Supporting Information for

Ligand-Controlled Regiodivergent Catalytic Amidation of Unactivated Secondary Alkyl Bromides

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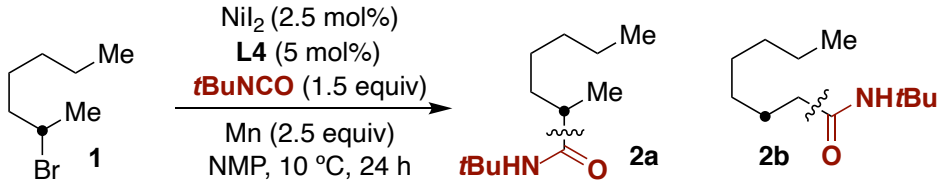
General considerations

Reagents. $NiBr_2$ (anhydrous, 98% purity), NiI_2 (anhydrous, 99% purity), manganese powder (99.9% trace metal basis), *tert*-butyl isocyanate (97% purity), cyclohexyl isocyanate (98% purity), adamantyl isocyanate (97% purity) and 1,1,3,3-tetramethylbutyl isocyanate (98% purity) were purchased from Aldrich. Ethyl 2-(1-isocyanatocyclohexyl) acetate was purchased from Fluorochem. (NOTE: *the purity of the isocyanates was found crucial for the reaction*; higher yields and better reproducibility were achieved by purifying the isocyanates through a short plug of dried neutral alumina inside a nitrogen-filled glovebox. Old batches of isocyanates provide consistently lower yields and variable results). 2-Bromoheptane (technical grade) was purchased form Aldrich, 3-bromoheptane (97% purity) and 4-bromoheptane (97% purity) were purchased from Alfa Aesar and used as received. Anhydrous *N,N*- dimethylformamide (DMF, 99.8% purity), anhydrous *N,N*-dimethylacetamide (DMA, 99.5% purity) and anhydrous 1-methyl-2-pyrrolidinone (NMP, 99.5% purity) were purchased from Acros Organics (NOTE: *it is critical to have appropriately dried DMF, DMA and NMP to obtain reproducible results*, since old batches of these solvents provided variable results). The temperature of the reactions was controlled by using a chiller (Huber Minichiller 300) connected to an aluminum block with an internal recirculation circuit.

Analytical methods. ^{1}H NMR and ^{13}C NMR spectra are included for all compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz, a Bruker 400 MHz or a Bruker 500 MHz at 20 ºC. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm) if not otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.2 ppm) and were obtained with ^{1}H decoupling. Coupling constants, *J*, are reported in hertz (Hz). Melting points were measured using open glass capillaries in a Büchi B540 apparatus. Infrared spectra (FT-IR) measurements were carried out on a Bruker Optics FT-IR Alpha spectrometer equipped with a DTGS detector, KBr beamsplitter at 4 cm^{-1} resolution using a one bounce ATR accessory with diamond windows. Mass spectra were recorded on a Waters LCT Premier spectrometer or in a MicroTOF Focus, Bruker Daltonics spectrometer. Flash chromatography was performed with EM Science silica gel 60 (230-400 mesh) using potassium permanganate, vanillin or cerium molybdate as TLC stains.

Optimization of the reaction conditions

General procedure. In a nitrogen-filled glovebox, an oven-dried screw-capped test tube containing a stirring bar was charged with the nickel source, ligand and Mn. The obtained mixture was stirred at rt, until a colored complex was obtained (*ca.* 5 to 10 min), after which *tert*- butyl isocyanate (0.75 mmol, 1.50 equiv) was added by syringe. Subsequently, the reaction mixture was cooled down to 10 °C outside the glovebox, and 2-bromoheptane was added by syringe (0.5 mmol, 1 equiv). The resulting mixture was stirred for 24 h at 10 °C using a chiller. The crude reaction mixture was carefully quenched with 5% aq. HCl (1 mL) and extracted with ethyl acetate. A sample of the obtained solution was filtered through a silica-celite plug, eluted with ethyl acetate and analyzed by GC-FID using anisole as internal standard.



entry	Deviation	yield **2a** + **2b** (%)	**2b:2a**
1	None	72	96:4
2	$NiBr_2$ (3 mol%), **L7** (4.5 mol%), DMF, rt[a]	25-30[a]	<1:99
3	**L7** instead of **L4**	62	<1:99
4	**L8** instead of **L4**	72	<1:99
5	with $NiBr_2$ and DMF at 3°C with **L8**	93	<1:99

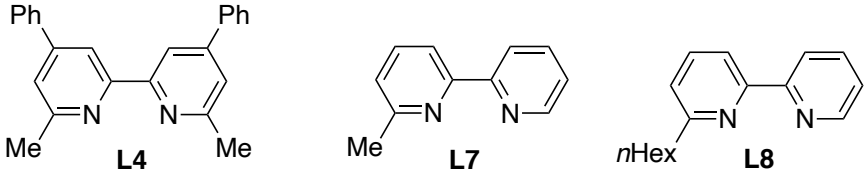
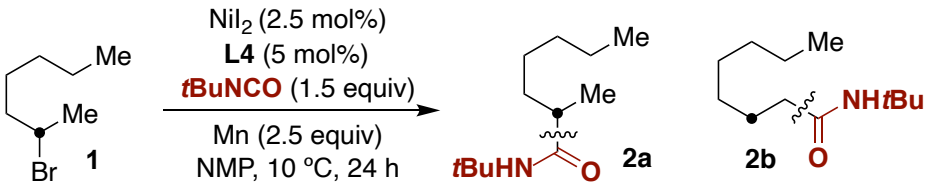


Table S1. Comparison of reaction conditions. [a] Using other Ni-catalyzed amidation protocols;[1] Variable yields were obtained, with a maximum value of 25-30%.

[1] Serrano, E.; Martin, R. *Angew. Chem. Int. Ed.* **2016**, *55* (37), 11207–11211.



entry	Deviation	Conversion	yield **2a** + **2b** (%)	**2b:2a**
1	None	100	72	96:4
2	**L9** instead of **L4**	93	15	1:99
3	**L10** instead of **L4**	56	3	—
4	**L11** instead of **L4**	79	27	89:11
5	**L12** instead of **L4**	53	4	—
6	**L13** instead of **L4**	97	62	77:23
7	**L14** instead of **L4**	100	39	72:28
8	**L15** instead of **L4**	90	5	—
9	**L16** instead of **L4**	100	4	—

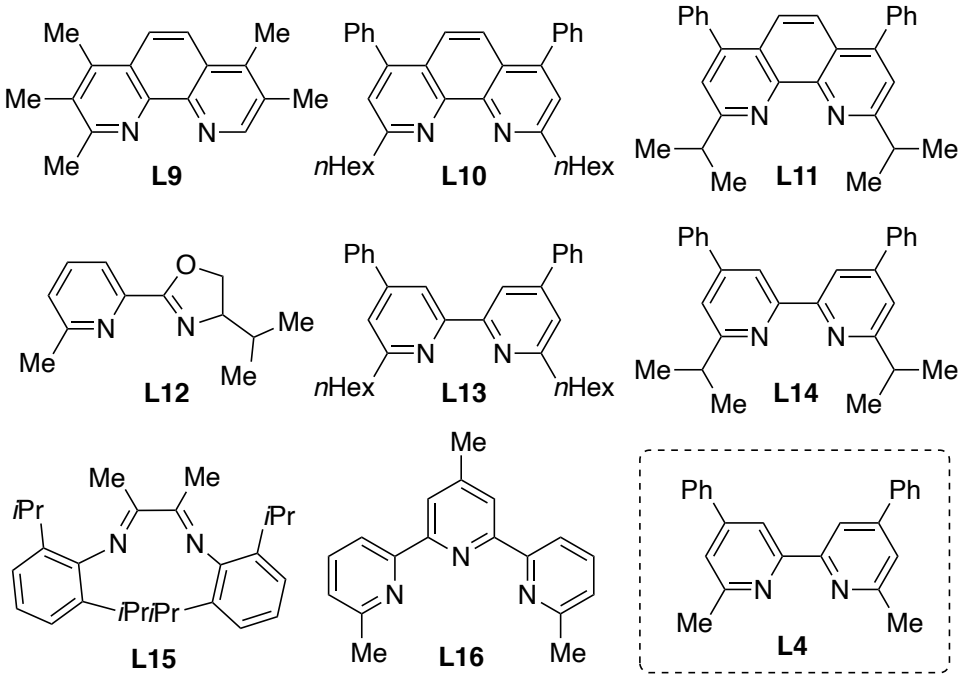
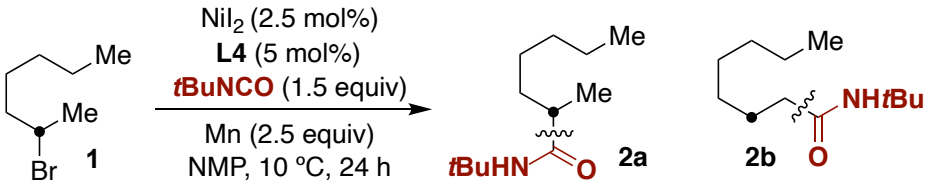


Table S2. Screening of nitrogen-containing ligands.



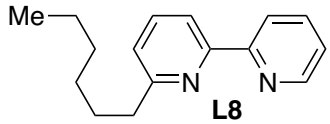
entry	Deviation	Conversion	yield **2a** + **2b** (%)	**2b:2a**
1	None	100	72	96:4
2	$NiBr_2$·dme	100	48	94:6
3	$NiCl_2$·dme	100	19	84:16
4	$Ni(acac)_2$	4	1	—
5	$Ni(COD)_2$	24	4	—
6	3 °C	92	68	91:9
7	+ TBAI (1 equiv)	82	49	96:4
8	+ TBABr (1 equiv)	86	36	94:6
9	+*i*PrBr (0.5 equiv)	100	67	96:4
10	2-iodoheptane	100	18	83:17

Table S3. Screening of different Nickel sources, ammonium salts and other additives.

Synthesis of ligands and starting materials

L4 was prepared according to a literature procedure.[2]

Synthesis of L8



L8

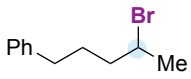
6-hexyl-2,2'-bipyridine (L8). *n*-Hexyl lithium (13.9 mL of a 2.3 M in hexane, 32 mmol; 1 equiv) was added slowly to a solution of bipyridine (5.0 g, 32 mmol, 1 equiv) in dry Et_2O (150 mL, 0.2 M) at −40 °C. The resulting red solution was stirred for 1 h under vigorous agitation. Then, the reaction mixture was quenched with brine (200 mL). The resulting biphasic yellow mixture was separated and the organic phase was extracted with diethyl ether (3 × 50 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The obtained dark orange crude product was dissolved in CH_2Cl_2 (50 mL) and MnO_2 (11.1 g, 128 mmol; 4 equiv) was added under vigorous agitation. After 3 h, the crude reaction mixture was filtered through a silica-celite plug, concentrated under reduced pressure and purified through column chromatography on silica gel (hexanes/ethyl acetate 99:5) to afford the title compound as a clear oil (4.38 g, 18.2 mmol, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H), 8.44 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.18 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 1H), 7.26 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.14 (dd, *J* = 7.7, 1.0 Hz, 1H), 2.89 – 2.81 (m, 2H), 1.86 – 1.72 (m, 2H), 1.45 – 1.25 (m, 6H), 0.93 – 0.84 (m, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.1, 156.8, 155.6, 149.2, 137.1, 136.9, 123.5, 122.8, 121.3, 118.2, 38.5, 31.9, 29.8, 29.2, 22.7, 14.2 ppm.
IR (neat, cm^{-1}): 2925, 2855, 1581, 1563, 1458, 1428, 773.
HRMS(ESI+): [$C_{16}H_{21}N_2$] (M+H) calcd. 241.1699, found 241.1693

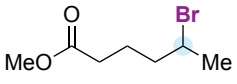
[2] Tortajada, A.; Duan, Y.; Sahoo, B.; Cong, F.; Toupalas, G.; Sallustrau, A.; Loreau, O.; Audisio, D.; Martin, R. *ACS Catal.* **2019**, *9, 7*, 5897.

Synthesis of secondary alkyl bromides

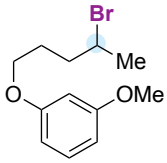
The following alkyl bromides were prepared following a literature procedure:[3,4,5]



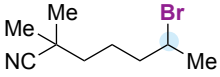
(4-bromopentyl)benzene[3]



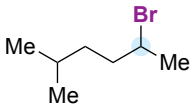
methyl 5-bromohexanoate[4]



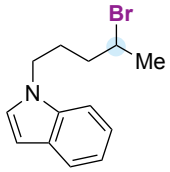
1-((4-bromopentyl)oxy)-3-methoxybenzene[4]



6-bromo-2,2-dimethylheptanenitrile[3]

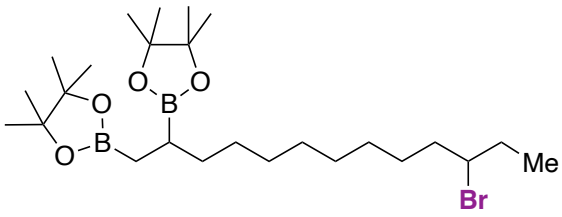


2-bromo-5-methylhexane[3]



1-(4-bromopentyl)-1*H*-indole[5]

Preparation of secondary alkyl bromides from the corresponding alcohols



2,2'-(11-bromotridecane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

Following up a known literature procedure,[6] 4-cyanopyridine (104.1 mg, 0.20 equiv), $NaBH_4$ (94.6 mg, 2.50 mmol, 0.5 equiv) and B_2pin_2 (2.54 g, 10mmol, 2 equiv) were placed in a round bottom flask under inert atmosphere. Subsequently, tridec-12-en-3-ol[7] (1.00 g, 5 mmol) and MeOH (5 mL) were added dropwise, and the mixture was heated to 100 ºC for 5 h. The reaction mixture was cooled down to rt, and brine was added to the reaction mixture. The aqueous layer was then extracted with EtOAc and the combined organic phases were dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude mixture was dissolved in a 2:1 hexane:EtOAc mixture, filtered through a pad of silica. The solvent was removed under reduced pressure and the crude was directly subjected to the general bromination conditions. Specifically, triphenylphosphine (1.15 g, 1.25 equiv.) was dissolved in CH_2Cl_2 (0.33M based on

[3] Sahoo, B.; Bellotti, P.; Juliá-Hernández, F.; Meng, Q.-Y.; Crespi, S.; König, B.; Martin, R. Site-Selective, *Chem. Eur. J.* **2019**, *25*, 9001.
[4] Juliá-Hernández, F.; Moragas, T.; Cornella, J.; Martin, R. *Nature* **2017**, *545*, 84
[5] Kaldas, S. J.; Cannillo, A.; McCallum, T.; Barriault, L. *Org. Lett.* **2015**, *17*, 2864.
[6] Xu, R.; Lu, G.; Cai, C. *New J. Chem.* **2018**, *42*, 16456.
[7] Cryle, M. J.; Matovic, N. J.; De Voss, J. J. *Org. Lett.* **2003**, *5* (18), 3341.

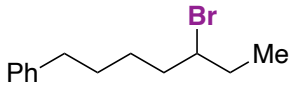
alcohol), and Br_2 (215 µL, 1.20 equiv.) was added dropwise at 0º C. After stirring the mixture for 10 min, pyridine (0.35 mL, 1.2 equiv.) and the crude alcohol (1.60 g, 1.0 equiv.) was added as a solution in CH_2Cl_2. The reaction mixture was allowed to warm up to rt and stirred overnight. The mixture was quenched with aq. saturated NH_4Cl and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica gel (hexane/ethyl acetate 100/0 to 95/5) to obtain the desired product as a colorless oil (966.7 mg, 38% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.95 (tt, *J* = 7.8, 4.9 Hz, 1H), 1.88 – 1.71 (m, 4H), 1.54 – 1.33 (m, 4H), 1.27 – 1.22 (m, 10H), 1.20 (s, 24H), 1.11 – 1.04 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H), 0.89 – 0.69 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.8, 82.7, 60.6, 38.8, 33.8, 32.1, 29.8, 29.5, 29.4, 29.0, 28.8, 27.6, 24.9, 24.8, 24.8, 24.7, 18.4 (br), 12.7 (br), 12.0 ppm.

IR (neat, cm^{-1}): 2976, 2924, 2854, 1462, 1369, 1310, 1214, 1140, 968, 846.

HRMS (ESI+): $[C_{25}H_{49}B_2BrNaO_4]^+$ (M+Na) calcd. 537.2893, found. 537.2897.



(6-bromooctyl)benzene. To a 250 mL round bottom flask containing a solution of triphenylphosphine (1.41g, 5,37 mmol) in DCM (30 mL) at 0 °C, bromine (858,6 mg, 5,37 mmol) was added dropwise and the mixture was stirred for 30 min. Then, a solution of 7-phenylheptan-3-ol[8] (861 mg, 4,48 mmol) in DCM (20 M) and pyridine (433,7 mL, 5,37 mmol) were subsequently added and the mixture was stirred for 4 h at rt. The mixture was partially concentrated and filtered through a plug of silica eluting with pentane. The filtrate was evaporated and the residue purified by flash column chromatography (EtOAc/Hexanes 5-10%), affording the corresponding bromide as a colorless oil (900 mg, 3,53 mmol, 79% yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 3.98 (tt, *J* = 7.9, 5.0 Hz, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.95 – 1.74 (m, 4H), 1.71 – 1.56 (m, 3H), 1.52 – 1.41 (m, 1H), 1.04 (t, *J* = 7.3 Hz, 3H) ppm.

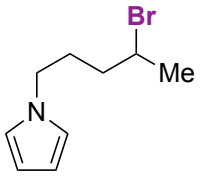
[8] Tanaka, K.; Ewing, W. R.; Yu, J.-Q. Hemilabile Benzyl Ether Enables γ-C(Sp^3)–H Carbonylation and Olefination of Alcohols. *J. Am. Chem. Soc.* **2019**, *141*, 15494.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.6, 128.5, 128.4, 125.9, 60.5, 38.8, 35.9, 32.3, 31.1, 27.5, 12.2 ppm

IR (neat, cm^{-1}): 3062, 3026, 2966, 2934, 2858, 1603, 1496, 1453, 745, 697.

HRMS (APCI+): $[C_{13}H_{19}]^+$ $(M\text{-}Br)^+$ calcd. 175.1481, found. 175.1476.

Synthesis of secondary alkyl bromides from 1,4-dibromopentane

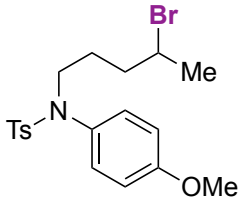


1-(4-bromopentyl)-1*H*-pyrrole. A solution of pyrrole (0.69 mL, 10 mmol; 1 equiv) in DMF (5 mL) was added slowly over a round bottom flask containing NaH (0.48 g of 60% NaH in mineral oil, 12 mmol; 1.20 equiv) in DMF (100 mL). The mixture was stirred at rt for 1h, and a solution of 1,4-dibromopentane (4 mL, 30 mmol; 3 equiv) in DMF (40 mL) was slowly added. After stirring at rt for 48h, the mixture was evaporated under reduced pressure, and the crude was purified through column chromatography to afford the title compound as a light-yellow oil (1.06 g, 4.9 mmol; 49% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.65 (s, 2H), 6.15 (s, 2H), 4.12 – 4.05 (m, 1H), 3.92 (td, *J* = 6.9, 1.3 Hz, 2H), 2.08 – 2.00 (m, 1H), 1.97 – 1.84 (m, 1H), 1.84 – 1.71 (m, 2H), 1.69 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 120.6, 108.3, 50.9, 49.0, 38.2, 29.9, 26.6 ppm.

IR (neat, cm^{-1}): 3099, 2924, 1684, 1499, 1445, 1280, 1088, 1066, 720, 617, 535. **HRMS (APCI$^+$):** $[C_9H_{15}BrN]^+$ (M+H) calcd. 216.0382, found. 216.0373.



***N*-(4-bromopentyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide**. A solution of *p*-MeO-Tosylaniline (1g, 3.61 mmol, 1.0 equiv) and K_2CO_3 (598 mg, 4,33 mmol, 1.2 equiv.) in DMF (6 mL) was stirred for 1 h at rt. Then, 1,4-dibromopentane (1.66 g, 7.21 mmol, 2.0 equiv) was added dropwise and stirred at rt for 24-48 h. Then, the mixture was extracted with EtOAc and washed with brine (3x). The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by flash column chromatography in silica gel with hexane/EtOAc, affording the title compound as a yellow viscous oil (800 mg, 1,88 mmol, 52% yield)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.45 (m, 2H), 7.30 – 7.21 (m, 2H), 6.98 – 6.91 (m, 2H), 6.86 – 6.79 (m, 2H), 4.12 (dqd, *J* = 8.5, 6.5, 4.6 Hz, 1H), 3.81 (s, 3H), 3.58 (dt,

J = 13.5, 6.9 Hz, 1H), 3.48 (dt, *J* = 13.0, 6.4 Hz, 1H), 2.43 (s, 3H), 1.98 – 1.73 (m, 2H), 1.69 (d, *J* = 6.6 Hz, 3H), 1.67 – 1.60 (m, 1H), 1.48 – 1.59 (m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 143.3, 135.2, 131.3, 129.9, 129.4, 127.7, 114.3, 55.4, 51.0, 49.8, 37.6, 26.6, 26.2, 21.6 ppm.

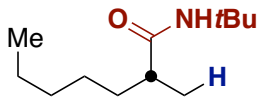
IR (neat, cm^{-1}): 2925, 2838, 1605, 1506, 1443, 1343, 1246, 1158, 1089, 1030, 902, 814, 676, 579, 545.

HRMS (ESI+): $[C_{19}H_{24}BrNNaO_3S]^+$ (M+Na) calcd. 448.0552, found. 448.0552.

Catalytic regiodivergent amidation of secondary alkyl bromides with isocyanates.

General Procedure A. In a nitrogen-filled glovebox, an oven-dried screw-capped test tube containing a stirring bar was charged with $NiBr_2$ (2.7 mg, 0.013 mmol; 2.5 mol%), 6-hexyl-2,2'-bipyridine (**L8**) (6.0 mg, 0.025, 5.0 mol%), Mn (41.2 mg, 0.750 mmol; 1.5 equiv) and DMF (0.5 mL). The mixture was stirred at rt until a deep green color was observed (30-45 min). Subsequently, the alkyl bromide (0.5 mmol, 1 equiv) and isocyanate (0.75 mmol, 1.5 equiv) were added dropwise, and the crude was stirred for 24 h at 3 °C. Then, the mixture was carefully quenched with 5% aq. HCl (1 mL) or saturated aq. NH_4Cl (2 mL) (if sensitive functional groups were present) followed by addition of distilled water (*ca*. 10 mL) and ethyl acetate (3 × 15 mL). The organic phase was washed with brine (40 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc or pentane/Et_2O).

General Procedure B. In a nitrogen-filled glovebox, an oven-dried screw-capped test tube containing a stirring bar was charged with NiI_2 (3.9 mg, 0.013 mmol; 2.5 mol%), 6,6'-dimethyl-4,4'-diphenyl-2,2'-bipyridine (**L4**) (8.4 mg, 0.025, 5.0 mol%), Mn (68.7 mg, 1.25 mmol; 2.5 equiv) and NMP (1.0 mL). The mixture was stirred at rt until a deep purple color was observed (20-30 minutes). Subsequently, the alkyl bromide (0.5 mmol, 1 equiv) and isocyanate (0.75 mmol, 1.5 equiv) were added dropwise, and the crude was stirred for 24 h at 3 °C. Then, the mixture was carefully quenched with 5% aq. HCl (1 mL) or saturated aq. NH_4Cl (2 mL) (if sensitive functional groups were present) followed by addition of distilled water (*ca*. 10 mL) and ethyl acetate (3 × 15 mL). The organic phase was washed with brine (40 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc or pentane/Et_2O).



2a

***N*-(*tert*-butyl)-2-methylheptanamide (2a).** Following general procedure A, starting from 2-bromoheptane (89.6 mg, 0.50 mmol, 1 equiv) and tert-butyl isocyanate (86.0 µL, 0.75 mmol, 1.50 equiv), compound **2a** was obtained as a white solid (91.6 mg, 92% yield).

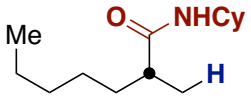
^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.21 (s, 1H), 2.07 – 1.93 (m, 1H), 1.65 – 1.50 (m, 1H), 1.34 (s, 9H), 1.33 – 1.21 (m, 7H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 176.1, 51.1, 42.5, 34.6, 32.0, 29.0, 27.3, 22.7, 18.1, 14.2 ppm.

mp: 57.9 – 60.2 °C.

IR (neat, cm^{-1}): 3314, 2961, 2928, 2859, 1646, 1543, 1453, 1362, 1226.

HRMS (ESI+): $[C_{12}H_{25}NNaO]^+$ (M+Na) calcd. 222.1828, found 222.1833.



3a

***N*-cyclohexyl-2-methylheptanamide (3a)** Following procedure A, starting from 2-bromoheptane (89.6 mg, 0.50 mmol; 1 equiv) and CyNCO (93.9 mg, 0.70 mmol, 1.50 equiv), compound **3a** was obtained as an off-white solid (47.3 mg, 42% yield).

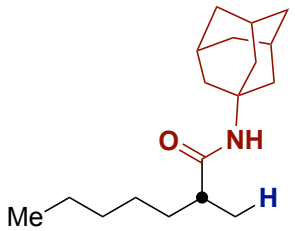
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.36 (s, 1H), 3.88 – 3.55 (m, 1H), 2.17 – 2.00 (m, 1H), 1.95 – 1.83 (m, 2H), 1.75 – 1.54 (m, 4H), 1.42 – 1.20 (m, 10H), 1.12 – 1.05 (m, 2H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm .

^{13}C NMR (1001 MHz, $CDCl_3$): δ = 175.7, 47.9, 41.9, 34.5, 33.5, 33.3, 31.9, 27.2, 25.7, 25.0, 25.0, 22.7, 18.1, 14.1 ppm.

mp: 85 – 87 ºC

IR (neat, cm^{-1}): 3282, 3086, 2959, 2925, 2852, 1636, 1547, 1444, 1349, 1272, 1235, 1155, 1099, 892, 712.

HRMS (ESI+): $[C_{14}H_{28}NO]^+$ (M+H) calcd. 226.2165, found 226.2161.



4a

***N*-(adamantan-1-yl)-2-methylheptanamide (4a).** Following procedure A, starting from 2-bromoheptane (89.6 mg, 0.50 mmol, 1 equiv) and 1-isocyanatoadamantane (158,4 mg, 0.75 mmol; 1.50 equiv), compound **4a** was obtained as a white solid (111,8 mg, 80 % yield).

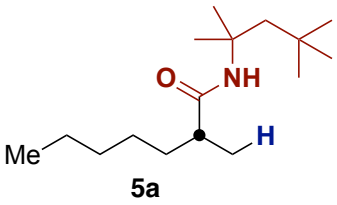
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.08 (s, 1H), 2.12 – 2.06 (m, 2H), 2.04 – 2.00 (m, 7H), 1.72– 1.52 (m, 8H), 1.39 – 1.19 (m, 7H), 1.10 (d, *J* = 6.8 Hz, 3H), 0.95 – 0.83 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 51.6, 42.4, 41.8, 41.8, 36.4, 36.3, 34.5, 31.9, 29.5, 27.1, 22.6, 18.1, 14.0 ppm.

m.p.: 99-101°C.

IR (neat, cm^{-1}): 2399, 2959, 2904, 2849, 1641, 1542, 1451, 1360, 1236, 1102, 670.

HRMS (ESI+): $[C_{18}H_{32}NO]^+$ (M+H) calcd. 278.2478, found 278.2470.



5a

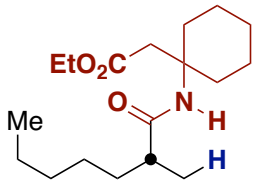
2-methyl-*N*-(2,4,4-trimethylpentan-2-yl)heptanamide (5a). Following procedure A, starting from 2-bromoheptane (89.6 mg, 0.50 mmol; 1 equiv) and *tert*-octyl isocyanate (127.0 mg, 0.75 mmol; 1.50 equiv), compound **5a** was obtained as a colorless oil (106,6 mg, 79 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.30 (s, 1H), 2.05 – 1.93 (m, 1H), 1.75 (d, *J* = 14.9 Hz, 1H), 1.61 (d, *J* = 14.9 Hz, 1H), 1.57 – 1.50 (m, 1H), 1.35 (d, *J* = 4.3 Hz, 6H), 1.31 – 1.16 (m, 7H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.96 (s, 9H), 0.82 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.6, 55.0, 52.1, 42.6, 34.4, 31.9, 31.7, 31.6, 29.3, 29.2, 27.2, 22.6, 17.9, 14.1 ppm.

IR (neat, cm^{-1}): 3325, 2956, 2930, 2872, 1644, 1541, 1458, 1387, 1364, 1253, 1227, 733.

HRMS (ESI+): $[C_{16}H_{33}NNaO]^+$ (M+Na) calcd. 278.2454, found 278.2455.



6a

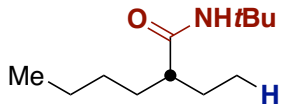
Ethyl 2-(1-(2-methylheptanamido)cyclohexyl)acetate (6a) Following procedure A, starting from 2-bromoheptane (132.9 mg, 0.50 mmol; 1 equiv) and ethyl 2-(1-isocyanatocyclohexyl)acetate (158,4 mg, 0.75 mmol; 1.50 equiv), compound **6a** was obtained as yellowish oil (70.1 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.34 (s, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 2.87 (d, *J* = 15.0 Hz, 1H), 2.75 (d, *J* = 15.1 Hz, 1H), 2.33 – 2.15 (m, 2H), 2.15 – 2.02 (m, 1H), 1.68 – 1.39 (m, 9H), 1.32 – 1.23 (m, 7H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.86 (t, *J* = 6.7 Hz, 3H) ppm .

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.5, 171.4, 60.1, 54.1, 42.6, 42.1, 34.9, 34.8, 34.3, 31.9, 27.3, 25.6, 22.6, 21.8, 21.6, 18.1, 14.3, 14.1 ppm.

IR (neat, cm^{-1}): 3338, 2928, 2857, 1730, 1650, 1529, 1450, 1369, 1249, 1214, 1133, 1032, 499, 469.

HRMS (ESI+): $[C_{18}H_{34}NO_3]^+$ (M+H) calcd. 312.2533, found 312.2539.



2a'

***N*-(*tert*-butyl)-2-ethylhexanamide (2a'** Following general procedure A, starting from 3-bromoheptane (89.6 mg, 0.50 mmol; 1 equiv), compound **2a'** was obtained as a white solid (79.5 mg, 80% yield).

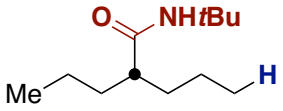
^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.21 (s, 1H), 1.78 – 1.70 (m, 1H), 1.63 – 1.50 (m, 2H), 1.35 (s, 9H), 1.32 – 1.20 (m, 6H), 0.88 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.3, 51.3, 50.7, 32.9, 30.0, 29.1, 26.4, 22.9, 14.2, 12.3 ppm.

m.p.: 78.2 − 80.0 °C.

IR (neat, cm^{-1}): 3308, 2958, 2928, 2872, 2859, 1644, 1544, 1456, 1358, 1270, 1253, 1224, 905, 675.

HRMS (ESI+): $[C_{12}H_{26}NO]^+$ (M+H) calcd. 200.2009, found 200.2009.



2a''

***N*-(*tert*-butyl)-2-propylpentanamide (2a'').** Following general procedure A, starting from 4-bromoheptane (89.6 mg, 0.500 mmol; 1 equiv), compound **2a''** was obtained as a colorless solid (75.3 mg, 76% yield).

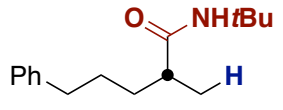
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (s, 1H), 1.91 – 1.77 (m, 1H), 1.59 – 1.43 (m, 2H), 1.29 (s, 9H), 1.26 – 1.13 (m, 6H), 0.83 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.4, 51.1, 48.4, 35.5, 28.9, 20.8, 14.2 ppm.

m.p.: 108.0 – 109.9 °C.

IR (neat, cm^{-1}): 3294, 3076, 2956, 2929, 2872, 1638, 1549, 1448, 1360, 1266, 1228, 1121, 938, 754, 682.

HRMS (ESI+): $[C_{12}H_{25}NNaO]^+$ (M+Na) calcd. 222.1828, found 222.1823.



7a

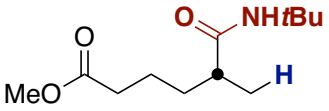
N-(tert-butyl)-2-methyl-5-phenylpentanamide (7a). Following general procedure A, starting from (4-bromopentyl)benzene (113.57 mg, 0,5 mmol), compound **7a** was obtained as a white solid (84.6 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.26 (m, 2H), 7.20 (m, 3H), 5.24 (s, 1H), 2.72 – 2.50 (m, 2H), 2.13 – 1.95 (m, 1H), 1.78 – 1.55 (m, 3H), 1.48 – 1.39 (m, 1H), 1.35 (s, 9H), 1.11 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 175.9, 142.5, 128.5, 128.4, 125.8, 51.1, 42.3, 36.1, 34.2, 29.4, 29.0, 18.2 ppm.

IR (neat, cm^{-1}): 3317, 3027, 2966, 2931, 2860, 1645, 1542, 1452, 1362, 1256, 1225, 747, 697.

HRMS (ESI+): $[C_{16}H_{25}NNaO]^+$ (M+H) calcd. 270.1828, found 270.1820.



8a

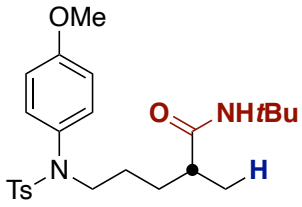
Methyl 6-(*tert*-butylamino)-5-methyl-6-oxohexanoate (8a). Following general procedure A, starting from methyl 5-bromohexanoate (104.5 mg, 0.50 mmol; 1 equiv), *tert*-butyl isocyanate (172 µL, 1.5 mmol, 3 equiv) and Mn (55.0 mg, 2 equiv), compound **8a** was obtained as a clear oil (87.7 mg , 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.32 (s, 1H), 3.65 (s, 3H), 2.37 – 2.22 (m, 2H), 2.10 – 1.98 (m, 1H), 1.68 – 1.52 (m, 3H), 1.39 – 1.34 (m, 1H), 1.33 (s, 9H), 1.09 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.6, 174.1, 51.6, 51.2, 42.2, 34.0, 33.9, 29.0, 22.9, 18.2 ppm.

IR (neat, cm^{-1}): 3320, 2965, 2874, 1738, 1647, 1536, 1452, 1224.

HRMS (ESI+): $[C_{12}H_{23}NNaO_3]^+$ (M+Na) calcd. 252.1570, found 252.1566



9a

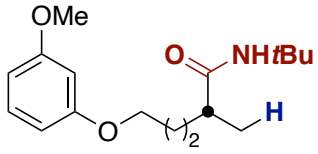
N-(tert-butyl)-5-(N-(4-methoxyphenyl)-4-methylphenylsulfonamido)-2-methylpentanamide (9a). Following procedure A, starting from *N*-(4-bromopentyl)-*N*-(4-methoxyphenyl)-4 methylbenzenesulfonamide (300 mg, 0,7 mmol; added as a 1 mL solution in DMF), compound **9a** was obtained as a colorless viscous oil (196.7 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 – 7.32 (m, 2H), 7.22 – 7.13 (m, 2H), 6.90 – 6.82 (m, 2H), 6.78 – 6.69 (m, 2H), 5.53 (s, 1H), 3.72 (s, 3H), 3.50 (dt, *J* = 13.4, 6.9 Hz, 1H), 3.35 (dt, *J* = 13.0, 6.4 Hz, 1H), 2.35 (s, 3H), 2.14 – 1.99 (m, 1H), 1.68 – 1.52 (m, 1H), 1.40 – 1.28 (m, 3H), 1.23 (s, 9H), 0.98 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ =175.6, 159.0, 143.3, 135.2, 131.3, 129.9, 129.4, 127.6, 114.2, 55.4, 50.8, 50.1, 40.7, 30.9, 28.7, 25.5, 21.5, 17.5 ppm.

IR (neat, cm^{-1}): 3388, 3322, 2965, 2931, 2871, 1649, 1507, 1340, 1248, 1159, 1089, 1031, 913, 678, 581, 559, 546.

HRMS (ESI+): $[C_{24}H_{35}N_2O_4S]^+$ (M+H) calcd. 447.2312, found 447.2313.



10a

***N*-(*tert*-butyl)-5-(3-methoxyphenoxy)-2-methylpentanamide (10a).** Following general procedure A and starting from 1-((4- bromopentyl)oxy)-3-methoxybenzene (136.6 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **10a** was obtained as a colorless solid (110.1 mg, 75% average yield).

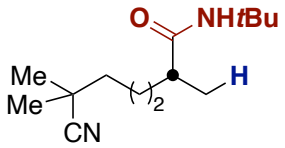
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17 (t, *J* = 8.2 Hz, 1H), 6.53 – 6.46 (m, 2H), 6.45 (t, *J* = 2.3 Hz, 1H), 5.31 (s, 1H), 4.02 – 3.95 (m, 1H), 3.95 – 3.88 (m, 1H), 3.79 (s, 3H), 2.16 – 2.10 (m, 1H), 1.82 – 1.72 (m, 3H), 1.59 – 1.50 (m, 1H), 1.35 (s, 9H), 1.13 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 175.7, 161.0, 160.3, 130.0, 106.8, 106.4, 101.1, 68.2, 55.4, 51.2, 42.1, 31.3, 29.0, 27.3, 18.3 ppm.

IR (neat, cm^{-1}): 3322, 2964, 2873, 1649, 1594, 1493, 1453, 1151, 1046.

HRMS (ESI+): $[C_{17}H_{27}NNaO_3]^+$ (M+Na) calcd. 316.1883, found 316.1870.

m.p.: 69.9 – 72.9 °C.



11a

***N*-(*tert*-butyl)-6-cyano-2,6-dimethylheptanamide (11a).** Following general procedure A and starting from 6-bromo-2,2-dimethylheptanenitrile (109.1 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **11a** was obtained as an off white solid (100.6 mg, 87% yield).

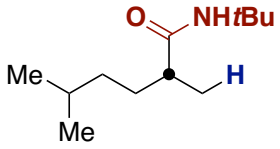
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.33 (s, 1H), 2.12 – 1.98 (m, 1H), 1.70 – 1.56 (m, 1H), 1.52 – 1.42 (m, 5H), 1.32 (s, 9H), 1.30 (s, 3H), 1.28 (s, 3H), 1.08 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.6, 125.2, 51.1, 42.2, 41.0, 34.2, 32.5, 28.9, 27.0, 26.5, 23.4, 18.2 ppm.

IR (neat, cm^{-1}): 3296, 3079, 2967, 2932, 2870, 2235, 1644, 1551, 1459, 1390, 1361, 1265, 1225, 687.

HRMS (ESI+): $[C_{14}H_{27}N_2O]^+$ (M+H) calcd. 239.2118, found 239.2118.

Mp: 86.1 – 88.4 °C



12a

N-(tert-butyl)-2,5-dimethylhexanamide (12a). Following general procedure A and starting from *2-bromo-5-methylhexane,* 90 mg (0,5 mmol), compound **12a** was obtained as a white solid (56.5 mg, 0,28 mmol, 57% yield).

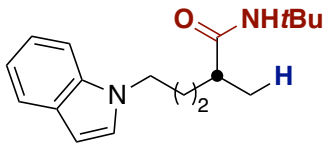
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.24 (s, 1H), 2.07 – 1.86 (m, 1H), 1.63 – 1.40 (m, 2H), 1.37 – 1.25(m, 10H), 1.19 – 1.09 (m, 2H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.85 (dd, *J* = 6.7, 0.9 Hz, 6H). ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 176.1, 51.0, 42.6, 36.8, 32.4, 29.0, 28.3, 28.2, 22.7, 22.7, 18.1 ppm.

IR (neat, cm^{-1}): 3312, 3076, 2961, 2930, 2870, 1644, 1546, 1451, 1390, 1360, 1263, 1227, 672.

HRMS (ESI+): $[C_{12}H_{26}NO]^+$ (M+H) calcd. 200.2009, found 200.2008.

mp: 52.2 – 54.0 °C



13a

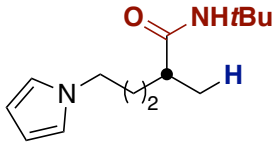
***N*-(*tert*-butyl)-5-(1H-indol-1-yl)-2-methylpentanamide (13a).** Following general procedure A and starting from 1-(4-bromopentyl)-1H-indole (133.1 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **13a** was obtained as a yellow oil (134.7, 93% average yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.23 – 7.17 (m, 1H), 7.12 – 7.07 (m, 2H), 6.49 (dd, *J* = 3.1, 0.8 Hz, 1H), 5.07 (s, 1H), 4.21 – 4.03 (m, 2H), 1.93 – 1.87 (m, 1H), 1.87 – 1.78 (m, 2H), 1.72 – 1.61 (m, 1H), 1.40 – 1.31 (m, 1H), 1.29 (s, 9H), 1.05 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.4, 136.0, 128.7, 127.9, 121.6, 121.1, 119.4, 109.5, 101.2, 51.2, 46.6, 42.0, 31.9, 28.9, 28.1, 18.4 ppm.

IR (neat, cm^{-1}): 3322, 2965, 2931, 2872, 1646, 1510, 1362, 1224, 737.

HRMS (ESI+): $[C_{18}H_{26}N_2NaO]^+$ (M+Na) calcd. 309.1937, found 309.1943.



14a

***N*-(*tert*-butyl)-2-methyl-5-(1H-pyrrol-1-yl)pentanamide (14a).** Following general procedure A and starting from 1-(4-bromopentyl)-1H-pyrrole (108.1 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **14a** was obtained as a beige solid (106.0 mg, 90% average yield).

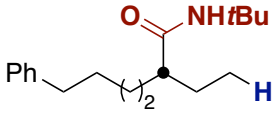
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.64 (s, 2H), 6.14 (s, 2H), 5.17 (s, 1H), 3.96 – 3.87 (m, 1H), 3.87 – 3.78 (m, 1H), 1.96 – 1.85 (m, 1H), 1.80 – 1.69 (m, 2H), 1.68 – 1.56 (m, 1H), 1.33 (s, 9H), 1.37 – 1.28 (m, 1H), 1.07 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.5, 120.6, 108.1, 51.2, 49.8, 41.9, 31.8, 29.5, 29.0, 18.3 ppm.

IR (neat, cm^{-1}): 3320, 2965, 2931, 2873, 1645, 1541, 1452, 1088, 719.

HRMS (ESI+): $[C_{14}H_{24}N_2NaO]^+$ (M+Na) calcd. 259.1781, found 259.1785.

m.p.: 59.5 – 61.9 °C.



15a

N-(tert-butyl)-2-ethyl-6-phenylhexanamide (15a). Following general procedure A and starting from (5-bromoheptyl)benzene (127.6 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **15a** was obtained as a white solid (113.0 mg, 82% average yield).

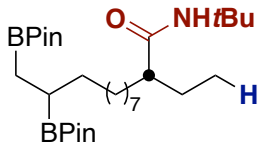
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 5.29 (s, 1H), 2.61 (t, *J* = 7.3 Hz, 2H), 1.83 – 1.72 (m, 1H), 1.67 – 1.52 (m, 4H), 1.35 (s, 9H), 1.45 – 1.22 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.2, 142.7, 128.5, 128.4, 125.8, 51.3, 50.6, 36.0, 33.0, 31.6, 29.0, 27.4, 26.4, 12.2 ppm.

IR (neat, cm^{-1}): 3320, 3026, 2962, 2930, 2858, 1644, 1540, 1453, 1391, 1361, 1225, 745, 697.

HRMS (ESI+): $[C_{18}H_{29}NNaO]^+$ (M+Na) calcd. 298.2141, found 298.2140.

mp: 68.1 – 70.2 ºC.



16a

***N*-(*tert*-butyl)-2-ethyl-12-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dodecanamide (16a).** Following general procedure A and starting from 2,2'-(11-bromotridecane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (258.0 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **16a** was obtained as a yellow oil (242.7 mg, 91% average yield).

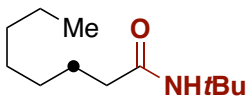
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (s, 1H), 1.71 (dq, *J* = 9.5, 4.7 Hz, 1H), 1.57 – 1.43 (m, 2H), 1.41 – 1.32 (m, 3H), 1.30 (s, 9H), 1.22 – 1.10 (m, 37H), 1.08 – 1.02 (m, 1H), 0.82 (t, *J* = 7.5 Hz, 3H), 0.75 (d, *J* = 5.8 Hzz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.2, 82.8, 82.7, 51.1, 50.4, 33.8, 33.0, 29.8, 29.7, 29.5, 29.5, 28.9, 28.8, 27.6, 26.2, 24.9, 24.8, 24.8, 24.7, 18.4, 12.7, 12.1 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 33.1 ppm.

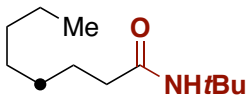
IR (neat, cm^{-1}): 3338, 2976, 2926, 2854, 2246, 1650, 1539, 1454, 1370, 1312, 1215, 1141, 968, 909, 846, 730.

HRMS (ESI+): $[C_{30}H_{60}NB_2O]^+$ (M+H) calcd. 536.4644, found 536.4645.



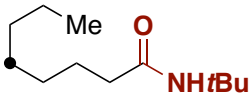
2b

***N*-(*tert*-butyl)octanamide (2b)** Following procedure B, starting from **2-bromoheptane** (89.6 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **2b** was obtained as a 24:1 **2b**:**2a** by GC analysis of the crude. Chromatographic purification provided the compound as a pale-yellow oil (71.8 mg, 72% yield).



2b

***N*-(*tert*-butyl)octanamide (2b)** Following procedure B, starting from **3-bromoheptane** (89.6 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **2b** was obtained as a 10:1 **2b**:(**2a**+**2a'**) by GC analysis of the crude. Chromatographic purification provided the compound as a pale-yellow oil (56.9 mg, 57% yield)

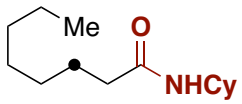


2b

***N*-(*tert*-butyl)octanamide (2b)** Following procedure B, starting from **4-bromoheptane** (89.6 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **2b** was obtained as a 8:1 **2b**:(**2a**+**2a'**+**2a''**) by GC analysis of the crude. Chromatographic purification provided the compound as a pale-yellow oil (66.1 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (s, 1H), 2.07 (d, *J* = 7.5 Hz, 2H), 1.58 (p, *J* = 7.0 Hz, 2H), 1.33 (s, 9H), 1.32 – 1.21 (m, 8H), 0.86 (t, *J* = 6.7 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.7, 51.2, 37.9, 31.8, 29.3, 29.2, 29.0, 25.9, 22.7, 14.2 ppm.



3b

***N*-cyclohexyloctanamide (3b).** Following procedure B and starting from 2-bromoheptane (89.6 mg, 0.500 mmol; 1 equiv) and cyclohexyl isocyanate (93.9 mg, 0.750 mmol; 1.50 equiv), compound **3b** was obtained as an off-white solid (57.5 mg, 51% yield).

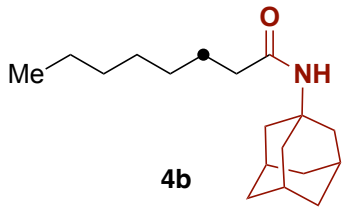
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.47 (s, 1H), 3.80 – 3.67 (m, 1H), 2.14 – 2.06 (m, 2H), 1.87 (dd, *J* = 12.6, 4.0 Hz, 2H), 1.72 – 1.58 (m, 2H), 1.61 – 1.52 (m, 3H), 1.47 – 1.17 (m, 10H), 1.18 – 1.04 (m, 3H), 0.84 (t, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 48.1, 37.2, 33.3, 31.8, 29.3, 29.1, 26.0, 25.7, 25.0, 22.7, 14.1 ppm.

m.p: 76-77 ºC

Spectroscopic data is in agreement with the literature.[9]

[9] Lücking, U.; Tucci, F. C.; Rudkevich, D. M.; Rebek, J. Self-Folding Cavitands of Nanoscale Dimensions. *J. Am. Chem. Soc.* **2000**, *122* (37), 8880–8889. https://doi.org/10.1021/ja001562l.



4b

***N*-(adamantan-1-yl)octanamide (4b).** Following general procedure B and starting from 2-bromoheptane (89.6 mg, 0.500 mmol; 1 equiv) and 1-isocyanatoadamantane (133 mg, 0.750 mmol; 1.50 equiv), compound **4b** was obtained as a white solid (97 mg, 70% yield).

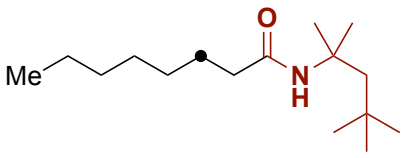
^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.17 (s, 1H), 2.11 – 2.03 (m, 5H), 1.99 (d, *J* = 2.9 Hz, 6H), 1.67 (t, *J* = 3.1 Hz, 6H), 1.58 (p, *J* = 7.0 Hz, 2H), 1.33 – 1.21 (m, 8H), 0.92 – 0.82 (m, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.4, 51.7, 41.7, 37.8, 36.4, 31.7, 29.5, 29.2, 29.1, 25.8, 22.6, 14.1 ppm.

m.p.: 69-71°C.

IR (neat, cm^{-1}): 3297, 3073, 2902, 2846, 1635, 1546, 1467, 1453, 1359, 1293, 691, 647.

HRMS (ESI+): $[C_{18}H_{32}NO]^+$ (M+H) calcd. 278.2478, found 278.2478.



5b

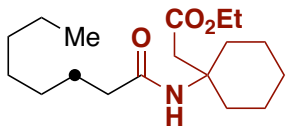
N-(2,4,4-trimethylpentan-2-yl)octanamide (5b). Following general procedure B and starting from t*ert*-octyl isocyanate (127 mg, 0.750 mmol; 1.50 equiv), compound **5b** was obtained as colorless oil (104,7 mg, 82 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (s, 1H), 2.11 – 1.99 (m, 2H), 1.72 (s, 2H), 1.56 (q, *J* = 7.3 Hz, 2H), 1.37 (s, 6H), 1.34 – 1.17 (m, 8H), 0.98 (s, 9H), 0.91 – 0.76 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.5, 55.4, 51.9, 38.3, 32.1, 32.0, 31.9, 31.8, 29.7, 29.6, 29.4, 26.0, 23.0, 14.4 ppm.

IR (neat, cm^{-1}): 3304, 2954, 2926, 2858, 1642, 1548, 1467, 1364, 1228.

HRMS (ESI+): $[C_{16}H_{33}NNaO]^+$ (M+Na) calcd. 278.2454, found 278.2455.



6b

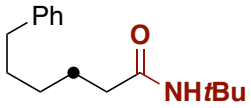
Ethyl 2-(1-octanamidocyclohexyl)acetate (**6b**). Following procedure B and starting from 2-bromoheptane (132.9 mg, 0.500 mmol; 1 equiv) and ethyl 2-(1-isocyanatocyclohexyl)acetate (158,4 mg, 0.750 mmol; 1.50 equiv), compound **6b** was obtained as yellowish oil (78.0 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.33 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.79 (s, 2H), 2.21 – 2.14 (m, 2H), 2.11 (t, *J* = 7.4 Hz, 2H), 1.62 – 1.36 (m, 9H), 1.30 – 1.21 (m, 9H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.0 Hz, 3H) ppm .

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.1, 171.4, 60.1, 54.3, 41.9, 37.8, 34.9, 31.8, 29.3, 29.1, 25.8, 25.5, 22.7, 21.7, 14.3, 14.1 ppm.

IR (neat, cm^{-1}):3309, 2926, 2855, 1731, 1645, 1538, 1450, 1369, 1179, 1132, 1033.

HRMS (ESI+): $[C_{18}H_{34}NO_3]^+$ (M+H) calcd. 312.2533, found 312.2541.



7b

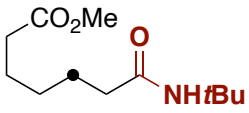
***N*-(*tert*-butyl)-6-phenylhexanamide (7b).** Following procedure B and starting from (4-bromopentyl)benzene (113.6 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), an inseparable mixture of compounds **7b:7a** (95:5) was obtained as a pale-yellow oil (61.1 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.22 (m, 2H), 7.19 – 7.11 (m, 3H), 5.35 (s, 1H), 2.65 – 2.56 (m, 2H), 2.07 (t, *J* = 7.5 Hz, 2H), 1.69 – 1.57 (m, 2H), 1.41 – 1.34 (m, 2H), 1.33 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.5, 142.6, 128.4, 128.3, 125.7, 51.1, 37.6, 35.8, 31.2, 29.7, 28.9, 28.8, 25.7 ppm.

IR (neat, cm^{-1}): 3307, 2964, 2929, 2858, 1643, 1544, 1453, 1361, 1224, 745, 697.

HRMS (ESI+): $[C_{16}H_{25}NNaO]^+$ (M+Na) calcd. 270.1828, found 2701818.



8b

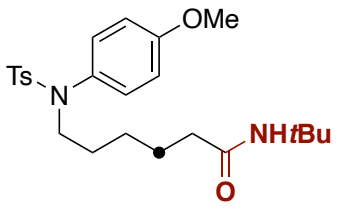
Methyl 7-(*tert*-butylamino)-7-oxoheptanoate (8b). Following procedure B and starting from methyl 5-bromohexanoate (104.5 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **8b** was obtained as a yellow oil (65.0 mg, 57%) as an inseparable 92:8 mixture of terminal amidation : amidation next to the carbonyl group.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.25 (s, 1H), 3.65 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.07 (t, *J* = 7.5 Hz, 2H), 1.68 – 1.53 (m, 4H), 1.38 – 1.26 (m, 2H), 1.33 (s, 9H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 174.3, 172.3, 51.6, 51.2, 37.5, 34.0, 29.0, 28.7, 25.4, 24.7 ppm.

IR (neat, cm^{-1}): 3315, 2957, 2865, 1737, 1645, 1542, 1454, 1362, 1223, 1172, 1088.

HRMS (ESI+): $[C_{12}H_{24}NO_3]^+$ (M+H) calcd. 230.1751, found 230.1744.



9b

N-(tert-butyl)-6-(N-(4-methoxyphenyl)-4-methylphenylsulfonamido)hexanamide (9b). Following general procedure B, starting from 213,18 mg (0,5 mmol) of *N*-(4-bromopentyl)-*N*-(4-methoxyphenyl)-4 methylbenzenesulfonamide which was added as an 0,7 mL solution in NMP to a 0,3 mL solution of reaction mixture (overall volume 1 mL). Compound **9b** was obtained as an off white solid (112,10 mg, 0,25 mmol, 50% yield).

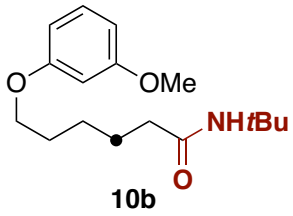
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 6.93 – 6.85 (m, 2H), 6.82 – 6.74 (m, 2H), 5.35 (s, 1H), 3.77 (d, *J* = 1.6 Hz, 3H), 3.44 (td, *J* = 6.8, 1.5 Hz, 2H), 2.39 (d, *J* = 1.7 Hz, 3H), 2.02 (td, *J* = 7.5, 1.5 Hz, 2H), 1.53 (p, *J* = 7.6, 7.1 Hz, 2H), 1.45 – 1.26 (m, 12H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.3, 159.1, 143.3, 135.4, 131.6, 130.0, 129.5, 129.4, 127.7, 127.7, 114.3, 114.2, 51.1, 50.5, 37.5, 28.9, 28.8, 27.9, 25.9, 25.2, 21.6 ppm.

IR (neat, cm^{-1}): 3284, 3075, 2963, 2929, 2862, 1644, 1605, 1553, 1505, 1455, 1339, 1247, 1150, 1029, 832, 815, 683, 579, 559, 545.

HRMS (ESI+): $[C_{24}H_{35}N_2O_4S]^+$ (M+H) calcd. 447.2312, found 447.2312.

mp: 119-121 °C



10b

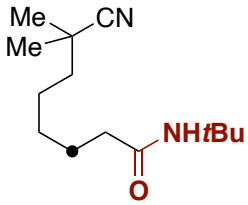
***N*-(*tert*-butyl)-6-(3-methoxyphenoxy)hexanamide (10b).** Following procedure B and starting from 1-((4-bromopentyl)oxy)-3-methoxybenzene (137 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **10b** was obtained as a pale-yellow oil (83.6 mg, 57%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 8.1 Hz, 1H), 6.53 – 6.41 (m, 3H), 5.29 (s, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 3.78 (s, 3H), 2.12 (t, *J* = 7.4 Hz, 2H), 1.85 – 1.61 (m, 4H), 1.56 – 1.42 (m, 2H), 1.34 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 161.0, 160.4, 130.0, 106.8, 106.3, 101.1, 67.8, 55.4, 51.4, 37.6, 29.2, 29.0, 25.8, 25.7 ppm.

IR (neat, cm^{-1}): 3313, 29362, 2867, 1645, 1591, 1544, 1492, 1453, 1363, 1285, 1264, 1199, 1149, 1044, 761, 686.

HRMS (ESI+): $[C_{17}H_{27}NNaO_3]^+$ (M+Na) calcd. 316.1883, found 316.1875.



11b

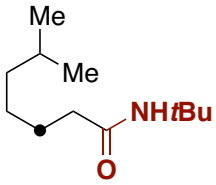
N-(tert-butyl)-7-cyano-7-methyloctanamide (11b). Following procedure B and starting from 6-bromo-2,2-dimethylheptanenitrile (109.1 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound 11b was obtained as a yellow oil (69.1 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.29 (s, 1H), 2.07 (t, *J* = 7.5 Hz, 2H), 1.68 – 1.56 (m, 2H), 1.55 – 1.40 (m, 4H), 1.32 (s, 9H), 1.31 (s, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 125.3, 51.2, 41.0, 37.4, 32.5, 29.1, 28.9, 26.8, 25.4, 25.1 ppm.

IR (neat, cm^{-1}): 3314, 2971, 2935, 2863, 2235, 1646, 1542, 1454, 1363, 1224.

HRMS (ESI+): $[C_{14}H_{26}N_2NaO]^+$ (M+Na) calcd. 261.1937, found 261.1925.



12b

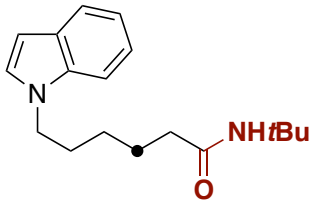
***N*-(*tert*-butyl)-6-methylheptanamide (12b).** Following procedure B and starting from 2-bromo-5-methylhexane (90 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **12b** was obtained as a pale-yellow oil (70.6 mg, 71%) as an inseparable mixture of 14:1 terminal amidation : retained amidation.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.46 (s, 1H), 2.05 (t, *J* = 7.6 Hz, 2H), 1.58 – 1.42 (m, 3H), 1.32 – 1.28 (m, 9H), 1.27 – 1.22 (m, 2H), 1.16 – 1.08 (m, 2H), 0.81 (d, *J* = 6.6 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 51.1, 38.7, 37.7, 28.9, 28.9, 27.9, 27.0, 26.1, 22.6 ppm.

IR (neat, cm^{-1}): 3307, 3077, 2957, 2929, 2869, 1644, 1546, 14541391, 1363, 1225.

HRMS (ESI+): $[C_{12}H_{26}NO]^+$ (M+H) calcd. 200.2009, found 200.2005.



13b

***N*-(*tert*-butyl)-6-(1*H*-indol-1-yl)hexanamide (13b).** Following procedure B and starting from 1-(4-bromopentyl)-1H-indole (133 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **13b** was obtained as a red solid (93.0 mg, 65%).

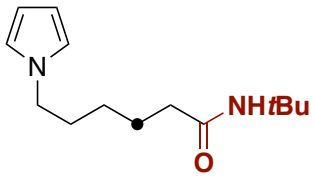
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.33 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.19 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.48 (dd, *J* = 3.1, 0.9 Hz, 1H), 5.13 (s, 1H), 4.13 (t, *J* = 7.0 Hz, 2H), 2.03 (t, *J* = 7.4 Hz, 2H), 1.92 – 1.79 (m, 2H), 1.69 – 1.56 (m, 2H), 1.39 – 1.27 (m, 11H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 136.0, 128.6, 127.9, 121.4, 121.0, 119.2, 109.4, 101.0, 51.1, 46.2, 37.3, 30.0, 28.9, 26.5, 25.3 ppm.

IR (neat, cm^{-1}): 3276, 3080, 2959, 2935, 2857, 1366, 1555, 1455, 1164, 955, 787, 694.

HRMS (ESI+): $[C_{18}H_{26}N_2NaO]^+$ (M+Na) calcd. 309.1937, found 309.1941.

mp: 71-73 °C



14b

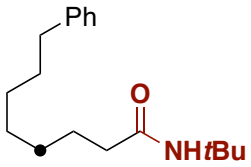
***N*-(*tert*-butyl)-6-(1*H*-pyrrol-1-yl)hexanamide (14b).** Following procedure B and starting from 1-(4-bromopentyl)-1*H*-pyrrole (108 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **14b** was obtained as a pale-yellow oil (60.2 mg, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.63 (t, *J* = 2.1 Hz, 2H), 6.11 (t, *J* = 2.1 Hz, 2H), 5.27 (s, 1H), 3.86 (t, *J* = 7.1 Hz, 2H), 2.05 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.71 (m, 2H), 1.66 – 1.54 (m, 2H), 1.32 (s, 9H), 1.30 – 1.21 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 120.6, 107.9, 51.2, 49.4, 37.5, 31.4, 28.9, 26.4, 25.3 ppm.

IR (neat, cm^{-1}): 3307, 2963, 2930, 2864, 1645, 1544, 1453, 1363, 1281, 1225, 1089, 722.

HRMS (ESI+): $[C_{14}H_{24}NNaO]^+$ (M+Na) calcd. 259.1781, found 259.1776.



15b

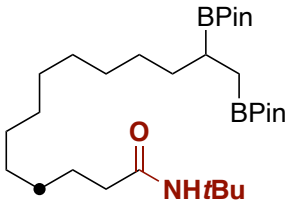
***N*-(*tert*-butyl)-8-phenyloctanamide (15b).** Following procedure B using 5 mol% of NiI_2 (7.8 mg), 10 mol% of **L4** (16.8 mg) and starting from (5-bromoheptyl)benzene (127.6 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **15b** was obtained as a pale-yellow oil (66.2 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 – 7.22 (m, 2H), 7.19 – 7.12 (m, 3H), 2.61 – 2.54 (m, 2H), 2.08 – 2.01 (m, 2H), 1.61 – 1.53 (m, 4H), 1.32 (s, 9H), 1.37 – 1.29 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 143.0, 128.5, 128.4, 125.7, 51.2, 37.9, 36.1, 31.6, 29.4, 29.3, 29.3, 29.0, 25.9 ppm.

IR (neat, cm^{-1}): 3307, 3026, 2964, 2927, 2855, 1644, 1545, 1453, 1391, 1362, 1224, 746, 697.

HRMS (ESI+): $[C_{18}H_{29}NNaO]^+$ (M+Na) calcd. 298.2141, found 298.2146.



16b

***N*-(*tert*-butyl)-13,14-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) tetradecanamide (16b).** Following procedure B using 5 mol% of NiI_2 (7.8 mg), 10 mol% of **L4** (16.8 mg) and starting from 2,2'-(11-bromotridecane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (258.0 mg, 0.500 mmol; 1 equiv) and *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv), compound **16b** was obtained as a pale-yellow oil (117.8 mg, 44%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.28 (s, 1H), 2.03 (t, *J* = 7.2 Hz, 2H), 1.58 – 1.51 (m, 2H), 1.45 – 1.31 (m, 2H), 1.30 (s, 9H), 1.27 – 1.12 (m, 40H), 1.11 – 1.02 (m, 1H), 0.88 – 0.69 (m, 2H) ppm.

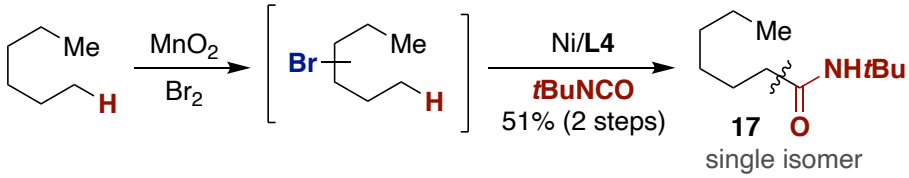
^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 82.9, 82.8, 51.1, 37.8, 33.9, 29.9, 29.7, 29.7, 29.6, 29.5, 29.3, 29.0, 25.9, 25.0, 24.9, 24.9, 24.8, 18.5, 12.8 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 32.8 ppm.

IR (neat, cm^{-1}): 3310, 2976, 2924, 2853, 1647, 1546, 1454, 1369, 1312, 1142, 968.

HRMS (ESI+): $[C_{30}H_{60}NB_2O]^+$ (M+H) calcd. 536.4652, found 536.4645.

Synthetic applications (Scheme 2).



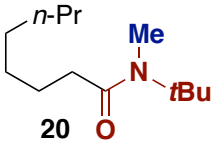
***N*-tertbutylheptanamide (17).** 2.5 mL of HPLC grade n-hexane were placed in a screw-capped vial with MnO_2 (87.0 mg, 1.0 mmol). Br_2 (79.9 mg, 25 µmol 0.500 mmol; 1 equiv) was added dropwise and stirred overnight. The resulting solution was filtered through a plug of SiO_2 and the crude was partially evaporated at 300 mbar/40 ºC to get approximately 300 µL of crude mixture. Following amidation procedure B using *tert*-butyl isocyanate (86.0 µL, 74.3 mg, 0.750 mmol; 1.50 equiv) and the crude alkyl bromide obtained before, compound **19** was obtained as a pale light-yellow oil (47.4 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.33 (s, 1H), 2.05 (t, *J* = 7.4 Hz, 2H), 1.55 (p, *J* = 7.7 Hz, 2H), 1.31 (s, 9H), 1.28 – 1.24 (m, 4H), 0.85 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.6, 51.1, 37.8, 31.7, 29.0, 28.9 (3C), 25.9, 22.6, 14.1 ppm.

IR (neat, cm^{-1}): 3306, 3076, 2959, 2927, 2859, 1643, 1546, 1453, 1362, 1225.

HRMS (ESI+): $[C_{11}H_{23}NNaO]^+$ (M+Na) calcd. 208.1672, found 208.1667.



N-(tert-butyl)-N-methyloctanamide (20). An oven-dried vial equipped with a stirring bar was directly transferred from the oven to the glovebox and charged with NiI_2 (3.91 mg, 0.012 mmol), Mn (68.67 mg, 1.25 mmol) and **L4** (8.41 mg, 0.025 mmol) and 1 mL of NMP. The suspension was left stirring time until its color turn to dark blue, moment in which the respective isocyanate (0.75 mmol) was added. The oven-dried screw-capped test was set in a temperature controlled (10 °C) reaction block outside the glovebox. The suspension was left to stir at this temperature for additional 15 min. Alkyl bromide **19** (0.5 mmol) was added dropwise. The reaction was left under stirring for additional 24 h at the same temperature, and after this period, it was treated with MeI and left to stirr for 24 h at 60 ºC. It was quenched then with NH_4Cl and extracted with EtOAc. The organic phase was dried over $MgSO_4$ and concentrated. The crude obtained was purified by flash

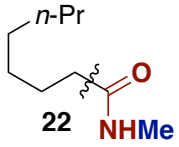
chromatography (Hex/Acet 5%) to afford compound **20** as colorless oil (48 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.88 (s, 3H), 2.31 – 2.23 (m, 2H), 1.58 (p, *J* = 7.9, 7.4 Hz, 2H), 1.39 (s, 9H), 1.32 – 1.24 (m, 8H), 0.86 (t, *J* = 6.6 Hz, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.0, 56.7, 37.0, 32.1, 31.9, 29.5, 29.3, 28.5, 25.5, 22.8, 14.2 ppm.

IR (neat, cm^{-1}): 2957, 2924, 2855, 1647, 1456, 1386, 1362, 1217, 1126, 1097, 731.

HRMS (ESI+): $[C_{13}H_{27}NNaO]^+$ (M+Na) calcd. 236.19875, found 236.1982.



22

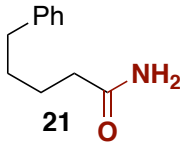
N-methyloctanamide (22). Starting from compound **20** (63 mg, 0,3 mmol), it was charged into a Schlenck with Cu(OTf)2 (21 mg, 0,06 mmol, 2 mol%) and DCM. The system was stirred at 80ºC for 36 h, cooled to room temperature and treated with water. The aqueous phase was extracted with DCM and the organic phases were collected together, dried over $MgSO_4$ and concentrated. The crude was purified by column chromatography to afford **22** as a white semi-solid (32 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (s, 1H), 2.76 (d, *J* = 4.8 Hz, 3H), 2.24 – 1.97 (m, 2H), 1.58 (td, *J* = 8.5, 7.9, 4.5 Hz, 2H), 1.34 – 1.14 (m, 8H), 0.91 – 0.73 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1, 36.8, 31.8, 29.4, 29.1, 26.3, 25.9, 22.7, 14.1.

IR (neat, cm^{-1}): 3293, 2956, 2927, 2857, 1649, 1560, 1465, 1411.

HRMS (ESI+): [C9H20NO]+ (M+H) calcd. 158.1539, found 158.1538.



21

5-phenylpentanamide (21). An oven-dried vial equipped with a stirring bar was directly transferred from the oven to the glovebox and charged with NiI_2 (3.91 mg, 0.012 mmol), Mn (68.67 mg, 1.25 mmol) and **L4** (8.41 mg, 0.025 mmol) and 1 mL of NMP. The suspension was left stirring time until its color turn to dark blue, moment in which the respective isocyanate (0.75 mmol) was added. The oven-dried screw-capped test was set in a temperature controlled (10 °C) reaction block outside the glovebox. The suspension was left to stir at this temperature for additional 15 min. Alkyl bromide **18** (0.5 mmol)

was added dropwise. The reaction was left under stirring for additional 24 h at the same temperature, and it was quenched then with NH_4Cl and extracted with EtOAc. The organic phase was dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude obtained was used in the next step without further purification. A microwave vial containing a stirring bar was charged with the crude, scandium(III) triflate (245 mg, 0.5 mmol, 1 equiv) and nitromethane (2.00 mL). The resulting mixture was heated at 170 ºC for 1 h at a Microwave Reactor. The reaction mixture was cooled to room temperature and the solvent removed under reduced pressure. The resulting residue was dissolved in dichloromethane, washed with water, dried over MgSO4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography, to obtain compound **21** as an off-white solid (39,8 mg, 40% overall yield).

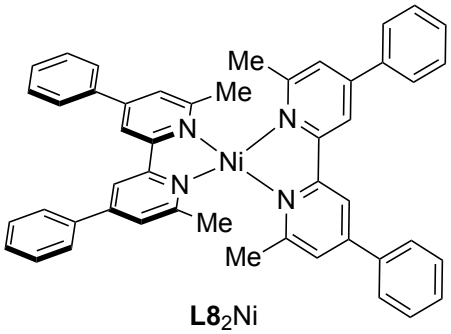
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.23 (m, 2H, Ar), 7.21 – 7.14 (m, 3H, Ar), 5.43 (d, J = 34.6 Hz, 2H), 2.70 – 2.58 (m, 2H), 2.28 – 2.19 (m, 2H), 1.68 (p, J = 3.7 Hz, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 175.4, 142.3, 128.5, 128.5, 125.9, 77.2, 35.9, 35.8, 31.1, 25.3 ppm.

m.p: 101.5 104 ºC

Spectroscopic data is in agreement with the literature[1].

Synthesis of Ni(0)L_2 complexes

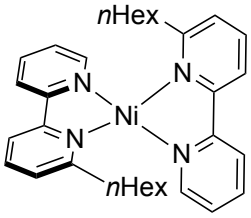


L8$_2$Ni

In the glovebox, **L8**$NiBr_2$ (383 mg, 0.29 mmol) was added to a 10 mL vial. A stirbar was added and it was charged with 3 mL of cold toluene (-36 °C), affording a pink suspension. $MgCl(CH_2SiMe_3)$ in THF (730 uL 0.84M, 2.1 equiv) was then added dropwise turning the pink suspension into a brown solution which then turned red. After the addition of Grignard, L7 (108 mg, 1.1 equiv) was added in 2 mL of cold toluene (-36 °C) as a suspension where the solution turned purple. After 3 h the now blue solution was filtered through a pipette plug of celite with black solid being filtered off and a blue solution collected. The solvent was removed to afford a blue powder and washed with cold (-36 °C) pentane (1 mL x 3) to give **L8**$_2$Ni (138 mg, 65 %) as a blue powder.

^{1}H NMR (400 MHz, THF-d_8) δ = 8.20 (d, J = 1.7 Hz, 4H), 8.14 – 7.94 (m, 12H), 7.60 (t, J = 7.4 Hz, 4H), 7.31 (t, J = 7.8 Hz, 8H), 2.65 (s, 12H) ppm.

^{13}C NMR (101 MHz, THF-d_8) δ = 159.6, 144.6, 140.0, 131.0, 130.5, 126.0, 124.1, 122.9, 119.1, 28.2 ppm.



L4$_2$Ni

In the glovebox, **L4**$NiBr_2$ (92 mg, 0.21 mmol) was added to a 10 mL vial. A stirbar was added and it was charged with 2.5 mL of cold toluene (-36 °C) and **L4** (94 mg, 42 mmol) affording a pink suspension. EtMgBr in THF (150 mL, 3M, 2.2 equiv) was then added dropwise turning the pink suspension, yellow and then blue. After 1 hour a black precipitate was filtered off through a celite plug and the blue filtrate was concentrated to dryness. The solid was redissolved in pentane and filtered through a celite plug and concentrated to dryness affording **L4**$_2$Ni (8 mg, 7 %) as a blue powder.

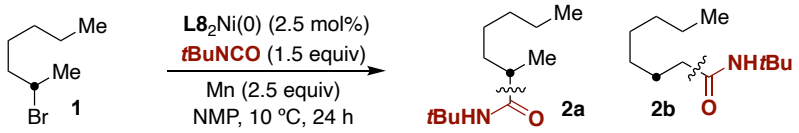
^{1}H NMR (500 MHz, C_6D_6) δ = 10.38 (dt, J = 5.9, 1.2 Hz, 2H), 8.29 – 8.03 (m, 4H), 7.63 (dd, J = 6.8, 1.1 Hz, 2H), 7.36 – 7.22 (m, 6H), 3.39 (dddd, J = 84.4, 13.6, 10.7, 5.4 Hz, 4H), 2.19 – 1.77 (m, 4H), 1.16 – 0.68 (m, 18H) ppm.

^{13}C NMR (126 MHz, C_6D_6) δ = 149.1, 136.8, 136.2, 123.2, 122.9, 122.5, 121.7, 120.8, 119.6, 118.3, 42.3, 38.5, 31.9, 29.8, 29.5, 29.2, 28.8, 22.7, 14.0 ppm.

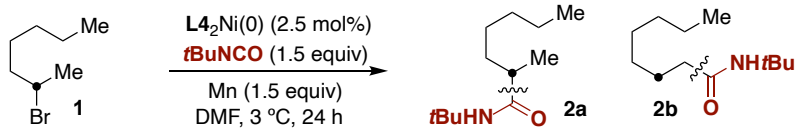
Mechanistic experiments

In a nitrogen-filled glovebox, an oven-dried screw-capped test tube containing a stirring bar was charged with the nickel complex and ligand and/or Mn (if necessary). The obtained mixture was stirred at rt (*ca.* 1 min), after which *tert*- butyl isocyanate (0.75 mmol; 1.5 equiv) was added. Subsequently, the reaction mixture was cooled down to the desired temperature outside the glovebox, and 2-bromoheptane was added (0.5 mmol; 1 equiv). The resulting mixture was stirred for 24 h, at the desired temperature using a metallic block with a recirculating liquid refrigerated by a chiller. The crude reaction mixture was carefully quenched with 5% aq. HCl (1 mL) and extracted with ethyl acetate. A sample of the obtained solution was filtered through a silica-celite plug, eluted with ethyl acetate and analyzed by GC-FID using anisole as internal standard.

❑ NiL_2 is catalitically competent

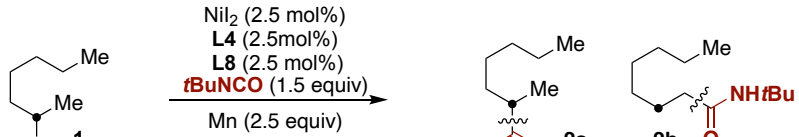


56% yield (7:93)



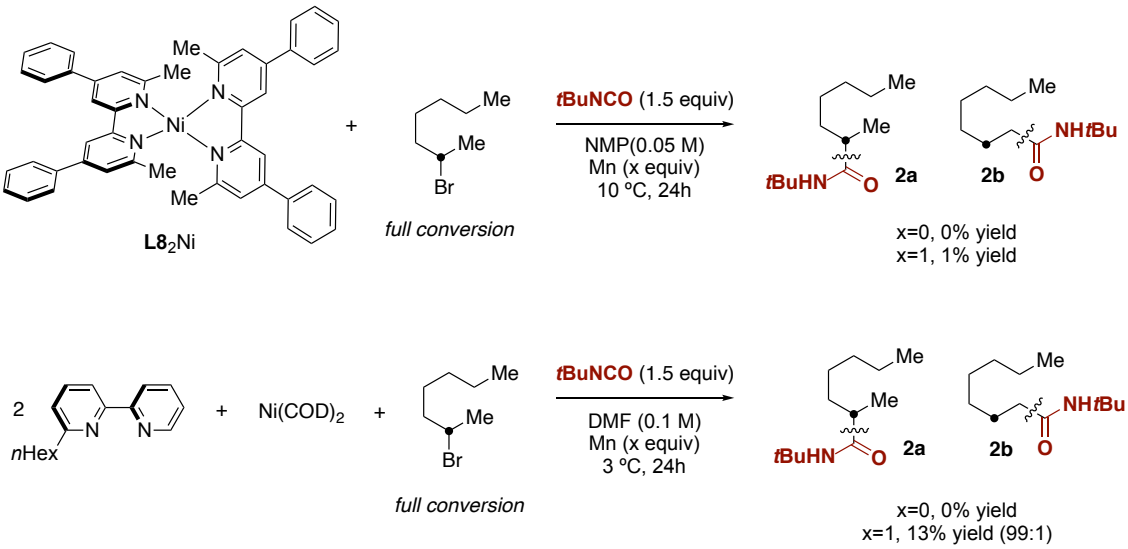
74% yield (99:1)

❑ Competitive experiment



72% yield (99:1)

❑ Stoichiometric experiments



X-Ray Structures

Crystal data and structure refinement for **L8**$_2$Ni.

Empirical formula	C48 H40 N4 Ni	
Formula weight	731.55	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 18.259(3)Å	a= 90°.
	b = 17.663(2)Å	b = 104.816(5)°.
	c = 11.5624(13)Å	g = 90°.
Volume	3604.9(8) Å^3	
Z	4	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.580 mm^{-1}	
F(000)	1536	
Crystal size	0.060 x 0.030 x 0.010 mm^3	
Theta range for data collection	2.156 to 25.713°.	
Index ranges	-21⩽h⩽22,-21⩽k⩽14,-10⩽l⩽13	
Reflections collected	21289	
Independent reflections	6750[R(int) = 0.1790]	
Completeness to theta =25.713°	98.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.74 and 0.61	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6750/ 488/ 528	
Goodness-of-fit on F^2	0.970	
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1124	
R indices (all data)	R1 = 0.2162, wR2 = 0.1530	
Largest diff. peak and hole	0.492 and -0.567 e.Å^{-3}	

Table S4. Bond lengths [Å] and angles [°] for **L8**$_2$Ni.

Bond lengths----

Ni1	N2	1.930(5)	N3	C25	1.381(6)
Ni1	N3	1.936(4)	N4	C34	1.359(6)
Ni1	N4	1.938(4)	N4	C30	1.388(7)
Ni1	N1	1.939(4)	C1	C2	1.378(7)
N1	C5	1.367(7)	C1	C11	1.470(8)
N1	C1	1.373(7)	C2	C3	1.408(8)
N2	C10	1.370(7)	C3	C4	1.396(7)
N2	C6	1.370(7)	C3	C12	1.480(8)
N3	C29	1.376(7)	C4	C5	1.385(7)

C5	C6	1.460(8)
C6	C7	1.388(8)
C7	C8	1.382(8)
C8	C9	1.422(8)
C8	C18	1.479(8)
C9	C10	1.344(8)
C10	C24	1.479(7)
C12	C17	1.372(8)
C12	C13	1.398(8)
C13	C14	1.383(8)
C14	C15	1.363(8)
C15	C16	1.381(8)
C16	C17	1.386(8)
C18	C19'	1.375(15)
C18	C23'	1.377(12)
C18	C19	1.43(3)
C18	C23	1.44(3)
C19	C20	1.29(4)
C20	C21	1.48(6)
C21	C22	1.26(5)
C22	C23	1.27(3)
C19'	C20'	1.372(18)
C20'	C21'	1.34(3)
C21'	C22'	1.44(2)
C22'	C23'	1.402(15)
C25	C26	1.363(7)
C25	C35	1.483(7)
C26	C27	1.407(7)
C27	C28	1.385(7)
C27	C36	1.483(7)
C28	C29	1.386(7)
C29	C30	1.449(7)
C30	C31	1.382(7)
C31	C32	1.395(7)
C32	C33	1.419(8)
C32	C42	1.478(7)
C33	C34	1.363(7)
C34	C48	1.493(7)
C36	C41	1.385(8)
C36	C37	1.385(7)
C37	C38	1.395(7)
C38	C39	1.363(8)
C39	C40	1.366(8)
C40	C41	1.374(7)
C42	C43	1.378(7)
C42	C47	1.396(7)
C43	C44	1.362(7)
C44	C45	1.375(7)
C45	C46	1.376(8)
C46	C47	1.376(8)

Angles----------

N2	Ni1	N3	115.23(18)
N2	Ni1	N4	126.6(2)
N3	Ni1	N4	82.76(18)
N2	Ni1	N1	82.7(2)
N3	Ni1	N1	131.06(19)
N4	Ni1	N1	124.18(18)
C5	N1	C1	117.6(5)
C5	N1	Ni1	114.9(4)
C1	N1	Ni1	127.4(4)
C10	N2	C6	117.6(5)
C10	N2	Ni1	127.3(4)
C6	N2	Ni1	115.0(4)
C29	N3	C25	117.3(5)
C29	N3	Ni1	114.9(3)
C25	N3	Ni1	127.4(4)
C34	N4	C30	117.1(5)
C34	N4	Ni1	128.2(4)
C30	N4	Ni1	114.5(3)
N1	C1	C2	120.7(6)
N1	C1	C11	116.4(5)
C2	C1	C11	122.9(6)
C1	C2	C3	122.6(6)
C4	C3	C2	115.5(5)
C4	C3	C12	121.5(6)

C2	C3	C12	123.0(5)
C5	C4	C3	120.7(6)
N1	C5	C4	122.8(5)
N1	C5	C6	113.5(5)
C4	C5	C6	123.7(6)
N2	C6	C7	121.7(5)
N2	C6	C5	113.6(5)
C7	C6	C5	124.7(5)
C8	C7	C6	121.6(6)
C7	C8	C9	114.6(6)
C7	C8	C18	122.2(5)
C9	C8	C18	123.2(5)
C10	C9	C8	123.0(6)
C9	C10	N2	121.4(5)
C9	C10	C24	123.3(5)
N2	C10	C24	115.3(5)
C17	C12	C13	117.6(5)
C17	C12	C3	121.9(5)
C13	C12	C3	120.5(6)
C14	C13	C12	119.6(6)
C15	C14	C13	122.0(6)
C14	C15	C16	119.1(6)
C15	C16	C17	119.0(6)
C12	C17	C16	122.7(6)
C19'	C18	C23'	117.3(9)
C19	C18	C23	113.4(18)
C19'	C18	C8	120.9(7)
C23'	C18	C8	121.7(7)
C19	C18	C8	123.8(14)
C23	C18	C8	122.8(12)
C20	C19	C18	122(3)
C19	C20	C21	119(4)
C22	C21	C20	118(5)
C21	C22	C23	125(4)
C22	C23	C18	122(2)
C20'	C19'	C18	121.5(12)
C21'	C20'	C19'	122.9(16)
C20'	C21'	C22'	117.9(19)
C23'	C22'	C21'	118.0(13)
C18	C23'	C22'	122.4(10)
C26	C25	N3	121.4(5)
C26	C25	C35	122.8(5)
N3	C25	C35	115.8(5)
C25	C26	C27	122.0(5)
C28	C27	C26	116.2(5)
C28	C27	C36	121.0(5)
C26	C27	C36	122.8(5)
C27	C28	C29	121.2(5)
N3	C29	C28	121.8(5)
N3	C29	C30	113.8(5)
C28	C29	C30	124.4(5)
C31	C30	N4	122.1(5)
C31	C30	C29	124.1(6)
N4	C30	C29	113.6(5)
C30	C31	C32	120.8(6)
C31	C32	C33	115.7(5)
C31	C32	C42	121.4(5)
C33	C32	C42	122.9(5)
C34	C33	C32	121.8(5)
N4	C34	C33	122.2(5)
N4	C34	C48	115.7(5)
C33	C34	C48	122.0(5)
C41	C36	C37	118.1(5)
C41	C36	C27	120.2(5)
C37	C36	C27	121.7(5)
C36	C37	C38	119.9(5)
C39	C38	C37	120.5(6)
C38	C39	C40	120.1(6)
C39	C40	C41	119.9(6)
C40	C41	C36	121.4(6)
C43	C42	C47	116.8(6)
C43	C42	C32	122.1(5)
C47	C42	C32	121.1(6)
C44	C43	C42	122.1(5)
C43	C44	C45	120.7(6)
C44	C45	C46	118.8(6)

C47	C46	C45	120.3(6)
C46	C47	C42	121.3(6)

Table S5. Torsion angles [°] for **L8**$_2$Ni.

C5	N1	C1	C2	2.0(8)	C6	N2	C10	C24	-178.7(5)
Ni1	N1	C1	C2	179.6(4)	Ni1	N2	C10	C24	-3.0(7)
C5	N1	C1	C11	-177.1(5)	C4	C3	C12	C17	18.7(8)
Ni1	N1	C1	C11	0.5(7)	C2	C3	C12	C17	-162.8(6)
N1	C1	C2	C3	-1.3(9)	C4	C3	C12	C13	-161.1(5)
C11	C1	C2	C3	177.7(5)	C2	C3	C12	C13	17.5(8)
C1	C2	C3	C4	-0.6(8)	C17	C12	C13	C14	0.8(9)
C1	C2	C3	C12	-179.3(5)	C3	C12	C13	C14	-179.4(5)
C2	C3	C4	C5	1.9(7)	C12	C13	C14	C15	-1.9(9)
C12	C3	C4	C5	-179.4(5)	C13	C14	C15	C16	1.0(10)
C1	N1	C5	C4	-0.7(8)	C14	C15	C16	C17	1.0(9)
Ni1	N1	C5	C4	-178.6(4)	C13	C12	C17	C16	1.1(9)
C1	N1	C5	C6	179.8(5)	C3	C12	C17	C16	-178.6(5)
Ni1	N1	C5	C6	1.9(6)	C15	C16	C17	C12	-2.1(10)
C3	C4	C5	N1	-1.4(8)	C7	C8	C18	C19'	12.1(12)
C3	C4	C5	C6	178.2(5)	C9	C8	C18	C19'	-169.1(9)
C10	N2	C6	C7	2.4(8)	C7	C8	C18	C23'	-163.4(8)
Ni1	N2	C6	C7	-173.8(4)	C9	C8	C18	C23'	15.3(11)
C10	N2	C6	C5	-179.0(5)	C7	C8	C18	C19	-15.2(16)
Ni1	N2	C6	C5	4.7(6)	C9	C8	C18	C19	163.6(14)
N1	C5	C6	N2	-4.3(7)	C7	C8	C18	C23	164.0(15)
C4	C5	C6	N2	176.2(5)	C9	C8	C18	C23	-17.2(16)
N1	C5	C6	C7	174.2(5)	C23	C18	C19	C20	3(3)
C4	C5	C6	C7	-5.3(9)	C8	C18	C19	C20	-177.4(17)
N2	C6	C7	C8	-0.8(9)	C18	C19	C20	C21	1(4)
C5	C6	C7	C8	-179.2(5)	C19	C20	C21	C22	-5(6)
C6	C7	C8	C9	-1.9(8)	C20	C21	C22	C23	4(7)
C6	C7	C8	C18	176.9(5)	C21	C22	C23	C18	0(5)
C7	C8	C9	C10	3.2(8)	C19	C18	C23	C22	-4(3)
C18	C8	C9	C10	-175.6(5)	C8	C18	C23	C22	176.8(18)
C8	C9	C10	N2	-1.7(9)	C23'	C18	C19'	C20'	1.8(15)
C8	C9	C10	C24	175.6(5)	C8	C18	C19'	C20'	-173.9(9)
C6	N2	C10	C9	-1.1(8)	C18	C19'	C20'	C21'	-3(2)
Ni1	N2	C10	C9	174.6(4)	C19'	C20'	C21'	C22'	1(3)

C20'	C21'	C22'	C23'	2(2)
C19'	C18	C23'	C22'	1.0(14)
C8	C18	C23'	C22'	176.8(8)
C21'	C22'	C23'	C18	-2.7(17)
C29	N3	C25	C26	2.8(8)
Ni1	N3	C25	C26	176.1(4)
C29	N3	C25	C35	-178.0(5)
Ni1	N3	C25	C35	-4.8(7)
N3	C25	C26	C27	-3.9(9)
C35	C25	C26	C27	177.0(6)
C25	C26	C27	C28	2.7(9)
C25	C26	C27	C36	-175.6(6)
C26	C27	C28	C29	-0.6(8)
C36	C27	C28	C29	177.7(5)
C25	N3	C29	C28	-0.8(8)
Ni1	N3	C29	C28	-174.9(4)
C25	N3	C29	C30	179.2(5)
Ni1	N3	C29	C30	5.1(6)
C27	C28	C29	N3	-0.3(9)
C27	C28	C29	C30	179.8(6)
C34	N4	C30	C31	-3.5(8)
Ni1	N4	C30	C31	173.1(5)
C34	N4	C30	C29	179.9(5)
Ni1	N4	C30	C29	-3.6(6)
N3	C29	C30	C31	-177.5(5)
C28	C29	C30	C31	2.4(9)
N3	C29	C30	N4	-0.9(7)
C28	C29	C30	N4	179.0(5)
N4	C30	C31	C32	1.6(9)
C29	C30	C31	C32	177.9(6)
C30	C31	C32	C33	1.2(9)
C30	C31	C32	C42	-179.2(6)
C31	C32	C33	C34	-2.1(9)
C42	C32	C33	C34	178.3(6)
C30	N4	C34	C33	2.6(9)
Ni1	N4	C34	C33	-173.4(5)
C30	N4	C34	C48	180.0(5)
Ni1	N4	C34	C48	3.9(8)
C32	C33	C34	N4	0.2(9)
C32	C33	C34	C48	-177.0(6)
C28	C27	C36	C41	-43.2(8)
C26	C27	C36	C41	135.0(6)
C28	C27	C36	C37	137.8(6)
C26	C27	C36	C37	-44.0(9)
C41	C36	C37	C38	0.5(9)
C27	C36	C37	C38	179.5(5)
C36	C37	C38	C39	-0.7(9)
C37	C38	C39	C40	-1.2(10)
C38	C39	C40	C41	3.3(10)
C39	C40	C41	C36	-3.6(9)
C37	C36	C41	C40	1.7(9)
C27	C36	C41	C40	-177.4(5)
C31	C32	C42	C43	28.7(9)
C33	C32	C42	C43	-151.7(6)
C31	C32	C42	C47	-152.2(6)
C33	C32	C42	C47	27.4(10)
C47	C42	C43	C44	-0.7(10)
C32	C42	C43	C44	178.4(6)
C42	C43	C44	C45	-1.0(11)
C43	C44	C45	C46	1.0(10)
C44	C45	C46	C47	0.9(11)
C45	C46	C47	C42	-2.7(11)
C43	C42	C47	C46	2.6(11)
C32	C42	C47	C46	-176.5(6)

Crystal data and structure refinement for **L4**$_2$Ni.

Empirical formula	C32 H40 N4 Ni	
Formula weight	539.39	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 17.2651(13)Å	a= 90°.
	b = 8.0978(6)Å	b = 102.933(2)°.
	c = 20.5663(16)Å	g = 90°.
Volume	2802.4(4) Å^3	
Z	4	
Density (calculated)	1.278 Mg/m^3	
Absorption coefficient	0.720 mm^{-1}	
F(000)	1152	
Crystal size	0.500 x 0.200 x 0.030 mm^3	
Theta range for data collection	2.032 to 33.945°.	
Index ranges	-26⩽h⩽26,-12⩽k⩽8,-32⩽l⩽32	
Reflections collected	58430	
Independent reflections	11254[R(int) = 0.0650]	
Completeness to theta =33.945°	98.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.74 and 0.64	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11254/ 246/ 392	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.0965	
R indices (all data)	R1 = 0.0863, wR2 = 0.1106	
Largest diff. peak and hole	0.567 and -0.336 e.Å^{-3}	

Table S6. Bond lengths [Å] and angles [°] for **L4**$_2$Ni.

Bond lengths					
Ni1	N1	1.9231(14)	C1	C2	1.379(3)
Ni1	N3	1.9252(14)	C2	C3	1.399(3)
Ni1	N4	1.9345(13)	C3	C4	1.368(3)
Ni1	N2	1.9470(15)	C4	C5	1.410(2)
N1	C1	1.362(2)	C5	C6	1.434(2)
N1	C5	1.369(2)	C6	C7	1.405(3)
N2	C10	1.374(2)	C7	C8	1.363(3)
N2	C6	1.377(2)	C8	C9	1.403(3)
N3	C17	1.361(2)	C9	C10	1.376(3)
N3	C21	1.373(2)	C10	C11	1.481(4)
N4	C26	1.3742(19)	C10	C11'	1.689(19)
N4	C22	1.378(2)	C11	C12	1.533(3)
			C12	C13	1.526(3)

C13	C14	1.528(3)
C14	C15	1.522(3)
C15	C16	1.530(7)
C11'	C12'	1.528(19)
C12'	C13'	1.538(17)
C13'	C14'	1.474(18)
C14'	C15'	1.580(19)
C15'	C16'	1.46(4)
C17	C18	1.373(3)
C18	C19	1.396(3)
C19	C20	1.371(3)
C20	C21	1.401(2)
C21	C22	1.440(2)
C22	C23	1.400(2)
C23	C24	1.371(2)
C24	C25	1.404(2)
C25	C26	1.382(2)
C26	C27	1.501(2)
C27	C28	1.535(2)
C28	C29	1.533(2)
C29	C30	1.514(3)
C30	C31	1.532(2)
C31	C32	1.523(3)

Angles

N1	Ni1	N3	108.98(6)
N1	Ni1	N4	139.32(6)
N3	Ni1	N4	82.78(6)
N1	Ni1	N2	82.33(6)
N3	Ni1	N2	136.96(6)
N4	Ni1	N2	116.03(6)
C1	N1	C5	117.83(15)
C1	N1	Ni1	126.52(13)
C5	N1	Ni1	115.46(11)
C10	N2	C6	117.37(15)
C10	N2	Ni1	128.50(11)
C6	N2	Ni1	114.11(11)
C17	N3	C21	117.42(15)
C17	N3	Ni1	127.33(13)
C21	N3	Ni1	115.19(10)
C26	N4	C22	117.48(13)
C26	N4	Ni1	128.05(11)
C22	N4	Ni1	114.23(10)
N1	C1	C2	122.79(19)
C1	C2	C3	119.30(19)
C4	C3	C2	118.91(17)
C3	C4	C5	119.99(19)
N1	C5	C4	121.11(17)
N1	C5	C6	113.79(14)
C4	C5	C6	125.06(17)
N2	C6	C7	121.60(16)
N2	C6	C5	114.01(15)
C7	C6	C5	124.38(16)
C8	C7	C6	119.99(17)
C7	C8	C9	118.85(18)
C10	C9	C8	119.89(18)
N2	C10	C9	122.22(16)
N2	C10	C11	116.8(2)
C9	C10	C11	121.0(2)
N2	C10	C11'	114.6(9)
C9	C10	C11'	122.0(9)
C10	C11	C12	112.8(3)
C13	C12	C11	112.1(2)
C12	C13	C14	112.48(17)
C15	C14	C13	114.05(18)
C14	C15	C16	114.4(3)
C12'	C11'	C10	113.5(13)
C11'	C12'	C13'	112.7(12)
C14'	C13'	C12'	115.3(10)
C13'	C14'	C15'	114.9(11)
C16'	C15'	C14'	114.8(19)
N3	C17	C18	123.19(19)
C17	C18	C19	119.16(18)
C20	C19	C18	118.91(18)
C19	C20	C21	119.97(19)
N3	C21	C20	121.32(15)

N3	C21	C22	113.43(14)	N4	C26	C27	117.37(13)
C20	C21	C22	125.25(16)	C25	C26	C27	120.74(14)
N4	C22	C23	121.99(14)	C26	C27	C28	112.69(14)
N4	C22	C21	114.14(14)	C29	C28	C27	112.78(15)
C23	C22	C21	123.83(15)	C30	C29	C28	114.07(14)
C24	C23	C22	119.81(16)	C29	C30	C31	113.02(14)
C23	C24	C25	118.70(15)	C32	C31	C30	111.72(15)
C26	C25	C24	120.07(15)				
N4	C26	C25	121.88(15)				

Table S7. Torsion angles [°] for **L4**$_2$Ni.

C5	N1	C1	C2	2.3(2)	C6	N2	C10	C11'	166.2(7)
Ni1	N1	C1	C2	177.11(14)	Ni1	N2	C10	C11'	-15.6(7)
N1	C1	C2	C3	-0.1(3)	C8	C9	C10	N2	-0.9(2)
C1	C2	C3	C4	-1.1(3)	C8	C9	C10	C11	178.8(2)
C2	C3	C4	C5	0.2(3)	C8	C9	C10	C11'	-167.8(7)
C1	N1	C5	C4	-3.2(2)	N2	C10	C11	C12	-68.2(4)
Ni1	N1	C5	C4	-178.60(12)	C9	C10	C11	C12	112.0(3)
C1	N1	C5	C6	174.48(14)	C10	C11	C12	C13	170.0(3)
Ni1	N1	C5	C6	-0.92(17)	C11	C12	C13	C14	-173.8(3)
C3	C4	C5	N1	2.0(3)	C12	C13	C14	C15	-177.8(2)
C3	C4	C5	C6	-175.37(16)	C13	C14	C15	C16	-64.4(4)
C10	N2	C6	C7	2.9(2)	N2	C10	C11'	C12'	-75.3(16)
Ni1	N2	C6	C7	-175.53(12)	C9	C10	C11'	C12'	92.5(16)
C10	N2	C6	C5	-175.76(13)	C10	C11'	C12'	C13'	178.4(12)
Ni1	N2	C6	C5	5.78(16)	C11'	C12'	C13'	C14'	-67.0(17)
N1	C5	C6	N2	-3.19(19)	C12'	C13'	C14'	C15'	-175.6(10)
C4	C5	C6	N2	174.38(15)	C13'	C14'	C15'	C16'	-179(2)
N1	C5	C6	C7	178.16(15)	C21	N3	C17	C18	1.2(3)
C4	C5	C6	C7	-4.3(3)	Ni1	N3	C17	C18	178.11(18)
N2	C6	C7	C8	-1.9(2)	N3	C17	C18	C19	-1.5(4)
C5	C6	C7	C8	176.67(16)	C17	C18	C19	C20	0.6(4)
C6	C7	C8	C9	-0.7(3)	C18	C19	C20	C21	0.6(4)
C7	C8	C9	C10	2.0(3)	C17	N3	C21	C20	0.1(3)
C6	N2	C10	C9	-1.5(2)	Ni1	N3	C21	C20	-177.22(15)
Ni1	N2	C10	C9	176.69(12)	C17	N3	C21	C22	-179.94(17)
C6	N2	C10	C11	178.68(18)	Ni1	N3	C21	C22	2.8(2)
Ni1	N2	C10	C11	-3.1(2)	C19	C20	C21	N3	-1.0(3)

C19	C20	C21	C22	179.1(2)	C22	N4	C26	C25	-2.9(2)
C26	N4	C22	C23	2.4(2)	Ni1	N4	C26	C25	170.99(13)
Ni1	N4	C22	C23	-172.37(14)	C22	N4	C26	C27	176.02(15)
C26	N4	C22	C21	-179.93(15)	Ni1	N4	C26	C27	-10.0(2)
Ni1	N4	C22	C21	5.31(19)	C24	C25	C26	N4	1.5(3)
N3	C21	C22	N4	-5.2(2)	C24	C25	C26	C27	-177.41(16)
C20	C21	C22	N4	174.74(18)	N4	C26	C27	C28	-73.20(18)
N3	C21	C22	C23	172.39(17)	C25	C26	C27	C28	105.79(18)
C20	C21	C22	C23	-7.6(3)	C26	C27	C28	C29	-171.57(13)
N4	C22	C23	C24	-0.4(3)	C27	C28	C29	C30	-64.7(2)
C21	C22	C23	C24	-177.86(18)	C28	C29	C30	C31	-178.05(15)
C22	C23	C24	C25	-1.1(3)	C29	C30	C31	C32	175.69(16)
C23	C24	C25	C26	0.5(3)					

^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra

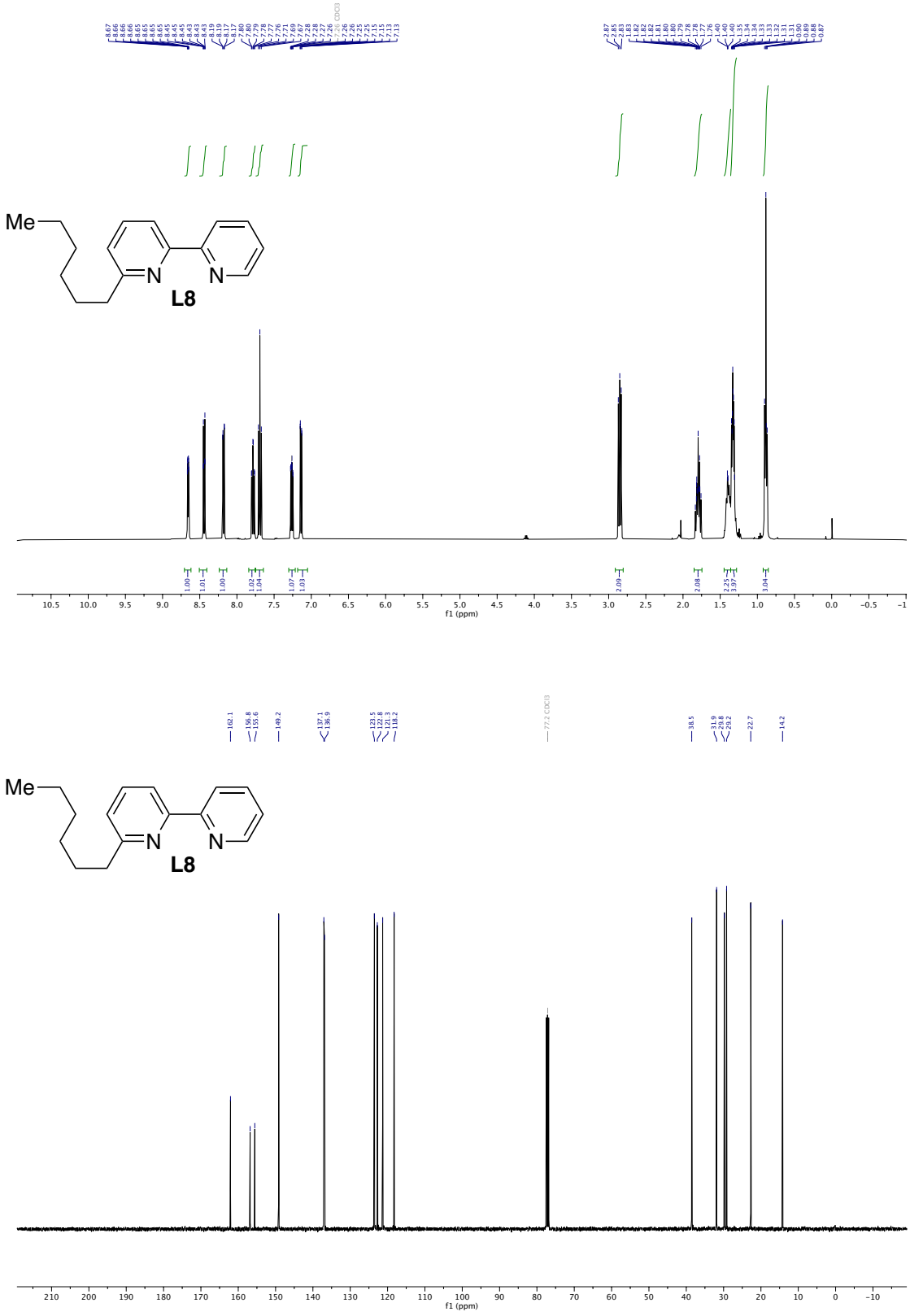
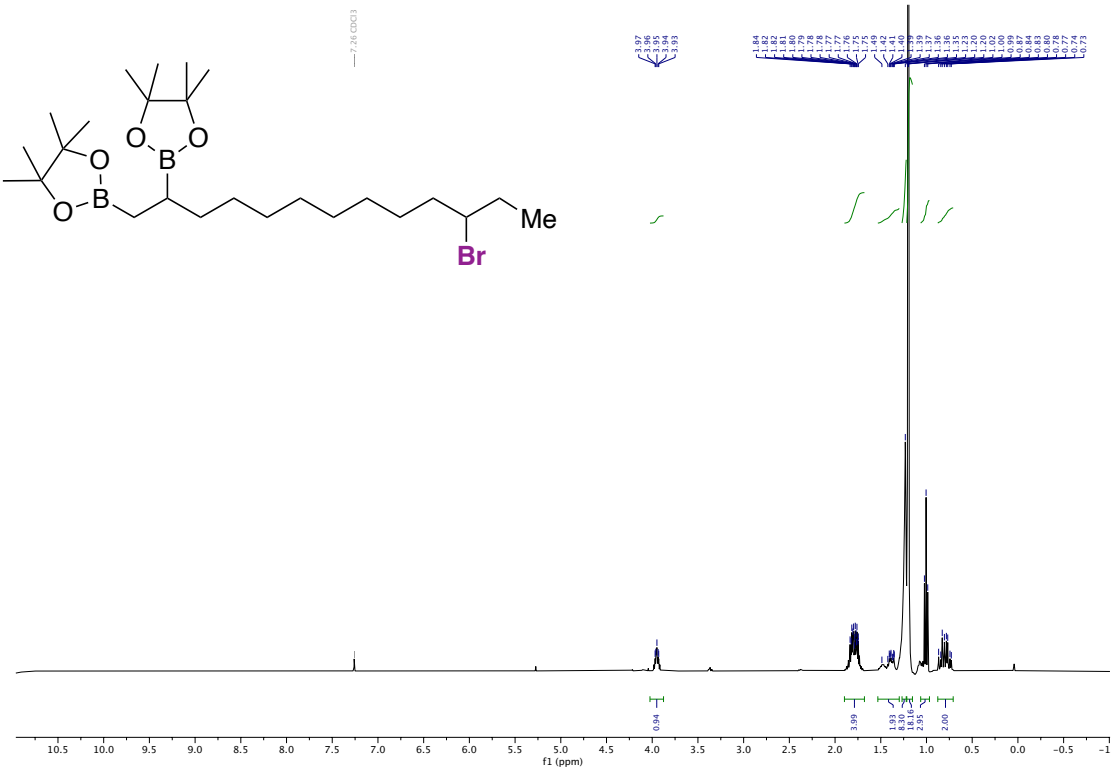
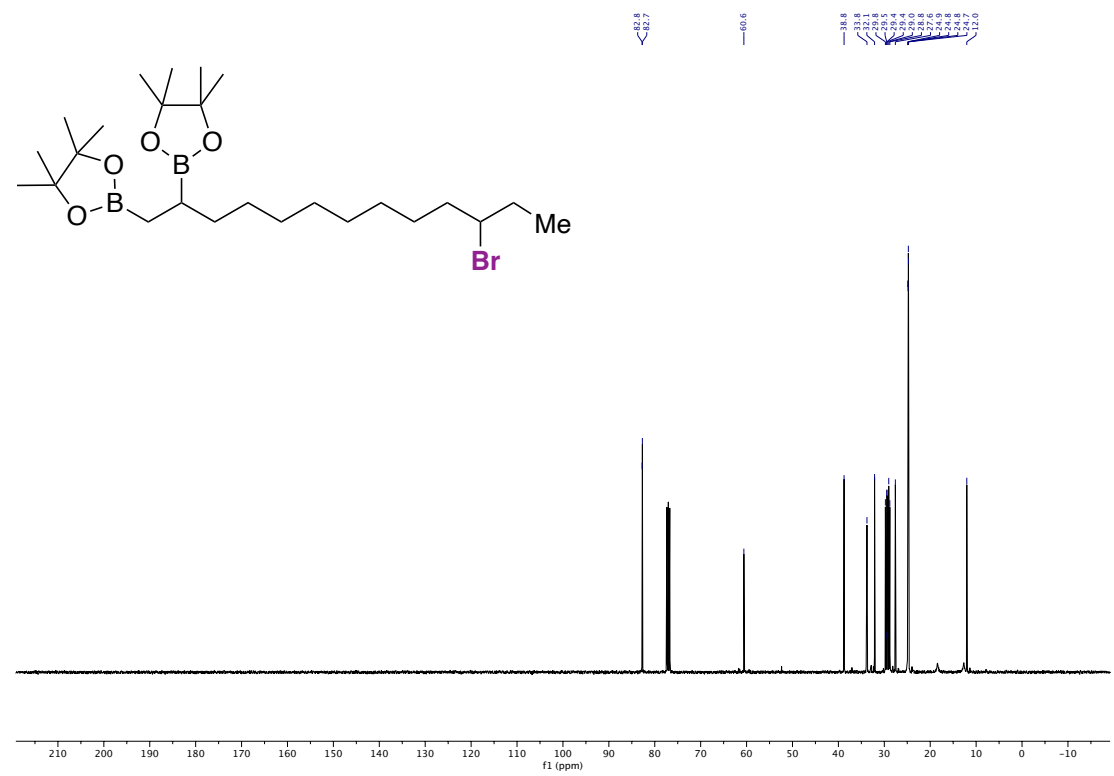


Figure 1. ^{1}H and ^{13}C NMR spectra of **L8**


Me
Br
f1 (ppm)


Me
Br
f1 (ppm)

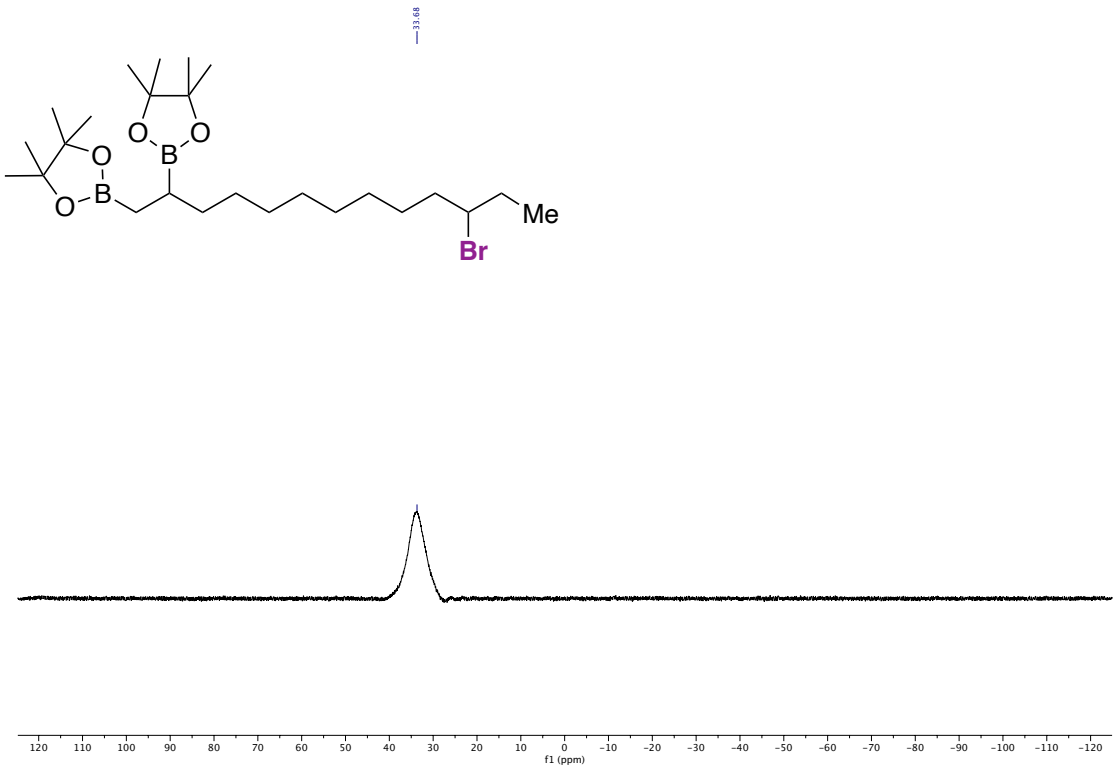


Figure 2.^{1}H, ^{13}C and ^{11}B NMR spectra of **2-(11-bromotridecyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane .**

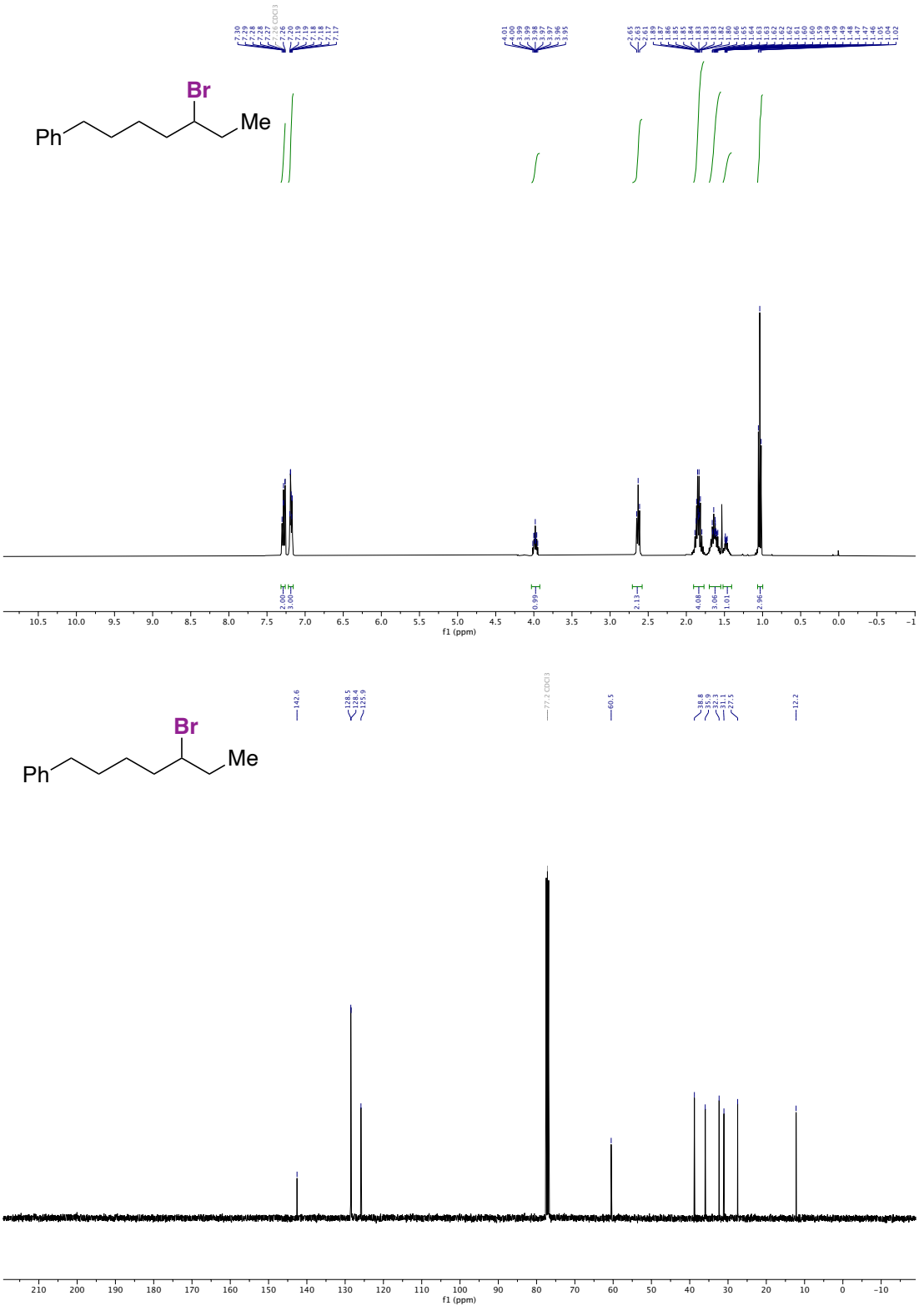


Figure 3. ^{1}H and ^{13}C NMR spectra of **(6-bromooctyl)benzene.**

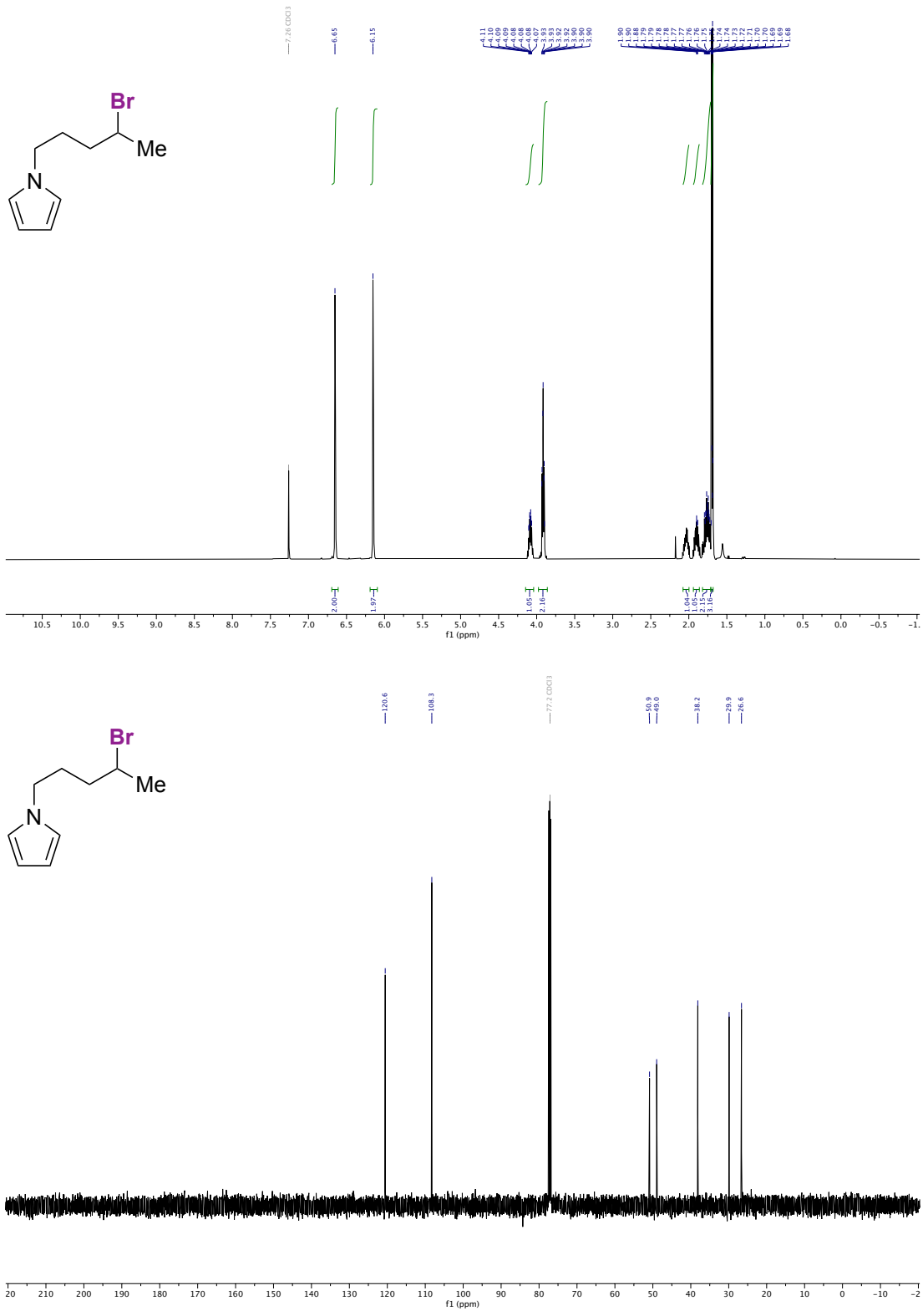


Figure 4.[1]H and [13]C NMR spectra of **1-(4-bromopentyl)-1*H*-pyrrole.**

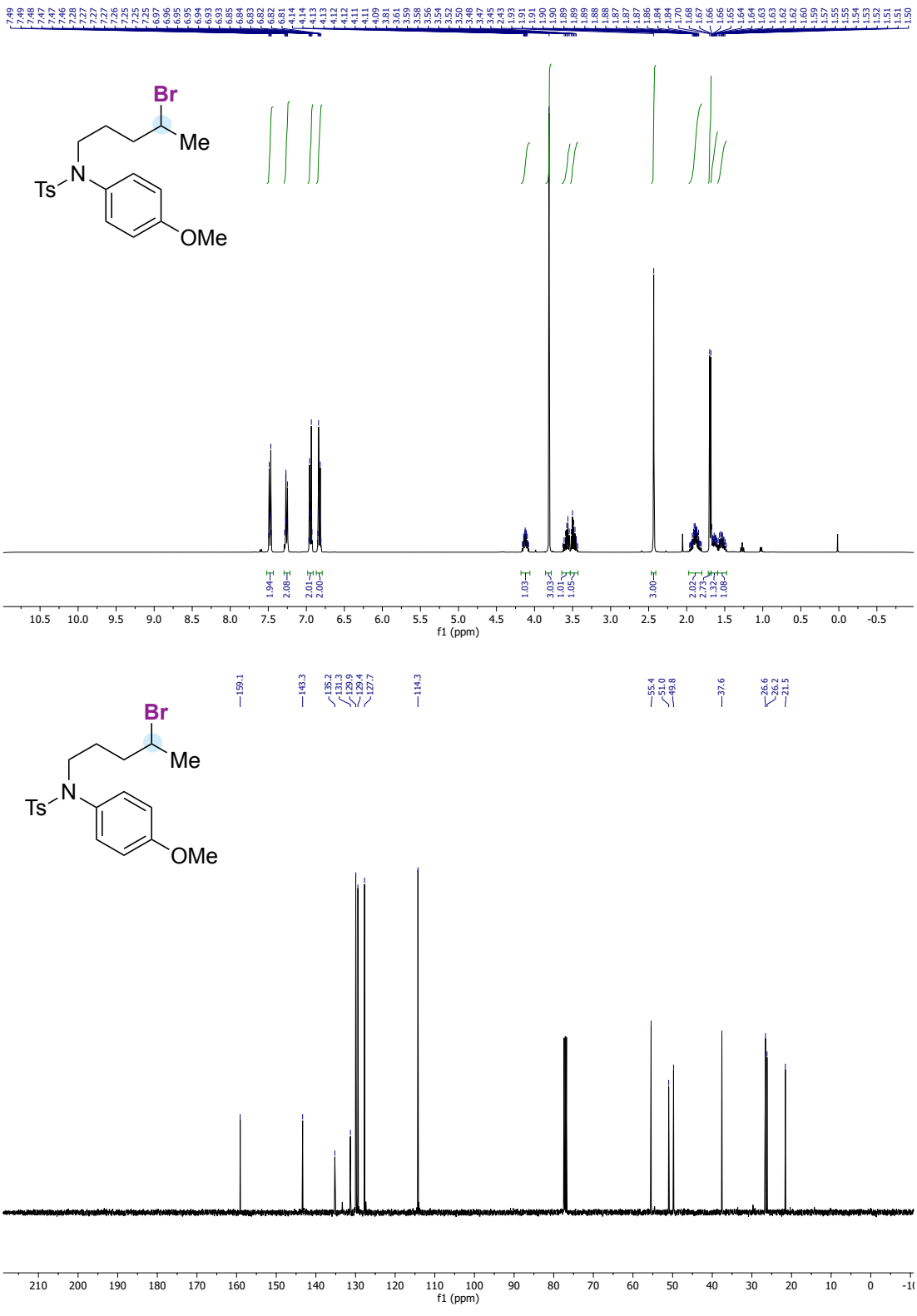


Figure 5. ^{1}H and ^{13}C NMR spectra of ***N*-(4-bromopentyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide.**

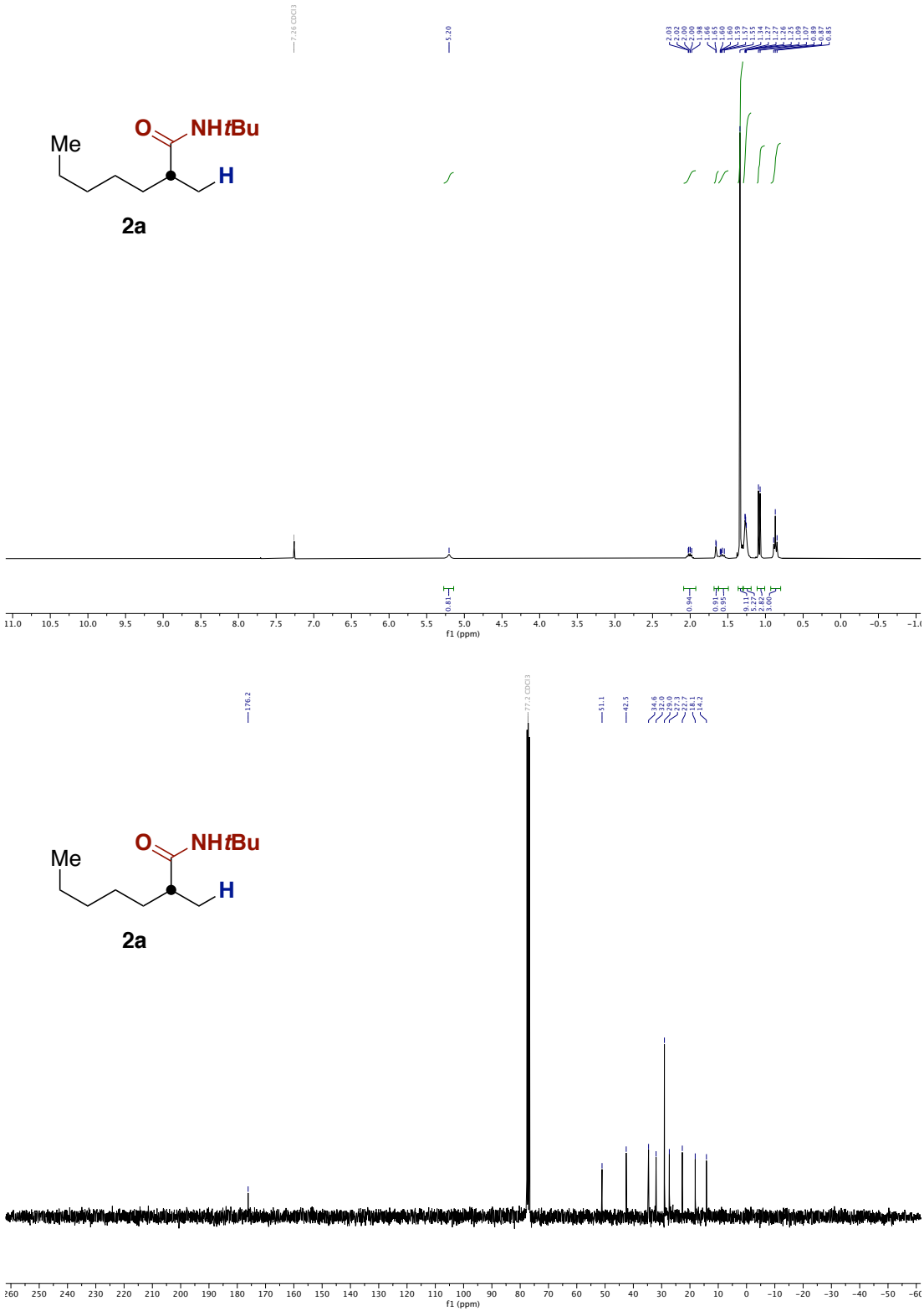


Figure 6. ^{1}H and ^{13}C NMR spectra of **2a**.

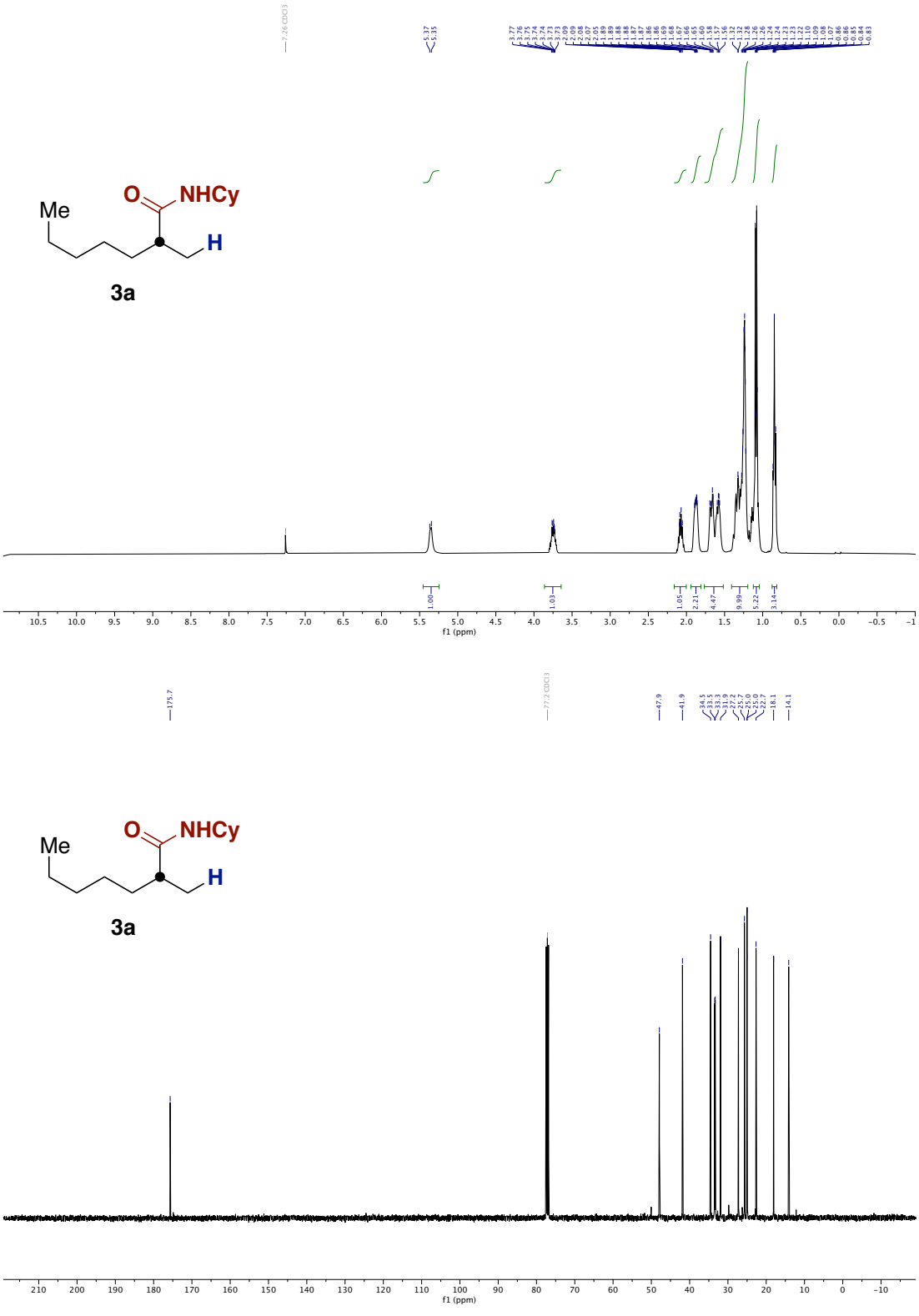


Figure 7. ^{1}H and ^{13}C NMR spectra of **3a**.

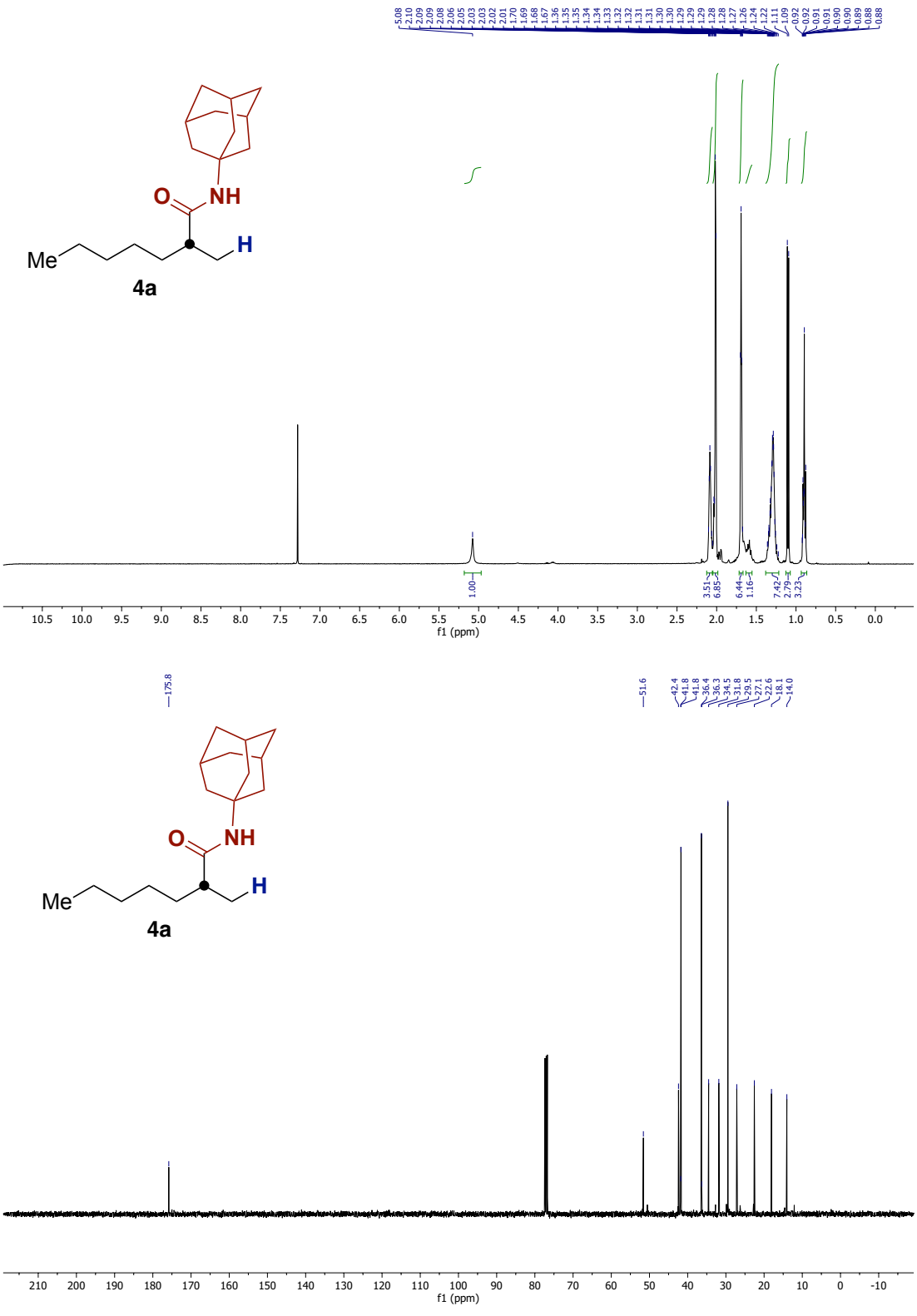


Figure 8. ^{1}H and ^{13}C NMR spectra of **4a**.

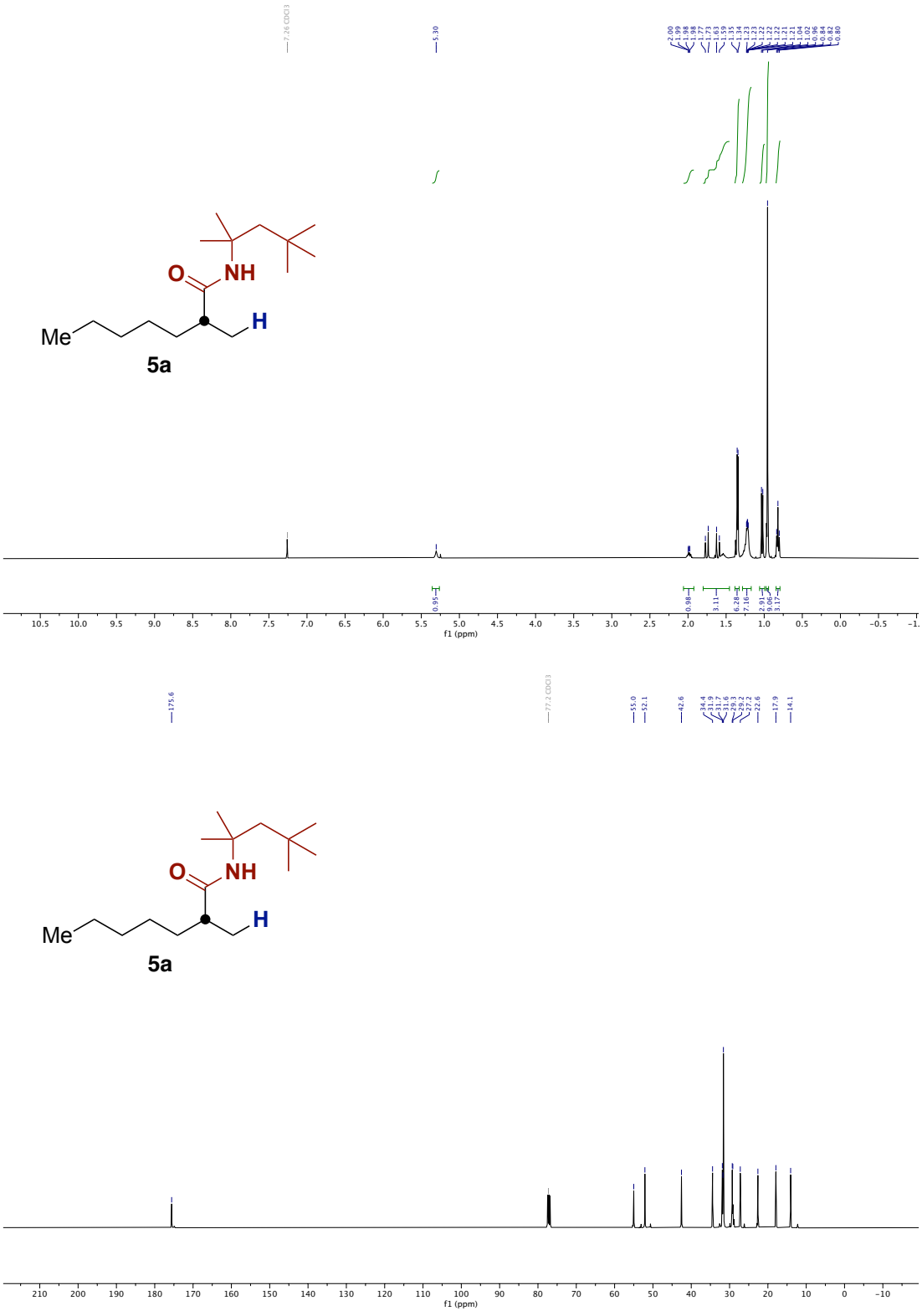


Figure 9. ^{1}H and ^{13}C NMR spectra of **6b**.

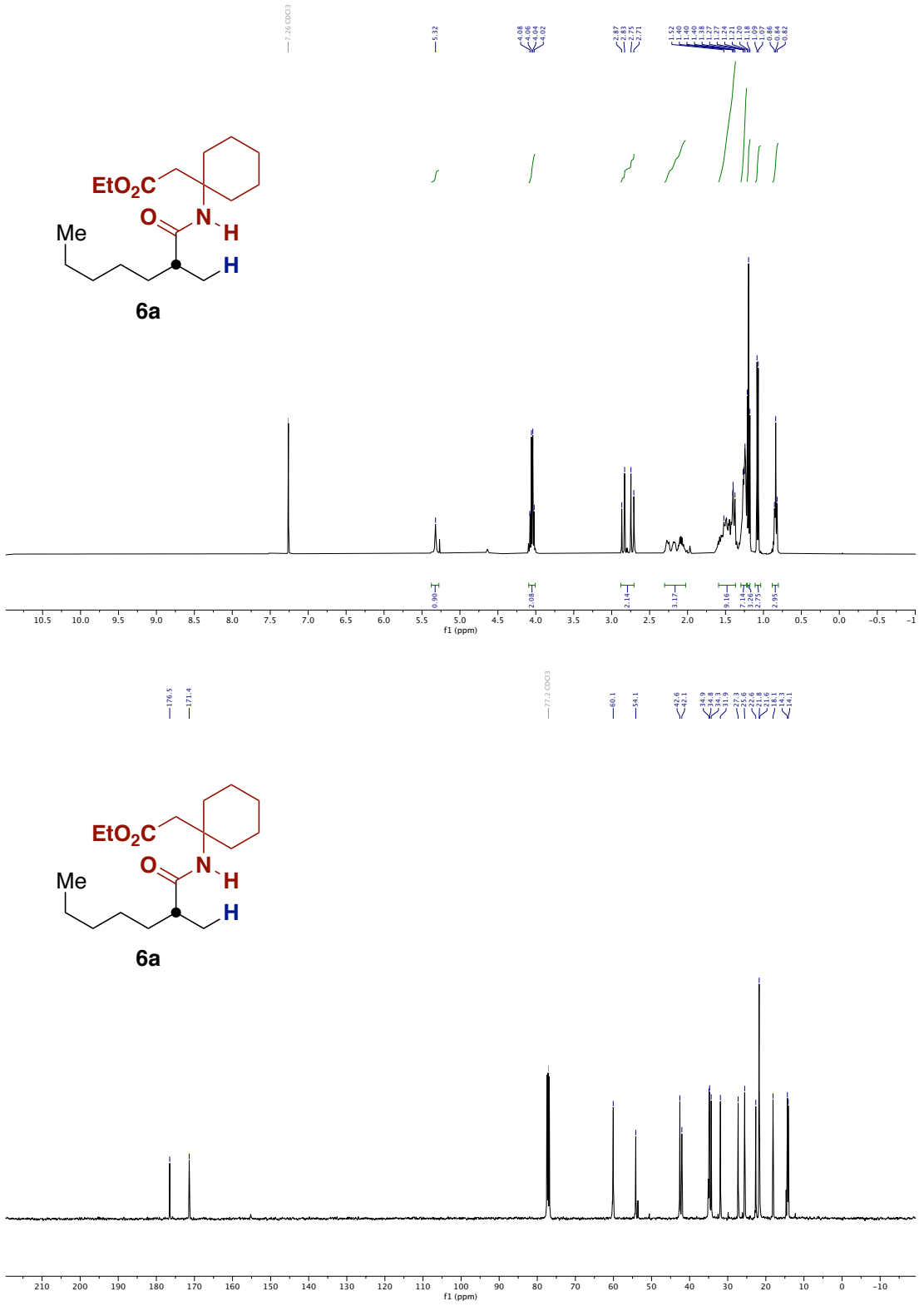
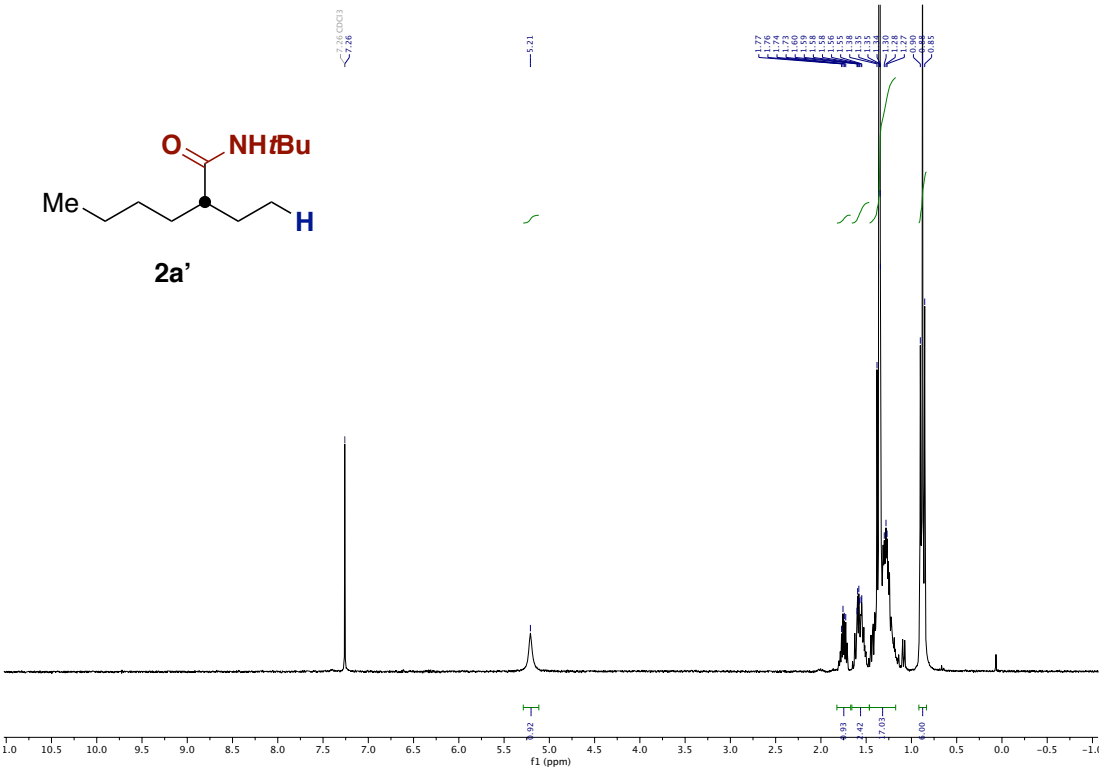


Figure 10. ^{1}H and ^{13}C NMR spectra of **6a**.



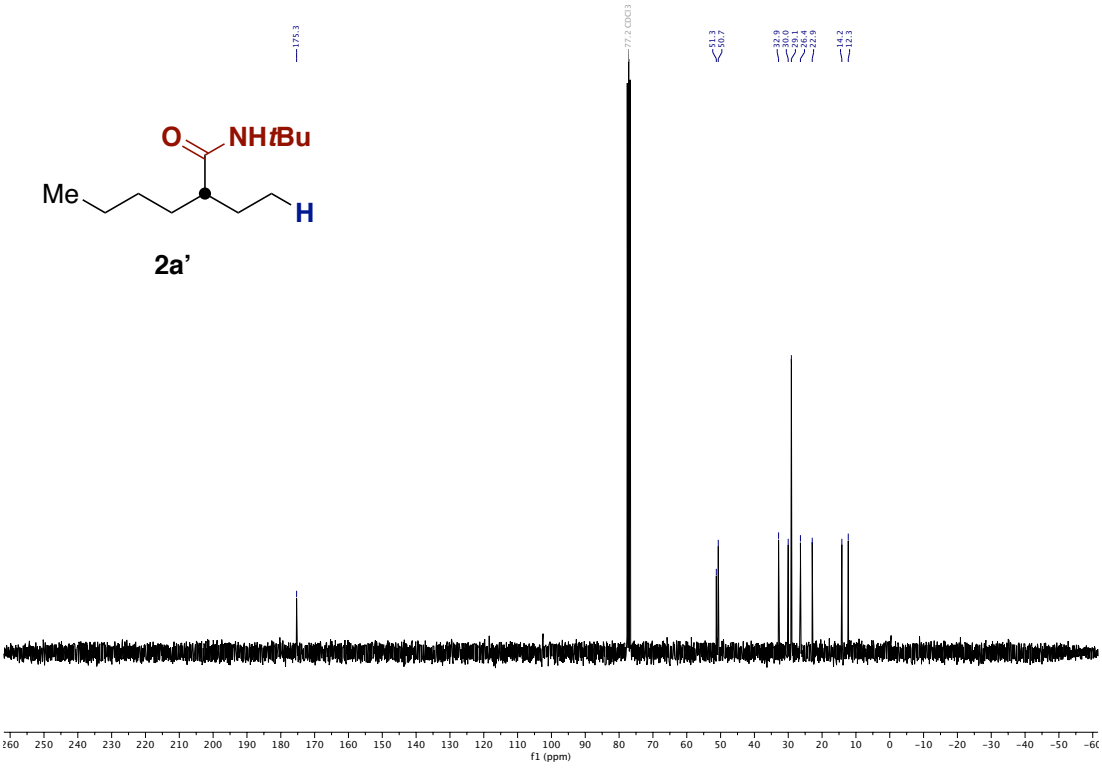
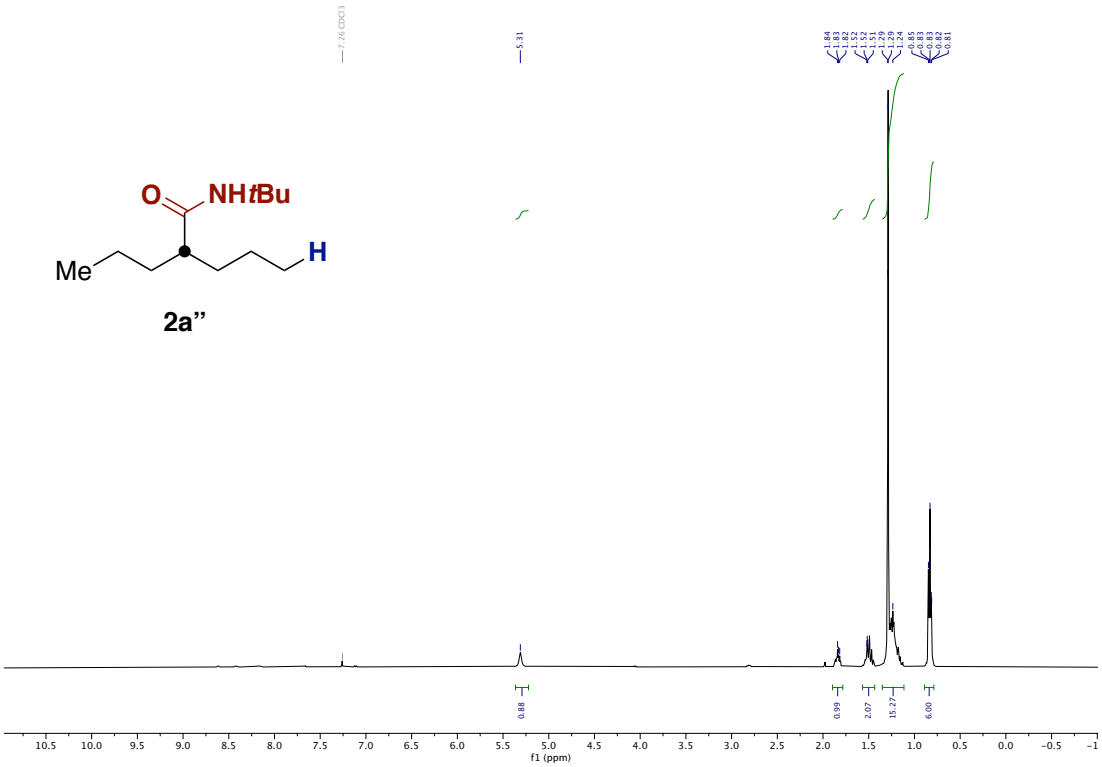


Figure 11. ^{1}H and ^{13}C NMR spectra of **2a'**.



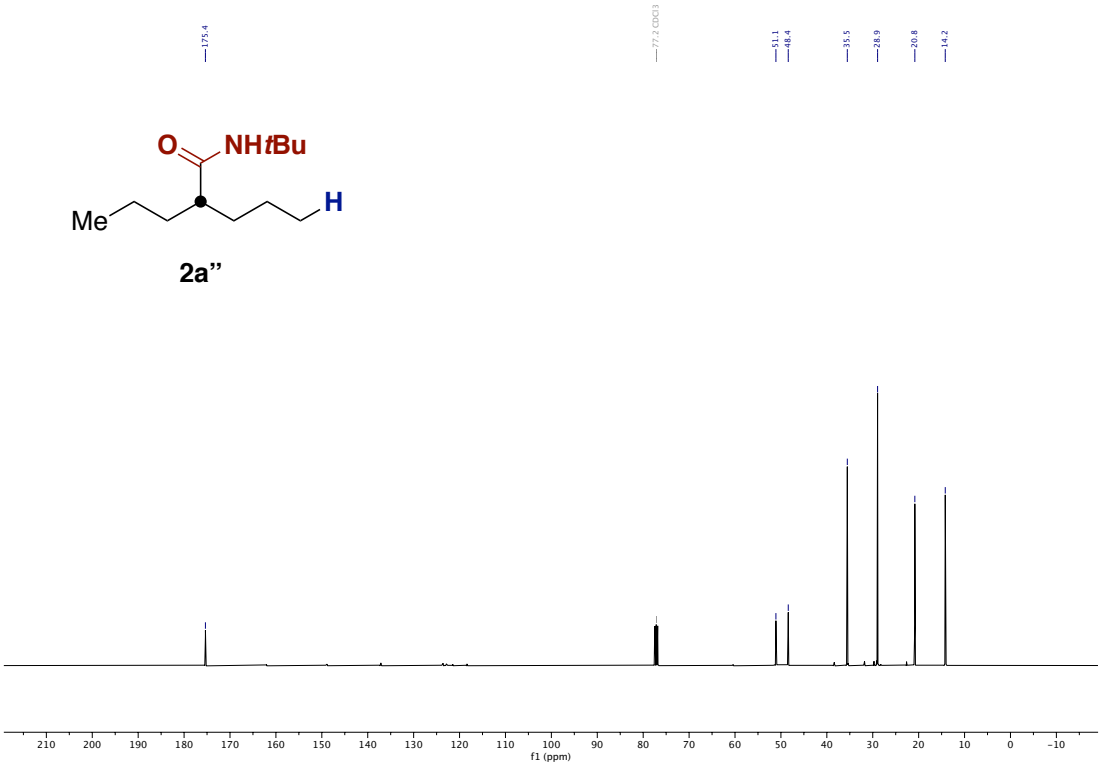


Figure 12. ^{1}H and ^{13}C NMR spectra of **2a''**.

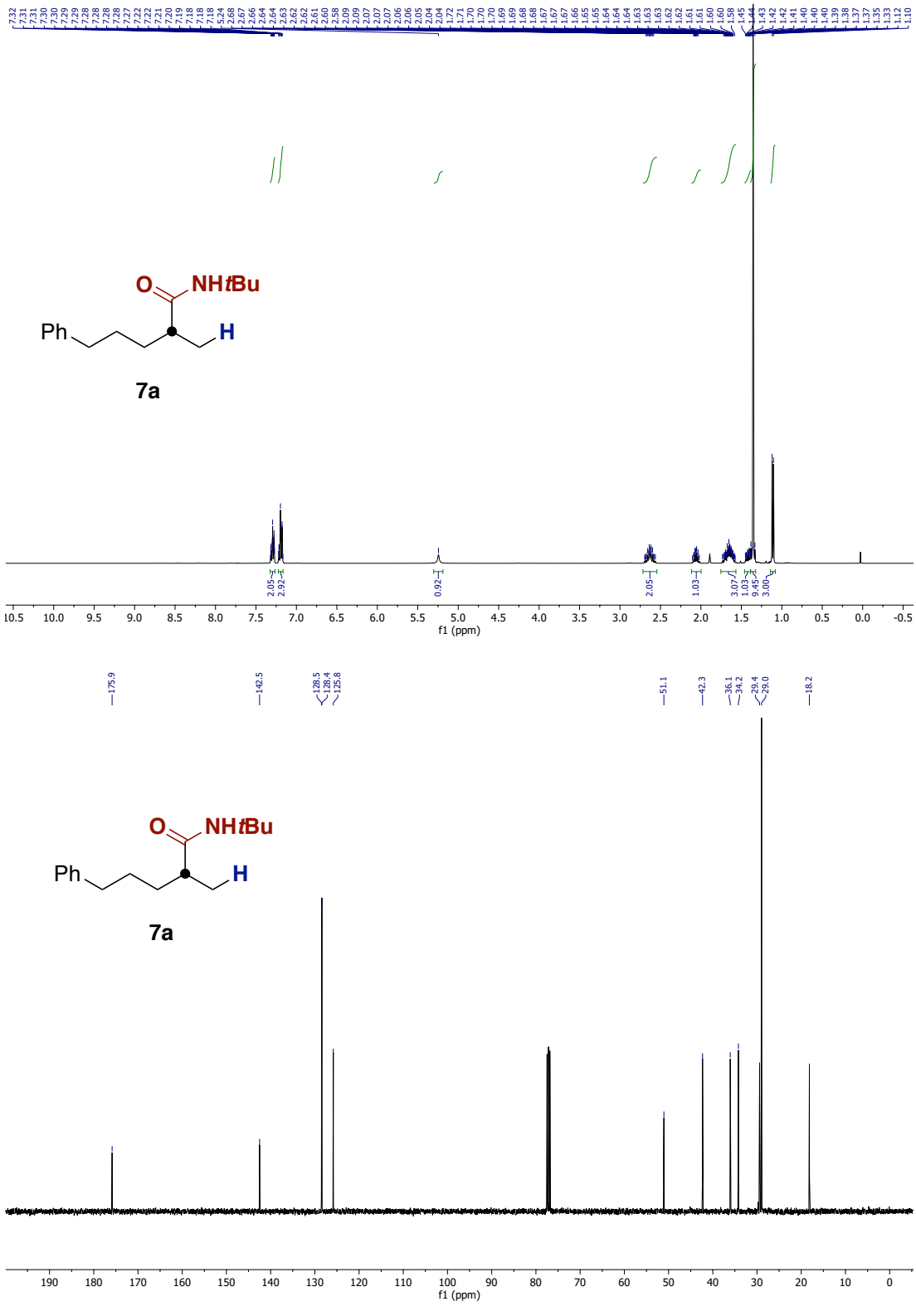


Figure 13. ^{1}H and ^{13}C NMR spectra of **7a**.

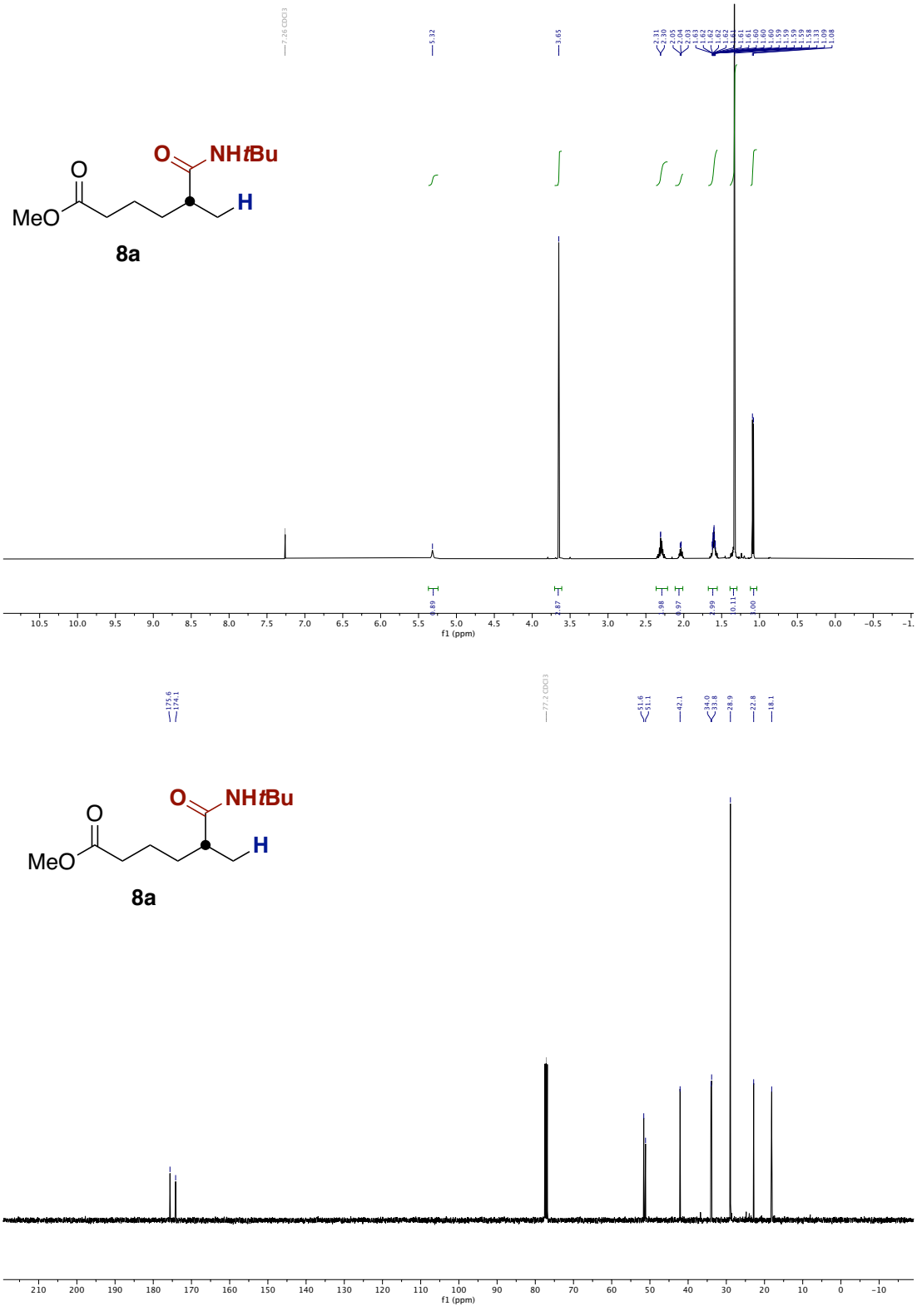


Figure 14. ^{1}H and ^{13}C NMR spectra of **8a**.

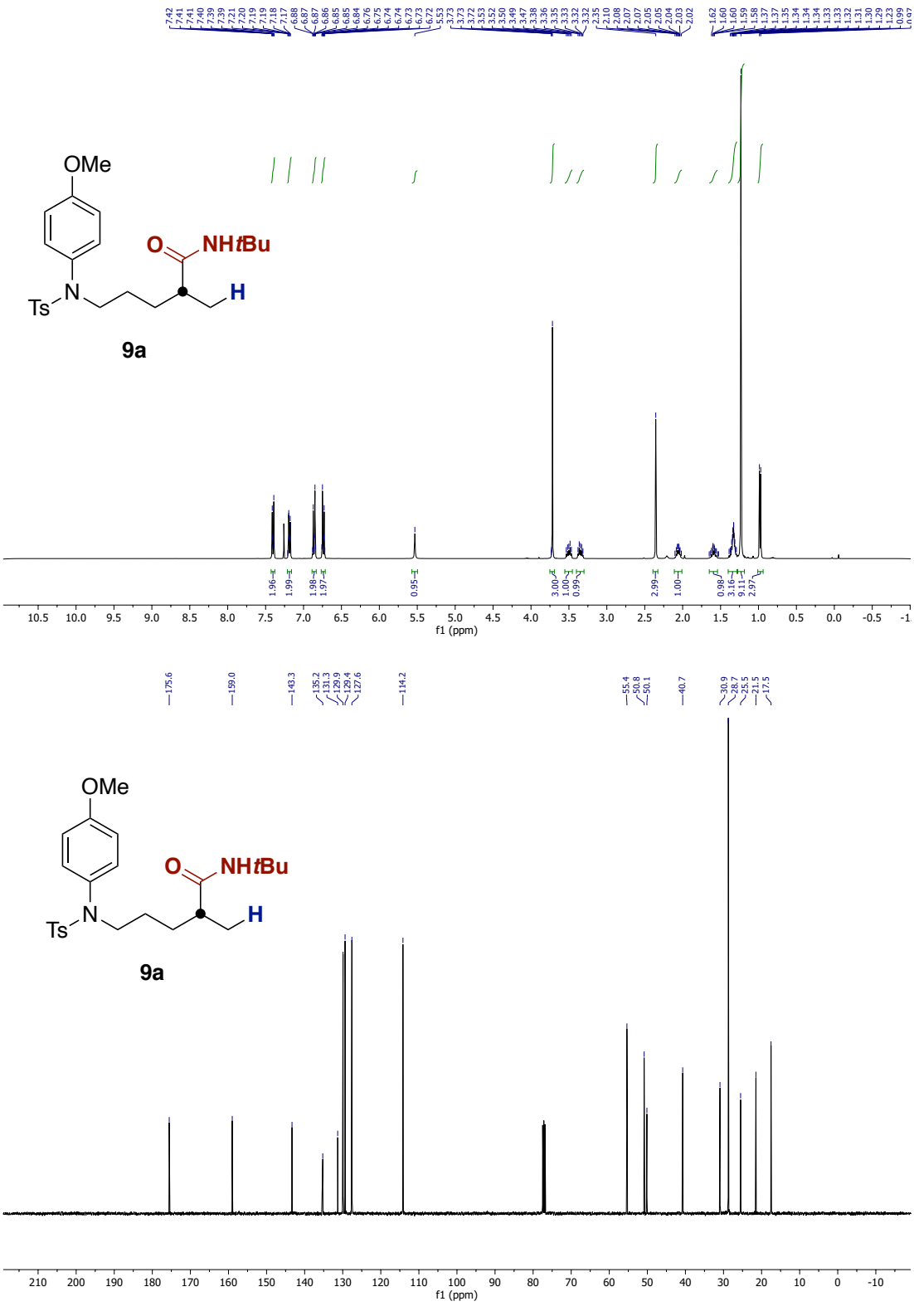


Figure 15. ^{1}H and ^{13}C NMR spectra of **9a**.

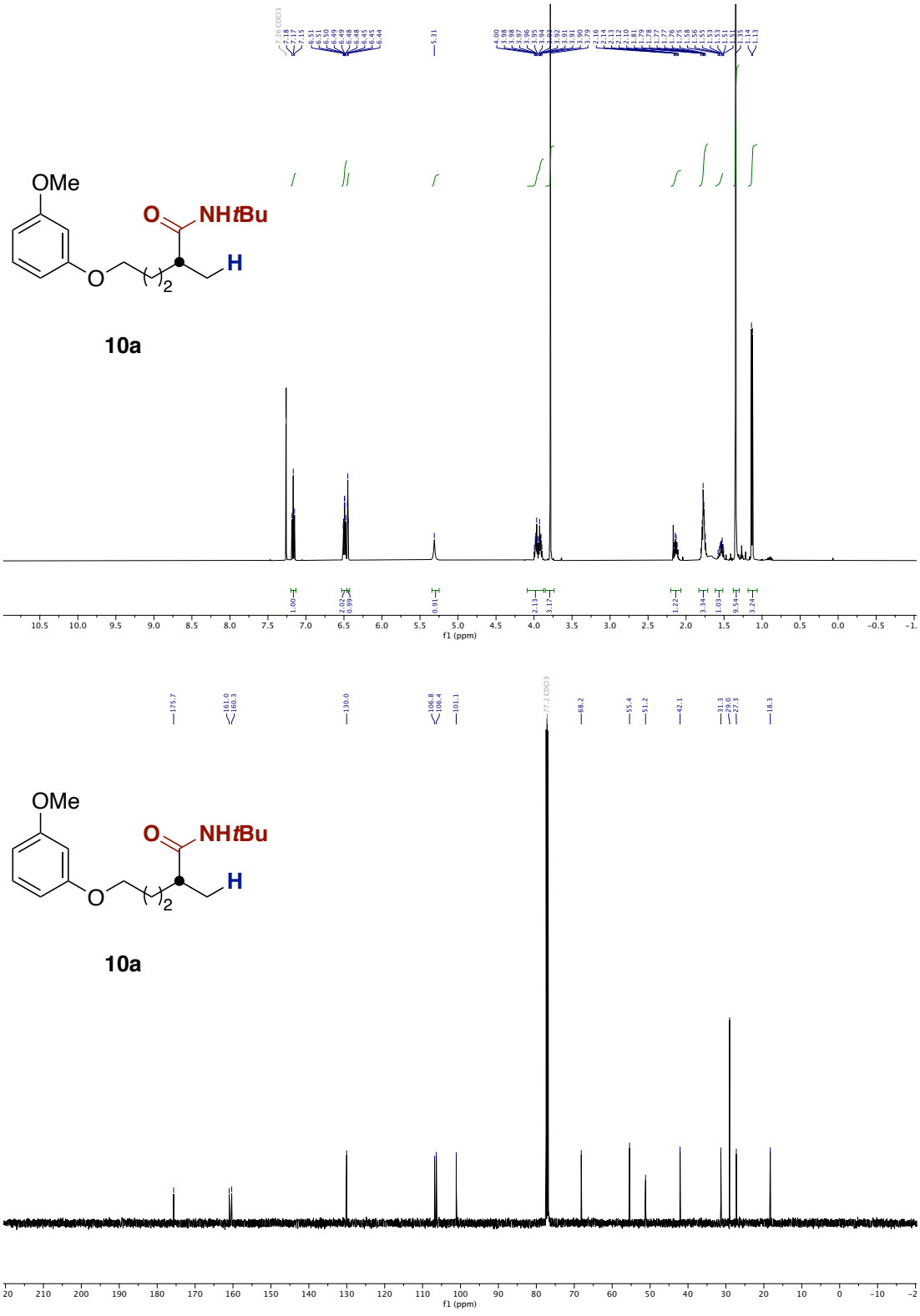
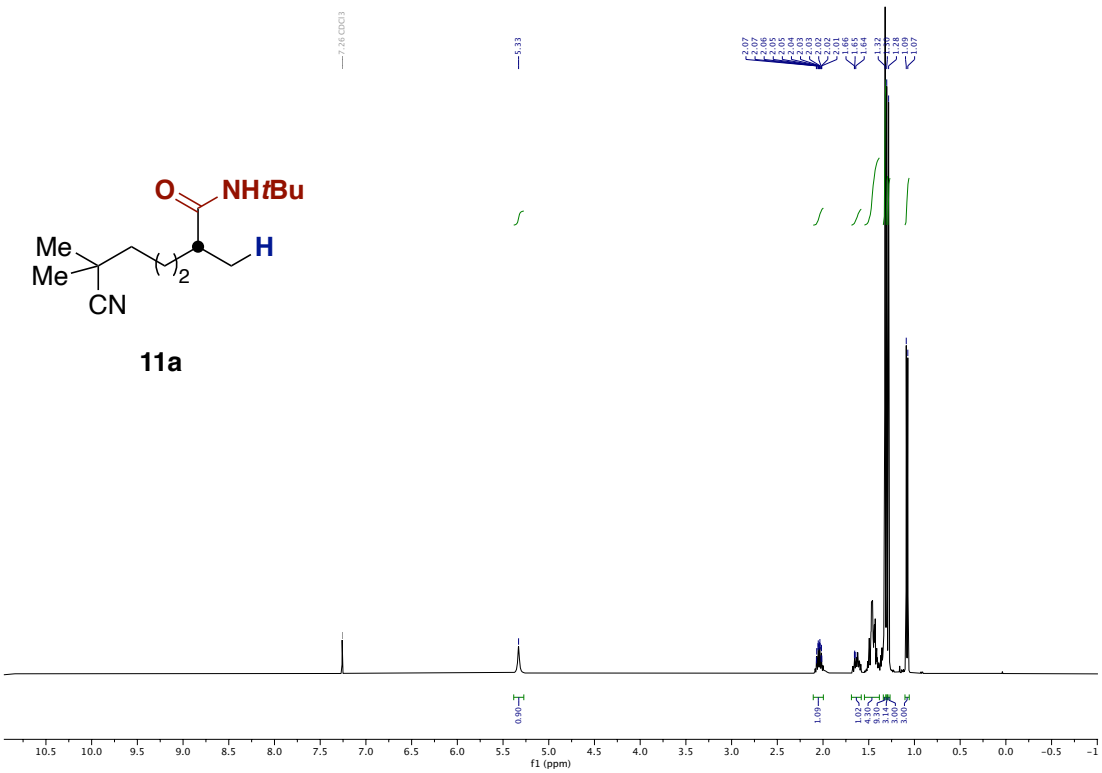


Figure 16. . ^{1}H and ^{13}C NMR spectra of **10a**.



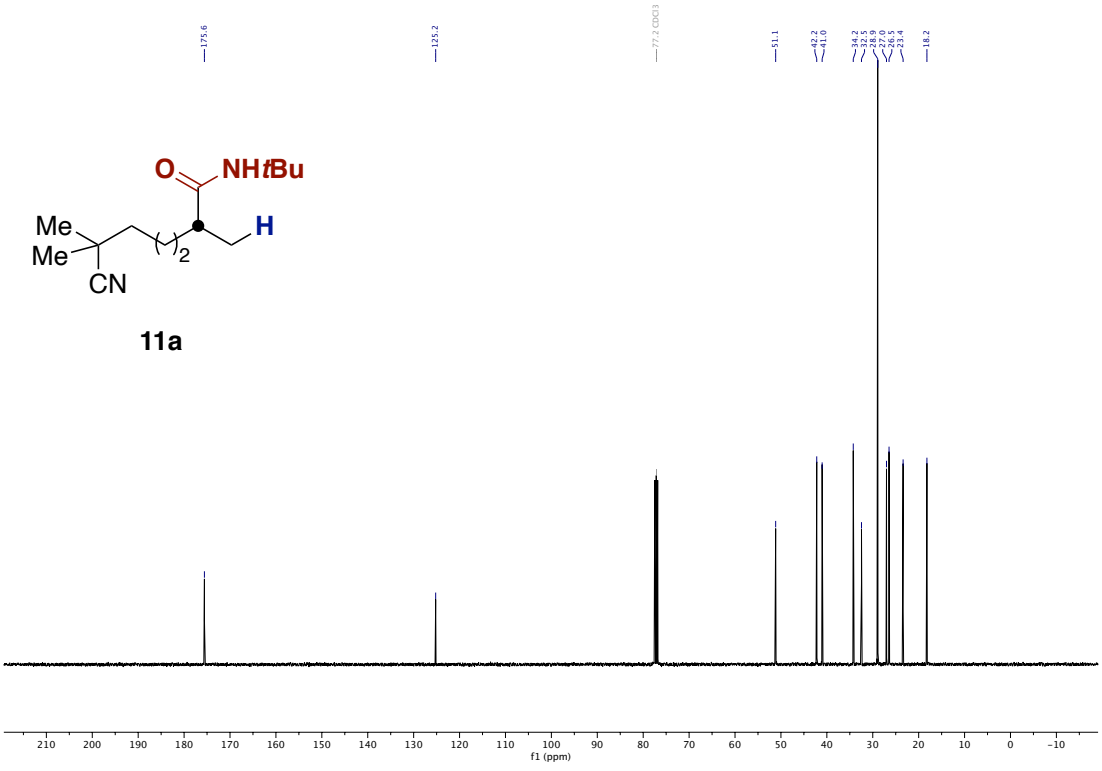


Figure 17. . ^{1}H and ^{13}C NMR spectra of **11a**.

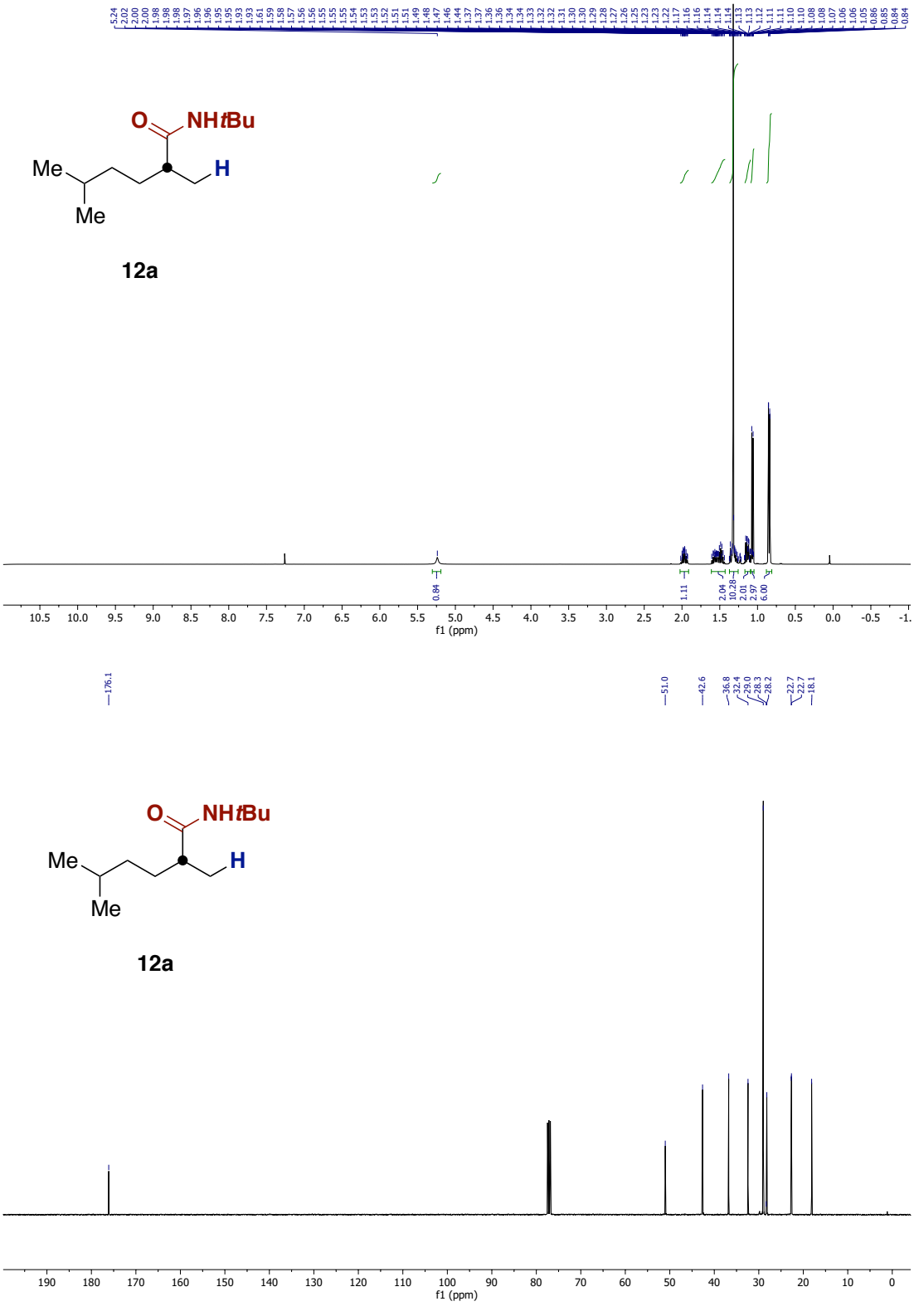


Figure 18. ^{1}H and ^{13}C NMR spectra of **12a**.

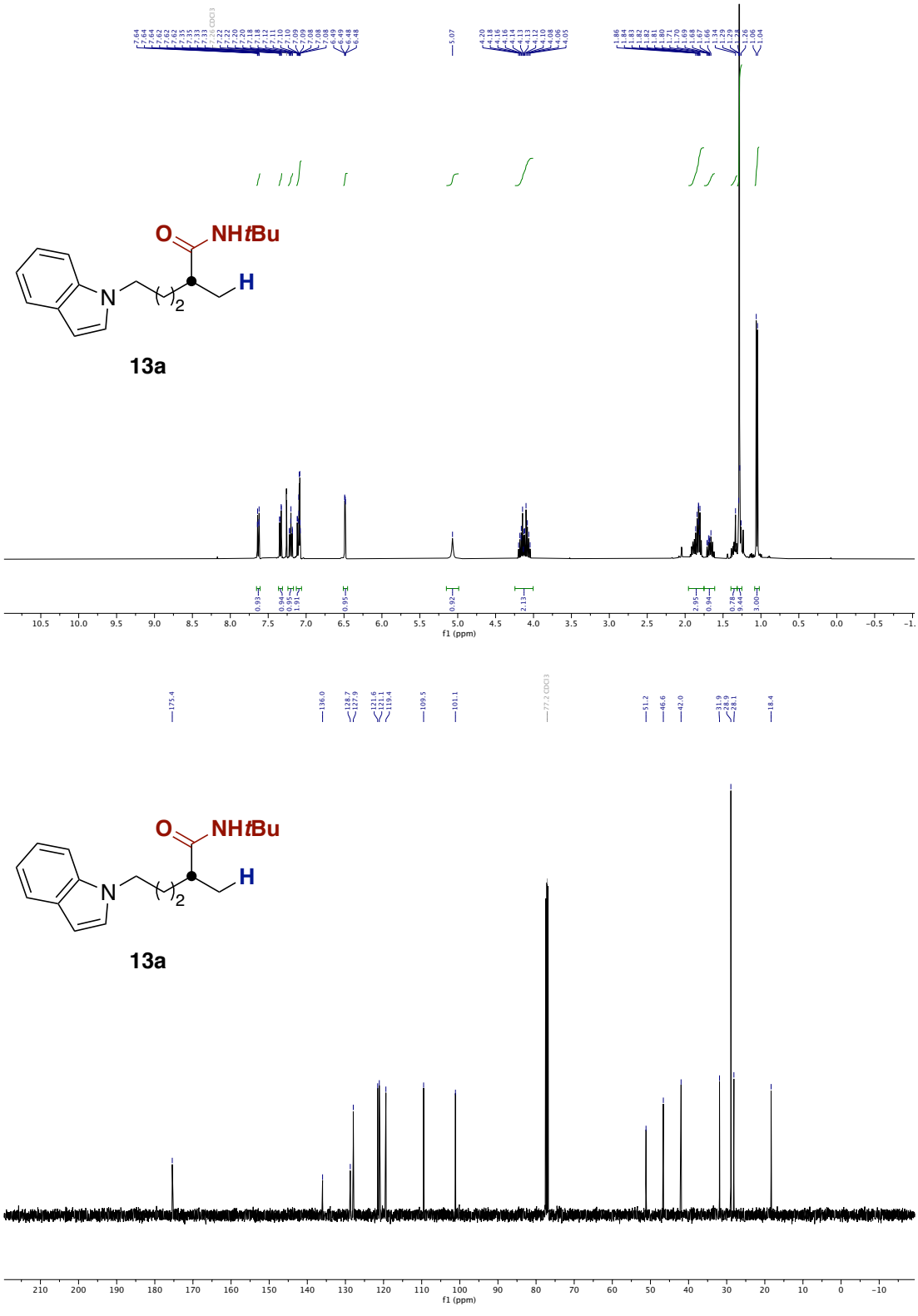


Figure 19. ^{1}H and ^{13}C NMR spectra of **13a**.

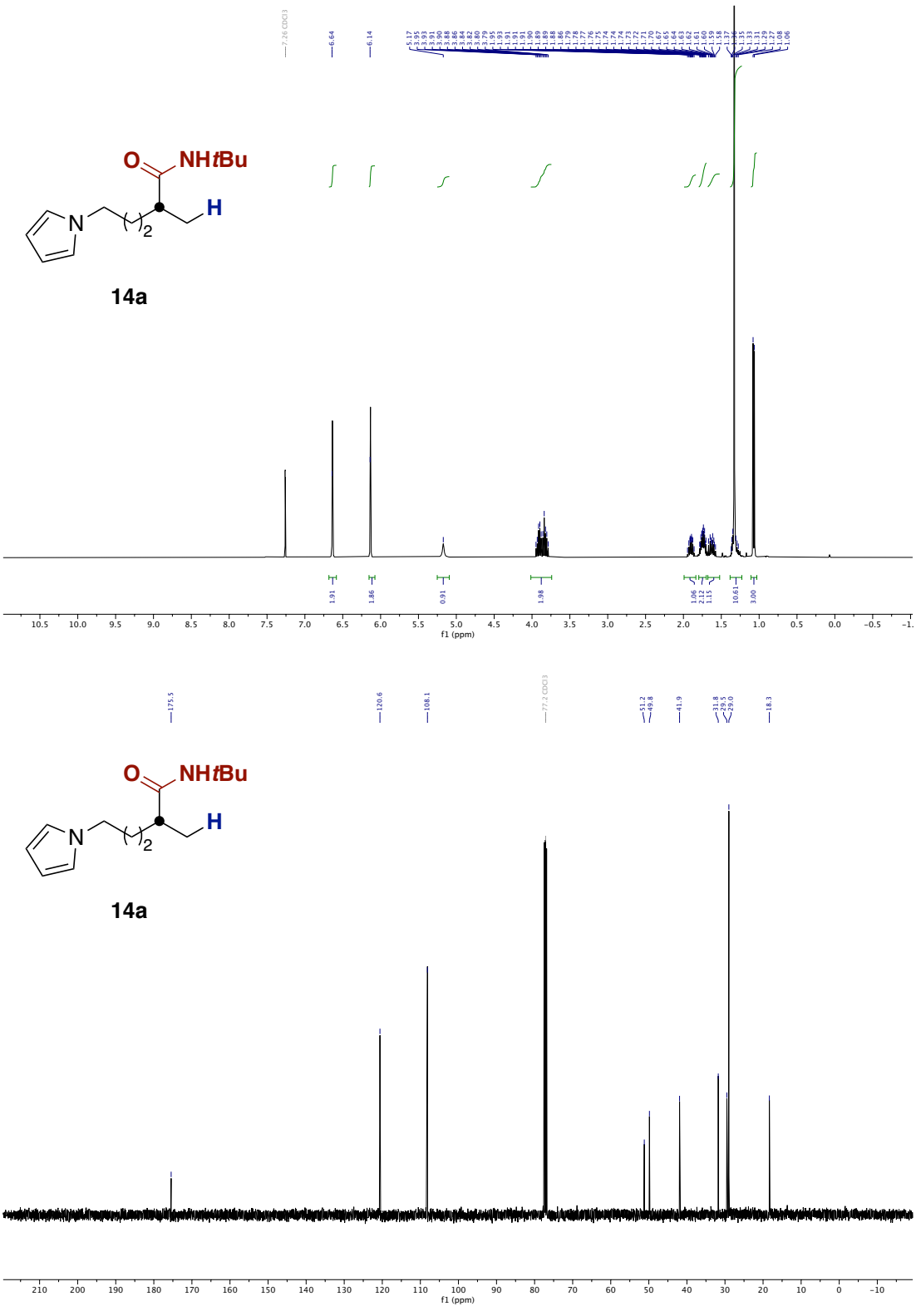


Figure 20. ^{1}H and ^{13}C NMR spectra of **14a**.

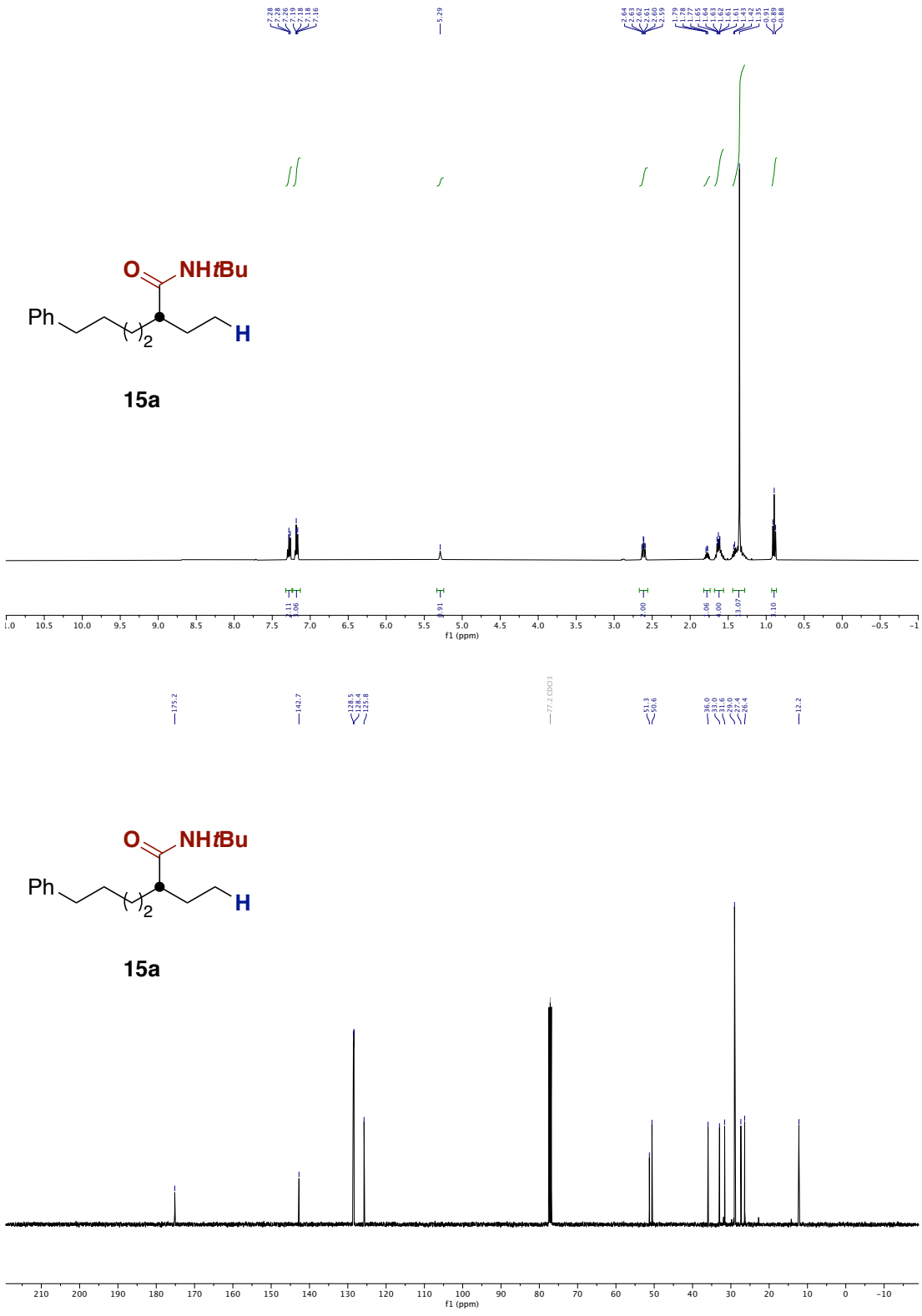
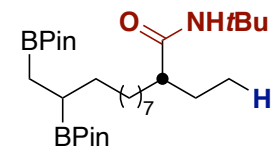
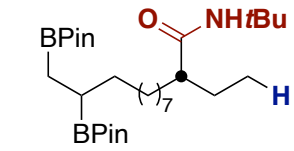


Figure 21. ^{1}H and ^{13}C NMR spectra of **15a**.


O
NHtBu
BPin
H
7
BPin

16a

7.26 CDCl3
5.25
1.73
1.72
1.71
1.70
1.52
1.39
1.38
1.18
1.17
1.13
1.12
0.84
0.82
0.80
0.78
0.75
0.74
0.85
1.00
2.14
2.89
2.80
37.15
1.07
5.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


O
NHtBu
BPin
H
7
BPin

16a

175.2
82.8
82.7
77.2 CDCl3
51.1
50.4
33.8
33.0
29.8
29.7
29.5
29.5
29.3
28.8
27.6
27.2
24.9
24.8
24.8
24.7
18.4
12.7
12.1
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−2
f1 (ppm)

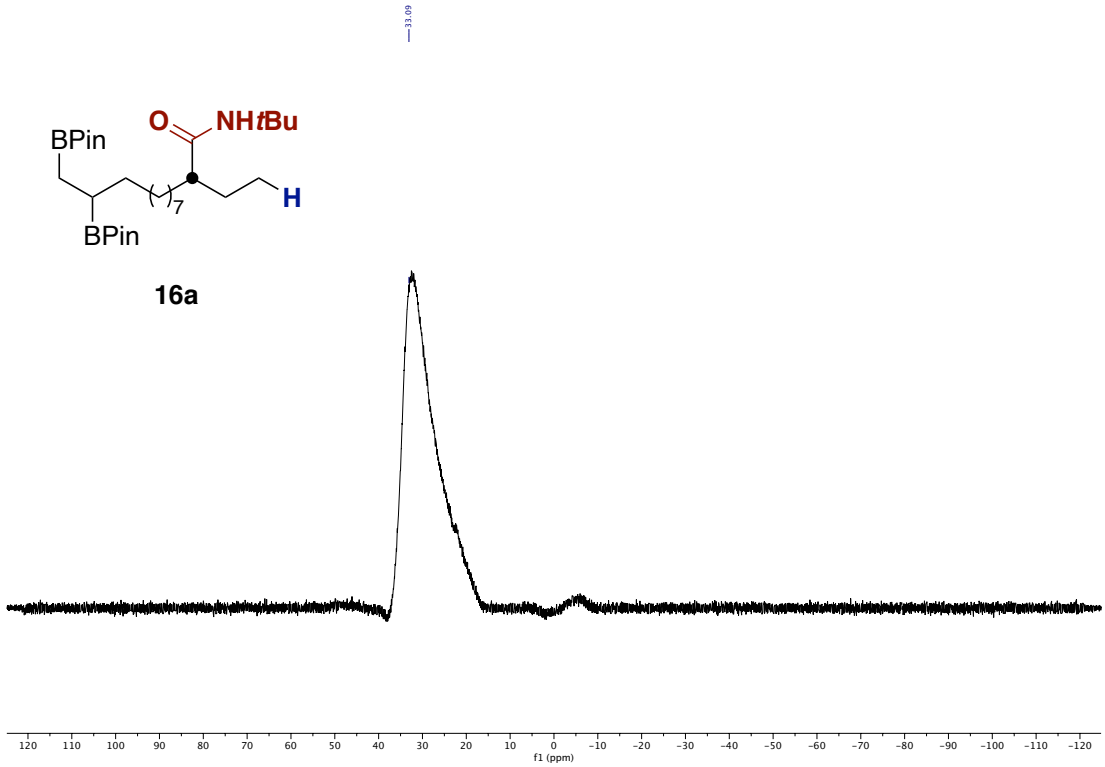
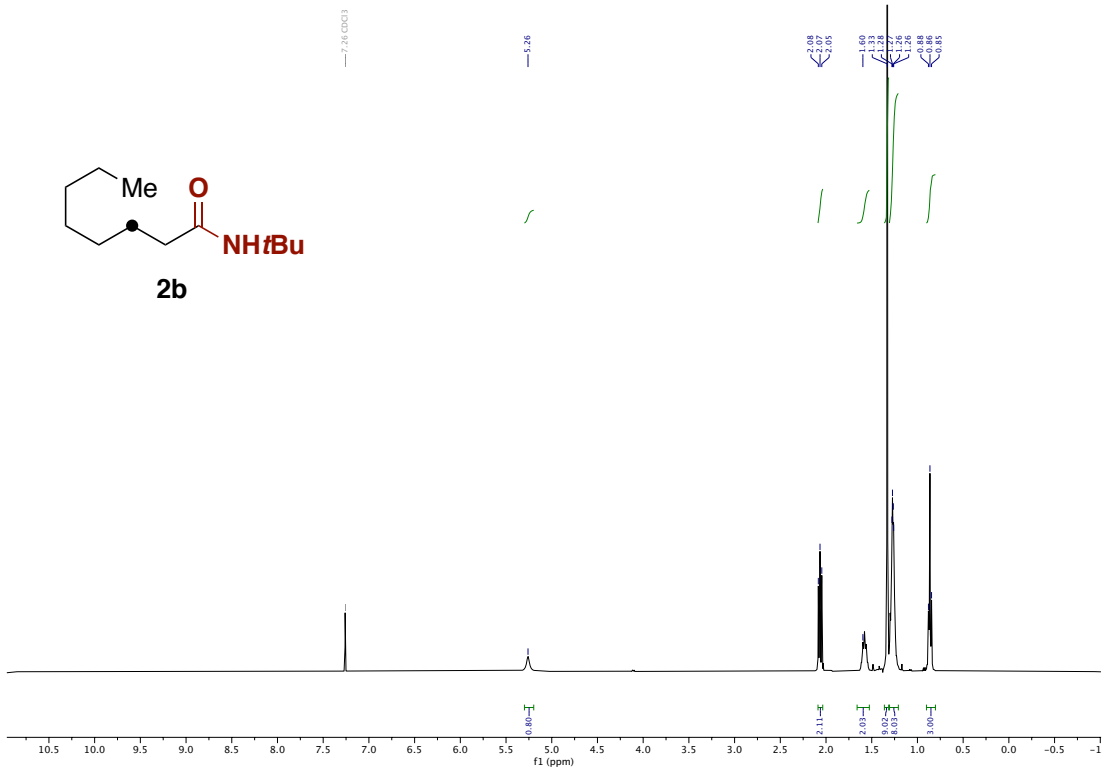


Figure 22. ^{1}H, ^{13}C and ^{11}B NMR spectra of **16a**.



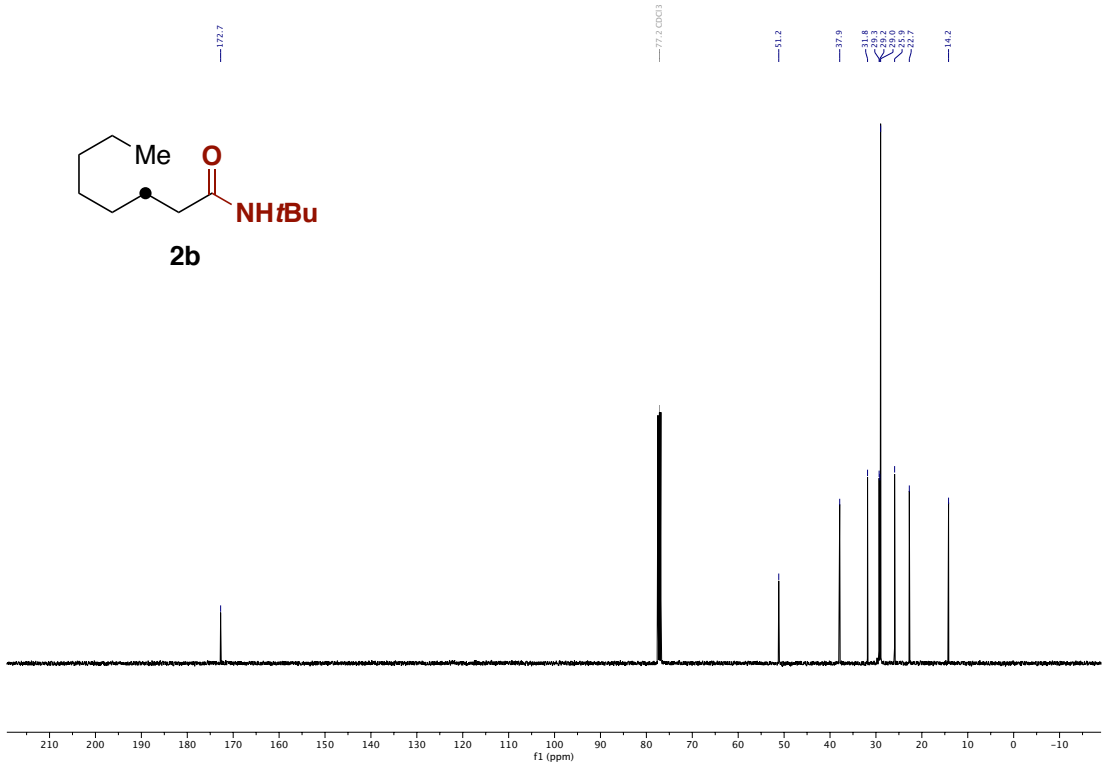


Figure 23. ^{1}H and ^{13}C NMR spectra of **2b**.

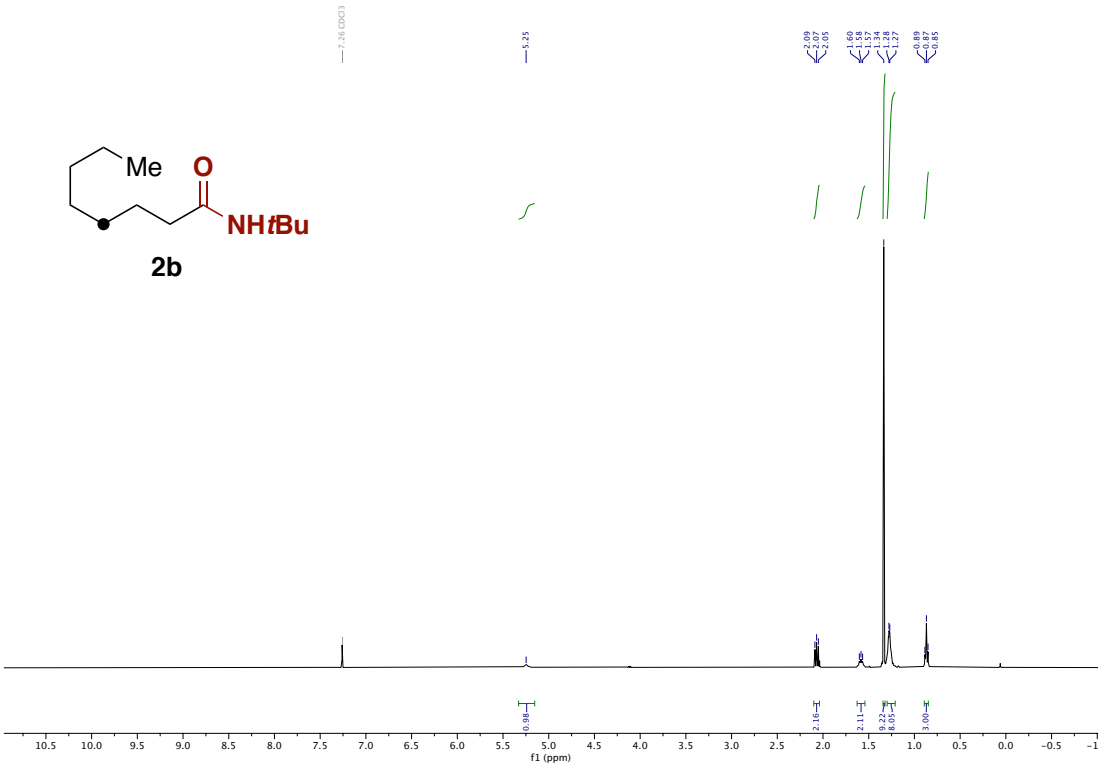


Figure 24. ^{1}H NMR spectrum of (Starting from 3-bromoheptane).

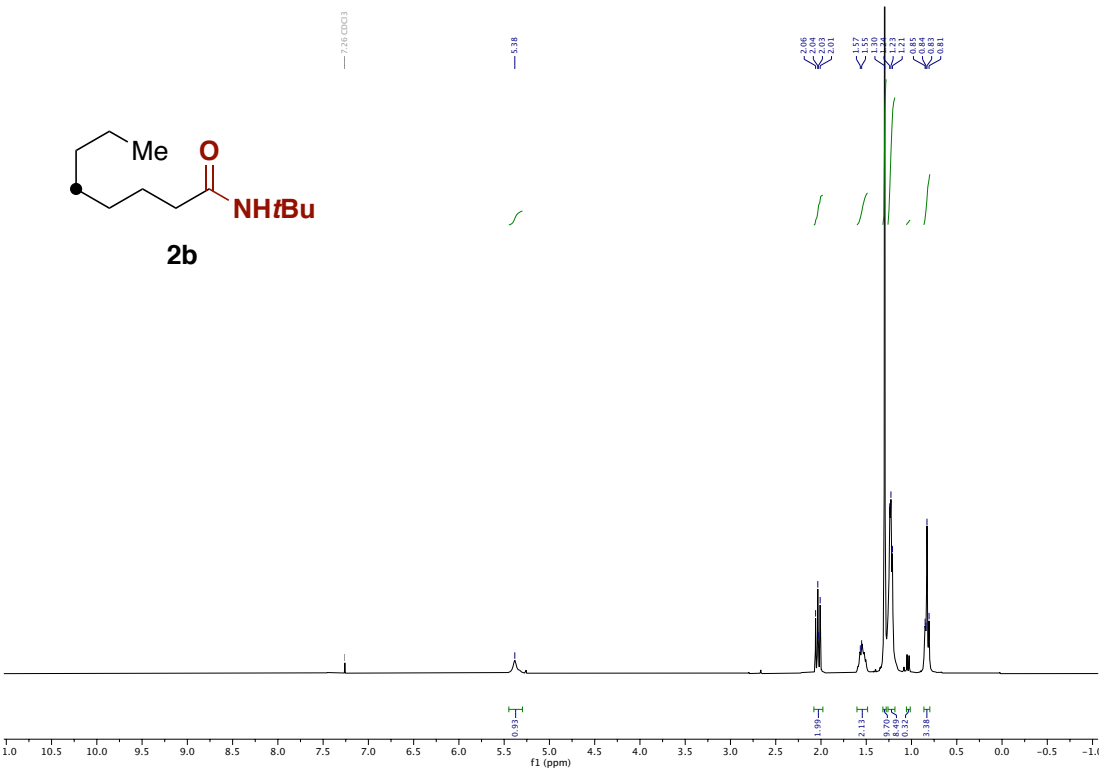


Figure 25. ^{1}H NMR spectrum of **2b** (Starting from 4-bromoheptane).

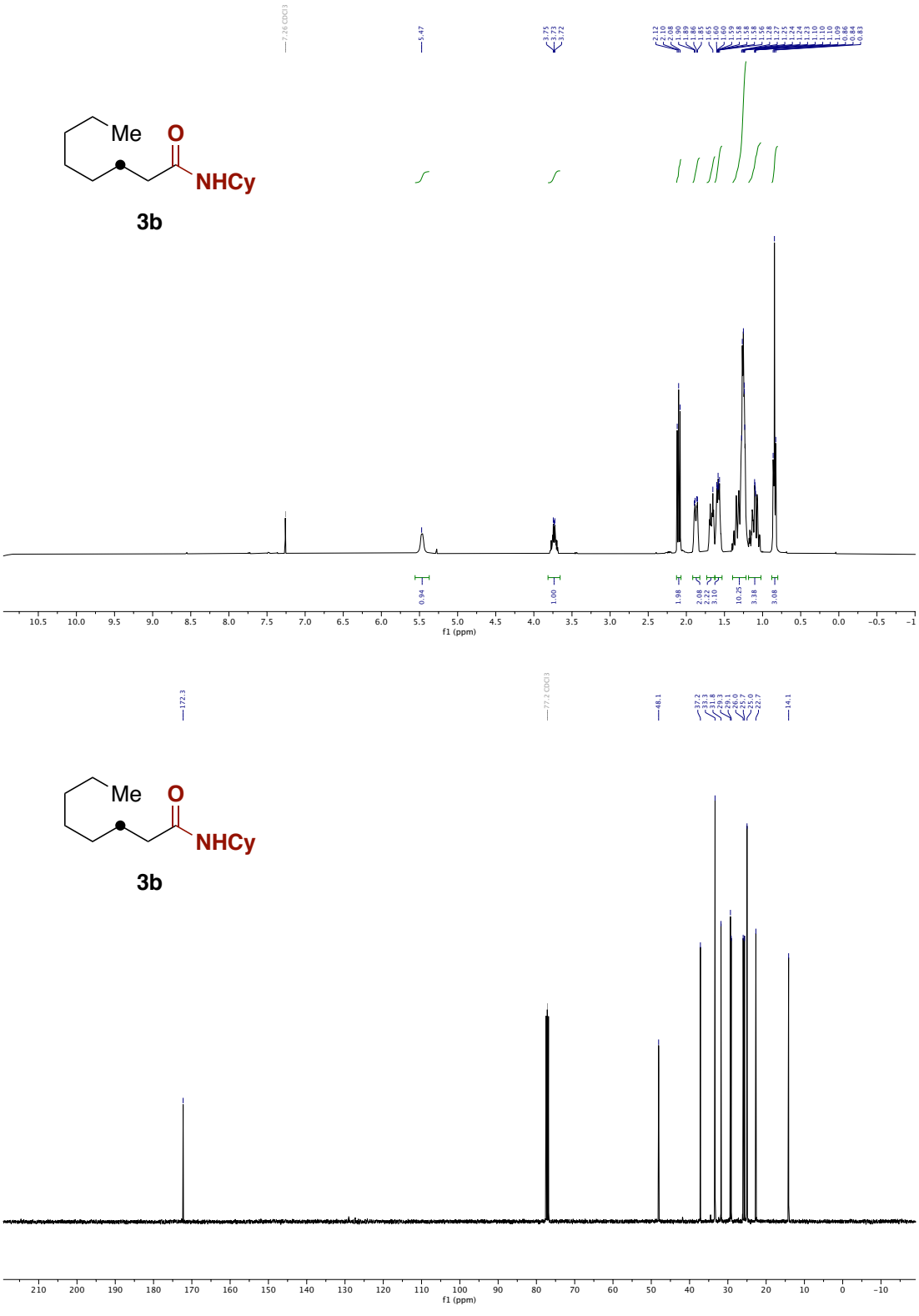


Figure 26. ^{1}H and ^{13}C NMR spectra of **3b**.

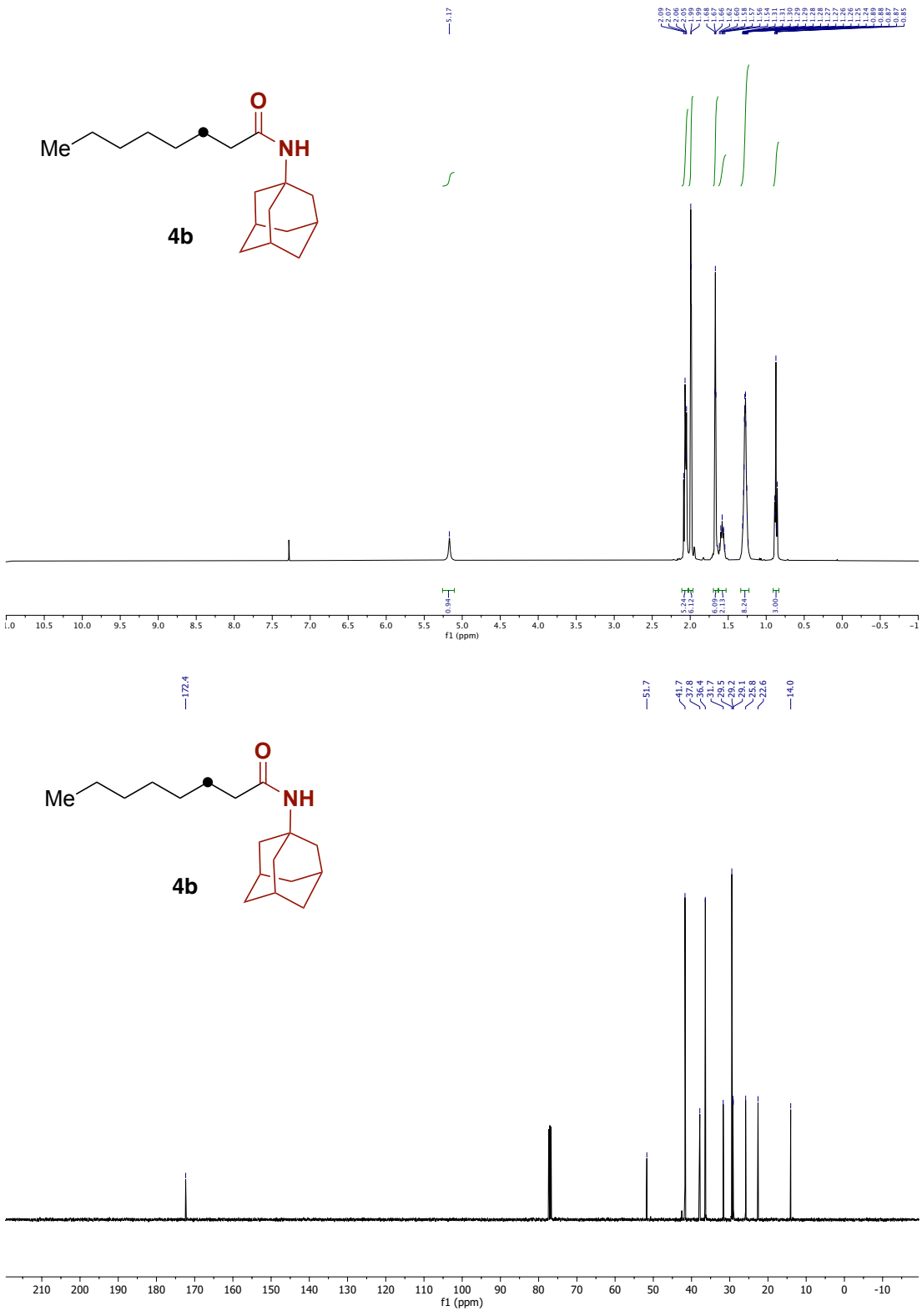


Figure 27. ^{1}H and ^{13}C NMR spectra of **4b**.

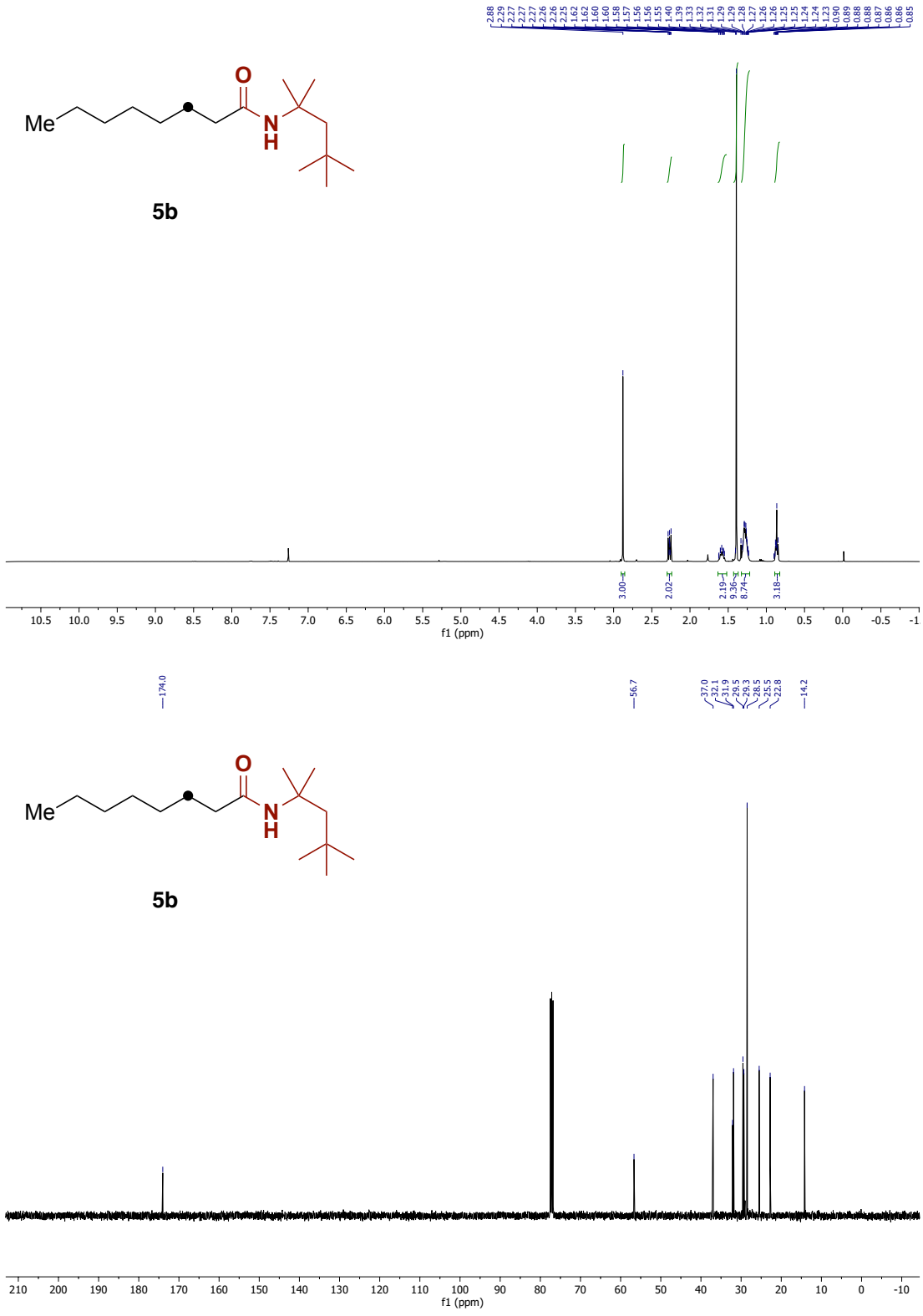


Figure 28. ^{1}H and ^{13}C NMR spectra of **5b**.

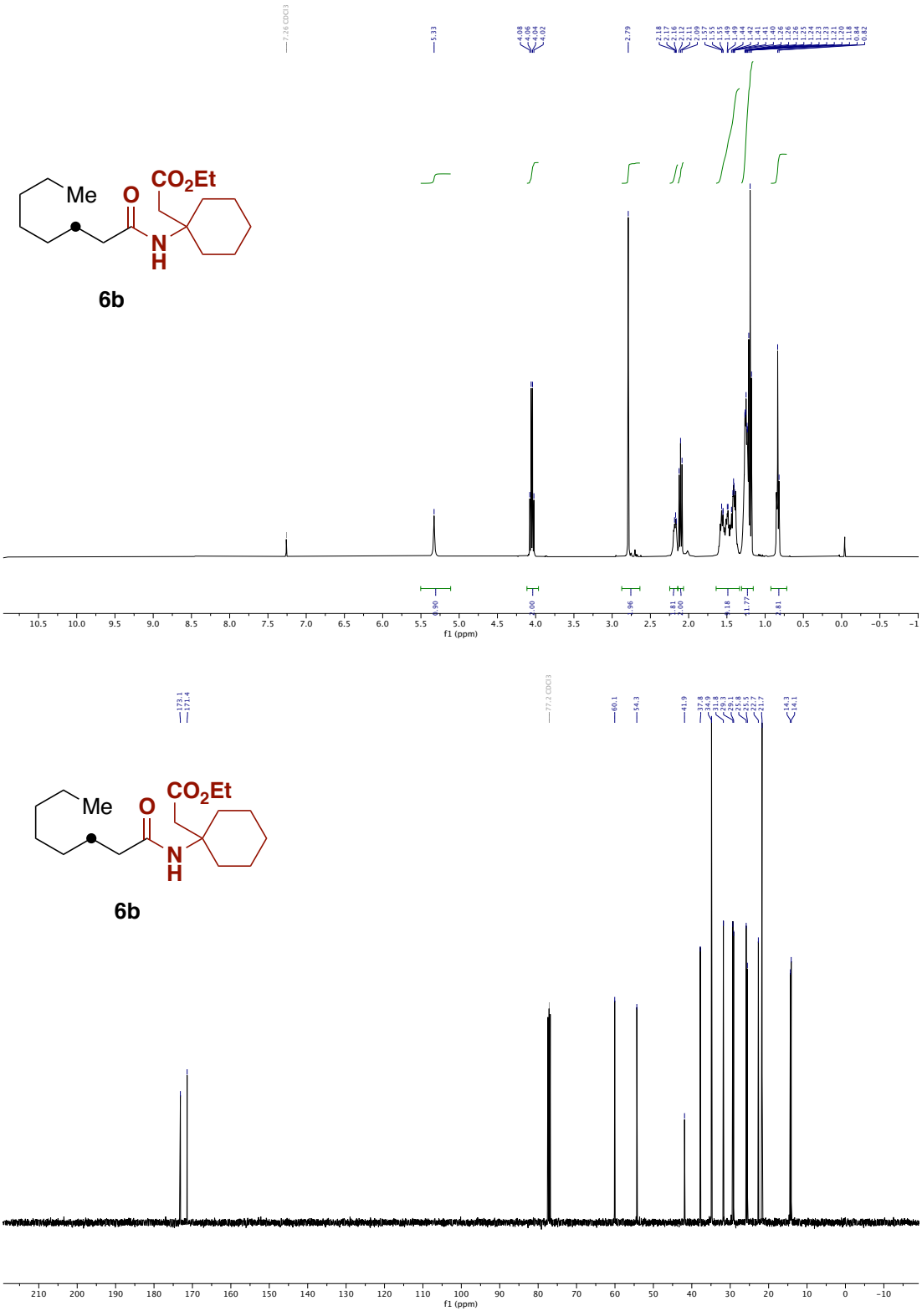


Figure 29. ^{1}H and ^{13}C NMR spectra of **6b**.

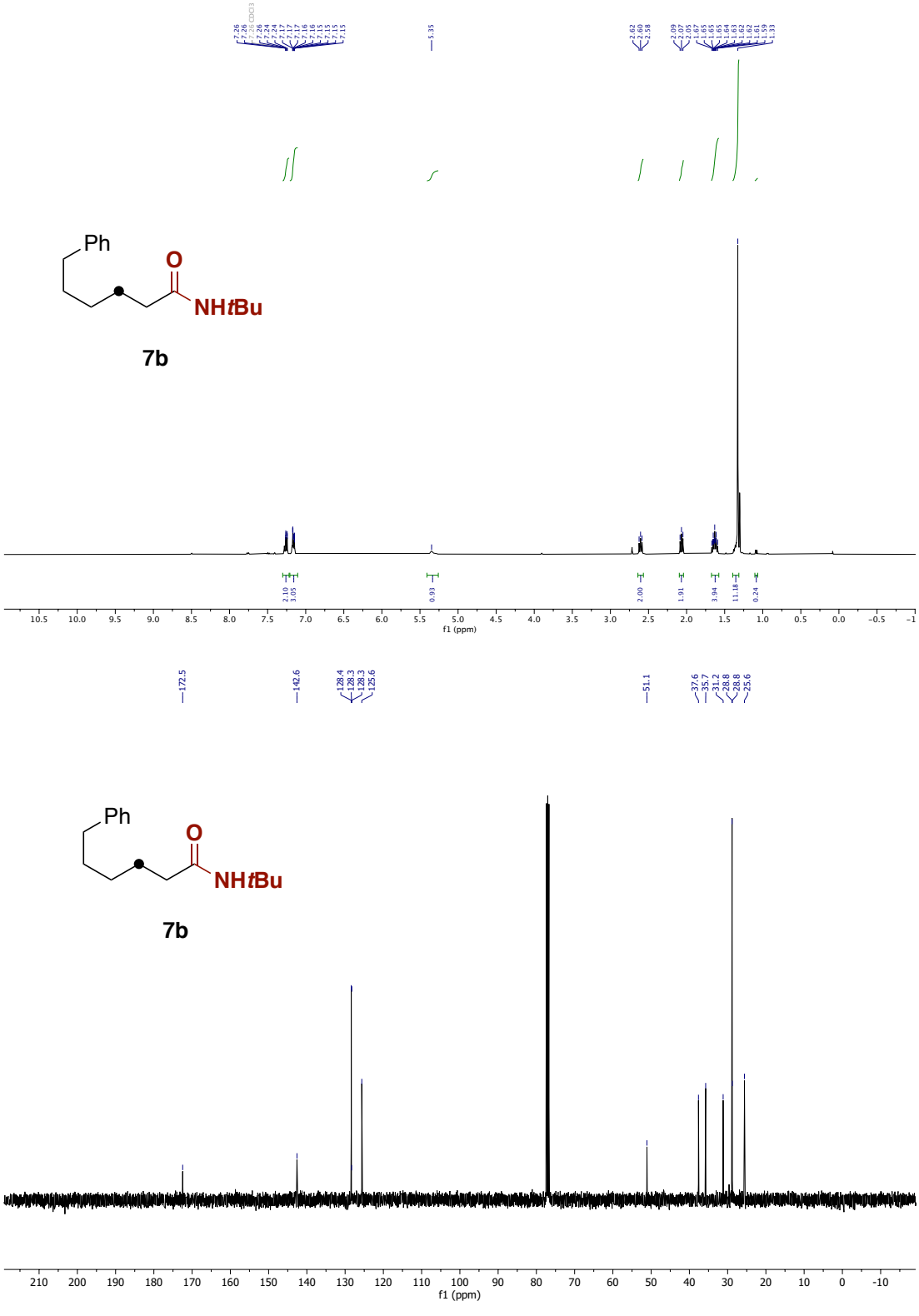


Figure 30. ^{1}H and ^{13}C NMR spectra of **7b**.

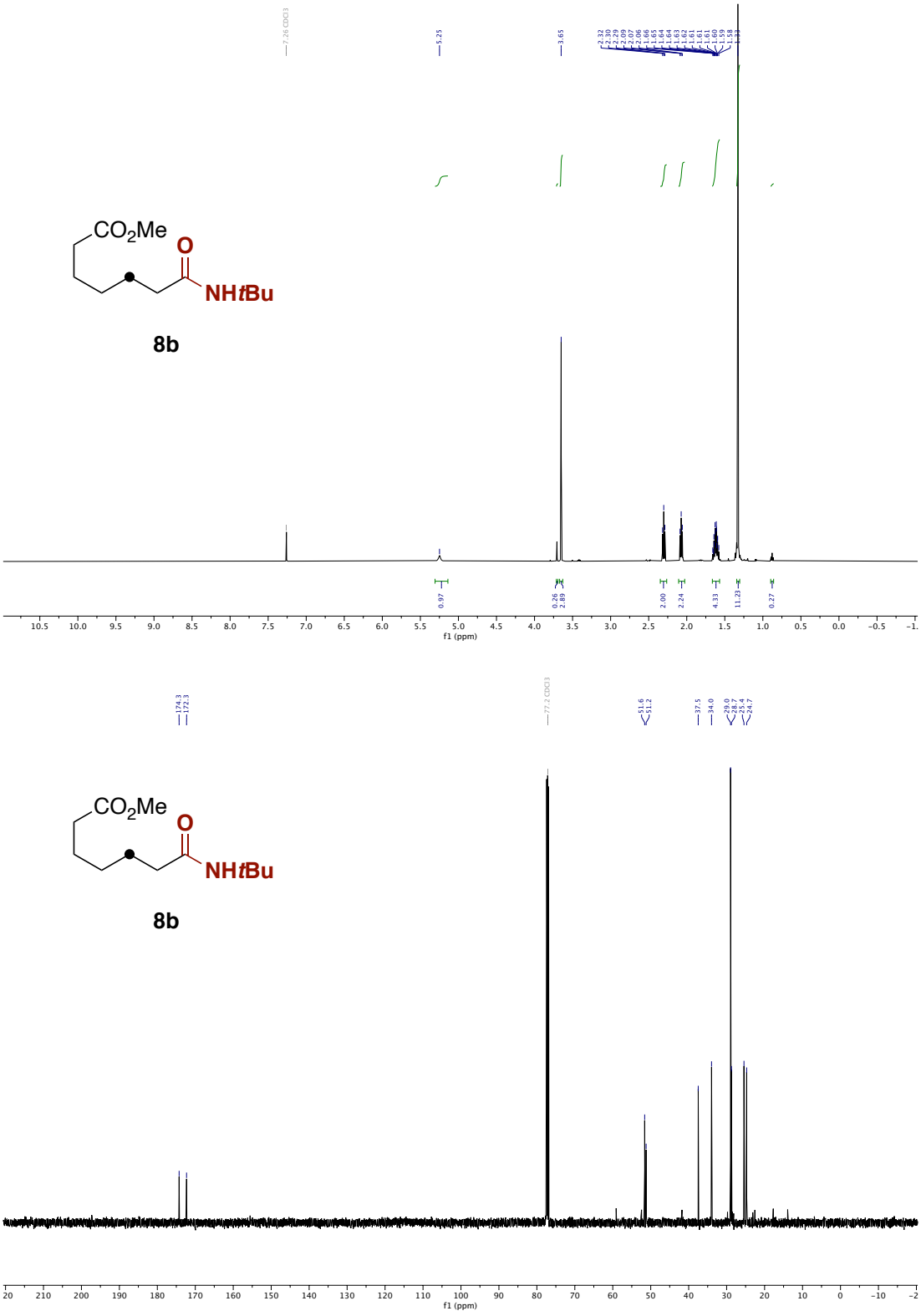


Figure 31. ^{1}H and ^{13}C NMR spectra of **8b**.

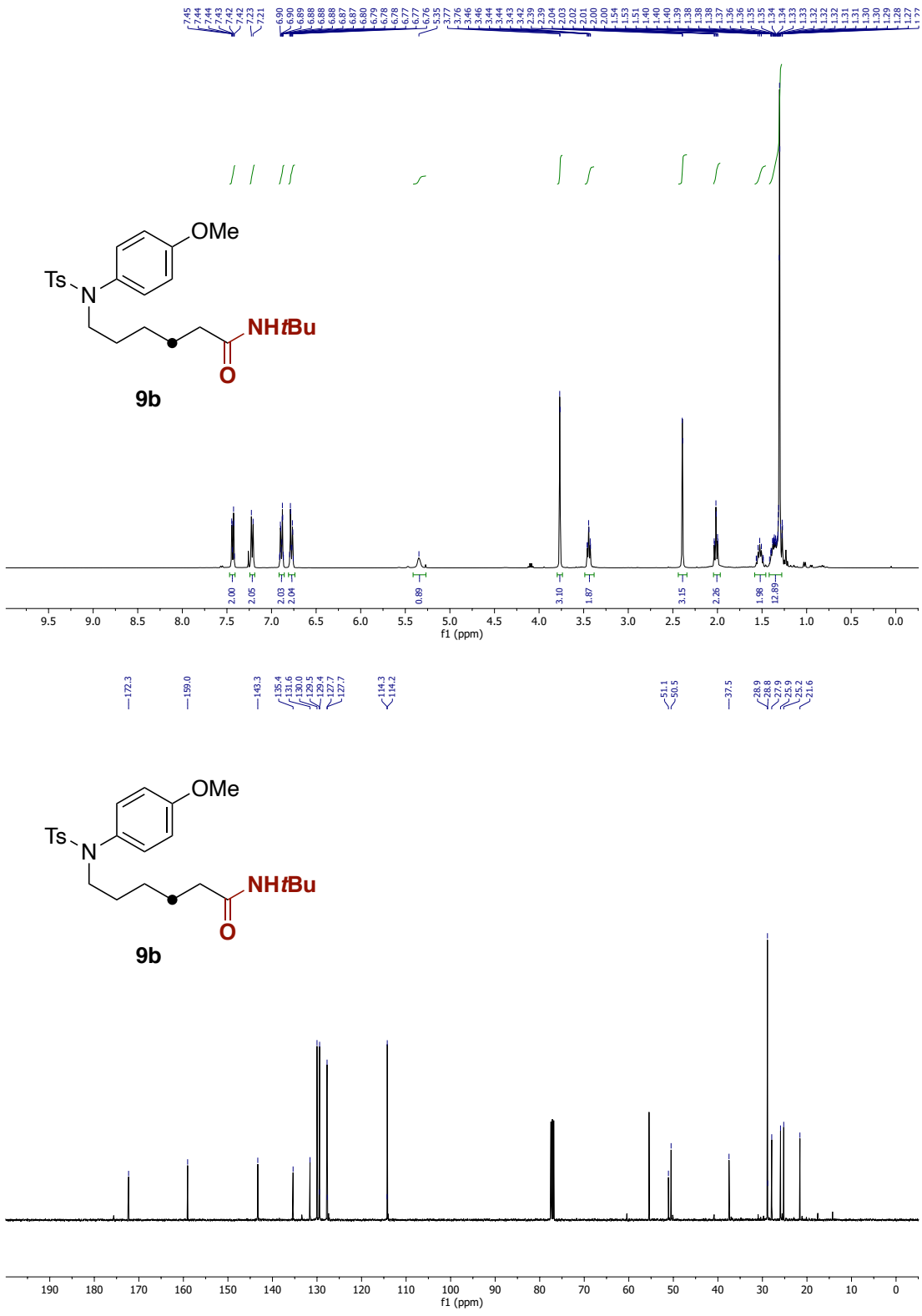


Figure 32. ^{1}H and ^{13}C NMR spectra of **9b**.

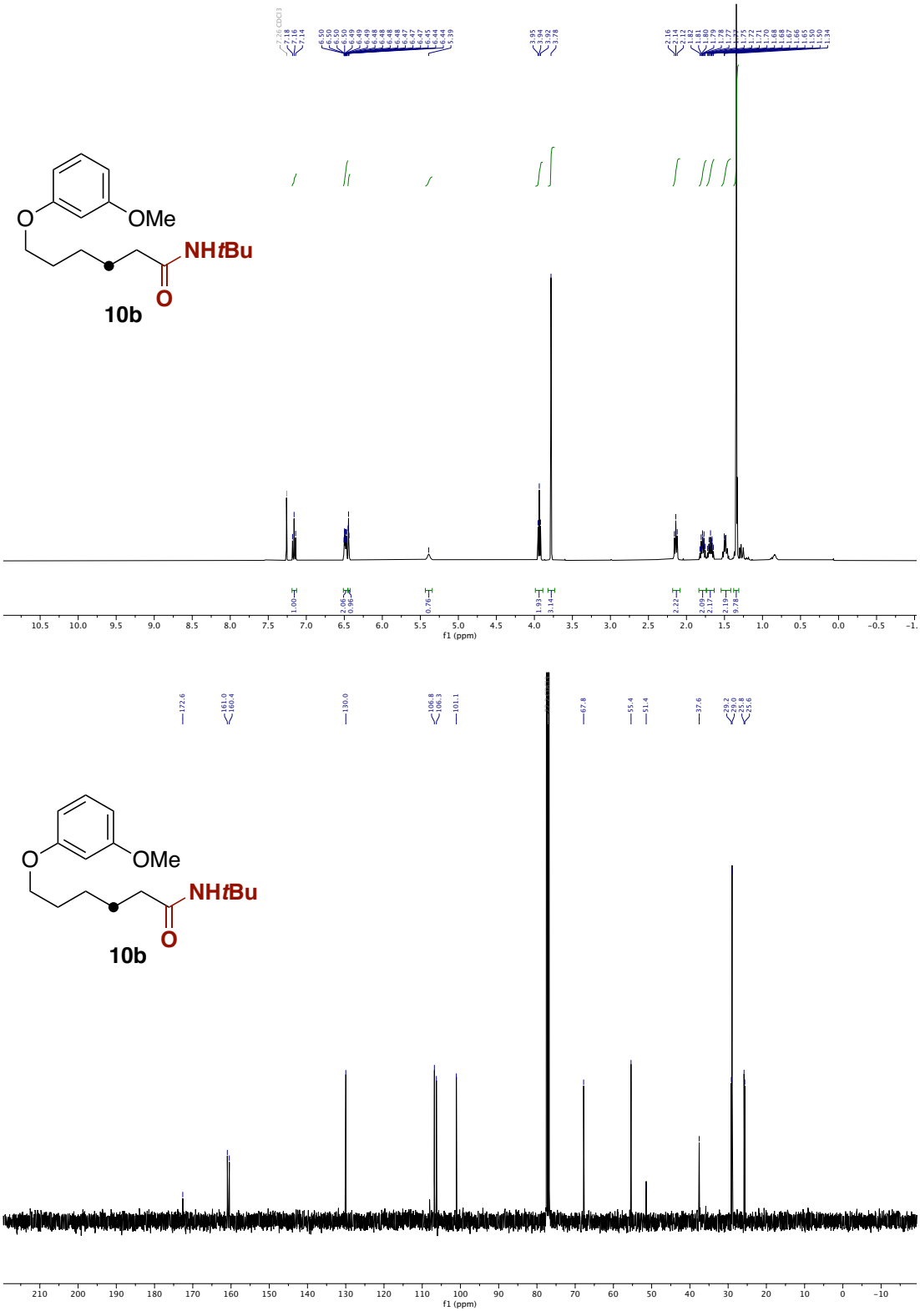


Figure 33. ^{1}H and ^{13}C NMR spectra of **10b**.

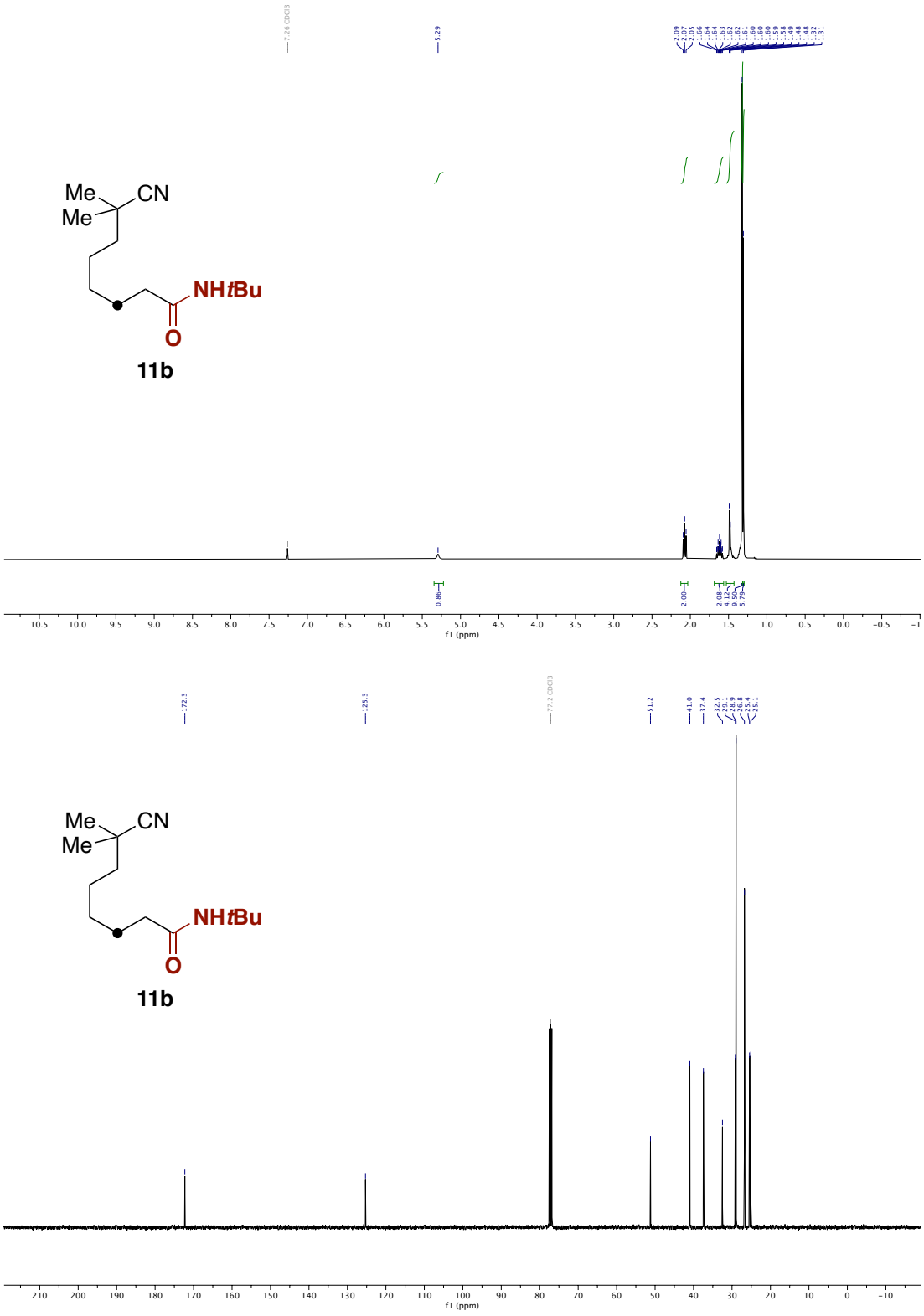


Figure 34. ^{1}H and ^{13}C NMR spectra of **11b**.

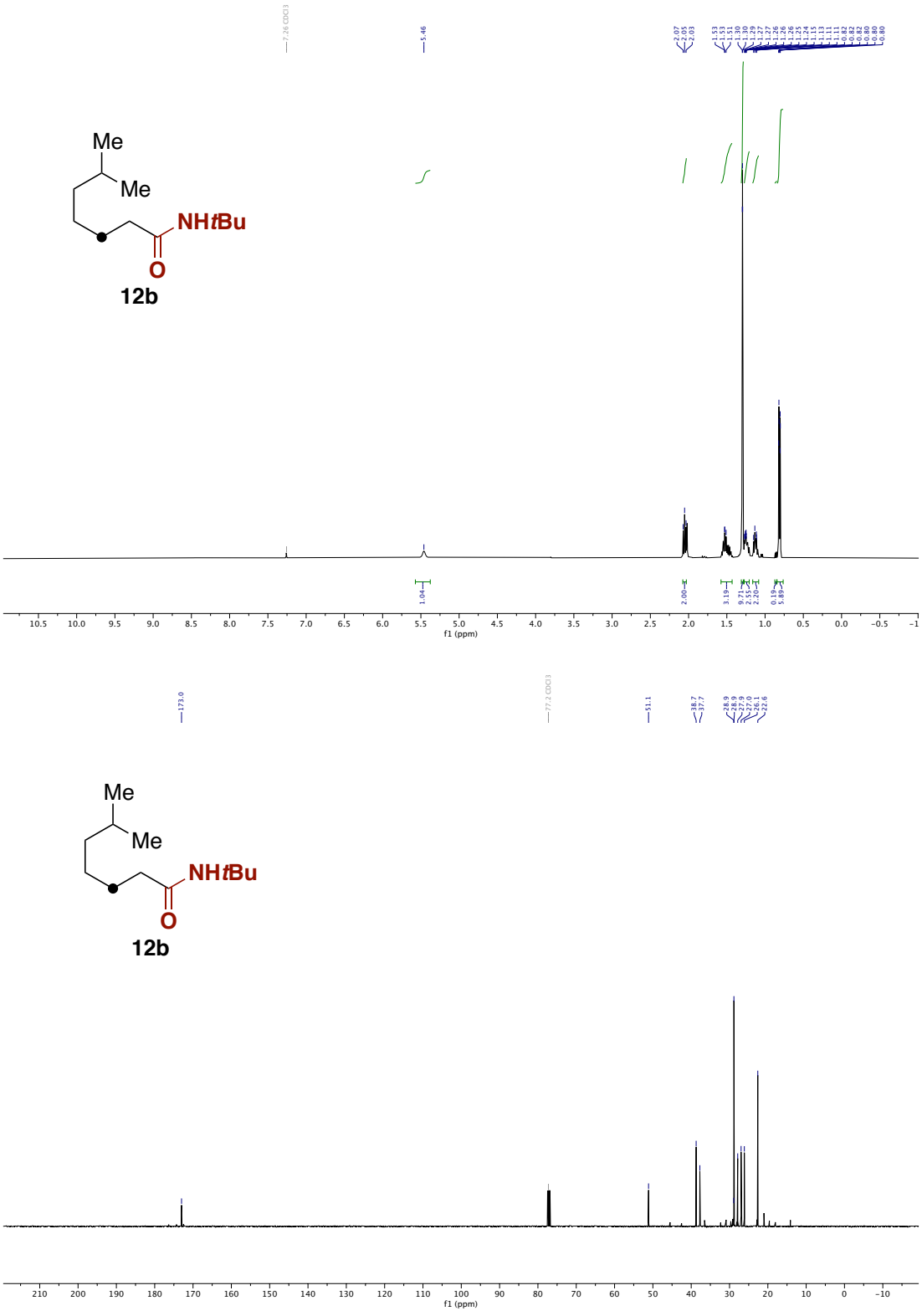


Figure 35. ^{1}H and ^{13}C NMR spectra of **12b**.

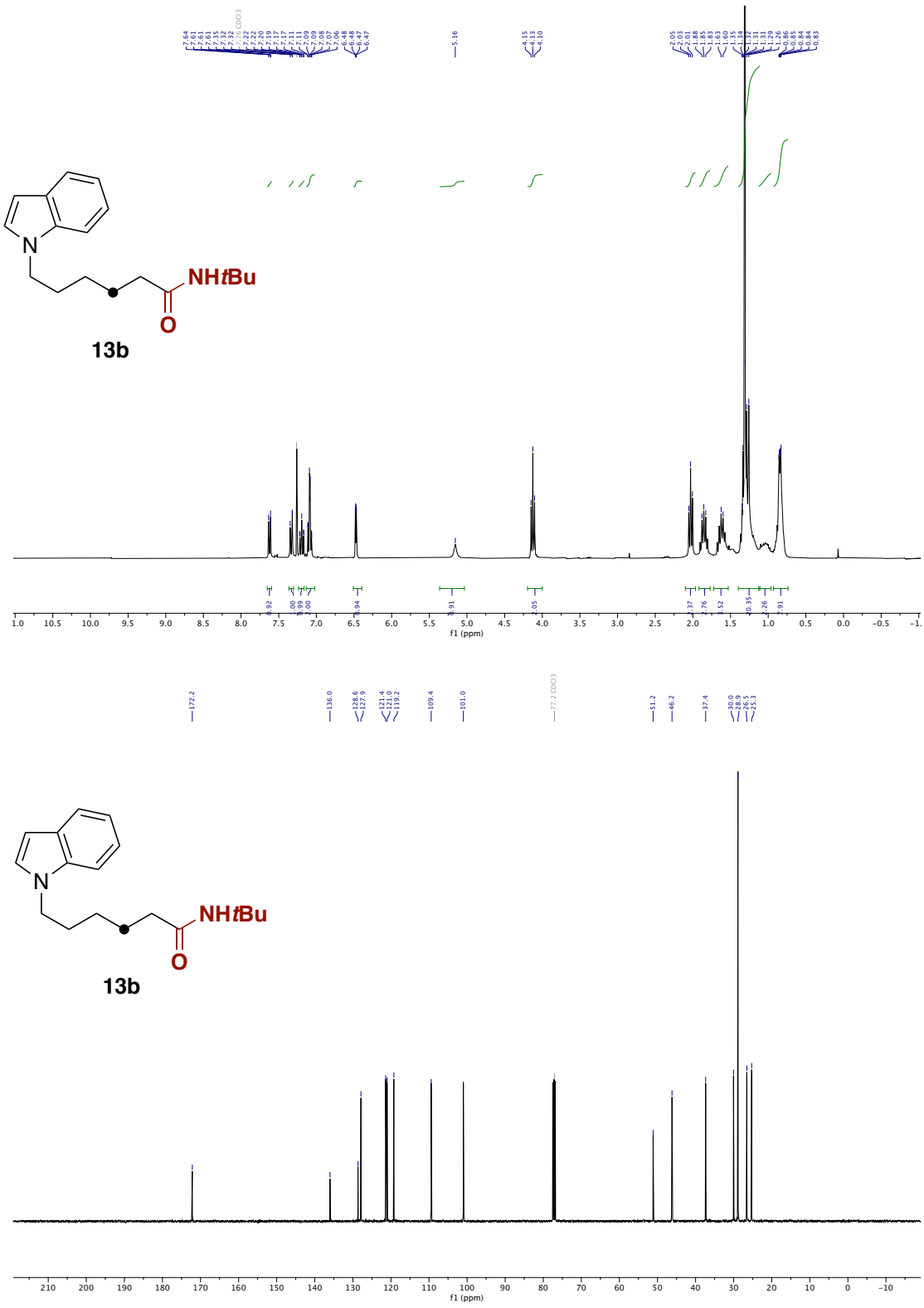


Figure 36. ^{1}H and ^{13}C NMR spectra of **13b**.

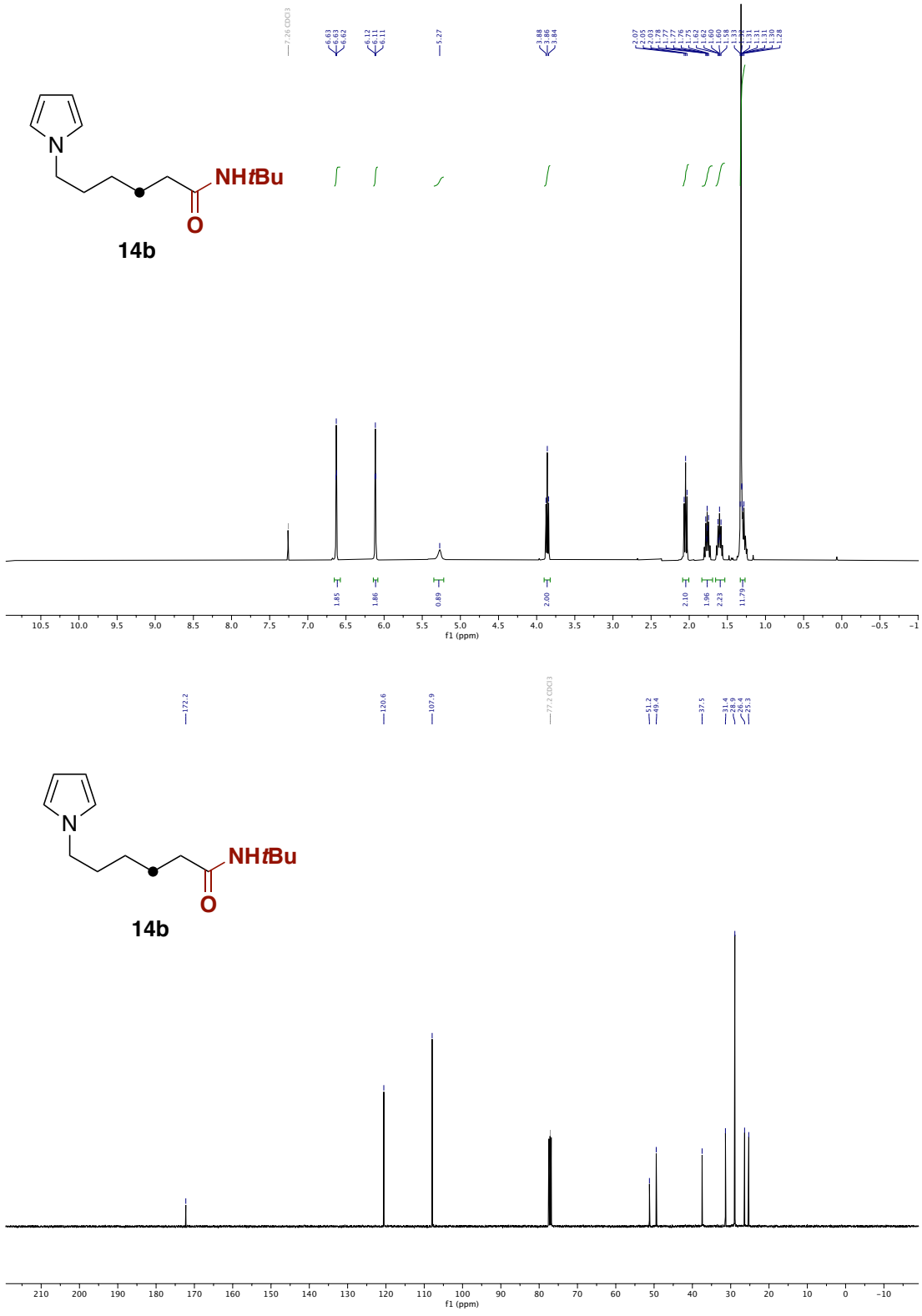


Figure 37. ^{1}H and ^{13}C NMR spectra of **14b**.

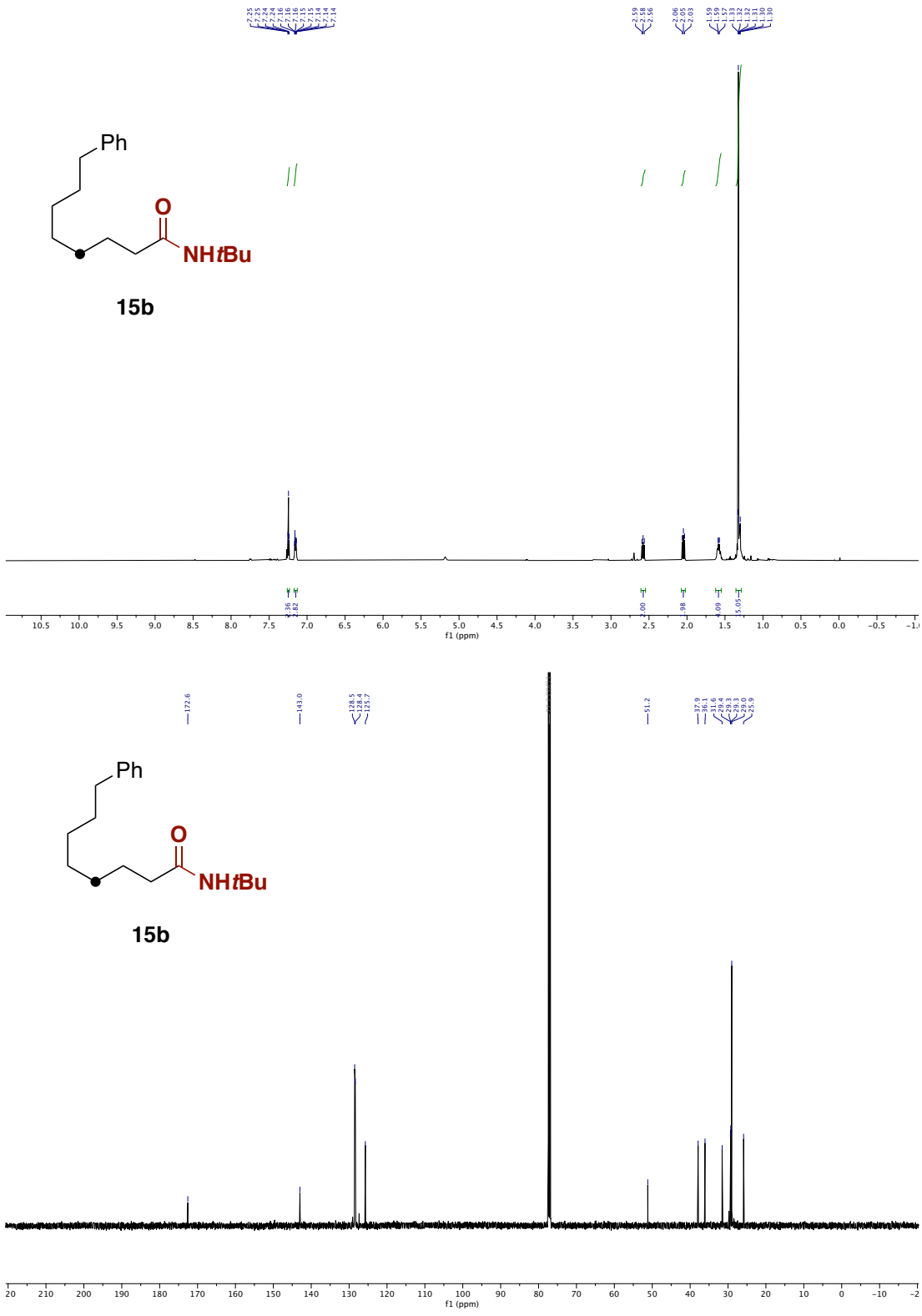
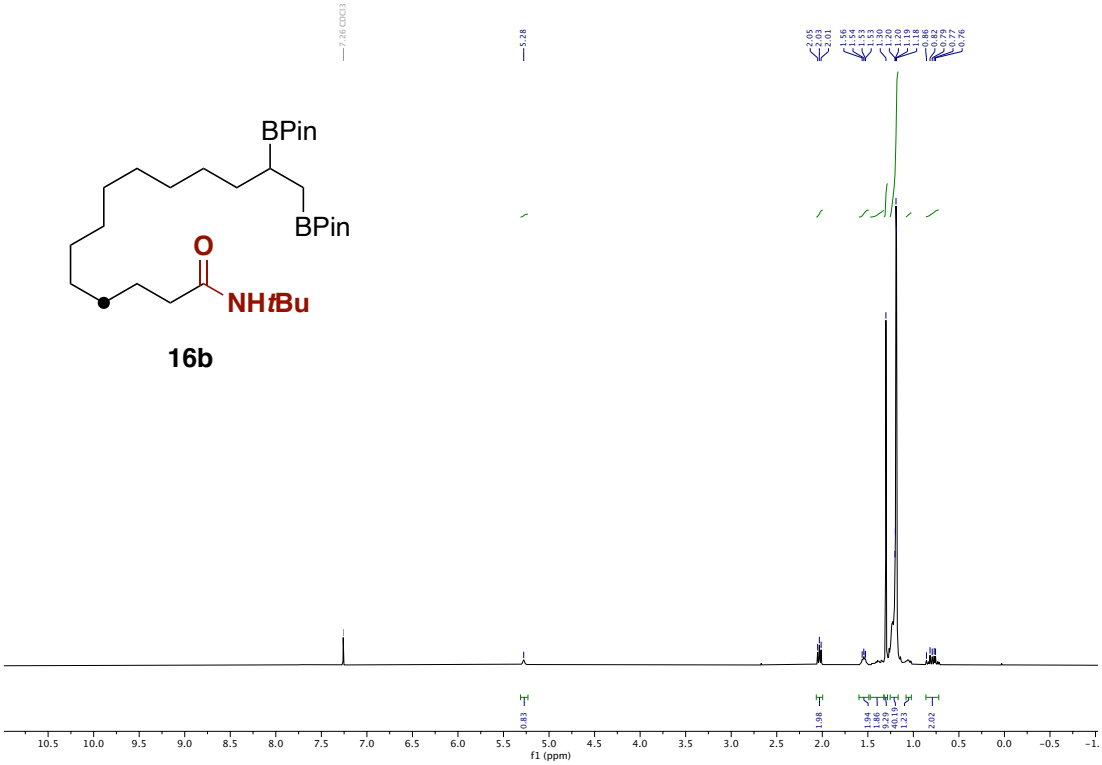
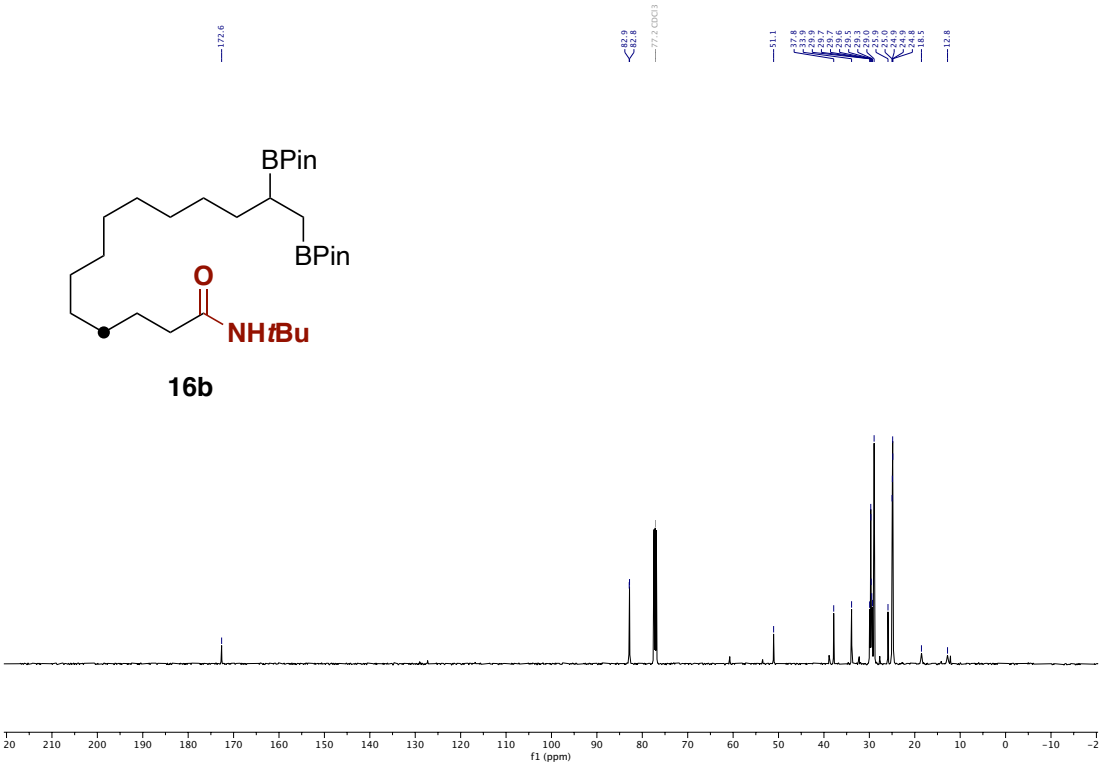


Figure 38. ^{1}H and ^{13}C NMR spectra of **15b**.



16b



16b

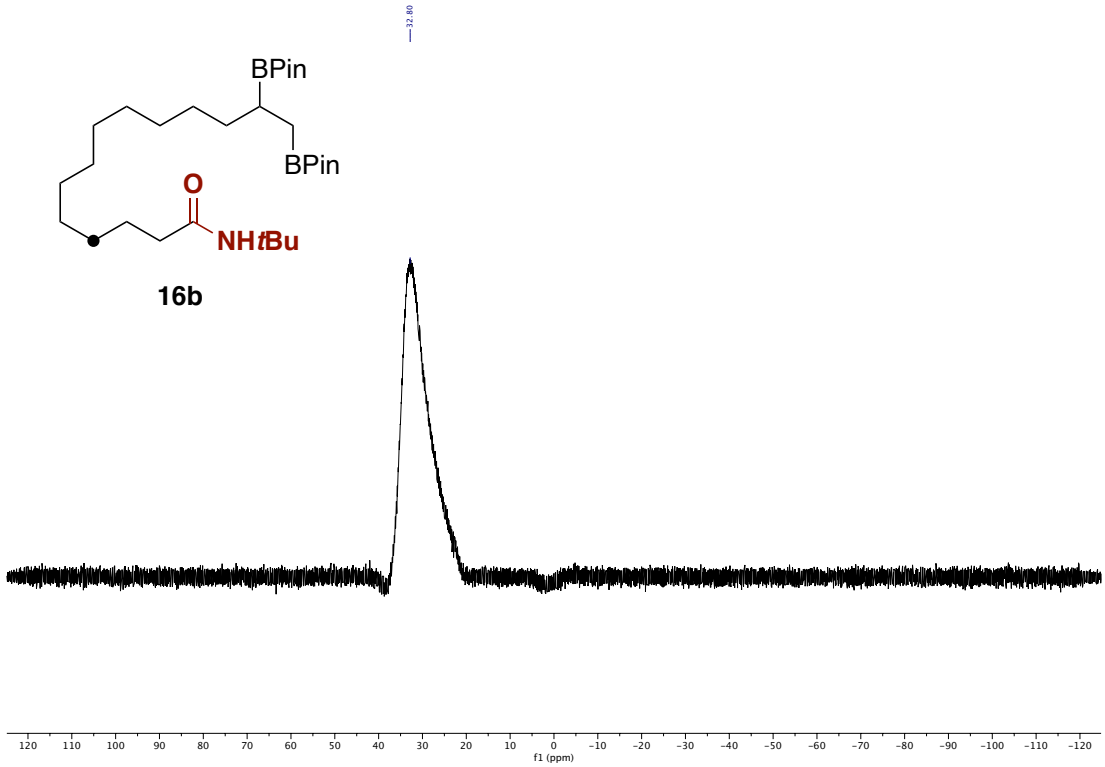
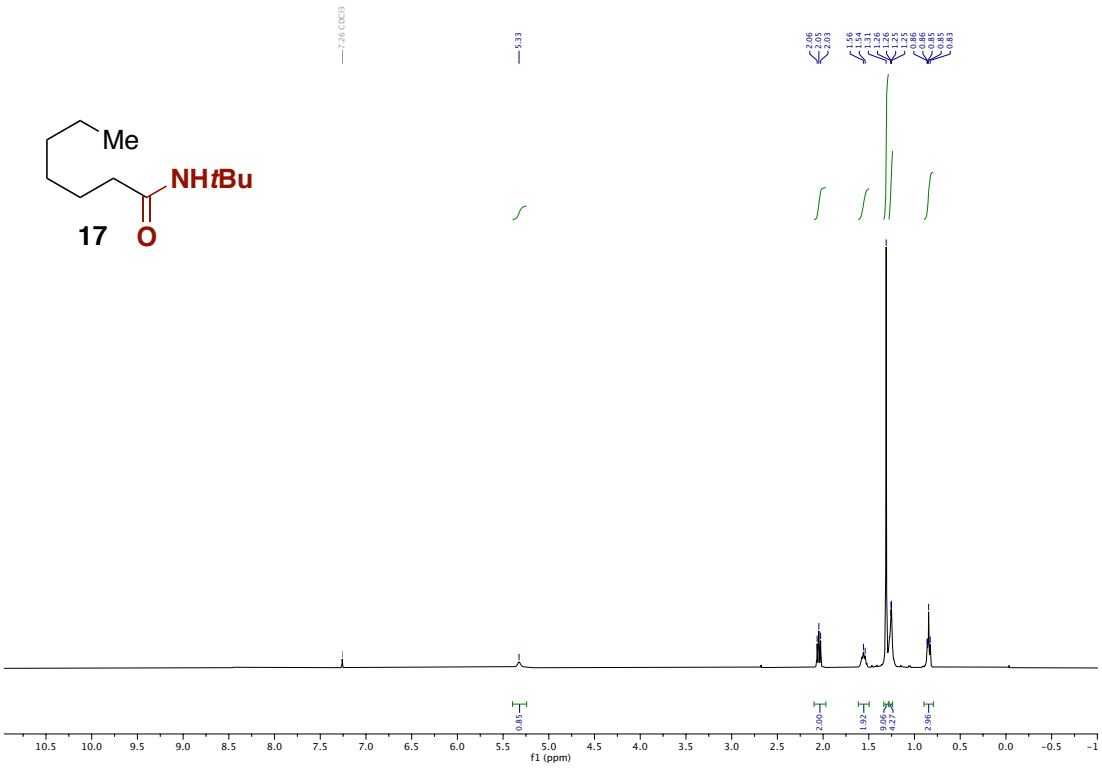


Figure 39. ^{1}H, ^{13}C and ^{11}B NMR spectra of **16b**.



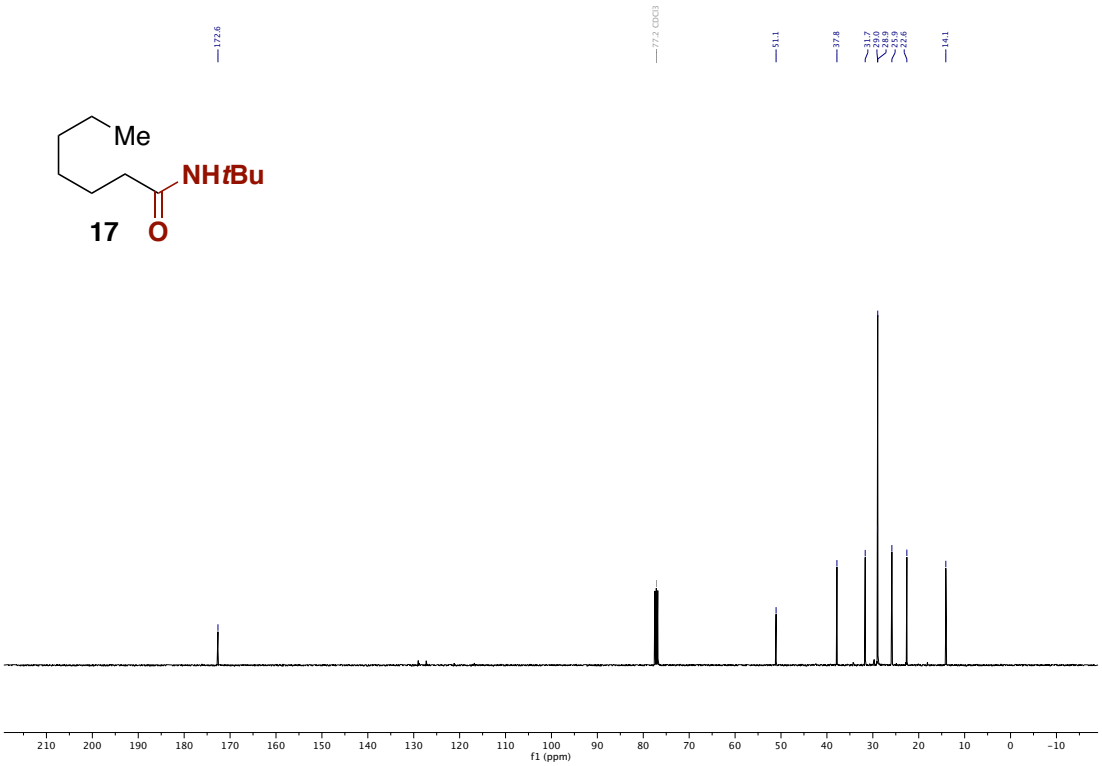


Figure 40. ^{1}H and ^{13}C NMR spectra of **17**.

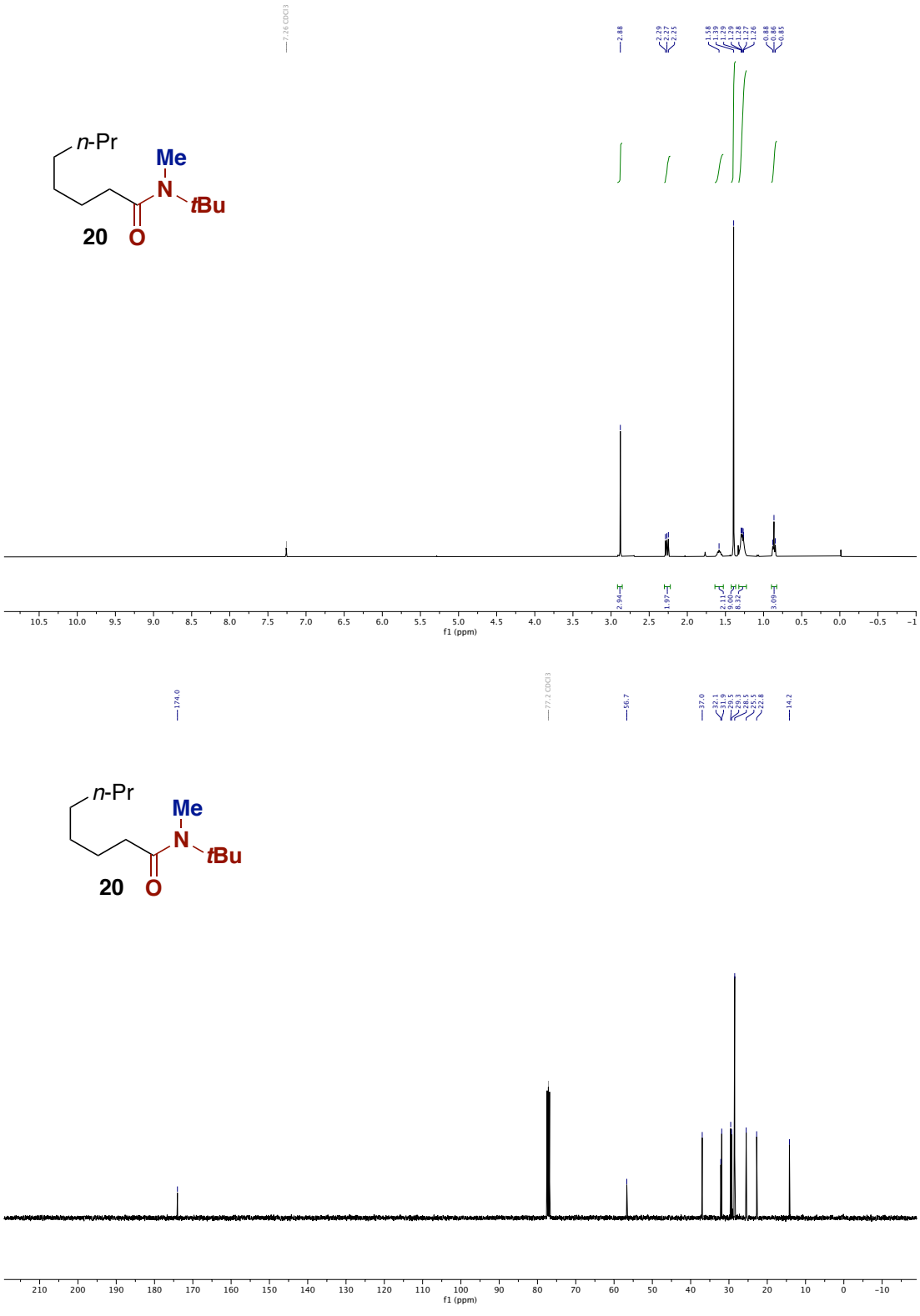


Figure 41. ^{1}H and ^{13}C NMR spectra of **20**.

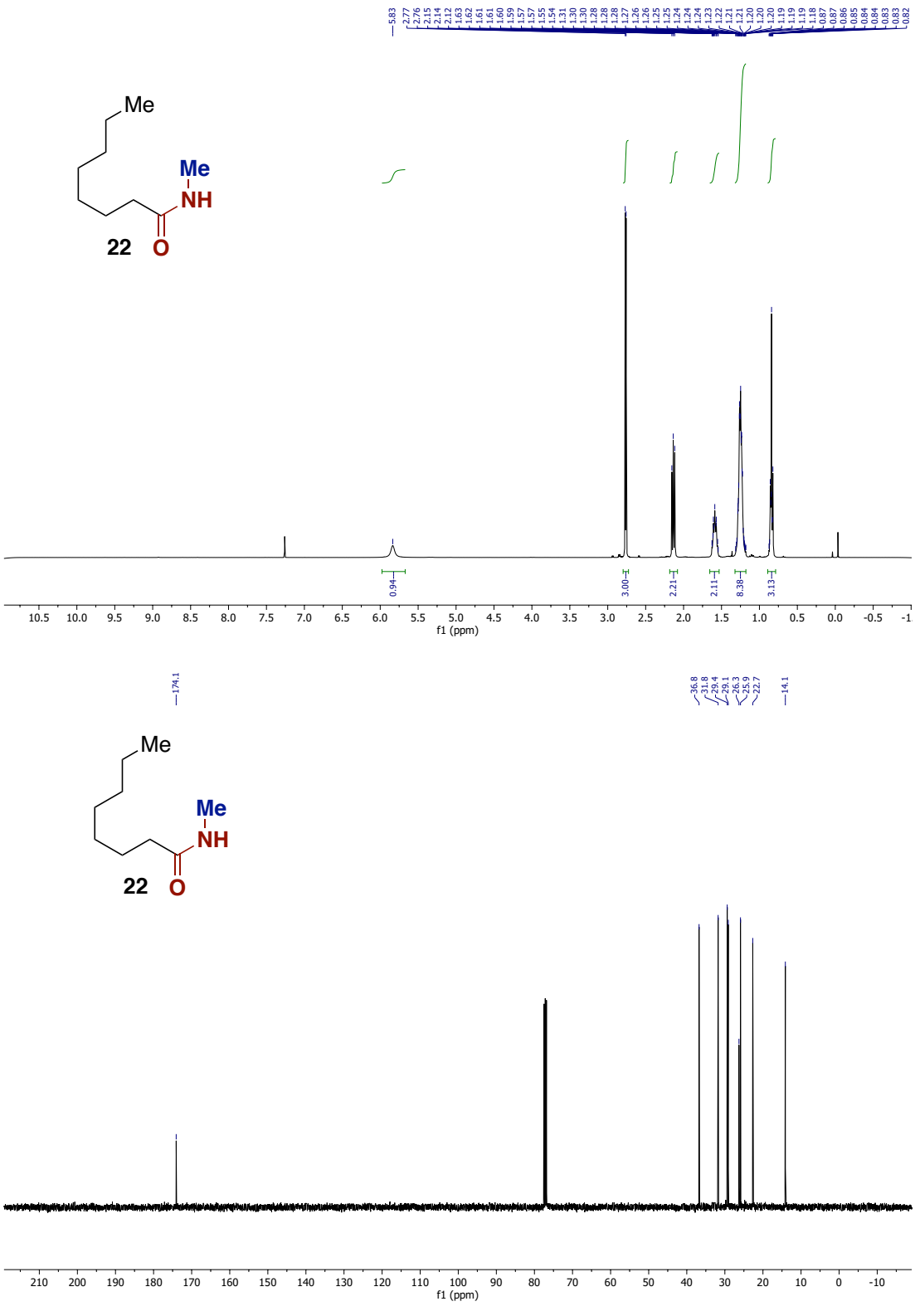


Figure 42. ^{1}H and ^{13}C NMR spectra of **22**.

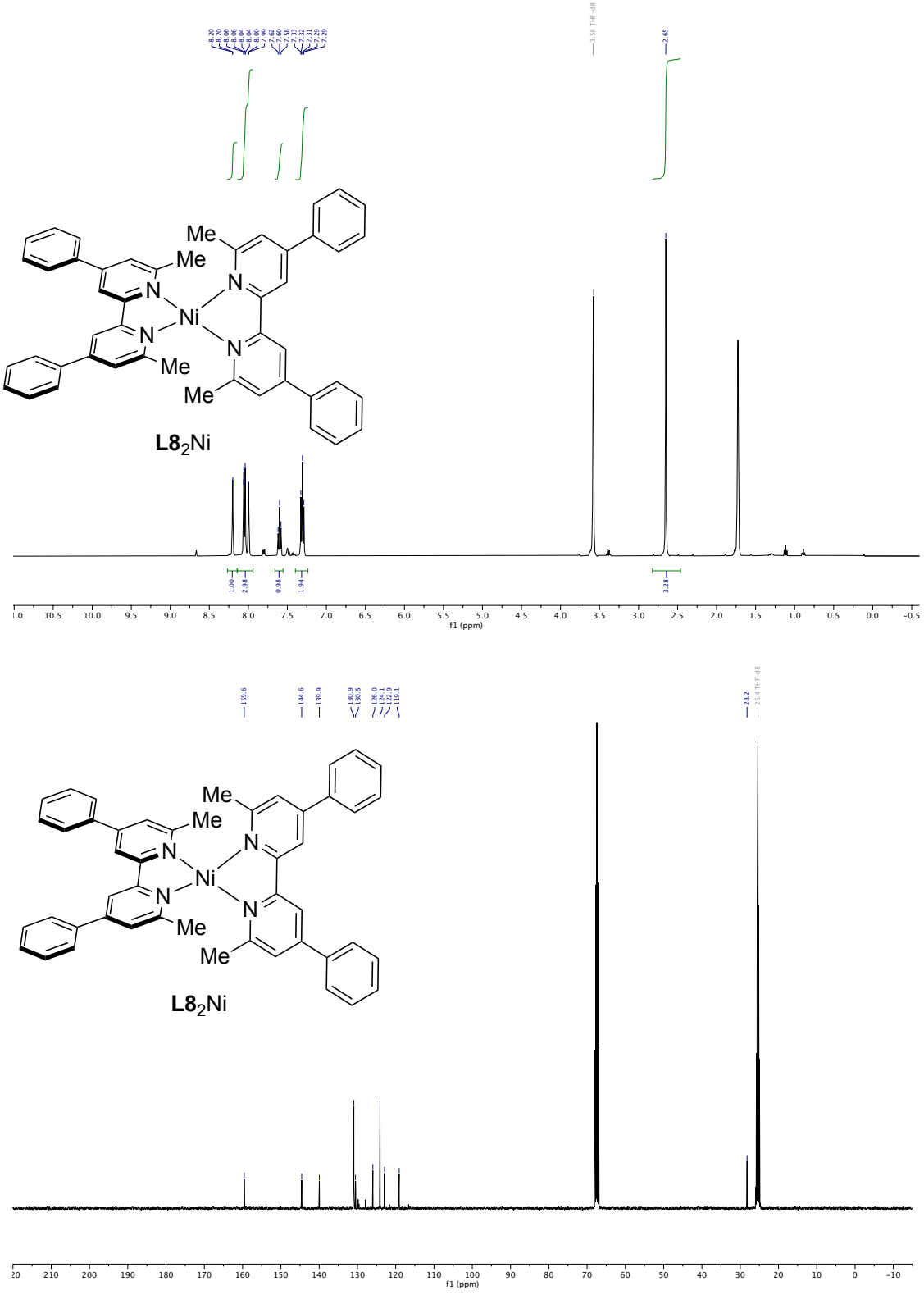


Figure 43. ^{1}H and ^{13}C NMR spectra of **L8**$_2$Ni.

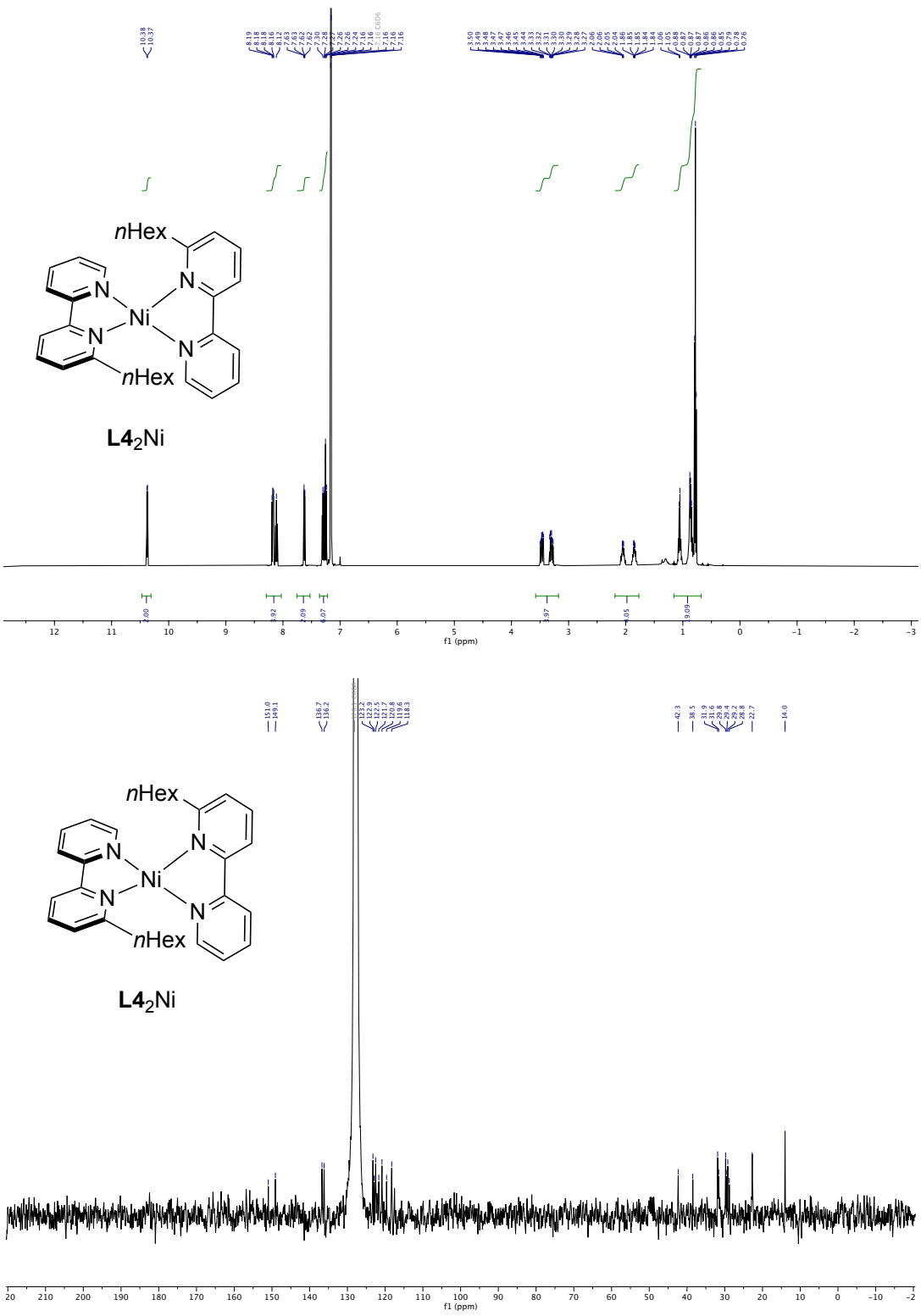


Figure 44. ^{1}H and ^{13}C NMR spectra of **L4**$_2$Ni.