Electronic Supplementary Information for:

Simple catalyst system involving boric acid and additives for the direct formation of amides from carboxylic acids and amines

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General.

All reagents and solvents were obtained from commercial suppliers and used without further purification. Thin-layer chromatography was carried out on 0.2-mm silica gel plates, with spots detected by UV light (254 nm). Column chromatography was performed on pore size 60 Å, 230-400 mesh silica gel.

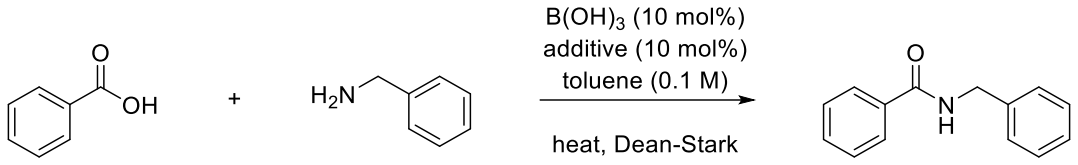
NMR spectra were recorded on a 400 MHz ECA-400 JEOL spectrometer. For ^{1}H NMR spectra, tetramethylsilane (0.00 ppm) or residual solvent signals ($CDCl_3$: 7.26 ppm, acetone-d_6: 2.05 ppm, DMSO-d_6: 2.50 ppm) were used as internal standard. Chemical shifts (δ) values are reported in parts per million (ppm) downfield from TMS and coupling constants *J* are reported in hertz (Hz). The following abbreviations are used: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), non (nonet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), br (broad). DEPTQ (^{13}C) NMR spectra were referenced to solvent signal ($^{13}CDCl_3$: 77.2 ppm, acetone-d_6: 29.8 ppm, DMSO-d_6: 39.5 ppm).

FT-IR spectra were recorded using a diamond attenuated total reflectance PerkinElmer UATR Two spectrometer and absorptions are reported in terms of wavenumbers ($\tilde{\nu}$, cm^{-1}).

HRMS data were obtained on a Waters Xevo G2 XS quadrupole-time of flight mass spectrometer equipped with an Atmospheric Solids Analysis Probe (ASAP). The corona pin was set to 3.0 mA and spectra were collected in continuum mode for 2 min with a solution of Leucine Enkephalin providing lockmass correction every 30 s.

Amide products **3**[1], **7**[2], **9**[3], **11**[4], **12**[5], **13**[6], **14**[7] and **15**[5] have previously been characterized.

Catalytic amidation screening procedure on benchmark reaction



6 **2** **7**

Benzoic acid **6** (0.100 g, 0.819 mmol) and boric acid (0.0051 g, 0.082 mmol, 10 mol%) were added to a flame-dried 25 mL round bottom flask with a stir bar under an inert atmosphere of N_2. When applicable, an additive (0.082 mmol, 10 mol%) was added. Toluene (8.2 mL, 0.1 M) was then added and the mixture was stirred for 10-20 minutes at room temperature. Benzylamine **2** (0.090 mL, 0.82 mmol) was added and the reaction flask was attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 °C temperature-controlled oil bath. A sample (0.4 mL) was taken out of the reaction mixture with a syringe after 2 and, when the 2-hour result warranted it, 4 hours of reflux. The solvent was removed under vacuum, and $CDCl_3$ (0.5 mL) was added. The samples were analyzed by ^1H NMR spectroscopy, using a relaxation delay of 20 s. The reactant-to-product ratio was calculated using the integrations of the following resonances: benzylamine **2** CH_2 singlet at ca. 3.9 ppm, and *N*-benzylbenzamide **7** CH_2 doublet at ca. 4.6 ppm. Ratios reported in Table 1 and Table S1 represent the average of at least two runs.

Table S1. Effect of Additives on the Boric Acid-Catalyzed Reaction Between Benzoic Acid and Benzylamine[a]

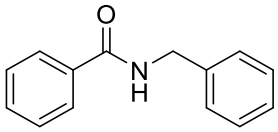
Entry	Additive	2/7 after 2 hours	2/7 after 4 hours
1	no catalyst	179.5:1	87.5:1
2	only boric acid (10 mol%), no additive	24.4:1	6.4:1
3	only boric acid (20 mol%), no additive	7.4:1	2.6:1
BRONSTED ACIDS			
4	phosphoric acid	156.1:1	
5	phosphorous acid	120.6:1	
6	phenylphosphonic acid	38.5:1	
7	phenylphosphinic acid	4.2:1	1.1:1
8	*p*-toluenesulfonic acid monohydrate	16.8:1	
9	sulfuric acid	1.4:1	1:3.5
10	sulfuric acid alone, no boric acid	144.3:1	
H-BONDING THIOUREA			
11	*N*,*N*'-bis[3,5-bis(trifluoromethyl)phenyl]-thiourea	16.3:1	6.8:1
AMINES, PYRIDINES, IMIDAZOLES			
12	*N*,*N*-diisopropylethylamine	42.4:1	12.8:1
13	*N*,*N*-dimethylhexylamine	58.9:1	17.2:1
14	pyridine	12.9:1	1.8:1
15	2,4,6-trimethylpyridine	50.1:1	14.0:1
16	4-dimethylaminopyridine	19.0:1	4.9:1
17	imidazole	128.8:1	26.9:1
18	1-methyl imidazole	49.7:1	
19	1,8-diazabicyclo[5.4.0]undec-7-ene	55.7:1	12.4:1
AMMONIUM AND PYRIDINIUM SALTS			
20	triethylammonium chloride	44.4:1	3.5:1
21	pyridinium chloride	from 1.8:1 to 86:1	from 55:1 to 1:3.4
22	pyridinium *p*-toluenesulfonate	from 3.7:1 to 30:1	from 9.6:1 to 1.1:1
CINCHONA ALKALOIDS			
23	quinine	12.5:1	3.4:1
24	quinine hydrochloride dihydrate	1.7:1	1:4.5
25	quinidine	4.4:1	1.4:1
26	cinchonine	2.5:1	1:1.4
27	cinchonidine	2.5:1	1:1.2
DIAMINES			
28	*N*,*N*,*N*',*N*'-teramethylethylenediamine	69.7:1	27.9:1
29	*N*,*N*,*N*',*N*'-tetramethyl-1,3-diaminopropane	67.0:1	
30	2,2'-bipyridine	68.1:1	
ETHYLENE GLYCOL, CATECHOLS AND OXALIC ACID			
31	ethylene glycol	13.1:1	4.1:1
32	catechol	98.8:1	
33	4-*tert*-butylcatechol	174.5:1	
34	oxalic acid	81.3:1	
ACTIVE OH/SH COMPOUNDS			
35	2-nitrophenol	94.5:1	
36	4-nitrophenol	31.2:1	
37	pentafluorophenol	98.5:1	31.4:1

38	2-hydroxypyridine	17.0:1	8.0:1
39	5-nitro-2-hydroxypyridine	16.2:1	8.4:1
40	4-hydroxypyridine	8.0:1	2.7:1
41	8-hydroxyquinoline	23.9:1	5.8:1
42	2-hydroxypyrimidine hydrochloride	9.4:1	2.5:1
43	1-hydroxybenzotriazole monohydrate	1.5:1	1:3.3
44	*N*-hydroxysuccinimide	1.5:1	1:1.9
45	2-mercaptopyridine	16.1:1	2.5:1
46	2-mercaptopyrimidine	44.9:1	
AMINE *N*-OXIDES			
47	pyridine *N*-oxide	74.1:1	36.9:1
48	2-methylpyridine *N*-oxide	82.8:1	13.9:1
49	4-(dimethylamino)pyridine *N*-oxide hydrate	49.6:1	
50	4-methylmorpholine *N*-oxide	38.4:1	20.8:1
51	2-mercaptopyridine *N*-oxide sodium salt	6.9:1	2.3:1
OTHERS			
52	triphenylphosphine	74.8:1	
53	trimethyl phosphite	6.9:1	4.1:1
54	triethyl phosphite	6.2:1	3.0:1
55	triphenyl phosphite	4.6:1	3.7:1
56	hydroxylamine hydrochloride	166.0:1	
57	sodium iodide	22.0:1	
AMINO ALCOHOLS			
58	2-dimethylaminoethanol	1:1.3	1:6.3
59	2-diethylaminoethanol	1:1.2	1:6.8
60	2-diethylaminoethanol alone, no boric acid	211.6:1	
61	2-diethylaminoethanol (5 mol%)	17.4:1	2.8:1
62	2-diethylaminoethanol (20 mol%)	1:1.5	1:5.8
63	2-(dibutylamino)ethanol	16.7:1	3.5:1
64	2-(diisopropylamino)ethanol	43.8:1	9.8:1
65	1-dimethylamino-2-propanol	5.2:1	1.3:1
66	2-morpholinoethanol	6.9:1	1.6:1
67	*N*-benzyl-*N*-methyl ethanolamine	14.3:1	3.2:1
68	*N*-methyldiethanolamine	131.8:1	68.9:1
69	*N*-phenyldiethanolamine	115.9:1	
70	triethanolamine	164.0:1	
71	*N*-benzylethanolamine	76.1:1	
72	2-{[2-(dimethylamino)ethyl]methylamino}ethanol	1:1.4	1:5.8
73	3-(dimethylamino)-1,2-propanediol	18.2:1	6.8:1
74	3-dimethylamino-1-propanol	1.2:1	1:4.3
75	2-[2-(dimethylamino)ethoxy]ethanol	3.8:1	1:1.3

[a] Reaction conditions: Benzoic acid (8.2 mmol), benzylamine (8.2 mmol), boric acid (10 mol%), additive (10 mol%), toluene (0.1 M), Dean-Stark, 150 °C. Ratios, which were averaged over at least two runs, were determined by ^{1}H NMR spectroscopy.

Gram-scale catalytic amidation procedures

***N*-Benzyl-benzamide (7)**



Gram-scale synthesis without additive

Benzoic acid (0.999 g, 8.18 mmol) and boric acid (0.0503 g, 0.814 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then benzylamine (0.90 mL, 8.2 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (3:7 ethyl acetate/hexanes), which yielded a white solid (0.590 g, 34%).

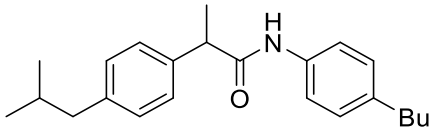
Gram-scale synthesis with sulfuric acid

Benzoic acid (1.00 g, 8.19 mmol) and boric acid (0.051 g, 0.82 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and sulfuric acid (0.040 mL, 0.82 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then benzylamine (0.90 mL, 8.2 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (3:7 ethyl acetate/hexanes), which yielded a white solid (0.965 g, 56%).

Gram-scale synthesis with 2-diethylaminoethanol

Benzoic acid (1.005 g, 8.230 mmol) and boric acid (0.0522 g, 0.844 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylaminoethanol (0.110 mL, 0.830 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then benzylamine (0.89 mL, 8.2 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ^oC oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (3:7 ethyl acetate/hexanes), which yielded a white solid (1.495 g, 86%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.49 (tt, J = 7.4, 1.4 Hz, 1H), 7,44-7.38 (m, 2H), 7.37-7.25 (m, 5H), 6.39 (br s, 1H), 4.65 (d, J = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 167.6, 138.4, 134.5, 131.7, 128.9, 128.7, 128.1, 127.8, 127.1, 44.3. IR (cm^{-1}, solid) 3321, 3059, 3029, 2928, 1818.54, 1715, 1638, 1601, 1577, 1540, 1497, 1489, 1452, 1418, 1362, 1312, 1299, 1258, 1185, 1151, 1075, 1054, 1027, 1001, 990, 928, 902, 849, 821. HRMS for $C_{14}H_{14}NO^+$ ($M+H^+$), calcd: 212.1070, found: 212.1074.

***N*-(4-Butylphenyl)-2-(4-isobutylphenyl)propanamide (8)**



Gram-scale synthesis without additive

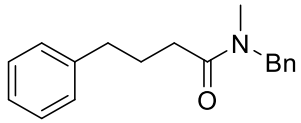
Ibuprofen (1.692 g, 8.202 mmol) and boric acid (0.0534 g, 0.864 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then 4-butylaniline (1.29 mL, 8.17 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ^oC oil bath to reflux for 24 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (12.5% ethyl acetate/hexanes), which yielded a light orange solid (1.240 g, 48%).

Gram-scale synthesis with 2-diethylaminoethanol

Ibuprofen (1.687 g, 8.177 mmol) and boric acid (0.0512 g, 0.828 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylaminoethanol (0.110 mL, 0.830 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then 4-butylaniline (1.29 mL, 8.17 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ^oC oil bath to reflux for 24 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (12.5% ethyl acetate/hexanes), which yielded a light orange solid (1.852 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 7.5 Hz, 2H), 7.17 (brs, 1H), 7.14 (d, J = 7.5 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 3.69 (q, J = 7.2 Hz, 1H), 2.54 (t, J = 7.6 Hz, 2H), 2.47 (d, J = 7.2 Hz, 2H), 1.86 (non, J = 6.8 Hz, 1H), 1.58 (d, J = 7.2 Hz, 3H), 1.54 (quint, J = 7.6 Hz, 2H), 1.31 (sext, J = 7.6 Hz, 2H), 0.91 (d, J = 6.8 Hz, 6H), 0.90 (t, J

= 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 172.7, 141.1, 140.0, 138.3, 135.7, 129.9, 128.9, 127.5, 119.8, 47.7, 45.1, 35.1, 33.8, 30.3, 22.5, 22.3, 18.6, 14.0. IR (cm^{-1}, solid) 3301, 3193, 3127, 2956, 2924, 2868, 1658, 1603, 1531, 1513, 1459, 1410, 1374, 1356, 1303, 1245, 1174, 1118, 1069, 1023, 1006, 917, 880, 829. HRMS for $C_{23}H_{32}NO^+$ ($M+H^+$), calcd: 338.2478, found: 338.2472.

***N*-Benzyl-*N*-methyl-4-phenylbutanamide (9)**



Gram-scale synthesis without additive

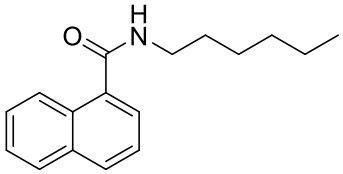
4-Phenylbutyric acid (1.365 g, 8.313 mmol) and boric acid (0.054 g, 0.87 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then *N*,*N*-benzylmethylamine (1.05 mL, 8.14 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 6 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (44:56 ethyl acetate:hexanes) which yielded (0.88 g, 40%).

Gram-scale synthesis with 2-diethylaminoethanol

4-Phenylbutyric acid (1.371 g, 8.350 mmol) and boric acid (0.0517 g, 0.836 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylaminoethanol (0.110 mL, 0.830 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then *N*,*N*-benzylmethylamine (1.05 mL, 8.14 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 6 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (44:56 ethyl acetate:hexanes) which yielded a light yellow oil (1.552 g, 70%). ^{1}H NMR, 2 rotamers (400 MHz, $CDCl_3$) δ 7.37-7.08 (m, 10H), 4.58 (s, 1.2H), 4.44 (s, 0.8H), 2.93 (s, 1.2H), 2.82 (s, 1.8H), 2.71 (t, J = 7.6 Hz, 1.2H), 2.65 (t, J = 7.6 Hz, 0.8H), 2.36 (t, J = 7.6 Hz, 2H), 2.06-1.96 (m, 2H). ^{13}C NMR, 2 rotamers (100 MHz, $CDCl_3$, ppm) δ = 173.3, 172.9, 141.9, 141.9, 137.7, 136.9, 129.0, 128.7, 128.7, 128.6, 128.5, 128.5,

128.2, 127.7, 127.4, 126.5, 126.0, 126.0, 53.5, 50.9, 35.5, 35.4, 34.9, 34.1, 32.8, 32.3, 26.9, 26.7. IR (cm^{-1}, neat): 3061, 3026, 2927, 1639, 1603, 1495, 1452, 1400, 1284, 1262, 1205, 1155, 1115, 1077, 1028, 986, 946, 910, 806. HRMS for $C_{18}H_{22}NO^{+}$ ($M+H^{+}$): calcd: 268.1696, found: 268.1690.

***N*-Hexyl-1-naphthamide (10)**



Gram-scale synthesis without additive

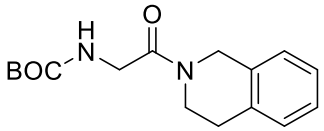
1-Naphthoic acid (1.417 g, 8.230 mmol) and boric acid (0.0594 g, 0.961 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then hexylamine (1.08 mL, 8.22 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 12 hours. The volatiles were removed under vacuum. The crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (30 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (30:70 ethyl acetate:hexanes) which yielded a white solid (0.966 g, 46%).

Gram-scale synthesis with 2-diethylaminoethanol

1-Naphthoic acid (1.413 g, 8.207 mmol) and boric acid (0.052 g, 0.84 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylaminoethanol (0.108 mL, 0.815 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then hexylamine (1.08 mL, 8.22 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 12 hours. The volatiles were removed under vacuum. The crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (30 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (20:80 ethyl acetate:hexanes) which yielded a white solid (1.309 g, 63%). ^{1}H NMR (400 MHz, acetone-d_6) δ 8.38-8.32 (m, 1H), 7.99-7.91 (m, 2H), 7.63 (br s, 1H), 7.61 (dd, J = 7.0, 1.2 Hz, 1H), 7.56-7.51 (m, 2H), 7.49 (dd, J = 8.2, 7.1 Hz, 1H), 3.48 (q, J = 6.8 Hz, 2H), 1.68 (quint, J = 7.2 Hz, 2H), 1.50-1.41 (m, 2H), 1.40-1.30 (m, 4H), 0.91 (t, J = 7.2

Hz, 3H). ^{13}C NMR (100 MHz, acetone-d_6, ppm) δ = 169.5, 136.5, 134.6, 131.3, 130.6, 129.0, 127.3, 127.0, 126.7, 125.7, 125.7, 40.3, 32.3, 30.4, 27.4, 23.3, 14.3. IR (cm^{-1}, solid): 3259, 3064, 2929, 2860, 1631, 1618, 1591, 1581, 1552, 1507, 1466, 1455, 1377, 1334, 1316, 1260, 1219, 1154, 1019, 973, 955, 897, 811. HRMS for $C_{17}H_{22}NO^+$ ($M+H^+$): calcd: 256.1696, found: 256.1694.

***N*-(1,2,3,4-Tetrahydroisoquinolinyl) BOC-glycineamide (11)**



Gram-scale synthesis without additive

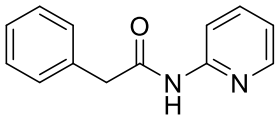
Boc-Gly-OH (1.436 g, 8.197 mmol) and boric acid (0.0522 g, 0.844 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then 1,2,3,4,-tetrahydroisoquinoline (1.03 mL, 8.23 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 °C oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 0.5 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (30 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (4:6 ethyl acetate/hexanes), which yielded a white solid (0.980 g, 41%).

Gram-scale synthesis with diethylamino ethanol

Boc-Gly-OH (1.437 g, 8.203 mmol) and boric acid (0.0517 g, 0.836 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylamino ethanol (0.108 mL, 0.815 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then 1,2,3,4-tetrahydroisoquinoline (1.03 mL, 8.23 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 °C oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 0.5 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (30 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (4:6 ethyl acetate/hexanes), which yielded a white solid (2.149 g, 90%). ^{1}H NMR, 2 rotamers (400 MHz, $CDCl_3$) δ 7.25-7.05 (m, 4H), 5.57 (br s, 1H), 4.74 (s, 1.1H), 4.54 (s, 0.9H), 4.09-4.01 (m, 2H), 3.84 (t, J = 6.0 Hz, 0.9H),

3.61 (t, J = 6.0 Hz, 1.1H), 2.91 (t, J = 6.0 Hz, 1.1H), 2.87 (t, J = 6.0 Hz, 0.9H), 1.46 (s, 9H). ^{13}C NMR, 2 rotamers (100 MHz, $CDCl_3$, ppm) δ = 167.5, 156.0, 134.9, 134.0, 133.0, 131.9, 129.1, 128.5, 127.3, 127.0, 126.9, 126.8, 126.3, 79.9, 46.1, 44.6, 42.9, 42.7, 42.2, 40.3, 29.3, 28.5, 28.5. IR (cm^{-1}, solid): 3277, 3033, 2977, 2932, 1704, 1632, 1581, 1525, 1497, 1484, 1461, 1452, 1430, 1404, 1387, 1362, 1291, 1273, 1249, 1222, 1206, 1167, 1109, 1066, 1044, 1027, 1004, 983, 942, 916, 867, 828, 809. HRMS for $C_{16}H_{23}N_2O_3^+$ ($M+H^+$): calcd: 291.1703, found: 291.1700.

***N*-(1-Pyridinyl)-2-phenylacetamide (12)**



Gram-scale synthesis without additive

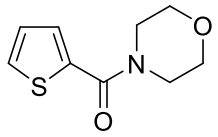
Phenylacetic acid (1.117 g, 8.204 mmol) and boric acid (0.0501 g, 0.810 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then p-xylene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then 2-aminopyridine (0.772 g, 8.20 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 190 ºC oil bath to reflux for 48 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (3:7 ethyl acetate:hexanes) which yielded a light yellow solid (1.076 g, 62%).

Gram-scale synthesis with 2-diethylaminoethanol

Phenylacetic acid (1.114 g, 8.182 mmol) and boric acid (0.0566 g, 0.915 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then p-xylene (82 mL) and diethylaminoethanol (0.109 mL, 0.822 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then 2-aminopyridine (0.772 g, 8.20 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 190 ºC oil bath to reflux for 48 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (3:7 ethyl acetate:hexanes) which yielded a light yellow solid (1.336 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (br s, 1H), 8.25-8.19 (m, 2H), 7.70-7.65 (m, 1H), 7.41-7.34 (m, 2H), 7.34-7.28 (m, 3H), 7.01 (ddd, J = 7.3, 4.9, 1.0 Hz, 1H), 3.74 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 169.8, 151.5, 147.8, 138.6, 134.1, 129.6, 129.3, 127.8, 120.0, 114.3, 45.0. IR (cm^{-1}, solid) 3231, 3050, 1657, 1599, 1578, 1533, 1495, 1458, 1432, 1325, 1291,

1240, 1196, 1149, 1097, 1073, 1032, 913, 881, 811. HRMS for $C_{13}H_{13}N_2O^+$ ($M+H^+$): calcd: 213.1022, found: 213.1038.

***N*-Morpholinyl-2-thiophenecarboxamide (13)**



Gram-scale synthesis without additive

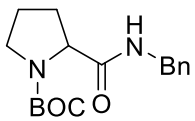
2-Thiophenecarboxylic acid (1.060 g, 8.272 mmol) and boric acid (0.0571 g, 0.923 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then morpholine (0.710 mL, 8.12 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 28 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (33:67 ethyl acetate:hexanes) which yielded a light brown oil (1.020 g, 63%).

Gram-scale synthesis with 2-diethylaminoethanol

2-Thiophenecarboxylic acid (1.052 g, 8.209 mmol) and boric acid (0.0524 g, 0.847 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylaminoethanol (0.110 mL, 0.830 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then morpholine (0.710 mL, 8.12 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for 36 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (4:6 ethyl acetate:hexanes) which yielded a light brown oil (1.288 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 5.0, 1.1 Hz, 1H), 7.29 (dd, J = 3.7, 1.1 Hz, 1H), 7.05 (dd, J = 5.0, 3.7 Hz, 1H), 3.79-3.69 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 163.8, 136.7, 128.1, 129.0, 126.9, 67.0. IR (cm^{-1}, solid) 3112, 2973, 2914, 2853, 1611, 1520,

1446, 1429, 1407, 1362, 1344, 1305, 1269, 1253, 1129, 1113, 1105, 1068, 1022, 1000, 929, 873, 853, 822. HRMS for $C_9H_{12}NO_2S^+$ ($M+H^+$): calcd: 198.0583, found: 198.0577.

***N*-Benzyl-*N*-boc proline amide (3)**



Gram-scale synthesis without additive

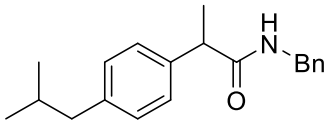
Boc-proline (1.571 g, 7.298 mmol) and boric acid (0.0457 g, 0.739 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (73 mL) was added. The mixture was stirred for 10 minutes at room temperature, then benzylamine (0.796 mL, 0.729 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for hours. The volatiles were removed under vacuum, and an ^{1}H NMR spectrum of the crude reaction mixture was acquired in DMSO-*d*$_6$. The crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (44% ethylacetate/hexane) which yielded a white solid (1.634 g, 74%).

Gram-scale synthesis with 2-diethylaminoethanol

Boc-proline (1.797 g, 8.348 mmol) and boric acid (0.0521 g, 0.843 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylaminoethanol (0.110 mL, 0.830 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then benzylamine (0.900 mL, 8.24 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ºC oil bath to reflux for hours. The volatiles were removed under vacuum, and an ^{1}H NMR spectrum of the crude reaction mixture was acquired in DMSO-*d*$_6$. The crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (44% ethylacetate/hexane) which yielded a white solid (2.035 g, 81%). ^{1}H NMR, mixture of rotamers (400 MHz, $CDCl_3$) δ = 7.37-7.20 (m, 5H), 6.35 (br s, 1H), 4.68-4.20 (m, 3H), 3.54-3.26 (m, 2H), 2.48-1.80 (m, 4H), 1.52-1.26 (m, 9H). ^{13}C NMR, mixture of rotamers (100 MHz, DMSO-

d$_6$, ppm) δ = 172.7, 172.5, 153.9, 153.6, 139.7, 128.3, 127.4, 126.9, 126.9, 126.7, 78.8, 78.7, 60.1, 59.9, 46.8, 46.6, 42.2, 41.9, 31.2, 30.2, 28.3, 28.1, 24.1, 23.3. IR (cm^{-1}, solid) = 3314, 2978, 2873, 1682, 1652, 1529, 1497, 1479, 1454, 1424, 1393, 1371, 1323, 1293, 1269, 1248, 1229, 1201, 1168, 1158, 1128, 1111, 1078, 1029, 1017, 974, 920, 899, 882, 872, 848, 827. HRMS for $C_{17}H_{25}N_2O_3^+$ ($M+H^+$): calcd: 305.1860, found: 305.1873.

***N*-Benzyl-2-(4-isobutylphenyl)propanamide (14)**



Gram-scale synthesis without additive

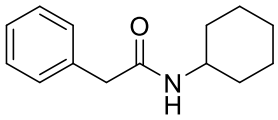
Ibuprofen (1.965 g, 9.525 mmol) and boric acid (0.0512 g, 0.828 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then benzylamine (0.890 mL, 8.15 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 °C oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (3:7 ethyl acetate:hexanes) which yielded a yellow, waxy solid (1.752 g, 62%).

Gram-scale synthesis with 2-diethylaminoethanol

Ibuprofen (1.691 g, 8.197 mmol) and boric acid (0.0507 g, 0.820 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and dimethylaminoethanol (0.110 mL, 0.830 mmol) were added. The mixture was stirred for 10 minutes at room temperature, then benzylamine (0.890 mL, 8.15 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 °C oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum- filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (3:7 ethyl acetate:hexanes) which yielded a yellow, waxy solid (2.020 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 5H), 7.12-7.09 (m, 4H), 5.68 (br s, 1H), 4.38 (d, J = 5.9 Hz, 2H), 3.57 (q, J = 7.1 Hz, 1H), 2.45 (d, J = 7.1 Hz, 2H), 1.83 (non, J = 6.9 Hz, 1H), 1.54 (d, J = 7.3 Hz, 3H), 0.88 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 174.5, 141.0, 138.6, 138.5, 129.8, 128.7, 127.5, 127.5, 47.0,

45.2, 43.7, 30.3, 22.5, 18.6. IR (cm^{-1}, solid) 3272, 3087, 3029, 2955, 2923, 2866, 1644, 1608, 1558, 1510, 1496, 1453, 1420, 1364, 1353, 1325, 1303, 1265, 1240, 1186, 1166, 1111, 1073, 1027, 1017, 991, 907, 882, 852. HRMS for $C_{20}H_{26}NO^+$ ($M+H^+$), calcd: 296.2009, found: 296.2012.

***N*-Cyclohexyl-2-phenylacetamide (15)**



Gram-scale synthesis without additive

Phenylacetic acid (1.119 g, 8.219 mmol) and boric acid (0.054 g, 0.87 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) was added. The mixture was stirred for 10 minutes at room temperature, then cyclohexylamine (0.94 mL, 8.2 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ^oC oil bath to reflux for 8 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (4:6 ethyl acetate:hexanes) which yielded a white solid (0.987 g, 55%).

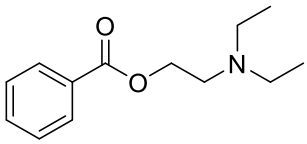
Gram-scale synthesis with 2-diethylaminoethanol

Phenylacetic acid (1.116 g, 8.190 mmol) and boric acid (0.0509 g, 0.823 mmol) were added to a flame-dried 250 mL round bottom flask with a stir bar under N_2 gas. Then toluene (82 mL) and diethylaminoethanol (0.108 mL, 0.815 mol) was added. The mixture was stirred for 10 minutes at room temperature, then cyclohexylamine (0.81 mL, 7.1 mmol) was added. The reaction flask was then attached to a Dean-Stark apparatus connected to a Schlenk line to maintain a N_2 atmosphere. The reaction flask was lowered into a 150 ^oC oil bath to reflux for 11 hours. The volatiles were removed under vacuum, and the crude solid was dissolved in dichloromethane (60 mL) and washed with 1 M HCl (2 x 30 mL) and 1 M NaOH (2 x 30 mL). The aqueous layers were each extracted with dichloromethane (15 mL). The combined organic layers were dried with $MgSO_4$ and vacuum-filtered and the dichloromethane was removed under vacuum. The product was purified by flash column chromatography on silica gel (35% ethyl acetate:hexanes) which yielded a white solid (1.421 g, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.32 (m, 2H), 7.31-7.21 (m, 3H), 5.28 (br s, 1H), 3.81-3.70 (m, 1H), 3.54 (s, 2H), 1.88-1.78 (m, 2H), 1.66-1.51 (m, 3H), 1.38-1.24 (m, 2H), 1.16-0.94 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 170.1, 135.3, 129.5, 129.1, 127.4, 48.3, 44.1, 33.0, 25.6, 24.8. IR (cm^{-1}, solid) 3268, 3084, 3027, 2930, 2853, 1666, 1634, 1603, 1554,

1495, 1447, 1432, 1350, 1257, 1170, 1155, 1100, 1073, 1031, 986, 966, 892, 844, 803. HRMS for $C_{14}H_{20}NO^+$ ($M+H^+$), calcd: 218.1539, found: 218.1539.

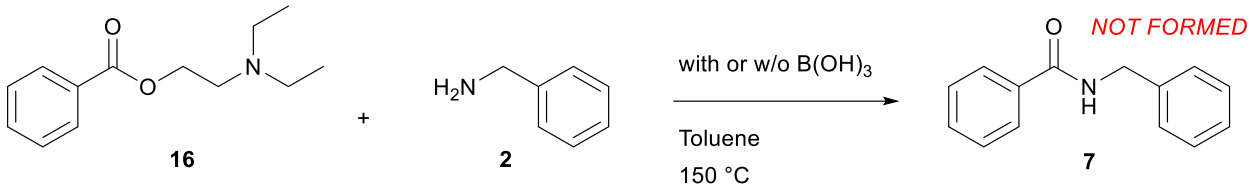
Studies involving 2-(diethylamino)ethyl benzoate (16)

Synthesis:



Compound **16** was synthesized by a previously published method.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.03 (m, 2H), 7.58-7.52 (m, 1H), 7.47-7.41 (m, 2H), 4.40 (t, *J* = 6.3 Hz, 2H), 2.01 (t, *J* = 6.3 Hz, 2H), 2.64 (q, *J* = 7.1 Hz, 4H), 1.07 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ = 166.7, 133.0, 130.4, 129.7, 128.4, 63.5, 51.1, 48.1, 12.2

Reaction of 16 with benzylamine



2-(Diethylamino)ethyl benzoate **16** (0.112 g, 0.506 mmol), benzylamine **2** (0.055 mL, 0.506 mmol) and toluene (5.0 mL) were added to a flame-dried 25 mL round bottom flask with a stir bar under N_2 gas. The reaction flask was attached to a reflux condenser connected to a Schlenk line to maintain a N_2 atmosphere and lowered into a 150 °C temperature-controlled oil bath. A sample (0.4 mL) was taken out of the reaction mixture with a syringe after 4 hours of reflux. The solvent was removed under vacuum, and $CDCl_3$ (0.5 mL) was added. The sample was analyzed by ^{1}H NMR spectroscopy, which did not show the presence of any *N*-benzylbenzamide **7**.

Boric acid (0.0031 g, 0.0501 mmol) was added to the reaction mixture, which was refluxed for a further 4 hours. NMR analysis of a 0.4 mL sample prepared as above did not reveal the presence of any *N*-benzylbenzamide **7**.

NMR Spectra

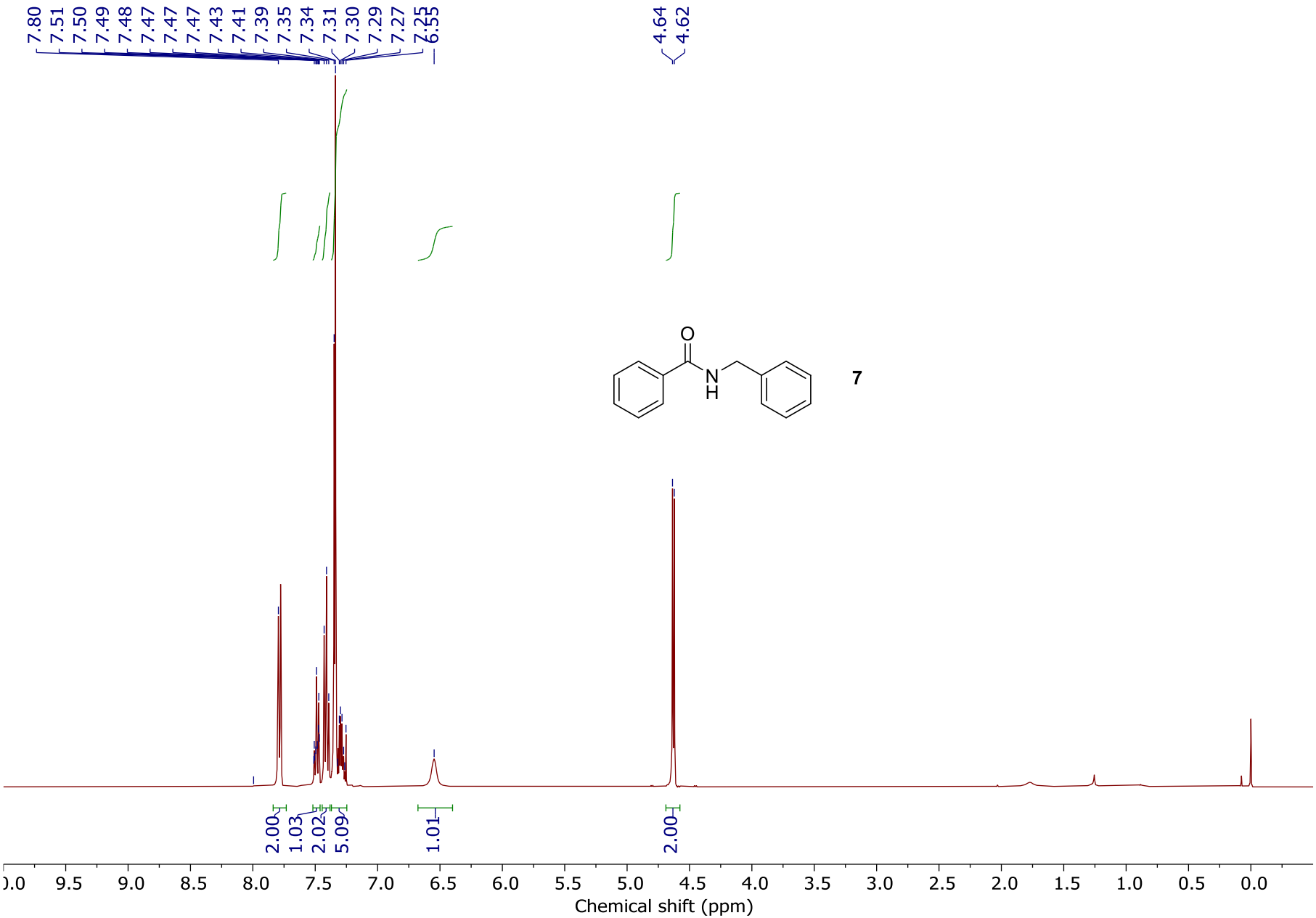


Figure S1a. ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$).

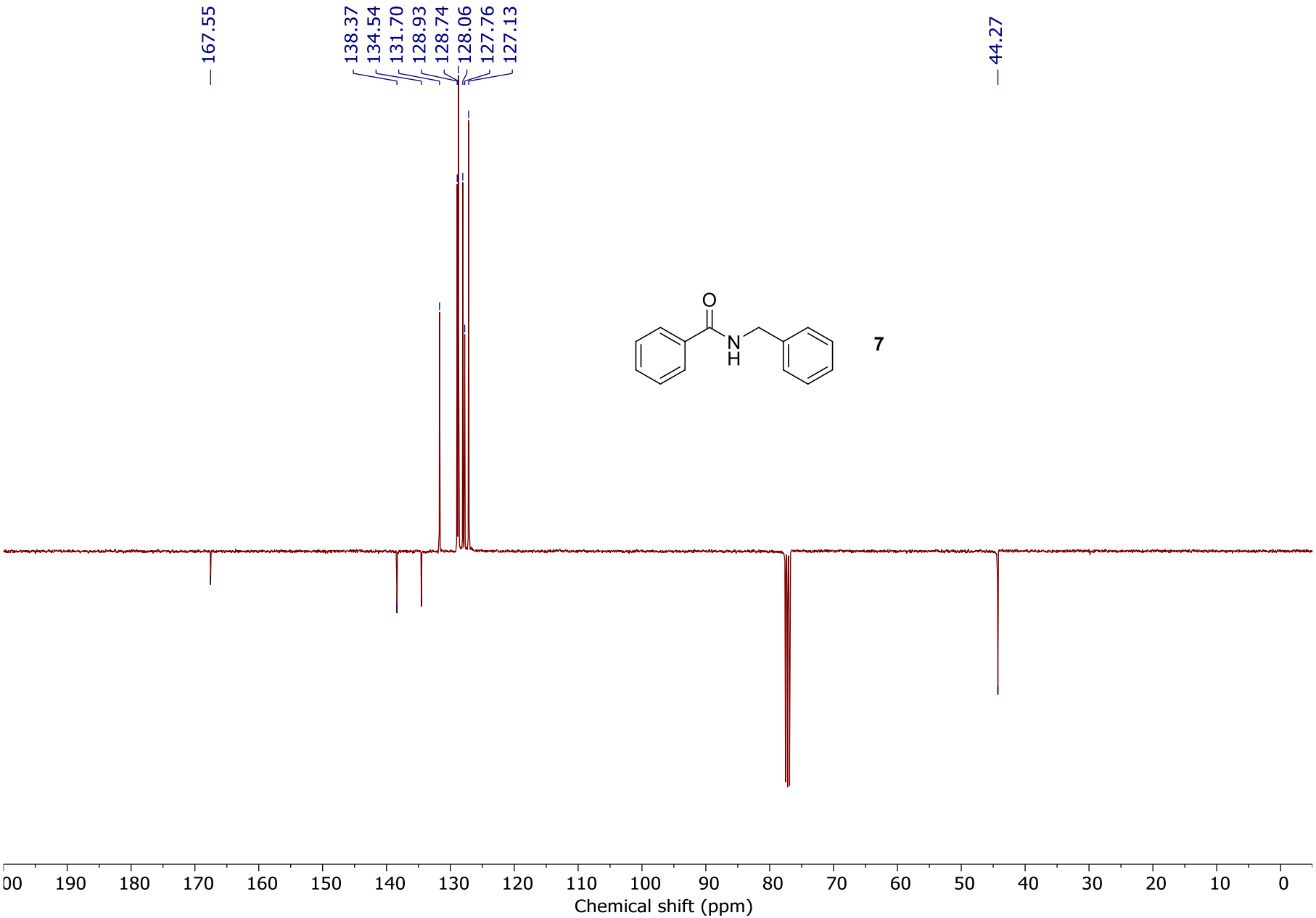


Figure S1b. DEPTQ NMR spectrum of compound **7** (100 MHz, $CDCl_3$).

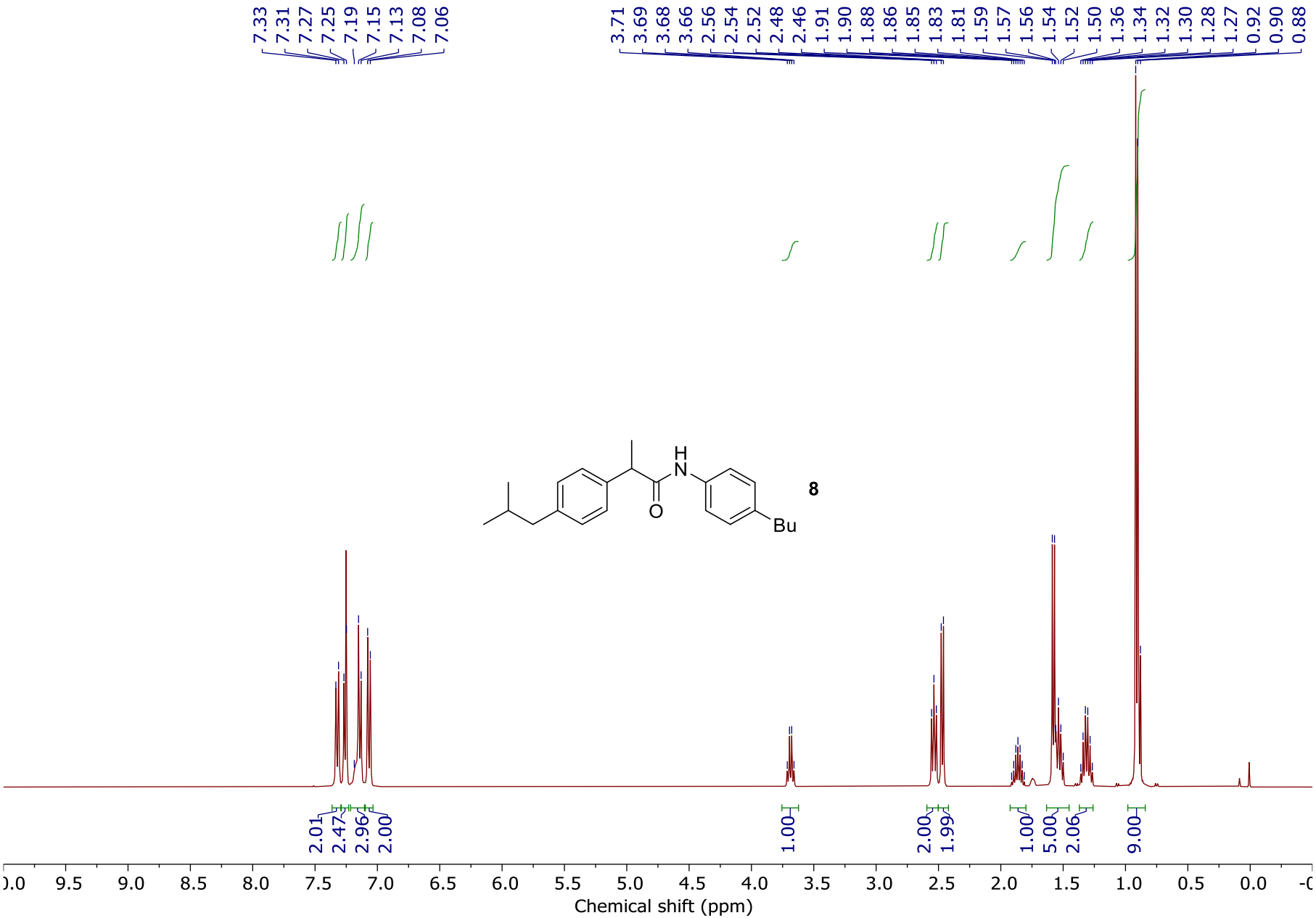


Figure S2a. ^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$).

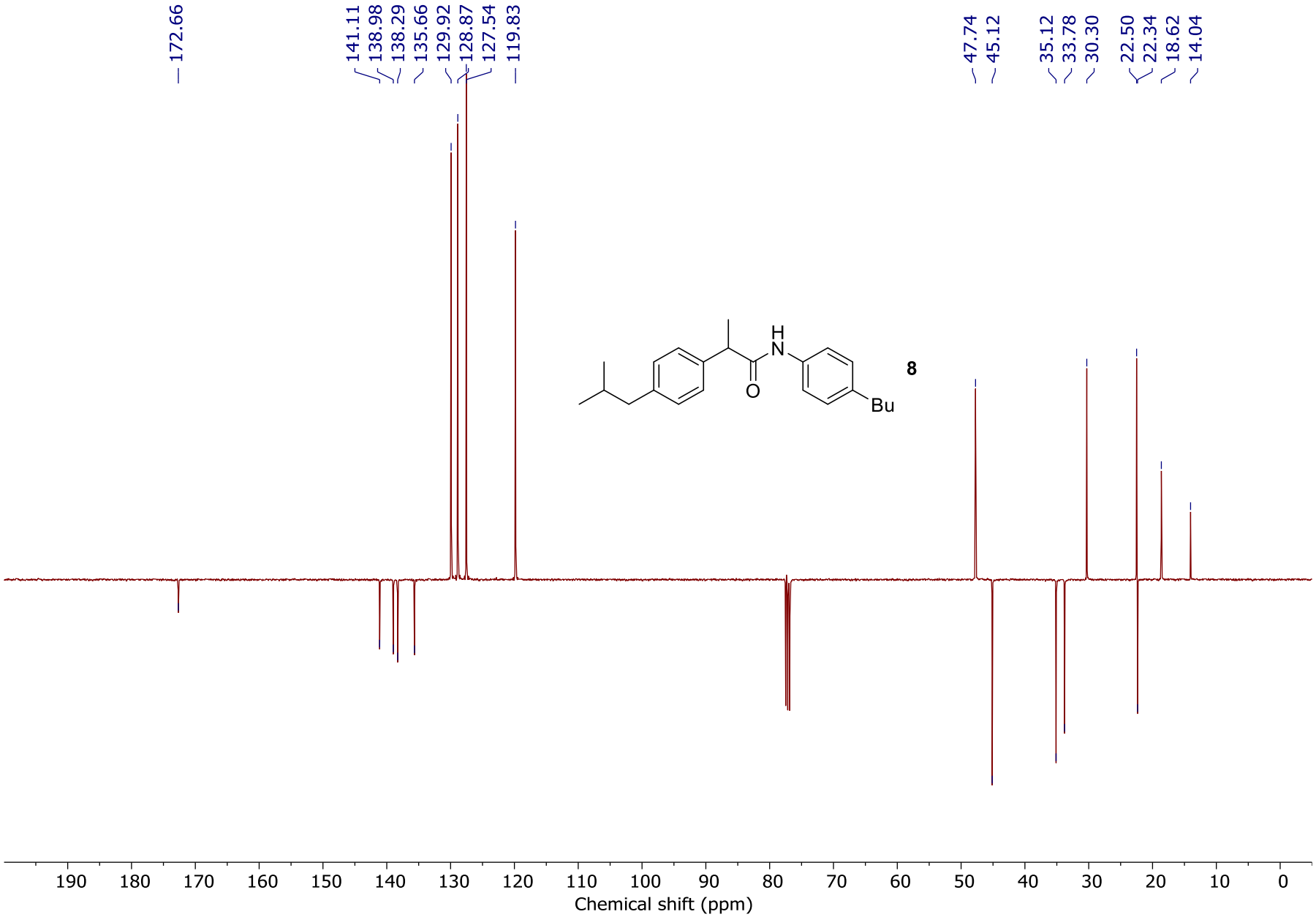


Figure S2b. DEPTQ NMR spectrum of compound **8** (100 MHz, $CDCl_3$).

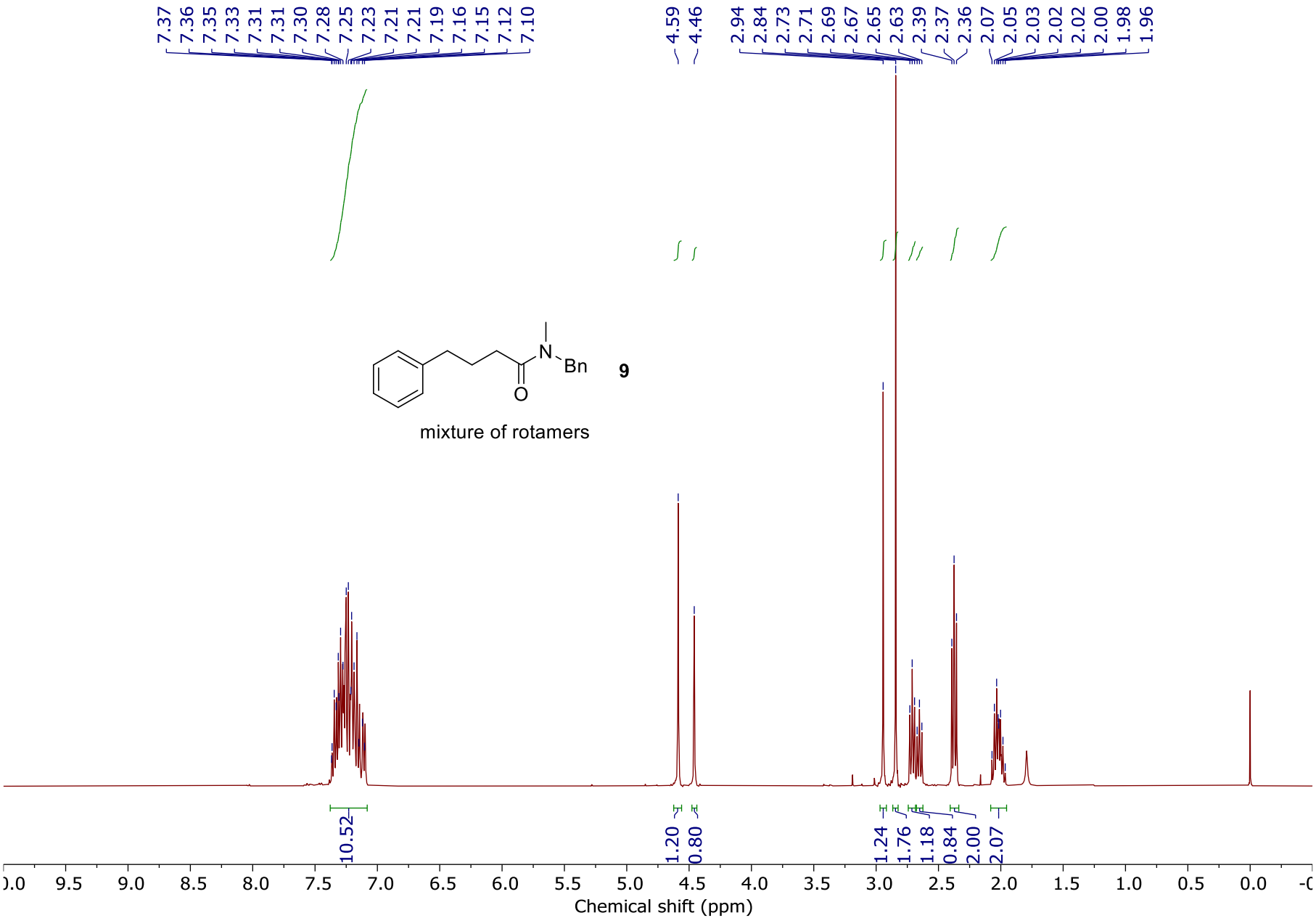


Figure S3a. ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$).

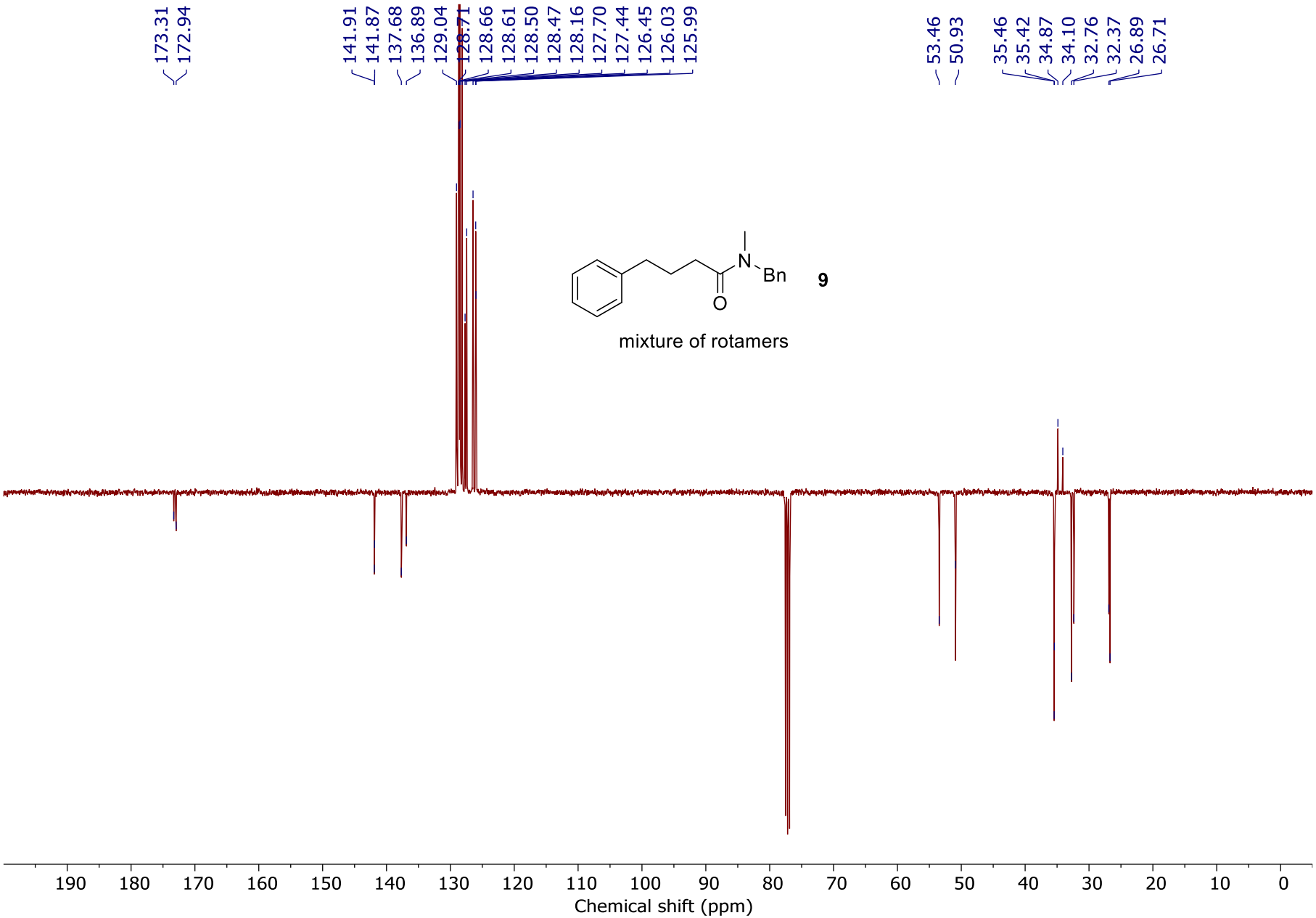


Figure S3b. DEPTQ NMR spectrum of compound **9** (100 MHz, $CDCl_3$).

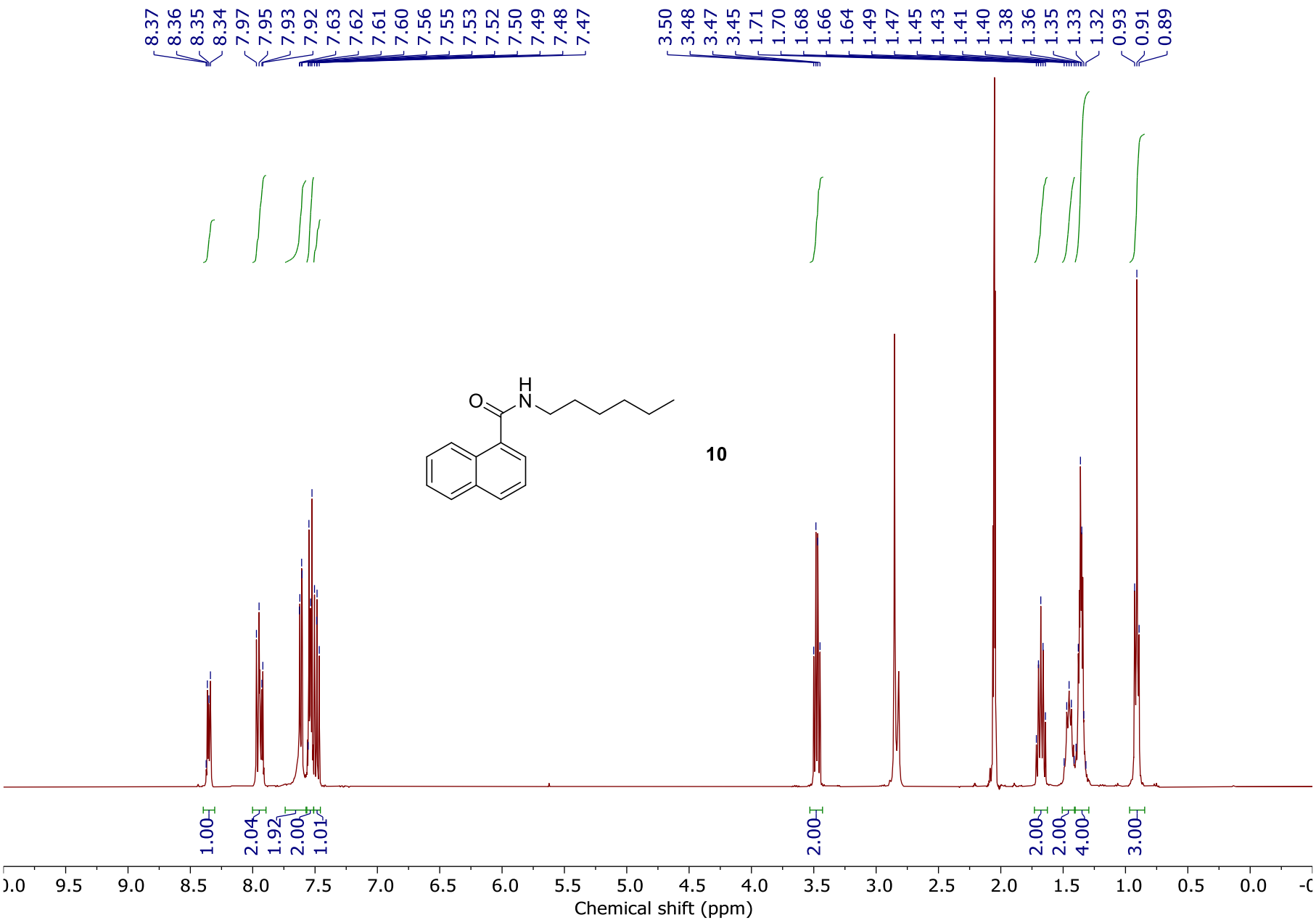


Figure S4a. ^{1}H NMR spectrum of compound **10** (400 MHz, acetone-d_6).

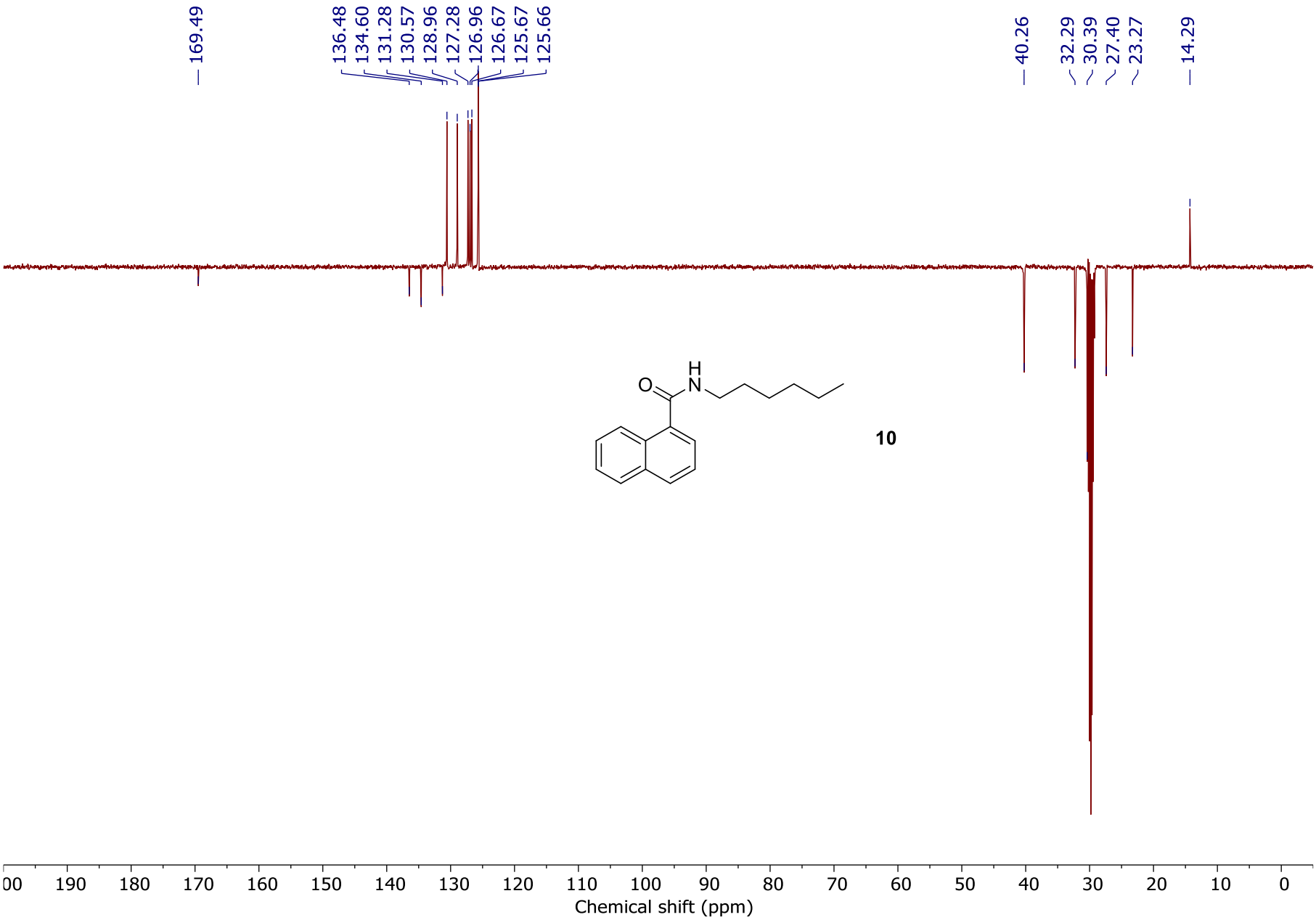


Figure S4b. DEPTQ NMR spectrum of compound **10** (100 MHz, acetone-d_6).

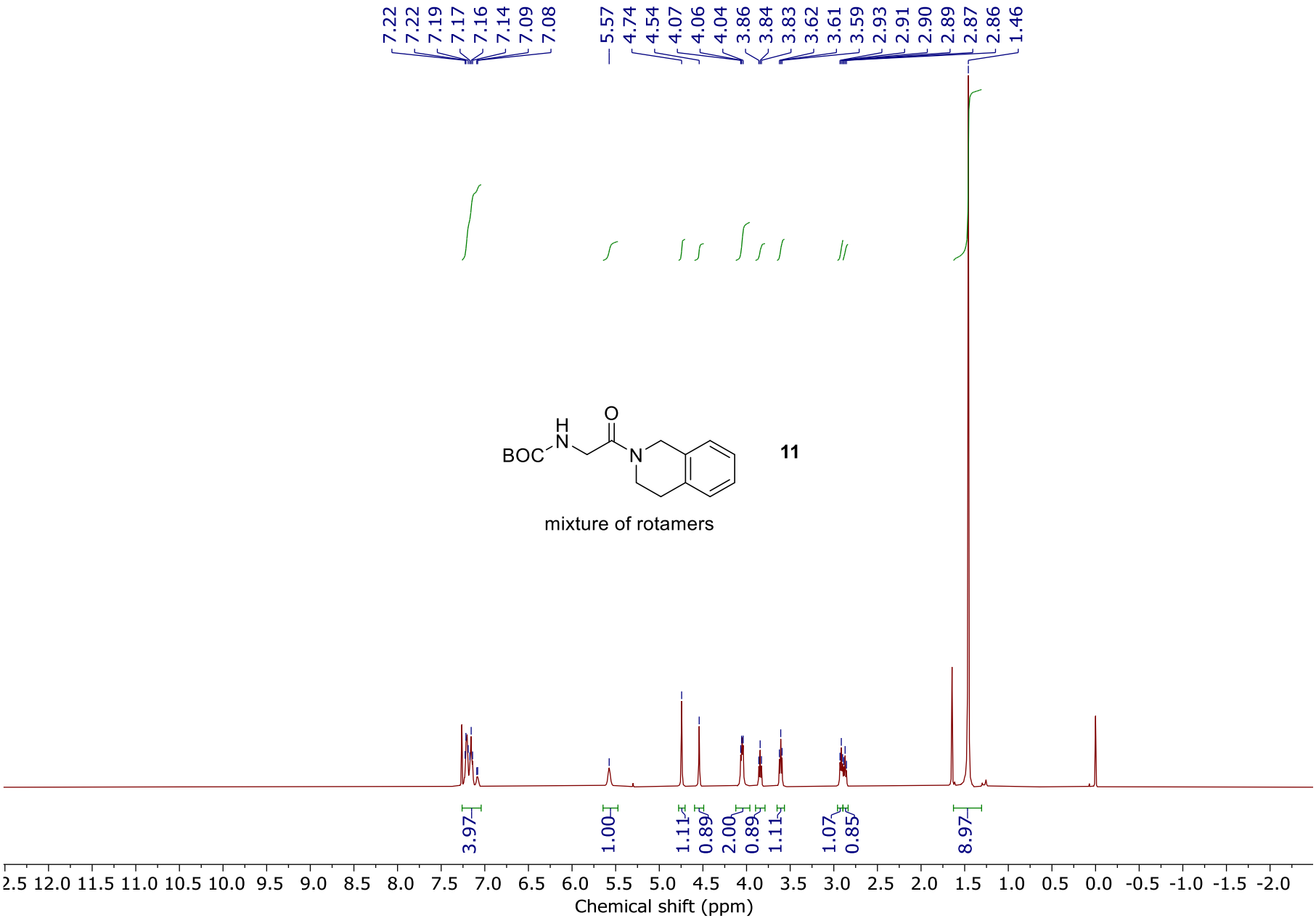


Figure S5a. ^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$).

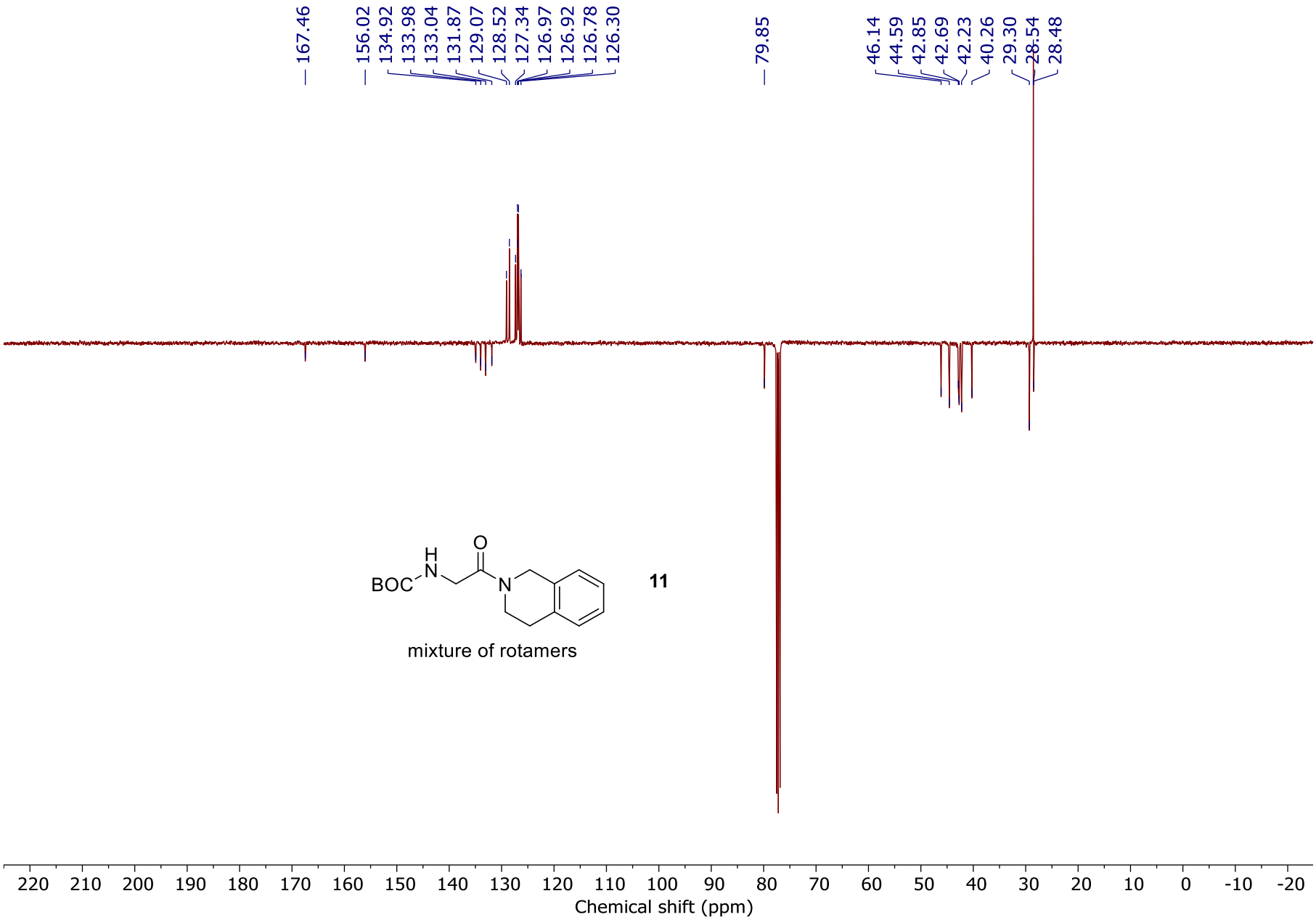


Figure S5b. DEPTQ NMR spectrum of compound **11** (100 MHz, $CDCl_3$).

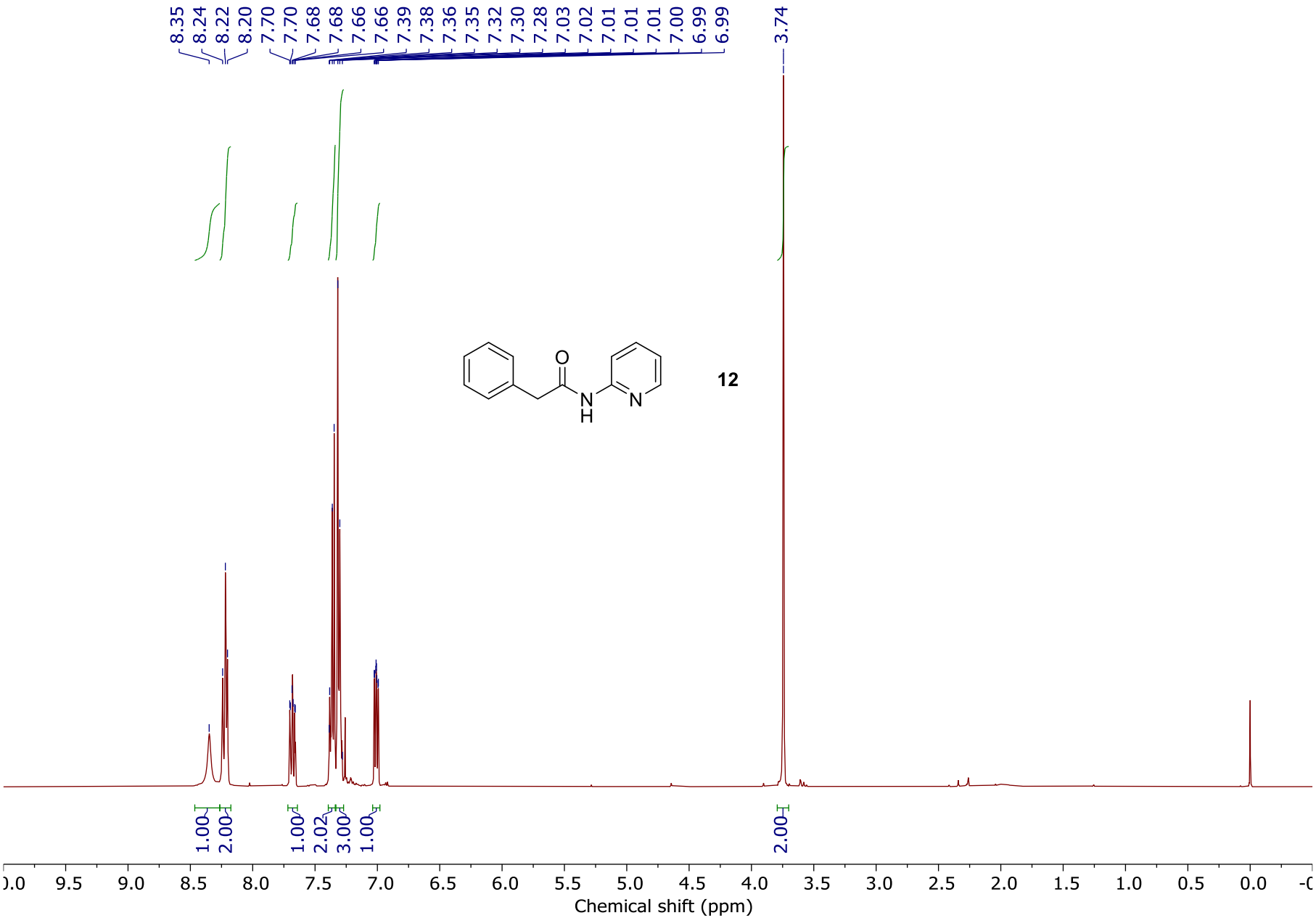


Figure S6a. ^{1}H NMR spectrum of compound **12** (400 MHz, $CDCl_3$).

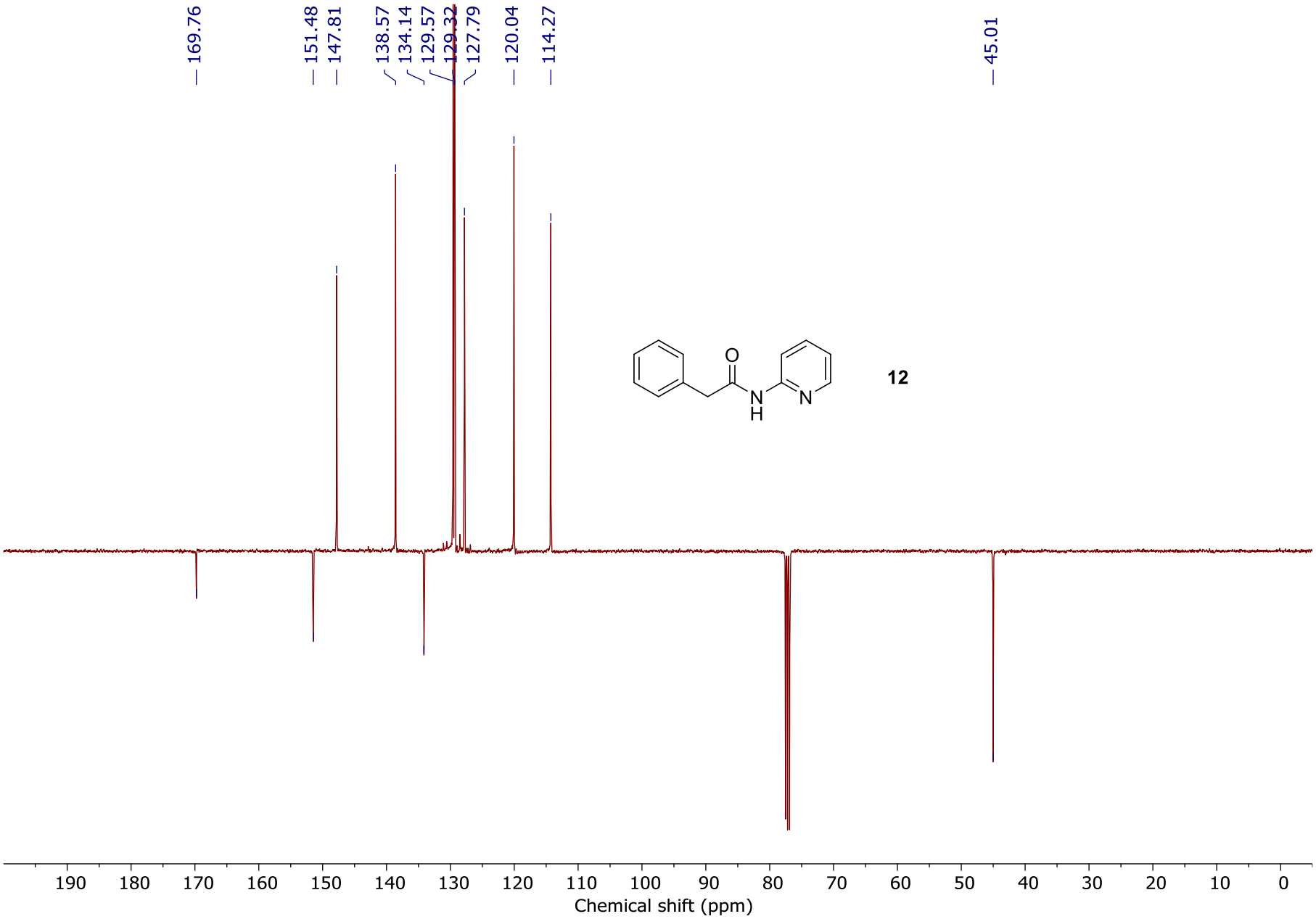


Figure S6b. DEPTQ NMR spectrum of compound **12** (100 MHz, $CDCl_3$).

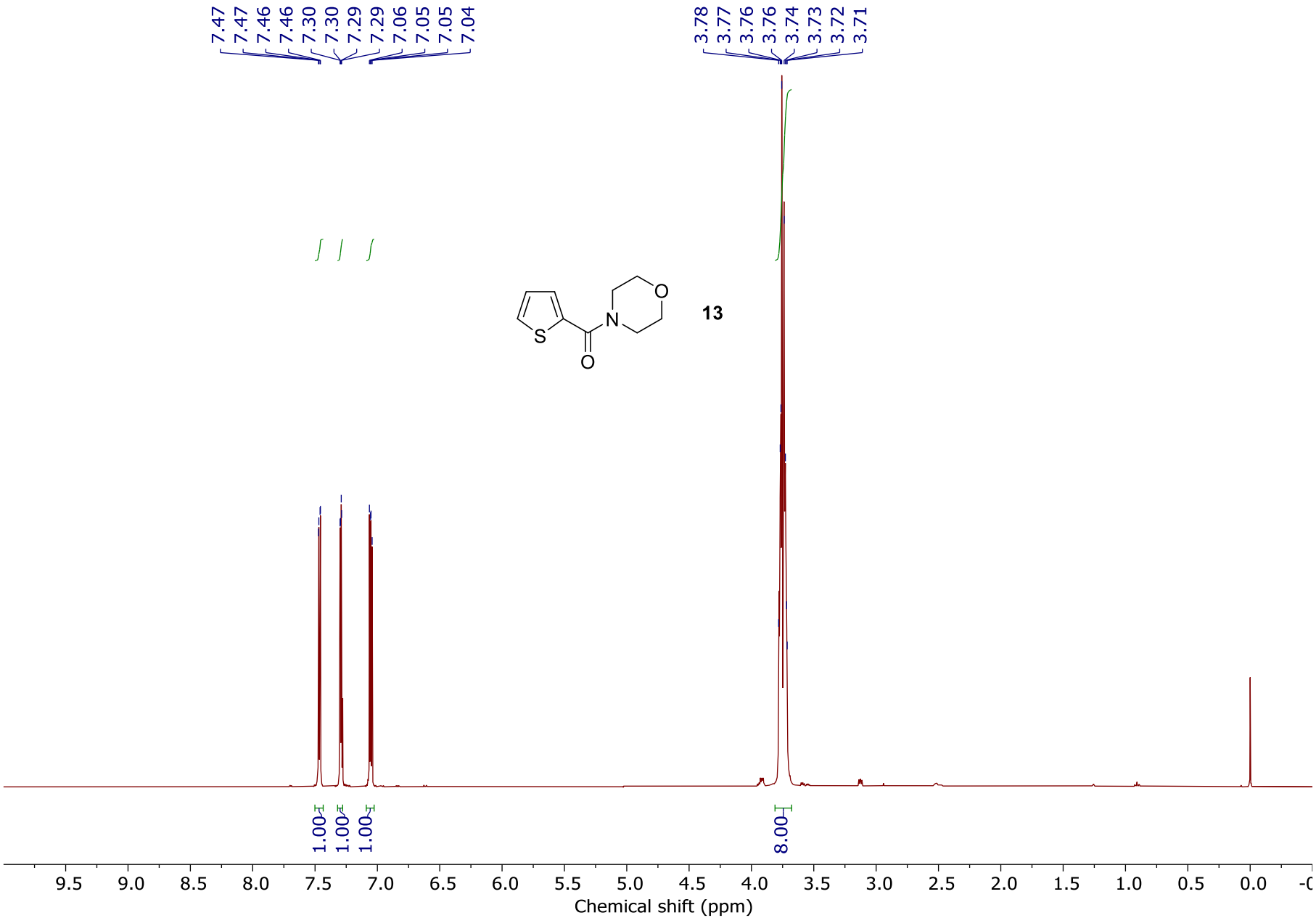


Figure S7a. ^{1}H NMR spectrum of compound **13** (400 MHz, $CDCl_3$).

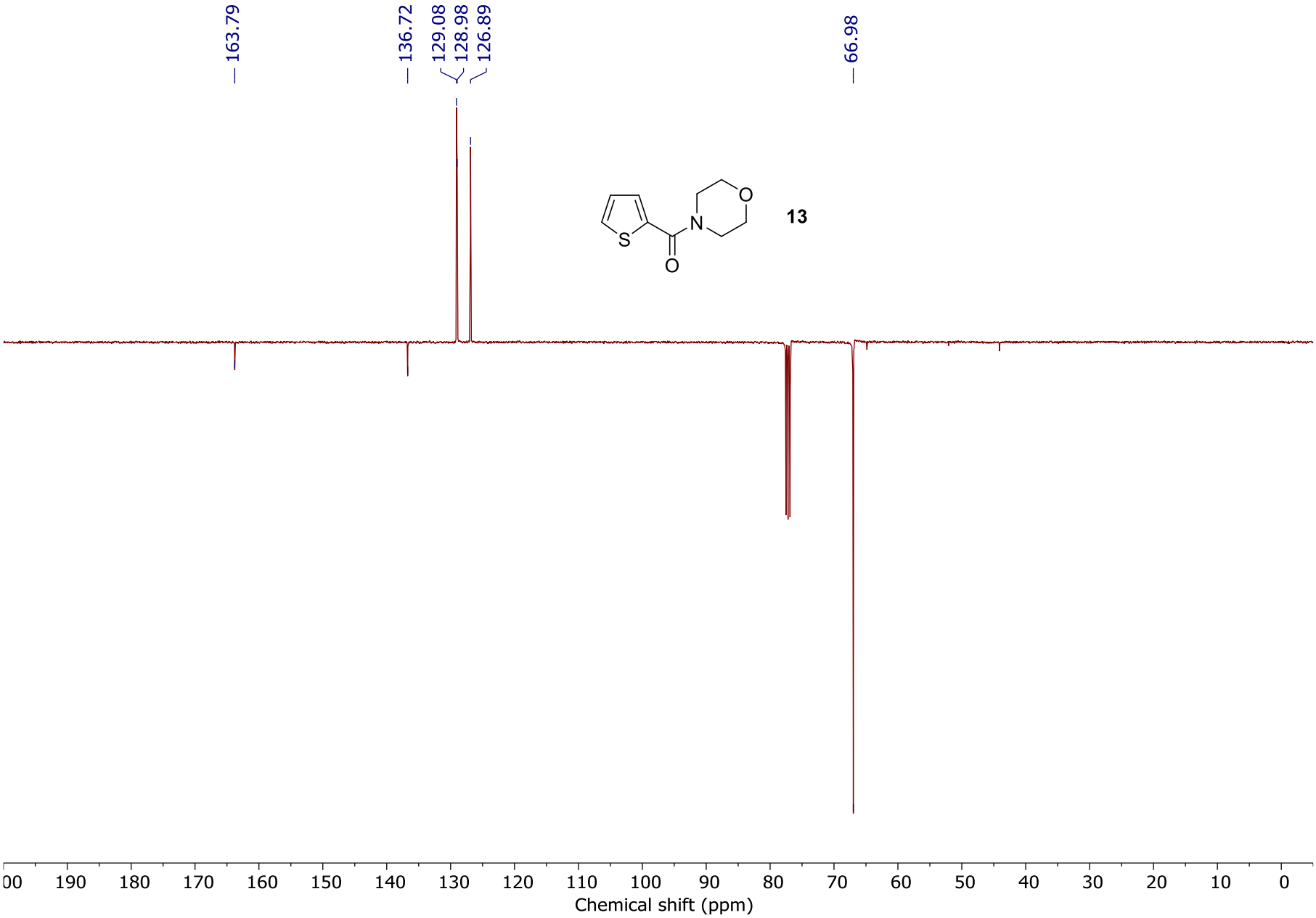


Figure S7b. DEPTQ NMR spectrum of compound **13** (100 MHz, $CDCl_3$).

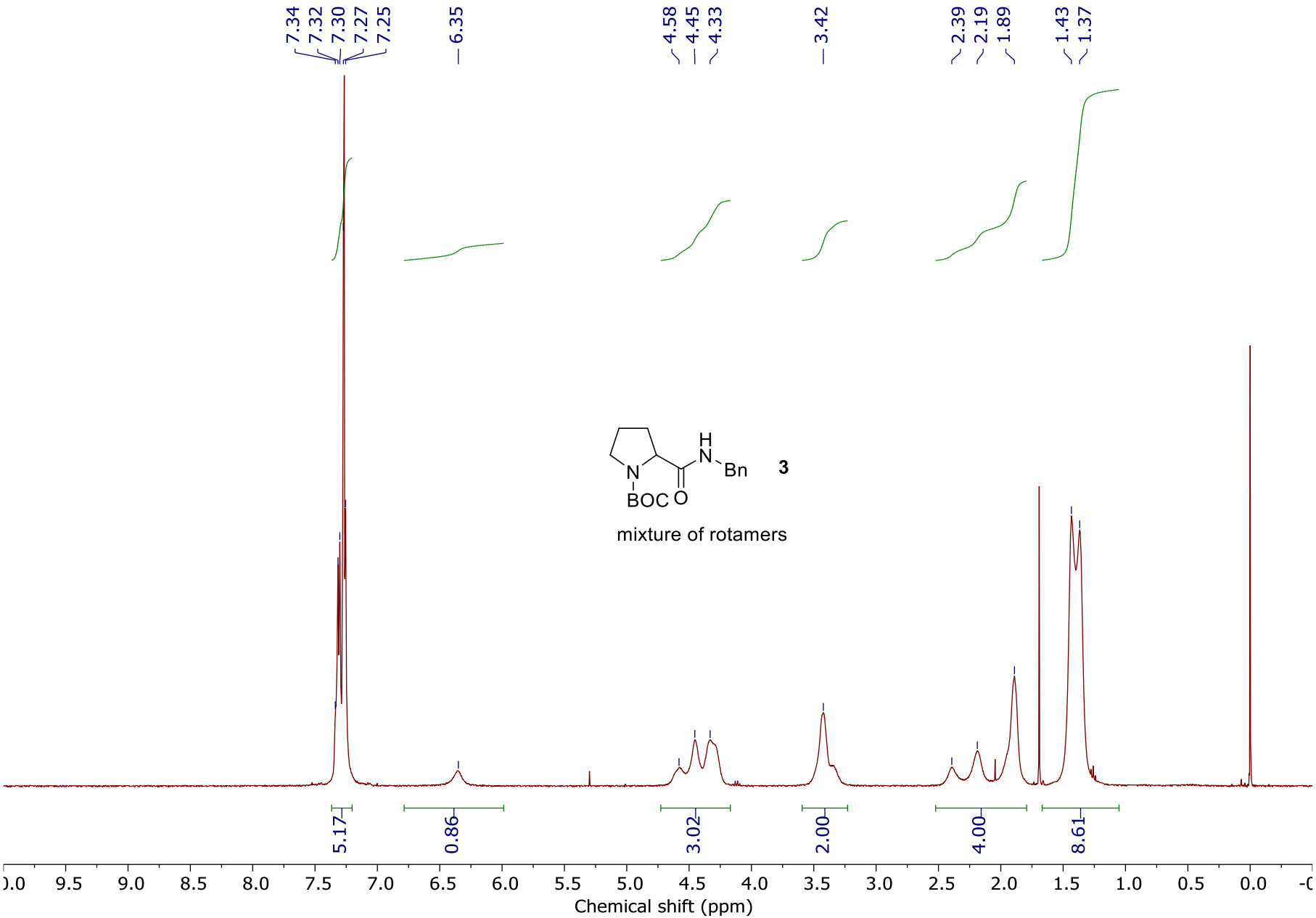


Figure S8a. ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$).

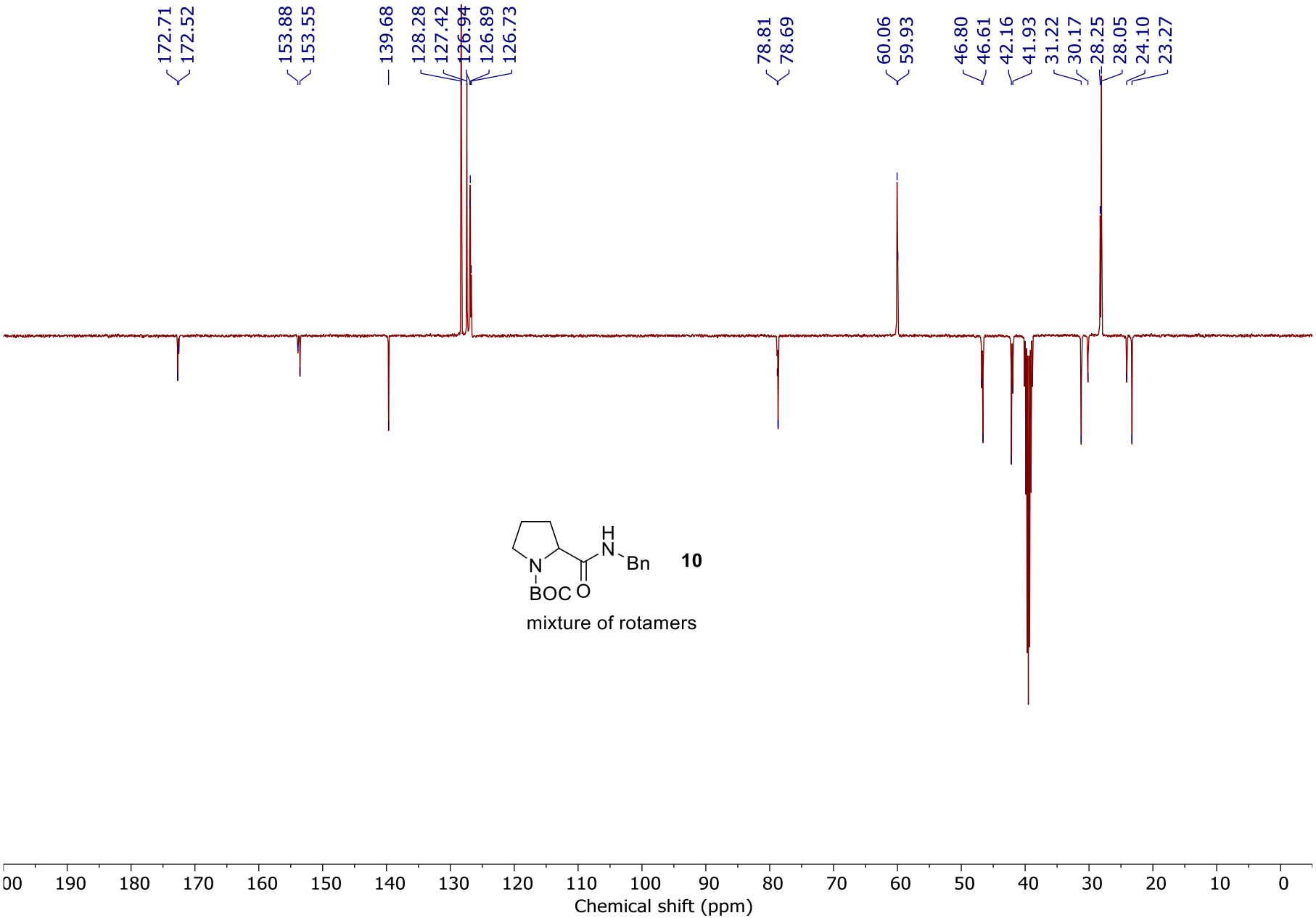


Figure S8b. DEPTQ NMR spectrum of compound **3** (100 MHz, DMSO-d_6).

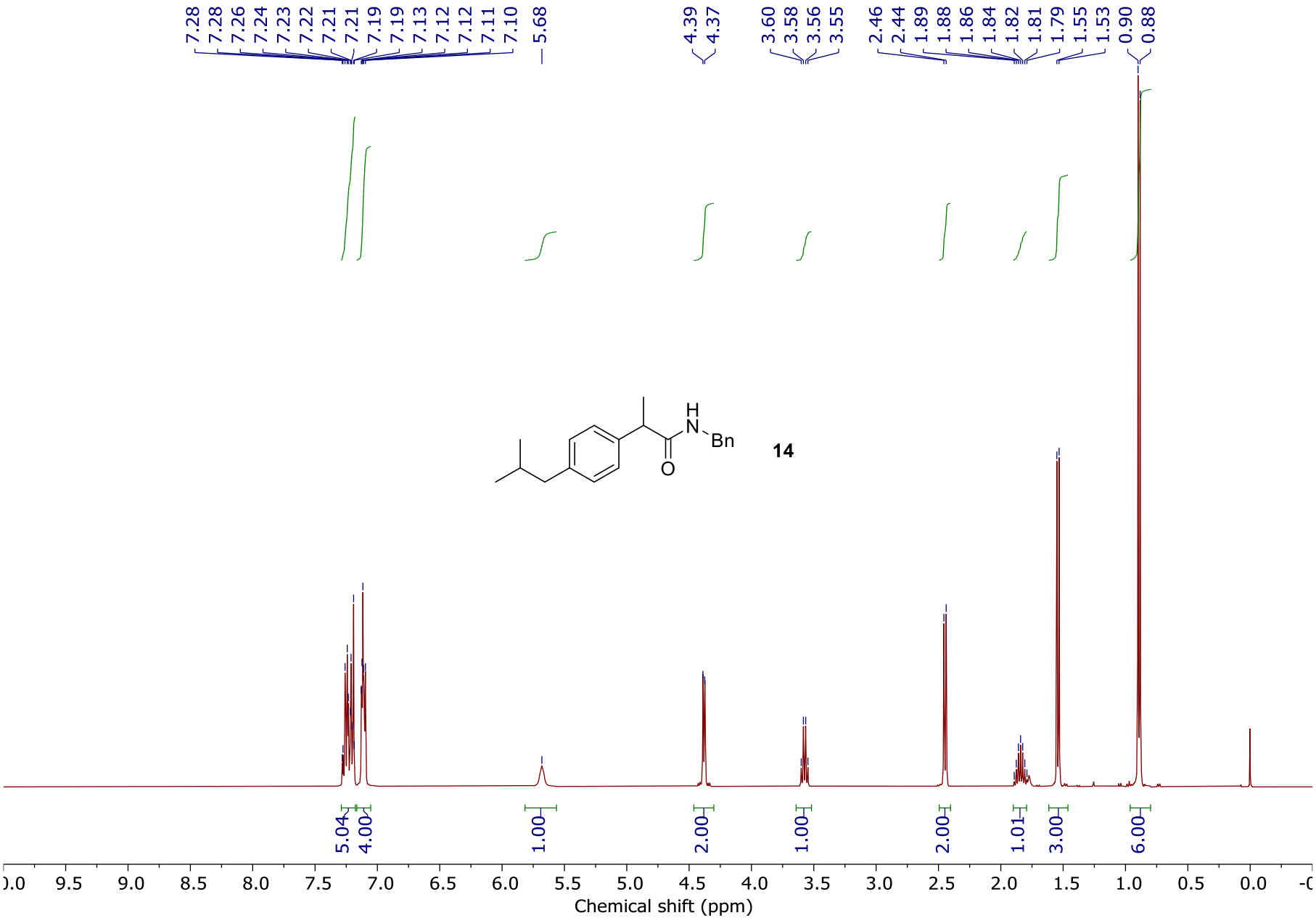


Figure S9a. ^{1}H NMR spectrum of compound **14** (400 MHz, $CDCl_3$).

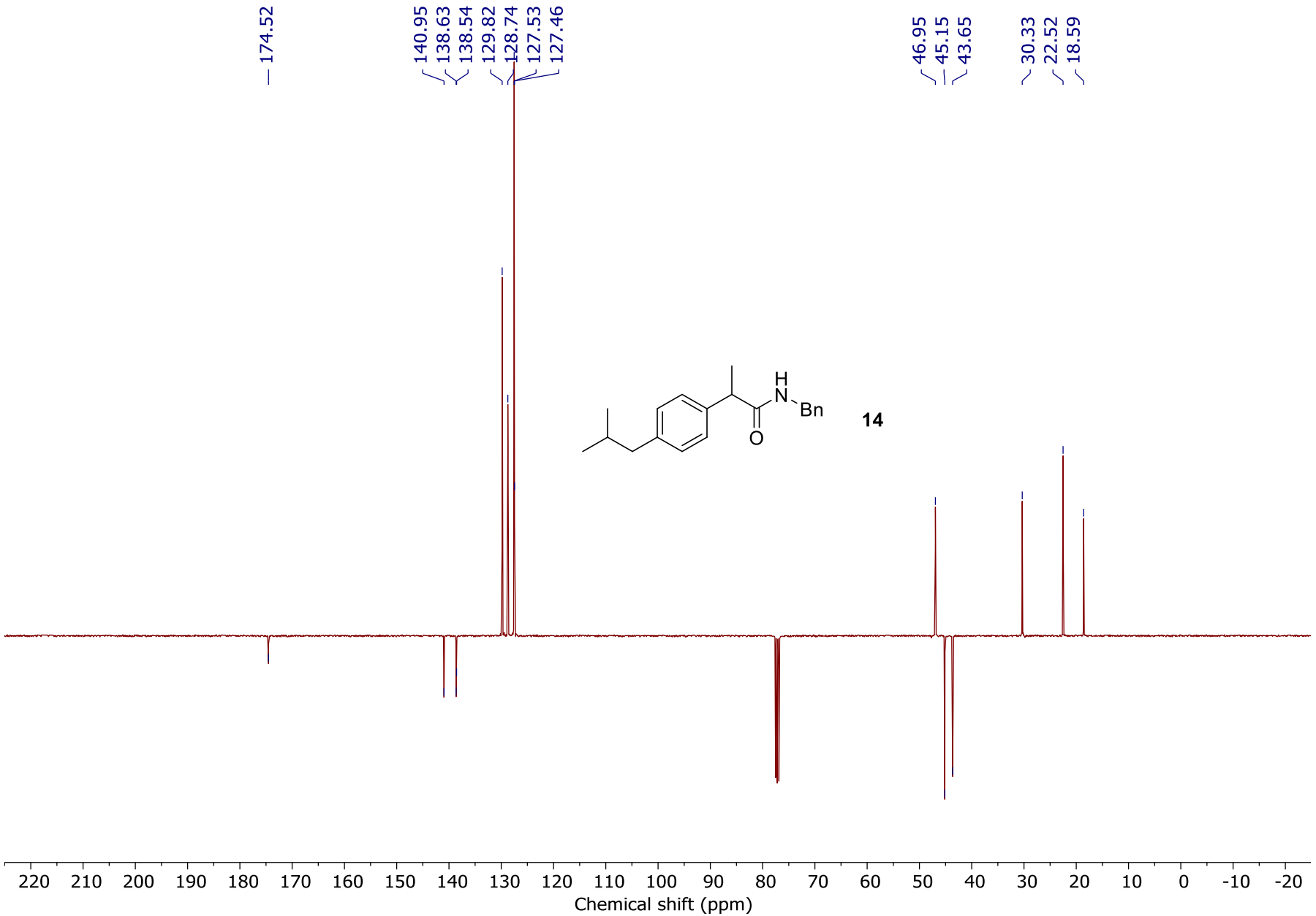


Figure S9b. DEPTQ NMR spectrum of compound **14** (100 MHz, $CDCl_3$).

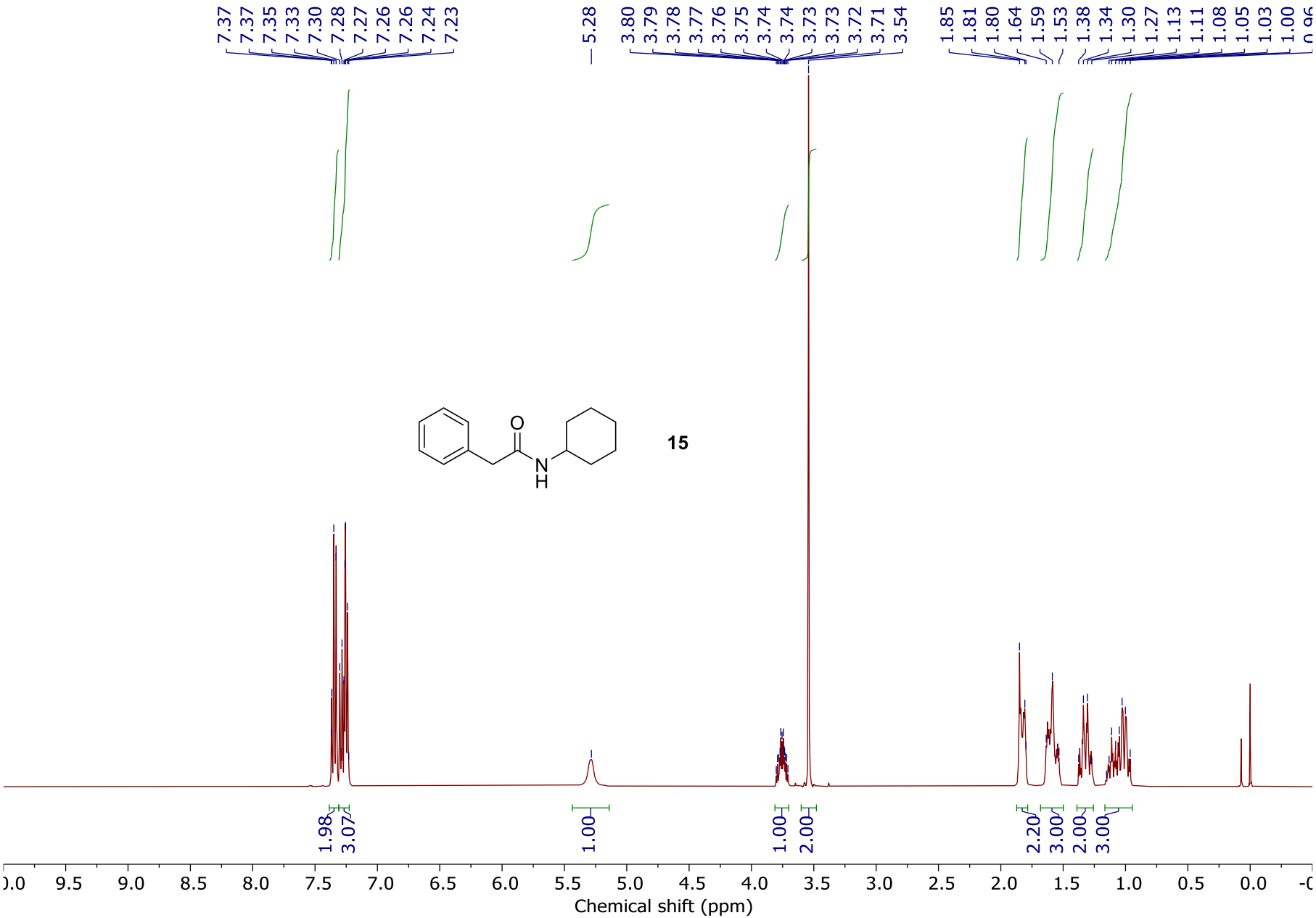


Figure S10a. ^{1}H NMR spectrum of compound **15** (400 MHz, $CDCl_3$).

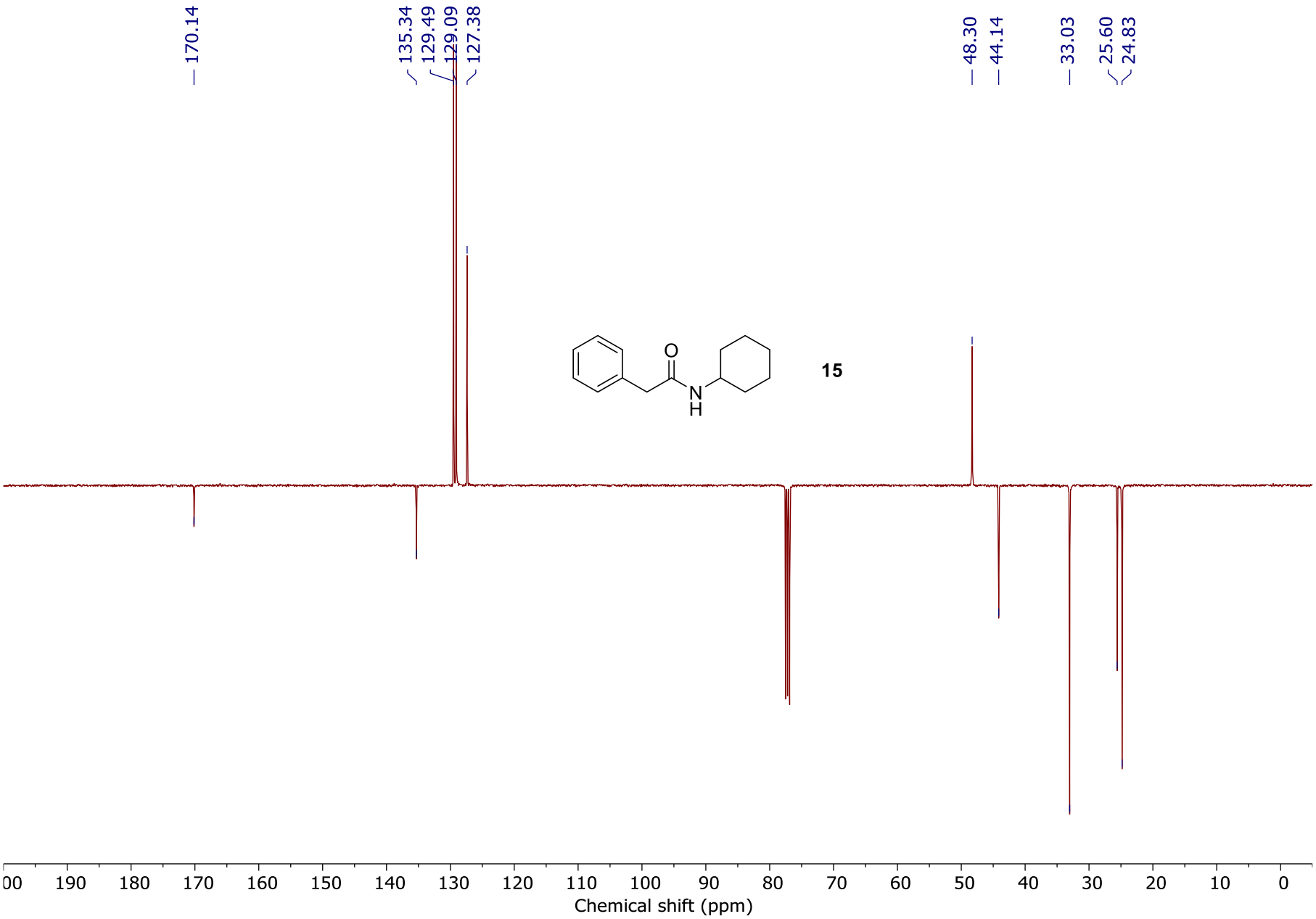


Figure S10b. DEPTQ NMR spectrum of compound **15** (100 MHz, $CDCl_3$).

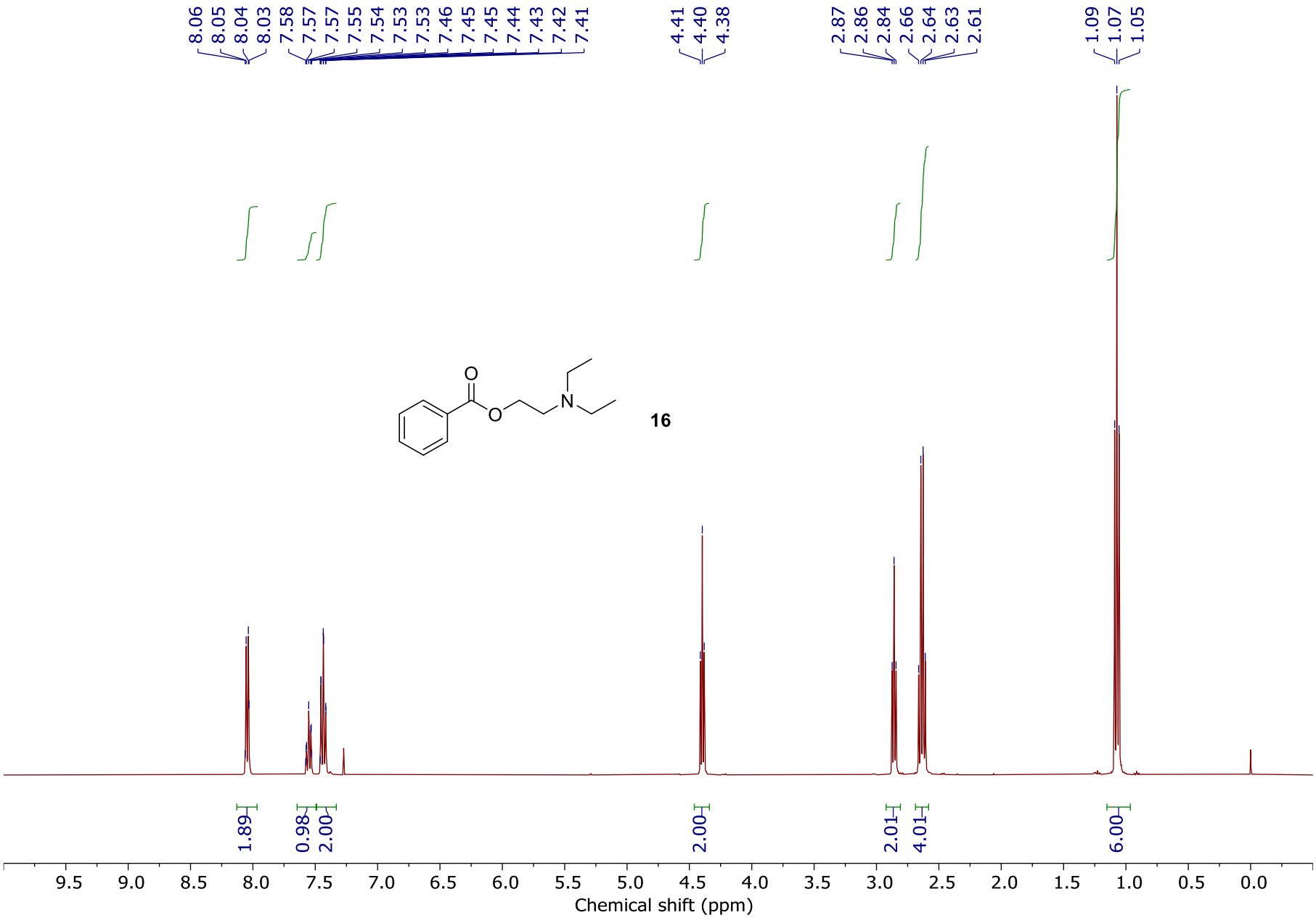


Figure S11a. ^{1}H NMR spectrum of compound **16** (400 MHz, $CDCl_3$).

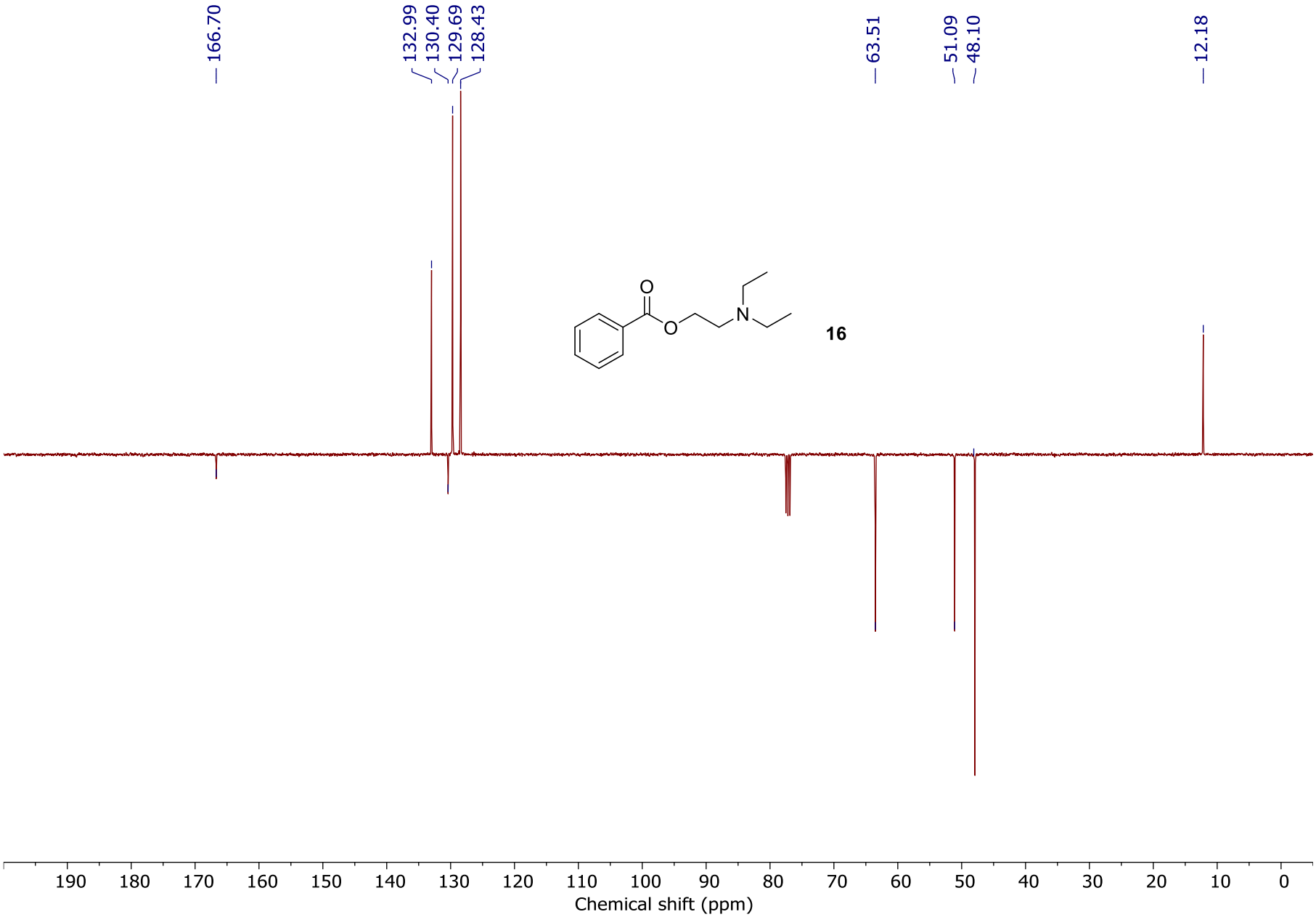


Figure S11b. DEPTQ NMR spectrum of compound **16** (100 MHz, $CDCl_3$).

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