Supporting Information for

α-Trideuteration of Methylarenes

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1. General information

Solvents were heated to reflux over CaH₂ (DMSO-d₆) under N₂ atmosphere and collected by distillation. All other reagents were used without purification as commercially available, such as NaOH, t-BuOK, NaH and 4-Phenyltoluene. All reactions were monitored and confirmed by TLC silica gel plate. The separation yield is obtained by using analytically pure reagents through silica gel under air conditions. ¹H, ¹³C{¹H} NMR spectra were recorded on Bruker 400/500 spectrometer. ²H NMR spectra were recorded on JNM-ECZ600R/S1 600 spectrometer. Chemical shifts are reported in δ units relative to CDCl₃ [¹H δ = 7.26, ¹³C δ = 77.36] and DMSO-d₆ [¹H δ = 2.50, ¹³C δ = 39.52]. HRMS and GC were recorded by the mass spectrometry service at University of Science and Technology of China.
2. Experimental procedures

2.1. Preparation of Starting Materials

To a solution of Cyclododecanol (55 mmol, 1.1 equiv), 4-bromo-3-methylphenol (50 mmol, 1.0 equiv) and PPh₃ (75 mmol, 1.5 equiv) in DCM (100 mL) was added DIAD (75 mmol, 1.5 equiv) under N₂ atmosphere. The mixture was stirred at 30 °C for 132 h. The resulting reaction mixture was monitored by TLC. After cooling, the reaction mixture was poured into H₂O and extracted with DCM (30 mL, three times). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation, then purified by flash column chromatography (PE/EA/DCM = 100:1:1) on silica gel to give the compound S₁ as white solid (10.4 g, 59% yield) m.p. 45-47 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.72 Hz, 1H), 6.79 (d, J = 2.76 Hz, 1H), 6.60 (dd, J = 8.72, 2.88 Hz, 1H), 4.39-4.33 (m, 1H), 2.35 (s, 3H), 1.81-1.73 (m, 2H), 1.66-1.59 (m, 2H), 1.47-1.38 (m, 18H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 157.6, 138.9, 132.9, 118.9, 115.2, 114.8, 75.8, 28.7, 24.7, 24.4, 23.3, 23.3, 23.2, 20.8. HRMS (EI) m/z: [M]+ calcd for C₁₉H₂₉OB₉Br⁺ 352.1396; found 352.1393.

To a solution of 1-iodo-4-methylbenzene (20 mmol, 1 equiv), Pd(OAc)₂ (1 mmol, 5 mol%), P(ο-tol)₃ (4 mmol, 20 mol%), styrene (40 mmol, 2 equiv) was added NEt₃ (20 mL) under N₂ atmosphere. The mixture was stirred at 125 °C for 16 h. After cooling, the reaction mixture was poured into water and then the product was extracted with DCM (30 mL, three times). The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography (PE) on silica gel to afford the corresponding S₂ as white solid (2.21 g, 57% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, J = 7.75 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.36 (t, J = 7.55 Hz, 2H), 7.27-7.24 (m, 1H), 7.18 (d, J = 7.8 Hz, 2H), 7.12-7.05 (m, 2H), 2.37 (s, 3H). ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 137.7, 134.7, 129.5, 128.8, 128.8, 127.8, 127.5, 126.6, 126.5, 21.4.
2.2. General procedure

**Condition A:** To a Schlenk tube charged with 1a (0.5 mmol, 1.0 equiv) and NaOH (2.0 equiv, 40.8 mg) was added solvent (1 mL) under N₂ atmosphere and the resulting reaction mixture was stirred at 110 °C for 6 h (oil bath). The reaction mixture was directly prified by silica gel column to give the pure product.

**Condition B:** To a Schlenk tube charged with 1a (0.5 mmol, 1.0 equiv) and tBuOK (20 mol%, 11.2 mg) was added solvent (1 mL) under N₂ atmosphere and the resulting reaction mixture was stirred at 30 °C for 6 h (oil bath). The reaction mixture was directly prified by silica gel column to give the pure product.

### 4-(methyl-d₃)-1,1'-biphenyl (1a-d₃)

Prepared according to the general procedure Condition A, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 84.7 mg, 99% yield, 97% D-rate. Condition B, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 83.7 mg, 98% yield, 98% D-rate. White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.62-7.60 (m, 2H, Ar C-H), 7.54-7.51 (m, 2H, Ar C-H), 7.47-7.43 (m, 2H, Ar C-H), 7.37-7.33 (m, 1H, Ar C-H), 7.29-7.26 (m, 2H, Ar C-H), 2.40-2.39 (m, 0.09H, 97% D, benzylic CH). ¹³C ¹H) NMR (100 MHz, CDCl₃): δ 141.3, 138.5, 137.0, 129.6, 128.8, 127.1, 20.9-20.0 (m). ²H NMR (92 MHz, MeCN): δ 4.09.

### 4-methoxy-4'-(methyl-d₃)-1,1'-biphenyl (1b-d₃)

Prepared according to the general procedure Condition A, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 92.6 mg, 92% yield, 90% D-rate. Condition B, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 100.3 mg, 100% yield, 97% D-rate. White solid (m.p. 94-95 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.55-7.52 (m, 2H, Ar C-H), 7.48-7.46 (m, 2H, Ar C-H), 7.26-7.24 (m, 2H, Ar C-H), 7.00-6.97 (m, 2H, Ar C-H), 3.86 (s, 3H, OCH₃), 2.39-2.36 (m, 0.08H, 97% D, benzylic CH). ¹³C ¹H) NMR (100 MHz, CDCl₃): δ 159.0, 138.1, 136.4, 133.9, 129.6, 128.1, 126.7, 114.3, 55.5, 21.0-20.3 (m). ²H NMR (92 MHz, MeCN): δ 4.08. HRMS (EI) m/z: [M]+ calcd for C₁₄H₁₁D₅O⁺ 201.1228; found 201.1224.

### 4-bromo-4'-(methyl-d₃)-1,1'-biphenyl (1c-d₃)

Prepared according to the general procedure Condition A, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 115.3 mg, 92% yield, 75% D-rate.
Condition B, T = 90 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 107.5 mg, 86% yield, 97% D-rate. White solid (m.p. 115-117 °C). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.56-7.54 (m, 2H, Ar C-H), 7.47-7.43 (m, 4H, Ar C-H), 7.26-7.24 (m, 2H, Ar C-H), 2.37-2.36 (m, 0.09H, 97% D, benzylic CH). \textsuperscript{13}C\textsuperscript{1}H NMR (100 MHz, CDCl\textsubscript{3}): δ 140.2, 137.5, 137.2, 131.9, 129.8, 128.7, 126.9, 121.3, 20.6-20.3 (m). \textsuperscript{2}H NMR (92 MHz, MeCN): δ 4.09. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C\textsubscript{13}H\textsubscript{8}D\textsubscript{3}Br\textsuperscript{+} 249.0227; found 249.0227.

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\text{4'-(methyl-d\textsubscript{3})-}[1,1'-biphenyl]-4-carbonitrile (1d-d\textsubscript{3})
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Prepared according to the general procedure Condition B, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 78.7 mg, 80% yield, 92% D-rate. White solid (m.p. 99-101 °C). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.72-7.66 (m, 4H, Ar C-H), 7.51-7.48 (m, 2H, Ar C-H), 7.31-7.27 (m, 2H, Ar C-H), 2.39-2.38 (m, 0.25H, 92% D, benzylic CH). \textsuperscript{13}C\textsuperscript{1}H NMR (100 MHz, CDCl\textsubscript{3}): δ 145.7, 138.8, 136.4, 132.7, 129.9, 127.6, 127.2, 119.2, 110.6, 20.8-20.3 (m). \textsuperscript{2}H NMR (92 MHz, MeCN): δ 4.09. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C\textsubscript{14}H\textsubscript{9}D\textsubscript{3}N\textsuperscript{+} 197.1153; found 197.1151.

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\text{toluene-d\textsubscript{3} (1e-d\textsubscript{3})}
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Prepared according to the general procedure Condition B, T = 90 °C, t = 6 h. Purification was performed by flash column chromatography (PE), GC: 97% yield, 97% D-rate. Colorless oil liquid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.30-7.25 (m, 2H, Ar C-H), 7.21-7.15 (m, 3H, Ar C-H), 2.35-2.34 (m, 0.1H, 97% D, benzylic CH). \textsuperscript{13}C\textsuperscript{1}H NMR (100 MHz, CDCl\textsubscript{3}): δ 137.9, 129.2, 128.4, 125.5, 21.0-20.6 (m). \textsuperscript{2}H NMR (92 MHz, DCM): δ 3.25. HRMS (EI) m/z: [M]+ calcd for C\textsubscript{13}H\textsubscript{8}D\textsubscript{3}N\textsuperscript{+} 95.0809; found 95.0804.

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\text{1-(methyl-d\textsubscript{3})-4-vinylbenzene (1f-d\textsubscript{3})}
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Prepared according to the general procedure Condition B, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 59% NMR yield, 96% D-rate. Colorless oil liquid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.33-7.31 (m, 2H, Ar C-H), 7.15-7.13 (m, 2H, Ar C-H), 6.70 (dd, J = 17.6, 10.88 Hz, 1H, C=CH), 5.70 (dd, J = 17.6, 0.88 Hz, 1H, C=CH), 5.19 (dd, J = 10.88, 0.88 Hz, 1H, C=CH), 2.32-2.31 (m, 0.11H, 96% D, benzylic CH). \textsuperscript{13}C\textsuperscript{1}H NMR (125 MHz, CDCl\textsubscript{3}): δ 137.6, 136.9, 135.0, 129.3, 126.2, 112.9, 20.8-20.2 (m). \textsuperscript{2}H NMR (92 MHz, DCM): δ 3.24. HRMS (EI) m/z: [M]+ calcd for C\textsubscript{9}H\textsubscript{7}D\textsubscript{3} 121.0965; found 121.0965.
1-(methyl-d₃)-4-phenoxybenzene (1g-d₃)

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 85.1 mg, 91% yield, 98% D-rate. Colorless oil liquid. 

¹H NMR (400 MHz, CDCl₃): δ 7.38-7.33 (m, 2H, Ar C-H), 7.25-7.21 (m, 1H, Ar C-H), 7.14-7.09 (m, 1H, Ar C-H), 7.05-7.02 (m, 2H, Ar C-H), 6.95-6.92 (m, 1H, Ar C-H), 6.86-6.83 (m, 2H, Ar C-H), 2.35-2.32 (m, 0.05H, 98% D, benzylic CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 157.5, 157.3, 139.9, 129.8, 129.6, 124.2, 123.2, 119.7, 119.0, 116.1, 21.1-20.3 (m). ²H NMR (92 MHz, MeCN): δ 4.00.

1,3-dimethoxy-5-(methyl-d₃)benzene (1h-d₃)

Prepared according to the general procedure **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 75.1 mg, 97% yield, 98% D-rate. Colorless oil liquid. 

¹H NMR (400 MHz, CDCl₃): δ 6.36-6.35 (m, 2H, Ar C-H), 6.31-6.30 (m, 1H, Ar C-H), 3.79 (s, 6H, OCH₃), 2.30-2.28 (m, 0.06H, 98% D, benzylic CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 160.8, 140.2, 107.2, 97.6, 55.3, 21.5-20.7 (m). ²H NMR (92 MHz, MeCN): δ 3.97. HRMS (EI) m/z: [M]+ calcd for C₁₃H₁₂D₃O₂⁺ 236.0812; found 236.0822.

1-(methyl-d₃)-4-(phenylsulfonyl)benzene (1i-d₃)

Prepared according to the general procedure **Condition A**, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 5:1:1), 110.2 mg, 94% yield, 97% D-rate. **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 5:1:1), 112.1 mg, 95% yield, 97% D-rate. White solid (m.p. 116-118 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.94-7.91 (m, 2H, Ar C-H), 7.84-7.81 (m, 2H, Ar C-H), 7.56-7.52 (m, 1H, Ar C-H), 7.50-7.46 (m, 2H, Ar C-H), 7.30-7.28 (m, 2H, Ar C-H), 2.36-2.35 (m, 0.08H, 97% D, benzylic CH). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 144.2, 142.1, 142.0, 138.8, 138.7, 133.1, 130.0, 129.9, 129.3, 129.2, 127.8, 127.6, 21.3-20.5 (m). ²H NMR (92 MHz, MeCN): δ 4.12. HRMS (ESI–TOF) m/z: [M+H]+ calcd for C₁₅H₁₂D₃O₂S⁺ 269.0878; found 269.0871.

(4-(methyl-d₃)phenyl)(phenyl)methanone (1j-d₃)

S-5
Prepared according to the general procedure **Condition A**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 91.3 mg, 92% yield, 96% D-rate. **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 92.7 mg, 93% yield, 97% D-rate. Colorless oil liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.80-7.77 (m, 2H, $Ar$ C-H), 7.74-7.71 (m, 2H, $Ar$ C-H), 7.60-7.55 (m, 1H, $Ar$ C-H), 7.50-7.45 (m, 2H, $Ar$ C-H), 7.30-7.27 (m, 2H, $Ar$ C-H), 2.42-2.41 (m, 0.11H, 96% D, benzylic CH). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 196.6, 143.2, 138.0, 135.0, 132.3, 130.1, 128.3, 21.3-20.5 (m). $^2$H NMR (92 MHz, MeCN): $\delta$ 4.15.

![tert-butyl 4-(methyl-d$_3$)benzoate (1k-d$_3$)](image)

Prepared according to the general procedure **Condition B**, T = 30 °C, $^t$BuOK (30mol%), t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 70.3 mg, 72% yield, 98% D-rate. Colorless oil liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90-7.87 (m, 2H, $Ar$ C-H), 7.22-7.19 (m, 2H, $Ar$ C-H), 2.37-2.36 (m, 0.05H, 98% D, benzylic CH), 1.59 (s, 9H, $CH_3$). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 166.0, 143.0, 129.5, 129.4, 129.0, 80.8, 28.3, 20.9-20.3 (m). $^2$H NMR (92 MHz, MeCN): $\delta$ 4.11. HRMS (EI) m/z: [M]$^+$ calcd for C$_{12}$H$_3$D$_2$O$_2$ $^+$ 195.1333; found 195.1333.

![4-(methyl-d$_3$)benzonitrile (1l-d$_3$)](image)

Prepared according to the general procedure **Condition A**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 20:1:1), 34.3 mg, 57% yield, 98% D-rate. Yellow oil liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.55-7.53 (m, 2H, $Ar$ C-H), 7.28-7.26 (m, 2H, $Ar$ C-H), 2.40-2.38 (m, 0.06H, 98% D, benzylic CH). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 143.7, 132.2, 130.0, 119.3, 109.5, 21.4-21.0 (m). $^2$H NMR (92 MHz, MeCN): $\delta$ 3.37. HRMS (EI) m/z: [M]$^+$ calcd for C$_8$H$_4$D$_3$N$^+$ 120.0761; found 120.0761.

![1-(methyl-d$_3$)naphthalene (1m-d$_3$)](image)

Prepared according to the general procedure **Condition A**, t = 110 °C, T = 6 h. Purification was performed by flash column chromatography (PE), 64.7 mg, 91% yield, 98% D-rate. **Condition B**, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 70.2 mg, 97% yield, 96% D-rate. Colorless oil liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 8.08$ Hz, 1H, $Ar$ C-H), 7.89 (d, $J = 8.16$ Hz, 1H, $Ar$ C-H), 7.75 (d, $J = 8.12$ Hz, 1H, $Ar$ C-H), 7.58-7.51 (m, 2H, $Ar$ C-H), 7.44-7.40 (m, 1H,
Ar C-H), 7.36-7.35 (m, 1H, Ar C-H), 2.71-2.70 (m, 0.06H, 98% D, benzylic CH). $^{13}$C $^{1}$H NMR (100 MHz, CDCl$_3$): $\delta$ 134.3, 133.6, 132.7, 128.6, 126.7, 126.5, 125.8, 125.7, 125.7, 124.2, 18.9-18.4 (m). $^{2}$H NMR (92 MHz, MeCN): $\delta$ 4.39.

9-(methyl-$d_3$)anthracene (1n-$d_3$)

Prepared according to the general procedure Condition B, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 80.2 mg, 82% yield, 98% D-rate. Yellow solid (m.p. 67-69 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.35 (s, 1H, Ar C-H), 8.30 (d, $J$ = 8.6 Hz, 2H, Ar C-H), 8.02 (d, $J$ = 7.88 Hz, 2H, Ar C-H), 7.55-7.46 (m, 4H, Ar C-H), 3.08-3.07 (m, 0.05H, 98% D, benzylic CH). $^{13}$C $^{1}$H NMR (100 MHz, CDCl$_3$): $\delta$ 131.6, 130.3, 130.2, 129.2, 125.4, 125.4, 124.9, 124.8, 13.6-12.9 (m). $^{2}$H NMR (92 MHz, MeCN): $\delta$ 4.80. HRMS (El) m/z: [M]$^+$ calcd for C$_{15}$H$_9$D$_3$$^+$ 195.1122; found 195.1119.

9-(methyl-$d_3$)phenanthrene (1o-$d_3$)

Prepared according to the general procedure Condition A, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 96.9 mg, 99% yield, 99% D-rate. Condition B, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 91.7 mg, 94% yield, 98% D-rate. White solid (m.p. 82-84 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.75-8.72 (m, 1H, Ar C-H), 8.68-8.66 (m, 1H, Ar C-H), 8.08-8.05 (m, 1H, Ar C-H), 7.83-7.81 (m, 1H, Ar C-H), 7.70-7.63 (m, 2H, Ar C-H), 7.63-7.56 (m, 3H, Ar C-H), 2.72-2.72 (m, 0.06H, 98% D, benzylic CH). $^{13}$C $^{1}$H NMR (100 MHz, CDCl$_3$): $\delta$ 132.5, 132.2, 132.1, 130.5, 129.8, 128.0, 126.9, 126.7, 126.6, 126.3, 125.9, 124.8, 123.1, 122.6, 19.6-19.2 (m). $^{2}$H NMR (92 MHz, DCM): $\delta$ 3.65. HRMS (El) m/z: [M]$^+$ calcd for C$_{15}$H$_9$D$_3$$^+$ 195.1122; found 195.1118.

8-(methyl-$d_3$)-1,9-dihydropyrene (1p-$d_3$)

Prepared according to the general procedure Condition B, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 107.7 mg, 97% yield, 98% D-rate. White solid (m.p. 58-60 °C). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.26-8.24 (m, 1H, Ar C-H), 8.21-8.18 (m, 1H, Ar C-H), 8.18-8.16 (m, 1H, Ar C-H), 8.13-8.09 (m, 2H, Ar C-H), 8.05-7.98 (m, 3H, Ar C-H), 7.88-7.87 (m, 1H, Ar C-H), 2.97-2.95 (m, 0.06H, 98% D, benzylic CH). $^{13}$C $^{1}$H NMR (100 MHz, CDCl$_3$): $\delta$ 132.3, 131.6, 131.1 129.9, 129.4, 128.0, 127.7, 127.2, 126.6, 125.9, 125.1, 125.0, 124.9, 124.9, 124.8, 123.8. $^{2}$H NMR (92 MHz,
DCM): δ 3.87. HRMS (El) m/z: [M]+ calcd for C_{17}H_{9}D_{3}+ 219.1122; found 219.1120.

2-(methyl-d_3)quinolone (1q-d_3)

Prepared according to the general procedure **Condition B**, T = 30 °C, 'BuOK (5 mol%), t = 3 h. Purification was performed by flash column chromatography (PE/EA/DCM = 3:1:1), 54.5 mg, 74% yield, 98% D-rate. Yellow oil liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.03-7.99 (m, 2H, Ar C-H), 7.76-7.74 (m, 1H, Ar C-H), 7.68-7.64 (m, 1H, Ar C-H), 7.48-7.43 (m, 1H, Ar C-H), 7.27-7.23 (m, 0.98H, Ar C-H), 2.70-2.69 (m, 0.07H, 98% D, benzylic CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 159.0, 147.8, 136.2, 129.5, 128.6, 127.5, 126.5, 125.7, 122.1, 24.8-24.4 (m). ²H NMR (92 MHz, MeCN): δ 4.94.

2-(4-(methyl-d_3)phenyl)pyridine (1r-d_3)

Prepared according to the general procedure **Condition B**, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 3:1:1), 86.7 mg, 100% yield, 97% D-rate. Colorless oil liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.69-8.67 (m, 1H, Ar C-H), 7.91-7.88 (m, 2H, Ar C-H), 7.75-7.69 (m, 2H, Ar C-H), 7.30-7.27 (m, 2H, Ar C-H), 7.22-7.19 (m, 1H, Ar C-H), 2.41-2.37 (m, 0.10H, 97% D, benzylic CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 157.6, 149.7, 139.0, 136.8, 136.7, 129.6, 126.9, 121.9, 120.4, 21.2-20.2 (m). ²H NMR (92 MHz, MeCN): δ 4.03. HRMS (ESI–TOF) m/z: [M+H]⁺ calcd for C₁₂H₉D₃N⁺ 173.1153; found 173.1153.

(4-bromo-3-(methyl-d_3)phenoxy)cyclododecane (1s-d_3)

Prepared according to the general procedure **Condition A**, t = 110 °C, T = 6 h. Purification was performed by flash column chromatography (PE), 178.6 mg, 100% yield, 98% D-rate. **Condition B**, T = 70 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 162.1 mg, 91% yield, 98% D-rate. White solid (m.p. 58-60 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.73 (d, J = 8.72 Hz, 1H, Ar C-H), 6.78 (d, J = 2.72 Hz, 1H, Ar C-H), 6.60 (dd, J = 8.64, 2.8 Hz, 1H, Ar C-H), 4.39-4.33 (m, 1H, CH), 2.32 (s, 0.07H, 98% D, benzylic CH), 1.81-1.72 (m, 2H, CH₂), 1.65-1.58 (m, 2H, CH₂), 1.45-1.27 (m, 18H, CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 157.6, 138.8, 132.9, 118.9, 115.2, 114.8, 75.8, 28.7, 24.7, 24.4, 23.3, 23.2, 20.8. ³H NMR (92 MHz, DCM): δ 3.72. HRMS (El) m/z: [M]⁺ calcd for C_{19}H_{26}D_{3}OBr⁺ 355.1585; found 355.1585.
(E)-1-(methyl-d$_3$)-4-styrylbenzene (1t-d$_3$)

Prepared according to the general procedure **Condition A**, $T = 110$ °C, $t = 6$ h. Purification was performed by flash column chromatography (PE), 87.6 mg, 89% yield, 98% D-rate. **Condition B**, $T = 30$ °C, $t = 6$ h. Purification was performed by flash column chromatography (PE), 87.0 mg, 88% yield, 98% D-rate. White solid (m.p. 105-107 °C). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.53-7.50 (m, 2H, Ar C-H), 7.47-7.42 (m, 2H, Ar C-H), 7.38-7.34 (m, 2H, Ar C-H), 7.31-7.21 (m, 1H, Ar C-H), 7.19-7.17 (m, 2H, Ar C-H), 7.13-7.04 (m, 2H, C=CH), 2.34 (s, 0.06H, 98% D, benzylic CH). $^{13}$C $^1$H NMR (125 MHz, CDCl$_3$) δ 137.6, 137.6, 134.7, 129.5, 128.8, 128.8, 127.8, 127.5, 126.6, 126.5. $^2$H NMR (92 MHz, DCM): δ 4.85. HRMS (EI) m/z: [M]$^+$ calcd for C$_{15}$H$_{11}$D$_3$+ 197.1278; found 197.1276.

4,4'-bis(methyl-d$_3$)-2,2'-bipyridine (1u-d$_6$)$^5$

Prepared according to the general procedure **Condition A**, $T = 110$ °C, $t = 6$ h. Purification was performed by flash column chromatography (EA), 91.0 mg, 96% yield, 96% D-rate. **Condition B**, $T = 90$ °C, $t = 6$ h. Purification was performed by flash column chromatography (EA), 88.9 mg, 93% yield, 96% D-rate. White solid. $^1$H NMR (400 MHz, CDCl$_3$): δ 8.54-8.52 (m, 2H, Ar C-H), 8.22-8.22 (m, 2H, Ar C-H), 7.13-7.12 (m, 2H, Ar C-H), 2.41-2.39 (m, 0.27H, 96% D, benzylic CH). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$): δ 156.1, 149.0, 148.1, 124.8, 122.1, 20.7-20.3 (m). $^2$H NMR (92 MHz, DCM): δ 4.09.

2,2'-bis(methyl-d$_3$)-1,1'-binaphthalene (1v-d$_6$)

Prepared according to the general procedure **Condition B**, $T = 30$ °C, $t = 6$ h. Purification was performed by flash column chromatography (PE), 144.3 mg, 100% yield, 96% D-rate. White solid (m.p. 75-77 °C). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.91-7.88 (m, 4H, Ar C-H), 7.53-7.51 (m, 2H, Ar C-H), 7.42-7.38 (m, 2H, Ar C-H), 7.26-7.19 (m, 2H, Ar C-H), 7.07-7.05 (m, 2H, Ar C-H), 2.02-2.01 (m, 0.24H, 96% D, benzylic CH). $^{13}$C $^1$H NMR (100 MHz, CDCl$_3$): δ 135.3, 134.3, 132.9, 132.3, 128.8, 128.1, 127.6, 126.2, 125.8, 125.0, 19.8-19.0 (m). $^2$H NMR (92 MHz, DCM): δ 2.99. HRMS (EI) m/z: [M]$^+$ calcd for C$_{22}$H$_{12}$D$_6$+ 288.1780; found 288.1778.
4-(ethyl-1,1-d₂)-1,1'-biphenyl (1w-d₂)

Prepared according to the general procedure Condition A, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 91.6 mg, 99% yield, 86% D-rate. Condition B, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 92.1 mg, 100% yield, 99% D-rate. Colorless oil liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.61-7.59 (m, 2H, Ar C-H), 7.55-7.53 (m, 2H, Ar C-H), 7.46-7.42 (m, 2H, Ar C-H), 7.36-7.32 (m, 1H, Ar C-H), 7.30-7.28 (m, 2H, Ar C-H), 2.72-2.68 (m, 0.03H, 99% D, benzylic CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.5, 141.3, 138.8, 128.8, 128.4, 127.2, 127.1, 28.2-27.8 (m), 15.6. ²H NMR (92 MHz, MeCN): δ 4.94.

4-(cyclopropylmethyl-d₂)-1,1'-biphenyl (1x-d₂)

Prepared according to the general procedure Condition A, T = 110 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 105.9 mg, 100% yield, 98% D-rate. Condition B, T = 30 °C, t = 6 h. Purification was performed by flash column chromatography (PE), 105.4 mg, 100% yield, 97% D-rate. Colorless oil liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.63-7.60 (m, 2H, Ar C-H), 7.56-7.54 (m, 2H, Ar C-H), 7.47-7.44 (m, 2H, Ar C-H), 7.37-7.33 (m, 3H, Ar C-H), 2.63-2.59 (m, 0.06H, 98% D, benzylic CH₃), 1.06-1.03 (m, 1H, CH₂), 0.60-0.55 (m, 2H, CH₂), 0.28-0.24 (m, 2H, CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 141.4, 141.3, 139.0, 128.9, 128.8, 127.2, 127.2, 127.1, 39.6-39.2 (m), 11.9, 4.8. ²H NMR (92 MHz, MeCN): δ 4.93. HRMS (EI) m/z: [M]⁺ calcd for C₁₆H₁₄D₂⁺ 210.1372; found 210.1371.

(methoxymethyl-d₂)benzene (1y-d₂)

Prepared according to the general procedure Condition B, T = 50 °C, t = 6 h. Purification was performed by flash column chromatography (PE/EA/DCM = 10:1:1), 34.0 mg, 55% yield (GC: 99%), 99% D-rate. Yellow oil liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.38-7.30 (m, 5H, Ar C-H), 4.45-4.45 (m, 0.03H, 99% D, benzylic CH₃), 3.40-3.39 (m, 3H, OCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 138.2, 128.5, 127.9, 127.8, 74.3-73.6 (m), 58.1. ²H NMR (92 MHz, DCM): δ 5.12. HRMS (EI) m/z: [M]⁺ calcd for C₈H₈D₂O⁺ 124.0852; found 124.0850.
Prepared according to the general procedure **Condition B**, $T=90\,^\circ\mathrm{C}$, $t=6\,\text{h}$. Purification was performed by flash column chromatography (PE), 102.1 mg, 99% yield, 98% D-rate. Colorless oil liquid. $^1\text{H}\ NMR$ ($400\ \text{MHz}, \text{CDCl}_3$): δ 7.29-7.26 (m, 2H, $Ar\ C-H$), 7.19-7.15 (m, 2.88H, $Ar\ C-H$), 2.60-2.56 (m, 0.03H, 98% D, benzylic $CH$), 1.60-1.58 (m, 2H, $CH_2$), 1.32-1.26 (m, 12H, $CH_2$), 0.90-0.86 (m, 3H, $CH_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl$_3$): δ 143.0, 128.5, 128.4, 125.7, 35.8-35.2 (m), 32.1, 31.5, 29.7, 29.7, 29.5, 29.4, 22.8, 14.3. $^2\text{H}\ NMR$ (92 MHz, MeCN): δ 4.94. HRMS (EI) m/z: [M]$^+$ calculd for C$_{15}$H$_{22}$D$_2$ 206.1998; found 206.1997.

3. **References**


Figure S1. $^1$H NMR spectra of S1 (CDCl$_3$, 400 M)
Figure S2. 13C NMR spectra of S1 (CDCl₃, 100 M)
Figure S3. $^1$H NMR spectra of S2 (CDCl$_3$, 500 M)
Figure S4. $^{13}$C NMR spectra of S2 (CDCl$_3$, 125 M)
Figure S5. $^1$H NMR spectra of 1a-$d_3$ (CDCl$_3$, 400 M)
Figure S6. $^{13}$C NMR spectra of 1a-$d_3$ (CDCl$_3$, 100 M)
Figure S7. $^2$H NMR spectra of 1a-$d_3$ (MeCN, 92 M)
Figure S8. $^1$H NMR spectra of $1b$-$d_3$ (CDCl$_3$, 400 M)
Figure S9. $^{13}$C NMR spectra of 1b-$d_3$ (CDCl$_3$, 100 M)
Figure S10. $^2$H NMR spectra of 1b-$d_3$ (MeCN, 92 M)
Figure S11. $^1$H NMR spectra of 1c-$d_3$ (CDCl$_3$, 400 M)
Figure S12. $^{13}$C NMR spectra of 1c-$d_3$ (CDCl$_3$, 100 M)
Figure S13. $^2$H NMR spectra of 1c-$d_3$ (MeCN, 92 M)
Figure S14. $^1$H NMR spectra of 1d-$d_3$ (CDCl$_3$, 400 M)
Figure S15. $^{13}$C NMR spectra of 1d-$d_3$ (CDCl$_3$, 100 M)
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Figure S18. $^{13}$C NMR spectra of 1e-$d_3$ (CDCl$_3$, 100 M)
Figure S19. $^2$H NMR spectra of 1e-$d_3$ (DCM, 92 M)
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Figure S22. $^2$H NMR spectra of 1f-$d_3$ (DCM, 92 M)
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Figure S25. $^2$H NMR spectra of 1g-$d_3$ (MeCN, 92 M)
Figure S26. $^1$H NMR spectra of 1h-$d_3$ (CDCl$_3$, 400 M)
Figure S27. $^{13}$C NMR spectra of 1h-$d3$ (CDCl$_3$, 100 M)
Figure S28. $^2$H NMR spectra of 1h-d$_3$ (MeCN, 92 M)
Figure S29. $^1$H NMR spectra of 1i-$d_3$ (CDCl$_3$, 400 M)
Figure S30. $^{13}$C NMR spectra of 1i-$d_3$ (CDCl$_3$, 100 M)
Figure S31. $^2$H NMR spectra of 1i-$d_3$ (MeCN, 92 M)
Figure S32. $^1$H NMR spectra of 1j-$d_3$ (CDCl$_3$, 400 M)
Figure S33. $^{13}$C NMR spectra of 1j-$d_3$ (CDCl$_3$, 100 M)
Figure S34. $^2$H NMR spectra of 1j-$d_3$ (MeCN, 92 M)
Figure S35. $^1$H NMR spectra of 1k-$d_3$ (CDCl$_3$, 400 M)
Figure S36. $^{13}$C NMR spectra of 1k-$d_3$ (CDCl$_3$, 100 M)
Figure S37. $^2$H NMR spectra of 1k-$d_3$ (MeCN, 92 M)
Figure S38. $^1$H NMR spectra of 11-\textit{d}$_3$ (CDCl$_3$, 400 M)
Figure S39. $^{13}$C NMR spectra of 11-$d_3$ (CDCl$_3$, 100 M)
Figure S40. $^2$H NMR spectra of 11-$d_3$ (MeCN, 92 M)
Figure S41. $^1$H NMR spectra of 1m-$d_3$ (CDCl$_3$, 400 M)
Figure S42. $^{13}$C NMR spectra of 1m-$d_3$ (CDCl$_3$, 100 M)
Figure S43. $^2$H NMR spectra of 1m-$d_3$ (MeCN, 92 M)
Figure S44. $^1$H NMR spectra of 1n-$d_3$ (CDCl$_3$, 400 M)
Figure S45. $^{13}$C NMR spectra of $1n-d_3$ (CDCl$_3$, 100 M)
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Figure S47. $^1$H NMR spectra of 1o-$d_3$ (CDCl$_3$, 400 M)
Figure S48. $^{13}$C NMR spectra of 1o-\textit{d}$_3$ (CDCl$_3$, 100 M)
Figure S49. $^2$H NMR spectra of 1o-$d_3$ (DCM, 92 M)
Figure S50. $^1$H NMR spectra of 1p-$d_3$ (CDCl$_3$, 400 M)
Figure S51. $^{13}$C NMR spectra of $1p-d_3$ (CDCl$_3$, 100 M)
Figure S52. $^2$H NMR spectra of 1p-$d_3$ (DCM, 92 M)
Figure S53. $^1$H NMR spectra of $1q$-$d_3$ (CDCl$_3$, 400 M)
Figure S5. $^{13}$C NMR spectra of 1q-$d_3$ (CDCl$_3$, 100 M)
Figure S55. $^2$H NMR spectra of 1q-$d_3$ (MeCN, 92 M)
Figure S56. $^1$H NMR spectra of 1r-$d_3$ (CDCl$_3$, 400 M)
Figure S57. $^{13}$C NMR spectra of 1r-$d_3$ (CDCl$_3$, 100 M)
Figure S58. $^2$H NMR spectra of 1r-$d_3$ (MeCN, 92 M)
Figure S59. $^1$H NMR spectra of 1s-$d_3$ (CDCl$_3$, 400 M)
Figure S60. $^{13}$C NMR spectra of 1s-$d_3$ (CDCl$_3$, 100 M)
Figure S61. $^2$H NMR spectra of 1s-$d_3$ (DCM, 92 M)
Figure S62. $^1$H NMR spectra of 1t-$d_3$ (CDCl$_3$, 400 M)
Figure S63. $^{13}$C NMR spectra of 1t-$d^3$ (CDCl$_3$, 100 M)
Figure S64. $^2$H NMR spectra of 1t-$d_3$ (DCM, 92 M)
Figure S65. $^1$H NMR spectra of 1u-d$_6$ (CDCl$_3$, 400 M)
Figure S66. $^{13}$C NMR spectra of 1u-$d_6$ (CDCl$_3$, 100 M)
Figure S67. $^2$H NMR spectra of 1u-$d_6$ (DCM, 92 M)
Figure S68. $^1$H NMR spectra of 1v-d$_6$ (CDCl$_3$, 400 M)
Figure S69. $^{13}$C NMR spectra of 1v-$d_6$ (CDCl$_3$, 100 M)
Figure S70. $^2$H NMR spectra of 1v-$d_6$ (DCM, 92 M)
Figure S71. $^1$H NMR spectra of 1w-$d_2$ (CDCl$_3$, 400 M)
Figure S72. $^{13}$C NMR spectra of 1w-d$_2$ (CDCl$_3$, 100 M)
Figure S73. $^2$H NMR spectra of 1w-$d_2$ (MeCN, 92 M)
Figure S74. $^1$H NMR spectra of $1x-d_2$ (CDCl$_3$, 400 M)
Figure S75. $^{13}$C NMR spectra of 1x-d$_2$ (CDCl$_3$, 100 M)
Figure S76. $^2$H NMR spectra of 1x-$d_2$ (MeCN, 92 M)
Figure S77. $^1$H NMR spectra of 1y-$d_2$ (CDCl$_3$, 400 M)
Figure S78. $^{13}$C NMR spectra of 1y-$d_2$ (CDCl$_3$, 100 M)
Figure S79. $^2$H NMR spectra of 1y-$d_2$ (DCM, 92M)
Figure S80. $^1$H NMR spectra of 1z-$d_2$ (CDCl$_3$, 400 M)
Figure S81. $^{13}$C NMR spectra of 1z-\textit{d}_2 (CDCl$_3$, 100 M)
Figure S82. $^2$H NMR spectra of 1z-$d_2$ (MeCN, 92 M)