

## Supporting Information

### Iodine Catalysed Transfer Hydrogenation of Carbon–Carbon $\sigma$ -Bond with Water

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## Computation and Isolobal Analogy

Figure S1 illustrates the computed SOMO of iodine radical and  $\text{Rh}^{\text{II}}(\text{ttp})$  (ttp = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion) metalloradical using Hartree Fock method with the LanL2DZ basis set in the gaseous state.

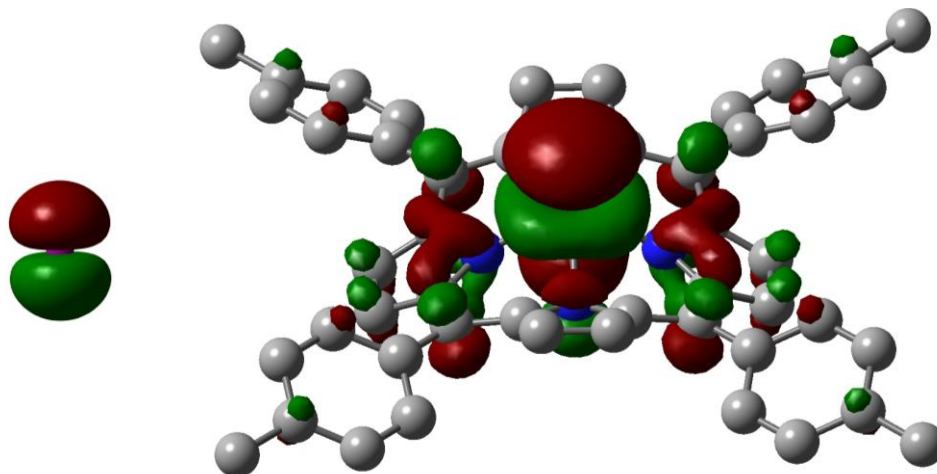
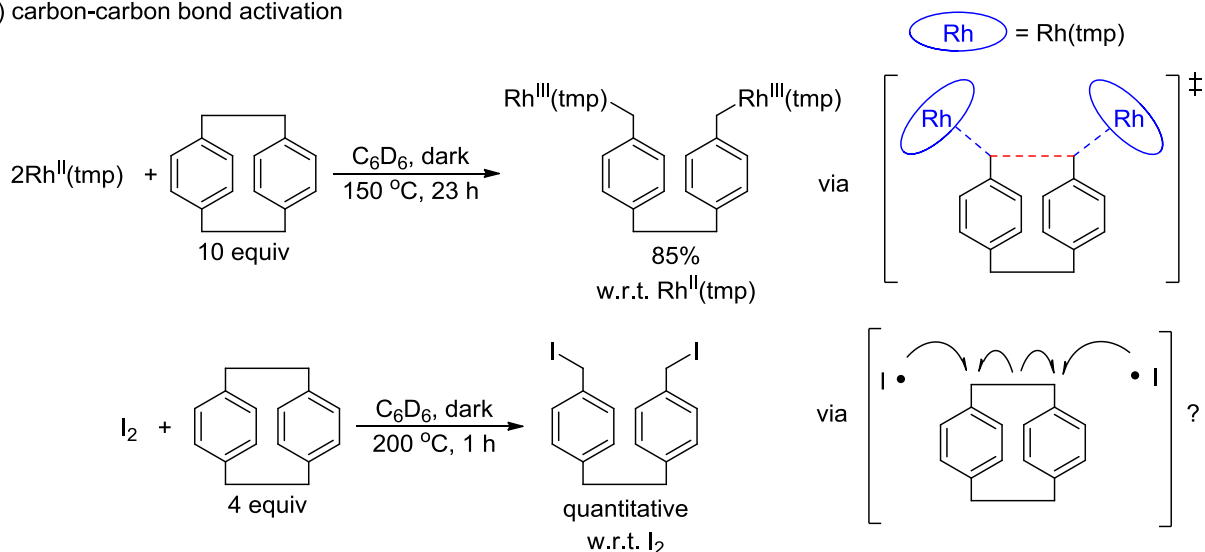


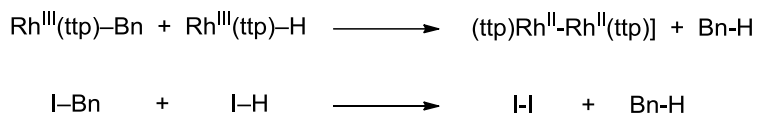
Figure S1. Computed SOMO for Iodine Radical (Left) and  $\text{Rh}^{\text{II}}(\text{ttp})$  Metalloradical (Right). Hydrogen Atoms are Omitted for Clarity.

The iodine radical may exhibit similar reactivity with the established reactivity of the isolobal  $d^7$   $\text{Rh}^{\text{II}}(\text{ttp})$  metalloradical, e.g. bi-metalloradical carbon-carbon bond activation (Scheme S1a) and bi-molecular C-H reductive elimination (Scheme S1b).<sup>1</sup> The BDEs of iodine and  $\text{Rh}(\text{ttp})$  species are shown in Table S1 and a similar trend is found.

(a) carbon-carbon bond activation



(b) C-H reductive elimination



Scheme S1. Similar Reactivity Patterns between Iodine Radical and Rhodium(II) Metalloporphyrin Radical Species.

Table S1. BDE of I-X Bonds and Rh(ttp)-X Bonds.<sup>2</sup>

bond	BDE (kcal/mol)	
	X = I	X = Rh <sup>III</sup> (ttp)
X-H	71.3	60
X-Me	57.1	54.3
X-OH	51.0	38 <sup>3</sup>
X-Bn	44.9	37.1
X-X	36.4	12

## Experimental Section

Unless otherwise specified, all reagents were purchased from commercial suppliers and directly used without further purification. Benzene- $d_6$  was distilled over sodium under nitrogen. Hexane for chromatography was distilled from anhydrous calcium chloride. Silica gel (Merck, 70–230 and 230–400 mesh) was used for column chromatography in air. Thin-layer chromatography (TLC) was performed on pre-coated silica gel 60 F254 plates. For the reaction conducted in a sealed NMR tube, the mixture was degassed by three freeze (77 K)–pump (0.005 mmHg)–thaw cycles, and then flame-sealed under vacuum, heated in oven in dark and wrapped with aluminum foil to protect from exposure to room light before  $^1\text{H}$  and  $^{13}\text{C}$  NMR measurements. The typical [PCP] employed in sealed NMR tube reaction is 8.9 mM unless otherwise specified. The NMR yields were with benzene residue as the internal standard. Benzene- $d_6$  stock solutions of [2.2]paracyclophane (10 mM and iodine were prepared separately and transferred to the reaction vessel using gas-tight syringe.

$^1\text{H}$  NMR spectra were recorded on a Bruker AV400 (400 MHz). Chemical shifts are reported with reference to the residual solvent protons in  $\text{C}_6\text{D}_6$  ( $\delta$  7.15 ppm) or in  $\text{CDCl}_3$  ( $\delta$  7.26 ppm) as the internal standard. Coupling constants ( $J$ ) are reported in hertz (Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AV400 (100 MHz) or Bruker AV700 (175 MHz) spectrometer and referenced to  $\text{CDCl}_3$  ( $\delta$  77.1 ppm) or  $\text{C}_6\text{D}_6$  ( $\delta$  128.1 ppm). High-resolution mass spectrometry (HRMS) was performed on a Bruker Solarix 9.4 Tesla FTICR MS / Thermofinnigan MAT 95 XL instrument in electrospray ionization (ESI) mode using  $\text{MeOH}/\text{CH}_2\text{Cl}_2$  (1/1) as the solvent.

## Preparation of Stock Solutions

**Stock Solution of PCP.** PCP (10.5 mg, 0.050 mmol) was dissolved in 5.0 mL C<sub>6</sub>D<sub>6</sub> to give a 10.0 mM PCP solution.

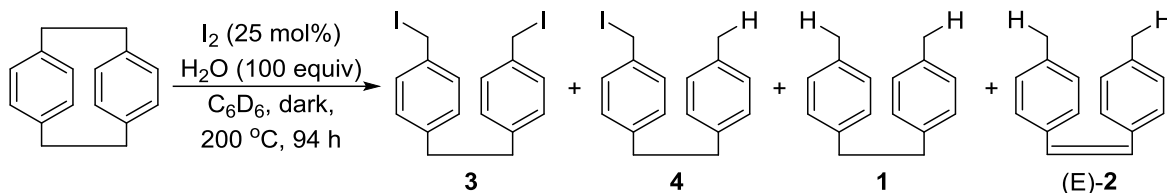
**Stock Solution of Iodine.** I<sub>2</sub> (10.0 mg, 0.039 mmol) was dissolved in 2.0 mL C<sub>6</sub>D<sub>6</sub> to give a 19.7 mM I<sub>2</sub> solution.

## Catalyst Loading Effect

**The Sealed NMR Tube Reaction between PCP and Water with 10 mol% of I<sub>2</sub>.** H<sub>2</sub>O (7.5 μL, 0.42 mmol), iodine stock solution (20 μL, 0.0004 mmol), PCP stock solution (400 μL, 0.0040 mmol) and 40 μL of C<sub>6</sub>D<sub>6</sub> were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 140 h, PCP was consumed to give **1** and **2** in 62%, 34% yields, respectively.

**The Sealed NMR Tube Reaction between PCP and Water with 25 mol% of I<sub>2</sub>.** H<sub>2</sub>O (7.5 μL, 0.42 mmol), iodine stock solution (50 μL, 0.0010 mmol) and PCP stock solution (400 μL, 0.0040 mmol) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 94 h, PCP was consumed to give **1** and **2** in 60%, 38% yields, respectively (Table S2, eq S1, Figure S2). The color of the reaction mixture turned from the characteristic reddish color of I<sub>2</sub> to colorless, and finally back to reddish (Figure S3).

Table S2. Reaction Time Profile of I<sub>2</sub> (25 mol%) Catalyzed Transfer Hydrogenation of PCP.



time / h	NMR yield / %					total organic
	PCP	di-iodo intermediate <b>3</b>	mono-iodo intermediate <b>4</b>	<b>1</b>	<b>2</b>	
0	100	0	0	0	0	100
1	65	31	0	0	0	96
7	65	31	0	0	0	97
23	46	21	18	8	3	97
49	20	15	26	26	8	96
69	1	1	8	56	31	97
94	0	0	0	60	38	98

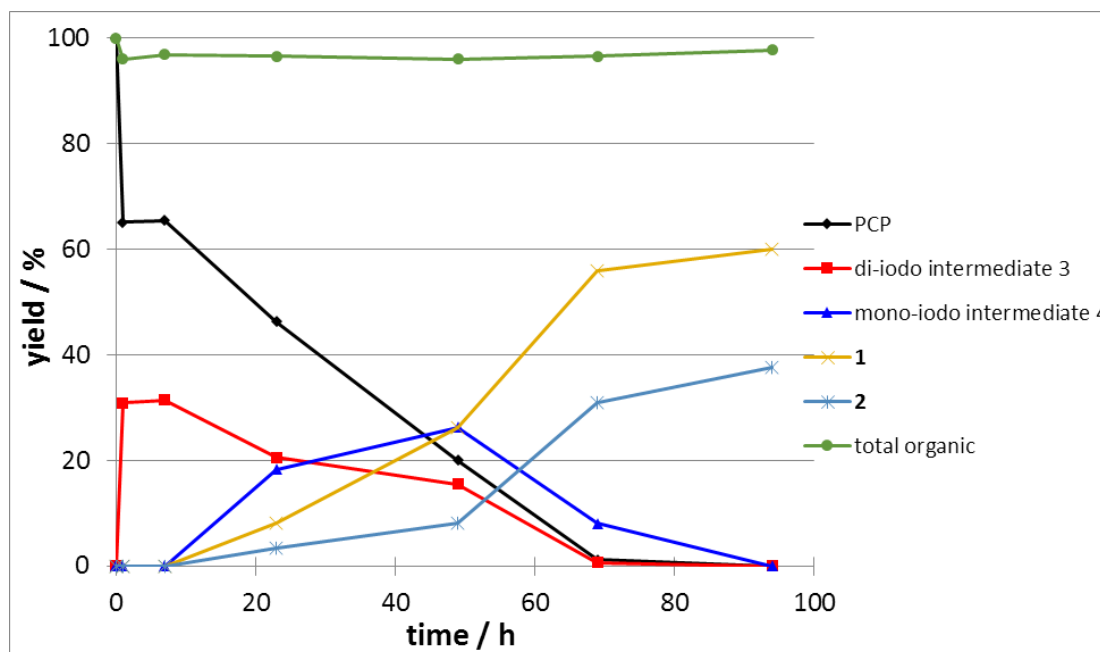


Figure S2. Reaction Time Profile of I<sub>2</sub> (25 mol%) Catalyzed Transfer Hydrogenation of PCP.

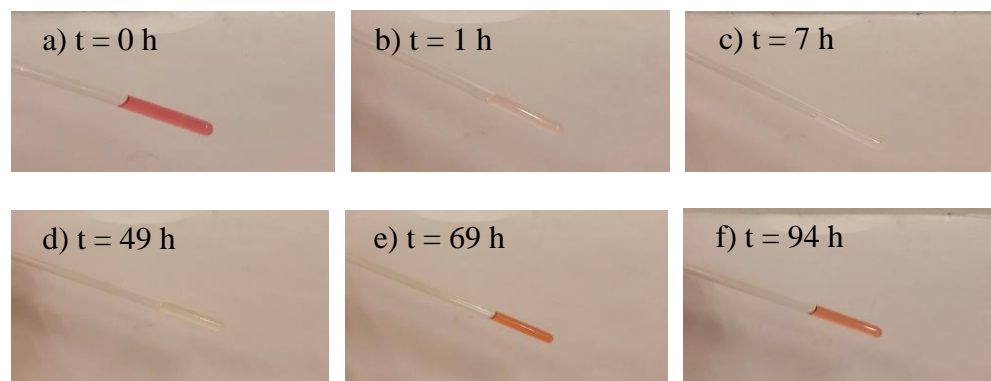
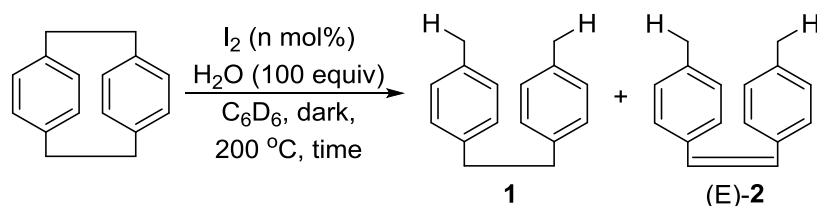


Figure S1. Color of reaction mixture at specific time interval.

**The Sealed NMR Tube Reaction between PCP and Water with 50 mol% of I<sub>2</sub>.** Iodine (4.7 mg, 0.019 mmol) stock solution in 0.5 mL C<sub>6</sub>D<sub>6</sub> was prepared. H<sub>2</sub>O (7.5 μL, 0.42 mmol), iodine stock solution (50 μL, 0.0019 mmol) and PCP stock solution (400 μL, 0.0040 mmol) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 180 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 72 h, PCP was consumed to give **1** and **2** in 48%, 40% yields, respectively.

Table S3. Catalyst Loading Effect of PCP Hydrogenation



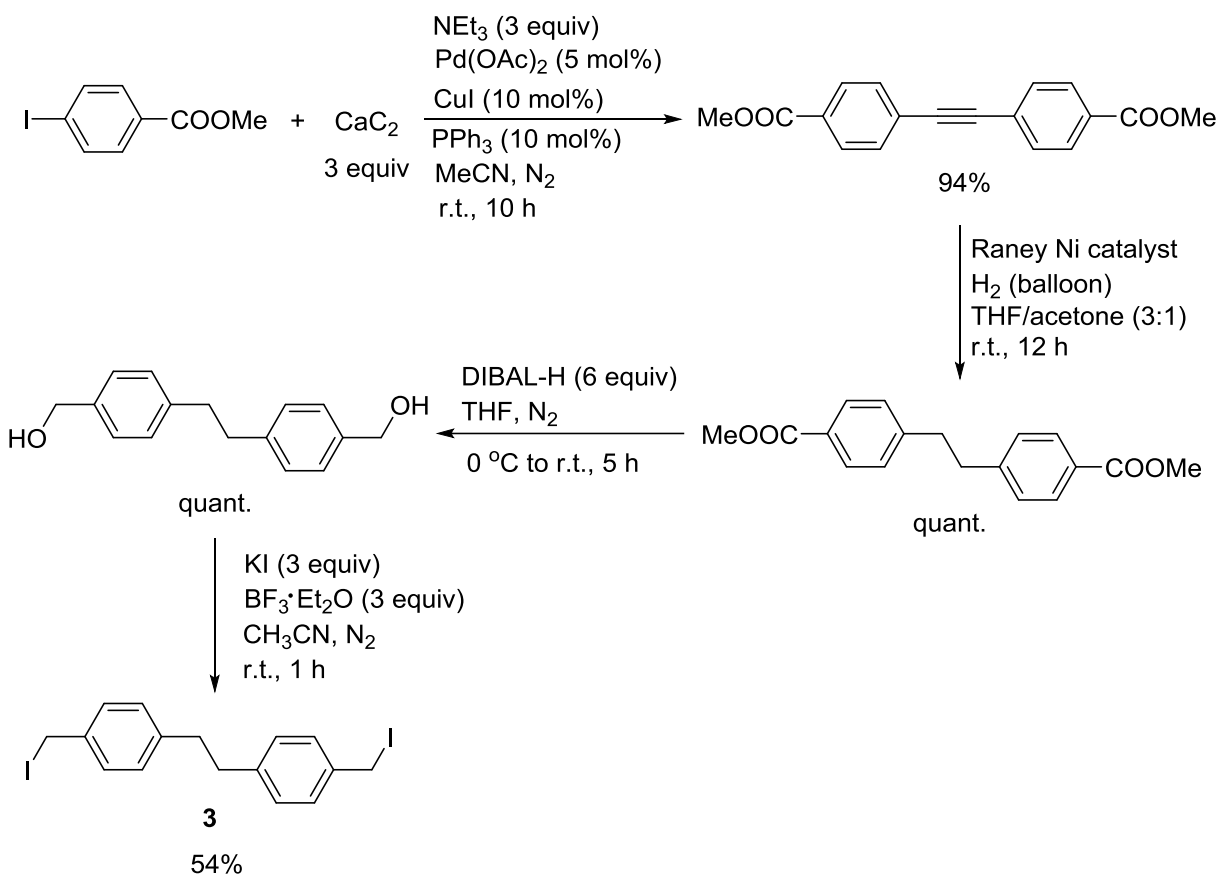
entry	n (I <sub>2</sub> )	temp (°C)	time (h)	<b>1</b> yield (%)	<b>2</b> yield (%)
1 <sup>b</sup>	0	200	108	0	0
2 <sup>c</sup>	10	200	140	62	34
3 <sup>c</sup>	25	200	94	60	38
4 <sup>c</sup>	50	180	72	48	40

<sup>b</sup>Quantitative recovery of PCP. <sup>c</sup>Trace amount formation of CH<sub>3</sub>-*p*-C<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>CH<sub>2</sub>-*p*-C<sub>6</sub>H<sub>4</sub>-CHO.

## Catalyst Effect

**The Sealed NMR Tube Reaction between PCP and Water with 50 mol% of HI.** HI (14.5  $\mu\text{L}$  57 wt% HI (aq)) stock solution in 405  $\mu\text{L}$   $\text{H}_2\text{O}$  was prepared. HI stock solution (7.5  $\mu\text{L}$ , 0.0020 mmol), PCP stock solution (400  $\mu\text{L}$ , 0.0040 mmol) and  $\text{C}_6\text{D}_6$  (50  $\mu\text{L}$ ) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200  $^\circ\text{C}$  and the reaction progress was monitored by  $^1\text{H}$  NMR spectroscopy. After 64 h, PCP was consumed to give **1** and **2** in 56%, 39% yields, respectively.

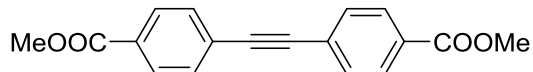
## Independent Synthesis of the Di-iodo Intermediate 3



Scheme S2. Independent Synthesis of the Di-iodo Intermediate **3**.

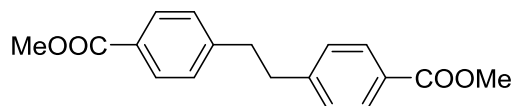


### Dimethyl 4,4'-(Ethyne-1,2-diyl)dibenzoate



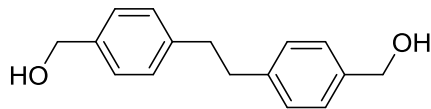
A 100 mL 2-necked round-bottomed flask with a magnetic stirrer was charged with methyl 4-iodobenzoate (202.3 mg, 0.77 mmol), PPh<sub>3</sub> (19.9 mg, 0.076 mmol), CuI (14.5 mg, 0.076 mmol), Pd(OAc)<sub>2</sub> (8.5 mg, 0.038 mmol), NEt<sub>3</sub> (320 μL, 2.30 mmol) and wet CH<sub>3</sub>CN (30 mL). The mixture was degassed by pump (low vacuum) and refilled with N<sub>2</sub> three times. Then CaC<sub>2</sub> (80 wt%, 194.6 mg, 2.43 mmol) was added under N<sub>2</sub>. The mixture was stirred at r.t. under N<sub>2</sub> for 10 h until the complete consumption of methyl 4-iodobenzoate monitored by TLC. The color changed to dark black at the end of the reaction. The reaction mixture was then filtered through a plug of silica gel and washed with DCM/EtOAc (v:v = 1:1). The filtrate was evaporated to dryness and further purified by column chromatography to give dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (106.6 mg, 0.36 mmol, 94%) as a yellow solid.<sup>4</sup>

### Dimethyl 4,4'-(Ethane-1,2-diyl)dibenzoate



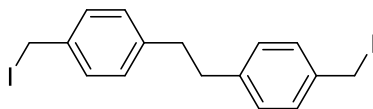
To a solution of dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate (30.0 mg, 0.102 mmol) in THF (6 mL)/acetone (v:v = 3:1) was added Raney nickel (~4 mg, 0.068 mmol) catalyst (activated, slurry in water). The reaction vessel was thrice evacuated and filled with H<sub>2</sub> gas (balloon). The mixture was stirred at r.t. for 12 h until the complete consumption of dimethyl 4,4'-(ethyne-1,2-diyl)dibenzoate monitored by TLC and GC-MS. Then the reaction mixture was filtered through a plug of silica gel (230–400 mesh). Concentration of the filtrate afforded dimethyl 4,4'-(ethane-1,2-diyl)dibenzoate (30.4 mg, 0.102 mmol, quant. yield) as a white solid.<sup>5</sup>

#### 4,4'-(Ethane-1,2-diyl)dibenzyl Alcohol



To an ice-cold solution of dimethyl 4,4'-(ethane-1,2-diyl)dibenzoate (29.7 mg, 0.10 mmol) in dry THF (4 mL) was added DIBAL-H (1.0 M in hexane, 0.6 mL, 0.6 mmol). After the addition, the solution was warmed to r.t. for 5 h. The reaction was monitored by TLC. After the complete reaction, the reaction was quenched sequentially with 24  $\mu\text{L}$   $\text{H}_2\text{O}$ , 24  $\mu\text{L}$  15% NaOH (aq), 60  $\mu\text{L}$   $\text{H}_2\text{O}$ . After stirring at r.t. for 30 min, anhydrous  $\text{MgSO}_4$  was added and the suspension stirred for another 30 min. The suspension was passed through a pad of Celite and evaporation of the solvent led to 4,4'-(ethane-1,2-diyl)dibenzyl alcohol (24.5 mg, 0.10 mmol, quant. yield) as a white solid.<sup>6,7</sup>

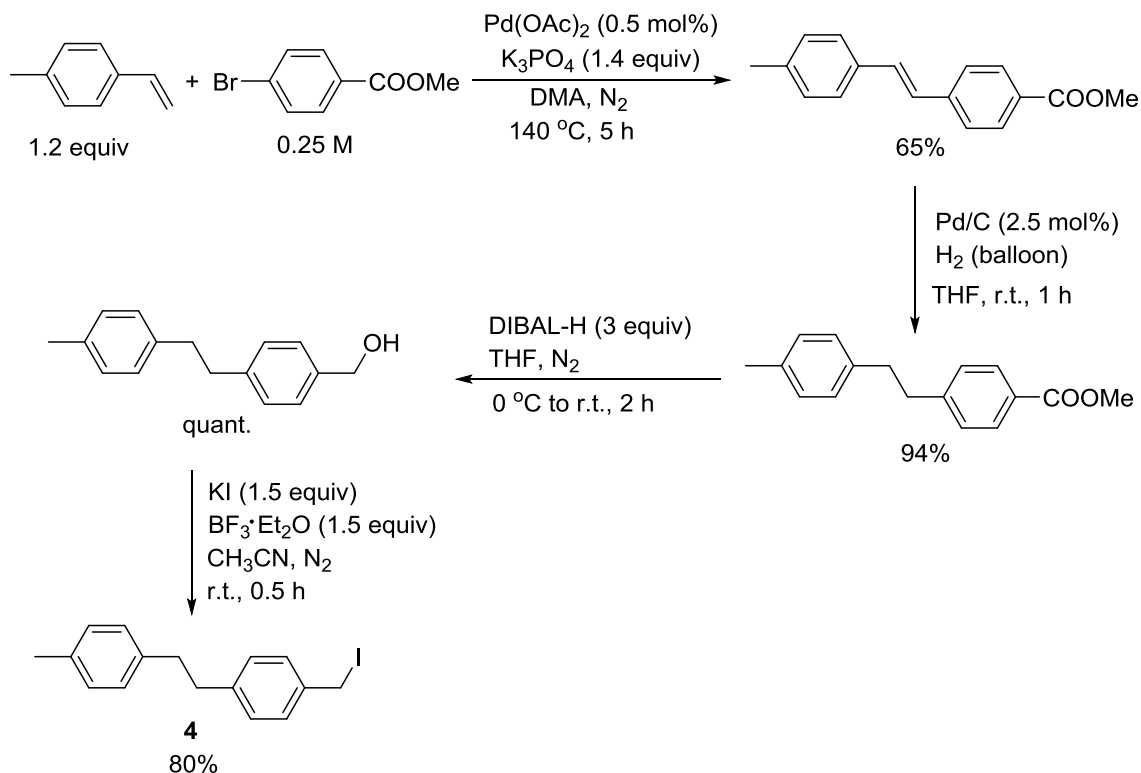
#### 4,4'-Diiodomethylbibenzyl



To a solution of 4,4'-(ethane-1,2-diyl)dibenzyl alcohol (24.5 mg, 0.10 mmol) and KI (51.2 mg, 0.31 mmol) in dry  $\text{CH}_3\text{CN}$  (6 mL) was added  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (38  $\mu\text{L}$ , 0.30 mmol). The mixture was stirred at r.t. under  $\text{N}_2$  for 1 h. The reaction mixture turned from initial colorless to reddish color. After the reaction,  $\text{H}_2\text{O}$  and sat.  $\text{Na}_2\text{S}_2\text{O}_3$  (aq) was added dropwise to the reaction mixture until it became colorless, and then it was extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. Further purification by column chromatography gave 4,4'-diiodomethylbibenzyl **3** (24.8 mg, 0.054 mmol, 54%) as a light yellow solid.<sup>8,9</sup>  $R_f = 0.77$  (hexane:DCM = 1:1).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  2.51 (s, 4H), 3.95 (s, 4H), 6.73 (d,  $J = 8.0$  Hz, 4H), 6.95 (d,  $J = 8.0$  Hz, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz)  $\delta$  5.7, 37.5,

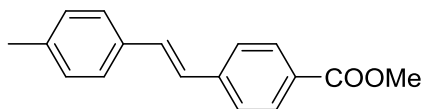
129.0, 129.0, 137.4, 141.4. HRMS (ESI-MS): calcd for C<sub>16</sub>H<sub>16</sub>I<sub>2</sub>Na ([M+Na]<sup>+</sup>) *m/z* 484.9234, found 484.9236.

### Independent Synthesis of the Mono-iodo Intermediate 4



Scheme S3. Independent Synthesis of the Mono-iodo Intermediate **4**.

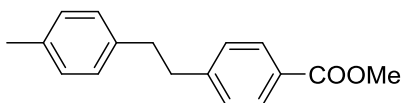
### Methyl (*E*)-4-(4-Methylstyryl)benzoate



A flame-dried 10 mL Schlenk flask was charged under N<sub>2</sub> with methyl 4-bromobenzoate (219.4 mg, 1.0 mmol), K<sub>3</sub>PO<sub>4</sub> (297.1 mg, 1.4 mmol), Pd(OAc)<sub>2</sub> (1.2 mg, 0.0053 mmol), 4-methylstyrene (158 μL, 1.2 mmol) and DMA (4 mL). The Schlenk flask was sealed and placed in an oil bath preheated to 140 °C. The reaction mixture was stirred at 140 °C for 5 h until the

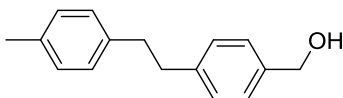
complete consumption of 4-bromobenzoate. After being cooled down to r.t., the mixture was poured into water, extracted with EtOAc three times. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness. Recrystallization from DCM/hexane gave methyl (*E*)-4-(4-methylstyryl)benzoate (163.2 mg, 0.65 mmol, 65%) as a white solid.<sup>10,11</sup>

### Methyl 4-(4-Methylphenethyl)benzoate



To a solution of methyl (*E*)-4-(4-methylstyryl)benzoate (25.5 mg, 0.10 mmol) in THF (3 mL) was added Pd/C (10 wt% Pd, 2.6 mg, 0.0024 mmol). The reaction vessel was thrice evacuated and filled with H<sub>2</sub> gas (balloon). The mixture was stirred at r.t. for 1 h until the complete consumption of methyl (*E*)-4-(4-methylstyryl)benzoate monitored by TLC and GC-MS. Then the reaction mixture was filtered through a plug of silica gel (230-400 mesh) and washed with DCM. Concentration of the filtrate afforded the desired product of methyl 4-(4-methylphenethyl)benzoate (24.0 mg, 0.094 mmol, 94%) as a white solid.<sup>12,13</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.32 (s, 3H), 2.89–2.97 (m, 4H), 3.91 (s, 3H), 7.04–7.10 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz) δ 21.1, 37.1, 38.1, 52.1, 128.0, 128.4, 128.7, 129.2, 129.8, 135.7, 138.2, 147.4, 167.3. HRMS (ESI-MS): calcd for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>Na ([M+Na]<sup>+</sup>) *m/z* 277.1199, found 277.1199.

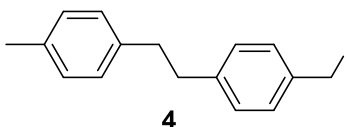
### 1-*p*-Tolyl-2-(*p*-(hydroxymethyl)phenyl)ethane



To an ice-cold solution of 4-(4-methylphenethyl)benzoate (22.0 mg, 0.0865 mmol) in dry THF (4

mL) was added DIBAL-H (1.0 M in hexane, 0.3 mL, 0.3 mmol). After the addition, the solution was warmed to r.t. for 2 h. The reaction was monitored by TLC. After the complete reaction, the reaction was quenched sequentially with 12  $\mu$ L H<sub>2</sub>O, 12  $\mu$ L 15% NaOH (aq), 30  $\mu$ L H<sub>2</sub>O. After stirring at r.t. for 30 min, anhydrous MgSO<sub>4</sub> was added and the suspension stirred for another 30 min. The suspension was passed through a pad of Celite and evaporation of the solvent gave 1-*p*-tolyl-2-(*p*-(hydroxymethyl)phenyl)ethane. (19.3 mg, 0.0853 mmol, quant. yield) as a white solid. <sup>14</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  1.67 (br, 1H), 2.33 (s, 3H), 2.84–2.94 (m, 4 H), 4.67 (d, *J* = 2.6 Hz, 2H), 7.07–7.12 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  21.1, 37.6, 37.9, 65.4, 127.3, 128.4, 128.8, 129.2, 135.5, 138.5, 138.7, 141.6. HRMS (ESI-MS): calcd for C<sub>16</sub>H<sub>18</sub>ONa ([M+Na]<sup>+</sup>) *m/z* 249.1250, found 249.1250.

#### 4-Iodomethyl-4'-methylbibenzyl

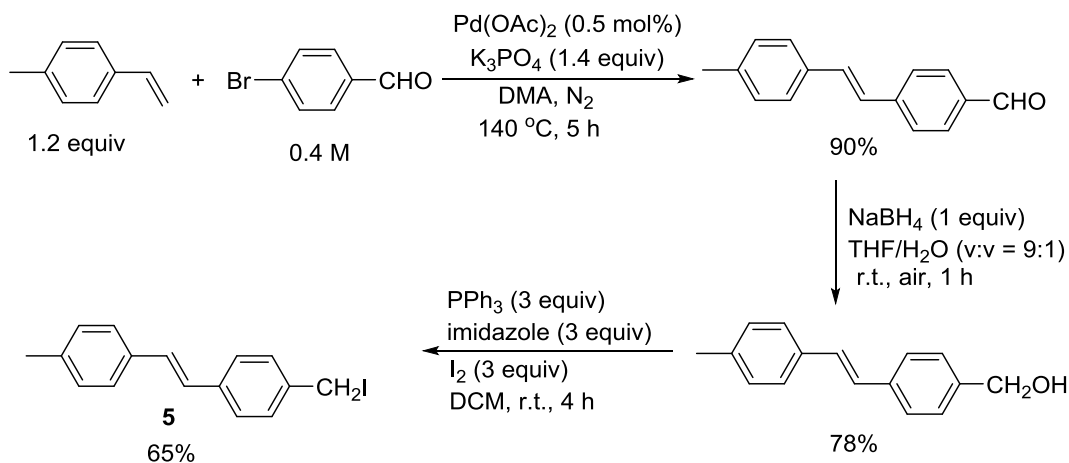


To a solution of 1-*p*-tolyl-2-(*p*-(hydroxymethyl)phenyl)ethane (18.3 mg, 0.081 mmol) and KI (22.0 mg, 0.132 mmol) in dry CH<sub>3</sub>CN (3 mL) was added BF<sub>3</sub>•Et<sub>2</sub>O (15  $\mu$ L, 0.12 mmol). The mixture was stirred at r.t. under N<sub>2</sub> for 0.5 h. The reaction mixture turned from initial colorless to reddish color. After the reaction, H<sub>2</sub>O and sat. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq) was added dropwise to the reaction mixture until it turned into colorless, and then it was extracted with Et<sub>2</sub>O. The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. Further purification by column chromatography gave 4-iodomethyl-4'-methylbibenzyl **4** (21.8 mg, 0.065 mmol, 80%) as a pale yellow solid. *R<sub>f</sub>* = 0.81 (hexane:DCM = 1:1). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta$  2.13 (s, 3H), 2.62–2.69 (m, 4H), 3.96 (s, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.96–6.98 (m,

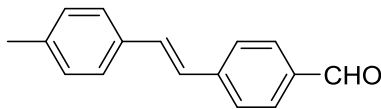
4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 100 MHz)  $\delta$  6.21, 21.2, 37.3, 37.9, 128.4, 128.9, 129.0, 129.2, 135.6, 136.9, 138.6, 141.9. HRMS (ESI-MS): calcd for  $\text{C}_{16}\text{H}_{17}\text{INa}$  ( $[\text{M}+\text{Na}]^+$ )  $m/z$  359.0267, found 359.0267.

### Independent Synthesis of (*E*)-1-(Iodomethyl)-4-(4-methylstyryl)benzene **5**

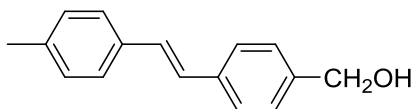
To probe whether compound **5** is a possible intermediate from dehydrogenation of mono-iodo intermediate **4**, compound **5** was independently synthesized (Scheme S4). From the  $^1\text{H}$  NMR analysis of the reaction mixture throughout the reaction process, compound **5** was not observed in the reaction of  $\text{I}_2$ -catalyzed transfer hydrogenation of PCP with  $\text{H}_2\text{O}$ . Therefore, **5** is unlikely an intermediate. This also indicates that the dehydrogenation of the diiodo intermediate **3** is not competitive with the hydrodeiodination of **3** to give **4**.



Scheme S4. Independent Synthesis of (*E*)-1-(Iodomethyl)-4-(4-methylstyryl)benzene **5**.

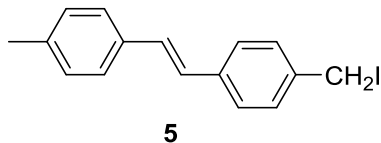
**(E)-4-(4-Methylstyryl)benzaldehyde**

A flame-dried Schlenk flask was charged under N<sub>2</sub> with 4-bromobenzaldehyde (373.1 mg, 2.0 mmol), K<sub>3</sub>PO<sub>4</sub> (599.0 mg, 2.8 mmol), Pd(OAc)<sub>2</sub> (2.2 mg, 0.01 mmol), 4-methylstyrene (315 μL, 2.4 mmol) and DMA (5 mL). The Schlenk flask was sealed and placed in an oil bath preheated to 140 °C. The reaction mixture was stirred at 140 °C for 5 h until the complete consumption of 4-bromobenzaldehyde. After being cooled down to r.t., the mixture was poured into water, extracted with EtOAc three times. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness. Further recrystallization from DCM/hexane gave (E)-4-(4-methylstyryl)benzaldehyde (406.5 mg, 1.8 mmol, 90%) as a light yellow solid.<sup>11,15</sup>

**(E)-(4-(4-Methylstyryl)phenyl)methanol**

To a stirred solution of (E)-4-(4-methylstyryl)benzaldehyde (110.1 mg, 0.5 mmol) in THF (4.5 mL)/H<sub>2</sub>O (v:v = 9:1) was added NaBH<sub>4</sub> (18.1 mg, 0.5 mmol) in one portion. The mixture was stirred at r.t. for 1 h. The reaction was then quenched with water, extracted with Et<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give (E)-(4-(4-methylstyryl)phenyl)methanol (86.6 mg, 0.39 mmol, 78%) as a white solid.<sup>16</sup>

### **(E)-1-(Iodomethyl)-4-(4-methylstyryl)benzene**



To a solution of PPh<sub>3</sub> (78.7 mg, 0.30 mmol), imidazole (20.4 mg, 0.30 mmol) in DCM (5 mL) was sequentially added iodine (76.1 mg, 0.30 mmol), and (E)-4-(4-methylstyryl)phenylmethanol (22.4 mg, 0.10 mmol). The reaction mixture was stirred at r.t. for 4 h. A reddish brown solution with yellow precipitates formed. The reaction was quenched by the addition of sat. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq). Upon quenching, the yellow precipitates disappeared and the color turned into colorless. Water was then added, and the aqueous phase was extracted with DCM three times. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure. The resulting residue was purified by pipet column chromatography eluting with the solvent of hexane:DCM (v:v 2:1) to afford (E)-1-(iodomethyl)-4-(4-methylstyryl)benzene **5** (21.7 mg, 0.065 mmol, 65%) as a white solid.  $R_f = 0.90$  (DCM). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz): δ 2.12 (s, 3H), 3.98 (s, 2H), 6.87–7.00 (m, 6H), 7.12 (d,  $J = 8.2$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100 MHz) δ 4.9, 20.3, 126.0, 126.1, 126.5, 128.4, 128.6, 128.8, 134.0, 136.6, 136.8, 137.8. HRMS (ESI-MS): calcd for C<sub>16</sub>H<sub>16</sub>I ([M+H]<sup>+</sup>)  $m/z$  335.0291, found 335.0289.

### **Reaction of Di-iodo Intermediate 3**

**The Sealed NMR Tube Reaction between 3 and Water.** **3** (1.0 mg, 0.0022 mmol), H<sub>2</sub>O (4 μL, 0.22 mmol), and C<sub>6</sub>D<sub>6</sub> (450 μL) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 180 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy.



After 76 h, **3** was consumed to give **1** and **2** in 48% and 44% yields, respectively, together with the formation of I<sub>2</sub> with characteristic reddish color (Figure S4, Table S4, eq S3 and Figure S5).

Prolonged heating to 100 h did not affect the yields of **1** and **2**.

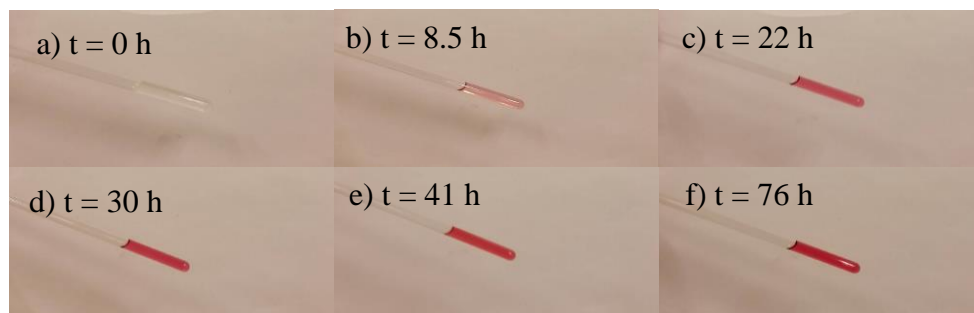
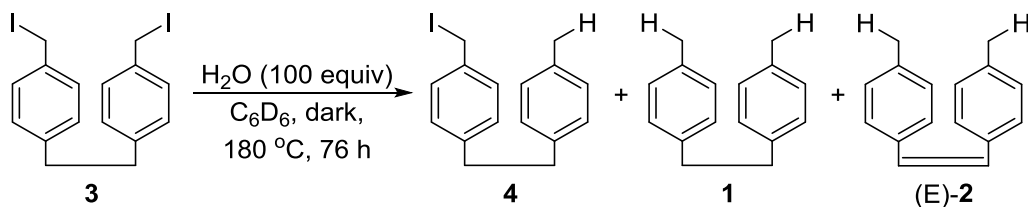


Figure S2. Color Change of the Reaction for the Transformation of the Diiodo Intermediate **3**

Table S4. Reaction Time Profile of Reaction between **3** and H<sub>2</sub>O.



time / h	NMR yield / %				
	<b>3</b>	<b>4</b>	<b>1</b>	<b>2</b>	total organic
0	100	0	0	0	100
8.5	77	22	1	0	100
22	41	37	11	9	98
30	24	35	23	16	98
41	6	26	39	27	99
48	2	16	46	33	97
56	0	15	45	36	96
76	0	0	48	44	92
100	0	0	46	44	90

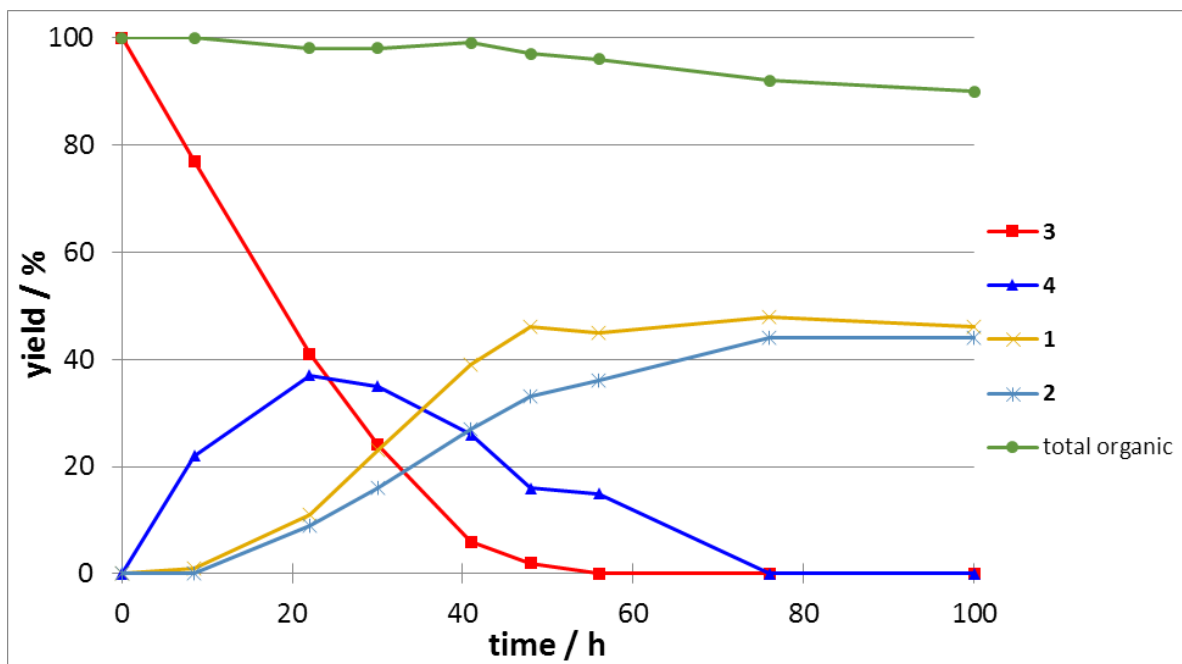
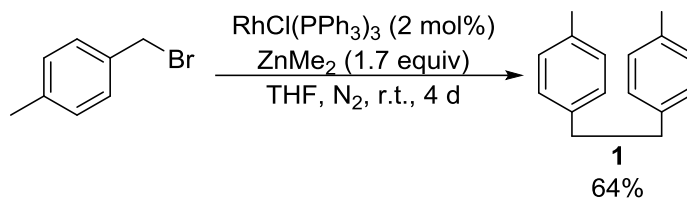


Figure S3. Reaction Time Profile of Reaction between **3** and H<sub>2</sub>O.

### Iodine Catalyzed Dehydrogenation of 4,4'-Dimethylbibenzyl to (E)-4,4'-Dimethylstilbene

#### Independent Synthesis of 4,4'-Dimethylbibenzyl **1**



To a stirred solution of RhCl(PPh<sub>3</sub>)<sub>3</sub> (8.5 mg, 0.02 mmol) and 4-methylbenzyl bromide (185.0 mg, 1.0 mmol) in anhydrous THF (5 mL) was added Me<sub>2</sub>Zn (1.2 M in hexane, 1450 μL, 1.74 mmol) at r.t.. The mixture was stirred at r.t. for 4 d until the complete consumption of 4-methylbenzyl bromide. The reaction mixture was quenched with 1 M HCl (aq), and extracted with EtOAc. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure. The resulting residue was purified by column chromatography to give 4,4'-dimethylbibenzyl **1** (66.7 mg, 0.32 mmol, 64%) as a white solid.<sup>6b</sup>

**The Sealed NMR Tube Reaction of Iodine Catalyzed Dehydrogenation of **1**.** **1** (2.1 mg, 0.010 mmol) stock solution in 1 mL C<sub>6</sub>D<sub>6</sub> was prepared. H<sub>2</sub>O (7.5 μL, 0.42 mmol), iodine stock solution (50 μL, 0.0010 mmol) and stock solution of **1** (400 μL, 0.0040 mmol) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 180 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 72 h, **2** was formed in 45% yield with 47% recovery yield of **1**. Prolonged heating did not show observable changes.

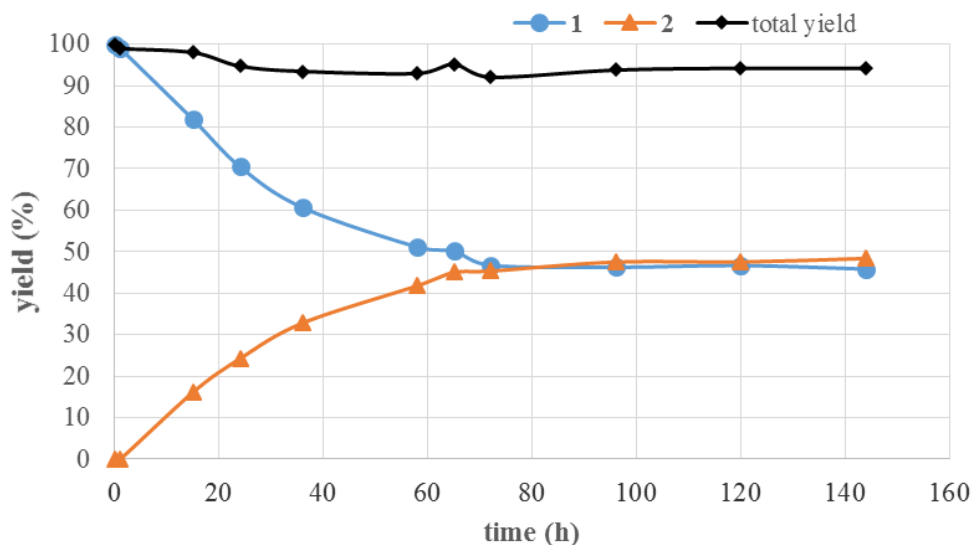
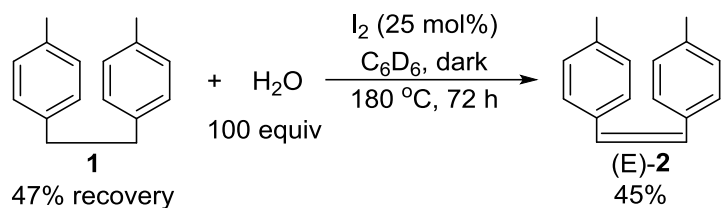
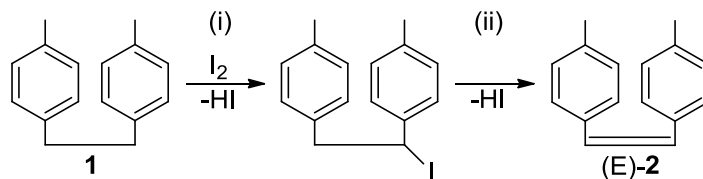
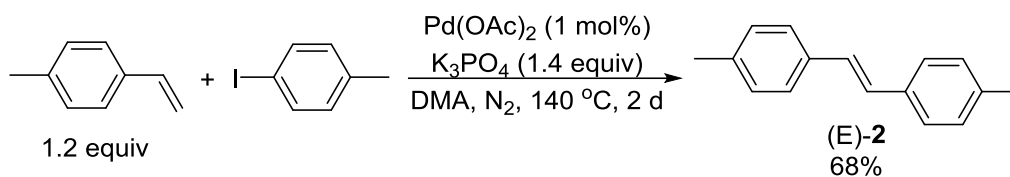


Figure S4. Reaction Time Profile of Iodine Catalyzed Dehydrogenation of **1** to **2**.



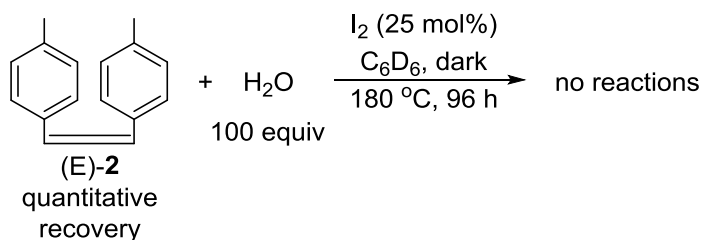
Scheme S5. Step (i) C-H Activation with Iodine; Step (ii) Dehydroiodination.

## Independent Synthesis of 4,4'-Dimethylstilbene



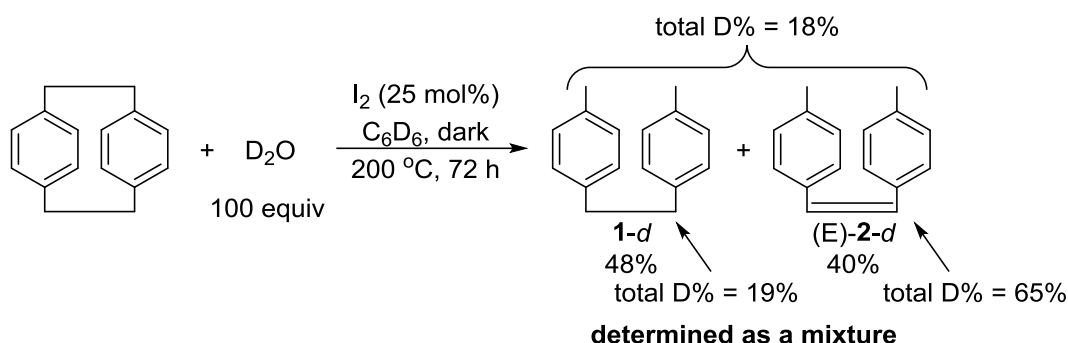
A flame-dried Schlenk flask was charged under N<sub>2</sub> with 4-iodotoluene (444.6 mg, 2.0 mmol), K<sub>3</sub>PO<sub>4</sub> (589.7 mg, 2.8 mmol), Pd(OAc)<sub>2</sub> (4.4 mg, 0.02 mmol), 4-methylstyrene (315 μL, 2.4 mmol) and DMA (5 mL). The Schlenk flask was sealed and placed in an oil bath preheated to 140 °C. The reaction mixture was stirred at 140 °C for 2 d until the complete consumption of 4-iodotoluene. After being cooled down to r.t., the mixture was poured into water, extracted with EtOAc three times. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness. Recrystallization from DCM/hexane gave the title compound of 4,4'-dimethylstilbene **2** (284.0 mg, 1.36 mmol, 68%) as a white solid.<sup>11,17</sup>

**The Sealed NMR Tube Reaction of Attempted Hydrogenation of 2.** **2** (2.1 mg, 0.010 mmol) stock solution in 1 mL C<sub>6</sub>D<sub>6</sub> was prepared. H<sub>2</sub>O (7.5 μL, 0.42 mmol), iodine stock solution (50 μL, 0.0010 mmol) and stock solution of **2** (400 μL, 0.0040 mmol) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 180 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 96 h, **2** was quantitatively recovered and **1** was not observed throughout the reaction.

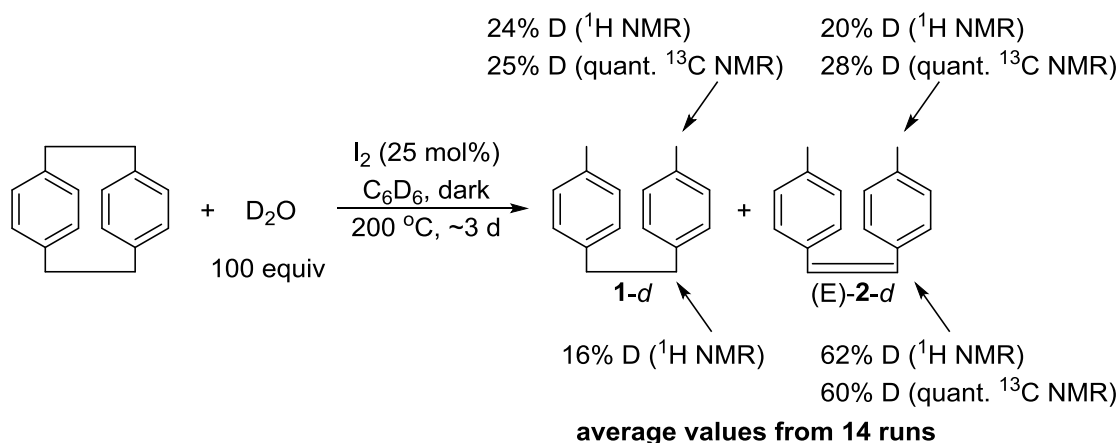


## Deuterium Labeling Experiments

**The Sealed NMR Tube Reaction of PCP with 100 equiv D<sub>2</sub>O at [PCP] = 8.9 mM and 25 mol% I<sub>2</sub>.** D<sub>2</sub>O (7.5 μL, 0.41 mmol), iodine stock solution (50 μL, 0.0010 mmol) and PCP stock solution (400 μL, 0.0040 mmol) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 72 h, PCP was consumed to give **1-*d*** and **2-*d*** in 48%, 40% yields, respectively. Based on the <sup>1</sup>H NMR spectrum, the terminal benzylic positions of **1-*d*** and **2-*d*** were 18% deuterated. The internal benzylic positions of **1-*d*** were 19% deuterated. The olefinic positions of **2-*d*** were 65% deuterated.



The above reaction was repeated for 14 times. The combined **1-*d*** and **2-*d*** was purified by HPLC for independent <sup>1</sup>H and quantitative <sup>13</sup>C NMR analysis (eq S7, Tables S5-S7, Figures S7 and S8).



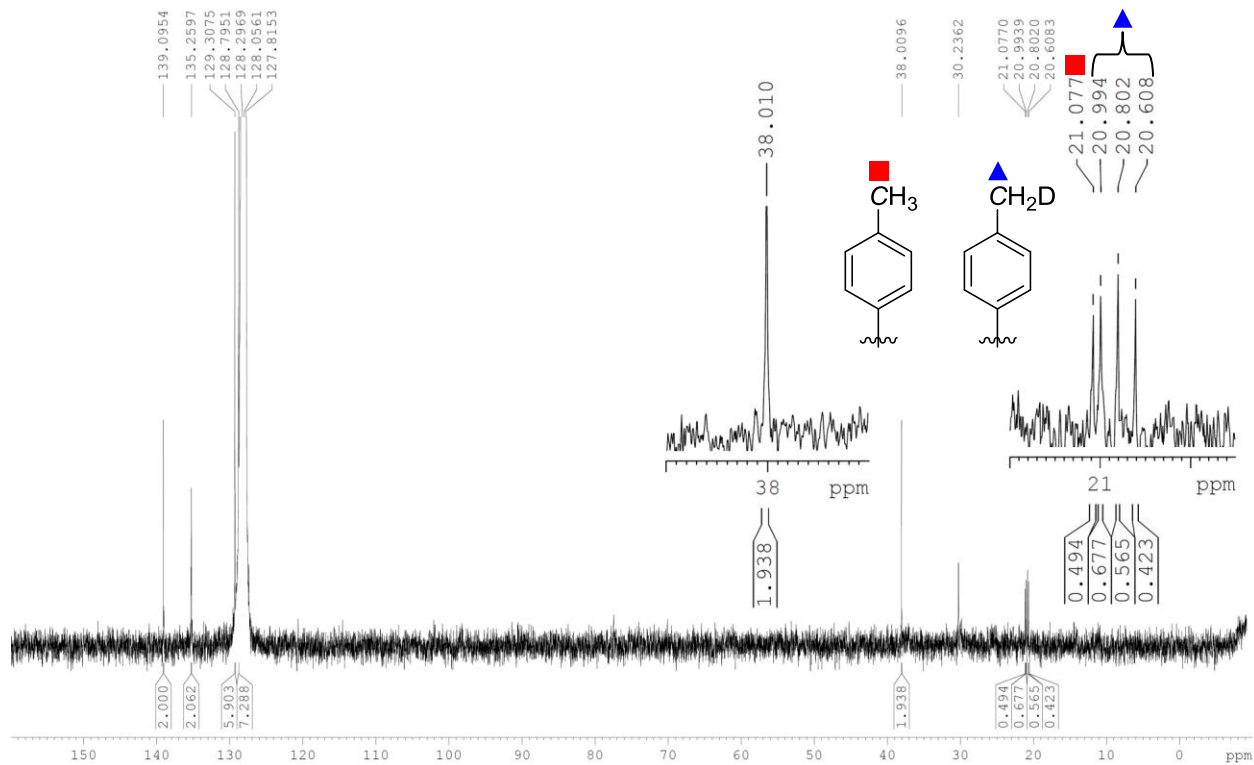


Figure S7. Quantitative  $^{13}\text{C}$  NMR Spectrum of Combined **1-d** and Assignment of Terminal Benzylic Isotopic Substitutions.

Table S5. Isotopic Substitution at the Terminal Benzylic Positions in **1-d** from Quantitative  $^{13}\text{C}$  NMR Analysis

isotopic substitution	splitting	peak integration	ratio
-CH <sub>3</sub>	Singlet	0.494	1.0
-CH <sub>2</sub> D	Triplet (1:1:1)	1.574	3.2
-CHD <sub>2</sub>	Quintet (1:2:3:2:1)		
-CD <sub>3</sub>	Septet (1:3:6:7:6:3:1)		not observed

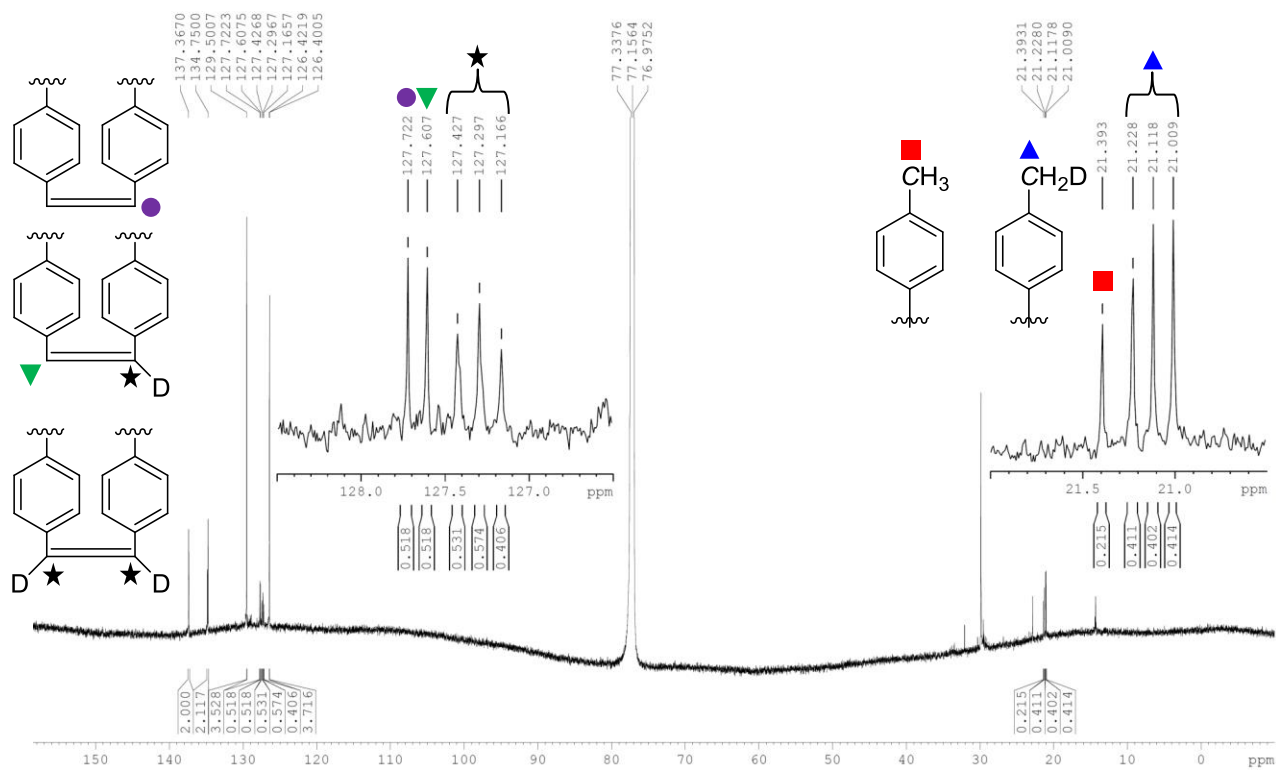


Figure S8. Quantitative  $^{13}\text{C}$  NMR Spectrum of Combined **2-d** and Assignment of Terminal Benzylic and Olefinic Isotopic Substitutions.

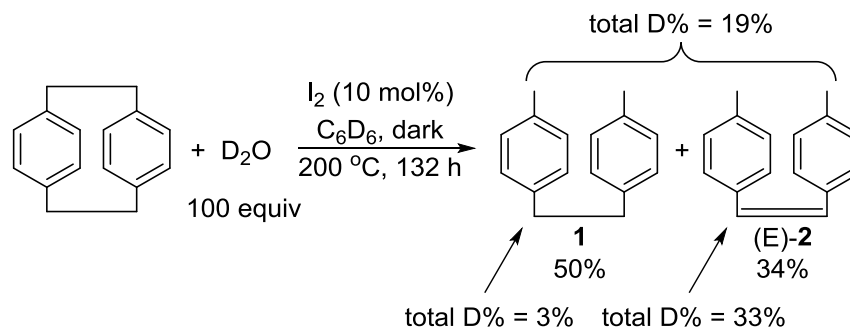
Table S6. Isotopic Substitution at the Terminal Benzylic Positions in **2-d** from Quantitative  $^{13}\text{C}$  NMR Analysis

isotopic substitution	splitting	peak integration	ratio
-CH <sub>3</sub>	Singlet	0.215	1.0
-CH <sub>2</sub> D	Triplet (1:1:1)	1.227	5.7
-CHD <sub>2</sub>	Quintet (1:2:3:2:1)		
-CD <sub>3</sub>	Septet (1:3:6:7:6:3:1)	not observed	

Table S7. Isotopic Substitution at the Olefinic Positions in **2-d** from Quantitative  $^{13}\text{C}$  NMR Analysis

isotopic substitution	splitting	peak integration	ratio
-CH	Singlet	1.036	1.0
-CD	Triplet (1:1:1)	1.511	1.5

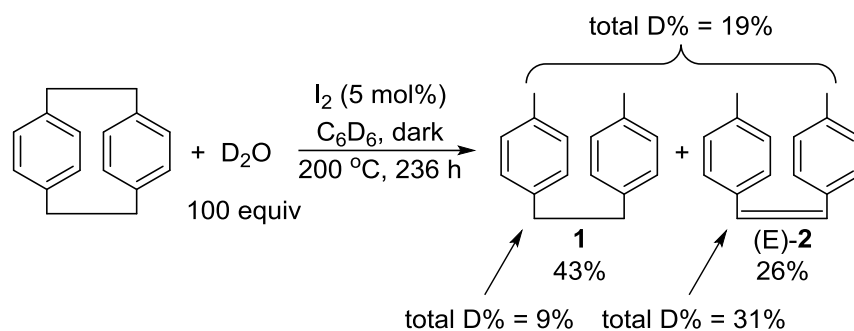
**The Sealed NMR Tube Reaction of PCP with 100 equiv  $\text{D}_2\text{O}$  at  $[\text{PCP}] = 8.9 \text{ mM}$  and 10 mol%  $\text{I}_2$ .**  $\text{D}_2\text{O}$  (7.5  $\mu\text{L}$ , 0.41 mmol), iodine stock solution (20  $\mu\text{L}$ , 0.0004 mmol), PCP stock solution (400  $\mu\text{L}$ , 0.004 mmol) and 30  $\mu\text{L}$   $\text{C}_6\text{D}_6$  were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200  $^\circ\text{C}$  and the reaction progress was monitored by  $^1\text{H}$  NMR spectroscopy. After 132 h, PCP was consumed to give **1-d** and **2-d** in 50%, 34% yields, respectively (eq S8). Based on the  $^1\text{H}$  NMR spectrum, the terminal benzylic positions of **1-d** and **2-d** were 19% deuterated. The internal benzylic positions of **1-d** were 3% deuterated. The olefinic positions of **2-d** were 33% deuterated.



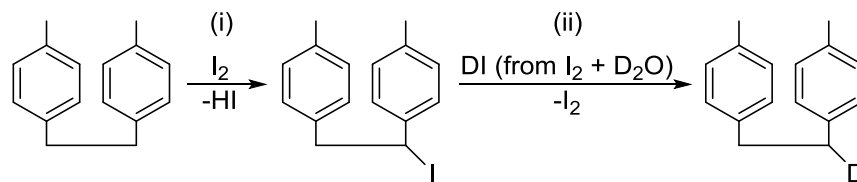
**The Sealed NMR Tube Reaction of PCP with 100 equiv  $\text{D}_2\text{O}$  at  $[\text{PCP}] = 8.9 \text{ mM}$  and 5 mol%  $\text{I}_2$ .**  $\text{D}_2\text{O}$  (7.5  $\mu\text{L}$ , 0.41 mmol), iodine stock solution (10  $\mu\text{L}$ , 0.0002 mmol), PCP stock



solution (400  $\mu\text{L}$ , 0.004 mmol) and 40  $\mu\text{L}$   $\text{C}_6\text{D}_6$  were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200  $^\circ\text{C}$  and the reaction progress was monitored by  $^1\text{H}$  NMR spectroscopy. After 236 h, PCP was consumed to give **1-d** and **2-d** in 43%, 26% yields, respectively (eq S9). Based on the  $^1\text{H}$  NMR spectrum, the terminal benzylic positions of **1-d** and **2-d** were 19% deuterated. The internal benzylic positions of **1-d** were 9% deuterated. The olefinic positions of **2-d** were 31% deuterated.



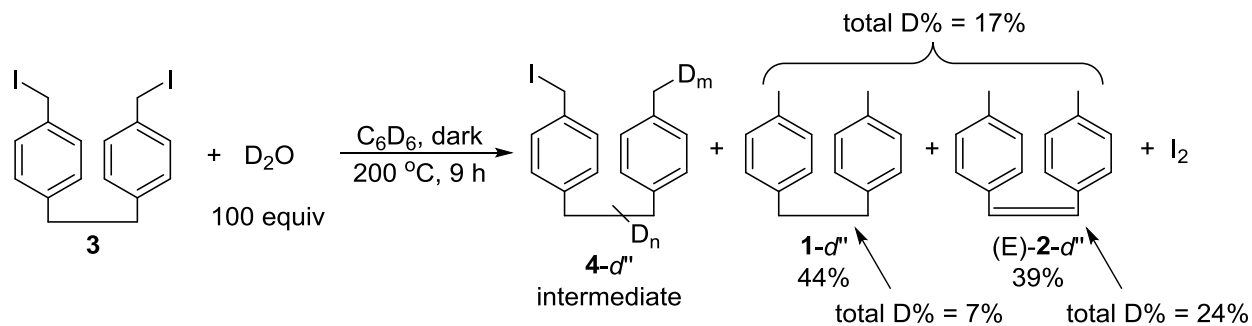
**The Sealed NMR Tube Reaction of  $\text{I}_2$  Catalyzed Post H/D Exchange of **1** with  $\text{D}_2\text{O}$ .** **1** (2.1 mg, 0.010 mmol) stock solution in 1 mL  $\text{C}_6\text{D}_6$  was prepared.  $\text{D}_2\text{O}$  (7.5  $\mu\text{L}$ , 0.41 mmol), iodine stock solution (50  $\mu\text{L}$ , 0.001 mmol), and stock solution of **1** (400  $\mu\text{L}$ , 0.004 mmol) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200  $^\circ\text{C}$  and the reaction progress was monitored by  $^1\text{H}$  NMR spectroscopy. After 94 h, **1-d'** and **2-d'** were formed in 75% and 20% yields, respectively. Negligible deuterations were found at the terminal benzylic positions of **1-d'** and **2-d'**. 70% D was incorporated at the internal benzylic positions of **1-d'**. 42% D was incorporated at the olefinic positions of **2-d'**.



Scheme S6. Proposed Mechanism for the I<sub>2</sub> Catalyzed Internal Benzylic H/D Exchange of **1** with D<sub>2</sub>O. Step (i) C-H Activation with Iodine; Step (ii) Reduction of C-I Bond with DI.

**The Sealed NMR Tube Reaction between 3 and 100 equiv of D<sub>2</sub>O.** **3** (1.0 mg, 0.0022 mmol), H<sub>2</sub>O (4 μL, 0.22 mmol), and C<sub>6</sub>D<sub>6</sub> (450 μL) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 9 h, **3** was consumed to give **1-d''** and **2-d''** in 44% and 39% yields, respectively, together with the formation of I<sub>2</sub>. Based on the <sup>1</sup>H NMR spectrum, the terminal benzylic positions of **1-d''** and **2-d''** were 17% deuterated. The internal benzylic positions of **1-d''** were 7% deuterated. The olefinic positions of **2-d''** were 24% deuterated.

Table S8. Reaction Time Profile of Reaction between **3** and D<sub>2</sub>O.



time	yield / %				
	<b>3</b>	4- <i>d</i> ''	1- <i>d</i> ''	(E)-2- <i>d</i> ''	total organic
0	100	0	0	0	100
30min	67	8	0	0	75
2h20min	56	37	8	7	108
3h50min	17	22	10	7	56
6h30min	3	14	23	17	57
9h	0	0	44	39	83

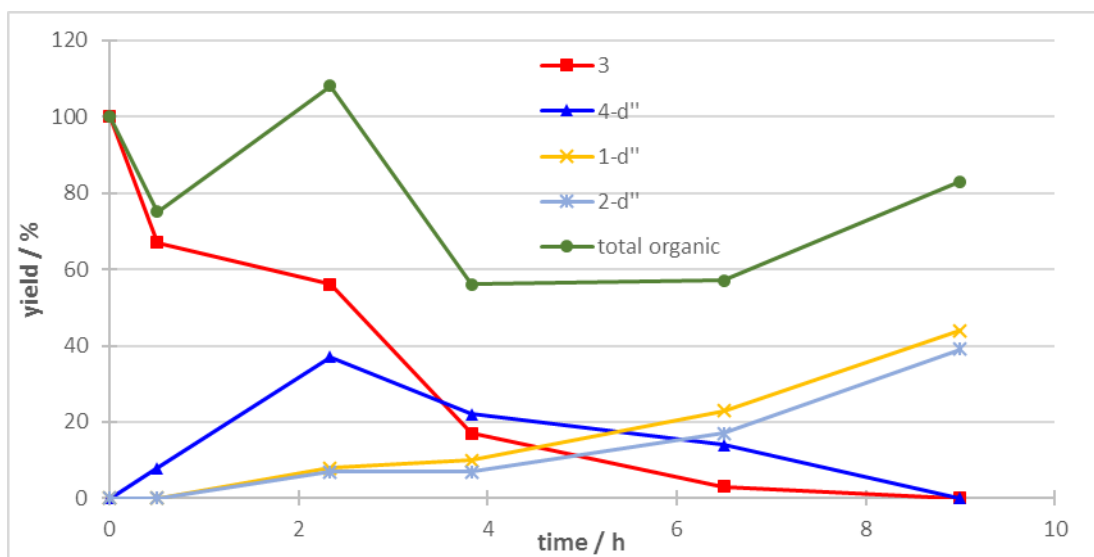
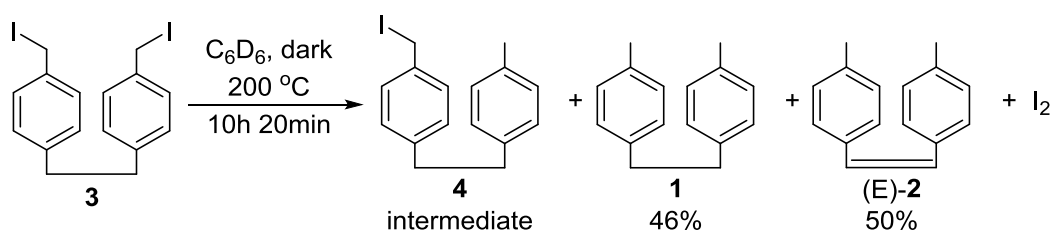


Figure S9. Reaction Time Profile of Reaction between **3** and D<sub>2</sub>O.

**The Sealed NMR Tube Reaction of only 3 in C<sub>6</sub>D<sub>6</sub>.** **3** (1.0 mg, 0.0022 mmol) and C<sub>6</sub>D<sub>6</sub> (450 μL) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 10 h 20 min, **3** was consumed to give **1** and **2** in 46% and 50% yields, respectively, together with the formation of I<sub>2</sub>. Prolonged heating to 100 h did not affect the yields of **1** and **2**.

Table S9. Reaction Time Profile of Reaction of only **3** and C<sub>6</sub>D<sub>6</sub>.



time	yield / %				
	<b>3</b>	<b>4</b>	<b>1</b>	(E)- <b>2</b>	total organic
0	100	0	0	0	100
30min	72	8	1	0	82
1h10min	72	16	3	0	92
2h40min	68	39	8	7	122
4h10min	42	40	14	13	109
5h40min	15	26	16	16	73
10h20min	0	0	44	50	96

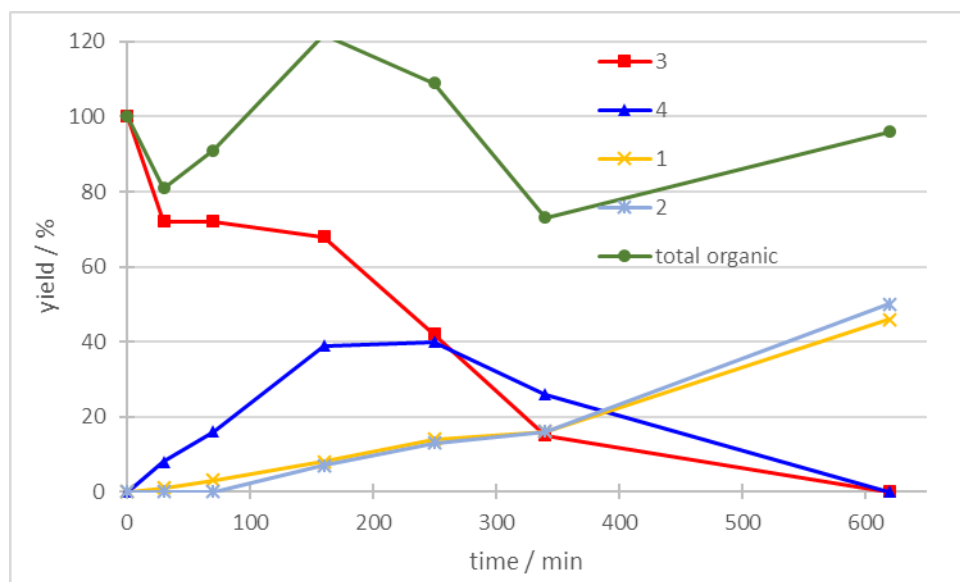
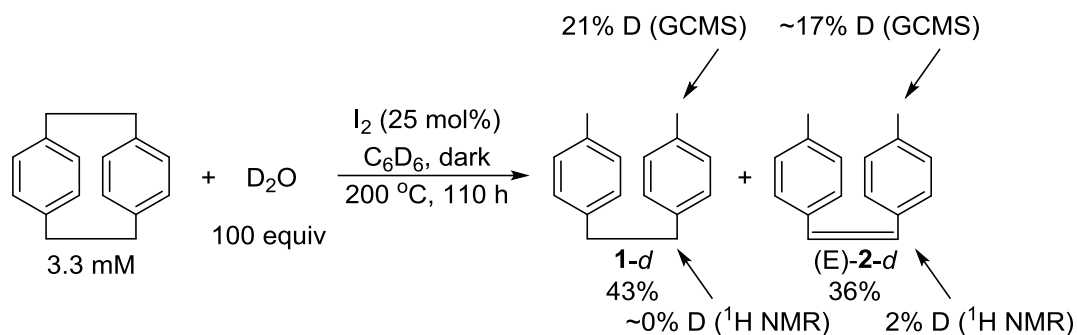
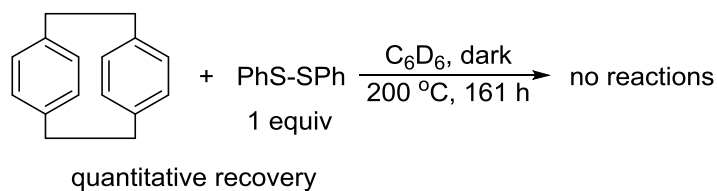


Figure S10. Reaction Time Profile of Reaction of only **3** and C<sub>6</sub>D<sub>6</sub>.

**The Sealed NMR Tube Reaction of PCP with 100 equiv D<sub>2</sub>O at [PCP] = 3.3 mM and 25 mol% I<sub>2</sub>.** D<sub>2</sub>O (2.8 μL, 0.15 mmol), iodine stock solution (20 μL, 0.0004 mmol), PCP stock solution (150 μL, 0.0015 mmol) and 280 μL of C<sub>6</sub>D<sub>6</sub> were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200 °C and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 110 h, PCP was consumed to give **1-d** and **2-d** in 43%, 36% yields, respectively. Based on the <sup>1</sup>H NMR spectrum and GC-MS analysis, the terminal benzylic positions of **1-d** and **2-d** were 21% and ~17% deuterated, respectively. The internal benzylic positions of **1-d** were negligibly deuterated. The olefinic positions of **2-d** were 2% deuterated.



**The Sealed NMR Tube Reaction of PCP with Diphenyl Disulfide.** Diphenyl disulfide (8.7 mg, 0.0098 mmol) stock solution in 0.5 mL  $C_6D_6$  was also prepared. Diphenyl disulfide stock solution (50  $\mu$ L, 0.004 mmol) and PCP stock solution (400  $\mu$ L, 0.004 mmol) were added into a Teflon screw head stoppered NMR tube. The reaction was heated at 200  $^\circ$ C and the reaction progress was monitored by  $^1H$  NMR spectroscopy. After 161 h, PCP and diphenyl disulfide were quantitatively recovered. PhS-SPh ( $S-S$  BDE = 51.2 kcal/mol)<sup>2</sup> can be a trapping agent in the homolysis of C-C bond.<sup>18</sup> The absence of reaction suggests that  $I_2$  is unlikely a radical trap under the current reaction conditions.



It is also unlikely that PCP undergoes oxidation with  $I_2$  to generate PCP radical cation prior to the C-C bond cleavage.<sup>19</sup> The 1<sup>st</sup> oxidation potential of PCP is 1.57 V in MeCN (vs SCE),<sup>20</sup> and the oxidation potential of  $I^-$  to  $I_2$  is 0.267 V in 1:1 MeCN/DMF (vs SCE).<sup>21</sup> This suggests that the oxidation of PCP with  $I_2$  is estimated to be endothermic by 1.303 V. Therefore, the possibility of single electron transfer from PCP to  $I_2$  is ruled out, particularly in non-polar benzene solvent.

## UV-Vis Spectroscopic Studies

### UV-Vis Absorption Spectroscopy for the Determination of [I<sub>2</sub>]

#### 1. UV-Vis Calibration Curve for [I<sub>2</sub>]

Stock solutions of I<sub>2</sub> was first prepared by dissolving I<sub>2</sub> (27.3 mg, 0.108 mmol) in 6.0 mL hexanes. To the four UV cells were added 50, 40, 30 and 20 μL of I<sub>2</sub> solutions, and diluted to 3.10 mL with hexanes. Finally, 0.450 mL C<sub>6</sub>H<sub>6</sub> was added to each UV cells to form the respective standards with [I<sub>2</sub>] = 0.253, 0.197, 0.141 and 0.084 mM for UV-Vis spectroscopic analysis. They absorb with  $\lambda_{\text{max}} = 516$  nm.

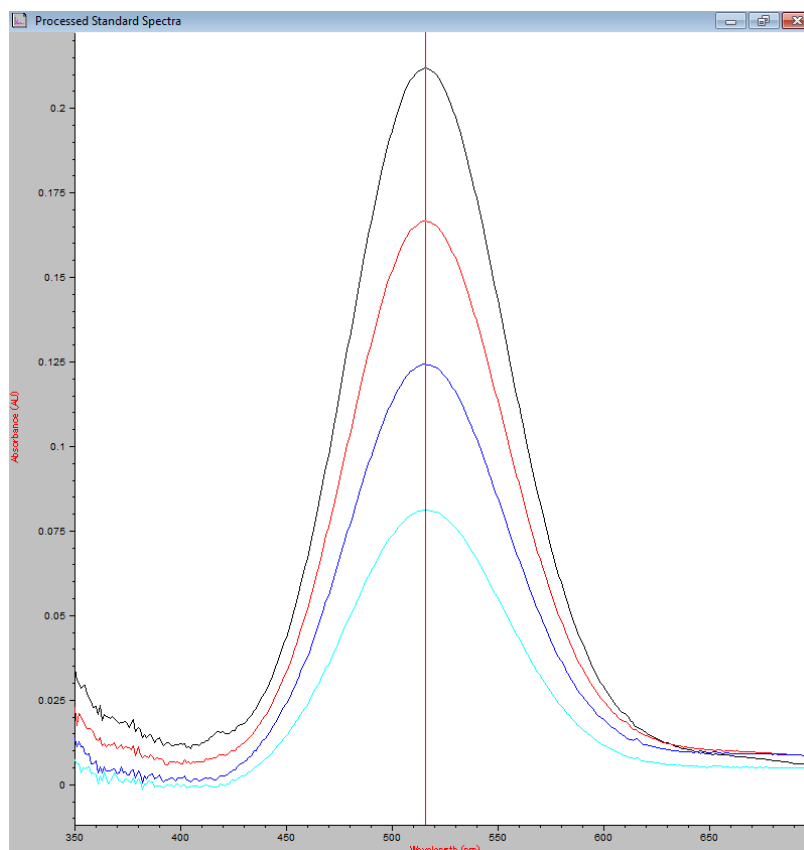


Figure S11. Stacked UV-Vis Absorption Spectra of I<sub>2</sub> Standards.

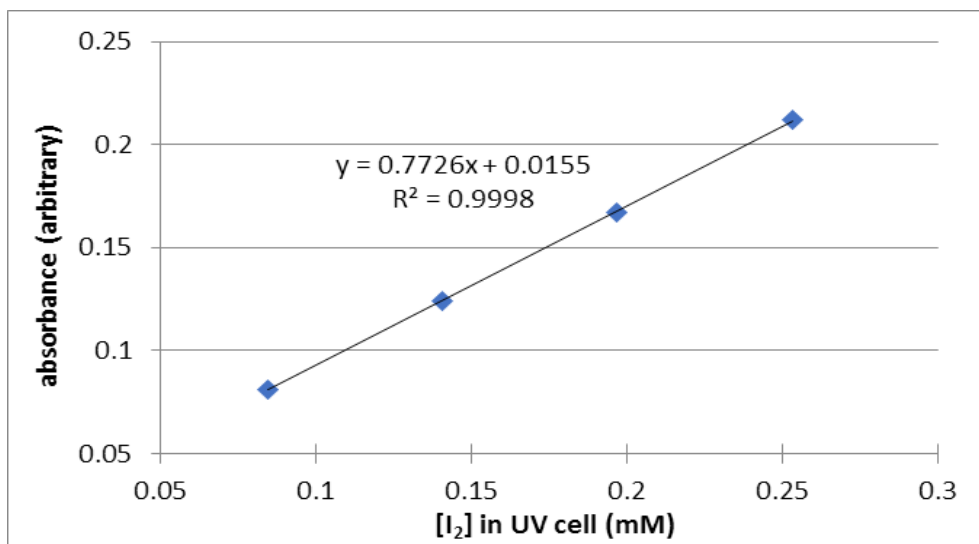


Figure S12. Calibration Curve for [I<sub>2</sub>] from 0.084 mM to 0.253 mM.

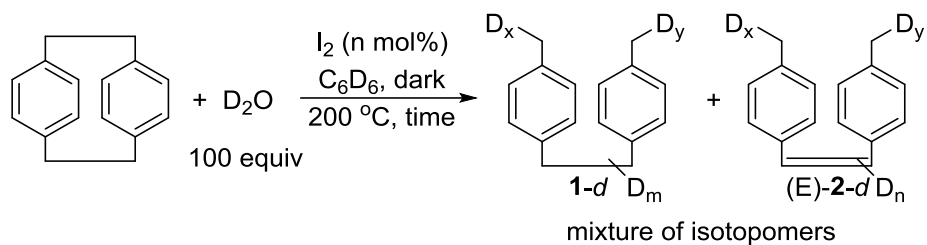
Table S10. Numerical Data for the Calibration.

entry	I <sub>2</sub> in UV cell / μmol	[I <sub>2</sub> ] in UV cell / mM	Absorbance / arbitrary
1	0.90	0.253	0.212
2	0.70	0.197	0.167
3	0.50	0.141	0.124
4	0.30	0.084	0.081



## 2. UV-Vis Determination of Recovered [I<sub>2</sub>] After Reactions:

Table S11. UV-Vis Spectroscopic Analysis Results.



entry	I <sub>2</sub> loading (n) / mol%	I <sub>2</sub> loading / μmol	time / h	absorbance at 516 nm	dilution factor	I <sub>2</sub> recovered / μmol
1	5	0.20	236	peak obscured <sup>a</sup>	1.00	N/A
2	10	0.40	132	0.105	0.55	0.226
3	25	1.00	72	0.084	2.33	0.732
4 <sup>b</sup>	25	1.00	72	0.237	1.00	1.017

<sup>a</sup> the absorption at 516 nm is probably too weak and obscured by the absorption of PCP

<sup>b</sup> no PCP added

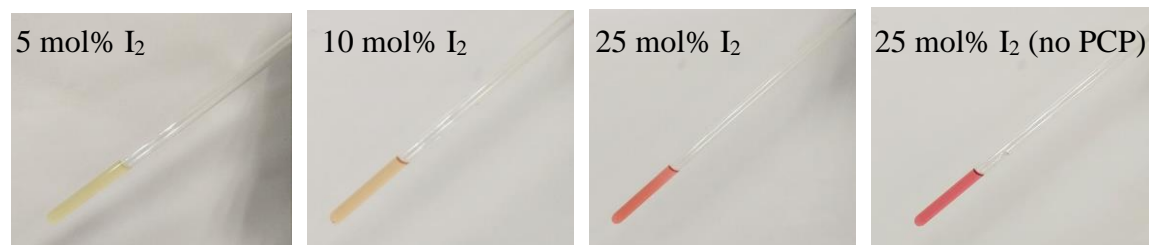
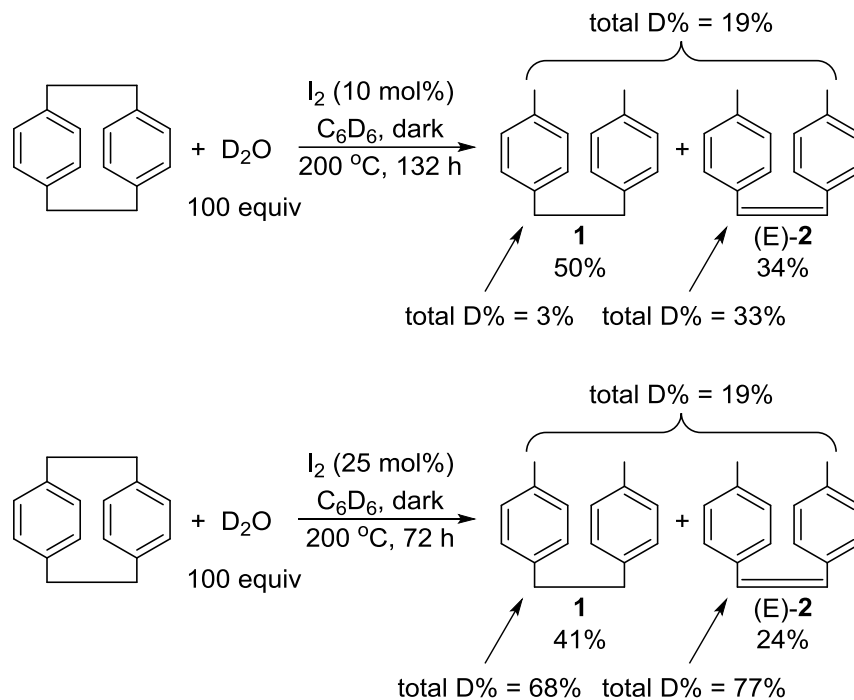


Figure S13. Color of Reaction Mixtures at the End of Reaction.

Table S12. Calculation of Ratio on Terminal Benzylic Deuterium Incorporated to I<sub>2</sub> Consumed.

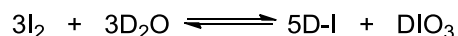


eq	I <sub>2</sub> loading / μmol	I <sub>2</sub> recovered / μmol	I <sub>2</sub> consumed / μmol	terminal benzylic deuterium introduced / μmol	(no. of mol of terminal benzylic deuterium) / (I <sub>2</sub> consumed)
S13	0.40	0.226	0.174	3.55	20.4
S14	1.00	0.732	0.268	2.75	10.2

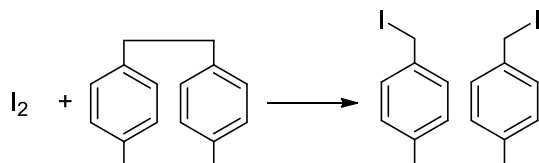
## Mechanistic Proposal Relating the I<sub>2</sub> Consumption and Terminal Benzylic Deuteration, and other I<sub>2</sub> Consuming Pathways

### Case 1:

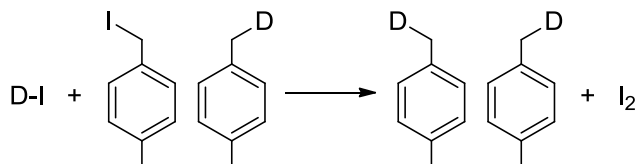
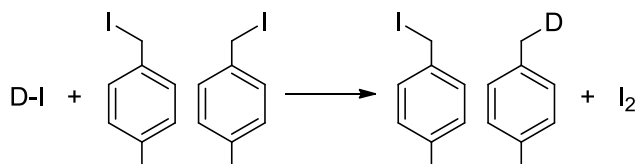
(i) generation of reductant D-I



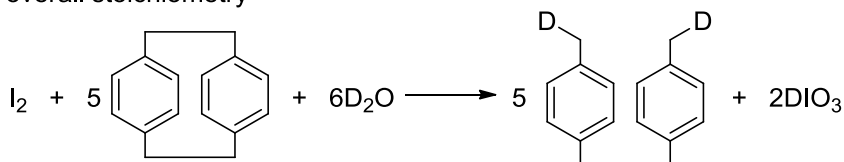
(ii) CCA of PCP



(iii) reduction of C-I bond to C-D bond with DI



overall stoichiometry

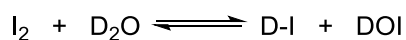


Based on this proposal, 3 moles of I<sub>2</sub> reacts with 3 moles D<sub>2</sub>O to generate 5 moles of DI. According to the overall stoichiometry, 1 mole of I<sub>2</sub> reacts with 5 moles of PCP to yield 5 moles of transfer hydrogenation product with 2 terminal benzylic deuterium, e.g. 10 moles of deuterium. If (no. of mol of terminal benzylic deuterium) / (I<sub>2</sub> consumed) > 10, I<sub>2</sub> is catalytic for the transfer hydrogenation. This is the maximum case. Since the I<sub>2</sub> consumption determined from the UV-Vis

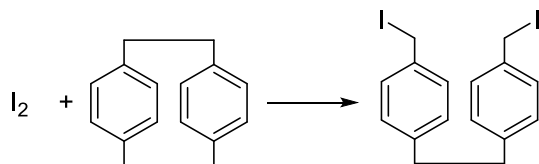
analysis covers other concurrent  $I_2$  consuming reactions, e.g. post H/D exchange, the results shown in Table S12 strongly indicate the catalytic role of  $I_2$ . However, we are unclear if there were additional pathways regenerating  $I_2$  in the reaction system based on the current understandings.

Case 2:

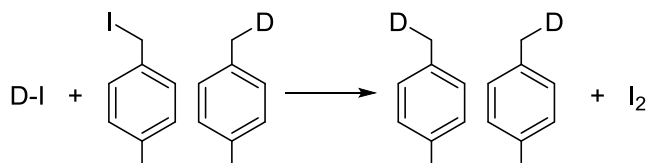
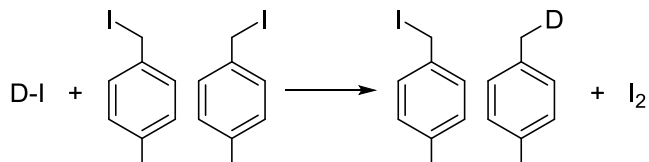
(i) generation of reductant D-I



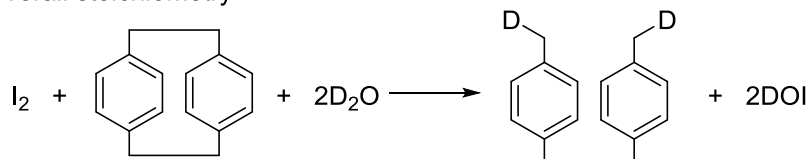
(ii) CCA of PCP



(iii) reduction of C-I bond to C-D bond with DI



overall stoichiometry

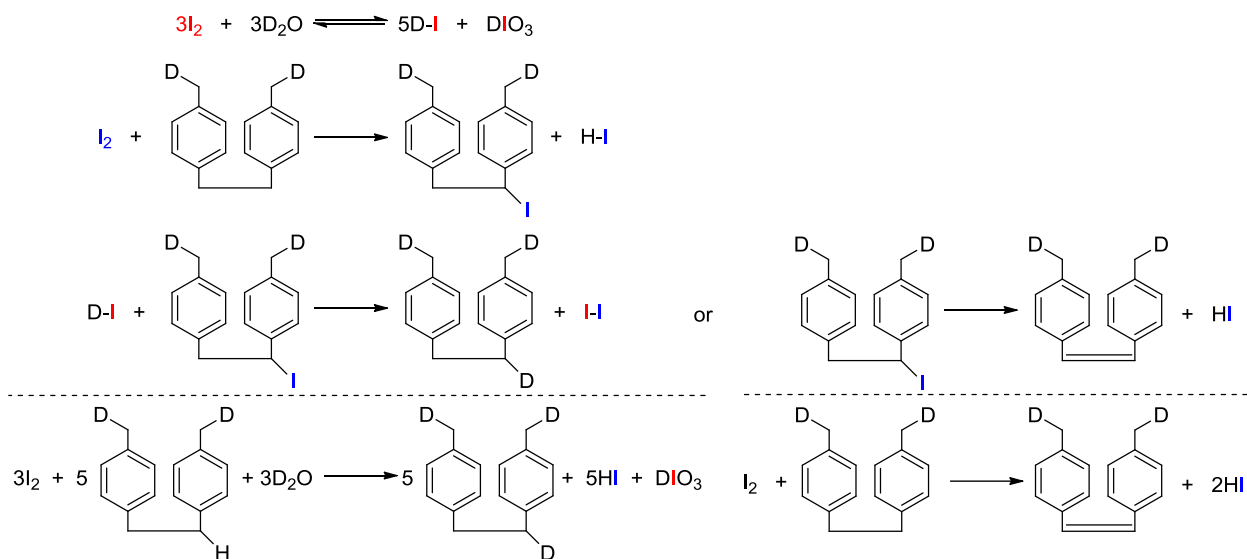


Based on this proposal, 1 mole of  $I_2$  reacts with 1 mole  $D_2O$  to generate 1 mole of DI. According to the overall stoichiometry, 1 mole of  $I_2$  reacts with 1 mole of PCP to yield 1 mole of transfer

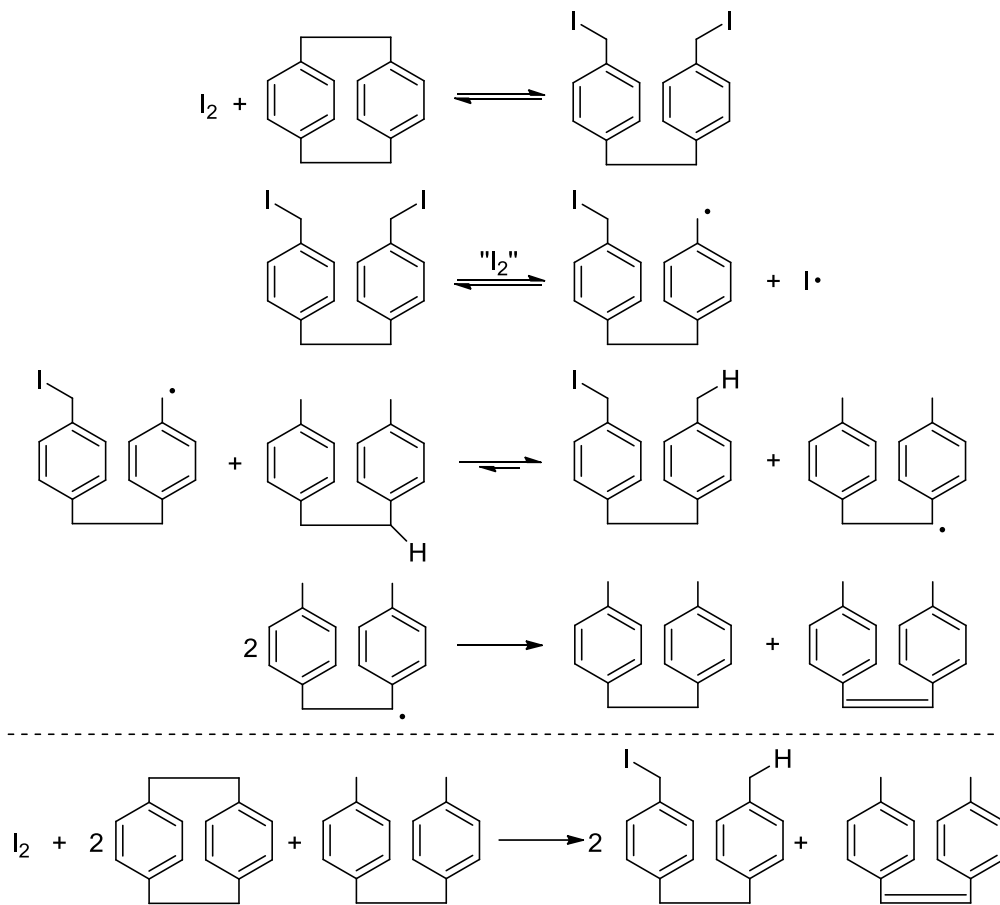
hydrogenation product with 2 terminal benzylic deuterium, e.g. 2 moles of deuterium. If (no. of mol of terminal benzylic deuterium) / (I<sub>2</sub> consumed) > 2, I<sub>2</sub> is catalytic for the transfer hydrogenation. This is the minimum case.

Other I<sub>2</sub> Consuming Pathways:

1. Post H/D exchange at the internal benzylic positions and dehydrogenation



2. Disproportionation Reactions (Deuterium Independent)



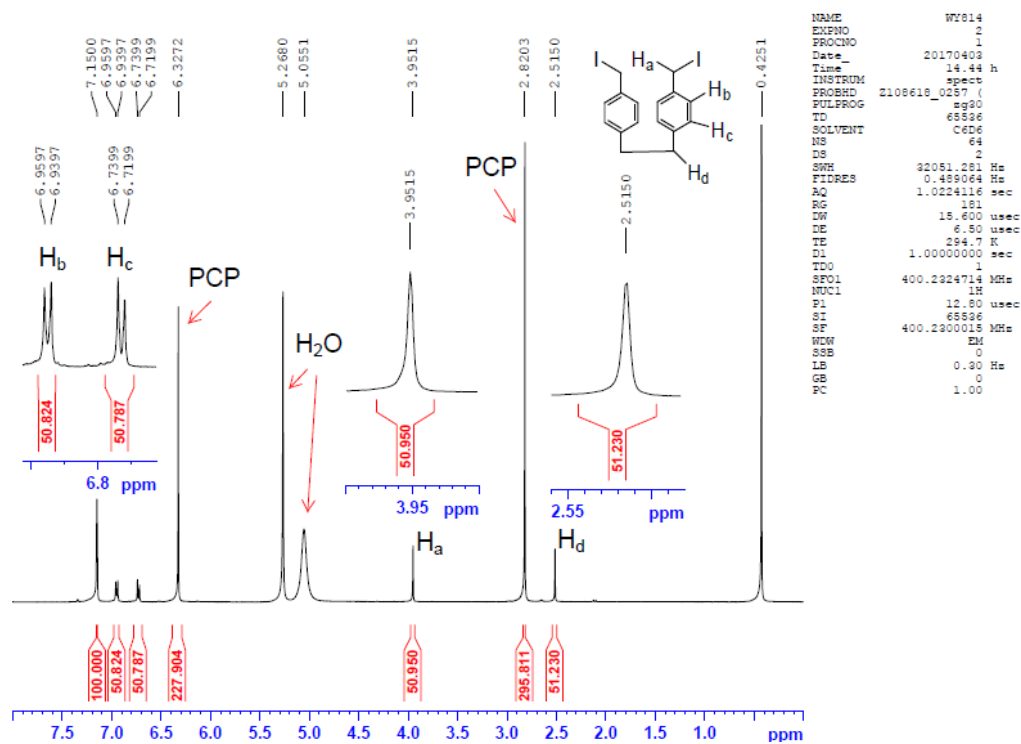
## NMR Spectra

No.	Spectra	Page
1	<sup>1</sup> H NMR Spectrum of <b>3</b> Intermediate	S41
2	<sup>1</sup> H NMR Spectrum of Dimethyl 4,4'-(Ethyne-1,2-diyl)dibenzoate	S41
3	<sup>1</sup> H NMR Spectrum of Dimethyl 4,4'-(Ethane-1,2-diyl)dibenzoate	S42
4	<sup>1</sup> H NMR Spectrum of 4,4'-(Ethane-1,2-diyl)dibenzyl Alcohol	S42
5	<sup>1</sup> H NMR Spectrum of 4,4'-Diiodomethylbibenzyl <b>3</b>	S43
6	<sup>13</sup> C{ <sup>1</sup> H} NMR Spectrum of 4,4'-Diiodomethylbibenzyl <b>3</b>	S43
7	<sup>1</sup> H NMR Spectrum of Methyl ( <i>E</i> )-4-(4-Methylstyryl)benzoate	S44
8	<sup>1</sup> H NMR Spectrum of Methyl 4-(4-Methylphenethyl)benzoate	S44
9	<sup>13</sup> C{ <sup>1</sup> H} NMR Spectrum of Methyl 4-(4-Methylphenethyl)benzoate	S45
10	<sup>1</sup> H NMR Spectrum of 1- <i>p</i> -Tolyl-2-( <i>p</i> -(hydroxymethyl)phenyl)ethane	S45
11	<sup>13</sup> C{ <sup>1</sup> H} NMR Spectrum of 1- <i>p</i> -Tolyl-2-( <i>p</i> -(hydroxymethyl)phenyl)ethane	S46
12	<sup>1</sup> H NMR Spectrum of 4-Iodomethyl-4'-methylbibenzyl <b>4</b>	S46
13	<sup>13</sup> C{ <sup>1</sup> H} NMR Spectrum of 4-Iodomethyl-4'-methylbibenzyl <b>4</b>	S47
14	<sup>1</sup> H NMR Spectrum of ( <i>E</i> )-4-(4-Methylstyryl)benzaldehyde	S47
15	<sup>1</sup> H NMR Spectrum of ( <i>E</i> )-(4-(4-Methylstyryl)phenyl)methanol	S48
16	<sup>1</sup> H NMR Spectrum of ( <i>E</i> )-1-(Iodomethyl)-4-(4-methylstyryl)benzene <b>5</b>	S48
17	<sup>13</sup> C{ <sup>1</sup> H} NMR Spectrum of ( <i>E</i> )-1-(Iodomethyl)-4-(4-methylstyryl)benzene <b>5</b>	S49
18	<sup>1</sup> H NMR Spectrum of 4,4'-Dimethylbibenzyl <b>1</b>	S49
19	<sup>1</sup> H NMR Spectrum of ( <i>E</i> )-4,4'-Dimethylstilbene <b>2</b>	S50
20	<sup>1</sup> H NMR Spectrum of mixture of <b>1-d</b> and <b>2-d</b> (eq 5)	S50
22	<sup>1</sup> H NMR Spectrum of isolated <b>1-d</b> from 14 runs (eq S7)	S51
23	<sup>1</sup> H NMR Spectrum of isolated <b>2-d</b> from 14 runs (eq S7)	S51

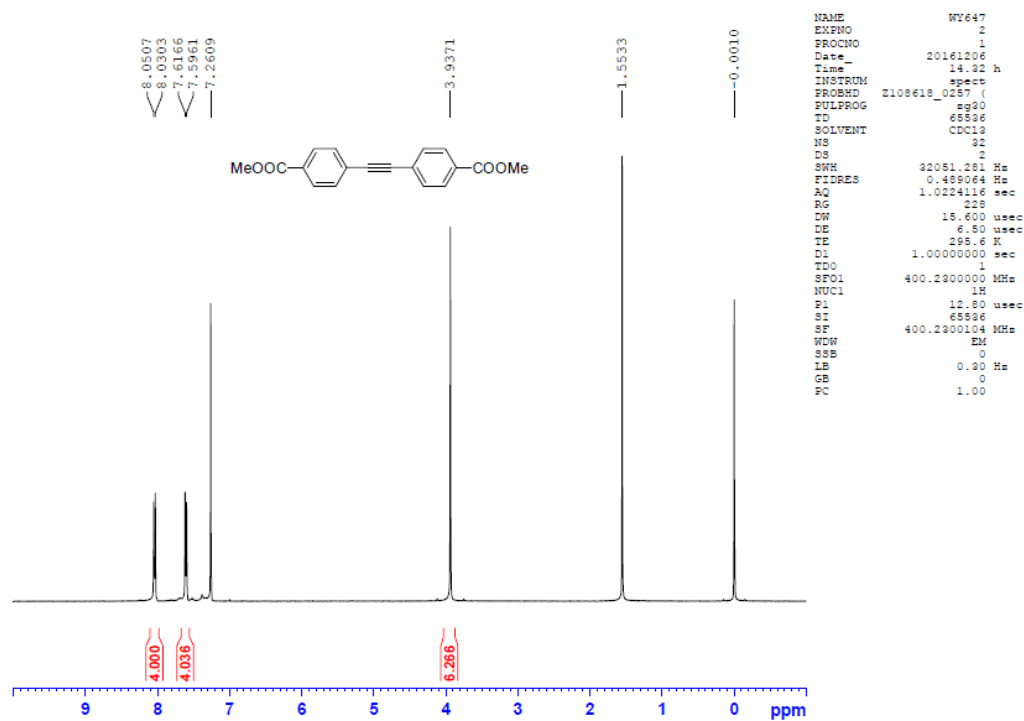




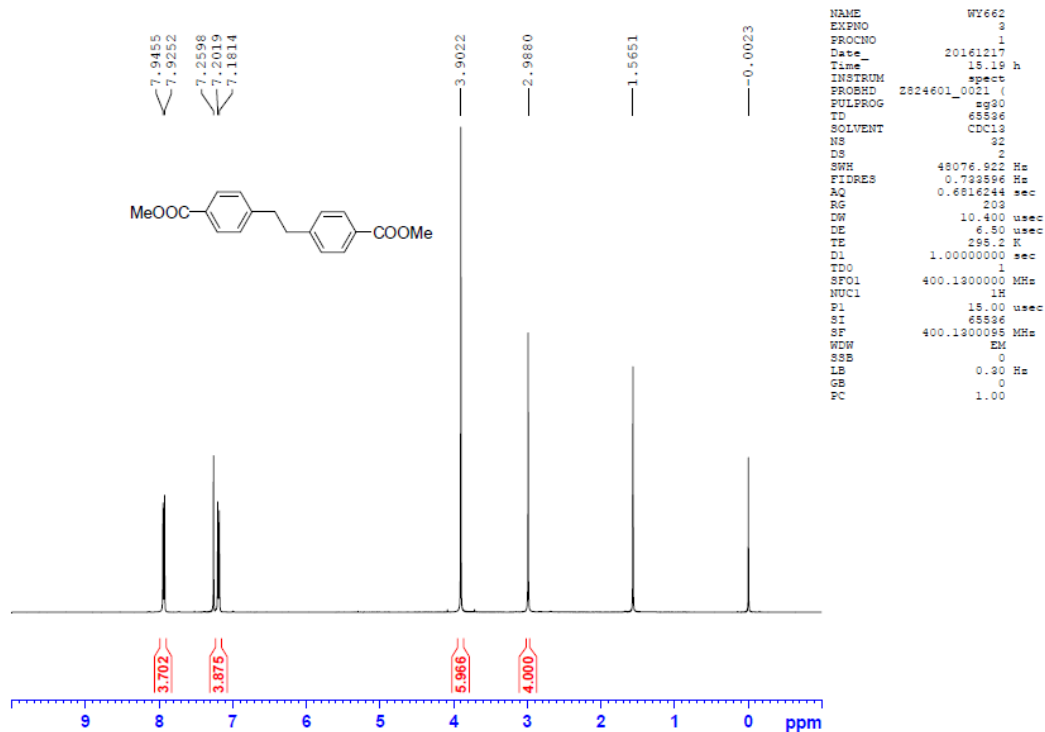
### <sup>1</sup>H NMR Spectrum of Diiodo Intermediate 3



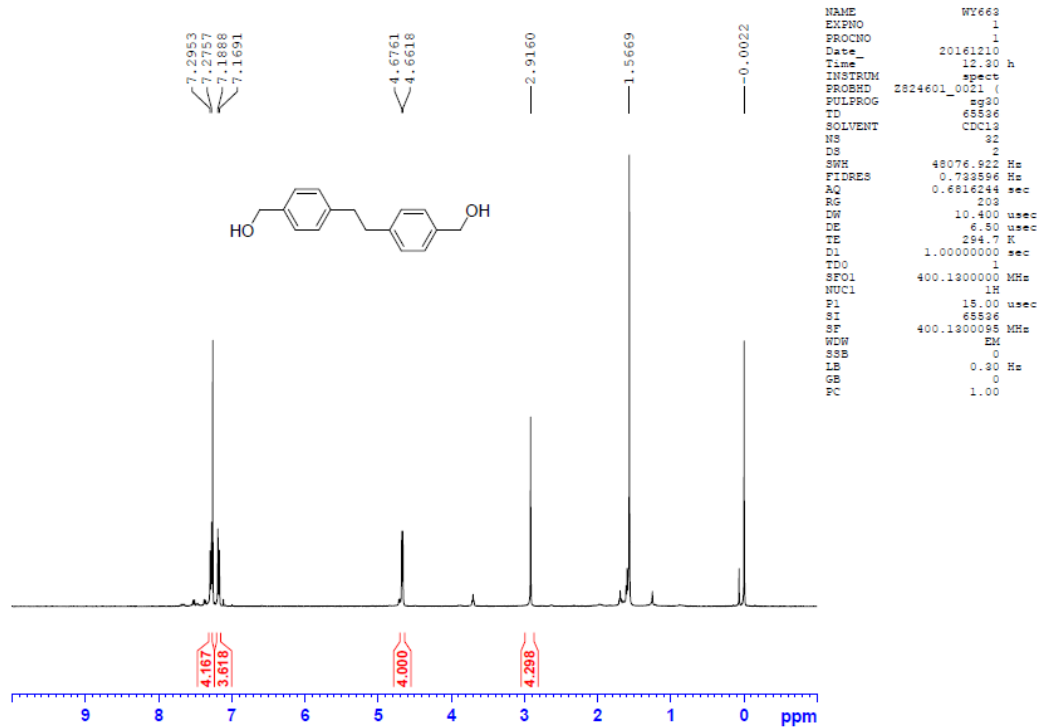
### <sup>1</sup>H NMR Spectrum of Dimethyl 4,4'-(Ethyne-1,2-diyl)dibenzoate



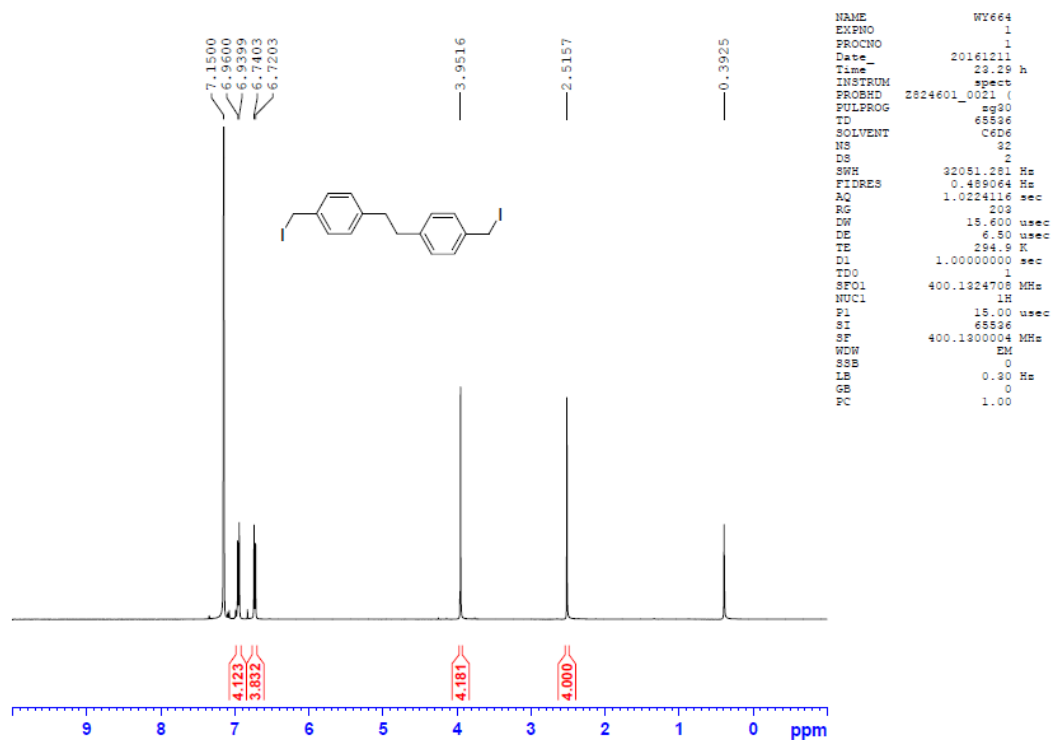
# <sup>1</sup>H NMR Spectrum of Dimethyl 4,4'-(Ethane-1,2-diyl)dibenzoate



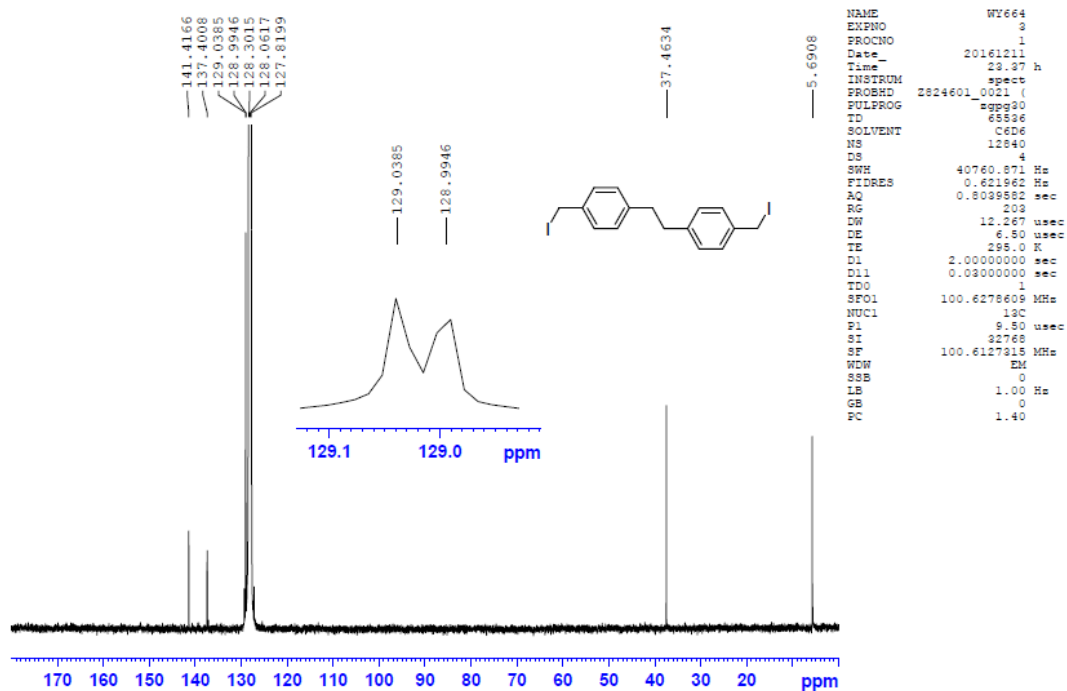
# <sup>1</sup>H NMR Spectrum of 4,4'-(Ethane-1,2-diyl)dibenzyl Alcohol



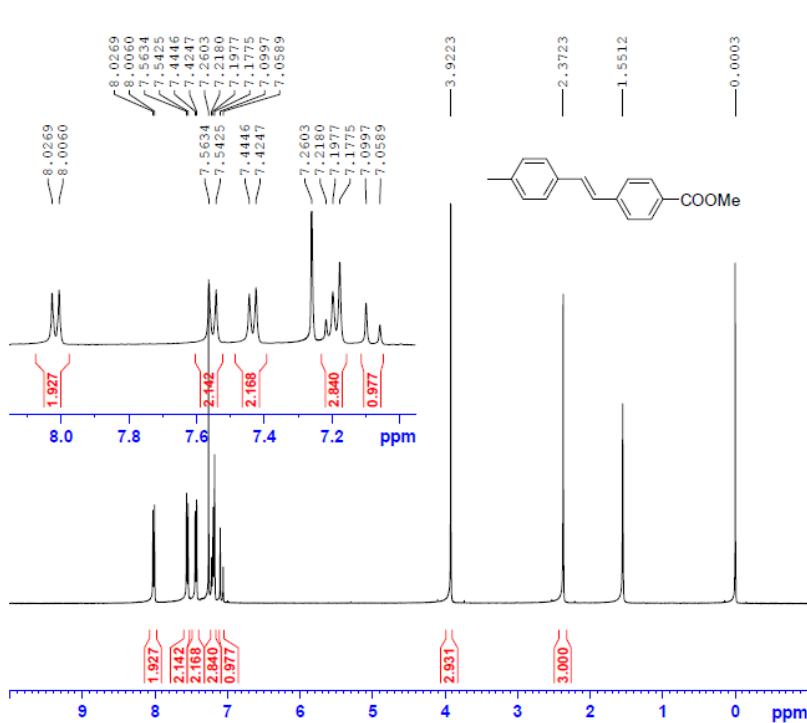
<sup>1</sup>H NMR Spectrum of 4,4'-Diiodomethylbibenzyl **3**



<sup>13</sup>C{<sup>1</sup>H} NMR Spectrum of 4,4'-Diiodomethylbibenzyl **3**



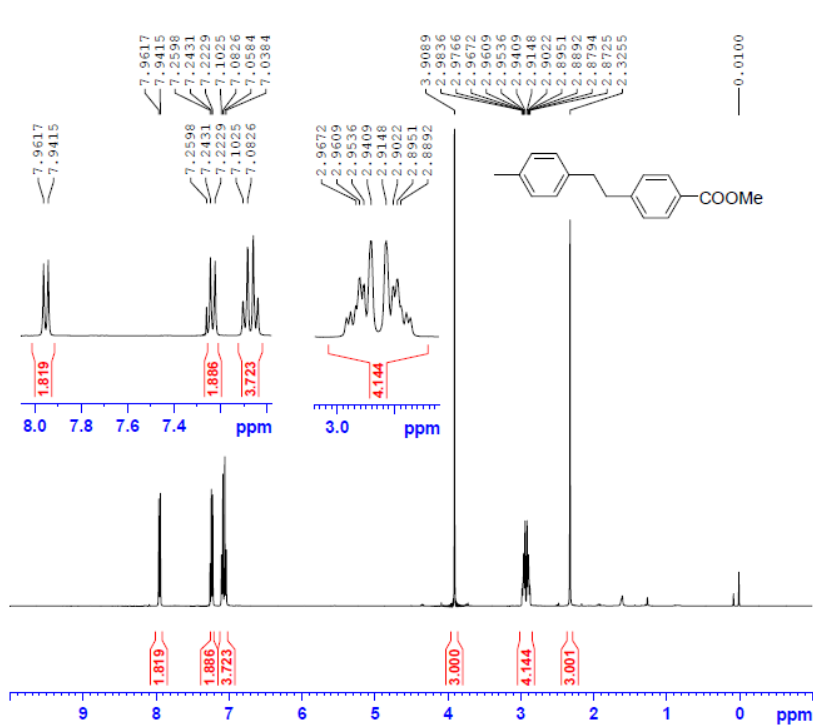
# <sup>1</sup>H NMR Spectrum of Methyl (E)-4-(4-Methylstyryl)benzoate



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EXPNO         1
PROCNO        1
Date_         20161115
Time          22.45 h
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PROBHD        2108618_0257 (
PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            2
DS            2
SWH           22051.251 Hz
FIDRES        0.489064 Hz
AQ            1.0224116 sec
RG            161
DW            15.600 usec
DE            6.50 usec
TE            296.3 K
D1            1.00000000 sec
TD0           1
SF01          400.2300000 MHz
NUC1          1H
P1            12.60 usec
SI            65536
SF            400.2300104 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
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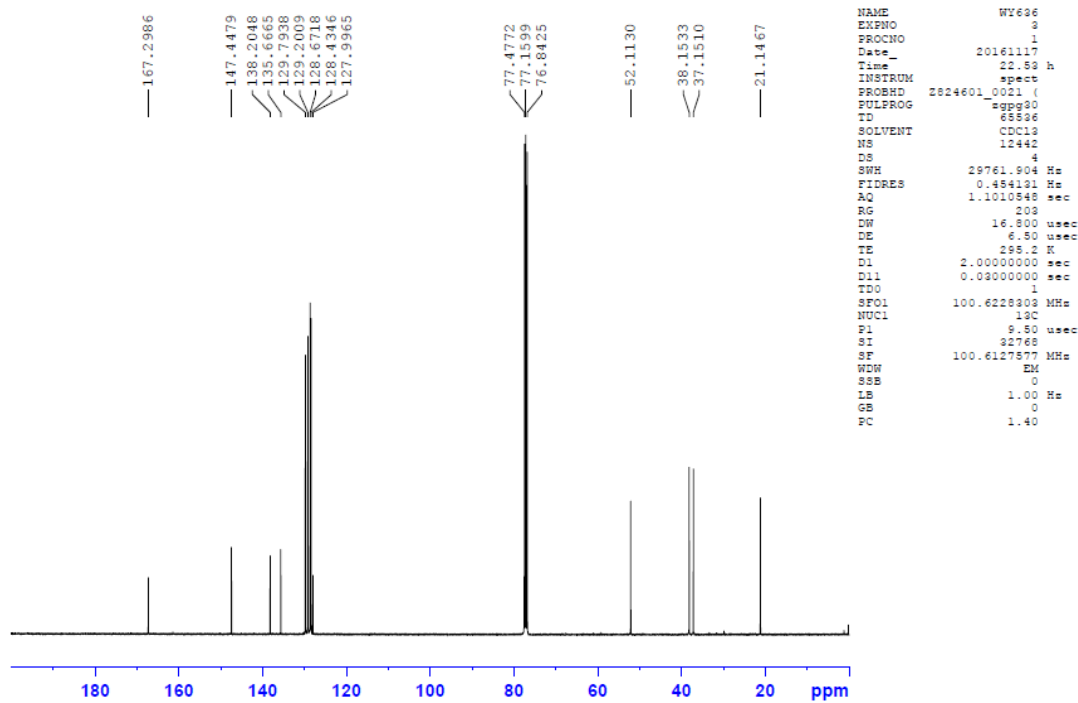
# <sup>1</sup>H NMR Spectrum of Methyl 4-(4-Methylphenethyl)benzoate



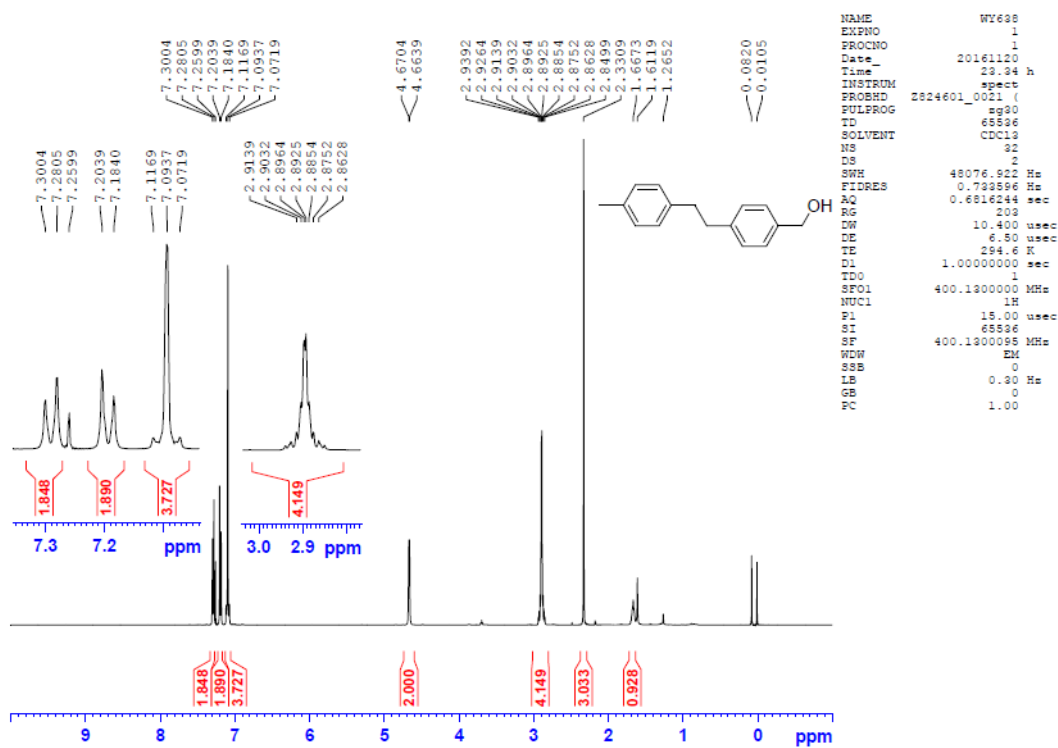
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PROCNO        1
Date_         20161117
Time          22.51 h
INSTRUM       spect
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PULPROG       zg30
TD            65536
SOLVENT       CDCl3
NS            2
DS            2
SWH           48076.922 Hz
FIDRES        0.793596 Hz
AQ            0.6816244 sec
RG            203
DW            10.400 usec
DE            6.50 usec
TE            295.1 K
D1            1.00000000 sec
TD0           1
SF01          400.1800000 MHz
NUC1          1H
P1            15.00 usec
SI            65536
SF            400.1800095 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            1.00
    
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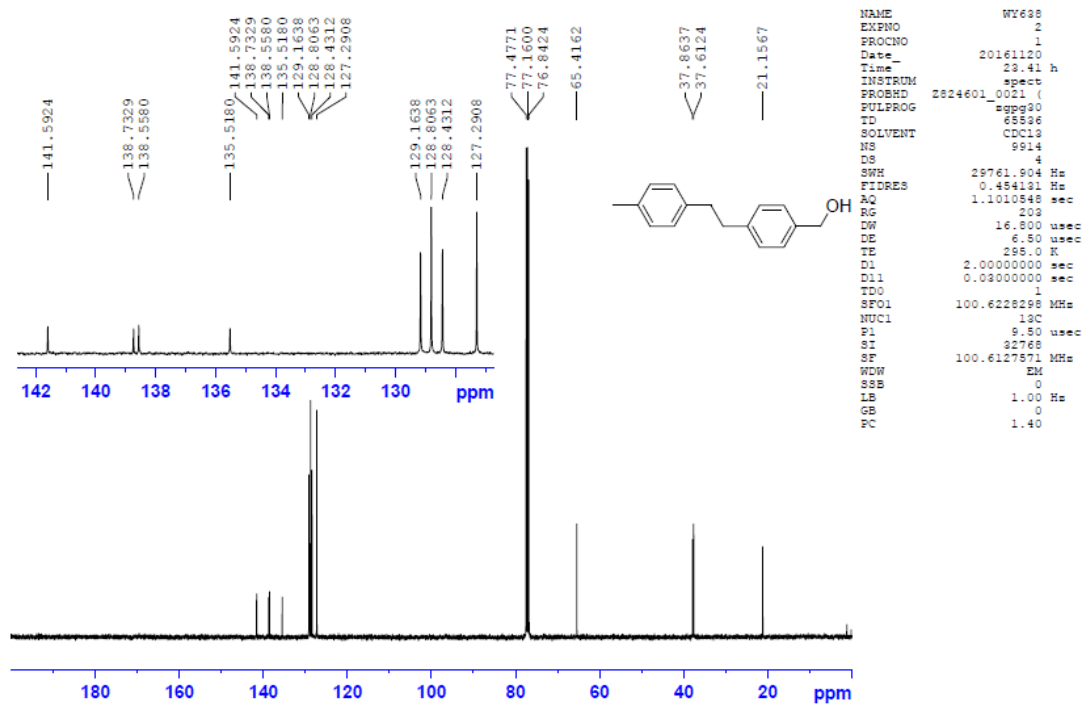
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of Methyl 4-(4-Methylphenethyl)benzoate



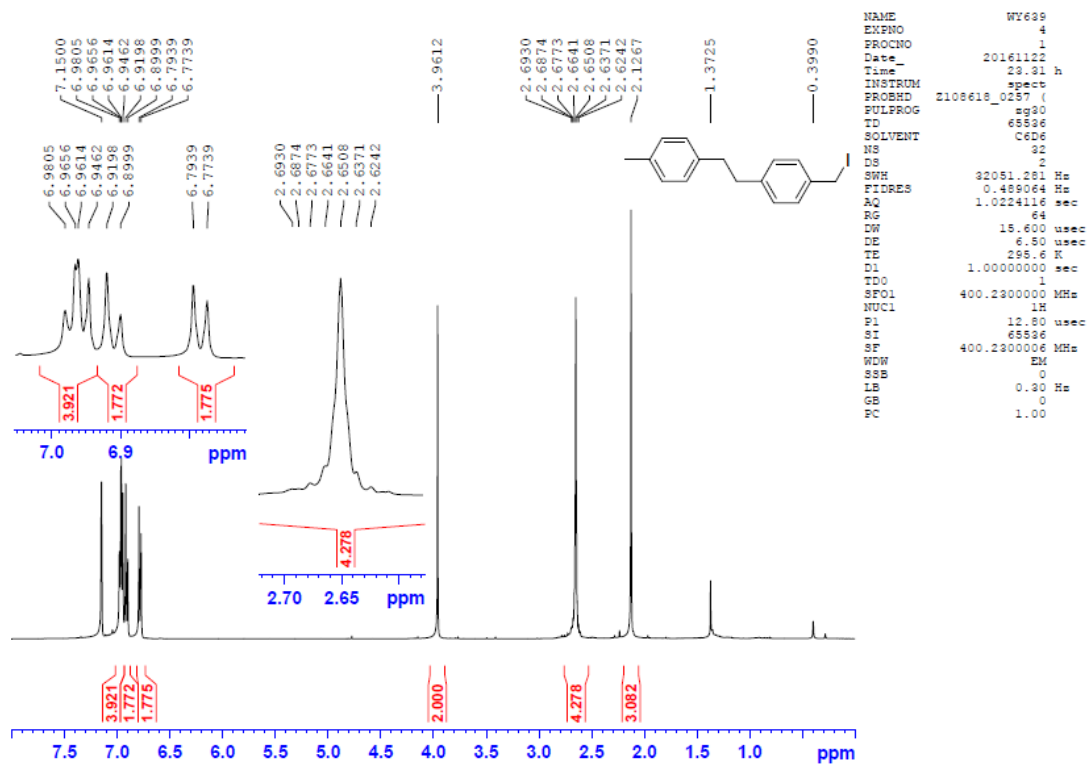
$^1\text{H}$  NMR Spectrum of 1-*p*-Tolyl-2-(*p*-(hydroxymethyl)phenyl)ethane



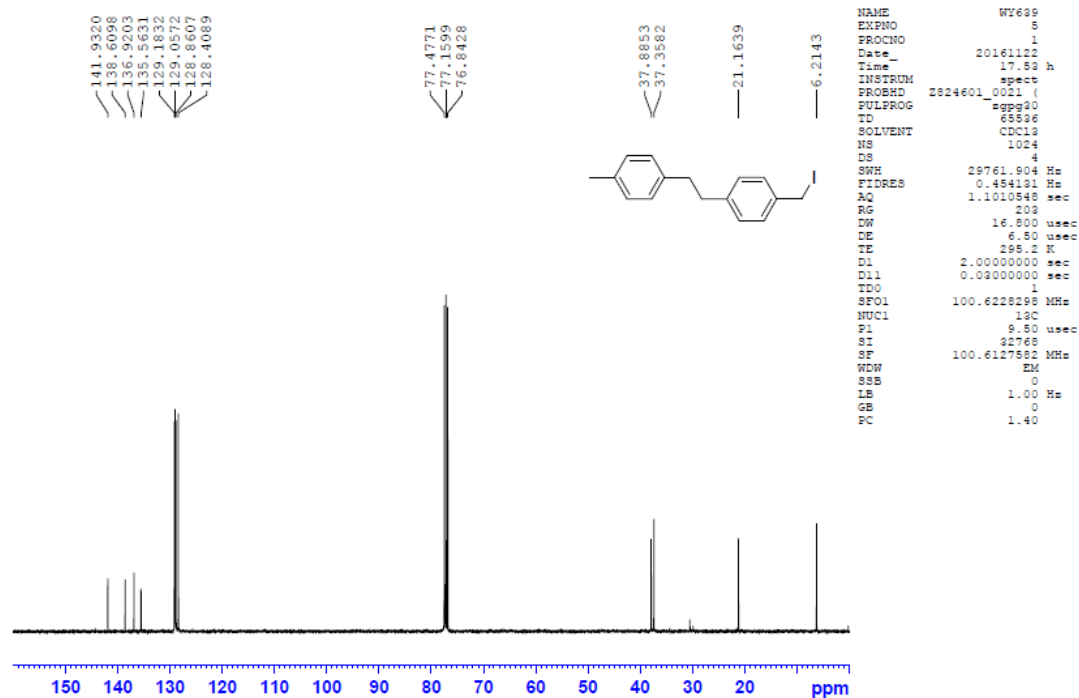
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of 1-*p*-Tolyl-2-(*p*-(hydroxymethyl)phenyl)ethane



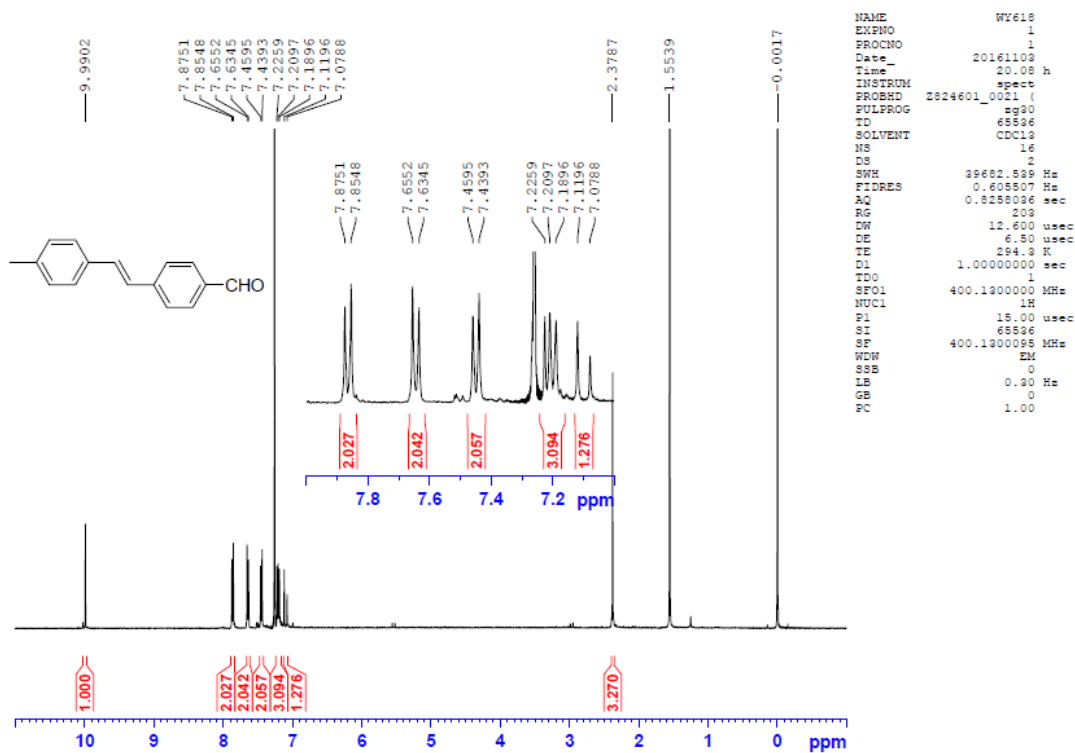
$^1\text{H}$  NMR Spectrum of 4-Iodomethyl-4'-methylbibenzyl 4



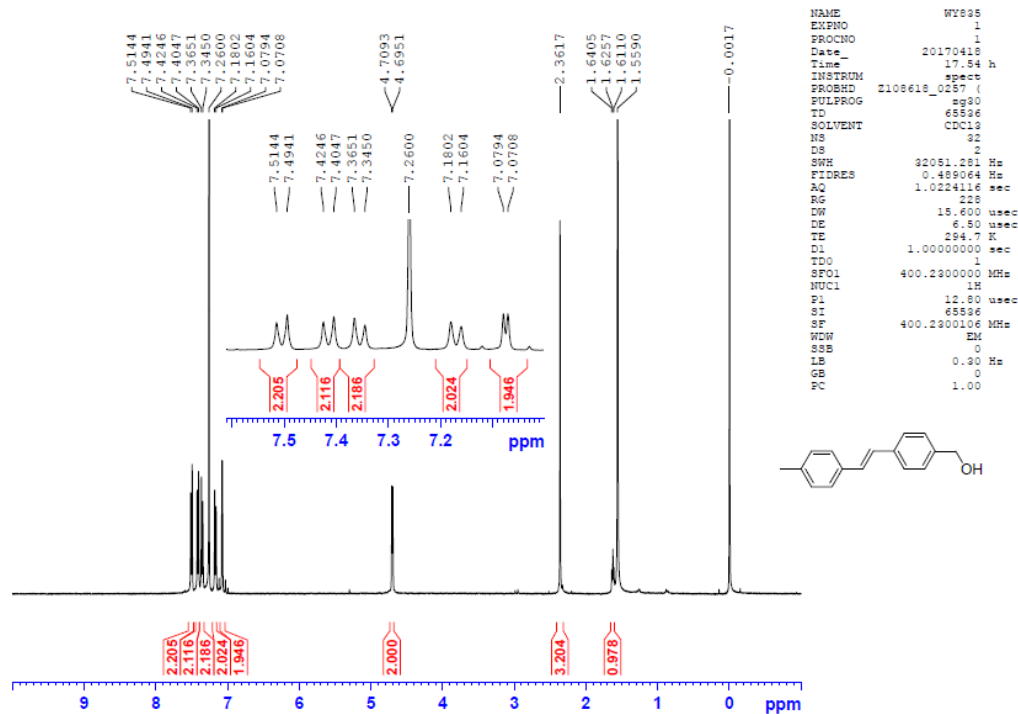
### <sup>13</sup>C NMR Spectrum of 4-Iodomethyl-4'-methylbibenzyl 4



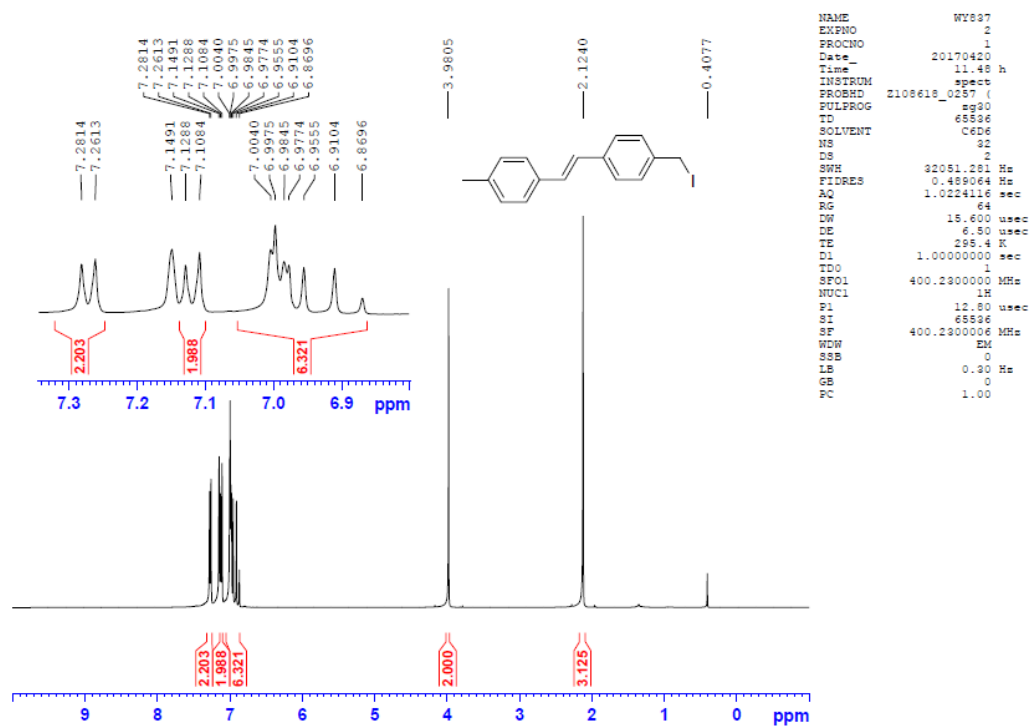
### <sup>1</sup>H NMR Spectrum of (E)-4-(4-Methylstyryl)benzaldehyde



<sup>1</sup>H NMR Spectrum of (E)-4-(4-Methylstyryl)phenylmethanol

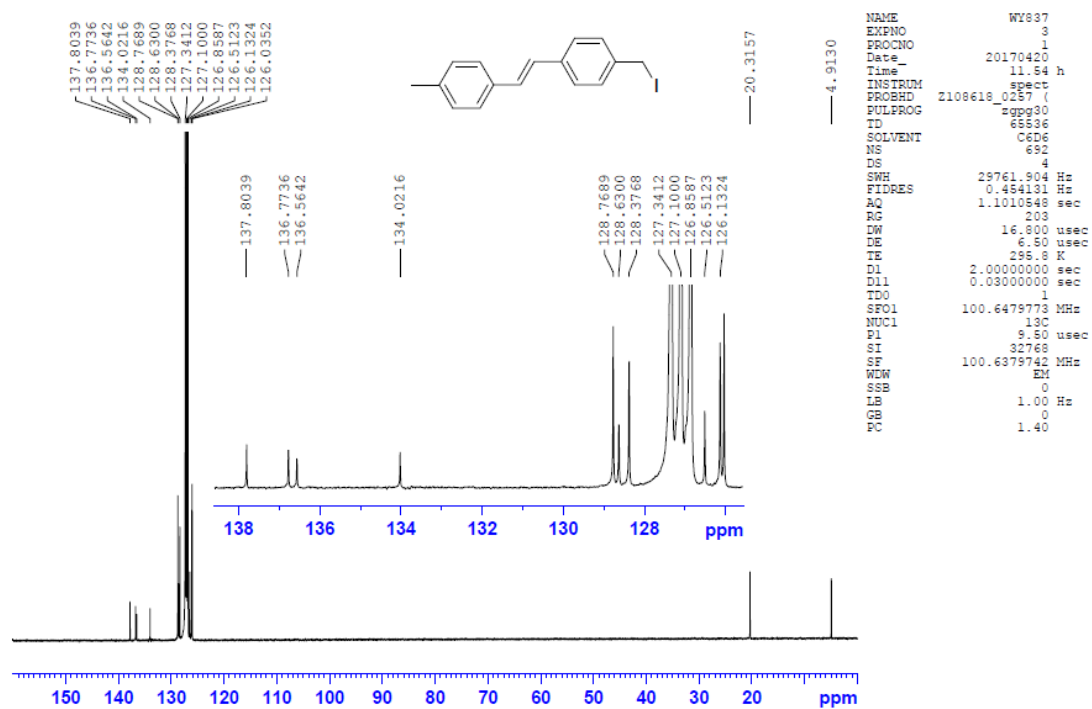


<sup>1</sup>H NMR Spectrum of (E)-1-(Iodomethyl)-4-(4-methylstyryl)benzene 5

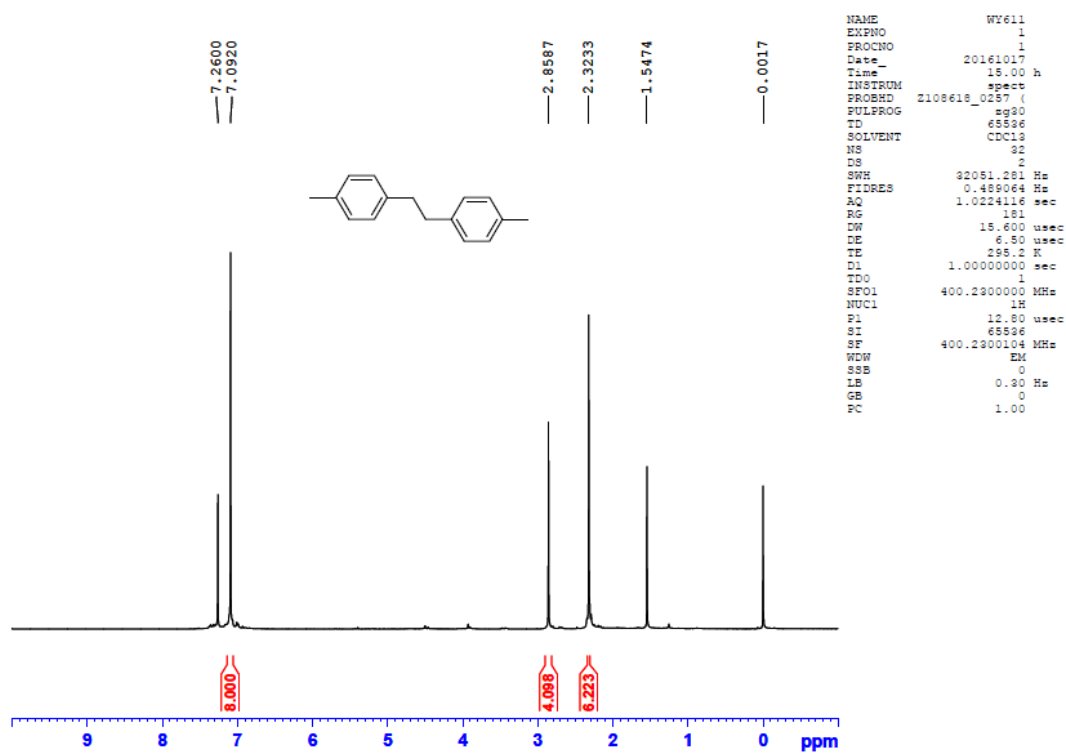




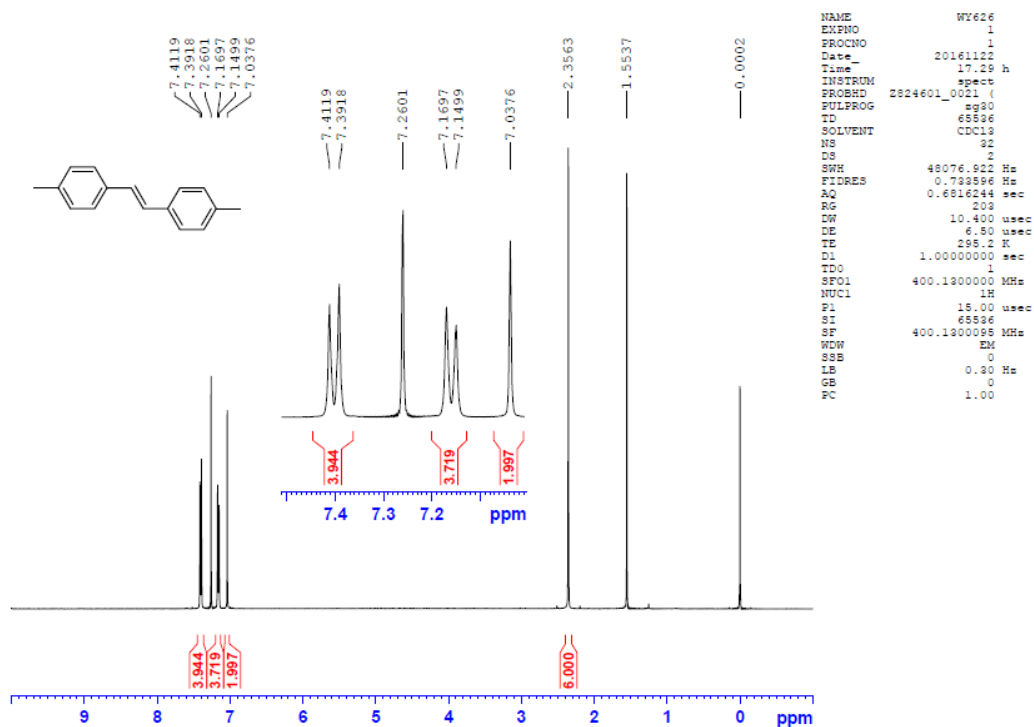
$^{13}\text{C}\{^1\text{H}\}$  NMR Spectrum of (*E*)-1-(Iodomethyl)-4-(4-methylstyryl)benzene **5**



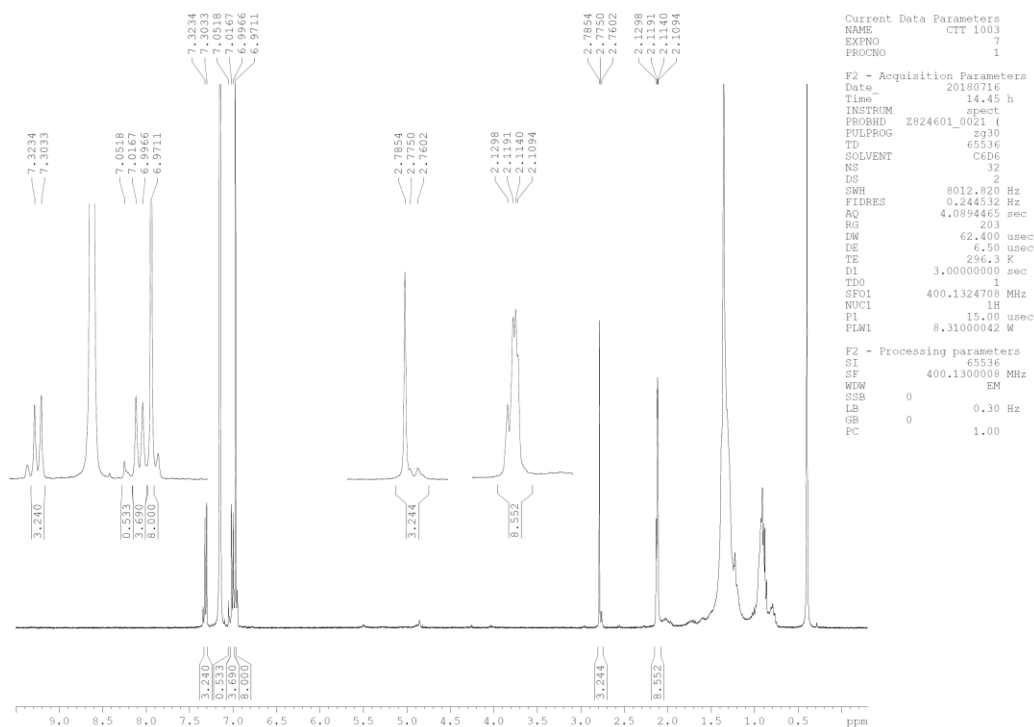
$^1\text{H}$  NMR Spectrum of 4,4'-Dimethylbibenzyl **1**



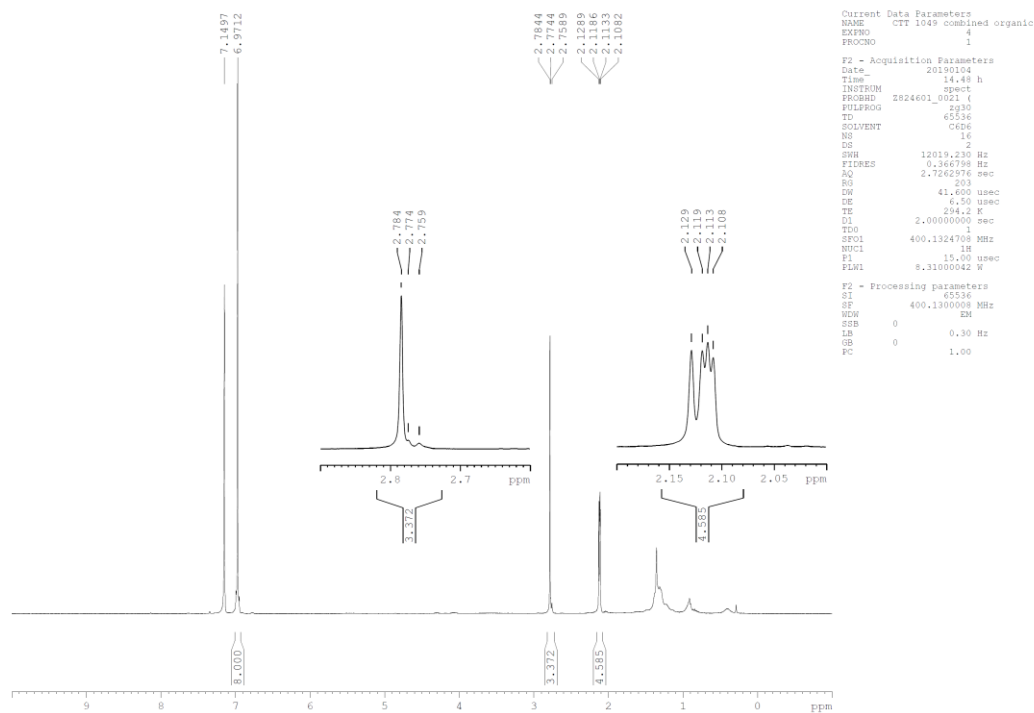
# <sup>1</sup>H NMR Spectrum of (E)-4,4'-Dimethylstilbene 2



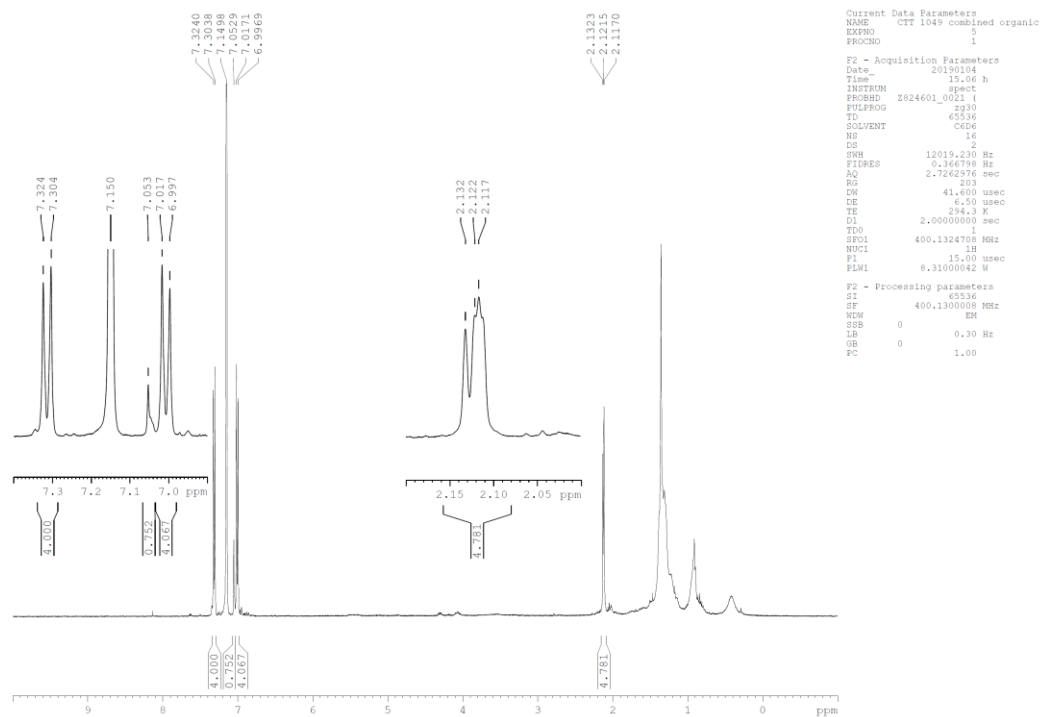
# <sup>1</sup>H NMR Spectrum of the Deuterium Labeling Reaction (eq 5)



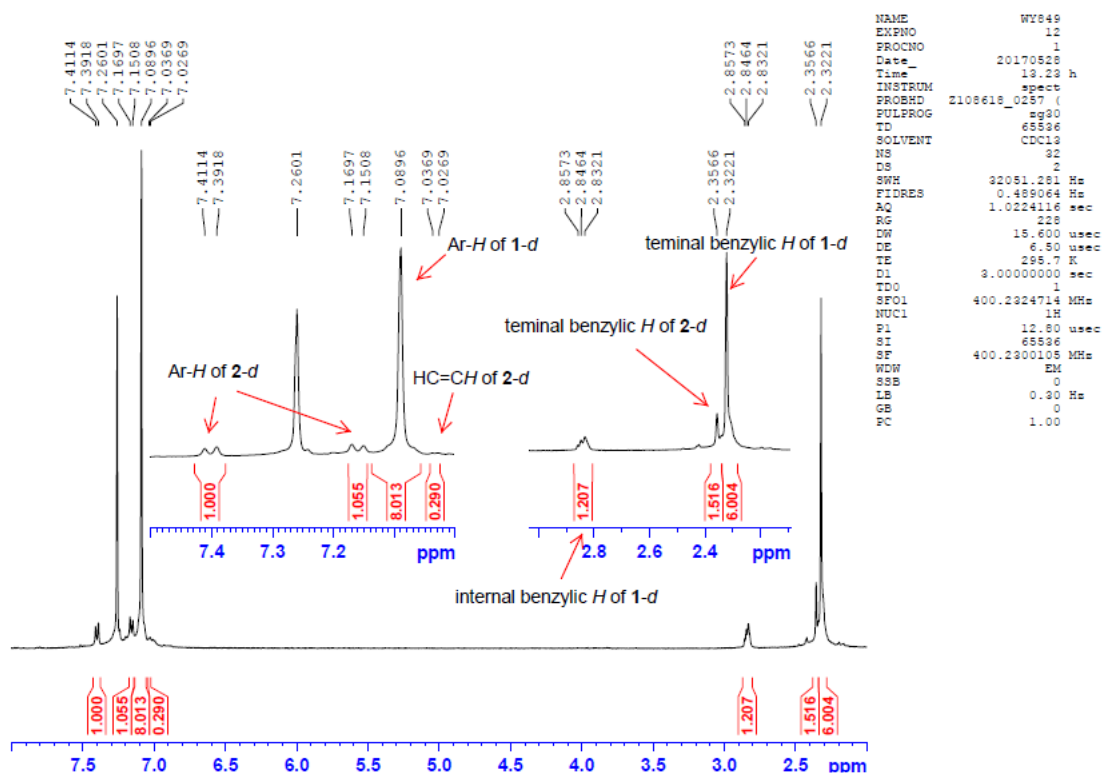
<sup>1</sup>H NMR Spectrum of isolated **1-d** from 14 runs (eq S7)



<sup>1</sup>H NMR Spectrum of isolated **2-d** from 14 runs (eq S7)



<sup>1</sup>H NMR Spectrum of the Post-Exchange Reaction of **1** with D<sub>2</sub>O (eq 6)



# MS Spectra

## HRMS Spectrum of 4,4'-Diiodomethylbibenzyl **3**

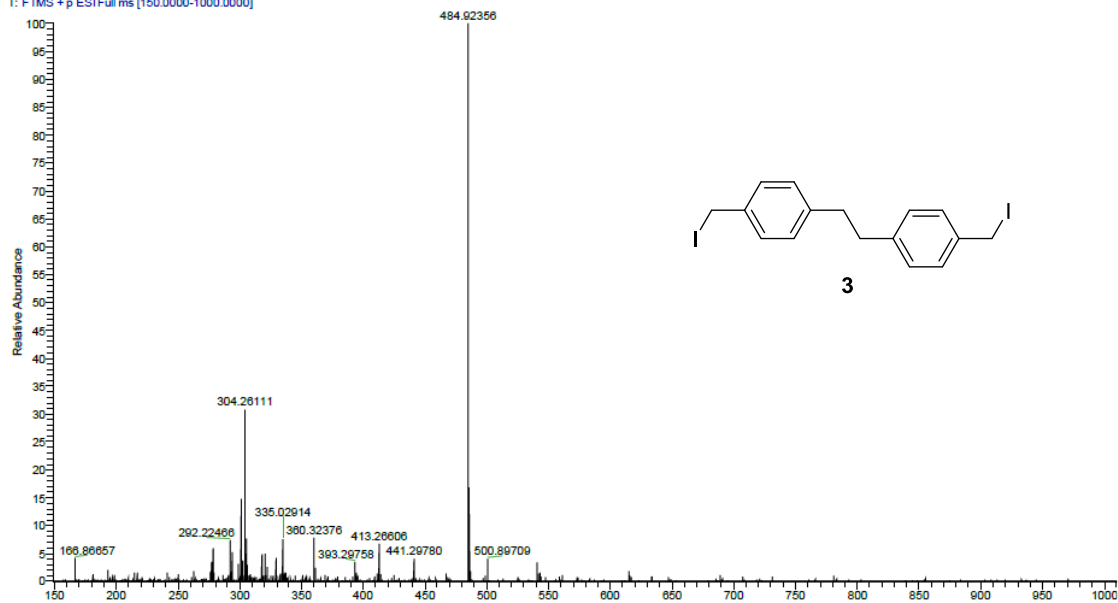
Molecular formula :	C <sub>16</sub> H <sub>16</sub> I <sub>2</sub>
Experimental Mass [M+Na] <sup>+</sup> :	484.92356
Theoretical Mass [M+Na] <sup>+</sup> :	484.92336
Error (ppm) :	0.4

D:\Raw data\qksc020

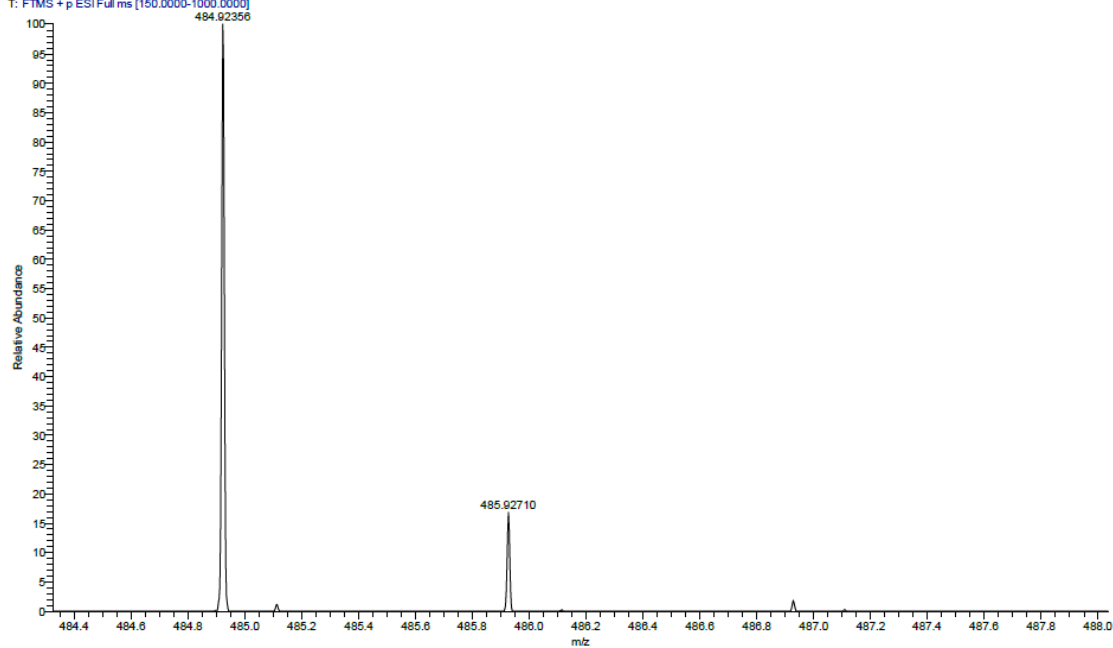
06/27/17 16:03:51

WY664

qksc020 #214 RT: 0.97 AV: 1 SB: 254 0.40-0.66 , 1.05-1.93 NL: 1.15E6  
T: FTMS + p ESI Full ms [150.0000-1000.0000]



qksc020 #214 RT: 0.97 AV: 1 SB: 254 0.40-0.66 , 1.05-1.93 NL: 1.15E6  
T: FTMS + p ESI Full ms [150.0000-1000.0000]



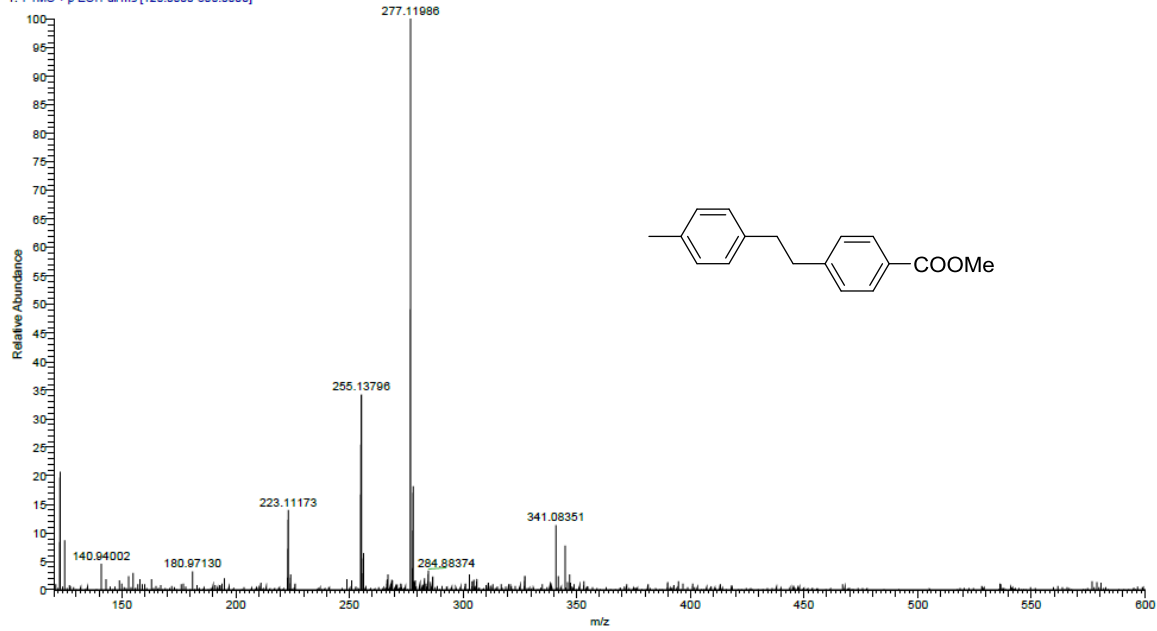
# HRMS Spectrum of Methyl 4-(4-Methylphenethyl)benzoate

Molecular formula :	C <sub>17</sub> H <sub>18</sub> O <sub>2</sub>
Experimental Mass (M+Na) <sup>+</sup> :	277.11986
Theoretical Mass (M+Na) <sup>+</sup> :	277.11990
Error (ppm) :	0.1

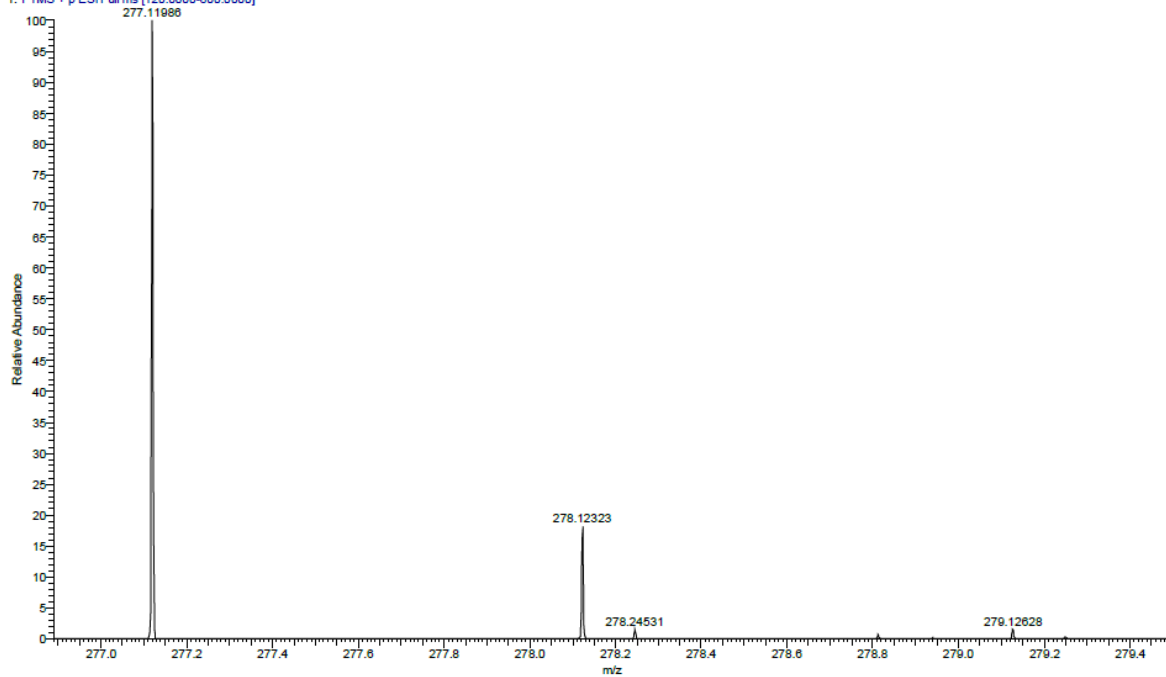
D:\Raw data\qksc007

11/30/16 17:11:58

qksc007 #197 RT: 0.88 AV: 1 SB: 182 0.41-0.76 , 1.04-1.49 NL: 1.63E8  
T: FTMS + p ESI Full ms [120.0000-800.0000]



qksc007 #197 RT: 0.88 AV: 1 SB: 182 0.41-0.76 , 1.04-1.49 NL: 1.63E8  
T: FTMS + p ESI Full ms [120.0000-800.0000]



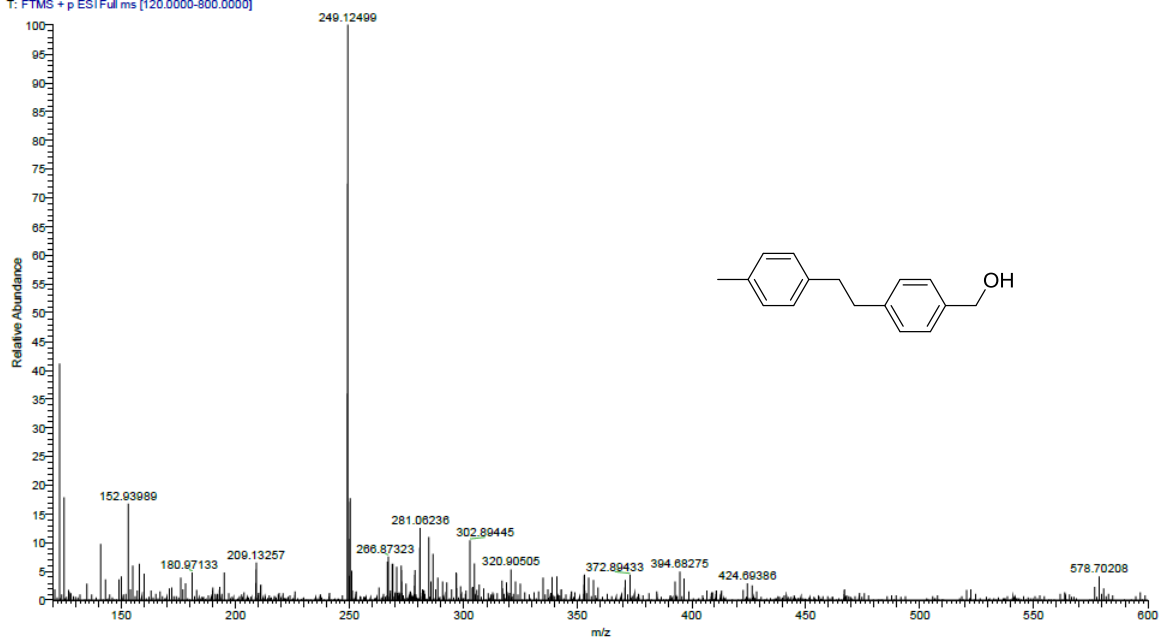
# HRMS Spectrum of 1-*p*-Tolyl-2-(*p*-(hydroxymethyl)phenyl)ethane

Molecular formula :	C <sub>16</sub> H <sub>18</sub> O
Experimental Mass (M+Na) <sup>+</sup> :	249.12499
Theoretical Mass (M+Na) <sup>+</sup> :	249.12499
Error (ppm) :	0.0

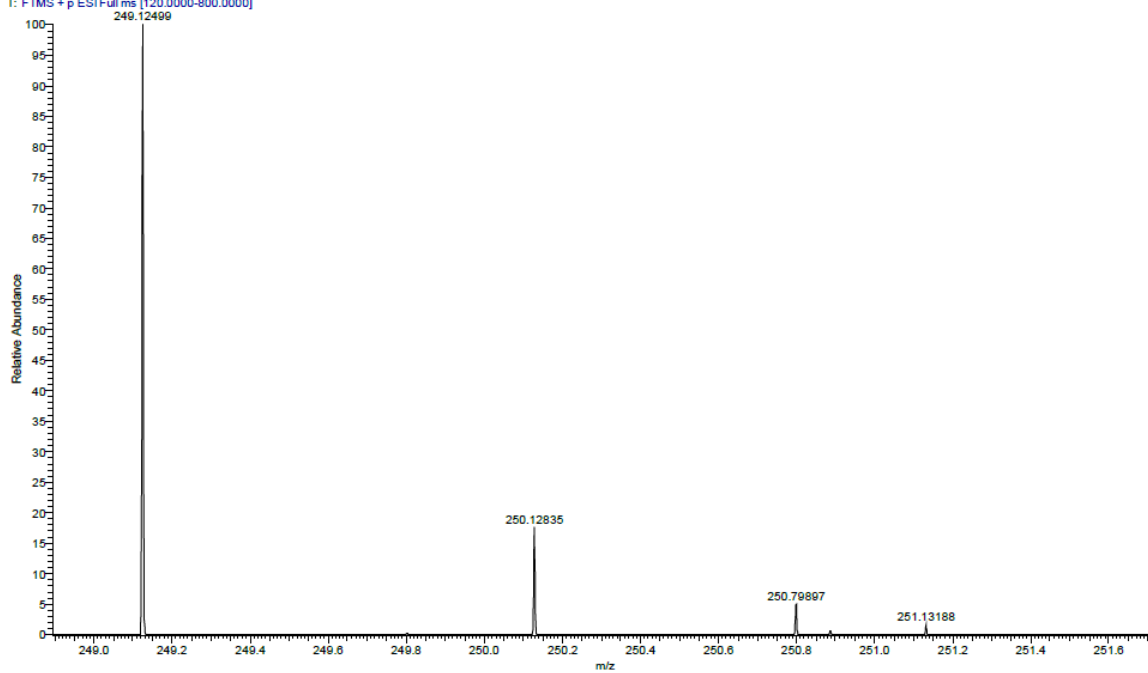
D:\Raw data\qksc008

11/30/16 17:24:13

qksc008 #199 RT: 0.89 AV: 1 SB: 183 0.38-0.79, 0.99-1.39 NL: 5.27E7  
T: FTMS + p ESI Full ms [120.0000-800.0000]



qksc008 #199 RT: 0.89 AV: 1 SB: 183 0.38-0.79, 0.99-1.39 NL: 5.27E7  
T: FTMS + p ESI Full ms [120.0000-800.0000]



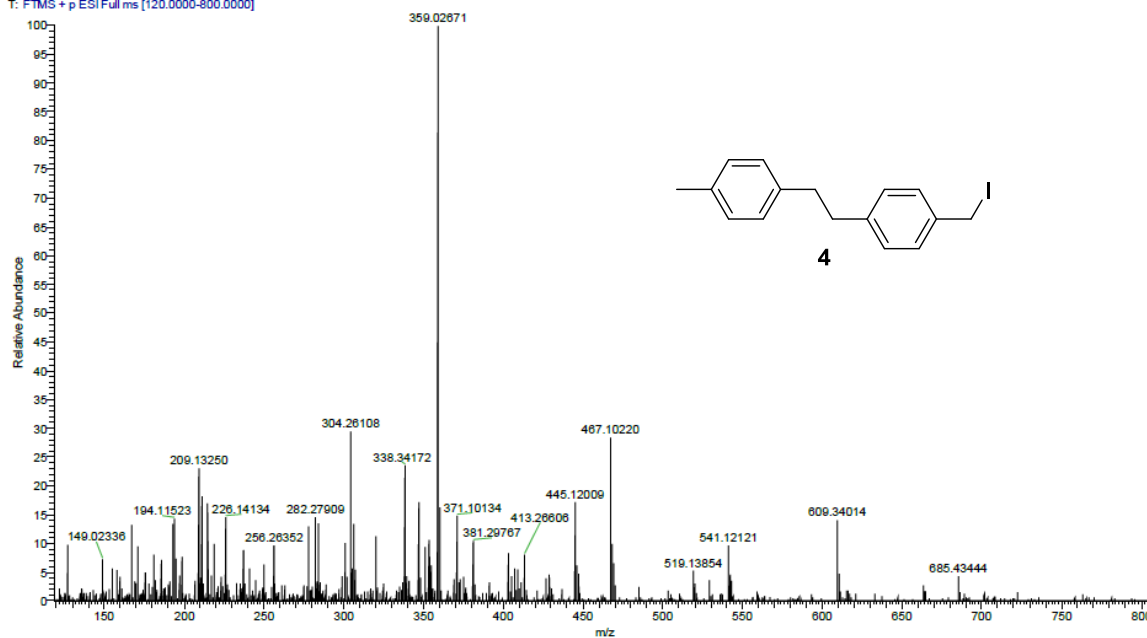
# HRMS Spectrum of 4-Iodomethyl-4'-methylbibenzyl 4

Molecular formula :	C <sub>16</sub> H <sub>17</sub> I
Experimental Mass (M+Na) <sup>+</sup> :	359.02671
Theoretical Mass (M+Na) <sup>+</sup> :	359.02671
Error (ppm) :	0.0

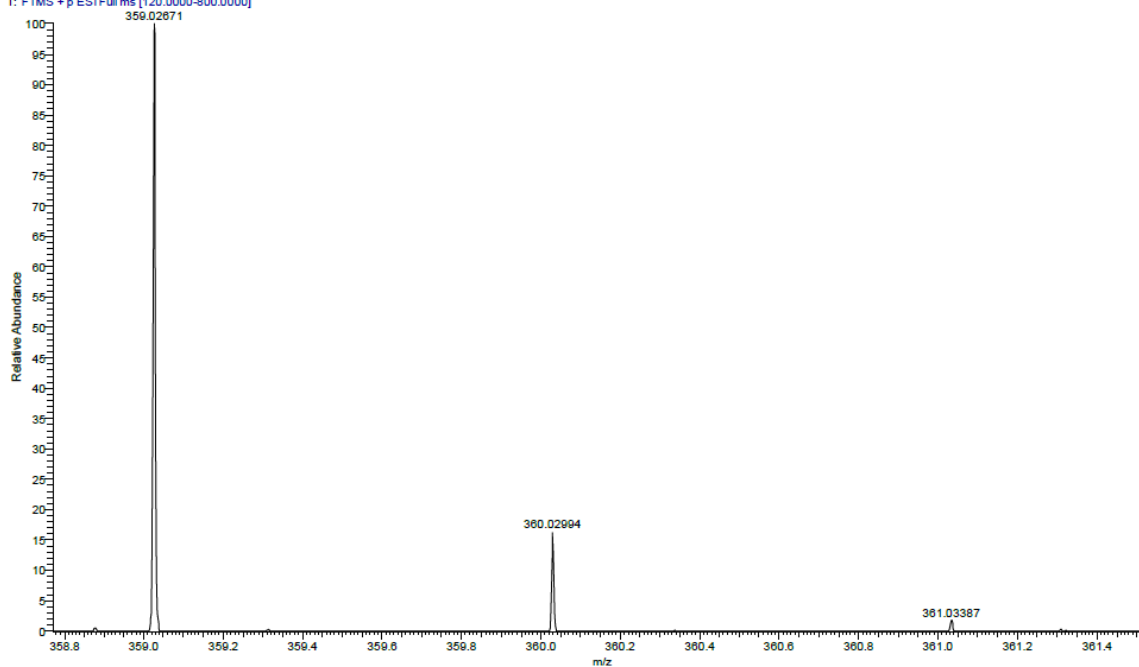
D:\Raw data\qksc009

11/30/16 17:36:33

qksc009 #194 RT: 0.87 AV: 1 SB: 142 0.51-0.74 , 0.96-1.36 NL: 1.18E7  
T: FTMS + p ESI Full ms [120.0000-800.0000]



qksc009 #194 RT: 0.87 AV: 1 SB: 142 0.51-0.74 , 0.96-1.36 NL: 1.18E7  
T: FTMS + p ESI Full ms [120.0000-800.0000]





# HRMS Spectrum of (E)-1-(Iodomethyl)-4-(4-methylstyryl)benzene 5

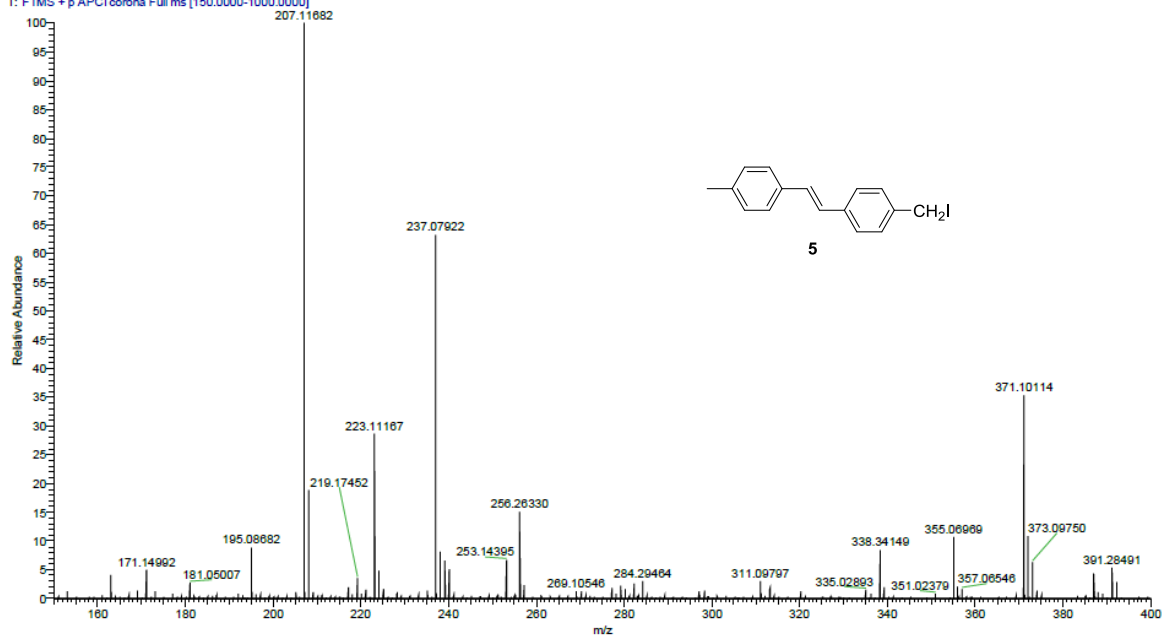
Molecular formula :	C <sub>16</sub> H <sub>15</sub> I
Experimental Mass [M+H] <sup>+</sup> :	335.02893
Theoretical Mass [M+H] <sup>+</sup> :	335.02912
Error (ppm) :	0.5

D:\Raw data\qksc018\_170427153039

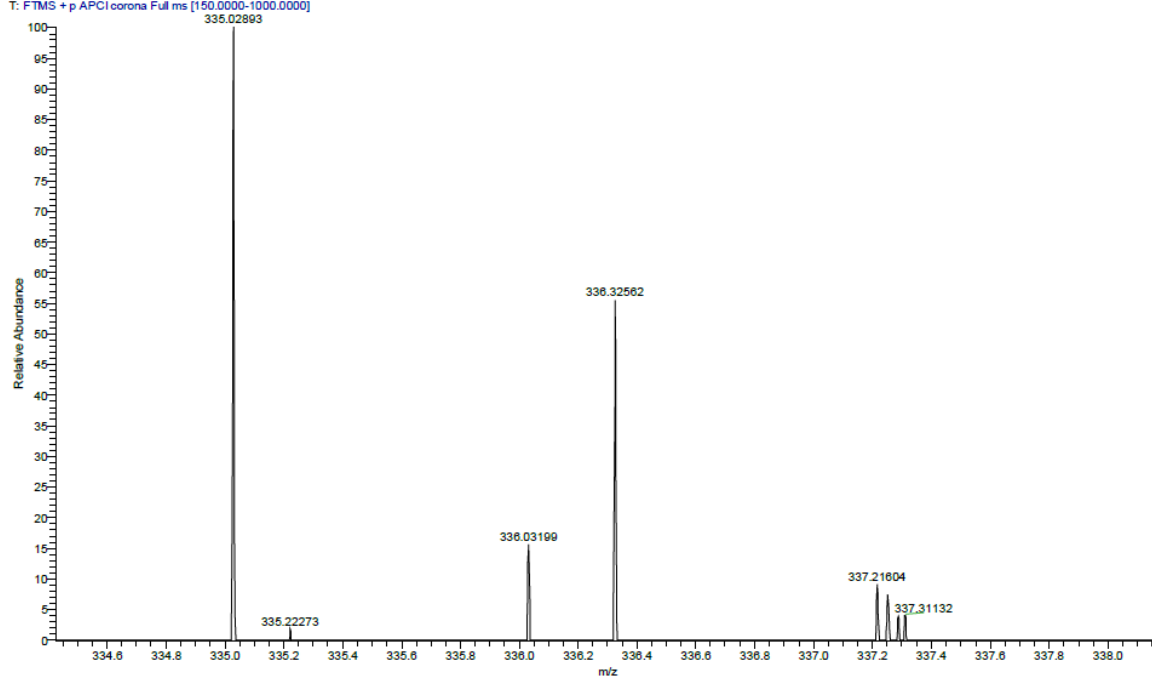
04/27/17 15:31:43

WY837

qksc018\_170427153039 #98 RT: 0.44 AV: 1 SB: 213 0.08-0.26 , 0.67-1.43 NL: 4.38E6  
T: FTMS + p APCI corona Full ms [150.0000-1000.0000]



qksc018\_170427153039 #98 RT: 0.44 AV: 1 SB: 213 0.08-0.26 , 0.67-1.43 NL: 6.91E4  
T: FTMS + p APCI corona Full ms [150.0000-1000.0000]



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