Anionic, *in situ* Generation of Formaldehyde. A Very Useful and Versatile Tool in Synthesis.

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SUPPORTING INFORMATION – ^1H & ^{13}C NMR, MS

NMR spectra were recorded on a 300 MHz Bruker Avance. Unless otherwise indicated, all spectra were recorded at 300 MHz for ^1H and 75 MHz for ^{13}C in CDCl_3 . All chemical shifts are given in ppm. R_f given for TLC analyses were measured on silica gel Merck Kieselgel F₂₅₄ aluminum plates.

Standard procedure for hydroxymethylation reaction:

To a stirred solution of n-butyllithium (4.02 mL, 10.05 mmol) in anhydrous THF (20 mL) was added dropwise 2,2,6,6-tetramethylpiperidine (1.72 mL, 10.05 mmol) at $-10\text{ }^\circ\text{C}$. The solution was allowed to stir at $0\text{ }^\circ\text{C}$ for 30 minutes then cooled to $-78\text{ }^\circ\text{C}$. Reactant (3.35 mmol) in anhydrous THF (4 mL) was added dropwise and stirred for an additional 1 hour. 1H-benzotriazole-methanol (1 g, 6.70 mmol) in anhydrous THF (30 mL) was added dropwise over a 30 minutes period and kept 2 hours at this temperature. The reaction was quenched with water (15 mL) extracted with diethyl ether (50 mL) then washed successively with 4N NaOH (15 mL) and brine (15 mL). The organic layer was dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification conditions for each compound are given in this supplementary material.

Procedure is the same if 1H-benzotriazole-methanol is replaced by *N*-hydroxymethyl phthalimide and if LTMP is replaced by LDA.

(2-bromopyridin-3-yl)methanol 4
Mol. Formula : C ₆ H ₆ BrNO Mol. Weight : 188.02
Flash chromatography eluting with dichloromethane : methanol 95 : 5 (R _f = 0.4) gave a white solid (497 mg, 79%)	
¹ H NMR (CDCl ₃ , 300 MHz): 2.23 (t, <i>J</i> = 6.0 Hz, 1H), 4.75 (d, <i>J</i> = 6.0 Hz, 2H), 7.30 (dd, <i>J</i> = 4.7 Hz, 7.3 Hz, 1H), 7.84 (d, <i>J</i> = 7.3 Hz, 1H), 8.29 (dd, <i>J</i> = 1.7 Hz, 4.7 Hz, 1H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 63.4, 123.2, 136.7, 137.5, 141.6, 148.7	
GC-MS <i>m/z</i> = 189, 187, 108, 106, 80, 78, 53, 51	
Anal. <i>calcd</i> for C ₆ H ₆ BrNO: C, 38.33; H, 3.22; N, 7.45 <i>found</i> C, 38.28; H, 3.17; N, 7.51	

GDE 4 #375 RT: 3.67 AV: 1 NL: 1.96E6
T: c Full [40.00-620.00]

The figure displays three stacked ^1H NMR spectra of compound **1**. The top spectrum shows the full range from 0.5 to 9.5 ppm. The middle spectrum is an expansion of the aromatic region (7.2–7.5 ppm), and the bottom spectrum is an expansion of the aliphatic region (2.0–2.5 ppm). Chemical shifts are indicated in ppm (ppm) on the x-axis. Integration values are provided for each major peak group.

Top Spectrum (Full ^1H NMR):

- Aromatic region (7.2–7.5 ppm):**
 - Peak at ~8.30 ppm: Integration 0.9534. Chemical shifts: 8.3000, 8.2944, 8.2843, 8.2793.
 - Peak at ~7.85 ppm: Integration 0.9606. Chemical shifts: 7.8550, 7.8505.
 - Peak at ~7.30 ppm: Integration 1.3204. Chemical shifts: 7.3334, 7.3177, 7.3083, 7.2926, 7.2600.
- Aliphatic region (2.0–2.5 ppm):**
 - Peak at ~4.75 ppm: Integration 2.0000. Chemical shifts: 4.7613, 4.7418.
 - Peak at ~2.25 ppm: Integration 0.9815. Chemical shifts: 2.2538, 2.2337, 2.2136.

Middle Spectrum (Aromatic Expansion):

- Peak at ~7.40 ppm: Integration 1.3204. Chemical shifts: 7.4000, 7.3944, 7.3843, 7.3793.
- Peak at ~7.85 ppm: Integration 0.9606. Chemical shifts: 7.8550, 7.8505.
- Peak at ~7.30 ppm: Integration 1.3204. Chemical shifts: 7.3334, 7.3177, 7.3083, 7.2926, 7.2600.

Bottom Spectrum (Aliphatic Expansion):

- Peak at ~4.75 ppm: Integration 2.0000. Chemical shifts: 4.7613, 4.7418.
- Peak at ~2.25 ppm: Integration 0.9815. Chemical shifts: 2.2538, 2.2337, 2.2136.

148.6870
141.5718
137.5184
136.7578
123.2303
77.5836
77.1000
76.7564
63.3630

(ppm)

4-(hydroxymethyl)- <i>N,N</i> -diisopropylnicotinamide 5
Mol. Formula : C ₁₃ H ₂₀ N ₂ O ₂ Mol. Weight : 236.31
Flash chromatography eluting with dichloromethane : methanol 95 : 5 (<i>R_f</i> = 0.3), gave a yellow oil (530 mg, 67%)	
¹ H NMR (CDCl ₃ , 300 MHz): 1.01 (m, 6H), 1.41 (d, <i>J</i> = 6.6 Hz, 6H), 3.45 (m, 2H), 4.5 (m, 2H), 7.33 (d, <i>J</i> = 5.0 Hz, 1H), 8.19 (s, 1H), 8.37 (d, <i>J</i> = 5.0 Hz, 1H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 20.3, 20.5, 46.1, 51.3, 60.5, 122.0, 131.7, 144.7, 147.7, 149.5, 167.7	
GC-MS <i>m/z</i> = 236, 193, 136, 86	
Anal. <i>calcd</i> for C ₁₃ H ₂₀ N ₂ O ₂ : C, 66.07; H, 8.53; N, 11.85 <i>found</i> C, 66.00 ; H, 8.45 ; N, 11.92

HM10-C

methyl 3-hydroxy-2-phenylpropanoate 6
Mol. Formula : C ₁₀ H ₁₂ O ₃ Mol. Weight : 180.20
Flash chromatography eluting with dichloromethane : methanol 95 : 5 (<i>R_f</i> = 0.3), gave a colorless oil (580 mg, 96%)	
¹ H NMR (CDCl ₃ , 300 MHz): 3.74 (s, 3H), 3.84 (m, 2H), 4.19 (dd, <i>J</i> = 8.5 Hz, 10.4 Hz, 1H), 7.33 (m, 5H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 52.4, 53.9, 64.5, 127.9, 128.2, 128.9, 135.5, 173.9	
GC-MS <i>m/z</i> = 180, 162, 150, 118, 91, 77, 51	
Anal. <i>calcd</i> for C ₁₀ H ₁₂ O ₃ : C, 66.65; H, 6.71 <i>found</i> C, 66.43 ; H, 6.59	

GDE1 #378 RT: 3.70 AV: 1 NL: 8.38E6
T: c Full [40.00-620.00]

HM1-H

HM1-C

2-(hydroxymethyl)-3,4-dihydronaphthalen-1(2H)-one 7
Mol. Formula : C ₁₁ H ₁₂ O ₂ Mol. Weight : 176.21
Flash chromatography eluting with ethyl acetate : cyclohexane 1 : 1 (R _f = 0.5), gave a colorless oil (372 mg, 63%)	
¹ H NMR (CDCl ₃ , 300 MHz): 1.90 (ddd, <i>J</i> = 5.1 Hz, 13.3 Hz, 18.4 Hz, 1H), 2.11 (m, 1H), 2.72 (m, 1H), 3.1 (m, 3H), 3.87 (ddd, <i>J</i> = 7.3 Hz, 11.3 Hz, 18.4 Hz, 2H), 7.27 (m, 2H), 7.50 (td, <i>J</i> = 1.3 Hz, 7.7 Hz, 1H), 8.01 (d, <i>J</i> = 7.7 Hz, 1H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 26.3, 29.1, 49.5, 63.8, 126.8, 127.3, 128.9, 132.4, 133.9, 144.4, 201.8	
GC-MS <i>m/z</i> = 176, 158, 130, 118, 90	
Anal. <i>calcd</i> for C ₁₁ H ₁₂ O ₂ : C, 74.98; H, 6.86 <i>found</i> C, 74.84; H, 6.75	

GDE2 #896-900 RT: 7.45-7.48 AV: 5 SB: 21 7.32-7.38, 7.67-7.77 NL: 2.44E5
T: c Full [20.00-500.00]

2,2-bis(hydroxymethyl)-3,4-dihydronaphthalen-1(2H)-one 8
Mol. Formula : C ₁₂ H ₁₄ O ₃
	Mol. Weight : 206.24
Deprotonation was accomplished with commercially available potassium tert-butoxide at –78°C. Flash chromatography eluting with ethyl acetate : cyclohexane 1 : 1 (R _f = 0.25), gave a colorless oil (636 mg, 92 %)	
¹ H NMR (CDCl ₃ , 300 MHz): 1.93 (t, <i>J</i> = 6.5 Hz, 2H), 2.97 (t, <i>J</i> = 6.5 Hz, 2H), 3.11 (bs, 1H), 3.69 (d, <i>J</i> = 11.3 Hz, 2H), 3.90 (d, <i>J</i> = 11.3 Hz, 2H), 7.19 (m, 2H), 7.45 (td, <i>J</i> = 1.2 Hz, 7.7 Hz, 1H), 7.94 (d, <i>J</i> = 7.7 Hz, 1H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 24.9, 26.5, 50.9, 64.9, 127.0, 127.7, 129.0, 131.7, 134.3, 143.7, 203.4	
IC(+)-MS MH ⁺ = 207	
Anal. <i>calcd</i> for C ₆ H ₇ NO: C, 69.88; H, 6.84 <i>found</i> C, 69.72; H, 6.75

2-(hydroxymethyl)-2-methyl-3,4-dihydronaphthalen-1(2H)-one 9
Mol. Formula : C ₁₂ H ₁₄ O ₂
	Mol. Weight : 190.24
Flash chromatography eluting with dichloromethane : methanol 95 : 5 (R _f = 0.6), gave a yellow oil (618 mg, 97%)	
¹ H NMR (CDCl ₃ , 300 MHz): 1.14 (s, 3H), 1.71 (td, <i>J</i> = 4.5 Hz, 8.5 Hz, 1H), 2.17 (td, <i>J</i> = 5.1 Hz, 13.2 Hz, 1H), 2.83 (td, <i>J</i> = 4.0 Hz, 4.4 Hz, 2H), 3.05 (m, 1H), 3.60 (dd, <i>J</i> = 11.1 Hz, 32.0 Hz, 2H), 7.19 (m, 2H), 7.40 (t, <i>J</i> = 7.3 Hz, 1H), 7.94 (d, <i>J</i> = 7.9 Hz, 1H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 17.7, 24.3, 30.5, 45.7, 67.9, 125.9, 126.7, 128.0, 130.6, 132.8, 142.7, 202.9	
GC-MS m/z= 190, 172, 160, 145, 118, 90	
Anal. <i>calcd</i> for C ₁₂ H ₁₄ O ₂ : C, 75.76; H, 6.86 <i>found</i> C, 75.66; H, 6.81

3-hydroxy-2-methylpropanenitrile 10
Mol. Formula : C ₄ H ₇ NO Mol. Weight : 85.1
Evaporation of the solvents and starting material gave a colorless oil (192 mg, 67%)	
¹ H NMR (CDCl ₃ , 300 MHz): 1.29 (d, <i>J</i> = 7.2Hz, 3H), 2.80 (m, 1H), 2.95 (m, 1H), 3.71 (d, <i>J</i> = 6.2 Hz, 1H), 3.71 (d, <i>J</i> = 6.2 Hz, 1H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 14.2, 29.0, 63.8, 121.8	
GC-MS m/z= not detected	
Anal. <i>calcd</i> for C ₄ H ₇ NO: C, 56.45; H, 8.29; N, 16.46 <i>found</i> C, 56.37; H, 8.22; N, 16.55	

HM12-H

HM12-C

2-(phenylsulfonyl)ethanol **11**

Mol. Formula : C₈H₁₀O₃S

Mol. Weight : 186.23

Flash chromatography eluting with dichloromethane : methanol 95 : 5 (*R_f* = 0.45), gave a colorless oil (330 mg, 53%)

¹H NMR (CDCl₃, 300 MHz): 3.29 (t, *J* = 5.6 Hz, 2H), 3.90 (t, *J* = 5.6 Hz, 2H), 7.50 (m, 2H), 7.57 (m, 1H), 7.84 (m, 2H)

¹³C NMR (CDCl₃, 75 MHz): 56.2, 58.2, 127.9, 129.5, 134.1, 138.9

GC-MS *m/z* = 186, 158, 143, 125, 77

Anal. *calcd* for C₈H₁₀O₃S: C, 51.60; H, 5.41; S, 17.22 *found* C, 51.55; H, 5.37; S, 17.15

GDE8 #1473-1487 RT: 12.22-12.34 AV: 15 SB: 81 11.76-11.97, 13.07-13.52 NL: 2.39E6
T: c Full [20.00-500.00]

HAS-C

2-(pyridin-2-yl)ethanol **12**

Mol. Formula : C₇H₉NO

Mol. Weight : 123.15

Evaporation of the solvents and starting material gave a colorless oil (268 mg, 65%)

¹H NMR (CDCl₃, 300 MHz): 2.98 (t, *J* = 5.5 Hz, 1H), 2.99 (t, *J* = 5.6 Hz, 1H), 3.98 (t, *J* = 5.6 Hz, 1H), 3.99 (t, *J* = 5.5 Hz, 1H), 7.12 (m, 2H), 7.61 (m, 1H), 8.44 (m, 1H)

¹³C NMR (CDCl₃, 75 MHz): 39.2, 61.7, 121.5, 123.5, 136.7, 148.7, 160.5

GC-MS *m/z*= 123, 106, 93, 79

Anal. *calcd* for C₇H₉NO: C, 68.27; H, 7.37; N, 11.37 *found* C, 68.19; H, 7.21; N, 11.45

GDE5 #420-427 RT: 3.50-3.56 AV: 8 SB: 18 3.33-3.37, 3.88-3.98 NL: 5.98E5
T: c Full [20.00-500.00]

HMS-H

HMS-C

3-phenylprop-2-yn-1-ol **13**

Mol. Formula : C₉H₈O

Mol. Weight : 132.16

Flash chromatography eluting with dichloromethane : methanol 95 : 5 (*R_f* = 0.6), gave a colorless oil (226 mg, 51%)

¹H NMR (CDCl₃, 300 MHz): 2.35 (bs, 1H), 4.50 (s, 2H), 7.29 (m, 3H), 7.45 (m, 2H)

¹³C NMR (CDCl₃, 75 MHz): 51.6, 85.7, 87.3, 122.6, 128.4, 128.6, 131.8

GC-MS *m/z*= 132, 103, 77

Anal. *calcd* for C₉H₈NO: C, 81.79; H, 6.10 *found* C, 81.71; H, 6.00

GDE9 #533-539 RT: 4.44-4.49 AV: 7 NL: 7.28E6
IT: c Full [20.00-500.00]

(2-phenyl-1,3-dithian-2-yl)methanol **14**

Mol. Formula : C₁₁H₁₄OS₂

Mol. Weight : 226.36

Flash chromatography eluting with ethyl acetate : cyclohexane (*R_f* = 0.65), gave a white solid (705 mg, 93%)

¹H NMR (CDCl₃, 300 MHz): 1.95-2.14 (m, 3H), 2.68 (ddd, *J* = 2.9 Hz, 7.4 Hz, 21.3 Hz, 2H) 2.92 (ddd, *J* = 2.9 Hz, 9.0 Hz, 23.2 Hz, 2H), 4.05 (s, 2H), 7.31 (m, 3H), 7.85 (d, *J* = 8.3 Hz, 2H)

¹³C NMR (CDCl₃, 75 MHz): 24.6, 27.3, 59.0, 66.2, 128.2, 128.6, 128.7, 139.6

GC-MS *m/z* = 226, 208, 195, 121

Anal. *calcd* for C₁₁H₁₄OS₂: C, 58.37; H, 6.23; S, 28.33 *found* C, 58.33; H, 6.20; S, 28.36

GDE 7 #1206 RT: 11.75 AV: 1 NL: 6.49E6
T: c Full [40.00-620.00]

(1<i>H</i>-indol-1-yl)methanol 15
Mol. Formula : C ₉ H ₉ NO
	Mol. Weight : 147.17
Flash chromatography eluting with ethyl acetate : cyclohexane 1 : 1 (<i>R_f</i> =0.65) gave a colorless oil (247 mg, 50%)	
¹ H NMR (CDCl ₃ , 300 MHz): 2.53 (bs, 1H), 5.53 (s, 2H), 6.46 (d, <i>J</i> = 3.2 Hz, 1H), 7.10 (m, 2H), 7.16 (t, <i>J</i> = 8.1 Hz, 1H), 7.39 (d, <i>J</i> = 8.1 Hz, 1H), 7.57 (d, <i>J</i> = 7.7 Hz, 1H)	
¹³ C NMR (CDCl ₃ , 75 MHz): 70.0, 103.1, 109.6, 120.5, 121.3, 122.3, 127.4, 129.4, 135.7	
GC-MS <i>m/z</i> = 147, 117, 90	
Anal. <i>calcd</i> for C ₉ H ₉ NO: C, 73.45; H, 6.16; N, 9.52 <i>found</i> C, 73.37; H, 6.09; N, 9.61	

GDE11 #823-828 RT: 6.84-6.88 AV: 6 SB: 60 6.56-6.80, 7.09-7.34 NL: 4.72E5
T: c Full [20.00-500.00]

HM11-H

HM11-C

1-methoxy-3-vinylbenzene **16**

Mol. Formula : C₉H₁₀O

Mol. Weight : 134.18

Filtration through a short plug of celite and silica gel eluting diethyl ether : cyclohexane 1 : 1 furnished **16** as a yellow oil (414 mg, 92%)

¹H NMR (CDCl₃, 300 MHz): 3.71 (s, 3H), 5.15 (d, *J* = 10.7 Hz, 1H), 5.65 (d, *J* = 17.5 Hz, 1H), 6.60 (dd, *J* = 10.7 Hz, 17.5 Hz, 1H), 6.71 (dd, *J* = 2.1 Hz, 7.9 Hz, 1H), 6.86 (m, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.9 Hz, 1H)

¹³C NMR (CDCl₃, 75 MHz): 54.3, 110.6, 112.5, 113.2, 117.9, 128.6, 135.8, 138.1, 158.8

GC-MS *m/z* = 134, 91

Anal. *calcd* for C₉H₁₀O: C, 80.56; H, 7.51 *found* C, 80.49 ; H, 7.44

GDE13 #410 RT: 3.42 AV: 1 NL: 8.09E6
T: c Full [20.00-500.00]