Supporting Information

Iodine-promoted transfer of dihydrogen from ketones to alkenes, triphenylmethyl and diphenylmethyl derivatives

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Supporting Information

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1. General Information

All reaction reagents or intermediates were carried out in dried glassware under atmosphere using 20 mL of Schlenk tube. n-Hexane was purchased from Shanghai Titan Scientific. Otherwise noted, other commercially available reagents were purchased from Energy Chemical, Sigma-Aldrich or Bidepharm in the highest purity grade and used without further purification. Thin layer chromatography (TLC) was performed on Energy Chemical silica gel GF-254 plates and visualized by fluorescence quenching under UV light (254/366 nm) or iodine quenching under silica gel and iodine mixture. Column chromatography was performed on Qingdao Ocean Chemical Co., Ltd. silica gel (300-400 mesh). 1H and 13C NMR spectra were recorded on a Bruker AC-400 FT or Bruker AC-300 FT spectrometer using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. High-resolution mass spectra (HRMS) measurement was performed on Agilent Q-TOF 6520 mass spectrometer with electron ionization (EI) and electrospray ion source (ESI) as the ion source.

Abbreviations: TH = transfer hydrogenation, NIS = N-iodosuccinimide, TBAI = tetrabutylammonium iodide, TIOH = trifluoromethanesulfonic acid, DCM = dichloromethane, EA = ethyl acetate, THF = tetrahydrofuran, MeCN = acetonitrile, DIDMH = 1,3-diiodo-5,5-dimethylimidazolidine-2,4-dione.

2. Preparation of Substrates

![Figure S1. Substrate structures.]

2.1. Preparation of 5b-e, 5m-n, 5u

To a solution of substituent aromatic ketones (10.0 mmol) in dry tetrahydrofuran (20 mL) under a nitrogen atmosphere at 0 °C was added dropwise a solution of phenyl magnesium bromide in tetrahydrofuran (2.0 M, 7.5 mL, 15.0 mmol). The mixture was stirred at 0 °C for 10 min and then for another 2 h at room temperature. The mixture was added a saturated aqueous NH4Cl solution (10 mL) carefully, then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated to give the crude product. Then added ethyl acetate (3 × 15 mL). The organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered,
and concentrated to give the crudes, which were purified by silica gel column chromatography, eluting with petroleum ether, to give desired products 1b-e, 1n, 1p-q.

2.2. Preparation of 1f-l, 1o

\[
\text{R}^1\text{O} + \text{R}^2\text{P(Ph)}_2\text{Br} \xrightarrow{\text{n-BuLi}, \text{THF}, 0\, ^\circ\text{C}, \text{N}_2} \text{1f-l, 1o}
\]

To a solution of R\(^3\)(Ph)\(_3\)Br (5.13 g, 15.0 mmol) in dry tetrahydrofuran (20 mL) under a nitrogen atmosphere at 0 °C was added dropwise a solution of n-BuLi in tetrahydrofuran (2.5 M, 6.0 mL, 15.0 mmol). The mixture was allowed to warm to room temperature and stirred for 0.5 h. Ketones (12.0 mmol) were dissolved in anhydrous and added into the above reaction mixture with a syringe, the results mixture was stirred with another 2 h. After the reaction was completed, the mixture was added a saturated aqueous NH\(_4\)Cl solution (10 mL) carefully, then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated to give the crudes, which were purified by silica gel column chromatography, eluting with petroleum ether, to give desired products 1f-l, 1o.

2.3. Preparation of 1r

\[
\text{O} + \text{Ph} + \text{P}_2\text{O}_5 \xrightarrow{\text{DCM, rt}, \text{H}} \text{1r}
\]

Cycloheptanone (1.12 g, 10.0 mmol) and P\(_2\)O\(_5\) (2.84 g, 20.0 mmol) were dissolved in 30 mL anhydrous DCM (30 mL), and \(p\)-toluenethiol (1.37 g, 11.0 mmol) was added dropwise. Then, the mixture was stirred for 5 h at room temperature. The mixture was quenched with 2N NaOH (30 mL) solution, then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated to give the crude, which was purified by silica gel column chromatography, eluting with petroleum ether, to give the desired product 1r.

2.4. Preparation of 5o, 5l, 5q

\[
\text{X} = \text{OH or NH}_2 \\
\text{R}^1 = \text{Ph or H} \\
\text{5o, 5l, 5q}
\]

Substituents benzyl alcohol (10.0 mmol) and Et\(_3\)N (2.77 mL, 20.0 mmol) were dissolved in anhydrous dichloromethane (30 mL) at 0 °C and acyl chloride/ sulfonyl chloride (15.0 mmol) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 3 h. Then, the mixture was extracted with dichloromethane (3 × 20 mL). The organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated to give the crude, which was purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (1: 5 to 1: 3 v/v), to give desired products 5o, 5l, 5q.

2.5. Preparation of 5k, 5m

\[
\text{5k, 5m}
\]
To a solution of benzhydrol (1.84 g, 10.0 mmol) in toluene (20 mL) was added methanol/ethanol (30.0 mmol) and 3 drops Con. HCl. The mixture was heated at 100 °C for 12 h, cooled to room temperature, and concentrated under reduced pressure to give the crudes, which as purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (1: 20 to 1: 10 v/v), to give desired products 5k, 5m.

2.6. Preparation of 5b-e, 5i

Ketones (10.0 mmol) were dissolved in MeOH (30 mL) at 0 °C, and NaBH₄ (757 mg, 20.0 mmol) was added slowly. The mixture was allowed to warm to room temperature and stirred for 2 h. The mixture was quenched with 10 mL saturated aqueous NH₄Cl solution, then extracted with ethyl acetate (3 × 20 mL). The organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated to give the crude, which was purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (1: 10 to 1: 4 v/v), to give desired product 5b-e, 5i.

3. Optimization of the Reaction Conditions

For the procedure, see below. The results are summarized in the following Table.

Table S1. optimization of the reaction condition

<table>
<thead>
<tr>
<th>Entry</th>
<th>Change from standard conditions</th>
<th>Yield of 3a [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>DCM instead of n-hexane</td>
<td>23</td>
</tr>
<tr>
<td>3</td>
<td>Toluene instead of n-hexane</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>CHCl₃ instead of n-hexane</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>MeCN instead of n-hexane</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>Lower the temperature to 90 °C</td>
<td>77</td>
</tr>
<tr>
<td>7</td>
<td>DIDMH instead of iodine</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>NIS instead of iodine</td>
<td>29</td>
</tr>
<tr>
<td>9</td>
<td>HI instead of iodine</td>
<td>37</td>
</tr>
<tr>
<td>10</td>
<td>TBAI instead of iodine</td>
<td>NR</td>
</tr>
<tr>
<td>11</td>
<td>TfOH instead of iodine</td>
<td>62 (48[b])</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (0.3 mmol), 2a (0.75 mmol), and Lewis acid (0.6 mmol) in n-hexane (0.5 mL), at 110 °C (oil bath), for 4 h. [b] Isolate yield. [c] 0.15 mmol TfOH, the isolated yield is 48%.

Table S2. Optimization of the reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>cycloheptanone (equiv)</th>
<th>Iodine (equiv)</th>
<th>Solvent (0.5 mL)</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>n-hexane</td>
<td>110</td>
<td>8</td>
<td>28</td>
</tr>
</tbody>
</table>
According to the results, the amount of iodine and ketones is critical factors influencing the efficiency of the reaction. The amount of cycloheptanone needs more than 2.0 equiv., otherwise the yield of 1,1-diphenylethane will reduced sharply. The amount of iodine is also very important to the yield. The solvent of this hydrogenation reaction was compatible with n-hexane, toluene and MeCN. The temperature of the reaction is also important, while the temperature is under 70 °C, the reaction will not take place.

4. General Procedure of Hydrogenation

4.1. General Procedure for the Hydrogenation of Alkenes and Alkynes

To a solution of alkene derivatives (0.3 mmol) in n-hexane (0.5 mL) was added cycloheptanone (88.5 μL, 0.75 mmol) and iodine (152.3 mg, 0.6 mmol). The mixture was heated at 110 °C (oil bath) under air in a sealed tube for 4 h, cooled to room temperature, and purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (0: 10 to 1: 10 v/v), to give the desired products.

4.2. General Procedure for Hydrogenation of alcohol, ether, ester, amine et al.

To a solution of benzhydrol derivatives (0.3 mmol) in n-hexane (0.5 mL) was added cycloheptanone (88.5 μL, 0.75 mmol) and iodine (152.3 mg, 0.6 mmol). The mixture was heated at 110 °C (oil bath) under air in a sealed tube for 4 h, cooled to room temperature, and purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (0: 10 to 1: 10 v/v), to give the desired products.
5. Mechanism Studies

5.1. Compound 8 NMR and MS Characterization

Compound 8 HRMS (ESI) calcd for C14H21O (M+H)+ 205.1587, found 205.1584.

\[\text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\text{)} \delta 2.73 – 2.65 (m, 4H), 2.43 – 2.26 (m, 4H), 1.79 – 1.63 (m, 12H).\]
$^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.42, 121.51, 30.99, 28.93, 28.84, 26.88, 23.90.

5.2. General Procedure for Compound 9 Derivatives Synthesis and Reaction of β-Hydroxyketones

To a solution of cyclododecanone (3.65 g, 20 mmol) in n-hexane (20 mL) was added iodine (10.15 g, 40 mmol). The mixture was heated at 90 °C (oil bath) for 2 h, cooled to room temperature, and concentrated under reduced pressure to give the crudes, which was purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (1:10), to give desired product 9.
$^1$H NMR (400 MHz, DMSO) δ 11.89 (s, 1H), 4.43 – 4.11 (m, 1H), 2.11 (t, $J = 7.3$ Hz, 2H), 1.91 – 1.70 (m, 3H), 1.44 – 1.37 (m, 3H), 1.27 – 1.05 (m, 34H).

Compound 9 HRMS (ESI) calcd for C$_{24}$H$_{45}$O$_2$ (M+H$^+$) 365.3431, found 365.3429.

5.3. General Procedure for Compound 9-1 Derivatives Synthesis
To a solution of cycloheptanone (1.12 g, 10 mmol) in THF, and the mixture was stirred at 0 °C for 10 min. Then, i-PrMgCl (7.5 mL, 2.0 M in THF) was added, the mixture was stirred another 4 h at 0 °C. After the reaction was completed, quenched with water and extracted with EA, the organic extracts were dried over Na$_2$SO$_4$. The crude product was purified by silica gel chromatography using a mixture of ethyl acetate and petroleum ether as eluent to get the desired products 9-1.

$^1$H NMR (400 MHz, DMSO) $\delta$ 4.31 (s, 1H), 2.70 (td, $J = 12.0, 2.9$ Hz, 1H), 2.30 (dd, $J = 11.7, 4.6$ Hz, 1H), 2.20 - 2.13 (m, 1H), 1.97 - 1.86 (m, 2H), 1.84 - 1.75 (m, 2H), 1.68 - 1.38 (m, 11H), 1.33 - 1.23 (m, 4H), 1.04 - 0.90 (m, 1H).

$^{13}$C NMR (101 MHz, DMSO) $\delta$ 216.7, 75.9, 62.7, 43.4, 39.4, 39.2, 30.3, 29.7, 29.6, 27.6, 26.6, 24.6, 22.2, 21.9.
5.4. General Procedure for Deuterium-Labeling Ketones 2k Synthesis

To a round bottom flask, cyclododecane (20 mmol, 3.65g) was dissolved in 10 mL anhydrous THF, D$_2$O (8.01g, 400 mmol) and tetrahydropyrrrole (142.2 mg, 2.0 mmol) was added. The reaction mixture was stirred at room temperature for 48 h. After the reaction was completed, the mixture was acidic with 2 N HCl and extracted with DCM, the organic extracts were dried over Na$_2$SO$_4$. The crude product was purified by silica gel chromatography using a mixture of ethyl acetate and petroleum ether as eluent to get the desired products.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.48 – 2.39 (m, 0H), 1.70 (t, $J = 6.4$ Hz, 4H), 1.37 – 1.21 (m, 16H).
6. Product Characterization

Ethane-1,1-diylidibenzene (3a)\(^1\) was obtained as a colorless oil (48.1 mg, 88%, from 1a; 53.0 mg, 97%, from 5g).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.45 – 7.09 (m, 10H), 4.18 (q, \(J = 7.2\) Hz, 1H), 1.67 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 146.4, 128.4, 127.6, 126.1, 44.8, 21.9.

1-Fluoro-4-(1-phenylethyl) benzene (3b)\(^2\) was obtained as a colorless oil (54.1 mg, 90% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.43 – 7.35 (m, 2H), 7.30 – 7.24 (m, 5H), 7.06 (t, \(J = 8.7\) Hz, 2H), 4.23 (q, \(J = 7.3\) Hz, 1H), 1.71 (d, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 162.5, 160.12, 146.2, 142.1, 142.1, 129.0, 128.5, 127.6, 126.2, 115.2, 115.0, 44.1, 22.1.

1-Chloro-4-(1-phenylethyl) benzene (3c)\(^2\) was obtained as a colorless oil (40.3 mg, 62% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.37 – 7.29 (m, 2H), 7.32 – 7.26 (m, 2H), 7.27 – 7.18 (m, 3H), 7.22 – 7.14 (m, 2H), 4.16 (q, \(J = 7.2\) Hz, 1H), 1.65 (d, \(J = 7.7\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.9, 144.9, 131.8, 129.1, 128.6, 128.5, 127.6, 126.3, 44.2, 21.9.

1-Bromo-4-(1-phenylethyl) benzene (3d)\(^3\) was obtained as a colorless oil (71.3 mg, 91% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.41 – 7.35 (m, 2H), 7.32 – 7.24 (m, 2H), 7.21 – 7.15 (m, 3H), 7.11 – 7.04 (m, 2H), 4.16 (q, \(J = 7.2\) Hz, 1H), 1.60 (d, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.8, 145.4, 131.5, 129.5, 128.6, 128.5, 127.6, 126.3, 119.9, 44.3, 21.8.

1-Iodo-4-(1-phenylethyl) benzene (3e)\(^4\) was obtained as a white solid at room temperature (60.1 mg, 65% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.68 – 7.65 (m, 2H), 7.40 – 7.31 (m, 2H), 7.29 – 7.24 (m, 3H), 7.06 - 7.02 (m, 2H), 4.16 (q, \(J = 7.1\) Hz, 1H), 1.68 (d, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 146.2, 145.8, 137.5, 129.9, 128.6, 127.7, 126.4, 91.4, 44.4, 21.8.

1-Methyl-4-(1-phenylethyl) benzene (3f)\(^2\) was obtained as a colorless oil (46.5 mg, 79% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 7.20 – 7.14 (m, 4H), 4.18 (q, \(J = 7.2\) Hz, 1H), 2.37 (s, 3H), 1.69 (d, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 146.7, 143.5, 135.6, 129.1, 128.4, 127.7, 127.6, 126.0, 44.5, 22.0, 21.1.
4,4′-(Ethane-1,1-diyl) bis(bromobenzene) (3g) was obtained as a white solid at room temperature (65.3 mg, 64% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.49 – 7.38 (m, 4H), 7.14 – 7.03 (m, 4H), 4.08 (q, $J$ = 7.2 Hz, 1H), 1.61 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.8, 131.6, 129.4, 120.1, 43.7, 21.7.

4,4′-(Ethane-1,1-diyl) bis(methylbenzene) (3h) was obtained as a colorless oil (34.7 mg, 55% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 – 7.14 (m, 8H), 4.16 (q, $J$ = 7.2 Hz, 1H), 2.38 (s, 6H), 1.68 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.6, 135.3, 128.9, 127.3, 43.8, 21.9, 20.9.

1-Bromo-3-(1-phenylethyl) benzene (3i) was obtained as a colorless oil (40.0 mg, 51% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J$ = 1.7 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.25 – 7.20 (m, 3H), 7.18 – 7.14 (m, 2H), 4.13 (q, $J$ = 7.3 Hz, 1H), 1.64 (d, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.8, 145.5, 130.7, 129., 129.2, 128.6, 127.6, 126.4, 126.4, 122.6, 44.6, 21.7.

1-Methyl-2-(1-phenylethyl) benzene (3j) was obtained as a colorless oil (53.0 mg, 90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.16 (m, 4H), 7.19 – 7.09 (m, 5H), 4.31 (q, $J$ = 7.2 Hz, 1H), 2.23 (s, 3H), 1.60 (d, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.3, 143.9, 136.2, 130.5, 128.4, 127.8, 126.8, 126.2, 126.1, 125.9, 41.1, 22.2, 19.8.

5-Methyl-10,11-dihydro-5H-dibenzo[a,d] [7]annulene (3k) was obtained as a colorless oil (41.8 mg, 67% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.26 – 7.17 (m, 2H), 7.18 – 7.04 (m, 6H), 4.42 (q, $J$ = 7.4 Hz, 1H), 3.20 (s, 4H), 1.71 (d, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 143.3, 139.3, 130.1, 127.5, 126.4, 126.2, 77.3, 43.7, 33.3, 22.0.

(1-Cyclohexylethyl) benzene (3l) was obtained as a colorless oil (24.8 mg, 44% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 – 7.27 (m, 2H), 7.25 – 7.15 (m, 3H), 2.48 (p, $J$ = 7.2 Hz, 1H), 1.99 – 1.87 (m, 1H), 1.83 – 1.73 (m, 1H), 1.72 – 1.60 (m, 2H), 1.50 – 1.40 (m, 2H), 1.36 – 1.22 (m, 1H), 1.27 (d, $J$ = 7.1 Hz, 3H), 1.25 – 1.05 (m, 2H), 1.03 – 0.93 (m, 1H), 0.92 – 0.78 (m, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.2, 128.0, 127.8, 125.7, 45.9, 44.2, 31.5, 30.7, 26.6, 26.6, 18.9.
Ethane-1,1,2-triyltribenzene (3m)\(^8\) was obtained as a white solid at room temperature (24.8 mg, 32% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.28 (m, 3H), 7.27 – 7.21 (m, 6H), 7.21 – 7.12 (m, 4H), 7.07 – 6.99 (m, 2H), 4.27 (t, \(J = 7.8\) Hz, 1H), 3.40 (d, \(J = 7.8\) Hz, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.6, 140.4, 129.2, 128.4, 128.2, 126.5, 126.3, 126.0, 53.2, 42.2.

(4-Iodobutane-1,1-diyl) dibenzene (3n)\(^9\) was obtained as a colorless oil (64.6 mg, 64% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.14 (m, 10H), 3.91 (t, \(J = 7.9\) Hz, 1H), 3.18 (t, \(J = 6.8\) Hz, 2H), 2.25 – 2.09 (m, 2H), 1.86 – 1.69 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.5, 128.6, 127.8, 126.4, 50.5, 36.5, 31.8, 7.0.

Butane-1,1-diyl dibenzene (3o)\(^{10}\) was obtained as a colorless oil (44.2 mg, 70% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.32 (m, 8H), 7.21 – 7.09 (m, 2H), 3.90 (t, \(J = 7.8\) Hz, 1H), 2.14 – 1.93 (m, 2H), 1.38 – 1.18 (m, 2H), 0.92 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.4, 128.4, 127.9, 126.1, 51.2, 38.0, 21.2, 14.2.

Dodecane-1,1-diyl dibenzene (3p)\(^{11}\) was obtained as a colorless oil (78.4 mg, 81% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.19 (m, 8H), 7.19 – 7.11 (m, 2H), 3.87 (t, \(J = 7.8\) Hz, 1H), 2.02 (q, \(J = 7.7\) Hz, 2H), 1.34 – 1.18 (m, 20H), 0.87 (t, \(J = 6.8\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.4, 128.4, 127.9, 126.0, 51.4, 35.8, 31.9, 29.7, 29.7, 29.5, 29.4, 28.1, 22.7, 14.2.

9-Butyl-9H-fluorene (3q)\(^{12}\) was obtained as a colorless oil with (46.7 mg, 70%, from 1q; 35.0 mg, 53%, from 5h).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 – 7.78 (m, 2H), 7.57 (d, \(J = 7.4\) Hz, 2H), 7.46 – 7.32 (m, 4H), 4.03 (t, \(J = 5.9\) Hz, 1H), 2.12 – 2.02 (m, 2H), 1.36 – 1.32 (m, 2H), 1.28 – 1.19 (m, 2H), 0.89 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 147.7, 141.2, 126.9, 126.8, 124.4, 119.8, 47.5, 32.8, 27.8, 23.1, 14.0.

Cycloheptyl (p-tolyl) sulfane (3r)\(^{13}\) was obtained as a colorless oil (52.2 mg, 79% yield).

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.24 – 7.15 (m, 2H), 7.01 (d, \(J = 7.9\) Hz, 2H), 3.17 (tt, \(J = 9.0, 4.1\) Hz, 1H), 2.23 (s, 3H), 1.99 – 1.83 (m, 2H), 1.67 – 1.57 (m, 2H), 1.55 – 1.26 (m, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 136.6, 132.0, 129.5, 48.6, 34.6, 28.2, 25.9, 21.0.
1,2-Diphenylethane (3s) was obtained as a colorless oil (13.1 mg, 24% from 1s; 4.9 mg, 9% from 1t; 20.8 mg, 38% from 1u).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.35 – 7.23 (m, 4H), 7.22 – 7.16 (m, 6H), 2.92 (s, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141., 128.5, 128.3, 125.9, 37.9.

Diphenylmethane (6a) was obtained as a colorless oil (31.8 mg, 63%, from 5a; 44.4 mg, 88%, from 5k; 38.5 mg, 76%, from 5l; 100.3 mg, 99%, from 5m; 11.1 mg, 22%, from 5n; 25.3 mg, 50%, from 5q; 47.1 mg, 93%, from 5s).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.32 – 7.24 (m, 4H), 7.22 – 7.17 (m, 6H), 3.98 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.2, 128.9, 128.5, 126.1, 42.0.

Bis(4-fluorophenyl) methane (6b) was obtained as a colorless oil (25.1 mg, 41% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29 (d, $J$ = 8.6 Hz, 3H), 7.24 – 7.14 (m, 6H), 3.97 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.3, 135.5, 128.9, 126.3, 42.2.

Di-p-tolylmethane (6c) was obtained as a colorless oil (31.2 mg, 53% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.15 (s, 8H), 3.98 (s, 2H), 2.38 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 138.5, 135.5, 129.2, 128.9, 41.2, 21.1.

Bis(4-bromophenyl) methane (6d) was obtained as a colorless oil (49.9 mg, 51% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 – 7.30 (m, 4H), 7.31 – 7.21 (m, 4H), 4.05 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.2, 129.0, 128.6, 126.2, 42.0.

1-Benzyl-4-chlorobenzene (6e) was obtained as a colorless oil (18.8 mg, 31% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29 (d, $J$ = 8.6 Hz, 3H), 7.24 – 7.14 (m, 6H), 3.97 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.3, 129.2, 128.7, 126.3, 42.2.

Triphenylmethane (6f) was obtained as a white solid at room temperature with (69.6 mg, 95%, from 5f; 71.8 mg, 98%, from 5p; 56.4 mg, 77%, from 5n; 71.8 mg, 98%, from 5o; 69.6 mg, 95%, from 5r).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.33 – 7.14 (m, 9H), 7.16 – 7.07 (m, 6H), 5.55 (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 143.7, 129.3, 128.1, 126.1, 56.7.

9H-xanthene (6g) was obtained as a colorless oil (24.0 mg, 44% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 – 7.16 (m, 4H), 7.11 – 7.01 (m, 4H), 4.08 (s, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 128.9, 127.6, 123.0, 116.5, 27.9.
Deuterium ethane-1,1-diyldibenzene (7a) was obtained as a colorless oil (42.9 mg, 78% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 (t, $J = 7.4$ Hz, 4H), 7.25 – 7.18 (m, 4H), 7.17 – 7.15 (m, 2H), 4.15 (q, $J = 6.7$ Hz, 1H), 1.63 (t, $J = 6.9$ Hz, 2H).

Deuterium 1-fluoro-4-(1-phenylethyl) benzene (7b) was obtained as a colorless oil (52.5 mg, 87% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 – 7.23 (m, 2H), 7.23 – 7.13 (m, 5H), 6.96 (t, $J = 8.7$ Hz, 2H), 4.12 (t, $J = 6.1$ Hz, 1H), 1.63 – 1.58 (m, 2H); IR (film): $\nu$ 2924, 2860, 1606, 1508, 1446 cm$^{-1}$; HRMS (EI) calcd for C$_{14}$H$_{12}$DF (M): 201.1064, found: 201.1075.

Deuterium 1-iodo-4-(1-phenylethyl) benzene (7c) was obtained as a colorless oil (45.4 mg, 49% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 8.1$ Hz, 2H), 7.25 (s, 2H), 7.21 – 7.15 (m, 3H), 6.96 (d, $J = 8.0$ Hz, 2H), 4.19 – 4.02 (m, 1H), 1.65 – 1.55 (m, 2H); IR (film): $\nu$ 3057, 3020, 2958, 2937, 1481, 1452, 1398 cm$^{-1}$; HRMS (EI) calcd for C$_{14}$H$_{12}$DI (M): 309.0125, found: 309.0121.

Deuterium 5-Methyl-10,11-dihydro-5H-dibenzo[a,d] [7]annulene (7d) was obtained as a colorless oil (47.7 mg, 76% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.21 – 7.13 (m, 2H), 7.12 – 6.99 (m, 6H), 4.44 – 4.33 (m, 1H), 3.15 (s, 4H), 1.67 – 1.63 (m, 2H); IR (film): $\nu$ 3053, 3014, 2926, 2248, 2220, 1489, 1460 cm$^{-1}$; HRMS (EI) calcd for C$_{16}$H$_{15}$D (M): 209.1315, found: 209.1325.

Deuterium 4,4'-(ethane-1,1-diyl) bis(bromobenzene) (7e) was obtained as a white solid at room temperature (59.3 mg, 58% yield).

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.40 – 7.36 (m, 4H), 7.04 (d, $J = 8.4$ Hz, 4H), 4.04 (t, $J = 6.1$ Hz, 1H), 1.58 – 1.54 (m, 2H); IR (film): $\nu$ 2353, 1485 cm$^{-1}$; HRMS (EI) calcd for C$_{14}$H$_{11}$DBr$_2$ (M): 338.9369, found: 338.9366.

Deuterium butane-1,1-diyldibenzene (7f) was obtained as a colorless oil (48.2 mg, 76% yield).
\[ ^1H \text{NMR (300 MHz, CDCl}_3 \delta 7.26 - 7.22 \text{ (m, 5H), 3.89 (d, } J = 6.8 \text{ Hz, 1H), 1.99 (d, } J = 7.6 \text{ Hz, 1H), 1.25 (d, } J = 7.1 \text{ Hz, 2H), 0.91 (t, } J = 7.3 \text{ Hz, 3H); IR (film): } \nu 3062, 3028, 2954, 2926, 2872, 1600, 1490, 1448 \text{ cm}^{-1}; \text{HRMS (EI) calcd for C}_{16}H_{17}D \text{ (M): 211.1471, found: 211.1470.} \]

7. References


8. Product NMR Spectra
$^{13}$C NMR

3a

f1 (ppm)
$^1$H NMR

3b
$^{13}$C NMR

3b
$^{13}$C NMR

3d

Chemical shifts:
- 145.8
- 145.5
- 131.5
- 129.5
- 128.5
- 127.5
- 126.3
- 119.9
- 44.3
- 21.8
$^{13}$C NMR

3o
$^{13}$C NMR

3p
$^{13}$C NMR

$3r$
\[ ^{13}\text{C NMR} \]

6c

- 138.5
- 133.5
- 129.2
- 128.9
- 41.2
- 21.1
$^{13}\text{C NMR}$

6d

-141.2
-129.1
-128.6
-126.2
-42.1

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)
$^1$H NMR

6g