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Supporting Information

Nanorod Photocatalysts for C–O Cross-Coupling Reactions

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[1] Supplementary Data

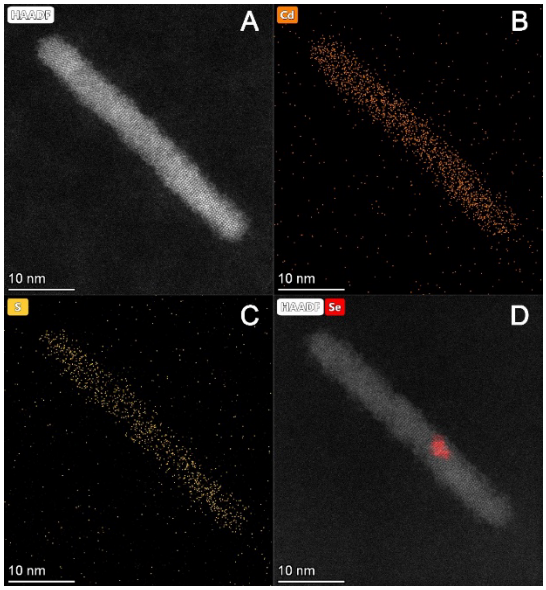


Figure S1 *(A) HAADF image of CdSe@CdS nanorods and EDX elemental mapping for Cd (B) and S (C); (D) Se EDX mapping and relative HAADF image, showing CdSe seed embedded in one third of one single nanorod.*

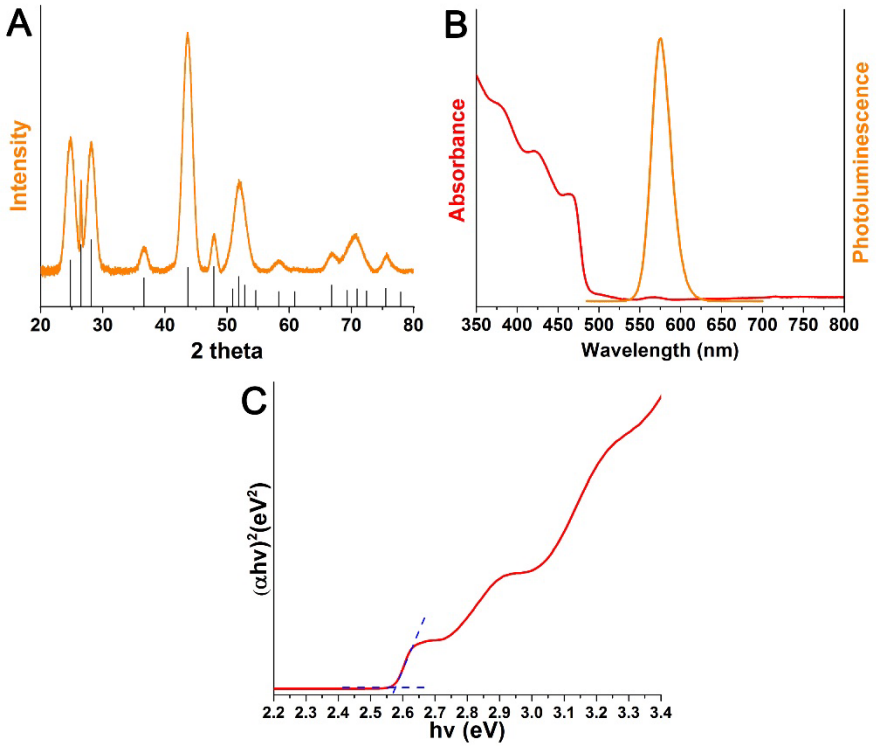
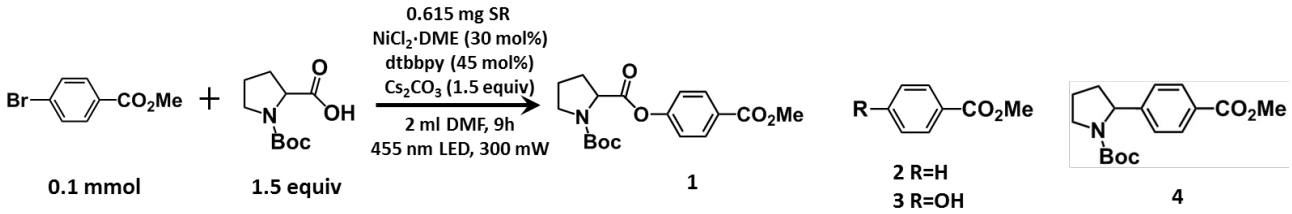


Figure S2 *(A) XRD pattern, (B) absorption and photoluminescence spectra of SR, (C) Tauc plot of colloidal SR. The intercept of the slope relative with first exciton absorption peak on the X-axis is 2.57 eV, indicating the optical band gap of CdS nanorods*

Table S1 *Optimization conditions*[a]



Entry	Deviation from standard conditions	1 [%][b]	2 [%][b]	3 [%][b]	4 [%][b]	Halide substrate[b]
1	Irradiation 3 hours	63%	0	0	0	34%
2	THF 2 mL, 3 h	14%	0	0	0	65%
3	acetone 2 mL, 3 h	0	0	0	0	100%
4	DMF 1 mL, 3 h	40%	0	0	0	53%
5	DMF 1 mL,0.02 mmol $NiCl_2$·DME, 6 h	36%	2%	0	0	54%
6	6 hours	80%	1.5%	0	0	9%
7	DMF 4 mL, 6 hours	81%	1%	0	0	8.5%
8	DMF 2 mL,0.05 mmol $NiCl_2$·DME, 6 h	65%	2%	0	0	20%

[a] Reaction conditions: methyl 4-bromobenzoate (0.1 mmol), Boc-Pro-OH (0.15 mmol), SR (0.615 mg, $2.7*10^{-7}$ mmol), $NiCl_2$·DME (0.03 mmol), dtbbpy (0.045 mmol), Cs_2CO_3 (0.15 mmol), DMF (2 mL, anhydrous), 455 nm LEDs with 300 mW at 40 ^{o}C. [b] calculated by ^{1}H-NMR using 0.1 mmol 1,3,5-trimethoxybenzene as internal standard.

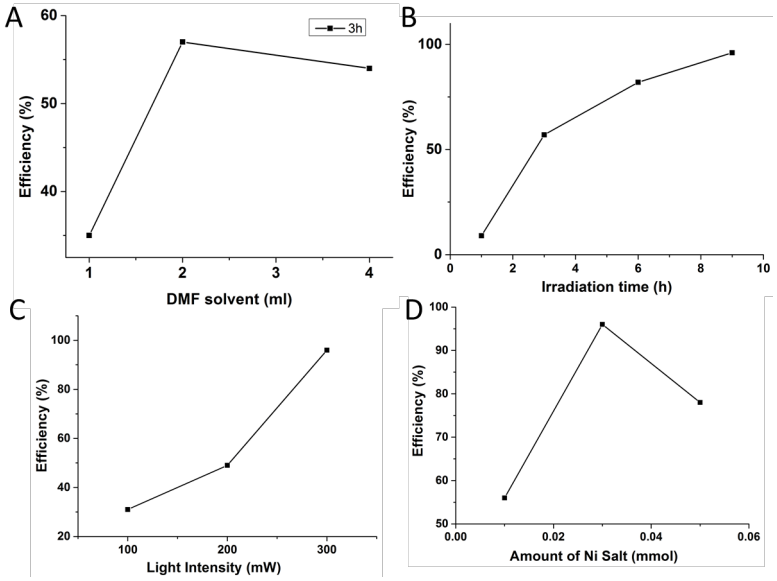
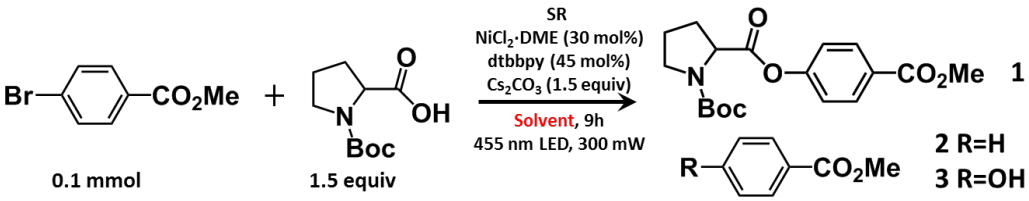


Figure S3 *Effect of solvent amount (A), irradiation time (B), light intensity (C), Ni salt amount (D) on the conversion efficiency, indicating the 2 mL DMF, 9 hours irradiation, 300 mW and 0.03 mmol Ni salt were optimal C-O cross coupling*

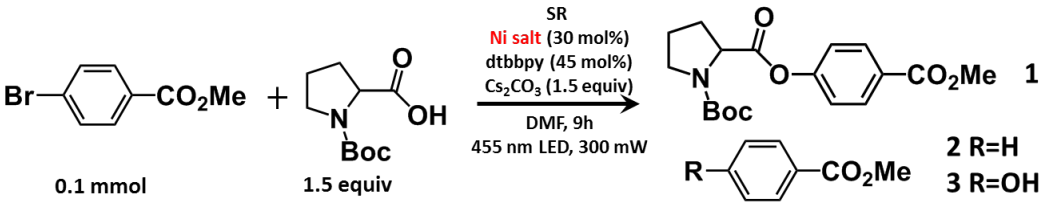
Table S2 *solvent screening*[a]



Entry	Screen solvent	1 [%][b]	2 [%][b]	3 [%][b]	Halide substrate[b]
1	DMF	96%	1.5%	0	0
2	DMSO	18%	2%	0	66%
3	THF	53%	0	0	46%
4	Acetonitrile	22%	3%	0	72%

[a] Reaction conditions: methyl 4-bromobenzoate (0.1 mmol), Boc-Pro-OH (0.15 mmol), SR (0.615 mg, $2.7*10^{-7}$ mmol), $NiCl_2$·DME (0.03 mmol), dtbbpy (0.045 mmol), Cs_2CO_3 (0.15 mmol), DMF (2 mL, anhydrous), 455 nm LEDs with 300 mW at 40 °C. [b] calculated by ^{1}H-NMR using 0.1 mmol 1,3,5-trimethoxybenzene as internal standard.

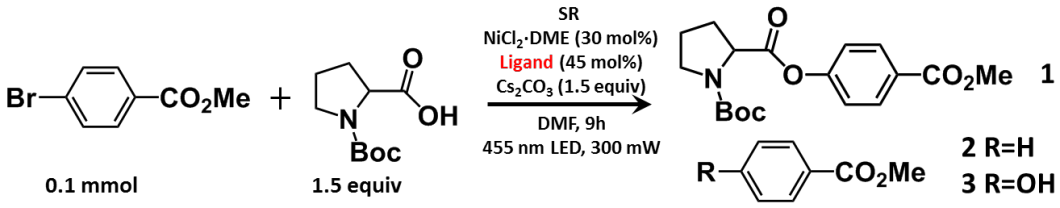
Table S3 *Ni salt screening*[a]



Entry	Screen Ni salt	1 [%][b]	2 [%][b]	3 [%][b]	Halide substrate[b]
1	$NiCl_2$·DME	96%	1.5%	0	0
2	Ni acetate·$4H_2O$	34%	4%	0	0
3	$Ni(AcAc)_2$	6%	2%	0	92%
4	$NiSO_4$·$6H_2O$	44%	2.5%	0	41%

[a] Reaction conditions: methyl 4-bromobenzoate (0.1 mmol), Boc-Pro-OH (0.15 mmol), SR (0.615 mg, $2.7*10^{-7}$ mmol), $NiCl_2$·DME (0.03 mmol), dtbbpy (0.045 mmol), Cs_2CO_3 (0.15 mmol), DMF (2 mL, anhydrous), 455 nm LEDs with 300 mW at 40 °C. [b] calculated by ^{1}H-NMR using 0.1 mmol 1,3,5-trimethoxybenzene as internal standard.

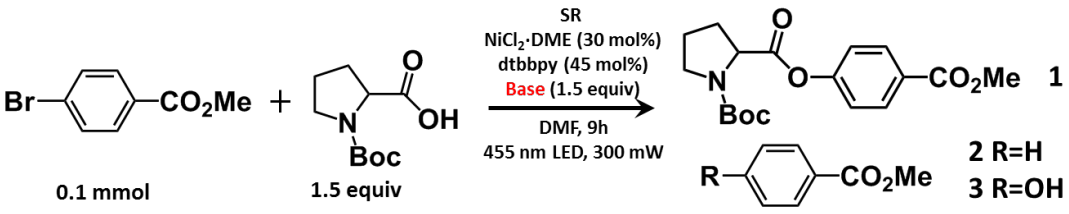
Table S4 *ligand screening*[a]



Entry	Screen ligand	1 [%][b]	2 [%][b]	3 [%][b]	Halide substrate[b]
1	dtbbpy	96%	1.5%	0	0
2	2,2′-Bipyridine	43%	4.5%	2%	38%
3	1,10-phenanthroline	<16%	13%	1.5%	60%
4	4,4‘-Dimethyl-2,2’-bipyridyl	70%	5.5%	4.5%	11.5%

[a] Reaction conditions: methyl 4-bromobenzoate (0.1 mmol), Boc-Pro-OH (0.15 mmol), SR (0.615 mg, $2.7*10^{-7}$ mmol), $NiCl_2$·DME (0.03 mmol), dtbbpy (0.045 mmol), Cs_2CO_3 (0.15 mmol), DMF (2 mL, anhydrous), 455 nm LEDs with 300 mW at 40 °C. [b] calculated by ^{1}H-NMR using 0.1 mmol 1,3,5-trimethoxybenzene as internal standard.

Table S5 *base screening*[a]



Entry	Screen base	1 [%][b]	2 [%][b]	3 [%][b]	Halide substrate[b]
1	Cs_2CO_3	96%	1.5%	0	0
2	1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)	25%	15%	0	2%
3	N-*tert*-butylisopropylamine	10%	14%	0	2%
4	N,N-Diisopropylethylamine	12%	15%	0	0
5	K_3PO_4	24%	3.5%	0	53%
6	Quinuclidine	6%	14%	0	15%

[a] Reaction conditions: methyl 4-bromobenzoate (0.1 mmol), Boc-Pro-OH (0.15 mmol), SR (0.615 mg, $2.7*10^{-7}$ mmol), $NiCl_2$·DME (0.03 mmol), dtbbpy (0.045 mmol), Cs_2CO_3 (0.15 mmol), DMF (2 mL, anhydrous), 455 nm LEDs with 300 mW at 40 °C. [b] calculated by ^{1}H-NMR using 0.1 mmol 1,3,5-trimethoxybenzene as internal standard.

Definition of Turnover Number (TON)) and (Turnover Frequency (TOF)

Turnover number (TON) for the SR photocatalytic system was calculated as the molar ratio between the C-O products that are detected and the rods:

$$TON=\frac{molar\ of\ C-O\ produt}{molar\ of\ nanorods}$$

In this regard is it vital to note that this is a photocatalytic system for which the limiting step is the absorption of light and generation of photoinduced charges. Since a single exciton is formed on each rod and sopportes the reaction, a rod is taken as a single catalytic site (as opposed to the number of atoms or surface active sites on the particle. We are awar of the fact that most heterogeneous photocatalytic systems are not based on individual particles that offer a single well-defined catalytic site. Hence we also provid activity quantified per unit of mass rather than molar ratio as in the TON definition.

Turnover frequency was used here as the number of generated products per unit of time (sec or hour) per catalytic site, again with a rod being defined as a single site.

$$TOF=\frac{TON}{reaction\ time}$$

Since this work offers a uniqe combination of a photocatalytic heterogenius system with a homoginus catalysis, we aqnoledge that some readers would experess interest in the TON calculated as per molar of Ni catalyst:

$$TON_{Ni}=\frac{molar\ of\ C-O\ product}{molar\ of\ Ni\ salt}$$

Though this data was also calculated and is provided in Table S6, it should be empasisyed that no optimization towards the Ni catalysts TON was performed in the course of this work.

Table S6 *comparison with other works in terms of photocatalyst concentration, substrates concentration, reaction time and yield*

	photocatalyst	Concentration of photocatalyst in solvent (mg/mL)	Aryl halide (mmol) /per mg of photocatalyst	Substrate aryl halide	Ni cocatalyst	Reaction time	Yield of C-O cross coupling	TON as per Ni salt	TOF as per Ni salt
MacMillan 's work	$Ir(ppy)_3$	1.3	0.153	0.8 mmol	0.04 mmol	18	94%	18.8	1.04 hr^{-1}
Pieber's work	C_3N_4	3.33	0.03	0.3 mmol	0.03 mmol	14	96%	9.6	0.69 hr^{-1}
This work	CdSe@CdS nanorods	0.3	0.163	0.1 mmol	0.03 mmol	9	96%	3.2	0.35 hr^{-1}
This work	CdSe@CdS nanorods	0.077	1.3	0.8 mmol	0.03 mmol	18	71%	18.9	1.05 hr^{-1}
This work	CdSe@CdS nanorods	0.038	2.6	1.6 mmol	0.03 mmol	18	61%	32.53	1.81 hr^{-1}

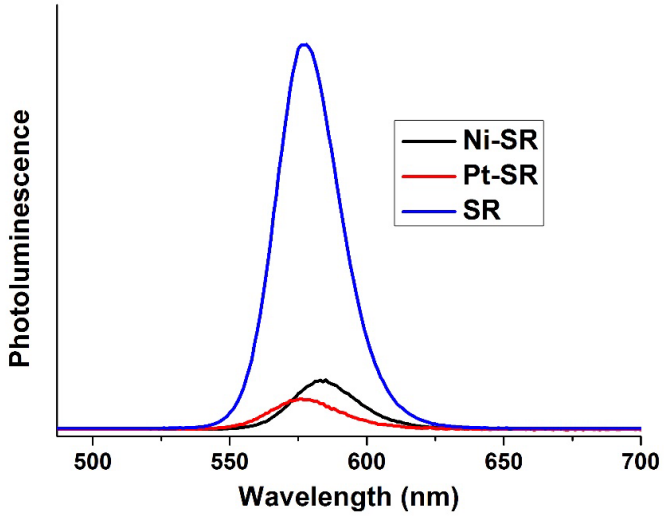


Figure S4 *Photoluminescence spectra of SR, Ni-SR and Pt-SR excited at 455 nm, indicating 40%, 5%, 3.4% quantum yield*

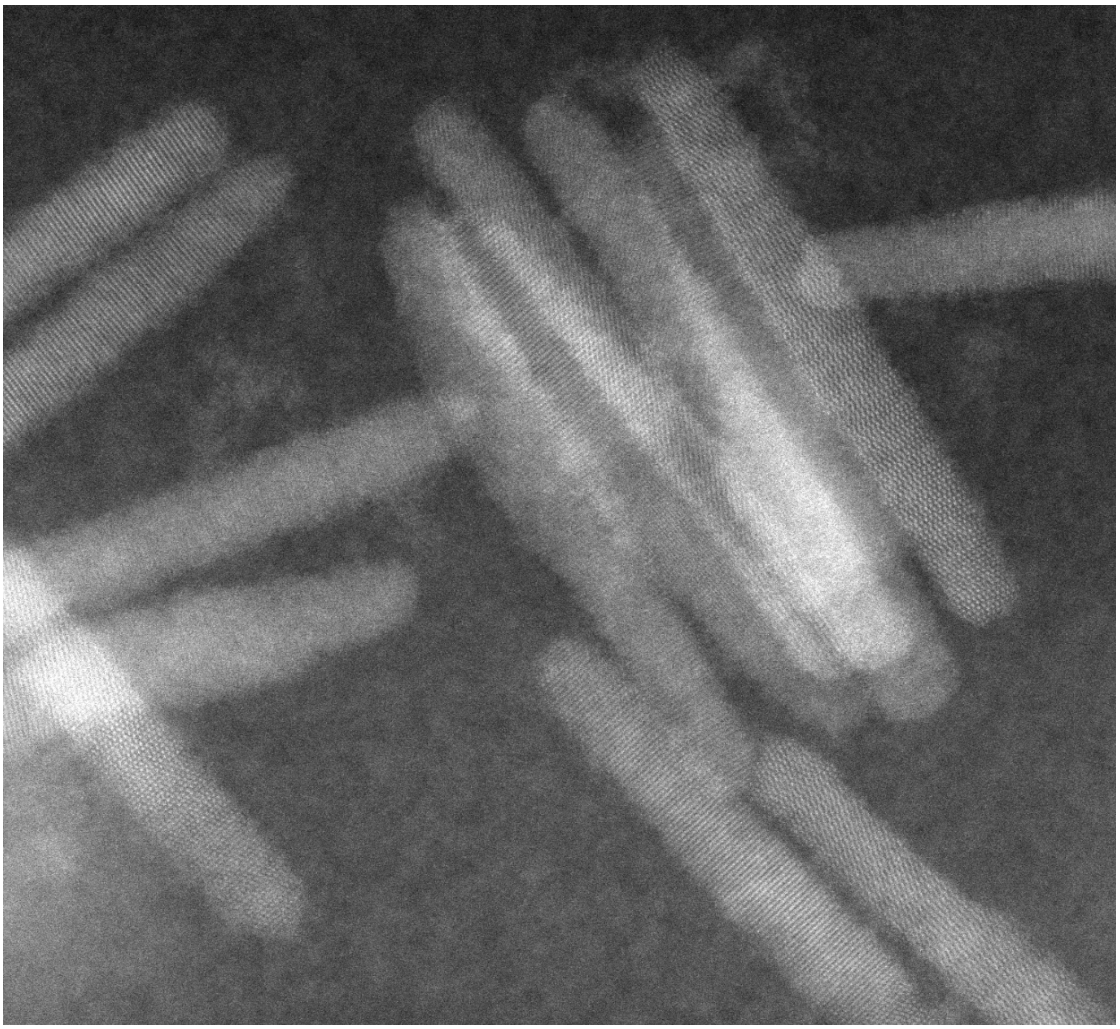


Figure S5 *High resolution STEM of nanorods after 132 hours illumination. There was no trace of Ni cluster or particles on crystalline lattice of nanorods*

A potential concern when using CdS nanorod photocatalysts is the toxicity of cadmium and potential trace contamination in the practical pharmaceutical synthesis. In our work, as Figure S5 showed, upon 132 hours irradiation under very strong light (300 mW, 455 nm LED), the surface of nanorods is still straight and well crystallized, with no evidence of photo-corrosion observed, as also indicated by the width of the nanorod that remained unchanged (confirmed also via absorption). Coupled with the stability of the yield over 10-recycles, this indicates a high level of robustness for CdS nanorods in our reaction system.

[2] The Ni-complex

Throughout the course of this work, the Ni-complex was produced in-situ via a simple mix the Ni salt and ligands in the presence of the substrates. The synthesis and efficient isolation of this complex are somewhat challenging since the coordination of the carboxylate nucleophile is rapid. Similar challenges were also reported in the literature.[1] Therefore, a similar approach was adopted here, and the energy transfer mechanism was investigated using a closely related alternative Ni complex as presented in Figure S6 A. This complex with *dtbbpy* ligand was utilized for the DFT calculation of the triplet energy state and absorption spectrum.

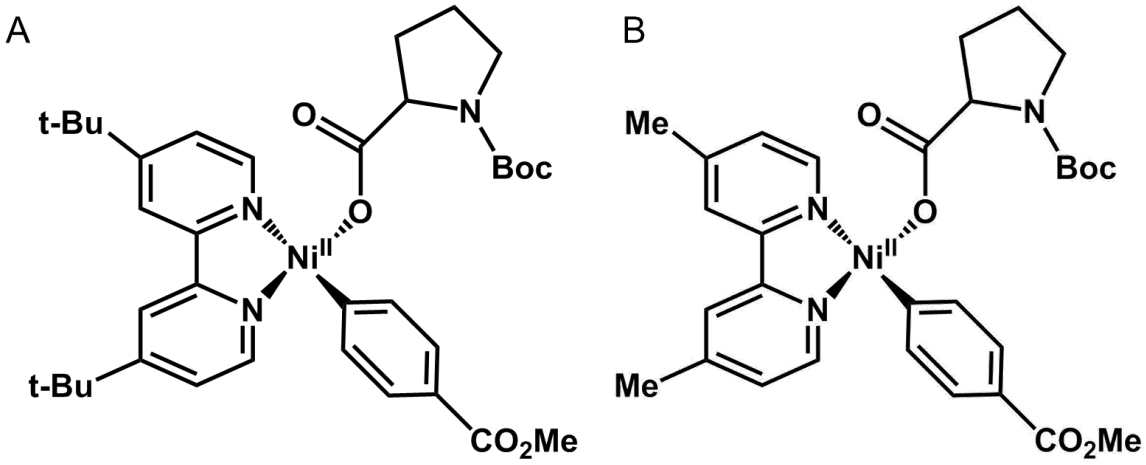


Figure S6 *(A) Chemical structure of Ni complex coordinated by ligand dtbbpy, and (B) 4,4'-dimethyl-2,2'-bipyridyl*

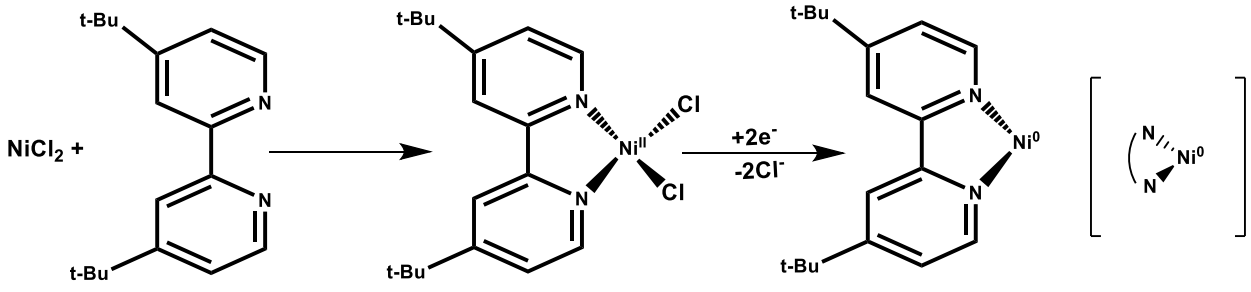


Figure S7 *Scheme of coordination of Ni^{2+} with ligand dtbbpy and in situ reduction of Ni(II) complex (pre-catalyst) to Ni(0) as shown in Figure 4*

[3] Computational Details

Given the lack of a thorough study with conclusive results regarding which of the known DFT functionals offers the best match with experimental spectra, especially for transition metal complexes, several options were considered here. From the survey done here[2-10] (see also the references below) there are three functionals that can be advised for the calculation of the first excitation energies and UV-Vis spectra:

1) B3LYP[3-5,9-11] – is the most studied functional, and it is often the first choice method for evaluation of electronic properties;
2) PBE0[2-6,9] – is also a very popular functional. In some cases it shows an even better match than the more widespread B3LYP, especially for electronic properties (including first excitation energies and UV-vis spectra) – is becoming more popular for el. Properties;
3) CAM-B3LYP[2,8,9] – is a relatively novel functional (range separated) which is more appropriate for the cases with charge transfer exciting states, which is, actually, the case for the studied complex and it can be requested by referees. However, it is less benchmarked than the previous two;

Separated references with TD-DFT functionals for: organic molecules[2,4,5,8,9]; TM complexes[3,5-7,11,12]

Table S7 *calculated S_0-S_1 energy gaps of Ni-complex in Figure S6*

Functional	*E[eV]*
B3LYP	2.2491
PBE0	2.4769
CAM-B3LYP	2.5382

Conformational search was performed by CREST[13] - computer code that uses the fast and reliable GFN$_n$-xTB methods. Geometry optimization of the lowest energy conformer and further frequency calculations were carried out using ORCA 4.2[14] software at BP86-D3(BJ)[15,16]/BS1 level of theory. Basis set BS1 refers to: for Ni Def2-TZVP and def2-SVP[17] for other elements. The optimized minima was verified by harmonic vibrational analysis to have no imaginary frequency. Absorption spectra and first excitation energies (S0-S1) were calculated by Gaussian (Revision D.01)[18] using

Tamm-Dancoff-approximated time-dependent DFT (TDA-DFT)[9,19] calculations by three functionals: B3LYP[20], PBE0[21] and CAM-B3LYP[22]; the functional used in conjunction with TZVP basis set; in DMF with CPCM model[23] as implemented in Gaussian.

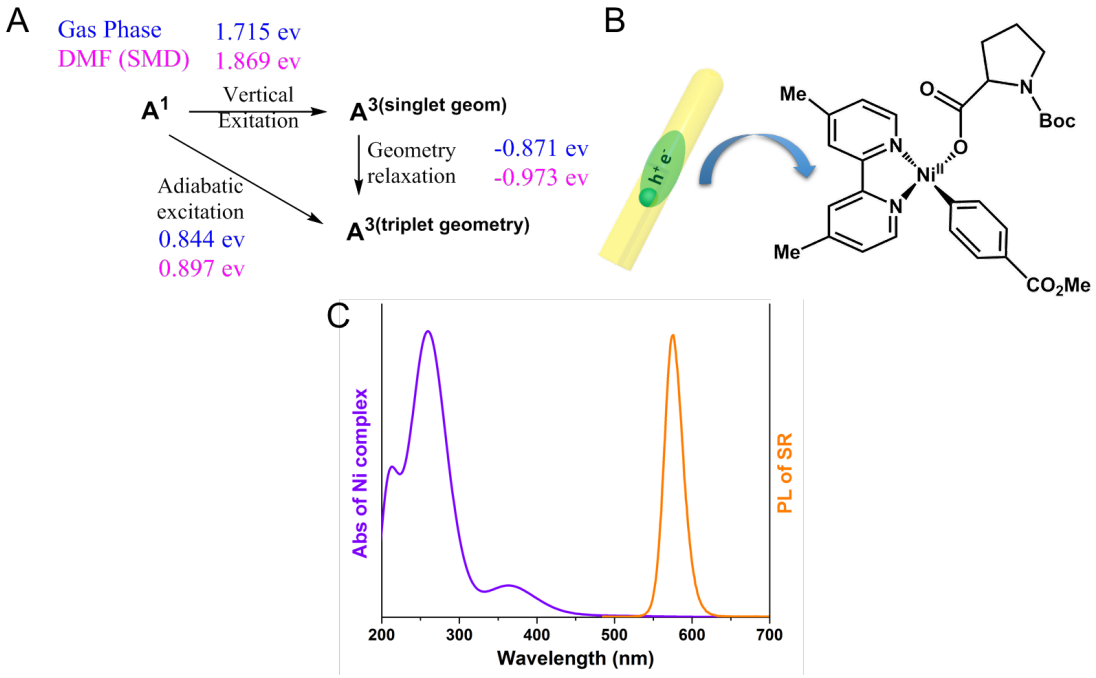


Figure S8 *(A) Adiabatic excitation, and vertical excitation plus geometry relaxation for triplet-singlet energy gap calculation; (B) Schematic diagram of Energy transfer from semiconductor nanocrystals CdSe@CdS nanorods to Ni-complex with ligand 4,4'-dimethyl-2,2'-bipyridyl; (C) calculated absorption spectrum of Ni complex in Figure S6 B by DFT/PBE0 and photoluminescence of SR*

Vertical excitation energy is a difference between the electronic energies of the excited state at the geometry of the ground state (before relaxation) and ground state at the geometry of the ground state. In contrast, evaluation of adiabatic excitation energy involves electronic energy of excited state at its geometry after relaxation, which follows the electron excitation being a much slower process. Generally, experimentally obtained spectra refer to vertical excitation energies; for adiabatic energies, more sophisticated spectroscopy is used.

[4] Ligands

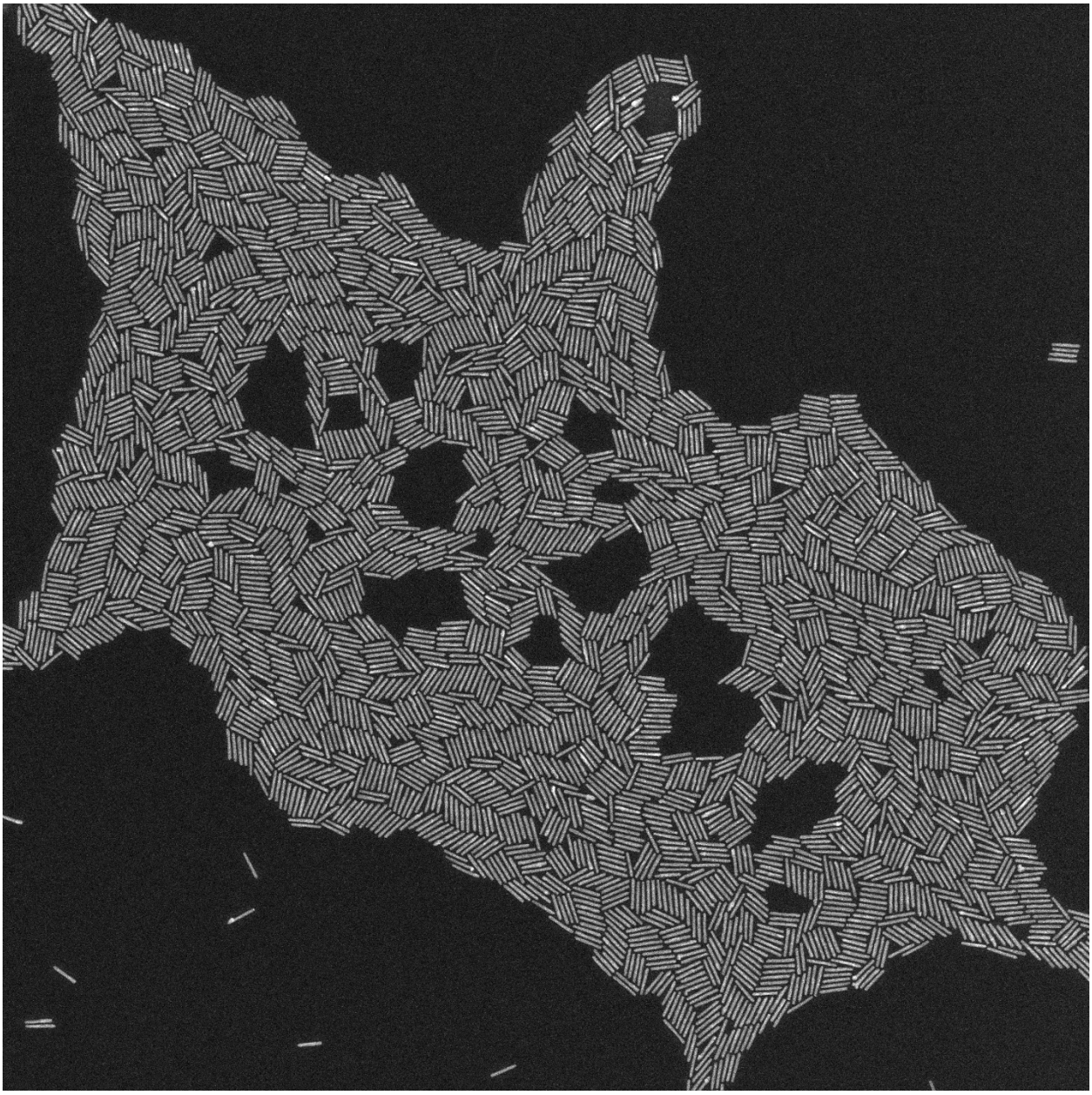


Figure S9 *STEM image of SR. A distance of 2.58 nm is estimated between two neighboring nanorods*

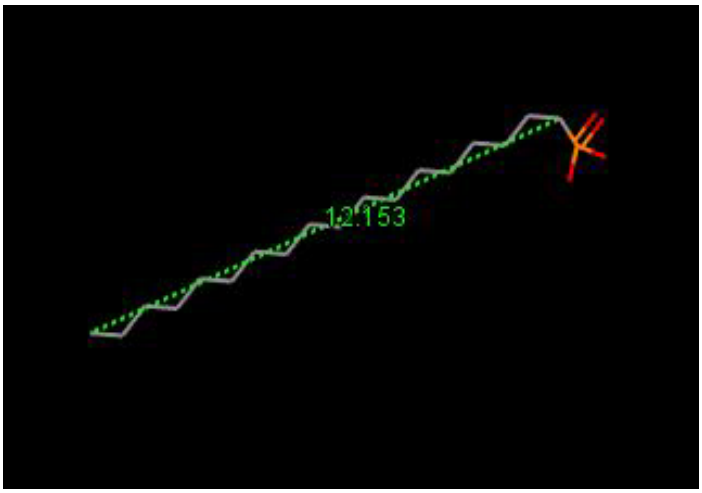


Figure S10 *Structure of octadecylphosphonic acid molecule, the distance of carbon chain was measured by "Mercury" software is 12.153 Å*

Ligand exchange protocols

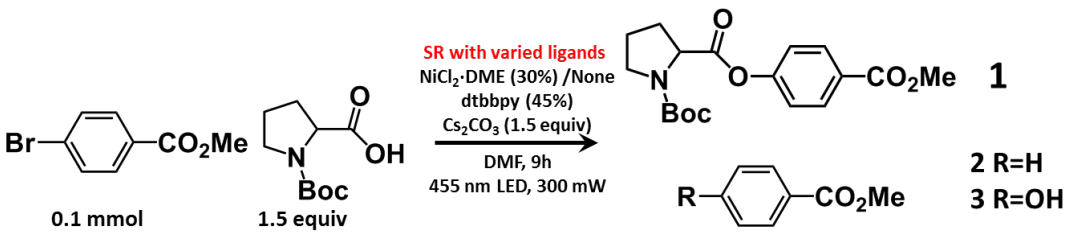
MUA ligand exchange:

0.2 mL original SR toluene solution was precipitated with methanol and dispersed into 2 mL methanol (containing 50 mg 11-mercaptoundecanoic acid (MUA) and 70 mg Tetramethylammonium hydroxide pentahydrate) and sat for 15 minutes. Then 6 ml toluene was added to precipitate the sample. The SR sample was finally into 0.2 mL DMF.

ACA ligand exchange:

0.2 mL original SR toluene solution was diluted to 1 mL, and 2 mL 9-ACA THF solution with concentration 120 mg/mL was added. The mixture was stirred for more than 24 hours, then 10 mL acetone was added to precipitate the SR, and the sample was finally dispersed into 0.2 mL toluene.

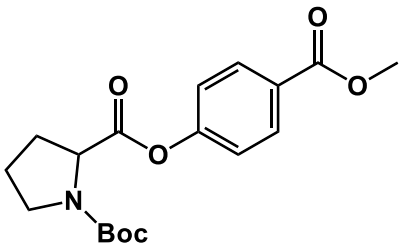
Table S8 *Ligand change on the surface of SR[a]*



Entry	Ligand on the nanorods	1 [%][b]	2 [%][b]	3 [%][b]	Halide substrate[b]
1	ODPA/TOP/ TOPO	96%	0	0	0
2	MUA	47%	3%	38%	0%
3	ACA	30%	1%	1%	50%

[a] Reaction conditions: methyl 4-bromobenzoate (0.1 mmol), Boc-Pro-OH (0.15 mmol), SR (0.615 mg, $2.7*10^{-7}$ mmol), $NiCl_2$·DME (0.03 mmol), dtbbpy (0.045 mmol), Cs_2CO_3 (0.15 mmol), DMF (2 mL, anhydrous), 455 nm LEDs with 300 mW at 40 °C. [b] calculated by ^{1}H-NMR using 0.1 mmol 1,3,5-trimethoxybenzene as internal standard.

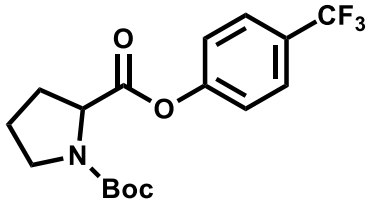
[5] NMR spectra



Product 6, 1-(tert-butyl) 2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and methyl 4-bromobenzoate or methyl 4-Iodobenzoate as substrates. The title compound was isolated as a yellowish solid using an elution of Dichloromethane: ethyl acetate (10:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, CDCl3) rotameric mixture, δ 8.12-8.02 (m, 2H), 7.23-7.14 (m, 2H), 4.53 (dd, *J* = 8.6, 4.3 Hz, 0.4H), 4.46 (dd, *J* = 8.7, 4.3 Hz, 0.6H), 3.91 (m, 3H), 3.69 – 3.40 (m, 2H), 2.48 – 2.29 (m, 1H), 2.17 (m, 1H), 2.11 – 1.88 (m, 2H), 1.47 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (171.31) 171.27, (166.50) 166.36, 154.61 (d, *J* = 16 Hz) (154.32), 153.79, 131.39 (131.26), 127.97 (127.81), (121.65) 121.28, 80.51 (80.29), 59.34 (59.23), 52.39 (52.34), (46.78) 46.60, 31.16 (30.11), 28.55, (24.69) 23.87.

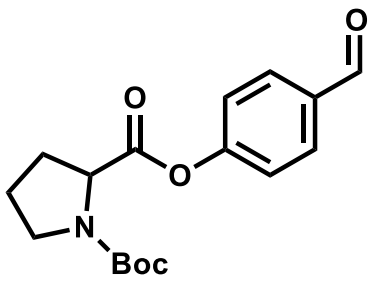


Product 5, 1-(tert-butyl) 2-(4-(trifluoromethyl)phenyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 4-Iodobenzotrifluoride or 4-Bromobenzotrifluoride as substrates. The title compound was isolated as yellowish oil using an elution of dichloromethane: hexane (volume ratio, 20:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, CDCl3) rotameric mixture δ 7.65 (m, 2H), 7.28-7.18 (m, 2H, contains residual solvent signal of CDCl3), 4.53 (dd, *J* = 8.5, 4.4 Hz, 0.4H), 4.47 (dd, *J* = 8.7, 4.4 Hz, 0.6H), 3.73-3.37 (m, 2H), 2.47-2.28 (m, 1H), 2.23-2.11 (m, 1H), 2.11-1.88 (m, 2H), 1.47 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (171.41) 171.30, (154.65) 153.78, (153.44) 153.18, 128.50 (128.16), 127.07 (127.03), 126.91 (126.87), (125.32) 122.50, (122.16) 121.78, 80.54 (80.35), 59.30 (59.21), (46.79) 46.61, 31.18 (30.12), 28.56, (24.72) 23.88.

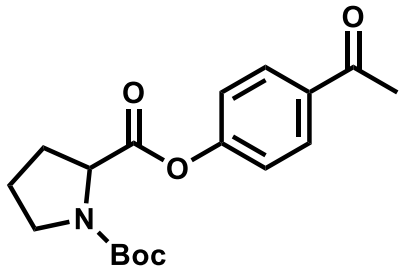
^{19}F NMR (377 MHz, $CDCl_3$) rotameric mixture δ -62.21, -62.26.



Product 7, 1-(tert-butyl) 2-(4-formylphenyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 4-iodobenzaldehyde or 4-bromobenzaldehyde as substrates. The title compound was isolated as yellowish oil using an elution of dichloromethane: hexane (volume ratio, 20:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture δ 10.00 (m, 1H), 7.93 (m, 2H), 7.34-7.25 (m, 2H, contains residual solvent signal of $CDCl_3$), 4.54 (dd, J = 8.5, 4.4 Hz, 0.4H), 4.47 (dd, J = 8.7, 4.4 Hz, 0.6H), 3.69-3.42 (m, 2H), 2.48-2.29 (m, 1H), 2.18 (m, 1H), 2.12 – 1.90 (m, 2H), 1.47 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (191.14) 190.96, (171.24) 171.15, 155.69 (155.38), (154.66) 153.77, 134.24 (134.15), 131.45 (131.34), (122.44) 122.06, 80.58 (80.39), 59.35 (59.25), (46.80) 46.61, 31.18 (30.12), 28.56, (24.72) 23.89.

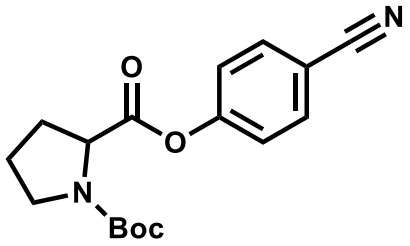


Product 8, 2-(4-acetylphenyl) 1-(tert-butyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 4'-iodo

or 4'-bromoacetophenone as substrates. The title compound was isolated as white solid using an elution of dichloromethane: hexane (volume ratio, 10:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, CDCl3) rotameric mixture δ 8.00 (m, 2H), 7.22 (m, 2H), 4.53 (dd, *J* = 8.6, 4.4 Hz, 0.4H), 4.46 (dd, *J* = 8.7, 4.4 Hz, 0.6H), 3.68-3.42 (m, 2H), 2.60 (m, 3H), 2.38 (m, 1H), 2.24-2.11 (m, 1H), 2.11-1.90 (m, 2H), 1.47 (m, 9H).

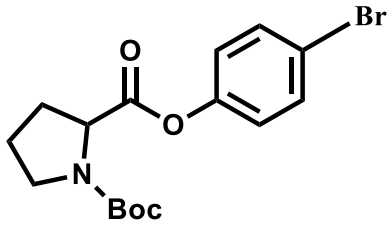
^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (197.10) 196.92, (171.34) 171.27, 154.68 (154.64), 154.40 (153.79), 134.98 (134.87), 130.18 (130.06), (121.83) 121.46, 80.52 (80.32), 59.35 (59.24), (46.79) 46.61, 31.18 (30.12), 28.56, 26.75, (24.71) 23.89.



Product 9, 1-(tert-butyl) 2-(4-cyanophenyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 4-iodobenzonitrile or 4-bromobenzonitrile as substrates. The title compound was isolated as white solid using an elution of dichloromethane: ethyl acetate (volume ratio, 5:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture, δ 7.70 (m, 2H), 7.31-7.18 (m, 2H, contains residual solvent signal of $CDCl_3$), 4.51 (dd, *J* = 8.6, 4.6 Hz, 0.5H), 4.46 (dd, *J* = 8.7, 4.4 Hz, 0.5H), 3.67-3.41 (m, 2H), 2.47-2.29 (m, 1H), 2.22-2.09 (m, 1H), 2.09-1.89 (m, 2H), 1.46 (m, 9H).

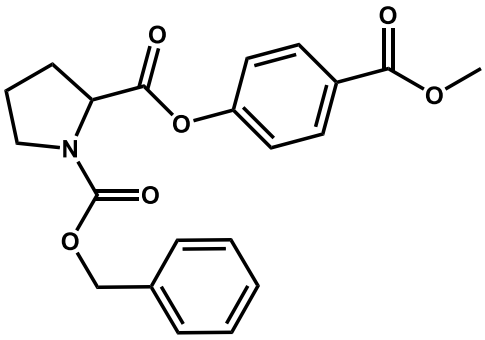
^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (171.13) 170.98, (154.64) 154.24, 153.95 (153.68), 133.92 (133.78), (122.82) 122.41, (118.42) 118.24, 110.06 (109.87), 80.60 (80.45), 59.28 (59.20), (46.78) 46.59, 31.15 (30.08), 28.53, (24.73) 23.87.



Product 10, 2-(4-bromophenyl) 1-(tert-butyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 1,4-dibromobenzene or 1-Bromo-4-Iodobenzene as substrates. The title compound was isolated as yellowish oil using an elution of Hexane: ethyl acetate (5:1) and dichloromethane: ethyl acetate (volume ratio, 50:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture δ 7.54-7.43 (m, 2H), 7.05-6.94 (m, 2H), 4.50 (dd, *J* = 8.6, 4.4 Hz, 0.4H), 4.44 (dd, *J* = 8.7, 4.3 Hz, 0.6H), 3.69-3.37 (m, 2H), 2.36 (m, 1H), 2.2-2.09 (m, 1H), 2.09-1.87 (m, 2H), 1.47 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (171.56) 171.47, (154.62) 153.81, (149.96) 149.74, 132.70 (132.54), (123.45) 123.05, 119.14 (119.02), 80.46 (80.26), 59.29 (59.18), (46.78) 46.59, 31.17 (30.12), 28.56, (24.68) 23.86.



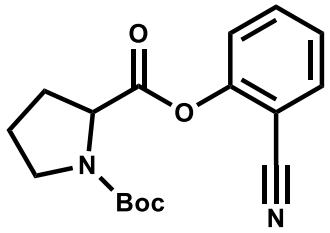
Product 19, 1-phenyl-2-(4-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate Cbz-Pro-OH and methyl 4-bromobenzoate as substrates. The title compound was isolated as yellowish oil using an elution of Dichloromethane: Hexane (volume ratio, 10:1).

1H NMR (400 MHz, $CDCl_3$) rotameric mixture δ 8.06 (m, 1H), 7.97 (m, 1H), 7.42-7.28 (m, 5H), 7.19 (m, 1H), 6.83 (m, 1H), 5.31-5.02 (m, 2H), 4.60 (dd, *J* = 8.6, 4.3 Hz, 0.5H), 4.56 (dd, *J* = 8.7, 4.2 Hz, 0.5H), 3.91 (s, 3H), 3.75-3.50 (m, 2H), 2.49-2.30 (m, 1H), 2.26-2.14 (m, 1H), 2.14-1.92 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ 170.99, 170.93, 166.46, 166.36, (155.10) 154.39, (154.32) 154.07, 136.68, 136.39,

131.26, 131.22, 128.70 (128.62), 128.36, (128.18) 128.02, 127.96 (127.92), 121.62, 121.38, 67.51, 67.35, 59.58, 59.05, 52.37, 52.34, 47.21, 46.67, 31.20, 30.12, 24.65, 23.81.

HRMS (ESI) m/z calcd for $C_{21}H_{21}NO_6Na^+$ [$(M+Na)^+$] 406.1267, found 406.1274

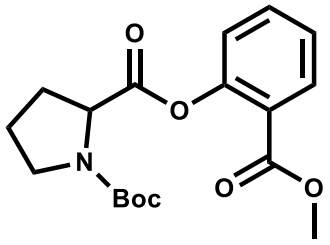


Product 11, 1-(tert-butyl) 2-(2-cyanophenyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 2-bromobenzonitrile as substrates. The title compound was isolated as pink liquid using an elution of Hexane: ethyl acetate (volume ratio, 5:2).

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture, δ 7.72-7.58 (m, 2H), 7.41-7.31 (m, 1H), 7.27 (m, 1H, contains residual solvent signal of $CDCl_3$), 4.62-4.51 (m, 1H), 3.70-3.40 (m, 2H), 2.51-2.32 (m, 2H), 2,14 (m, 1H), 1.99 (m, 1H), 1.48 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ 170.73, (154.71) 153.77, (152.44) 152.18, (134.37) 134.32, 133.55 (133.17), 126.64 (126.47), (123.67) 123.00, (115.25) 115.08, 107.08 (106.96), 80.57 (80.36), 59.15, (46.84) 46.62, 31.16 (30.12), 28.57 (28.54), (24.65) 23.77.

HRMS (ESI) m/z calcd for $C_{17}H_{20}N_2O_4Na^+$ [$(M+Na)^+$] 339.1321, found 339.1321

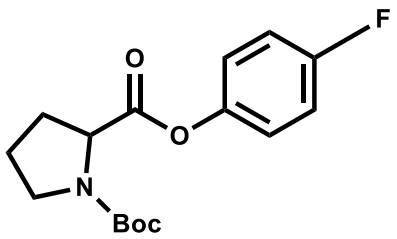


Product 12, 1-(tert-butyl) 2-(2-(methoxycarbonyl)phenyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and methyl 2-bromobenzoate as substrates. The title compound was isolated as a yellowish solid using an elution of Dichloromethane: ethyl acetate (5:3).

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture, δ 8.01-7.95 (m, 1H), 7.60-7.51 (m, 1H), 7.36-7.27 (m, 1H), 7.18 (d, *J*= 12 Hz, 0.45H), 7.09 (d, *J*=8.1 Hz, 0.55H), 4.57 (dd, *J* = 8.7, 3.9 Hz, 0.45H), 4.52 (dd, *J* = 8.8, 3.6 Hz, 0.55H), 3.86 (m, 3H), 3.68 – 3.38 (m, 2H), 2.60 – 2.42 (m, 1H), 2.40-2.23 (m, 1H), 2.20-2.06 (m, 1H), 2.02 – 1.89 (m, 1H), 1.48 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (171.22) 171.10, (165.18) 164.90, (154.62) 154.01, (150.57) 150.38, (133.91) 133.81, 131.75 (131.58), 126.22 (126.11), 124.23, (123.70) 123.56, 80.24 (79.99), 59.39 (59.29), 52.30, (46.83) 46.61, 30.32 (29.43), 28.60, (24.60) 23.72.

HRMS (ESI) m/z calcd for $C_{18}H_{23}NO_6Na^+$ [$(M+Na)^+$] 372.1423, found 372.1422

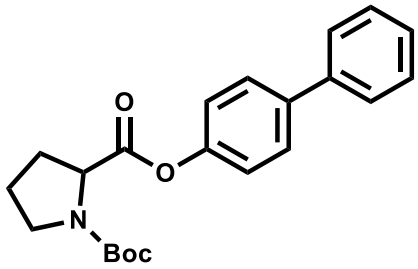


Product 14, 2-(4-fluorophenyl) 1-(tert-butyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 1-fluoro-4-Iodobenzene as substrates. The title compound was isolated as colorless liquid using an elution of Hexane: ethyl acetate (5:2).

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture δ 7.12-7.00 (m, 4H), 4.51 (dd, *J* = 8.5, 4.2 Hz, 0.42H), 4.44 (dd, *J* = 8.7, 4.3 Hz, 0.58H), 3.68-3.39 (m, 2H), 2.45-2.26 (m, 1H), 2.21-2.09 (m, 1H), 2.09-1.87 (m, 2H), 1.46 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ (171.85) 171.77, 161.56 (159.13), (154.61) 153.85, (146.70, 146.68) 146.51 (146.48) (123.03) 122.68, (122.95) 122.60, 116.41 (116.22), 116.18 (115.99), 80.41 (80.21), 59.23 (59.14), (46.76) 46.58, 31.16 (30.12), 28.54, (24.64) 23.83.

HRMS (ESI) m/z calcd for $C_{16}H_{20}NO_4Na^+F$ [$(M+Na)^+$] 332.1274, found 332.1274

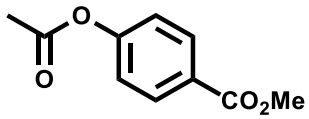


Product 13, 2-(biphenyl) 1-(tert-butyl) pyrrolidine-1,2-dicarboxylate. Boc-Pro-OH and 4-bromobipehnyl as substrates. The title compound was isolated as white solid using an elution of Hexane: ethyl acetate (5:3).

^{1}H NMR (400 MHz, $CDCl_3$) rotameric mixture δ 7.63-7.52 (m, 4H), 7.47-7.40 (m, 2H), 7.38-7.31 (m, 1H), 7.22-7.13 (m, 2H), 4.55 (dd, *J* = 8.6, 4.2 Hz, 0.38H), 4.48 (dd, *J* = 8.7, 4.3 Hz, 0.62H), 3.69-3.40 (m, 2H), 2.47-2.28 (m, 1H), 2.26-2.13 (m, 1H), 2.12-1.88 (m, 2H), 1.49 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) rotameric mixture, resonances for minor rotamer are enclosed in parenthesis δ 171.82, (154.62) 153.90, (150.32) 150.09, (140.55) 140.37, 139.24 (139.07), 128.94 (128.89), 128.36 (128.23), 127.54 (127.42), 127.23, (121.86) 121.53, 80.41 (80.16), 59.34 (59.22), (46.77) 46.59, 31.20 (30.16), 28.57, (24.63) 23.85.

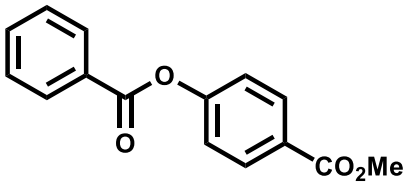
HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_4Na^+$ [$(M+Na)^+$] 390.1681, found 390.1681



Product 15, Methyl 4-acetoxybenzoate. acetic acid and methyl 4-bromobenzoate as substrate The title compound was isolated as a white solid using an elution dichloromethane: Hexane (volume ratio, 1:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H), 2.32 (s, 3H).

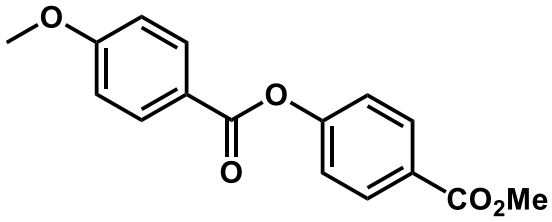
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.03, 166.46, 154.42, 131.31, 127.85, 121.74, 52.36, 21.30.



Product 16, Methyl 4-(benzoyloxy)benzoate. benzoic acid and methyl 4-bromobenzoate as substrate. The title compound was isolated as a white solid using an elution of Hexane and ethyl acetate (5:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.17 (m, 2H), 8.13 (d, J = 8 Hz, 2H), 7.70-7.61 (m, 1H), 7.58-7.47 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 3.94 (s, 3H).

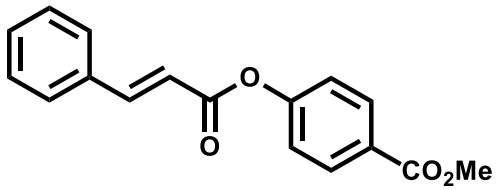
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 164.80, 154.76, 134.04, 131.38, 130.39, 129.24, 128.82, 127.92, 121.92, 52.38.



Product 18, 4-(methoxycarbonyl)phenyl 4-methoxybenzoate. 4-methoxybenzoic acid and methyl 4-bromobenzoate as substrate. The title compound was isolated as a white solid using an elution of dichloromethane and Hexane (volume ratio, 10:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 12 Hz, 2H), 8.12 (d, J = 6 Hz, 2H), 7.29 (d, J = 12 Hz, 2H), 7.00 (d, J = 8 Hz, 2H), 3.93 (s, 3H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.57, 164.50, 164.27, 154.91, 132.55, 131.32, 127.72, 121.98, 121.48, 114.09, 55.70, 52.35.

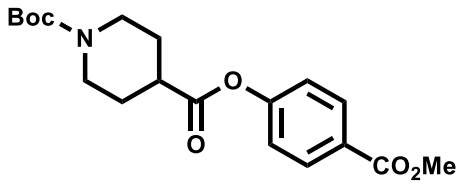


Product 17, Methyl 4-(cinnamoyloxy)benzoate. *trans*-cinnamic acid and methyl 4-bromobenzoate. The title compound was isolated as a white solid using an elution of

Dichloromethane: Hexane (volume ratio, 10:1) and Hexane: ethyl acetate (volume ratio, 5:1), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 16.0 Hz, 1H), 7.65-7.55 (m, 2H), 7.48-7.39 (m, 3H), 7.30-7.23 (d, *J* = 12 Hz, 2H, contains residual solvent signal of $CDCl_3$), 6.63 (d, *J* = 16.0 Hz, 1H), 3.93 (s, 3H).

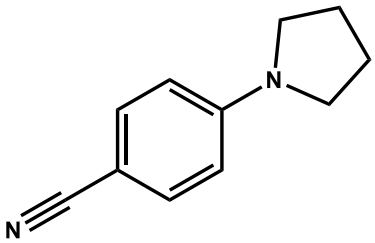
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.52, 164.96, 154.61, 147.41, 134.13, 131.33, 131.07, 129.19, 128.53, 127.77, 121.80, 116.92, 52.35.



Product 20, 1-(tert-butyl) 4-(4-(methoxycarbonyl)phenyl) piperidine-1,4-dicarboxylate. 1-Boc-iperidine-4-carboxylic acid and methyl 4-bromobenzoate as substrates. The title compound was isolated as a white solid using an elution of Hexane and ethyl acetate (volume ratio, 5:1 and 5:2 (for the second isolation, scrape the relative silica part from glass plate and then extract the product with purity to do the purification again with elution of Hexane and ethyl acetate (volume ratio, 5:2), and is identical with the spectra of the known compound.[24]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8 Hz, 2H), 7.15 (d, *J* = 8 Hz, 2H), 4.10 (br, 2H), 3.92 (s, 3H), 2.92 (m, 2H), 2.73 (tt, *J* = 11.0, 3.9 Hz, 1H), 2.04 (m, 2H), 1.78 (dtd, *J* = 13.3, 11.2, 4.3 Hz, 2H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.69, 166.42, 154.81, 154.40, 131.33, 127.92, 121.61, 79.93, 52.37, 43.02 (br), 41.40, 28.57, 28.02.



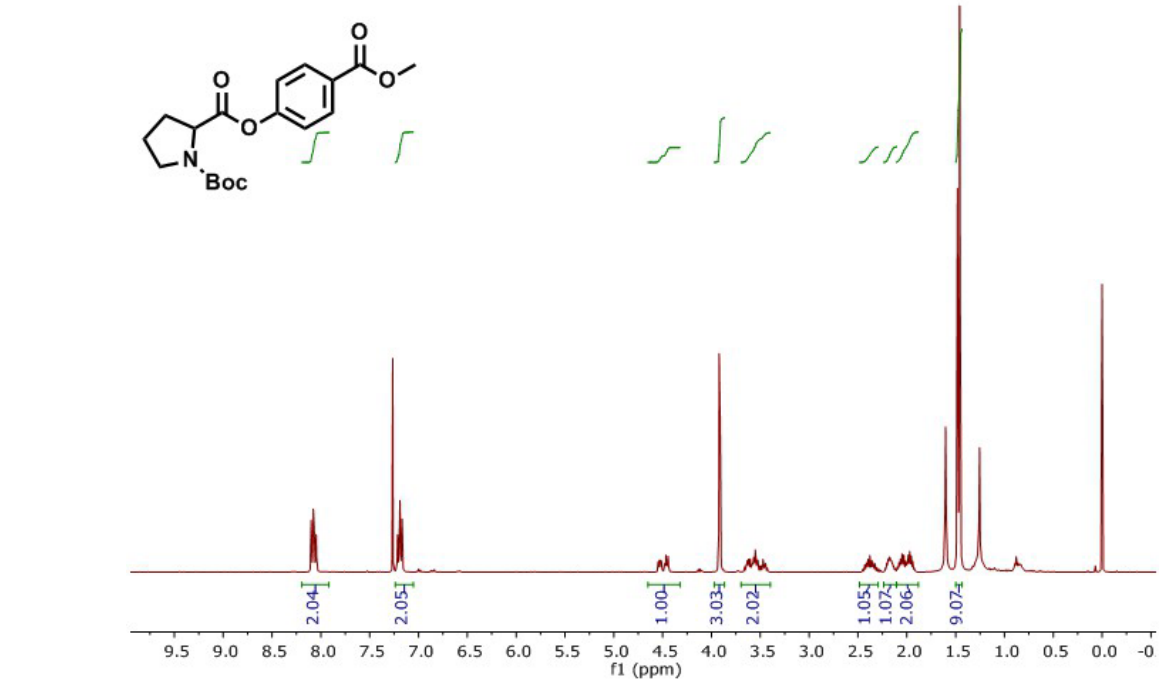
Product **24**. The synthesis procedure was in term of the standard condition with twice amounts. after the purification with Hexane and ethyl acetate (10:1), the final product was white solid and is identical with the spectra of the known compound.[25] The NMR yield is 25%. ^{1}H NMR (400 MHz,

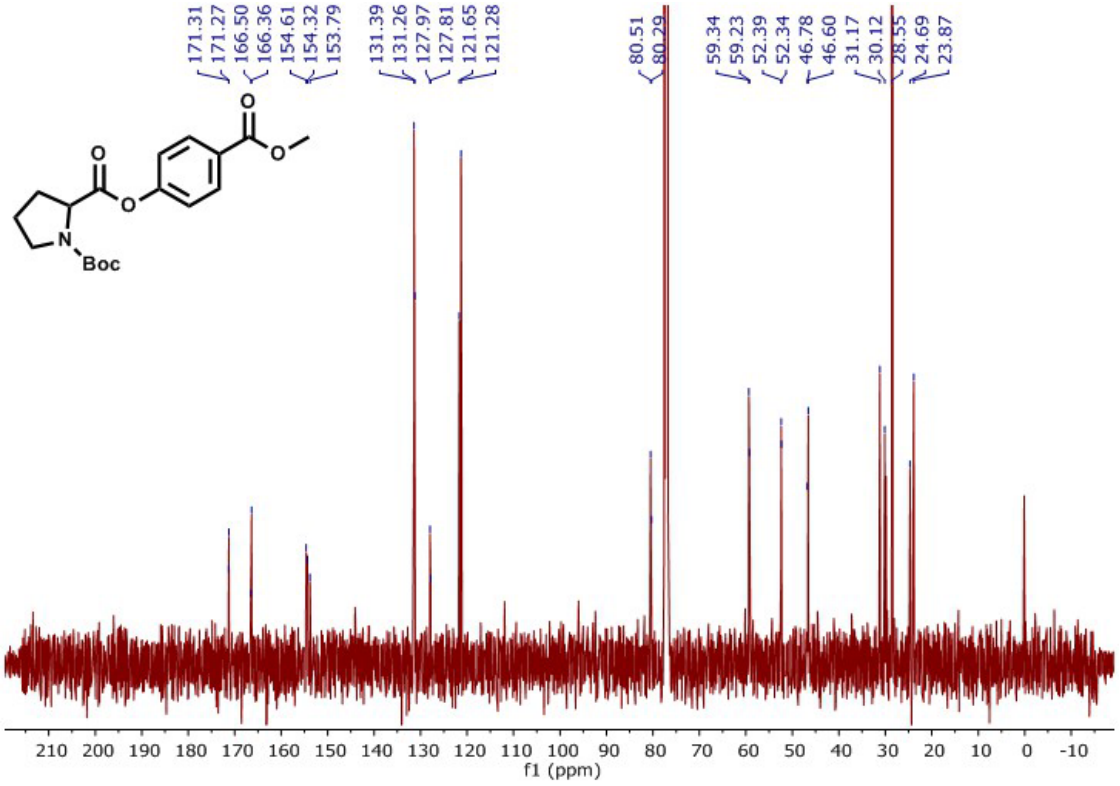
$CDCl_3$) δ (ppm) 7.45 (d, *J* = 8.9 Hz, 2H), 6.50 (d, *J* = 8.9 Hz, 2H), 3.33 (t, *J* = 6.8 Hz, 4H), 2.05 (t, *J* = 6.3 Hz, 4H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.15, 133.61, 121.17, 111.58, 96.70, 47.62, 25.56.

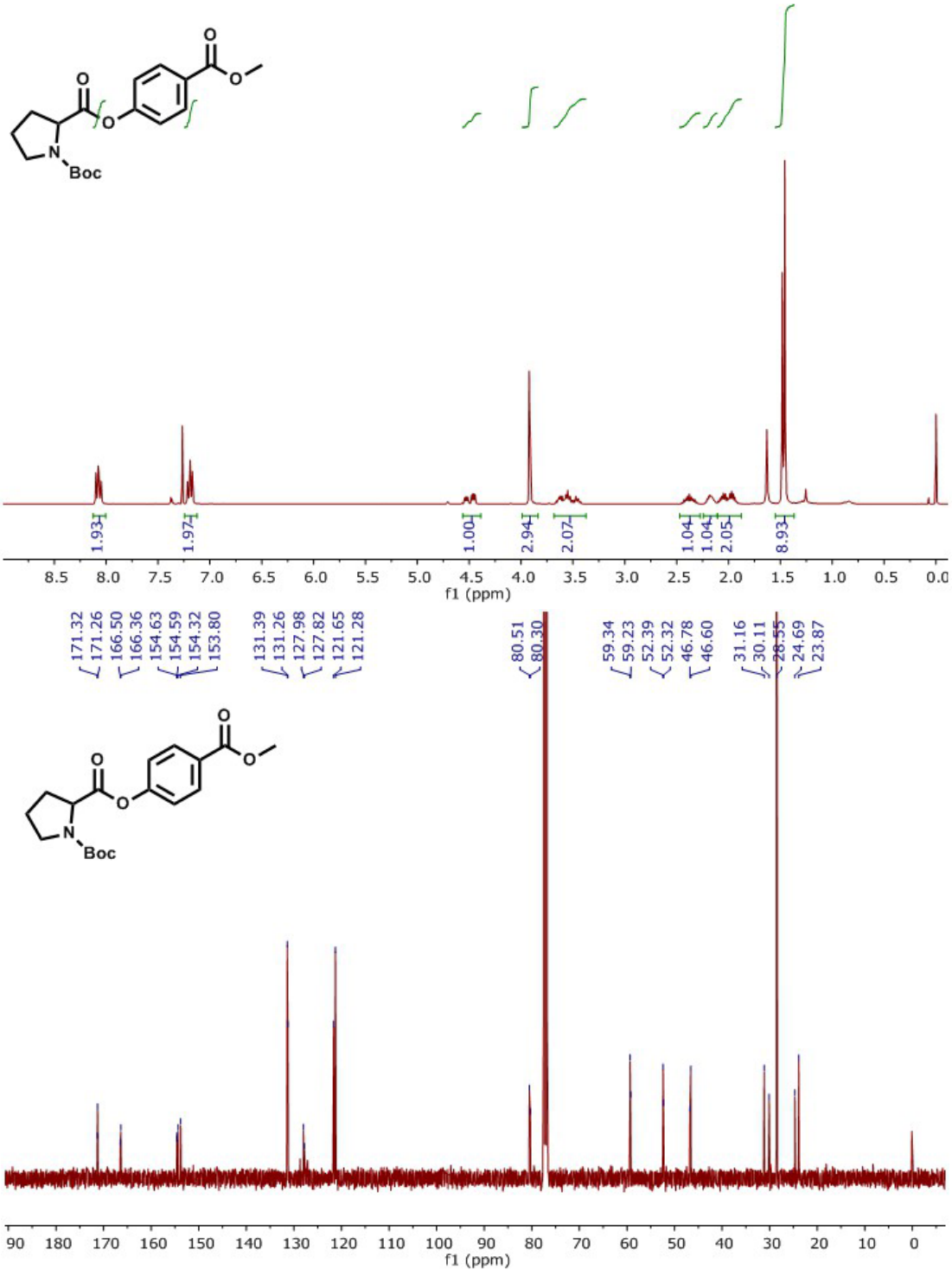
NMR spectra of isolated compounds

Substrate: methyl 4-bromobenzoate, product **6**

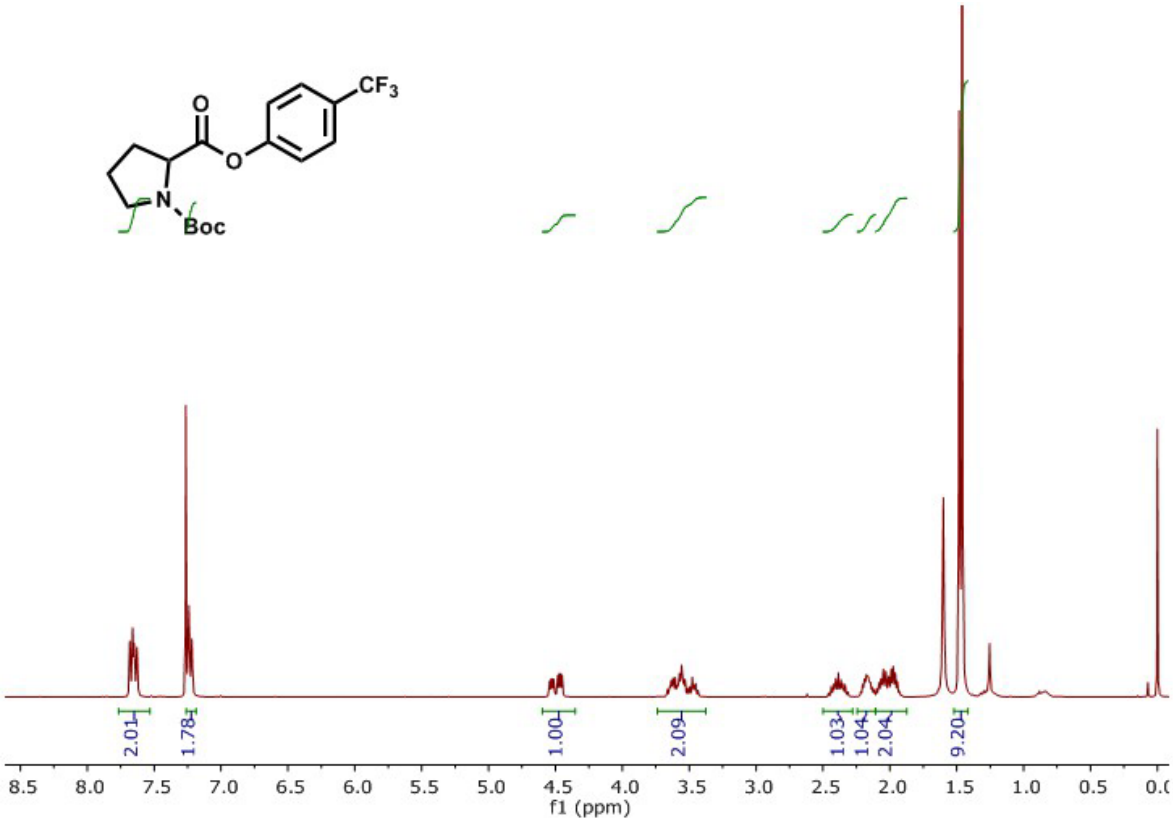


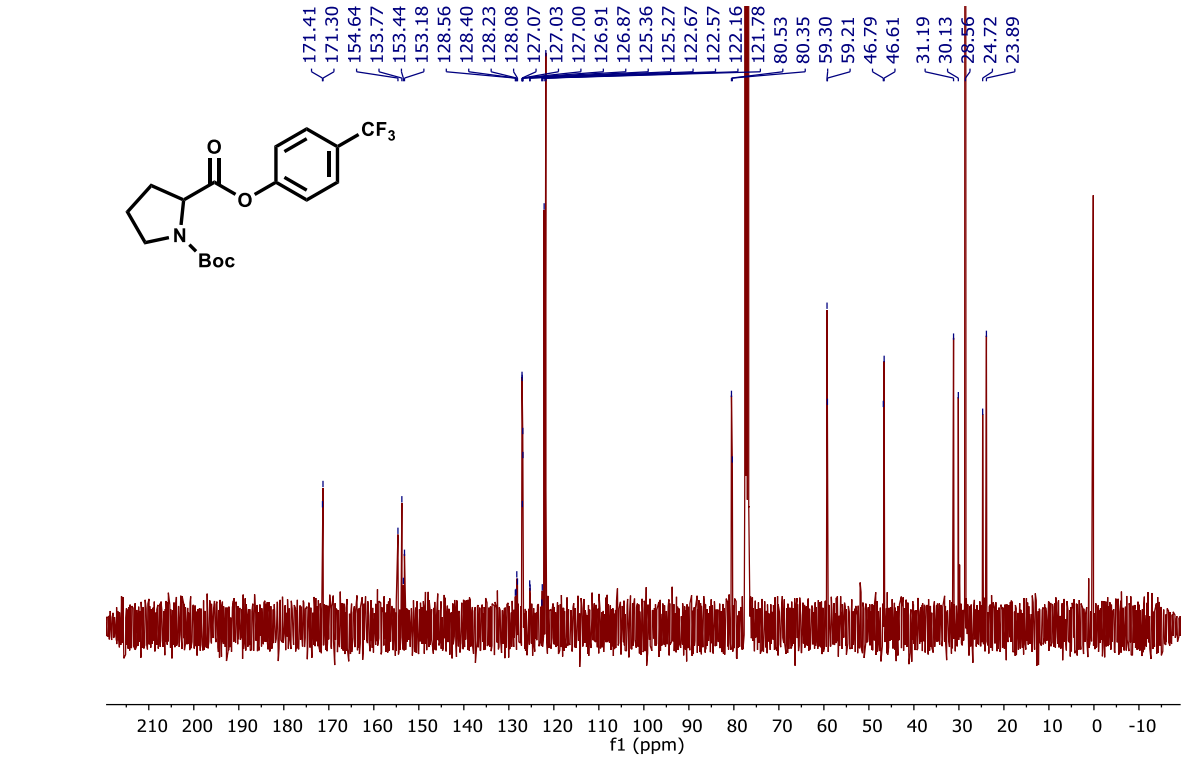


Substrate: methyl 4-Iodobenzoate, product **6**

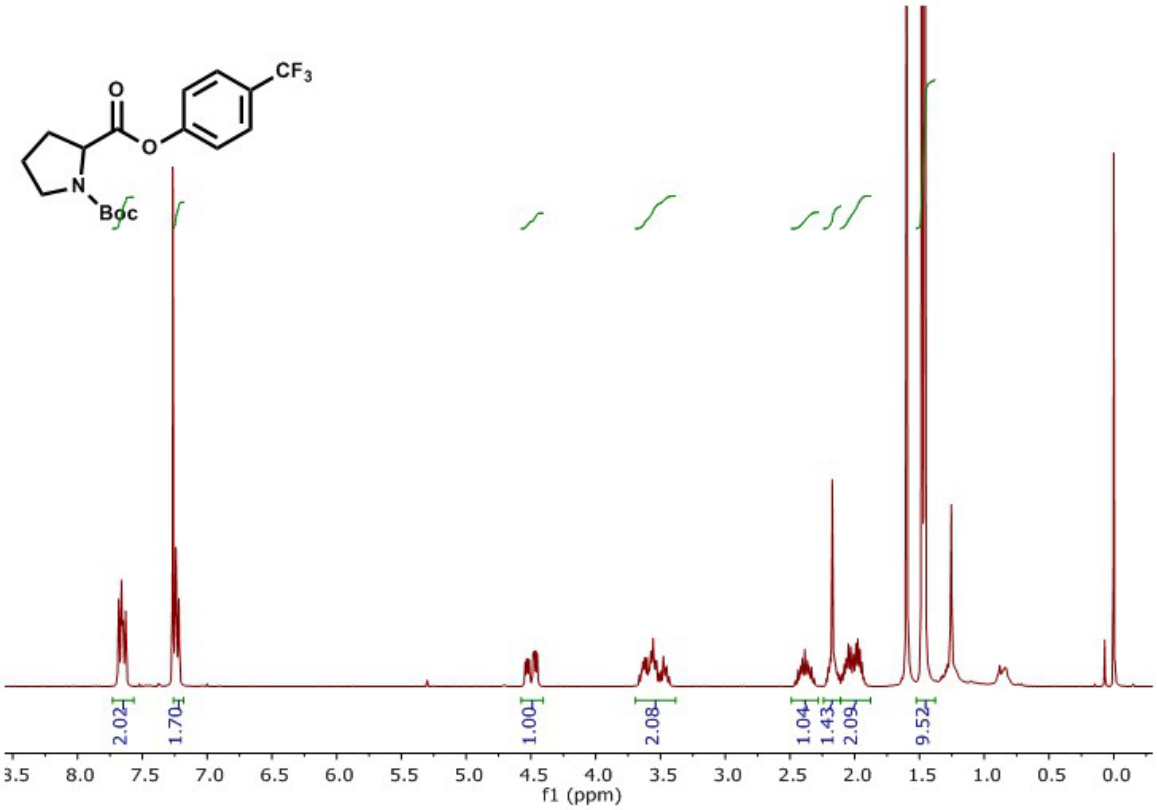


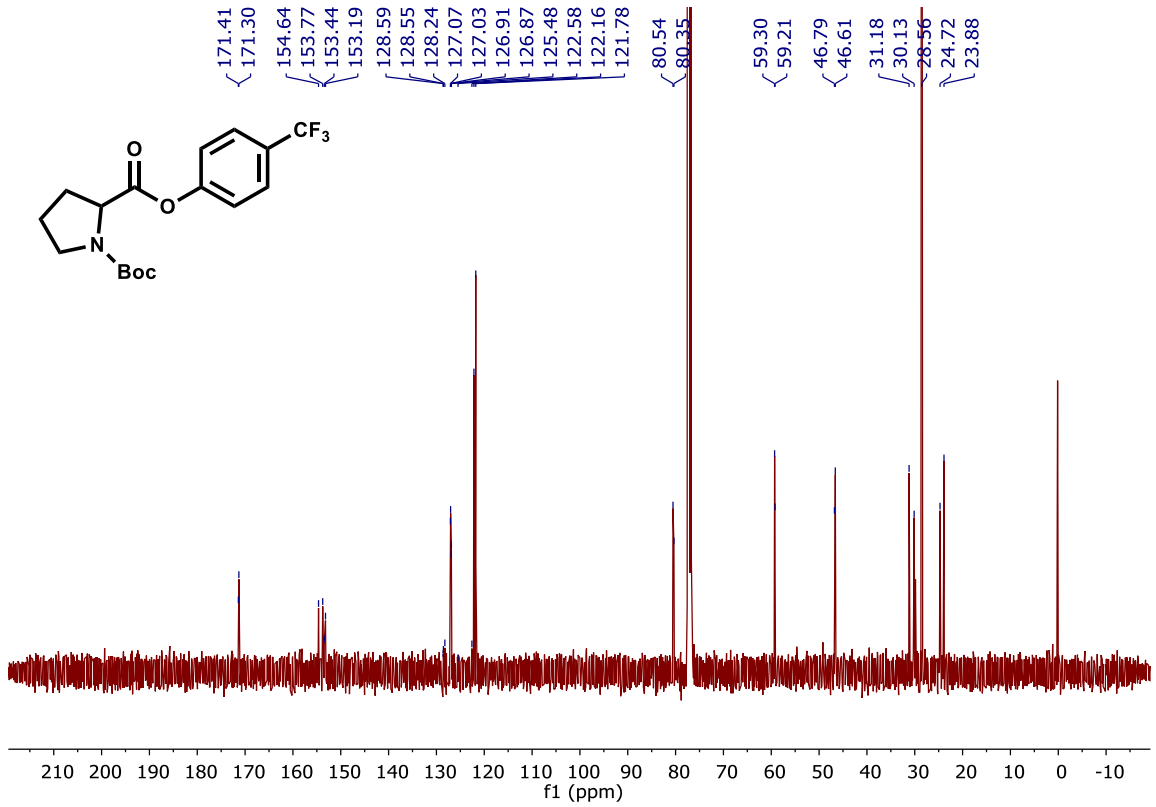
Substrate: 4-Bromobenzotrifluoride, product **5**

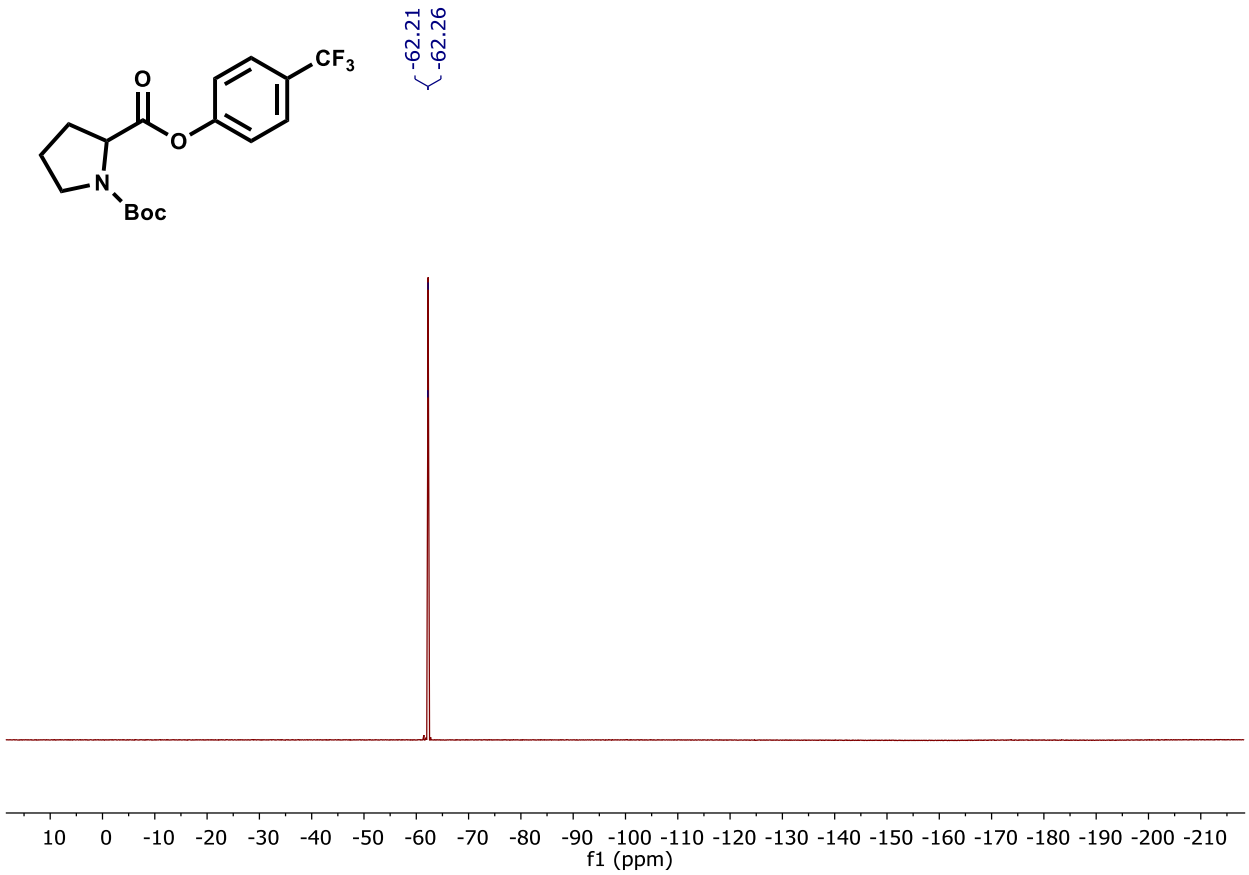




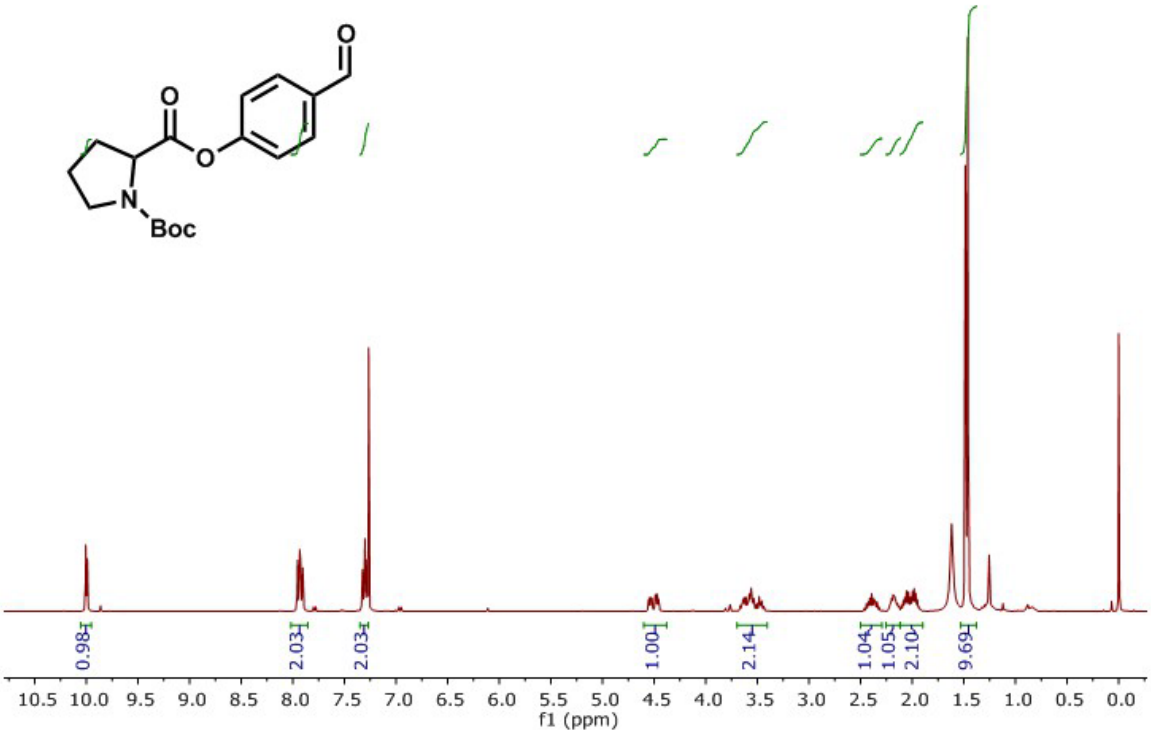
Substrate: 4-Iodobenzotriluoride, product **5**

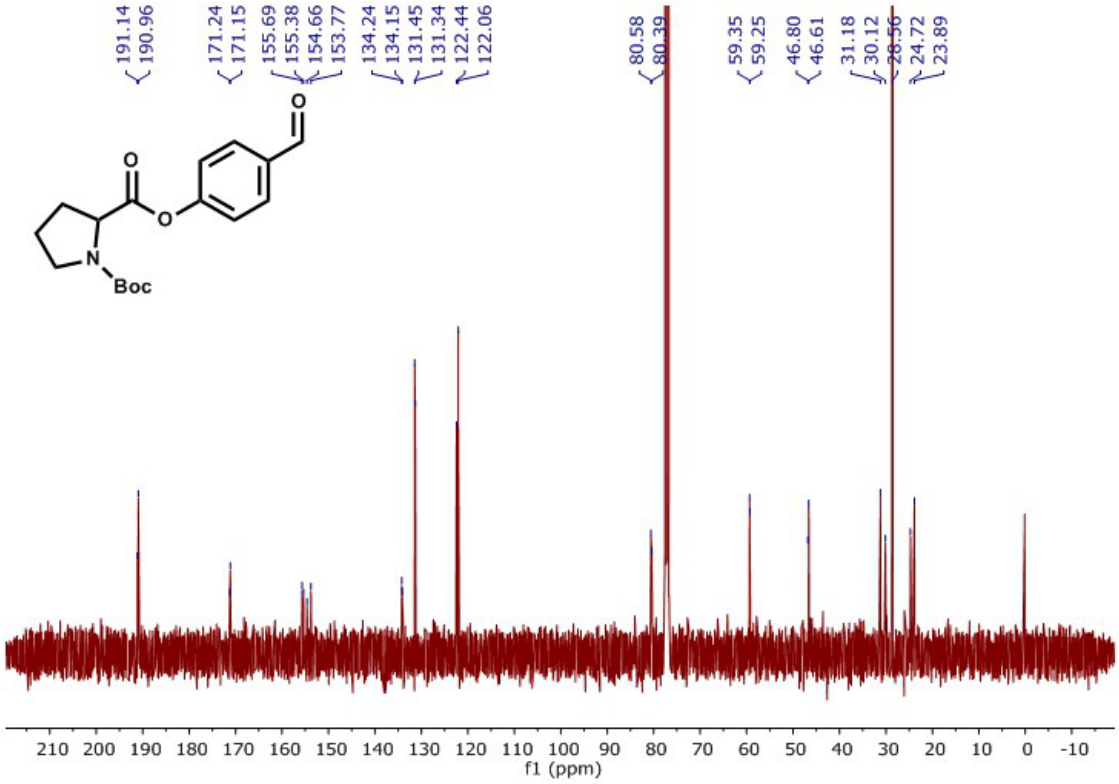




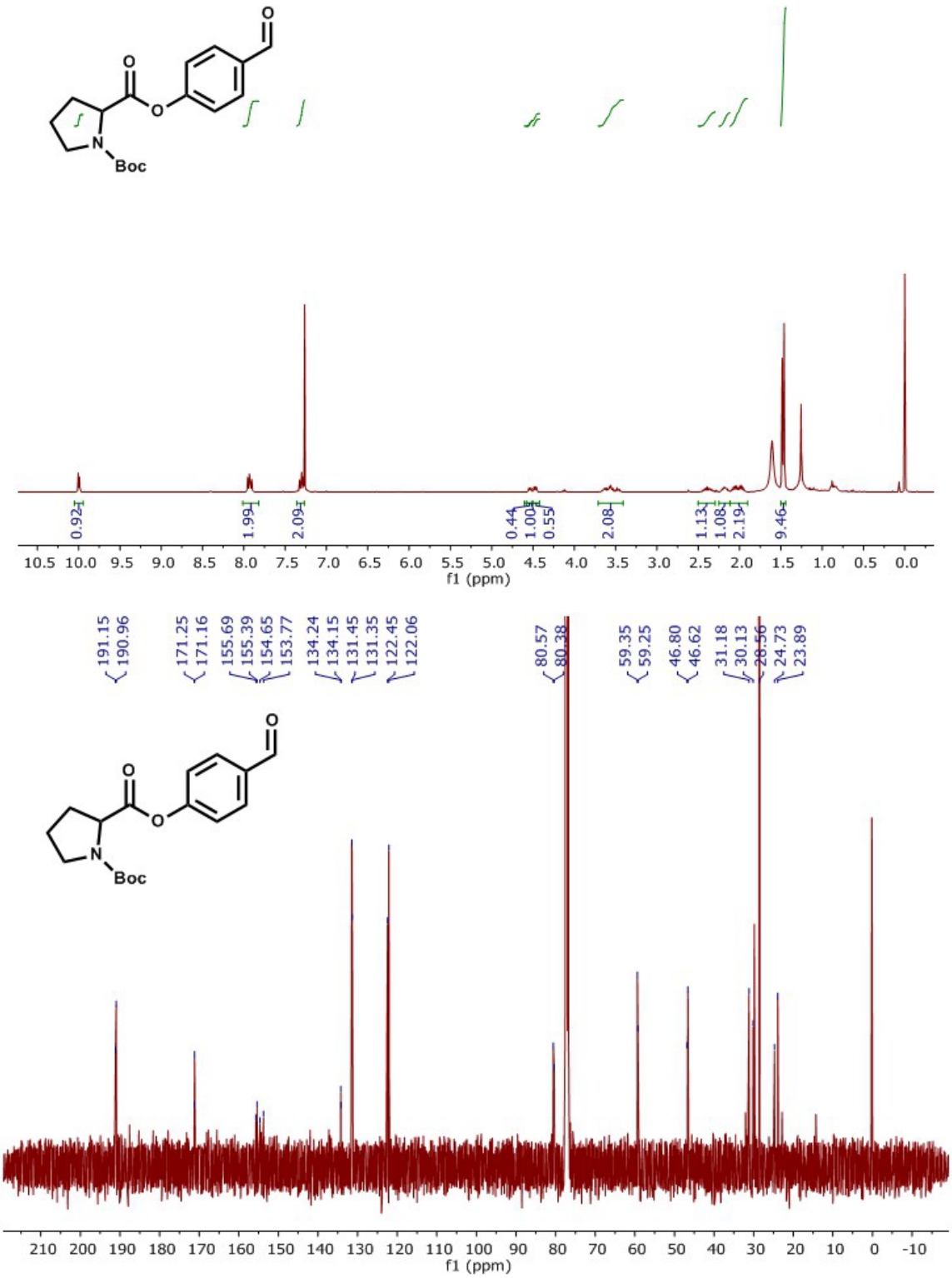

-62.21
-62.26
CF3
O
O
N
Boc
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Substrate: 4-bromobenzaldehyde, product **7**

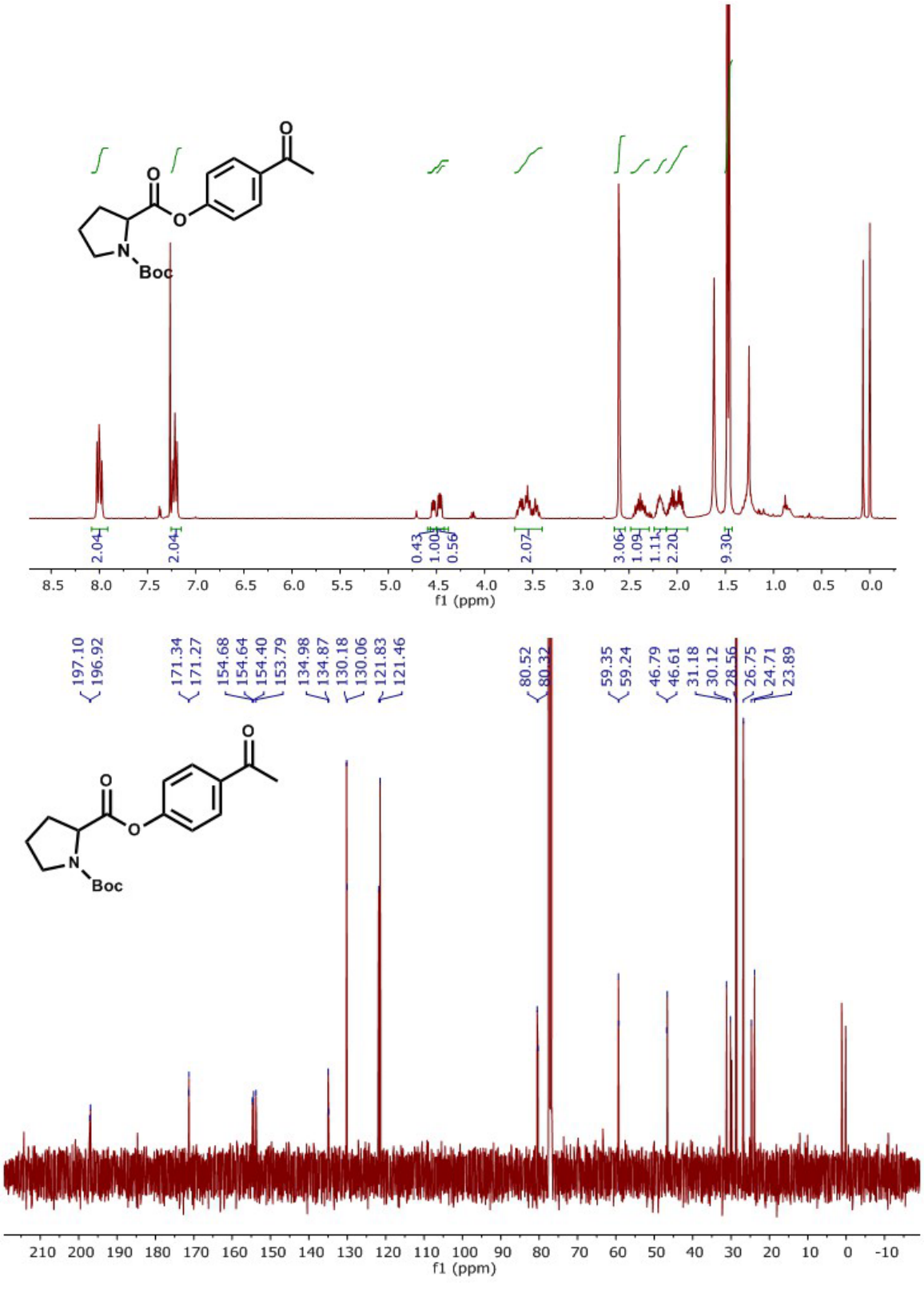




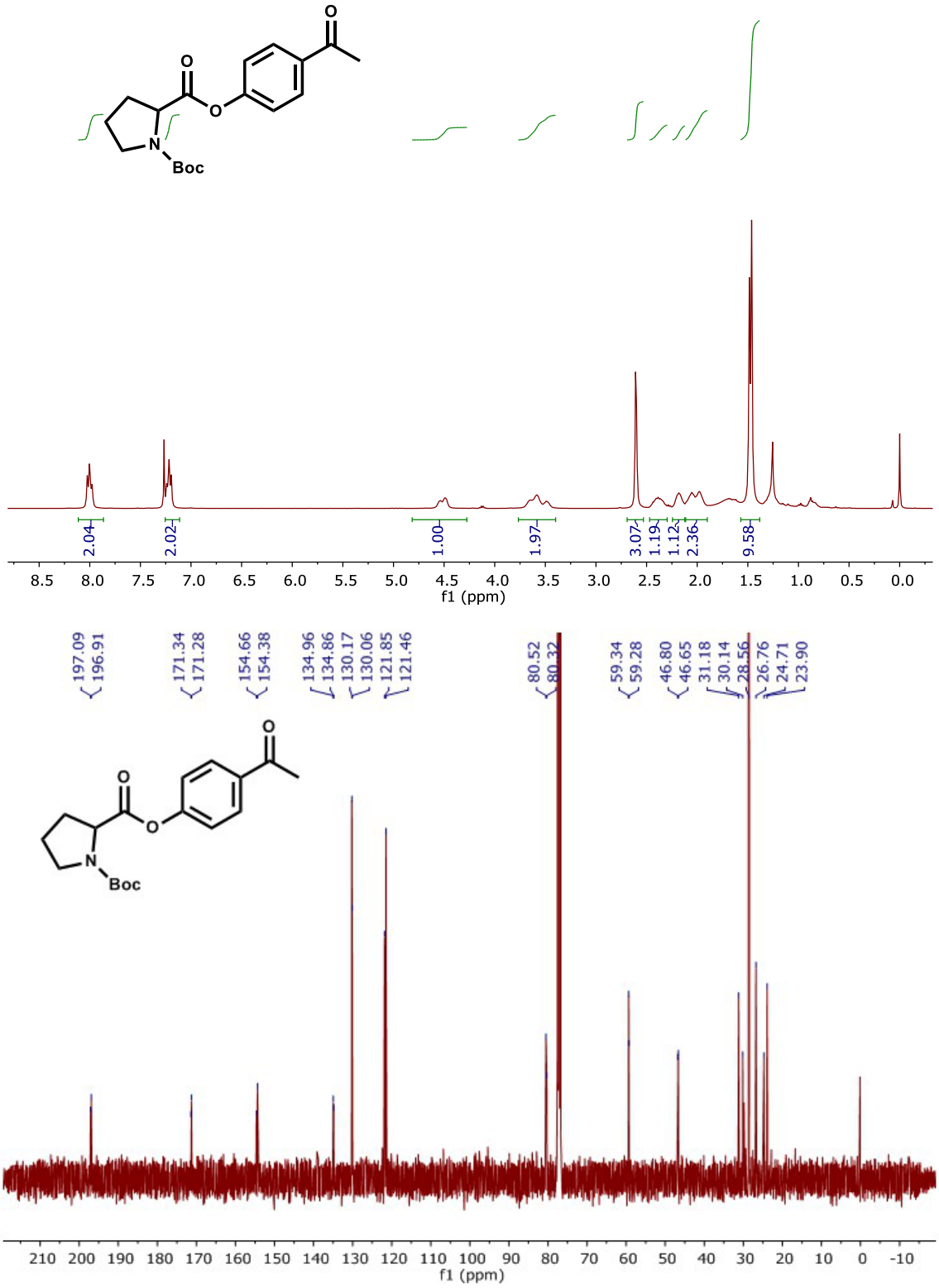
Substrate: 4-Iodobenzaldehyde, product **7**



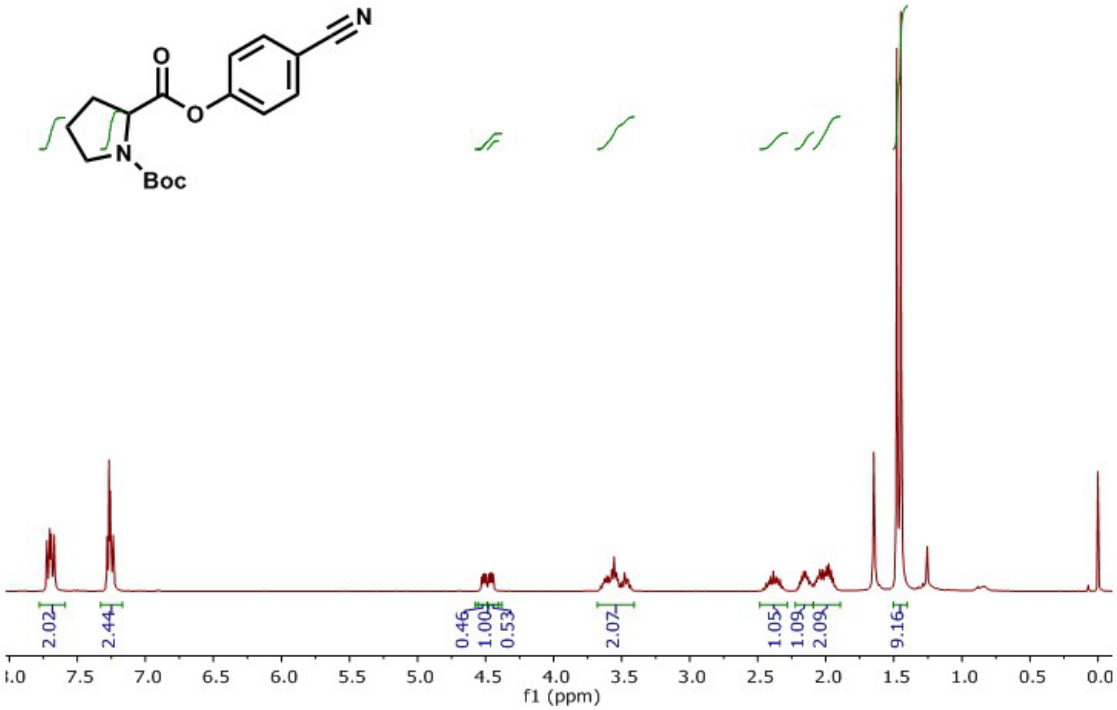
Substrate: 4’-Iodoacetohenone, product **8**

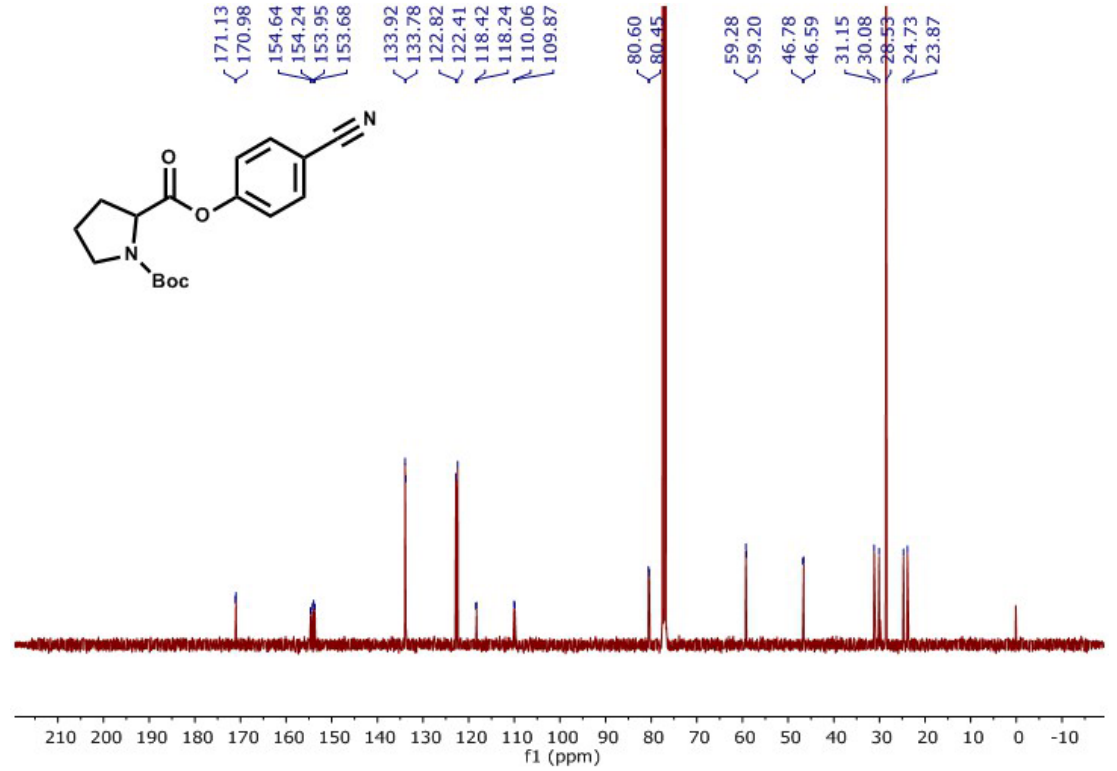


Substrate: 4’-Bromoacetophenone, product **8**

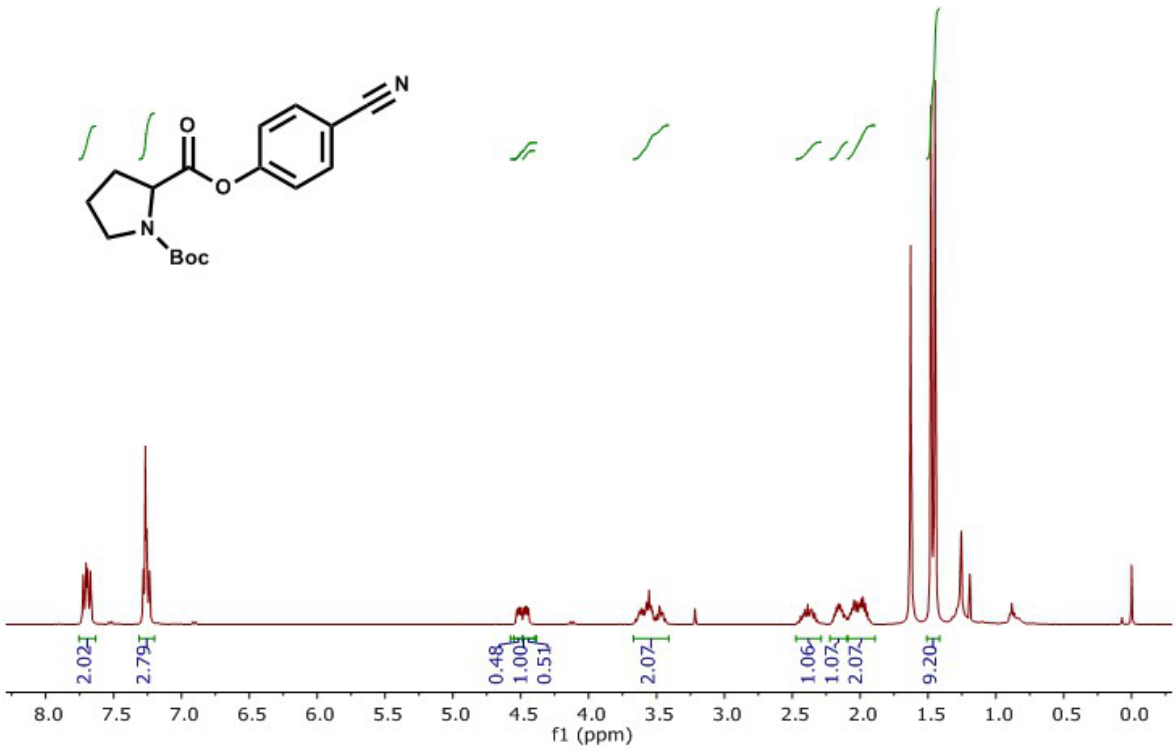


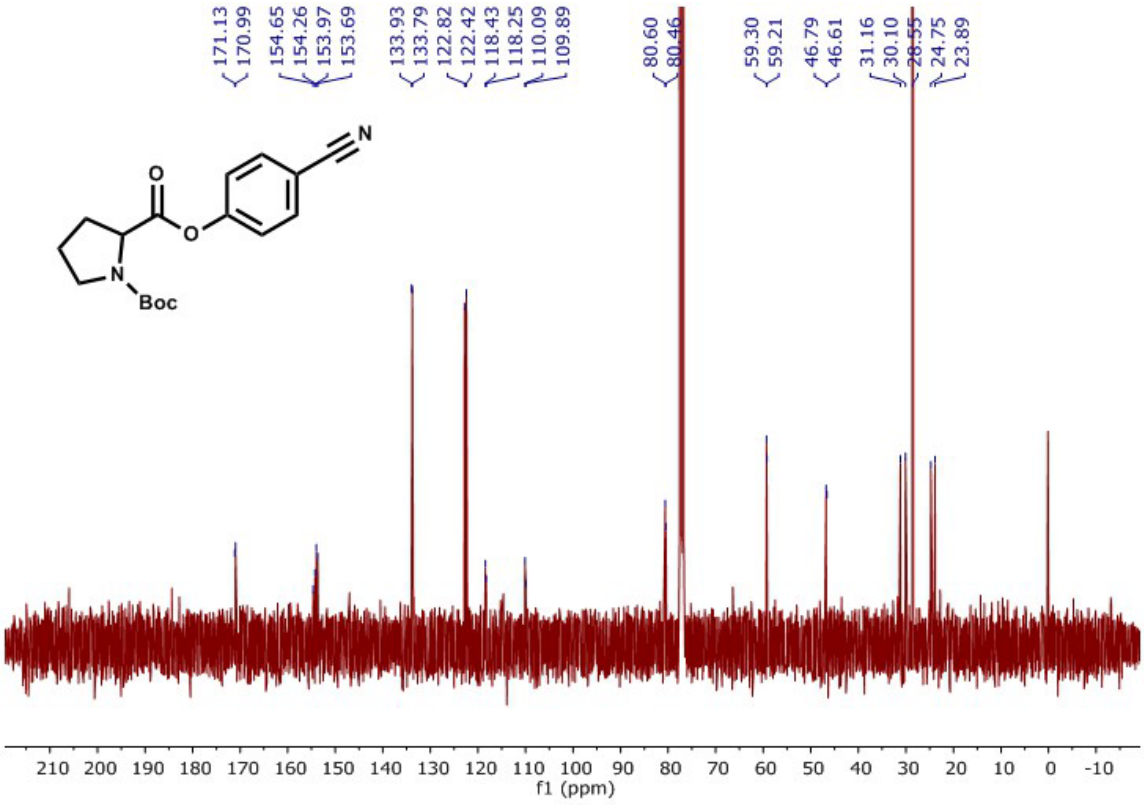
Substrate: 4-bromobenzonitrile, product **9**



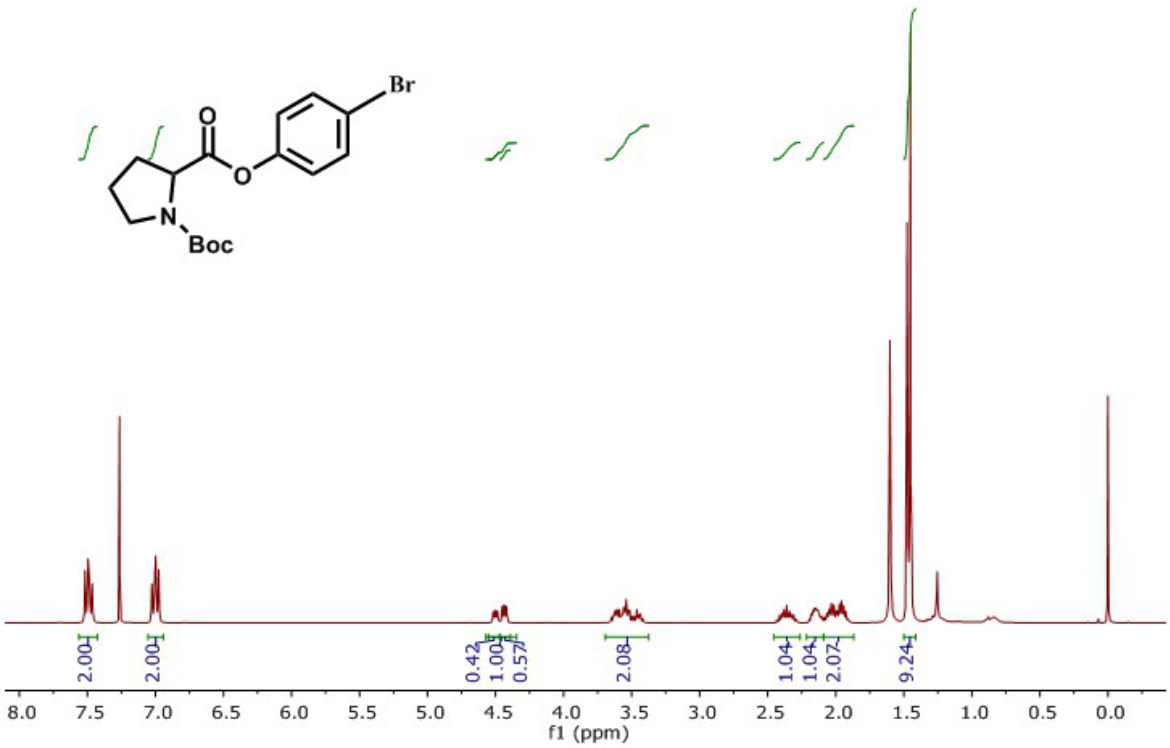


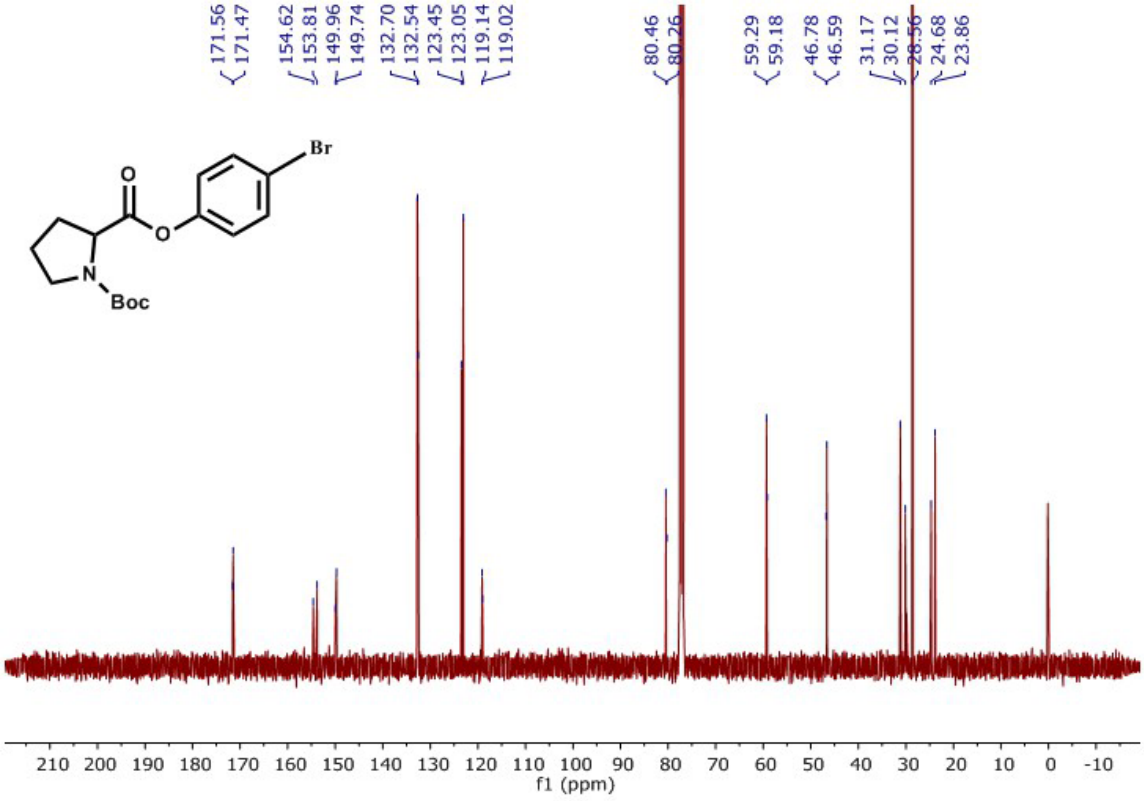
Substrate: 4-Iodobenzonitrile, product **9**



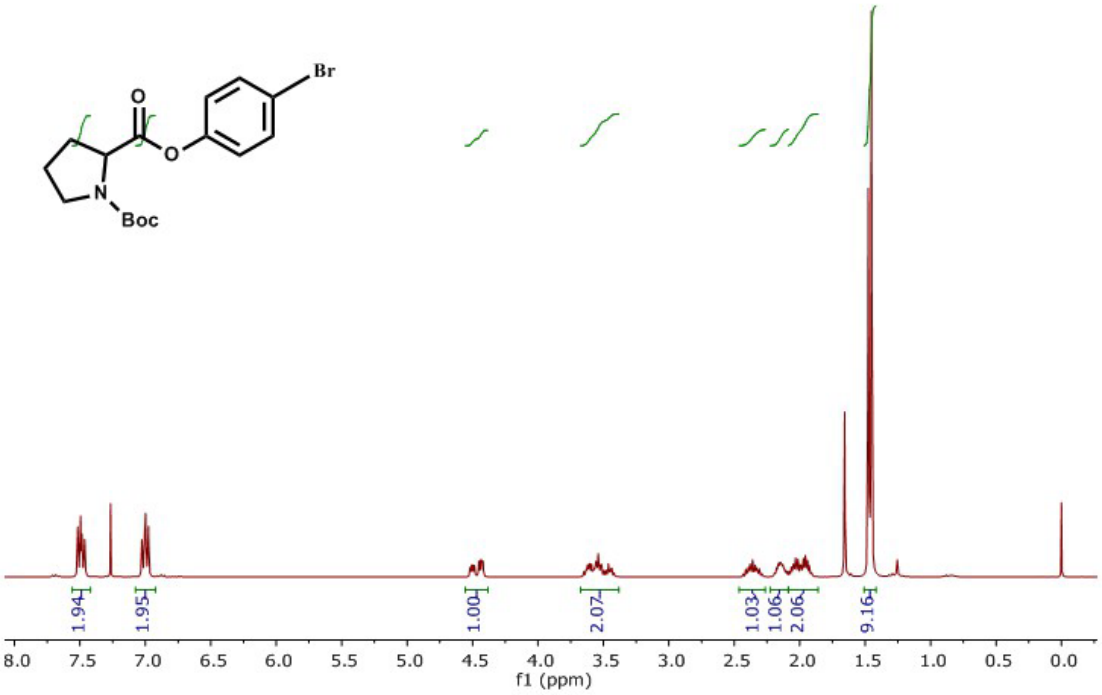


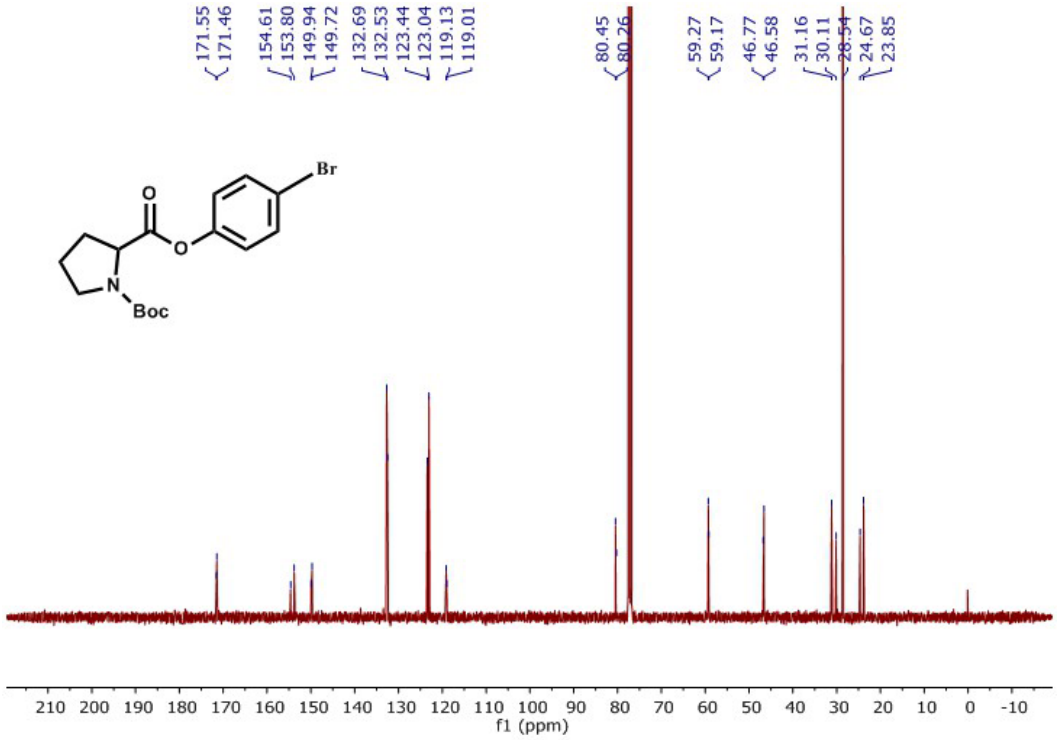
Substrate: 1,4-dibromobenzene, product **10**



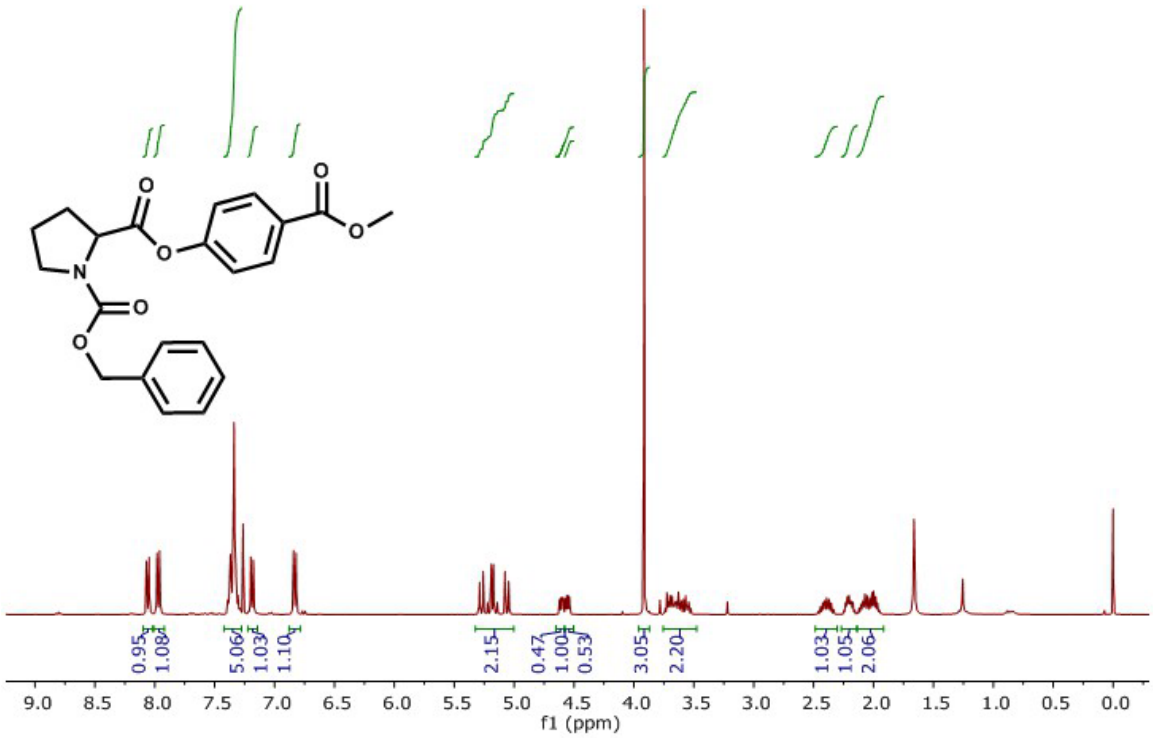


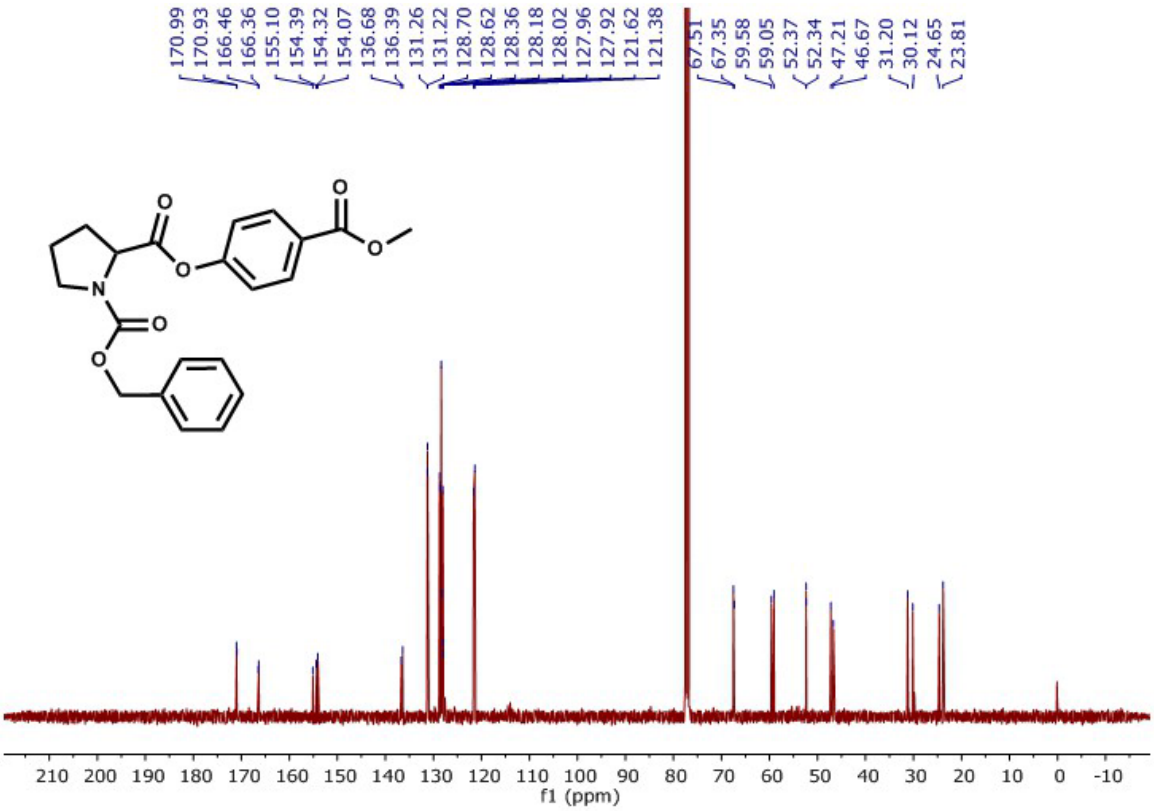
Substrate: 1-Bromo-4-Iodobenzene, product **10**



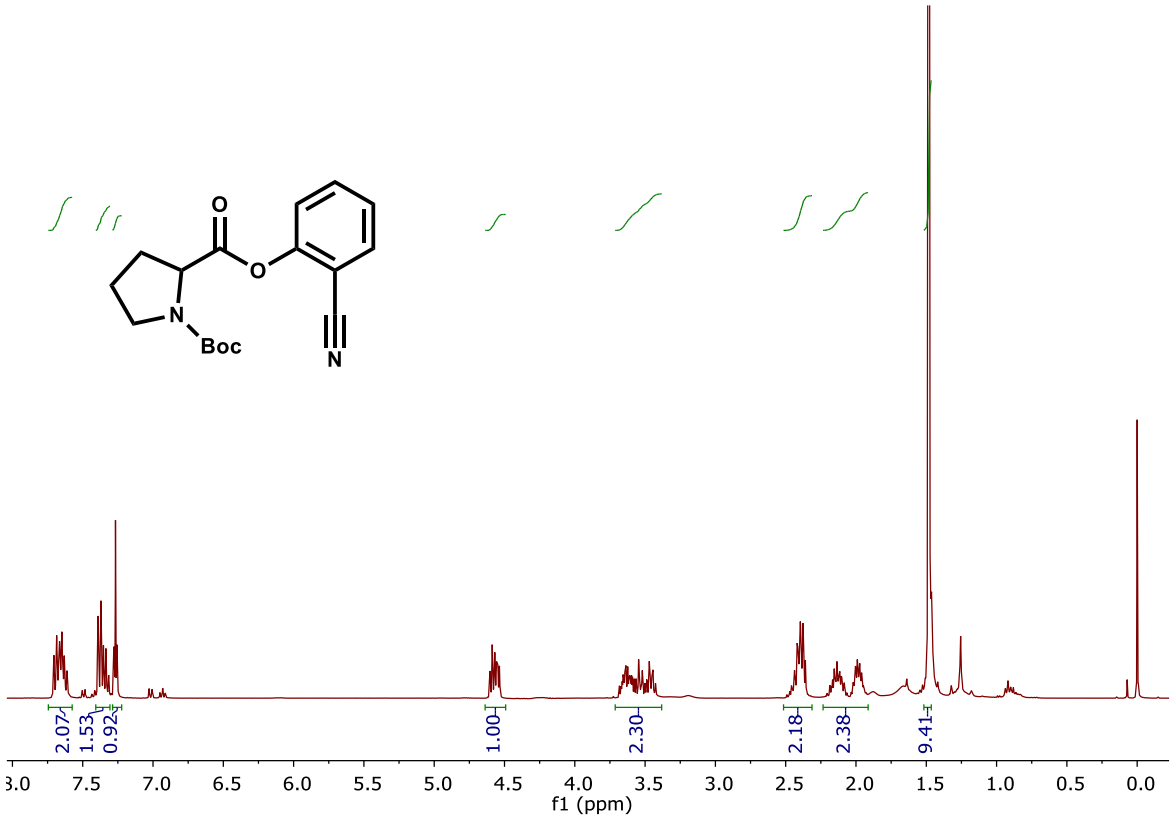


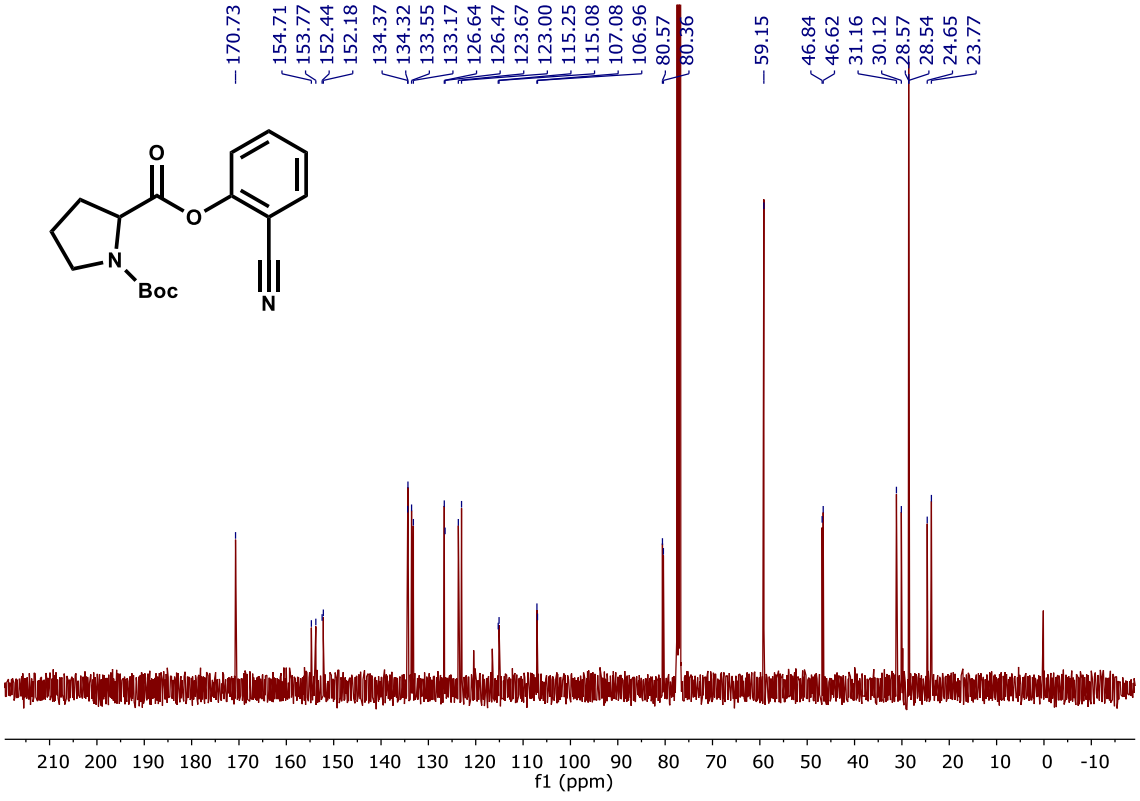
Product **19**


0.95
1.08
5.06
1.03
1.10
2.15
0.47
1.00
0.53
3.05
2.20
1.03
1.05
2.06
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)

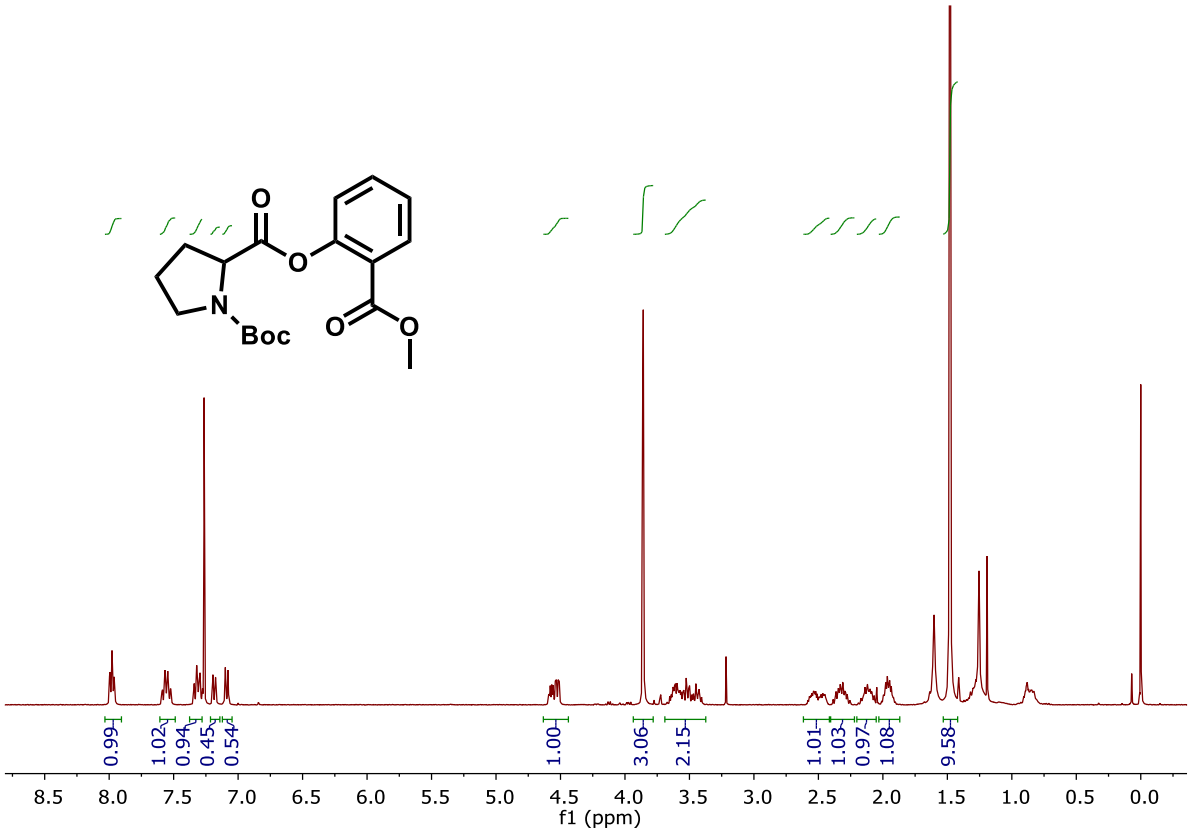

170.99
170.93
166.46
166.36
155.10
154.39
154.32
154.07
136.68
136.39
131.26
131.22
128.70
128.62
128.36
128.18
128.02
127.96
127.92
121.62
121.38
67.51
67.35
59.58
59.05
52.37
52.34
47.21
46.67
31.20
30.12
24.65
23.81
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

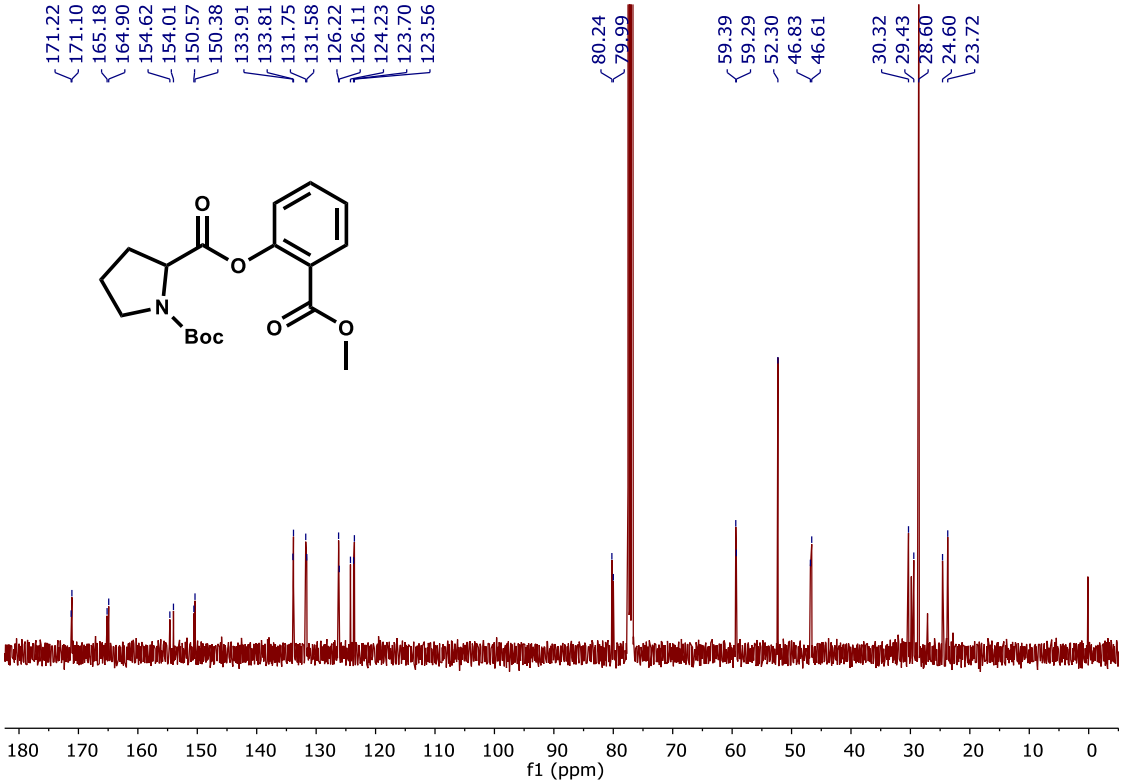
Product **11**


O
O
N
Boc
N
2.07
1.53
0.92
1.00
2.30
2.18
2.38
9.41
f1 (ppm)

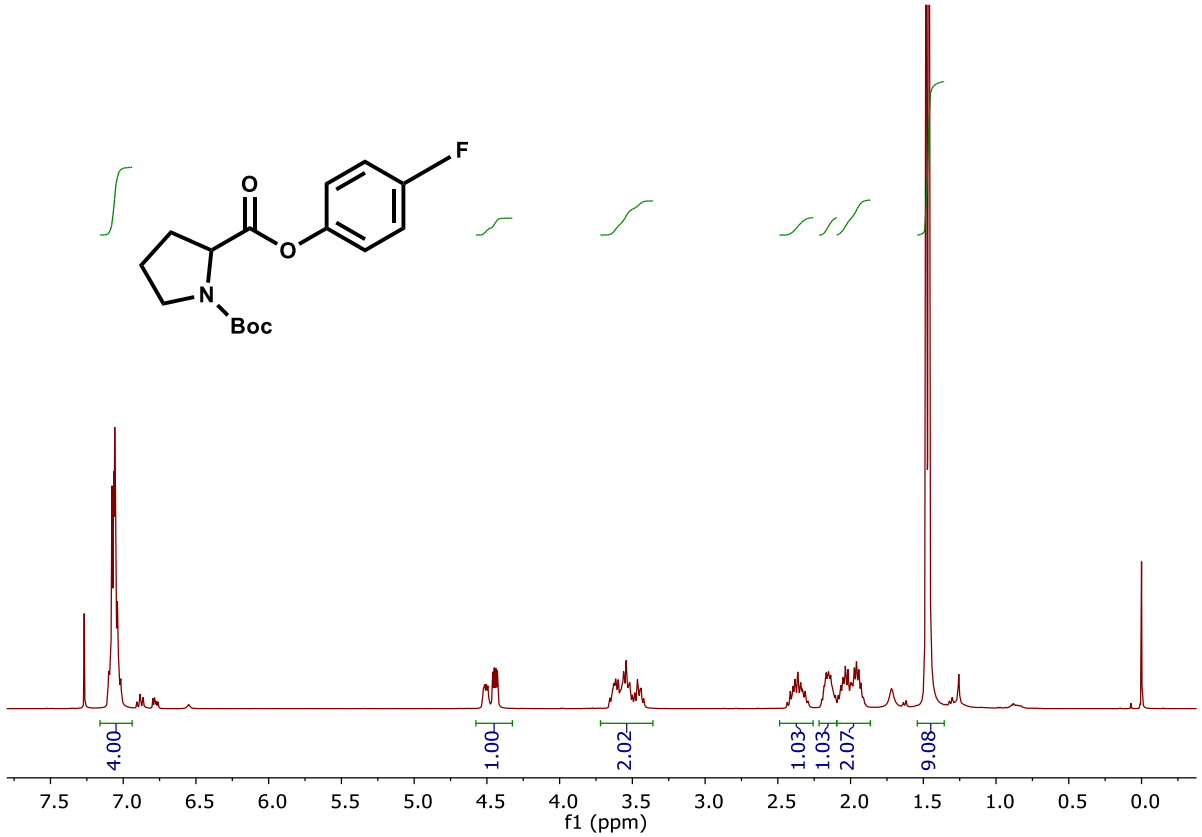

170.73
154.71
153.77
152.44
152.18
134.37
134.32
133.55
133.17
126.64
126.47
123.67
123.00
115.25
115.08
107.08
106.96
80.57
80.36
59.15
46.84
46.62
31.16
30.12
28.57
28.54
24.65
23.77
O
O
N
Boc
N
f1 (ppm)

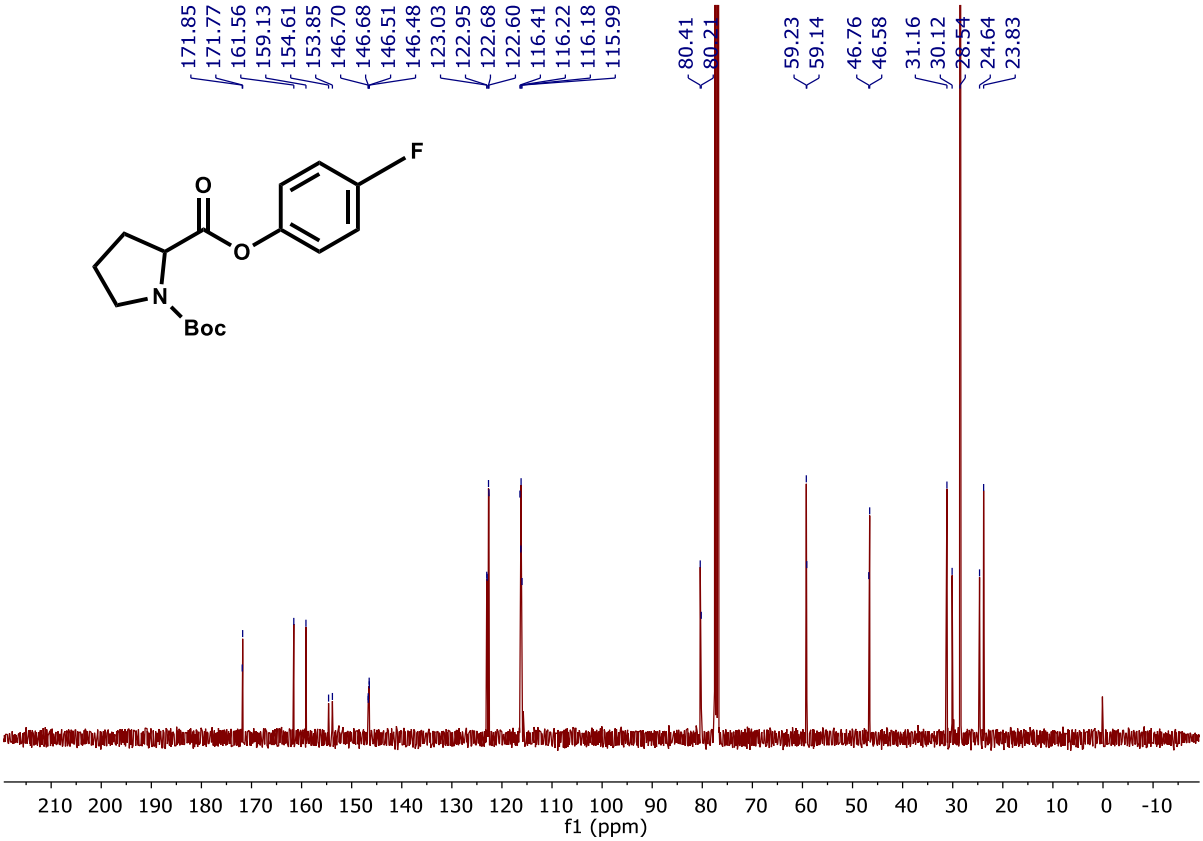
Product **12**


O
O
N
Boc
O
O
0.99
1.02
0.94
0.45
0.54
1.00
3.06
2.15
1.01
1.03
0.97
1.08
9.58
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)

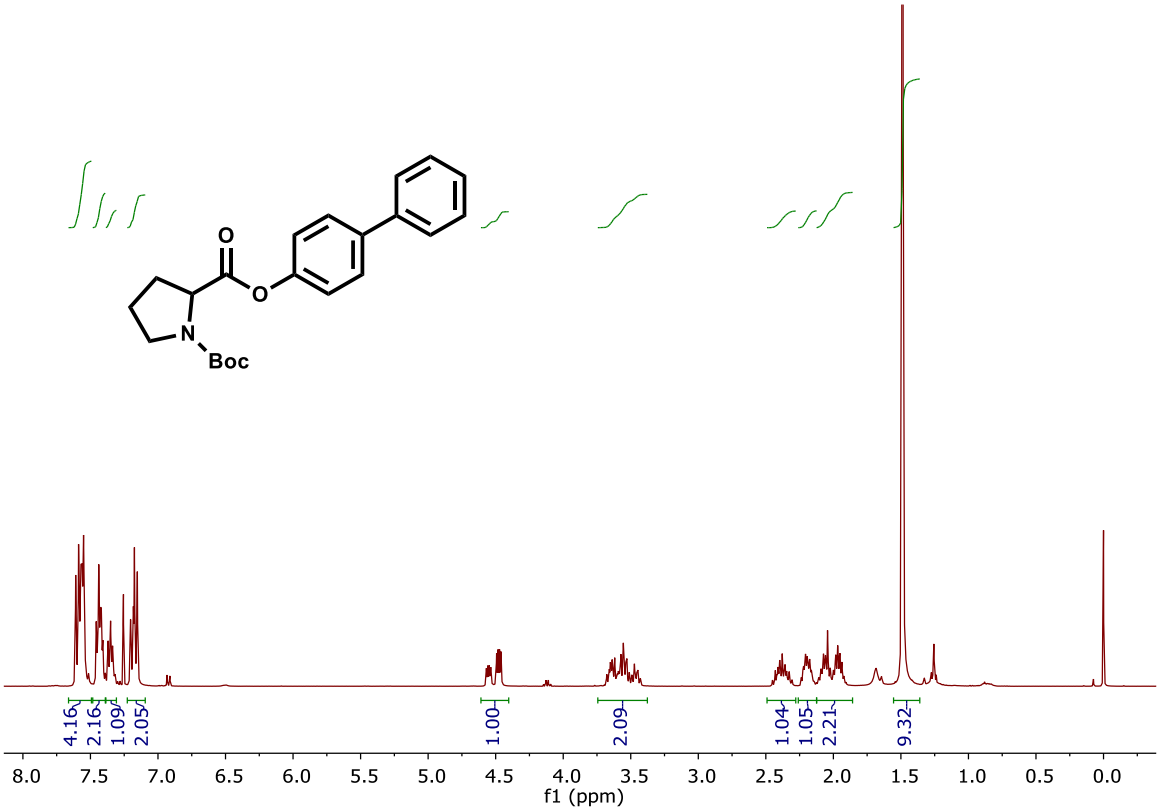

171.22
171.10
165.18
164.90
154.62
154.01
150.57
150.38
133.91
133.81
131.75
131.58
126.22
126.11
124.23
123.70
123.56
80.24
79.99
59.39
59.29
52.30
46.83
46.61
30.32
29.43
28.60
24.60
23.72
O
O
N
Boc
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

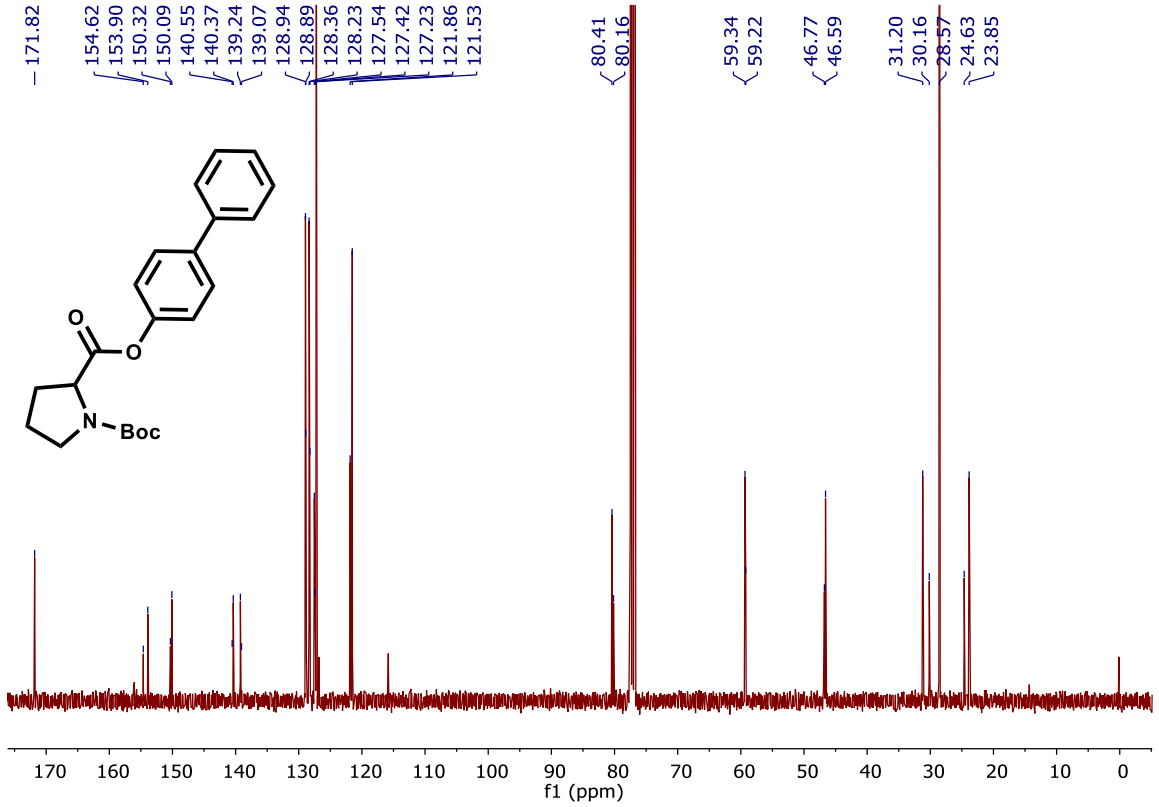
Product **14**


F
O
O
N
Boc
4.00
1.00
2.02
1.03
1.03
2.07
9.08
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)

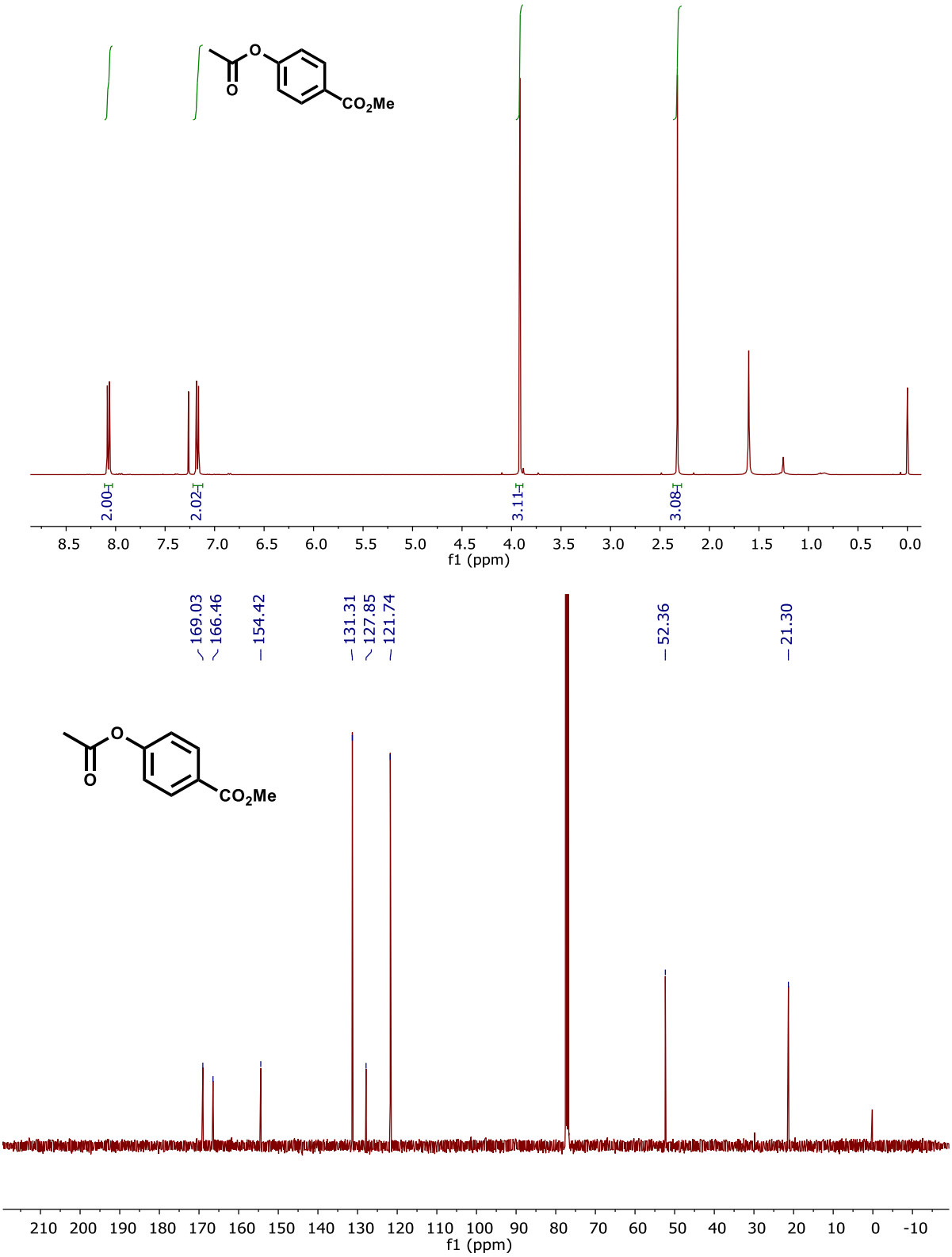

171.85
171.77
161.56
159.13
154.61
153.85
146.70
146.68
146.51
146.48
123.03
122.95
122.68
122.60
116.41
116.22
116.18
115.99
80.41
80.21
59.23
59.14
46.76
46.58
31.16
30.12
28.54
24.64
23.83
F
O
O
N
Boc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Product **13**

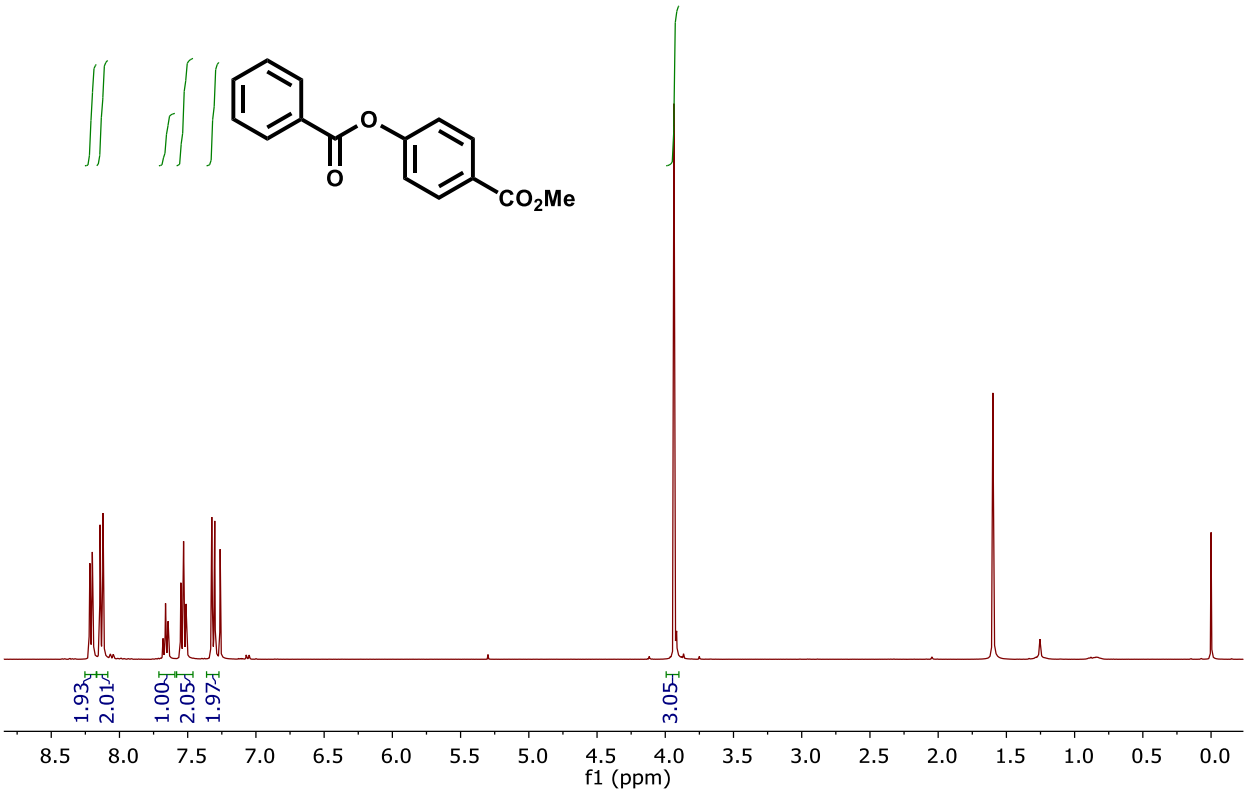

O
O
N
Boc
4.16
2.16
1.09
2.05
1.00
2.09
1.04
1.05
2.21
9.32
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

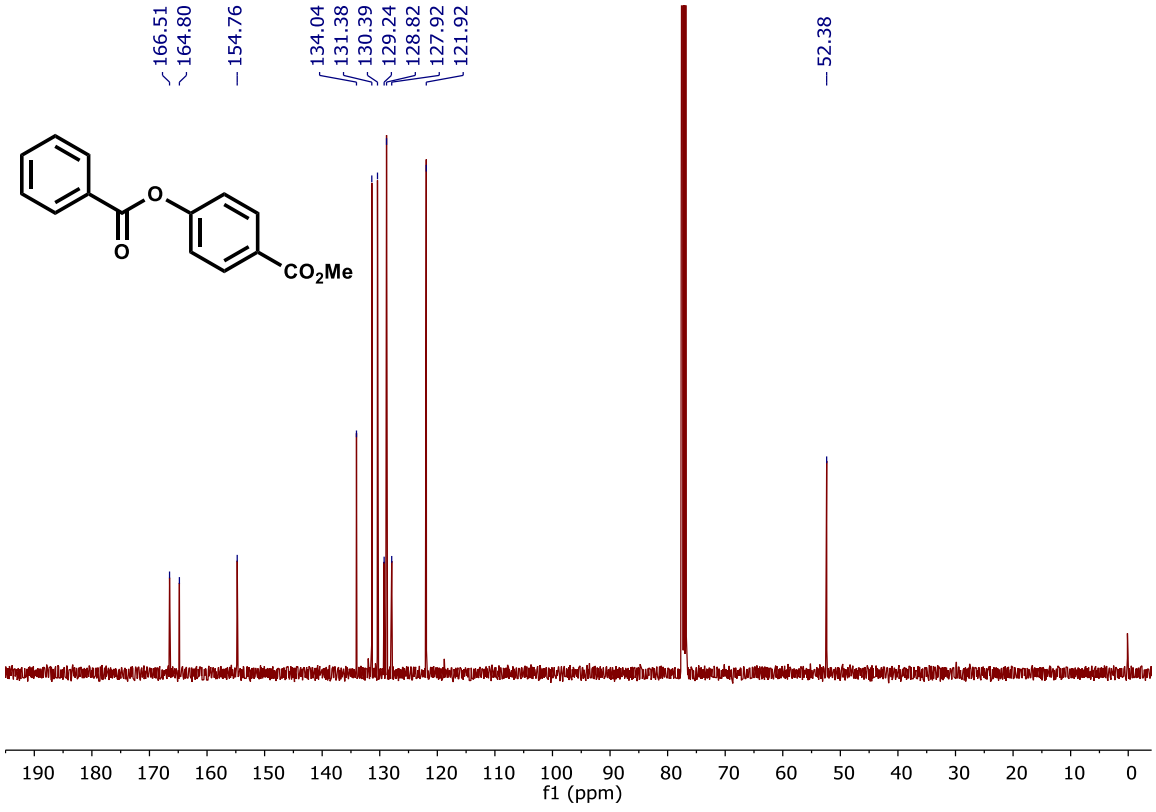

171.82
154.62
153.90
150.32
150.09
140.55
140.37
139.24
139.07
128.94
128.89
128.36
128.23
127.54
127.42
127.23
121.86
121.53
80.41
80.16
59.34
59.22
46.77
46.59
31.20
30.16
28.57
24.63
23.85
O
O
N
Boc
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Product **15**

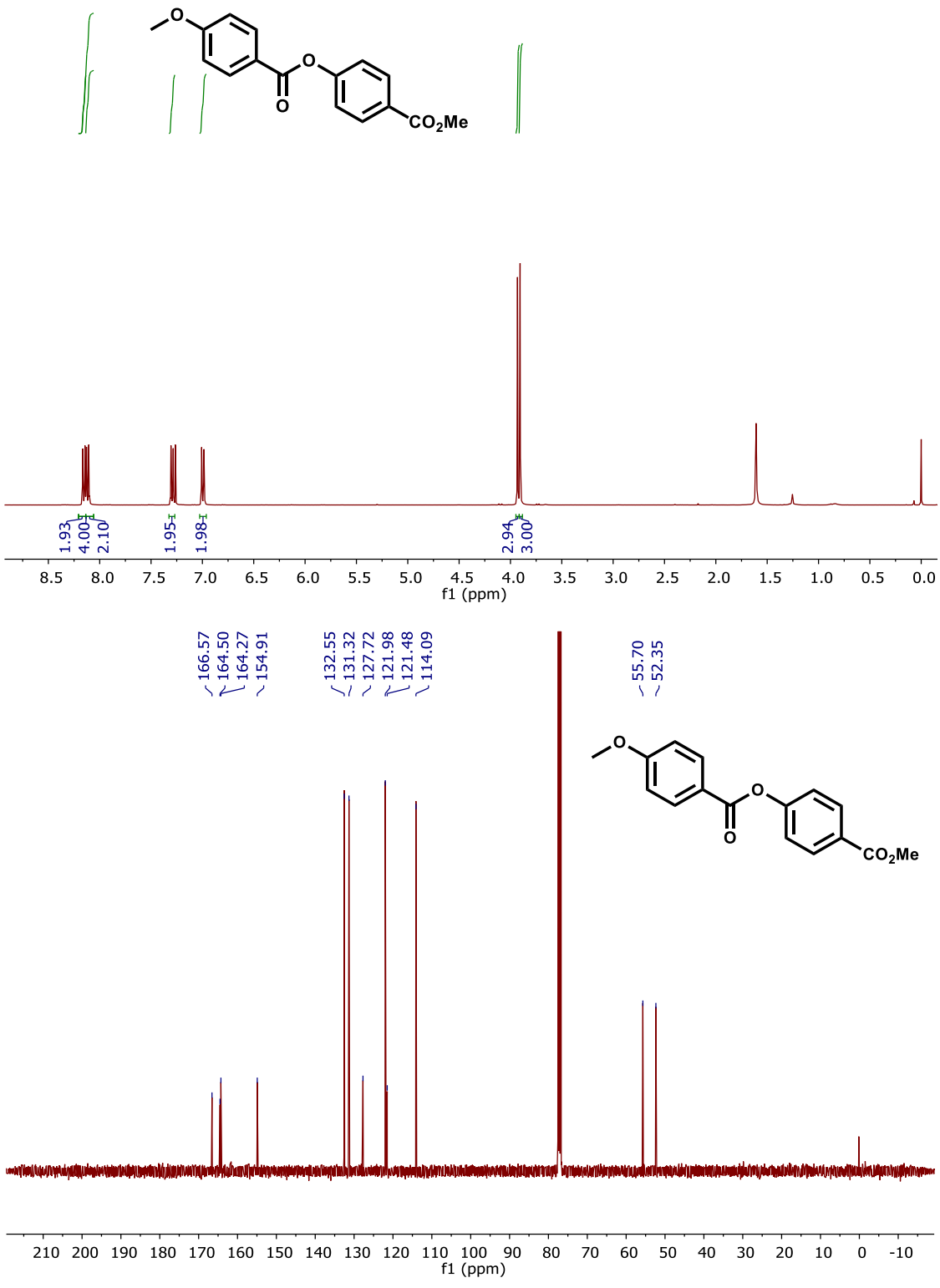

O
O
CO2Me
2.00
2.02
3.11
3.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
169.03
166.46
154.42
131.31
127.85
121.74
52.36
21.30
O
O
CO2Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Product **16**

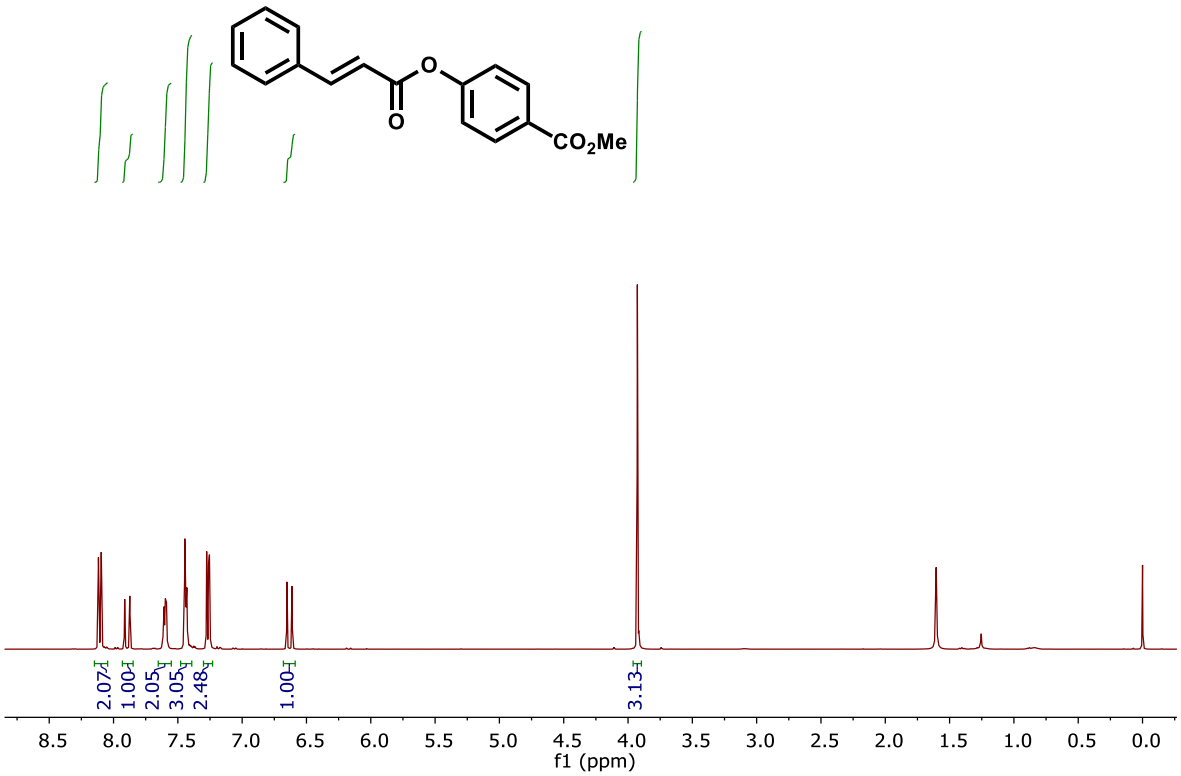

O
O
CO2Me
1.93
2.01
1.00
2.05
1.97
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

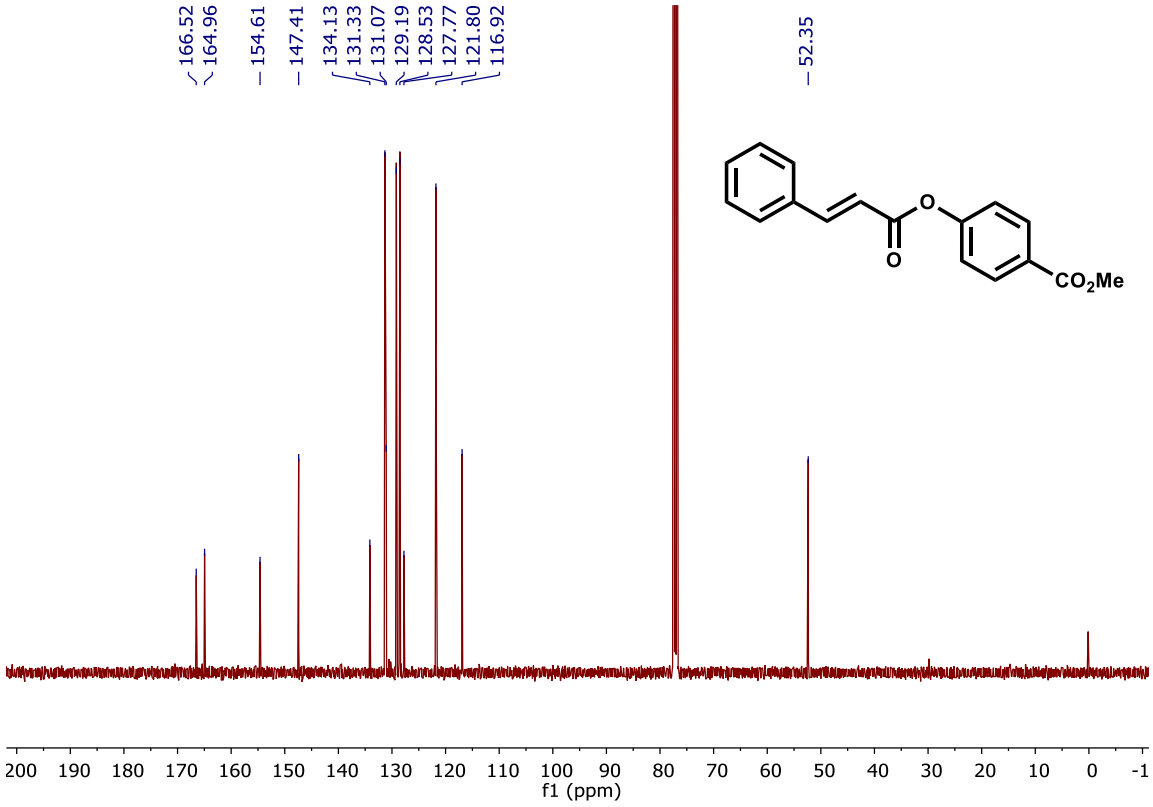

166.51
164.80
154.76
134.04
131.38
130.39
129.24
128.82
127.92
121.92
52.38
O
O
CO2Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Product **18**

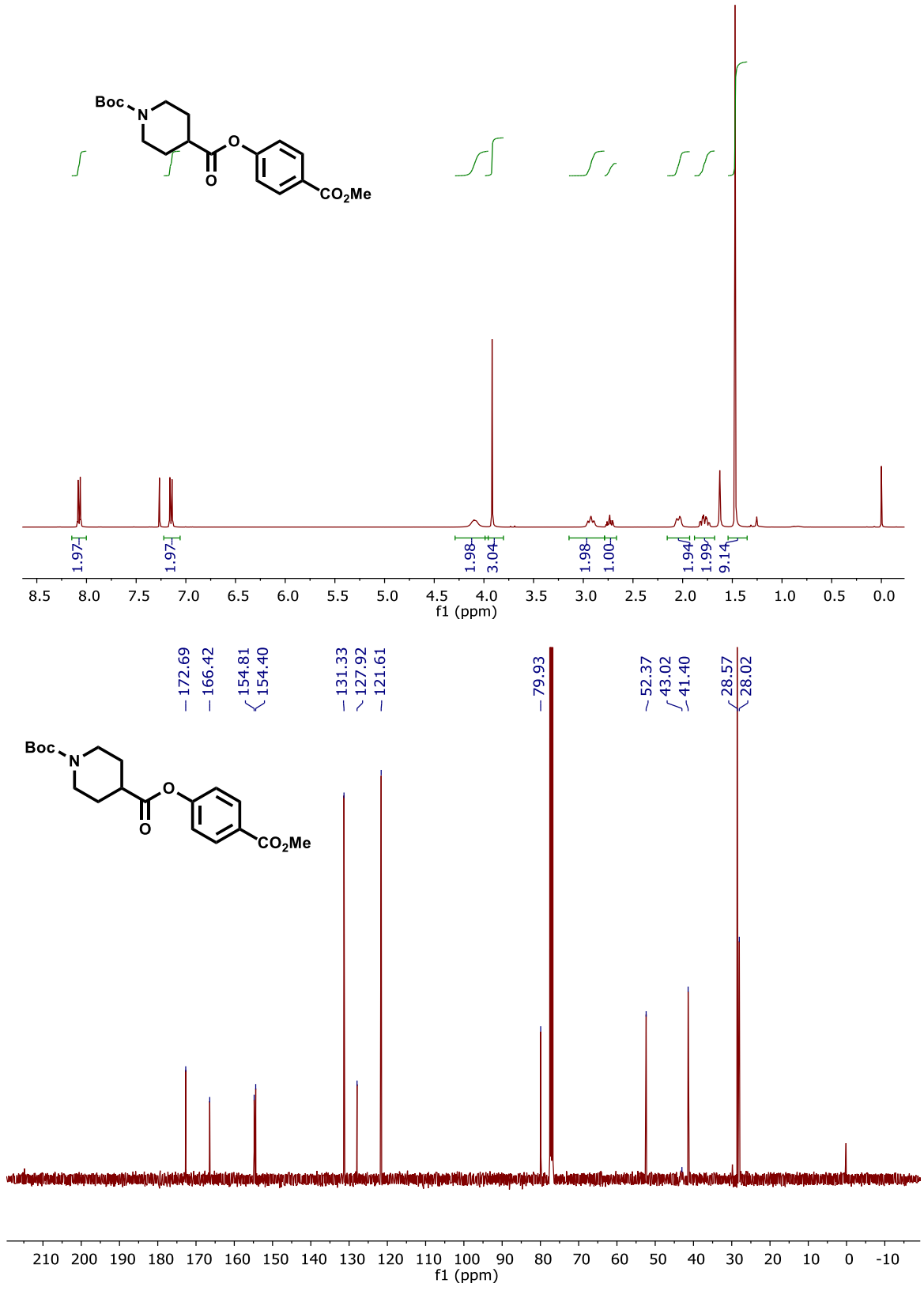

O
O
O
CO2Me
1.93
4.00
2.10
1.95
1.98
2.94
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
166.57
164.50
164.27
154.91
132.55
131.32
127.72
121.98
121.48
114.09
55.70
52.35
O
O
O
CO2Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Product **17**

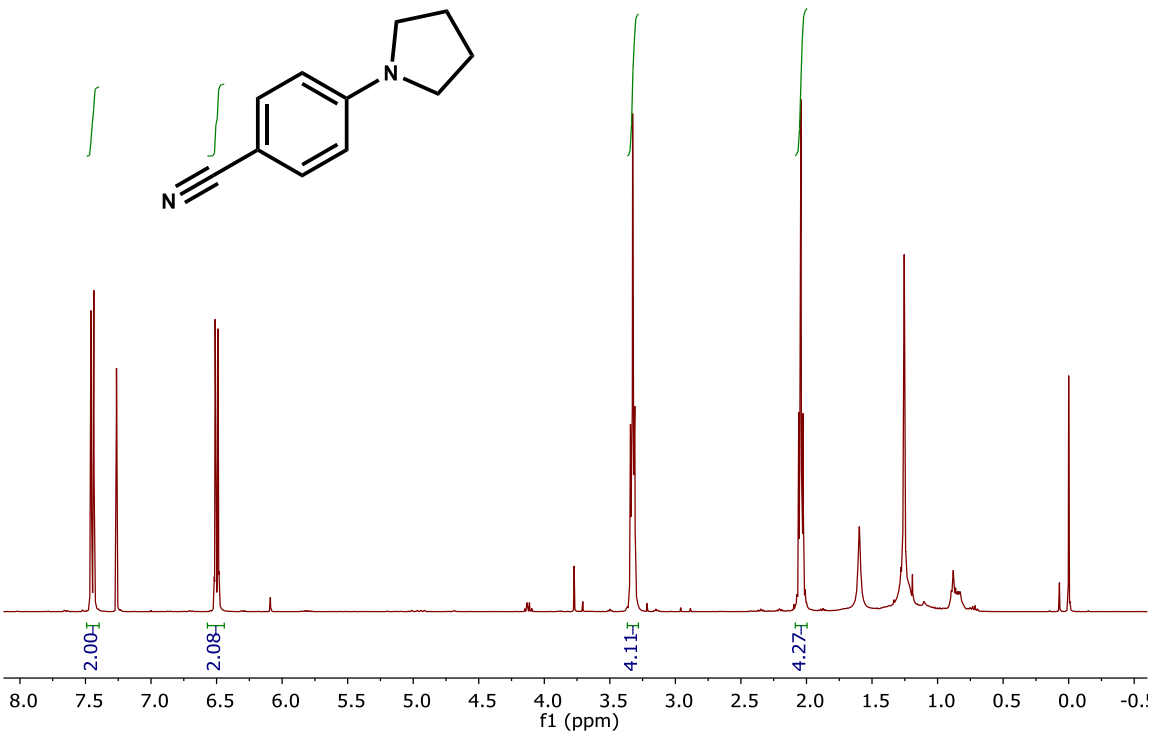

O
O
CO2Me
2.07
1.00
2.05
3.05
2.48
1.00
3.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

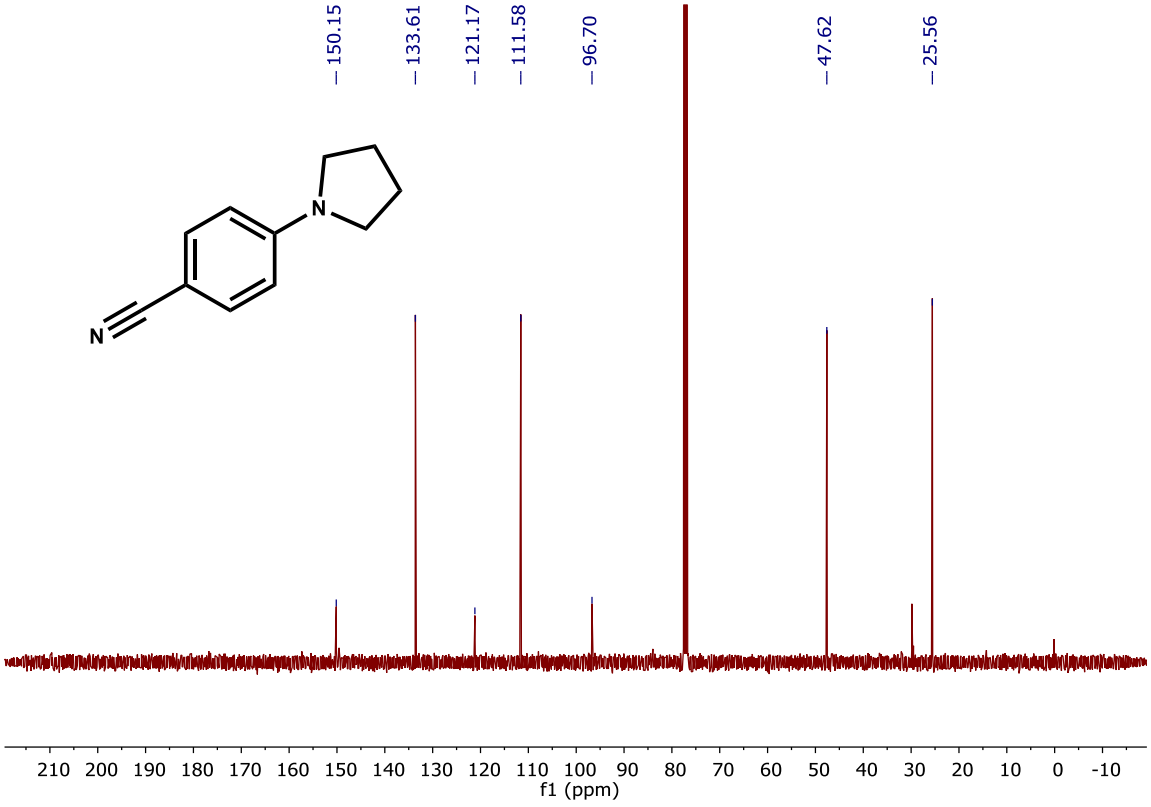

166.52
164.96
154.61
147.41
134.13
131.33
131.07
129.19
128.53
127.77
121.80
116.92
52.35
O
O
CO2Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

Product **20**


Boc
N
O
O
CO2Me
1.97
1.97
1.98
3.04
1.98
1.00
1.94
1.99
9.14
f1 (ppm)
172.69
166.42
154.81
154.40
131.33
127.92
121.61
79.93
52.37
43.02
41.40
28.57
28.02
f1 (ppm)

Product **24**


N
N
2.00
2.08
4.11
4.27
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)


150.15
133.61
121.17
111.58
96.70
47.62
25.56
N
N
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)

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