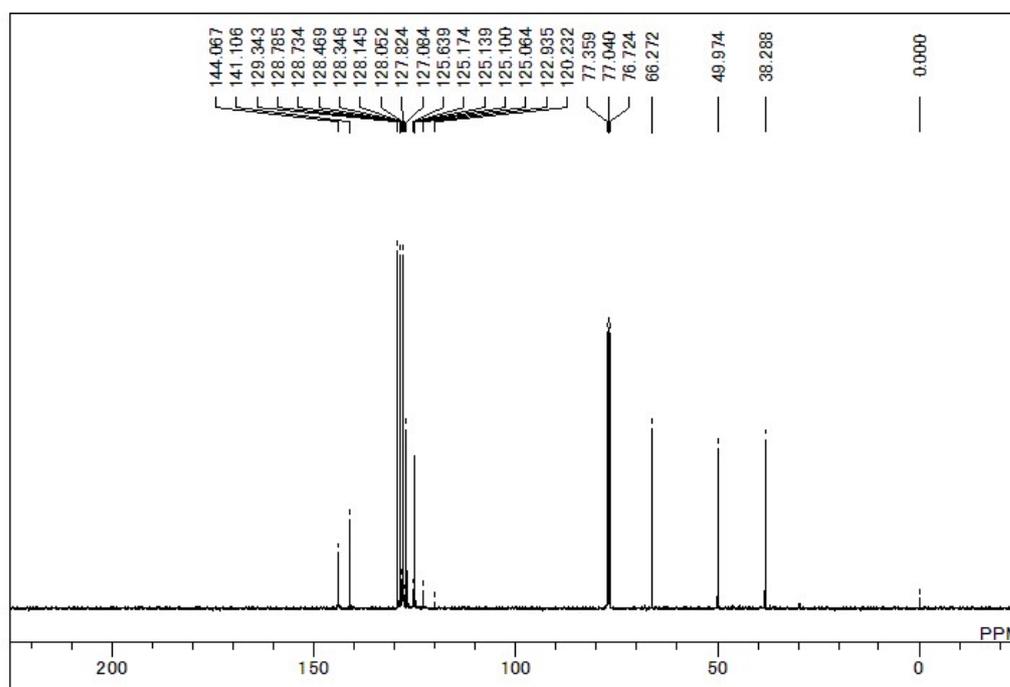
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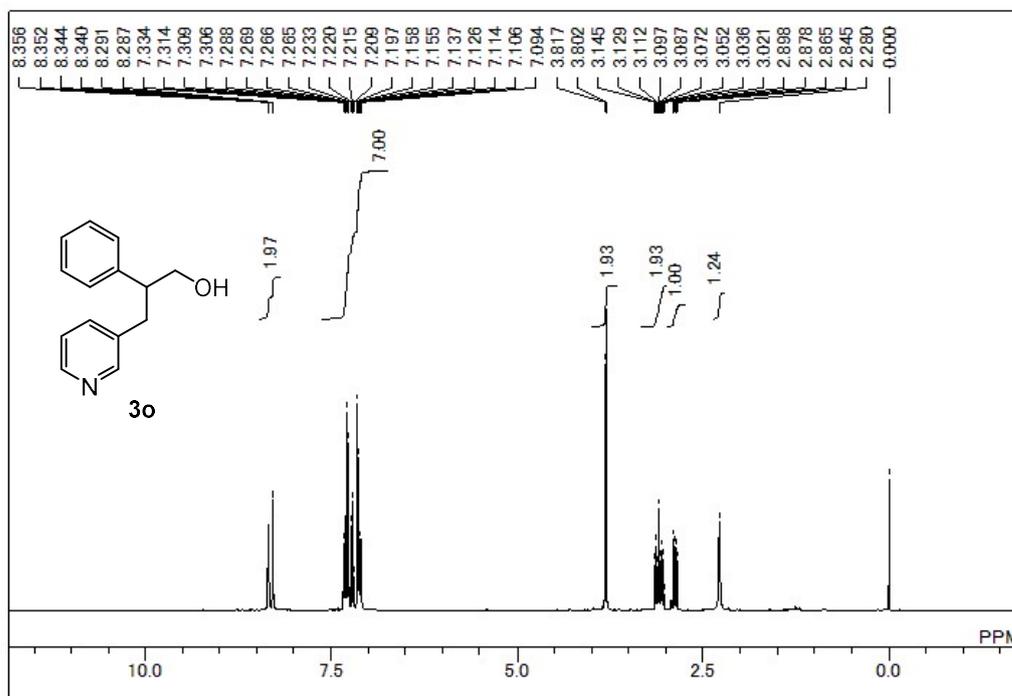
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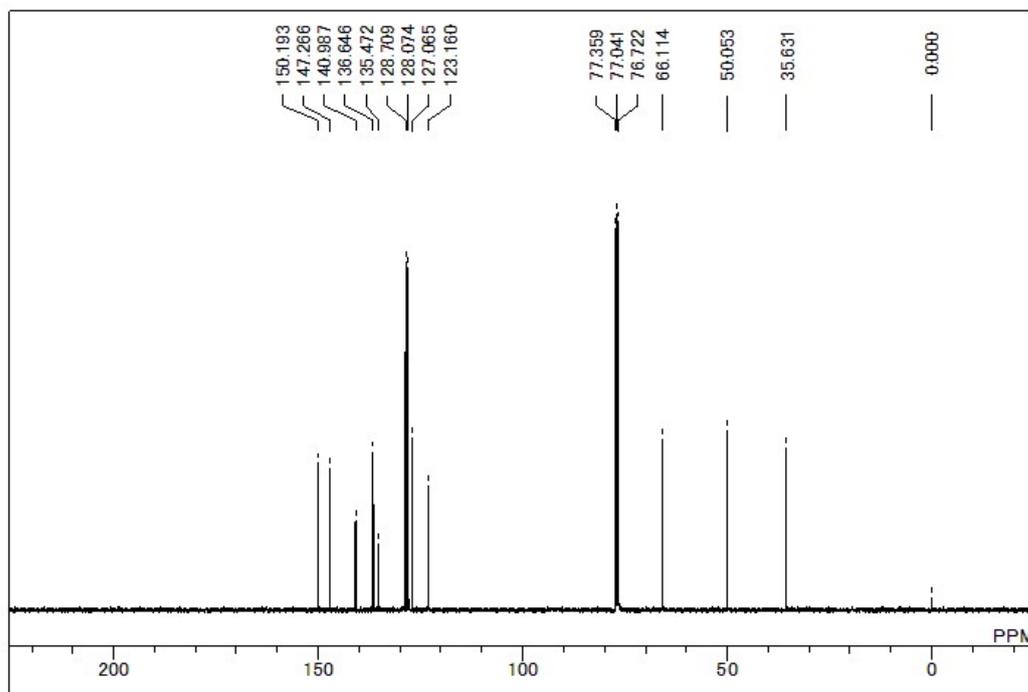
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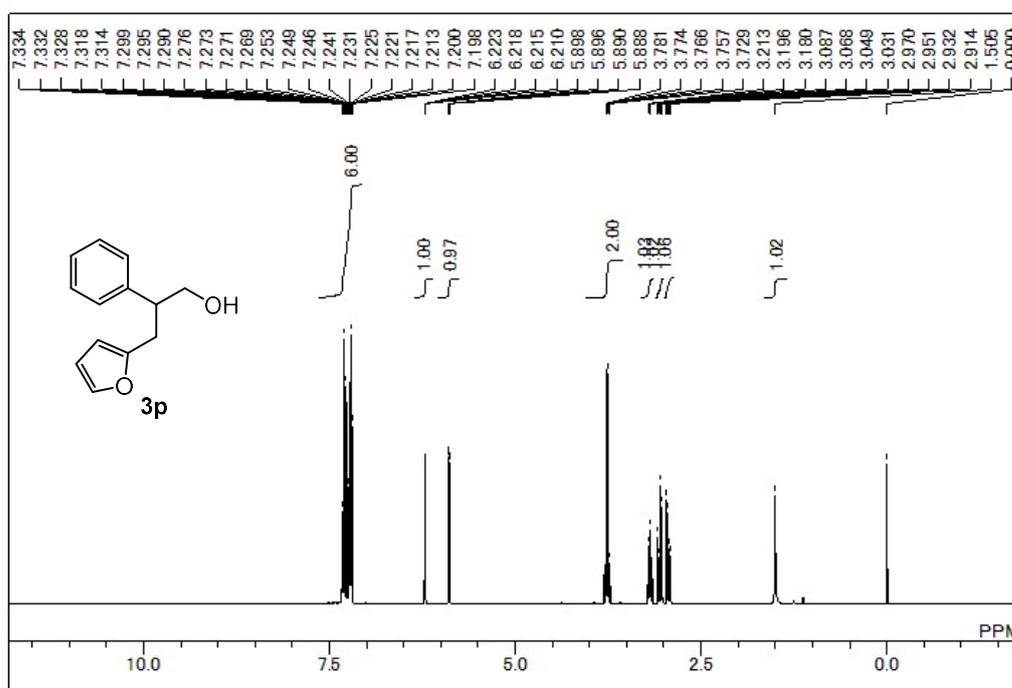
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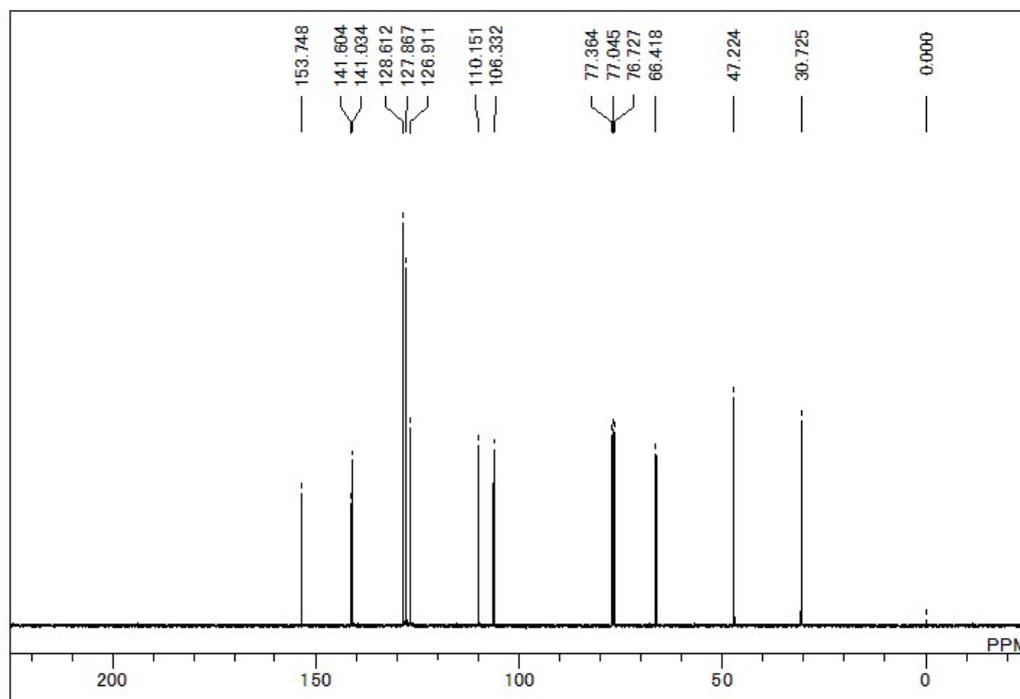
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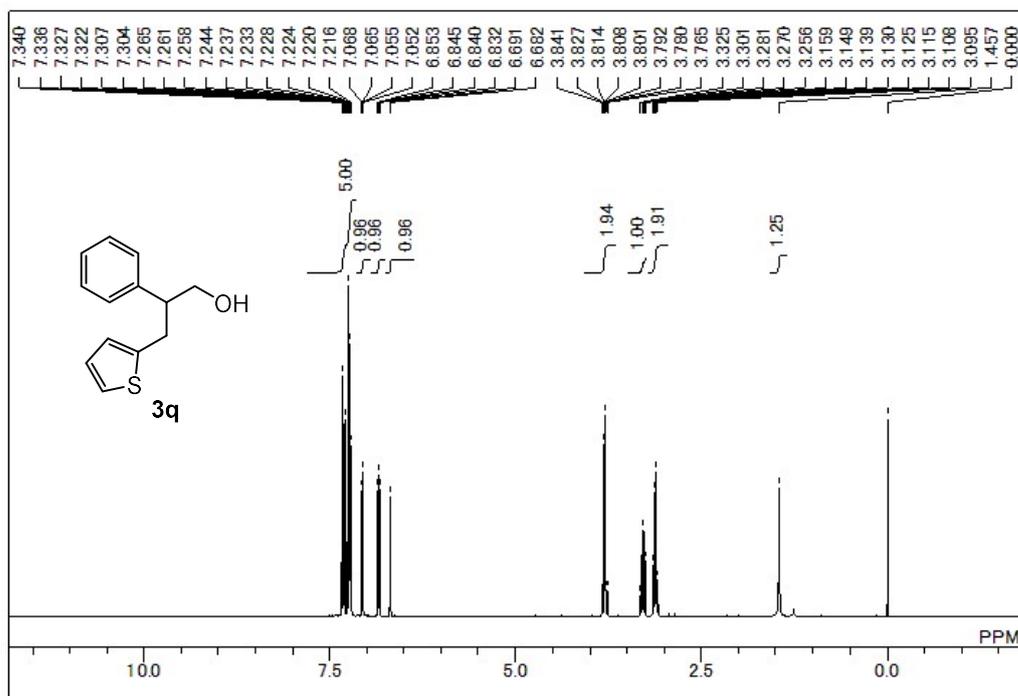
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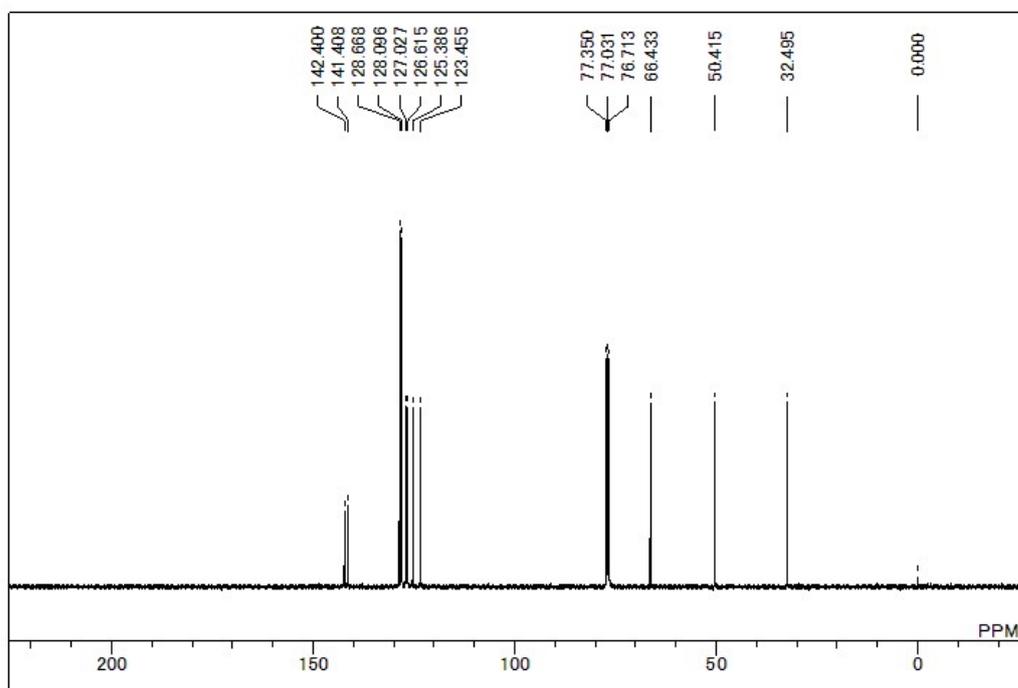
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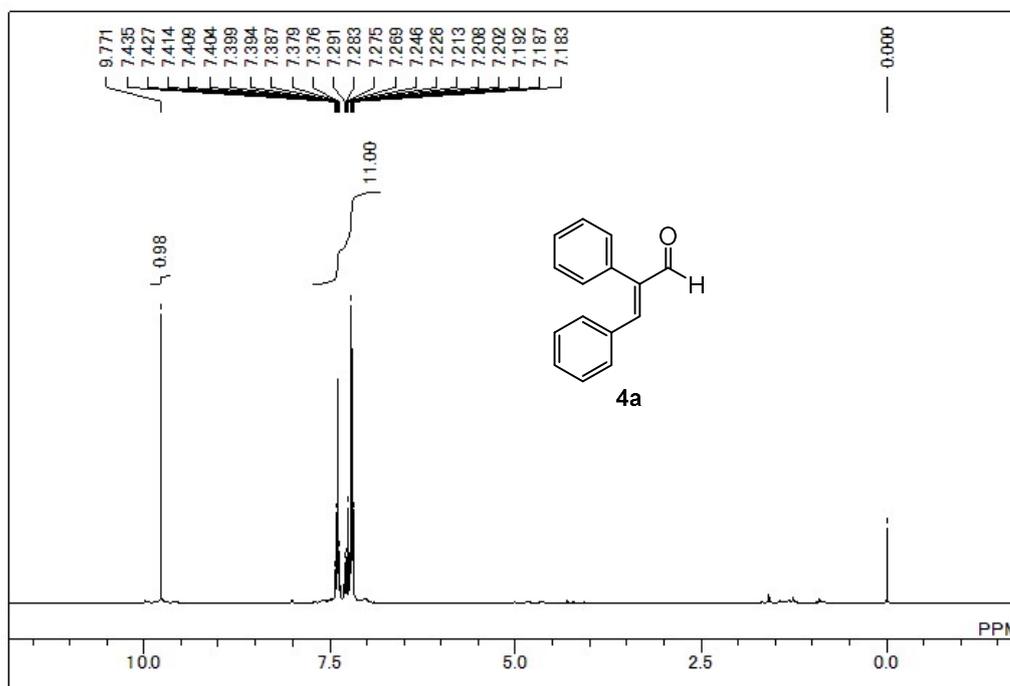
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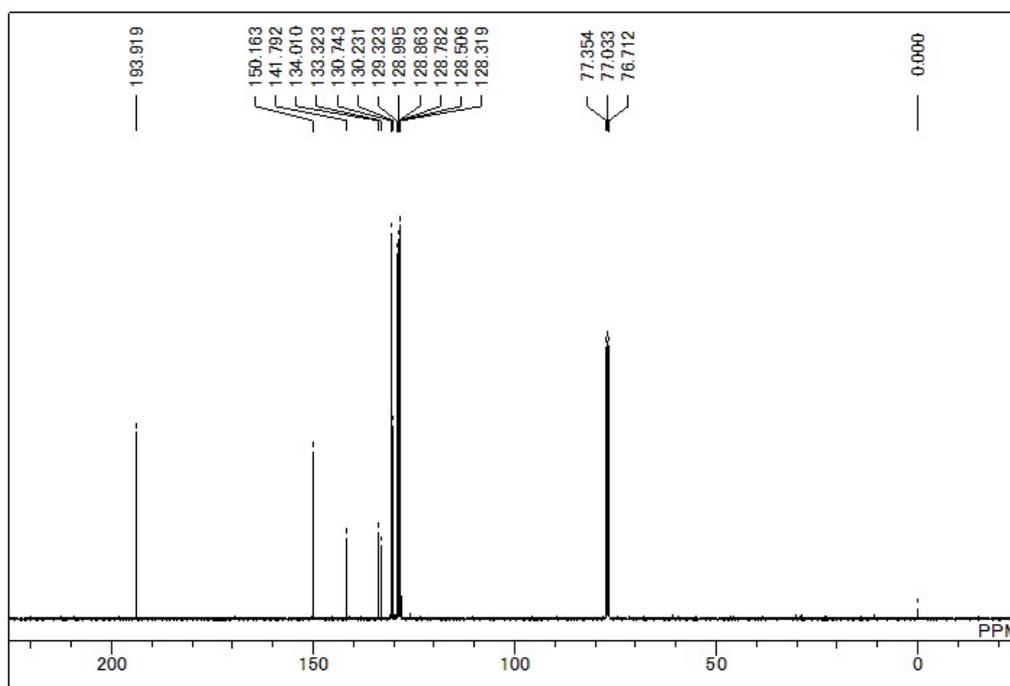
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¹H NMR



¹³C NMR



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