Nucleophilic Acyl Substitutions of Anhydrides with Protic Nucleophiles Catalyzed by Amphoteric, Oxomolybdenum Species

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SUPPORTING INFORMATION

Representative experimental procedures, spectral data, and ^{1}H and ^{13}C NMR spectra for all the acylation products are included (148 pages).

General. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterochloroform with chloroform as an internal reference unless otherwise stated. Chemical shifts are reported in ppm (δ). Coupling constants, *J*, are reported in Hz. Infrared spectra were reported with peaks in units of cm^{-1} with the following relative intensities: br (broad), s (strong 67-100 %), m (medium 33-67 %), or w (weak 0-33 %). Mass spectra were recorded with an ionization voltage of 70 or 20 eV unless otherwise stated. Combustion analyses were performed by the Northern Instrument Center of Taiwan. Fast atom bombardment (FAB) and electrospray (ESI) mass spectra were reported with data in the form m/e (intensity relative to base peak). Gel permeation chromatography (GPC) data were obtained by using THF as eluting solvent at room temperature and a polystyrene calibration curve for analyses. Analytical TLC was visualized with UV light or with phosphomolybdic acid (PMA) and $KMnO_4$ staining agents. Column (flash) chromatography was performed using 32-63 μm silica gel. Solvents for extraction and chromatography were reagent grade. Dichloromethane was dried over CaH_2 before use. THF was dried over Na with benzophenone-ketyl intermediate as indicator. All reactions were run under nitrogen and the acylation products were isolated as chromatographically pure materials. The VOX_2 series of compounds (brand name as *Clip-all*® series, US patent # 6,541,659 B1, **2003**) is now available directly from the institution (e-mail: chefv043@scc.ntnu.edu.tw).

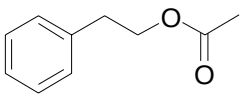
General procedure for acylation reactions

In a dry 50-mL, two-necked, round-bottomed flask was placed MoO_2Cl_2 (1.9 mg, 0.01 mmol) in 3 mL of anhydrous solvent (CH_2Cl_2 was used unless it is stated otherwise). To the above solution, anhydride (1.5 mmol) was slowly added at ambient temperature. After for 30 min, a solution of nucleophile (1.0 mmol in CH_2Cl_2, 2 mL) was slowly added to the above bluish solution and the reaction mixture was stirred for indicated time periods. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with cold, saturated aqueous $NaHCO_3$ solution (5 mL). For the acylation of β-hydroxy ketones or esters, ice-cold water was used to quench the reaction to prevent β-elimination. The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography on silica gel if required (in most of the acetylation reactions, essentially pure material was obtained without further purification). The product obtained was characterized by routine spectroscopic methods.

General procedure for catalyst recovery

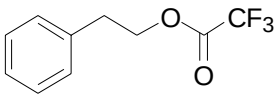
In a dry 250-mL, two-necked, round-bottomed flask was placed MoO_2Cl_2 (100 mg, 0.5 mmol) in 50 mL of anhydrous solvent (CH_2Cl_2 was used unless it is stated otherwise). To the above solution, anhydride (75 mmol) was slowly added at ambient temperature. After for 30 min, a solution of nucleophile (50 mmol in CH_2Cl_2, 20 mL) was slowly added to the above bluish solution and the reaction mixture was stirred for indicated time periods. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with ice-cold water (100 mL). The separated aqueous layer was concentrated by rotatory evaporator at 40 ^oC. Subsequently, the recovered catalyst was dried in *vacuo* at ambient temperature for 2 hours to get bluish solid (100 mg) in essentially quantitative recovery.

2-Phenylethyl Acetate[1]



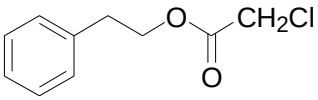
Data: ^1H NMR (200 MHz, $CDCl_3$) 7.34-7.22 (m, 5H), 4.30 (t, J = 7.2, 2H), 2.95 (t, J = 7.2, 2H), 2.05 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) 171.96, 137.80, 128.85, 128.47, 126.53, 64.89, 35.07, 20.93; TLC R_f 0.62 (EtOAc/hexane, 1/ 20).

Trifluoroacetic acid phenethyl ester[2]



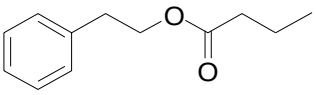
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.39-7.20 (m, 5H), 4.55 (t, J = 7.0, 2H), 3.05 (t, J = 7.0, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 157.35 ($J_{C\text{-}F}$ = 41.8), 136.35, 128.87, 128.69, 127.01, 114.68 ($J_{C\text{-}F}$ = 283.7), 68.17, 34.38; MS (70 eV) 218 (M^+, 60), 206 (10), 192 (15), 191 (64), 178 (12), 151 (12), 141 (16), 131 (100), 124 (16); TLC R_f 0.31 (EtOAc/hexane, 1/20).

Chloroacetic acid phenethyl ester[3]



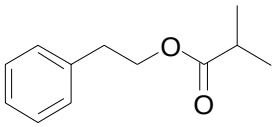
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.35-7.23 (m, 5H), 4.42 (t, J = 6.8, 2H), 4.04 (s, 2H), 2.99 (t, J = 6.8, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 167.09, 137.10, 128.8, 128.47, 126.64, 66.42, 40.72, 34.79; MS (FAB) 265 (100), 221 (M+Na^+, 51); TLC R_f 0.31 (EtOAc/hexane, 1/20).

Butanoic acid phenethyl ester[4]



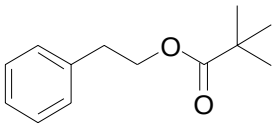
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.33-7.22 (m, 5H), 4.30 (t, J = 7.2, 2H), 2.95 (t, J = 7.2, 2H), 2.28 (t, J = 7.2, 2H), 1.68-1.59 (m, 2H), 0.93 (t, J = 7.6, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 173.55, 137.85, 128.85, 128.42, 126.47, 64.62, 36.15, 35.12, 18.35, 13.59; IR (CH_2Cl_2) 3061 (s), 2988 (s), 1730 (s), 1423 (s), 1281 (s), 1181 (s), 1089 (m), 991 (m), 897(s), 764 (s), 454 (w); MS (70 eV) 192 (M^+, 4), 149 (11), 120 (9), 104 (100), 91 (89), 77 (12), 71 (52), 57 (55); TLC R_f 0.32 (EtOAc/hexane, 1/20).

Isobutyric acid phenethyl ester[5]



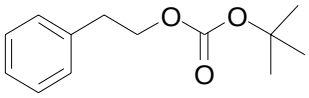
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.35-7.21 (m, 5H), 4.30 (t, J = 7.0, 2H), 2.95 (t, J = 7.0, 2H), 2.62-2.42 (sept, J = 7.0, 1H), 1.14 (d, J = 7.0, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) 177.14, 137.95, 128.93, 128.45, 126.51, 64.64, 35.05, 33.90, 18.82; MS (20 eV) 193 (M+1^+, 92), 191 (78), 190 (35), 188 (14), 184 (25), 183 (46), 178 (37), 175 (86), 137 (29), 168 (46); TLC R_f 0.36 (EtOAc/hexane, 1/20).

2-Phenylethyl 2, 2-Dimethylpropanoate[6]



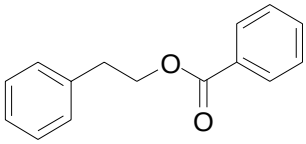
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.34-7.24 (m, 5H), 4.31 (t, J = 7.0, 2H), 2.96 (t, J = 7.0, 2H), 1.20 (s, 9H, CH_3×3); ^{13}C NMR (50 MHz, $CDCl_3$) 178.31, 137.92, 128.87, 128.32, 126.39, 64.72, 38.6, 35.09, 27.08; TLC R_f 0.54 (EtOAc/hexane, 1/20).

Carbonic acid *tert*-butyl ester phenethyl ester[7]



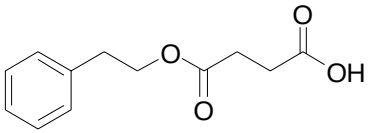
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.32-7.22 (m, 5H), 4.29 (t, *J* = 7.4, 2H), 2.98 (t, *J* = 7.4, 2H), 1.49 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 153.39, 137.32, 128.83, 128.40, 126.46, 81.67, 67.15, 35.02, 27.51; MS (70 eV) 223 ($M+1^+$, 18), 222 (M^+, 10), 207 (14), 167 (100), 160 (10), 145 (10); TLC R_f 0.55 (EtOAc/hexane, 1/20).

2-Phenylethyl Benzoate[8]



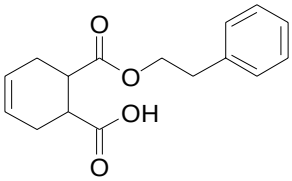
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.08-8.03 (m, 2H), 7.61-7.26 (m, 8H), 4.53 (t, *J* = 7.0, 2H), 3.11 (t, *J* = 7.0, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 166.58, 137.95, 132.92, 130.33, 128.59, 128.98, 128.57, 128.36, 126.61, 65.41, 35.16; TLC R_f 0.32 (EtOAc/hexane, 1/40).

Succinic acid monophenethyl ester[9]



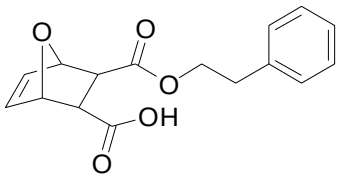
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 10.81 (bs, 1H), 7.36-7.20 (m, 5H), 4.33 (t, *J* = 7.0, 2H), 2.94 (t, *J* = 7.2, 2H) 2.68-2.62 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) 178.26, 172.16, 137.64, 128.86, 128.48, 126.55, 65.23, 34.85, 28.75, 28.69. MS (70 eV) 222 (M^+, 88), 216 (78), 210 (78), 208 (88), 206 (56), 200 (44), 198 (100), 193 (65), 186 (44), 185 (65), 183 (88); TLC R_f 0.22 (EtOAc/hexane, 1/4).

Cyclohex-4-ene-1, 2-dicarboxylic acid monophenethyl ester



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.19 (m, 5H), 5.66 (s, 2H), 4.33-4.29 (m, 2H), 3.06-3.01 (m, 2H), 2.92 (t, *J* = 6.8, 2H), 2.59-2.53 (m, 2H), 2.38-2.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 179.42, 173.06, 137.72, 128.81, 128.40, 126.45, 125.13, 65.17, 39.50, 39.47, 34.86, 25.70, 25.50; IR (CH_2Cl_2) 3495-2750 (br, m), 3055 (m), 2926 (m), 2254 (m), 1731 (s), 1710 (s), 1498 (m), 1390 (m), 1300 (m), 1270 (m), 1198 (s), 1031 (m), 911 (s), 702 (s); MS (70 eV) 275 ($M+1^+$, 6), 124 (13), 104 (100), 91 (20), 79 (48), 77 (28); TLC R_f 0.36 (EtOAc/hexane, 1/2).

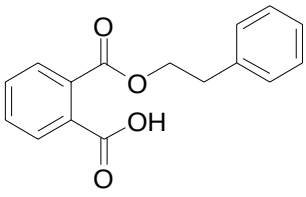
7-Oxa-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid monophenethyl ester



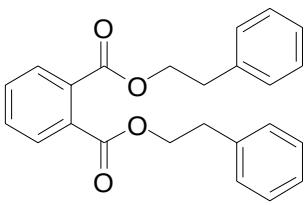
Data: ^{1}H NMR (400 MHz, d_6-Acetone) 7.31-7.19 (m, 5H), 6.45 (ddd, *J* = 9.8, 5.6, 1.2, 2H), 5.15 (s, 1H), 5.11 (d, *J* = 1.2, 1H), 4.24-4.18 (m, 2H), 2.91 (td, *J* = 7.6, 1.8, 2H), 2.82 (d, *J* = 9.2, 1H), 2.75 (d, *J* = 8.8, 1H); ^{13}C NMR (100 MHz, d_6-Acetone) 173.04, 172.30, 139.23, 137.55, 129.84, 129.28, 127.23, 81.45, 81.08, 65.83, 47.63, 47.39, 35.53; IR (CH_2Cl_2) 3498-2710 (br, m), 3055 (s), 2685 (s), 2306 (s), 1731 (s), 1717 (s), 1424 (s), 1282 (s), 1248 (s), 1171 (s), 997 (m), 896 (s), 496 (w); MS (ESI) 333 (33), 311 ($M+Na^+$, 100); TLC R_f 0.34 (EtOAc/hexane, 1/9).

Phthalic acid monophenethyl ester and diphenethyl ester

In a dry 50-mL, two-necked, round-bottomed flask was placed MoO_2Cl_2 (4 mg, 0.02 mmol) in 20 mL of anhydrous CH_2Cl_2. To the above solution, phthalic anhydride (444.3 mg, 3.0 mmol) was added at ambient temperature and stirred for one hour. The reaction flask was cooled to 10 ^{o}C. A solution of 2-phenylethanol (239 μL, 2.0 mmol) in CH_2Cl_2 (5 mL) was slowly added to the above dark green solution. The resultant reaction mixture was stirred at this temperature for 78 hours. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with 1N HCl (10 mL) and stirred for one hour. The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography on silica gel (EtOAc/hexane, 1/5) to give the mono-phenethyl ester in 92 % (497 mg) along with di-phenethyl ester (<1 %).



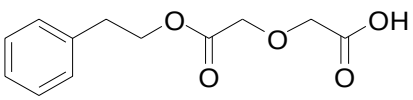
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 11.69 (bs, 1H), 7.94-7.89 (m, 1H), 7.66-7.54 (m, 3H), 7.31-7.22 (m, 5H), 4.56 (t, *J* = 7.2, 2H), 3.08 (t, *J* = 7.2, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 172.04, 168.14, 137.58, 133.26, 132.06, 130.82, 130.18, 129.75, 128.92, 128.69, 128.49, 126.55, 66.24, 34.62; IR (CCl_4) 3500-2700 (br, m), 1738 (s), 1701 (s), 1600 (w), 1580 (w), 1495 (w), 1450 (w), 1409 (w), 1369 (w), 1281 (s), 1239 (m), 1125 (m), 1073 (m), 1044 (m); MS (70 eV) 271 ($M+1^+$, 100), 270 (M^+, 22), 253 (15); TLC R_f 0.25 (EtOAc/hexane,1/10).



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.68-7.49 (m, 4H), 7.34-7.22 (m,

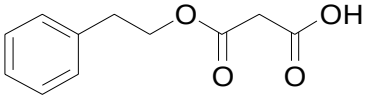
10H), 4.45 (t, *J* = 7.1, 2H), 3.02 (t, *J* = 7.0, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 167.55, 137.70, 132.15, 131.07, 129.00, 128.93, 128.57, 126.64, 66.05, 34.88; IR (CCl_4) 3066 (w), 3026 (w), 2923 (s), 2851 (m), 1735 (m), 1703 (w), 1600 (w), 1580 (w), 1496 (w), 1456 (w), 1408 (w), 1376 (w), 1280 (m), 1241 (m), 1121 (m), 1069 (w), 1045 (w); MS (70 eV) 375 ($M+1^+$, 100), 365 (30), 361 (18), 359 (15), 351 (65), 348 (24), 345 (16), 337 (40), 325 (22); TLC R_f 0.57 (EtOAc/hexane, 1/5).

Phenethyloxycarbonylmethoxy-acetic acid



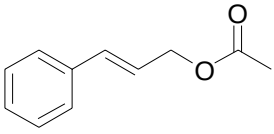
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 9.89 (bs, 1H), 7.32-7.19 (m, 5H), 4.39 (t, *J* = 7.2, 2H), 4.20 (s, 4H), 2.96 (t, *J* = 7.2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 173.78, 170.15, 137.11, 128.75, 128.49, 126.66, 68.18, 65.63, 34.81; IR (CH_2Cl_2) 3500-2710 (br, m), 3056 (w), 2915 (w), 1753 (s), 1709 (s), 1606 (w), 1364 (m), 1223 (m), 1143 (s), 1053 (w), 1001 (w); MS (20 eV) 239 ($M+1^+$, 6), 104 (100), 91 (16); TLC R_f 0.36 (EtOAc/hexane, 1/4).

Malonic acid monophenethyl ester



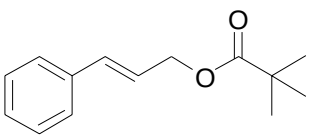
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 11.54 (bs, 1H), 7.34-7.21 (m, 5H), 4.40 (t, *J* = 6.8, 2H), 3.43 (s, 2H), 2.98 (t, *J* = 6.8, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 171.90, 166.51, 137.23, 128.85, 128.54, 126.70, 66.27, 40.90, 34.82; IR (CH_2Cl_2) 3473-2710 (br, w), 3032 (w), 2961 (w), 1733 (s), 1605 (s), 1498 (w), 1455 (w), 1330 (m), 1154 (m), 1011 (w), 878 (w); MS (ESI) 231 (M^++ Na, 5), 209 ($M+1^+$, 11); TLC R_f 0.32 (EtOAc/hexane, 1/4).

***trans*-3-Phenyl-2-propen-1-yl Acetate**[10]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.42-7.26 (m, 5H), 6.57 (d, *J* = 15.6, 1H), 6.28 (dt, *J* = 15.8, 6.4, 1H), 4.73 (dd, *J* = 6.4, 1.2, 2H), 2.10 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.75, 136.20, 134.14, 128.56, 128.01, 126.55, 123.17, 64.91, 20.77; MS (70 eV) 176 (M^+, 44), 134 (67), 133 (53), 117 (83), 115 (100), 105 (50), 92 (48), 77 (28), 57 (28); TLC R_f 0.29 (EtOAc/hexane, 1/20).

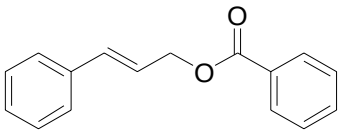
3-Phenyl-2-propen-1-yl 2, 2-Dimethylproponate[11]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.43-7.26 (m, 5H), 6.66 (d, *J* = 15.6,

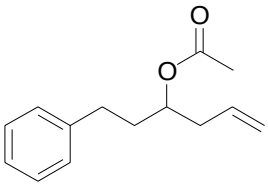
1H), 6.36-6.22 (dt, *J* = 15.8, 6.0, 1H), 4.73 (dd, *J* = 6.0, 1.2, 2H), 1.25 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 178.34, 136.40, 133.62, 128.60, 127.98, 126.60, 123.62, 64.82, 38.72, 27.11; MS (70 eV) 218 (M^+, 10), 138 (30), 123 (23), 117 (58), 115 (34), 96 (22), 95 (100), 85 (27), 81 (62), 67 (21), 57 (74), 55 (22); TLC R_f 0.35 (EtOAc/hexane, 1/20).

3-Phenyl-2-propen-1-yl benzoate[12]



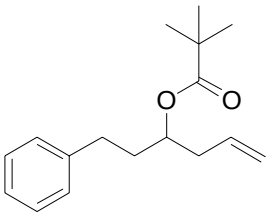
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 8.12 (dd, *J* = 8.2,1.2, 2H), 7.58 (t, *J* = 7.4, 1H), 7.48-7.26 (m, 7H), 6.77 (d, *J* = 15.8, 1H), 6.43 (dt, *J* = 15.8, 6.4, 1H), 5.01 (dd, *J* = 6.4, 1.3, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.25, 136.13, 134.15, 132.88, 130.12, 129.56, 128.51, 128.27, 127.98, 126.55, 123.16, 56.41; MS (20 eV) 238 (M^+, 15), 117 (67), 105 (100), 77 (24); TLC R_f 0.23 (EtOAc/hexane, 1/9).

Acetic acid 1-phenethyl-but-3-enyl ester[13]



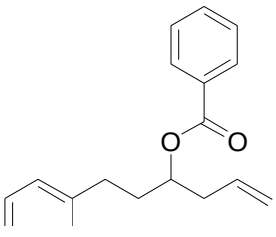
Data: ^{1}H NMR (400 MHz, CD_2Cl_2) 7.25-7.21 (m, 2 H), 7.15-7.12 (m, 3 H), 5.76-5.69 (m, 1 H), 5.07-5.00 (m, 2H), 4.90-4.87, (m, 1 H), 2.63-2.55 (m, 2 H), 2.30-2.28, (m, 2H), 1.9 (s, 3H), 1.85-1.79 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2) 172.31, 143.30, 135,21, 129.86, 129.66, 127.15, 118.59, 73.26, 38.84, 35.47, 31.77, 20.90; MS (20 eV) 219 ($M+1^+$, 30), 159 (100), 129 (12), 117 (10), HR-MS calcd for $C_{14}H_{18}O_2$: 218.1307; found: 218.1311; TLC R_f 0.32 (EtOAc/hexane, 1/20).

2,2-Dimethylpropanoic acid 1-phenethyl-but-3-enyl ester



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.34-7.16 (m, 5 H), 5.88-5.67 (m, 1 H), 5.13-5.01 (m, 2 H), 2.74-2.52 (m, 2 H) 2.39-2.33 (m, 2 H), 2.00-1.84 (m, 2 H), 1.24 (s, 9 H); ^{13}C NMR (50 MHz, $CDCl_3$) 178.06, 141.65, 133.58, 128.45, 128.37, 125.96, 117.74, 72.20, 38.77, 38.60, 35.44, 31.65, 27.13; IR (CH_2Cl_2) 3056 (s), 2987 (s), 1730 (m), 1550 (m), 1422 (s), 1250 (s), 1156 (m), 897 (s); MS (20 eV) 259 ($M-1^+$, 1), 178 (16), 149 (76), 107 (100), 57 (12); TLC R_f 0.36 (EtOAc/hexane, 1/20).

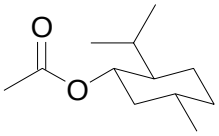
1-Phenethyl-but-3-enyl benzoate



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 8.08 (dd, *J* = 8.2, 1.2, 2H), 7.59 (t, *J* =

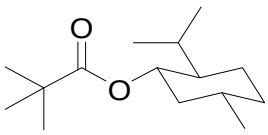
7.4, 1H), 7.49-7.45 (m, 2H), 7.31-7.18 (m, 5H), 5.91-5.81 (m, 1H), 5.29-5.23 (m, 1H), 5.17-5.09 (m, 2H), 2.82-2.67 (m, 2H), 2.52 (dd, *J* = 7.0, 6.0, 2H), 2.14-2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.13, 141.46, 133.35, 132.80, 131.01, 130.55, 129.53, 128.39, 128.29, 125.90, 117.99, 73.47, 38.67, 35.36, 31.73; IR (CH_2Cl_2) 3056 (s), 2988 (s), 1714 (s), 1603 (m), 1424 (s), 1281 (s), 1116 (s), 1071 (m), 1026 (m), 896 (s); MS (FAB) 304 ($M+Na^+$, 100); TLC R_f 0.28 (EtOAc/hexane, 1/9).

(2*R*,5*S*)-2-Isopropyl-5-methyl-cyclohexyl Acetate[14]



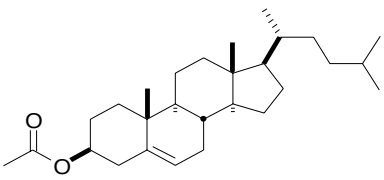
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 4.62 (dt, *J* = 11.0, 4.4, 1H), 1.97 (s, 3H), 1.93-1.86 (m, 1H), 1.86-1.71 (m, 1H), 1.70-1.54 (m, 2H), 1.52-1.13 (m, 2H), 1.11-0.90 (m, 2H), 0.84 (d, *J* = 7.4, 6H), 0.80-0.74 (m, 1H), 0.70 (d, *J* = 7.0, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.80, 74.13, 46.93, 34.17, 31.29, 26.22, 23.40, 21.91, 21.23, 20.64, 16.28; MS (70 eV) 198 (M^+, 5), 183 (13), 177 (12), 165 (17), 159 (10), 156 (54), 155 (100), 154 (22), 149 (14), 146 (52), 145 (66); TLC R_f 0.35 (EtOAc/hexane, 1/60).

(2*R*,5*S*) 2-Isopropyl-5-methyl-cyclohexyl 2,2-Dimethylpropanoate[15]



Data: ^{1}H NMR ($CDCl_3$, 200 MHz) 4.61 (dt, *J* = 10.8, 4.4, 1H), 2.20-1.78 (m, 2H), 1.74-1.58 (m, 2H), 1.58-1.29 (m, 2H), 1.17 (s, 9H), 1.15-0.98 (m, 1H), 0.98-0.92 (m, 1H), 0.88 (d, *J* = 7.6, 6H), 0.84-0.78 (m, 1H), 0.73 (d, *J* = 7.0, 3H), ^{13}C NMR ($CDCl_3$, 50 MHz) 178.02, 73.66, 46.99, 40.62, 34.25, 31.23, 27.02, 26.02, 23.17, 21.91, 20.70, 15.95; MS (70 eV) 240 (M^+, 12), 225 (61), 218 (12), 197 (14), 183 (74), 165 (15), 157 (15), 156 (77), 155 (100), 154 (55), 148 (13); TLC R_f 0.4 (EtOAc/hexane, 1/60).

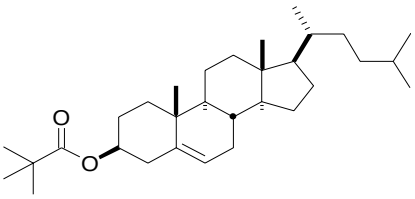
Acetic acid 17 -(1,5 –dimethyl-hexyl) -10,13-dimethyl-2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl ester[16]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 5.35 (d, *J* = 4.4, 1H), 4.62-4.54 (m, 1H), 2.30 (d, *J* = 7.2, 2H), 2.00 (s, 3H), 1.99-1.77 (m, 6H), 1.66-1.04 (m, 20H), 1.00 (s, 3H), 0.90 (d, *J* = 6.4, 3H), 0.85 (d, *J* = 6.8, 3H), 0.84 (d, *J* = 6.8, 3H), 0.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.31, 139.54, 122.55, 73.87, 56.63, 56.10, 49.98, 42.24, 39.68, 39.47, 38.07, 36.95,

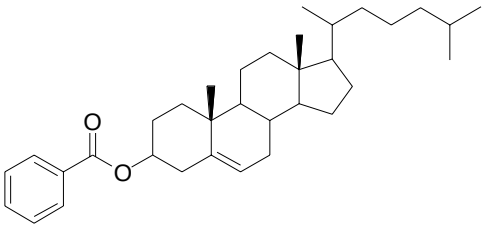
36.51, 36.14, 35.75, 31.83, 31.80, 28.18, 27.94, 27.71, 24.22, 23.80, 22.76, 22.51, 21.32, 20.98, 19.24, 18.67, 11.79; IR (CH_2Cl_2) 3060 (s), 2984 (s), 2305 (m), 1727 (s), 1469 (s), 1420 (s), 1375 (s), 1267 (s), 1137 (m), 1033 (s), 894 (s); MS (70 eV) 428 (M^+, 5), 368 (100), 352 (18), 247 (13), 147 (20); TLC R_f 0.57 (EtOAc/hexane, 1/9).

2,2-Dimethyl-propanoic acid 17- (1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10, 11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl ester



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 5.36 (d, *J* = 4.2, 1H), 4.58-4.55 (m, 1H), 2.29 (d, *J* = 7.7, 2H), 2.02-1.81 (m, 6H), 1.58-1.33 (m, 14H), 1.18 (s, 9H), 1.15-1.04 (m, 6H), 1.02 (s, 3H), 0.91 (d, *J* = 6.5, 3H), 0.86 (d, *J* = 6.6, 3H), 0.86 (d, *J* = 6.6, 3H), 0.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 177.94, 139.79, 122.47, 73.53, 56.70, 56.16, 50.04, 42.32, 39.75, 39.52, 38.59, 38.02, 37.00, 36.61, 36.20, 35.80, 28.22, 28.00, 27.67, 27.15, 24.28, 23.84, 22.81, 22.55, 21.05, 19.35, 18.72, 11.85; IR (CH_2Cl_2) 3057 (s), 2987 (s), 2305 (m), 1715 (s), 1420 (s), 1263 (s), 1169 (m), 896 (s); MS (70 eV) 470 (M^+, 5), 368 (100), 352 (18), 260 (14), 147 (19), 145 (15), 81 (13), 57 (20); TLC R_f 0.67 (EtOAc/hexane, 1/9).

Benzoic acid 17-(1,5-dimethyl-hexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15, 16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl ester

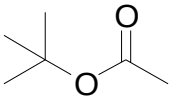


Data: ^{1}H NMR (400 MHz, $CDCl_3$) 8.05 (d, *J* = 7.6, 2H), 7.56-7.41 (m, 3H), 5.42 (d, *J* = 4.0, 1H), 4.91-4.83 (m, 1H), 2.47 (d, *J* = 7.6, 2H), 2.04-0.99 (m, 29H), 0.93 (d, *J* = 6.4, 3H), 0.87 (d, *J* = 6.8, 3H), 0.87 (d, *J* = 6.8, 3H), 0.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.99, 139.68, 132.68, 130.88, 129.53, 128.24, 122.77, 74.59, 56.72, 56.18, 50.08, 42.34, 39.77, 39.53, 38.23, 37.06, 36.67, 36.20, 35.80, 28.23, 28.01, 27.90, 24.30, 23.84, 22.80, 22.56, 21.07, 19.37, 18.73, 11.87; IR (CH_2Cl_2) 3051 (s), 2985 (s), 2306 (m), 1711 (m), 1603 (w), 1423 (s), 1279 (s), 1263 (s), 1119 (m), 896 (s); MS (70 eV) 490 (M^+, 5), 368 (100), 353 (15), 260 (14), 147 (14), 105 (20); TLC R_f 0.62 (EtOAc/hexane, 1/9).

General procedure for acylation of *tert*-butanol and trityl alcohol

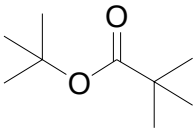
In a dry 50-mL, two-necked, round-bottomed flask was placed MoO_2Cl_2 (19 mg, 0.1 mmol) in 5 mL of anhydrous toluene. A solution of anhydride (15 mmol) and a given 3^o alcohol (10 mmol) in toluene (5 mL) was slowly added to the above solution and the reaction mixture was stirred for 30 min to 1 hour. To the above solution, diisopropylethylamine (1750 μL, 10 mmol) was slowly added at ambient temperature. This mixture was refluxed for 1 to 24 hours. After completion of the reaction as monitored by TLC (for the benzoylation of tryl alcohol), the reaction mixture was quenched with cold, saturated aqueous $NaHCO_3$ solution (50 mL) at room temperature. The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by distillation. The product obtained was characterized by routine spectroscopic methods.

Acetic acid *tert*-butyl ester[17]



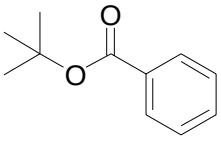
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 1.95 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.53, 80.12, 28.03, 22.49

2, 2-Dimethyl-propionic acid *tert*-butyl ester[18]



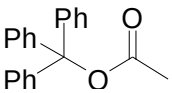
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 1.43 (s, 9H), 1.15 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) 177.95, 79.46, 39.14, 27.92, 27.13.

Benzoic acid *tert*-butyl ester[19]



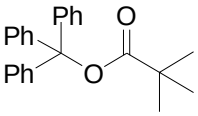
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 8.02-7.99 (m, 2H), 7.51-7.38 (m, 3H), 1.60 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.65, 132.30, 131.94, 129.31, 128.07, 80.78, 28.09; TLC R_f 0.61 (EtOAc/hexane, 1/9).

Acetic acid trityl ester[20]



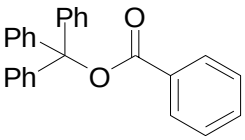
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.44-7.28 (m, 15H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 168.70, 143.34, 128.32, 127.69, 127.22, 89.81, 22.49; TLC R_f 0.47 (EtOAc/hexane, 1/20).

2, 2-Dimethyl-propionic acid trityl ester[21]



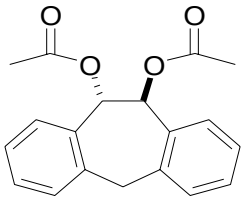
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.39-7.25 (m, 15H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 175.52, 143.57, 128.15, 127.66, 127.11, 89.21, 39.56, 27.10; TLC R_f 0.47 (EtOAc/hexane, 1/20).

Benzoic acid trityl ester[22]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 8.15-8.13 (m, 2H), 7.58-7.45 (m, 9 H), 7.35-7.25 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 164.41, 143.39, 132.96, 131.28, 129.80, 128.41, 128.37, 127.80, 127.31, 90.50; TLC R_f 0.41 (EtOAc/hexane, 1/20).

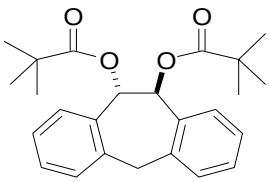
***trans*-11-Acetoxy-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-10-yl Acetate**[23]



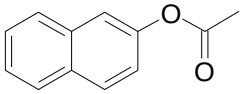
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.32-7.20 (m, 8H), 6.53 (s, 2H), 4.18 (s, 2H), 2.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 171.41, 138.22, 137.58, 128.56, 127.98, 127.71, 127.02, 75.24, 40.8, 22.18; TLC R_f 0.32 (EtOAc/hexane, 1/9); Anal. Calcd. For $C_{19}H_{18}O_4$ (310.33): C, 73.53; H, 5.85, Found: C, 73.47; H, 5.28.

***trans*-11-(2,2-Dimethyl-propanoyloxy)-10,11-dihydro-5H-dibenzo[a,d]cyclohepten-10-yl 2,2-Dimethylpropanoate**

Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.27-7.14 (m, 8H), 6.54 (s, 2H), 4.18 (s, 2H), 1.23 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) 178.60, 140.34, 135.23, 129.21, 128.90, 128.81, 127.52, 73.62, 40.09, 38.39, 26.55; MS (70 eV) 394 (2), 293 (49), 190 (27), 178 (35), 137 (37); TLC R_f 0.58 (EtOAc/hexane, 1/9); Anal. Calcd. for $C_{25}H_{30}O_4$ (394.49): C, 76.11; H, 7.66. Found: C, 76.04; H, 7.71.

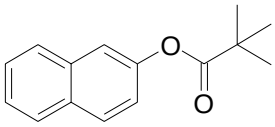


Naphthalen-2-yl Acetate[24]



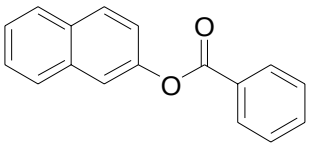
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.88-7.79 (m, 3H), 7.57-7.46 (m, 3H), 7.24 (dd, J = 9.0, 2.4, 1H), 2.36 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 175.90, 148.41, 133.82, 131.52, 129.45, 127.81, 127.69, 126.59, 125.74, 121.16, 118.55, 21.10; TLC R_f 0.39 (EtOAc/hexane, 1/ 4).

Naphthalen-2-yl 2, 2-Dimethylpropanoate[25]



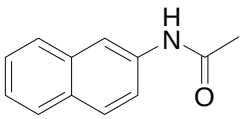
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.89-7.80 (m, 3H), 7.57-7.46 (m, 3H), 7.23 (dd, *J* = 9.0, 2.4, 1H), 1.44 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 177.30, 148.85, 133.85, 131.42, 129.31, 127.78, 127.58, 126.50, 125.56, 121.18, 118.39, 39.05, 27.10; TLC R_f 0.54 (EtOAc/hexane, 1/ 4).

2-Naphthyl benzoate[26]



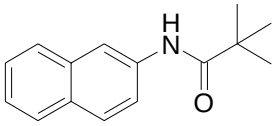
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.29-8.24 (m, 2H), 7.92 (d, *J* = 8.6, 1H), 7.94-7.82 (m, 2H), 7.71-7.48 (m, 6H), 7.38 (dd, *J* = 8.8, 2.3, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) 165.42, 148.66, 133.85, 133.67, 131.54, 130.24, 129.59, 129.50, 128.63, 127.83, 127.71, 126.60, 125.75, 121.26, 118.71; MS (20 eV) 248 (M^+, 35), 115 (18), 105 (100), 77 (27); TLC R_f 0.65 (EtOAc/hexane, 1/ 4).

***N*-Naphthalen-2-yl-acetamide**[27]



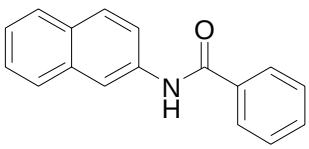
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.17 (bd, *J* = 1.4, 1H), 8.06 (bs, 1H), 7.77-7.70 (m, 3H), 7.49-7.38 (m, 3H), 2.20 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 168.94, 135.44, 133.80, 130.65, 128.69, 127.63, 127.54, 126.46, 125.01, 120.03, 116.81, 24.47; TLC R_f 0.29 (EtOAc/hexane, 1/4).

***N*-Naphthalen-2-yl-2, 2-dimethyl-propanamide**[28]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.27 (d, *J* = 2.2, 1H), 7.81-7.77 (m, 3H), 7.49-7.39 (m, 4H), 1.36 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 176.91, 135.44, 133.93, 130.63, 128.69, 127.69, 126.54, 126.51, 124.97, 120.01, 116.74, 39.64, 27.58; TLC R_f 0.26 (EtOAc/hexane, 1/4).

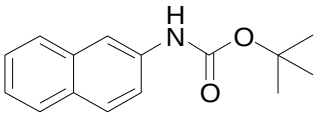
***N*-2-Napthalenyl-benzamide**[29]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.35 (d, *J* = 2.2, 1H), 7.98-7.78 (m, 6H), 7.62-7.42 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) 166.05, 135.43, 135.02, 133.93, 131.95, 130.86, 128.87, 128.51, 127.78, 127.63, 127.11,

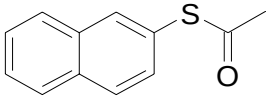
126.60, 125.19, 120.18, 117.16; MS (20 eV) 247 (M^+, 86), 115 (20), 105 (100), 77 (37); TLC R_f 0.24 (EtOAc/hexane, 1/4).

Naphthalen-2-yl-carbamic acid *tert*-butyl ester[30]



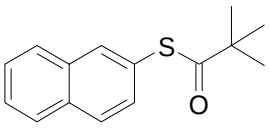
Data: ^{1}H NMR (200 MHz, CD_2Cl_2) 8.26 (d, J = 2.0, 1H), 7.80-7.76 (m, 3 H) 7.47-7.40 (m, 4H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) 176.77, 135.42, 133.86, 130.58, 128.58, 127.60, 127.46, 126.41, 124.88, 120.03, 116.74, 39.66, 27.62; TLC R_f 0.30 (EtOAc/hexane, 1/4).

***S*-Naphthalen-2-yl Thioacetate**[31]



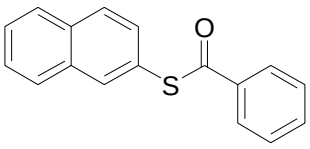
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.97-7.82 (m, 4H), 7.58-7.45 (m, 3H), 2.47 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 194.43, 134.35, 133.55, 133.36, 130.91, 128.84, 128.01, 127.81, 127.19, 126.60, 125.26, 30.18; TLC R_f 0.42 (EtOAc/hexane, 1/20).

***S*-Naphthalen-2-yl 2, 2-Dimethyl-thiopropanoate**[32]



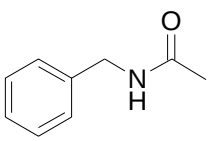
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.91 (dd, J = 10.0, 1.4, 1H), 7.88-7.82 (m, 3H), 7.54-7.49 (m, 2H), 7.43 (dd, J = 8.6, 1.8, 1H), 1.36 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 204.98, 134.79, 133.65, 133.29, 131.50, 128.65, 127.95, 127.81, 127.01, 126.46, 125.51, 46.96, 27.37; TLC R_f 0.46 (EtOAc/hexane, 1/40).

***S*-[2]-Naphthyl thiobenzoate**[37]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.10-8.05 (m, 3H), 7.95-7.84 (m, 3H), 7.64-7.46 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) 190.47, 136.73, 135.05, 133.76, 133.70, 133.50, 131.45, 128.87, 128.83, 128.04, 127.87, 127.57, 127.22, 126.60, 124.73; MS (20 eV) 264 (M^+, 18), 115 (17), 105 (100), 77 (24); TLC R_f 0.40 (EtOAc/hexane, 1/40).

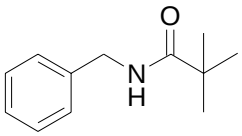
***N*-Benzyl-acetamide**[33]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.33-7.24 (m, 5H), 6.11 (s, 1H), 4.38 (d, J = 5.7, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.05, 138.21, 128.55,

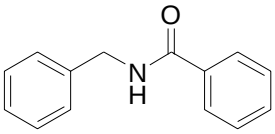
127.68, 127.31, 43.56, 23.01; MS (ESI) 172 ($M+Na^+$, 62), 155 (31); TLC R_f 0.43 (EtOAc/hexane, 1/1).

_N_-Benzyl-2, 2-dimethyl-propionamide[34]



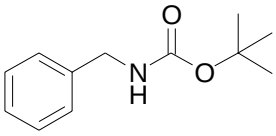
Data: ^1H NMR (400 MHz, $CDCl_3$) 7.32-7.22 (m, 5H), 6.15 (s, 1H), 4.40 (d, *J* = 5.5, 2H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 178.25, 138.62, 128.57, 127.47, 127.26, 43.44, 38.60, 27.51; MS (ESI) 214 ($M+Na^+$, 100), 192 (M^+, 15), 185 (10); TLC R_f 0.20 (EtOAc/hexane, 1/10).

_N_-Benzyl-benzamide[35]



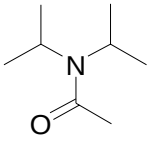
Data: ^1H NMR (400 MHz, $CDCl_3$) 7.79 (dd, *J* =8.0, 1.4, 2H), 7.50 (t, *J* = 7.4, 1H), 7.45-7.30 (m, 7H), 6.44 (bs, 1H), 4.65 (d, *J* = 5.6, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 167.31, 138.20, 134.43, 131.52, 128.79, 128.59, 127.92, 127.63, 126.94, 44.15; MS (20 eV) 211 (M^+, 75), 105 (100), 77 (51), 51 (14); TLC R_f 0.40 (EtOAc/hexane, 1/10).

Benzyl-carbamic acid *tert*-butyl ester[36]



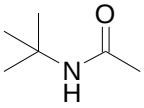
Data: ^1H NMR (400 MHz, $CDCl_3$) 7.34-7.23 (m, 5H), 5.01 (s, 1H), 4.30 (d, *J* = 5.5, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.82, 138.88, 128.34, 127.23, 127.02, 79.13, 44.42, 28.22; MS (ESI) 230 ($M+Na^+$, 35), 181 (13); TLC R_f 0.43 (EtOAc/hexane, 1/10).

_N,N_-Diisopropyl-acetamide[37]



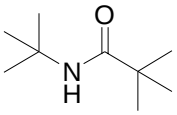
Data: ^1H NMR (200 MHz, $CDCl_3$) 3.92-3.82 (m, 1H), 3.56-3.49 (m, 1H), 2.07 (s, 3H), 1.35 (d, *J* = 6.4, 6H), 1.19 (d, *J* = 6.6, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) 169.66, 48.98, 45.15, 23.23, 20.41, 20.11; MS (20 eV) 143 (M^+, 13), 135 (17), 134 (11), 117 (22), 104 (100); TLC R_f 0.31 (EtOAc/hexane, 1/20).

N-tert-Butyl-acetamide[38]



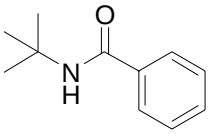
Data: ^1H NMR (400 MHz, $CDCl_3$) 5.33 (bs, 1H), 1.90 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 169.42, 51.11, 28.75, 24.51; TLC R_f 0.5 (EtOAc/hexane, 1/4).

***N*-*tert*-Butyl-2,2-dimethyl-propionamide**[39]



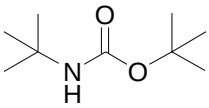
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 5.38 (bs, 1H), 1.32 (s, 9H), 1.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 177.77, 50.64, 38.94, 28.71, 27.64; TLC R_f 0.45 (EtOAc/hexane, 1/4).

***N*-*tert*-Butyl-benzamide**[40]



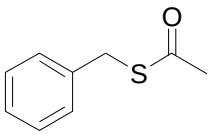
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.71 (dd, J = 8.4, 1.3, 2H), 7.47-7.37 (m, 3H), 5.97 (bs, 1H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.85, 135.92, 130.99, 128.40, 126.65, 51.53, 28.83; TLC R_f 0.25 (EtOAc/hexane, 1/4).

***tert*-Butyl-carbamic acid-*tert*-butyl ester**[41]



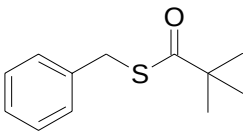
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 4.45 (bs, 1H), 1.42 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 154.44, 78.43, 49.84, 28.93, 28.36; TLC R_f 0.40 (EtOAc/hexane, 1/4).

Thioacetic acid *S*-benzyl ester[42]



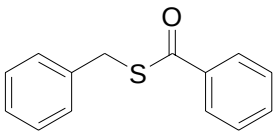
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.31-7.26 (m, 5H), 4.13 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 195.05, 137.57, 128.78, 128.60, 127.24, 33.44, 30.27; MS (20 eV) 167 ($M+1^+$, 27), 123 (19), 91 (100), 77 (10), 65 (17); TLC R_f 0.2 (hexane).

2, 2-Dimethyl-thiopropionic acid *S*-benzyl ester[43]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.33-7.25 (m, 5H), 4.13 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 205.65, 137.64, 128.66, 128.39, 126.95, 46.17, 32.84, 27.22; MS (20 eV) 209 ($M+1^+$, 100), 91 (92), 85 (100), 65 (18), 57 (100); TLC R_f 0.6 (hexane).

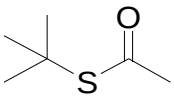
***S*-Benzyl-thiobenzoate**[44]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.98 (dd, J = 8.4, 1.3, 2H), 7.57 (t, J = 7.4, 1H), 7.47-7.24 (m, 7H), 4.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.26, 137.46, 136.82, 133.40, 128.96, 128.63, 128.60, 127.30, 127.28, 33.33; MS (20 eV) 228 (M^+, 18), 65 (55), 105 (100), 91 (60), 77 (27); TLC R_f 0.46

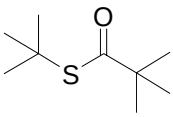
(EtOAc/hexane, 1/20).

S-tert-butyl Thioacetate[45]



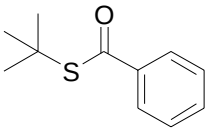
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 2.26 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 195.53, 47.17, 30.76, 29.27; TLC R_f 0.33 (hexane).

S-tert-butyl 2, 2-Dimethyl-thiopropanoate[46]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 1.44 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 207.97, 65.83, 46.96, 29.77, 27.37; MS (70 eV) 174 (M^+, 10), 85 (18), 72 (14), 57 (100); TLC R_f 0.26 (hexane).

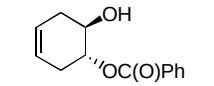
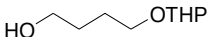
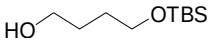
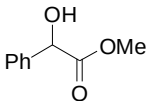
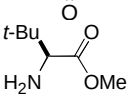
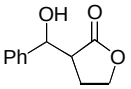
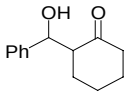
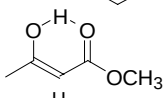
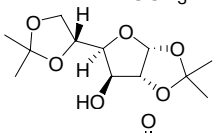
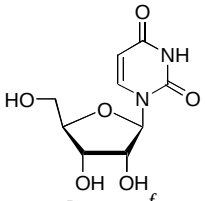
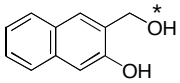
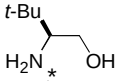
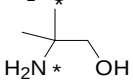
S-tert-butyl thiobenzoate[47]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.92 (dd, J = 8.4, 1.8, 2H), 7.53-7.38 (m, 3H), 1.58 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 192.41, 138.10, 132.74, 128.27, 126.78, 47.73, 29.72; MS (70 eV) 194 (M^+, 8), 138 (15), 105 (100), (51), 57 (24), 51 (22); TLC R_f 0.67 (EtOAc/hexane, 1/4).

On-line text and Table 4' for a complete study regarding the scope of functional group compatibility

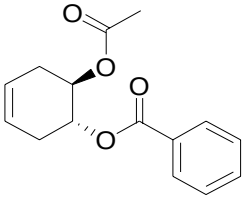
Table 4'. Acetylation, pivalation, and chemoselective acylation of functionalized substrates

entry	substrate[a]	time, h	yield,[b] %
1		3 (54/38[c])	99 (98/98[c])
2		6 (13)	95 (95)
3		1 (15)	98 (99)
4		6 (14)	99 (99)
5		2 (8/12/16[d])	100 (99/100/99[d])
6		5 (32)	99 (98)
7		8 (14)	98 (99)
8		72	20
9		60	71
10		107[e]	92
11	glucose[f]	43	93
12	lactose[e,f]	70	97
13	β-cyclodextrin[f]	120	87
14	cellulose[g]	6	95
15		3[h](49/12)	98 (99/98)
16		2[h,i] (6/12/12[d])	99 (99/96/99[d])
17		0.5 (1/12/10[d])	100 (100/96/99[d])

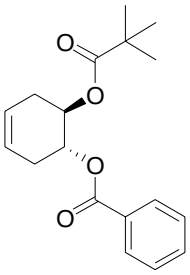
[a] 1.5 equiv of anhydride was used unless otherwise stated. [b] Isolated yields and characterized spectroscopically. [c] The data in parentheses correspond to pivalation and benzoylation, respectively, unless otherwise stated [d] The third data in parentheses represent *t*-Boc protection. [e] Three equiv of anhydride was used. [f] No solvent was used. [g] Carried out at 100-110 ^{o}C. [h] Asterisk signifies the reactive site. [i] For effective mono-acylation, 0.95 equiv of anhydride was used.

6-Acetoxy-cyclohex-3-enyl benzoate

Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.01 (dd, *J* = 8.4, 1.4, 2H), 7.55-7.40 (m, 3H), 5.63 (d, *J* = 2.4, 2H), 5.35-5.25 (m, 2H), 2.70-2.55 (m, 2H), 2.35-2.25 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.46, 165.89, 133.01, 130.03, 129.57, 128.36, 123.73, 123.67, 70.78, 69.73, 30.03, 20.85; IR (CH_2Cl_2) 3052 (w), 1735 (s), 1720 (s), 1609 (w), 1525 (w), 1316 (m), 1265 (s), 1243 (s), 1119 (m), 1046 (m), 910 (s), 735 (s); MS (70 eV) 261 ($M+1^+$, 100), 259 (18), 139 (10), 105 (100), 78 (98); TLC R_f 0.35 (EtOAc/hexane, 1/15).

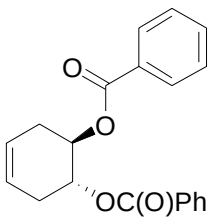


6-(2,2-Dimethyl-propanoyloxy)-cyclohex-3-enyl benzoate



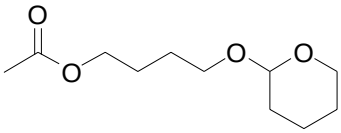
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 8.01 (dd, *J* = 8.4, 1.6, 2H), 7.55-7.38 (m, 3H), 5.62 (d, *J* = 2.4, 2H), 5.37-5.25 (m, 2H), 2.75-2.55 (m, 2H), 2.40-2.18 (m, 2H), 1.06 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 177.96, 165.92, 133.06, 130.06, 129.71, 128.36, 123.84, 123.79, 70.86, 69.65, 38.57, 30.30, 30.16, 26.85; IR (CH_2Cl_2) 3045 (m), 2985 (s), 1723 (s), 1422 (s), 1282 (s), 1251 (s), 1160 (s), 1117 (s), 1028 (m), 896 (s); MS (70 eV) 303 ($M+1^+$, 22), 201 (70), 181 (100), 77 (5); TLC R_f 0.32 (EtOAc/hexane, 1/15).

***trans*-4,5-bis-Benzoyloxy-cyclohexene**[48]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.98 (dd, *J* = 8.4, 1.6, 4H), 7.52-7.48 (m, 2H), 7.39-7.35 (m, 4H), 5.69-5.68 (m, 2H), 5.53-5.50 (m, 2H), 2.81-2.76 (m, 2H), 2.44-2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 166.01, 132.95, 130.01, 129.60, 128.29, 123.77, 70.66, 30.22; TLC R_f 0.30 (EtOAc/hexane, 1/20).

Acetic acid 4-(tetrahydro-pyran-2-yloxy)-butyl ester[49]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 4.44 (t, *J* = 1.6, 1 H), 3.96 (t, *J* = 6.8, 2H), 3.71-3.61 (m, 2H), 3.28-3.25 (m, 2H), 1.91 (s, 3H), 1.59-1.38 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) 171.11, 98.82, 66.89, 64.32, 62.28, 30.68, 26.21, 25.56, 25.43, 20.93, 19.57; MS (20 eV) 217 ($M+1^+$, 58), 175 (100), 133 (56), 115 (34), 85 (32); TLC R_f 0.4 (EtOAc/hexane, 1/10).

2, 2-Dimethyl-propionic acid 4-(tetrahydro-pyran-2-yloxy)-butyl ester

Data: ^{1}H NMR (400 MHz, $CDCl_3$) 4.55 (dd, *J* = 4.4, 2.8, 1H), 4.06 (t, *J* = 6.0, 2H), 3.86-3.71 (m, 2H), 3.50-3.38 (m, 2H), 1.82-1.48 (m, 10 H), 1.17 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 178.34, 98.67, 66.80, 64.02, 62.13, 38.55, 30.56, 27.03, 26.11, 25.48, 25.31, 19.46; IR (CH_2Cl_2) 3066 (s), 2961 (s), 1721 (s), 1442 (s), 1289 (s), 1265 (m), 1245 (s), 1166 (s), 1076 (s), 1034 (s), 973 (s), 900 (s); MS (20 eV) 259 ($M+1^+$, 6), 175 (32), 157 (34), 118 (8), 101 (36), 85 (84), 57 (100); TLC R_f 0.4 (EtOAc/hexane, 1/4).

Acetic acid 4-(*tert*-butyl-dimethyl-silanyloxy)-butyl ester[503]

Data: ^{1}H NMR (400 MHz, $CDCl_3$) 4.03 (t, *J* = 6.5, 2H), 3.58 (t, *J* = 6.2, 2H), 1.98 (s, 3H), 1.67-1.60 (m, 2H), 1.55-1.48 (m, 2H), 0.84 (s, 9H), -0.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.81, 64.20, 62.39, 29.06, 25.76, 25.09, 20.73, 18.13, -5.51; MS (20 eV) 246 (M^+, 4), 149 (8), 111 (16), 99 (18), 71 (52), 57 (100); TLC R_f 0.4 (EtOAc/hexane, 1/10).

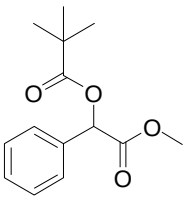
2, 2-Dimethyl-propionic acid 4-(*tert*-butyl-dimethyl-silanyloxy)-butyl ester

Data: ^{1}H NMR (400 MHz, $CDCl_3$) 4.07 (t, *J* = 6.4, 2H), 3.63 (t, *J* = 6.4, 2H), 1.71-1.65 (m, 2H), 16.1-1.54 (m, 2H), 1.19 (s, 9H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 178.58, 64.23, 62.23, 38.71, 29.28, 27.18, 25.92, 25.26, 18.30, -5.33; IR (CH_2Cl_2) 2998 (w), 2957 (m), 2856 (m), 1719 (s), 1602 (w), 1481 (m), 1287 (m), 1266 (m), 1167 (s), 1094 (m), 838 (s); MS (20 eV) 289 ($M+1^+$, 100), 187 (16); TLC R_f 0.42 (EtOAc/hexane, 1/4).

Methyl 2-Acetoxy-2-phenyl-aceate[51]

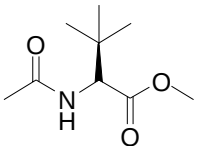
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.47-7.36 (m, 5H), 5.93 (s, 1H), 3.70 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.29, 169.32, 133.73, 129.22, 128.75, 127.60, 74.36, 52.45, 20.50; MS (20 eV) 209 ($M+1^+$, 18), 166 (27), 150 (91), 121 (50); TLC R_f 0.35 (EtOAc/hexane, 1/9).

1-Methoxycarbonyl-1-phenyl-methyl 2, 2-Dimethyl-propanoate[52]



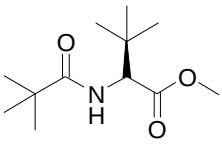
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.34-7.33 (m, 5H), 5.18 (d, *J* = 4.4, 1H), 3.76 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 177.9, 169.47, 138.24, 128.60, 128.49, 126.57, 72.88, 52.99, 41.17, 26.49; IR (CH_2Cl_2) 2937 (m), 2856 (m), 1771 (m), 1742 (m), 1698 (m), 1595 (m), 1347 (m), 1265 (s), 1233 (w), 740 (s); MS (20 eV) 250 (M^+, 4), 154 (12), 149 (15), 136 (13), 107 (14); TLC R_f 0.62 (EtOAc/hexane, 1/9).

(*S*)-Methyl 2-Acetylamino-3, 3-dimethyl-butanoate[53]



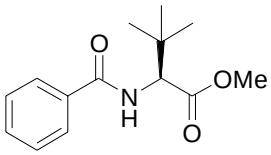
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 5.97 (bs, 1H), 4.48 (d, *J* = 9.4, 1H), 3.72 (s, 3H), 2.03 (s, 3H), 0.97 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 172.30, 169.88, 59.78, 51.56, 34.41, 26.31, 22.96; TLC R_f 0.25 (EtOAc/hexane, 1/10).

(*S*)-Methyl 2-(2, 2-Dimethyl-propanoylamino)-3, 3-dimethyl-butanoate



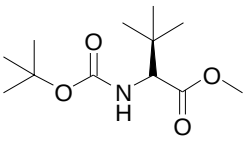
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 6.14 (bd, *J* = 8.0, 1H), 4.47 (d, *J* = 9.4, 1H), 3.72 (s, 3H), 1.22 (s, 9H), 0.96 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 178.06, 172.49, 59.48, 51.69, 38.81, 34.82, 27.40, 26.45; MS (ESI) 459 (100), 230 ($M+1^+$, 45); TLC R_f 0.23 (EtOAc/hexane, 1/10).

(2*S*)-Methyl 2-benzoylamino-3,3-dimethylbutanoate[54]



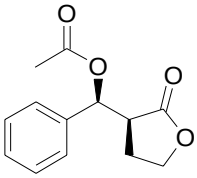
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.80 (dd, *J* = 7.8, 1.6, 2H), 7.56-7.40 (m, 3H), 6.65 (bd, *J* = 8.2, 1H), 4.71 (d, *J* = 9.6, 1H), 3.76 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 172.16, 167.12, 134.09, 131.62, 128.49, 126.95, 60.05, 51.69, 34.93, 26.40; TLC R_f 0.35 (EtOAc/hexane, 1/5).

2-*tert*-Butoxycarbonylamino-3, 3-dimethyl-butyric acid methyl ester[55]



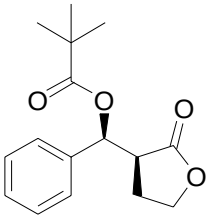
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 5.09 (bd, *J* = 8.4, 1H), 4.10 (d, *J* = 9.6, 1H), 3.72 (s, 3H), 1.45 (s, 9H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 172.51, 155.50, 77.33, 61.64, 51.64, 34.63, 28.33, 26.48; MS (ESI) 268 ($M+Na^+$, 100), 246 (M^+, 10), 244 (50), 146 (21); TLC R_f 0.23 (EtOAc/hexane, 1/9).

(3-Acetoxy-3-phenyl)methyl-dihydrofuran-2-one (syn isomer)



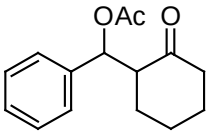
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.32-7.22 (m, 5H), 6.20 (d, *J* = 3.8, 1H), 4.27 (dt, *J* = 8.0, 4.0, 1H), 4.12 (dt, *J* = 8.0, 4.0, 1H), 2.95 (dt, *J* = 12.0, 4.0, 1H), 2.42-2.37 (m, 1H), 2.08 (s, 3H), 2.10-2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 175.27, 169.62, 136.77, 128.63, 128.59, 126.78, 73.56, 66.37, 44.35, 24.67, 21.02; IR (CH_2Cl_2) 3945 (s), 2987 (s), 2686 (s), 2411 (s), 2306 (s), 1771 (s), 1742 (s), 1422 (s), 1281 (s), 1251 (s), 1163 (m), 1026 (m), 896 (s), 453 (w); MS (20 eV) 234 (M^+, 10), 191 (50), 174 (98), 129 (35), 115 (64); TLC R_f 0.30 (ether/hexane, 1/20); HR-MS Calcd. For $C_{18}H_{14}O_3$: 278.0943, found: 278.0943.

(3-Pivaloyloxy-3-phenyl)methyl-dihydrofuran-2-one (syn isomer)



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.39-7.25 (m, 5H), 6.23 (d, *J* = 3.0, 1H), 4.34 (dt, *J* = 8.8, 3.6, 1H), 4.17 (dt, *J* = 8.8, 7.4, 1H), 3.01 (dt, *J* = 9.6, 3.4, 1H), 2.48-2.33 (m, 1H), 2.20-2.09 (m, 1H), 1.23 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 178.23, 175.85, 139.83, 128.75, 128.11, 125.35, 72.64, 66.55, 45.81, 40.51, 26.93, 23.06; IR (CH_2Cl_2) 3055 (m), 2254 (w), 1771 (w), 1742 (w), 1591 (w), 1373 (w), 1270 (m), 909 (s), 720 (m), 651 (m); MS (70 ev) 276 (M^+, 5), 191 (100), 174 (48), 131 (20), 115 (48), 105 (20), 91 (20), 57 (68); TLC R_f 0.33 (ether/hexane, 1/20).

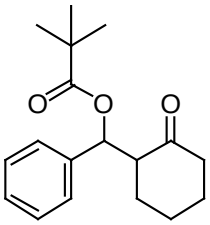
(2-Oxo-cyclohexyl)-phenyl-methyl Acetate[56]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.41-7.24 (m, 5H), 6.29 (d, *J* = 5.4, 1H, syn), 6.07 (d, *J* = 9.4, 1H, anti), 2.95-2.62 (m, 2H), 2.58-2.22 (m, 3H), 2.20-1.59 (m, 4H), 2.07 (s, 3H, syn), 2.00 (s, 3H, anti); ^{13}C NMR (50 MHz, $CDCl_3$) syn: 209.15, 169.63, 139.57, 128.16, 127.49, 126.26, 72.45, 55.53, 42.04, 27.57, 27.18, 24.35, 20.74. anti: 210.15, 169.63, 138.19, 128.31, 127.33, 126.26, 73.98, 54.94, 41.80, 30.19, 27.95, 23.96, 23.09; IR (CH_2Cl_2) 2987 (s), 1771 (m), 1742 (m), 1422 (s), 1250 (s), 1159 (m), 896 (s); MS (70 eV) 246 (M^+, 84), 219 (19), 218 (35), 212 (33), 208 (100); TLC R_f 0.52 (syn), 0.58 (anti) (EtOAc/hexane, 1/6).

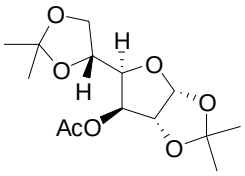
(2-Oxo-cyclohexyl)-phenyl-methyl 2,2-dimethylpropanoate

Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.51-7.23 (m, 5H), 6.26 (d, *J* = 4.6, 1H, syn), 6.03 (d, *J* = 9.2, 1H, anti), 2.92-2.67 (m, 2H), 2.59-2.25 (m, 3H), 2.02-1.20 (m, 4H), 1.21 (s, 9H, syn), 1.14 (s, 9H,

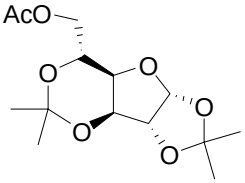


anti); ^{13}C NMR (50 MHz, $CDCl_3$) syn: 208.97, 177.06, 139.89, 136.67, 128.51, 128.25, 127.48, 126.11, 72.12, 55.84, 42.15, 38.69, 28.80, 26.99, 24.52, 23.73. anti: 209.95, 177.06, 138.61, 135.56, 128.39, 128.31, 128.03, 127.19, 73.92, 55.35, 41.62, 38.42, 27.99, 26.83, 23.82, 23.23; IR (CH_2Cl_2) 3032 (w), 2945 (m), 2863 (m), 1725(m), 1698 (s), 1595 (m), 1522 (m), 1451 (m), 1347 (s), 1266 (m), 1131 (m), 853 (w); MS (70 eV) 288 (M^+, 9), 271 (20), 270 (100); TLC R_f 0.67 (syn), 0.60 (anti) (EtOAc/hexane, 1/6).

Dicetone-D-glucose-3-acetate[57] **and 6-acetate**[58]

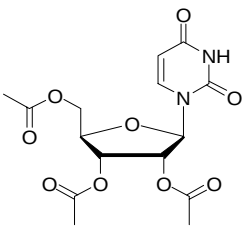


In a dry 25-mL, two-necked, round-bottomed flask was placed MoO_2Cl_2 (1.9 mg, 0.01 mmol) in 5 mL of anhydrous CH_2Cl_2. To the above solution, acetic anhydride (140 µL, 1.5 mmol) was added at ambient temperature and stirred for one hour. A solution of diacetone-D-glucose (260 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was slowly added to the above bluish solution. The reaction mixture was stirred for 60 hours at ambient temperature. After completion of the reaction as monitored by TLC, the reaction mixture was quenched with cold, saturated aqueous $NaHCO_3$ solution (20 mL). The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography on silica gel (EtOAc/*n*-hexane, 1/5) to give the 3- and 6-acetate in 71 % (214.2 mg) and 27 % (82.5 mg) yields, respectively: ^{1}H NMR (200 MHz, $CDCl_3$) 5.84 (d, *J* = 3.8, 1H), 5.21 (d, *J* = 2.2, 1H), 4.46 (d, *J* = 3.6, 1H), 4.20-4.13 (m, 2H), 4.08-3.94 (m, 2H), 2.06 (s, 3H), 1.48 (s, 3H), 1.37 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 169.68, 112.29, 109.35, 105.04, 83.33, 79.67, 76.11, 72.40, 67.14, 26.75, 26.63, 26.11, 25.17, 20.77; MS (70 eV) 303 ($M+1^+$, 100), 298 (42), 293 (10); TLC R_f 0.26 (EtOAc/hexane,1/5).



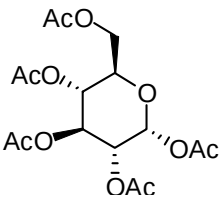
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 5.98 (d, *J* = 3.6, 1H), 4.56 (d, *J* = 3.8, 1H), 4.34-4.09 (m, 5H), 3.80-3.71 (m, 1H), 2.07 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.92, 112.29, 106.45, 101.09, 83.92, 79.41, 74.98, 70.14, 64.45, 27.07, 26.43, 23.82, 20.76; MS (70 eV) 303 ($M+1^+$, 100), 298 (16), 289 (20); TLC R_f 0.36 (EtOAc/hexane, 1/5).

$O^{2'}$, $O^{3'}$, $O^{5'}$ -Triacetyl-uridine[59]



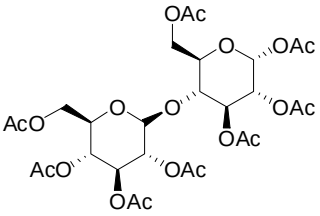
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 9.97 (s, 1H), 7.38 (d, *J* = 8.0, 2H), 5.99 (d, *J* = 4.0, 2H), 5.75 (d, *J* = 8.0, 2H), 5.34-5.30 (m, 2H), 4.29 (bs, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.14, 169.57, 163.24, 150.36, 139.43, 103.14, 87.23, 79.59, 72.43, 69.92, 62.94, 20.42, 20.17, 20.06; MS (70 eV) 371 ($M+1^+$, 100), 329 (44), 327 (23); TLC R_f 0.25 (EtOAc/hexane, 2/1).

Acetic acid 4, 5, 6-triacetoxy-2-acetoxymethyl-tetrahydro-pyran-3-yl ester[60]



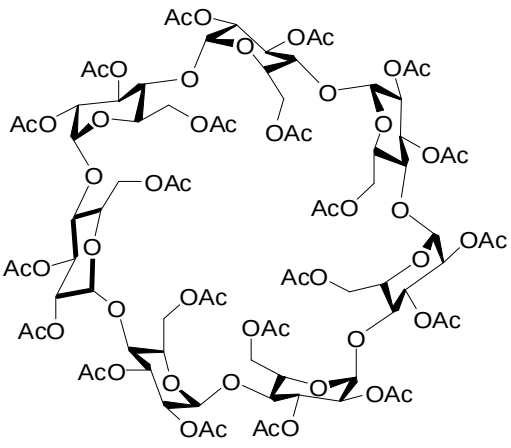
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 6.30 (d, *J* = 3.8, 1H, α-form), 5.68 (dd, *J* = 8.0, 1.6, 1H, β-form), 5.45 (t, *J* = 8.2, 1H, β-form), 5.27-5.03 (m, 2H), 4.32-4.20 (m, 1H), 4.17-4.04 (m, 1H), 3.84-3.77 (m, 1H), 2.16, 2.15, 2.09, 2.07, 2.05, 2.00, 1.99, 1.98 (s, 15H, α+β forms); ^{13}C NMR (50 MHz, $CDCl_3$): 170.70, 170.19, 169.34, 169.05, 168.84, 91.70, 89.06, 72.77, 72.71, 69.81, 67.87, 67.73, 61.42, 20.79, 20.71, 20.61, 20.47, 20.35; TLC R_f 0.35 (ether/hexane, 1/2)

***O*^{1},*O*^{2},*O*^{3},*O*^{6}-Tetraacetyl-*O*^{4}-(tetra-*O*-acetyl-β-Δ-galactopyranosyl)-α-D-glucopyran-ose**[61]



Data: ^{1}H NMR (200 MHz, $CDCl_3$) 6.25 (d, *J* = 3.6, 1H), 5.46 (t, *J* = 9.2, 1H), 5.35 (d, *J* = 2.8, 1H), 5.17-4.92 (m, 3H), 4.51-4.40 (m, 2H), 4.20-3.95 (m, 3H), 3.90-3.74 (m, 2H), 2.18, 2.16, 2.12, 2.06, 2.05, 2.00, 1.96 (s, 24H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.28, 170.25, 170.10, 170.01, 169.88, 169.57, 169.08, 168.88, 101.05, 88.82, 75.64, 70.84, 70.55, 69.44, 69.26, 68.97, 66.47, 61.31, 60.66, 20.71, 20.62, 20.42, 20.27; MS (70 eV) 678 (M^+, 10), 677 (25), 662 (54), 648 (33), 647 (79), 636 (27), 635 (100); TLC R_f 0.26 (EtOAc/hexane, 1/1).

Heneicosa-*O*-acetyl-cyclo-*lin*-hepta[1α=>4]-D-glucopyranosyl[62]

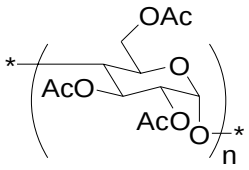


Data: ^{1}H NMR (400 MHz, $CDCl_3$) 5.29 (t, *J* = 9.4, 7H), 5.08 (d, *J* = 3.5, 7H), 4.79 (dd, *J* = 9.6, 4.0, 7H), 4.56 (d, *J* = 12.4, 7H), 4.26 (dd, *J* = 12.5, 4.0, 7H), 4.16-4.13 (m, 7H), 3.70 (t, *J* = 8.2, 7H), 2.12 (s, 21H), 2.09 (s, 21H), 2.05 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.75, 170.45, 169.46, 96.77, 76.76, 70.84, 70.40, 69.58, 62.45,

20.62; IR (KBr) 2940 (m), 2340 (w), 1740 (s, C=O), 1370 (m), 1230 (s), 1040 (s), 900 (m); MS (FAB) 2017 (M^+, 12), 517 (10), 169 (100); TLC R_f 0.32 (EtOAc/hexane, 4/1).

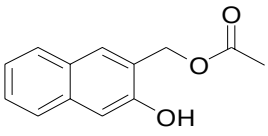
Cellulose Tricetate[63]

In a dry 50-mL, round-bottomed flask was placed cellulose (500 mg) in a 1:1 solution of acetic acid and acetic anhydride (10mL). The mixture was heated at 140 ^oC for 8 hours, then gradually cooled down to room temperature. A solution of MoO_2Cl_2 (10 mg) in acetic anhydride (1 mL) was slowly added at ambient temperature to above cellulose solution. The resultant mixture was heated at 100-110 ^oC for 6 hours. The reaction mixture was quenched with cold, saturated aqueous $NaHCO_3$ solution (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude white product was re-crystallized from CH_2Cl_2/ether to give 850 mg (96 % yield) of cellulose triacetate as white powder.



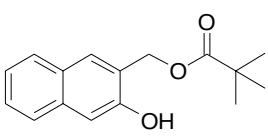
Data: ^1H NMR (400 MHz, $CDCl_3$) 5.05 (t, J = 9.1, 1H), 4.78 (t, J = 8.0, 1H), 4.38-4.35 (m, 2H), 4.09-4.03 (m, 1H), 3.70 (t, J = 9.0, 1H), 3.53 (bs, 1H), 2.11 (s, 3H), 1.99 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 170.18, 169.70, 169.26, 100.47, 76.05, 72.80, 72.49, 71.82, 62.00, 20.76, 20.54, 20.44; IR (CH_2Cl_2) 3454 (m), 2959 (m), 2893 (m), 2118 (w), 1751 (s), 1369 (s), 1232 (s), 1159 (s), 1123 (s), 1053 (s), 898 (m); TLC R_f 0.52 (MeOH/CH_2Cl_2, 1/9); GPC t_R 7.11 min (M_n 8697, M_w 28811, M_w/M_n = 3.31).

(3-Hydroxy-[2]naphthyl)-methyl Acetate[64]



Data: ^1H NMR (200 MHz, $CDCl_3$) 7.78 (s, 1H), 7.76-7.64 (m, 2H), 7.45-7.23 (m, 2H), 7.26 (s, 1H), 5.29 (s, 2H), 3.40 (bs, OH), 2.10 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 172.98, 152.62, 135.12, 131.21, 128.48, 127.77, 126.85, 126.14, 124.15, 123.77, 111.38, 63.04, 20.80; IR (CH_2Cl_2) 3050 (s), 2987 (s), 1715 (m), 1640 (m), 1509 (m), 1422 (s), 1278 (s), 1106 (m), 1025 (m), 953 (m), 896 (s); MS (70 eV) 216 (M^+, 38), 156 (38), 128 (100); TLC R_f 0.30 (EtOAc/hexane, 1/3).

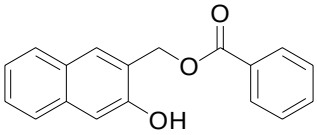
(3-Hydroxy-[2]naphthyl)-methyl 2,2-Dimethyl-propanoate



Data: ^1H NMR (200 MHz, $CDCl_3$) 7.81 (s, 1H), 7.74-7.65 (m, 2H),

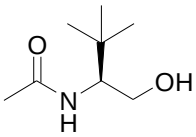
7.43-7.26 (m, 2H), 7.26 (s, 1H), 5.30 (s, 2H), 1.20 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 180.62, 152.82, 135.22, 131.24, 128.51, 127.78, 126.84, 126.23, 124.46, 123.75, 111.70, 63.21, 38.87, 27.00; IR (CH_2Cl_2) 3062 (s), 2988 (s), 2686 (m), 2410 (m), 2306 (s), 1668 (w), 1554 (m), 1422 (s), 1281 (s), 1159 (m), 895 (s); MS (70 eV) 258 (M^+, 25), 156 (100), 149 (10), 128 (82), 105 (39), 57 (40); TLC R_f 0.32 (EtOAc/hexane, 1/3).

(3-Hydroxy-[2]naphthyl)-methyl benzoate



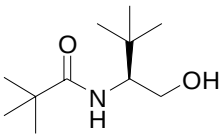
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 8.09 (d, *J* = 8.0, 2H), 7.91 (s, 1H), 7.78 (d, *J* = 8.0, 1H), 7.68 (dd, *J* = 10.0, 8.4, 2H), 7.58 (dd, *J* = 8.0, 7.2, 2H), 7.46-7.41 (m, 3H), 7.35-7.31 (m, 2H), 5.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 168.36, 152.76, 135.35, 133.57, 131.87, 129.94, 129.32, 128.54, 128.46, 127.78, 126.96, 126.26, 124.13, 123.84, 112.06, 63.74; IR (CH_2Cl_2) 3299 (w), 3020 (w), 2361 (w), 2254 (m), 1724 (w), 1687 (w), 1604 (w), 1380 (w), 1140 (w), 890 (s); MS (70 eV) 278 (M^+, 58), 156 (85), 128 (100), 105 (38), 77 (22); TLC R_f 0.35 (EtOAc/hexane, 1/3).

***N*-(1-Hydroxymethyl-2,2-dimethyl-propyl)-acetamide**[654]



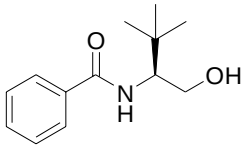
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 5.82 (bd, *J* = 8.9, 1H), 3.88-3.77 (m, 2H), 3.57-3.47 (m, 1H), 2.05 (s, 3H), 0.94 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 170.14, 63.69, 55.84, 33.71, 26.61, 20.85; TLC R_f 0.35 (EtOAc/hexane, 1/2).

***N*-(1-Hydroxymethyl-2,2-dimethyl-propyl)-2,2-dimethyl-propanamide**[66]



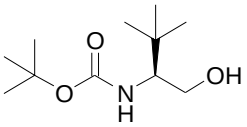
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 5.84 (bs, 1H), 3.90-3.75 (m, 2H), 3.59-3.50 (m, 1H), 2.63 (bs, 1H), 1.24 (s, 9H), 0.96 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 180.11, 63.71, 59.52, 38.98, 33.43, 27.57, 26.87; R_f 0.20 (EtOAc/hexane, 1/5).

***N*-(1-Hydroxymethyl-2,2-dimethyl-propyl)-benzamide**[67]



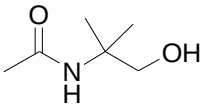
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.77 (dd, *J* = 7.2, 1.8, 2H), 7.50-7.37 (m, 3H), 6.38 (bd, *J* = 6.8, 1H), 4.09-3.88 (m, 2H), 3.72-3.62 (m, 1H), 2.83 (bs, 1H), 1.03 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) 168.84, 134.72, 131.59, 128.65, 126.99, 63.06, 59.81, 33.87, 30.79, 26.98; R_f 0.18 (EtOAc/hexane, 1/1).

(1-Hydroxymethyl-2,2-dimethyl-propyl)-carbamic acid *tert*-butyl ester[68]



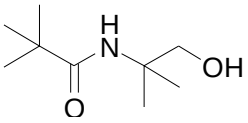
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 4.61 (bs, 1H), 3.85 (t, J = 7.0, 1H), 3.49 (d, J = 7.6, 2H), 2.10 (bs, 1H), 1.46 (s, 9H), 0.94 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 157.13, 79.41, 62.88, 60.88, 33.66, 28.32, 26.75; MS (20 eV) 218 ($M+1^+$, 5), 186 (15), 162 (35), 144 (15), 130 (39), 104 (13), 86 (45), 60 (37), 57 (100); R_f 0.26 (EtOAc/hexane, 1/5).

***N*-(2-Hydroxy-1,1-dimethyl-ethyl)-acetamide**[69]



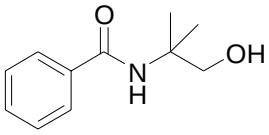
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 6.26 (s, 1 H), 5.28 (s, 1H), 3.49 (s, 2H), 1.92 (s, 3H), 1.23 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) 171.45, 70.50, 55.87, 24.29, 23.74; MS (20 eV) 132 ($M+1^+$, 4), 128 (16), 118 (24), 98 (20), 91 (44), 72 (38), 57 (100); TLC R_f 0.4 (EtOAc/hexane, 1/4).

***N*-(2-Hydroxy-1,1-dimethyl-ethyl)-2, 2-dimethyl-propionamide**



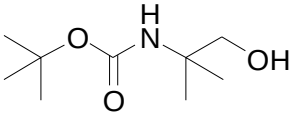
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 5.62 (s, 1H), 4.98 (s, 1H), 3.57 (s, 2H), 1.28 (s, 6H), 1.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 179.54, 70.74, 55.47, 38.86, 27.50, 24.39; IR (CH_2Cl_2) 3449 (m), 3314 (m), 2967 (s), 2878 (m), 1643 (s), 1472 (m), 1368 (m), 1210 (m), 1073 (m); MS (20 eV) 174 ($M+1^+$, 100), 142 (32), 102 (33), 69 (26), 57 (98); TLC R_f 0.36 (EtOAc/hexane, 1/4).

***N*-(2-Hydroxy-1,1-dimethyl-ethyl)-Benzoate**[70]



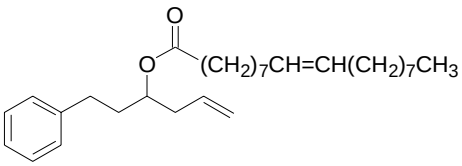
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.71-7.23 (m, 2H), 7.49-7.38 (m, 3H), 6.31 (bs, 1H), 5.08 (bs, 1H), 3.68 (s, 2H), 1.41 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) 168.41, 134.80, 131.54, 128.53, 126.86, 70.56, 56.34, 24.66, 24.56; MS (20 eV) 194 ($M+1^+$, 15), 162 (51), 122 (14), 105 (100), 77 (28); R_f 0.38 (EtOAc/hexane, 1/4).

(2-Hydroxy-1,1-dimethyl-ethyl)-carbamic acid *tert*-butyl ester[71]



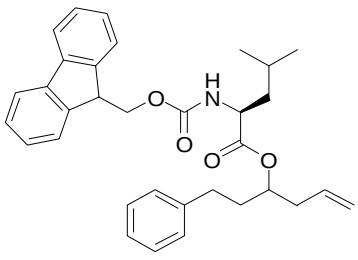
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 4.76 (s, 1H), 3.53 (s, 2H), 1.42 (s, 6H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.08, 79.61, 70.66, 54.15, 28.31, 24.53; MS (20 eV) 190 ($M+1^+$, 39), 158 (13), 134 (36), 116 (16), 102 (17), 86 (42), 84 (100), 58 (44); TLC R_f 0.33 (EtOAc/hexane, 1/9).

***cis*-octadec-9-enoic acid 1-phenethyl-but-3-enyl ester (1a)**



In a dry 50-mL, two-necked, round-bottomed flask was charged with MoO_2Cl_2 (9.5 mg, 0.05 mmol) in anhydrous CH_2Cl_2 (2 mL). To the above solution of catalyst, oleic acid (297 mg, 1.05 mmol in 2 mL of CH_2Cl_2) was added at ambient temperature followed by addition of benzoic anhydride (249 mg, 1.1 mmol in 2 mL of CH_2Cl_2). A solution of 1-phenethyl-but-3-en-1-ol (176.2 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) was added after 15 min. The resultant reaction mixture was stirred for 6 h and then quenched with cold, saturated aqueous $NaHCO_3$ solution (10 mL). The separated organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The resultant crude product was purified by column chromatography (EtOAc/hexane, 3/97) on silica gel to furnish 338 mg (95 % yield) of the pure oleate: ^{1}H NMR (200 MHz, $CDCl_3$) 7.32-7.14 (m, 5H), 5.82-5.68 (m, 1H), 5.34 (t, *J* = 5.4, 2H), 5.12-4.95 (m, 3H), 2.63 (q, *J* = 7.0, 2H), 2.35 (t, *J* = 6.8, 2H), 2.28 (t, *J* = 7.6, 2H), 2.02-1.81 (m, 3H), 1.65-1.62 (m, 2H), 1.38-1.22 (m, 21H), 0.88 (t, *J* = 6.5, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) 173.30, 141.45, 133.50, 129.89, 129.65, 128.32, 128.27, 125.84, 117.65, 72.31, 38.60, 35.22, 34.37, 31.76, 31.62, 29.60, 29.54, 29.38, 29.16, 29.03, 28.98, 28.95, 27.05, 26.99, 24.90, 22.52, 13.93; IR (CH_2Cl_2) 3029 (m), 2937 (s), 2856 (s), 1713 (s), 1606 (m), 1447 (m), 1316 (m), 1266 (w), 1174 (m), 1116 (m), 867 (w); MS (70 eV) 356 (M^+, 5), 355 (16), 341 (17), 298 (32), 296 (100), 292 (56), 281 (32), 280 (48), 177 (18), 158 (20), 149 (50), 117 (100), 105 (64), 91 (36); R_f 0.5 (EtOAc/hexane, 3/97).

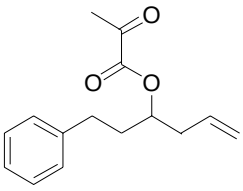
2-(9H-Fluoren-9-yl-methoxycarbonylamino)-4-methyl-pentanoic acid 1-phenethyl-but-3-enyl ester (1b)



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.80 (d, *J* = 7.6, 2H), 7.67-7.62 (m, 2H), 7.45-7.18 (m, 9H), 5.81-5.74 (m, 1H), 5.29-5.04 (m, 4H), 4.47-4.42 (m, 3H), 4.27 (t, *J* = 6.8, 1H), 2.75-2.61 (m, 2H), 2.42 (t, *J* = 6.8, 2H), 2.02-1.91 (m, 2H), 1.79-1.51 (m, 3H), 1.04-1.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 172.69, 155.86, 143.87, 143.70, 141.23, 133.06, 132.96, 128.32, 127.60, 126.96, 125.90, 124.98, 119.88, 118.09, 73.97, 66.82, 52.62, 47.14, 41.80, 38.46, 35.11, 31.52, 24.72, 22.84, 21.77; IR (CH_2Cl_2) 3945 (m), 3056 (s), 2960 (s), 1726 (s), 1648 (m), 1422 (s), 1277 (s), 1252 (s), 896 (s); MS (ESI) 543 (M^++MeOH, 30),

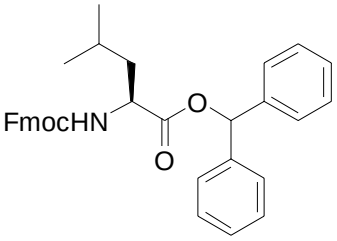
542 (M^++OMe, 37), 399 (17), 181 (100); TLC R_f 0.21 (EtOAc/hexane, 1/9).

2-Oxo-propionic acid 1-phenethyl-but-3-enyl ester (1c)



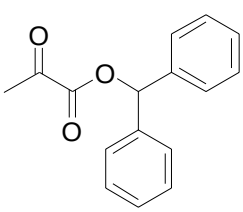
Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.30-7.15 (m, 5H), 5.79-5.69 (m, 1H), 5.13-5.05 (m, 3H), 2.72-2.60 (m, 2H), 2.45-2.41 (m, 2H), 2.44 (s, 3H), 2.12-1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.97, 160.54, 140.92, 132.72, 128.50, 128.30, 126.13, 118.57, 75.77, 38.50, 34.97, 31.67, 26.74; IR (CH_2Cl_2) 3491 (m), 3052 (s), 1738 (s), 1694 (s), 1605 (m), 1585 (m), 1420 (s), 1319 (s), 1287 (s), 1250 (s), 1177 (m), 1071 (m), 1026 (m), 896 (s); MS (70 eV) 246 (M^+, 2), 205 (13), 158 (24), 133 (13), 117 (100), 104 (21), 91 (69); TLC R_f 0.31 (EtOAc/hexane, 1/9).

2-(9H-Fluoren-9-yl-methoxycarbonylamino)-4-methyl-pentanoic acid benzhydryl ester (2a)



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (d, *J* = 7.5, 2H), 7.59 (d, *J* = 7.4, 2H), 7.42-7.28 (m, 14H), 6.91 (s, 1H), 5.19 (d, *J* = 8.7, 1H), 4.57-4.52 (m, 1H), 4.39 (d, *J* = 6.8, 2H), 4.21 (t, *J* = 7.0, 1H), 1.70-1.53 (m, 3H), 0.95-0.92 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 172.11, 155.89, 143.90, 143.70, 141.25, 139.59, 139.52, 128.49, 128.06, 127.99, 127.63, 127.14, 127.00, 126.94, 125.03, 119.91, 77.91, 66.95, 52.67, 47.15, 41.58, 24.68, 22.79, 21.83; IR (CH_2Cl_2) 3439 (m), 3057 (s), 2986 (s), 1726 (s), 1609 (m), 1511 (m), 1422 (s), 1384 (m), 1250 (s), 912 (s); MS (20 eV) 519 (M^+, 5), 178 (100), 165 (10), 91 (10) ; TLC R_f 0.28 (EtOAc/hexane, 1/9).

2-Oxo-propionic acid benzhydryl ester (2b)

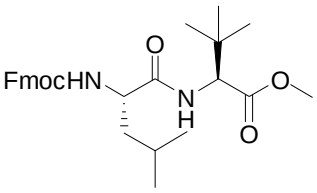


Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.41-7.30 (m, 10H), 6.96 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 191.43, 159.85, 138.93, 128.65, 128.35, 127.12, 78.98, 26.73; IR (CH_2Cl_2) 3033 (m), 2958 (m), 1735 (s), 1598 (m), 1495 (w), 1360 (w), 1266 (w), 1138 (s); MS (ESI) 277 (M+Na^+, 100), 167 (33); TLC R_f 0.26 (EtOAc/hexane, 1/9).

***N*-Fmoc-*L*-leucyl-*L*-*tert*-leucine methyl ester (3)**

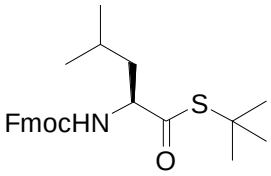
In a dry 50-mL, two-necked, round-bottomed flask was charged with MoO_2Cl_2 (5.0 mg, 0.025 mmol, 5 mol %) in anhydrous CH_2Cl_2 (5 mL). To the above solution of catalyst,

Fmoc-*L*-leucine (176 mg, 0.5 mmol in 5 mL of CH_2Cl_2) was added at ambient temperature followed by addition of benzoic anhydride (170 mg, 0.75 mmol in 5 mL of CH_2Cl_2). A solution of methyl *L*-*tert*-leucinate (80.2 mg, 0.6 mmol) in CH_2Cl_2 (5 mL) was added after 60 min. The resultant reaction mixture was stirred for 8 h and then quenched with cold, saturated aqueous $NaHCO_3$ solution (20 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and evaporated. The resultant crude product was purified by column chromatography (EtOAc/*n*-hexane, 1/4) on silica gel to furnish 216 mg (90 % yield) of the pure di-peptide.



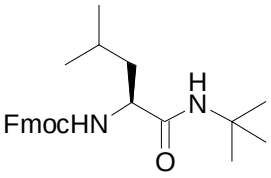
Data: ^{1}H NMR (200 MHz, $CDCl_3$) 7.75 (d, *J* = 7.4, 2H), 7.57 (d, *J* = 7.2, 2H), 7.40 (t, *J* = 7.2, 2H), 7.30 (t, *J* = 7.2, 2H), 6.56 (d, *J* = 9.4, 1H), 5.25, (d, *J* = 8.4, 1H), 4.46-4.39 (m, 3H), 4.21 (t, *J* = 6.8, 2H), 3.71 (s, 3H), 1.72-1.48 (m, 3H), 0.95 (bs, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) 171.89, 171.75, 156.34, 143.88, 143.77, 141.36, 127.77, 127.13, 125.07, 120.01, 67.11, 60.04, 53.56, 51.74, 47.10, 40.97, 34.75, 26.43, 24.58, 22.82, 21.94; IR (CCl_4) 3424 (m), 3334 (m), 3062 (m), 3025 (m), 2959 (s), 2872 (m), 1946 (w), 1901 (w), 1740 (s), 1681 (s), 1512 (s), 1478 (s), 1450 (s), 1436 (s), 1401 (m), 1370 (m), 1340 (m), 1218 (s), 1166 (s), 1105 (m), 1044 (m), 995 (w), 936 (w), 856 (w); MS (70 eV) 480 (M^+, 12), 465 (30), 449 (10), 424 (15), 386 (10), 308 (100), 285 (25), 269 (92), 264 (84), 243 (22), 237 (72); TLC R_f 0.3 (EtOAc/hexane, 1/4).

2-(9H-Fluoren-9-yl-methoxycarbonylamino)-4-methyl-pentanethioic acid *S*–*tert*- butyl ester (4)



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.77 (d, *J* = 7.6, 2H), 7.61 (t, *J* = 7.6, 2H), 7.40 (t, *J* = 7.4, 2H), 7.31 (d, *J* = 7.4, 2H), 5.09 (d, *J* = 9.0, 1H), 4.82-4.34 (m, 3H), 4.25 (t, *J* = 7.0, 2H), 1.72-1.64 (m, 3H), 1.47 (s, 9H), 0.96 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 201.46, 155.71, 143.95, 143.77, 141.34, 127.69, 127.05, 125.09, 119.97, 66.99, 59.69, 48.19, 47.25, 42.27, 29.78, 24.77, 23.10, 21.69; IR (CH_2Cl_2) 3431 (m), 3225 (m), 2989 (s), 2871 (s), 1955 (m), 1725 (s), 1681 (m), 1491 (s), 1448 (s), 1381 (s), 1351 (s), 1298 (s), 1119 (s), 1041 (s), 934 (s), 917 (m), 844 (s); MS (ESI) 425 (M^+, 100); TLC R_f 0.46 (EtOAc/hexane, 1/20).

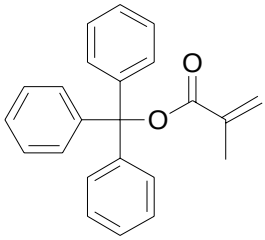
(1-*tert*-Butylcarbamoyl-3-methyl-butyl)-carbamic acid 9H-fluoren-9-ylmethyl ester (5)[72]



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.76 (d, *J* = 7.5, 2H), 7.59 (t, *J* = 7.5, 2H), 7.40 (t, *J* = 7.4, 2H), 7.31 (t, *J* = 7.4, 2H), 5.71 (bs, 1H), 5.22 (bd, *J* = 6.9, 1H), 4.41 (d, *J* = 6.8, 2H), 4.22 (t, *J* = 7.0, 1H), 4.04-4.03 (m, 1H), 1.64-1.51 (m, 3H), 1.34 (s, 9H), 0.95 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 171.27, 156.22, 143.81, 143.74, 141.29, 127.70, 127.05, 125.01, 119.96, 119.95, 66.93, 54.02, 51.38, 47.17, 41.77, 28.67, 24.70, 22.90, 22.14; IR (CH_2Cl_2) 3425 (m), 3052 (s), 2959 (m), 2748 (w), 2598 (w), 2483 (w), 2082 (w), 1718 (s), 1680 (s), 1560 (m), 1508 (s), 1422 (m), 1265 (s), 1216 (m), 1121 (m), 1050 (m), 896 (s); MS (ESI) 432 ($M+Na^+$, 100), 410 ($M+H^+$, 35);TLC R_f 0.38 (EtOAc/hexane, 1/9).

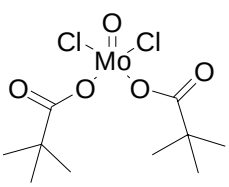
2-Methyl-acrylic acid trityl ester (6)[73]

In a dry 50 mL, two-necked, round-bottomed flask was placed MoO_2Cl_2 (4 mg, 0.02 mmol, 1mol%) in 5 mL of anhydrous toluene. A solution of methacrylic acid (205 μL, 2.4 mmol, 1.2 equiv) and benzoic anhydride (543 mg, 2.4 mmol, 1.2 equiv) in toluene (5 mL) was slowly added to the above solution. The resulting reaction mixture was stirred for 1 hour. To the above solution was slowly added a solution of diisopropylethylamine (350 μL, 2 mmol, 1 equiv) and trityl alcohol (520 mg, 2 mmol) in toluene (5 mL) at ambient temperature. This mixture was heated to reflux for 3 hours. After completion of the reaction as monitored by TLC, the reaction mixture was gradually warmed to room temperature and quenched with cold, saturated aqueous $NaHCO_3$ solution (20 mL). The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography on silica gel to give 571 mg (87%) of colorless oil along with 33 mg (9%) benzoylation side product.



Data: ^{1}H NMR (400 MHz, $CDCl_3$) 7.41-7.25 (m, 15H), 6.25-6.24 (m, 1H), 5.62-5.61 (m, 1H), 2.00 (dd, *J* = 1.24, 1.20, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 165.23, 143.41, 137.49, 128.30, 127.91, 127.23, 125.58, 89.97, 18.56; TLC R_f 0.52 (EtOAc/hexane/Et_3N, 10/90/5).

Molybdenum dichloride dipivalate oxide-I



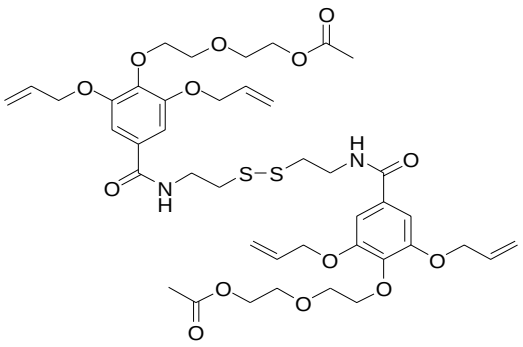
In a dry 50-mL, round-bottomed flask was placed $MoOCl_4$ (127 mg, 0.5 mmol) in 5 mL of anhydrous CH_2Cl_2. Silver pivalate (209 mg, 1.0 mmol) was added

as a solid to the above solution and the reaction mixture was refluxed for 8 hours. This solution was allowed to cool down to the room temperature. White precipitate was observed and filtered. The filtrate was concentrated and dried in vacuo to give **I** as dark-green power (173 mg, 90 %): ^{1}H NMR (400 MHz, $CDCl_3$) 1.251 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) 185.87, 38.75, 26.89; MS (ESI) 450 ($M+CH_3CN+Na^+$, 100), 410 ($M+ Na^+$, 6).

Applications on Highly Functionalized Substrates:

Acetic acid 2-(2-{4-[2-(2-{4-[2-(2-acetoxy-ethoxy)-ethoxy]-3,5-bis- allyloxy-benzoyl amino}-ethyldisulfanyl)-ethylcarbamoyl]-2,6-bis-allyloxy-phenoxy}-thoxy)-ethyl ester (7a)

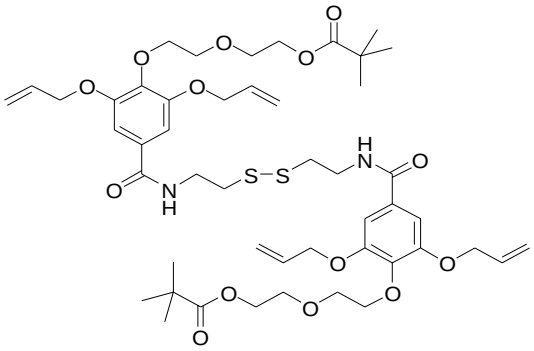
In a dry 50 mL, two-necked, round-bottomed flask was placed molybdenum dioxydichloride (2 mg, 0.01 mmol, 13mol%, 0.065 equiv) in 15 mL of anhydrous CH_2Cl_2. To the above solution, acetic anhydride (35 μL, 0.37 mmol, 2.5 equiv) was slowly added at ambient temperature. After for 10 min, a solution of corresponding alcohol (60 mg, 0.076 mmol in CH_2Cl_2, 2 mL) was slowly added to the above dark bluish green solution and the reaction mixture were stirred for 30 hours at room temperature. After completion, reaction mixture was quenched with cold, saturated aqueous NH_4Cl solution (5 mL) and extracted with dichloromethane (2 × 5 mL). The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography. The product obtained as colorless oil (63 mg, 95 %) was characterized by routine spectroscopic methods.



Data: ^{1}H NMR (500 MHz, $CDCl_3$) 7.53 (t, J = 5.6, 1H), 7.09 (s, 2H), 5.95-5.87 (m, 2H), 5.30 (dd, J = 17.2, 1.0, 2H), 5.17 (dd, J = 10.6, 1.0, 2H), 4.46 (d, J = 5.1, 4H), 4.16-4.13, (m, 4H), 3.76 (t, J = 5.0, 2H), 3.72 (t, J = 4.9, 2H), 3.69 (t, J = 6.1,2H), 2.89 (t, J = 6.4, 2H), 2.01 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 170.94, 167.26, 152.17, 140.90, 132.77, 129.11, 117.48, 106.54, 72.26, 70.34, 69.78, 68.88, 63.60, 39.32, 37.76, 20.80; IR (CCl_4) 3355 (w), 2927 (m), 1743 (s), 1649 (m), 1581 (m), 1493 (s), 1421 (m), 1364 (w), 1330 (s), 1232 (s), 1132 (s), 929 (m); MS (70 eV) 439 ($M/2^+$, 40), 423 (38), 362 (20), 232 (20), 215 (22), 87 (100); Anal. Calcd. for $C_{42}H_{56}N_2O_{14}S_2$ (877.02): C: 57.52%, H: 6.44%, N: 3.19%, S: 7.31%; Found: C: 57.85%, H: 7.76%, N: 3.18%, S: 7.03%; TLC R_f 0.67 (EtOAc/hexane, 1/4).

2,2-Dimethyl-propionic acid 2-[2-(2,6-bis-allyloxy-4-{2-[2-(3,5-bis-allyloxy-4-{2-[2-(2, 2-dimethyl-propionyloxy)-ethoxy]-ethoxy}-benzoylamino)-ethyldisulfanyl]-ethylcarbamoyl }-phenoxy)-ethoxy]-ethyl ester (7b)

In a dry 50 mL, two-necked, round-bottomed flask was placed molybdenum dioxydichloride (2 mg, 0.01 mmol, 8.7 mol%, 0.045 equiv) in 15 mL of anhydrous dichloromethane. To the above solution, pivalic anhydride (112 μL, 0.55 mmol, 2.4 equiv) was slowly added at ambient temperature. After for 10 min, a solution of corresponding alcohol (90 mg, 0.115 mmol in CH_2Cl_2, 2 mL) was slowly added to the above dark bluish green solution and the reaction mixture were stirred for 48 hours at room temperature. After completion, reaction mixture was quenched with cold, saturated aqueous NH_4Cl solution (5 mL) and extracted with dichloromethane (2 × 5 mL). The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography. The product obtained as colorless oil (92 mg, 84 %) was characterized by routine spectroscopic methods.

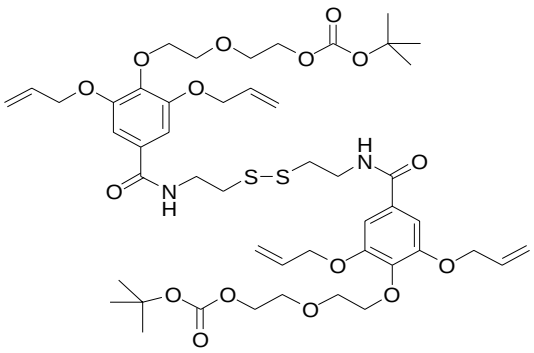


Data: ^{1}H NMR (500 MHz, $CDCl_3$) 7.22 (t, *J* = 6.6, 1H), 7.08 (s, 2H), 6.00-5.92 (m, 2H), 5.35 (dd, *J* = 17.0, 1.0, 2H), 5.21 (dd, *J* = 10.5, 1.0, 2H), 4.51 (d, *J* = 5.1, 4H), 4.19-4.15 (m, 4H), 3.78 (t, *J* = 5.1, 2H), 3.76-3.72 (m, 4H), 2.95 (t, *J* = 6.2, 2H), 1.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) 178.48, 167.37, 152.33, 141.17, 132.89, 129.24, 117.62, 106.69, 72.36, 70.45, 69.99, 69.08, 63.57, 39.36, 38.66, 37.90, 27.12; IR (CCl_4) 3303 (w), 2931 (m), 1730 (m), 1650 (m), 1581 (m), 1492 (m), 1420 (m), 1330 (m), 1284 (m), 1225 (w), 1132 (s), 930 (w); MS (70 eV) 482 ((M/2)+1$^+$, 98), 466 (50), 448 (40), 404 (35), 294 (35), 232 (40), 215 (25), 129 (100); Anal. Calcd. For $C_{48}H_{68}N_2O_{14}S_2$ (961.18): C: 59.98%, H: 7.13%, N: 2.91%, S: 6.67%; Found: C: 59.57%, H: 7.69%, N: 2.54%, S: 6.09%; TLC R_f 0.85 (EtOAc/hexane, 1/4).

Carbonic acid 2(2-{2,6-bis-llyloxy-4-[2-(2-{3,5-bis-allyloxy-4-[2-(2-*tert*-butoxycarb onyloxy-ethoxy)-ethoxy]-benzoylamino}-ethyldisulfanyl)-ethylcarbamoyl]-phenoxy}-ethoxy)-ethyl ester *tert*-butyl ester (7c)

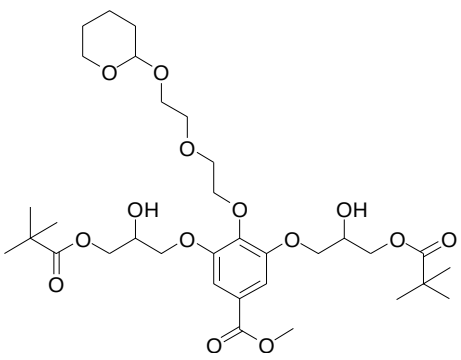
In a dry 50 mL, two-necked, round-bottomed flask was placed molybdenum dioxydichloride

(2 mg, 0.01 mmol, 8.5 mol%, 0.044 equiv) in 15 mL of anhydrous dichlorometane. To the above solution, di-*t*-butyl-dicarbonate (134 μL, 0.58 mmol, 2.5 equiv) was slowly added at ambient temperature. After for 10 min, a solution of corresponding alcohol (93 mg, 0.118 mmol in CH_2Cl_2, 2 mL) was slowly added to the above dark bluish green solution and the reaction mixture were refluxed for 48 hours. After completion, reaction mixture was quenched with cold, saturated aqueous NH_4Cl solution (5mL) and extracted with dichloromethane (2 × 5 mL). The separated organic layer was washed with brine, dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography. The product obtained as colorless oil (104 mg, 90 %) was characterized by routine spectroscopic methods.



^{1}H NMR (500 MHz, $CDCl_3$) 7.09 (t, *J* = 6.2, 1H), 7.07 (s, 2H), 6.08-5.94 (m, 2H), 5.36 (dd, *J* = 17.2, 1.0, 2H), 5.23 (dd, *J* = 10.8, 1.0, 2H), 4.53 (d, *J* = 5.1, 4H), 4.18, (t, *J* = 5.0, 4H), 3.79 (t, *J* = 5.0, 2H), 3.77-3.75 (m, 4H), 2.96 (t, *J* = 6.3, 2H), 1.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) 167.36, 153.49, 152.38, 141.19, 132.93, 129.28, 117.69, 106.67, 82.08, 72.38, 70.45, 70.04, 68.92, 66.07, 39.34, 37.92, 27.73; IR (CCl_4) 3354 (w), 2929 (w), 1742 (s), 1650 (m), 1581 (m), 1492 (s), 1420 (m), 1368 (m), 1330 (s), 1279 (s), 1133 (s), 929 (w); MS (70eV) 498 ($M/2^+$, <1), 453 (15), 397 (100), 382 (70), 320 (45), 234 (40), 215 (35), 199 (20); Anal. Calcd. For $C_{48}H_{68}N_2O_{16}S_2$ (993.18): C: 58.05%, H: 6.90%, N: 2.82%, S: 6.46%; Found: C: 57.79%, H: 7.19%, N: 2.73%, S: 6.12%; TLC R_f 0.72 (EtOAc/hexane, 1/4).

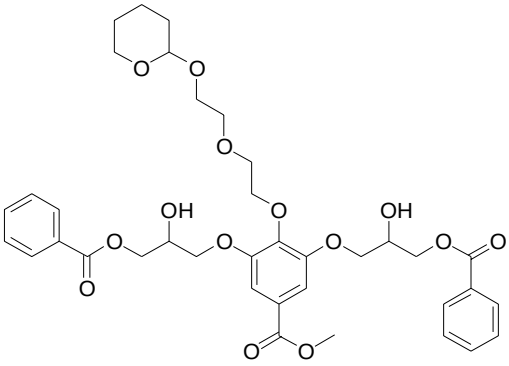
3,5-Bis-[3-(2,2-dimethyl-propionyloxy)-2-hydroxy-propoxy]-4-{2-[2-(tetrahydro-pyran-2-yl oxy)-ethoxy]-ethoxy}-benzoic acid methyl ester (8a)



In a dry 50 mL, two-necked, round bottom flask was placed MoO_2Cl_2 (14 mg, 0.07 mmol, 15 mol%) in 15 mL of anhydrous CH_2Cl_2. To the above solution, pivalic anhydride (90 mg, 0.48 mmol), was slowly added at ambient temperature. After for 45 min, a solution of the corresponding tetraol (123 mg, 0.24 mmol in CH_2Cl_2, 5 mL) was slowly added to the above dark bluish green solution

and the reaction mixture were stirred at ambient temperature for 32 hours. After completion, reaction mixture was quenched with cold, saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with dichloromethane (2 x 15 mL). The separated organic layer was washed with brine, dried ($MgSO_4$), filtered and evaporated. The crude product was purified by column chromatography on silica gel. The product-**8a** was obtained as colorless oil (118 mg, 73 %): ^{1}HNMR (500 MHz, d_6-DMSO) 7.24 (s, 2H), 5.31(bs, 2H), 4.53-4.52 (t, *J* = 3.5Hz, 1H), 4.14-4.08 (m, 6H), 4.05-3.99 (m, 6H), 3.82 (s, 3H), 3.73 (m, 4H), 3.58-3.56 (t, *J* = 4.4Hz, 2H), 3.46-3.34 (m, 2H), 1.45-1.12 (m, 6H), 1.10(s, 9H); ^{13}C NMR (125 MHz, d_6-DMSO) 177.27, 165.69, 152.09, 141.94, 124.49, 108.20, 98.03, 71.98, 70.24, 69.85, 69.65, 66.75, 66.06, 64.93, 61.17, 52.18, 30.15, 26.82, 24.98, 19.05; IR (CH_2Cl_2) 3466 (br, m), 2926 (m), 1722 (s), 1648 (m), 1590 (m), 1502 (m), 1481 (m), 1365 (m), 1342 (m), 1124 (m), 1035 (m), 938 (m), 886 (m); MS (70 eV) 672 (M^+, 5), 533 (7), 455 (7), 243 (20), 159 (100); HRMS Calcd for ($C_{33}H_{52}O_{14}$) 672.3357 found 672.3352; TLC R_f 0.49 **(**EtOAc/hexane, 1/2)

3,5-Bis-(3-benoyloxy)-2-hydroxy-propoxy)-4-{2-[2-(tetrahydro-pyran-2-yloxy)-ethoxy]-ethoxy}-benzoic acid methyl ester (**8b**)



In a dry 50 mL, two-necked, round bottom flask was placed MoO_2Cl_2 (23 mg, 0.12 mmol, 15 mol%) in 15 mL of anhydrous CH_2Cl_2. To the above solution, benzoic anhydride (179 mg, 0.79 mmol), was slowly added at ambient temperature. After for 45 min, a solution of the corresponding tetraol (200 mg, 0.39 mmol in CH_2Cl_2, 5 mL) was slowly added to the above dark bluish green solution and the reaction mixture were stirred at ambient temperature for 47 hours. The reaction mixture was quenched with cold, saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with dichloromethane (2 x 15 mL). The separated organic layer was washed with brine, dried ($MgSO_4$), filtered and evaporated. The crude product was purified by column chromatography on silica gel. The product-**8b** was obtained as colorless oil (237 mg, 85 %): ^{1}H NMR (500 MHz, d_6-DMSO) 8.01-7.99 (dd, *J* = 7.1Hz, *J* = 1.3Hz, 4H), 7.66-7.63 (m, 2H), 7.53-7.50 (m, 4H), 7.29 (s, 2H), 5.48 (bs, 2H), 4.46-4.34 (m, 5H), 4.21-4.19 (m, 2H), 4.15-4.10 (m, 6H), 3.80 (s, 3H), 3.70-3.61 (m, 4H), 3.56-3.54 (t, *J* = 4.3Hz), 3.42-3.30 (m,2H), 1.59-1.34 (m,

6H); ^{13}C NMR (125 MHz, d_6-DMSO) 165.70, 165.66, 152.08, 141.97, 133.26, 129.67, 129.24, 128.78, 124.52, 108.35, 98.03, 72.03, 70.34, 69.88, 69.64, 66.89, 66.03, 65.89, 61.16, 52.12, 30.11, 24.94, 19.03; IR (CH_2Cl_2) 3472 (br, m), 2877 (m), 1723 (s), 1650 (m), 1589 (m), 1503 (m), 1342 (m), 1211 (m), 1114 (m), 1033 (m), 937(m), 869 (m); MS (70 eV) 712 (M^+, 5), 283 (20), 179 (100), 105 (50), 85(22); TLC R_f 0.39 (EtOAc/hexane, 1/2).

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