Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Reductive amidation of alkyl tosylates with isocyanates by Ni/Co-dual catalytic system

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1. General information

All reactions were performed on oven-and flame-dried glassware under argon using standard Schlenk techniques. Flash-column chromatography was performed with silica-gel 60 (KANTO Chemical Co. Inc., 40–50 nm). TLC monitoring was carried out with silica-gel aluminum sheets (Merck, type 60 F_{254}). Gas chromatography (GC) monitoring was carried out on Shimadzu GC-2014. Nuclear magnetic resonance (NMR) spectra were recorded with Varian-400 (^{1}H NMR: 400 MHz; ^{13}C NMR: 101 MHz) spectrometer or Varian-500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 126 MHz) spectrometers, calibrated from residual deuterated chloroform as an internal standard at 7.26 ppm for ^{1}H NMR spectra and at 77.0 ppm for ^{13}C NMR spectra, respectively. Low-resolution mass spectrum (LRMS) was recorded on Shimadzu GCMS-QP2010SE (EI, 70 eV). High-resolution mass spectrum (HRMS) was performed by the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University using LTQ Orbitrap XL from Thermo Fisher Scientific.

2. Materials

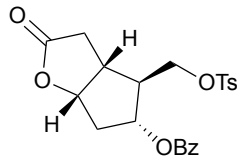
All nickel catalysts were synthesised based on the reported method.[1] Vitamin B_{12} and methylcobalamin were purchased from Nacalai tesque. Inc. (Product No.: 36323-54) and TCI Co. LTD. (Product No: M2742), respectively. All solvents were dried over activated MS 4Å, distilled and stored with activated MS 4Å under argon. Unless otherwise noted, commercially available reagents were used as received without further purification.

3. Synthetic methods for alkyl tosylates

Unless otherwise noted, alkyl tosylates were prepared in one of the following methods.

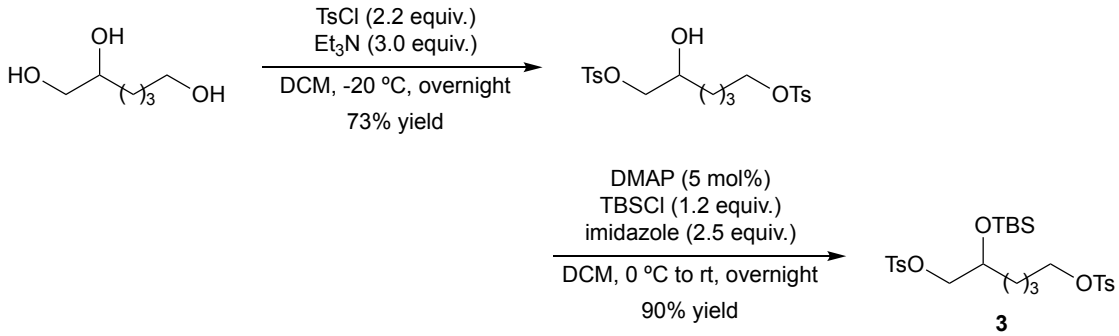
General procedure 1: The alcohol (1.0 equiv.), dichloromethane (DCM, 0.45 mol/L), Et_3N (1.3 equiv.) and *N*,*N*-dimethylaminopyridine (DMAP, 2 mol%) were added to a round-bottom flask and the mixture was cooled to 0 ºC. TsCl (1.1 equiv.) was added and the reaction mixture was stirred overnight at rt. After the reaction, water was added to the reaction mixture and the aqueous phase was extracted with DCM. The combined organic phases were washed with saturated $NaHCO_3$ (aq., 1 M HCl aq.) and brine. The obtained organic phase was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography or recrystallisation.

General procedure 2: alcohol (1.0 equiv.) and pyridine (1 mol/L) were added and cooled to 0 ºC. TsCl (1.5 equiv.) was added to a round-bottom flask and the mixture was stirred overnight at rt. After completion of the reaction, water was added to the reaction mixture and the aqueous phases were extracted with DCM. The combined organic phase was washed with 1 M HCl aq. and brine and dried over $MgSO_4$. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography or recrystallisation.



1u. was prepared by the general procedure 1. Isolated as a white solid (Mp. 138.0 – 138.5 ºC) in 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.44 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.20 (dt, *J* = 6.3, 3.9 Hz, 1H), 5.10 – 5.03 (m, 1H), 4.16 (dd, *J* = 10.2, 4.7 Hz, 1H), 4.09 (dd, *J* = 10.2, 5.7 Hz, 1H), 2.97 – 2.84 (m, 2H), 2.57 – 2.35 (m, 2H), 2.43 – 2.37 (m, 4H), 2.30 (dd, *J* = 16.0, 3.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 165.8, 145.4, 133.5, 132.2, 130.1, 129.6, 129.2, 128.5, 127.9, 84.0, 69.1, 51.7, 40.2, 38.3, 35.6, 21.6. HRMS calcd for $C_{22}H_{26}NO_7S$ $[M+NH_4]^+$: 448.14300, found 448.14245.

Synthesis of alkyl ditosylate 3



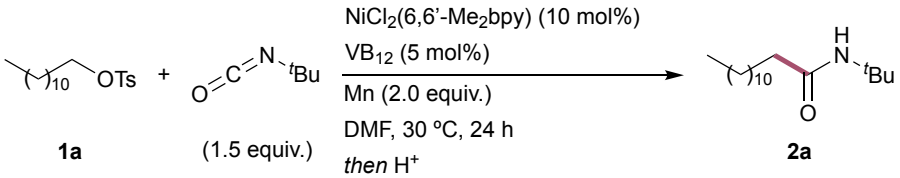
3

1,2,6-Hexanetriol (1.21 g, 9.04 mmol, 1.0 equiv.), DCM (5 mL), and Et_3N (3.78 mL, 27.1 mmol, 3.0 equiv.) were added to a round-bottom flask and the mixture was cooled to -20 ºC. TsCl (3.79 g, 19.9 mmol, 2.2 equiv.) in DCM (15 mL) was added slowly and the reaction mixture was stirred overnight at -20 ºC. After the reaction, water was added to the reaction mixture and the aqueous phase was extracted with DCM. The combined organic phases were washed with 1 M HCl aq. and brine. The obtained organic phase was dried over

anhydrous Na_2SO_4. After filtration and removing the solvent, the residue was purified by silica-gel column chromatography (hexane/DCM = 3:7) to obtain the hydroxyl ditosylate as a white solid in 73% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 4H), 7.40 – 7.31 (m, 4H), 4.06 – 3.95 (m, 3H), 3.90 – 3.83 (m, 1H), 3.85 – 3.74 (m, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 1.71 – 1.52 (m, 2H), 1.47 (dtd, *J* = 10.6, 8.6, 8.1, 5.6 Hz, 1H), 1.53 – 1.30 (m, 4H).

The ditosylate (2.0 g, 4.52 mmol, 1.0 equiv.), DCM (13 mL), DMAP (27.6 mg, 0.226 mmol, 5 mol%) and imidazole (769.3 mg, 11.3 mmol, 2.5 equiv.) were added to a round-bottom flask and the mixture was cooled to 0 ºC. TBSCl (817.5 mg, 5.42 mmol, 1.2 equiv.) was added and the reaction mixture was stirred overnight at rt. After the reaction, water was added to the reaction mixture and the aqueous phase was extracted with DCM. The combined organic phases were washed with brine. The obtained organic phase was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography (hexane/DCM = 1:1) to obtain **3** as a colorless oil in 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 4H), 7.39 – 7.30 (m, 4H), 4.07 (dd, *J* = 7.0, 5.5 Hz, 2H), 3.99 – 3.89 (m, 1H), 3.85 (dd, *J* = 9.9, 5.5 Hz, 1H), 3.80 (dd, *J* = 9.9, 5.0 Hz, 1H), 2.46 (s, 3H), 2.45 (s, 3H), 1.89 – 1.64 (m, 2H), 0.77 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 144.9, 132.8, 132.6, 129.9, 129.9, 127.9, 127.9, 72.5, 66.4, 66.3, 33.3, 25.6, 21.6, 21.6, 17.8, -4.7, -5.2. HRMS calcd for $C_{26}H_{44}NO_7S_2Si$ $[M+NH_4]^+$: 574.23285, found 574.23236.

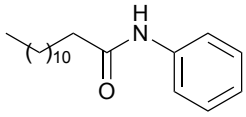
4. General procedure for the Ni/Co-catalysed reductive amidation of alkyl tosylates



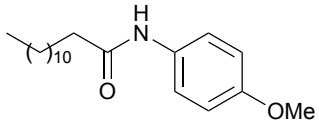
In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 ºC for 3 min under vacuum. After cooling, the Schlenk tube was charged with $NiCl_2$(6,6'-Me_2bpy) (7.8 mg, 0.025 mmol, 10 mol%), vitamin B_{12} (VB_{12}, 18.9 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 μL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, dodecyl tosylate (**1a**, 85.1 mg, 0.25 mmol, 1.0 equiv.) and ^{t}Bu-isocyanate (47 μL, 0.375 mmol, 1.5 equiv.) were added into

the solution. The reaction mixture was stirred at 30 ºC for 24 h. The obtained mixture was quenched by saturated NH_4Cl aq. and diluted with EtOAc. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over $MgSO_4$. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography (Hexane/EtOAc = 5:1) to give the product **2a** as a white solid (Mp. 45.0 – 45.5 ºC) in 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (s, 1H), 2.07 (t, *J* = 7.6 Hz, 2H), 1.34 (s, 9H), 1.32 – 1.22 (m, 19H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 51.0, 37.8, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 25.8, 22.7, 14.1. HRMS calcd for $C_{17}H_{36}NO$ $[M+H]^+$: 270.27269, found 270.27939.

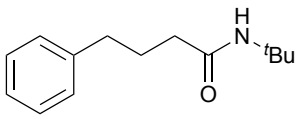
5. Characterisation of alkyl amides



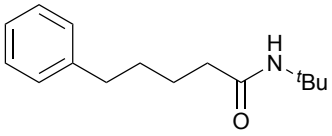
2b. Isolated as a white solid (Mp.: 76.5 – 77.0 ºC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.20 (s, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.72 (p, *J* = 7.5 Hz, 2H), 1.47 – 1.14 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 137.9, 129.0, 124.1, 119.7, 37.9, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 25.6, 22.7, 14.1. HRMS calcd for $C_{19}H_{32}NO$ $[M+H]^+$: 290.24839, found 290.24805.



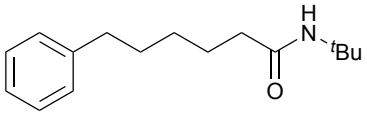
2c. Isolated as a white solid (Mp.: 104.5 – 105.0 ºC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.9 Hz, 2H), 7.19 (s, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.71 (p, *J* = 7.5 Hz, 2H), 1.39 –1.16 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 156.3, 131.1, 121.7, 114.1, 55.4, 37.6, 31.9, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 25.7, 22.7, 14.1. HRMS calcd for $C_{20}H_{34}NO_2$ $[M+H]^+$: 320.25895, found 320.25833.



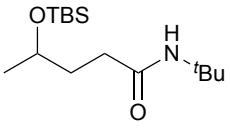
2d. Isolated as a white solid (Mp.: 69.5 – 70.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.15 (m, 3H), 5.18 (s, 1H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.12 – 2.02 (m, 2H), 2.01 – 1.88 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 141.6, 128.5, 128.3, 125.9, 51.1, 36.8, 35.1, 28.8, 27.1. HRMS calcd for $C_{14}H_{22}NO$ $[M+H]^+$: 220.17014, found 220.16975.



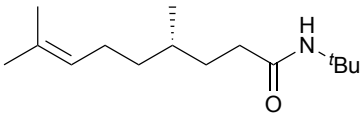
2e. Isolated as a white solid (Mp.: 61.5 – 62.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.20 – 7.13 (m, 3H), 5.19 (s, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.07 (t, *J* = 7.5 Hz, 2H), 1.63 (tt, *J* = 9.1, 6.6 Hz, 3H), 1.40 – 1.28 (m, 11H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 142.3, 128.4, 128.3, 125.7, 51.0, 37.5, 35.7, 31.0, 28.8, 25.4. HRMS calcd for $C_{15}H_{24}NO$ $[M+H]^+$: 234.18579, found 234.18550.



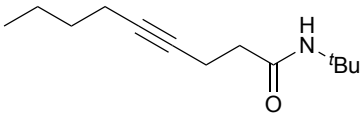
2f. Isolated as a white solid (Mp.: 44.5 – 45.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.20 – 7.14 (m, 3H), 5.19 (s, 1H), 2.62 (t, *J* = 7.1 Hz, 2H), 2.10 (t, *J* = 7.2 Hz, 2H), 1.71 – 1.59 (m, 6H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 142.3, 128.4, 128.3, 125.7, 51.0, 37.5, 35.7, 31.0, 28.8, 25.4. HRMS calcd for $C_{16}H_{26}NO$ $[M+H]^+$: 248.20144, found 248.20103.



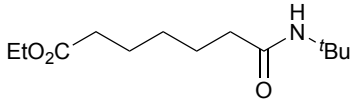
2g. Isolated as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (s, 1H), 3.88 – 3.78 (m, 1H), 2.26 – 2.02 (m, 2H), 1.82 – 1.71 (m, 1H), 1.69 – 1.52 (m, 2H), 1.34 (s, 9H), 1.13 (d, *J* = 6.1 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 67.8, 51.0, 35.2, 33.6, 28.8, 25.9, 23.8, 18.1, -4.3, -4.7. HRMS calcd for $C_{15}H_{34}NO_2Si$ $[M+H]^+$: 288.23588, found 288.23569.



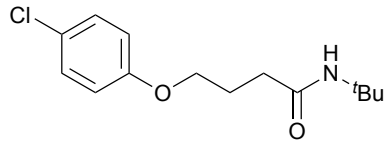
2h. Isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 (s, 1H), 5.10 – 5.02 (m, 1H), 2.19 – 1.85 (m, 4H), 1.66 (s, 3H), 1.58 (s, 3H), 1.32 (m, 13H), 1.20 – 1.03 (m, 1H), 0.86 (d, *J* = 6.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 131.2, 124.7, 51.0, 36.8, 35.4, 32.7, 32.1, 28.8, 25.7, 25.4, 19.3, 17.6. HRMS calcd for $C_{15}H_{30}NO$ $[M+H]^+$: 240.23247, found 240.23203.



2i. Isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (s, 1H), 2.44 (tt, *J* = 6.8, 2.3 Hz, 2H), 2.25 (t, *J* = 7.0 Hz, 2H), 2.17 – 2.09 (m, 2H), 1.51 – 1.28 (m, 13H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 81.5, 78.6, 51.1, 37.0, 31.0, 28.8, 21.9, 18.3, 15.4, 13.6. HRMS calcd for $C_{13}H_{24}NO$ $[M+H]^+$: 210.18579, found 210.18541.

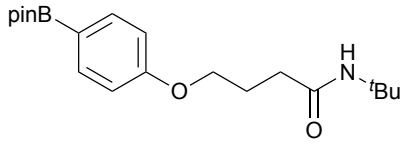


2j. Isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.06 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.54 (m, 4H), 1.31 (s, 9H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 172.2, 60.4, 60.2, 60.0, 51.0, 37.3, 34.1, 34.1, 29.6, 29.0, 28.8, 28.7, 28.5, 28.4, 25.5, 25.3, 25.1, 24.7, 24.6, 24.4, 14.4, 14.3, 14.1, 14.0. HRMS calcd for $C_{13}H_{26}NO_3$ $[M]^+$: 244.19127, found 244.19107.

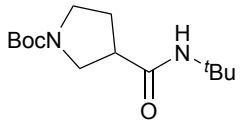


2k. Isolated as a white solid (Mp.: 91.5 – 92.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.1 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.29 (s, 1H), 3.97 (t, *J* = 6.0 Hz, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 2.14 – 2.02 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 157.5, 129.3,

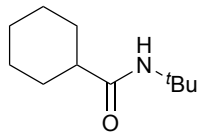
125.5, 115.7, 67.2, 51.2, 33.7, 28.8, 25.3, 25.1. HRMS calcd for $C_{14}H_{21}ClNO_2$ $[M+H]^+$: 270.12608, found 270.12592.



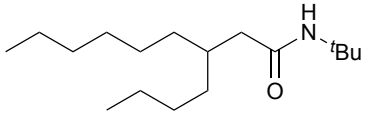
2l. Isolated as a white solid (Mp.: 95.5 – 96.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.30 (s, 1H), 4.02 (t, *J* = 5.9 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 2.10 (p, *J* = 6.3 Hz, 2H), 1.33 (s, 12H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 161.4, 136.5, 113.8, 83.6, 66.6, 51.2, 33.8, 29.6, 28.8, 25.2, 24.8. HRMS calcd for $C_{20}H_{33}BNO_4$ $[M+H]^+$: 362.25026, found 362.25043.



2m. Isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 3.65 – 3.44 (m, 2H), 3.44 – 3.35 (m, 1H), 3.35 – 3.21 (m, 1H), 2.80 – 2.63 (m, 1H), 2.20 – 1.94 (m, 2H), 1.44 (s, 9H), 1.34 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 154.4, 79.4, 51.3, 48.6, 37.3, 36.4, 28.7, 28.4, 27.9. HRMS calcd for $C_{14}H_{27}N_2O_3$ $[M+H]^+$: 271.20217, found 271.20157.

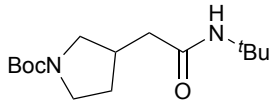


2n. Isolated as a white solid (Mp.: 104.5 – 105.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (s, 1H), 1.94 (tt, *J* = 11.7, 3.4 Hz, 1H), 1.86 – 1.72 (m, 4H), 1.68 – 1.61 (m, 1H), 1.51 – 1.34 (m, 2H), 1.33 (s, 9H), 1.31 – 1.12 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 50.8, 46.3, 29.8, 28.9, 25.8. HRMS calcd for $C_{11}H_{22}NO$ $[M+H]^+$: 184.17014, found 184.16972.

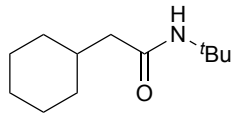


2o. Isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1H), 1.98 (d, *J* = 7.0 Hz, 2H), 1.89 – 1.77 (m, 1H), 1.34 (s, 6H), 1.34 (s, 9H), 1.30 – 1.19 (m, 16H); ^{13}C NMR (126

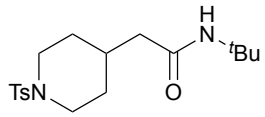
MHz, $CDCl_3$) δ 172.3, 51.0, 42.9, 35.4, 33.8, 33.4, 31.8, 29.6, 28.8, 28.7, 28.2, 26.5, 23.0, 22.6, 14.1. HRMS calcd for $C_{17}H_{36}NO$ $[M+H]^+$: 270.27969, found 270.27939.



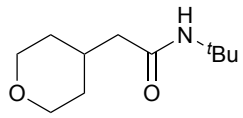
2p. Isolated as a white solid (Mp.: 111.5 – 112.0 ºC); ^1H NMR (400 MHz, $CDCl_3$) δ 5.38 (s, 1H), 3.68 – 3.20 (m, 4H), 2.90 (d, *J* = 30.3 Hz, 2H), 2.79 – 2.64 (m, 1H), 2.16 – 1.93 (m, 2H), 1.43 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 154.6, 79.1, 51.3, 51.1, 50.7, 45.5, 44.9, 40.4, 40.7, 35.9, 35.1, 31.5, 30.7, 28.8, 28.5. HRMS calcd for $C_{15}H_{29}N_2O_3$ $[M+H]^+$: 285.21782, found 285.21760.



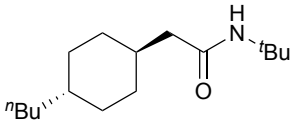
2q. Isolated as a white solid (Mp.: 115.5 – 116.0 ºC); ^1H NMR (400 MHz, $CDCl_3$) δ 5.20 (s, 1H), 1.93 (d, *J* = 6.9 Hz, 2H), 1.81 – 1.61 (m, 6H), 1.34 (s, 9H), 1.32 – 1.21 (m, 2H), 1.19 – 1.06 (m, 1H), 0.97 – 0.86 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 51.1, 45.9, 35.4, 33.1, 28.9, 26.3, 26.1. HRMS calcd for $C_{12}H_{24}NO$ $[M+H]^+$: 198.18579, found 198.18542.



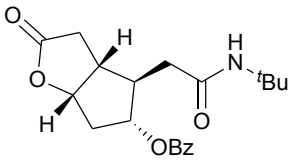
2r. Isolated as a white solid (Mp.: 143.5 – 144.0 ºC); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.22 (s, 1H), 3.76 (d, *J* = 11.5 Hz, 2H), 2.43 (s, 3H), 2.23 (td, *J* = 12.0, 2.4 Hz, 2H), 1.96 (d, *J* = 6.7 Hz, 2H), 1.79 – 1.65 (m, 3H), 1.38 – 1.21 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 143.5, 132.9, 129.6, 127.7, 51.3, 46.3, 44.0, 32.6, 31.2, 28.8, 21.5. HRMS calcd for $C_{18}H_{28}N_2O_3S$ $[M+H]^+$: 353.18989, found 353.18994.



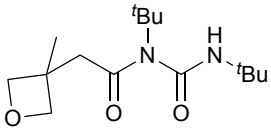
2s. Isolated as a white solid (Mp.: 88.5 – 89.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1H), 3.94 (ddt, *J* = 11.7, 4.5, 1.2 Hz, 2H), 3.40 (td, *J* = 11.9, 2.1 Hz, 2H), 2.12 – 1.92 (m, 3H), 1.68 – 1.58 (m, 2H), 1.34 (s, 9H), 1.33 – 1.22 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 67.9, 51.3, 45.0, 32.8, 32.5, 28.8. HRMS calcd for $C_{11}H_{22}NO_2$ $[M+H]^+$: 200.16505, found 200.16406.



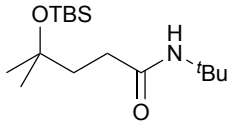
2t. Isolated as a white solid (Mp.: 103.5 – 104.0 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (s, 1H), 1.93 (d, *J* = 6.9 Hz, 2H), 1.79 – 1.65 (m, 6H), 1.34 (s, 9H), 1.28 – 1.07 (m, 6H), 0.99 – 0.84 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8, 51.1, 45.9, 37.5, 37.0, 35.6, 33.0, 33.0, 29.2, 28.9, 23.0, 14.1. HRMS calcd for $C_{16}H_{32}NO$ $[M+H]^+$: 254.24839, found 254.24814.



2u. Isolated as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.55 (ddt, *J* = 8.7, 7.0, 1.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 5.67 (s, 1H), 5.21 (dt, *J* = 6.1, 4.1 Hz, 1H), 5.05 (td, *J* = 6.4, 1.9 Hz, 1H), 2.89 (d, *J* = 12.2 Hz, 2H), 2.65 – 2.56 (m, 1H), 2.56 – 2.43 (m, 2H), 2.40 – 2.21 (m, 2H), 2.14 (dd, *J* = 14.8, 8.5 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.8, 169.3, 166.3, 133.4, 129.7, 128.5, 83.8, 79.4, 51.5, 49.2, 42.8, 39.6, 37.8, 35.8, 28.7. HRMS calcd for $C_{20}H_{26}NO_5$ $[M+H]^+$: 360.18110, found 360.18005.



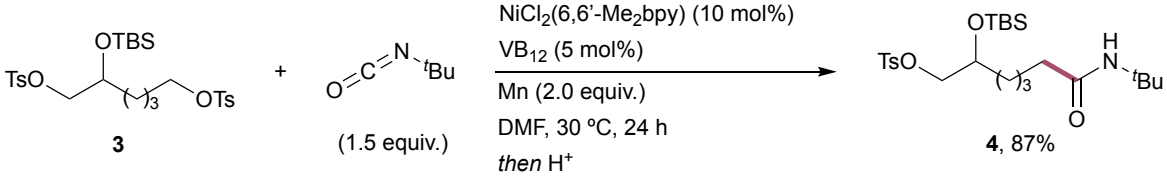
2v. Isolated as a white solid (Mp.: 100.5 – 101.0 ºC); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.64 (s, 1H), 3.96 – 3.83 (m, 1H), 3.34 (d, *J* = 9.8 Hz, 1H), 3.10 (d, *J* = 9.8 Hz, 1H), 2.38 (d, *J* = 16.6 Hz, 1H), 2.11 (d, *J* = 16.6 Hz, 1H), 1.38 (s, 9H), 1.32 (s, 9H), 1.13 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 154.6, 54.8, 53.9, 50.4, 43.4, 35.1, 29.6, 28.9, 27.7, 23.5. HRMS calcd for $C_{15}H_{29}N_2O_3$ $[M+H]^+$: 285.21782, found 285.21759.



2w. Isolated as a colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.30 (s, 1H), 2.32 – 2.23 (m, 2H), 1.87 – 1.78 (m, 2H), 1.44 (s, 9H), 1.30 (s, 6H), 0.96 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 72.9, 51.0, 40.4, 32.7, 29.7, 28.8, 28.2, 25.9, 18.1, -2.1. HRMS calcd for $C_{16}H_{36}NO_2Si$ $[M+H]^+$: 302.25153, found 302.25125.

6. Regioselective functionalisation of the alkyl ditosylate 3

6-1. Ni/Co-catalysed regioselective amidation of alkyl ditosylate 3



In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 ºC for 3 min under vacuum. After cooling, the Schlenk tube was charged with $NiCl_2$(6,6'-Me_2bpy) (7.8 mg, 0.025 mmol, 10 mol%), vitamin B_{12} (VB_{12}, 18.9 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 μL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, ditosylate **3** (139.2 mg, 0.25 mmol, 1.0 equiv.) and ^{t}Bu-isocyanate (47 μL, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 ºC for 24 h. The obtained mixture was quenched by saturated NH_4Cl aq. and diluted with EtOAc. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over $MgSO_4$. After filtration and removing the solvent, the residue was purified by silica-gel column chromatography (chloroform) to give the product **4** as a colorless oil in 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 5.21 (s, 1H), 3.90 – 3.77 (m, 3H), 2.45 (s, 3H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.07 (m, 16H), 0.82 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 144.8, 132.9, 129.8, 127.9, 73.0, 69.8, 51.1, 37.4, 33.8, 28.8, 25.7, 25.6, 24.4, 21.6, 18.0, -4.6, -4.8. HRMS calcd for $C_{24}H_{43}NO_5SSi$ $[M+H]^+$: 486.27095, found 486.27023.

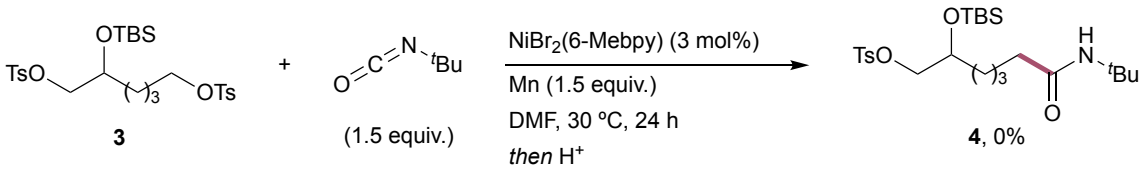
6-2. Cyanation of compound 4

This reaction was carried out following the literature.[2] To a solution of **4** (102.0 mg, 0.21 mmol) in 3 mL of DMSO was added KCN (27.4 mg, 0.42 mmol, 2.0 equiv.), and the mixture was stirred at 60 °C for 12 h. After the reaction, the reaction mixture was extracted with Et_2O. The ethereal layer was washed with brine, dried over $MgSO_4$ and evaporated to remove solvent. The residue was purified by silica-gel column chromatography (Hexane/EtOAc = 5:1) to give the product **5** as a colorless oil in 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1H), 3.97 – 3.89 (m, 1H), 2.45 (dd, *J* = 5.5, 4.8 Hz, 2H), 2.09 (t, *J* = 7.4 Hz, 2H), 1.69 – 1.53 (m, 5H), 1.34 (s, 9H), 0.89 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 117.7, 68.1, 51.1, 37.3, 36.7, 28.8, 26.0, 25.7, 25.4, 24.5, 17.9, -4.7, -4.7. HRMS calcd for $C_{18}H_{37}N_2O_2Si$ $[M+H]^+$: 341.26243, found 341.26221.

6-3. Thiophenylation of compound 4

This reaction was carried out following the literature.[3] To a solution of **4** (100 mg, 0.21 mmol) in EtOH (2.5 mL) was added NaOH (12.6 mg, 0.315 mmol, 1.5 equiv.). After the reaction mixture became homogeneous upon heating (40 ºC), thiophenol (32 µL, 0.135 mmol, 1.5 equiv.) was added. The reaction mixture was heated (50 ºC) for 24 h. After cooling to rt, the reaction mixture was concentrated in vacuo and diluted with H_2O. The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, filtered, and concentrated in vacuo. Purification of the resultant residue by silica-gel chromatography (Hexane/EtOAc = 5:1) afforded the product **6** as a colorless oil in 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.31 – 7.21 (m, 2H), 7.19 – 7.11 (m, 1H), 5.26 (s, 1H), 3.80 (tt, *J* = 6.6, 4.9 Hz, 1H), 3.05 – 2.86 (m, 2H), 2.06 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.46 (m, 4H), 1.44 – 1.24 (m, 11H), 0.86 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 136.9, 129.1, 128.8, 125.8, 71.2, 51.0, 40.7, 37.6, 35.9, 28.8, 25.8, 25.7, 24.5, 18.0, -4.5, -4.6. HRMS calcd for $C_{23}H_{41}NNaO_2SSi$ $[M+Na]^+$: 446.25250, found 446.25217.

7. Reductive amidation of ditosylate 3 by Martin's method using $NiBr_2$(6-Mebpy) catalyst[4]



In a flame dried Schlenk tube, Mn powder (20.6 mg, 0.375 mmol, 1.5 equiv.) was added and heated at 400 ºC for 3 min under vacuum. After cooling, the Schlenk tube was charged with $NiBr_2$(6-Mebpy) (2.9 mg, 0.0075 mmol, 3 mol%), DMF (0.5 mL), and TMSCl (6.3 μL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, ditosylate **3** (139.2 mg, 0.25 mmol, 1.0 equiv.) and ^{t}Bu-isocyanate (47 μL, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 ºC for 24 h. The obtained mixture was quenched by saturated NH_4Cl aq. and diluted with EtOAc. The organic phase was analysed by GC using mesitylene as an internal standard. As a result, the reaction afforded complex mixture, in which a part of ditosylate **3** remained unchanged (Figure S1, a).

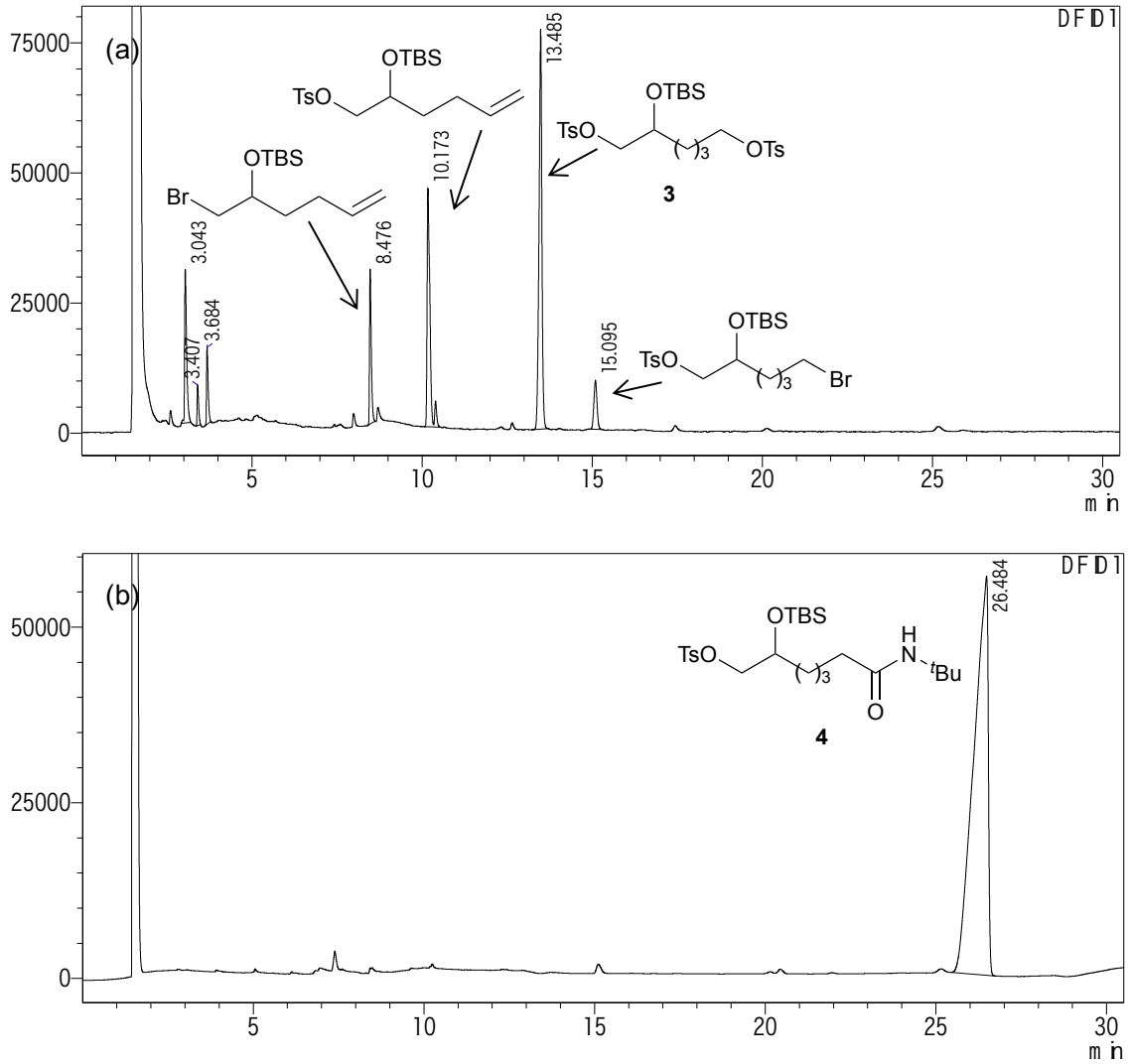
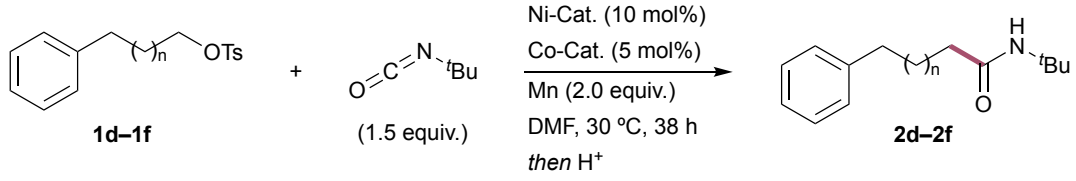


Figure S1. (a) A GC chart of the reaction mixture in the amidation of ditosylate **3** by $NiBr_2$(6-Mebpy) under Martin's conditions. (b) A GC chart of the mono-amidation product **4**.

8. Effect of counter anions in the reductive amidation of alkyl tosylates

As shown in Table S1, careful selection of counter anion on nickel catalysts is essential in the present amidation because alkyl tosylates would be converted into alkyl halides via a tosylate–halogen exchange reaction with the anion. Thus, $NiBr_2$(6-Mebpy) catalyst gave alkyl amide **2e** in the amidation of alkyl tosylate **1e** in 18% yield with 32% conversion of **1e** (Entry 1, Table S1). In contrast, $NiCl_2$(6-Mebpy) and $NiCl_2$(6,6'-Me_2bpy) catalysts afforded a negligible amount of **2e**, in which most of **1e** remained unchanged (Entries 2 and 3). These results would indicate that Br anion on $NiBr_2$ or in-situ generated $MnBr_2$ displaced TsO group to Br during reaction. Additionally, low-reactivities of $NiCl_2$ complexes were repeated in the cases of alkyl tosylates **1d** and **1f** (Entries 5 and 7), whereas $NiCl_2$(6,6'-Me_2bpy)/VB_{12}-dual catalytic system led to complete conversion of **1** and good product yields in all cases (Entries 4, 6 and 8).

Table S1 Examination for the effect of the counter anions



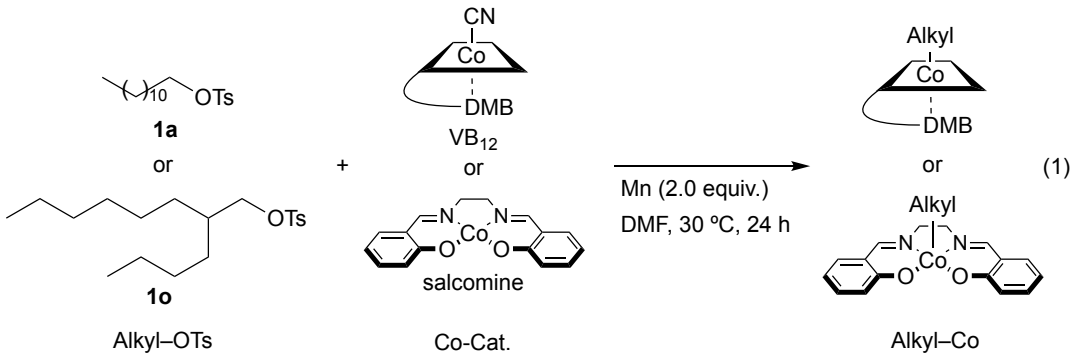
Entry	**1** (n)	Ni-Cat.	Co-Cat.	Conv. of **1** (%)	**2** and yield (%) [a]	
1	**1e** (2)	$NiBr_2$(6-Mebpy)	none	32	**2e**	18
2	**1e** (2)	$NiCl_2$(6-Mebpy)	none	<1	**2e**	trace
3	**1e** (2)	$NiCl_2$(6,6'-Me_2bpy)	none	<1	**2e**	trace
4	**1e** (2)	$NiCl_2$(6,6'-Me_2bpy)	VB_{12}	100	**2e**	86[b]
5	**1d** (1)	$NiCl_2$(6,6'-Me_2bpy)	none	<1	**2d**	Trace
6	**1d** (1)	$NiCl_2$(6,6'-Me_2bpy)	VB_{12}	100	**2d**	80[b]
7	**1f** (3)	$NiCl_2$(6,6'-Me_2bpy)	none	<1	**2f**	Trace
8	**1f** (3)	$NiCl_2$(6,6'-Me_2bpy)	VB_{12}	100	**2f**	76[b]

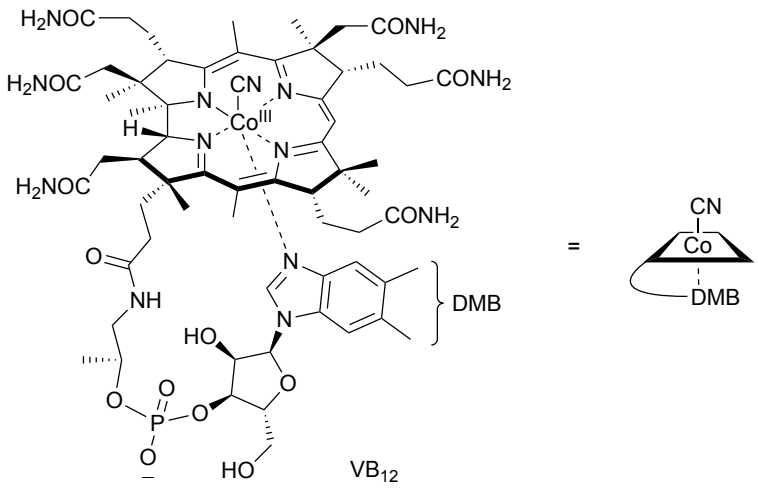
[a] Yields were determined by GC using mesitylene as an internal standard. [b] Isolated yields.

9. Stoichiometric reactions of cobalt complexes with alkyl tosylates

In order to investigate a relationship between the steric hindrance of cobalt catalysts and alkyl tosylates, we carried out stoichiometric reactions of cobalt catalysts with alkyl tosylates

(Eq. 1). That is, in a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 ºC for 3 min. under vacuum. After cooling, the Schlenk tube was charged with cobalt catalyst (VB_{12} or salcomine), DMF (1.5 mL), and TMSCl (6.3 μL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, alkyl tosylate **1** (**1a**: 0.25 mmol or **1o**: 0.25 mmol) and mesitylene (0.25 mmol) as an internal standard were added into the solution. The recovery of alkyl tosylates was monitored by GC measurement. These results were graphically showed in Figure S2. As a result, the rate of reaction progress in the two S_N2-type oxidative addition (S_N2-type OA) between cobalt complexes and alkyl tosylates was quite similar. These results indicate that the S_N2-type OA would not be the rate-determining step in the present amidation and that the transalkylation between alkyl-Co(III) and Ni(0) might be the rate-determining step.





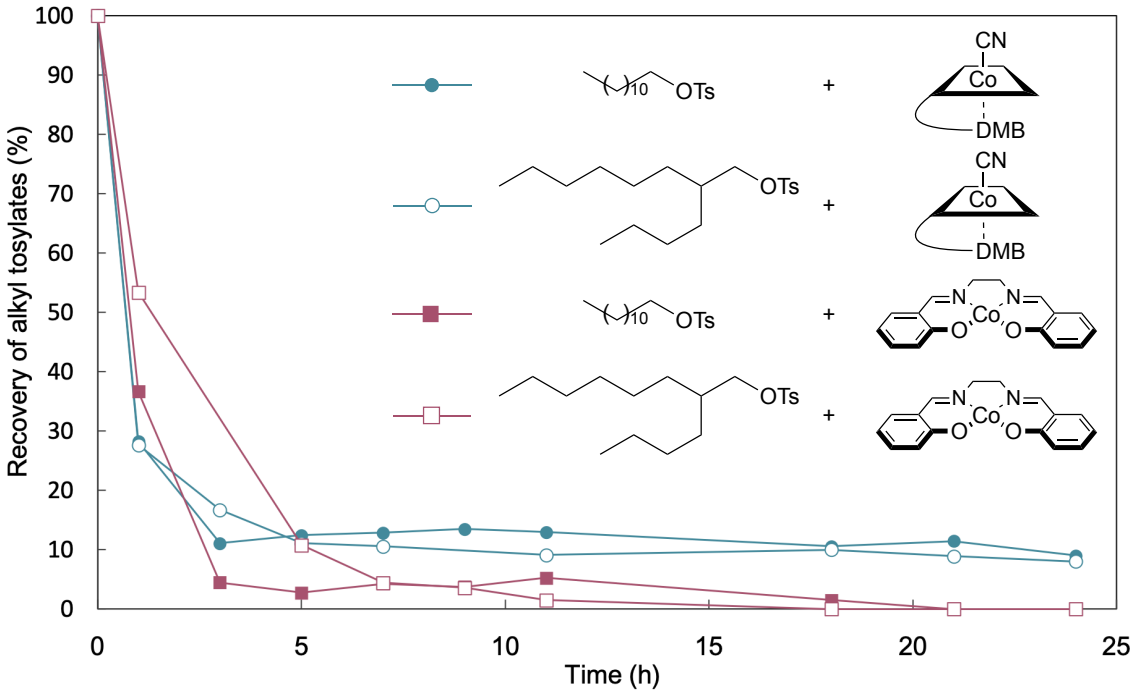
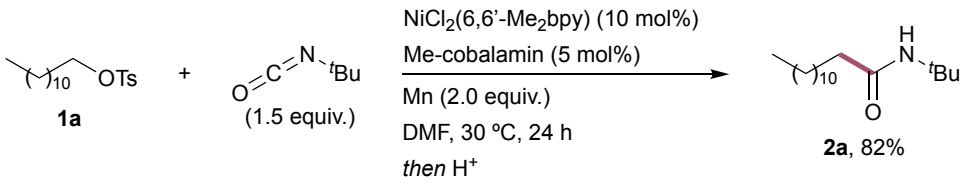
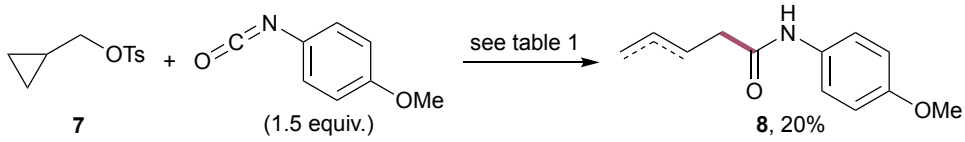


Figure S2 Stoichiometric reactions between alkyl tosylates and cobalt catalysts.

10. Mechanistic investigation

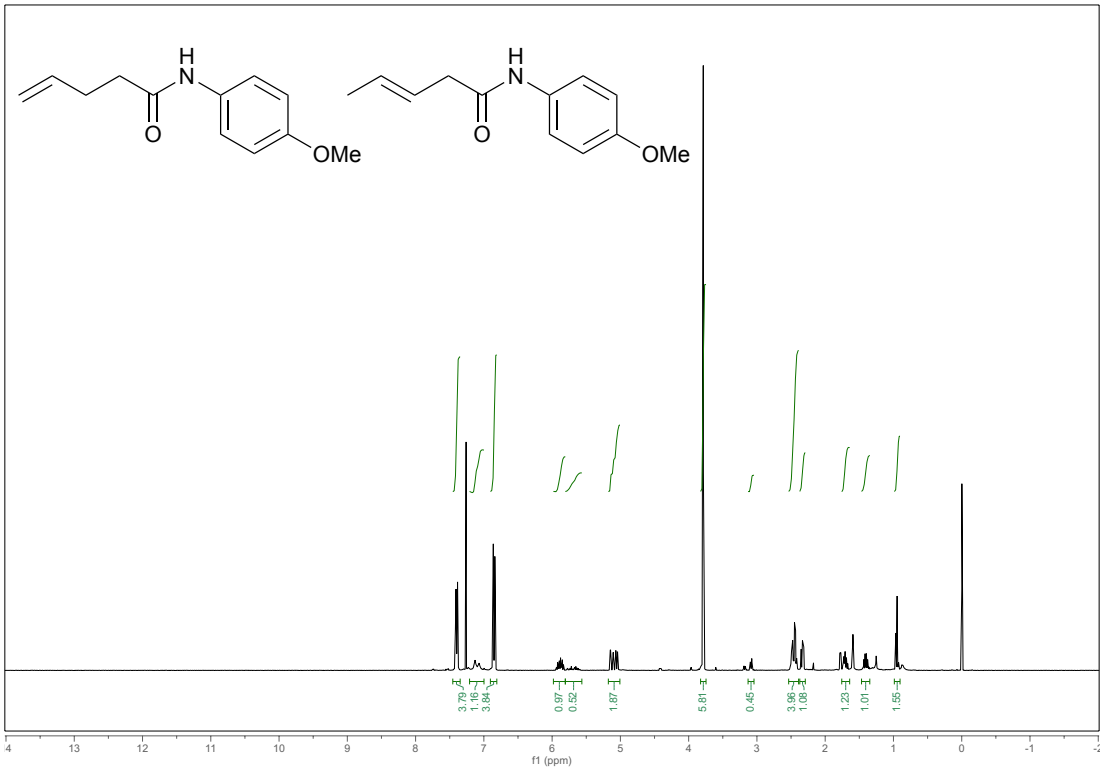


In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 ºC for 3 min under vacuum. After cooling, the Schlenk tube was charged with $NiCl_2$(6,6'-Me_2bpy) (7.8 mg, 0.025 mmol, 10 mol%), Me-cobalamin (16.8 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 μL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, dodecyl tosylate (**1a**, 85.1 mg, 0.25 mmol, 1.0 equiv.) and ^{t}Bu-isocyanate (47 μL, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 ºC for 24 h. The obtained mixture was quenched by saturated NH_4Cl aq. and diluted with EtOAc. The organic phase was taken up and analysed by GC using mesitylene as an internal standard.

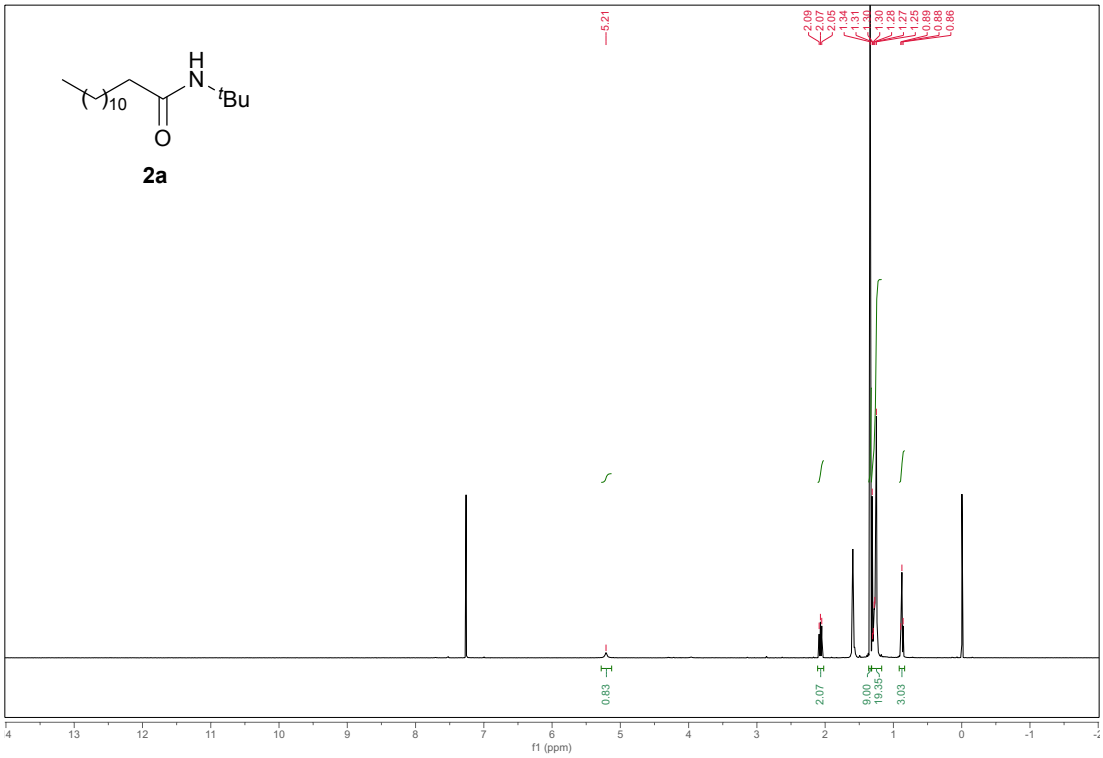


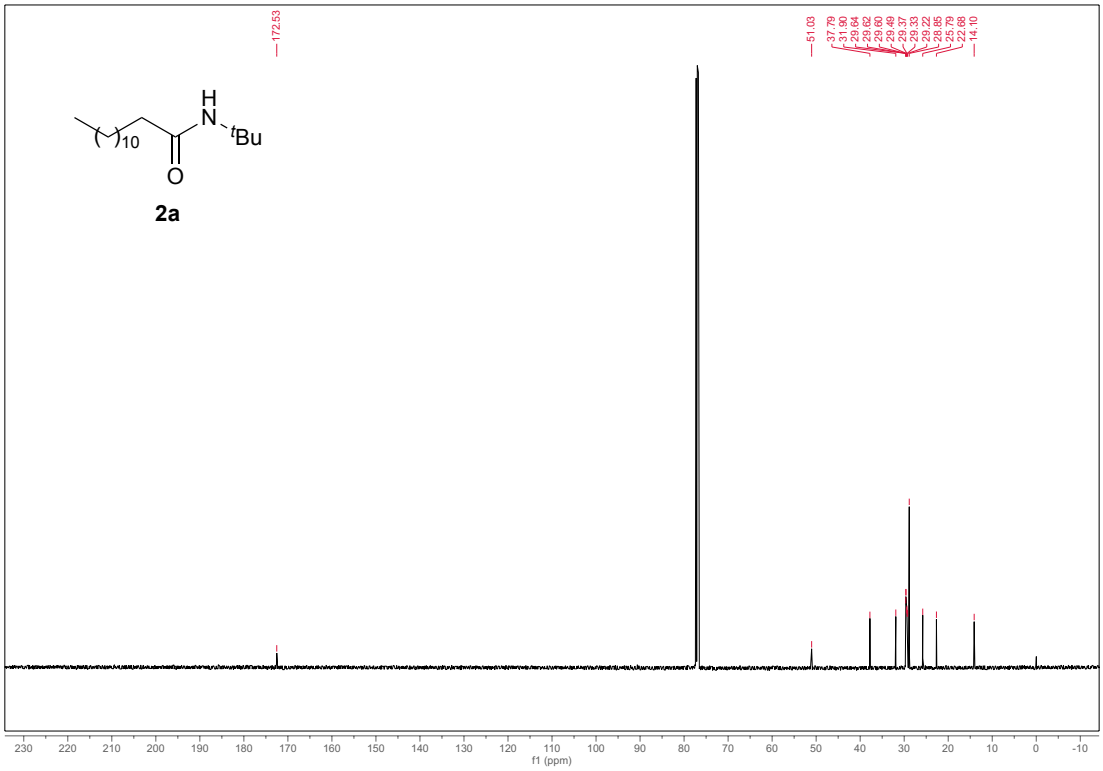
7 **8**, 20%

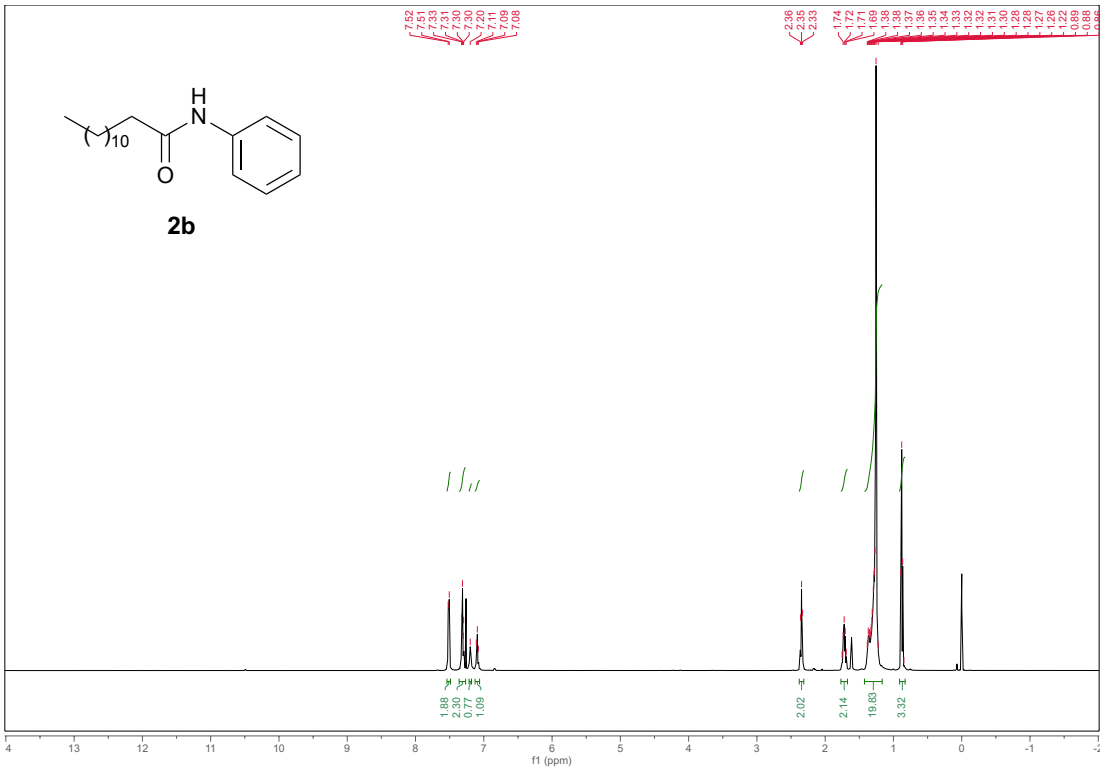
In a flame dried Schlenk tube, Mn powder (27.5 mg, 0.5 mmol, 2.0 equiv.) was added and heated at 400 ºC for 3 min under vacuum. After cooling, the Schlenk tube was charged with $NiCl_2$(6,6'-Me_2bpy) (7.8 mg, 0.025 mmol, 10 mol%), vitamin B_{12} (VB_{12}, 18.9 mg, 0.0125 mmol, 5 mol%), DMF (1.5 mL), and TMSCl (6.3 μL, 0.05 mmol, 20 mol%) and then followed by stirring for 10 min until the solution color turned to black. Then, cyclopropylmethyl tosylate (**7**, 56.6 mg, 0.25 mmol, 1.0 equiv.) and 4-anisyl isocyanate (55.9 mg, 0.375 mmol, 1.5 equiv.) were added into the solution. The reaction mixture was stirred at 30 ºC for 24 h. The obtained mixture was quenched by saturated NH_4Cl aq. and diluted with EtOAc. The aqueous phase was extracted with EtOAc and the combined organic phase was dried over $MgSO_4$. After filtration and removal of the solvent, the residue was purified by silica-gel column chromatography (Hexane/EtOAc = 5:1) to give the mixture of isomers **8** as a colorless oil. The ^{1}H NMR data is consistent with the literature: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.88 (ddt, *J* = 16.8, 10.2, 6.1 Hz, 1H), 5.26 – 4.89 (m, 2H), 3.79 (s, 3H), 2.65 – 2.33 (m, 4H).[5]



11. Spectral data for products



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O
2b
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7.30
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7.20
7.11
7.09
7.08
2.36
2.35
2.33
1.74
1.72
1.71
1.69
1.38
1.38
1.37
1.36
1.35
1.34
1.33
1.32
1.32
1.31
1.30
1.28
1.28
1.27
1.26
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0.77
1.09
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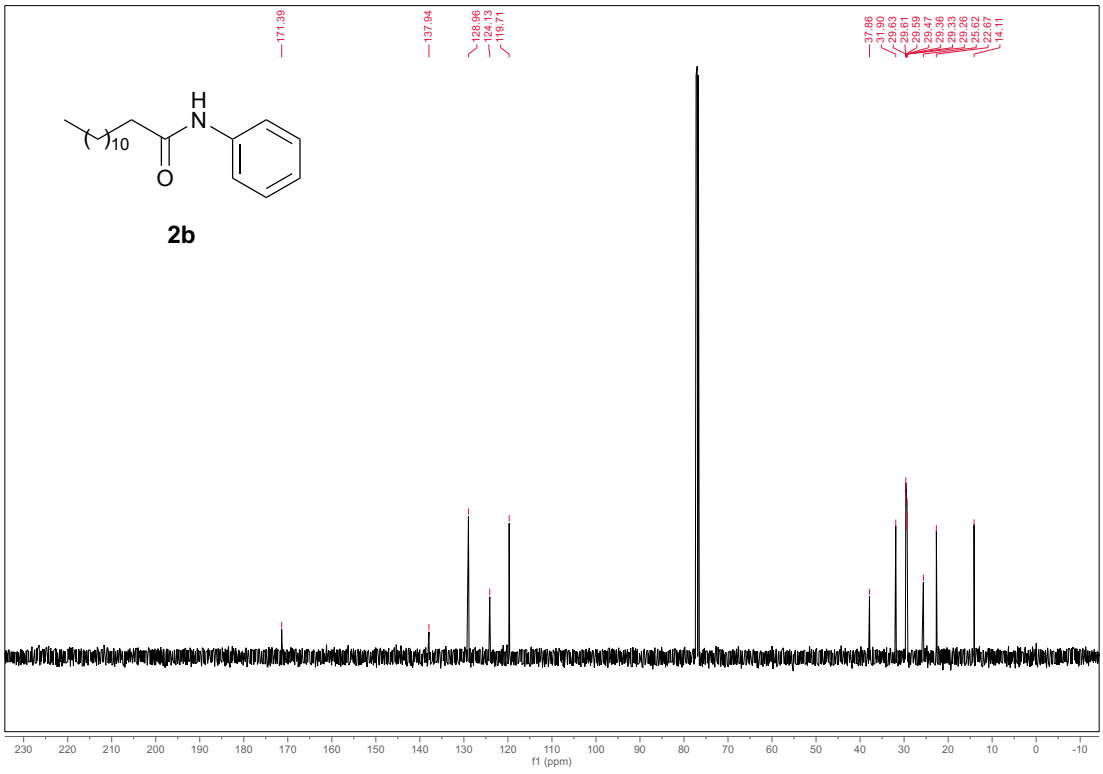
2.14
19.83
3.32
f1 (ppm)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O
2b
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29.26
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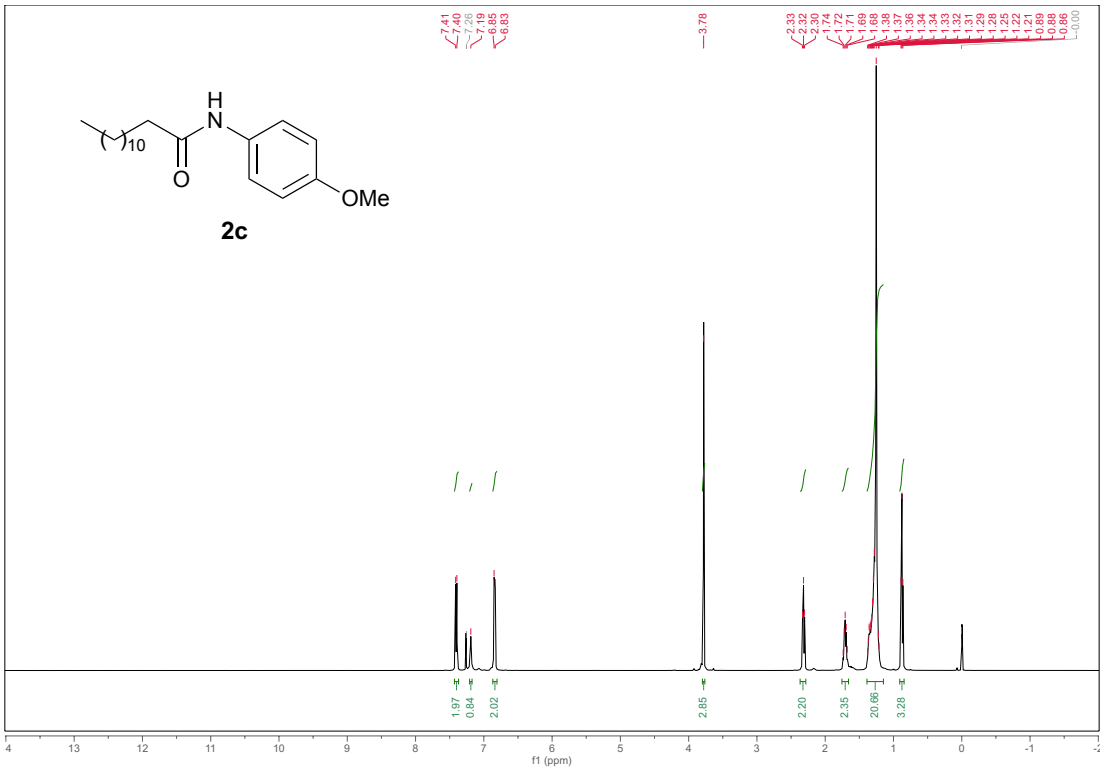
f1 (ppm)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1.38
1.37
1.36
1.34
1.34
1.33
1.32
1.31
1.29
1.28
1.25
1.22
1.21
0.89
0.88
0.86
0.00
H
N
O
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OMe
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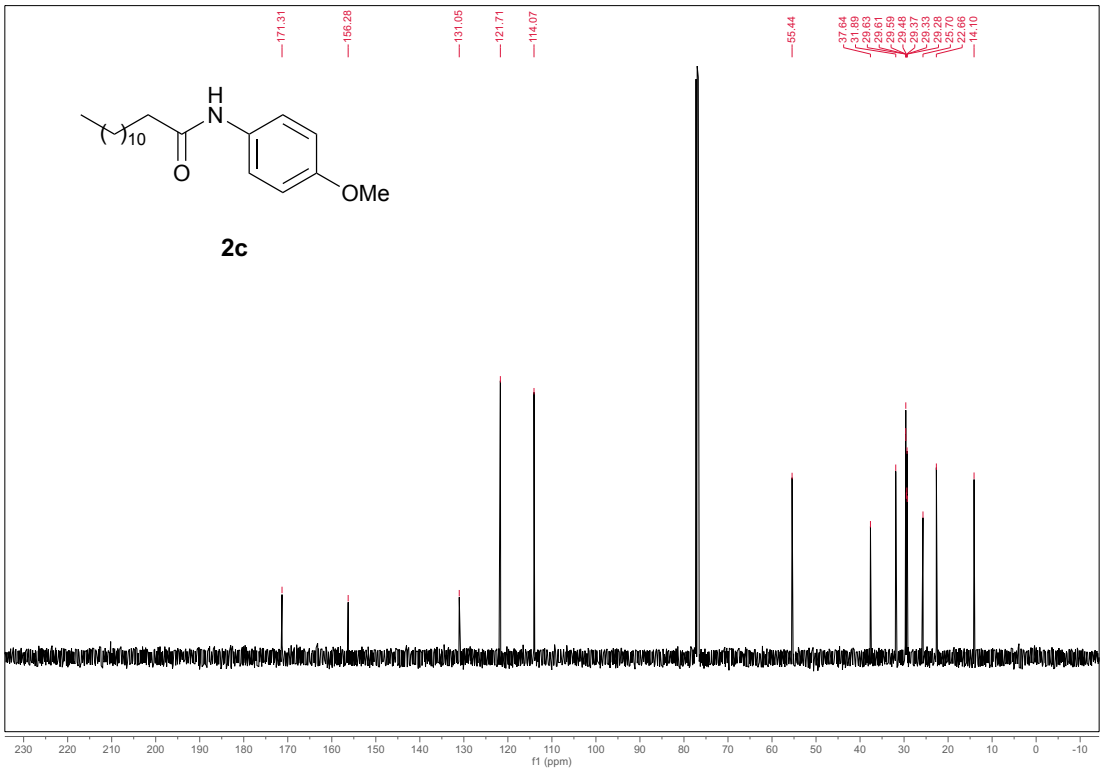
f1 (ppm)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121.71
114.07
55.44
37.64
31.89
29.63
29.61
29.59
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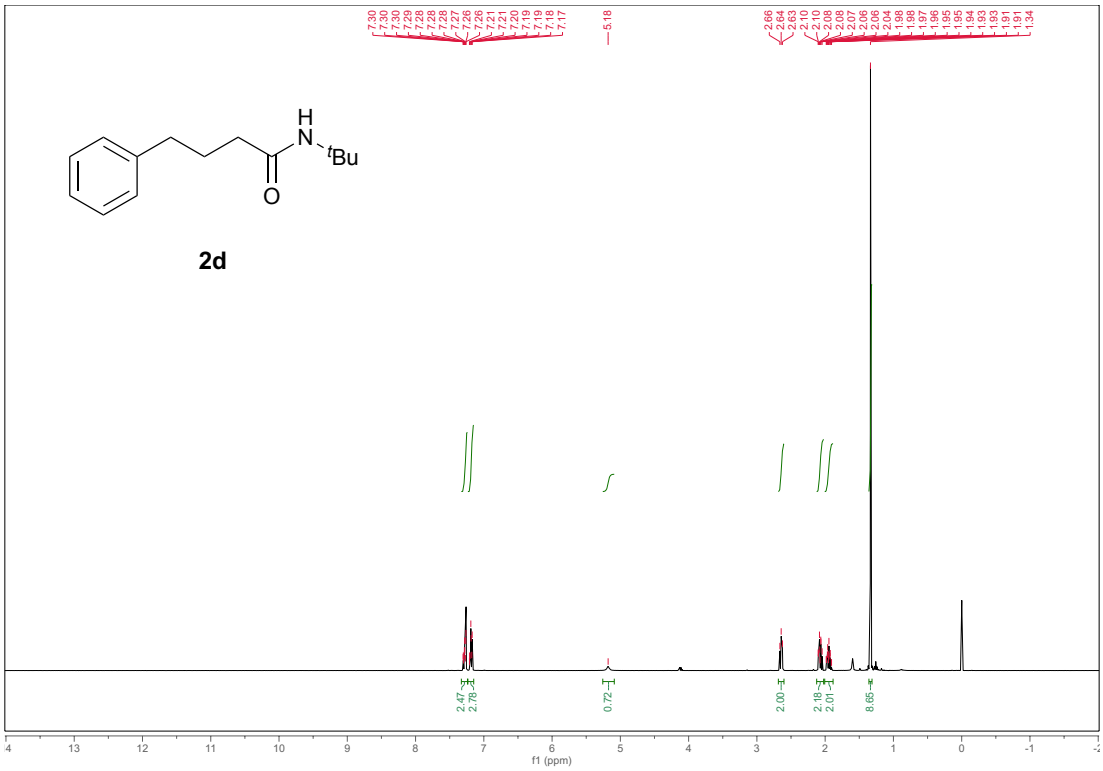
29.37
29.33
29.28
25.70
22.66
14.10
H
N
O
10
OMe
2c
f1 (ppm)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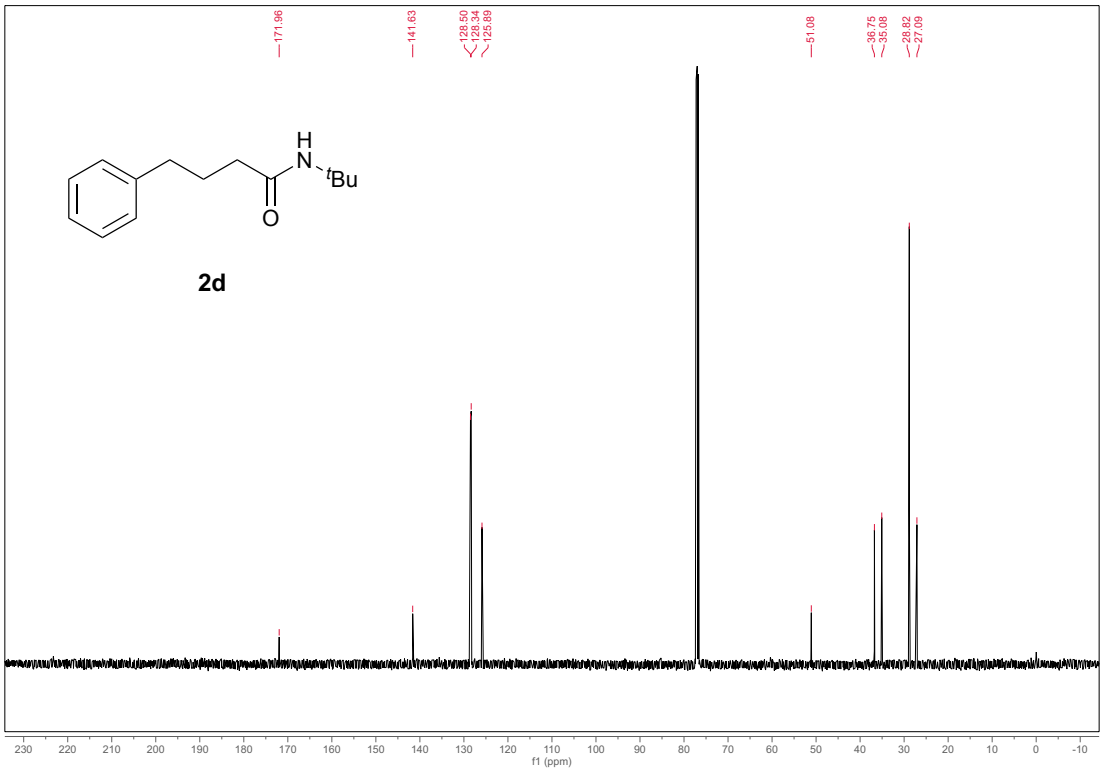
tBu
O
2d
f1 (ppm)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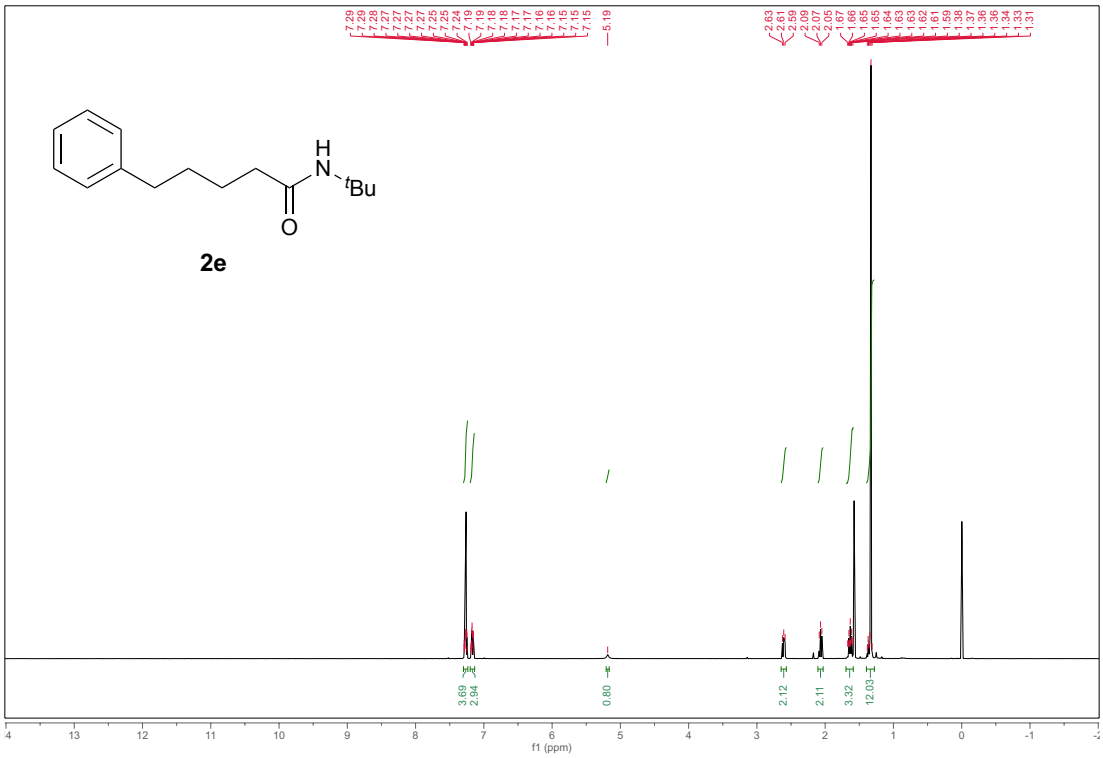
tBu
O
2d
f1 (ppm)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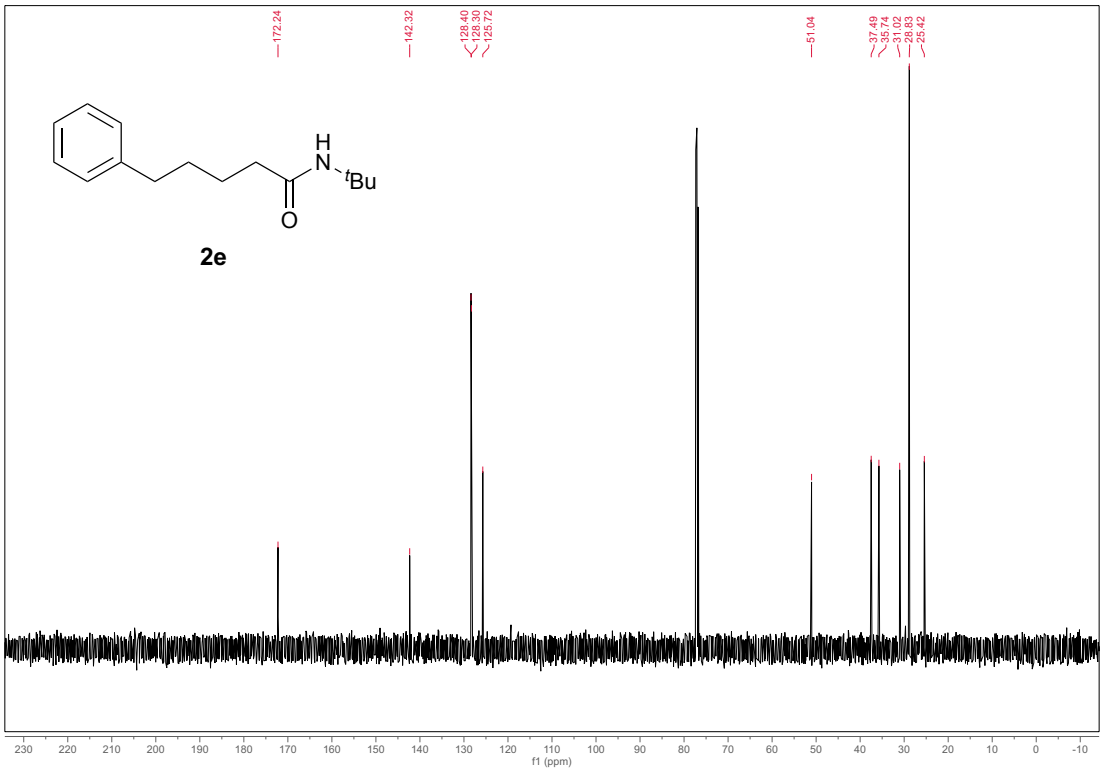
tBu
O
2e
f1 (ppm)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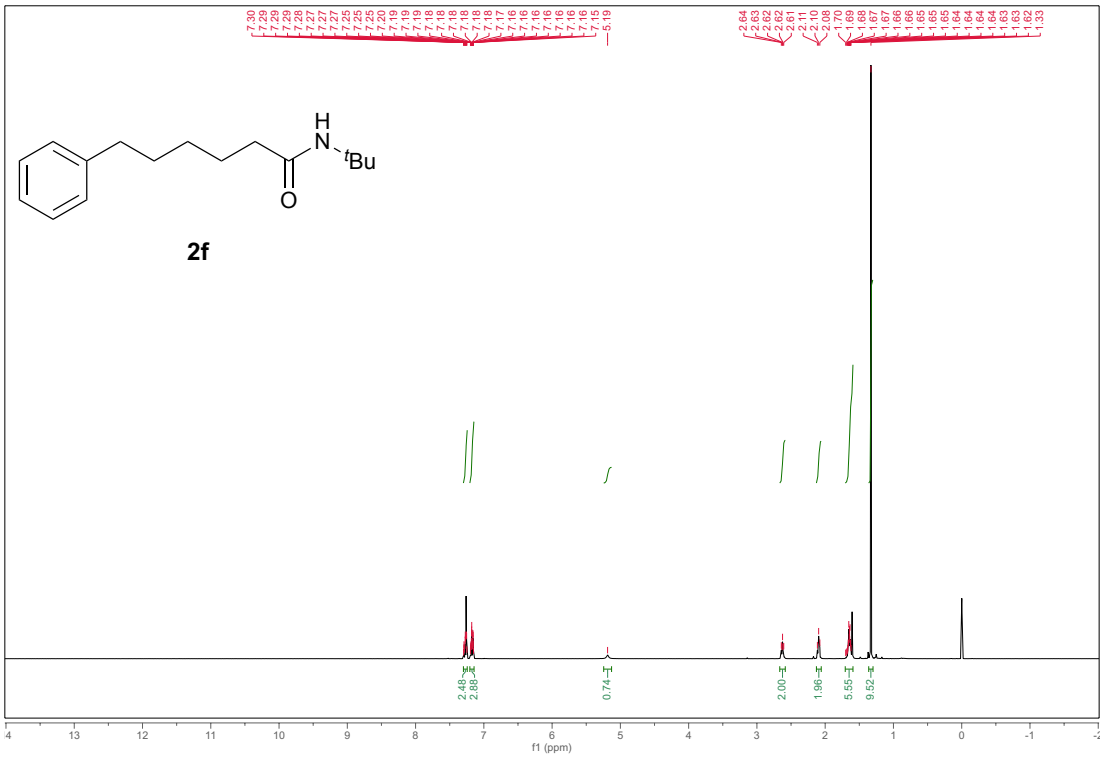
tBu
O
2e
f1 (ppm)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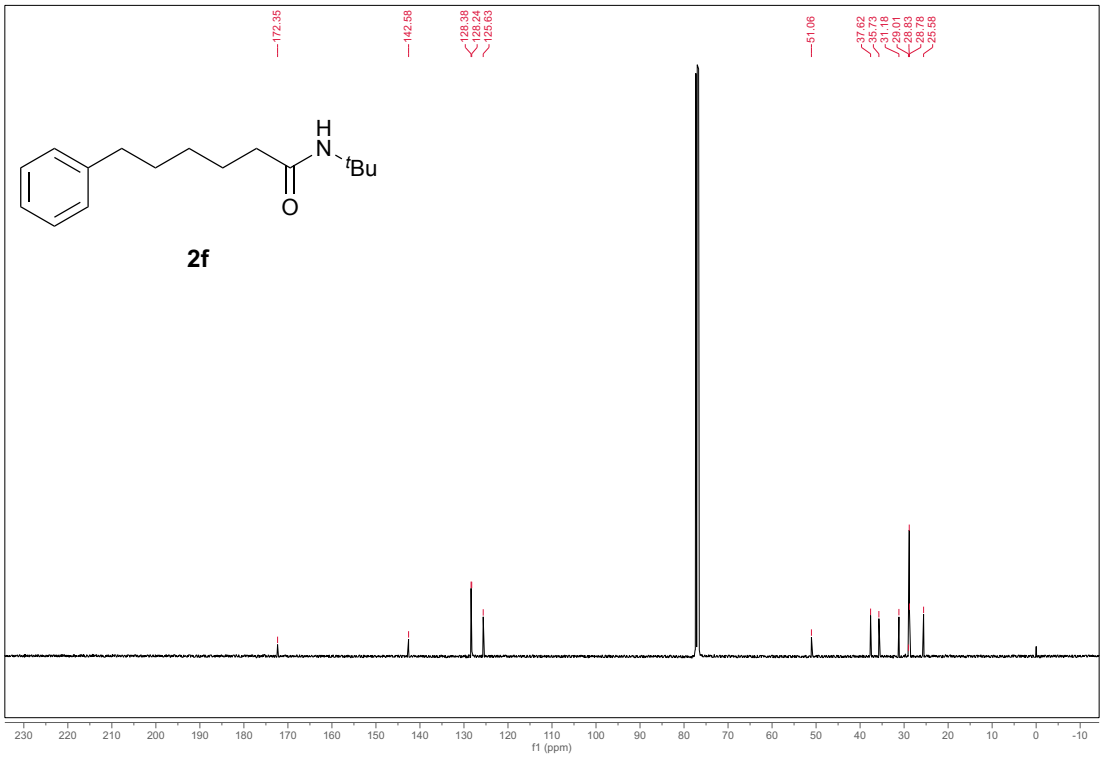
2f
f1 (ppm)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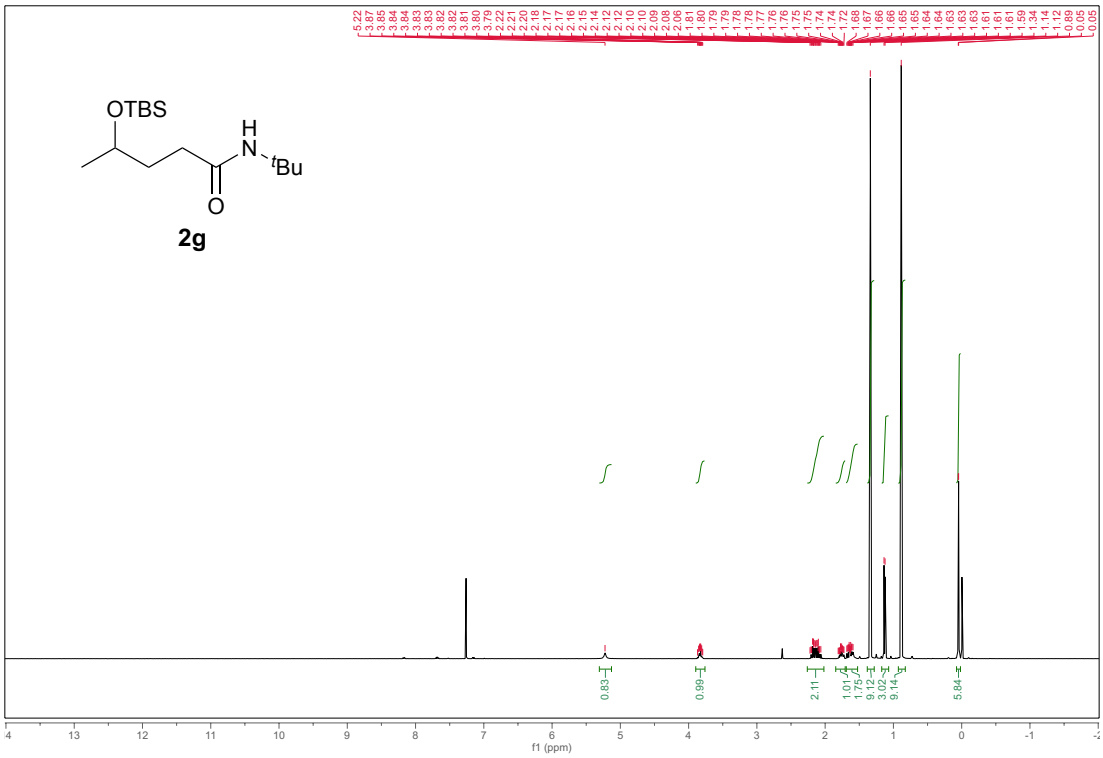
2f
f1 (ppm)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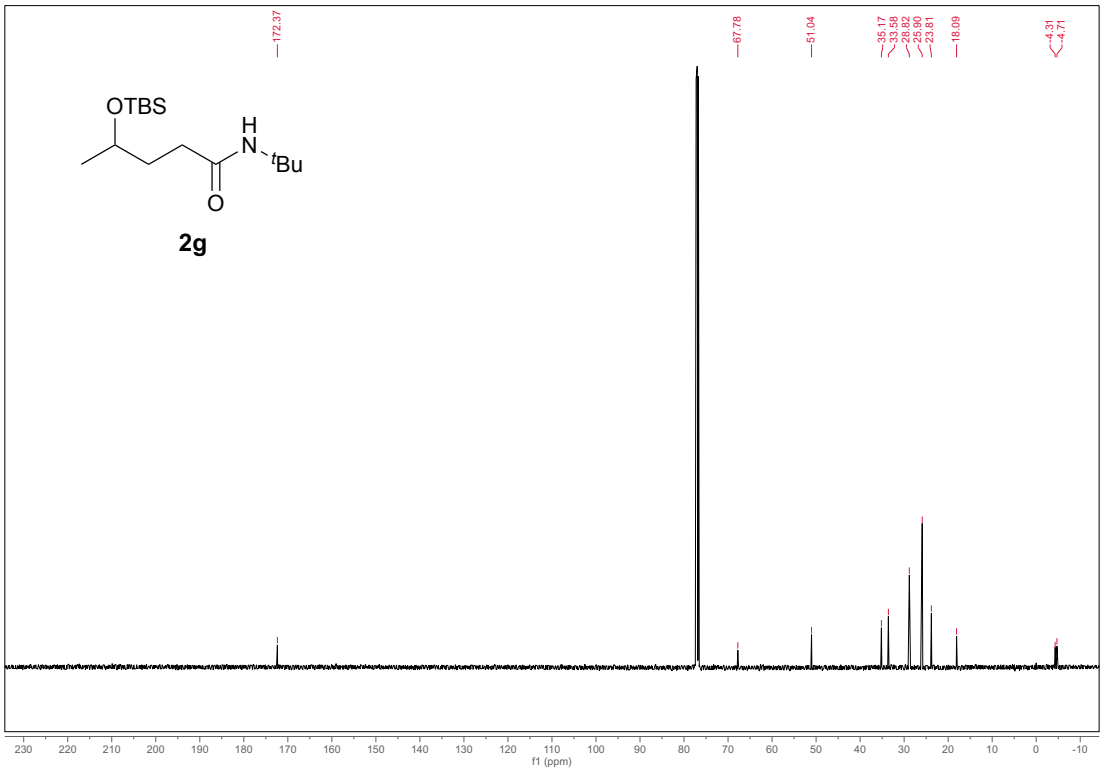
tBu
O
2g
f1 (ppm)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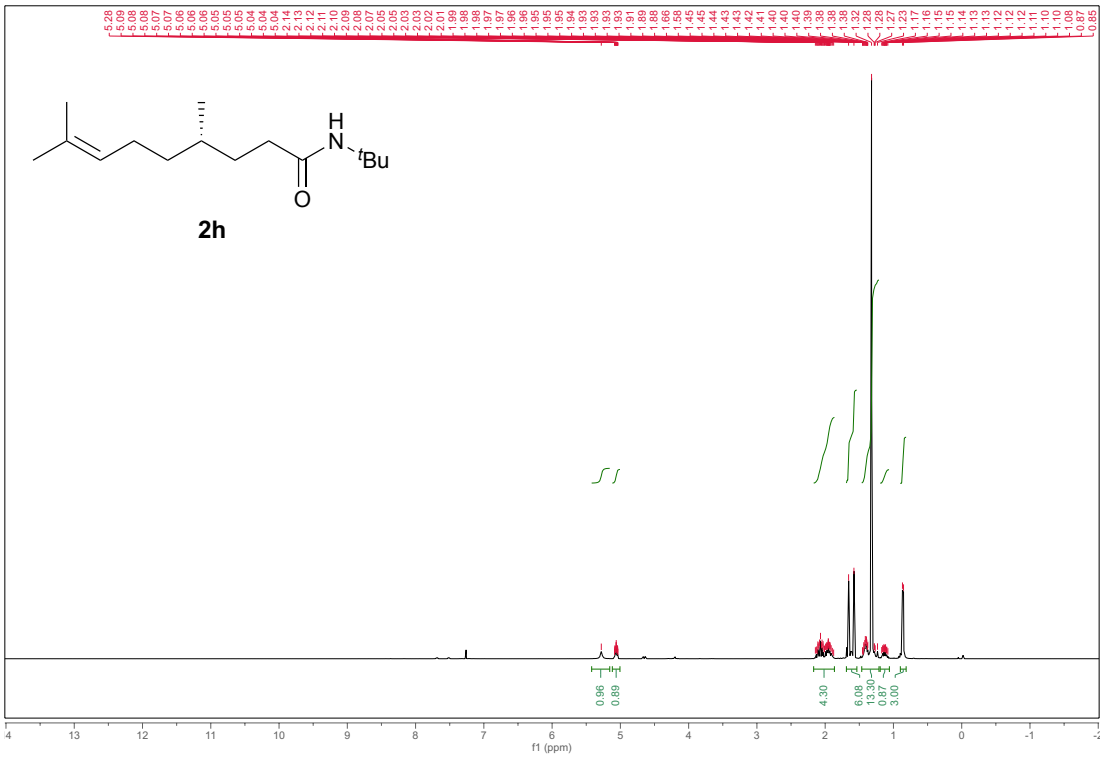
f1 (ppm)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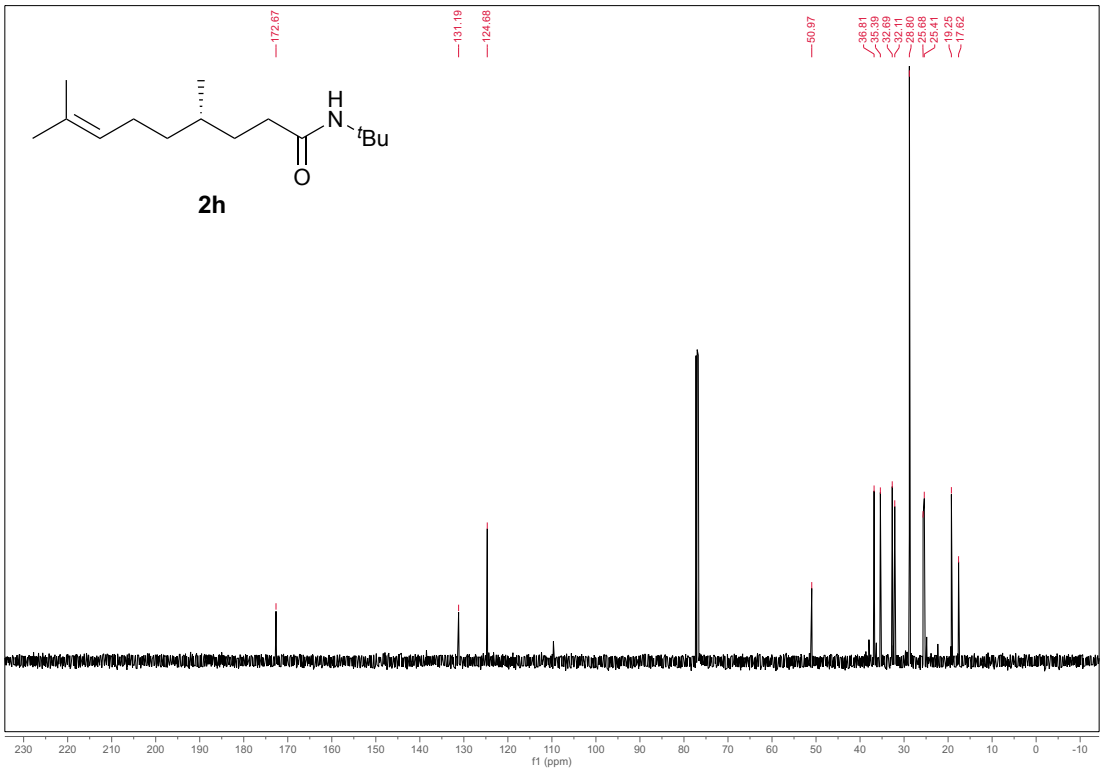
tBu
O
2h
f1 (ppm)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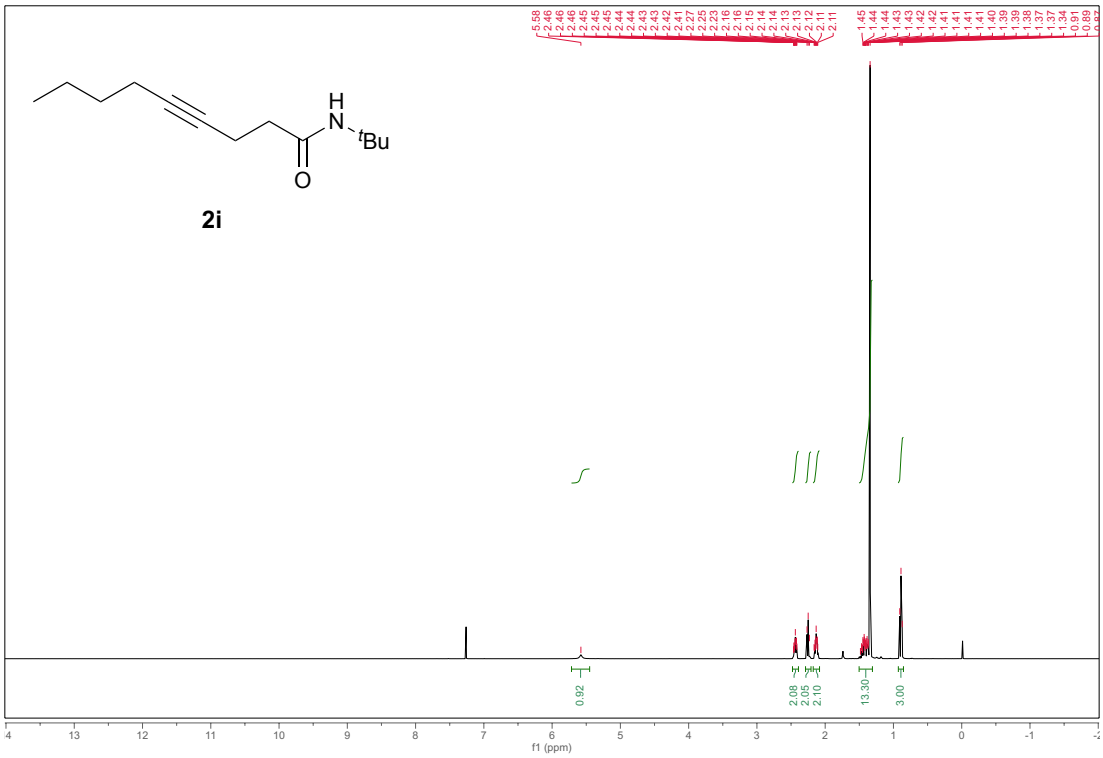
35.39
32.69
32.11
28.80
25.68
25.41
19.25
17.62
H
N
tBu
O
2h
f1 (ppm)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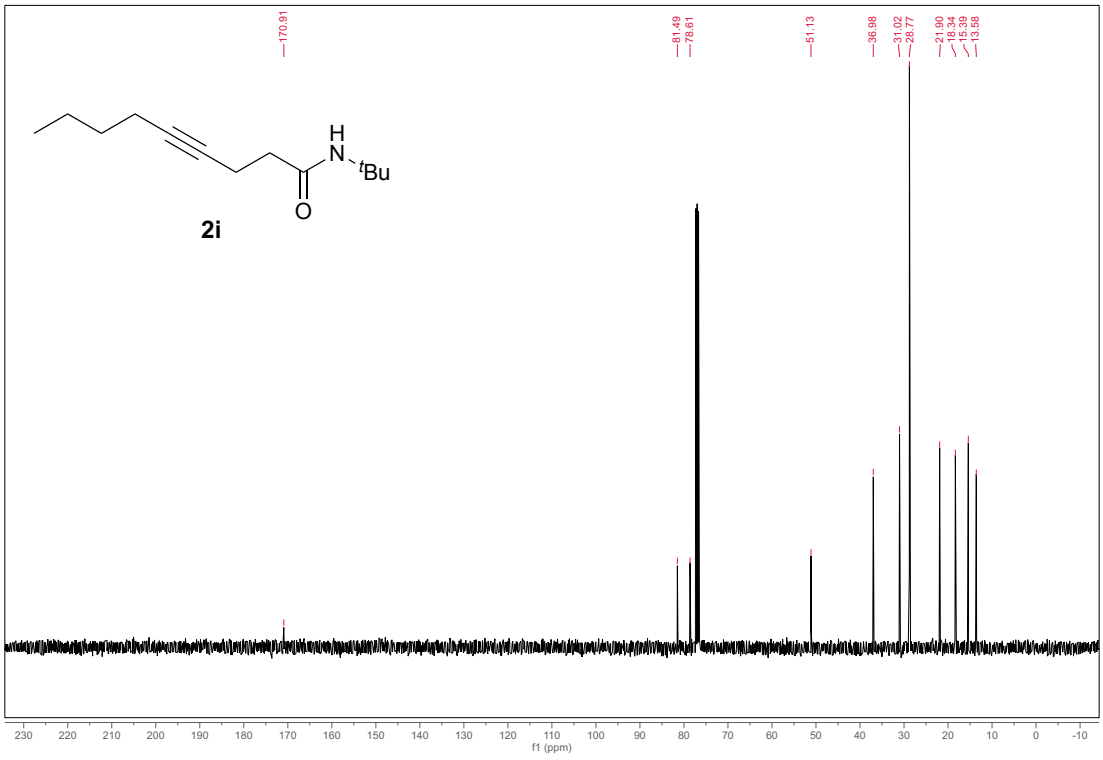
O
2i
f1 (ppm)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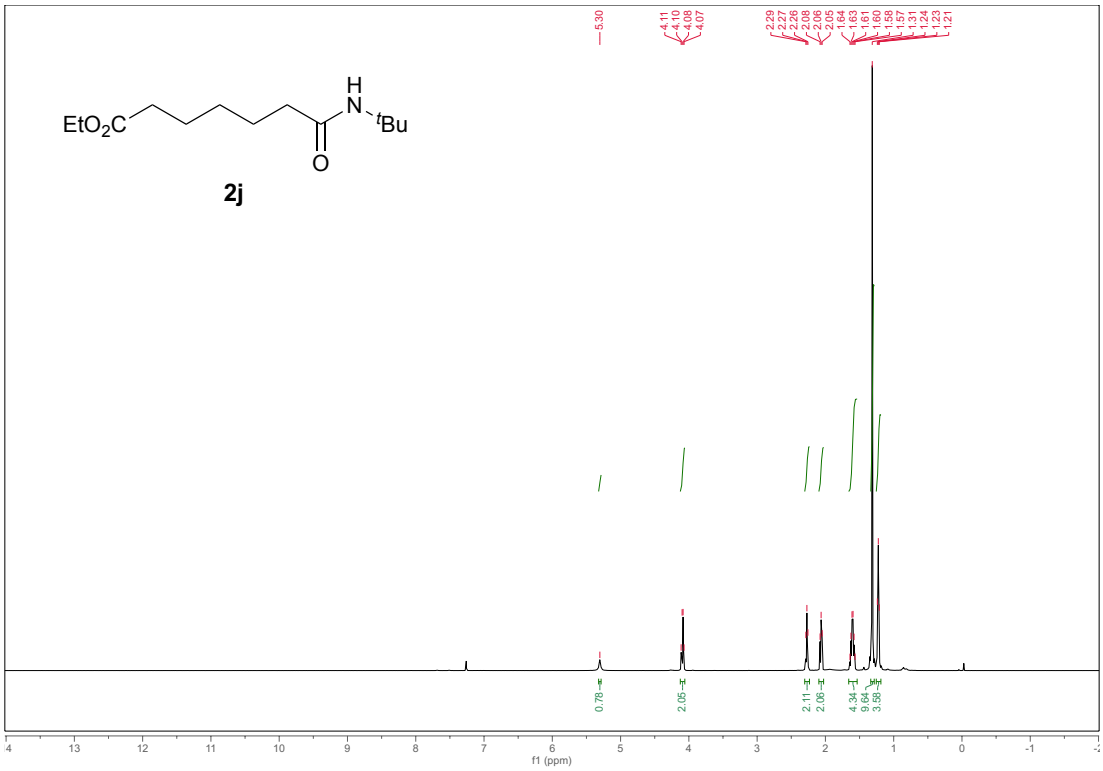
O
2i
f1 (ppm)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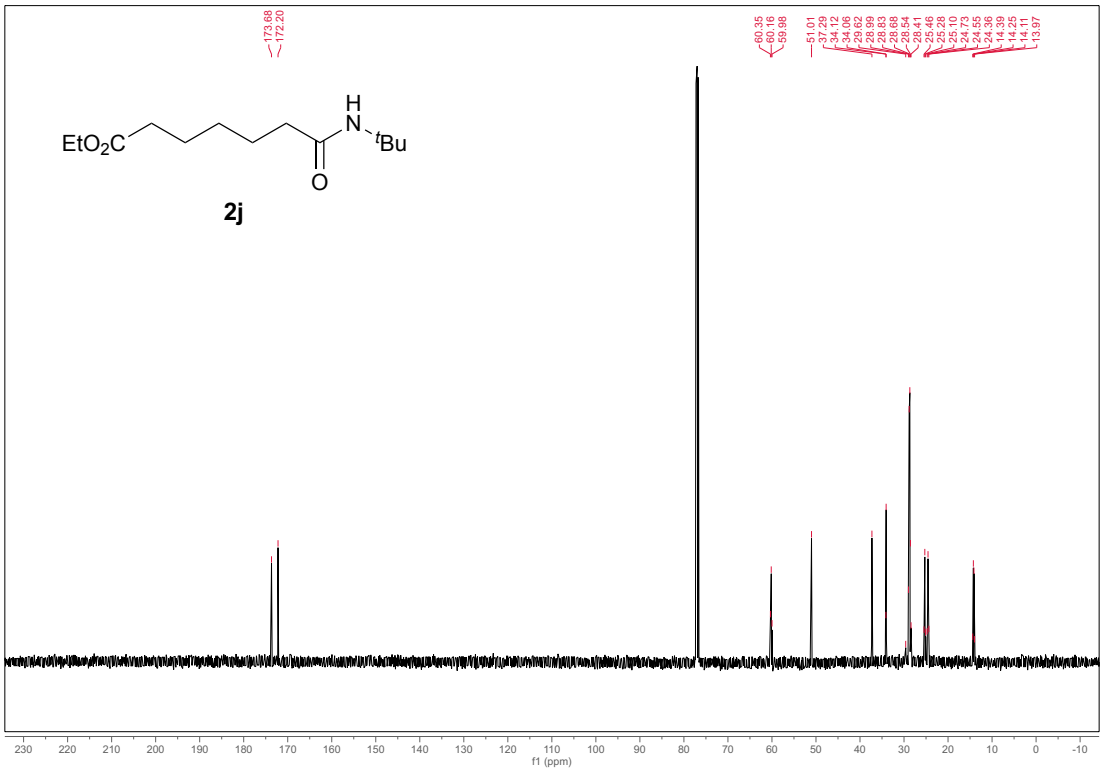
N
tBu
O
2j
f1 (ppm)


EtO2C
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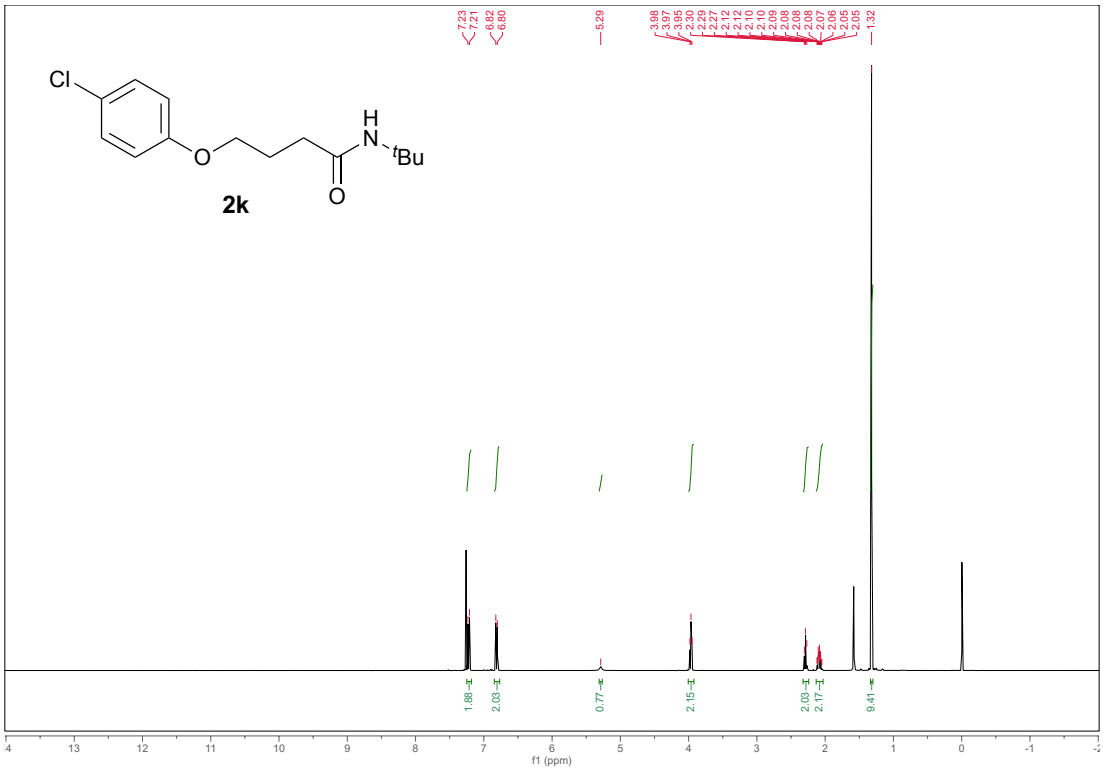
N
tBu
O
2j
f1 (ppm)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N
tBu
O
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6.82
6.80
5.29
3.98
3.97
3.95
2.30
2.29
2.27
2.12
2.12
2.10
2.10
2.09
2.08
2.08
2.08
2.07
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2.05
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2.03
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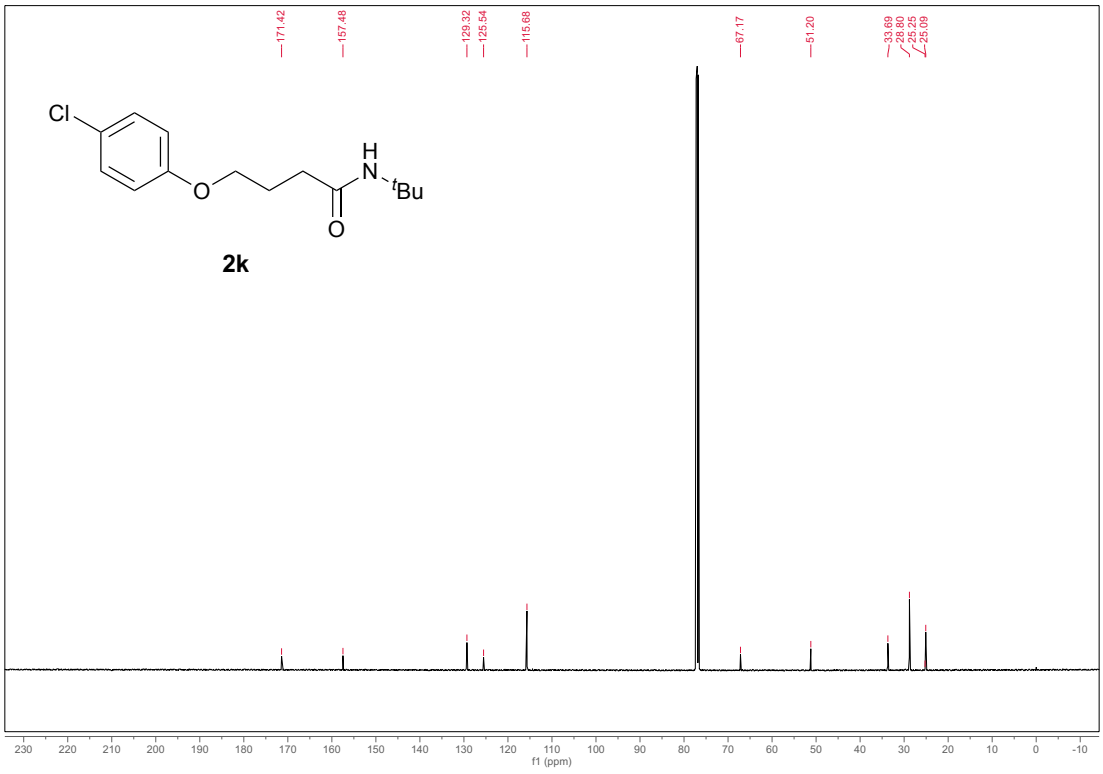
2.03
2.17
9.41
f1 (ppm)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N
tBu
O
2k
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67.17
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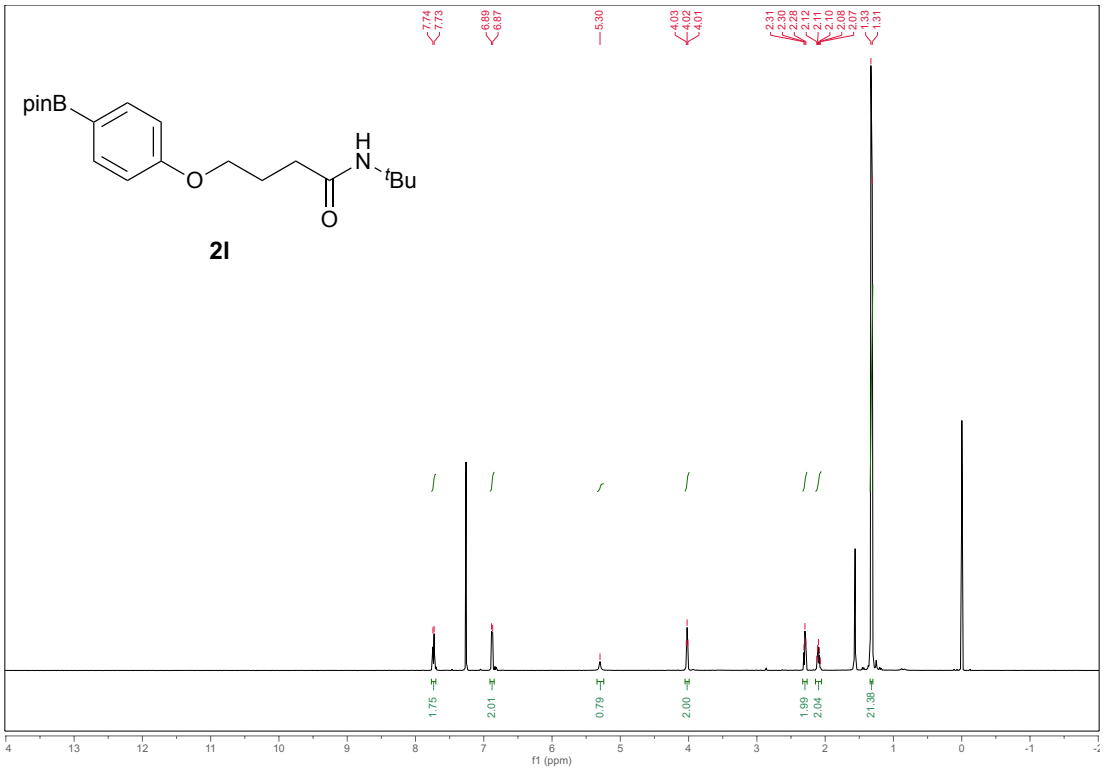
28.80
25.25
25.09
f1 (ppm)


pinB
O
H
N
tBu
O
2l
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6.87
5.30
4.03
4.02
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2.31
2.30
2.28
2.12
2.11
2.10
2.08
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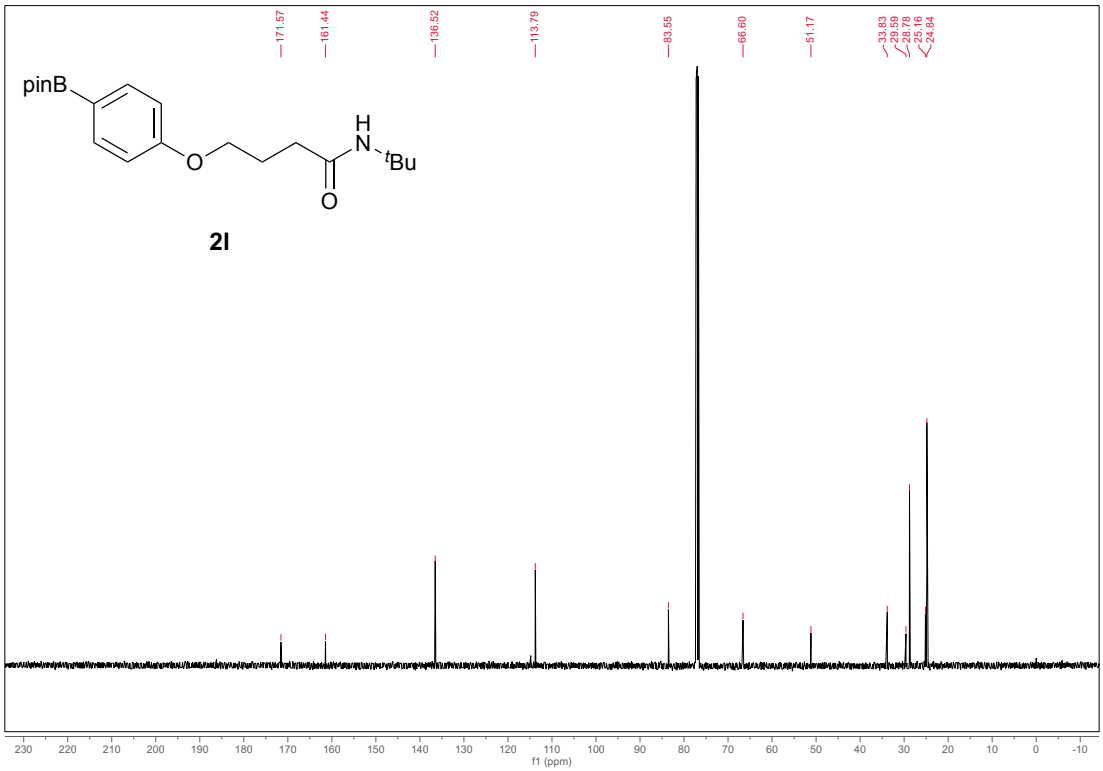
2.01
0.79
2.00
1.99
2.04
21.38
f1 (ppm)


pinB
O
H
N
tBu
O
2l
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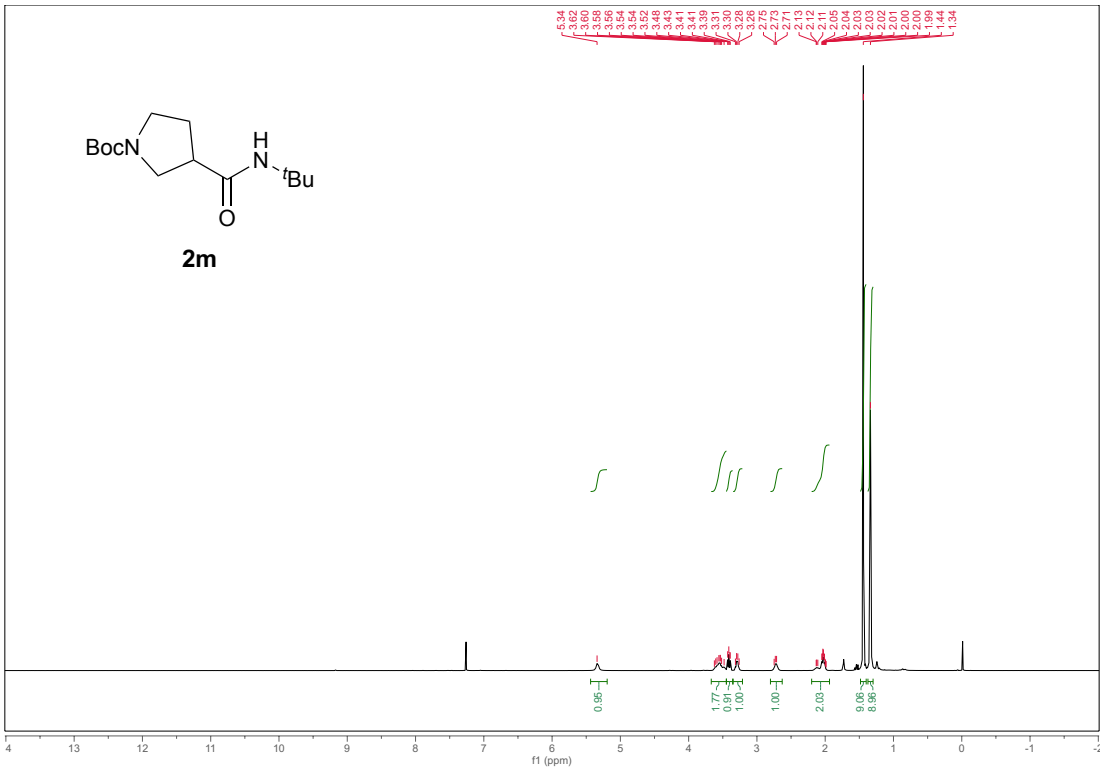
24.84
f1 (ppm)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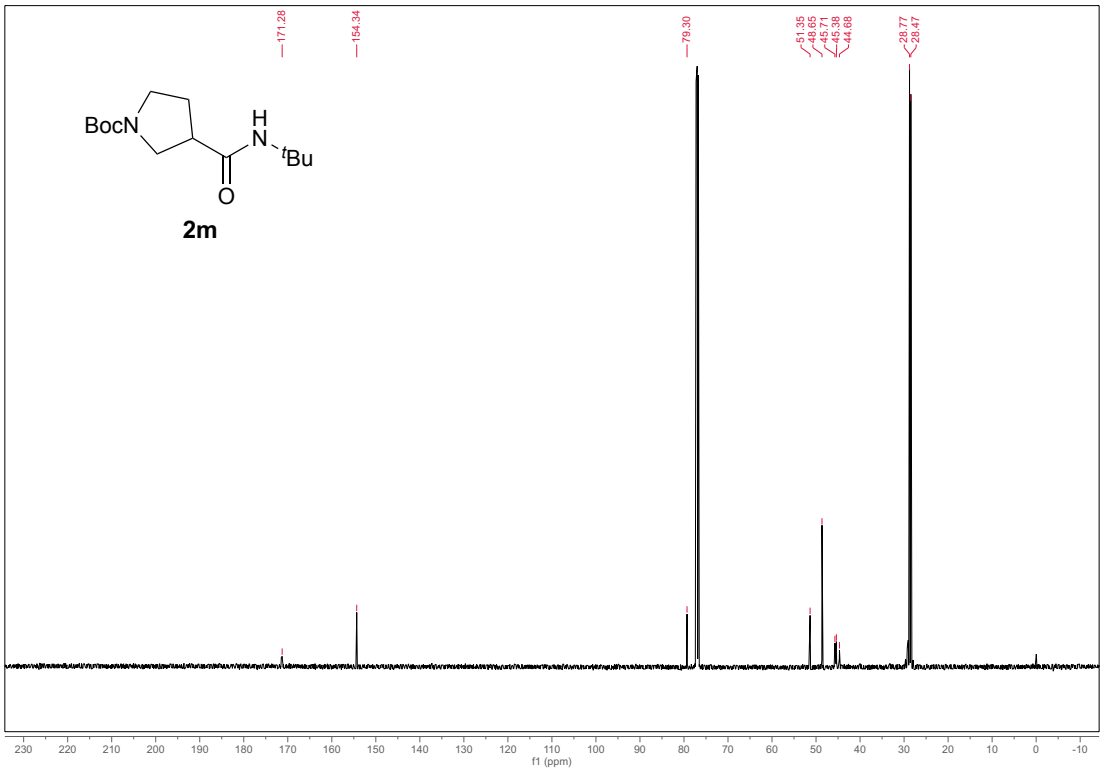
tBu
O
2m
f1 (ppm)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tBu
O
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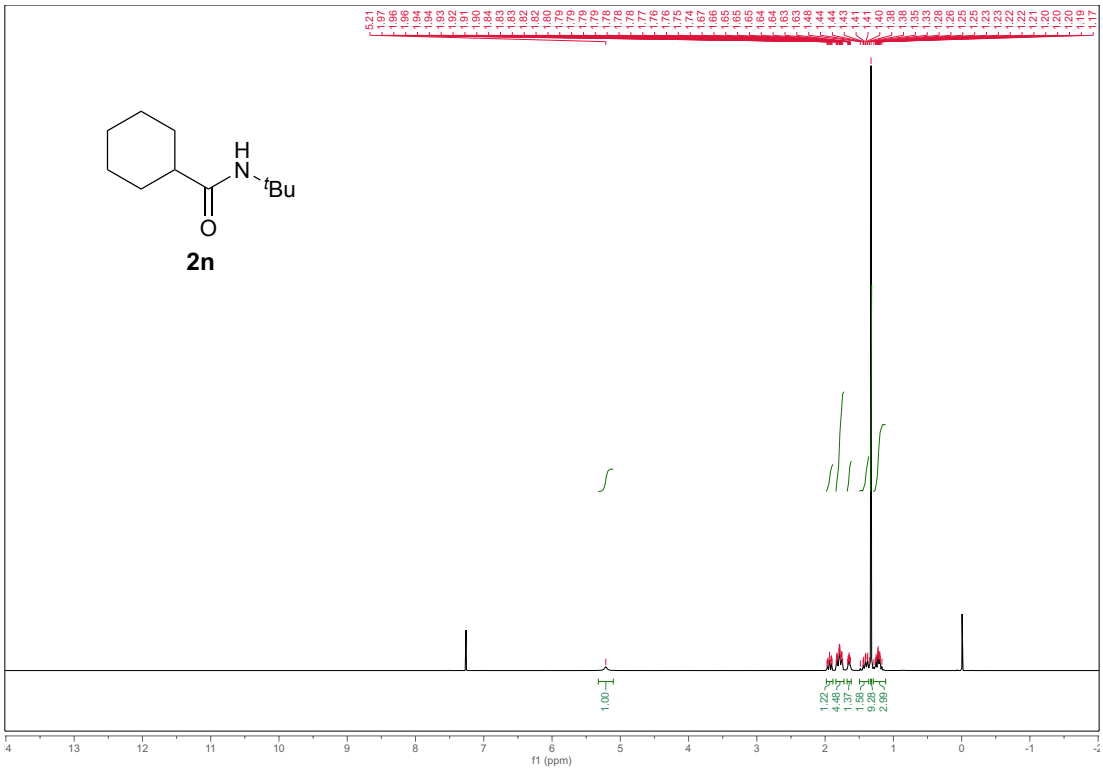
f1 (ppm)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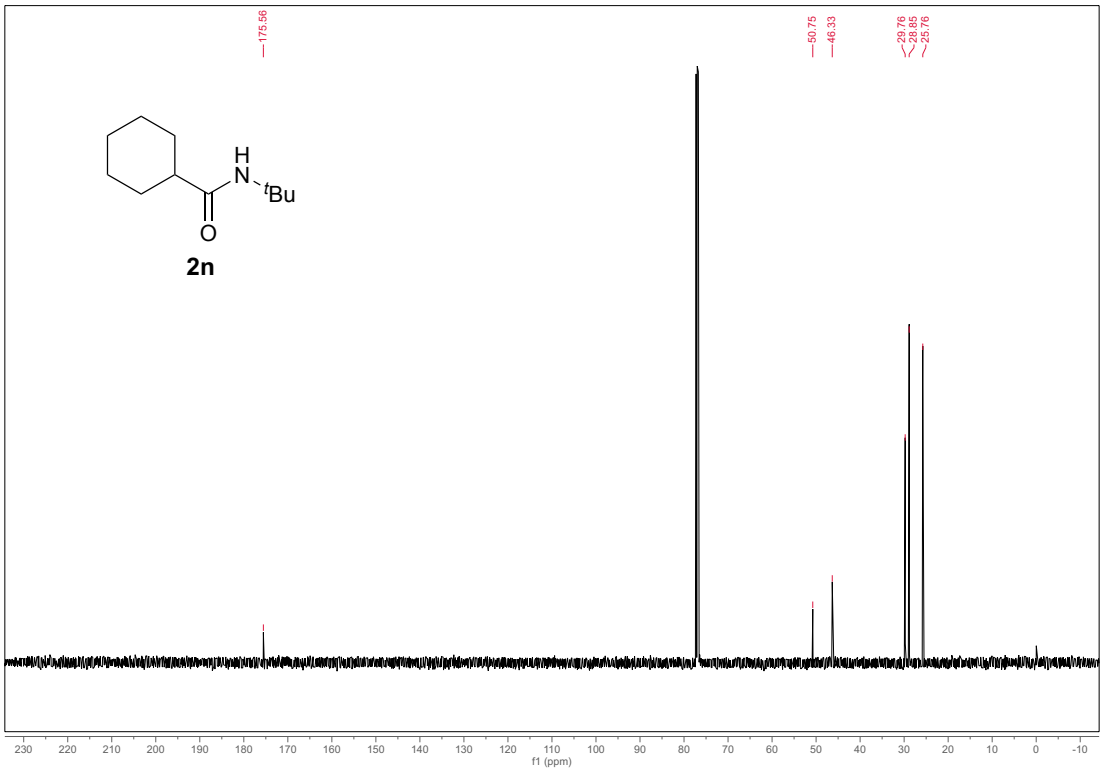
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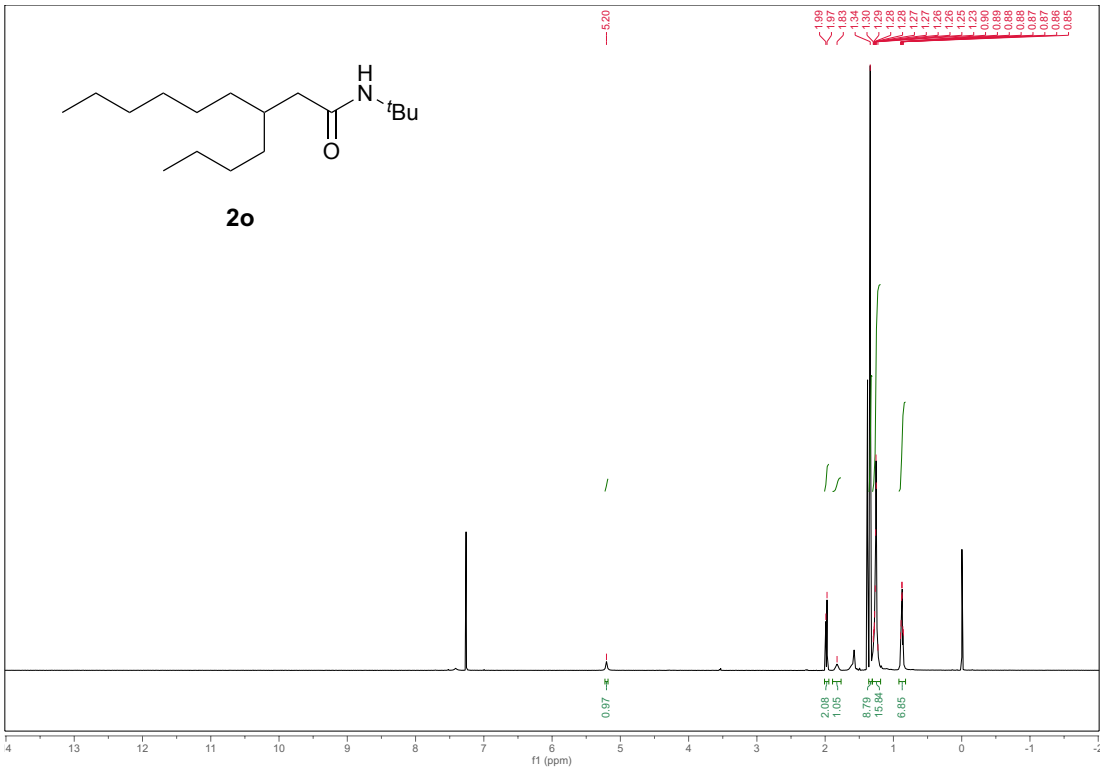
O
2n
f1 (ppm)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1.27
1.27
1.26
1.26
1.25
1.23
0.90
0.89
0.88
0.88
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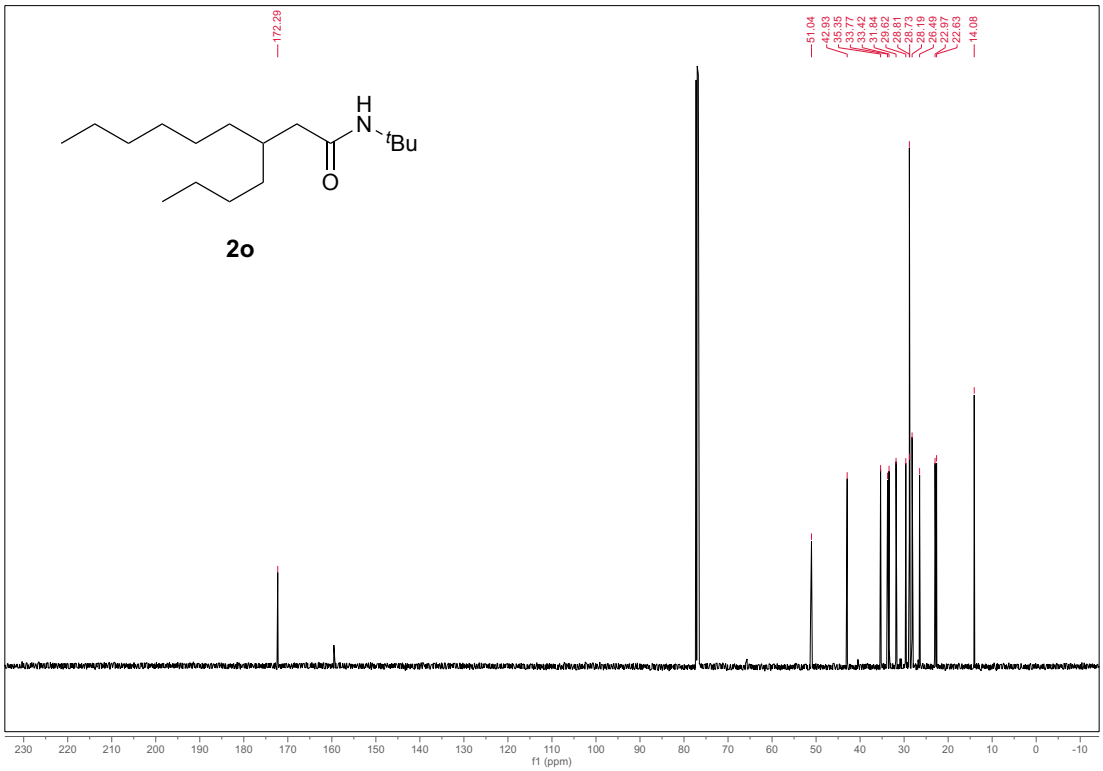
2.08
1.05
8.79
15.84
6.85
f1 (ppm)

2o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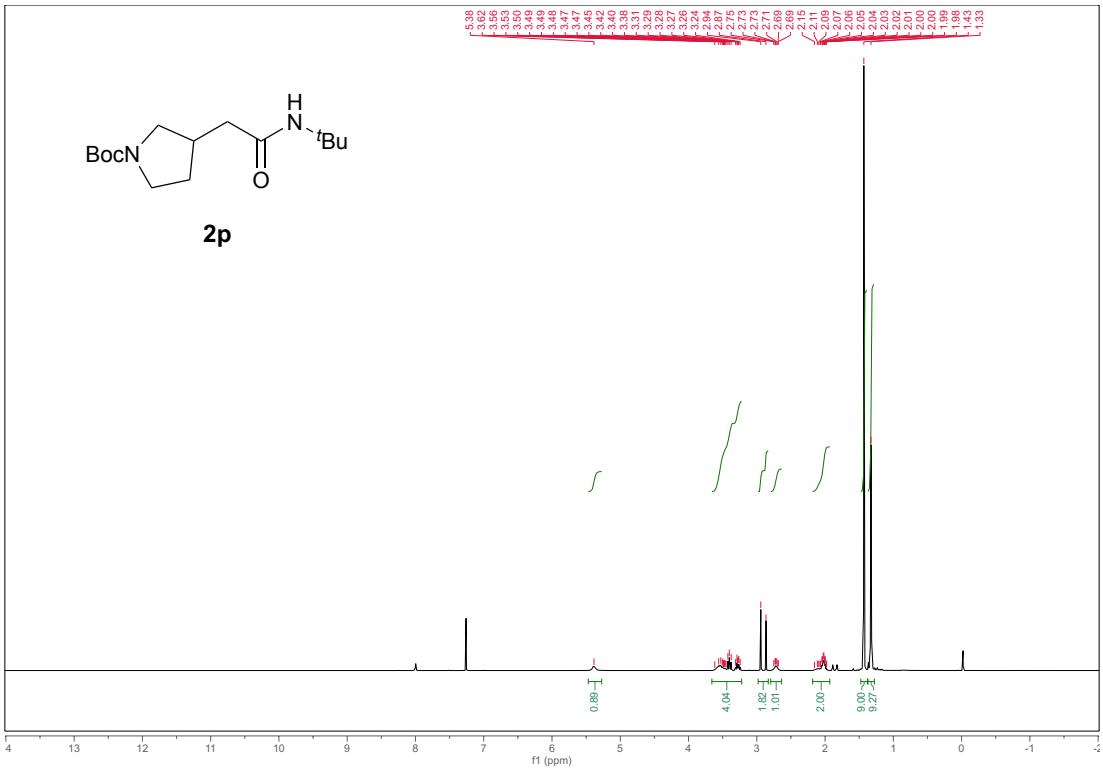
22.63
14.08
f1 (ppm)

2o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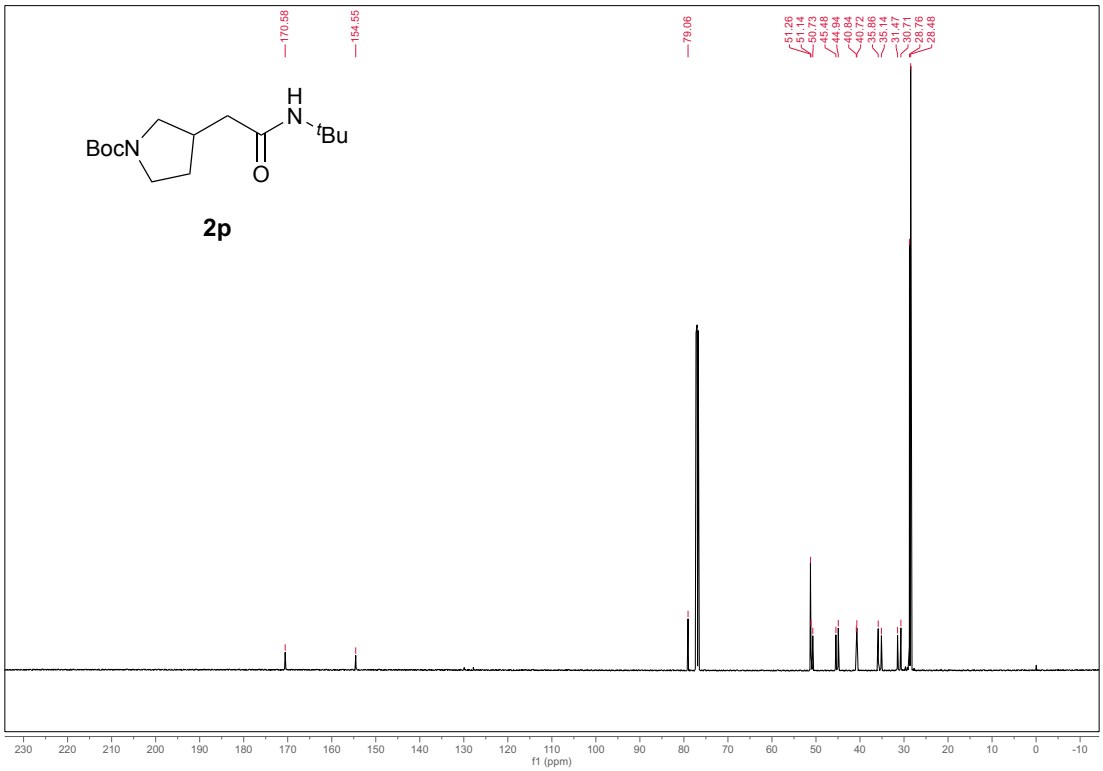
N
tBu
O
2p
f1 (ppm)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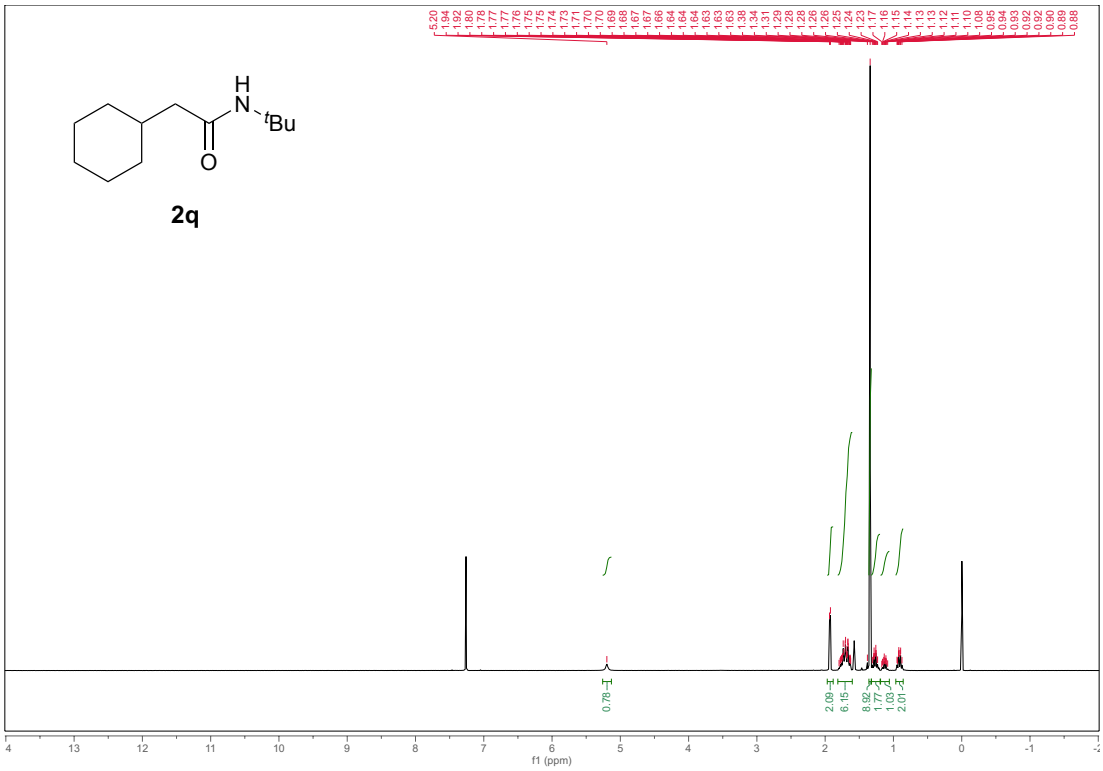
tBu
O
2p
f1 (ppm)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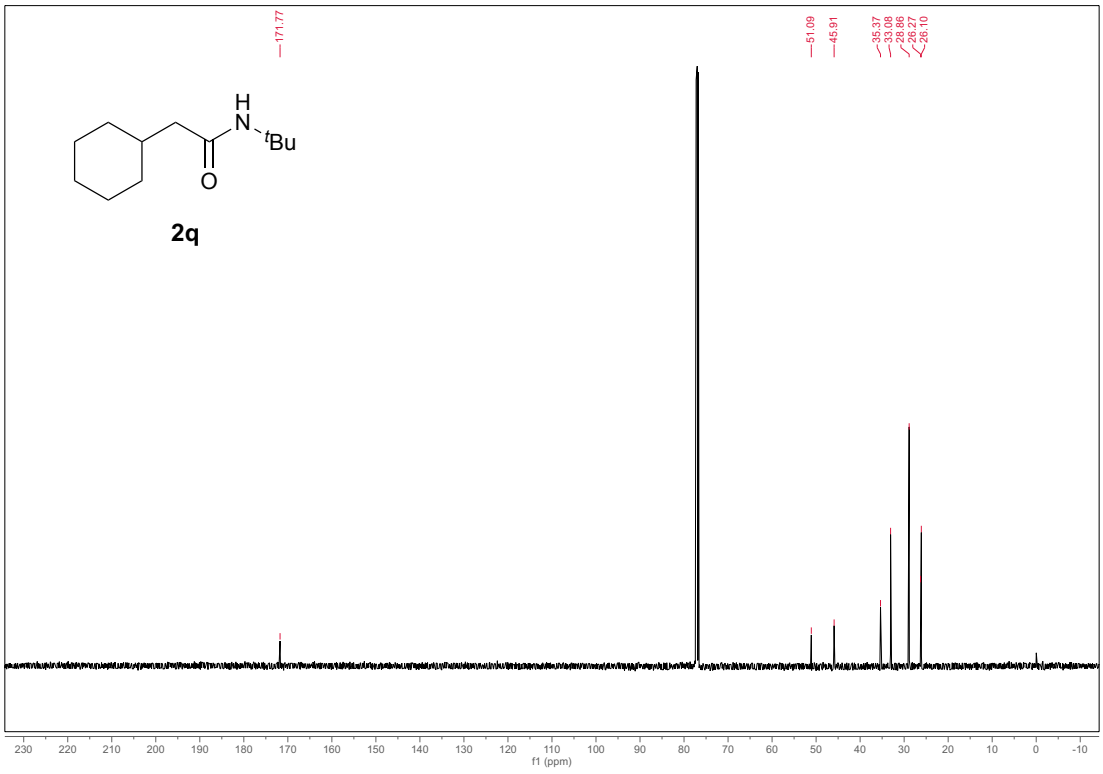
tBu
O
2q
f1 (ppm)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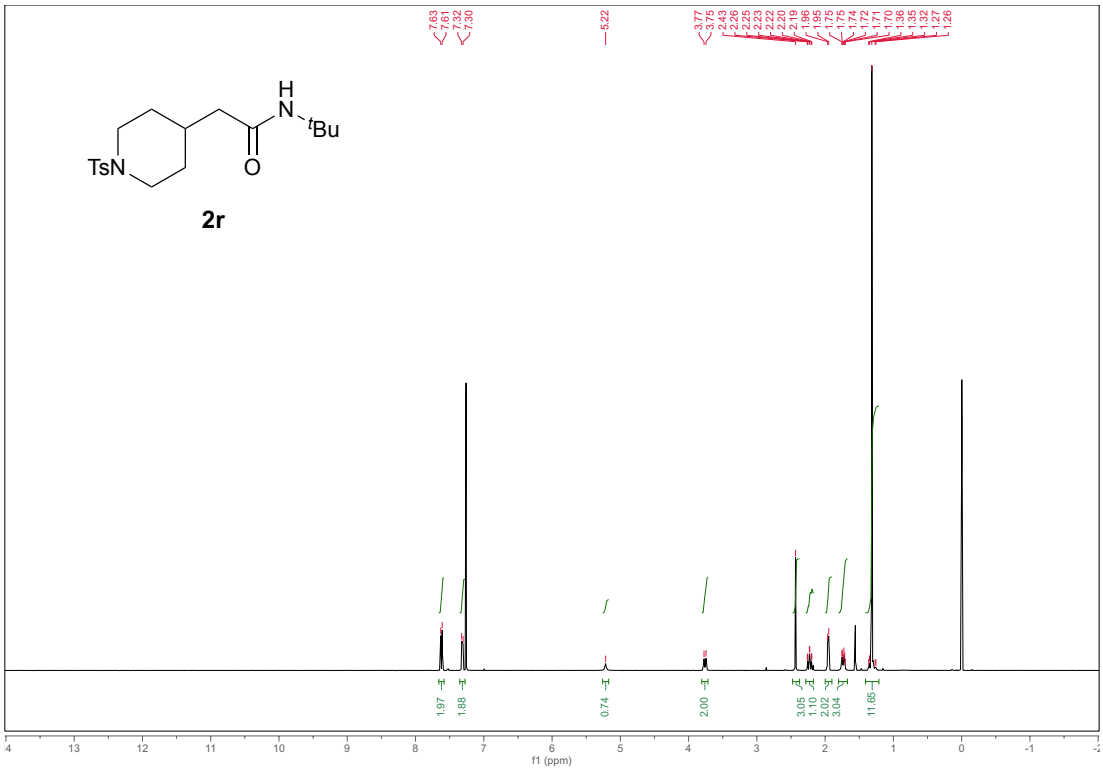
26.10
H
N
tBu
O
2q
f1 (ppm)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2.23
2.22
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1.75
1.74
1.72
1.71
1.70
1.36
1.35
1.32
1.27
1.26
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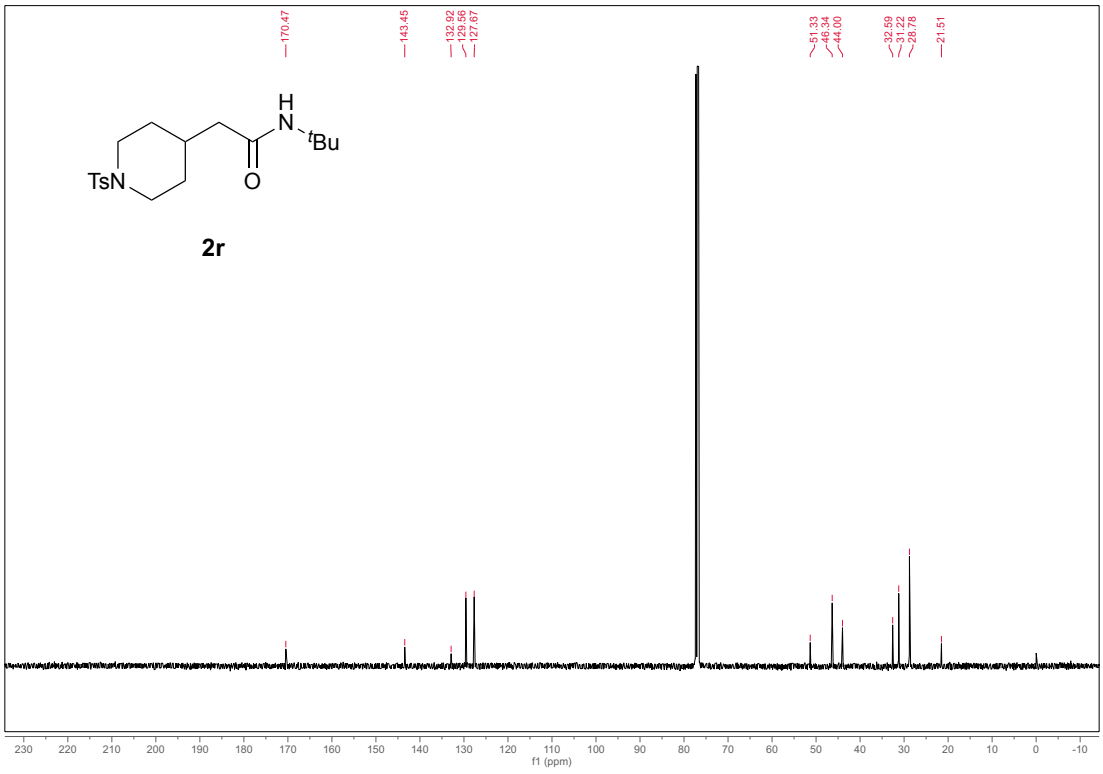
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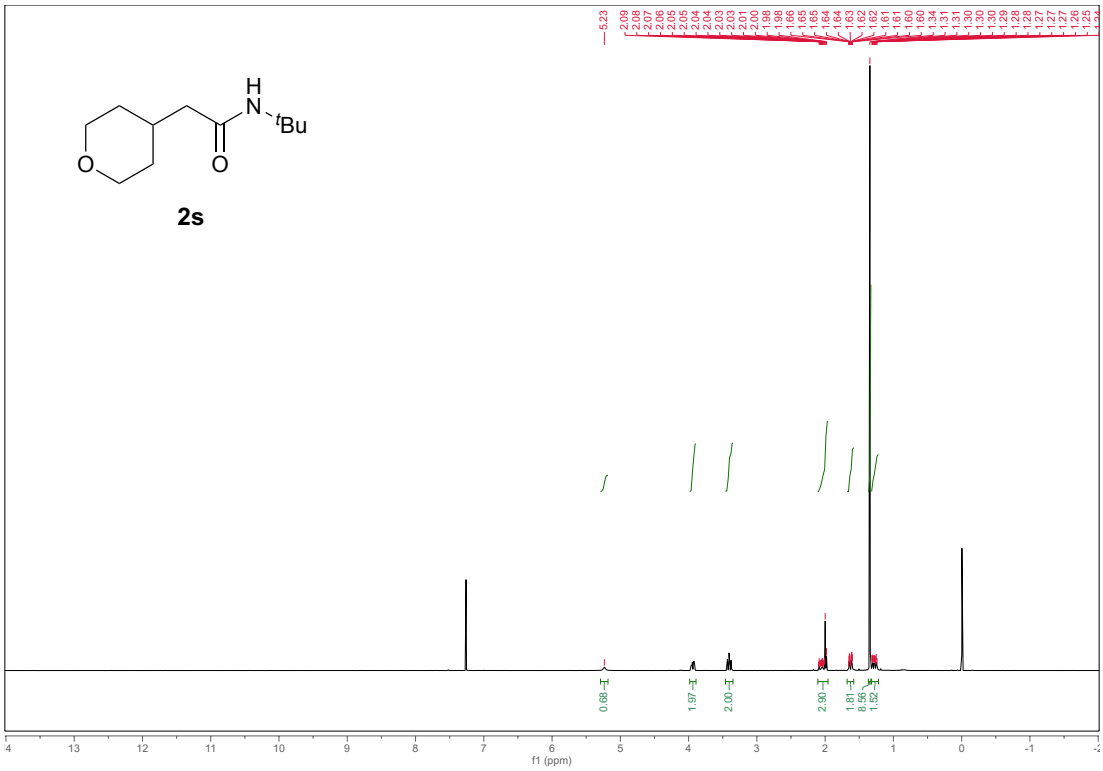
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O
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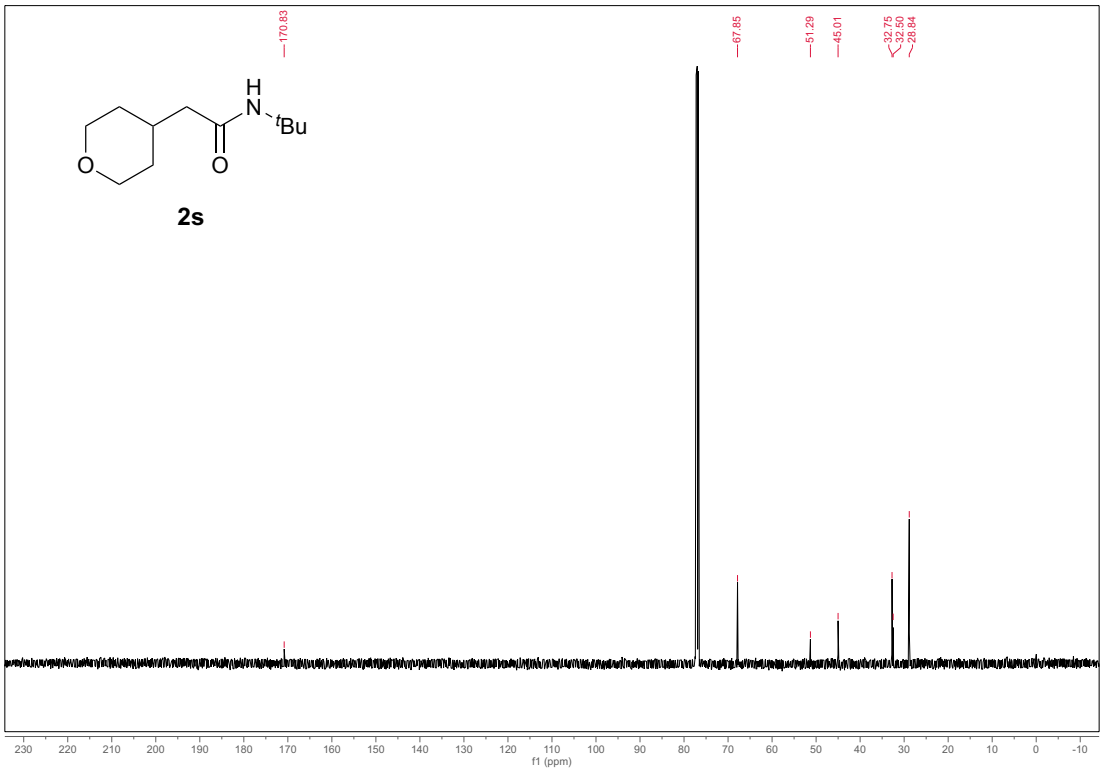
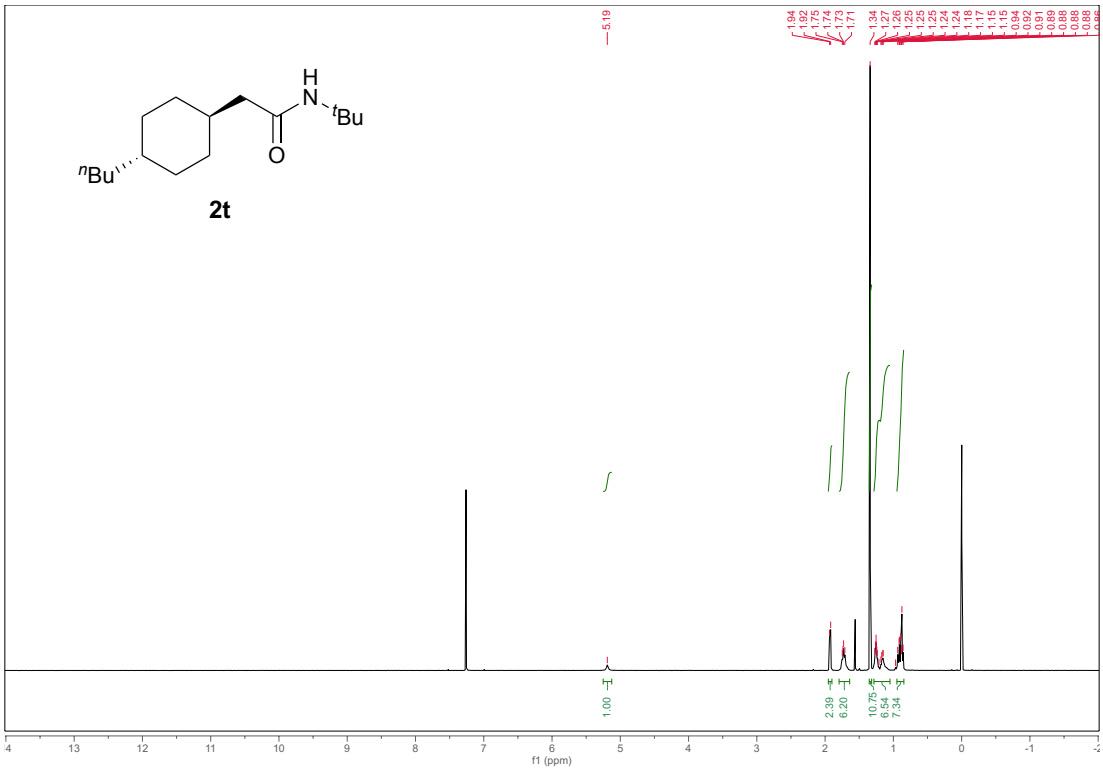
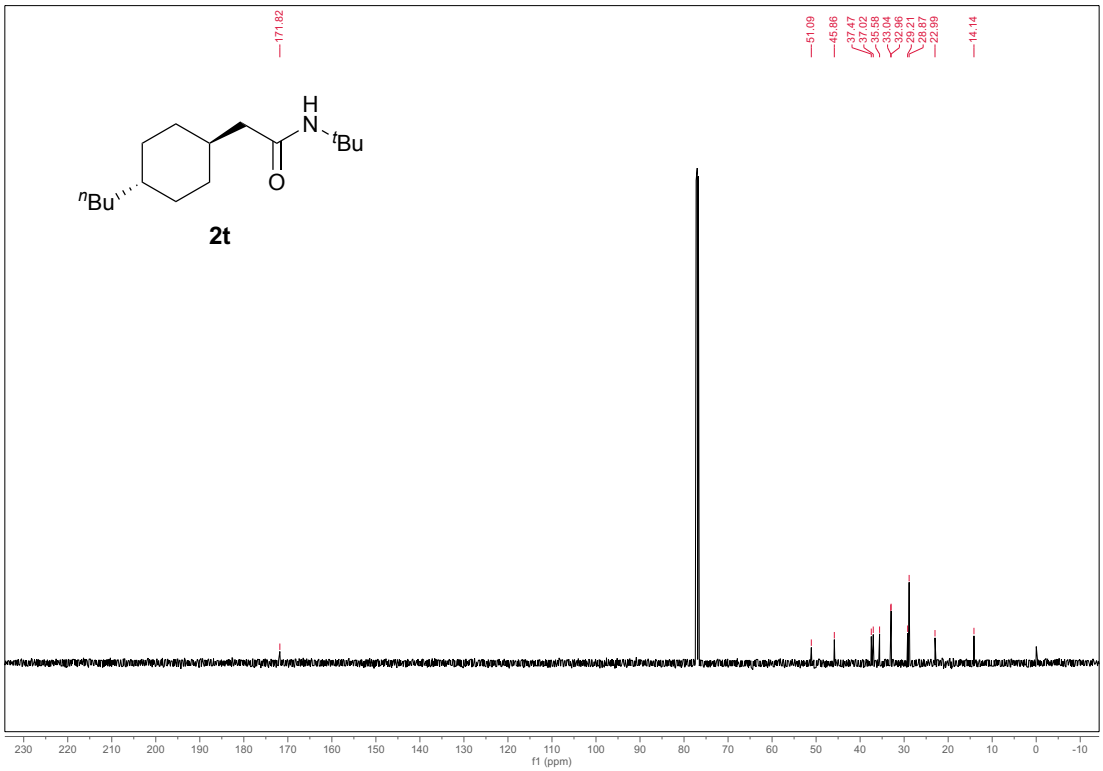
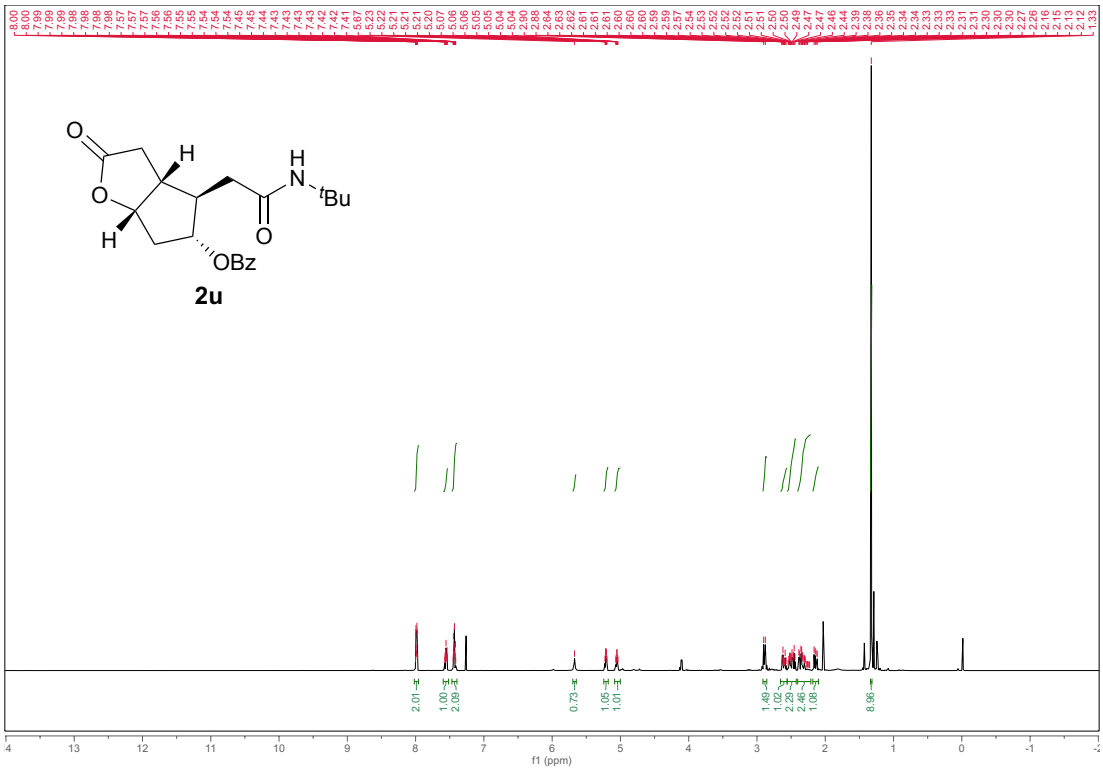
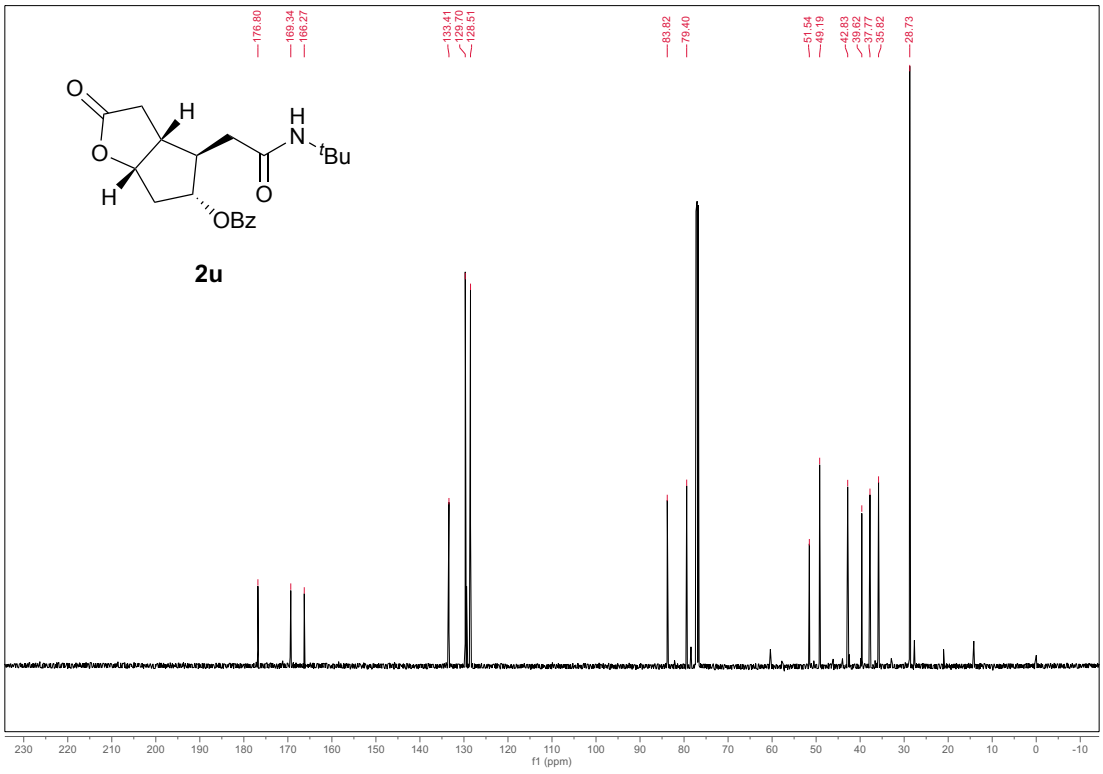
f1 (ppm)

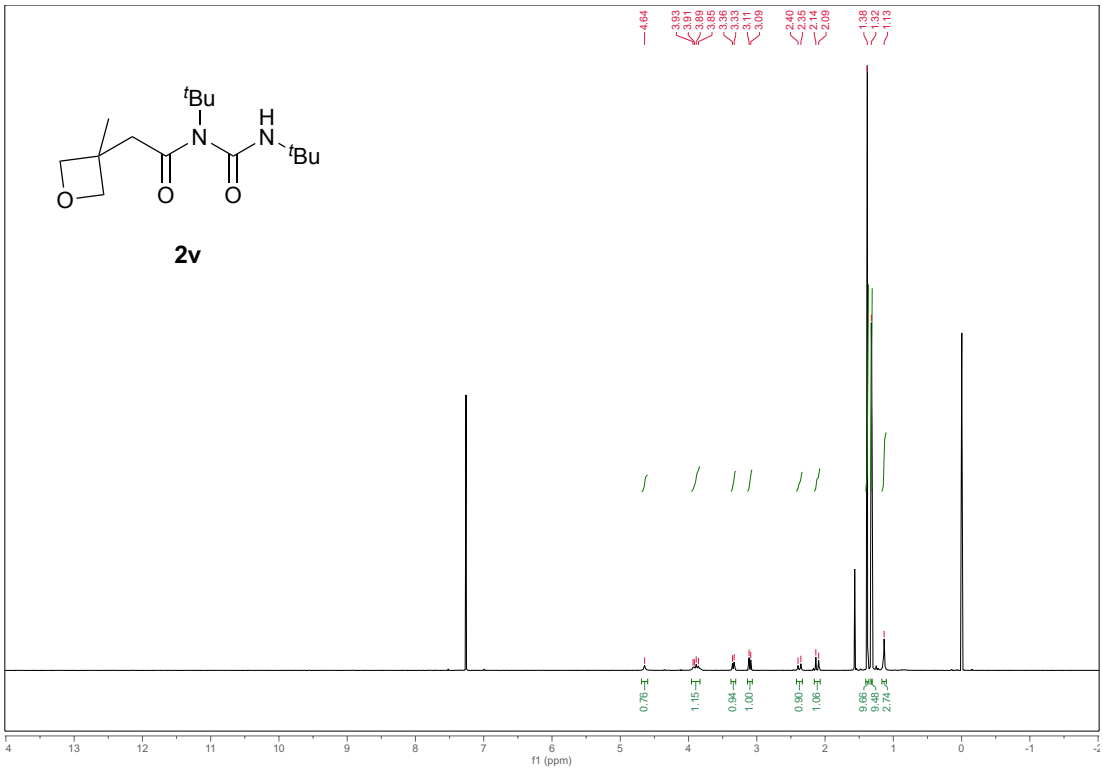

H
N
tBu
O
O
2s
f1 (ppm)


H
N
tBu
O
nBu
2t
5.19
1.94
1.92
1.75
1.74
1.73
1.71
1.34
1.27
1.26
1.25
1.25
1.25
1.24
1.24
1.18
1.17
1.15
1.15
1.00
2.39
6.20
10.75
6.54
7.34
f1 (ppm)

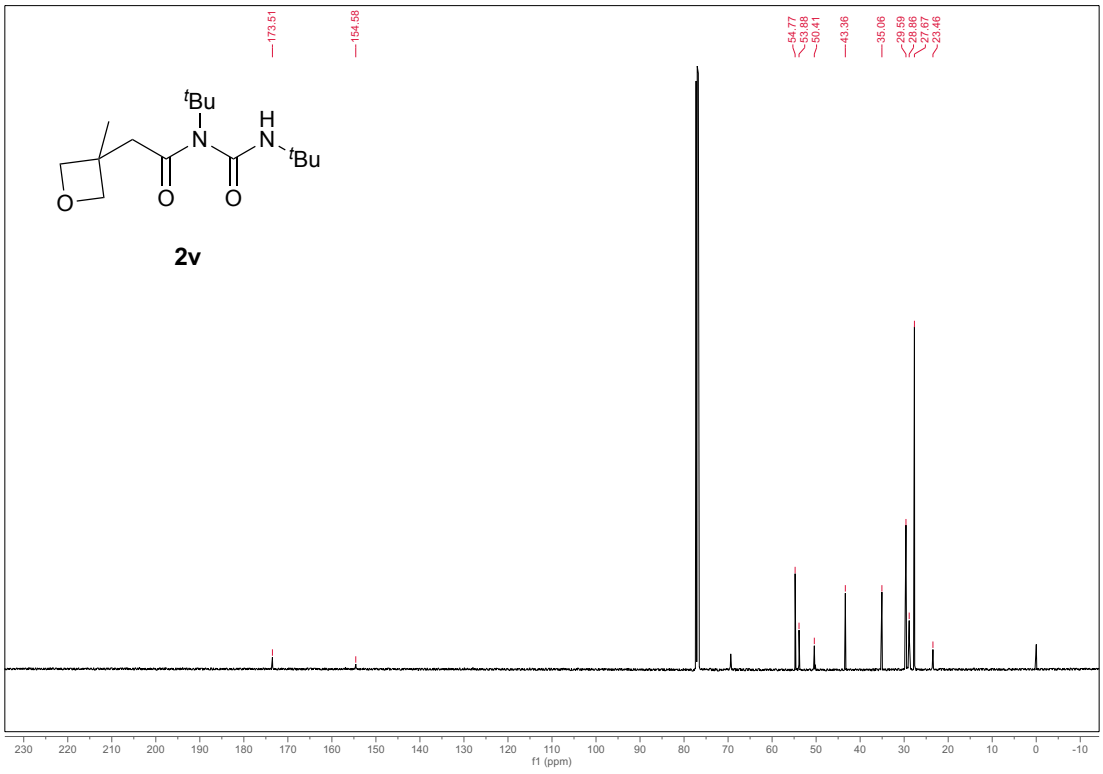

H
N
tBu
O
nBu
2t
171.82
51.09
45.86
37.47
37.02
35.58
33.04
32.96
29.21
26.87
22.99
14.14
f1 (ppm)


O
H
O
H
H
N
tBu
O
OBz
2u
f1 (ppm)

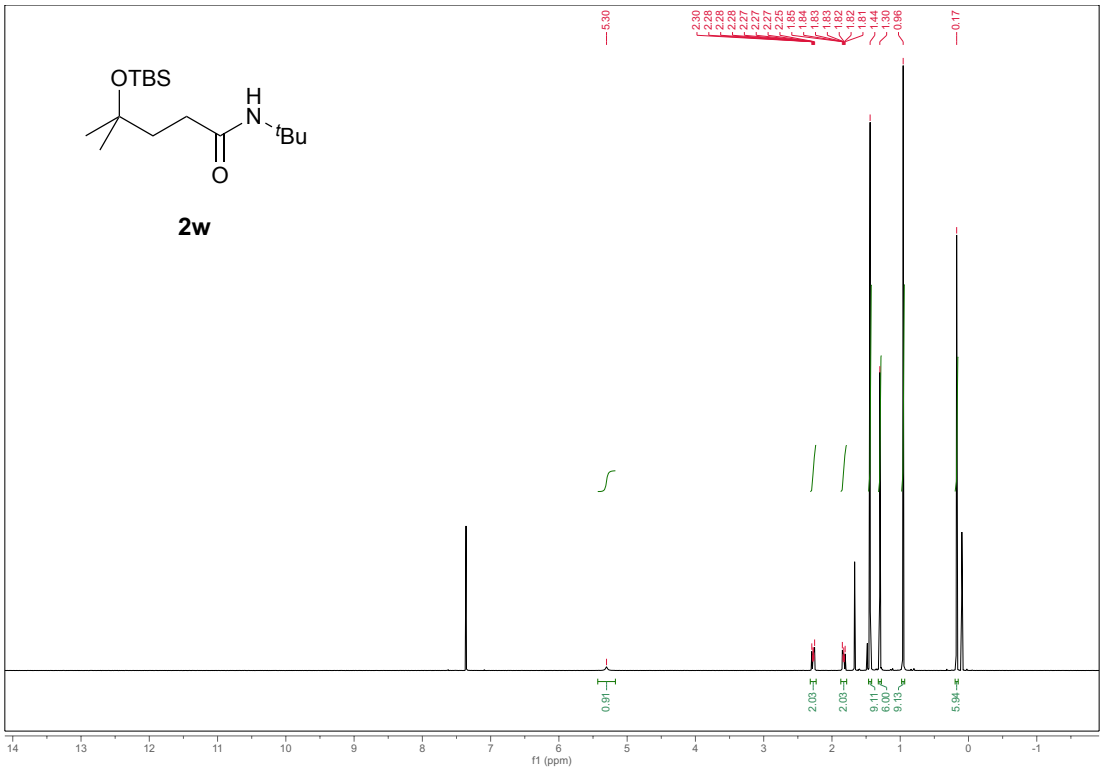

176.80
169.34
166.27
133.41
129.70
128.51
83.82
79.40
51.54
49.19
42.83
39.62
37.77
35.82
28.73
O
H
O
H
H
N
tBu
O
OBz
2u
f1 (ppm)

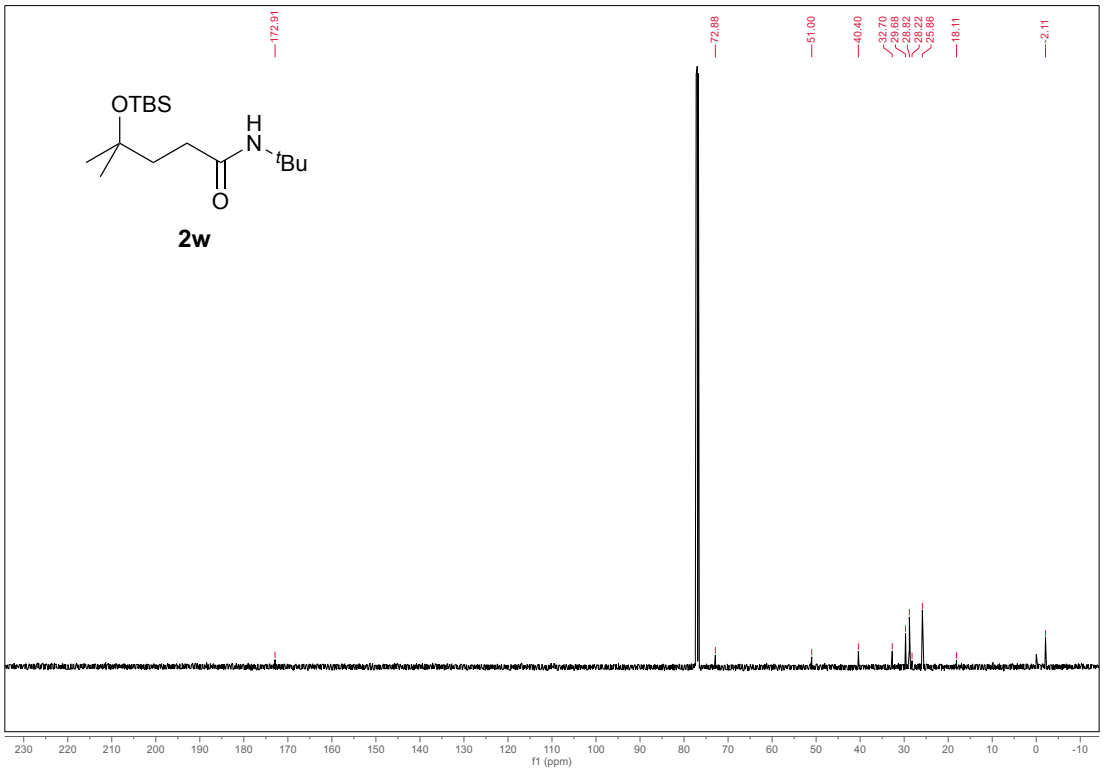

4.64
3.93
3.91
3.89
3.85
3.35
3.33
3.11
3.09
2.40
2.35
2.14
2.09
1.38
1.32
1.13
0.76
1.15
0.94
1.00
0.90
1.06
9.66
9.48
2.74
f1 (ppm)

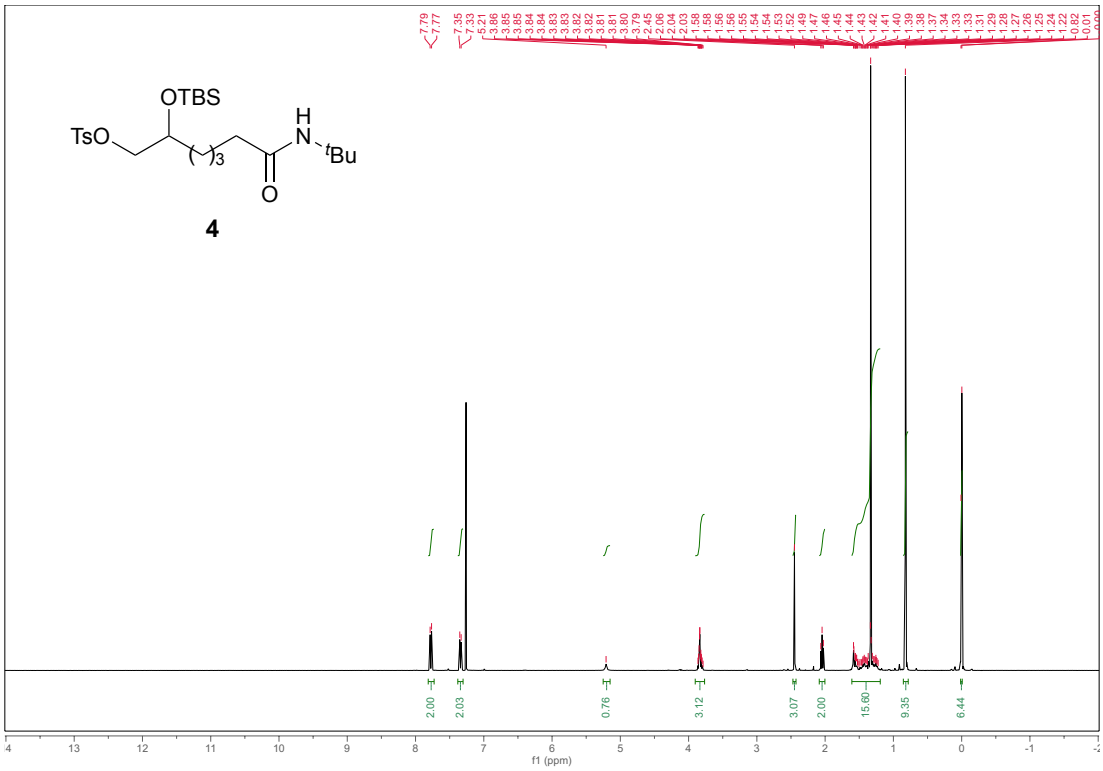
2v

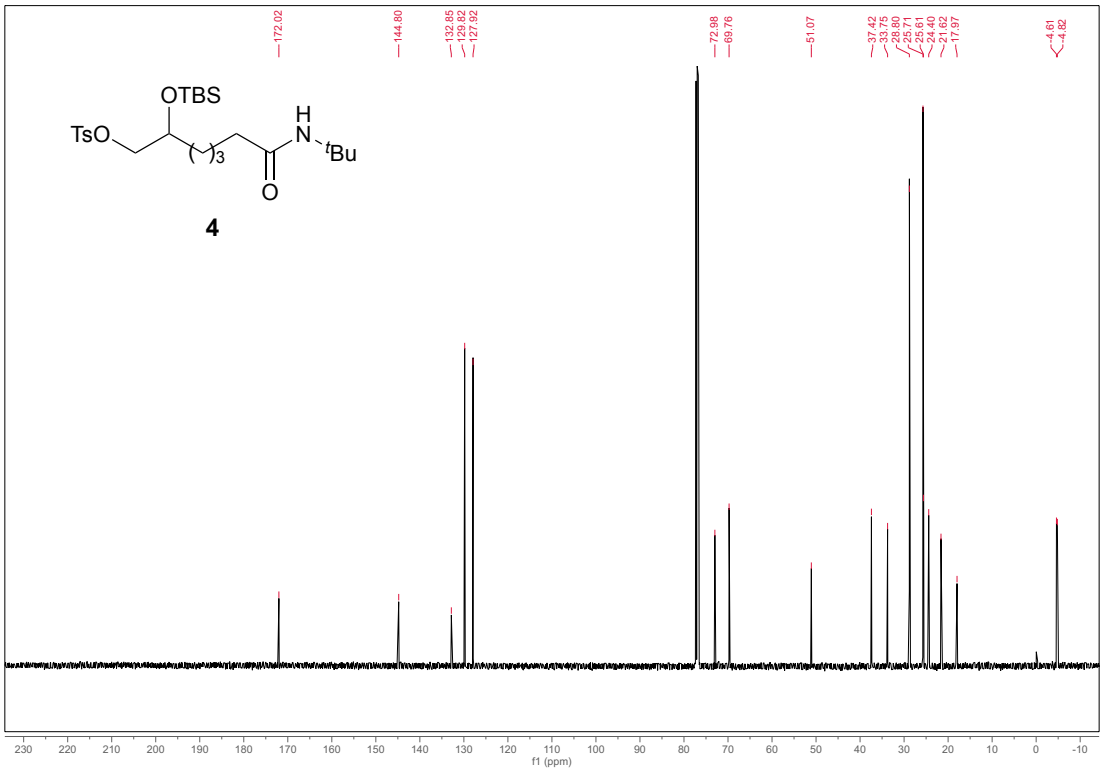

173.51
154.58
54.77
53.88
50.41
43.36
35.06
29.59
28.86
27.67
23.46
f1 (ppm)

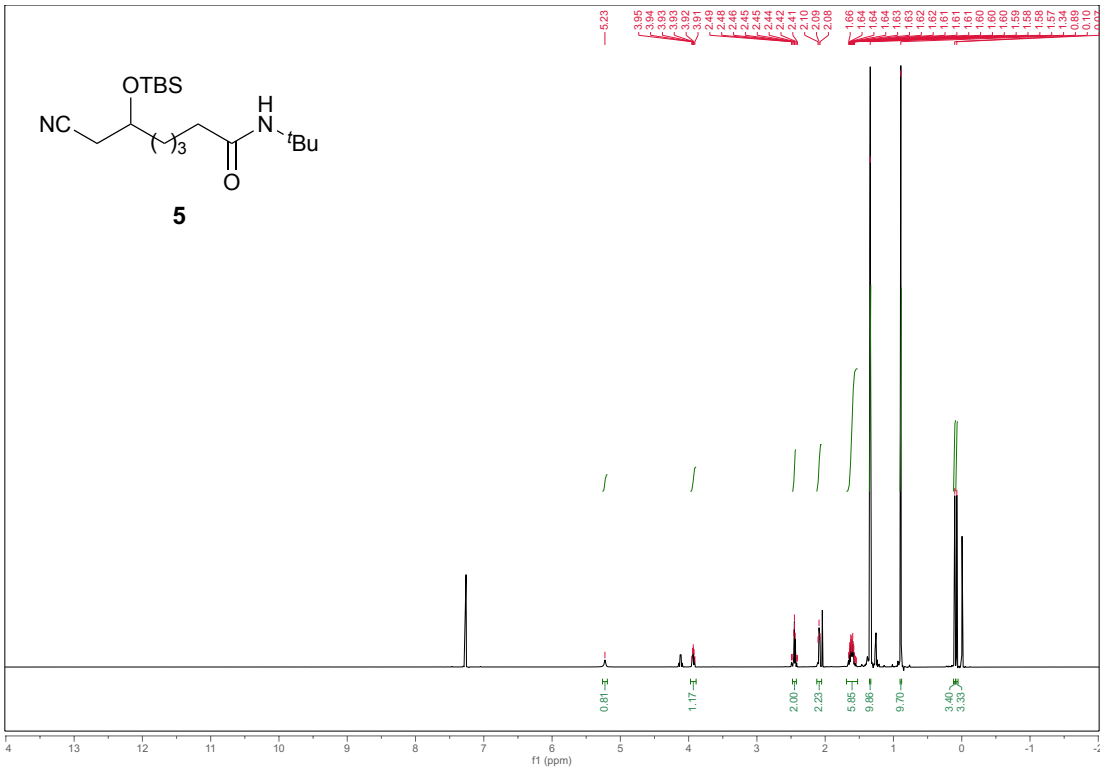
2v

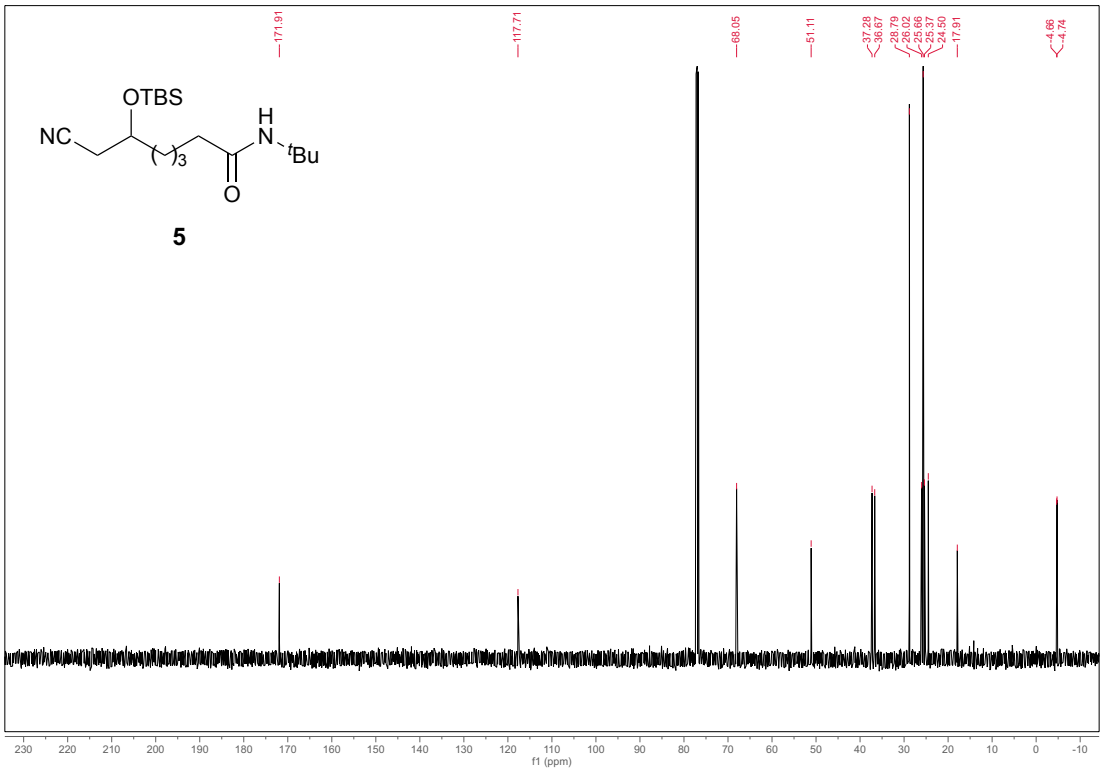

OTBS
H
N
tBu
O
2w
5.30
2.30
2.28
2.28
2.28
2.27
2.27
2.27
2.25
1.85
1.84
1.83
1.82
1.82
1.81
1.44
1.30
0.96
0.17
0.91
2.03
2.03
9.11
6.00
9.13
5.94
f1 (ppm)

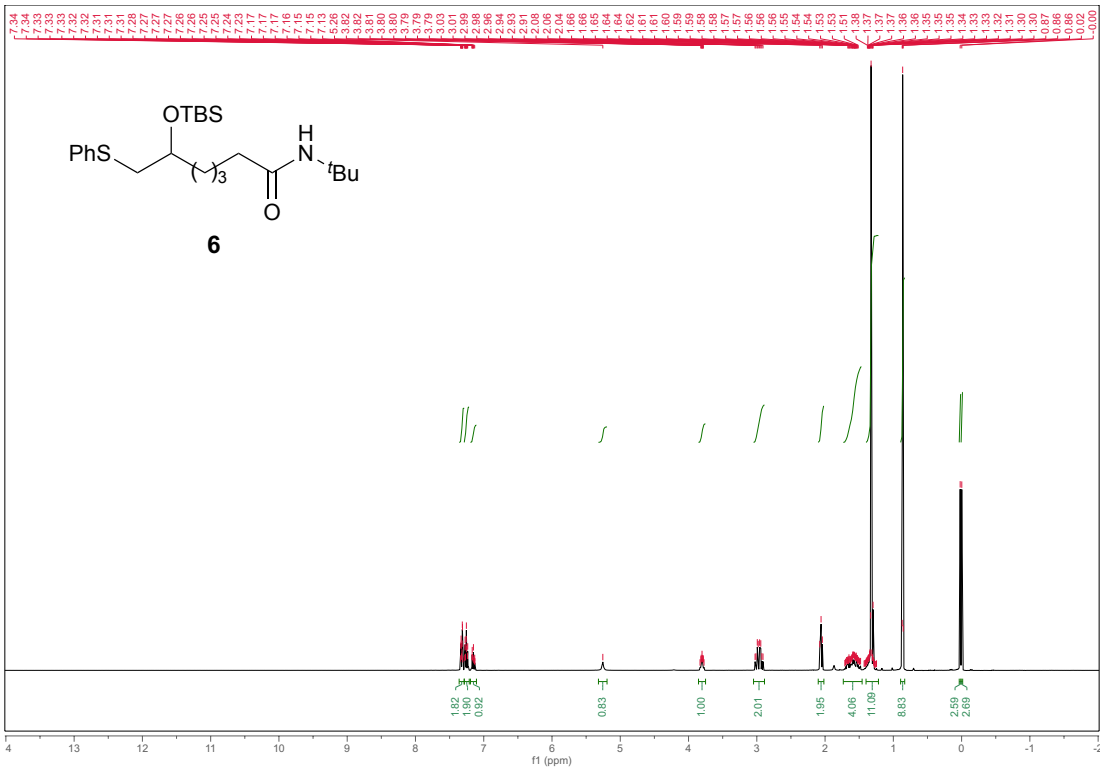

OTBS
H
N
tBu
O
2w
172.91
72.88
51.00
40.40
32.70
29.68
29.32
28.22
25.86
18.11
-2.11
f1 (ppm)

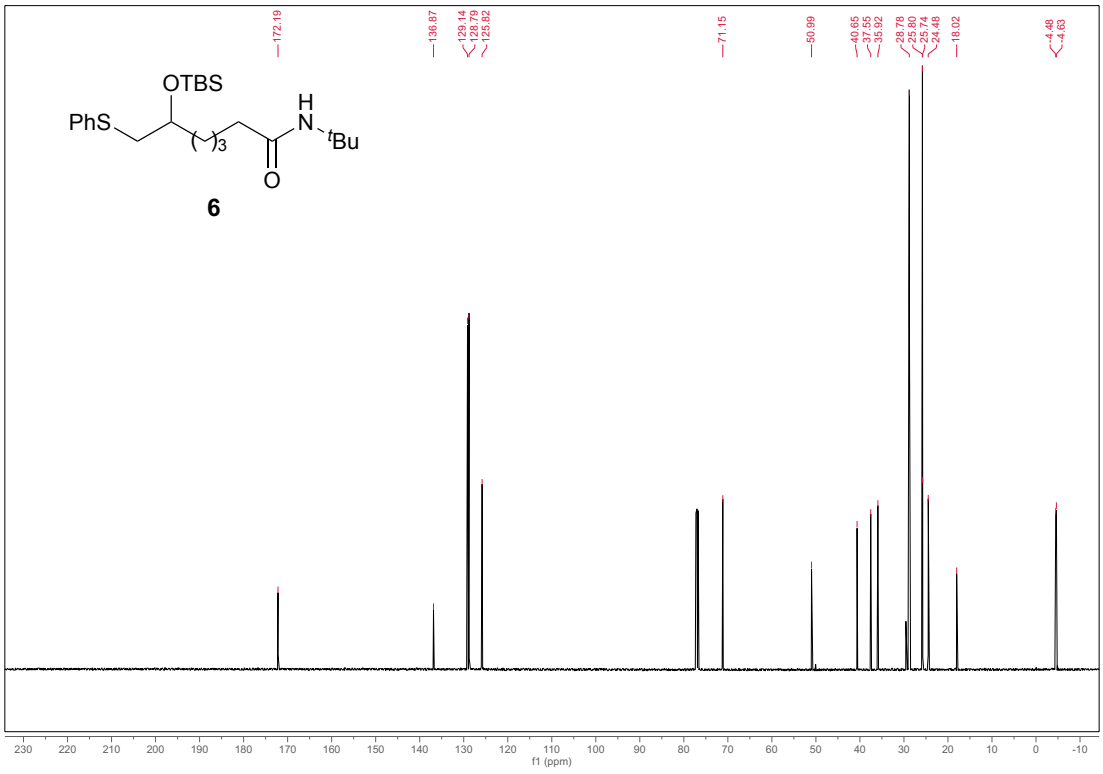

OTBS
TsO
H
N
tBu
O
3
4
f1 (ppm)


OTBS
TsO
H
N
tBu
O
3
4
f1 (ppm)


OTBS
NC
H
N
tBu
O
3
5
f1 (ppm)


OTBS
NC
H
N
tBu
O
3
5
f1 (ppm)


OTBS
PhS
H
N
tBu
O
6
f1 (ppm)


OTBS
PhS
H
N
tBu
O
6
f1 (ppm)

12. References

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