# 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 CDCl<sub>3</sub> (7.26 ppm) for <sup>1</sup>H NMR, and CDCl<sub>3</sub> (77.16 ppm) for <sup>13</sup>C 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.<sup>*a*</sup>

		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 <sub>3</sub> 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 <sub>3</sub> /1	NaI/0.5	29
6	DMF/1	HNEt <sub>2</sub> /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 <sub>3</sub> COONa/1	64
14	DMF/2	DMAP/2	KCl/1	68
15	DMF/2	DMAP/2	KNO <sub>3</sub> /1	61
16	DMF/2	DMAP/2	CaCl <sub>2</sub> /1	61
17	DMF/2	DMAP/2	Na <sub>3</sub> PO <sub>4</sub> ·12 H <sub>2</sub> O/1	73
18	DMF/2	DMAP/2	CaSO <sub>4</sub> /1	64
19	DMF/2	DMAP/2	NaNO <sub>2</sub> /1	65
20	DMF/2	DMAP/2	KBr/1	65
21	DMF/2	DMAP/2	Rb <sub>2</sub> CO <sub>3</sub> /1	73
22	DMF/2	DMAP/2	Na3PO4 <sup>·</sup> 12 H2O/0.5	75
23 <sup>b</sup>	DMF/2	DMAP/2	Na <sub>3</sub> PO <sub>4</sub> ·12 H <sub>2</sub> O/0.5	75

<sup>*a*</sup> 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. <sup>*b*</sup> *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 <sub>3</sub> OD	-	-	0	-
2	DMSO-d <sub>6</sub>	-	-	22	96
3	acetone- $d_6$	-	-	Trace	-
4	DMF/D <sub>2</sub> O (9:1)	-	-	57	10
5	CH <sub>3</sub> CN/D <sub>2</sub> O (9:1)	-	-	0	-
6	CD <sub>3</sub> 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 <sub>3</sub> PO <sub>4</sub> /0.5	70	96
11	DMSO-d <sub>6</sub>	DMAP/2	Na <sub>3</sub> PO <sub>4</sub> /1	78	96
12	DMSO- $d_6$	DMAP/2	Na <sub>3</sub> PO <sub>4</sub> /1.5	74	96
13	DMSO- $d_6$	DMAP/2	K <sub>3</sub> PO <sub>4</sub> /1	72	96
14	DMSO- $d_6$	DMAP/2	K <sub>2</sub> CO <sub>3</sub> /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.<sup>a</sup>

<sup>*a*</sup> 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 <sup>1</sup>H 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 <sub>3</sub> /0.5	-	trace	-
2	acetone-d <sub>6</sub> /0.5	-	52	99
3	DMSO- <i>d</i> <sub>6</sub> /0.5	-	10	99
4	CD <sub>3</sub> 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 <sub>3</sub> /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 <sub>3</sub> PO <sub>4</sub> /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 <sub>2</sub> CO <sub>3</sub> /1	50	99
16	acetone- $d_6/0.5$	Rb <sub>2</sub> CO <sub>3</sub> /1	53	99
17	acetone- $d_6/0.5$	Na <sub>2</sub> SO <sub>4</sub> /0.5	trace	-
18	acetone- $d_6/0.5$	K <sub>2</sub> CO <sub>3</sub> /1	60	99
19	acetone- $d_6/0.5$	Na <sub>2</sub> CO <sub>3</sub> /1	63	99
20	acetone-d <sub>6</sub> /0.5	Na <sub>2</sub> CO <sub>3</sub> /2	75	99
21	acetone- $d_6/0.5$	Na <sub>2</sub> CO <sub>3</sub> /3	70	99
22	CD <sub>3</sub> OD/0.5	Na2CO3/2	54	99

Table S3. Optimization of conditions for the reductive deuteration of aryl halide.<sup>a</sup>

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 <sup>1</sup>H 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:<sup>1</sup> To a solution of ArNH<sub>2</sub> (1 mmol) in CH<sub>3</sub>CN (2 mL) was added MeOTf (3.2 mmol, 362  $\mu$ L) and Na<sub>2</sub>CO<sub>3</sub> (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 CD<sub>3</sub>OD (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 <sup>1</sup>H NMR spectroscopy or GC-MS.

#### CH<sub>2</sub>Cl<sub>2</sub>, 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) Na<sub>3</sub>PO<sub>4</sub> (1 equiv) DMSO-d<sub>6</sub> (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:<sup>2</sup> To a solution of ArOH (1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) at 0 °C was added pyridine (2 or 4 mmol, 163 or 326  $\mu$ L) and triflic anhydride (2 equiv, 2 or 4 mmol, 335 or 670  $\mu$ 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.<sup>2</sup>

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), Na<sub>3</sub>PO<sub>4</sub>·12 H<sub>2</sub>O (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 Na<sub>2</sub>SO<sub>4</sub>. 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), Na<sub>3</sub>PO<sub>4</sub> (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 Na<sub>2</sub>SO<sub>4</sub>. 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 <sup>1</sup>H 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), Na<sub>2</sub>CO<sub>3</sub> (0.2 mmol, 21 mg) and CD<sub>3</sub>OD (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 <sup>1</sup>H 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.<sup>3</sup>

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

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

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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 132.9, 130.6, 129.6, 128.4, 61.1, 14.5. These data were agreed with literature.<sup>4</sup>



Methyl benzoate (2d/2j)

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 133.0, 130.2, 129.7, 128.5, 52.2. These data were agreed with literature.<sup>4</sup>

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

Colorless liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 134.2, 129.4, 128.7, 127.2, 61.0, 41.6, 14.3. These data were agreed with literature.<sup>4</sup>



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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 128.2, 125.5, 125.4, 34.8, 31.5. These data were agreed with literature.<sup>3</sup>



Benzonitrile (2g)

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  132.9, 132.3, 129.2, 119.0, 112.5. These data were agreed with literature.<sup>3</sup>



Off-white powder, m.p. 80.8-82.0 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92-7.83 (m, 4H), 7.55-7.46 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.5, 128.0, 126.0. These data were agreed with literature.<sup>3</sup>



Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.7, 147.3, 137.3, 130.2, 128.8, 128.4, 128.0, 127.1, 121.2. These data were agreed with literature.<sup>3</sup>



1H-Indole (2n)

Brown powder, m.p. 52.2-53.4 °C. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  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). <sup>13</sup>C NMR (101 MHz, DMSO- $d_6$ )  $\delta$  136.0, 127.7, 125.3, 121.0, 120.1, 118.9, 111.5, 101.1. These data were agreed with literature.<sup>3</sup>



Methyl 2-phenylacetate (2u)

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 – 7.26 (m, 5H), 3.70 (s, 2H), 3.64 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 134.1, 129.4, 128.7, 127.2, 52.2, 41.3. These data were agreed with literature.<sup>5</sup>



Phenyl benzoate (2v)

Off-white powder, m.p. 69.5-71.2 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.3, 151.0, 133.7, 130.3, 129.6, 128.7, 126.0, 121.8. These data were agreed with literature.<sup>6</sup>



Phenyl acetate (**2w**)

Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (t, *J* = 7.9 Hz, 2H), 7.24 (m, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 2.31 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  169.7, 150.7, 129.5, 125.9, 121.7, 21.2. These data were agreed with literature.<sup>7</sup>



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

Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.29 (t, *J* = 8.0 Hz, 2H), 6.82-6.76 (m, 3H), 2.98 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 129.2, 117.1, 113.0, 40.9. These data were agreed with literature.<sup>3</sup>

2-Methoxynaphthalene (**2y**)

Off-white powder, m.p. 72.4-73.6 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>8</sup>

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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.84 (s, 4H), 5.95 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.5, 121.7, 108.8, 100.7. These data were agreed with literature.<sup>9</sup>



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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -72.85.



Propane-2,2-diyldibenzene (2ac)

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) *δ* 7.32-7.23 (m, 8H), 7.21-7.16 (m, 2H), 1.71 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) *δ* 150.8, 128.1, 126.9, 125.7, 43.1, 30.9.



Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (t, *J* = 7.4 Hz, 4H), 7.22 (t, *J* = 6.7 Hz, 6H), 4.00 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.2, 129.1, 128.6, 126.2, 42.1. These data were agreed with literature.<sup>10</sup>



2-Methylquinoline (**2ae**)

Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>11</sup>

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

Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45-7.38 (m, 1H), 6.91 (d, *J* = 7.5 Hz, 2H), 2.49 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.6, 136.7, 120.3, 24.5. These data were agreed with literature.<sup>12</sup>



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

Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.5, 152.3, 133.5, 126.6, 125.9, 123.4, 122.1. These data were agreed with literature.<sup>13</sup>



2-Phenylbenzo[d]thiazole (2ah)

Off-white powder, m.p. 114.9-115.8 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>13</sup>

(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, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz,CDCl<sub>3</sub>)  $\delta$  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. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -73.58. HRMS m/z (ESI) calcd. for C<sub>19</sub>H<sub>21</sub>F<sub>3</sub>O<sub>3</sub>S<sup>+</sup> [M]<sup>+</sup>: 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.<sup>14</sup>



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

Off-white powder, m.p. 69.7-70.5 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.69 (d, J = 7.7 Hz, 4H), 7.58-7.50 (m, 4H), 7.44 (t, J = 7.4 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.3, 128.9, 128.8, 127.4, 127.3, 126.8 (t, J = 23.1 Hz). These data were agreed with literature.<sup>15</sup>



Ethyl benzoate-4-d (3c)

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>16</sup>



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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 3.92 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.3, 132.8 (t, J = 24.7 Hz), 130.2, 129.7, 128.4, 52.3. These data were agreed with literature.<sup>15</sup>



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

Off-white powder, m.p. 69.4-70.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>16</sup>



Methyl benzoate-3-d (3j)

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>15</sup>



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



Naphthalene-1-d (3l)

Naphthalene-2-d (3k)

Off-white powder, m.p. 80.6-81.5 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93-7.87 (m, 3H), 7.58-7.50 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>15</sup>



Quinoline-3-d (3m)

Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>15</sup>



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

Yellow liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>17</sup>



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

Off-white powder, m.p. 70.1-71.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63 (d, J = 7.9 Hz, 3H), 7.48 (t, J = 7.4 Hz, 4H), 7.38 (t, J = 7.3 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>18</sup>



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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>16</sup>



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

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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>19</sup>



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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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 C<sub>13</sub>H<sub>15</sub>DNO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 219.1238; found: 219.1239.

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Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.84 (s, 3H), 5.95 (s, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (d, J = 8.1 Hz, 4H), 7.50 (d, J = 7.7 Hz, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.3, 128.8, 127.3, 126.8 (t, J = 23.1 Hz). These data were agreed with literature.<sup>15</sup>



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

Off-white powder, m.p. 37.8-38.7 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>17</sup>



N-(Phenyl-4-d)acetamide (**3ak**) <sup>20</sup>

Off-white powder, m.p. 112.1-113.3 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>16</sup>



2-Methoxynaphthalene-1-d (3al)

Off-white powder, m.p. 72.1-73.3 °C.<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>17</sup>



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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.3, 129.2, 119.9 (t, J = 24.8 Hz), 115.8, 67.0, 49.4. These data were agreed with literature.<sup>17</sup>



2-Methoxynaphthalene-6-d (3an)

Off-white powder, m.p. 71.9-73.1 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.82-7.78 (m, 3H), 7.50 (d, J = 8.2 Hz, 1H), 7.24-7.16 (m, 2H), 3.94 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>17</sup>



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

Colorless liquid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.8, 129.2, 115.1 (t, *J* = 25.5 Hz), 111.9, 44.4, 12.6. These data were agreed with literature.<sup>17</sup>

# 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 CH<sub>3</sub>CN (1 mL), DMF (1 mL), or CH<sub>3</sub>OH (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.<sup>20</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>20</sup>

Figure S2. GC-MS and <sup>1</sup>H NMR spectrum of 7.
(a) GC-MS report of 7 (t<sub>R</sub>=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 CH<sub>3</sub>CN (1 mL), DMF (1 mL), or CH<sub>3</sub>OH (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,<sup>21</sup> which had the same retention time and MS spectrum in GC-MS. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  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.<sup>21</sup>





(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<sub>R</sub>=20.502 min) from the reaction of **5ae** with compound **8**.







(e) <sup>1</sup>H NMR of **9** prepared according to literature.<sup>21</sup>



#### (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) CH<sub>3</sub>OD 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%.

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# 6. NMR Spectra <sup>1</sup>H NMR of compound 2b/2h/2ab/2q:



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<sup>1</sup>H NMR of compound 2d/2j:



<sup>1</sup>H NMR of compound 2e/2i:







#### <sup>1</sup>H NMR of compound 2g:



#### <sup>1</sup>H NMR of compound 2k/2l:



<sup>1</sup>H NMR of compound 2m:



<sup>1</sup>H NMR of compound 2n:



<sup>1</sup>H NMR of compound 2u:



# <sup>1</sup>H NMR of compound 2v:



# <sup>13</sup>C 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
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fl (ppm)

<sup>1</sup>H NMR of compound 2w:



<sup>1</sup>H NMR of compound 2x:







# <sup>1</sup>H NMR of compound 2z:



<sup>1</sup>H NMR of compound 2aa:






<sup>13</sup>C NMR of compound 2ad:



# <sup>13</sup>C NMR of compound 2ae:





### <sup>13</sup>C NMR of compound 2ag:



<sup>13</sup>C NMR of compound 2ah:



<sup>13</sup>C NMR of compound 2ai:





<sup>1</sup>H NMR of compound 3b:



<sup>1</sup>H NMR of compound 3c:



## <sup>13</sup>C NMR of compound 3c:





<sup>1</sup>H NMR of compound 3d:



### <sup>1</sup>H NMR of compound 3h:



<sup>13</sup>C NMR of compound 3h:

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



<sup>1</sup>H NMR of compound 3i:





<sup>1</sup>H NMR of compound 3k:







<sup>1</sup>H NMR of compound 3m:



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

<sup>1</sup>H NMR of compound 30:



<sup>1</sup>H NMR of compound 3p:









S57



<sup>1</sup>H NMR of compound 3t:



### <sup>1</sup>H NMR of compound 3z:



<sup>1</sup>H NMR of compound 3ab:



<sup>13</sup>C NMR of compound 3ab:



<sup>1</sup>H NMR of compound 3aj:













<sup>1</sup>H NMR of compound 3an:





7. Deuterium Ratios Determined by <sup>1</sup>H NMR Spectroscopy Table 1, entry 10, 3b (ArNMe<sub>3</sub>OTf to ArD)





Table 5, 3b (ArCl to ArD)






















Table 5, 3j (ArI to ArD)



Table 5, 3j (ArCl to ArD)











Table 2, 3p (ArNMe<sub>3</sub>OTf to ArD)













Table 4, 3s (ArOTf to ArD)













