

## Supporting Information

### A Novel [2+2] Photodimerization of N-[(E)-3,4-Methylenedioxcinnamoyl]dopamine in the Solid State

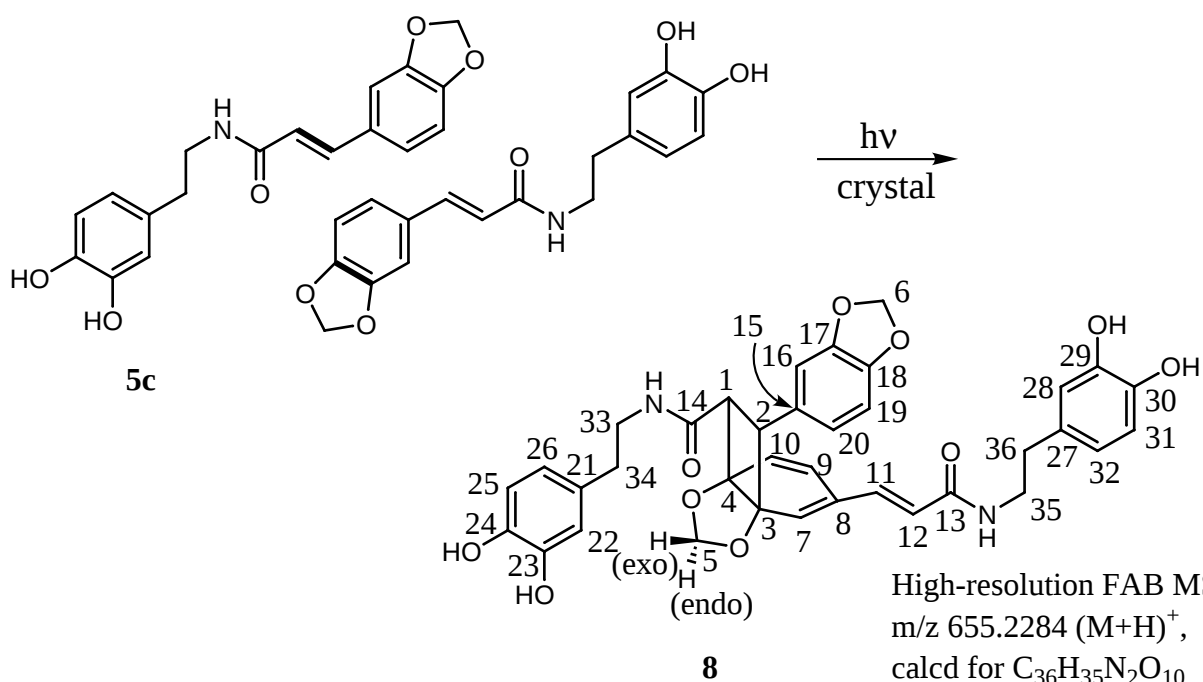
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**6**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  7.27 (4 H, d,  $J$  = 8.6 Hz), 7.20 (4 H, d,  $J$  = 8.6 Hz), 6.74 (2 H, d,  $J$  = 8.2 Hz), 6.53 (2 H, d,  $J$  = 2.0 Hz), 6.48 (2 H, dd,  $J$  = 8.2, 2.0 Hz), 5.09 (2 H, t,  $J$  = 5.7 Hz, NH), 4.37 (2 H, dd,  $J$  = 10.2, 7.2 Hz, cyclobutane), 3.86 (6 H, s), 3.82 (6 H, s), 3.57 (2 H, dd,  $J$  = 10.2, 6.9 Hz, cyclobutane), 3.21 (4 H, quar,  $J$  = 6.4 Hz,  $\text{CH}_2\text{NH}$ ), 2.45 (2 H, dt,  $J$  = 13.9, 6.9 Hz,  $\text{CH}_2\text{Ph}$ ), 2.31 (2 H, dt,  $J$  = 13.9, 6.9 Hz,  $\text{CH}_2\text{Ph}$ ); IR (KBr) 3310, 1637, 1518, 1264, 1238, 1157, 1141, 1028, 814  $\text{cm}^{-1}$ ; MS (FAB, thioglycerol)  $m/z$  (rel intensity) 691 (9,  $(\text{M}+\text{H})^+$ ), 346 (5), 208 (7), 165 (100), 164 (90); HRMS calcd for  $\text{C}_{38}\text{H}_{41}\text{O}_6\text{N}_2\text{Cl}_2$  691.2341, found 691.2324. The structure of **6** was confirmed by single crystal X-ray analysis.<sup>12</sup>

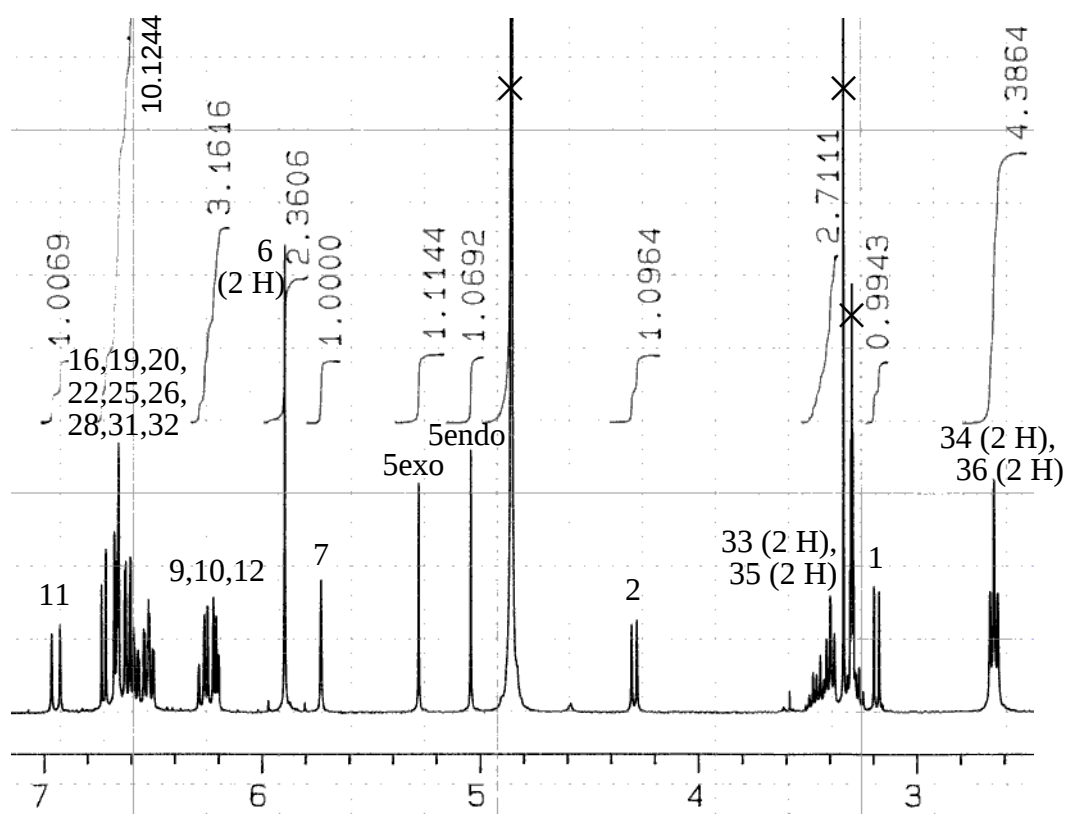
**7**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 270 MHz)  $\delta$  6.72 (2 H, d,  $J$  = 8.1 Hz), 6.69 (2 H, d,  $J$  = 2.0 Hz), 6.65 (2 H, dd,  $J$  = 8.1, 2.0 Hz), 6.56 (2 H, d,  $J$  = 8.0 Hz), 6.35 (2 H, dd,  $J$  = 8.0, 1.7 Hz), 6.33 (2 H, d,  $J$  = 1.7 Hz), 5.84 (4 H, s), 5.81 (2 H, t,  $J$  = 5.9 Hz, NH), 4.12 (2 H, d,  $J$  = 6.2 Hz, cyclobutane), 3.82 (6 H, s), 3.81 (6 H, s), 3.50 (2 H, d,  $J$  = 6.2 Hz, cyclobutane), 3.47 (4 H, quar,  $J$  = 6.7 Hz,  $\text{CH}_2\text{NH}$ ), 2.71 (4 H, t,  $J$  = 7.0 Hz,  $\text{CH}_2\text{Ph}$ ); IR (KBr) 1654, 1637, 1519, 1262, 1238, 1040  $\text{cm}^{-1}$ ; MS (FAB, NBA)  $m/z$  (rel intensity) 711 (32,  $(\text{M}+\text{H})^+$ ), 355 (14), 262 (35), 208 (11), 175 (43), 165 (97), 164 (100); HRMS calcd for  $\text{C}_{40}\text{H}_{43}\text{O}_{10}\text{N}_2$  711.2917, found 711.2900. The  $\beta$ -truxinic dimer of (E)-3,4-methylenedioxcinnamic acid<sup>18</sup> was heated with thionyl chloride in benzene and then treated with O,O'-dimethyldopamine under solvent-free conditions to afford **7**.

(18) Desiraju, G. R.; Kamala, R.; Kumari, B. H.; Sarma, J. A. R. P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 181-189.

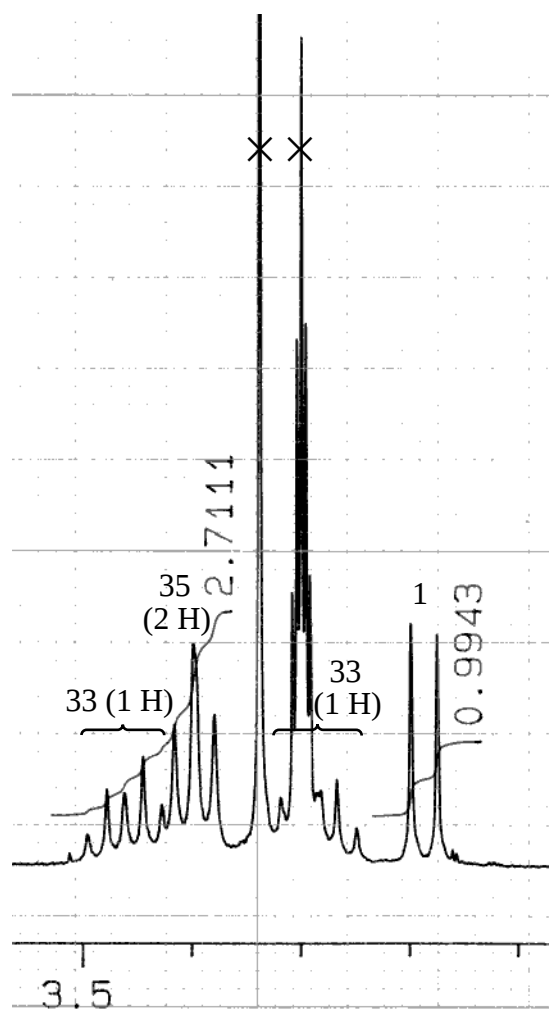
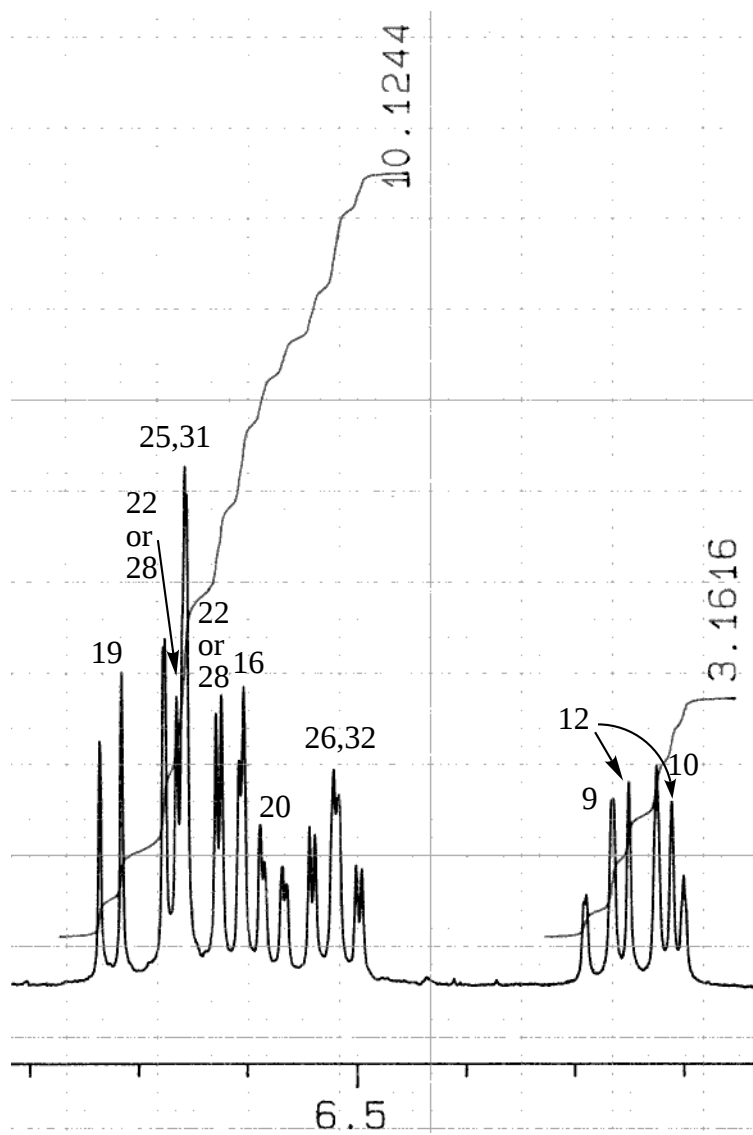
**8**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$  6.94 (1 H, d,  $J$  = 15.8 Hz, H-11), 6.73 (1 H, d,  $J$  = 8.1 Hz, H-19), 6.67 (2 H, d,  $J$  = 8.1 Hz, H-25, H-31), 6.66 (1 H, d,  $J$  = 2.0 Hz, H-22 or H-28), 6.63 (1 H, d,  $J$  = 2.0 Hz, H-22 or H-28), 6.61 (1 H, d,  $J$  = 1.6 Hz, H-16), 6.58 (1 H, dd,  $J$  = 8.1, 1.5 Hz, H-20), 6.53 and 6.51 (2 H, dd x 2,  $J$  = 8.1, 2.0 Hz, H-26, H-32), 6.28 (1 H, d,  $J$  = 10.0 Hz, H-9), 6.23 (1 H, d,  $J$  = 15.8 Hz, H-12), 6.22 (1 H, d,  $J$  = 10.0 Hz, H-10), 5.90 (2 H, s, H-6), 5.73 (1 H, s, H-7), 5.28 (1 H, s, H-5<sub>exo</sub>), 5.05 (1 H, s, H-5<sub>endo</sub>), 4.30 (1 H, d,  $J$  = 9.9 Hz, H-2), 3.46 (1 H, dt,  $J$  = 13.4, 7.0 Hz, H-33), 3.40 (2 H, t,  $J$  = 7.0 Hz, H-35), 3.28 (1 H, dt,  $J$  = 13.4, 7.0 Hz, H-33), 3.19 (1 H, d,  $J$  = 9.9 Hz, H-1), 2.65 (4 H, t,  $J$  = 7.0 Hz, H-34 x 2, H-36 x 2);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 100 MHz)  $\delta$  170.12 (C-14), 168.15 (C-13), 149.32 (C-17), 148.19 (C-18), 146.272 and 146.265 (C-23, C-29), 144.81 and 144.80 (C-24, C-30), 140.17 (C-11), 133.70 (C-8), 132.09 (C-21), 131.97 (C-27), 131.25 (C-15), 128.37 (C-10), 127.89 (C-7), 123.15 (C-12), 122.21 (C-20), 121.26 and 121.03 (C-26, C-32), 121.23 (C-9), 117.04 and 116.85 (C-22, C-28), 116.40 and 116.35 (C-25, C-31), 109.15 and 109.14 (C-16, C-19), 102.42 (C-6), 94.02 (C-5), 82.51 (C-3), 80.12 (C-4), 52.67 (C-2), 51.18 (C-1), 42.56 (C-33), 42.53 (C-35), 35.92 (C-34), 35.86 (C-36); IR (KBr) 3387, 1654, 1637, 1608, 1523, 1445, 1288, 1255, 1239, 1075, 1040, 810  $\text{cm}^{-1}$ ; MS (FAB, glycerol)  $m/z$  (rel intensity) 655 (3,  $(\text{M}+\text{H})^+$ ), 328 (26), 282 (19), 175 (100); HRMS calcd for  $\text{C}_{36}\text{H}_{35}\text{N}_2\text{O}_{10}$  655.2292, found 655.2284.



**<sup>1</sup>H NMR (400 MHz) of 8 in CD<sub>3</sub>OD**



**$^1\text{H}$  NMR (400 MHz) of 8 in  $\text{CD}_3\text{OD}$**



**$^{13}\text{C}$  NMR (100 MHz) of 8 in  $\text{CD}_3\text{OD}$**

