Supporting Information

Light-Mediated Reductive Debromination of Unactivated Alkyl and Aryl Bromides.

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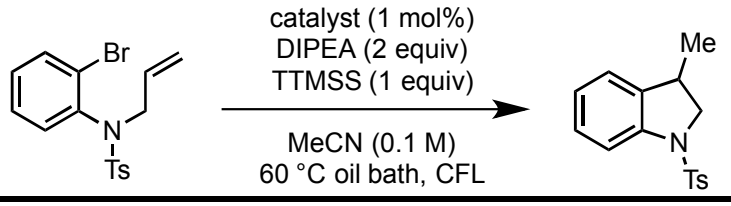
General Information:
Chemicals were either used as received or purified according to the procedures outlined in *Purification of Common Laboratory Chemicals.* Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp and stained with an ethanolic solution of potassium permanganate, ceric ammonium molybdate, or anisaldehyde. Column flash chromatography was performed using Teledyne ISCO Combiflash® Rf. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise noted. 4W LED lights (CL-FRS5050-12WP-12V) and 12 V DC power supplies (CL-PS94670-25W) were purchased from Creative Lighting Solutions (http://www.creativelightings.com) .

^{1}H and ^{13}C NMR spectra were recorded using an internal deuterium lock on Varian Unity Plus 400, Varian 500, or Varian 700 spectrometers. All signals are reported in ppm with the internal reference of the specified solvent. J couplings are reported in Hz. Data are presented as follows: integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent, dd = doublet of doublet, dt = doublet of triplet, etc) and coupling constant (J/Hz).

Infrared spectra were recorded on a Perkin Elmer BX FT-IR fitted with an ATR accessory. Absorptions are given in wavenumbers (cm^{-1}). High resolution mass spectra were obtained on a Waters® Micromass® AutoSpec Ultima*TM* high resolution mass spectrometer. UPLC analysis was conducted on a Waters® Acuity H-Class UPLC with a Acquity UPLC BEH C18 column 1.7 µm 2.1 x 50mm, using a photodiode array detector.

Table S1. Reaction Optimization and Catalyst Selection.



Entry	Catalyst	Alteration	SM:PDT[a]
1	$[Ir(ppy)_2(dtbbpy)]PF_6$ (**2**)	None	0:1 (88%)[b]
2	**2**	no TTMSS	1:trace
3	**2**	no DIPEA	1:1
4	**2**	sparged with N_2	1:2
5	**2**	freeze-pump-thaw	1:4
6	**2**	no light	1:trace
7	None	None	2:1
8	$Ir(ppy)_3$	None	1:2.5
9	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	None	1:1.1
10	$[Ru(bpy)_3]Cl_2$	None	4:1
11	$[Cu(dap)_2]Cl_2$	None	NR
12	rose bengal	None	19:1
13	methylene blue	None	NR
14	eosin Y	None	14:1
15	fluoroscein	None	>19:1

[a]Calculated by ^{1}H NMR. [b]Isolated yield.

Procedure for Kinetic Analysis:

A 20 mL vial equipped with a magnetic stir bar was charged with **2** and solid substrate. MeCN (5 mL) was added to the vial followed by **1**, DIPEA, and liquid substrate. It was sealed with a septum cap. An 18 G x 1.5" needle was pierced through the septum and left open to air. The solution was allowed to stir for 5 min. The reaction was then illuminated with a 4W blue LED strip and stirred open to air. 0.05 mL aliquots were sampled via syringe. 10 µL reaction solution was dissolved 990 µL 2:1 MeCN:H_2O containing 10 µL of 5 mg/mL benzophenone in 2:1 MeCN:H_2O. Samples were analyzed via reverse-phase UPLC.

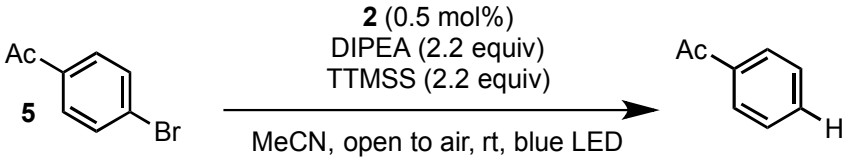
Rate orders

Rate orders in Table 3, unless otherwise noted, were determined using equation S1.

$$ln\left(\frac{(\text{slope})_a}{(\text{slope})_b}\right) = y\, ln\left(\frac{(\text{concentration})_a}{(\text{concentration})_b}\right) \qquad \text{(S1)}$$

where y = order.

Kinetic Studies of 5.



Scheme S1. Hydrodebromination of **5**.

Table S2. Raw data for impact of [**2**] on reductive debromination of **5**.

0.0005 M **2**			0.00025 M **2**		
Time (s)	[**5**] (M)	ln[**5**]	Time (s)	[**5**] (M)	ln[**5**]
0	0.025	-3.688879454	0	0.025	-3.688879454
120	0.023333	-3.757886611	180	0.026524	-3.629705295
240	0.023153	-3.765630917	240	0.023582	-3.74727157
360	0.020456	-3.889479041	360	0.025862	-3.654980569
480	0.018819	-3.972888281	480	0.023589	-3.746974777
600	0.015777	-4.149202096	600	0.022983	-3.773000467
1200	0.009847	-4.620588439	1200	0.013969	-4.27091469
1800	0.007053	-4.954302221	2400	0.00649	-5.037492748
2400	0.004837	-5.331460585	3600	0.003737	-5.589472128
3600	0.002939	-5.829685892	4800	0.002485	-5.997482619
4800	0.001047	-6.861826347	6000	0.00201	-6.209620557
6000	0.000361	-7.9266326			
7200	0.000072	-9.538844439			

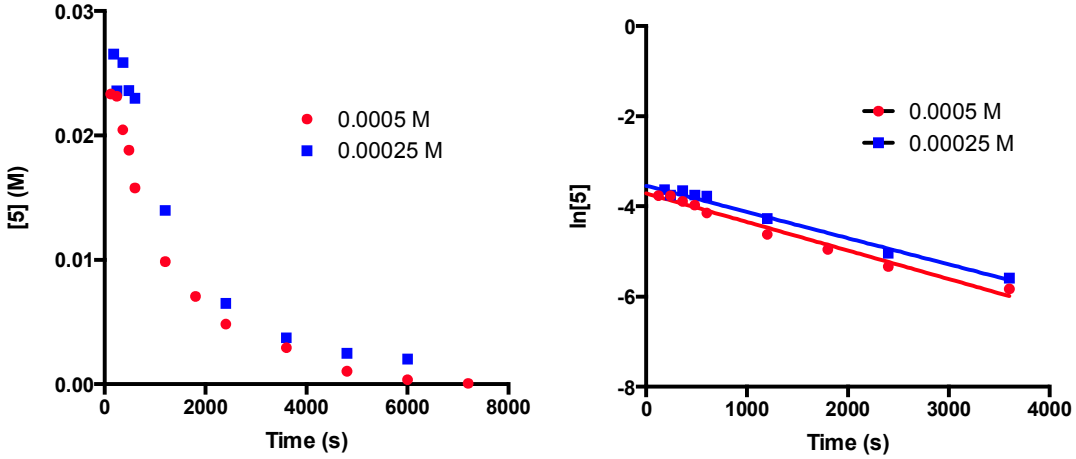


Figure S1. Impact of [**2**] on reductive debromination of **5**. [**5**] vs time (left). Ln[**5**] vs time (right).

Table S3. Trendline data for ln[**5**] vs time for effect of **2**.

	0.0005 M **2**	0.00025 M **2**
Slope	-0.0006321 ± 2.956e-005	-0.0005808 ± 2.861e-005
Y-intercept	-3.713 ± 0.04597	-3.542 ± 0.04367
R square	0.9828	0.9833

Table S4. Raw data for impact of [**DIPEA**] on reductive debromination of **5**.

0.03 M DIPEA			0.06 M DIPEA		
Time (s)	[**5**] (M)	ln[**5**]	Time (s)	[**5**] (M)	ln[**5**]
0	0.025	-3.688879454	0	0.025	-3.688879454
120	0.023333	-3.757886611	120	0.024178	-3.72231215
240	0.023153	-3.765630917	240	0.02247	-3.795574193
360	0.020456	-3.889479041	360	0.017686	-4.034981913
480	0.018819	-3.972888281	480	0.014952	-4.202910209
600	0.015777	-4.149202096	600	0.012417	-4.388688778
1200	0.009847	-4.620588439	1200	0.007899	-4.84101911
1800	0.007053	-4.954302221	2400	0.002878	-5.850659671
2400	0.004837	-5.331460585	3600	0.00092	-6.991136888
3600	0.002939	-5.829685892	4800	0.000344	-7.974868901
4800	0.001047	-6.861826347	6000	0.000214	-8.449534543
6000	0.000361	-7.9266326	7200	0.0002	-8.517193191
7200	0.000072	-9.538844439			

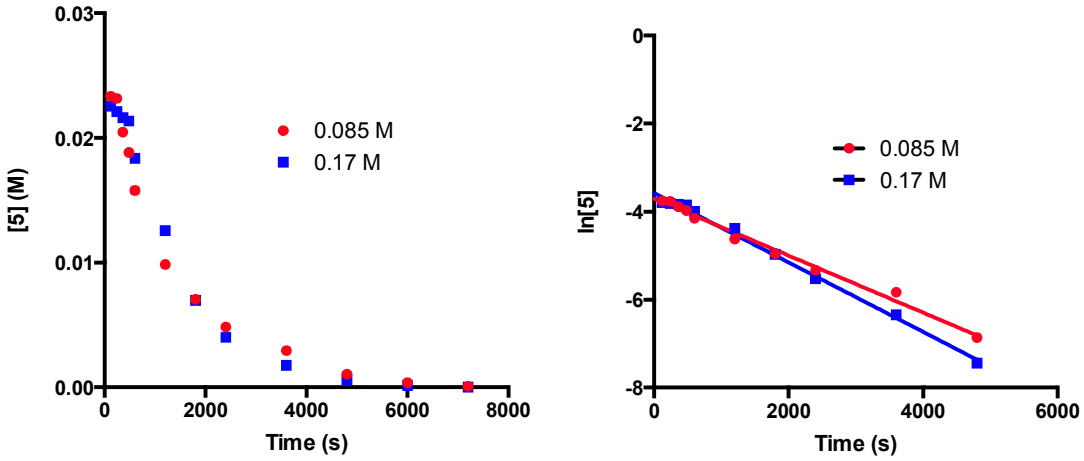


Figure S2. Impact of [DIPEA] on reductive debromination of **5**. [**5**] vs time (left). Ln[**5**] vs time (right).

Table S5. Trendline data for ln[**5**] vs time for effect of DIPEA.

	0.085 M DIPEA	0.17 M DIPEA
Slope	-0.0006475 ± 2.034e-005	-0.0007885 ± 1.890e-005
Y-intercept	-3.702 ± 0.04215	-3.575 ± 0.03916
R square	0.9912	0.9949

Table S6. Raw data for impact of [**1**] on reductive debromination of **5**.

0.03 M **1**			0.06 M **1**		
Time (s)	[**5**] (M)	ln[**5**]	Time (s)	[**5**] (M)	ln[**5**]
0	0.025	-3.688879454	0	0.025	-3.688879454
120	0.023333	-3.757886611	120	0.024178	-3.72231215

240	0.023153	-3.765630917	240	0.02247	-3.795574193
360	0.020456	-3.889479041	360	0.017686	-4.034981913
480	0.018819	-3.972888281	480	0.014952	-4.202910209
600	0.015777	-4.149202096	600	0.012417	-4.388688778
1200	0.009847	-4.620588439	1200	0.007899	-4.84101911
1800	0.007053	-4.954302221	2400	0.002878	-5.850659671
2400	0.004837	-5.331460585	3600	0.00092	-6.991136888
3600	0.002939	-5.829685892	4800	0.000344	-7.974868901
4800	0.001047	-6.861826347	6000	0.000214	-8.449534543
6000	0.000361	-7.9266326	7200	0.0002	-8.517193191
7200	0.000072	-9.538844439			

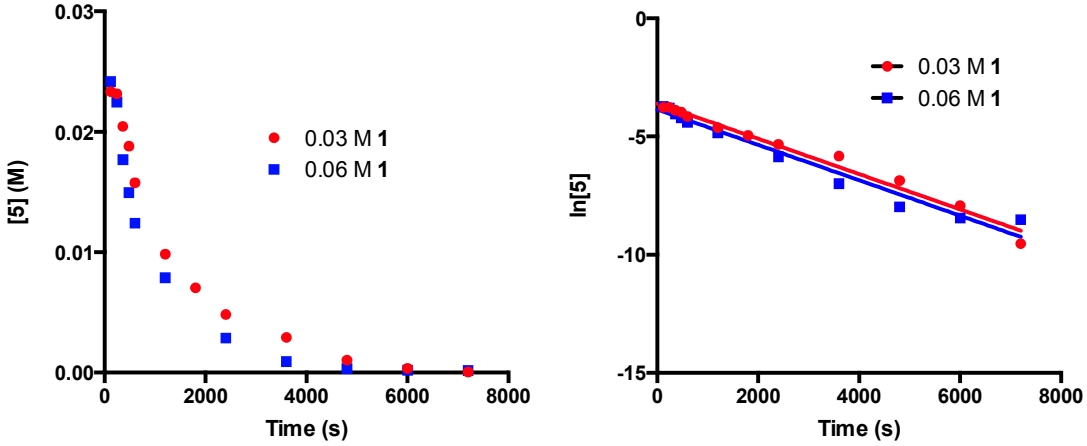
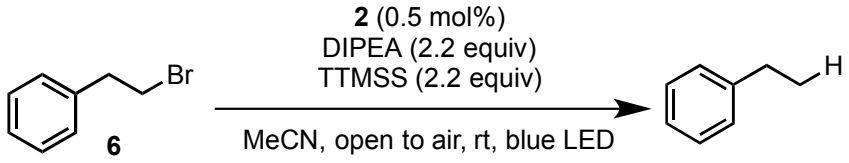


Figure S3. Impact of [**1**] on reductive debromination of **5**. [**5**] vs time (left). Ln[**5**] vs time (right).

Table S7. Trendline data for ln[**5**] vs time for effect of **1**.

	0.03 M **1**	0.06 M **1**
Slope	-0.0007477 ± 2.982e-005	-0.0007491 ± 4.124e-005
Y-intercept	-3.596 ± 0.09611	-3.853 ± 0.1367
R square	0.9828	0.9706

Kinetic Studies of 6.



Scheme S2. Hydrodebromination of 5.

Table S8. Raw data for impact of [**2**] on reductive debromination of **6**.

	0.0005 M **2**			0.00025 M **2**	
Time (s)	[**6**] (M)	ln[**6**]	Time (s)	[**6**] (M)	ln[**6**]
240	0.044294	-3.116906051	360	0.045613	-3.087562515
360	0.035893	-3.327212989	480	0.03566	-3.333725667

480	0.031238	-3.466119977	600	0.029708	-3.516338909
600	0.024018	-3.72895173	900	0.019638	-3.930288814
900	0.014559	-4.22954592	1200	0.016147	-4.126021005
1200	0.009851	-4.620182306	1500	0.010505	-4.555903945
			1800	0.008701	-4.744317317

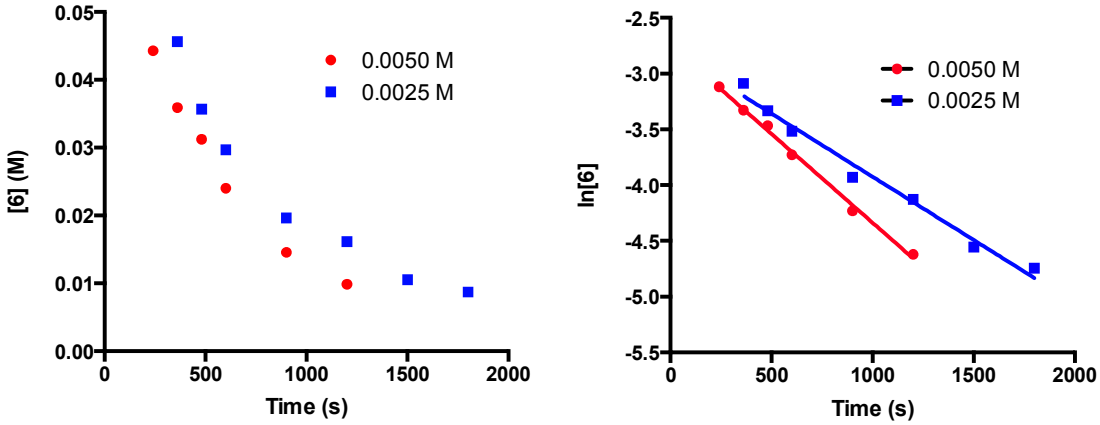


Figure S4. Impact of [**2**] on reductive debromination of **6**. [**6**] vs time (left). Ln[**6**] vs time (right).

Table S9. Trendline data for ln[**6**] vs time for effect of **2**.

	0.005 M **2**	0.0025 M **2**
Slope	-0.001594 ± 5.122e-005	-0.001133 ± 6.799e-005
Y-intercept	-2.744 ± 0.03638	-2.792 ± 0.07474
R square	0.9828	0.9833

Table S10. Raw data for impact of [DIPEA] on reductive debromination of **6**.

0.172 M DIPEA		0.086 M DIPEA	
Time (s)	[**6**] (M)	Time (s)	[**6**] (M)
360	0.035893	360	0.035596
480	0.031238	480	0.028569
600	0.024018	600	0.022913
900	0.014559	900	0.013972
1200	0.009851	1200	0.008215

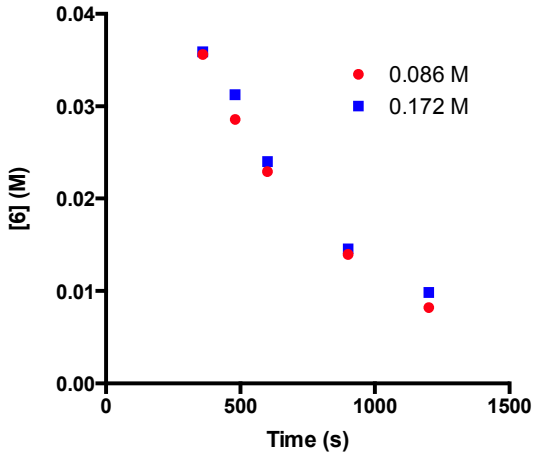


Figure S5. Impact of [DIPEA] on reductive debromination of **6**. [**6**] vs time.

Table S11. Raw data for impact of [**1**] on reductive debromination of **6**.

0.095 M **1**			0.127 M **1**		
Time (s)	[**6**] (M)	ln[**6**]	Time (s)	[**6**] (M)	ln[**6**]
600	0.041794	-3.17500249	360	0.042514	-3.157921846
900	0.033143	-3.406923746	480	0.041118	-3.191309297
1200	0.028557	-3.555853189	600	0.03765	-3.279422325
1500	0.023198	-3.763689211	900	0.029762	-3.514522867
1800	0.02304	-3.770523443	1200	0.02429	-3.717690536
2400	0.019356	-3.94475283	1500	0.018954	-3.965740288
3000	0.014549	-4.230233016	1800	0.01558	-4.161767239
			2400	0.011132	-4.497931435

0.16 M **1**			0.192 M **1**		
Time (s)	[**6**] (M)	ln[**6**]	Time (s)	[**6**] (M)	ln[**6**]
360	0.040324	-3.210808454	360	0.043188	-3.1421926
480	0.037584	-3.281176851	480	0.032778	-3.41799772
600	0.03319	-3.405506653	600	0.027574	-3.590881979
900	0.022608	-3.789451453	900	0.01695	-4.077487445
1200	0.015823	-4.146290701	1200	0.008358	-4.784536115
1500	0.010533	-4.553242093			

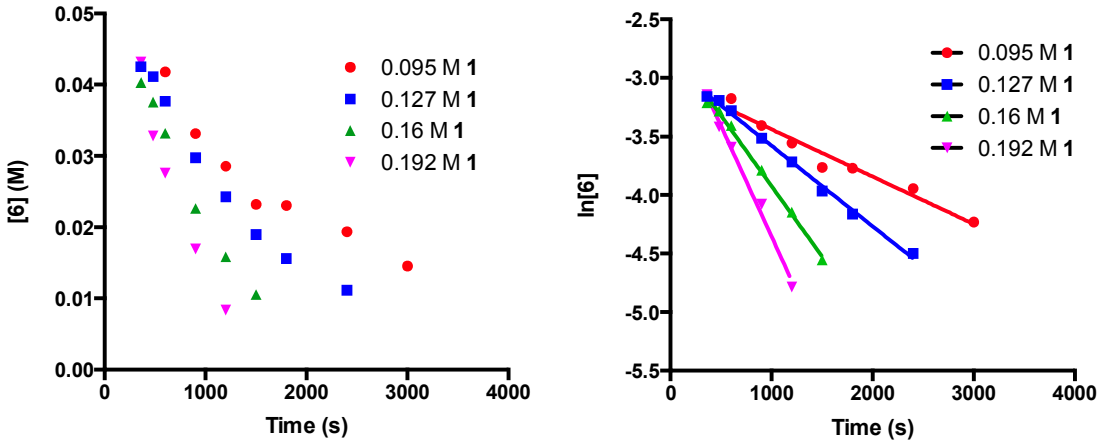


Figure S6. Impact of [**1**] on reductive debromination of **6**. [**6**] vs time (left). Ln[**6**] vs time (right).

Table S12. Trendline data for ln[**6**] vs time for effect of **1**.

	0.095 M **1**	0.127 M **1**
Slope	-0.0004041 ± 3.790e-005	-0.0006874 ± 1.776e-005
Y-intercept	-3.034 ± 0.06848	-2.892 ± 0.02368
R square	0.9579	0.996

	0.16 M **1**	0.192 M **1**
Slope	-0.001202 ± 3.968e-005	-0.001890 ± 9.541e-005
Y-intercept	-2.722 ± 0.03701	-2.465 ± 0.07353
R square	0.9957	0.9924

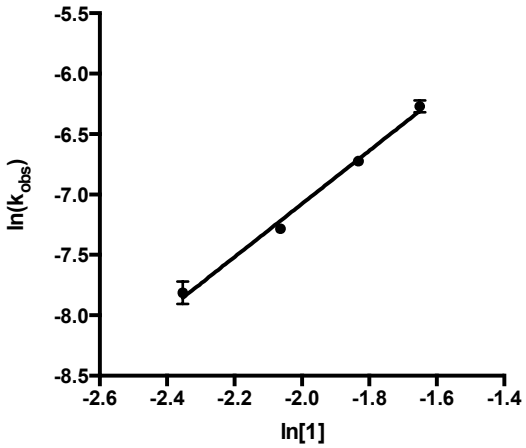
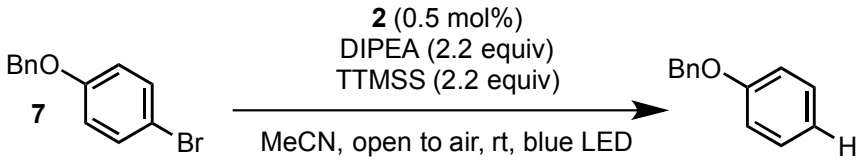


Figure S7. ln(k_{obs}) vs ln[**1**] for the reductive debromination of **6**.

Table S13. Trendline data for Ln(k_{obs}) vs ln[**1**] for the reductive debromination of **6**.

Slope	2.199 ± 0.1172
Y-intercept	-2.680 ± 0.2335
R square	0.9944

Kinetic Studies of 7.



Scheme S3. Hydrodebromination of **7**.

Table S14. Raw data for impact of [**2**] on reductive debromination of **7**.

0.005 M **2**		0.0025 M **2**	
Time (s)	[**7**] (M)	Time (s)	[**7**] (M)
0	0.05	660	0.049724
300	0.046465	900	0.04618
600	0.043239	1260	0.042241
900	0.039876	1500	0.038972
1200	0.038426	1800	0.035815
1500	0.038024	2100	0.031947
1800	0.033693	2700	0.028732
2100	0.031452	3000	0.025373
2400	0.028607	3300	0.019487
2700	0.025503	3600	0.016922
3000	0.021721		
3300	0.02026		
3600	0.017875		

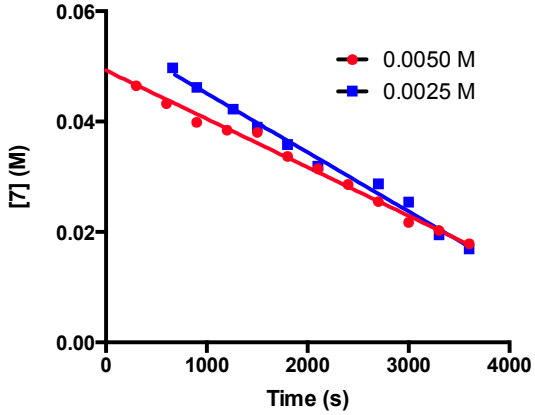


Figure S8. Impact of [**2**] on reductive debromination of **7**. [**7**] vs time (left). Ln[**7**] vs time (right).

Table S15. Trendline data for ln[**7**] vs time for effect of **2**.

	0.0050 M **2**	0.0025 M **2**
Slope	-8.776e-006 ± 2.270e-007	-1.068e-005 ± 3.845e-007
Y-intercept	0.04927 ± 0.0004815	0.05578 ± 0.0008842
R square	0.9927	0.9897

Table S16. Raw data for impact of [DIPEA] on reductive debromination of **7**.

0.086 M DIPEA		0.172 M DIPEA	
Time (s)	[**7**] (M)	Time (s)	[**7**] (M)
0	0.05	0	0.05
300	0.042753	300	0.047422
660	0.040812	600	0.0448415
900	0.037379	900	0.039877
1260	0.032032	1200	0.039089
1500	0.028122	1500	0.0377775
1800	0.024781	1800	0.0344985
2100	0.020897	2100	0.0319015
2400	0.01665	2400	0.029395
2700	0.0146	2700	0.028588
3000	0.011781	3000	0.0256225
3300	0.009657	3300	0.024175
3600	0.007922	3600	0.0224615

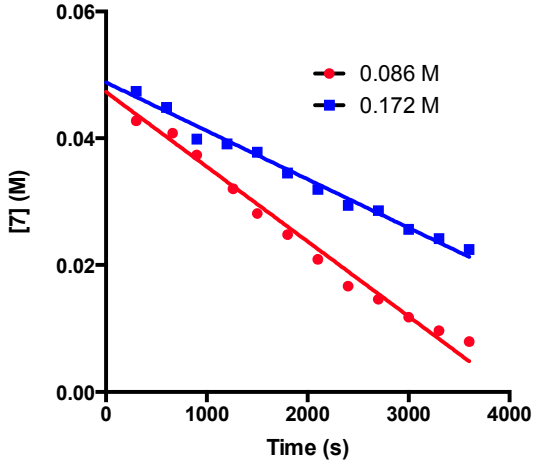


Figure S9. Impact of [DIPEA] on reductive debromination of **7**. [**7**] vs time.

Table S17. Trendline data for ln[**7**] vs time for effect of DIPEA.

	0.0050 M **2**	0.0025 M **2**
Slope	-8.776e-006 ± 2.270e-007	-1.068e-005 ± 3.845e-007
Y-intercept	0.04927 ± 0.0004815	0.05578 ± 0.0008842
R square	0.9927	0.9897

Table S18. Raw data for impact of [**1**] on reductive debromination of **7**

0.071 M **1**

Time (s)	[**7**] (M)
0	0.05
5400	0.042475
9000	0.037413
14400	0.03282
21600	0.026227

0.128 M **1**

Time (s)	[**7**] (M)
0	0.05
300	0.046633
600	0.045246
900	0.04413
1500	0.042514
2400	0.040853
3300	0.037318
3600	0.035885
2160	0.040769
1800	0.041217

0.160 M **1**

Time (s)	[**7**] (M)
0	0.05
300	0.047787
600	0.04733
900	0.044696
1200	0.041881
1500	0.040747
1800	0.038855
2100	0.037347
2400	0.036023
2700	0.034801
3000	0.033504
3300	0.033523
3600	0.032125

0.190 M **1**

Time (s)	[**7**] (M)
0	0.05
900	0.043628
1800	0.036512
2700	0.030691
3600	0.024022

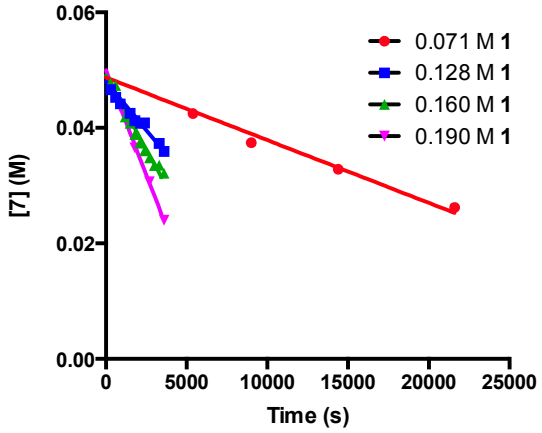


Figure S10. Impact of [**1**] on reductive debromination of **7**. [**7**] vs time.

Table S19. Trendline data for [**7**] vs time for effect of **1**.

	0.095 M **1**	0.127 M **1**
Slope	-1.084e-006 ± 7.871e-008	-3.369e-006 ± 2.560e-007
Y-intercept	0.04872 ± 0.0009856	0.04803 ± 0.0005185
R square	0.9844	0.9558

	0.16 M **1**	0.192 M **1**
Slope	-5.104e-006 ± 2.474e-007	-7.210e-006 ± 1.085e-007
Y-intercept	0.04908 ± 0.0005248	0.04995 ± 0.0002392
R square	0.9748	0.9993

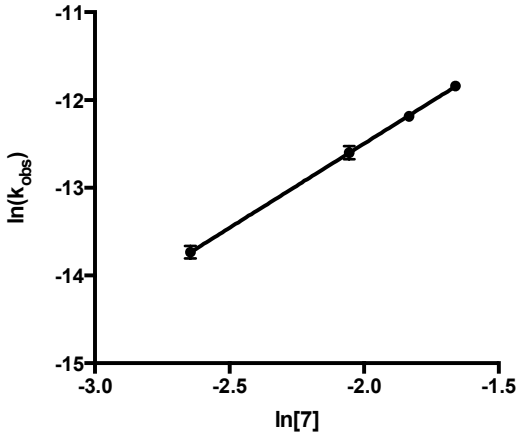


Figure S11. Ln(k_{obs}) vs ln[**1**] for the reductive debromination of **7**.

Table S20. Trendline data for Ln(k_{obs}) vs ln[**1**]

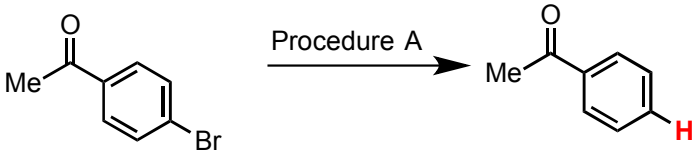
Slope	1.919 ± 0.01122
Y-intercept	-8.659 ± 0.02337
R square	0.9999

General Procedure A for aryl and alkyl bromides:
A 20 mL vial equipped with a magnetic stir bar was charged with **2** (2.3 mg, 0.0025 mmol, 0.50 mol%). Solid bromide substrate (0.500 mmol) was added at this time. MeCN (5 mL) was added to the vial followed by **1** (340 μL, 274 mg, 1.10 mmol, 2.2 equiv), DIPEA (192 μL, 142 mg, 1.10 mmol, 2.2 equiv). Liquid bromide substrate was added at this time. The vial was sealed with a septum cap. An 18 G x 1.5" needle was pierced through the septum and left open to air. The solution was allowed to stir for 5 min at 100 rpm. The reaction was then illuminated with a 4W blue LED strip and stirred open to air for 10 h at 100 rpm. Upon completion, turn off LEDs and add 3 g of 37 wt% KF on Alumina. Stir for 5 min. Filter off solid. Concentrate via rotary evaporation. The residue was purified via chromatography, using hexanes/ethyl acetate gradient.

General Procedure B for dibromocyclopropanes:
A 20 mL vial equipped with a magnetic stir bar was charged with **2** (2.3 mg, 0.0025 mmol, 0.50 mol%). Solid bromide substrate (0.500 mmol) was added at this time. MeCN

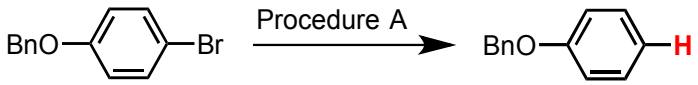
(5 mL) was added to the vial followed by **1** (680 µL, 274 mg, 1.10 mmol, 4.4 equiv), DIPEA (192 µL, 142 mg, 1.10 mmol, 2.2 equiv). Liquid bromide substrate was added at this time. The vial was sealed with a septum cap. An 18 G x 1.5" needle was pierced through the septum and left open to air. The solution was allowed to stir for 5 min at 100 rpm. The reaction was then illuminated with a 4W blue LED strip and stirred open to air for 10 h at 100 rpm. Upon completion, turn off LEDs and add 3 g of 37 wt% KF on Alumina. Stir for 5 min. Filter off solid. Concentrate via rotary evaporation. The residue was purified via chromatography, using hexanes/ethyl acetate gradient.

Compound Characterization:



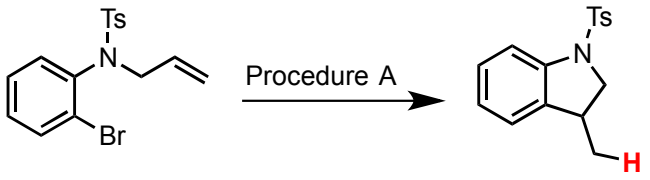
Acetophenone (Table 1, Entry 1): According to General Procedure A, 1-(4-bromophenyl)ethan-1-one (99 mg, 0.5 mmol) afforded acetophenone in 99% yield by UPLC (PDA). Spectroscopic properties consistent with commercial sample.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98 (d, J=7.3 Hz, 2H), 7.60-7.54 (m, 1H), 7.50-7.47 (m, 2H), 2.63 (s, 3H).



(Benzyloxy)benzene (Table 1, Entry 2): According to General Procedure A, 1-(benzyloxy)-4-bromobenzene[1] (131 mg, 0.5 mmol) afforded (benzyloxy)benzene (86 mg, 94%) as a yellow oil. Spectroscopic properties consistent with those reported in the literature.[2]

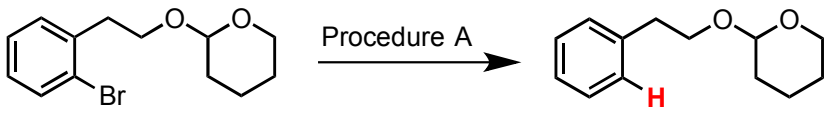
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54-7.33 (m, 7H) 7.08-7.03 (m, 3H) 5.16 (s, 2H).



3-methyl-1-tosylindoline (Table 1, Entry 3): According to General Procedure A, *N*-allyl-*N*-(2-bromophenyl)-4-methylbenzenesulfonamide[3] (183 mg, 0.5 mmol) afforded 3-methyl-1-tosylindoline (118 mg, 82%). Spectroscopic properties consistent with those reported in the literature.[4]

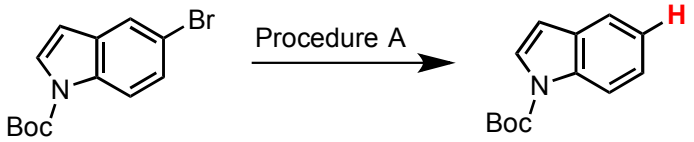
^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.68 (d, J=8.3 Hz, 2H), 7.64 (d, J=8.0 Hz, 1H) 7.22 (d, J=8.3 Hz, 2H) 7.19 (d, J=7.8 Hz, 1H), 7.05 (d, J=7.6 Hz, 1H), 7.00 (t, J=6.6 Hz, 1H), 4.08

(dd, J=10.4, 9.2 Hz, 1H), 3.42 (dd, J=10.5, 7.1 Hz, 1H), 3.19 (m, 1H) 2.36 (s, 3H), 1.11 (d, J=6.8 Hz, 3H).



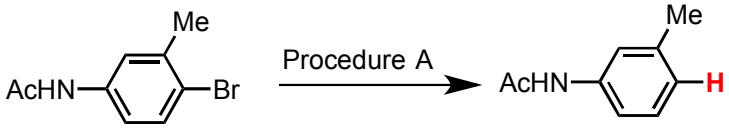
2-Phenethoxytetrahydro-2*H*-pyran (Table 1, Entry 4): According to General Procedure A, 2-(2-bromophenethoxy)tetrahydro-2*H*-pyran[5] (142 mg, 0.5 mmol) afforded 2-phenethoxytetrahydro-2*H*-pyran in (87 mg, 84%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[6]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32-7.20 (m, 5H), 4.61 (t, J=3.5 Hz, 1H), 3.97 (dt, J=9.6, 7.4 Hz, 1H) 3.77 (ddd, J=11.2, 8.3, 3.2 Hz, 1H) 3.64 (dt, J=9.6, 7.3 Hz, 1H), 3.49-3.45 (m, 1H), 2.93 (t, J=7.3 Hz, 2H), 1.87-1.79 (m, 1H), 1.74-1.69 (m, 1H) 1.63-1.48 (m, 4H).



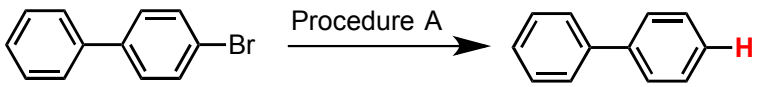
***tert*-Butyl 1*H*-indole-1-carboxylate (Table 1, Entry 5):** According to General Procedure A, *tert*-butyl 5-bromo-1*H*-indole-1-carboxylate (148 mg, 0.5 mmol) afforded *tert*-butyl 1*H*-indole-1-carboxylate in (103 mg, 83%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[7]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15 (d, J=7.3 Hz, 1H), 7.60 (d, J=3.4 Hz, 1H), 7.56 (d, J=7.8 Hz, 1H) 7.33-7.30 (m, 1H), 7.24-7.21 (m, 1H), 6.57 (d, J=3.4 Hz, 1H), 1.68 (s, 9H)



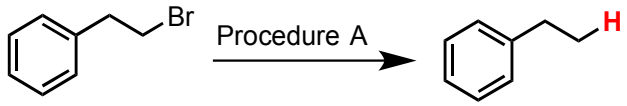
***N*-(*m*-Tolyl)acetamide (Table 1, Entry 6):** According to General Procedure A, *N*-(4-bromo-3-methylphenyl)acetamide (114 mg, 0.5 mmol) afforded *N*-(*m*-tolyl)acetamide in (62 mg, 83%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[8]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 (bs, 1H), 7.27 (m, 1H), 7.22-7.19 (m, 1H), 7.14 (bs, 1H), 6.93 (d, J=7.3 Hz, 1H), 2.35 (s, 3H), 2.18 (s, 3H).



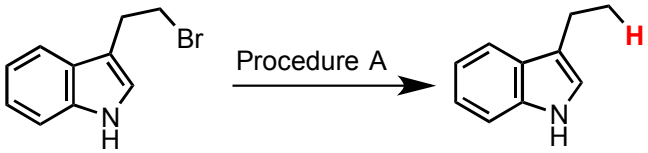
Biphenyl (Table 1, Entry 7): According to General Procedure A, 4-bromo-1,1'-biphenyl (116 mg, 0.5 mmol) afforded biphenyl in (70 mg, 91%) as a white solid. Spectroscopic properties consistent with commercial sample.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, J=7.1 Hz, 4H), 7.46 (t, J=7.7 Hz, 4H), 7.37 (t, J=7.6 Hz, 2H).



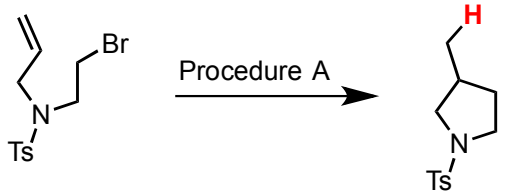
Ethylbenzene (Table 2, Entry 1): According to General Procedure A, (2-bromoethyl)benzene (92 mg, 0.5 mmol) afforded ethylbenzene in in 99% yield by UPLC (PDA). Spectroscopic properties consistent with commercial sample.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32-7.29, (m, 2H), 7.23-7.18 (m, 3H); 2.67 (q, J=7.6 Hz, 2H), 1.26 (t, J=7.6 Hz, 3H).



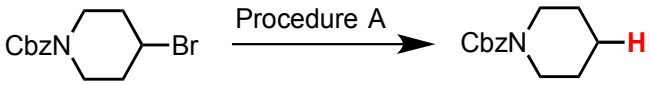
3-Ethyl-1*H*-indole (Table 2, Entry 2): According to General Procedure A, 3-(2-bromoethyl)-1*H*-indole (112 mg, 0.5 mmol) afforded 3-ethyl-1*H*-indole in (62 mg, 85%) as a white solid. Spectroscopic properties consistent with those reported in the literature.[9]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90 (bs, 1H), 7.65 (d, J=8.1 Hz, 1H), 7.37 (d, J=8.1 Hz, 1H), 7.22 (t, J=7.4 Hz, 1H), 7.14 (t, J=7.4 Hz, 1H), 7.00 (s, 1H), 2.82 (q, J=7.6 Hz, 2H), 1.36 (t, J=7.6 Hz, 3H).



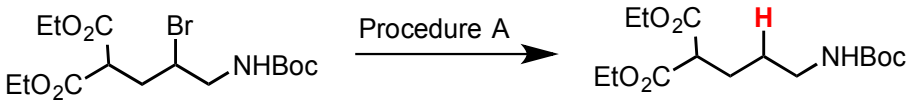
3-Methyl-1-tosylpyrrolidine (Table 2, Entry 3): According to General Procedure A, *N*-allyl-*N*-(2-bromoethyl)-4-methylbenzenesulfonamide[10] (158 mg, 0.5 mmol) afforded 3-methyl-1-tosylpyrrolidine in (102 mg, 85%) as a white solid. Spectroscopic properties consistent with those reported in the literature.[11]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.71, d, 8.3, 2h; 7.32, d, 8.1, 2H; 3.42, dd, 9.7, 7.2, 1H; 3.34, ddd, 9.8, 8.2, 4, 1H; 3.22, dt, 9.5, 7.9, 1H; 2.75, dd, 9.8, 7.8, 1h; 2.43, s, 3h; 2.12, dq, 14.8, 7.3, 1H, 1.87-1.93, m, 1H; 1.35, dq, 12.3, 8.4, 1H; 0.92, d, 6.6, 3H.



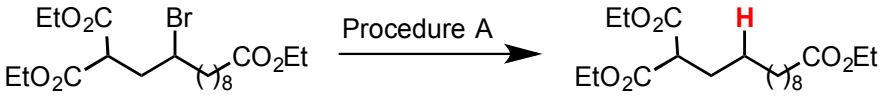
Benzyl piperidine-1-carboxylate (Table 2, Entry 4): According to General Procedure A, benzyl 4-bromopiperidine-1-carboxylate (149 mg, 0.5 mmol) afforded benzyl piperidine-1-carboxylate in (100 mg, 91%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[12]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 (d, J=4.4 Hz, 4H), 7.34-7.29 (m, 1H), 5.13 (s, 2H), 3.45 (m, 4H), 1.62-1.56 (m, 2H), 1.56-1.50 (m, 4H).



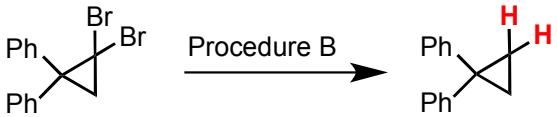
Diethyl 2-(3-((*tert*-butoxycarbonyl)amino)propyl)malonate (Table 2, Entry 5): According to General Procedure A, diethyl 2-(2-bromo-3-((*tert*-butoxycarbonyl)amino)propyl)malonate[13] (198 mg, 0.5 mmol) afforded diethyl 2-(3-((*tert*-butoxycarbonyl)amino)propyl)malonate in (141 mg, 89%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[14]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.19 (overlapping q, J=7.1 Hz, 4H), 3.33 (t, J=7.5 Hz, 1H) 3.14 (m, 2H), 1.91 (m, 2H) 1.52 (m, 2H), 1.43 (s, 9H), 1.23 (t, J=7.2 Hz, 6H).



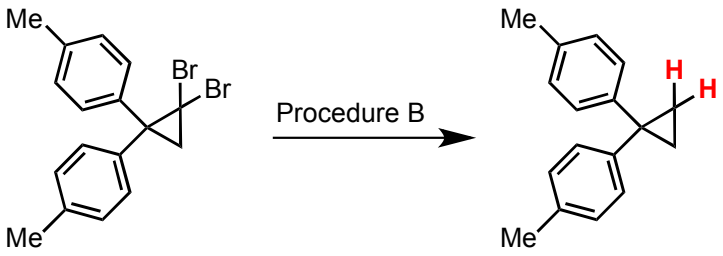
Triethyl undecane-1,1,11-tricarboxylate (Table 2, Entry 6): According to General Procedure A, triethyl 3-bromoundecane-1,1,11-tricarboxylate[15] (225 mg, 0.5 mmol) afforded triethyl undecane-1,1,11-tricarboxylate in (171 mg, 92%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[16]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.20 (overlapping q, J=7.1 Hz, 4H), 4.13 (q, J=7.1 Hz, 2H), 3.32 (t, J=7.6 Hz, 1H), 2.29 (t, J=7.6 Hz, 2H), 1.89 (q, J=7.3 Hz, 2H), 1.62 (m, 2H) 1.33-1.25 (bm, 21H, 3 -CH_3, 6 -CH_2-).



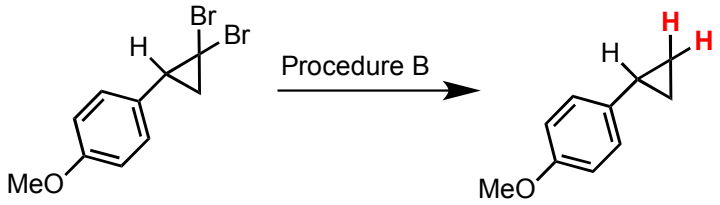
Cyclopropane-1,1-diyldibenzene (Table 2, Entry 7): According to General Procedure B, (2,2-dibromocyclopropane-1,1-diyl)dibenzene[17] (175 mg, 0.5 mmol) afforded cyclopropane-1,1-diyldibenzene in (86 mg, 89%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[18]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29-7.23 (m, 8H), 7.20-7.17 (m, 2H), 1.31 (s, 4H).



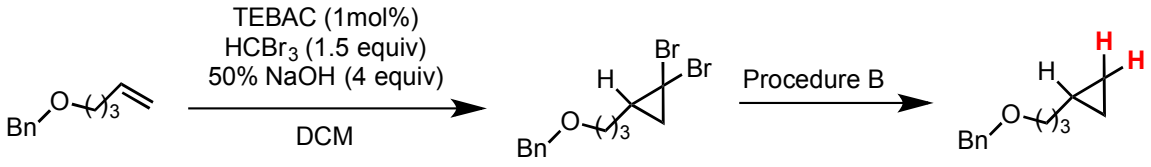
4,4'-(Cyclopropane-1,1-diyl)bis(methylbenzene) (Table 2, Entry 8): According to General Procedure B, 4,4'-(2,2-dibromocyclopropane-1,1-diyl)bis(methylbenzene)[19] (189 mg, 0.5 mmol) afforded 4,4'-(cyclopropane-1,1-diyl)bis(methylbenzene) in (94 mg, 85%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[20]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.25 (d, J=8.1 Hz, 4H), 7.20 (d, J=8.1 Hz, 4H), 2.43 (s, 6H), 1.38 (s, 4H).



1-Cyclopropyl-4-methoxybenzene (Table 2, Entry 9): According to General Procedure B, 1-(2,2-dibromocyclopropyl)-4-methoxybenzene[21] (198 mg, 0.5 mmol) afforded 1-cyclopropyl-4-methoxybenzene in (141 mg, 89%) as a colorless oil. Spectroscopic properties consistent with those reported in the literature.[22]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.03 (d, J=8.4 Hz, 2H), 6.82 (d, J=8.6 Hz, 2H), 3.78 (s, 3H), 1.86 (m, 1H), 0.91 (m, 2H) 0.62 (m, 2H).



((3-Cyclopropylpropoxy)methyl)benzene (Table 2, Entry 10): ((Pent-4-en-1-yloxy)methyl)benzene[23] (1.76 g, 10 mmol), bromoform (1.3 mL, 15 mmol, 1.5 equiv.) and triethylbenzylammonium chloride (25 mg, 0.1 mmol, 0.01 equiv.) were dissolved in DCM and stirred vigorously. A 50% solution of sodium hydroxide (1.6 g, 40 mmol, 4 equiv.) in water (1.6 mL) was then added dropwise at room temperature. The reaction was stirred for 2 h at room temperature. The reaction was quenched by addition of water (20 mL) and product was extracted with dichloromethane (3 x 50 mL). The combined organic fractions dried over Na_2SO_4 and concentrated via rotary evaporation. The residue

was purified via chromatography, using hexanes/ethyl acetate gradient to afford ((3-(2,2-dibromocyclopropyl)propoxy)methyl)benzene (1.83 g, 52%) as a colorless oil.

IR (neat): 2942, 2854, 1703, 1453, 1363, 1204, 1102, 1028, 734, 696, 677 cm^{-1};

^1H NMR ($CDCl_3$, 500 MHz): δ 7.37-7.35 (m, 4H), 7.28-7.33 (m, 1H), 4.51-4.56 (m, 2H), 3.6053-3.53 (m, 2H), 1.86-1.92 (m, 1H), 1.83-1.78 (m, 1H), 1.75 (dd, J=9.9, 7.2 Hz, 1H), 1.72-1.67 (m, 1H; 1.56-1.63, m, 2H; 1.23, t, 7.3, 1H.

^{13}C NMR ($CDCl_3$, 175 MHz): δ 138.5, 128.4, 127.7, 127.6, 72.9, 69.6, 31.1, 29.5, 28.4.

HRMS (ESI) *m/z* calculated for $C_{13}H_{17}Br_2O^+$ ([M+H]+) 346.9646, found 346.9649.

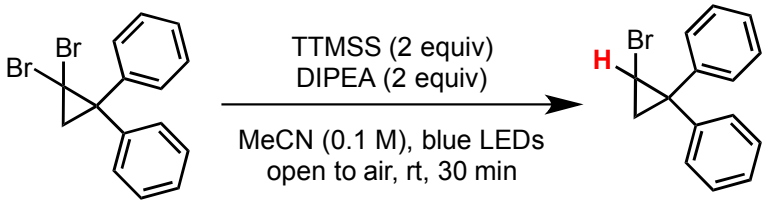
According to General Procedure B, ((3-(2,2-dibromocyclopropyl)propoxy)methyl)benzene (173 mg, 0.5 mmol) afforded ((3-cyclopropylpropoxy)methyl)benzene in (84 mg, 88%) as a colorless oil.

IR (neat): 3074, 3031, 2998, 2933, 2853, 1721, 1496, 1453, 1363, 1274, 1100, 1013, 8542, 821, 732, 696 cm^{-1};

^1H NMR ($CDCl_3$, 500 MHz): δ 7.37-7.34 (m, 4H), 7.32-7.27 (m, 1H), 4.52 (s, 2H), 3.52 (t, J=6.6 Hz, 2H), 1.74 (m, 2H), 1.30 (q, J=7.2 Hz, 2H), 0.67 (m, 1H), 0.41 (m, 2H), 0.03 (m, 2H).

^{13}C NMR ($CDCl_3$, 175 MHz): 138.3, 127.9, 127.0, 72.4, 69.9, 30.8, 29.4, 10.2, 4.0.

HRMS (ESI) *m/z* calculated for $C_{13}H_{19}O^+$ ([M+H]+) 191.1436, found 191.1435.



1-cyclopropyl-4-methoxybenzene (4, Scheme 3): A 20 mL vial equipped with a magnetic stir bar was charged with (2,2-dibromocyclopropane-1,1-diyl)dibenzene (**3**)[24] (189 mg, 0.5 mmol). MeCN (5 mL) was added to the vial followed by **1** (340 µL, 274 mg, 1.10 mmol, 2.2 equiv), DIPEA (192 µL, 142 mg, 1.10 mmol, 2.2 equiv). The vial was sealed with a septum cap. An 18 G x 1.5" needle was pierced through the septum and left open to air. The solution was allowed to stir for 5 min. The reaction was then illuminated with a 4W blue LED strip and stirred open to air for 30 min. Upon completion, the LEDs were turned off and 3 g of 37 wt% KF on Alumina was added. The slurry was stirred for 5 min. The solid was filtered off and the solution was concentrated via rotary evaporation. The residue was purified via chromatography, using hexanes/ethyl acetate gradient, affording 1-cyclopropyl-4-methoxybenzene (**4**) in (113 mg, 83%) as a white solid. Spectroscopic properties consistent with those reported in the literature.[25]

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (d, J=7.1 Hz, 2H), 7.35 (t, J=7.8 Hz, 2H), 7.22-7.30 (m, 5H), 7.20-7.16 (m, 1H), 3.69 (dd, J=7.8, 4.9 Hz, 1H), 1.89 (dd, J=7.8, 6.6 Hz, 1H), 1.83 (dd, J=6.6, 4.8 Hz, 1H).

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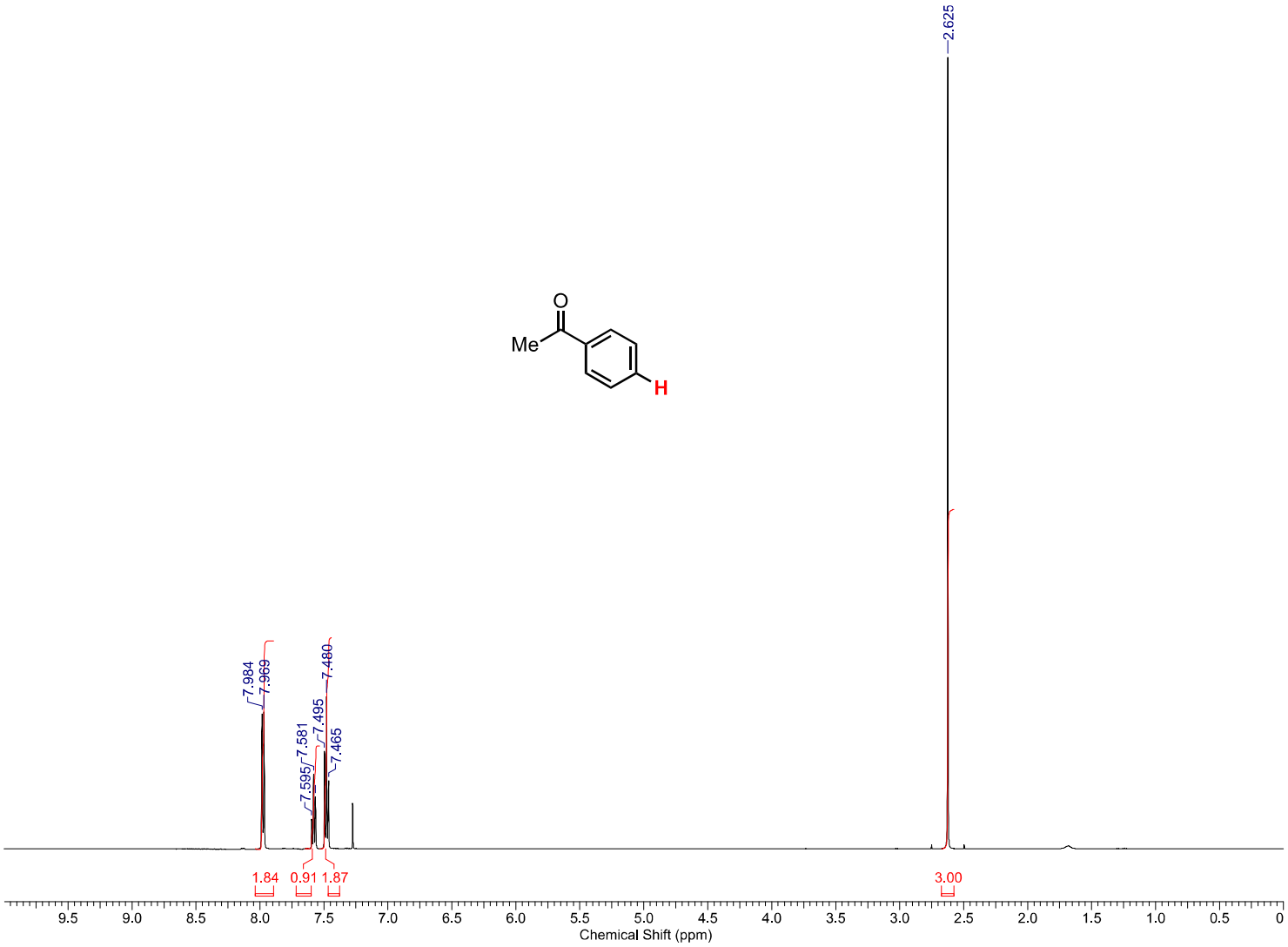
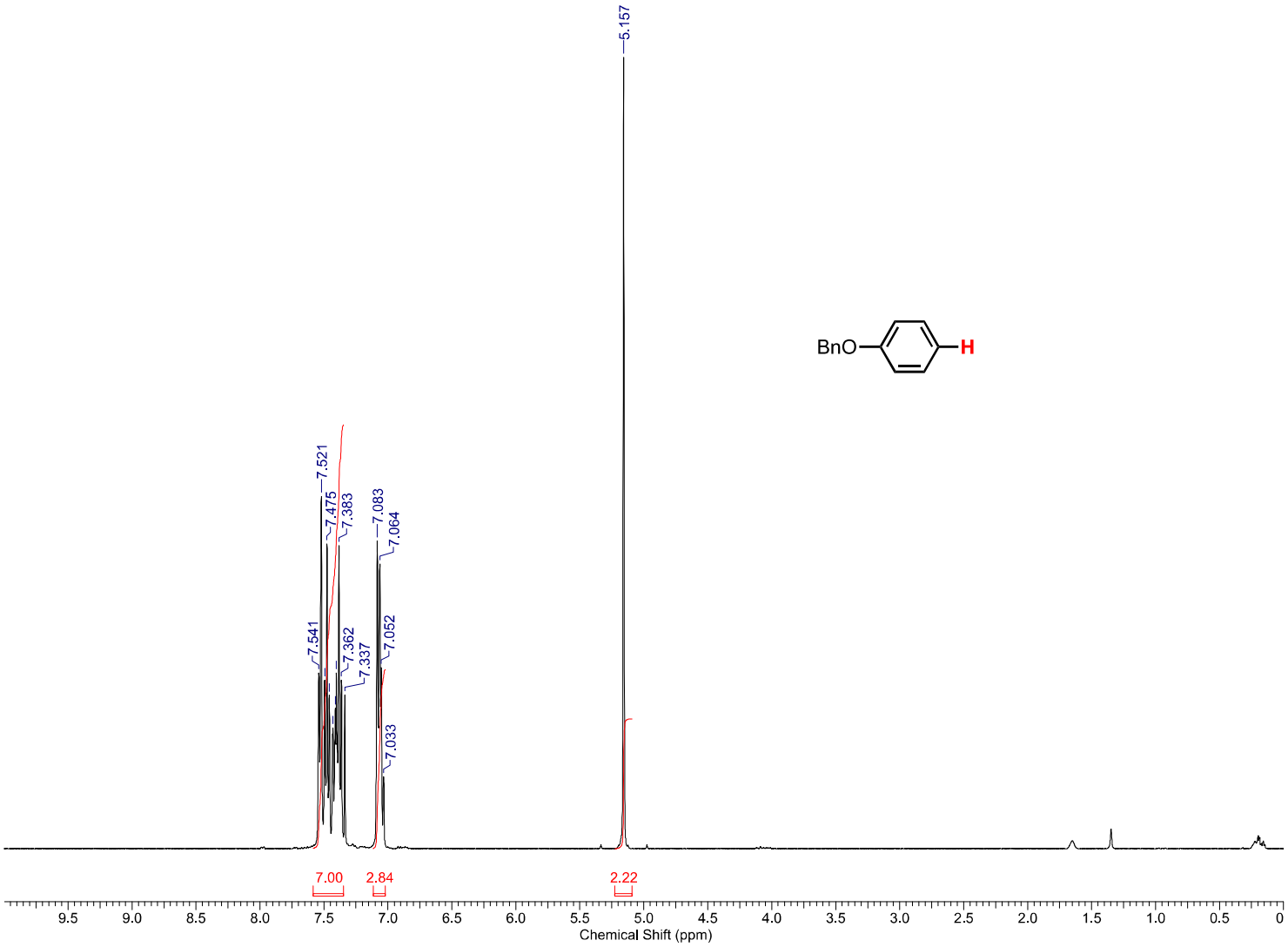
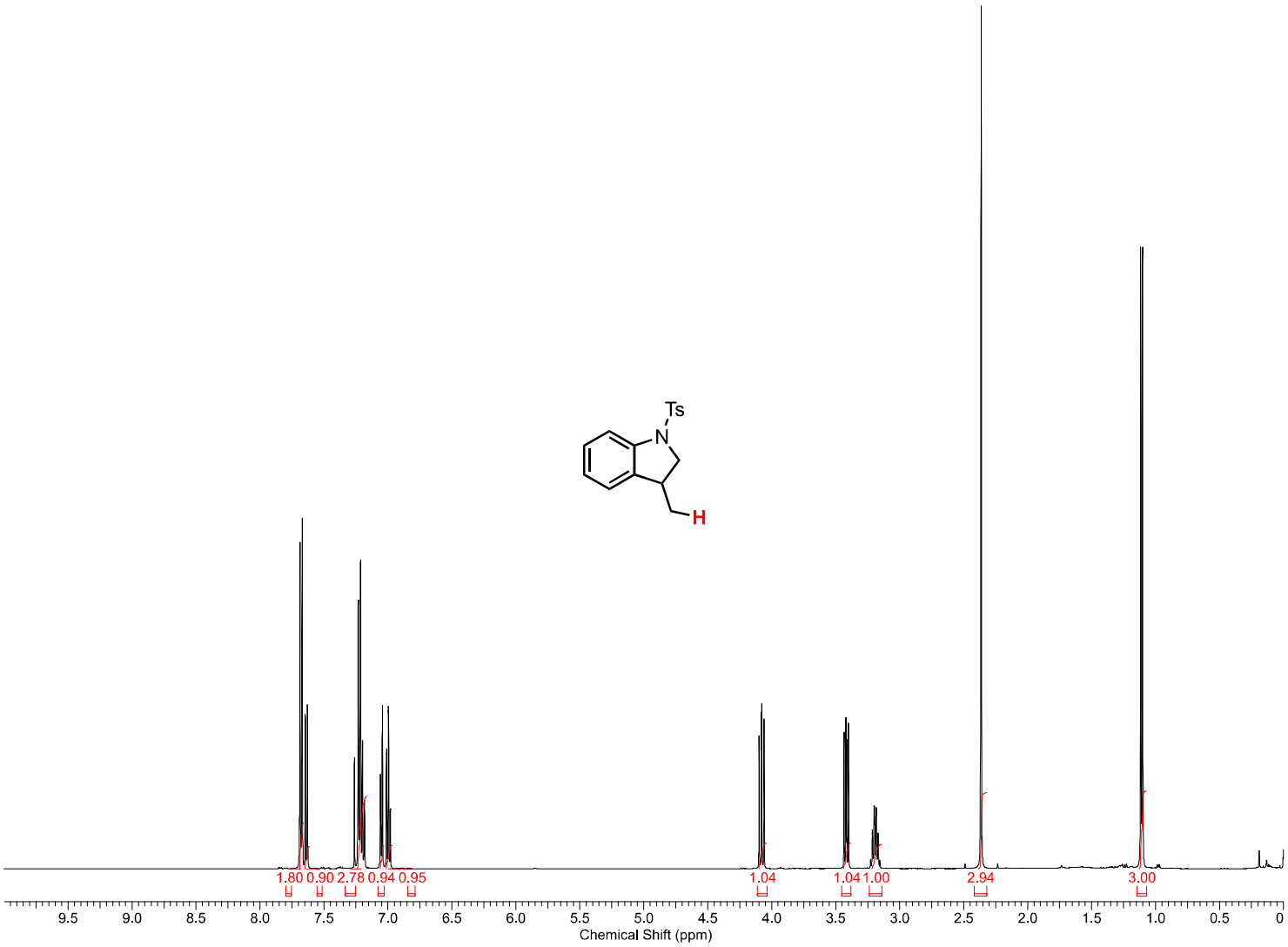
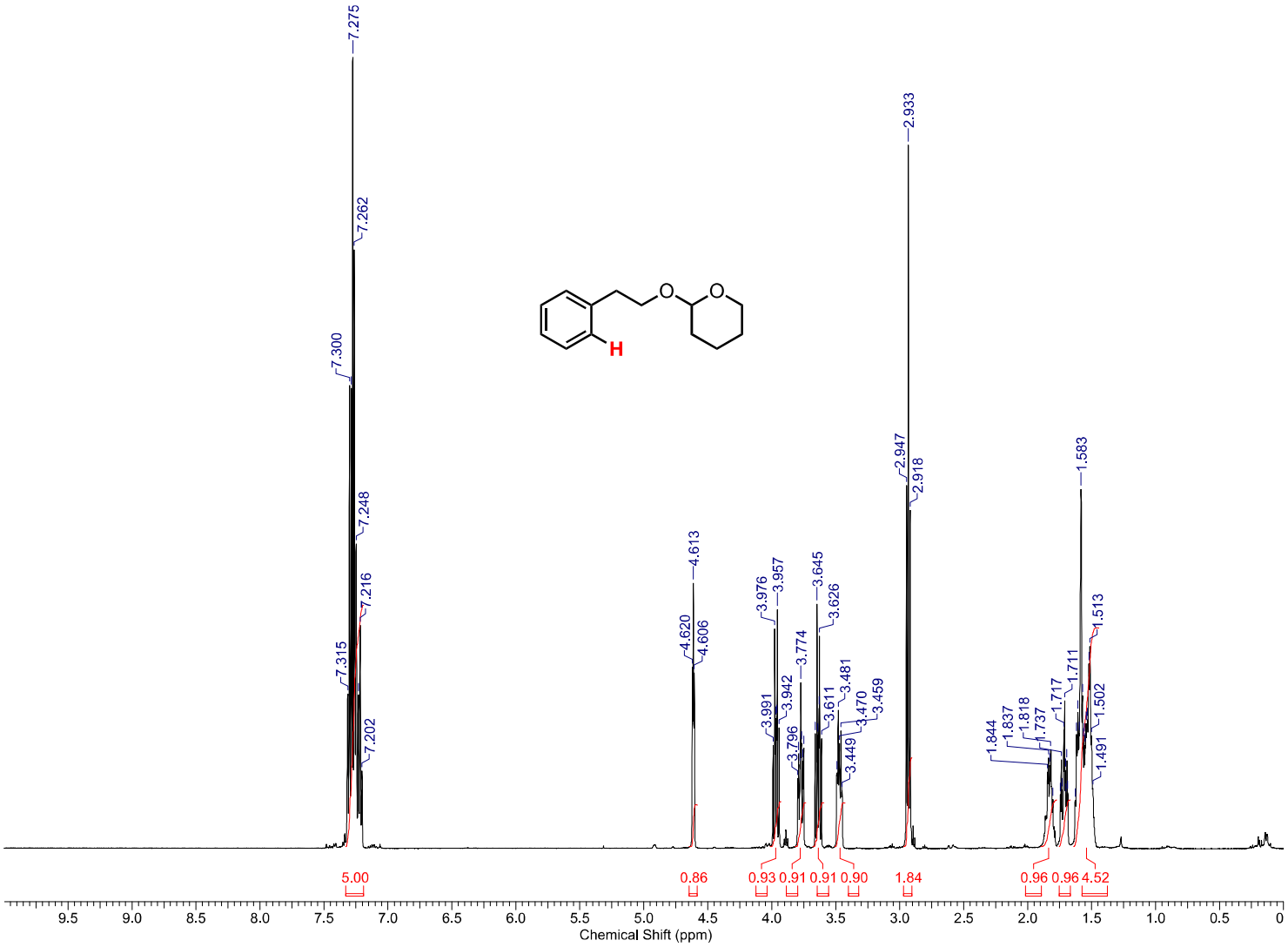
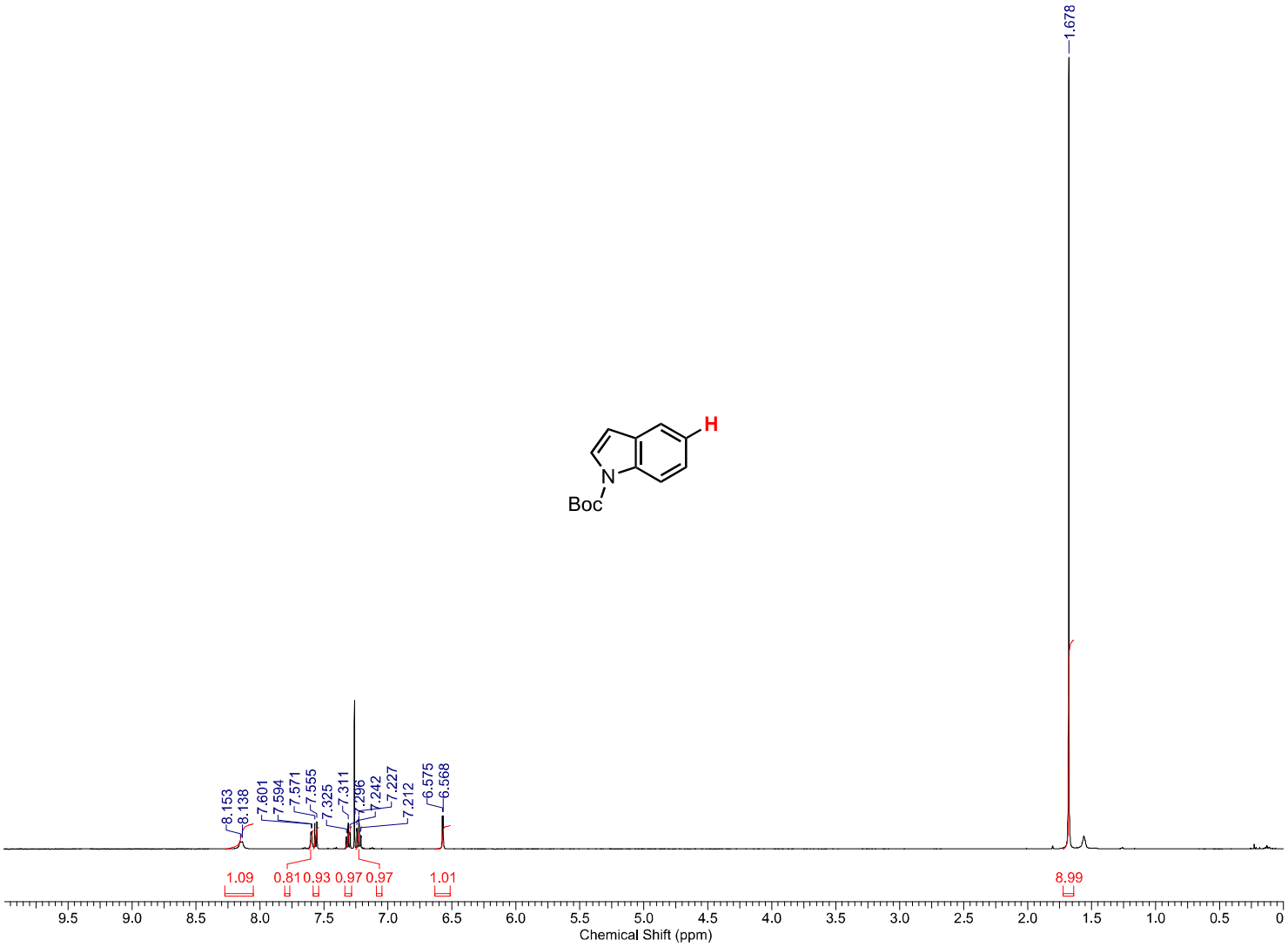
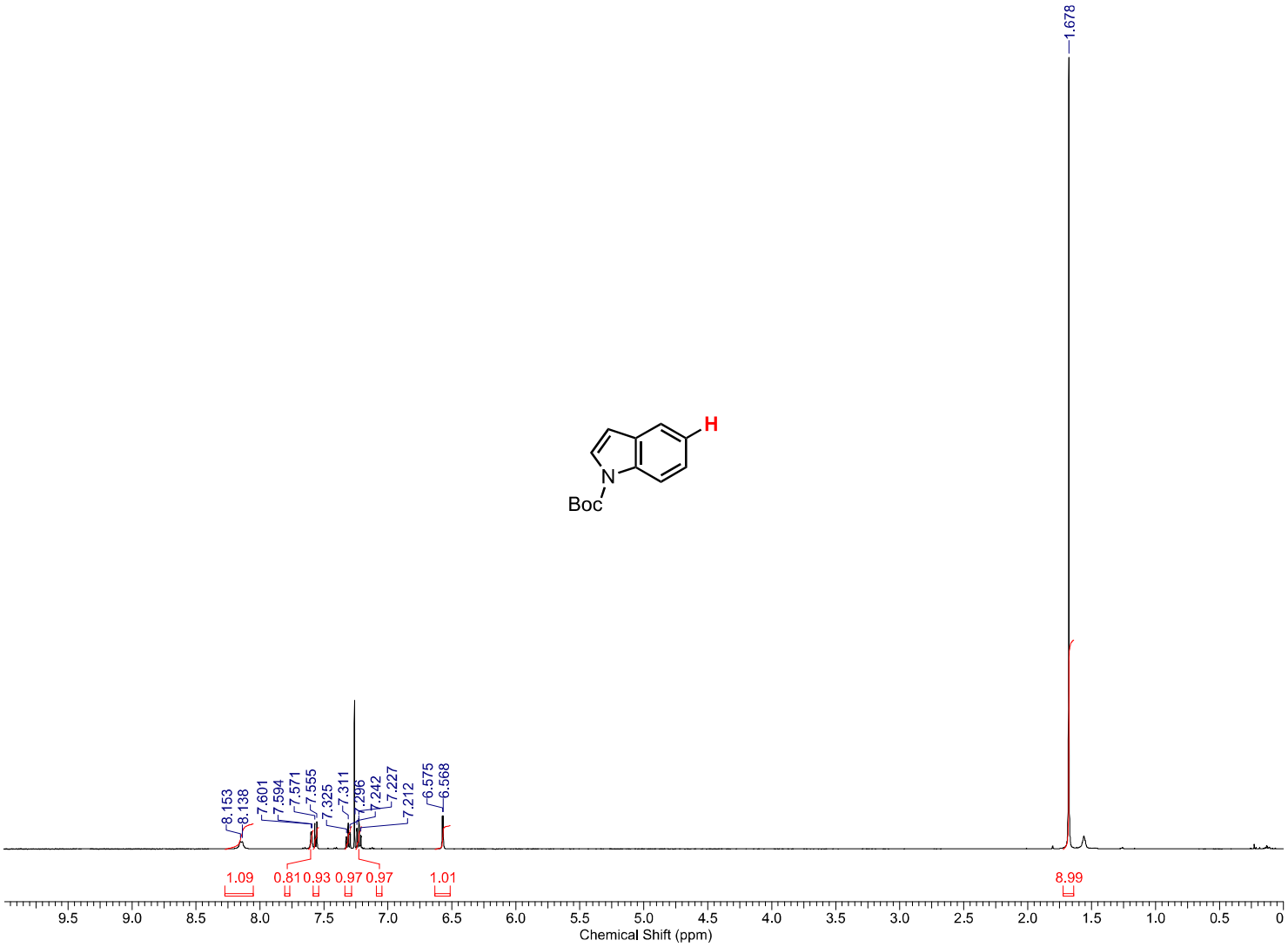

O
Me
H
2.625
7.984
7.969
7.595
7.581
7.495
7.480
7.465
1.84
0.91
1.87
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

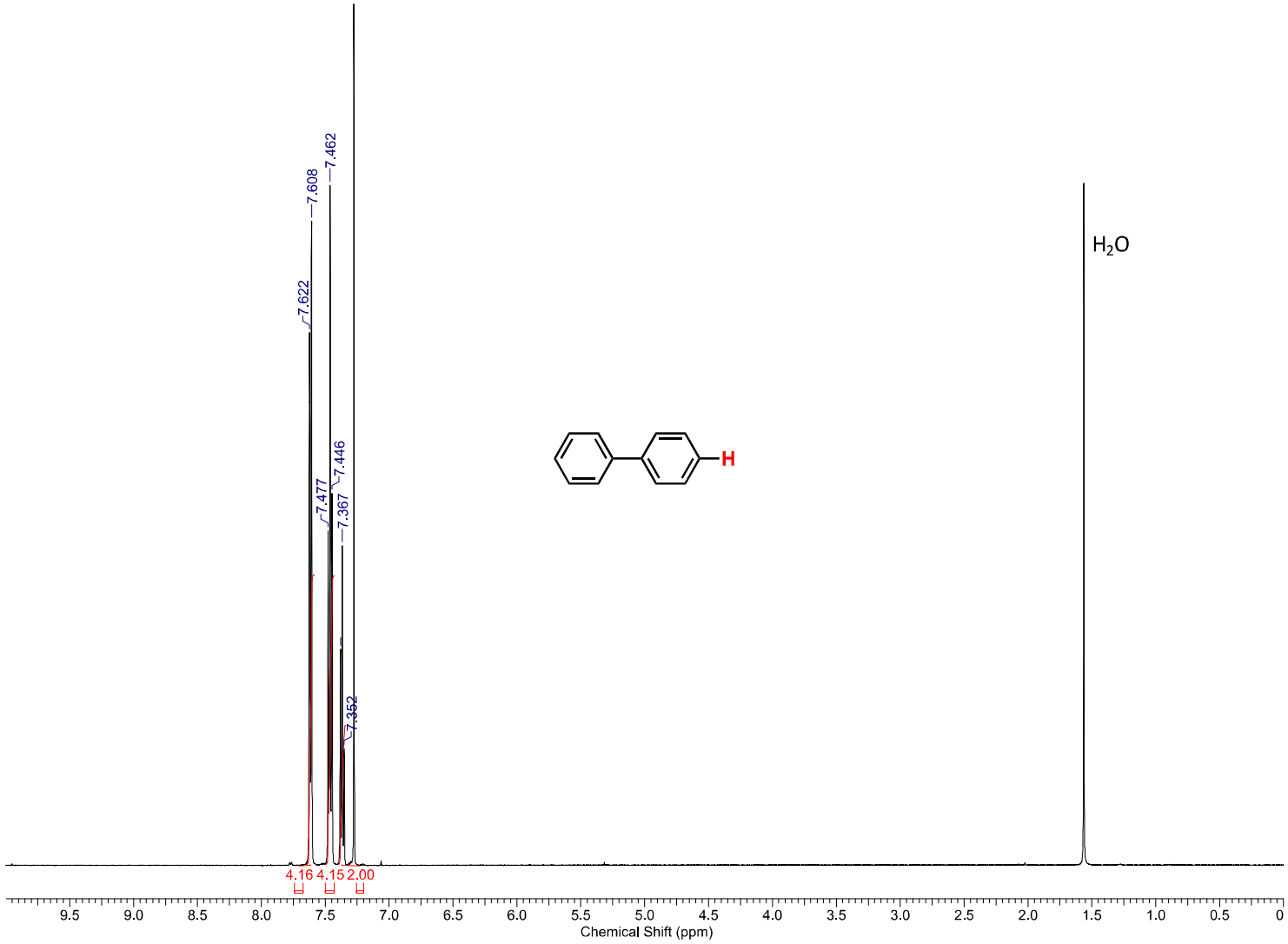

5.157
7.521
7.475
7.383
7.083
7.064
7.541
7.362
7.337
7.052
7.033
BnO
H
7.00
2.84
2.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

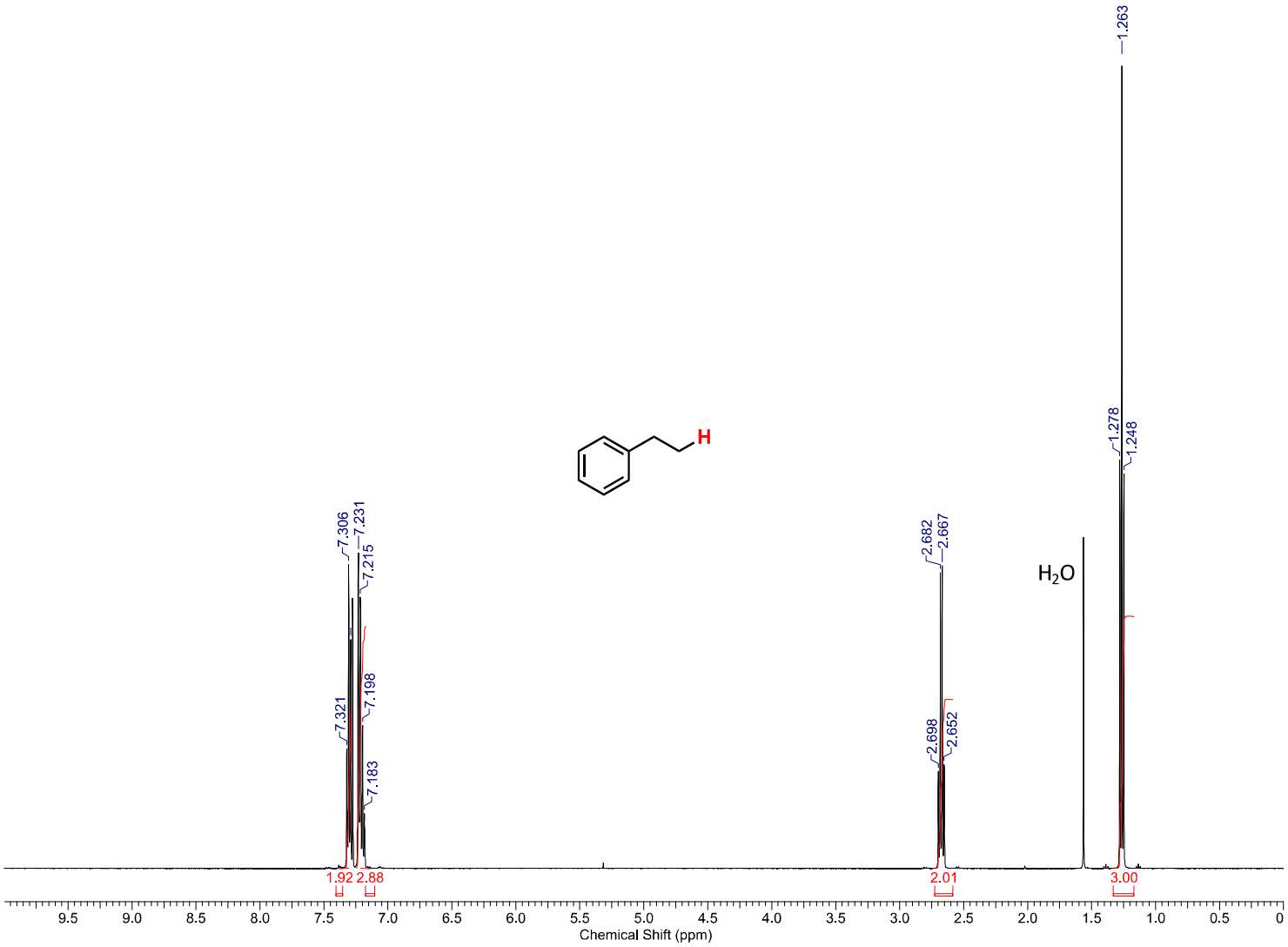

Ts
N
H
1.80 0.90 2.78 0.94 0.95
1.04
1.04 1.00
2.94
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

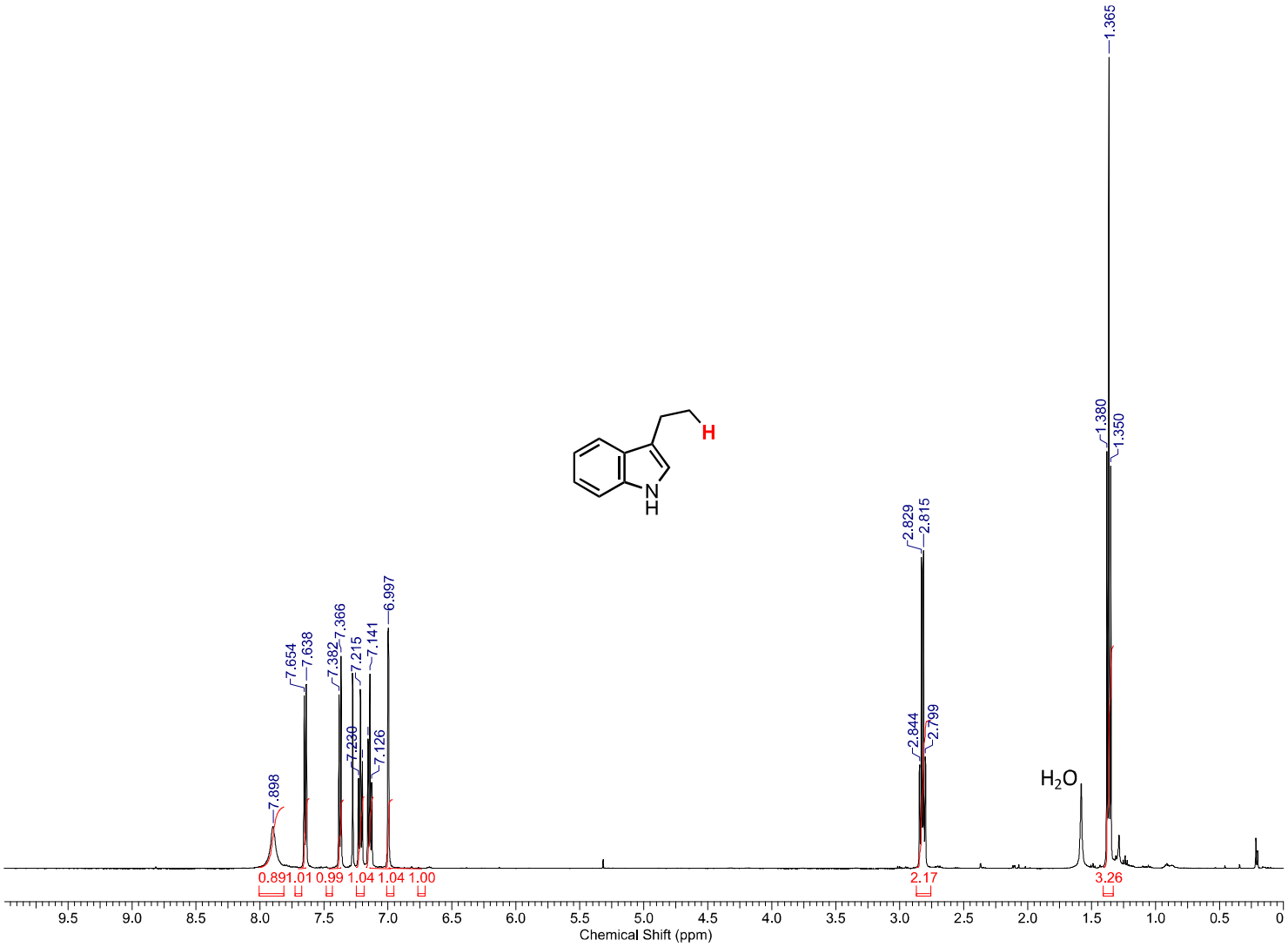

7.275
7.262
7.300
7.248
7.216
7.315
7.202
4.613
4.620
4.606
3.976
3.957
3.645
3.626
3.774
3.481
3.942
3.991
3.611
3.470
3.459
3.796
3.449
2.933
2.947
2.918
1.583
1.513
1.844
1.837
1.818
1.737
1.717
1.711
1.502
1.491
H
O
O
5.00
0.86
0.93
0.91
0.91
0.90
1.84
0.96
0.96
4.52
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

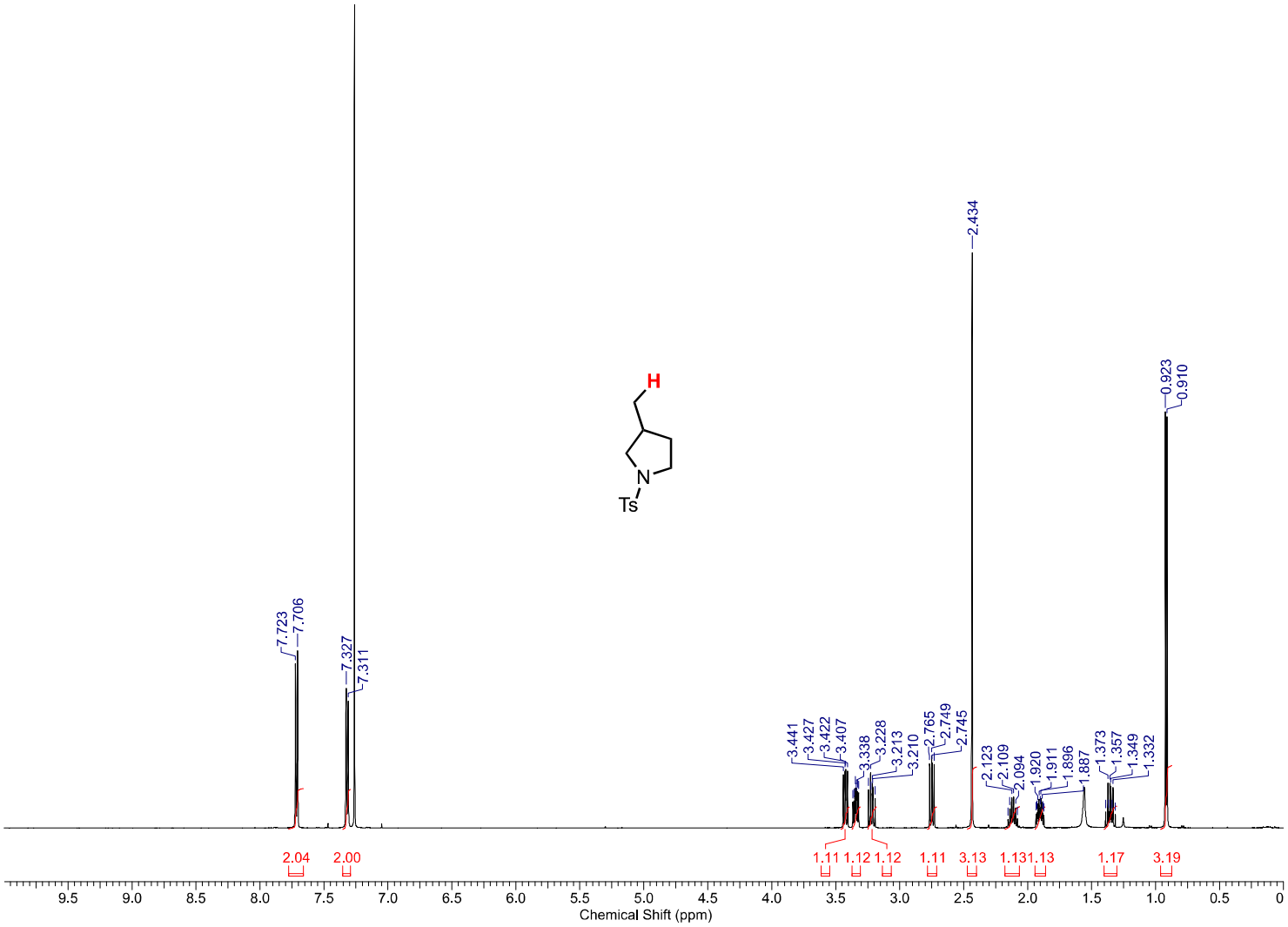

H
N
Boc
1.678
8.153
8.138
7.601
7.594
7.571
7.555
7.325
7.311
7.296
7.242
7.227
7.212
6.575
6.568
1.09
0.81
0.93
0.97
0.97
1.01
8.99
Chemical Shift (ppm)

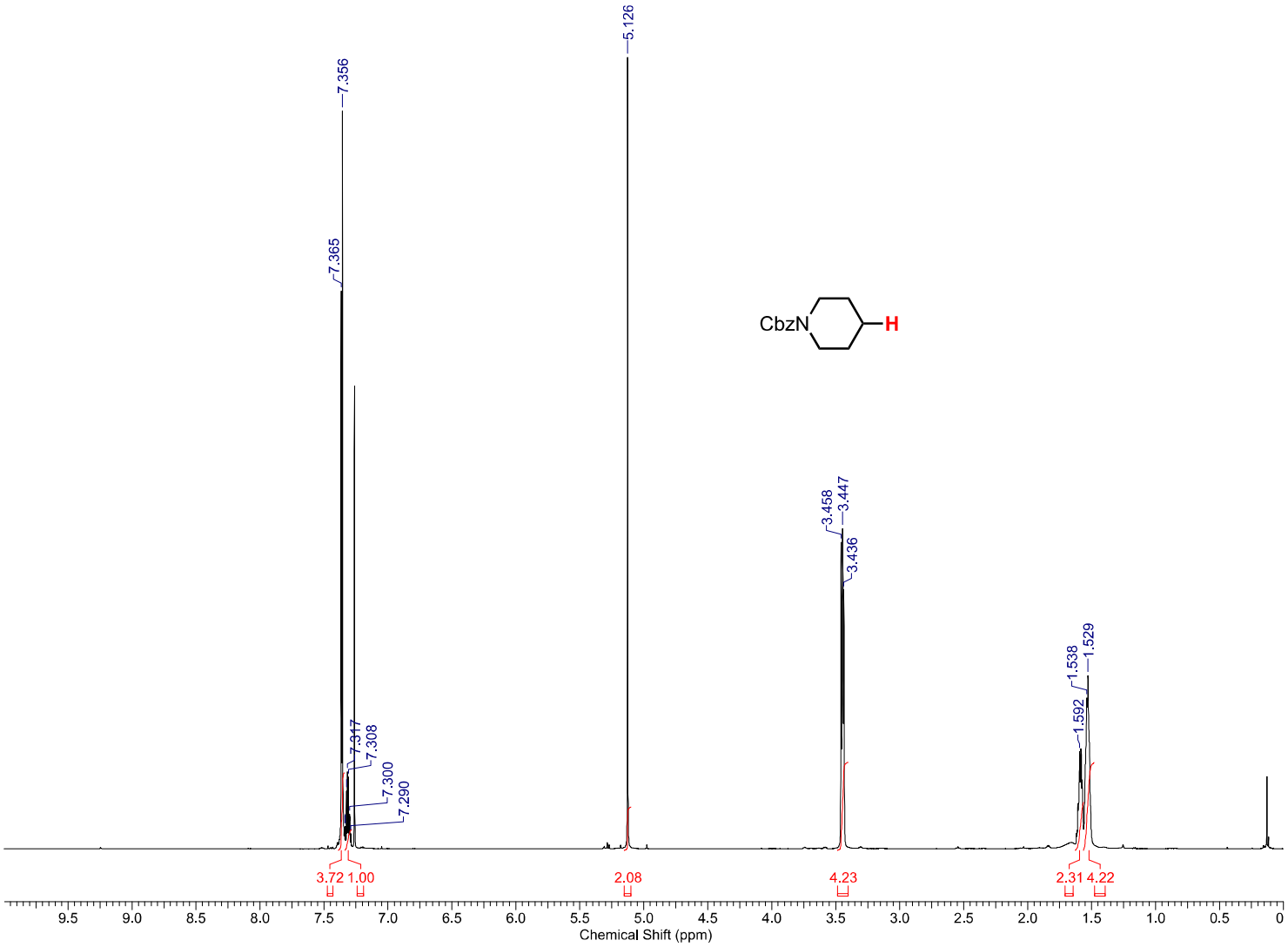

H
N
Boc
1.678
8.153
8.138
7.601
7.594
7.571
7.555
7.325
7.311
7.296
7.242
7.227
7.212
6.575
6.568
1.09
0.81
0.93
0.97
0.97
1.01
8.99
Chemical Shift (ppm)

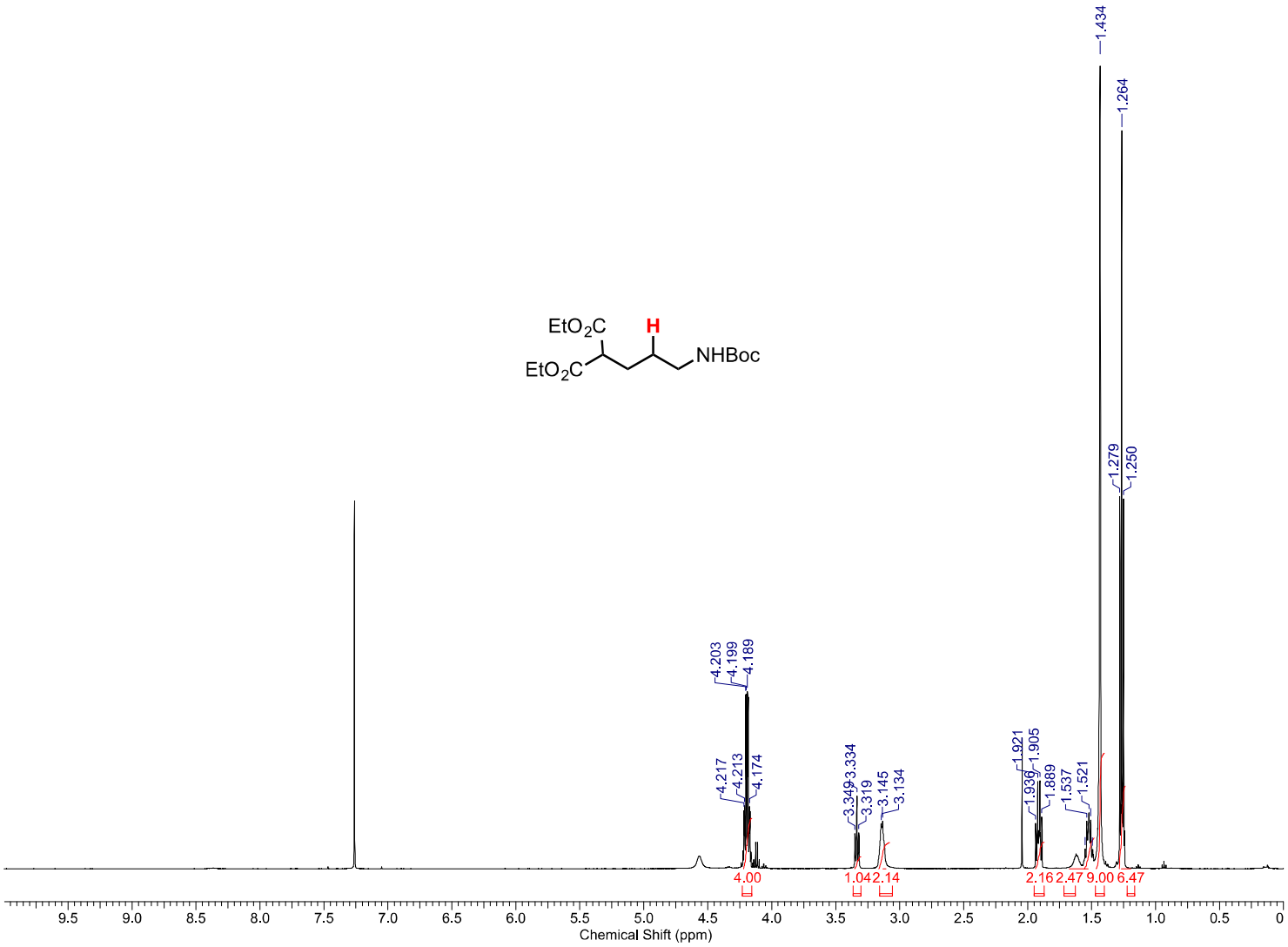

7.622
7.608
7.462
7.477
7.446
7.367
7.352
H
H2O
4.16
4.15
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

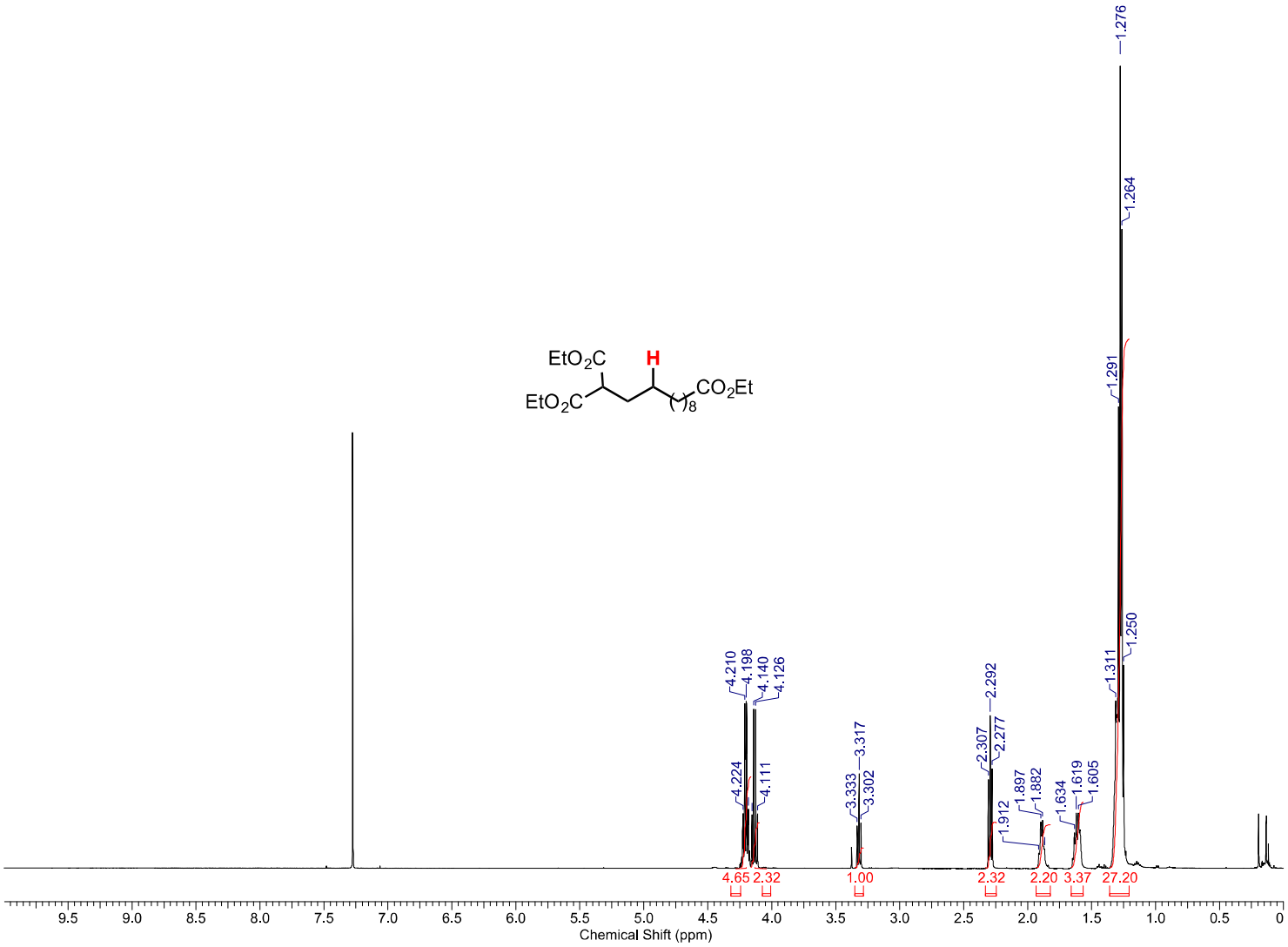

H
7.306
7.231
7.215
7.321
7.198
7.183
2.682
2.667
2.698
2.652
H2O
1.263
1.278
1.248
1.92
2.88
2.01
3.00
Chemical Shift (ppm)

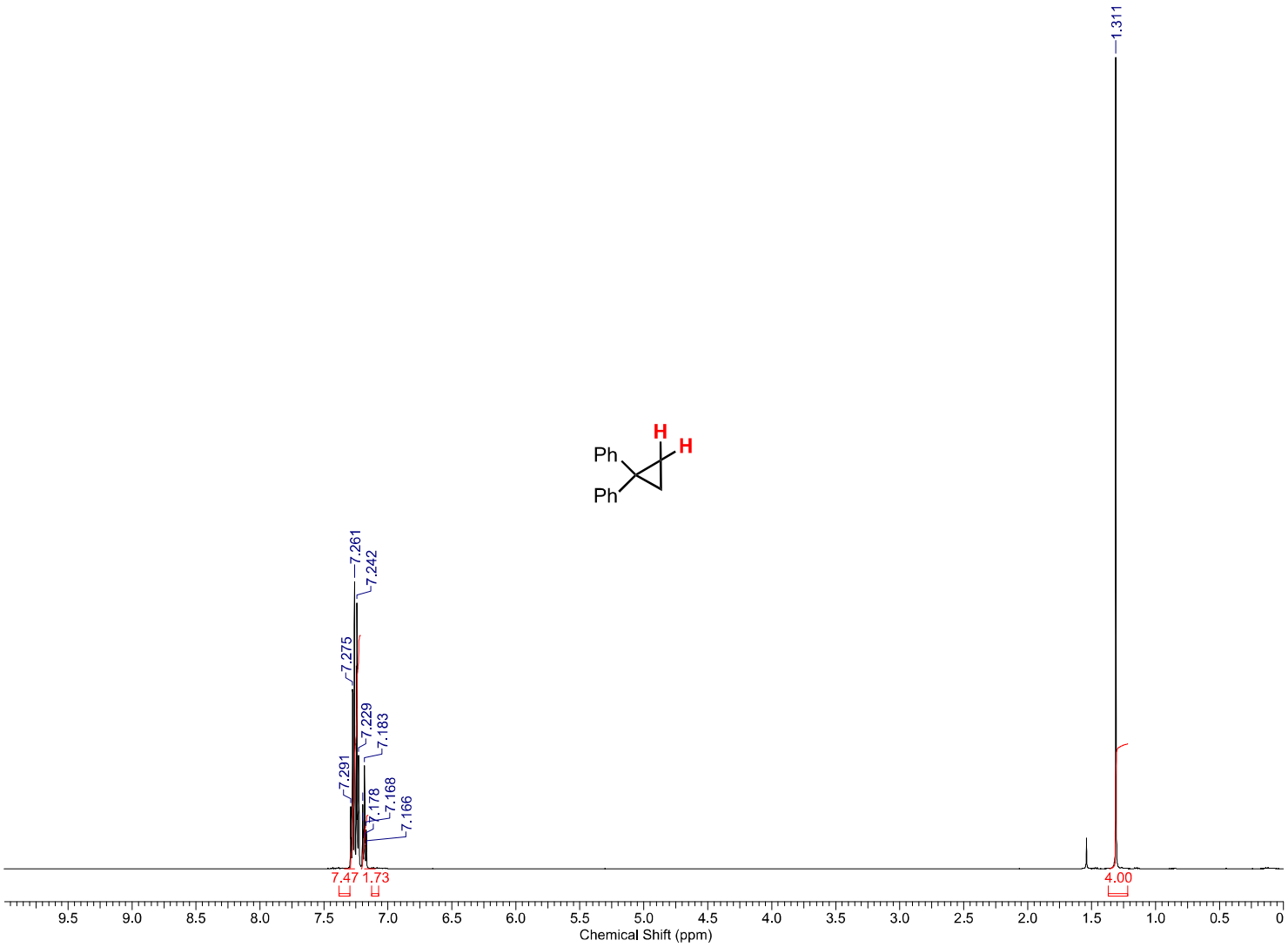

H
N
H
1.365
1.380
1.350
2.829
2.815
2.844
2.799
7.898
7.654
7.638
7.382
7.366
7.230
7.215
7.141
7.126
6.997
H2O
0.89 1.01 0.99 1.04 1.04 1.00
2.17
3.26
Chemical Shift (ppm)

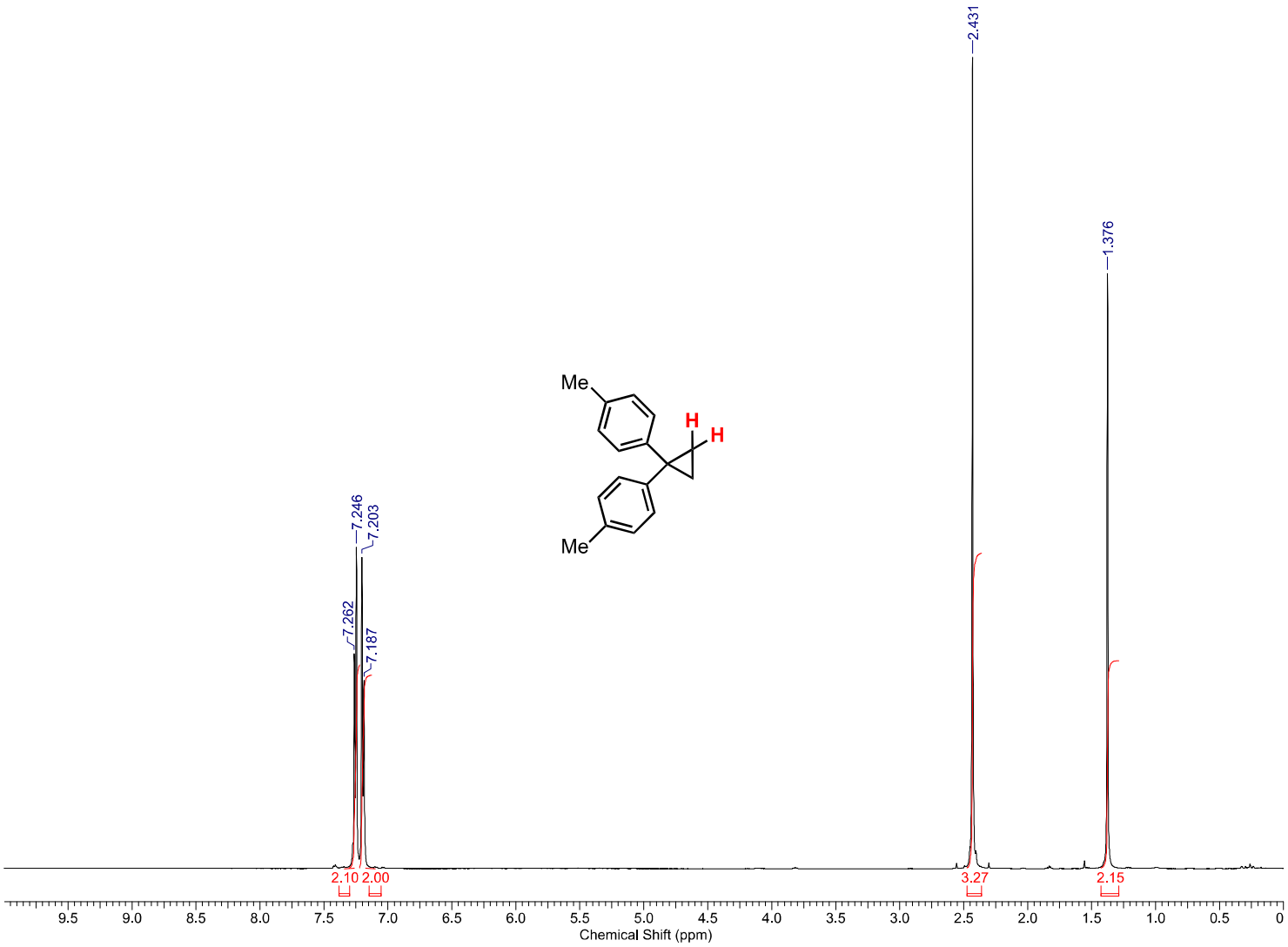

H
N
Ts
7.723
7.706
7.327
7.311
2.434
0.923
0.910
3.441
3.427
3.422
3.407
3.338
3.228
3.213
3.210
2.765
2.749
2.745
2.123
2.109
2.094
1.920
1.911
1.896
1.887
1.373
1.357
1.349
1.332
2.04
2.00
1.11
1.12
1.12
1.11
3.13
1.13
1.13
1.17
3.19
Chemical Shift (ppm)

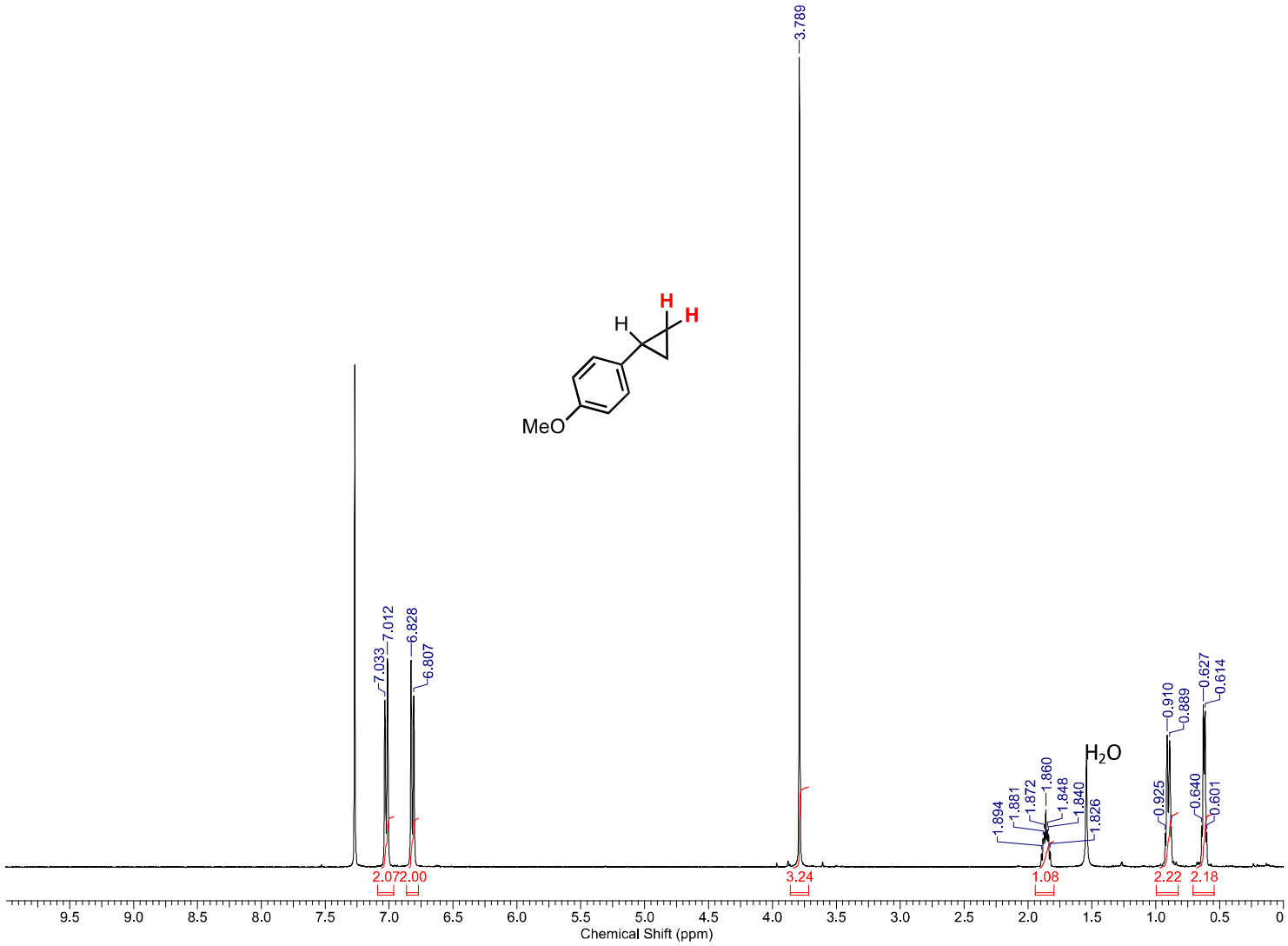

7.356
5.126
7.365
CbzN
H
3.458
3.447
3.436
1.538
1.529
1.592
7.317
7.308
7.300
7.290
3.72 1.00
2.08
4.23
2.31 4.22
Chemical Shift (ppm)

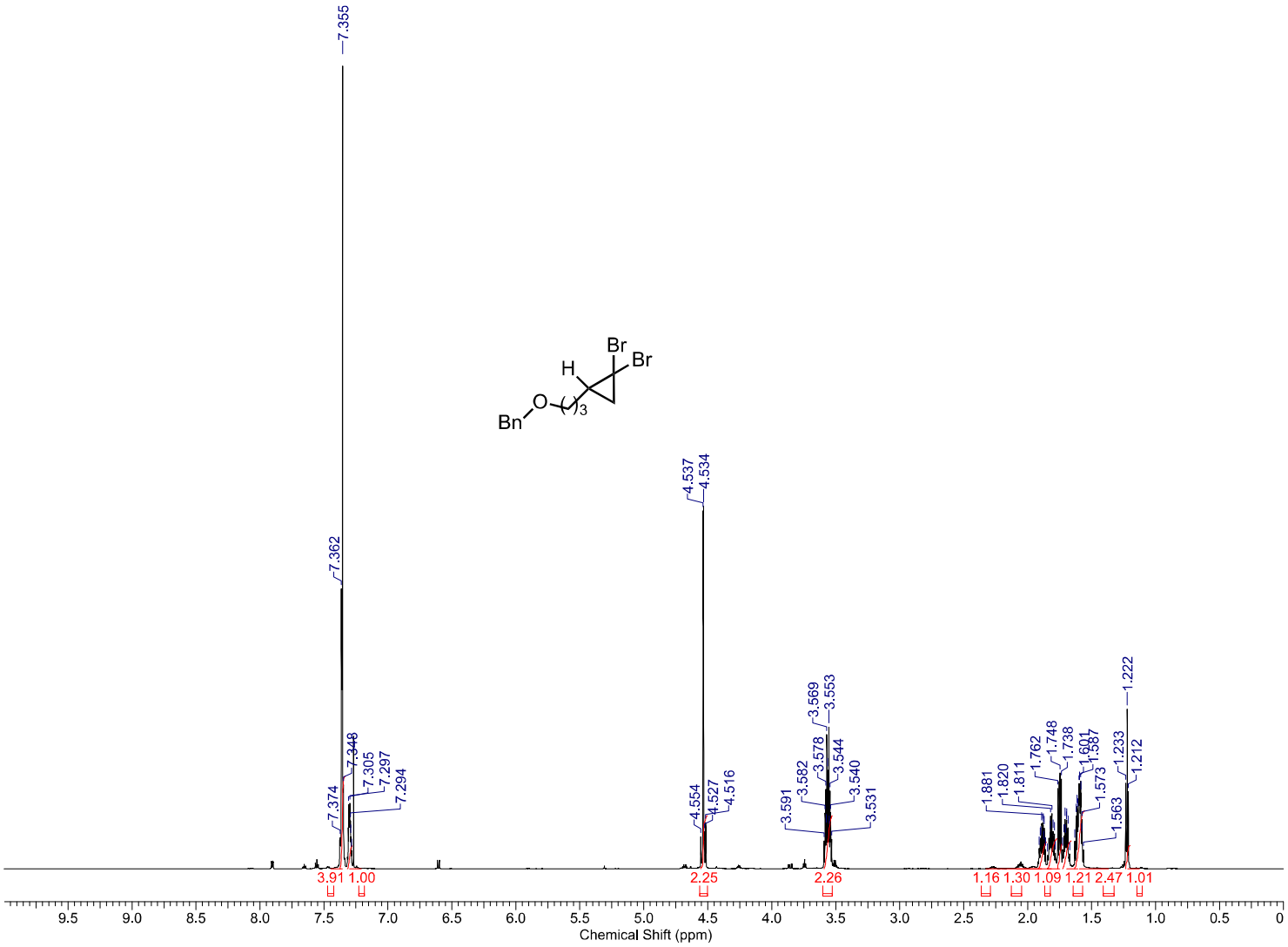

EtO2C
H
EtO2C
NHBoc
1.434
1.264
1.279
1.250
4.203
4.199
4.189
4.217
4.213
4.174
3.349
3.334
3.319
3.145
3.134
1.921
1.936
1.905
1.889
1.537
1.521
4.00
1.04
2.14
2.16
2.47
9.00
6.47
Chemical Shift (ppm)

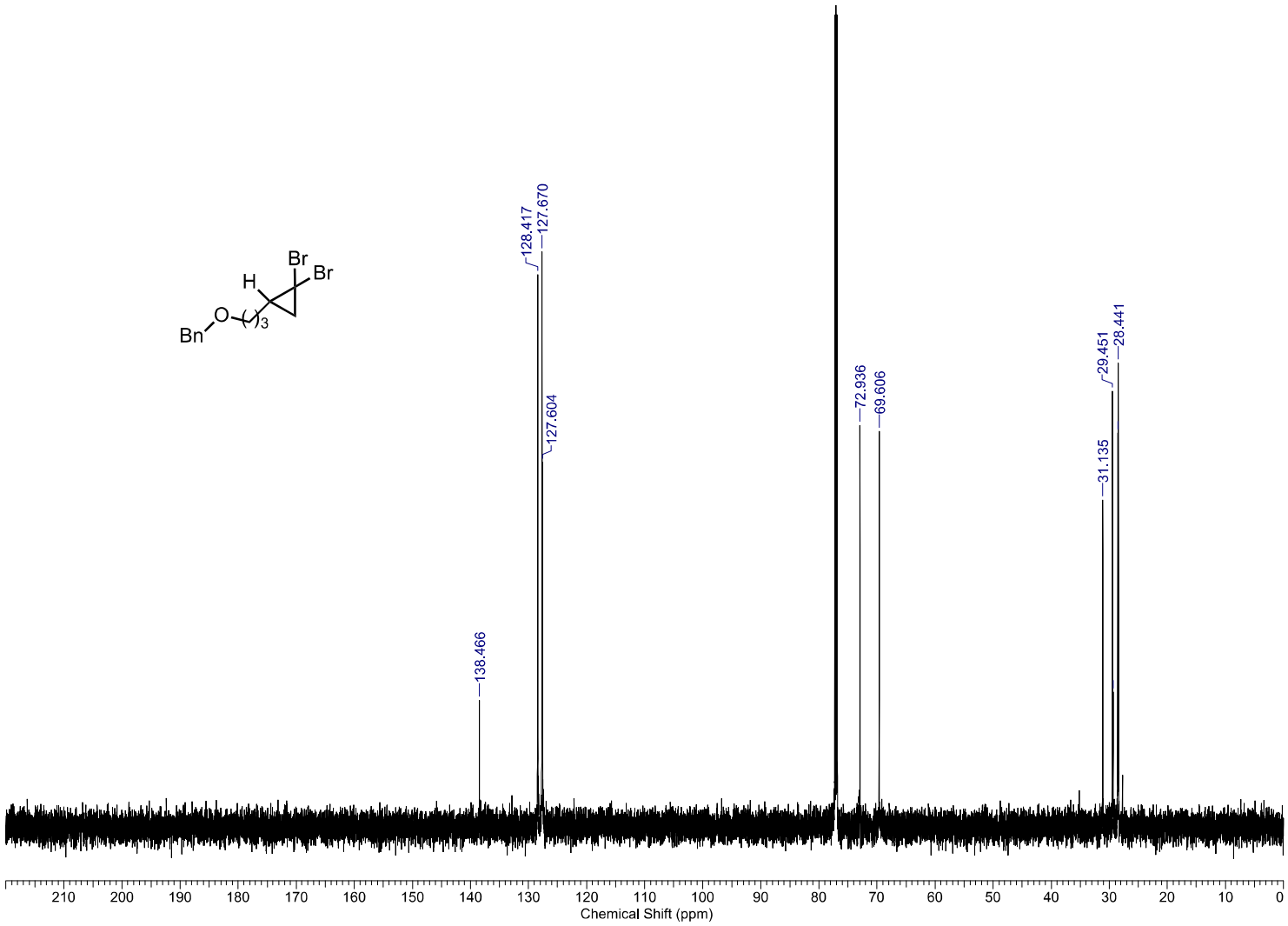

EtO2C
H
EtO2C
CO2Et
8
1.276
1.264
1.291
1.250
1.311
4.210
4.198
4.140
4.126
4.224
4.111
3.333
3.317
3.302
2.307
2.292
2.277
1.912
1.897
1.882
1.634
1.619
1.605
4.65
2.32
1.00
2.32
2.20
3.37
27.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

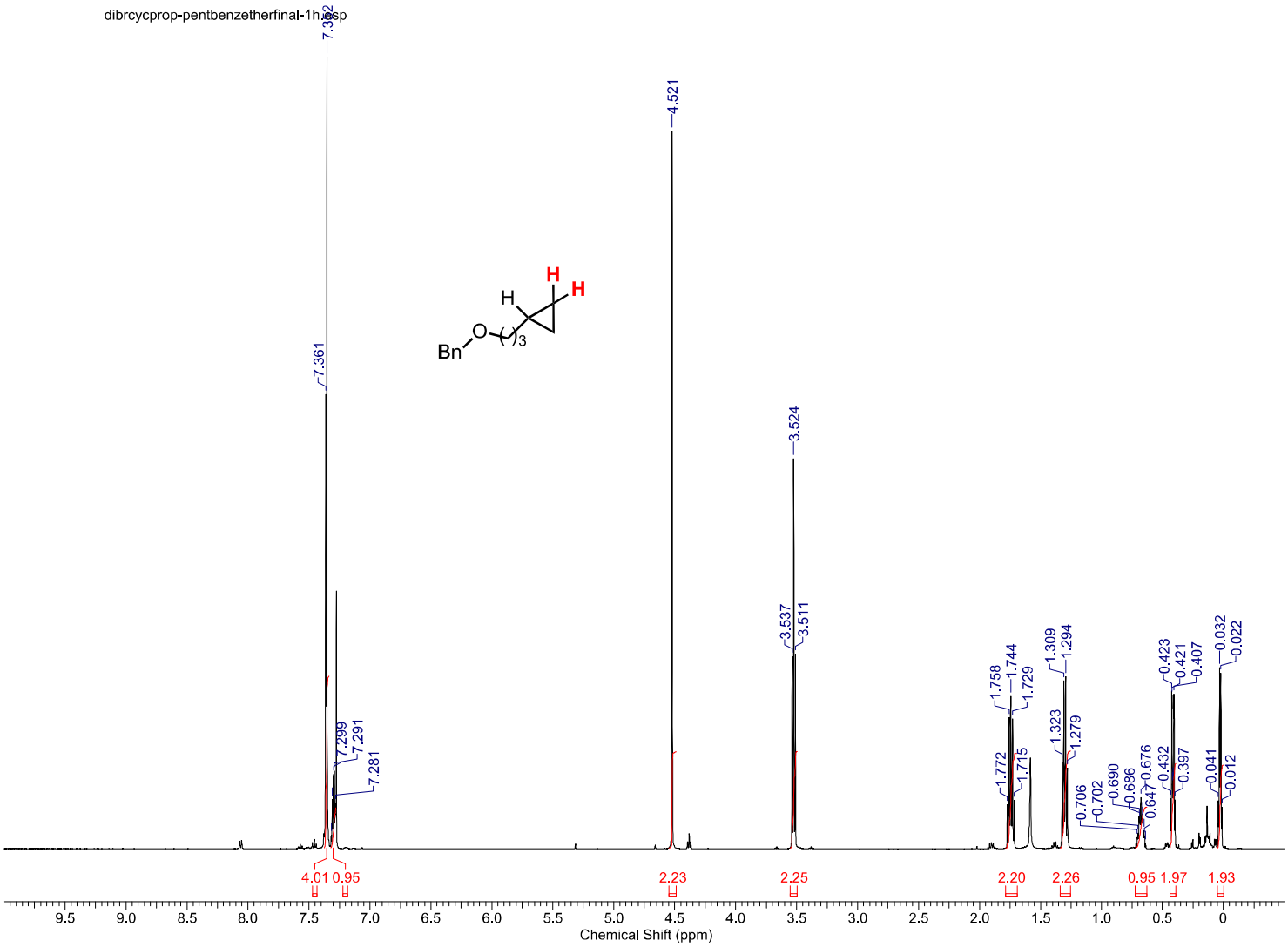

1.311
H
H
Ph
Ph
7.261
7.242
7.275
7.229
7.183
7.291
7.178
7.168
7.166
7.47
1.73
4.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

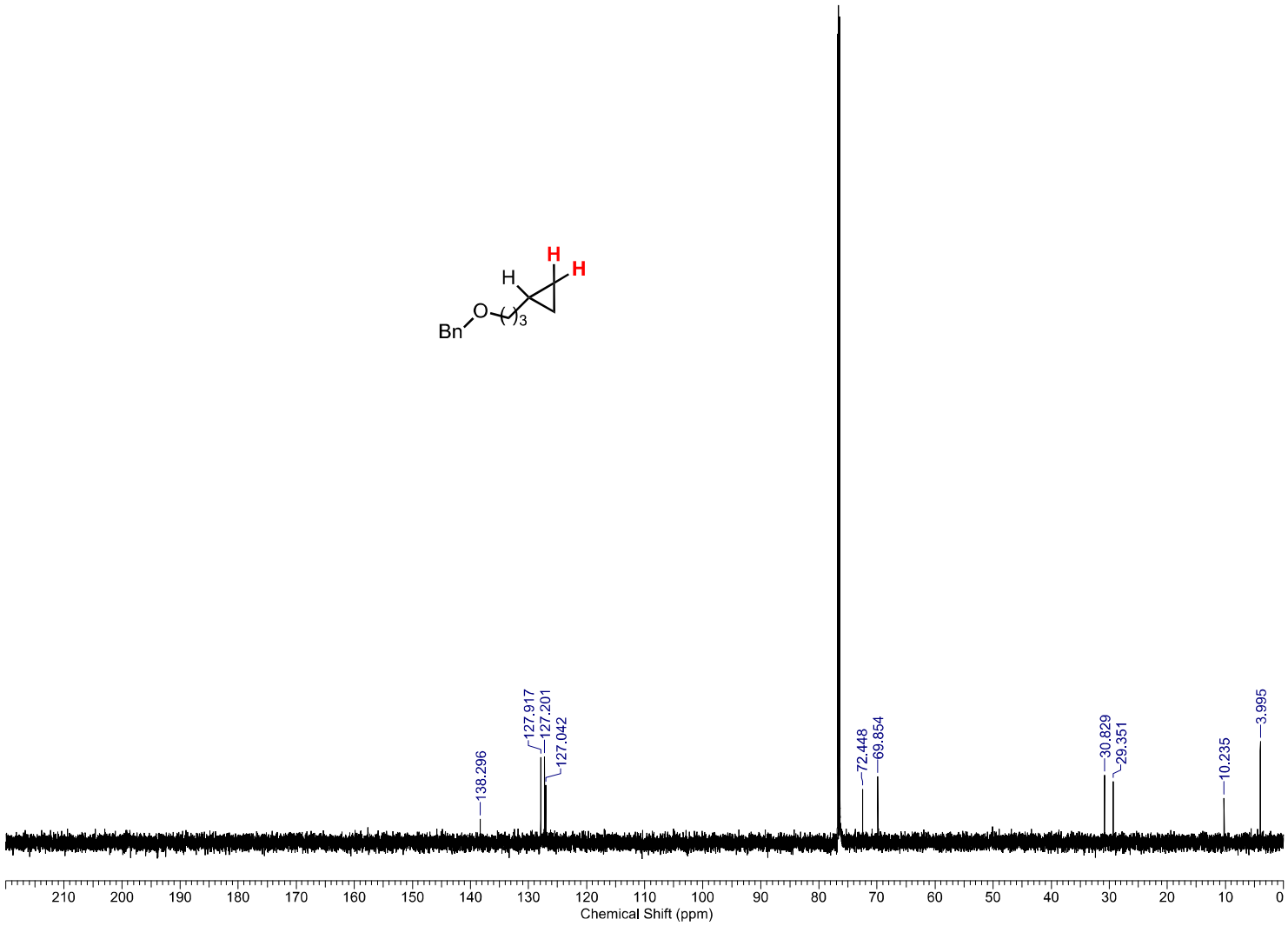

2.431
1.376
7.246
7.203
7.262
7.187
Me
Me
H
H
2.10
2.00
3.27
2.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

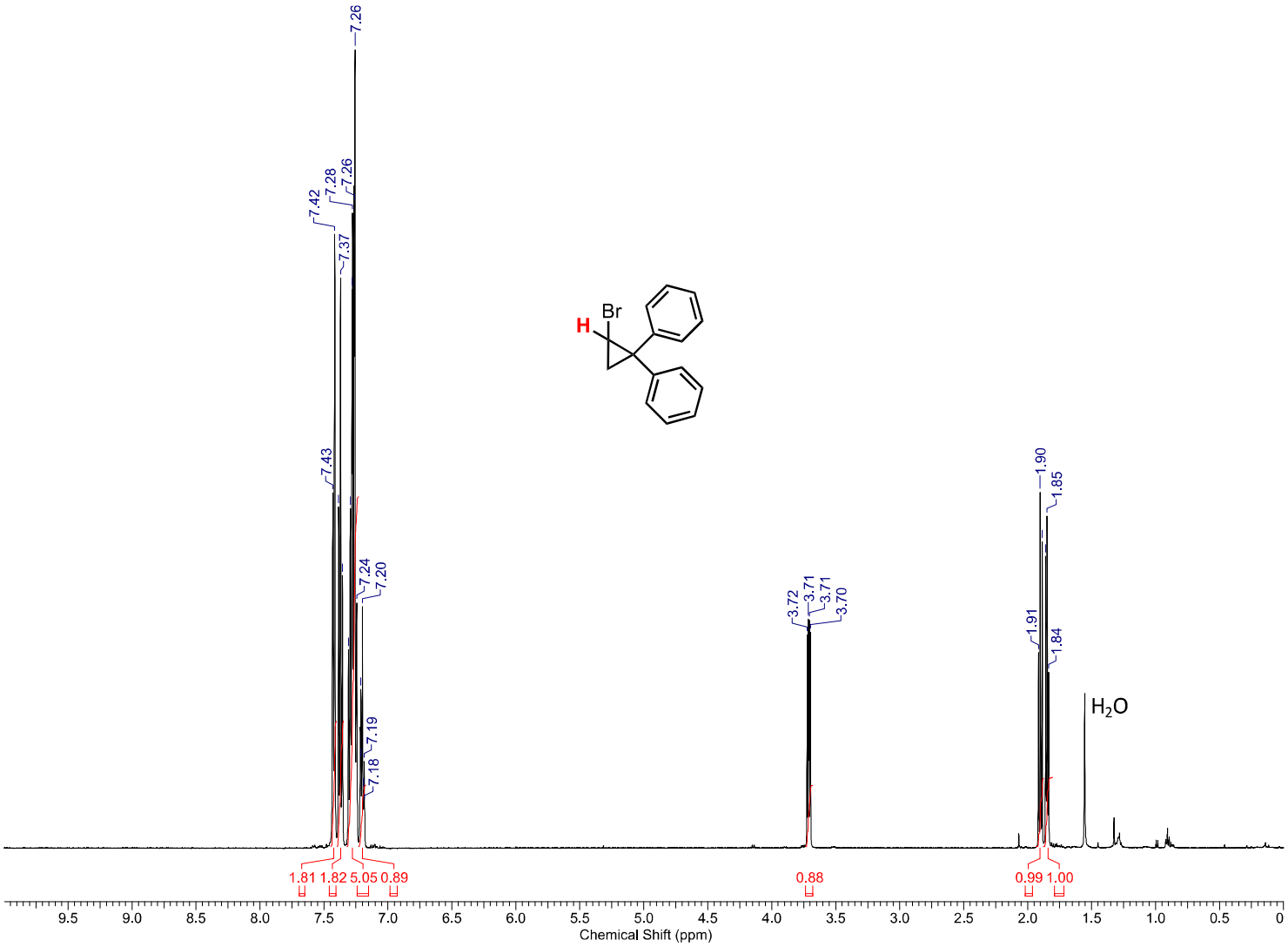

3.789
7.033
7.012
6.828
6.807
1.894
1.881
1.872
1.860
1.848
1.840
1.826
H2O
0.925
0.910
0.889
0.640
0.627
0.614
0.601
2.07
2.00
3.24
1.08
2.22
2.18
Chemical Shift (ppm)
MeO
H
H
H


7.355
7.362
7.374
7.348
7.305
7.297
7.294
4.537
4.534
4.554
4.527
4.516
3.591
3.582
3.578
3.569
3.553
3.544
3.540
3.531
1.881
1.820
1.811
1.762
1.748
1.738
1.601
1.587
1.573
1.563
1.233
1.222
1.212
3.91 1.00
2.25
2.26
1.16 1.30 1.09 1.21 2.47 1.01
Chemical Shift (ppm)
Br
Br
H
O
Bn
3


Br
Br
H
O
Bn
3
128.417
127.670
127.604
138.466
72.936
69.606
31.135
29.451
28.441
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


dibrcycprop-pentbenzetherfinal-1h.esp
7.361
4.521
3.524
3.537
3.511
7.299
7.291
7.281
1.758
1.744
1.729
1.772
1.715
1.323
1.309
1.294
1.279
0.706
0.702
0.690
0.686
0.676
0.647
0.432
0.423
0.421
0.407
0.397
0.041
0.032
0.022
0.012
H
H
H
O
Bn
3
4.01
0.95
2.23
2.25
2.20
2.26
0.95
1.97
1.93
Chemical Shift (ppm)


H
H
H
O
Bn
3
138.296
127.917
127.201
127.042
72.448
69.854
30.829
29.351
10.235
3.995
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)


7.26
7.42
7.28
7.26
7.37
7.43
7.24
7.20
7.19
7.18
3.72
3.71
3.71
3.70
1.90
1.85
1.91
1.84
H2O
Br
H
1.81 1.82 5.05 0.89
0.88
0.99 1.00
Chemical Shift (ppm)