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## Supporting Information

### Characterization data for cyclohexenones 3a, 4a-i and 10.

**5-Methyl-2-cyclohexen-1-one (4a):**  $R_f = 0.43$  (2:8 EtOAc:hexanes); **bp** 50 °C/3 mmHg (lit.<sup>23</sup> 54 °C/5 mmHg); **IR** 1671, 1645  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**   $\delta$  1.08 (3H, d,  $J = 6.6$  Hz), 2.04 (1H, ddd of A part of ABq,  $J_d = 2.7, 2.7, 9.7, J_{AB} = 18.6$  Hz), 2.12 (1H, d of A part of ABq,  $J_d = 12.2, J_{AB} = 15.8$  Hz), 2.22 (1H, m), 2.42 (1H, dd of B part of ABq,  $J_d = 4.5, 5.6, J_{AB} = 18.6$  Hz), 2.48 (1H, d of B part of ABq,  $J_d = 3.6, J_{AB} = 15.8$  Hz), 6.01 (1H, ddd,  $J = 1.3, 1.3, 10.1$  Hz), 6.96 (1H, ddd,  $J = 2.7, 5.6, 10.1$ ).

**6-Carboethoxy-5-methyl-2-cyclohexen-1-one (3a):**  $R_f = 0.22$  (2:8 EtOAc:hexanes); **IR** 1731, 1677  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**   $\delta$  1.09 (3H, d,  $J = 6.4$  Hz), 1.30 (3H, t,  $J = 7.2$  Hz), 2.05~2.22 (1H, m), 2.43~2.69 (2H, m), 3.12 (1H, d,  $J = 11.8$  Hz), 4.26 (2H, q,  $J = 7.2$  Hz), 6.08 (1H, ddd,  $J = 1.3, 1.3, 10.1$  Hz), 7.01 (1H, ddd,  $J = 2.7, 5.7, 10.1$ ).  **$^{13}\text{C NMR}$**   $\delta$  14.2, 19.6, 32.7, 33.0, 60.9, 61.6, 128.7, 149.8, 169.9, 194.5. **HRMS** calcd for  $\text{C}_{10}\text{H}_{14}\text{O}_3$  182.0943, found 182.0956.

**4-Methyl-2-cyclohexen-1-one (4b):**  $R_f = 0.42$  (2:8 EtOAc:hexanes); **bp** 58 °C/5 mmHg (lit.<sup>27</sup> 45.0-45.5 °C/4.5 mmHg); **IR** 1683  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**   $\delta$  1.16 (3H, d,  $J = 7.3$  Hz), 1.68 (1H, dddd,  $J = 5.0, 12.0, 12.2, 13.2$  Hz), 2.12 (1H, ddddd,  $J = 1.2, 4.8, 5.0, 5.0, 13.2$  Hz), 2.37 (1H, dd of A part of ABq,  $J_d = 4.8, 12.2, J_{AB} = 16.8$  Hz), 2.49 (1H, dd of B part of ABq,  $J_d = 5.0, 5.0, J_{AB} = 16.8$  Hz), 2.55 (1H, m), 5.95 (1H, ddd,  $J = 0.6, 1.9, 10.1$  Hz), 6.80 (1H, ddd,  $J = 1.5, 3.0, 10.1$  Hz).

**3-Methyl-2-cyclohexen-1-one (4c):**  $R_f = 0.42$  (2:8 EtOAc:hexanes); **IR** 1665, 1626  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**   $\delta$  1.96 (3H, s), 1.99 (2H, t,  $J = 6.5$  Hz), 2.29 (2H, t,  $J = 6.2$  Hz), 2.34 (2H, t,  $J = 6.7$  Hz), 5.88 (1H, s).

**Isophorone (4d):**  $R_f = 0.42$  (2:8 EtOAc:hexanes); **IR** 1663  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**   $\delta$  1.04 (6H, s), 1.94 (3H, s), 2.17 (2H, s), 2.19 (2H, s), 5.88 (1H, s).

**3-Ethyl-2-cyclohexen-1-one (4e):**  $R_f = 0.37$  (2:8 EtOAc:hexanes); **IR** 1648  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**   $\delta$  1.10 (3H, t,  $J = 7.2$  Hz), 1.99 (2H, dddd,  $J = 5.3, 5.7, 6.2, 7.1$  Hz), 2.25 (2H, q,  $J = 7.2$  Hz), 2.30 (2H, dd,  $J = 5.3, 5.7$  Hz), 2.37 (2H, dd,  $J = 6.2, 7.1$  Hz), 5.89 (1H, t,  $J = 1.5$  Hz);  **$^{13}\text{C NMR}$**   $\delta$  11.2, 22.7, 29.7, 30.8, 37.4, 124.5, 168.0, 200.1.

**6-Methyl-2-cyclohexen-1-one (4f):**  $R_f = 0.41$  (2:8 EtOAc:hexanes); **IR** 1676  $\text{cm}^{-1}$ ;  **$^1\text{H NMR}$**   $\delta$  1.15 (3H, d,  $J = 6.8$  Hz), 1.74 (1H, m), 2.08 (1H, dddd,  $J = 4.2, 4.5, 4.8, 13.2$  Hz), 2.36~2.45 (3H, m), 5.99 (1H, dt,  $J_d = 10.0, J_t = 2.0$  Hz), 6.93 (1H, ddt,  $J_d = 1.0, 10.0, J_t = 4.5$  Hz).

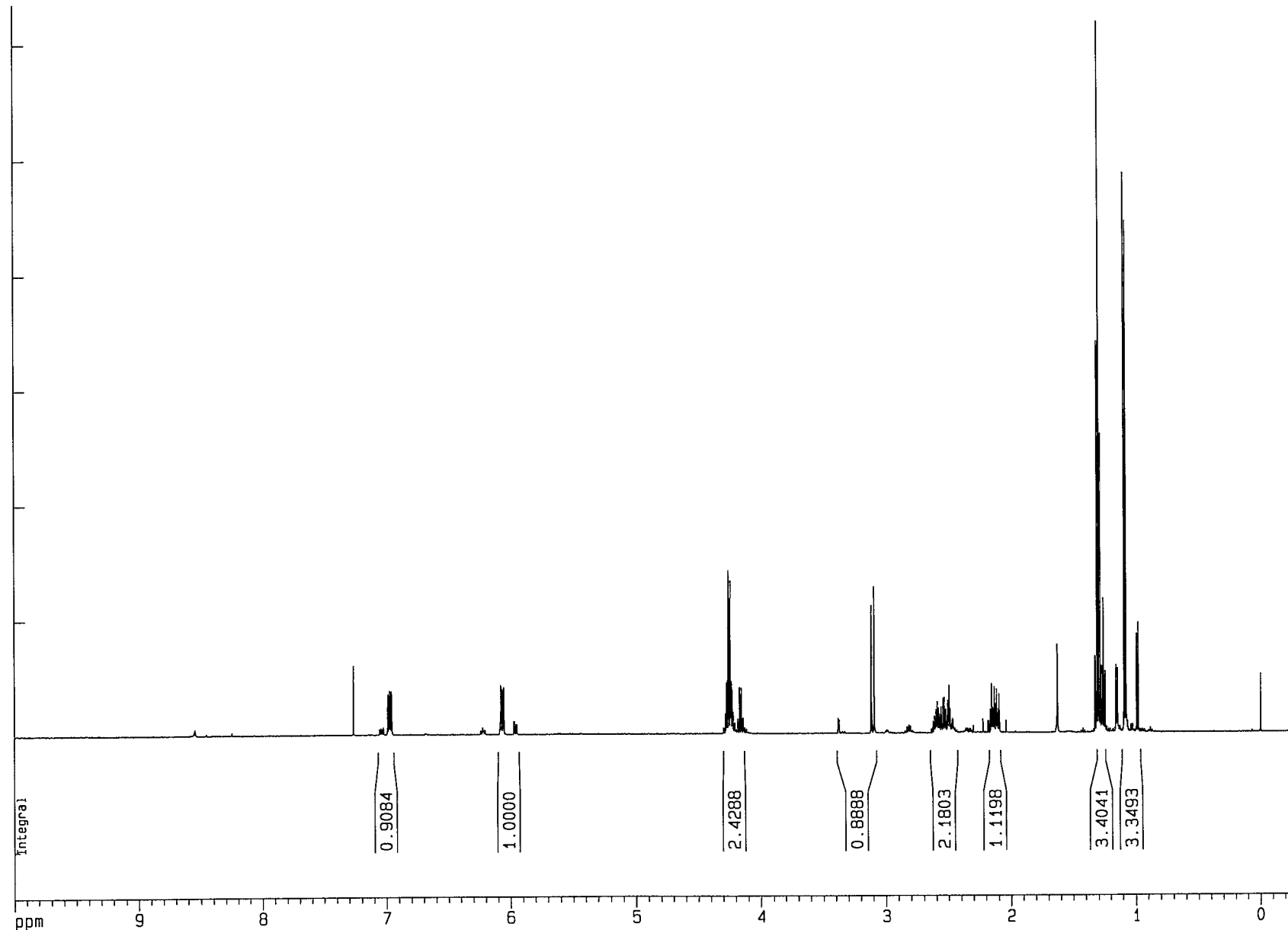
**3,6-Dimethyl-2-cyclohexen-1-one (4g):**  $R_f = 0.42$  (2:8 EtOAc:hexanes); **IR** 1671  $\text{cm}^{-1}$ ;  
 **$^1\text{H}$  NMR**  $\delta$  1.13 (3H, d,  $J = 6.9$  Hz), 1.70 (1H, dddd,  $J = 5.1, 10.1, 11.6, 13.2$  Hz), 1.94 (3H, s), 2.06  
(1H, dddd,  $J = 4.2, 4.5, 4.8, 13.2$  Hz), 2.24~2.40 (3H, m), 5.84 (1H, s).

**2,3-Dimethyl-2-cyclohexen-1-one (4h):**  $R_f = 0.39$  (2:8 EtOAc:hexanes); **IR** 1666  $\text{cm}^{-1}$ ;  
 **$^1\text{H}$  NMR**  $\delta$  1.76 (3H, s), 1.93 (3H, s), 1.91~1.96 (2H, m), 2.33 (2H, br t,  $J = 5.7$  Hz), 2.38 (2H, t,  $J =$   
6.7 Hz);  **$^{13}\text{C}$  NMR**  $\delta$  10.4, 21.1, 22.0, 32.4, 37.3, 130.7, 154.7, 198.5.

**2,6-Dimethyl-2-cyclohexen-1-one (4i):**  $R_f = 0.40$  (2:8 EtOAc:hexanes); **IR** 1679  $\text{cm}^{-1}$ ;  
 **$^1\text{H}$  NMR**  $\delta$  1.14 (3H, d,  $J = 6.8$  Hz), 1.72 (1H, dddd,  $J = 5.8, 9.2, 11.9, 13.0$  Hz), 1.77 (3H, ddd,  $J =$   
1.3, 1.5, 1.8 Hz), 2.04 (1H, dddd,  $J = 4.0, 5.0, 5.0, 13.0$  Hz), 2.31~2.42 (3H, m), 6.68 (1H, dddd,  $J =$   
1.3, 1.4, 3.5, 4.6 Hz).

**4-Carboethoxy-3,5-dimethyl-2-cyclohexen-1-one (10):**  $R_f = 0.22$  (2:8 EtOAc:hexanes);  
**IR** 1717, 1663  $\text{cm}^{-1}$ ;  **$^1\text{H}$  NMR major**  $\delta$  1.08 (3H, d,  $J = 6.6$  Hz), 1.31 (3H, t,  $J = 7.2$  Hz), 1.96 (3H,  
dd,  $J = 1.1, 1.3$  Hz), 2.09 (1H, dd,  $J = 6.8, 17.2$  Hz), 2.53~2.64 (2H, m), 3.02 (1H, d,  $J = 6.8$  Hz),  
4.24 (2H, q,  $J = 7.1$  Hz), 5.97 (1H, t,  $J = 1.5$  Hz); **minor**  $\delta$  1.10 (3H, d,  $J = 6.7$  Hz), 1.29 (3H, t,  $J =$   
7.1 Hz), 1.97 (3H, d,  $J = 1.2$  Hz), 2.28 (1H, dd,  $J = 4.0, 16.3$  Hz), 2.38~2.51 (1H, m), 3.18 (1H, d,  $J$   
 $= 5.2$  Hz), 4.21 (2H, dq,  $J_d = 1.8, J_q = 7.2$  Hz);  **$^{13}\text{C}$  NMR major**  $\delta$  14.2, 19.7, 22.6, 32.8, 43.0,  
54.4, 61.2, 128.0, 155.9, 171.9, 198.0; **minor**  $\delta$  14.2, 18.5, 23.3, 32.0, 40.7, 52.2, 61.1, 128.2,  
156.6, 170.1, 199.7; **HRMS** calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_3$  196.1099, found 196.1107.

6-Carboethoxy-5-methyl-2-cyclohexen-1-one / 1H



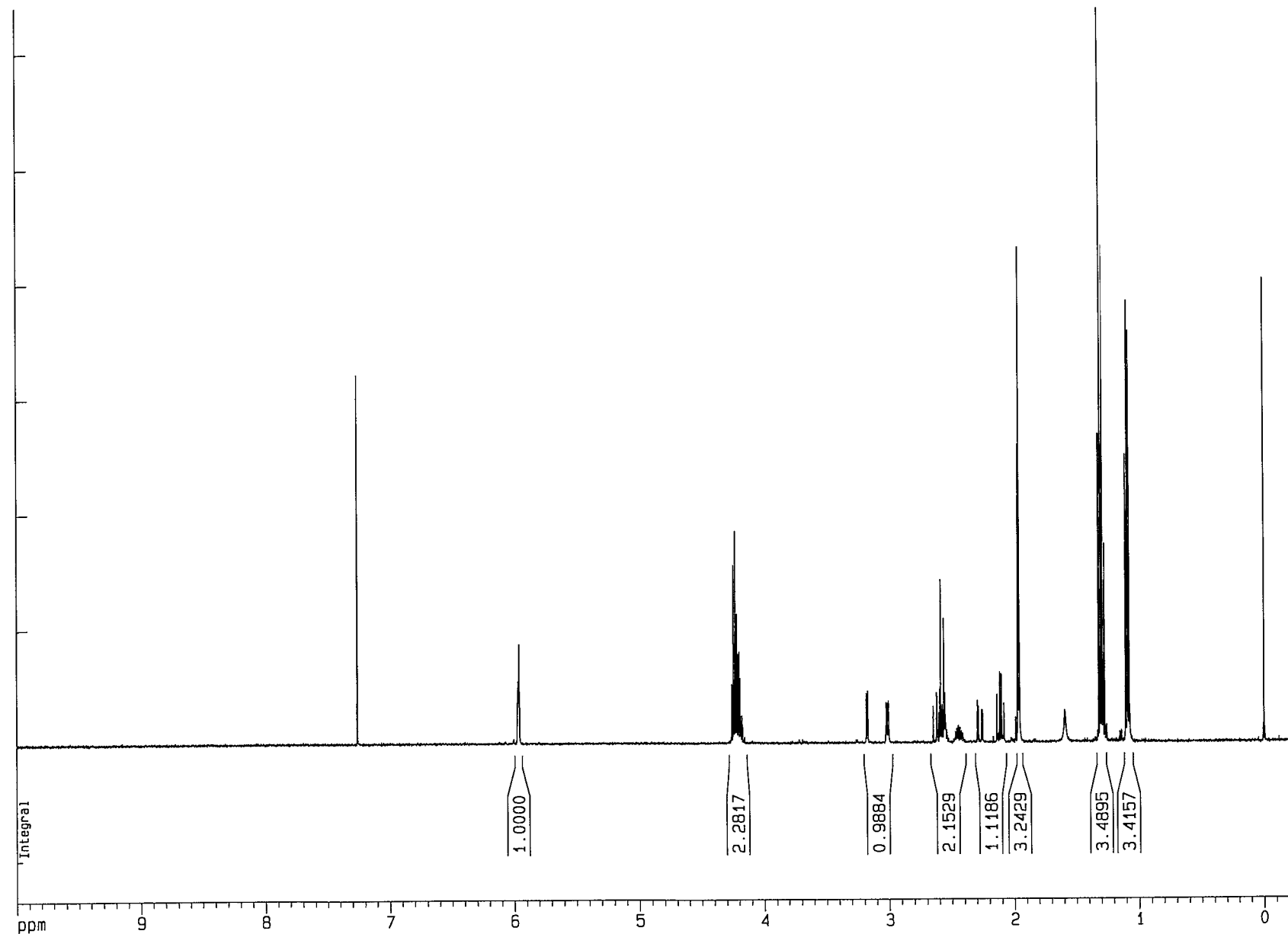
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4-Carboethoxy-3,5-dimethyl-2-cyclohexen-1-one / 1H



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