Electronic Supplementary Material (ESI) for Green Chemistry
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Electronic Supplementary Information

Carbon dioxide as a reversible amine-protecting agent in selective Michael additions and acylations

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NMR study of compounds under air and under CO_2 atmosphere

^{1}H-NMR spectra of products were recorded on a Bruker AMX-300 at 300 MHz and ^{13}C-NMR spectra at 75.5 MHz. Samples were prepared by dissolution of 20 µl of the sample in 600 µl of *d*-DMSO or *d*-acetonitrile. To study the reaction of the product with CO_2, samples were bubbled at room temperature with CO_2 for approximately 2 minutes. After bubbling, the solution was transferred to an NMR tube and sealed immediately and spectra were recorded as soon as possible.

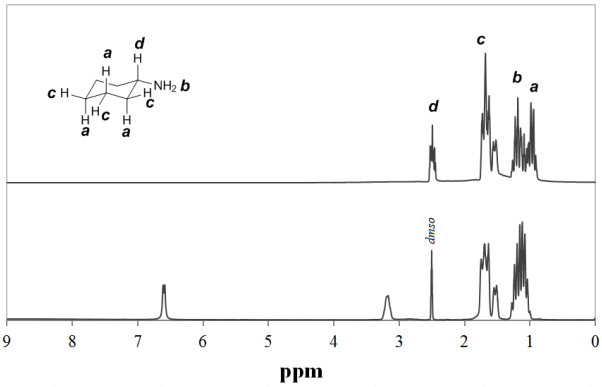

Figure SI.1 ^{1}H NMR spectra of cyclohexylamine in *d*-DMSO (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

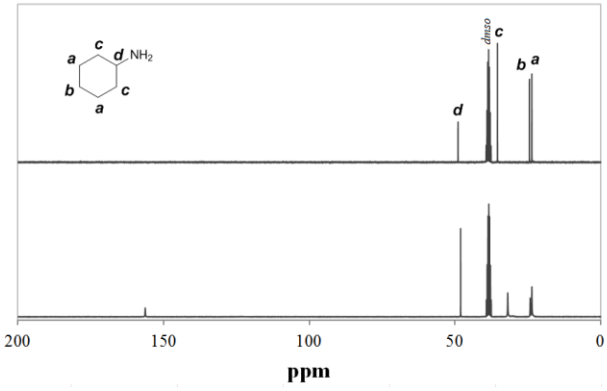

Figure SI.2 ^{13}C-NMR spectra of cyclohexylamine in *d*-DMSO (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

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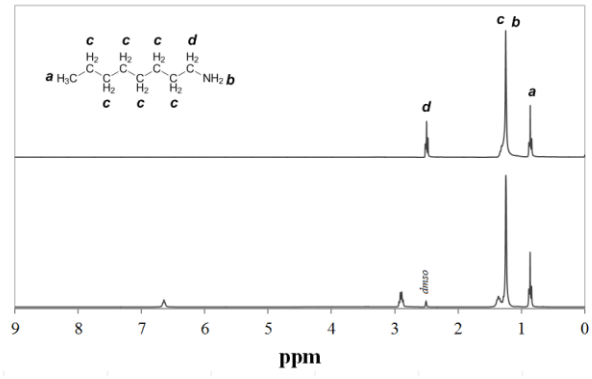

Figure SI.3 ^{1}H NMR spectra of octylamine in *d*-DMSO (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

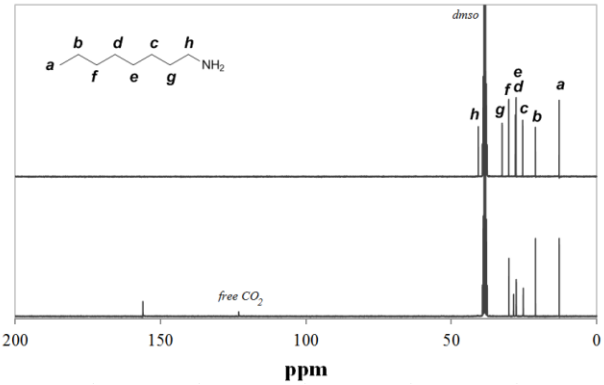

Figure SI.4 ^{13}C-NMR spectra of octylamine in *d*-DMSO (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

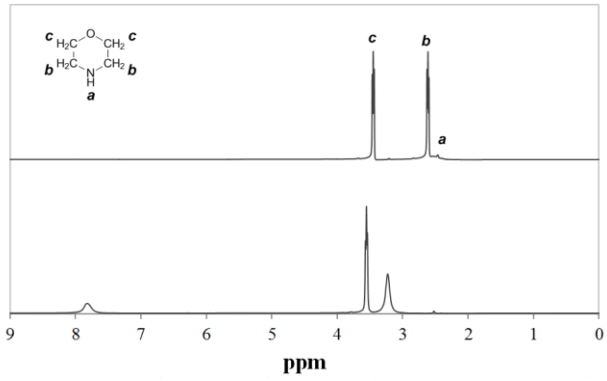

Figure SI.5 ^{1}H NMR spectra of morpholine in *d*-DMSO (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

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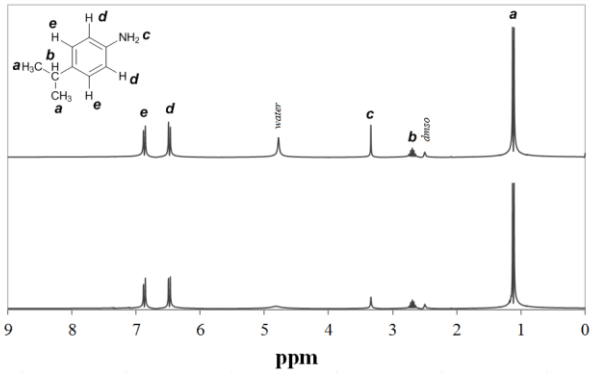

Figure SI.6 ^{1}H NMR spectra of *p*-isopropylaniline in *d*-DMSO (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

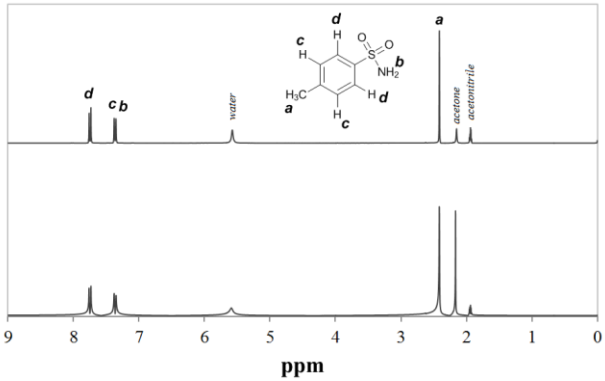

Figure SI.7 ^{1}H NMR spectra of *p*-toluenesulfonamide in *d*-acetonitrile (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

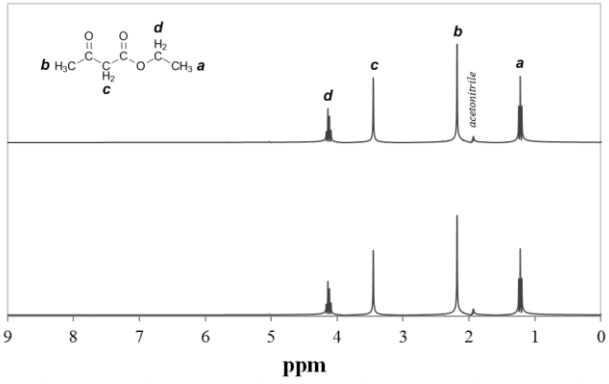

Figure SI.8 ^{1}H NMR spectra of ethylacetoacetate in *d*-acetonitrile (top) and after flushing with CO_2 at room temperature and atmospheric pressure (bottom)

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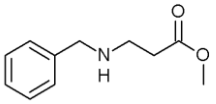
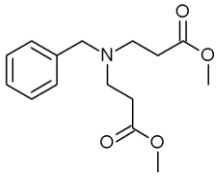
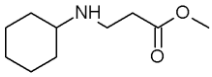
Identification of products



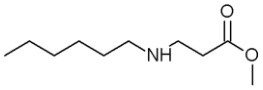
methyl 3-(*N*-benzylamino)propionate
GC-MS (EI, 70eV): *m/z* (rel. int.): 193 (1 %) [M^+], 192 (2), 120 (16), 106 (28), 102 (5), 91 (100), 77 (6), 65 (18).



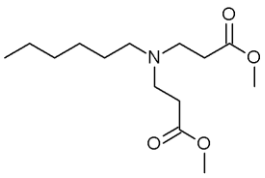
3,3'-(*N*-benzylimino)dipropionic acid dimethyl ester
GC-MS (EI, 70eV): *m/z* (rel. int.): 279 (2 %) [M^+], 206 (55), 192 (11), 91 (100), 65 (6).



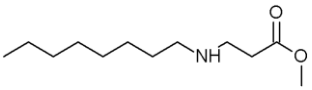
methyl 3-(*N*-cyclohexylamino)propionate
GC-MS (EI, 70eV): *m/z* (rel. int.): 185 (11 %) [M^+], 156 (6), 142 (100), 129 (4), 112 (26), 110 (21), 82 (16), 68 (42), 56 (47), 41 (62).



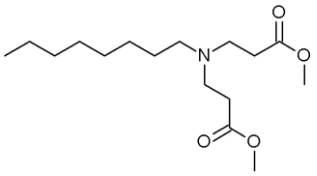
methyl 3-(*N*-hexylamino)propionate
GC-MS (EI, 70eV): *m/z* (rel. int.): 187 (2 %) [M^+], 172 (2), 158 (2), 144 (1), 130 (2), 116 (100), 114 (21), 102 (5), 84 (77), 70 (9), 56 (33), 42 (99).



3,3'-(*N*-hexylimino)dipropionic acid dimethyl ester
GC-MS (EI, 70eV): *m/z* (rel. int.): 273 (1 %) [M^+], 202 (100), 200 (57), 160 (9), 130 (50), 116 (11), 98 (7), 84 (22), 70 (6), 59 (30), 55 (40), 42 (69).



methyl 3-(*N*-octylamino)propionate
GC-MS (EI, 70eV): *m/z* (rel. int.): 215 (2 %) [M^+], 172 (2), 158 (2), 142 (15), 128 (3), 116 (100), 84 (55), 70 (10), 56 (21), 42 (71).



3,3'-(*N*-octylimino)dipropionic acid dimethyl ester
GC-MS (EI, 70eV): *m/z* (rel. int.): 301 (1 %) [M^+], 258 (1), 228 (36), 202 (100), 160 (8), 130 (35), 116 (9), 84 (16), 55 (22), 42 (39).

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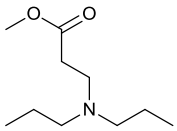
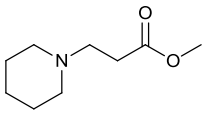
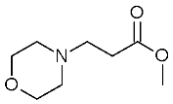
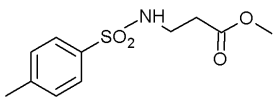
methyl 3-(dipropylamino)propionate 

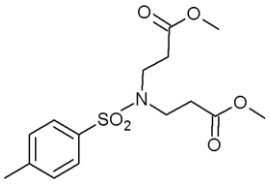
GC-MS (EI, 70eV): *m/z* (rel. int.): 187 (4 %) [M^+], 172 (2), 158 (100), 144 (1), 130 (7), 114 (48), 84 (26), 70 (7), 59 (5), 42 (42).

methyl 3-(piperidino)propionate 

GC-MS (EI, 70eV): *m/z* (rel. int.): 171 (6 %) [M^+], 156 (2), 98 (100), 96 (8), 84 (3), 70 (3), 59 (4), 55 (12), 44 (9), 42 (18).

methyl 3-(morpholinyl)propionate 
GC-MS (EI, 70eV): *m/z* (rel. int.): 173 (4 %) [M^+], 142 (2), 115 (2), 100 (100), 88 (4), 84 (6), 70 (10), 56 (55), 42 (61).

methyl 3-(*p*-toluenesulfonylamino)propionate 
GC-MS (EI, 70eV): *m/z* (rel. int.): 257 (1 %) [M^+], 226 (2), 184 (18), 155 (58), 102 (100), 91 (94), 77 (3), 70 (19), 65 (22).

3,3'-[*p*-toluenesulfonylimino]dipropionic acid dimethyl ester 
GC-MS (EI, 70eV): *m/z* (rel. int.): 343 (1 %) [M^+], 312 (2), 270 (29), 188 (87), 155 (65), 114 (35), 91 (100), 84 (20), 65 (16).

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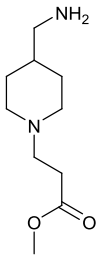
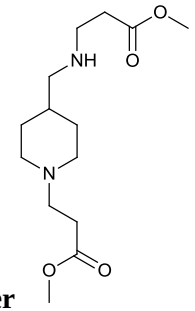


4-(aminomethyl)-1-piperidine propanoic acid methyl ester

GC-MS (EI, 70eV): *m/z* (rel. int.): 200 (11 %) [M^+], 182 (5), 170 (5), 168 (5), 155 (3), 142 (11), 127 (89), 116 (22), 110 (100), 96 (51), 84 (20), 82 (15), 68 (8), 59 (7), 55 (23), 42 (32), 30 (24).

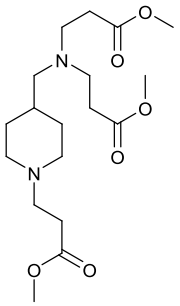
NMR analysis of CO_2-protected product.

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.74 (N*H*-CO), 3.59 (*s*, O-CH_3), 2.8 (*m*, -CH_2-NH-CO and N-CH_2- in ring), 2.49 (*m*, N-CH_2- in ring and N-CH_2-CH2-CO-), 1.86 (*t*, *J* = 10.7 Hz, CH_2-CO), 1.58 (*d*, *J* = 12.1, -CH_2- in ring), 1.33 (*m*, -C*H*- in ring), 1.06 (*m*, -CH_2- in ring).



4-[[(3-methoxy-3-oxopropyl)amino]methyl]-1-piperidine propanoic acid methyl ester

GC-MS (EI, 70eV): *m/z* (rel. int.): 286 (7 %) [M^+], 255 (7), 227 (2), 213 (43), 133 (21), 182 (53), 171 (20), 155 (16), 142 (45), 116 (60), 112 (47), 110 (100), 98 (44), 96 (49), 84 (46), 82 (18), 70 (24), 55 (26), 42 (55), 30 (6).



3-3'-(((1-(3-methoxy-3-oxopropyl)piperidine-4-ylmethyl)azanediyl) dipropionic acid dimethyl ester

GC-MS (EI, 70eV): *m/z* (rel. int.): 372 (2 %) [M^+], 341 (1), 313 (1), 299 (7), 285 (7), 202 (100), 182 (26), 170 (4), 155 (5), 142 (8), 110 (16), 96 (10), 55 (9), 42 (12), 30 (2).

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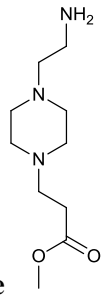
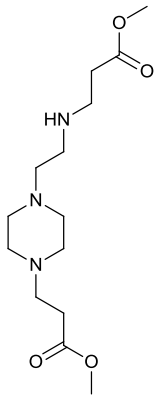


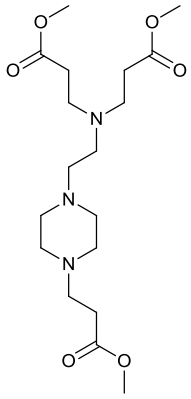
methyl 3-(4-(2-aminoethyl)piperazine-1-yl)propanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 215 (1 %) [M^+], 198 (8), 185 (94), 170 (15), 155 (8), 153 (8), 142 (46), 130 (9), 125 (4), 111 (50), 98 (100), 87 (11), 70 (35), 56 (37), 42 (47), 30 (21).



methyl 3- (4-(2-((3-methoxy-3-oxopropyl)aminoethyl)piperazine-1-yl)propanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 302 (1 %) [M^+*+1*], 270 (7), 228 (16), 198 (8), **185** (100), 173 (11), 159 (8), 153 (8), 142 (10), 130 (8), 111 (31), 98 (59), 84 (13), 70 (19), 56 (24), 42 (31), 30 (3).



dimethyl 3,3'-((2-4-(3-methoxy-3-oxopropyl)piperazin-1-yl)ethyl)azanediyl) dipropanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 387 (1 %) [M^+], 314 (11), 245 (2), 228 (3), 216 (4), 202 (60), 185 (100), 170 (7), 153 (4), 142 (8), 130 (6), 111 (19), 98 (33), 84 (7), 70 (13), 55 (23), 42 (22), 30 (2).

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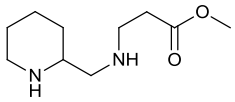
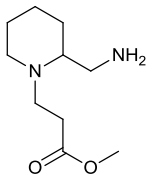


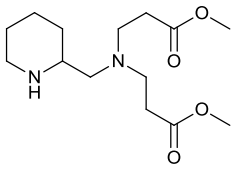
methyl 3-((piperidine-2-ylmethyl)amino)propanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 200 (1 %) [M^+], 169 (2), 127 (4), 118 (3), 96 (2), 84 (100), 56 (13), 42 (9), 30 (5).



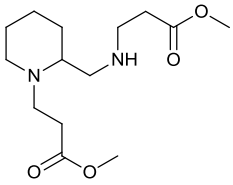
methyl 3-(2-(aminomethyl)piperidine-1-yl)propanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 200 (1 %) [M^+], 170 (100), 142 (3), 127 (11), 110 (5), 96 (69), 84 (7), 68 (4), 55 (13), 42 (8), 30 (8).



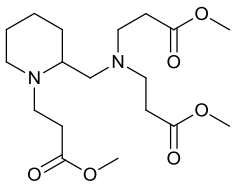
dimethyl 3,3'-((piperidine-2-ylmethyl)azanediyl)dipropanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 286 (1 %) [M^+], 255 (2), 213 (6), 202 (11), 170 (1), 130 (33), 116 (2), 98 (2), 84 (100), 56 (11), 42 (9), 30 (4).



methyl 3-(2-(((3-methoxy-3-oxopropyl)amino)methyl)piperidine-1-yl) propanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 286 (1 %) [M^+], 255 (2), 213 (5), 170 (100), 142 (2), 110 (3), 96 (35), 84 (10), 68 (2), 55 (8), 42 (8), 30 (2).



dimethyl 3,3'-(((1-(3-methoxy-3-oxopropyl)piperidine-2-yl)methyl)azanediyl) dipropanoate

GC-MS (EI, 70eV): *m/z* (rel. int.): 372 (1 %) [M^+], 341 (1), 299 (4), 213 (1), 202 (4), 170 (100), 130 (2), 110 (2), 96 (20), 84 (4), 55 (8), 42 (7).

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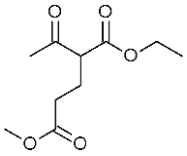
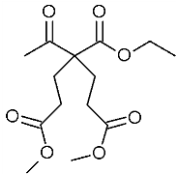
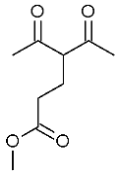


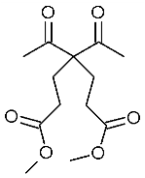
2-acetyl-pentanedioic acid 1-ethyl 5-methyl ester
GC-MS (EI, 70eV): *m/z* (rel. int.): 216 (1 %) [M^+], 185 (2), 174 (6), 139 (11), 128 (7), 114 (6), 100 (21), 85 (6), 73 (5), 59 (13), 55 (20), 43 (100).



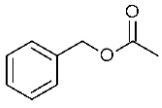
3-acetyl-1,3,5-pentanetricarboxylic acid 3-ethyl, 1,5 dimethyl ester
GC-MS (EI, 70eV): *m/z* (rel. int.): 302 (1 %) [M^+], 271 (2), 214 (7), 200 (5), 186 (16), 171 (7), 155 (7), 143 (7), 127 (7), 113 (17), 97 (7), 81 (7), 67 (7), 59 (16), 55 (16), 43 (100).



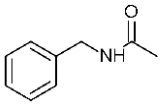
methyl 4-acetyl-5-oxohexanoate
GC-MS (EI, 70eV): *m/z* (rel. int.): 186 (1 %) [M^+], 144 (13), 139 (1), 113 (11), 112 (12), 84 (15), 74 (3), 71 (11), 59 (9), 55 (18), 43 (10).



4,4-(diacetyl)heptanedioic acid dimethyl ester
GC-MS (EI, 70eV): *m/z* (rel. int.): 272 (1 %) [M^+], 230 (3), 199 (5), 198 (5), 167 (3), 155 (2), 138 (7), 125 (13), 110 (4), 97 (13), 81 (2), 59 (7), 55 (7), 43 (100).



acetic acid, phenylmethyl ester
GC-MS (EI, 70eV): *m/z* (rel. int.): 150 (29%) [M^+], 108 (100), 91 (73), 90 (40), 79 (29), 77 (23), 65 (16), 63 (7), 51 (16), 43 (46).



***N*-(phenylmethyl)-acetamide**
GC-MS (EI, 70eV): *m/z* (rel. int.): 149 (70%) [M^+], 106 (100), 91 (29), 79 (14), 77 (14), 65 (8), 51 (9), 43 (26).