Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Metal-Free Direct C (sp^3)–H Cyanation Reaction with Cyanobenziodoxolones

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Supporting Information

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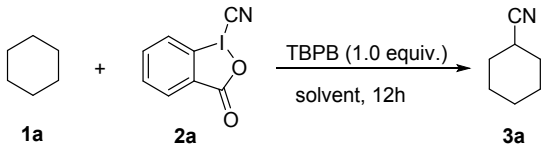
1. General Procedures and Instrumentation.

All reactions were carried out in a dry argon atmosphere using an MBraun glovebox. 4 Å molecular sieves were activated in muffle furnace at 400 °C for 5 h. Solvent was dried and stored over activated 4 Å molecular sieves prior to use. The following instruments were used for physical characterization of the compounds. NMR spectra were recorded on a Bruker ASCEND spectrometer (^{1}H, 600 MHz; ^{13}C{^{1}H}, 151 MHz) or a JEOL JNM-ECA600 spectrometer (^{1}H, 600 MHz; ^{13}C{^{1}H}, 151 MHz). ^{1}H NMR and ^{13}C NMR, chemical shift δ was given relative to TMS and referenced to the solvent signal. ESI-MS analysis was performed on a Bruker time of flight mass spectrometer microTOF-Q II using an electro spray ionization (ESI) source. GC analysis was performed using Aglient GC-7890B equipped with a DB-FFAP capillary column, 30 m×0.32 mm; FID detector: 280 °C; injection: 220 °C; oven temperature: 85 °C for 15 min, raised to 190 °C at a rate of 30 °C/min, and held for 15 min. GC-MS analysis was performed using Shimadzu GCMS-QP2020 with HP-5MS column, 30 m×0.32 mm; FID detector: 250 °C; injection: 250 °C; oven temperature: 40 °C for 2 min, raised to 100 °C at a rate of 10 °C/min, then to 240 °C at a rate of 20 °C/min, and held for 8 min. Column chromatography was performed using silica gel. Analytical TLC was done using pre-coated silica gel 60 F254 plates.

General procedure: A ethyl acetate (EtOAc) solution (0.6 mL) was prepared under argon consisting of cyclohexane **1a** (1.0 mmol, 10.0 equiv.), 1-cyano-1,2-benziodoxole (**2a**, 0.1 mmol) and TBPB (4 μL, 0.01 mmol, 0.2 equiv.), in a sealed reaction tube with a stirbar. The mixture was then heated to 110°C and reacted for 16 h. Afterwards, the combined organic filtrate was dried by Na_2SO_4 overnight and concentrated, which was analyzed by a combination of GC with cyclohexanone as internal standard or ^{1}H NMR ($CDCl_3$) with CH_2Br_2 as internal standard.

2. Efforts on optimization of solvent and time of cyclohexane.

Table S1. The preliminary screening of cyanation of cyclohexane with solvent and time.



Entry	Solvent	Temp. (°C)	Yield (%)
1	EtOAc	110	78
2	CH_3CN	110	29
3	CH_3OH	110	9
4	DCE	110	65
5	Acetone	110	41
6	EtOAc	90	48
7	EtOAc	100	75
8	EtOAc	120	78
9	EtOAc	130	71

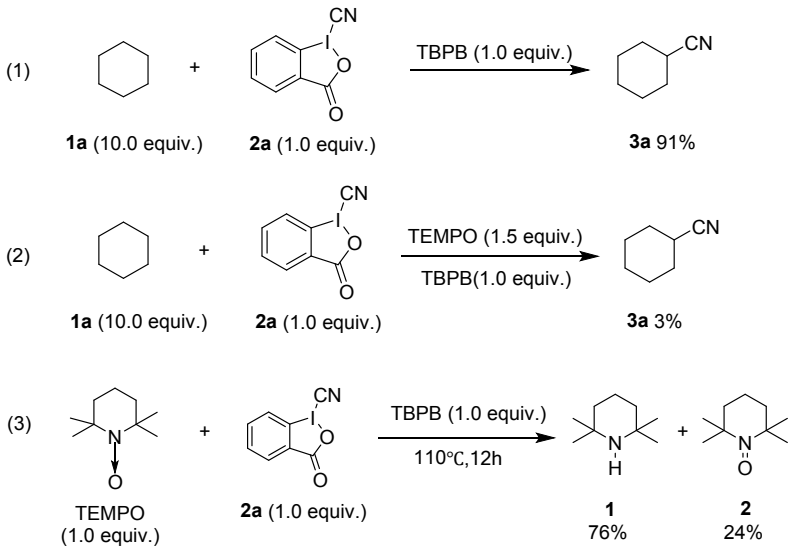
General conditions: **1a (**1.0 mmol, 10 equiv.), **2a** (0.1mmol, 10 equiv.), TBPB (1.0 equiv.), Solvent (0.3 mL), 110 °C, 12 h, under Argon, GC yield**,** cyclohexanone as internal standard.

DCE = 1,2-dichloroethane.

3. Mechanism investigation experiment.

3.1 Investigation of the reaction mechanism.

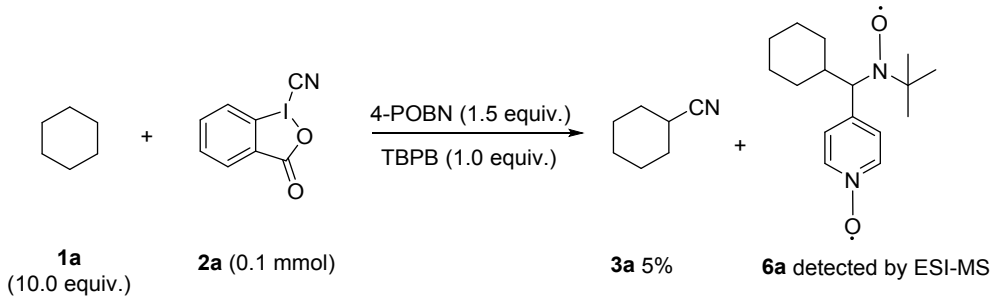
When we added 1.5 equiv. of 2,2,6,6-tetramethyl-piperidine 1-oxyl (TEMPO) to the reaction system, we found that the yield was reduced from 91% to 3% compared to the result which in the absences of TEMPO. Unexpectedly, the TEMPO adduct cyclohexane was not obtained (Scheme S1, (1) and (2)), determined by GC-MS analysis and ESI-MS). We further studied the reaction of TEMPO, **2a** and TBPB under the reaction conditions, found that TEMPO was oxidized by **2a** and TBPB (Scheme S1, (3)).



Scheme S1. Investigation of the Reaction Mechanism.

3.2 Control experiments for mechanistic studies.

The addition of cyclohexane to 4-POBN was trapped when the free radical scavenger was added. **6a** ESI-MS: calc. for $C_{16}H_{25}N_2O_2$ $[M]^+$: 277.1916 found: 277.1946.



Scheme S2. Radical-trapping experiment of cyclohexane.

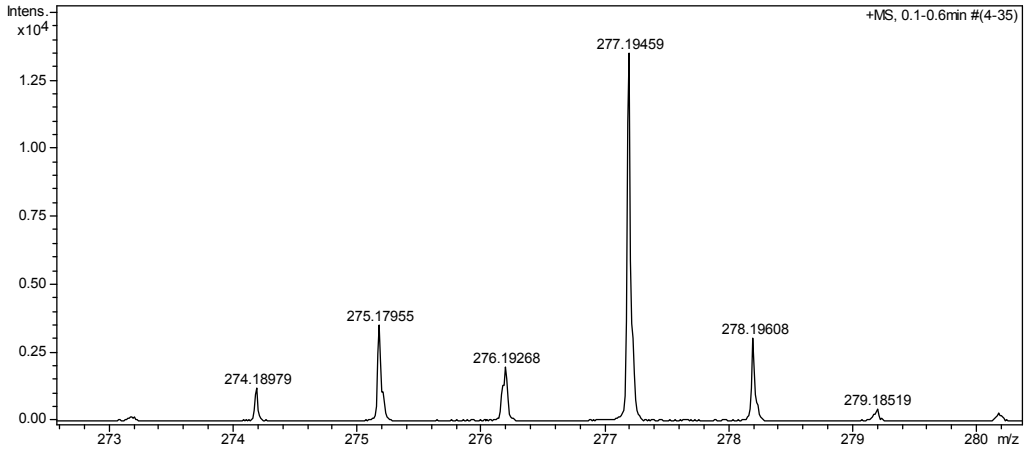
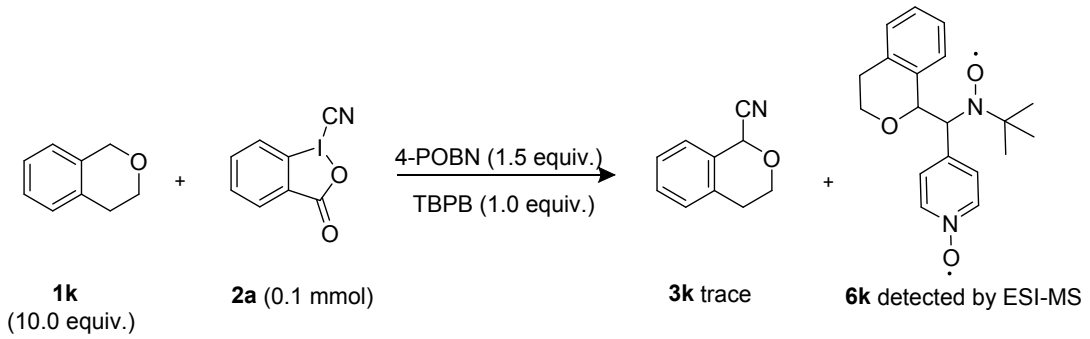


Fig 1. ESI-MS of 4-POBN adduct cyclohexane (**6a**)

The addition of isochroman to 4-POBN was trapped when the free radical scavenger was added. **6k** ESI-MS: calc. for $C_{19}H_{23}N_2O_3$ $[M]^+$: 327.1781 found: 327.1776.



Scheme S3. Radical-trapping experiment of isochroman.

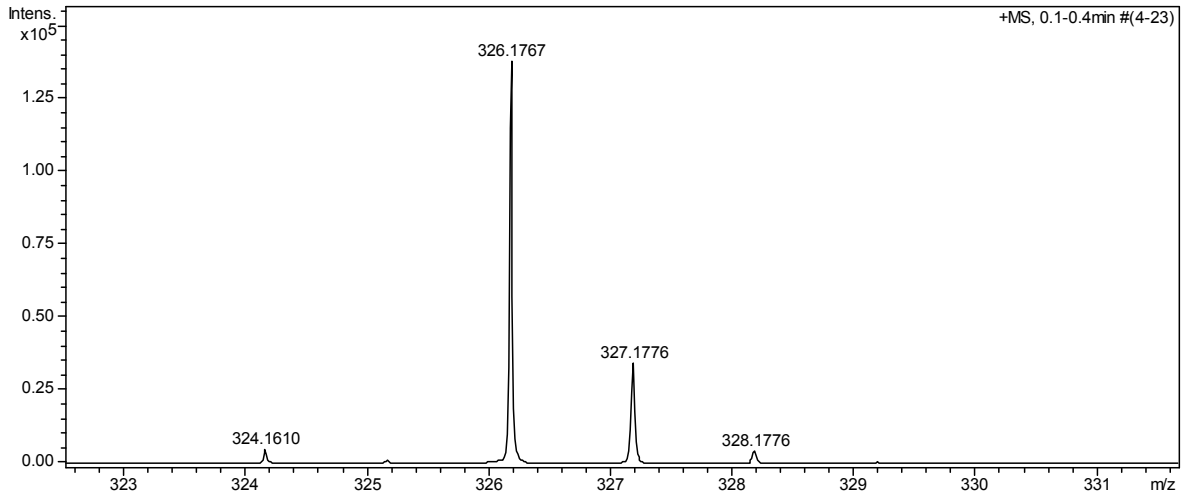
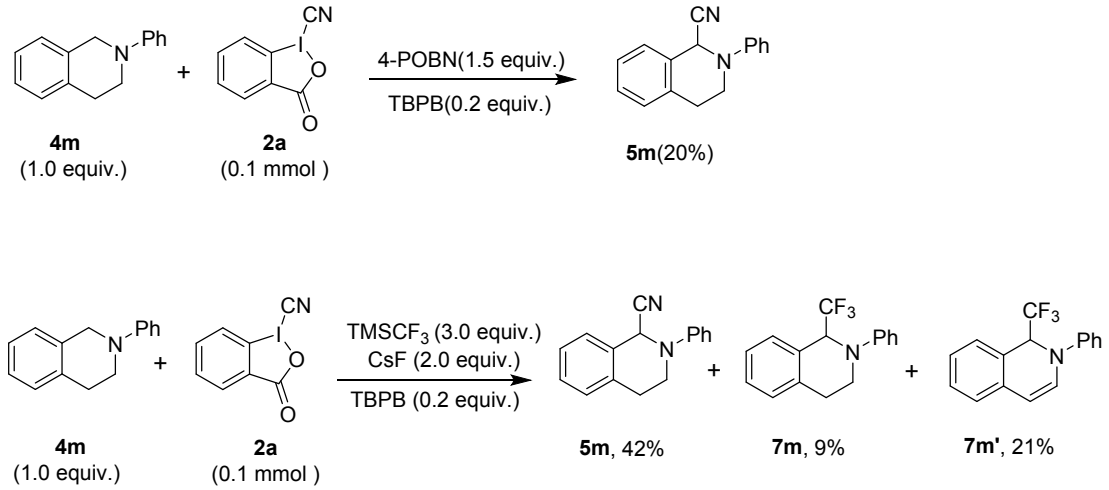


Fig 2. ESI-MS of 4-POBN adduct isochroman (**6k**)

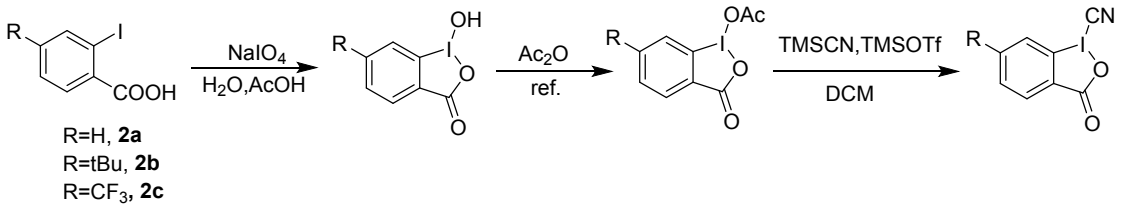
Competitive experiment



Scheme S4. Study on competitive experiment of **4m**.

4. Preparation and Characterization data

4.1 The procedures for the synthesis of cyanation-transfer reagents



Scheme S5. The procedures for the synthesis of cyanation-transfer reagents.

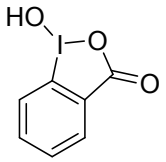
Following a reported procedure,[1] $NaIO_4$ (4.04 mmol,) and 2-iodo benzoic acid derivatives (4 mmol) were suspended in AcOH / H_2O (2.5 mL: 5.0 mL) under air with vigorous stirring. The mixture was refluxed for 4 h, then diluted with cold water (50 mL). After vigorous stirring for 15 minutes, the precipitation was suction filtered and washed with ice water and cold acetone, respectively. The pure 1-Hydroxy-1,2-benziodoxol-3-(1H)-one derivatives were obtained by vacuum desiccation at 50 ^oC as a white solid.

The 1-Hydroxy-1,2-benziodoxol-3-(1H)-one derivatives (2 mmol) was put into 2 mL Ac_2O, then the suspension was heated at 140 ^oC, turning clear after several minutes when the reaction was over. The mixture was cooled and crystallized at -18 ^oC for 5 h. The crystal was further dried by vacuum desiccation to 1-Acetoxy-1,2-benziodoxol-3-(1H)-one derivatives.

To the 5 mL DCM solution of 1-Acetoxy-1,2-benziodoxol-3-(1H)-one derivatives (1 mmol) under Argon, added was 2 mmol TMSCN. Then TMSOTf (1 mol%) was added by syringe, with solid appearing. After 15-30 minutes stirring, the mixture was diluted with 15 mL PE and filtered. And the collection was further washed by PE to give the desired product 1-Cyanyo-1,2-benziodoxol-3-(1H)-one derivative.

4.1.1 Preparation and characterization of 2a.

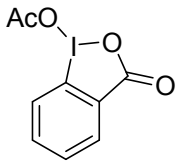
1-Hydroxy-1,2-benziodoxol-3-(1H)-one (2aa)



2aa

^{1}H NMR (600 MHz, DMSO-D^{6}, 298 K): δ = 8.02 (s, 1 H), 8.01 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ =1.2 Hz, 2H), 7.96 (m, 1H), 7.84 (d, $^{3}J_{HH}$ =7.8 Hz, 1H), 7.70 (td, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 0.6 Hz, 1H). **^{13}C{^{1}H} NMR** (600 MHz, DMSO-D^{6}, 298 K): δ = 167.7 (C=O), 134.5, 131.5, 131.1, 130.4, 126.3, 120.4. NMR data correspond to the reported values.[1]

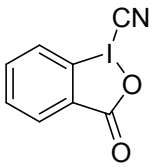
1-Acetoxy-1,2-benziodoxol-3-(1H)-one (2ab)



2ab

^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ = 8.26 (dd, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H), 8.00 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.93 (td, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.72 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 2.26 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 176.2 (C=O), 168.3, 136.3, 133.4, 131.5, 129.5, 129.2, 118.5, 20.5 (CH_3). NMR data correspond to the reported values.[1]

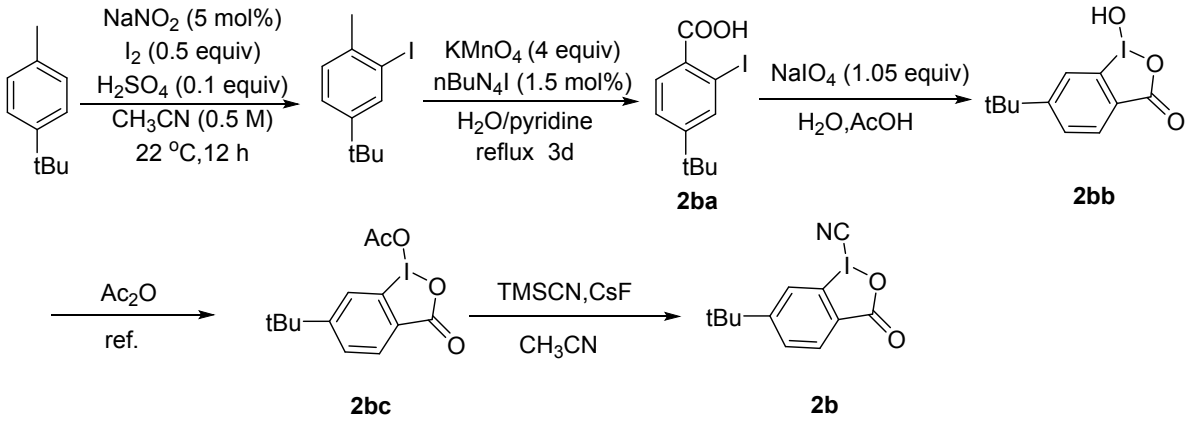
1-Cyano-1,2-benziodoxol-3-(1H)-one (**2a**)



2a

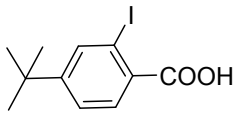
Isolated yield from 1-Acetoxy-1,2-benziodoxol-3-(1H)-one is 90% as white solid. **^{1}H-NMR** (600 MHz, DMSO-D^6, 298 K): δ = 8.31 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 8.14 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 8.03 (m, 1H), 7.89 (t, $^3J_{HH}$ = 7.2 Hz, 1H). **^{13}C {^{1}H} NMR** (151 MHz, DMSO-D^6, 298 K): δ = 166.7 (C=O), 135.4, 132.0, 131.8, 130.3, 127.8, 117.5, 87.9 (CN). NMR data correspond to the reported values.[1]

4.1.2 Preparation and characterization of 2b.



Scheme S6. The procedures for the synthesis of **2b**.

4-tert-butyl-2-iodobenzoic acid (2ba)

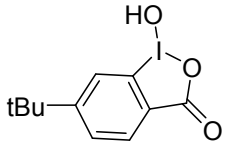


2ba

From a modification of known procedures,[1] to the solution of 4-tert-butyl-2-iodo-1-methylbenzene (30 mmol, 8.22 g) in H_2O/ pyridine (96 mL:120 mL), was added $KMnO_4$ (19 g, 120 mmol) and $nBuN_4I$ (110 mg, 1 mol%). The mixture was heated to reflux for 3 days when the solution turned clear. The hot solution was collected, while the black solid was extracted by EtOAc. Then the former and latter was combined to get layered, the aqueous phase was further extracted by EtOAc. The combined organic phase washed by 10 N HCl to adjust pH 4. Then it was basified by 50% KOH solution to adjust pH 10. The organic phase was collected, washed by brine and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure, to provide the

unreacted staring material 3.6 g. While the aqueous phase was acidified by 2 N HCl to adjust pH 10, it was extracted by EtOAc, which was washed by brine and dried over anhydrous Na_2SO_4, and concentrated under reduced pressure, to provide the 4-tert-butyl-2-iodobenzoic acid 4.5 g as a colorless solid, 49% yield. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.05 (d, $^1J_{HH}$ = 1.8 Hz, 1H), 7.97 (d, ^{3}J = 8.4 Hz, 1H), 7.45 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 1.33 (s, 9H, CH_3). **^{13}C {^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ =170.8 (C=O), 157.8, 139.5, 132.1, 130.1, 125.4, 95.4, 35.1 (C^{CH_3}), 31.1 (CH_3). NMR data correspond to the reported values.[1]

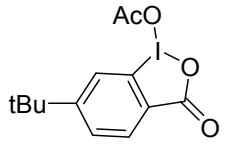
4-tBu-1-hydroxy-1,2-benziodoxol-3-(1H)-one (2bb)



2bb

White solid. **^{1}H NMR** (600 MHz, DMSO-D^6, 298 K): δ = 7.99 (s, 1H, OH), 7.93 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.81 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 7.74 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, CH_3), 1.35 (s, 9H, CH_3). **^{13}C {^{1}H} NMR** (151 MHz, DMSO-D^6, 298 K): δ = 167.7 (C=O), 157.9, 130.8, 129.1, 127.8, 122.4, 120.5, 35.5(C^{CH_3}), 30.8 (CH_3). NMR data correspond to the reported values.[1]

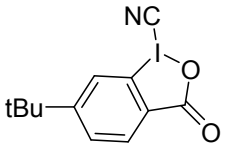
4-tBu-1-Acetoxy-1,2-benziodoxol-3-(1H)-one (2bc)



2bc

White solid. Yield 95%. **^{1}H-NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.14 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.94 (s, 1H), 7.71 (d, $^3J_{HH}$ = 9 Hz, 1H), 2.26 (s, 3H, CH_3), 1.41 (s, 9H, CH_3). **^{13}C {^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ =176.3 (C=O), 168.4, 161.2, 132.9, 129.0, 126.3, 125.8, 119.2, 36.3 (C^{CH_3}), 31.2(CH_3), 20.5 (CH_3). NMR data correspond to the reported values.[1]

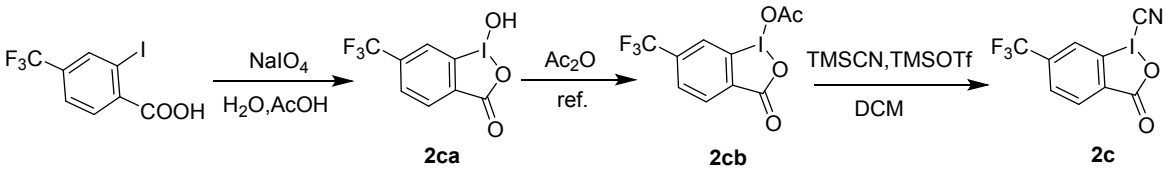
4-tBu-1-Acetoxy-1,2-benziodoxol-3-(1H)-one (2b)



2b

White solid. **^{1}H-NMR** (600 MHz, $CDCl_3$, 298 K): δ = 8.41 (d, $^{4}J_{HH}$ = 1.1 Hz, 1H), 8.30 (d, $^{3}J_{HH}$ = 7.9 Hz, 1H), 7.88 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 1.2 Hz, 1H), 1.45 (s, 9H, CH_3). **^{13}C {^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ =166.3 (C=O), 162.5, 133.0, 130.4, 126.8, 123.8, 116.7, 86.6 (CN), 36.7 (C^{CH_3}), 31.3(CH_3). NMR data correspond to the reported values.[1]

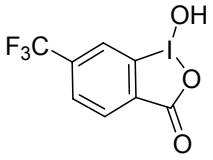
4.1.3 Preparation and characterization of 2c.



2ca **2cb** **2c**

Scheme S7. The procedures for the synthesis of **2c**.

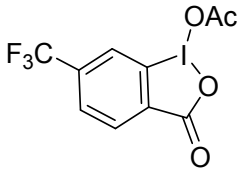
4-Trifluoromethyl-1-hydroxy-1,2-benziodoxol-3-(1H)-one (2ca)



2ca

White solid. **^{1}H NMR** (600 MHz, DMSO-D^{6}, 298 K): δ = 8.38 (s, 1H, OH), 8.19 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.09 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 8.05 (s, 1H). **^{13}C{^{1}H} NMR** (151 MHz, DMSO-D^{6}, 298 K): δ = 166.5 (C=O), 135.4, 134.1, 133.8, 132.0, 127.8, 124.4, 123.2, 122.5, 121.6. NMR data correspond to the reported values.[1]

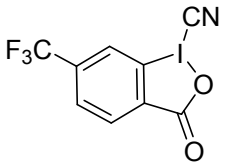
4-Trifluoromethyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one (2cb)



2cb

White solid. **^{1}H-NMR** (600 MHz, $CDCl_3$, 298K): δ = 8.39 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 8.26 (s, 1H), 7.99 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 2.29 (s, 3H, CH_3). **^{13}C {^{1}H} NMR** (151 MHz, $CDCl_3$, 298K): δ = 176.8 (C=O), 166.8, 138.2, 138.0, 133.7, 132.4, 128.9, 128.8, 127.2, 127.1, 122.1, 123.9, 122.1, 118.8, 20.4 (CH_3). NMR data correspond to the reported values.[1]

4-Trifluoromethyl-1-cyano-1,2-benziodoxol-3-(1H)-one (2c)

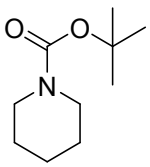


2c

white solid. **^{1}H-NMR** (600 MHz, DMSO-D^6, 298 K): δ = 8.47 (s, 1H), 8.29(m, 2H). **^{13}C {^{1}H} NMR** (151 MHz, DMSO-D^6, 298 K): δ = 165.6 (C=O), 135.2, 134.9, 134.3, 132.5, 129.2, 124.9, 123.9, 122.1, 119.0, 87.9. NMR data correspond to the reported values.[1]

4.2 Synthesis and characterization of substrates.

4.2.1 Preparation of tert-butyl piperidine-1-carboxylate (4k)

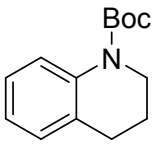


4k

Following a reported procedure,[2, 3] a mixture of piperidine (3.3 mL, 33 mmol) and BoC_2O (6.55 g, 30 mmol) in CH_2Cl_2 (100 mL) was stirred for 4 h at room temperature.

The solvent was removed under reduced pressure and the residue was purified by flash silica gel column chromatography (hexane/EtOAc = 10/1) to give **4k**. Spectroscopic data were identical to the reported values. Colorless oil (5.32 g, 96% yield). **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K) δ = 3.35 (t, $^3J_{HH}$ = 5.7 Hz, 4H, CH_2^N), 1.56 (m, 2H, CH_2), 1.49 (m, 4H, CH_2), 1.45 (s, 9H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 155.1 (C=O), 79.2 (C^{CH_3}), 44.8 (CH_2), 28.6 (CH_3), 25.9 (CH_2), 24.6 (CH_2). NMR data correspond to the reported values.[2]

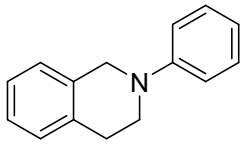
4.2.2 Preparation of (tert-butyl 3,4-dihydro-1(2H)-quinolinecarboxylate) (4l)



4l

Following a reported procedure,[4] to a solution of 1,2,3,4-tetrahydroquinoline (6.66 g, 50 mmol) in 100 mL of methylene chloride at ambient temperature was added di-tert-butyl dicarbonate (12.0 g, 55 mmol) and triethylamine (7.7 mL, 55 mmol). The resulting mixture was allowed to stir at 40 °C for 24 h. The reaction was allowed to cool to ambient temperature and the methylene chloride was removed under reduced pressure. The residue was dissolved in ethyl acetate, washed with 10% aqueous HCl, saturated aqueous sodium bicarbonate and brine, dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography (elution with 60:1 hexane/ethyl acetate) to afford the title compound. Oil. **^{1}H NMR** (600 MHz, $CDCl_3$, 298 K): δ = 7.64 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ph), 7.13 (t, $^3J_{HH}$ = 8.4 Hz, 1H, Ph), 7.07 (d, $^3J_{HH}$ =7.2 Hz, 1H, Ph), 6.98 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ph), 3.71 (t, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2^N), 2.77 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2^{Ph}), 1.93 (m, 2H, CH_2), 1.53 (s, 9H, CH_3). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 154.1 (C=O), 138.8 (Ph^N), 130.0, 128.6, 125.8, 124.3, 123.3, 80.8 (C^{CH_3}), 44.8 (CH_2), 28.5 (CH_3), 27.6 (CH_2), 23.7 (CH_2). NMR data correspond to the reported values.[4]

4.2.3 Preparation of N-Phenyl-1,2,3,4-tetrahydroisoquinoline (4m)



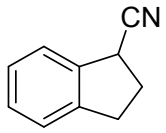
4m

Following a reported procedure,[5, 6] copper(I) iodide (39.8 mg, 0.21 mmol, 0.1 equiv.) and potassium phosphate (887.3 mg, 4.18 mmol, 2.09 equiv.) were weighed into a round bottom flask which was evacuated and back filled with nitrogen for 3 times. 2-Propanol (2 mL), ethylene glycol (0.23 mL), iodobenzene (426.4 mg, 0.23 mL, 2.09 mmol, 1.05 equiv.) and 1,2,3,4-tetrahydroisoquinoline (0.27 g, 0.26 mL, 2.0 mmol, 1 equiv.) were added via a syringe at room temperature. The reaction mixture was heated to 85–90 °C, stirred for 24 h and then allowed to cool to room temperature. Diethyl ether (5 mL) and water (5 mL) were then added to the reaction mixture. The organic layer was extracted by diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over magnesium sulfate. The solvent was removed under vacuo and the crude mixture purified by column chromatography on silica gel (PE: EtOAc = 20:1). Compound **4m** was obtained as light brown solid in 83% yield (347 mg, 1.66 mmol). **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.30 (m, 2H), 7.19 (m, 4H), 7.01 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.84 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 4.43 (s, 2H, CH_2^{Ph}), 3.59 (t, $^{3}J_{HH}$ = 6.0 Hz, 2H, CH_2^{N}), 3.00 (t, $^{3}J_{HH}$ = 5.9 Hz, 2H); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 150.7 (Ph^{N}), 135.0, 134.6, 129.4, 128.6, 126.7, 126, 126.2, 118.8, 115.3, 50.9, 46.7, 29.3 (CH_2). NMR data correspond to the reported values.[5,6]

5. Characterization of cyanide products

5.1 C (sp^3)-H cyanidation of 2a with various hydrocarbons.

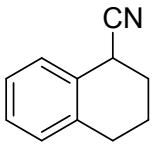
2,3-Dihydro-1H-indene-1-carbonitrile (3d)



3d

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **3d**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.44 (d, $^3J_{HH}$ = 6.0 Hz, 1H), 7.29 (m, 3H), 4.11 (t, $^3J_{HH}$ =8.1 Hz, 1H, CH^{CN}), 3.09 (m, 1H, CH_2), 2.96 (m, 1H, CH_2), 2.59 (m, 1H, CH_2), 2.38 (m, 1H, CH_2); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 143.0, 137.7, 128.7, 127.4, 125.1, 124.5, 121.2 (CN), 34.7 (CH), 31.6 (CH_2), 31.3 (CH_2). NMR data correspond to the reported values.[7]

Tetrahydronaphthalene- 1-carbonitrile (3e).

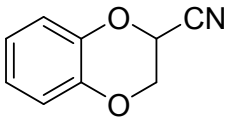


3e

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **3e**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.36 (m, 2H, ArH), 7.22 (m, 2H, ArH), 7.13 (m, 1H, ArH), 3.99 (t, $^3J_{HH}$ = 6.3 Hz, 1H, CH^{CN}), 2.79 (m, 2H, CH_2), 2.16 (m, 2H, CH_2), 2.04 (m, 1H, CH_2), 1.85 (m, 1H, CH_2); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 136.6, 129.9, 129.0, 128.2, 126.7, 121.9 (CN), 31.0, 28.6, 27.5, 21.0 (CH_2). ESI-MS: calc. for $C_{11}H_{11}N$ $[M+H]^+$: 158.0964 found: 158.0915. NMR data correspond to the reported values.[8]

5.2 C (sp^3)-H cyanidation of 2a with various ethers.

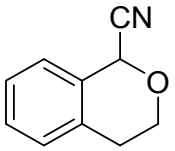
1,4-Benzodioxan-2-carbonitrile (3j)



3j

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **3j**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 6.95 (m, 4H), 5.11 (dd, $^1J_{HH}$ = 3.6 Hz, $^1J_{HH}$ = 3.0 Hz, 1H, CH^{CN}), 4.42 (dd, $^3J_{HH}$ = 11.4 Hz, $^4J_{HH}$ = 3.6 Hz, 1H, CH_2), 4.35 (dd, $^3J_{HH}$ = 12.9 Hz,$^4J_{HH}$ = 2.4 Hz, 1H, CH_2); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 142.4, 140.6, 123.4, 122.8, 117.9 (CN), 114.9, 64.8 (CH), 62.0 (CH_2). NMR data correspond to the reported values.[9]

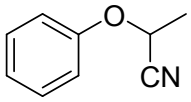
1-Cyanoisochroman (3k)



3k

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **3k**. White solid. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.29 (m, 2H, Ph), 7.20 (m, 2H, Ph), 5.65(s, 1 H, CH^{CN}), 4.16 (m, 2 H, O-CH_2), 3.05 (ddd, $^2J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 6.0 Hz, 1H), 2.77 (dt, $^2J_{HH}$ = 16.2 Hz, $^3J_{HH}$ = 3.0 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 133. 1, 129.6, 129.2, 128.9, 127.2, 125.6, 118.3 (CN), 65.4 (CH^{CN}), 63.5 (O-CH_2), 27.4. NMR data correspond to the reported values.[10]

2-Phenoxy-propanenitrile (3l)

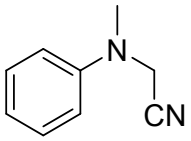


3l

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **3l**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.35 (m, 2H, Ph), 7.09 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ph), 7.01 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Ph), 4.90 (q, $^3J_{HH}$ = 6.7, 1H, CH^{CN}), 1.80 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 156.5, 130.0, 123.3, 118.4 (CN), 116.0, 62.6 (CH^{CN}), 20.1 (CH_3). ESI-MS: calc. for C_9H_9NO $[M]^+$: 147.0679 found: 147.0802. NMR data correspond to the reported values.[11]

5.3 C (sp^3)-H cyanidation of 2a with various tertiary amines.

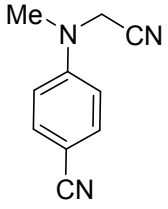
N-Methyl-N-phenylaminoacetonitrile (5a)



5a

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5a**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.32 (m, 2 H), 6.92 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.87 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 4.8 Hz, 2H), 4.18 (s, 2H, CN), 3.01 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 147.9 (Ph^N), 129.6, 120.4, 115.6 (CN), 115.1, 42.5 (CH_2), 39.4 (CH_3). NMR data correspond to the reported values.[12]

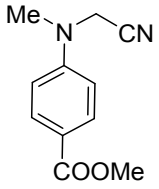
4-[(cyanomethyl)methylamino]-benzonitrile (5b)



5b

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate10:1) and provided **5b**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.58 (d, $^3J_{HH}$ =12 Hz, 2 H), 6.82 (d, $^3J_{HH}$ = 12 Hz, 1H), 4.25 (s, 2H, CH_2), 3.12 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 150.4 (Ph), 133.9, 119.6 (CN), 114.8 (CN), 113.5, 102.0, 41.2 (CH_2), 39.1 (CH_3).

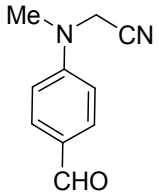
4-[(cyanomethyl)methylamino]-benzoic acid, methyl ester (5c)



5c

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) and provided **5c**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.98 (s, 2 H, Ph), 6.81 (s, 2H, Ph), 4.25 (s, 2H, CH_2), 3.87 (s, 3H, CH_3), 3.10 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 167.0 (C=O), 151.0 (Ph), 131.6, 121.0, 115.2 (CN), 112.9 (CN), 51.9 (CH_3), 41.3 (CH_2), 39.2 (CH_3).

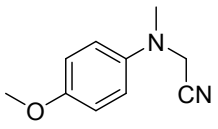
2-[(4-formylphenyl)methylamino]-acetonitrile (5d)



5d

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) and provided **5d**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 9.84 (s, 1H, CHO), 7.83 (d, $^3J_{HH}$ = 9 Hz, 2 H), 6.88 (d, $^3J_{HH}$ = 9 Hz, 2H), 4.30 (s, 2H, CH_2), 3.17 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 190.6 (CHO), 152.0, 132.1, 128.2, 115.1(CN), 113.1, 102.0, 41.2 (CH_2), 39.3 (CH_3).

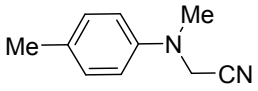
(4-Methoxyphenyl)-methyl-amino]acetonitrile (5e)



5e

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5e**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 6.88 (s, 4H, Ph), 4.08 (s, 2H, CH_2), 3.78 (s, 3H, CH_3), 2.92 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 154.5 (C-O), 142.3, 118.0, 115.5 (CN), 114.9, 55.7, 44.1 (CH_2), 40.1 (CH_3). NMR data correspond to the reported values.[12]

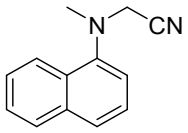
(Methyl-p-tolyl-amino)acetonitrile (5f)



5f

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5f**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.12 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 6.81 (d, 7.12 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 4.14 (s, 2H, CN), 2.97 (s, 3H, CH_3), 2.30 (s, 3H, CH_3^{Ph}); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 145.8, 130.1, 115.6, 115.6 (CN), 43.0 (CH_2), 39.6 (CH_3), 20.5 (CH_3^{Ph}). NMR data correspond to the reported values.[13]

2-(methyl-1-naphthalenylamino)acetonitrile (5g)

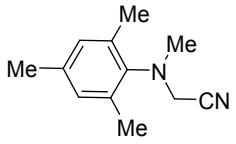


5g

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5g**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 8.12 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.87 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.67 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.50-7.56 (m, 2H), 7.46 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.34 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 4.11 (s, 2H, CH_2), 3.06 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 146.4, 134.9, 128.8, 128.7, 127.3,

126.3, 125.8, 125.5, 122.8, 117.3, 115.5 (CN), 46.3 (CH_2), 41.5 (CH_3). ESI-MS: calc. for $C_{13}H_{12}N_2$ $[M+H]^+$: 197.1073 found: 197.1022.

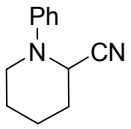
2-[Methyl(2,4,6-trimethylphenyl)amino]acetonitrile (5h)



5h

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5h**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 6.85 (s, 2H, Ph), 3.93 (s, 2H, CH_2), 2.94 (s, 3H, CH_3), 2.28 (s, 6H, CH_3), 2.25 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 144.3, 136.9, 136.0, 129.8, 117.7 (CN), 44.1 (CH_2), 40.4 (CH_3), 20.8 (CH_3), 19.0 (CH_3). NMR data correspond to the reported values.[13]

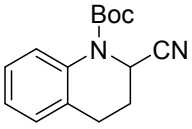
1-p-Phenylpiperidine-2-carbonitrile (5j)



5j

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5j**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.31 (t, $^3J_{HH}$ = 7.8 Hz, 2H, Ph), 7.00 (m, 3H, Ph), 4.63 (s, 1H, CH^{CN}), 3.45 (d, $^3J_{HH}$ = 12.0 Hz, 1H), 3.04 (td, $^3J_{HH}$ = 12.0 Hz, $^4J_{HH}$ = 2.4 Hz, 1H), 2.03 (m, 2H), 1.86 (m, 2H), 1. 71 (m, 2H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 149.9, 129.5, 122.3, 118.5, 117.3 (CN), 52.2 (CH^{CN}), 46.8 (CH_2^N), 29.4, 25.3, 20.3. NMR data correspond to the reported values.[12]

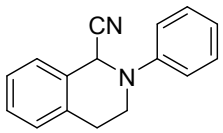
tert-Butyl 3,4-dihydro-1(2H)-quinolinecarboxylate-6-carbonitrile (5l)



5l

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5l**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.65 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.20 (m, 1H), 7.12 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.07 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 5.39 (t, $^{3}J_{HH}$ = 6.0 Hz, 1H, CH^{CN}), 2.97 (m, 1H), 2.77 (m, 1H), 2.33 (m, 1H), 2.17 (m, 1H), 1.56 (s, 9H, CH_3); **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 152.5 (C=O), 135.5, 128.7, 128.4, 126.7, 124.6, 118.4 (CN), 83.1 (C^{CH_3}), 44.8 ($C^{CN)}$, 28.2 (CH_3), 27.8, 24.9. ESI-MS: calc. for $C_{15}H_{18}N_2O_2$ $[M+H]^+$: 259.1441 found: 259.1193.

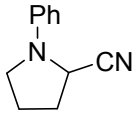
2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (5m)



5m

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5m**. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.38 (m, 2H), 7.28 (m, 4H), 7.06 (m, 2H), 7.03 (m, 1H), 5.52 (s, 1H, CH), 3.79 (m, 1H), 3.50 (m, 1H), 3.17 (m, 1H), 2.98 (dt, $^{2}J_{HH}$ = 16.2 Hz, $^{3}J_{HH}$ = 3.6 Hz, 1H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ = 148.5, 134.7, 129.7, 129.5, 128.9, 127.1, 127.0, 122.0 (CN), 117.8, 117.7, 53.3 (CH^{CN}), 44.3 (CH_2^{N}), 28.6 (CH_2). NMR data correspond to the reported values.[12]

1-Phenylpyrrolidine-2-carbonitrile (5n)



5n

Purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1) and provided **5n**. Yellow liquid. **^{1}H NMR** (600 MHz, $CDCl_3$, 298): δ = 7.2 30 (m, 2H), 6.84 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H), 6.69 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 4.44 (m, 1H, CH^{CN}), 3.47 (m, 1H), 3.38 (m, 1H), 2.43 (m, 1H), 2.21 (m, 3H). **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 298 K): δ =145.4 (Ph^{N}), 129.6, 119.4, 118.4, 112.9 (CN), 49.3 (CH^{CN}), 47.6, 31.7, 24.1. NMR data correspond to the reported values.[12]

References

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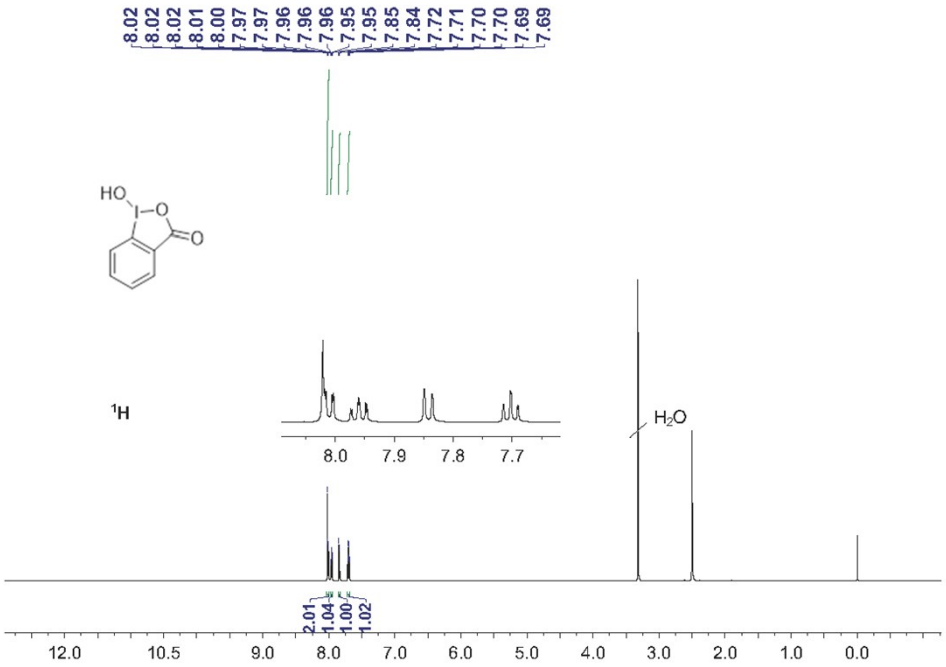
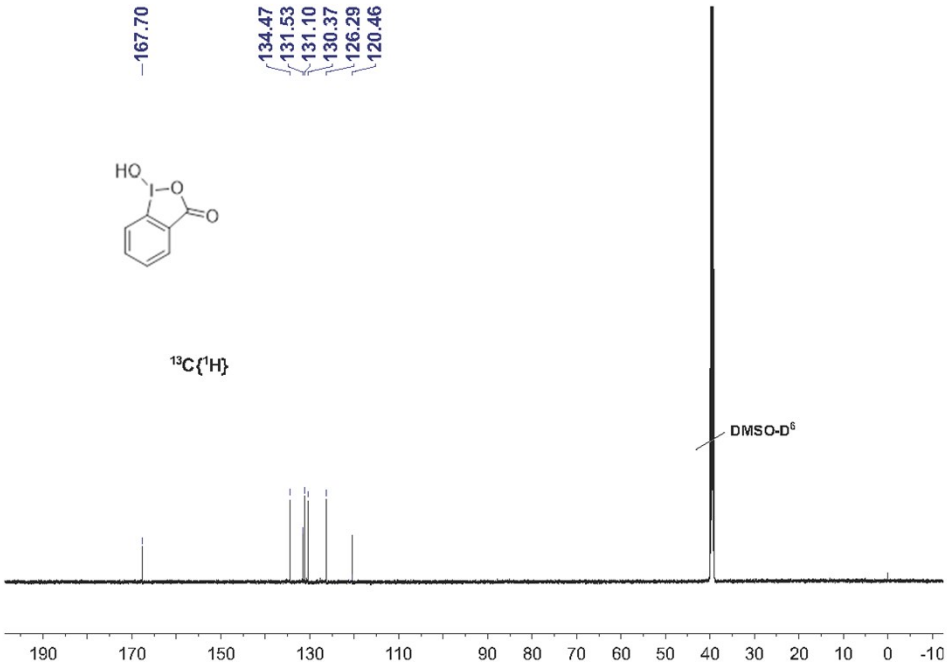
6 ^{1}H and ^{13}C NMR spectra

1-Hydroxy-1,2-benziodoxol-3-(1H)-one (2aa)

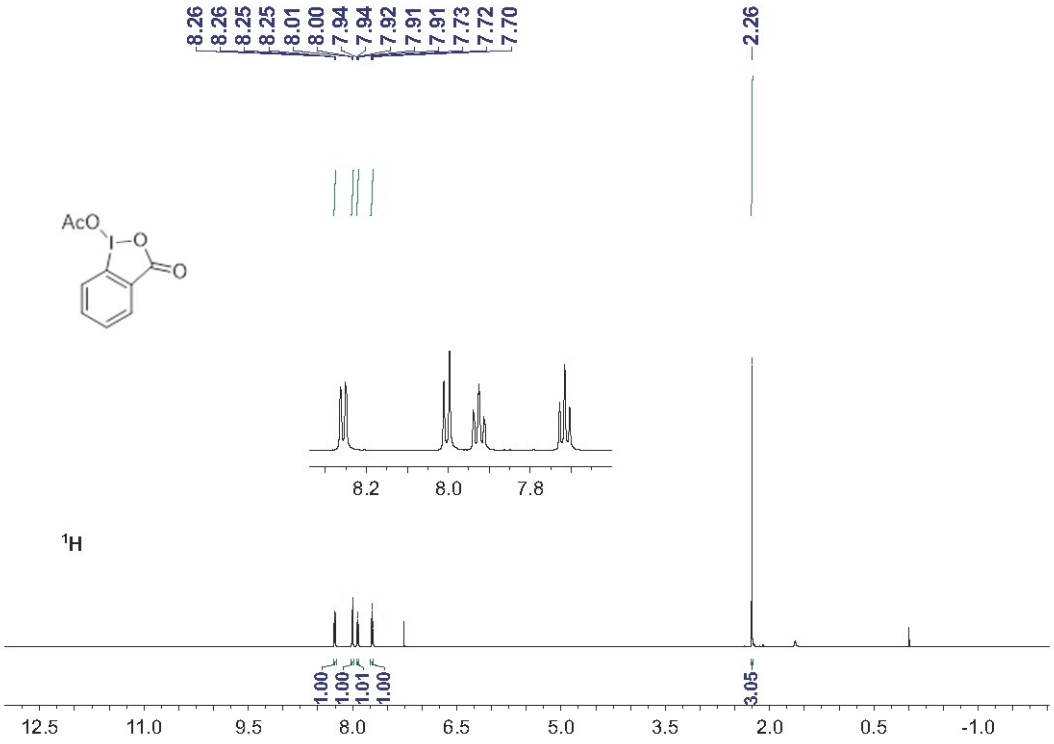


^{1}H NMR (600 MHz, DMSO-D^{6}, 298 K) of **2aa**

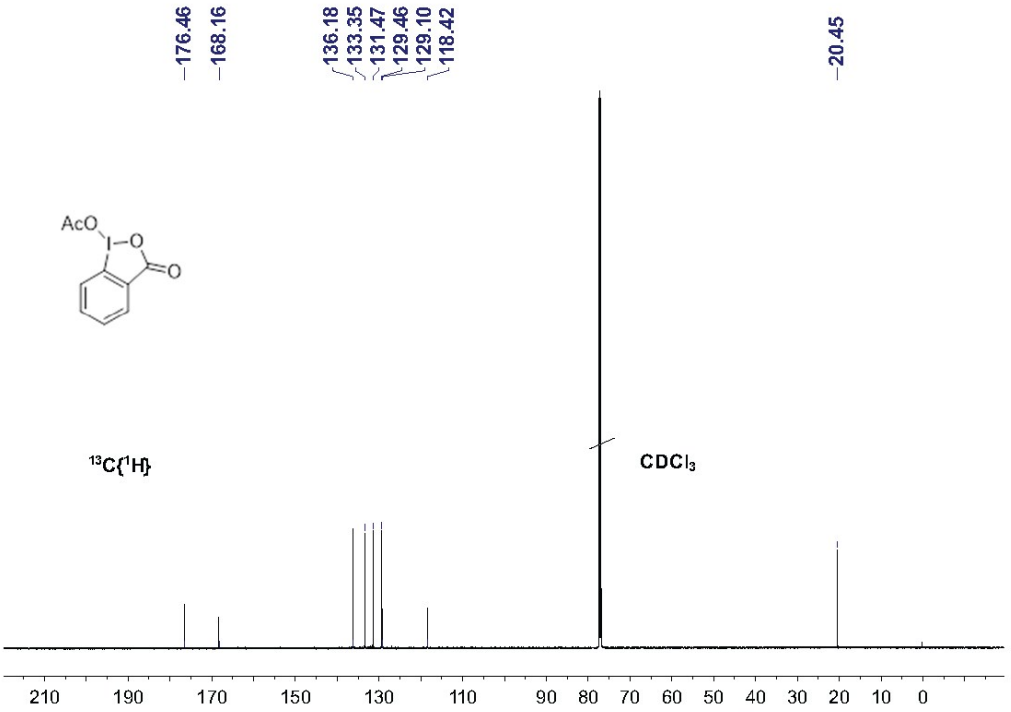


$^{13}C\{^{1}H\}$ (600 MHz, DMSO-D^{6}, 298 K) of 2aa

1-Acetoxy-1,2-benziodoxol-3-(1H)-one (2ab)

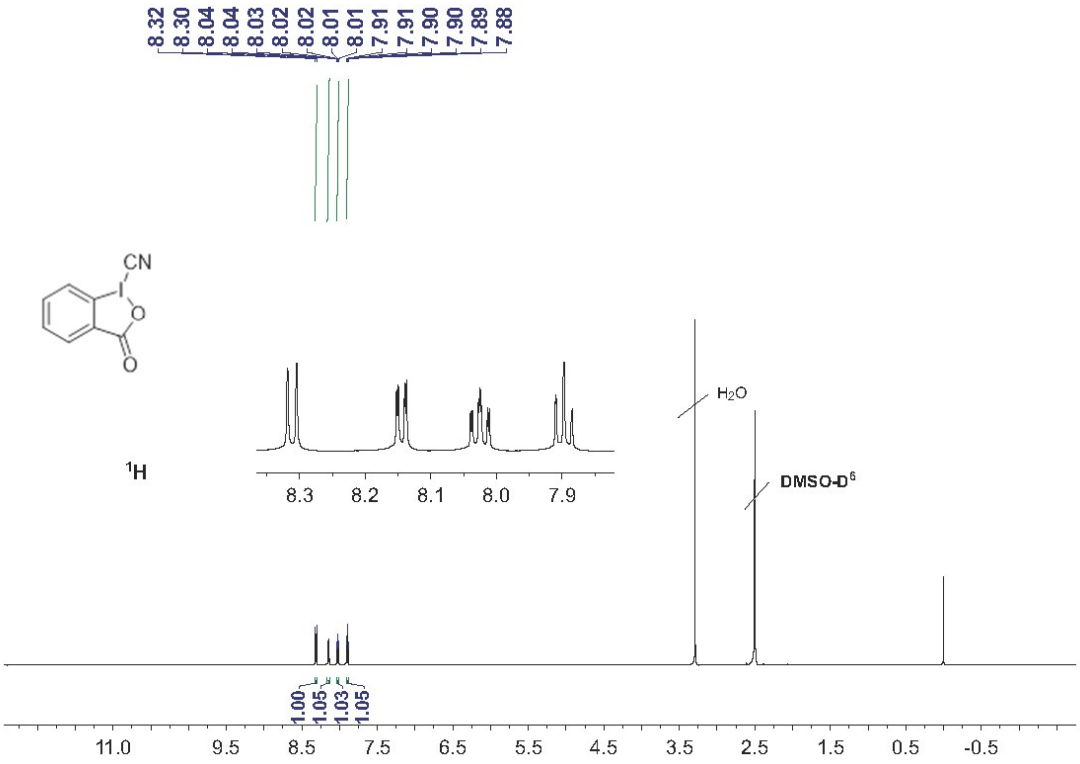


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **2ab**

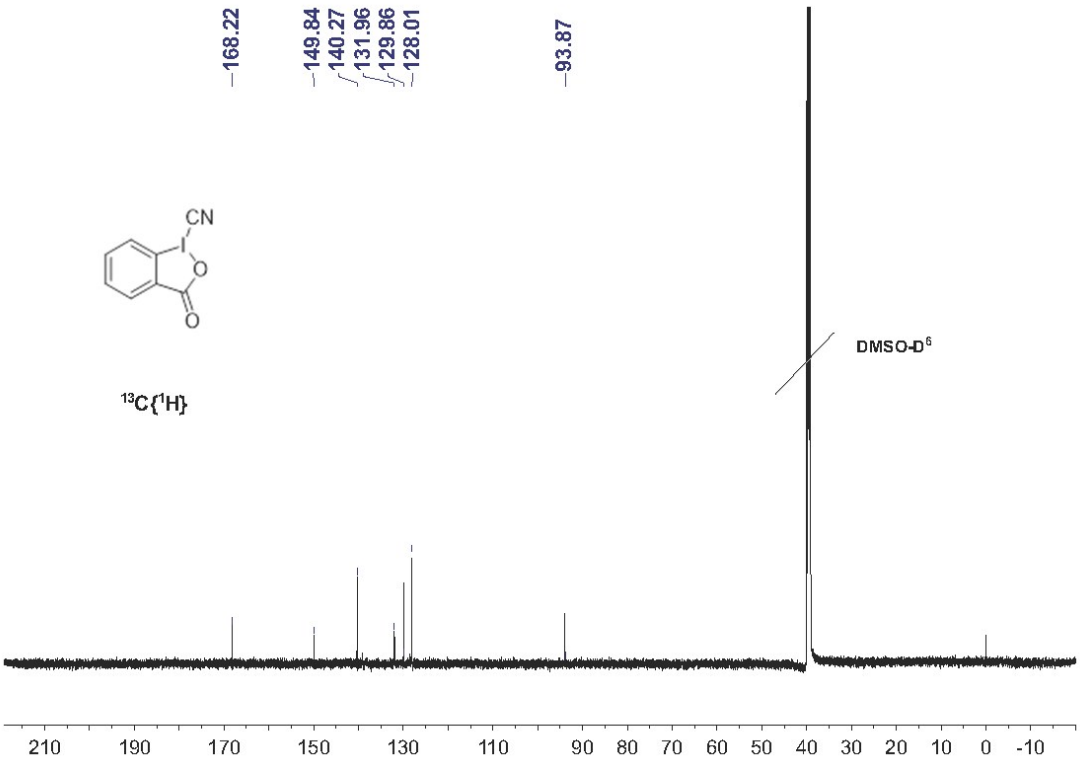


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **2ab**

1-Cyano-1,2-benziodoxol-3-(1H)-one (2a)

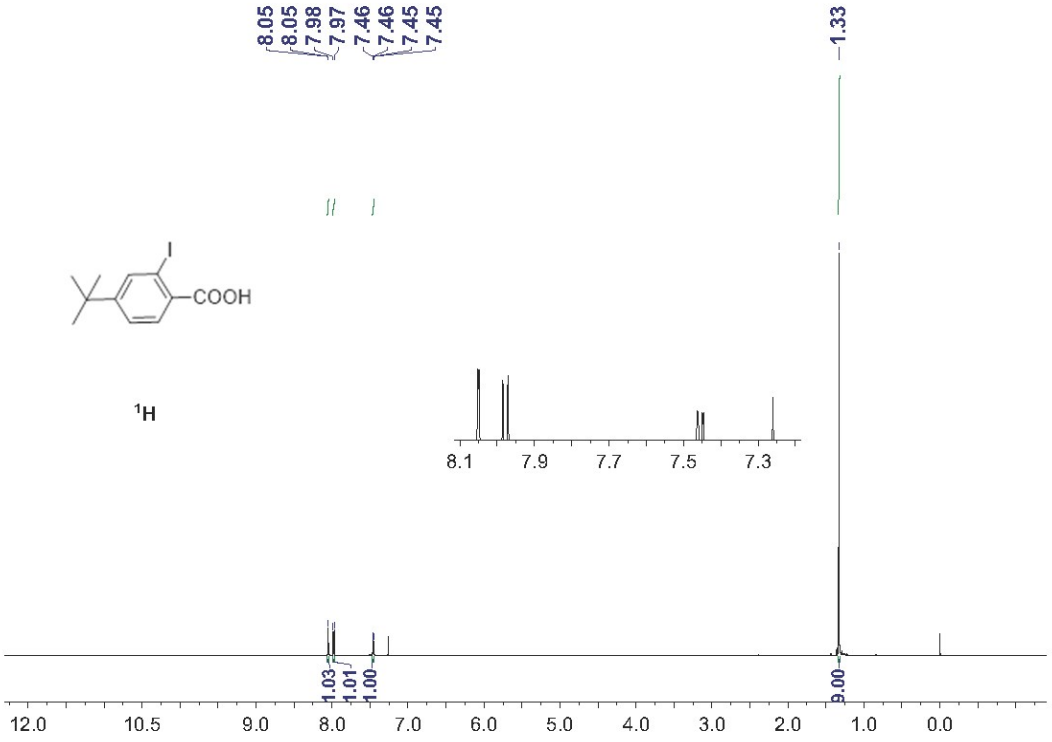


^{1}H NMR (600 MHz, DMSO-D^6, 298 K) of **2a**

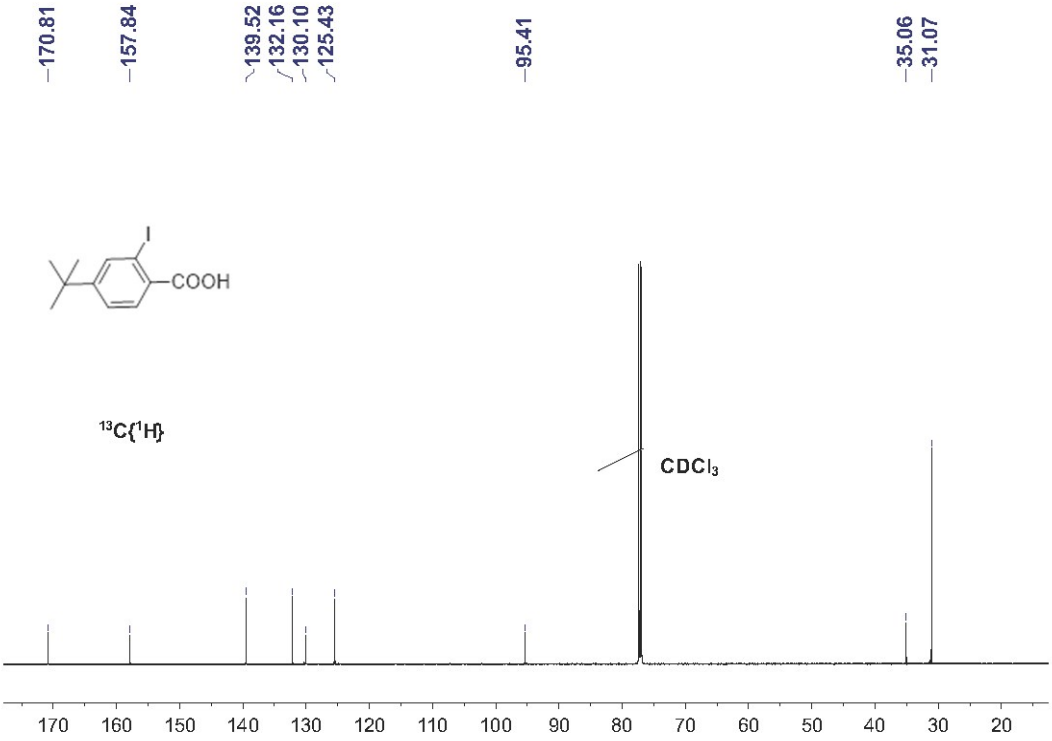


^{13}C{^{1}H} (600 MHz, DMSO-D^6, 298 K) of **2a**

4-tert-butyl-2-iodobenzoic acid (2ba)

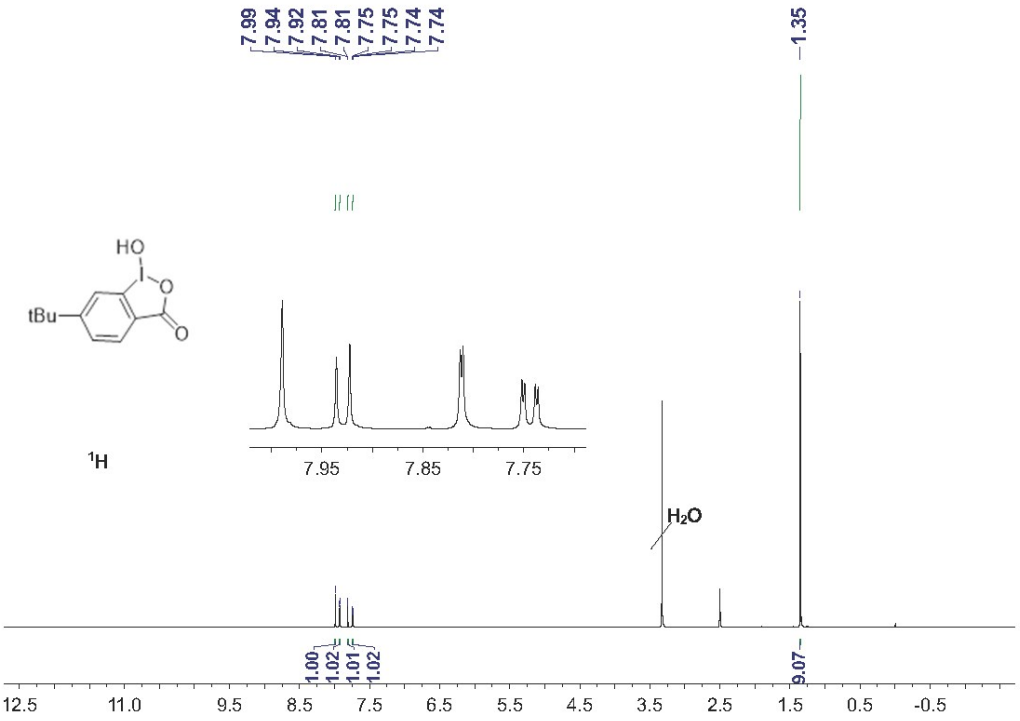


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **2ba**

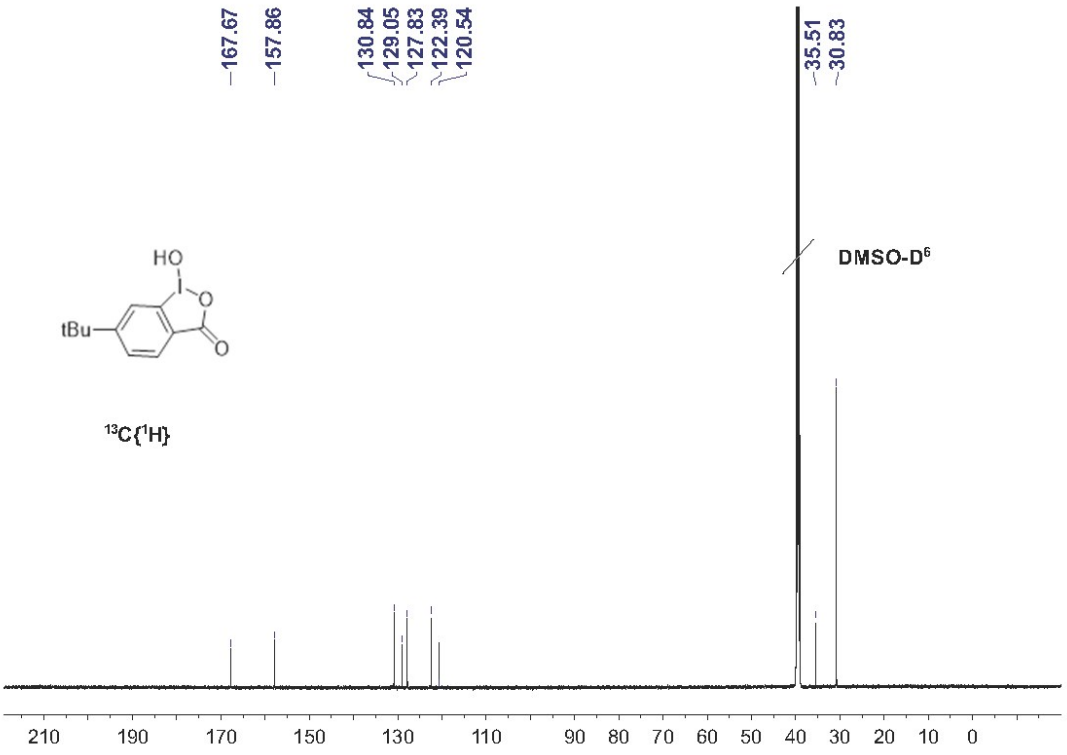


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **2ba**

4-tBu-1-hydroxy-1,2-benziodoxol-3-(1H)-one (2bb)

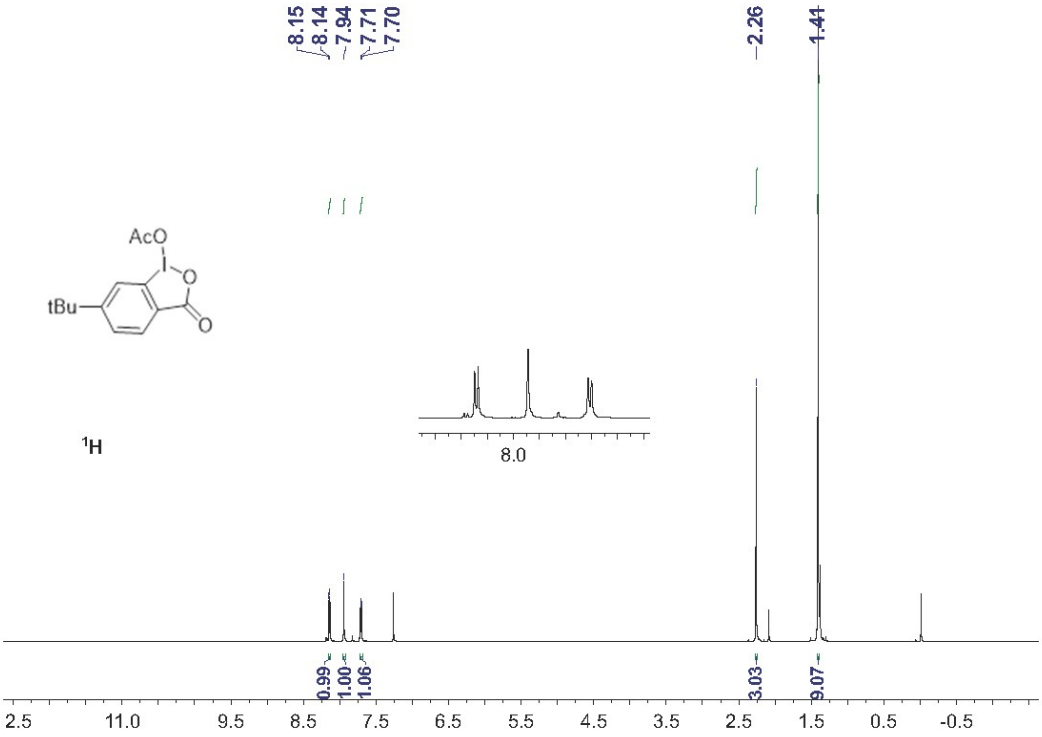


^{1}H NMR (600 MHz, DMSO-D^{6}, 298 K) of **2bb**

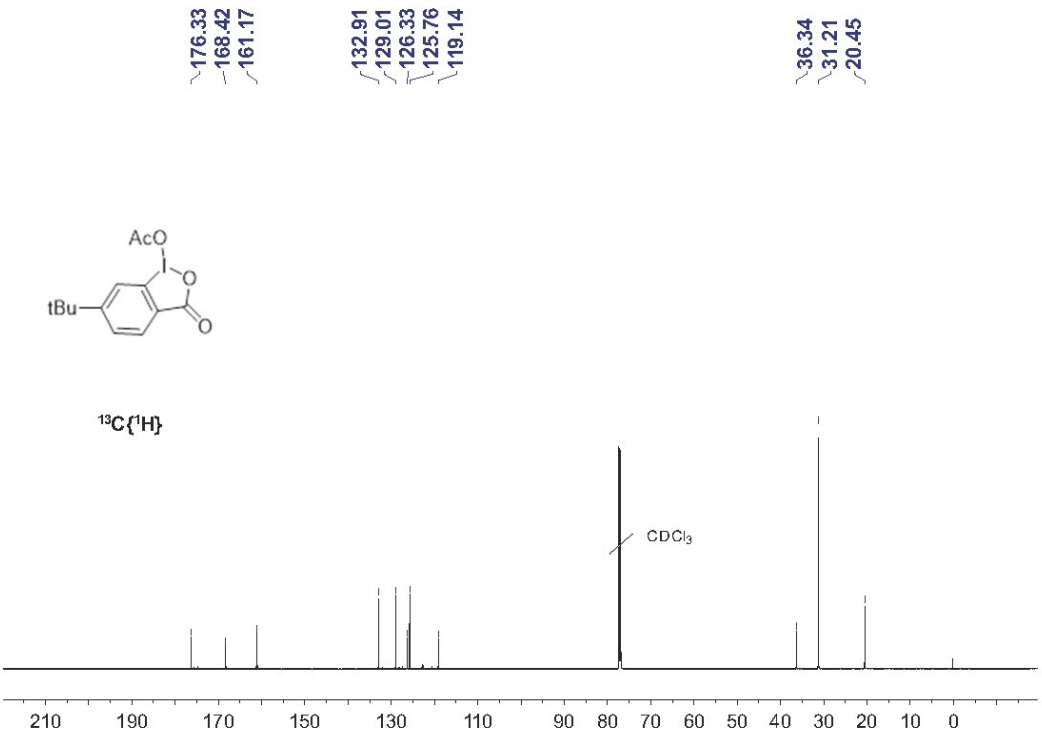


^{13}C{^{1}H} (600 MHz, DMSO-D^{6}, 298 K) of **2bb**

4-tBu-1-Acetoxy-1,2-benziodoxol-3-(1H)-one (2bc)

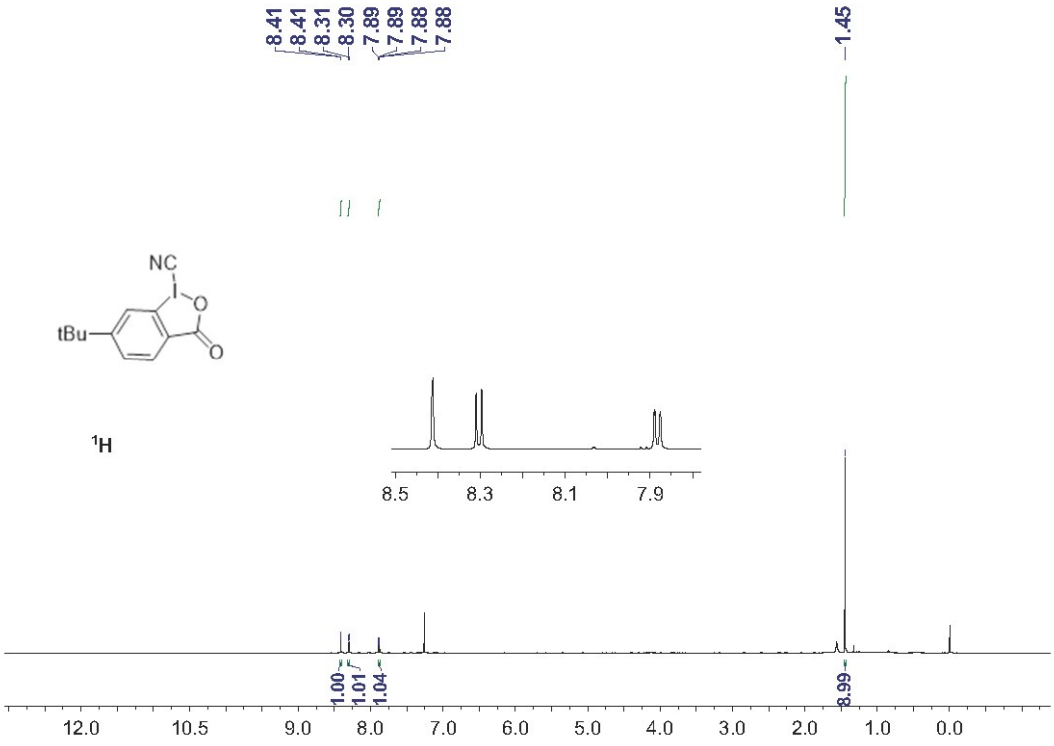


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **2bc**

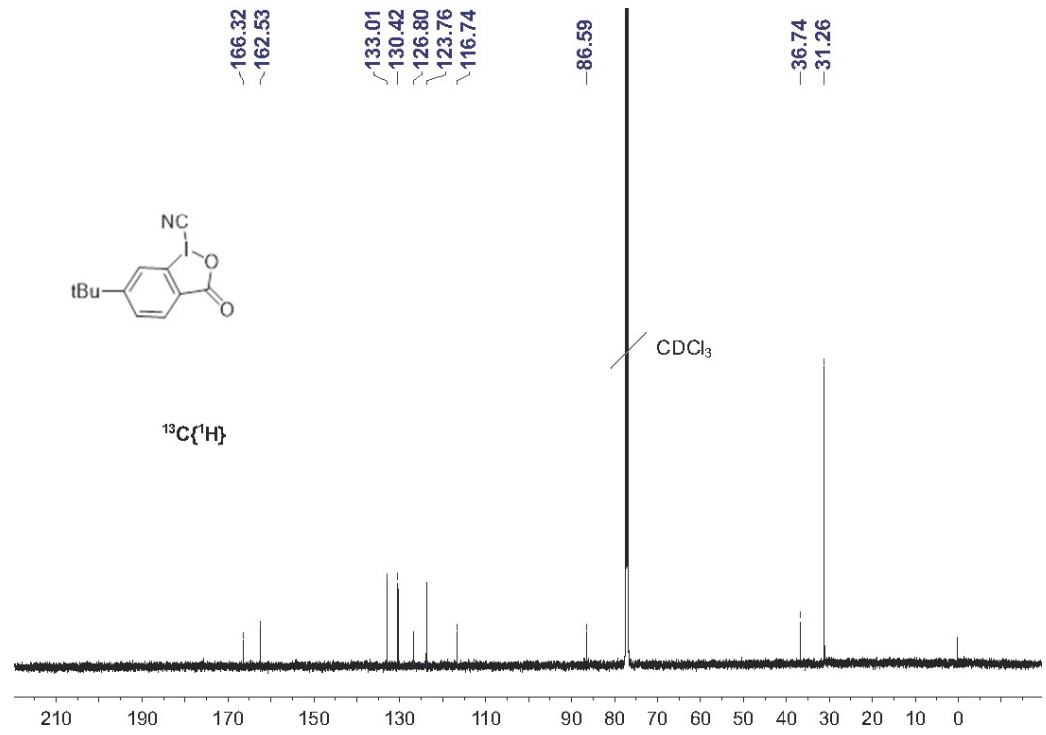


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **2bc**

4-tBu-1-Acetoxy-1,2-benziodoxol-3-(1H)-one (2b)

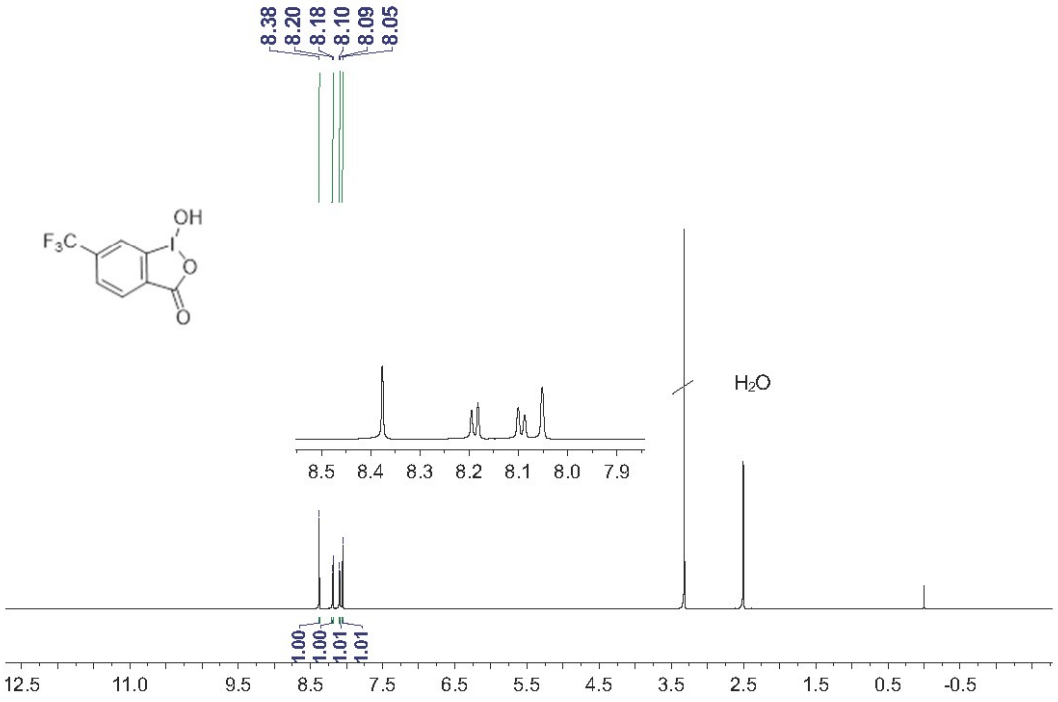


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **2b**

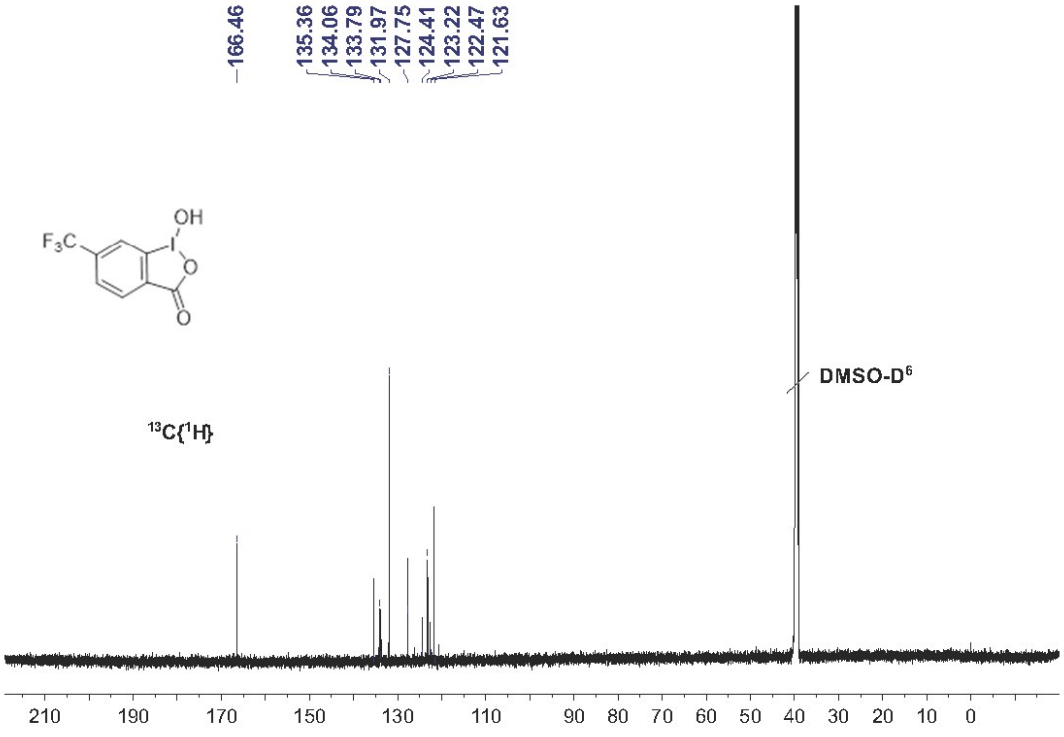


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **2b**

4-Trifluoromethyl-1-hydroxy-1,2-benziodoxol-3-(1H)-one (2ca)

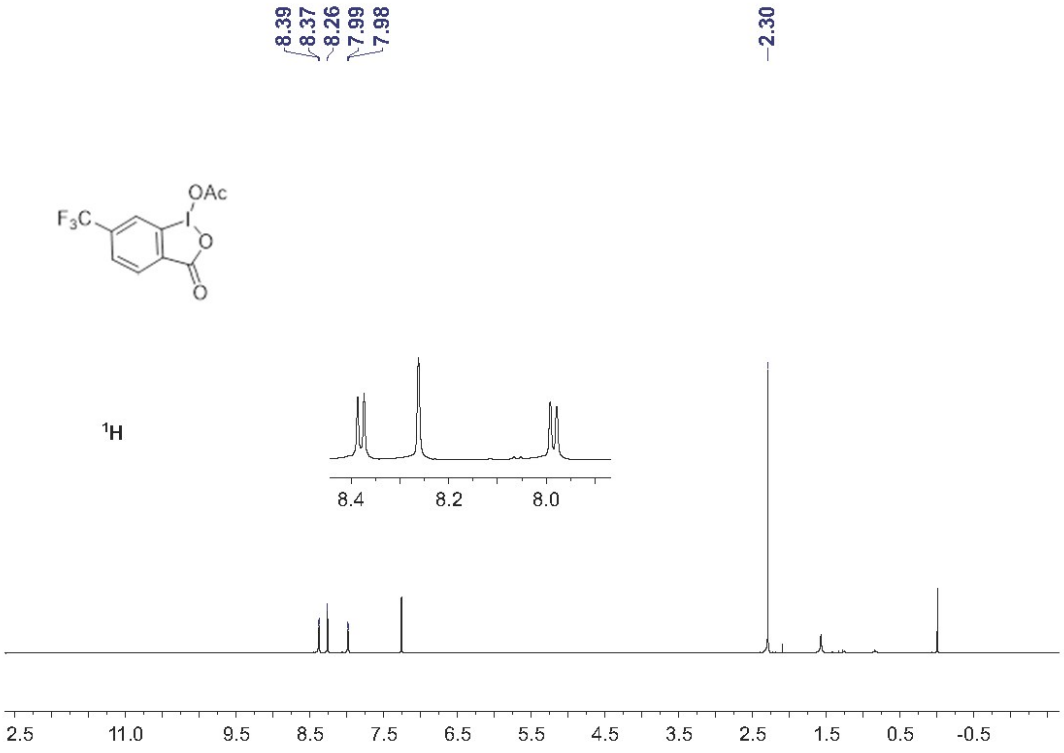


^{1}H NMR (600 MHz, DMSO-D^{6}, 298 K) of **2ca**

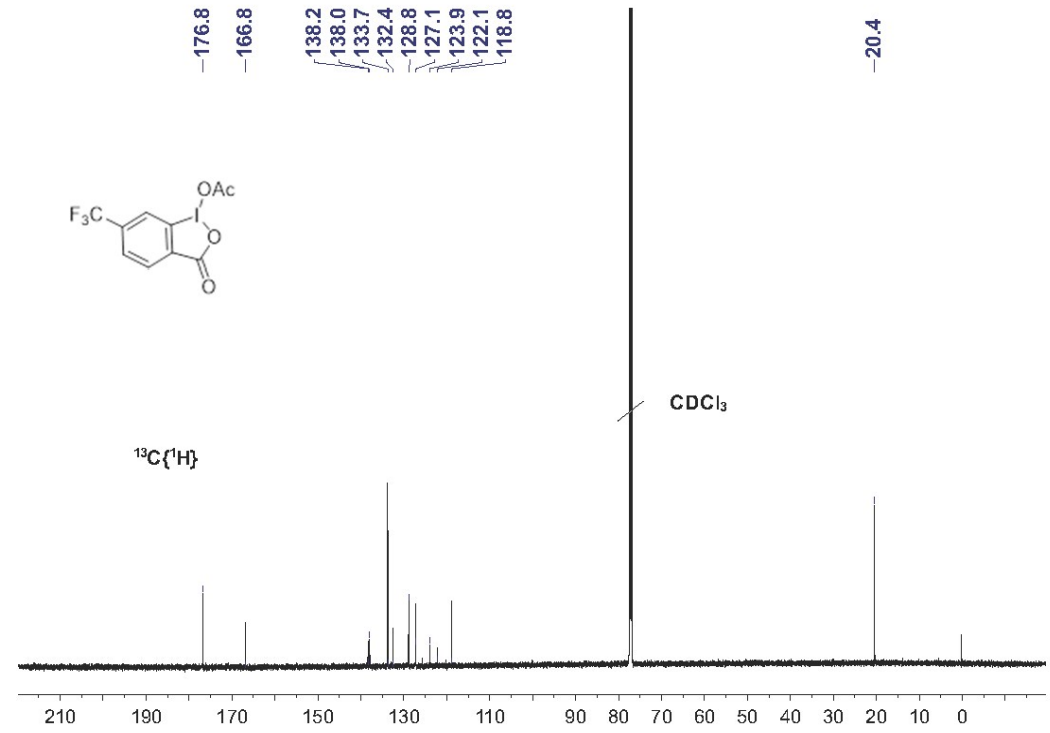


^{13}C{^{1}H} (600 MHz, DMSO-D^{6}, 298 K) of **2ca**

4-Trifluoromethyl-1-acetoxy-1,2-benziodoxol-3-(1H)-one (2cb)

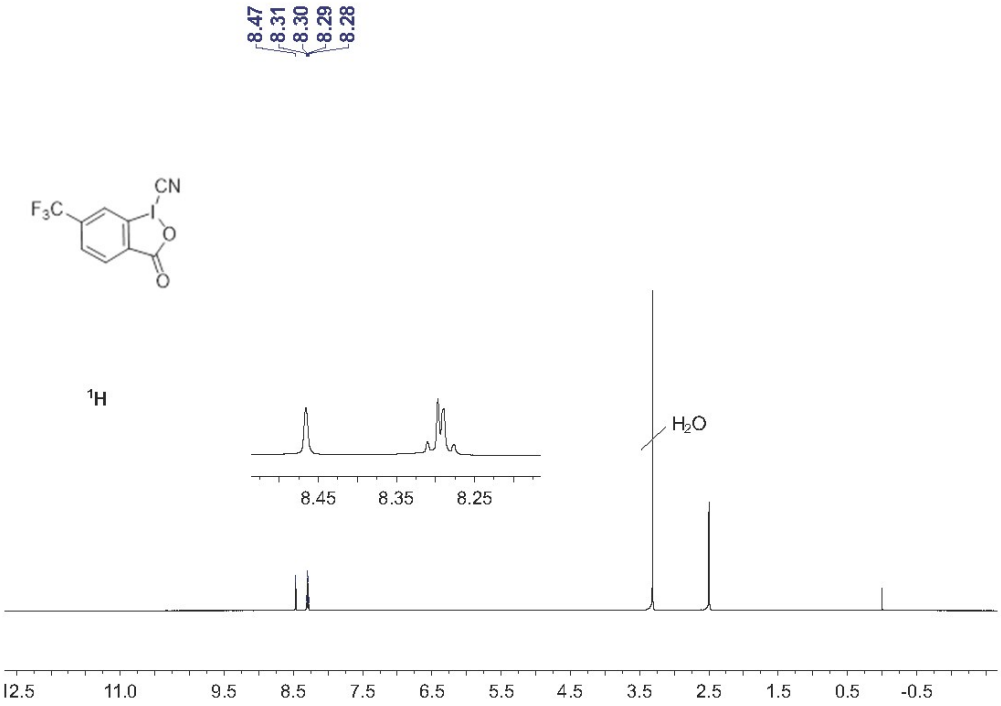


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **2cb**

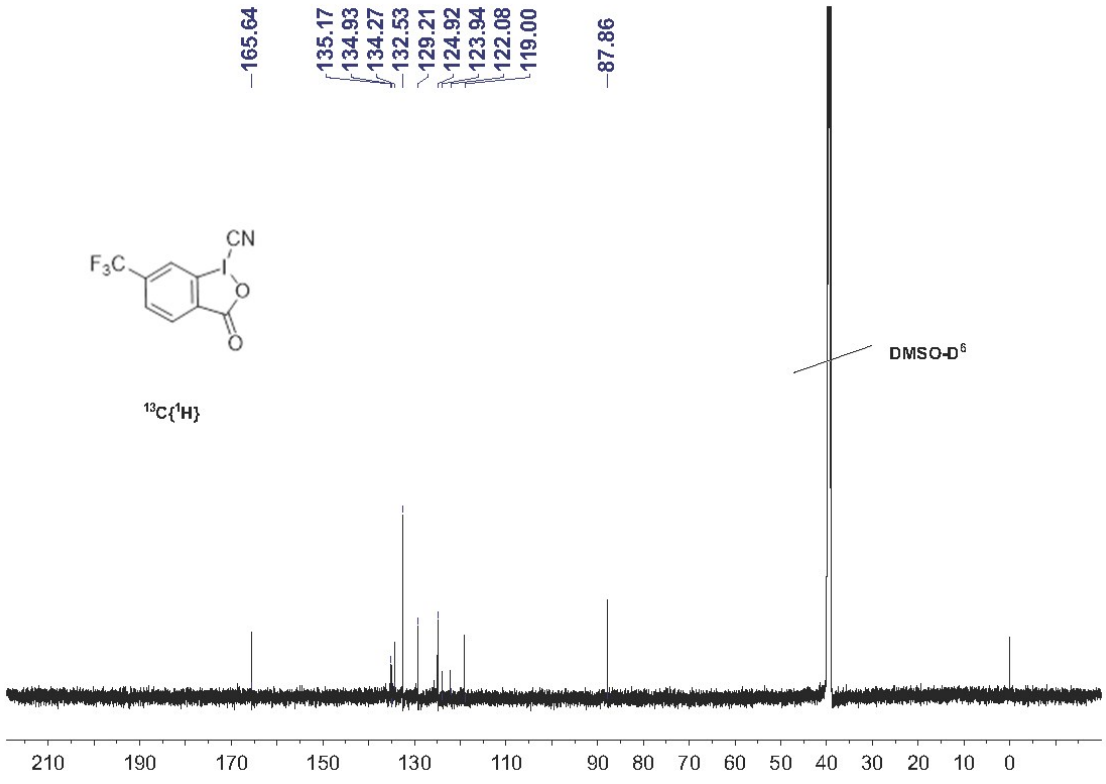


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **2cb**

4-Trifluoromethyl-1-cyano-1,2-benziodoxol-3-(1H)-one (2c)

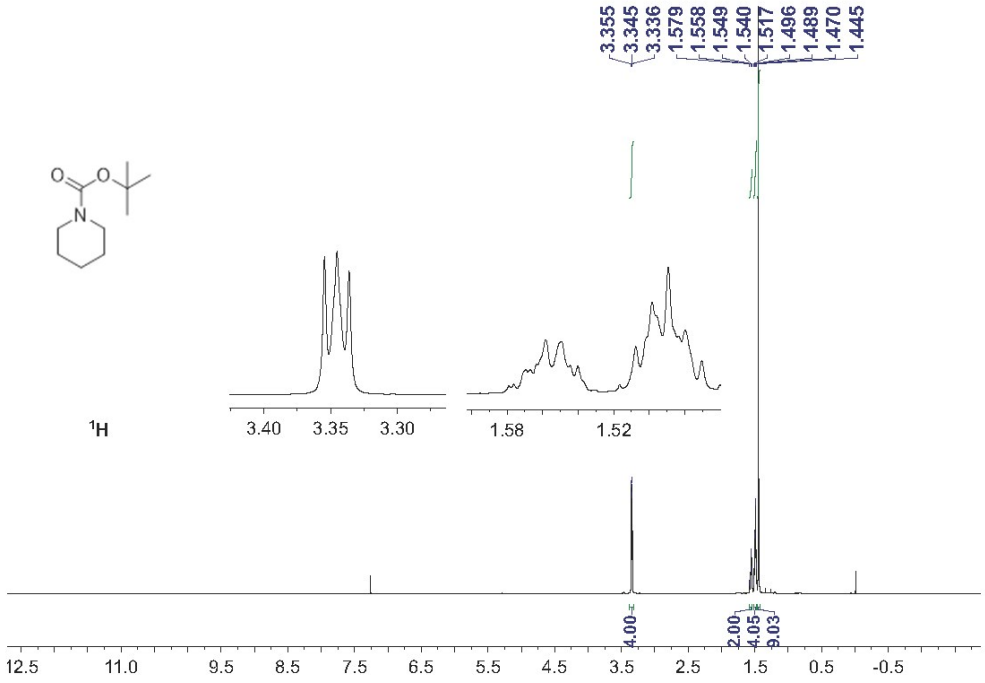


^{1}H NMR (600 MHz, DMSO-D^{6}, 298 K) of **2c**

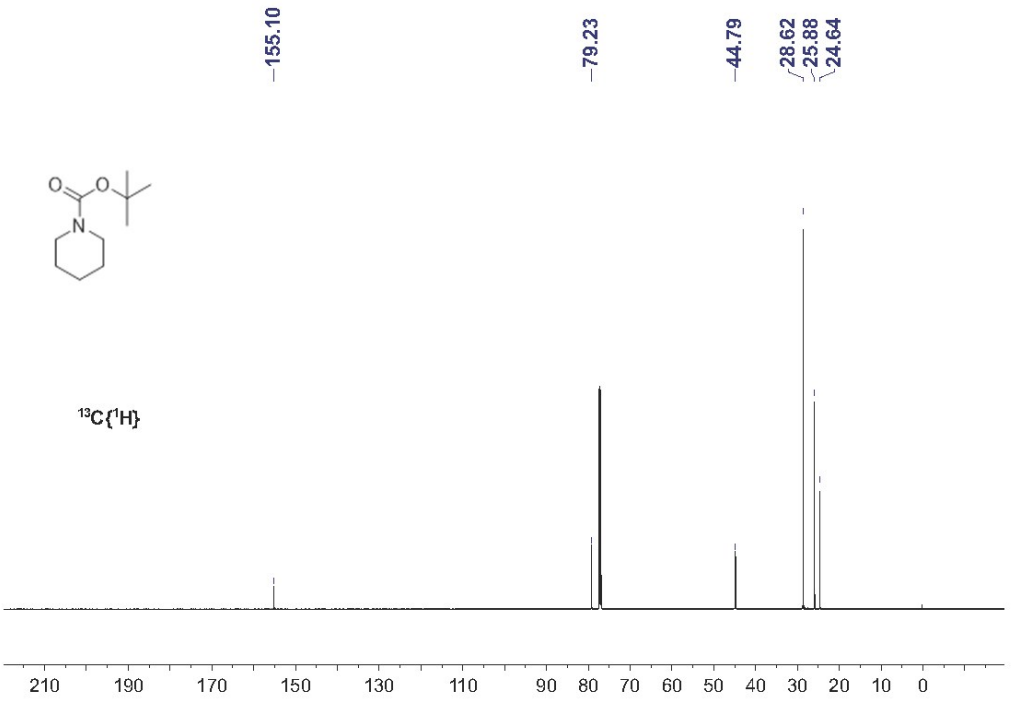


^{13}C{^{1}H} (600 MHz, DMSO-D^{6}, 298 K) of **2c**

tert-butyl piperidine-1-carboxylate (4k)

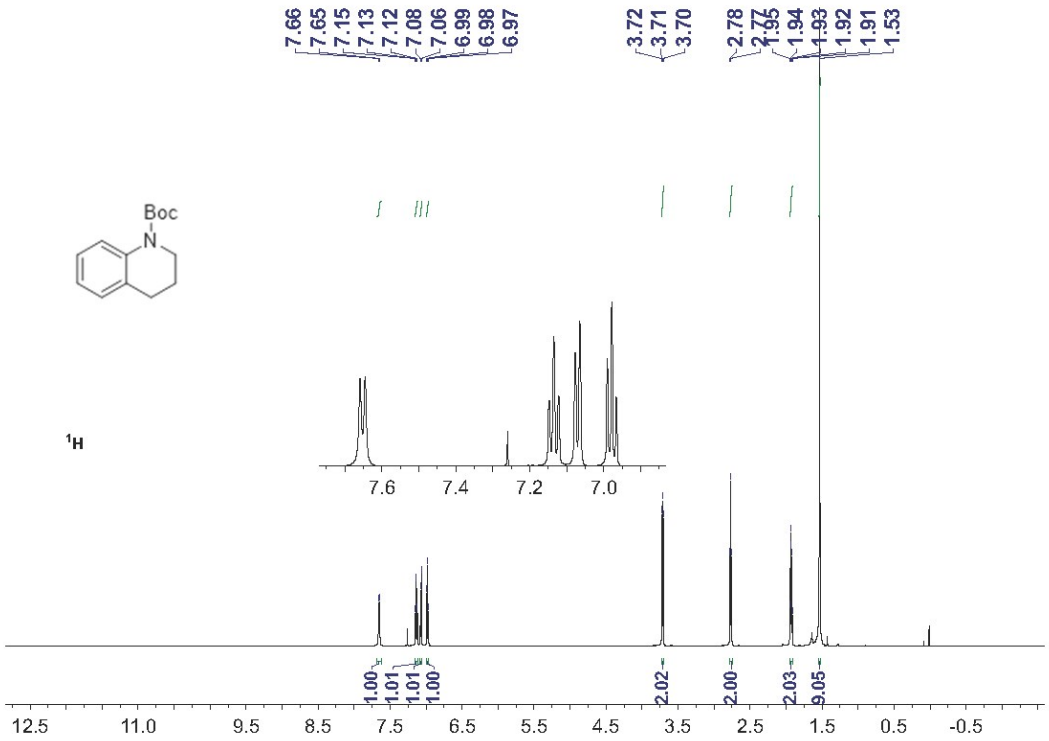


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4k**

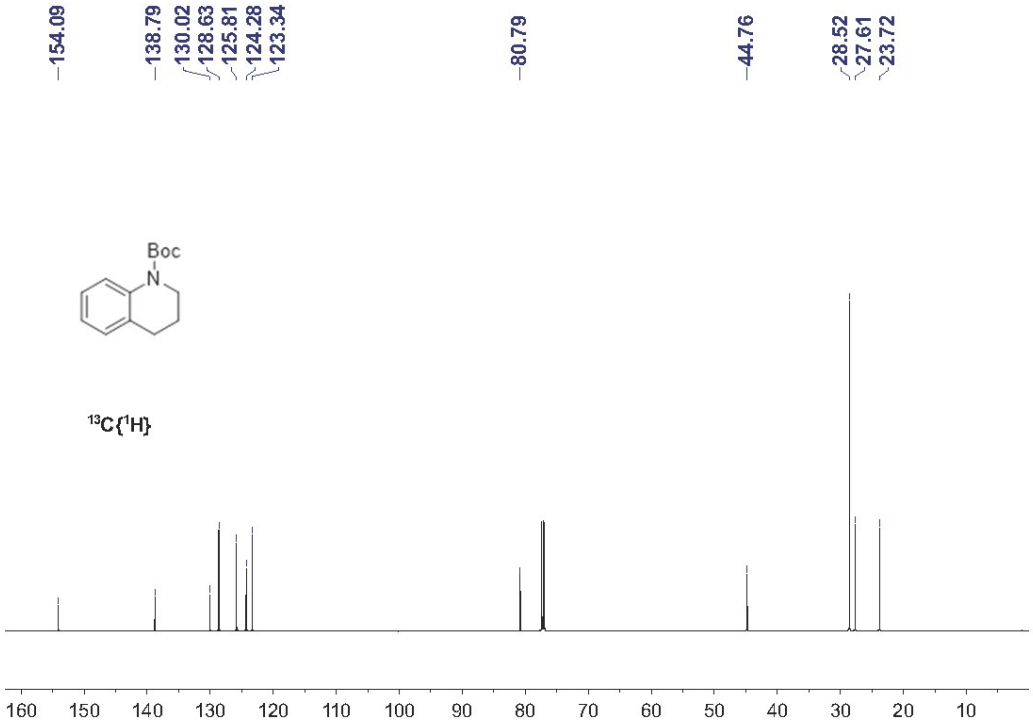


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **4k**

(tert-butyl 3,4-dihydro-1(2H)-quinolinecarboxylate) (4l)

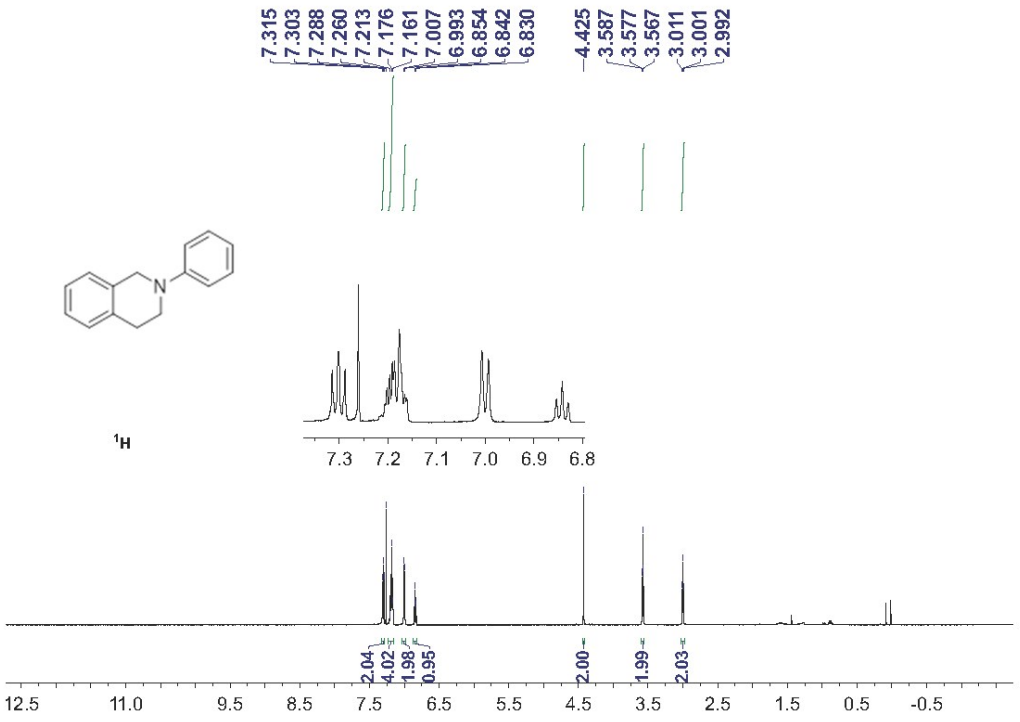


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4l**

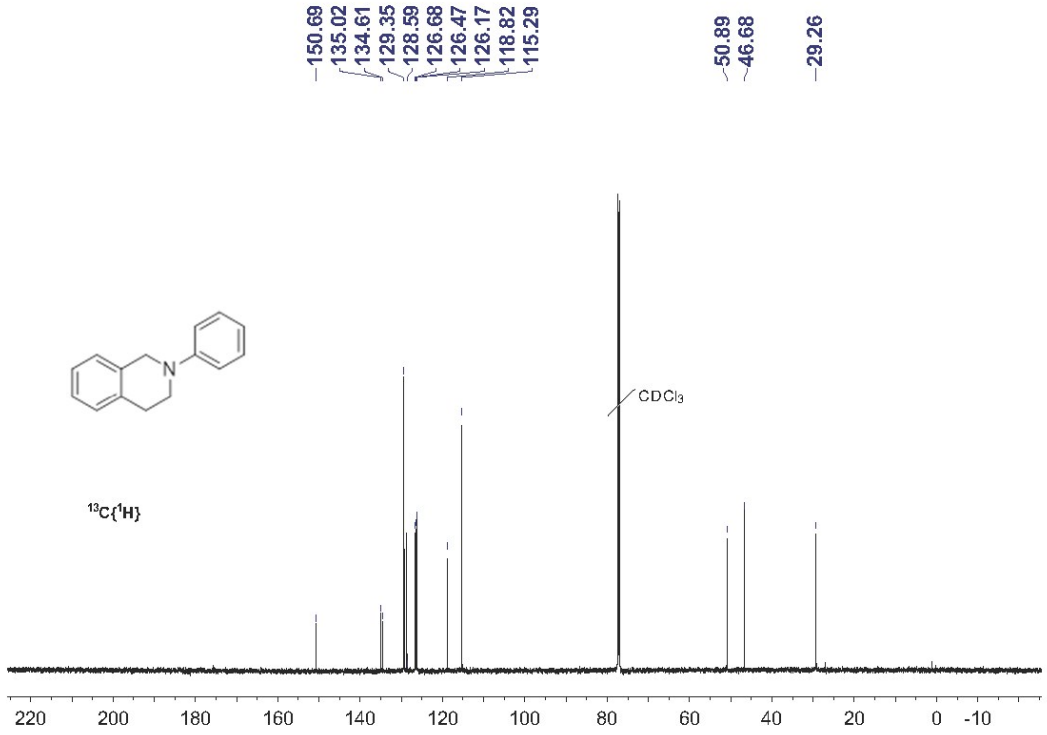


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **4l**

N-Phenyl-1,2,3,4-tetrahydroisoquinoline (4m)

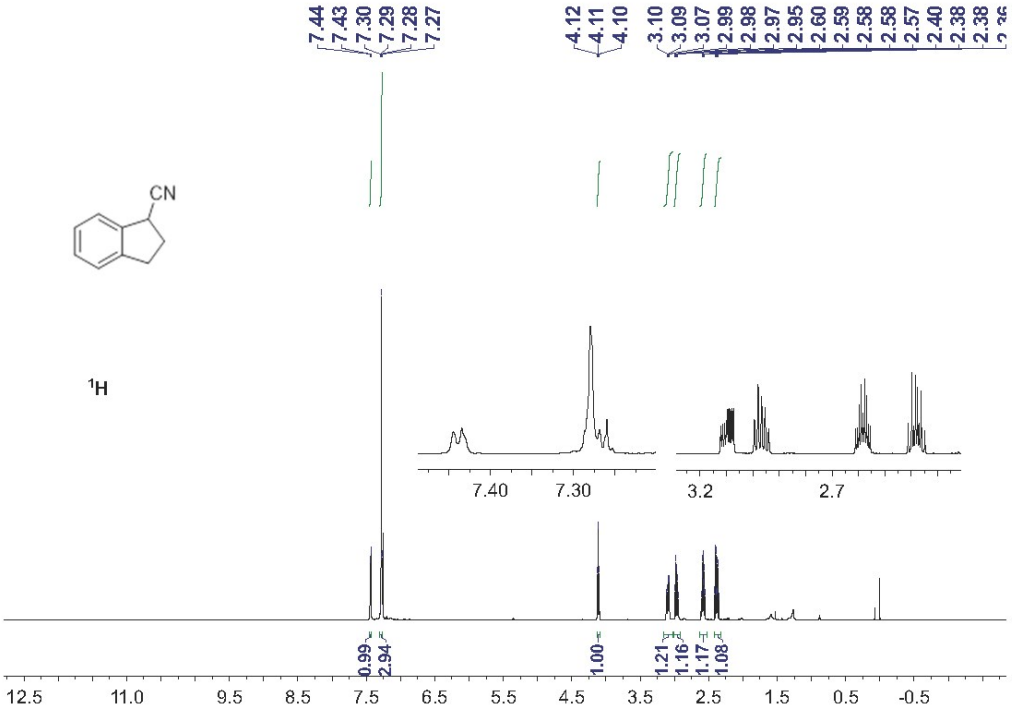


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **4m**

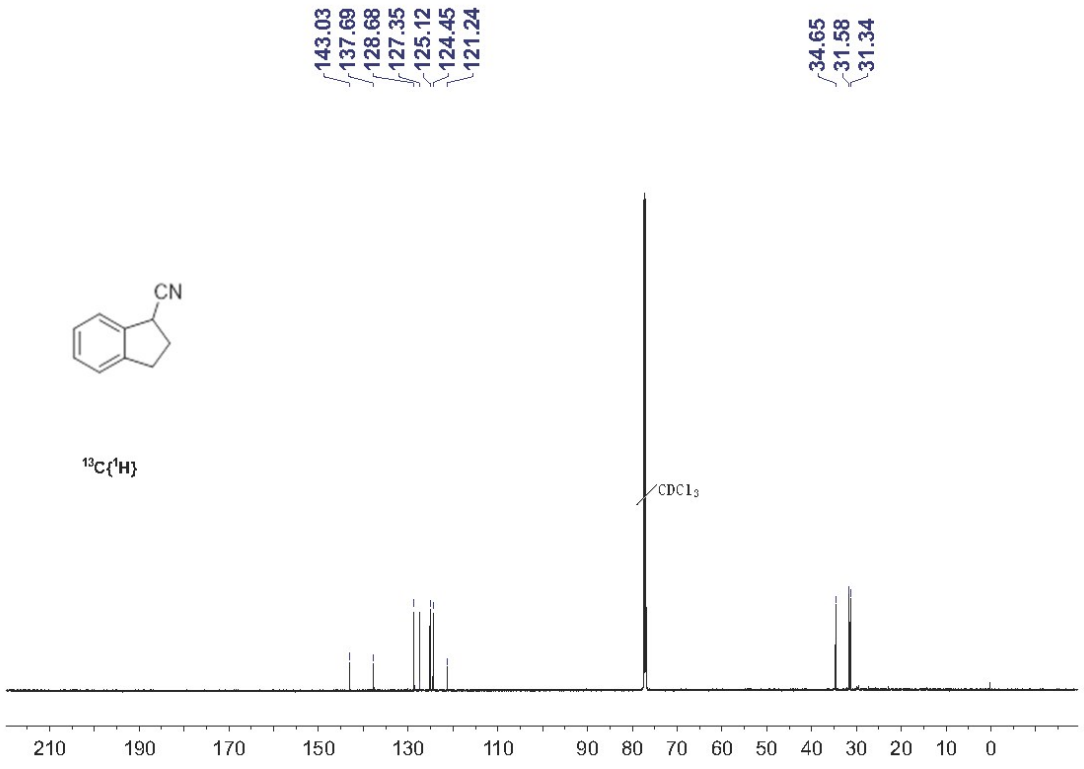


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **4m**

2,3-Dihydro-1H-indene-1-carbonitrile (3d)

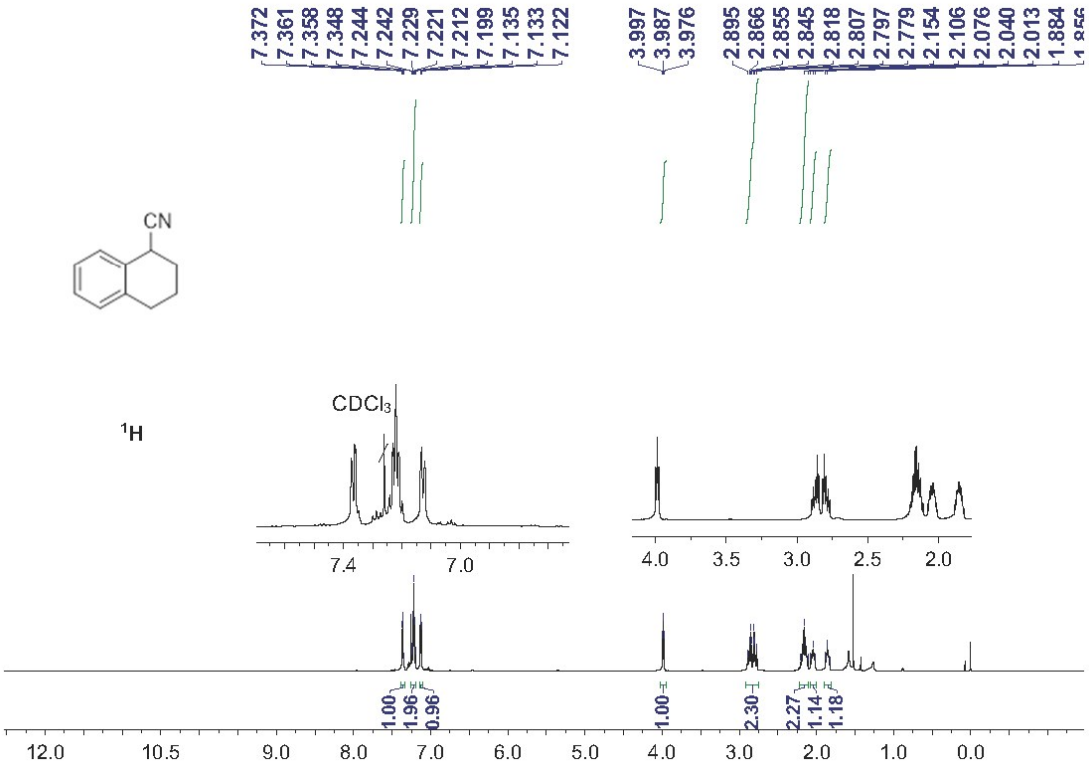


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3d**

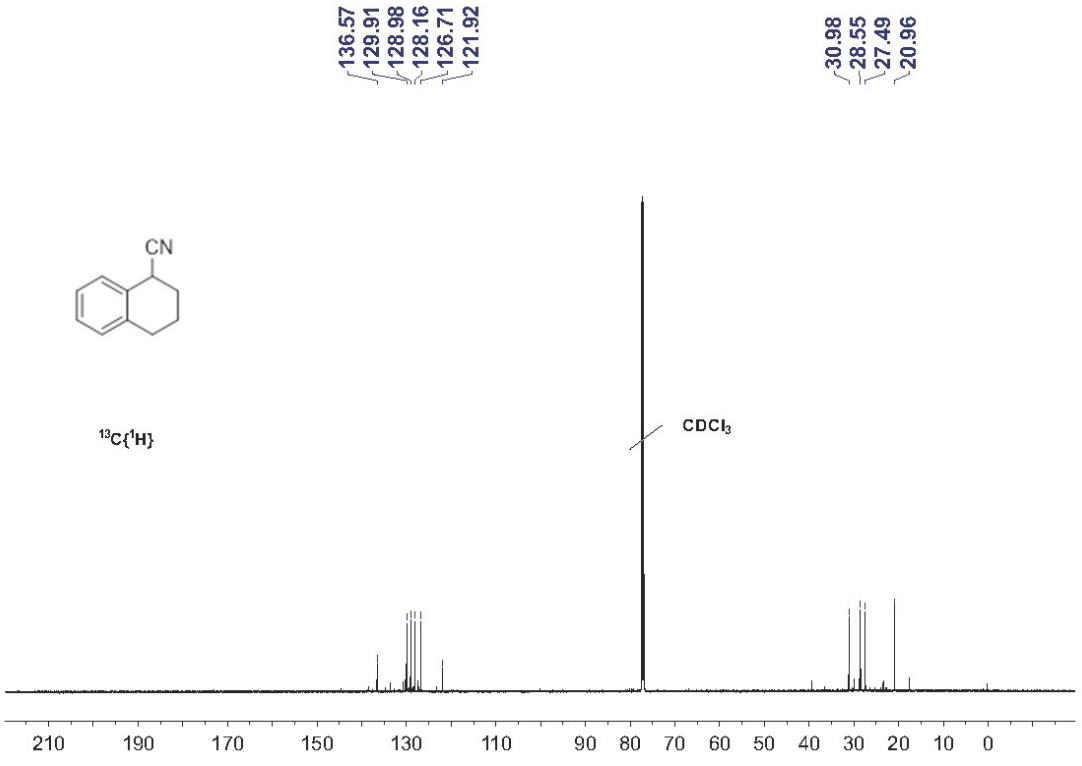


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **3d**

Tetrahydronaphthalene- 1-carbonitrile (3e)

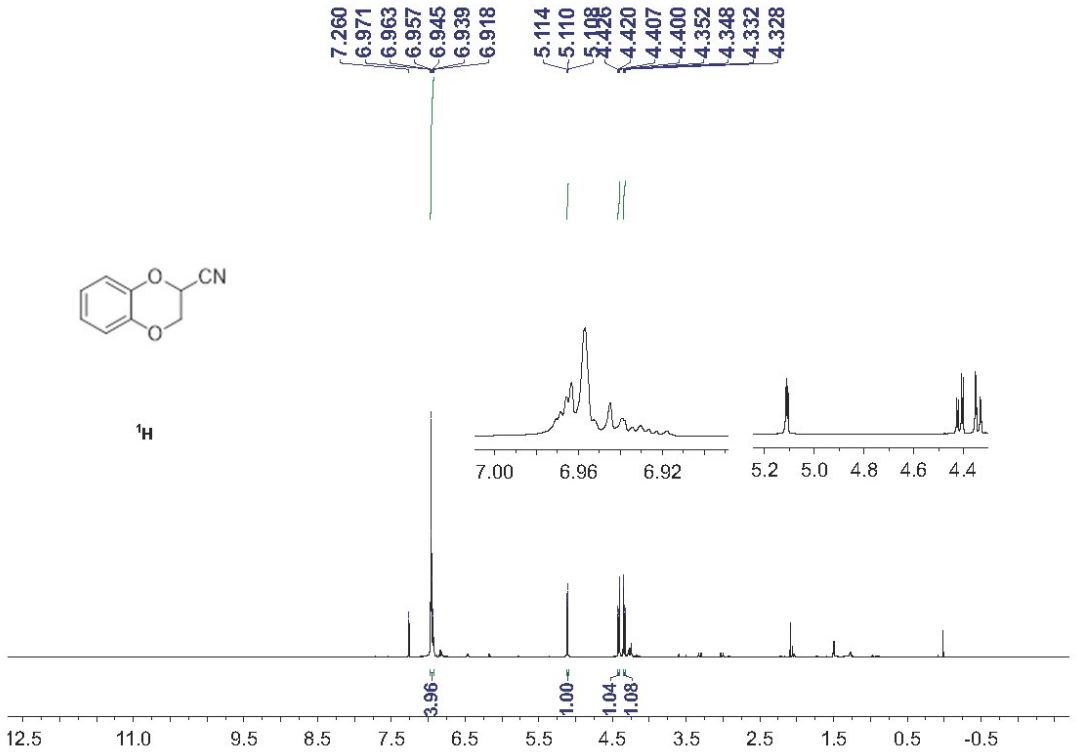


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3e**

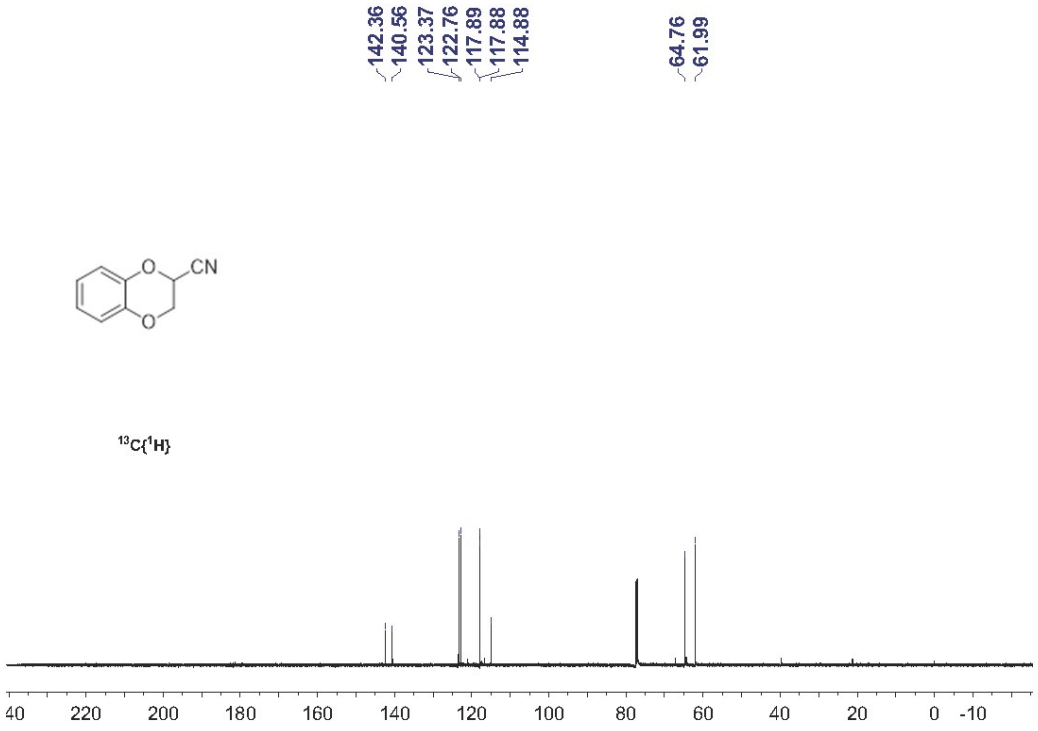


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **3e**

1,4-Benzodioxan-2-carbonitrile (3j)



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3j**



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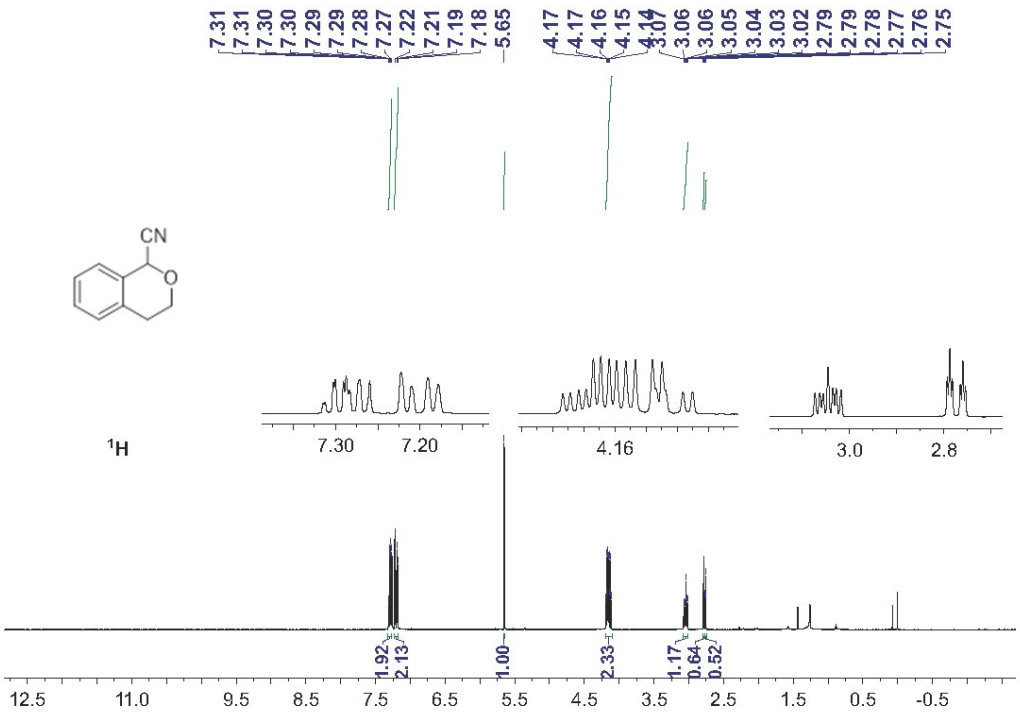
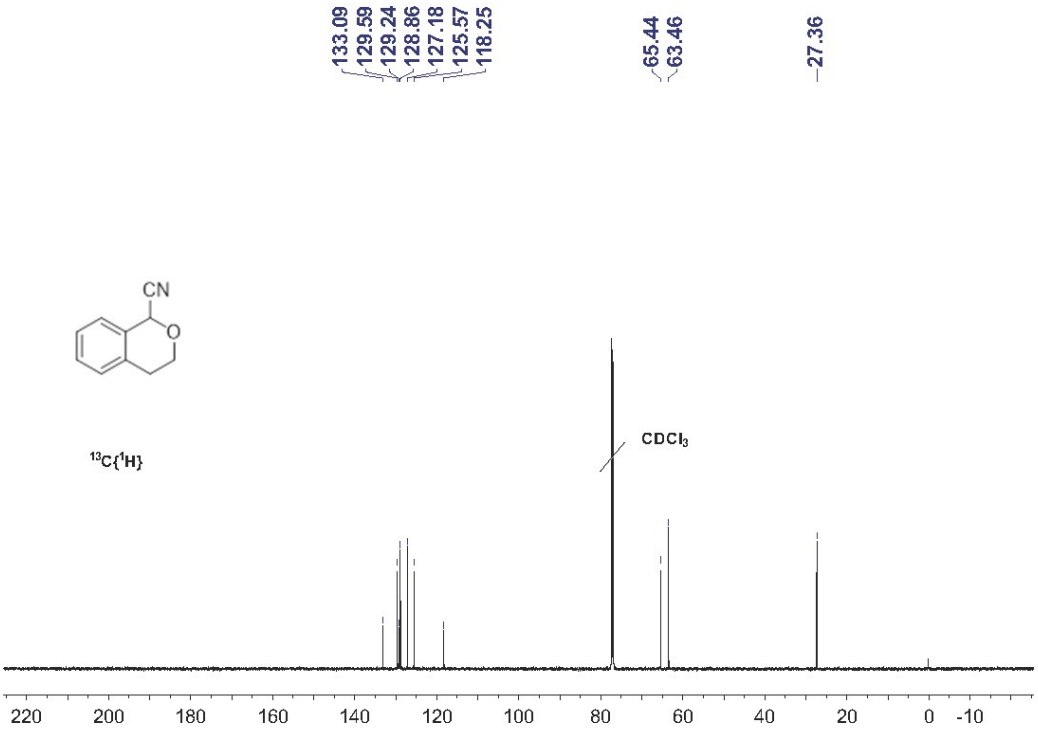
1-Cyanoisochroman (3k)

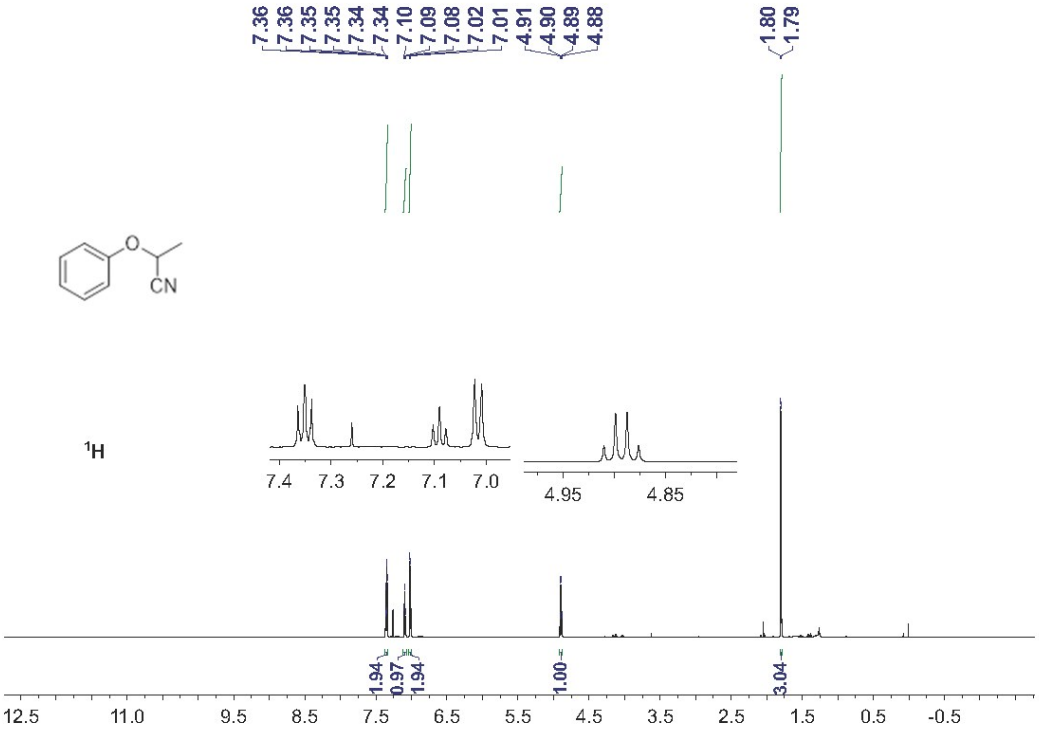


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3k**

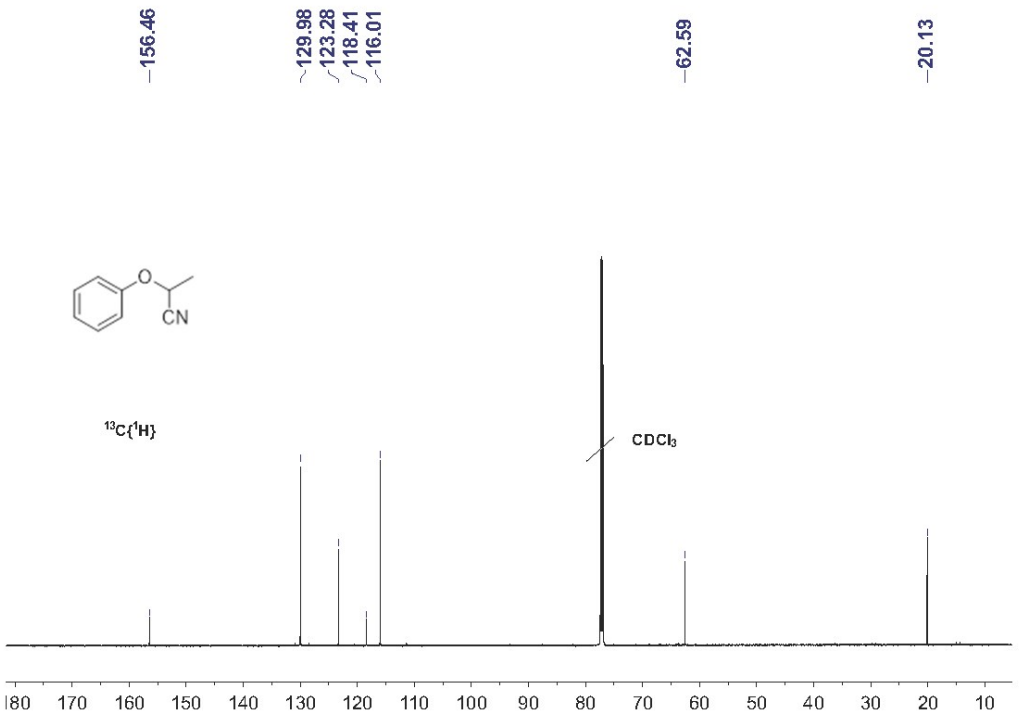


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **3k**

2-Phenoxy-propanenitrile (3l)

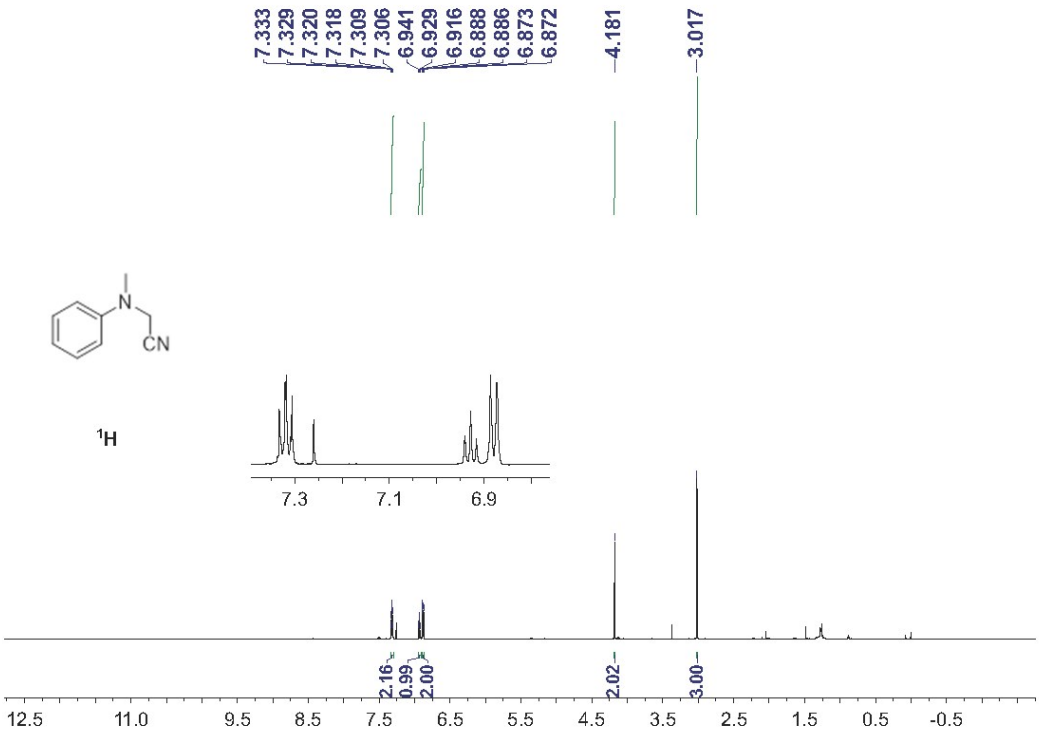


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **3l**

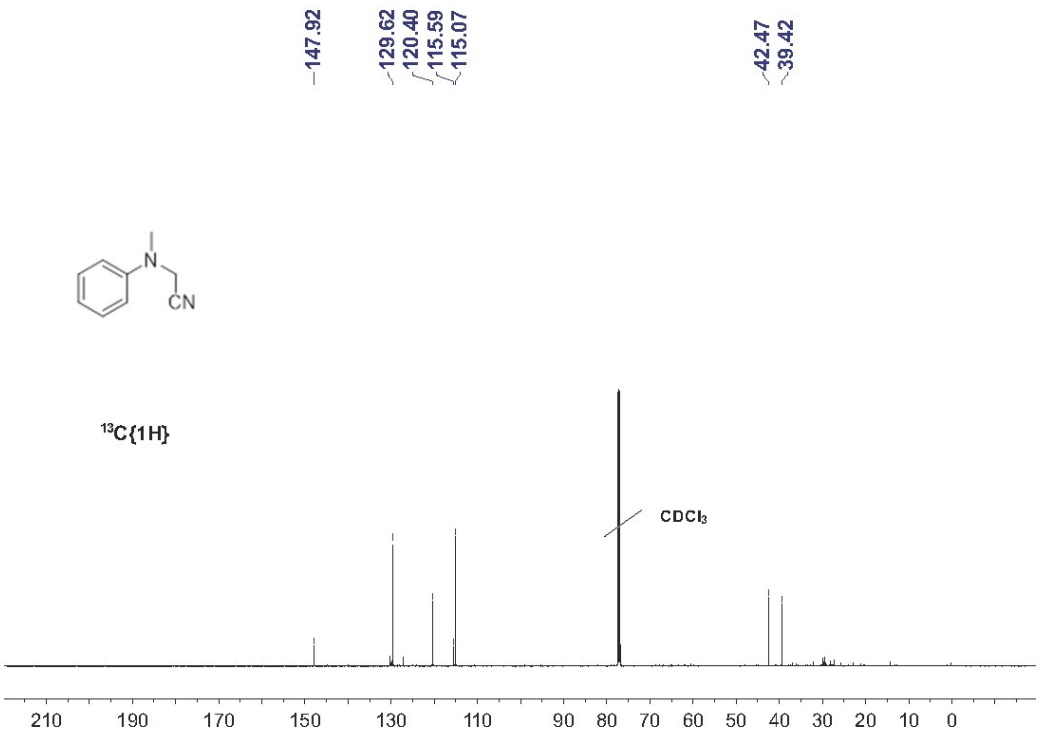


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **3l**

N-Methyl-N-phenylaminoacetonitrile (5a)

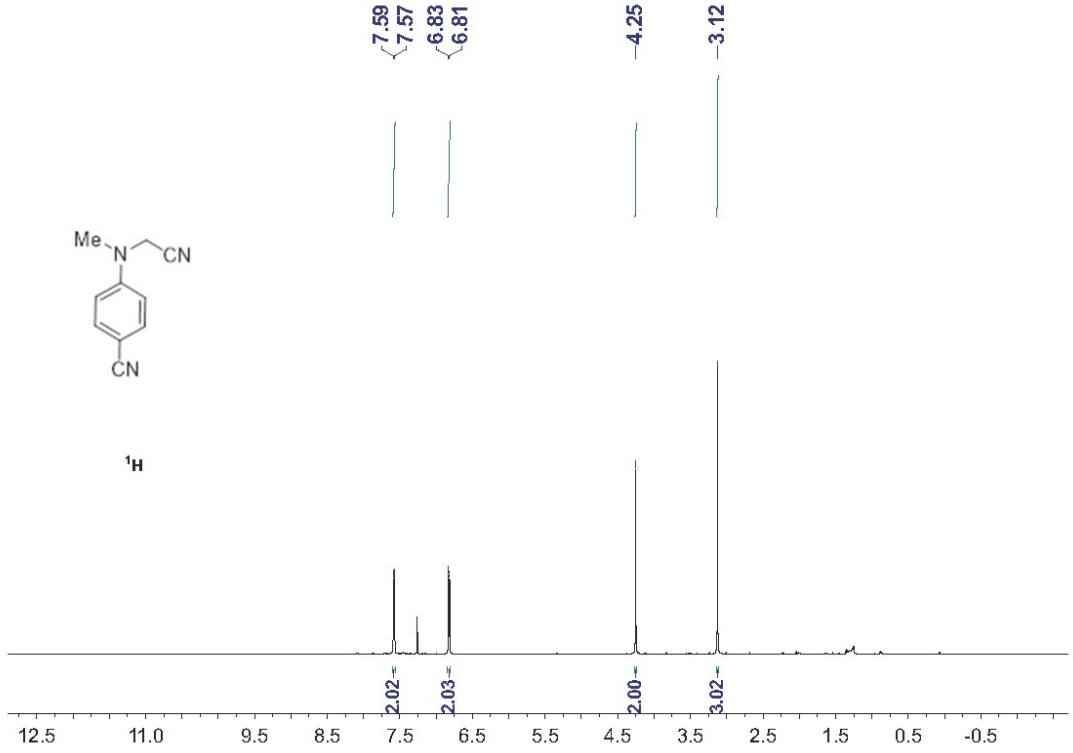


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5a**

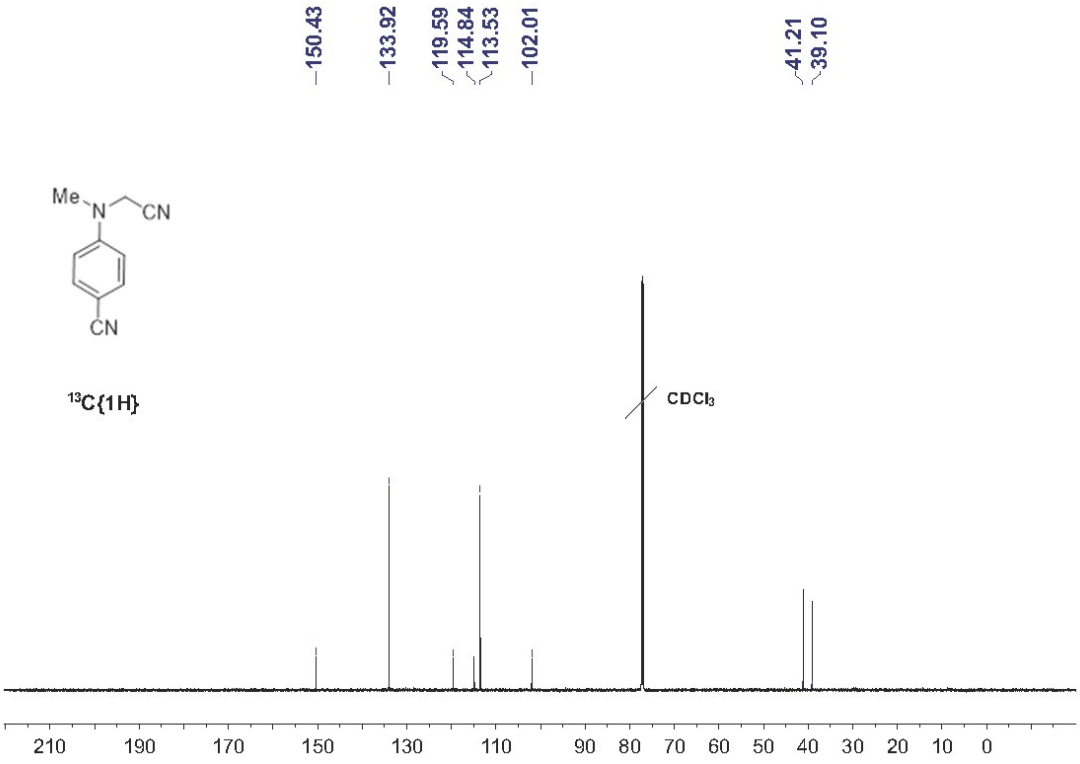


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5a**

4-[(cyanomethyl)methylamino]-benzonitrile (5b)

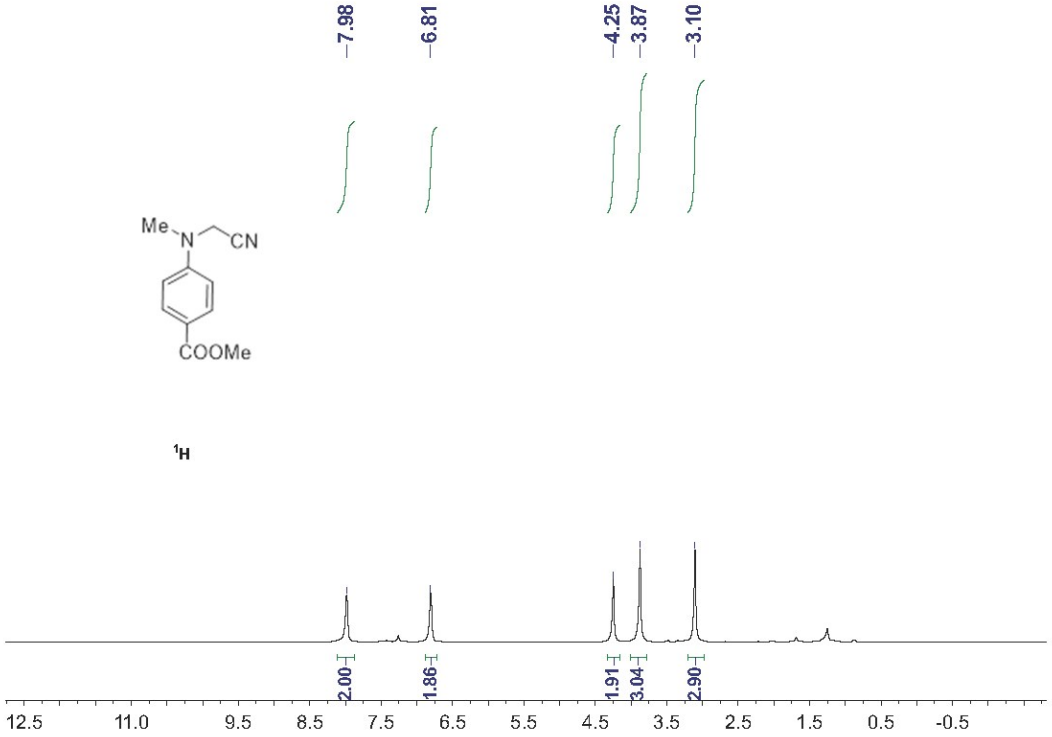


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5b**

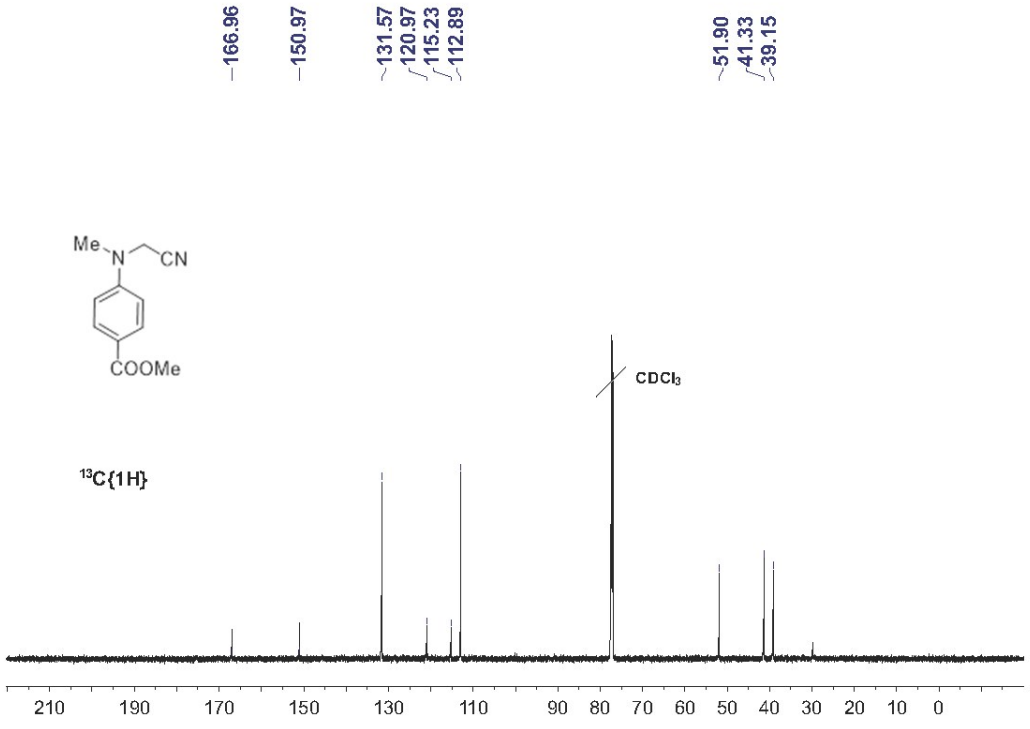


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5b**

4-[(cyanomethyl)methylamino]-benzoic acid, methyl ester (5c)

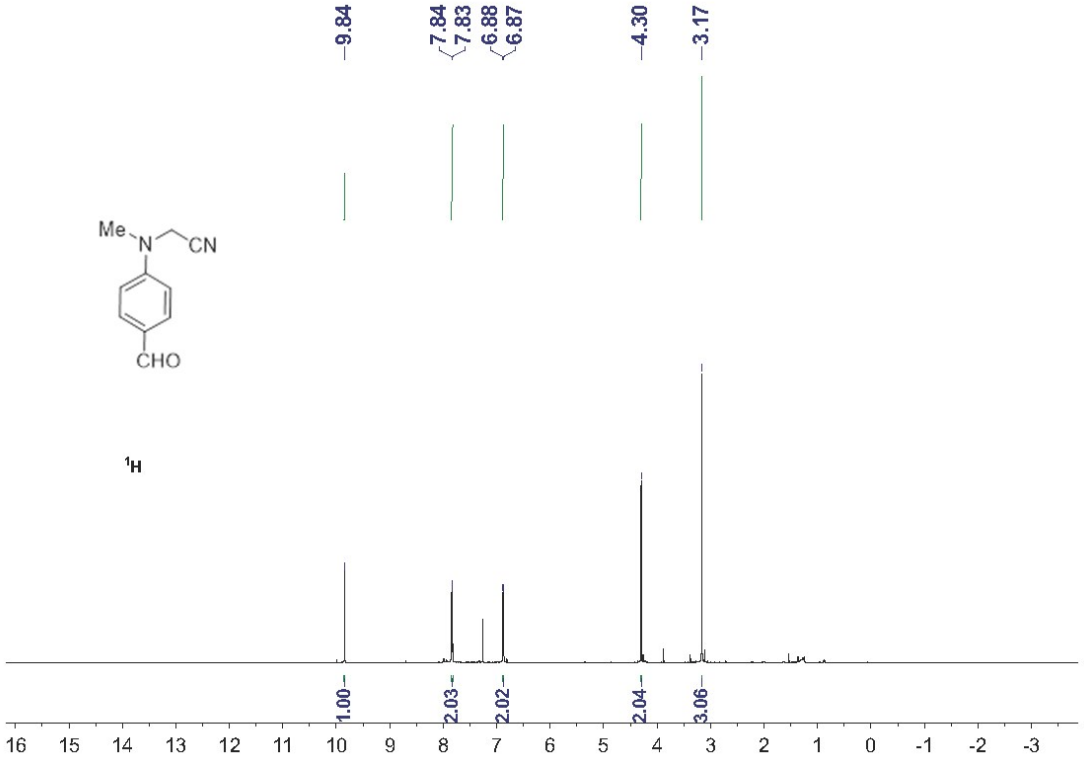


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5c**

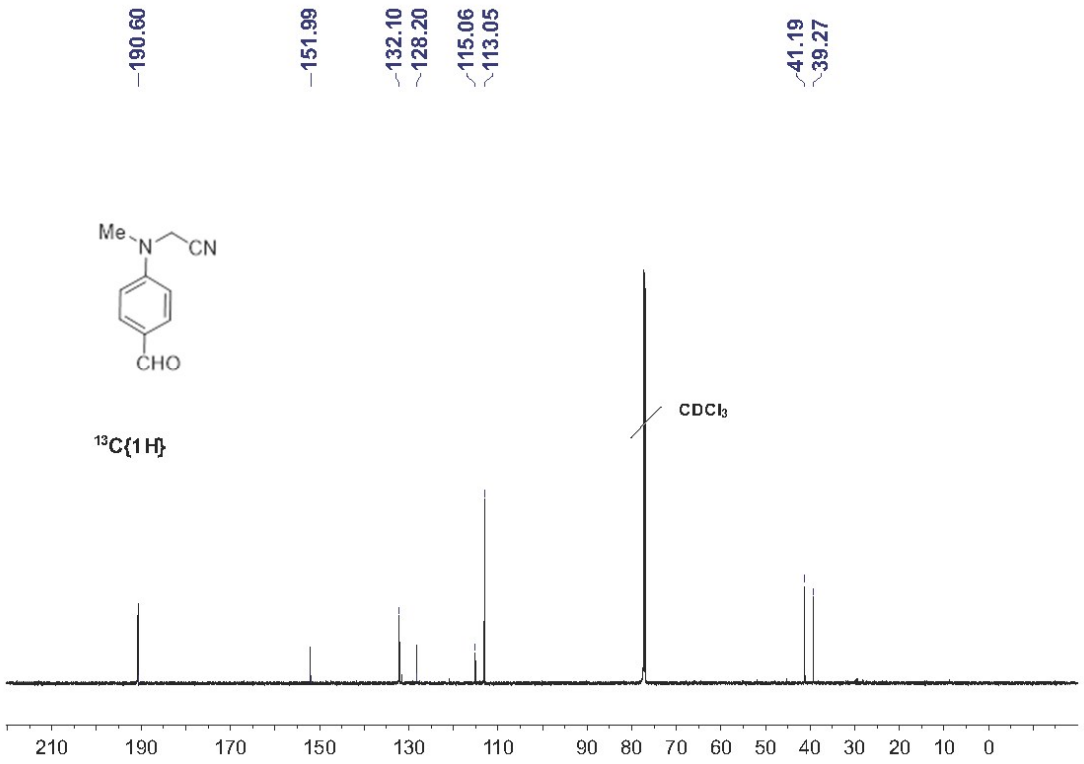


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5c**

2-[(4-formylphenyl)methylamino]-acetonitrile (5d)

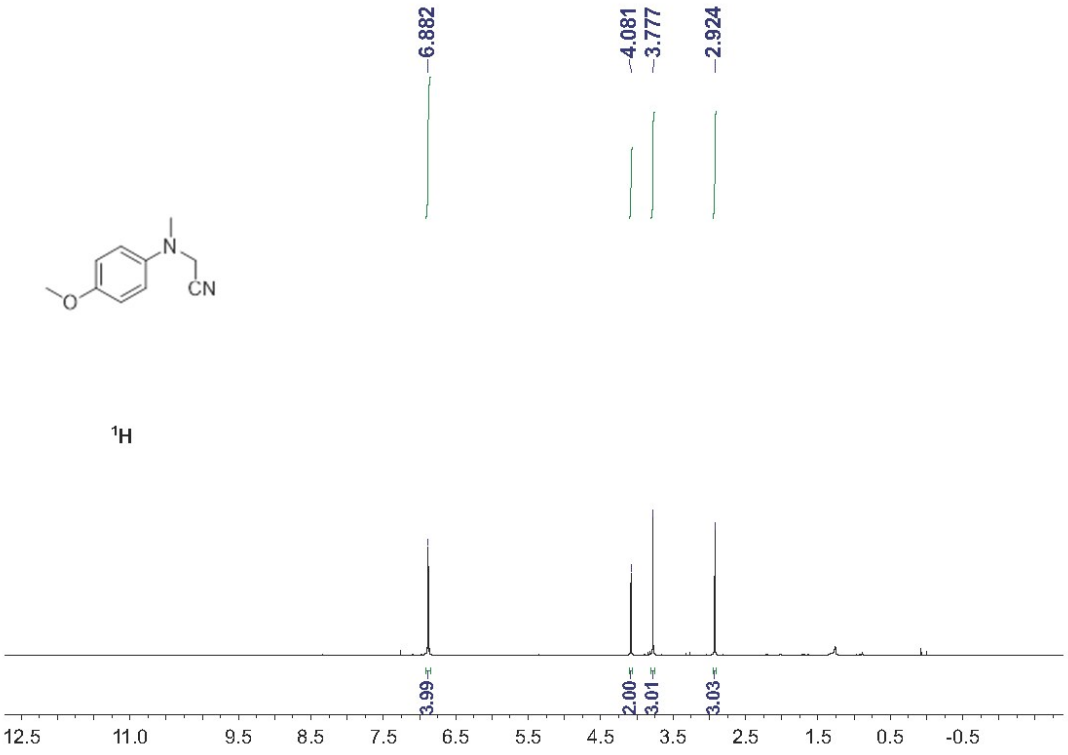


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5d**

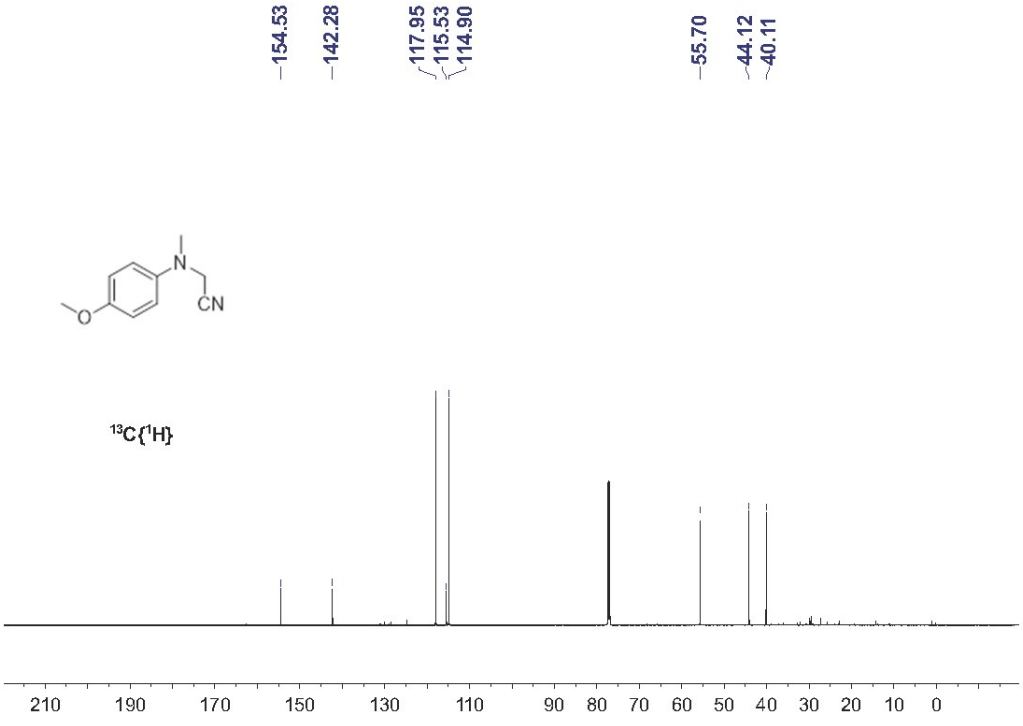


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5d**

(4-Methoxyphenyl)-methyl-amino]acetonitrile (5e)

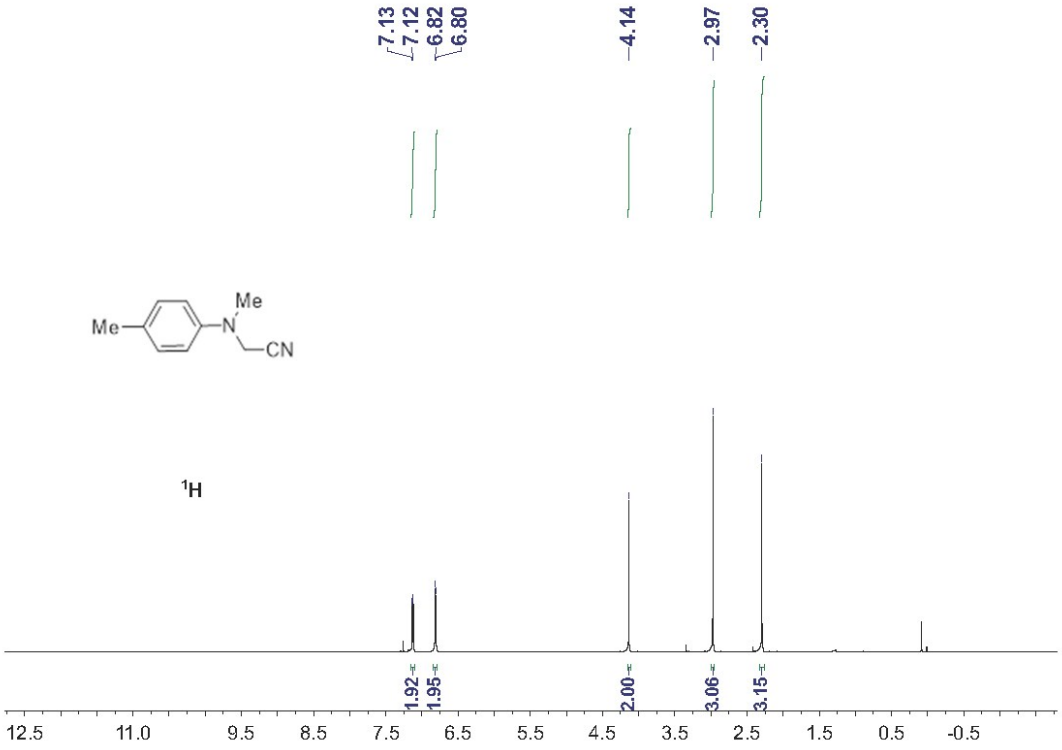


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5e**

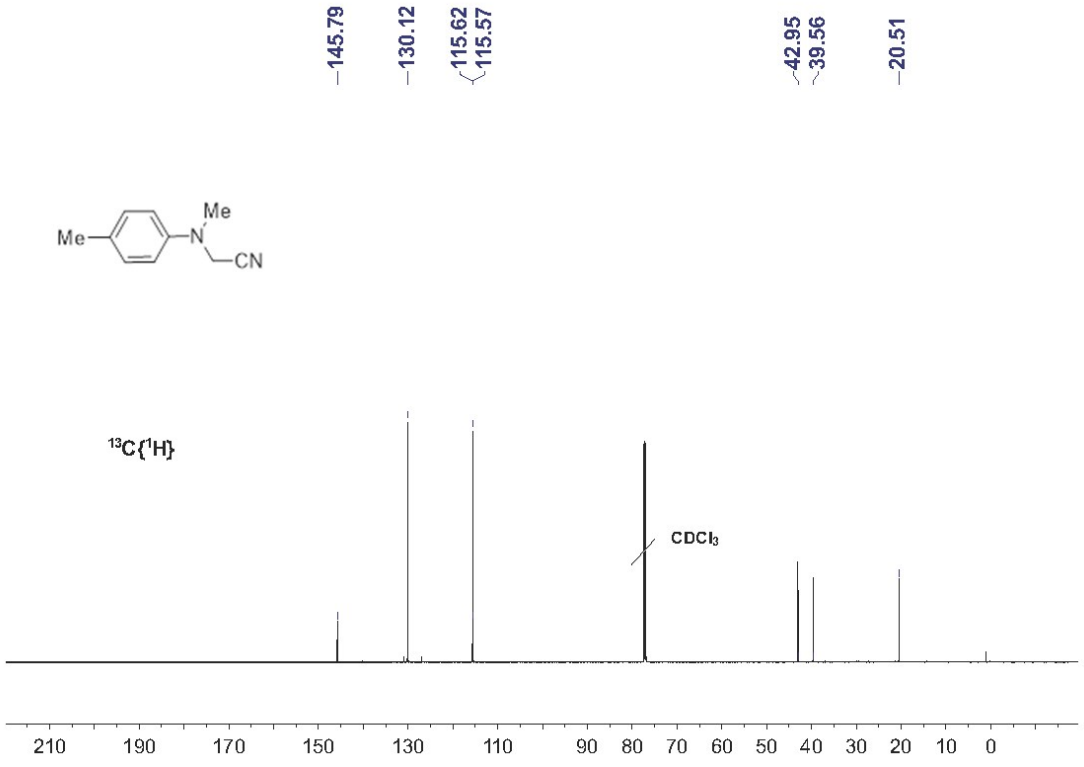


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5e**

(Methyl-p-tolyl-amino)acetonitrile (5f)

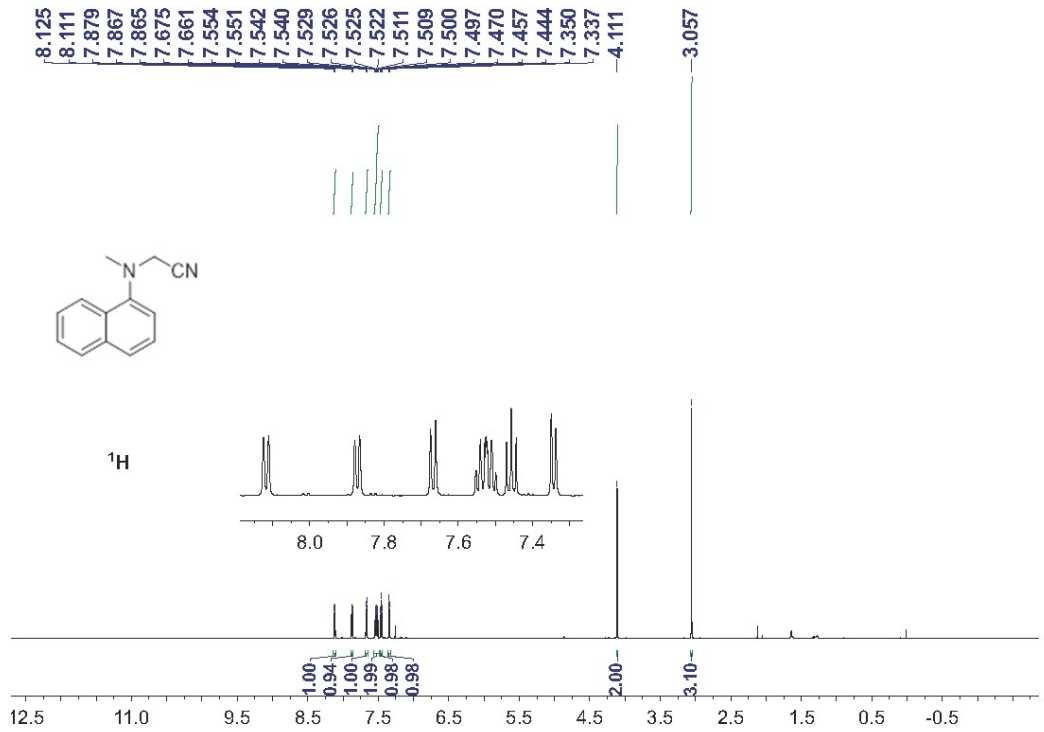


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5f**

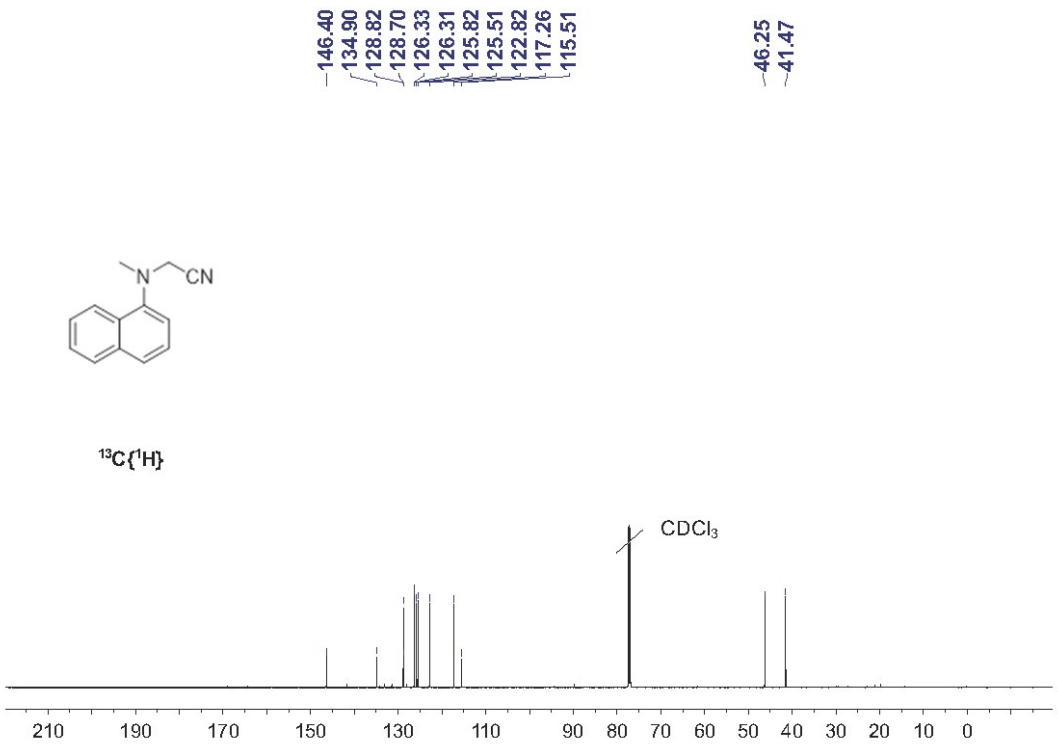


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5f**

2-(methyl-1-naphthalenylamino)acetonitrile (5g)

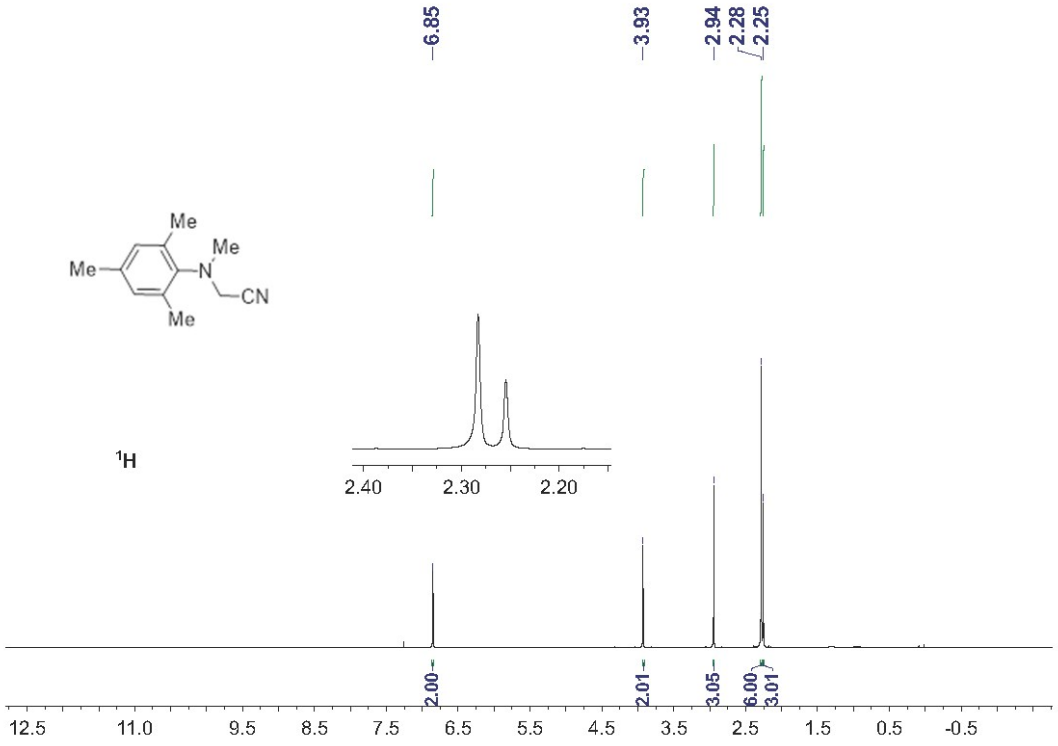


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5g**

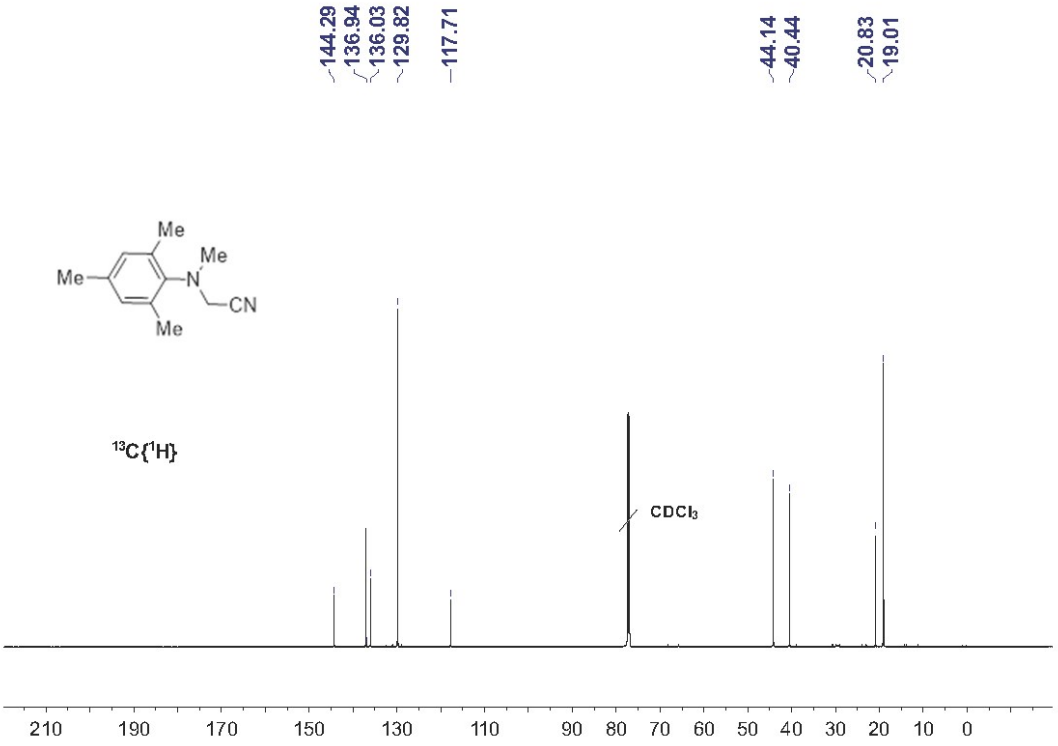


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5g**

2-[Methyl(2,4,6-trimethylphenyl)amino]acetonitrile (5h)

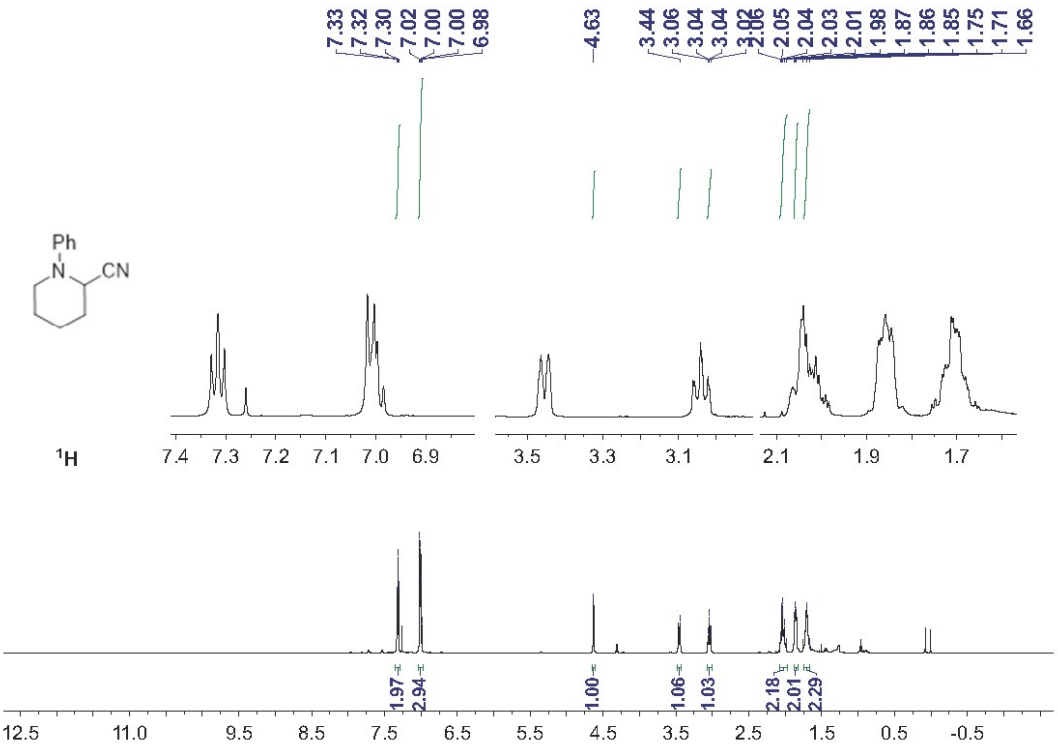


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5h**

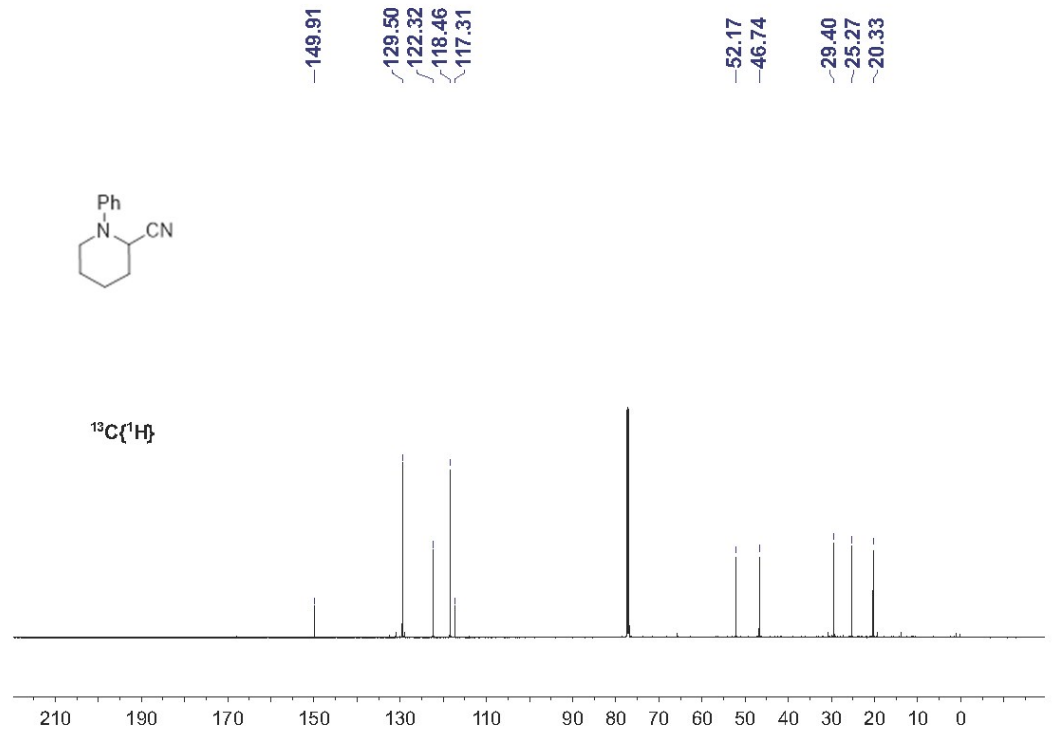


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5h**

1-p-Phenylpiperidine-2-carbonitrile (5j)

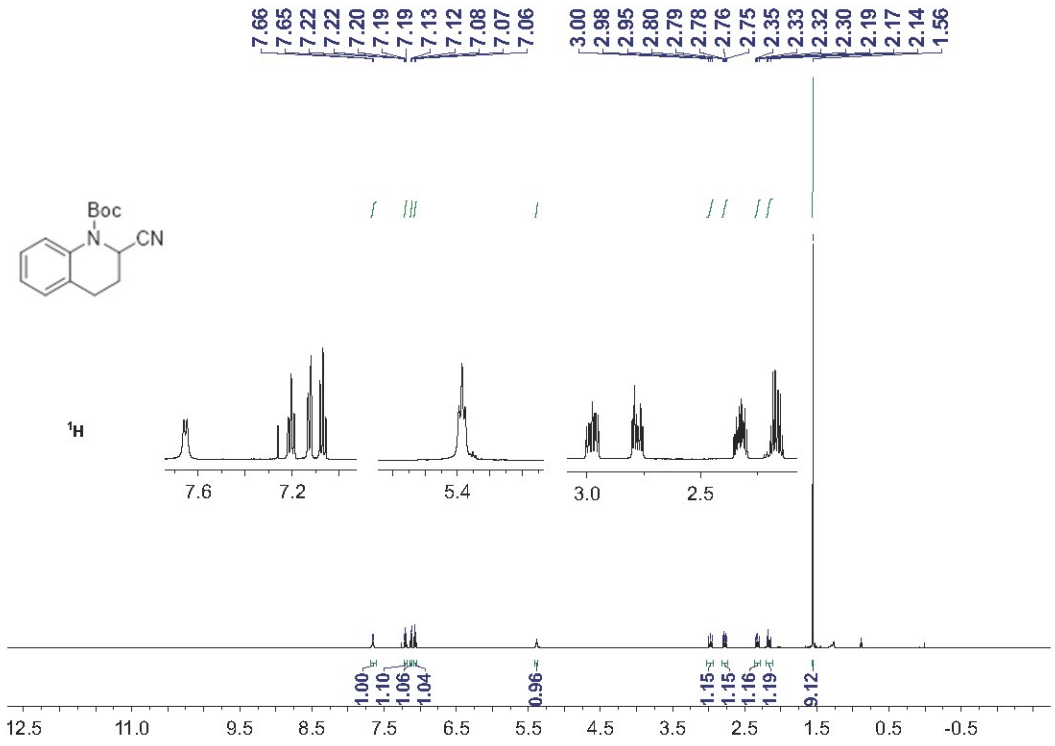


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5j**

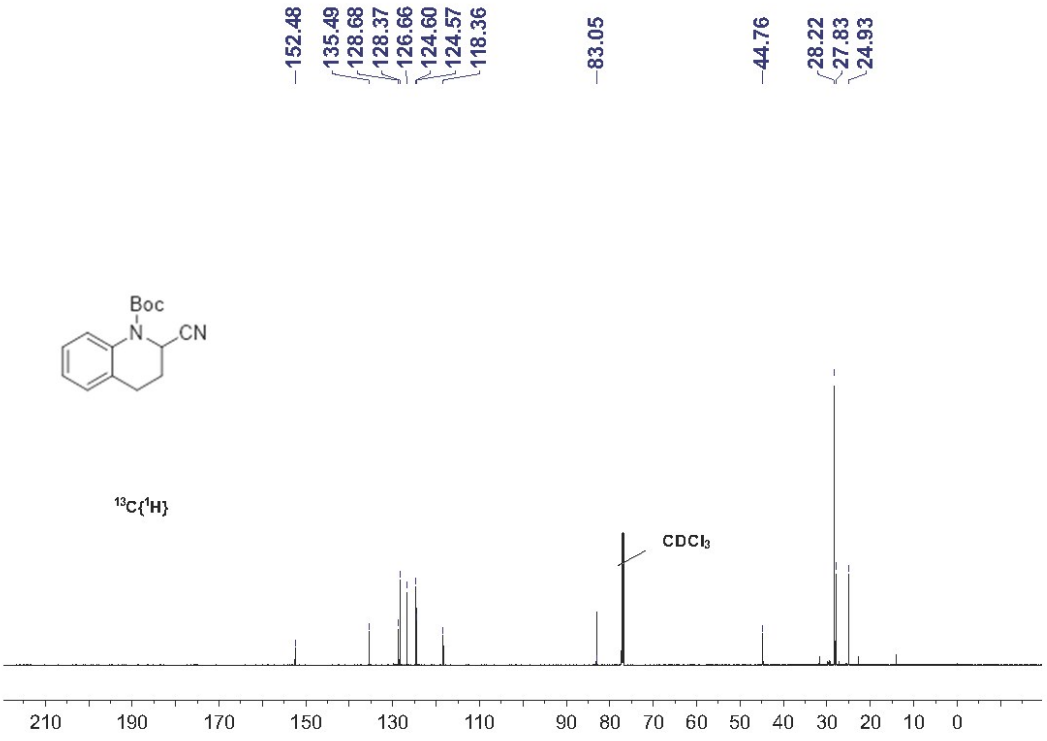


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5j**

tert-Butyl 3,4-dihydro-1(2H)-quinolinecarboxylate-6-carbonitrile (5l)

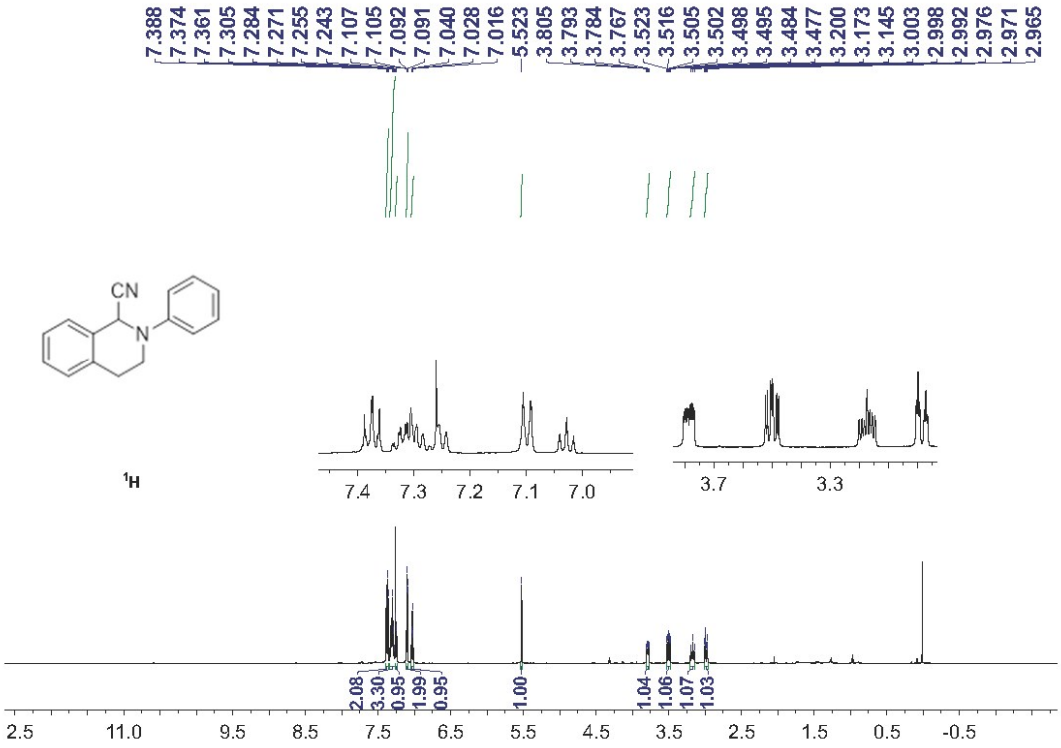


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5l**

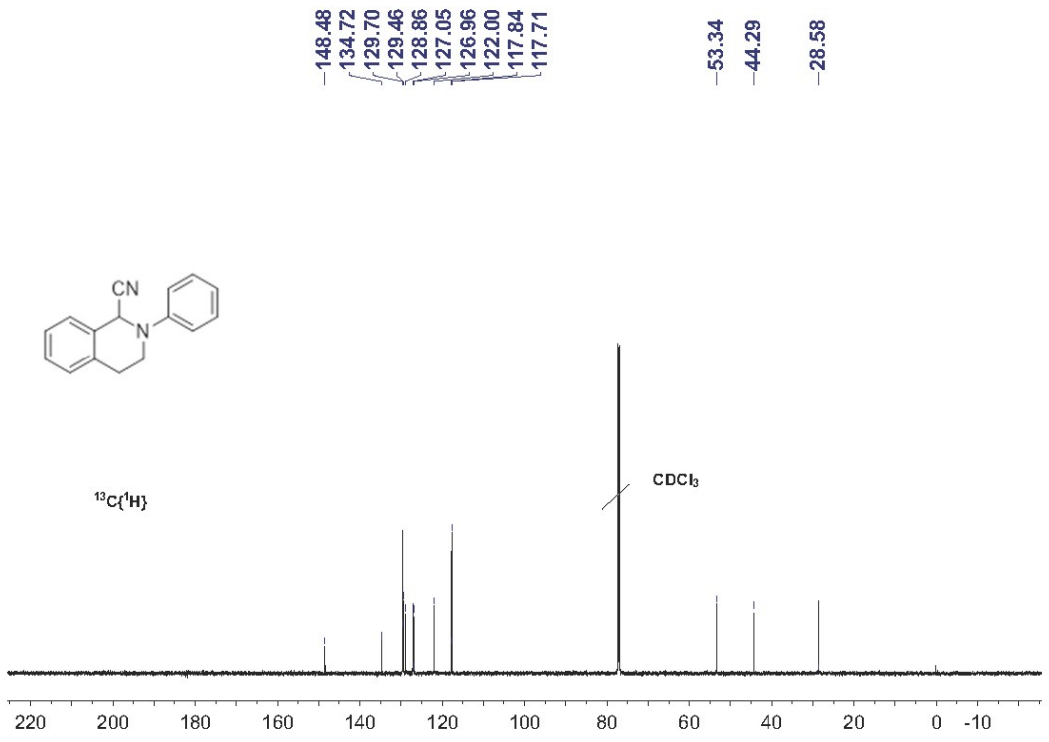


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5l**

2-Phenyl-1,2,3,4-tetrahydroisoquinoline-1-carbonitrile (5m)

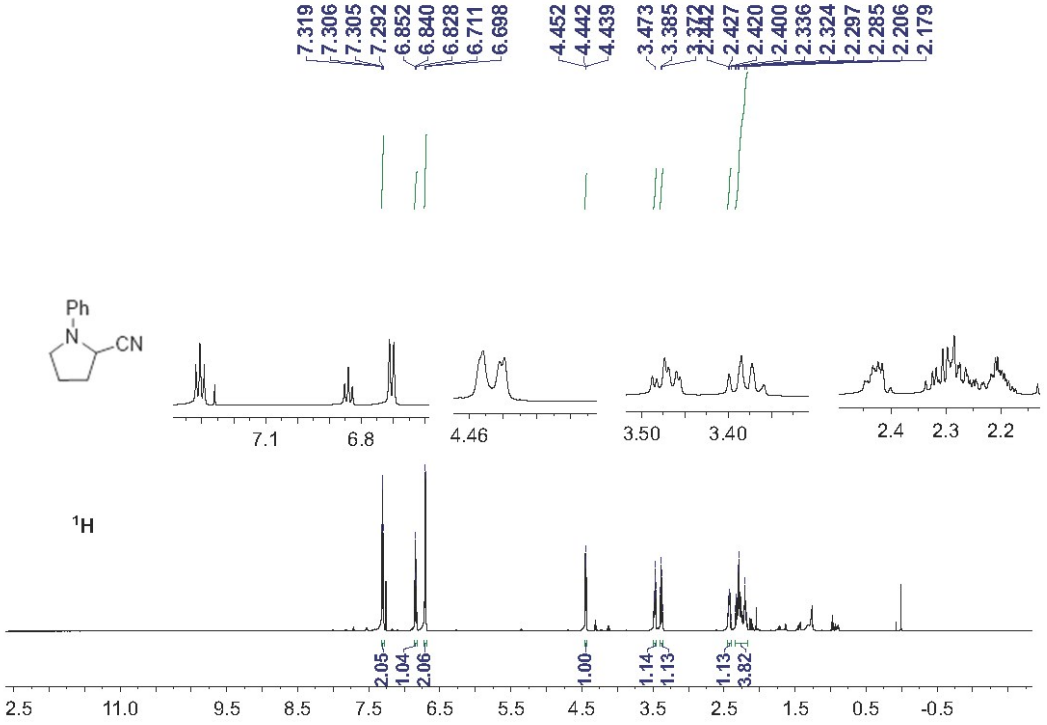


^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5m**

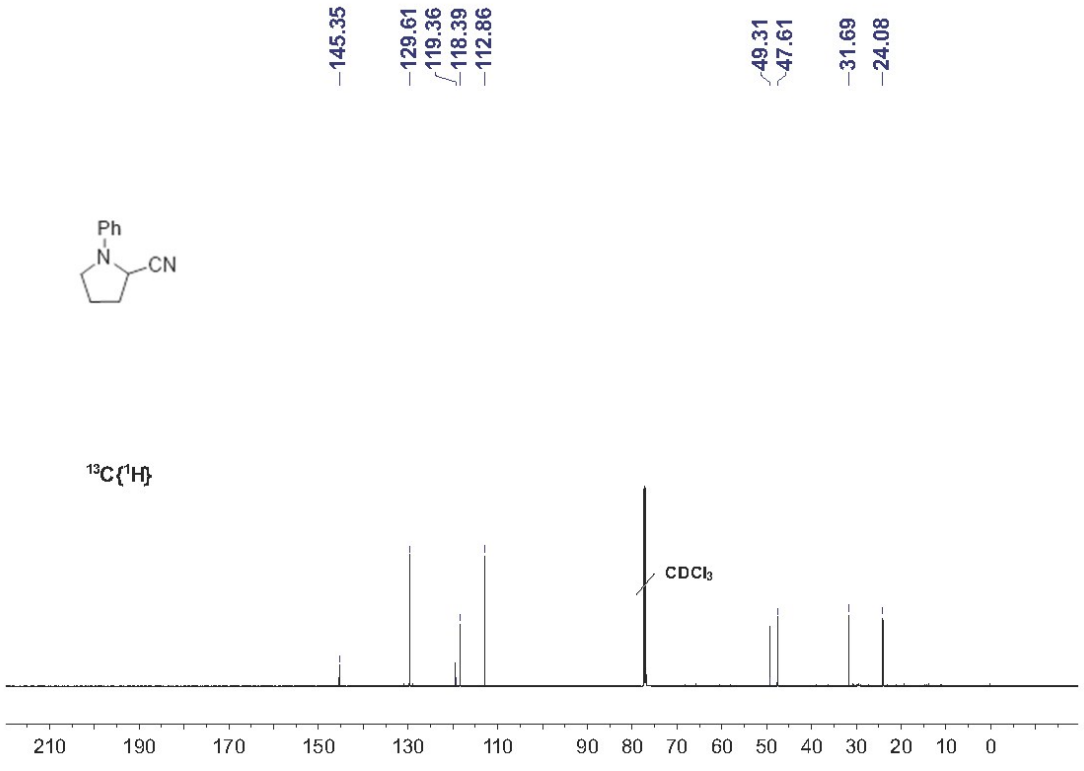


^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5m**

1-Phenylpyrrolidine-2-carbonitrile (5n)



^{1}H NMR (600 MHz, $CDCl_3$, 298 K) of **5n**



^{13}C{^{1}H} (600 MHz, $CDCl_3$, 298 K) of **5n**