Electronic Supporting Information for

Trityl isocyanide as a general reagent for visible light mediated photoredox-catalyzed cyanations

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1. General Considerations

1.1 General: All reactions sensitive to air or moisture were carried out in flame-dried glassware under argon pressure using standard Schlenk techniques. NMR spectra were acquired on a Bruker Avance 300 MHz spectrometer running at 300 and 75 MHz for ^{1}H and ^{13}C, respectively or a 500 MHz spectrometer running at 500 and 126 MHz for ^{1}H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to the respective residual solvent signals of $CDCl_3$ [δ (^{1}H) = 7.26 ppm, δ (^{13}C) = 77.16 ppm] or CD_3OD [δ (^{1}H) = 3.31 ppm, δ (^{13}C) = 49.00 ppm]. Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; br, broad signal. Flash column chromatography was performed on silica gel 60 (VWR, 230-400 mesh) or on RediSep® Bronze columns (Teledyne, ISCO, 230-400 mesh) with the indicated eluent mixtures. Thin layer chromatography (TLC) was performed on silica coated aluminum plates (silica 60 F254) with detection by UV-light (λ = 254 nm) and employing potassium permanganate ($KMnO_4$), cerium ammonium molybdate (CAM), phosphomolybdic acid, ninhydrin or *p*-anisaldehyde stain developer solutions followed by heat treatment. High Resolution Mass Spectrometry (HRMS) were registered in a GCT Agilent Technologies 6890 N spectrometer using Electronic Impact (EI+) techniques at 70 eV and electrospray (ESI+) or Bruker maXis II™ (APCI+). Melting points (ºC) were determined in a Stuart™ melting point SMP3 apparatus in open capillary tubes and are uncorrected.

1.2 Chemicals: Deuterated NMR solvents were purchased and used as received. Dry acetone, DMA, DMF, DMSO, THF, MeCN and DCM were obtained from Acros Organics or Merck and used as received. All the reagents were purchased from commercial suppliers (Merck, TCI Chemicals, BLDpharm, Acros Organics, Fluorochem) and used as received.

1.3 Reaction set-up: All photoredox reactions were performed with a Kessil PR160L-blue LED lamp (max 45 W High Luminous DEX 2100 LED, λmax = 440 nm). The lamp was placed 4.0 cm away from the reaction vials. Photoredox-catalyzed reactions were performed using 4 mL Screw Neck Vial (clear glass, 45 x 14.7 mm) with screw cap 13 mm black Sil/PTFE septa. A typical reaction setup is shown below (***Figure S1***).

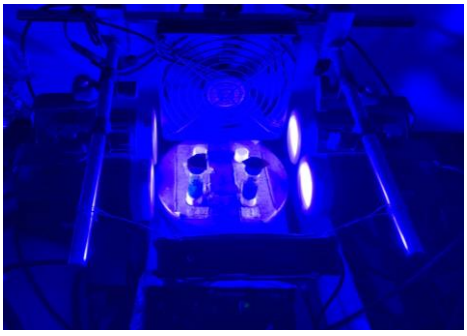


Figure S1. Reaction setup.

2. General Procedures for the Synthesis of Starting Materials

Starting materials (***Figure S2***) were prepared according to literature procedures,[1-9] purchased from suppliers, or synthesized as indicated below.

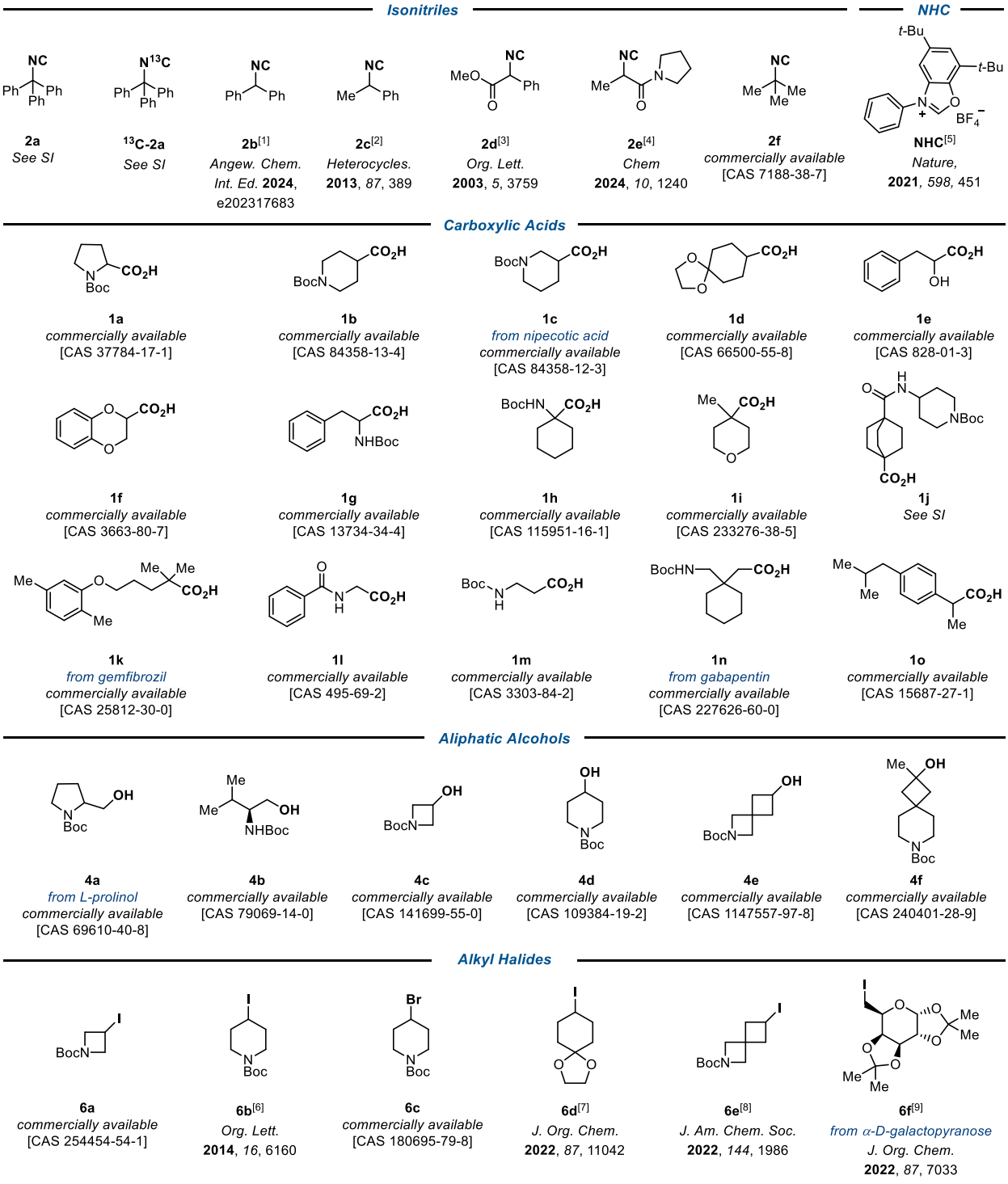
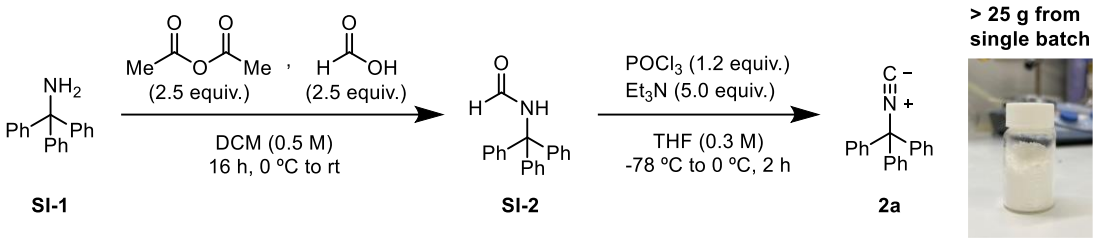


Figure S2: Synthesis of starting materials.

A. Synthesis of (isocyanomethanetriyl)tribenzene 2a



According to a modified literature procedure,[3] acetic anhydride (27.3 mL, 289.2 mmol, 2.5 equiv.) and formic acid (10.9 mL, 289.2 mmol, 2.5 equiv.) were stirred for 2 h at 55 °C to prepare acetic formic anhydride. The corresponding acetic formic anhydride was added dropwise to a stirred solution of triphenylmethanamine **SI-1** (30.0 g, 115.7 mmol, 1.0 equiv.) in dry DCM (231.0 mL, 0.5 M) at 0 °C. The mixture was stirred for 15 min to 0 °C and then, the reaction was allowed to warm room temperature and stirred a further 16 h. The resulting mixture was quenched with cold water. The aqueous layer was extracted with DCM (x3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the corresponding formamide **SI-2** that was directly used in the next step without further purification.

Et_3N (80.6 mL, 578.5 mmol, 5.0 equiv.) was added to a stirred solution of **SI-2** (33.3 g, 115.7 mmol, 1.0 equiv.) in dry THF (290.0 mL, 0.4 M) at -78 ºC. Then, $POCl_3$ (12.9 mL, 138.8 mmol, 1.2 equiv.) in dry THF (92.0 mL, 1.5 M) was added dropwise and the reaction mixture was stirred for 1 h at -78 ºC. Then the reaction mixture was let warm to 0 ºC and stirred for a further

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hour before cold water was added. The resulting mixture was extracted with Et_2O (x3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash column chromatography (SiO_2; 0 – 2% EtOAc in cyclohexane) to afford pure product **2a** (25.3 g, 93.9 mmol) in 82% yield. $\mathbf{R_f}$ = 0.60 (9:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 9H), 7.25 – 7.21 (m, 6H). *Spectrum*

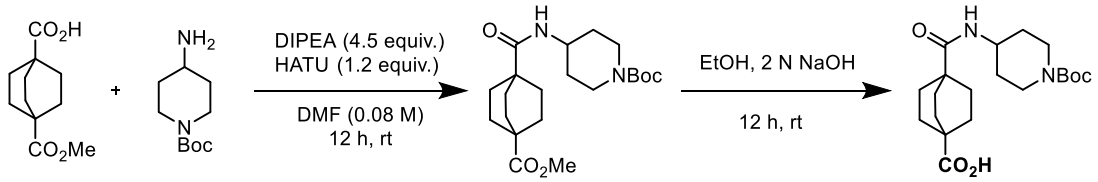
^{13}C NMR (75 MHz, $CDCl_3$): δ 157.7 (br s, -N**C**), 141.7, 128.5, 128.4, 128.2, 75.1 (m, **C**-NC). *Spectrum*

HRMS (APCI+): calculated for $C_{20}H_{15}N$ $[M]^+$: 269.1199; found: 269.1201.

m.p.: 136 – 137 ºC.

Spectroscopic data are in agreement with those in literature.[3b]

B. Synthesis of 4-((1-(*tert*-butoxycarbonyl)piperidin-4-yl)carbamoyl)bicyclo[2.2.2]octane-1-carboxylic acid 1j



SI-3 (2.0 equiv.) **SI-4** **1j**

Step 1: *N*,*N*-Diisopropylethylamine (DIPEA) (1.85 mL, 10.6 mmol, 4.5 equiv.) was added dropwise to a solution of **SI-3** (500.0 mg, 2.4 mmol, 1.0 equiv.), *tert*-butyl 4-aminopiperidine-1-carboxylate (943.7 mg, 4.7 mmol, 2.0 equiv.) and hexafluorophosphate azabenzotriazole tetramethyl uronium (HATU) (1.07 g, 2.8 mmol, 1.2 equiv.) in dry DMF (29.5 mL). The mixture was stirred at rt for 12 hours. The reaction was diluted with water and EtOAc, then extracted with EtOAc. The combined organic layers were washed with saturated NaCl (aq), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to obtain the corresponding **SI-4** product that was directly used in the next step without further purification.

Step 2: The crude compound **SI-4** was dissolved in 12 mL of EtOH and 4.8 mL of a 2 N NaOH solution were added. The resulting reaction mixture was stirred for 12 hours at rt. Then, the solvents were removed at reduced pressure and the resulting solid was dissolved in water. The aqueous solution was washed twice with DCM. Then, the aqueous phase was acidified with 1 N HCl and extracted with DCM:MeOH (10:1) three times. The combined organic phases were

washed with brine and dried over Na_2SO_4. After removal of the solvents at reduced pressure 429.0 mg (48% yield) of the crude acid **1j** were obtained as a white solid.

^{1}H NMR (500 MHz, CD_3OD): δ 7.20 (d, *J* = 7.9 Hz, 1H), 4.86 (br s, 2H), 4.07 – 4.04 (m, 2H), 3.87 – 3.79 (m, 1H), 2.82 (br s, 2H), 1.82 – 1.80 (m, 6H), 1.78 – 1.74 (m, 6H), 1.45 (s, 9H), 1.42 – 1.34 (m, 2H). *Spectrum*

^{13}C NMR (126 MHz, CD_3OD): δ 181.3, 179.7, 156.4, 81.1, 48.3, 44.4, 43.8, 39.9, 39.6, 32.5, 29.1, 29.0, 28.7. *Spectrum*

HRMS (APCI+): calculated for $C_{20}H_{33}N_2O_5$ $[M+H]^+$: 381.2384; found: 381.2387.

m.p.: 235 – 236 ºC.

3. Synthesis of Cyanides from Carboxylic Acids

A. Reaction Optimization

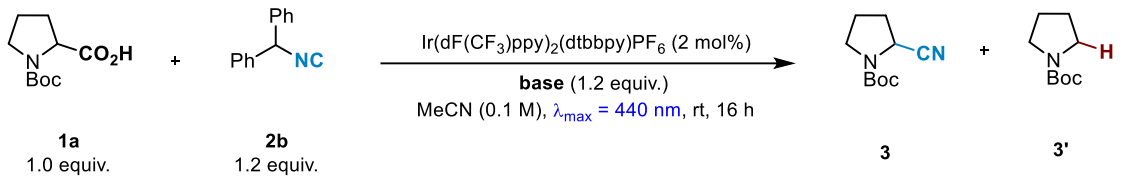


Table 1. Screening of bases[a]

Base	**2b** (equiv.)	Yield **3** (%)[b]	Yield **3'** (%)[b]
K_3PO_4	1.2	42 (40)[c]	38
K_2HPO_4	1.2	29[c]	40
Na_2CO_3	1.2	24	18
$CsCO_3$	1.2	37	36

[a]Optimization reactions were performed using carboxylic acid **1a** (0.10 mmol), isonitrile **2b** (0.12 mmol), **base** (0.12 mmol), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (2 mol%) in dry degassed MeCN (0.1 M), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]The yield was calculated by ^{1}H-NMR analysis using CH_2Br_2 as internal standard. [c]Isolated yield.

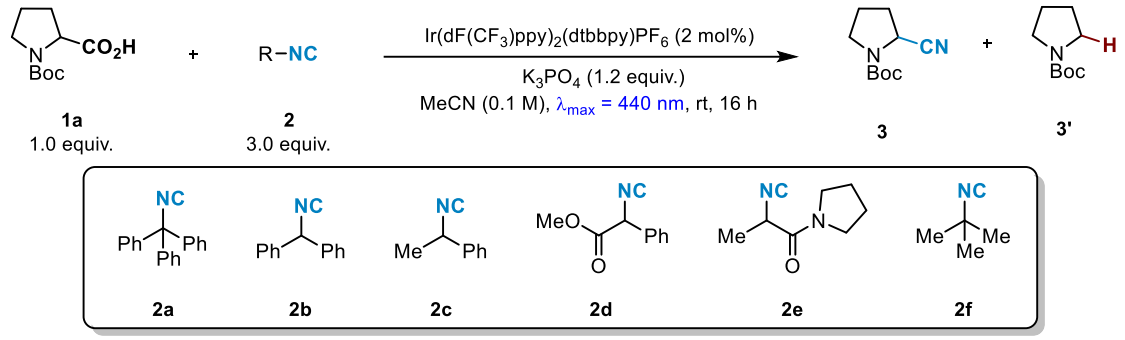


Table 2. Screening of isonitriles[a]

Isonitrile (2)	Yield **3** (%)[b]	Yield **3'** (%)[b]
2a	68	14
2b	55	35
2c	30	5
2d	48	52
2e	24	0
2f	4	12

[a]Optimization reactions were performed using carboxylic acid **1a** (0.10 mmol), **isonitrile 2** (0.30 mmol), K_3PO_4 (0.12 mmol), Ir(dF(CF_3)ppy)$_2$(dtbbpy)PF_6 (2 mol%) in dry degassed MeCN (0.1 M), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]The yield was calculated by ^{1}H-NMR analysis using CH_2Br_2 as internal standard. nd = not detected.

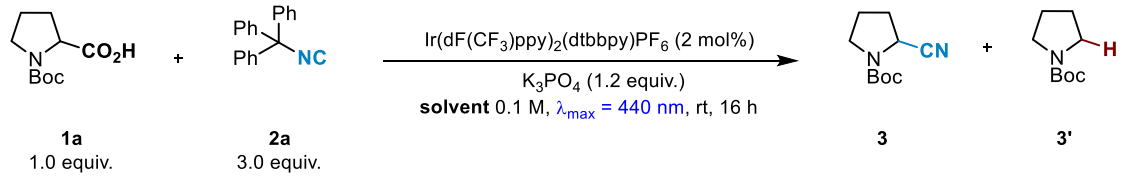


Table 3. Solvent[a]

Solvent	Yield **3** (%)[b]	Yield **3'** (%)[b]
MeCN	68	14
THF	53	15
DCM	0	5
DMF	61	14
DMSO	74	12

Toluene	36	30
MeOH	14	nd

[a]Optimization reactions were performed using carboxylic acid **1a** (0.10 mmol), isonitrile **2a** (0.30 mmol), K_3PO_4 (0.12 mmol), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (2 mol%) in dry degassed **solvent** (0.1 M), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]The yield was calculated by ^{1}H-NMR analysis using CH_2Br_2 as internal standard. nd = not detected.

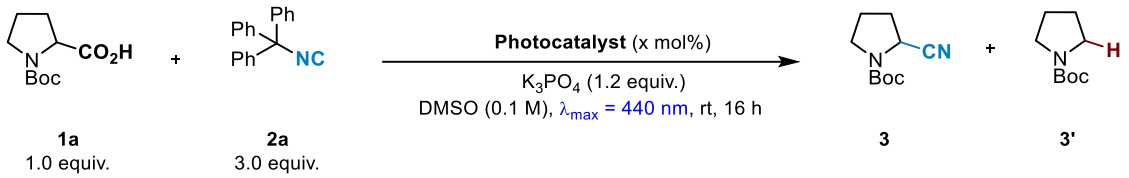


Table 4. Photocatalyst and loading[a]

Catalyst	**(mol%)**	Yield **3** (%)[b]	Yield **3'** (%)[b]
$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	2	74	12
$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	1	80	7
4CzIPN	1	47	7
$Ir(ppy)_3$	1	11	traces
$Ru(bpy)_3(PF_6)_2$	1	10	traces
9-mesityl-10-methylacridinium BF_4	1	39	13

[a]Optimization reactions were performed using carboxylic acid **1a** (0.10 mmol), isonitrile **2a** (0.30 mmol), K_3PO_4 (0.12 mmol), **photocatalyst** (x mol%) in dry degassed DMSO (0.1 M), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]The yield was calculated by ^{1}H-NMR analysis using CH_2Br_2 as internal standard. nd = not detected.

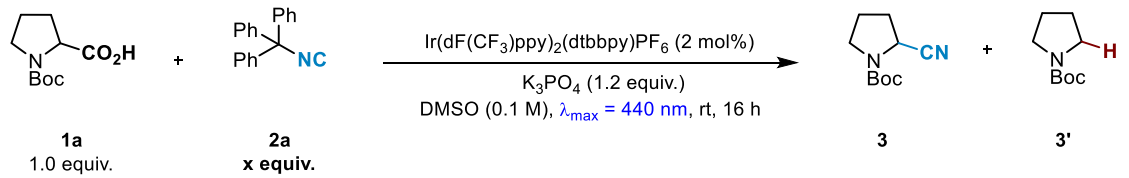


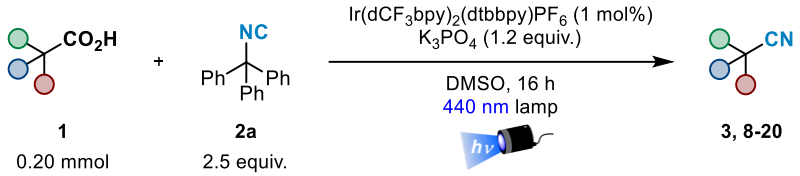
Table 5. Equivalents of isonitrile **2a**[a]

2a (equiv.)	Yield **3** (%)[b]	Yield **3'** (%)[b]
3.0	74	7

5.0	90	5
2.0	81[c]	8
2.5	89[c]	8
2.5	(82)[c,d,e]	-

[a]Optimization reactions were performed using carboxylic acid **1a** (0.10 mmol), isonitrile **2a** (x equiv.), K_3PO_4 (0.12 mmol), $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (2 mol%) in dry degassed DMSO (0.1 M), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]The yield was by ^{1}H-NMR analysis calculated using CH_2Br_2 as internal standard. [c]1 mol% of catalyst $Ir(dF(CF_3)ppy_2)_2(dtbbpy)PF_6$. [d]Isolated yield after flash chromatography. [e]0.20 mmol scale reaction.

B. General Procedure A



In an oven-dried 4 mL vial were weighted the corresponding acid **1** (0.20 mmol, 1.0 equiv.), isonitrile **2a** (0.50 mmol, 2.5 equiv.), K_3PO_4 (0.24 mmol, 1.2 equiv.) and the photocatalyst $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (0.002 mmol, 0.01 equiv.) and dissolved in 2.0 mL of dry, degassed DMSO, under argon. The vial was sealed with parafilm and placed in front of a Kessil PR160L-blue LED lamp (max 45 W High Luminous DEX 2100 LED, λ_{max} = 440 nm) as shown in the reaction setup (see ***Figure S1***) and irradiated for 16 hours. Upon completion, the reaction mixture was diluted with water and extracted with ethyl acetate three times. Then, the combined organic phases were washed with brine three times and dried over Na_2SO_4. The solvents were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography.

4. Synthesis of Cyanides from Alcohols

A. Reaction Optimization

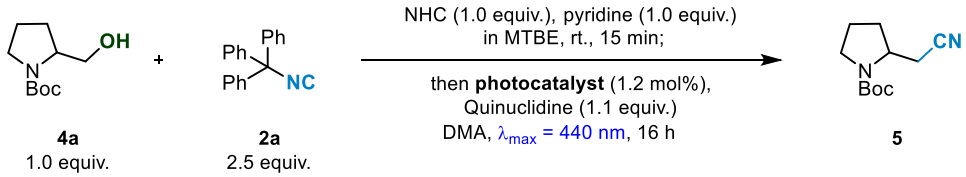


Table 6. Screening of photocatalysts[a]

photocatalyst (1.2 mol%)	**Base (1.1 equiv.)**	Yield **5** (%)[b]
$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	Quinuclidine	0
$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	-	0
$Ir(ppy)_2(dtbbpy)PF_6$	Quinuclidine	26
$Ir(ppy)_2(dtbbpy)PF_6$	-	0
4CzIPN	Quinuclidine	30
4CzIPN	-	0

[a]Optimization reactions were performed using alcohol **4a** (0.10 mmol), isonitrile **2a** (0.25 mmol), NHC precursor (0.10 mmol), pyridine (0.10 mmol), dry MTBE (1.0 mL), quinuclidine (0.11 mmol), **photocatalyst** (1.2 mol%) in dry degassed DMA (1.0 mL), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]Isolated yield.

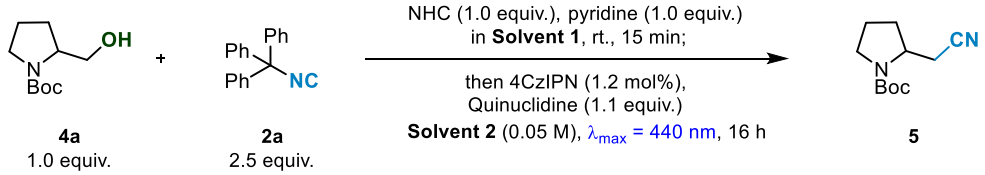


Table 7. Screening of solvents[a]

Solvent 1	**Solvent 2**	**Ratio**	Yield **5** (%)[b]
MTBE	MTBE	-	46
Dioxane	Dioxane	-	52
Dioxane	DMA	1:1	0
Dioxane	MeCN	1:1	0
Dioxane	Acetone	1:1	40
Dioxane	DMSO	1:1	75

[a]Optimization reactions were performed using alcohol **4a** (0.10 mmol), isonitrile **2a** (0.25 mmol), NHC precursor (0.10 mmol), pyridine (0.10 mmol), **solvent 1** (1.0 mL), quinuclidine (0.11 mmol), 4CzIPN (1.2 mol%) in dry degassed **solvent 2** (1.0 mL), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]Isolated yield.

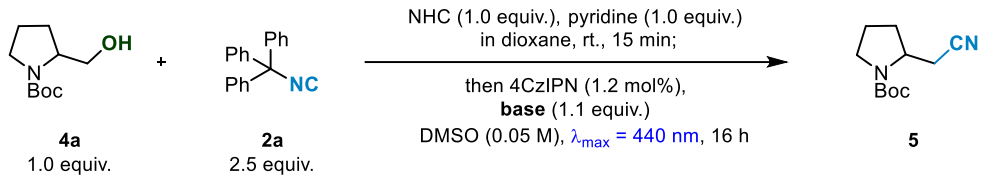
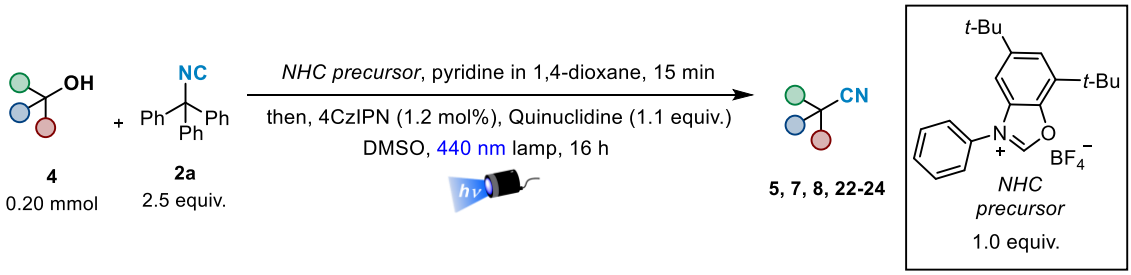


Table 8. Screening of bases[a]

Base	Yield **5** (%)[b]
Quinuclidine	75 (60)[c]
DABCO	0
K_3PO_4	0

[a]Optimization reactions were performed using alcohol **4a** (0.10 mmol), isonitrile **2a** (0.25 mmol), NHC precursor (0.10 mmol), pyridine (0.10 mmol), dry dioxane (1.0 mL), **base** (0.11 mmol), 4CzIPN (1.2 mol%) in dry degassed DMSO (1.0 mL), under blue light irradiation (λ_{max} = 440 nm) for 16 h. [b]Isolated yield. [c]0.20 mmol reaction scale.

B. General Procedure B



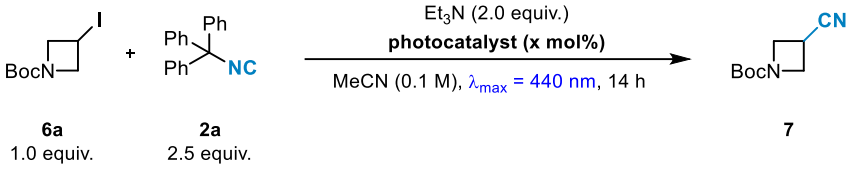
An oven-dried 8 mL vial was charged with 4CzIPN (2.40 µmol, 0.012 equiv.), isonitrile **2a** (0.50 mmol, 2.5 equiv.), quinuclidine (0.22 mmol, 1.1 equiv.) and a magnetic stir bar. Degassed DMSO (2.0 mL) was added to this vial under inert atmosphere of argon.

An oven-dried 4 mL vial was charged with the corresponding alcohol **4** (0.20 mmol, 1.0 equiv.), the NHC precursor (0.20 mmol, 1.0 equiv.) and a magnetic stir bar. The vial was evacuated and refilled with argon three times, dry 1,4-dioxane (0.5 mL) was added and the reaction stirred at rt for 5 min. Then, a pyridine solution (0.20 mmol, 1.0 equiv. in 1.0 mL of dry 1,4-dioxane) was added dropwise at room temperature. The resulting solution was stirred at rt for 10 minutes during which a white solid precipitated. The mixture was filtered with a syringe filter and added to the DMSO solution, employing further 0.5 mL of dry 1,4-dioxane to rinse the vial and to transfer quantitatively its content. The resulting reaction mixture was sparged with argon for 15 minutes. Then the vial was sealed with parafilm and placed in front of a Kessil PR160L-blue LED lamp (max 45 W High Luminous DEX 2100 LED, λ_{max} = 440 nm) as shown in the reaction setup (see ***Figure S1***) and irradiated for 16 hours.

The reaction was quenched with water and the aqueous layer was extracted with Et_2O three times. The combined organic layers were washed with brine three times and dried over anhydrous $MgSO_4$ before being concentrated under reduced pressure. The residue was subjected to purification by flash column chromatography.

5. Synthesis of Cyanides from Alkyl Iodides

A. Reaction Optimization

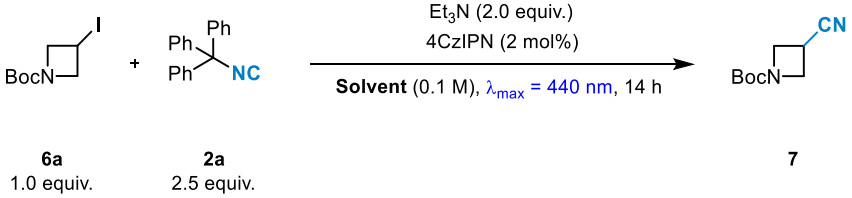


6a 1.0 equiv. **2a** 2.5 equiv. **7**

Table 9. Photocatalyst screening[a]

photocatalyst	**mol%**	Yield **7** (%)[b]
$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	1	(96), 86[c]
4CzIPN	5	(90), 88[c]
4CzIPN	2	91[c]

[a]Optimization reactions were performed using alkyl iodide **6a** (0.20 mmol), isonitrile **2a** (0.50 mmol), Et_3N (0.40 mmol), **photocatalyst (x mol%)** in dry degassed MeCN (0.1 M), under blue light irradiation (λ_{max} = 440 nm) for 14 h. [b]The yield was calculated by ^{1}H-NMR analysis using CH_2Br_2 as internal standard. [c]Isolated yield.



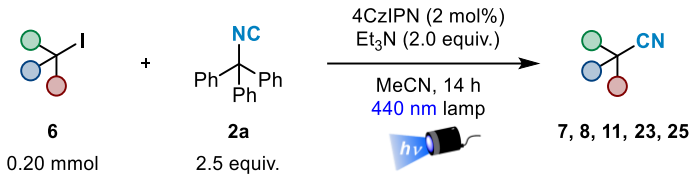
6a 1.0 equiv. **2a** 2.5 equiv. **7**

Table 10. Solvent screening[a]

Solvent	Yield **7** (%)[b]
MeCN	91
DMSO	50
Acetone	69

[a]Optimization reactions were performed using alkyl iodide **6a** (0.20 mmol), isonitrile **2a** (0.50 mmol), Et_3N (0.40 mmol), 4CzIPN (2 mol%) in dry degassed **solvent** (0.1 M), under blue light irradiation (λ_{max} = 440 nm) for 14 h. [b]Isolated yield after flash chromatography.

B. General Procedure C



In an oven-dried 4 mL vial were weighted the corresponding iodide **6** (0.20 mmol, 1.0 equiv.), isonitrile **2a** (0.50 mmol, 2.5 equiv.) and the photocatalyst 4CzIPN (0.004 mmol, 0.02 equiv.) and dissolved in 2.0 mL of dry MeCN. Then triethylamine (0.4 mmol, 2.0 equiv.) was added and the reaction mixture was degassed by three cycles of "freeze-pump-thaw". The vial was sealed with parafilm and placed in front of a Kessil PR160L-blue LED lamp (max 45 W High Luminous DEX 2100 LED, λ_{max} = 440 nm) as shown in the reaction setup (see ***Figure S1***) and irradiated for 14 hours. The solvents were removed at reduced pressure and the residue was purified by flash chromatography.

6. Scale-Up Synthesis

A. Scale-up of compound 3

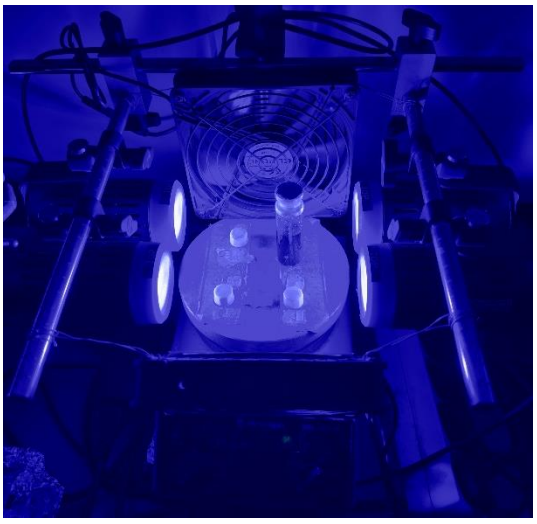
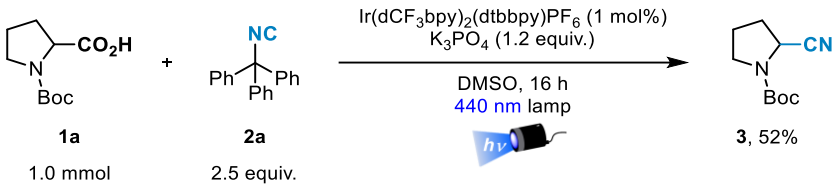
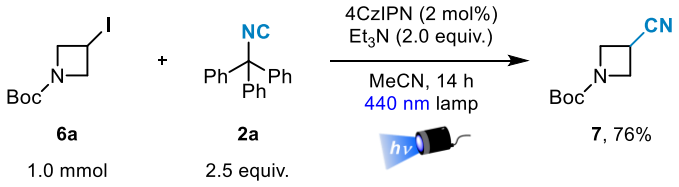


Figure S3. Scale-up synthesis reaction setup.



In an oven-dried 20 mL vial were weighted the corresponding acid **1a** (215.3 mg, 1.00 mmol, 1.0 equiv.), isonitrile **2a** (673.4 mg, 2.50 mmol, 2.5 equiv.), K_3PO_4 (254.7 mg, 1.20 mmol, 1.2 equiv.) and the photocatalyst $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (11.2 mg, 10.0 µmol, 0.01 equiv.) and dissolved in 10.0 mL of dry, degassed DMSO, under argon. The vial was sealed with parafilm and placed in front of a Kessil PR160L-blue LED lamp (max 45 W High Luminous DEX 2100 LED, λ_{max} = 440 nm) as shown in the reaction setup (see ***Figure S3***) and irradiated for 16 hours. Upon completion, the reaction mixture was diluted with water and extracted with ethyl acetate three times. Then, the combined organic phases were washed with brine three times and dried over Na_2SO_4. The solvents were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography.

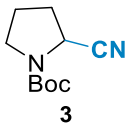
B. Scale-up of compound 7



In an oven-dried 20 mL vial were weighted the corresponding iodide **6a** (283.1 mg, 1.00 mmol, 1.0 equiv.), isonitrile **2a** (673.4 mg, 2.50 mmol, 2.5 equiv.) and the photocatalyst 4CzIPN (15.8 mg, 20.0 µmol, 0.02 equiv.) and dissolved in 10.0 mL of dry MeCN. Then triethylamine (0.28 mL, 2.00 mmol, 2.0 equiv.) was added and the reaction mixture was degassed by three cycles of "freeze-pump-thaw". The vial was sealed with parafilm and placed in front of a Kessil PR160L-blue LED lamp (max 45 W High Luminous DEX 2100 LED, λ_{max} = 440 nm) as shown in the reaction setup (see ***Figure S3***) and irradiated for 14 hours. Upon completion, all the volatiles were removed under reduced pressure, and the crude mixture was subjected to purification by column chromatography.

7. Characterization Data of Nitriles

tert-Butyl 2-cyanopyrrolidine-1-carboxylate (3)



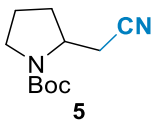
3

Prepared following the general procedure A using carboxylic acid **1a** (43.1 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (32.3 mg, 0.17 mmol) was obtained in 82% yield as a yellow oil, after purification by flash column chromatography (SiO_2; 5 – 15 % EtOAc in cyclohexane). **1.0 mmol scale**: The title compound (101.7 mg, 0.52 mmol) was obtained in 52% yield as a yellow oil, after purification by flash column chromatography. $\mathbf{R_f}$ = 0.51 (3:2 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.56 – 4.45 (m, 1H), 3.51 – 3.35 (m, 2H), 2.25 – 2.03 (m, 4H), 1.51 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[10]

tert-Butyl 2-(cyanomethyl)pyrrolidine-1-carboxylate (5)



5

Prepared following the general procedure B using alcohol **4a** (40.3 mg, 0.20 mmol, 1.0 equiv.), NHC precursor (79.1 mg, 0.20 mmol, 1.0 equiv.), pyridine (16.2 µL, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (135.0 mg, 0.50 mmol, 2.5 equiv.), quinuclidine (24.5 mg, 0.22 mmol, 1.1 equiv.) and 4CzIPN (1.9 mg, 2.4 mmol, 0.012 equiv.). The title compound (25.3 mg, 0.12 mmol) was obtained in 60% yield as a colorless oil, after purification by flash column chromatography (SiO_2; 5 – 15 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.58 (4:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.00 (s, 1H), 3.43 – 3.38 (m, 2H), 2.88 – 2.57 (m, 2H), 2.18 – 2.11 (m, 1H), 2.03 – 1.81 (m, 3H), 1.47 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[11]

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[10] N. P. Ramirez, B. König and J. C. Gonzalez-Gomez, Decarboxylative Cyanation of Aliphatic Carboxylic Acids via Visible-Light Flavin Photocatalysis. *Org. Lett*. 2019, **21**, 1368-1373.

[11] C. K. Mahato, S. Mukherjee, M. Kundu and A. Pramanik, Pyrrolidine-Oxadiazolone Conjugates as Organocatalysts in Asymmetric Michael Reaction. *J. Org. Chem.* 2019, **84**, 1053-1063.

***tert*-Butyl 3-cyanoazetidine-1-carboxylate (7)**

7

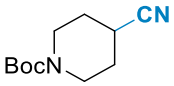
Prepared following the general procedure B using alcohol **4c** (34.6 mg, 0.20 mmol, 1.0 equiv.), NHC precursor (79.1 mg, 0.20 mmol, 1.0 equiv.), pyridine (16.2 µL, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (135.0 mg, 0.50 mmol, 2.5 equiv.), quinuclidine (24.5 mg, 0.22 mmol, 1.1 equiv.) and 4CzIPN (1.9 mg, 2.4 mmol, 0.012 equiv.). The title compound (17.3 mg, 0.12 mmol) was obtained in 48% yield as a white solid, after purification by flash column chromatography (SiO_2; 5 – 30 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.58 (4:1 cyclohexane/EtOAc).

Prepared following the general procedure C using iodide **6a** (56.6 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), Et_3N (55.8 µL, 0.40 mmol, 2.0 equiv.) and 4CzIPN (3.2 mg, 4.0 µmol, 0.02 equiv.). The title compound (33.1 mg, 0.18 mmol) was obtained in 91% yield as a white solid, after purification by flash column chromatography (SiO_2; 5 – 30 % EtOAc in cyclohexane). **1.0 mmol scale**: The title compound (138.7 mg, 0.76 mmol) was obtained in 76% yield as a white solid, after purification by flash column chromatography. $\mathbf{R_f}$ = 0.58 (4:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.23 – 4.13 (m, 4H), 3.43 – 3.33 (m, 1H), 1.44 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[12]

***tert*-Butyl 4-cyanopiperidine-1-carboxylate (8)**



8

Prepared following the general procedure A using carboxylic acid **1b** (45.9 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (27.7 mg, 0.13 mmol) was obtained in 66% yield as a yellow oil, after purification by flash column chromatography (SiO_2; 0 – 40 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.32 (4:1 cyclohexane/EtOAc).

Prepared following the general procedure B using alcohol **4d** (40.3 mg, 0.20 mmol, 1.0 equiv.), NHC precursor (79.1 mg, 0.20 mmol, 1.0 equiv.), pyridine (16.2 µL, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (135.0 mg, 0.50 mmol, 2.5 equiv.), quinuclidine (24.5 mg, 0.22 mmol, 1.1 equiv.) and 4CzIPN (1.9 mg, 2.4 mmol, 0.012 equiv.). The title compound (25.8 mg, 0.12 mmol) was

[12] Y. Ji, L. Wojtas and J. M. Lopchuk, An improved, gram-scale synthesis of protected 3-haloazetidines: rapid diversified synthesis of azetidine-3-carboxylic acids. *ARKIVOC* 2018, **iv**, 195-214.

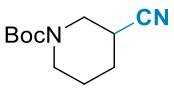
obtained in 61% yield as a yellow oil, after purification by flash column chromatography (SiO_2; 2 – 20 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.32 (4:1 cyclohexane/EtOAc).

Prepared following the general procedure C using iodide **6b** (62.2 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), Et_3N (55.8 µL, 0.40 mmol, 2.0 equiv.) and 4CzIPN (3.2 mg, 4.0 µmol, 0.02 equiv.). The title compound (26.6 mg, 0.16 mmol) was obtained in 82% yield as a yellow oil, after purification by flash column chromatography (SiO_2; 0 – 40 % EtOAc in cyclohexane). Starting from bromide **6c** (52.8 mg, 0.20 mmol, 1.0 equiv.), the title compound (22.2 mg, 0.11 mmol) was obtained in 53% yield. $\mathbf{R_f}$ = 0.32 (4:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.64 (ddd, *J* = 13.9, 7.1, 3.8 Hz, 2H), 3.32 (ddd, *J* = 13.8, 7.7, 3.7 Hz, 2H), 2.78 (tt, *J* = 7.9, 4.3 Hz, 1H), 1.91 – 1.71 (m, 4H). 1.44 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[10]

***tert*-Butyl 3-cyanopiperidine-1-carboxylate (9)**



9

Prepared following the general procedure A using carboxylic acid **1c** (45.9 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (27.3 mg, 0.13 mmol) was obtained in 65% yield as a yellowish oil, after purification by flash column chromatography (SiO_2; 10 – 40 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.35 (4:1 cyclohexane/EtOAc).

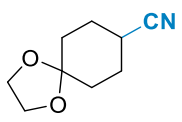
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.72 – 3.32 (m, 4H), 2.65 (dq, *J* = 11.3, 3.9 Hz, 1H), 2.01 – 1.66 (m, 4H), 1.45 (s, 9H). *Spectrum*

^{1}H NMR (500 MHz, DMSO), T = 90 ºC: δ 3.67 (dd, *J* = 13.2, 5.8 Hz, 1H), 3.54 – 3.49 (m, 1H), 3.42 (dd, *J* = 13.4, 3.5 Hz, 1H), 3.17 (ddd, *J* = 12.9, 8.5, 3.7 Hz, 1H), 2.98 – 2.94 (m, 1H), 1.91 – 1.85 (m, 1H), 1.84 – 1.79 (m, 1H), 1.65 – 1.57 (m, 1H), 1.56 – 1.47 (m, 1H), 1.43 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[13]

[13] N. Nakajima, M. Saito and M. Ubukata, Activated dimethyl sulfoxide dehydration of amide and its application to one-pot preparation of benzyl-type perfluoroimidates. *Tetrahedron*, 2022, **58**, 3561-3577.

1,4-Dioxaspiro[4.5]decane-8-carbonitrile (10)



10

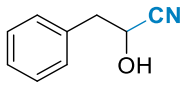
Prepared following the general procedure A using carboxylic acid **1d** (37.2 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (28.0 mg, 0.17 mmol) was obtained in 84% yield as a yellow oil, after purification by flash column chromatography (SiO_2; 0 – 20 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.21 (4:1 cyclohexane/EtOAc).

Prepared following the general procedure C using iodide **6d** (53.6 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), Et_3N (55.8 µL, 0.40 mmol, 2.0 equiv.) and 4CzIPN (3.2 mg, 4.0 µmol, 0.02 equiv.). The title compound (26.6 mg, 0.16 mmol) was obtained in 80% yield as a yellow oil, after purification by flash column chromatography (SiO_2; 0 – 20% EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.21 (4:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.97 – 3.91 (m, 4H), 2.69 – 2.61 (m, 1H), 2.04 – 1.79 (m, 6H), 1.66 – 1.57 (m, 2H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[14]

2-Hydroxy-3-phenylpropanenitrile (11)



11

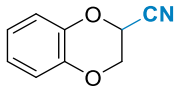
Prepared following the general procedure A using carboxylic acid **1e** (33.2 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (21.9 mg, 0.15 mmol) was obtained in 74% yield as a yellowish oil, after purification by flash column chromatography (SiO_2; 10 – 30 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.20 (4:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.29 (m, 5H), 4.65 (t, J = 6.4 Hz, 1H), 3.12 (d, J = 6.4 Hz, 2H), 2.79 (br s, 1H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[15]

[14] G. R. Harris, A. D. Trowbridge and M. J. Gaunt, A Chiral Amine Transfer Approach to the Photocatalytic Asymmetric Synthesis of α-Trialkyl-α-tertiary Amines. *Org. Lett*. 2023, **25**, 861-866.
[15] A. Dickschat and A. Studer, Radical Addition of Arylboronic Acids to Various Olefins under Oxidative Conditions. *Org. Lett.* 2010, **12**, 3972-3974.

2,3-Dihydrobenzo[b][1,4]dioxine-2-carbonitrile (12)



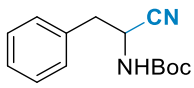
12

Prepared following the general procedure A using carboxylic acid **1f** (36.0 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (16.5 mg, 0.10 mmol) was obtained in 51% yield as a yellowish solid, after purification by flash column chromatography (SiO_2; 0 – 5% EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.29 (9:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98 – 6.91 (m, 4H), 5.11 (dd, *J* = 3.8, 2.6 Hz, 1H), 4.42 (dd, *J* = 11.7, 3.8 Hz, 1H), 4.35 (dd, *J* = 11.8, 2.6 Hz, 1H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[10]

***tert*-Butyl (1-cyano-2-phenylethyl)carbamate (13)**



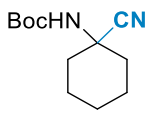
13

Prepared following the general procedure A using carboxylic acid **1g** (53.1 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (30.8 mg, 0.13 mmol) was obtained in 63% yield as a white solid, after purification by flash column chromatography (SiO_2; 5 – 10 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.51 (4:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 – 7.27 (m, 5H), 4.79 (br s, 2H), 3.15 – 3.01 (m, 2H), 1.44 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[10]

***tert*-Butyl (1-cyanocyclohexyl)carbamate (14)**



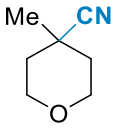
14

Prepared following the general procedure A using carboxylic acid **1h** (48.7 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (35.7 mg, 0.16 mmol) was obtained in 80% yield as a white solid, after purification by flash column chromatography (SiO_2; 0 – 20 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.52 (7:3 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.67 (br s, 1H), 2.33 – 2.27 (m, 2H), 1.76 – 1.55 (m, 8H), 1.48 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[10]

4-Methyltetrahydro-2H-pyran-4-carbonitrile (15)



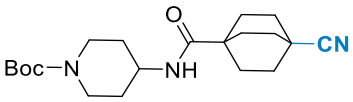
15

Prepared following the general procedure A using carboxylic acid **1i** (28.8 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound was obtained in 61% yield. In this case, the yield was calculated by ^1H NMR using CH_2Br_2 as internal standard since we could not isolate it due to its suspected volatility. For this reason, crude ^1H NMR is provided.

^1H NMR (300 MHz, $CDCl_3$): δ 4.08 – 4.02 (m, 2H), 3.82 (td, *J* = 12.1, 2.1 Hz, 2H), 1.97 – 1.91 (m, 2H), 1.75 – 1.65 (m, 2H), 1.51 (s, 3H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[16]

***tert*-Butyl 4-(4-cyanobicyclo[2.2.2]octane-1-carboxamido)piperidine-1-carboxylate (16)**



16

Prepared following the general procedure A using carboxylic acid **1j** (76.1 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (37.2 mg, 0.10 mmol) was obtained in 52% yield as a yellowish solid, after purification by flash column chromatography (SiO_2; 90 – 100% Et_2O in pentane). $\mathbf{R_f}$ = 0.14 (1:1 cyclohexane/EtOAc).

^1H NMR (300 MHz, $CDCl_3$): δ 5.33 (d, *J* = 7.8 Hz, 1H), 4.04 – 3.99 (m, 2H), 3.93 – 3.80 (m, 1H), 2.86 – 2.77 (m, 2H), 1.99 – 1.93 (m, 6H), 1.87 – 1.75 (m, 8H), 1.44 (s, 9H), 1.24 – 1.16 (m, 2H). *Spectrum*

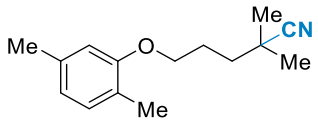
^{13}C NMR (75 MHz, $CDCl_3$): δ 175.4, 154.8, 124.5, 79.8, 46.8, 42.8, 37.7, 32.2, 29.4, 28.5, 27.5, 27.3. *Spectrum*

HRMS (APCI+): calculated for $C_{20}H_{32}N_2O_3$ $[M+H]^+$: 362.2438; found: 362.2439.

m.p.: 176 – 177 ºC.

[16] K. Le, M. J. Soth, G. Liu, P. Jones, J. B. Cross, T. J. McAfoos, C. L. Carroll and R. T. Lewis, US2019/308978, A1.

5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanenitrile (17)



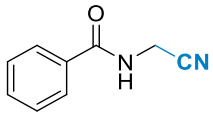
17

Prepared following the general procedure A using carboxylic acid **1k** (50.1 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (36.9 mg, 0.16 mmol) was obtained in 80% yield as a yellowish oil, after purification by flash column chromatography (SiO_2; 0 – 4% EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.55 (4:1 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (d, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 3.99 (t, *J* = 6.0 Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 2.03 – 1.97 (m, 2H), 1.77 – 1.74 (m, 2H), 1.40 (s, 6H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[17]

***N*-(Cyanomethyl)benzamide (18)**



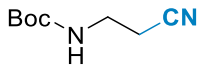
18

Prepared following the general procedure A using carboxylic acid **1l** (35.8 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (4.5 mg, 4.0 µmol, 0.02 equiv.). The title compound (14.7 mg, 0.09 mmol) was obtained in 46% yield as a yellowish solid, after purification by flash column chromatography (SiO_2; 0 – 40% EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.32 (3:2 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 – 7.77 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 6.59 (br s, 1H), 4.40 (d, *J* = 5.9 Hz, 2H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[18]

***tert*-Butyl (2-cyanoethyl)carbamate (19)**



19

Prepared following the general procedure A using carboxylic acid **1m** (37.8 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2

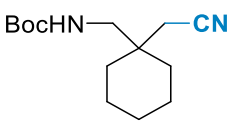
[17] G. Zhang, C. Zhang, Y. Tian and F. Chen, Fe-Catalyzed Direct Synthesis of Nitriles from Carboxylic Acids with Electron-Deficient *N*-Cyano-*N*-aryl-arylsulfonamide. *Org. Lett*. 2023, **25**, 917-922.
[18] G. S. Kumar, P. S. Shinde, H. Chen, K. Muralirajan, R. Kancherla and M. Rueping, Paired Electrolysis for Decarboxylative Cyanation: 4-CN-Pyridine, a Versatile Nitrile Source. *Org. Lett.* 2022, **24**, 6357-6363.

mg, 2.0 μmol, 0.01 equiv.). The title compound (14.7 mg, 0.09 mmol) was obtained in 43% yield as a yellowish oil, after purification by flash column chromatography (SiO_2; 10 – 40 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.24 (3:2 cyclohexane/EtOAc).

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.95 (br s, 1H), 3.39 (q, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 6.3 Hz, 2H), 1.45 (s, 9H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[19]

***tert*-Butyl ((1-(cyanomethyl)cyclohexyl)methyl)carbamate (20)**



20

Prepared following the general procedure A using carboxylic acid **1n** (54.3 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 μmol, 0.01 equiv.). The title compound (24.2 mg, 0.10 mmol) was obtained in 48% yield as a yellowish solid, after purification by flash column chromatography (SiO_2; 0 – 40 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.33 (4:1 cyclohexane/EtOAc).

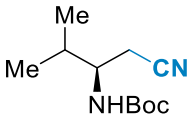
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.63 (br s, 1H), 3.18 (d, *J* = 6.9 Hz, 2H), 2.33 (s, 2H), 1.55 – 1.39 (m, 19H). *Spectrum*

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 118.2, 79.8, 47.2, 37.3, 32.9, 28.5, 25.7, 21.5. *Spectrum*

HRMS (APCI+): calculated for $C_{14}H_{25}N_2O_2$ $[M+H]^+$: 253.1911; found: 253.1913.

m.p.: 55 – 56 ºC.

***tert*-Butyl (1-cyano-3-methylbutan-2-yl)carbamate (22)**



22

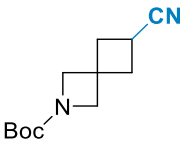
Prepared following the general procedure B using alcohol **4b** (40.7 mg, 0.20 mmol, 1.0 equiv.), NHC precursor (79.1 mg, 0.20 mmol, 1.0 equiv.), pyridine (16.2 μL, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (135.0 mg, 0.50 mmol, 2.5 equiv.), quinuclidine (24.5 mg, 0.22 mmol, 1.1 equiv.) and 4CzIPN (1.89 mg, 2.4 mmol, 0.012 equiv.). The title compound (19.3 mg, 0.09 mmol) was obtained in 46% yield as a white solid, after purification by flash column chromatography (SiO_2; 5 –15 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.60 (4:1 cyclohexane/EtOAc).

[19] A. J. C. Sarris, T. Hansen, M. A. R. de Geus, E. Maurits, W. Doelman, H. S. Overkleeft, J. D. C. Codée, D. V. Filippov and S. I. van Kasteren, Fast and pH-Independent Elimination of trans-Cyclooctene by Using Aminoethyl-Functionalized Tetrazines. *Chem. Eur. J.* 2018, **24**, 18075-18081.

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.64 (br d, *J* = 9.1 Hz, 1H), 3.64 – 3.55 (m, 1H), 2.69 (dd, *J* = 17.0, 5.3 Hz, 1H), 2.57 (dd, *J* = 16.9, 4.9 Hz, 1H), 1.94 – 1.83 (m, 1H), 1.45 (s, 9H), 0.99 (d, *J* = 6.8 Hz, 6H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[20]

***tert*-Butyl 6-cyano-2-azaspiro[3.3]heptane-2-carboxylate (23)**



23

Prepared following the general procedure B using alcohol **4e** (42.7 mg, 0.20 mmol, 1.0 equiv.), NHC precursor (79.1 mg, 0.20 mmol, 1.0 equiv.), pyridine (16.2 µL, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (135.0 mg, 0.50 mmol, 2.5 equiv.), quinuclidine (24.5 mg, 0.22 mmol, 1.1 equiv.) and 4CzIPN (1.9 mg, 2.4 mmol, 0.012 equiv.). The title compound (26.3 mg, 0.12 mmol) was obtained in 59% yield as a white solid, after purification by flash column chromatography (SiO_2; 0 – 20 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.32 (3:2 cyclohexane/EtOAc).

Prepared following the general procedure C using iodide **6e** (64.6 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), Et_3N (55.8 µL, 0.40 mmol, 2.0 equiv.) and 4CzIPN (3.2 mg, 4.0 µmol, 0.02 equiv.). The title compound (30.5 mg, 0.14 mmol) was obtained in 69% yield as a white solid, after purification by flash column chromatography (SiO_2; 0 – 40% EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.32 (3:2 cyclohexane/EtOAc).

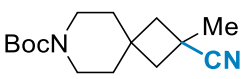
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (d, *J* = 3.6 Hz, 4H), 2.97 (p, *J* = 8.2 Hz, 1H), 2.63 – 2.51 (m, 4H), 1.42 (s, 9H). *Spectrum*

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 121.8, 79.8, 61.0, 37.3, 35.9, 28.4, 17.3. *Spectrum*

HRMS (APCI+): calculated for $C_{12}H_{18}N_2O_2$ $[M+H]^+$: 223.1441; found: 223.1442.

m.p.: 93 – 94 ºC.

***tert*-Butyl 2-cyano-2-methyl-7-azaspiro[3.5]nonane-7-carboxylate (24)**



24

Prepared following the general procedure B using alcohol **4f** (51.1 mg, 0.20 mmol, 1.0 equiv.), NHC precursor (79.1 mg, 0.20 mmol, 1.0 equiv.), pyridine (16.2 µL, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (135.0 mg, 0.50

[20] Y. Sohtome, B. Shin, N. Horitsugi, R. Takagi, K. Noguchi and K. Nagasawa, Entropy-Controlled Catalytic Asymmetric 1,4-Type Friedel-Crafts Reaction of Phenols Using Conformationally Flexible Guanidine/Bisthiourea Organocatalyst. *Angew. Chem. Int. Ed*. 2010, **49**, 7299-7303.

mmol, 2.5 equiv.), quinuclidine (24.5 mg, 0.22 mmol, 1.1 equiv.) and 4CzIPN (1.89 mg, 2.4 mmol, 0.012 equiv.). The title compound (20.9 mg, 0.12 mmol) was obtained in 40% yield as a yellow solid, after purification by flash column chromatography (SiO_2; 0 – 20 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.72 (7:3 cyclohexane/EtOAc).

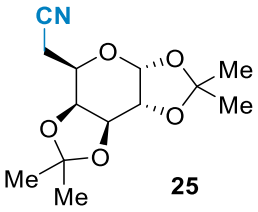
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 – 3.33 (m, 2H), 3.29 – 3.25 (m, 2H), 2.45 – 2.41 (m, 2H), 1.94 – 1.89 (m, 2H), 1.76 – 1.72 (m, 2H), 1.53 – 1.49 (m, 5H), 1.44 (s, 9H). *Spectrum*

^{13}C NMR (75 MHz, $CDCl_3$): δ 155.0, 126.3, 79.7, 43.7, 39.0, 37.5, 32.7, 28.6, 27.4, 25.0. *Spectrum*

HRMS (APCI+): calculated for $C_{15}H_{25}N_2O_2$ $[M+H]^+$: 265.1904; found: 265.1911.

m.p.: 106 – 107 ºC.

2-((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b4',5'-d]pyran-5-yl)acetonitrile (25)



25

Prepared following the general procedure C using iodide **6f** (74.0 mg, 0.20 mmol, 1.0 equiv.), isonitrile **2a** (134.7 mg, 0.50 mmol, 2.5 equiv.), Et_3N (55.8 µL, 0.40 mmol, 2.0 equiv.) and 4CzIPN (3.2 mg, 4.0 µmol, 0.02 equiv.). The title compound (26.6 mg, 0.16 mmol) was obtained in 37% yield as a yellow oil, after purification by flash column chromatography (SiO_2; 0 – 20 % EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.20 (4:1 cyclohexane/EtOAc).

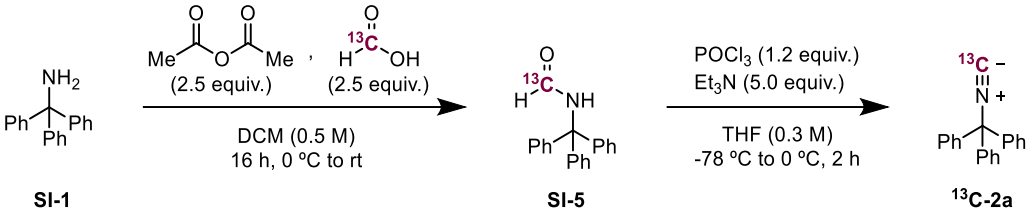
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.50 (d, J = 5.0 Hz, 1H), 4.65 (dd, J = 7.8, 2.4 Hz, 1H), 4.33 (dd, J = 5.0, 2.5 Hz, 1H), 4.24 (dd, J = 7.8, 2.0 Hz, 1H), 4.05 (td, J = 7.1, 2.0 Hz, 1H), 2.80–2.57 (m, 2H), 1.54 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). *Spectrum*

Spectroscopic data are in agreement with those in literature.[21]

[21] L. Xu, Q. Li, D. Li, X. Zhou, N. Song, P. Wang and M. Li, Radical Decarboxylative Cyanomethylation of Aliphatic Carboxylic Acids and Uronic Acids via Vinyl Azide Cascade Fragmentation. *Chin. J. Chem.*, 2023, **41**, 1191-1197.

8. Synthesis of ^{13}C Isotopically Labeled Cyanides

A. Synthesis of ((isocyano-^{13}C)methanetriyl)tribenzene



According to a modified literature procedure,[22] acetic anhydride (1.3 mL, 13.9 mmol, 2.5 equiv.) and ^{13}C-formic acid (2.5 equiv.) were stirred for 2 h at 55 °C to prepare ^{13}C- acetic formic anhydride. The corresponding compound was added dropwise to a stirred solution of triphenylmethanamine (1.44 g, 5.55 mmol, 1.0 equiv.) in dry DCM (11.1 mL, 0.5 M) at 0 °C. The mixture was stirred for 15 min to 0 °C and then, the reaction was allowed to warm room temperature and stirred a further 16 h. The resulting mixture was quenched with cold water. The aqueous layer was extracted with DCM (x3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the corresponding formamide **SI-5** that was directly used in the next step without further purification.

Et_3N (3.9 mL, 27.7 mmol, 5.0 equiv.) was added to a stirred solution of **SI-5** (1.60 g, 5.55 mmol, 1.0 equiv.) in dry THF (13.9 mL, 0.4 M) at -78 ºC. Then, $POCl_3$ (0.62 mL, 6.66 mmol, 1.2 equiv.) in dry THF (3.7 mL, 1.5 M) was added dropwise and the reaction mixture was stirred for 1 h at -78 ºC. Then the reaction mixture was let warm to 0 ºC and stirred for a further hour before cold water was added. The resulting mixture was extracted with Et_2O (x3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash column chromatography (SiO_2; 0 – 2% EtOAc in cyclohexane) to afford pure product **^{13}C-2a** (1.23 g, 4.6 mmol) in 82% yield. $\mathbf{R_f}$ = 0.60 (9:1 cyclohexane/EtOAc).

^1H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 9H), 7.25 – 7.21 (m, 6H). *Spectrum*

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.7 (s, -N**^{13}C**), 141.7, 128.44, 128.38, 128.2, 75.1 (m, **C**-N^{13}C). *Spectrum*

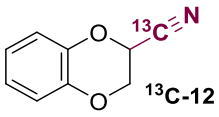
HRMS (APCI+): calculated for $C_{19}{}^{13}CH_{15}N$ $[M]^+$: 270.1238; found: 270.1236.

m.p.: 136 – 137 ºC.

[22] R. S. Bon, C. Hong, M. J. Bouma, R. F. Schmitz, F. J. J. de Kanter, M. Lutz, A. L. Spek and R. V. A. Orru, Novel Multicomponent Reaction for the Combinatorial Synthesis of 2-Imidazolines. *Org. Lett.* 2003, **5**, 3759-3762.

B. Charaterization Data of ^{13}C Isotopically Labeled Compounds

2,3-Dihydrobenzo[b][1,4]dioxine-2-carbonitrile-^{13}C (^{13}C-12)



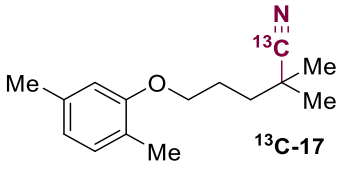
Prepared following the general procedure A using carboxylic acid **1f** (36.0 mg, 0.20 mmol, 1.0 equiv.), isonitrile **^{13}C-2a** (135.2 mg, 0.50 mmol, 2.5 equiv.), K_3PO_4 (50.9 mg, 0.24 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (2.2 mg, 2.0 µmol, 0.01 equiv.). The title compound (18.9 mg, 0.12 mmol) was obtained in 58% yield as an orange oil, after purification by flash column chromatography (SiO_2; 0 – 8% EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.35 (4:1 cyclohexane/EtOAc).

^1H NMR (300 MHz, $CDCl_3$): δ 6.98 – 6.91 (m, 4H), 5.11 (ddd, *J* = 6.6, 3.7, 2.6 Hz, 1H), 4.42 (ddd, *J* = 11.8, 3.7, 1.8 Hz, 1H), 4.34 (ddd, *J* = 11.8, 6.3, 2.6 Hz, 1H). *Spectrum*

^{13}C NMR (75 MHz, $CDCl_3$): δ 142.4, 140.6 (d, *J* = 1.4 Hz), 123.4, 122.8, 117.92, 117.90, 114.9, 64.8, 62.0 (d, *J* = 66.2 Hz). *Spectrum*

HRMS (APCI+): calculated for $C_8{}^{13}CH_8NO_2$ $[M+H]^+$: 163.0589; found: 163.0586.

5-(2,5-Dimethylphenoxy)-2,2-dimethylpentanenitrile-1-^{13}C (^{13}C-17)



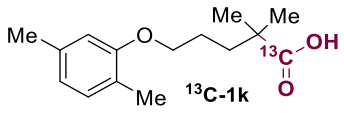
Prepared following the general procedure A using carboxylic acid **1k** (100.1 mg, 0.40 mmol, 1.0 equiv.), isonitrile **^{13}C-2a** (270.3 mg, 1.00 mmol, 2.5 equiv.), K_3PO_4 (101.9 mg, 0.48 mmol, 1.2 equiv.) and $Ir(dCF_3bpy)_2(dtbbpy)PF_6$ (4.5 mg, 4.0 µmol, 0.01 equiv.). The title compound (65.2 mg, 0.28 mmol) was obtained in 70% yield as a yellowish oil, after purification by flash column chromatography (SiO_2; 0 – 1% EtOAc in cyclohexane). $\mathbf{R_f}$ = 0.24 (9:1 cyclohexane/EtOAc).

^1H NMR (300 MHz, $CDCl_3$): δ 7.01 (d, *J* = 7.7 Hz, 1H), 6.67 (d, *J* = 7.4 Hz, 1H), 6.62 (s, 1H), 3.99 (t, *J* = 6.0 Hz, 2H), 2.31 (s, 3H), 2.17 (s, 3H), 2.04 – 1.95 (m, 2H), 1.79 – 1.71 (m, 2H), 1.40 (d, $^3J_{H,13C}$ = 5.4 Hz, 6H). *Spectrum*

^{13}C NMR (75 MHz, $CDCl_3$): δ 156.9, 136.7, 130.5, 125.1, 123.7, 121.1, 112.1, 67.3, 38.0 (d, *J* = 0.9 Hz), 32.4 (d, *J* = 54.5 Hz), 26.8 (d, *J* = 1.3 Hz), 25.7 (d, *J* = 1.7 Hz), 21.5, 15.9. *Spectrum*

HRMS (APCI+): calculated for $C_{14}{}^{13}CH_{22}NO$ $[M+H]^+$: 233.1735; found: 233.1725.

Gemfibrozil-^{13}C (^{13}C-1k)



To a solution of **^{13}C-17** (62.2 mg, 0.27 mmol, 1.0 equiv.) in EtOH (1.2 mL, 0.22 M) and H_2O (1.2 mL, 0.22 M), was added KOH (600.9 mg, 10.7 mmol, 40.0 equiv.). The reaction mixture was stirred for 24 h at reflux and then the solvents were removed under reduced pressure. The residue was redissolved in water and washed with DCM (x2). The combined aqueous layers were acidified with concentrated HCl and extracted with DCM (x3). The combined organic layers were washed with saturated NaCl (aq), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to obtain the corresponding product **^{13}C-1k** (60.2 mg, 0.24 mmol) in 90% yield. $\mathbf{R_f}$ = 0.46 (3:1 cyclohexane/EtOAc).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (d, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.94 (t, *J* = 5.9 Hz, 2H), 2.32 (s, 3H), 2.19 (s, 3H), 1.86 – 1.73 (m, 4H), 1.27 (d, $^3J_{H,13C}$ = 4.5 Hz, 6H). *Spectrum*

^{13}C NMR (126 MHz, $CDCl_3$): δ 184.7, 157.1, 136.6, 130.4, 123.7, 120.8, 112.1, 68.0, 42.1 (d, *J* = 53.9 Hz), 37.0, 25.3 (d, *J* = 1.0 Hz), 25.1, 21.5, 15.9. *Spectrum*

HRMS (APCI-): calculated for $C_{14}{}^{13}CH_{21}O_3$ $[M-H]^+$: 250.1529; found: 250.1526.

9. Cyclic Voltammetry of Isonitriles 2a-d

Cyclic Voltammograms were obtained in a *Ivium CompaqStat* potentiostat interfaced with a computer. All cyclic voltammetry experiments were performed using a conventional three-electrode system, containing a Pt wire as counter electrode, a silver wire coated with AgCl immersed in a 3.0 M aqueous solution of KCl as reference electrode and a glassy carbon as working electrode. The measurements were taken with a scanning speed of 200 mV/s.

Cyclic voltammetry of isonitriles **2a-d** were performed in a three-electrode cell, after solutions were deaerated by argon bubbling for 10 minutes. Oxidation and reduction scans of isonitriles **2a-d**, in DMSO (0.01 M) with $TBAPF_6$ (0.1 M) as electrolyte, were performed.

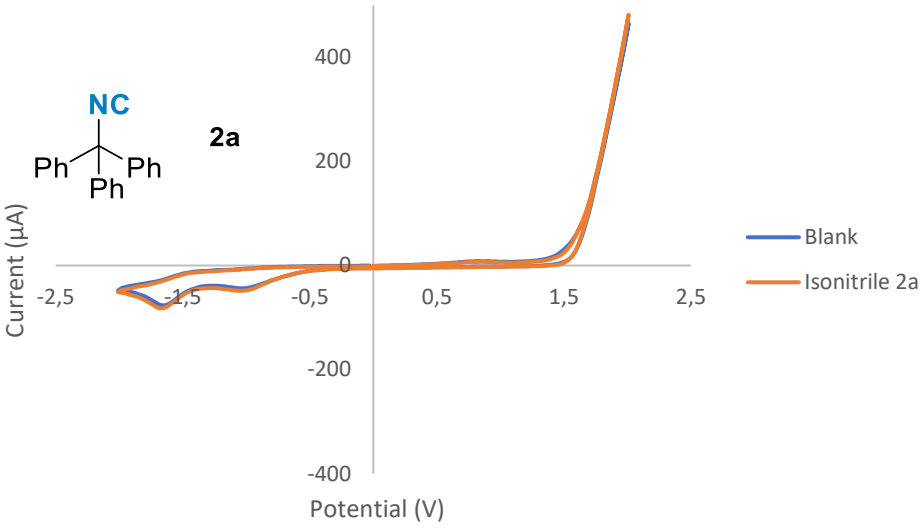


Figure S4. Cyclic voltammetry of isonitrile **2a** at 200 mV/s.

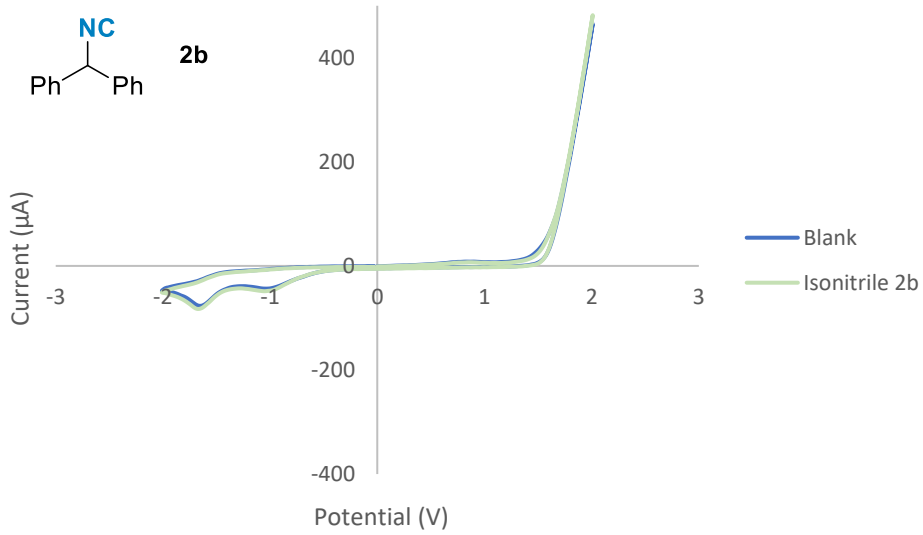


Figure S5. Cyclic voltammetry of isonitrile **2b** at 200 mV/s.

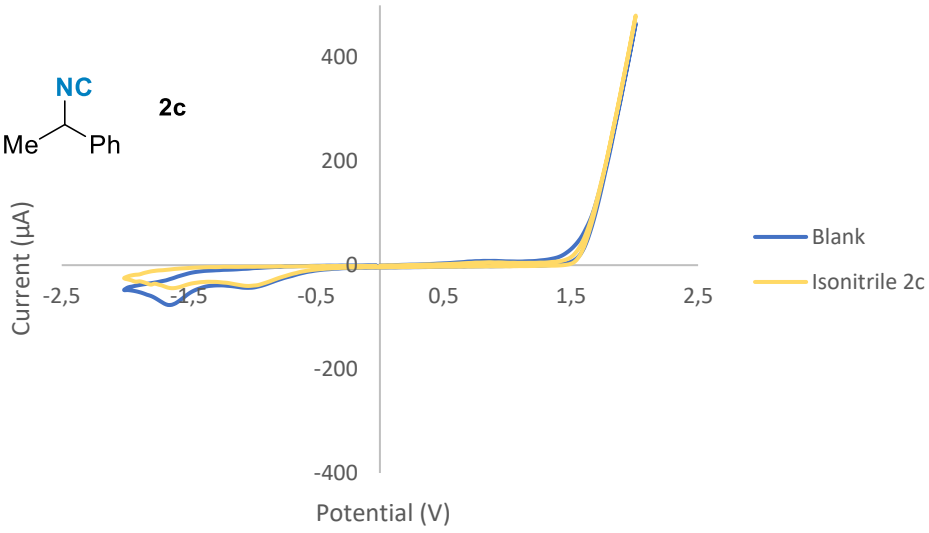


Figure S6. Cyclic voltammetry of isonitrile **2c** at 200 mV/s.

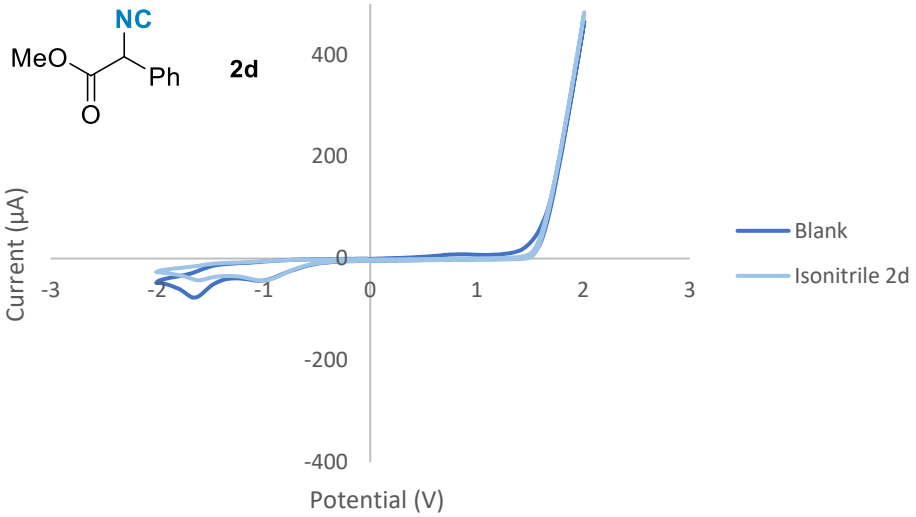


Figure S7. Cyclic voltammetry of isonitrile **2d** at 200 mV/s.

10. Proposed Mechanisms for the Individual Reactions

According to the reported literatures[23,24,25] and the cyclic voltammograms above, we proposed the following mechanisms for the decarboxylative, deoxygenative and dehalogenative cyanation reactions (**Figure S8-10**).

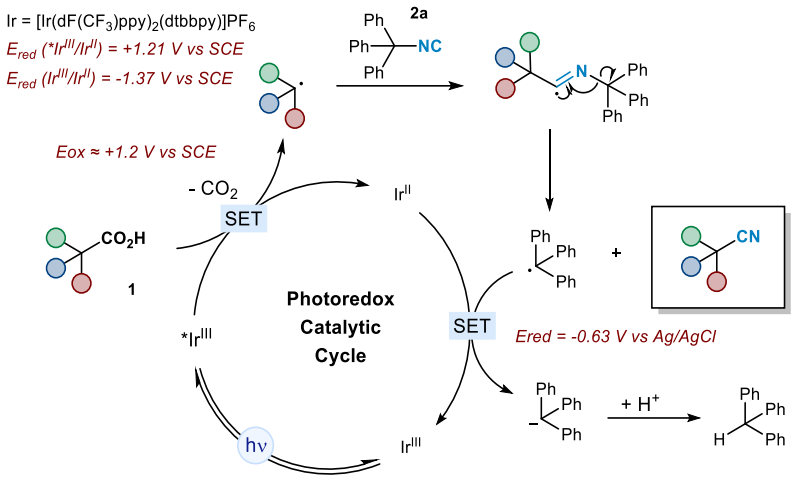


Figure S8. Proposed mechanism of the decarboxylative cyanation reaction.

[23] (a) L. Chu, C. Ohta, Z. Zuo and D. W. C. MacMillan, Carboxylic Acids as A Traceless Activation Group for Conjugate Additions: A Three-Step Synthesis of (±)-Pregabalin. *J. Am. Chem. Soc*., 2014, **136**, 10886-10889 (b) S. B. Beil, T. Q. Chen, N. E. Intermaggio and D. W. C. MacMillan, Carboxylic Acids as Adaptive Functional Groups in Metallaphotoredox Catalysis. *Acc. Chem. Res.*, 2022, **55**, 3481-3494.

[24] Z. Dong and D. W. C. MacMillan, Metallaphotoredox-enabled deoxygenative arylation of alcohols. *Nature*, 2021, **598**, 451-456.

[25] T. Constantin, M. Zanini, A. Regni, N. S. Sheikh, F. Juliá and D. Leonori, Aminoalkyl radicals as halogen-atom transfer agents for activation of alkyl and aryl halides. *Science*, 2020, **367**, 1021-1026.

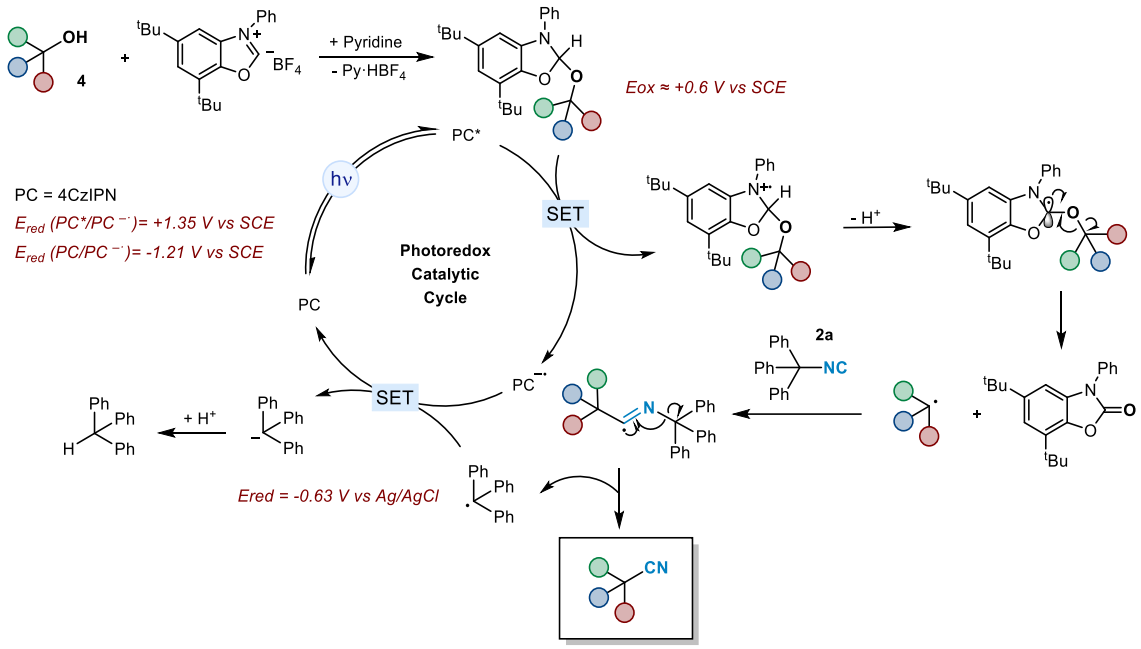


Figure S9. Proposed mechanism of the deoxygenative cyanation reaction.

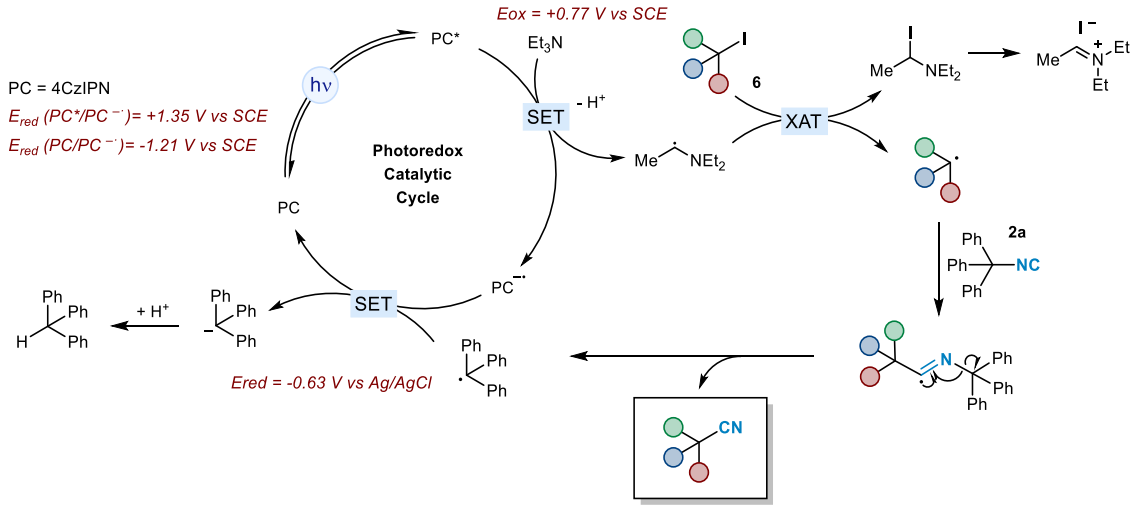
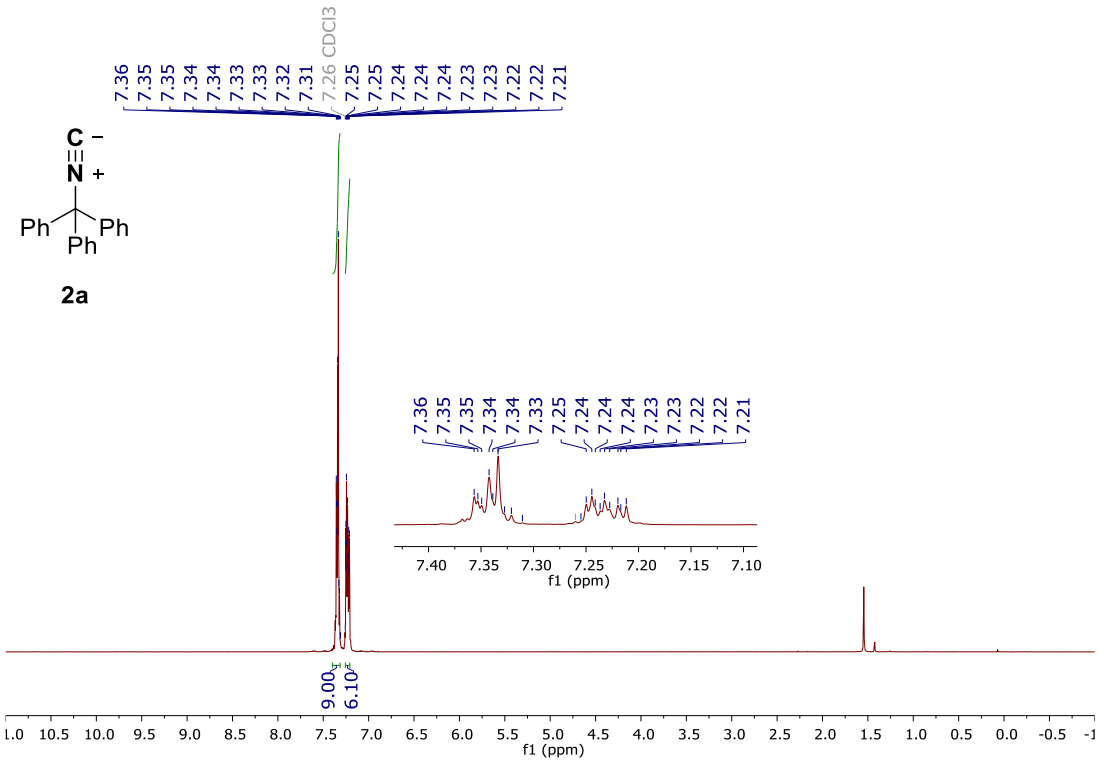


Figure S10. Proposed mechanism of the dehalogenative cyanation reaction.

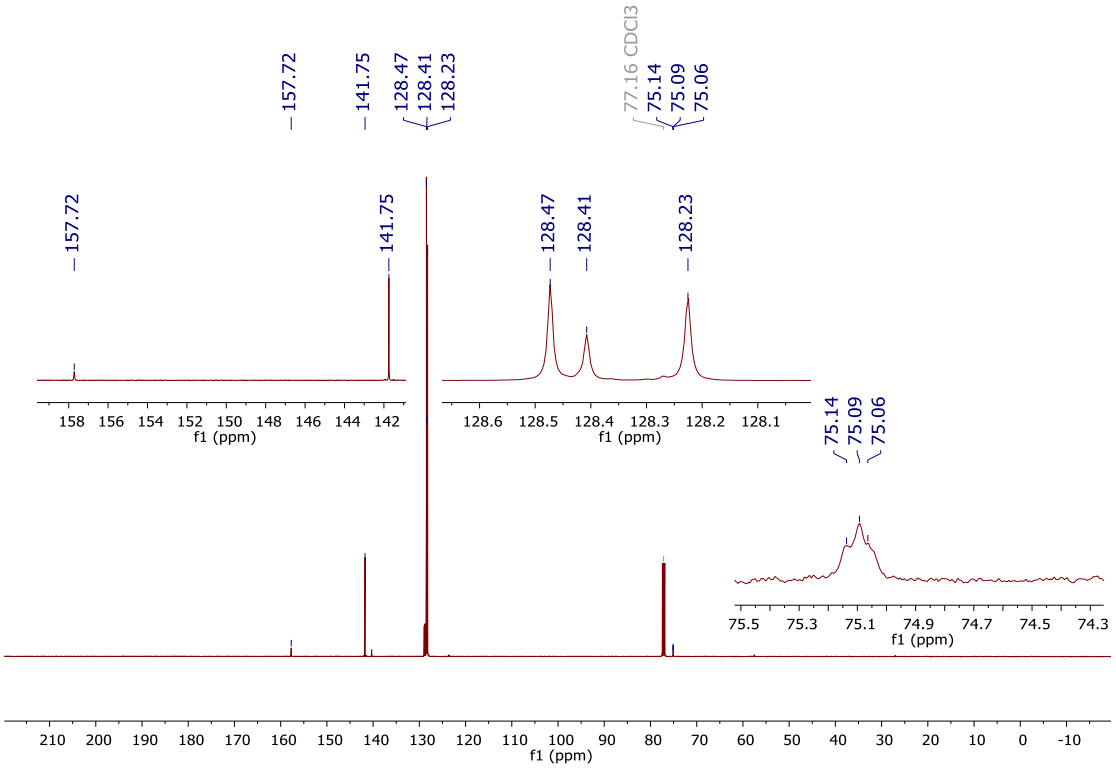
11. NMR Spectra

For known compounds, only ^{1}H NMR spectra is provided. For new compounds, full characterization is provided.

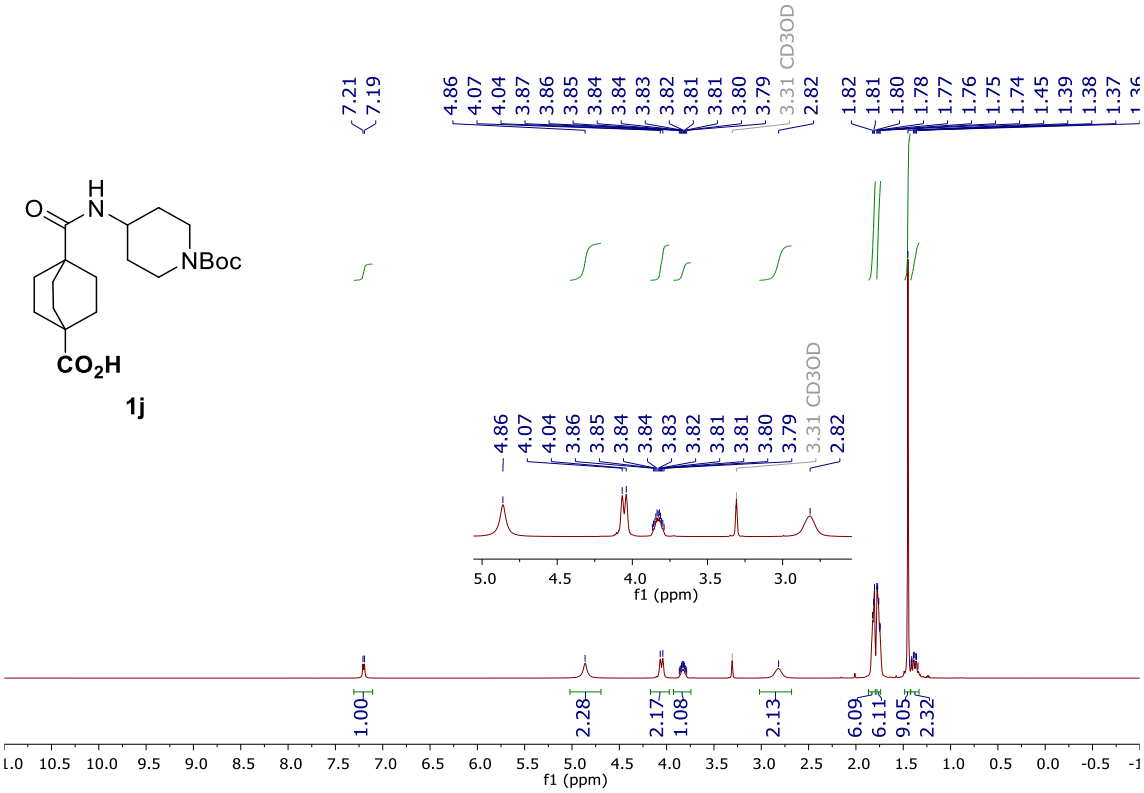
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **2a**



^{13}C-NMR (75 MHz, $CDCl_3$) of compound **2a**

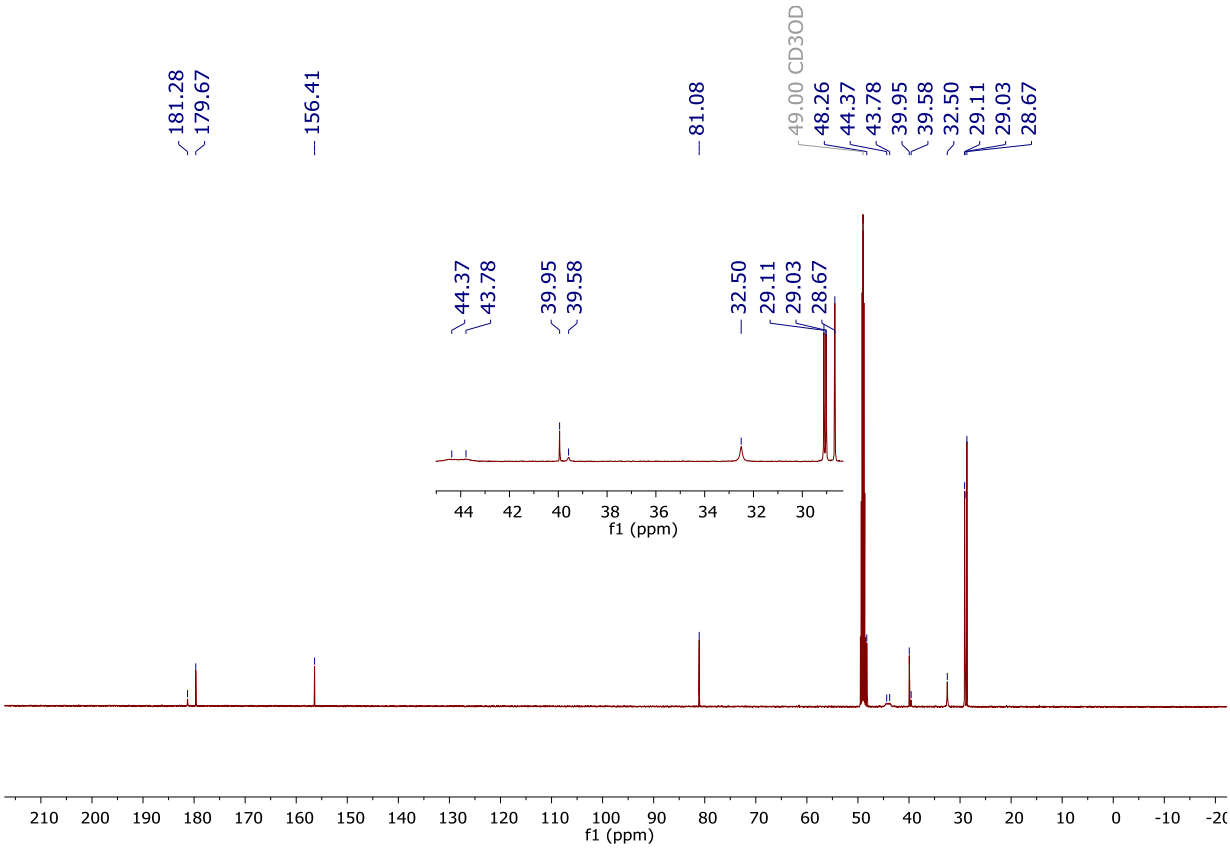


^{1}H-NMR (500 MHz, CD_3OD) of compound **1j**

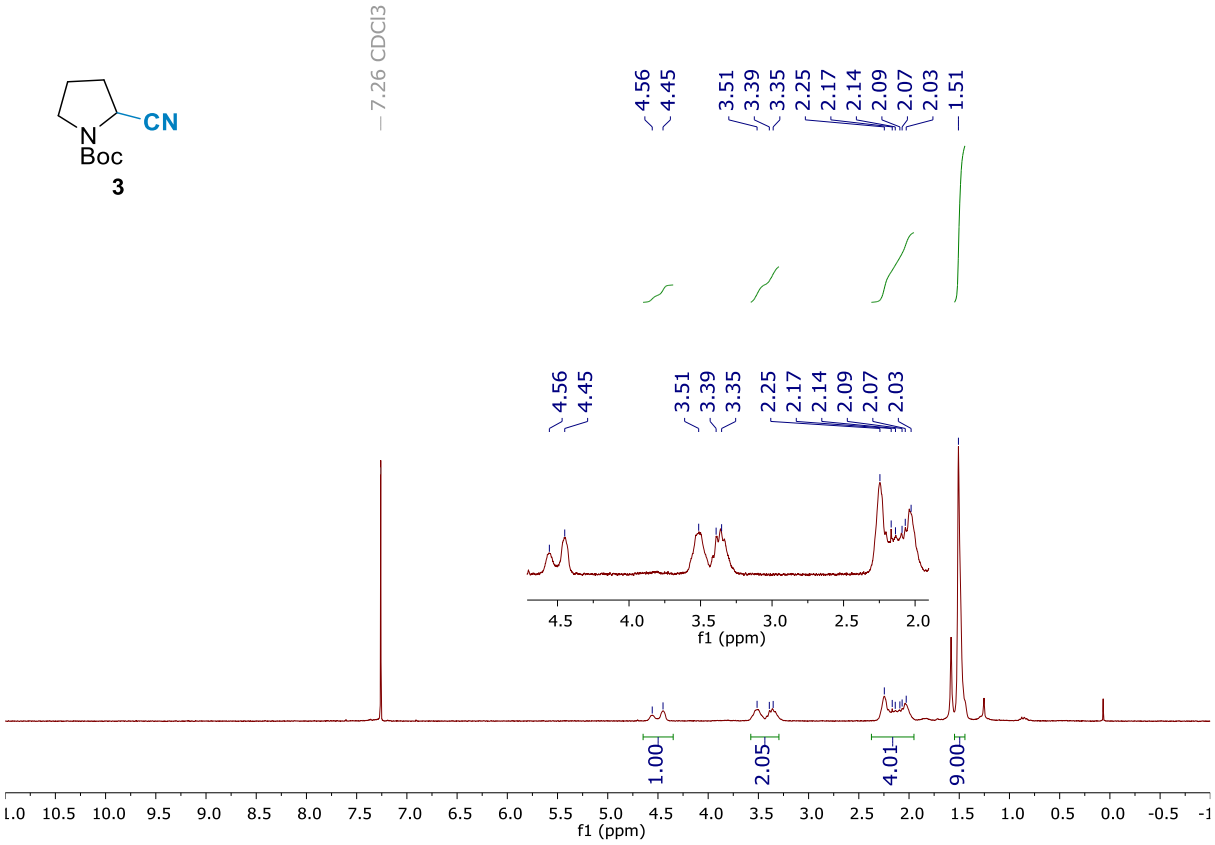


1j

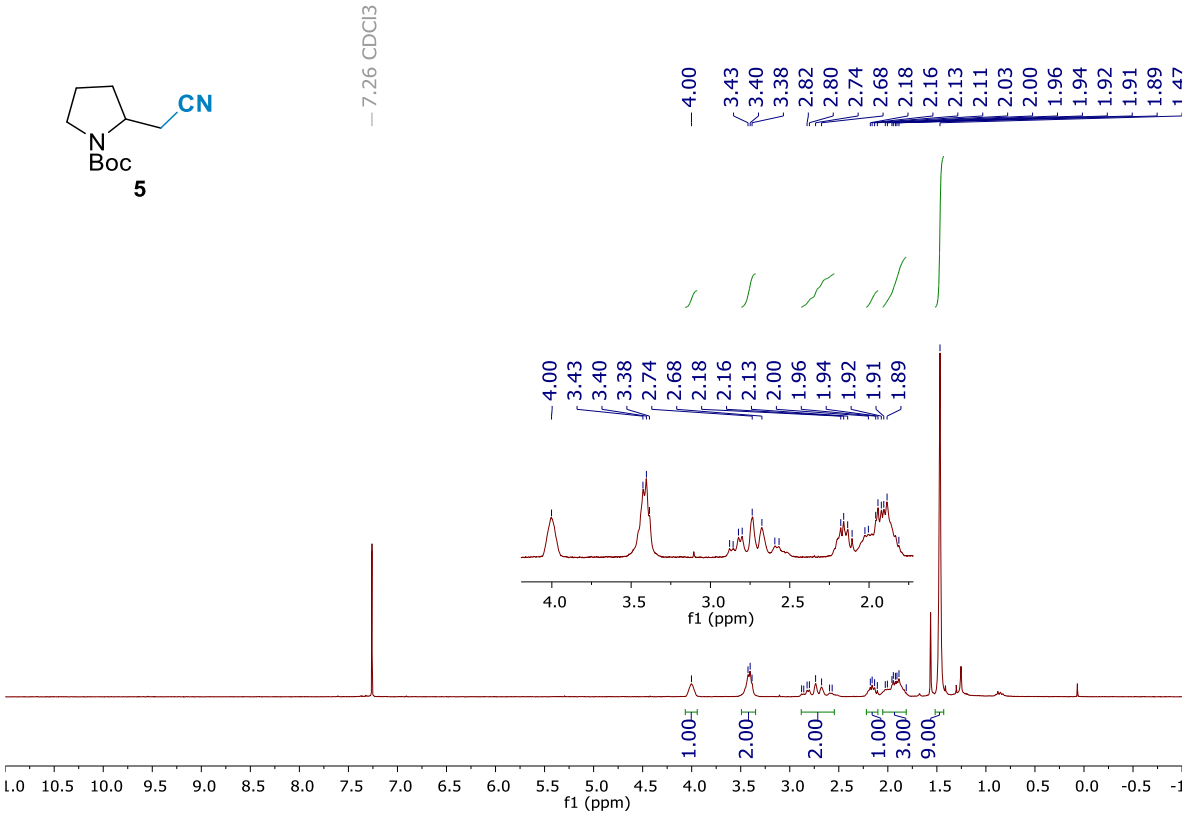
^{13}C-NMR (126 MHz, CD_3OD) of compound **1j**



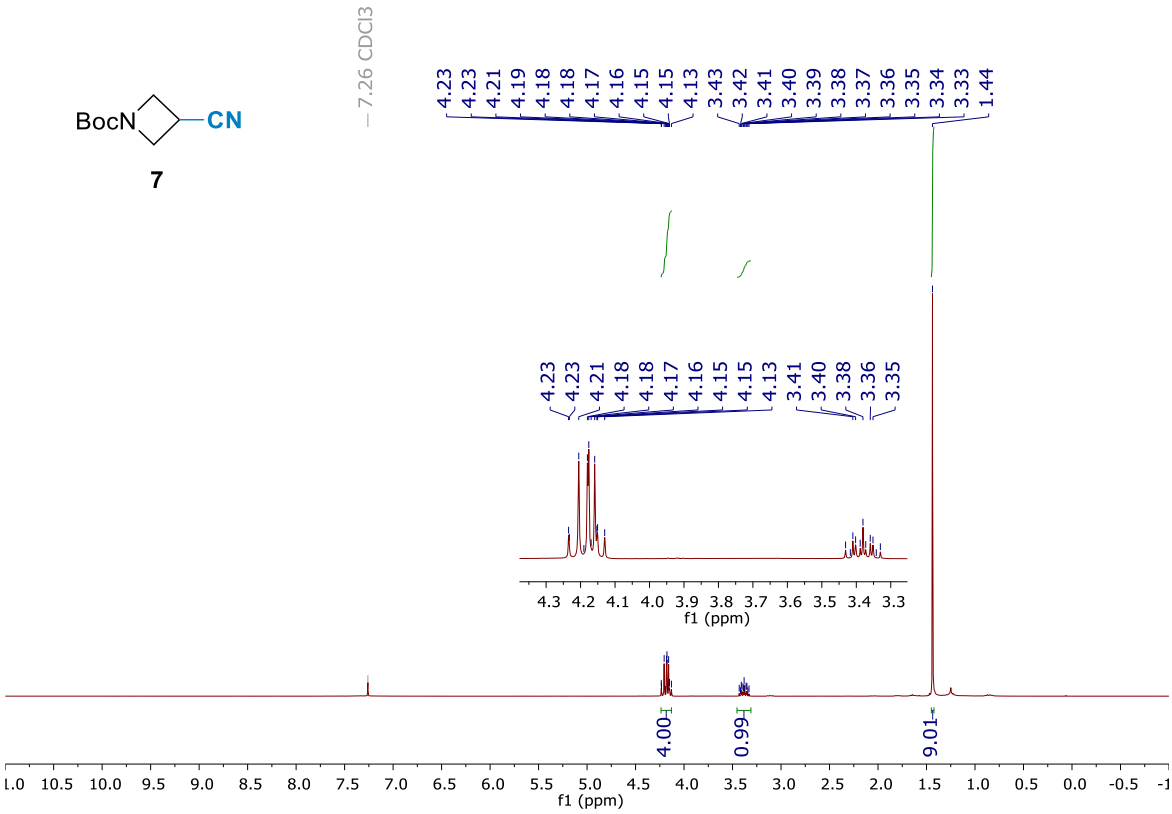
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **3**



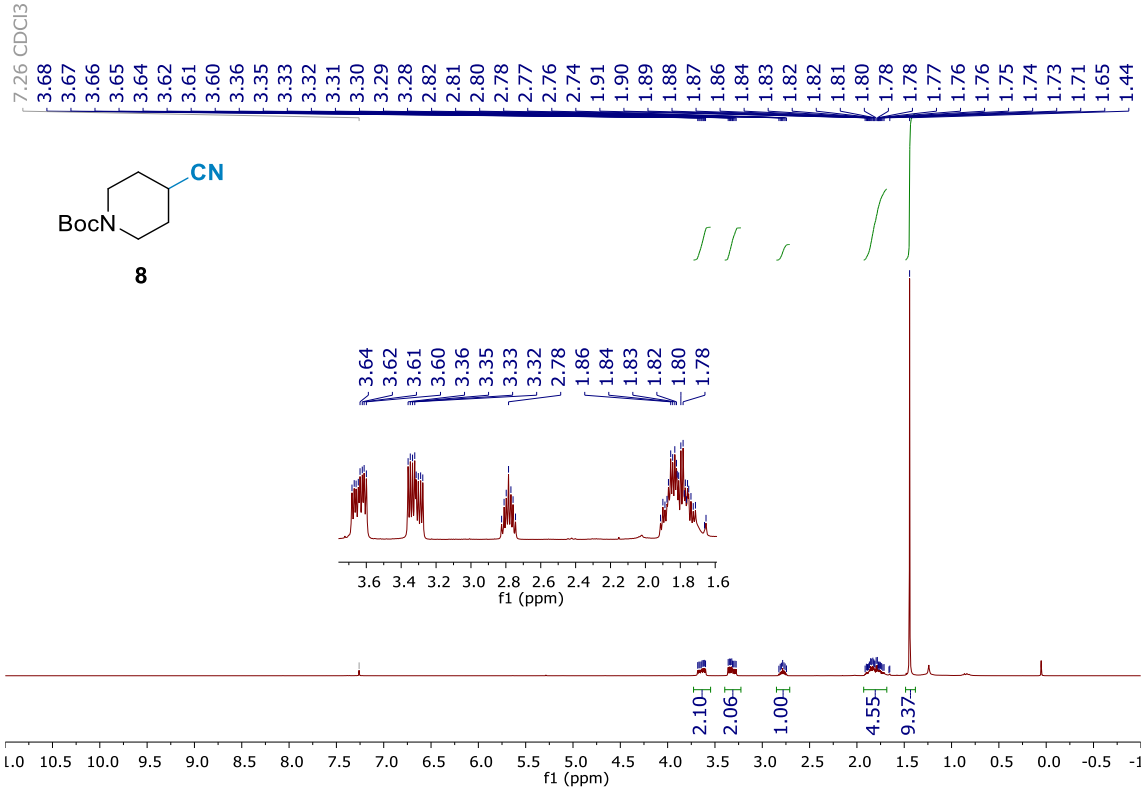
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **5**



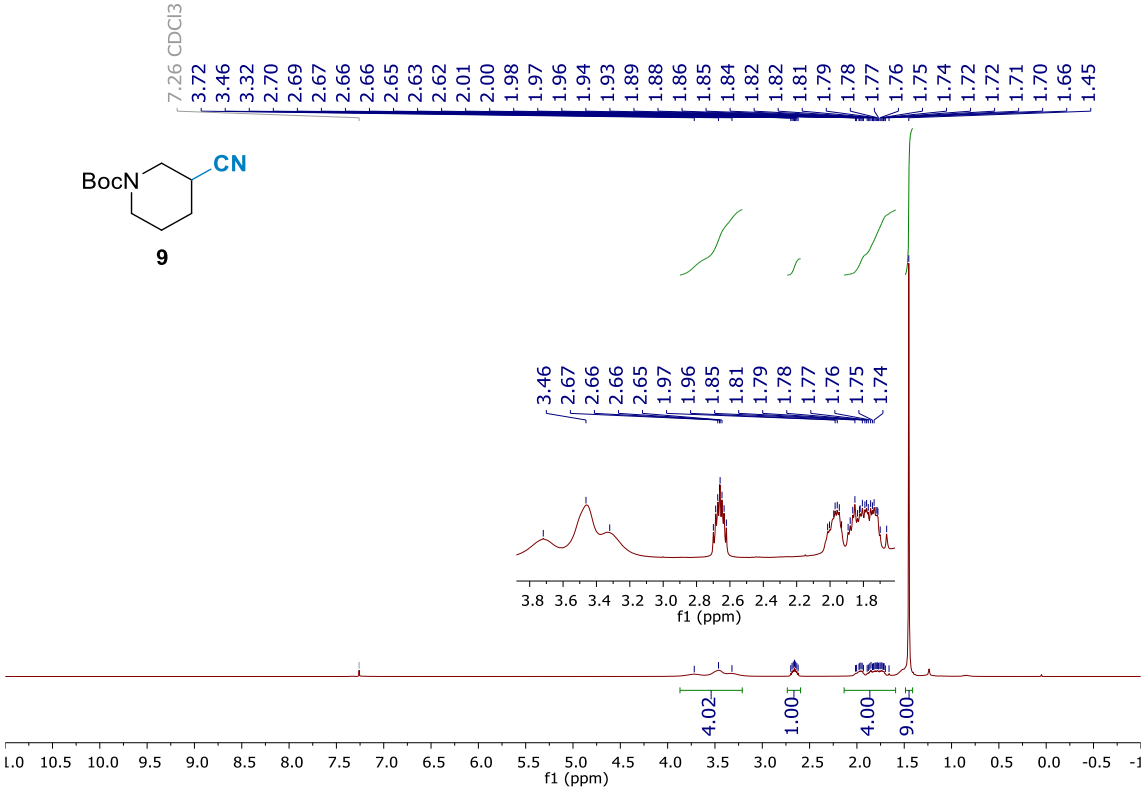
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **7**



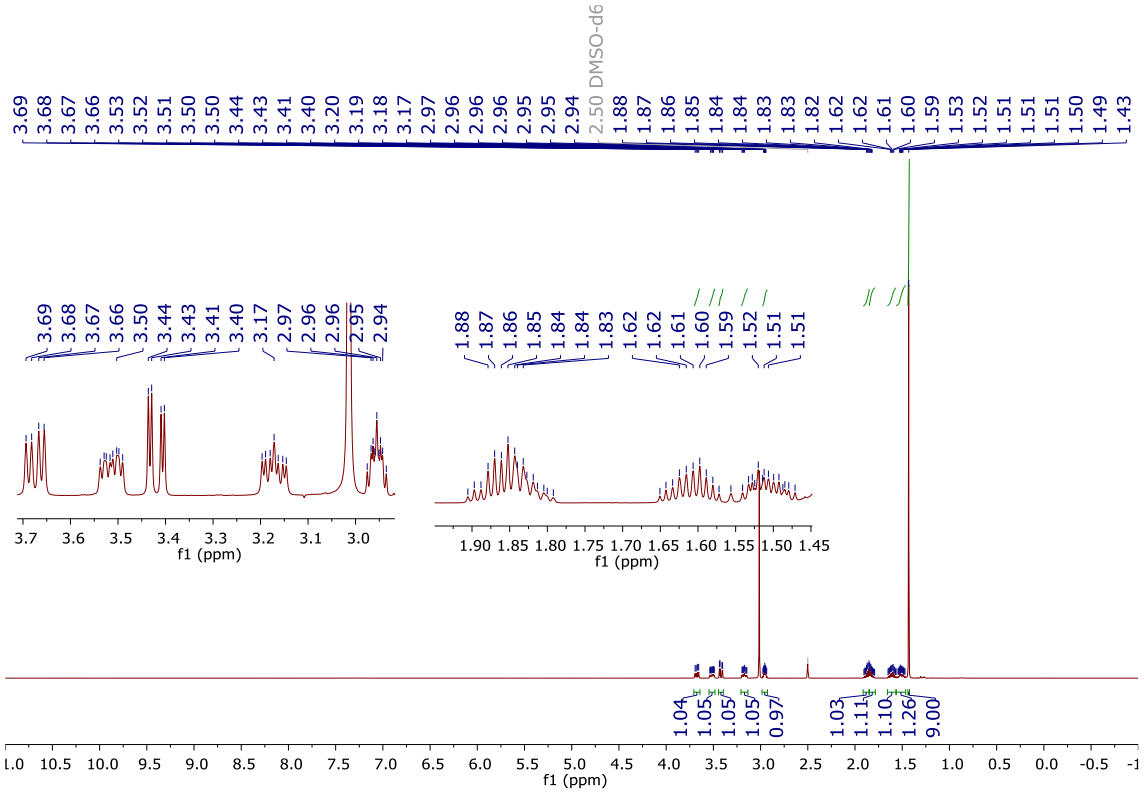
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **8**



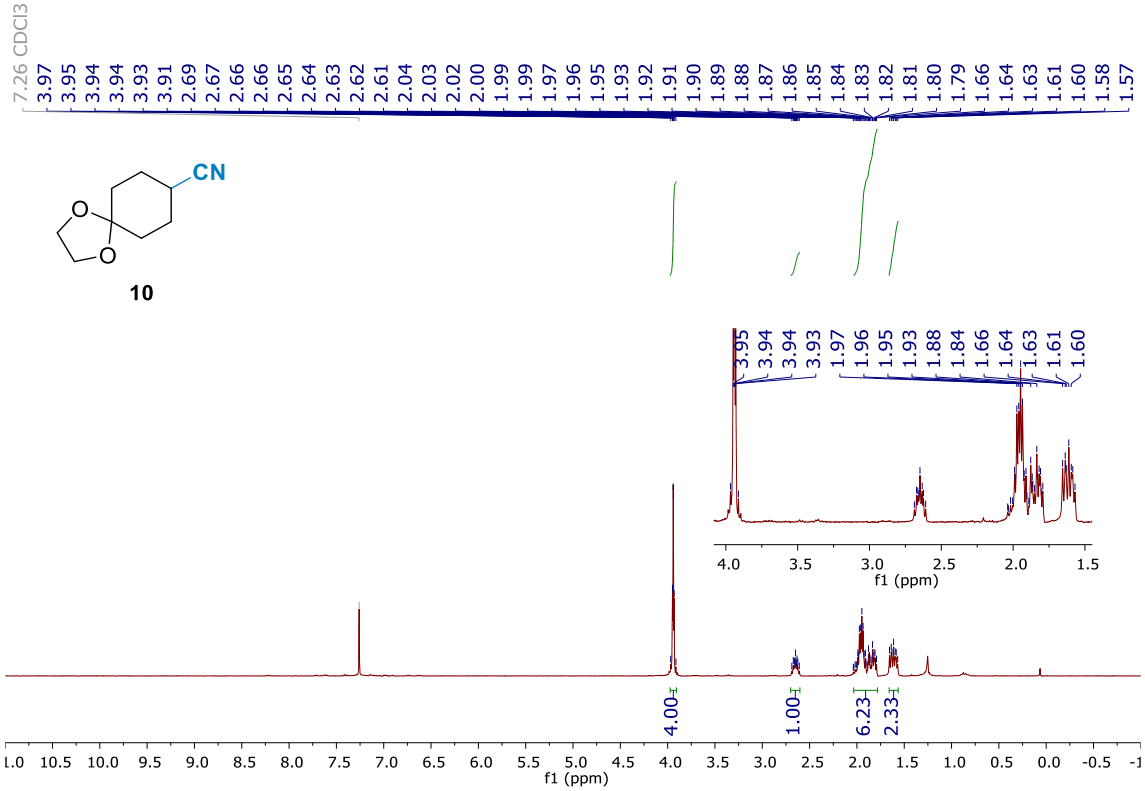
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **9**



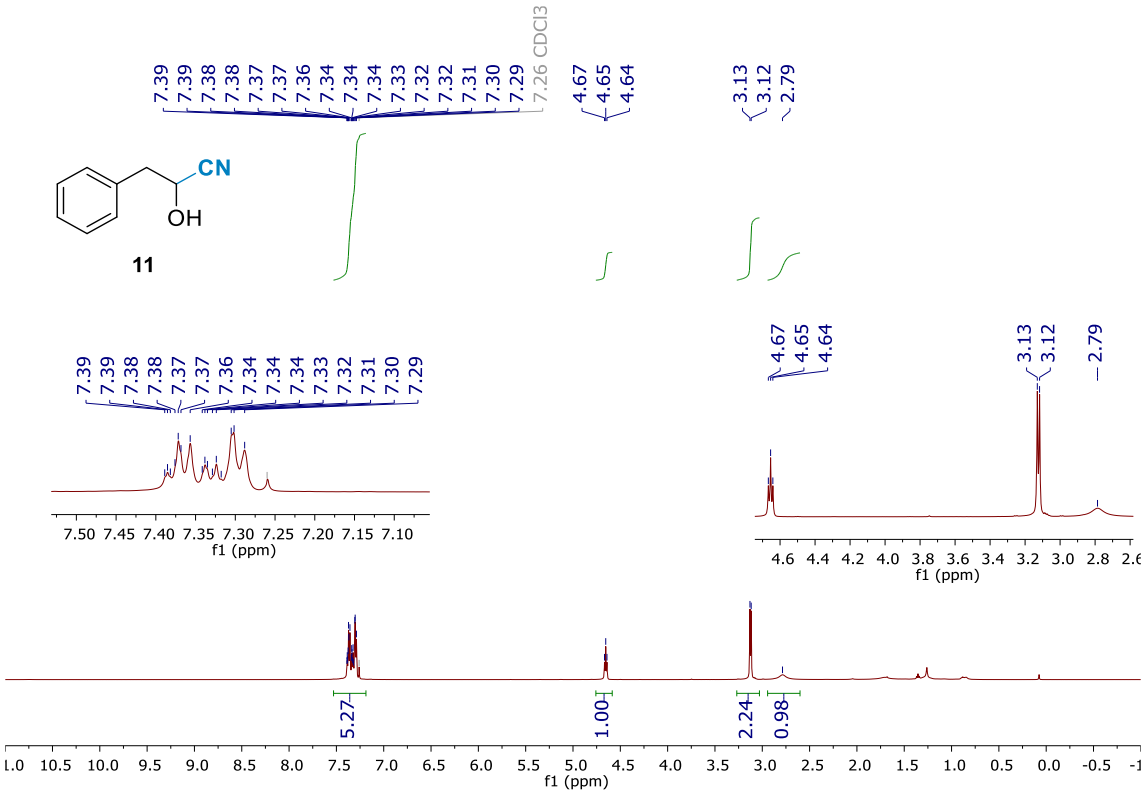
^{1}H-NMR (500 MHz, DMSO) of compound **9, T = 90 ºC**



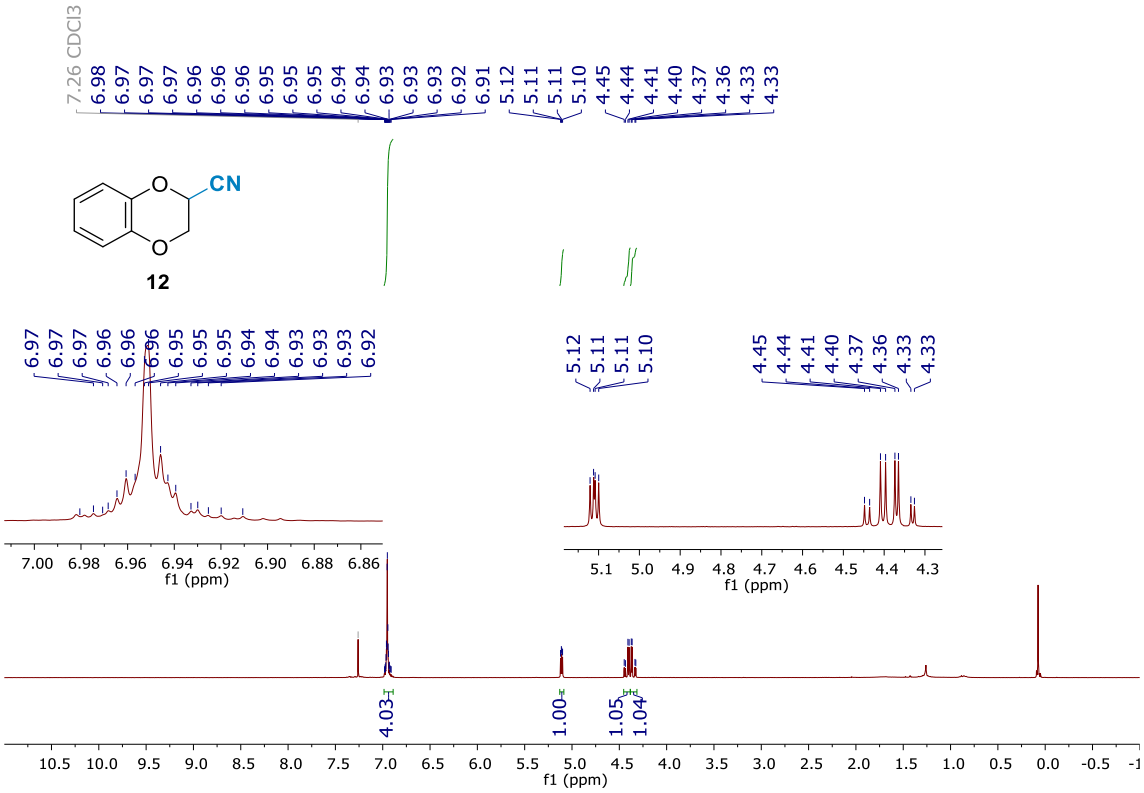
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **10**



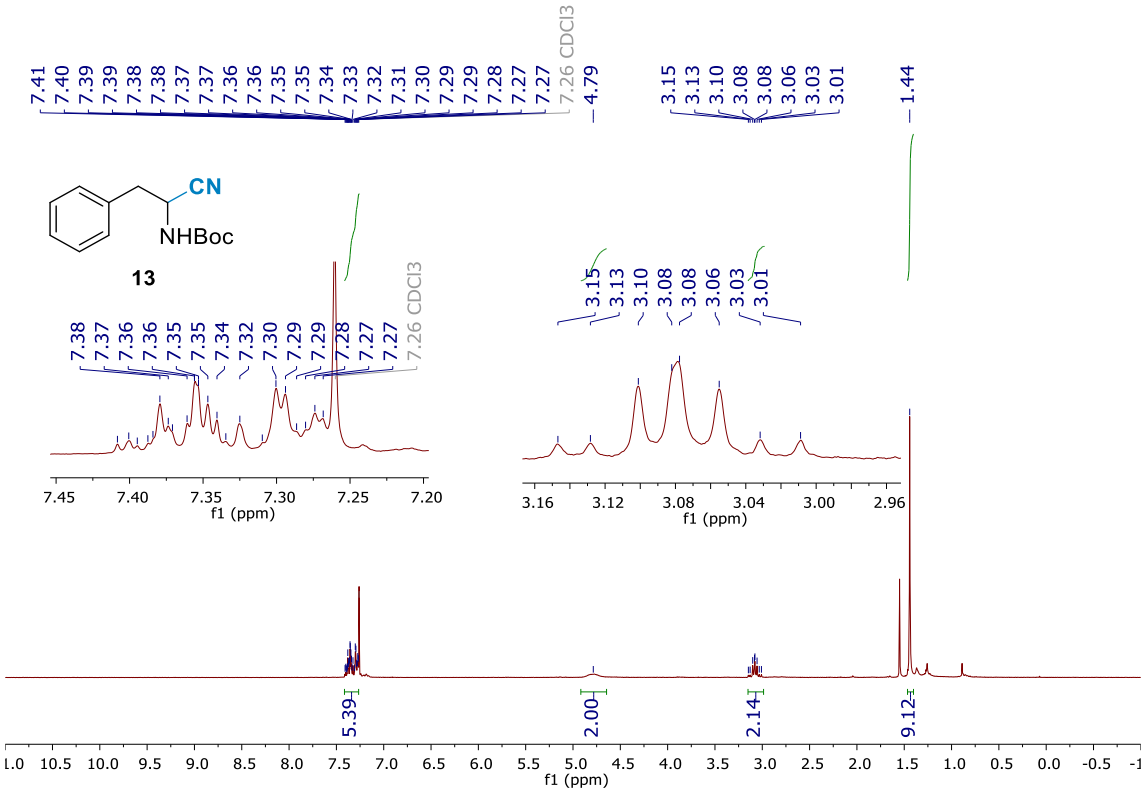
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **11**



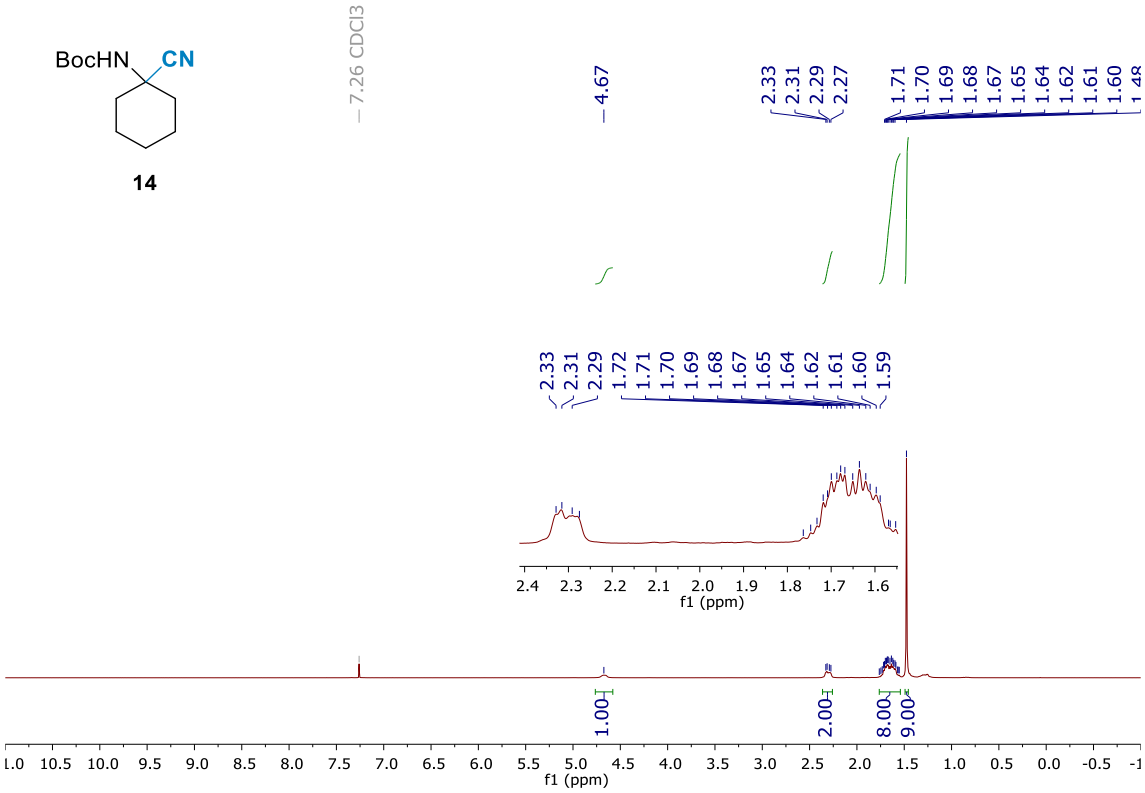
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **12**



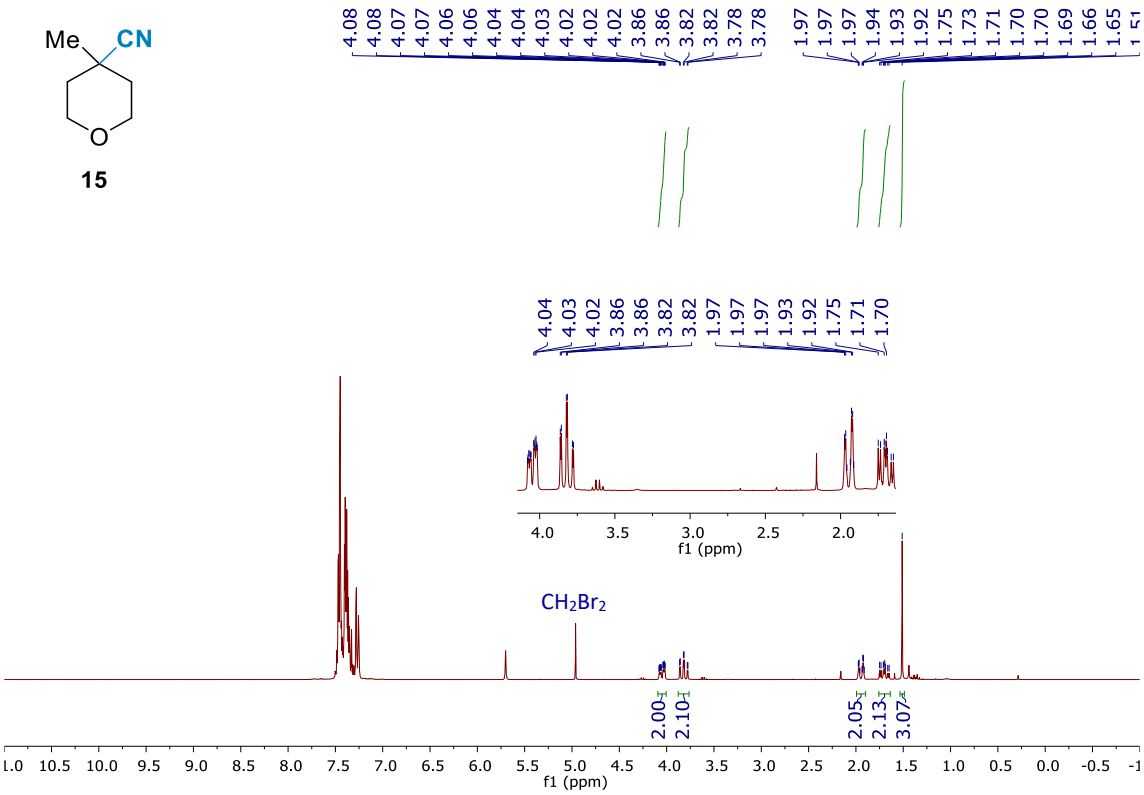
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **13**



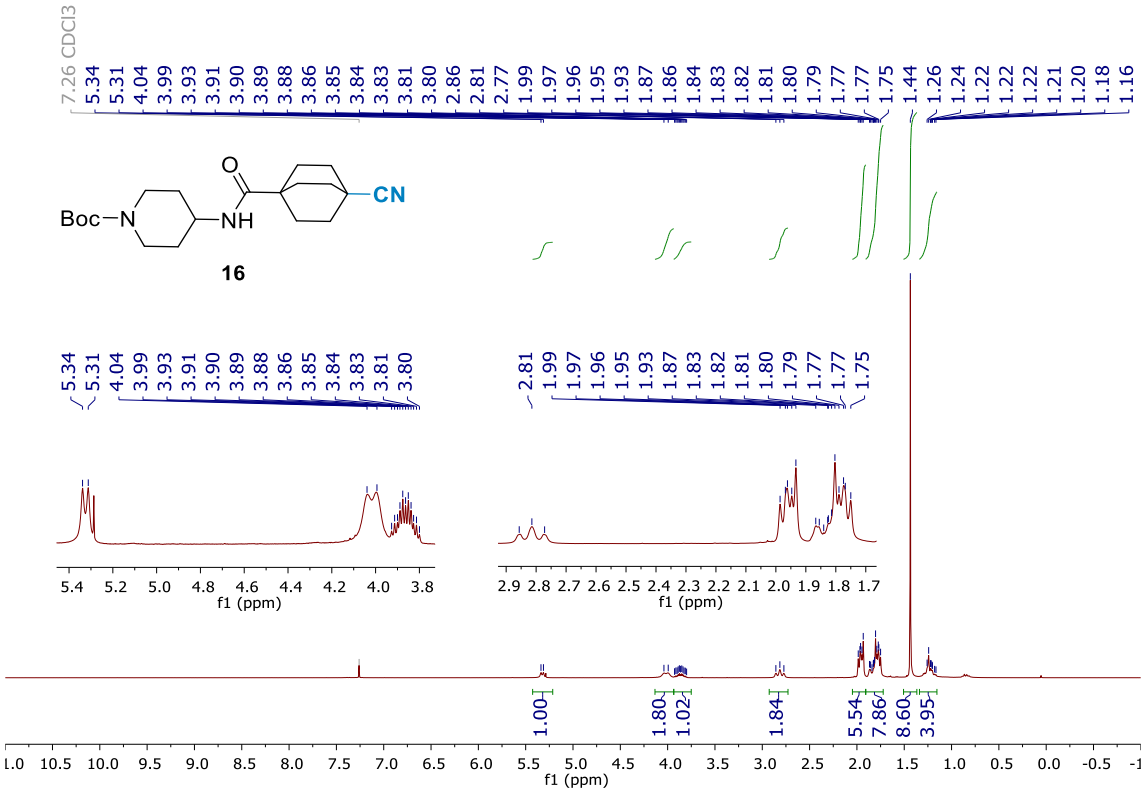
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **14**



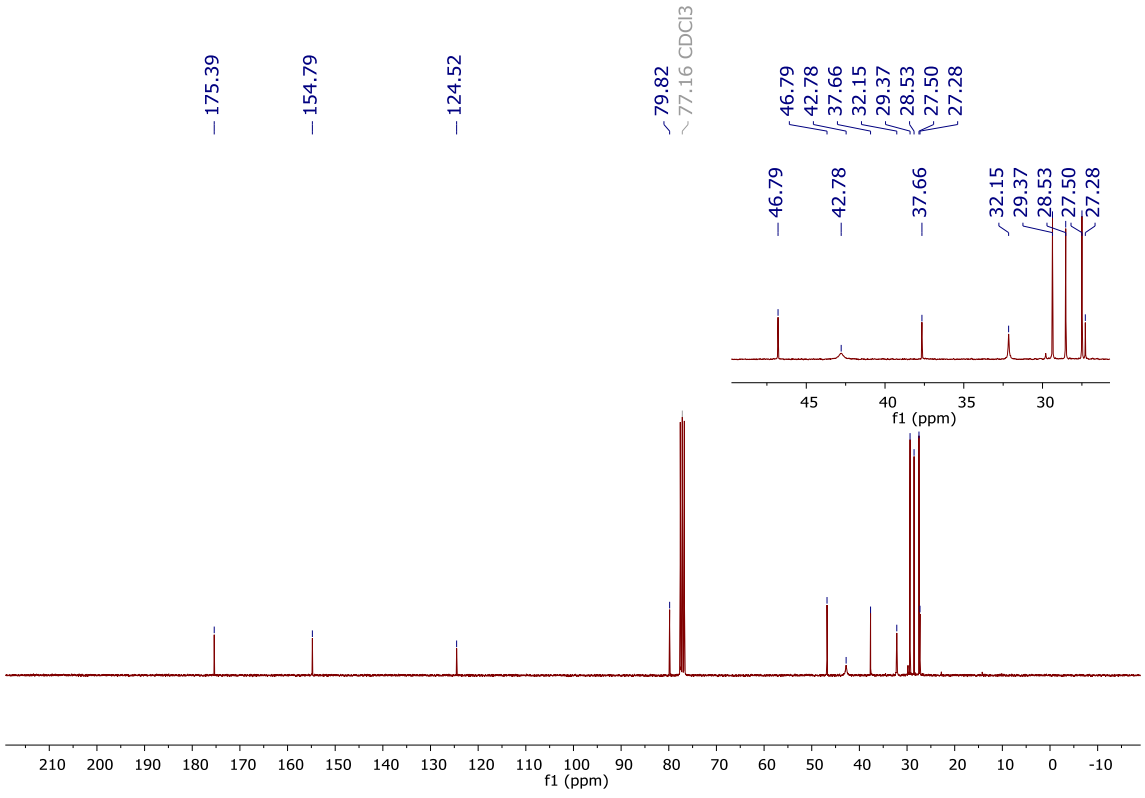
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **15** (Crude ^{1}H NMR with CH_2Br_2 as internal standard)



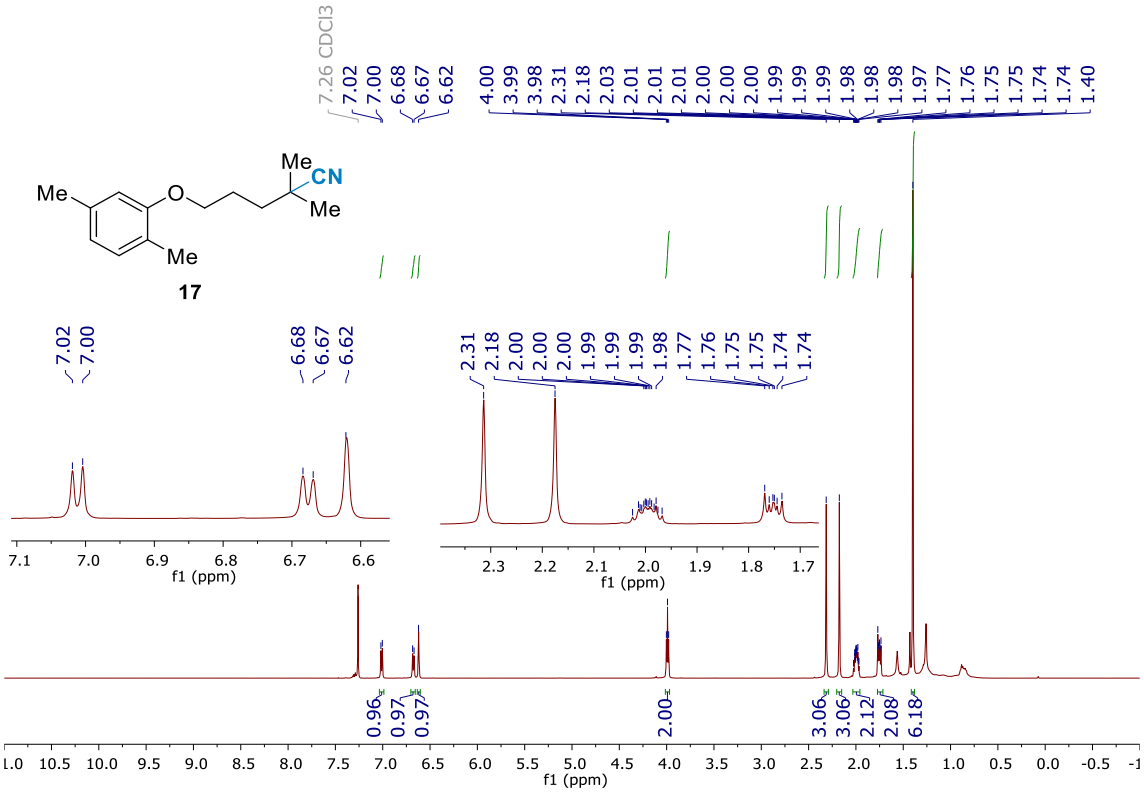
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **16**



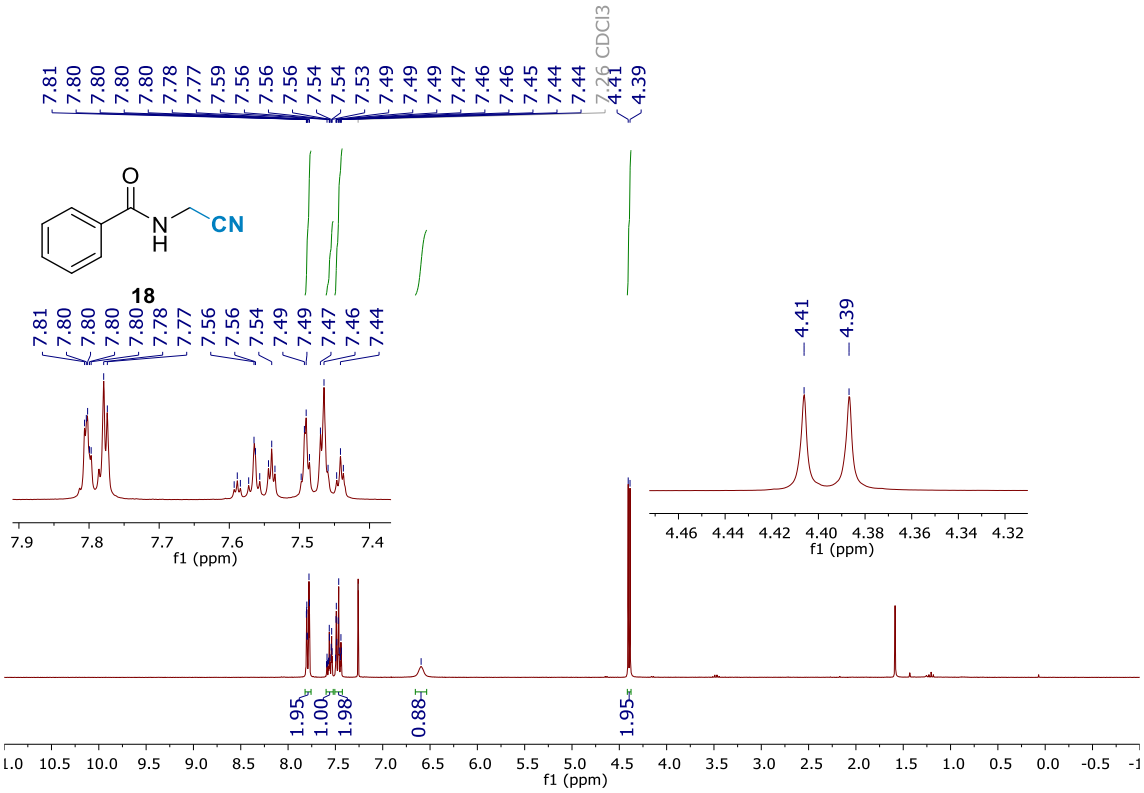
^{13}C-NMR (75 MHz, $CDCl_3$) of compound **16**



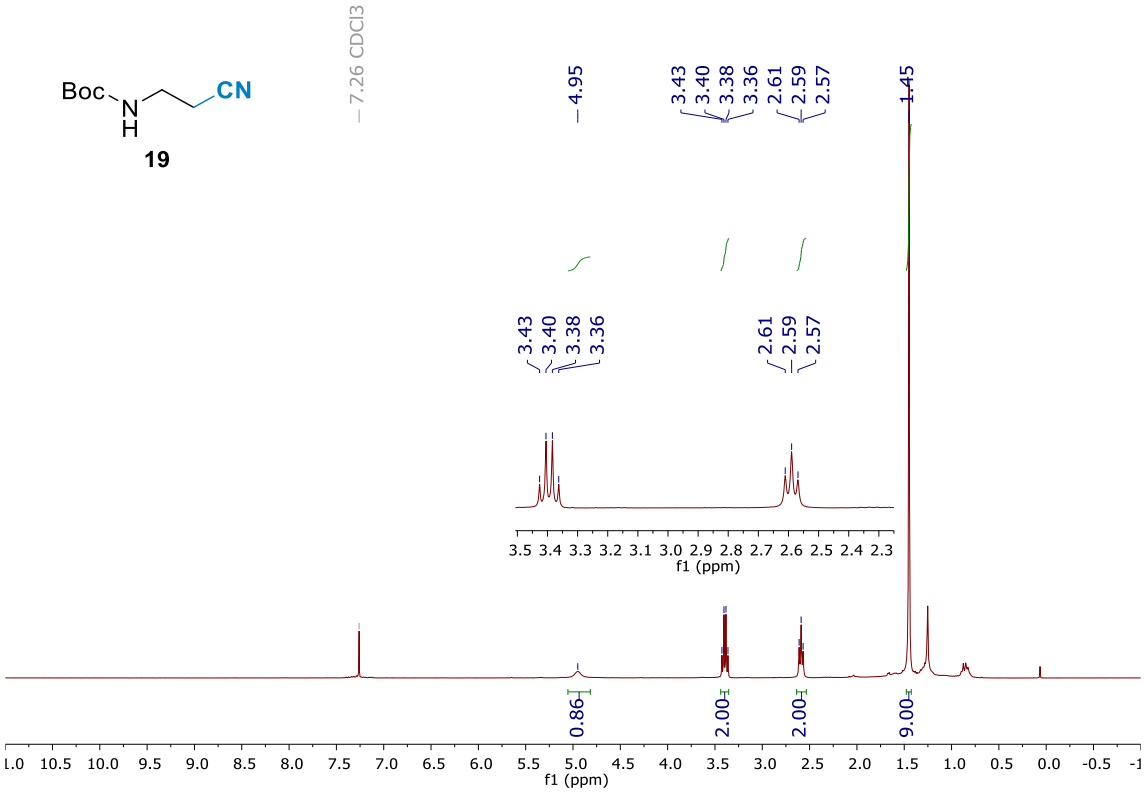
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **17**



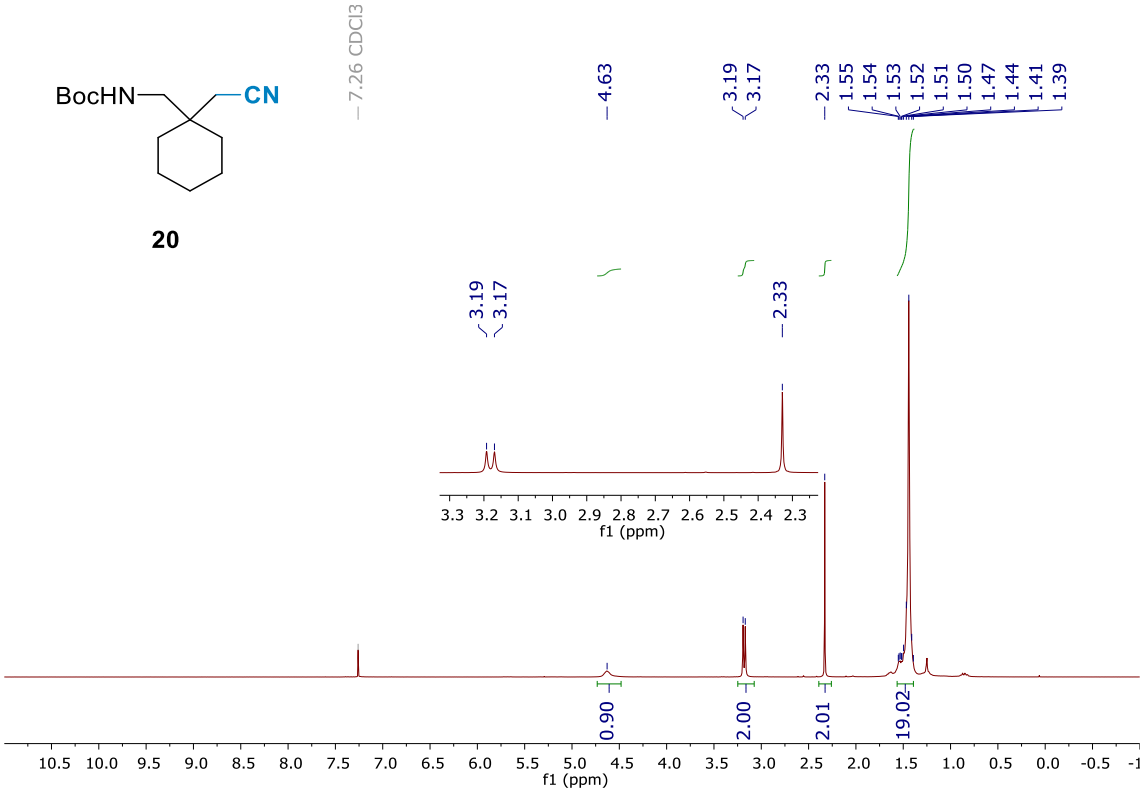
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **18**



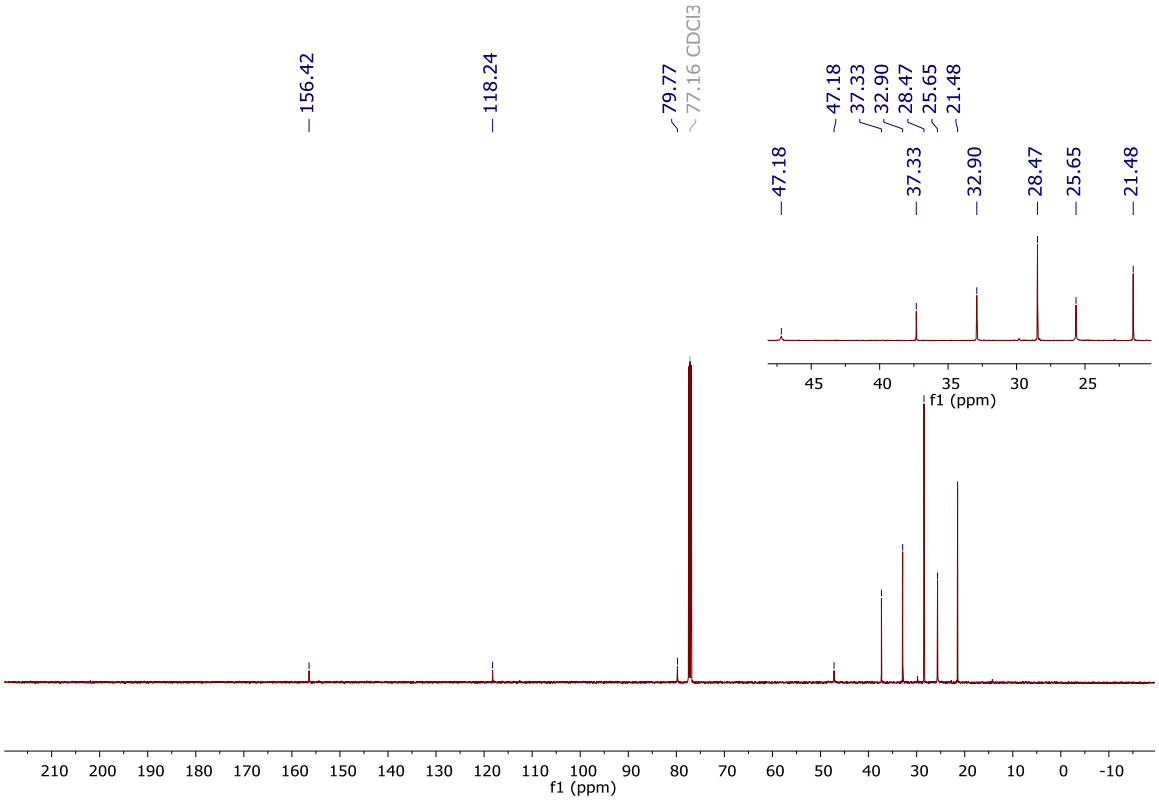
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **19**



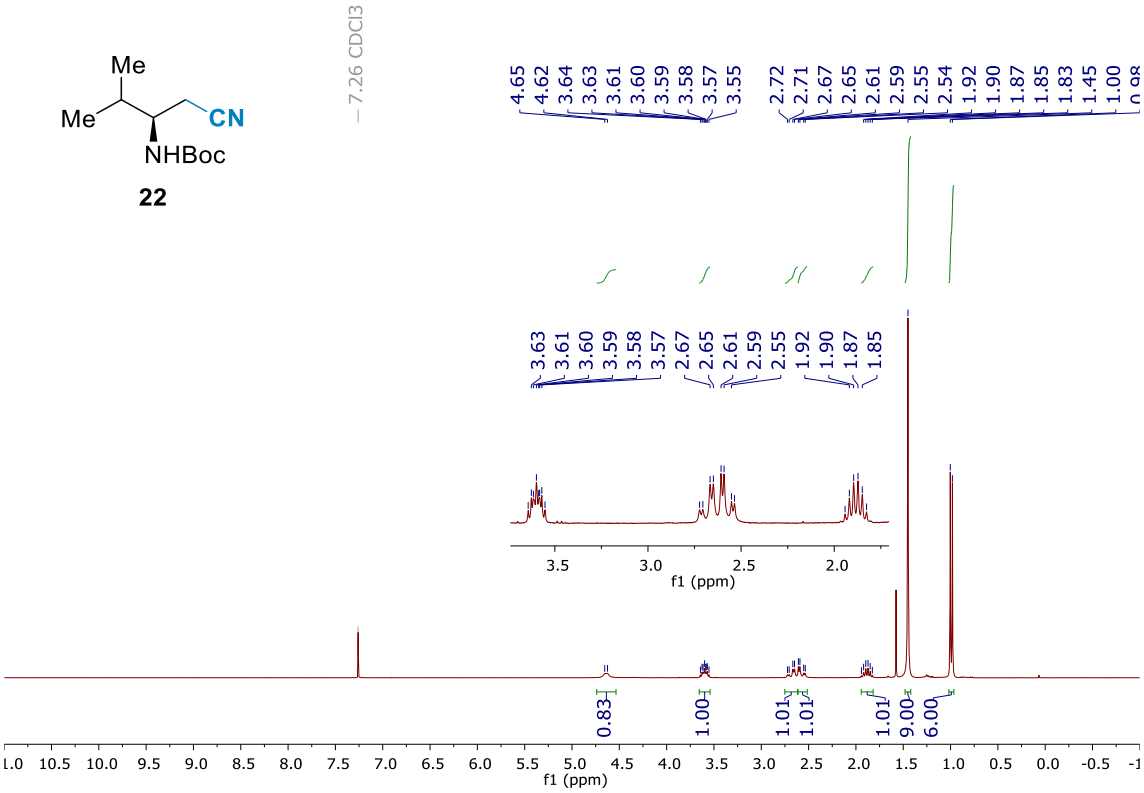
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **20**



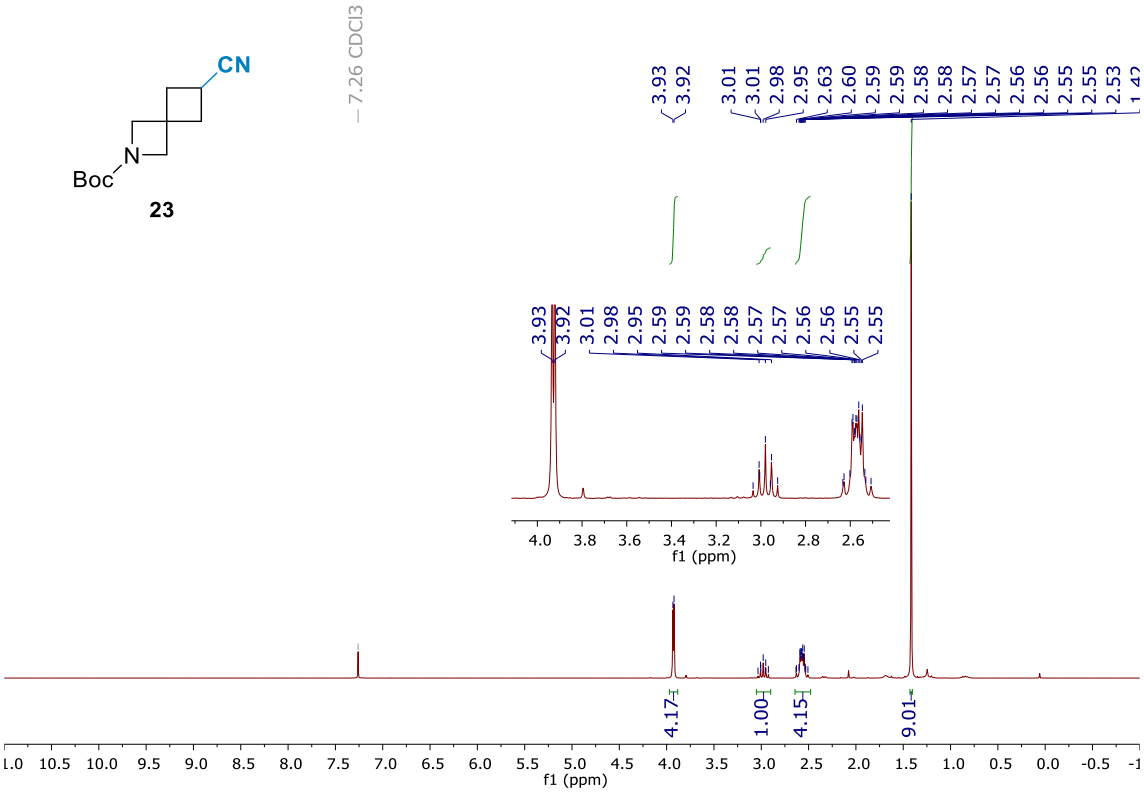
^{13}C-NMR (75 MHz, $CDCl_3$) of compound **20**



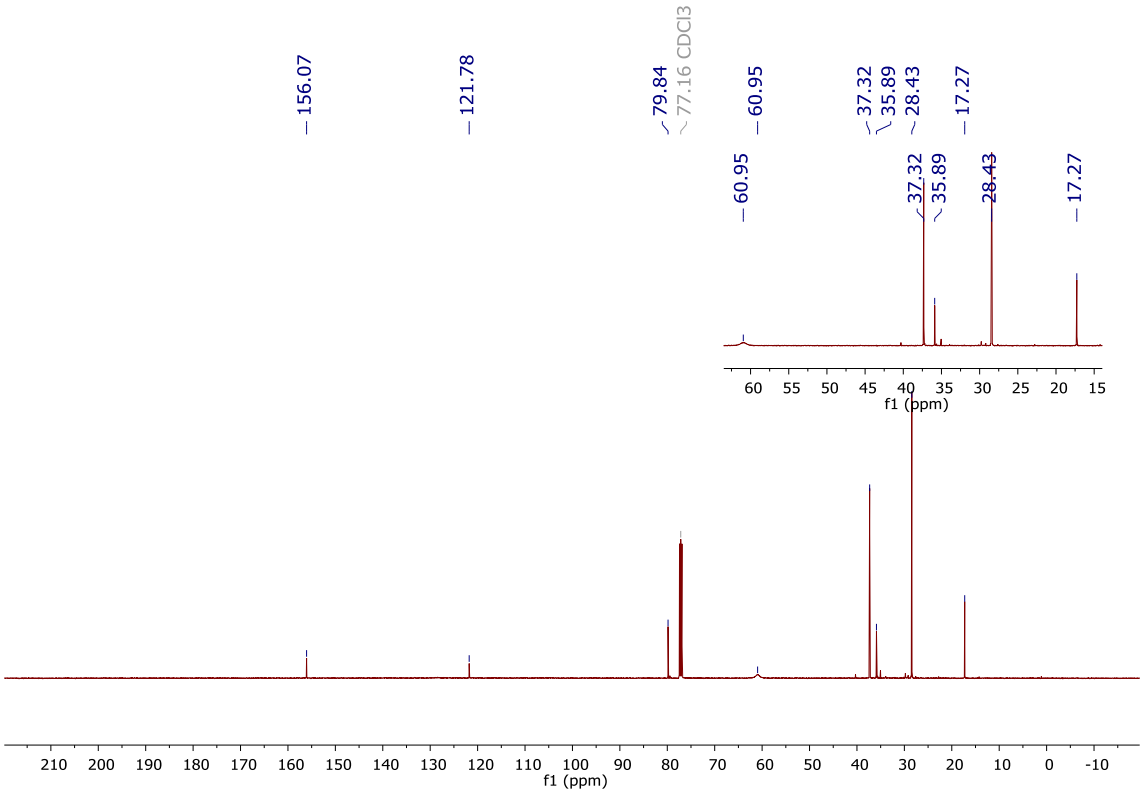
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **22**



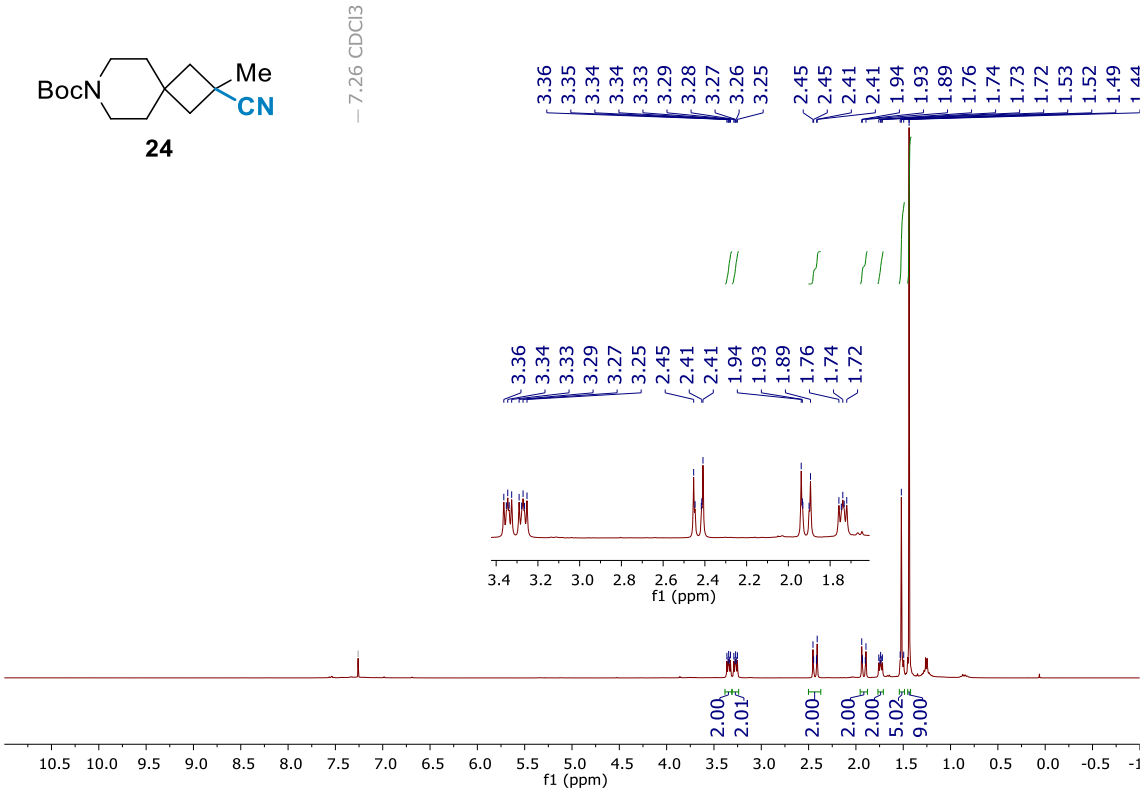
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **23**



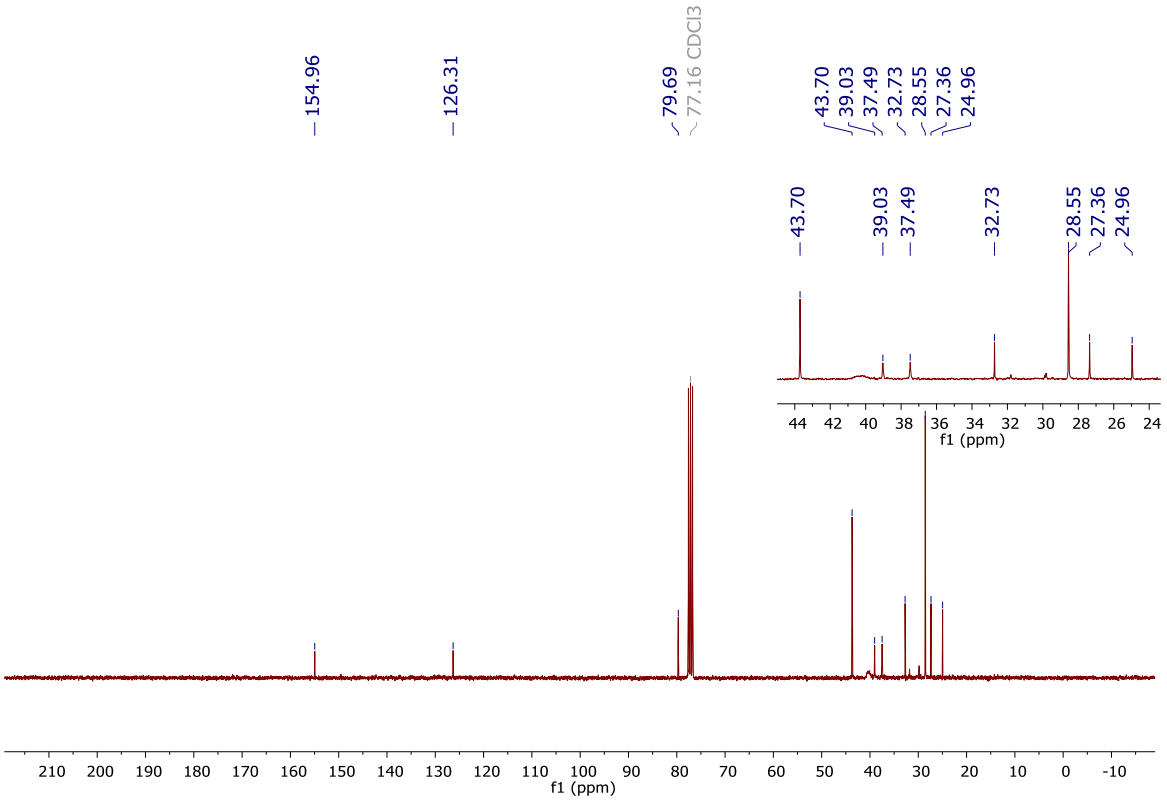
^{13}C-NMR (75 MHz, $CDCl_3$) of compound **23**



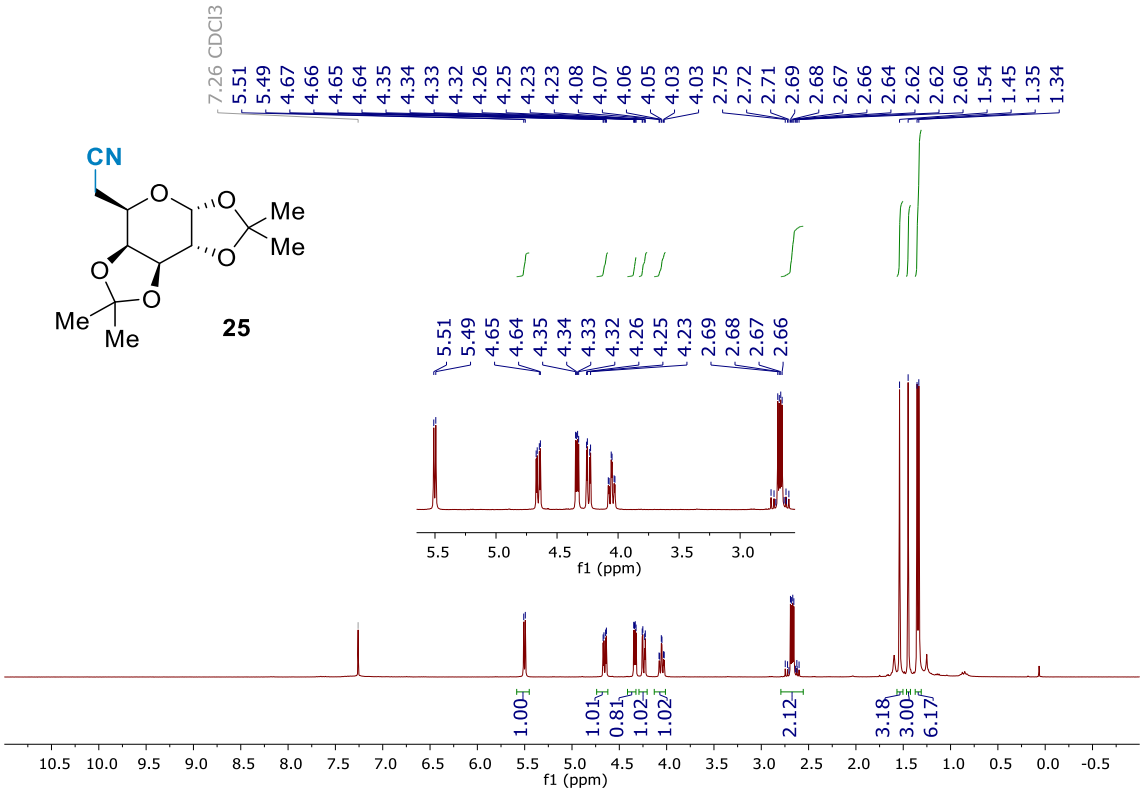
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **24**



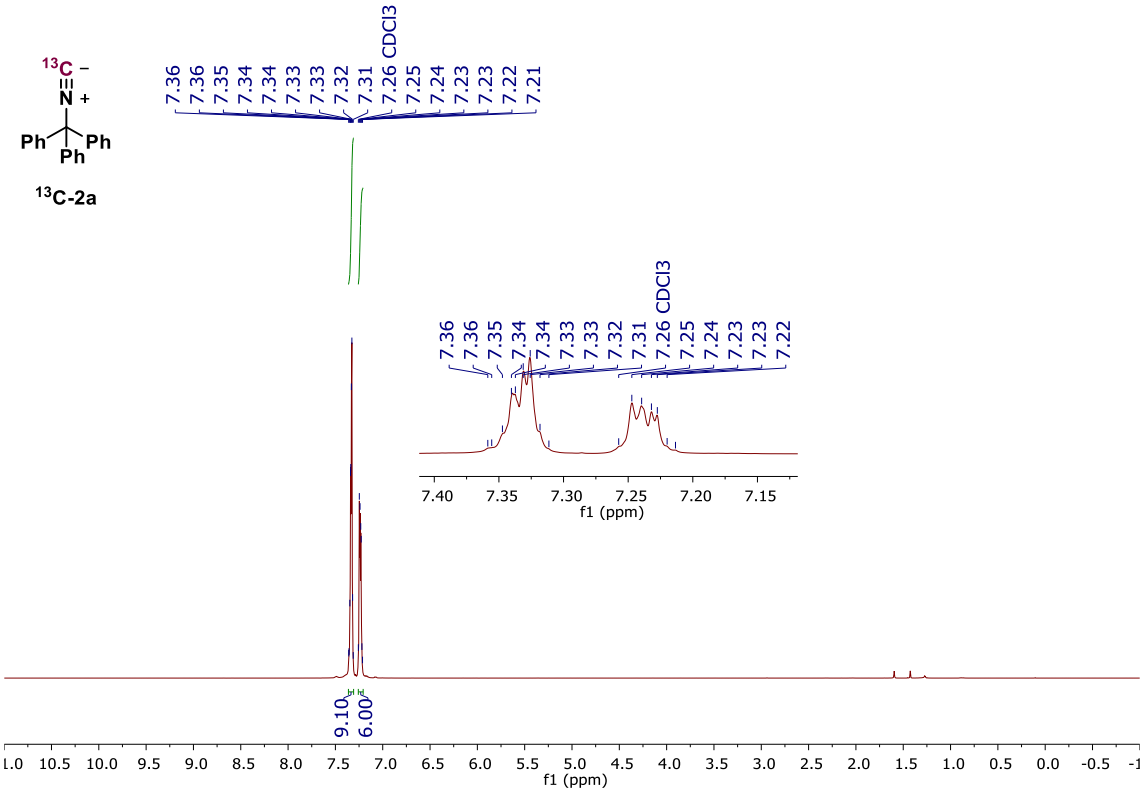
^{13}C-NMR (75 MHz, $CDCl_3$) of compound **24**



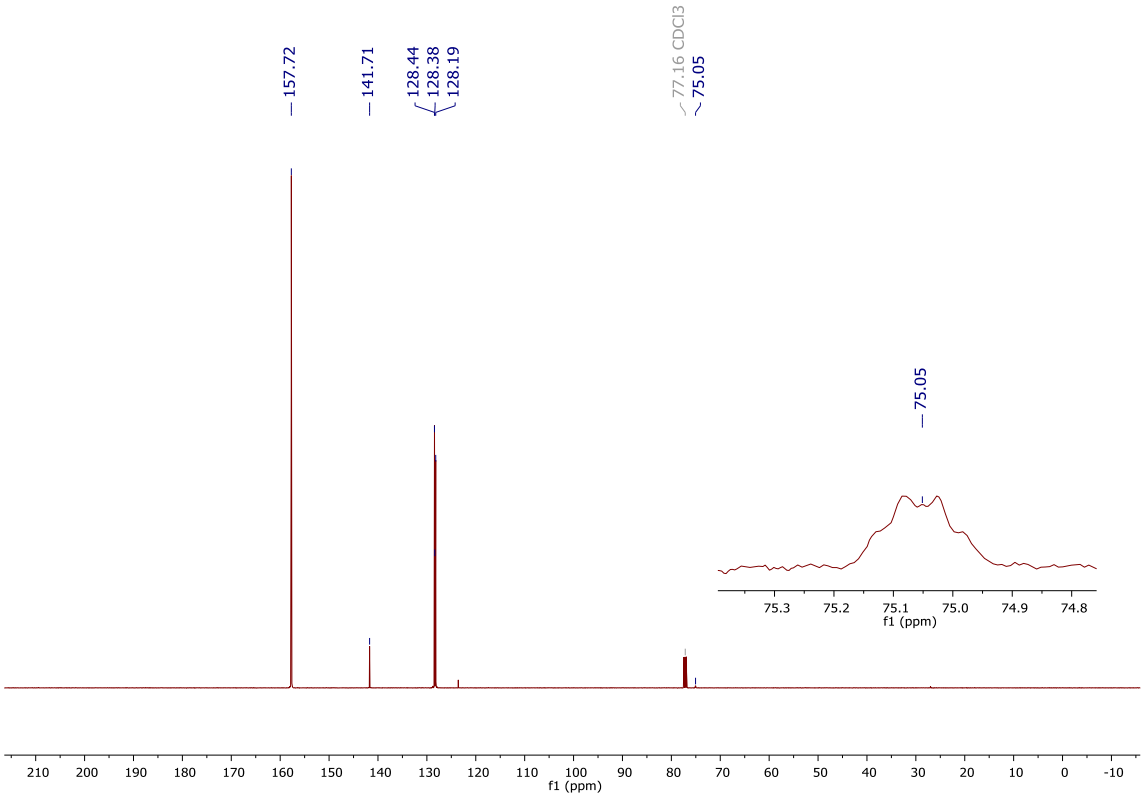
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **25**



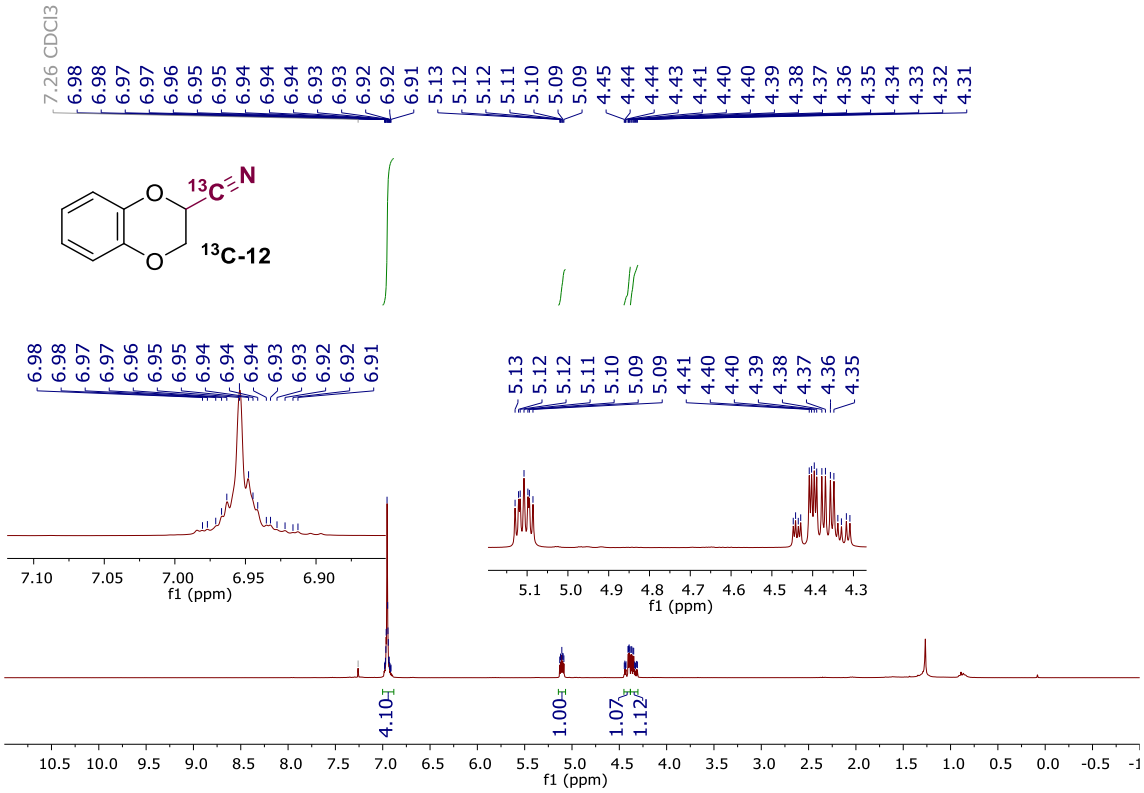
^{1}H-NMR (500 MHz, $CDCl_3$) of compound **^{13}C-2a**



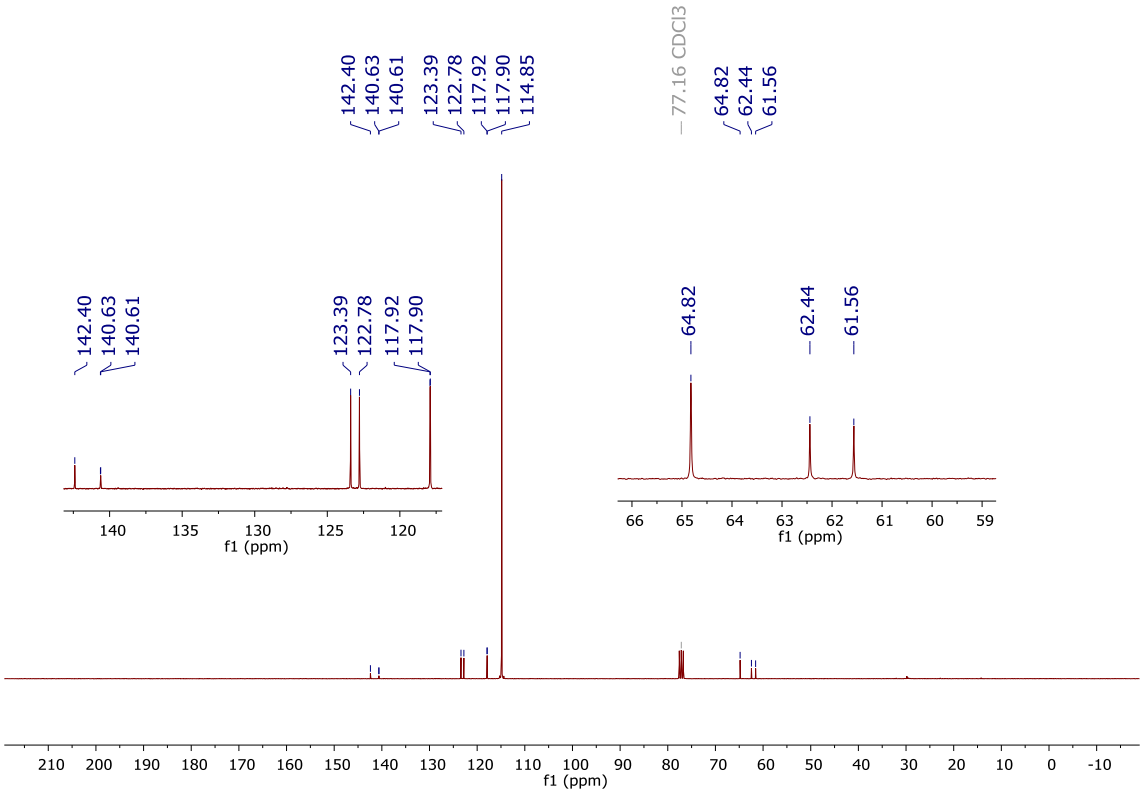
^{13}C-NMR (126 MHz, $CDCl_3$) of compound **^{13}C-2a**



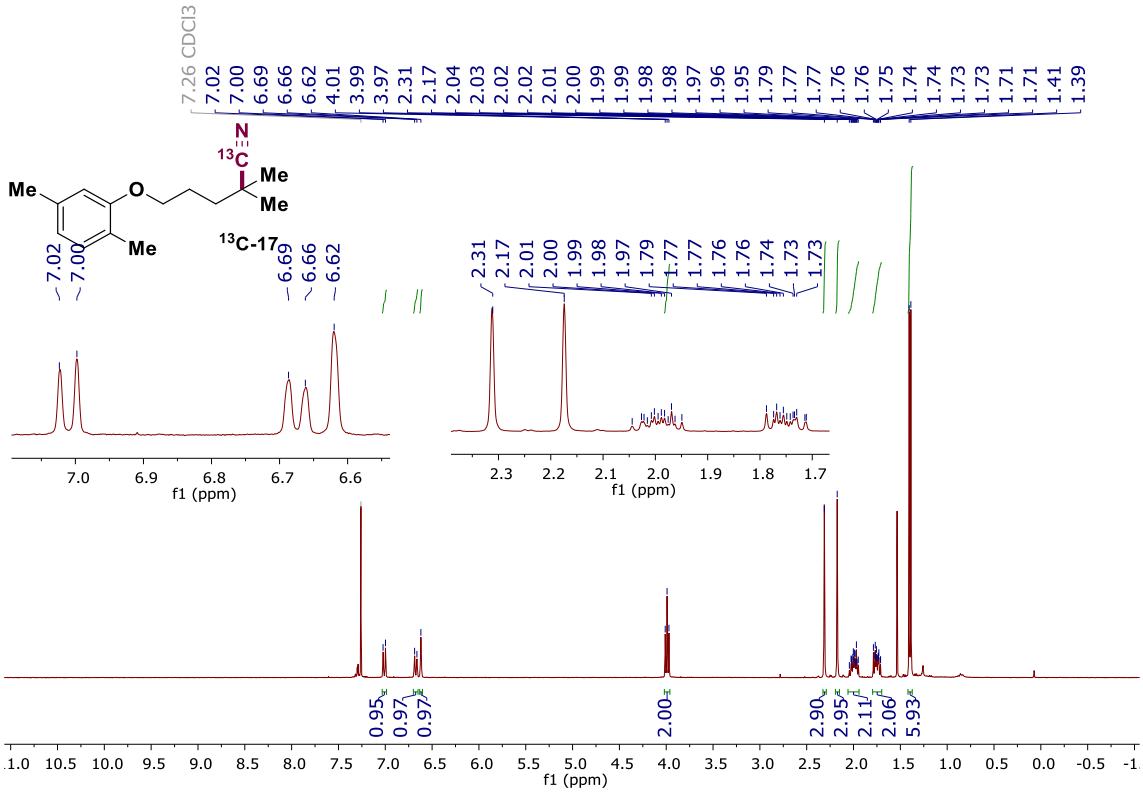
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **^{13}C-12**



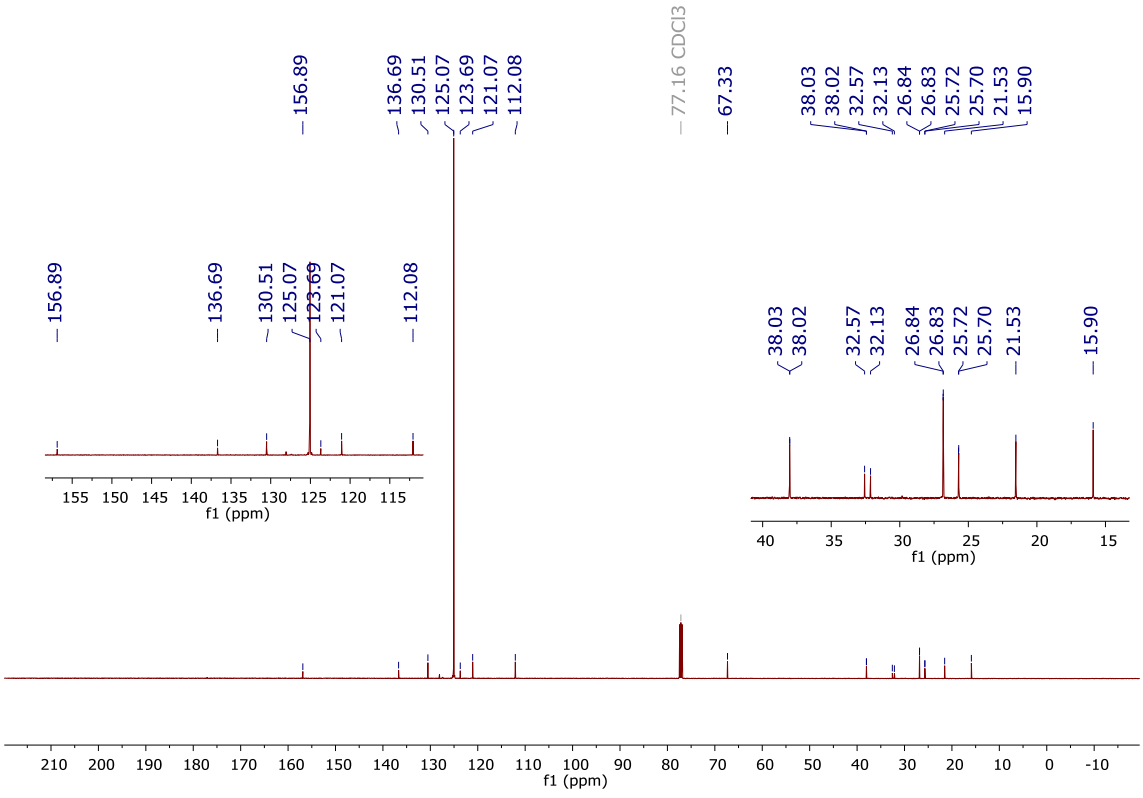
^{13}C-NMR (75 MHz, $CDCl_3$) of compound **^{13}C-12**



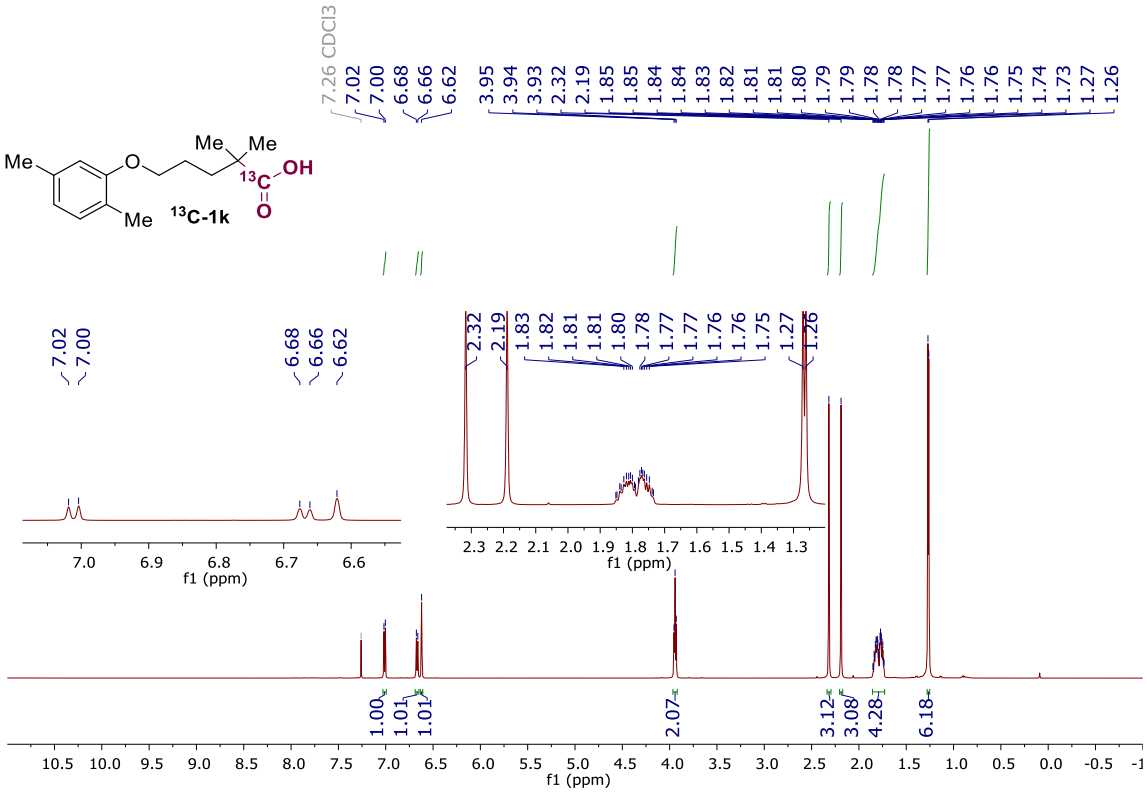
^{1}H-NMR (300 MHz, $CDCl_3$) of compound **^{13}C-17**



^{13}C-NMR (75 MHz, $CDCl_3$) of compound **^{13}C-17**



^{1}H-NMR (500 MHz, $CDCl_3$) of compound **^{13}C-1k**



^{13}C-NMR (126 MHz, $CDCl_3$) of compound **^{13}C-1k**