

Supporting Information
Design, Synthesis and DNA-Cleaving Efficiency of
Photoswitchable Dimeric Azobenzene Based Eneidyne
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Page No. 31: Figure S83: DNA binding study of compound **1a** by UV

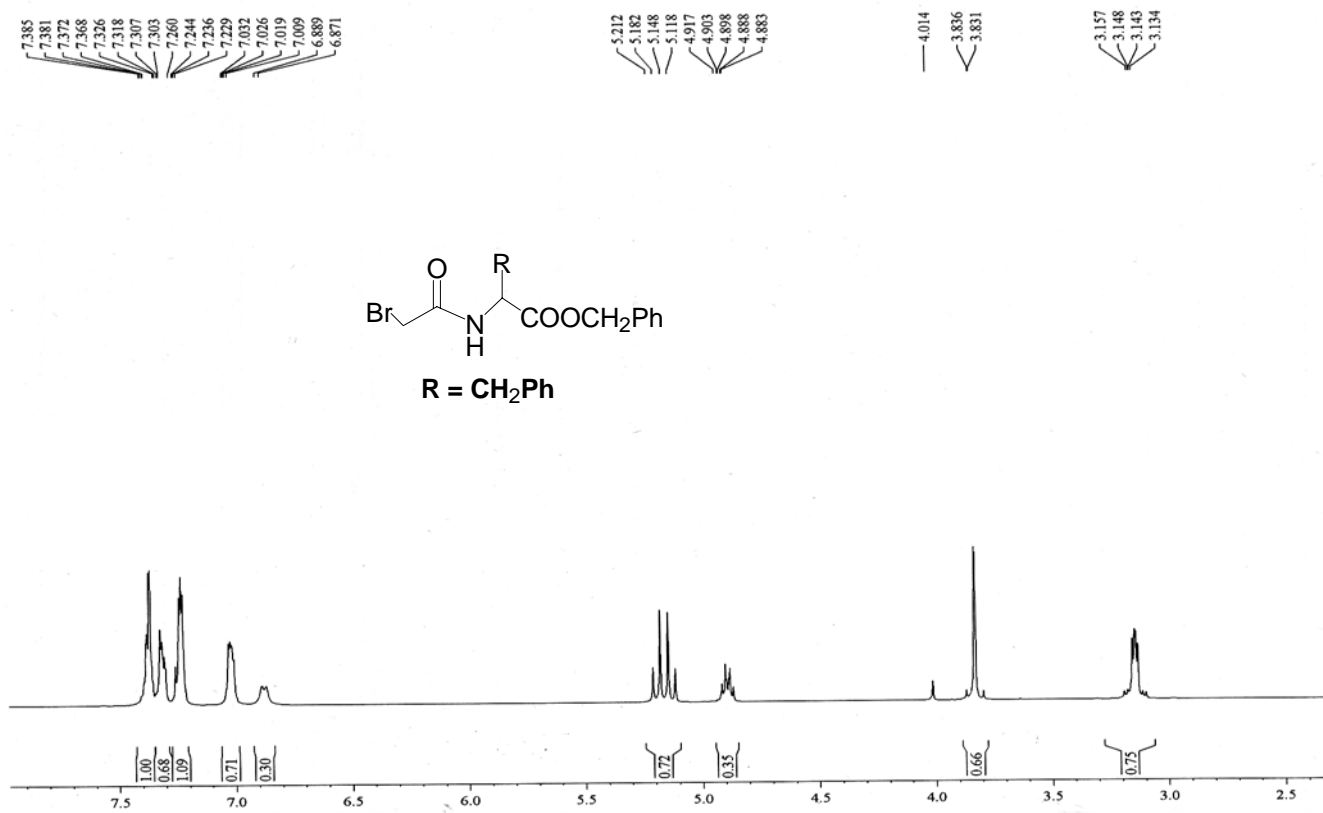
Page No. 32:: Figure S84 to S87: DNA binding plots of compounds **2a-2b** and **2i-2j**

Page No. 33: Figure S88 to S91: DSC of enediynes **1a**, **1b**, **1c** and **1e** respectively

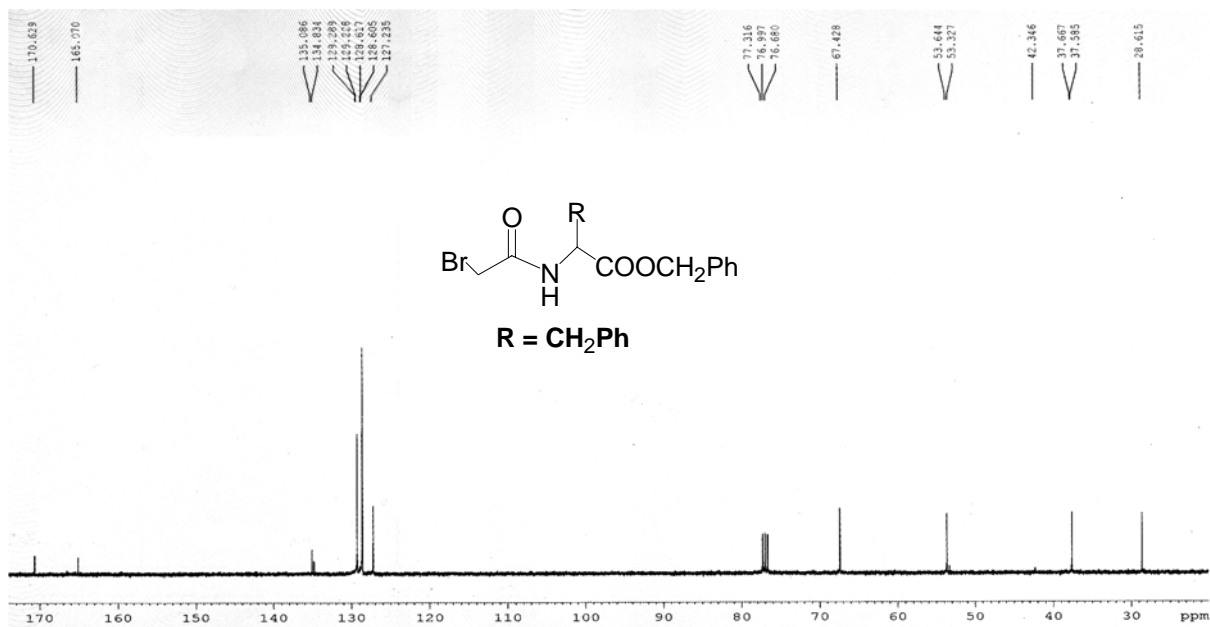
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Page No. 35: Figure S93: Energy minimized conformations of **1a**, **2a**, **1d**, **2d**, **1e** and **2e**

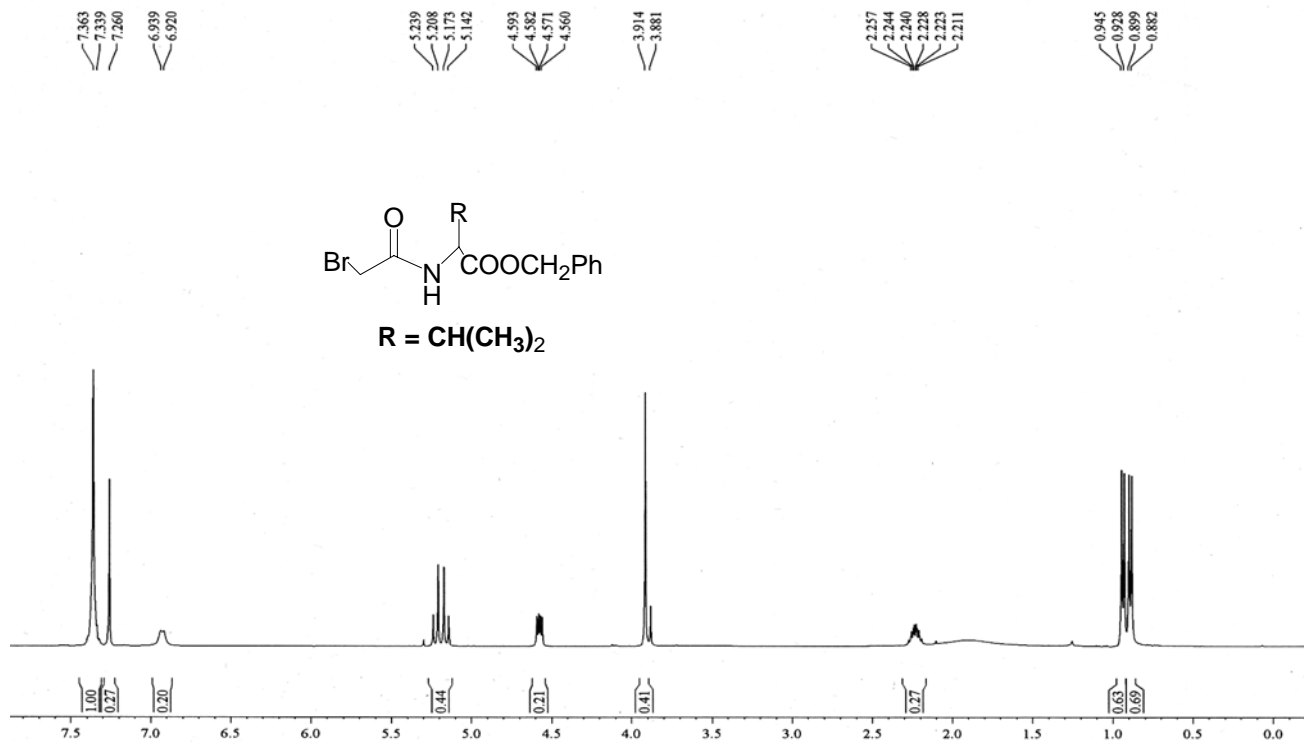
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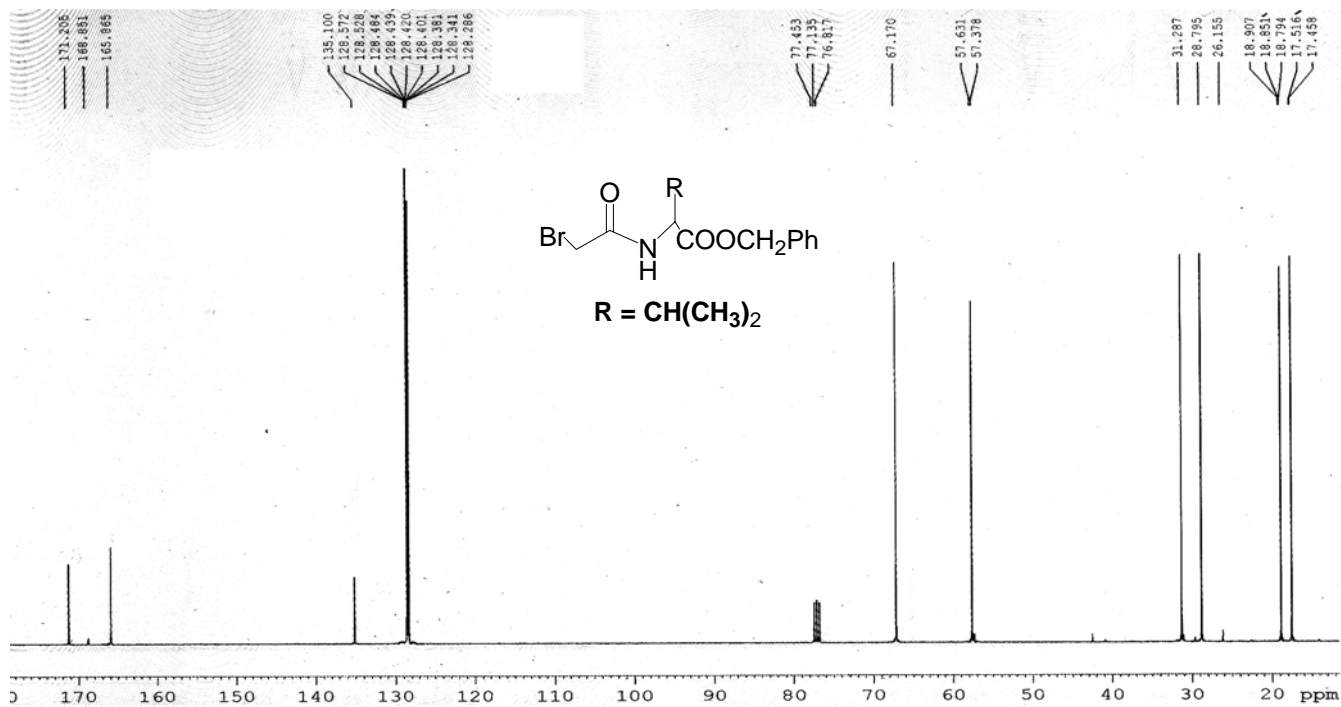
Figures S2



Figures S3



Figures S4

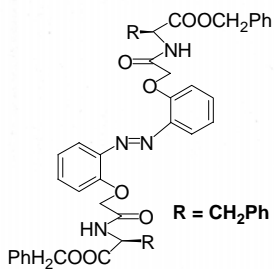


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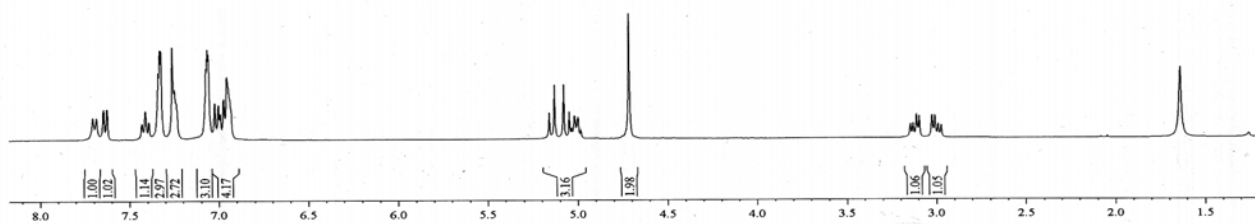
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7.430
7.411
7.392
7.330
7.324
7.260
7.247
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7.072
7.064
7.058
7.023
7.002
6.992
6.972
6.954

5.159
5.128
5.078
5.047
5.018
4.998
4.713

3.144
3.129
3.110
3.095
3.025
3.008
2.990
2.974



3a



Figures S6

170.798
167.872

155.155

142.623

135.474
135.029
132.602
129.006
128.474
128.350
128.332
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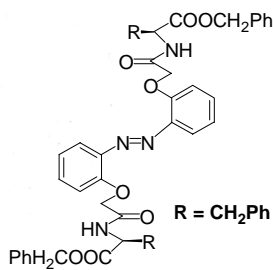
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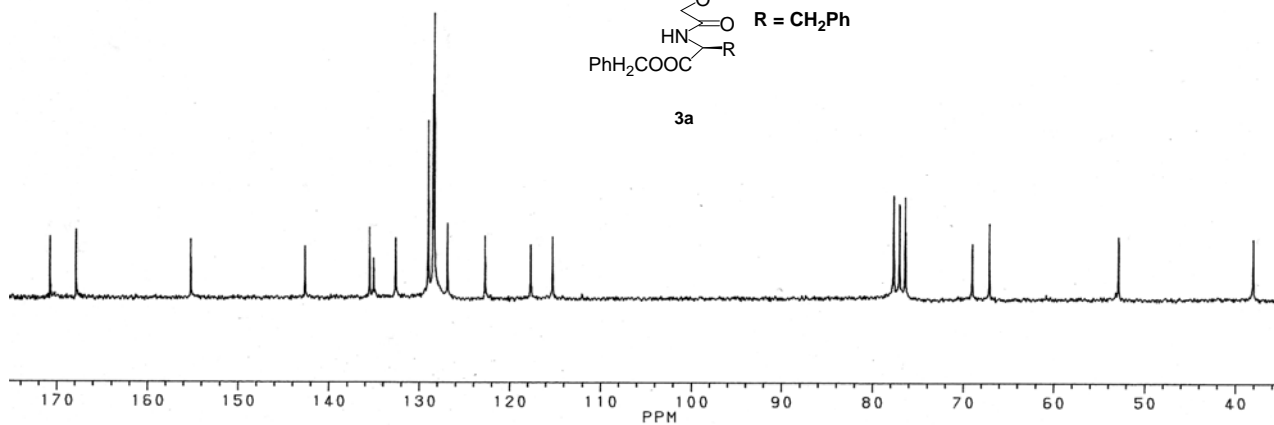
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52.829

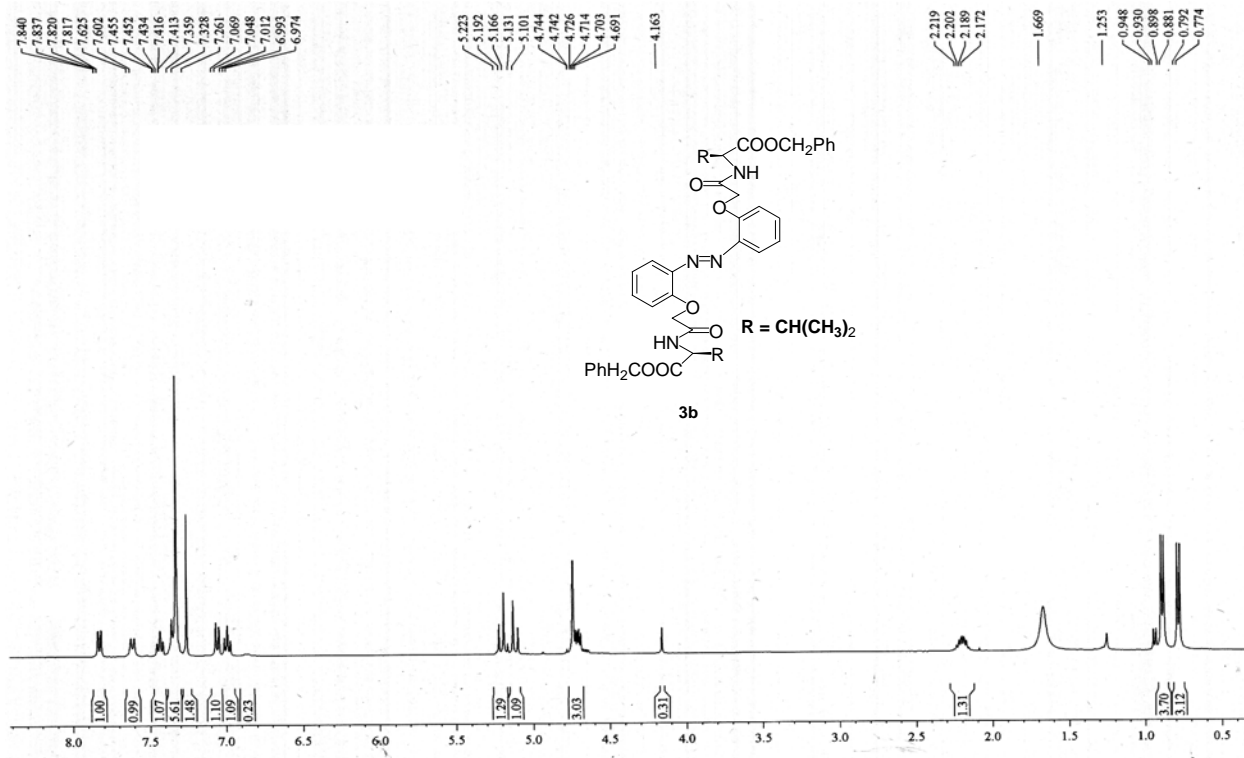
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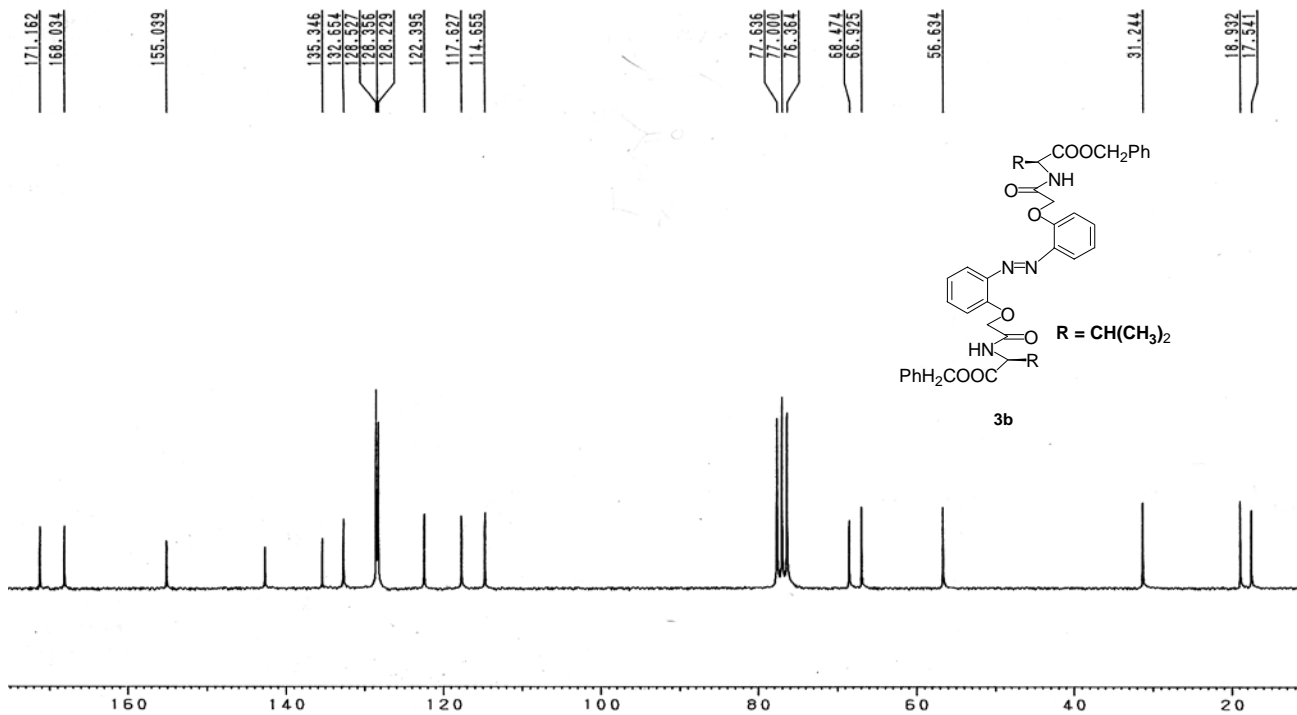
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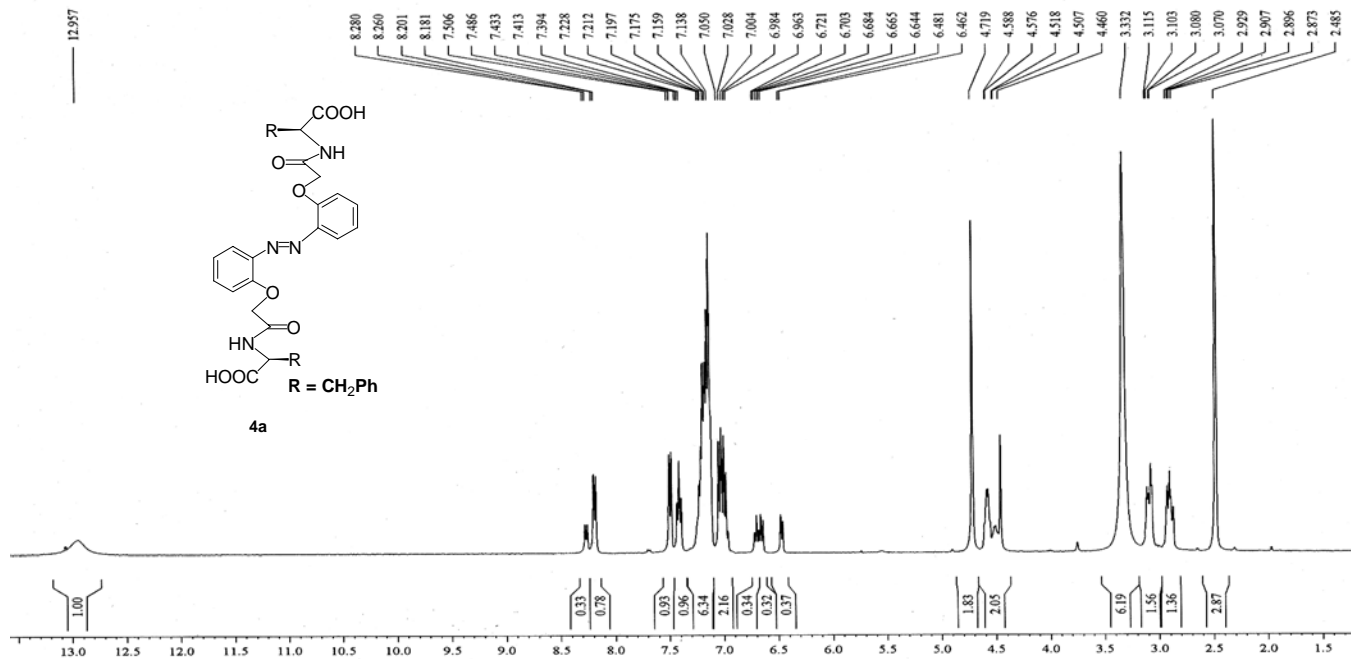
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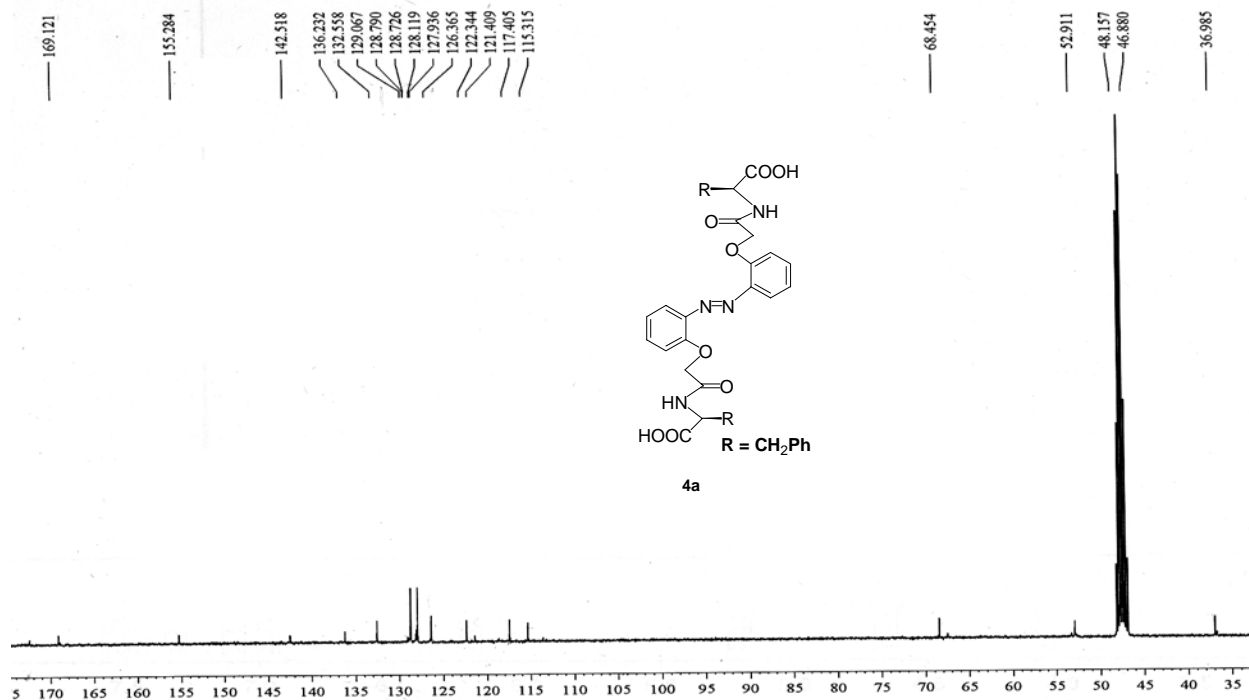
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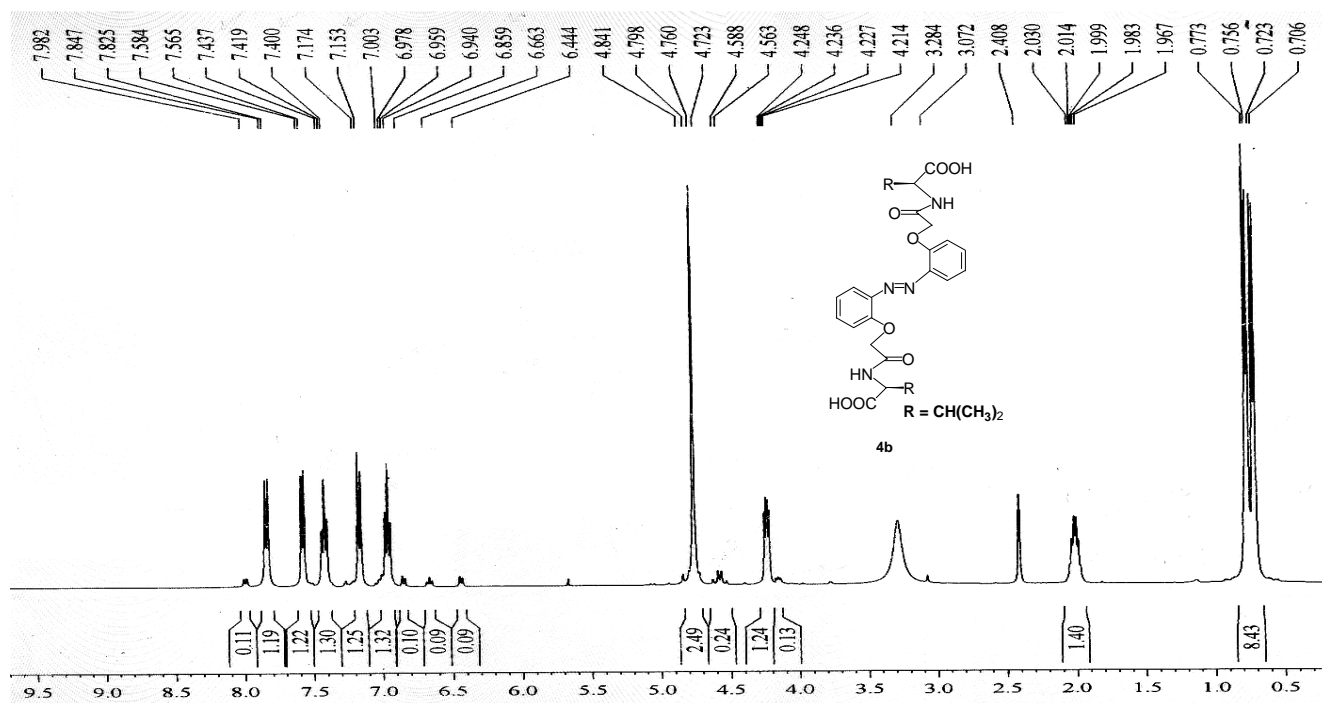
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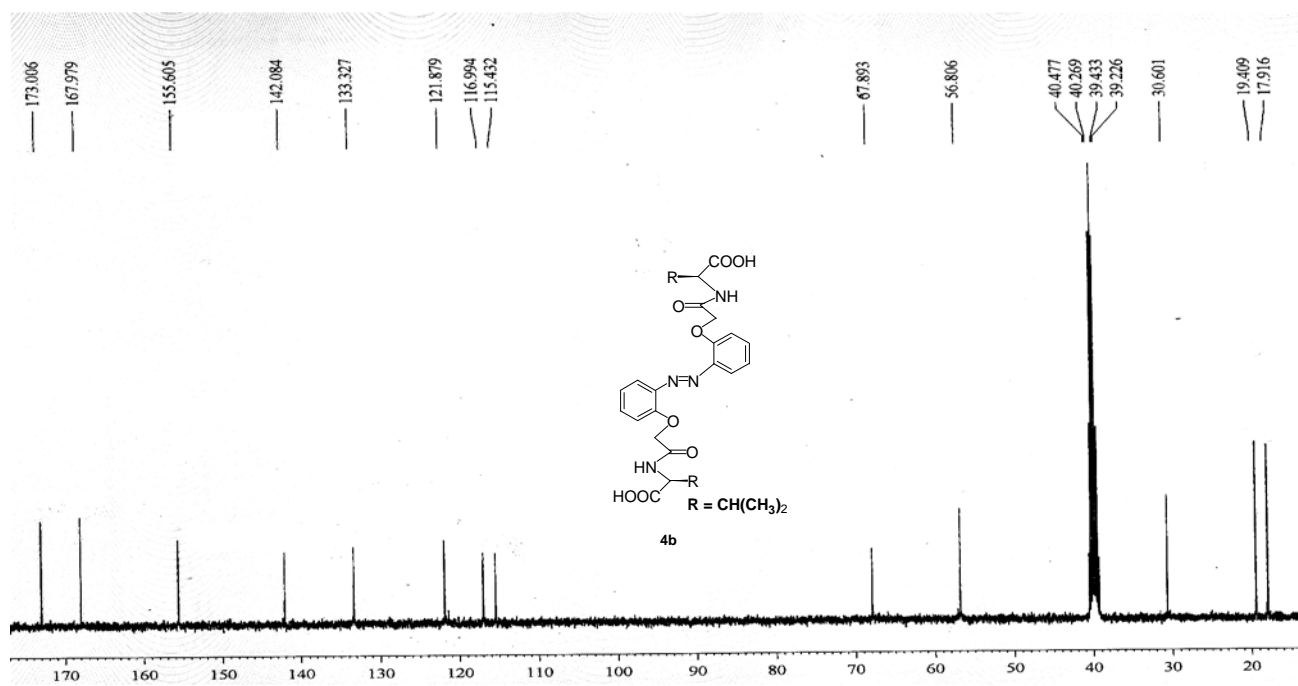
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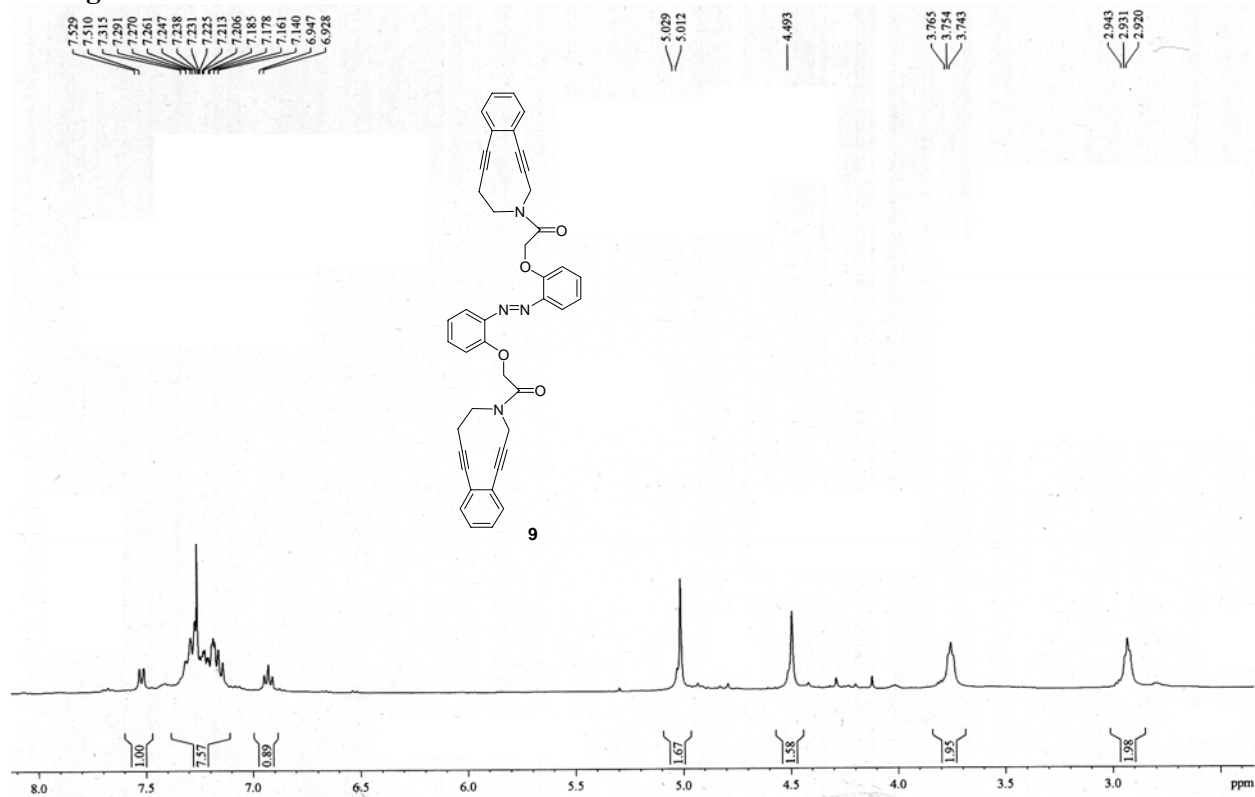
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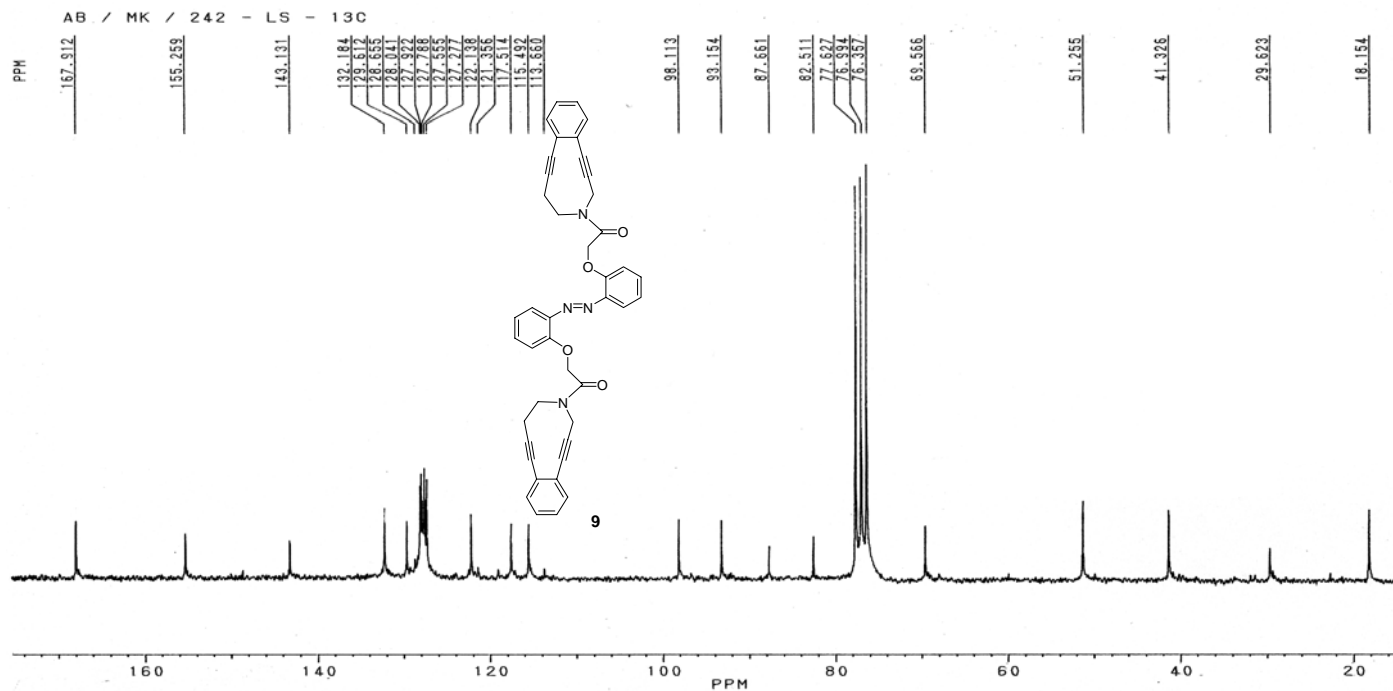
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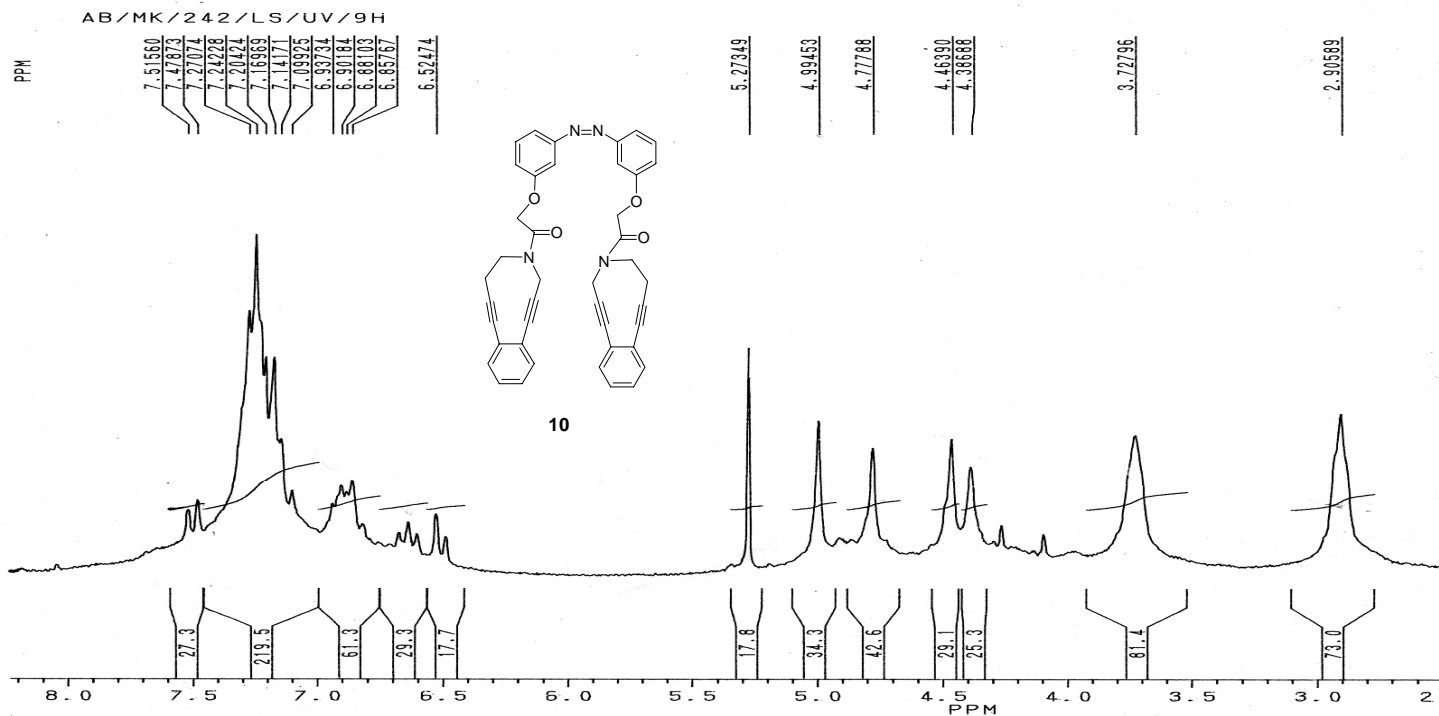
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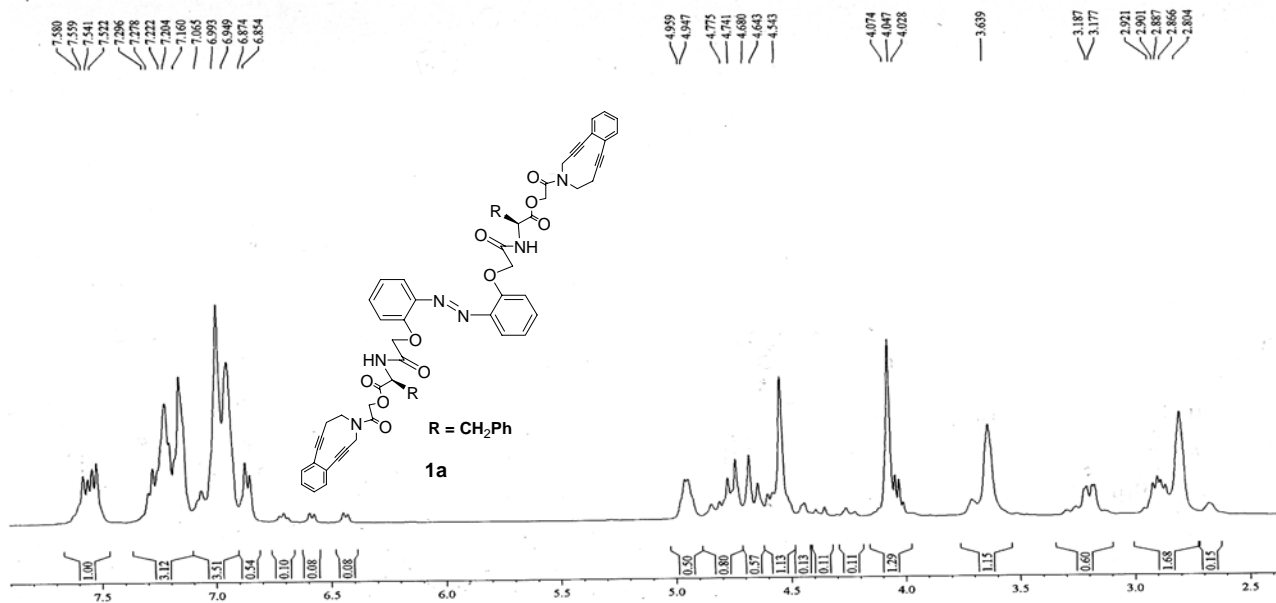
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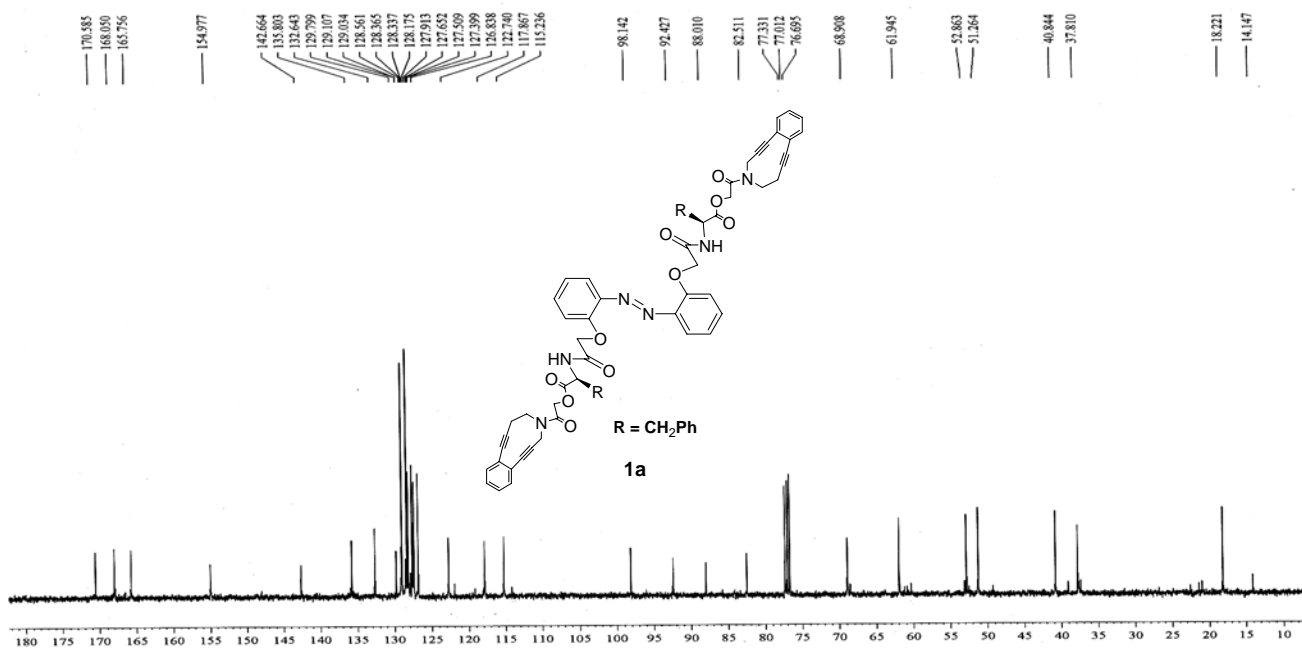
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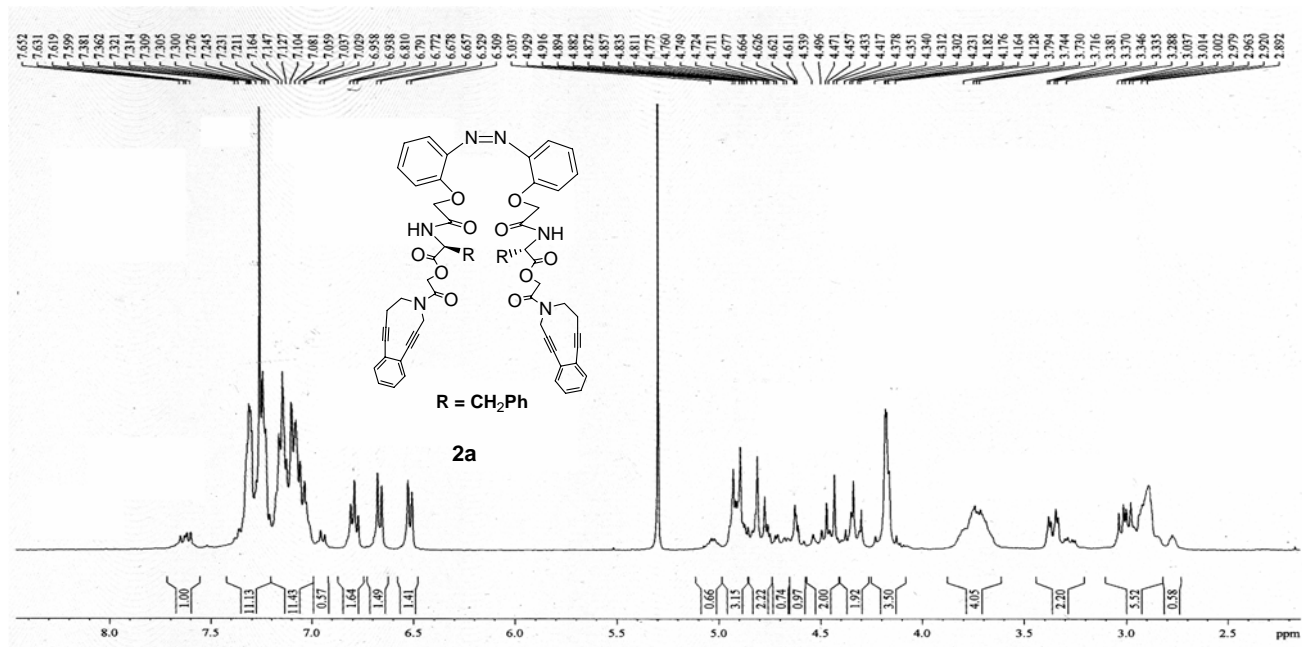
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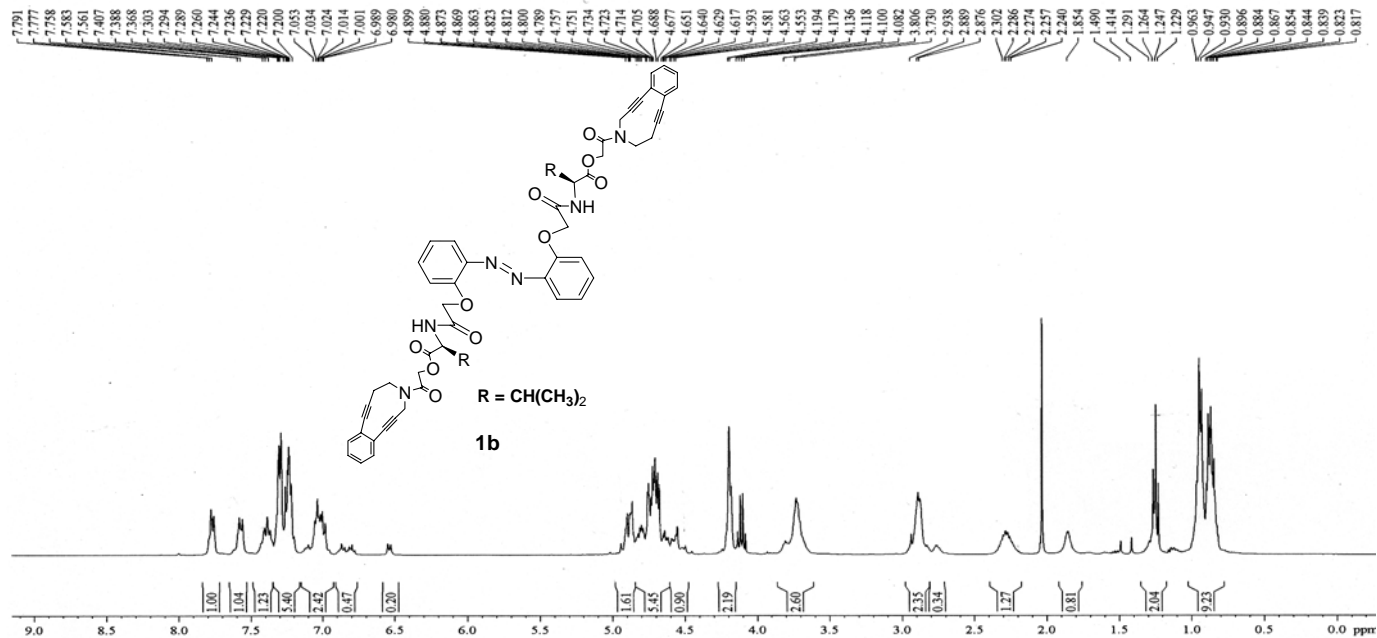
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Figures S18

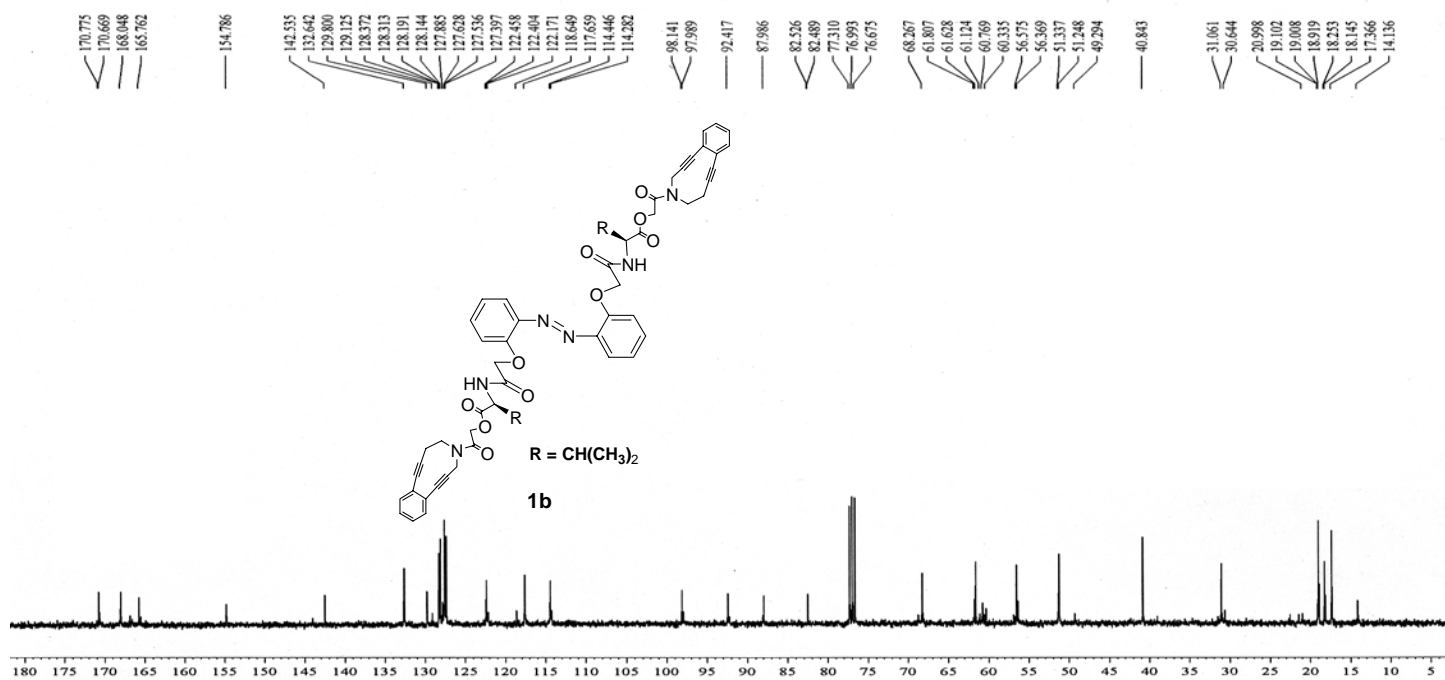


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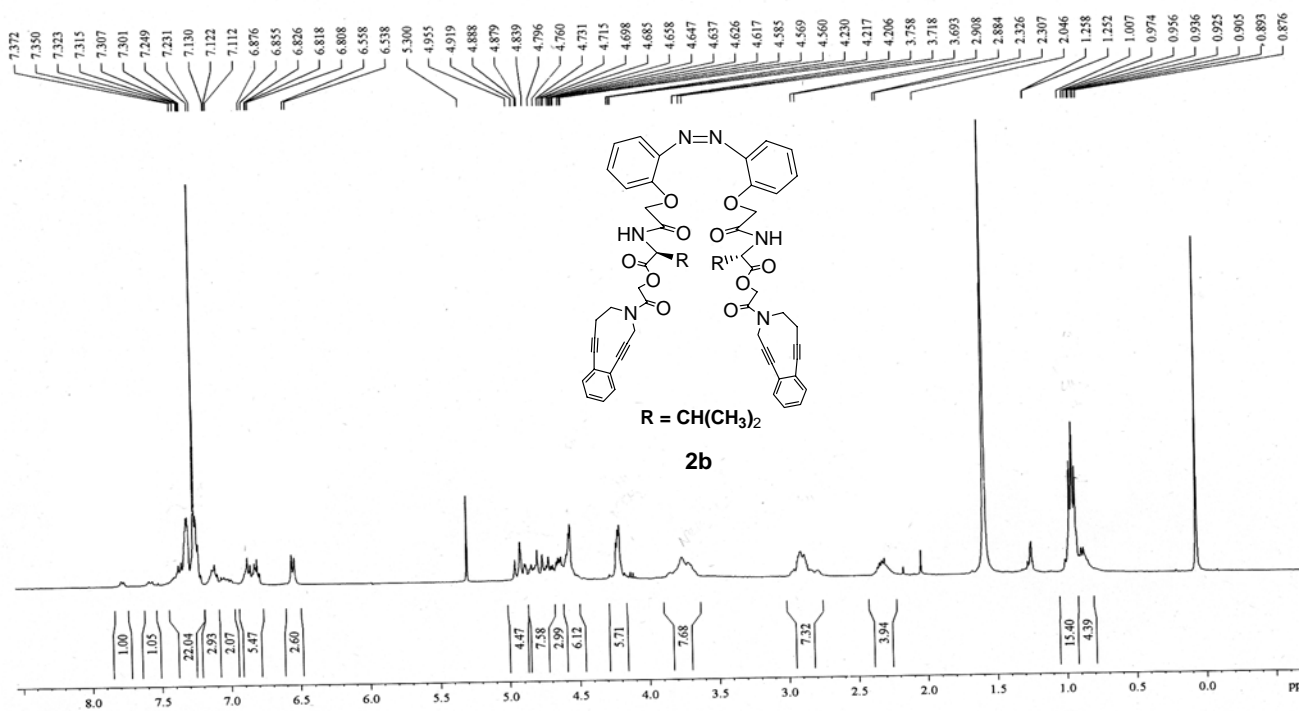


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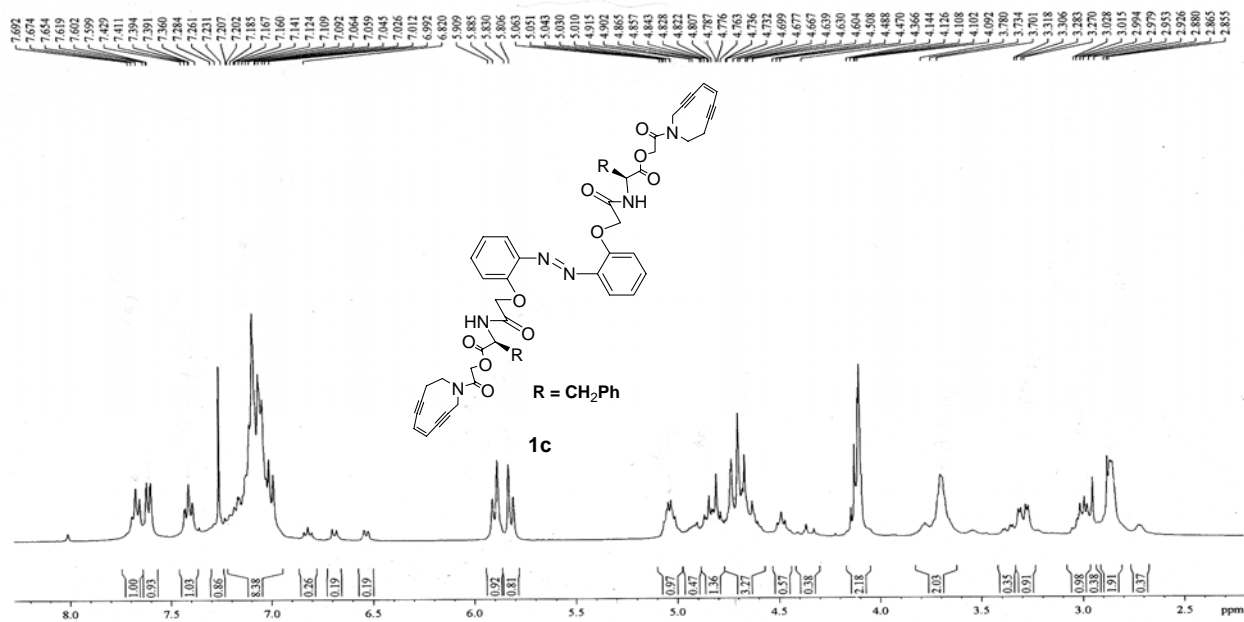
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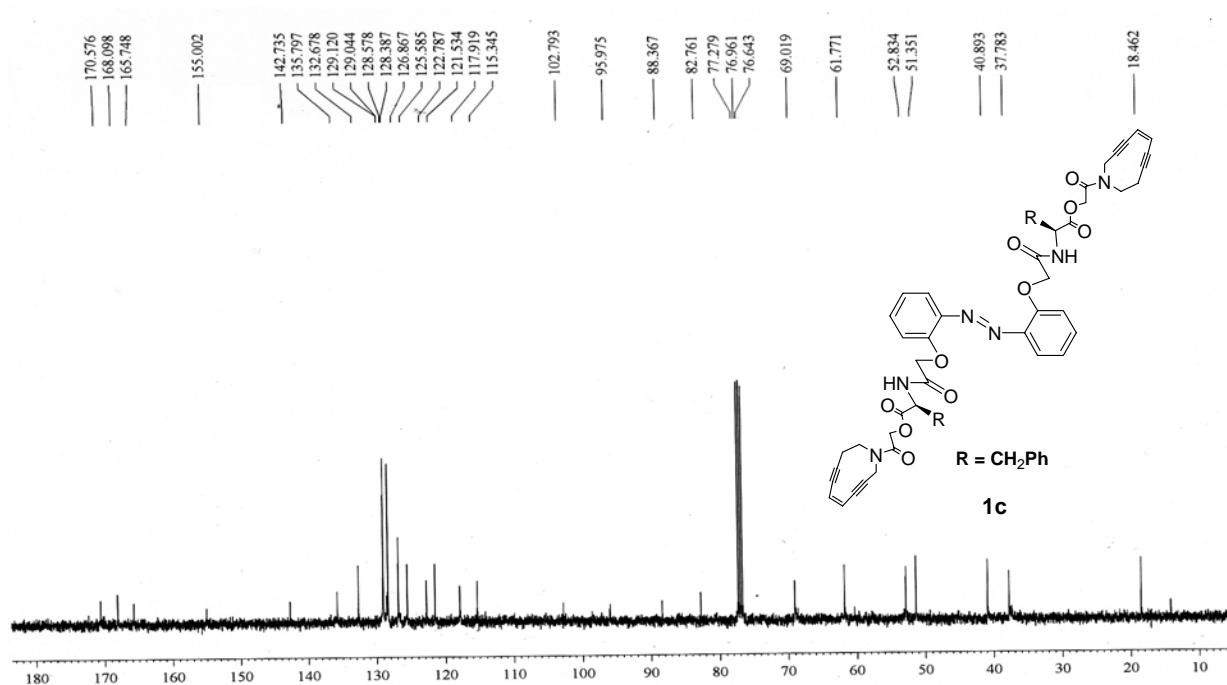
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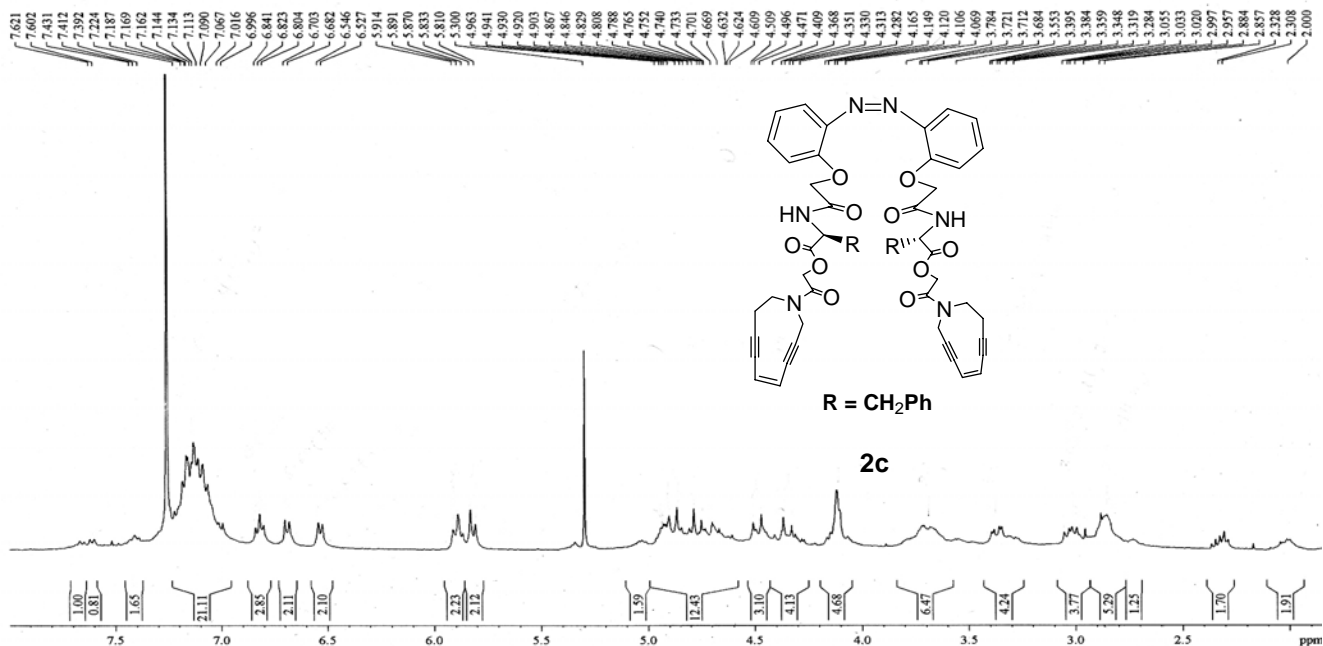
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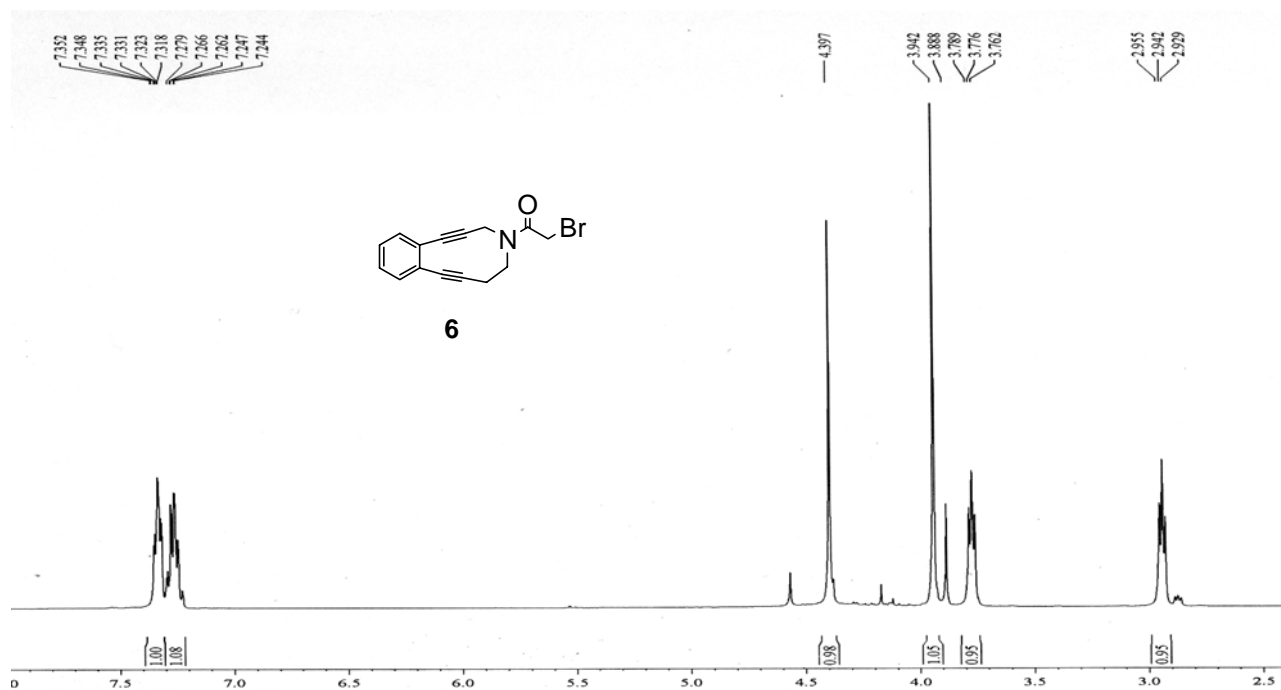
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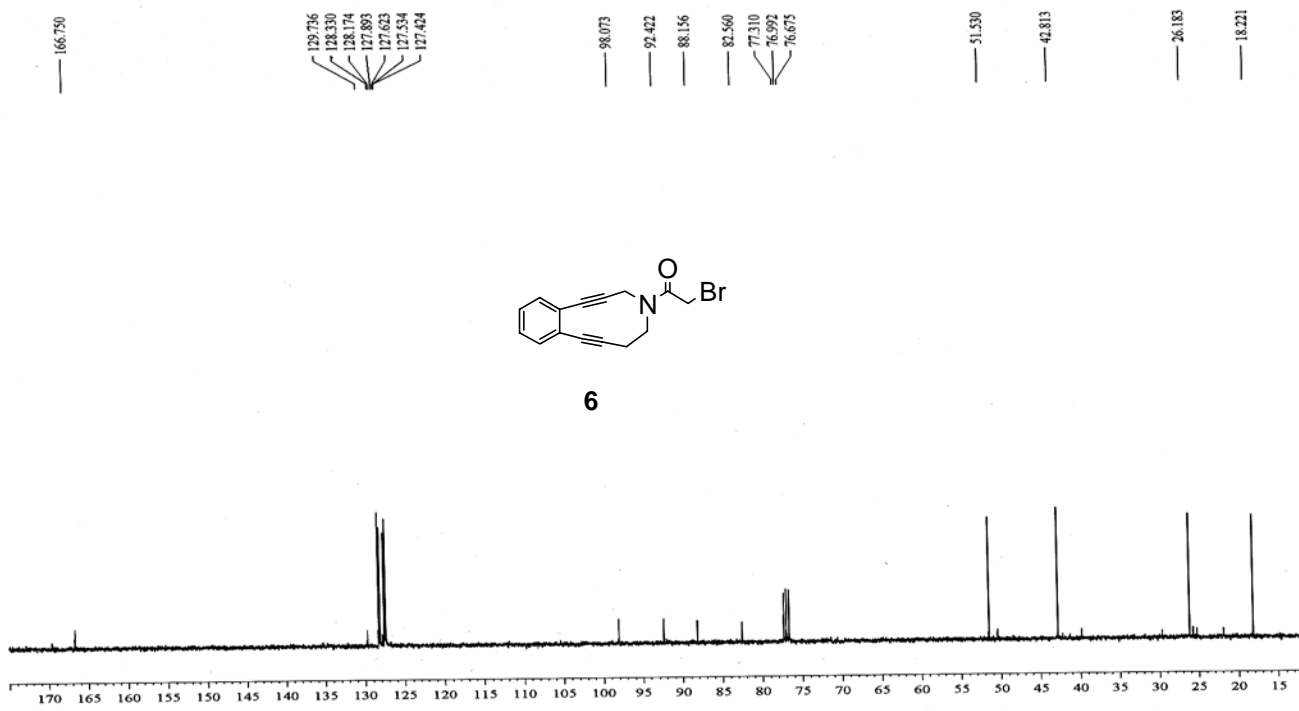
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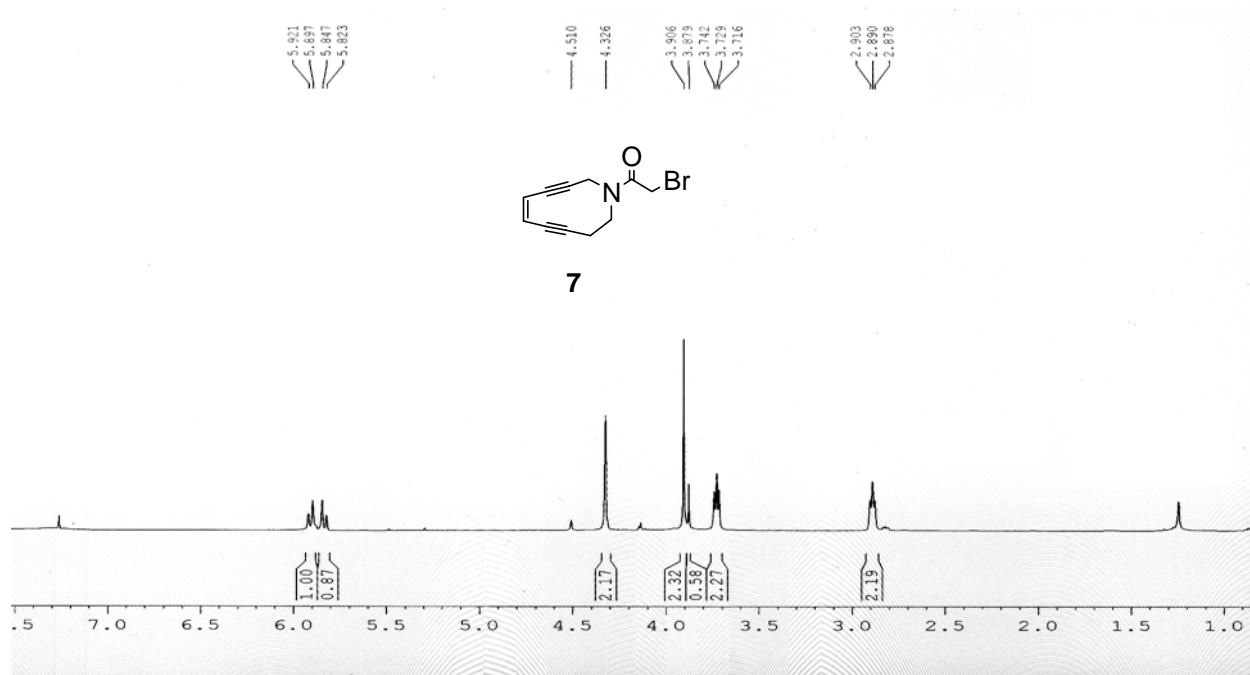
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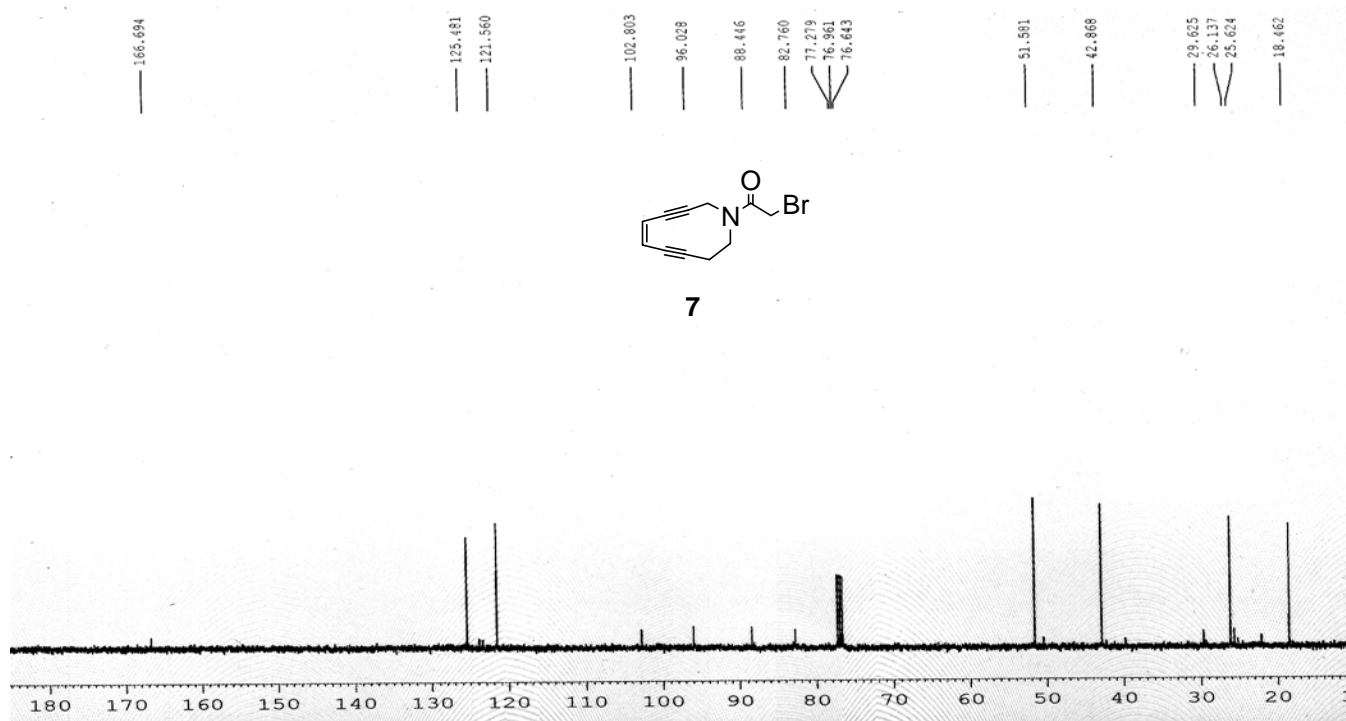
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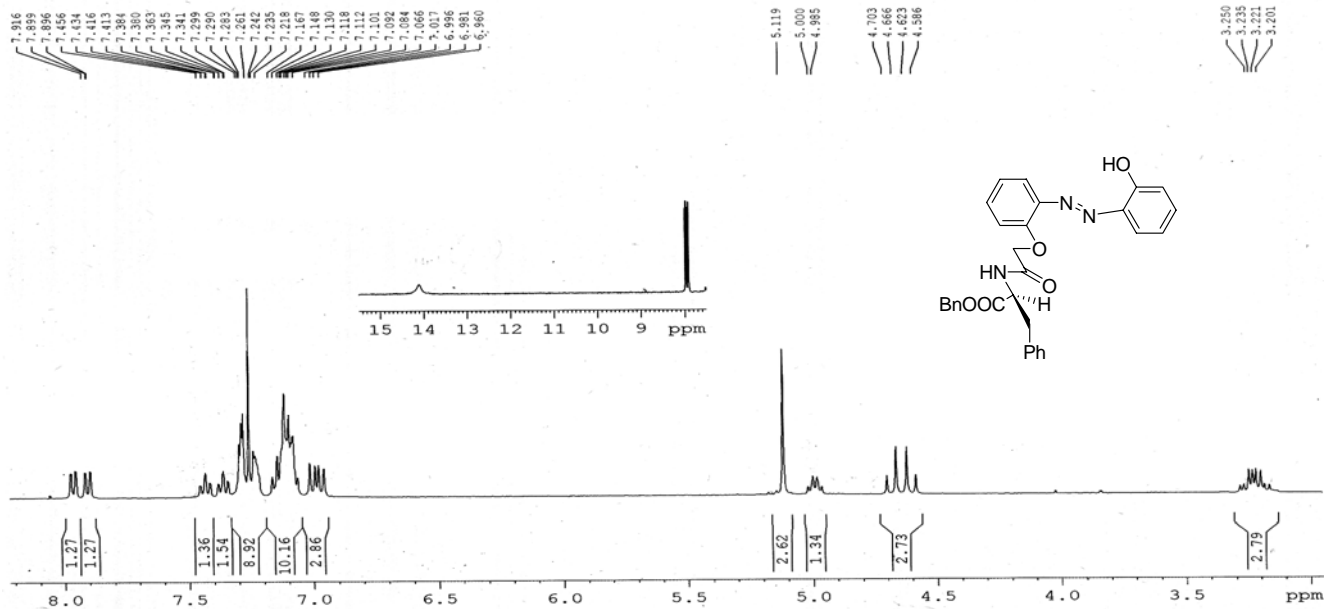
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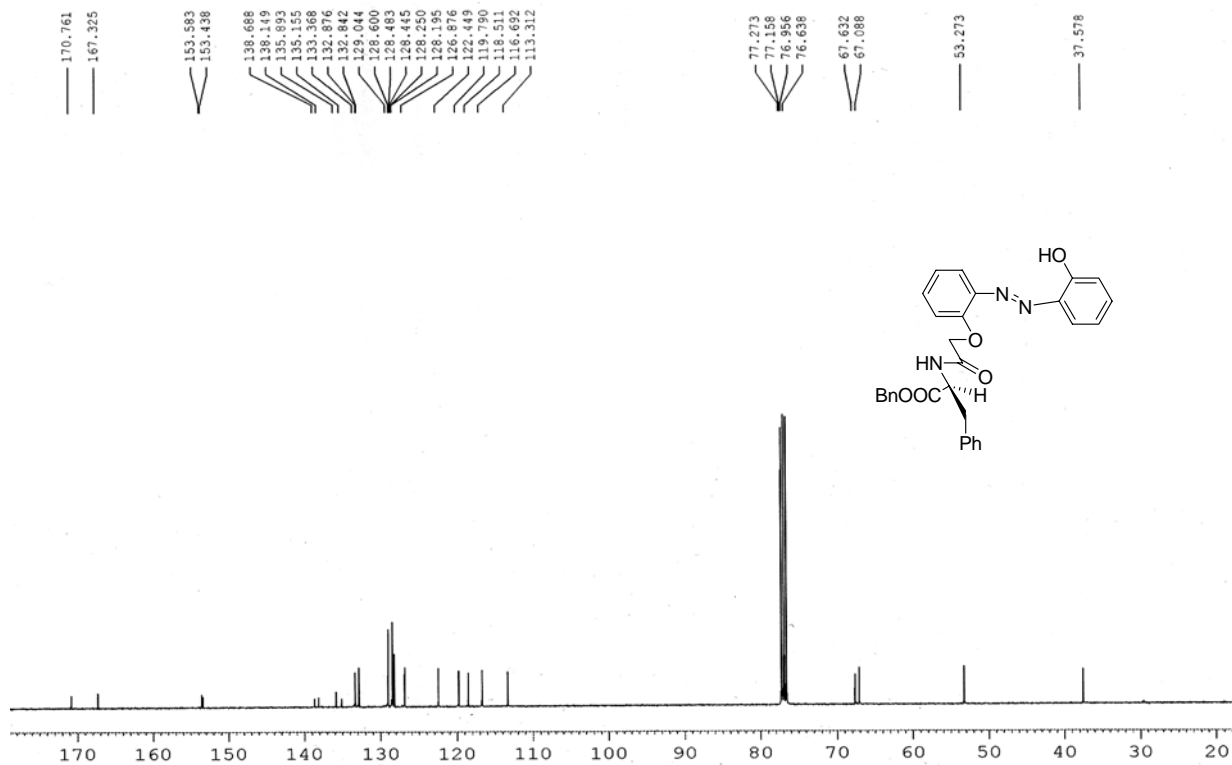
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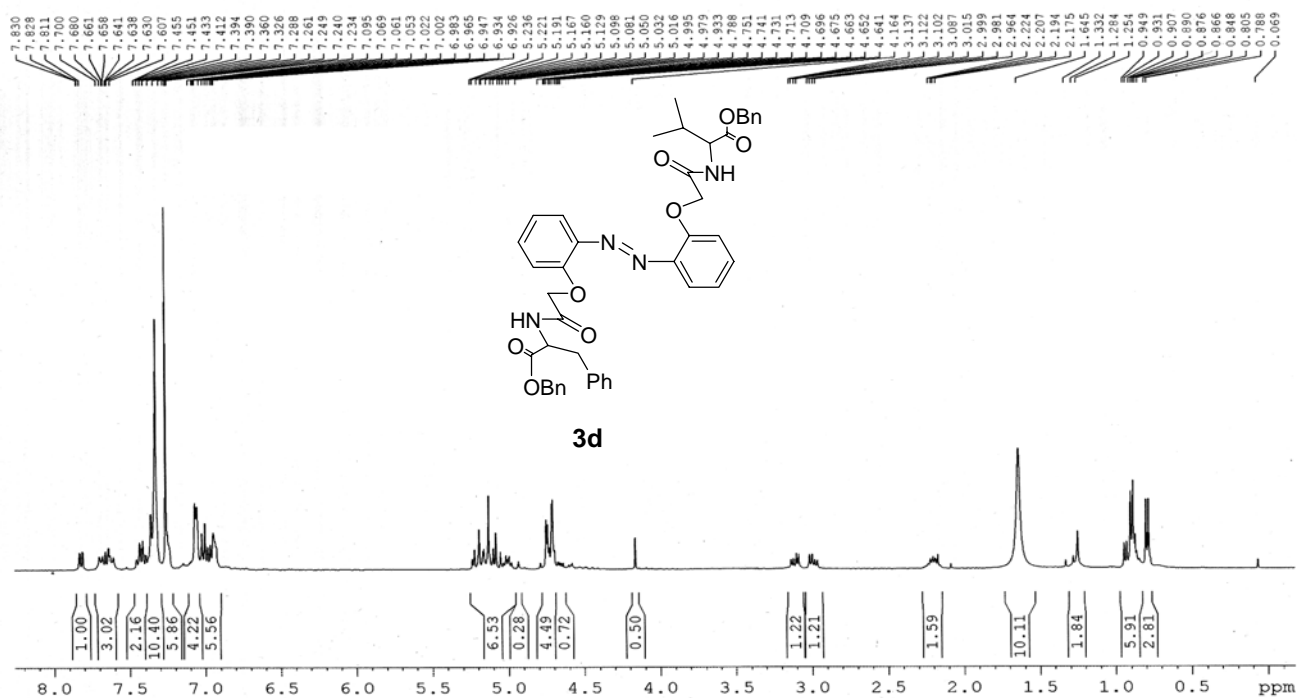
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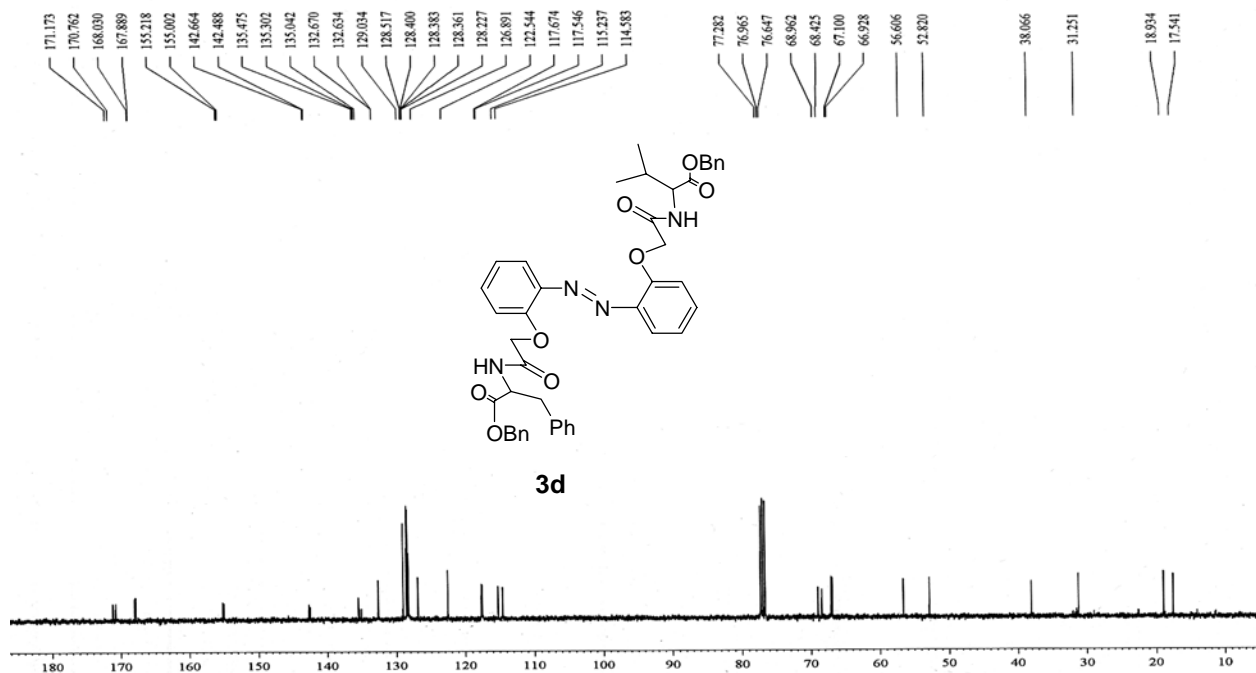
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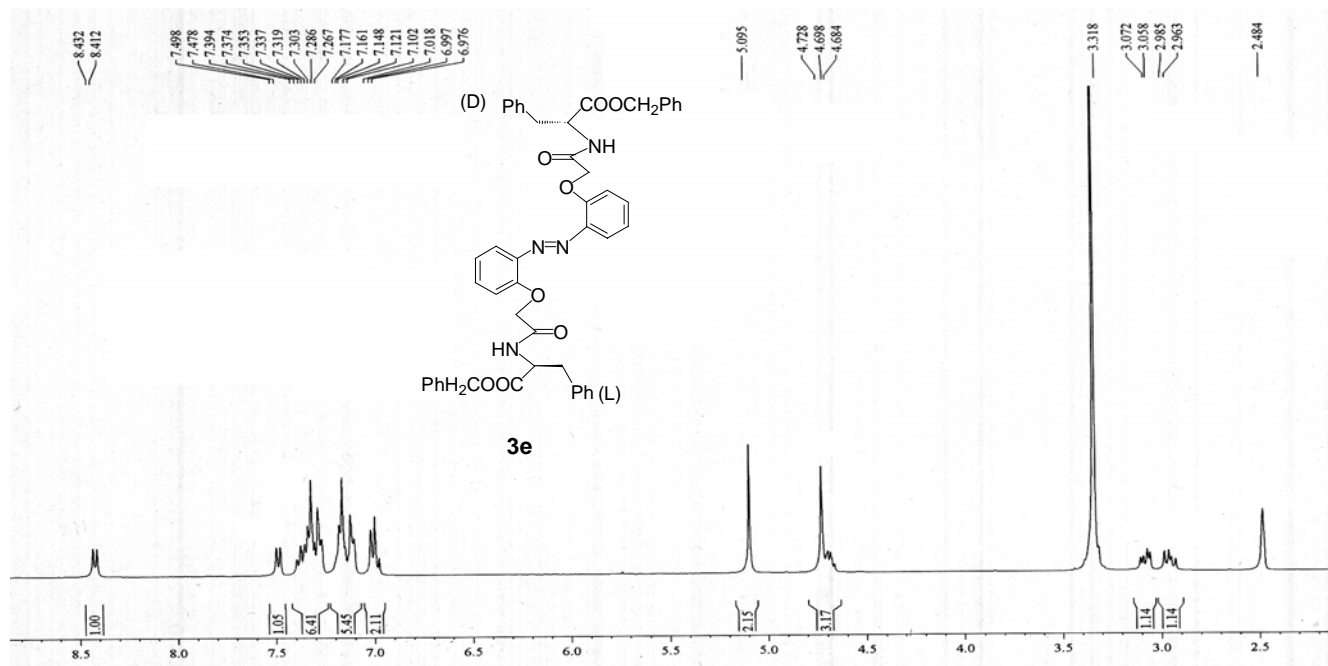
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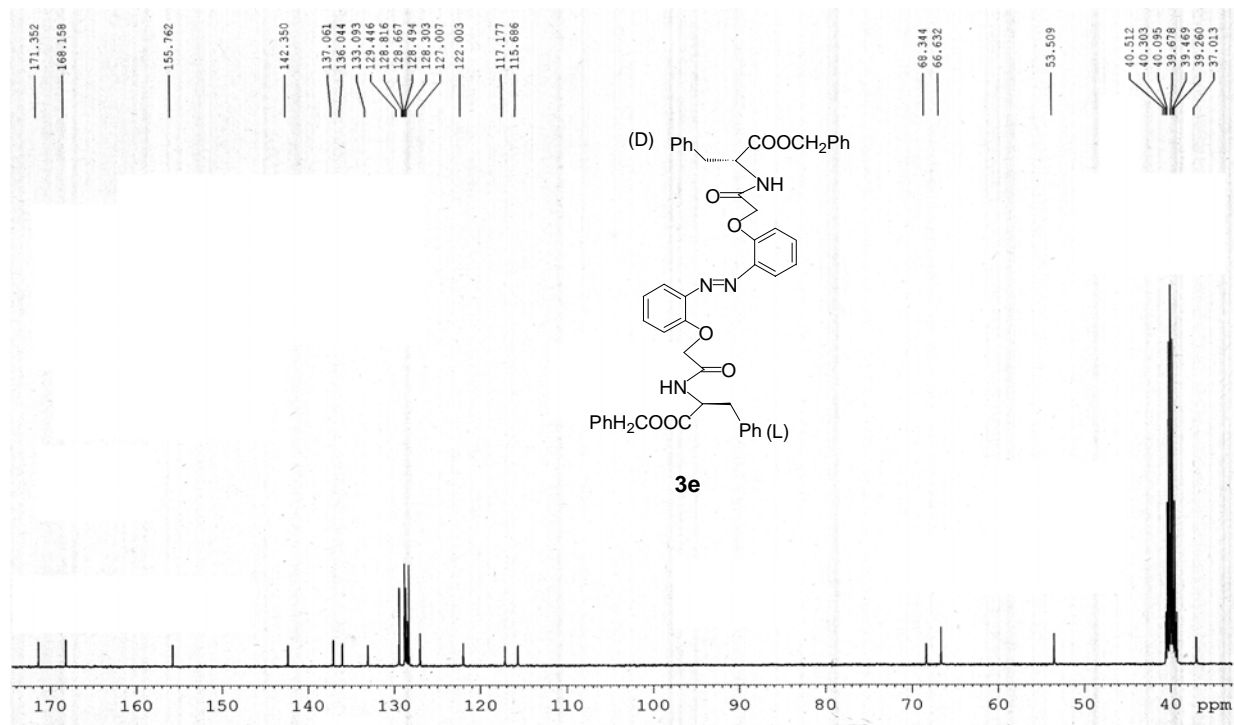
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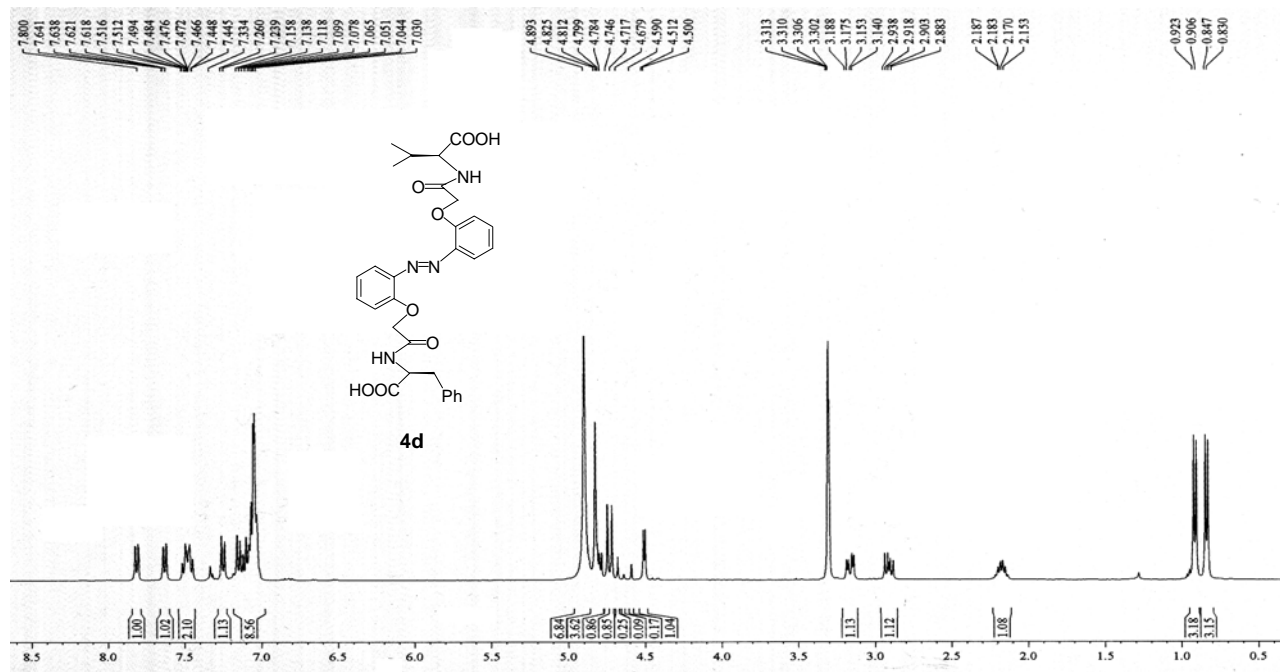
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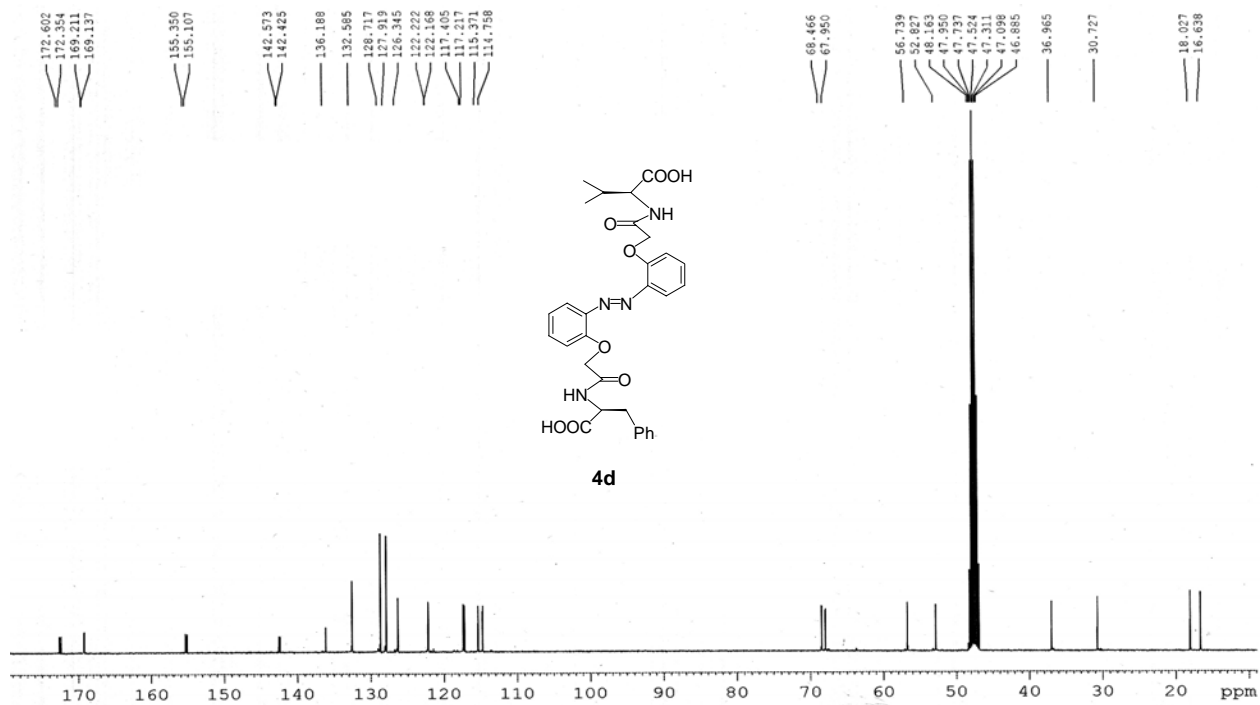
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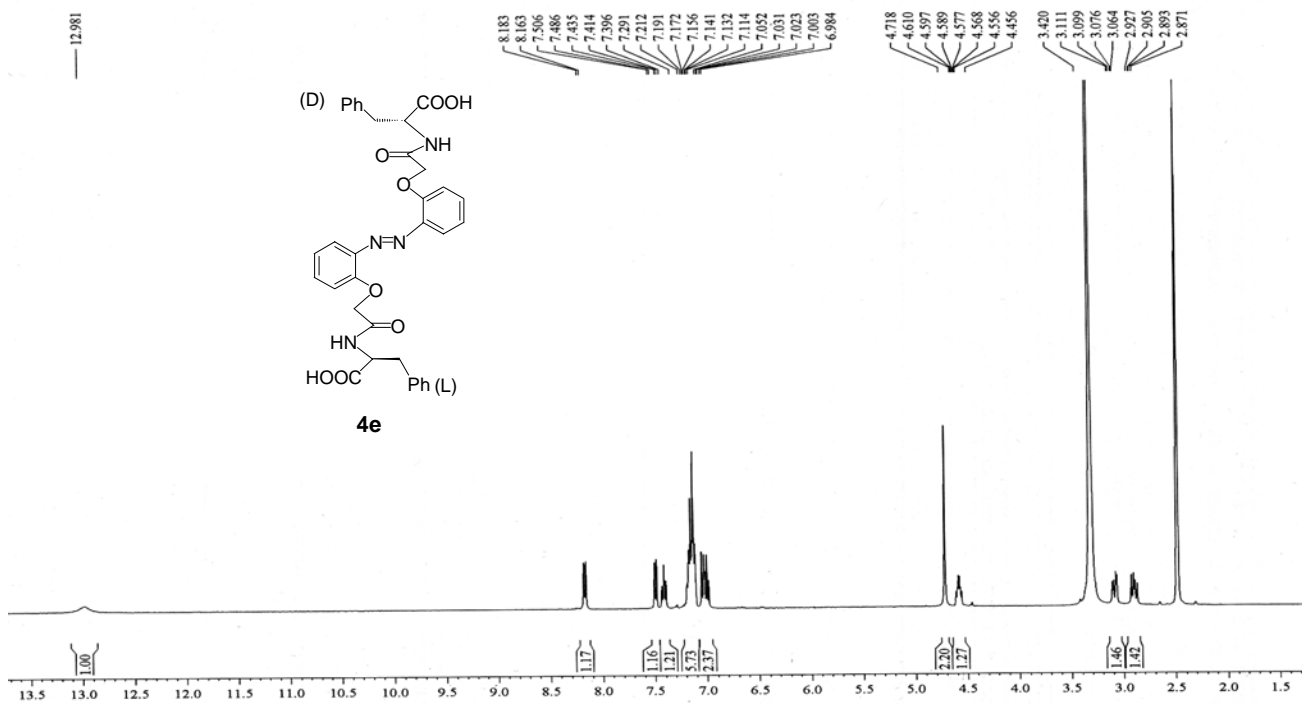
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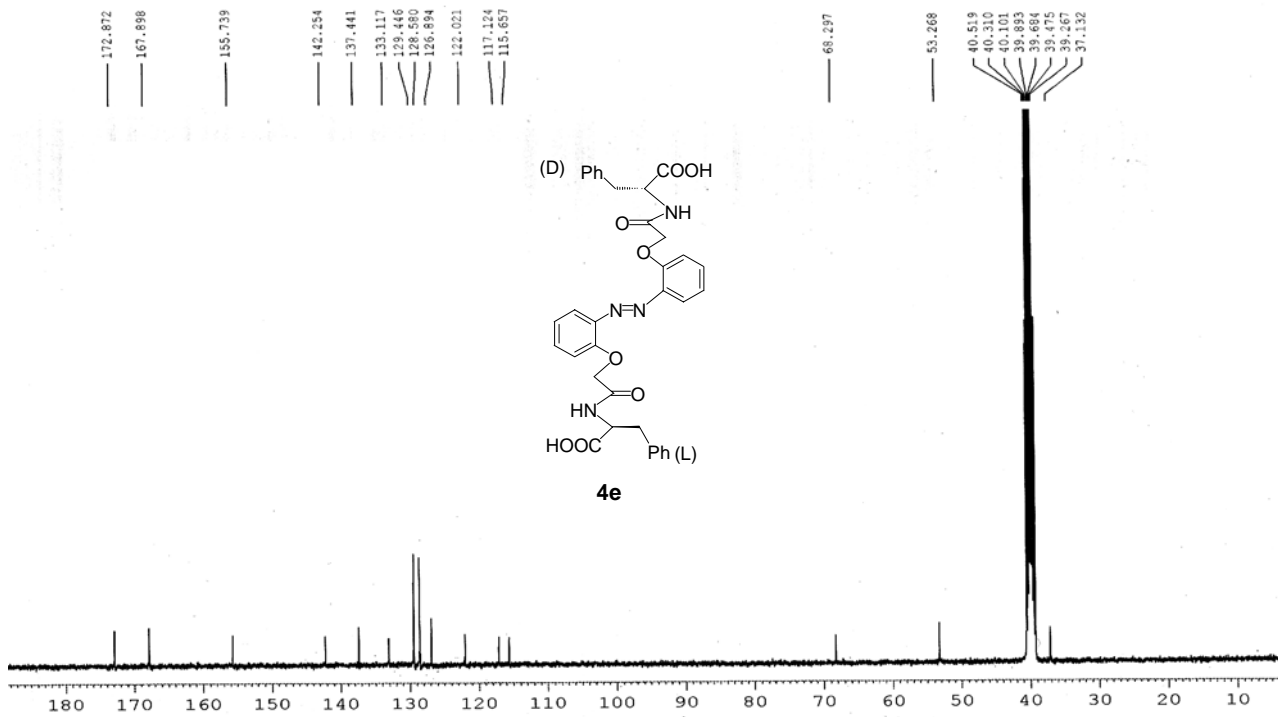
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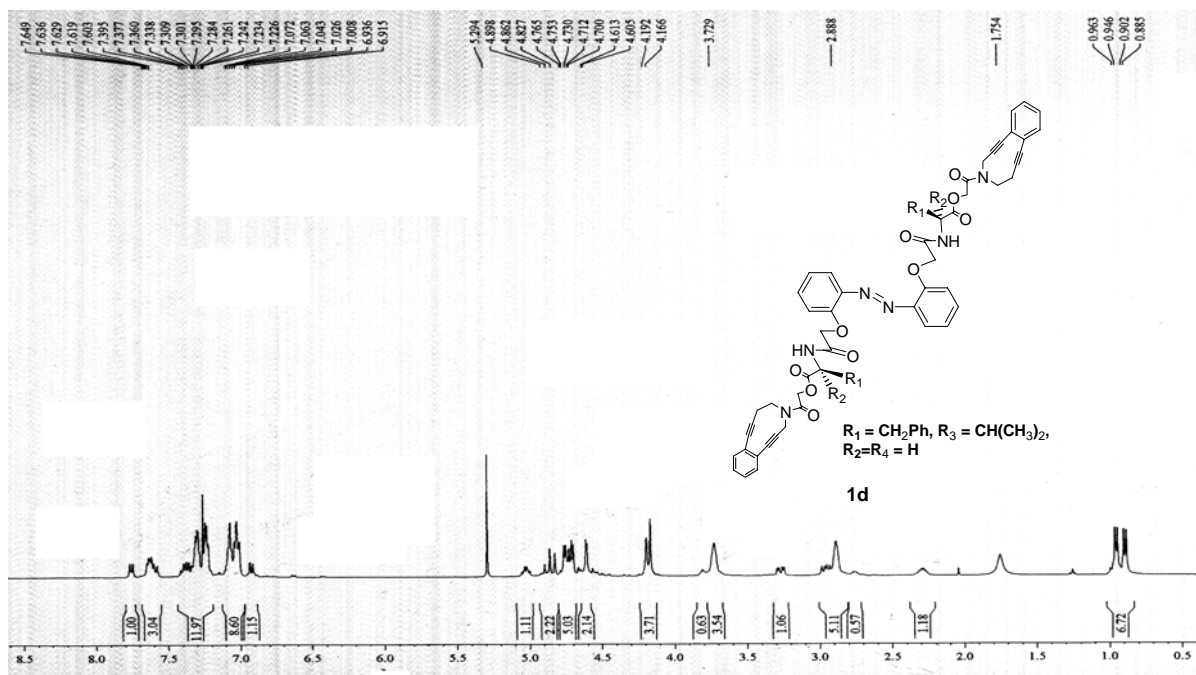
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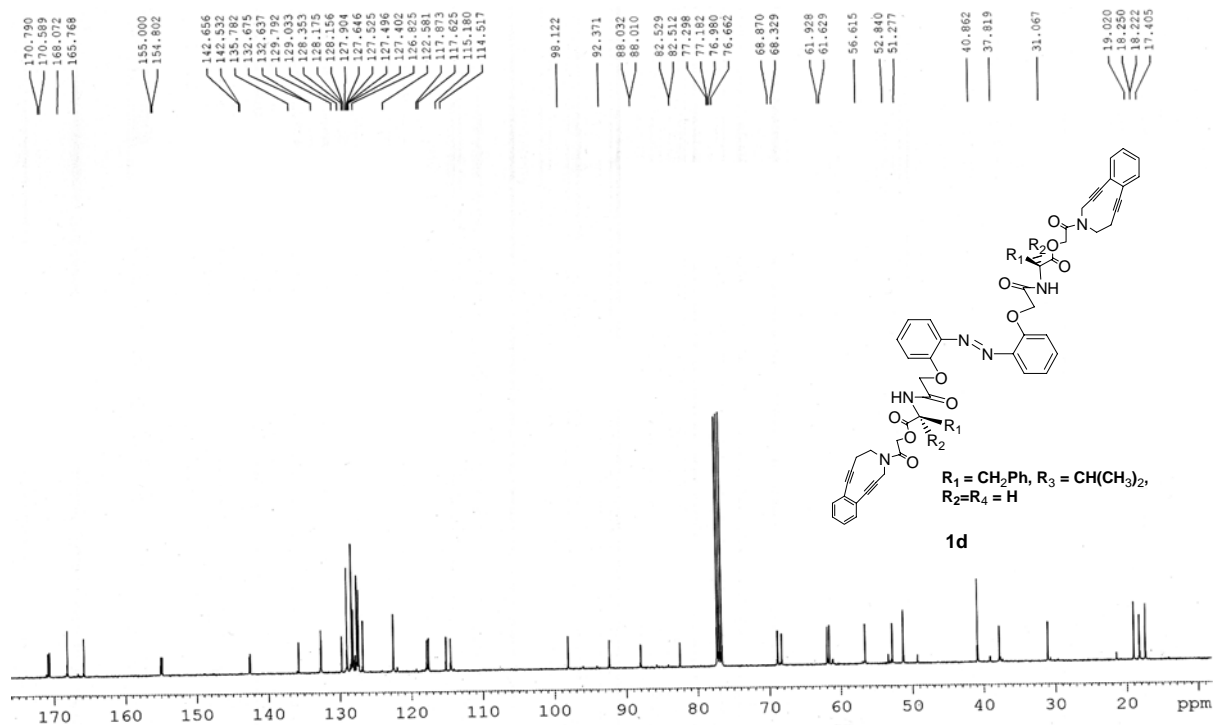
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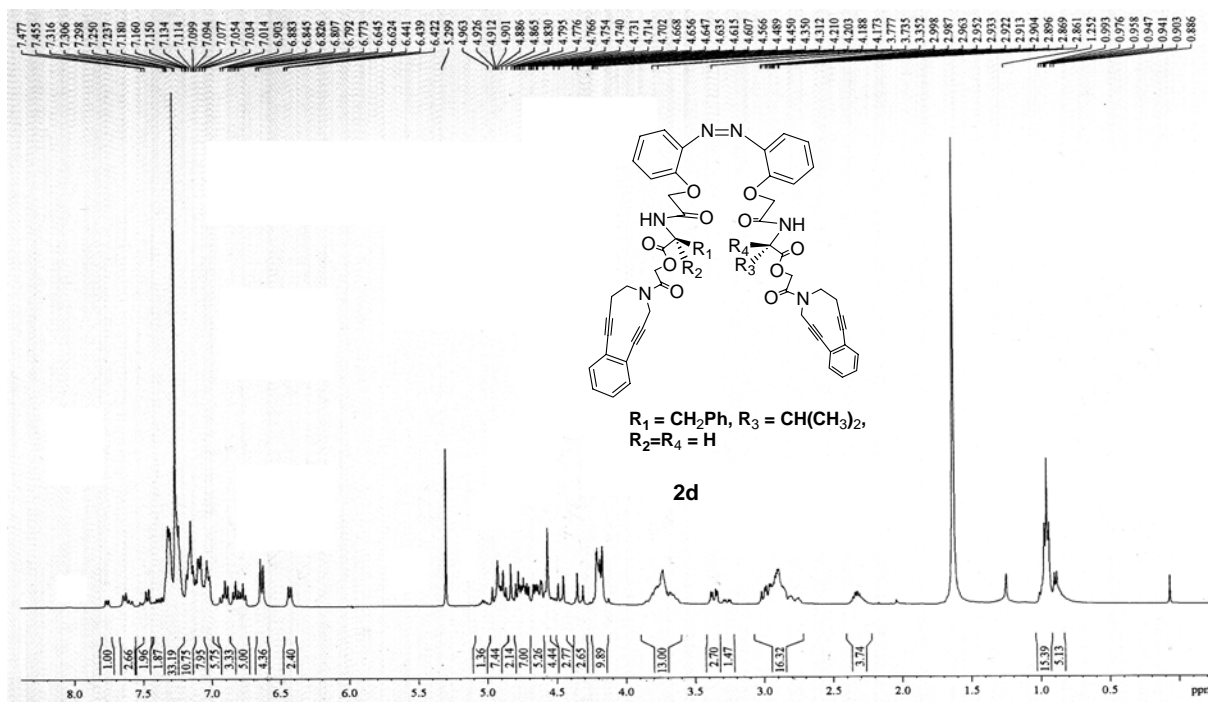
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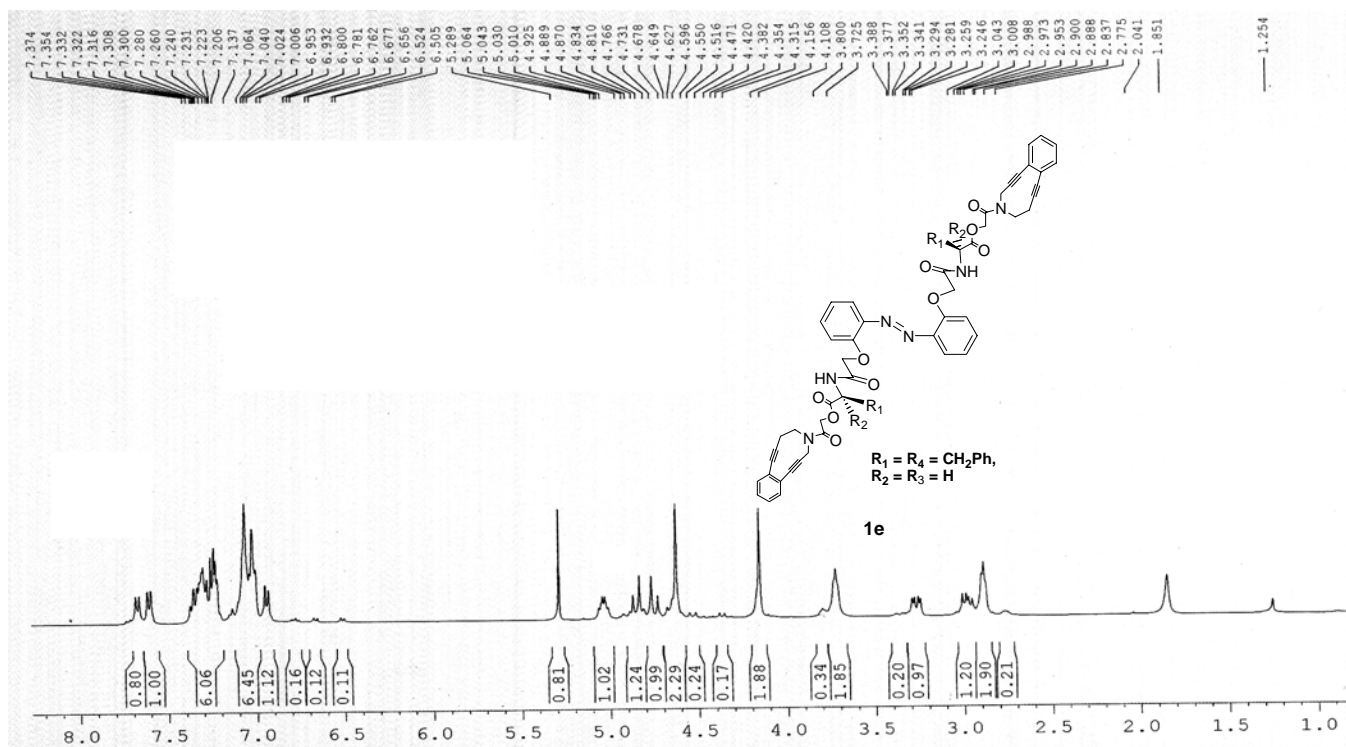
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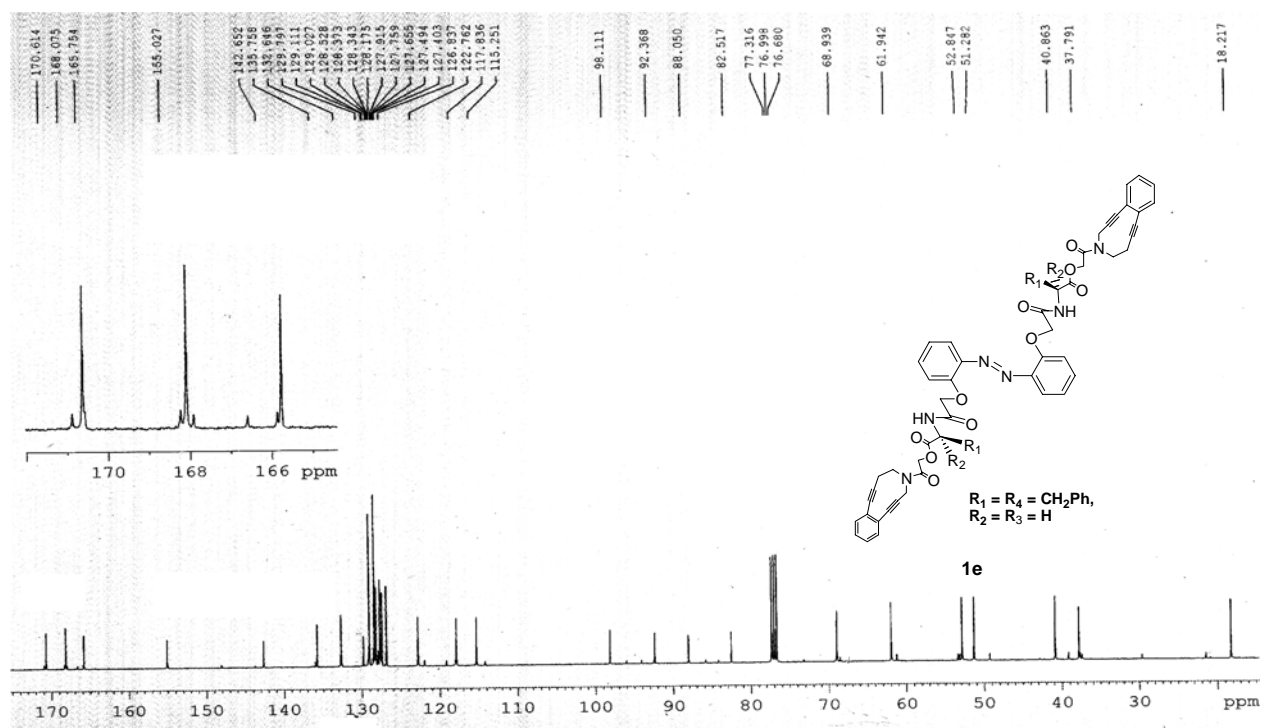
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Figures S42

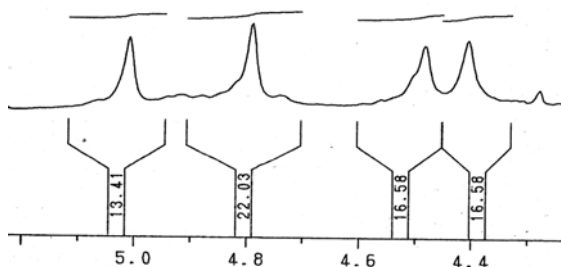


Figures S43



Thermal Isomerization Kinetics of 10 at 20 °C

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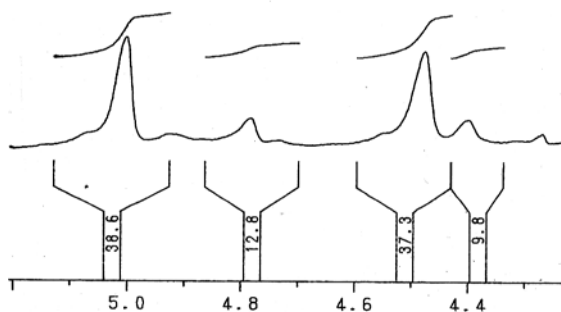
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T = 60 min



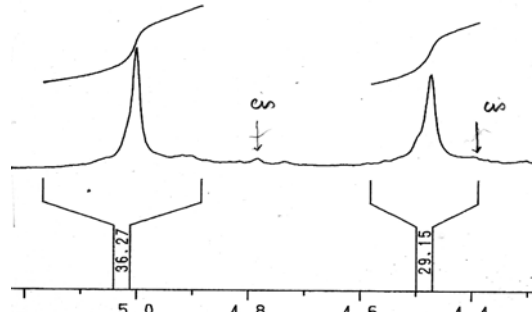
Figures S45

T = 180 min



Figures S46

T = 1800 min



Figures S47

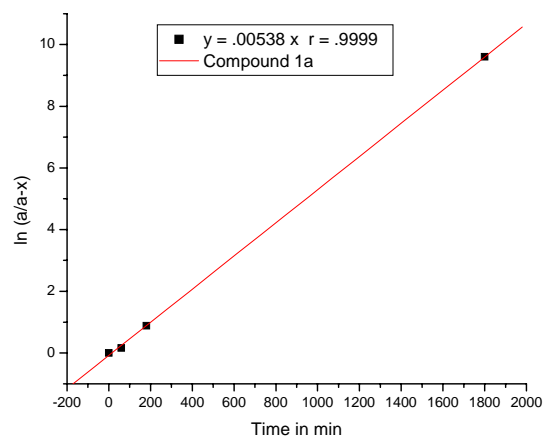
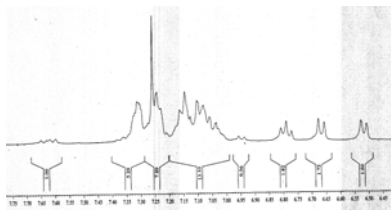


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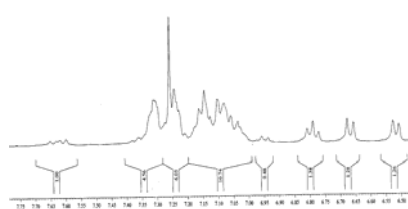
Thermal Isomerization Kinetics of 2a at 20 °C

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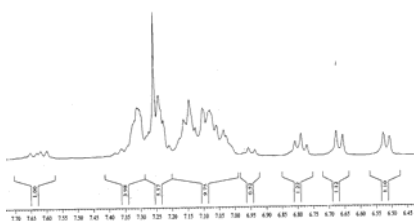
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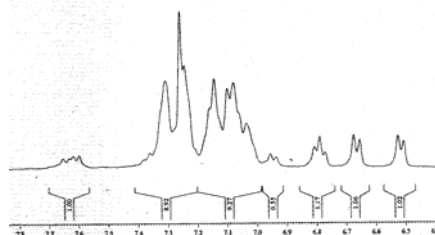
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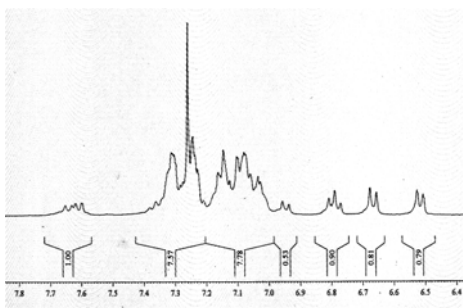
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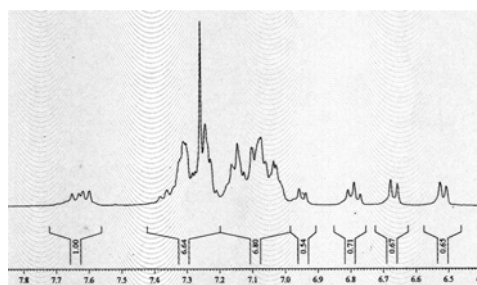
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Figures S52

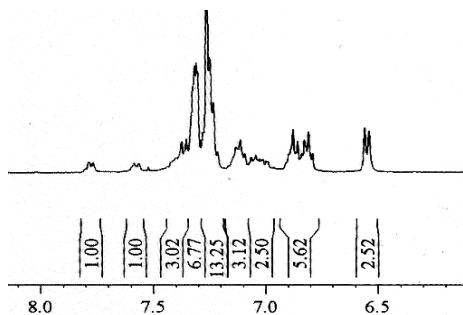
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Figures S53

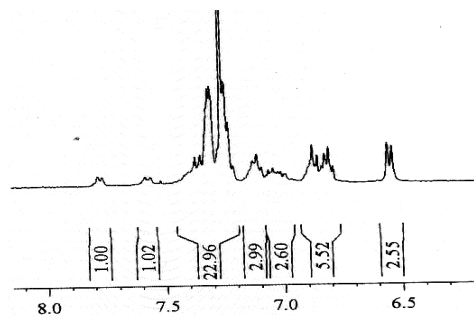
Thermal Isomerization Kinetics of 2b at 20 °C

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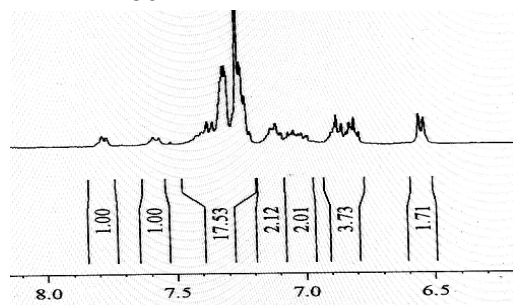
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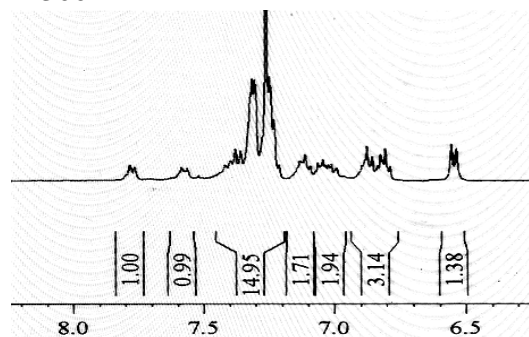
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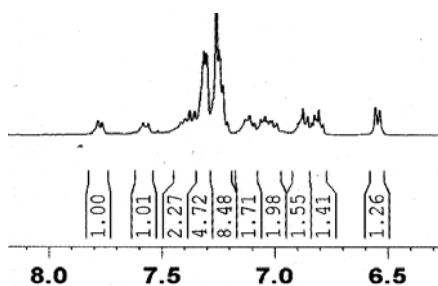
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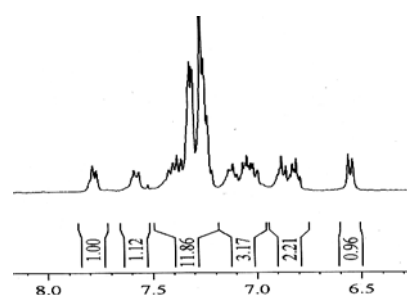
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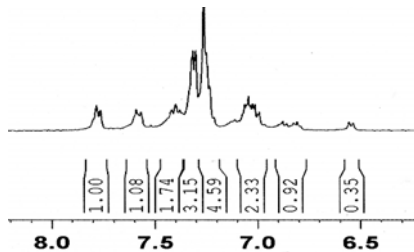
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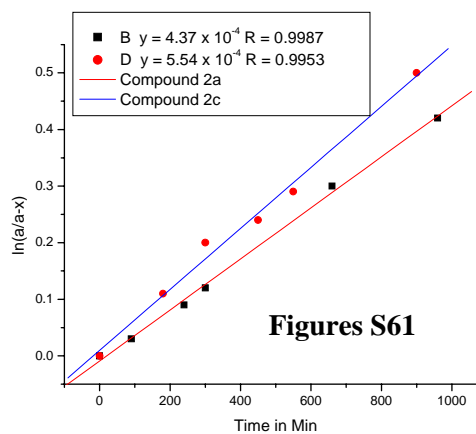


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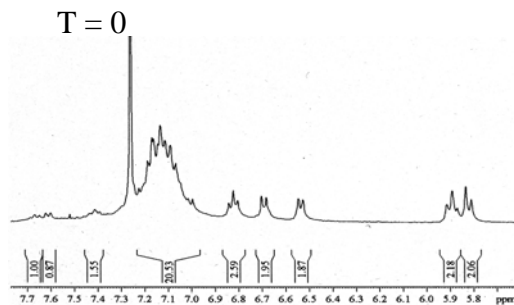


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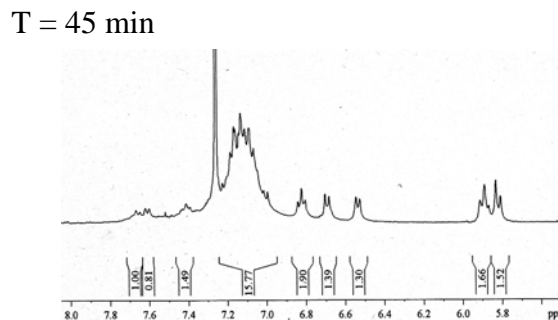


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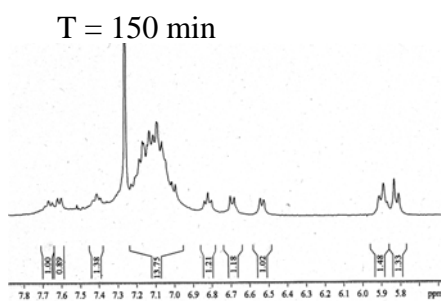
Thermal Isomerization Kinetics of 2c at 20 °C



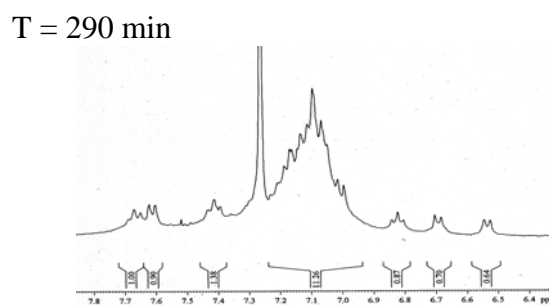
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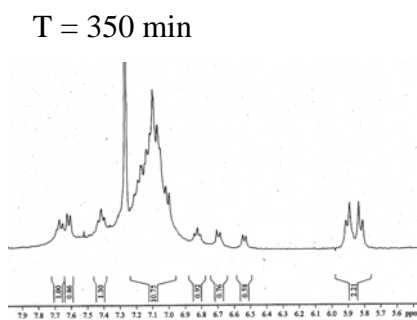
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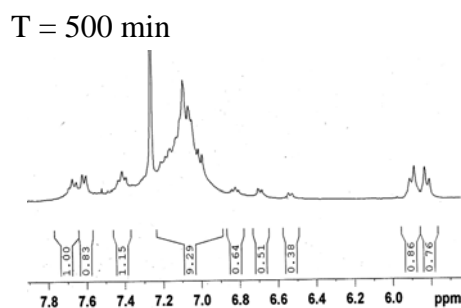
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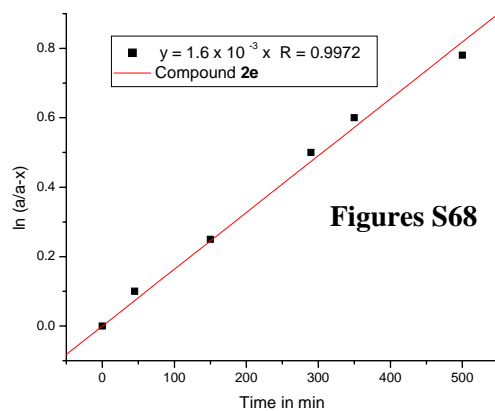
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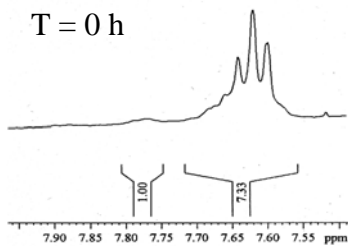
Figures S66



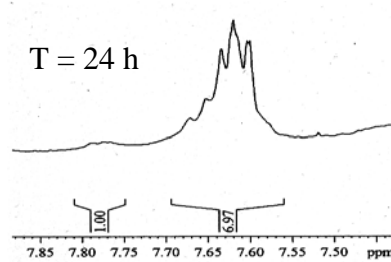
Figures S67



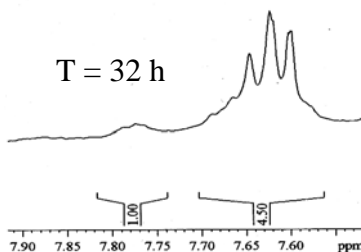
Bergman Cyclization Kinetics of 1a at 45 °C



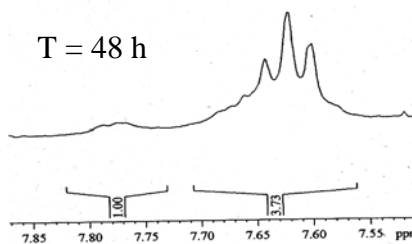
Figures S69



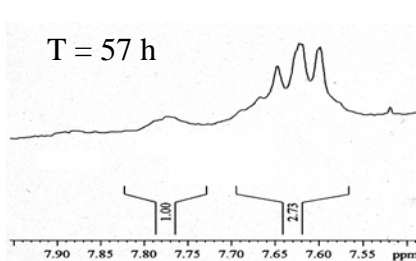
Figures S70



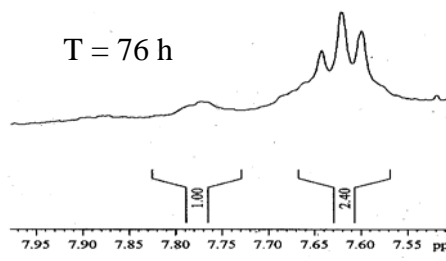
Figures S71



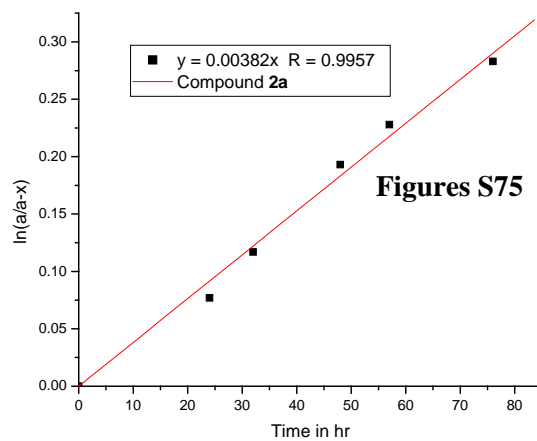
Figures S72



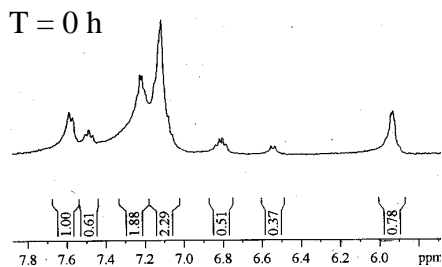
Figures S73



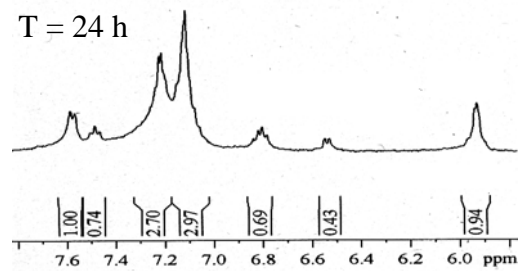
Figures S74



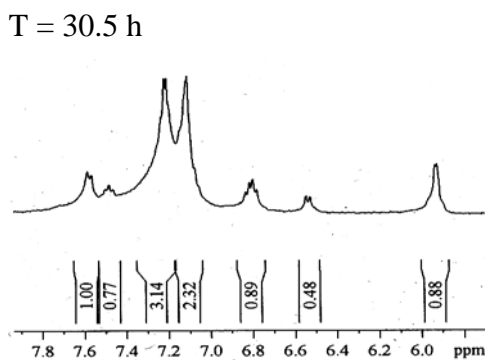
Bergman Cyclization Kinetics of aliphatic 1c at 30 °C



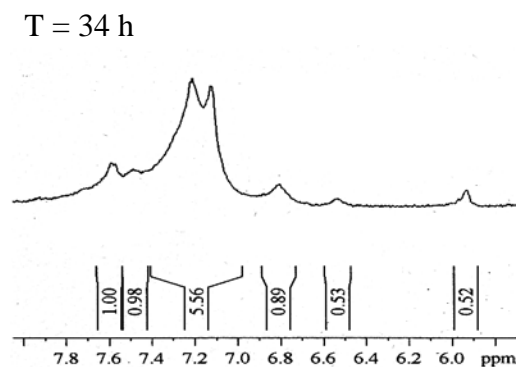
Figures S76



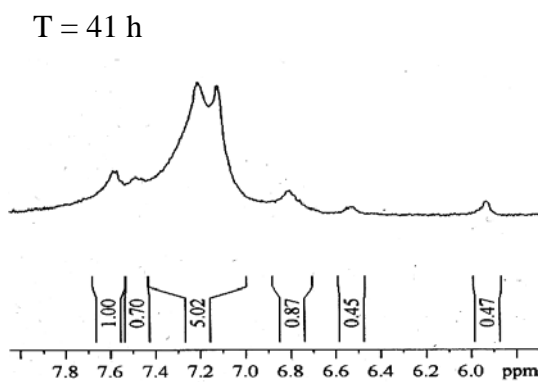
Figures S77



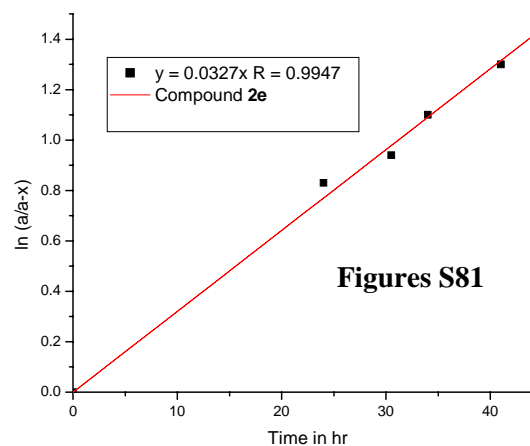
Figures S78



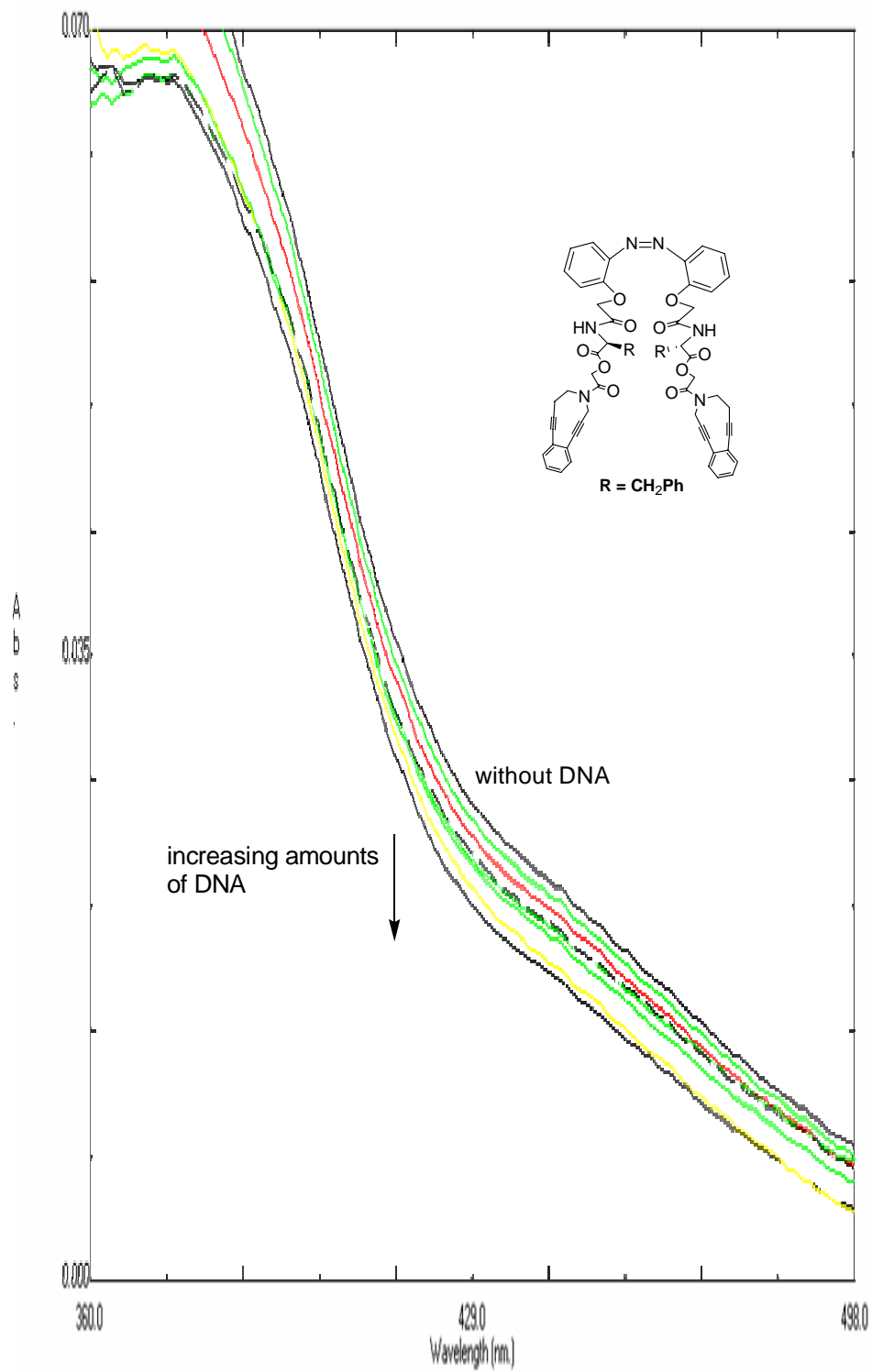
Figures S79



Figures S80

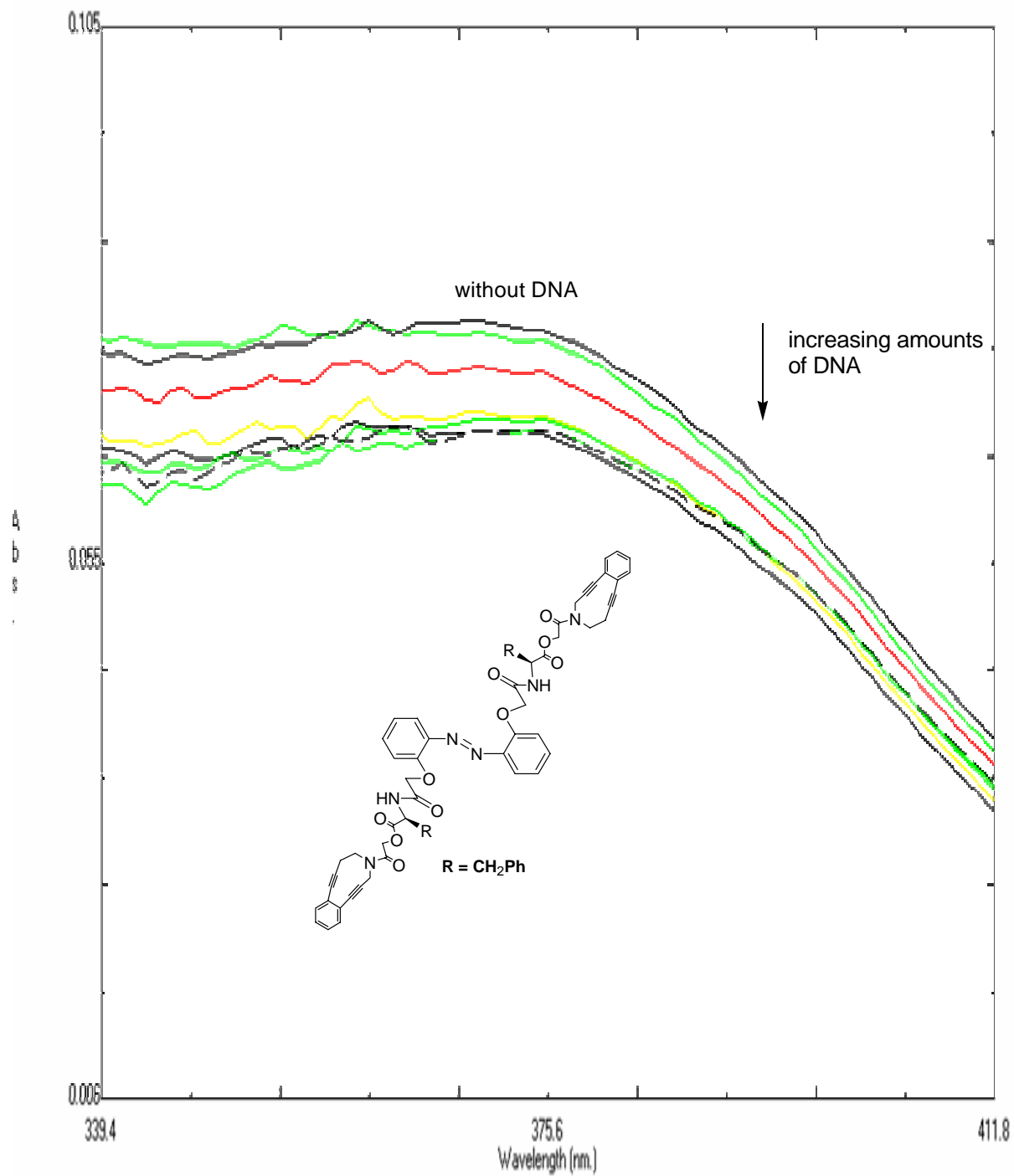


DNA binding study of compound 2a by UV



Figures S82

DNA binding study of compound 1a by UV



Figures 83

DNA-Binding Plots

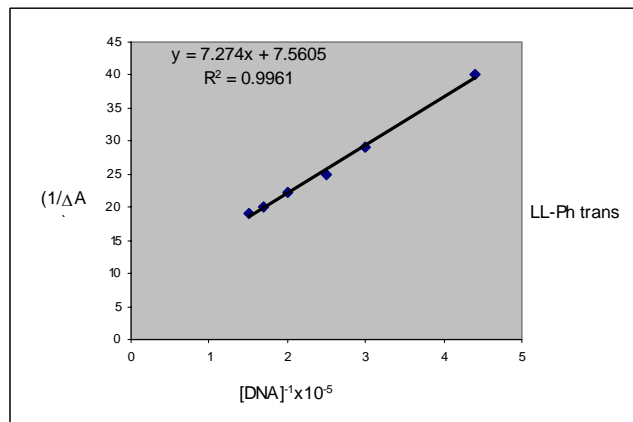


Figure S84: For 1a

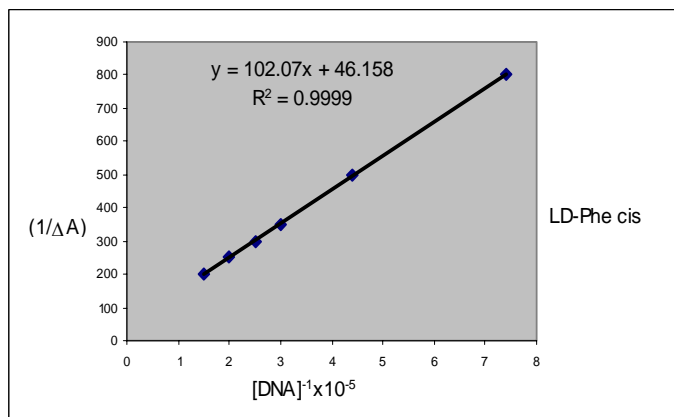


Figure S85: For 2a

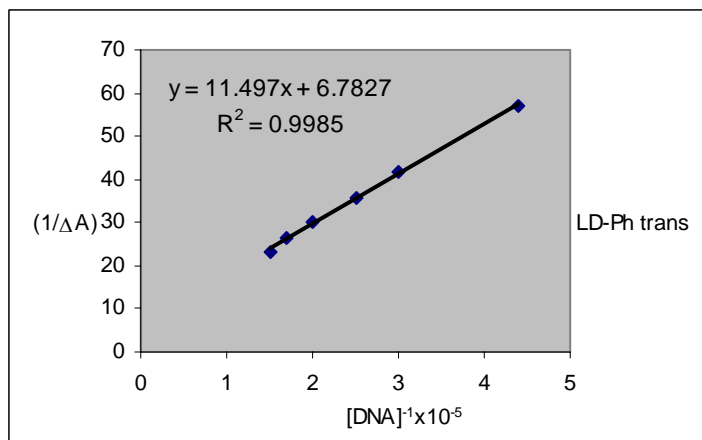


Figure S86: For 1e

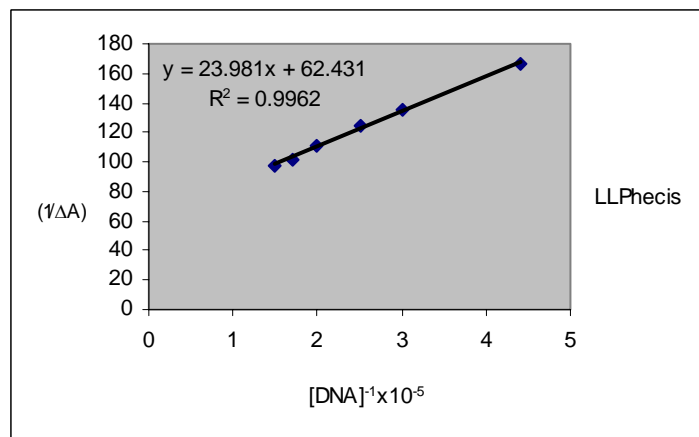


Figure S87: For 2e

DSC of enediynes 1a, 1b, 1c and 1e respectively

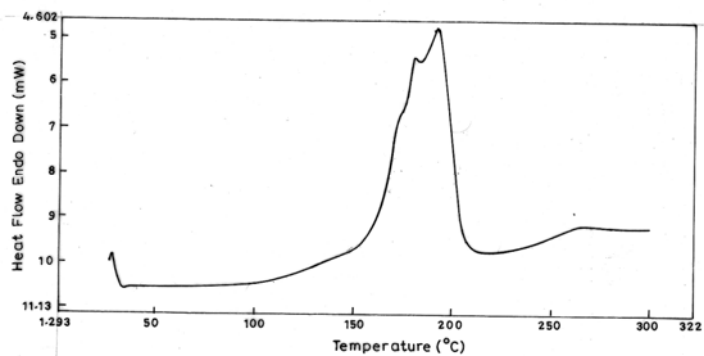


Figure S88

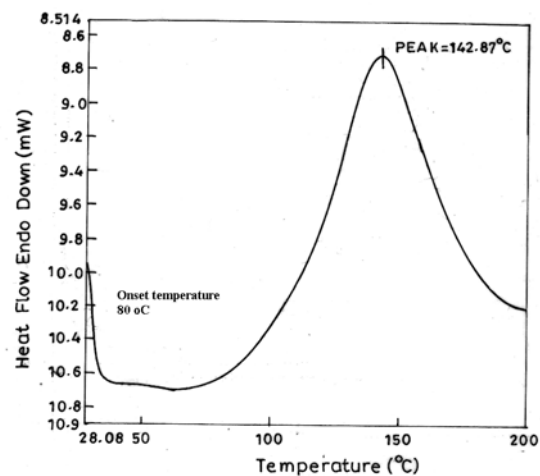


Figure S89

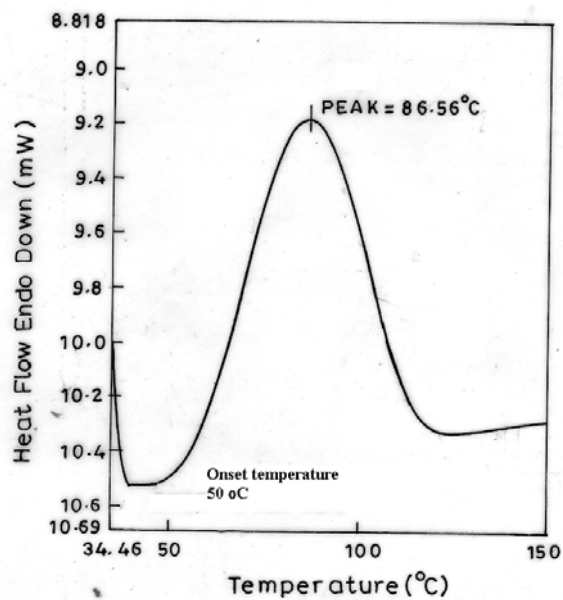


Figure S90

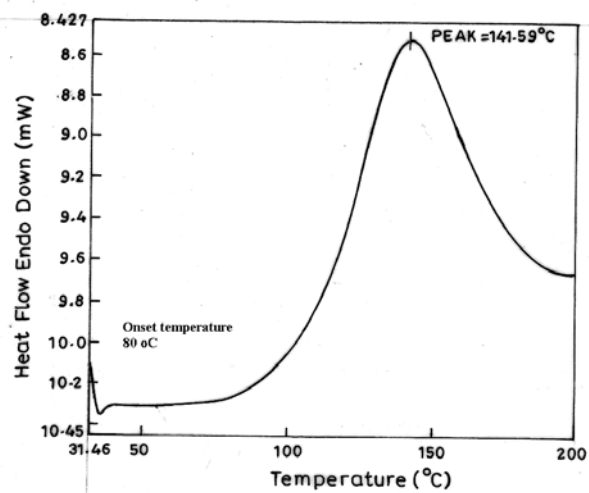


Figure S91

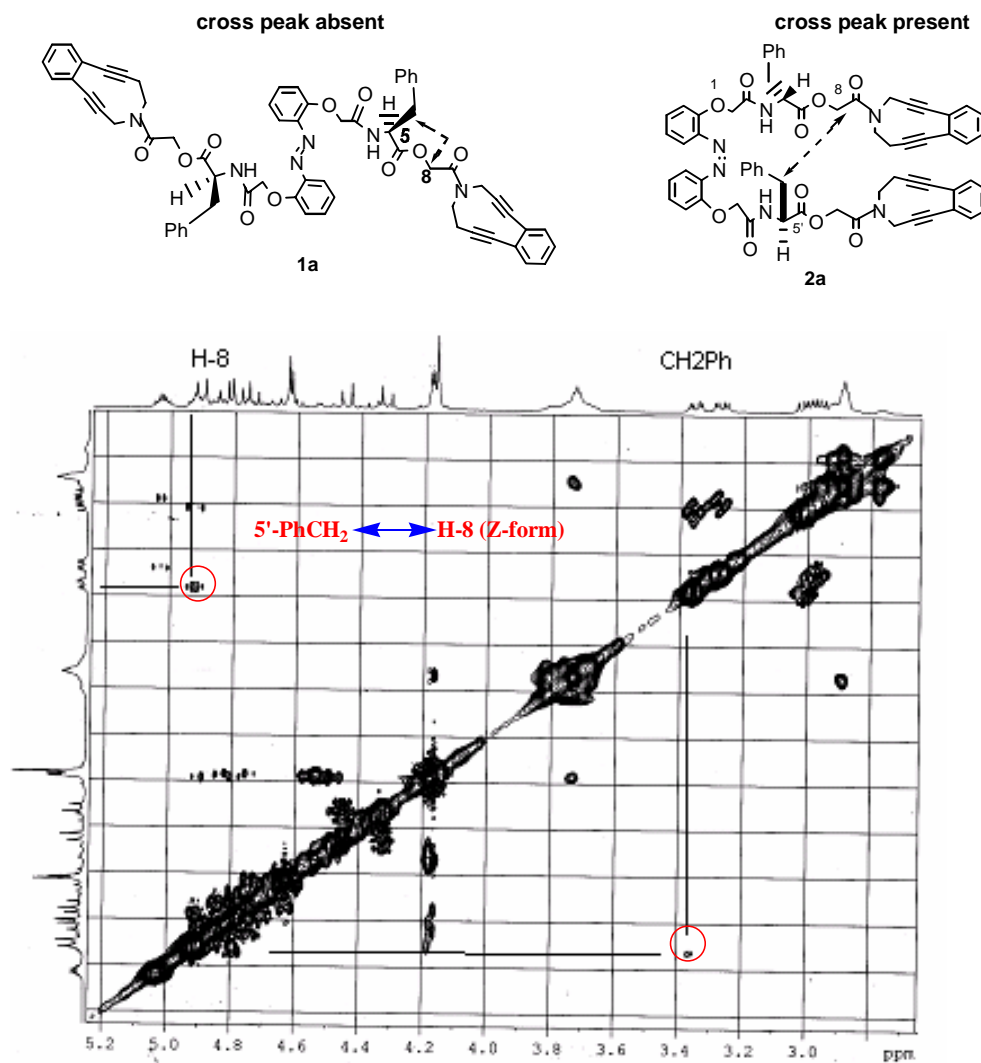


Figure S92: NOESY spectrum of enediynes 1a/2a

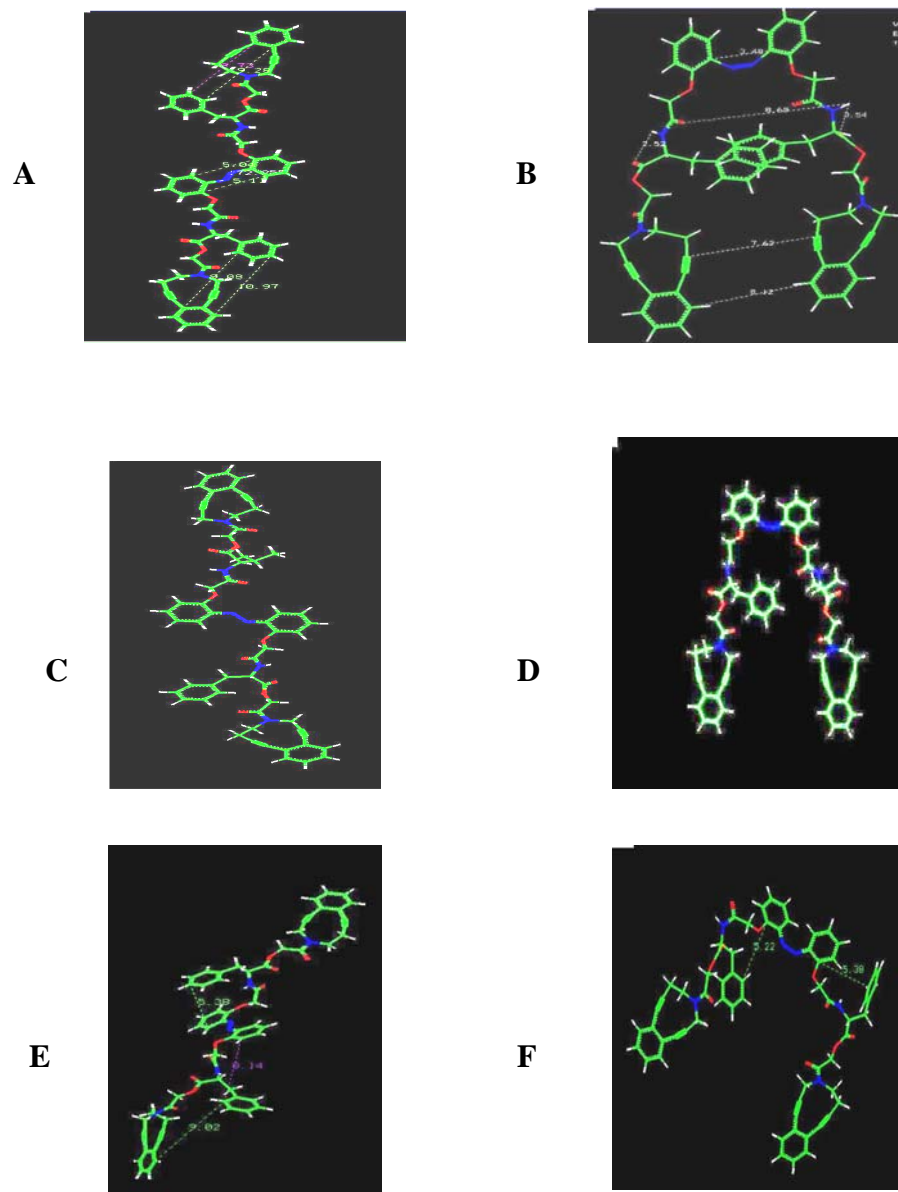


Figure S93: Energy minimized conformations of **1a** (A), **2a** (B), **1d** (C)/ **2d** (D), and **1e** (E)/**2e** (F)

Gel Documentation

The gel documentation was carried with UVP-GELDOC, Cambridge UK. The cleavage efficiency was measured by densitometry using image processing software (Kodak 1D version V.3.6.3).

Energy Minimization

The energy minimizations were carried out in Silicon Graphics using PDB coordinates from the Dundee PRODRG 2.5 Server (beta).

Selected spectral data

For compound **1a**: δ_{H} (400 MHz, CDCl_3) 7.55 (dd, $J = 8.4$ Hz, 15.6 Hz, 2 x 2H), 7.29-7.16 (m, 12H), 6.99-6.94 (m, 10H), 6.86 (d, $J = 8$ Hz, 2H), 4.95 (m, 2H), 4.76 (d, $J = 13.6$ Hz, 2H), 4.66 (d, $J = 13.6$ Hz, 2H), 4.54 (s, 4H), 4.05 (s, 4H), 3.64 (bs, 4H), 3.18 (d, $J = 4$ Hz, 2H), 2.89 (dd, $J = 8, 13.6$ Hz, 2H), 2.80 (bs, 4H); δ_{C} (100 MHz, CDCl_3) 170.5, 168.0, 165.7, 154.9, 142.6, 135.8, 132.6, 129.7, 129.1, 129.03, 128.5, 128.3, 128.3, 128.1, 127.9, 127.6, 127.5, 127.3, 126.8, 122.7, 117.8, 115.2, 98.1, 92.4, 88.0, 82.5, 68.9, 61.9, 52.8, 51.2, 40.8, 37.8, 18.2; HRMS: calcd for $\text{C}_{64}\text{H}_{54}\text{N}_6\text{O}_{10} + \text{H}^+$ 1067.3983 found 1067.3987.

For compound **2a**: δ_{H} (400 MHz, CDCl_3) 7.38-7.08 (m, 22H), 6.79 (t, $J = 7.6$ Hz, 2H), 6.66 (d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 8$ Hz, 2H), 4.89, 4.83 (ABq, $J = 16.0$ Hz, 2 x 2H), 4.71 (m, 2H), 4.48, 4.38 (ABq, $J = 16.0$ Hz, 2 x 2H), 4.16 (m, 4H), 3.75 (bm, 4H), 3.35 (m, 2H), 3.01 (m, 2H), 2.94 (bm, 4H).

For compound **1c**: δ_{H} (400 MHz, CDCl_3) 7.67 (t, $J = 7.6$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.28-6.99 (m, 14H), 5.89, 5.81 (ABq, $J = 9.6$ Hz, 2 x 2H), 5.04 (2H, m), 4.84 (2H, m), 4.76, 4.73 (ABq, $J = 12.6$ Hz, 2 x 2H), 4.75 (m, obscured, 2H), 4.11 (s, 4H), 3.75 (bs, 4H), 3.29 (dd, $J = 4.8, 14.0$ Hz, 2H), 2.99 (dd, $J = 4.0, 14.0$ Hz, 2H), 2.86 (bs, 4H); δ_{C} (100 MHz, CDCl_3) 170.5, 168.0, 165.7, 155.0, 142.7, 135.7, 132.6, 129.1, 129.0, 128.5, 128.3, 126.8, 125.5, 122.7, 121.5, 117.9, 115.3, 102.7, 95.9, 88.4, 82.7, 69.0, 61.7, 52.8, 51.3, 40.8, 37.7, 18.4; HRMS: calcd for $\text{C}_{56}\text{H}_{50}\text{N}_6\text{O}_{10} + \text{H}^+$ 967.3669 found 967.3673.

For compound **2c**: δ_{H} (400 MHz, CDCl_3) 7.22-6.99 (m, 14H), 6.82 (t, $J = 7.4$ Hz, 2H), 6.69 (d, $J = 8.4$ Hz, 2H), 6.53 (d, $J = 7.6$ Hz, 2H), 5.90, 5.82 (ABq, $J = 9.2$ Hz, 4H), 4.87 (m, 2H), 4.84,

4.77 (ABq, $J = 14.2$ Hz, 4H), 4.50, 4.37 (ABq, $J = 14.8$ Hz, 4H), 4.12 (m, 4H), 3.70 (m, 4H), 3.37 (dd, $J = 4.4, 14.4$ Hz, 2H), 3.03 (dd, $J = 8.8, 14.0$ Hz, 2H), 2.88 (m, 4H).

For compound **2i**: δ_{H} (400 MHz, CDCl_3) 7.66 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.38-7.21 (m, 12H), 7.15-7.0 (m, 10H), 6.94 (d, $J = 8.0$ Hz, 2H), 5.04 (m, 2H), 4.82, 4.75 (ABq, $J = 14.4$ Hz, 2H), 4.64 (s, 4H), 4.36 (s, 4H), 3.73 (t, $J = 4.6$ Hz, 4H), 3.26 (dd, $J = 5.4, 14.4$ Hz, 2H), 3.01-2.9 (m, 2H), 2.89 (t, $J = 4.8$ Hz, 4H); δ_{C} (100 MHz, CDCl_3) 170.6, 168.1, 165.8, 155.0, 142.7, 135.8, 132.6, 129.8, 129.1, 129, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.5, 127.4, 126.8, 122.8, 117.8, 115.3, 98.1, 92.4, 88, 82.5, 68.9, 61.9, 52.8, 51.3, 40.9, 37.8, 18.2; MS (ES^+) m/z 1067 (MH^+), 1089 (MNa^+); HRMS Calcd. For $\text{C}_{64}\text{H}_{54}\text{N}_6\text{O}_{10} + \text{H}^+$ 1067.3982 found 1067.3969.

For compound **2j**: δ_{H} (400 MHz, CDCl_3) 7.40-7.21 (m, 10H), 7.15-7.03 (m, 10H), 6.79 (t, $J = 7.6$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 6.51 (d, $J = 7.6$ Hz, 2H), 4.95-4.80 (m, 6H), 4.47 (d, $J = 15.6$ Hz, 2H), 4.32 (d, $J = 15.6$ Hz, 4H), 4.18 (s, 4H), 3.75 (m, 4H), 3.38 (dd, $J = 4.4, 14.0$ Hz, 2H), 3.05 (dd, $J = 5.2, 14.0$ Hz, 2H), 2.92 (m, 4H).