Supporting Information

For

Photoinduced Catalytical Reduction of Carbonyl Compounds by Water as Hydrogen Source

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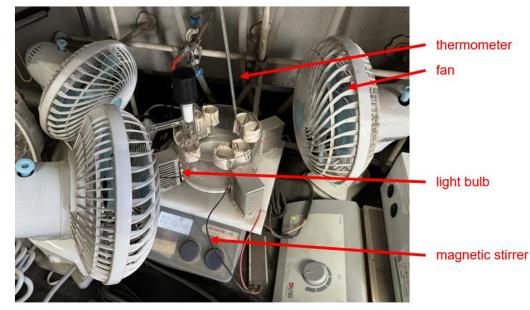
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1. General Information

Unless otherwise noted, all the reactions were carried out in oven-dried sealed tube with Teflon-lined-septum under N₂ atmosphere. Materials were obtained from commercial sources and used as received, or synthesized according to previous literatures. Super dry acetonitrile with molecular sieves was use in the reaction. ¹H NMR, ¹³C NMR, and ¹⁹F NMR spectra were recorded on 400 MHz at ambient temperature with CDCl₃ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of CDCl₃ (7.26), to the carbon resonance of CDCl₃ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, and s referred to multiplet, quartet, triplet, doublet, and singlet. The reaction progress was monitored by GC-MS if applicable. Column chromatography was performed with silica gel (200-300 meshes). Thin layer chromatography (TLC) was visualized using UV light. HRMS(EI⁺) analysis was performed on a Shimadzu GCMS-FT/TOF spectrometer.

The photoreactor used in this research was built by our group, which was made up of 4 blue LED bulbs (30 W for each) with 3 cooler fans to keep room temperature. Spectral distribution: 425 nm. In the reaction, each Schlenk tube is mainly irradiated by one of the light bulbs. The approximate distance of the tube to the closest light bulb is 2 cm. A magnetic stirrer is placed under the photoreactor to keep the reaction being stirred.



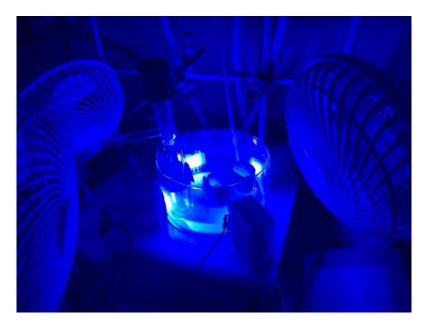
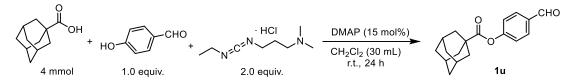


Fig. S1 Photos of the photoreactor

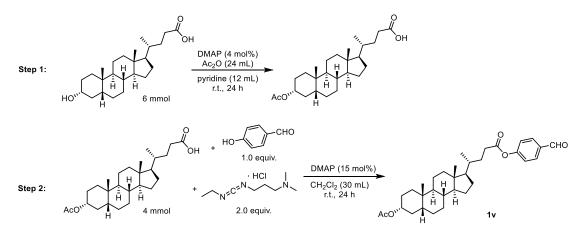
2. General Procedures for Synthesis of Substrates 1:^[1]

General procedures for synthesis of substrates 1u:



To a stirred of solution of adamantane acid (4.00 mmol, 1.00 equiv.) and EDC·HCl (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride) (6.00 mmol, 2.00 equiv.) in CH₂Cl₂ (30 mL) were added DMAP (4-dimethylaminepyridine) (0.60 mmol, 0.15 equiv) and 4-hydroxybenzaldehyde (4.00 mmol, 1.00 equiv). The reaction mixture was stirred at 23 °C for 24 h, then concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give products **1u**, which were identified by ¹H and ¹³C NMR.

General procedures for synthesis of substrates 1v:

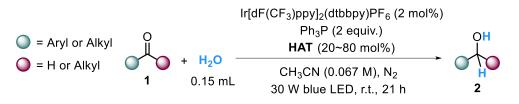


Step 1: To a solution of lithocholic acid (6.00 mmol) in pyridine (12 mL) was added acetic anhydride (24 mL) and DMAP (4-dimethylaminepyridine) (0.16 mmol). The reaction mixture was stirred at 23 °C for 24 h. The reaction was quenched with saturated CuSO₄ solution (120 mL) and extracted with ethyl acetate (180 mL). The organics was washed with H₂O (120 mL) and brine (120 mL), dried over Na₂SO₄, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel.

Step 2: To a stirred of solution of acetate protected lithocholic acid (4.00 mmol, 1.00 equiv.) and EDC·HCl (6.00 mmol, 2.00 equiv.) in CH₂Cl₂ (30 mL) were added

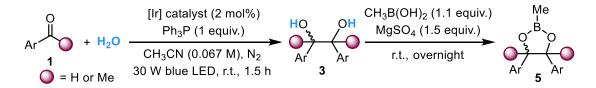
DMAP (4-dimethylaminepyridine) (0.60 mmol, 0.15 equiv.) and 4hydroxybenzaldehyde (4.00 mmol, 1.00 equiv.). The reaction mixture was stirred at 23 °C for 24 h, then concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give product **1v**, which was identified by ¹H and ¹³C NMR.

3. General Procedures for Synthesis of Products 2 - 4:



General procedures for synthesis of products 2 and 4 (alcohols from unimolecular reduction and amines): A sealed tube equipped with a stirrer bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6(4.4 mg, 2.0 mol\%)$, PPh₃ (104.9 mg, 2.0 equiv.), substrate 1 (0.2 mmol, for solid substrates), then degassed and refilled with N₂ for 3 times. After that, anhydrous CH₃CN (3 mL), 4-*tert*-butylthiophenol (6.7 – 26.6 mg, 20 – 80 mol%), H₂O (0.15 mL), and substrate 1 (0.2 mmol, for liquid substrates) were added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give products 2 and 4, which were identified by ¹H, ¹³C, and ¹⁹F NMR.

General procedures for the gram-scale synthesis of products 2*a*: A sealed tube equipped with a stirrer bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6(0.176 g, 2.0 mol%)$, PPh₃ (4.196 g, 2.0 equiv.), then degassed and refilled with N₂ for 3 times. After that, anhydrous CH₃CN (120 mL), 4-*tert*-butylthiophenol (1.064 g, 80 mol%), H₂O (6.0 mL), and substrate 1a (8 mmol, 0.960 g) were added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give products 2a (0.899 g, 92%), which was identified by ¹H and ¹³C NMR.



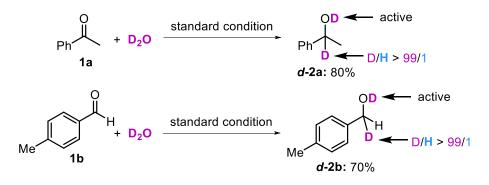
General procedures for synthesis of products 3 (pinacols): A sealed tube equipped with a stirrer bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.4 mg, 2.0 mol%), PPh₃ (52.5 mg, 1.0 equiv.), substrate 1 (0.2 mmol, for solid substrates), then degassed

and refilled with N₂ for 3 times. After that, anhydrous CH₃CN (3 mL), H₂O (0.15 mL), and substrate **1** (0.2 mmol, for liquid substrates) were added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 1.5 hours, after which the reaction was concentrated *in vacuo*. The residue was purified by chromatography on silica gel to give product **3**, which was identified by ¹H and ¹³C NMR.

General procedures for synthesis of products **5** (borate esters): A sealed tube equipped with a stirrer bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6(4.4 mg, 2.0 mol%)$, PPh₃ (52.5 mg, 1.0 equiv.), substrate **1** (0.2 mmol, for solid substrates), then degassed and refilled with N₂ for 3 times. After that, anhydrous CH₃CN (3 mL), H₂O (0.15 mL), and substrate **1** (0.2 mmol, for liquid substrates) were added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 1.5 hours, after which CH₃B(OH)₂ (13.2 mg, 1.1 equiv.), MgSO₄ (36.1 mg, 1.5 equiv.) were added, then stirred overnight. The residue was concentrated in vacuo and purified by chromatography on silica gel to give products **5**, which were identified by ¹H and ¹³C NMR.

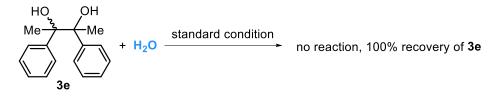
4. General Procedures for Mechanism Studies

4.1 Deuterium-labelled experiments

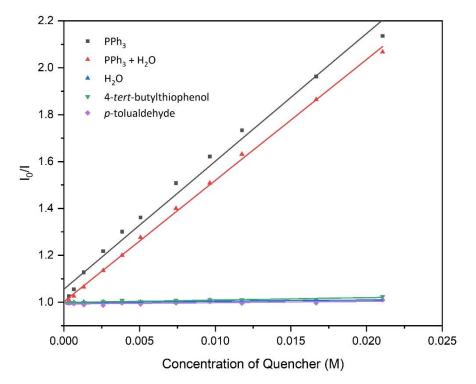


А sealed tube equipped with stirrer bar а was charged with Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.4 mg, 2.0 mol%), PPh₃ (104.9 mg, 2.0 equiv.), then degassed and refilled with N₂ for 3 times. After that, anhydrous CH₃CN (3 mL), 4-tertbutylthiophenol (6.7 - 26.6 mg, 20 - 80 mol%), H₂O (0.15 mL), and substrate **1a** or **1b** (0.2 mmol) were added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated in *vacuo*. The residue was tested by ¹H NMR to determine the deuterium ratio.

4.2 Intermediate study



sealed equipped with А tube а stirrer charged with bar was Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (4.4 mg, 2.0 mol%), PPh₃ (104.9 mg, 2.0 equiv.), pinacol **3e** (0.2 mmol), then degassed and refilled with N_2 for 3 times. After that, anhydrous CH₃CN (3 mL), 4-tert-butylthiophenol (26.6 mg, 80 mol%), H₂O (0.15 mL) were added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated in vacuo. The residue was tested by ¹H NMR to determine the result.



5. Stern-Volmer Fluorescence Quenching Experiments

Fig. S2 Fluorescence quenching experiment between photocatalyst and substrate

Fluorescence quenching experiments were measured on an Ahilent Technologies Cary Eclipse Fluorescence Spectrophotometer. The complex $Ir[dF(CF_3)ppy]_2(dtbbpy)$ was excited at 375 nm and the emission spectrum max = 475 nm was recorded. Gradient dilution to get 1.0 x 10⁻⁵ M $Ir[dF(CF_3)ppy]_2(dtbbpy)$ solution in CH₃CN, 0.1 M *p*-tolualdehyde (**2b**) solution in CH₃CN, 0.1 M 4-*tert*-butylthiophenyl (**1a**) solution in CH₃CN, 0.1 M PPh₃ (**3a**) solution in CH₃CN, 0.1 M H₂O (**3a**) solution in CH₃CN, and 0.1 M PPh₃ + 0.1 M H₂O solution in CH₃CN. 3.0 mL 1.0 x 10⁻⁵ M $Ir[dF(CF_3)ppy]_2(dtbbpy)$ solution in CH₃CN and a stirrer bar were added into the 4.0 mL quartz cuvette covered with Teflon cap. 10 µL of the above solutions were added each time, separately. Then, the emission spectrum of the solution was collected at each addition.

Quenching effects of various quenchers under different concentration were shown in Fig S1. Linear fit based on the Stern-Volmer equation was performed to calculate the Stern-Volmer constant (listed in Table S1).

 $\frac{I_0}{I} = 1 + K_{sv} \cdot [Q], \quad Q$ represents quencher

Table S1 Stern-Volmer constant of varie	ous quenchers
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Quencher	Ph ₃ P	$Ph_3P + H_2O$	H_2O	4-tert-butylthiophenol	<i>p</i> -tolualdehyde
K_{sv} (M ⁻¹)	54.6	51.7	0.583	1.05	0.563

	Ir[dF(CF ₃)ppy] ₂ (dtbbpy)PF ₆ (2 mol%) Ph ₃ P (2 equiv.) HAT1 (80 mol%)		OH	^t Bu—	
Ph + H ₂ O — 1a: 0.2 mmol 0.15 mL	CH ₃ CN (0.067 M), N ₂ 30 W blue LED, r.t., 21 h		► Ph (\ H 2a: 97%	HAT1	
Agents	Agents		HAT1	POPh ₃	
Additive Amount		2.00 equiv.	0.80 equiv.	-	
Theoretically Remaining Amount		1.03 equiv.	0.80 equiv.	0.97 equiv.	
Experimentally Recovered Amount		0.60 equiv.	0.56 equiv.	1.35 equiv.	
Recovery Yield		58%	70%	140%	
Pacona	ru rata -	Theoratica	l Remaing		

6. Experiments for The Recovery of PPh₃, POPh₃, and Thiophenol

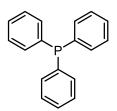
 $Recovery \ rate = \frac{1}{Experimentally \ Recovered \ Amount}$

A sealed tube equipped with a stirrer bar was charged with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (4.4 mg, 2.0 mol%), PPh₃ (104.9 mg, 2.0 equiv.), then degassed and refilled with N₂ for 3 times. After that, anhydrous CH₃CN (3 mL), 4-*tert*-butylthiophenol (26.6 mg, 80 mol%), H₂O (0.15 mL), and substrate **1a** (0.2 mmol, for liquid substrates) were added under N₂. The reaction mixture was irradiated by 30 W blue LEDs at room temperature for 21 hours, after which the reaction was concentrated in vacuo. The residue was purified by chromatography on silica gel to recover PPh₃, **HAT1**, and POPh₃, which were identified by ¹H and ¹³C NMR.

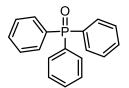
PPh₃ could be recovered at a 58% yield (31.5 mg), while POPh₃ was recovered at a 140% yield (75.1 mg), among them, the excess 40% of POPh₃ was from the oxidation of PPh₃ by air at the work-up stage. The total recovery rate of phosphorus species was (58% + 140%) / 2 = 99%, indicating that PPh₃ and POPh₃ were quantificationally recyclable from the reaction.

HAT1 could be recovered at a 70% yield, while about 30% of the **HAT1** was converted into diaryl disulfide through radical coupling reaction of the thiophenol radical as a side-reaction.

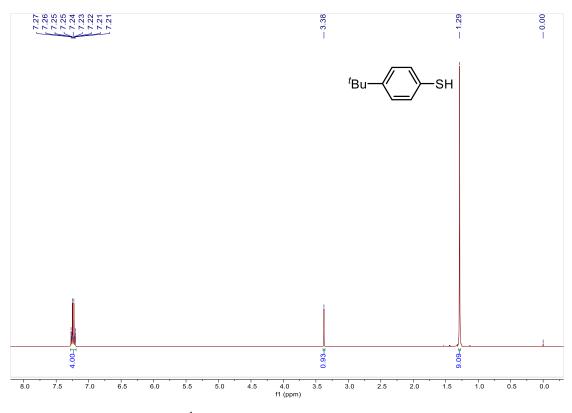
4-*Tert*-**butylthiophenol (HAT1):** colorless oil (18.6 mg, 0.56 equiv.). Eluent for the flash chromatography with silica gel: hexane / EA: 60/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.27 – 7.21 (m, 4H), 3.38 (s, 1H), 1.29 (s, 9H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 149.1, 129.7, 127.0, 126.3, 34.5, 31.4. The spectroscopic data corresponds to the reported data.^[2]

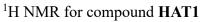


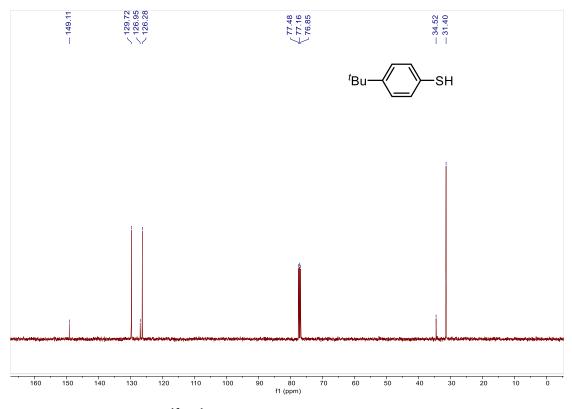
Triphenylphosphine (PPh₃): white solid (31.5 mg, 0.60 equiv.). Eluent for the flash chromatography with silica gel: hexane / EA: 10/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.32 – 7.29 (m, 15H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 137.3 (d, *J* = 11.1 Hz), 133.9 (d, *J* = 20.2 Hz), 128.8, 128.6 (d, *J* = 7.1 Hz). The spectroscopic data corresponds to the reported data.^[3]



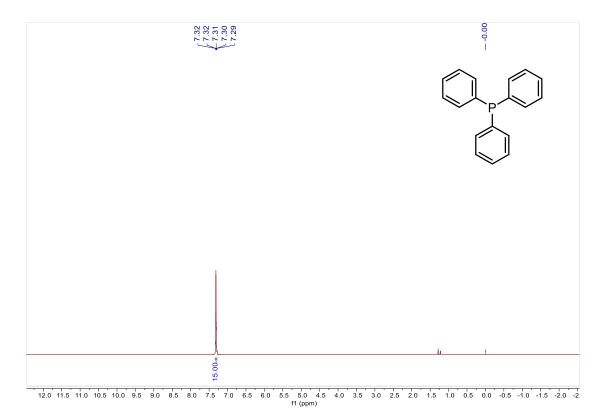
Triphenylphosphine oxide (POPh₃): white solid (75.1 mg, 1.35 equiv.). Eluent for the flash chromatography with silica gel: CH₂Cl₂ / MeOH: 10/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.70 – 7.64 (m, 6H), 7.53 – 7.49 (m, 3H), 7.45 – 7.41 (m, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 132.9, 131.9 (d, *J* = 10.1 Hz), 131.8 (d, *J* = 3.0 Hz), 128.4 (d, *J* = 13.1 Hz). The spectroscopic data corresponds to the reported data.^[4]



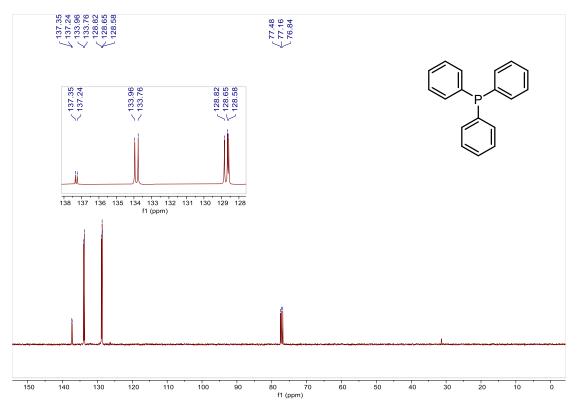




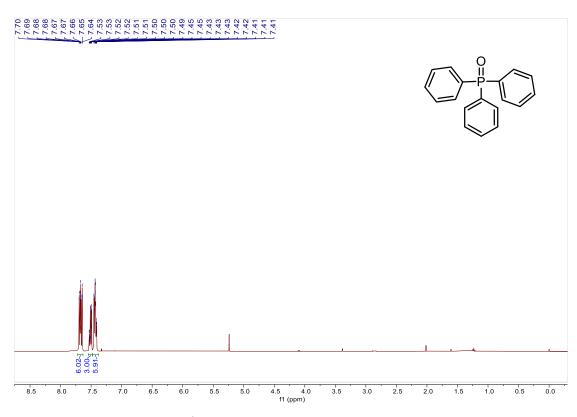
 $^{13}C\{^1H\}$ NMR for compound HAT1

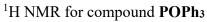


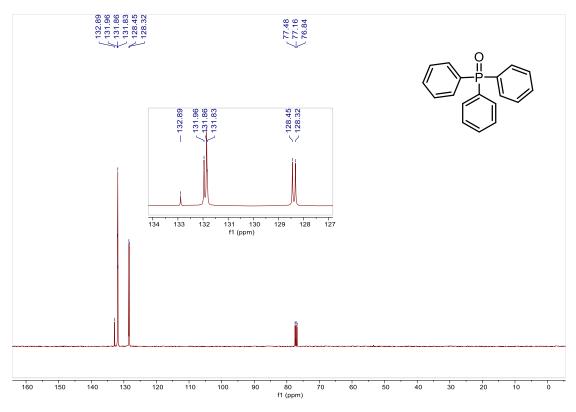
¹H NMR for compound **PPh**₃



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound PPh₃

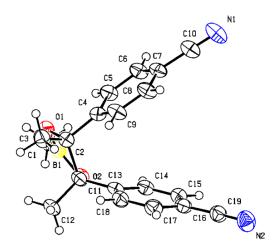






 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound POPh₃

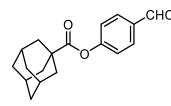
7. X-Ray Crystallography of the meso Isomer of 5d



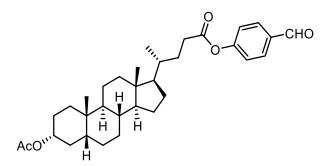
*ORTEP diagram of **5d** (*meso*) with the thermal ellipsoids shown at the 30% probability level. All hydrogen atoms have been omitted for clarity.

Crystal data and structure refinement for 5d (<i>meso</i>)			
Empirical formula	$C_{38}H_{34}B_2N_4O_4$		
Formula weight	632.31		
Temperature/K	169.98(10)		
Crystal system	triclinic		
Space group	P-1		
a/Å	8.1573(4)		
b/Å	9.2437(8)		
c/Å	24.5989(10)		
α/°	86.636(5)		
β/°	89.592(4)		
$\gamma/^{o}$	66.992(6)		
Volume/Å ³	1704.1(2)		
Z	2		
$\rho_{calc} g/cm^3$	1.232		
μ/mm^{-1}	0.637		
F(000)	664.0		
Crystal size/mm ³	0.18 imes 0.15 imes 0.1		
Radiation	Cu Ka ($\lambda = 1.54184$)		
2Θ range for data collection/°	3.598 to 172.506		
Index ranges	$-9 \le h \le 10, -11 \le k \le 11, -30 \le l \le 30$		
Reflections collected	18711		
Independent reflections	6844 [$R_{\text{int}} = 0.0636$, $R_{\text{sigma}} = 0.0571$]		
Data/restraints/parameters	6844/0/439		
Goodness-of-fit on F ²	1.097		
Final R indexes [I>=2 σ (I)]	$R_1 = 0.0891, wR_2 = 0.2375$		
Final R indexes [all data]	$R_1 = 0.1099, wR_2 = 0.2502$		
Largest diff. peak/hole / e Å ⁻³	0.41/-0.41		
CCDC Number: 2328828			

8. Spectra Data for Synthesized Substrates



4-Formylphenyl adamantane-1-carboxylate (**1u**): ¹H NMR (400 MHz, CHLOROFORM-D) δ 9.99 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 2.10 (s, 3H), 2.06 (s, 6H), 1.81 – 1.74 (m, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 191.1, 175.6, 156.1, 133.9, 131.3, 122.5, 41.3, 38.8, 36.5, 27.9. The spectroscopic data corresponds to the reported data.^[1]



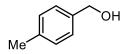
4-Formylphenyl (*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-acetoxy-10,13dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (1v): ¹H NMR (400 MHz, CHLOROFORM-D) δ 9.98 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 4.71 (dq, *J* = 11.5, 5.7 Hz, 1H), 2.64 (ddd, *J* = 15.1, 9.9, 5.0 Hz, 1H), 2.55 - 2.46 (m, 1H), 2.03 (s, 3H), 1.97 - 1.79 (m, 6H), 1.56 - 1.37 (m, 11H), 1.28 -1.06 (m, 9H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.93 (s, 3H), 0.67 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 190.9, 172.0, 170.6, 155.5, 133.9, 131.2, 122.4, 74.4, 56.5, 56.0, 42.8, 41.9, 40.4, 40.2, 35.8, 35.4, 35.0, 34.6, 32.2, 31.4, 28.3, 27.0, 26.6, 26.3, 24.2, 23.4, 21.5, 20.8, 18.3, 12.1. The spectroscopic data corresponds to the reported data.^[1]

9. Spectral Data for All Products

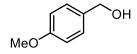
For products with diastereoisomers, **3a-3c**, **3f** were isolated and characterized as the mixture of the *dl* and *meso* isomer, while the *dl* and *meso* isomer of **3d**, **3e**, **5a-5d** were isolated and characterized separately.



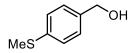
1-Phenylethanol (2a): colorless oil (24.2 mg, 99%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.37 – 7.32 (m, 4H), 7.28 – 7.23 (m, 1H), 4.86 (q, *J* = 6.4 Hz, 1H), 2.09 (s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 145.9, 128.6, 127.6, 125.5, 70.5, 25.2. The spectroscopic data corresponds to the reported data.^[5]



4-Methylbenzyl alcohol (2b): colorless oil (23.7 mg, 99%). Eluent for the flash chromatography with silica gel: hexane / ethyl acetate (EA): 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.60 (s, 2H), 2.34 (s, 3H), 1.96 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.0, 137.4, 129.3, 127.2, 65.3, 21.2. The spectroscopic data corresponds to the reported data.^[5]



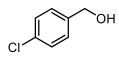
4-Methoxybenzyl alcohol (2c): colorless oil (25.9 mg, 95%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.30 – 7.25 (m, 2H), 6.91 – 6.85 (m, 2H), 4.59 (s, 2H), 3.80 (s, 3H), 1.85 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 159.3, 133.2, 128.8, 114.0, 65.1, 55.4. The spectroscopic data corresponds to the reported data.^[5]



4-(Methylthio)benzyl alcohol (2d): light yellow solid (30.5 mg, 99%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.29 – 7.23 (m, 4H), 4.63 (s, 2H), 2.48 (s, 3H), 1.83 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 137.9, 137.9, 127.8, 126.9, 65.0, 16.1. The spectroscopic data corresponds to the reported data.^[6]

N,N-dimethyl-4-hydroxymethylaniline (2e): colorless oil (29.9 mg, 99%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.25 – 7.19 (m, 2H), 6.74 – 6.68 (m, 2H), 4.53 (s, 2H), 2.93 (s, 6H), 1.82 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 150.4, 129.0, 128.7, 112.7, 65.4, 40.8. The spectroscopic data corresponds to the reported data.^[6]

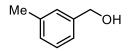
Biphenyl-4-yl methanol (2f): white solid (24.0 mg, 65%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.57 (m, 4H), 7.47 – 7.41 (m, 4H), 7.37 – 7.32 (m, 1H), 4.73 (d, J = 4.6 Hz, 2H), 1.75 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 141.0, 140.8, 140.0, 128.9, 127.6, 127.5, 127.5, 127.2, 65.2. The spectroscopic data corresponds to the reported data.^[7]



4-Chlorobenzyl alcohol (2g): colorless oil (15.1 mg, 53%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.35 – 7.26 (m, 4H), 4.66 (s, 2H), 1.75 (s, 1H). ¹³C NMR (101

MHz, CHLOROFORM-D) δ 139.4, 133.5, 128.8, 128.4, 64.7. The spectroscopic data corresponds to the reported data.^[7]

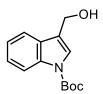
4-(Methoxycarbonyl)benzyl alcohol (2h): white solid (7.0 mg, 21%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 4.77 (s, 2H), 3.92 (s, 3H), 1.87 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 167.1, 146.1, 130.0, 129.5, 126.6, 64.9, 52.3. The spectroscopic data corresponds to the reported data.^[7]



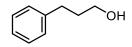
3-Methylbenzyl alcohol (2i): colorless oil (22.7 mg, 93%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.20 – 7.07 (m, 3H), 4.63 (s, 2H), 2.35 (s, 3H), 1.84 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 140.9, 138.4, 128.6, 128.5, 127.9, 124.2, 65.5, 21.5. The spectroscopic data corresponds to the reported data.^[5]



2-Methylbenzyl alcohol (2j): colorless oil (22.5 mg, 92%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.37 – 7.31 (m, 1H), 7.24 – 7.14 (m, 3H), 4.67 (s, 2H), 2.35 (s, 3H), 1.72 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.8, 136.2, 130.4, 127.9, 127.6, 126.2, 63.6, 18.8. The spectroscopic data corresponds to the reported data.^[5]

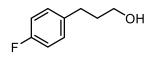


Tert-butyl 3-hydroxymethylindole-1-carboxylate (2k): colorless oil (28.5 mg, 58%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.57 (s, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 4.83 (s, 2H), 1.66 (s, 9H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 149.8, 135.9, 129.3, 124.8, 123.9, 122.8, 120.6, 119.4, 115.4, 83.9, 57.3, 28.3. The spectroscopic data corresponds to the reported data.^[8]

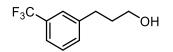


3-Phenyl-1-propanol (2l): colorless oil (25.9 mg, 95%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.32 – 7.26 (m, 2H), 7.21 – 7.17 (m, 3H), 3.67 (t, *J* = 6.4 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 1.89 (tt, *J* = 7.6, 6.4 Hz, 2H), 1.40 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 142.0, 128.5, 128.5, 126.0, 62.4, 34.4, 32.2. The spectroscopic data corresponds to the reported data.^[5]

3-(4-Bromophenyl)propan-1-ol (2m): colorless oil (40.4 mg, 94%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.42 – 7.37 (m, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.70 – 2.62 (m, 2H), 1.89 – 1.81 (m, 2H), 1.56 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 140.9, 131.6, 130.3, 119.7, 62.1, 34.1, 31.5. The spectroscopic data corresponds to the reported data.^[9]



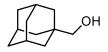
3-(4-fluorophenyl)propan-1-ol (2n): colorless oil (27.8 mg, 90%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.16 – 7.11 (m, 2H), 7.02 – 6.91 (m, 2H), 3.65 (t, J = 6.4 Hz, 2H), 2.72 – 2.63 (m, 2H), 1.90 – 1.81 (m, 2H), 1.75 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 161.3 (d, J = 243.4 Hz), 137.5 (d, J = 4.0 Hz), 129.8 (d, J = 8.1 Hz), 115.2 (d, J = 21.2 Hz), 62.09, 34.38, 31.29. ¹⁹F NMR (376 MHz, CHLOROFORM-D) δ -117.5 – -117.7 (m). The spectroscopic data corresponds to the reported data.^[10]



3-[3-(trifluoromethyl)phenyl]propan-1-ol (20): colorless oil (32.7 mg, 80%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.46 – 7.44 (m, 2H), 7.42 – 7.38 (m, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.81 – 2.74 (m, 2H), 1.95 – 1.86 (m, 2H), 1.55 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 142.9, 132.0, 130.8 (q, *J* = 32.3 Hz), 128.9 (q, *J* = 8.1 Hz), 125.2 (q, *J* = 3.5 Hz), 124.4 (q, *J* = 273.7 Hz), 122.9 (q, *J* = 3.6 Hz), 62.0, 34.1, 32.0. ¹⁹F NMR (376 MHz, CHLOROFORM-D) δ -62.4. The spectroscopic data corresponds to the reported data.^[11]

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Cyclohexylmethyl alcohol (2p): colorless oil (17.8 mg, 78%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 3.44 (d, J = 6.4 Hz, 2H), 1.76 – 1.72 (m, 4H), 1.71 – 1.65 (m, 1H), 1.52 – 1.43 (m, 1H), 1.40 (s, 1H), 1.30 – 1.14 (m, 3H), 0.93 (qd, J = 12.8, 3.4 Hz, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 68.9, 40.6, 29.7, 26.7, 26.0. The spectroscopic data corresponds to the reported data.^[12]



1-Adamantanemethanol (**2q**): white solid (32.9 mg, 99%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 3.19 (s, 2H), 1.99 (s, 3H), 1.73 (d, J = 12.4 Hz, 3H), 1.65 (d, J = 11.5 Hz, 3H), 1.51 (d, J = 2.8 Hz, 7H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 73.9, 39.1, 37.3, 34.6, 28.3. The spectroscopic data corresponds to the reported data.^[6]

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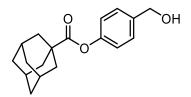
5-Chloro-1-pentanol (2r): colorless oil (22.8 mg, 93%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 3.66 (t, J = 6.2 Hz, 2H), 3.55 (t, J = 6.6 Hz, 2H), 1.82 (dt, J = 14.2, 6.9 Hz, 2H), 1.64 – 1.48 (m, 5H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 62.7, 45.1, 32.4, 32.0, 23.2. The spectroscopic data corresponds to the reported data.^[13]

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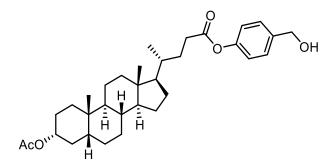
3-(*t*-Butyldimethylsilyloxy)propanol (2t): colorless oil (37.3 mg, 98%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 3.84 (t, *J* = 5.7 Hz, 2H), 3.80 (t, *J* = 5.3 Hz, 2H), 2.76 (s, 1H), 1.78 (tt, *J* = 5.7, 5.3 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 63.0, 62.5, 34.3, 26.0, 18.3, -5.4. The spectroscopic data corresponds to the reported data.^[14]

2-(Hydroxymethyl)cyclohexanone (2t): Colorless oil (21.0 mg, 82%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 3.80 – 3.69 (m, 1H), 3.67 – 3.55 (m, 1H), 2.70 (s, 1H), 2.52 (ddt, J = 11.9, 6.4, 4.6 Hz, 1H), 2.46 – 2.24 (m, 2H), 2.15 – 1.99 (m, 2H), 1.97 – 1.88 (m,

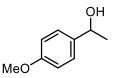
1H), 1.76 - 1.60 (m, 2H), 1.48 (qd, J = 12.8, 3.7 Hz, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 215.0, 62.9, 52.4, 42.3, 30.2, 27.6, 24.8. The spectroscopic data corresponds to the reported data.^[15]



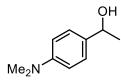
4-(Hydroxymethyl)phenyl adamantane-1-carboxylate (2u): white solid (55.6 mg, 97%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.33 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 4.63 (s, 2H), 2.20 – 2.05 (m, 10H), 1.80 – 1.73 (m, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 176.5, 150.6, 138.3, 128.1, 121.7, 64.8, 41.1, 38.8, 36.5, 28.0. The spectroscopic data corresponds to the reported data.^[16]



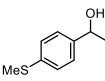
4-(Hydroxymethyl)phenyl (*R*)-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-acetoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (2v): white solid (73.5mg, 70%). Melting point: 138.4 – 140.9 °C. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.35 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 4.71 (td, *J* = 11.5, 5.7 Hz, 1H), 4.64 (s, 2H), 2.60 (ddd, *J* = 15.1, 9.6, 4.8 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.02 (s, 3H), 2.00 – 1.74 (m, 6H), 1.68 (d, *J* = 10.1 Hz, 1H), 1.61 – 1.37 (m, 10H), 1.35 – 1.02 (m, 10H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.93 (s, 3H), 0.67 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 173.0, 170.8, 150.1, 138.6, 128.1, 121.7, 74.5, 64.6, 56.6, 56.0, 42.8, 41.9, 40.5, 40.2, 35.8, 35.4, 35.1, 34.6, 32.3, 31.4, 31.0, 28.3, 27.1, 26.7, 26.4, 24.2, 23.4, 21.6, 20.9, 18.4, 12.1. HRMS (EI+) calculated *m*/*z* for C₃₃H₄₈O₅⁺ [M]⁺: 524.3496, found 524.3498.



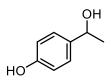
1-(4-Methoxyphenyl)ethanol (2w): colorless oil (30.1 mg, 99%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.31 – 7.26 (m, 2H), 6.90 – 6.84 (m, 2H), 4.83 (q, J = 6.4 Hz, 1H), 3.79 (s, 3H), 1.97 (s, 1H), 1.46 (d, J = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 159.1, 138.2, 126.8, 114.0, 70.0, 55.4, 25.1. The spectroscopic data corresponds to the reported data.^[5]



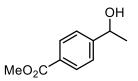
1-[4-(*N*,*N***-dimethylamino**)**phenyl]ethanol** (**2x**)**:** colorless oil (26.8 mg, 81%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 4.81 (q, *J* = 6.4 Hz, 1H), 2.93 (s, 6H), 1.79 (s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 150.3, 133.9, 126.6, 112.7, 70.2, 40.8, 24.8. The spectroscopic data corresponds to the reported data.^[17]



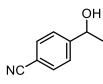
1-(4-(Methylthio)phenyl)ethanol (2y): white solid (33.3 mg, 99%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 4.83 (q, *J* = 6.4 Hz, 1H), 2.47 (s, 3H), 2.08 (s, 1H), 1.46 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 142.9, 137.4, 126.9, 126.1, 70.1, 25.2, 16.1. The spectroscopic data corresponds to the reported data.^[18]



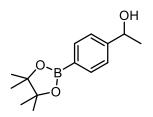
1-(4-Hydroxyphenyl)ethanol (2z): white solid (27.1 mg, 98%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, METHANOL- D_4) δ 7.23 – 7.13 (m, 2H), 6.76 – 6.72 (m, 2H), 4.77 – 4.70 (m, 1H), 1.43 – 1.39 (m, 3H). ¹³C NMR (101 MHz, METHANOL- D_4) δ 157.6, 138.3, 127.8, 115.9, 70.6, 25.4. The spectroscopic data corresponds to the reported data.^[19]



Methyl 4-(1-hydroxy ethyl)benzoate (2aa): colorless oil (22.3 mg, 62%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.03 – 7.97 (m, 2H), 7.43 (d, J = 8.3 Hz, 2H), 4.95 (q, J = 6.4Hz, 1H), 3.90 (s, 3H), 2.16 (s, 1H), 1.50 (d, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 167.1, 151.1, 130.0, 129.3, 125.4, 70.1, 52.2, 25.4. The spectroscopic data corresponds to the reported data.^[20]



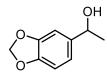
4-(1-Hydroxyethyl)benzonitrile (2ab): colorless oil (15.6 mg, 53%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 4.96 (q, *J* = 6.4 Hz, 1H), 2.07 (s, 1H), 1.50 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 151.2, 132.5, 126.2, 119.0, 111.2, 69.8, 25.5. The spectroscopic data corresponds to the reported data.^[18]



1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethanol (2ac): white solid (25.3 mg, 51%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.80 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 7.8 Hz, 2H), 4.91 (q, J = 6.4 Hz, 1H), 1.93 (s, 1H), 1.49 (d, J = 6.4 Hz, 3H), 1.34 (s, 12H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 149.1, 135.2, 124.8, 83.9, 70.5, 25.3, 25.0. The spectroscopic data corresponds to the reported data.^[21]



1-(1-Naphthyl)ethanol (2ad): colorless oil (11.4 mg, 33%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.12 (d, J = 8.3 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.68 (d, J = 7.3 Hz, 1H), 7.55 – 7.45 (m, 3H), 5.68 (q, J = 6.4 Hz, 1H), 1.97 (s, 1H), 1.67 (d, J = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 141.5, 133.9, 130.4, 129.5, 129.0, 128.0, 126.2, 125.7, 123.3, 122.1, 67.2, 24.5. The spectroscopic data corresponds to the reported data.^[22]



1-Benzo[1,3]dioxol-5-yl-ethanol (2ae): colorless oil (31.6 mg, 95%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 6.86 (s, 1H), 6.81 – 6.73 (m, 2H), 5.92 (s, 2H), 4.78 (q, *J* = 6.4 Hz, 1H), 2.20 (s, 1H), 1.43 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-

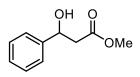
D) δ 147.8, 146.8, 140.1, 118.8, 108.1, 106.1, 101.0, 70.2, 25.2. The spectroscopic data corresponds to the reported data.^[23]



1,2,3,4-Tetrahydro-1-naphthol (2af): colorless oil (24.3 mg, 82%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.43 – 7.39 (m, 1H), 7.21 – 7.18 (m, 2H), 7.11 – 7.08 (m, 1H), 4.75 (s, 1H), 2.81 (dt, *J* = 16.0, 5.0 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.00 – 1.86 (m, 4H), 1.81 – 1.73 (m, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.9, 137.2, 129.1, 128.8, 127.7, 126.3, 68.2, 32.3, 29.3, 18.9. The spectroscopic data corresponds to the reported data.^[18]

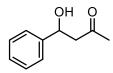


1-Indanol (2ag): colorless oil (24.7 mg, 92%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.40 (d, J = 6.0 Hz, 1H), 7.24 7.20 (m, 3H), 5.21 (t, J = 5.5 Hz, 1H), 3.04 (ddd, J = 16.0, 8.7, 4.8 Hz, 1H), 2.80 (dt, J = 15.6, 7.3 Hz, 1H), 2.46 (dtd, J = 13.3, 7.6, 5.0 Hz, 1H), 2.01 (s, 1H), 1.97 – 1.86 (m, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 145.1, 143.4, 128.4, 126.8, 125.0, 124.3, 76.5, 36.0, 29.9. The spectroscopic data corresponds to the reported data.^[18]

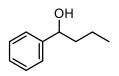


Methyl 3-hydroxy-3-phenylpropionate (2ah): colorless oil (31.0 mg, 86%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.37 – 7.25 (m, 5H), 5.14 – 5.10 (m, 1H), 3.70 (s, 3H), 3.32 (s,

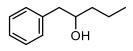
1H), 2.79 – 2.67 (m, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 172.9, 142.6, 128.6, 127.9, 125.7, 70.4, 52.0, 43.3. The spectroscopic data corresponds to the reported data.^[24]



1-Hydroxy-1-phenyl-3-butanone (2ai): colorless oil (23.0 mg, 70%). Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.35 (d, *J* = 4.6 Hz, 4H), 7.30 – 7.25 (m, 1H), 5.14 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.35 (s, 1H), 2.88 (dd, *J* = 17.4, 9.2 Hz, 1H), 2.80 (dd, *J* = 17.4, 3.2 Hz, 1H), 2.18 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 209.2, 142.8, 128.6, 127.8, 125.7, 69.9, 52.1, 30.9. The spectroscopic data corresponds to the reported data.^[25]

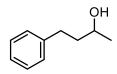


1-Phenyl-1-butanol (2aj): colorless oil (29.4 mg, 98%). Eluent for the flash chromatography with silica gel: hexane / EA: 10/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.35 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 4.64 (t, *J* = 6.6 Hz, 1H), 2.02 (s, 1H), 1.77 (dtd, *J* = 10.1, 7.8, 5.0 Hz, 1H), 1.66 (ddt, *J* = 13.3, 10.1, 5.5 Hz, 1H), 1.48 – 1.36 (m, 1H), 1.34 – 1.24 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 145.0, 128.5, 127.6, 126.0, 74.5, 41.3, 19.1, 14.1. The spectroscopic data corresponds to the reported data.^[26]

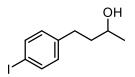


1-Phenyl-2-pentanol (2ak): colorless oil (15.8 mg, 48%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.34 – 7.29 (m, 2H), 7.26 – 7.20 (m, 3H), 3.91 – 3.75 (m, 1H),

2.83 (dd, J = 13.5, 4.4 Hz, 1H), 2.64 (dd, J = 13.5, 8.5 Hz, 1H), 1.54 – 1.47 (m, 4H), 1.41 – 1.37 (m, 1H), 0.94 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.8, 129.6, 128.7, 126.6, 72.6, 44.2, 39.1, 19.1, 14.2. The spectroscopic data corresponds to the reported data.^[27]



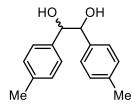
1-Phenyl-3-butanol (2al): colorless oil (15.0 mg, 50%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.16 (m, 3H), 3.86 – 3.78 (m, 1H), 2.80 – 2.62 (m, 2H), 1.77 (ddt, J = 9.2, 7.3, 5.3 Hz, 2H), 1.53 (s, 1H), 1.22 (d, J = 6.0 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 142.2, 128.5, 128.5, 125.9, 67.6, 41.0, 32.2, 23.7. The spectroscopic data corresponds to the reported data.^[18]



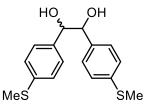
4-(4-Iodophenyl)-2-butanol (2am): colorless oil (11.6 mg, 21%). Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.64 – 7.54 (m, 2H), 7.03 – 6.88 (m, 2H), 3.81 (dq, *J* = 12.4, 6.0 Hz, 1H), 2.75 – 2.57 (m, 2H), 1.77 – 1.68 (m, 2H), 1.22 (d, *J* = 6.4 Hz, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 141.8, 137.6, 130.7, 90.9, 67.4, 40.7, 31.7, 23.9. HRMS (EI+) calculated *m/z* for C₁₀H₁₃IO⁺ [M]⁺: 276.0006, found 276.0009.

1,1,1-Trifluoro-3-phenylpropan-2-ol (2an): colorless oil (34.6 mg, 91%). Eluent for the flash chromatography with silica gel: hexane / EA: 10/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.36 – 7.24 (m, 5H), 4.18 – 4.08 (m, 1H), 3.05 (dd, *J* = 14.2, 2.8 Hz, 1H), 2.84 (dd, *J* = 14.2, 10.1 Hz, 1H), 2.15 (d, *J* = 5.0 Hz, 1H). ¹³C NMR (101 MHz,

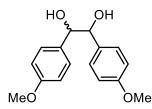
CHLOROFORM-D) δ 135.8, 129.6, 128.9, 127.4, 125.0 (q, *J* = 282.8 Hz), 71.6 (q, *J* = 31.3 Hz), 36.2. The spectroscopic data corresponds to the reported data.^[28]



1,2-Bis(4-methylphenyl)-1,2-ethanediol (*dl* and *meso*) (**3a**): White solid. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.25 – 7.13 (m, 8H), 7.06 – 6.99 (m, 8H), 4.72 (s, 2H), 4.64 (s, 2H), 2.86 (s, 2H), 2.34 (s, 6H), 2.29 (s, 6H), 2.16 (s, 2H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 137.9, 137.6, 137.1, 129.1, 128.9, 127.2, 127.0, 78.9, 78.2, 21.3, 21.3. The spectroscopic data corresponds to the reported data.^[29]

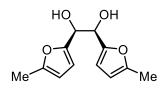


1,2-Bis(4-(methylthio)phenyl)-1,2-ethanediol (*dl* and *meso*) (**3b):** White solid. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.11 (d, *J* = 8.3 Hz, 4H), 7.03 (d, *J* = 8.7 Hz, 4H), 4.62 (s, 2H), 2.89 (s, 2H), 2.45 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.3, 136.6, 127.6, 126.2, 78.8, 15.8. (*R*,*S*)-287a was assigned, while (*R*,*R*)/(*S*,*S*)-287a was not assigned due to the weak signal caused by extremely low soluability. The spectroscopic data corresponds to the reported data.^[30]

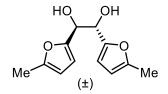


1,2-Bis(4-methoxyphenyl)-1,2-ethanediol (*dl* and *meso*) (**3c**): White solid. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz,

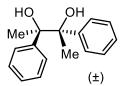
CHLOROFORM-D) δ 7.18 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 8.7 Hz, 4H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 4H), 4.72 (s, 2H), 4.60 (s, 2H), 3.79 (s, 6H), 3.75 (s, 6H), 2.94 (s, 2H).¹³C NMR (101 MHz, CHLOROFORM-D) δ 159.5, 159.3, 132.2, 132.2, 128.5, 128.3, 113.8, 113.6, 78.9, 77.9, 55.4, 55.3. The spectroscopic data corresponds to the reported data.^[31]



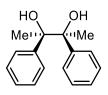
(*R*,*S*)-1,2-bis(5-methylfuran-2-yl)-1,2-ethanediol (*dl*-3d): Colorless oil. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 6.21 (d, *J* = 3.2 Hz, 2H), 5.93 (d, *J* = 2.8 Hz, 2H), 4.91 (s, 2H), 2.32 (s, 2H), 2.29 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 152.6, 151.0, 109.7, 106.5, 70.0, 13.7. The spectroscopic data corresponds to the reported data.^[30]



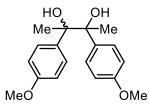
(*R*,*R*)/(*S*,*S*)-1,2-bis(5-methylfuran-2-yl)-1,2-ethanediol (*meso*-3d): Colorless oil. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 6.13 (d, *J* = 2.8 Hz, 2H), 5.87 (d, *J* = 2.8 Hz, 2H), 4.92 (s, 2H), 2.81 (s, 2H), 2.26 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 152.3, 150.9, 109.0, 106.4, 69.9, 13.7. The spectroscopic data corresponds to the reported data.^[30]



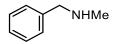
(R,R)/(S,S)-2,3-diphenylbutane-2,3-diol (*dl*-3e): White solid. Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.25 – 7.23 (m, 6H), 7.21 – 7.18 (m, 4H), 2.59 (s, 2H), 1.50 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 143.6, 127.5, 127.3, 127.2, 79.0, 25.1. The spectroscopic data corresponds to the reported data.^[29]



(*R*,*S*)-2,3-diphenylbutane-2,3-diol (*meso-3e*): White solid. Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.25 – 7.21 (m, 10H), 2.25 (s, 2H), 1.58 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 143.9, 127.4, 127.0, 127.0, 78.7, 25.3. The spectroscopic data corresponds to the reported data.^[29]



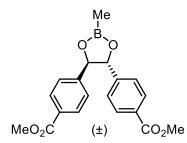
1,2-Bis(4-methoxyphenyl)butane-2,3-ethanediol (*dl* and *meso*) (**3f**): White solid. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.14 – 7.07 (m, 8H), 6.79 – 6.73 (m, 8H), 3.79 (s, 6H), 3.78 (s, 6H), 2.56 (s, 2H), 2.28 (s, 2H), 1.54 (s, 6H), 1.45 (s, 6H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 158.7, 158.6, 136.2, 135.8, 128.7, 128.2, 112.7, 112.5, 78.8, 78.6, 55.3, 55.3, 25.3, 25.1. The spectroscopic data corresponds to the reported data.^[32]



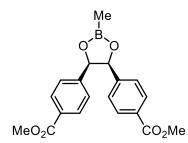
N-Methylbenzylamine (4a): white solid (10.2 mg, 42%). Eluent for the flash chromatography with silica gel: CH₂Cl₂ / MeOH: 20/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.35 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 3.74 (s, 2H), 2.45 (s,

3H), 1.41 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 140.3, 128.5, 128.3, 127.0, 56.2, 36.2. The spectroscopic data corresponds to the reported data.^[33]

N-Benzylaniline (4b): white solid (33.7 mg, 92%). Eluent for the flash chromatography with silica gel: hexane / EA: 10/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.34 (q, *J* = 8.0 Hz, 4H), 7.26 (t, *J* = 6.6 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.74 – 6.68 (m, 1H), 6.62 (d, *J* = 8.3 Hz, 2H), 4.31 (s, 2H), 4.00 (s, 1H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 148.2, 139.6, 129.4, 128.8, 127.6, 127.3, 117.7, 112.9, 48.4. The spectroscopic data corresponds to the reported data.^[34]

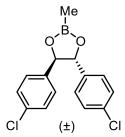


(*R*,*R*)/(*S*,*S*) dimethyl 4,4'-(2-methyl-1,3,2-dioxaborolane-4,5-diyl)dibenzoate (*dl*-5a): White solid. Melting point: 109.6 – 111.5 °C. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.07 (d, J = 8.3 Hz, 4H), 7.35 (d, J = 8.3 Hz, 4H), 5.15 (s, 2H), 3.93 (s, 6H), 0.57 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 166.8, 144.9, 130.4, 130.3, 125.8, 85.9, 52.4. HRMS (EI+) calculated *m*/*z* for C₁₉H₁₉BO₆⁺ [M]⁺: 354.1269, found 354.1267.

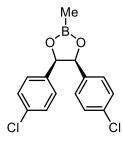


(*R*,*S*) dimethyl 4,4'-(2-methyl-1,3,2-dioxaborolane-4,5-diyl)dibenzoate (*meso*-5a): White solid. Melting point: 223.9 – 225.2 °C. Eluent for the flash chromatography with

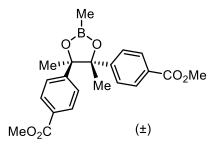
silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.74 (d, *J* = 8.3 Hz, 4H), 6.98 (d, *J* = 8.3 Hz, 4H), 5.80 (s, 2H), 3.84 (s, 6H), 0.63 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 166.7, 142.4, 129.5, 129.3, 126.3, 82.4, 52.2. HRMS (EI+) calculated *m*/*z* for C₁₉H₁₉BO₆⁺ [M]⁺: 354.1269, found 354.1267.



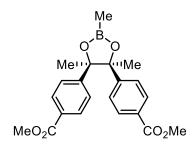
(R,R)/(S,S)-4,5-bis(4-chlorophenyl)-2-methyl-1,3,2-dioxaborolane (*dl*-5b): Light yellow oil. Eluent for the flash chromatography with silica gel: hexane / EA: 15/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.36 (d, J = 8.3 Hz, 4H), 7.20 (d, J = 8.3 Hz, 4H), 5.05 (s, 2H), 0.53 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 138.5, 134.5, 129.2, 127.3, 85.8. HRMS (EI+) calculated m/z for C₁₅H₁₃BCl₂O₂⁺ [M]⁺: 306.0380, found 306.0377.



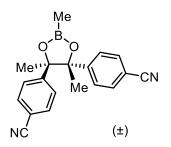
(*R*,*S*)-4,5-bis(4-chlorophenyl)-2-methyl-1,3,2-dioxaborolane (*meso*-5b): White solid. Melting point: 89.1 – 91.4 °C. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.10 – 7.06 (m, 4H), 6.85 – 6.80 (m, 4H), 5.68 (s, 2H), 0.59 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 128.5, 128.5, 128.2, 127.7, 82.1. HRMS (EI+) calculated *m*/*z* for C₁₅H₁₃BCl₂O₂⁺ [M]⁺: 306.0380, found 306.0377.



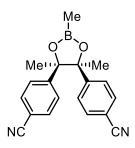
(R,R)/(S,S) dimethyl 4,4'-(2,4,5-trimethyl-1,3,2-dioxaborolane-4,5-diyl)dibenzoate (*dl*-5c): White solid. Melting point: 152.0 – 153.9 °C. Eluent for the flash chromatography with silica gel: hexane / EA: 10/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 8.08 (d, J = 8.7 Hz, 4H), 7.53 (d, J = 8.3 Hz, 4H), 3.95 (s, 6H), 1.15 (s, 6H), 0.55 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 166.9, 147.5, 129.6, 125.8, 87.8, 52.3, 27.5. HRMS (EI+) calculated m/z for C₂₁H₂₃BO₆⁺ [M]⁺: 382.1582, found 382.1585.



(*R*,*S*) dimethyl 4,4'-(2,4,5-trimethyl-1,3,2-dioxaborolane-4,5-diyl)dibenzoate (*meso*-5c): White solid. Melting point: 103.2 – 105.4 °C. Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.68 (d, *J* = 8.3 Hz, 4H), 6.99 (d, *J* = 8.3 Hz, 4H), 3.85 (s, 6H), 1.83 (s, 6H), 0.64 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 166.7, 147.5, 128.9, 128.7, 125.5, 88.6, 52.1, 25.0. HRMS (EI+) calculated *m*/*z* for C₂₁H₂₃BO₆⁺ [M]⁺: 382.1582, found 382.1585.



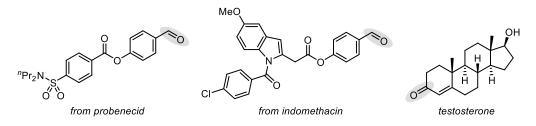
(R,R)/(S,S)-4,4'-(2,4,5-trimethyl-1,3,2-dioxaborolane-4,5-diyl)dibenzonitrile (*dl*-5d): White solid. Melting point: 212.0 – 213.4 °C. Eluent for the flash chromatography with silica gel: hexane / EA: 5/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.73 (d, J = 7.3 Hz, 4H), 7.57 (d, J = 7.8 Hz, 4H), 1.14 (s, 6H), 0.55 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 147.5, 132.3, 126.5, 118.6, 112.0, 87.5, 27.4. HRMS (EI+) calculated m/z for C₁₉H₁₇BN₂O₂⁺ [M]⁺: 316.1378, found 316.1380.



(*R*,*S*)-4,4'-(2,4,5-trimethyl-1,3,2-dioxaborolane-4,5-diyl)dibenzonitrile (*meso*-5d): White solid. Melting point: 141.7 – 143.2 °C. Eluent for the flash chromatography with silica gel: hexane / EA: 2/1. ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.37 – 7.32 (m, 4H), 7.04 – 7.00 (m, 4H), 1.82 (s, 6H), 0.63 (s, 3H). ¹³C NMR (101 MHz, CHLOROFORM-D) δ 147.6, 131.6, 126.3, 118.4, 111.2, 88.4, 24.8. HRMS (EI+) calculated *m*/*z* for C₁₉H₁₇BN₂O₂⁺ [M]⁺: 316.1378, found 316.1380.

10. Scope of Unsuccessful Derivatized Examples

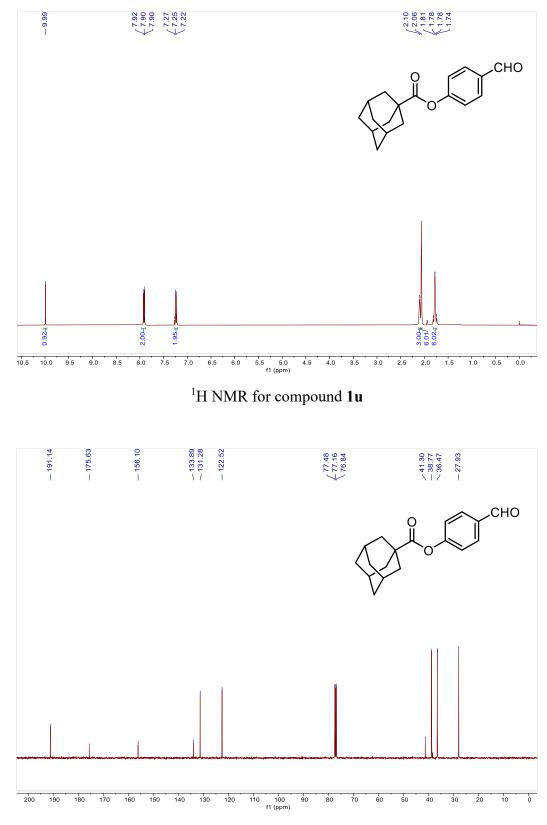
The following bioactive compounds or drugs did not proceed well in the hydrogenated reaction for different reasons. The probenecid derivative suffered from competitive reductive coupling and reduction of the sulfonyl group, and the indomethacin derivative was interrupted by the dearomatized hydrogenation of the indole motif, while testosterone resulted in hydrogenation of the C=C double bond.



11. References

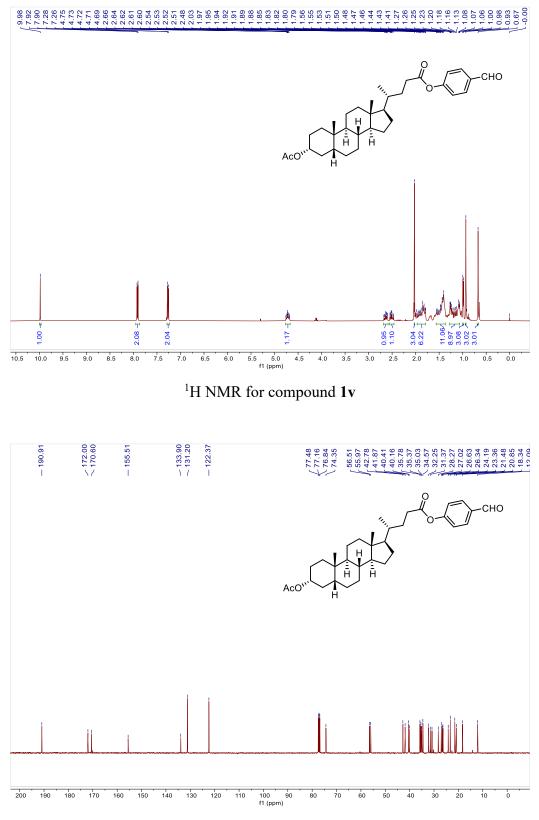
- [1] S. Mukherjee, R. A. Garza-Sanchez, A. Tlahuext-Aca, F. Glorius, Angew. Chem. Int. Ed. 2017, 56, 14723-14726.
- [2] M. Zhang, B. Wang, Y. Cao, Y. Liu, Z. Wang, Q. Wang, Org. Lett. 2022, 24, 8895-8900.
- [3] H. Jin, C. Gu, Z. Xiao, Q. Tan, L. Liu, L.-B. Han, W.-H. Chen, T. Chen, *Eur. J. Org. Chem.* 2023, 26, e202300397.
- [4] L. Tang, G. Lv, F. Jia, R. Zhao, X. Wang, Q. Zhou, Adv. Synth. Catal. 2024, 366, 70-76.
- [5] A. Call, C. Casadevall, F. Acuña-Parés, A. Casitas, J. Lloret-Fillol, *Chem. Sci.* 2017, 8, 4739-4749.
- [6] Z. Wei, H. Li, Y. Wang, Q. Liu, Angew. Chem. Int. Ed. 2023, 62, e202301042.
- [7] Q. Yu, D. Zhou, Y. Liu, X. Huang, C. Song, J. Ma, J. Li, Org. Lett. 2023, 25, 47-52.
- [8] A. R. White, R. A. Kozlowski, S.-C. Tsai, C. D. Vanderwal, *Angew. Chem. Int. Ed.* 2017, 56, 10525-10529.
- [9] K. S. Iyer, C. Nelson, B. H. Lipshutz, Green Chem. 2023, 25, 2663-2671.
- [10] M. Shibuya, T. Orihashi, Y. Li, Y. Yamamoto, Chem. Commun. 2021, 57, 8742-8745.
- [11] A. Nair, V. Tiwari, S. Rath, P. Saini, A. Verma, A. J. Elias, *Chem. Commun.* 2023, 59, 11117-11120.
- [12] Q. Chen, X. Kang, X. Zhang, Y. Cao, L. He, J. Org. Chem. 2023, 88, 5044-5051.
- [13] G. B. af Gennäs, V. Talman, O. Aitio, E. Ekokoski, M. Finel, R. K. Tuominen, J. Yli-Kauhaluoma, J. Med. Chem. 2009, 52, 3969-3981.
- [14] J.-C. Han, L.-Z. Liu, Y.-Y. Chang, G.-Z. Yue, J. Guo, L.-Y. Zhou, C.-C. Li, Z. Yang, J. Org. Chem. 2013, 78, 5492-5504.
- [15] M. Lenze, E. B. Bauer, Chem. Commun. 2013, 49, 5889-5891.
- [16] C. M. Levinn, A. K. Steiger, M. D. Pluth, ACS Chemical Biology 2019, 14, 170-175.
- [17] D. Peng, M. Zhang, Z. Huang, Chem. Eur. J. 2015, 21, 14737-14741.
- [18] Q. Xuan, C. Zhao, Q. Song, Org. Biomol. Chem. 2017, 15, 5140-5144.
- [19] B. Bueno, S. Heurtaux, A. Gagnon, J. Org. Chem. 2023, 88, 13351-13357.
- [20] T.-S. Chen, H. Long, Y. Gao, H.-C. Xu, Angew. Chem. Int. Ed. 2023, 62, e202310138.
- [21] J. M. Paolillo, A. D. Duke, E. S. Gogarnoiu, D. E. Wise, M. Parasram, J. Am. Chem. Soc. 2023, 145, 2794-2799.
- [22] L. Hackl, L. P. Ho, D. Bockhardt, T. Bannenberg, M. Tamm, Organometallics 2022, 41, 836-851.
- [23] T. B. Boit, M. M. Mehta, N. K. Garg, Org. Lett. 2019, 21, 6447-6451.
- [24] Z. Peralta-Neel, K. A. Woerpel, Org. Lett. 2021, 23, 5002-5006.
- [25] R. A. Fernandes, G. V. Ramakrishna, V. Bethi, Org. Biomol. Chem. 2020, 18, 6115-6125.
- [26] S. Yadav, M. Rao Kuram, Eur. J. Org. Chem. 2023, 26, e202201344.
- [27] B. Ardiansah, H. Tanimoto, T. Tomohiro, T. Morimoto, K. Kakiuchi, *Chem. Commun.* 2021, 57, 8738-8741.
- [28] N. F. Both, A. Spannenberg, H. Jiao, K. Junge, M. Beller, Angew. Chem. Int. Ed. 2023, 62, e202307987.
- [29] M. Billamboz, N. Sotto, C. Chevrin-Villette, C. Len, RSC Adv. 2015, 5, 46026-46030.
- [30] Y. Yan, G. Li, J. Ma, C. Wang, J. Xiao, D. Xue, Green Chem. 2023, 25, 4129-4136.

- [31] S. Okamoto, H. Tsujioka, A. Sudo, *Chem. Lett.* **2018**, *47*, 369-372.
- [32] C. Yang, G. Magallanes, S. Maldonado, C. R. J. Stephenson, J. Org. Chem. 2021, 86, 15927-15934.
- [33] X. Guo, Y. Zuo, G. A. Alvarez, E. Mejía, *Eur. J. Org. Chem.* **2023**, *26*, e202300904.
- [34] D. J. Scott, N. A. Phillips, J. S. Sapsford, A. C. Deacy, M. J. Fuchter, A. E. Ashley, *Angew. Chem. Int. Ed.* **2016**, *55*, 14738-14742.

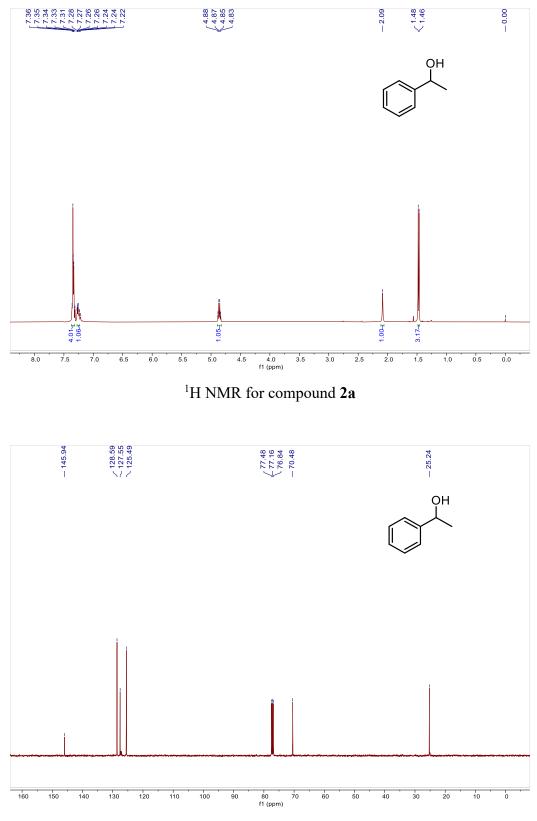


12. Copies of ¹H, ¹³C{¹H}, ¹⁹F NMR Spectra for Synthesized Compounds

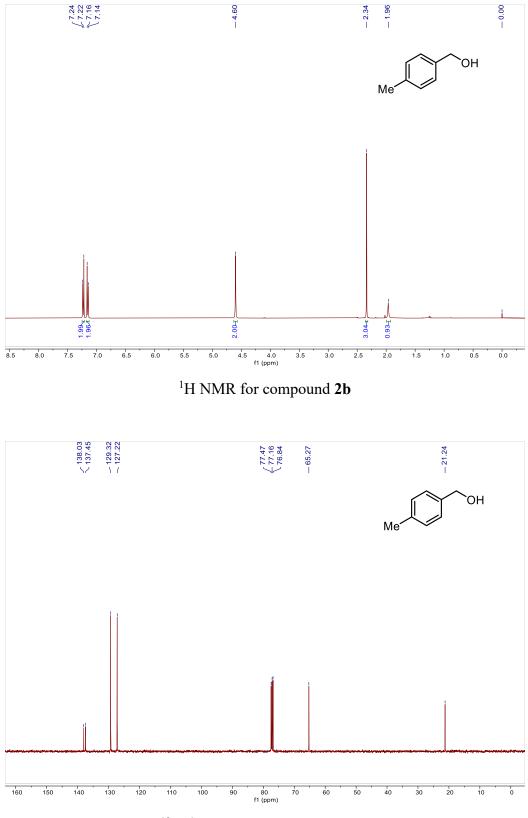
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 1u



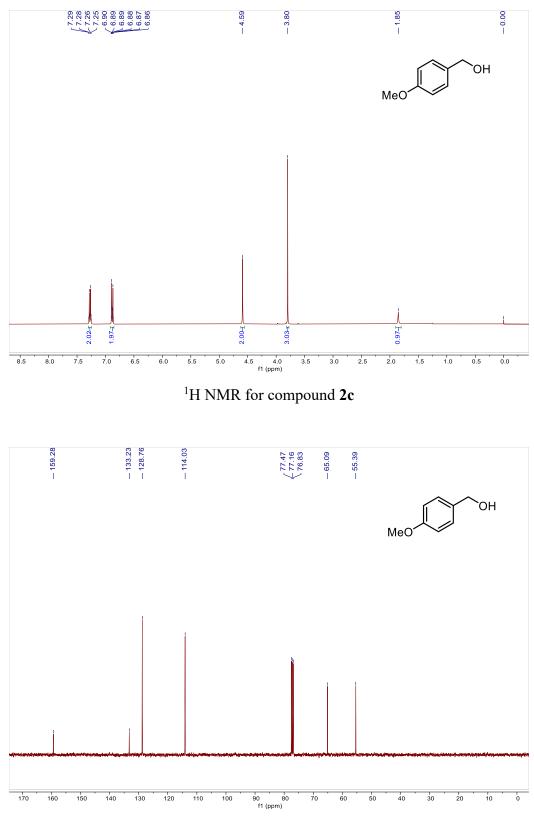
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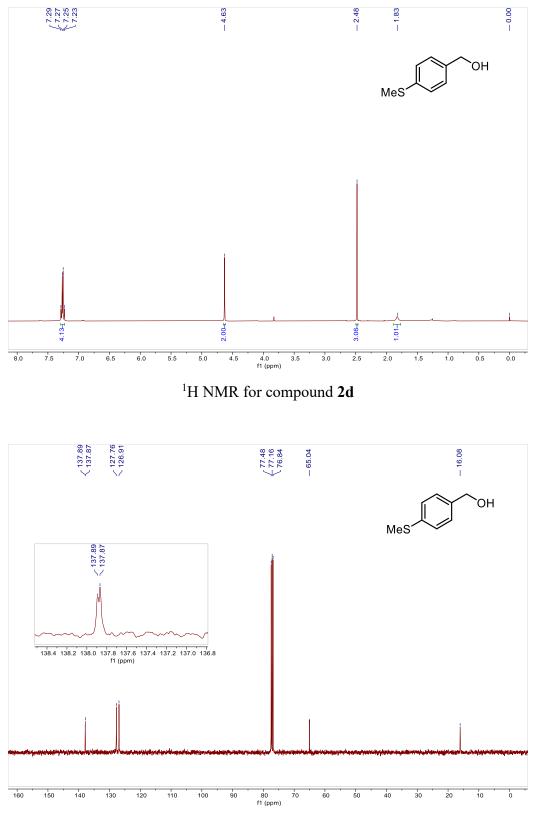
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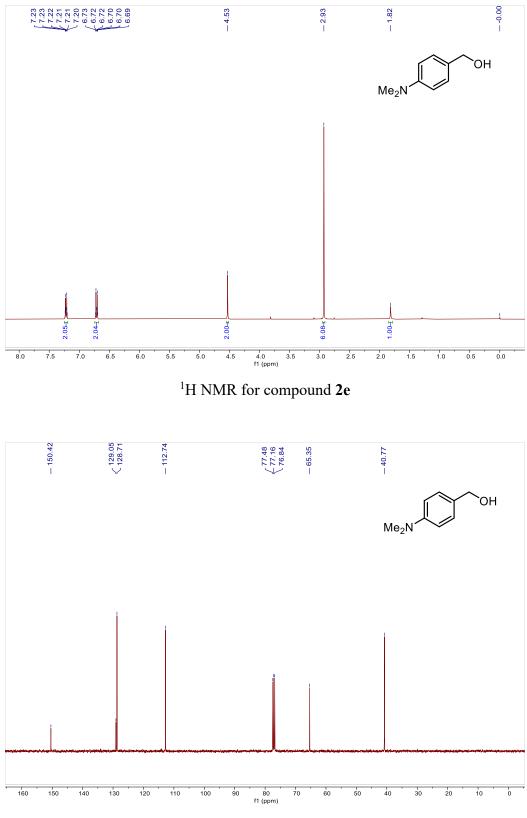
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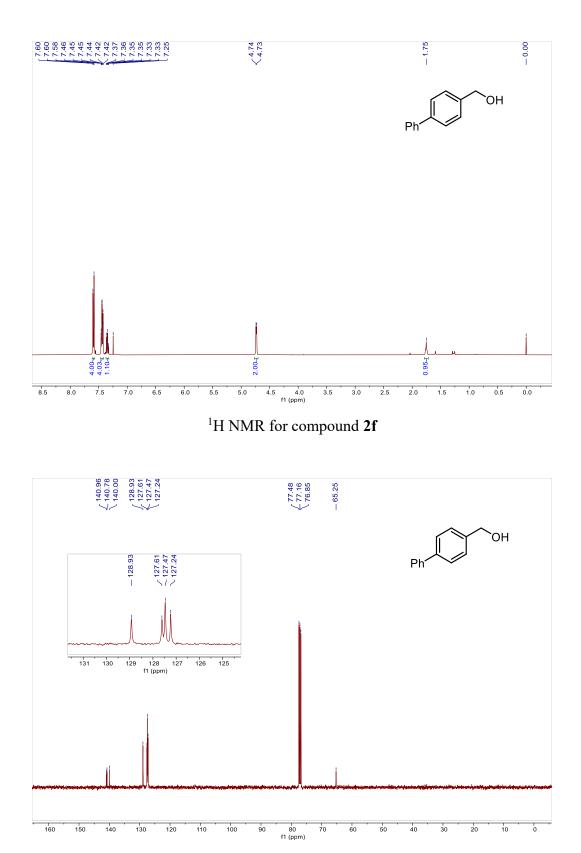
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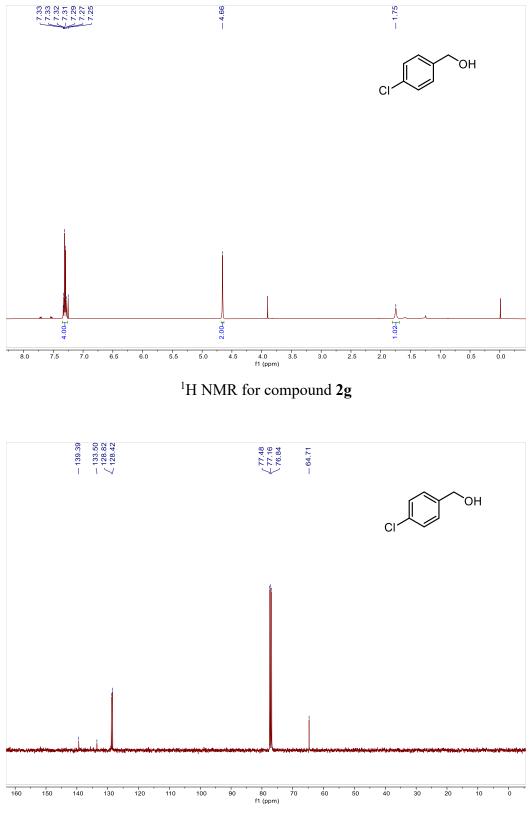
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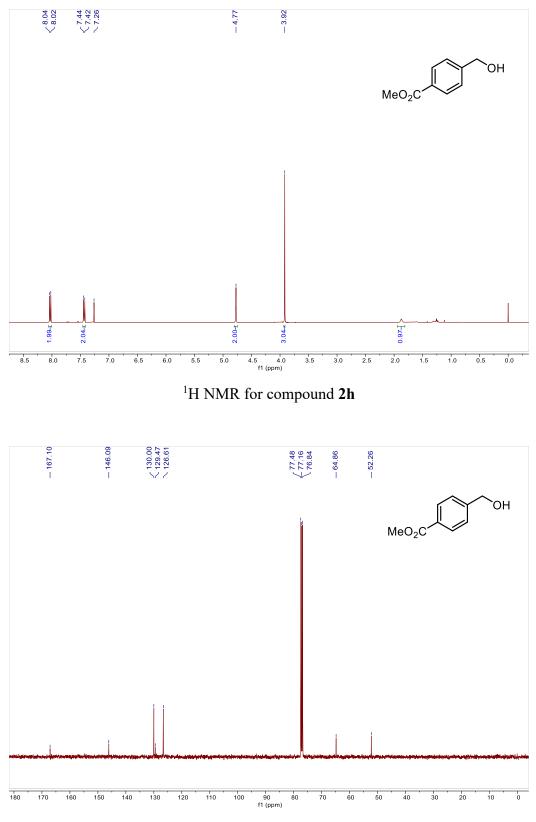
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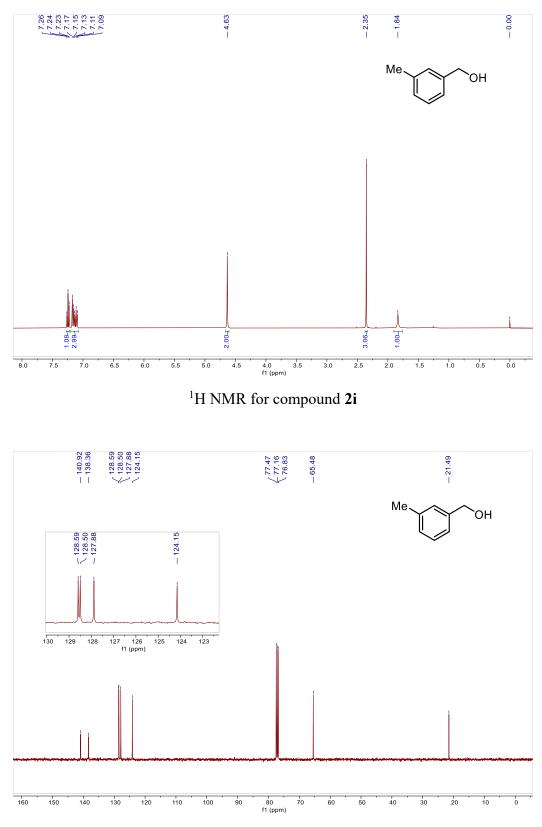
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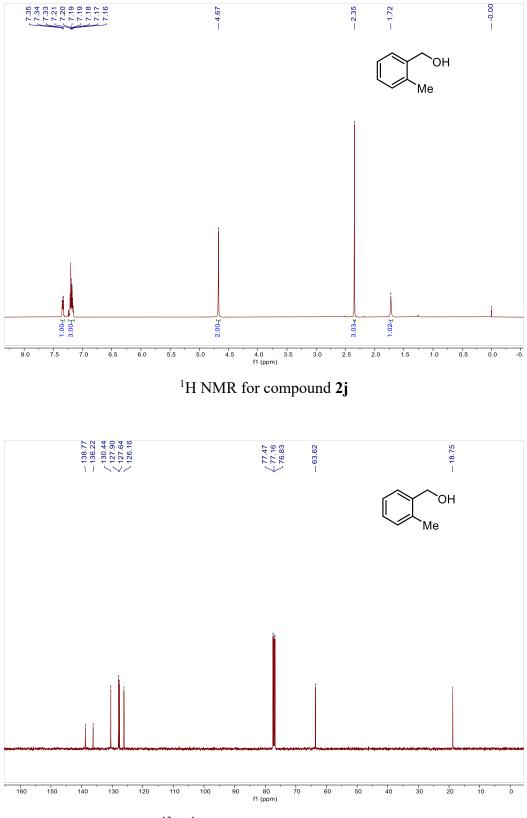
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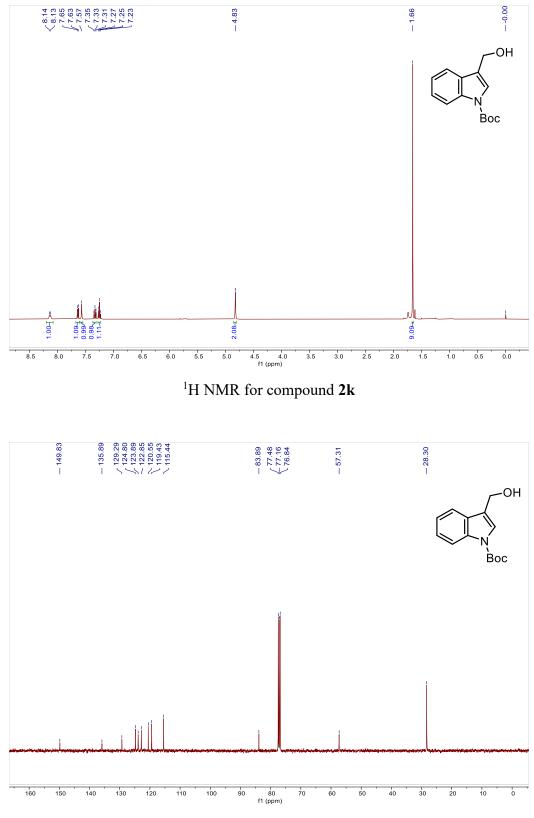
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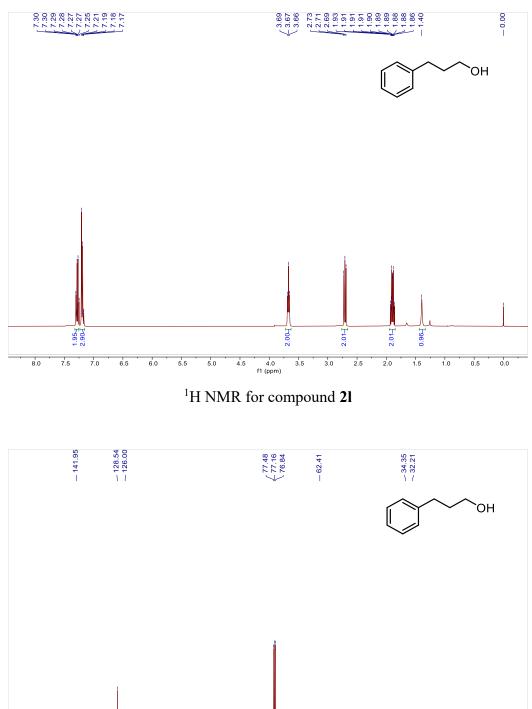
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2i



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2j

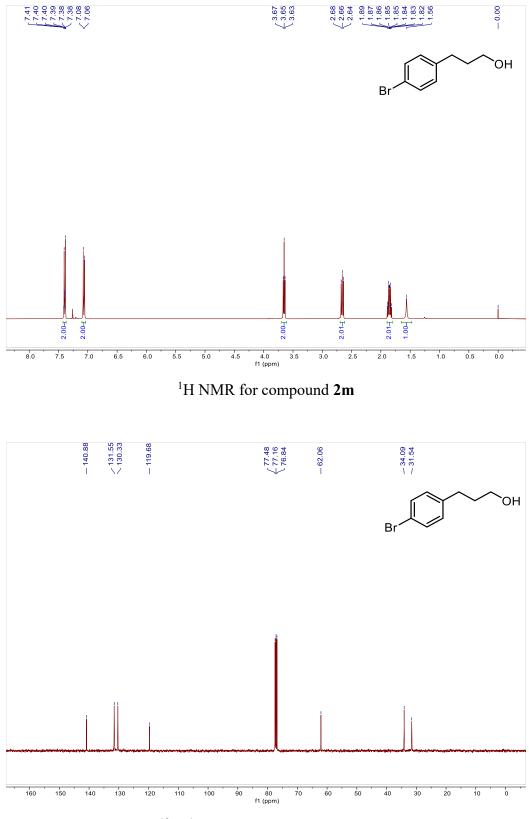


 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2k

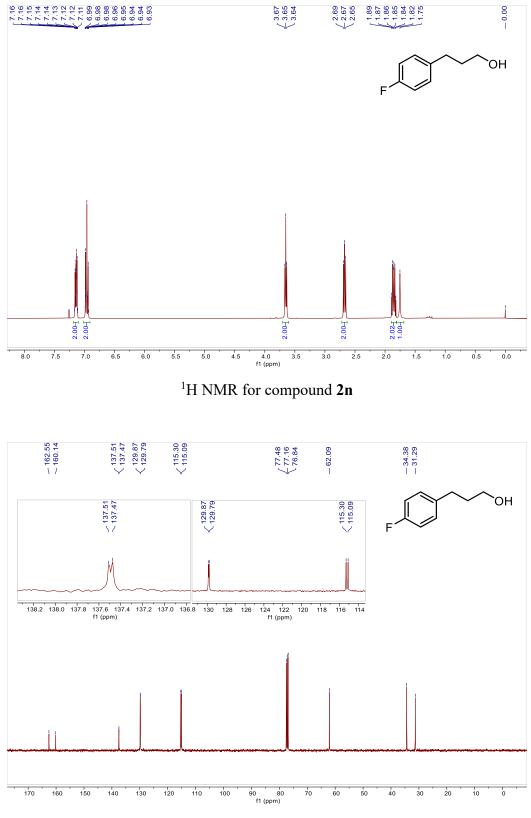


130 120 110 100 90 80 70 60 50 40 f1(ppm)

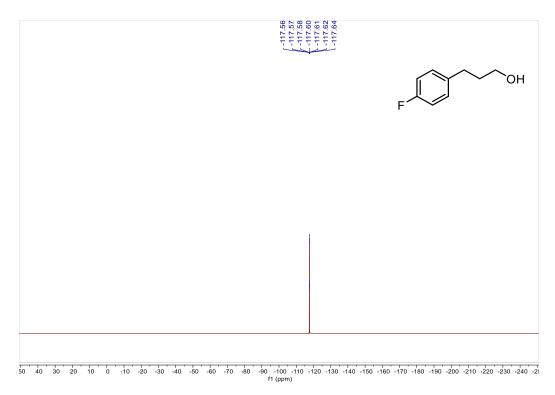
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound **21**



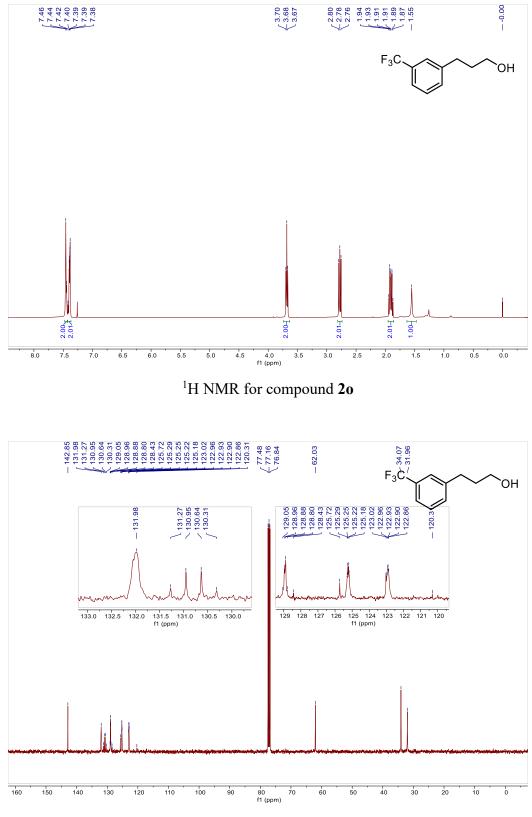
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2m



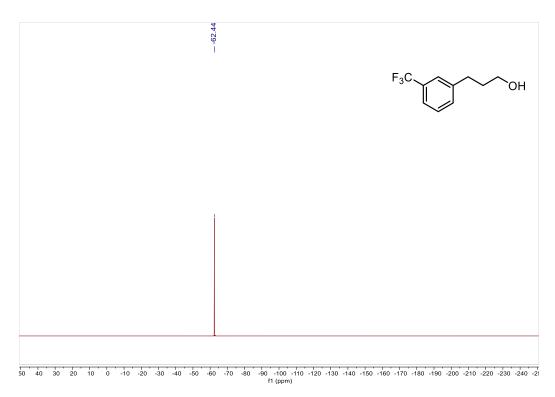
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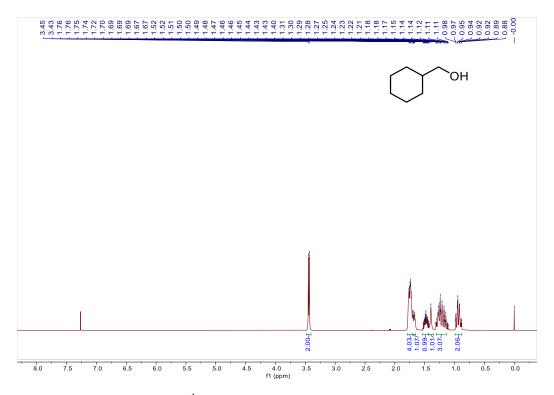
¹⁹F NMR for compound **2n**



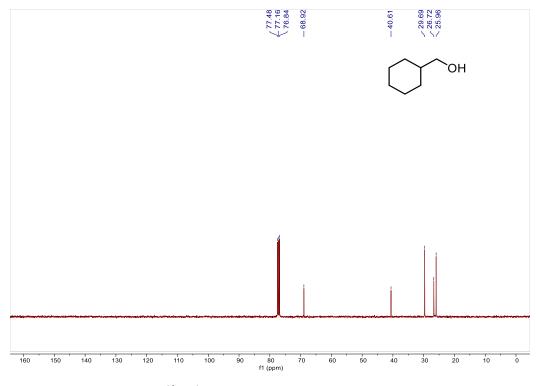
 $^{13}C\{^1H\}$ NMR for compound $\bf 2o$



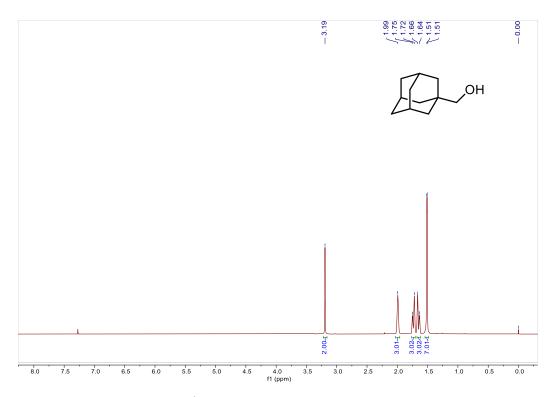
¹⁹F NMR for compound **20**



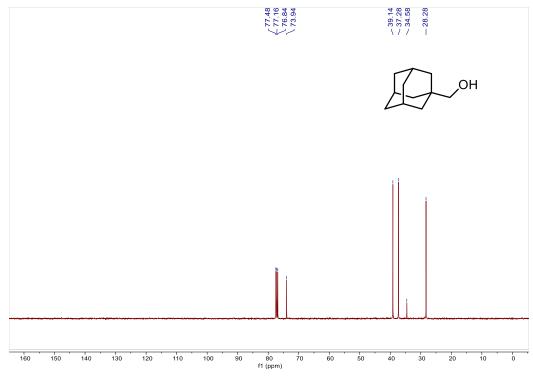
 1 H NMR for compound **2p**



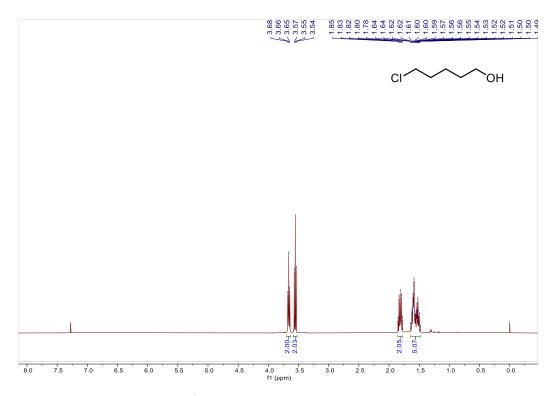
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound $\mathbf{2p}$



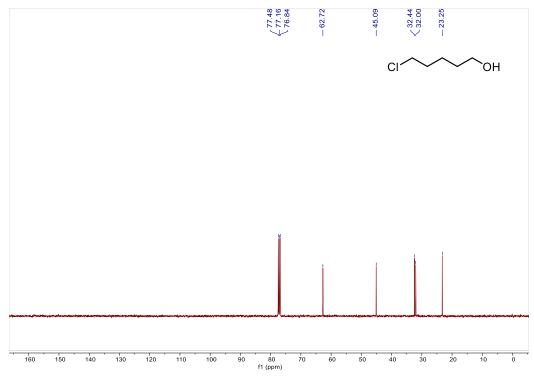
¹H NMR for compound **2**q



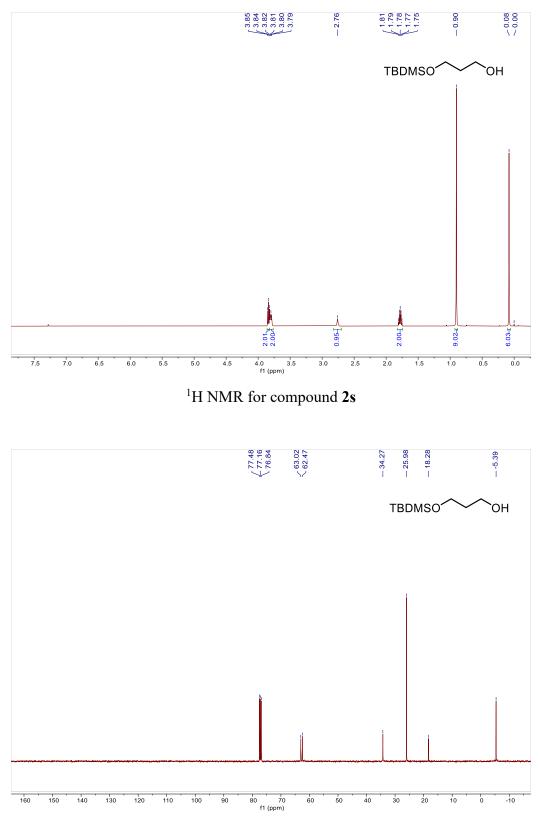
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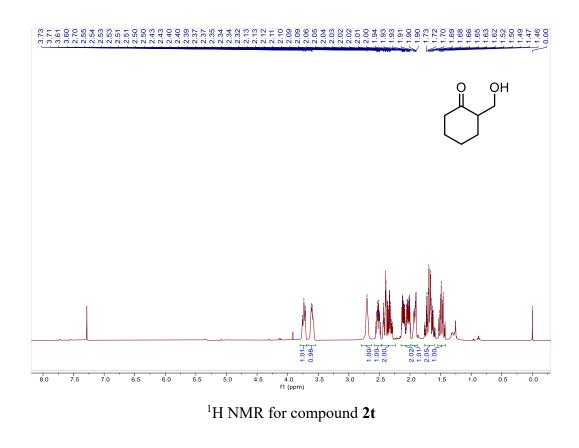
¹H NMR for compound 2r

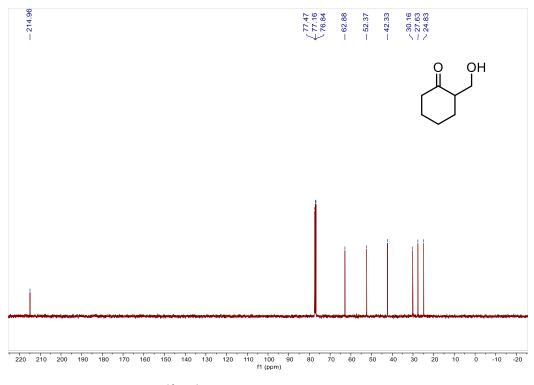


 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2r

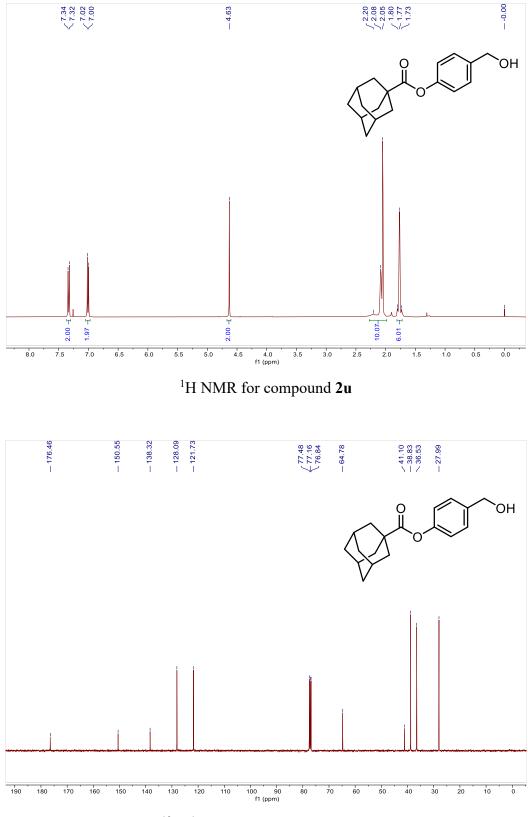


 $^{13}C\{^{1}H\}$ NMR for compound **2s**

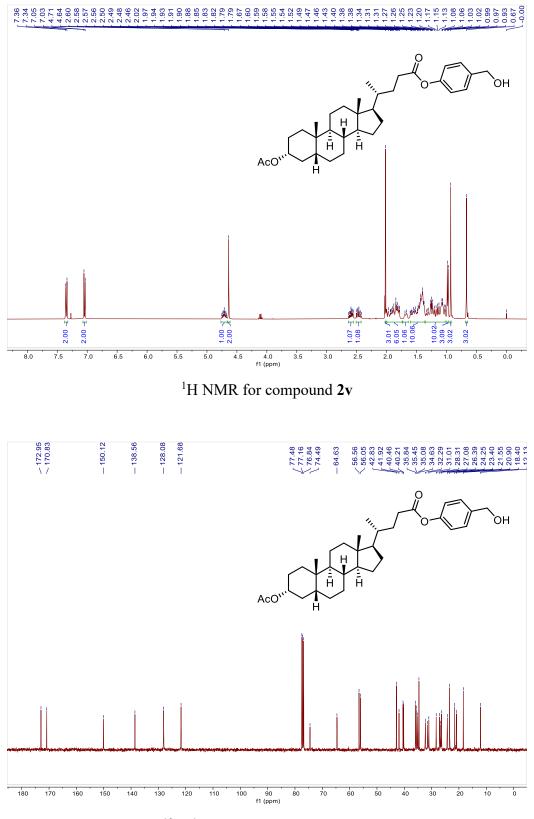




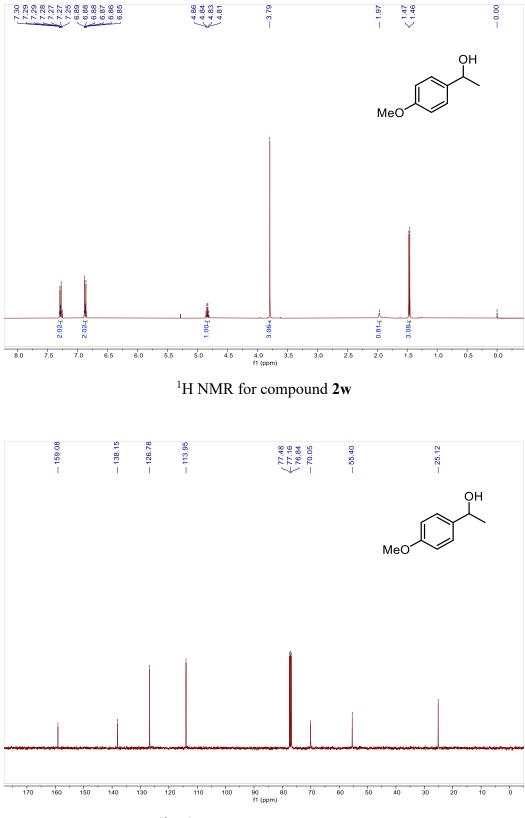
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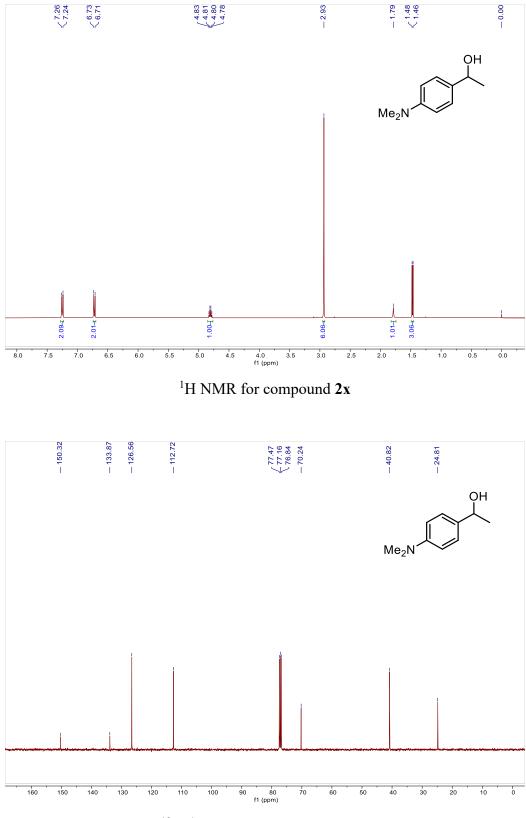
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2u



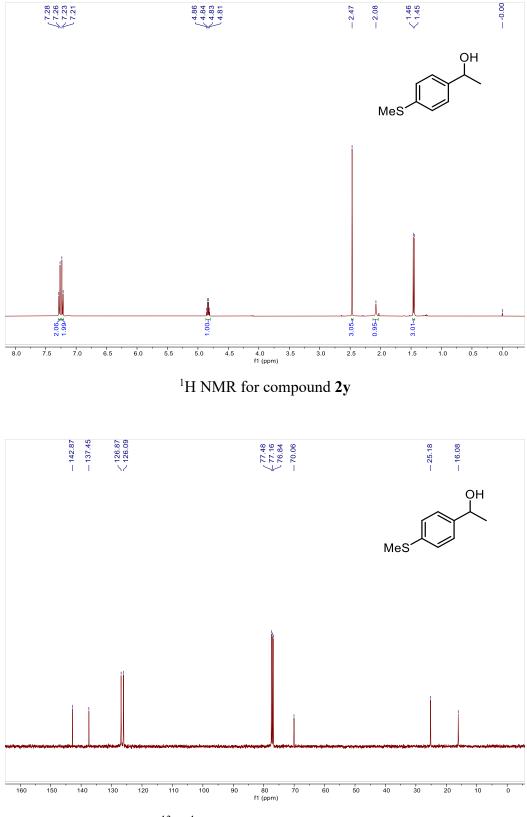
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2v



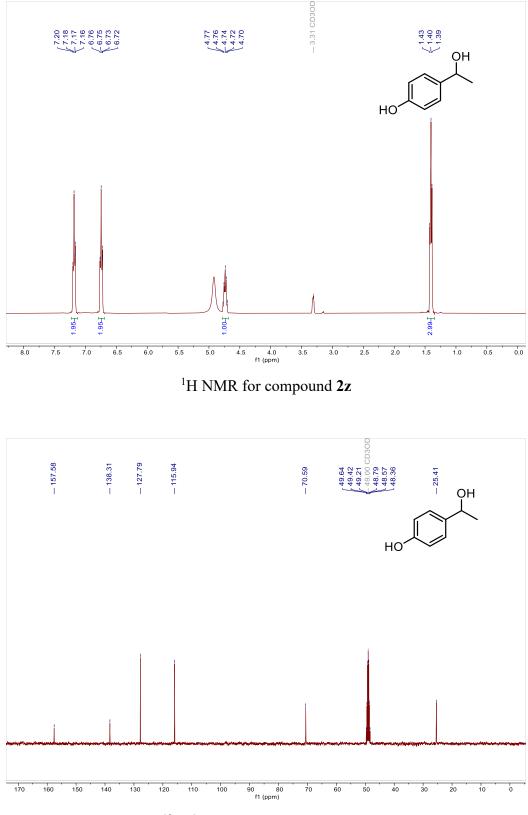
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2w



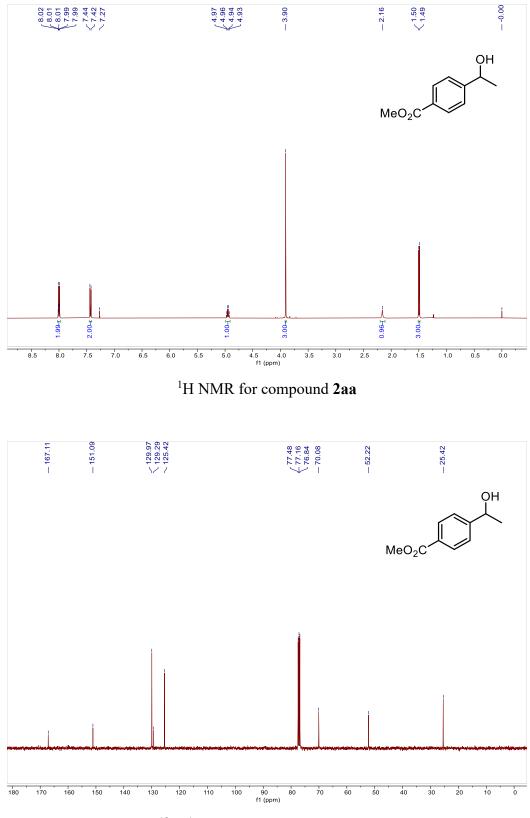
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2x



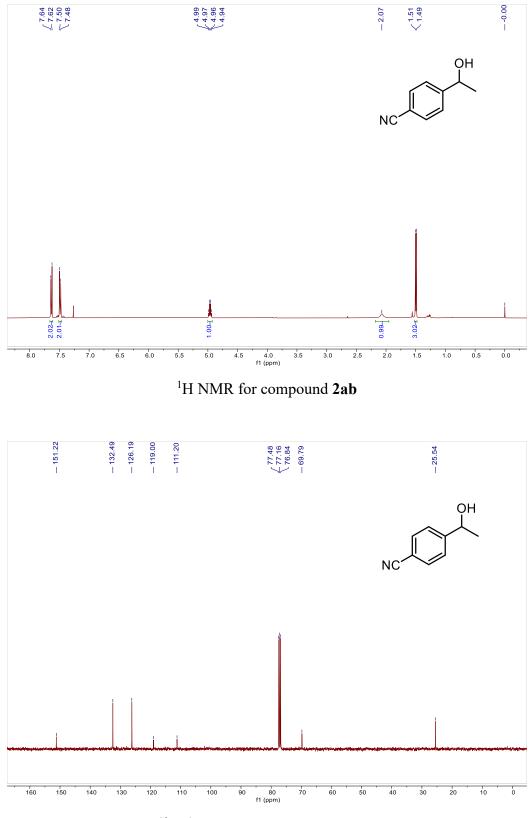
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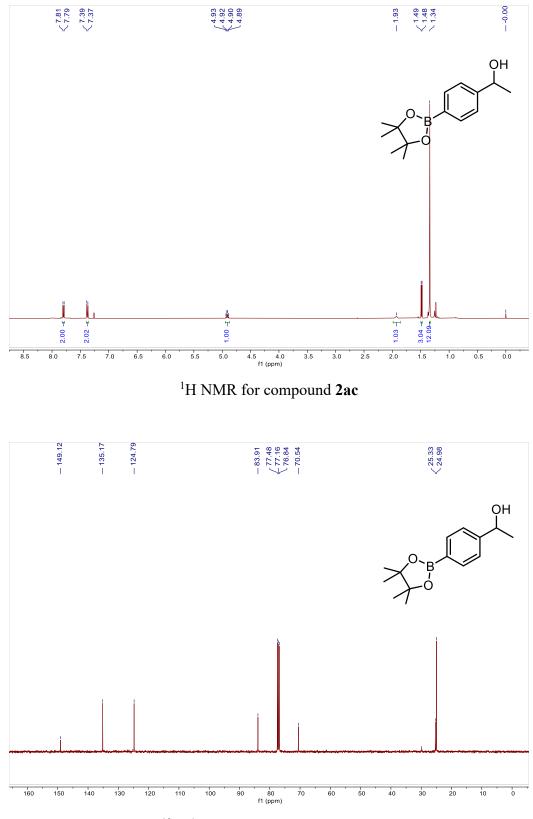
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2z



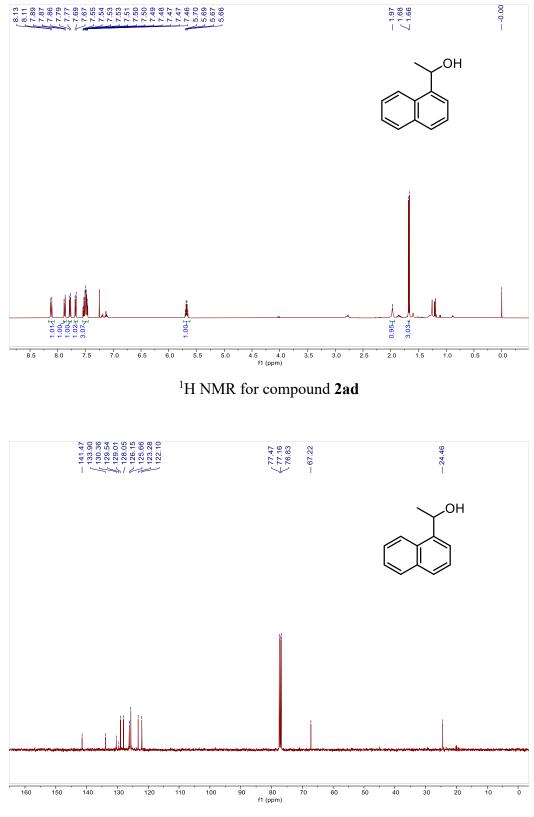
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound **2aa**



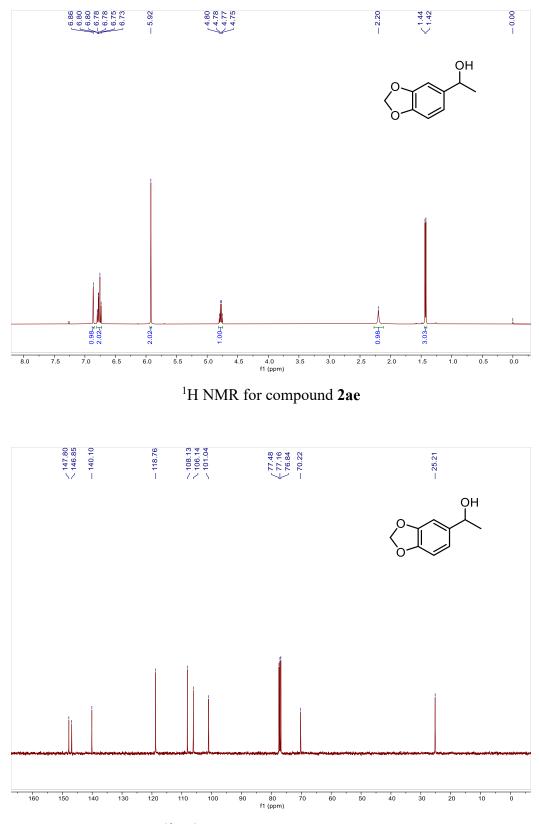
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound **2ab**



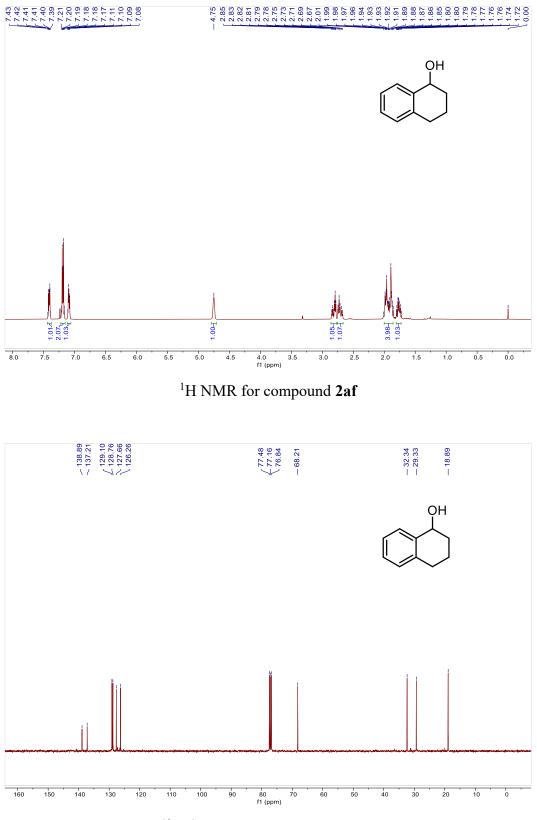
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound **2ac**



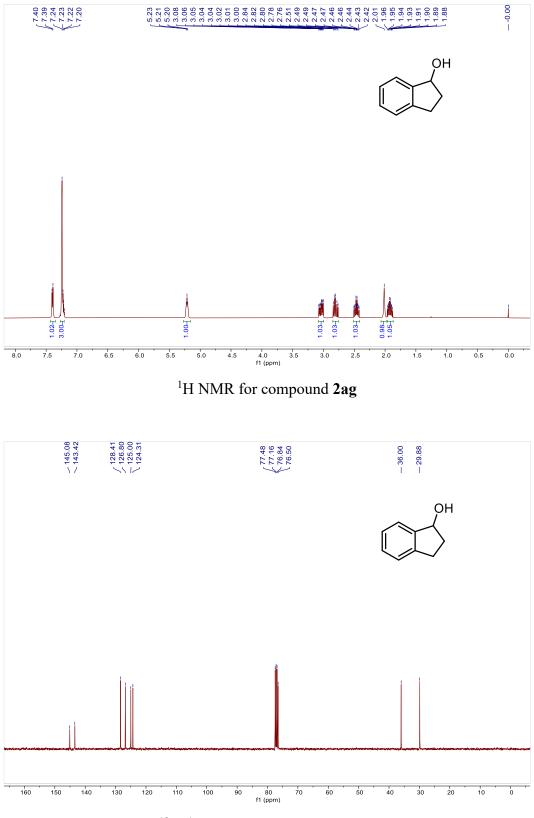
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound $\mathbf{2ad}$



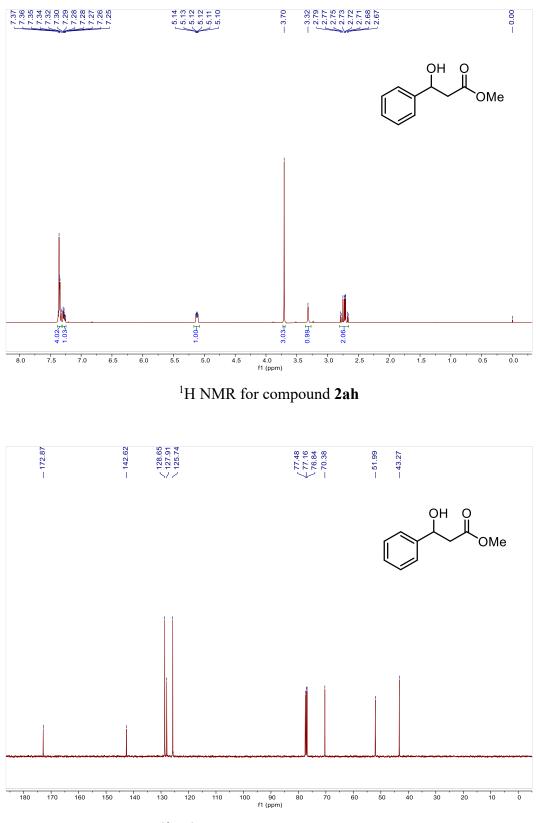
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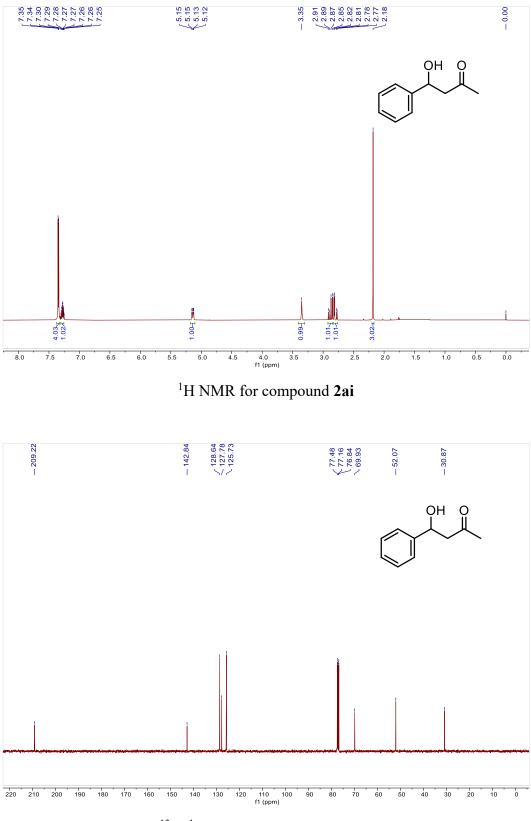
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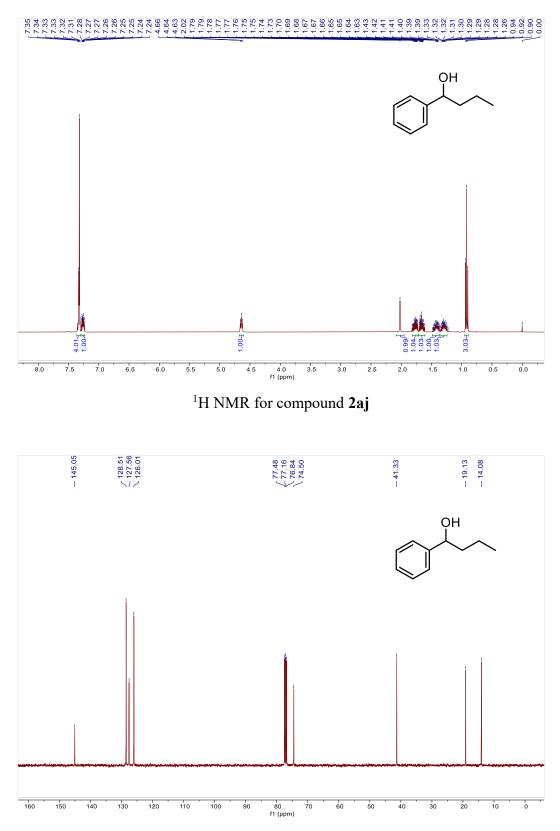
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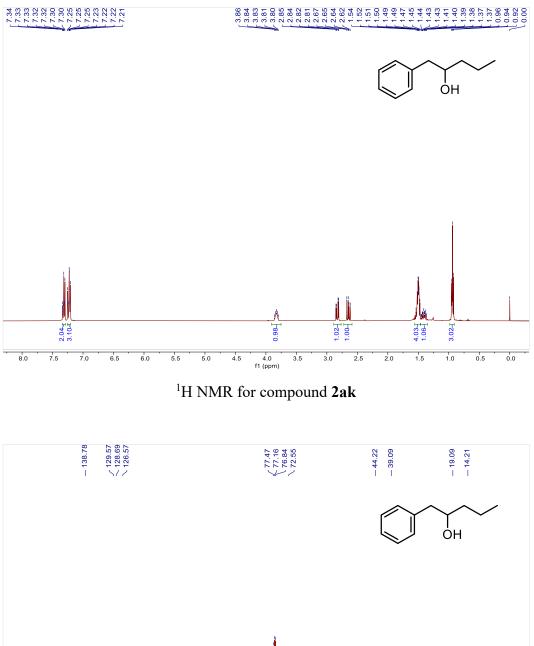
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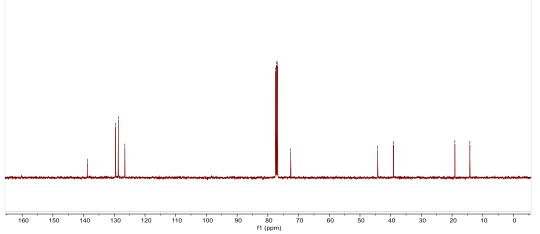


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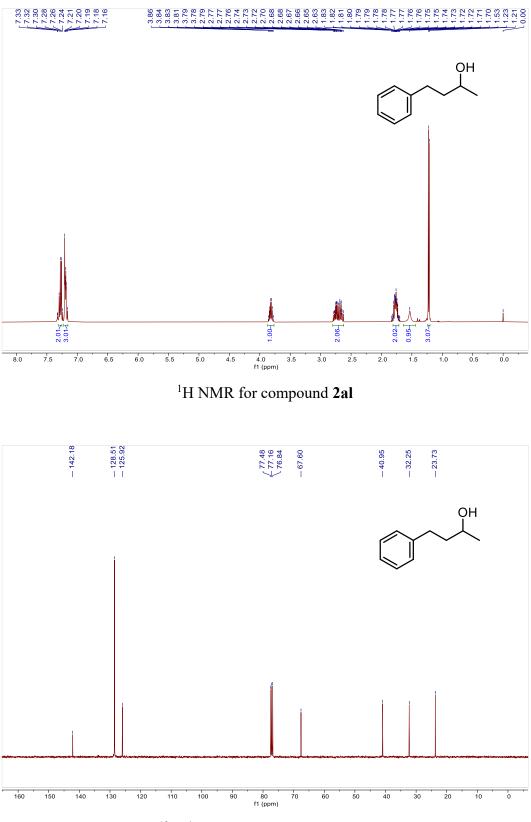


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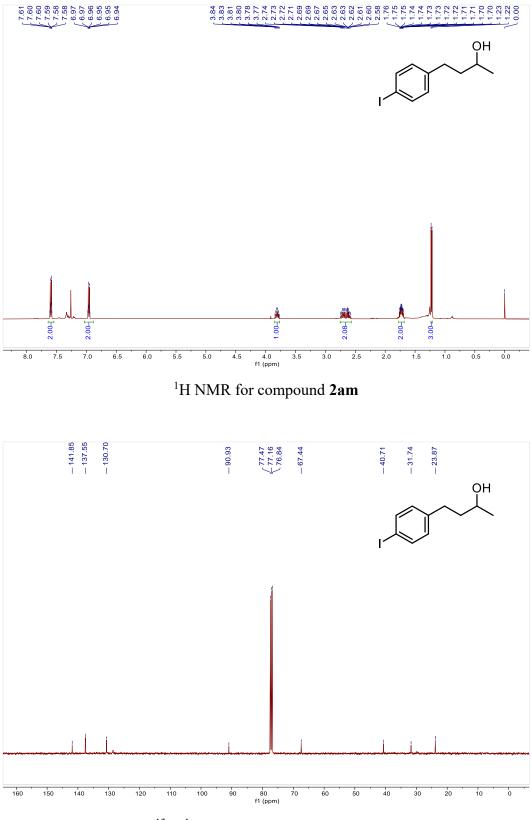




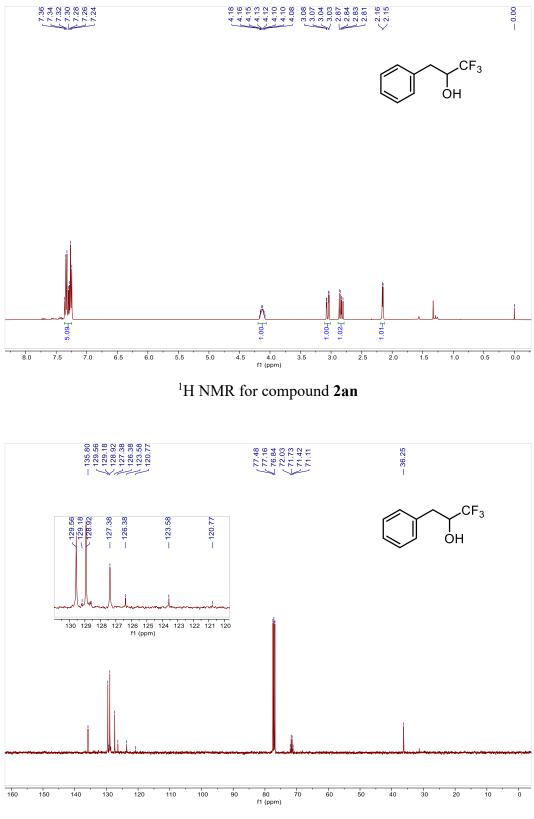
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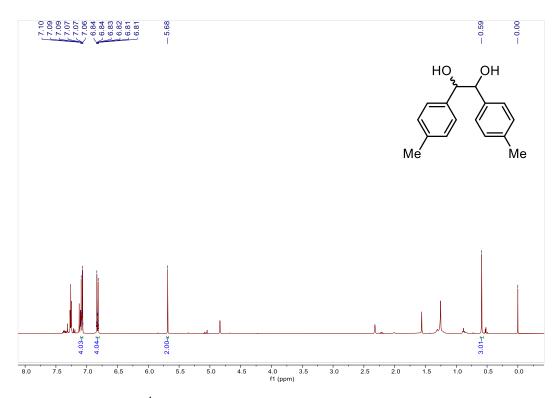
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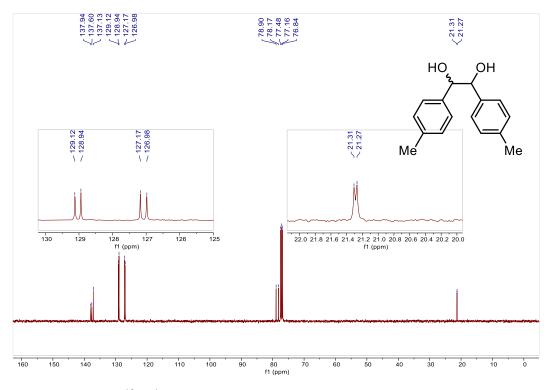
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 2am



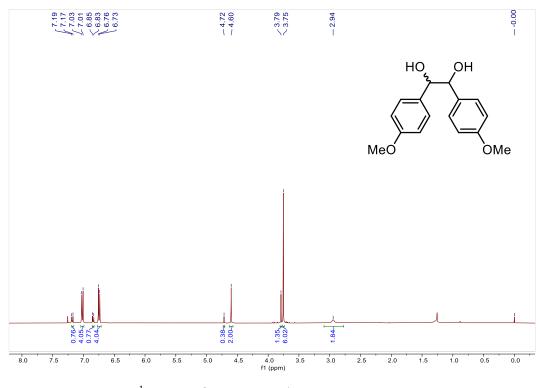
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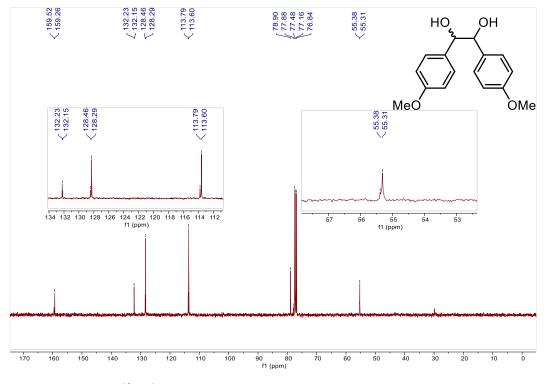
¹H NMR for compound **3a** (*dl* and *meso*)



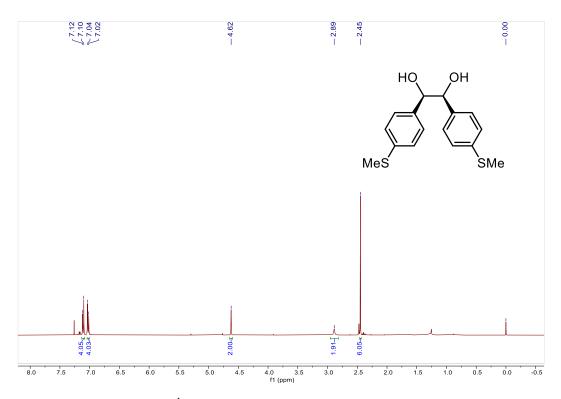
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound **3a** (*dl* and *meso*)



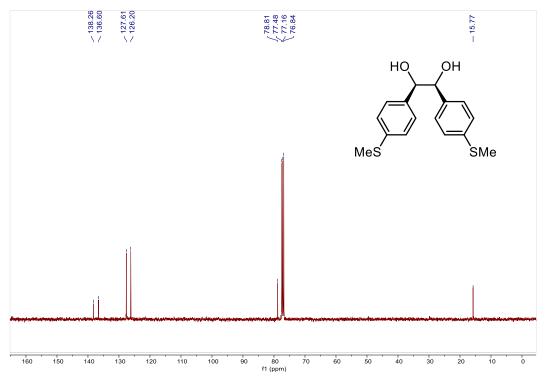
¹H NMR for compound **3b** (*dl* and *meso*)



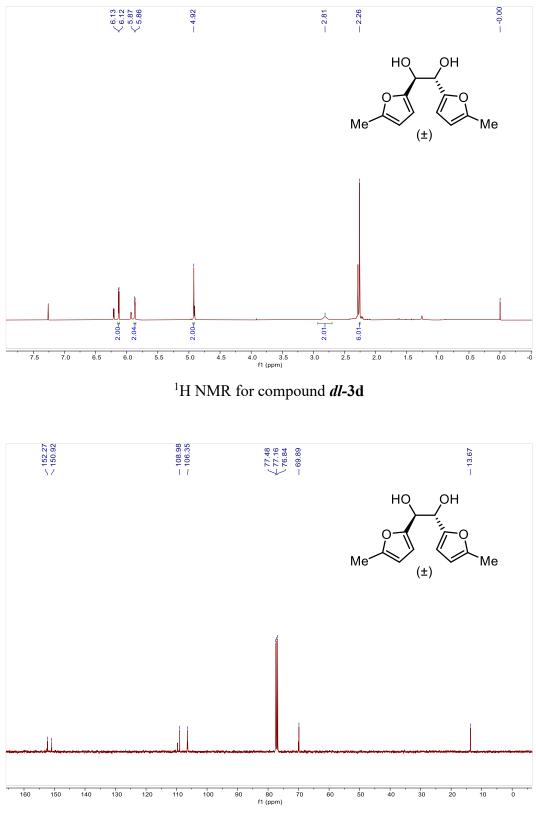
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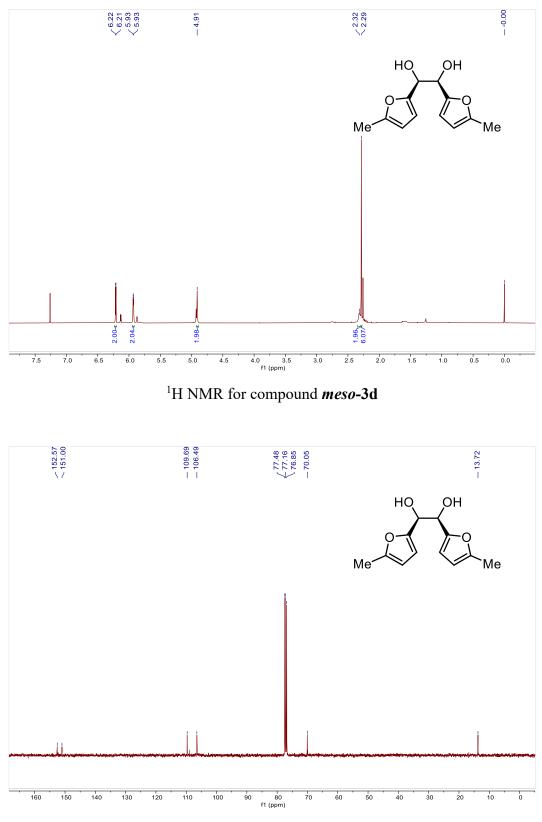
¹H NMR for compound *meso-*3c



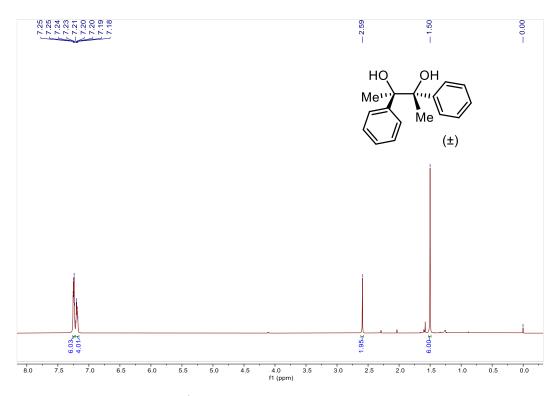
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound <code>meso-3c</code>



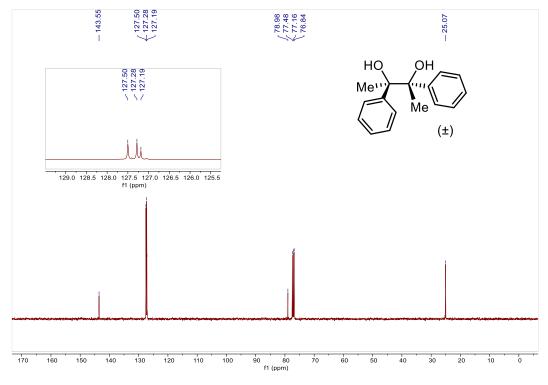
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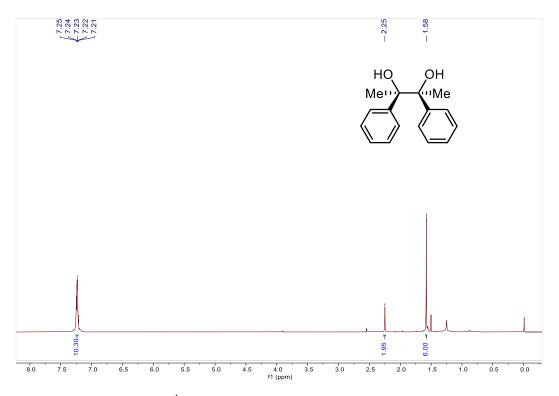
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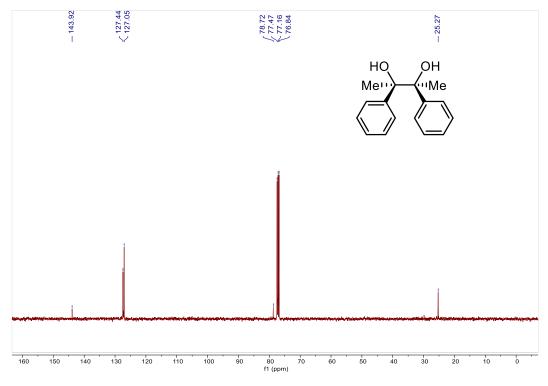
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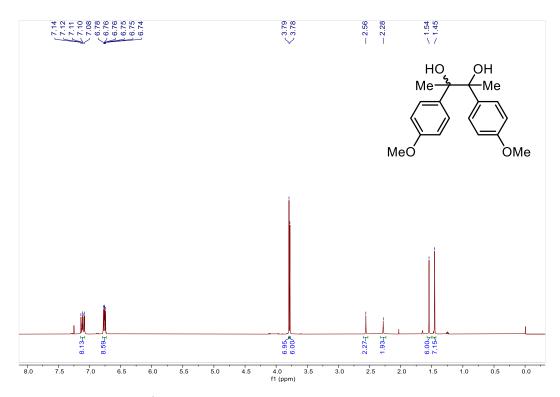
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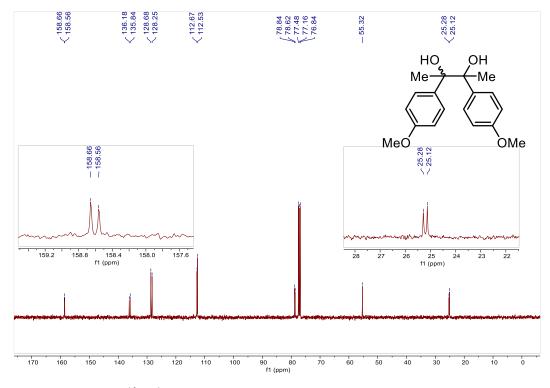
¹H NMR for compound *meso-3*e



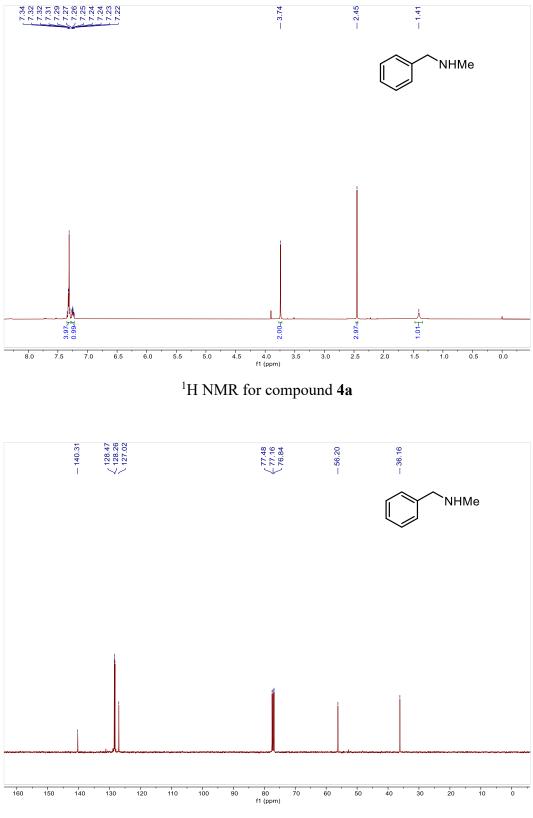
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound *meso-3e*



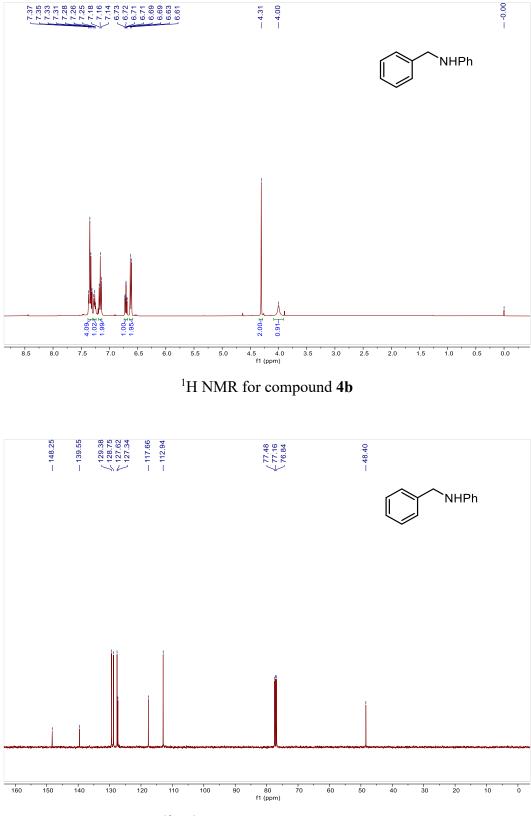
¹H NMR for compound **3f** (*dl* and *meso*)



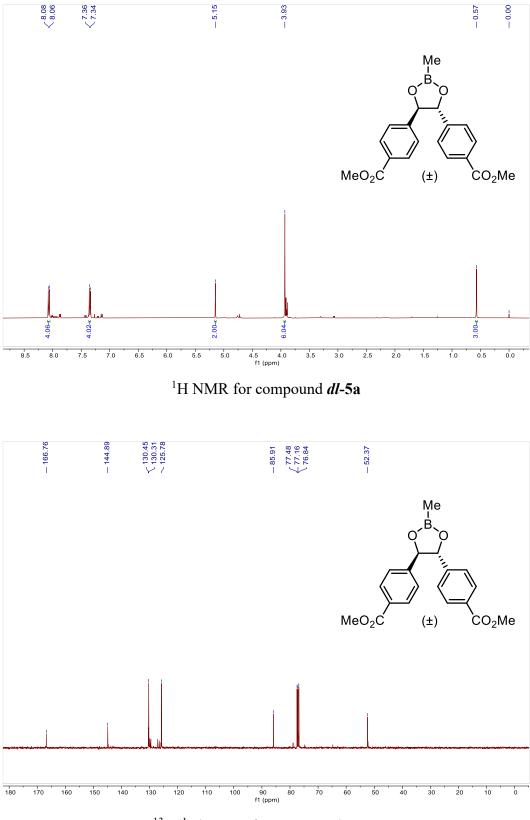
 $^{13}C\{^{1}H\}$ NMR for compound **3f** (*dl* and *meso*)



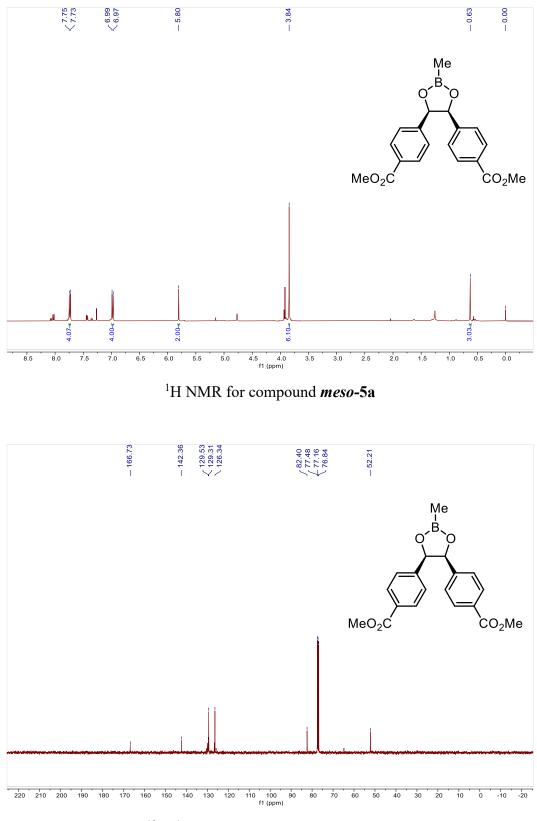
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound 4a



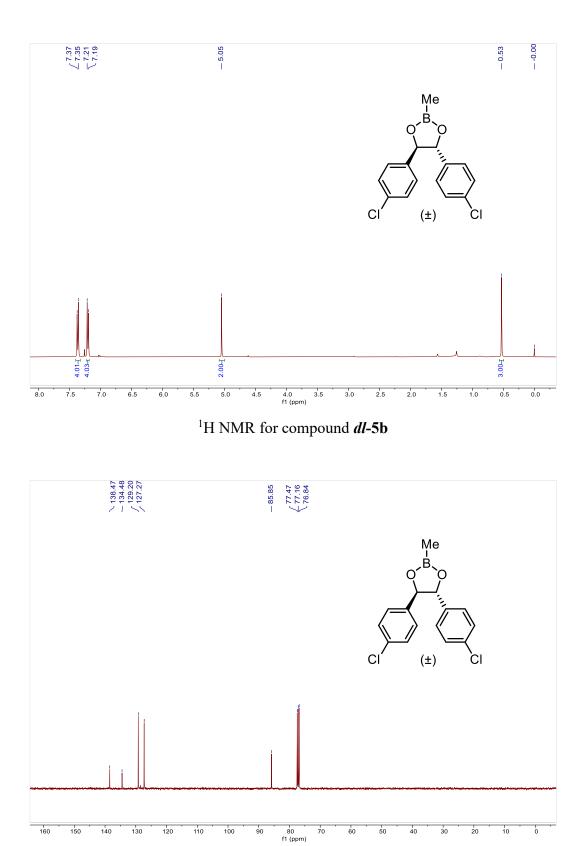
 $^{13}C\{^{1}H\}$ NMR for compound $\boldsymbol{4b}$



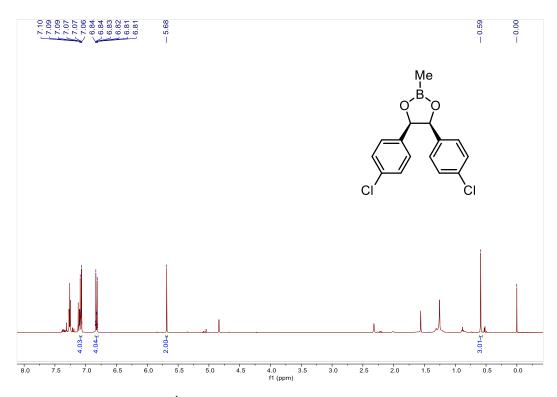
¹³C{¹H} NMR for compound *dl*-5a



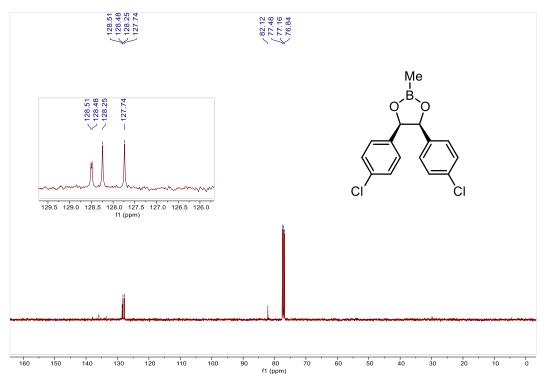
 $^{13}C\{^{1}H\}$ NMR for compound *meso-5*a



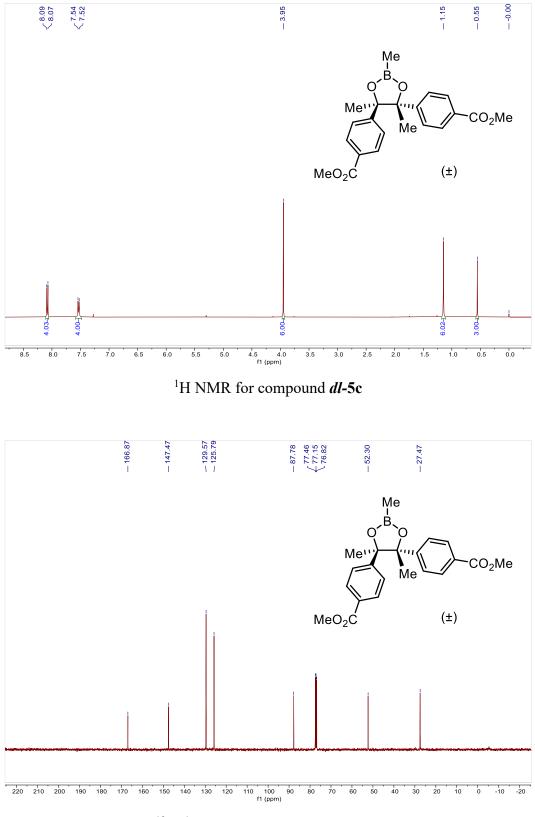
¹³C{¹H} NMR for compound *dl*-5b



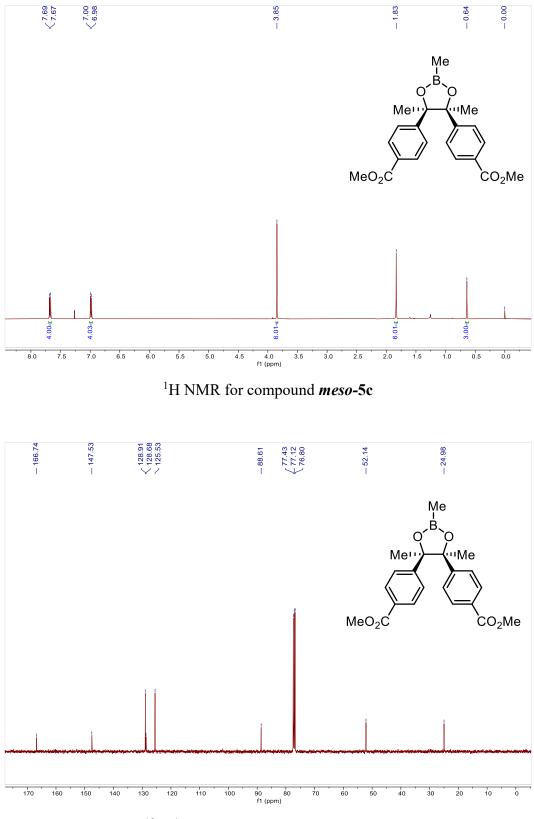
¹H NMR for compound *meso-5*b



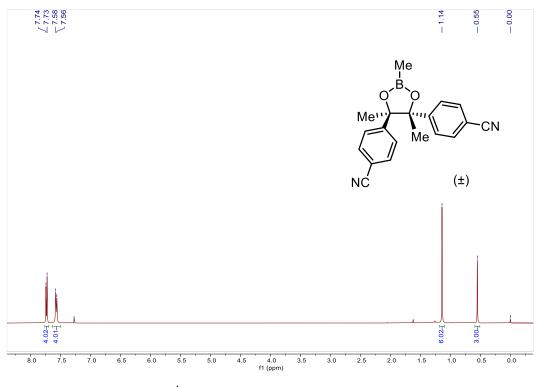
 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound meso-5b



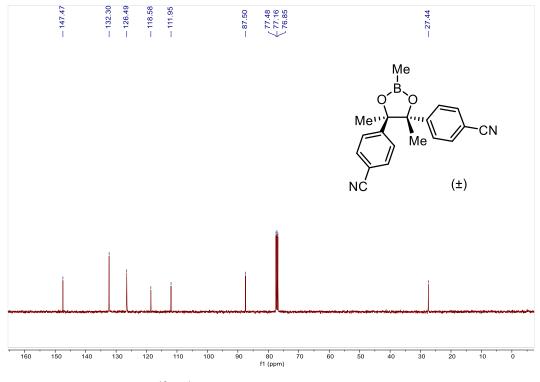
 $^{13}C{^{1}H}$ NMR for compound *dl*-5c



 $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR for compound *meso-5*c



¹H NMR for compound *dl*-5d



¹³C{¹H} NMR for compound *dl*-5d

