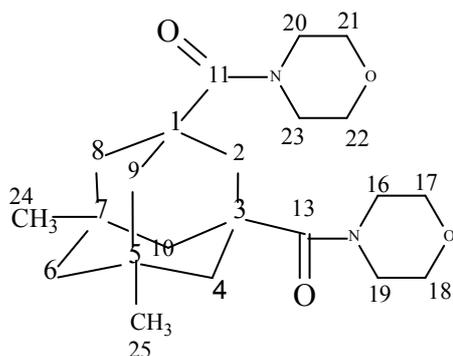


The first one-pot synthesis of 1,3-dicarbonyl adamantanes from 1-bromoadamantanes

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All experiments with 1-AdBr **1a** and 1,3-Me₂-5-Br -adamantane **1b** were carried out under atmospheric CO pressure with CBr₄·2AlBr₃ (E) for 3h according to the general procedure. If the other conditions were used, they are described. NMR spectra were recorded on a Bruker Avance spectrometer (¹H, 400 MHz; ¹³C, 100 MHz, TMS, CDCl₃). Mass spectra were measured on a Finnigan Polaris GCO Plus instrument, m/z (*I*_{rel} %). The conversions and the yields of products were determined by GC or both GC and ¹H NMR (with mesitylene as an internal standard). The yields of isolated products are marked by asterisk.

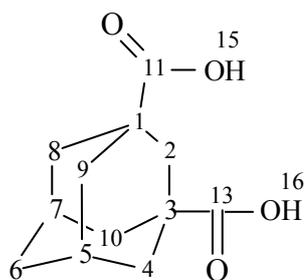
Typical procedures 1. At 0 °C under atmospheric CO pressure, **1b** (0.83 mmol) was added to the stirred solution of the complex CBr₄·2AlBr₃, freshly prepared from AlBr₃ (2.50 mmol) and CBr₄ (1.25 mmol) in anhydrous CH₂Br₂ (1.3 ml) at room temperature. After 3 h stirring at 0 °C under CO atmosphere, morpholine (5.0 mmol) was added to the *in situ* prepared carbonylation intermediate. The mixture was left to warm up to 0 °C during 20-30 min. After this, 10 ml of water and 20 ml of CHCl₃ were carefully added under stirring. Organic layer was separated. The remaining aqueous layer was extracted with CHCl₃ (2x20 ml). Combined organic extracts were dried over Na₂SO₄, the solvent was removed under reduced pressure and the residue was purified by crystallization from EtOH. The yield of **9c** was 85%. White powder, mp 222–224 °C. Calc. for C₂₂H₃₄N₂O₄, M. 390.46, (%): C, 67.67; H, 8.77; N, 7.17. Found (%): C, 67.85; H, 8.94; N, 7.14.



^1H NMR: 0.91 (6H, m., $^{24,25}\text{CH}_3$); 1.16 (2H, m., $^6\text{CH}_2$); 1.57, 1.59 (8H, AB system, q., $^2J_{\text{HH}}$ 12.8, $^{4,8-10}\text{CH}_2$); 2.03 (2H, bs., $^2\text{CH}_2$); 3.65 (16H, m., $^{16-19,20-23}\text{CH}_2$). ^{13}C : 30.28 ($^{24,25}\text{CH}_3$); 31.82 (^5C); 38.88 ($^{1,3}\text{C}$); 44.09 ($^{16,19,20,23}\text{CH}_2$); 44.31 ($^6\text{CH}_2$); 45.98 ($^{4,8-10}\text{CH}_2$); 49.66 ($^2\text{CH}_2$); 66.86 ($^{17,18,21,22}\text{CH}_2$); 174.58 ($^{11,13}\text{C}$). MS: 390, M^+ (0.7); 375, $\text{M}^+ - \text{CH}_3$ (2); 360 (9); 359 (6); 347 (3); 319 (4); 292 (3); 278 (6); 277 (38); 276, $\text{M}^+ - \text{CONC}_4\text{H}_8\text{O}$ (100); 248 (3); 247 (4); 246 (8); 232 (3); 207 (3); 192 (9); 190 (4); 189 (11); 163 (10); 162 (5); 161 (26); 133 (19); 121 (5); 119 (12); 114, $^+\text{CONC}_4\text{H}_8\text{O}$ (7); 105 (8); 91 (6); 88 (4); 86, $\text{NC}_4\text{H}_8\text{O}^+$ (5); 85 (5); 70, NC_4H_8^+ (5); 69 (3).

2. Similarly, **4b** was prepared in 82% yield from **1a** (0.469g, 2.18 mmol), aniline (6 mmol) in the presence of $\text{CBr}_4 \cdot 2\text{AlBr}_3$ (2.62 mmol) in CH_2Br_2 (1.8 ml). White powder, mp 279 °C. Calc. for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2$, M. 374.49, (%): C, 76.98; H, 6.99; N, 7.48. Found (%): C, 76.97; H, 6.91; N, 7.35. ^1H NMR: 1.70 - 1.80 (2H, m., CH_2); 1.80 - 2.60 (12H, m., CH_2 , CH); 7.10 (2H, t., $^3J_{\text{HH}}$ 7.3, CH); 7.31 (4H, t., $^3J_{\text{HH}}$ 7.3, CH); 7.39 (2 H, bs., CH); 7.52 (4H, d, CH). ^{13}C : 28.12 (CH); 35.21 (CH_2); 38.26 (CH_2); 40.37 (C); 41.93 (CH_2); 120.09 (CH); 124.32 (CH); 128.89 (CH); 137.61 (C); 174.85 (C). MS: 374, M^+ (45); 281, $\text{M}^+ - \text{C}_6\text{H}_4\text{NH}_2$ (1); 255 (17); 254, $\text{M}^+ - \text{CONHC}_6\text{H}_5$ (100); 253 (7); 207 (4); 199 (3); 191 (3); 185 (6); 183 (3); 174 (4); 170 (6); 167 (4); 163 (3); 161 (8); 149 (13); 143 (5); 139 (3); 135 (12); 134 (5); 133 (14); 129 (3); 121 (5); 120 (4); 119 (3); 115 (3); 111 (5); 109 (3); 107 (8); 105 (12); 97 (5); 95, $^+\text{NHC}_6\text{H}_5$ (6); 91 (11); 85 (5); 83 (4); 81 (8); 79 (7); 77 (7); 71 (6); 69 (5).

For 2. (a). **1a** (2.47 mmol), **E** (3.70mmol), CH_2Br_2 (3 ml), H_2O (15 ml); 1-2 days, (until the termination of precipitation). Yield 80%*. White solid, mp 285–286 °C (AcOH). Calc. for $\text{C}_{12}\text{H}_{16}\text{O}_4$, M. 224.26 (%): C, 64.27; H, 7.19. Found (%): C, 64.21; H, 7.24.

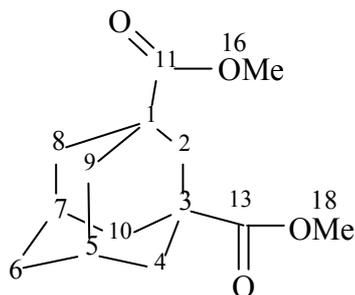


¹H NMR (CD₃OD): 1.74 (2H, ⁶CH₂); 1.84 – 1.94 (8H, AB-system, ^{4,8-10}CH₂); 2.02 (2H, bs., ²CH₂); 2.15 (2H, bs., ^{5,7}CH). **¹³C NMR**: 28.00 (^{5,7}CH); 35.12 (⁶CH₂); 37.83 (^{4,8-10}CH₂); 39.83 (²CH₂); 40.48 (^{1,3}C); 179.42 (^{11,13}C). **MS**: 224, M⁺ (5); 207, M⁺-OH (4); 180, M⁺-CO₂ (13); 179, M⁺-CO₂H (100); 162, M⁺-CO₂H-OH (5); 133, M⁺-2CO₂H-H (38); 105 (15); 91 (19); 79 (9); 77 (9); 65 (3).

(b). Under similar conditions, at a molar ratio **E** : **1a** = 1.2, yield 71%.*

(c). Carbonylation at 20 °C, 2 h. **1a** (1.78 mmol), **E** (2.14 mmol), CH₂Br₂ (2.2 ml), **H₂O** (10 ml); yield 66%*.

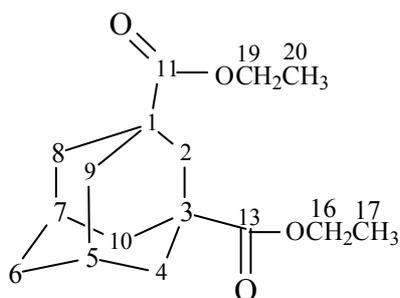
For 3a. (a). **1a** (2.98 mmol), **E** (3.57 mmol), CH₂Br₂ (3.8 ml), **MeOH** (1 ml); yield 83%.



¹H NMR: 1.60 (2H, ⁶CH₂); 1.67 – 1.81 (8H, m., ^{4,8-10}CH₂); 1.94 (2H, s., ^{5,7}CH); 2.07 (2H, bs., ²CH₂); 3.58 (6H, s. ^{16,18}CH₃). **¹³C NMR**: 27.47 (^{5,7}CH); 35.07 (⁶CH₂); 37.66 (^{4,8-10}CH₂); 39.50 (²CH₂); 40.65 (^{1,3}C); 51.44 (^{16,18}C); 176.96 (^{11,13}C). **MS**: 252, M⁺ (56); 221, M⁺-OMe (3); 207, M⁺-COOH (4); 194 (36); 193, M⁺-COOMe (100); 192 (3); 165 (3); 162, M⁺-COOMe-OMe (4); 161, M⁺-HCOOMe-OMe (36); 151 (3); 137 (7); 135 (4); 134 (19); 133 (87); 132 (10); 131 (6); 120 (4); 119 (9); 118 (4); 117 (19); 115 (5); 107 (5); 106 (7); 105 (24); 103 (3); 93 (16); 92 (9); 91 (41); 81 (9); 80 (3); 79 (19); 78 (12); 77 (18); 65 (8); 63 (3); 59, COOMe (15); 55 (10); 53 (7).

(b). Carbonylation at 20 °C, 0.5 h., [**1a**] : [**E**] = 1; **1a** (2.72 mmol), **E** (2.72 mmol), CH₂Br₂ (3.5 ml), **MeOH** (1 ml); yield 83%.

For 3b. **1a** (1.66 mmol), **E** (2.0 mmol), CH₂Br₂ (2 ml), **EtOH** (2 ml); yield 81%.



$^1\text{H NMR}$: 1.20 (6H, t., $^3J_{\text{HH}}$ 7.1, $^{17,20}\text{CH}_3$); 1.62 (2H, m., $^6\text{CH}_2$); 1.72 – 2.01 (10H, m., $^{4,8-10}\text{CH}_2$, $^{5,7}\text{CH}$); 2.11 (2H, m., $^2\text{CH}_2$); 4.07 (4H, q. $^3J_{\text{HH}}$ 7.1, $^{16,19}\text{CH}_2$). $^{13}\text{C NMR}$: 13.79 ($^{17,20}\text{CH}$); 27.31 ($^{5,7}\text{CH}_2$); 34.92 ($^6\text{CH}_2$); 37.47 ($^{4,8-10}\text{CH}_2$); 39.28 ($^2\text{CH}_2$); 40.24 ($^{1,3}\text{C}$); 59.87 ($^{16,19}\text{CH}_2$); 176.20 ($^{11,13}\text{C}$). **MS**: 281, $\text{M}^+ + 1$ (5); 252, $\text{M}^+ - \text{C}_2\text{H}_4$ (19); 234, $\text{M}^+ - \text{C}_2\text{H}_4 - \text{H}_2\text{O}$ (3); 224 (17); 208, $\text{M}^+ - \text{HCO}_2\text{Et}$ (15); 207, $\text{M}^+ - \text{CO}_2\text{Et}$ (100); 179, $\text{M}^+ - \text{CO}_2\text{Et} - \text{C}_2\text{H}_4$ (31); 161, $\text{M}^+ - \text{CO}_2\text{Et} - \text{C}_2\text{H}_5\text{OH}$ (54); 133 (55); 105 (16); 91 (19); 77 (6).

For 3c. (a). **1a** (1.55 mmol), **E** (1.97 mmol), CH_2Br_2 (2 ml), $^i\text{PrOH}$ (1 ml); yield 97%.

NMR: 1.12 (12H, d., $^3J_{\text{HH}}$ 6.2, $^{13,14,17,18}\text{CH}_3$); 1.59 (2H, m., $^6\text{CH}_2$); 1.69, 1.73 (8H, AB system, $^2J_{\text{HH}}$ 13.8, $^{4,8-10}\text{CH}_2$); 1.89 (2H, m., $^{5,7}\text{CH}$); 2.05 (2H, m., $^2\text{CH}_2$); 4.89 (2H, sept., $^3J_{\text{HH}}$ 6.2, $^{16,12}\text{CH}_2$). $^{13}\text{C NMR}$: 21.44 ($^{13,14,17,18}\text{CH}_3$); 27.63 ($^{5,7}\text{CH}_2$); 35.20 ($^6\text{CH}_2$); 37.66 ($^{4,8-10}\text{CH}_2$); 39.37 ($^2\text{CH}_2$); 40.54 ($^{1,3}\text{C}$); 66.95 ($^{16,12}\text{CH}_2$); 176.07 ($^{11,13}\text{C}$). **MS**: 309, $\text{M}^+ + \text{H}$ (21); 308, M^+ (3); 268 (3); 267, $\text{M}^+ - \text{C}_3\text{H}_5$ (16); 226 (5); 225 (42); 222 (6); 221, $\text{M}^+ - \text{COOC}_3\text{H}_7$ (31); 207 (4); 180, $\text{M}^+ - \text{CO}_2\text{C}_3\text{H}_7 - \text{C}_3\text{H}_5$ (15); 179, $\text{M}^+ - \text{CO}_2\text{C}_3\text{H}_7 - \text{C}_3\text{H}_6$ (100); 162, (6); 161 (48); 151 (5); 134 (9); 133 (46); 119 (3); 105 (13); 93 (3); 92 (3); 91 (14); 79 (4); 77 (3).

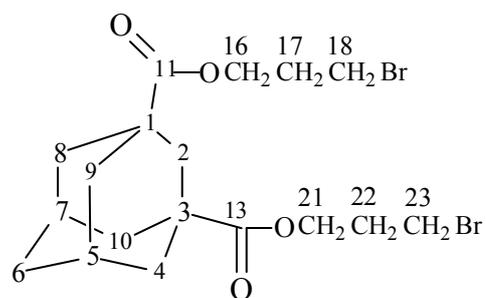
(b). Carbonylation at 20 °C, 0.5 h. **1a** (2.72 mmol), **E** (3.27 mmol), CH_2Br_2 3.5 ml), $^i\text{PrOH}$ (1.5 ml); yield 76%, conversion of **1a** 97%.

(c). Carbonylation at 20 °C, 0.45 h. **1a** (2.18 mmol), **E** (2.18 mmol), CH_2Br_2 2.2 ml), $^i\text{PrOH}$ (2 ml); yield 55%, conversion of **1a** 83%.

For 3d. **1a** (1.70 mmol), **E** (2.04 mmol), CH_2Br_2 (2 ml), $^s\text{BuOH}$ (1 ml); yield 84%.

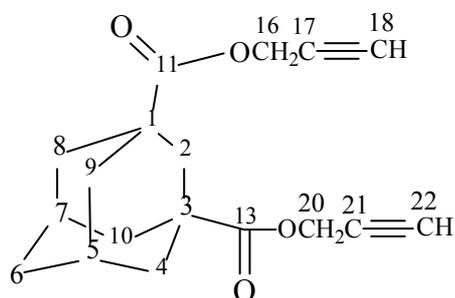
MS: 281, $\text{M}^+ - \text{C}_4\text{H}_7$ (16); 235, $\text{M}^+ - \text{COOC}_4\text{H}_9$ (35); 226, $\text{M}^+ - 2\text{C}_4\text{H}_7$ (13); 225, $\text{M}^+ - \text{C}_4\text{H}_7 - \text{C}_4\text{H}_8$ (92); 180, $\text{M}^+ - \text{COOC}_4\text{H}_9 - \text{C}_4\text{H}_7$ (13); 179, $\text{M}^+ - \text{COOC}_4\text{H}_9 - \text{C}_4\text{H}_8$ (100); 134 (9); 133 (42); 105 (10); 105 (10); 93 (5); 91 (12); 79 (4); 77 (4).

For 3e. **1a** (2.14 mmol), **E** (2.58 mmol), CH_2Br_2 (2.7ml), $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{OH}$ (10 mmol); yield 75%.



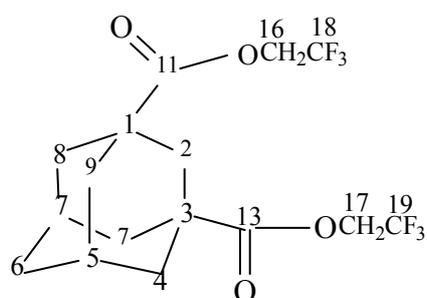
$^1\text{H NMR}$: 1.49 (2H, m., $^6\text{CH}_2$); 1.66 (8H, AB system, $^2J_{\text{HH}}$ 13.8, $^{4,8-10}\text{CH}_2$); 1.80 (2H, m., $^2\text{CH}_2$); 1.99 (6H, m., $^{17,22}\text{CH}_2$, $^{5,7}\text{CH}$); 3.27 (4H, t. $^3J_{\text{HH}}$ 5.9, $^{18,23}\text{CH}_2$); 3.99 (4H, t., $^3J_{\text{HH}}$ 5.9, $^{16,21}\text{CH}_2$). $^{13}\text{C NMR}$: 27.06 ($^{5,7}\text{CH}_2$); 29.04 ($^{18,23}\text{CH}_2$); 30.96 ($^{17,22}\text{CH}_2$); 34.60 ($^6\text{CH}_2$); 37.18 ($^{4,8-10}\text{CH}_2$); 38.94 ($^2\text{CH}_2$); 40.22 ($^{1,3}\text{C}$); 61.43 ($^{16,21}\text{CH}_2$); 175.70 ($^{11,13}\text{C}$). **MS**: 387, 385, M^+-Br (2); 301, 299, $\text{M}^+-\text{COO}(\text{CH}_2)_3\text{Br}$ (34), 266 (17); 265, $\text{Ad}(\text{COOH})(\text{COOC}_3\text{H}_6)^+$ (100); 219 (2); 205 (3); 186 (4); 179, $\text{Ad}(\text{COOH})^+$ (30); 162 (5); 161 (47); 134 (7); 133 (42); 119 (2); 105 (9); 93 (2); 91 (11); 79 (3); 77 (3).

For **3f**. **1a** (2.24 mmol), **E** (2.70 mmol), CH_2Br_2 (2.9 ml), $\text{CH}\equiv\text{CCH}_2\text{OH}$ (10.78 mmol); yield 74%.



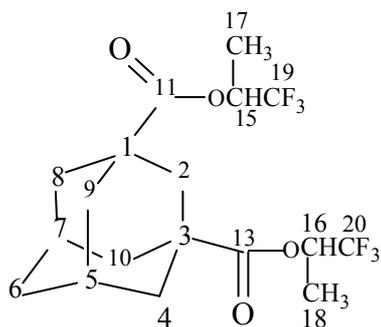
$^1\text{H NMR}$: 1.55 (2H, m., $^6\text{CH}_2$); 1.74 (8H, AB - system, $^2J_{\text{HH}}$ 13.8, $^{4,8-10}\text{CH}_2$); 1.91 (2H, m., $^2\text{CH}_2$); 2.03 (2H, m., $^{5,7}\text{CH}$); 2.41 (2H, t., $^4J_{\text{HH}}$ 2.5, $^{18,22}\text{C}$); 4.51- 4.52 (4H, d., $^4J_{\text{HH}}$ 2.6, $^{16,20}\text{CH}_2$). $^{13}\text{C NMR}$: 27.30 ($^{5,7}\text{CH}_2$); 34.88 ($^6\text{CH}_2$); 37.49 ($^{4,8-10}\text{CH}_2$); 39.13 ($^2\text{CH}_2$); 40.55 ($^{1,3}\text{C}$); 51.80 ($^{16,20}\text{CH}_2$); 75.03 ($^{18,22}\text{C}$); 77.86 ($\text{C}^{17,21}$); 176.14 ($^{11,13}\text{C}$). **MS**: 300, M^+ (12); 218 (16); 217, $\text{M}^+-\text{COOCH}_2\text{C}_2\text{H}$ (100), 207 (2); 161 (11); 135 (2); 134 (5); 133 (31); 105 (6); 93 (4); 92 (3); 91 (13); 79 (7); 77 (5); 55 (4)

For **3g**. **1a** (1.89 mmol), **E** (2.27 mmol), CH_2Br_2 (2.4 ml), $\text{CF}_3\text{CH}_2\text{OH}$ (2 ml); yield 92%.



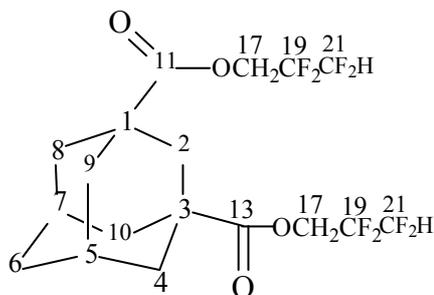
¹H NMR: 1.65–1.71 (2H, ⁶CH₂); 1.80–1.95 (8H, AB-system, ²J_{HH} 13.0, ^{4,8-10}CH₂); 2.05 (2H, bs., ²CH₂); 2.16 (2H, sept., ³J_{HH} 2.9, ^{5,7}CH); 4.43 (4H, q., ³J_{HF} 8.5, ^{16,17}CH₂). **¹³C NMR:** 27.38 (^{5,7}CH); 34.87 (⁶CH₂); 37.38 (^{4,8-10}CH₂); 38.91 (²CH₂); 40.86 (^{1,3}C); 60.05 (q., ²J_{CF} 36.5, ^{16,17}CH₂); 122.87 (q., ¹J_{CF} 277.1, ^{18,19}CF₃); 174.62 (^{11,13}C). **¹⁹F NMR:** - 74.08 (t., ³J_{HF} 8.5, ^{18,19}CF₃). **MS:** 388, M⁺ (3); 387, M⁺-H (9); 369, M⁺-F (4); 341, M⁺-F-CO (2); 287, M⁺-CH₂CF₂-H₂O (9); 261, M⁺-CH₂CF₂-CO₂ (100); 259 (7); 233, M⁺-CH₂CF₂-CO₂-CO (3); 185 (3); 162 (8); 161 (55); 134 (6); 133 (48); 131 (8); 105 (17); 91 (16); 79 (2); 77 (4).

For **3h**. **1a** (1.04 mmol), **E** (1.25 mmol), CH₂Br₂ (1.3 ml), CF₃CH(CH₃)OH (5 mmol); yield 94%.



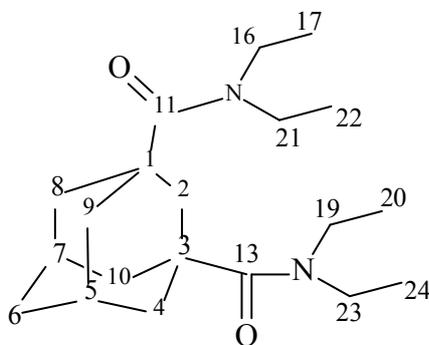
¹H NMR: 1.34 (6H, d., ^{17,18}CH₃); 1.65 – 1.71 (2H, ⁶CH₂); 1.78 - 1.93 (8H, AB system, ²J_{HH} 13.8, ^{4,8-10}CH₂); 2.02 (2H, bs., ²CH₂); 2.12 - 2.19 (2H, m, ^{5,7}CH); 5.26 (2H, qq, ³J_{HF} ~ ³J_{HF} 6.60, ^{15,16}CH). **¹³C NMR:** 13.23 (q., ³J_{CF} 1.8, ^{17,18}CH₃); 27.46 (s., ^{5,7}CH); 34.98 (s., ⁶CH₂); 37.40-37.42 (^{4,8-10}CH₂); 38.87 (²CH₂); 40.84 (^{1,3}C); 66.50 (q., ²J_{CF} 33.3, ^{15,16}CH); 123.87 (q., ¹J_{CF} 279.7, ^{19,20}C); 174.58 (^{11,13}C). **¹⁹F NMR:** - 78.87 (s., ^{19,20}C). **MS:** 417, M⁺+H (5); 397, M⁺-HF (3); 276, M⁺-COOCHCH₃ (16); 275, M⁺-COOCH₂CH₃ (100); 162 (8); 161 (75); 134 (8); 133 (67); 131 (8); 105 (18); 91 (20); 79 (5); 77 (7).

For **3i**. **1a** (1.98 mmol), **E** (2.38 mmol), CH₂Br₂ (2.6 ml), HCF₂CF₂CH₂OH (9,5 mmol); yield 90%.



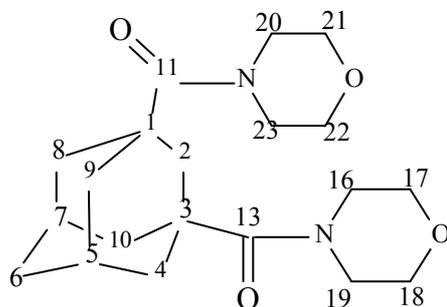
¹H NMR: 1.65 – 1.70 (2H, sept., ⁶CH₂); 1.78 - 1.93 (8H, AB system, ²J_{HH} 13.8, ^{4,8-10}CH₂); 2.03 (2H, bs., ²CH₂); 2.16 (2H, sept., ³J_{HH} 2.8, ^{5,7}CH); 4.43 (4H, tt, ³J_{HF} 12.8, ⁴J_{HF} 1.3, ^{16,17}CH₂); 5.82 (2H, tt., ²J_{HF} 53.1, ³J_{HF} 3.8, ^{20,21}CH). **¹³C NMR:** 27.50 (^{5,7}CH); 34.99 (⁶CH₂); 37.53 (^{4,8-10}CH₂); 39.10 (s., ²CH₂); 41.00 (^{1,3}C); 59.47 (t., ²J_{CF} 29.2, ^{16,17}CH₂); 109.36 (tt., ¹J_{CF} 250.1, ²J_{CF} 37.0, ^{20,21}CH); 114.13 (tt., ¹J_{CF} 249.4.1, ²J_{CF} 28.2, ^{18,19}CF₂); 174.72 (^{11,13}C). **MS:** 452, M⁺ (0.7); 433, M⁺-F (2); 401, M⁺-CF₂H (1); 294, M⁺-CO₂--CH₂CF₂CF₂ (15); 293, M⁺-CO₂--CH₂CF₂CF₂H (100); 265 (2); 237 (2); 162 (8); 161 (67); 134 (8); 133 (59); 131 (4); 119 (3); 105 (15); 91 (15); 79 (2); 77 (2); 51, CF₂H⁺ (2).

For 4a. Carbonylation at 0 °C, 1 h., **1a** (1.72 mmol), **E** (2.06 mmol), CH₂Br₂ (2 ml), **Et₂NH** (8 mmol); yield 75%*. White solid, mp 115 °C. (precipitated from diethyl ether by pentane). Calc. for C₂₀H₃₄N₂O₂, M. 334.50, (%): C, 71.81; H, 10.25; N, 8.37. Found (%): C, 71.84; H, 10.27; N, 8.37.



¹H NMR: 1.02 (12H, t., ³J_{HH} 6.7, ^{17,22,20,24}CH₃); 1.57 (2H, m., ⁶CH₂); 1.83, 1.85 (8H, AB system, ²J_{HH} 12.4, ^{4,8-10}CH₂), 2.07 (4H, m., ^{5,7}CH, ²CH₂); 3.30 (8H, q., ³J_{HH} 6.7, ^{16,21,19,23}CH₂). **¹³C NMR:** 13.30 (^{17,22,20,24}CH₃); 28.49 (^{5,7}CH₂); 35.33 (⁶CH₂); 37.97 (^{16,21,19,23}CH₂); 40.03 (^{1,3}C); 41.56 (^{4,8-10}CH₂); 42.26 (²CH₂); 174.85 (^{11,13}C). **MS:** 334, M⁺ (5); 305, M⁺-C₂H₅ (12); 236 (21); 235 (67); 234, M⁺-CONEt₂ (100); 206, M⁺-CONEt₂-C₂H₄ (10), 204 (3); 178, M⁺-CONEt₂-2C₂H₄ (4); 164 (5); 162 (4); 161 (18); 143 (4); 135 (20); 134 (4); 133 (18); 119 (3); 107 (5); 105 (16); 100, ⁺CONEt₂ (23); 93 (7); 91 (13); 79 (5); 77 (4); 74 (5); 72, ⁺NEt₂ (23); 71 (8).

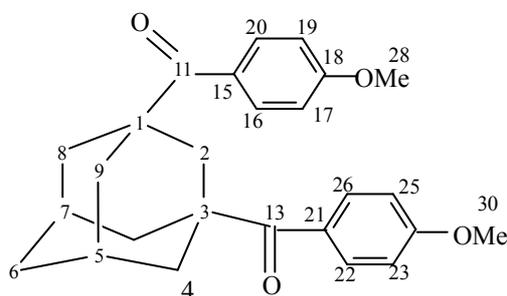
For **4c**. (a) **I** (1.73 mmol), **E** (2.08 mmol), CH_2Br_2 (2.2 ml), **morpholine** (8.20 mmol); yield 86%.* White solid, mp 184–185 °C (precipitated from dioxane by pentane). Calc. for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_4$, M. 362.47, (%): C, 66.27; H, 8.34; N, 7.73. Found (%): C, 66.31; H, 8.32; N, 7.59.



$^1\text{H NMR}$: 1.68 (2H, m., $^6\text{CH}_2$); 1.94–1.96 (8H, AB -system, $^2J_{\text{HH}}$ 13.3, $^{4,8-10}\text{CH}_2$); 2.17 (4H, m., $^2\text{CH}_2$, $^{5,7}\text{CH}$); 3.66 (16H, m., $^{16-19, 20-23}\text{CH}_2$). $^{13}\text{C NMR}$: 28.26 ($^{5,7}\text{CH}$); 35.43 ($^6\text{CH}_2$); 37.96 ($^{4,8-10}\text{CH}_2$); 42.20 ($^{16,19,20,23}\text{CH}_2$); 45.89 ($^2\text{CH}_2$); 66.85 ($^{21,22,17,18}\text{CH}_2$); 174.74 ($^{11,13}\text{C}$). **MS**: 362, M^+ (1); 333, $\text{M}^+ - \text{C}_2\text{H}_6$ (5); 332 (15); 331 (13); 319, $\text{M}^+ - \text{C}_3\text{H}_7$ (8); 291 (6); 290 (4); 250 (6); 249 (58); 248, $\text{M}^+ - \text{CONC}_4\text{H}_8\text{O}$ (100); 247 (5); 234 (4); 220 (10); 219 (6); 218 (12); 217 (4); 206 (3); 205 (3); 204 (3); 190 (4); 165 (3); 164 (9); 162 (6); 161 (43); 143 (4); 135 (17); 134 (6); 133 (25); 131 (4); 119 (5); 118 (4); 114, $^+\text{CONC}_4\text{H}_8\text{O}$ (13); 107 (6); 105 (27); 93 (4); 91 (13); 86, $\text{NC}_4\text{H}_8\text{O}^+$ (7); 88 (6); 86, $\text{NC}_4\text{H}_8\text{O}^+$ (7); 85 (15); 83 (10); 77 (7); 70, NC_4H_8^+ (9); 69 (5).

(b) Carbonylation at 20 °C, 45 min. **1a** (2.28 mmol), **E** (2.74 mmol), CH_2Br_2 (3 ml), **morpholine** (10.9 mmol); yield 64%.*

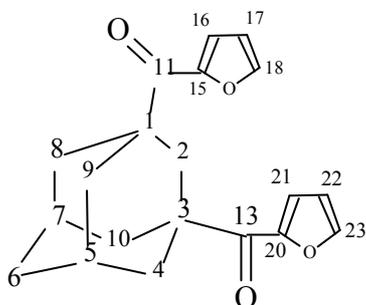
For **5**. **1a** (2.15 mmol), **E** (2.58 mmol), CH_2Br_2 (2.8 ml), **C₆H₅OMe** (10.4 mmol); yield 69%*. White solid, mp 144–145 °C (precipitated from dioxane by hexane). Calc. for $\text{C}_{26}\text{H}_{28}\text{O}_4$, M. 404.46, (%): C, 77.20; H, 6.98. Found (%): C, 77.33; H, 6.82.



$^1\text{H NMR}$: 1.75 (2H, m., $^6\text{CH}_2$); 2.04 – 2.06 (8H, AB- system, $^2J_{\text{HH}}$ 12.7, $^{4,8-10}\text{CH}_2$); 2.25 (2H, m., $^2\text{CH}_2$); 2.31 (2H, m., $^{5,7}\text{CH}$); 3.79 (6H, s., $^{28,30}\text{CH}_3$); 6.85 (4H, m., $^3J_{\text{HH}}$ 8.6, $^{17,19,23,25}\text{CH}$); 7.74 (4H, m., $^3J_{\text{HH}}$ 8.6, $^{16,20,22,26}\text{CH}$). $^{13}\text{C NMR}$: 28.26 ($^{5,7}\text{CH}$); 35.43 ($^6\text{CH}_2$); 38.82 ($^{4,8-10}\text{CH}_2$); 40.74 ($^2\text{CH}_2$); 47.00 ($^{1,3}\text{C}$); 55.12 ($^{28,30}\text{CH}_3$); 113.07 ($^{17,19,23,25}\text{CH}$); 130.22 ($^{16,20,22,26}\text{CH}$); 130.29

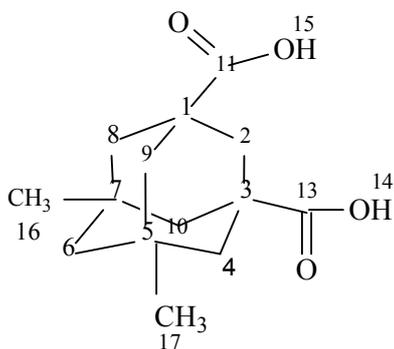
($^{15}, ^{21}\text{C}$); 161.60 ($^{18,24}\text{C}$); 205.58 ($^{11,13}\text{C}$). **MS**: 404, M^+ (5); 342, M^+-2OMe (3); 270 (5); 269, $\text{M}^+-\text{COC}_6\text{H}_4\text{OMe}$ (23); 268, $\text{M}^+-\text{COC}_6\text{H}_4\text{OMe}-\text{H}$ (15); 252 (10); 196 (4); 161 (5); 149 (4); 136 (9); 135, $^+\text{COC}_6\text{H}_4\text{OMe}$ (100); 107, $\text{C}_6\text{H}_4\text{OMe}^+$ (7); 91 (6); 77 (14).

For **6**. **1a** (1.02 mmol), **E** (1.25 mmol), CH_2Br_2 (1.3ml), **furan** (4.1 mmol); yield 30-45%.



$^1\text{H NMR}$: 1.40 – 2.05 (10H, m., $^{6,4,8-10}\text{CH}_2$); 3.57 - 4.00 (4H, m., $^2\text{CH}_2$, $^{5,7}\text{CH}$); 7.07 (2H, dd, $^3J_{\text{HH}}$ 4.9, $^4J_{\text{HH}}$ 3.0, $^{17,22}\text{CH}$); 7.53 (2H, dd, $^3J_{\text{HH}}$ 4.9, $^4J_{\text{HH}}$ 0.8, $^{16,21}\text{CH}$); 7.75 (2H, dd., $^3J_{\text{HH}}$ 3.0, $^4J_{\text{HH}}$ 0.8, $^{18,23}\text{CH}$). $^{13}\text{C NMR}$: 27.74 ($^{5,7}\text{CH}$); 37.34 ($^6\text{CH}_2$); 37.35 ($^{4,8-10}\text{CH}_2$); 45.85 ($^2\text{CH}_2$); 49.07 ($^{1,3}\text{C}$); 111.81 ($^{17,22}\text{CH}$); 118.47 ($^{16,21}\text{CH}$); 145.09 ($^{18,23}\text{CH}$); 152.52 ($^{15,20}\text{C}$); 193.64 ($^{11,13}\text{C}$). **MS**: 324, M^+ (44); 256, $\text{M}^+-\text{C}_4\text{H}_3\text{O}$ (22); 230 (17); 229, $\text{M}^+-\text{COC}_4\text{H}_3\text{O}$ (100); 201, $\text{M}^+-\text{M}^+-\text{C}_4\text{H}_3\text{O}-\text{CO}$ (12); 174 (10); 173 (7); 169 (3); 161 (13); 159 (6); 155 (5); 145 (13); 143 (7); 133 (13); 131 (6); 123 (5); 119 (11); 107 (5); 105 (9); 95, $\text{C}_4\text{H}_3\text{OCO}^+$ (62); 93 (8); 91 (13); 79 (5); 77 (7); 67, $\text{C}_4\text{H}_3\text{O}^+$ (2).

For **7**. (a). **1b** (1.88 mmol), **E** (2.82 mmol), CH_2Br_2 (2.8 ml), **H₂O** (10 ml) (until the termination of precipitation); yield 53%*. White solid, mp 273–274 °C (AcOH). Calc. for $\text{C}_{14}\text{H}_{20}\text{O}_4$, M. 252.31, (%): C, 66.64; H, 7.99. Found (%): C, 66.85; H, 8.14.

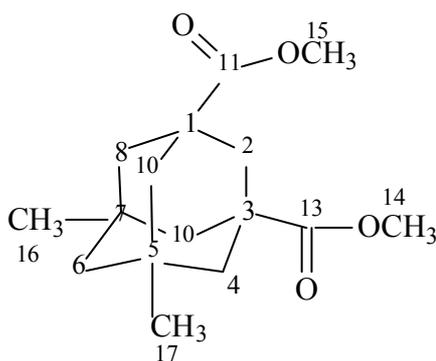


$^1\text{H NMR}$: 0.93 (6H, m., $^{16,17}\text{CH}_3$); 1.20 (2H, $^6\text{CH}_2$); 1.48, 1.52 (8H, AB system, $^2J_{\text{HH}}$ 11.9; $^{4,8-10}\text{CH}_2$); 1.88 (2H, m., $^2\text{CH}_2$). $^{13}\text{C NMR}$: 29.06 ($^{16,17}\text{CH}_3$); 30.93 ($^{5,7}\text{CH}$); 38.75 ($^2\text{CH}_2$); 42.41 ($^{1,3}\text{C}$); 44.07 ($^{4-8}\text{CH}_2$); 47.60 ($^6\text{CH}_2$); 179.23 ($^{11,13}\text{C}$). **MS**: 252, M^+ (0.4); 237, M^+-Me (2); 219, $\text{M}^+-\text{Me}-\text{H}_2\text{O}$ (8); 208, M^+-CO_2 (14); 207, $\text{M}^+-\text{CO}_2\text{H}$ (100); 189, $\text{M}^+-\text{CO}_2\text{H}-\text{H}_2\text{O}$ (41); 179,

M^+-CO_2H-CO (43); 161, M^+-2CO_2H-H (77); 133 (5); 121 (9); 119 (17); 107 (32); 105 (21); 93 (9); 91 (27); 79 (10); 77 (7); 65 (4).

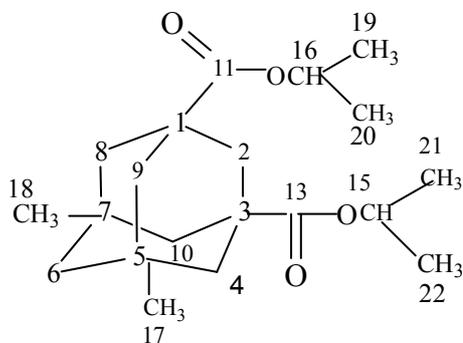
(b). Carbonylation at 20 °C, 45 min., **1b** (2.18 mmol), **E** (3.92 mmol), CH_2Br_2 (4 ml), H_2O (20 ml). Yield 60% for 3 days.

For 8a. **1b** (2.47 mmol), **E** (2.47 mmol), CH_2Br_2 (2.6 ml), **MeOH** (2 ml); yield of pure compound 65%*. White solid, mp 105 °C (hexane). Calc. for $C_{16}H_{24}O_4$, M. 280.36 (%): C, 68.54; H, 8.63. Found (%): C, 68.56; H, 8.63.



1H NMR: 0.88 (6H, m., $^{16,17}CH_2$); 1.14 (2H, 6CH_2); 1.48, 1.49 (8H, AB system., $^2J_{HH}$ 11.9; $^{4,8-10}CH_2$); 1.93 (2H, m., 2CH_2); 3.64 (6H, m., $^{14,15}CH_3$). ^{13}C NMR: 29.77 ($^{16,17}CH_3$); 31.24 ($^{5,7}CH$); 38.65 (2CH_2); 42.75 ($^{1,3}C$); 44.09 ($^{4,8-10}CH_2$); 49.59 (6CH_2); 51.63 ($^{14,15}CH_3$); 176.98 ($^{11,13}C$). **MS**: 280, M^+ (2); 265, M^+-CH_3 (3); 233 (3); 222 (16); 221, $M^+-COOCH_3$ (100); 205 (3); 190 (8); 189 (53); 165 (10); 163 (3); 162 (13); 161 (63); 145 (4); 134 (5); 134 (3); 133 (5); 121 (10); 120 (4); 119 (4); 107 (4); 106 (6); 105 (13); 91 (9); 77 (4).

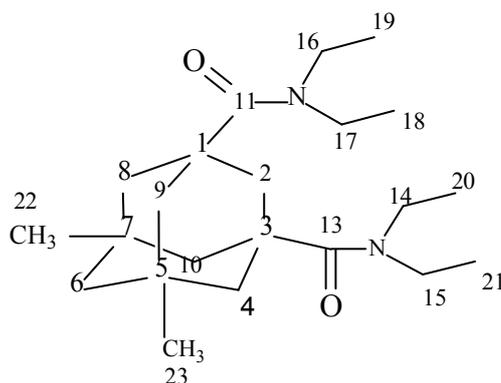
For 8b. **1b** (1.80 mmol), **E** (2.16 mmol), CH_2Br_2 (2.5 ml), iPrOH (2 ml); yield 79%.



1H NMR: 0.85 (6H, s., $^{17,18}CH_3$); 1.10 (2H, m., 6CH_2); 1.16 (12H, d., $^3J_{HH}$ 6.2, $^{19-22}CH_3$); 1.42, 1.44 (8H, AB - system, q., $^2J_{HH}$ 12.4, $^{4,8-10}CH_2$); 1.79 (2H, m., 2CH_2); 4.93 (2H, sept., $^3J_{HH}$ 6.2, $^{15,16}CH$). ^{13}C NMR: 21.56 ($^{19-22}CH_3$); 29.79 ($^{17,18}CH_3$); 31.18 ($^{5,7}C$); 38.40 (2CH_2); 42.55 ($^{1,3}C$);

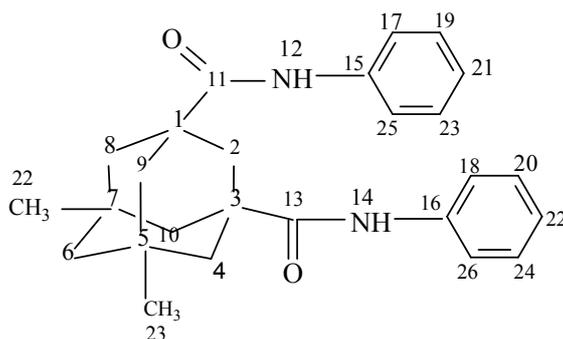
43.95 ($^{4,8-10}\text{CH}_2$); 49.61 ($^6\text{CH}_2$); 67.17 ($^{15,16}\text{CH}_3$); 176.10 ($^{11,13}\text{C}$). **MS**: 337, M^+H (33); 296 (4); 295 (22); 254 (11); 253 (68); 250 (8); 249 (37); 248 (3); 209 (3); 208 (17); 207 (100); 205 (3); 191 (3); 190 (9); 189 (49); 180 (7); 179 (41); 163 (7); 162 (22); 161 (74); 151 (10); 133 (4); 121 (11); 120 (5); 119 (13); 107 (25); 106 (5); 105 (17); 93 (4); 92 (3); 91 (16); 79 (6); 77 (6).

For 9a. 1b (1.30 mmol), **E** (1.96 mmol), CH_2Br_2 (2 ml), HNEt_2 (3.90 mmol); yield 75%.* White solid, mp 129–130 °C. (hexane). Calc. for $\text{C}_{22}\text{H}_{38}\text{N}_2\text{O}_2$, M. 362.55, (%): C, 72.88; H, 10.56; N, 7.73. Found (%): C, 72.75; H, 10.55; N, 7.69.



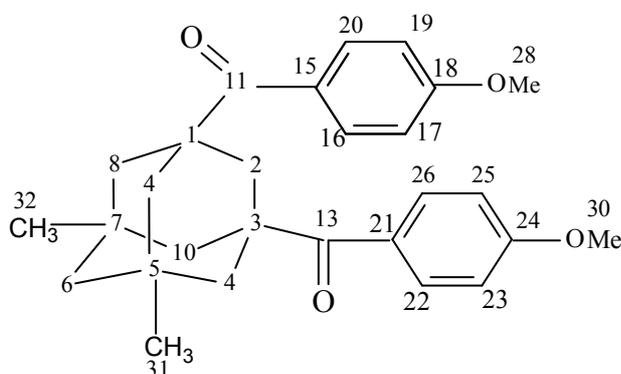
$^1\text{H NMR}$: 0.91 (6H, m., $^{22,23}\text{CH}_3$); 1.12 (2H, t., $^6\text{CH}_2$); 1.16 (12H, t., $^3J_{\text{HH}}$ 7.0, $^{18-21}\text{CH}_3$); 1.57, 1.62 (10H, AB system, q., $^2J_{\text{HH}}$ 13.6, $^{4,8-10}\text{CH}_2$); 2.04 (2H, m., $^2\text{CH}_2$); 3.58 (8H, q., $^3J_{\text{HH}}$ 7.0, $^{14-17}\text{CH}_2$). $^{13}\text{C NMR}$: 13.55 ($^{18-21}\text{CH}_3$); 30.45 ($^{22,23}\text{CH}_3$); 31.84 ($^{5,7}\text{C}$); 38.99 ($^{1,3}\text{C}$); 41.88 ($^{14-17}\text{C}$); 44.38 ($^6\text{CH}_2$); 44.60 ($^{4,8-10}\text{CH}_2$); 49.73 ($^2\text{CH}_2$); 174.91 ($^{11,13}\text{C}$). **MS**: 363, M^+H (1); 362, M^+ (1); 333 (9); 265 (3); 264 (19); 263 (64); 262, $\text{M}^+\text{-CONEt}_2$ (100); 207 (3); 206 (7); 192 (4); 189 (5); 164 (3); 163 (10); 162 (8); 161 (15); 134 (5); 133 (12); 121 (4); 120 (5); 119 (8); 107 (5); 106 (3); 105 (6); 100 (17); 91 (4); 74 (4); 72, $^+\text{NEt}_2$ (17); 71 (7).

For 9b. 1b (1.56 mmol), **E** (2.35 mmol), CH_2Br_2 (2.5 ml), $\text{C}_6\text{H}_5\text{NH}_2$ (4.35 mmol); yield 88%*. White solid, mp 280–281 °C (precipitated from dioxane by pentane). Calc. for $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_2$, M. 402.54, (%): C, 75.58; H, 7.51; N, 6.96. Found (%): C, 77.54; H, 7.52; N, 6.91.



¹H NMR: 0.99 (6H, s., ^{22,23}CH₃); 1.27 (2H, s., ⁶CH₂), 1.58 (2H, s., ²CH); 1.61, 1.63 (8H, AB system, q., ²J_{HH} 12.4, ^{4,8-10}CH₂); 2.04 (2H, ⁴CH₂); 7.11 (2H, t., ³J_{HH} 7.3, ^{21,22}CH); 7.32 (4H, dd., ³J_{HH} 8.0, ³J_{HH} 7.3 ^{19,20,23,24}CH); 7.52 (4H, d., ³J_{HH} 8.0, ^{17,18,25,26}CH). **¹³C NMR:** 29.84 (^{22,23}CH₃); 31.88 (^{5,7}CH); 39.33 (⁶CH₂); 43.88 (²CH₂); 44.53 (^{4,8-10}CH₂); 49.48 (^{1,3}C); 120.01 (^{17,18,25,26}CH); 124.36 (^{21,22}CH); 128.89 (^{19,20,23,24}CH); 137.54 (^{15,16}C); 174.85 (^{11,13}C). **MS:** 402, M⁺ (24); 374, M⁺-CO (2); 283 (21); 282, M⁺-CONHC₆H₅ (100); 281 (4); 254, M⁺-CONHC₆H₅-CO(2); 226 (15); 189 (5); 163 (3); 161 (10); 133 (7); 120, ⁺CONHC₆H₅ (4); 119 (6); 107 (11); 105 (5); 93 (3); 91 (4); 79 (2); 77 (2).

For **10. 1b** (1.09 mmol), **E** (1.55 mmol), CH₂Br₂ (1.6 ml), **C₆H₅OMe** (6.20 mmol); yield 73%. * White solid, mp. 120-121 °C (precipitated. from dioxane by pentane). Calc. for C₂₈H₃₂O₄, M. 432.56, (%): C, 77.75; H, 7.46. Found (%): C, 77.69; H, 7.32.



¹H NMR: 0.95 (6H, s., ^{31,32}CH₃); 1.70 (4H, ^{4,8}CH₂); 2.13 (2H, m.) and 2.19, (2H, m.) ^{4,10}CH₂); 3.84 (6H, s., ^{28,30}CH₃); 6.89 (4H, d., ³J_{HH} 8.9, ^{18,22,24,28}CH); 7.38 (4H, d., ³J_{HH} 8.9, ^{19,21,25,27}CH). **¹³C NMR:** 30.29 (^{31,33}CH₃); 31.94 (^{5,7}C); 39.89 (²CH₂); 44.93 (^{4,8-10}CH₂); 49.18 (^{1,3}C); 49.88 (⁶CH₂); 55.27 (^{30,32}CH₂); 113.26 (^{17,19,23,25}CH); 130.28 (^{16,20,22,26}CH); 130.76 (^{15,21}C); 164.76 (^{18,24}C); 205.68 (^{11,13}C). **MS:** 433, M⁺+ H (2); 432, M⁺ (7); 299 (3); 298 (18); 297 (46); 296 (33); 281 (3); 280 (11); 271 (3); 270 (13); 269 (4); 267 (4); 241 (4); 225 (3); 224 (7); 213 (14); 199 (11); 164 (5); 163 (36); 162 (11); 161 (4); 160 (4); 149 (4); 147 (3); 136 (11); 135, ⁺COC₆H₄OMe (100); 121 (11); 119 (4); 108 (4); 107, C₆H₄OMe⁺ (29); 106 (5); 105 (9); 95 (4); 93 (6); 92 (5); 91 (17); 81 (3); 79 (8); 77 (18); 65 (3).