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A three-component novel synthesis of 1-carbamato-alkyl-2-naphthol derivatives

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ABSTRACT

A new one-pot, efficient three-component condensation of benzaldehydes, 2-naphthol, and carbamates in the presence of silica supported sodium hydrogen sulfate as an effective heterogeneous catalyst for the synthesis of novel 1-carbamato-alkyl-2-naphthol derivatives under solvent-free conditions is described. The present methodology offers several advantages, such as high yields, short reaction times, and very easy workup.

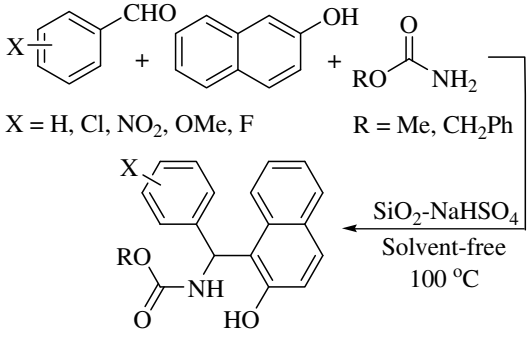
Multi-component reactions have attracted considerable attention in organic synthesis as they can produce target products in a single operation without isolating the intermediates and thus reducing the reaction times and energy input.[1,2] Heterogeneous catalysts have gained much importance in recent years due to economic and environmental considerations.[3] These catalysts are generally less expensive, highly reactive, eco-friendly, easy to handle, reduce reaction times, impart greater selectivity, and lead to simple workup and recoverability of the catalysts.[4–11]

Compounds bearing 1,3-amino-oxygenated functional motifs are common in a variety of biologically important natural products and potent drugs, including a number of nucleoside antibiotics and HIV protease inhibitors, such as ritonavir and lipinavir.[12] It is noteworthy that 1-carbamato-alkyl-2-naphthols can be converted to important biologically active 1-aminomethyl-2-naphthol derivatives by carbamate hydrolysis. The hypotensive and bradycardiac effects of these compounds have been evaluated.[13] It is noteworthy that aminotetralin derivatives manifest a number of important and therapeutically useful biological activities such as antidepressant, immunomodulator, and antitumor.[14] Despite this broad range of applications, only a few members of this family of compounds have been reported. The development of new methods for their assembly is therefore of considerable synthetic importance.[15]

Recently, we reported the reaction of 2-naphthol, aromatic aldehydes, and amides to form amidoalkyl naphthol derivatives.[16] The reaction proceeds through the in situ formation of *ortho*-quinone methides (*o*-QMs), and the amide acted as a nucleophile. The use of carbamates instead of amides leads to 1-carbamato-alkyl-2-naphthols. Carbamates, which can be deprotected more easily than an amide group,[17] are important for the preparation of biologically active 1-aminomethyl-2-naphthol derivatives.[14,15]

Silica supported sodium hydrogen sulfate can be prepared easily from the readily available inexpensive ingredients, $NaHSO_4{\cdot}H_2O$ and silica gel.[18]

With the aim to develop a more efficient synthetic process, we herein describe a practical and inexpensive method for the preparation of new 1-carbamato-alkyl-2-naphthol derivatives via a three-component condensation reaction between aryl aldehydes, 2-naphthol, and carbamates in the presence of SiO_2–$NaHSO_4$ as a heterogeneous catalyst under thermal and solvent-free conditions (Scheme 1).



Scheme 1.

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Table 1
Optimization of the amount of SiO_2–$NaHSO_4$ and the reaction temperature for the preparation of methyl (2-hydroxynaphthalen-1-yl)(phenyl)methyl carbamate

Entry	Catalyst (g)	Temperature (°C)	Time (min)	Yield[a] (%)
1	0.03	100	5.5	76
2	0.05	100	3.5	81
3	0.07	100	3.5	84
4	0.10	100	2.5	83
5	0.05	75	10	71
6	0.05	130	3	73

[a] Yields refer to isolated pure products.

To optimize the amount of catalyst and the reaction temperature, the reaction of benzaldehyde (1 equiv), 2-naphthol (1 equiv), and methyl carbamate (1.2 equiv) under thermal solvent-free conditions was selected as a model. The best result was obtained by carrying out the reaction using 0.05 g of SiO_2–$NaHSO_4$ at 100 °C under solvent-free conditions (Table 1).

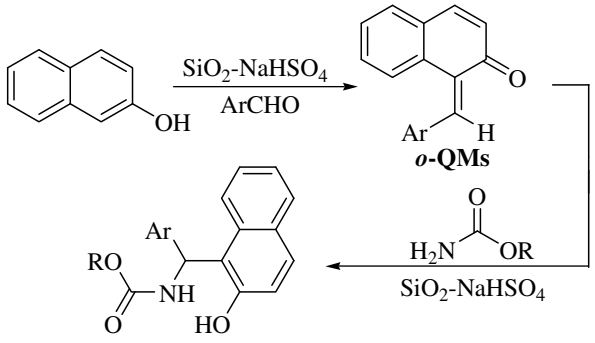
Using these optimized reaction conditions, the scope and efficiency of the reaction were explored for the synthesis of a wide variety of substituted 1-carbamato-alkyl-2-naphthols using various aryl aldehydes, 2-naphthol, and methyl/benzyl carbamates.[19–32] The results are summarized in Table 2.

As shown in Table 2, the direct three-component reactions worked well with a variety of aryl aldehydes including those bearing electron-withdrawing and electron-donating groups such as OMe, Cl, F, and NO_2, and the desired compounds were obtained in good to high yields. Under the same conditions, this reaction did not proceed when aliphatic aldehydes such as propionaldehyde or heptaldehyde (Table 2, entries 8 and 9) and heterocyclic 2-pyridinecarbaldehyde (Table 2, entry 10) were used as the starting material.

Table 2
Preparation of 1-carbamato-alkyl-2-naphthols

Entry	Aldehyde	R	Time (min)/Yield[a] (%)	Mp (°C)
1	Benzaldehyde	Me	3.5/ 81	217-218
2	4-Nitrobenzaldehyde	Me	2.5/89	205–207
3	4-Chlorobenzaldehyde	Me	6.0/92	198–200
4	2,4-Dichlorobenzaldehyde	Me	6.0/84	192 dec
5	3-Chlorobenzaldehyde	Me	4.5/79	196–198
6	3-Nitrobenzaldehyde	Me	2.0/87	252 dec
7	2,5-Dimethoxybenzaldehyde	Me	3.0/83	215 dec
8	Propionaldehyde	Me	30.0/—	—
9	Heptaldehyde	Me	30.0/—	—
10	2-Pyridinecarbaldehyde	Me	30.0/—	—
11	Benzaldehyde	CH_2Ph	10.0/75	179–180
12	2-Chlorobenzaldehyde	CH_2Ph	25.0/60	163–165
13	3-Chlorobenzaldehyde	CH_2Ph	20.0/80	203 dec
14	3-Methoxybenzaldehyde	CH_2Ph	3.0/95	182–184
15	4-Fluorobenzaldehyde	CH_2Ph	15.0/67	185–186

[a] Yields refer to isolated pure products.



Scheme 2.

In conclusion, we have developed a highly efficient synthesis of 1-carbamato-alkyl-2-naphthol derivatives from arylaldehydes, 2-naphthol and methyl/benzyl carbamates under solvent-free conditions. These products can be deprotected and used to prepare potentially biologically active 1-aminomethyl-2-naphthol derivatives.

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19. SiO_2-$NaHSO_4$ was prepared according to the reported procedure.[18] All yields refer to isolated products after purification.
20. *General procedure for the preparation of 1-carbamato-alkyl-2-naphthol derivatives*: To a mixture of 2-naphthol (1 mmol), aldehyde (1 mmol), and methyl/benzyl carbamate (1.2 mmol), silica supported sodium hydrogen sulfate (0.05 g) was added. The mixture was stirred at 100 °C in an oil bath and the reaction was followed by TLC. After completion, the mixture was cooled to room temperature, and then ethanol was added to dissolve the precipitated product. The catalyst was filtered and the filtrate evaporated. Then, the solid product was purified by recrystallization from aqueous EtOH (20%). Spectral data are given below.

21. *Methyl (2-hydroxynaphthalen-1-yl)(phenyl)methyl carbamate (Table 2, entry 1)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.57 (s, 3H), 6.87 (d, J = 8.4 Hz, 1H), 7.18–7.29 (m, 7H), 7.38 (d, J = 7.4 Hz, 1H), 7.65–7.84 (m, 3H), 7.92 (d, J = 7.7 Hz, 1H), 10.12 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.8, 52.1, 118.9, 119.3, 123.0, 123.5, 126.5, 126.8, 127.0, 128.6, 128.8, 129.0, 129.8, 132.5, 142.8, 153.4, 157.0 ppm; IR (KBr, cm^{-1}): 3423, 3202, 1677, 1630, 1585, 1518, 1438, 1335, 1272, 1066, 1042, 937, 811, 743, 697; MS (EI, 70 eV): m/z (%) = 307 (M$^+$, 13), 295 (9), 279 (15), 232 (79), 231 (100), 202 (16), 167 (31), 149 (76), 115 (10), 104 (10), 71 (14), 57 (18), 43 (10); Anal. Calcd for: $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56%. Found: C, 74.23; H, 5.57; N, 4.52%.
22. *Methyl (2-hydroxynaphthalen-1-yl)(4-nitrophenyl)methyl carbamate (Table 2, entry 2)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.60 (s, 3H), 6.95 (d, J = 8.3 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.78–7.87 (m, 4H), 8.15 (d, J = 8.6 Hz, 2H), 10.22 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.6, 52.3, 118.4, 118.8, 123.1, 123.3, 123.8, 127.3, 127.6, 128.8, 129.1, 130.4, 132.4, 146.5, 151.2, 153.6, 157.2 ppm; IR (KBr, cm^{-1}): 3422, 3265, 1683, 1628, 1604, 1518, 1438, 1346, 1272, 1247, 1068, 1046, 852, 823, 782, 741, 704; MS (EI, 70 eV): m/z (%) = 352 (M$^+$, 17), 276 (21), 260 (85), 231 (36), 230 (100), 202 (25), 115 (10); Anal. Calcd for: $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95%. Found: C, 64.75; H, 4.58; N, 7.91%.
23. *Methyl (4-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl carbamate (Table 2, entry 3)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.57 (s, 3H), 6.84 (d, J = 8.2 Hz, 1H), 7.20–7.41 (m, 7H), 7.71–7.81 (m, 3H), 7.89 (d, J = 7.3 Hz, 1H, NH), 10.16 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.3, 52.1, 118.9, 123.0, 123.4, 127.1, 128.4, 128.5, 128.8, 129.1, 130.0, 131.4, 132.4, 141.9, 153.4, 157.1 ppm; IR (KBr, cm^{-1}): 3422, 3225, 2951, 1685, 1629, 1583, 1516, 1491, 1438, 1330, 1273, 1245, 1182, 1144, 1088, 1014, 963, 852, 807, 749, 708; MS (EI, 70 eV): m/z (%) = 341 (M$^+$, 7), 266 (33), 265 (50), 231 (100), 202 (18); Anal. Calcd for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10%. Found: C, 66.71; H, 4.68; N, 4.10%.
24. *Methyl (2,4-dichlorophenyl)(2-hydroxynaphthalen-1-yl)methyl carbamate (Table 2, entry 4)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.54 (s, 3H), 6.83 (d, J = 8.1 Hz, 1H), 7.13 (d, J = 8.9 Hz, 1H), 7.28 (t, J = 7.3 Hz, 1H), 7.38–7.57 (m, 4H), 7.75 (d, J = 8.7 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H, NH), 8.01 (d, J = 8.6 Hz, 1H), 9.93 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 49.9, 52.0, 116.8, 119.0, 122.9, 123.1, 127.0, 127.1, 128.7, 129.0, 129.1, 130.2, 131.7, 132.4, 133.0, 133.6, 139.3, 154.0, 156.6 ppm; IR (KBr, cm^{-1}): 3404, 3259, 1677, 1626, 1620, 1469, 1437, 1319, 1273, 1236, 1190, 1054, 1035, 815, 853; MS (EI, 70 eV): m/z (%) = 376 (M$^+$, 1), 375 (6), 267 (59), 266 (33), 265 (100), 231 (18), 202 (14), 115 (10), 101 (6); Anal. Calcd for $C_{19}H_{15}Cl_2NO_3$: C, 60.65; H, 4.02; N, 3.72%. Found: C, 60.61; H, 4.04; N, 3.75%.
25. *Methyl (3-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl carbamate (Table 2, entry 5)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.58 (s, 3H), 6.86 (d, J = 8.6 Hz, 1H), 7.13–7.31 (m, 6H), 7.41 (t, J = 7.6 Hz, 1H), 7.77–7.83 (m, 3H), 7.92 (d, J = 8.0 Hz, 1H, NH), 10.19 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.4, 52.2, 118.7, 118.9, 123.1, 123.3, 125.3, 126.2, 126.8, 127.2, 128.8, 129.1, 130.1, 130.5, 132.4, 133.3, 145.6, 153.4, 157.1 ppm; IR (KBr, cm^{-1}): 3417, 3293, 3070, 1688, 1628, 1596, 1572, 1516, 1474, 1438, 1335, 1274, 1241, 1190, 1045, 808, 748; MS (EI, 70 eV): m/z (%) = 341 (M$^+$, 20), 265 (40), 231 (100), 202 (18), 170 (5), 115 (11), 59 (8); Anal. Calcd for $C_{19}H_{16}ClNO_3$: C, 66.77; H, 4.72; N, 4.10%. Found: C, 67.02; H, 4.75; N, 4.11%.
26. *Methyl (2-hydroxynaphthalen-1-yl)(3-nitrophenyl)methyl carbamate (Table 2, entry 6)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.60 (s, 3H), 6.96 (d, J = 8.6 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.79–7.97 (m, 4H), 8.07 (d, J = 8.0 Hz, 1H, NH), 8.12 (s, 1H) 10.23 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.5, 52.3, 118.3, 118.9, 121.0, 122.0, 123.0, 123.1, 127.3, 128.8, 129.1, 130.2, 130.4, 132.4, 133.3, 145.5, 148.2, 153.6, 157.2 ppm; IR (KBr, cm^{-1}): 3389, 3290, 3088, 1687, 1630, 1578, 1525, 1440, 1340, 1278, 1246, 1138, 1044, 923, 806, 733, 634; MS (EI, 70 eV): m/z (%) = 352 (M$^+$, 28), 335 (18), 295 (40), 277 (33), 276 (57), 260 (87), 231 (80), 230 (100), 202 (39), 149 (12), 115 (15); Anal. Calcd for $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95%. Found: C, 64.80; H, 4.57; N, 7.92%.
27. *Methyl (2,5-dimethoxyphenyl)(2-hydroxynaphthalen-1-yl)methyl carbamate (Table 2, entry 7)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.54 (s, 3H), 3.56 (s, 3H), 3.64 (s, 3H), 6.73 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 8.8 Hz, 1H), 7.02 (d, J = 9.1 Hz, 1H), 7.17 (d, J = 8.9 Hz, 2H), 7.27 (t, J = 7.0 Hz, 1H),7.43–7.54 (m, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.6 Hz, 1H, NH), 10.07 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 47.1, 51.9, 55.7, 56.4, 111.9, 112.2, 116.0, 119.1, 119.2, 122.8, 123.7, 126.5, 128.6, 128.7, 129.4, 131.8, 132.8, 151.0, 153.2, 153.5, 156.4 ppm; IR (KBr, cm^{-1}): 3403, 3245, 3019, 2952, 2908, 1679, 1626, 1578, 1526, 1498, 1405, 1307, 1296, 1245, 1194, 1090, 856, 818, 750, 719; MS (EI, 70 eV): m/z (%) = 367 (M$^+$, 7), 335 (16), 262 (42), 261 (100), 218 (18); Anal. Calcd for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81%. Found: C, 68.58; H, 5.75; N, 3.83%.
28. *Benzyl (2-hydroxynaphthalen-1-yl)(phenyl)methyl carbamate (Table 2, entry 11)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.04 (d, J = 12.5 Hz, 1H), 5.11 (d, J = 12.5 Hz, 1H), 6.92 (d, J = 8.6 Hz, 1H), 7.16–7.36 (m, 13H), 7.76–7.82 (m, 3H), 7.92 (d, J = 7.5 Hz, 1H, NH), 10.13 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.8, 66.1, 118.9, 119.3, 122.9, 126.5, 126.8, 126.9, 128.2, 128.6, 128.8, 128.9, 129.0, 129.8, 132.5, 137.5, 142.8, 153.4, 156.5 ppm; IR (KBr, cm^{-1}): 3423, 3200, 3064, 3034, 1675, 1629, 1581, 1514, 1438, 1328, 1271, 1221, 1132, 1040, 943, 808, 753, 697; MS (EI, 70 eV): m/z (%) = 383 (M$^+$, 7), 281 (9), 232 (74), 231 (100), 202 (13), 115 (9), 91 (47); Anal. Calcd for $C_{25}H_{21}NO_3$: C, 78.31; H, 5.52; N, 3.65%. Found: C, 78.25; H, 5.69; N, 3.64%.
29. *Benzyl (2-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl carbamate (Table 2, entry 12)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.02 (d, J = 12.7 Hz, 1H), 5.10 (d, J = 12.9 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 8.7 Hz, 1H), 7.24–7.53 (m, 11H), 7.76 (d, J = 9.1 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H, NH), 8.04 (t, J = 8.1 Hz, 2H), 9.96 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.2, 65.8, 117.4, 119.0, 122.8, 123.4, 126.8, 127.0, 127.9, 128.1, 128.7, 128.9, 129.1, 129.8, 130.0, 130.4, 133.0, 133.1, 137.6, 139.8, 154.0, 156.1 ppm; IR (KBr, cm^{-1}): 3421, 3170, 3062, 3030, 1700, 1627, 1579, 1516, 1476, 1437, 1375, 1335, 1274, 1247, 1050, 819, 753, 733; MS (EI, 70 eV): m/z (%) = 417 (M$^+$, 7), 282 (12), 232 (32), 231 (100), 202 (12), 115 (8), 91 (61); Anal. Calcd for $C_{25}H_{20}ClNO_3$: C, 71.85; H, 4.82; N, 3.35%. Found: C, 71.65; H, 4.77; N, 3.30%.
30. *Benzyl (3-chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl carbamate (Table 2, entry 13)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.00 (d, J = 12.8 Hz, 1H), 5.08 (d, J = 12.8 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 7.15 (d, J = 8.6 Hz, 1H), 7.26–7.37 (m, 10H), 7.52 (s, 1H), 7.74–7.81 (m, 2 H), 8.02–8.05 (m, 2H) 9.93 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.2, 65.8, 117.4, 119.0, 122.8, 123.4, 126.8, 127.0, 127.9, 128.1, 128.7, 128.9, 129.1, 129.8, 130.0, 130.4, 133.1, 137.6, 139.8, 154.0, 156.1 ppm; IR (KBr, cm^{-1}): 3421, 3170, 1701, 1628, 1579, 1517, 1438, 1377, 1335, 1275, 1248, 1050, 940, 819, 753, 734, 694, 530; MS (EI, 70 eV): m/z (%) = 417 (M$^+$, 4), 415 (6), 295 (8), 282 (6), 232 (22), 231 (100), 202 (13), 115 (8), 91 (40), 77 (7); Anal. Calcd for $C_{25}H_{20}ClNO_3$: C, 71.85; H, 4.82; N, 3.35%. Found: C, 71.82; H, 4.85; N, 3.33%.
31. *Benzyl (2-hydroxynaphthalen-1-yl)(3-methoxyphenyl)methyl carbamate (Table 2, entry 14)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.66 (s, 3H), 5.03 (d, J = 12.6 Hz, 1H), 5.11 (d, J = 12.6 Hz, 1H), 6.74–6.88 (m, 4H), 7.13–7.35 (m, 9H), 7.74–7.81 (m, 3H), 7.90 (d, J = 7.9 Hz, 1H, NH), 10.06 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.7, 55.3, 66.1, 111.6, 112.8, 118.9, 119.2, 122.9, 123.6, 126.9, 128.2, 128.8, 129.0, 129.7, 129.8, 132.5, 137.5, 144.5, 153.4, 156.5, 159.6 ppm; IR (KBr, cm^{-1}): 3406, 3274, 3063, 3008, 2945, 1699, 1625, 1609, 1582, 1508, 1454, 1326, 1294, 1244, 1129, 1040, 961, 816, 771, 744; MS (EI, 70 eV): m/z (%) = 413 (M$^+$, 10), 278 (14), 262 (62), 261 (61), 232 (21), 231 (100), 91 (62); Anal. Calcd for $C_{26}H_{23}NO_4$: C, 75.53; H, 5.61; N, 3.39%. Found: C, 75.45; H, 5.58; N, 3.40%.
32. *Benzyl (4-fluorophenyl)(2-hydroxynaphthalen-1-yl)methyl carbamate (Table 2, entry 15)*: ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.04 (d, J = 12.6 Hz, 1H), 5.10 (d, J = 12.6 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 7.05–7.12 (m, 2H), 7.21–7.35 (m, 10H), 7.76–7.86 (m, 3H), 7.92 (d, J = 8.0 Hz, 1H, NH), 10.2 (s, 1H, OH) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 50.38, 66.2, 115.1, 115.4, 118.9, 119.0, 123.0, 123.5, 127.0, 128.3, 128.4, 128.5, 128.5, 128.9, 129.0, 129.9, 132.4, 137.4, 138.8, 153.4, 156.5, 159.7 ppm; IR (KBr, cm^{-1}): 3424, 3247, 3072, 2968, 1676, 1268, 1562, 1507, 1455, 1438, 1327, 1273, 1219, 1160, 1066, 944, 854, 815, 755, 703; MS (EI, 70 eV): m/z (%) = 401 (M$^+$, 6), 250 (77), 249 (100), 220 (11), 91 (57); Anal. Calcd for $C_{25}H_{20}FNO_3$: C, 74.80; H, 5.02; N, 3.49%. Found: C, 74.71; H, 4.97; N, 3.44%.