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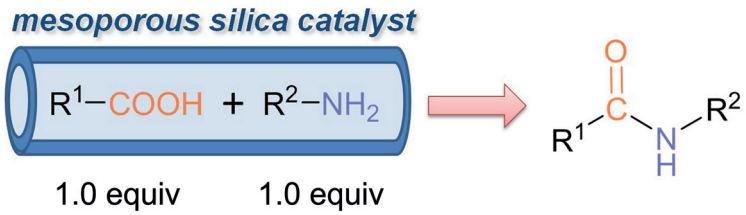
Direct Amide Synthesis from Equimolar Amounts of Carboxylic Acid and Amine Catalyzed by Mesoporous Silica SBA-15

Mizuki Tamura
Daisuke Murase
Kenichi Komura*

Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu City, 501-1193, Japan
kkomura@gifu-u.ac.jp



Received: 15.10.2014
Accepted after revision: 09.12.2014
Published online: 26.01.2015
DOI: 10.1055/s-0034-1379966; Art ID: ss-2014-f0617-op

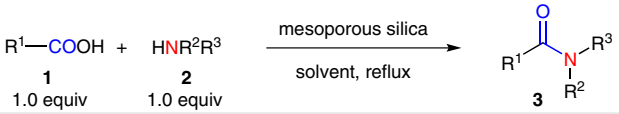
Abstract Direct amide synthesis from equimolar amounts of carboxylic acid and amine using mesoporous silica as a versatile heterogeneous catalyst is reported.

Key words amides, amines, carboxylic acids, heterogeneous catalysis, green chemistry

Amidation reaction of carboxylic acids with amines is one of the pivotal tools in organic synthesis, providing amides as valuable chemicals, which are found in the fields of life science, medicines, and engineering polymers, etc. Conventionally, the activation of a carboxylic acid by adding hazardous or toxic reagents such as $SOCl_2$ or *N*,*N*′-dicyclohexylcarbodiimide (DCC) has been required to achieve sufficient formation of amides, and this process always suffers from huge waste production.[1,2] However, with widespreading demands for environmental benign chemical processes, a sophisticated reaction system has been desired; that is, the *direct amidation reaction* – the amide formation utilizing an equimolar amount of a carboxylic acid and an amine in the presence of catalytic amount of an activator.[3] Of course, the utilization of homogeneous activators seems to be attractive; however, there are still drawbacks such as recovery and reusability after the reaction. Thus, the development for heterogeneous catalysts is a challenging task, and some potential reports have appeared. For example, the polymer-supported boronopyridinium ion as an organic heterogeneous catalyst has been reported by Ishihara and Yamamoto et al.[3g,4] The use of inorganic catalysts, for example, activated silica gel,[5] sulfated tungstate,[6] and molecular sieves (3Å MS)[7] in the amidation process has also been revealed. Recently the application of Ph_3P as well as and boronic acid anchored onto the inorganic support catalysts has been reported.[8]

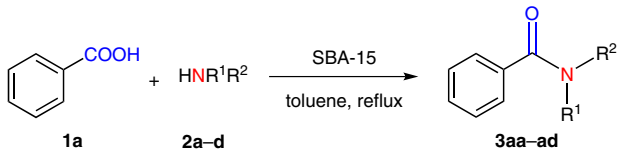
Our group is interested in condensation reactions such as esterification and amidation using an equimolar amounts of substrates and has reported that multi-valent metal salt such as $FeCl_3{\cdot}6H_2O$ is a highly active homogeneous catalyst for producing esters or amides in good to excellent yields.[3d,9] In addition, we have recently reported the direct amidation of fatty acids with long-chain amines over mesoporous silica MCM-41 catalyst and claimed that only siliceous material with mesoporosity exhibited the highest catalytic activity to afford the amides in excellent yields, and that the catalyst can be easily separated from the reaction medium and reused without loss of its catalytic activity.[10] The catalytic activity of mesoporous silica catalyst results from the surface silanol (SiOH), which has an extremely weak acidity. It is interesting that uniformed pore structure and proper pore size trigger the sufficient catalytic performance; however, detailed reasons as to why extremely weak silanol should act as an acid catalyst is unclear.

Here, we report the heterogeneous direct amidation over mesoporous silica SBA-15 catalyst using lower molecular weight substrates by varying combinations of acids and amines as illustrated in Scheme 1 to disclose the substrates scope of limitations in this reaction system over mesoporous silica catalyst.



Scheme 1 Direct amidation reaction of an equimolar amount of carboxylic acid and amine over mesoporous silica SBA-15 catalyst

Table 1 Results of Direct Amidation of Benzoic Acid (**1a**) with Amines in the Presence of SBA-15 Catalyst[a]



1a **2a–d** **3aa–ad**

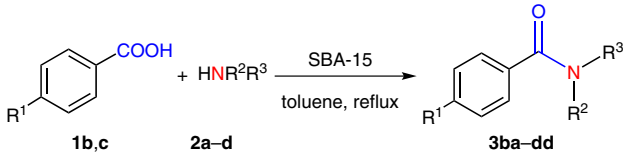
Entry	Amine	Product	R^1, R^2	Yield (%)[b]
1	**2a**	**3aa**	H, Ph	26 (0)[c] 50[d] 58[e]
2[f]	**2b**	**3ab**	H, Bn	>99
3	**2c**	**3ac**	H, $(CH_2)_5Me$	>99
4[f]	**2d**	**3ad**	$-(CH_2)_2O(CH_2)_2-$	78

[a] Reactions were performed by using benzoic acid (**1a**; 3.0 mmol) and amine (3.0 mmol) in anhydrous toluene (15mL) in the presence of the catalyst (0.5 g) under reflux for 24 h.
[b] Isolated yield.
[c] The yield obtained in the absence of catalyst is indicated between parentheses.
[d] Under *m*-xylene reflux.
[e] Under mesitylene reflux.
[f] Reaction time: 8 h.

Mesoporous silica SBA-15 is also a siliceous material having the same structural group (*p6mm*) as MCM-41; however, SBA-15 has higher hydrothermal stability and larger pore size than that of MCM-41. Mesoporous silica SBA-15 was used in our amidation reaction as the catalyst, which was prepared according to the reported procedure and characterized by powder-XRD, nitrogen isotherm, and TG-DTA analyses.[11]

Table 1 shows the results of the direct amidation of benzoic acid (**1a**) with various amines such as aniline (**2a**), benzylamine (**2b**), *n*-hexylamine (**2c**), and morpholine (**2d**). First, the reaction of **1a** with **2a** was demonstrated as a model reaction. In the absence of the SBA-15 catalyst, no amide formation was observed; however, the catalyst gave the amide **3aa** in a low 26% yield (Table 1, entry 1). Our recent finding revealed that the reaction is strongly dependent on the reaction temperature. Therefore, use of higher boiling point aromatic solvent such as *m*-xylene and mesitylene was examined.[3d,9g] A two-fold enhanced yield of **3aa** in 50% was obtained under refluxing *m*-xylene; unfortunately, further increase of the temperature did not afford **3aa** in sufficiently excellent yield. Aliphatic amines with higher basicity such as **2b** and **2c** gave quantitative yields of amides **2ab** and **2ac** by conducting the reaction for 8 hours (entries 2 and 3). However, reaction of secondary amine **2d** showed only moderate amide formation due to its steric hindrance. Nevertheless, the reaction of the sterically hindered secondary amine (*N*,*N*′-dihexylamine) with **1a** gave

Table 2 Results of Direct Amidation Reaction of **1b–d** and **2a–d** over SBA-15 Catalyst[a]



1b,c **2a–d** **3ba–dd**

Entry	Acid	R^1	Amine	R^2	R^3	Product	Yield (%)[b]
1	**1b**	4-MeO	**2a**	H	Ph	**3ba**	24
2[c]	**1b**	4-MeO	**2b**	H	Bn	**3bb**	63
3[c]	**1b**	4-MeO	**2c**	H	$(CH_2)_5Me$	**3bc**	75
4	**1b**	4-MeO	**2d**	$-(CH_2)_2O(CH_2)_2-$		**3bd**	76
5	**1c**	4-F	**2a**	H	Ph	**3ca**	56
6	**1c**	4-F	**2b**	H	Bn	**3cb**	87
7	**1c**	4-F	**2c**	H	$(CH_2)_5Me$	**3cc**	62
8	**1c**	4-F	**2d**	$-(CH_2)_2O(CH_2)_2-$		**3cd**	88
9	**1d**	4-O_2N	**2a**	H	Ph	**3da**	24
10	**1d**	4-O_2N	**2b**	H	Bn	**3db**	78
11	**1d**	4-O_2N	**2c**	H	$(CH_2)_5Me$	**3dc**	58
12	**1d**	4-O_2N	**2d**	$-(CH_2)_2O(CH_2)_2-$		**3dd**	64

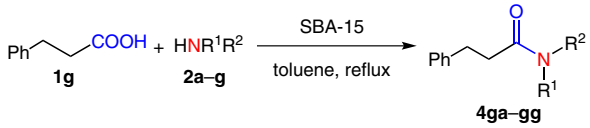
[a] Reactions were performed by using benzoic acid (**1a**; 3.0 mmol) and amine (3.0 mmol) in anhydrous toluene (15mL) in the presence of the catalyst (0.5 g) under reflux for 24 h.
[b] Isolated yield.
[c] Reaction time: 8 h.

the corresponding amide in 15% by refluxing in xylene for 24 hours (data not shown). This result is similar to our original report.[10]

Table 2 shows the results of direct amidation of three aromatic carboxylic acids bearing selected substituents at *para*-position (MeO, **1b**; F, **1c**; and NO_2, **1d**) and four amines **2a–d** over SBA-15 catalyst. All yields are isolated yields after column chromatography. The yields from the less reactive aniline **2a** are low as in the cases of **3ba** (24%) and **3da** (24%); however, the use of **1c** with a highly electron-withdrawing group fluorine exhibited an increasing yield of the amide **3ca** up to 56% (entries 1, 5, and 9). Other results by varying the combination of aromatic acids and amines are found to be moderate to good with respect to the yields of the corresponding amides. These results evidently demonstrate the effectiveness of mesoporous silica catalyst in a heterogeneous amidation reaction.

Interestingly, 3-phenylpropionic acid (**1g**), a more flexible aliphatic carboxylic acid, was used as a substrate in this reaction with amines **2a–g** to furnish the corresponding amides **4ga–gg** in quantitative yields within 8 hours (Table 3). Further, aromatic amines **2e–g** possessing either an electron-donating group and or an electron-withdrawing group at the *para*-position afforded the corresponding amides **4ge–gg** in excellent yields (GC) irrespective of their electronic environment associated with nucleophilicity (Table 3, entries 5–7). Thus, aliphatic carboxylic acids seem to be more favorable substrates for this reaction system. This is because the less steric hindrance of **1g** enables for sufficient acceptance of nucleophilic attack of amine.

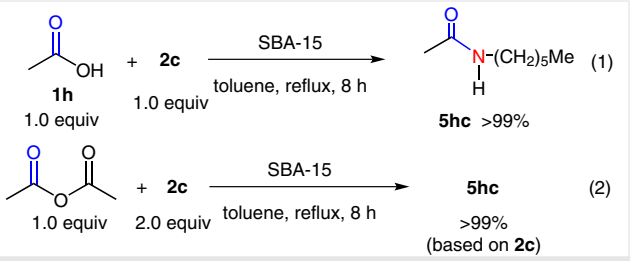
Table 3 Results of Direct Amidation of 3-Phenylpropionic Acid (**1g**) with Amine in the Presence of SBA-15 Catalyst[a]



Entry	Amine	R^1	R^2	Product	Yield (%)[b]
1	**2a**	H	Ph	**4ga**	>99
2	**2b**	H	Bn	**4gb**	>99
3	**2c**	H	$(CH_2)_5Me$	**4gc**	>99
4	**2d**	$-(CH_2)_2O(CH_2)_2-$		**4gd**	>99
5	**2e**	H	4-$MeOC_6H_4$	**4ge**	>99
6	**2f**	H	4-$Me_2NC_6H_4$	**4gf**	>99
7	**2g**	H	4-FC_6H_4	**4gg**	>99

[a] Reactions were performed by using benzoic acid (1a; 3.0 mmol) and amine (3.0 mmol) in anhydrous toluene (15mL) in the presence of the catalyst (0.5 g) under reflux for 8 h.
[b] Yield was determined by GC by comparing with an authentic sample.

The direct amidation of acetic acid (**1h**) with hexylamine (**2c**) for 8 hours proceeded well to afford **5hc** in quantitative yield (>99%, Scheme 2, eq. 1). It is interesting to note that the reaction of acetic anhydride with a two-fold amount of **2c** for 8 hours also gave the amide **5hc** in excellent yield. This indicates that the excess hexylamine (**2c**) reacted with acetic anhydride to afford **2hc** via a noncatalytic manner at the first step, and then, the amidation of acetic acid (**1h**) formed in this process reacted with **2c** in the presence of SBA-15 catalyst. These results obviously imply that mesoporous silica is a versatile catalyst for acetylation reaction of amine, which is often utilized in the acetyl protection of, for example, amino acids. This part of research topic is in progress and will be reported in near future.

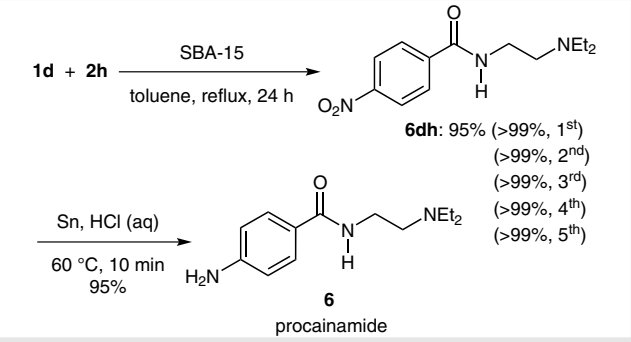


Scheme 2 Direct amidation of acetic acid (**1h**) with **2c**, and acetic anhydride with **2c** over SBA-15 catalyst

With an efficient heterogeneous amidation reaction catalyzed by mesoporous silica SBA-15 in hand, the reaction was applied to valuable and practical chemical synthesis. Procainamide (**6**) is one of the widely used important pharmaceuticals as arrhythmic agent and conventionally synthesized via acid chloride of **1d** and amine **2h** accompanied by hazardous waste of gaseous HCl. Thus, the reaction must require the neutralization by base, which then produces a huge amount of salt and/or polluted water as a waste.

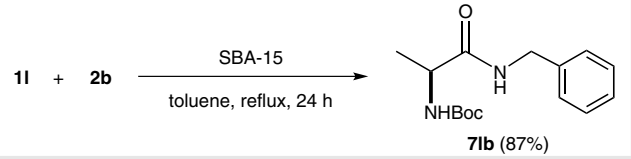
The direct amidation reaction of **1d** with *N*,*N*-diethylethylenediamine (**2h**) over SBA-15 catalyst is shown in Scheme 3. The corresponding amide **6dh**, an important intermediate of procainamide, can be obtained in 95% isolated yield after 24 hours, and this is subjected to reduction to afford procainamide **6** in 95% yield. The reduction step by Sn catalyst is also a heterogeneous reaction medium, thus our new heterogeneous synthetic strategy allows to obtain the procainamide from **1d** in two steps in 90% total yield in heterogeneous manners, and the calculated environmental-factor (E-factor) value and atom economy are found to be 0.07 and 94%, respectively[12] (E-factor and atom economy of conventional method via acid chloride activation are 0.80 and 54%). In addition, the reusability of the catalyst reveals that the activity did not decline and the yields of **6dh** were >99% (GC) until the 5th recycle. It obviously suggests that this synthetic method should be an alternative method for practical production of procainamide (**6**) as an environmentally benign process. This result encouraged us to ex-

amine the direct amidation reactions of **2h** with aromatic acids **1a**–**c**, **1e**, **1f**, and **1i**–**1k**, which can produce the procainamide derivatives. In the absence of the catalyst, the reaction of benzoic acid (**1a**) and **2h** allowed the formation of the product only in poor yield (23%). However, the SBA-15 catalyst sufficiently promoted the reaction in quantitative yield (96%, Table 4, entry 1). Further, the reactions utilizing **2h** for synthesizing the procainamide derivatives gave the corresponding amides in good to excellent yields (entries 2 to 5). The effect of the isomers on this reaction were performed by using toluic acids (*ortho*, **1i**; *meta*, **1j**; *para*, **1k**); of note are the excellent yields of **6jh** and **6kh** in 89% and 88% (entries 7 and 8). However, the reaction of **1i** having a steric methyl group at the *ortho*-position gave only a moderate yield of the corresponding **6ih** due to the effect of steric hindrance via promotion of catalysis at the surface.



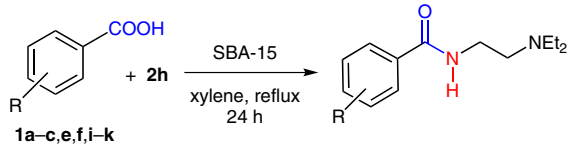
Scheme 3 Preparation of procainamide intermediate (**6dh**) by the direct amidation **1d** with **2h** over SBA-15 catalyst, and the preparation of procainamide (**6**). Numbers in parentheses are the GC yields of **6dh** in recycled experiments.

The amidation of the selected *N*-Boc (*tert*-butoxycarbonyl)-protected amino acid **1l** with **2b** was examined and the result is shown in Scheme 4. The benzyl esters of *N*-Boc-protected amino acids are versatile intermediates, because the benzyl moiety and Boc protecting group allow for facile deprotection to the corresponding acid or amine for connecting further molecular units. The reaction of *N*-Boc-L-Ala-OH with **2b** over SBA-15 gave the corresponding amide **7lb** in 87% isolated yield without formation of by-products (i.e., deprotected compounds), indicating that mesoporous silica catalyst is tolerant for substrates having acid sensitive moiety. Further investigation on valuable amino acid derivatives by this system are in progress in our laboratory.



Scheme 4 Direct amidation of *N*-Boc-Ala-OH (**1l**) with **2b** over SBA-15 catalyst

Table 4 Results of Direct Amidation of Various Carboxylic Acids with *N*,*N*-Diethylethylenediamine (**2h**) in the Presence of SBA-15 Catalyst[a]



Entry	Acid	Product	R	Yield (%)[b]
1	**1a**	**6ah**	H	96 (23)[c]
2	**1b**	**6bh**	4-MeO	88
3[d]	**1c**	**6ch**	4-F	99
4[d]	**1e**	**6eh**	4-F_3C	90
5[d]	**1f**	**6fh**	4-NC	77
6[d]	**1i**	**6ih**	2-Me	65
6[d]	**1j**	**6jh**	3-Me	89
6[d]	**1k**	**6kh**	4-Me	88

[a] Reactions were performed by using acid **1** (3.0 mmol) and amine **2h** (3.0 mmol) in anhydrous *m*-xylene (15 mL) in the presence of the catalyst (0.10 g) under reflux for 24 h.
[b] Isolated yield.
[c] The yield obtained in the absence of the catalyst SBA-15 is given in parentheses.
[d] Reaction was performed under refluxing toluene.

In conclusion, the heterogeneous direct amidation reactions of various combinations of carboxylic acids and amines were examined over mesoporous silica SBA-15 catalyst. The reaction proceeds in moderate to excellent yields, except for aniline, affording the corresponding amides over mesoporous silica SBA-15 catalyst. By demonstrating the synthesis of procainamide and its derivatives, the efficient availability and potentials as a green chemical process are obviously suggested. Mesoporous silica catalyst is a siliceous material having recyclability and reusability, thus it can be an alternative synthetic strategy for amide production with environmentally benign chemistry. Further investigations are ongoing in our laboratory.

Powder X-ray diffraction (XRD) was measured by a Shimadzu XRD-6000 diffractometer with Kα radiation (α = 1.5418 Å). Nitrogen adsorption isotherm measurements were carried out on a Belsorp 28SA apparatus (Bel, Japan). Thermal gravimetric (TGA) and differential thermal (DTA) analyses were carried out by using a Shimadzu DTG-50 analyzer at a ramping rate of 10 K/min under an air stream. ^{1}H and ^{13}C NMR spectra were recorded at 500 and 125 MHz on a JEOL ECA-500 NMR spectrometer. FT-IR spectra were recorded on PerkinElmer Spectrum 100 by KBr technique for solids and neat for liquid compounds. All reagents are commercially available and used without purification.

Direct Amide Synthesis from Carboxylic Acids and Amines Catalyzed by Mesoporous Silica SBA-15; General Procedure

The amidation was carried out in a 50 mL single-necked round-bottomed flask equipped with a Teflon-coated magnetic stirring bar and a Dean–Stark apparatus. Unless otherwise noted, all reactions were performed by using the carboxylic acid **1** (3.0 mmol) and amine **2** (3.0 mmol) in anhydrous toluene (15 mL) in the presence of catalyst (0.5 g) under reflux conditions for the prescribed reaction period (Tables 1–4). After cooling to r.t., the suspended catalyst was removed by filtration and rinsed with $CHCl_3$ (10 mL). The collected small amount of an aliquot filtrate was then analyzed by gas chromatography to determine the yield of amide (Shimadzu 18A, column: Ultra ALLOY$^+$-65) by comparing with an authentic sample. All reactions produce the corresponding amide without any by-product and residual substrate. The remaining filtrate was purified by column chromatography to give the pure product. The filtered catalyst was subjected to calcination under air flow (10 mL/min) at 550 °C for 5 h to evacuate the occluded organic residue.[10]

***N*-Phenylbenzamide (3aa)**

[CAS Reg. No.: 93-98-1]

Yield: 155 mg (26%); white solid; mp 161–163 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.10 (1 H, t, *J* = 7.5 Hz), 7.35 (2 H, t, *J* = 8.0 Hz), 7.53 (2 H, t, *J* = 7.5 Hz), 7.59 (1 H, t, *J* = 7.2 Hz), 7.79 (2 H, d, *J* = 8.0 Hz), 7.96 (2 H, d, *J* = 6.9 Hz), 10.23 (1 H, br s).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 120.3, 123.6, 127.6, 128.3, 128.5, 131.5, 135.0, 139.1, 165.5.

***N*-Benzylbenzamide (3ab)**

[CAS Reg. No.: 1485-70-7]

Yield: 630 mg (>99%); white solid; mp 104–106 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.63 (2 H, d, *J* = 5.7 Hz), 6.55 (1 H, br s), 7.28–7.34 (5 H, m), 7.40 (2 H, t, *J* = 7.5 Hz), 7.48 (2 H, t, *J* = 7.5 Hz), 7.78 (2 H, d, *J* = 8.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.2, 127.1, 127.7, 128.0, 128.7, 128.9, 131.7, 134.5, 138.3, 167.5.

***N*-Hexylbenzamide (3ac)**

[CAS Reg. No.: 4773-75-5]

Yield: 610 mg (>99%); yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.9 Hz), 1.28–1.37 (6 H, m), 1.60 (2 H, quint, *J* = 7.3 Hz), 3.42 (2 H, q, *J* = 6.9 Hz), 6.44 (1 H, br s), 7.39 (2 H, t, *J* = 7.4 Hz), 7.47 (1 H, t, *J* = 6.5 Hz), 7.77 (2 H, d, *J* = 7.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.8, 29.7, 31.6, 40.2, 127.0, 128.6, 131.3, 135.0, 167.7.

***N*-Morpholinylbenzamide (3ad)**

[CAS Reg. No.: 1468-28-6]

Yield: 550 mg (78%); yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.45–3.75 (8 H, br), 7.39–7.42 (5 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 42.6, 48.3, 66.9, 127.1, 128.6, 130.0, 135.4, 170.5.

***N*-Phenyl-4-methoxybenzamide (3ba)**

[CAS Reg. No.: 7465-88-5]

Yield: 160 mg (24%); white solid; mp 172–173 °C.

IR (KBr): 3335, 1635, 1542, 1226, 1159 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.83 (3 H, s), 7.04–7.08 (3 H, m), 7.32 (2 H, t, *J* = 7.8 Hz), 7.75 (2 H, d, *J* = 7.5 Hz), 7.95 (2 H, d, *J* = 9.2 Hz).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 55.4, 113.6, 120.3, 123.4, 127.0, 128.5, 129.6, 139.3, 161.9, 164.9.

***N*-Benzyl-4-methoxybenzamide (3bb)**

[CAS Reg. No.: 7465-87-4]

Yield: 450 mg (63%); white solid; mp 124–125 °C.

IR (KBr): 3266, 1632, 1559, 1254, 1180 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.82 (3 H, s), 4.60 (2 H, d, *J* = 5.7 Hz), 6.53 (1 H, br s), 6.89 (2 H, d, *J* = 9.2 Hz), 7.26–7.33 (5 H, m), 7.75 (2 H, d, *J* = 8.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.1, 55.5, 113.8, 126.8, 127.6, 128.0, 128.8, 128.9, 138.6, 162.3, 167.0.

***N*-Hexyl-4-methoxybenzamide (3bc)**

[CAS Reg. No.: 330467-48-6]

Yield: 525 mg (75%); white solid; mp 59–60 °C.

IR (KBr): 3330, 1633, 1533, 1253, 1107 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (3 H, t, *J* = 6.9 Hz), 1.30–1.37 (6 H, m), 1.59 (2 H, q, *J* = 7.4 Hz), 3.42 (2 H, q, *J* = 6.9 Hz), 3.84 (3 H, s), 6.21 (1 H, br s), 6.90 (2 H, d, *J* = 8.6 Hz), 7.74 (2 H, d, *J* = 9.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.4, 22.7, 26.8, 29.8, 31.6, 40.2, 55.5, 113.8, 127.3, 128.7, 162.1, 167.1.

***N*-Morpholinyl-4-methoxybenzamide (3bd)**

[CAS Reg. No.: 7504-58-7]

Yield: 500 mg (76%); yellow liquid.

IR (neat): 1633, 1114 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.69 (8 H, br s), 3.83 (3 H, s), 6.92 (2 H, d, *J* = 9.2 Hz), 7.39 (2 H, d, *J* = 8.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.0, 55.5, 67.0, 113.9, 127.4, 129.3, 161.0, 170.5.

***N*-Phenyl-4-fluorobenzamide (3ca)**

[CAS Reg. No.: 366-63-2]

Yield: 360 mg (56%); white solid; mp 157–159 °C.

IR (KBr): 3351, 1655, 1531, 1227 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.09 (1 H, t, *J* = 7.5 Hz), 7.35 (4 H, m), 7.75 (2 H, d, *J* = 8.6 Hz), 8.01–8.04 (2 H, m), 10.3 (1 H, br s).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 115.3 (d, $^2J_{C,F}$ = 21.5 Hz), 120.4, 123.7, 128.6, 130.4 (d, $^3J_{C,F}$ = 8.4 Hz), 131.4, 139.0, 164.0 (d, $^1J_{C,F}$ = 246.8 Hz).

***N*-Benzyl-4-fluorobenzamide (3cb)**

[CAS Reg. No.: 725-38-2]

Yield: 595 mg (87%); white solid; mp 144–145 °C.

IR (KBr): 3324, 1642, 1553, 1255 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.61 (2 H, d, *J* = 5.9 Hz), 6.52 (1 H, br s), 7.07–7.10 (2 H, m), 7.29–7.36 (5 H, m), 7.78–7.81 (2 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 44.3, 115.7 (d, $^2J_{C-F}$ = 21.5 Hz), 127.8, 128.0, 128.9, 129.4 (d, $^3J_{C-F}$ = 8.4 Hz), 130.6, 138.2, 164.9 (d, $^1J_{C-F}$ = 250.4 Hz), 166.4.

***N*-Hexyl-4-fluorobenzamide (3cc)**

[CAS Reg. No.: 234449-90-2]

Yield: 418 mg (62%); white solid; mp 43–44 °C.

IR (KBr): 3332, 1635, 1535, 1245 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.89 (3 H, t, *J* = 7.2 Hz), 1.29–1.37 (6 H, m), 1.60 (2 H, quint, *J* = 7.5 Hz), 3.42 (2 H, q, *J* = 6.7 Hz), 6.27 (1 H, br s), 7.07–7.10 (2 H, m), 7.76–7.79 (2 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.8, 29.8, 31.6, 40.3, 115.6 (d, $^2J_{C,F}$ = 22.7 Hz), 129.3 (d, $^3J_{C,F}$ = 8.4 Hz), 164.7 (d, $^1J_{C,F}$ = 249.2 Hz).

***N*-Morpholinyl-4-fluorobenzamide (3cd)**

[CAS Reg. No.: 1978-65-0]

Yield: 555 mg (88%); yellow liquid.

IR (neat): 1634 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.50–3.71 (8 H, br), 7.09–7.12 (2 H, m), 7.41–7.44 (2 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 67.0, 115.8 (d, $^2J_{C,F}$ = 21.5 Hz), 129.6 (d, $^3J_{C,F}$ = 8.4 Hz), 131.4, 163.6 (d, $^1J_{C,F}$ = 248.0 Hz), 169.6.

***N*-Phenyl-4-nitrobenzamide (3da)**

[CAS Reg. No.: 3460-11-5]

Yield: 177 mg (24%); yellow solid; mp 218–219 °C.

IR (KBr): 3322, 1652, 1533, 1519, 1348, 1264 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 7.13 (1 H, t, *J* = 7.5 Hz), 7.37 (2 H, t, *J* = 8.0 Hz), 7.77 (2 H, d, *J* = 7.5 Hz), 8.17 (2 H, d, *J* = 8.6 Hz), 8.36 (2 H, d, *J* = 8.6 Hz), 10.6 (1 H, br s).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 120.5, 123.6, 124.2, 128.7, 129.2, 138.7, 140.6, 149.1, 163.9.

***N*-Benzyl-4-nitrobenzamide (3db)**

[CAS Reg. No.: 2585-26-4]

Yield: 600 mg (78%); white solid; mp 141–142 °C.

IR (KBr): 3309, 1640, 1537, 1514, 1356, 1278 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 4.50 (2 H, d, *J* = 6.3 Hz), 7.23–7.27 (1 H, m), 7.33 (4 H, d, *J* = 4.6 Hz), 8.11 (2 H, d, *J* = 9.2 Hz), 8.32 (2 H, d, *J* = 8.6 Hz), 9.38 (1 H, br t, *J* = 5.7 Hz).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 42.8, 123.6, 126.9, 127.3, 128.4, 128.8, 139.1, 139.9, 149.0, 164.6.

***N*-Hexyl-4-nitrobenzamide (3dc)**

[CAS Reg. No.: 89399-21-3]

Yield: 430 mg (58%); white solid; mp 80–81 °C.

IR (KBr): 3281, 1631, 1537, 1515, 1347, 1283 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 0.85 (3 H, t, *J* = 6.9 Hz), 1.28–1.30 (6 H, m), 1.592 (2 H, quint, *J* = 6.9 Hz), 3.26 (2 H, q, *J* = 6.5 Hz), 8.77 (1 H, br t, *J* = 5.3 Hz).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 13.9, 22.0, 26.1, 28.9, 31.0, 123.5, 128.6, 140.3, 148.9, 164.4.

***N*-Morpholinyl-4-nitrobenzamide (3dd)**

[CAS Reg. No.: 5397-76-2]

Yield: 470 mg (64%); yellow solid; mp 104–105 °C.

IR (KBr): 1636, 1521, 1353 cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 3.26 (2 H, br s), 3.53 (2 H, br s), 3.64–3.65 (4 H, br), 7.68 (2 H, d, *J* = 8.6 Hz), 8.27 (2 H, d, *J* = 8.6 Hz).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 42.0, 47.4, 65.9, 123.8, 141.9, 147.8, 167.2.

***N*-Phenyl-3-phenylpropanamide (4ga)**

[CAS Reg. No.: 3271-81-6]

Yield: 580 mg (86%); white solid; mp 97–98 °C.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.63 (2 H, t, *J* = 7.7 Hz), 2.92 (2 H, t, *J* = 7.7 Hz), 7.02 (1 H, t, *J* = 7.2 Hz), 7.18 (1 H, t, *J* = 6.9 Hz), 7.25–7.30 (6 H, m), 7.58 (2 H, d, *J* = 8.0 Hz), 9.89 (1 H, br s).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 30.8, 37.9, 119.0, 123.0, 125.9, 128.2, 128.3, 128.6, 139.2, 141.2, 170.3.

***N*-Benzyl-3-phenylpropanamide (4gb)**

[CAS Reg. No.: 10264-10-5]

Yield: 600 mg (83%); white solid; mp 80–82 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.48 (2 H, t, *J* = 7.5 Hz), 2.96 (2 H, t, *J* = 7.7 Hz), 4.35 (2 H, d, *J* = 5.7 Hz), 5.88 (1 H, br s), 7.14–7.28 (10 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.8, 38.5, 43.6, 126.3, 127.5, 127.8, 128.5, 128.6, 128.7, 138.3, 140.8, 172.1.

***N*-Hexyl-3-phenylpropanamide (4gc)**

[CAS Reg. No.: 10264-22-9]

Yield: 550 mg (80%); yellow liquid.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.87 (3 H, t, *J* = 6.9 Hz), 1.22–1.29 (6 H, m), 1.40 (2 H, quint, *J* = 7.2 Hz), 2.46 (2 H, t, *J* = 7.7 Hz), 2.96 (2 H, t, *J* = 7.7 Hz), 3.19 (2 H, q, *J* = 6.9 Hz), 5.46 (1 H, br s), 7.18–7.29 (5 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.6, 29.6, 31.6, 31.9, 38.6, 39.7, 126.3, 128.4, 128.6, 141.0, 172.2.

***N*-Morpholinyl-3-phenylpropanamide (4gd)**

[CAS Reg. No.: 17077-46-2]

Yield: 440 mg (80%); yellow liquid.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.61 (2 H, t, *J* = 8.0 Hz), 2.98 (2 H, t, *J* = 7.7 Hz), 3.34 (2 H, t, *J* = 4.9 Hz), 3.50 (2 H, t, *J* = 4.9 Hz), 3.61 (4 H, s), 7.19–7.30 (5 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.5, 34.8, 42.0, 46.0, 66.5, 66.9, 126.3, 128.5, 128.6, 141.1, 170.9.

***N*-(4-Methoxyphenyl)-3-phenylpropanamide (4ge)**

[CAS Reg. No.: 97754-31-9]

Yield: 700 mg (92%); white solid; mp 130–131 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.61 (2 H, t, *J* = 7.7 Hz), 3.02 (2 H, t, *J* = 7.7 Hz), 3.76 (3 H, s), 6.80 (2 H, d, *J* = 9.2 Hz), 7.20–7.31 (8 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.8, 39.3, 55.6, 114.2, 122.1, 126.5, 128.5, 128.7, 131.0, 140.9, 156.6, 170.5.

***N*-(4-Dimethylaminophenyl)-3-phenylpropanamide (4gf)**

[CAS Reg. No.: 349431-89-6]

Yield: 800 mg (99%); light purple solid; mp 157–158 °C.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.60 (2 H, t, *J* = 7.7 Hz), 2.88 (6 H, s), 3.02 (2 H, t, *J* = 7.7 Hz), 6.65 (2 H, d, *J* = 9.2 Hz), 7.12 (1 H, br s), 7.18–7.29 (8 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.9, 39.4, 41.2, 113.1, 122.1, 126.4, 127.7, 128.5, 128.7, 141.0, 148.2, 170.3.

***N*-(4-Fluorophenyl)-3-phenylpropanamide (4gg)**

[CAS Reg. No.: 5298-86-2]

Yield: 700 mg (97%); white solid; mp 116–118 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.63 (2 H, t, *J* = 7.7 Hz), 3.02 (2 H, t, *J* = 7.7 Hz), 6.95 (2 H, d, *J* = 8.6 Hz), 7.20–7.37 (8 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.7, 39.4, 115.7 (d, $^2J_{C,F}$ = 21.5 Hz), 122.0 (d, $^3J_{C,F}$ = 7.2 Hz), 126.6, 128.5, 128.8, 133.8, 140.6, 159.5 (d, $^1J_{C,F}$ = 242.0 Hz), 170.7.

***N*-[2-(Diethylamino)ethyl]-4-aminobenzamide (6, Procainamide)**

[CAS Reg. No.: 51-06-9]

Yield: 223 mg (95%); yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.00 (6 H, t, *J* = 7.2 Hz), 2.52 (4 H, q, *J* = 7.1 Hz), 2.59 (2 H, t, *J* = 6.3 Hz), 3.43 (2 H, q, *J* = 5.7 Hz), 4.35 (2 H, br s), 6.59 (2 H, d, *J* = 8.6 Hz), 7.00 (1 H, br s), 7.59 (2 H, d, *J* = 8.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.8, 37.1, 46.6, 51.3, 113.8, 123.3, 128.4, 149.9, 167.2.

***N*-[2-(Diethylamino)ethyl]benzamide (6ah)**

[CAS Reg. No.: 3690-53-7]

Yield: 637 mg (96%); dark yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.06 (6 H, t, *J* = 7.2 Hz), 2.60 (4 H, q, *J* = 7.1 Hz), 2.69 (2 H, t, *J* = 6.0 Hz), 3.51 (2 H, q, *J* = 5.7 Hz), 7.26 (1 H, br s), 7.40 (2 H, t, *J* = 7.4 Hz), 7.47 (1 H, t, *J* = 7.5 Hz), 7.81 (2 H, d, *J* = 7.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.6, 37.0, 46.7, 51.2, 126.8, 128.3, 131.1, 134.5, 167.2.

***N*-[2-(Diethylamino)ethyl]-4-methoxybenzamide (6bh)**

[CAS Reg. No.: 32276-18-9]

Yield: 665 mg (88%); dark yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (6 H, t, *J* = 7.2 Hz), 2.56 (4 H, q, *J* = 7.1 Hz), 2.64 (2 H, t, *J* = 6.0 Hz), 3.47 (2 H, q, *J* = 5.5 Hz), 3.84 (3 H, s), 6.86 (1 H, br s), 6.92 (2 H, d, *J* = 9.2 Hz), 7.75 (2 H, d, *J* = 8.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.2, 37.3, 46.9, 51.5, 55.5, 113.8, 127.3, 128.7, 162.1, 167.0.

***N*-[2-(Diethylamino)ethyl]-4-fluorobenzamide (6ch)**

[CAS Reg. No.: 120690-13-3]

Yield: 700 mg (99%); dark yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.04 (6 H, t, *J* = 5.0 Hz), 2.60 (4 H, q, *J* = 8.3 Hz), 2.66 (2 H, t, *J* = 7.5 Hz), 3.48 (2 H, q, *J* = 5.0 Hz), 7.08 (2 H, t, *J* = 7.5 Hz), 7.27 (1 H, br s), 7.82 (2 H, m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.8, 37.3, 46.8, 51.3, 115.4 (d, $^2J_{C,F}$ = 21.5 Hz), 129.2 (d, $^3J_{C,F}$ = 8.4 Hz), 130.9, 164.5 (d, $^1J_{C,F}$ = 249.2 Hz), 166.3.

***N*-[2-(Diethylamino)ethyl]-4-nitrobenzamide (6dh)**

[CAS Reg. No.: 1664-52-4]

Yield: 530 mg (95%); yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 (6 H, t, *J* = 7.2 Hz, CH_3), 2.62 (4 H, q, *J* = 7.2 Hz, CH_2), 2.71 (2 H, *J* = 6.0 Hz, CH_2), 3.53 (2 H, *J* = 5.5 Hz, CH_2), 7.93 (1 H, br s, NH), 7.99 (2 H, d, *J* = 8.6 Hz, CH), 8.28 (2 H, d, *J* = 9.2 Hz, CH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.8, 37.4, 46.9, 51.3, 123.8, 140.3, 149.5, 165.2.

***N*-[2-(Diethylamino)ethyl]trifluoromethylbenzamide (6eh)**

[CAS Reg. No.: 827582-99-0]

Yield: 780 mg (90%); dark yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 (6 H, t, *J* = 7.2 Hz), 2.60 (4 H, q, *J* = 7.1 Hz), 2.69 (2 H, t, *J* = 5.7 Hz), 3.50 (2 H, q, *J* = 5.5 Hz), 7.16 (1 H, br s), 7.70 (2 H, d, *J* = 8.1 Hz), 7.89 (2 H, d, *J* = 8.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.0, 37.4, 46.9, 51.2, 123.9 (d, $^1J_{C,F}$ = 270.7 Hz), 125.7 (d, $^3J_{C,F}$ = 3.6 Hz), 127.5, 133.1 (d, $^2J_{C,F}$ = 32.2 Hz), 138.2, 166.1.

***N*-[2-(Diethylamino)ethyl]-4-cyanobenzamide (6fh)**

[CAS Reg. No.: 1016671-87-6]

Yield: 567 mg (77%); dark yellow liquid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.04 (6 H, t, *J* = 7.2 Hz), 2.66 (4 H, q, *J* = 7.1 Hz), 2.73 (2 H, t, *J* = 6.9 Hz), 3.43 (2 H, q, *J* = 6.5 Hz), 7.98 (2 H, d, *J* = 8.0 Hz), 8.02 (2 H, d, *J* = 8.1 Hz), 8.35 (1 H, br s).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 11.2, 37.2, 46.7, 51.0, 113.5, 118.3, 128.0, 132.4, 138.4, 164.8.

***N*-[2-(Diethylamino)ethyl]-2-methylbenzamide (6ih)**

[CAS Reg. No.: 62556-26-7]

Yield: 457 mg (65%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (6 H, t, *J* = 7.1 Hz), 2.46 (3 H, s), 2.57 (4 H, q, *J* = 7.2 Hz), 2.66 (2 H, t, *J* = 5.9 Hz), 3.49 (2 H, q, *J* = 5.7 Hz), 6.59 (1 H, br s), 7.20 (2 H, t, *J* = 8.5 Hz), 7.30 (1 H, m), 7.38 (1 H, d, *J* = 7.3 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.8, 20.0, 37.2, 46.7, 51.5, 125.8, 127.0, 129.8, 131.1, 136.1, 136.8, 170.1.

***N*-[2-(Diethylamino)ethyl]-3-methylbenzamide (6jh)**

[CAS Reg. No.: 93808-02-7]

Yield: 620 mg (89%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (6 H, t, *J* = 7.1 Hz), 2.40 (3 H, s), 2.57 (4 H, q, *J* = 7.0 Hz), 2.65 (2 H, t, *J* = 6.0 Hz), 3.48 (2 H, q, *J* = 5.7 Hz), 6.94 (1 H, br s), 7.31 (2 H, m), 7.54 (1 H, d, *J* = 6.0 Hz), 7.62 (1 H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.1, 21.5, 46.9, 51.5, 55.5, 113.8, 127.3, 128.7, 162.1, 167.0.

***N*-[2-(Diethylamino)ethyl]-4-methylbenzamide (6kh)**

[CAS Reg. No.: 58028-41-4]

Yield: 620 mg (88%); yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (6 H, t, *J* = 7.1 Hz), 2.39 (3 H, s), 2.57 (4 H, q, *J* = 7.2 Hz), 2.65 (2 H, t, *J* = 6.2 Hz), 3.48 (2 H, q, *J* = 5.7 Hz), 6.97 (1 H, br s), 7.23 (2 H, d, *J* = 8.2 Hz), 7.68 (2 H, d, *J* = 8.4 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.1, 21.5, 46.9, 51.5, 55.5, 113.8, 127.3, 128.7, 162.1, 167.0.

***tert*-Butyl (*S*)-[1-(Benzylamino)-1-oxopropan-2-yl]carbamate (7lb)**

[CAS Reg. No.: 51814-55-2]

Yield: 726 mg (87%); white solid; mp 105–107 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (3 H, d, *J* = 6.9 Hz), 1.40 (9 H, s), 4.23 (1 H, br s), 4.42 (2 H, s), 5.20 (1 H, br s), 6.82 (1 H, br s), 7.56 (5 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.5, 28.4, 43.4, 50.2, 80.2, 127.5, 127.6, 128.7, 138.2, 155.7, 172.8.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1379966.

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