

Supporting Information

Influence of Michael Acceptor Stereochemistry on Intramolecular Morita-Baylis-Hillman Reactions

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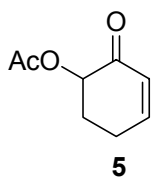
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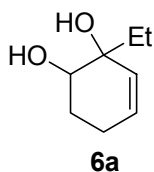
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General Methods. ¹H and ¹³C NMR spectra were recorded on a 300 MHz spectrometer in CDCl₃ with tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded using the EI method. Tetrahydrofuran and toluene were distilled from Na/benzophenone under an Ar atmosphere. Acetonitrile and 1,2-dichloroethane were distilled from CaH₂ under an Ar atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC analysis using GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

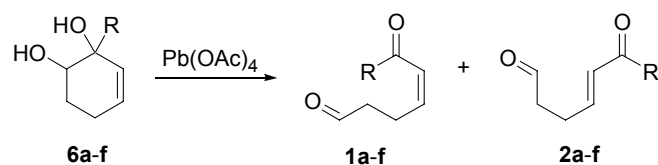
Representative reports of intermolecular MBH reactions where cycloalkenenones were used as the Michael acceptor: (a) Kataoka, T.; Iwama, T.; Tsujiyama, S.-I.; Iwamura, T.; Watanabe, S.-I. *Tetrahedron* **1998**, *54*, 11813-11824. (b) Kataoka, T.; Iwama, T.; Tsujiyama, S.-I. *Chem. Commun.* **1998**, 197-198. (c) Rezgui, F.; El Gaied, M. M. *Tetrahedron Lett.* **1998**, *39*, 5965-5966. (d) Kawamura, M.; Kobayashi, S. *Tetrahedron Lett.* **1999**, *40*, 1539-1542. (e) Aggarwal, V. K.; Mereu, A. *Chem. Commun.* **1999**, 2311-2312. (f) Li, G.; Wei, H.-X.; Gao, J. J.; Caputo, T. D. *Tetrahedron Lett.* **2000**, *41*, 1-5. (g) Yamada, Y. M. A.; Ikegami, S. *Tetrahedron Lett.* **2000**, *41*, 2165-2169. (h) Iwamura, T.; Fujita, M.; Kawakita, T.; Kinoshita, S.; Watanabe, S.-I.; Kataoka, T. *Tetrahedron* **2001**, *57*, 8455-8462. (i) Bauer, T.; Tarasuik, J. *Tetrahedron: Asymmetry* **2001**, *12*, 1741-1745. (j) Jauch, J. *J. Org. Chem.* **2001**, *66*, 609-611. (k) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295-4298. (l) Pei, W.; Wei, H.-X.; Li, G. *Chem. Commun.* **2002**, 2412-2413. (m) Patra, A.; Batra, S.; Joshi, B. S.; Roy, R.; Kundu, B.; Bhaduri, A. P. *J. Org. Chem.* **2002**, *67*, 5783-5788. (n) Franck, X.; Figadère, B. *Tetrahedron Lett.* **2002**, *43*, 1449-1451. (o) Luo, S.; Zhang, B.; He, J.; Janczuk, A.; Wang, P. G.; Cheng, J.-P. *Tetrahedron Lett.* **2002**, *43*, 7369-7371. (p) Gatri, R.; El Gaied, M. M. *Tetrahedron Lett.* **2002**, *43*, 7835-7836. (q) McDougal, N. T.; Schaus, S. E. *J. Am. Chem. Soc.* **2003**, *125*, 12094-12095. (r) McDougal, N. T.; Trevellini, W. L.; Rodgen, S. A.; Kliman, L. T.; Schaus, S. E. *Adv. Synth. Catal.* **2004**, *346*, 1231-1240.



6-Acetoxy-2-cyclohexene-1-one (5).¹ To a stirred solution of 2-cyclohexene-1-one (3.06 g, 30.00 mmol) in toluene (60 mL) was added Pb(OAc)₄ (28.00 g, 60.00 mmol). The mixture was then heated to reflux for 4 h, and cooled to room temperature. The resulting mixture was diluted with ether, washed with 1 M HCl, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford **5** (2.31 g, 15.00 mmol) in 50% yield.

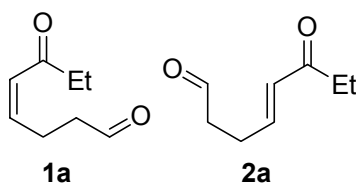


Typical reaction procedure for nucleophilic 1,2-addition to 5: 2-ethyl-3-cyclohexene-1,2-diol (6a).¹ To a stirred solution of **5** (2.44 g, 15.84 mmol) in THF (30 mL) was added 1 M THF solution of EtMgBr (50 mL, 47.53 mmol) at 0 °C. The mixture was stirred at that temperature for 0.5 h and then stirred at room temperature for 0.5 h. It was then quenched by the addition of a saturated aq solution of NH₄Cl (40 mL). The resulting mixture was stirred for 1 h more, diluted with ethyl acetate, wash with saturated aq NaCl solution, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford diol **6a** (1.079 g, 7.60 mmol) in 48 % yield as a mixture of diastereoisomers.

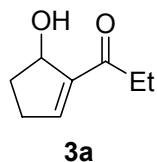
Table 1. Synthesis of intramolecular MBH reaction substrates.

Entry	Compounds	1:2	Combined yield (%) ^a
1	1a + 2a , R = -Et	4.1:1	53
2	1b + 2b , R = -Bu	8.8:1	40
3	1c + 2c , R = -Ph	4.8:1	57
4	1d + 2d , R = -C ₆ H ₄ -4-Cl	1.9:1	39
5	1e + 2e , R = -C ₆ H ₄ -3-Me	9.7:1	66
6	1f + 2f , R = -C ₆ H ₄ -4-Me	6.7:1	57

^a Isolated yield.



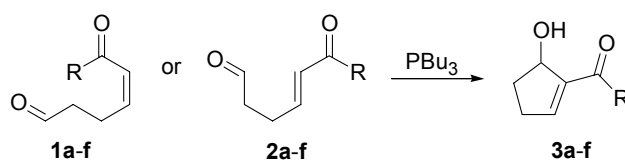
Typical reaction procedure for oxidative cleavage reactions: (Z)-6-oxo-4-octenal (1a) and (E)-6-oxo-4-octenal (2a).¹ To a stirred solution of **6a** (253 mg, 1.78 mmol) in MeCN (20 mL) was added Pb(OAc)₄ (830 mg, 1.78 mmol). The reaction mixture was stirred at room temperature for 15 min, diluted with ethyl acetate, washed with 1 M aq HCl solution, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford **1a** (106 mg, 0.76 mmol) in 42% yield and **2a** (26 mg, 0.19 mmol) in 10% yield. These dicarbonyl compounds were found to be relatively unstable and had to be used in the intramolecular MBH reactions soon after preparation.



Typical reaction procedure for the intramolecular Morita-Baylis-Hillman reactions:

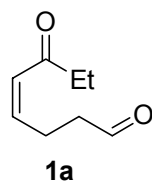
1-(5-hydroxy-1-cyclopentenyl)-1-propanone (3a).¹ To a stirred solution of **1a** (105 mg, 0.75 mmol) in *t*-BuOH (7.5 mL) was added PPh₃ (197 mg, 0.75 mmol) at 40 °C. The mixture was stirred at that temperature for 60 h, diluted with ethyl acetate, washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford **3a** (76 mg, 0.54 mmol) in 72% yield.

Table 2. Intramolecular MBH reaction results using PBU₃ as the catalyst.

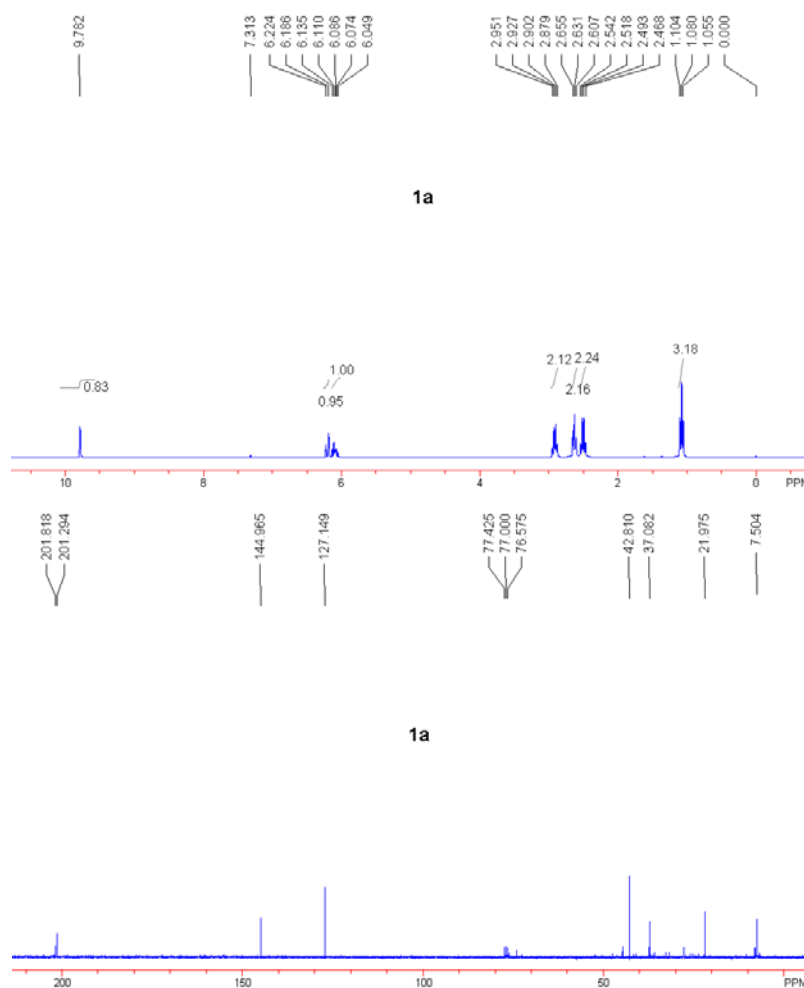


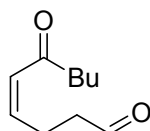
Entry	Substrate	Solvent	Conc.	Temp.	Time	Product	Yield (%) ^a
3	1a , R = -Et	<i>t</i> -BuOH	0.1 M	40 °C	48 h	3a	17
4	2a , R = -Et	<i>t</i> -BuOH	0.1 M	40 °C	48 h	3a	0
11	1c , R = -Ph	CH ₃ CN	0.1 M	rt	12 h	3c	27
12	2c , R = -Ph	CH ₃ CN	0.1 M	rt	12 h	3c	0

^a Isolated yield.



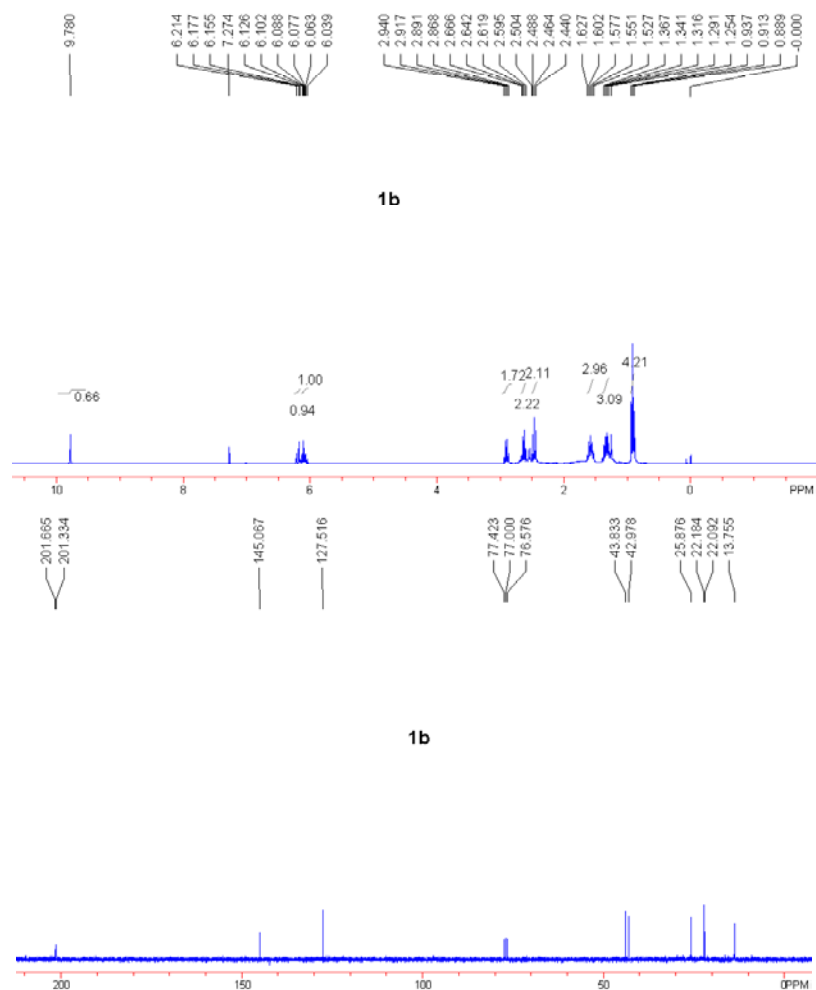
(Z)-6-Oxo-4-octenal (1a).¹ Yellow oil; IR (CH₂Cl₂): ν 3448, 2973, 2938, 2728, 1748, 1697, 1631, 1374, 1074, 982, 817 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.08 (3H, t, $J = 7.4$ Hz, CH₃), 2.51 (2H, q, $J = 7.2$ Hz, CH₂), 2.63 (2H, t, $J = 7.2$ Hz, CH₂), 2.92 (2H, q, $J = 7.2$ Hz, CH₂), 6.09 (1H, dt, $J_d = 11.1$ Hz, $J_t = 7.5$ Hz, CH), 6.21 (1H, t, $J = 11.4$ Hz, CH), 9.78 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 7.5, 22.0, 37.1, 42.8, 127.1, 145.0, 201.3, 201.8; MS (EI) m/z (%): 140 (1.2) [M⁺], 111 (14.5), 83 (25.2), 66 (100), 57 (30.2); HRMS (EI) calcd. for C₈H₁₂O₂ (M⁺) requires 140.0837, found 140.0818.

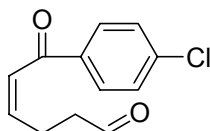




1b

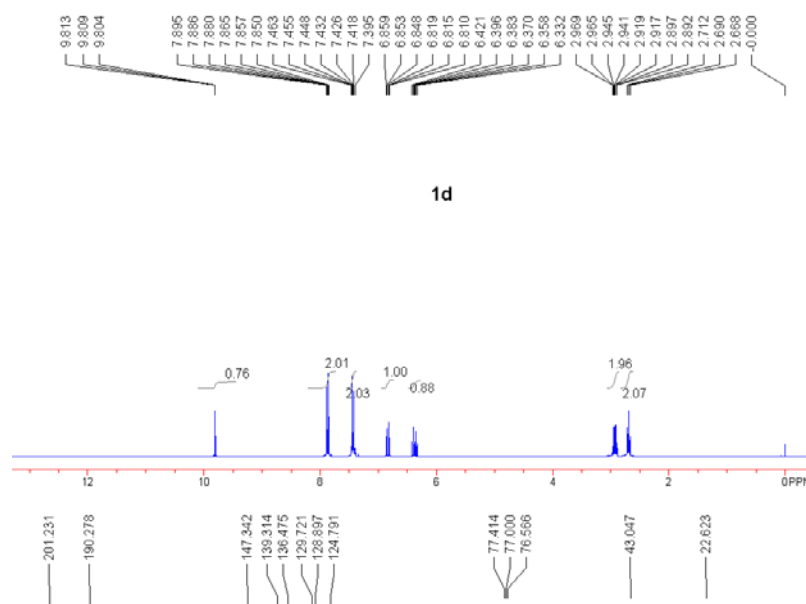
(Z)-6-Oxo-4-decenal (1b).¹ Yellow oil; IR (CH₂Cl₂): ν 3431, 2958, 2932, 2724, 1725, 1691, 1618, 1412, 1379, 1062, 980, 751 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.91 (3H, t, J = 7.2 Hz, CH₃), 1.25-1.37 (2H, m, CH₂), 1.53-1.63 (2H, m, CH₂), 2.44-2.50 (2H, m, CH₂), 2.60-2.67 (2H, m, CH₂), 2.90 (2H, q, J = 7.2 Hz, CH₂), 6.08 (1H, dt, J_d = 11.4 Hz, J_t = 7.4 Hz, CH), 6.20 (1H, t, J = 11.1 Hz, CH), 9.78 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.8, 22.1, 22.2, 25.9, 43.0, 43.8, 127.5, 145.1, 201.3, 201.7; MS (EI) m/z (%): 168 (0.9) [M⁺], 139 (9.5), 93 (13.2), 85 (20.7), 66 (100), 57 (29.6); HRMS (EI) calcd. for C₁₀H₁₆O₂ (M⁺) requires 168.1150, found: 168.1131.



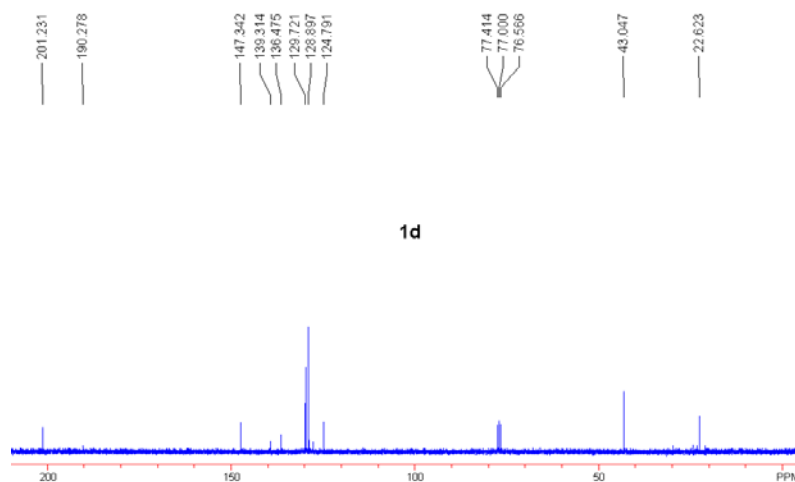


1d

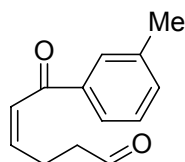
(Z)-6-(4-Chlorophenyl)-6-oxo-4-hexenal (1d). Yellow oil; IR (CH₂Cl₂): ν 3460, 3063, 2932, 2853, 2726, 1725, 1668, 1490, 1401, 1092, 1010, 828, 530 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.69 (2H, t, J = 6.6 Hz, CH₂), 2.93 (2H, ddd, J_d = 1.2 Hz, J_d = 7.2 Hz, J_d = 13.7 Hz, CH₂), 6.38 (1H, dt, J_d = 11.4 Hz, J_t = 7.5 Hz, CH), 6.83 (1H, dt, J_d = 11.7 Hz, J_t = 1.5 Hz, CH), 7.42-7.46 (2H, m, ArH), 7.85-7.90 (2H, m, ArH), 9.81 (1H, t, J = 1.4 Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 22.6, 43.0, 124.8, 128.9, 129.7, 136.5, 139.3, 147.3, 190.3, 201.2; MS (EI) m/z (%): 222 (0.7) [M⁺], 204 (3.5), 141 (26.5), 139 (100), 111 (26.9), 75 (8.3); HRMS (EI) calcd. for C₁₂H₁₁O₂Cl (M⁺) requires 222.0448, found: 222.0447.



1d

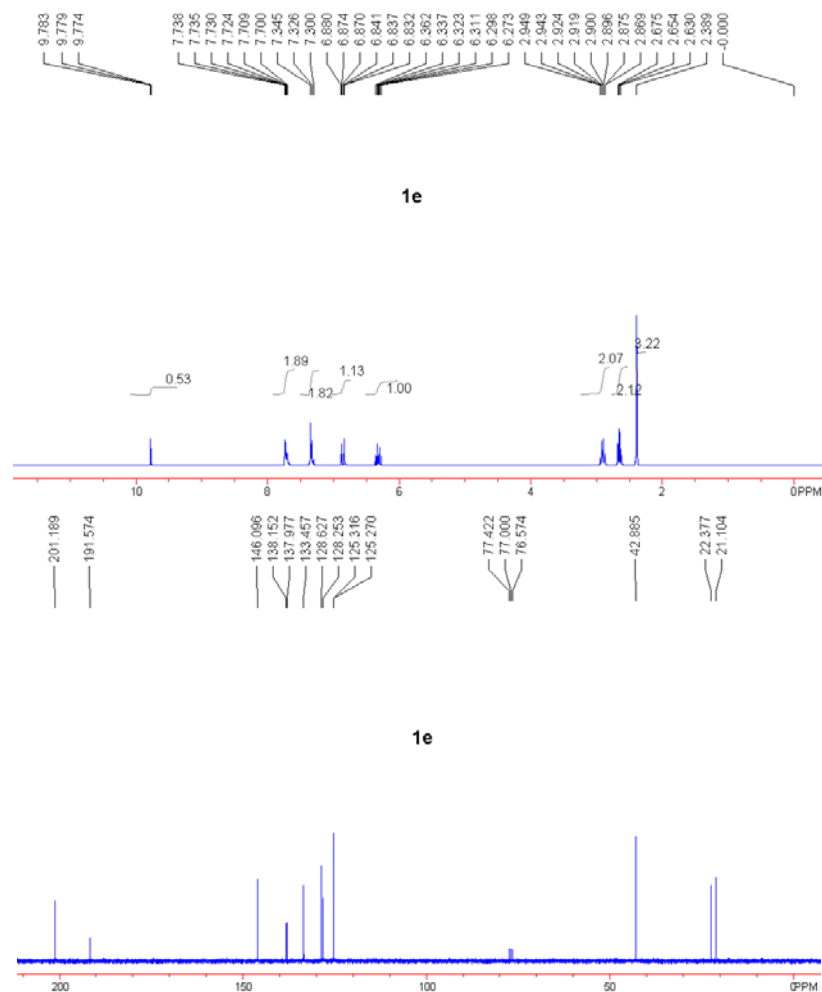


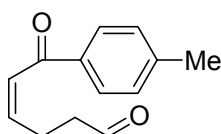
1d



1e

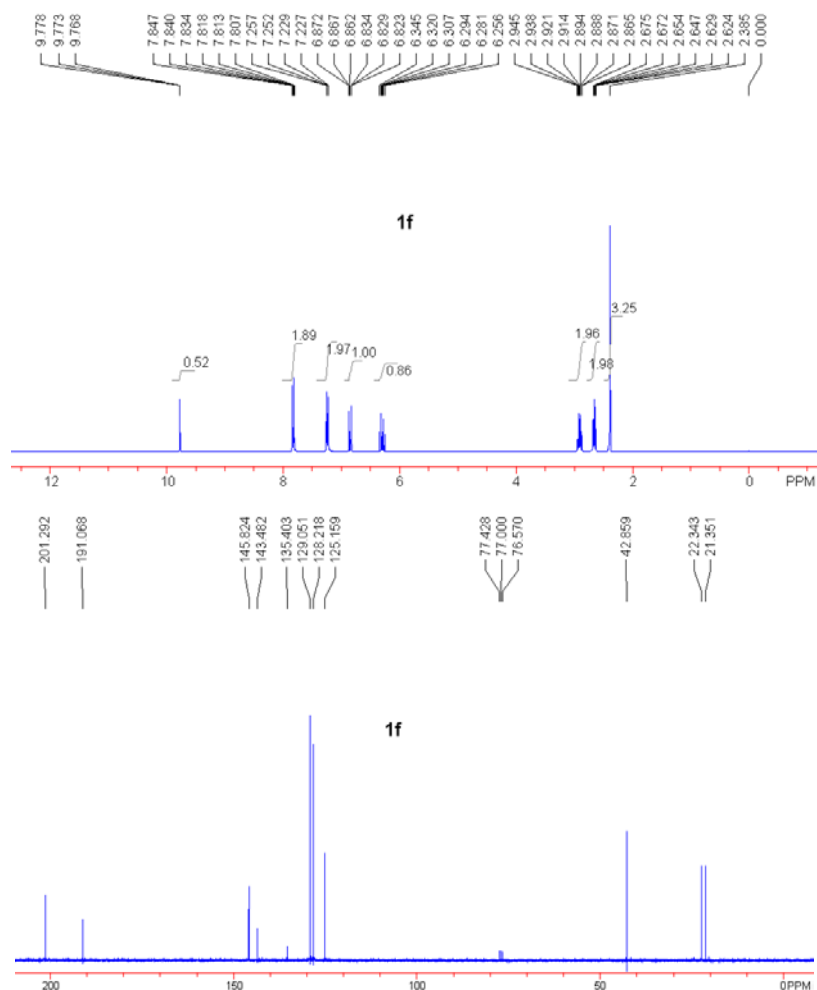
(Z)-6-Oxo-6-m-tolyl-4-hexenal (1e). Yellow oil; IR (CH₂Cl₂): ν 3424, 3056, 2924, 2832, 2727, 1724, 1666, 1613, 1437, 1051, 1022, 767, 613 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.39 (3H, s, CH₃), 2.65 (2H, t, $J = 6.8$ Hz, CH₂), 2.91 (2H, ddd, $J_d = 1.5$ Hz, $J_d = 7.5$ Hz, $J_d = 14.7$ Hz, CH₂), 6.32 (1H, dt, $J_d = 11.7$ Hz, $J_t = 7.5$ Hz, CH), 6.86 (1H, dt, $J_d = 11.6$ Hz, $J_t = 1.5$ Hz, CH), 7.30-7.35 (2H, m, ArH), 7.70-7.74 (2H, m, ArH), 9.78 (1H, t, $J = 1.4$ Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.1, 22.4, 42.9, 125.3, 125.3, 128.3, 128.6, 133.5, 138.0, 138.2, 146.1, 191.6, 201.2; MS (EI) m/z (%): 202 (1.5) [M⁺], 184 (10.1), 119 (100), 91 (80.8), 65 (27.8); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0991.

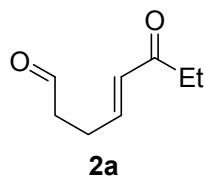




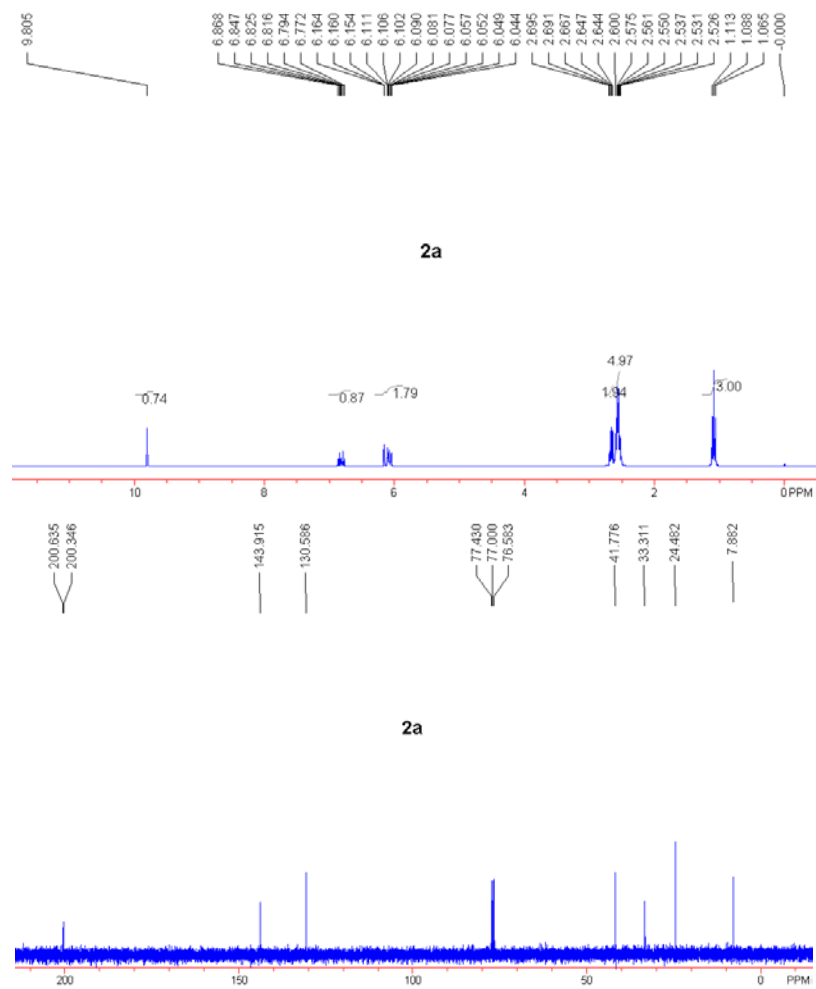
1f

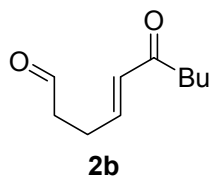
(Z)-6-Oxo-6-p-tolyl-4-hexenal (1f). Yellow oil; IR (CH₂Cl₂): ν 3428, 3031, 2923, 2827, 2727, 1723, 1662, 1608, 1422, 1181, 1010, 778 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.39 (3H, s, CH₃), 2.65 (2H, dt, $J_d = 1.5$ Hz, $J_t = 7.1$ Hz, CH₂), 2.90 (2H, ddd, $J_d = 2.0$ Hz, $J_d = 7.1$ Hz, $J_d = 15.0$ Hz, CH), 6.30 (1H, dt, $J_d = 11.7$ Hz, $J_t = 7.7$ Hz, CH), 6.85 (1H, dt, $J_d = 11.7$ Hz, $J_t = 7.5$ Hz, CH), 7.23-7.26 (2H, m, ArH), 7.81-7.85 (2H, m, ArH), 9.77 (1H, t, $J = 1.5$ Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.4, 22.3, 42.9, 125.2, 128.2, 129.1, 135.4, 143.5, 145.8, 191.1, 201.3; MS (EI) m/z (%): 202 (1.2) [M⁺], 173 (12.1), 119 (100), 91 (53.1), 65 (16.1); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0997.



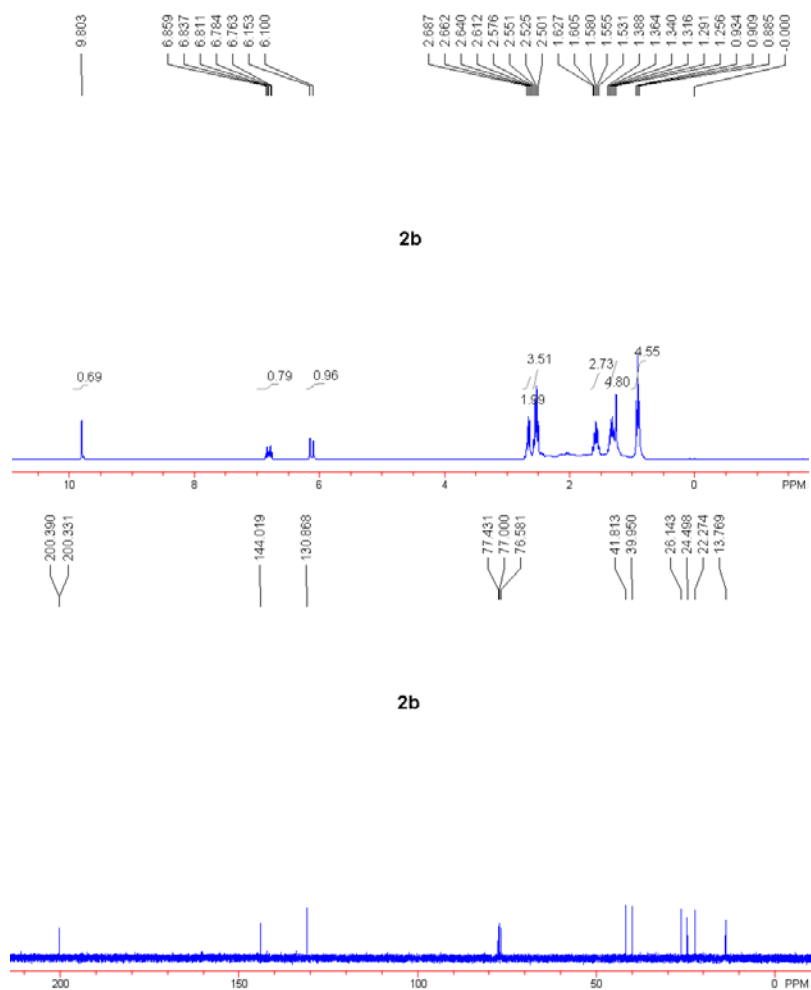


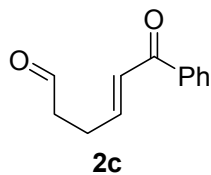
(E)-6-Oxo-4-octenal (2a).¹ Yellow oil; IR (CH₂Cl₂): ν 3429, 2974, 2937, 2726, 1724, 1693, 1622, 1459, 1413, 1379, 1121, 1040, 980, 816 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.09 (3H, t, $J = 7.2$ Hz, CH₃), 2.53-2.60 (4H, m, CH₂), 2.64-2.70 (2H, m, CH₂), 6.12 (1H, dt, $J_d = 15.4$ Hz, $J_t = 1.5$ Hz, CH), 6.82 (1H, dt, $J_d = 15.9$ Hz, $J_t = 6.6$ Hz, CH), 9.81 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 7.9, 24.5, 33.3, 41.8, 130.6, 143.9, 200.3, 200.6; MS (EI) m/z (%): 140 (2.5) [M⁺], 111 (57.3), 83 (85.2), 57 (20.5), 55 (100); HRMS (EI) calcd. for C₈H₁₂O₂ (M⁺) requires 140.0837, found: 140.0851.



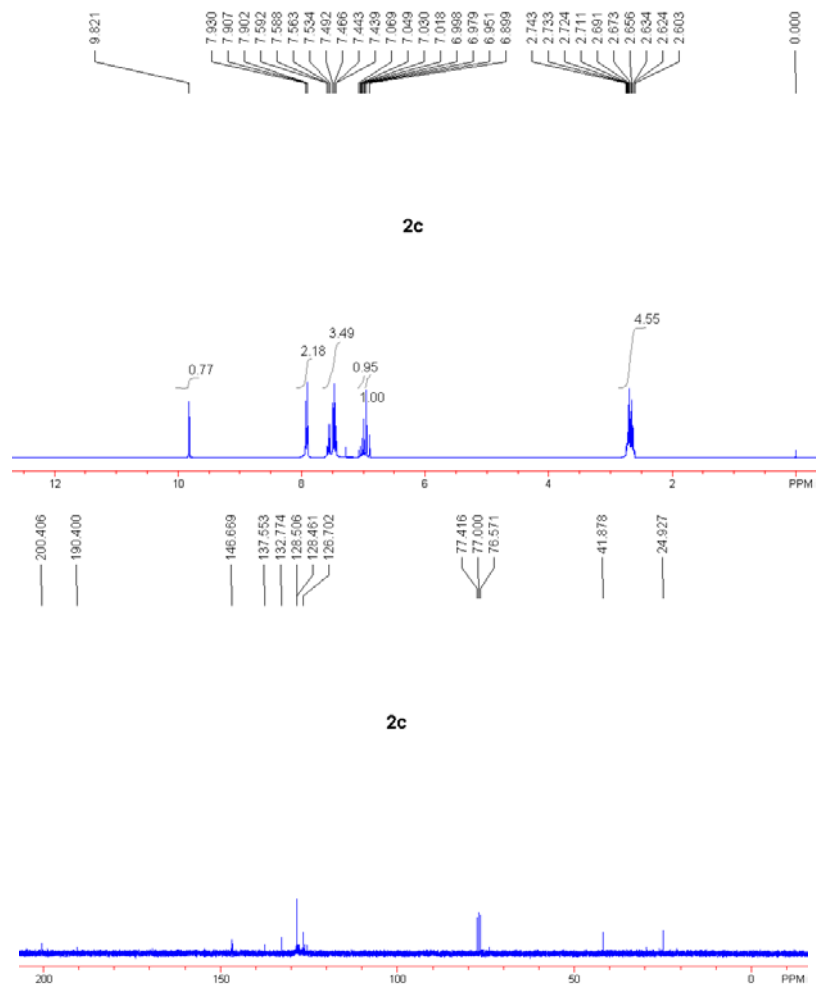


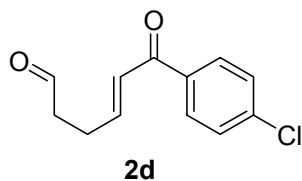
(E)-6-Oxo-4-decenal (2b).¹ Yellow oil; IR (CH₂Cl₂): ν 3448, 2932, 2871, 2727, 1728, 1655, 1629, 1458, 1374, 1045, 748, 606 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.91 (3H, t, J = 7.4 Hz, CH₃), 1.26-1.39 (4H, m, CH₂), 1.53-1.63 (2H, m, CH₂), 2.50-2.57 (2H, m, CH₂), 2.61-2.69 (2H, m, CH₂), 6.13 (1H, d, J = 15.9 Hz, CH), 6.81 (1H, dt, J_d = 15.0 Hz, J_t = 6.9 Hz, CH), 9.80 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.8, 22.3, 24.5, 26.1, 40.0, 41.8, 130.9, 144.0, 200.3, 200.4; MS (EI) m/z (%): 168 (1.6) [M⁺], 143 (9.5), 129 (26.1), 109 (27.7), 69 (46.8), 55 (100), 41 (62.6); HRMS (EI) calcd. for C₁₀H₁₆O₂ (M⁺) requires 168.1150, found: 168.1127.



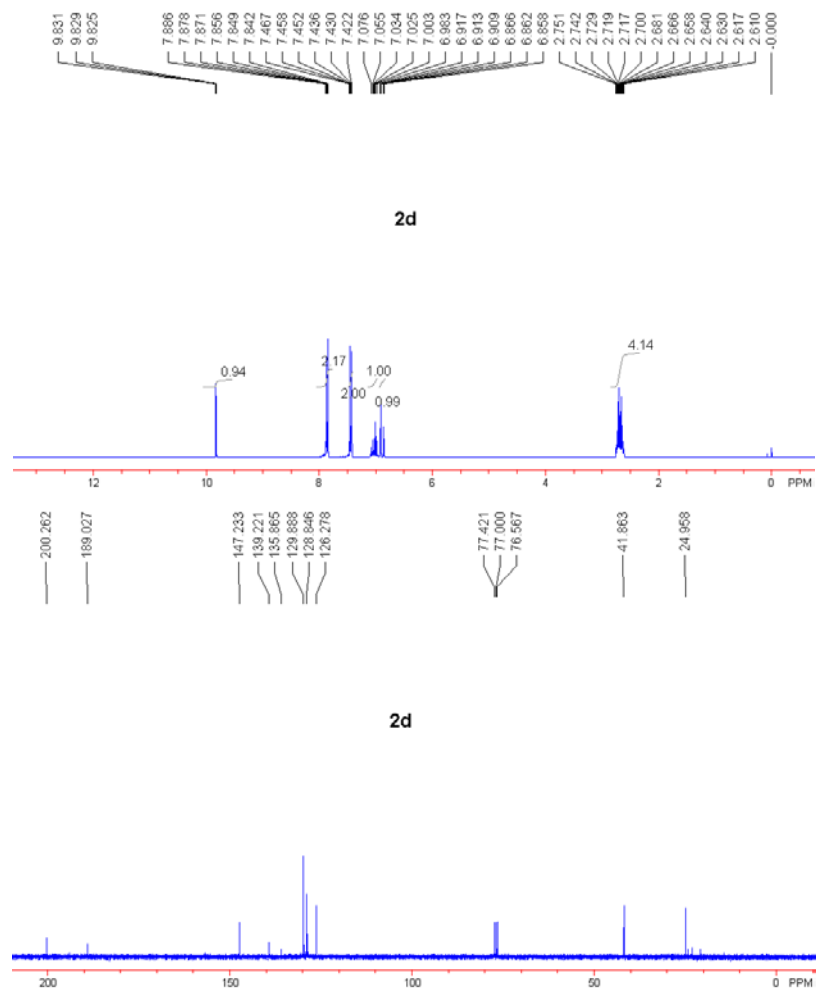


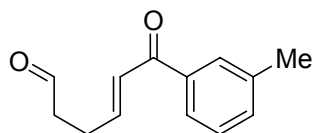
(E)-6-Oxo-6-phenyl-4-hexenal (2c).¹ Yellow oil; IR (CH₂Cl₂): ν 3426, 3060, 2925, 2854, 2727, 1723, 1668, 1620, 1448, 1005, 977, 742, 694 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.60-2.74 (4H, m, CH₂), 6.93 (1H, d, $J = 15.6$ Hz, CH), 7.01 (1H, dt, $J_d = 15.3$ Hz, $J_t = 5.9$ Hz, CH), 7.45-7.59 (3H, m, ArH), 7.90-7.93 (2H, m, ArH), 9.82 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 24.9, 41.9, 126.7, 128.5, 128.5, 132.8, 137.6, 146.7, 190.4, 200.4; MS (EI) m/z (%): 188 (1.6) [M⁺], 159 (28.6), 105 (100), 77 (41.5), 55 (10.1); HRMS (EI) calcd. for C₁₂H₁₂O₂ (M⁺) requires 188.0837, found: 188.0839.





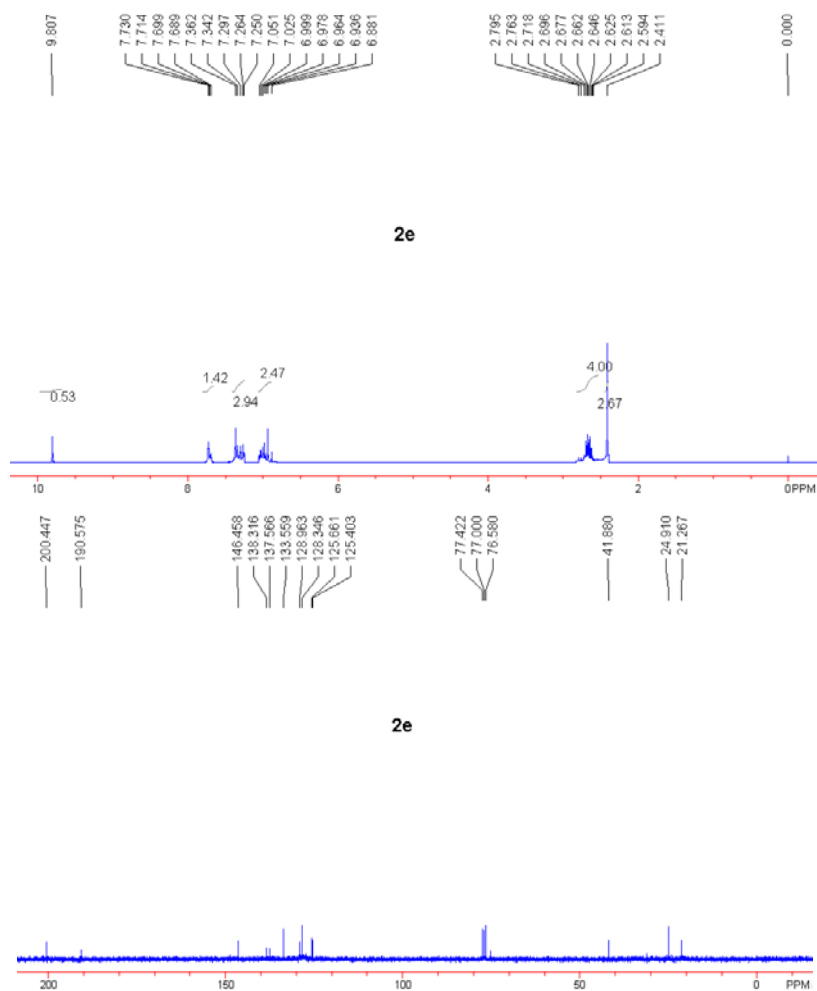
(E)-6-(4-Chlorophenyl)-6-oxo-4-hexenal (2d). Yellow oil; IR (CH₂Cl₂): ν 3475, 3034, 2936, 2875, 1748, 1695, 1618, 1428, 1373, 1074, 1042, 919, 816, 747 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.61-2.75 (4H, m, CH₂), 6.89 (1H, dt, $J_d = 15.3$ Hz, $J_t = 1.2$ Hz, CH), 7.03 (1H, dt, $J_d = 15.6$ Hz, $J_t = 6.5$ Hz, CH), 7.42-7.47 (2H, m, ArH), 7.84-7.89 (2H, m, ArH), 9.83 (1H, t, $J = 1.1$ Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 25.0, 41.9, 126.3, 128.8, 129.9, 135.9, 139.2, 147.2, 189.0, 200.3; MS (EI) m/z (%): 222 (16.9) [M⁺], 193 (35.3), 180 (12.1), 138 (100), 111 (25.5); HRMS (EI) calcd. for C₁₂H₁₁O₂Cl (M⁺) requires 222.0448, found: 222.0444.

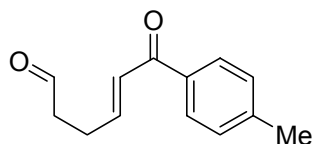




2e

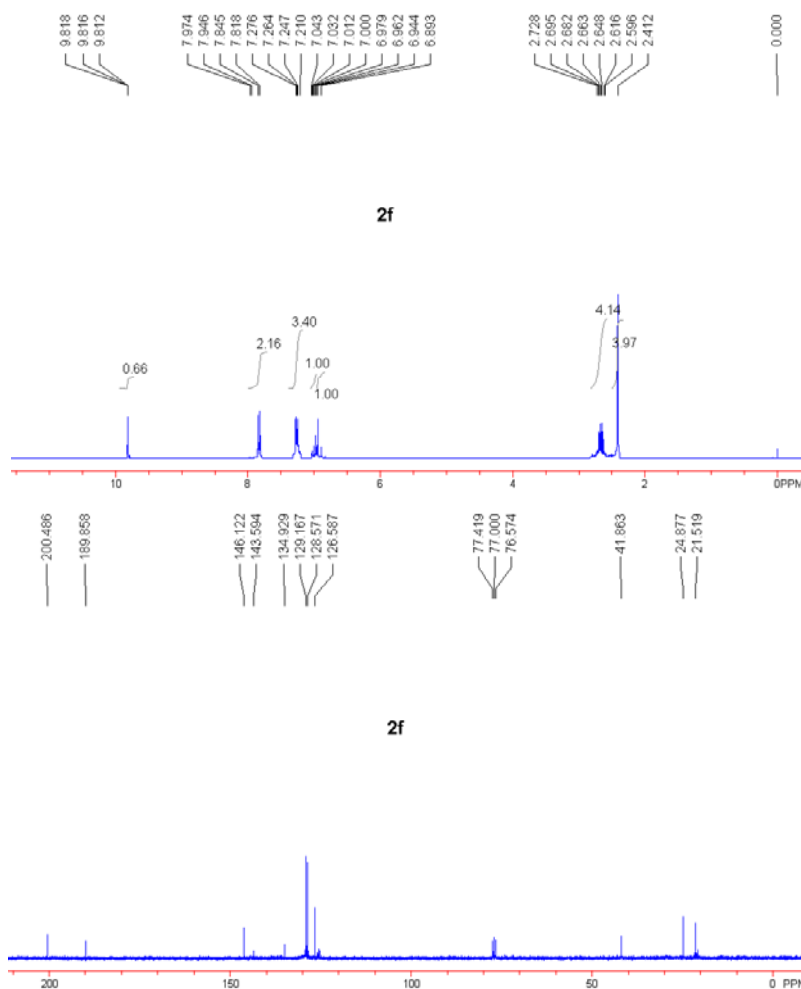
(E)-6-Oxo-6-m-tolyl-4-hexenal (2e). Yellow oil; IR (CH₂Cl₂): ν 3450, 2925, 2875, 2720, 1721, 1668, 1622, 1429, 1054, 1009, 781 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.41 (3H, s, CH₃), 2.59-2.80 (4H, m, CH₂), 6.88-7.05 (2H, m, CH), 7.25-7.36 (3H, m, ArH), 7.69-7.73 (1H, m, ArH), 9.81 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.3, 24.9, 41.9, 125.4, 125.7, 128.3, 129.0, 133.6, 137.6, 138.3, 146.5, 190.6, 200.4; MS (EI) m/z (%): 202 (2.1) [M⁺], 173 (9.0), 119 (100), 91 (36.2), 65 (8.9); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0995.

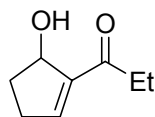




2f

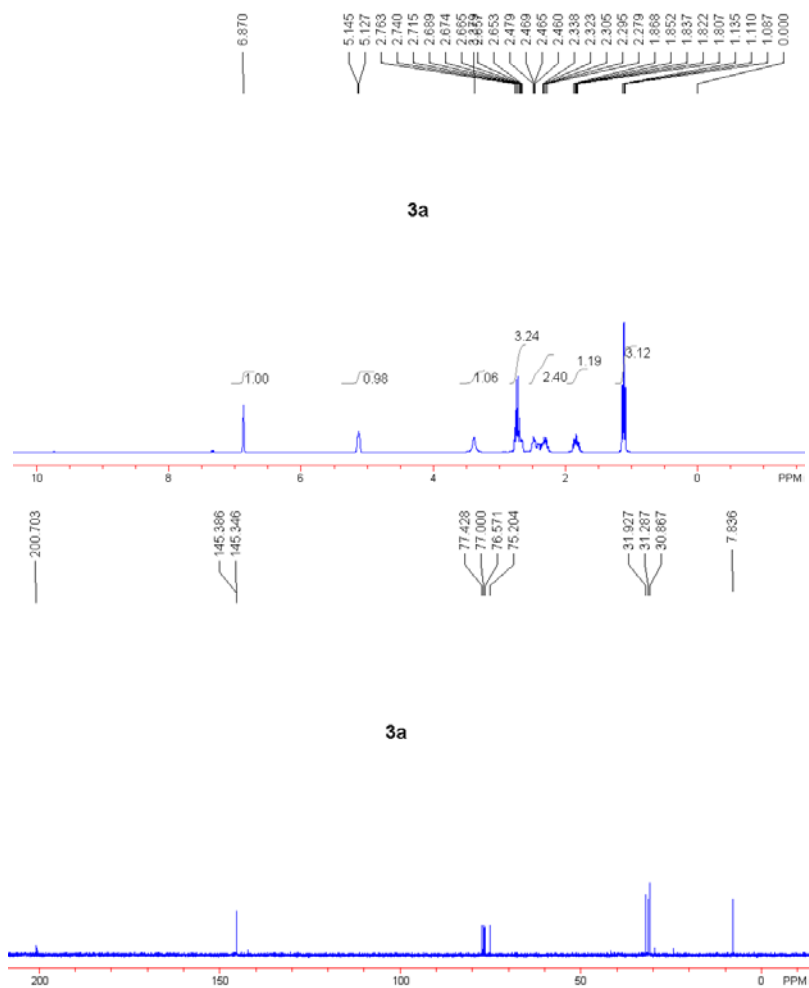
(E)-6-Oxo-6-p-tolyl-4-hexenal (2f). Yellow oil; IR (CH₂Cl₂): ν 3428, 3031, 2922, 2828, 2726, 1724, 1669, 1621, 1571, 1410, 1181, 1042, 977, 810, 726 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 2.41 (3H, s, CH₃), 2.60-2.73 (4H, m, CH₂), 6.92 (1H, d, J = 15.3 Hz, CH), 6.96-7.04 (1H, m, CH), 7.21-7.28 (2H, m, ArH), 7.82-7.97 (2H, m, ArH), 9.82 (1H, t, J = 1.5 Hz, CHO); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.5, 24.9, 41.9, 126.6, 128.6, 129.2, 134.9, 143.6, 146.1, 189.9, 200.5; MS (EI) m/z (%): 202 (3.0) [M⁺], 173 (21.8), 119 (100), 91 (32.6), 65 (9.5); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.1005.

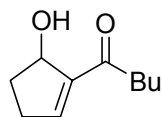




3a

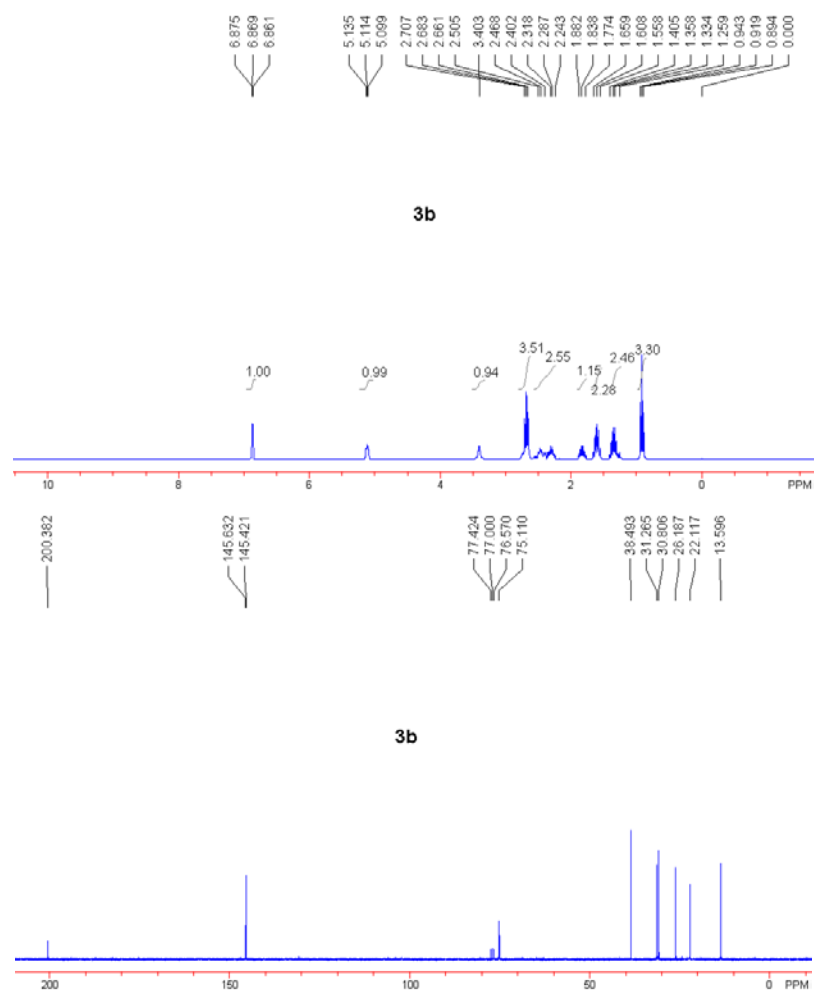
1-(5-Hydroxy-1-cyclopentenyl)propanone (3a).¹ Yellow oil; IR (CH₂Cl₂): ν 3463, 3055, 2981, 2939, 2844, 1659, 1621, 1378, 1055, 739, 704 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.11 (3H, t, J = 7.2 Hz, CH₃), 1.81-1.87 (1H, m, CH₂), 2.28-2.48 (2H, m, CH₂), 2.65-2.76 (3H, m, CH₂), 3.38 (1H, s, OH), 5.13 (1H, br s, CH), 6.87 (1H, s, CH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 7.8, 30.9, 31.3, 31.9, 75.2, 145.3, 145.4, 200.7; MS (EI) m/z (%): 140 (3.5) [M⁺], 111 (100), 93 (17.2), 83 (79.2), 67 (20.6), 55 (29.6); HRMS (EI) calcd. for C₈H₁₂O₂ (M⁺) requires 140.0837, found: 140.0853.

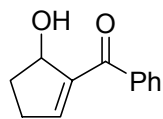




3b

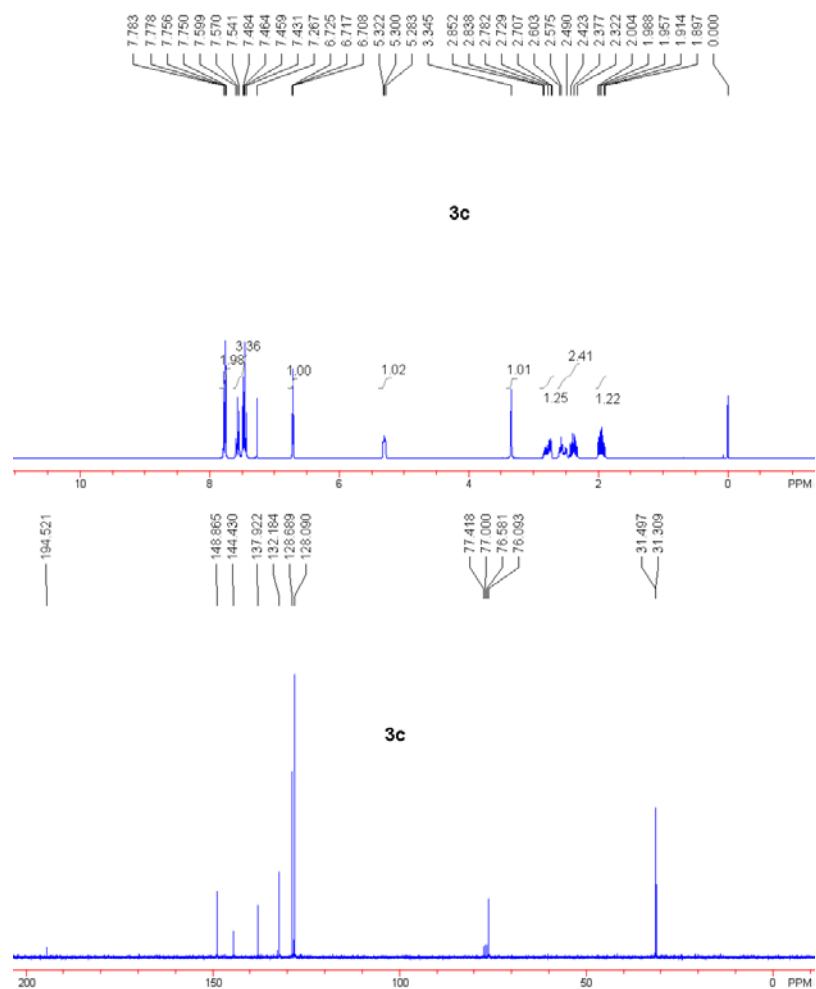
1-(5-Hydroxy-1-cyclopentenyl)pentanone (3b).¹ Yellow oil; IR (CH₂Cl₂): ν 3487, 3055, 2933, 2871, 1659, 1619, 1455, 1380, 1055, 982, 739 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 0.92 (3H, t, J = 7.4 Hz, CH₃), 1.26-1.41 (2H, m, CH₂), 1.56-1.66 (2H, m, CH₂), 1.77-1.88 (1H, m, CH₂), 2.24-2.51 (2H, m, CH₂), 2.66-2.71 (3H, m, CH₂), 3.40 (1H, s, OH), 5.12 (1H, br s, CH), 6.87 (1H, t, J = 2.1 Hz, CH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 13.6, 22.1, 26.2, 30.8, 31.3, 38.5, 75.1, 145.4, 145.6, 200.4; MS (EI) m/z (%): 168 (0.6) [M⁺], 150 (13.0), 126 (15.7), 111 (100), 83 (48.7), 55 (30.2); HRMS (EI) calcd. for C₁₀H₁₆O₂ (M⁺) requires 168.1150, found: 168.1130.

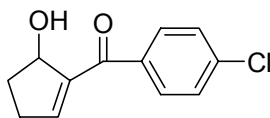




3c

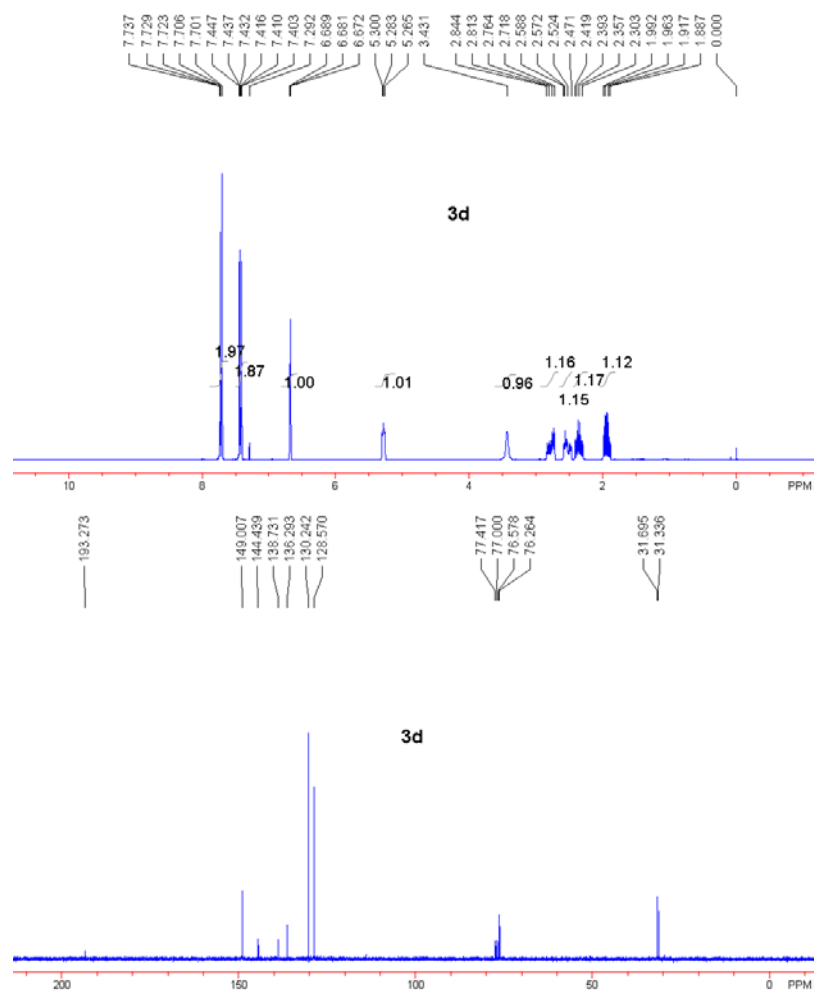
(5-Hydroxy-1-cyclopentenyl)-phenyl-methanone (3c).¹ Yellow oil; IR (CH₂Cl₂): ν 3441, 3059, 2937, 1641, 1598, 1446, 1352, 1053, 931, 724, 697 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.90-2.00 (1H, m, CH₂), 2.32-2.60 (2H, m, CH₂), 2.71-2.85 (1H, m, CH₂), 3.35 (1H, s, OH), 5.30 (1H, br s, CH), 6.72 (1H, t, J = 2.6 Hz, CH), 7.43-7.60 (3H, m, ArH), 7.75-7.78 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 31.3, 31.5, 76.1, 128.1, 128.7, 132.2, 137.9, 144.4, 148.9, 194.5; MS (EI) m/z (%): 188 (65.8) [M⁺], 170 (26.1), 128 (45.0), 105 (92.3), 83 (100), 77 (81.8); HRMS (EI) calcd. for C₁₂H₁₂O₂ (M⁺) requires 188.0837, found: 188.0842.

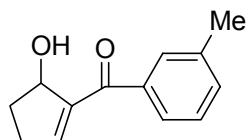




3d

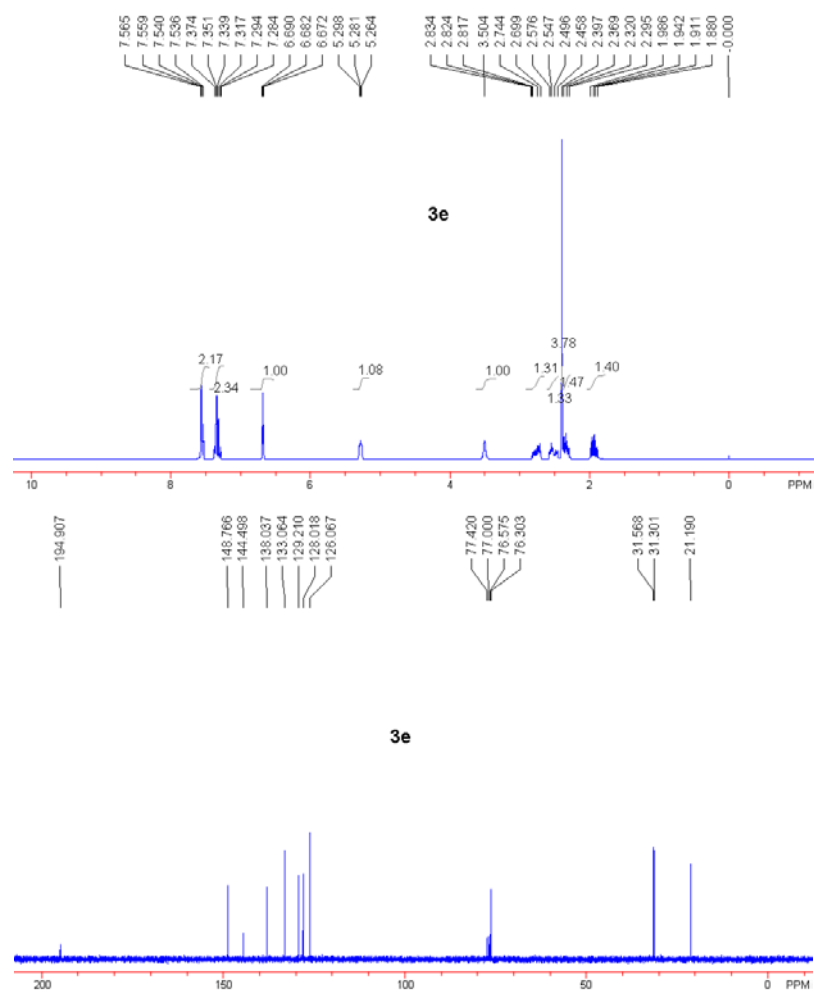
(5-Hydroxy-1-cyclopenteny)-4-chlorophenyl-methanone (3d).² Yellow oil; IR (CH₂Cl₂): ν 3443, 3056, 2930, 1639, 1586, 1486, 1400, 1347, 1175, 1014, 931, 839, 695 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.89-1.99 (1H, m, CH₂), 2.30-2.42 (1H, m, CH₂), 2.47-2.59 (1H, m, CH₂), 2.72-2.84 (1H, m, CH₂), 3.43 (1H, s, OH), 5.28 (1H, br s, CH), 6.68 (1H, t, $J = 2.6$ Hz, CH), 7.40-7.45 (2H, m, ArH), 7.70-7.74 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 31.3, 31.7, 76.3, 128.6, 130.2, 136.3, 138.7, 144.4, 149.0, 193.3; MS (EI) m/z (%): 222 (34.9) [M⁺], 204 (19.4), 187 (65.0), 139 (100), 111 (74.8), 83 (84.7); HRMS (EI) calcd. for C₁₂H₁₁O₂Cl (M⁺) requires 222.0448, found: 222.0448.

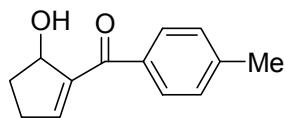




3e

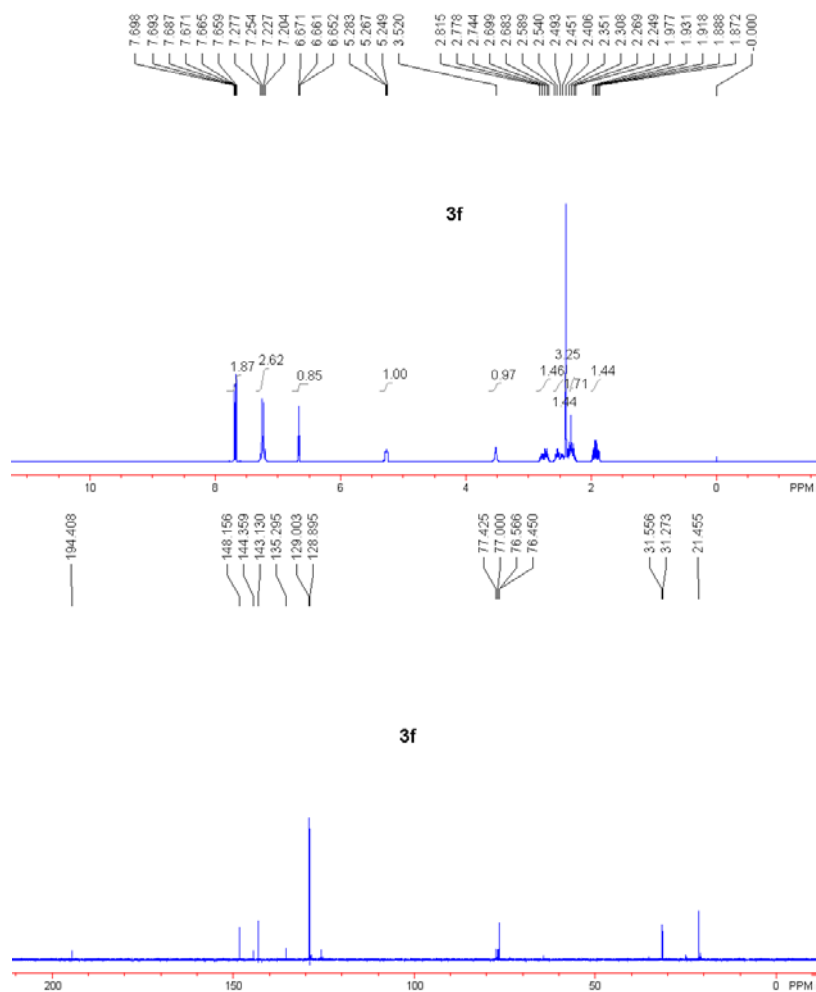
(5-Hydroxy-1-cyclopentenyl)-m-tolyl-methanone (3e). Yellow oil; IR (CH₂Cl₂): ν 3430, 3056, 2934, 1730, 1644, 1584, 1427, 1347, 1189, 1053, 931, 775 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.88-1.99 (1H, m, CH₂), 2.30-2.37 (1H, m, CH₂), 2.40 (3H, s, CH₃), 2.46-2.58 (1H, m, CH₂), 2.70-2.83 (1H, m, CH₂), 3.50 (1H, s, OH), 5.28 (1H, br s, CH), 6.68 (1H, t, J = 2.7 Hz, CH), 7.28-7.37 (2H, m, ArH), 7.54-7.57 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.2, 31.3, 31.6, 76.3, 126.1, 128.0, 129.2, 133.1, 138.0, 144.5, 148.8, 194.9; MS (EI) m/z (%): 202 (70.5) [M⁺], 187 (26.4), 159 (37.4), 119 (100), 83 (58.6); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0996.





3f

(5-Hydroxy-1-cyclopentenyl)-p-tolyl-methanone (3f). Yellow oil; IR (CH₂Cl₂): ν 3485, 3055, 2925, 2854, 1723, 1633, 1605, 1457, 1351, 1180, 1052, 739 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, TMS): δ 1.87-1.98 (1H, m, CH₂), 2.25-2.35 (1H, m, CH₂), 2.41 (3H, s, CH₃), 2.45-2.59 (1H, m, CH₂), 2.68-2.82 (1H, m, CH₂), 3.52 (1H, s, OH), 5.27 (1H, br s, CH), 6.66 (1H, t, *J* = 2.9 Hz, CH), 7.20-7.28 (2H, m, ArH), 7.66-7.70 (2H, m, ArH); ¹³C NMR (75 MHz, CDCl₃, TMS): δ 21.5, 31.3, 31.6, 76.5, 128.9, 129.0, 135.3, 143.1, 144.4, 148.2, 194.4; MS (EI) *m/z* (%): 202 (44.4) [M⁺], 187 (40.7), 159 (32.9), 119 (100), 83 (35.7); HRMS (EI) calcd. for C₁₃H₁₄O₂ (M⁺) requires 202.0994, found: 202.0991.



References:

1. Yeo, J. E.; Yang, X.-L.; Kim, H. J.; Koo, S. *Chem. Commun.* **2004**, 236-237.
2. Daniel, L. R.; Loraine, L.,-D.; Manuel G., V.; Craig, M. *Tetrahedron Lett.* **1983**, 24, 4499-4502.