

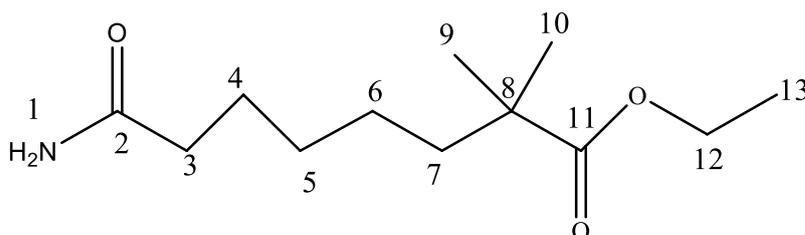
Chemo- and regioselective remote functionalization of nonanamides via sp^3 C–H bond cleavage under superelectrophilic conditions

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The experiments with amides, $R_2NC(O)C_8H_{17}$ [R= H (I); Et (II)] were carried out according to the typical procedure that was presented in the paper. The carbonylation was carried out under atmospheric CO pressure, with $CBr_4 \cdot 2AlBr_3$ (E) in anhydrous CH_2Br_2 , at a molar ratio [E] : [amide] = 2: 1 and at 0 °C for 1h. All NMR spectra were recorded on a Bruker Avance in $CDCl_3$ (1H NMR 400.13 MHz; ^{13}C NMR 100.61 MHz in δ from Me_4Si ; ^{19}F 376.49 MHz, δ from $CFCl_3$, J , Hz). The GC – MS spectra were recorded on a Finnigan Polaris GCO Plus.

1. Synthesis of $H_2NCO(CH_2)_5C(Me)_2COOCH_2CH_3$ (3a)

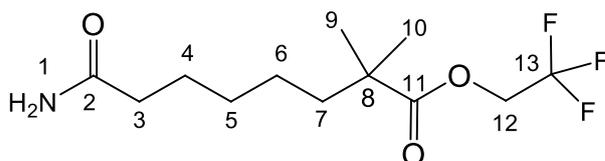
$H_2NCO C_8H_{17}$ (0.11g, 0.68 mol), E (1.16, 1.35 mmol), CH_2Br_2 (1.5 mL), EtOH (2mL), 0 °C, 1 h. Yield 48%.



1H NMR: 1.13 (s., $^{9,10}CH_3$); 1.23 (t., $^3J_{HH} = 7.1$, $^{13}CH_2$); 1.08–1.63 (m., $^{4-7}CH_2$); 2.20 (t., $^3J_{HH} = 7.4$, 3CH_2); 4.09 (q., $^3J_{HH} = 7.0$, $^{12}CH_2$); 5.86, 6.61 (bs., 1NH_2). ^{13}C NMR: 14.03 ($^{13}CH_3$); 24.38 ($^{9,10}CH_3$); 24.93 (6CH_2); 25.12 (5CH_2); 29.36 (4CH_2); 35.54 (3CH_2); 40.23 (7CH_2); 41.90 (8C); 60.01 ($^{12}CH_2$); 175.92 (2CO); 177.87 (^{11}CO). MS: 230, $M^+ + H$ (23); 212 (9); 184 (10); 171 (9); 166 (13); 157 (7); 156 (64); 155 (10); 154 (3); 151 (16); 143 (9); 142 (5); 141 (3); 140 (12); 139 (67); 138 (27); 137 (5); 130 (9); 129 (5); 128 (4); 127 (6); 126 (4); 125 (3); 124 (3); 123 (6); 122 (4); 121 (31); 116 (30); 115 (26); 114 (65); 113 (3); 112 (10); 111 (17); 110 (23); 109 (7); 102 (6); 101 (11); 100 (48); 99 (12); 98 (14); 97 (100); 96 (11); 95 (35); 94 (4); 93 (39); 91 (5); 88 (41); 87 (16); 86 (21); 85 (8); 84 (10); 83 (24); 82 (10); 81 (39); 80 (4); 79 (15); 77 (4); 74 (4); 73 (33); 72 (79); 71 (17); 70 (16); 69 (74); 68 (5); 67 (27); 65 (4); 66 (8); 59 (72); 58 (10); 57 (39); 56 (12); 55 (81).

2. Synthesis of $H_2NCO(CH_2)_5C(Me)_2COOCH_2CF_3$ (3b)

$H_2NCO C_8H_{17}$ (0.11g, 0.68 mol), E (1.18, 1.37 mmol), CH_2Br_2 (1.1 mL), CF_3CH_2OH (0.16 mL), 0 °C, 1 h. Yield 89%.

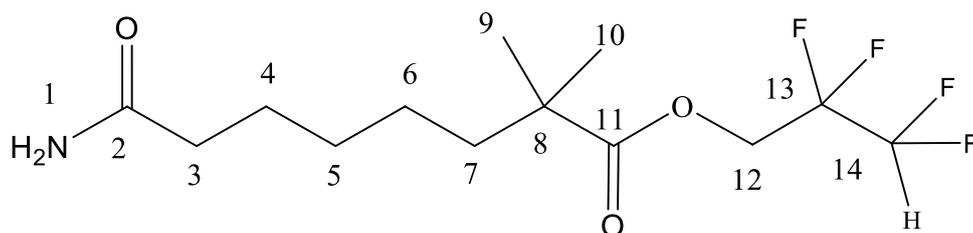


1H NMR: 1.24 ($^{9,10}CH_3$); 1.15 – 1.65 (m., $^{4-7}CH_2$); 2.20 (t., $^3J_{HH} = 7.4$, 3CH_2); 4.47 (q., $^3J_{HF} = 8.5$, $^{12}CH_2$); 5.66, 6.03 (bs., 1NH_2). ^{13}C NMR: 24.36 (6CH_2); 24.79 ($^{9,10}CH_3$); 25.06 (5CH_2); 29.30

(⁴CH₂); 35.55 (³CH₂); 40.03 (⁷CH₂); 42.32 (⁸C); 59,90 (q., ²J_{CF}= 36.3, ¹²CH₂); 125.66 (q., ¹J_{CF} = 277.3, ¹³CH₃); 175.43 (²CO); 175.66 (¹¹CO). MS: 284, M⁺ +H (4); 184 (5); 170 (3); 166 (6); 156 (11); 155 (4); 151 (8); 141 (4); 140 (3); 139 (16); 138 (8); 137 (2); 135 (4); 127 (4); 126 (2); 123 (4); 121 (7); 114 (19); 112 (3); 111 (3); 110 (7); 109 (3); 107 (2); 105 (2); 101 (2); 100 (19); 99 (6); 98 (4); 97 (24); 96 (5); 95 (12); 94 (3); 93 (12); 91 (2); 86 (12); 85 (2); 84 (3); 83 (17); 82 (4); 81 (13); 80 (2); 79 (9); 77 (2); 73 (3); 72 (35); 71 (9); 70 (6); 69 (31); 68 (2); 67 (11); 61 (3); 60 (6); 59 (100); 58 (4); 57 (13); 56 (6); 55 (33).

3. Synthesis of H₂NCO(CH₂)₅C(Me)₂C(O)CH₂(CF₂)₂H (3c)

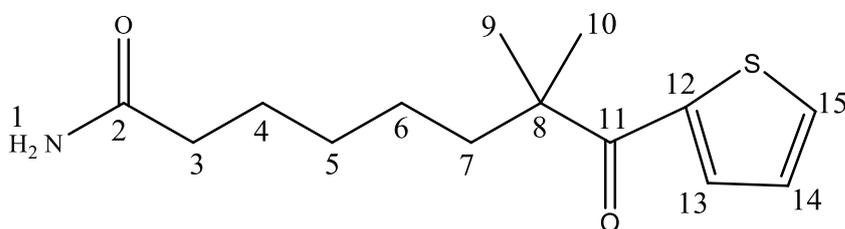
H₂NCOC₈H₁₇ (0.12 g, 0.73 mmol), E (1.26 , 1.46 mmol), CH₂Br₂ (1.1 mL), HCF₂CF₂CH₂OH (0.20 mL), 0 °C, 1 h. Yield 67%.



¹H NMR: 1.16 (s, ^{9,10}CH₃); 1.11-1.61 (m., ⁴⁻⁷CH₂); 2,17 (t., ³J_{HH} = 7.4, ³CH₂); 4.42 (t., ³J_{HH}=13.0, ¹²CH₂); 5,85 (tt., ²J_{HF} = 53,0, ³J_{HF}=3.7, ¹⁴CHF₂); 6,29 (bs., ¹NH₂). ¹³C NMR: 24.28 (⁶CH₂); 24.10 (^{9,10}CH₃); 25.01 (⁵CH₂); 29.23 (⁴CH₂); 35.47 (³CH₂); 40.02 (⁷CH₂); 42.24 (⁸C); 59.26 (t., ³J_{CF}= 29.0 ¹²CH₂); 109.11 (tt., ¹J_{CF} = 250.1, ³J_{CF} = 37.0, ¹⁴CF₂H); 113,71 (tt., ¹J_{CF} = 212.4, ³J_{CF} = 28.4, ¹³CF₂); 175.86 (²CO); 176.18 (¹¹CO). ¹⁹F: -65.13 (¹³CF₂); -78.93 (¹⁴CF₂H). MS: 316, M⁺ +H (5), 202 (4); 201 (3); 187 (3); 184 (5); 173 (5); 167 (2); 166 (9); 159 (3); 157 (2); 156 (21); 155 (3); 151 (8); 140 (4); 139 (19); 138 (11); 137 (4); 123 (4); 121 (11); 114 (22); 113 (3); 112 (4); 111(7); 110 (12); 109 (4); 101 (3); 100 (43); 99 (6); 98 (6); 97 (26); 96 (7); 95 (19); 93 (16); 86 (10); 85 (5); 84 (7); 83 (12); 82 (8); 81 (18); 79 (11); 77 (4); 73 (5); 72 (41); 71 (12); 70 (7); 69 (43); 67 (13); 65 (4); 60 (8); 59 (100); 58 (6); 57 (23); 56 (9); 55 (42).

4. Synthesis of H₂NCO(CH₂)₅C(Me)₂C(O)C₄H₃S (3d).

H₂NCOC₈H₁₇ (0.13 g, 0,82 mmol), E (1.41g, 1.63 mmol), CH₂Br₂ (1.3 mL), thiophene (0.2 mL), 0 °C, 1 h. Yield 50 %

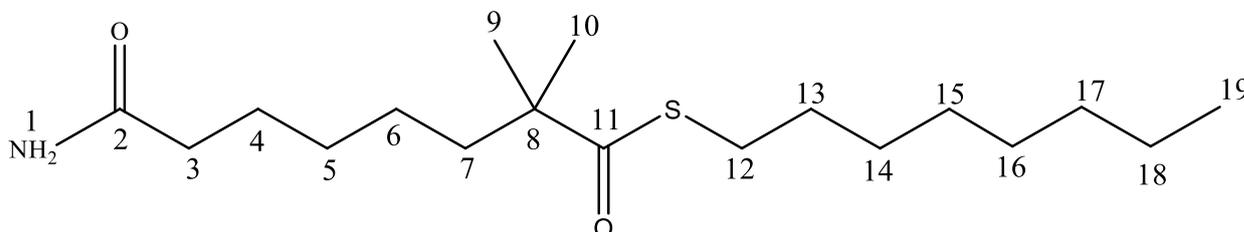


¹H NMR: 0,89-1,89 (m., ⁴⁻⁷CH₂); 1.37 (s, ^{9,10}CH₃); 2,36 (t, ³J_{HH} =7,3, ³CH₂); 6.82, 6.85 ¹NH₂); 7.11 (t., ³J_{HH} = 3.9, ¹⁴CH); 7,58 (t., ³J_{HH} = 3.8, ¹³CH); 7.79 (d., ³J_{HH} =3.9, ¹⁵CH). ¹³C NMR: 22.77 (⁶CH₂); 24.19 (⁵CH₂); 24.96 (^{9,10}CH₃); 29.33 (⁴CH₂); 35.10 (³CH₂); 41.72 (⁷CH₂); 47.33 (⁸C); 126.73 (¹⁴CH); 131.39 (¹³CH); 132.26 (¹⁵CH); 167.82 (²CO); 217.26 (¹¹CO). MS: 268, M⁺ +H (1); 157 (3); 156 (25); 155 (3); 154 (32); 153 (3); 141 (3); 140 (13); 139 (36); 138 (5); 126 (5); 121 (16); 114 (3); 113 (6); 112 (10); 111 (100); 110 (4); 100 (8); 98 (4); 97 (32); 96 (3); 95

(12); 93 (17); 86 (4); 85 (3); 84 (3); 83 (15); 82 (4); 81 (12); 79 (7); 72 (6); 71 (4); 70 (3); 69 (26); 67 (9); 59 (6); 58 (5); 57 (13); 56 (3); 55 (21).

5. Synthesis of $\text{H}_2\text{NCO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{C}(\text{O})\text{SC}_8\text{H}_{17}$ (**3e**)

$\text{H}_2\text{NCOC}_8\text{H}_{17}$ (0.20 g, 1.30 mmol), **E** (2.25 g, 2.60 mmol), CH_2Br_2 (2 mL), $\text{HSC}_8\text{H}_{17}$ (0.67 g, 0.57 mmol), 0°C , 1 h. Yield 73 %.

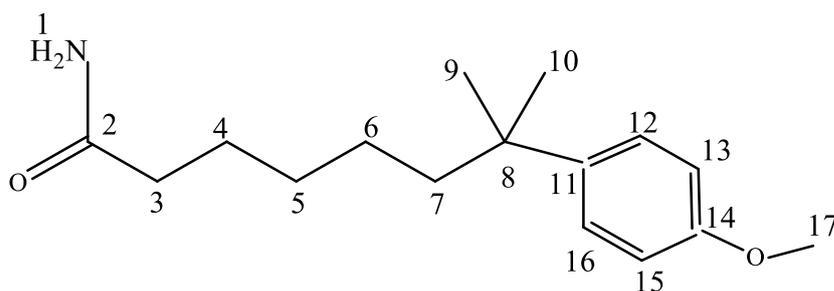


^1H NMR: 0.85 (t., $^3J_{\text{HH}} = 6.5$, $^{19}\text{CH}_3$); 1.17 (s., $^{9,10}\text{CH}_3$); 1.21 – 1.62 (m., $^{4-7, 12-18}\text{CH}_2$); 2.18 (t., $^3J_{\text{HH}} = 7.5$, $^3\text{CH}_2$); 2.79 (t., $^3J_{\text{HH}} = 7.5$, $^{12}\text{CH}_2$); 5.81– 6.29 (bs, $^1\text{H}_2\text{N}$). ^{13}C NMR: 13.94 ($^{19}\text{CH}_3$); 22.46 ($^{17}\text{CH}_2$); 24.14 ($^6\text{CH}_2$); 25.17 ($^{9,10}\text{CH}_3$); 28.36 ($^5\text{CH}_2$); 29.49 ($^4\text{CH}_2$); 28.76, 28.93, 29.00, 29.41 ($^{13-16}\text{CH}_2$); 31.62 ($^{12}\text{CH}_2$); 35.62 ($^3\text{CH}_2$); 40.73 ($^7\text{CH}_2$); 176.42 (^2CO); 206.60 (^{11}CO). MS: 330, $\text{M}^+ + \text{H}$ (2); 184 (6); 167 (3); 157 (11); 156 (97); 140 (10); 139 (100); 138 (9); 122 (4); 121 (46); 114 (5); 111 (16); 110 (3); 105 (3); 100 (13); 98 (6), $\text{C}_7\text{H}_{14}^+$; 97 (60); 96 (5); 95 (32); 94 (5); 93 (52); 91 (10); 86 (11); 84 (5); 83 (18); 82 (6); 81 (41); 79 (20); 77 (6); 73 (4); 72 (17); 71 (13), 70 (7); 69 (60); 68 (4); 67 (29); 65 (3); 59 (10), 58 (10); 57 (20); 56 (8); 55 (47).

6. Reaction of $\text{H}_2\text{NCOC}_8\text{H}_{17}$ with CO and anisole

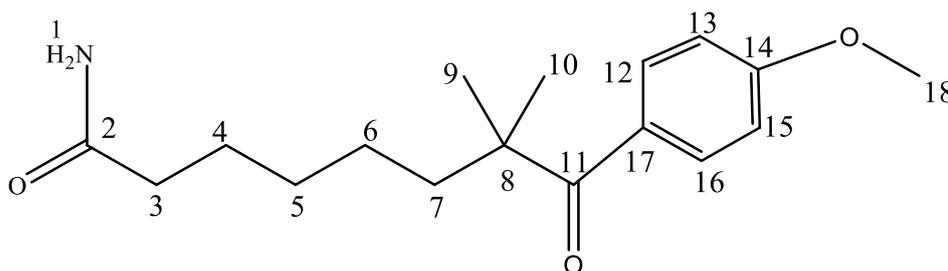
$\text{H}_2\text{NCOC}_8\text{H}_{17}$ (0.18 g, 1.14 mmol), **E** (1.98 g, 2.28 mmol), CH_2Br_2 (2.5 mL), anisole (0.37 g, 0.34 mmol), 0°C , 1 h. Anisole was added at -20°C . The total yield of **3g** and **5** is 60%. A molar ratio $[\text{NH}_2\text{CO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{C}_6\text{H}_4\text{OMe-p}] : [\text{NH}_2\text{CO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{COC}_6\text{H}_4\text{OMe-p}] = 1 : 1.6$. The products were separated by column chromatography (silica gel) using hexane - acetone (2 : 1) as the eluent.

$\text{H}_2\text{NCO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{C}_6\text{H}_4\text{OMe-4}$ (**5**)



^1H NMR: 1.10-1.57 (m., $^{4-7}\text{CH}_2$); 1.28 (s., $^{9,10}\text{CH}_3$); 2.16 (t., $^3J_{\text{HH}} = 7.4$, $^3\text{CH}_2$); 3.81 ($^{17}\text{CH}_3$); 5.92 ($^1\text{NH}_2$); 6.84 (d., $^3J_{\text{HH}} = 9.0$, $^{13,15}\text{CH}$); 7.27 (d., $^3J_{\text{HH}} = 9.0$, $^{12,16}\text{CH}$). ^{13}C NMR: 24.28 ($^6\text{CH}_2$); 25.26 ($^5\text{CH}_2$); 29.0 ($^{9,10}\text{CH}_3$); 29.70 ($^4\text{CH}_2$); 35.75 ($^3\text{CH}_2$); 44.36 ($^7\text{CH}_2$); 55.09 ($^{17}\text{CH}_3$); 113.19 ($^{13,15}\text{CH}$); 126.65 ($^{12,16}\text{CH}$); 141.55 (^{11}C); 157.89 (^{14}C); 175.91 (^2CO). MS: 263, M^+ (2); 245 (2); 156 (5); 149 (2); 138 (5); 94 (4); 93 (3); 91 (12); 84 (3); 81 (9); 80 (2); 79 (29); 78 (19); 77 (72); 76 (3); 72 (9); 70 (3); 69 (10); 68 (4); 67 (18); 66 (12); 65 (43); 64 (9); 63 (16); 58 (5); 57 (13); 56 (15); 55 (75); 41 (100).

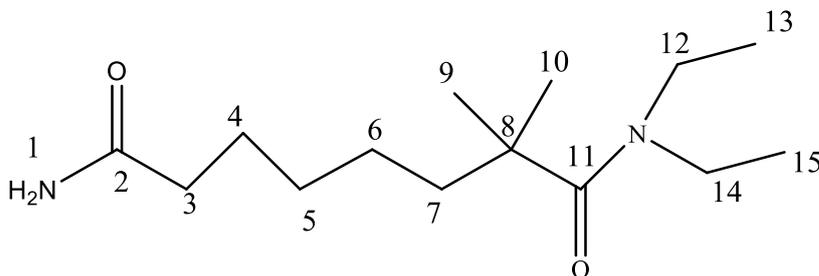
H₂NCO(CH₂)₅C(Me)₂COC₆H₄OMe-4 (3g)



¹H NMR: 1.21-1.78 (m, ⁴⁻⁷CH₂); 1.35 (s, ^{9,10}CH₃); 2.20 (t, ³J_{HH} = 6.9, ³CH₂); 3.89 (s, ¹⁸CH₃); 5.76 (bs., ¹NH₂); 6.87 (d., ³J_{HH} = 8.8, ^{13,15}CH); 7.85 (d., ³J_{HH} = 8.8, ^{12,16}CH). ¹³C NMR: 24.33 (⁶CH₂); 25.06 (⁵CH₂); 26.55 (^{9,10}CH₃); 29.52 (⁴CH₂); 35.70 (³CH₂); 41.16 (⁷CH₂); 47.45 (⁸C); 55.44 (¹⁸CH₃); 113.23 (^{13,15}CH); 130.52 (^{12,16}CH); 176.01 (²CO); 200.26 (¹¹CO). MS: 292, M⁺ + H (1); 138 (3); 81 (3); 79 (8); 78 (9); 77 (100); 76 (5); 72 (7); 71 (3); 70 (5); 69 (22); 68 (3); 67 (14); 65 (19); 64 (39); 63 (37); 60 (4); 59 (14); 58 (8); 57 (18); 56 (18); 55 (53).

7. Synthesis of H₂NCO(CH₂)₅C(Me)₂C(O)NEt₂ (3f)

H₂NCOC₈H₁₇ (0.108 g, 0.69 mmol), E (1.20 g, 1.39 mmol), CH₂Br₂ (1.5 mL), Et₂NH (2 mL), 0 °C, 1 h. The product **3f** was isolated by column chromatography (silica gel) using hexane - acetone (2 : 1) as the eluent .



3f

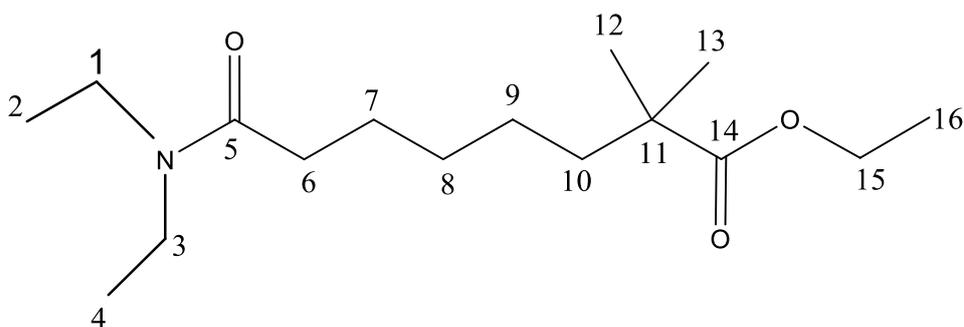
(**3f**). 1.15 (t., ³J_{HH} = 6.5, ^{13,15}CH₃); 1.26 (s, ^{9,10}CH₃); 1.21-1.67 (m., ⁴⁻⁷CH₂); 2.22 (t., ³J_{HH} = 7.5, ³CH₂); 3.40 (bs., ^{12,14}CH₂); 5.86 (bs., ¹NH₂). ¹³C NMR: 13.94 (^{13,15}CH₃); 24.48 (⁶CH₂); 27.02 (^{9,10}CH₃); 25.18 (⁵CH₂); 27.02 (^{9,10}CH₃); 29.47 (⁴CH₂); 38.49 (⁸C); 40.84 (³CH₂); 41.34 (^{12,14}CH₂); 42.44 (⁷CH₂); 175.62 (²CO); 175.72 (¹¹CO). MS: 257, M⁺ + H (3); 239 (8); 156 (3); 59 (2); 58 (26), 57 (5); 56 (4); 55 (21); 44 (100).

Product of dehydration of **3f**. MS: 239, M⁺ + H (12); 156 (5); 138 (2); 58 (17), 56 (4); 55 (12); 44 (100).

Product of cyclization of **1**. MS: 156, M⁺ + H (56); 155 (2); 154 (2); 142 (3); 140 (2); 139 (8); 138 (10); 137 (2); 121 (2); 95 (2); 59 (17); 57 (7); 56 (10); 55 (52); 41 (100).

8. Synthesis of Et₂NCO(CH₂)₅C(Me)₂COOCH₂CH₃ (4a)

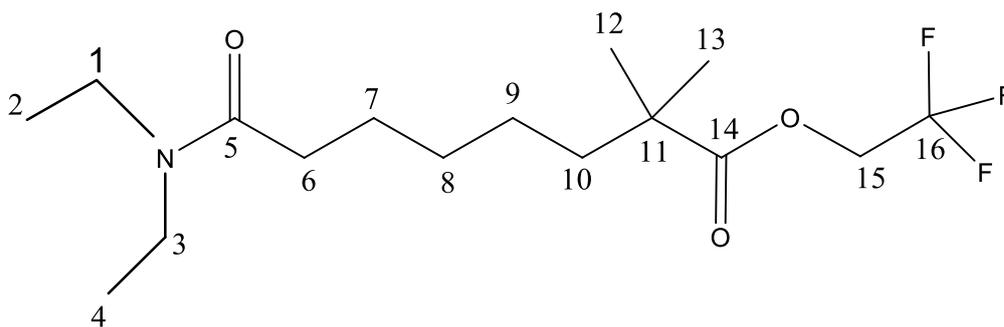
NEt₂COC₈H₁₇ (0.17 g, 0.81 mmol), E (1.41 g, 1.63 mmol), CH₂Br₂ (1.8 mL), EtOH (2 mL), 0 °C, 1 h. Yield 90%.



$^1\text{H NMR}$: 1.09 – 1.80 (m., $^{2,4}\text{CH}_3$, $^{7-10}\text{CH}_2$); 1.14 (s., $^{12,13}\text{CH}_3$); 1.24 (t., $^3J_{\text{HH}} = 7.2$, $^{16}\text{CH}_2$); 2.44 (t., $^3J_{\text{HH}} = 7.7$, $^6\text{CH}_2$); 3.39 (bs., $^{1,3}\text{CH}_2$); 4.12 (q., $^3J_{\text{HH}} = 7.2$, $^{15}\text{CH}_2$). $^{13}\text{C NMR}$: 12.72, 14.11 ($^{2,4}\text{CH}_3$); 14.05 ($^{16}\text{CH}_3$); 24.47 ($^9\text{CH}_2$); 24.94 ($^{12,13}\text{CH}_3$); 25.47 ($^7\text{CH}_2$); 29.63 ($^8\text{CH}_2$); 32.28 ($^6\text{CH}_2$); 40.24 ($^{10}\text{CH}_2$); 40.79, 42.53 ($^{1,3}\text{CH}_2$); 47.03 (^{11}C); 59.98 ($^{15}\text{CH}_2$); 173.35 (^5CO); 177.83 (^{14}CO). MS: 286, $\text{M}^+ + \text{H}$ (3); 212 (8); 170 (20); 156 (4); 142, $\text{Et}_2\text{N}^+\text{COC}_2\text{H}_4$ (6); 139 (3); 128 (15); 116 (5); 115 (33); 101 (6); 100, Et_2NCO^+ (100); 97 (3); 95 (4); 93 (3); 87 (6); 86 (10); 83 (3); 81 (3); 79 (3); 74 (37); 73 (8); 72, Et_2N^+ (60); 69 (14); 67 (6); 58 (85), 57 (3); 56 (5); 55 (13).

9. Synthesis of $\text{Et}_2\text{NCO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{COOCH}_2\text{CF}_3$ (4b)

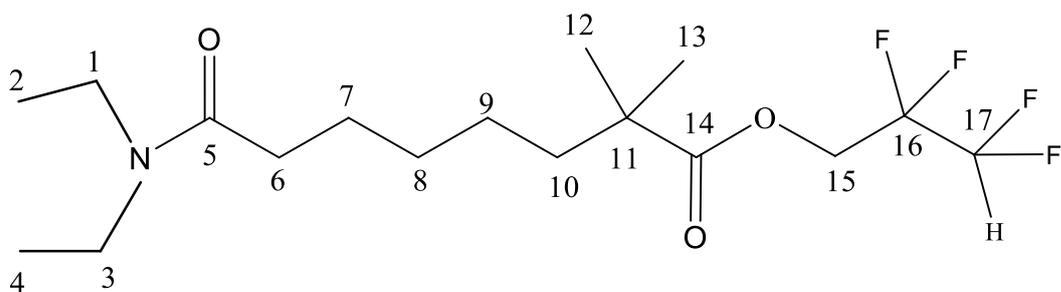
$\text{NEt}_2\text{COC}_8\text{H}_{17}$ (0.17 g, 0.81 mmol), E (1.41 g, 1.63 mmol), CH_2Br_2 (1.8 mL), $\text{CF}_3\text{CH}_2\text{OH}$ (0.18 g, 1.84 mmol), 0 °C, 1 h. Yield 89 %.



$^1\text{H NMR}$: 1.07 – 1.59 (m., $^{2,4}\text{CH}_3$, $^{7-10}\text{CH}_2$); 1.17 (s., $^{12,13}\text{CH}_3$); 2.25 (t., $^3J_{\text{HH}} = 7.5$, $^6\text{CH}_2$); 3.26, -3.33 ($^{1,3}\text{CH}_2$); 4.44 (q., $^3J_{\text{HH}} = 8.2$, $^{15}\text{CH}_2$). $^{13}\text{C NMR}$: 12.87, 14.14 ($^{2,4}\text{CH}_3$); 24.43 ($^9\text{CH}_2$); 24.71 ($^{12,13}\text{CH}_3$); 24.99 ($^7\text{CH}_2$); 29.56 ($^8\text{CH}_2$); 32.67 ($^6\text{CH}_2$); 39.84, 41.98 ($^{1,3}\text{CH}_2$); 40.21 ($^{10}\text{CH}_2$); 46.33 (^{11}C); 59.84 (q., $^2J_{\text{CF}} = 36.3$, $^{15}\text{CH}_2$); 122.84 (q., $^7J_{\text{CF}} = 278.3$, $^{16}\text{CF}_3$); 171.92 (^5CO); 176.08 (^{14}CO). $^{19}\text{F NMR}$: -15.44. MS: 340, $\text{M}^+ + \text{H}$ (5); 212 (5); 170 (15); 156 (3); 142, $\text{Et}_2\text{N}^+\text{COC}_2\text{H}_4$ (6); 128 (12); 116 (2); 115 (35); 101 (6); 100, Et_2NCO^+ (100); 97 (2); 95 (2); 93 (2); 87 (7); 86 (10); 83 (6); 81 (3); 79 (3); 74 (29); 73 (5); 72, Et_2N^+ (53); 70 (3); 69 (18); 67 (4); 59 (42), 58 (88); 56 (5); 55 (16).

10. Synthesis of $\text{Et}_2\text{NCO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{COOCH}_2\text{CF}_2\text{CF}_2\text{H}$ (4c)

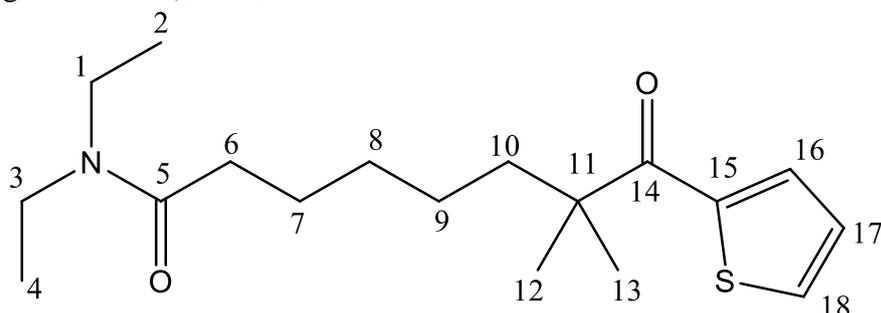
$\text{NEt}_2\text{COC}_8\text{H}_{17}$ (0.165 g, 0.81 mmol), E (1.34 g, 1.55 mmol), CH_2Br_2 (1.44 mL), $\text{H}(\text{CF}_2)_2\text{CH}_2\text{OH}$ (0.40 g, 2.33 mmol), 0 °C, 1 h. Yield 57 %.



^1H NMR: 1.18 (s, $^{12,13}\text{CH}_3$); 1.09 - 1.62 (m., $^{2,4}\text{CH}_3$, $^{7-10}\text{CH}_2$); 2.27 (t., $^3J_{\text{HH}} = 7.4$, $^6\text{CH}_2$); 3.28, 3.35 ($^{1,3}\text{CH}_2$); 4.44 (t., $^3J_{\text{HH}}=12.9$, $^{15}\text{CH}_2$); 5.85 (tt., $^3J_{\text{HF}} = 53.2$, $^3J_{\text{HF}}=3.9$, $^{17}\text{CHF}_2$); ^{13}C NMR: 12.84, 14.15 ($^{2,4}\text{CH}_3$); 24.45 ($^9\text{CH}_2$); 24.74 ($^{12,13}\text{CH}_3$); 25.02 ($^7\text{CH}_2$); 29.57 ($^8\text{CH}_2$); 32.66 ($^6\text{CH}_2$); 40.13 ($^{10}\text{CH}_2$); 41.80, 42.29 ($^{1,3}\text{CH}_2$); 59.31 (t., $^2J_{\text{CF}}=29.0$, $^{15}\text{CH}_2$); 106.65 (tt., $^1J_{\text{CF}} = 260.1$, $^2J_{\text{CF}} = 37.0$, $^{14}\text{CF}_2\text{H}$); 111.62 (tt., $^1J_{\text{CF}}=250.0$, $^2J_{\text{CF}} = 28.2$, $^{16}\text{CF}_2$); 172.02 (^5CO); 176.22 (^{14}CO). ^{19}F : -65.07 ($^{16}\text{CF}_2$); -78.85 ($^{17}\text{CF}_2\text{H}$). MS: 372, $\text{M}^+ + \text{H}$ (3), 212 (7); 170 (15); 156 (3); 142 (6); 128 (14); 116 (4); 115 (36); 101 (7); 100 (100); 95 (4); 93 (3); 87 (5); 86 (9); 83 (4); 81 (4); 74 (32); 73 (4); 72 (55); 70 (3); 69 (17); 67 (6); 59 (5); 58 (90); 56 (4); 55 (17).

11. Synthesis of $\text{Et}_2\text{NCO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{C}(\text{O})\text{C}_4\text{H}_3\text{S}$ (4d)

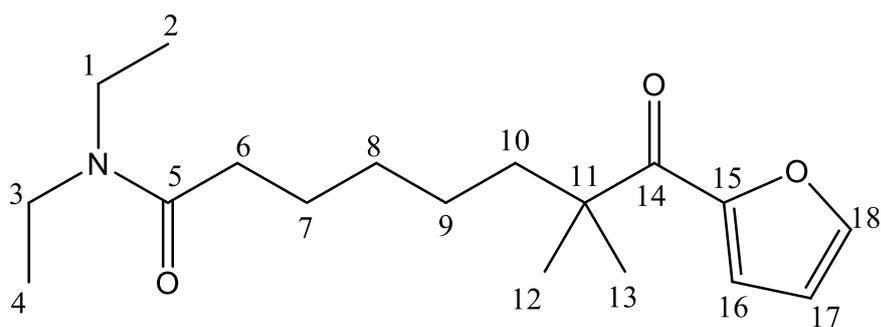
$\text{NEt}_2\text{COC}_8\text{H}_{17}$ (0.165 g, 0.78 mmol), E (1.34 g, 1.55 mmol), CH_2Br_2 (1.44 mL), thiophene (0.195 g, 2.33 mmol), 0 °C, 1 h. Yield 62 %.



^1H NMR: 1.15 - 1.86 (m., $^{2,4}\text{CH}_3$, $^{7-10}\text{CH}_2$); 1.30 (s., $^{12,13}\text{CH}_3$); 2.31 (t., $^3J_{\text{HH}} = 7.4$, $^6\text{CH}_2$); 3.36, ($^{1,3}\text{CH}_2$); 7.11 (t., $^3J_{\text{HH}}=5.0$, ^{17}CH); 7.56 (d., $^3J_{\text{HH}} = 4.9$, ^{16}CH); 7.79 (d., $^3J_{\text{HH}} = 5.0$, ^{18}CH). ^{13}C NMR: 12.88, 14.13 ($^{2,4}\text{CH}_3$); 24.27 ($^9\text{CH}_2$); 25.02 ($^7\text{CH}_2$); 26.03 ($^{12,13}\text{CH}_3$); 29.63 ($^8\text{CH}_2$); 32.38 ($^6\text{CH}_2$); 41.17 ($^{10}\text{CH}_2$); 40.29, 42.10 ($^{1,3}\text{CH}_2$), 47.30 (^{11}C), 127.52 (^{17}CH); 131.38 (^{16}CH); 132.05 (^{18}CH); 142.65 (^{15}C); 172.57 (^5CO); 198.59 (^{14}CO). MS: 324, $\text{M}^+ + \text{H}$ (0.5); 212 (10); 170 (11); 156 (8); 142, $\text{Et}_2\text{N}^+\text{COC}_2\text{H}_4$ (13); 128 (14); 116 (3); 115 (22); 112 (3); 111 (37); 100, Et_2NCO^+ (100); 97 (7); 93 (3); 91 (3); 86 (3); 83 (6); 81 (3); 79 (3); 75 (4); 74 (93); 73 (4); 72, Et_2N^+ (72); 69 (11); 67 (5); 58 (33); 56 (3); 55 (10).

12. Synthesis of $\text{Et}_2\text{NCO}(\text{CH}_2)_5\text{C}(\text{Me})_2\text{C}(\text{O})\text{C}_4\text{H}_3\text{O}$ (4e)

$\text{NEt}_2\text{COC}_8\text{H}_{17}$ (0.18 g, 0.85 mmol), E (1.47 g, 1.71 mmol), CH_2Br_2 (1.47 mL), furan (0.18 mL, 2.56 mmol), 0 °C, 1 h. Yield 42 %.



^1H NMR: 1.15 – 1.83 (m., $^{2,4}\text{CH}_3$, $^{7-10}\text{CH}_2$); 1.30 (s., $^{12,13}\text{CH}_3$); 2.33 (t., $^3J_{\text{HH}} = 7.5$, $^6\text{CH}_2$); 3.39, ($^{1,3}\text{CH}_2$); 6.50 (t., $^3J_{\text{HH}} = 3.6$, ^{17}CH); 7.20 (d., $^3J_{\text{HH}} = 3.60$, ^{16}CH); 7.54 (d., $^3J_{\text{HH}} = 3.6$, ^{18}CH). ^{13}C NMR: 12.74, 14.06 ($^{2,4}\text{CH}_3$); 24.24 ($^9\text{CH}_2$); 24.73 ($^{12,13}\text{CH}_3$); 25.14 ($^7\text{CH}_2$); 29.64 ($^8\text{CH}_2$); 32.31 ($^6\text{CH}_2$); 39.58 ($^{10}\text{CH}_2$); 40.45, 42.20 ($^{1,3}\text{CH}_2$), 46.35 (^{11}C), 111.47 (^{17}CH); 117.62 (^{16}CH); 144.77 (^{18}CH); 152.50 (^{15}C); 172.86 (^5CO); 194.56 (^{14}CO). MS: 308, $\text{M}^+ + \text{H}$ (3); 212 (7); 184 (5); 175 (9); 174 (5); 170 (10); 156 (6); 142, $\text{Et}_2\text{N}^+\text{COC}_2\text{H}_4$ (11); 138 (3); 128 (12); 123 (5); 115 (20); 109 (4); 101 (7); 100, Et_2NCO^+ (100); 97 (5); 95 (34); 93 (4); 91 (4); 86 (4); 79 (7); 77 (5); 75 (4); 74 (88); 73 (4); 72, Et_2N^+ (75); 69 (10); 67 (8); 58 (43); 56 (4); 55 (12).