Supporting Information For

Catalyst-free selective N-formylation and N-methylation of amines using CO₂ as a sustainable C1 source

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1. General information

All amines are analytically pure agents purchased from TCI Chemical and are used without further purification unless otherwise indicated. The deuterated solvents are purchased from CIL (Cambridge Isotope Laboratories). All the solvents used for reactions were distilled after drying over an appropriate drying agent. CO\(_2\) (99.99 vt.%.) and N\(_2\) (99.999%) are purchased from Guiyang Shengjian Gas Center, Guizhou University. The products were determined using Shimadzu GC2014 gas chromatograph and Shimadzu GC-MS-QP2010. The NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (\(^1\)H NMR) and 101 MHz (\(^{13}\)C NMR). The NMR multiplicities are abbreviated as follows: \(s\) = singlet, \(d\) = doublet, \(t\) = triplet, \(q\) = quartet, \(sept\) = septet, \(m\) = multiplet, \(br\) = broad signal. Chemical shifts are given in ppm and are referenced to SiMe\(_4\) (\(^1\)H and \(^{13}\)C) and BF\(_3\)·Et\(_2\)O (\(^{11}\)B NMR).

2. Typical procedure for selective N-formylation of amine

\[
\text{CO}_2 + \text{NaBH}_4 (2.5 \text{ eq.}), 50^\circ\text{C}, 24 \text{ h} \rightarrow \text{DMF, Catalyst-free} \rightarrow \text{N} = \text{O}
\]

A stainless autoclave (25 mL teflon inner tube) was charged with 2.5 mmol of NaBH\(_4\), 1 mmol of substrate 1\(\text{a}\), and solvent of DMF. The reactor was pressurized with 10 bar of CO\(_2\) gas at ambient temperature. The reactor was heated and stirred at 50 \(^\circ\)C for 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. The mixture was quenched with water and extracted with ethyl acetate. The yield of 2\(\text{a}\) was determined by GC/MS using dodecane as the internal standard. The isolated 2\(\text{a}\) was obtained after purification by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. Particularly, all formylated products were identified through comparisons with the corresponding \(^1\)H NMR, \(^{13}\)C NMR data reported in the literatures.\(^1\)\(^-5\)

The solvent effect on selective N-formylation and N-methylation of amine is shown in Table S1. We found that both water and methanol (CH\(_3\)OH) are ineffective (Entry 1 and 2). Diglyme, acetonitrile (CH\(_3\)CN), and tetrahydrofuran (THF) afforded moderate yields of 2\(\text{a}\) (Entry 3-5), but
they are not optimal due to the inferior selectivity. To our delight, both DMSO and DMF are effective for the selective N-formylation of amines (Entry 7 and 8).

**Table S1.** The solvent effect on selective N-formylation and N-methylation of amine.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of 2a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield of 3a (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>CH₃OH</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Diglyme</td>
<td>81</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>CH₃CN</td>
<td>74</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>75</td>
<td>18</td>
</tr>
<tr>
<td>6</td>
<td>1,4-dioxane</td>
<td>47</td>
<td>33</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>DMF</td>
<td>94</td>
<td>6</td>
</tr>
</tbody>
</table>

*Reaction conditions: amine 1a (1.0 mmol), solvent (3 mL), CO₂ (10 bar), NaBH₄ (2.5 mmol), 50 °C, 24 h. *<sup>a</sup>The yields were determined by GC/MS using dodecane as the internal standard.*

3. **Typical procedure for selective N-methylation of amine**

A stainless autoclave (25 mL teflon inner tube) was charged with 4 mmol of NaBH₄, 1 mmol of substrate 1a, and solvent of 1,4-dioxane. The reactor was pressurized with 10 bar of CO₂ gas at ambient temperature. The reactor was heated and stirred at 100 °C for 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. The mixture was quenched with water and extracted with ethyl acetate. The yield of 3a was determined by GC/MS using dodecane as the internal standard. The isolated 3a was obtained after purification by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. All methylated products were identified through comparisons with the corresponding <sup>1</sup>H NMR, <sup>13</sup>C NMR data reported in the literatures.¹⁻⁵
4. Selective N-methylation of aniline

For the selective N-methylation of aniline, we performed the kinetic control experiments and analyzed the yields of various potential products (3q, A, B, and C) in the reaction system. The mole fraction of aniline, 3q and A in reaction system was determined at the desired time by GC using dodecane as the internal standard. As shown in illustration, most of the aniline did not react, and the reaction produces methylated products of 3q as major and A as minor. No formylation products (B or C) was formed. The yield of 3q increases over time in the first 48 h, followed by reaching equilibrium after 48 h.

Illustration: The change of mole fraction of aniline, 3q and A in reaction system over reaction time.

5. Gram scale reaction

A stainless autoclave reactor coupled with a magnetic stirrer was charged with 1d (10 mmol, 1.21 g), quantitative NaBH₄, and solvent (20 mL). The resulting mixture was stirred for 24 h at stated temperature under 10 bar of CO₂. After the reaction, excess CO₂ was vented discretely. The reaction mixture was quenched by water and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The
product of 2d and 3d was obtained respectively in yield of 85% and 78% after purification by flash chromatography on silica gel with petroleumether/ethyl acetate.

6. Reaction of NaBH₄ and CO₂ in DMF

A stainless autoclave reactor coupled with a magnetic stirrer was charged with NaBH₄ (3 mmol) and DMF (3 mL). The reactor was pressurized with 10 bar of CO₂ at ambient temperature, and then was heated and stirred at 50 °C for 24 h. After the reaction, excess CO₂ was vented discreetly, about 0.1 mL of mixture was dissolved in 0.4 mL of D₂O for NMR experiment analysis. The ¹H NMR, ¹³C NMR and ¹¹B NMR spectra are measured at 298.15 K and shown in Fig. S1.
In addition, the effects of the amount of the NaBH$_4$, solvent, reaction temperature and time were examined, respectively. The specific experimental conditions and products Int.1 and Int. 2 are shown in Table S2.

$$\text{CO}_2 + \text{NaBH}_4 \xrightarrow{\text{Solvent (3 mL)}} \xrightarrow{T, t} \text{NaH}_{4-n}\text{B(OCOH)}_n + \text{NaH}_{4-n}\text{B(OCH}_3)_n$$

Int. 1 \hspace{2cm} Int. 2
Table S2 Control experiment on formation of Int. 1 and Int. under different conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>NaBH₄ (mmol)</th>
<th>Solvent (mL)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Int.1ᵃ</th>
<th>Int.2ᵃ</th>
</tr>
</thead>
<tbody>
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<td>DMF (3 mL)</td>
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<td>24</td>
<td>major</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>DMF (3 mL)</td>
<td>50</td>
<td>5</td>
<td>major</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>DMF (3 mL)</td>
<td>50</td>
<td>24</td>
<td>moiety</td>
<td>moiety</td>
</tr>
<tr>
<td>4</td>
<td>2.0</td>
<td>DMF (3 mL)</td>
<td>100</td>
<td>24</td>
<td>moiety</td>
<td>moiety</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>1,4-dioxane (3 mL)</td>
<td>100</td>
<td>24</td>
<td>trace</td>
<td>major</td>
</tr>
<tr>
<td>6</td>
<td>4.0</td>
<td>1,4-dioxane (3 mL)</td>
<td>100</td>
<td>24</td>
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</tr>
<tr>
<td>7</td>
<td>4.0</td>
<td>1,4-dioxane (3 mL)</td>
<td>50</td>
<td>24</td>
<td>minor</td>
<td>major</td>
</tr>
</tbody>
</table>

ᵃDetermined by the $^{11}$B NMR.

The $^{11}$B NMR spectra for the reaction of NaBH₄ and CO₂ in DMF (The experimental conditions are shown in Table S2, Entry 1).

The $^{11}$B NMR spectra for the reaction of NaBH₄ and CO₂ in DMF (The experimental conditions are shown in Table S2, Entry 2).
The $^{11}$B NMR spectra for the reaction of NaBH$_4$ and CO$_2$ in DMF (The experimental conditions are shown in Table S2, Entry 4).

The $^{11}$B NMR spectra for the reaction of NaBH$_4$ and CO$_2$ in DMF (The experimental conditions are shown in Table S2, Entry 5).
The $^{11}$B NMR spectra for the reaction of NaBH$_4$ and CO$_2$ in DMF (The experimental conditions are shown in Table S2, Entry 7).

7. Isotope labeling experiment with NaBD$_4$

A stainless autoclave (25 mL teflon inner tube) was charged with 2.5 mmol of NaBD$_4$, 1 mmol of substrate 1a, and solvent of DMF (3 mL). The reactor was pressurized with 10 bar of CO$_2$ gas at ambient temperature. The reactor was heated and stirred at 50 °C for 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. The mixture was quenched with water and extracted with ethyl acetate. The yield of 2a’ was determined by GC/MS using dodecane as the internal standard. The isolated 2a’ was obtained after purification by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, and the structure confirmed by NMR (Fig. S2).
8. Reaction of NaBH₄ and CO₂ in 1,4-dioxane

Analogously, a stainless autoclave reactor coupled with a magnetic stirrer was charged with NaBH₄ (3 mmol) and 1,4-dioxane (3 mL). The reactor was pressurized with 10 bar of CO₂ at ambient temperature, and then was heated and stirred at 100°C for 24 h. After the reaction, excess CO₂ was vented discreetly, about 0.1 mL of mixture was dissolved in 0.4 mL of D₂O for NMR experiment analysis. The ¹H NMR, ¹³C NMR and ¹¹B NMR spectra are measured at 298.15 K and shown in Fig. S3.
Fig. S3 The $^1$H NMR, $^{13}$C NMR and $^{11}$B NMR spectra for the reaction of NaBH$_4$ and CO$_2$ in 1,4-dioxane.
9. Details on stepwise reaction of 1r, CO$_2$ and NaBH$_4$

A stainless autoclave reactor coupled with a magnetic stirrer was charged with 1r (1 mmol), DMF (3 mL), and 10 bar of CO$_2$. The resulting mixture was stirred for 24 h at room temperature. After the reaction, residual CO$_2$ was completely removed through the pump at low temperature (ice-salt baths), and 2.5 eq. NaBH$_4$ (2.5 mmol) and 1 bar of N$_2$ were introduced into the reactor. Then, it was heated and stirred at 50°C for another 24 h. After the reaction, the conversion and yield of the 2r was resolved by GC/MS analysis using dodecane as the internal standard.
10. The NMR information of formamides and methylamines

2a: $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 8.41$ (s, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 7.16 – 7.07 (m, 2H), 3.25 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 162.46$ (s), 142.04 (s), 129.59 (s), 126.41 (s), 122.28 (s), 32.02 (s) ppm.

2a*: $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.42$ (t, $J = 7.9$ Hz, 2H), 7.28 (s, 1H), 7.22 – 7.15 (m, 2H), 3.33 (s, 3H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta = 162.37$ (s), 142.15 (s), 129.63 (s), 126.40 (s), 122.32 (s), 32.00 (s) ppm.

2e: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.13$ (s, 1H), 6.94 – 6.87 (m, 2H), 6.77 – 6.69 (m, 2H), 3.60 (s, 3H), 3.06 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 162.24$ (s), 158.05 (s), 135.02 (s), 124.29 (s), 114.57 (s), 55.29 (s), 32.32 (s) ppm.

2n: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.44$ (s, 1H), 7.44 – 7.28 (m, 6H), 7.26 – 7.16 (m, 4H), 4.43 (s, 2H), 4.28 (s, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 162.90$ (s), 136.04 (s), 135.66 (s), 77.50 (s), 77.18 (s), 76.86 (s), 50.28 (s), 44.66 (s) ppm.
2q: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.89$ (s, 1H), 3.52 (ddd, $J = 16.4, 7.2, 3.8$ Hz, 4H), 3.43 – 3.36 (m, 2H), 3.26 (dd, $J = 6.4, 3.3$ Hz, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 160.75$ (s), 67.09 (s), 66.26 (s), 45.64 (s), 40.42 (s) ppm.

2r: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.83$ (s, 1H), 3.35 – 3.27 (m, 2H), 3.20 – 3.12 (m, 2H), 1.60 – 1.45 (m, 2H), 1.45 – 1.31 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 160.75$ (s), 67.09 (s), 66.26 (s), 45.64 (s), 40.42 (s) ppm.

2s: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.77$ (s, 1H), 8.53 (s, 1H), 8.08 (d, $J = 8.5$ Hz, 1H), 7.31 – 7.11 (m, 3H), 7.12 – 6.99 (m, 1H), 4.20 – 3.96 (m, 2H), 3.24 – 3.06 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 159.35$ (s), 157.57 (s), 141.06 (s), 131.93 (s), 127.56 (d, $J = 2.4$ Hz), 126.06 (s), 124.87 (s), 124.56 (s), 124.25 (s), 116.60 (s), 109.40 (s), 46.95 (s), 44.64 (s), 27.74 (s), 27.17 (s) ppm.

3a (colourless liquid, 80% yield, 97 mg): $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.94$ (s, 1H), 8.53 (s, 1H), 8.08 (d, $J = 8.5$ Hz, 1H), 7.31 – 7.11 (m, 3H), 7.12 – 6.99 (m, 1H), 4.20 – 3.96 (m, 2H), 3.24 – 3.06 (m, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 150.58$ (s), 129.00 (s), 116.54 (s), 112.57 (s), 40.56 (s).

3b (colourless liquid, 85% yield, 115 mg): $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.34 – 7.22$ (m, 2H), 7.20 – 7.02 (m, 2H), 2.82 (s, 6H), 2.46 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 152.80$ (s), 132.19 (s), 131.25 (s), 126.53 (s), 122.67 (s), 118.44 (s), 44.32 (s), 18.47 (s) ppm.

3c (colourless liquid, 82% yield, 110 mg): $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.27$ (d, $J = 2.0$ Hz, 1H), 6.70 (dd, $J = 4.7, 3.5$ Hz, 3H), 3.06 (s, 6H), 2.46 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 150.87$ (s), 138.79 (s), 129.05 (s), 117.78 (s), 113.59 (s), 110.07 (s), 40.79 (s), 22.02 (s) ppm.
3d (colourless liquid, 93% yield, 125 mg): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 6.95 (dt, $J$ = 4.9, 1.4 Hz, 2H), 6.70 – 6.52 (m, 2H), 2.78 (s, 6H), 2.16 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 148.95 (s), 129.72 (s), 126.21 (s), 113.35 (s), 41.17 (s), 20.39 (s) ppm.

3e (white solid, 78% yield, 118 mg): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 6.80 – 6.65 (m, 4H), 3.68 (s, 3H), 2.79 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 152.13 (s), 145.66 (s), 115.03 (s), 114.66 (s), 55.77 (s), 41.93 (s).

3f (light yellow solid, 64% yield, 89 mg): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 6.76 (t, $J$ = 8.8 Hz, 2H), 6.57 – 6.38 (m, 2H), 2.70 (s, 6H) ppm.$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 156.84 (s), 154.50 (s), 147.57 (s), 115.53 (s), 115.31 (s), 113.99 (d, $J$ = 7.4 Hz), 41.35 (s) ppm.

3g: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.24 (d, $J$ = 9.2 Hz, 2H), 6.69 (d, $J$ = 9.1 Hz, 2H), 2.97 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 149.21 (s), 128.85 (s), 121.39 (s), 113.69 (s), 40.67 (s) ppm.

3h: $^1$H NMR (400 MHz, DMSO) $\delta$ = 8.17 – 8.05 (m, 2H), 6.66 – 6.54 (m, 2H), 3.11 (s, 6H) ppm. $^{13}$C NMR (101 MHz, DMSO) $\delta$ = 149.46 (s), 121.34 (s), 105.50 (s), 35.52 (s) ppm.

3i: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.35 (d, $J$ = 4.4 Hz, 4H), 7.28 (ddd, $J$ = 8.7, 5.0, 3.8 Hz, 1H), 3.46 (s, 2H), 2.28 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 138.96 (s), 129.11 (s), 128.27 (s), 127.07 (s), 64.47 (s), 45.41 (s) ppm.

3j: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 6.80 – 6.65 (m, 4H), 3.68 (s, 3H), 2.79 (s, 6H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 138.38 (s), 127.97 (s), 127.28 (s), 125.99 (s), 60.93 (s), 41.29 (s) ppm.

3k: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.25 (dd, $J$ = 8.7, 6.6 Hz, 4H), 2.14 (s, 3H), 1.44 – 1.32 (m, 4H), 1.24 (dq, $J$ = 14.3, 7.2 Hz, 4H), 0.85 (t, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 57.62 (s), 42.31 (s), 29.43 (s), 20.77 (s), 14.06 (s).

3l: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.29 (s, 6H), 2.16 (dt, $J$ = 14.0, 6.9 Hz, 1H), 1.83 (dd, $J$ = 37.9, 12.3 Hz, 4H), 1.63 (d, $J$ = 12.9 Hz, 1H), 1.30 – 1.10 (m, 5H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 63.76 (s), 41.48 (s), 28.85 (s), 26.21 (s), 25.70 (s) ppm.
**3m**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 2.16$ (s, 3H), 1.45 (tdd, $J = 7.1$, 3.4, 1.5 Hz, 2H), 1.38 (dd, $J = 6.6$, 3.6 Hz, 4H), 0.97 (s, 12H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 53.73$ (s), 41.21 (s), 31.46 (s), 28.48 (s), 26.29 (s), 17.90 (s) ppm.

**3n**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.24$ (t, $J = 7.7$ Hz, 1H), 7.12 (d, $J = 7.0$ Hz, 1H), 6.84 – 6.69 (m, 2H), 3.42 – 3.32 (m, 2H), 3.04 (s, 3H), 2.93 (t, $J = 6.4$ Hz, 2H), 2.14 (tt, $J = 10.1$, 5.0 Hz, 2H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 146.90$ (s), 128.96 (s), 127.21 (s), 122.98 (s), 116.37 (s), 111.11 (s), 51.43 (s), 39.26 (s), 27.97 (s), 22.65 (s) ppm.

**3o**: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 7.20 – 7.05$ (m, 2H), 6.71 (dd, $J = 11.0$, 3.7 Hz, 1H), 6.54 (d, $J = 8.1$ Hz, 1H), 3.32 (dd, $J = 11.0$, 5.3 Hz, 2H), 2.98 (t, $J = 8.0$ Hz, 2H), 2.80 (s, 3H) ppm. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 153.42$ (s), 130.36 (s), 127.37 (s), 124.32 (s), 117.85 (s), 107.31 (s), 56.21 (s), 36.35 (s), 28.79 (s) ppm.
Fig. S4 The $^1$H NMR and $^{13}$C NMR spectra of 2a.
Fig.S5 The $^1$H NMR and $^{13}$C NMR spectra of 2a'.
Fig. S6 The $^1$H NMR and $^{13}$C NMR spectra of 2e.
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Fig. S8 The $^1$H NMR and $^{13}$C NMR spectra of 2q.
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