Supplementary Information

Boric Acid-Grafted Biochar (BoAB) for the Direct Amidation of Carboxylic Acids and Amines

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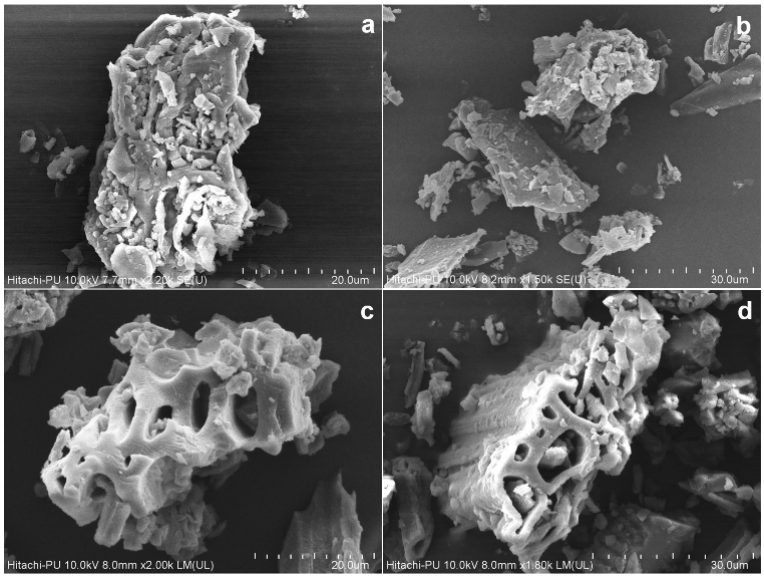


Figure S1 FESEM images of NBC (a, b) and BoAB (c, d) catalysts.

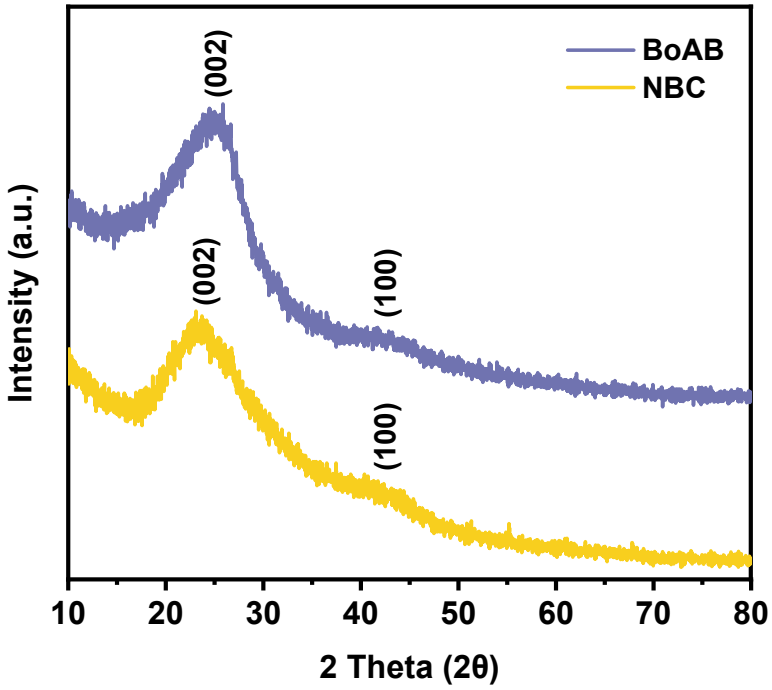


Figure S2 XRD spectra of BoAB and NBC catalysts

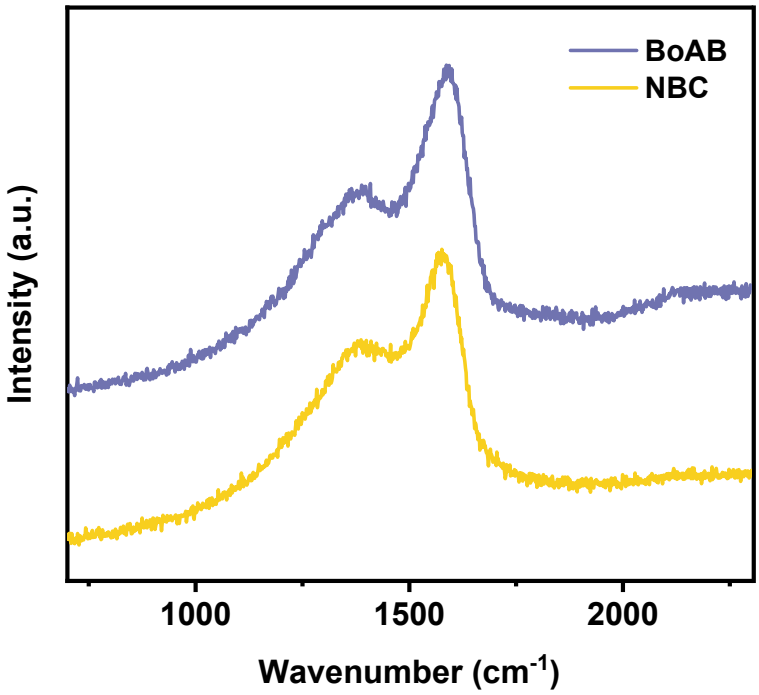


Figure S3 Raman spectra of BoAB and NBC catalysts

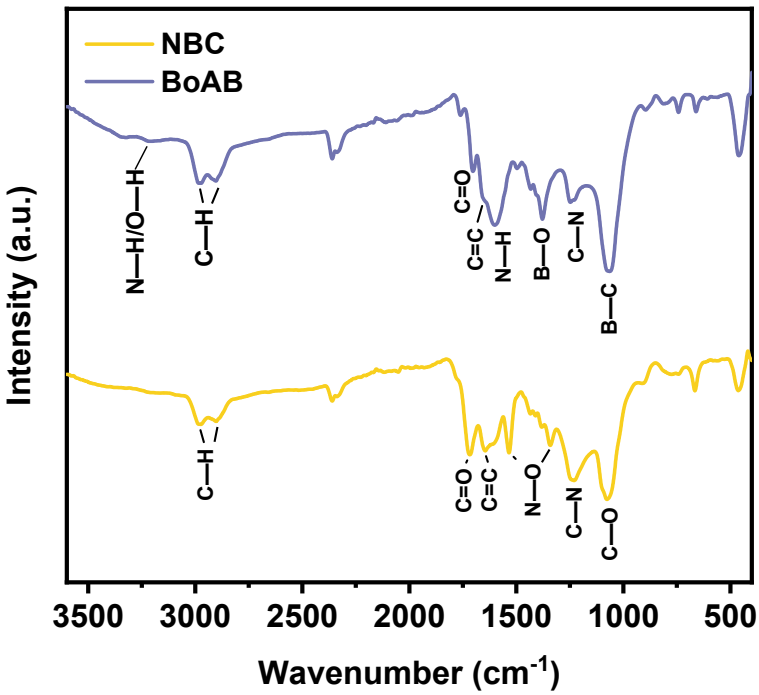


Figure S4 FTIR spectra of BoAB and NBC catalysts

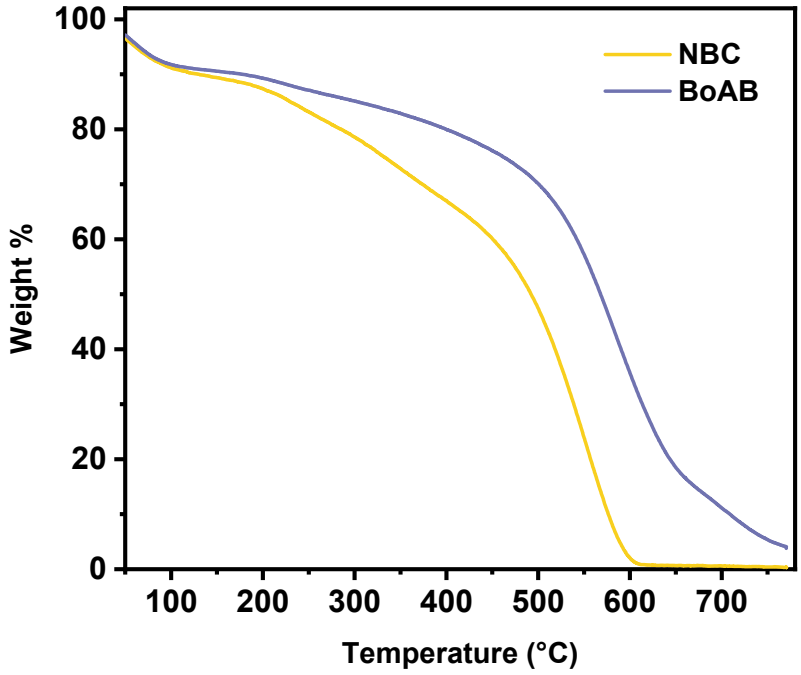


Figure S5 TGA of BoAB and NBC catalysts

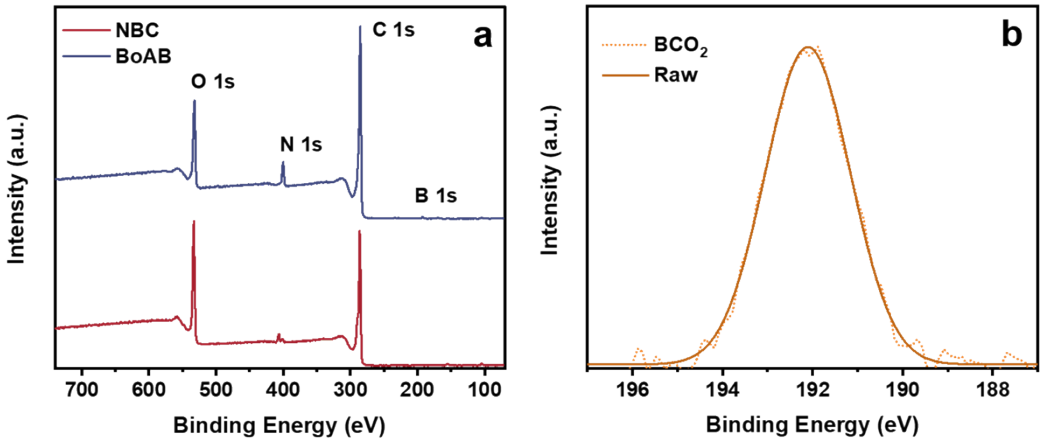


Figure S6 (a) XPS survey spectra of NBC and BoAB, (b) B 1s spectra of BoAB

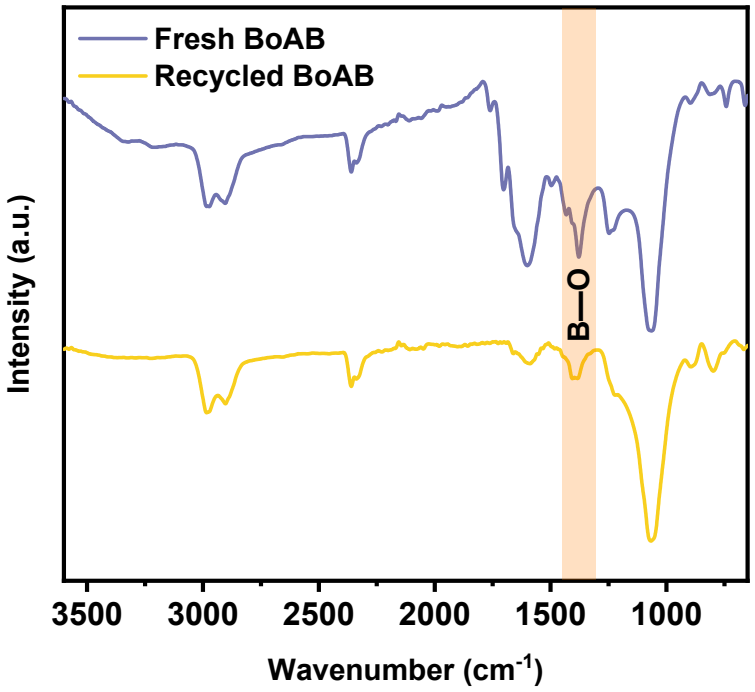


Figure S7 FTIR spectra of fresh and recycled BoAB catalyst

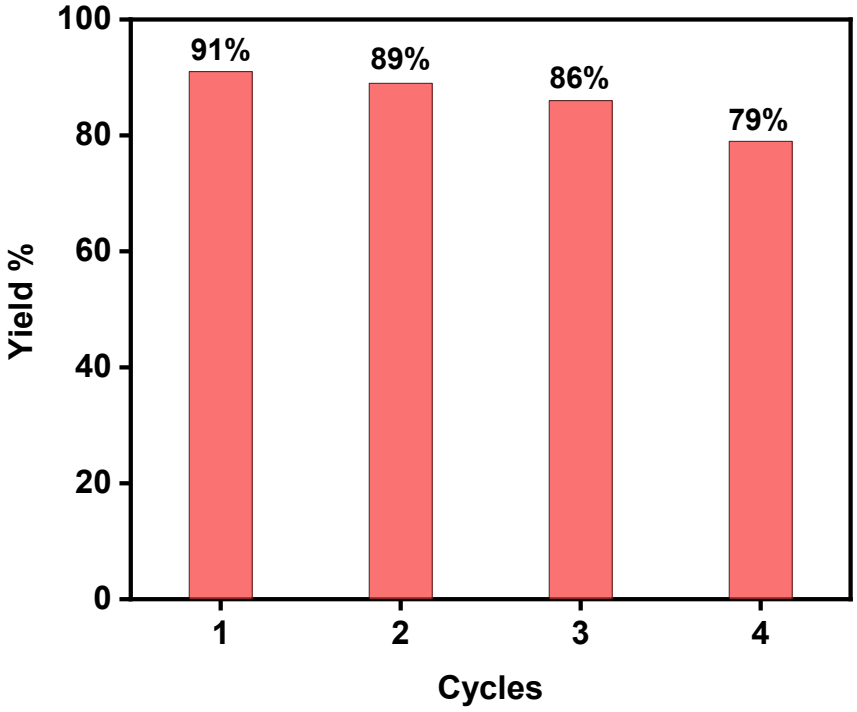


Figure S8 Recyclability study of BoAB for amidation

Table S1 Screening of reaction conditions for the amidation of benzoic acid with N-benzylamine using biochar catalysts

Entry	Catalyst	Solvent	Yield (%)
1	$B(OH)_3$	PhMe	68
2	BC-BA_P	PhMe	30
3	BC-PBA_P	PhMe	32
4	BC-BA	PhMe	44
5	BC-PBA	PhMe	45
6	NBC	PhMe	51
7	BC	PhMe	29
8	BoAB	PhMe	74
9	BoAB	MeCN	25
10	BoAB	DCM	49

Reaction conditions: benzoic acid (1 mmol), benzylamine (1 mmol), catalyst (5 wt. %), solvent (5 mL), Dean-Stark assembly; time: 12 h, temp: 110 °C

Table S2 BET surface area and pore volume estimation from N_2 adsorption/desorption isotherm

BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
65.93	7.36

NMR spectra of the obtained compounds

N-benzylbenzamide (3a)[1] The compound was obtained as white solids with a yield of 91%. R_f = 0.53 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.56 Hz, 1H), 7.52 – 7.27 (m, 5H), 6.51 (s, 1H), 4.64 (d, *J* = 5.67 Hz, 1H).

N-benzyl-4-fluorobenzamide (3b)[2] The compound was obtained as white solids with a yield of 82%. R_f = 0.30 (hexane/ethyl acetate 8:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.8 (m, 2H), 7.3 (m, 5H), 7.0 (t, *J* = 8.6 Hz, 2H), 6.9 (s, 1H), 4.6 (d, *J* = 5.7 Hz, 2H). HRMS (EIQTOF, $[M+H]^+$) calculated for $C_{14}H_{12}FNO$: 230.1049. found:

N-benzyl-2-chlorobenzamide (3c)[3] The compound was obtained as off-white solids with a yield of 88%. R_f =0.45 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.55, 1.72 Hz, 1H), 7.33 – 7.18 (m, 8H), 6.83 (s, 1H), 4.52 (d, *J* = 5.82 Hz, 2H). HRMS (TOF MS ES+, $[M+H]^+$) calculated for $C_{14}H_{12}ClNO$: 246.0726.

N-benzyl-4-chlorobenzamide (3d)[4] The compound was obtained as off-white solids with a yield of 87%. R_f = 0.45 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, 2H), 7.41 – 7.27 (m, 7H), 6.53 (s, 1H), 4.61 (d, *J* = 5.68 Hz, 2H). HRMS (EIQTOF, $[M+H]^+$) calculated for $C_{14}H_{12}ClNO$: 246.1342.

N-benzyl-2,4-dichlorobenzamide (3e)[5] The compound was obtained as off-white solids with a yield of 74%. R_f = 0.45 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.99 Hz, 1H), 7.43 – 7.10 (m, 7H), 6.82 (s, 1H), 4.55 (d, *J* = 5.39 Hz, 2H).

N-benzyl-2-methylbenzamide (3f)[6] The compound was obtained as orange solids with a yield of 85%. R_f = 0.53 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.2 (m, 7H), 7.0 (m, 1H), 7.0 (t, 1H), 6.5 (s, 1H), 4.4 (d, *J* = 5.7 Hz, 2H), 2.2 (s, 3H). HRMS (EIQTOF, $[M+H]^+$) calculated for $C_{15}H_{15}NO$: 226.1992.

N-benzyl-4-methoxybenzamide (3g)[6] The compound was obtained as white solids with a yield of 83%. R_f = 0.33 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 (m, 2H), 7.2 (m, 4H), 7.1 (m, 1H), 6.8 (t, *J* = 5.8 Hz, 1H), 6.7 (m, 2H), 4.4 (d, *J* = 5.8 Hz, 2H), 3.7 (s, 3H). HRMS (EIQTOF, $[M+H]^+$) calculated for $C_{15}H_{15}NO_2$: 242.1873.

N-benzyl-2-mercaptobenzamide (3h) The compound was obtained as orange solids with a yield of 86%. R_f = 0.53 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.0 (d, 1H), 7.5 (t, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.4 (d, *J* = 8.1 Hz, 1H), 7.4 – 7.2 (m, 6H), 5.0 (s, 2H).

N-benzyl-4-nitrobenzamide (3i)[7] The compound was obtained as off-white solids with a yield of 90%. R_f = 0.53 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.82 Hz, 2H), 7.93 (d, *J* = 8.83 Hz, 2H), 7.39 – 7.26

(m, 5H), 6.81 – 6.70 (m, 1H), 4.63 (d, *J* = 5.68 Hz, 2H). HRMS (EIQTOF, $[M+H]^+$) calculated for $C_{14}H_{12}N_2O_3$: 257.0968.

N-Benzylpicolinamide (3j)[8] The compound was obtained as white solids with a yield of 78%. R_f = 0.53 (hexane/ethyl acetate 6:4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.4 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.3 (s, 1H), 8.1 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.7 (td, *J* = 7.7, 1.7 Hz, 1H), 7.3 – 7.2 (m, 6H), 4.6 (d, *J* = 6.1 Hz, 2H).

N-benzylbutyramide (3k)[9] The compound was obtained as off-white solids with a yield of 79%. R_f = 0.53 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.3 – 7.1 (m, 5H), 6.0 (s, 1H), 4.3 (d, *J* = 5.7 Hz, 2H), 2.1 (t, *J* = 7.2 Hz, 2H), 1.6 – 1.5 (m, 2H), 0.9 (t, *J* = 7.4 Hz, 3H).

N-Benzyl-2-(4-isobutylphenyl)propanamide (3l)[10] The compound was obtained as white solids with a yield of 68%. R_f = 0.53 (hexane/ethyl acetate7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.2 – 7.1 (m, 5H), 7.0 – 7.0 (m, 4H), 5.9 (s, 1H), 4.2 (d, *J* = 5.86 Hz, 2H), 3.5 (q, *J* = 7.16 Hz, 1H), 2.3 (d, *J* = 7.20 Hz, 2H), 1.8 – 1.7 (m, 1H), 1.4 (d, *J* = 7.21 Hz, 3H), 0.8 (d, *J* = 6.68 Hz, 6H).

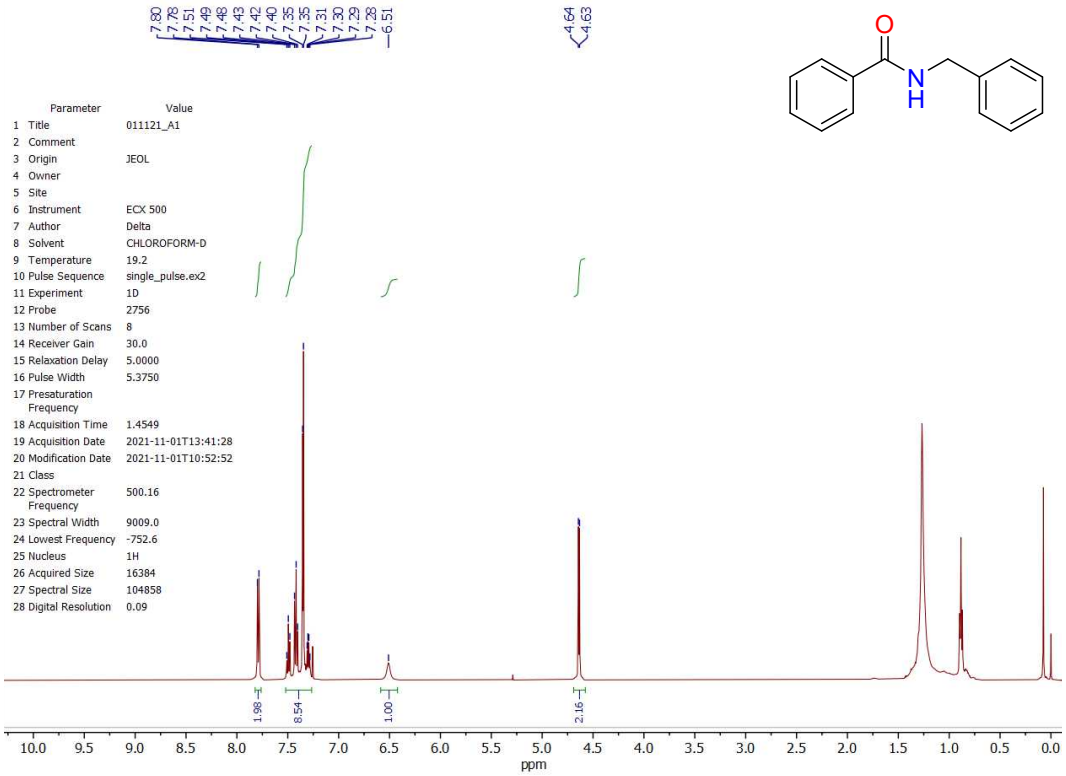
N-benzyl-N-methylbenzamide (5a)[11] The compound was obtained as colorless oil with a yield of 84%. R_f =0.53 (hexane/ethyl acetate 8:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.5 – 7.0 (m, 10H), 4.6 (s, 1H), 4.4 (s, 1H), 2.9 (s, 1H), 2.7 (s, 2H).

N-(4-fluorobenzyl)benzamide (5b)[9] The compound was obtained as off-white solids with a yield of 82%. R_f = 0.53 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.7 – 7.7 (m, 2H), 7.4 – 7.4 (m, 1H), 7.3 – 7.3 (m, 2H), 7.3 – 7.2 (m, 2H), 7.0 – 6.8 (m, 2H), 6.7 (s, 1H), 4.5 (d, *J* = 5.8 Hz, 2H).

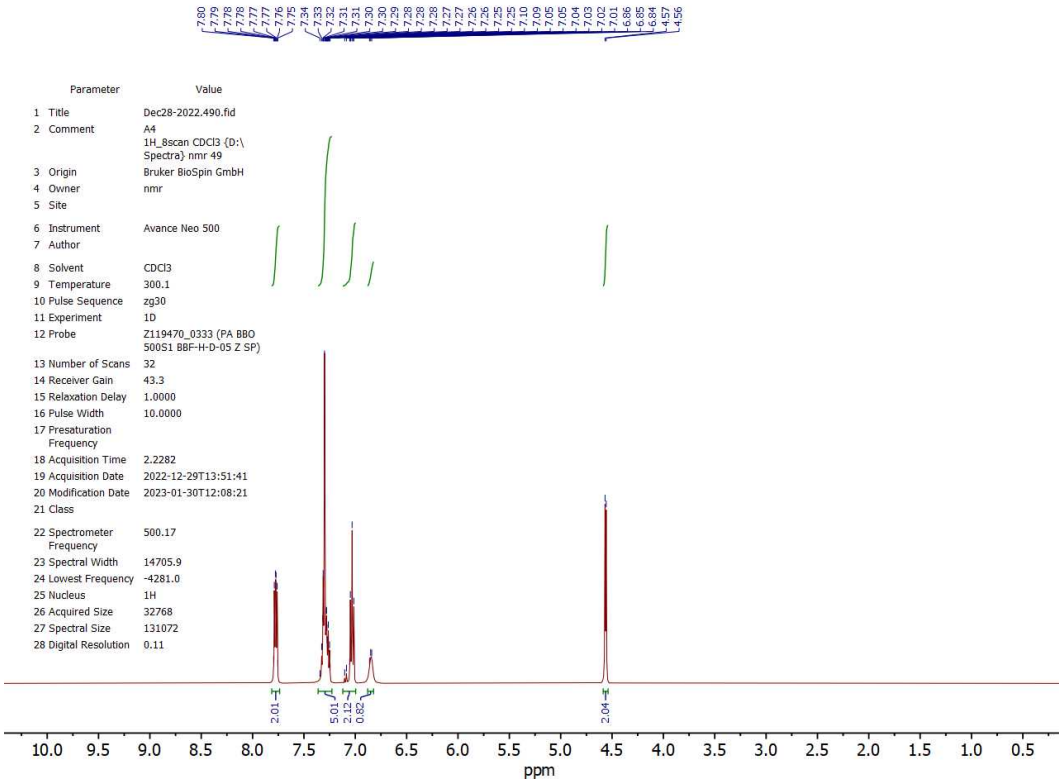
N-(2-chlorobenzyl)benzamide (5c)[12] The compound was obtained as off-orange solids with a yield of 81%. R_f = 0.53 (hexane/ethyl acetate 9:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 6.96 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.39 – 7.30 (m, 4H), 7.20 – 7.15 (m, 2H), 7.04 (s, 1H), 4.65 (d, *J* = 5.98 Hz, 2H).

N-phenylbenzamide (5d)[13] The compound was obtained as off-white solids with a yield of 76%. R_f = 0.53 (hexane/ethyl acetate 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 3H), 7.66 – 7.61 (m, 2H), 7.58 – 7.51 (m, 1H), 7.51 – 7.44 (m, 2H), 7.36 (d, *J* = 7.48 Hz, 2H), 7.15 (t, *J* = 7.38 Hz, 1H).

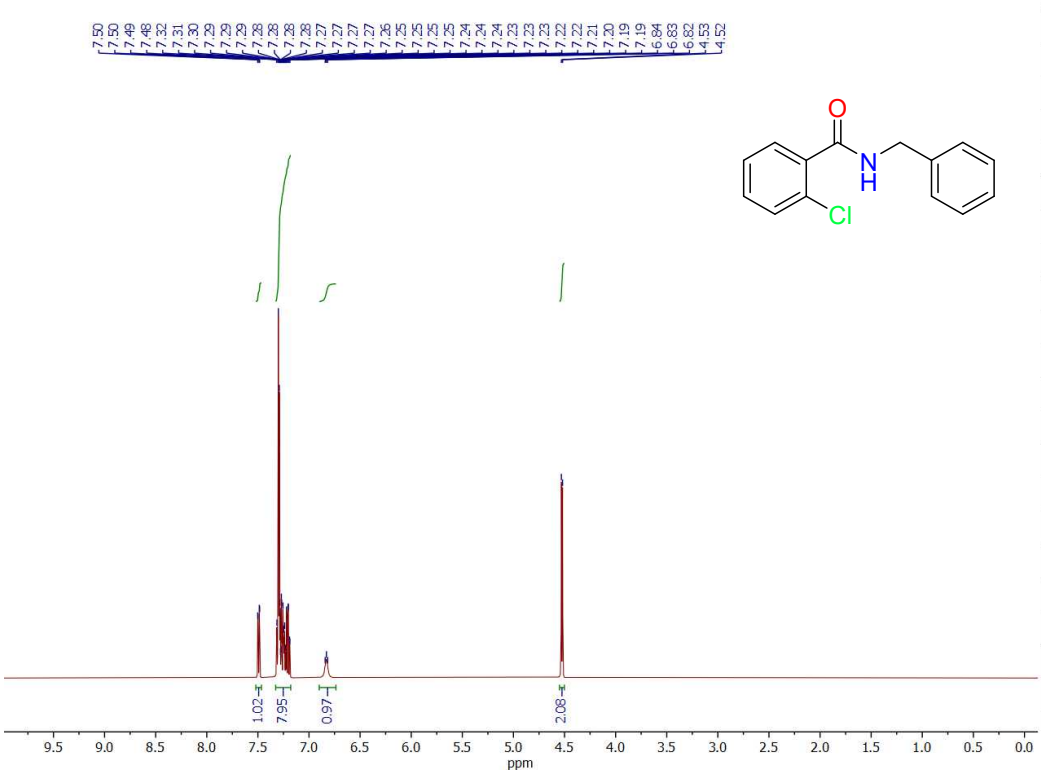
N-benzylbenzamide (3a)



N-benzyl-4-fluorobenzamide (3b)



N-benzyl-2-chlorobenzamide (3c)



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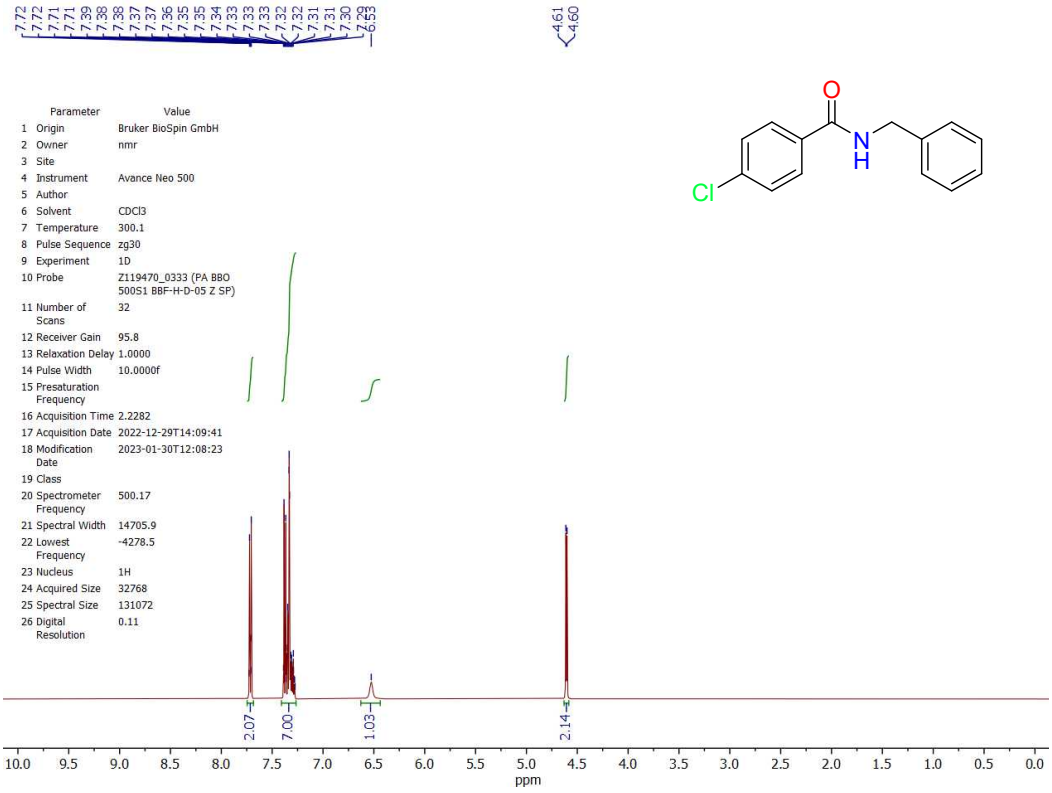
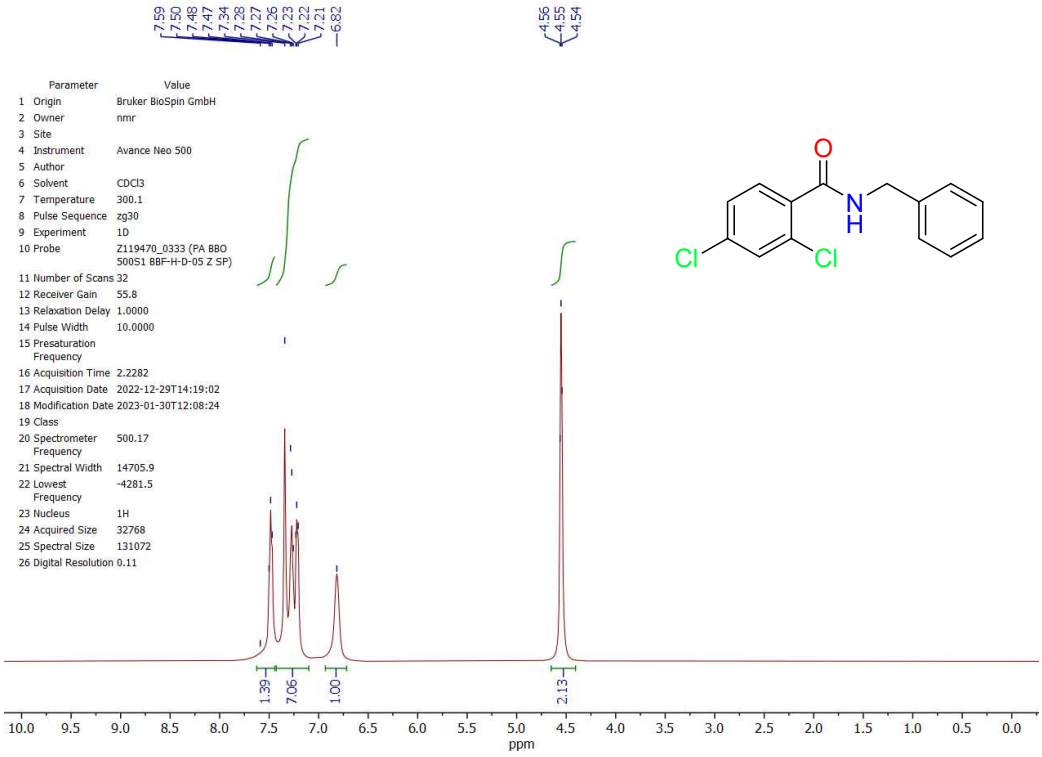


N-benzyl-2,4-dichlorobenzamide (3e)



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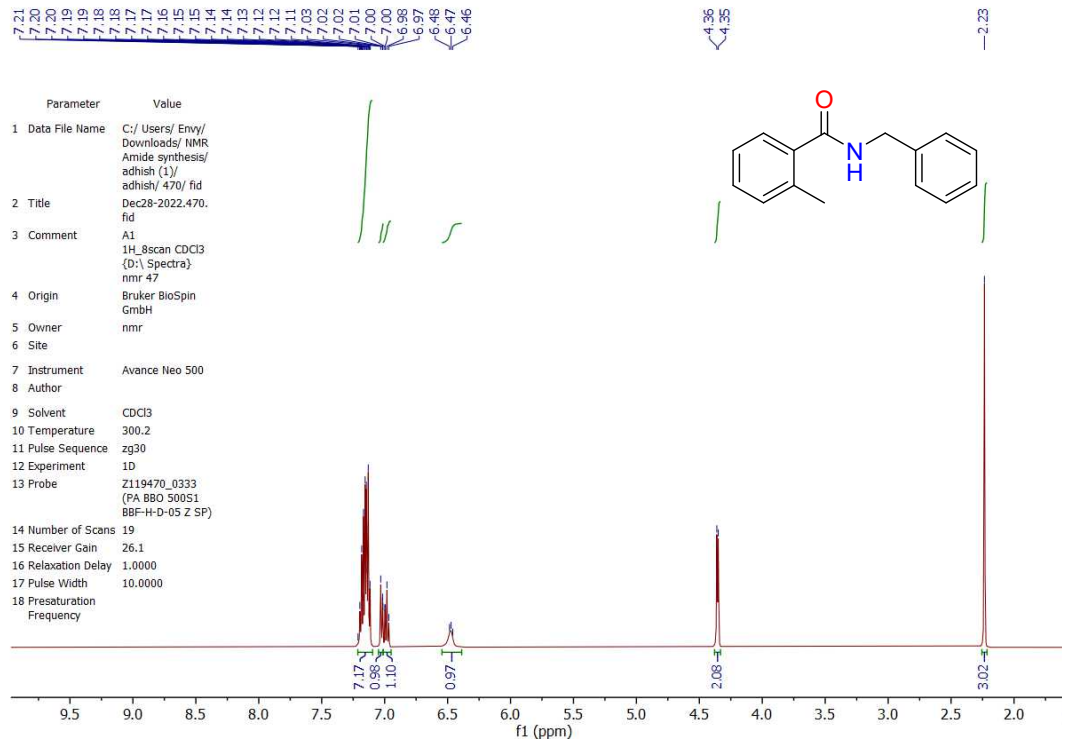

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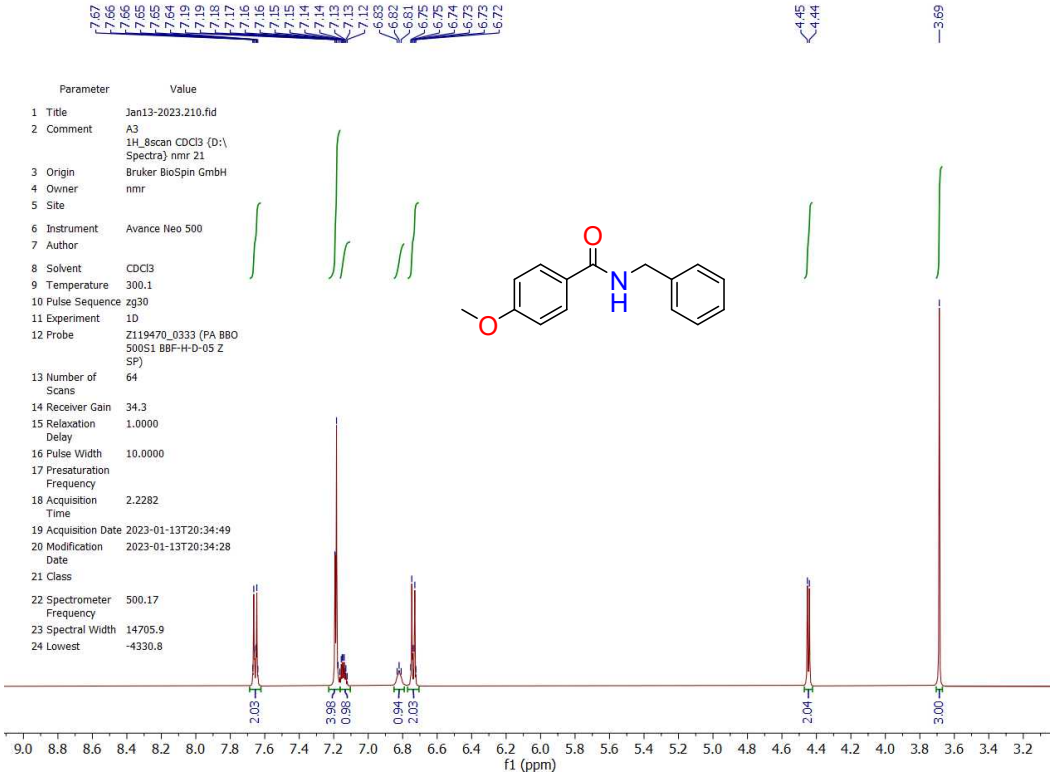

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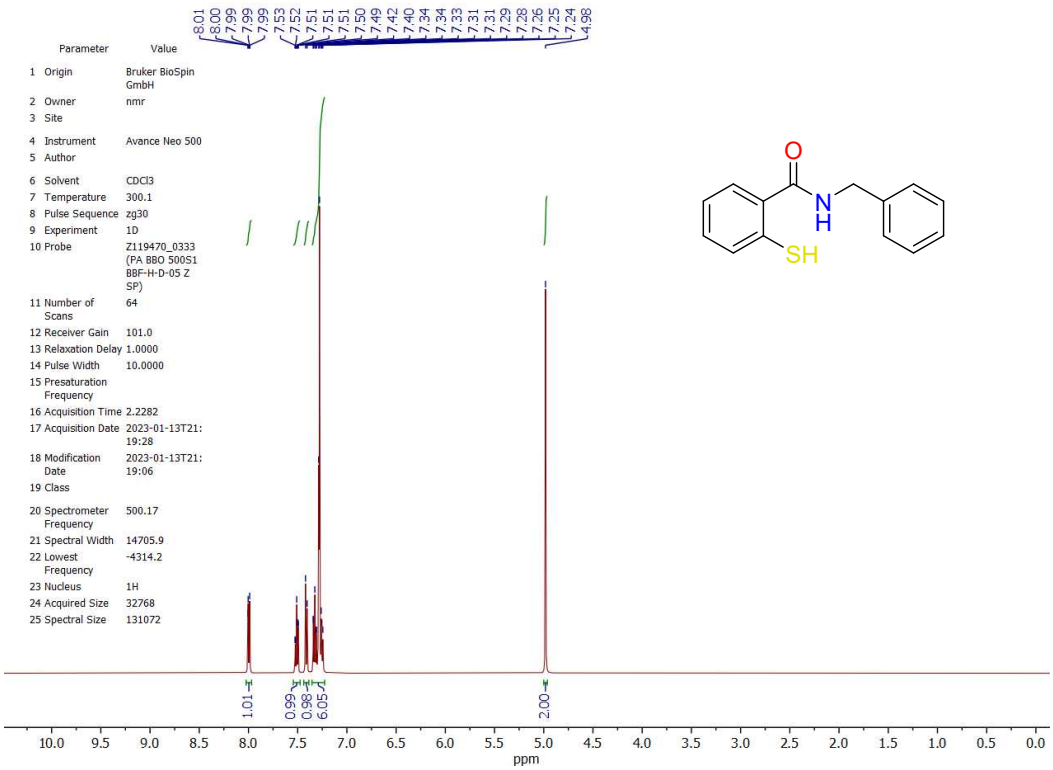

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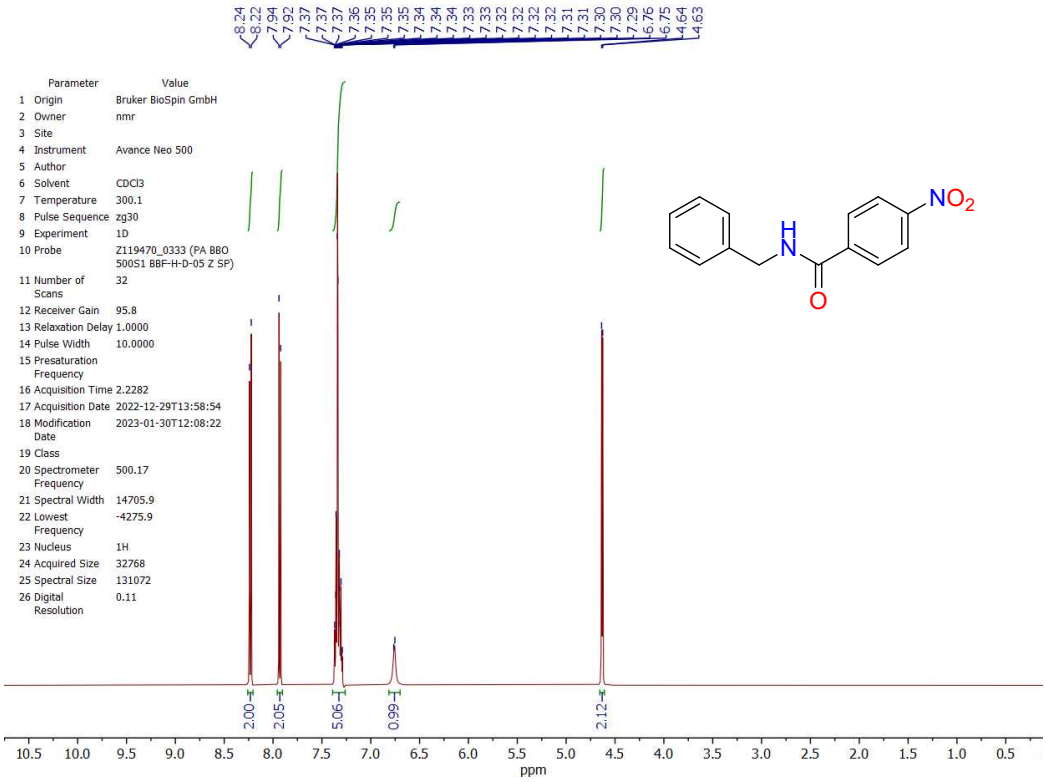

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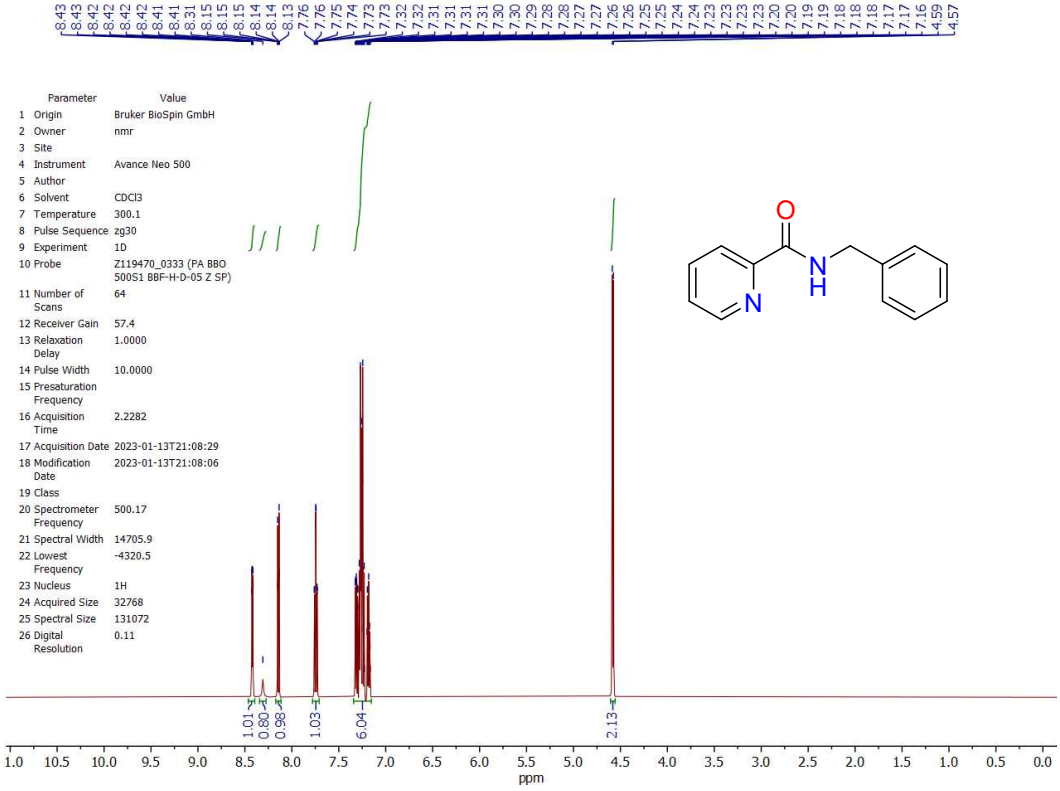
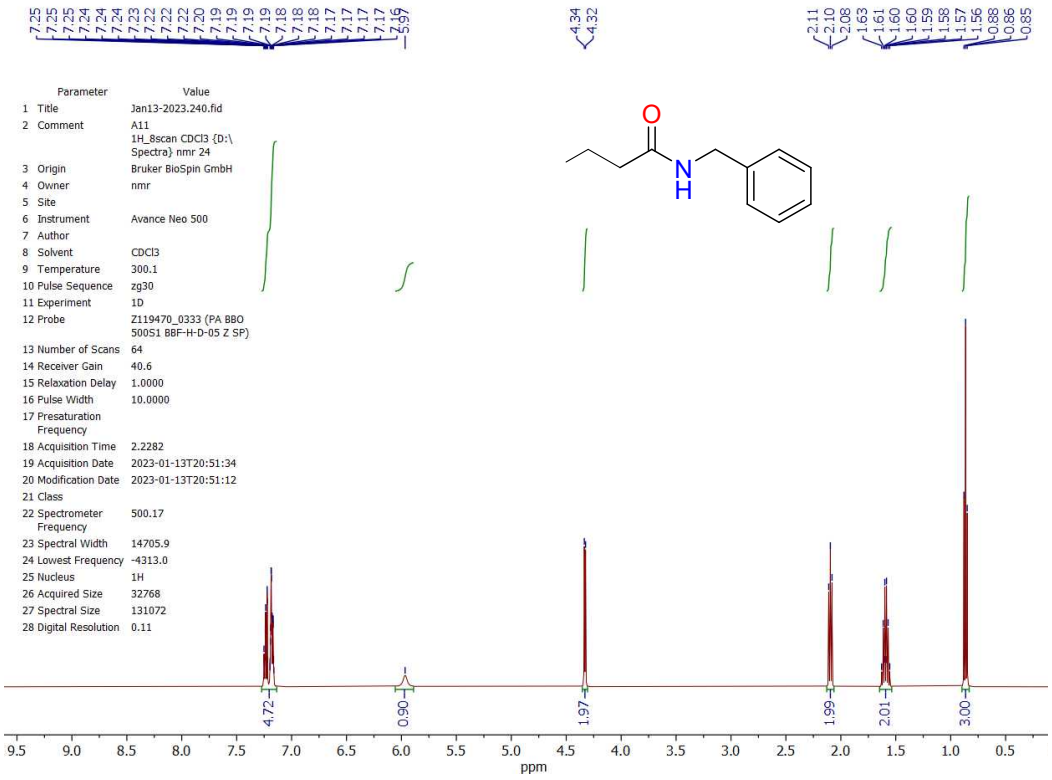
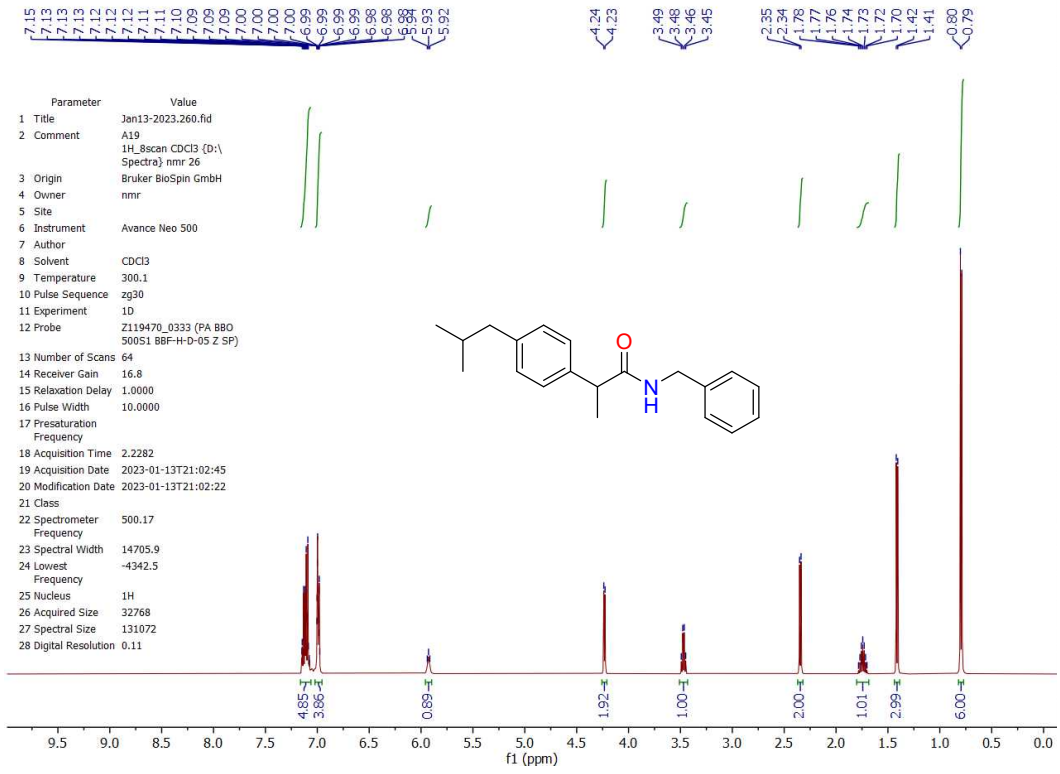


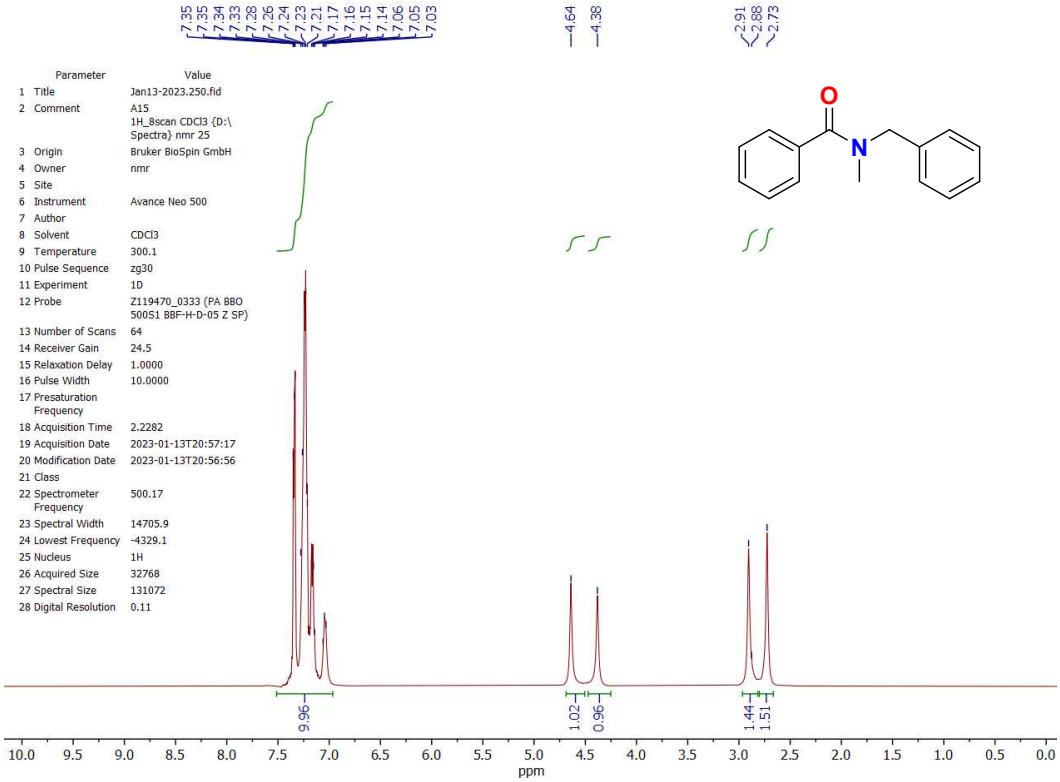
N-benzylbutyramide (3k)



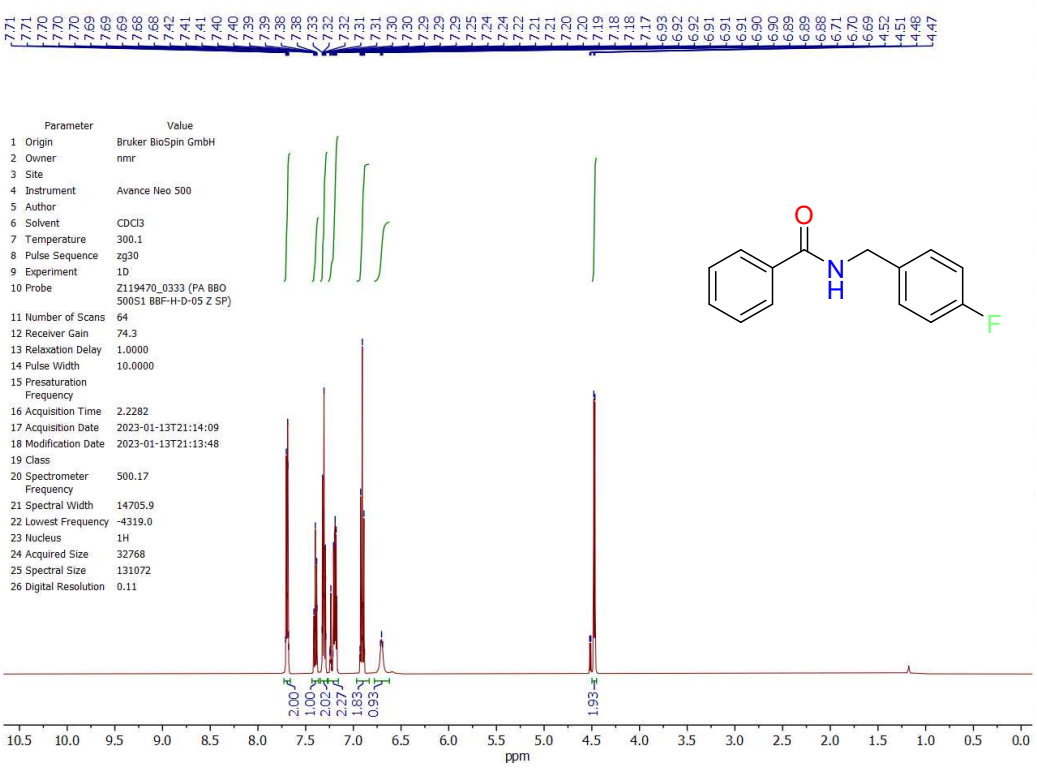
N-Benzyl-2-(4-isobutylphenyl)propanamide (3l)



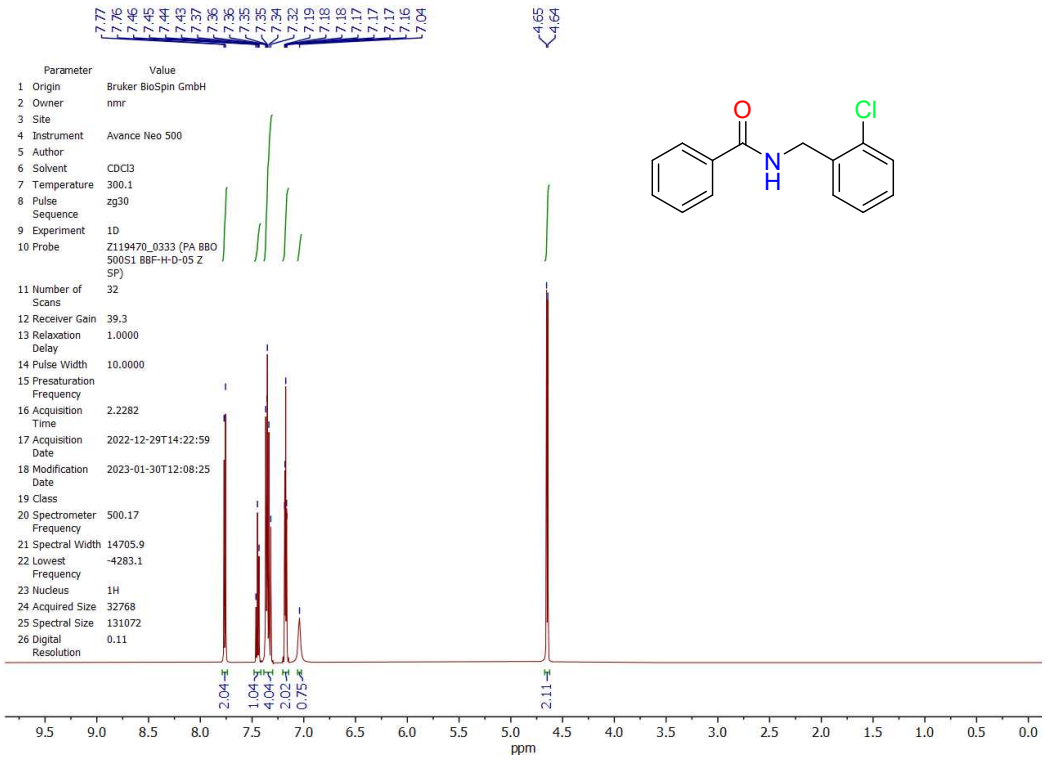
N-benzyl-N-methylbenzamide (5a)



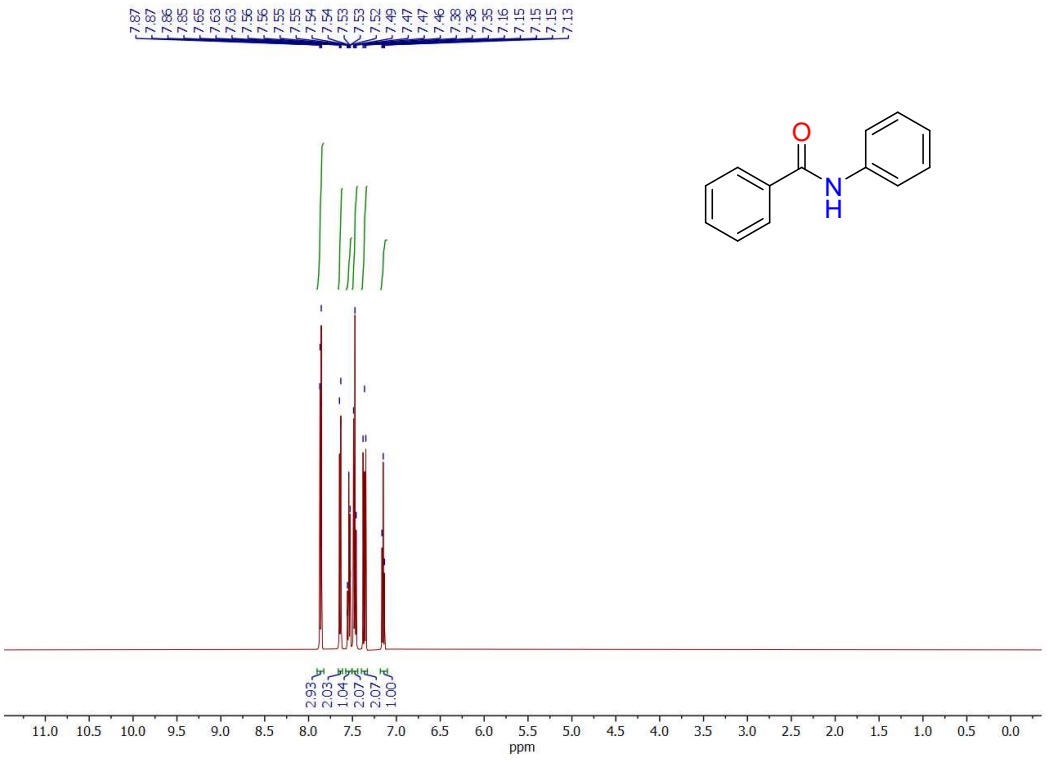
N-(4-fluorobenzyl)benzamide (5b)



N-(2-chlorobenzyl)benzamide (5c)



N-phenylbenzamide (5d)



References

1 A. Ojeda-Porras, A. Hernández-Santana and D. Gamba-Sánchez, *Green Chem.*, 2015, **17**, 3157–3163.

2 C. J. Smedley, A. S. Barrow, C. Spiteri, M.-C. Giel, P. Sharma and J. E. Moses, *Chem. Eur. J.*, 2017, **23**, 9990–9995.

3 P. Thansandote, D. G. Hulcoop, M. Langer and M. Lautens, *J. Org. Chem.*, 2009, **74**, 1673–1678.

4 B. N. Atkinson, A. Rosie Chhatwal, H. V. Lomax, J. W. Walton and J. M. J. Williams, *Chem. Commun.*, 2012, **48**, 11626–11628.

5 N. Iqbal and E. J. Cho, *J. Org. Chem.*, 2016, **81**, 1905–1911.

6 Z. Huang, J. E. Reilly and R. N. Buckle, *Synlett*, 2007, **2007**, 1026–1030.

7 S. Jamalifard, J. Mokhtari and Z. Mirjafary, *RSC Adv.*, 2019, **9**, 22749–22754.

8 H. Morimoto, R. Fujiwara, Y. Shimizu, K. Morisaki and T. Ohshima, *Org. Lett.*, 2014, **16**, 2018–2021.

9 N. Wang, X. Zou, J. Ma and F. Li, *Chem. Commun.*, 2014, **50**, 8303–8305.

10 M. T. Sabatini, L. T. Boulton and T. D. Sheppard, *Sci. Adv.*, 2017, **3**, e1701028.

11 Z. Lu, G. P. A. Yap and D. S. Richeson, *Organometallics*, 2001, **20**, 706–712.

12 P. Xu, F.-S. Han and Y.-H. Wang, *Adv. Synth. Catal.*, 2015, **357**, 3441–3446.

13 A. Kumar and A. K. Bishnoi, *RSC Adv.*, 2014, **4**, 41631–41635.