Supplementary Information (SI) for Organic Chemistry Frontiers.

Beyond HAT: Harnessing TBADT for Photocatalyzed Giese-type C(sp^3)-C(sp^3) Bond Formation through Reductive Decarboxylation

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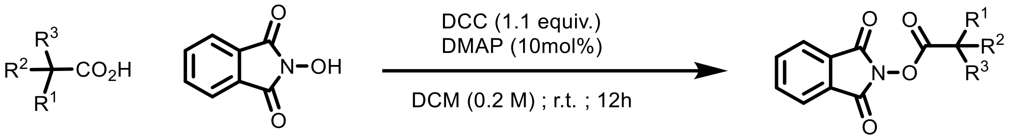
General information

All the solvent and reagents are commercially available and used as received (unless otherwise noted). TBADT was already available in the laboratory and prepared according to a reported procedure.[1] Analytical thin layer chromatography (TLC) plates (silica gel 60 F254) were visualized either with a UV lamp (254 nm), or by submersion in the chosen stain for TLC. Flash column chromatography was carried out by using an automatic LC system. NMR experiments were carried out in the deuterated solvent of choice. Proton ^{1}H NMR spectra were recorded on a Bruker Avance Neo 400 MHz and proton-decoupled carbon ^{13}C{1H} NMR spectra were recorded at 75 MHz. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent as the internal reference. The following abbreviations are used for the multiplicity: s: singlet; d: doublet; t: triplet; q: quadruplet; p: pentuplet; h: heptaplet; m: multiplet or overlap of non-equivalent resonances; br s: broad singlet. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra were determined on an AEI MS-9 using electrospray ionization (ESI) and a time-of-flight (TOF). Photochemical reactions have been carried out in a homemade photobox, equipped with a 3D-printed vial holder, a 370 nm Kessil lamp as the light source and a fan as the cooling system and placed on a stirrer plate. (for more details see Figures S1, S2).

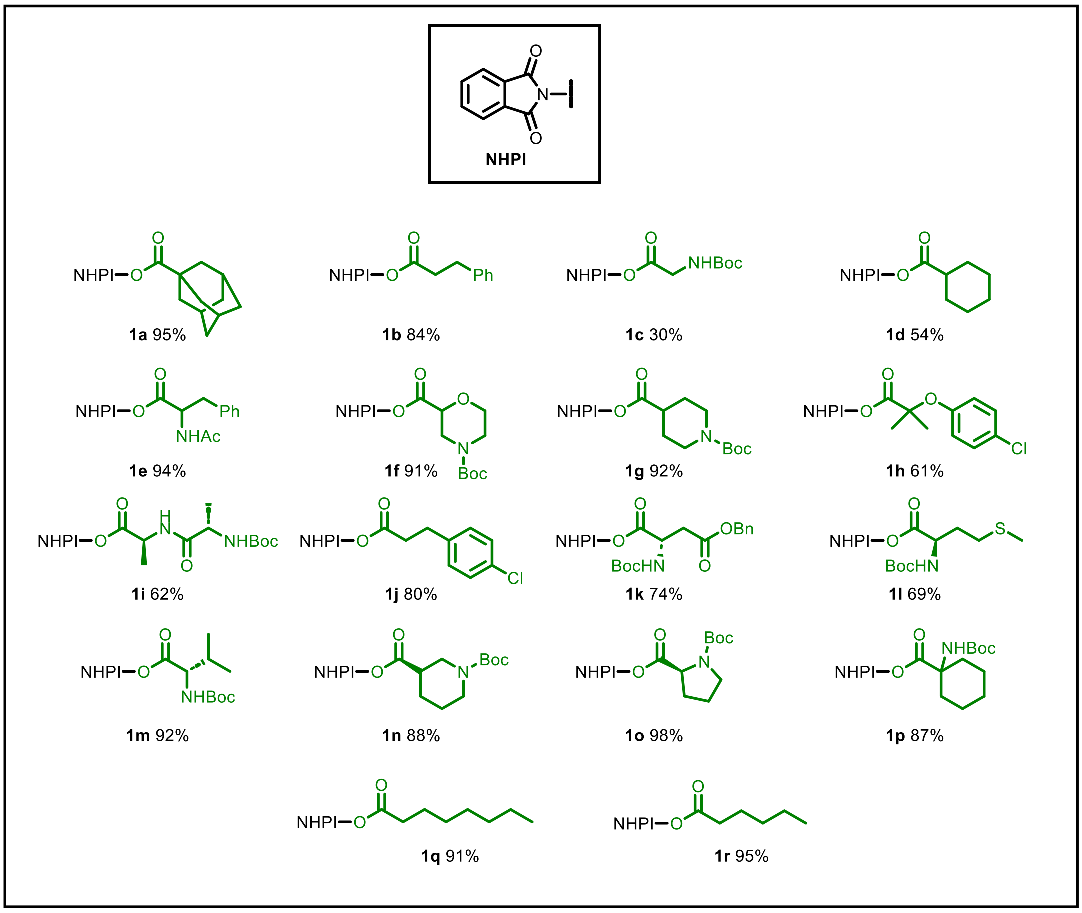
Preparation of Substrates

General procedure for the preparation of NHPI Redox Active Esters (RAEs)

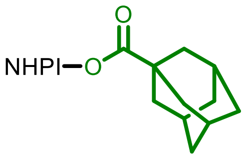


In a round bottomed flask, equipped with a magnetic stirrer were placed: carboxylic acid (1.0 equiv.), 4-dimethylaminopyridine (0.1 equiv.), *N*-hydroxyphthalimide (1.0 equiv.) and *N,N'*-dicyclohexylcarbodiimide (1.1 equiv.) in CH_2Cl_2 (0.2 M). Then, the reaction mixture was stirred overnight at room temperature. Upon completion, the crude mixture was filtered and the filtrate washed with DCM. The solvent was then removed under reduced pressure. Purification via silica gel column chromatography afforded the desired product. (Eluent C.Hex/EtOAc or DCM/MeOH).

The following NHPI Redox Active Esters (**1a-1p**) were prepared according to the general procedure and NMR spectra agree with the previously reported data.[2-12]



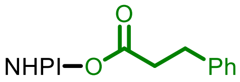
Scheme S1. Preparation of Redox Active Esters (RAEs).



1,3-Dioxoisoindolin-2-yl-adamantane-1-carboxylate (1a)[2]

Eluent: C.Hex/EtOAc (9:1); White solid (95%). Mp: 144 °C. The data are in accordance with previously reported data.[2]

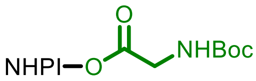
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (dd, *J* = 4.8, 3.1 Hz, 2H), 7.81 (dd, *J* = 4.9, 3.1 Hz, 2H), 2.18–2.10 (m, 6H), 2.09–2.06 (m, 3H), 1.79–1.72 (m, 6H).



1,3-Dioxoisoindolin-2-yl 3-phenylpropanoate (1b)[3]

Eluent: C.Hex/EtOAc (9:1); White solid (84%). Mp: 83 °C. The data are in accordance with previously reported data.[3]

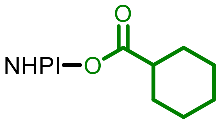
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.40–7.33 (m, 2H), 7.32–7.29 (m, 2H), 7.29–7.27 (m, 1H), 3.18–3.10 (m, 2H), 3.05–2.97 (m, 2H).



1,3-Dioxoisoindolin-2-yl (tert-butoxycarbonyl)glycinate (1c)[4]

Eluent: C.Hex/EtOAc (8:2); White solid (30%). Mp: 188-189 °C. The data are in accordance with previously reported data.[4]

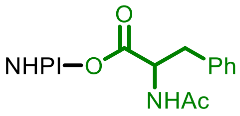
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92–7.85 (m, 2H), 7.84–7.77 (m, 2H), 5.21–4.77 (m, 1H), 4.44–4.18 (m, 2H), 1.56–1.50 (m, 9H).



1,3-Dioxoisoindolin-2-yl cyclohexanecarboxylate (1d)[4]

Eluent: C.Hex/EtOAc (9:1); White solid (54%). Mp: 67-68 °C. The data are in accordance with previously reported data.[4]

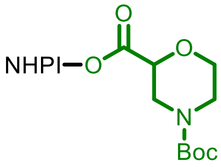
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90–7.87 (m, 2H), 7.83–7.73 (m, 2H), 2.73 (tt, *J* = 10.9, 3.5 Hz, 1H), 2.15–2.06 (m, 2H), 1.84–1.81 (m, 2H), 1.72–1.63 (m, 3H), 1.45–1.30 (m, 3H).



1,3-Dioxoisoindolin-2-yl 2-acetamido-3-phenylpropionate (1e)[5]

Eluent: C.Hex/EtOAc (8:2); White solid (94%). Mp: 172-173 °C. The data are in accordance with previously reported data.[5]

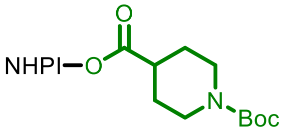
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.87 (m, 2H), 7.84–7.78 (m, 2H), 7.40–7.29 (m, 5H), 5.83 (d, *J* = 7.8 Hz, 1H), 5.37 (m, 1H), 3.33 (qd, *J* = 14.0, 5.6 Hz, 2H), 2.01 (s, 3H)



4-tert-Butyl 2-(1,3-dioxoisoindolin-2-yl) morpholine-2,4-dicarboxylate (1f)[6]

Eluent: C.Hex/EtOAc (8:2); White solid (91%). Mp: 112 °C. The data are in accordance with previously reported data.[6]

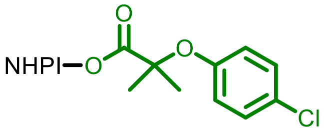
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.85 (m, 2H), 7.83–7.76 (m, 2H), 4.55 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.36–4.01 (m, 2H), 3.80–3.61 (m, 2H), 3.57–3.36 (m, 1H), 3.28–3.20 (m, 1H), 1.48 (s, 9H).



1-tert-Butyl 4-(1,3-dioxoisoindolin-2-yl) piperidine-1,4-dicarboxylate (1g)[6]

Eluent: C.Hex/EtOAc (8:2); White solid (92%). Mp: 112 °C. The data are in accordance with previously reported data.[6]

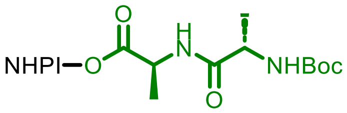
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 2H), 7.82–7.75 (m, 2H), 4.04 (dt, *J* = 13.6, 3.9 Hz, 2H), 3.0 (ddd, *J* = 13.6, 10.6, 3.0 Hz, 2H), 2.89 (tt, *J* = 10.2, 4.0 Hz, 1H), 2.10–2.06 (m, 2H), 1.87–1.82 (m, 2H), 1.47 (s, 9H).



1,3-Dioxoisoindolin-2-yl 2-(4-chlorophenoxy)-2-methylpropanoate (1h)[7]

Eluent: C.Hex/EtOAc (8:2); White solid (61%). Mp: 103 °C. The data are in accordance with previously reported data.[7]

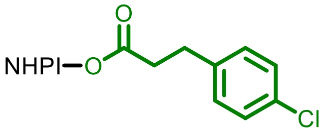
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.86 (m, 2H), 7.83–7.78 (m, 2H), 7.32–7.30 (m, 2H), 7.06–7.04 (m, 2H), 1.77 (s, 6H).



1,3-Dioxoisoindolin-2-yl (tert-butoxycarbonyl)-L-alanyl-L-alaninate (1i)

Eluent: DCM/MeOH 95/5 White solid (60 %). Mp: 84°C.

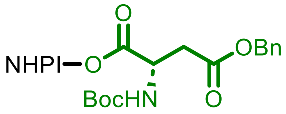
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 3.13 Hz, 2H), 7.77 (dd, *J* = 5.55, 3.09 Hz, 2H), 7.05–7.00 (m, 1H), 5.19 (dd, *J* = 29.16, 7.28 Hz, 1H), 4.99 (p, *J* = 7.32 Hz, 1H), 4.30 (d, *J* = 44.21 Hz, 1H), 1.63 (dd, *J* = 7.25, 4.32 Hz, 3H), 1.41 (s, 9H), 1.37 (d, *J* = 7.05 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.7, 169.4, 161.6, 155.8, 135.0, 128.9, 124.1, 80.3, 49.3, 46.5, 28.4, 25.0, 18.2. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{19}H_{23}N_3O_7Na^+$ 428.1428; Found 428.1436.



1,3-Dioxoisoindolin-2-yl 3-(4-chlorophenyl)propanoate (1j)[3]

Eluent: C.Hex/EtOAc (9:1); White solid (80%). Mp: 121-123 °C. The data are in accordance with previously reported data.[3]

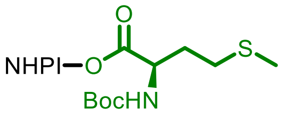
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.87 (m, 2H), 7.83–7.79 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H).



4-Benzyl 1-(1,3-dioxoisoindolin-2-yl) (tert-butoxycarbonyl)aspartate (1k)[4]

Eluent: DCM/MeOH (95:5); Yellowish gel (74%). The data are in accordance with previously reported data.[4]

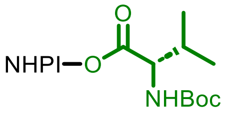
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.82 (m, 2H), 7.83–7.77 (m, 2H), 7.47–7.30 (m, 5H), 5.63–5.30 (m, 1H), 5.30–5.21 (m, 2H), 5.15–4.32 (m, 1H), 3.25–3.01 (m, 2H), 1.47 (s, 9H).



1,3-Dioxoisoindolin-2-yl-(tert-butoxycarbonyl)methioninate (1l)[8]

Eluent: DCM/MeOH (95:5); Yellowish gel (69%). Mp: 92-94 °C. The data are in accordance with previously reported data.[8]

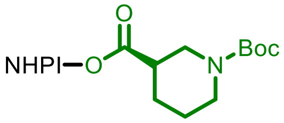
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93–7.86 (m, 2H), 7.85–7.80 (m, 2H), 5.41–4.72 (m, 2H), 2.80–2.63 (m, 2H), 2.38–2.05 (m, 5H), 1.50 (s, 9H).



1,3-Dioxoisoindolin-2-yl (tert-butoxycarbonyl)valinate (1m)[4]

Eluent: C.Hex/EtOAc (8:2); White solid (92%). Mp: 82 °C. The data are in accordance with previously reported data.[4]

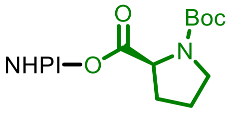
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96–7.88 (m, 2H), 7.83–7.79 (m, 2H), 5.35–4.61 (m, 2H), 2.44–2.30 (m, 1H), 1.46 (s, 9H), 1.13 (t, J = 7.0 Hz, 6H).



1-(tert-Butyl) 3-(1,3-dioxoisoindolin-2-yl) piperidine-1,3-dicarboxylate (1n)[9]

Eluent: C.Hex/EtOAc (8:2); White solid (88%). Mp: 158-160 °C. The data are in accordance with previously reported data.[9]

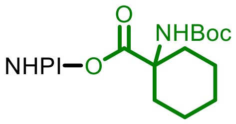
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.87 (m, 2H), 7.83–7.77 (m, 2H), 4.32 (s, 1H), 3.95 (d, J = 13.1 Hz, 1H), 3.20–3.17 (m, 1H), 2.99–2.85 (m, 2H), 2.35–2.26 (m, 1H), 1.93–1.82 (m, 2H), 1.67–1.59 (m, 1H), 1.50 (s, 9H).



1-(tert-Butyl)-2-(1,3-dioxoisoindolin-2-yl)-pyrrolidine-1,2-dicarboxylate (1o)[4]

Eluent: C.Hex/EtOAc (8:2); White solid (98%). Mp: 152-154 °C. The data are in accordance with previously reported data.[4]

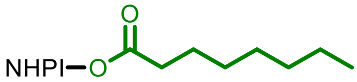
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98–7.88 (m, 2H), 7.78–7.66 (m, 2H), 4.77–4.50 (m, 1H), 3.63–3.38 (m, 2H), 2.58–2.31 (m, 2H), 2.13–1.86 (m, 2H), 1.51 (s, 9H).



1,3-Dioxoisoindolin-2-yl 1-((tert-butoxycarbonyl)amino)cyclohexane-1-carboxylate (1p)[10]

Eluent: C.Hex/EtOAc (8:2); White solid (87%). Mp: 149 °C. The data are in accordance with previously reported data.[10]

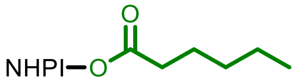
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.89 (m, 2H), 7.75–7.76 (m, 2H), 4.92 (s, 1H), 2.23–2.05 (m, 4H), 1.75–1.66 (m, 2H), 1.64–1.59 (m, 2H), 1.51 (s, 9H), 1.46–1.32 (m, 2H)



1,3-Dioxoisoindolin-2-yl octanoate (1q)[11]

Eluent: C.Hex/EtOAc (8:2); White solid (91%). Mp: 44 °C. The data are in accordance with previously reported data.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.86 (m, 2H), 7.78–7.74 (m, 2H), 2.66–2.64 (m, 2H), 1.79–1.74 (m, 2H), 1.42 (s, 2H), 1.33–1.29 (m, 6H), 0.91 (t, J = 3.5 Hz, 3H)

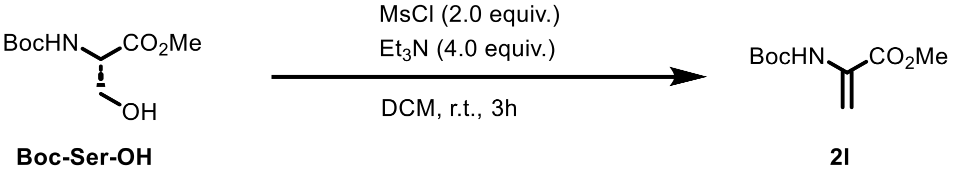


1,3-dioxoisoindolin-2-yl hexanoate (1r)[12]

Eluent: C.Hex/EtOAc (8:2); White solid (95%). Mp: 42 °C. The data are in accordance with previously reported data.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.86 (m, 2H), 7.80–7.76 (m, 2H), 2.66 (t, J = 7.4 Hz, 2H), 1.82–1.75 (m, 2H), 1.46–1.36 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H)

General procedure for the synthesis of 2l

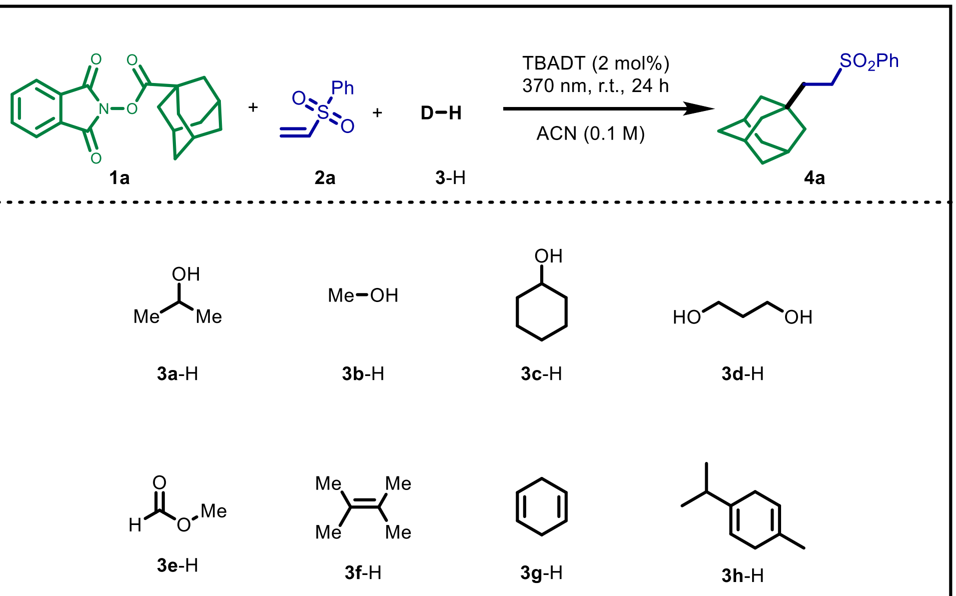


Compound **2l** was prepared following a reported procedure.[13] In round bottomed flask, equipped with a magnetic stirring bar was added *N*-Boc-L-Serine (1 equiv.) followed by the solvent DCM (0.2 M) and Et_3N (4.0 equiv.). Next, MsCl was added dropwise (2.0 equiv.) and the reaction was followed by TLC. After 3h, full conversion of starting material was observed, and the crude was quenched with a saturated solution of $NaHCO_3$ and extracted with DCM (×3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude was purified by column chromatography (C.Hex/EtOAc from 100:0 to 80:20). Compound **2l** was obtained as a colorless oil in 97% yield and stored in freezer. **2l** is not highly stable, it degradates easily, it mantains its purity for 4 weeks when stored in freezer. The data are in accordance with previously reported data.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.20 (d, *J* = 1.3 Hz, 1H), 5.75 (d, *J* = 1.4 Hz, 1H), 3.80 (s, 3H,), 1.52 (s, 9H).

Optimization for photocatalyzed reductive decarboxylative C(sp^3)-C(sp^3) coupling

Screening of hydrogen donors

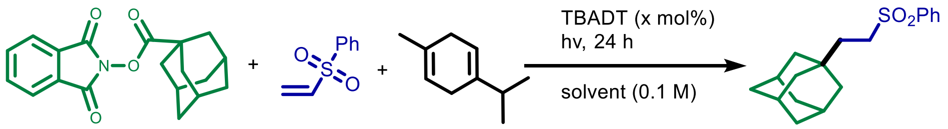


Entry	D-H	yield (%)
1	**3a**-H	20%
2	**3b**-H	15%
3	**3c**-H	25%
4	**3d**-H	< 5%
5	**3e**-H	< 5%
6	**3f**-H	41%
7	**3g**-H	54%
8	**3h**-H	60%

Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), **D-H** (1.0 mmol), TBADT (2 mol%) in ACN (0.1M) under 370 nm 40W Kessil LED lamp for 24 h at room temperature. Yield determined by ^{1}H NMR with CH_2Br_2 as internal standard

Table S1. Optimization with various hydrogen donors

Screening of additional conditions



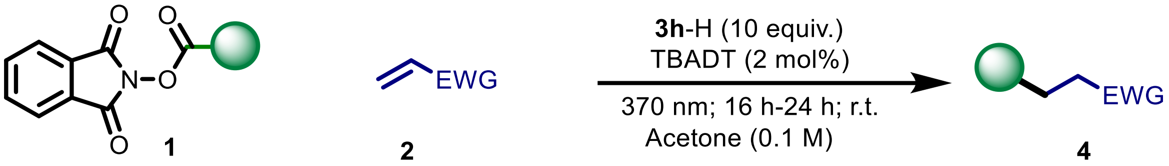
1a **2a** **3h**-H **4a**

Entry	1	2	3-H	TBADT (mol%)	Solvent (0.1 M)	yield %
1	1 equiv	1.2 equiv	10 equiv	2	ACN/DCM 9/1	92%
2	1 equiv	1.2 equiv	10 equiv	1	ACN/DCM 9/1	59%
3	1 equiv	1.2 equiv	5 equiv	2	ACN/DCM 9/1	69%
4	1 equiv	1.0 equiv	10 equiv	2	ACN/DCM 9/1	70%
5[a]	1 equiv	1.2 equiv	10 equiv	2	ACN/DCM 9/1	53%
6	1 equiv	1.2 equiv	10 equiv	2	Acetone	95%
7[b]	1 equiv	1.2 equiv	10 equiv	-	ACN/DCM 9/1	-
8[c]	1 equiv	1.2 equiv	10 equiv	2	ACN/DCM 9/1	-
9[d]	1 equiv	1.2 equiv	-	2	ACN/DCM 9/1	-

Reaction run in 0.1mmol scale in solvent (0.1M) for 24h at room temperature under 370 nm 40W Kessil LED lamp irradiation, if otherwise noted. Yield determined by ^{1}H NMR with CH_2Br_2 as internal standard. [a] 390 nm 40W Kessil LED lamp. [b] no photocatalyst [c] no light [d] no H-donor

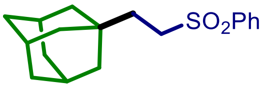
Table S2 Optimization table with screening of additional conditions

General procedure for photocatalyzed reductive decarboxylative C(sp^3)-C(sp^3) coupling



A dried 10 mL (Pyrex® Boro 3.3) tube was charged with a magnetic stirring bar, **1** (0.2 mmol), **2** (0.24 mmol), TBADT (0.004 mmol) and Acetone (2 mL 0.1M). The tube was sealed with a rubber septum and N_2 was bubbled in the solution for 2 min, followed by the addition of **3h**-H (2 mmol). The tube was placed in a 3D printed reactor, stirred inside a photobox, equipped with a cooling fan, (see Figure S1) and irradiated with a 370 nm 40W Kessil LED lamp. The lamp was placed at distance of 6 cm from the reactor. After completion the crude mixture was purified by column chromatography to afford the pure **4**.

Figure S1. Photochemical set-up for the scope in batch.



1-(2-(Phenylsulfonyl)ethyl)adamantane (4a)

Eluent: C.Hex/EtOAc (8:2); Obtained as a white solid (0.176 mmol; 53.5 mg) in 87% yield. Mp: 100-102 °C. The data are in accordance with previously reported data.[14]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.86 (m, 2H), 7.70–7.61 (m, 1H), 7.57 (dd, J = 8.3, 6.8 Hz, 2H), 3.09–3.01 (m, 2H), 1.93 (p, J = 3.1 Hz, 3H), 1.72–1.52 (m, 6H), 1.51–1.43 (m, 2H), 1.40 (d, J = 2.9

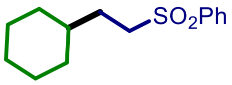
Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.4, 133.7, 129.4, 128.1, 51.4, 42.1, 36.9, 36.0, 32.0, 28.5. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{18}H_{24}O_2SNa^+$ 327.1389; Found 327.1385.

((4-Phenylbutyl)sulfonyl)benzene (4b)

Eluent: C.Hex/EtOAc (8:2); Obtained as a pale yellow oil (0.08 mmol; 22.0 mg) in 40% yield. The data are in accordance with previously reported data.[15]
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92–7.85 (m, 2H), 7.69–7.52 (m, 3H), 7.28–7.22 (m, 3H), 7.20–7.08 (m, 2H), 3.12–3.06 (m, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 1.82–1.66 (m, 4H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 141.2, 139.2, 133.6, 129.3, 128.4, 128.3, 128.1, 126.0, 56.1, 35.3, 30.0, 22.3. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{16}H_{18}O_2SNa^+$ 297.0920; Found 297.0923.

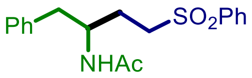
tert-Butyl (3-(phenylsulfonyl)propyl)carbamate (4c)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.136 mmol; 40.77 mg) in 68% yield. The data are in accordance with previously reported data.[16]
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94–7.86 (m, 2H), 7.67–7.62 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 2H), 4.76 (t, *J* = 6.4 Hz, 1H), 3.21 (d, *J* = 6.7 Hz, 2H), 3.15–3.10 (m, 2H), 2.08–1.79 (m, 2H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.0, 139.0, 133.8, 129.4, 128.0, 79.6, 53.7, 38.8, 28.3, 23.6. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{14}H_{21}NO_4SNa^+$ 322.1084; Found 322.1088.



((2-Cyclohexylethyl)sulfonyl)benzene (4d)

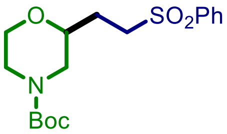
Eluent: C.Hex/EtOAc (8:2); Obtained as a white solid (0.108 mmol; 27.2 mg) in 54% yield. Mp: 51°C. The data are in accordance with previously repoted data.[17]
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92–7.86 (m, 2H), 7.70–7.61 (m, 1H), 7.56 (dd, *J* = 8.3, 6.8 Hz, 2H), 3.21–3.03 (m, 2H), 1.86–1.57 (m, 7H), 1.25 (dtd, *J* = 12.4, 7.9, 3.5 Hz, 1H), 1.21–1.08 (m, 3H), 0.91–0.79 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.4, 133.7, 129.3, 128.1, 54.5, 36.7, 32.8, 29.7, 26.3, 26.1. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{14}H_{20}O_2SNa^+$ 275.1076; Found 275.1071.



***N*-(1-Phenyl-4-(phenylsulfonyl)butan-2-yl)acetamide (4e)**

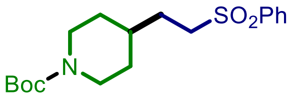
Eluent: C.Hex/EtOAc (8:2); Obtained as a yellowish oil (0.146 mmol; 48.3 mg) in 73% yield.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89–7.80 (m, 2H), 7.69–7.60 (m, 1H), 7.55 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.35–7.19 (m, 3H), 7.16–7.08 (m, 2H), 5.64 (d, *J* = 9.0 Hz, 1H), 4.26–4.13 (m, 1H), 3.13 (dt, *J* = 9.8,

5.7 Hz, 2H), 2.86–2.70 (m, 2H), 2.05–1.94 (m, 1H), 1.88 (s, 3H), 1.87–1.78 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.2, 139.1, 137.0, 134.0, 129.5, 129.3, 128.7, 128.0, 126.9, 53.6, 49.1, 41.3, 27.1, 23.4. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{18}H_{21}NO_3SNa^+$ 354.1134; Found 354.1130.



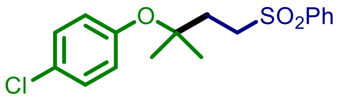
tert-Butyl-2-(2-(phenylsulfonyl)ethyl)morpholine-4-carboxylate (4f)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.15 mmol; 53.3 mg) in 75% yield.
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92–7.87 (m, 2H), 7.67–7.61 (m, 1H), 7.55 (dd, *J* = 8.3, 6.8 Hz, 2H), 3.89–3.70 (m, 3H), 3.42–3.25 (m, 3H), 3.14 (ddd, *J* = 14.1, 10.4, 5.7 Hz, 1H), 2.84 (s, 1H), 2.53 (s, 1H), 1.99–1.84 (m, 1H), 1.84–1.73 (m, 1H), 1.43 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 154.6, 139.1, 133.8, 129.4, 128.1, 80.3, 73.4, 66.5, 52.5, 49.6, 34.0, 28.4, 26.2. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{17}H_{25}NO_5SNa$ 378.1346; Found 378.1340.



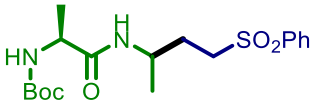
tert-Butyl 4-(2-(phenylsulfonyl)ethyl)piperidine-1-carboxylate (4g)

Eluent: C.Hex/EtOAc (8:2); Obtained as a pale yellow solid (0.184 mmol; 65.0 mg) in 92% yield. Mp: 55°C. The data are in accordance with previously reported data.[18]
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93–7.87 (m, 2H), 7.68–7.62 (m, 1H), 7.56 (dd, *J* = 8.3, 6.8 Hz, 2H), 4.04 (d, *J* = 12.1 Hz, 2H), 3.19–3.02 (m, 2H), 2.61 (t, *J* = 12.6 Hz, 2H), 1.71–1.61 (m, 2H), 1.61–1.54 (m, 2H), 1.47 (dt, *J* = 7.3, 3.8 Hz, 1H), 1.41 (s, 9H), 1.04 (qd, *J* = 12.4, 4.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 154.8, 139.2, 133.8, 129.4, 128.1, 79.5, 54.0, 43.7, 35.0, 31.7, 29.0, 28.5. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{18}H_{27}NO_4SNa^+$ 376.1553; Found 376.1561.



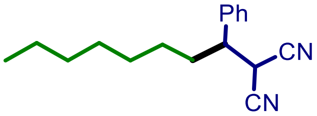
1-Chloro-4-((2-methyl-4-(phenylsulfonyl)butan-2-yl)oxy)benzene (4h)

Eluent: C.Hex/EtOAc (8:2); Obtained as a white waxy solid (0.166 mmol; 56.1 mg) in 83% yield.
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00–7.89 (m, 2H), 7.72–7.66 (m, 1H), 7.63–7.55 (m, 2H), 7.19–7.15 (m, 2H), 6.80–6.72 (m, 2H), 3.44–3.30 (m, 2H), 2.12–1.99 (m, 2H), 1.23 (s, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 153.2, 139.2, 133.9, 129.5, 129.3, 129.2, 128.2, 125.0, 79.0, 52.1, 34.6, 26.6. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{17}H_{19}ClO_3SNa^+$ 361.0636; Found 361.0631.



tert-Butyl ((*S*)-1-oxo-1-((-4-(phenylsulfonyl)butan-2-yl)amino)propan-2-yl)carbamate (4i)

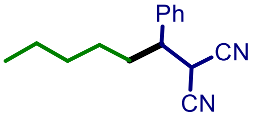
Eluent: DCM/MeOH (95:5); Obtained as a yellow oil (0.162 mmol; 62.2 mg) in 81% yield (d.r. 1.1:1). **^{1}H NMR (400 MHz, CDCl$_3$)** mixture of diastereoisomers δ 7.89 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.65 (td, *J* = 7.3, 1.4 Hz, 1H), 7.55 (td, *J* = 7.4, 6.9, 1.3 Hz, 2H), 6.32–6.20 (m, 1H), 4.98 (dd, *J* = 18.4, 7.6 Hz, 1H), 4.11–3.94 (m, 2H), 3.13 (ddd, *J* = 8.2, 6.5, 3.6 Hz, 2H), 1.99–1.78 (m, 2H), 1.42 (d, *J* = 3.0 Hz, 9H), 1.30 (dd, *J* = 7.1, 1.6 Hz, 3H), 1.15 (dd, *J* = 6.7, 2.7 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** mixture of diastereoisomers δ 172.5, 155.7, 139.2, 133.9, 129.5, 128.1, 80.4, 53.4, 50.4, 44.1, 29.8, 28.4, 21.2, 21.1. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{18}H_{28}N_2O_5SNa^+$ 407.1611; Found 407.1615.



2-(1-Phenyloctyl)malononitrile (4j)

Eluent: n-Hex/EtOAc (90:10); Obtained as a pale yellow oil (0.106 mmol; 26.9 mg) in 53% yield. The data are in accordance with previously reported data.[19]

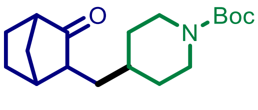
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45–7.37 (m, 3H), 7.34–7.26 (m, 2H), 3.88 (d, *J* = 6.25 Hz, 1H), 3.20 (dt, *J* = 8.78, 6.46 Hz, 1H), 1.99 (td, *J* = 8.81, 6.25 Hz, 2H), 1.46–1.10 (m, 10H), 0.86 (t, *J* = 6.95 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 137.0, 129.4, 129.0, 127.9, 112.1, 46.7, 32.2, 31.8, 30.4, 29.2, 29.0, 27.1, 22.7, 14.1. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{17}H_{22}N_2Na^+$ 277.1675; Found 277.1672.



2-(1-Phenylhexyl)malononitrile (4k)

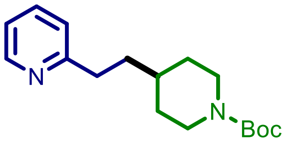
Eluent: n-Hex/EtOAc (90:10); Obtained as a pale yellow oil (0.12 mmol; 27.1 mg) in 60% yield. The data are in accordance with previously reported data.[20]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46–7.36 (m, 3H), 7.31 (dd, *J* = 7.98, 1.70 Hz, 2H), 3.88 (d, *J* = 6.30 Hz, 1H), 3.20 (dt, *J* = 8.62, 6.51 Hz, 1H), 2.07–1.94 (m, 2H), 1.37–1.16 (m, 6H), 0.86 (dq, *J* = 8.87, 2.97 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 137.0, 129.4, 128.9, 127.9, 112.1, 46.7, 32.2, 31.4, 30.3, 26.7, 22.4, 14.0. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{15}H_{18}N_2Na^+$ 249.1362; Found 249.1360.



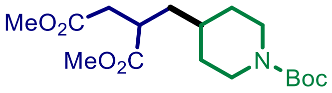
tert-Butyl 4-((3-oxobicyclo[2.2.1]heptan-2-yl)methyl)piperidine-1-carboxylate (4l)

Eluent: C.Hex/EtOAc (8:2); Obtained as a white solid (0.146 mmol; 44.9 mg) in 73% of yield. Mp: 75°C. Based on data provided in literature, **4l** has an endo configuration.[21] The data are in accordance with previously reported data.[22]
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.13–3.74 (m, 2H), 2.80–2.31 (m, 4H), 2.06 (dtd, *J* = 13.1, 9.5, 8.7, 5.4 Hz, 1H), 1.78 (dtd, *J* = 18.0, 9.2, 6.9, 4.4 Hz, 2H), 1.71–1.50 (m, 7H), 1.42 (s, 9H), 1.39–1.31 (m, 2H), 1.15–1.02 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 154.9, 154.9, 79.4, 51.4, 50.5, 38.7, 37.1, 34.5, 30.4, 30.0, 28.5, 25.4, 21.3, 21.3. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{18}H_{29}NO_3Na^+$ 330.2040; Found 330.2038.



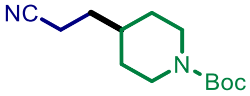
tert-Butyl 4-(2-(pyridin-2-yl)ethyl)piperidine-1-carboxylate (4m)

Eluent: C.Hex/EtOAc (1:1); Obtained as a white solid (0.162 mmol; 47.0 mg) in 81% yield. Mp: 62°C. The data are in accordance with previously reported data.[23]
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.48 (dt, *J* = 4.8, 1.5 Hz, 1H), 7.55 (td, *J* = 7.7, 1.9 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.06 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 3.88 (dt, *J* = 13.4, 4.1 Hz, 2H), 2.79 (t, *J* = 8.2 Hz, 2H), 2.74–2.70 (m, 1H), 2.49 (s, 1H), 1.85 (dt, *J* = 12.9, 4.0 Hz, 1H), 1.61 (dtd, *J* = 14.5, 7.8, 6.2, 3.5 Hz, 3H), 1.42 (s, 11H), 1.17–1.05 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.1, 155.0, 149.3, 136.4, 122.8, 121.1, 79.3, 35.8, 35.6, 33.8, 31.0, 28.6, 25.0. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{17}H_{26}N_2O_2Na^+$ 313.1886; Found 313.1882.



Dimethyl 2-((1-(tert-butoxycarbonyl)piperidin-4-yl)methyl)succinate (4n)

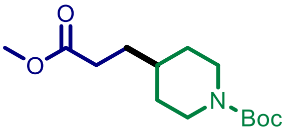
Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.196 mmol; 67.3 mg) in 98% yield.
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.06 (s, 2H), 3.70 (s, 3H), 3.67 (s, 3H), 2.93 (tt, *J* = 8.5, 5.6 Hz, 1H), 2.68 (td, *J* = 20.4, 18.5, 11.0 Hz, 3H), 2.42 (dd, *J* = 16.5, 5.4 Hz, 1H), 1.74 (dt, *J* = 13.2, 2.8 Hz, 1H), 1.67 – 1.55 (m, 3H), 1.44 (s, 9H), 1.34 (ddd, *J* = 13.7, 7.8, 5.9 Hz, 1H), 1.07 (pd, *J* = 12.3, 4.4 Hz, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 175.5, 172.3, 154.9, 79.4, 52.1, 52.0, 38.9, 38.6, 36.5, 33.9, 32.3, 31.8, 28.6. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{17}H_{29}NO_6Na^+$ 366.1887; Found 366.1891.



tert-Butyl 4-(2-cyanoethyl)piperidine-1-carboxylate (4o)

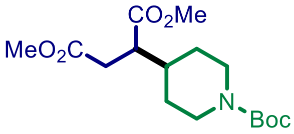
Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.162 mmol; 38.6 mg) in 81% yield. The data are in accordance with previously reported data.[16]

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.95–3.72 (m, 2H), 2.89 (ddd, *J* = 13.6, 10.4, 3.2 Hz, 1H), 2.72–2.51 (m, 1H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.92–1.77 (m, 1H), 1.68–1.50 (m, 4H), 1.44 (s, 10H), 1.22–1.09 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 154.9, 119.6, 79.7, 34.8, 30.2, 28.8, 28.5, 24.3, 14.9. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{13}H_{22}N_2O_2Na^+$ 261.1573; Found 261.1577.



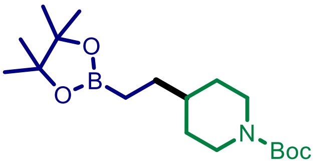
tert-Butyl 4-(3-methoxy-3-oxopropyl)piperidine-1-carboxylate (4p)

Eluent: C.Hex/EtOAc (8:2); Obtained as a yellow oil (0.154 mmol; 41.8 mg) in 77% yield. The data are in accordance with previously reported data.[16]
^{1}H NMR (400 MHz, CDCl$_3$) δ 3.84 (dt, *J* = 13.1, 4.0 Hz, 2H), 3.64 (s, 3H), 2.76 (t, *J* = 12.3 Hz, 2H), 2.32 (t, *J* = 7.8 Hz, 2H), 1.96–1.73 (m, 1H), 1.67–1.45 (m, 3H), 1.42 (s, 11H), 1.07 (tt, *J* = 12.9, 5.9 Hz, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.1, 154.9, 79.4, 51.7, 44.5, 35.5, 31.5, 30.7, 28.5. One aliphatic carbon is missing due to overlap of signals. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{14}H_{25}NO_4Na^+$ 294.1676; Found 294.1677.



Dimethyl-2-(1-(tert-butoxycarbonyl)piperidin-4-yl)succinate (4q)

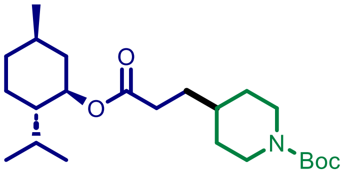
Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.128 mmol; 42.1 mg) in 64% yield as a mixture of rotamers. The data are in accordance with previously reported data.[24]
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.00 (d, *J* = 13.4 Hz, 1H), 3.84 (dt, *J* = 13.5, 4.1 Hz, 1H), 3.70 (d, *J* = 2.7 Hz, 3H), 3.65 (d, *J* = 1.2 Hz, 3H), 2.76 (qt, *J* = 10.0, 4.3 Hz, 3H), 2.65–2.42 (m, 2H), 1.84–1.61 (m, 4H), 1.43 (d, *J* = 1.1 Hz, 9H), 1.31–1.11 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 174.4, 174.2, 172.5, 172.5, 154.8, 79.7, 79.6, 52.0, 52.0, 51.9, 44.5, 38.0, 34.1, 33.5, 28.6, 28.5, 28.4. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{16}H_{27}NO_6Na^+$ 352.1731; Found 352.1726.



tert-Butyl 4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)piperidine-1-carboxylate (4r)

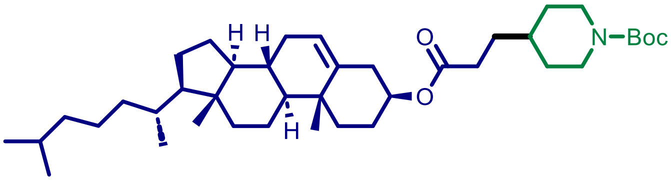
Eluent: C.Hex/EtOAc (8:2); Obtained as a reddish gel (0.076 mmol; 25.8 mg) in 38% yield. The data are in accordance with previously reported data.[16]
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.03 – 3.84 (m, 2H), 2.70 (t, *J* = 11.7 Hz, 1H), 2.55–2.34 (m, 1H), 1.82 (d, *J* = 13.2 Hz, 1H), 1.61 (dt, *J* = 13.2, 3.7 Hz, 1H), 1.44 (s, 9H), 1.32 (q, *J* = 9.0 Hz, 3H), 1.23

(s, 13H), 1.05–0.97 (m, 1H), 0.77 (dd, *J* = 8.8, 7.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.0, 83.1, 79.2, 38.2, 30.8, 28.6, 28.6, 27.9, 24.9, 24.9. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{18}H_{34}BNO_4Na^+$ 362.2473; Found 362.2477.



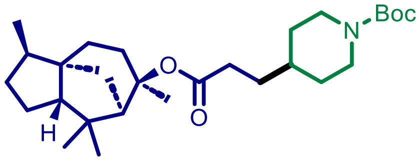
tert-Butyl 4-(3-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-3-oxopropyl)piperidine-1-carboxylate (4s)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.170 mmol; 67.2 mg) in 85% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (td, *J* = 10.8, 4.4 Hz, 1H), 4.06 (d, *J* = 10.2 Hz, 2H), 2.63 (t, *J* = 12.9 Hz, 2H), 2.39–2.24 (m, 2H), 2.01–1.91 (m, 1H), 1.82 (ddd, *J* = 10.9, 6.9, 3.4 Hz, 2H), 1.64 (ddt, *J* = 9.8, 6.7, 3.3 Hz, 3H), 1.56 (q, *J* = 7.3 Hz, 2H), 1.43 (s, 9H), 1.34 (ddt, *J* = 12.6, 11.0, 3.2 Hz, 2H), 1.14–0.97 (m, 3H), 0.87 (dd, *J* = 6.8, 3.5 Hz, 9H), 0.73 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.3, 154.9, 79.3, 74.2, 47.1, 41.0, 35.6, 34.3, 32.0, 31.6, 31.5, 28.5, 26.4, 23.5, 22.1, 20.9, 16.4. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{23}H_{41}NO_4Na^+$ 418.2928; Found 418.2923.



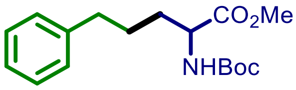
tert-Butyl 4-(3-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-3-oxopropyl)piperidine-1-carboxylate (4t)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.182 mmol; 113.8 mg) in 90% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (dd, *J* = 4.7, 1.9 Hz, 1H), 4.60 (ddq, *J* = 16.0, 8.1, 4.1 Hz, 1H), 3.85 (dt, *J* = 13.2, 4.2 Hz, 1H), 2.78 (s, 1H), 2.34–2.26 (m, 4H), 1.97 (ddt, *J* = 20.4, 11.5, 4.3 Hz, 2H), 1.89–1.72 (m, 4H), 1.68–1.38 (m, 19H), 1.39–0.93 (m, 22H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.85 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.66 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.1, 154.9, 139.8, 122.8, 79.4, 74.0, 56.8, 56.3, 50.2, 42.4, 39.9, 39.6, 38.3, 37.1, 36.7, 36.3, 35.9, 35.5, 32.2, 32.0, 32.0, 30.8, 28.6, 28.3, 28.1, 27.9, 24.4, 24.0, 22.9, 22.7, 21.2, 19.4, 18.8, 12.0. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{40}H_{67}NO_4Na^+$ 648.4962; Found 648.4968.



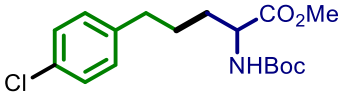
tert-Butyl 4-(3-oxo-3-(((3R,3aS,6R,7R,8aS)-3,6,8,8-tetramethyloctahydro-1H-3a,7-methanoazulen-6-yl)oxy)propyl)piperidine-1-carboxylate (4u)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.194 mmol; 89.5 mg) in 97% yield.
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.14–3.71 (m, 2H), 2.95–2.67 (m, 1H), 2.59–2.32 (m, 2H), 2.29–2.17 (m, 2H), 2.13–1.73 (m, 5H), 1.70–1.22 (m, 25H), 1.19–1.13 (m, 3H), 1.07 (d, *J* = 10.8 Hz, 1H), 0.96 (s, 3H), 0.83 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 172.8, 155.0, 86.5, 79.4, 57.2, 56.8, 54.1, 53.5, 43.5, 41.4, 41.1, 37.1, 35.59, 35.57, 33.3, 33.25, 33.23, 31.4, 28.6, 27.3, 27.0, 26.0, 25.4, 18.6, 15.6. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{28}H_{47}NO_4Na^+$ 484.3397; Found 484.3392.



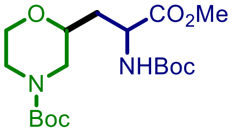
Methyl 2-((tert-butoxycarbonyl)amino)-5-phenylpentanoate (4v)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.120 mmol; 36.9 mg) in 60% yield. The data are in accordance with previously reported data.[25]
^{1}H NMR (400 MHz, CDCl$_3$). δ 7.31–7.24 (m, 2H), 7.22–7.14 (m, 3H), 4.98 (d, *J* = 8.6 Hz, 1H), 4.33 (s, 1H), 3.72 (s, 3H), 2.63 (h, *J* = 6.0 Hz, 2H), 1.91–1.54 (m, 4H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)**. One carbon is missing due to overlapping of signals. δ 173.5, 155.5, 141.8, 128.5, 126.0, 80.0, 53.4, 52.3, 35.4, 32.5, 28.5, 27.2. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{17}H_{25}NO_4Na^+$ 330.1676; Found 330.1684.



Methyl 2-((tert-butoxycarbonyl)amino)-5-(4-chlorophenyl)pentanoate (4w)

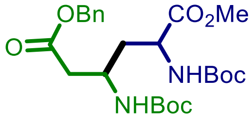
Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.128 mmol; 43.7 mg) in 64% yield.
^{1}H NMR (400 MHz, CDCl$_3$). δ 7.25–7.22 (m, 2H), 7.11–7.06 (m, 2H), 4.98 (d, *J* = 8.4 Hz, 1H), 4.32 (s, 1H), 3.72 (s, 3H), 2.59 (dt, *J* = 14.2, 7.3 Hz, 2H), 1.90–1.50 (m, 4H), 1.44 (s, 9H). **^{13}C NMR (101 MHz, CDCl$_3$)**. One carbon is missing due to overlapping of signals δ 173.4, 155.5, 140.2, 131.8, 129.8, 128.6, 80.1, 53.3, 52.4, 34.7, 32.4, 28.5, 27.1. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{17}H_{24}NO_4ClNa^+$ 364.1286; Found 364.1292.



tert-Butyl-2-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)morpholine-4-carboxylate (4x)

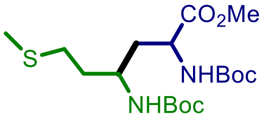
Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless gel (0.136 mmol; 52.8 mg) in 68% yield as a mixture of diastereoisomers (1:1.2)
^{1}H NMR (400 MHz, CDCl$_3$) mixture of diastereoisomers δ 5.47 (major d, *J* = 8.9 Hz, 0.55H), 5.32 (minor d, *J* = 7.3 Hz, 0.45H), 4.50 (major s, 0.55H), 4.39 (minor d, *J* = 6.6 Hz, 0.45H), 3.91–3.75 (m,

3H), 3.72 (d, *J* = 5.7 Hz, 3H), 3.51–3.37 (m, 2H), 2.89 (s, 1H), 2.66–2.51 (m, 1H), 1.89 (ddd, *J* = 14.1, 10.2, 4.6 Hz, 2H), 1.49–1.40 (m, 18H). **^{13}C NMR (101 MHz, CDCl$_3$)** mixture of diastereoisomers δ 173.0, 172.8, 154.7, 80.3, 80.2, 66.6, 66.5, 52.5, 35.4, 35.2, 34.1, 28.5, 28.5, 27.0. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{18}H_{32}N_2O_7Na^+$ 411.2102; Found 411.2106.



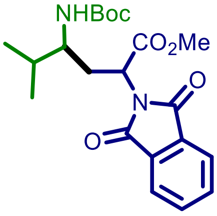
6-Benzyl 1-methyl (4R)-2,4-bis((tert-butoxycarbonyl)amino)hexanedioate (4y)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.122 mmol; 60.3mg) in 61% yield as a mixture of diastereoisomers (1:1.4)
^{1}H NMR (400 MHz, CDCl$_3$) mixture of diastereoisomers δ 7.42–7.31 (m, 5H), 5.47 (d, *J* = 8.5 Hz, 1H), 5.12 (s, 2H), 5.06 (d, *J* = 9.6 Hz, 1H), 4.42 (dd, *J* = 9.2, 4.9 Hz, 1H), 4.09 (dq, *J* = 9.8, 4.7 Hz, 1H), 3.71 (s, 3H), 2.62 (t, *J* = 4.8 Hz, 2H), 2.18–1.95 (m, 2H), 1.43 (d, *J* = 5.3 Hz, 18H). **^{13}C NMR (101 MHz, CDCl$_3$)** mixture of diastereoisomers δ 172.8, 171.4, 155.7, 155.3, 135.7, 128.8, 128.5, 128.4, 80.1, 79.9, 66.7, 60.5, 52.6, 51.0, 44.2, 38.9, 36.5, 28.5. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{24}H_{36}N_2O_8Na^+$ 503.2364; Found 503.2370.



Methyl-2,4-bis((tert-butoxycarbonyl)amino)-6-(methylthio)hexanoate (4z)

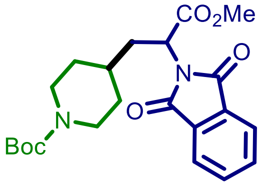
Eluent: C.Hex/EtOAc (8:2); Obtained as a pale yellow oil (0.18 mmol; 73.1mg) in 90% yield as a mixture of diastereoisomers (1:1.1)
^{1}H NMR (400 MHz, CDCl$_3$) mixture of diastereoisomers δ 5.50 (minor d, *J* = 8.5 Hz, 0.48H), 5.24 (major d, *J* = 6.4 Hz, 0.52H), 4.68 (minor d, *J* = 8.1 Hz, 0.48H), 4.41 (dd, *J* = 9.3, 4.2 Hz, 1H), 4.28 (major s, 0.52H), 3.86–3.76 (minor m, 0.5H), 3.73 (d, *J* = 4.7 Hz, 3.5H), 2.50 (dtd, *J* = 10.3, 8.5, 7.7, 5.4 Hz, 2H), 2.14–2.08 (m, 3H), 2.02–1.91 (m, 2H), 1.89–1.72 (m, 2H), 1.49 – 1.39 (m, 18H). **^{13}C NMR (101 MHz, CDCl$_3$)** mixture of diastereoisomers δ 173.2, 173.1, 155.6, 79.8, 79.8, 70.7, 52.6, 51.0, 30.8, 30.7, 28.5, 28.5, 28.4, 28.4, 15.7. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{18}H_{34}N_2O_6SNa^+$ 429.2030; Found 429.2036.



Methyl-4-((tert-butoxycarbonyl)amino)-2-(1,3-dioxoisoindolin-2-yl)-5-methylhexanoate (4aa)

Eluent: C.Hex/EtOAc (8:2); Obtained as a white solid (0.182 mmol; 73.6mg) in 91% of yield as a mixture of diastereoisomers (1:1.1)

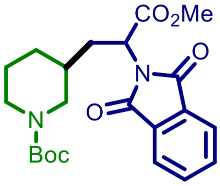
^{1}H NMR (400 MHz, CDCl$_3$) mixture of diastereoisomers δ 7.83 (ddd, *J* = 12.4, 7.0, 4.2 Hz, 2H), 7.72 (tdd, *J* = 8.3, 5.4, 3.2 Hz, 2H), 5.03 (minor dd, *J* = 12.3, 4.5 Hz, 0.3H), 4.97 (major dd, *J* = 8.2, 6.4 Hz, 0.7H), 4.35 (major d, *J* = 10.1 Hz, 0.7H), 4.20 (s, 0.3H), 3.71 (d, *J* = 5.4 Hz, 3H), 3.69 – 3.62 (major m, 0.7H), 3.40 – 3.29 (minor m, 0.73H), 2.76 (minor ddd, *J* = 15.0, 12.3, 3.2 Hz, 0.3H), 2.52 (major ddd, *J* = 14.6, 6.4, 3.4 Hz, 0.7H), 2.13–1.96 (m, 1H), 1.83–1.64 (m, 1H), 1.45–1.18 (m, 9H), 1.02–0.81 (m, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** mixture of diastereoisomers δ 170.5, 169.8, 167.8, 167.7, 155.8, 155.6, 134.3, 134.2, 134.1, 132.1, 123.6, 123.5, 79.4, 79.1, 54.0, 52.9, 52.1, 50.4, 49.6, 33.2, 32.8, 32.6, 31.0, 28.4, 28.2, 27.0, 19.1, 19.0, 18.0, 17.4. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{21}H_{28}N_2O_6Na^+$ 427.1840; Found 427.1846.



tert-Butyl 4-(2-(1,3-dioxoisoindolin-2-yl)-3-methoxy-3-oxopropyl)piperidine-1-carboxylate (4ab)

Eluent: C.Hex/EtOAc (8:2). Obtained as a colorless oil (0.196 mmol; 81.6 mg) in 98% yield (two rotational isomers are present in solution). The data are in accordance with previously reported data.[26]

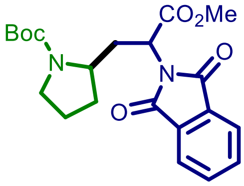
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (ddd, *J* = 4.9, 3.0, 1.6 Hz, 2H), 5.05–4.89 (m, 1H), 3.94–3.79 (m, 1H), 3.71 (d, *J* = 1.9 Hz, 3H), 3.57 (dt, *J* = 14.3, 4.9 Hz, 1H), 3.12–2.86 (m, 1H), 2.78–2.46 (m, 1H), 2.32–1.80 (m, 3H), 1.75–1.58 (m, 2H), 1.40 (d, *J* = 31.5 Hz, 10H), 1.26–1.15 (m, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.0, 170,0, 167.7, 167.7, 154.9, 154.9, 134.4, 134.3, 131.9, 131.9, 123.7, 123.7, 79.6, 79.5, 52.9, 52.9, 50.1, 49.7, 32.8, 32.4, 31.6, 31.0, 29.5, 28.5, 28.5, 24.5, 23.9. **HRMS** (EI) m/z: [M+Na]$^+$ Calculated for $C_{22}H_{28}N_2O_6Na^+$ 439.1840; Found 439.1846.



tert-butyl-3-(2-(1,3-dioxoisoindolin-2-yl)-3-methoxy-3-oxopropyl)piperidine-1-carboxylate (4ac)

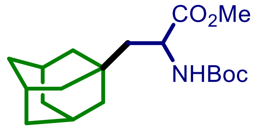
Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.19 mmol; 79.1 mg) in 95% yield as a mixture of diastereoisomers (1:1.1).

^{1}H NMR (400 MHz, CDCl$_3$) mixture of diastereoisomers δ 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.94 (dd, *J* = 11.3, 4.4 Hz, 1H), 4.05 (d, *J* = 23.6 Hz, 2H), 3.70 (s, 3H), 2.67–2.51 (m, 2H), 2.30 (ddd, *J* = 14.3, 11.3, 4.2 Hz, 1H), 2.07 (ddd, *J* = 14.3, 9.7, 4.5 Hz, 1H), 1.81 (dt, *J* = 13.0, 2.8 Hz, 1H), 1.56 (dt, *J* = 12.7, 2.8 Hz, 1H), 1.41 (s, 9H), 1.31 (dtd, *J* = 9.1, 7.4, 3.5 Hz, 1H), 1.23–1.02 (m, 2H). **^{13}C NMR (101 MHz, CDCl$_3$)** mixture of diastereoisomers δ 170.0, 167.8, 154.8, 134.4, 131.8, 123.7, 79.4, 52.9, 49.7, 43.8, 35.3, 32.9, 32.4, 30.8, 28.5, 26.9. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{22}H_{28}N_2O_6Na^+$ 439.1840; Found 439.1843.



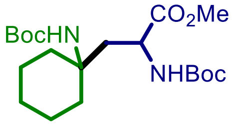
tert-Butyl-2-(2-(1,3-dioxoisoindolin-2-yl)-3-methoxy-3-oxopropyl)pyrrolidine-1-carboxylate (4ad)

Eluent: C.Hex/EtOAc (8:2); Obtained as a colorless oil (0.192 mmol; 77.2 mg) in 96% yield as a mixture of diastereoisomers (1:1.1) and rotamers.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.80 (m, 2H), 7.76–7.68 (m, 2H), 5.02–4.80 (m, 1H), 4.02–3.83 (m, 1H), 3.70 (s, 3H), 3.45–3.29 (m, 1H), 3.23 (ddd, *J* = 10.8, 7.2, 5.4 Hz, 1H), 2.8–2.15 (m, 2H), 2.00–1.52 (m, 4H), 1.49–1.26 (m, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 168.3, 167.7, 167.4, 154.6, 134.3, 134.2, 132.8, 131.9, 123.64, 123.5, 79.7, 79.2, 56.1, 55.3, 54.5, 52.9, 50.5, 49.7, 46.5, 46.1, 34.2, 33.1, 31.3, 3.7, 28.5, 28.4, 23.9, 23.4. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{21}H_{26}N_2O_6Na^+$ 425.1683; Found 425.1680.



Methyl 3-adamantan-1-yl)-2-((tert-butoxycarbonyl)amino)propanoate (4ae)

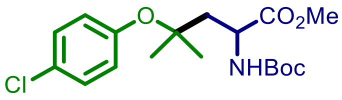
Eluent: C.Hex/EtOAc (85:15); Obtained as a white solid (0.08 mmol; 27.0 mg) in 40% yield. Mp: 126°C. The data are in accordance with previously reported data.[27]
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 (d, *J* = 8.9 Hz, 1H), 4.35 (dt, *J* = 9.0, 5.4 Hz, 1H), 3.71 (s, 3H), 1.96 (t, *J* = 3.2 Hz, 3H), 1.81–1.59 (m, 7H), 1.54 (d, *J* = 2.9 Hz, 6H), 1.44 (s, 9H), 1.33–1.24 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.7, 155.2, 80,0, 52.3, 50,0, 47.3, 42.5, 37.0, 32.7, 29.8, 28.7, 28.5. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{19}H_{31}NO_4Na^+$ 360.2145; Found 360.2141.



Methyl-2-((tert-butoxycarbonyl)amino)-3-(1-((tert-butoxycarbonyl)amino)cyclohexyl) propanoate (4af)

Eluent: C.Hex/EtOAc (85:15); Obtained as a colorless oil (0.102 mmol; 40.8 mg) in 51% yield.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.04 (d, *J* = 8.5 Hz, 1H), 4.45–4.24 (m, 2H), 3.71 (s, 3H), 2.17–1.94 (m, 4H), 1.72 (d, *J* = 25.8 Hz, 1H), 1.61–1.49 (m, 4H), 1.43 (d, *J* = 2.9 Hz, 18H), 1.39–1.29 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.1, 155.6, 154.6, 79.9, 53.7, 52.4, 50.2, 40.1, 35.2, 29.8, 28.6,

28.5, 27.0, 25.7, 21.5, 21.5. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{20}H_{36}N_2O_6Na^+$ 423.2466; Found 423.2462.

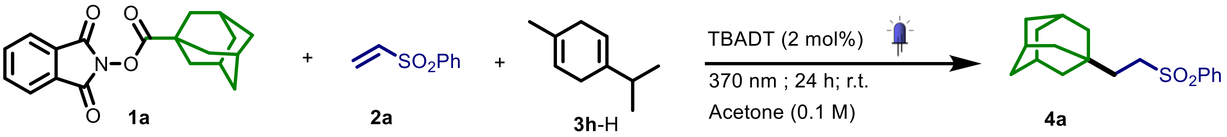


Methyl 2-((tert-butoxycarbonyl)amino)-4-(4-chlorophenoxy)-4-methylpentanoate (4ag)

Eluent: C.Hex/EtOAc (85:15); Obtained as a colorless oil (0.140 mmol; 52.0 mg) in 70% yield as a mixture of rotamers.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26–7.20 (m, 2H), 6.94–6.89 (m, 2H), 5.44 (d, *J* = 7.5 Hz, 1H), 4.52 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 2.17 (dd, *J* = 14.5, 4.9 Hz, 1H), 2.04 (dd, *J* = 14.5, 8.4 Hz, 1H), 1.43 (d, *J* = 6.1 Hz, 9H), 1.29 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 173.6, 155.4, 153.2, 134.4, 129.1, 125.6, 80.3, 80.0, 52.4, 51.3, 44.2, 28.5, 26.8, 26.1. **HRMS** (EI) m/z: $[M+Na]^+$ Calculated for $C_{18}H_{26}NO_5ClNa^+$ 394.1392; Found 394.1397.

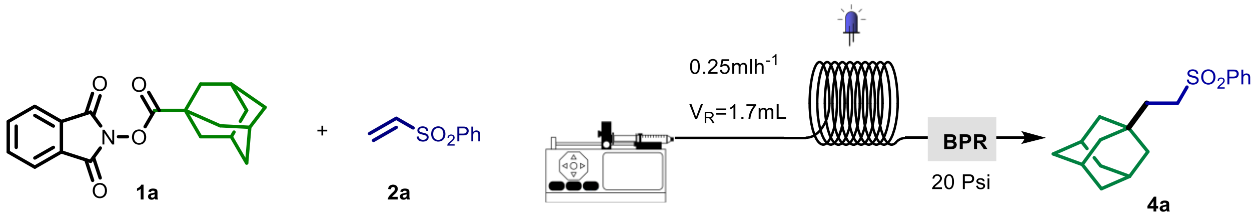
Scale up in batch



A dried 100 mL (Pyrex®) vessel was charged with a magnetic stirring bar, **1a** (325 mg; 1 mmol), **2a** (201.6 mg; 1.2 mmol), TBADT (66.4 mg 0.02 mmol) and Acetone (10 mL 0.1M). The vessel was sealed with a rubber septum and N_2 was bubbled in the solution for 5 min, followed by the addition of **3h**-H (1.6 mL 10 mmol). The vessel was placed in a photo-box, equipped with a cooling fan (see Figure S2) and irradiated with a 370 nm 40W Kessil LED lamp. The lamp was placed at 1 cm distance from the upper part of the vessel. After completion the crude mixture was purified by column chromatography to afford pure **4a** (243.3 mg 0.8 mmol, 80% yield.)

Figure S2. Set-up for the scale-up reaction in batch

Scale up in flow



In an oven dried 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with **1a** (325 mg; 1 mmol) **2a** (201.6 mg; 1.2 mmol), TBADT (66.4 mg, 0.02 mmol) and Acetone (5 mL 0.2M). The flask was sealed with a rubber septum and N_2 was bubbled in the solution for 5 min, followed by the addition of **3h**-H (1.6 mL 10 mmol). The solution was stirred until the mixture was completely homogeneous. The solution was taken up with a 10 mL syringe, mounted on a syringe pump and pushed into a MR-LAB-V microreactor (**Little Things Factory GmbH)** (volume 1.7 mL, Figure S3). For all the additional information visit (https://ltf-gmbh.com/product/mr-lab-v/). The system was equipped with a BPR (back pressure resistance) of 20 Psi and the optimal flow rate is 0.25mL/h. A 370 nm 40W Kessil LED lamp was placed at 5 cm distance from the reactor. After completion the crude mixture was purified by column chromatography to afford the pure **4a** (270.7 mg, 0.89 mmol, 89% yield).

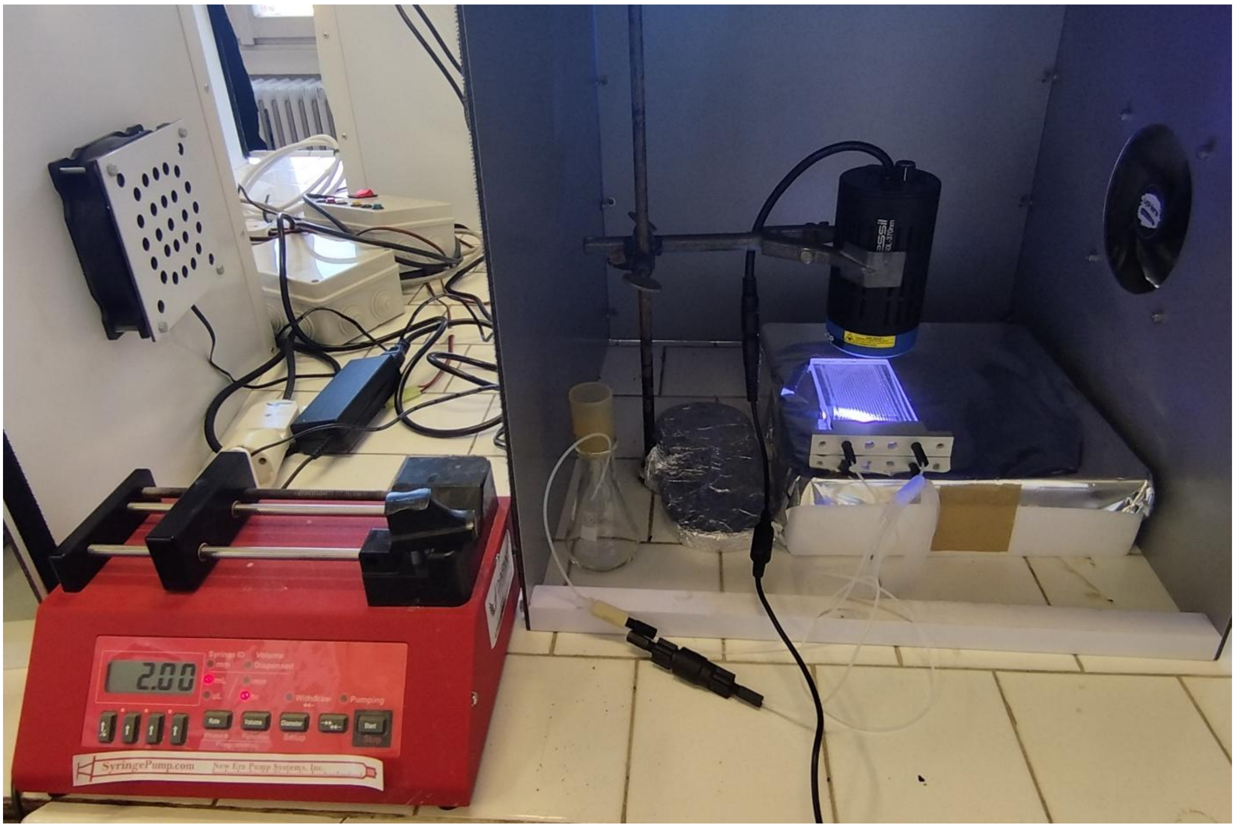
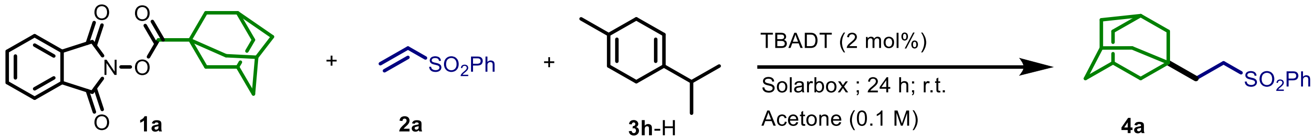


Figure S3. Set up for the scale-up reaction under flow conditions

Scale up in Solarbox



A dried 100 mL (Pyrex®) vessel was charged with a magnetic stirring bar, **1a** (325 mg; 1 mmol), **2a** (201.6 mg; 1.2 mmol), TBADT (66.4 mg, 0.02 mmol) and Acetone (10 mL 0.1M). The vessel was sealed with a rubber septum and N_2 was bubbled in the solution for 5 min, followed by the addition of **3h**-H (1.6 mL, 10 mmol). The vessel was placed in a Solarbox (Solarbox 1500e; Co.Fo.Me.Gra., Italy, Milan), equipped with a cooling fan, (see Figure S4) and irradiated with a 1.5 kW Xenon lamp, with light intensity: 500 W·m^{-2} (the emission spectrum of the employed lamp is available online at: https://cofomegra.it/). After completion the crude mixture was purified by column chromatography to afford the pure **4a** (267.7 mg, 0.88 mmol, 88% yield).

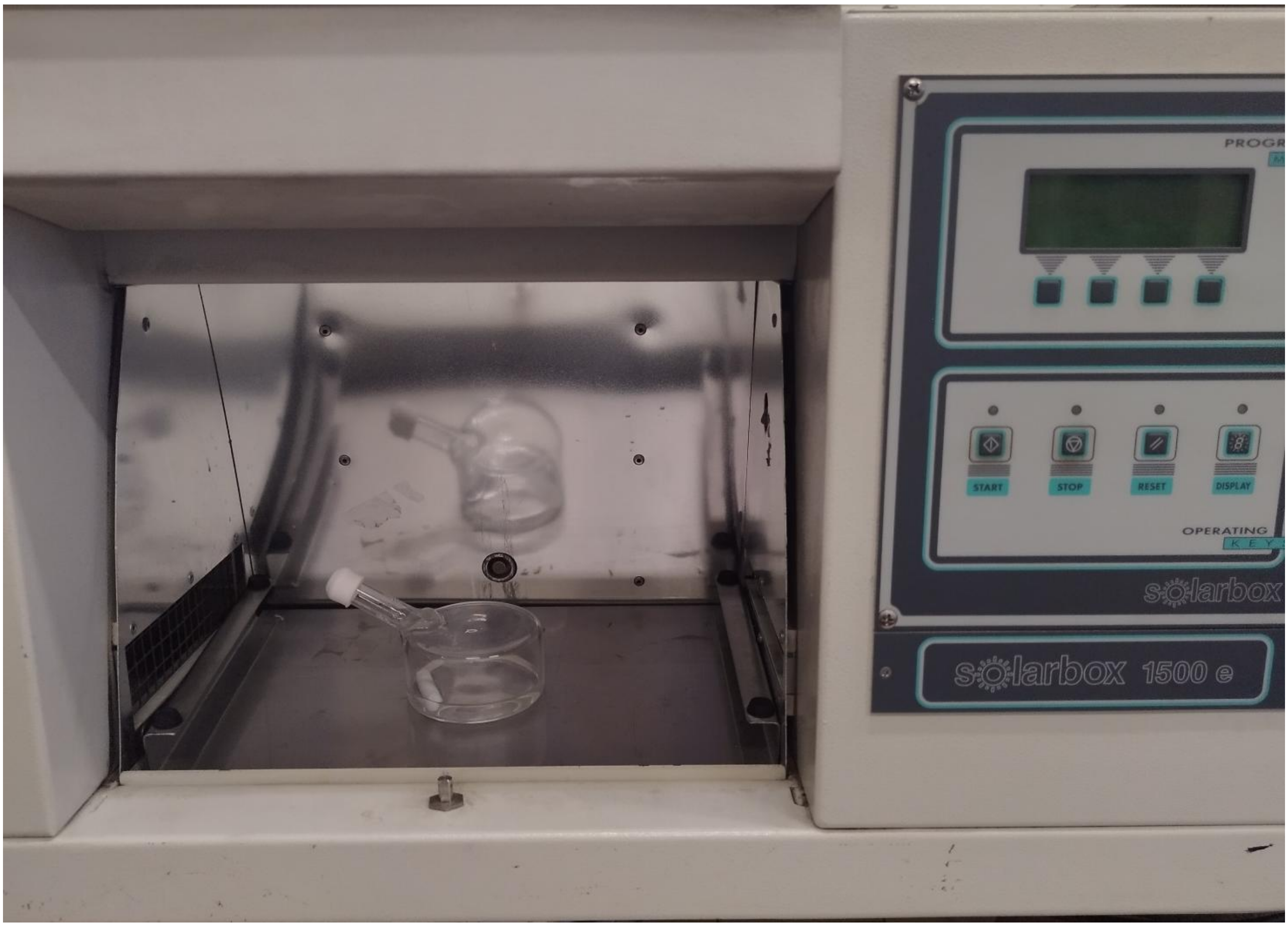
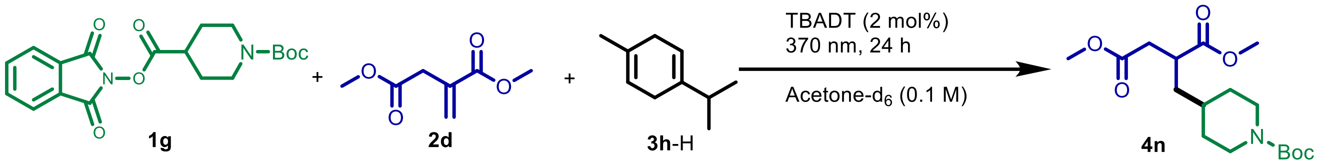


Figure S4. Set-up for the scale-up reaction in Solarbox 1500e

Mechanistic Studies

Light ON-OFF



A dried 10 mL (Pyrex® Boro 3.3) tube was charged with a magnetic stirring bar, **1g** (75 mg, 0.2 mmol), **2d** (38 mg, 0.24 mmol), TBADT (13.2 mg, 0.004 mmol) and Acetone-d_6 (2 mL, 0.1M). The tube was sealed with a rubber septum and N_2 was bubbled in the solution for 2 min, followed by the addition of **3h**-H (320 µL, 2 mmol). The tube was placed in a 3D printed reactor, stirred inside a photo-box, equipped with a cooling fan, and irradiated with a 370 nm 40W Kessil LED lamp. The lamp was placed at 6 cm distance from the reactor. At fixed amount of time a little aliquot of the reaction crude was taken with a syringe from the tube. The crude was subjected to ^{1}H NMR analysis to calculate the % of conversion of **1g** to **4n**. The tube was then let it stir in the darkness for a determined amount of time after which an ^{1}H NMR was recorded again. These processes were repeated several times as depicted in Figure S5. For each spectrum was calculated the conversion of **1g** in **4n** taking as a reference the (9H δ-1.32 **1g**) and (9H δ-1.29 **4n**) signals. From the experiment a radical chain pathway may be safely excluded.

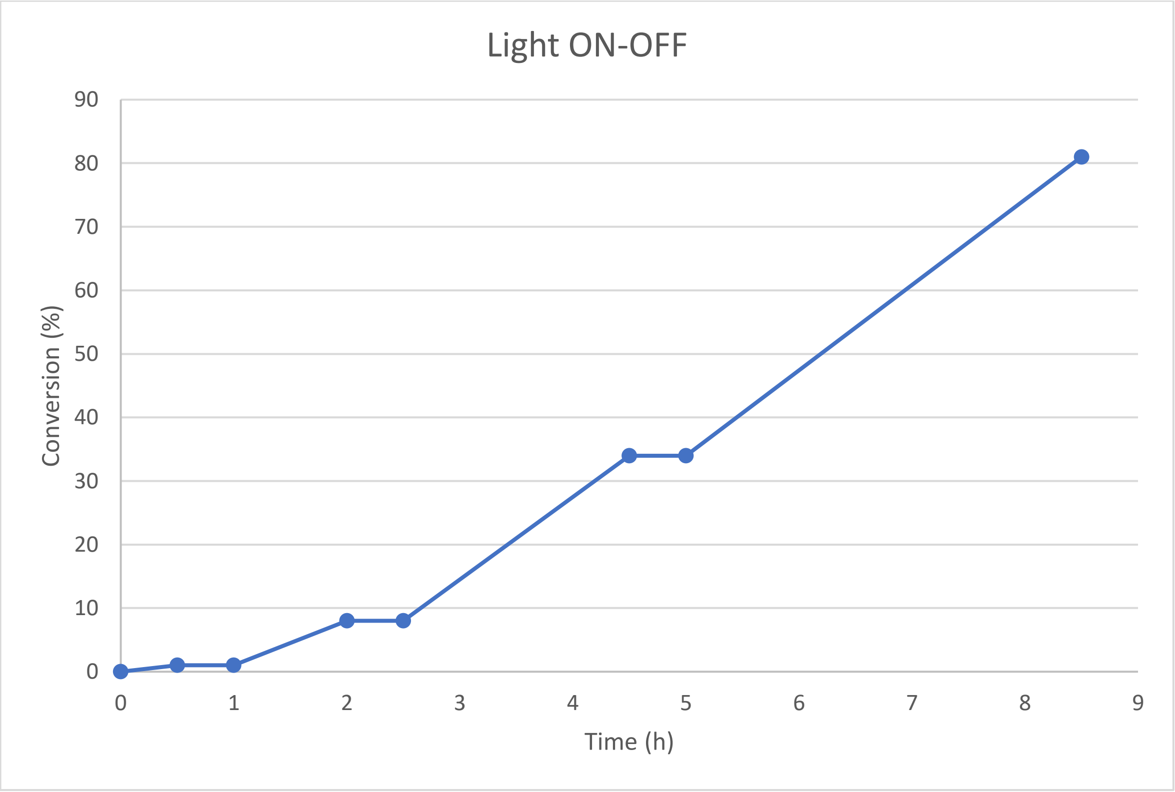
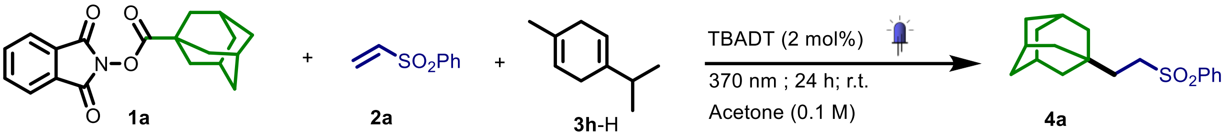


Figure S5. Light ON-OFF experiment

Reaction with TEMPO

To have more insights into the effect of the TEMPO (2,2,6,6-tetramethylpyrrolidine-*N*-oxyl) additive on the reaction outcome, we performed the GC-MS analysis of a selected reaction of **1a** and **2a** following the general procedure for the photocatalyzed reaction.



We performed several reactions: 1) in the absence of the radical scavenger TEMPO to highlight the formation of the desired product **4a** (See Figure S6); 2) With 1 equiv. of TEMPO. (See figure S7). 3) With 5 equiv. of TEMPO (See Figure S8). We could observe a slower conversion of **1a** when 1 equiv. of TEMPO was used, while the presence of 5 equiv. of TEMPO fully inhibited the formation of product **4a**.

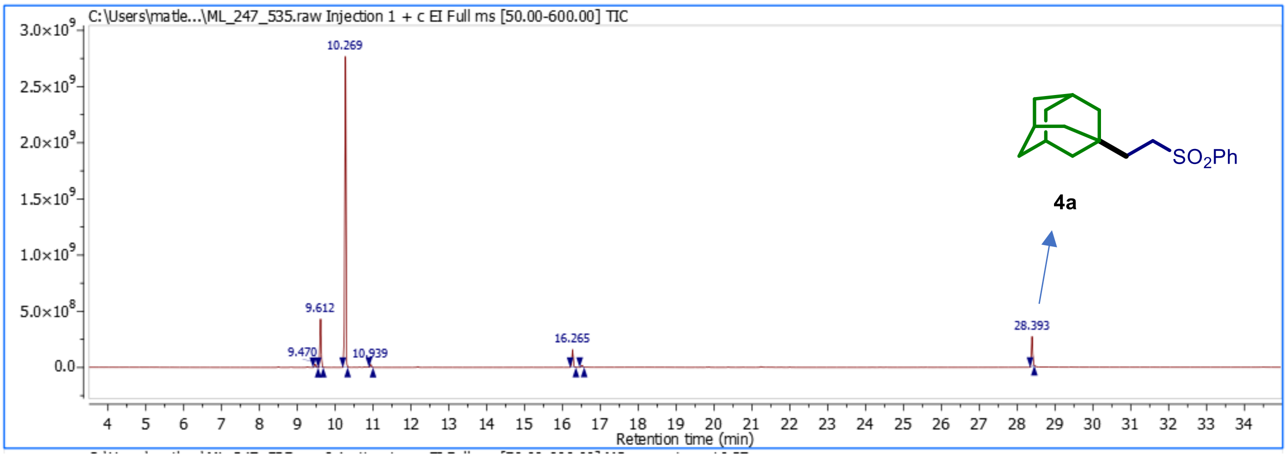


Figure S6. GC-MS in the absence of TEMPO

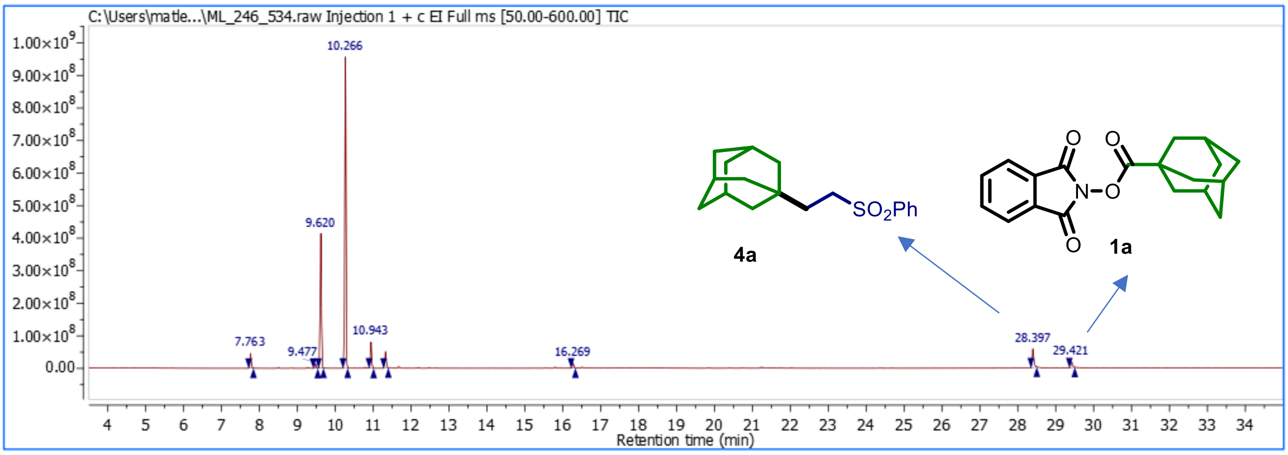


Figure S7. GC-MS in the presence of 1 equiv. of TEMPO

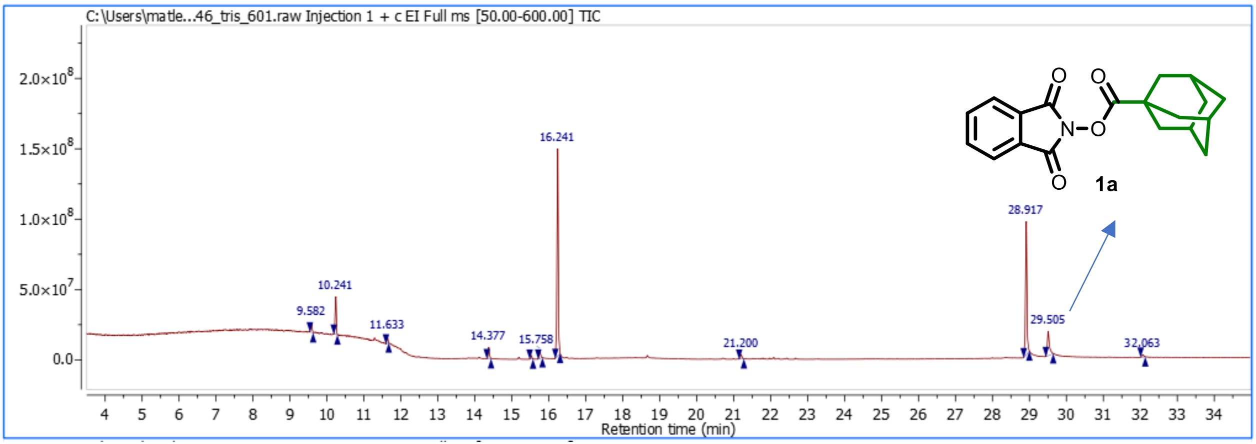
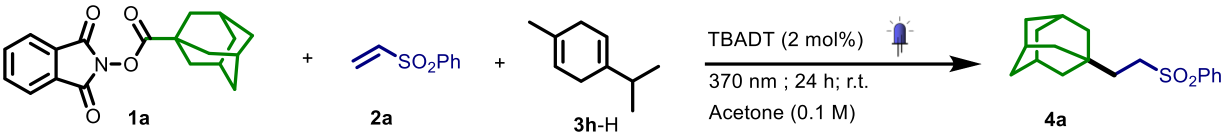


Figure S8. GC-MS in the presence of 5 equiv. of TEMPO

Detection of p-cymene in GC-MS

Analysis performed on the following reaction.



GC-MS analyses were carried out using a Thermo Scientific DSQII single quadrupole GC-MS system.

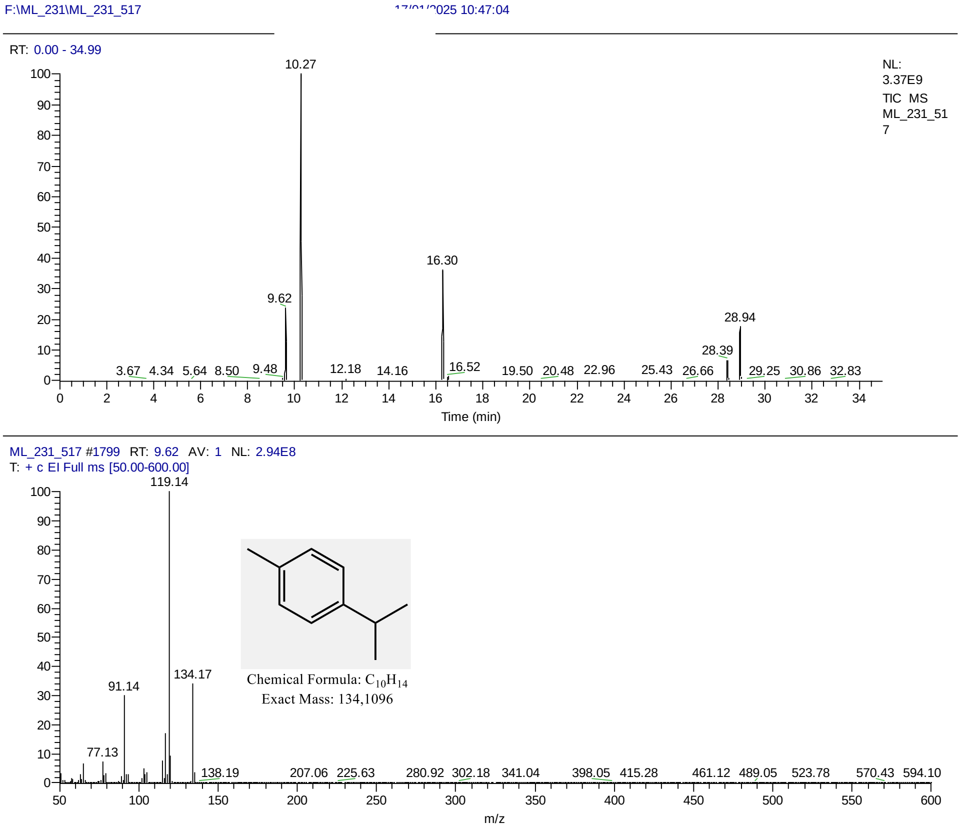
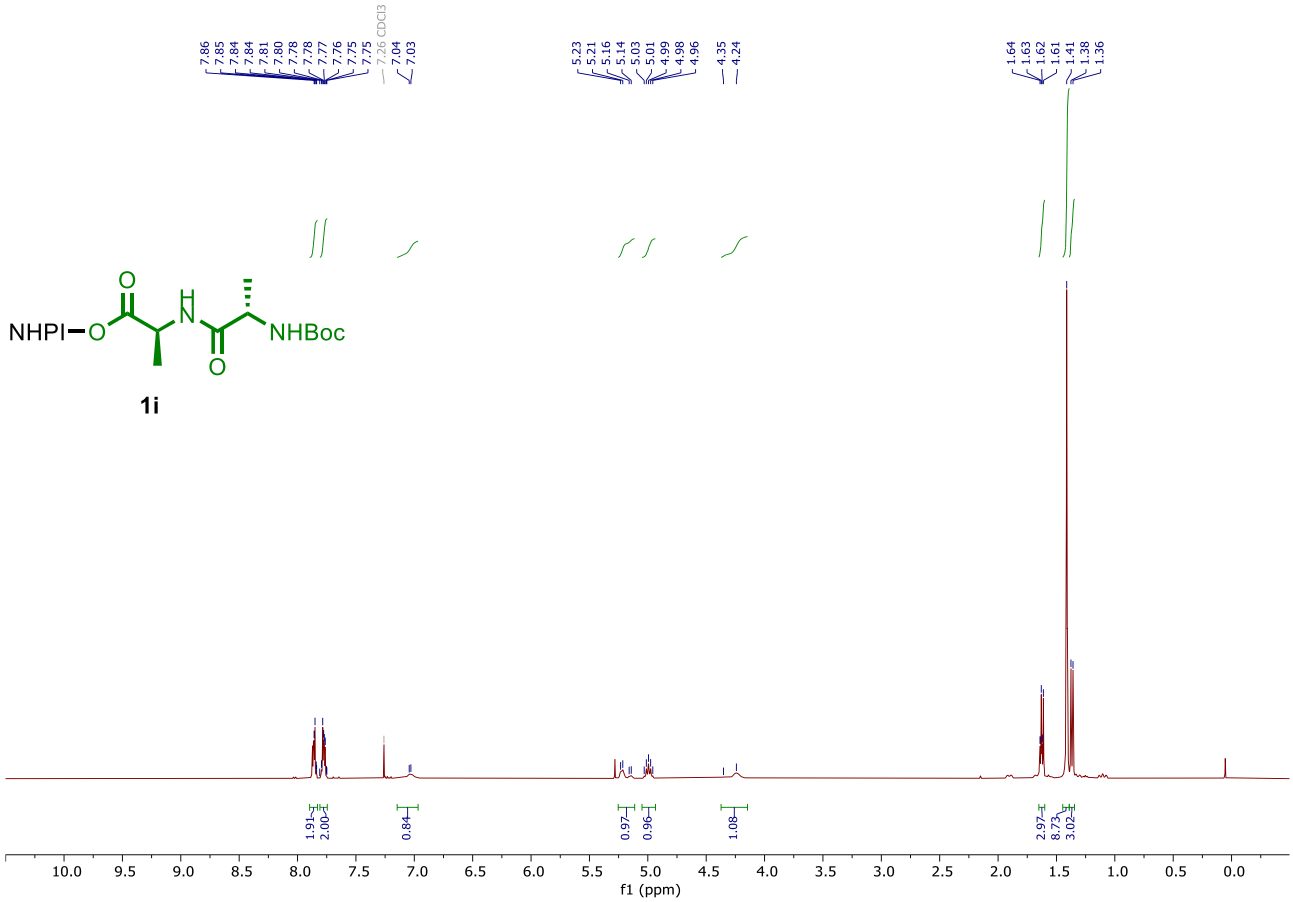
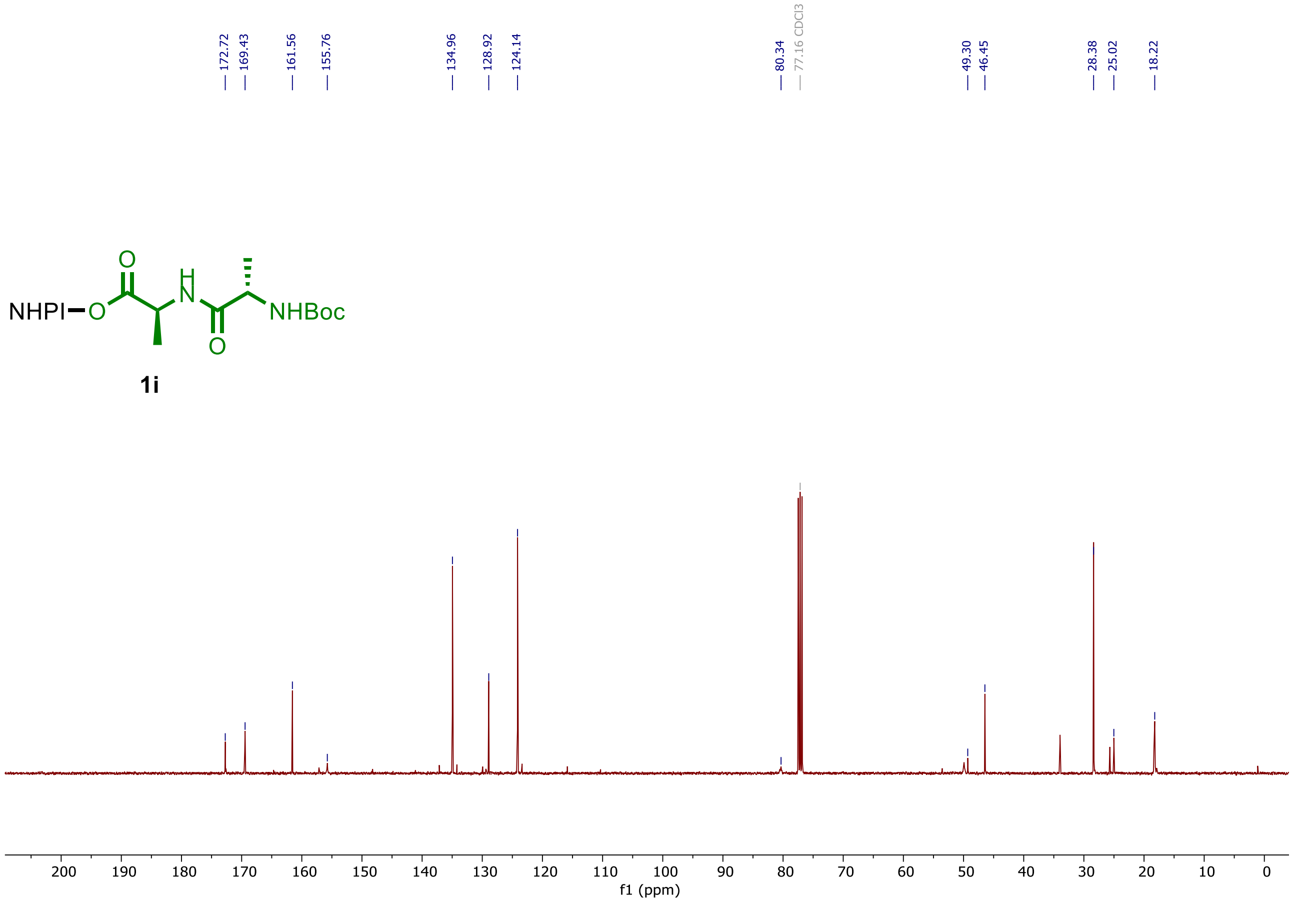


Figure S9. Detection of p-cymene with a r.t. of 9.62 (min).

Copy of ^{1}H and ^{13}C NMR Spectra



1i



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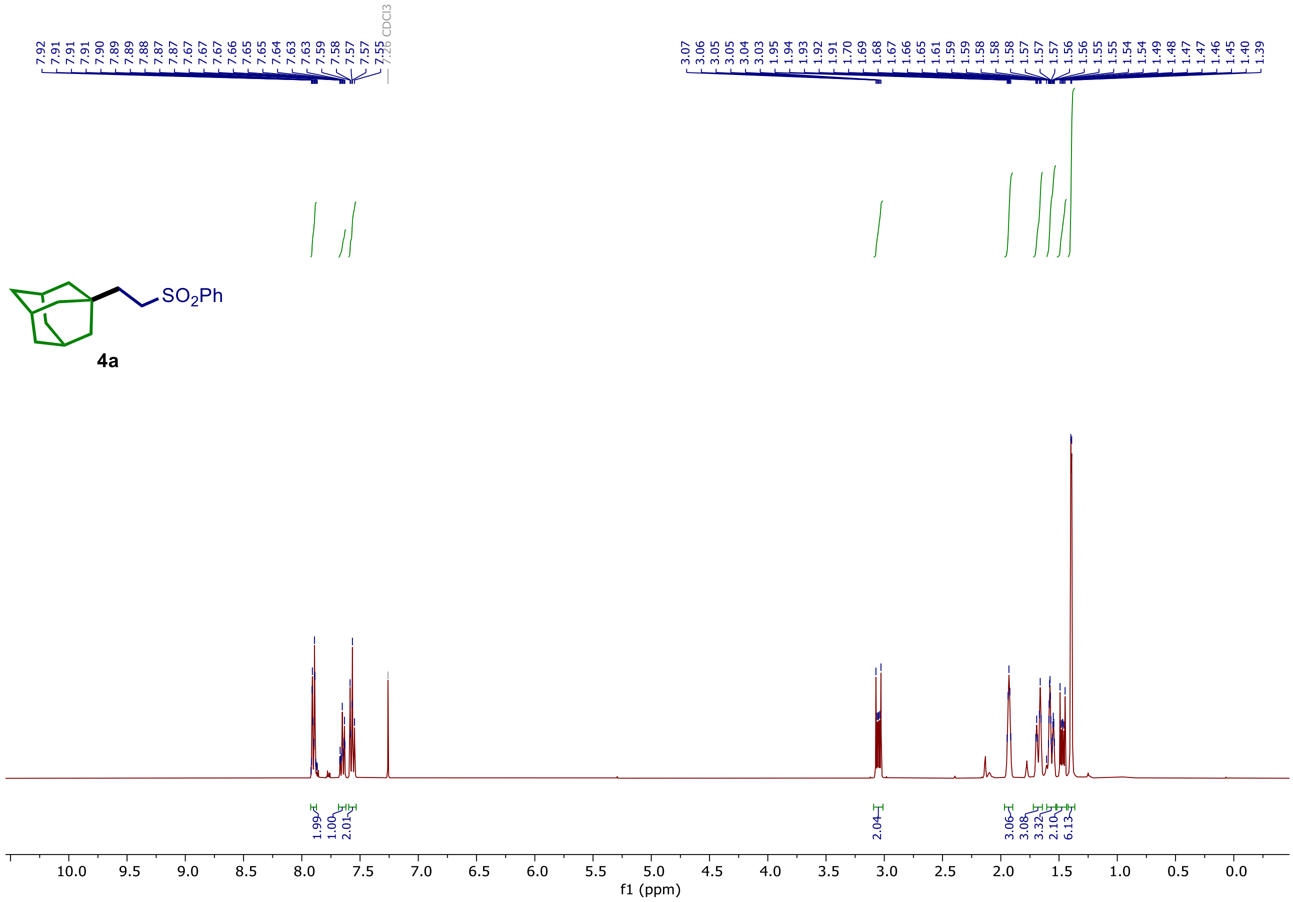
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2.04
3.06
3.08
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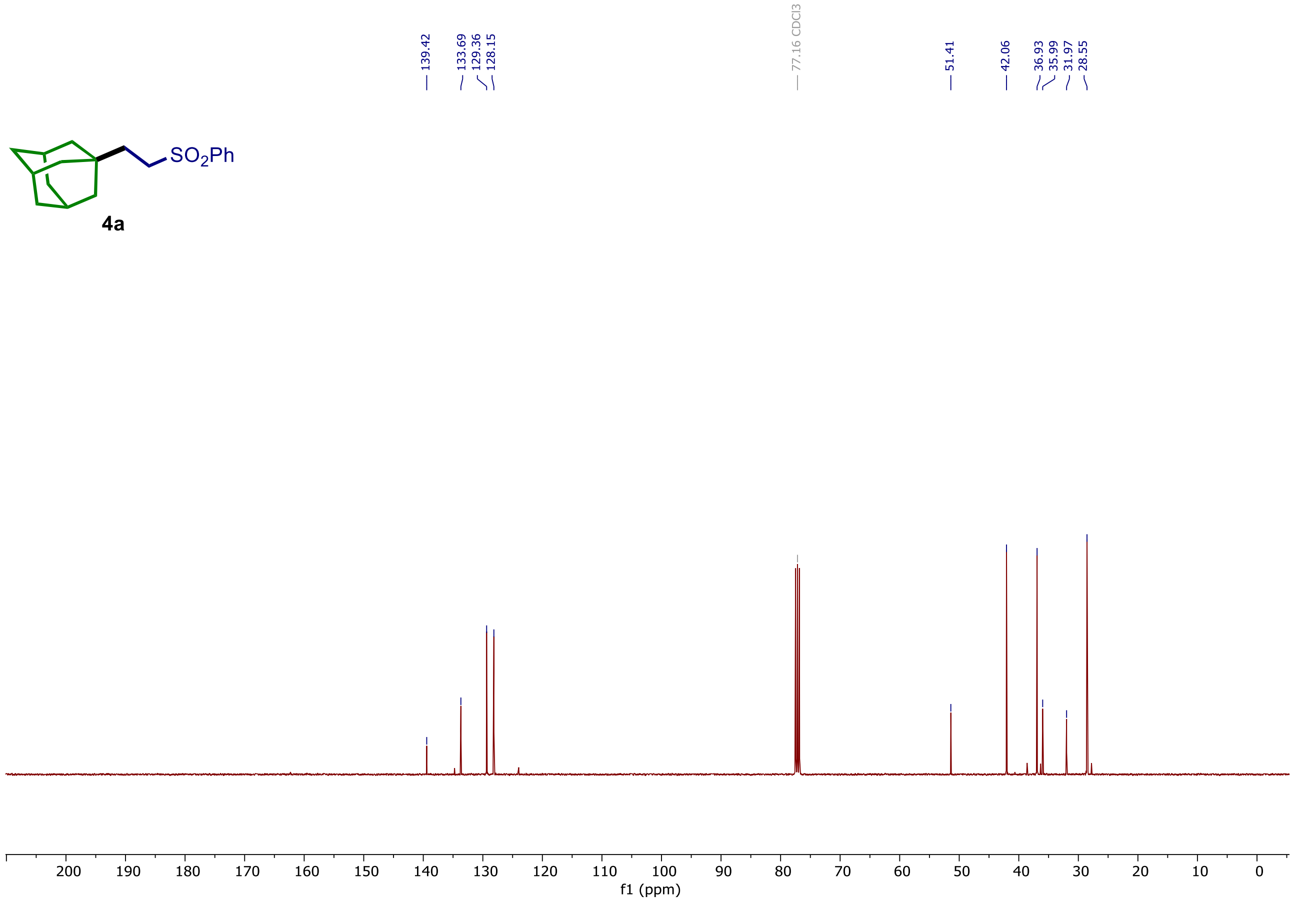
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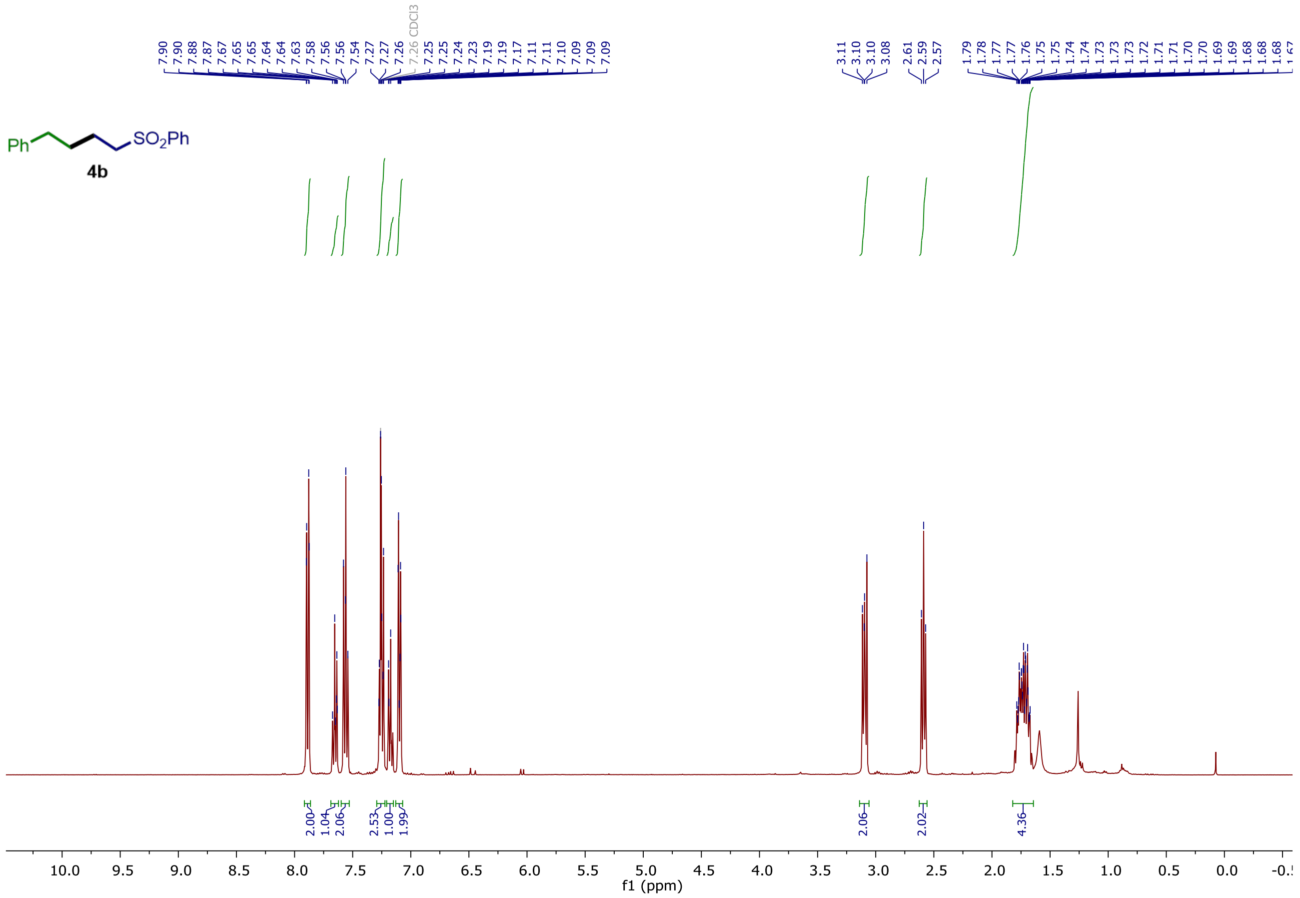
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1.00
1.99
2.06
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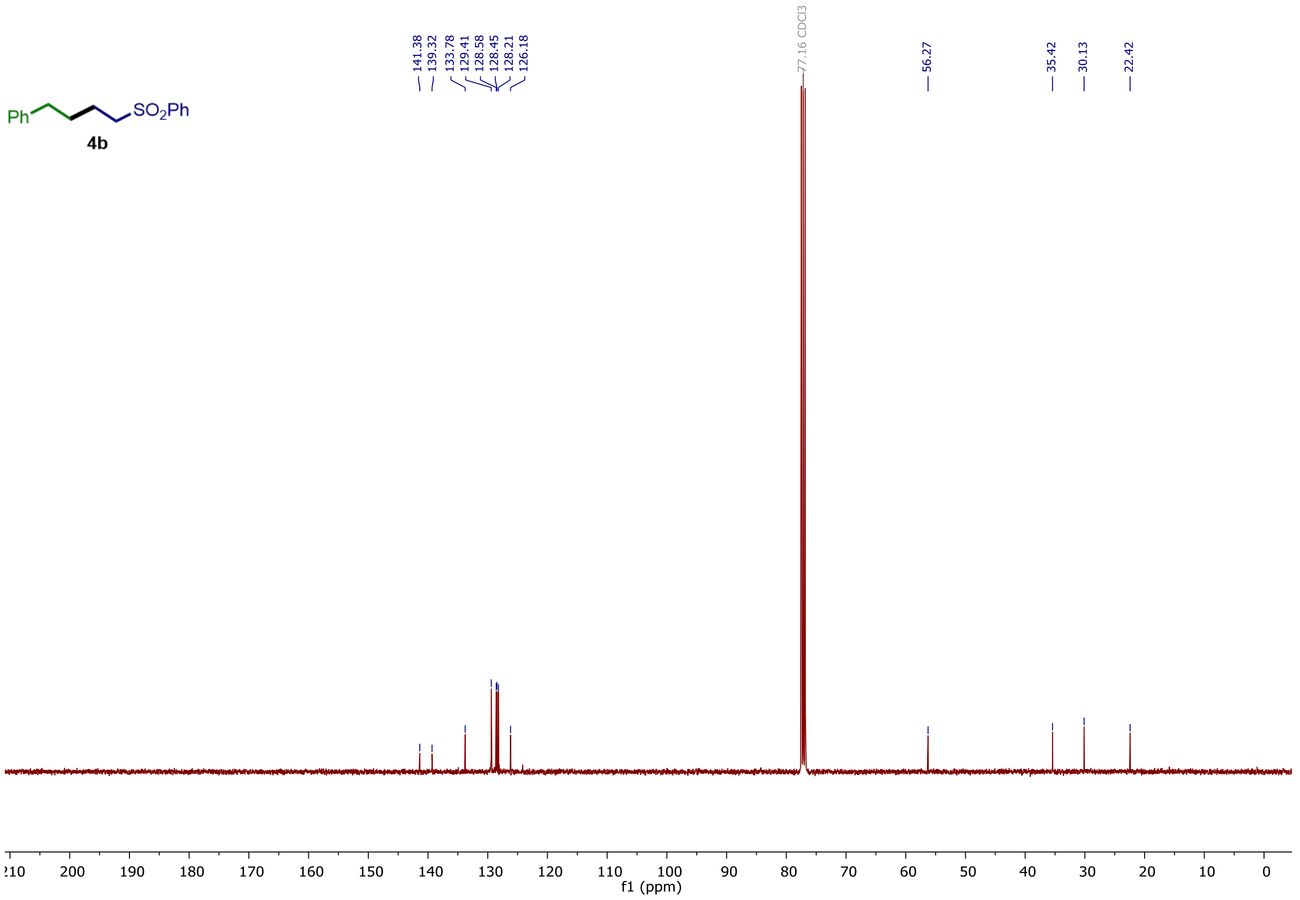
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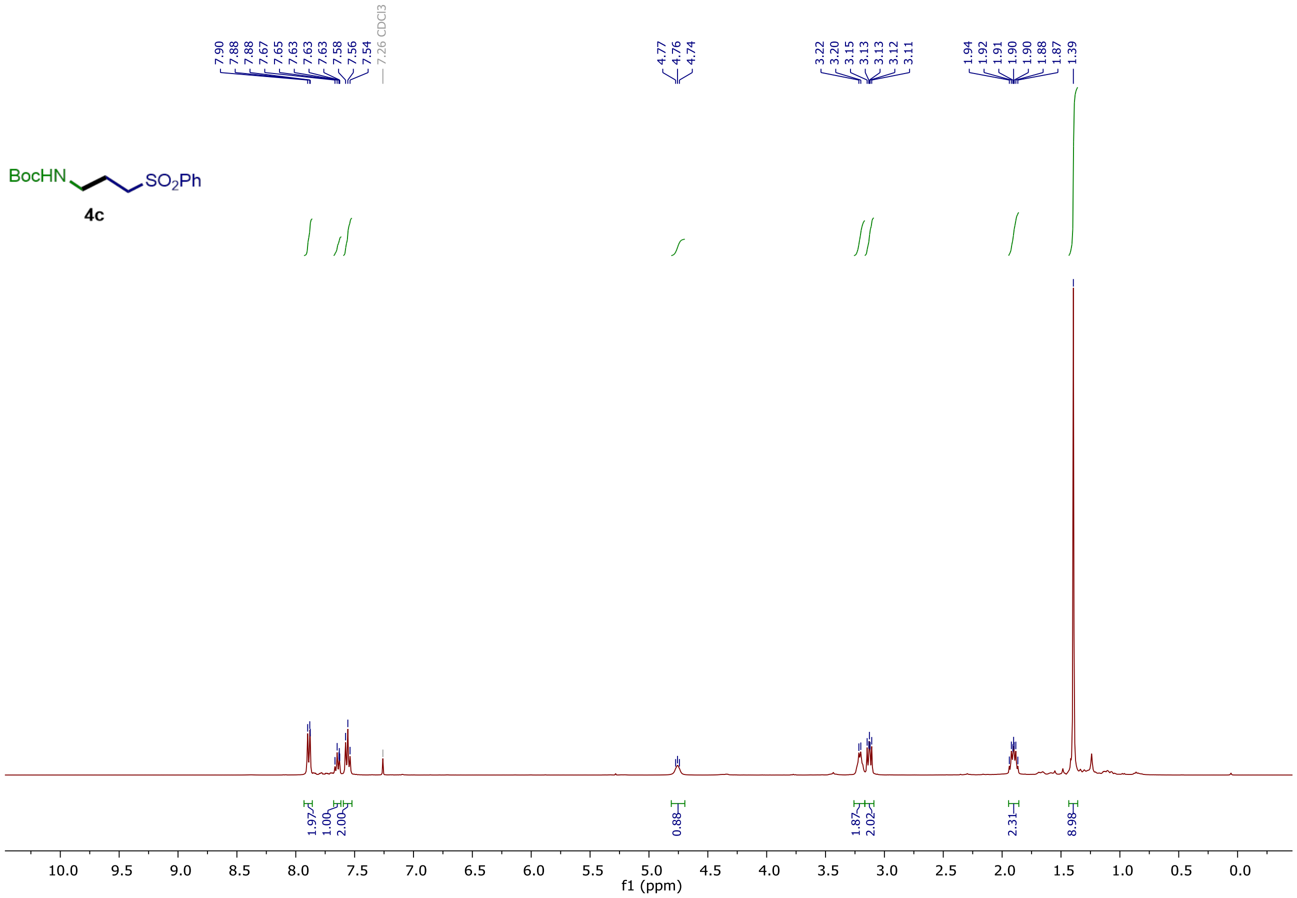
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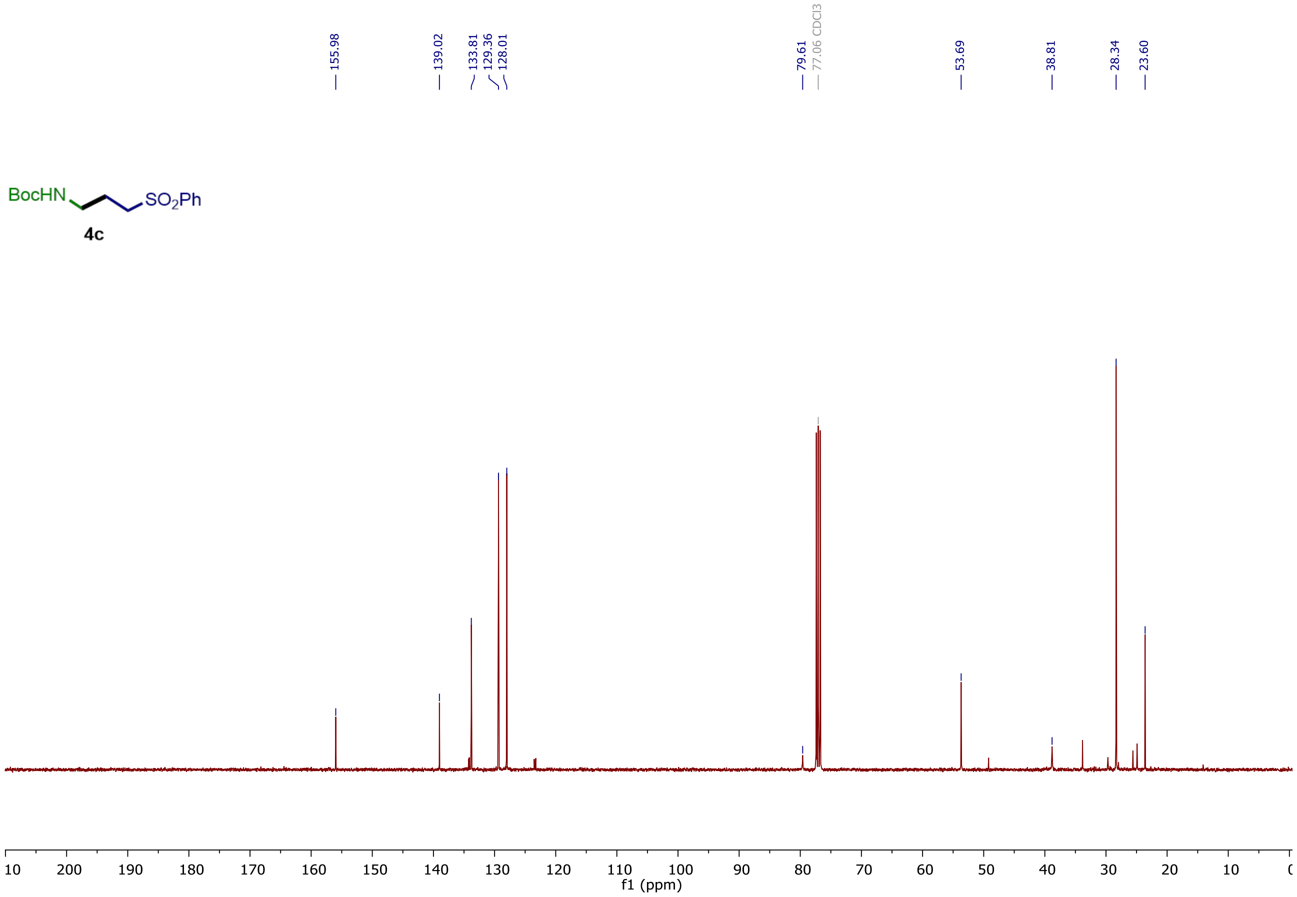
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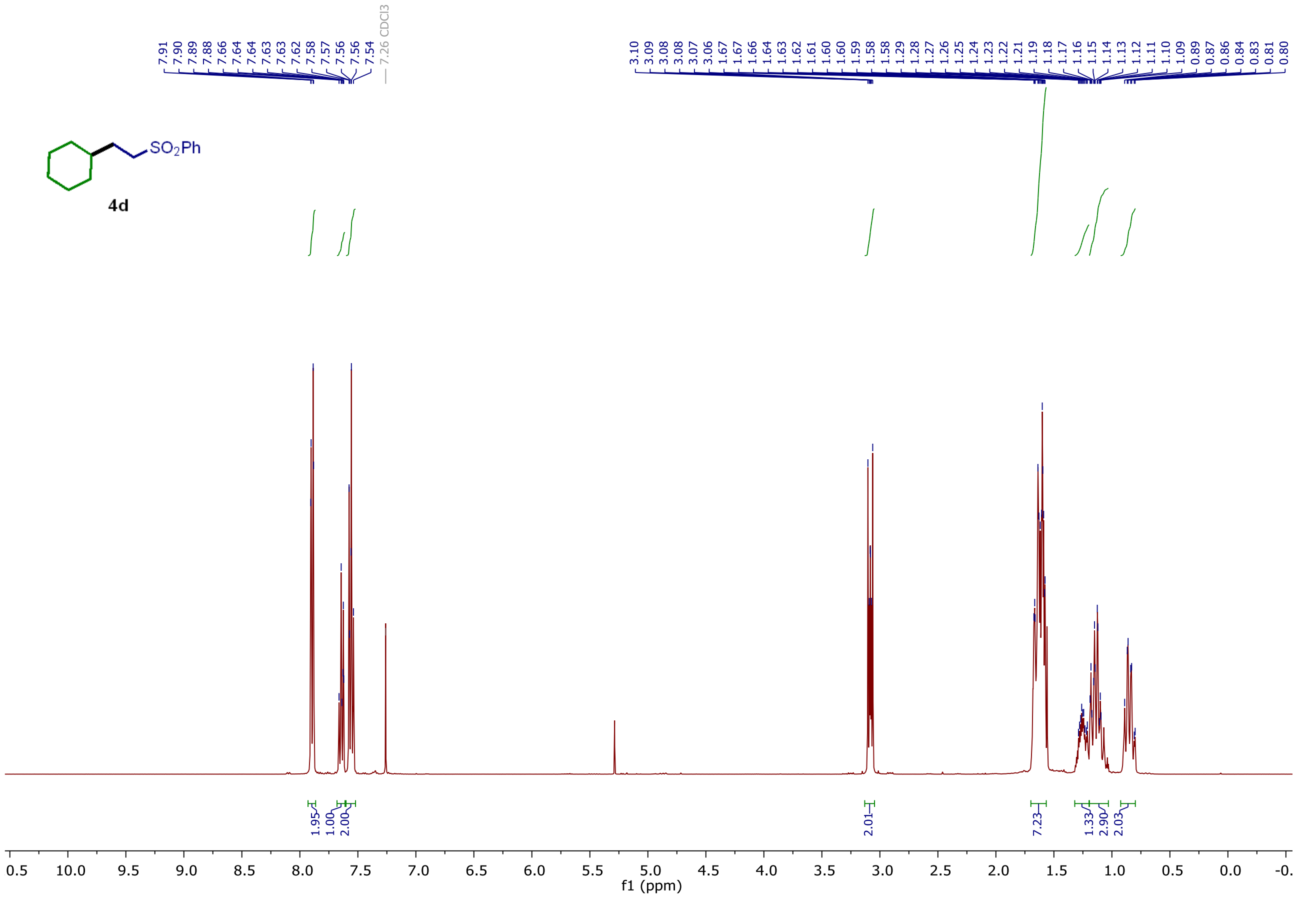
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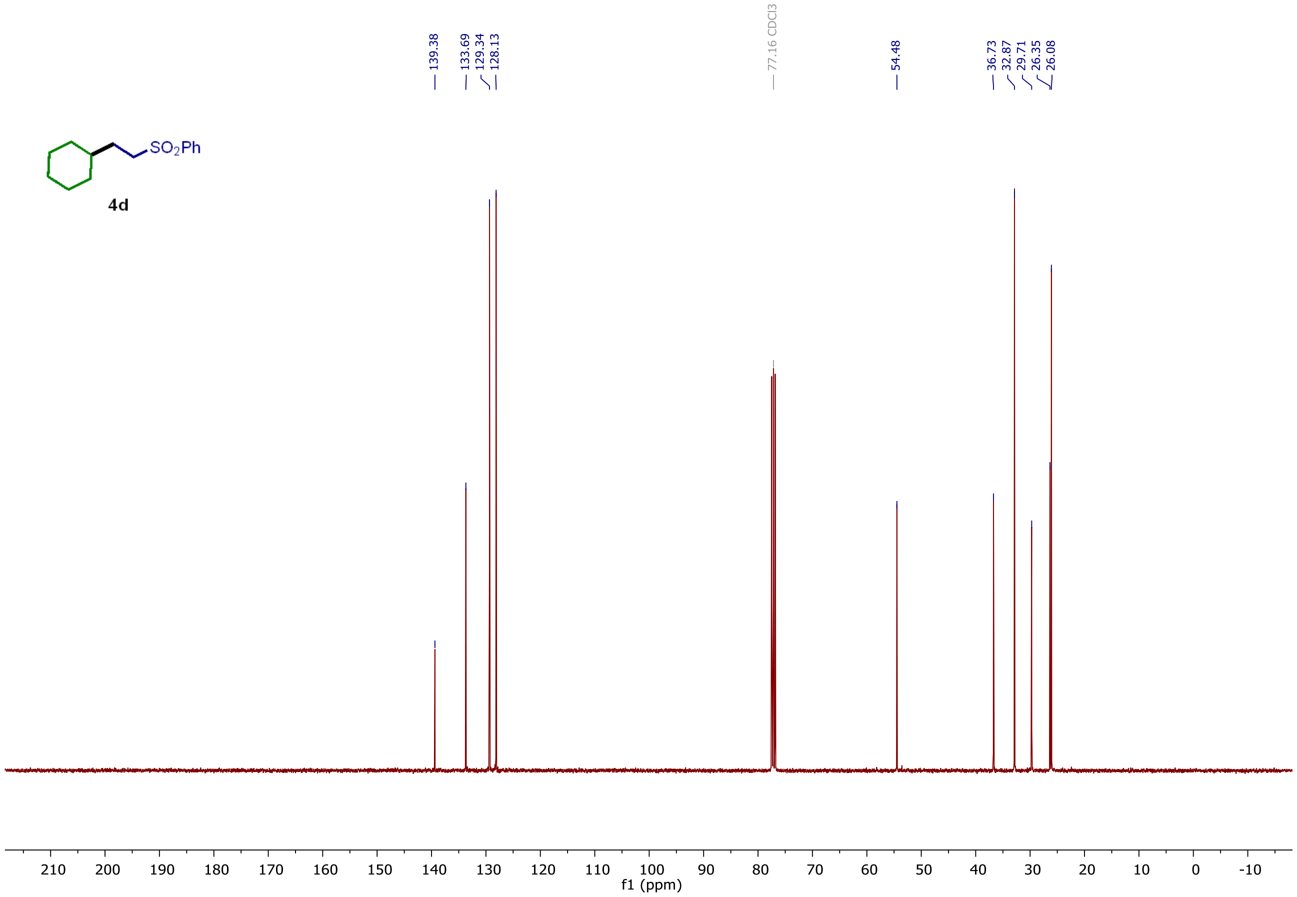
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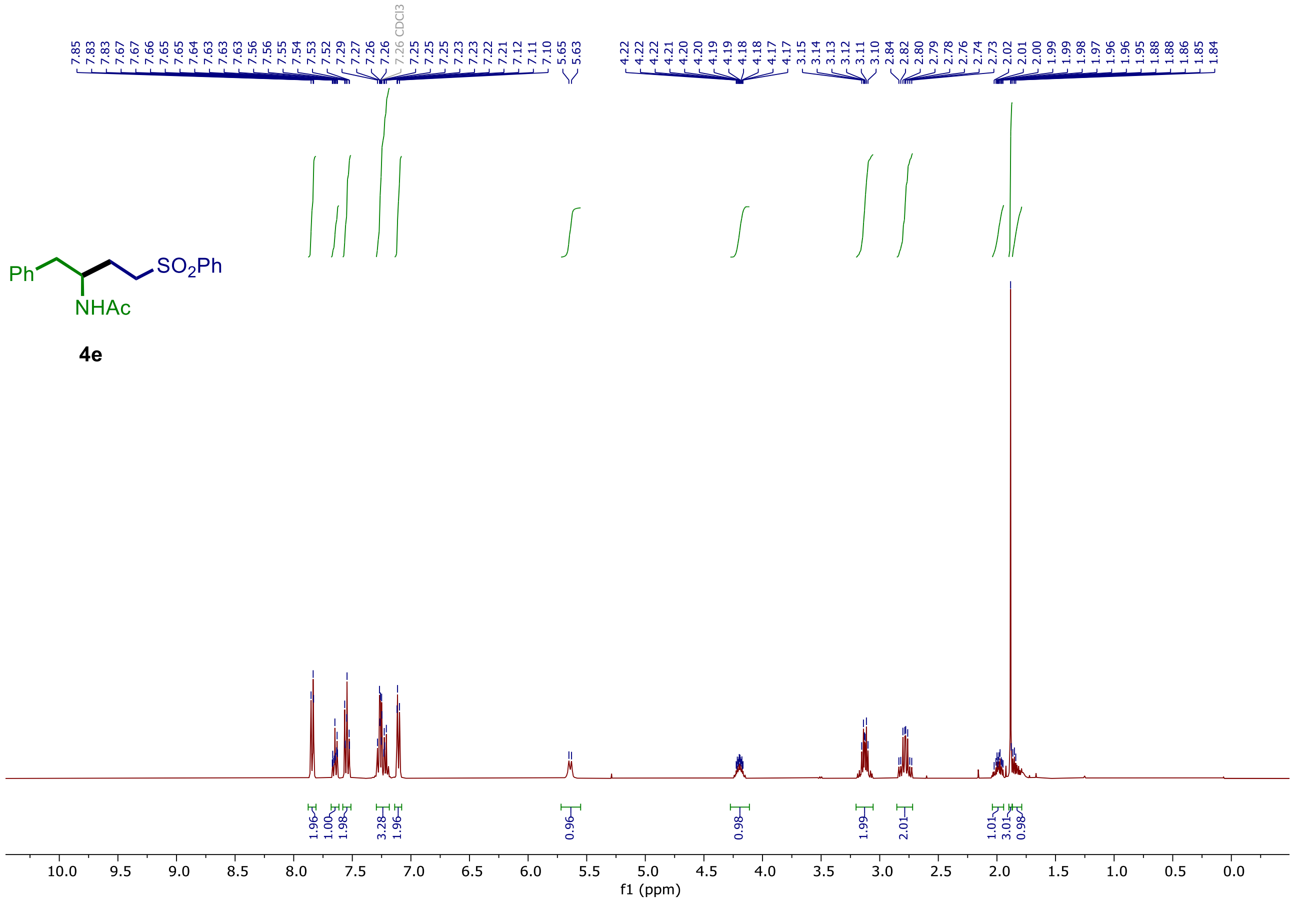
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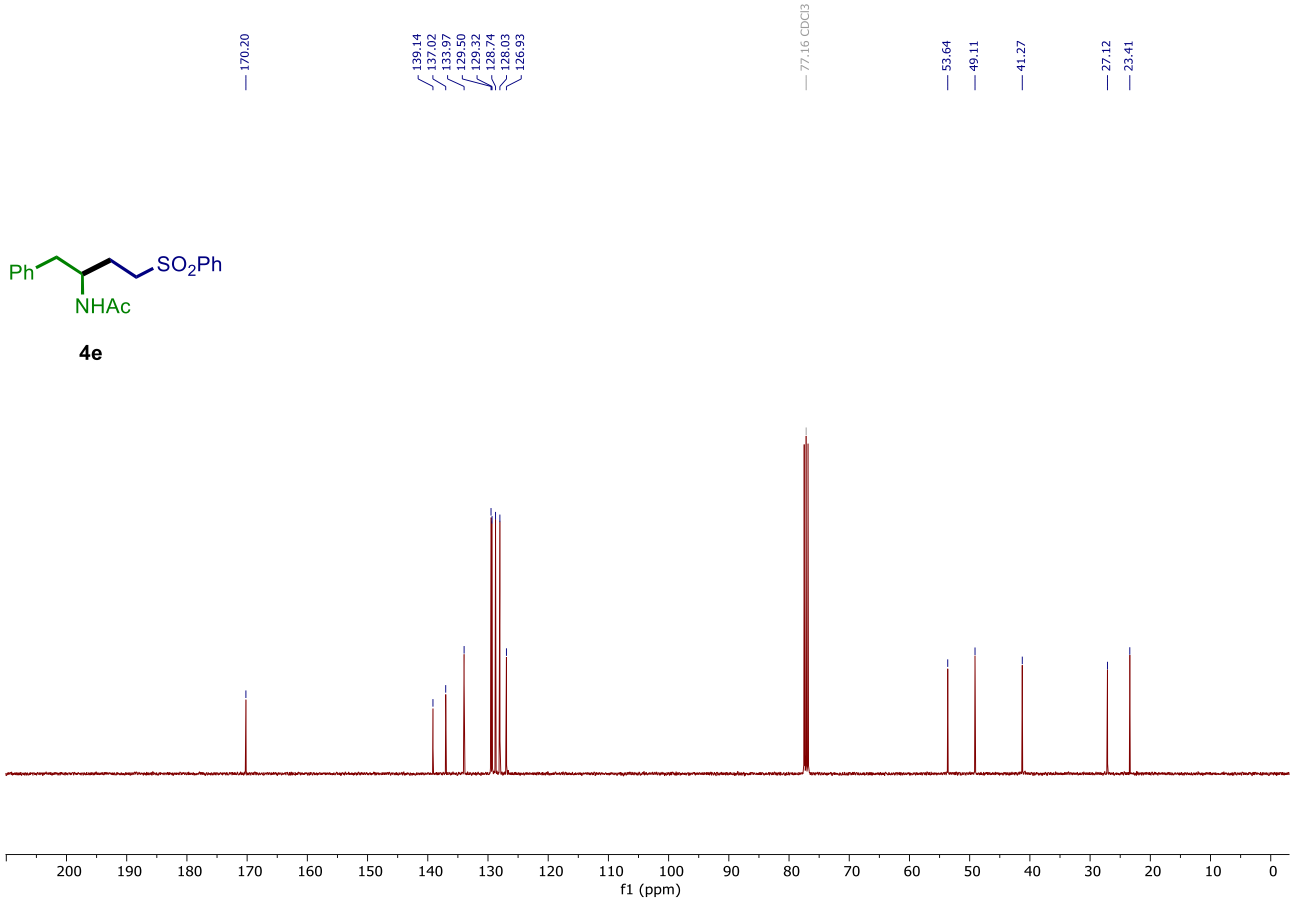
4e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27.12
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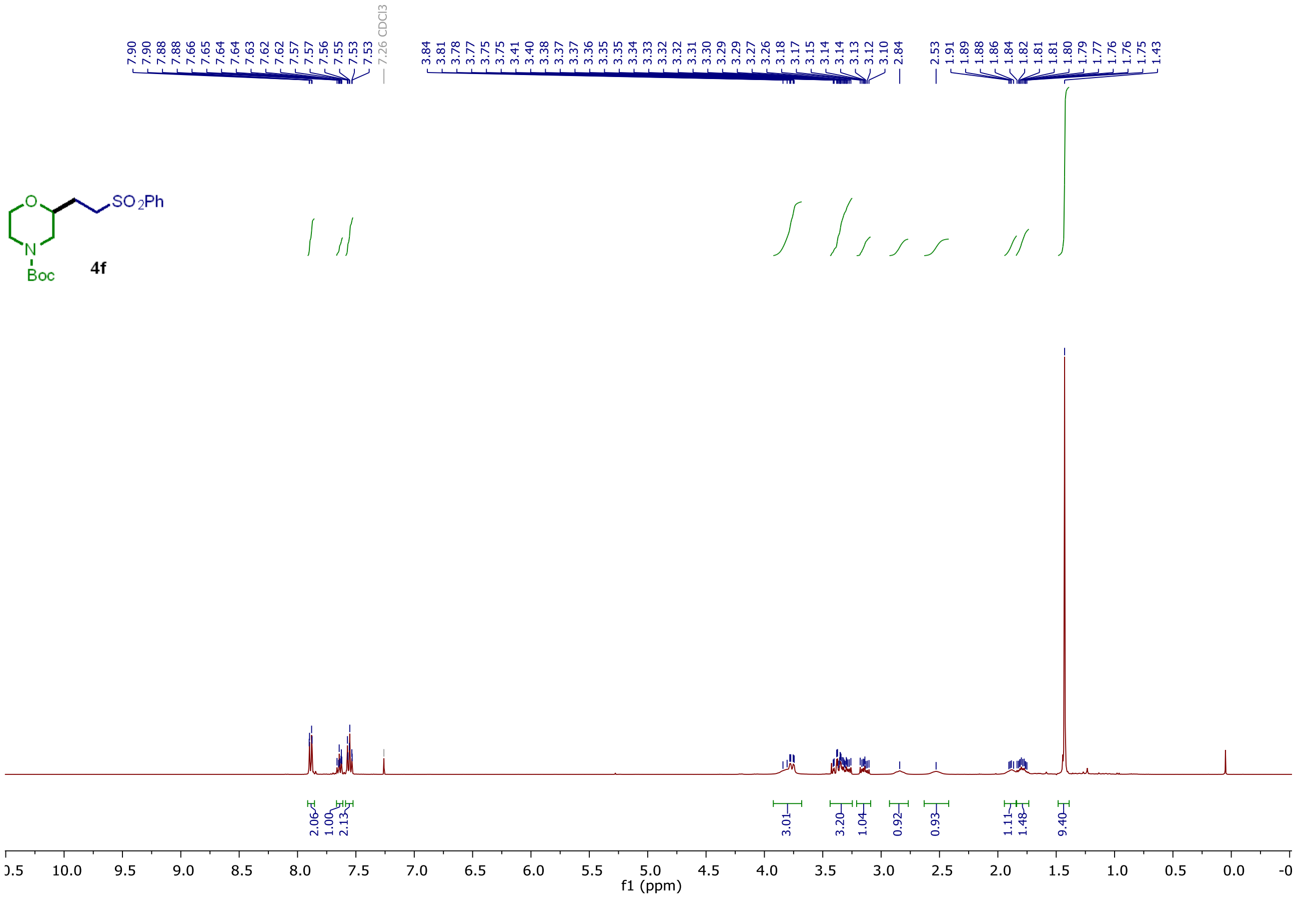
f1 (ppm)

4e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3.0
2.5
2.0
1.5
1.0
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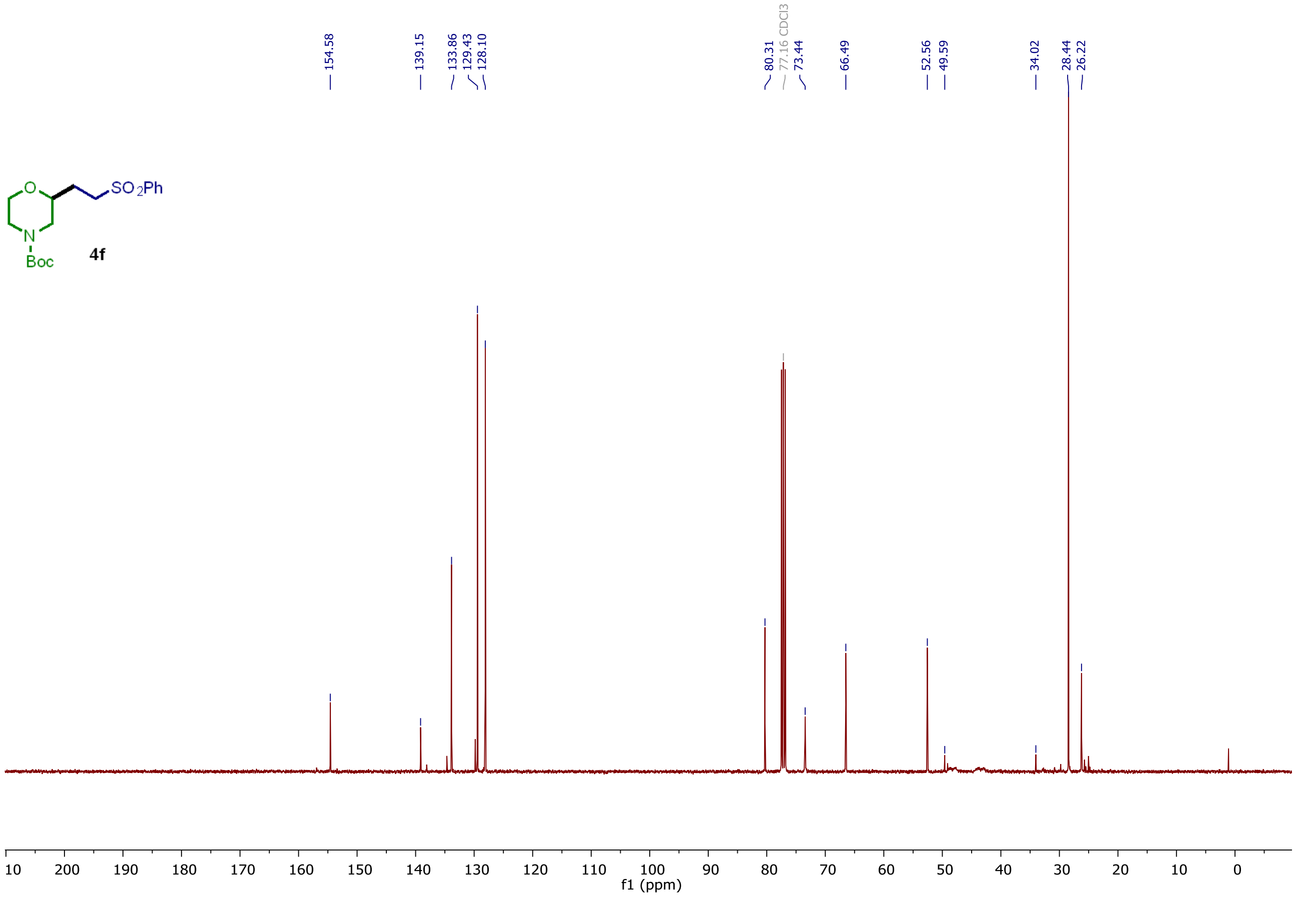
-0
f1 (ppm)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128.10
80.31
77.16 CDCl3
73.44
66.49
52.56
49.59
34.02
28.44
26.22
SO2Ph
O
N
Boc
4f
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
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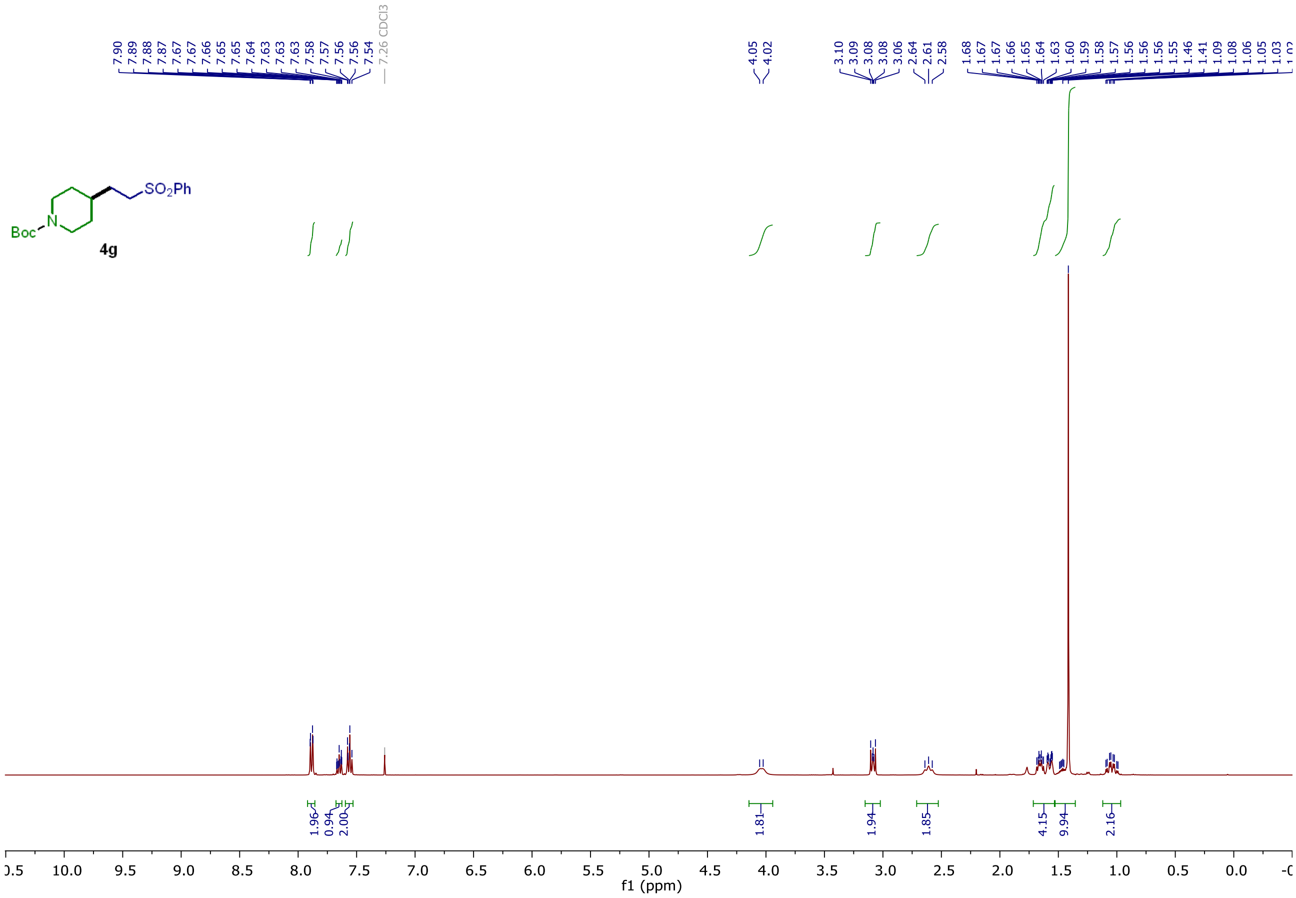
10
0
f1 (ppm)



SO2Ph
Boc
N
4g
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7.89
7.88
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7.67
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7.65
7.65
7.64
7.63
7.63
7.63
7.58
7.57
7.56
7.56
7.54
7.26 CDCl3
4.05
4.02
3.10
3.09
3.08
3.08
3.06
2.64
2.61
2.58
1.68
1.67
1.67
1.66
1.65
1.64
1.63
1.60
1.59
1.58
1.57
1.56
1.56
1.56
1.55
1.46
1.41
1.09
1.08
1.06
1.05
1.03
1.96
0.94
2.00
1.81
1.94
1.85
4.15
9.94
2.16
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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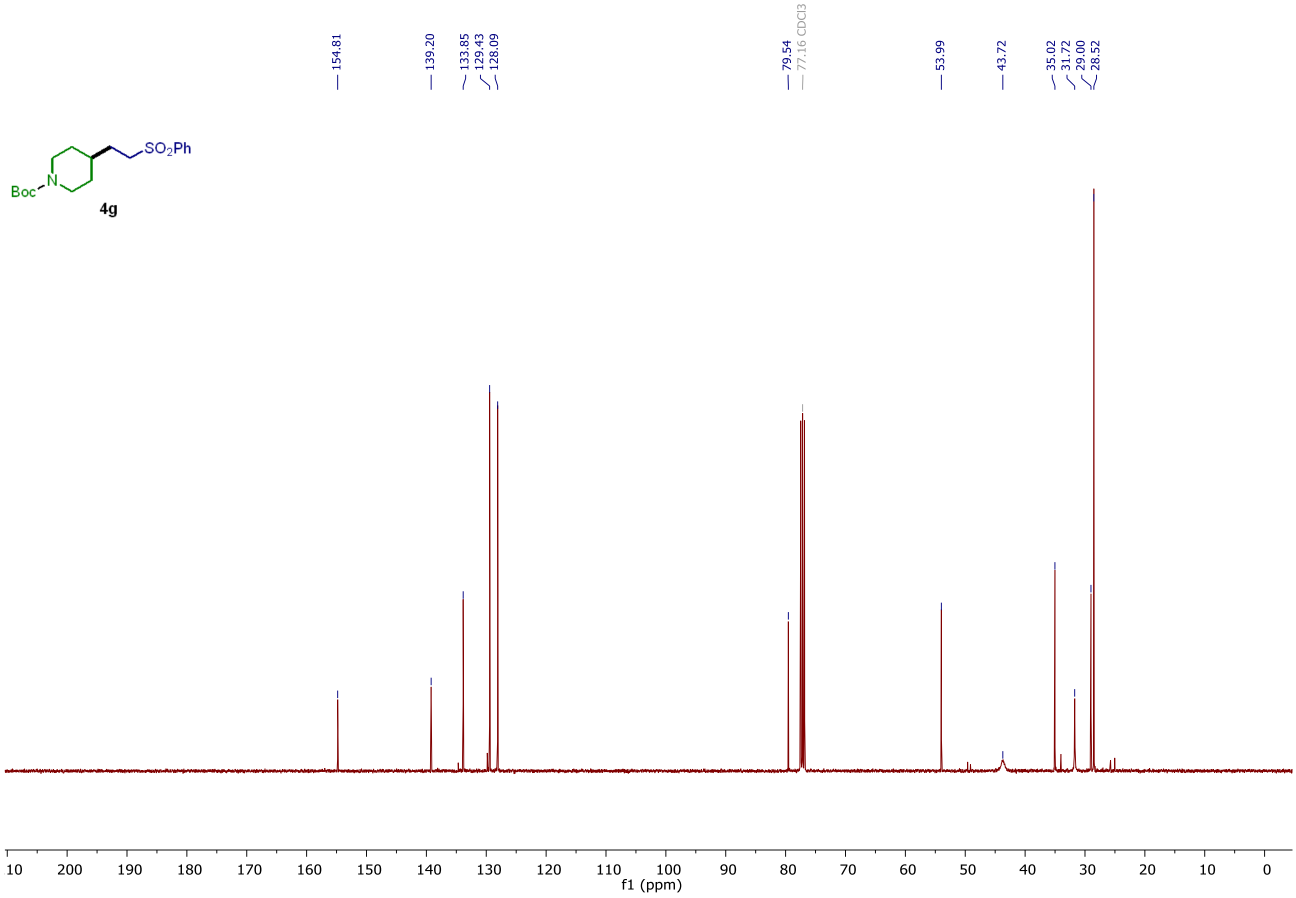
f1 (ppm)



SO2Ph
Boc
N
4g
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128.09
79.54
77.16 CDCl3
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43.72
35.02
31.72
29.00
28.52
200
190
180
170
160
150
140
130
120
110
100
90
80
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50
40
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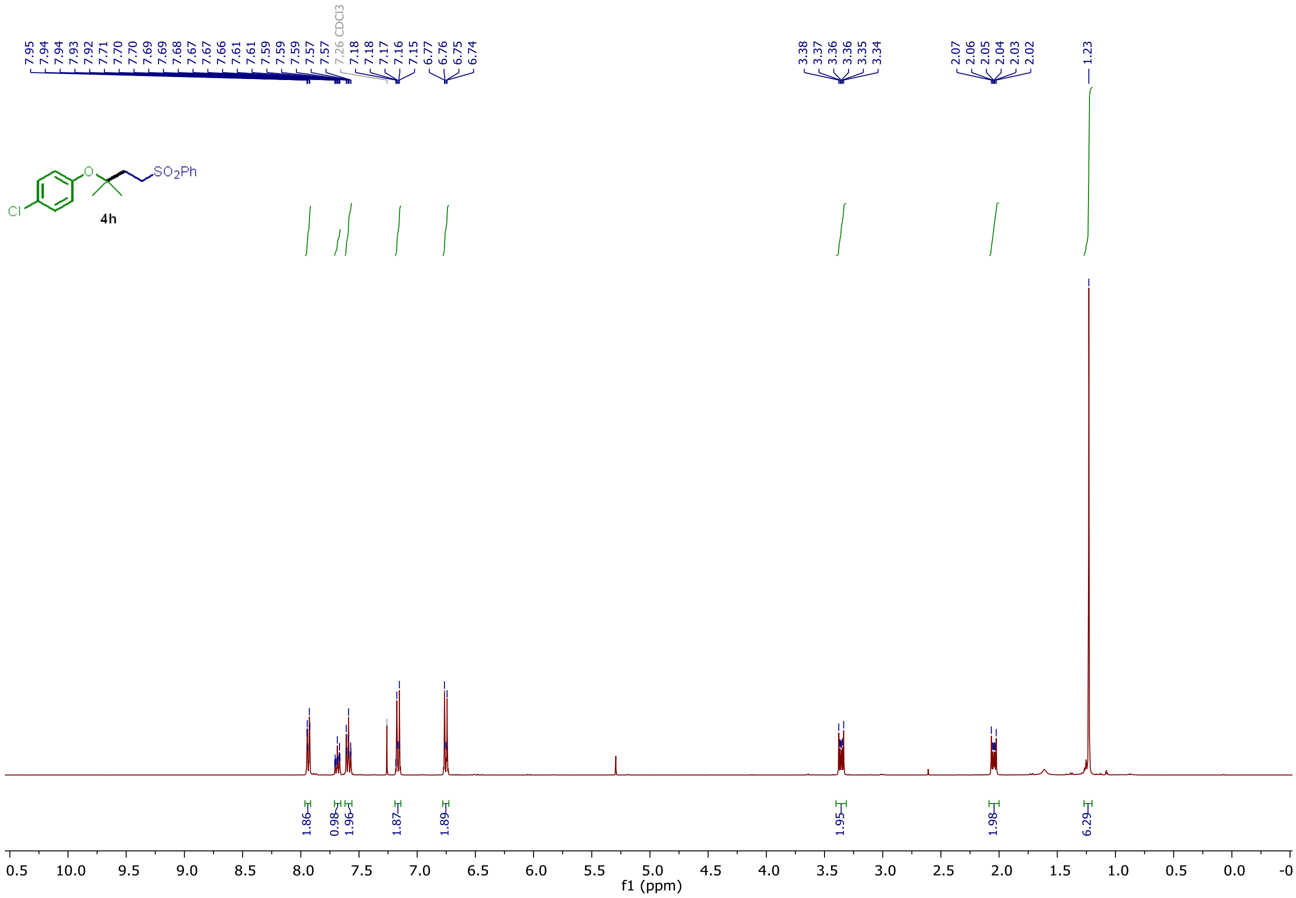
20
10
0
f1 (ppm)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7.68
7.67
7.67
7.66
7.61
7.61
7.59
7.59
7.59
7.57
7.57
7.26 CDCl3
7.18
7.18
7.17
7.16
7.15
6.77
6.76
6.75
6.74
3.38
3.37
3.36
3.36
3.35
3.34
2.07
2.06
2.05
2.04
2.03
2.02
1.23
Cl
O
SO2Ph
4h
1.86
0.98
1.96
1.87
1.89
1.95
1.98
6.29
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
1.5
1.0
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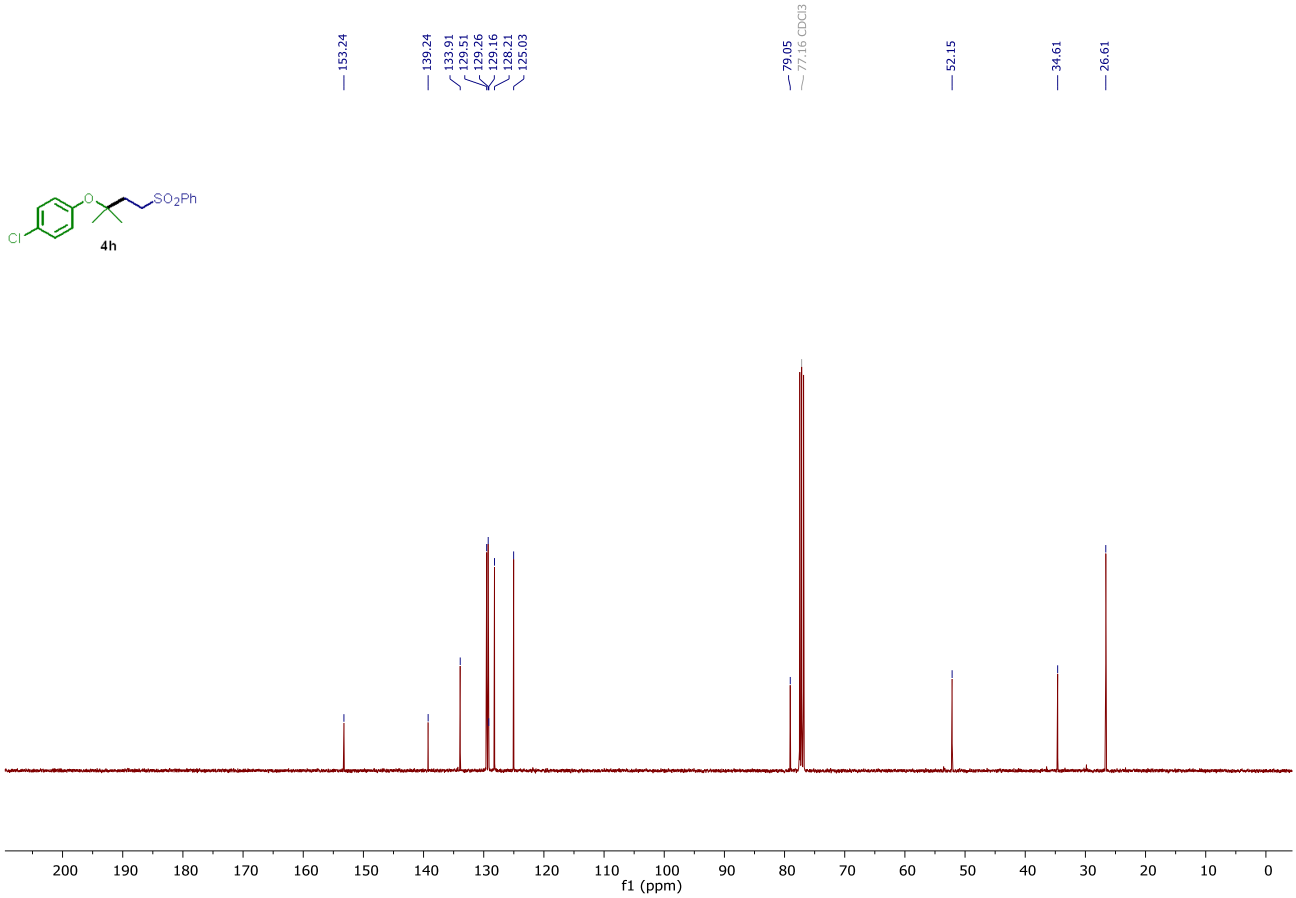
0.0
-0
f1 (ppm)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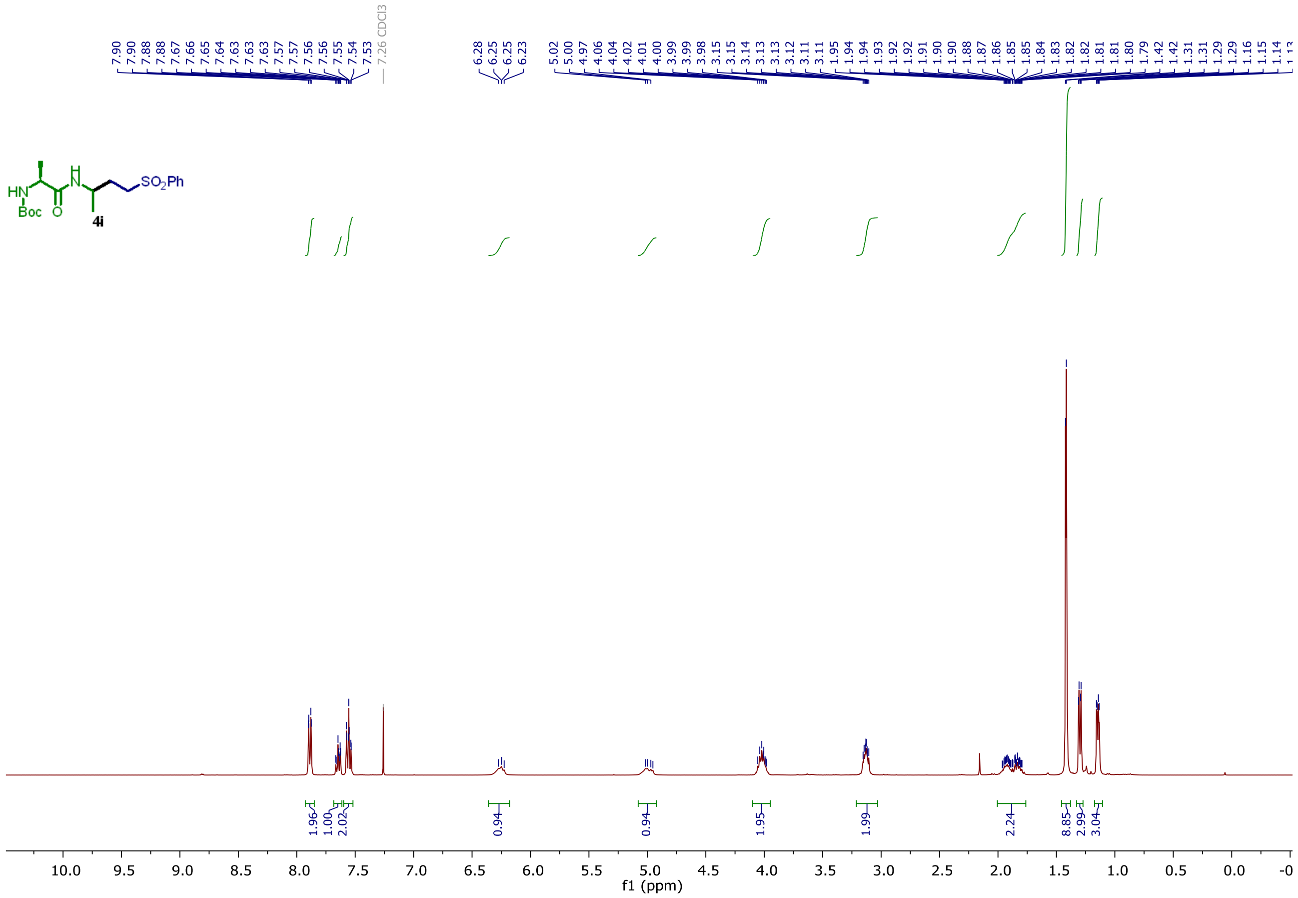
129.16
128.21
125.03
79.05
77.16 CDCl3
52.15
34.61
26.61
Cl
O
SO2Ph
4h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.90
7.88
7.88
7.67
7.65
7.64
7.63
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7.63
7.57
7.56
7.56
7.55
7.54
7.53
7.26 CDCl3
6.28
6.25
6.25
6.23
5.02
5.00
4.97
4.06
4.04
4.02
4.01
4.00
3.99
3.99
3.98
3.15
3.15
3.14
3.13
3.13
3.12
3.11
3.11
1.95
1.94
1.94
1.93
1.92
1.92
1.91
1.90
1.90
1.88
1.87
1.86
1.85
1.85
1.84
1.83
1.82
1.82
1.81
1.81
1.80
1.79
1.42
1.42
1.31
1.31
1.29
1.16
1.15
1.14
HN
Boc
O
H
N
SO2Ph
4i
1.96
1.00
2.02
0.94
0.94
1.95
1.99
2.24
8.85
2.99
3.04
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
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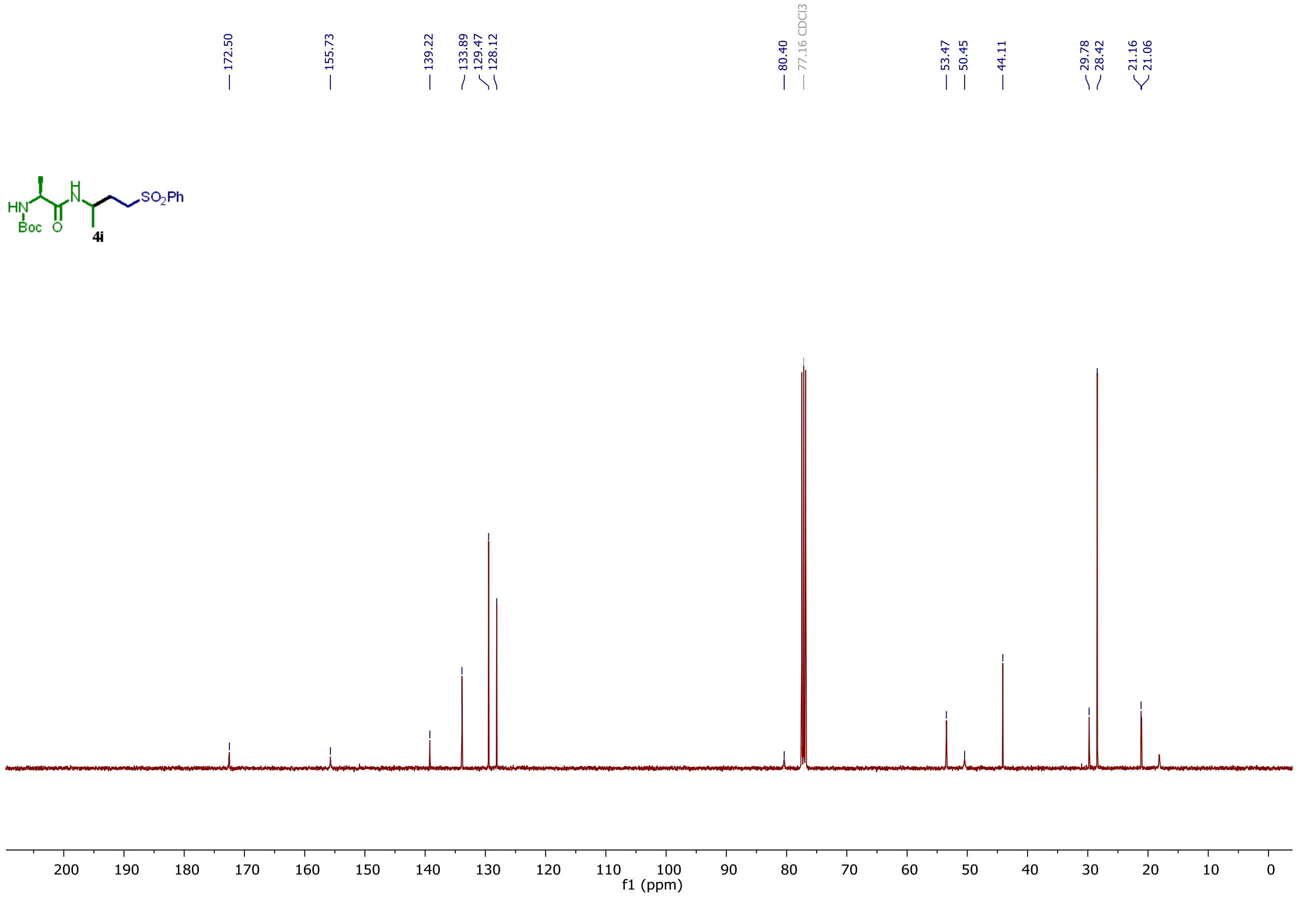
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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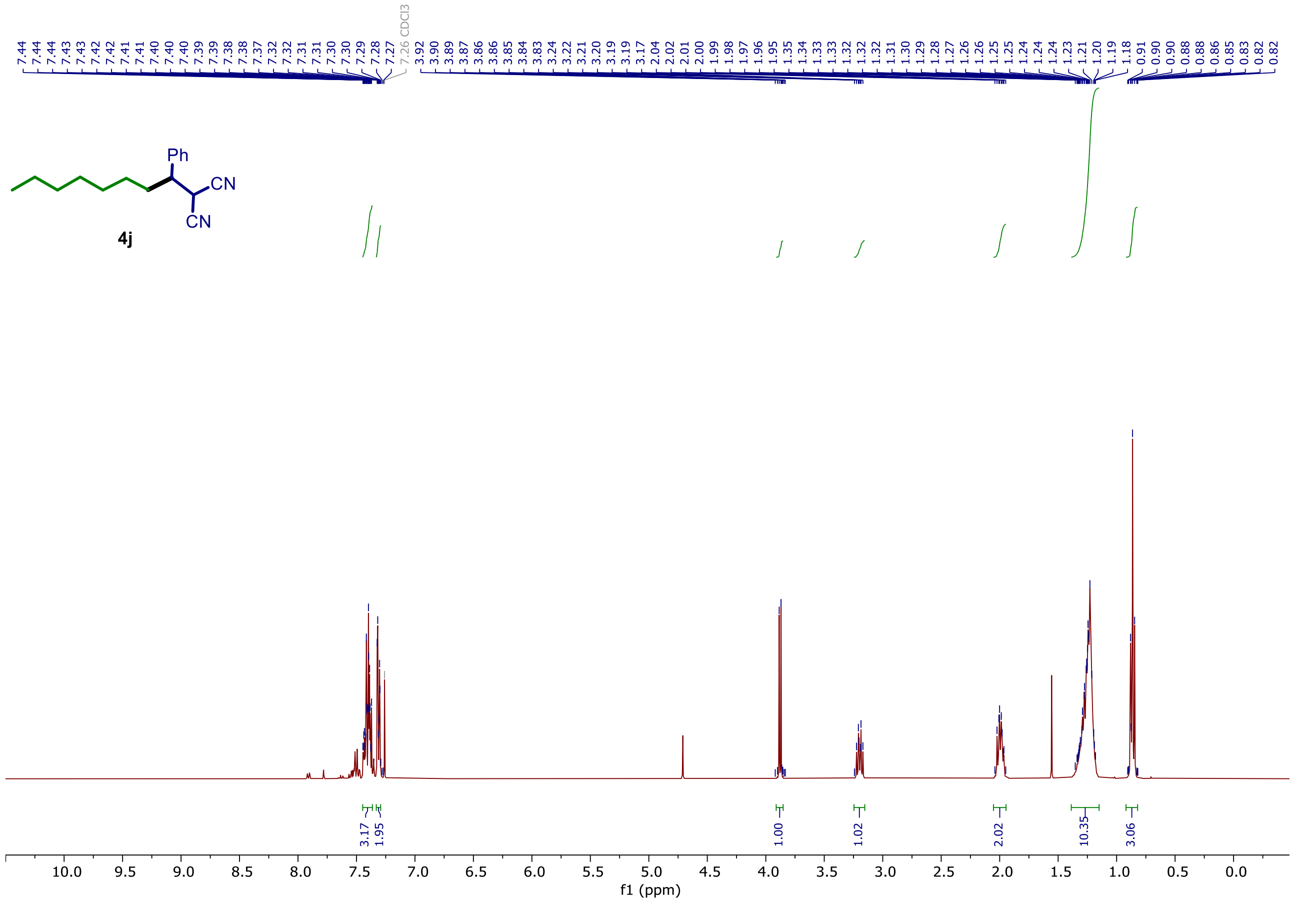
129.47
128.12
80.40
77.16 CDCl3
53.47
50.45
44.11
29.78
28.42
21.16
21.06
HN
Boc
O
H
N
SO2Ph
4i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


4j
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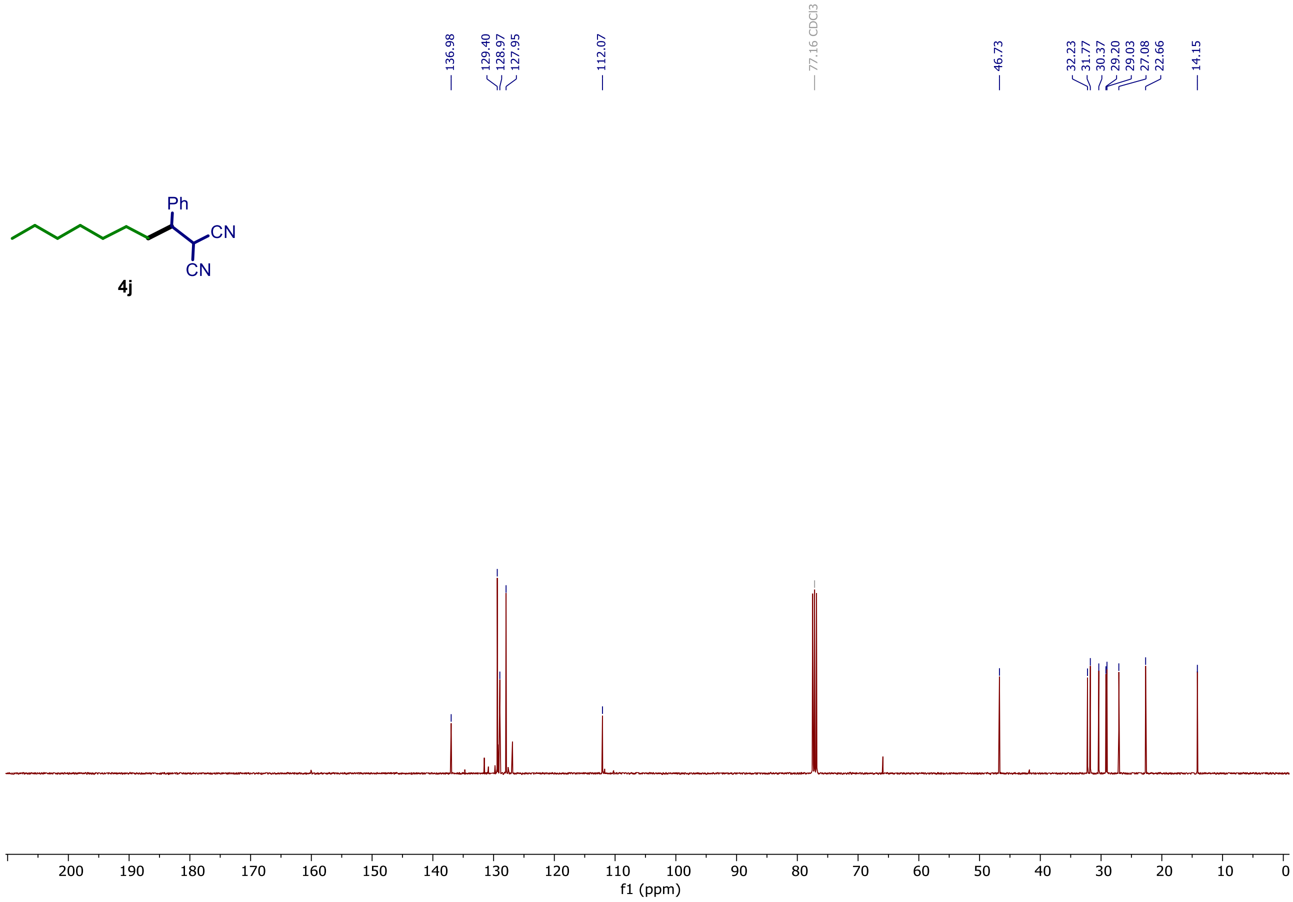
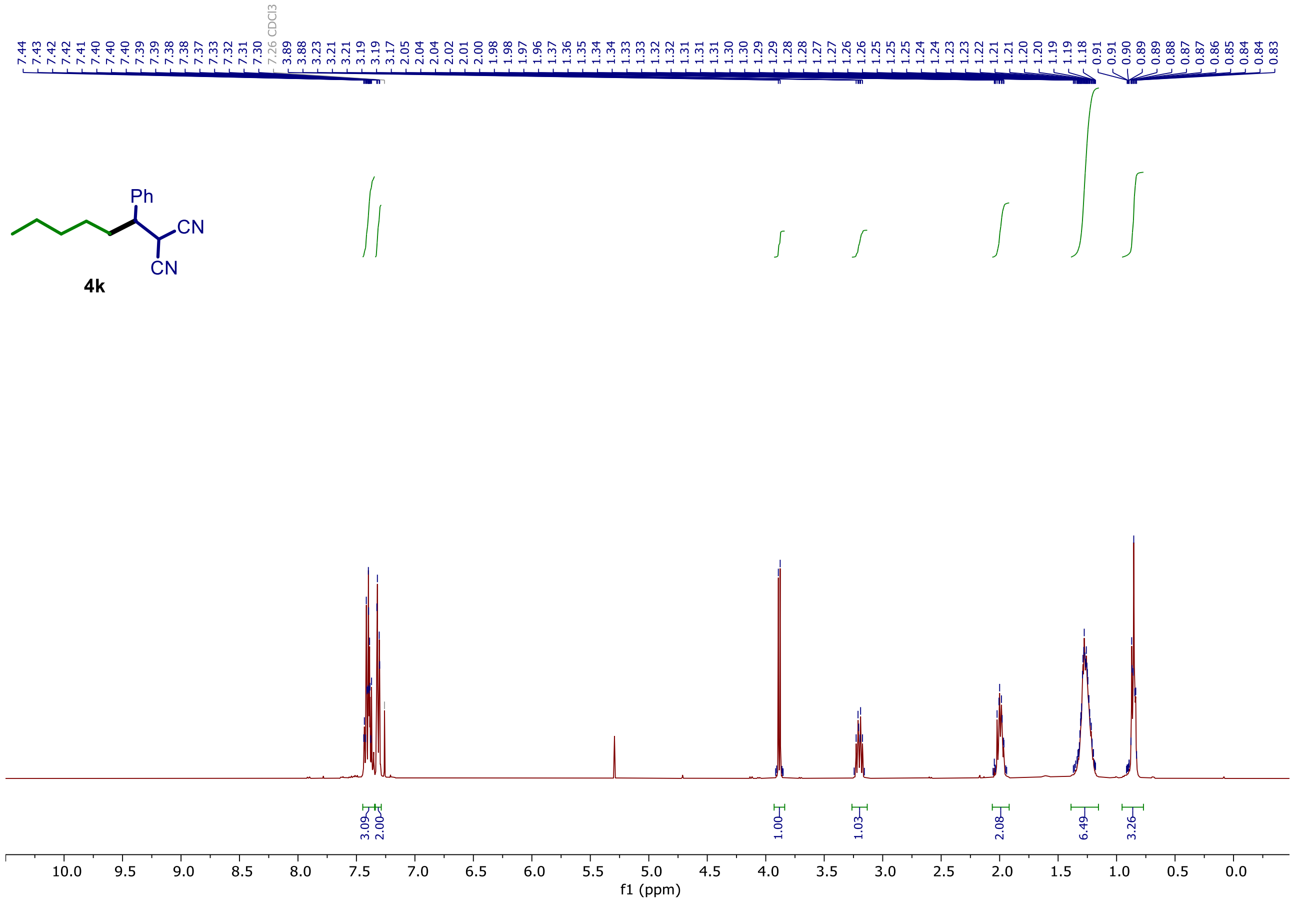
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.37
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.27
7.26 CDCl3
3.92
3.90
3.89
3.87
3.86
3.85
3.84
3.83
3.24
3.22
3.21
3.20
3.19
3.19
3.17
2.04
2.02
2.01
2.00
1.99
1.98
1.97
1.96
1.95
1.35
1.34
1.33
1.33
1.32
1.32
1.32
1.31
1.30
1.29
1.28
1.27
1.26
1.26
1.25
1.25
1.24
1.24
1.23
1.21
1.20
1.19
1.18
0.91
0.90
0.90
0.88
0.86
0.85
0.83
0.82
0.82
Ph
CN
CN
3.17
1.95
1.00
1.02
2.02
10.35
3.06
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
f1 (ppm)


4j
136.98
129.40
128.97
127.95
112.07
77.16 CDCl3
46.73
32.23
31.77
30.37
29.20
29.03
27.08
22.66
14.15
Ph
CN
CN
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.43
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7.40
7.39
7.39
7.38
7.38
7.37
7.33
7.32
7.31
7.30
7.26 CDCl3
3.89
3.88
3.23
3.21
3.21
3.19
3.19
3.17
2.05
2.04
2.04
2.02
2.01
2.00
1.98
1.98
1.97
1.96
1.37
1.36
1.35
1.34
1.34
1.33
1.33
1.32
1.31
1.31
1.31
1.30
1.30
1.29
1.29
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1.28
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1.27
1.26
1.26
1.25
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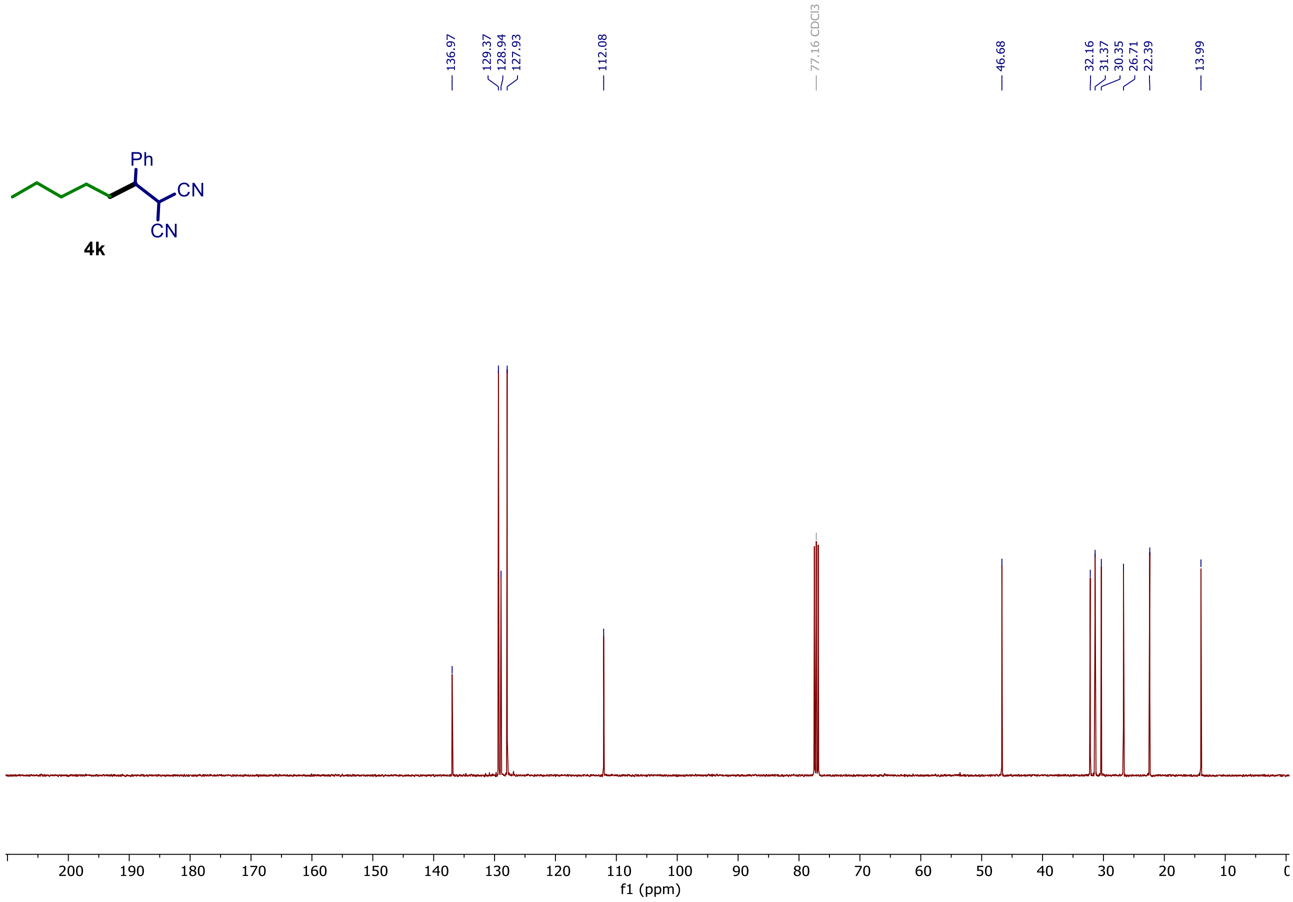
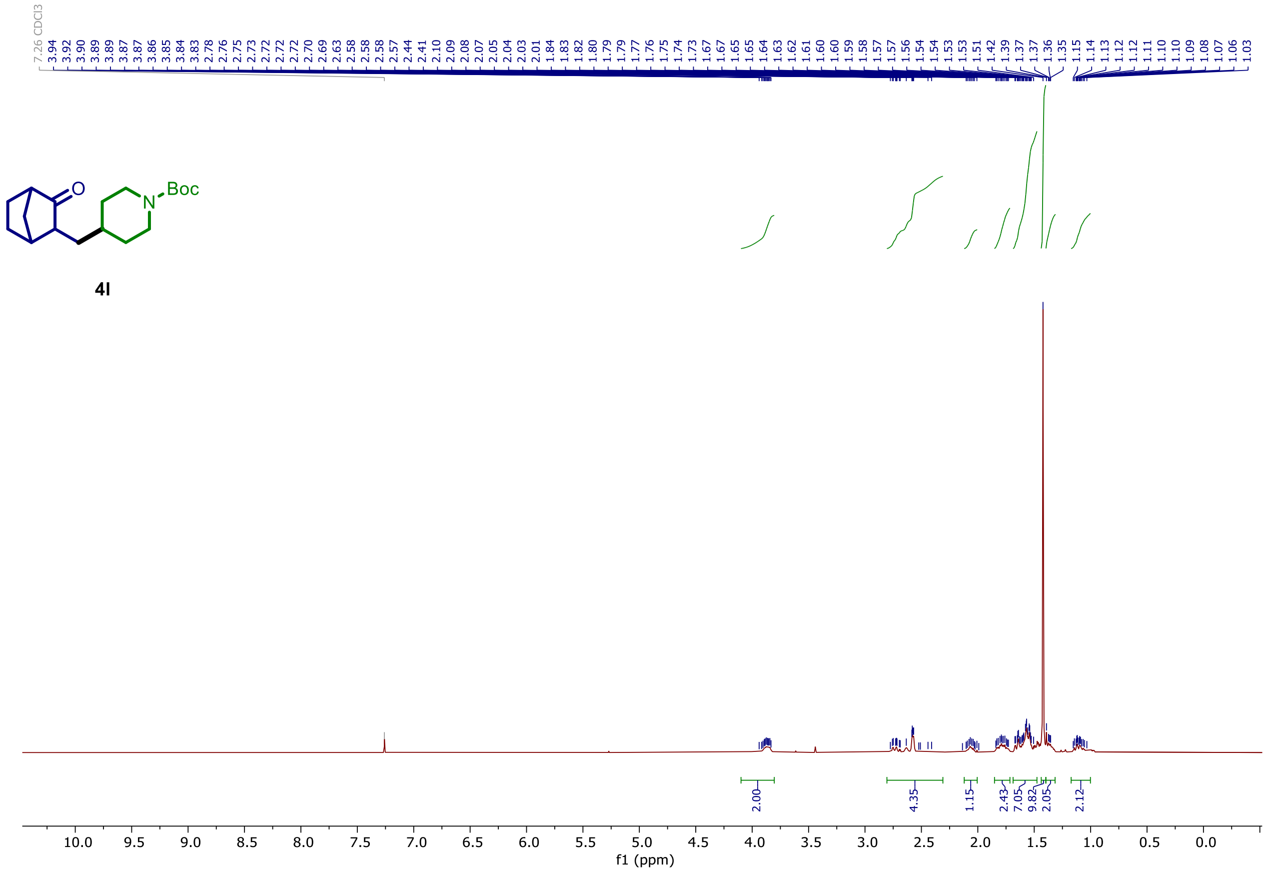
1.25
1.24
1.24
1.23
1.23
1.22
1.21
1.21
1.20
1.20
1.19
1.19
1.18
0.91
0.91
0.90
0.89
0.89
0.88
0.87
0.87
0.86
0.85
0.84
0.84
0.83
Ph
CN
CN
4k
3.09
2.00
1.00
1.03
2.08
6.49
3.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


136.97
129.37
128.94
127.93
112.08
77.16 CDCl3
46.68
32.16
31.37
30.35
26.71
22.39
13.99
Ph
CN
CN
4k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4l
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3.94
3.92
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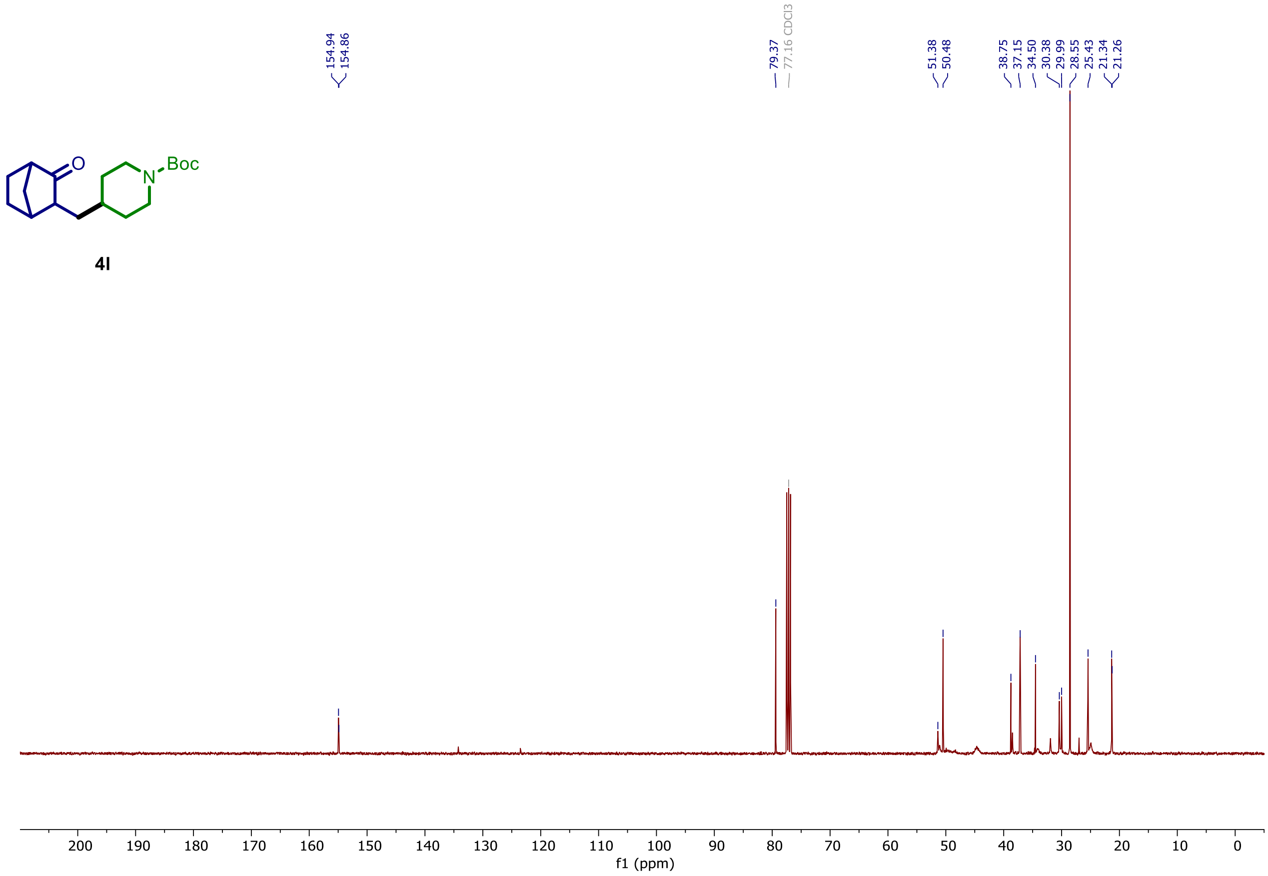
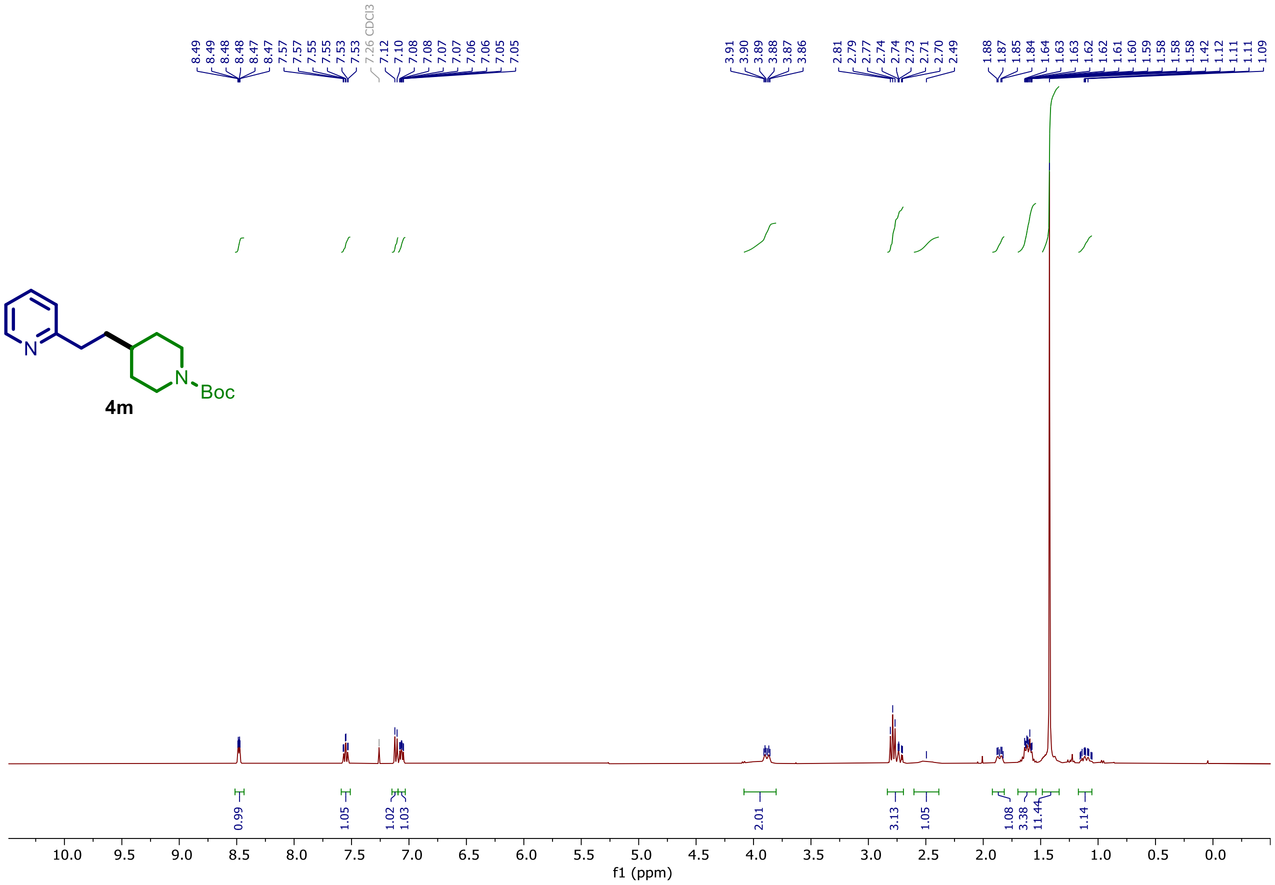
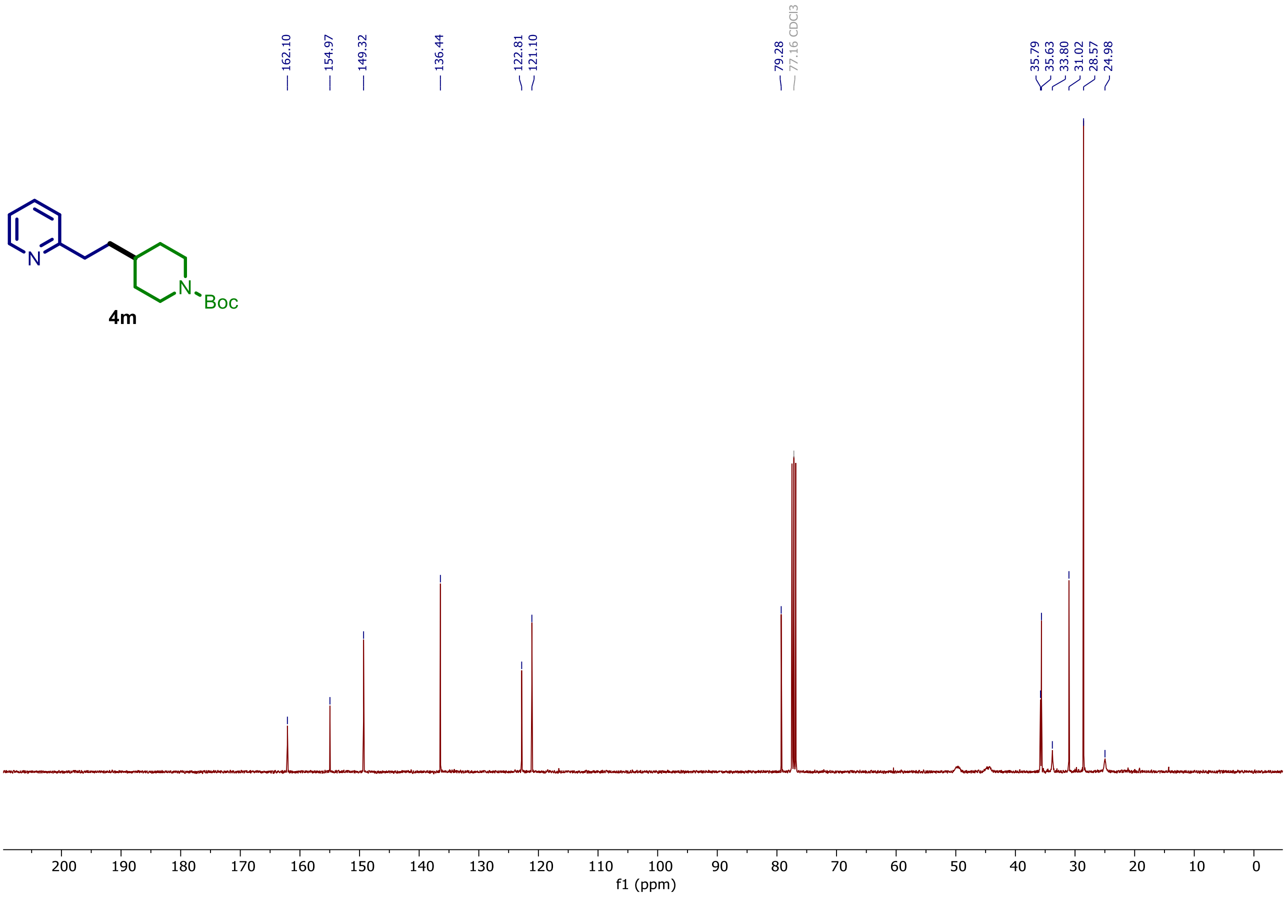
3.89
3.89
3.87
3.87
3.86
3.85
3.84
3.83
2.78
2.76
2.75
2.73
2.72
2.72
2.72
2.70
2.69
2.63
2.58
2.58
2.58
2.57
2.44
2.41
2.10
2.09
2.08
2.07
2.05
2.04
2.03
2.01
1.84
1.83
1.82
1.80
1.79
1.79
1.77
1.76
1.75
1.74
1.73
1.67
1.65
1.65
1.64
1.63
1.62
1.61
1.60
1.60
1.59
1.58
1.57
1.57
1.56
1.54
1.54
1.53
1.53
1.51
1.42
1.39
1.37
1.37
1.36
1.35
1.15
1.14
1.13
1.12
1.12
1.11
1.11
1.10
1.10
1.09
1.08
1.07
1.06
1.03
2.00
4.35
1.15
2.43
7.05
9.82
2.05
2.12
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
f1 (ppm)



4l
154.94
154.86
79.37
77.16 CDCl3
51.38
50.48
38.75
37.15
34.50
30.38
29.99
28.55
25.43
21.34
21.26
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.49
8.49
8.48
8.48
8.47
7.57
7.57
7.55
7.55
7.53
7.53
7.26 CDCl3
7.12
7.10
7.08
7.08
7.07
7.07
7.06
7.06
7.05
7.05
3.91
3.90
3.89
3.88
3.87
3.86
2.81
2.79
2.77
2.74
2.74
2.73
2.71
2.70
2.49
1.88
1.87
1.85
1.84
1.64
1.63
1.63
1.62
1.62
1.61
1.60
1.59
1.58
1.58
1.58
1.42
1.12
1.11
1.11
1.09
N
Boc
4m
0.99
1.05
1.02
1.03
2.01
3.13
1.05
1.08
3.38
11.44
1.14
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
f1 (ppm)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136.44
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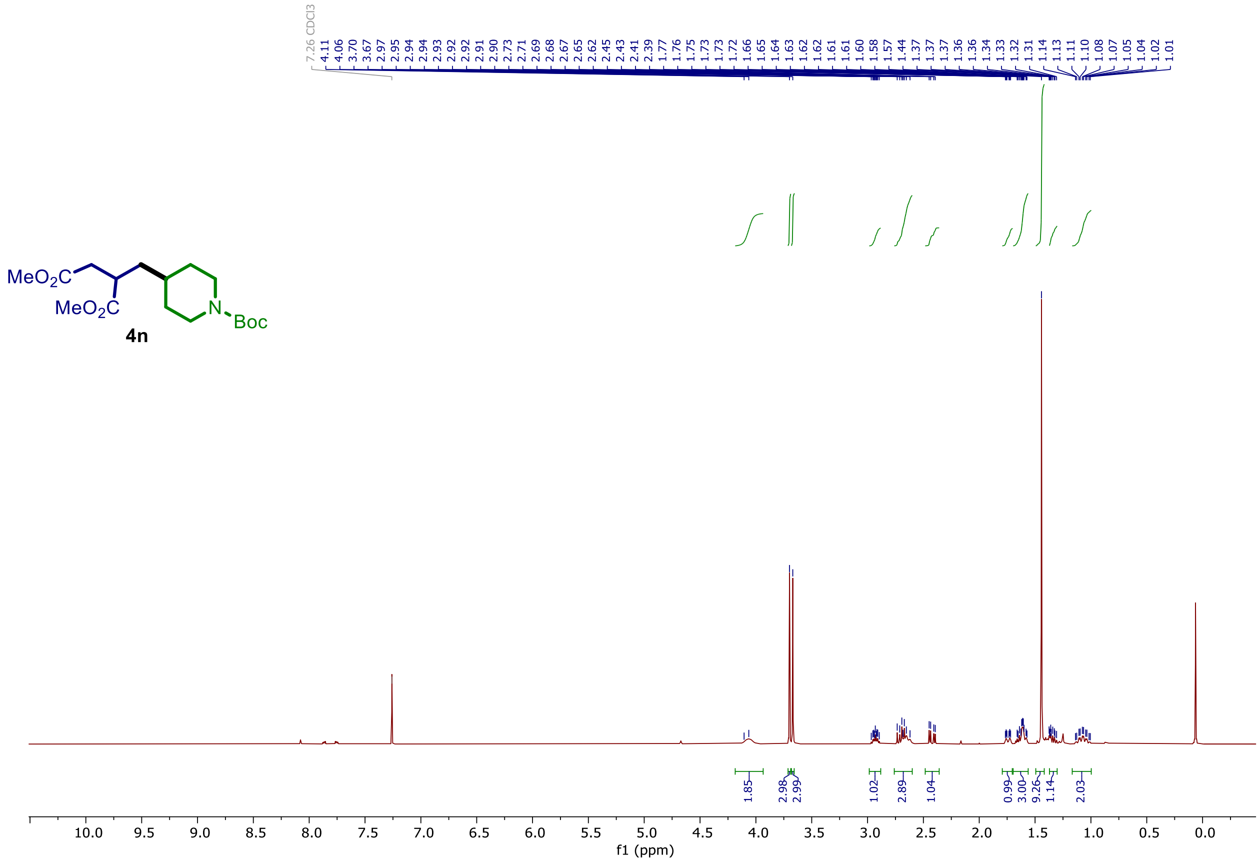
121.10
79.28
77.16 CDCl3
35.79
35.63
33.80
31.02
28.57
24.98
N
Boc
4m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
4.11
4.06
3.70
3.67
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2.95
2.94
2.94
2.93
2.92
2.92
2.91
2.90
2.73
2.71
2.69
2.68
2.67
2.65
2.62
2.45
2.43
2.41
2.39
1.77
1.76
1.75
1.73
1.73
1.72
1.66
1.65
1.64
1.63
1.62
1.62
1.61
1.61
1.60
1.58
1.57
1.44
1.37
1.37
1.37
1.36
1.34
1.33
1.32
1.31
1.14
1.13
1.11
1.10
1.08
1.07
1.05
1.04
1.02
1.01
MeO2C
MeO2C
N
Boc
4n
1.85
2.98
2.99
1.02
2.89
1.04
0.99
3.00
9.26
1.14
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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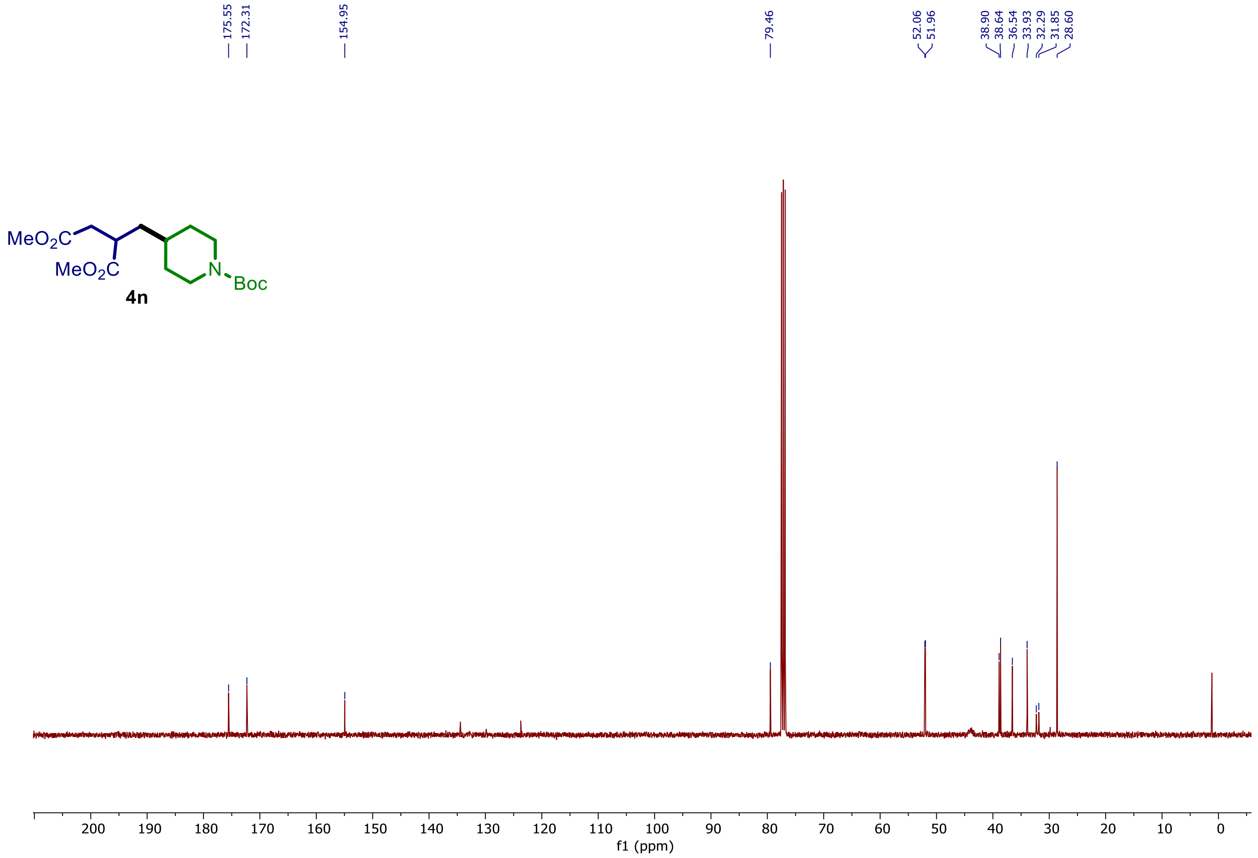
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.55
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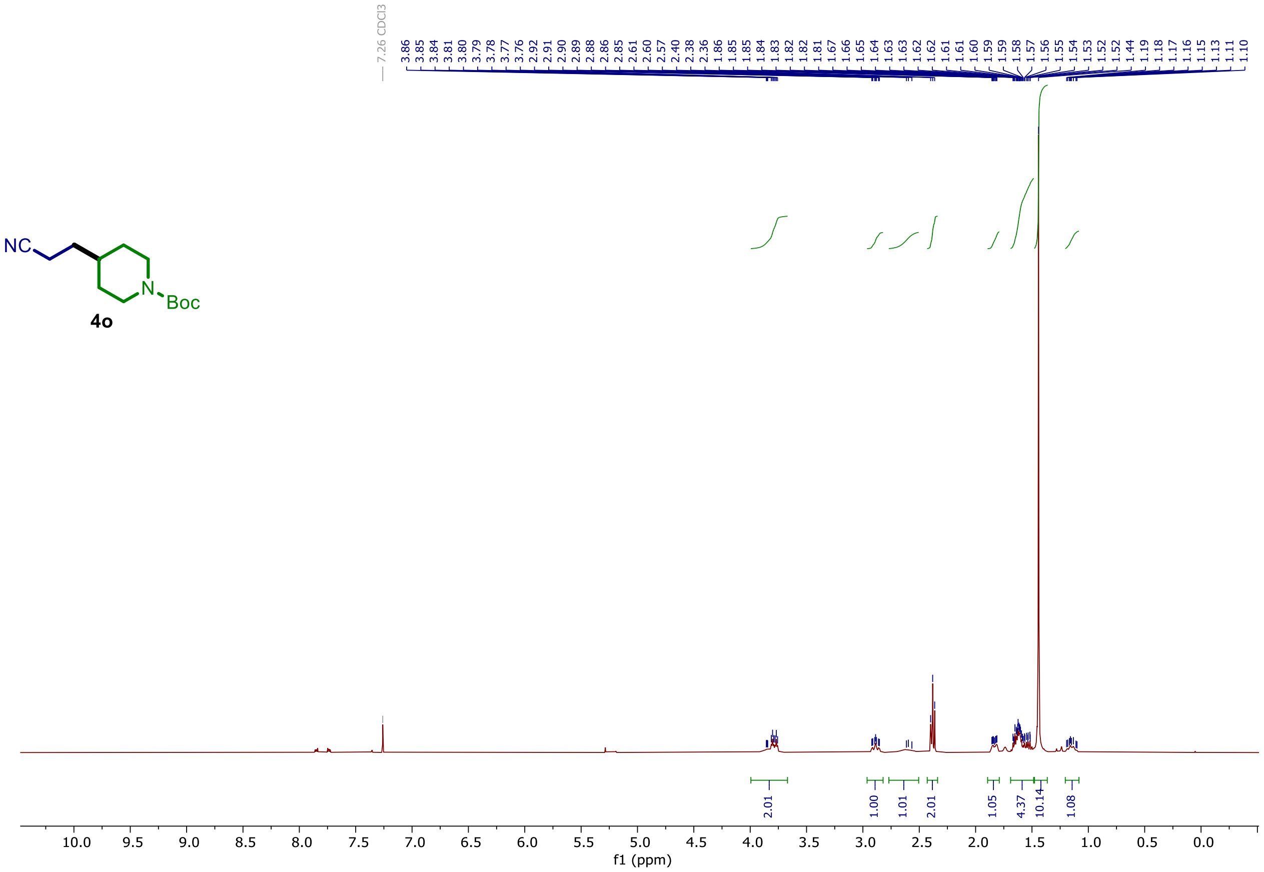
79.46
52.06
51.96
38.90
38.64
36.54
33.93
32.29
31.85
28.60
MeO2C
MeO2C
N
Boc
4n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



4o
7.26 CDCl3
3.86
3.85
3.84
3.81
3.80
3.79
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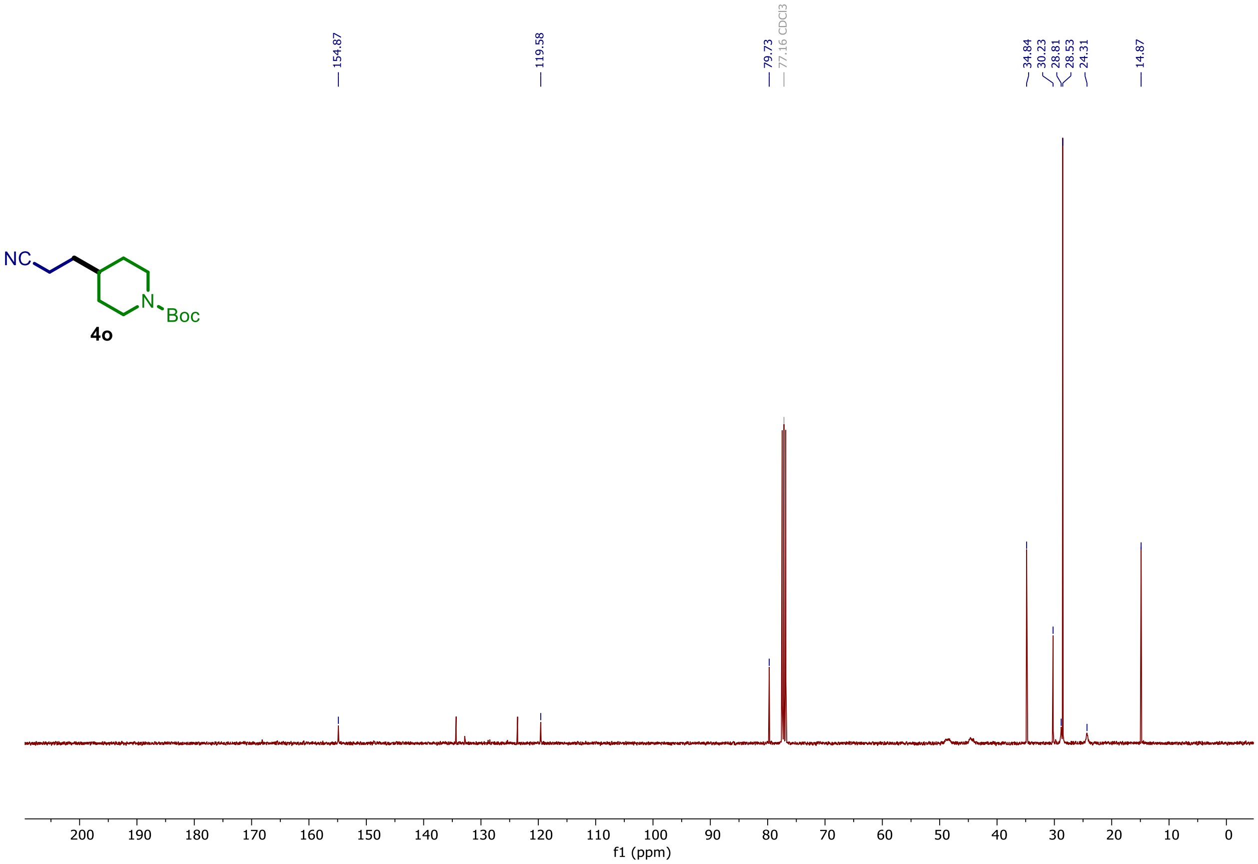
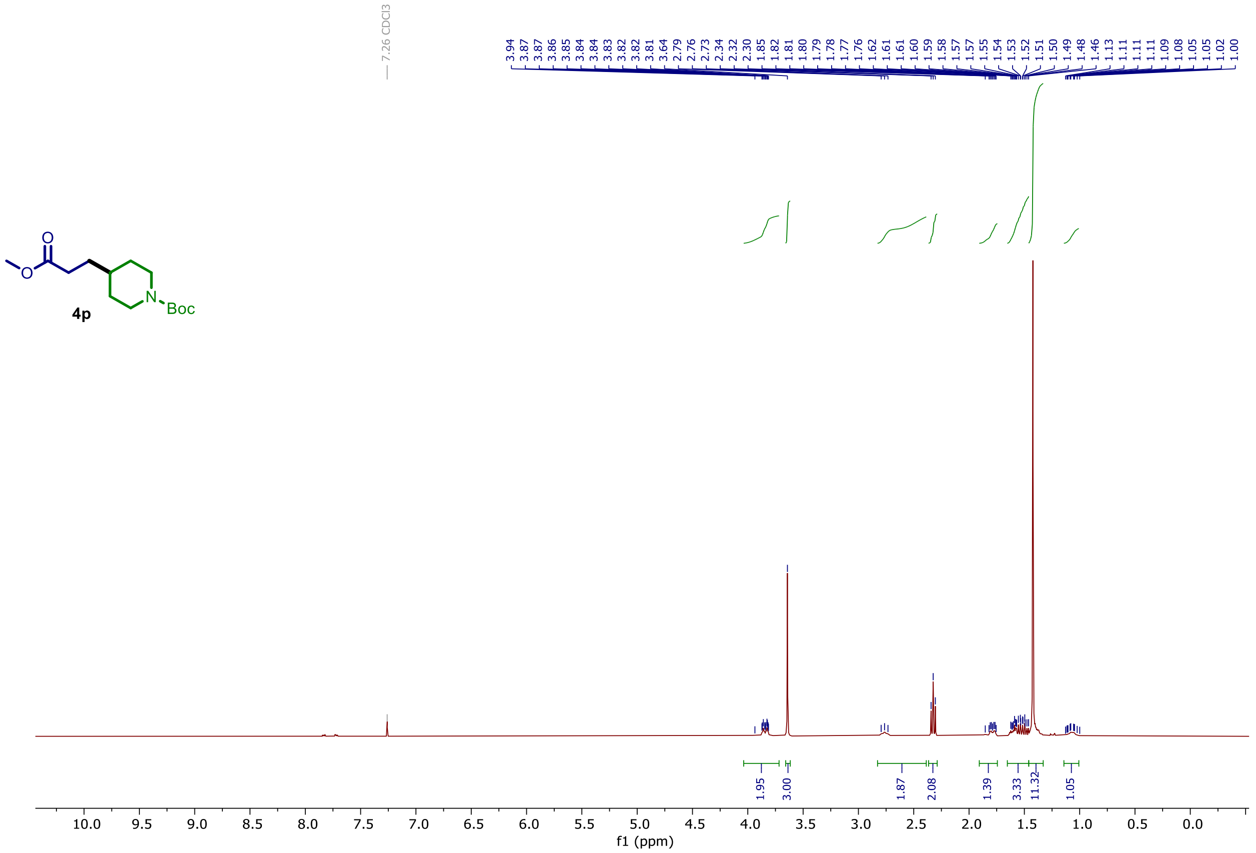
3.77
3.76
2.92
2.91
2.90
2.89
2.88
2.86
2.85
2.61
2.60
2.57
2.40
2.38
2.36
1.86
1.85
1.84
1.83
1.82
1.82
1.81
1.67
1.66
1.65
1.64
1.63
1.63
1.62
1.62
1.61
1.61
1.60
1.59
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.52
1.44
1.19
1.18
1.17
1.16
1.15
1.13
1.11
1.10
2.01
1.00
1.01
2.01
1.05
4.37
10.14
1.08
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
f1 (ppm)

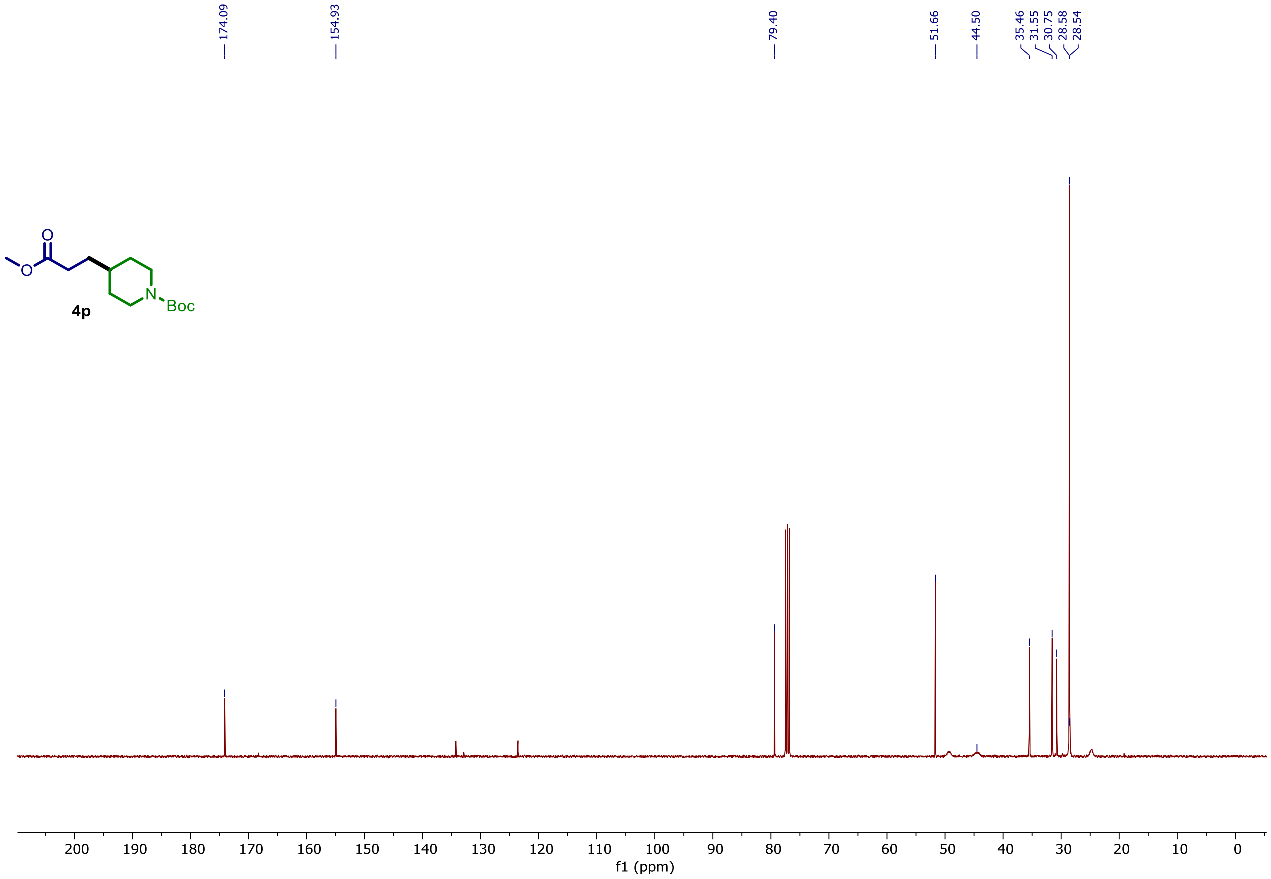


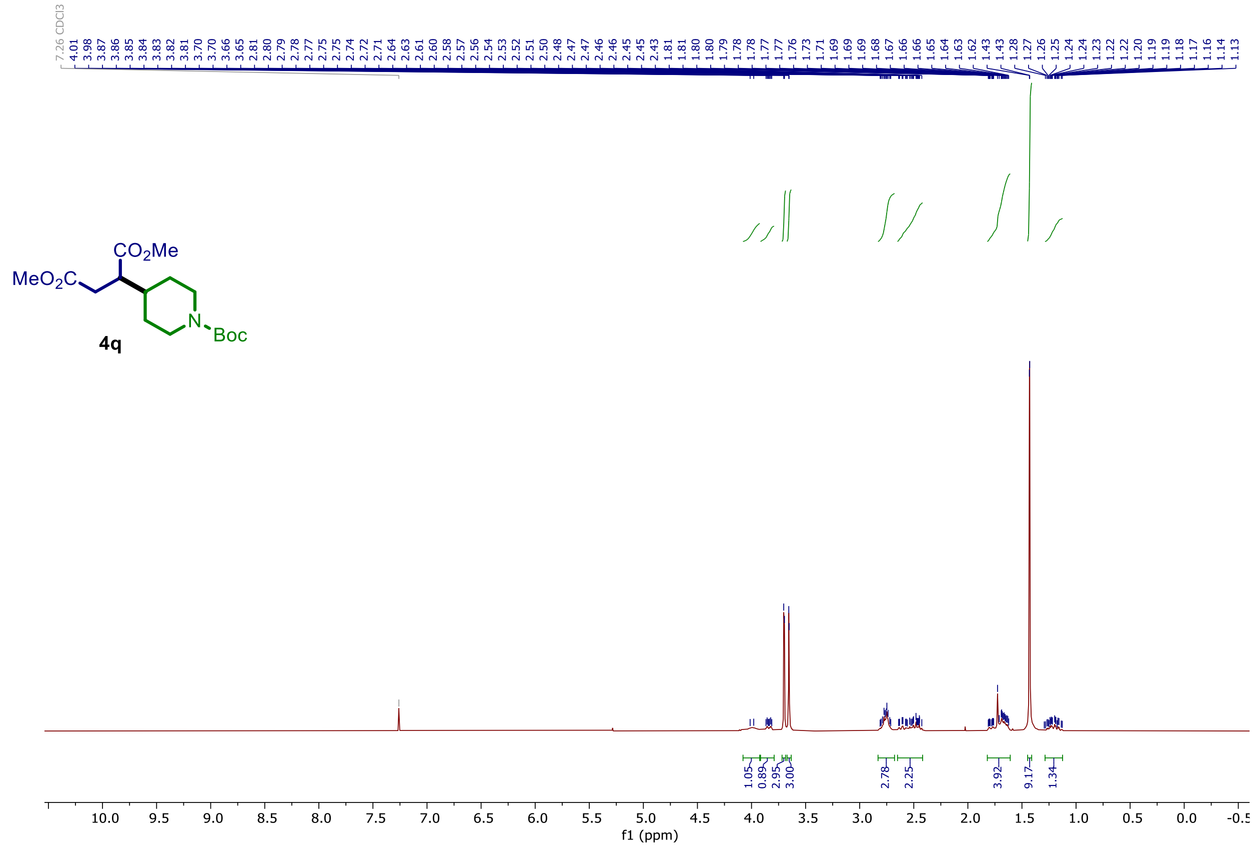
4o
154.87
119.58
79.73
77.16 CDCl3
34.84
30.23
28.81
28.53
24.31
14.87
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

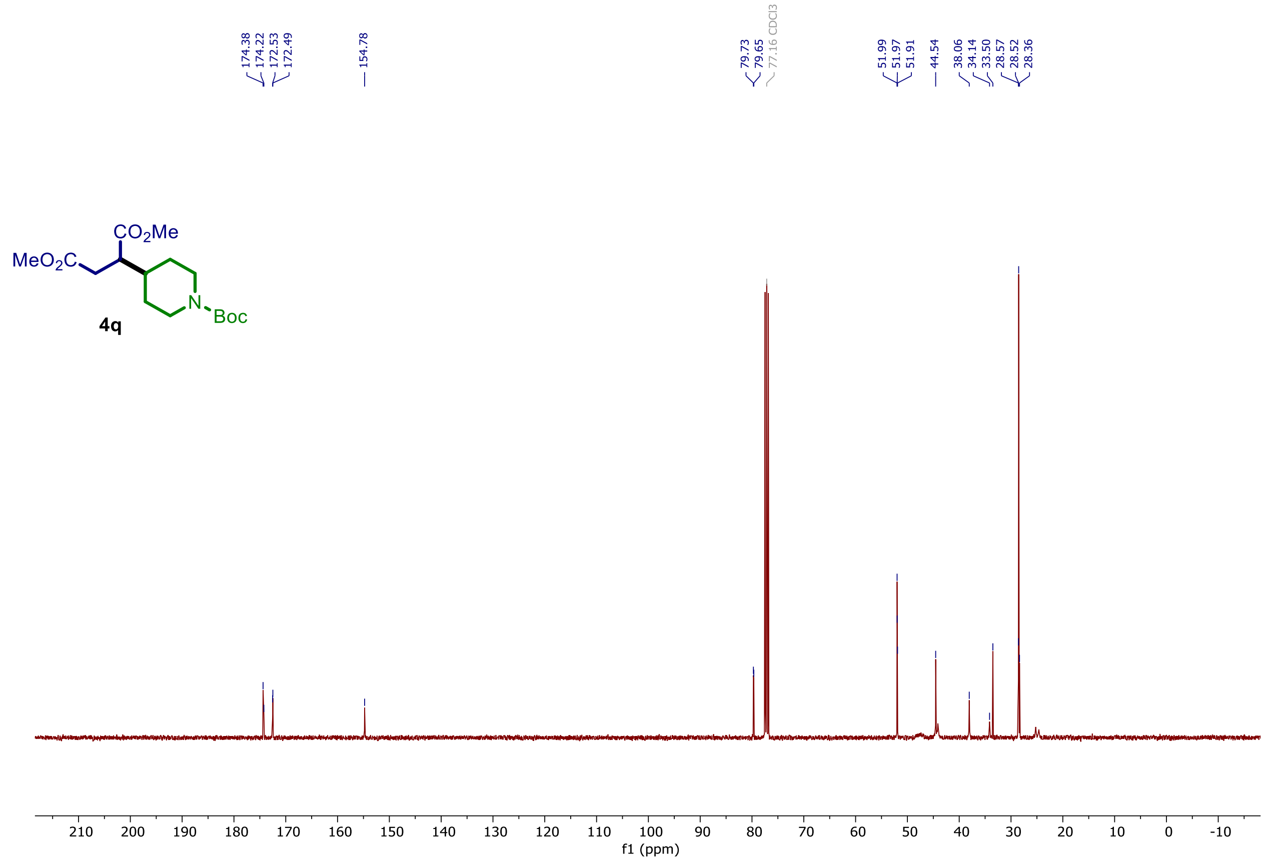
4p

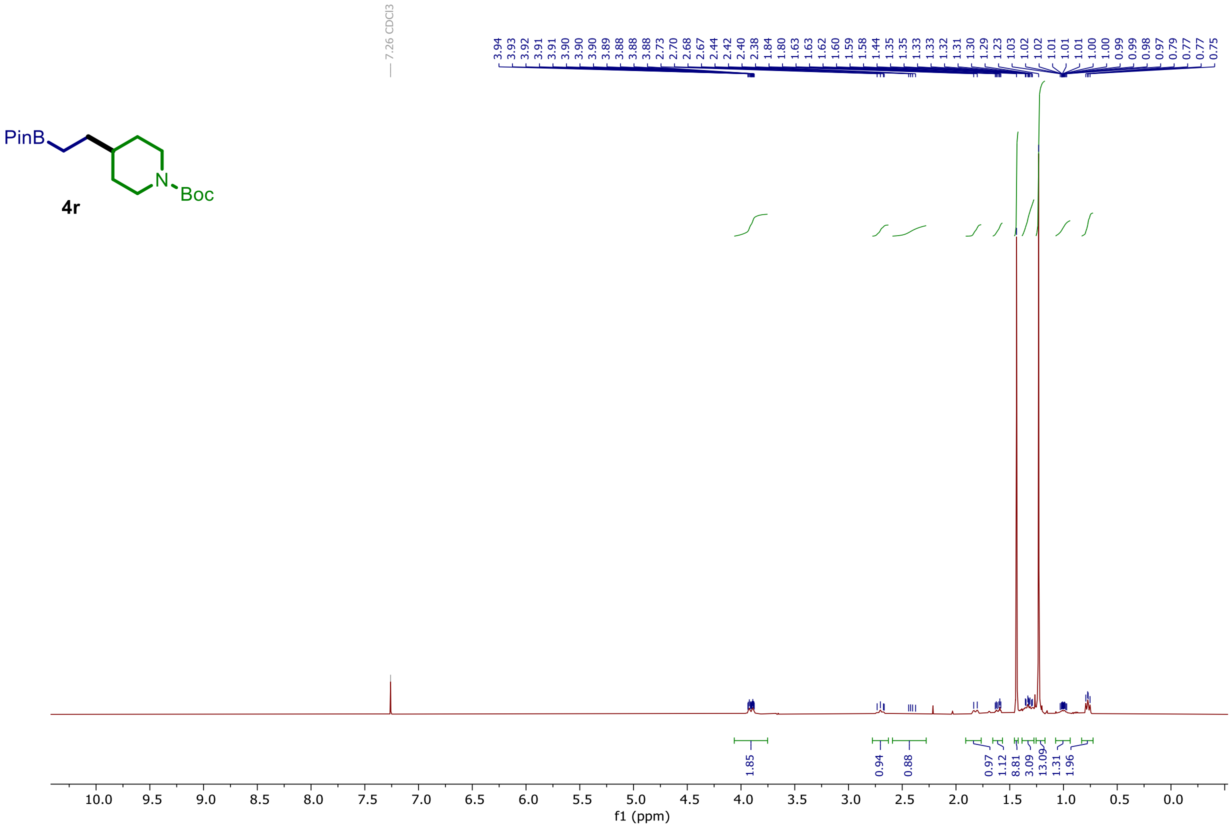

7.26 CDCl3
3.94
3.87
3.87
3.86
3.85
3.84
3.84
3.83
3.82
3.82
3.81
3.64
2.79
2.76
2.73
2.34
2.32
2.30
1.85
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.62
1.61
1.61
1.60
1.59
1.58
1.57
1.57
1.55
1.54
1.53
1.53
1.52
1.51
1.50
1.49
1.48
1.46
1.13
1.11
1.11
1.11
1.09
1.08
1.05
1.05
1.02
1.00
1.95
3.00
1.87
2.08
1.39
3.33
11.32
1.05
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
f1 (ppm)

4p

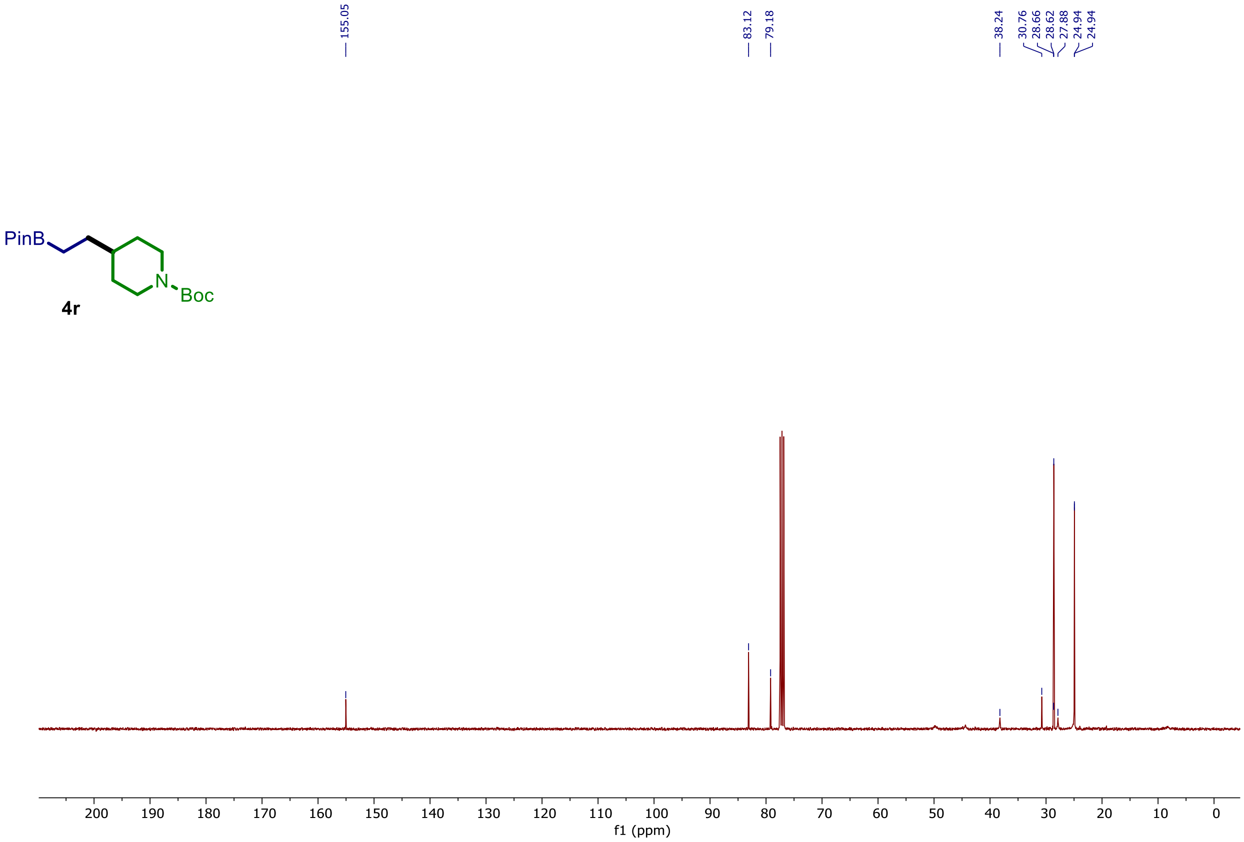

174.09
154.93
79.40
51.66
44.50
35.46
31.55
30.75
28.58
28.54
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
4.01
3.98
3.87
3.86
3.85
3.84
3.83
3.82
3.81
3.70
3.66
3.65
2.81
2.80
2.79
2.78
2.77
2.75
2.75
2.74
2.72
2.71
2.64
2.63
2.61
2.60
2.58
2.57
2.56
2.54
2.53
2.52
2.51
2.50
2.48
2.47
2.47
2.46
2.46
2.45
2.45
2.43
1.81
1.81
1.80
1.80
1.79
1.78
1.78
1.77
1.77
1.76
1.73
1.71
1.69
1.69
1.69
1.68
1.67
1.66
1.66
1.65
1.64
1.63
1.62
1.43
1.43
1.28
1.27
1.26
1.25
1.24
1.24
1.23
1.22
1.22
1.20
1.19
1.19
1.18
1.17
1.16
1.14
1.13
CO2Me
MeO2C
N
Boc
4q
1.05
0.89
2.95
3.00
2.78
2.25
3.92
9.17
1.34
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)

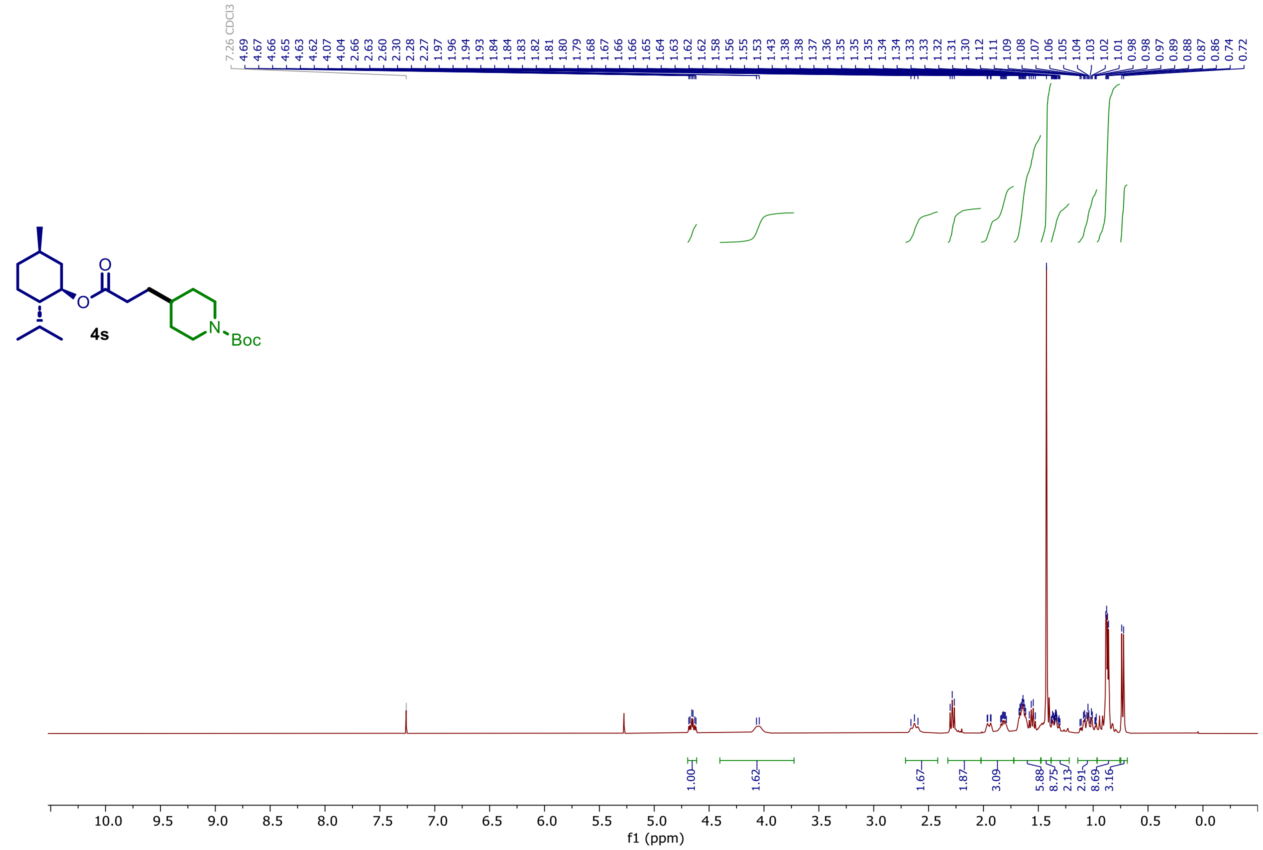

174.38
174.22
172.53
172.49
154.78
79.73
79.65
77.16 CDCl3
51.99
51.97
51.91
44.54
38.06
34.14
33.50
28.57
28.52
28.36
CO2Me
MeO2C
N
Boc
4q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

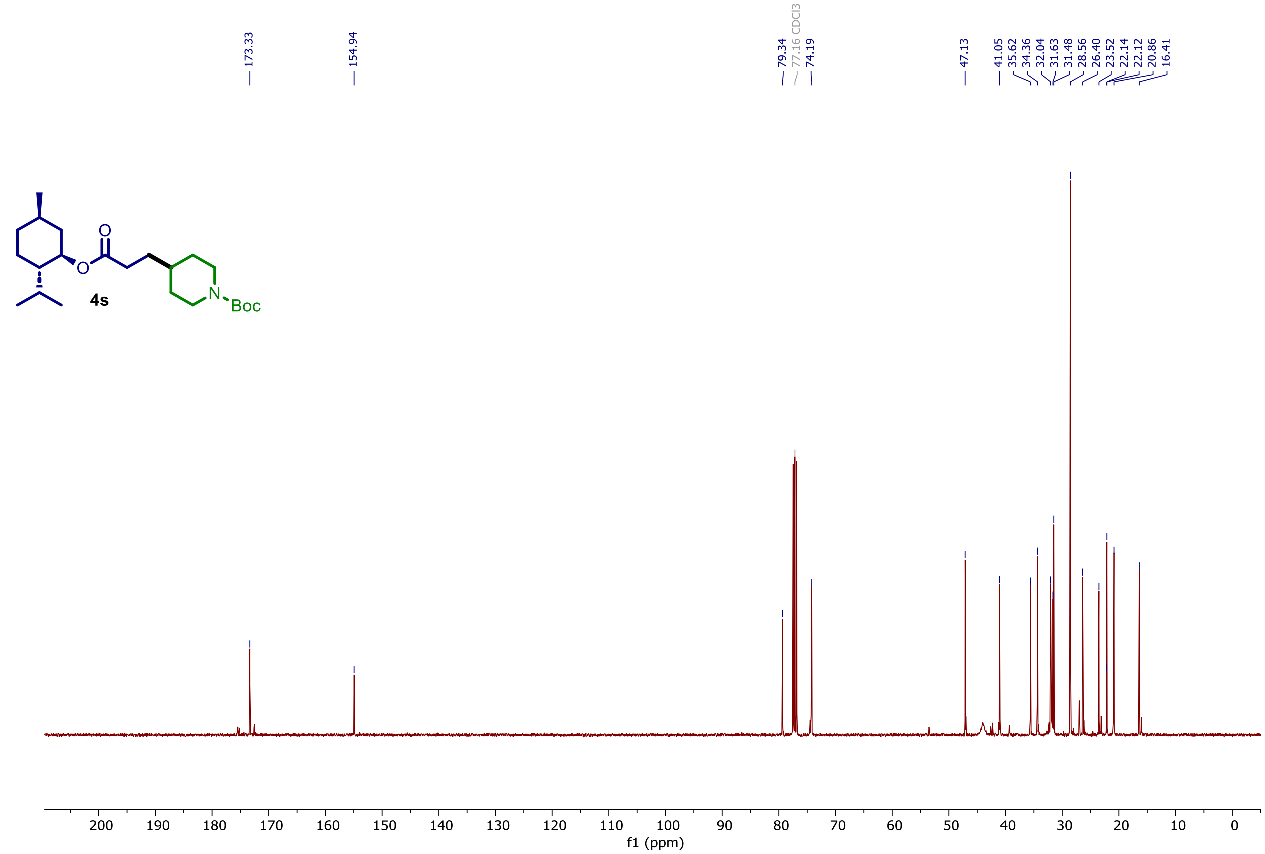

PinB
N
Boc
7.26 CDCl3
3.94 3.93 3.92 3.91 3.91 3.90 3.90 3.90 3.89 3.88 3.88 3.88 2.73 2.70 2.68 2.67 2.44 2.42 2.40 2.38 1.84 1.80 1.63 1.63 1.62 1.60 1.59 1.58 1.44 1.35 1.35 1.33 1.33 1.32 1.31 1.30 1.29 1.23 1.03 1.02 1.02 1.02 1.01 1.01 1.01 1.00 1.00 0.99 0.99 0.98 0.97 0.79 0.77 0.77 0.75
1.85
0.94
0.88
0.97
1.12
8.81
3.09
13.09
1.31
1.96
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
f1 (ppm)

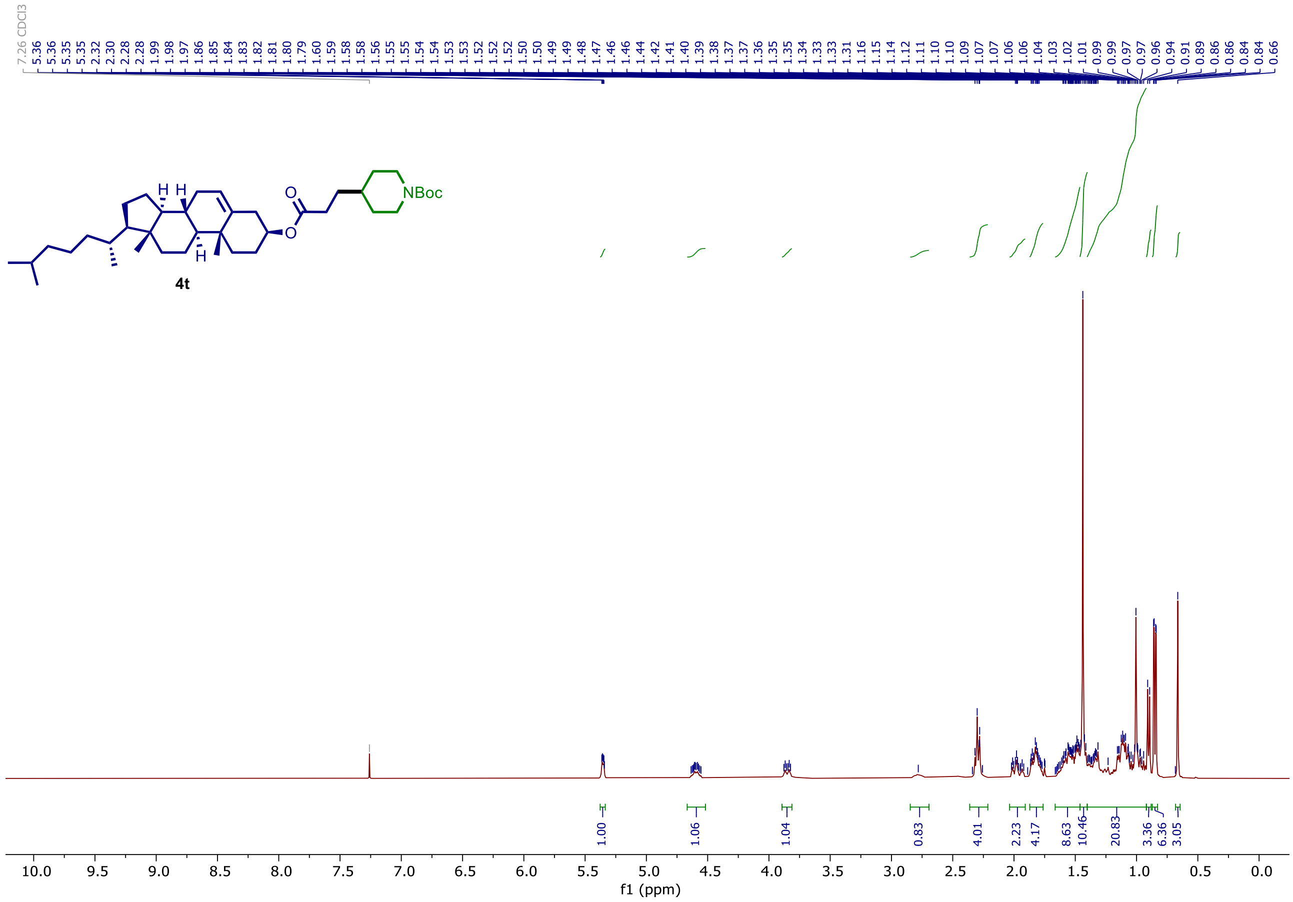
4r

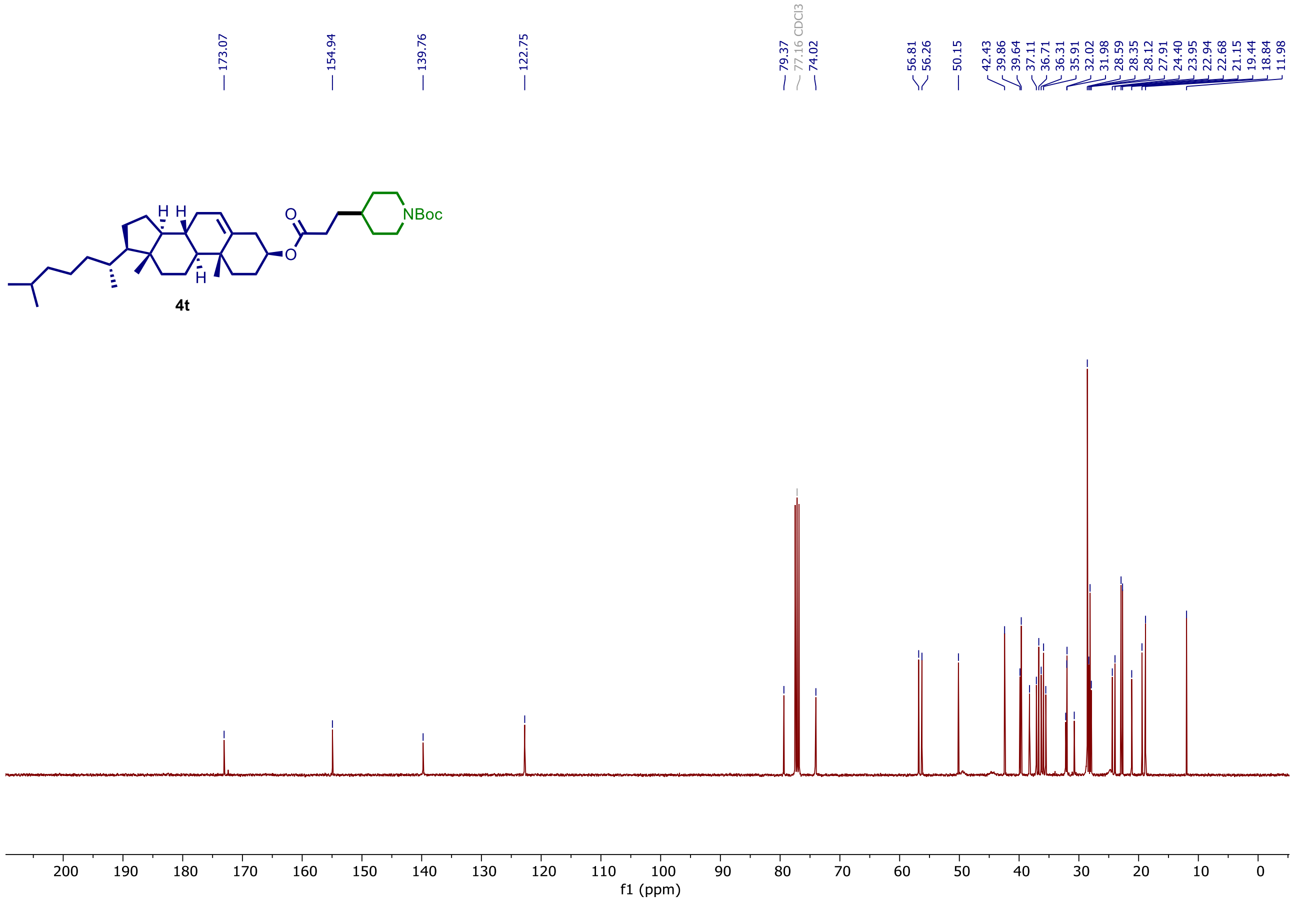

155.05
83.12
79.18
38.24
30.76
28.66
28.62
27.88
24.94
24.94
PinB
N
Boc
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

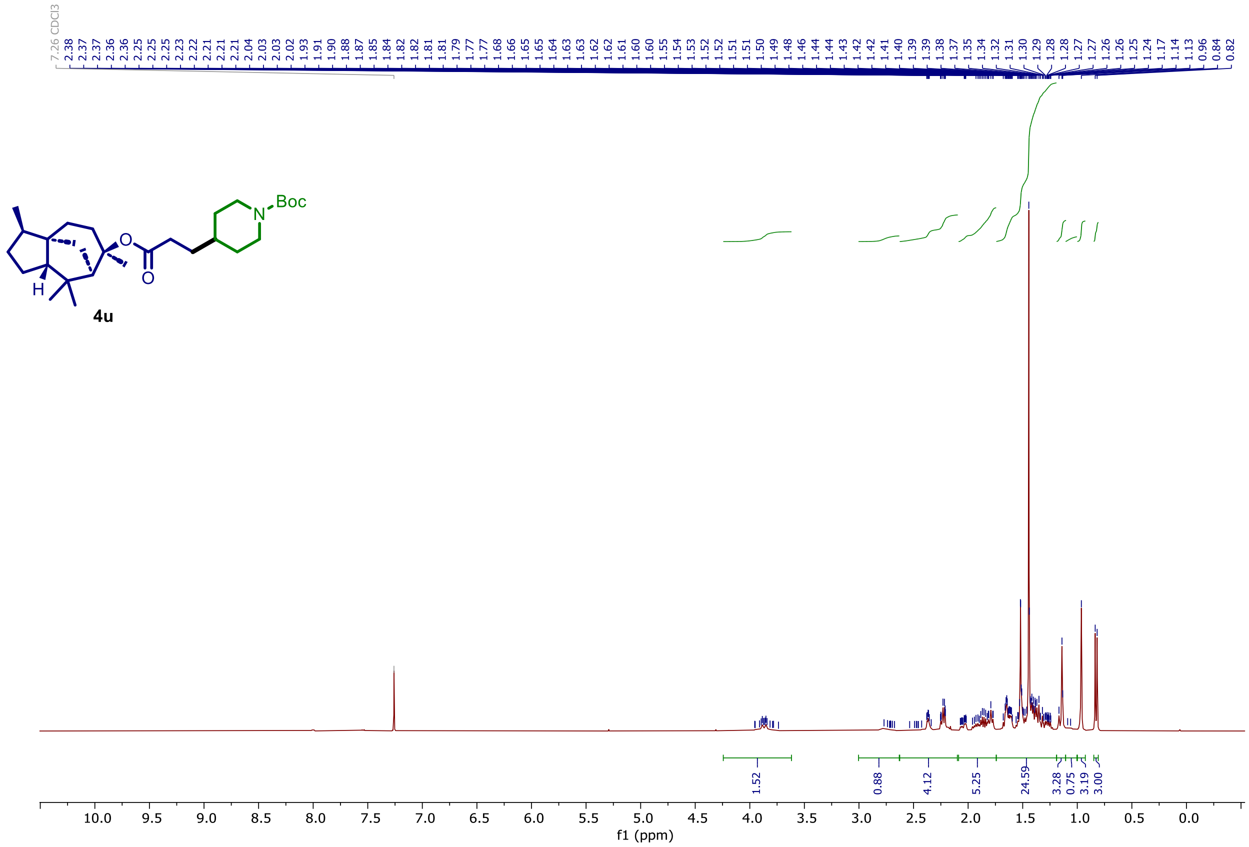
4r


7.26 CDCl3
4.69
4.67
4.66
4.65
4.63
4.62
4.07
4.04
2.66
2.63
2.60
2.30
2.28
2.27
1.97
1.96
1.94
1.93
1.84
1.84
1.83
1.82
1.81
1.80
1.79
1.68
1.67
1.66
1.66
1.65
1.64
1.63
1.62
1.62
1.58
1.56
1.55
1.53
1.43
1.38
1.38
1.37
1.36
1.35
1.35
1.35
1.34
1.34
1.33
1.33
1.32
1.31
1.30
1.12
1.11
1.09
1.08
1.07
1.06
1.05
1.04
1.03
1.02
1.01
0.98
0.98
0.97
0.89
0.88
0.87
0.86
0.74
0.72
O
O
N
Boc
4s
1.00
1.62
1.67
1.87
3.09
5.88
8.75
2.13
2.91
8.69
3.16
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
f1 (ppm)

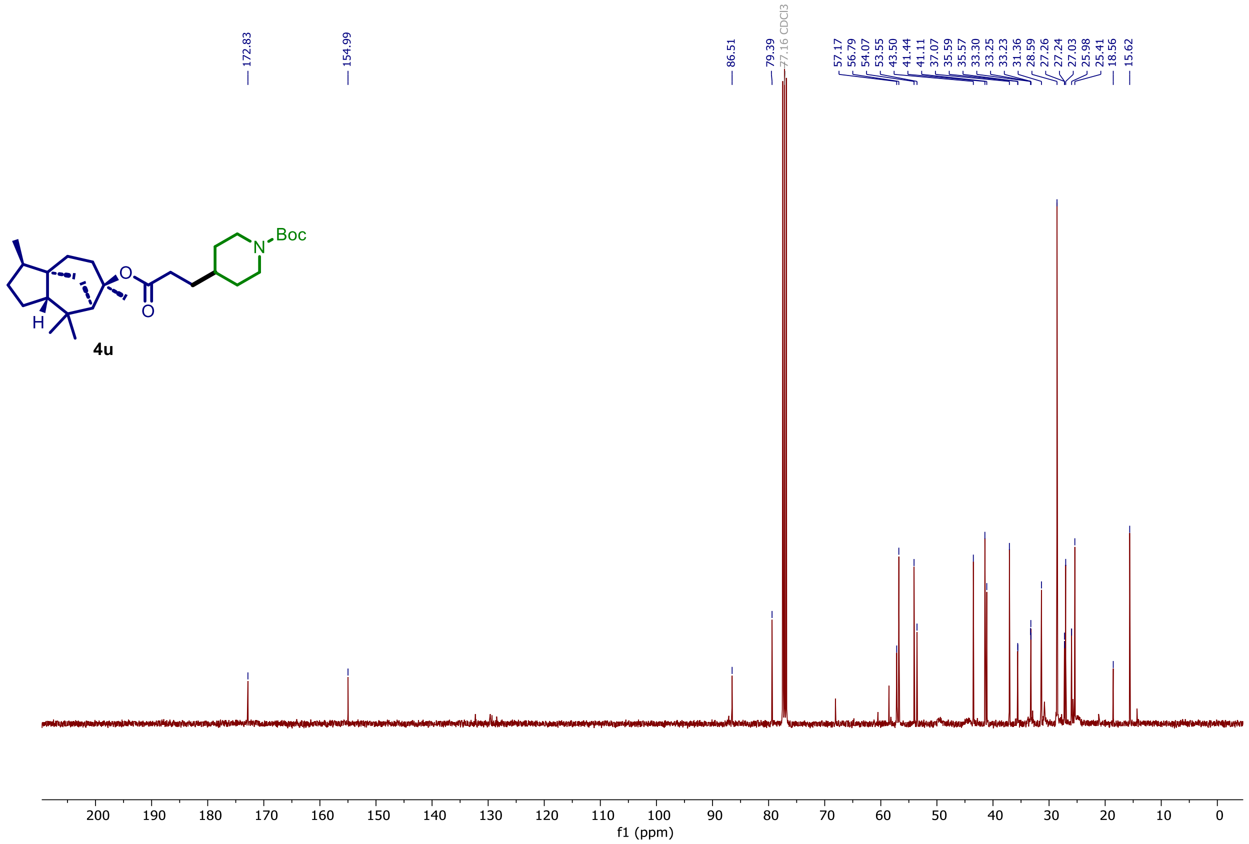

173.33
154.94
79.34
77.16 CDCl3
74.19
47.13
41.05
35.62
34.36
32.04
31.63
31.48
28.56
26.40
23.52
22.14
22.12
20.86
16.41
O
O
N
Boc
4s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
5.36
5.36
5.35
5.35
2.32
2.30
2.28
2.28
1.99
1.98
1.97
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.60
1.59
1.58
1.58
1.56
1.55
1.55
1.54
1.54
1.53
1.53
1.52
1.52
1.52
1.50
1.50
1.49
1.49
1.48
1.47
1.46
1.46
1.44
1.42
1.41
1.40
1.39
1.38
1.37
1.37
1.36
1.35
1.35
1.34
1.33
1.33
1.31
1.16
1.15
1.14
1.12
1.11
1.11
1.10
1.10
1.09
1.07
1.07
1.06
1.06
1.04
1.03
1.02
1.01
0.99
0.97
0.97
0.96
0.94
0.91
0.89
0.86
0.86
0.84
0.84
0.66
H
H
O
O
NBoc
H
4t
1.00
1.06
1.04
0.83
4.01
2.23
4.17
8.63
10.46
20.83
3.36
6.36
3.05
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
f1 (ppm)

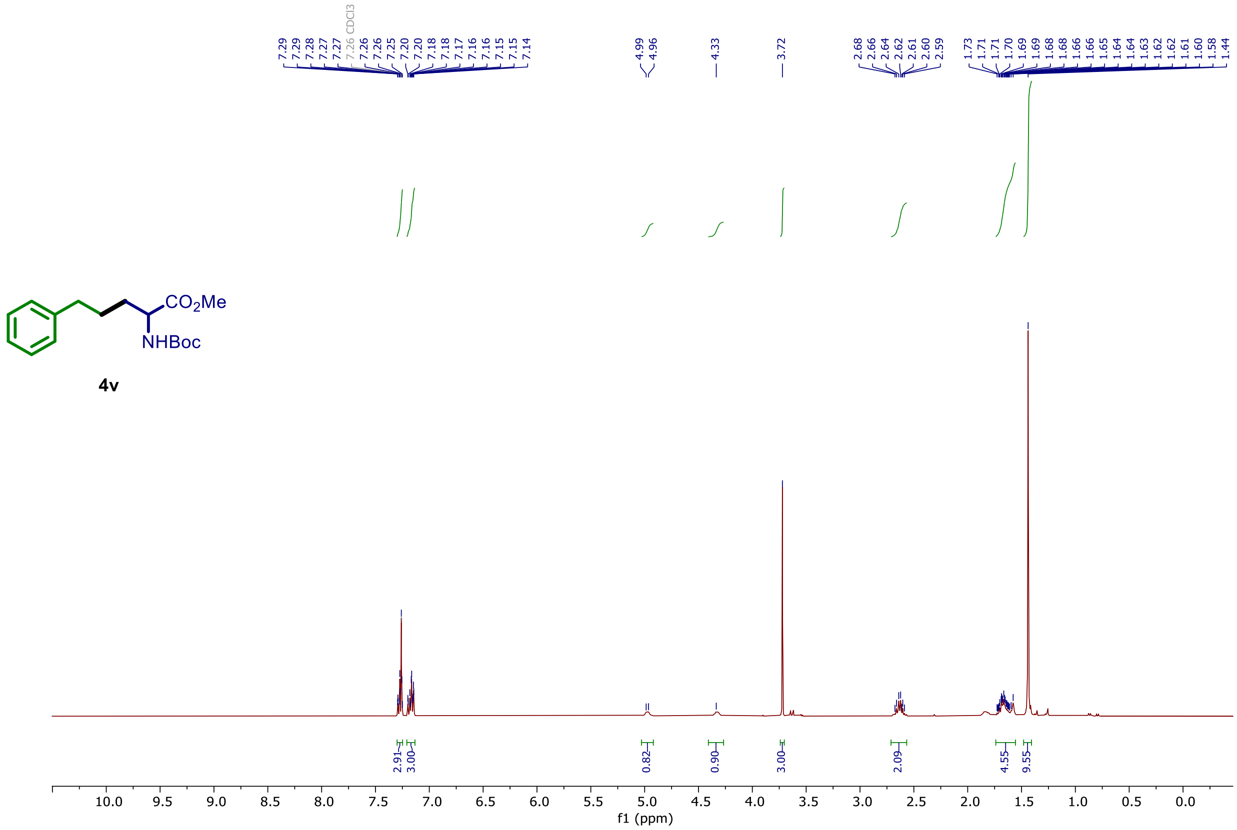

173.07
154.94
139.76
122.75
79.37
77.16 CDCl3
74.02
56.81
56.26
50.15
42.43
39.86
39.64
37.11
36.71
36.31
35.91
32.02
31.98
28.59
28.35
28.12
27.91
24.40
23.95
22.94
22.68
21.15
19.44
18.84
11.98
H
H
O
O
NBoc
H
4t
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

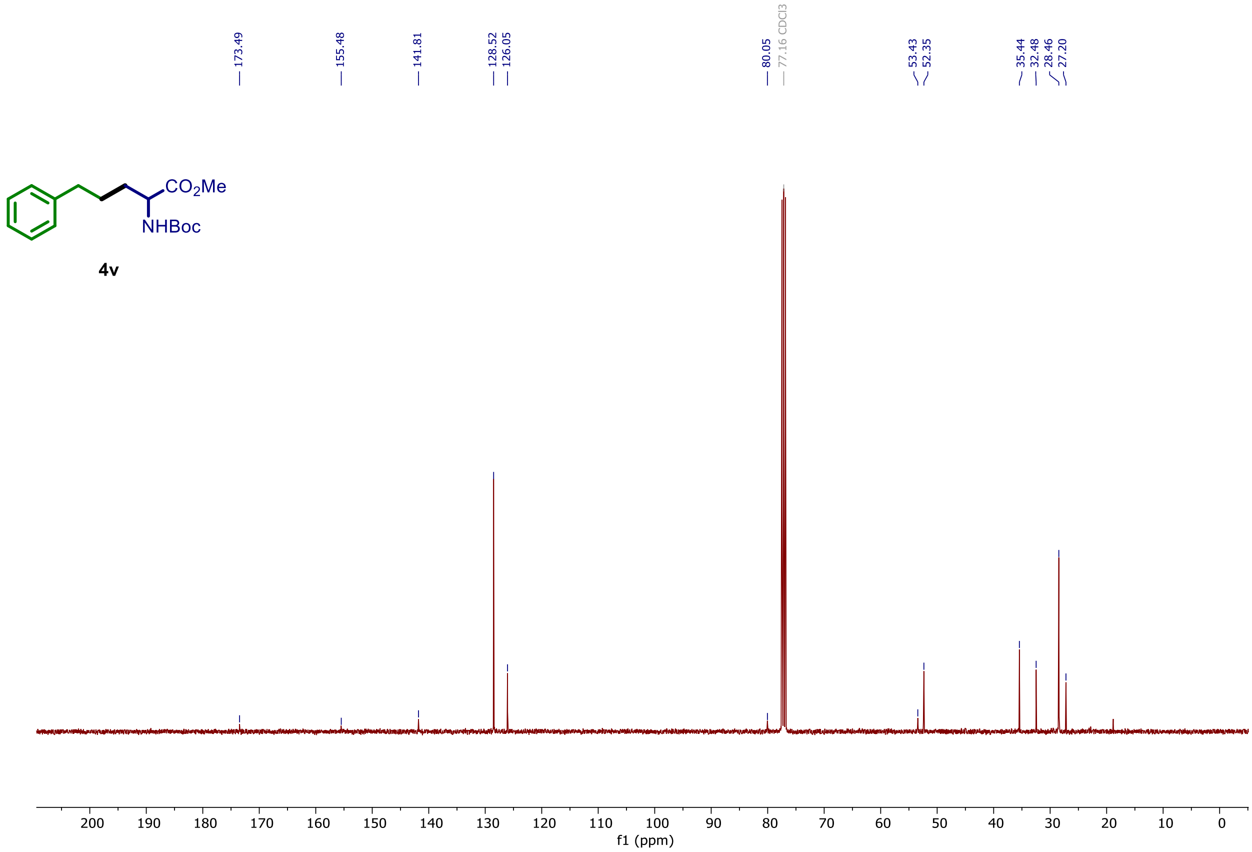

7.26 CDCl3
2.38
2.37
2.37
2.36
2.36
2.25
2.25
2.25
2.23
2.22
2.21
2.21
2.21
2.04
2.03
2.03
2.02
1.93
1.91
1.90
1.88
1.87
1.85
1.84
1.82
1.82
1.81
1.79
1.77
1.68
1.66
1.65
1.65
1.64
1.63
1.63
1.62
1.62
1.61
1.60
1.60
1.55
1.54
1.53
1.52
1.52
1.51
1.51
1.50
1.49
1.48
1.46
1.44
1.44
1.43
1.42
1.42
1.41
1.40
1.39
1.39
1.38
1.37
1.35
1.34
1.32
1.31
1.30
1.29
1.28
1.28
1.27
1.27
1.26
1.25
1.24
1.17
1.14
1.13
0.96
0.84
0.82
N
Boc
O
O
H
1.52
0.88
4.12
5.25
24.59
3.28
0.75
3.19
3.00
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
f1 (ppm)

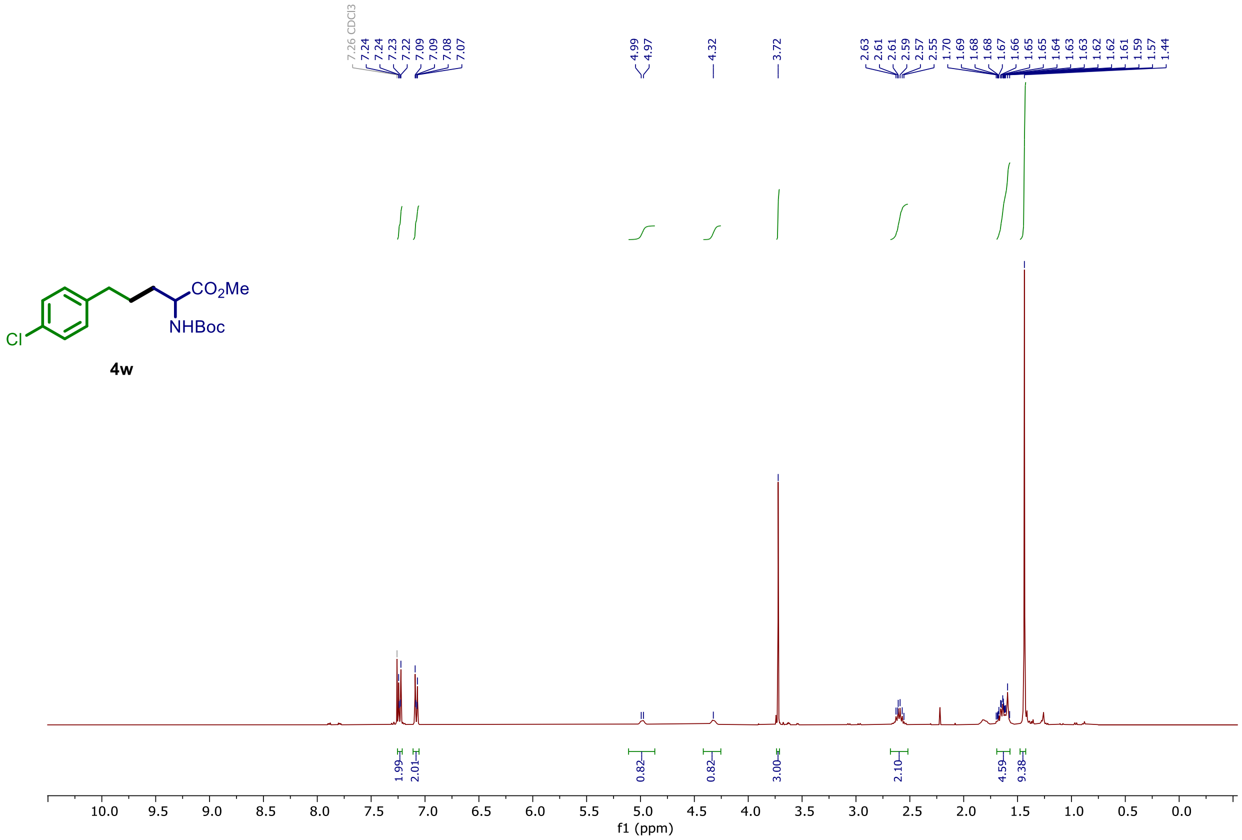
4u

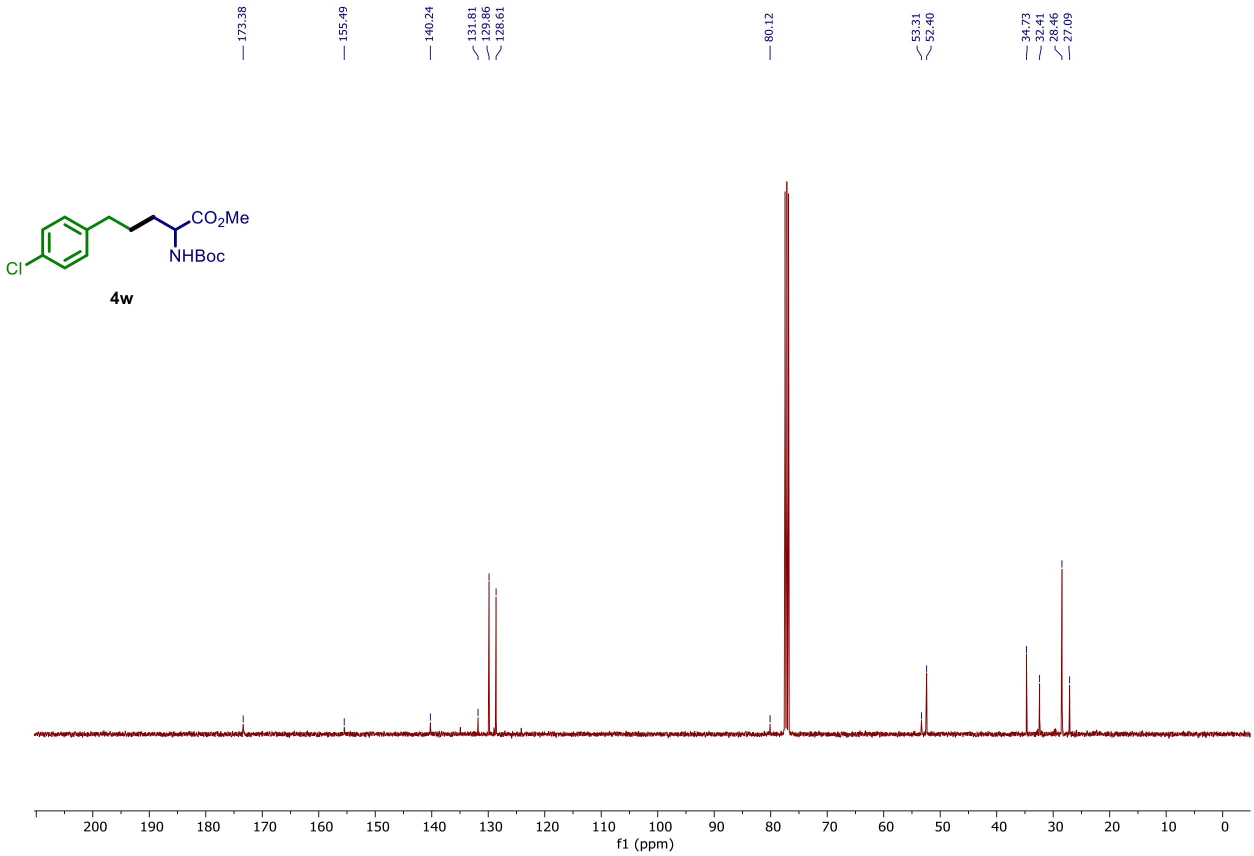

172.83
154.99
86.51
79.39
77.16 CDCl3
57.17
56.79
54.07
53.55
43.50
41.44
41.11
37.07
35.59
35.57
33.30
33.25
33.23
31.36
28.59
27.26
27.24
27.03
25.98
25.41
18.56
15.62
N
Boc
O
O
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

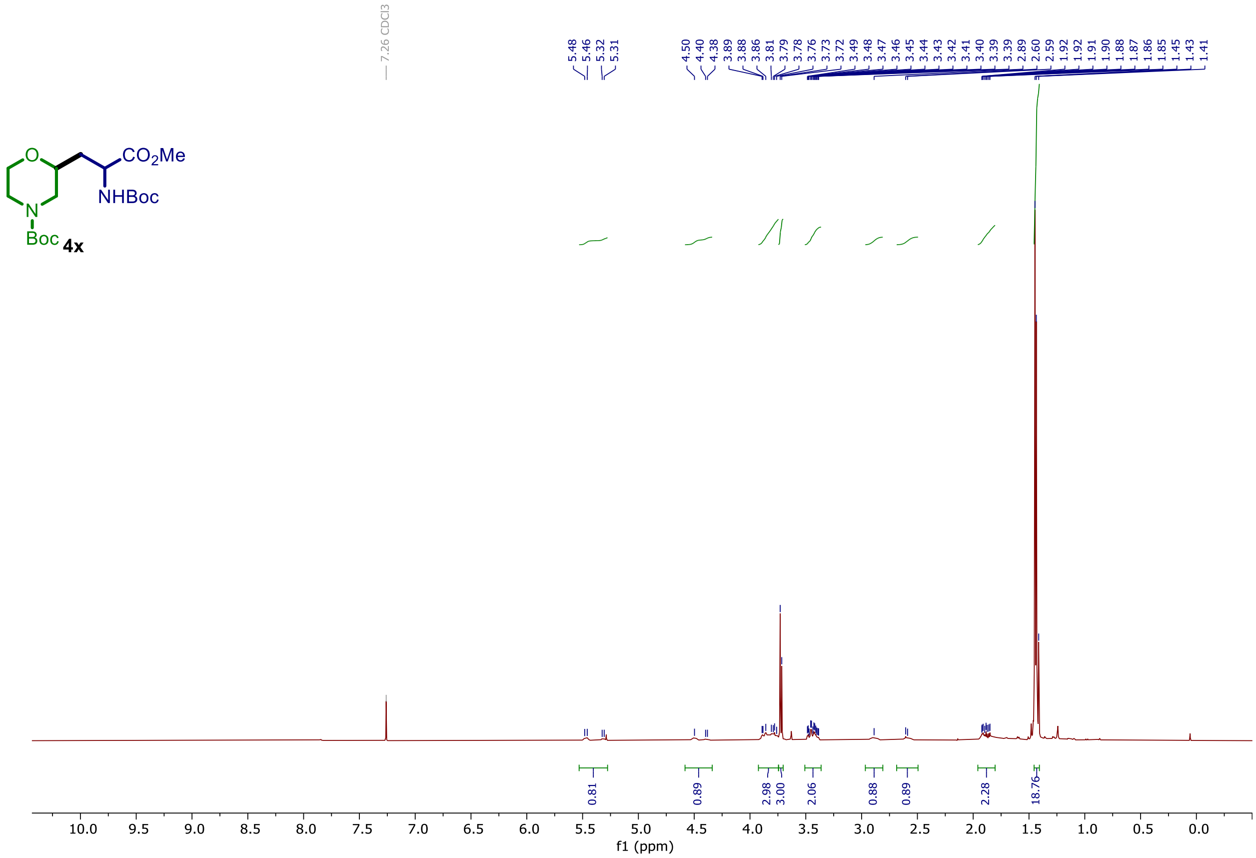
4u


7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
7.26
7.26
7.25
7.20
7.20
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.14
4.99
4.96
4.33
3.72
2.68
2.66
2.64
2.62
2.62
2.61
2.60
2.59
1.73
1.71
1.70
1.69
1.69
1.68
1.68
1.66
1.66
1.65
1.64
1.64
1.63
1.62
1.62
1.61
1.60
1.58
1.44
CO2Me
NHBoc
4v
2.91
3.00
0.82
0.90
3.00
2.09
4.55
9.55
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
f1 (ppm)


173.49
155.48
141.81
128.52
126.05
80.05
77.16 CDCl3
53.43
52.35
35.44
32.48
28.46
27.20
CO2Me
NHBoc
4v
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

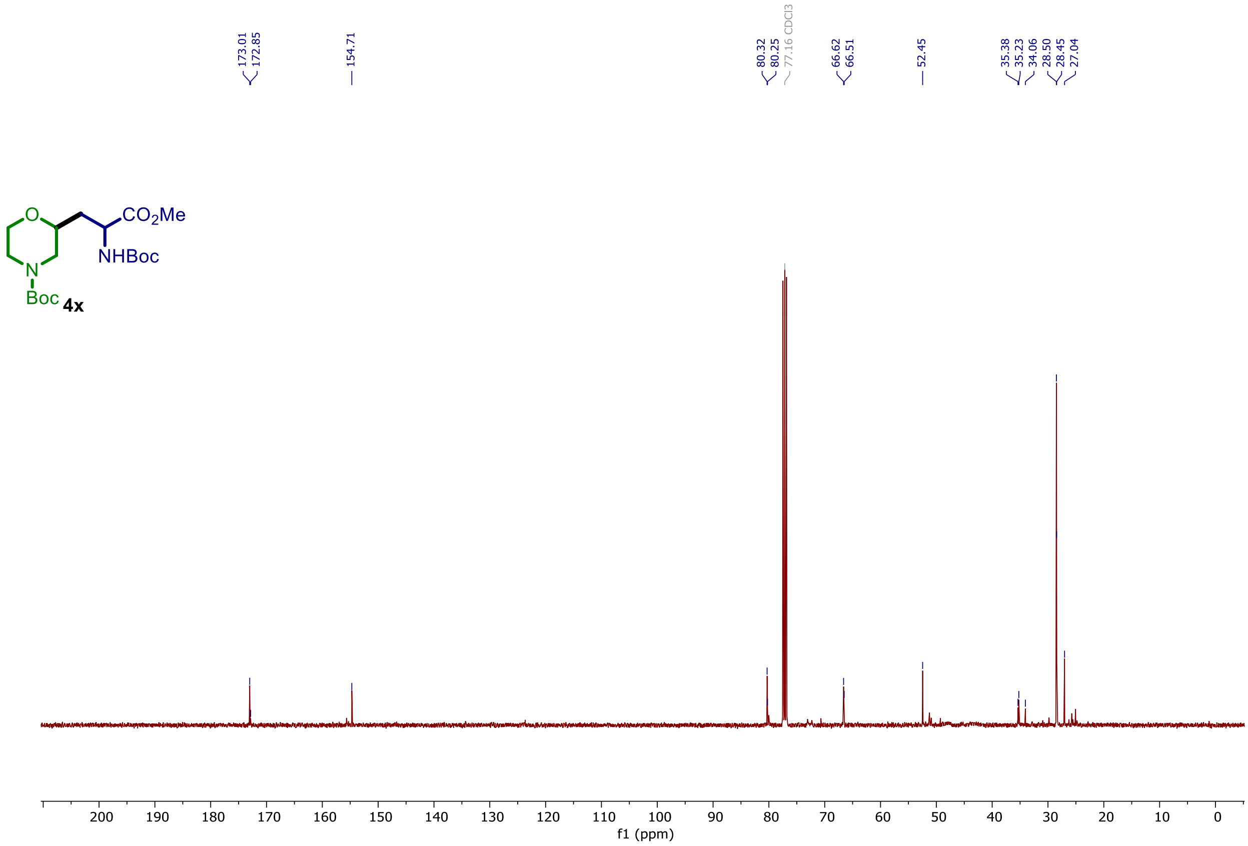

7.26 CDCl3
7.24
7.24
7.23
7.22
7.09
7.09
7.08
7.07
4.99
4.97
4.32
3.72
2.63
2.61
2.61
2.59
2.57
2.55
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.65
1.64
1.63
1.63
1.62
1.62
1.61
1.59
1.57
1.44
CO2Me
NHBoc
Cl
4w
1.99
2.01
0.82
0.82
3.00
2.10
4.59
9.38
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


173.38
155.49
140.24
131.81
129.86
128.61
80.12
53.31
52.40
34.73
32.41
28.46
27.09
CO2Me
NHBoc
Cl
4w
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
CO2Me
NHBoc
N
Boc

4x

7.26 CDCl3
5.48
5.46
5.32
5.31
4.50
4.40
4.38
3.89
3.88
3.86
3.81
3.79
3.78
3.76
3.73
3.72
3.49
3.48
3.47
3.46
3.45
3.44
3.43
3.42
3.41
3.40
3.39
3.39
2.89
2.60
2.59
1.92
1.92
1.91
1.90
1.88
1.87
1.86
1.85
1.45
1.43
1.41
0.81
0.89
2.98
3.00
2.06
0.88
0.89
2.28
18.76
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
f1 (ppm)

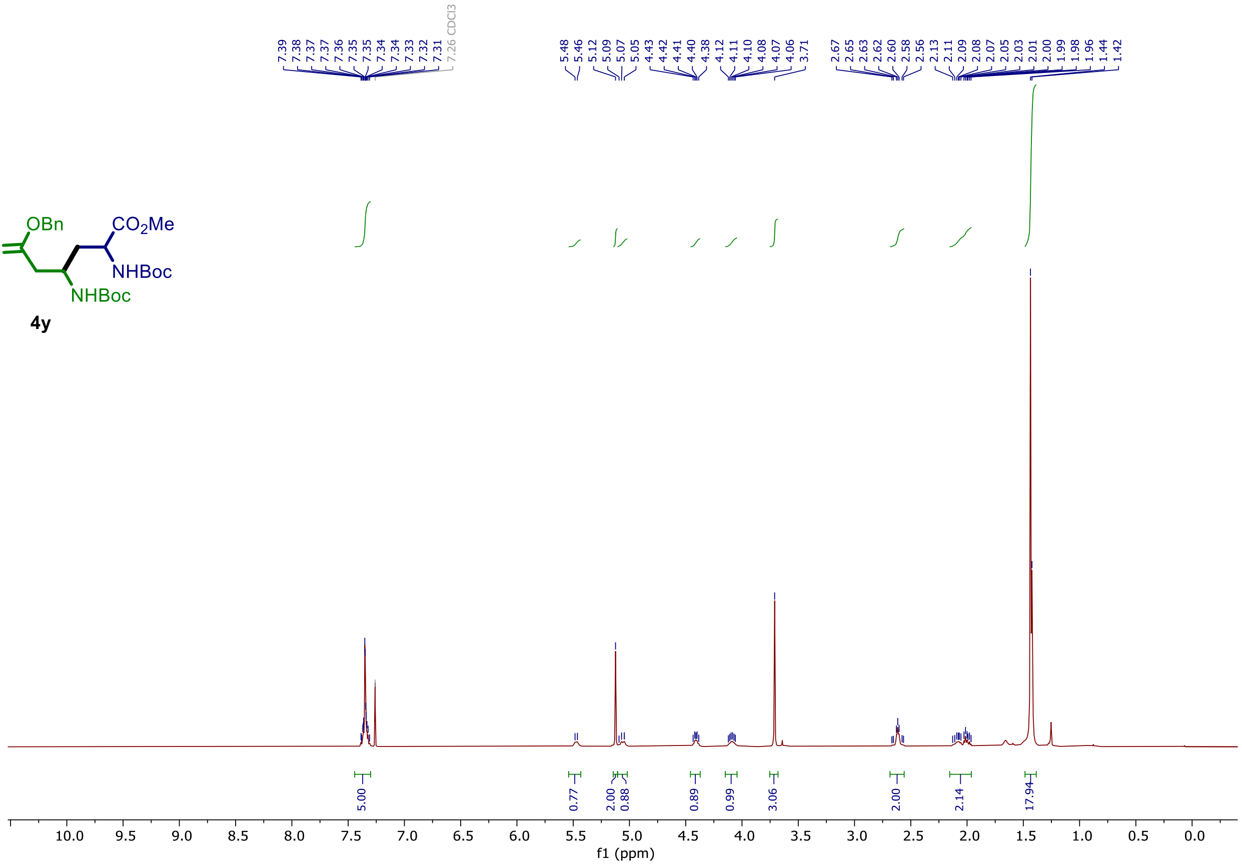

O
CO2Me
NHBoc
N
Boc

4x

173.01
172.85
154.71
80.32
80.25
77.16 CDCl3
66.62
66.51
52.45
35.38
35.23
34.06
28.50
28.45
27.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

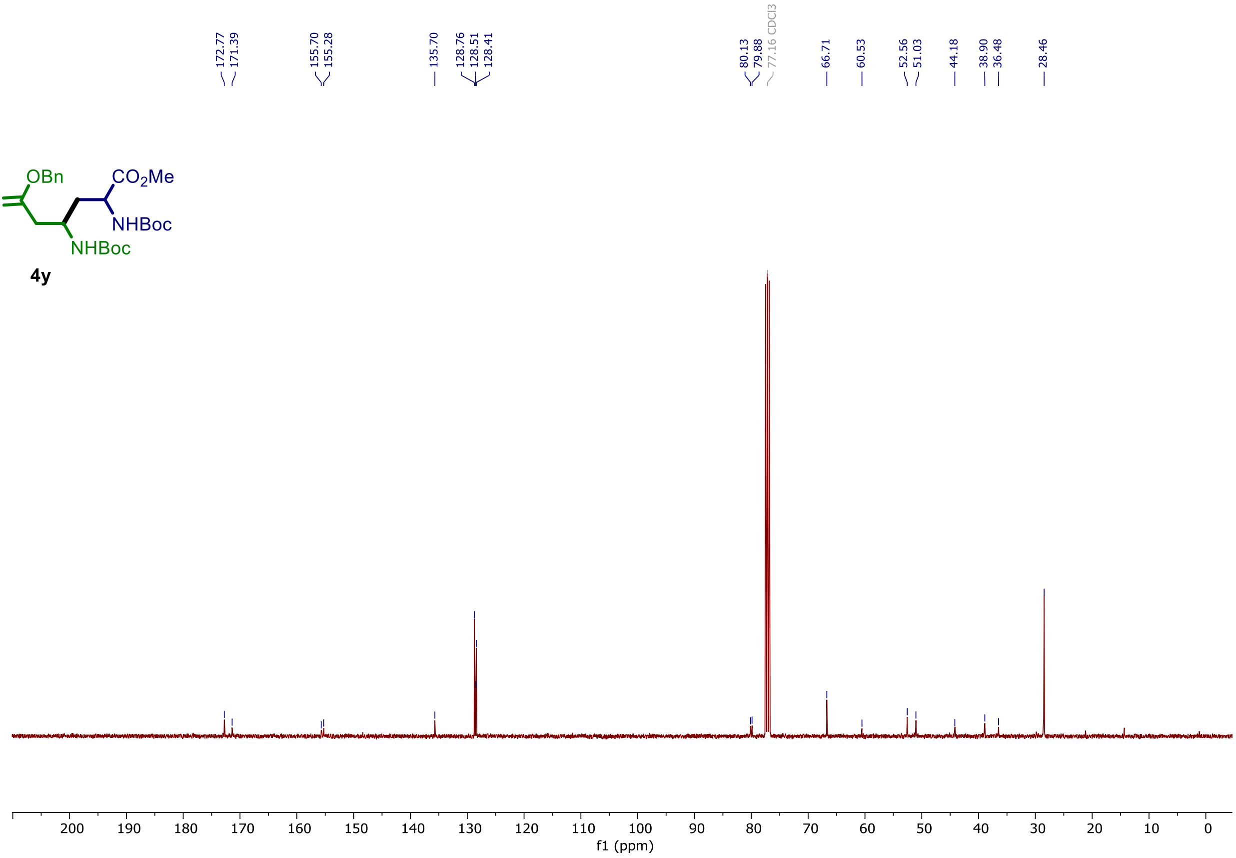
OBn
O
CO2Me
NHBoc
NHBoc

4y


7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.26 CDCl3
5.48
5.46
5.12
5.09
5.07
5.05
4.43
4.42
4.41
4.40
4.38
4.12
4.11
4.10
4.08
4.07
4.06
3.71
2.67
2.65
2.63
2.62
2.60
2.58
2.56
2.13
2.11
2.09
2.08
2.07
2.05
2.03
2.01
2.00
1.99
1.98
1.96
1.44
1.42
5.00
0.77
2.00
0.88
0.89
0.99
3.06
2.00
2.14
17.94
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
f1 (ppm)

OBn
O
CO2Me
NHBoc
NHBoc

4y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171.39
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155.28
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128.76
128.51
128.41
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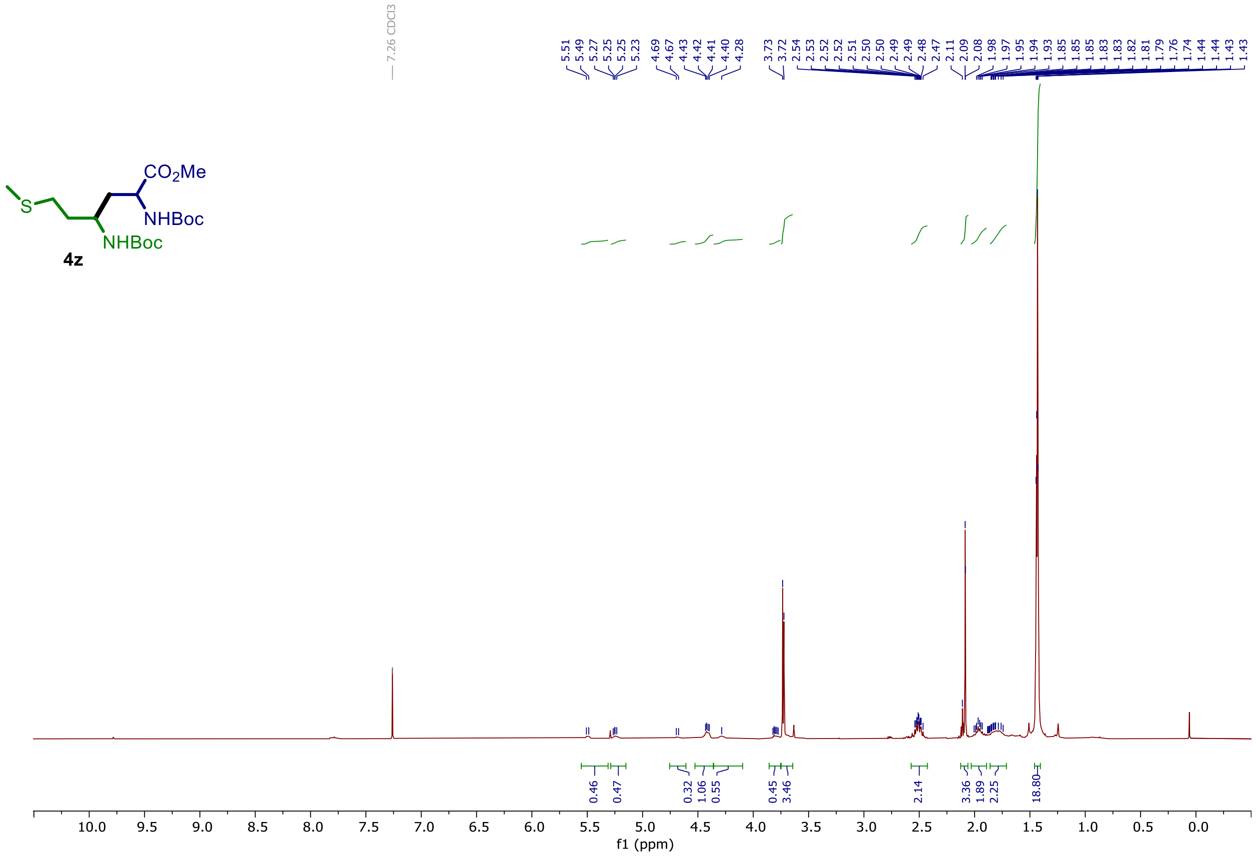
79.88
77.16 CDCl3
66.71
60.53
52.56
51.03
44.18
38.90
36.48
28.46
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



CO$_2$Me
S
NHBoc
NHBoc
4z
7.26 CDCl3
5.51
5.49
5.27
5.25
5.25
5.23
4.69
4.67
4.43
4.42
4.41
4.40
4.28
3.73
3.72
2.54
2.53
2.52
2.52
2.51
2.50
2.49
2.49
2.48
2.47
2.11
2.09
2.08
1.98
1.97
1.95
1.94
1.93
1.85
1.85
1.85
1.83
1.83
1.82
1.81
1.79
1.76
1.74
1.44
1.43
1.43
0.46
0.47
0.32
1.06
0.55
0.45
3.46
2.14
3.36
1.89
2.25
18.80
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
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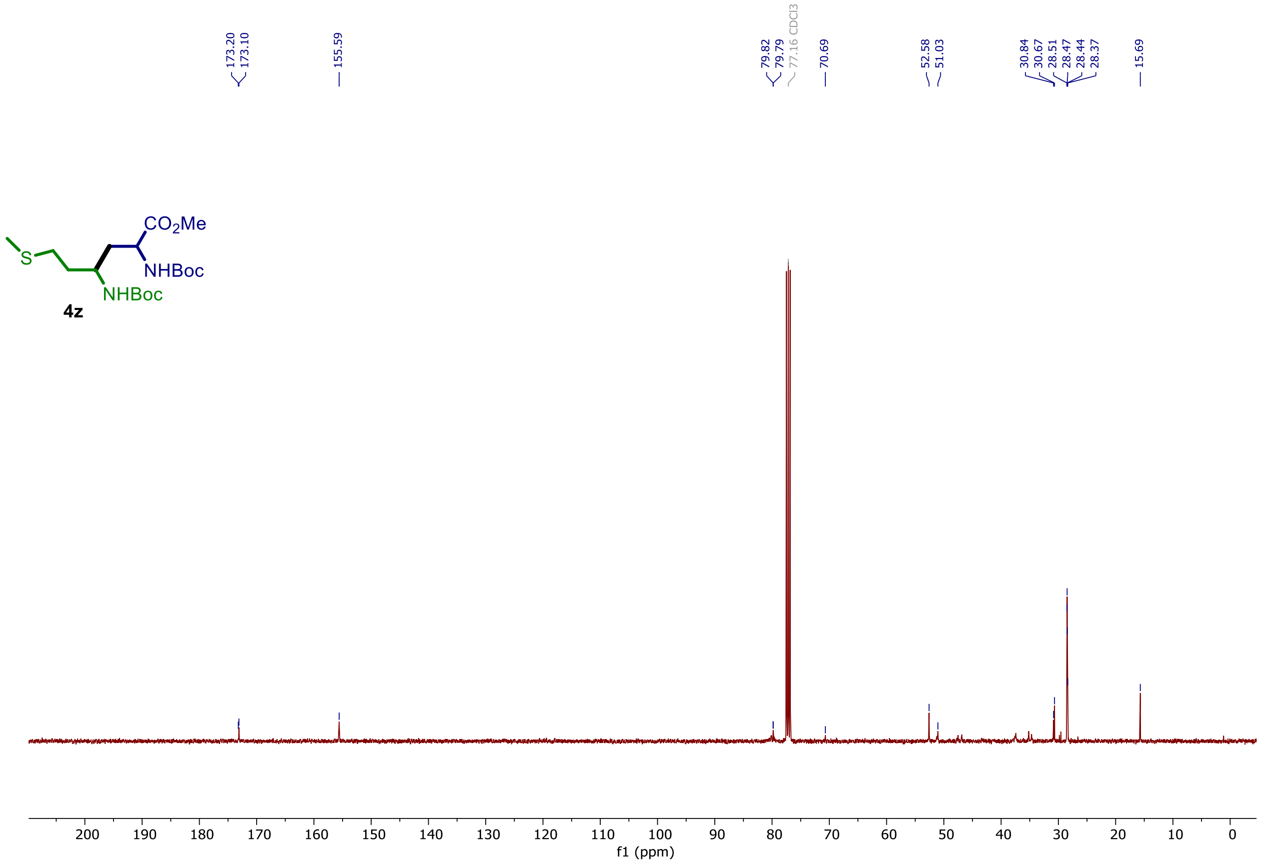
1.0
0.5
0.0
f1 (ppm)



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79.82
79.79
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70.69
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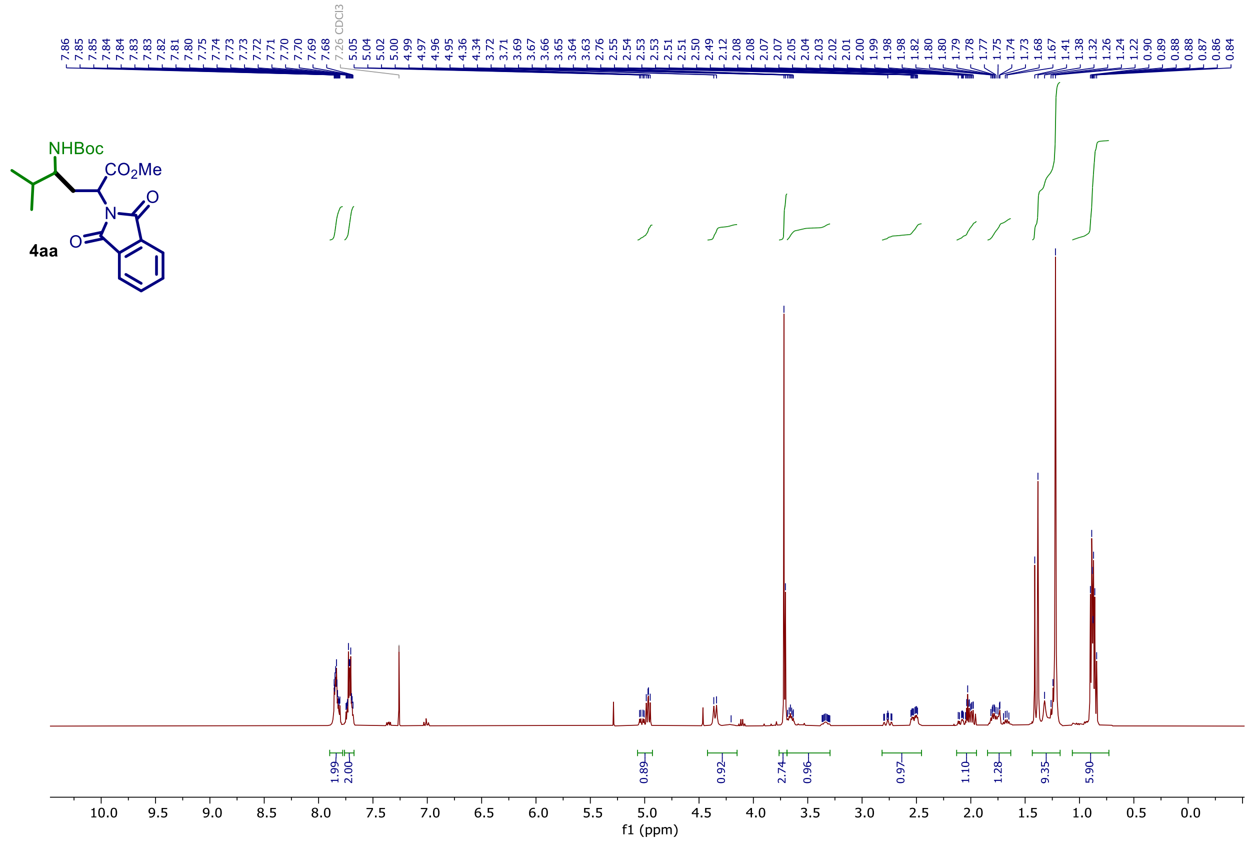
51.03
30.84
30.67
28.51
28.47
28.44
28.37
15.69
CO$_2$Me
S
NHBoc
NHBoc
4z
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NHBoc
CO$_2$Me
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O
O
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7.81
7.80
7.75
7.74
7.73
7.73
7.72
7.71
7.70
7.70
7.69
7.68
7.26 CDCl3
5.05
5.04
5.02
5.00
4.99
4.97
4.96
4.95
4.36
4.34
3.72
3.71
3.69
3.67
3.66
3.65
3.64
3.63
2.76
2.55
2.54
2.53
2.53
2.51
2.51
2.50
2.49
2.12
2.08
2.08
2.07
2.07
2.05
2.04
2.03
2.02
2.01
2.00
1.99
1.98
1.98
1.82
1.80
1.80
1.79
1.78
1.77
1.75
1.74
1.73
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1.67
1.41
1.38
1.32
1.26
1.24
1.22
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0.89
0.88
0.88
0.87
0.86
0.84
1.99
2.00
0.89
0.92
2.74
0.96
0.97
1.10
1.28
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9.5
9.0
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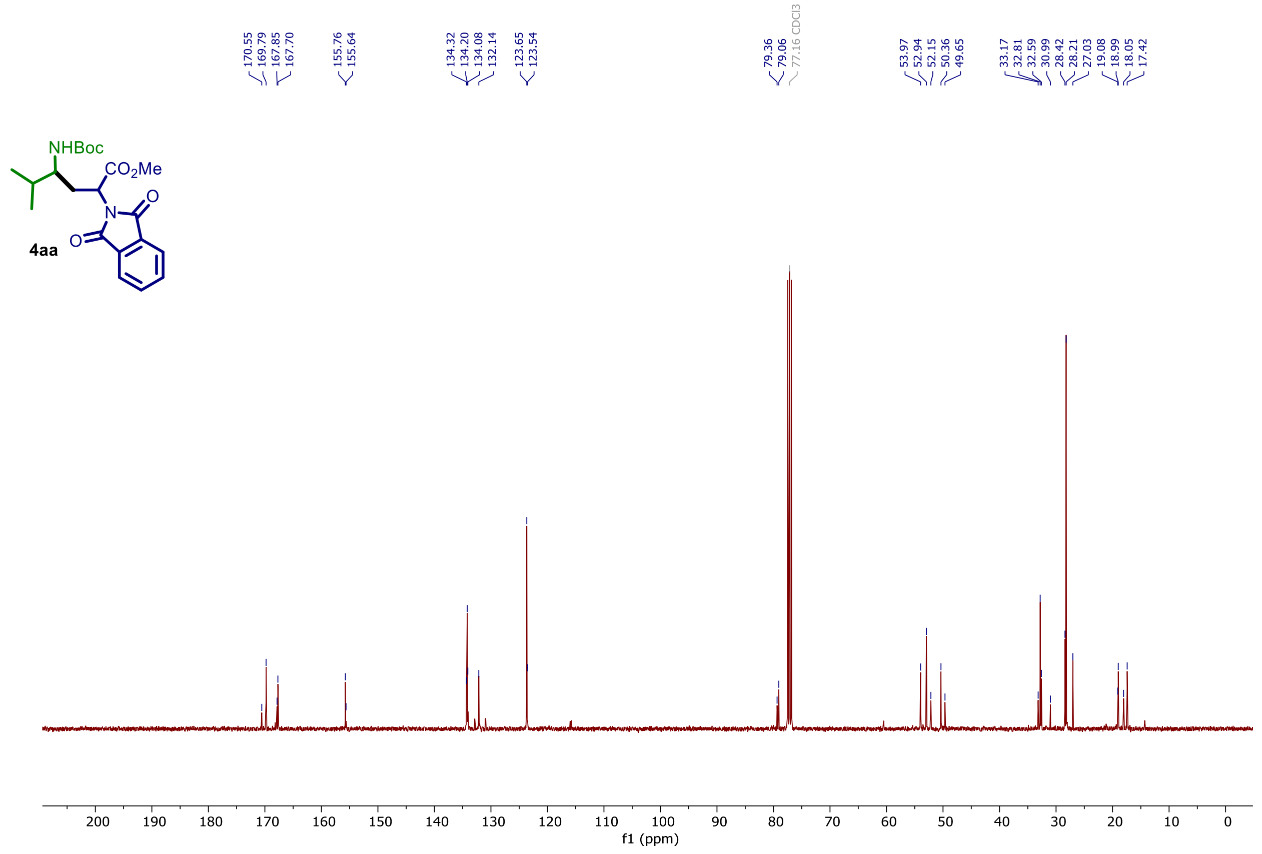
0.0
f1 (ppm)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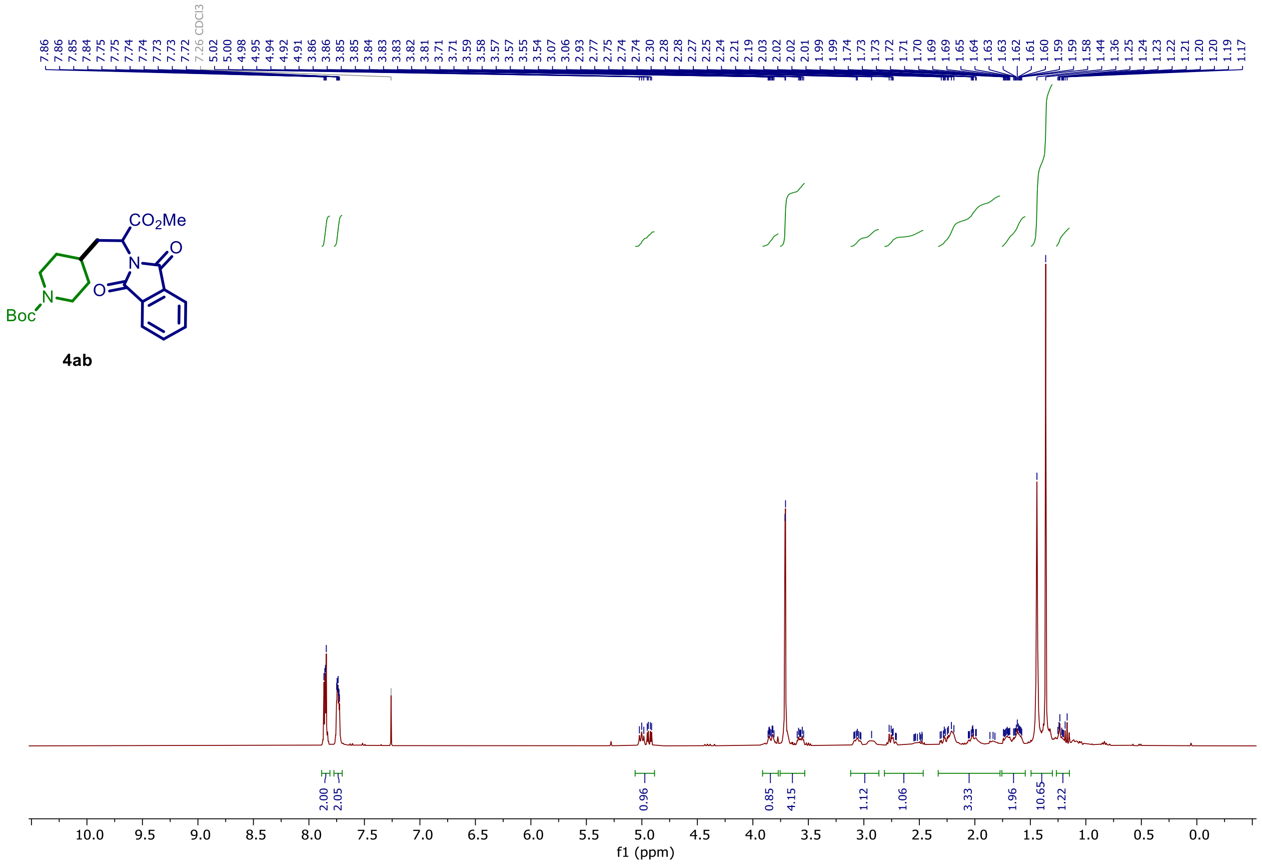
134.32
134.20
134.08
132.14
123.65
123.54
79.36
79.06
77.16 CDCl3
53.97
52.94
52.15
50.36
49.65
33.17
32.81
32.59
30.99
28.42
28.21
27.03
19.08
18.99
18.05
17.42
NHBoc
CO$_2$Me
N
O
O
4aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



7.86
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7.84
7.75
7.75
7.74
7.74
7.73
7.73
7.72
7.26 CDCl3
5.02
5.00
4.98
4.95
4.94
4.92
4.91
3.86
3.86
3.85
3.85
3.84
3.83
3.83
3.82
3.81
3.71
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3.58
3.57
3.57
3.55
3.54
3.07
3.06
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2.77
2.75
2.74
2.74
2.30
2.28
2.28
2.27
2.25
2.24
2.21
2.19
2.03
2.02
2.02
2.01
1.99
1.99
1.74
1.73
1.73
1.72
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1.69
1.69
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1.64
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1.61
1.60
1.59
1.59
1.58
1.44
1.36
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.17
CO2Me
N
O
O
N
Boc
2.00
2.05
0.96
0.85
4.15
1.12
1.06
3.33
1.96
10.65
1.22
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
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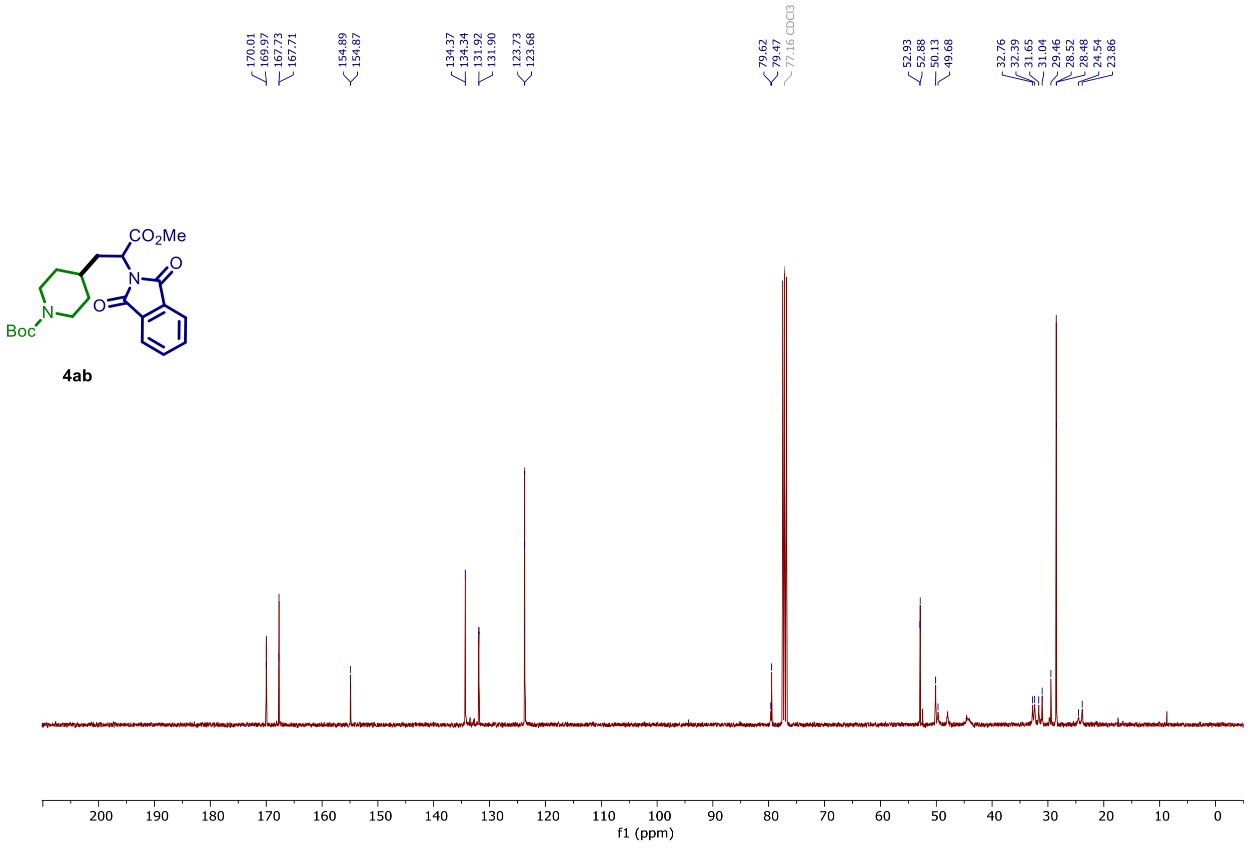
f1 (ppm)

4ab



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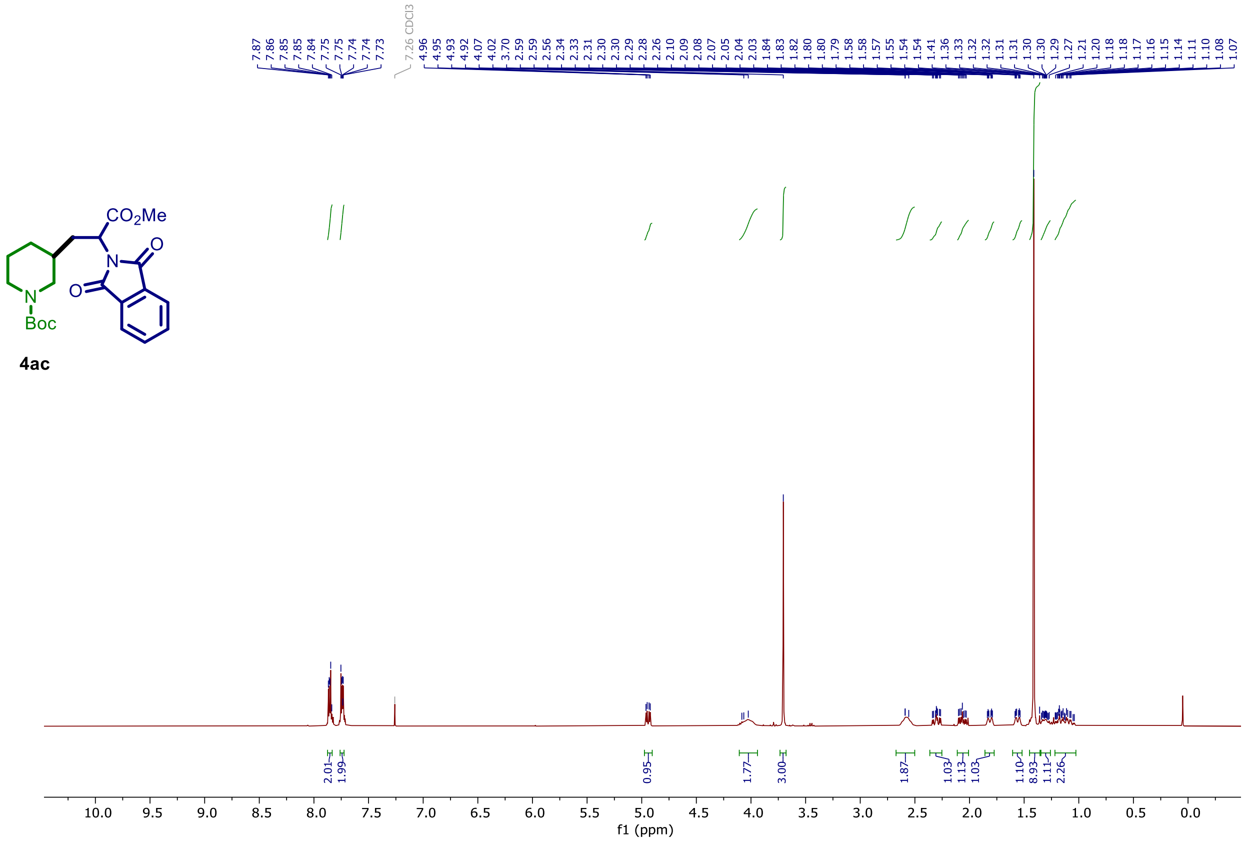
134.34
131.92
131.90
123.73
123.68
79.62
79.47
77.16 CDCl3
52.93
52.88
50.13
49.68
32.76
32.39
31.65
31.04
29.46
28.52
28.48
24.54
23.86
CO2Me
N
O
O
N
Boc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4ab

CO$_2$Me
N
O
O
N
Boc

4ac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7.75
7.74
7.74
7.73
7.26 CDCl3
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4.95
4.93
4.92
4.07
4.02
3.70
2.59
2.59
2.56
2.34
2.33
2.31
2.30
2.30
2.29
2.28
2.26
2.10
2.09
2.08
2.07
2.05
2.04
2.03
1.84
1.83
1.82
1.80
1.80
1.79
1.58
1.58
1.57
1.55
1.54
1.54
1.41
1.36
1.33
1.32
1.32
1.31
1.31
1.30
1.30
1.29
1.27
1.21
1.20
1.18
1.18
1.17
1.16
1.15
1.14
1.11
1.10
1.08
1.07
2.01
1.99
0.95
1.77
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1.03
1.13
1.03
1.10
8.93
1.11
2.26
10.0
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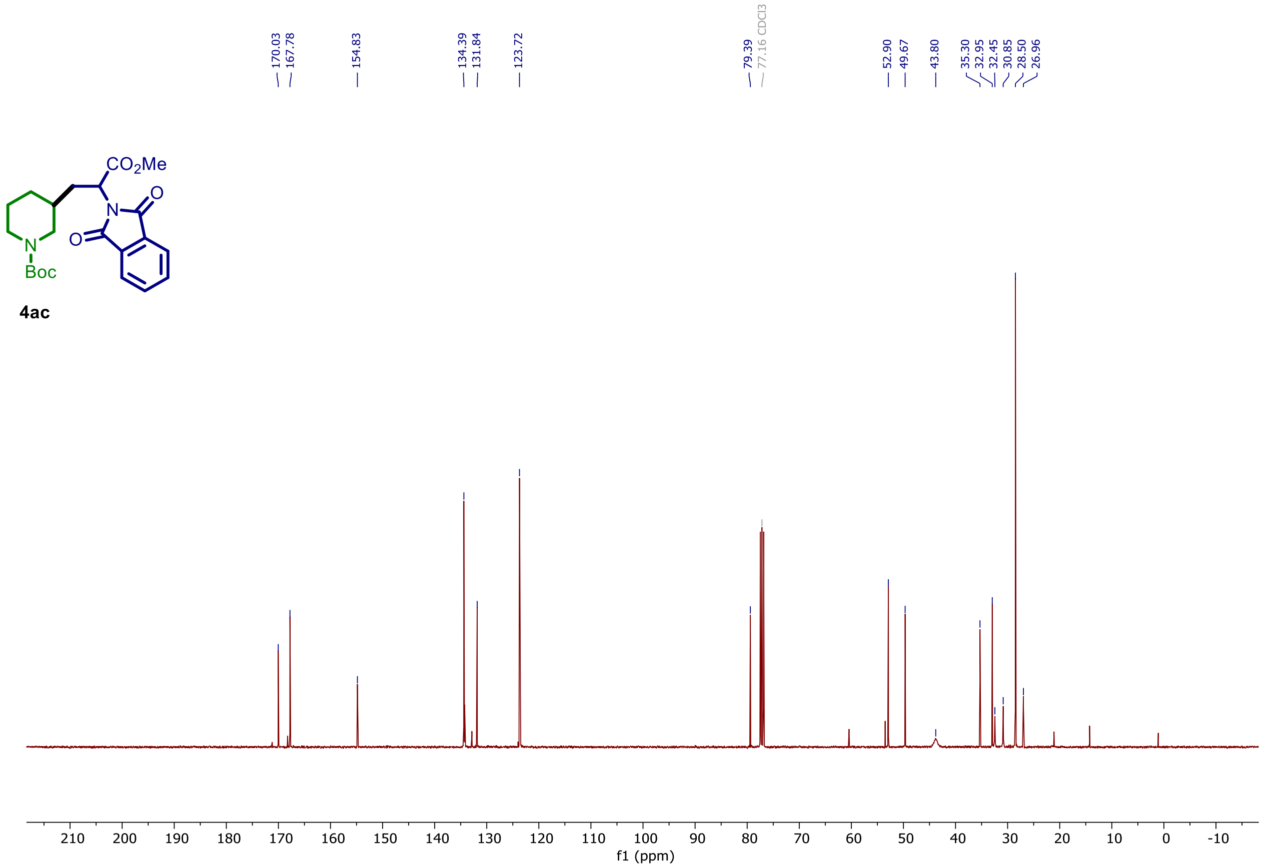
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

CO$_2$Me
N
O
O
N
Boc

4ac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77.16 CDCl3
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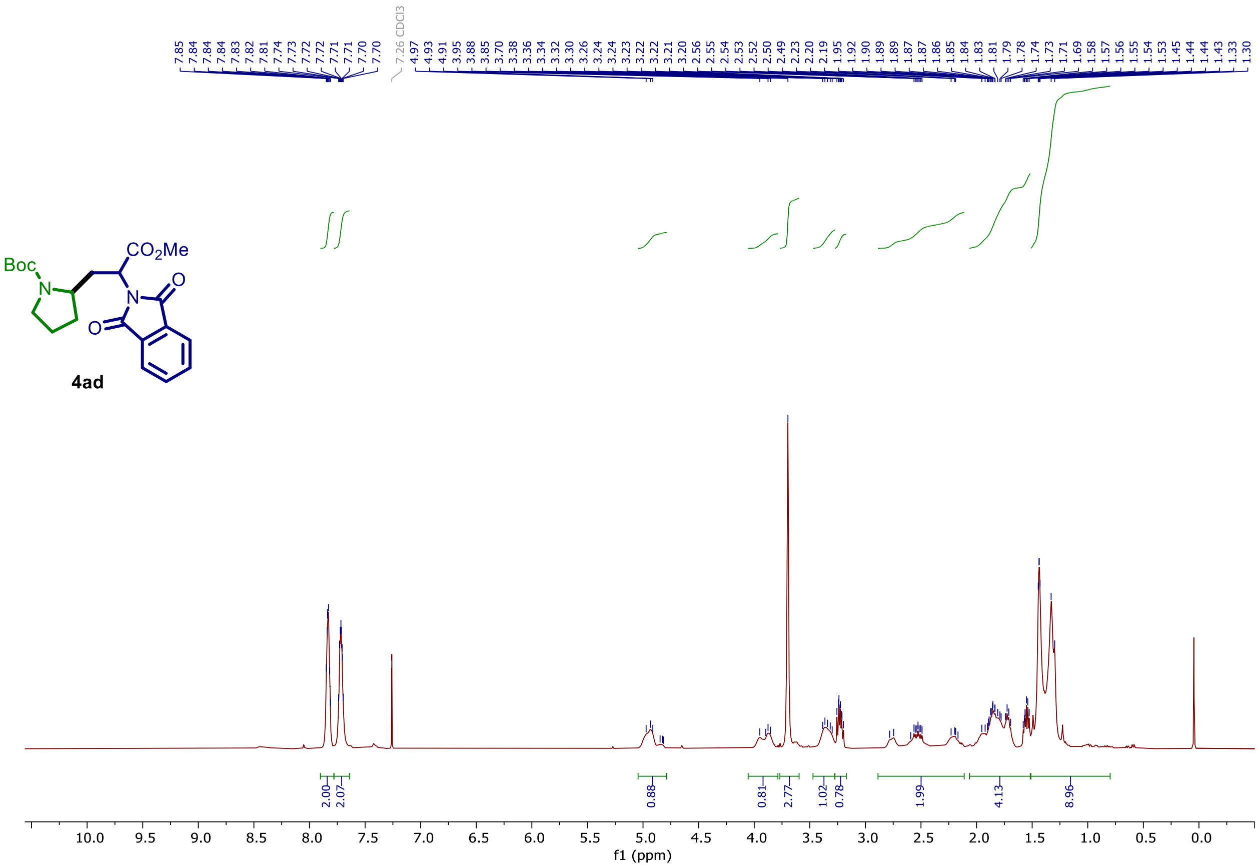
49.67
43.80
35.30
32.95
32.45
30.85
28.50
26.96
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


4ad

Boc
N
CO$_2$Me
N
O
O
7.85
7.84
7.84
7.83
7.82
7.81
7.74
7.73
7.72
7.72
7.71
7.71
7.70
7.26 CDCl3
4.97
4.93
4.91
3.95
3.88
3.85
3.70
3.38
3.36
3.34
3.32
3.30
3.26
3.24
3.24
3.23
3.22
3.22
3.21
3.20
2.56
2.55
2.54
2.53
2.52
2.50
2.49
2.23
2.20
2.19
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1.90
1.89
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1.83
1.81
1.79
1.78
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1.69
1.58
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1.55
1.54
1.53
1.45
1.44
1.43
1.33
1.30
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0.81
2.77
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0.78
1.99
4.13
8.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
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1.0
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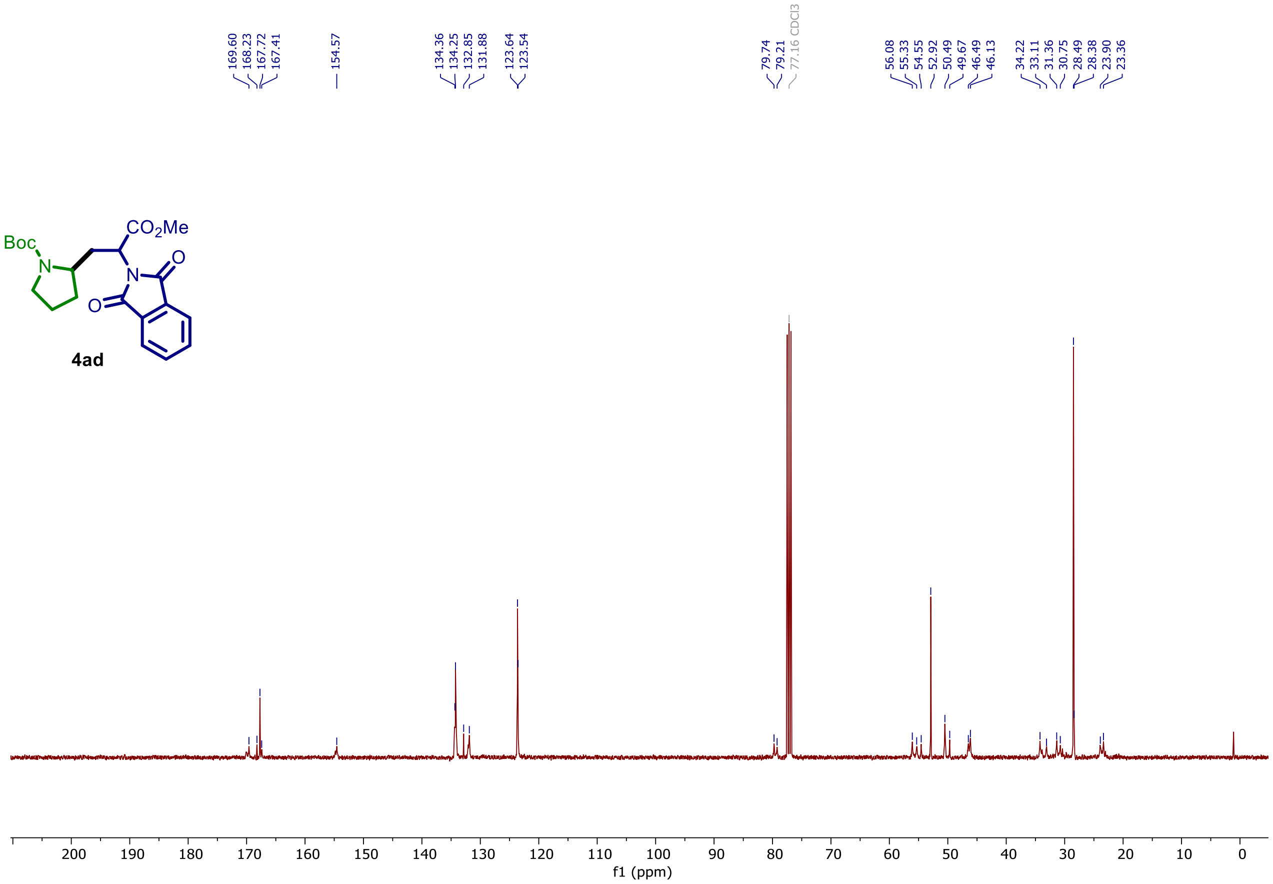
0.0
f1 (ppm)


4ad

Boc
N
CO$_2$Me
N
O
O
169.60
168.23
167.72
167.41
154.57
134.36
134.25
132.85
131.88
123.64
123.54
79.74
79.21
77.16 CDCl3
56.08
55.33
54.55
52.92
50.49
49.67
46.49
46.13
34.22
33.11
31.36
30.75
28.49
28.38
23.90
23.36
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
40
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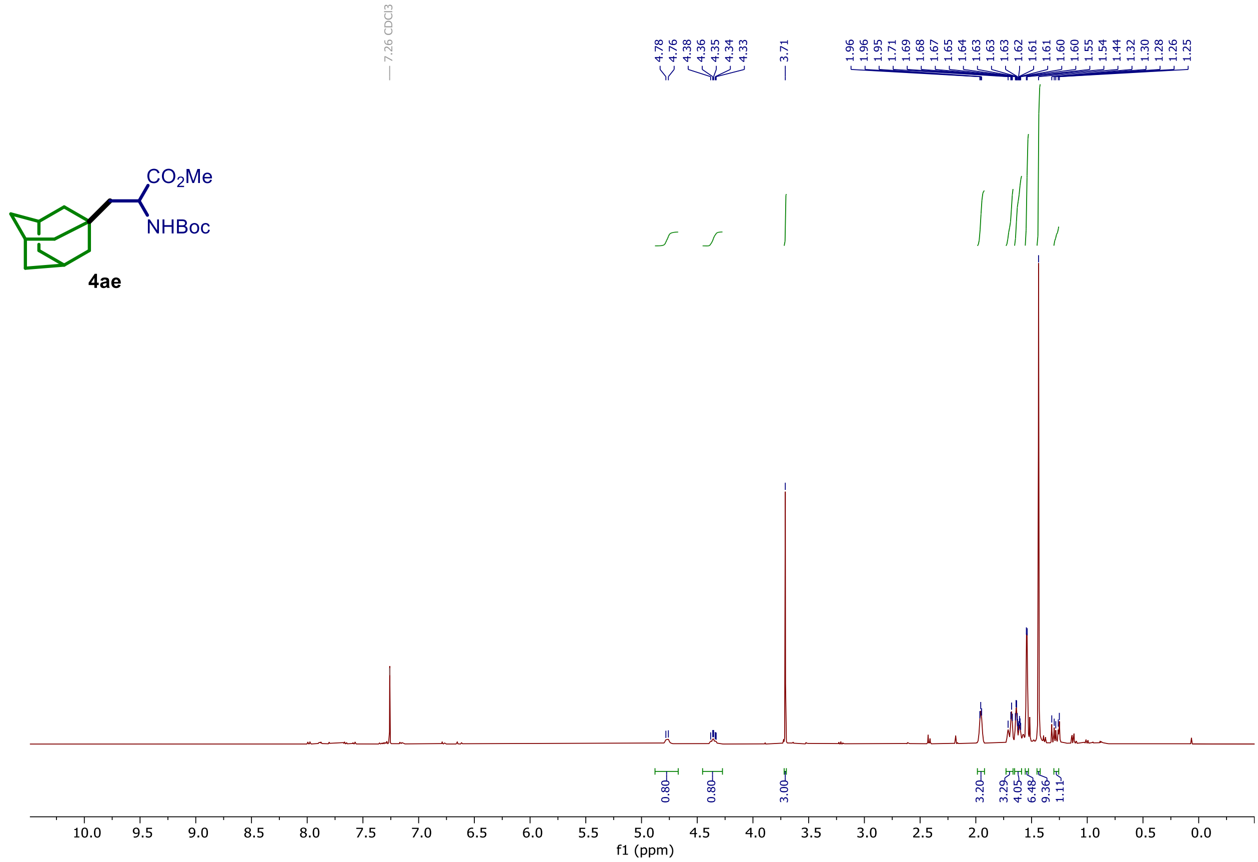
20
10
0
f1 (ppm)



4ae

CO2Me
NHBoc
7.26 CDCl3
4.78
4.76
4.38
4.36
4.35
4.34
4.33
3.71
1.96
1.96
1.95
1.71
1.69
1.68
1.67
1.65
1.64
1.63
1.63
1.63
1.62
1.61
1.61
1.60
1.60
1.55
1.54
1.44
1.32
1.30
1.28
1.26
1.25
0.80
0.80
3.00
3.20
3.29
4.05
6.48
9.36
1.11
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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3.5
3.0
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2.0
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1.0
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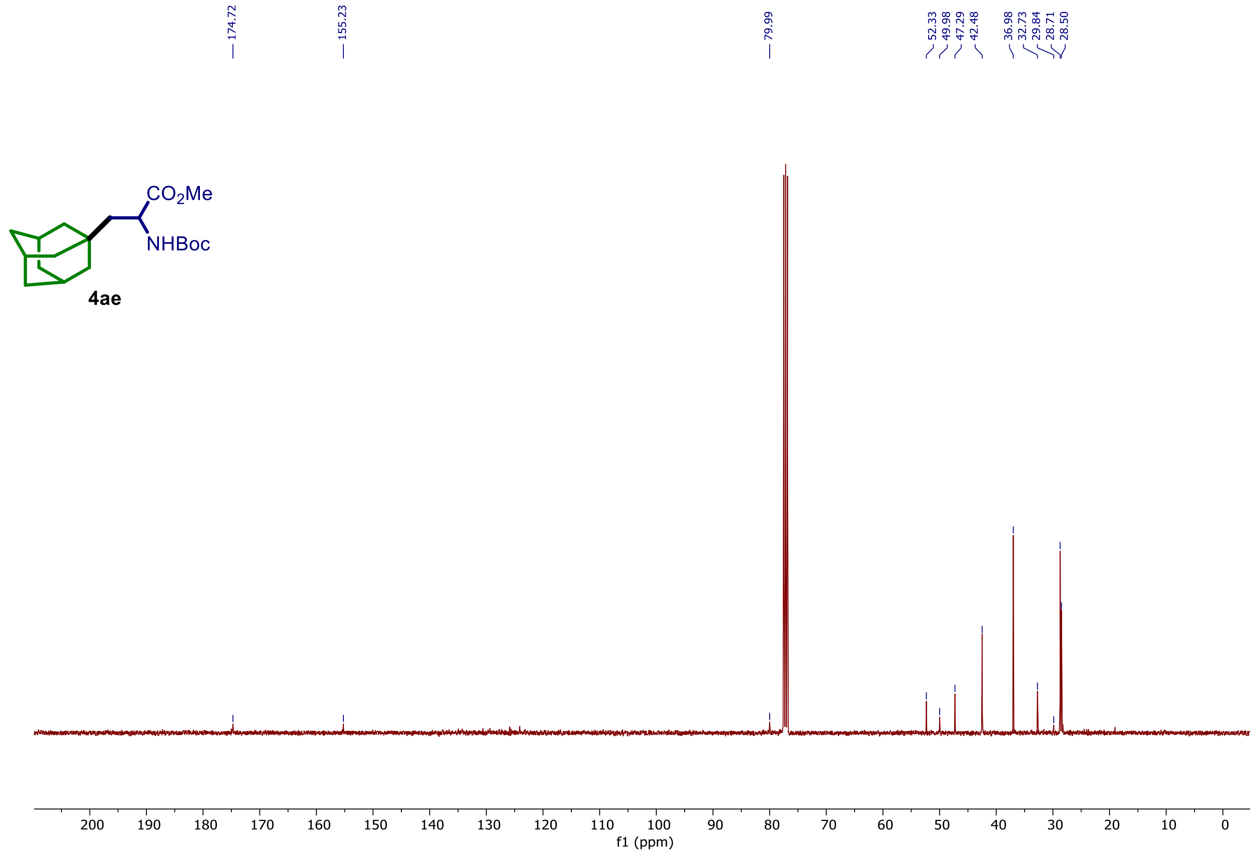
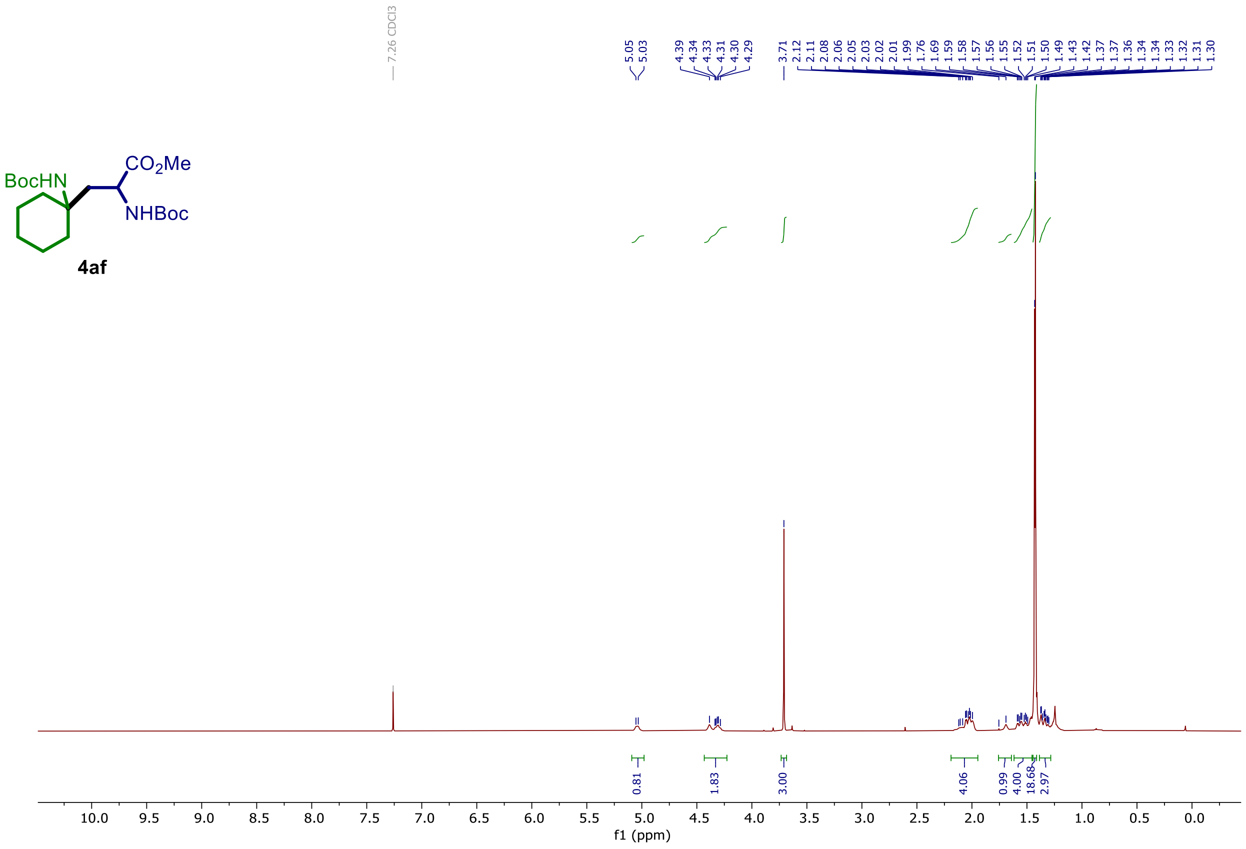
0.0
f1 (ppm)



4ae

CO2Me
NHBoc
174.72
155.23
79.99
52.33
49.98
47.29
42.48
36.98
32.73
29.84
28.71
28.50
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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5.05
5.03
4.39
4.34
4.33
4.31
4.30
4.29
3.71
2.12
2.11
2.08
2.06
2.05
2.03
2.02
2.01
1.99
1.76
1.69
1.59
1.58
1.57
1.56
1.55
1.52
1.51
1.50
1.49
1.43
1.42
1.37
1.37
1.36
1.34
1.34
1.33
1.32
1.31
1.30
BocHN
CO2Me
NHBoc
4af
0.81
1.83
3.00
4.06
0.99
4.00
18.68
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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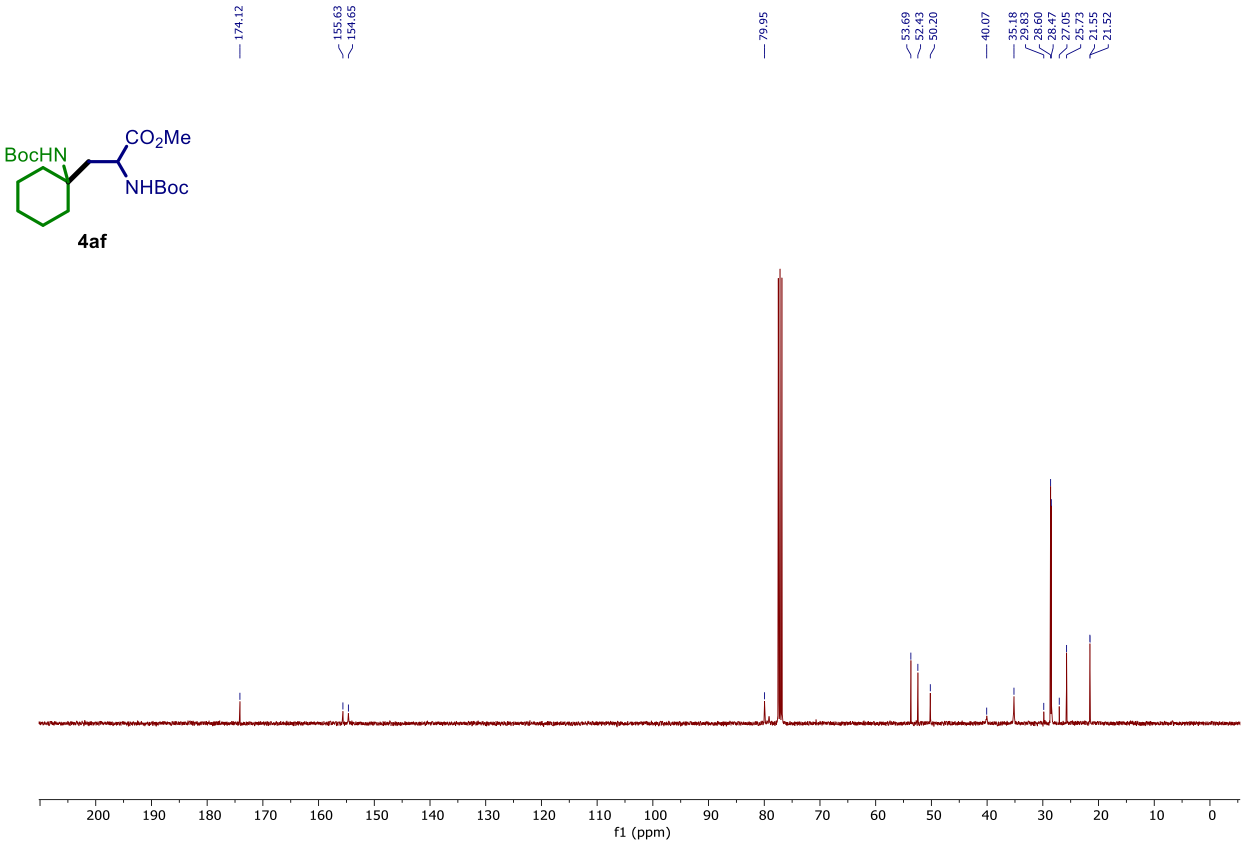
1.0
0.5
0.0
f1 (ppm)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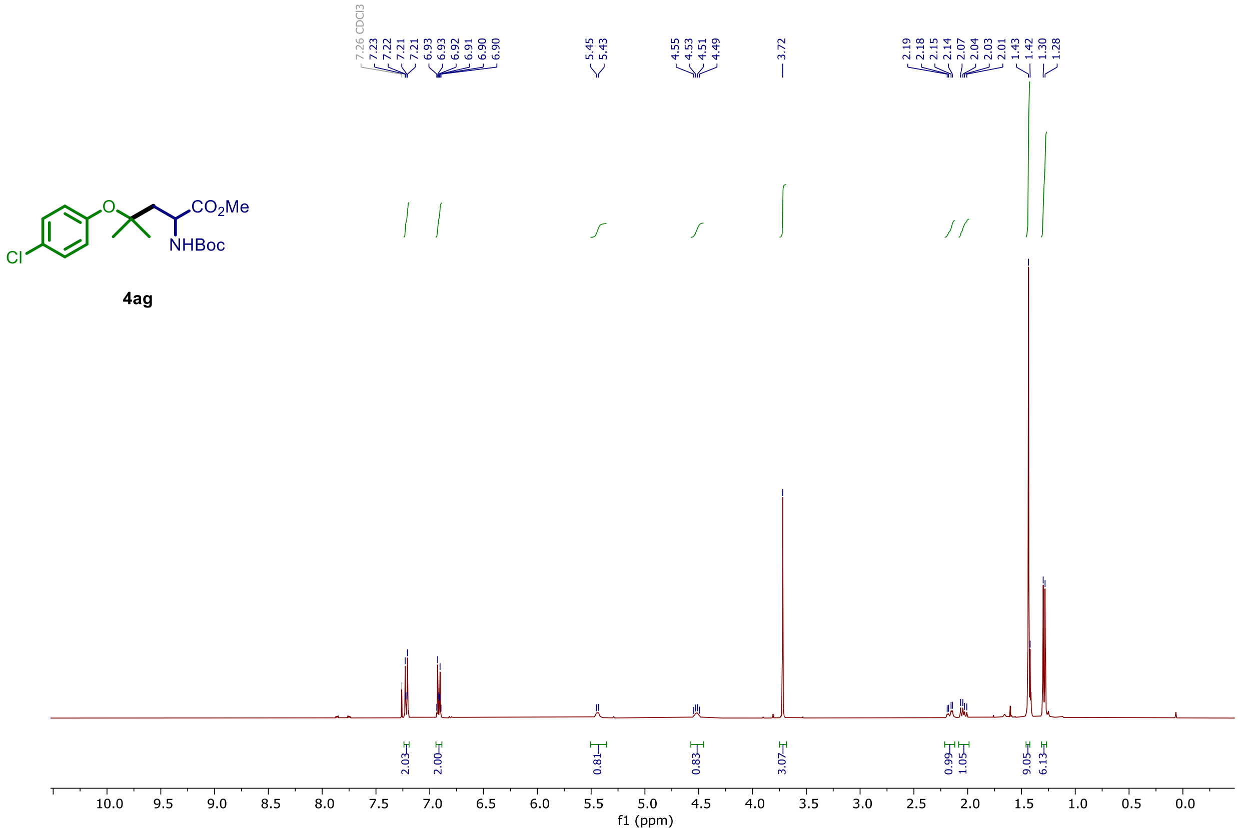
40.07
35.18
29.83
28.60
28.47
27.05
25.73
21.55
21.52
BocHN
CO2Me
NHBoc
4af
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26 CDCl3
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7.22
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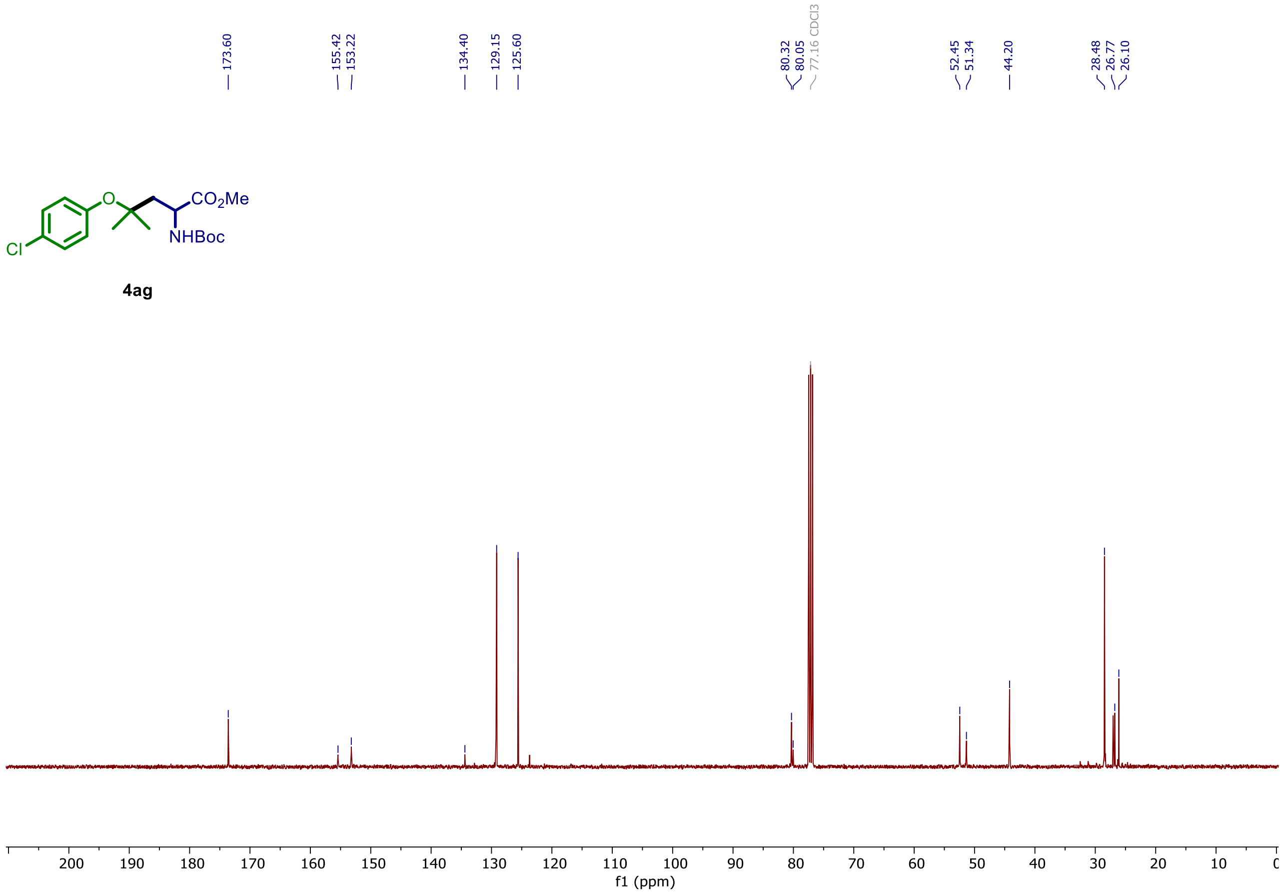
7.21
6.93
6.93
6.92
6.91
6.90
6.90
5.45
5.43
4.55
4.53
4.51
4.49
3.72
2.19
2.18
2.15
2.14
2.07
2.04
2.03
2.01
1.43
1.42
1.30
1.28
2.03
2.00
0.81
0.83
3.07
0.99
1.05
9.05
6.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
CO2Me
NHBoc
Cl

4ag


173.60
155.42
153.22
134.40
129.15
125.60
80.32
80.05
77.16 CDCl3
52.45
51.34
44.20
28.48
26.77
26.10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
CO2Me
NHBoc
Cl

4ag

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