Supporting Information

Two-Photon Photochemical Generation of Reactive Enediyne

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Two-photon Induced Enediyne Generation. TPE experiments were conducted using 800 nm pulses generated by an amplified Ti:Sapphire laser operating at 1 kHz. The laser beam was attenuated by a diaphragm with a 6.15 mm opening. The power output of the laser after the diaphragm is 0.61 W, which is reduced to 0.55 W after passing through the sample. At the concentration of the substrate used in these experiments the loss of energy after the sample is mostly due to the losses on the phase boundaries, which allows us to evaluate the laser power within the sample as 0.58 W or 580 μJ per pulse^{-1}. The shape of the laser pulse was determined to be close to Gaussian with the half-height width of 94 fs. Using these parameters we have calculated the distribution of light intensity and squared light intensity within the pulse assuming ideal Gaussian shape of the pulse. For the integration of the squared light intensity we have selected the integration limits of ± 100 fs from the center of the pulse, as the value I^2 at these extremes drops to less than 0.2% of the maximum.

The degassed 1 mL samples of ca. 10^{-3} M methanol solutions of **1** were irradiated in 1x1 cm quartz cell. The cross-section of the solution in the cell is 1 cm^2, while the cross-section of the beam is 0.297 cm^2. Thus, the irradiated volume was 30% of the total volume. Durations of irradiation experiments required to achieve certain conversion were therefore scaled down by the factor of 0.3. The progress of the reaction was followed by measuring the concentration of the starting material (**1**) and the product, the 2,3-(octa-1,7-diyne-1,8-diyl)-5,6-dimethyl-1,4-benzoquinone (**2**), by HPLC. We have not observed decomposition of **2** under the 800 nm irradiation.

Table S1. Two-photon Induced Decarbonylation of Cyclopropenone **1** (580 μJ/pulse).

Time of Irradiation (s)	[2] / mM
0	0.0
445	0.348
624	0.466
802	0.546
1247	0.778
1782	0.885
2317	0.959
2851	0.958

Table S2. Formation of enediyne **2** in two-photon induced decarbonylation of **1** (486s of irradiation, variable pulse energy).

Pulse Energy (μJ/pulse)	Rate of formation of **2** (s^{-1}) / 10^{-6}
115	3.01
225	34.0
285	104
395	332
475	556
560	950

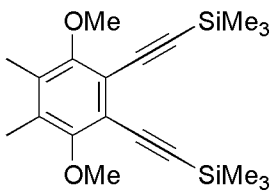
*Bergman Cyclization of enediyne **2**.* 1.85 mM solution of **2** in 2-propanol was kept at 40 ± 0.25^{0}C using a constant temperature bath. The progress of the reaction was followed by HPLC.

Table S3. Bergman Cyclization of enediyne **2** at 40^{0}C in 2-propanol

Time (s)	[**2**] / mM
0	0.00185
9000	0.00175
18000	0.00161
62280	0.0014
73800	0.00134
88200	0.00126
108000	0.00122
156600	0.0011
235800	9.31865E-4
318600	7.80315E-4
439200	5.68512E-4
604800	4.04916E-4
698400	3.19739E-4
806400	2.77905E-4
1.368E6	9.77804E-5

Complete Ref. 16b:

Cumpston,B.H.; Ananthavel,S.P.; Barlow, S.; Dyer, D.L.; Ehrlich, J.E.; Erskine, L.L.; Heikal, A.A.; Kuebler, S.M.; Lee, I-Y.S.; McCord-Maughon, D.; Qin, J.; Rockel, H.; Rumi, M.; Wu, X-L.; Marder, S.R.; Perry, J.W. *Nature* **1999**, *398*, 51



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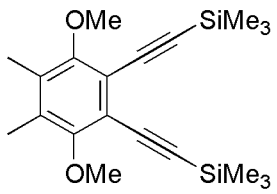
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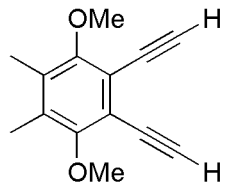
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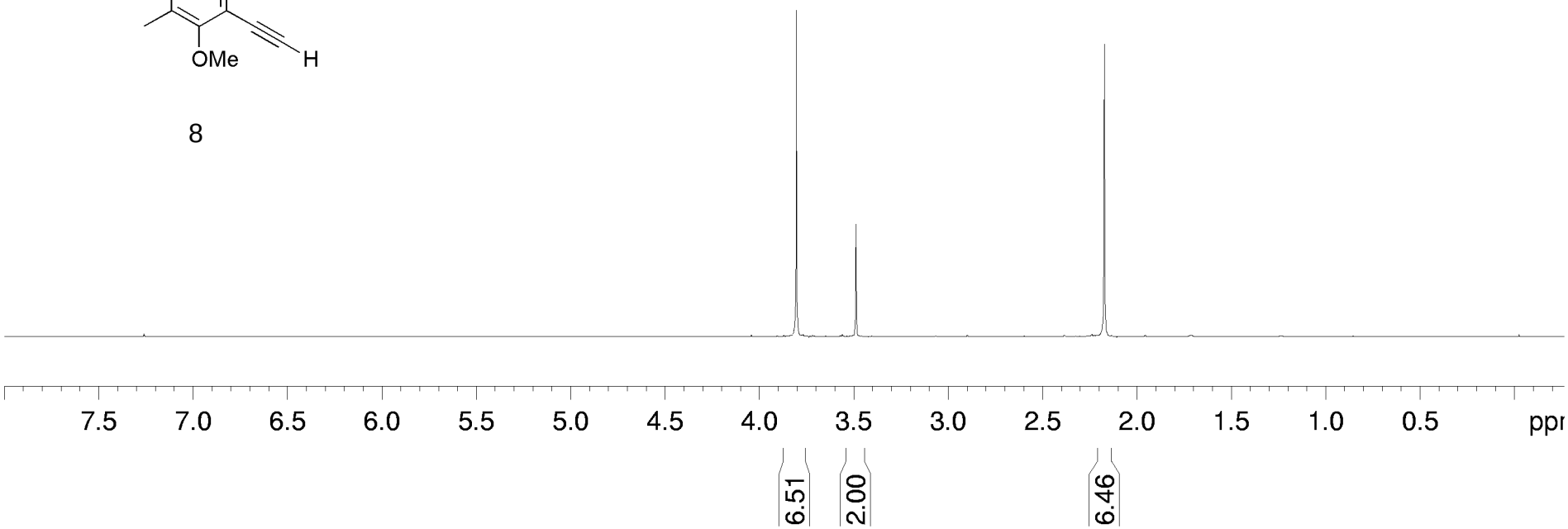
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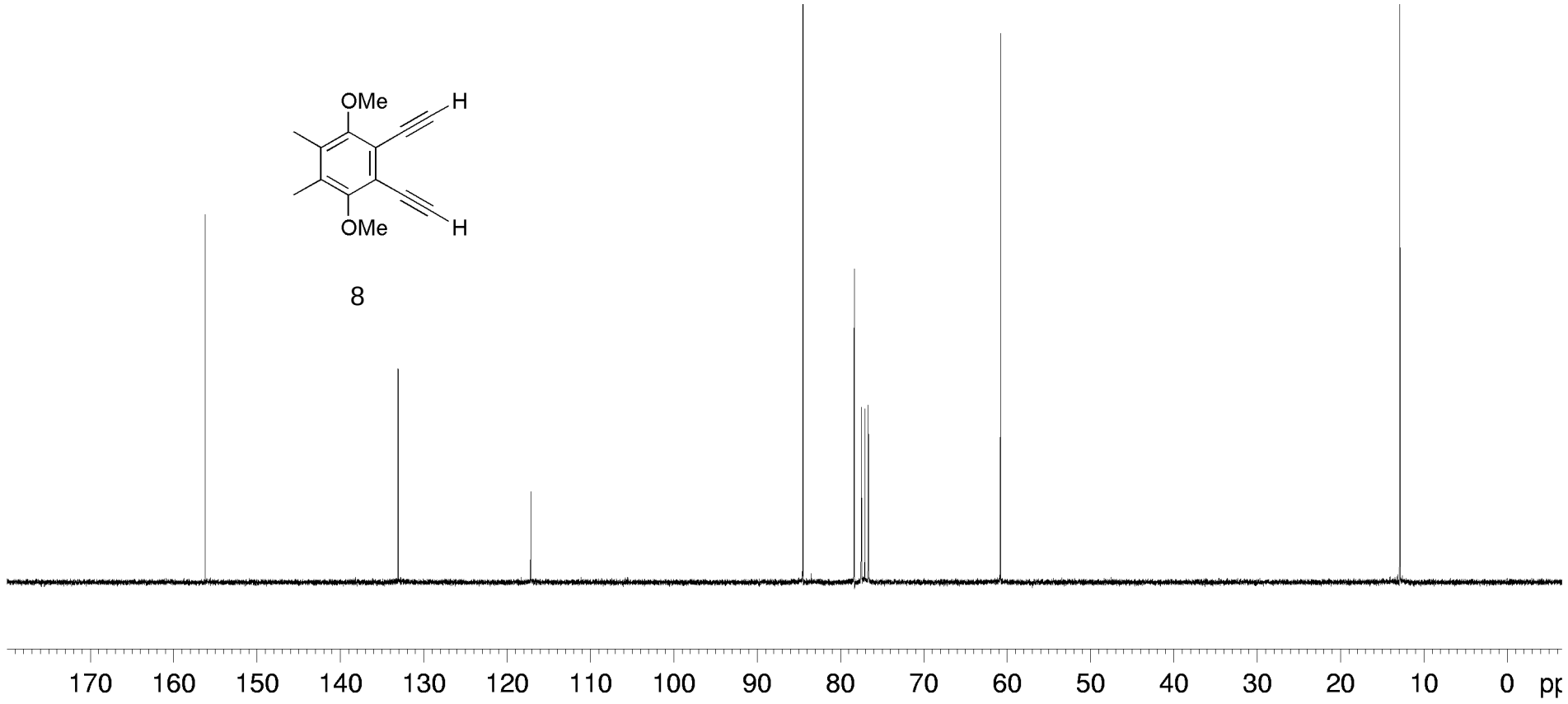
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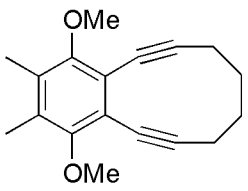
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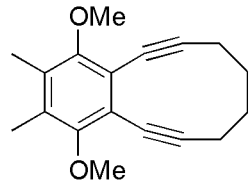
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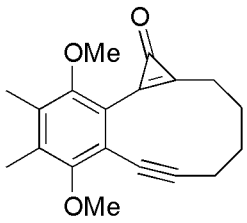
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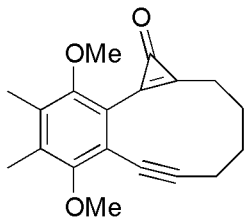
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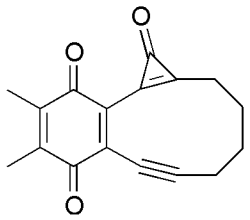

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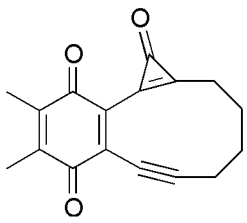

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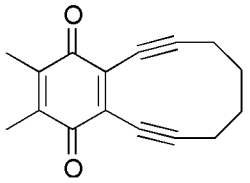

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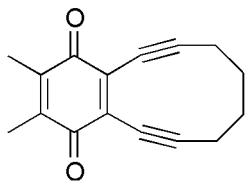

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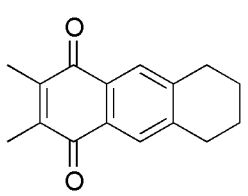

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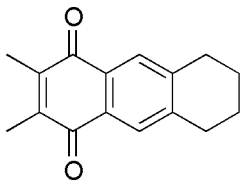

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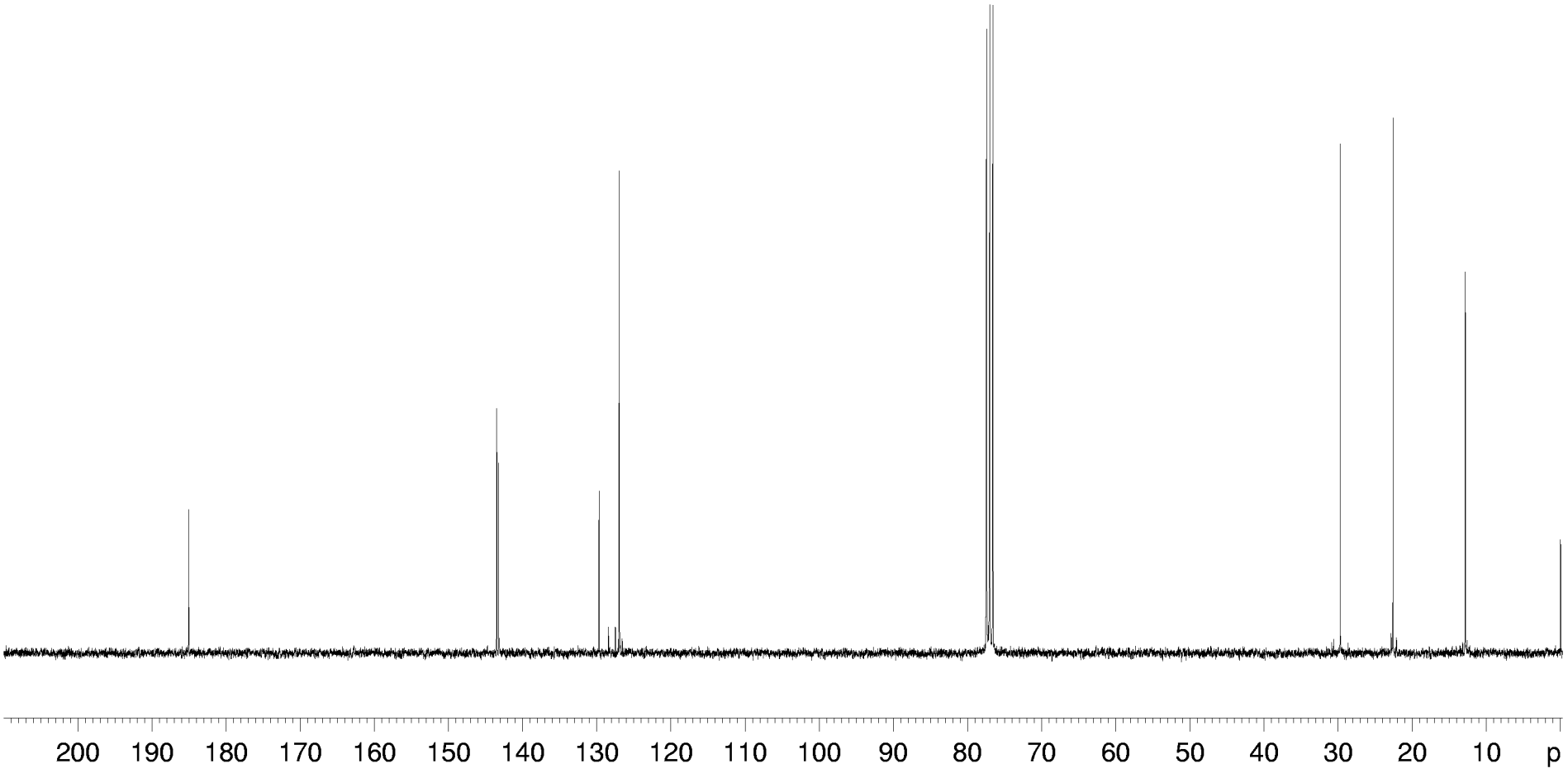
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