Catalyst-Free Reductive Hydrogenation or Deuteration of Aryl-Heteroatom

Bonds Induced by Light

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1. General Experiments

NMR spectra were recorded on an Agilent-NMR-VNMRs 400 MHz spectrometer or Bruker Advance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced to CDCl₃ (7.26 ppm) for ¹H NMR, and CDCl₃ (77.16 ppm) for ¹³C NMR. GC-MS analyses were performed with an Agilent 8890-597BGCMSD spectrometer. High-resolution mass spectrometry used electro-spraying ionization (ESI) on a Thermo Scientific LTQ Orbitrap XL. Column chromatography or preparative thin-layer chromatography (TLC) was performed with Qing Dao silica gel. All reagents and solvents were used directly as purchased. DMSO- d_6 (99.8% deuterium, containing 0.03% (v/v) TMS), acetone- d_6 (99.8% deuterium, containing 0.03% (v/v) TMS) were used directly as purchased in deuteration reactions.

2. Supplement Figures and Tables

Figure S1. Photoreactors with household UV lamps (254 nm, 8 W each lamp): (a) 4*8 W; (b) 20*8 W.





(a)

Table S1. Optimization of conditions for the reduction of aryl triflates.^{*a*}

| | | OTf solve bas additi r.t., / | $\begin{array}{c} \text{ent} \\ \text{e} \\ \text{ive} \\ \text{hv} \\ \text{hv} \\ 2a \end{array}$ | |
|-----------------|----------------------|---------------------------------------|---|---------|
| entry | solvent/mL | base/equiv | additive/equiv | yield/% |
| 1 | CH ₃ CN/1 | DIPEA/1 | NaI/0.5 | 13 |
| 2 | DMF/1 | DIPEA/1 | NaI/0.5 | 26 |
| 3 | DMSO/1 | DIPEA/1 | NaI/0.5 | 13 |
| 4 | $H_2O/1$ | DIPEA/1 | NaI/0.5 | trace |
| 5 | DMF/1 | NEt ₃ /1 | NaI/0.5 | 29 |
| 6 | DMF/1 | HNEt ₂ /1 | NaI/0.5 | 26 |
| 7 | DMF/1 | DMAP/1 | NaI/0.5 | 41 |
| 8 | DMF/1 | Pyridine/1 | NaI/0.5 | 24 |
| 9 | DMF/1 | TMEDA/1 | NaI/0.5 | 23 |
| 10 | DMF/1 | DMAP/2 | NaI/0.5 | 55 |
| 11 | DMF/1 | DMAP/2 | - | 49 |
| 12 | DMF/2 | DMAP/2 | - | 57 |
| 13 | DMF/2 | DMAP/2 | CH ₃ COONa/1 | 64 |
| 14 | DMF/2 | DMAP/2 | KCl/1 | 68 |
| 15 | DMF/2 | DMAP/2 | KNO ₃ /1 | 61 |
| 16 | DMF/2 | DMAP/2 | CaCl ₂ /1 | 61 |
| 17 | DMF/2 | DMAP/2 | Na ₃ PO ₄ ·12 H ₂ O/1 | 73 |
| 18 | DMF/2 | DMAP/2 | CaSO ₄ /1 | 64 |
| 19 | DMF/2 | DMAP/2 | NaNO ₂ /1 | 65 |
| 20 | DMF/2 | DMAP/2 | KBr/1 | 65 |
| 21 | DMF/2 | DMAP/2 | Rb ₂ CO ₃ /1 | 73 |
| 22 | DMF/2 | DMAP/2 | Na3PO4 [·] 12 H2O/0.5 | 75 |
| 23 ^b | DMF/2 | DMAP/2 | Na ₃ PO ₄ ·12 H ₂ O/0.5 | 75 |

^{*a*} Reaction conditions: **4a** (0.1 mmol), solvent, air, r.t., *hv* (254 nm, 20*8 W), 20 h, GC-MS yield with 1,3,5-trimethylbenzene as internal standard. ^{*b*} *hv* (254 nm, 4*8 W).

| | MeO | OTf - | solvent base additive r.t., hv | D | |
|-------|---|------------|---|---------|-------------|
| | | 4d | 3d | | |
| entry | solvent | base/equiv | additive/equiv | yield/% | D-content/% |
| 1 | CD ₃ OD | - | - | 0 | - |
| 2 | DMSO-d ₆ | - | - | 22 | 96 |
| 3 | acetone- d_6 | - | - | Trace | - |
| 4 | DMF/D ₂ O (9:1) | - | - | 57 | 10 |
| 5 | CH ₃ CN/D ₂ O (9:1) | - | - | 0 | - |
| 6 | CD ₃ CN | - | - | 10 | 96 |
| 7 | DMSO- d_6 | DMAP/1 | - | 44 | 96 |
| 8 | DMSO- d_6 | DMAP/2 | - | 62 | 96 |
| 9 | DMSO- d_6 | DMAP/3 | - | 51 | 96 |
| 10 | DMSO- d_6 | DMAP/2 | Na ₃ PO ₄ /0.5 | 70 | 96 |
| 11 | DMSO-d ₆ | DMAP/2 | Na ₃ PO ₄ /1 | 78 | 96 |
| 12 | DMSO- d_6 | DMAP/2 | Na ₃ PO ₄ /1.5 | 74 | 96 |
| 13 | DMSO- d_6 | DMAP/2 | K ₃ PO ₄ /1 | 72 | 96 |
| 14 | DMSO- d_6 | DMAP/2 | K ₂ CO ₃ /1 | 69 | 96 |
| 15 | DMSO- d_6 | DMAP/2 | NaOH/1 | 55 | 96 |

Table S2. Optimization of conditions for the reductive deuteration of aryl triflates.^a

^{*a*} Reaction conditions: **4d** (0.1 mmol), solvent (0.5 mL), base, additive, *hv* (254 nm, 4*8 W), 24 h, r.t., Ar. The yields were obtained after purified by preparative TLC, and the deuterium incorporation was determined by ¹H NMR spectroscopy of the product.

| | Br | base, <i>hv</i> solvent, Ar, 18 h | | |
|-------|----------------------------------|--------------------------------------|---------|-------------|
| | | | 3al | |
| entry | solvent/mL | base/equiv | yield/% | D-content/% |
| 1 | CDCl ₃ /0.5 | - | trace | - |
| 2 | acetone-d ₆ /0.5 | - | 52 | 99 |
| 3 | DMSO- <i>d</i> ₆ /0.5 | - | 10 | 99 |
| 4 | CD ₃ OD/0.5 | - | 33 | 99 |
| 5 | acetone- $d_6/0.35$ | - | 35 | 99 |
| 6 | acetone- $d_6/0.15$ | - | 25 | 99 |
| 5 | acetone- $d_6/0.5$ | N-Methylpyrrole/1 | 13 | 50 |
| 6 | acetone- $d_6/0.5$ | N-Methylpiperidine/1 | 50 | 10 |
| 7 | acetone- $d_6/0.5$ | Pyrrolidine/1 | 70 | 50 |
| 8 | acetone- $d_6/0.5$ | NEt ₃ /1 | 31 | 20 |
| 9 | acetone- $d_6/0.5$ | Pyridine/1 | trace | - |
| 10 | acetone- $d_6/0.5$ | DMAP/1 | trace | - |
| 11 | acetone- $d_6/0.5$ | DBU/1 | 43 | 20 |
| 12 | acetone- $d_6/0.5$ | K ₃ PO ₄ /1 | 60 | 80 |
| 13 | acetone- $d_6/0.5$ | $Cs_2CO_3/1$ | 43 | 99 |
| 14 | acetone- $d_6/0.5$ | KI/1 | 44 | 99 |
| 15 | acetone- $d_6/0.5$ | Li ₂ CO ₃ /1 | 50 | 99 |
| 16 | acetone- $d_6/0.5$ | Rb ₂ CO ₃ /1 | 53 | 99 |
| 17 | acetone- $d_6/0.5$ | Na ₂ SO ₄ /0.5 | trace | - |
| 18 | acetone- $d_6/0.5$ | K ₂ CO ₃ /1 | 60 | 99 |
| 19 | acetone- $d_6/0.5$ | Na ₂ CO ₃ /1 | 63 | 99 |
| 20 | acetone-d ₆ /0.5 | Na ₂ CO ₃ /2 | 75 | 99 |
| 21 | acetone- $d_6/0.5$ | Na ₂ CO ₃ /3 | 70 | 99 |
| 22 | CD ₃ OD/0.5 | Na2CO3/2 | 54 | 99 |

Table S3. Optimization of conditions for the reductive deuteration of aryl halide.^a

Reaction conditions: 5a (0.1 mmol), hv (254 nm, 20*8 W), 18 h, r.t., Ar. The yields were obtained after purified by preparative TLC, and the deuterium incorporation was determined by ¹H NMR spectroscopy of the product.

3. Experimental procedure(1) General procedure for the reduction of C–N bond

 $ArNH_{2} + MeOTf \xrightarrow{Na_{2}CO_{3}} Ar - NMe_{3}OTf$ $Ar - NMe_{3}OTf \xrightarrow{Condition A: THF (1 mL), hv, air, 5 h, r.t.} Ar - H (2)$ or $Ar - DMe_{3}OTf \xrightarrow{Condition B: CD_{3}OD (0.5 mL), hv, Ar, 5 h, r.t.} Ar - H (2)$ (3)

Aryltrimethylammonium triflates (1) were prepared according to the literature:¹ To a solution of ArNH₂ (1 mmol) in CH₃CN (2 mL) was added MeOTf (3.2 mmol, 362 μ L) and Na₂CO₃ (3 mmol, 318 mg) under air atmosphere. The mixture was stirred for 2 h at room temperature, and then filtrated through a celite pad. The filtrate was concentrated and washed with diethyl ether (5 mL*3) to afford the desired aryl trimethylammonium salts (1) which were used directly in the next step without further purification.

To a 10 mL quartz tube charged with a magnetic stir-bar was added 1 (0.1 mmol) and THF (1 mL) under air atmosphere or CD₃OD (0.5 mL) under argon atmosphere. Then the reaction mixture was irradiated by UV light (254 nm, 4*8 W) for 5 h at room temperature. The mixture was concentrated and purified by preparative TLC with petroleum ether/EtOAc (100:1~5:1) to afford the desired products 2 or 3 in yields as indicated in Table 2. The deuterium incorporation of 3 was determined by ¹H NMR spectroscopy or GC-MS.

CH₂Cl₂, pyridine Ar-OH Ar -OTf TfOTf, 0 °C to r.t. 4 Condition A: DMAP (2 equiv) $Na_{3}PO_{4} \cdot 12 H_{2}O(0.5 equiv)$ Ar-H (2) DMF, hv, air, 20 h, r.t. Ar OTf or Condition B: DMAP (2 equiv) 4 Ar - D (3) Na₃PO₄ (1 equiv) DMSO-d₆ (0.5 mL), hv, Ar, 24 h, r.t.

(2) General procedure for the reduction of C-O bond

Aryl triflates (**4**) were prepared according to literature:² To a solution of ArOH (1 mmol) in CH₂Cl₂ (4 mL) at 0 °C was added pyridine (2 or 4 mmol, 163 or 326 μ L) and triflic anhydride (2 equiv, 2 or 4 mmol, 335 or 670 μ L) dropwise. After 5 minutes, the ice bath was removed and the mixture was stirred at room temperature for 12 h. The mixture was concentrated and purified by flash column chromatography with petroleum ether/EtOAc (20:1~10:1) to afford the desired aryl triflates **4** which have data in according with reported literature.²

Reductive hydrogenation of **4** to **2**: To a 15 mL quartz tube charged with a magnetic stir-bar under air atmosphere was added **4** (0.2 mmol), Na₃PO₄·12 H₂O (0.1 mmol, 38 mg), DMAP (0.4 mmol, 49 mg) and DMF (4 mL) sequentially. The reaction mixture was irradiated by UV light (254 nm, 8*4 W) for 20 h at room temperature. Then EtOAc (10 mL) was added and the mixture was washed with brine (2 mL*3), dried with anhydrous Na₂SO₄. The filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC with petroleum ether/EtOAc (100:1-5:1) to afford the products **2** in yields as indicated in Table 3.

Reductive deuteration of **4** to **3**: To a 10 mL quartz tube charged with a magnetic stir-bar under argon atmosphere was added **4** (0.1 mmol), Na₃PO₄ (0.1 mmol, 16 mg), DMAP (0.2 mmol, 24 mg) and DMSO- d_6 (0.5 mL) sequentially. The reaction mixture was irradiated by UV light (254 nm, 4*8 W) for 24 h at room

temperature. Then EtOAc (10 mL) was added and the mixture was washed with brine (2 mL*3), dried with anhydrous Na₂SO₄. The filtrate was concentrated under reduced pressure, and the residue was purified by preparative TLC with petroleum ether/EtOAc (100:1-5:1) to afford the products **3** in yields as indicated in Table 4. The deuterium incorporation of **3** was determined by ¹H NMR spectroscopy.

(3) General procedure for the reductive deuteration of aryl halides

Ar-x
$$\begin{array}{c} Na_2CO_3 (2 \text{ equiv}), CD_3OD (0.5 \text{ mL}) \\ \hline hv, Ar, r.t. \\ 3 \end{array}$$

To a 10 mL quartz tube charged with a magnetic stir-bar under argon atmosphere was added aryl halide (5, 0.1 mmol), Na₂CO₃ (0.2 mmol, 21 mg) and CD₃OD (0.5 mL) sequentially. The reaction mixture was irradiated by UV light (254 nm, 20*8 W) for 12 h (Ar-I) or 18 h (Ar-Br/Ar-Cl) at room temperature. Then the reaction mixture was filtrated through a celite pad. The filtrate was concentrated and purified by preparative TLC with petroleum ether/EtOAc (100:1-5:1) to afford the products **3** in yields as indicated in Table 5. The deuterium incorporation of **3** was determined by ¹H NMR spectroscopy.

Anisole (2a)

The yield of **2a** was determined by GC-MS using 1,3,5-trimethylbenzene as an internal standard and its structure was confirmed by comparison with standard anisole sample via GC-MS analysis. EI (m/z) 108.0. These data were agreed with literature.³

1,1'-Biphenyl (2b/2h/2ab/2q)

Off-white powder, m.p. 69.8-70.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J*=7.1 Hz, 4H), 7.47 (t, *J*=7.8 Hz, 4H), 7.37 (t, *J*=7.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 128.9, 127.4, 127.3. These data were agreed with literature.³

Eto

Ethyl benzoate (2c/2i/2r)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 132.9, 130.6, 129.6, 128.4, 61.1, 14.5. These data were agreed with literature.⁴



Methyl benzoate (2d/2j)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.1 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 133.0, 130.2, 129.7, 128.5, 52.2. These data were agreed with literature.⁴

Ethyl 2-phenylacetate (2e/2i) EtO

Colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.23 (m, 5H), 4.15 (q, J = 7.1 Hz, 2H), 3.62 (s, 2H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 171.8, 134.2, 129.4, 128.7, 127.2, 61.0, 41.6, 14.3. These data were agreed with literature.⁴



*t*ert-Butylbenzene (**2f**)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 1.34 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 151.2, 128.2, 125.5, 125.4, 34.8, 31.5. These data were agreed with literature.³



Benzonitrile (2g)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, J = 8.0, 1.0 Hz, 2H), 7.61 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 132.9, 132.3, 129.2, 119.0, 112.5. These data were agreed with literature.³



Off-white powder, m.p. 80.8-82.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.92-7.83 (m, 4H), 7.55-7.46 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 133.5, 128.0, 126.0. These data were agreed with literature.³



Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.95-8.91 (m, 1H), 8.25-8.18 (m, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 8.3 Hz, 1H), 7.46 (dd, *J* = 8.1, 4.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 149.7, 147.3, 137.3, 130.2, 128.8, 128.4, 128.0, 127.1, 121.2. These data were agreed with literature.³



1H-Indole (2n)

Brown powder, m.p. 52.2-53.4 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 11.10 (s, 1H), 7.54 (t, J = 6.7 Hz, 1H), 7.39 (t, J = 8.4 Hz, 1H), 7.35-7.31 (m, 1H), 7.11-7.04 (m, 1H), 7.02-6.94 (m, 1H), 6.45-6.39 (m, 1H). ¹³C NMR (101 MHz, DMSO- d_6) δ 136.0, 127.7, 125.3, 121.0, 120.1, 118.9, 111.5, 101.1. These data were agreed with literature.³



Methyl 2-phenylacetate (2u)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.26 (m, 5H), 3.70 (s, 2H), 3.64 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 172.2, 134.1, 129.4, 128.7, 127.2, 52.2, 41.3. These data were agreed with literature.⁵



Phenyl benzoate (2v)

Off-white powder, m.p. 69.5-71.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.25 (d, *J*=7.3 Hz, 2H), 7.66 (t, *J*=7.4 Hz, 1H), 7.54 (t, *J*=7.7 Hz, 2H), 7.46 (t, *J*=7.8 Hz, 2H), 7.30 (t, *J*=7.4 Hz, 1H), 7.25 (d, *J*=8.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 165.3, 151.0, 133.7, 130.3, 129.6, 128.7, 126.0, 121.8. These data were agreed with literature.⁶



Phenyl acetate (**2w**)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.39 (t, *J* = 7.9 Hz, 2H), 7.24 (m, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 2.31 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.7, 150.7, 129.5, 125.9, 121.7, 21.2. These data were agreed with literature.⁷



N, *N*-Dimethylaniline (**2x**)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.29 (t, *J* = 8.0 Hz, 2H), 6.82-6.76 (m, 3H), 2.98 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 150.5, 129.2, 117.1, 113.0, 40.9. These data were agreed with literature.³

2-Methoxynaphthalene (**2y**)

Off-white powder, m.p. 72.4-73.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81-7.73 (m, 3H), 7.46 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.4 Hz, 1H), 7.19-7.13 (m, 2H), 3.94 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.7, 134.7, 129.5, 129.0, 127.8, 126.9, 126.5, 123.7, 118.8, 105.8, 55.4. These data were agreed with literature.⁸

Benzo[d][1,3]dioxole (**2z**)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 6.84 (s, 4H), 5.95 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 121.7, 108.8, 100.7. These data were agreed with literature.⁹



Ethyl 3-(((trifluoromethyl)sulfonyl)oxy)benzoate (2aa)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 8.7 Hz, 1H), 7.93 (s, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.47 (dd, J = 8.3, 2.4 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 149.5, 133.2, 130.5, 129.6, 125.8, 122.6, 118.9 (q, J = 322.2 Hz), 61.9, 14.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -72.85.



Propane-2,2-diyldibenzene (2ac)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) *δ* 7.32-7.23 (m, 8H), 7.21-7.16 (m, 2H), 1.71 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) *δ* 150.8, 128.1, 126.9, 125.7, 43.1, 30.9.



Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, *J* = 7.4 Hz, 4H), 7.22 (t, *J* = 6.7 Hz, 6H), 4.00 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.2, 129.1, 128.6, 126.2, 42.1. These data were agreed with literature.¹⁰



2-Methylquinoline (**2ae**)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 6.7 Hz, 2H), 7.74 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 8.3 Hz, 1H), 2.73 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.0, 147.7, 136.4, 129.6, 128.6, 127.6, 126.5, 125.8, 122.1, 25.4. These data were agreed with literature.¹¹

2,6-Dimethylpyridine (**2af**)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.38 (m, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 2.49 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 136.7, 120.3, 24.5. These data were agreed with literature.¹²



Benzo[d]thiazole (**2ag**)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 9.10 (s, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 154.5, 152.3, 133.5, 126.6, 125.9, 123.4, 122.1. These data were agreed with literature.¹³



2-Phenylbenzo[d]thiazole (2ah)

Off-white powder, m.p. 114.9-115.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.15-8.08 (m, 3H), 7.91 (d, J = 8.0 Hz, 1H), 7.55-7.48 (m, 4H), 7.40 (t, J = 7.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 168.3, 154.0, 135.0, 133.5, 131.2, 129.2, 127.7, 126.5, 125.4, 123.3, 121.8. These data were agreed with literature.¹³

(8R,9S,13S,14S)-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-17-yl



trifluoromethanesulfonate (2ai)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.27 (dd, J = 8.8, 2.4 Hz, 1H), 7.20-7.08 (m, 3H), 5.63 (dd, J = 3.3, 1.7 Hz, 1H), 2.93 (dd, J = 8.4, 3.5 Hz, 2H), 2.46-2.31 (m, 3H), 2.11 (ddd, J = 14.9, 11.1, 1.7 Hz, 1H), 1.97-1.89 (m, 1H), 1.81 (td, J = 11.3, 6.3 Hz, 1H), 1.71-1.57 (m, 3H), 1.51-1.41 (m, 1H), 1.01 (s, 3H). ¹³C NMR (101 MHz,CDCl₃) δ 159.4, 139.9, 136.5, 129.2, 126.0, 125.9, 125.1, 118.7 (q, J = 320.5 Hz), 114.6, 53.8, 45.2, 44.8, 36.5, 32.9, 29.3, 28.5, 26.8, 25.7, 15.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -73.58. HRMS m/z (ESI) calcd. for C₁₉H₂₁F₃O₃S⁺ [M]⁺: 386.1158; found: 386.1160.



Anisole-4-d (3a) D

The yield and structure of **3a** were determined by GC-MS analysis using 1,3,5-trimethylbenzene as an internal standard. EI (m/z) 109.1. These data were agreed with literature.¹⁴



1,1'-Biphenyl-4-*d* (**3b**)

Off-white powder, m.p. 69.7-70.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 7.7 Hz, 4H), 7.58-7.50 (m, 4H), 7.44 (t, J = 7.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 128.9, 128.8, 127.4, 127.3, 126.8 (t, J = 23.1 Hz). These data were agreed with literature.¹⁵



Ethyl benzoate-4-d (3c)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 7.9 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 132.6 (t, J = 24.6 Hz), 130.6, 129.6, 128.3, 61.1, 14.5. These data were agreed with literature.¹⁶



Methyl benzoate-4-d (**3d**)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 3.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 132.8 (t, J = 24.7 Hz), 130.2, 129.7, 128.4, 52.3. These data were agreed with literature.¹⁵



1,1'-Biphenyl-3-d (3h)

Off-white powder, m.p. 69.4-70.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 5.9 Hz, 4H), 7.53 (t, J = 7.8 Hz, 3H), 7.44 (dd, J = 6.5, 2.6 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 128.9, 128.6 (J = 24.6 Hz), 127.4, 127.28, 127.26, 127.2.



Ethyl benzoate-3-d (3i)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.07-8.03 (m, 2H), 7.55 (d, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 132.8, 130.5, 129.6, 129.5, 128.4, 128.1 (t, J = 24.7 Hz), 61.1, 14.4. These data were agreed with literature.¹⁶



Methyl benzoate-3-d (3j)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.07-8.02 (m, 2H), 7.56 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 3.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 132.9, 130.2, 129.7, 129.6, 128.5, 128.2 (t, J = 23.4 Hz), 52.2. These data were agreed with literature.¹⁵



Off-white powder, m.p. 80.1-81.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (dd, J = 5.5, 3.0 Hz, 4H), 7.53 (dd, J = 6.3, 3.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 133.5, 128.0, 127.9, 125.9, 125.8, 125.7 (t, J = 24.5 Hz). These data were agreed with literature.¹⁵



Naphthalene-1-d (3l)

Naphthalene-2-d (3k)

Off-white powder, m.p. 80.6-81.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.93-7.87 (m, 3H), 7.58-7.50 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 133.52, 133.46, 128.00, 127.95, 127.7 (t, *J* = 24.5 Hz), 125.9, 125.8. These data were agreed with literature.¹⁵



Quinoline-3-d (3m)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.88 (s, 1H), 8.11 (d, J = 6.1 Hz, 1H), 8.08 (s, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.69 (m, 1H), 7.51 (t, J = 7.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 148.2, 136.1, 129.6 129.4, 128.3, 127.9, 126.6, 120.9 (t, J = 24.6 Hz). These data were agreed with literature.¹⁵



1-(Phenyl-3-d)ethan-1-one (**3o**)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.00-7.94 (m, 2H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 2.61 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.4, 137.1, 133.1 128.7, 128.40, 128.37 (t, *J* = 24.8 Hz), 128.3 26.8.



Quinoline-4-*d* (**3p**)

Yellow liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.90 (d, J = 4.2 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.38 (d, J = 3.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 148.2, 135.9 (t, J = 24.9 Hz), 129.6, 129.4, 128.3, 127.8, 126.6, 121.0. These data were agreed with literature.¹⁷



1,1'-Biphenyl-2-*d* (**3q**)

Off-white powder, m.p. 70.1-71.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J = 7.9 Hz, 3H), 7.48 (t, J = 7.4 Hz, 4H), 7.38 (t, J = 7.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.29, 141.26, 141.2, 128.9, 128.8, 127.3, 127.2, 126.9 (t, J = 24.3 Hz). These data were agreed with literature.¹⁸



Ethyl benzoate-2-d (**3r**)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, J = 8.1, 1.1 Hz, 1H), 7.55 (td, J = 7.6, 1.3 Hz, 1H), 7.47-7.41 (m, 2H), 4.38 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 132.9, 130.5, 129.6, 129.4 (t, J = 23.6 Hz, 2H), 128.4, 128.3, 61.1, 14.5. These data were agreed with literature.¹⁶



Methyl benzoate-2-d (**3s**)

1,3-Benzodioxole-5-d (3z)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, J = 8.1 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 6.0 Hz, 2H), 3.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 133.0, 130.1, 129.6, 129.4 (t, J = 23.7 Hz), 128.5, 128.4, 52.2. These data were agreed with literature.¹⁹



4-Ethyl-4-(phenyl-4-d)piperidine-2,6-dione (3t)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ (400 MHz, DMSO-*d*₆) δ 10.89 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.48-2.29 (m, 2H), 2.12 (dtd, *J* = 34.2, 13.1, 4.4 Hz, 2H), 1.94-1.69 (m, 2H), 0.75 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 175.6, 173.1, 138.8, 129.0, 128.9, 127.6, 127.3 (t, *J* = 24.8 Hz), 126.2, 51.1, 32.9, 29.3, 27.0, 9.1. HRMS m/z (ESI) calcd. for C₁₃H₁₅DNO₂⁺ [M+H]⁺: 219.1238; found: 219.1239.

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 6.84 (s, 3H), 5.95 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 121.6, 121.5 (t, *J* = 24.8 Hz), 108.8, 108.7, 100.7.



1,1'-Biphenyl-4,4'- d_2 (**3ab**) D

Off-white powder, m.p. 70.0-71.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.1 Hz, 4H), 7.50 (d, J = 7.7 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 128.8, 127.3, 126.8 (t, J = 23.1 Hz). These data were agreed with literature.¹⁵



1-(Benzyloxy)benzene-4-d (**3aj**)

Off-white powder, m.p. 37.8-38.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.42-7.33 (m, 3H), 7.05 (d, J = 8.6 Hz, 2H), 5.12 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 158.8, 137.1, 129.5, 128.7, 128.0, 127.6, 120.8 (t, J = 23.1 Hz), 114.9, 70.0. These data were agreed with literature.¹⁷



N-(Phenyl-4-d)acetamide (**3ak**) ²⁰

Off-white powder, m.p. 112.1-113.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 2.13 (s, 2.22 H). ¹³C NMR (101 MHz, CDCl₃) δ 169.2, 138.1, 128.8, 124.0 (t, J = 24.9 Hz), 120.2, 24.5, 24.2 (t, J = 19.8 Hz). These data were agreed with literature.¹⁶



2-Methoxynaphthalene-1-d (3al)

Off-white powder, m.p. 72.1-73.3 °C.¹H NMR (400 MHz, CDCl₃) δ 7.80-7.72 (m, 3H), 7.44 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.15 (d, J = 8.9 Hz, 1H), 3.93 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 134.6, 129.5, 129.0, 127.8, 126.8, 126.5, 123.7, 118.8, 105.8 (t, J = 23.3 Hz), 55.4. These data were agreed with literature.¹⁷



4-(Pheny-4-*d*)morpholine (**3am**)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 8.4 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.88 (t, J = 4.6 Hz, 4H), 3.18 (t, J = 4.8 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 151.3, 129.2, 119.9 (t, J = 24.8 Hz), 115.8, 67.0, 49.4. These data were agreed with literature.¹⁷



2-Methoxynaphthalene-6-d (3an)

Off-white powder, m.p. 71.9-73.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.78 (m, 3H), 7.50 (d, J = 8.2 Hz, 1H), 7.24-7.16 (m, 2H), 3.94 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.6, 134.6, 129.5, 129.0, 127.6, 126.8, 126.4, 123.4 (t, J = 24.6 Hz), 118.8, 105.8, 55.3. These data were agreed with literature.¹⁷



N, *N*-Diethylaniline-4-*d* (**3ao**)

Colorless liquid, ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 7.7 Hz, 2H), 3.41 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 129.2, 115.1 (t, *J* = 25.5 Hz), 111.9, 44.4, 12.6. These data were agreed with literature.¹⁷

4. Mechanistic Studies(1) Radical clock experiments



The procedures for the radical clock experiments were the same as the above reductive hydrogenative reactions with **1ap**, **4ap**, or **5ae** (0.1 mmol) and (1-cyclopropylvinyl)benzene (**6**, 0.2 mmol) in CH₃CN (1 mL), DMF (1 mL), or CH₃OH (0.5 mL), respectively. The reaction mixture was analyzed by GC-MS: Trace of product **7** was detected in a molecular weight of 220.0 at 18.974 min. The structure of **7** was further confirmed with the standard substance that was prepared according to literature which had the same retention time and MS spectrum in GC-MS.²⁰ ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 4.4 Hz, 1H), 7.30-7.24 (m, 4H), 7.22-7.19 (m, 2H), 7.16-7.11 (m, 2H), 5.81 (t, *J* = 4.5 Hz, 1H), 3.80 (s, 2H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.32 (dd, *J* = 12.5, 7.9 Hz, 2H). GC-MS (EI): m/z 220.0, 129.0, 91.0. These data were in agreement with literature.²⁰

Figure S2. GC-MS and ¹H NMR spectrum of 7.
(a) GC-MS report of 7 (t_R=18.974 min) from the reaction of 1ap with compound 6









(c) GC-MS report of 7 (t_R =18.974 min) from the reaction of **5ae** with compound **6**





(2) Radical trapping experiments



The procedures for the radical trapping experiments were the same as the above reductive hydrogenative reactions with **1ap**, **4ap**, or **5ae** (0.1 mmol) and 2,6-di-tert-butylphenol (**8**, 0.2 mmol) in CH₃CN (1 mL), DMF (1 mL), or CH₃OH (0.5 mL), respectively. The reaction mixture was analyzed by GC-MS: Trace of product **9** was detected in a molecular weight of 282.2 at 20.502 min. The structure of **9** was further confirmed with the standard substance that was prepared according to literature,²¹ which had the same retention time and MS spectrum in GC-MS. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.47-7.40 (m, 4H), 7.32 (t, *J* = 7.3 Hz, 1H), 5.29 (s, 1H), 1.52 (s,18H). GC-MS (EI): m/z 282.2, 267.1, 207.1. These data were in agreement with literature.²¹





(b) GC-MS report of product 9 ($t_R=20.502$ min) from the reaction of 4ap with compound 8.



(c) GC-MS report of product 9 (t_R=20.502 min) from the reaction of **5ae** with compound **8**.







(e) ¹H NMR of **9** prepared according to literature.²¹



(3) TEMPO as an additive



The procedures with TEMPO as radical-trapping agents were the same as the above reductive hydrogenation of C-O bond with the presence of TEMPO (0/1/2/3 equiv), which afforded **2a** in a yield of 85%, 59%, 29%, or 19%, respectively as determined by GC-MS with 1,3,5-trimethylbenzene as internal standard.

(4) CH₃OD as H/D-source



The procedure with CH_3OD as H/D-source was the same as the above reductive deuteration of aryl halides with CH_3OD (0.5 mL) as a solvent, which afforded 12.9 mg **2b** in a yield of 84%.

5. References

- S. Jin, H. T. Dang, G. C. Haug, R. He, V. D. Nguyen, V. T. Nguyen, H. D. Arman, K. S. Schanze and O. V. Larionov, *J. Am. Chem. Soc.*, 2020, **142**, 1603-1613.
- (2) Z. Huang, Z. Liu and J. S. Zhou, J. Am. Chem. Soc., 2011, 133, 15882-15885.
- (3) T.-H. Ding, J.-P. Qu and Y.-B. Kang, Org. Lett., 2020, 22, 3084-3088.
- (4) B. Rammurthy, S. Peraka, A. Vasu, G. Krishna Sai, Y. Divya Rohini and N. Narender, *Asian J. Org. Chem.*, 2021, **10**, 594-601.
- (5) W. R. Harker, E. L. Carswell and D. R. Carbery, Org. Lett., 2010, 12, 3712-3715.
- (6) L. Zheng, C. Sun, W. Xu, A. V. Dushkin, N. Polyakov, W. Su and J. Yu, RSC Adv., 2021, 11, 5080-5085.
- (7) C. K. Lee, J. S. Yu and H.-J. Lee, J. Heterocyclic Chem., 2002, 39, 1207-1217.
- (8) F. Rajabi and M. R. Saidi, Syn. Comm., 2004, 34, 4179-4188.
- (9) A. R. Katritzky, J. Ellison, J. Frank, P. Rákóczy, L. Radics and E. Gács-Baitz, Org. Magn. Reson., 1981, 16, 280-284.
- (10) J. Shi, T. Yuan, M. Zheng and X. Wang, ACS Catal., 2021, 11, 3040-3047.
- (11) Q. Liu, R.-G. Xing, Y.-N. Li, Y.-F. Han, X. Wei, J. Li and B. Zhou, Synthesis, 2011, 2011, 2066-2072.
- (12) M. Zheng, P. Chen, W. Wu and H. Jiang, Chem. Commun., 2016, 52, 84-87.
- (13) A. Monga, S. Bagchi, R. K. Soni and A. Sharma, Adv. Synth. Catal., 2020, 362, 2232-2237.
- (14) T. Mutsumi, H. Iwata, K. Maruhashi, Y. Monguchi and H. Sajiki, Tetrahedron, 2011, 67, 1158-1165.
- (15) 1. Y. Lang, X. Peng, C.-J. Li and H. Zeng, Green Chem. 2020, 22, 6323-6327.
- (16) A. Enomoto, S. Kajita and K.-i. Fujita, Chem. Lett., 2019, 48, 106-109.
- (17) X. Wang, M. H. Zhu, D. P. Schuman, D. Zhong, W. Y. Wang, L. Y. Wu, W. Liu, B. M. Stoltz and W. B. Liu, *J. Am. Chem. Soc.*, 2018, **140**, 10970-10974.
- (18) E. Tatunashvili, B. Chan, P. E. Nashar and C. S. P. McErlean, Org. Biomol. Chem., 2020, 18, 1812-1819.
- (19) A. M. Majek, F. Filace and A. Jacobi von Wangelin, Chem. Eur. J., 2015, 21, 4518-4522.
- (20) Z. Sun, C. Du, P. Liu, Y. Wei, L. Xu and B. Dai, ChemistrySelect, 2018, 3, 900-903.
- (21) K. Liang, Q. Liu, L. Shen, X. Li, D. Wei, L. Zheng and C. Xia, Chem. Sci., 2020, 11, 6996-7002.

6. NMR Spectra ¹H NMR of compound 2b/2h/2ab/2q:



| \sim | $\infty \infty \odot$ | |
|------------|-----------------------|-------|
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| ÷ | 8 1 1 1 8 | 4 - 8 |
| 4 | 000 | 6 1 1 |
| _ | | |
| | \searrow | |





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¹H NMR of compound 2d/2j:



¹H NMR of compound 2e/2i:







¹H NMR of compound 2g:



¹H NMR of compound 2k/2l:



¹H NMR of compound 2m:



¹H NMR of compound 2n:



¹H NMR of compound 2u:



¹H NMR of compound 2v:



¹³C NMR of compound 2v:

| 55.29 | 51.00 | 33.69 30.25 29.60 28.66 25.99 21.82 | 7.48 7.16 5.84 |
|-------|--------|--|----------------------|
| Ē | - - | | |



fl (ppm)

¹H NMR of compound 2w:



¹H NMR of compound 2x:







¹H NMR of compound 2z:



¹H NMR of compound 2aa:






¹³C NMR of compound 2ad:



¹³C NMR of compound 2ae:





¹³C NMR of compound 2ag:



¹³C NMR of compound 2ah:



¹³C NMR of compound 2ai:





¹H NMR of compound 3b:



¹H NMR of compound 3c:



¹³C NMR of compound 3c:





¹H NMR of compound 3d:



¹H NMR of compound 3h:



¹³C NMR of compound 3h:

| -141.32 128.88 | -128.34 -127.37 -127.28 -127.28 -127.26 | ר77.48 -77.16 ר76.84 |
|-------------------|---|----------------------------|
| | | |



¹H NMR of compound 3i:





¹H NMR of compound 3k:







¹H NMR of compound 3m:



| · · · | | | | | | | - | | · · · · | | | · · · | | | | · · · |
|-------|-----|-----|-----|-----|-----|-----|----|----------------|---------|----|----|-------|----|----|----|-------|
| 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 f1 (ppm) | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| | | | | | | | | S53 | | | | | | | | |

¹H NMR of compound 30:



¹H NMR of compound 3p:









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¹H NMR of compound 3t:



¹H NMR of compound 3z:



¹H NMR of compound 3ab:



¹³C NMR of compound 3ab:



¹H NMR of compound 3aj:













¹H NMR of compound 3an:





7. Deuterium Ratios Determined by ¹H NMR Spectroscopy Table 1, entry 10, 3b (ArNMe₃OTf to ArD)





Table 5, 3b (ArCl to ArD)






















Table 5, 3j (ArI to ArD)



Table 5, 3j (ArCl to ArD)











Table 2, 3p (ArNMe₃OTf to ArD)













Table 4, 3s (ArOTf to ArD)













