Supporting Information For

Hydride-catalyzed selectively reductive cleavage of unactivated tertiary amides using hydrosilane

Wubing Yao*, Rongrong Li, Jianguo Yang, and Feiyue Hao

School of Pharmaceutical and Materials Engineering, Taizhou University, Jiaojiang
318000, China

E-mail: icyyw2010@yeah.net
## Table of Contents

1. General considerations ........................................................................................................... S3
2. Typical procedures for the cleavage of C-N bonds .......................................................... S4
3. The unreactive substrates ................................................................................................... S4
4. Mechanistic studies .......................................................................................................... S5
5. NMR spectra data ............................................................................................................. S9
6. References ......................................................................................................................... S15
7. NMR spectra ..................................................................................................................... S16
1. General considerations

1.1 Materials

All manipulations were carried out using standard Schlenk, high vacuum, and glovebox techniques. Glassware was dried in a 140 °C oven over 4 h prior to use. LiBEt₃H (1.7 M solution in THF), NaBEt₃H (1M solution in THF), KOtBu (98%), NaOH (98%) and PMe₃ (97%) were purchased from Acros and used as received. KBEt₃H (1M solution in THF), BEt₃ (1M solution in THF) and Hg (99.999%) were purchased from Aladdin and used as received. BPh₃ (96%), Boron trifluoride etherate (98+%), (EtO)₃SiH (96%), and B(C₆F₅)₃ (97%) were purchased from Alfa and used as received. Poly(methylhydrosiloxane) (98%) was purchased from Chembee and used as received. Flash column chromatography was performed on silica gel (particle size 300-400 mesh ASTM), purchased from Yantai, China. The other bases and silanes were obtained from commerical sources and used as received. All solvents were obtained from commercial sources and dried and degassed according to standard procedures. Tertiary aromatic amides were synthesized according to literature procedures.¹

1.2 Analytical Methods

NMR spectra data were obtained on AVANCE (III) HD 400 MHz instruments. ¹H NMR and ¹³C NMR spectra were referenced to residual protio solvent peaks or TMS signal (0 ppm). Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). GC was performed on a Shimadzu GC-2010 plus spectrometer. GC/MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer.
2. Typical procedures for the cleavage of C-N bonds

In an argon filled glovebox, a 10 mL dried Schlenk tube equipped with a magnetic stir bar was charged with NaBEt₃H (20 µL, 20 µmol), amide (0.5 mmol), silane (1.25 mmol, 2.5 equiv.), MTBE (2.0 mL). The tube was then sealed with a Teflon plug under an argon atmosphere, and removed from the glovebox. Then, the solution was stirred at 80 °C for 6-24 h. After the allotted time, the reaction was quenched by adding 1 M aqueous HCl (1 mL) at room temperature. The mixture stirred for 1 h at room temperature, and was extracted with dichloromethane (DCM). Then, the organic layer was filtra-ted though Celite, and dried over MgSO₄. The combined organic layers were analyzed by GC analysis, with p-xylene an internal standard to obtain the GC yield. After that, the crude product was purified by silica gel column chromatography using an ethyl acetate/petroleum ether mixture.

3. The unreactive substrates

![Chemical structures]

Reaction conditions: amides (0.5 mmol), (EtO)₂SiH (1.25 mmol), NaBEt₃H (20 µmol), MTBE (2 mL), at 80 °C, 6 h, then 1M HCl/H₂O, rt, 1 h. Yields were determined by GC-MS.
4. Mechanistic studies

4.1 Homogeneity test with Hg and PMe₃

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<th>Yield (%)</th>
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Reaction conditions: 1a (0.5 mmol), (EtO₂)₂SiH (1.25 mmol), NaBEt₂H (20 μmol), MTBE (2 mL), at 80 °C, 6 h. Yields were determined by GC analysis with p-xylene as an internal standard.

4.2 Effects of radical scavengers on the reduction reactions

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Reaction conditions: 1a (0.5 mmol), (EtO₂)₂SiH (1.25 mmol), NaBEt₂H (20 μmol), MTBE (2 mL), at 80 °C, 6 h. Yields were determined by GC analysis with p-xylene as an internal standard.
4.3 The kinetic profiles for the reduction reactions

**Figure S1.** Reaction conditions: 1a (0.5 mmol), LiBEt₃H (20 μmol), (EtO)₃SiH (1.25 mmol, 2.5 equiv.), MTBE (2 mL), at 80 °C, 0.5-12 h, then 1M HCl/H₂O, rt, 1 h. Yields were determined by GC analysis with p-xylene as an internal standard. All points were taken as an average after repeating the experiments in triplicate.

**Figure S2.** Reaction conditions: 1a (0.5 mmol), KBEt₃H (20 μmol), (EtO)₃SiH (1.25 mmol, 2.5 equiv.), MTBE (2 mL), at 80 °C, 0.5-12 h, then 1M HCl/H₂O, rt, 1 h. Yields were determined by GC analysis with p-xylene as an internal standard. All points were taken as an average after repeating the experiments in triplicate.
4.4 The less likely pathway

\[ \text{NaBEt}_3 \text{H} + 1.0 \text{ equiv. Ph}_2\text{NC(O)Me in MTBE, rt, 1 h.} \]
\[ \text{NaBEt}_3 \text{H} + 1.0 \text{ equiv. Ph}_2\text{NC(O)Me in MTBE, rt, 6 h.} \]
\[ \text{NaBEt}_3 \text{H} + 1.0 \text{ equiv. PhNH in MTBE, rt, 1 h.} \]

**Figure S3.** $^{11}$B NMR spectra. (a) NaBEt$_3$H $+$ 1.0 equiv. Ph$_2$NC(O)Me in MTBE, rt, 1 h. (b) NaBEt$_3$H $+$ 1.0 equiv. Ph$_2$NC(O)Me in MTBE, rt, 6 h. (c) NaBEt$_3$H $+$ 1.0 equiv. Ph$_2$NH in MTBE, rt, 1 h. (d) BEt$_3$ in MTBE. Not observed the formation of NaBEt$_3$NPh$_2$ (-11.9 ppm) and NaBEt$_3$OEt (0.15 ppm).

\[ \text{NaBEt}_3(R^*) \]
\[ R^* = \text{OCH}_2\text{R or NR'R}^* \]

Not observed by $^{11}$B NMR

[Diagram showing reaction pathways and intermediates]
4.5 The energy barrier profile

Table S1. Zero-point energies ($E_{ZEP}$), total electronic energies ($E_T$), Gibbs free energies ($G$), and relative energies calculated by DFT/B3LYP/6-31+G*. Gibbs free energies $\Delta G$ and imaginary frequencies $\nu$ of the transition state offered in the reaction pathway via intramolecular proton transfer in gas phase.

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<th>$E_T$/Hartree</th>
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\[(\text{EtO})_2\text{SiH} + \text{NaBE}_3\text{H} \rightarrow (\text{EtO})_3\text{Si}--\text{H} \rightarrow \begin{array}{c} \text{H} \cdots \text{BE}_3 \\ (\text{EtO})_3\text{Si}--\text{H} \end{array} \rightarrow (\text{EtO})_3\text{Si}--\text{H} \cdots \text{BE}_3\]
5. NMR spectra data

\[ \text{\includegraphics[width=0.1\textwidth]{image.png}} \]

2a. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 0.1 g, 91%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.11-7.02 (m, 2H), 6.95 (d, $J$ = 8.0 Hz, 1H), 6.81 (s, 1H), 6.74 (m, 3H), 3.04 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 143.5, 141.9, 132.1, 132.0, 130.8, 129.1, 127.1, 127.0, 120.3, 119.3, 118.3, 117.6, 34.8, 34.7. These spectroscopic data correspond to reported data.$^2$

\[ \text{\includegraphics[width=0.1\textwidth]{image.png}} \]

2b. Purification by silica gel column chromatography using petroleum ether/EtOAc gave pale yellow solid, 96 mg, 99%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.12-7.06 (m, 4H), 6.83-6.82 (m, 4H), 3.12 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 142.5, 130.8, 128.8, 126.9, 119.6, 118.1, 35.0. These spectroscopic data correspond to reported data.$^2$

\[ \text{\includegraphics[width=0.1\textwidth]{image.png}} \]

2f. Purification by silica gel column chromatography using petroleum ether/EtOAc gave pale yellow solid, 95 mg, 99%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.07 (t, $J$ = 8.0, 2H), 6.94-6.90 (m, 4H), 6.73 (d, $J$ = 8.0 Hz, 2H), 6.42 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 148.5, 132.3, 130.6, 129.9, 129.6, 123.2, 119.5. These spectroscopic data correspond to reported data.$^3$
2g. Purification by silica gel column chromatography using petroleum ether/EtOAc gave pale yellow solid, 66 mg, 59%. \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) δ 7.50-7.47 (m, 1H), 7.21-7.17 (m, 1H), 7.06-6.99 (m, 3H), 6.97-6.92 (m, 1H), 6.68 (t, \(J = 10\) Hz, 2H), 5.88 (s, 1H), 5.17 (s, 1H), 3.87 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\), 20 °C) δ 156.2, 149.2, 146.6, 130.4, 129.6, 128.7, 128.9, 127.6, 127.3, 123.6, 123.1, 119.8, 119.4, 103.4, 55.5. These spectroscopic data correspond to reported data.\(^4\)

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\text{2g}
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2h. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 54 mg, 65%. \(^1\)H NMR (400 MHz, DMSO-\(d_6\), 20 °C) δ 11.26 (s, 1H), 8.11 (d, \(J = 8.0\) Hz, 2H), 7.49 (d, \(J = 8.0\) Hz, 2H), 7.39 (t, \(J = 6.0\) Hz, 2H), 7.16 (t, \(J = 8.0\) Hz, 2H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\), 20 °C) δ 139.7, 125.5, 122.4, 120.2, 118.5, 110.9. These spectroscopic data correspond to reported data.\(^2\)

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2i. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 69 mg, 56%. \(^1\)H NMR (400 MHz, DMSO-\(d_6\), 20 °C) δ 11.45 (s, 1H), 8.36 (s, 1H), 8.16 (d, \(J = 8.0\) Hz, 1H), 7.52-7.49 (m, 2H), 7.47 (t, \(J = 8.0\) Hz, 1H), 7.42 (t, \(J = 8.0\) Hz, 1H), 7.17 (t, \(J = 8.0\) Hz, 1H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\), 20 °C) δ 140.1, 138.4, 127.9, 126.3, 124.4, 122.8, 121.5, 120.7, 118.9, 112.9, 111.2, 110.6. These spectroscopic data correspond to reported data.\(^5\)

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\text{2i}
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2j. Purification by silica gel column chromatography using petroleum ether/EtOAc gave pale yellow solid, 66 mg, 61%. \(^1\)H NMR (400 MHz, DMSO-\(d_6\), 20 °C) δ 11.22 (s, 1H), 8.68 (s, 1H), 8.25 (d, \(J = 8.0\) Hz, 1H), 8.05 (d, \(J = 8.0\) Hz, 1H), 8.00 (d, \(J = 8.0\) Hz, 1H), 7.86 (s, 1H), 7.50-7.43 (m, 3H), 7.36 (t, \(J = 8.0\) Hz, 1H), 7.21-7.17 (m, 1H). \(^{13}\)C
NMR (101 MHz, DMSO-\textit{d}_6, 20 °C) δ 142.5, 139.6, 132.2, 128.3, 127.5, 127.3, 126.9, 125.1, 124.8, 122.2, 121.0, 118.6, 118.3, 110.5, 105.1. These spectroscopic data correspond to reported data.\textsuperscript{6}

2k. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 61 mg, 67%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 20 °C) δ 7.09-7.04 (m, 4H), 6.84 (t, \textit{J} = 8.0 Hz, 2H), 6.66 (d, \textit{J} = 8.0 Hz, 2H), 4.04 (s, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}, 20 °C) δ 140.2, 128.7, 127.1, 120.7, 120.1, 113.6, 31.5. These spectroscopic data correspond to reported data.\textsuperscript{7}

2l. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 63 mg, 69%. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6, 20 °C) δ 8.17 (s, 1H), 6.73-6.69 (m, 2H), 6.60-6.53 (m, 4H), 6.45-6.43 (m, 2H). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6, 20 °C) δ 142.8, 132.4, 123.9, 120.3, 115.1, 113.3. These spectroscopic data correspond to reported data.\textsuperscript{8}

2m. Purification by silica gel column chromatography using petroleum ether/EtOAc gave pale yellow solid, 77 mg, 77%. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6, 20 °C) δ 8.59 (s, 1H), 6.98 (t, \textit{J} = 8.0 Hz, 2H), 6.90 (d, \textit{J} = 4.0 Hz, 2H), 6.74 (t, \textit{J} = 6.0 Hz, 2H), 6.69 (d, \textit{J} = 8.0 Hz, 2H). \textsuperscript{13}C NMR (101 MHz, DMSO-\textit{d}_6, 20 °C) δ 142.1, 127.5, 126.2, 121.8, 116.3, 114.4. These spectroscopic data correspond to reported data.\textsuperscript{9}
2n. Purification by silica gel column chromatography using petroleum ether/EtOAc gave pale yellow solid, 80 mg, 60%. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) δ 8.88 (s, 1H), 7.09 (d, J = 8.0 Hz, 1H), 7.03-6.99 (m, 2H), 6.93-6.91 (m, 2H), 6.79 (t, J = 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H). $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) δ 142.7, 140.9, 128.1, 126.9, 126.4, 125.4, 122.7, 122.6, 122.0, 118.0, 115.3, 114.7, 110.1. These spectroscopic data correspond to reported data.$^9$

2o. Purification by silica gel column chromatography using petroleum ether/EtOAc gave pale yellow solid, 63 mg, 49%. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) δ 8.61 (s, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.75 (t, J = 8.0 Hz, 1H), 6.70-6.64 (m, 3H), 2.89 (q, J = 16.0 Hz, J = 8.0 Hz, 2H), 1.22 (t, J = 8.0 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) δ 142.6, 141.7, 135.3, 127.6, 126.6, 126.3, 121.9, 121.3, 116.4, 114.5, 113.7, 113.6, 26.3, 14.3. These spectroscopic data correspond to reported data.$^9$

2p. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 87 mg, 88%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.21 (t, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 1H), 7.03 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.86-6.82 (m, 3H), 5.28 (s, 1H), 2.30 (s, 3H), 2.21 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 145.1, 138.4, 132.4, 131.8, 129.9, 129.4, 127.4, 120.9, 119.8, 116.4, 20.9, 18.0. These spectroscopic data correspond to reported data.$^2$
2q. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 69 mg, 70%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.09 (d, $J = 8.0$ Hz, 4H), 6.97 (d, $J = 8.0$ Hz, 4H), 5.53 (s, 1H), 2.32 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 141.2, 130.3, 129.9, 118.0, 20.8. These spectroscopic data correspond to reported data.$^2$

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2r. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 74 mg, 74%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.20 (t, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.91-6.80 (m, 5H), 5.48 (s, 1H), 3.78 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 155.4, 145.3, 135.8, 129.4, 122.3, 119.7, 115.7, 114.8, 55.7. These spectroscopic data correspond to reported data.$^2$

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2s. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 70 mg, 83%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.30-7.23 (m, 4H), 7.15-7.08 (m, 4H), 6.95 (t, $J = 7.3$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 143.2, 129.5, 121.1, 117.9. These spectroscopic data correspond to reported data.$^2$

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\text{\includegraphics[width=0.2\textwidth]{image}}
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2w. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 98 mg, 89%. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.75 (d, 4.0 Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.62 (s, 1H), 7.46-7.38 (m, 2H), 7.33 (m, 6H), 7.07 (t, $J = 6.0$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) δ 142.5, 140.4, 134.6, 129.6, 129.5,
129.4, 127.8, 126.7, 126.6, 123.9, 122.1, 120.2, 118.8, 112.5. These spectroscopic data correspond to reported data.²

2x. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 101 mg, 75%. ¹H NMR (400 MHz, CDCl₃, 20 °C) δ 7.78 (t, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.54 (s, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃, 20 °C) δ 139.9, 134.5, 130.0, 129.6, 127.8, 126.9, 126.7, 124.3, 120.5, 113.7. These spectroscopic data correspond to reported data.¹⁰

2y. Purification by silica gel column chromatography using petroleum ether/EtOAc gave white solid, 125 mg, 88%. ¹H NMR (400 MHz, CDCl₃, 20 °C) δ 7.62 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.32 (dd, J = 12.0, J = 3.0 Hz, 3H), 7.13 (s, 3H), 6.96 (s, 1H), 1.48 (s, 6H). ¹³C NMR (101 MHz, CDCl₃, 20 °C) δ 155.4, 153.2, 139.4, 129.5, 127.1, 126.2, 122.5, 121.0, 119.2, 117.8, 112.5, 46.9, 27.4. These spectroscopic data correspond to reported data.¹¹
6. References


7. NMR spectra

Figure S4. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2a

Figure S5. $^{13}$C NMR ( MHz, CDCl$_3$, 20 °C) of 2a
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2b

Figure S7. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2b
Figure S8. $^1$H NMR (400 MHz, CDCl$_3$, 20 $^\circ$C) of 2f

Figure S9. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 $^\circ$C) of 2f
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2g

Figure S11. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2g
Figure S12. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) of 2h

Figure S13. $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) of 2h
Figure S14. $^{1}$H NMR (400 MHz, DMSO-$d_6$, 20 °C) of 2i

Figure S15. $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) of 2i
Figure S16. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) of 2j

Figure S17. $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) of 2j
Figure S18. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2k

Figure S19. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2k
Figure S20. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) of 2l

Figure S21. $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) of 2l
Figure S22. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) of 2m

Figure S23. $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) of 2m
Figure S24. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) of 2n

Figure S25. $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) of 2n
Figure S26. $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) of 2o

Figure S27. $^{13}$C NMR (101 MHz, DMSO-$d_6$, 20 °C) of 2o
Figure S28. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2p

Figure S29. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2p
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2q

Figure S31. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2q
Figure S32. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2r

Figure S33. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2r
Figure S34. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2s

Figure S35. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2s
Figure S36. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2w

Figure S37. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2w
Figure S38. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2x

Figure S39. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2x
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 2y

Figure S31. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 2y