

## Supporting Information

### Photo-induced, strain-promoted cycloadditions of trans-cycloheptenones and azides

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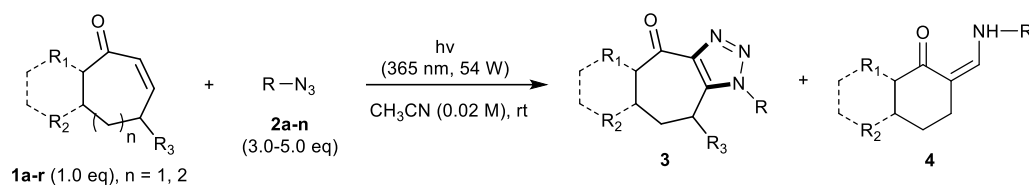
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## 1. General Information

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR were recorded on Bruker AV400 spectrometer. TMS was used as internal standard for  $^1\text{H}$  NMR (7.26 ppm), and solvent signal was used as reference for  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, qd = quarter doublet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2 QTOF MS. UV-Visible absorption spectrum were recorded on U-3900H spectrometer. The commercially available UV lamp (model: Philips PL-L 18W/10/4P, emission wave-length range: 350-400 nm;  $\lambda_{\text{max}}$ : 365 nm) was used as light resource. Reactions were monitored by Thin Layer Chromatography on plates ( $\text{GF}_{254}$ ) supplied by Yantai Chemicals (China) using UV light as visualizing agent and an ethanolic solution of Potassium permanganate, and heat as developing agents. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China).

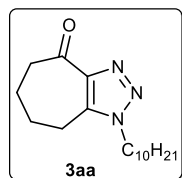
Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically ( $^1\text{H}$  NMR) homogeneous materials.

## 2. General Procedure for Cycloaddition of Cycloheptenones and Azides

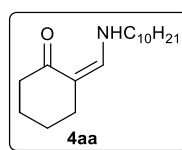


A quartz tube was charged with a solution of cycloheptenone (1.0 equiv) and azide derivatives (3.0-5.0 equiv) in anhydrous  $\text{CH}_3\text{CN}$  (0.02 M of cycloheptenone). The tube was irradiated with 365 nm UV lamps (3 x 18 W) at room temperature. The progress of the reaction was monitored by TLC. After completion, the crude reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography to give the triazolines and enamines.

## 3. Analysis Data of 1,2,3-triazole and Enaminones

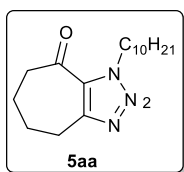


**3aa** (65%) : Following the general procedure, the product was obtained as a white solid (86.3 mg, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 4.24 (t,  $J$  = 7.4 Hz, 2H), 2.91 (t,  $J$  = 6.2 Hz, 2H), 2.80 (t,  $J$  = 5.6 Hz, 2H), 2.11-2.06 (m, 2H), 1.98-1.93 (m, 2H), 1.89-1.82 (m, 2H), 1.32-1.24 (m, 14H), 0.86 (t,  $J$  = 6.6 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  193.2, 144.1, 139.4, 48.2, 43.7, 31.8, 29.7, 29.4, 29.3, 29.2, 29.0, 26.5, 25.3, 24.7, 22.6, 22.3, 14.0; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{17}\text{H}_{29}\text{N}_3\text{O}$  292.2389, found 292.2376.

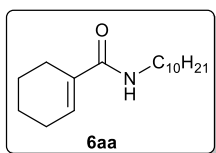


**4aa** (16%) : Following the general procedure, the product was obtained as brown oil (19.4 mg, 16%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 10.20 (brs, 1H), 6.60 (d,  $J$  = 12.4 Hz, 1H), 3.16 (t + t,  $J$  = 6.4, 6.4 Hz, 2H), 2.30 (t + t,  $J$  = 6.0, 6.4 Hz, 4H), 1.77-1.71 (m, 2H), 1.69-1.63 (m, 2H), 1.60-1.53 (m, 2H), 1.36-

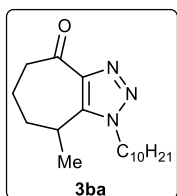
1.28 (m, 14H), 0.88 (t,  $J = 6.4$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 197.2, 153.3, 101.1, 49.1, 37.6, 31.9, 31.2, 29.5, 29.49, 29.3, 29.2, 27.8, 26.6, 24.1, 22.9, 22.7, 14.1$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{17}\text{H}_{31}\text{NO}$  266.2484, found 266.2472.



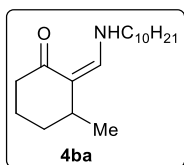
**5aa** (6%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 4.61$  (t,  $J = 7.4$  Hz, 2H), 3.12 (dd,  $J = 5.6$  Hz, 2H), 2.79-2.76 (m, 2H), 2.02-1.91 (m, 4H), 1.85-1.78 (m, 2H), 1.31-1.25 (m, 14H), 0.87 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 192.2, 152.0, 131.1, 51.0, 43.9, 31.9, 30.2, 29.5, 29.4, 29.3, 29.1, 26.4, 24.9, 22.7, 22.3, 14.1$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{17}\text{H}_{29}\text{N}_3\text{O}$  292.2389, found 292.2376.



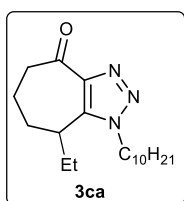
**6aa** (3%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 6.61$ -6.59 (m, 1H), 5.69 (brs, 1H), 3.28 (t + t,  $J = 6.8, 7.2$  Hz, 2H), 2.24-2.18 (m, 2H), 2.17-2.11 (m, 2H), 1.70-1.64 (m, 2H), 1.61-1.55 (m, 2H), 1.52-1.47 (m, 2H), 1.32-1.24 (m, 14H), 0.86 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 168.6, 133.2, 133.17, 39.6, 31.9, 29.7, 29.5, 29.3, 29.3, 27.0, 25.3, 24.3, 22.7, 22.66, 22.2, 21.6, 14.1$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{17}\text{H}_{31}\text{NO}$  266.2484, found 266.2472.



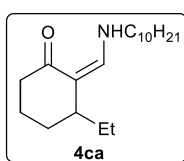
**3ba** (40%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.31$  (ddd,  $J = 14.2, 8.4, 6.4$  Hz, 1H), 4.13 (ddd,  $J = 14.2, 8.3, 6.8$  Hz, 1H), 3.33-3.22 (m, 1H), 2.88 (ddd,  $J = 17.0, 6.8, 2.8$  Hz, 1H), 2.73-2.65 (m, 1H), 2.14-2.01 (m, 3H), 1.99-1.85 (m, 3H), 1.37-1.24 (m, 17H), 0.86 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 193.8, 143.4, 143.0, 48.1, 44.2, 33.0, 31.8, 30.2, 29.4, 29.3, 29.2, 29.0, 28.7, 26.7, 22.6, 20.4, 17.6, 14.1$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{31}\text{N}_3\text{O}$  306.2545, found 306.2545.



**4ba** (38%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.17$  (brs, 1H), 6.60 (d,  $J = 12.4$  Hz, 1H), 3.15 (t + t,  $J = 6.8, 6.8$  Hz, 2H), 2.35-2.23 (m, 3H), 1.95-1.85 (m, 1H), 1.79-1.69 (m, 1H), 1.62-1.49 (m, 4H), 1.34-1.25 (m, 14H), 1.16 (d,  $J = 7.2$  Hz, 3H), 0.87 (t,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 197.2, 153.4, 107.00, 49.2, 37.8, 31.9, 31.86, 31.2, 29.5, 29.49, 29.3, 29.2, 26.6, 23.6, 22.7, 19.6, 14.1$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{33}\text{NO}$  280.2640, found 280.2642.

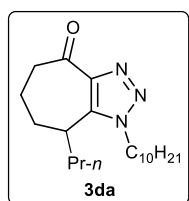


**3ca** (28%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.33$  (ddd,  $J = 13.6, 8.0, 6.4$  Hz, 1H), 4.10 (ddd,  $J = 13.6, 7.6, 6.8$  Hz, 1H), 3.02-2.96 (m, 1H), 2.86 (ddd,  $J = 16.4, 6.8, 2.8$  Hz, 1H), 2.76-2.62 (m, 1H), 2.24 (ddd,  $J = 13.2, 7.7, 4.4$  Hz, 1H), 2.06-1.82 (m, 4H), 1.74-1.49 (m, 3H), 1.40-1.19 (m, 14H), 1.00 (t,  $J = 7.4$  Hz, 3H), 0.87 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 194.1, 143.43, 143.2, 48.2, 44.1, 35.3, 31.8, 30.2, 29.4, 29.3, 29.2, 29.0, 28.4, 27.3, 26.6, 22.6, 17.8, 14.1, 11.9$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}$  320.2702, found 320.2702.

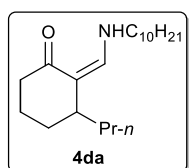


**4ca** (52%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.40$  (brs, 1H), 6.65 (d,  $J = 12.5$  Hz, 1H), 3.18 (t + t,  $J = 6.4, 6.8$  Hz, 2H), 2.31-2.25 (m, 2H), 2.24-2.18 (m, 1H), 1.70-1.59 (m, 4H), 1.58-1.51 (m, 2H), 1.45-1.37 (m, 2H), 1.33-1.25 (m, 14H), 0.88 (t,  $J = 6.8$  Hz, 3H), 0.87 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 197.1, 154.3, 105.9, 49.3, 38.2, 37.4, 31.9, 31.2, 30.2, 29.5, 29.49, 29.3, 29.2,$

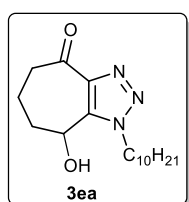
27.4, 26.6, 22.7, 18.6, 14.1, 11.7; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>35</sub>NO 294.2797, found 294.2796.



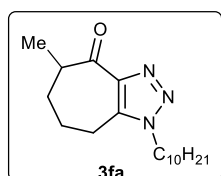
**3da** (27%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 4.32 (ddd, *J* = 14.0, 8.0, 6.8 Hz, 1H), 4.09 (ddd, *J* = 14.0, 8.0, 7.2 Hz, 1H), 3.12-3.06 (m, 1H), 2.85 (ddd, *J* = 16.6, 6.6, 2.7 Hz, 1H), 2.73-2.64 (m, 1H), 2.24-2.17 (m, 1H), 2.09-1.80 (m, 5H), 1.70-1.59 (m, 1H), 1.53-1.39 (m, 2H), 1.35-1.20 (m, 15H), 0.94 (t, *J* = 7.1 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 194.0, 143.5, 143.3, 48.1, 44.1, 36.2, 33.3, 31.8, 30.1, 29.4, 29.3, 29.2, 29.0, 28.7, 26.6, 22.6, 20.3, 17.8, 14.0, 13.7; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>35</sub>N<sub>3</sub>O 334.2858, found 334.2852.



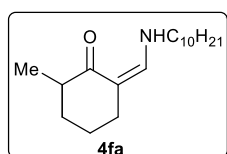
**4da** (52%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 10.43 (brs, 1H), 6.67 (d, *J* = 12.4 Hz, 1H), 3.21 (t + t, *J* = 6.8, 6.8 Hz, 2H), 2.37-2.28 (m, 3H), 1.86-1.54 (m, 9H), 1.43-1.28 (m, 15H), 0.93 (t, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 197.1, 154.2, 106.1, 49.3, 40.1, 37.3, 36.3, 31.9, 31.2, 29.5, 29.5, 29.3, 29.2, 27.9, 26.6, 22.7, 20.3, 18.5, 14.3, 14.1; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>37</sub>NO 308.2953, found 308.2952.



**3ea** (82%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 4.51 (dt, *J* = 13.8, 7.6 Hz, 1H), 4.42 (dt, *J* = 13.8, 7.5 Hz, 1H), 3.97 (d, *J* = 8.4 Hz, 1H), 2.79 (ddd, *J* = 18.2, 8.1, 2.8 Hz, 1H), 2.65 (ddd, *J* = 18.2, 9.2, 3.6 Hz, 1H), 2.36-2.16 (m, 3H), 2.00-1.93 (m, 2H), 1.78-1.73 (m, 1H), 1.39-1.27 (m, 14H), 0.89 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 193.7, 142.0, 139.9, 63.4, 43.7, 35.1, 31.8, 29.9, 29.5, 29.4, 29.3, 29.1, 26.7, 22.6, 16.7, 14.1; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>29</sub>N<sub>3</sub>O<sub>2</sub> 308.2338, found 308.2339.

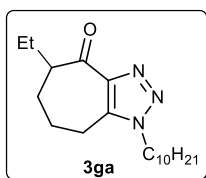


**3fa** (47%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 4.23 (t, *J* = 7.4 Hz, 2H), 2.80-2.85 (m, 2H), 2.78-2.69 (m, 1H), 2.13-1.98 (m, 3H), 1.86-1.79 (m, 2H), 1.72-1.64 (m, 1H), 1.29-1.22 (m, 17H), 0.85 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 196.6, 144.3, 139.3, 48.1, 46.2, 31.7, 30.7, 29.7, 29.3, 29.28, 29.1, 28.9, 26.4, 24.1, 23.8, 22.6, 17.3, 14.0; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>31</sub>N<sub>3</sub>O 306.2545, found 306.2543.

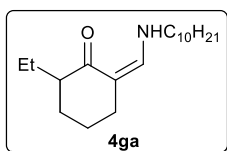


**4fa** (20%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 9.69 (brs, 1H), 6.58 (d, *J* = 12.4 Hz, 1H), 3.13 (t + t, *J* = 6.4, 6.8 Hz, 2H), 2.33-2.26 (m, 3H), 1.93-1.86 (m, 1H), 1.78-1.70 (m, 1H), 1.60-1.50 (m, 4H), 1.35-1.25 (m, 14H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 200.2, 153.1, 100.5, 49.1, 40.9, 31.9, 31.4, 31.1, 29.5, 29.5, 29.3, 29.2, 28.3, 26.6, 22.7, 22.6, 17.6, 14.1; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>18</sub>H<sub>33</sub>NO 280.2640, found 280.2638.

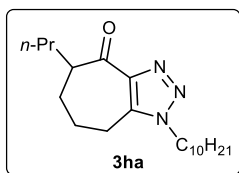




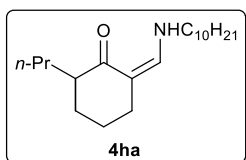
**3ga** (52%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.25$  (td,  $J = 7.2, 3.4$  Hz, 2H), 2.88-2.86 (m, 2H), 2.62-2.55 (m, 1H), 2.10-1.98 (m, 3H), 1.96-1.89 (m, 1H), 1.87-1.81 (m, 2H), 1.77-1.72 (m, 1H), 1.62-1.55 (m, 1H), 1.31-1.25 (m, 14H), 0.96 (t,  $J = 7.4$  Hz, 3H), 0.87 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 195.6, 144.6, 139.1, 52.9, 48.2, 31.8, 29.8, 29.4, 29.3, 29.2, 29.0, 27.7, 26.5, 24.5, 24.2, 23.1, 22.6, 14.1, 11.5$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}$  320.2702, found 320.2702.



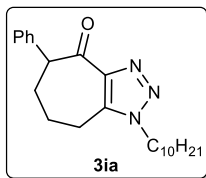
**4ga** (21%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.21$  (brs, 1H), 6.62 (d,  $J = 12.4$  Hz, 1H), 3.18 (td + td,  $J = 6.8, 2.4$  Hz, 2H), 2.34-2.30 (m, 2H), 2.17-2.10 (m, 1H), 1.96-1.88 (m, 2H), 1.83-1.74 (m, 1H), 1.57-1.51 (m, 3H), 1.49-1.42 (m, 2H), 1.36-1.28 (m, 14H), 0.95 (t,  $J = 7.5$  Hz, 3H), 0.90 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 199.7, 153.1, 101.0, 49.1, 47.4, 31.9, 31.2, 29.5, 29.5, 29.3, 29.25, 28.2, 27.5, 26.6, 24.7, 22.7, 22.7, 14.1, 11.7$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{35}\text{NO}$  294.2797, found 294.2787



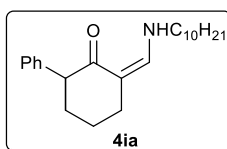
**3ha** (43%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.24$  (td,  $J = 7.3, 4.2$  Hz, 2H), 2.89-2.84 (m, 2H), 2.70-2.63 (m, 1H), 2.10-1.97 (m, 3H), 1.89-1.81 (m, 3H), 1.75-1.68 (m, 1H), 1.53-1.44 (m, 1H), 1.42-1.35 (m, 2H), 1.32-1.24 (m, 14H), 0.91 (t,  $J = 7.3$  Hz, 3H), 0.86 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 195.8, 144.5, 139.1, 51.2, 48.2, 33.6, 31.8, 29.8, 29.4, 29.3, 29.2, 29.0, 28.0, 26.5, 24.2, 23.0, 22.6, 20.2, 14.1$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{20}\text{H}_{35}\text{N}_3\text{O}$  334.2858, found 334.2856.



**4ha** (34%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.19$  (brs, 1H), 6.59 (d,  $J = 12.4$  Hz, 1H), 3.15 (td + td,  $J = 6.8, 2.3$  Hz, 2H), 2.31-2.27 (m, 2H), 2.21-2.14 (m, 1H), 1.92-1.82 (m, 2H), 1.79-1.71 (m, 1H), 1.57-1.50 (m, 3H), 1.45-1.33 (m, 4H), 1.31-1.25 (m, 14H), 0.92 (t,  $J = 7.1$  Hz, 3H), 0.88 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 199.86, 153.12, 100.91, 49.09, 45.77, 34.17, 31.87, 31.16, 29.53, 29.48, 29.28, 29.25, 28.15, 28.09, 26.64, 22.66, 20.42, 14.26, 14.10$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{20}\text{H}_{37}\text{NO}$  308.2953, found 308.2947.

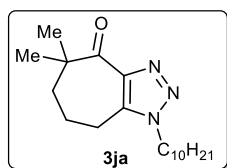


**3ia** (72%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.33$ -7.28 (m, 2H), 7.26-7.21 (m, 1H), 7.16-7.14 (m, 2H), 4.28 (td,  $J = 7.2, 2.7$  Hz, 2H), 3.99 (dd,  $J = 9.5, 4.0$  Hz, 1H), 3.0-2.87 (m, 2H), 2.34-2.14 (m, 3H), 2.07-1.98 (m, 1H), 1.93-1.85 (m, 2H), 1.34-1.26 (m, 14H), 0.88 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 193.6, 144.6, 140.6, 139.1, 128.6, 128.4, 126.9, 58.2, 48.3, 31.8, 30.9, 29.7, 29.4, 29.36, 29.2, 29.0, 26.5, 24.6, 23.0, 22.6, 14.1$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{23}\text{H}_{33}\text{N}_3\text{O}$  368.2702, found 368.2703.

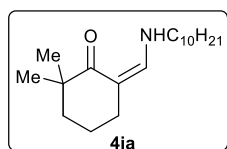


**4ia** (11%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.33$  (brs, 1H), 7.32-7.28 (m, 2H), 7.21-7.18 (m, 3H), 6.70 (d,  $J = 12.5$  Hz, 1H), 3.52 (dd,  $J = 9.8, 6.2$  Hz, 1H), 3.20-3.13 (m, 2H), 2.54-2.46 (m, 1H), 2.42-2.36 (m, 1H), 2.17-2.10 (m, 1H), 1.93-1.84 (m, 2H), 1.71-1.64 (m, 1H), 1.56-1.48 (m, 2H), 1.31-

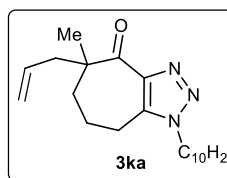
1.25 (m, 14H), 0.88 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 196.8, 153.9, 143.8, 128.7, 128.3, 126.1, 101.1, 53.6, 49.2, 32.2, 31.9, 31.0, 29.5, 29.46, 29.3, 29.2, 28.1, 26.6, 23.0, 22.7, 14.1$ .; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{23}\text{H}_{35}\text{NO}$  342.2797, found 342.2795.



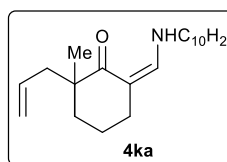
**3ja** (45%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.20$  (t,  $J = 7.4$  Hz, 2H), 2.82 (t,  $J = 6.3$  Hz, 2H), 2.07-1.97 (m, 2H), 1.86-1.73 (m, 4H), 1.30-1.23 (m, 14H), 1.23 (s, 6H), 0.85 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 198.9, 143.4, 138.0, 48.2, 47.2, 37.5, 31.8, 29.6, 29.4, 29.3, 29.2, 29.0, 27.0, 26.5, 25.3, 22.6, 20.4, 14.0$ .; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}$  320.2702, found 320.2702.



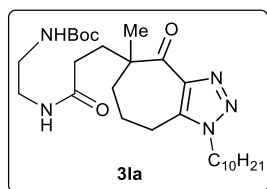
**4ja** (32%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.25$  (brs, 1H), 6.62 (d,  $J = 12.1$  Hz, 1H), 3.14 (t + t,  $J = 6.6, 6.4$  Hz, 2H), 2.31 (t,  $J = 6.2$  Hz, 2H), 1.69-1.63 (m, 2H), 1.61-1.57 (m, 2H), 1.55-1.50 (m, 2H), 1.32-1.25 (m, 14H), 1.13 (s, 6H), 0.87 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 202.7, 153.9, 99.3, 49.1, 41.0, 38.5, 31.9, 31.1, 29.5, 29.46, 29.3, 29.2, 28.8, 27.7, 26.7, 22.7, 20.7, 14.1$ .; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{35}\text{N}_3\text{O}$  294.2797, found 294.2790.



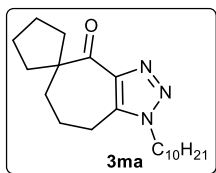
**3ka** (30%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 5.76$ -5.65 (m, 1H), 5.04 (d,  $J = 11.8$  Hz, 2H), 4.21 (t,  $J = 7.4$  Hz, 2H), 2.87-2.77 (m, 2H), 2.49 (dd,  $J = 13.7, 7.2$  Hz, 1H), 2.27 (dd,  $J = 13.7, 7.7$  Hz, 1H), 2.12-1.71 (m, 6H), 1.31-1.24 (m, 14H), 1.21 (s, 3H), 0.86 (t,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 198.3, 143.7, 138.1, 133.5, 118.5, 50.4, 44.1, 34.4, 31.8, 29.6, 29.4, 29.3, 29.2, 9.0, 26.5, 25.4, 24.5, 22.6, 20.0, 14.0$ .; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{21}\text{H}_{35}\text{N}_3\text{O}$  346.2858, found 346.2855.



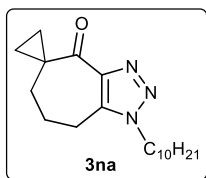
**4ka** (38%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 10.28$  (brs, 1H), 6.62 (d,  $J = 12.5$  Hz, 1H), 5.79-5.69 (m, 1H), 5.05-5.02 (m, 1H), 5.01-4.99 (m, 1H), 3.15 (t + t,  $J = 6.8, 6.4$  Hz, 2H), 2.42 (ddt,  $J = 13.5, 6.8, 1.3$  Hz, 1H), 2.31-2.27 (m, 2H), 2.17 (ddt,  $J = 13.5, 8.0, 1.1$  Hz, 1H), 1.76-1.62 (m, 2H), 1.56-1.50 (m, 2H), 1.48-1.42 (m, 2H), 1.31-1.25 (m, 14H), 1.10 (s, 3H), 0.88 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 201.7, 153.8, 135.5, 117.0$ KK, 99.9, 49.1, 44.2, 44.0, 34.6, 31.9, 31.1, 29.5, 29.46, 29.3, 29.2, 28.7, 26.7, 25.7, 22.7, 20.5, 14.1; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{21}\text{H}_{37}\text{N}_3\text{O}$  320.2953, found 320.2958.



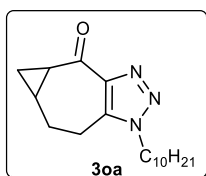
**3la** (80%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 6.40$  (d,  $J = 26.8$  Hz, 1H), 5.12 (brs, 1H), 4.28-4.16 (m, 2H), 3.33-3.29 (m, 2H), 3.24-3.19 (m, 2H), 2.87-2.83 (m, 2H), 2.20-2.12 (m, 3H), 2.06-1.95 (m, 2H), 1.91-1.81 (m, 5H), 1.42 (s, 9H), 1.32-1.25 (m, 14H), 1.22 (s, 3H), 0.87 (t,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 198.5, 173.5, 156.6, 143.6, 138.4, 79.4, 49.8, 48.3, 40.4, 40.2, 35.5, 35.3, 31.8, 31.4, 29.7, 29.6, 29.4, 29.36, 29.2, 29.0, 28.4, 26.6, 25.2, 24.5, 22.6, 20.0, 14.1$ .; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{28}\text{H}_{49}\text{N}_5\text{O}_4$  520.3863, found 520.3861.



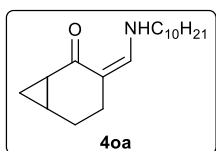
**3ma** (47%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.22 (t,  $J$  = 7.6 Hz, 2H), 2.83 (t,  $J$  = 6.2 Hz, 2H), 2.23-2.17 (m, 2H), 2.05-1.99 (m, 2H), 1.89-1.79 (m, 6H), 1.67-1.62 (m, 2H), 1.49-1.43 (m, 2H), 1.31-1.24 (m, 14H), 0.86 (t,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 199.2, 144.2, 138.1, 58.8, 48.2, 38.5, 36.0, 31.8, 29.6, 29.4, 29.3, 29.2, 29.0, 26.5, 25.5, 25.1, 22.6, 21.7, 14.1; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{21}\text{H}_{35}\text{N}_3\text{O}$  346.2858, found 346.2858.



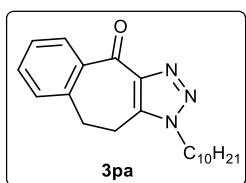
**3na** (70%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.22 (t,  $J$  = 8 Hz, 2H), 2.91 (t,  $J$  = 6.4 Hz, 2H), 2.12 (dt,  $J$  = 10.6, 5.2 Hz, 2H), 1.90-1.79 (m, 4H), 1.52 (dt,  $J$  = 3.2, 3.6 Hz, 2H), 1.31-1.23 (m, 14H), 0.86 (t,  $J$  = 6.8 Hz, 3H), 0.79 (dt,  $J$  = 3.2, 3.6 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 193.9, 144.0, 138.8, 48.2, 32.9, 32.03, 31.8, 29.5, 29.4, 29.3, 29.2, 28.9, 26.5, 25.3, 23.3, 22.6, 21.0, 14.1; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{31}\text{N}_3\text{O}$  318.2545, found 318.2545.



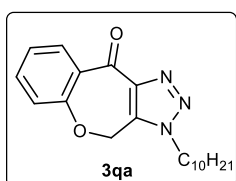
**3oa** (50%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.27 (dt,  $J$  = 14.4, 7.5 Hz, 1H), 4.18 (dt,  $J$  = 14.4, 7.3 Hz, 1H), 2.91 (dt,  $J$  = 17.1, 3.6 Hz, 1H), 2.66 (ddd,  $J$  = 17.1, 13.2, 3.9 Hz, 1H), 2.52-2.46 (m, 1H), 2.23-2.15 (m, 2H), 1.87-1.79 (m, 3H), 1.32-1.23 (m, 14H), 1.19-1.15 (m, 2H), 0.86 (t,  $J$  = 6.7 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 192.4, 142.7, 137.6, 48.2, 31.8, 29.7, 29.4, 29.3, 29.2, 29.1, 28.9, 26.5, 22.6, 21.8, 20.9, 20.3, 14.0, 11.8; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{29}\text{N}_3\text{O}$  304.2389, found 304.2384.



**4oa** (17%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 9.69 (brs, 1H), 6.48 (d,  $J$  = 12.4 Hz, 1H), 3.13 (t + t,  $J$  = 6.6, 6.8 Hz, 2H), 2.35 (dt,  $J$  = 15.2, 7.5 Hz, 1H), 2.20-2.11 (m, 1H), 1.99-1.94 (m, 2H), 1.73-1.67 (m, 2H), 1.59-1.54 (m, 2H), 1.33-1.22 (m, 14H), 1.14-1.10 (m, 2H), 0.87 (t,  $J$  = 6.7 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 197.1, 152.0, 97.6, 49.0, 31.9, 31.3, 29.5, 29.5, 29.3, 29.27, 26.6, 23.4, 23.00, 22.7, 21.3, 16.6, 14.1, 7.5; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{31}\text{NO}$  278.2484, found 278.2479.

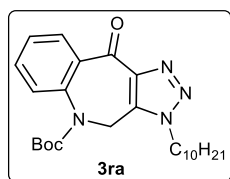


**3pa** (70%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.99 (d,  $J$  = 7.7 Hz, 1H), 7.47 (dd,  $J$  = 7.7, 7.2 Hz, 1H), 7.40 (dd,  $J$  = 7.2, 7.7 Hz, 1H), 7.27 (d,  $J$  = 7.7 Hz, 1H), 4.29 (t,  $J$  = 7.3 Hz, 2H), 3.23-3.20 (m, 2H), 3.07-3.04 (m, 2H), 1.88-1.81 (m, 2H), 1.30-1.22 (m, 14H), 0.85 (t,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 184.3, 144.2, 141.1, 138.4, 137.9, 132.7, 130.4, 130.0, 127.8, 48.4, 33.3, 31.8, 29.8, 29.4, 29.3, 29.2, 29.0, 26.5, 23.7, 22.6, 14.1; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}$  340.2389, found 340.2386.

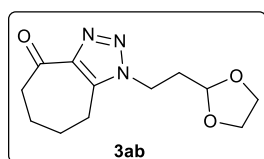


**3qa** (60%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 8.21 (dd,  $J$  = 8.0, 1.8 Hz, 1H), 7.55 (td,  $J$  = 8.0, 1.8 Hz, 1H), 7.32 (td,  $J$  = 8.1, 0.9 Hz, 1H, 1H), 7.20 (dd,  $J$  = 8.1, 0.9 Hz, 1H), 5.26 (s, 2H), 4.35 (t,  $J$  = 7.3 Hz, 2H), 1.92-1.85 (m, 2H), 1.32-1.25 (m, 14H), 0.87 (t,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 179.2, 157.7, 145.2, 139.0, 134.9, 131.7, 130.1, 125.5, 122.4, 64.0, 48.9, 31.8, 30.2, 29.4, 29.3, 29.2, 28.92, 26.4, 22.6, 14.1; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for

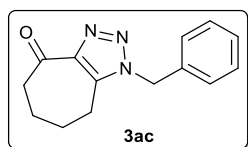
C<sub>20</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub> 342.2182, found 342.2180.



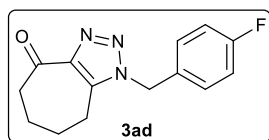
**3ra** (51%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 8.12 (d, *J* = 7.6 Hz, 1H), 7.55 (dd, *J* = 7.2, 7.6 Hz, 1H), 7.44 (dd, *J* = 7.7, 7.2 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 5.61 (d, *J* = 16.7 Hz, 1H), 4.46 (dt, *J* = 14.5, 7.3 Hz, 1H), 4.32 (dt, *J* = 14.5, 7.2 Hz, 1H), 4.28 (d, *J* = 16.7 Hz, 1H), 1.93-1.89 (m, 2H), 1.32-1.27 (m, 14H), 1.23 (s, 9H), 0.85 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 180.9, 153.6, 144.3, 140.7, 139.4, 135.1, 133.0, 131.0, 129.4, 128.1, 82.2, 48.9, 41.5, 31.8, 29.9, 29.4, 29.3, 29.2, 28.9, 27.9, 26.4, 22.6, 14.0; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>36</sub>N<sub>4</sub>O<sub>3</sub> 441.2866, found 441.2883.



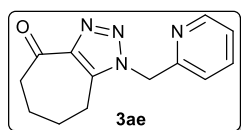
**3ab** (50%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 4.89 (t, *J* = 4.1 Hz, 1H), 4.38 (t, *J* = 7.4 Hz, 2H), 3.98-3.94 (m, 2H), 3.86-3.83 (m, 2H), 2.92 (t, *J* = 6.2 Hz, 2H), 2.79-2.76 (m, 2H), 2.29-2.24 (m, 2H), 2.09-2.03 (m, 2H), 1.96-1.90 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 193.2, 144.0, 139.9, 101.3, 65.1, 43.6, 42.9, 33.2, 25.1, 24.6, 22.2; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub> 252.1348, found 252.1347.



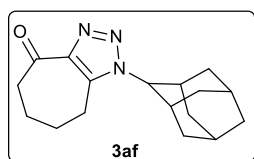
**3ac** (49%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.38-7.30 (m, 3H), 7.17 (d, *J* = 6.7 Hz, 2H), 5.53 (s, 2H), 2.81-2.76 (m, 4H), 2.01-1.96 (m, 2H), 1.91-1.86 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 193.3, 144.4, 140.2, 133.8, 129.1, 128.5, 127.1, 52.0, 43.7, 25.0, 24.7, 22.0; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O 242.1293, found 242.1291.



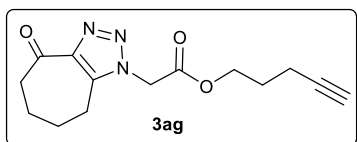
**3ad** (66%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.16 (d + d, *J* = 5.2 Hz, 2H), 7.02 (d + d, *J* = 5.2 Hz, 2H), 5.48 (s, 2H), 2.78-2.75 (m, 4H), 2.00-1.95 (m, 2H), 1.90-1.85 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 193.3, 163.8, 161.4, 139.9, 129.6, 129.1, 129.0, 116.2, 116.0, 51.4, 43.7, 25.0, 24.8, 22.0; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>14</sub>FN<sub>3</sub>O 260.1199, found 260.1205.



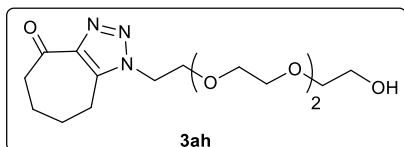
**3ae** (27%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.51 (d, *J* = 4.5 Hz, 1H), 7.66 (ddd, *J* = 7.7, 7.8, 1.2 Hz, 1H), 7.23 (dd, *J* = 7.2, 5.2 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 5.60 (s, 2H), 2.92 (t, *J* = 6.2 Hz, 2H), 2.76 (t, *J* = 6.0 Hz, 2H), 2.02-1.96 (m, 2H), 1.92-1.86 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ = 193.3, 153.9, 149.7, 144.4, 140.9, 137.4, 123.5, 122.0, 53.6, 43.8, 25.1, 24.9, 22.2. HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>4</sub>O 243.1246, found 243.1247.



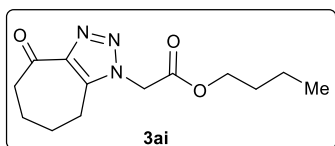
**3af** (35%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 3.23 (t, *J* = 5.6 Hz, 2H), 2.80 (t, *J* = 6.0 Hz, 2H), 2.40 (s, 6H), 2.30 (s, 3H), 2.07-2.01 (m, 2H), 1.97-1.91 (m, 2H), 1.81 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 194.0, 146.2, 140.3, 62.9, 42.4, 41.8, 35.8, 29.7, 26.1, 25.4, 21.7; HRMS (m/z): [M+H]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>23</sub>N<sub>3</sub>O 286.1919, found 286.1929.



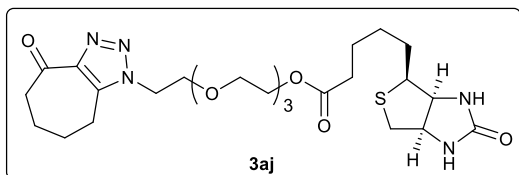
**3ag** (28%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 5.12 (s, 2H), 4.32 (t,  $J$  = 6.3, 6.3, 2H), 2.88 (t,  $J$  = 6.1, 6.4, 2H), 2.82-2.79 (m, 2H), 2.26 (td,  $J$  = 6.9, 2.7 Hz, 2H), 2.10-2.04 (m, 2H), 1.99-1.93 (m, 3H), 1.87 (tt,  $J$  = 6.4, 6.6, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.1, 165.7, 144.2, 141.2, 82.3, 69.6, 65.0, 49.1, 43.8, 27.1, 25.1, 24.6, 22.2, 15.0 ppm; HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{17}\text{N}_3\text{O}_3$  276.1348, found 276.1354.



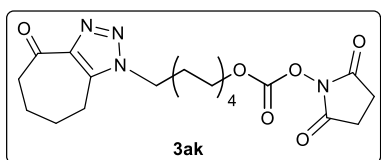
**3ah** (43%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 4.45 (t,  $J$  = 5.2 Hz, 2H), 3.90 (t,  $J$  = 5.2 Hz, 2H), 3.71-3.69 (m, 2H), 3.63-3.54 (m, 11H), 3.02-2.99 (dd,  $J$  = 6.8, 6.0 Hz, 2H), 2.82-2.79 (m, 2H), 2.07-2.01 (m, 2H), 1.98-1.91 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 193.4, 143.9, 141.5, 72.4, 70.5, 70.4, 70.2, 69.8, 61.6, 48.1, 43.6, 25.2, 24.7, 22.2; HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{15}\text{H}_{25}\text{N}_3\text{O}_5$  328.1872, found 328.1871.



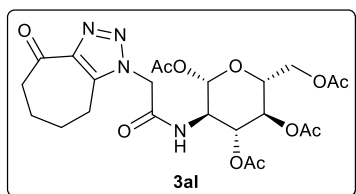
**3ai** (75%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 5.10 (s, 2H), 4.19 (t,  $J$  = 6.7 Hz, 2H), 2.88 (t,  $J$  = 6.3 Hz, 2H), 2.84-2.81 (m, 2H), 2.11-2.05 (m, 2H), 2.00-1.94 (m, 2H), 1.67-1.59 (m, 2H), 1.40-1.30 (m, 2H), 0.91 (t,  $J$  = 7.4 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 193.0, 165.7, 144.2, 141.0, 66.4, 49.1, 43.7, 30.4, 25.1, 24.6, 22.1, 18.9, 13.6; HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{13}\text{H}_{19}\text{N}_3\text{O}_3$  266.1505, found 266.1501.



**3aj** (52%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 5.81 (brs, 1H), 5.19 (brs, 1H), 4.50 (dd,  $J$  = 7.6, 5.2 Hz, 1H), 4.46 (t,  $J$  = 5.1 Hz, 2H), 4.31 (dd,  $J$  = 6.8, 4.8 Hz, 1H), 4.22-4.20 (m, 2H), 3.91 (t,  $J$  = 5.1 Hz, 2H), 3.66 (t,  $J$  = 4.6 Hz, 3H), 3.61-3.58 (m, 2H), 3.57-3.54 (m, 6H), 3.17-3.12 (m, 1H), 3.01 (t,  $J$  = 6.2 Hz, 2H), 2.90 (dd,  $J$  = 12.8, 4.9 Hz, 1H), 2.84-2.79 (m, 2H), 2.34 (t,  $J$  = 7.5 Hz, 2H), 2.07-2.02 (m, 2H), 1.97-1.91 (m, 2H), 1.73-1.63 (m, 4H), 1.47-1.39 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 193.5, 173.6, 143.9, 141.5, 70.6, 70.5, 70.4, 69.9, 69.1, 63.3, 61.9, 60.0, 55.4, 48.2, 43.6, 40.5, 33.7, 28.3, 28.2, 25.1, 24.8, 24.7, 22.2; HRMS (m/z):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{25}\text{H}_{39}\text{N}_5\text{O}_7\text{S}$  487.2355, found 487.2363.

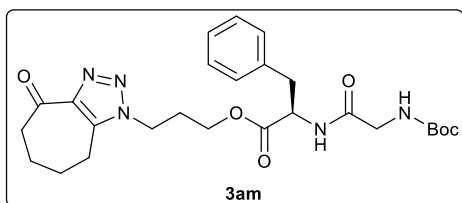


**3ak** (60%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 4.28 (t,  $J$  = 6.6, 2H), 4.22 (t,  $J$  = 7.4, 2H), 2.90 (t,  $J$  = 6.3, 2H), 2.81 (s, 4H), 2.78-2.75 (m, 2H), 2.09-2.03 (m, 2H), 1.96-1.90 (m, 2H), 1.87-1.81 (m, 2H), 1.73-1.66 (m, 2H), 1.31-1.26 (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 193.4, 168.8, 151.6, 144.1, 139.6, 71.5, 48.2, 43.7, 29.6, 29.1, 28.8, 28.3, 26.4, 25.5, 25.48, 25.3, 25.2, 24.7, 22.3 ppm; HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{30}\text{N}_4\text{O}_6$  435.2244, found 435.2234.



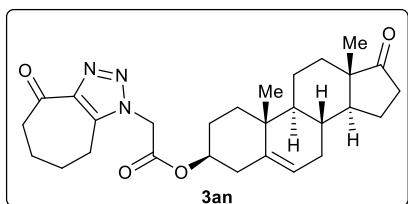
**3al** (54%):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.27 (d,  $J$  = 9.0 Hz, 1H), 5.97 (d,  $J$  = 8.8 Hz, 1H), 5.48 (t,  $J$  = 9.8 Hz, 1H), 5.15 (s, 2H), 5.07 (t,  $J$  = 9.7 Hz, 1H), 4.28 (dd,  $J$  = 12.5, 4.4 Hz, 1H), 4.22-4.15 (m, 1H), 4.09-4.05 (m, 1H), 3.96-3.92 (m, 1H), 2.95-2.91 (m, 2H), 2.81-2.78 (m, 2H), 2.09-2.05 (m + s, 6H), 2.03-1.99 (m + s + s, 7H), 1.93 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  = 194.0, 170.8, 170.5, 169.5, 169.3, 165.5, 143.9, 142.2, 91.8, 72.3, 72.28, 68.3, 61.7, 53.6, 51.0, 43.8, 25.0, 24.6, 22.0, 20.9, 20.8, 20.7, 20.66. HRMS (m/z):  $[\text{M}-\text{H}]^+$  calcd. for  $\text{C}_{23}\text{H}_{30}\text{N}_4\text{O}_{11}$  537.1833, found 537.1833.



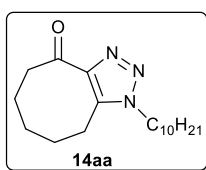
**3am** (70%):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.29-7.13 (m, 5H), 6.95 (d,  $J$  = 7.4 Hz, 1H), 5.44 (t,  $J$  = 5.0 Hz, 1H), 4.75 (dt,  $J$  = 7.4, 6.8 Hz, 1H), 4.24-4.10 (m, 3H), 4.08-4.02 (m, 1H), 3.86-3.72 (m, 2H), 3.08 (d,  $J$  = 6.8 Hz, 2H), 2.88-2.84 (m, 2H), 2.80-2.77 (m, 2H), 2.23-2.11 (m, 2H), 2.09-2.03 (m, 2H), 1.96-1.90 (m, 2H),

1.41 (s, 9H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 193.3, 171.2, 169.6, 143.9, 140.1, 135.7, 129.0, 128.6, 127.1, 61.6, 53.4, 44.5, 43.6, 37.7, 28.3, 28.2, 25.0, 24.4, 22.1; HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{26}\text{H}_{35}\text{N}_5\text{O}_6$  514.2666, found 514.2660.

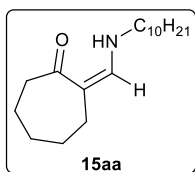


**3an** (27%):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 5.41 (d,  $J$  = 4.8 Hz, 1H), 5.09 (s, 2H), 4.75-4.67 (m, 1H), 2.88 (t,  $J$  = 6.2 Hz, 2H), 2.85-2.82 (m, 2H), 2.46 (dd,  $J$  = 19.2, 8.8 Hz, 1H), 2.36-2.33 (m, 2H), 2.14-2.06 (m, 4H), 2.00-1.82 (m, 6H), 1.68-1.63 (m, 4H), 1.57-1.46 (m, 2H), 1.31-1.23 (m, 2H), 1.18-1.10 (m, 1H), 1.04 (s, 3H), 1.02-0.98 (m, 1H), 0.88 (s,

3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 220.9, 193.1, 165.0, 144.2, 141.0, 139.0, 122.7, 76.5, 51.6, 50.0, 49.3, 47.5, 43.7, 37.8, 36.7, 36.6, 35.8, 31.4, 31.3, 30.7, 27.5, 25.1, 24.7, 22.2, 21.8, 20.3, 19.3, 13.5; HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{28}\text{H}_{37}\text{N}_3\text{O}_4$  480.2862, found 480.2866.

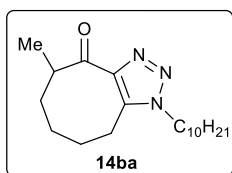


**14aa** (51%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.30 (t,  $J$  = 7.1 Hz, 2H), 3.11 (t,  $J$  = 6.3 Hz, 2H), 2.86 (t,  $J$  = 6.5 Hz, 2H), 1.90-1.78 (m, 6H), 1.58-1.49 (m, 2H), 1.32-1.25 (m, 14H), 0.87 (t,  $J$  = 6.6 Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 193.4, 145.8, 138.2, 48.1, 40.7, 31.8, 30.4, 29.4, 29.3, 29.2, 29.0, 26.5, 24.4, 23.8, 23.4, 22.6, 22.56, 14.1; HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{18}\text{H}_{31}\text{N}_3\text{O}$  306.2545, found 306.2551.

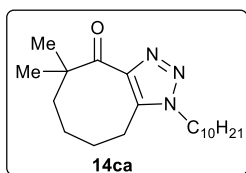


**15aa** (16%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 9.67 (brs, 1H), 6.61 (d,  $J$  = 12.4 Hz, 1H), 3.13 (t + t,  $J$  = 6.8, 6.8 Hz, 2H), 2.49-2.47 (m, 2H), 2.24-2.22 (m, 2H), 1.714-1.51 (m, 8H), 1.33-1.25 (m, 14H), 0.88 (t,  $J$  = 6.6 Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 202.7, 152.3, 106.1, 48.9, 44.5, 32.6, 32.0, 31.9, 31.3, 31.1, 29.5, 29.5, 29.3, 29.3, 26.7, 25.1, 22.7, 14.1. HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd.

for  $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}$  280.2640, found 280.2643.

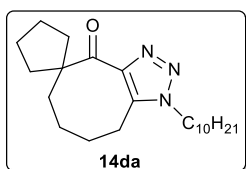


**14ba** (49%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.29$  (t,  $J = 7.4$  Hz, 2H), 3.28-3.12 (m, 2H), 3.02 (ddd,  $J = 15.6, 6.5, 2.6$  Hz, 1H), 1.92-1.72 (m, 4H), 1.68-1.57 (m, 3H), 1.30-1.22 (m, 15H), 1.19 (d,  $J = 6.4$  Hz, 3H), 0.85 (t,  $J = 6.4, 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 195.7, 146.3, 137.5, 48.1, 43.0, 33.5, 31.8, 30.5, 29.4, 29.3, 29.2, 29.0, 26.5, 24.5, 23.0, 22.6, 22.6, 16.8, 14.1$  ppm; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{19}\text{H}_{33}\text{N}_3\text{O}$  320.2702, found 320.2705.



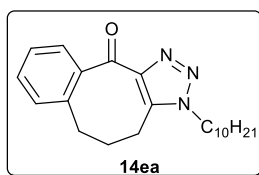
**14ca** (49%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.17$  (t,  $J = 7.5$  Hz, 2H), 2.68-2.66 (m, 2H), 1.90-1.83 (m, 2H), 1.80-1.70 (m, 6H), 1.37-1.25 (m, 14H), 1.19 (s, 6H), 0.86 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 206.40, 142.20, 136.64, 47.89, 46.98, 35.49, 31.80, 29.59, 29.41, 29.34, 29.20, 29.01, 26.58, 25.54, 23.13, 22.61, 22.23, 14.05$ ; HRMS ( $m/z$ ):

$[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{20}\text{H}_{35}\text{N}_3\text{O}$  334.2858, found 334.2865.



**14da** (61%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 4.18$  (t,  $J = 7.4$  Hz, 2H), 2.67 (d,  $J = 9.0$  Hz, 2H), 2.22-2.14 (m, 2H), 1.90-1.85 (m, 2H), 1.82-1.75 (m, 7H), 1.66-1.60 (m, 3H), 1.45-1.38 (m, 2H), 1.29-1.25 (m, 14H), 0.87 (t,  $J = 6.7$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 205.5, 142.9, 136.4, 100.0, 58.7, 47.9, 34.8, 31.8, 29.6, 29.4, 29.36, 29.2, 29.0, 26.6, 26.4, 25.7,$

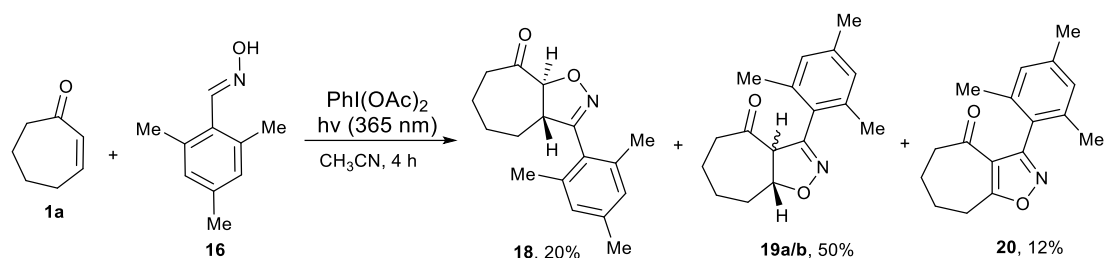
23.1, 22.6, 22.5, 14.1; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{22}\text{H}_{37}\text{N}_3\text{O}$  360.3015, found 360.3024.



**14ea** (60%):  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.75$  (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.48 (ddd,  $J = 7.7, 7.2, 1.4$  Hz, 1H), 7.35 (ddd,  $J = 7.6, 7.6, 1.2$  Hz, 1H), 7.20 (dd,  $J = 7.6, 0.8$  Hz, 1H), 4.31 (t,  $J = 7.6$  Hz, 2H), 2.73 (t,  $J = 6.5$  Hz, 2H), 2.61 (t,  $J = 6.6$  Hz, 2H), 1.98-1.92 (m, 2H), 1.90-1.82 (m, 2H), 1.31-1.23 (m, 14H), 0.85 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100

MHz):  $\delta = 186.2, 146.2, 139.4, 138.0, 137.7, 132.2, 130.2, 129.3, 127.1, 48.1, 31.8, 30.3, 30.0, 29.7, 29.4, 29.3, 29.2, 29.0, 26.5, 22.6, 19.6, 14.0$ .

## 4. Procedure for Cycloaddition of Cycloheptenone and Nitrile Oxide

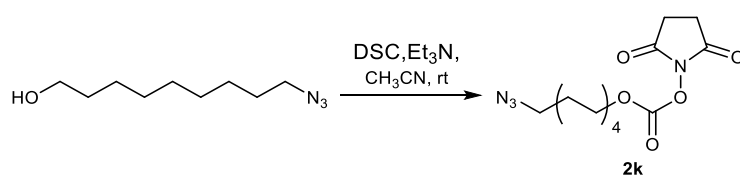


To a solution of cycloheptenone (33.7 mg, 0.306 mmol, 1.0 eq) was added mesitylene hydroxime (50 mg, 0.306 mmol, 1.0 eq) and  $\text{PhI}(\text{OAc})_2$  (98.6 mg, 0.306 mmol, 1.0 eq). The tube was irradiated with 365 nm UV lamps (3 x 18 W) at room temperature. After 10 h, the crude reaction mixture was concentrated under reduced pressure and purified by silica gel chromatography (PE:EA=20:1-4:1) to give compound **18** (16.6 mg, 20%), **19a/b** (41.5 mg, 50%) and **20** (9.9 mg, 12%)<sup>[1]</sup>.

**Dihydroisoxazole (18)**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 6.88 (d,  $J$  = 18.8 Hz, 2H), 5.17 (d,  $J$  = 15.2 Hz, 1H), 3.45 (ddd,  $J$  = 15.2, 12.3, 2.7 Hz, 1H), 2.79-2.72 (m, 1H), 2.47 (ddd,  $J$  = 19.4, 12.8, 3.2 Hz, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 2.15 (s, 3H), 2.10-1.91 (m, 3H), 1.78-1.67 (m, 1H), 1.65-1.54 (m, 1H), 1.34-1.23 (m, 1H),  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 204.4, 161.3, 139.1, 137.3, 136.0, 128.7, 128.6, 124.5, 90.1, 54.3, 41.3, 29.5, 28.1, 22.2, 21.0, 20.5, 19.8; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{17}\text{H}_{21}\text{NO}_2$  272.1651, found 272.1660.

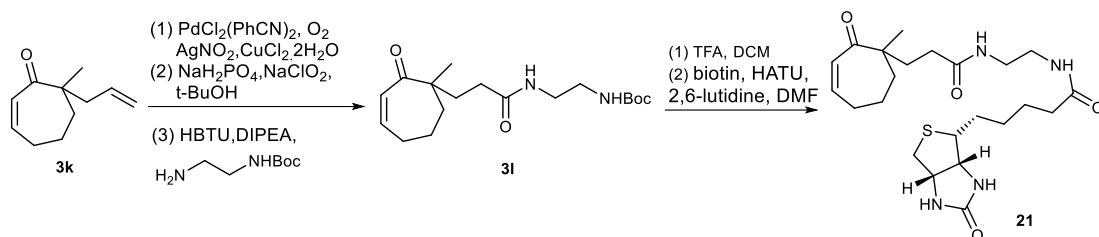
**isoxazole (20)**:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 6.90 (s, 2H), 3.21 (t,  $J$  = 6.4 Hz, 2H), 2.71-2.68 (m, 2H), 2.30 (s, 3H), 2.13-2.07 (m, 2H), 2.03 (s, 6H), 2.01-1.95 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 194.1, 176.5, 162.2, 138.5, 136.6, 128.0, 125.2, 117.7, 44.7, 29.7, 28.2, 24.2, 22.7, 21.2, 20.0; HRMS ( $m/z$ ):  $[\text{M}+\text{H}]^+$  calcd. for  $\text{C}_{17}\text{H}_{19}\text{NO}_2$  270.1494, found 270.1495.

## 5. Synthesis of Azide-derived DSC and HCO-modified Biotin-tag



9-azidononan-1-ol (1.02 g, 5.5 mmol) and  $\text{Et}_3\text{N}$  (1.14 mL, 8.3 mmol) were dissolved in anhydrous DCM (10 mL), and then N,N'-disuccinimidyl carbonate (2.12 g, 8.3 mmol) was added. The reaction mixture was stirred for overnight at room temperature. After the removal of the solvent, the residue was purified by silica gel flash column chromatography to give compound **2k** as a faint yellow oil (1.47 g, 82%)<sup>[2]</sup>.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.31 (t,  $J$  = 6.7 Hz, 2H), 3.25 (t,  $J$  = 7.0 Hz, 2H), 2.83 (s, 4H), 1.78-1.71 (m, 2H), 1.63-1.56 (m, 2H), 1.41-1.32 (m, 10H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 168.7, 151.6, 71.6, 51.4, 29.2, 28.9, 28.9, 28.8, 28.3, 26.6, 25.4, 25.3.  $[\text{M}-\text{H}]^+$  calcd. for  $\text{C}_{14}\text{H}_{22}\text{N}_4\text{O}_5$  325. 1512, found 325. 1515.





$\text{PdCl}_2(\text{PhCN})_2$  (138.1 mg, 0.36 mmol),  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (61.4 mg, 0.36 mmol) and  $\text{AgNO}_2$  (28.1 mg, 0.18 mmol) were weighed into a 50 mL vial charged with a stir bar. The vial was sparged for 2 minutes with oxygen (1 atm, balloon). Premixed and oxygen saturated *t*BuOH (7.5 mL) and  $\text{MeNO}_2$  (0.5 mL) followed by the alkene **3k** (500 mg, 3.04 mmol) were added via syringe. The solution was saturated with oxygen by an additional 45 seconds of sparging. The reaction was then allowed to stir at room temperature for 20 h. Next, the reaction was quenched with water (100 mL) and extracted three times with dichloromethane (50 mL). The combined organic layers were subsequently washed with a saturated solution of  $\text{NaHCO}_3$  and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the product was purified by flash column chromatography to afford the desired aldehyde (274 mg, 50%)<sup>[3]</sup>.

The above aldehyde (270 mg, 1.5 mmol), 2-methyl-2-butene (1.05 g, 15 mmol),  $\text{NaH}_2\text{PO}_4$  (0.8 M, 9.4 mL, 7.5 mmol) and  $\text{NaClO}_2$  (0.5 M, 9 mL, 4.5 mmol) were dissolved in *t*-BuOH (20 mL). The reaction mixture was stirred for 20 min at room temperature. After completion, the mixture was extracted with EtOAc (3 x 20 mL). The organic layer was dried over  $\text{MgSO}_4$  and concentrated under reduced pressure. The product was purified by flash column chromatography to afford acid (265 mg, 90%)<sup>[4]</sup>.

To a stirred solution of above acid (265 mg, 1.35 mmol) and *N*-Boc-ethylenediamine (261 mg, 1.63 mmol) in DMF (10 mL) at 25 °C were added DIPEA (350 mg, 2.72 mmol) and HBTU (620 mg, 1.63 mmol). The mixture was stirred for overnight. After completion, the mixture was quenched with saturated aqueous solution of  $\text{NaHCO}_3$  and extracted with EtOAc, washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The product was purified by flash column chromatography to afford amide **31** (407 mg, 89%)<sup>[5]</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 6.26 (dt + brs,  $J$  = 12.5, 4.2 Hz, 2H), 5.88 (d,  $J$  = 12.5 Hz, 1H), 5.07 (brs, 1H), 3.34-3.29 (m, 2H), 3.26-3.21 (m, 2H), 2.38-2.33 (m, 2H), 2.09 (t,  $J$  = 7.9 Hz, 2H), 1.87-1.79 (m, 3H), 1.72-1.61 (m, 3H), 1.42 (s, 9H), 1.11 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 209.1, 173.4, 156.8, 142.1, 130.1, 79.5, 51.7, 40.5, 40.3, 36.1, 35.6, 33.1, 31.5, 28.3, 23.6, 22.1; HRMS ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{18}\text{H}_{30}\text{N}_2\text{O}_4$  361.2103, found 361.2114.

To a solution of **31** (500 mg, 1.48 mmol) in DCM (10 mL) was added TFA (1.69 g, 14.8 mmol). After stirred for 30 min,  $\text{Et}_3\text{N}$  was added until pH turned to 10. The crude mixture was concentrated under reduced pressure and was directly used without purified. The biotin (370 mg, 1.51 mmol), HATU (570 mg, 1.51 mmol) and 2,6-lutidine (260 mg, 2.46 mmol) were dissolved in DMF (5 mL) and stirred for 30 min at room temperature under  $\text{N}_2$  atmosphere. The above crude primary amine dissolved in DMF (1 mL) was added to the reaction mixture and stirred for overnight. After completion, reaction was quenched with saturated aqueous solution of  $\text{NaHCO}_3$  and extracted with EtOAc, washed with water and brine, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure. The product was purified by flash column chromatography to afford amide **21** (260 mg, 45%)<sup>[5]</sup>;  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz):  $\delta$  = 6.45-6.39 (m, 1H), 5.93 (d,  $J$  = 12.4 Hz, 1H), 4.91 (s, 4H), 4.57-4.53 (m, 1H), 4.38-4.34 (m, 1H), 3.39 (d,  $J$  = 4.4 Hz, 1H), 3.36-3.35 (m, 1H), 3.30-3.23 (m, 1H),

2.98 (dt,  $J = 12.7, 4.7$  Hz, 1H), 2.75 (dd,  $J = 12.7, 4.1$  Hz, 1H), 2.49-2.43 (m, 2H), 2.27-2.23 (m, 2H), 2.19-2.14 (m, 2H), 1.96-1.59 (m, 8H), 1.52-1.43 (m, 2H), 1.18 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz):  $\delta = 211.1, 176.3, 176.1, 166.1, 144.2, 130.9, 63.3, 61.6, 57.0, 53.0, 41.1, 40.1, 40.0, 37.1, 36.9, 36.8, 34.3, 32.1, 29.8, 29.5, 26.8, 24.1, 23.2$ ; HRMS ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd. for  $\text{C}_{23}\text{H}_{36}\text{N}_4\text{O}_4\text{S}$  487.2235, found 487.2363.

## 6. In Vitro Labeling of DSC-Modified BSA with Biotin-tag

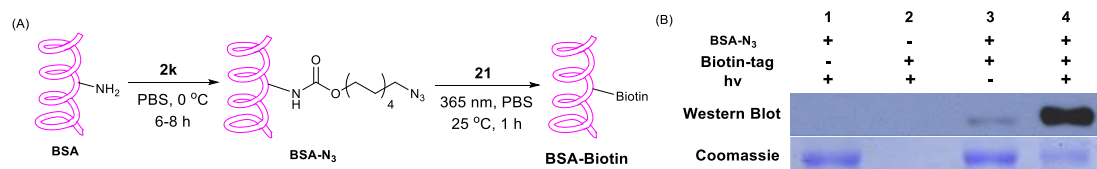


Figure S1. (A) Modification of free lysine residues on BSA with **2k** and subsequent labeling with **21**; (B) Western blot analysis of biotin-labeled BSA using Biotin-Tag **21** (240 μM) in PBS buffer with anti-biotin antibody. Protein loading was assessed by Coomassie staining (lower panel).

## Protein Modification

Bovine serum albumin conjugates were prepared by the treatment of BSA (10 mg/mL) with compound **2k** (150 μM) using a standard coupling protocol. Then the DSC-modified BSA was subsequently reacted with **21** at 25 °C.

## Labeling of DSC-Modified BSA in PBS buffer

A 210 μL aliquot of PBS buffer was added with compound **2k**-modified BSA (250 μL, 4 mg/mL in PBS) for a final concentration of the functionalized BSA (2 mg/mL). Biotin-tag **21** (40 μL, 3 mM) was then added and the reaction sample was shaken for 2 h under 365 nm UV. An equal amount of proteins was separated by SDS-polyacrylamide gels and was transferred to nitrocellulose membrane. After blocking with 5% nonfat milk in PBST (PBS containing 0.1% Tween 20), the membrane was incubated for 2 h at room temperature with HRP-conjugated anti-biotin antibody, washed thrice with PBST and developed using Super Signal West Dura Extended Duration Substrate (Thermo). X-OMAT film (Kodak) was used to detect the chemiluminescence.

## 7. References

- [1] B. C. Sanders, F. Friscourt, P. A. Ledin, N. E. Mbua, S. Arumugam, J. Guo, T. J. Boltje, V. V. Popik, G.-J. Boons, *J. Am. Chem. Soc.*, 2011, **133**, 949-957.
- [2] R. Baba, Y. Hori, S. Mizukami, K. Kikuchi, *J. Am. Chem. Soc.*, 2012, **134**, 14310-14313.
- [3] Z. K. Wickens, B. Morandi, R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2013, **52**, 11257-11260.
- [4] Y. Schmidt, K. Lehr, U. Breuninger, G. Brand, T. Reiss, B. Breit, *J. Org. Chem.*, 2010, **75**, 4424-4433.
- [5] K. C. Nicolaou, G. S. Tria, D. J. Edmonds, M. Kar, *J. Am. Chem. Soc.*, 2009, **131**, 15909-15917.

## 8. Computational Details

All calculations were run using Gaussian 09, Revision D.01<sup>S1</sup>, Equilibrium structures and transition states were fully optimized using B3LYP density functional method<sup>S2</sup> with the 6-311+g(d,p) basis sets. Frequency analyses at 298 K were performed on B3LYP/6-311+g(d,p) optimized geometries to obtain thermodynamic corrections and to confirm the nature of the stationary points as equilibrium structures (with all real frequencies) or transition states (with only one imaginary frequency), and relative free energies,  $\Delta G_{298}$ , were reported in all cases. All transition states were confirmed with IRC at the same level<sup>S3</sup>. For all calculations mentioned above, the solvent effect was modeled using the SMD model with acetonitrile as the solvent<sup>S4</sup>. Structural images were created using *Ball & Stick*.<sup>S5</sup>

### S1. Full Reference of Gaussian 09:

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

### S2. B3LYP references

- (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648-5652;
- (b) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 1372-1377;
- (c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785-789;
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### S3. IRC reference

- (a) C. Gonzalez,; H. B. Schlegel, *J. Phys. Chem.* 1990, **94**, 5523-5527.
- (b) K. Fukui, *Acc. Chem. Res.* 1981, **14**, 363-368.

### S4. Ball & Stick reference

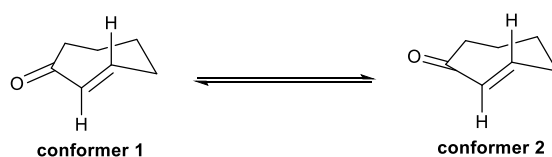
Müller, N.; Falk, A. *Ball & Stick 4.0 a12*, molecular graphics software for MacOS, Johannes Kepler University Linz, 2000.

### S5. SMD reference

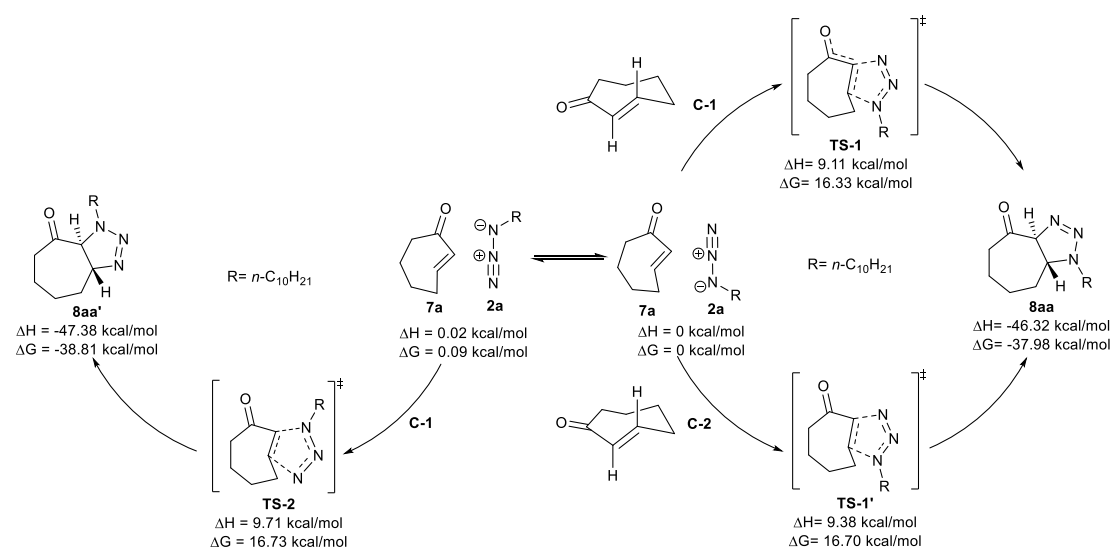
- (a) Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory Comput.* 2006, **2**, 364;
- (b) A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* 2009, **113**, 6378.

## Cycloadditions of *trans*-cycloheptenones and C<sub>10</sub>H<sub>21</sub>N<sub>3</sub>

### A) Proposed reaction pathways



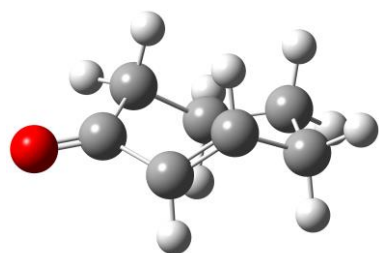
Calculations reveal the two low-energy conformers of *trans*-cycloheptenone exist in the reaction condition. **Conformer 1** has a more pronounced conjugation between C=O and C=C, whereas the **conformer 2** has no significant conjugation between C=O and C=C.



While undergoing cycloaddition with C<sub>10</sub>H<sub>21</sub>N<sub>3</sub>, *trans*-cycloheptenone has two options. Adopting **conformer 1** reveals a strong conjugation, benefiting to a concerted asynchronous process. As a result, for **conformer 1**, we can find **TS-1** as a reasonable transition state but can't find a TS corresponding to **TS-2** due to the unfavorable electronic distribution. At the same time, adopting **conformer 2** reveals no conjugation and a weak regioselectivity, manifested as **TS-1'** and **TS-2** with a similar  $\Delta G$  ( $\Delta\Delta G = 0.03$  kcal/mol).

### B) Geometries, structure images and energies

#### Conformer 1



C	-1.51717900	-0.16920900	0.04329700
O	-2.72219100	-0.23763200	-0.11568900

C	-0.49964500	-1.21475400	-0.28084600
C	0.61256400	-1.23685600	0.47046700
H	-0.44130400	-1.44719500	-1.34456100
H	0.51475100	-0.98193900	1.52544200
C	-0.78265800	1.13613400	0.39217400
H	-0.56624000	1.11019300	1.46894100
H	-1.47075700	1.96908000	0.22778700
C	1.94083200	-0.89505500	-0.10152900
H	2.80824800	-1.27267600	0.44400200
H	2.02251700	-1.17532800	-1.15454800
C	1.86807600	0.67590200	0.04637100
H	2.69033500	1.10613700	-0.53494500
H	2.05982400	0.92604600	1.09501700
C	0.55134500	1.37848900	-0.40223400
H	0.74918700	2.45313700	-0.34601800
H	0.37095500	1.16570200	-1.46179900

Zero-point correction = 0.154022 (Hartree/Particle)

Thermal correction to Energy = 0.161352

Thermal correction to Enthalpy = 0.162296

Thermal correction to Gibbs Free Energy = 0.122415

Sum of electronic and zero-point Energies = -347.870685

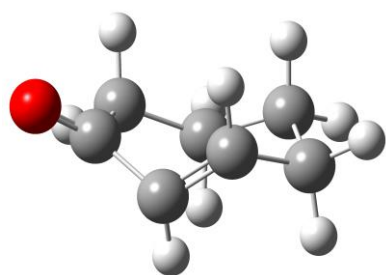
Sum of electronic and thermal Energies = -347.863354

Sum of electronic and thermal Enthalpies = -347.862410

Sum of electronic and thermal Free Energies = -347.902292

Imaginary Frequencies: 0

## Conformer 2



C	1.48359200	-0.12520700	0.09602400
O	2.58747700	-0.38530600	-0.33606600
C	0.45625800	-1.02545300	0.68618000
C	-0.47382900	-1.40609600	-0.20509000
H	0.11378700	-0.73013000	1.67650100
H	-0.17797200	-1.56472500	-1.24189800
C	0.82875600	1.26576200	-0.06560600
H	0.97423100	1.52055300	-1.12252100

H	1.42424200	1.98831500	0.50373500
C	-1.87676200	-0.92726100	0.00895100
H	-2.62634900	-1.42995500	-0.60604800
H	-2.17300200	-1.00148200	1.05950300
C	-1.76955300	0.58377800	-0.40241000
H	-2.73782300	1.05558000	-0.20526800
H	-1.61436800	0.64105200	-1.48570600
C	-0.67729800	1.43439900	0.31592500
H	-0.91726200	2.48170100	0.10744900
H	-0.79227700	1.32201000	1.39894400

Zero-point correction = 0.154224 (Hartree/Particle)

Thermal correction to Energy = 0.161526

Thermal correction to Enthalpy = 0.162470

Thermal correction to Gibbs Free Energy = 0.122603

Sum of electronic and zero-point Energies = -347.870726

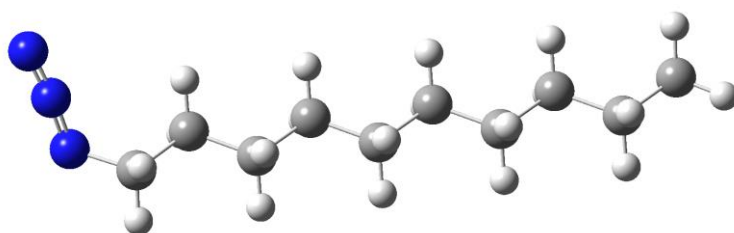
Sum of electronic and thermal Energies = -347.863425

Sum of electronic and thermal Enthalpies = -347.862480

Sum of electronic and thermal Free Energies = -347.902347

Imaginary Frequencies: 0

### C<sub>10</sub>H<sub>21</sub>N<sub>3</sub>



C	-7.19433700	0.60253500	0.11691700
H	-7.26008400	0.66745500	1.20786500
H	-7.15891700	1.62467600	-0.27382300
H	-8.11726600	0.14005500	-0.24469500
C	-5.96091400	-0.19643500	-0.31500700
H	-6.04169500	-1.22343600	0.06184200
H	-5.94118600	-0.27353900	-1.40903000
C	-4.64181300	0.41544000	0.17028100
H	-4.56246800	1.44407200	-0.20557600
H	-4.66214400	0.49162800	1.26542600
C	-3.40108500	-0.37601000	-0.25836600
H	-3.48142100	-1.40431000	0.11775300
H	-3.38205000	-0.45201900	-1.35339500
C	-2.08273000	0.23707600	0.22732400
H	-2.00239700	1.26544300	-0.14841800
H	-2.10145300	0.31250400	1.32233800

C	-0.84236000	-0.55474100	-0.20229000
H	-0.82248200	-0.62911000	-1.29728800
H	-0.92277100	-1.58325900	0.17281400
C	0.47492900	0.05846200	0.28566300
H	0.45619600	0.13231500	1.38041500
H	0.55730300	1.08634900	-0.08999300
C	1.71333000	-0.73645500	-0.14463800
H	1.73523800	-0.80812600	-1.23915200
H	1.63147000	-1.76422800	0.23050600
C	3.02642500	-0.11910800	0.35163200
H	3.01599500	-0.04951100	1.44460600
H	3.11920000	0.90321200	-0.03296300
C	4.24493400	-0.93582700	-0.08074300
H	4.30117100	-1.00775000	-1.17209500
H	4.19000300	-1.94785500	0.32003700
N	5.52763700	-0.38844600	0.44442400
N	5.94843300	0.63344800	-0.08408000
N	6.44271500	1.57011400	-0.49774500

Zero-point correction = 0.305085 (Hartree/Particle)

Thermal correction to Energy = 0.321438

Thermal correction to Enthalpy = 0.322382

Thermal correction to Gibbs Free Energy = 0.258307

Sum of electronic and zero-point Energies = -557.775859

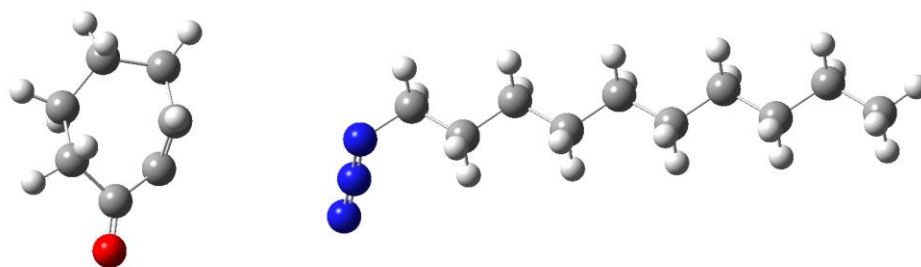
Sum of electronic and thermal Energies = -557.759506

Sum of electronic and thermal Enthalpies = -557.758562

Sum of electronic and thermal Free Energies = -557.822637

Imaginary Frequencies: 0

### (Reactant) 1



C	7.33467700	1.30243900	0.39387200
O	7.54505200	2.49989100	0.44494600
C	6.32921500	0.58969300	-0.45266300
C	5.80185700	-0.53980600	0.04419100
H	6.53416100	0.66634100	-1.52101000
H	5.63389000	-0.59091600	1.11969700

C	6.08519200	-1.85984400	-0.57878400
H	5.36983700	-2.65515200	-0.35865600
H	6.22362600	-1.78436100	-1.66021000
C	7.46003300	-2.17435800	0.13032800
H	7.91587400	-3.02751600	-0.38315600
H	7.24657100	-2.50151400	1.15328400
C	8.51791100	-1.03099100	0.18073800
H	9.43130600	-1.48256200	0.57938700
H	8.76256400	-0.72059800	-0.84115000
C	-11.44523800	0.28960700	0.35299400
H	-11.46612200	0.55681700	1.41454100
H	-11.49758500	1.21896000	-0.22333000
H	-12.34963200	-0.28666300	0.13749500
C	-10.18071200	-0.50298600	0.00787800
H	-10.17361200	-1.44269400	0.57363000
H	-10.20539700	-0.78496600	-1.05190600
C	-8.88600500	0.26655400	0.29363600
H	-8.89572500	1.20856600	-0.27027400
H	-8.86079200	0.54657900	1.35503100
C	-7.61463000	-0.51642000	-0.05296500
H	-7.60533500	-1.45797900	0.51141800
H	-7.64157400	-0.79655400	-1.11414400
C	-6.32091200	0.25515200	0.23163800
H	-6.33148400	1.19755700	-0.33118500
H	-6.29244700	0.53343900	1.29319100
C	-5.04978100	-0.52670000	-0.11912900
H	-5.07892800	-0.80580500	-1.18039100
H	-5.03731900	-1.46833000	0.44480700
C	-3.75739000	0.24774600	0.16285000
H	-3.72436400	0.52311900	1.22465600
H	-3.77070400	1.19052800	-0.39864100
C	-2.48792500	-0.53388300	-0.19531800
H	-2.52058400	-0.80967300	-1.25669300
H	-2.47117500	-1.47511500	0.36808400
C	-1.20020700	0.24945700	0.08723200
H	-1.15213700	0.51811400	1.14793500
H	-1.21092900	1.18738700	-0.48000300
C	0.05126000	-0.54965700	-0.27895700
H	0.04564000	-0.82099100	-1.34008700
H	0.10294000	-1.46985400	0.30260500
N	1.31616800	0.17182500	0.03840600
N	1.60661700	1.11559700	-0.68696000
N	1.98372900	2.00140700	-1.29165000
C	8.25132200	0.25305300	1.04506700



H	7.78257100	-0.03802200	1.99519900
H	9.19884300	0.73659100	1.29608300

Zero-point correction = 0.459438 (Hartree/Particle)

Thermal correction to Energy = 0.485689

Thermal correction to Enthalpy = 0.486633

Thermal correction to Gibbs Free Energy = 0.391670

Sum of electronic and zero-point Energies = -905.646423

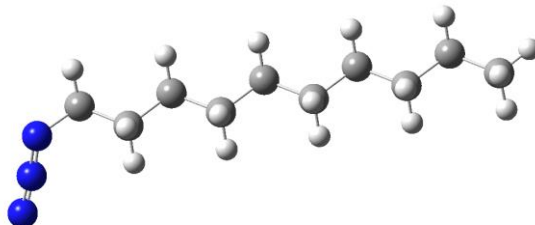
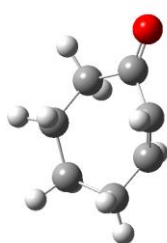
Sum of electronic and thermal Energies = -905.620172

Sum of electronic and thermal Enthalpies = -905.619228

Sum of electronic and thermal Free Energies = -905.714191

Imaginary Frequencies: 0

### (Reactant) 2



C	6.22987600	1.72706800	-0.09844700
O	5.69403500	2.75272100	-0.47447600
C	5.82047400	0.32080400	-0.39938900
C	6.06461200	-0.60313300	0.54260500
H	5.92236600	0.05861900	-1.45304200
H	5.97848600	-0.29931400	1.58557000
C	7.05776000	-1.68660600	0.31696200
H	6.95144700	-2.57085200	0.94897400
H	7.10430200	-1.99227000	-0.73121000
C	8.36911900	-0.90443400	0.71904400
H	9.22871000	-1.50581700	0.40478700
H	8.40855500	-0.84774400	1.81190200
C	8.55398100	0.52914900	0.13652000
H	9.56745300	0.83792000	0.41003500
H	8.54506900	0.47807500	-0.95786300
C	-11.31520000	0.09163900	0.42119200
H	-11.49664700	-0.18388100	-0.62276700
H	-11.35711100	-0.82556300	1.01752100
H	-12.13891400	0.73536400	0.74301700
C	-9.96222400	0.79189300	0.58024500
H	-9.96307700	1.72283500	0.00006200
H	-9.82465400	1.08549400	1.62815200
C	-8.77603200	-0.07403900	0.14063200

H	-8.77719900	-1.00655400	0.72022800
H	-8.91387900	-0.36684400	-0.90855200
C	-7.41690100	0.61692400	0.29836600
H	-7.41659900	1.54946700	-0.28089400
H	-7.28024100	0.90912700	1.34772900
C	-6.23195600	-0.25049000	-0.14160900
H	-6.23405500	-1.18422400	0.43562600
H	-6.36702600	-0.54020600	-1.19180200
C	-4.87232000	0.43879400	0.02068000
H	-4.73619000	0.72623800	1.07129100
H	-4.86961900	1.37330300	-0.55512300
C	-3.68937200	-0.42986100	-0.42169800
H	-3.82078500	-0.71167800	-1.47411900
H	-3.69445700	-1.36664000	0.14993400
C	-2.32984900	0.25766500	-0.24945000
H	-2.19595200	0.53583600	0.80327600
H	-2.32287500	1.19477900	-0.81984400
C	-1.15320400	-0.61743200	-0.69817100
H	-1.27020200	-0.88663400	-1.75334800
H	-1.15432800	-1.55341200	-0.12757200
C	0.19127500	0.08734100	-0.51262900
H	0.35253600	0.35310000	0.53749500
H	0.22843300	1.00421500	-1.10050000
N	1.34365900	-0.72291800	-0.99879700
N	1.67221500	-1.68087500	-0.30972700
N	2.07357200	-2.58782500	0.24632800
C	7.60326800	1.69312300	0.59308400
H	7.41758400	1.60828400	1.67268200
H	8.09064000	2.65809500	0.43189900

Zero-point correction = 0.459503 (Hartree/Particle)

Thermal correction to Energy = 0.485735

Thermal correction to Enthalpy = 0.486679

Thermal correction to Gibbs Free Energy = 0.391828

Sum of electronic and zero-point Energies = -905.646366

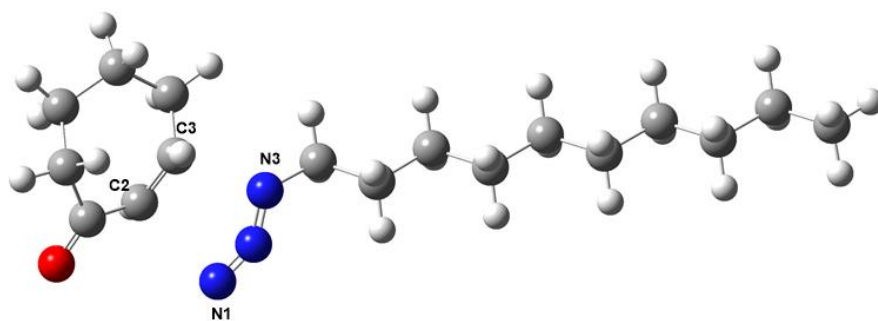
Sum of electronic and thermal Energies = -905.620134

Sum of electronic and thermal Enthalpies = -905.619190

Sum of electronic and thermal Free Energies = -905.714041

Imaginary Frequencies: 0

TS-1



C	10.52648100	0.07480200	0.66392600
H	10.47814500	0.41135100	1.70465600
H	10.63447900	-1.01467700	0.67323800
H	11.43377000	0.49495400	0.22036800
C	9.27558300	0.49892200	-0.11174100
H	9.21438800	1.59390500	-0.13414300
H	9.36776500	0.17691300	-1.15626900
C	7.97745400	-0.06557100	0.47655700
H	8.03861600	-1.16165100	0.49707800
H	7.88796300	0.25452900	1.52305100
C	6.71850400	0.35614900	-0.28952500
H	6.65804000	1.45215600	-0.30860100
H	6.80852100	0.03684200	-1.33603400
C	5.42238100	-0.21020700	0.30133000
H	5.48031000	-1.30636900	0.31402500
H	5.33678600	0.10324000	1.34994100
C	4.16081900	0.21941300	-0.45635900
H	4.24593500	-0.08991300	-1.50612300
H	4.09985200	1.31540100	-0.46401400
C	2.86860500	-0.35394100	0.13598000
H	2.78971600	-0.05501900	1.18899900
H	2.92396900	-1.44996100	0.13166900
C	1.60378200	0.09030500	-0.60824100
H	1.68216400	-0.20114100	-1.66300300
H	1.54185400	1.18567400	-0.59401300
C	0.32128600	-0.49880200	-0.01019500
H	0.23668000	-0.21707000	1.04475100
H	0.36544000	-1.59320400	-0.04560900
C	-0.93467000	-0.02680800	-0.74801800
H	-0.89655000	-0.30111100	-1.80748100
H	-1.01892100	1.05946600	-0.68888400
N	-2.18030700	-0.53105200	-0.14127000
N	-2.51436600	-1.72408300	-0.28902900
N	-3.37238000	-2.49511400	-0.30364000
C	-6.20094800	-0.82424100	0.44245600

O	-6.95635100	-1.78584000	0.32766800
C	-4.98757300	-0.61118800	-0.36482500
C	-4.12676300	0.40237500	0.02452400
H	-5.14618400	-0.78727500	-1.42748100
H	-4.00305800	0.52581400	1.09746600
C	-6.61778100	0.43575600	1.21005700
H	-5.95004600	0.59185000	2.06565500
H	-7.62114900	0.27058400	1.60871700
C	-4.12705600	1.71644100	-0.68445500
H	-3.20711800	2.29725000	-0.57852600
H	-4.35231200	1.59937200	-1.74765600
C	-5.28559200	2.47265800	0.05514200
H	-5.51832600	3.37813300	-0.51469700
H	-4.89989500	2.80544500	1.02507500
C	-6.61572100	1.70731400	0.29222400
H	-7.30580200	2.42584800	0.74485700
H	-7.05759700	1.43687500	-0.67378400

Zero-point correction = 0.460496 (Hartree/Particle)

Thermal correction to Energy = 0.484806

Thermal correction to Enthalpy = 0.485750

Thermal correction to Gibbs Free Energy = 0.402302

Sum of electronic and zero-point Energies = -905.629968

Sum of electronic and thermal Energies = -905.605658

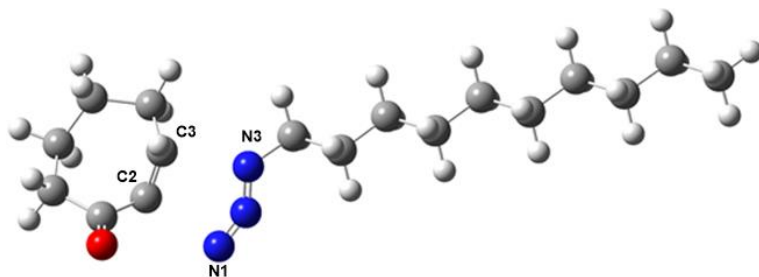
Sum of electronic and thermal Enthalpies = -905.604714

Sum of electronic and thermal Free Energies = -905.688163

Imaginary Frequencies: 1 (-289.62 cm<sup>-1</sup>)

Selected length: C2-N1= 2.48229 Å      C3-N3= 2.16506 Å

### TS-1'



C	10.64724700	-0.27416600	0.32763400
H	10.66560600	-0.52477900	1.39326900
H	10.70853900	-1.21192100	-0.23399600
H	11.54840000	0.30519100	0.10689900
C	9.37844800	0.50381500	-0.03477800
H	9.36212200	1.45198100	0.51647600
H	9.40552600	0.76968600	-1.09865800

C	8.08840500	-0.27104600	0.25747800
H	8.10774700	-1.22158800	-0.29165700
H	8.06081900	-0.53480000	1.32297900
C	6.81216300	0.49610800	-0.10646500
H	6.79246300	1.44599700	0.44349600
H	6.84137200	0.76020400	-1.17168600
C	5.52430800	-0.28278300	0.18450200
H	5.54656700	-1.23386000	-0.36320500
H	5.49368900	-0.54466000	1.25017000
C	4.24651100	0.47994100	-0.18405900
H	4.27793800	0.74397600	-1.24911800
H	4.22024000	1.42933000	0.36623300
C	2.96256300	-0.30661900	0.10274000
H	2.92819800	-0.56715300	1.16830000
H	2.99148200	-1.25740600	-0.44455500
C	1.68288600	0.45032900	-0.27241000
H	1.71635700	0.71121100	-1.33761800
H	1.64851500	1.39929600	0.27723400
C	0.40880500	-0.35144500	0.01586600
H	0.35683000	-0.60132300	1.08101600
H	0.43727000	-1.29969100	-0.53278400
C	-0.86190000	0.40891300	-0.37641100
H	-0.84932200	0.66433800	-1.44186500
H	-0.93262900	1.34019000	0.18812600
N	-2.09832600	-0.32277100	-0.04713900
N	-2.41508800	-1.33248300	-0.70591300
N	-3.29007700	-2.00782300	-1.05916800
C	-6.06449800	-1.11746300	0.35363700
O	-6.05128300	-2.11281200	1.05541700
C	-4.94460100	-0.53718000	-0.42878300
C	-4.25903900	0.39212800	0.32648900
H	-5.22712400	-0.21592300	-1.42870100
H	-4.16223200	0.20237100	1.39286800
C	-7.26349100	-0.15067600	0.33382300
C	-4.44240300	1.83387000	-0.04762800
H	-3.74752100	2.50634200	0.46168900
H	-4.33493500	1.97691200	-1.12739200
C	-5.90744000	2.16944100	0.38165800
H	-6.10977400	3.20664200	0.09529400
H	-5.96943800	2.13602800	1.47571100
C	-7.03603300	1.28595400	-0.22302100
H	-7.97695400	1.82109400	-0.06128900
H	-6.91104400	1.24184200	-1.30983900
H	-7.61622500	-0.10235100	1.37003400

H -8.06937000 -0.62787600 -0.23685100

Zero-point correction = 0.460530 (Hartree/Particle)

Thermal correction to Energy = 0.484845

Thermal correction to Enthalpy = 0.485789

Thermal correction to Gibbs Free Energy = 0.402492

Sum of electronic and zero-point Energies = -905.629535

Sum of electronic and thermal Energies = -905.605221

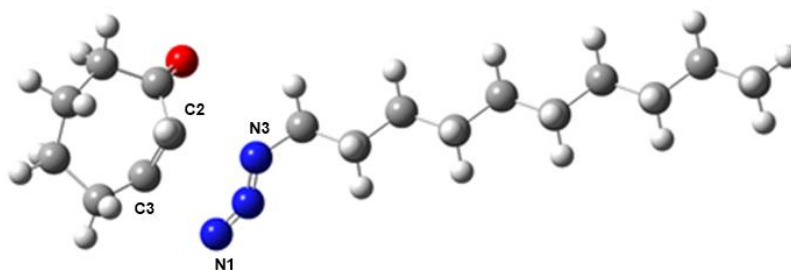
Sum of electronic and thermal Enthalpies = -905.604277

Sum of electronic and thermal Free Energies = -905.687573

Imaginary Frequencies: 1 (-286.33 cm<sup>-1</sup>)

Selected length: C2-N1= 2.30166 Å C3-N3= 2.30637 Å

### TS-2



C	10.53285500	0.02420400	0.39978800
H	10.54972200	-0.04429700	1.49234900
H	10.65902700	-0.98836400	0.00287500
H	11.40116200	0.61297200	0.09016300
C	9.22582900	0.65189400	-0.09381300
H	9.14521700	1.67611300	0.29065000
H	9.25266100	0.73763000	-1.18704900
C	7.97919900	-0.13948600	0.31842200
H	8.05982000	-1.16426500	-0.06753100
H	7.95422800	-0.22677100	1.41264800
C	6.66602600	0.48281400	-0.16889000
H	6.58744800	1.50766800	0.21690400
H	6.69177700	0.56961400	-1.26298200
C	5.41952600	-0.30790800	0.24493700
H	5.49574000	-1.33169800	-0.14395500
H	5.39558300	-0.39757600	1.33879000
C	4.10686300	0.31918400	-0.23811700
H	4.13013100	0.40887600	-1.33191300
H	4.03093900	1.34280400	0.15110200
C	2.86050200	-0.47102500	0.17668200
H	2.83754500	-0.56288900	1.27006700
H	2.93270200	-1.49343500	-0.21569400
C	1.54971300	0.16278200	-0.30345700

H	1.57032600	0.25165900	-1.39680400
H	1.47799300	1.18548200	0.08761900
C	0.30716500	-0.62917500	0.11980600
H	0.27050700	-0.71230900	1.21135300
H	0.36536900	-1.64943200	-0.27600100
C	-0.98782700	0.02435900	-0.37116700
H	-0.99756900	0.10260600	-1.46336500
H	-1.07855800	1.03277900	0.03448200
N	-2.20171900	-0.67198000	0.09588000
N	-2.53164700	-1.75576200	-0.42485800
N	-3.41390500	-2.45210300	-0.70981700
C	-4.53417400	1.46338000	-0.31297000
O	-3.90317300	2.00920000	-1.19918300
C	-4.31736000	0.12126900	0.27756900
C	-5.07004800	-0.83972000	-0.36235000
H	-4.34353100	0.10629700	1.36375300
H	-5.24659300	-0.71128400	-1.42894500
C	-5.85696600	2.04187600	0.22794800
C	-6.23703400	-1.39079600	0.41143000
H	-6.69055100	-2.26518800	-0.06296200
H	-5.93681800	-1.67110500	1.42658700
C	-7.27617800	-0.22904000	0.47512500
H	-8.12830600	-0.56473500	1.07585200
H	-7.66480800	-0.04949500	-0.53437900
C	-6.78004700	1.11719000	1.07649400
H	-7.67174800	1.71199200	1.29782100
H	-6.31326500	0.92469500	2.04840500
H	-6.39643800	2.40169900	-0.65539900
H	-5.61169200	2.93445600	0.81597300

Zero-point correction = 0.460349 (Hartree/Particle)

Thermal correction to Energy = 0.484698

Thermal correction to Enthalpy = 0.485642

Thermal correction to Gibbs Free Energy = 0.401876

Sum of electronic and zero-point Energies = -905.629053

Sum of electronic and thermal Energies = -905.604704

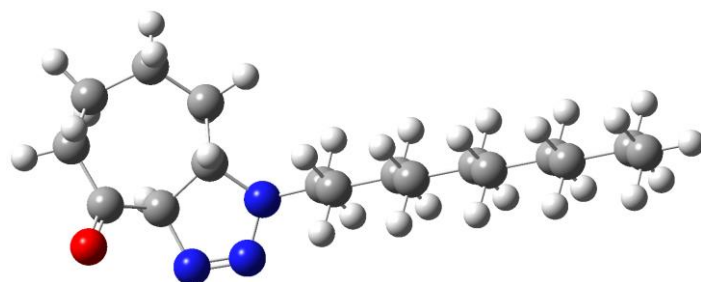
Sum of electronic and thermal Enthalpies = -905.603760

Sum of electronic and thermal Free Energies = -905.687525

Imaginary Frequencies: 1 (-292.82 cm<sup>-1</sup>)

Selected length: C2-N3= 2.26676 Å    C3-N1= 2.33738 Å

**(Product) 8aa**



C	-5.00964300	0.52581700	1.45020300
O	-4.92911800	0.42283800	2.65771900
C	-4.51417800	-0.55687600	0.50908100
C	-3.37582500	-0.08953100	-0.42220200
H	-5.37054100	-0.88681900	-0.09703900
H	-2.73779100	0.64502500	0.09167400
C	-5.60100500	1.77525700	0.81046800
H	-4.94065600	2.60232200	1.10073800
H	-6.54323400	1.95813400	1.33734100
C	-3.83994600	0.48795400	-1.75447800
H	-2.97400500	0.63829100	-2.40610900
H	-4.48976800	-0.24260700	-2.24868100
C	-4.57494100	1.82890200	-1.59607600
H	-4.86357700	2.16730300	-2.59538000
H	-3.87955900	2.58367500	-1.20908700
C	-5.83585400	1.80613700	-0.71057800
H	-6.40352400	2.71817300	-0.91555500
H	-6.48940300	0.97943800	-1.01094300
C	9.83039600	1.07204400	0.74854900
H	9.67494000	2.15424300	0.80656200
H	9.84928300	0.68514700	1.77259200
H	10.81797300	0.90102300	0.31048400
C	8.72814200	0.39949800	-0.07537900
H	8.75705000	0.78105900	-1.10340100
H	8.92900500	-0.67671600	-0.14354100
C	7.32387900	0.61345300	0.50128700
H	7.29596400	0.23192400	1.53048700
H	7.12351000	1.69082800	0.56977600
C	6.21395000	-0.05650900	-0.31637900
H	6.24291800	0.32512300	-1.34537300
H	6.41580100	-1.13349100	-0.38429800
C	4.80998700	0.15733100	0.26098800
H	4.78164600	-0.22245100	1.29060600
H	4.60666500	1.23412200	0.32678200
C	3.70152100	-0.51674200	-0.55557100
H	3.90554000	-1.59332200	-0.62151100



H	3.72869100	-0.13668100	-1.58509700
C	2.29791500	-0.30479700	0.02309600
H	2.09056500	0.77114900	0.08559700
H	2.27053800	-0.68281700	1.05305700
C	1.19317000	-0.98565300	-0.79296500
H	1.40220000	-2.06098300	-0.85754600
H	1.21696100	-0.60555500	-1.82219900
C	-0.20866600	-0.77821500	-0.20825400
H	-0.42165400	0.29481800	-0.15029700
H	-0.24438300	-1.16584800	0.81612400
C	-1.28570300	-1.48310700	-1.04298800
H	-1.07020400	-2.55175200	-1.11158100
H	-1.29620300	-1.09314700	-2.06387800
N	-2.64853700	-1.37110600	-0.52065900
N	-2.96134900	-2.15608400	0.53928000
N	-3.97168300	-1.76739600	1.17354000

Zero-point correction = 0.465882 (Hartree/Particle)

Thermal correction to Energy = 0.489130

Thermal correction to Enthalpy = 0.490074

Thermal correction to Gibbs Free Energy = 0.408414

Sum of electronic and zero-point Energies = -905.717243

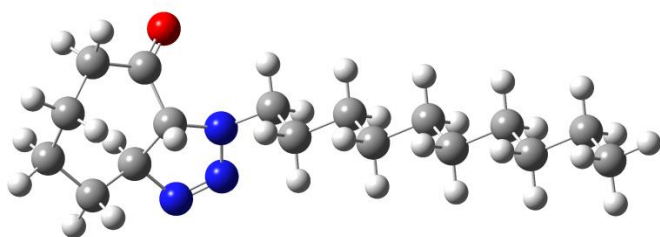
Sum of electronic and thermal Energies = -905.693995

Sum of electronic and thermal Enthalpies = -905.693051

Sum of electronic and thermal Free Energies = -905.774711

Imaginary Frequencies: 0

### (Product) 8aa'



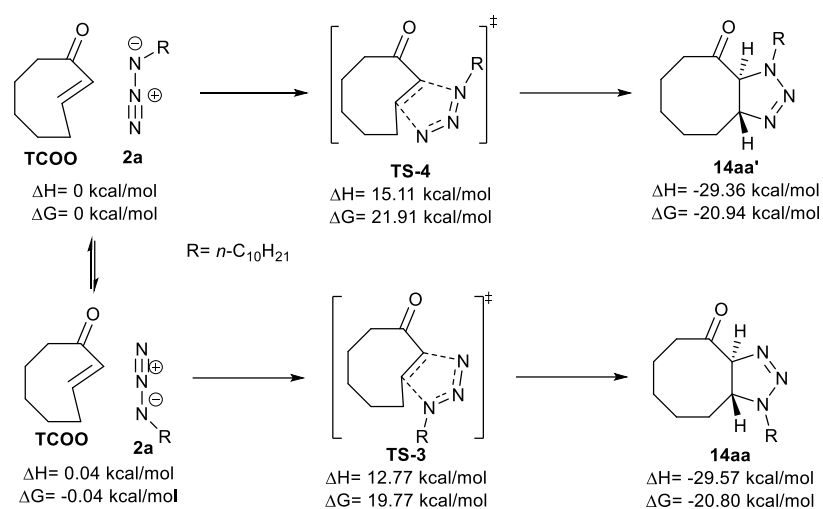
C	4.01151900	0.50517000	1.37973300
O	3.92416000	-0.05219400	2.45625200
C	3.46189400	-0.10431700	0.10580800
C	4.59795800	-0.55591500	-0.84205500
H	2.83242900	0.64661400	-0.39362300
H	5.45567500	-0.90991100	-0.25201900
C	4.70880100	1.85170900	1.24341300
H	5.68818000	1.73234800	1.72110300
H	4.15177800	2.53932400	1.89043300

C	5.06732800	0.49478500	-1.83655900
H	5.77032300	0.02727700	-2.53207100
H	4.20915700	0.83400500	-2.42770900
C	5.74418700	1.69816700	-1.15927700
H	6.05767500	2.38884200	-1.94744100
H	6.66374400	1.36790000	-0.66082700
C	4.87486700	2.47976300	-0.15309500
H	5.33957300	3.45702300	0.00529600
H	3.89432300	2.68985000	-0.59485600
C	-9.77808100	1.02755900	-0.62420000
H	-9.62648400	2.10601300	-0.73680400
H	-9.83904000	0.59542100	-1.62831100
H	-10.74637500	0.87696500	-0.13821100
C	-8.64170500	0.39159800	0.18224800
H	-8.62622600	0.82080100	1.19155900
H	-8.83975600	-0.67980300	0.30908500
C	-7.26340400	0.57519100	-0.46351700
H	-7.27979400	0.14602200	-1.47397400
H	-7.06589700	1.64777900	-0.59061900
C	-6.11975900	-0.05857000	0.33635700
H	-6.10509600	0.37001500	1.34693800
H	-6.31844500	-1.13093200	0.46217800
C	-4.74138200	0.12576800	-0.30899600
H	-4.75677400	-0.29973100	-1.32080700
H	-4.54048700	1.19809200	-0.43124000
C	-3.60011800	-0.51410500	0.48969600
H	-3.80066500	-1.58667000	0.60968900
H	-3.58565600	-0.09050700	1.50228000
C	-2.22098100	-0.32882700	-0.15353300
H	-2.01589300	0.74332500	-0.26779300
H	-2.23526600	-0.74844400	-1.16749500
C	-1.08516000	-0.97866400	0.64491400
H	-1.29083200	-2.05064600	0.75810300
H	-1.07008300	-0.56002300	1.65914300
C	0.29400400	-0.79504400	0.00102700
H	0.50561900	0.27529200	-0.10017300
H	0.29039600	-1.21631500	-1.01053900
C	1.39901500	-1.47429300	0.82038000
H	1.19054100	-2.54190900	0.92103300
H	1.44540100	-1.05772500	1.82866100
N	2.74501200	-1.36870700	0.25527900
N	3.03210300	-2.16708700	-0.80867900
N	4.02299800	-1.78029000	-1.46875300

Zero-point correction = 0.465888 (Hartree/Particle)  
 Thermal correction to Energy = 0.489119  
 Thermal correction to Enthalpy = 0.490063  
 Thermal correction to Gibbs Free Energy = 0.408757  
 Sum of electronic and zero-point Energies = -905.718906  
 Sum of electronic and thermal Energies = -905.695675  
 Sum of electronic and thermal Enthalpies = -905.694731  
 Sum of electronic and thermal Free Energies = -905.776037  
 Imaginary Frequencies: 0

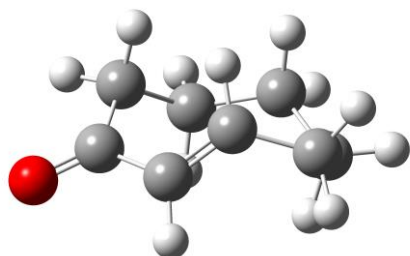
## Cycloadditions of *trans*-cyclooctenones and C<sub>10</sub>H<sub>21</sub>N<sub>3</sub>

### A) Proposed reaction pathways



### B) Geometries, structure images and energies

#### *Trans*-cyclooctenone



C	-1.71699700	-0.32291600	0.02315000
O	-2.85074100	-0.47803900	-0.41699300
C	-0.64730800	-1.33012800	-0.11587400
C	0.46425400	-1.17695000	0.61767000
H	-0.67995200	-1.96288700	-0.99961500

H	0.38002700	-0.57174200	1.51357400
C	-1.24181200	1.03924800	0.54104000
H	-0.98643500	0.96446000	1.60461600
H	-2.09632700	1.71595600	0.47257400
C	1.86381500	-1.33189500	0.15578700
H	2.55927800	-1.46854300	0.98711900
H	2.00583100	-2.14093900	-0.56358300
C	1.44203000	1.31063300	0.08313300
H	2.01890000	2.16219700	-0.29143000
H	1.59090300	1.32136100	1.16935000
C	-0.04411700	1.65739500	-0.25216500
H	-0.13459600	2.73850700	-0.10837900
H	-0.20969800	1.49089300	-1.32322800
C	2.11344800	0.05242000	-0.54624400
H	3.19333400	0.22481700	-0.58411000
H	1.76478200	-0.03660700	-1.57991900

Zero-point correction = 0.183786 (Hartree/Particle)

Thermal correction to Energy = 0.192134

Thermal correction to Enthalpy = 0.193078

Thermal correction to Gibbs Free Energy = 0.151090

Sum of electronic and zero-point Energies = -387.185413

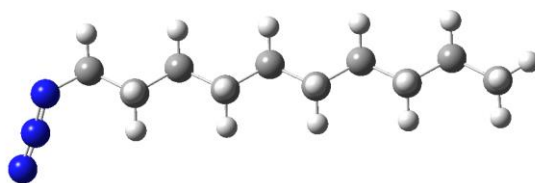
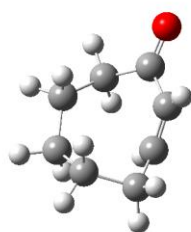
Sum of electronic and thermal Energies = -387.177064

Sum of electronic and thermal Enthalpies = -387.176120

Sum of electronic and thermal Free Energies = -387.218109

Imaginary Frequencies: 0

### (Reactant) 5



C	6.02311000	1.65681300	-0.09084200
O	5.52373400	2.71338600	-0.46137900
C	5.57929800	0.33471800	-0.57351000
C	6.00556200	-0.75329500	0.08353100
H	5.18418200	0.28677700	-1.58539000
H	6.32708600	-0.61168600	1.10955600
C	7.32235200	1.62987500	0.72215500
H	7.13631900	1.18238900	1.70550900
H	7.60194000	2.67041200	0.90072600

C	6.51982900	-2.00913300	-0.51225600
H	6.49658900	-2.84079400	0.19580500
H	6.00583400	-2.30744000	-1.42818700
C	8.72772000	-0.64376500	0.14309300
H	9.79678200	-0.79401600	-0.03779600
H	8.56637700	-0.96230800	1.17987000
C	8.51447500	0.89919700	0.02188100
H	9.41587400	1.35653100	0.44135500
H	8.51682000	1.17058600	-1.04053900
C	8.00499200	-1.61185300	-0.84230700
H	8.59552800	-2.53031500	-0.91274300
H	8.00818000	-1.14992500	-1.83465500
C	-11.87101100	-0.30004900	-0.28869600
H	-11.89748300	-0.59262700	-1.34340900
H	-11.92386500	-1.21510400	0.31005000
H	-12.77258500	0.28423200	-0.08318300
C	-10.60248100	0.49646000	0.03172400
H	-10.59569400	1.42292700	-0.55550200
H	-10.62093300	0.80281100	1.08484900
C	-9.31143900	-0.28313400	-0.24298500
H	-9.32107000	-1.21228600	0.34192900
H	-9.29229400	-0.58696900	-1.29794100
C	-8.03606200	0.50349900	0.07970300
H	-8.02740300	1.43270500	-0.50484400
H	-8.05628400	0.80647600	1.13473500
C	-6.74612900	-0.27765200	-0.19564100
H	-6.75606400	-1.20781000	0.38726900
H	-6.72461600	-0.57870100	-1.25113500
C	-5.47069000	0.50763900	0.13087400
H	-5.49233200	0.80894800	1.18622700
H	-5.45912100	1.43726100	-0.45268700
C	-4.18244900	-0.27643900	-0.14320800
H	-4.15745900	-0.57416000	-1.19920000
H	-4.19478300	-1.20724700	0.43800200
C	-2.90807400	0.50832200	0.18968000
H	-2.93158200	0.80536100	1.24554700
H	-2.89294700	1.43809600	-0.39250400
C	-1.62511700	-0.28462000	-0.08753800
H	-1.58755100	-0.57602600	-1.14265000
H	-1.63304800	-1.21025600	0.49963700
C	-0.36786900	0.51817500	0.24961300
H	-0.36183000	0.81214000	1.30463000
H	-0.31895500	1.42546000	-0.35215600
N	0.89070600	-0.21530800	-0.06530700

N	1.19661400	-1.13119400	0.68835100
N	1.58702600	-1.99365200	1.31813200

Zero-point correction = 0.489272 (Hartree/Particle)

Thermal correction to Energy = 0.516534

Thermal correction to Enthalpy = 0.517478

Thermal correction to Gibbs Free Energy = 0.420754

Sum of electronic and zero-point Energies = -944.961095

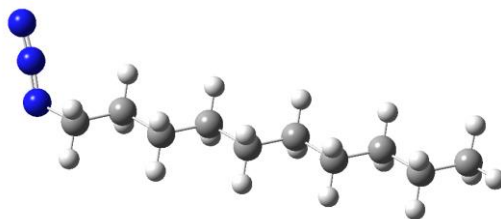
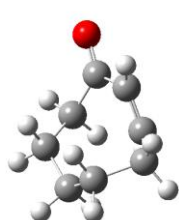
Sum of electronic and thermal Energies = -944.933833

Sum of electronic and thermal Enthalpies = -944.932889

Sum of electronic and thermal Free Energies = -945.029613

Imaginary Frequencies: 0

### (Reactant) 6



C	7.04229900	1.31255200	0.38059000
O	7.42518500	2.46213600	0.19357200
C	6.03392700	0.64425500	-0.46476100
C	5.50329500	-0.50515300	-0.02357000
H	5.98842700	0.94485700	-1.50872200
H	5.54831400	-0.68662500	1.04459100
C	7.76208500	0.38134900	1.36273300
H	7.07688500	0.08933900	2.16735700
H	8.55705200	0.96882200	1.82705500
C	5.27655600	-1.74232400	-0.80724600
H	4.55508900	-2.40730700	-0.32681700
H	4.96345700	-1.56265500	-1.83770700
C	7.56916900	-2.20497900	0.49571100
H	8.31845300	-3.00198900	0.45726900
H	6.96999400	-2.41934000	1.38869200
C	8.39011000	-0.89306500	0.70968800
H	9.22314900	-1.16850500	1.36380900
H	8.85004800	-0.60817500	-0.24399800
C	6.71035700	-2.38715100	-0.79257400
H	6.60331900	-3.45939100	-0.98259000
H	7.26837700	-1.96482700	-1.63417100
C	-11.77549000	-0.23670500	0.54321500
H	-11.77014800	-0.21141800	1.63774000
H	-11.92546500	0.78845400	0.18929400

H	-12.64098300	-0.82690600	0.22850800
C	-10.46966700	-0.82311500	-0.00177800
H	-10.36476500	-1.86006400	0.34027000
H	-10.51868700	-0.86645800	-1.09674800
C	-9.22714400	-0.02769400	0.41505500
H	-9.33321400	1.01025100	0.07295700
H	-9.17890600	0.01581200	1.51111300
C	-7.91528500	-0.60690900	-0.12596700
H	-7.81101000	-1.64499900	0.21577800
H	-7.96455600	-0.64968000	-1.22186400
C	-6.67295200	0.18813500	0.29206000
H	-6.77655100	1.22616600	-0.04982900
H	-6.62347900	0.23080000	1.38788600
C	-5.36198600	-0.39300300	-0.24954600
H	-5.41029200	-0.43329800	-1.34544900
H	-5.25942100	-1.43165000	0.09058800
C	-4.11953600	0.39985800	0.17172800
H	-4.06860000	0.43774000	1.26730200
H	-4.22061600	1.43877500	-0.16711600
C	-2.81123700	-0.18402900	-0.37393800
H	-2.85870900	-0.21608200	-1.46951200
H	-2.71151700	-1.22394500	-0.03867400
C	-1.57140500	0.60788500	0.05925100
H	-1.50932600	0.63411100	1.15242200
H	-1.66212200	1.64604500	-0.28086900
C	-0.28131900	0.00203500	-0.49533800
H	-0.29607700	-0.01621500	-1.59027700
H	-0.15786200	-1.02231300	-0.14419800
N	0.94276500	0.71325200	-0.02966700
N	1.17163000	1.80493300	-0.53630800
N	1.49240600	2.81923200	-0.93753300

Zero-point correction = 0.489425 (Hartree/Particle)

Thermal correction to Energy = 0.516636

Thermal correction to Enthalpy = 0.517580

Thermal correction to Gibbs Free Energy = 0.420727

Sum of electronic and zero-point Energies = -944.960975

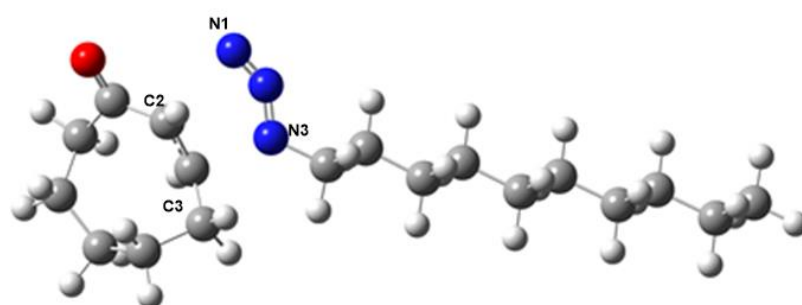
Sum of electronic and thermal Energies = -944.933764

Sum of electronic and thermal Enthalpies = -944.932820

Sum of electronic and thermal Free Energies = -945.029673

Imaginary Frequencies: 0

TS-3



C	10.75647400	0.08297500	0.73535400
H	10.70349800	0.44672900	1.76665500
H	10.85837900	-1.00646000	0.77360700
H	11.66882000	0.48656900	0.28681500
C	9.51286900	0.49344700	-0.05911600
H	9.45732600	1.58780400	-0.10956700
H	9.61037500	0.14476200	-1.09457200
C	8.20792400	-0.04981600	0.53409200
H	8.26345300	-1.14533400	0.58233900
H	8.11260600	0.29674800	1.57159900
C	6.95688000	0.35868700	-0.25175800
H	6.90103600	1.45417300	-0.29708800
H	7.05439500	0.01463400	-1.28973600
C	5.65320500	-0.18877000	0.34033400
H	5.70741800	-1.28446200	0.38067200
H	5.55773300	0.15087100	1.37988600
C	4.40167800	0.22561000	-0.44197300
H	4.50023600	-0.10662300	-1.48355500
H	4.34227300	1.32122800	-0.47452300
C	3.10039800	-0.33359200	0.14404100
H	3.00319700	-0.00830300	1.18764900
H	3.15640700	-1.42933300	0.16808000
C	1.84941100	0.09035200	-0.63449100
H	1.95214400	-0.22158200	-1.68131300
H	1.78268800	1.18547800	-0.64369400
C	0.55584800	-0.49339600	-0.05540500
H	0.43945000	-0.18658800	0.98946900
H	0.60909100	-1.58785300	-0.06288300
C	-0.68057500	-0.04998400	-0.84255400
H	-0.59591500	-0.33169200	-1.89749800
H	-0.78475300	1.03499800	-0.79687500
N	-1.93941600	-0.57263400	-0.28275400
N	-2.22447600	-1.78817900	-0.39535500
N	-3.10793400	-2.53717900	-0.39941800
C	-5.74431200	-1.13568600	0.39334100



O	-6.54101200	-2.04316700	0.14226600
C	-4.68161600	-0.75249100	-0.53375400
C	-3.83376500	0.30192600	-0.21168300
H	-4.87806300	-0.98779800	-1.57642800
H	-3.73266700	0.51036100	0.84534300
C	-5.99560600	-0.21182400	1.58456400
H	-5.09247300	-0.08704400	2.19066100
H	-6.73928400	-0.70565700	2.21363300
C	-3.75399500	1.54705400	-1.03907700
H	-2.91874000	2.17800900	-0.72309200
H	-3.63920300	1.33511900	-2.10529300
C	-5.62039800	2.32191700	0.67116800
H	-6.21441300	3.23618400	0.76889300
H	-4.78460700	2.44851300	1.37015400
C	-6.55613400	1.18319400	1.16804600
H	-7.06219700	1.57425000	2.05650400
H	-7.34651700	1.03033600	0.42329800
C	-5.09843900	2.29541300	-0.79272000
H	-4.97323800	3.32751200	-1.13470300
H	-5.86665800	1.84564000	-1.43033400

Zero-point correction = 0.490076 (Hartree/Particle)

Thermal correction to Energy = 0.515415

Thermal correction to Enthalpy = 0.516359

Thermal correction to Gibbs Free Energy = 0.430786

Sum of electronic and zero-point Energies = -944.938817

Sum of electronic and thermal Energies = -944.913478

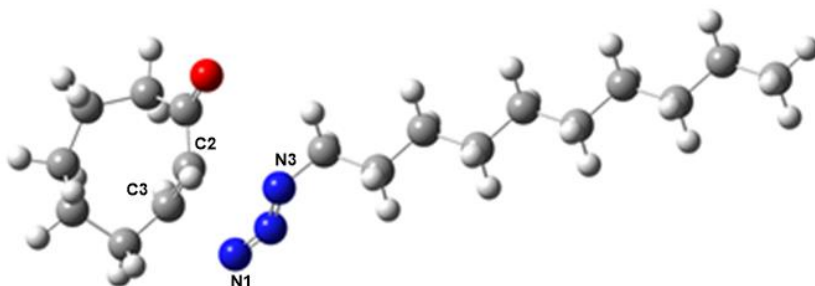
Sum of electronic and thermal Enthalpies = -944.912534

Sum of electronic and thermal Free Energies = -944.998108

Imaginary Frequencies: 1 (-341.87 cm<sup>-1</sup>)

Selected length: C2-N1= 2.38320 Å      C3-N3= 2.08769 Å

#### TS-4



C	10.82548000	0.09858600	0.31044200
H	10.84666600	0.04022800	1.40352100
H	10.97349500	-0.91436100	-0.07786400

H	11.67940300	0.70412000	-0.00674700
C	9.50327700	0.69208800	-0.18509800
H	9.39995300	1.71717500	0.19148100
H	9.52584400	0.76973200	-1.27903100
C	8.27610400	-0.12447900	0.23622400
H	8.37833700	-1.14955200	-0.14380900
H	8.25682200	-0.20559900	1.33103300
C	6.94759400	0.46563300	-0.24959000
H	6.84737200	1.49018200	0.13199100
H	6.96755600	0.54808500	-1.34413500
C	5.72060600	-0.35078200	0.17252400
H	5.81418600	-1.37229400	-0.21857100
H	5.70720200	-0.44245100	1.26638500
C	4.39172700	0.25135000	-0.29782900
H	4.40386500	0.34616700	-1.39136200
H	4.29883900	1.27157100	0.09662000
C	3.16484400	-0.56479500	0.12472800
H	3.16190300	-0.67370600	1.21676100
H	3.24569500	-1.57982200	-0.28473600
C	1.83649000	0.05751200	-0.32120000
H	1.83543400	0.16748800	-1.41280800
H	1.75732400	1.07133400	0.09099600
C	0.61407700	-0.76023200	0.11092300
H	0.61306600	-0.88379900	1.19912400
H	0.66376500	-1.76444200	-0.32462500
C	-0.70149600	-0.09720000	-0.30991300
H	-0.75166000	0.02420400	-1.39692600
H	-0.78459300	0.89300300	0.14253900
N	-1.88687900	-0.82037200	0.17968800
N	-2.33513300	-1.80002800	-0.45220300
N	-3.34543800	-2.33190000	-0.71282100
C	-3.89709300	1.43018600	0.25113600
O	-3.17026600	2.22220900	0.84520100
C	-3.97983700	0.00548500	0.62517900
C	-4.73655900	-0.87160000	-0.13498400
H	-3.83135400	-0.18756800	1.68373200
H	-4.91818600	-0.57036400	-1.15997700
C	-4.93229800	1.92470800	-0.75432700
H	-4.83575900	1.38938400	-1.70453000
H	-4.70445700	2.97455100	-0.95032200
C	-5.88424500	-1.64378700	0.44487000
H	-6.23575700	-2.39636200	-0.26658000
H	-5.61318700	-2.15827500	1.37098900
C	-7.21479300	0.50277400	-0.34093200

H	-8.26257900	0.81051400	-0.26435900
H	-7.11261500	0.08237000	-1.34883700
C	-6.40197500	1.82501800	-0.23610800
H	-6.96083000	2.57083000	-0.80996700
H	-6.42992700	2.17429900	0.80305300
C	-7.00737900	-0.60508800	0.72897400
H	-7.95048400	-1.14732500	0.85226200
H	-6.79820700	-0.12315700	1.69032600

Zero-point correction = 0.489787 (Hartree/Particle)

Thermal correction to Energy = 0.515110

Thermal correction to Enthalpy = 0.516054

Thermal correction to Gibbs Free Energy = 0.430162

Sum of electronic and zero-point Energies = -944.935073

Sum of electronic and thermal Energies = -944.909749

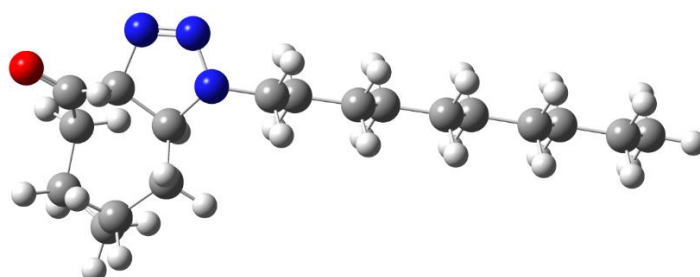
Sum of electronic and thermal Enthalpies = -944.908805

Sum of electronic and thermal Free Energies = -944.994698

Imaginary Frequencies: 1 (-372.02 cm<sup>-1</sup>)

Selected length: C2-N3= 2.29368 Å      C3-N1= 2.09800 Å

### (Product) 14aa



C	9.97035200	1.22281600	0.68047800
H	9.77836700	2.30042900	0.65649200
H	10.00929700	0.91694900	1.73100600
H	10.96021100	1.05177000	0.24761100
C	8.88622600	0.45207300	-0.07895100
H	8.89584600	0.75320800	-1.13369900
H	9.12296700	-0.61890200	-0.06527900
C	7.47901900	0.66366700	0.49152800
H	7.47023100	0.36465800	1.54797900
H	7.24206500	1.73566300	0.47581800
C	6.38824000	-0.10645700	-0.26105000
H	6.40256000	0.18867800	-1.31841800
H	6.62390200	-1.17848500	-0.24017700
C	4.97935900	0.11105900	0.30294400
H	4.96443800	-0.18024800	1.36126900

H	4.74170200	1.18250700	0.27737200
C	3.89263700	-0.66510000	-0.44960000
H	4.12620200	-1.73714800	-0.41628200
H	3.91455300	-0.38040900	-1.50961700
C	2.48042700	-0.43936500	0.10235600
H	2.24347800	0.63156500	0.06342300
H	2.45574000	-0.72094400	1.16281000
C	1.40146200	-1.22319500	-0.65350000
H	1.63376000	-2.29462200	-0.60661000
H	1.43337000	-0.94833000	-1.71549100
C	-0.01393300	-0.98857900	-0.11351600
H	-0.24943500	0.08003500	-0.16782300
H	-0.06150300	-1.27216600	0.94400900
C	-1.05993400	-1.79610500	-0.89301000
H	-0.83380600	-2.86304500	-0.83569600
H	-1.04340400	-1.52155300	-1.95088700
N	-2.43782800	-1.63992200	-0.42716200
N	-2.80022400	-2.32595000	0.67648200
N	-3.85623400	-1.90709100	1.20969700
C	-5.05523900	0.28059400	1.26631800
O	-6.11156900	-0.01069100	1.79711800
C	-4.38190200	-0.76563400	0.37848100
C	-3.17943600	-0.36009800	-0.47225300
H	-5.17366500	-1.19834200	-0.24823400
H	-2.57986700	0.39739000	0.04675900
C	-4.43020600	1.64559600	1.46438500
H	-3.34488600	1.56609500	1.56851800
H	-4.82835300	2.02516300	2.40756300
C	-3.51338800	0.13295400	-1.87660800
H	-2.58654900	0.42269800	-2.38259200
H	-3.94625400	-0.69390100	-2.44910700
C	-4.08306900	2.54056800	-1.01859800
H	-4.33090400	3.45193700	-1.57090300
H	-2.99505100	2.56732100	-0.88555700
C	-4.77839900	2.67073400	0.34968300
H	-4.52820100	3.65431900	0.75775000
H	-5.86437500	2.67017300	0.20314400
C	-4.48699300	1.32572400	-1.88887100
H	-4.58279300	1.64941700	-2.92880400
H	-5.48842400	0.98689300	-1.59770800

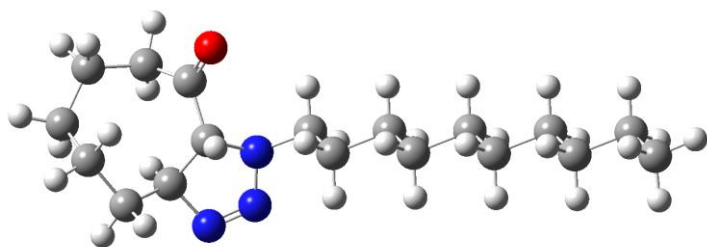
Zero-point correction = 0.495104 (Hartree/Particle)

Thermal correction to Energy = 0.519384

Thermal correction to Enthalpy = 0.520328

Thermal correction to Gibbs Free Energy = 0.437583  
 Sum of electronic and zero-point Energies = -945.005233  
 Sum of electronic and thermal Energies = -944.980954  
 Sum of electronic and thermal Enthalpies = -944.980010  
 Sum of electronic and thermal Free Energies = -945.062755  
 Imaginary Frequencies: 0

**(Product) 14aa'**



C	10.13591800	0.46313000	1.12396400
H	9.97409600	1.17340800	1.94132900
H	10.21836700	-0.53554700	1.56510400
H	11.09772200	0.70246800	0.66126600
C	8.99369200	0.52419100	0.10531100
H	8.96036000	1.52361900	-0.34550900
H	9.19948500	-0.17413600	-0.71520900
C	7.62333600	0.19930200	0.71080600
H	7.65924600	-0.79909000	1.16638500
H	7.41690000	0.90093900	1.52980700
C	6.47344900	0.25100000	-0.30128200
H	6.43915900	1.24831400	-0.75895200
H	6.67988500	-0.45306700	-1.11798100
C	5.10438500	-0.07166000	0.30827700
H	5.14246400	-1.06479800	0.77458700
H	4.89410400	0.63830800	1.11881500
C	3.95455600	-0.03569600	-0.70478900
H	4.16269500	-0.74923800	-1.51265100
H	3.91620500	0.95577800	-1.17442400
C	2.58775500	-0.35571700	-0.08904600
H	2.37414700	0.36496100	0.71074300
H	2.62957000	-1.34209300	0.39042700
C	1.43876700	-0.33866900	-1.10362900
H	1.64904400	-1.06383900	-1.90002300
H	1.39589500	0.64553100	-1.58704900
C	0.07613200	-0.65566400	-0.47659500
H	-0.14078800	0.08068900	0.30474100
H	0.11245300	-1.63633100	0.01095400
C	-1.04827900	-0.66073200	-1.51893900

H	-0.83891000	-1.39681200	-2.29854600
H	-1.12459200	0.31314000	-2.00698700
N	-2.38004300	-0.98519800	-0.99502600
N	-2.57609900	-2.29028000	-0.62605800
N	-3.51436700	-2.43944000	0.18370000
C	-3.57125200	1.18193300	-0.66065800
O	-2.78870300	2.11329100	-0.72595500
C	-3.08676400	-0.12573000	-0.02305700
C	-4.15381400	-1.11677700	0.44616100
H	-2.40893500	0.15500800	0.79574200
H	-5.00497100	-1.09554000	-0.24400400
C	-4.99703200	1.32553400	-1.14620100
H	-5.37241900	0.39135100	-1.56979400
H	-4.97546800	2.06947700	-1.94527900
C	-4.66421200	-0.92962300	1.86559200
H	-5.41345000	-1.70173600	2.06748300
H	-3.84300600	-1.08645300	2.57275000
C	-6.38248200	0.88226200	1.08999800
H	-7.17047800	1.40078100	1.64432200
H	-6.86376400	-0.00669500	0.66513300
C	-5.96370600	1.84076300	-0.04242500
H	-6.87223200	2.15930600	-0.56182700
H	-5.53078500	2.74671300	0.39612900
C	-5.28178000	0.46277500	2.09614600
H	-5.70108600	0.46858100	3.10589900
H	-4.48974200	1.22136500	2.10813900

Zero-point correction = 0.495009 (Hartree/Particle)

Thermal correction to Energy = 0.519314

Thermal correction to Enthalpy = 0.520258

Thermal correction to Gibbs Free Energy = 0.436955

Sum of electronic and zero-point Energies = -945.004930

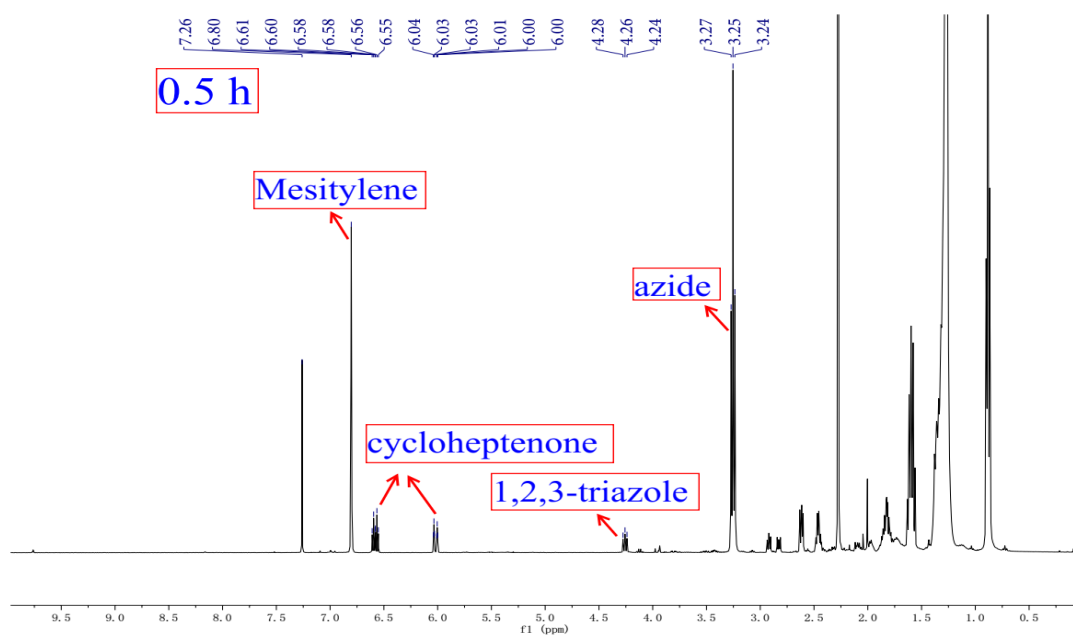
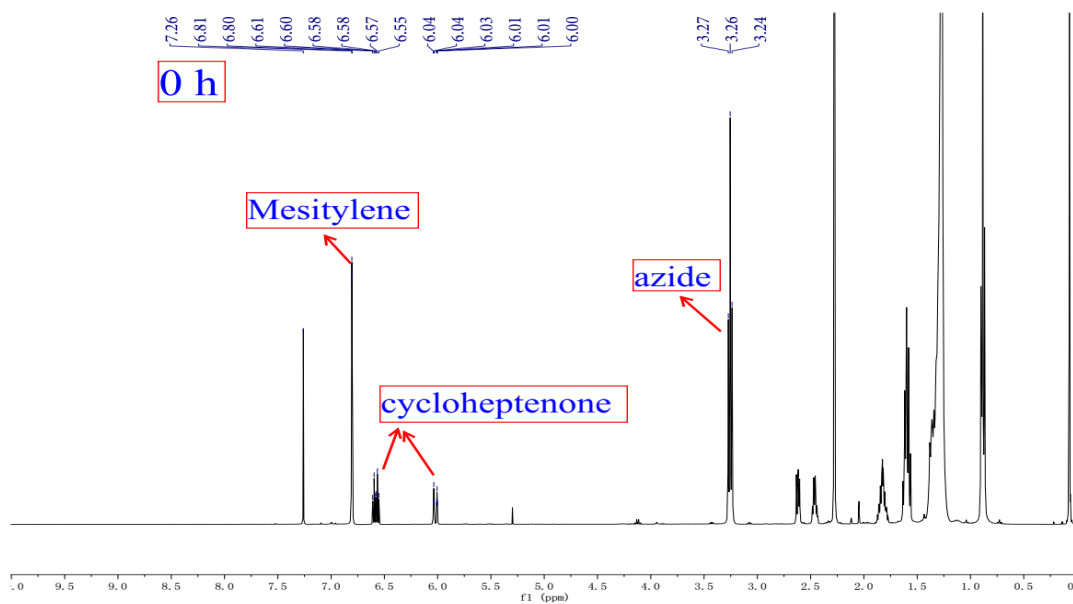
Sum of electronic and thermal Energies = -944.980625

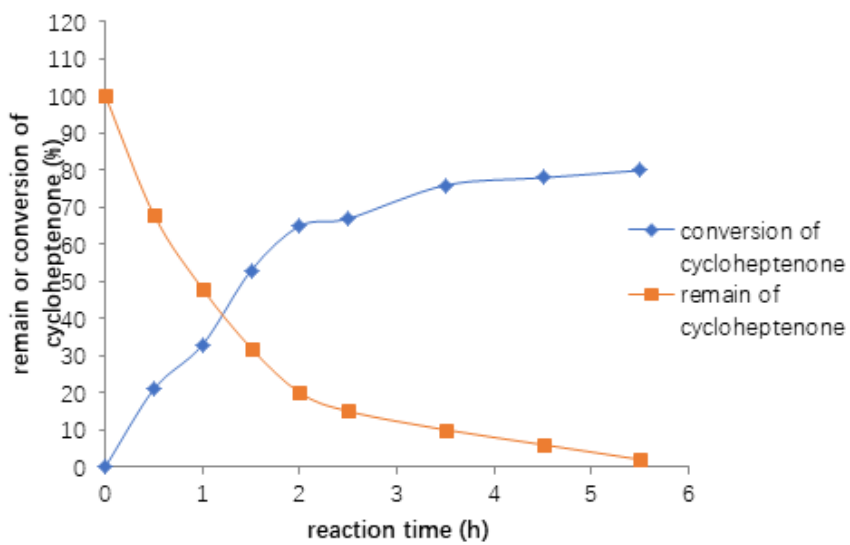
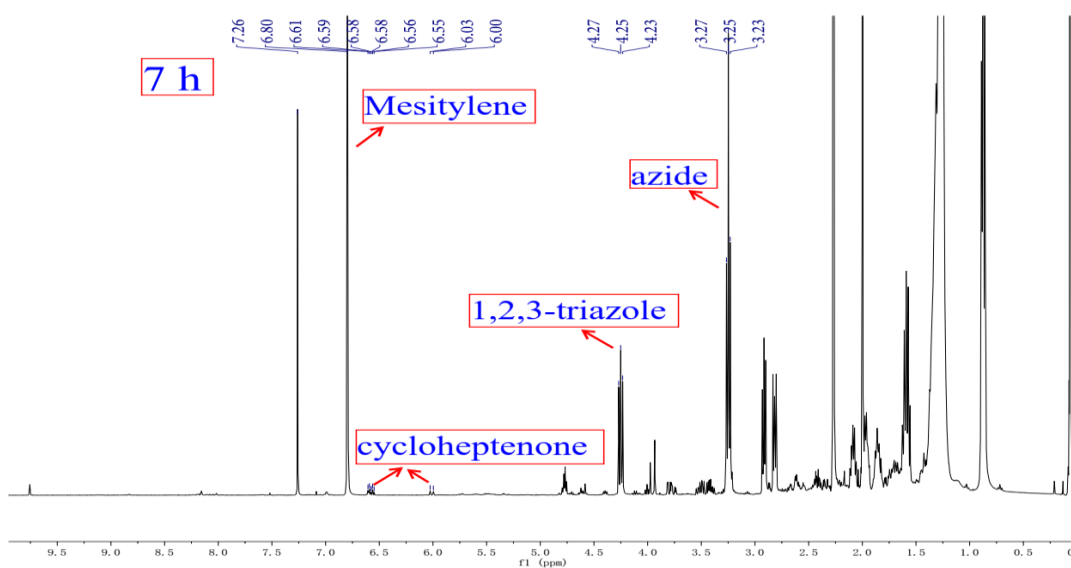
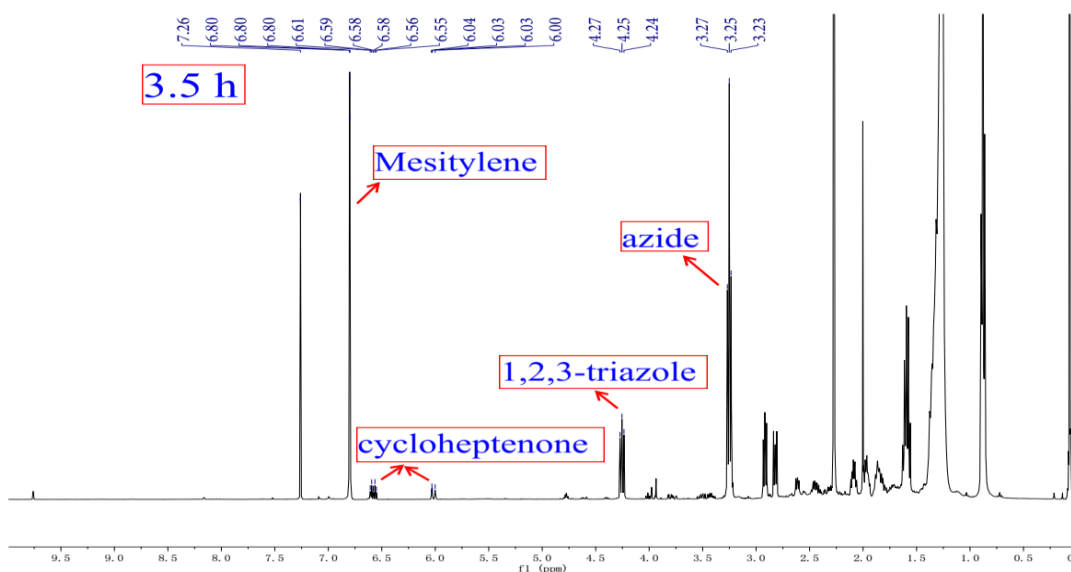
Sum of electronic and thermal Enthalpies = -944.979680

Sum of electronic and thermal Free Energies = -945.062984

Imaginary Frequencies: 0

## 9. Time Scale Study of the Photo-induced [3+2]-Cycloaddition



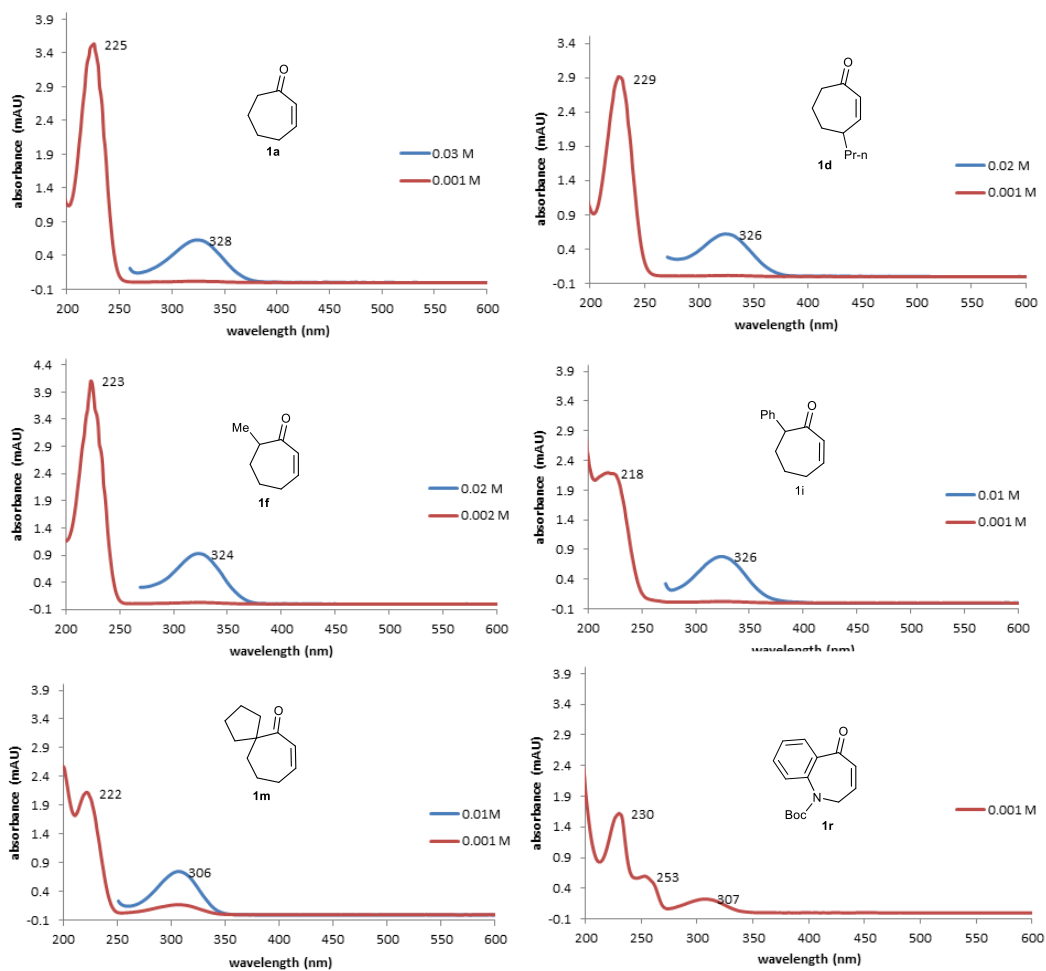


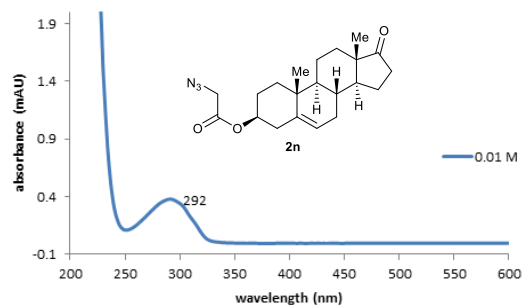
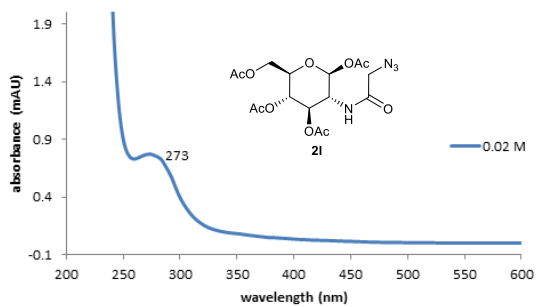
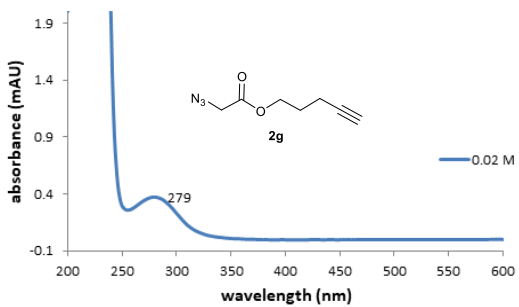
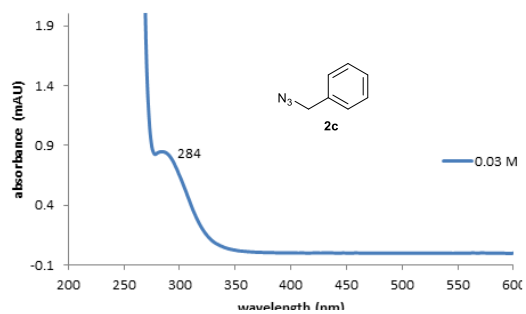
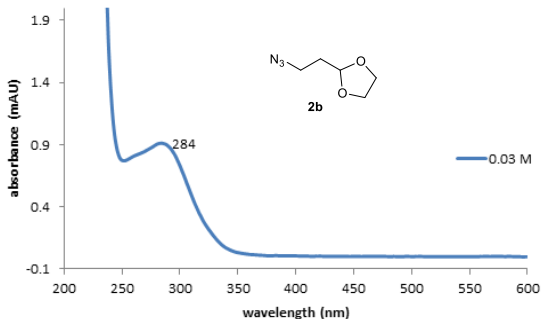
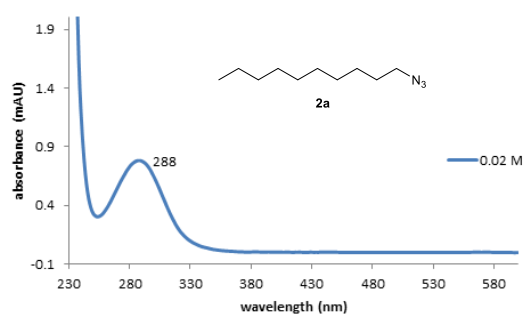
Time scale study of the photo-induced [3+2]-cycloaddition



## 10. UV Spectra of Representative Cycloheptenones and Azides

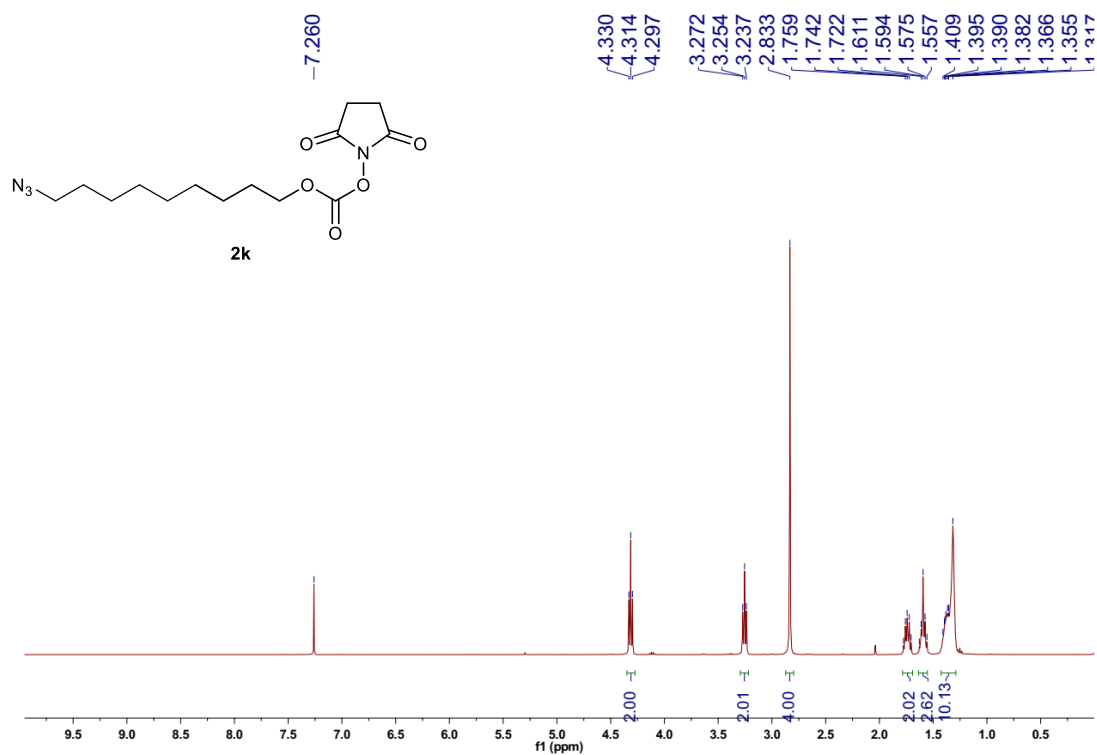
The UV-Vis measurement was performed with a CH<sub>3</sub>CN solution of representative cycloheptenones and azides.



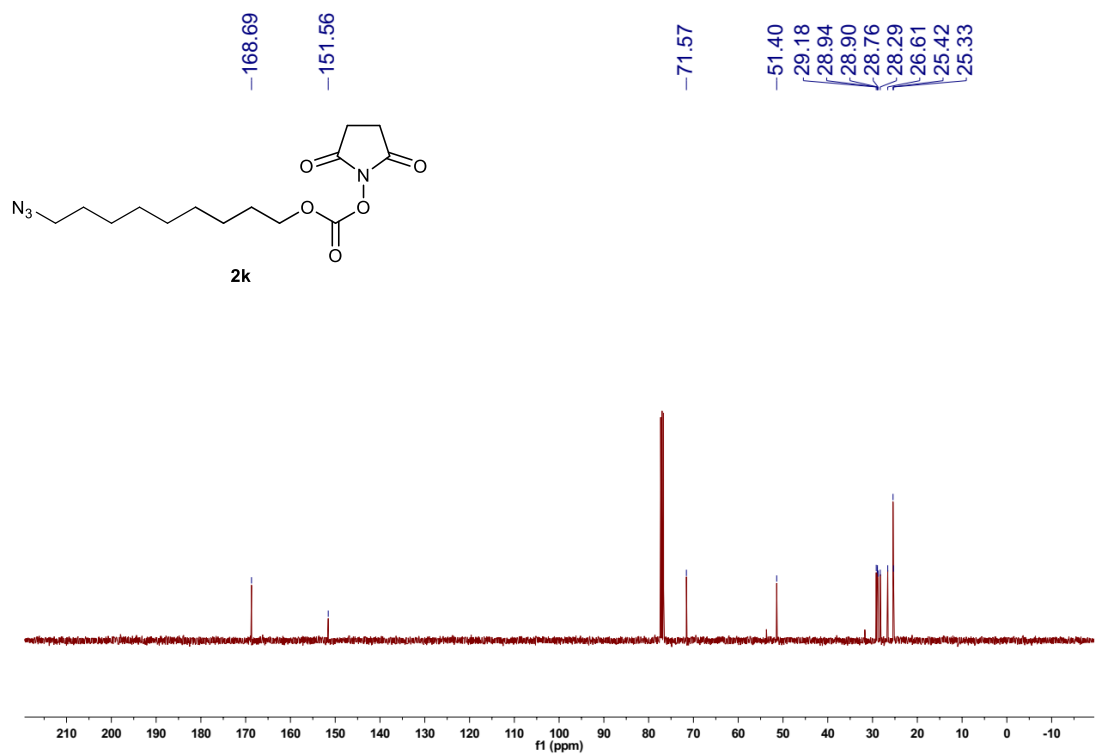


## 11. NMR Spectra

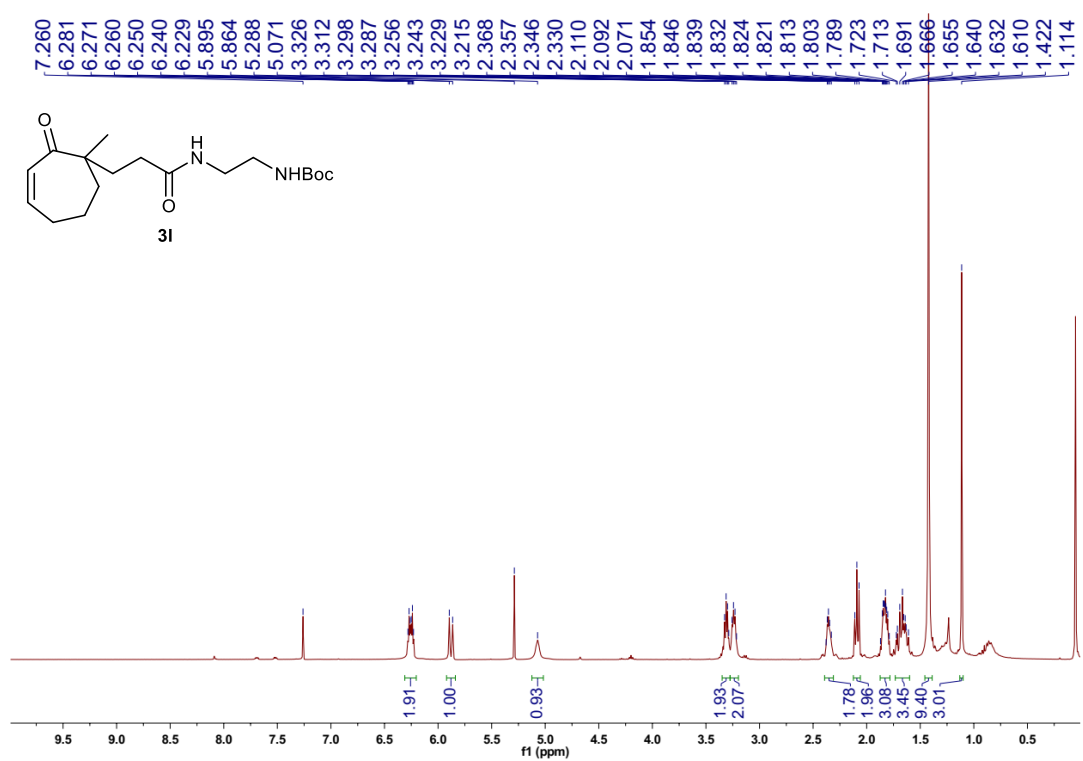
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



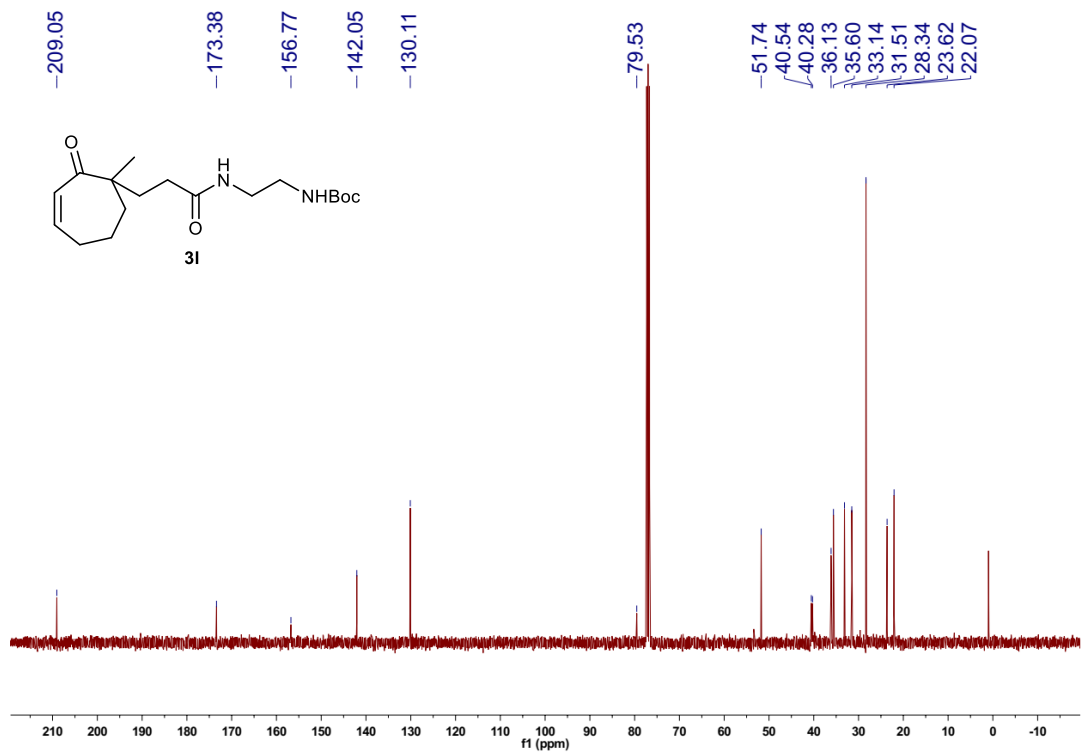
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



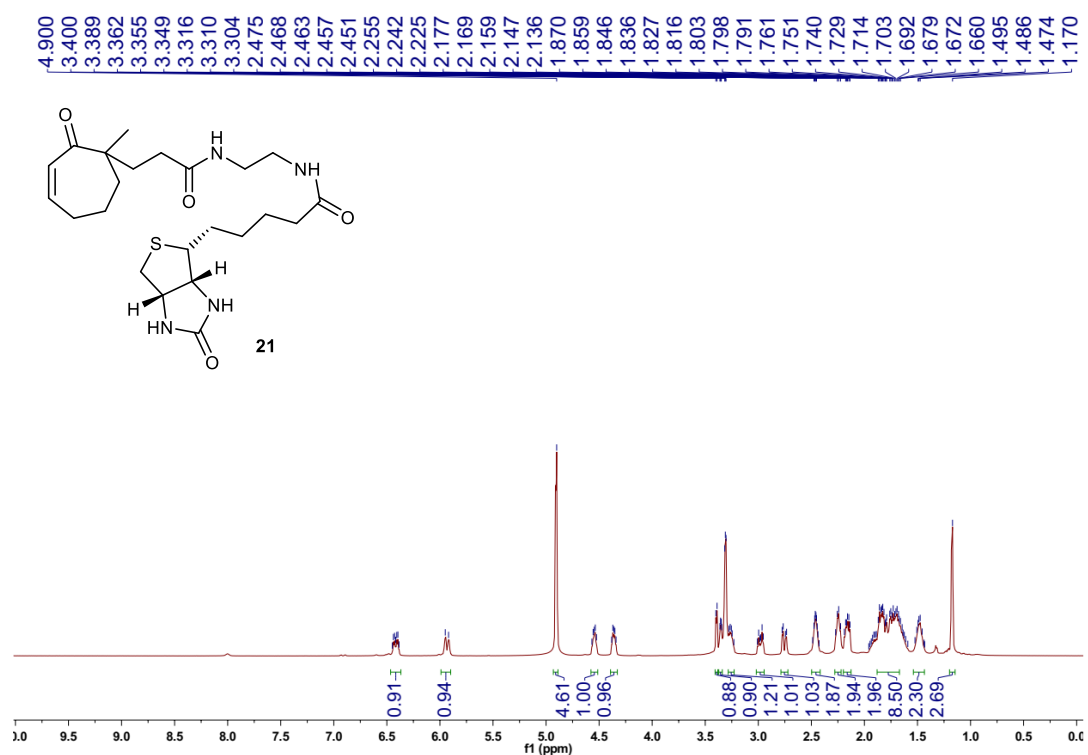
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



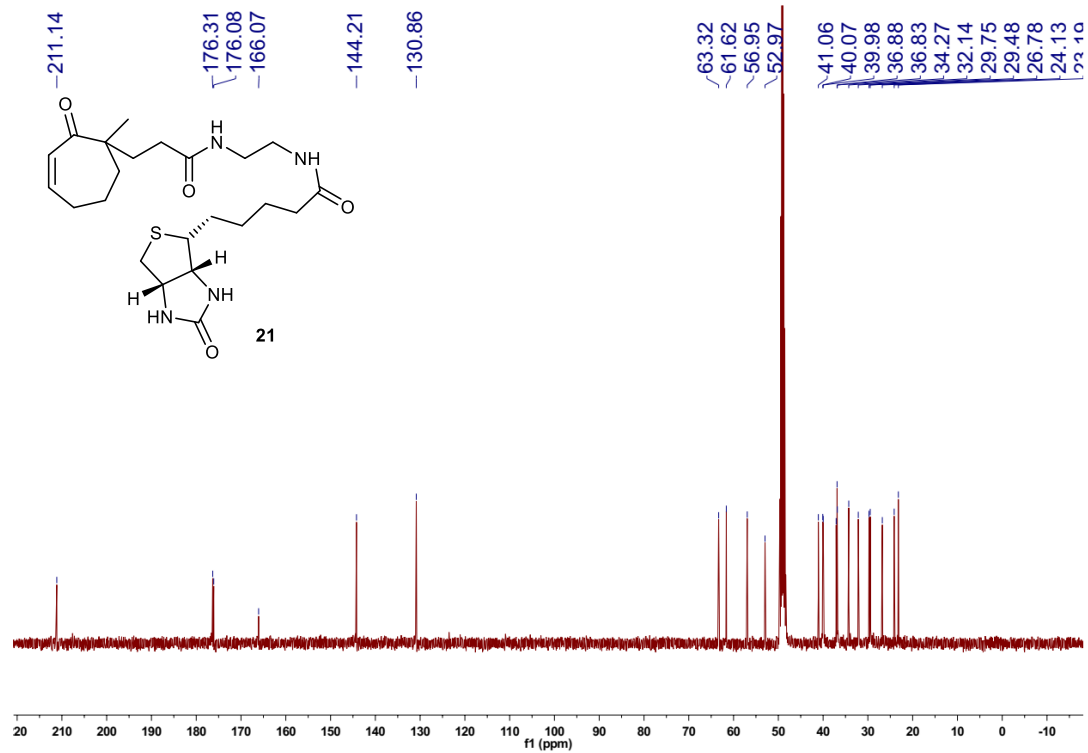
### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



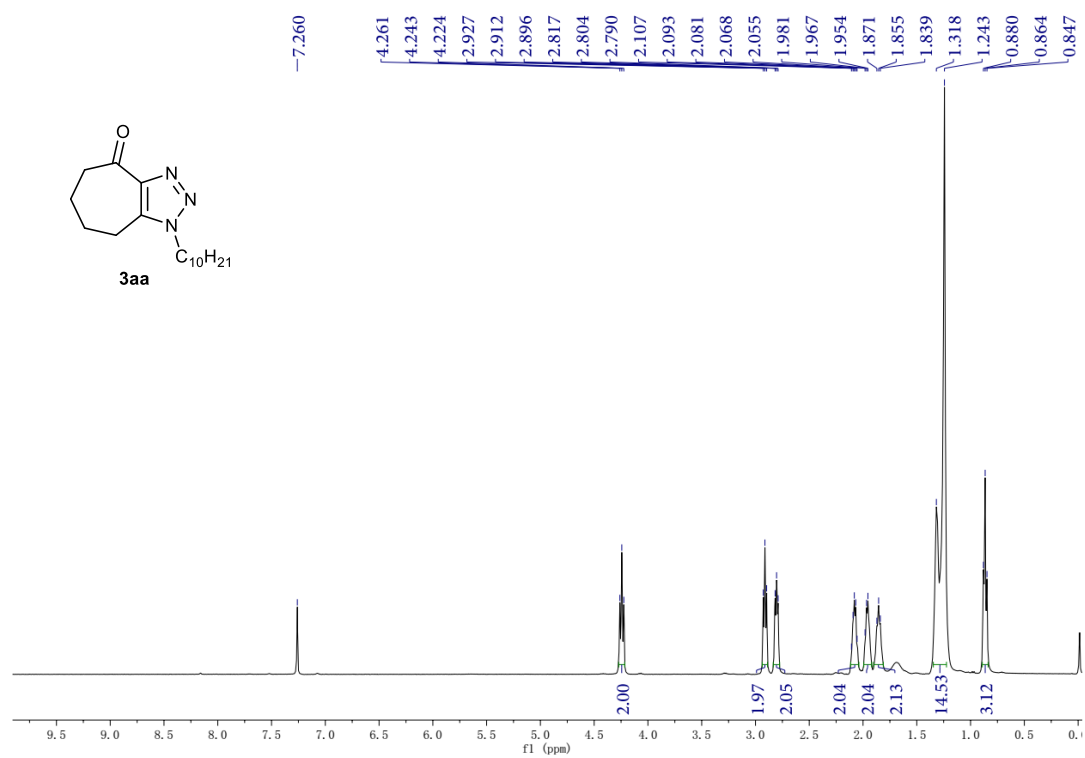
### <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)



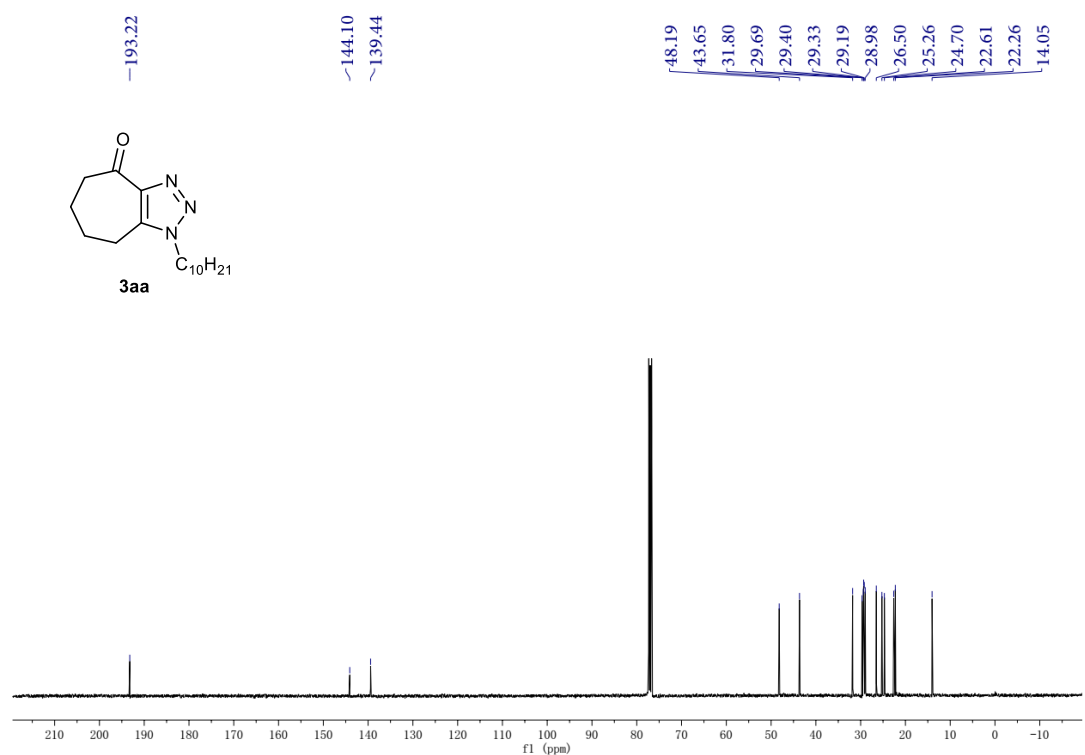
### <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD)



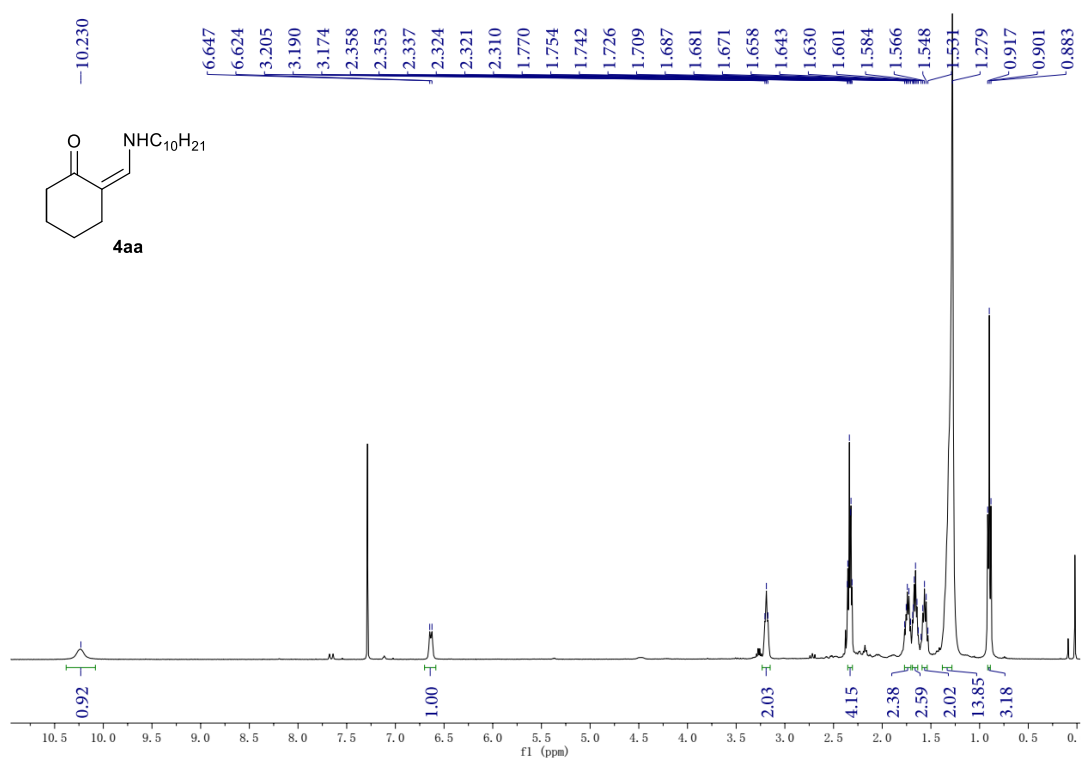
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



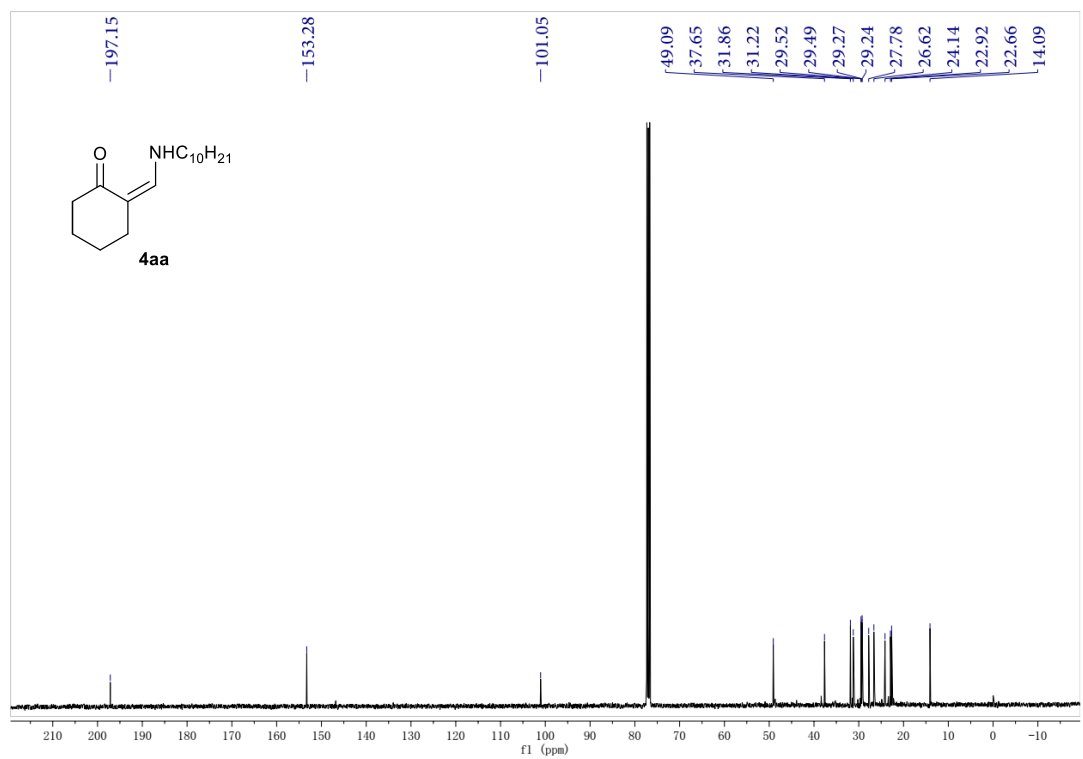
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



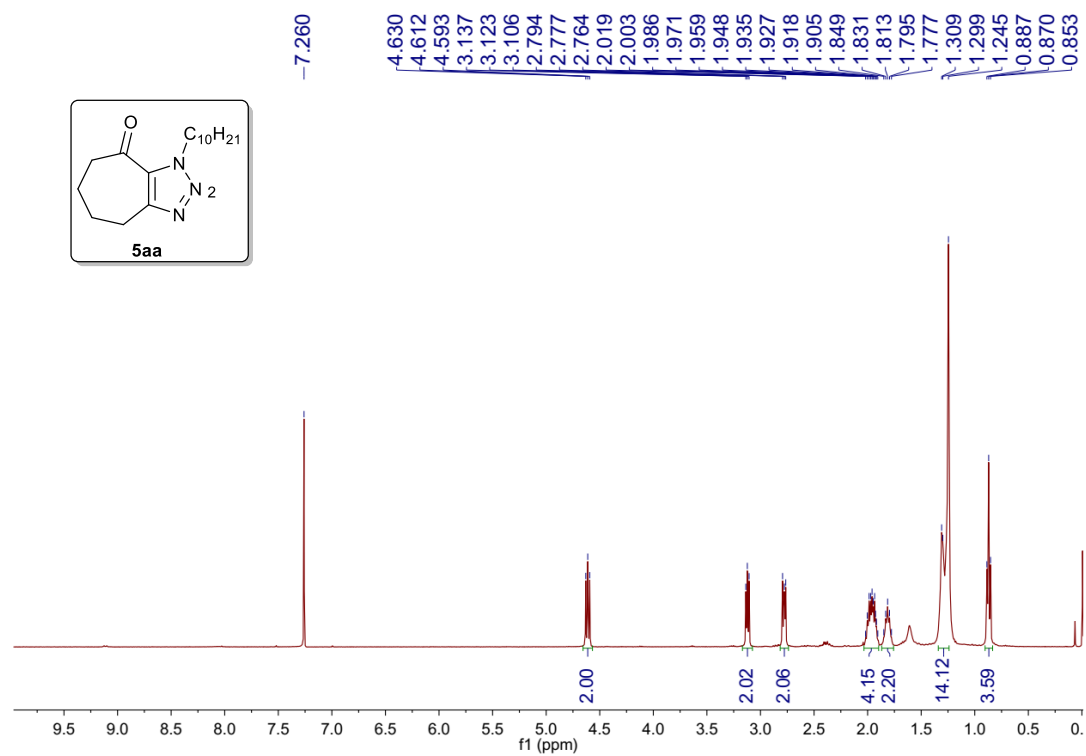
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



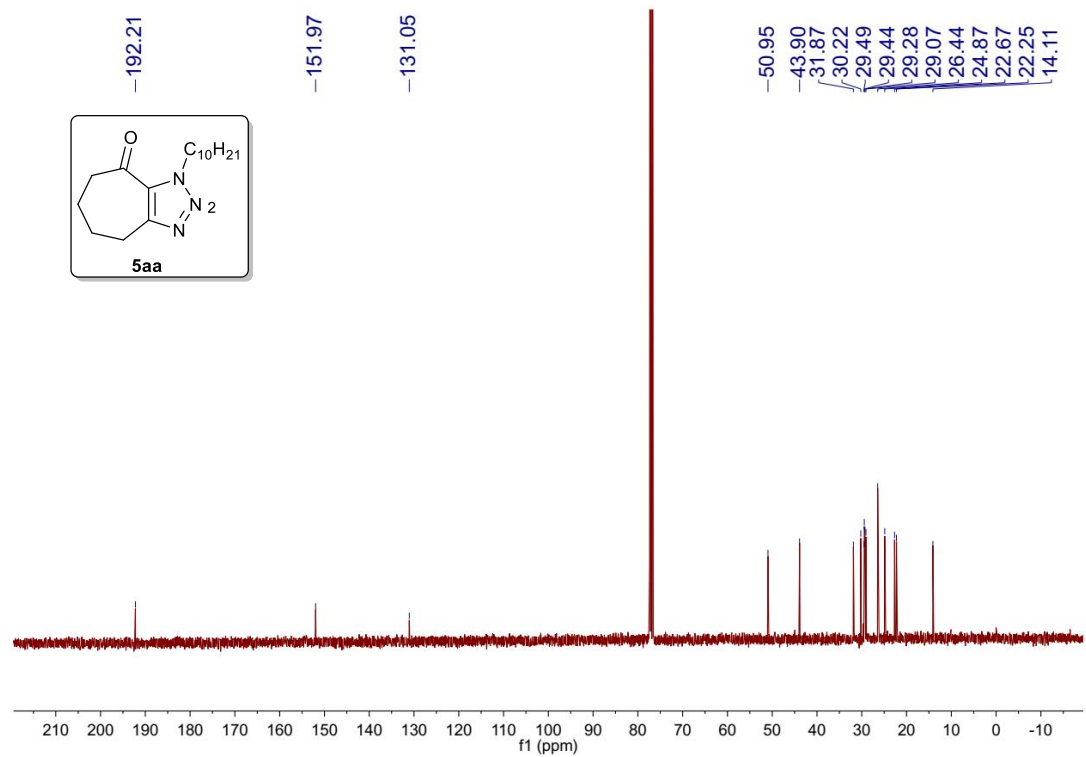
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

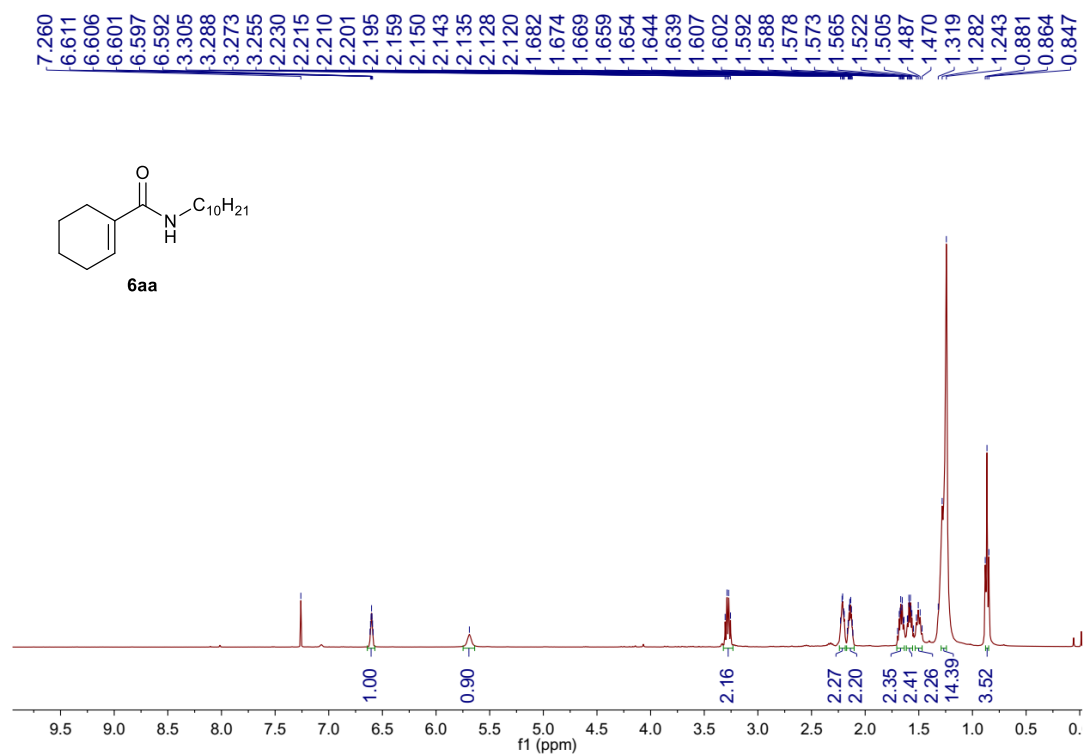


### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )

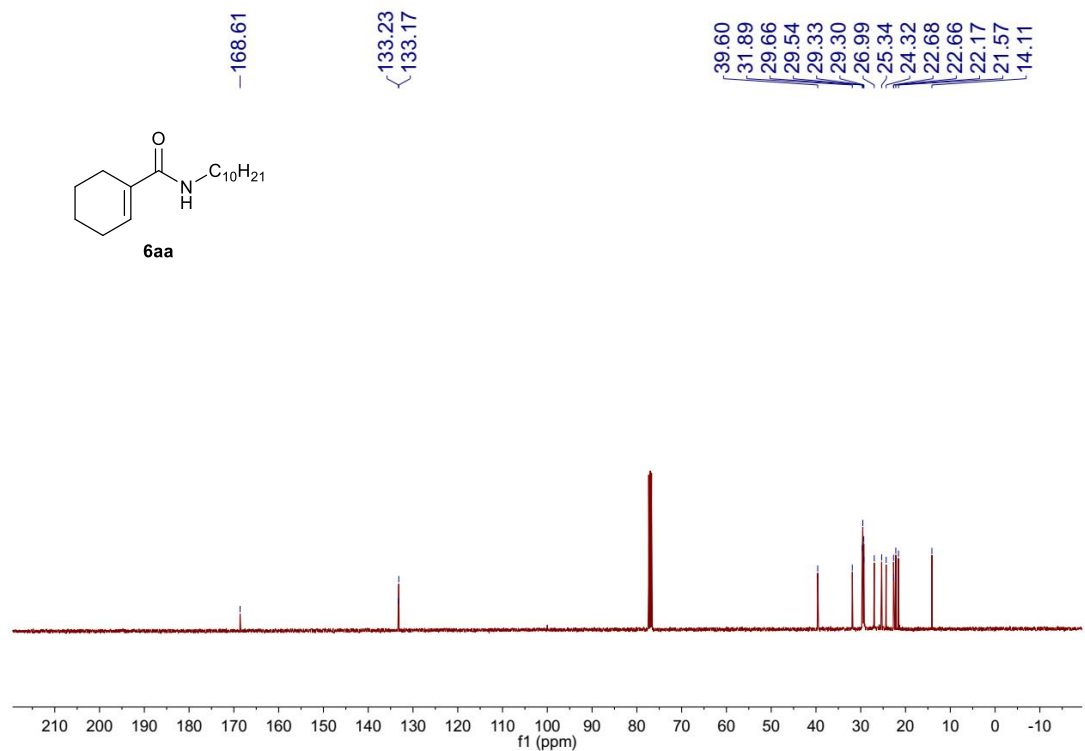




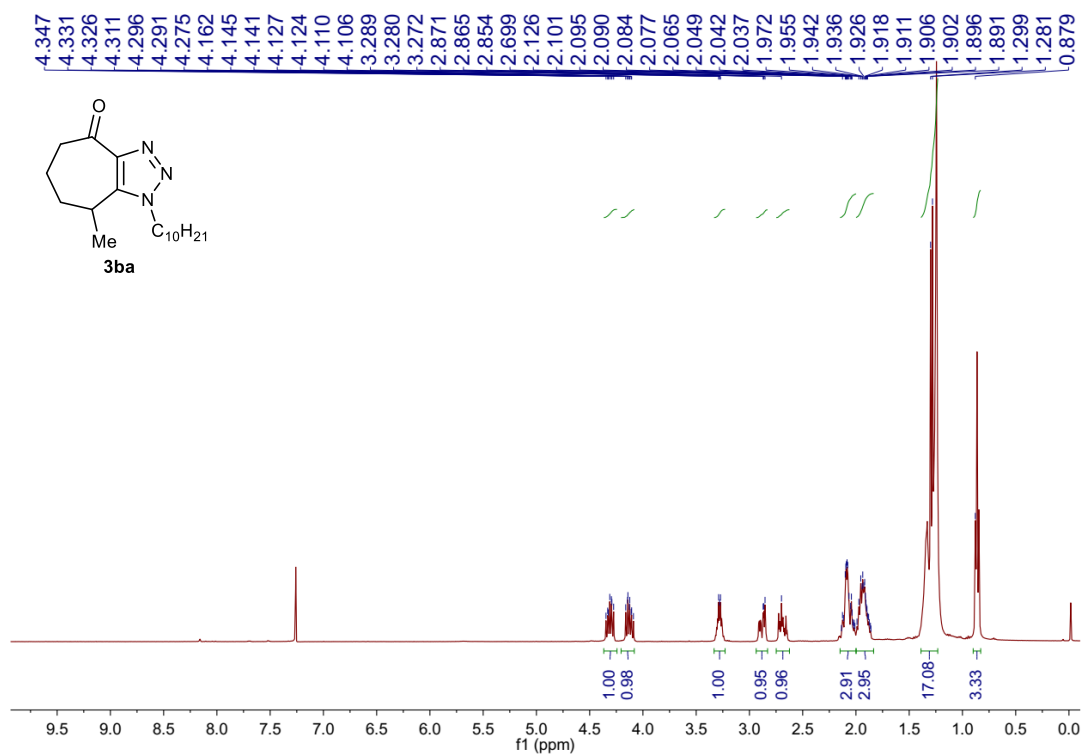
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



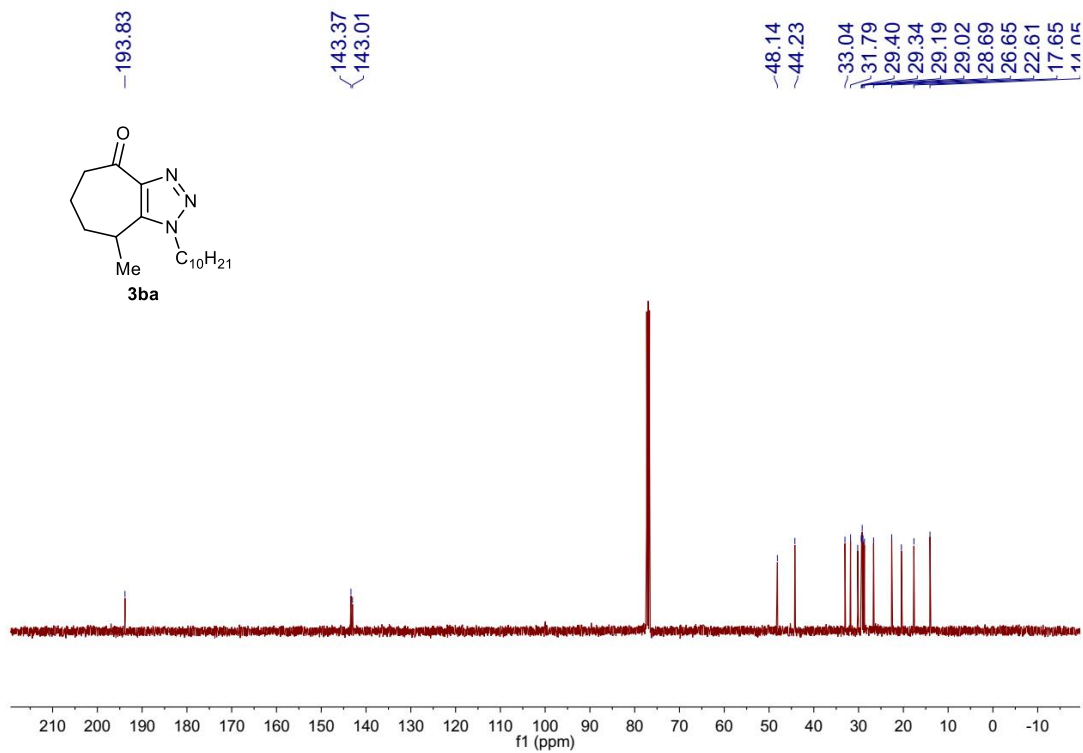
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



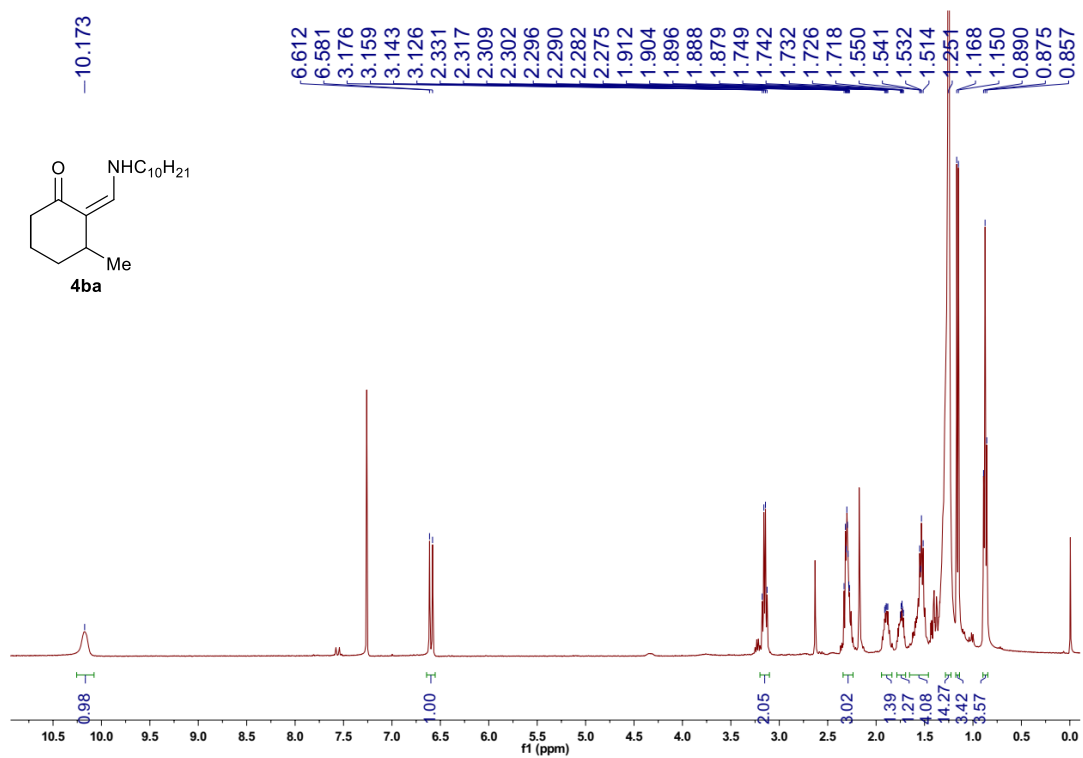
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



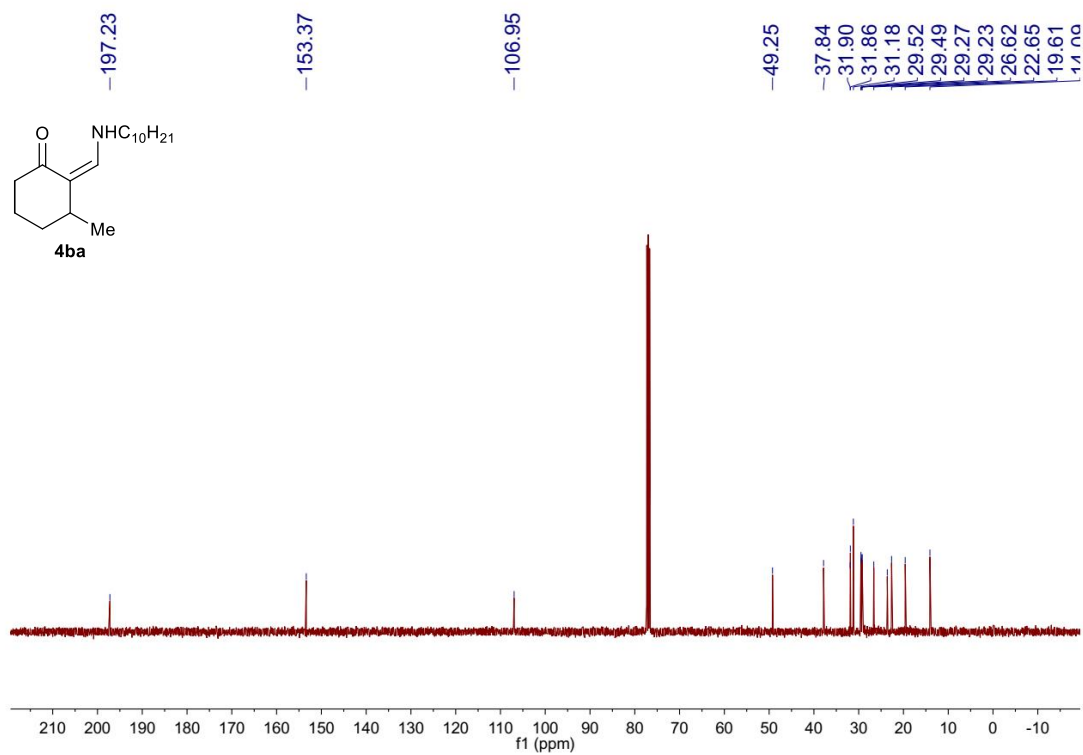
### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



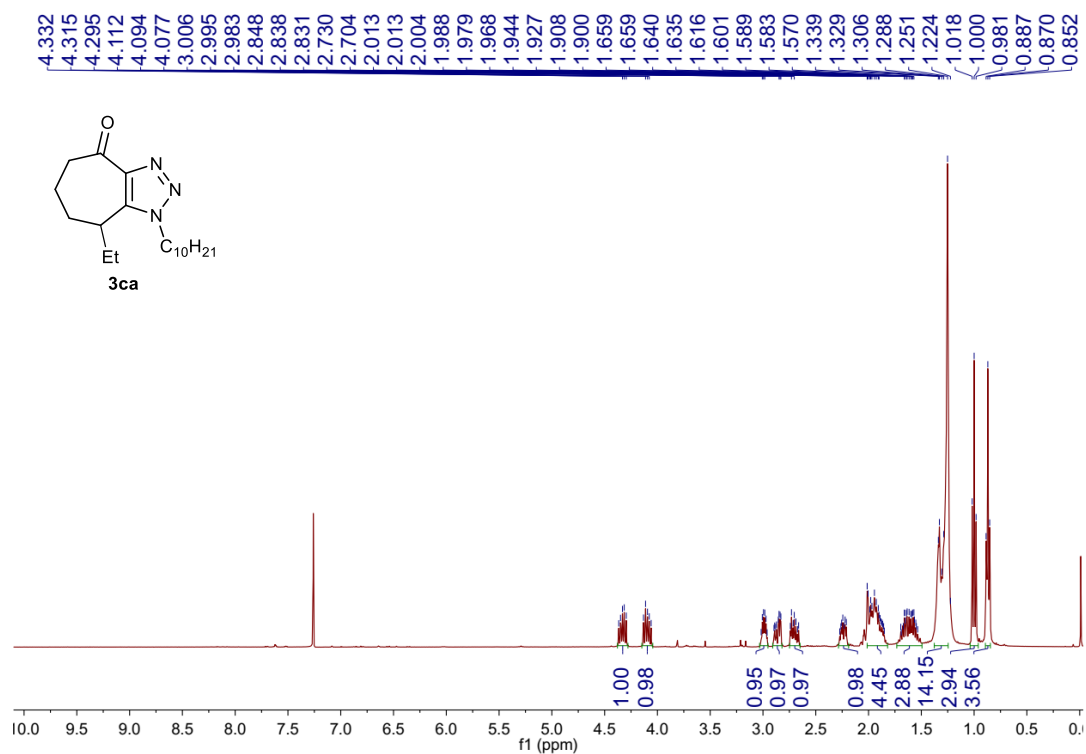
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



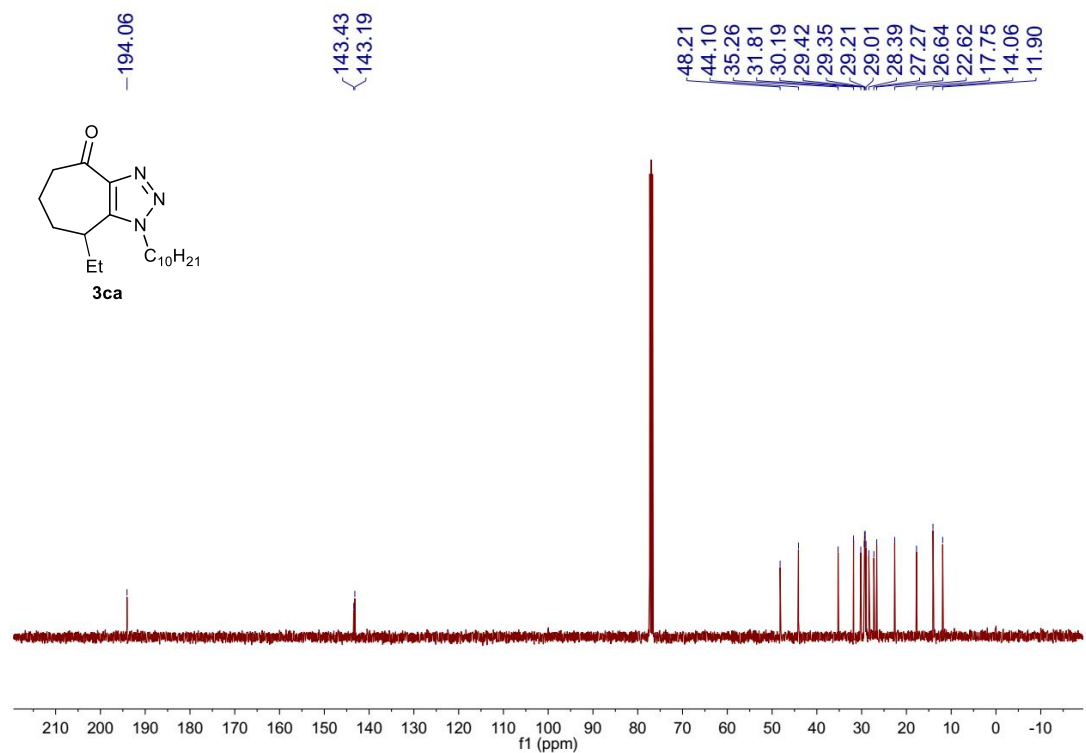
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



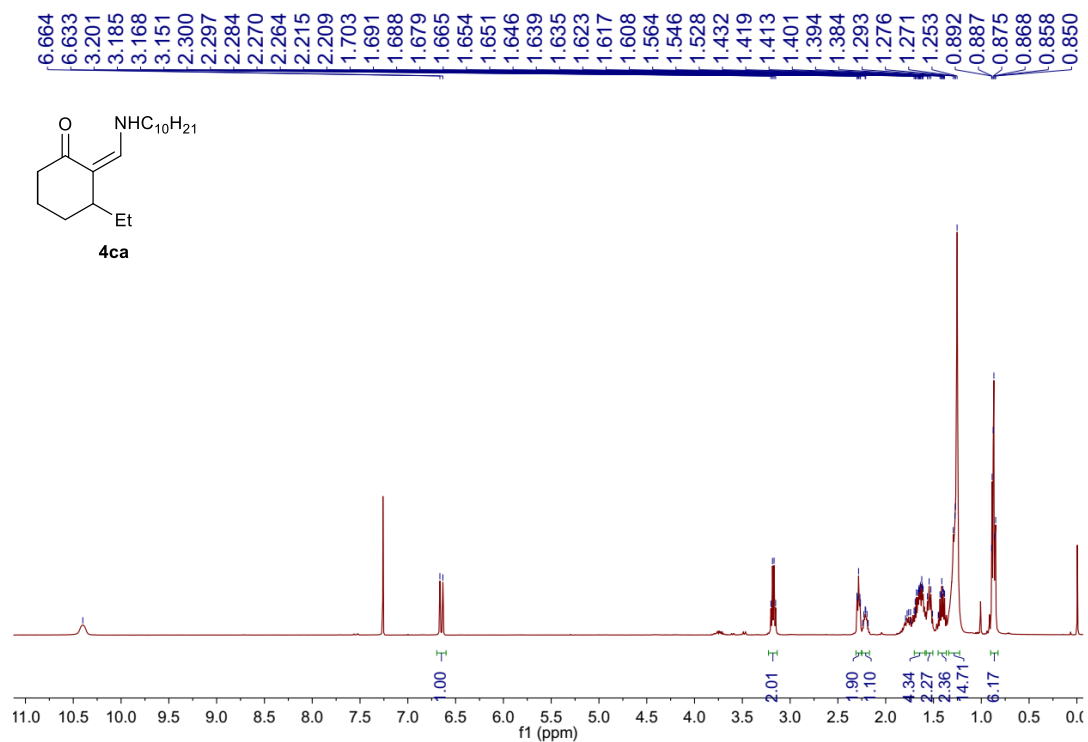
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



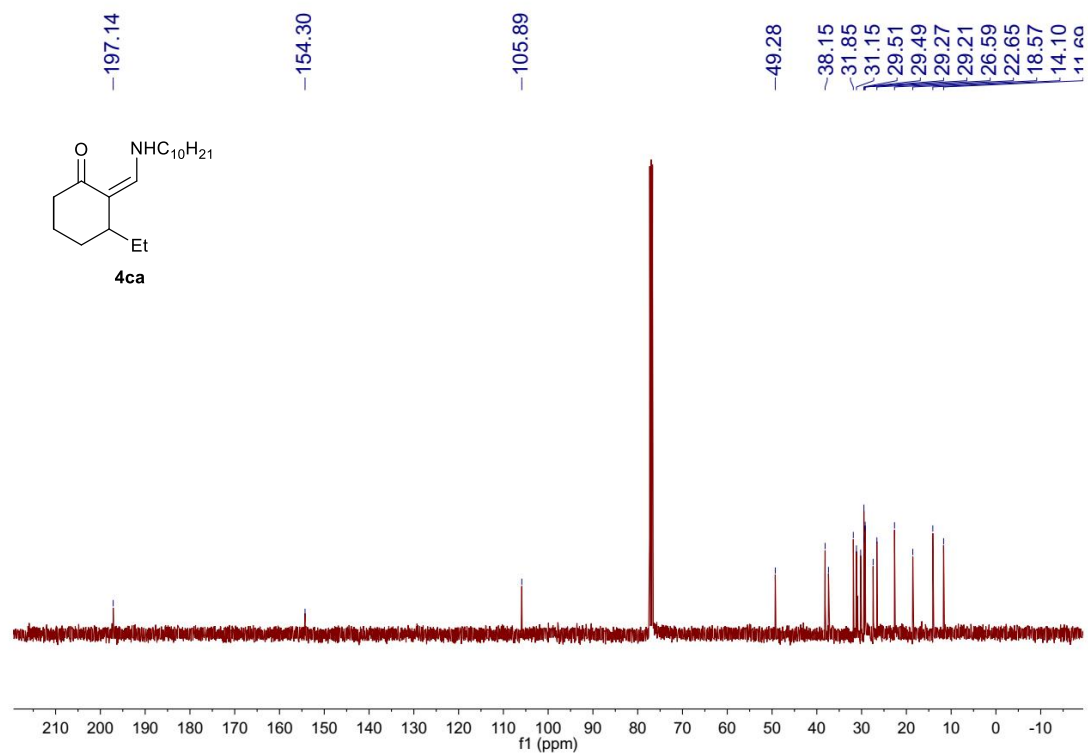
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



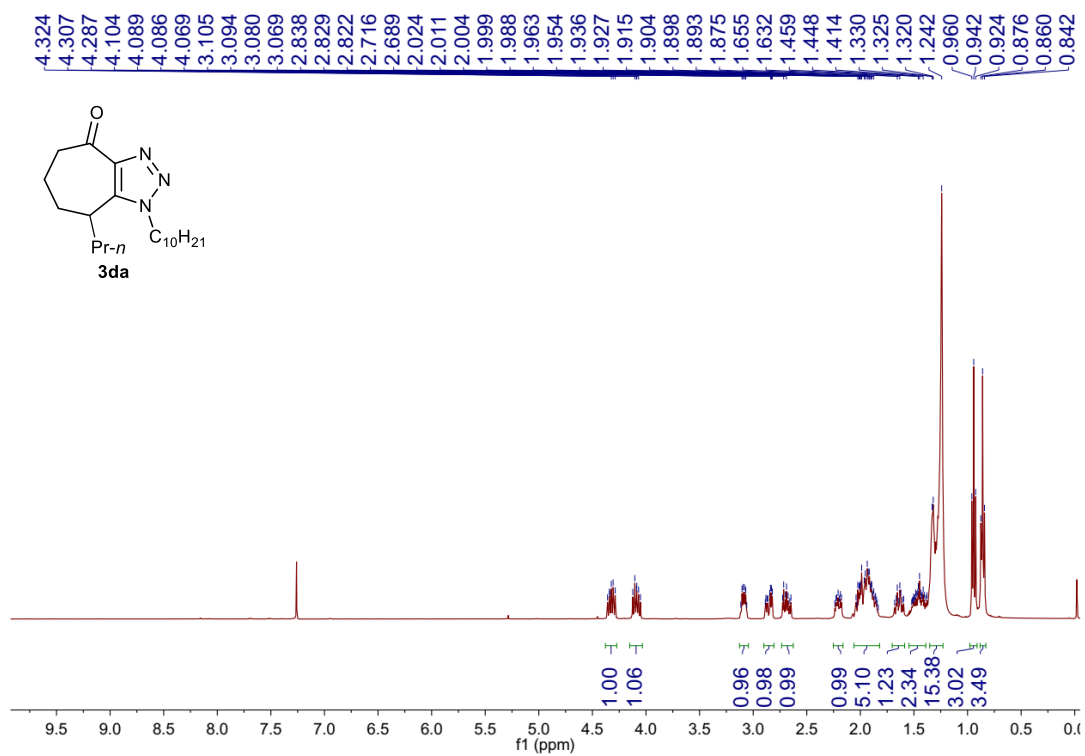
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



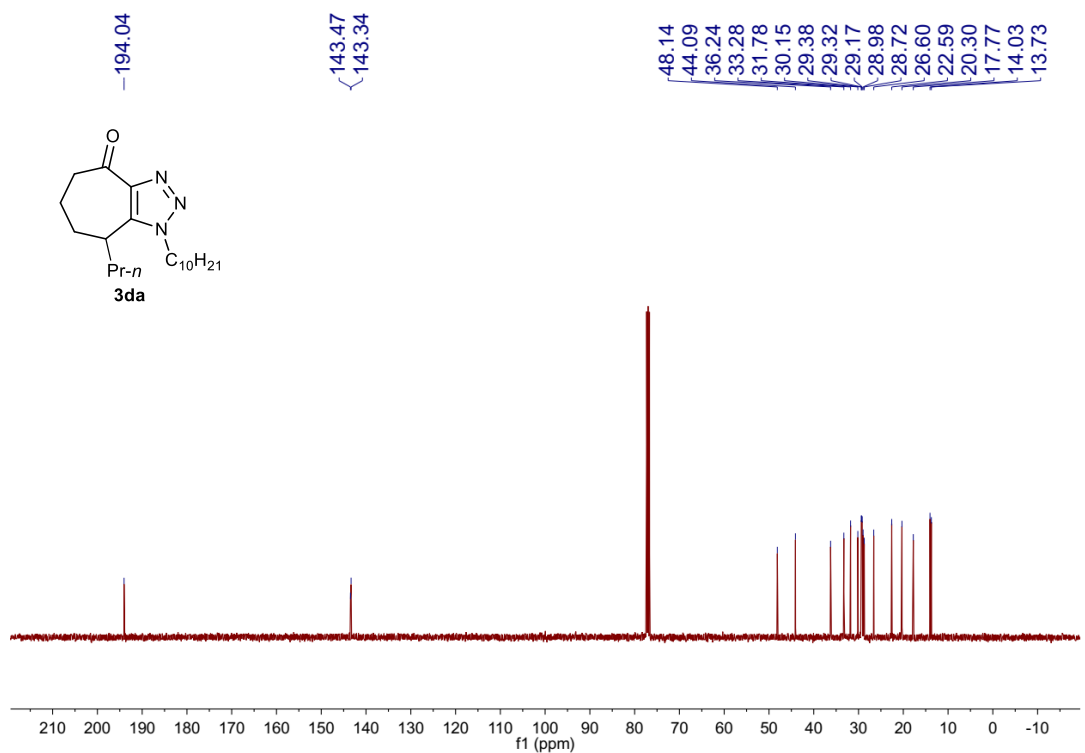
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



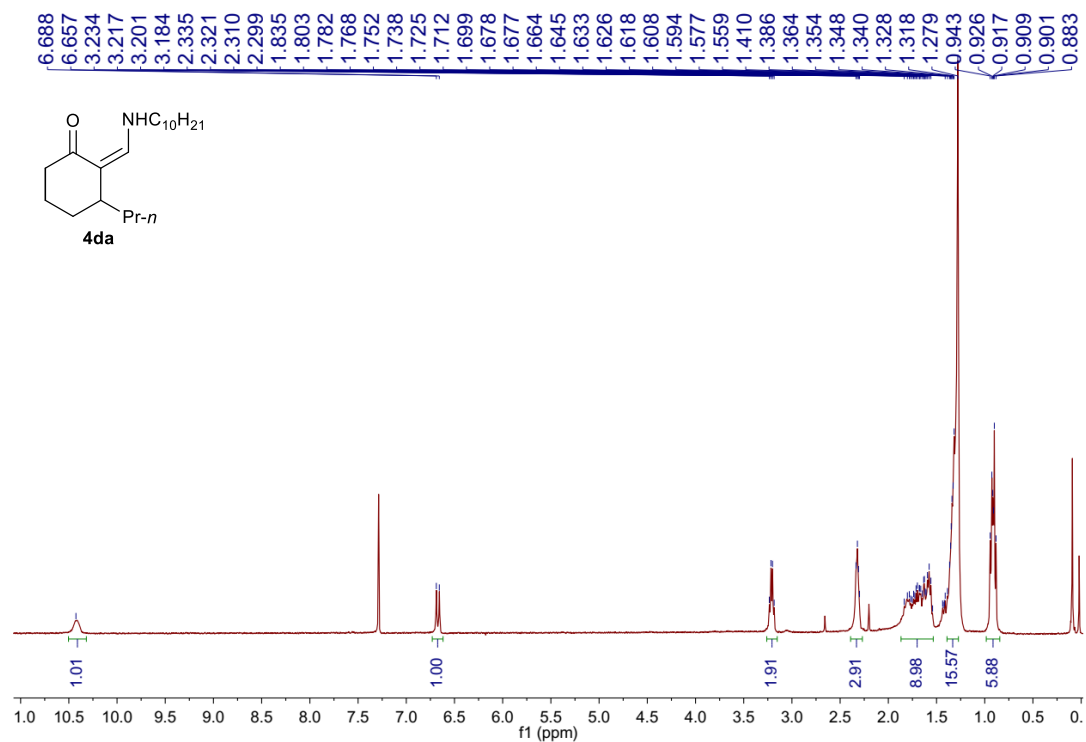
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



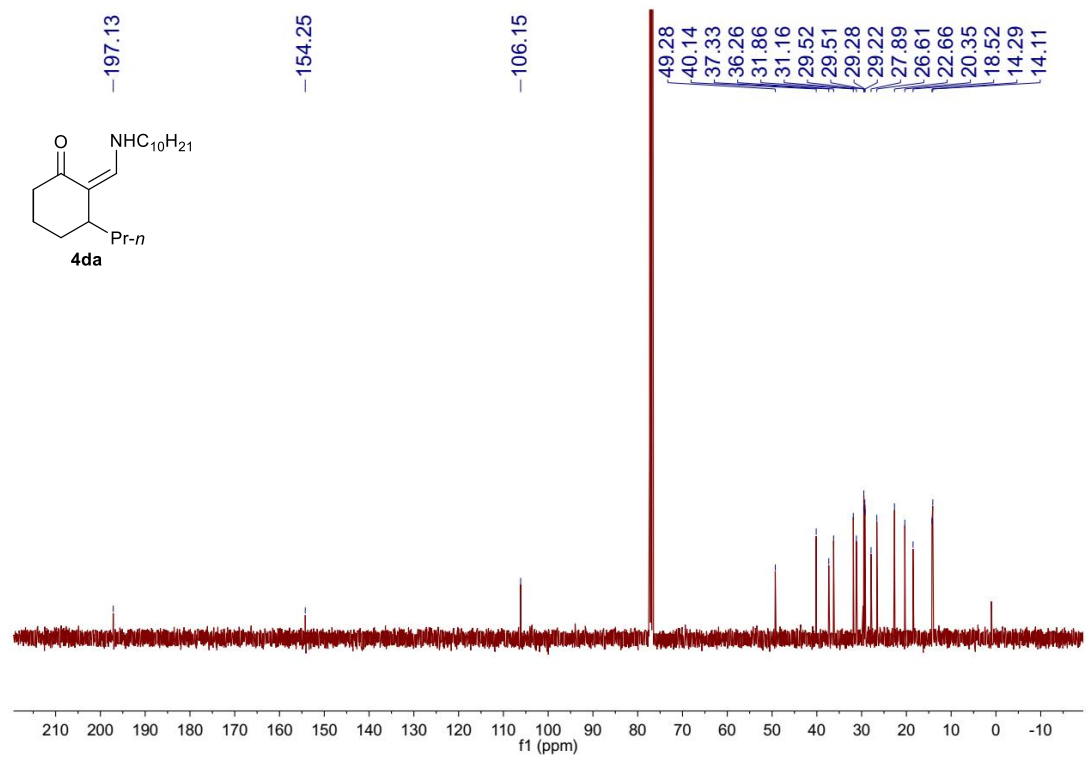
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



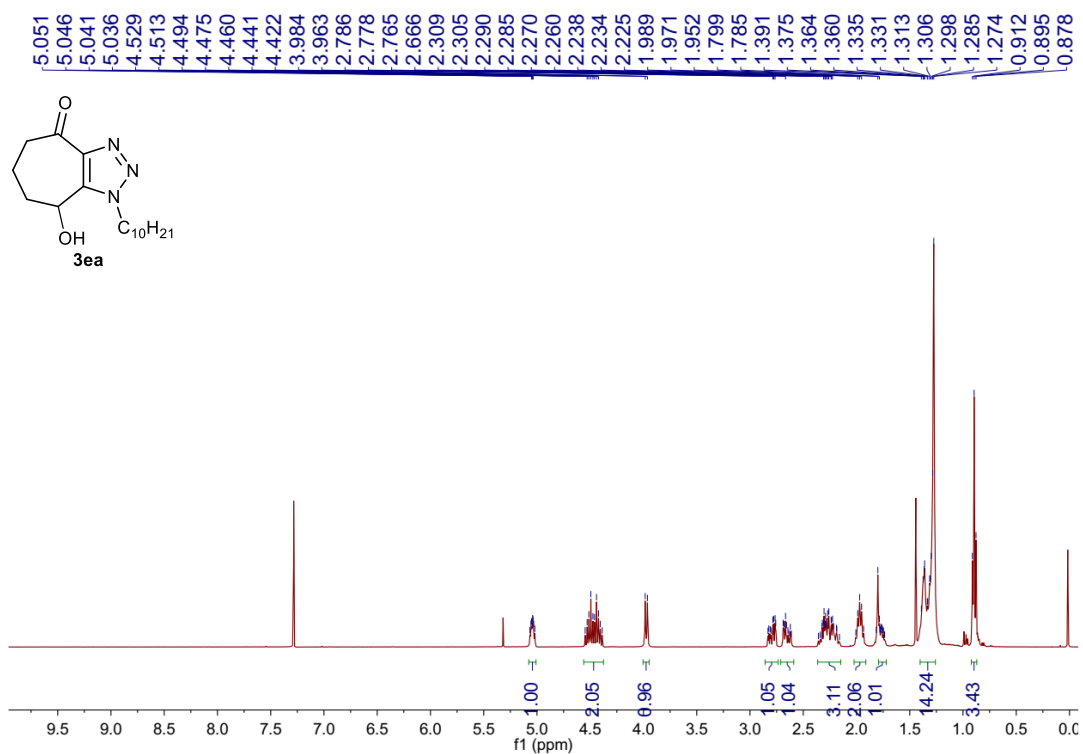
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



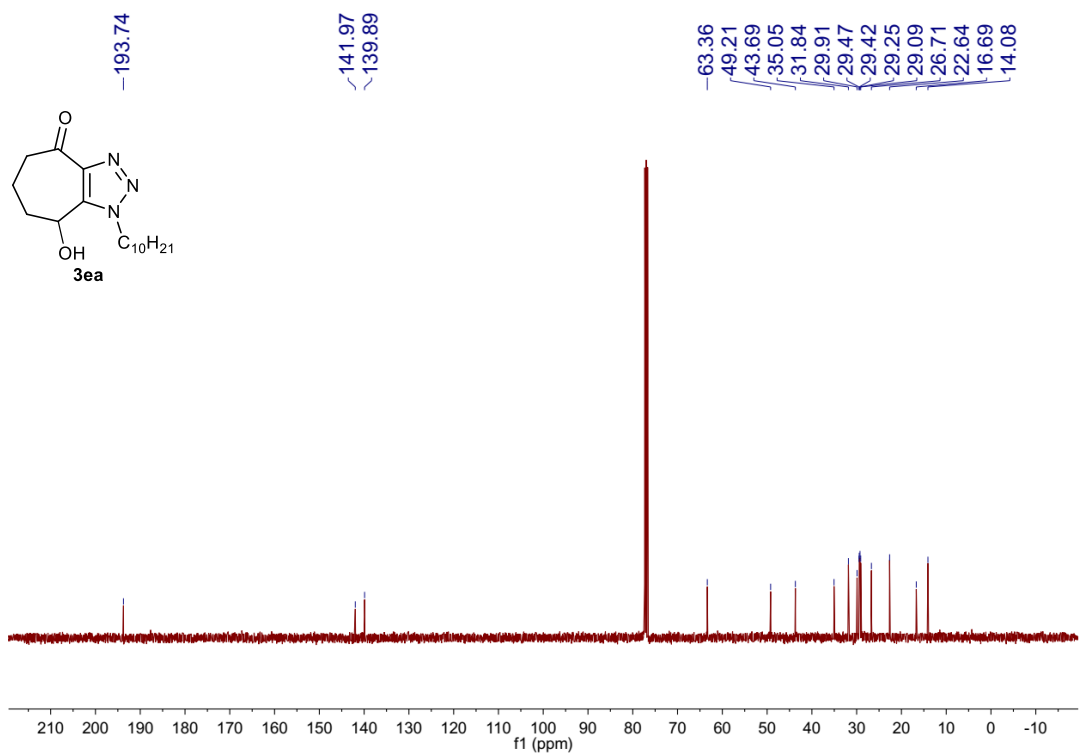
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

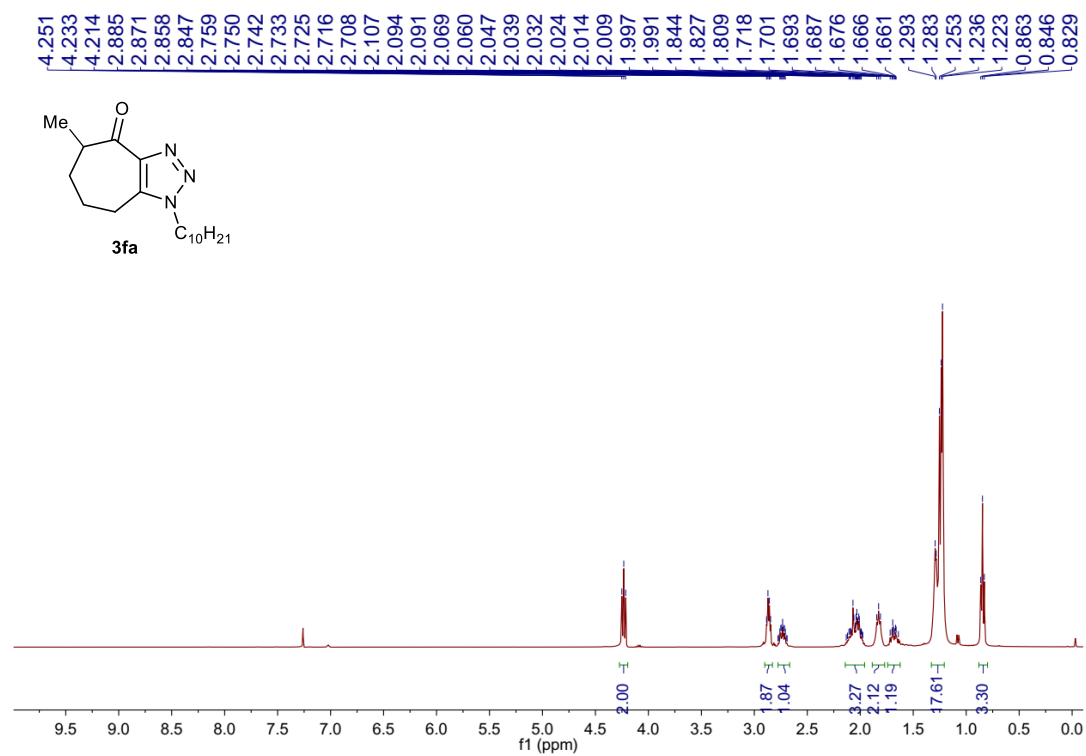


# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

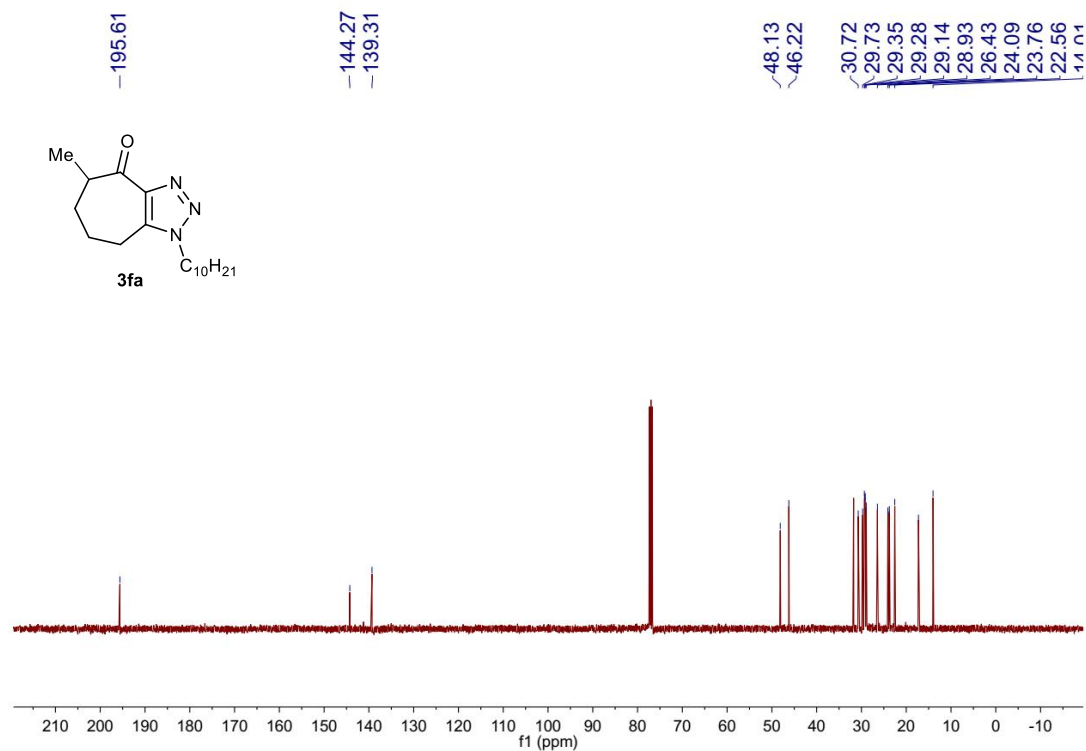




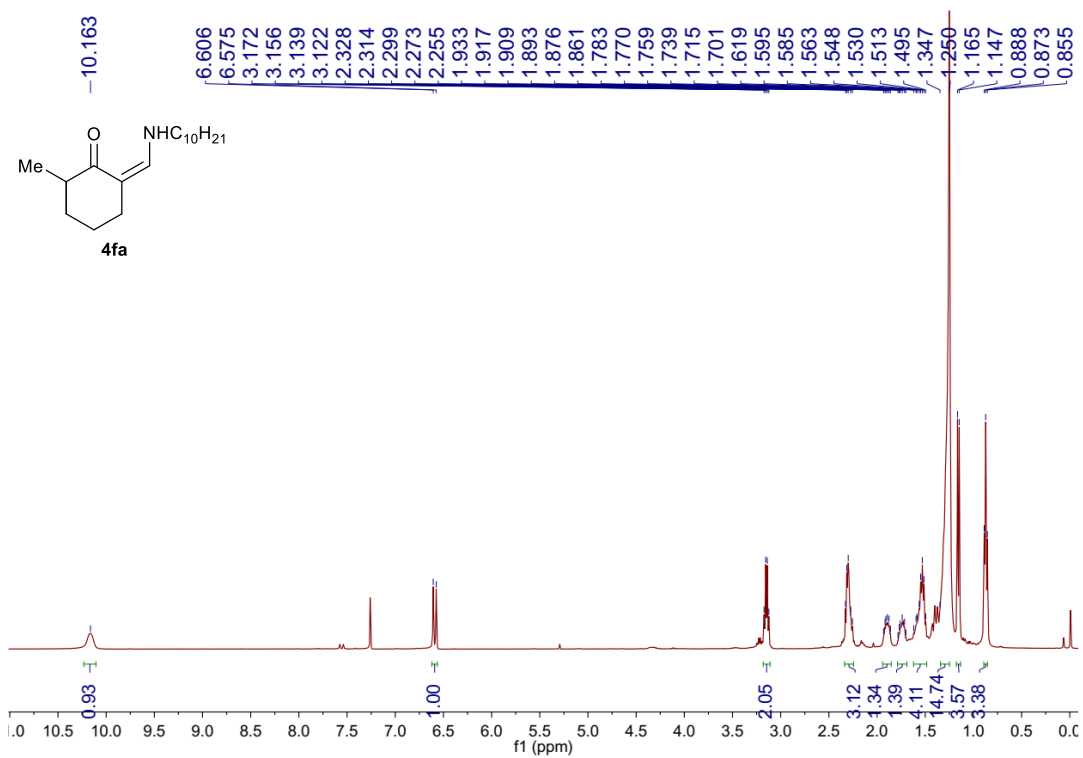
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



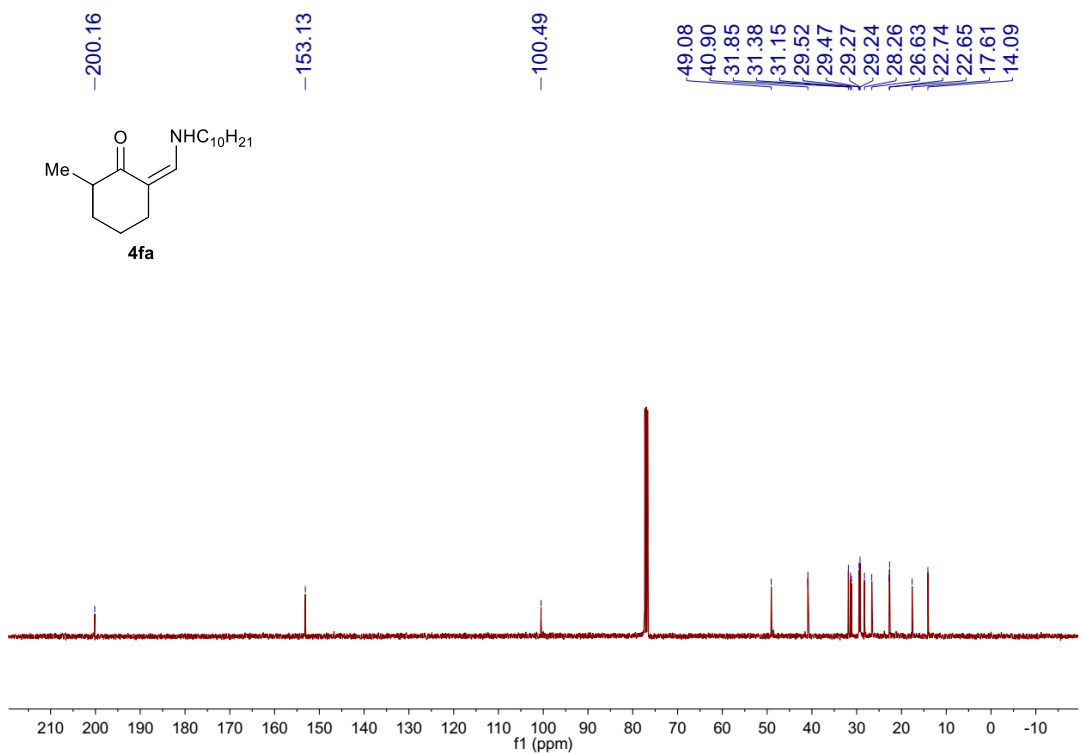
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



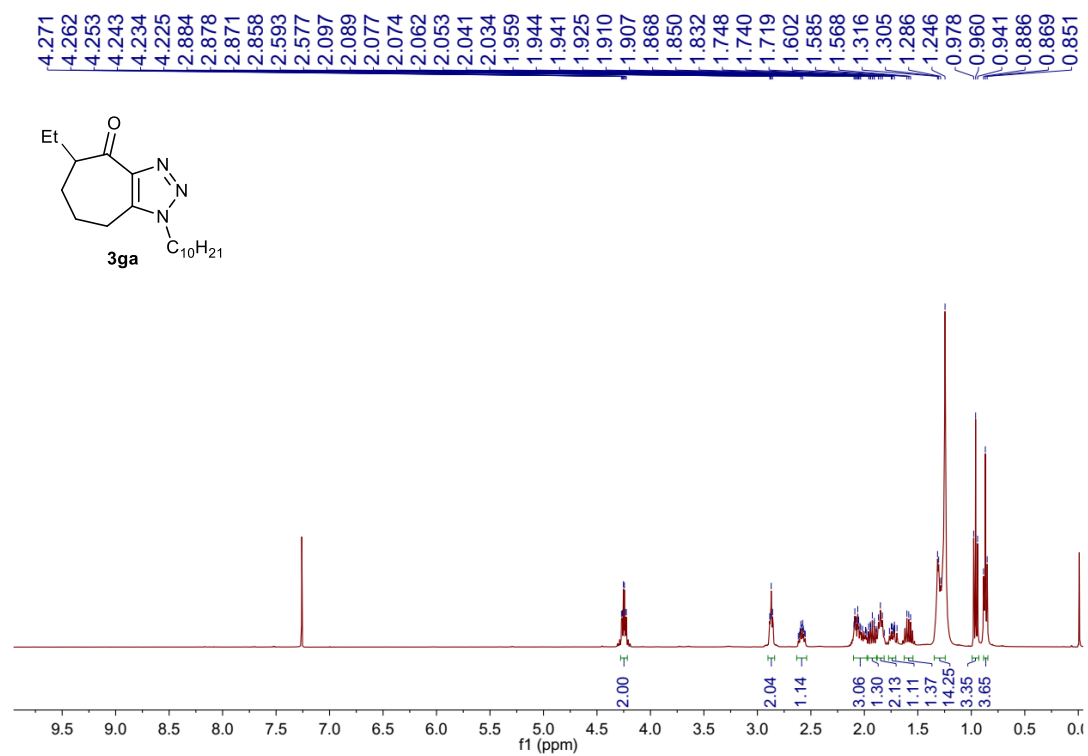
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



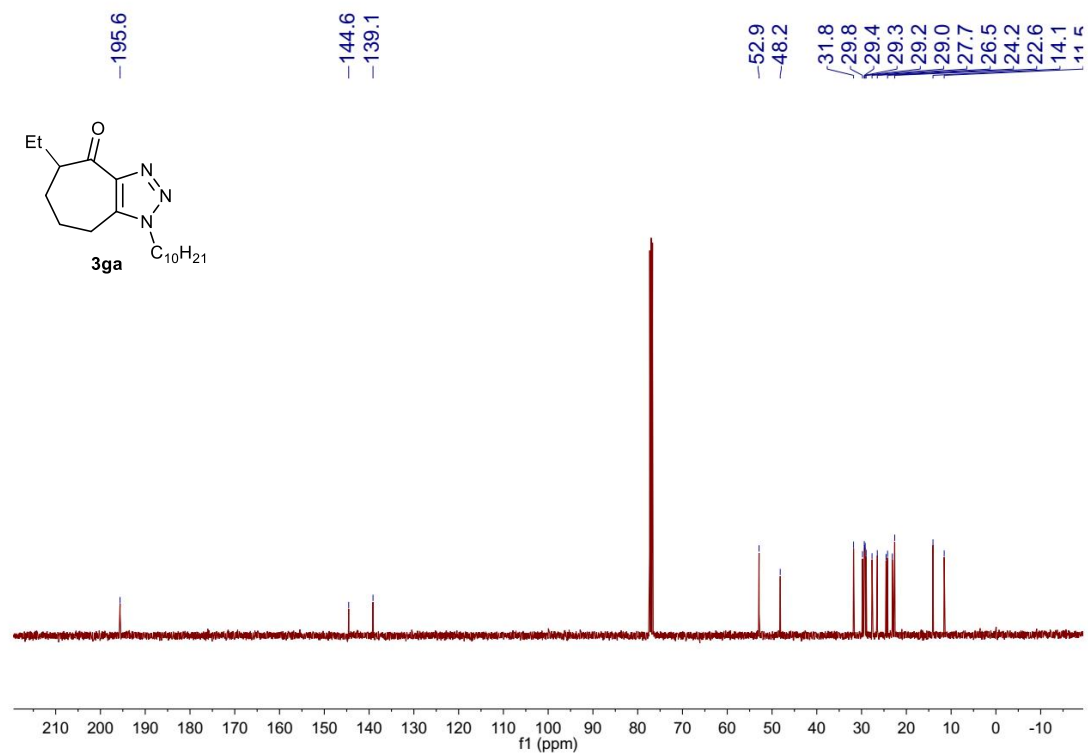
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



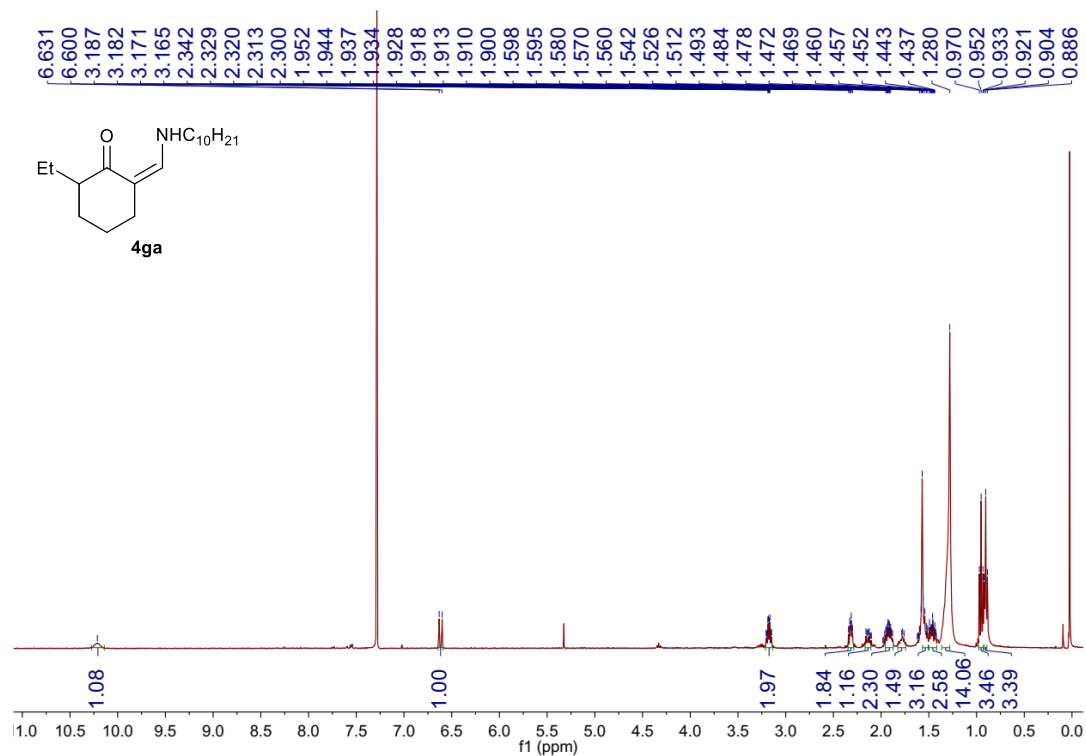
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



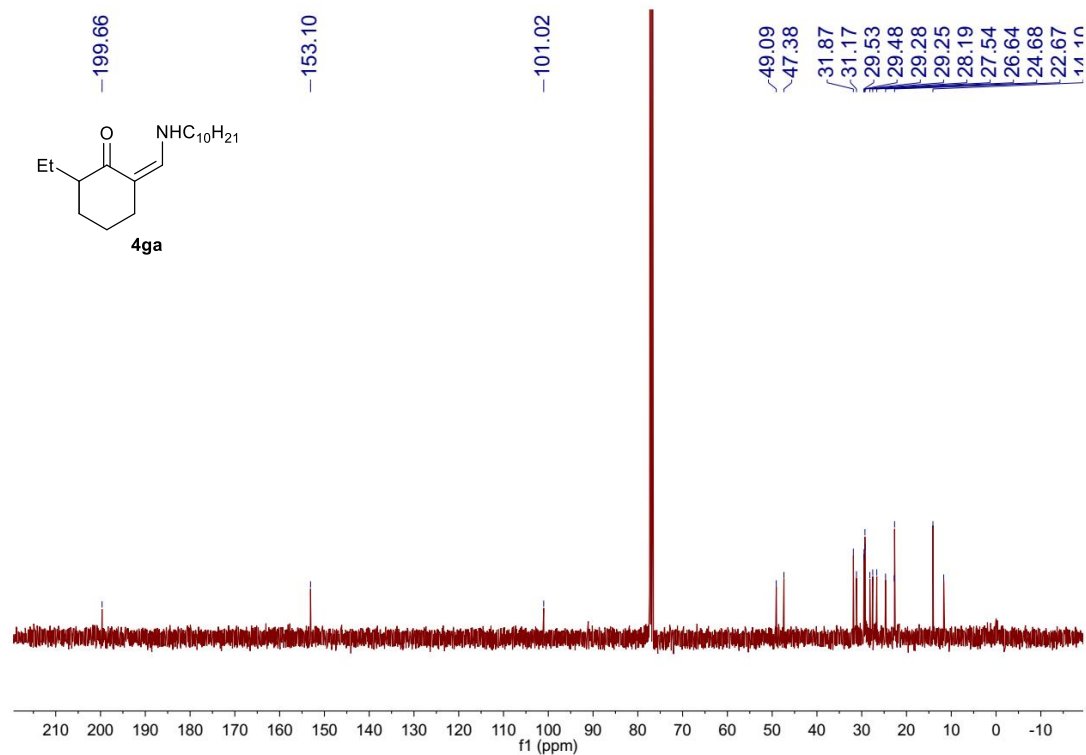
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



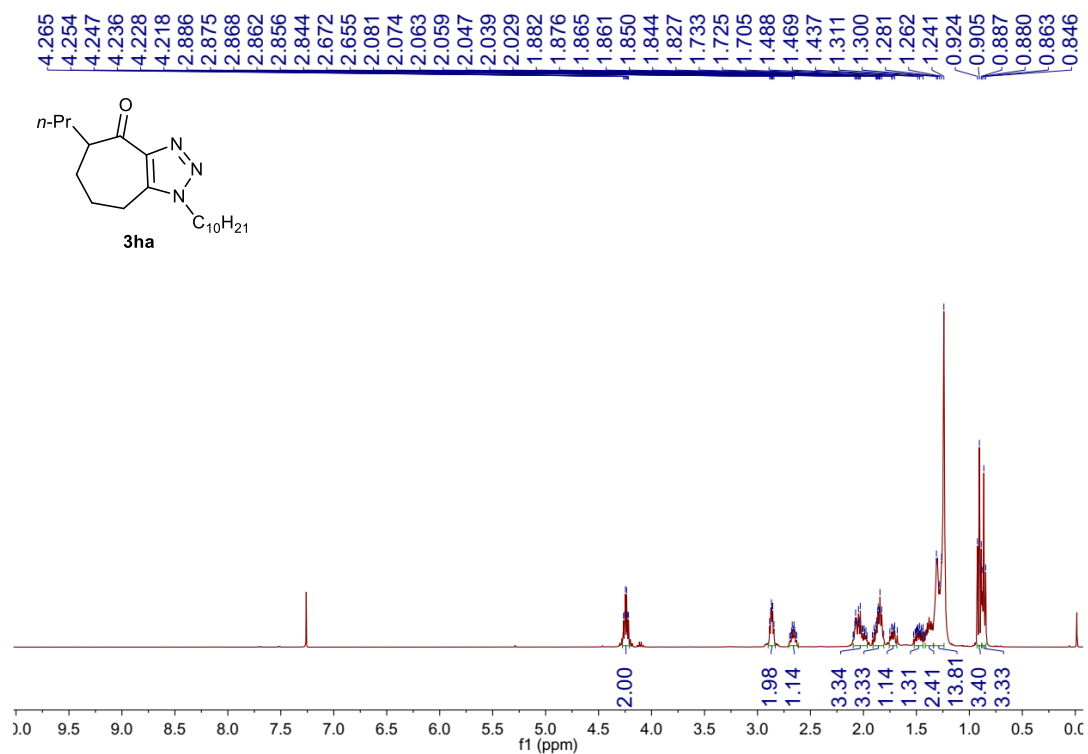
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



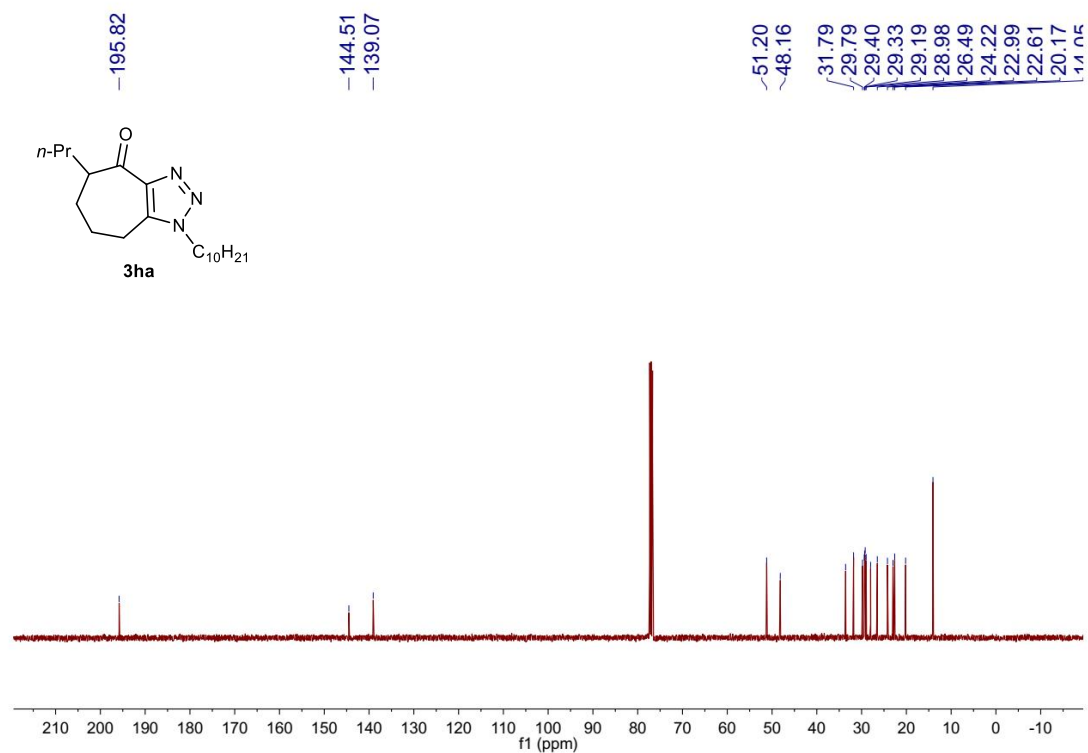
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



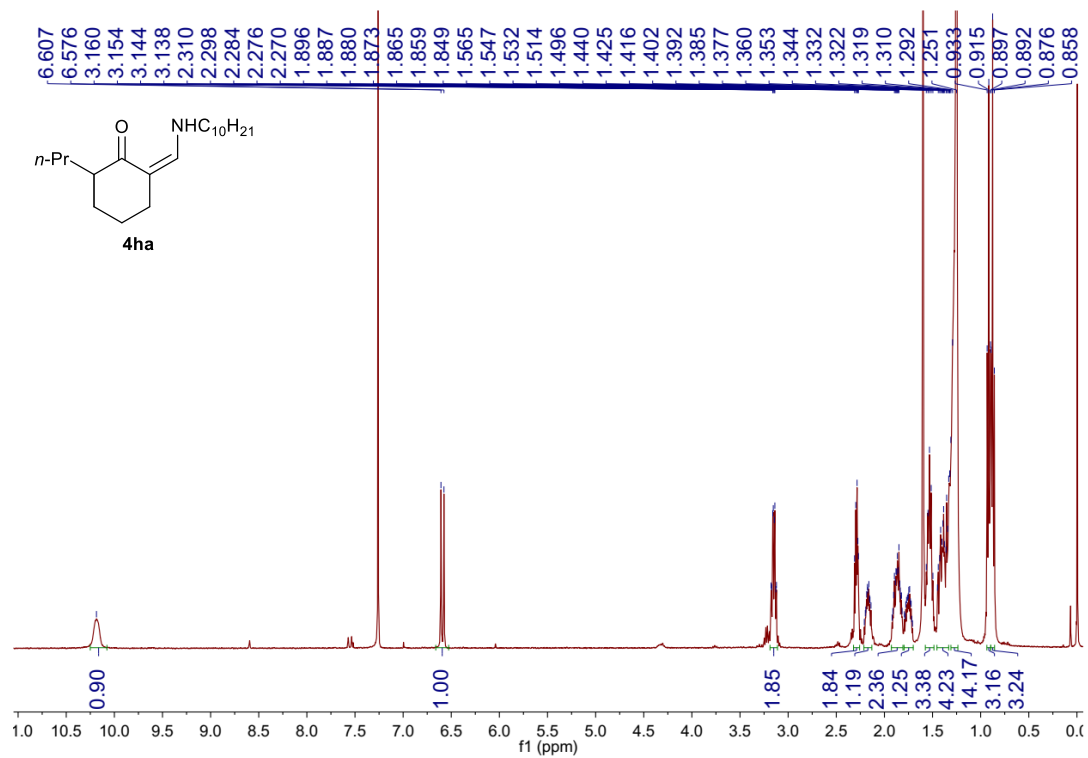
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



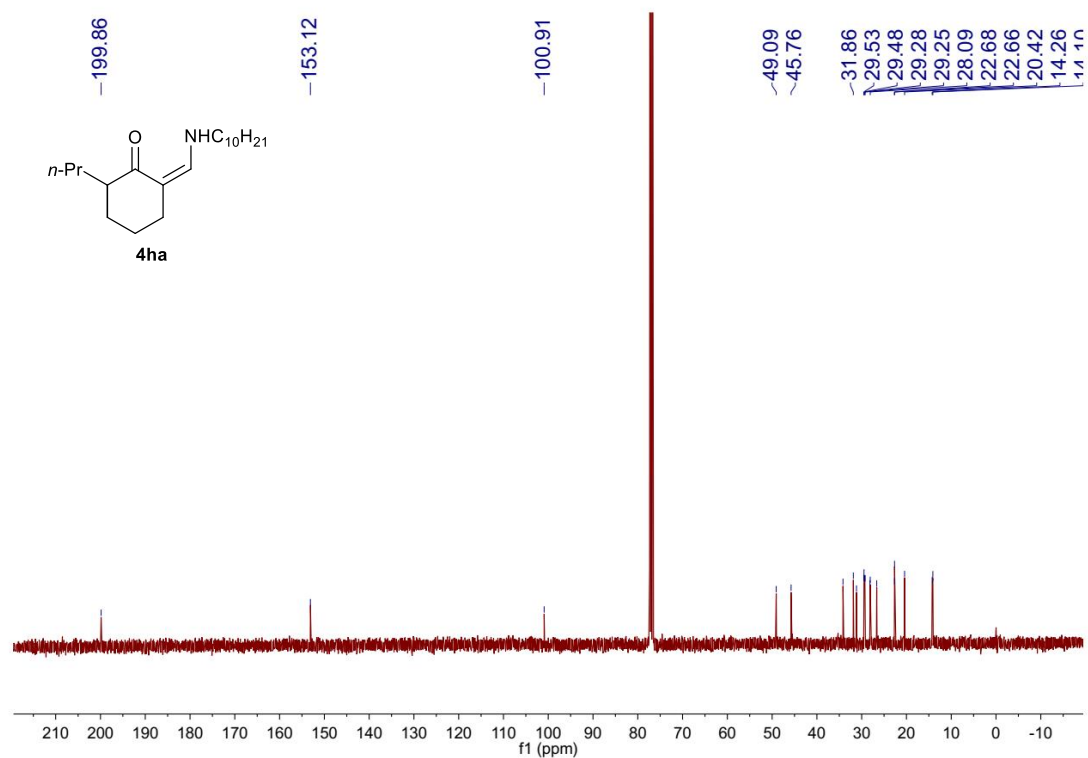
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



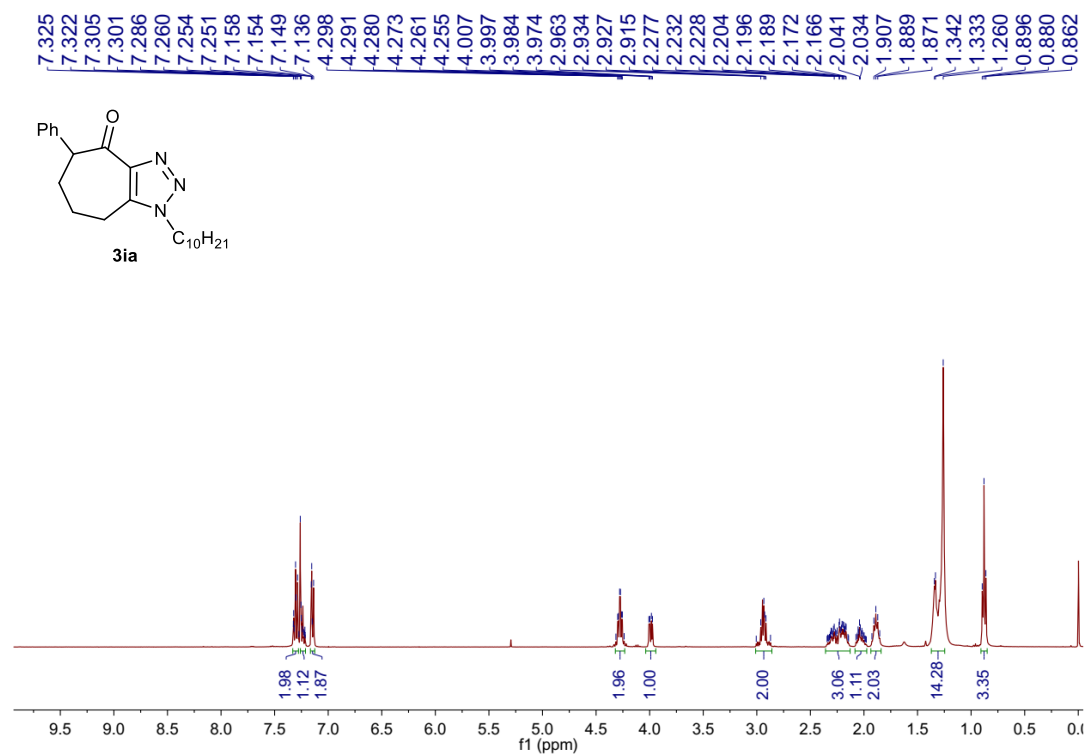
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



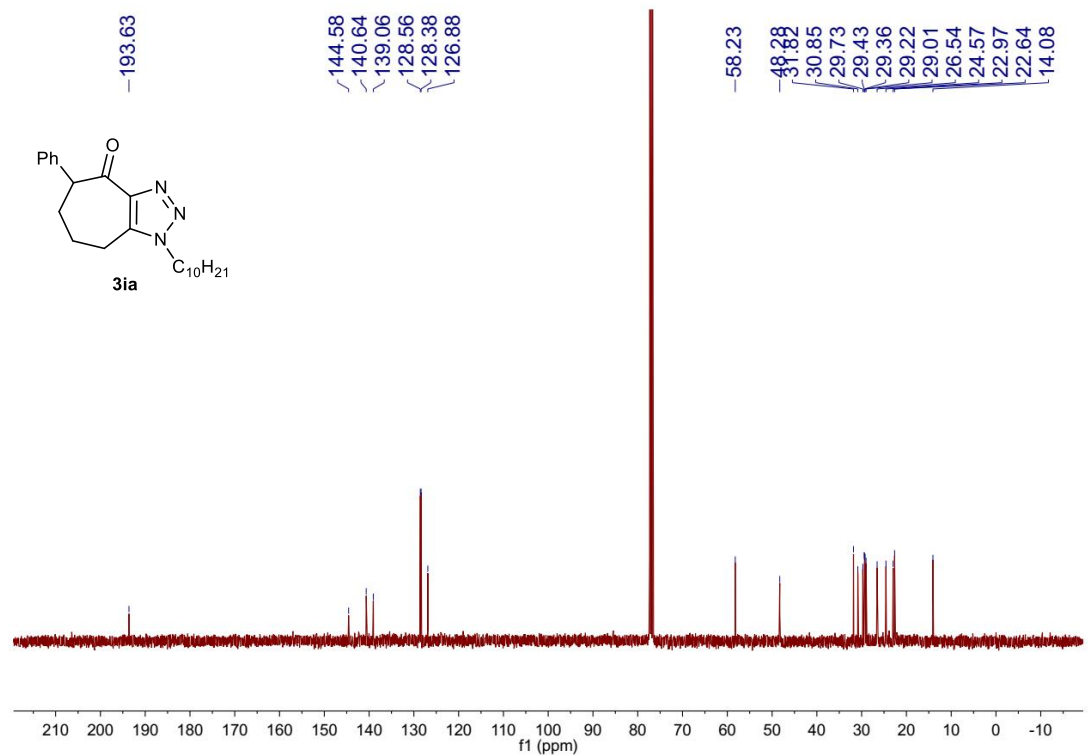
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



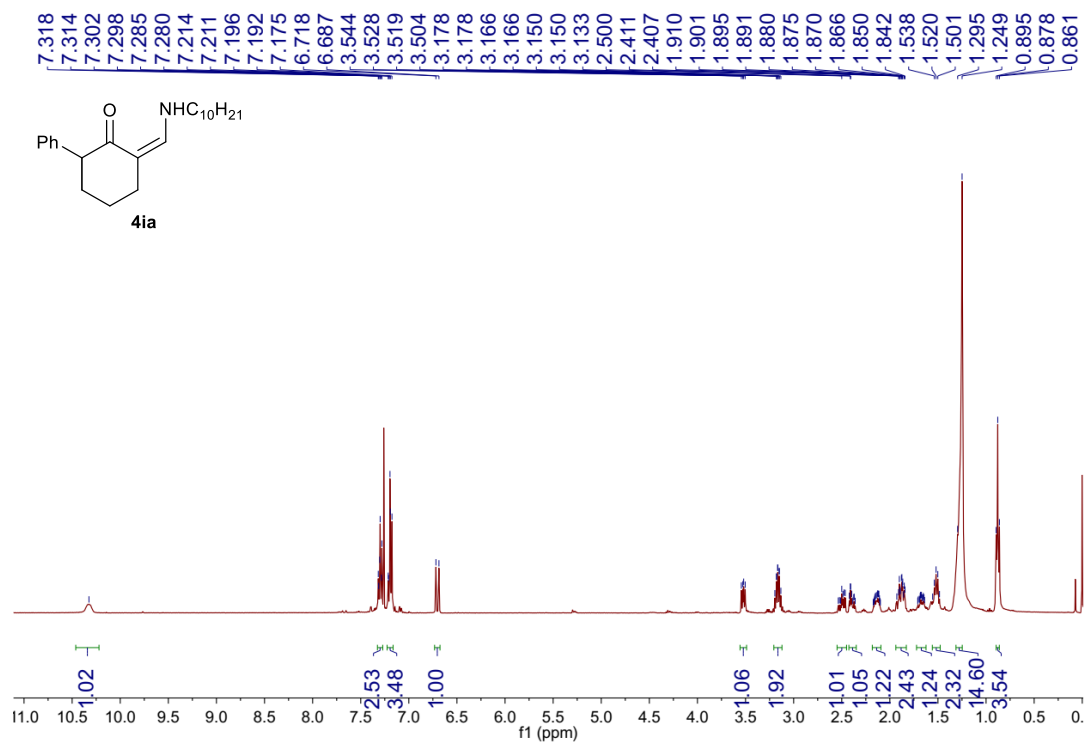
# $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



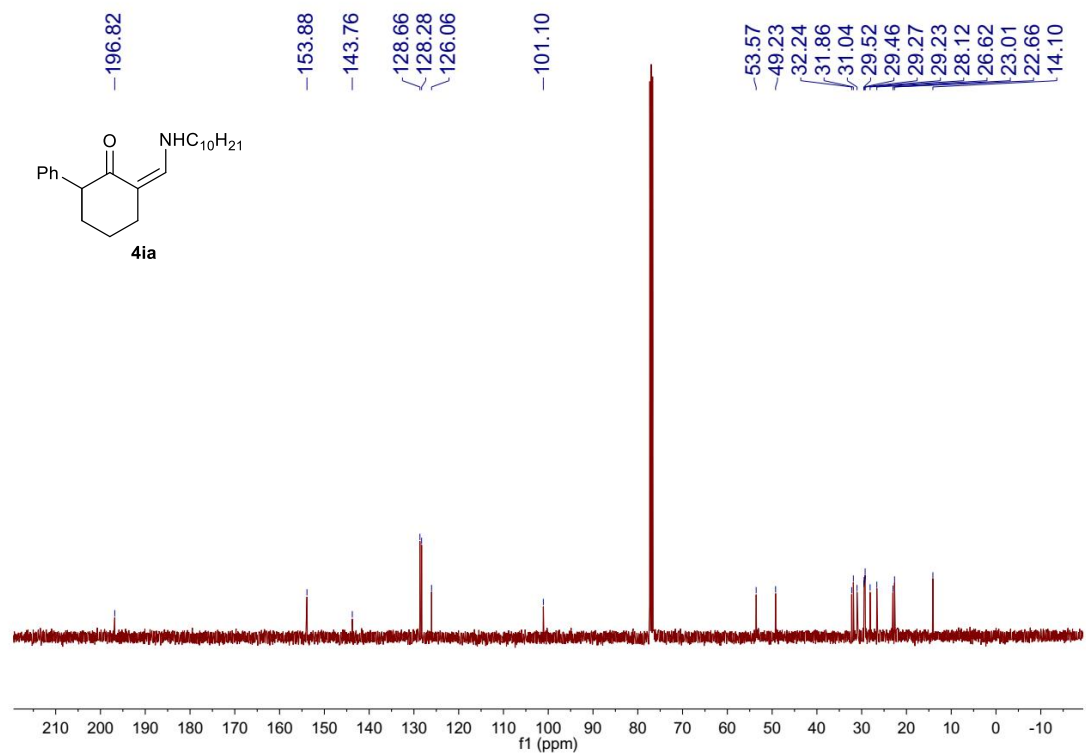
# $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

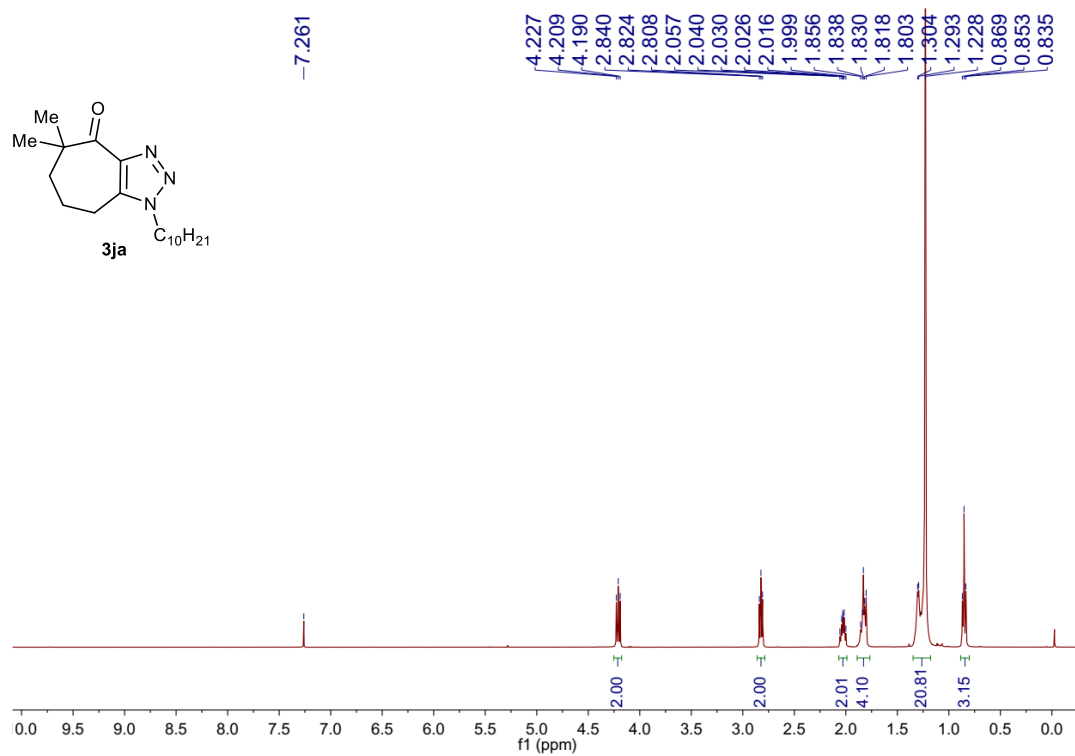


# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

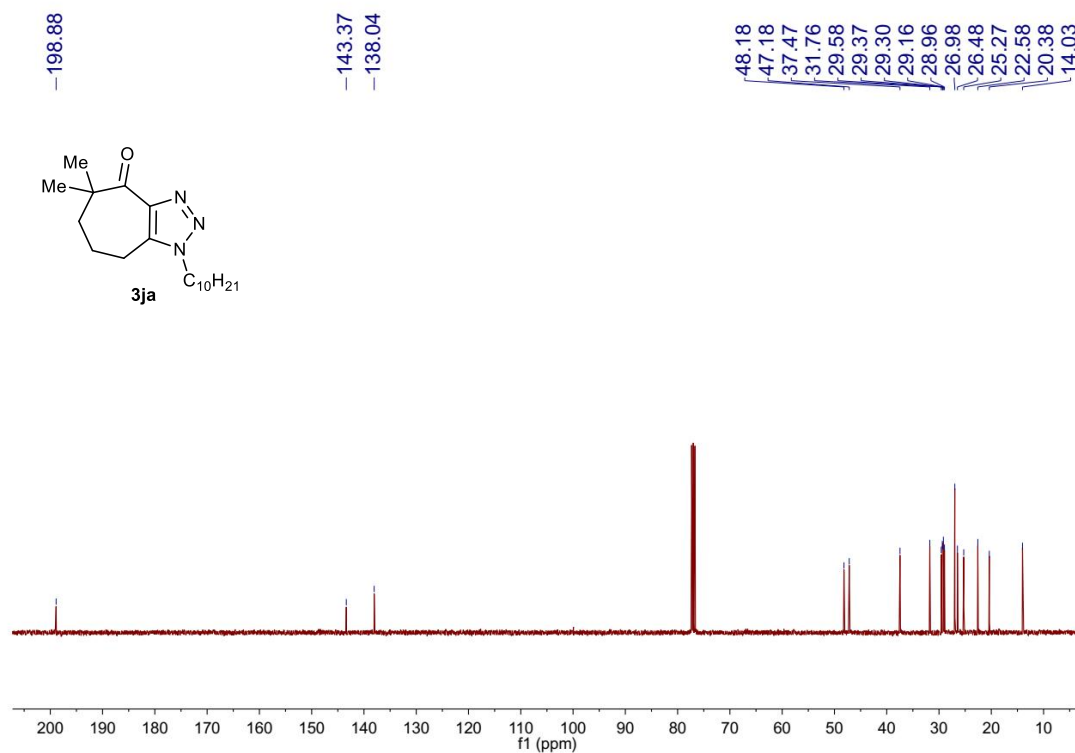




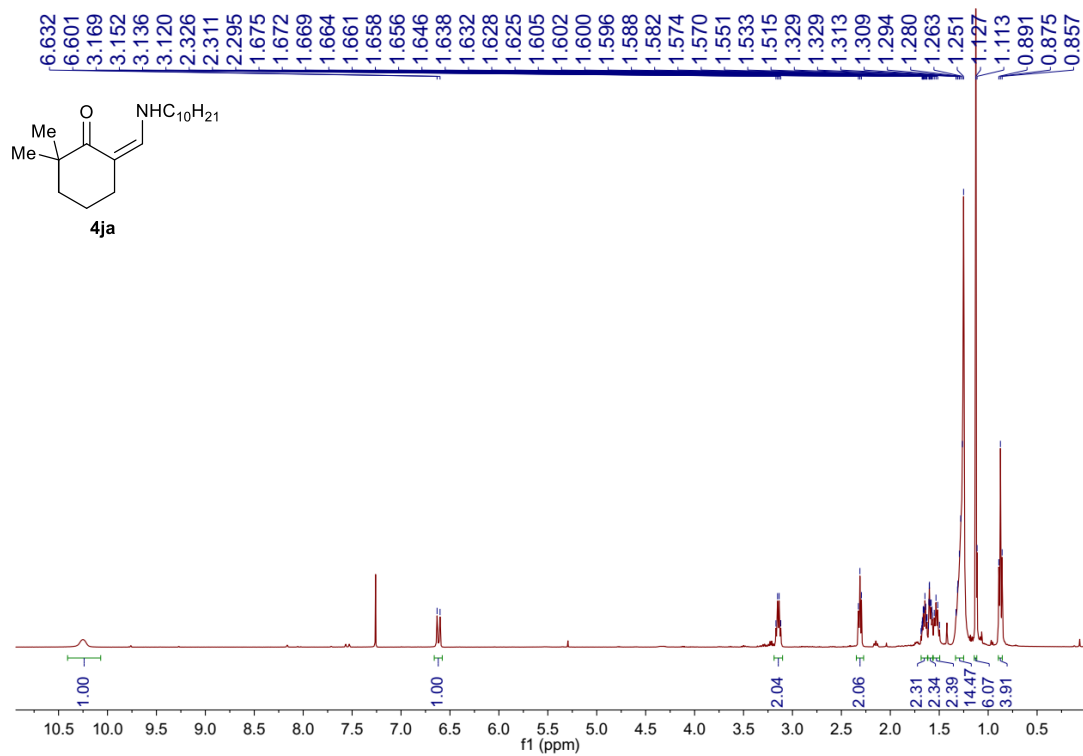
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



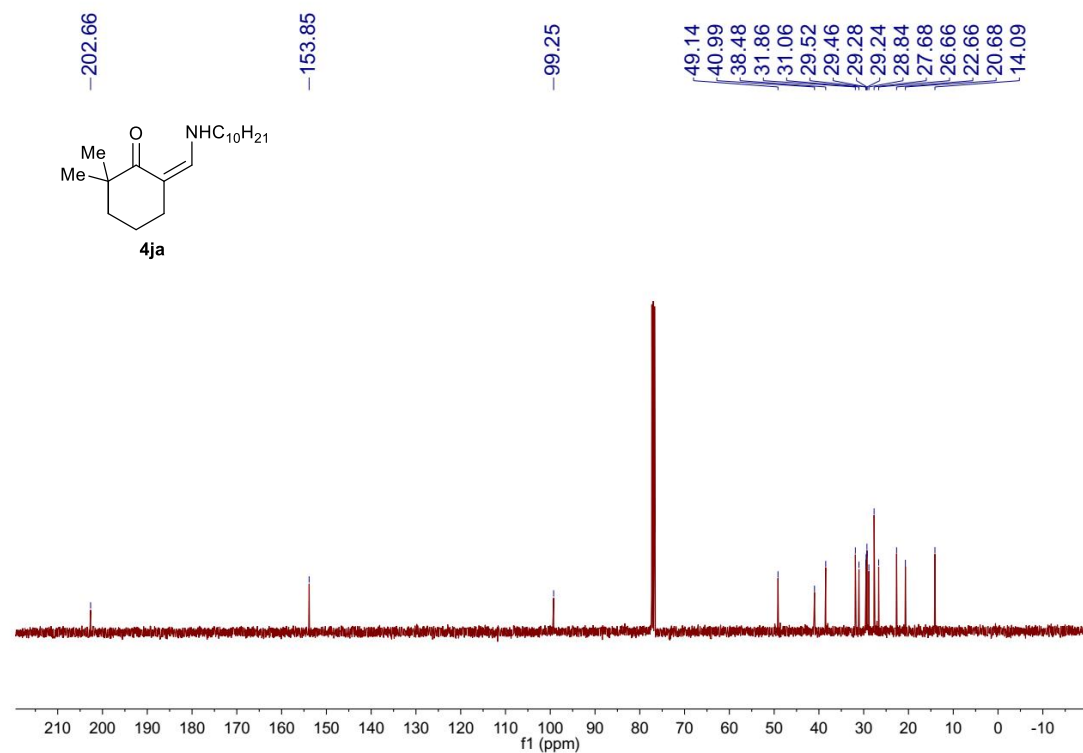
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



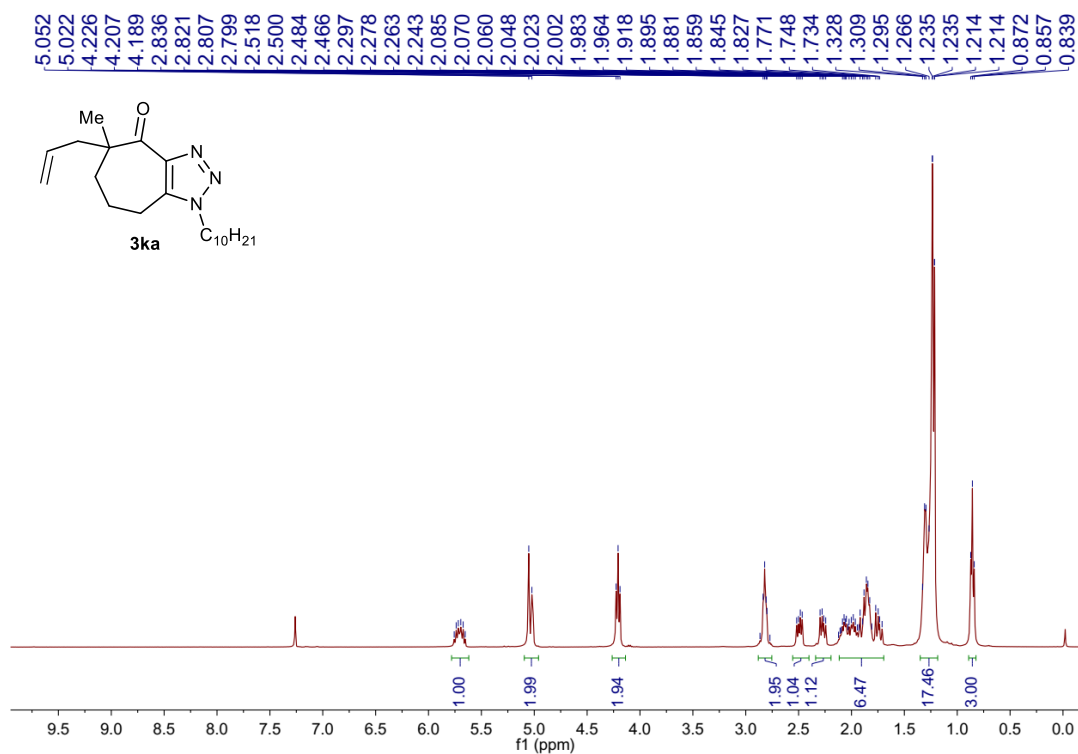
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



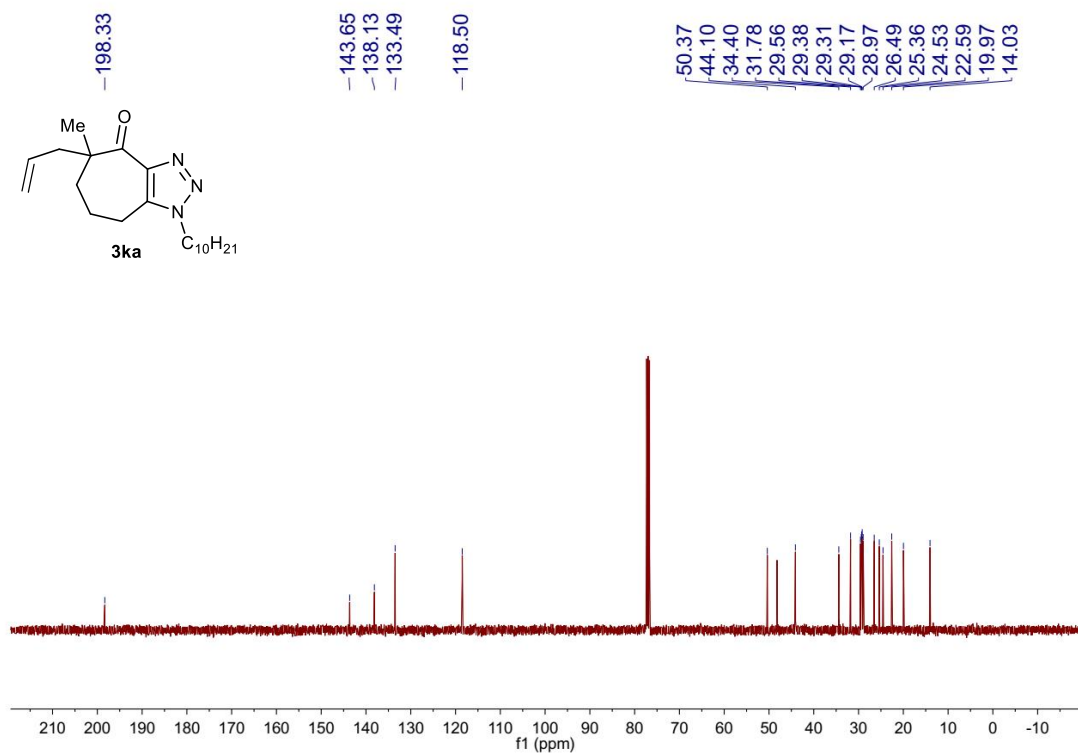
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



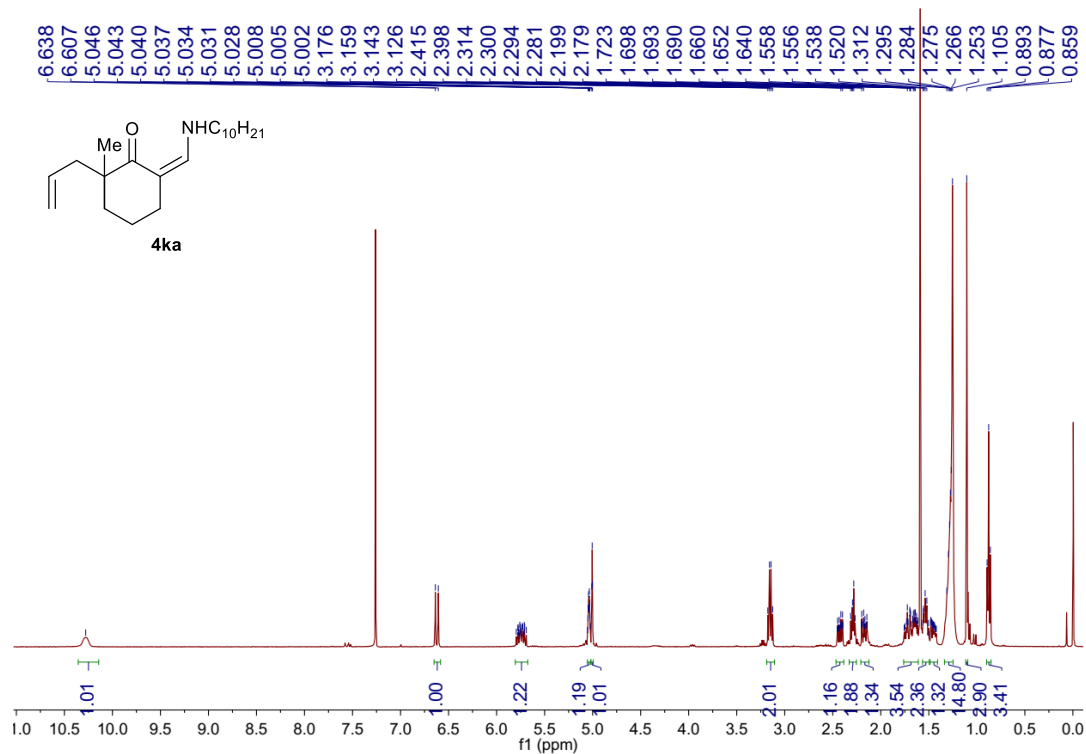
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



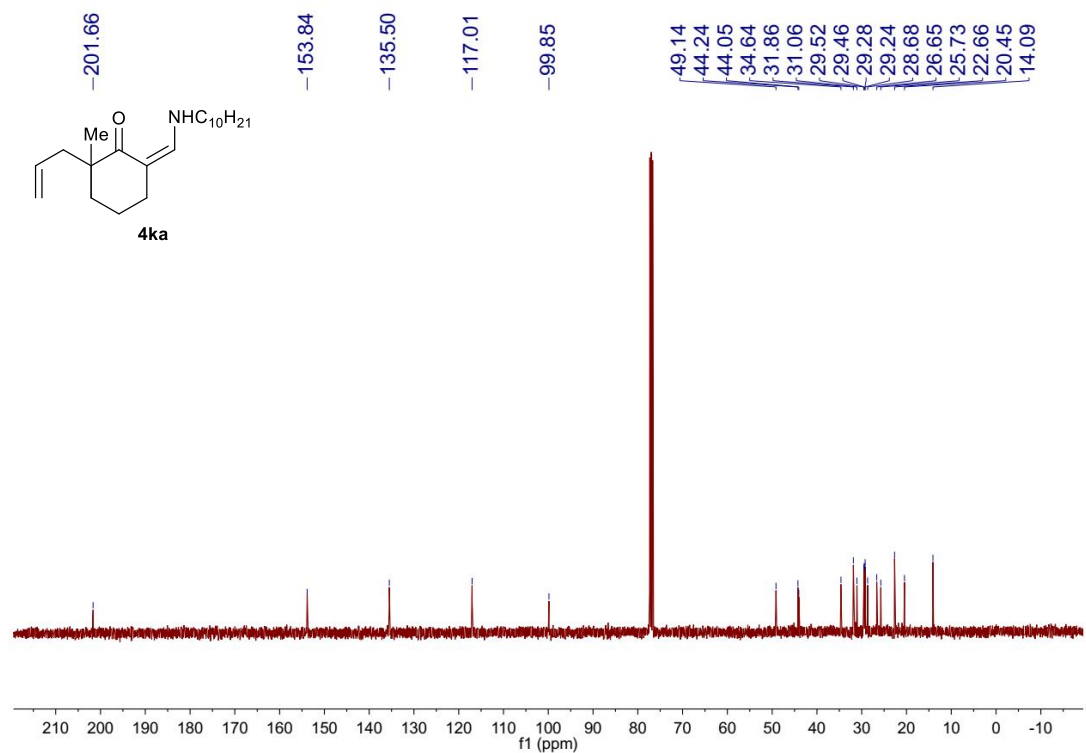
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



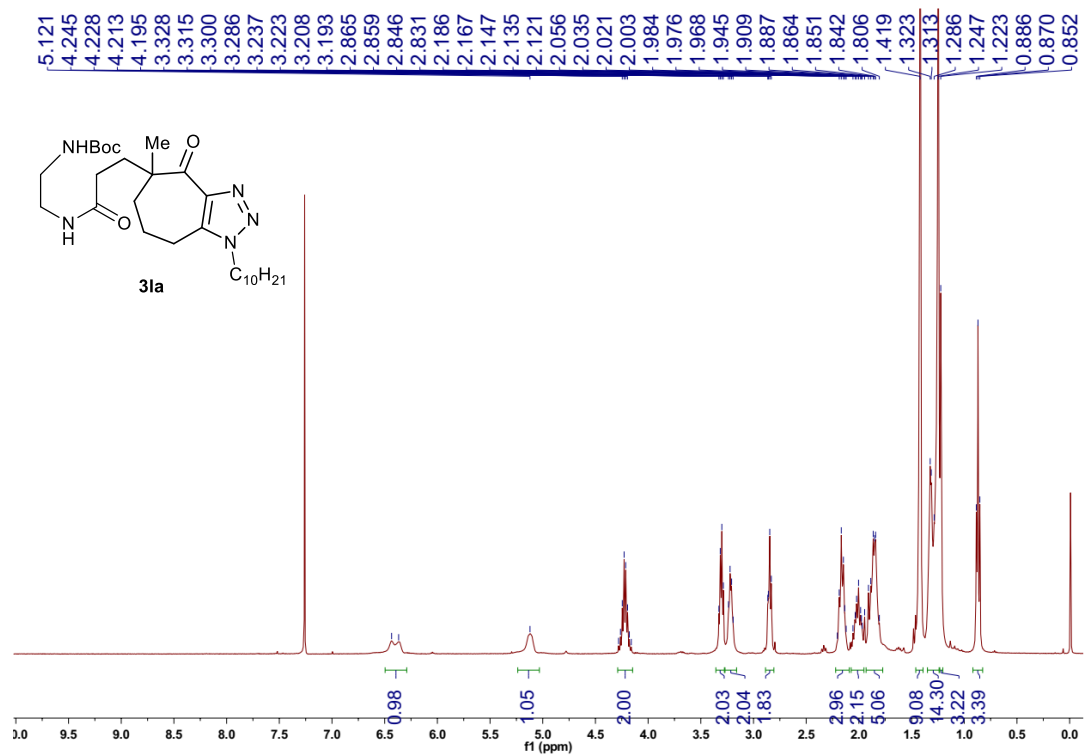
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



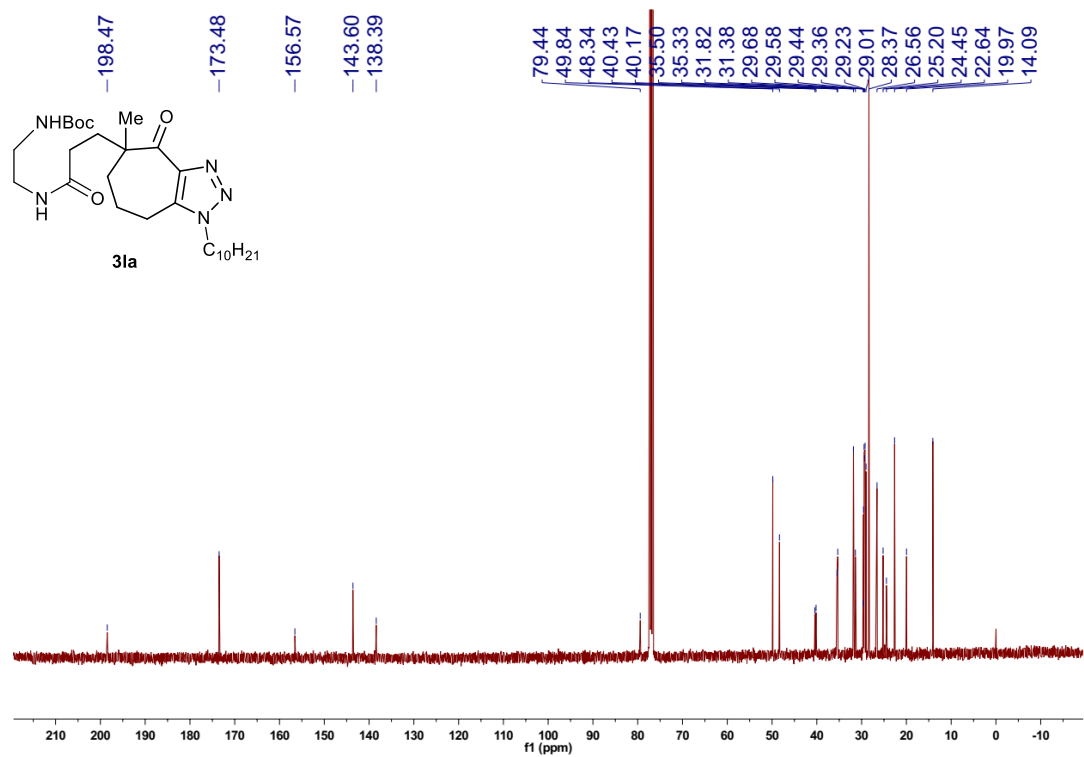
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



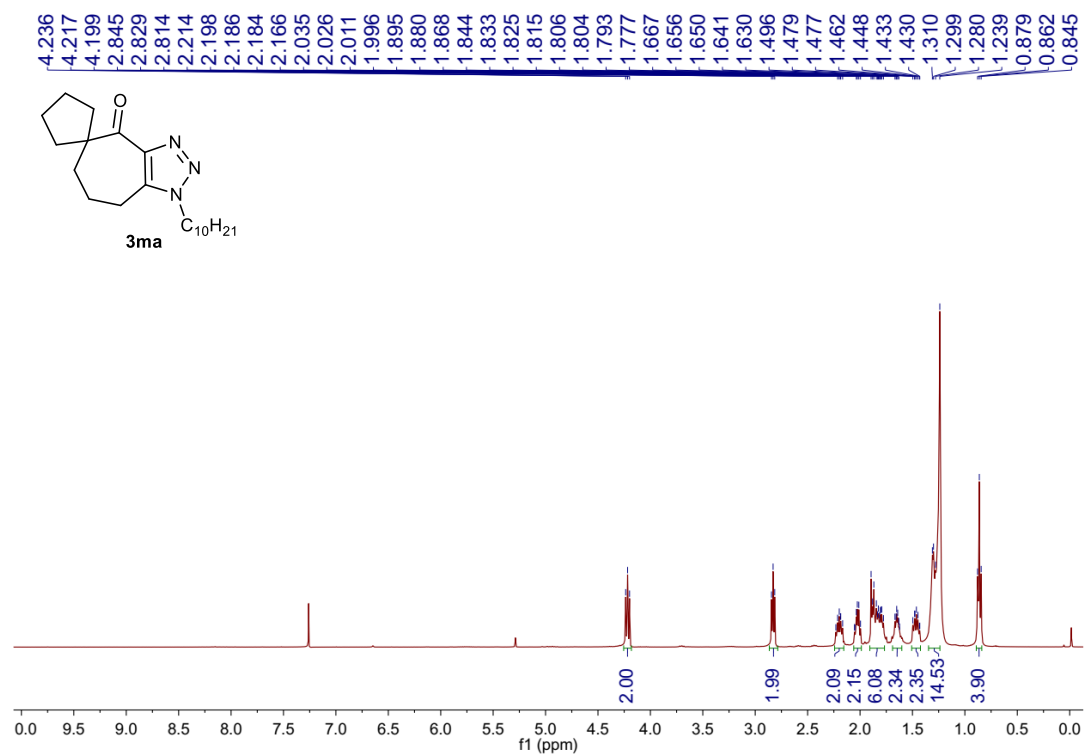
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



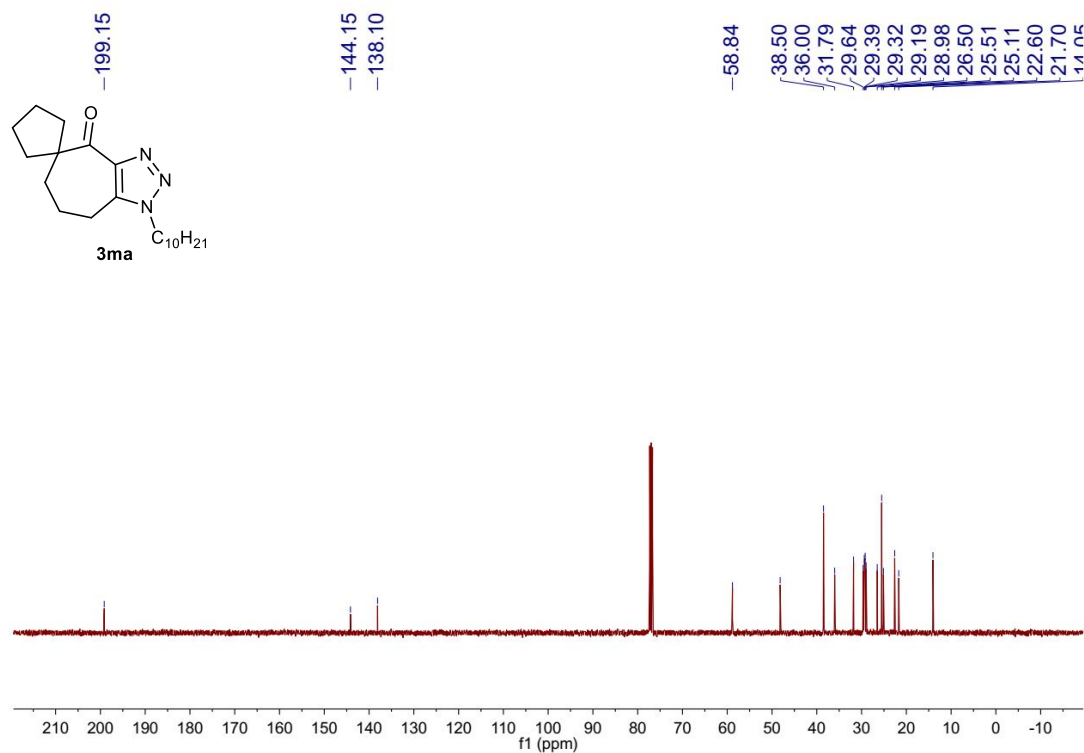
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



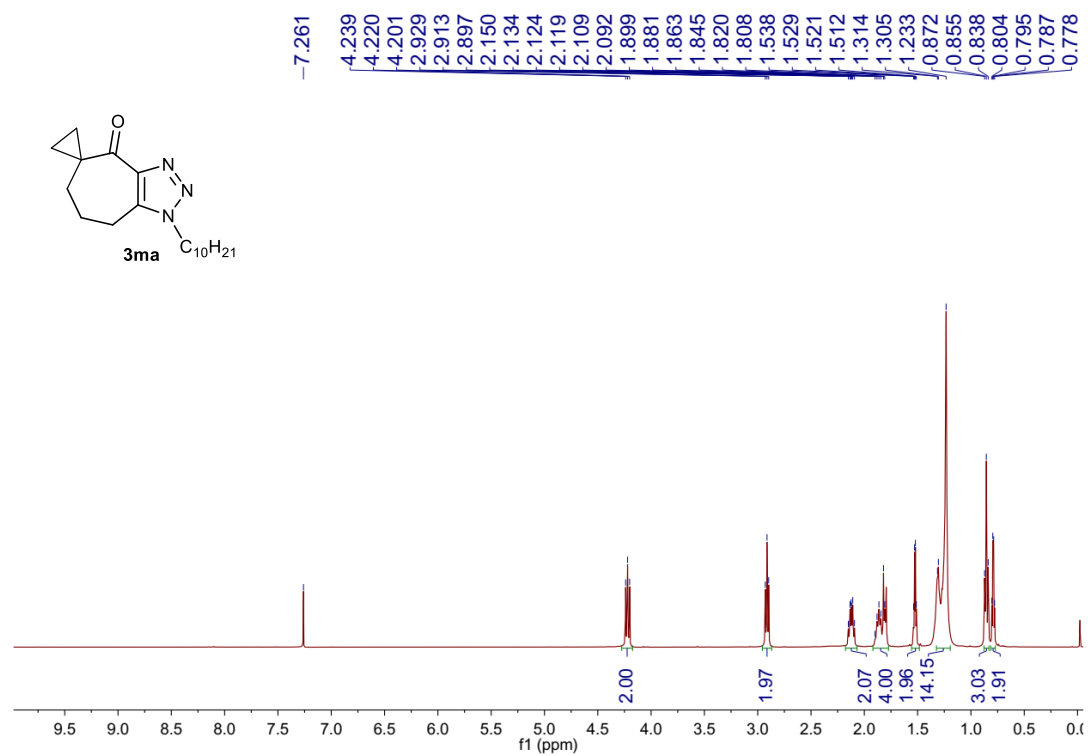
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



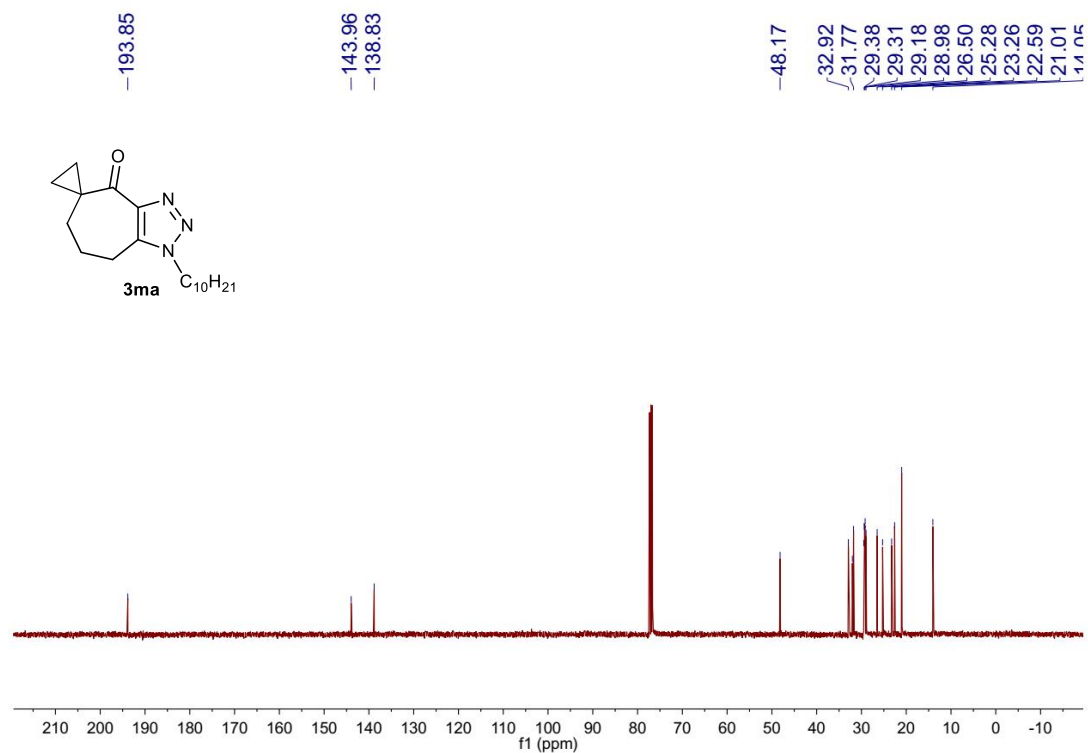
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



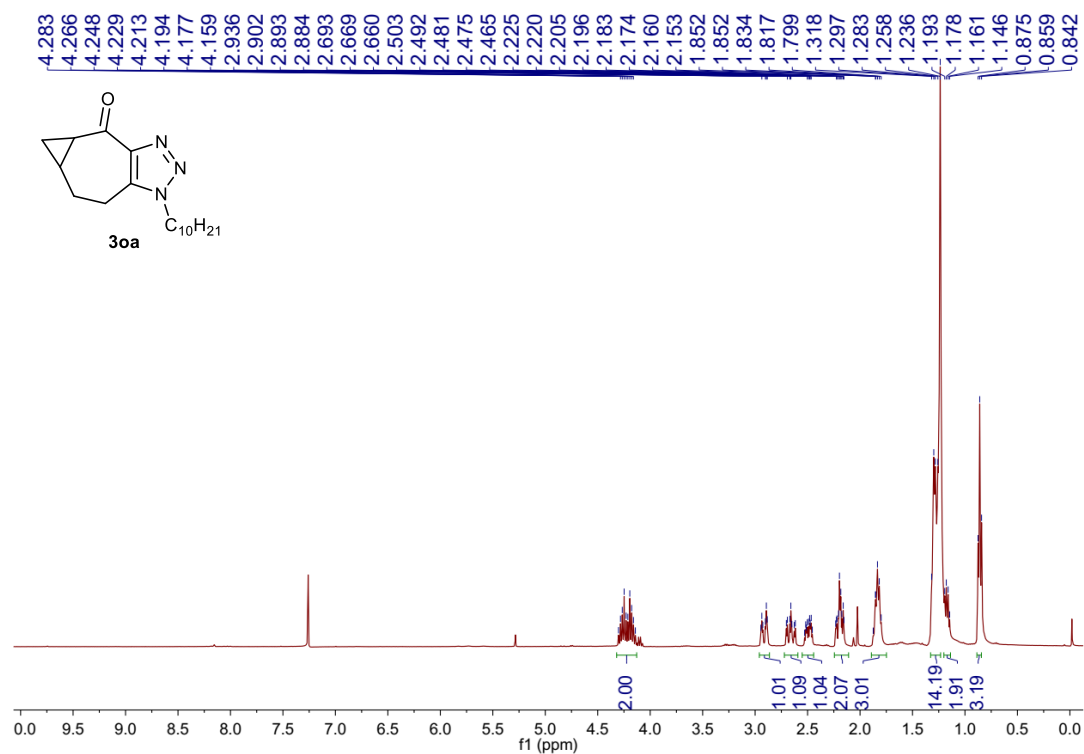
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



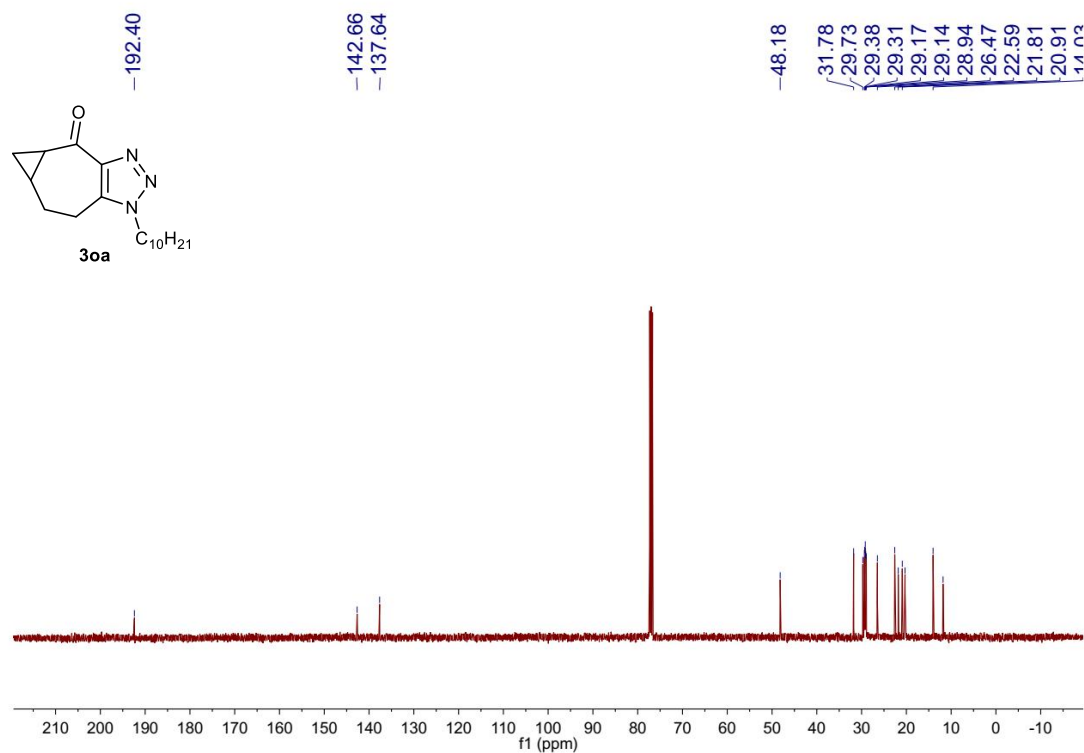
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

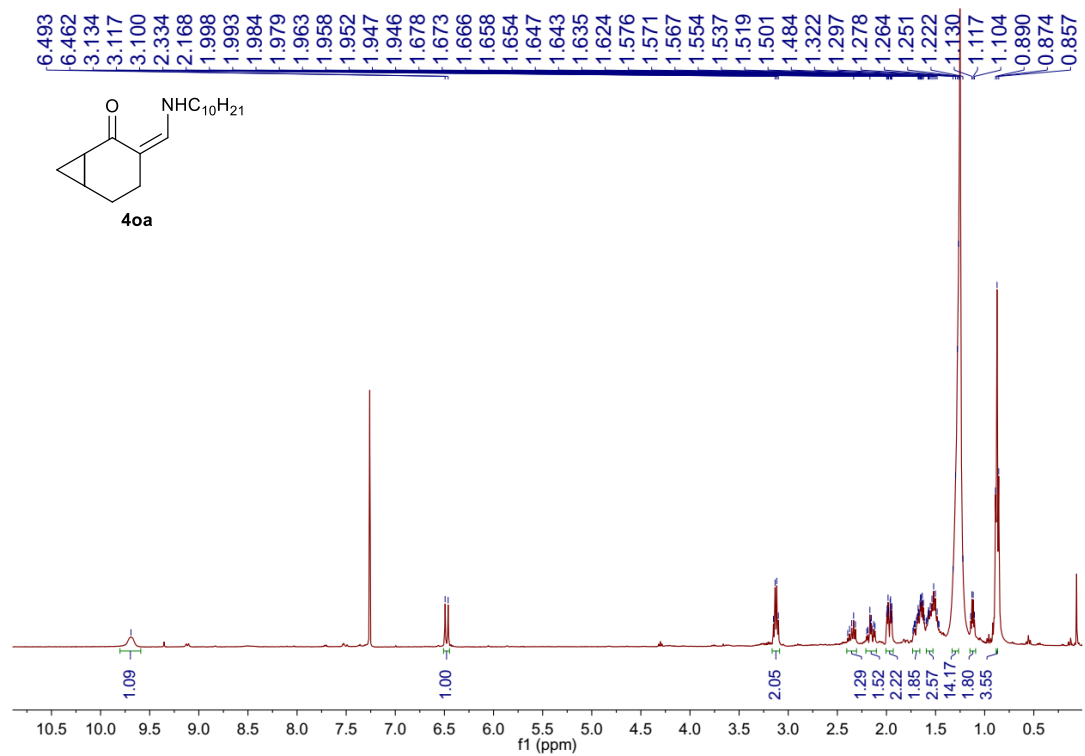


### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )

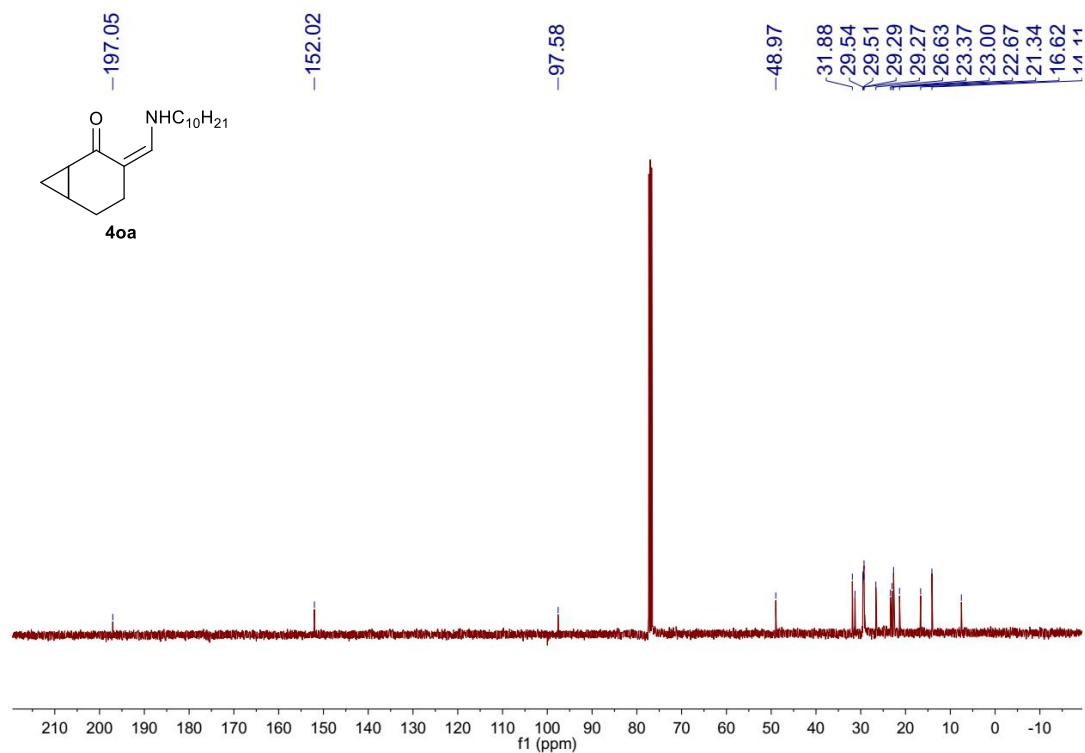




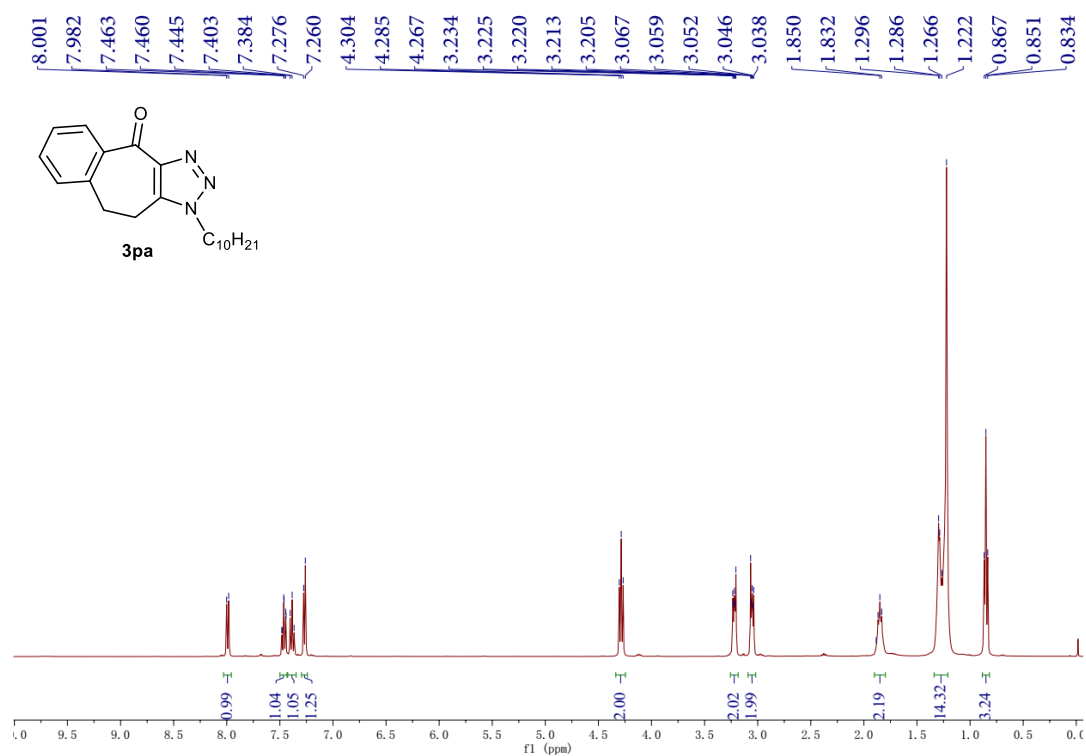
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



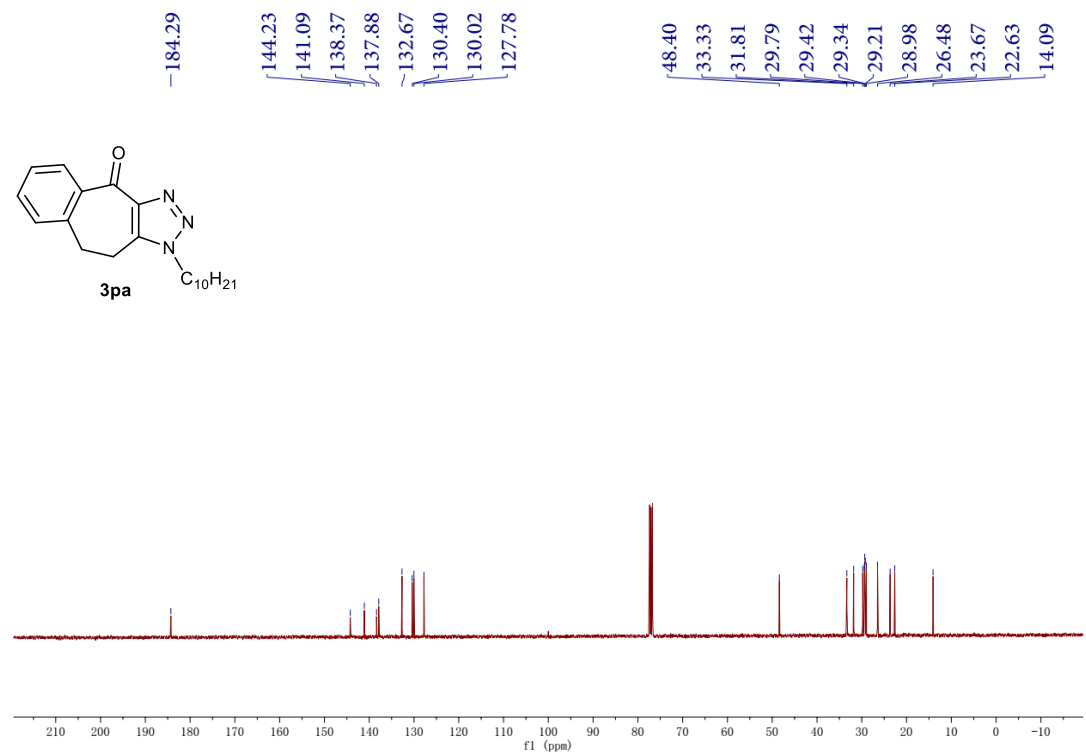
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



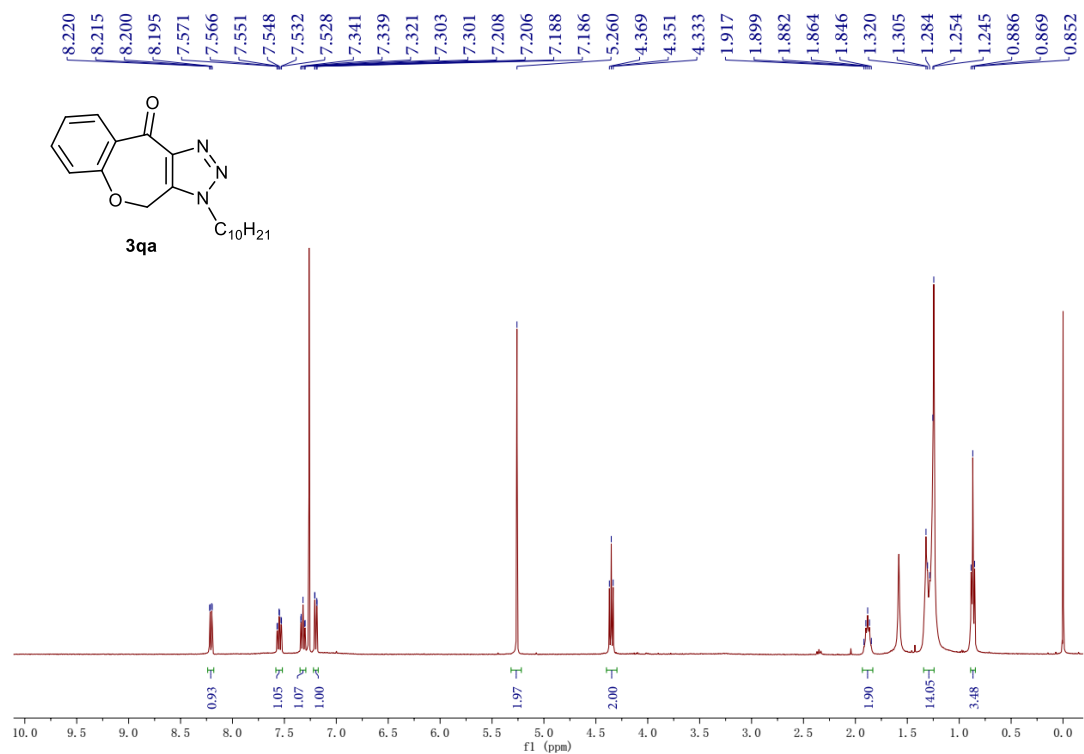
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



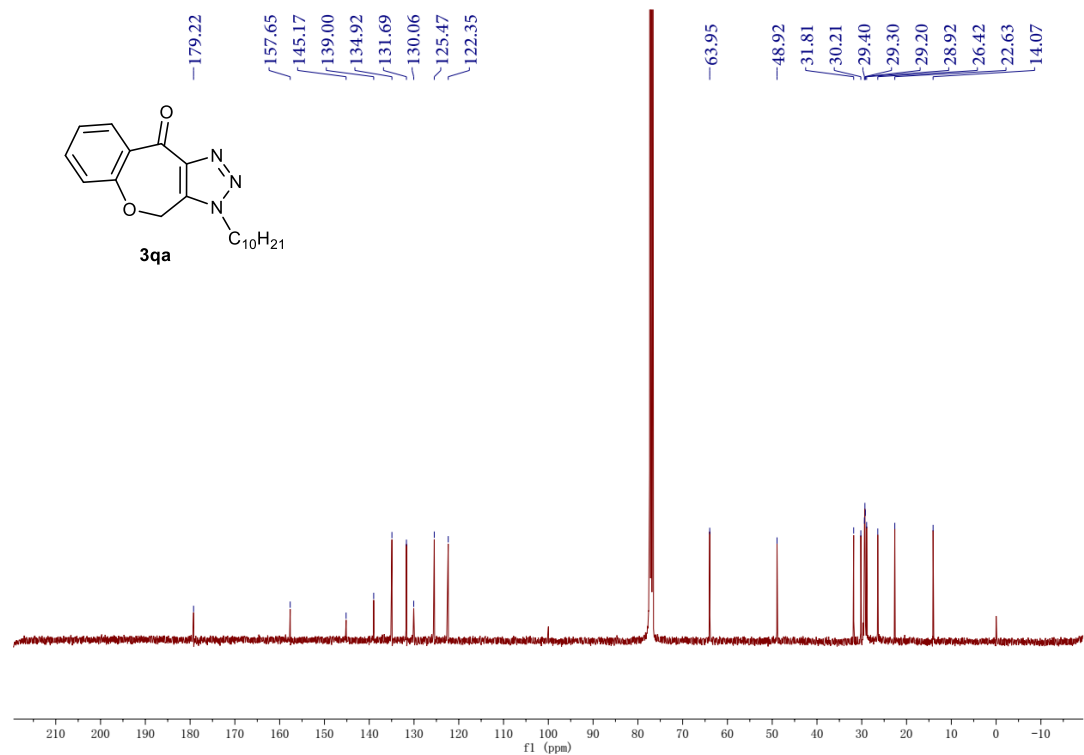
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



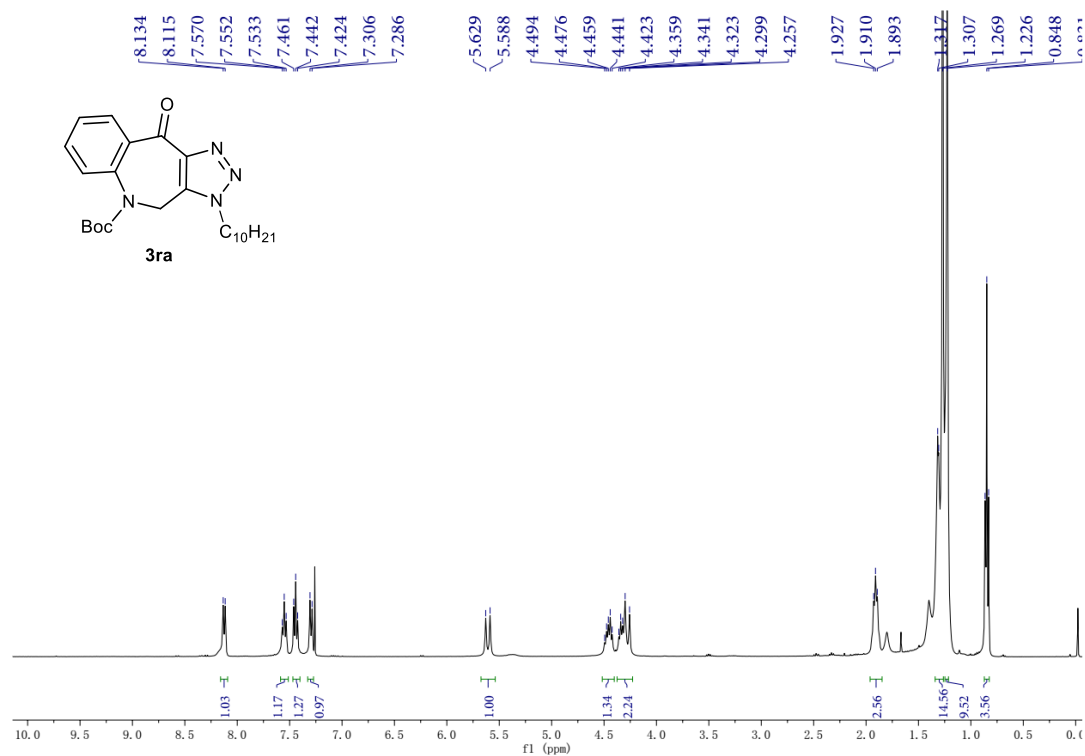
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



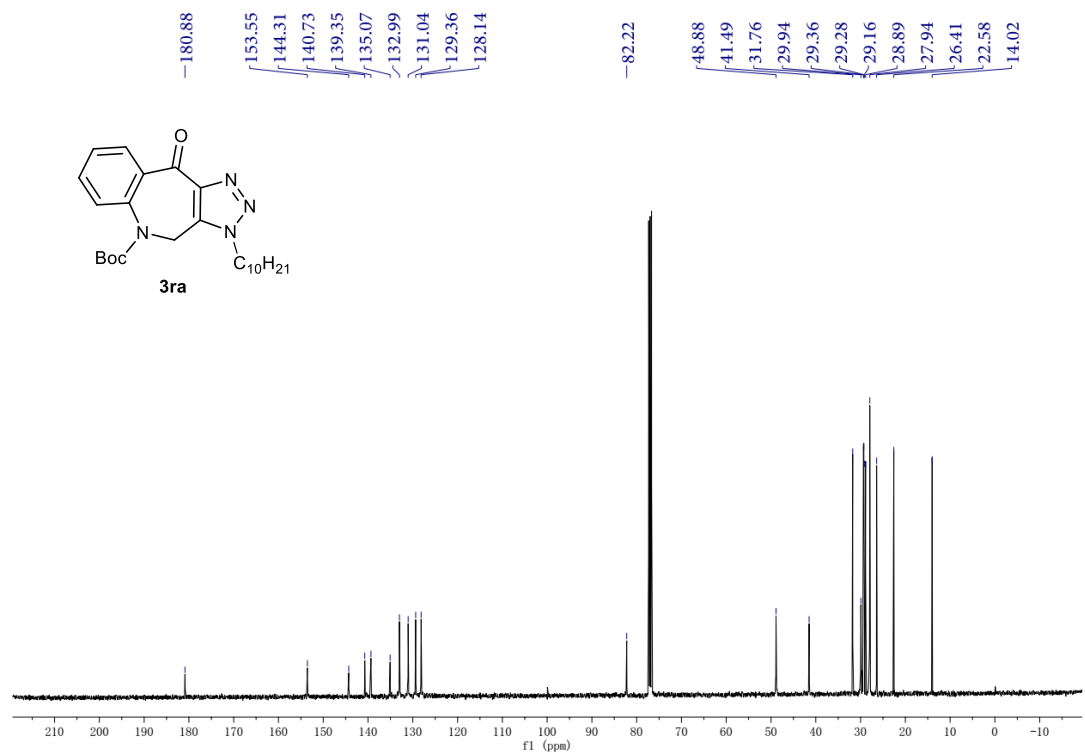
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



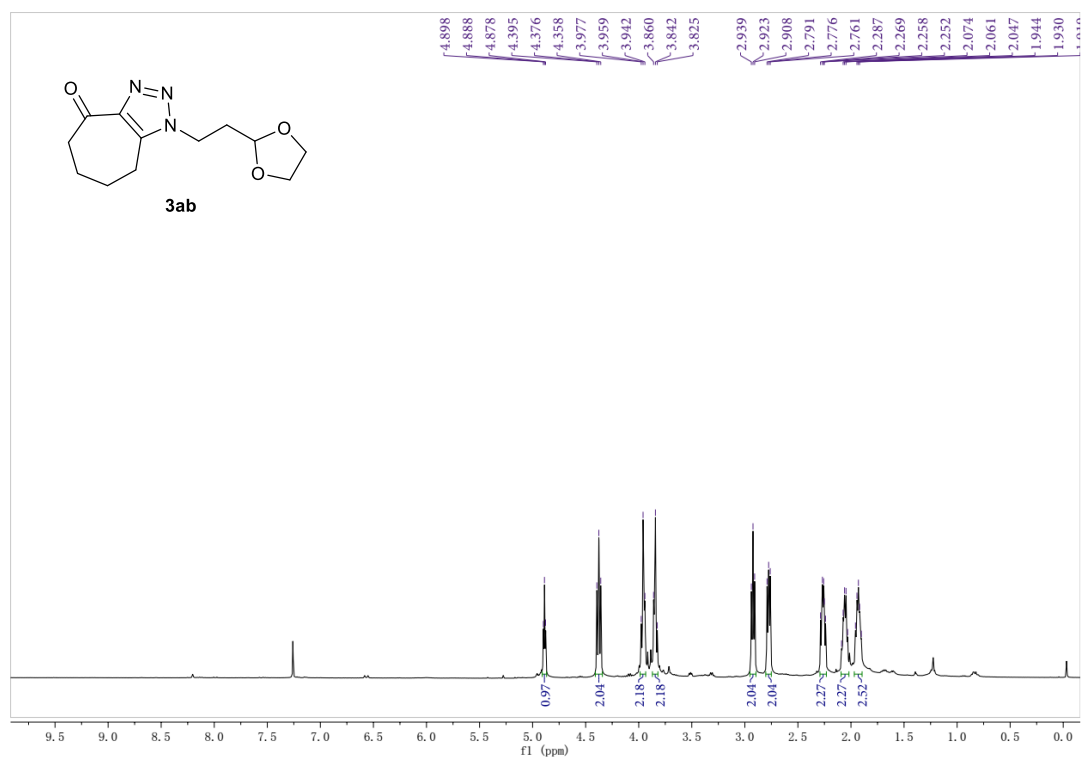
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



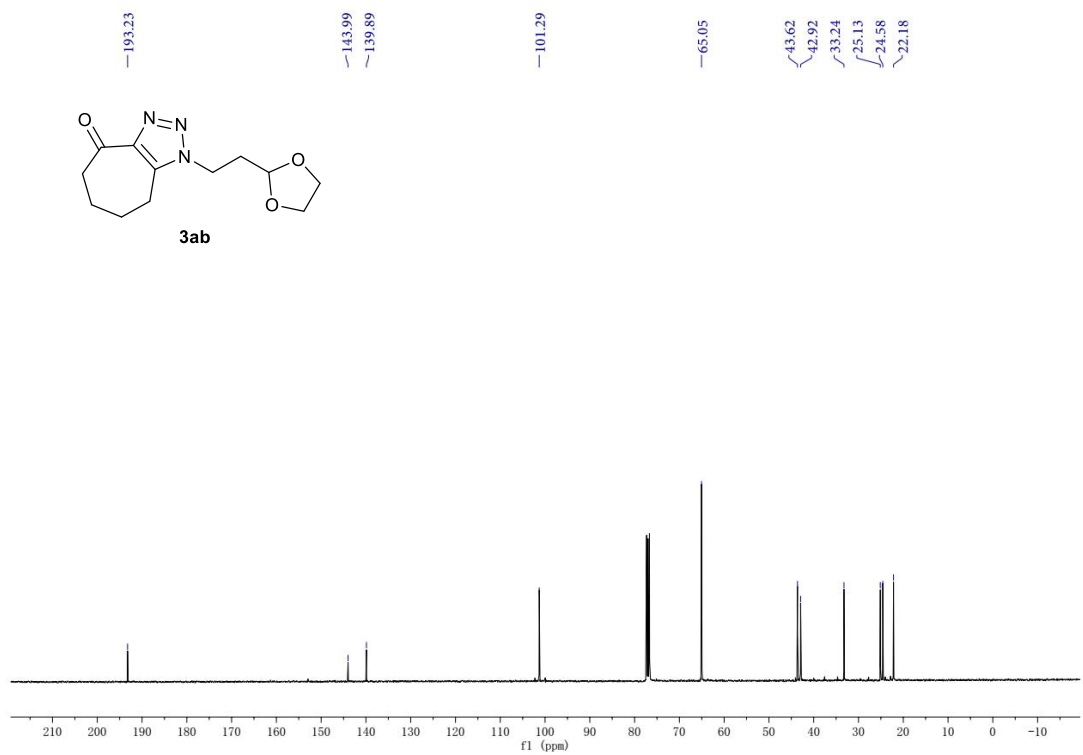
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



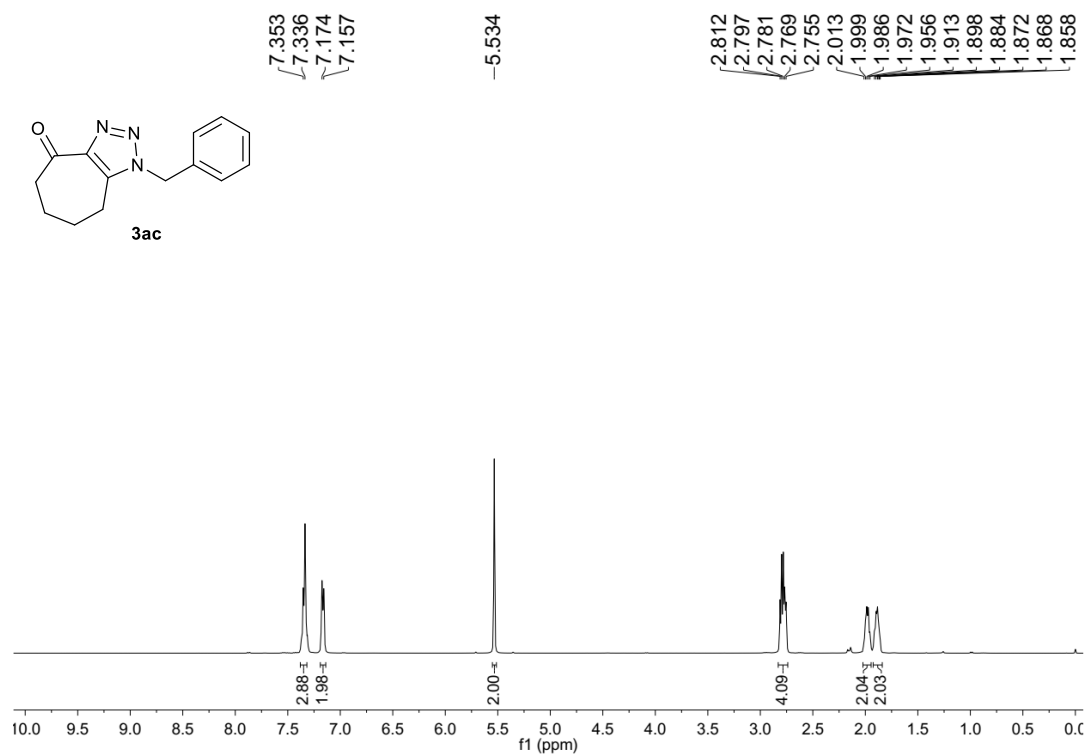
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



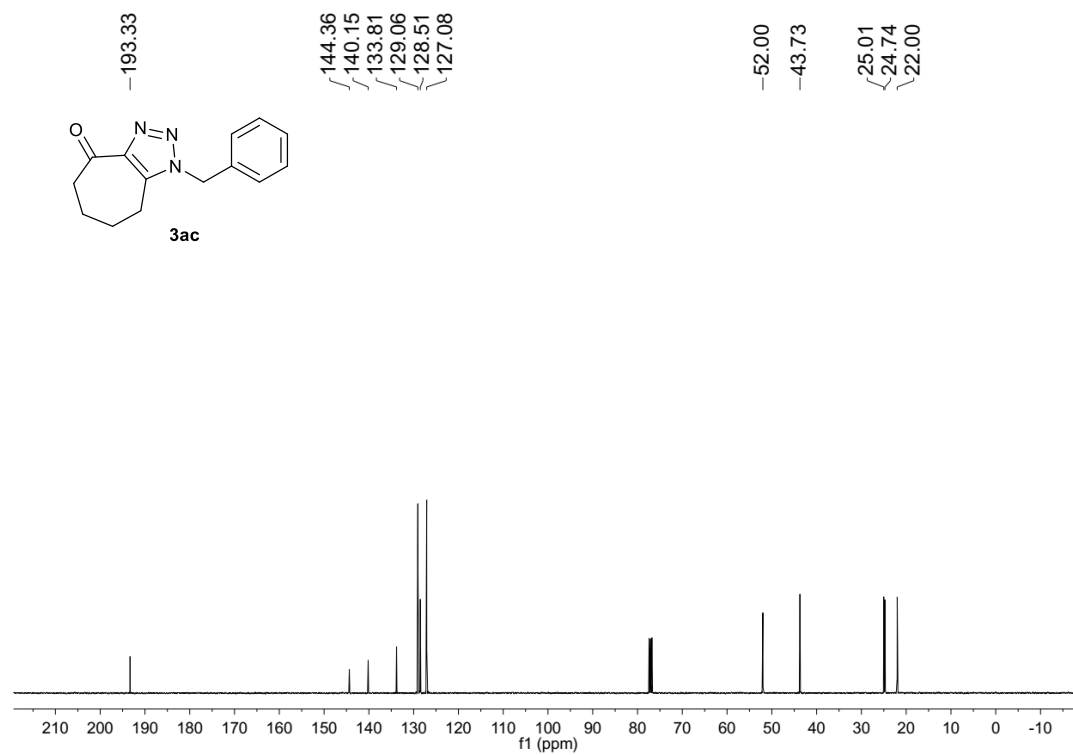
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



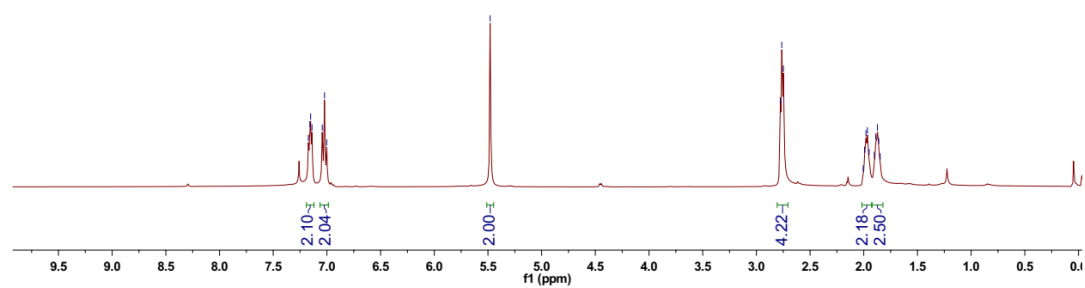
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



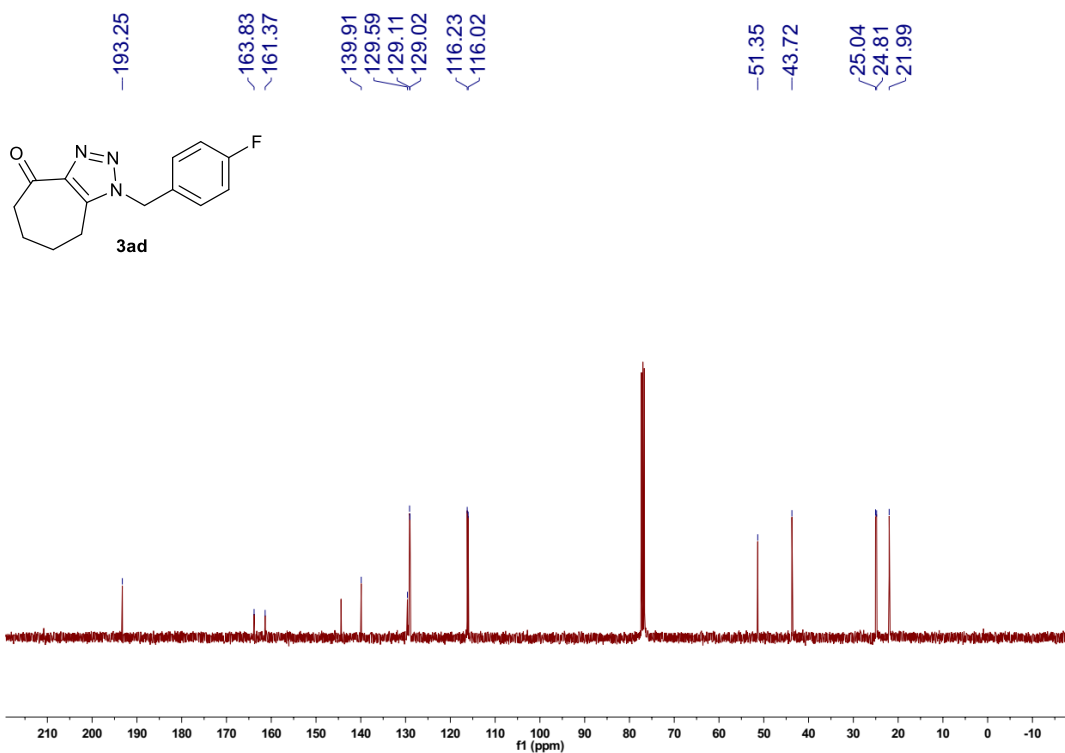
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



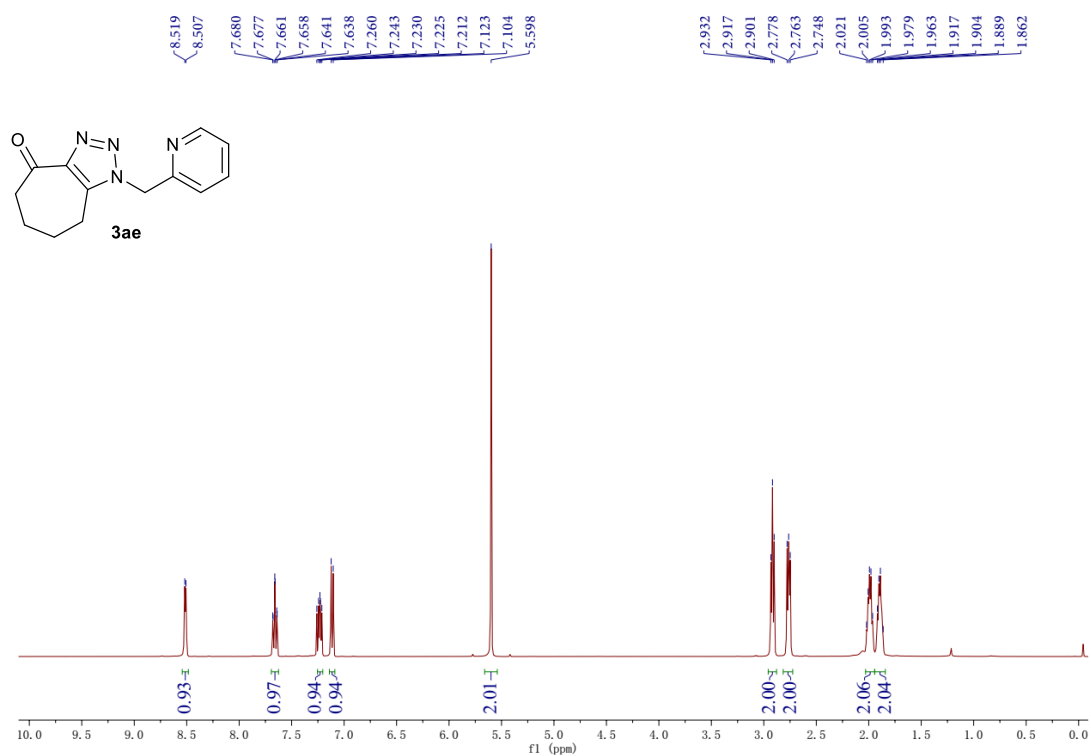
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



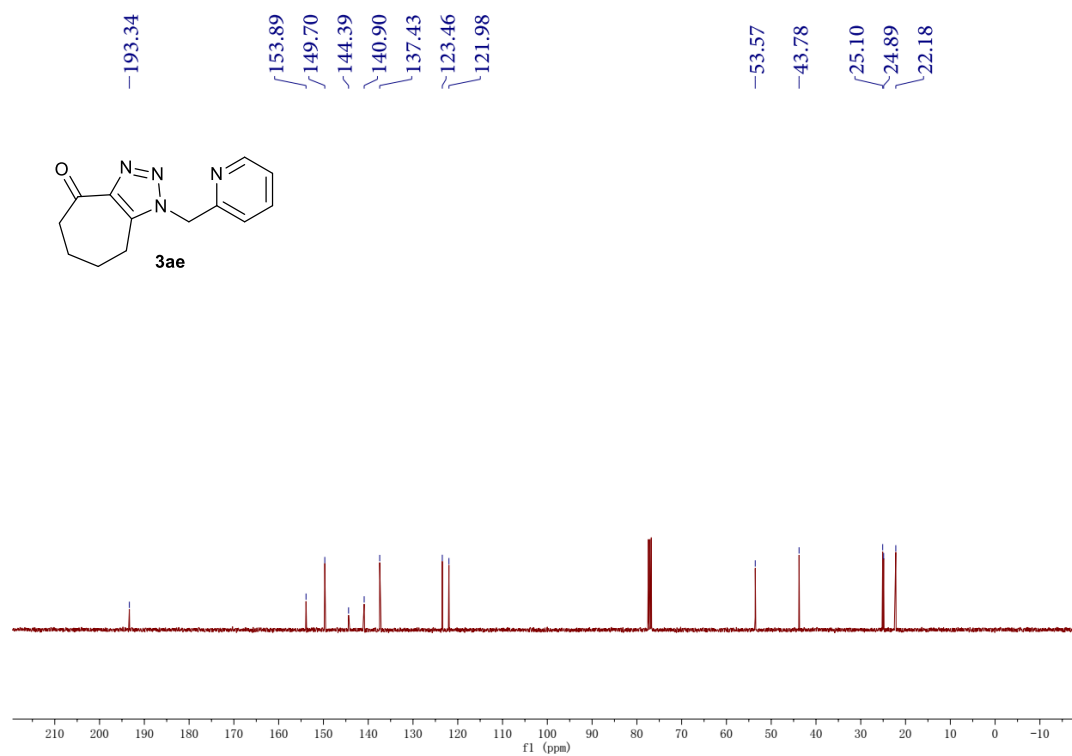
### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

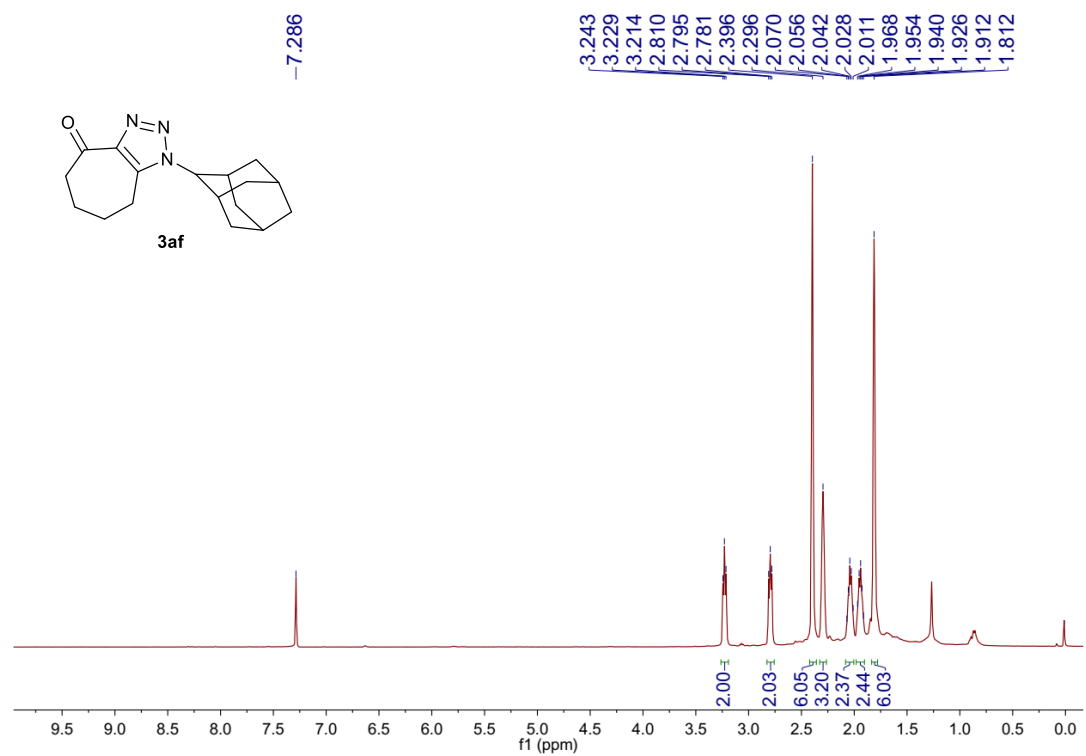


### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )

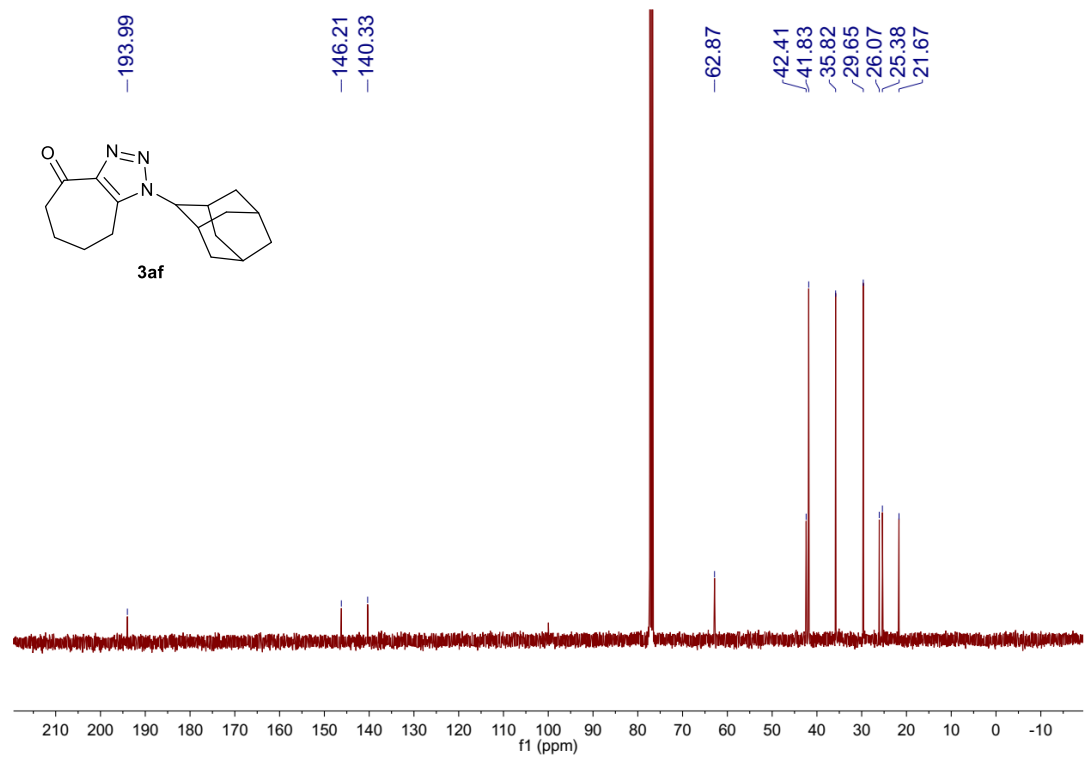




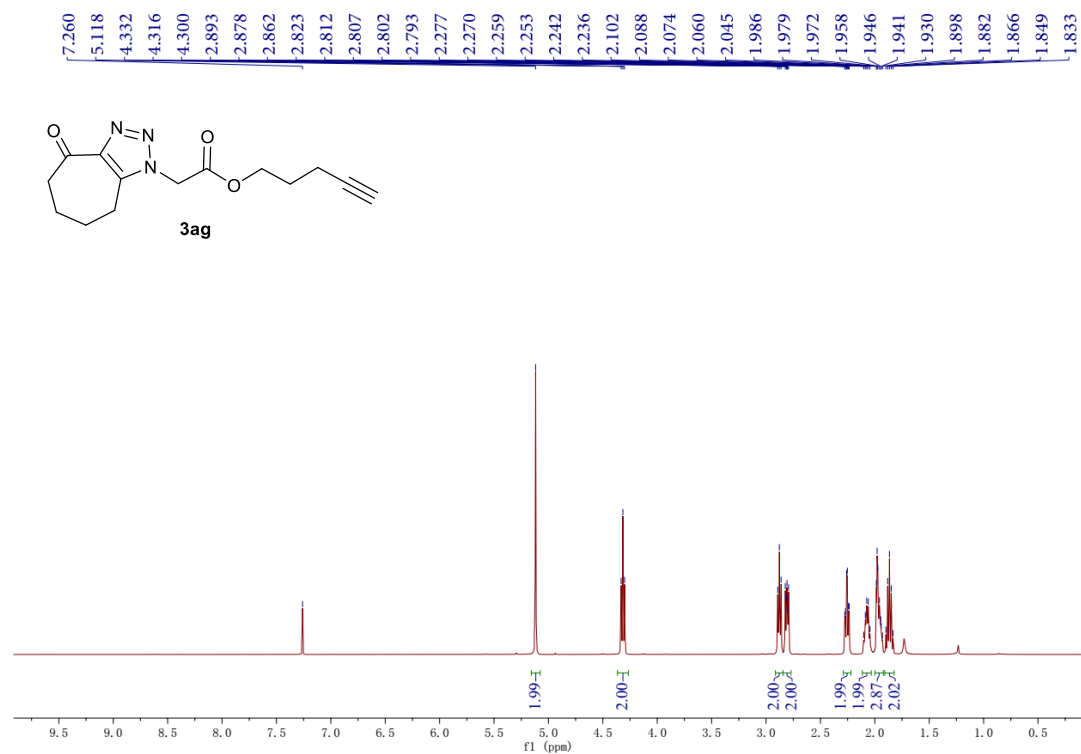
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



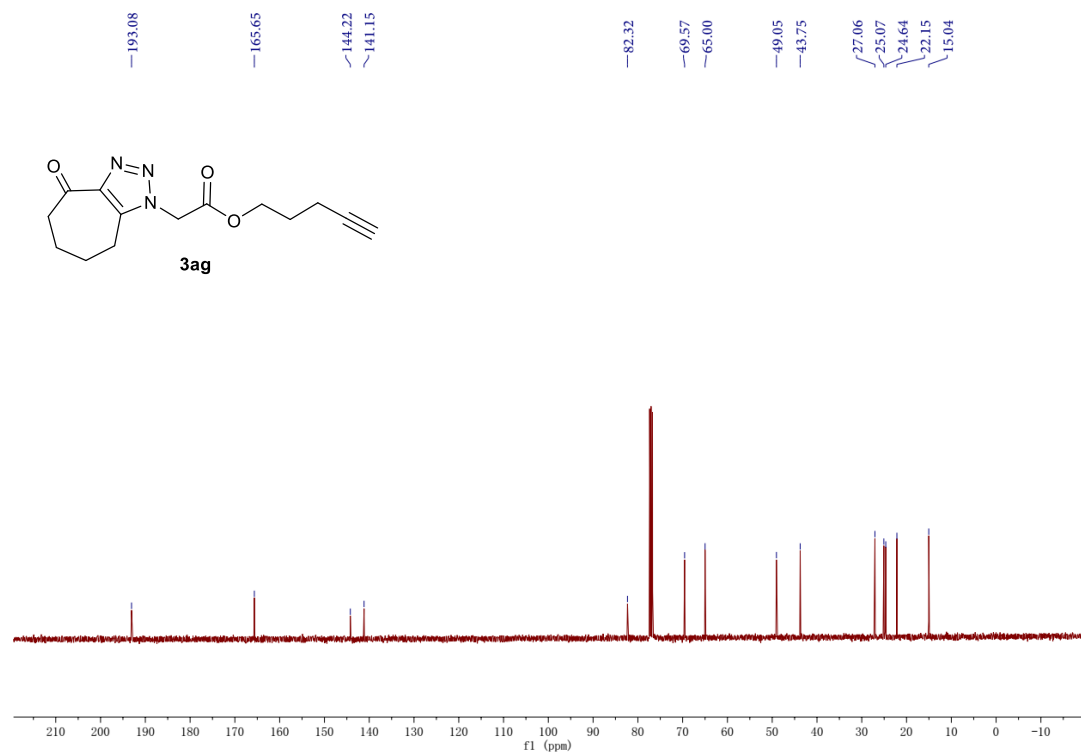
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



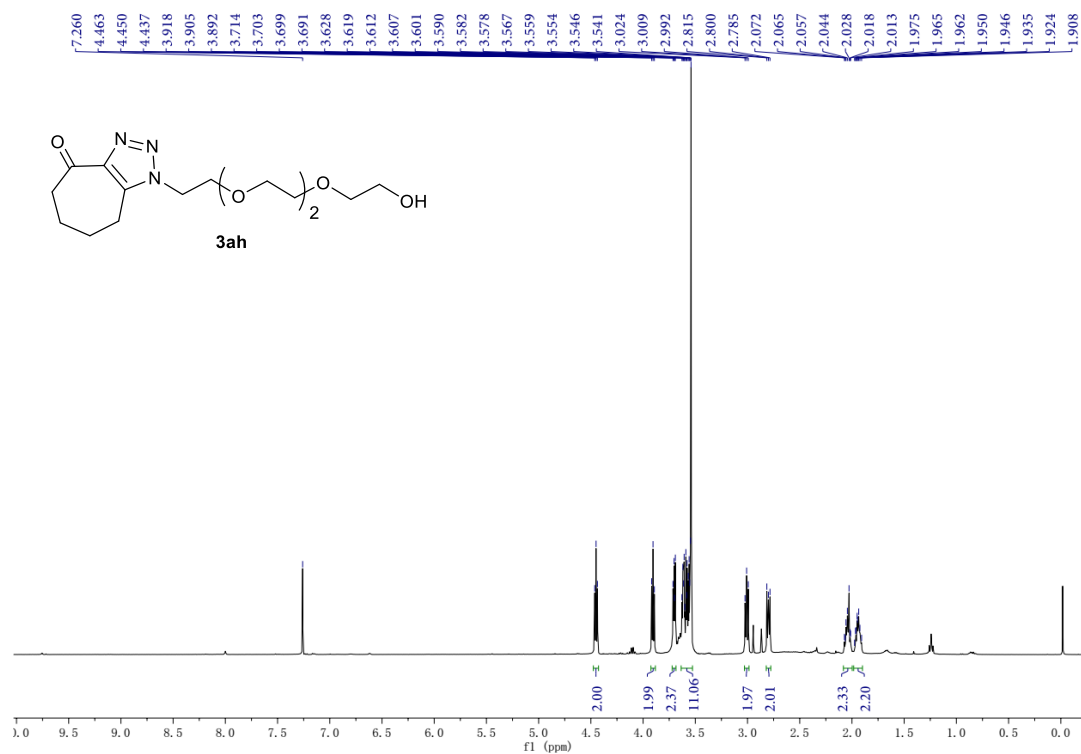
### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



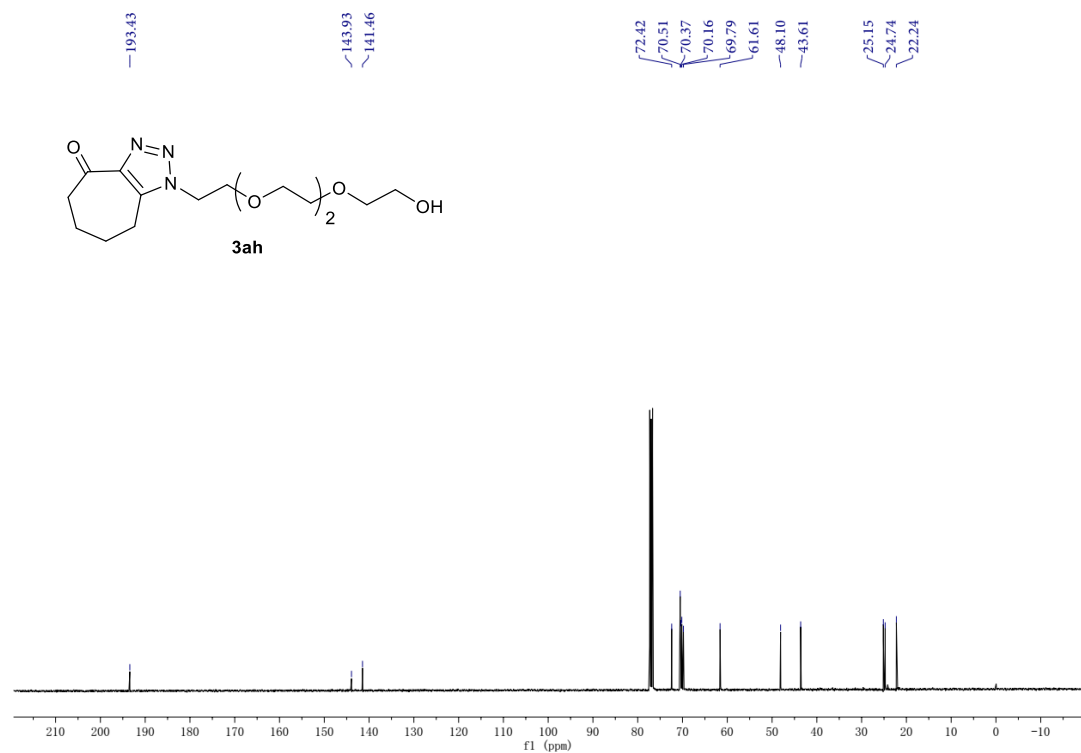
### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



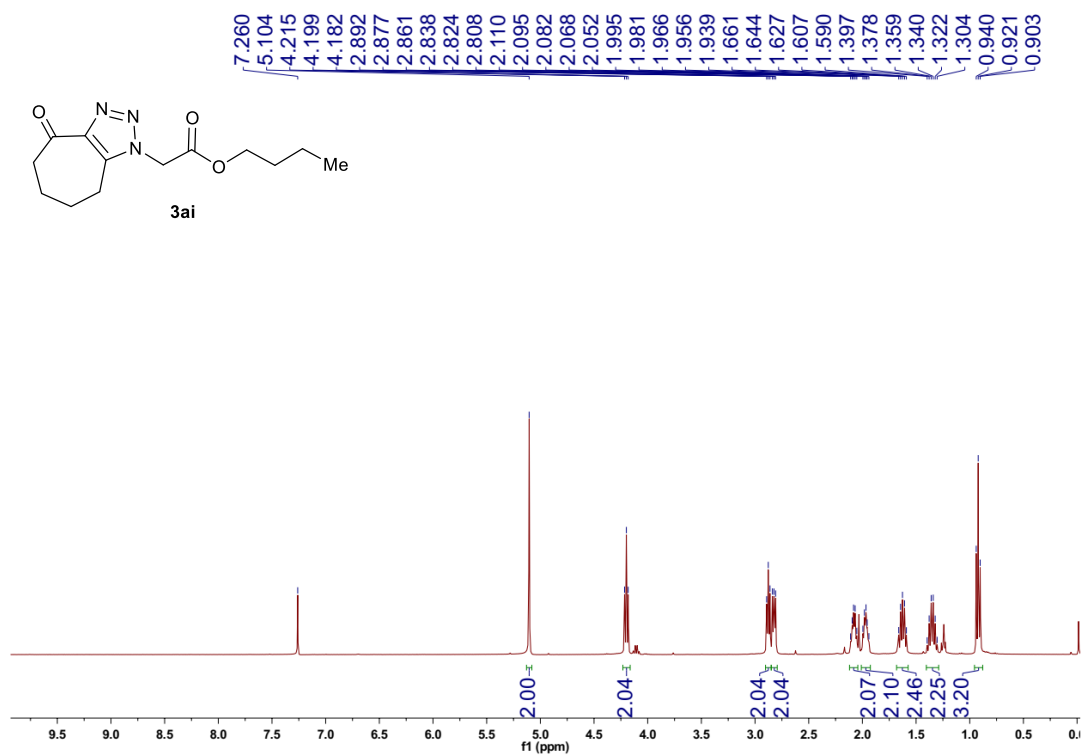
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



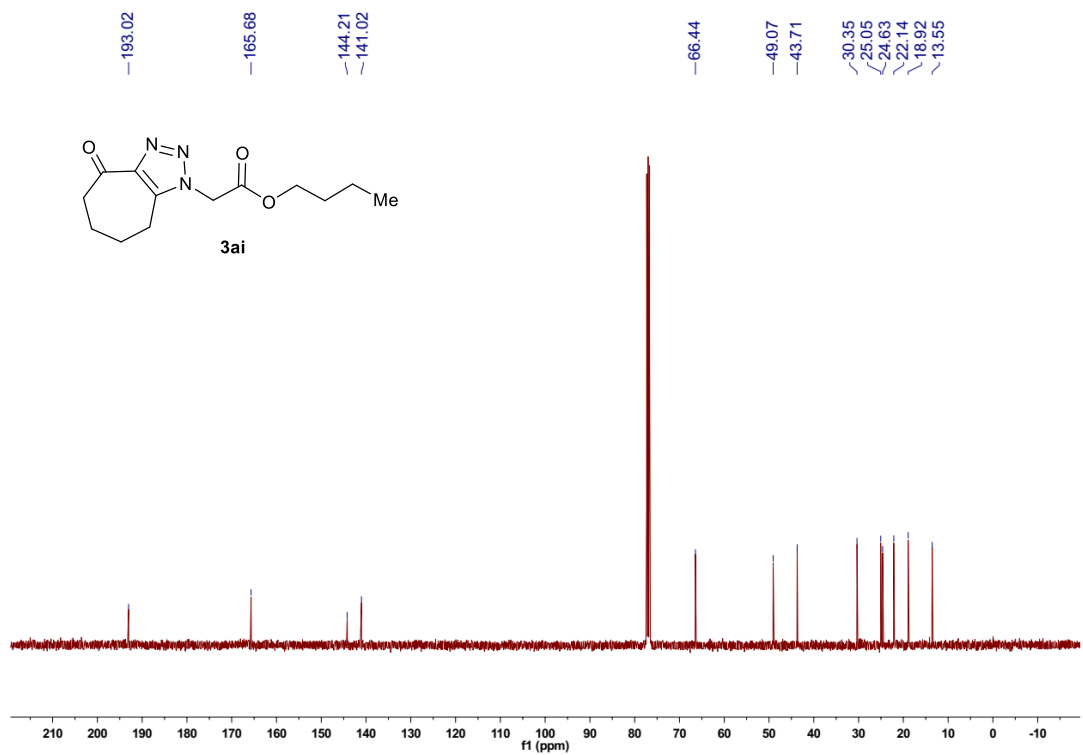
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



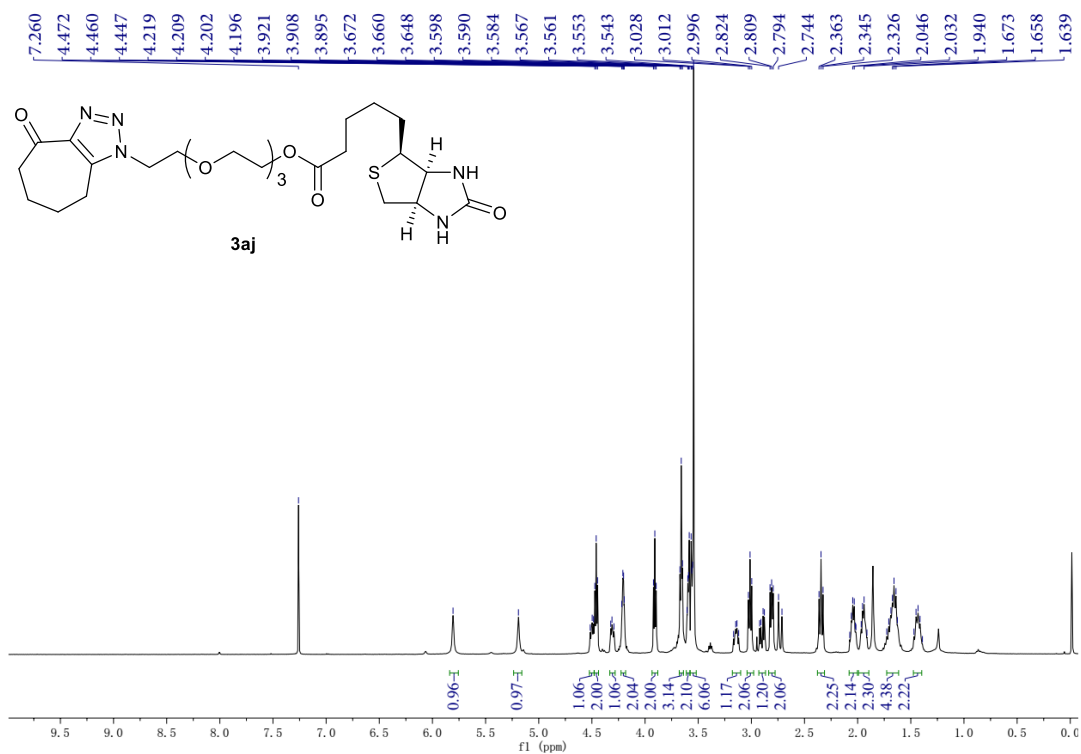
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



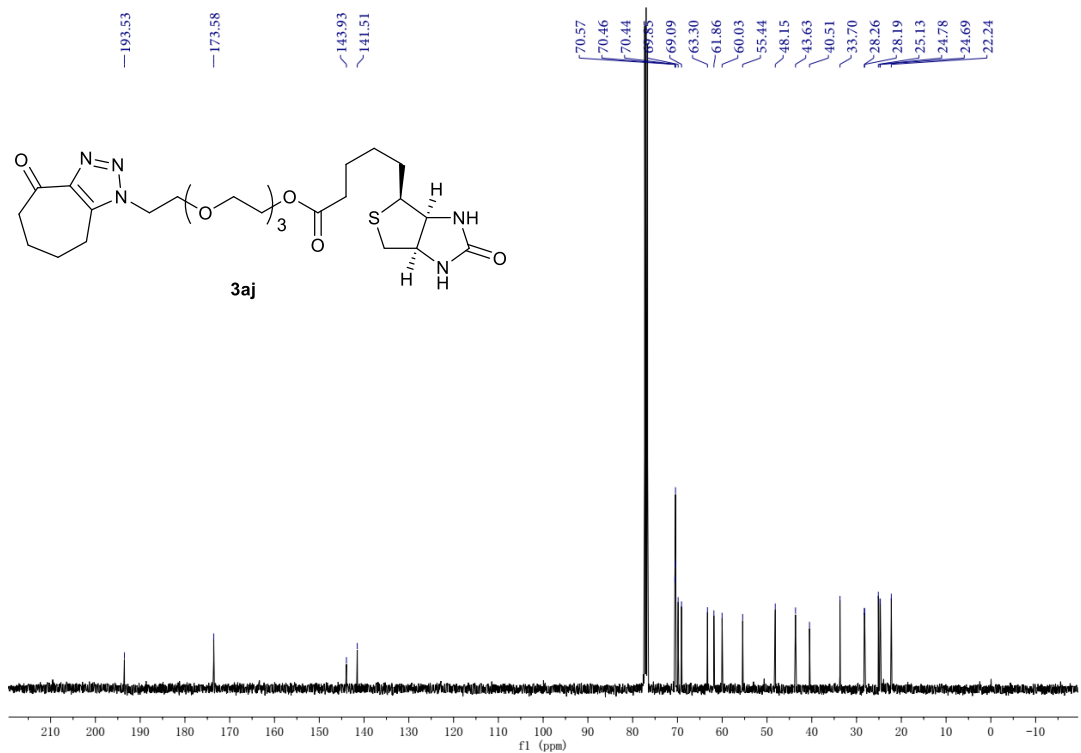
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



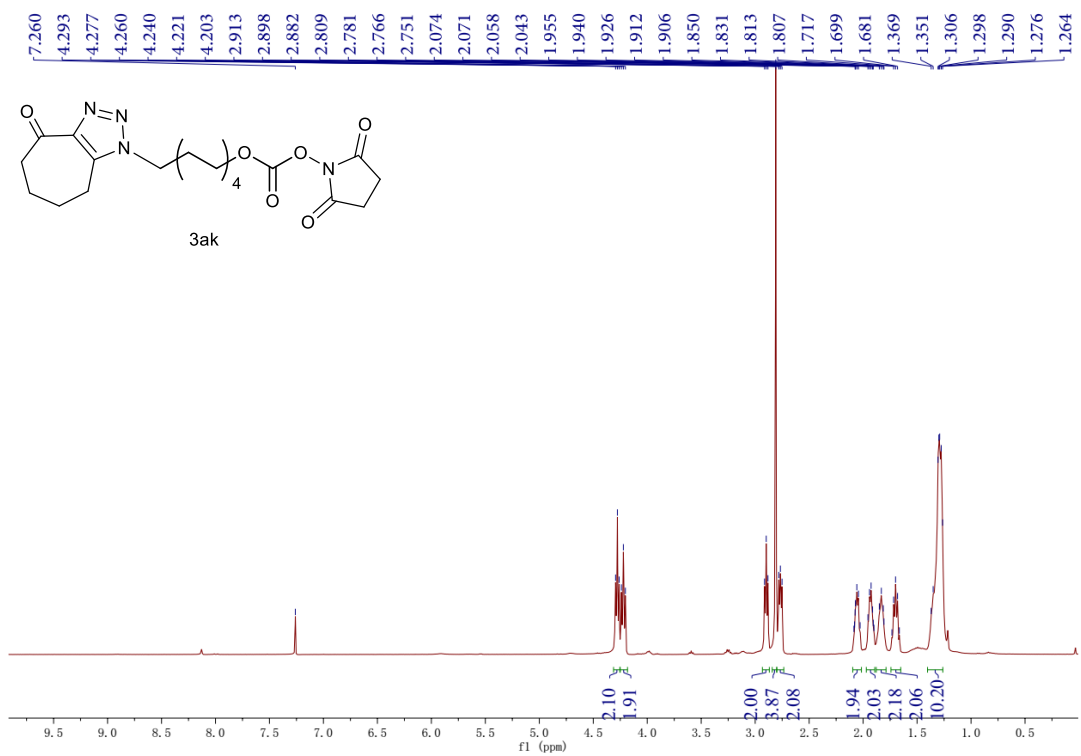
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



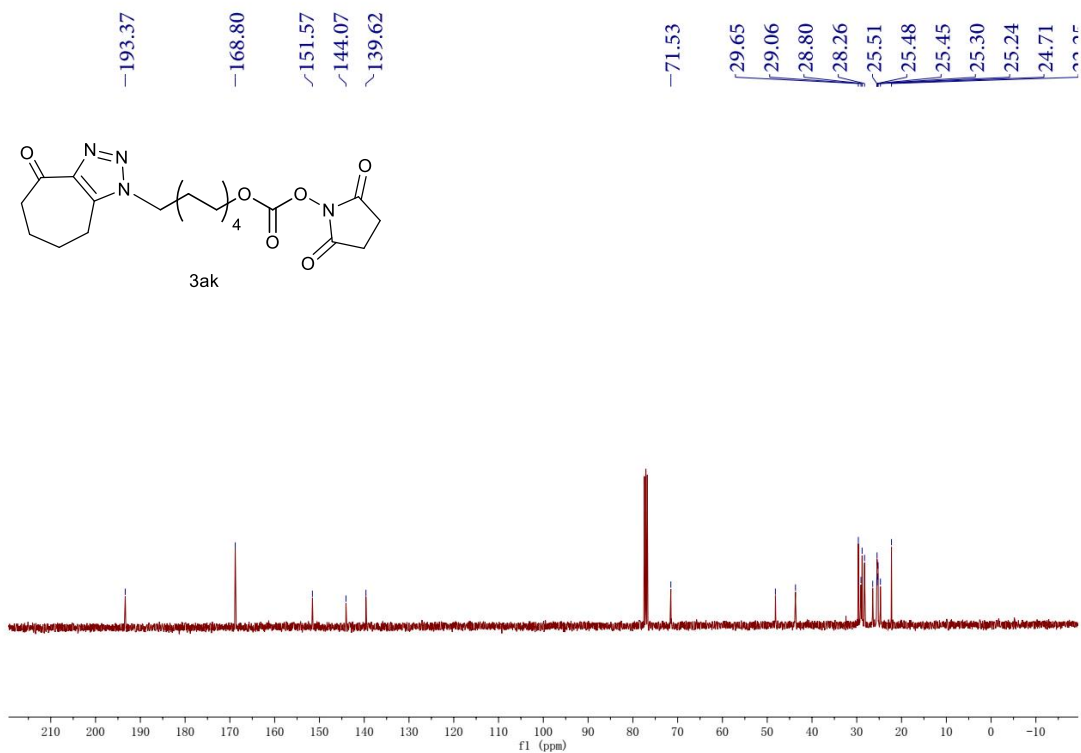
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



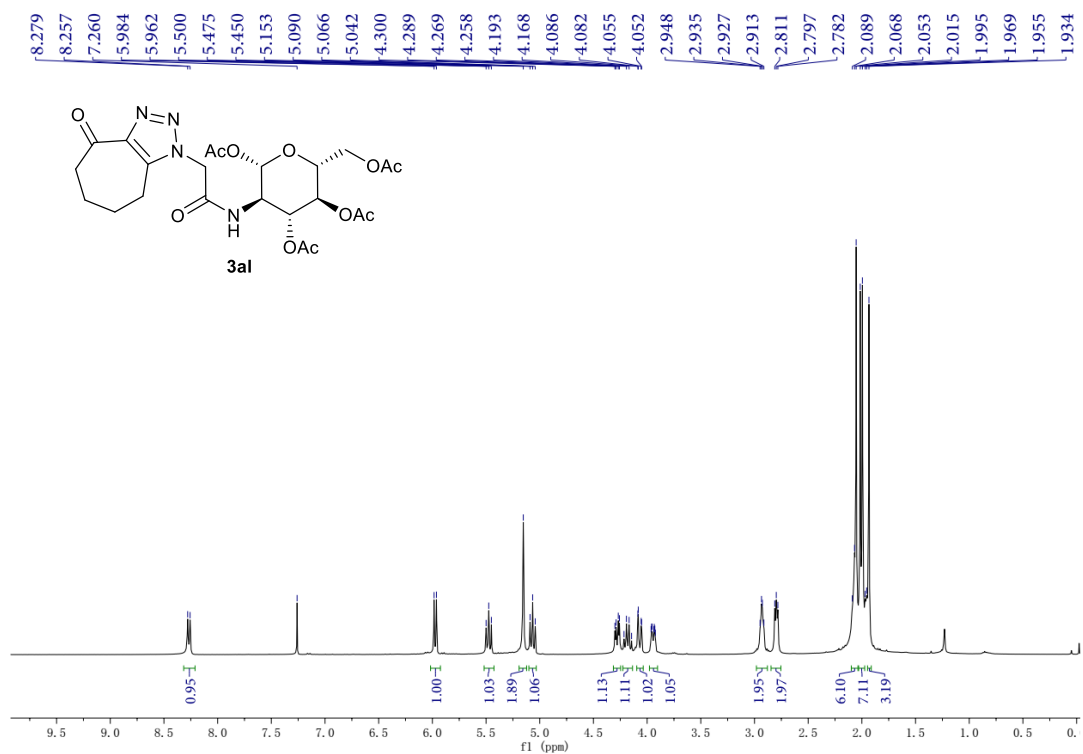
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



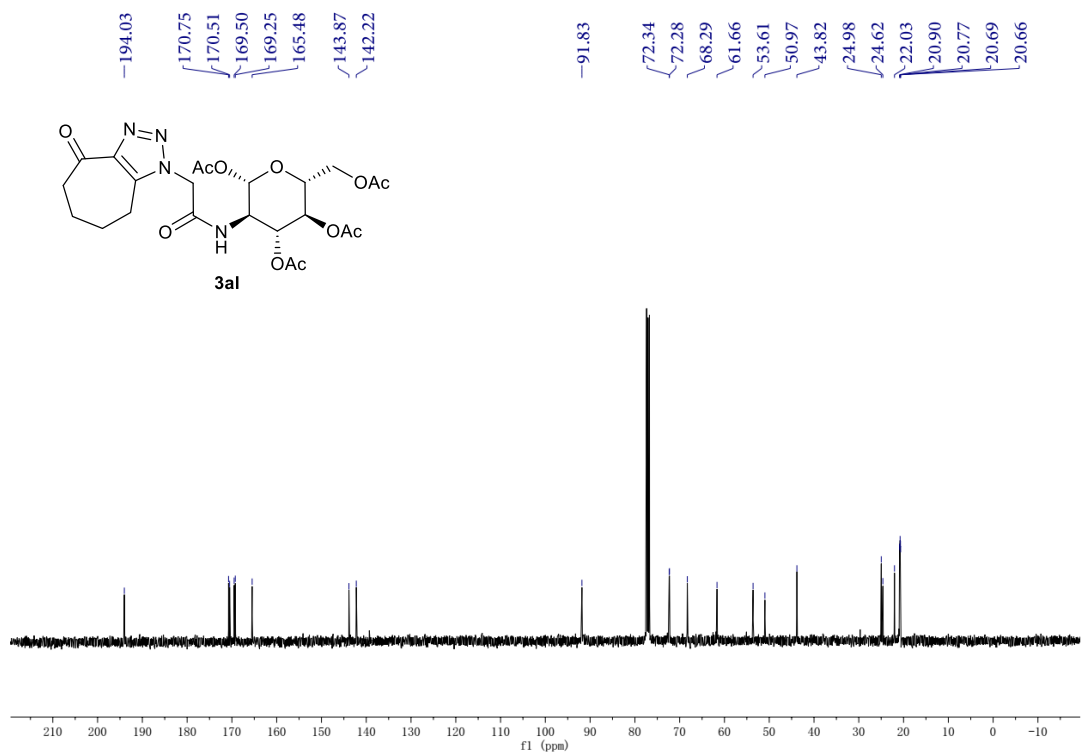
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



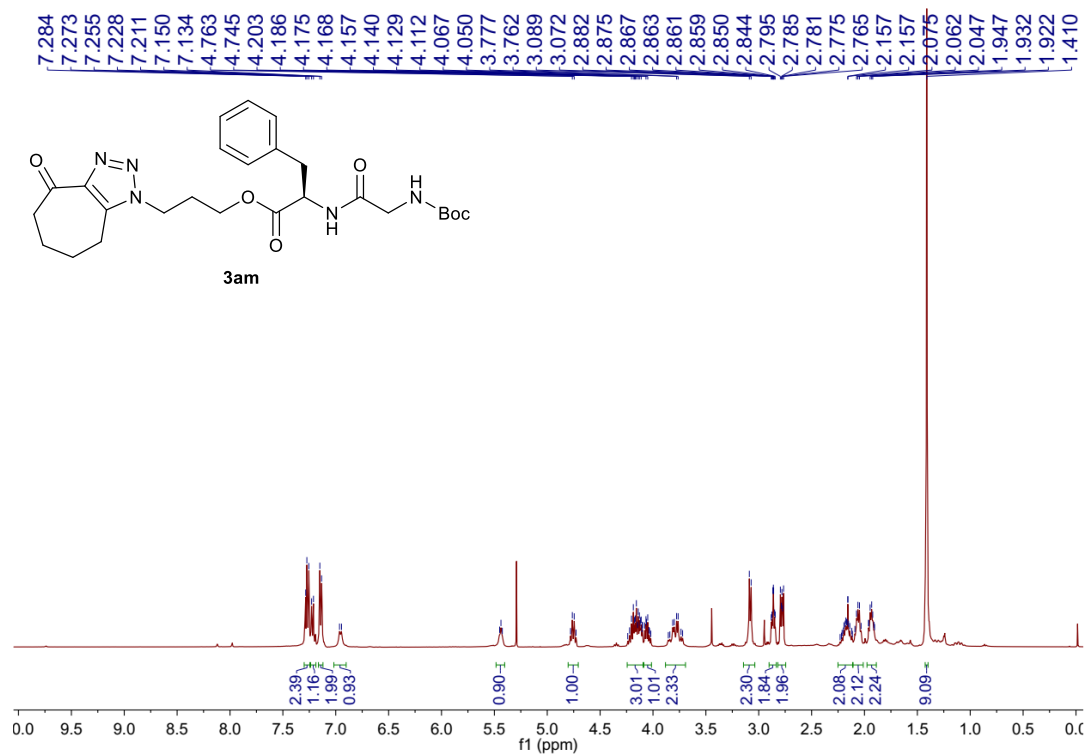
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



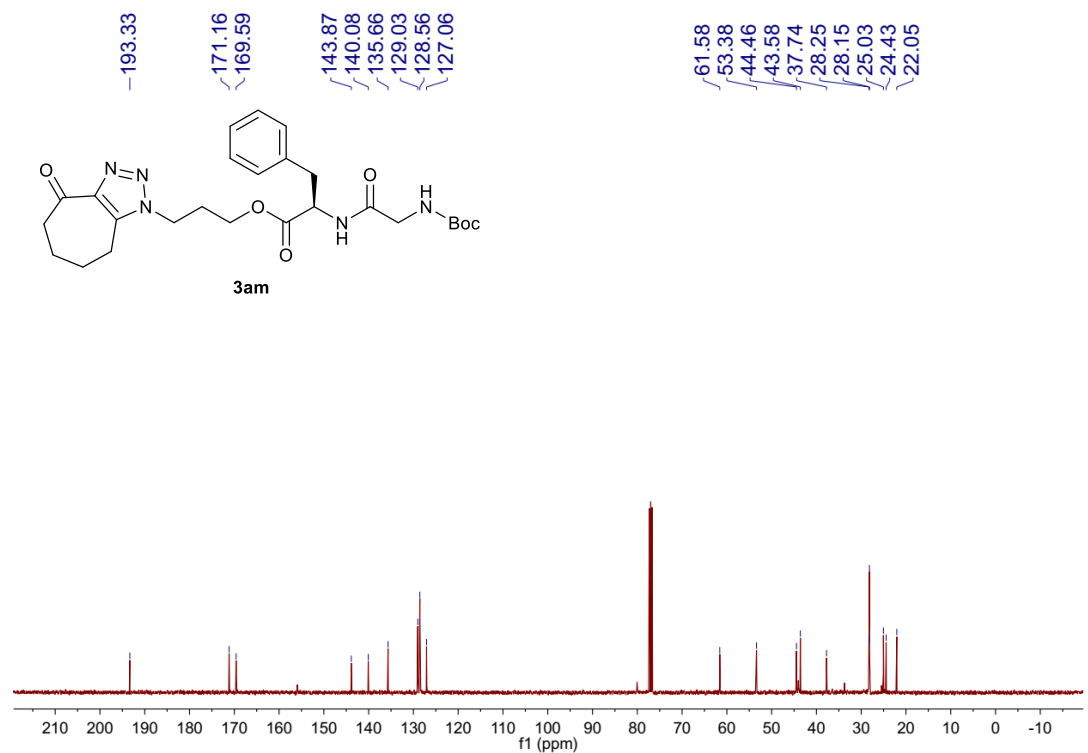
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



### <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

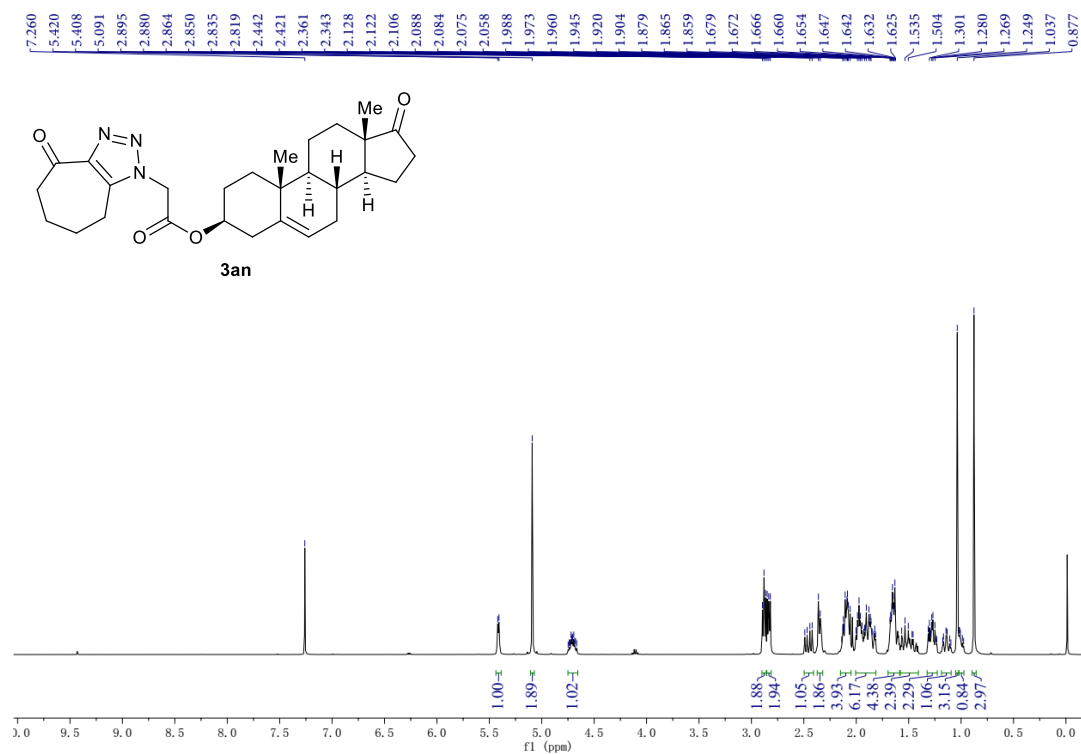


### <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

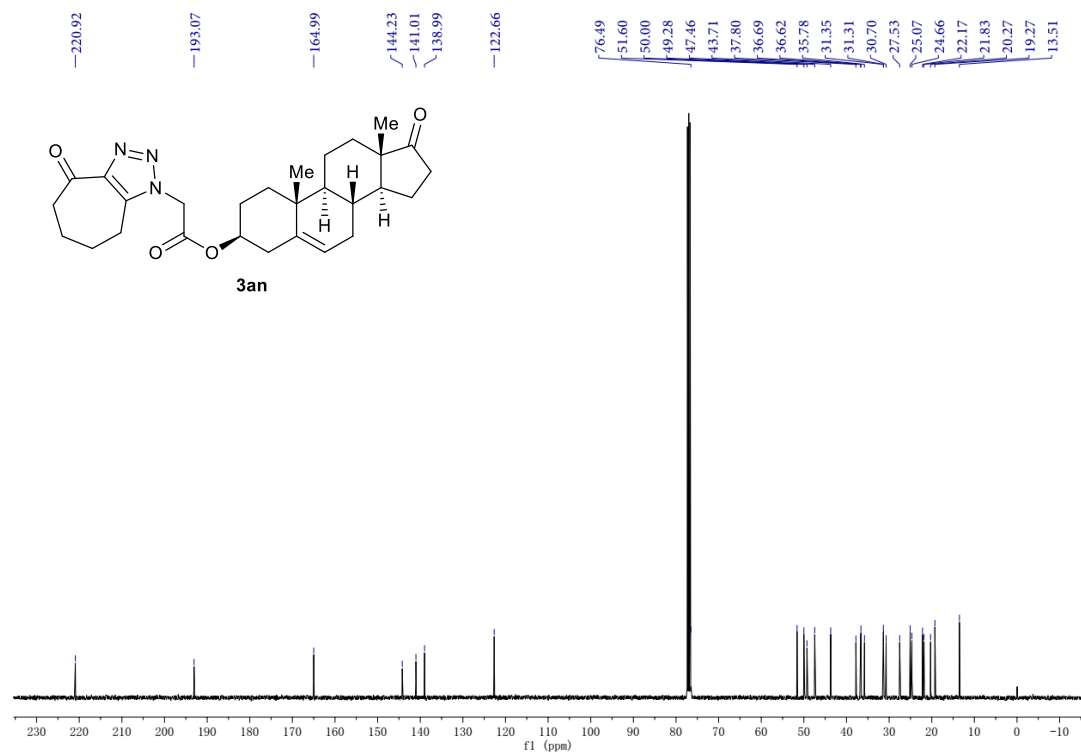




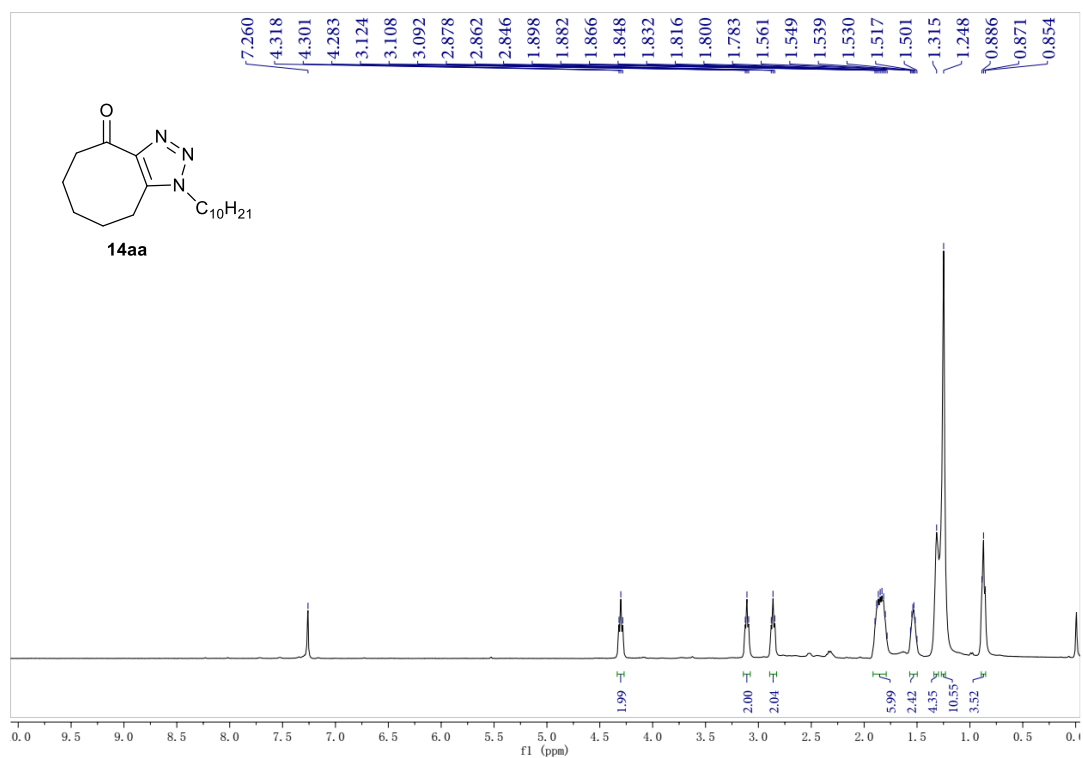
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



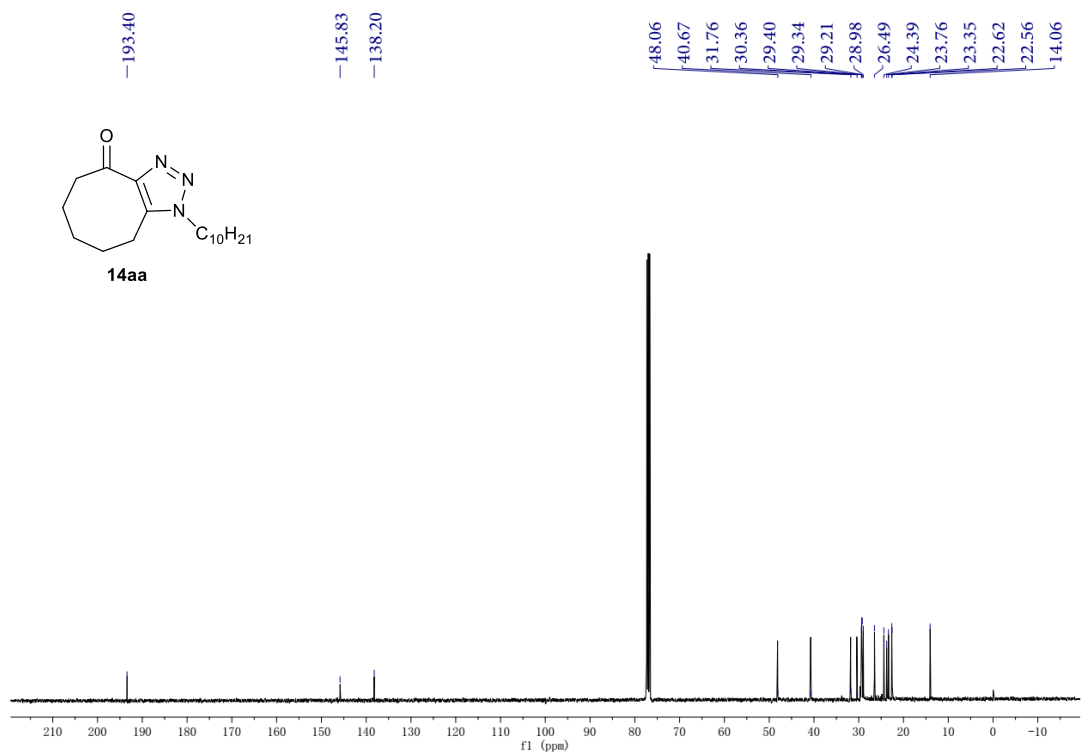
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



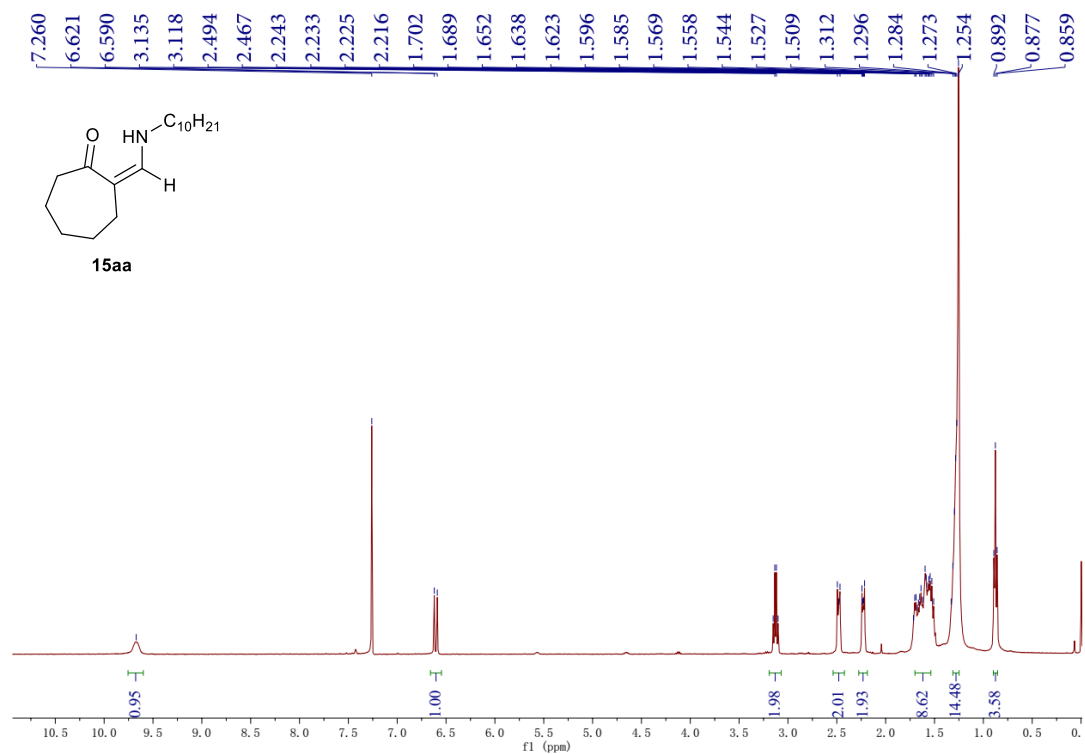
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



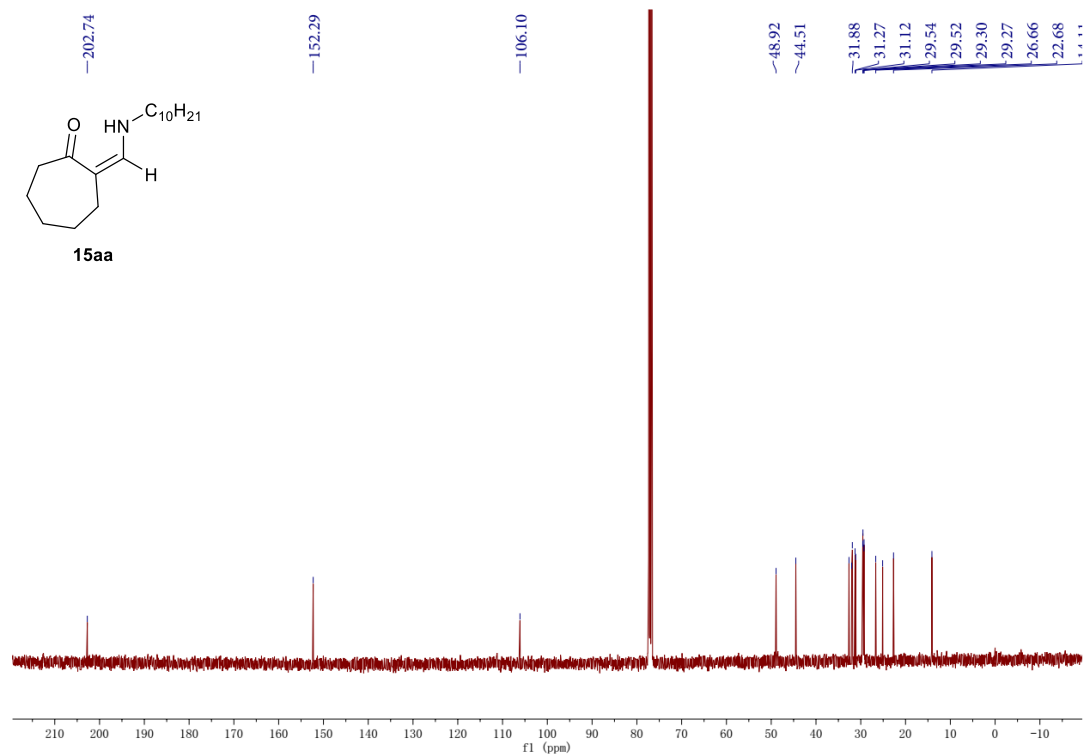
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



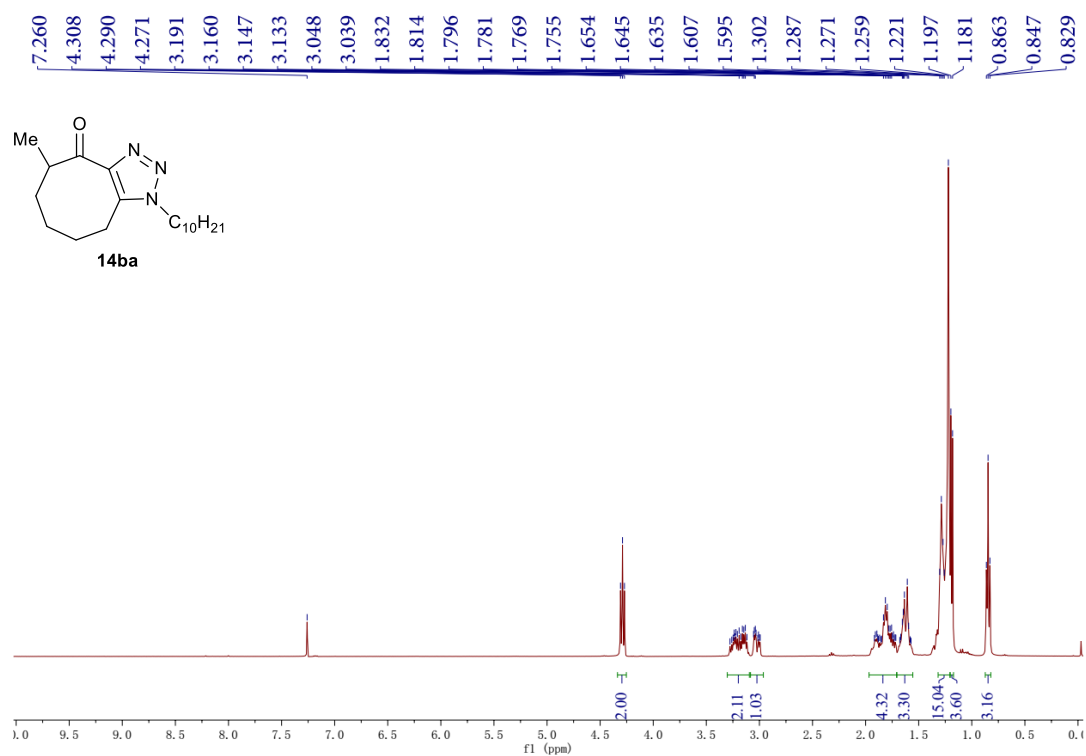
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



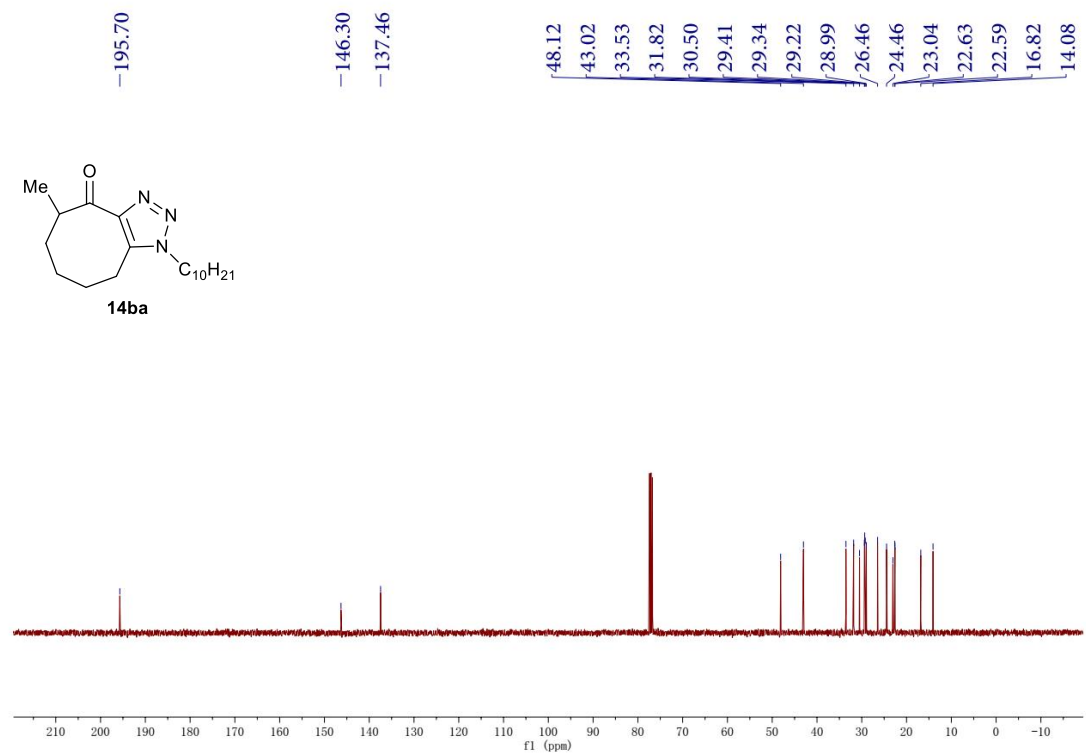
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



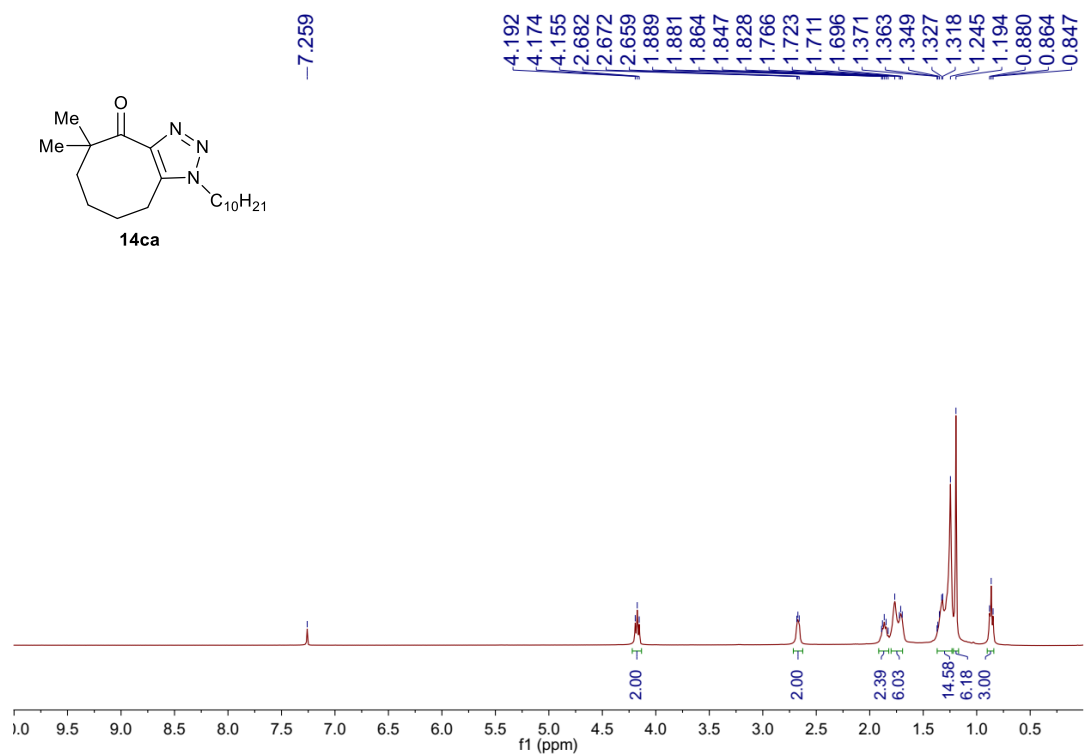
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



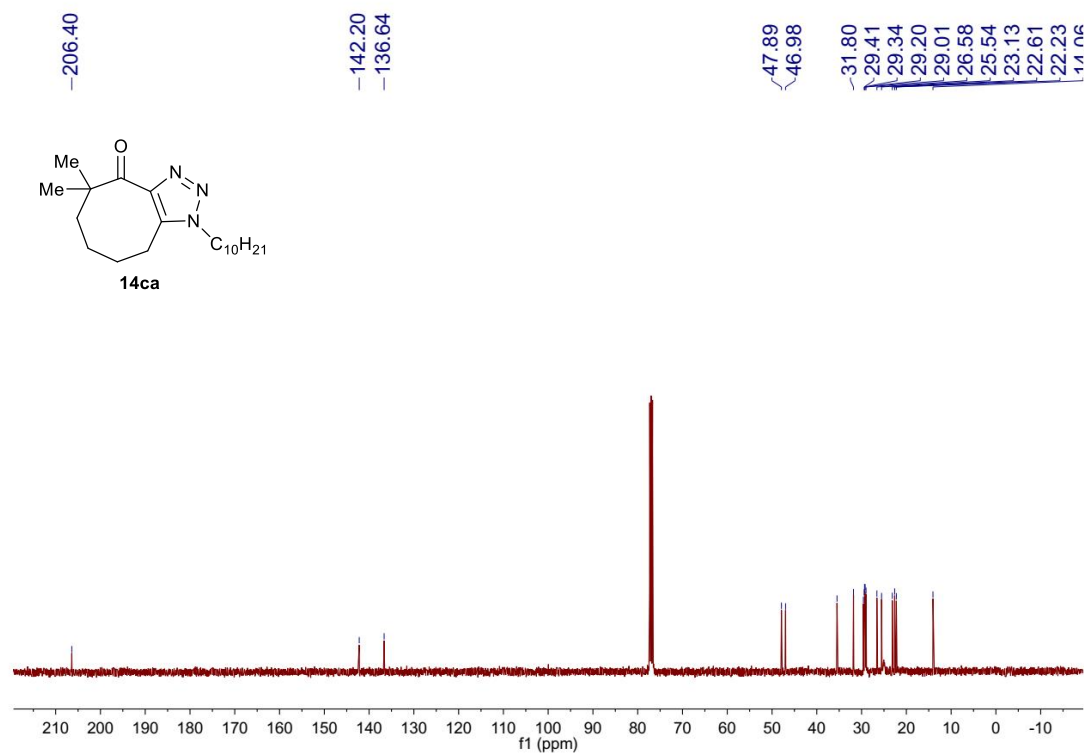
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



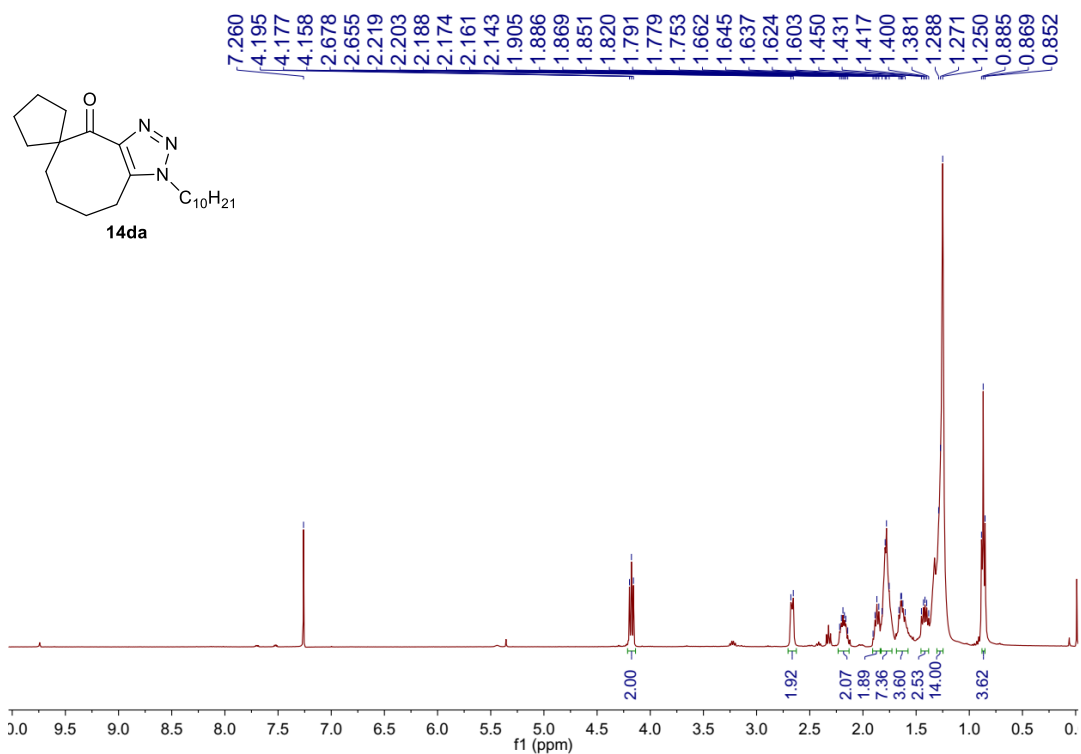
# $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



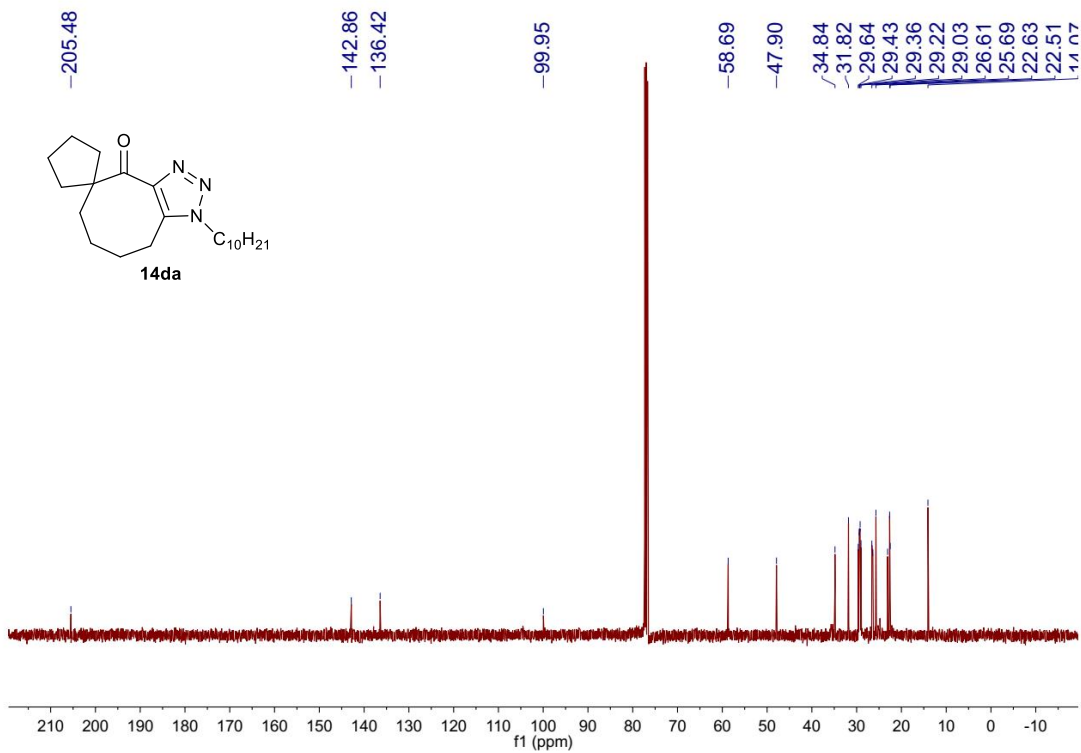
# $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



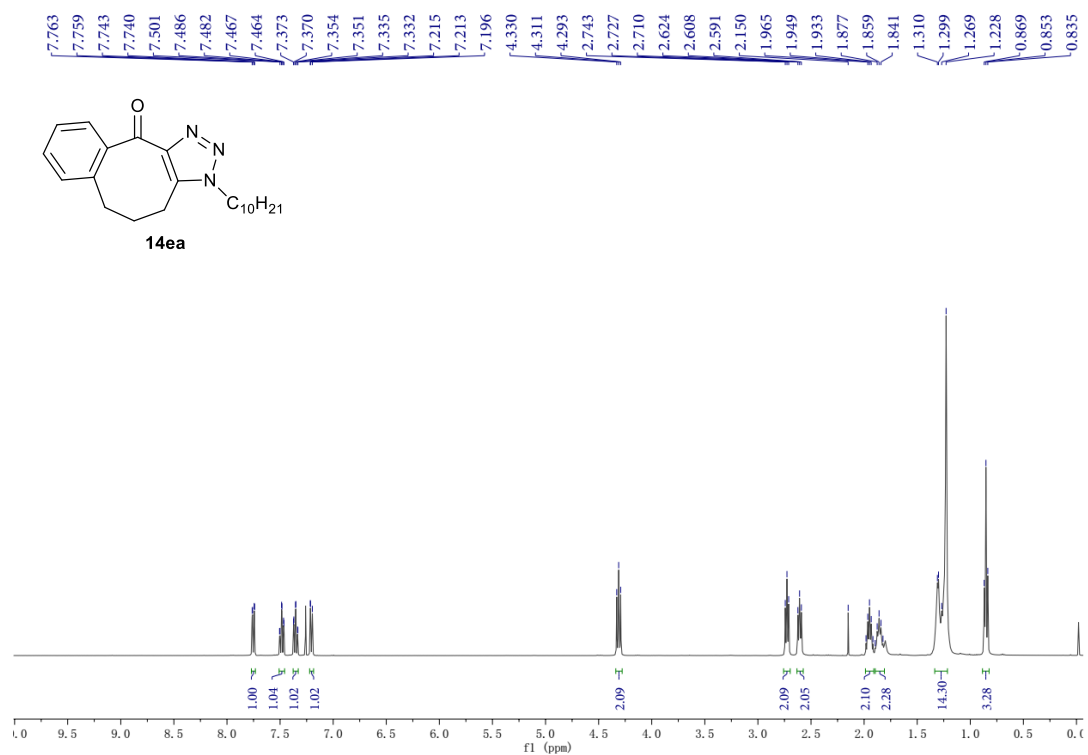
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



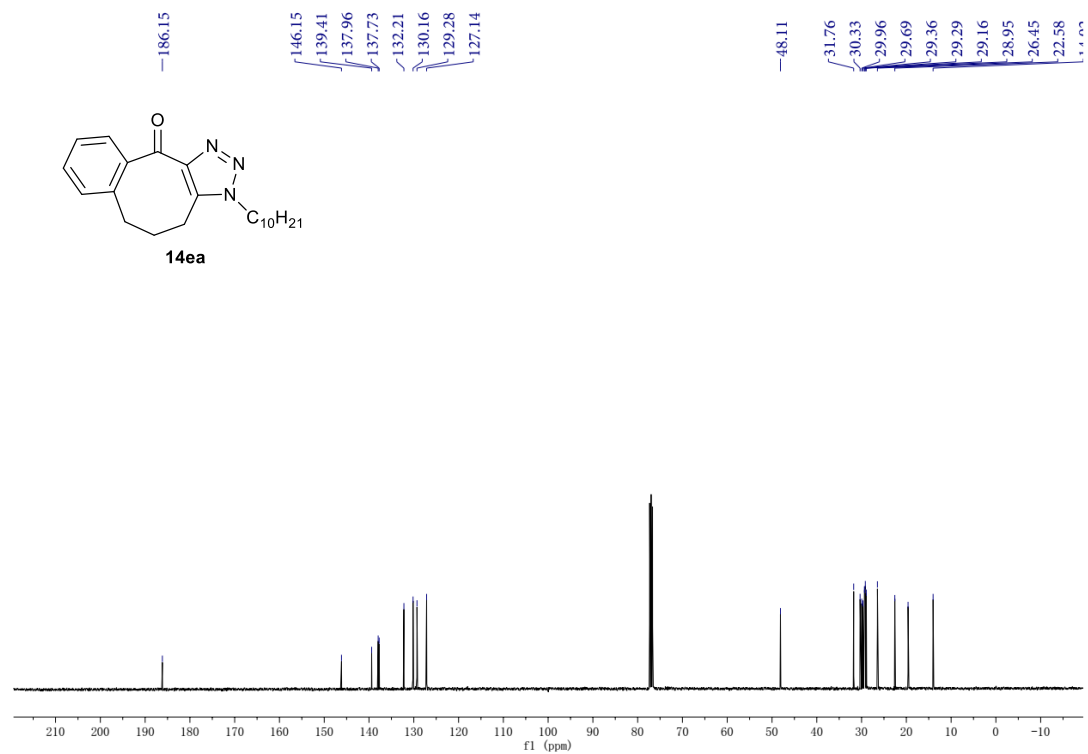
# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



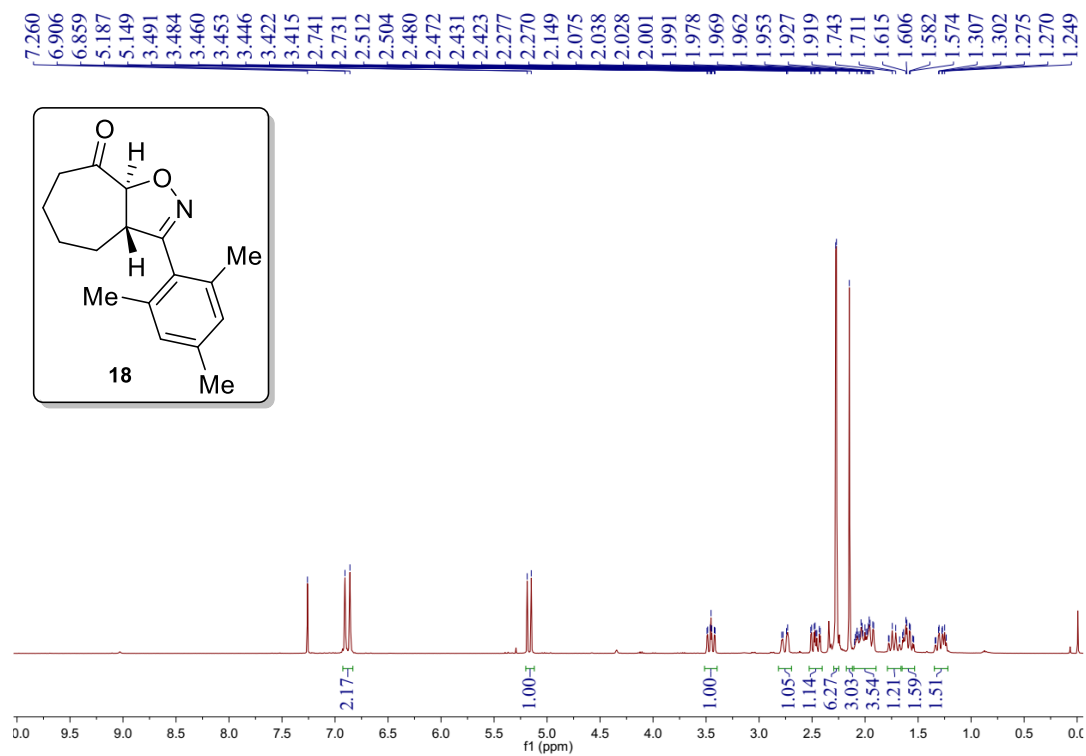
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )



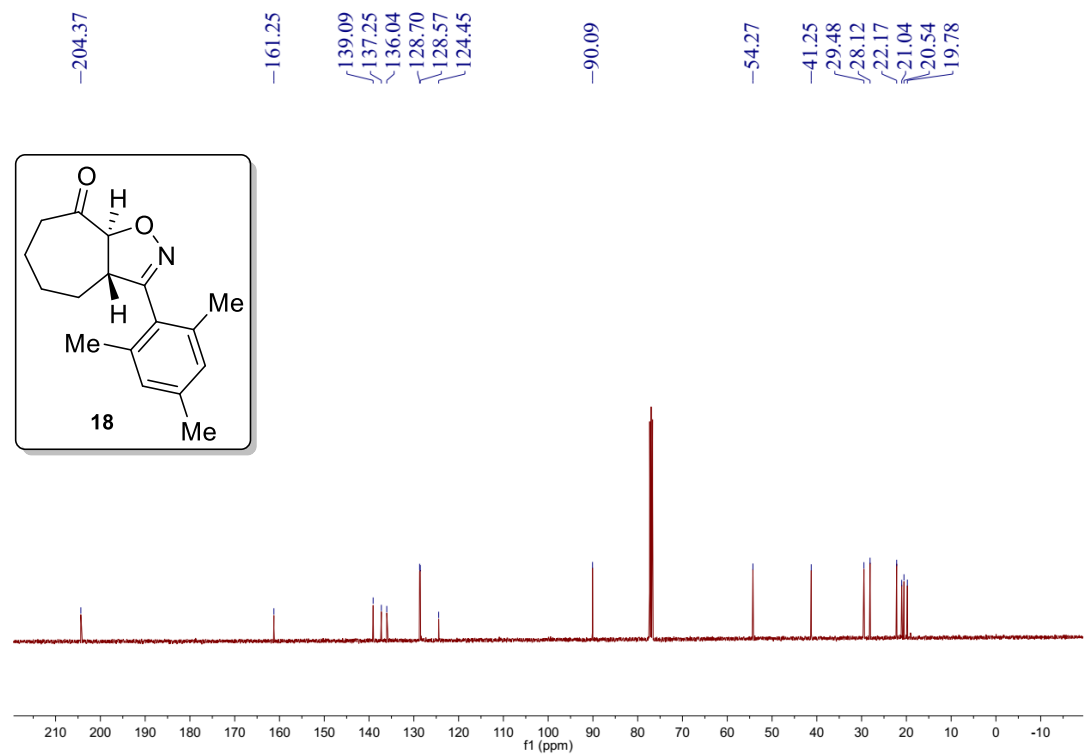
### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )



### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ )

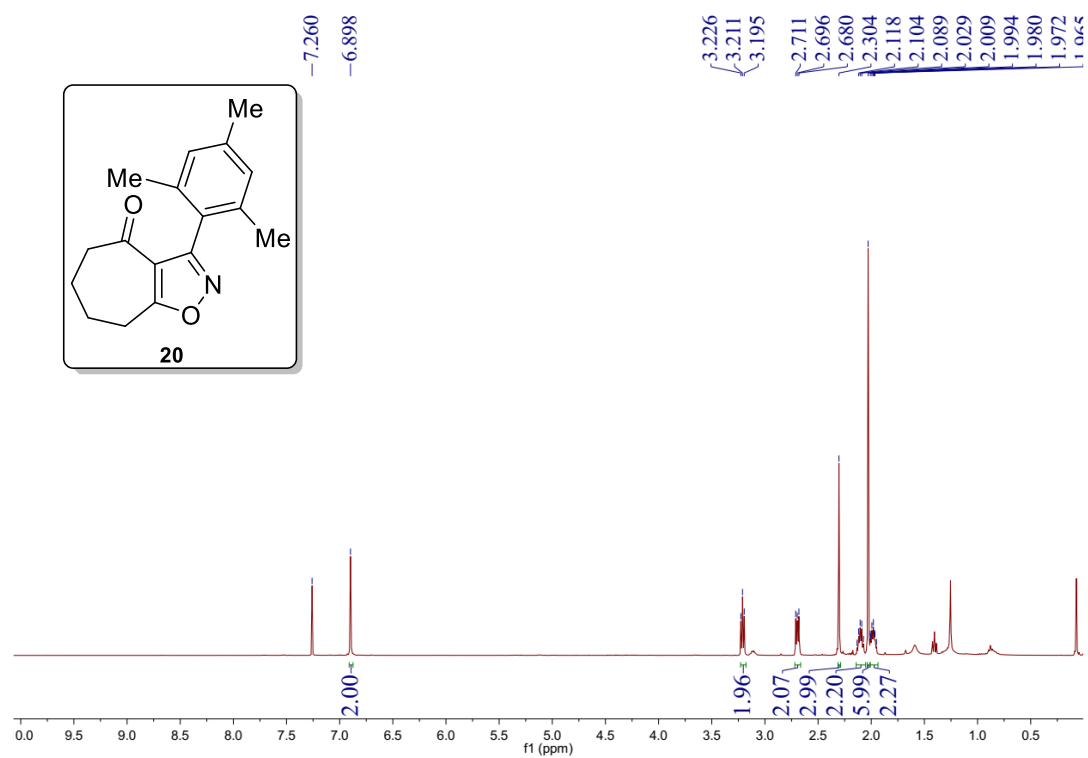


### $^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )

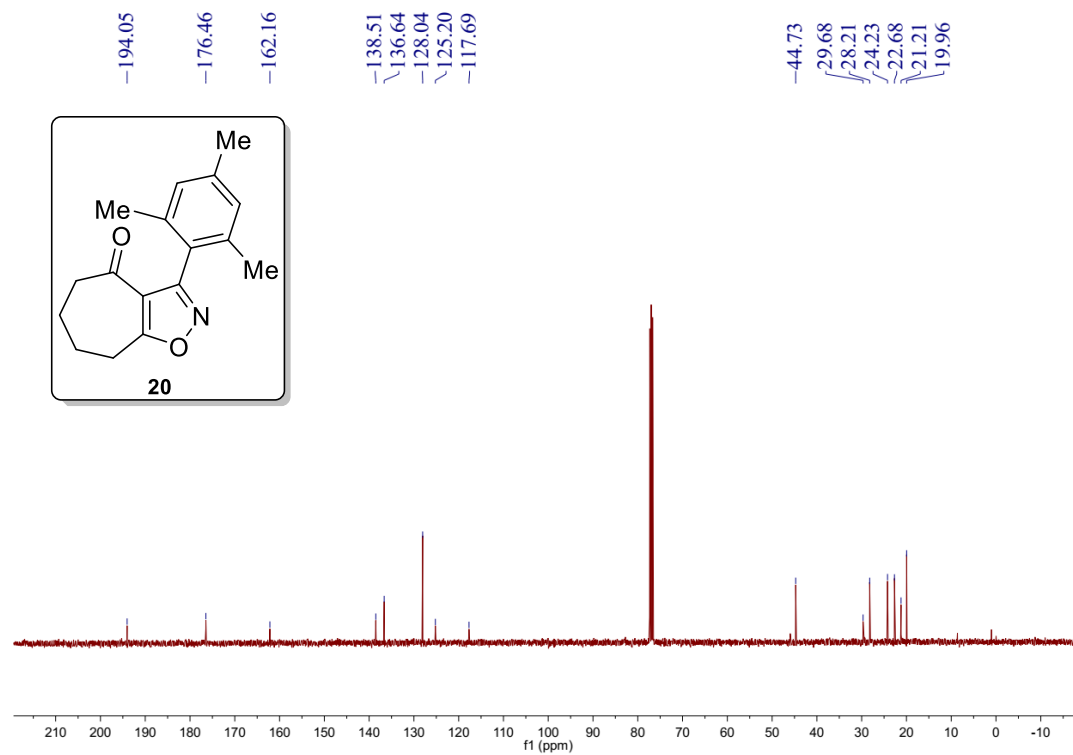




# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

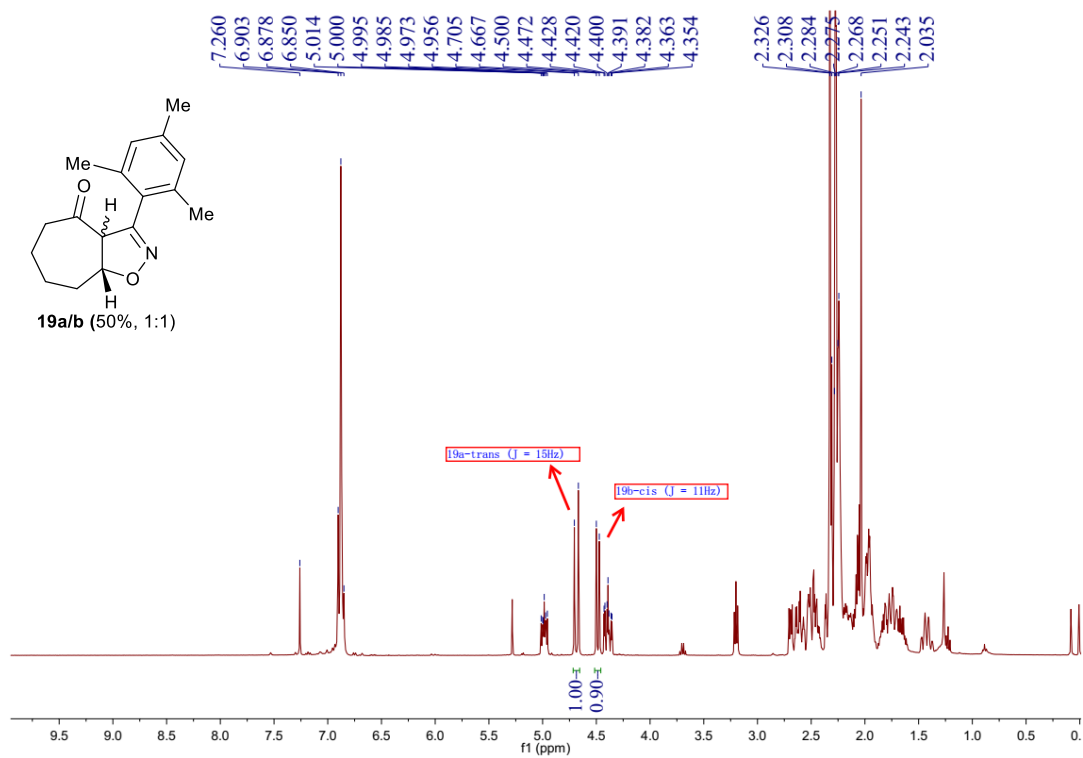


# <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

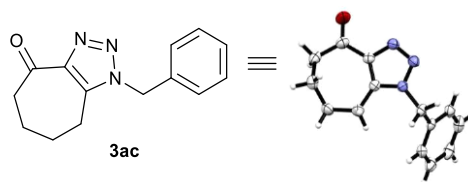


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

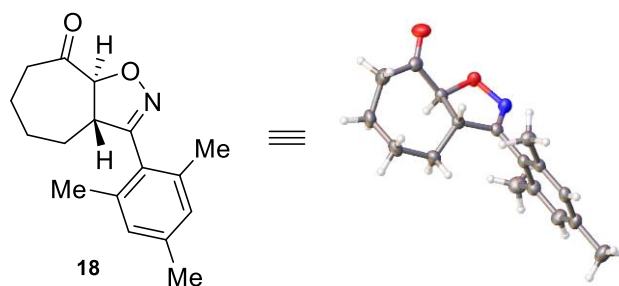
**19a-trans/19b-cis**



## 12. X-ray Crystallographic Structures of 3ac and 18



Compound	<b>3ac</b>
formula	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O
FW	241.29
crystal system	monoclinic
space group	<i>P 1 21/c 1</i>
<i>a</i> /Å	10.3653 (3)
<i>b</i> /Å	21.9057 (7)
<i>c</i> /Å	11.1008 (4)
<i>α</i> /deg	90
<i>β</i> /deg	104.043 (4)
<i>γ</i> /deg	90
<i>V</i> /Å <sup>3</sup>	2445.21 (14)
<i>Z</i>	8
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.311
<i>μ</i> /mm <sup>-1</sup>	0.684
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2σ)	0.0455 (3629)
w <i>R</i> <sub>2</sub> <sup>b</sup> (all data)	0.1169 (4562)
GOF	1.045



Compound	<b>18</b>
formula	C <sub>17</sub> H <sub>21</sub> NO <sub>2</sub>
FW	271.35
crystal system	monoclinic
space group	<i>P 1 21/n 1</i>
<i>a</i> /Å	13.1208 (3)
<i>b</i> /Å	7.6644 (1)
<i>c</i> /Å	15.2725 (4)
<i>α</i> /deg	90
<i>β</i> /deg	111.229 (3)
<i>γ</i> /deg	90
<i>V</i> /Å <sup>3</sup>	1431.63 (6)
<i>Z</i>	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.259
<i>μ</i> /mm <sup>-1</sup>	0.649
<i>R</i> <sub>1</sub> <sup>a</sup> ( <i>I</i> > 2σ)	0.0376 (2457)
w <i>R</i> <sub>2</sub> <sup>b</sup> (all data)	0.0972 (2665)
GOF	1.020