Electronic Supporting Information (ESI) for:

Formation of β-cyano-ketones through cyanide-promoted ring-opening of cyclic organic carbonates

Jixiang Ni,[a] Àlex Cristòfol,[a] and Arjan W. Kleij[a,b*]

[a] *Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Av. Països Catalans 16, 43007 Tarragona, Spain*

[b] *Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain;*

**E-mail: akleij@iciq.es*

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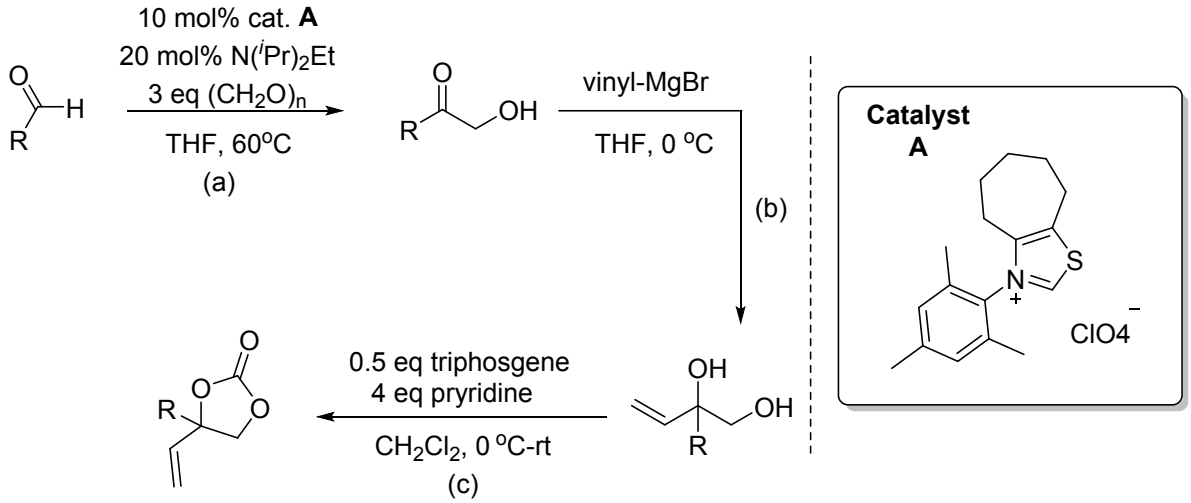
S2. General comments

Potassium cyanide (≥98.0%) was purchased from Sigma Aldrich and was stored in an N_2-filled glovebox. The carbonate was prepared according to a reported procedure1 and 2. Solvents were dried using an Innovative Technology PURE SOLV solvent purification system. Air and water-sensitive reactions were carried out in heat-gun-dried glassware under an Ar or N_2 atmosphere using standard Schlenk manifold techniques. Reactions were monitored by TLC and ^{1}H NMR. TLC was carried out on 0.25 mm Merck aluminum-backed sheets coated with 60 F254 silica gel. Visualization of the silica plates was achieved using a UV lamp (λ = 254 nm) and/or by heating plates that were dipped in a ceric ammonium molybdate stain. Flash chromatography was carried out on Sigma-Aldrich silica gel 60 (70-230 mesh) using the indicated eluent system.^{1}H NMR, ^{13}C NMR spectra were recorded at room temperature on a Bruker AV-400 spectrometer and referenced to the residual deuterated solvent signals. All reported NMR values are given in parts per million (ppm). FT-IR spectra were collected using a Bruker Optics FTIR Alpha spectrometer. Mass spectrometric analyses (including the HRMS measurements), and X-ray diffraction studies were performed by the Research Support Area (RSA) at ICIQ.

S2. Typical procedure for the preparation of starting materials

1. General procedure for the preparation of vinyl cyclic carbonates [1]

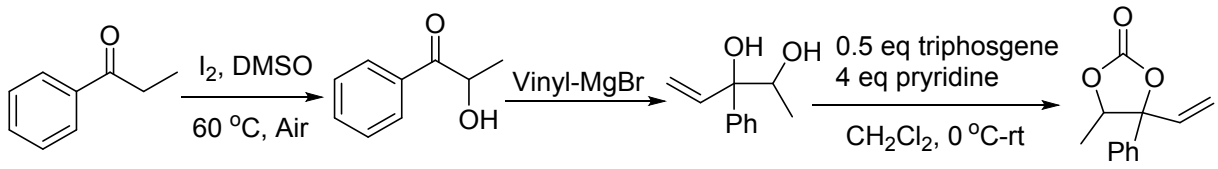


Step (a): In an oven-dried Schlenk-flask sealed with a rubber septum and equipped with a magnetic stirring bar, thiazolium salt **A** (0.1 mmol, 0.1 equiv), paraformaldehyde (3.0 mmol, 3.0 equiv) and the aldehyde (1.0 mmol, 1.0 equiv) were suspended in dry THF (4 mL). N(*i*-Pr)$_2$Et (0.2 mmol, 0.2 equiv) was added and the resulting mixture was heated to 60 °C. In the case of aliphatic aldehydes, the aldehyde was added after stirring the other reactants for 5 min at room temperature. After a reaction time of 24 h, the solvent was evaporated and the crude product was purified by flash chromatography.

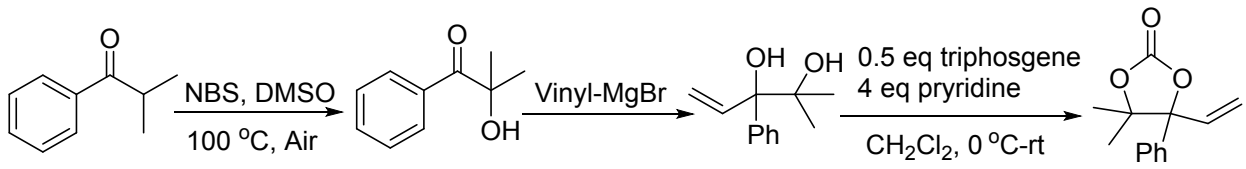
Step (b): To a solution of the respective hydroxy methyl ketone (5 mmol, 1 equiv) in THF (20 mL) was added vinyl magnesium bromide (1.0 M in THF, 2.5 equiv) at 0 °C. The reaction was stirred under an N_2 atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated affording the crude product which was directly used in step (c).

Step (c): To a solution of diol (5 mmol, 1 equiv) and pyridine (20 mmol, 4 equiv) in CH_2Cl_2 (20 mL) was added triphosgene (2.5 mmol, 0.5 equiv, 1.0 M in CH_2Cl_2) at 0 °C. The reaction was stirred under an N_2 atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica to afford the corresponding carbonate.

2. Procedure for the preparation of other vinyl cyclic carbonates [2]

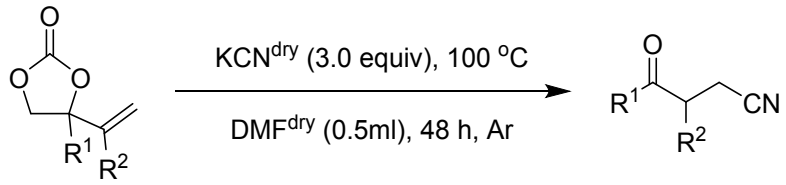


This vinyl carbonate was prepared according to a reported procedure: Propiophenone (1.34 g, 10 mmol), I_2 (508 mg, 20 mol%), and DMSO (20 mL) and a stirring bar were added to a round-bottom flask under air. The mixture was stirred at 60 °C for 24 h and monitored by TLC. After cooling down to room temperature, the mixture was diluted with ethyl acetate (10 mL) and washed with 0.1 mol/L $Na_2S_2O_3$ (5 mL) aqueous solution, extracted with ethyl acetate (3 × 100 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20:1) to get the desired 2-hydroxypropiophenone. The next synthetic step is the same as reported above under **1**.



This vinyl carbonate was prepared according to a reported procedure: Isobutyrophenone (1.48 g, 10 mmol), NBS (356 mg, 20 mol%), and DMSO (20 mL) and a stirring bar were added to a round-bottom flask under air. The mixture was stirred at 100 °C for 24 h and monitored by TLC. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL) and washed with water (5 mL), extracted with ethyl acetate (3 × 5 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20:1) to get the desired product. The next synthetic step is the same as reported above under **1**.

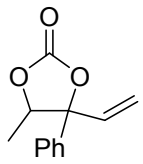
S4. Typical procedure for the preparation of the β-cyano ketones



In an N_2-filled glovebox, to a Schlenk tube equipped with a magnetic stirring bar, the respective vinyl carbonate (0.2 mmol, 1.0 equiv), KCN (0.6 mmol, 3.0 equiv), and dry DMF (0.5 mL) were added. The resulting mixture was stirred at 100 ºC for 48 h, and then the reaction mixture was cooled to room temperature, the product extracted with EtOAc, and the organic phase washed with H_2O (3 times to remove DMF). The organic phase was dried with Na_2SO_4, filtered, and concentrated, after which the product was purified by flash column chromatography on silica gel (eluent hexane/ethyl acetate, Hex/EA) to afford the pure β-cyano ketone product.

S5. Characterization data for non-reported starting materials

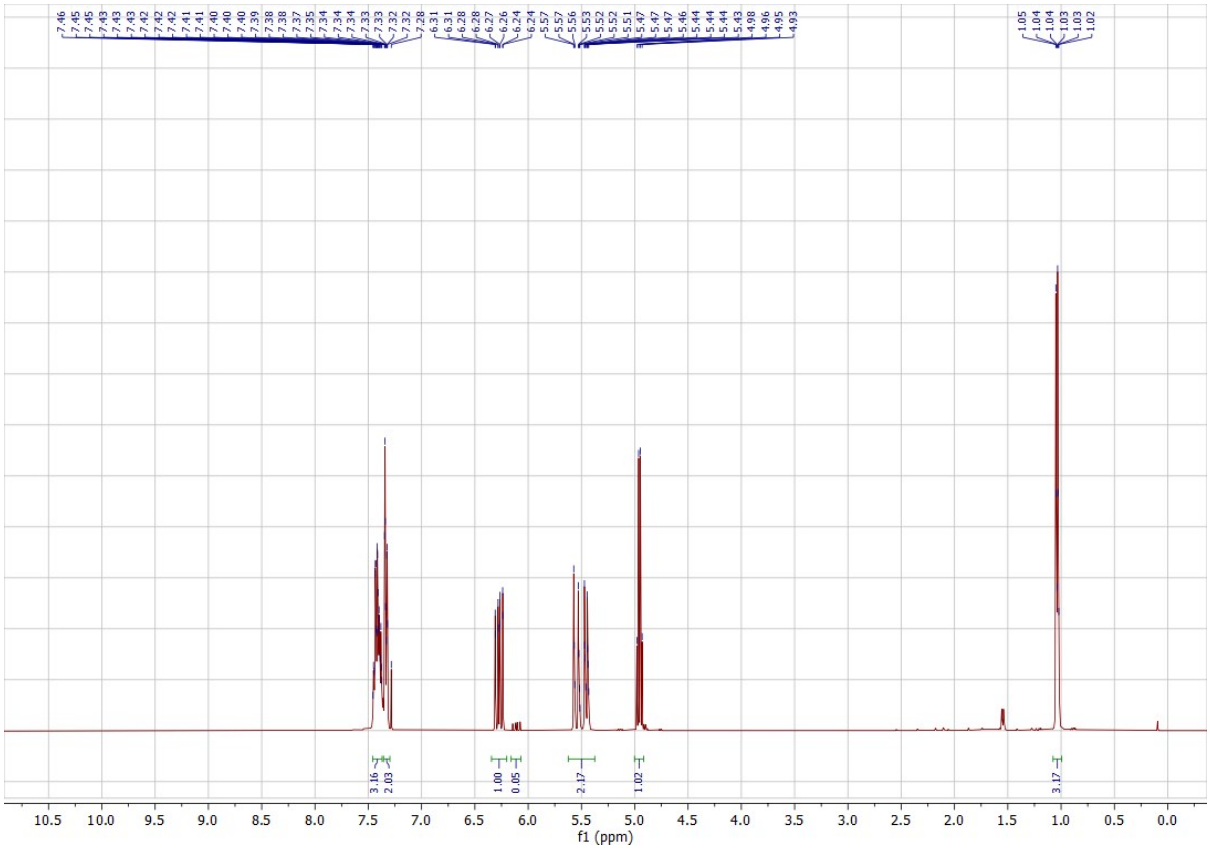
Note that most vinyl cyclic carbonates were prepared according to a previously reported procedure.[3] Unless stated otherwise, all spectra were recorded in $CDCl_3$ (^1H NMR at 400 MHz, and ^{13}C NMR at 100 MHz).



1u

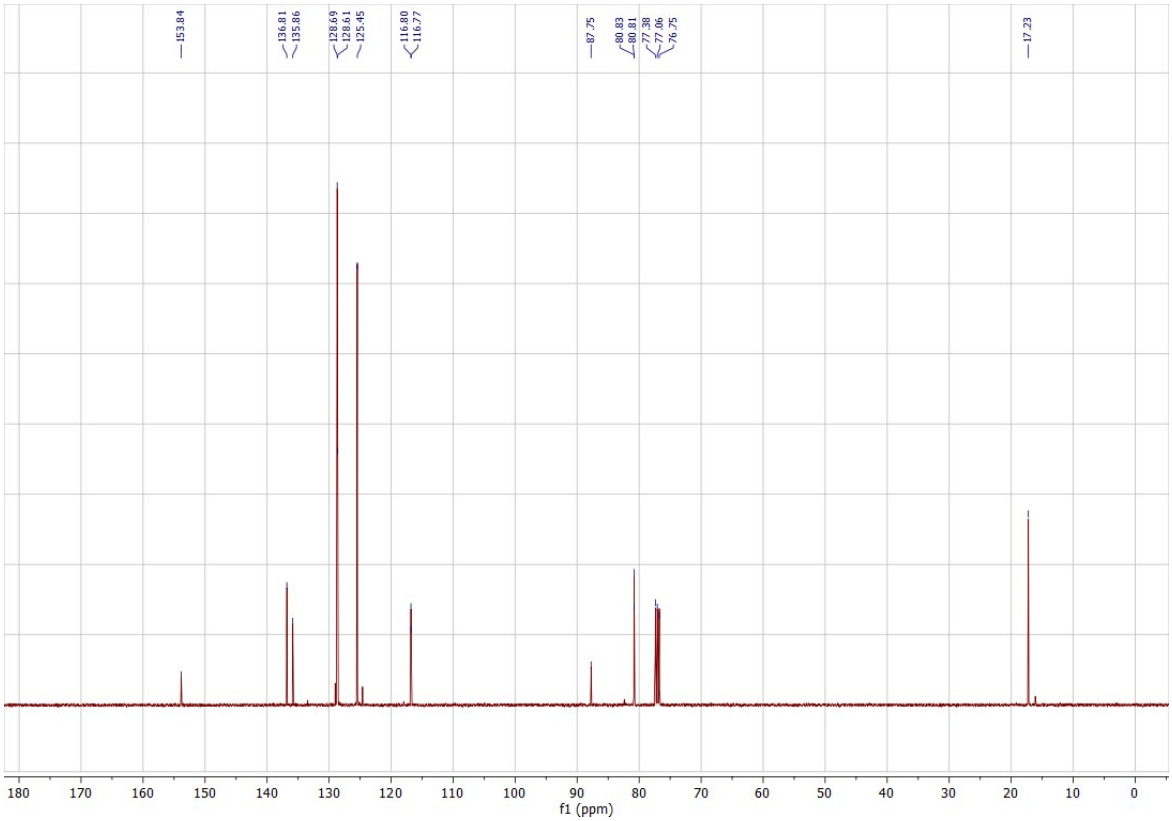
20:1 mixture of diastereoisomers

^1H NMR spectrum ($CDCl_3$)



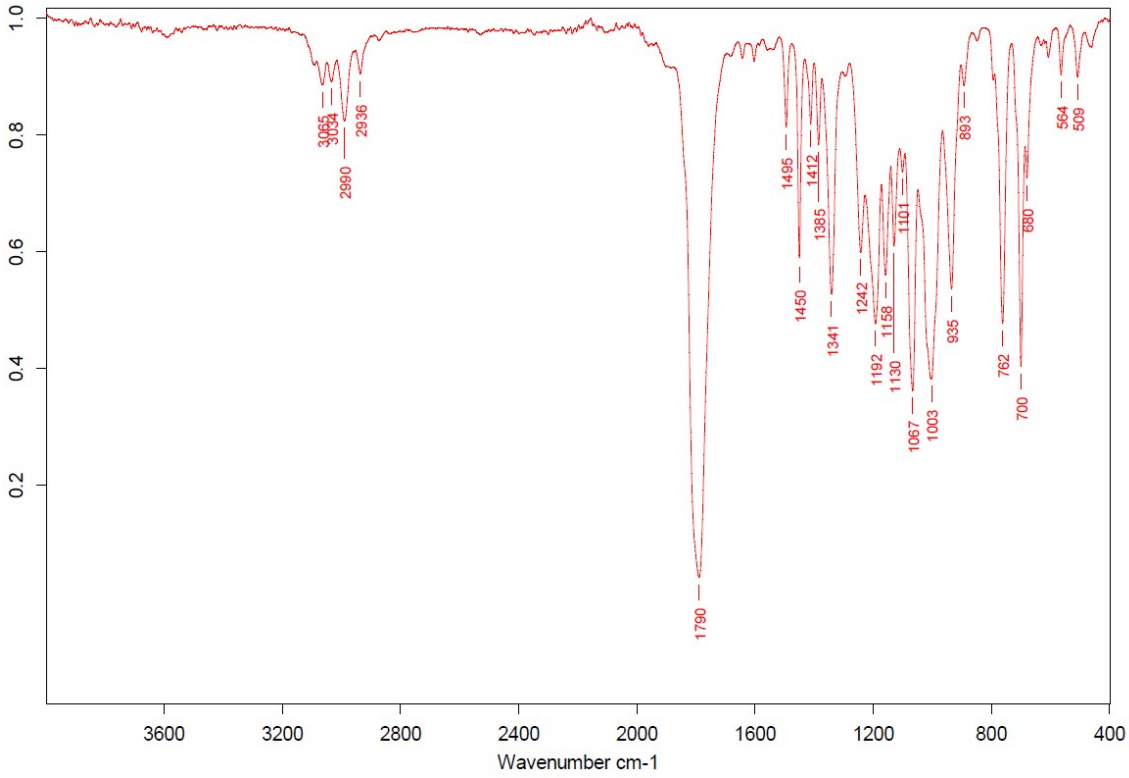
^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.37 (m, 3H), 7.35-7.32 (m, 2H), 6.31-6.24 (m, 2H), 5.57-5.43 (m, 2H), 4.98-4.93 (m, 1H), 1.05-1.02 (m, 3H). The carbonate is a mixture of two stereoisomers with ratio of 20:1, only the data for the major diastereoisomer is listed here.

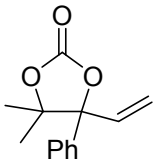
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 153.84, 136.81, 135.86, 128.69, 128.61, 125.45, 116.80, 116.77, 87.75, 80.83, 80.81, 17.23.

IR spectrum (neat)

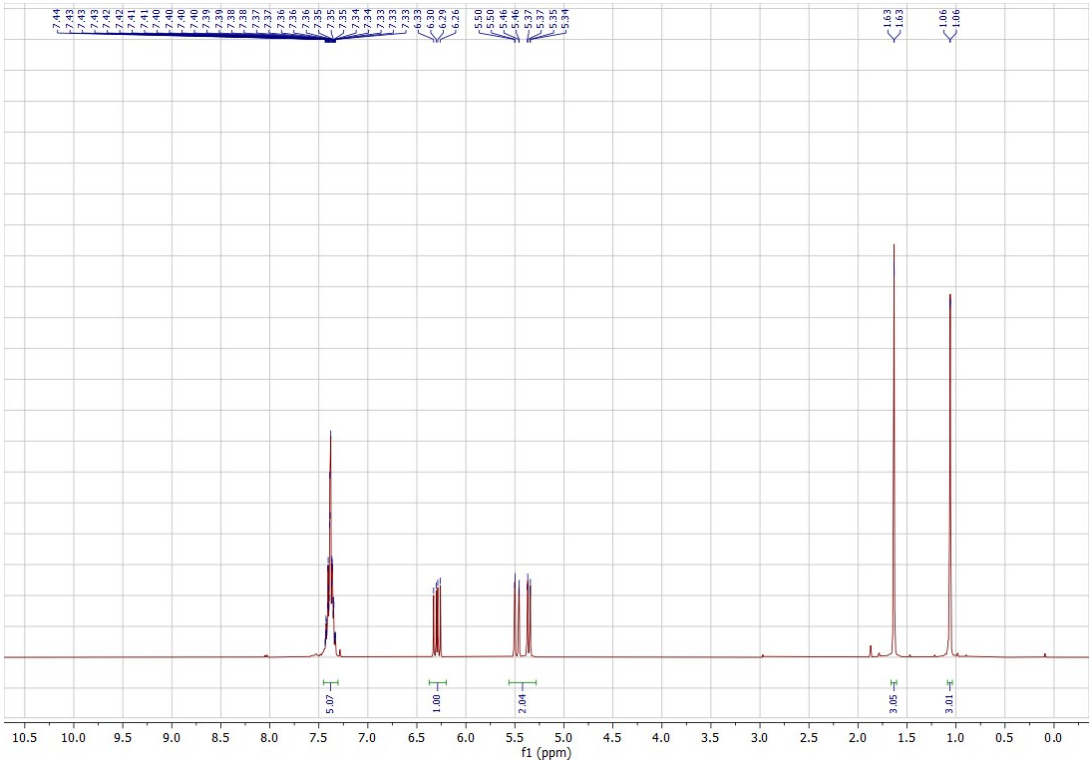




1v

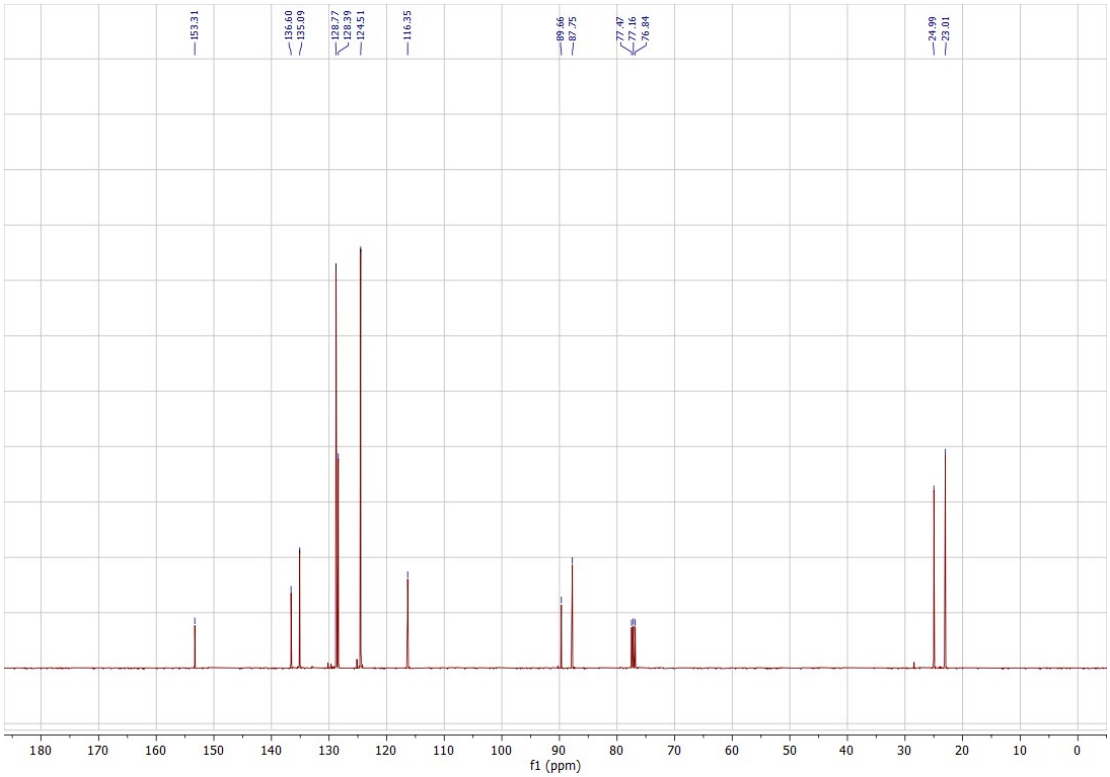
Original data: Y. Mao, X. Zhai, A. Khan, J. Cheng, X. Wu, Y.-J. Zhang, *Tetrahedron Lett.* **2016**, *57*, 3268-3271.

^{1}H NMR spectrum ($CDCl_3$)



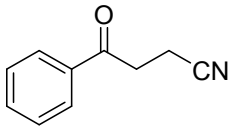
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 5H), 6.33-6.26 (m, 1H), 5.50-5.34 (m, 2H), 1.63 (s, 3H), 1.06 (s, 3H).

^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 153.31, 136.60, 135.09, 128.77, 128.39, 124.51, 116.35, 89.66, 87.75, 24.99, 23.01.

S9: Characterization data for the β-cyano ketone products

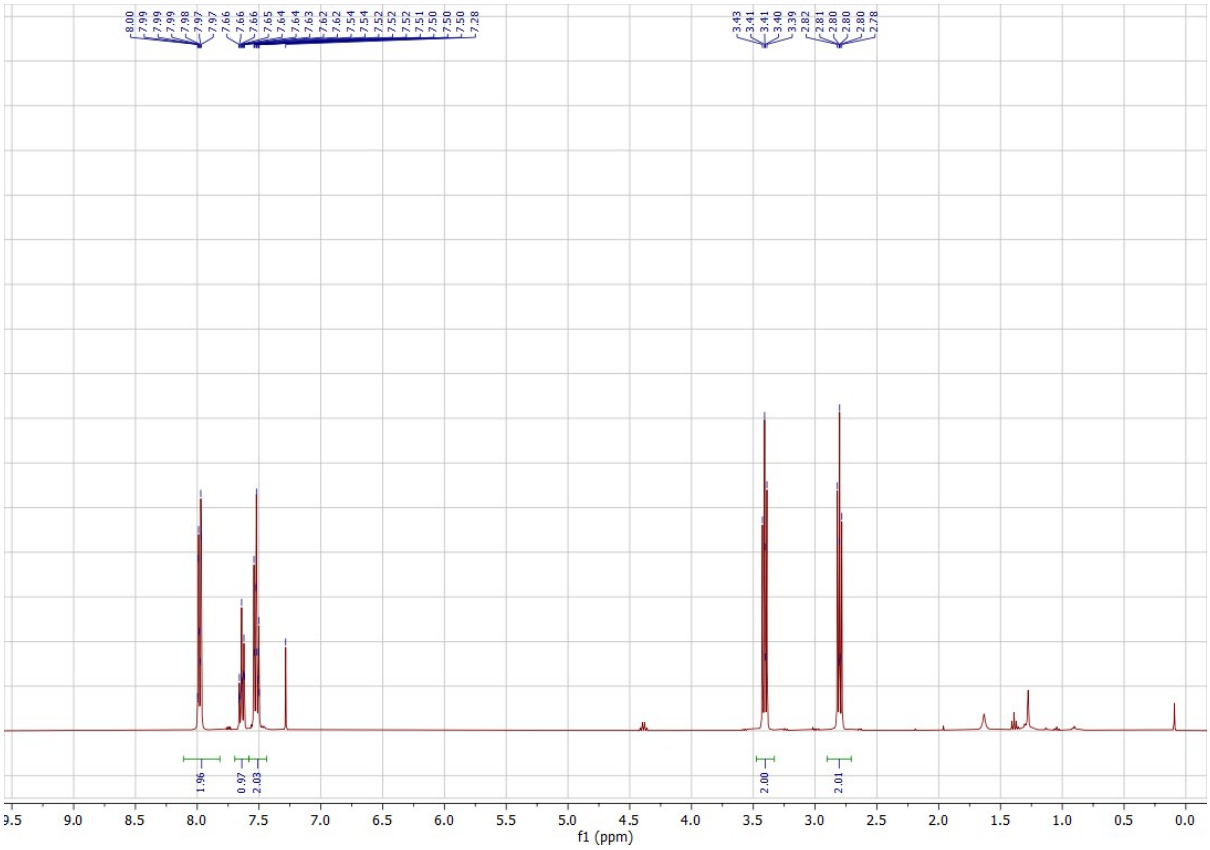


2a

The product was isolated as a white solid. Yield: 72%

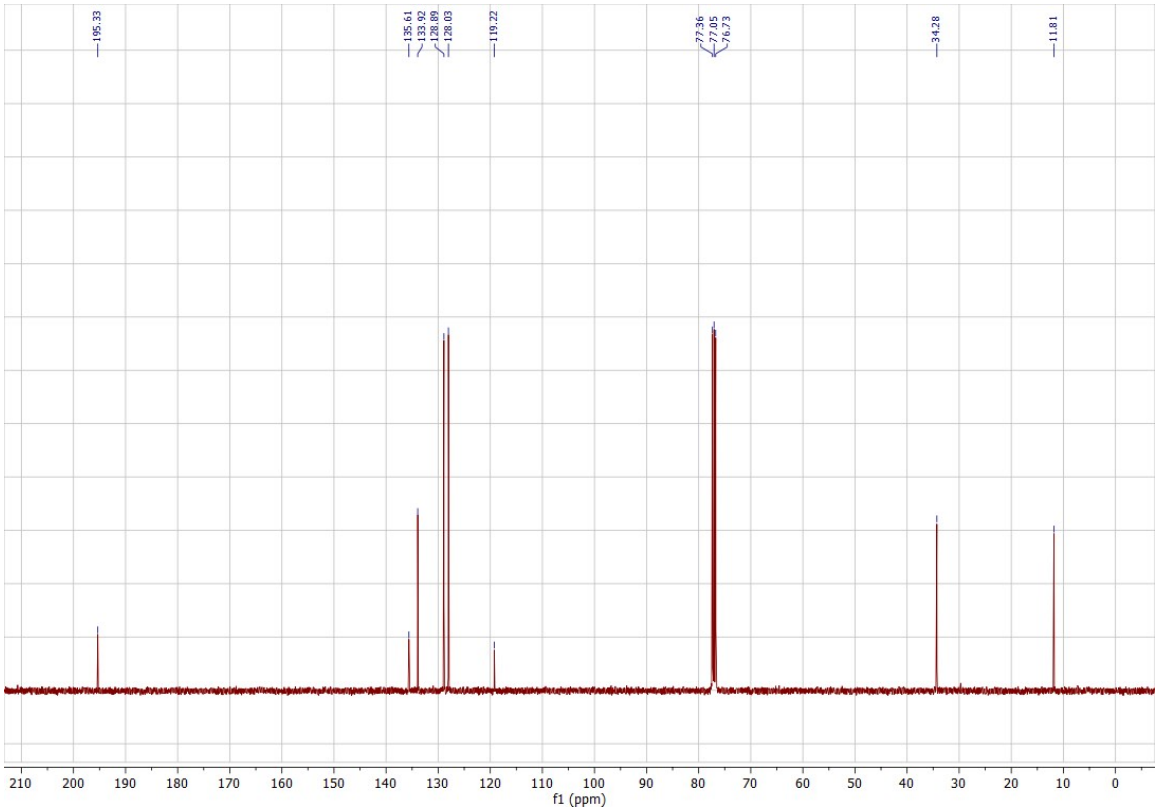
Characterization data matching data reported in the literature.[4,5,7,9,10,13]

^{1}H NMR spectrum ($CDCl_3$)



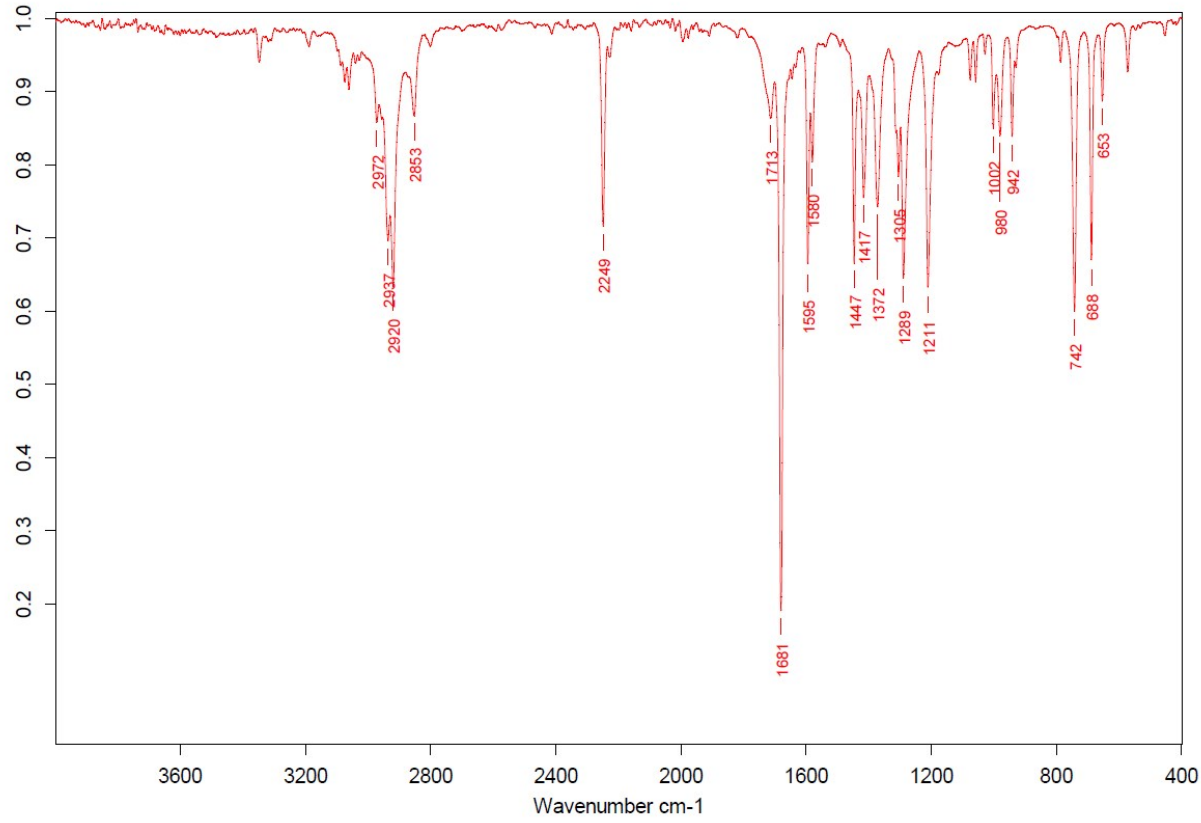
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 2H), 7.66-7.62 (m, 1H), 7.54-7.50 (m, 2H), 3.41 (t, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H).

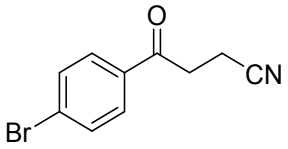
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 195.33, 135.61, 133.92, 128.89, 128.03, 119.22, 34.28, 11.81.

IR spectrum (neat)



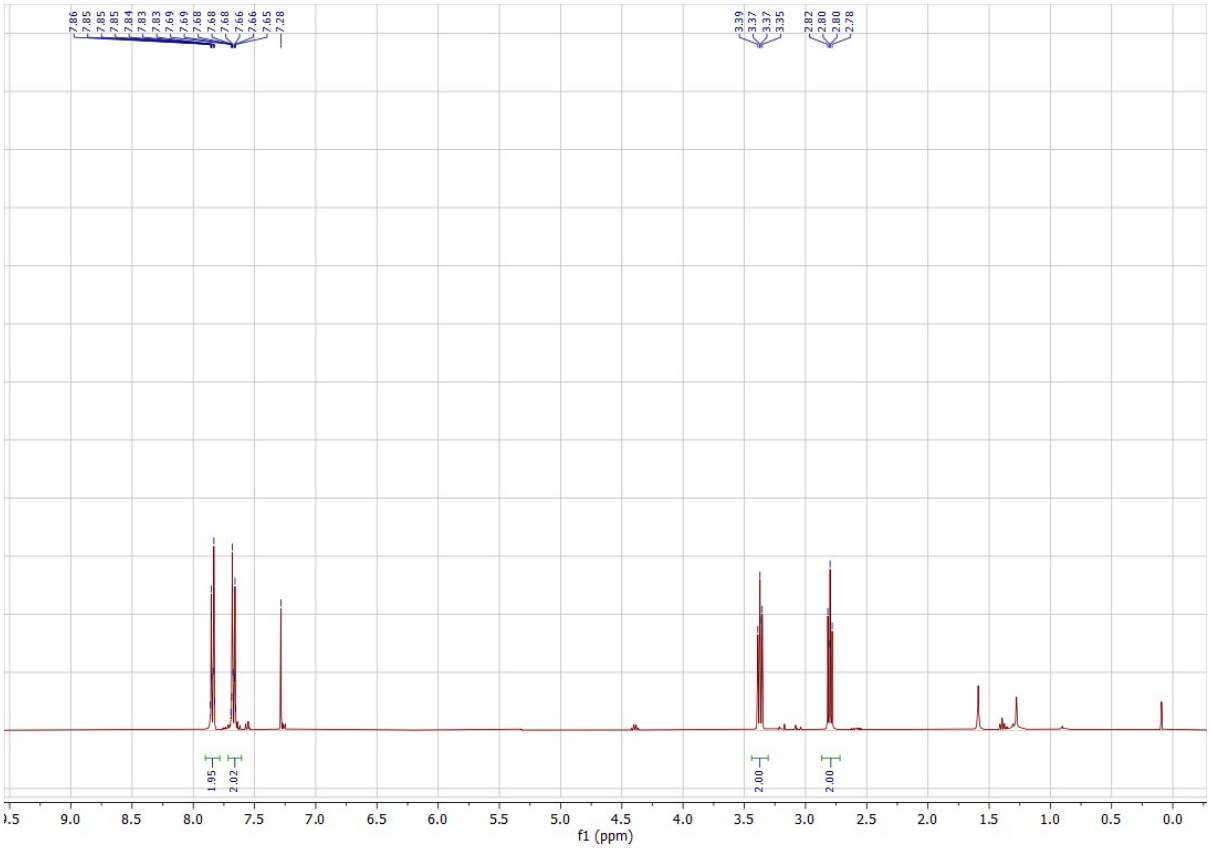


2b

The product was isolated as a white solid. Yield: 63%

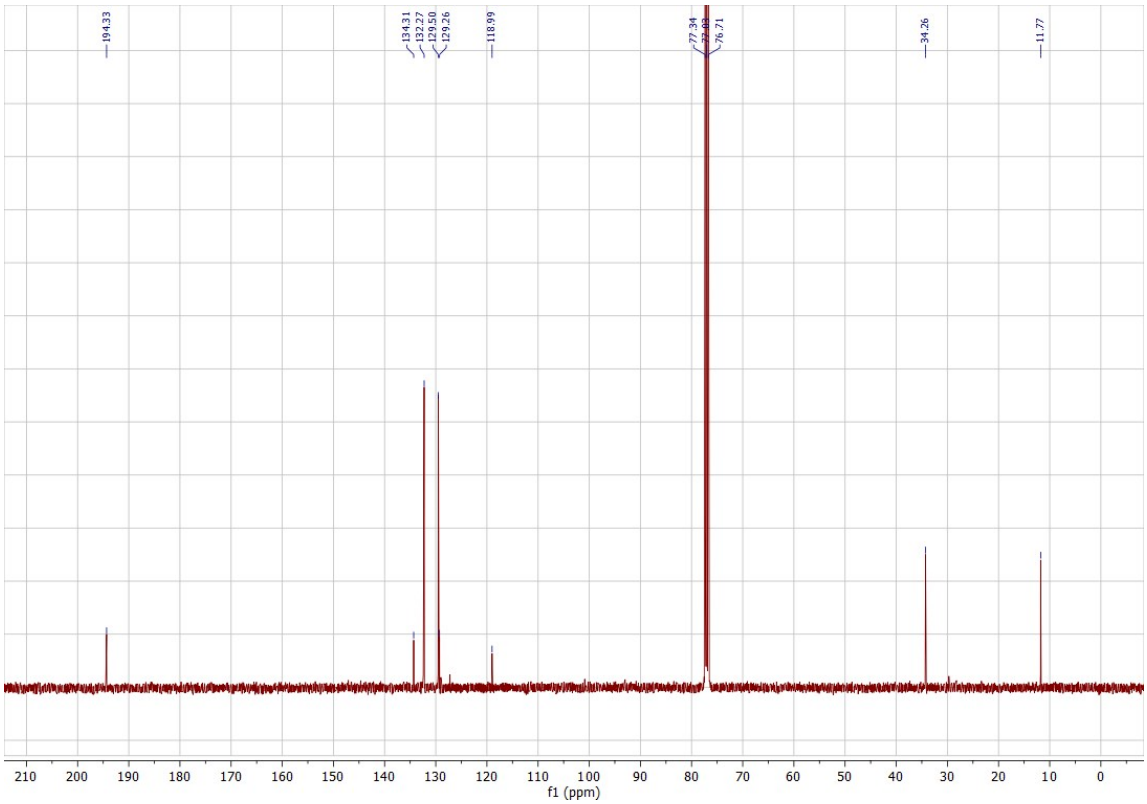
Characterization data matching data reported in the literature.[4,10]

^{1}H NMR spectrum ($CDCl_3$)



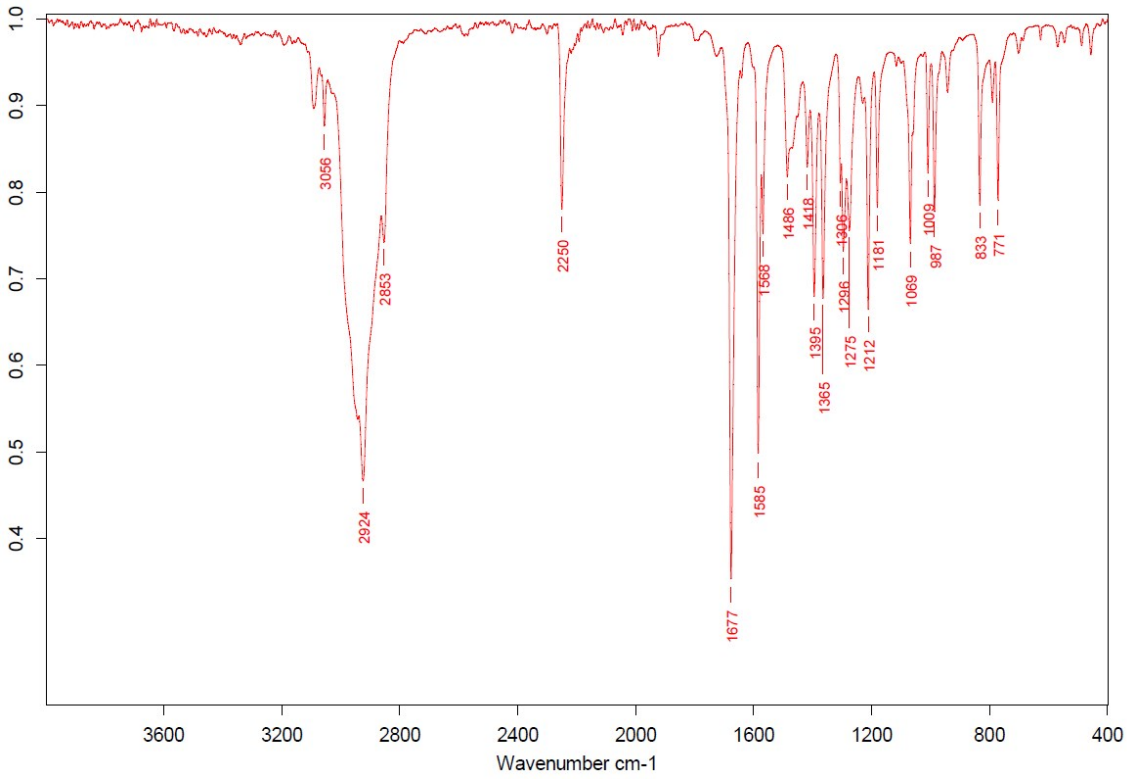
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.69-7.65 (m, 2H), 3.37 (t, J = 8.0 Hz, 2H), 2.80 (t, J = 8.0 Hz, 2H).

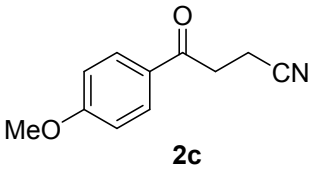
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 194.33, 134.31, 132.27, 129.50, 129.26, 118.99, 34.26, 11.77.

IR spectrum (neat)





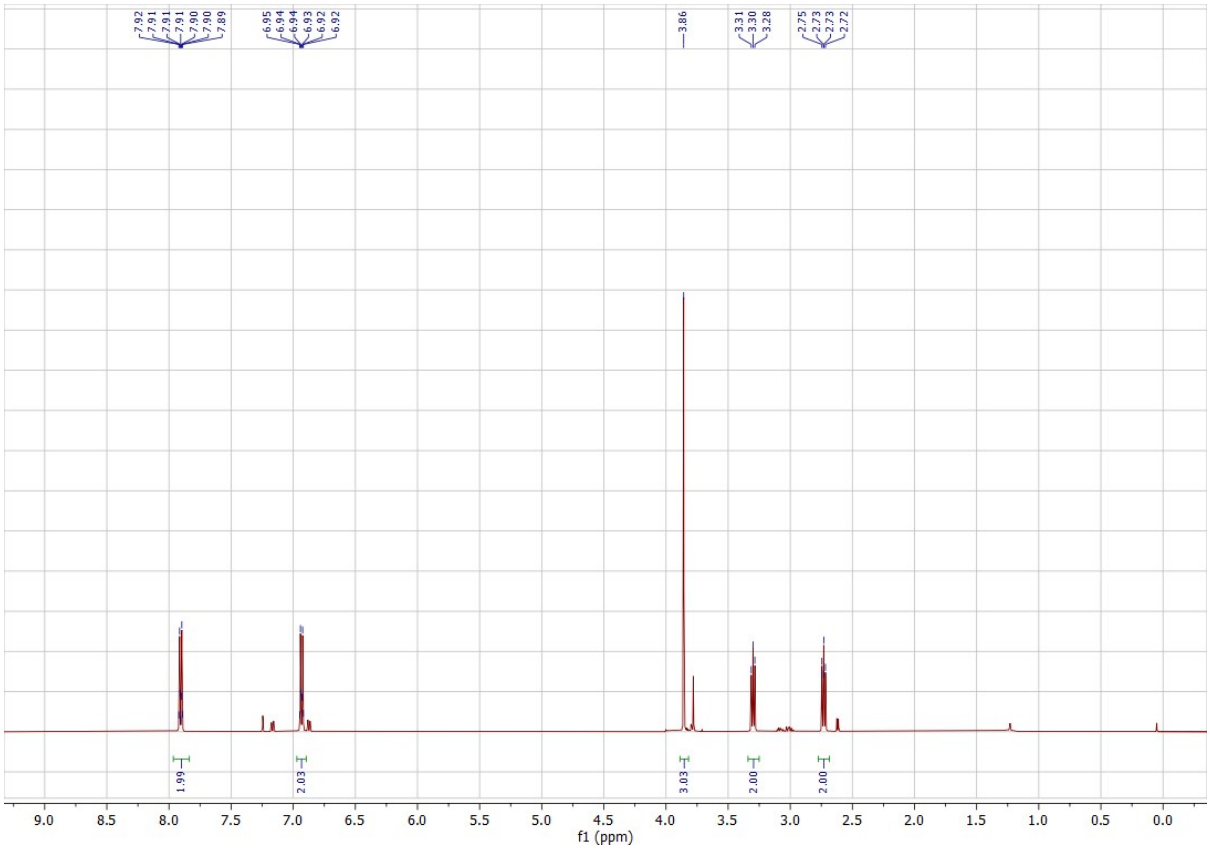
2c

The product was isolated as a white solid. Yield: 70%

PLEASE NOTE: the product was purified several times by column chromatography without changing (virtually) the outcome. The main impurity is ascribed to the dicyanated product such as **4** (see main text).

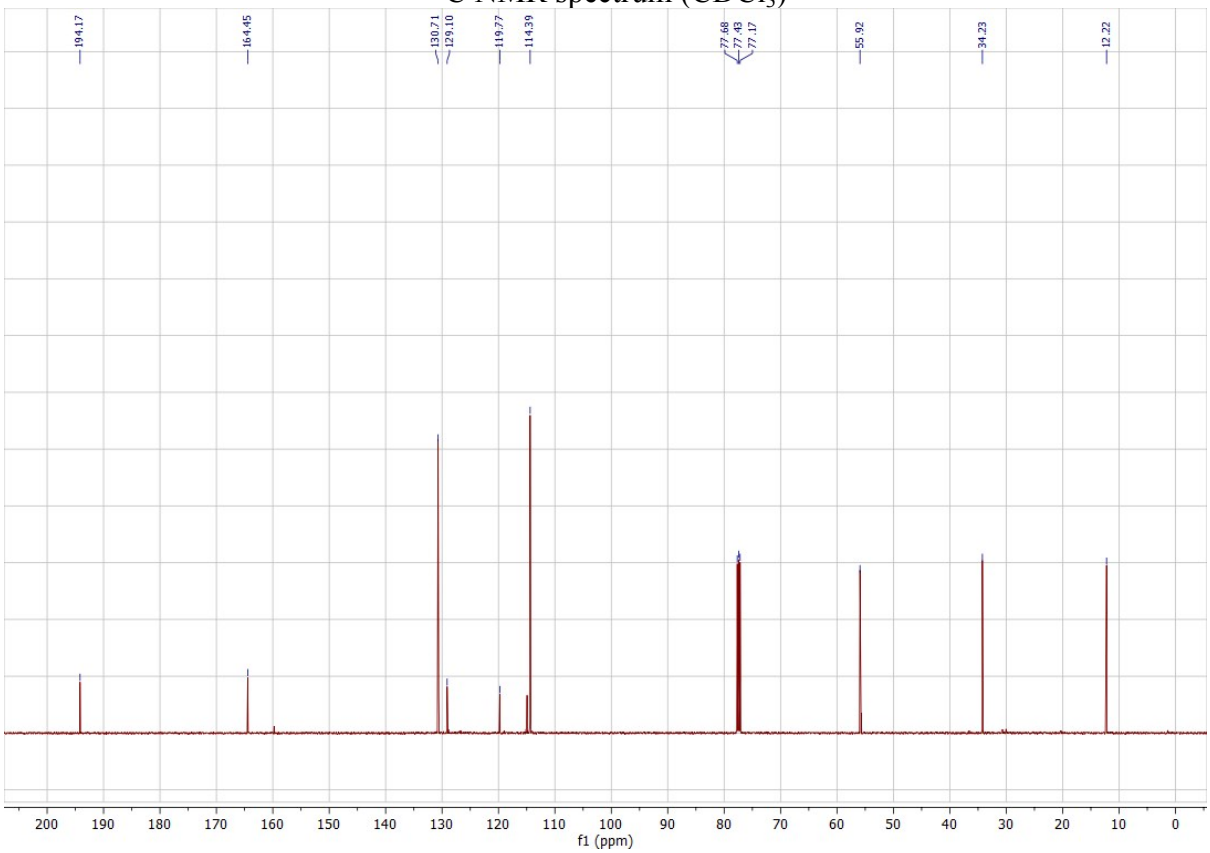
Characterization data matching data reported in the literature.[4,9,10,13]

^{1}H NMR spectrum ($CDCl_3$)



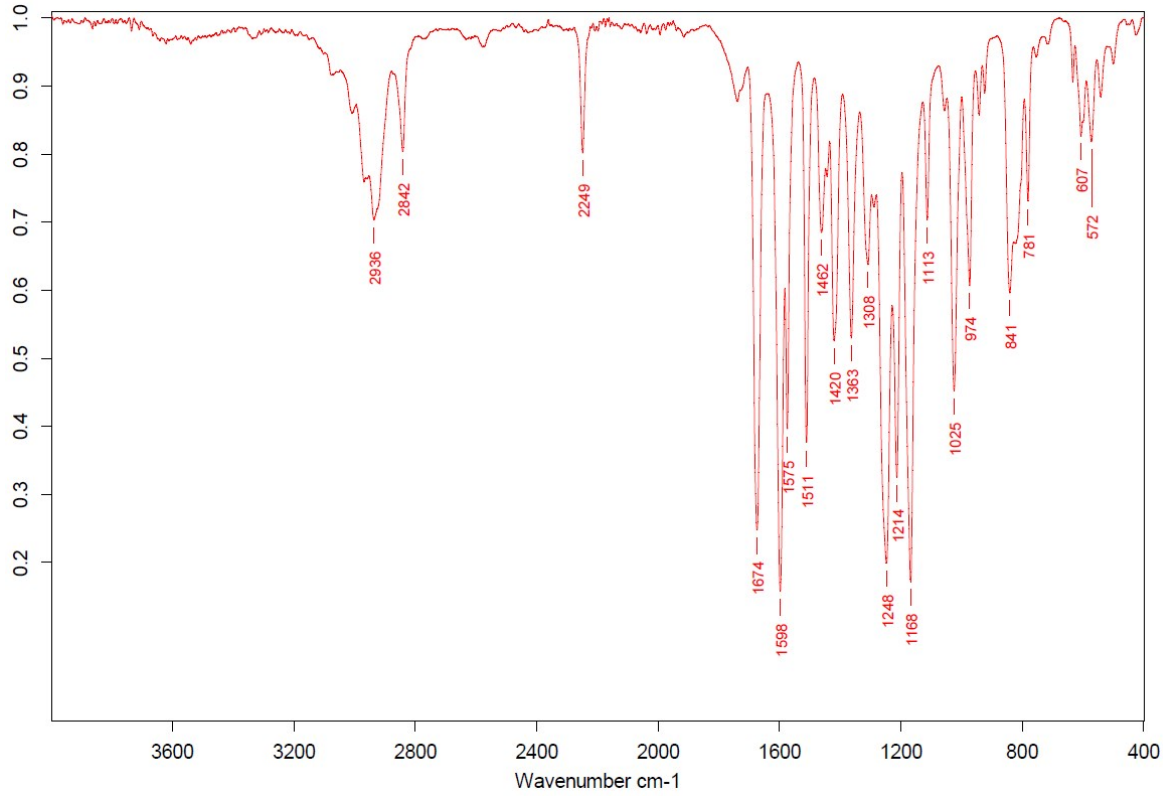
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H), 6.95-6.92 (m, 2H), 3.86 (s, 3H), 3.30 (t, J = 8.0 Hz, 2H), 2.73 (t, J = 8.0 Hz, 2H). The product is a mixture of two compounds with ratio of 8:1.

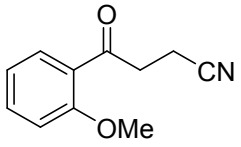
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 194.17, 164.45, 130.71, 129.10, 119.77, 114.39, 55.92, 34.23, 12.22.

IR spectrum (neat)





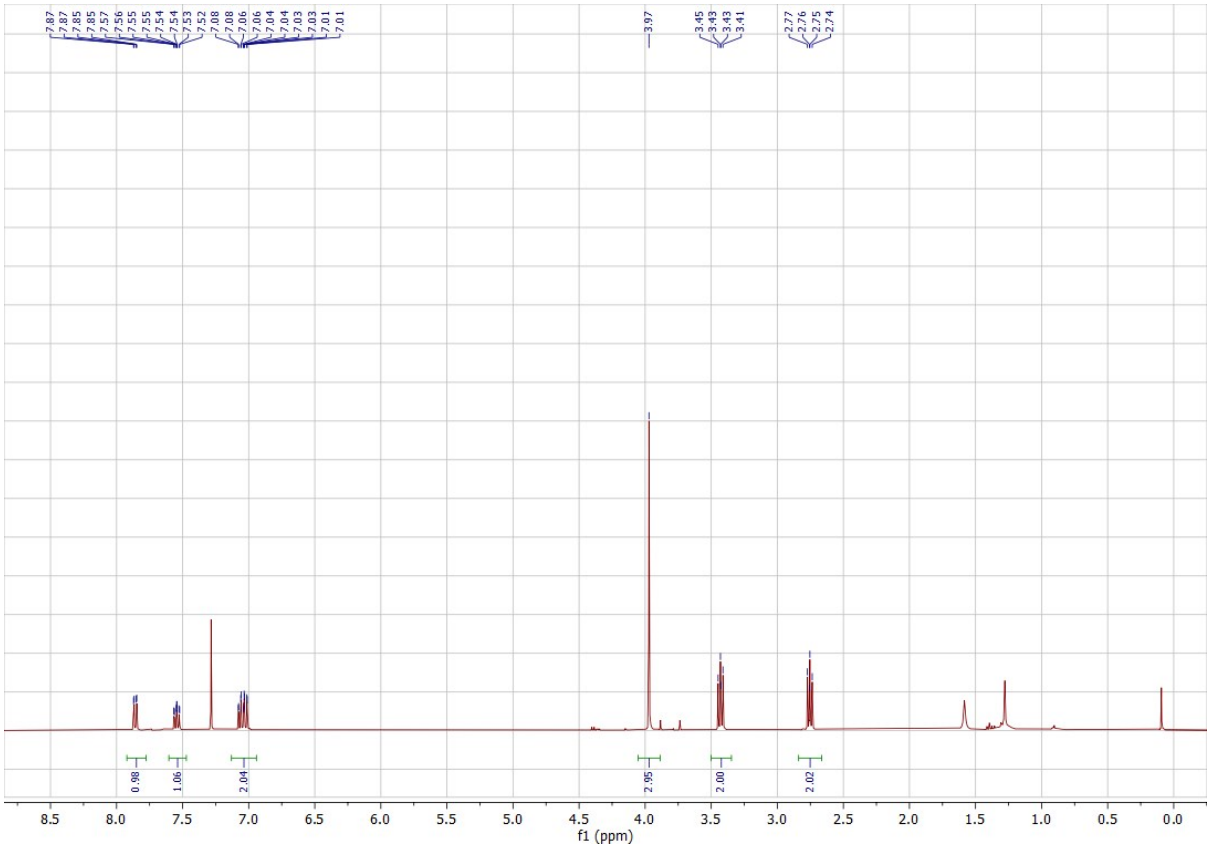
2d

The product was isolated as a light yellow oil. Yield: 35%

PLEASE NOTE: the product was purified several times by column chromatography without changing (virtually) the outcome.

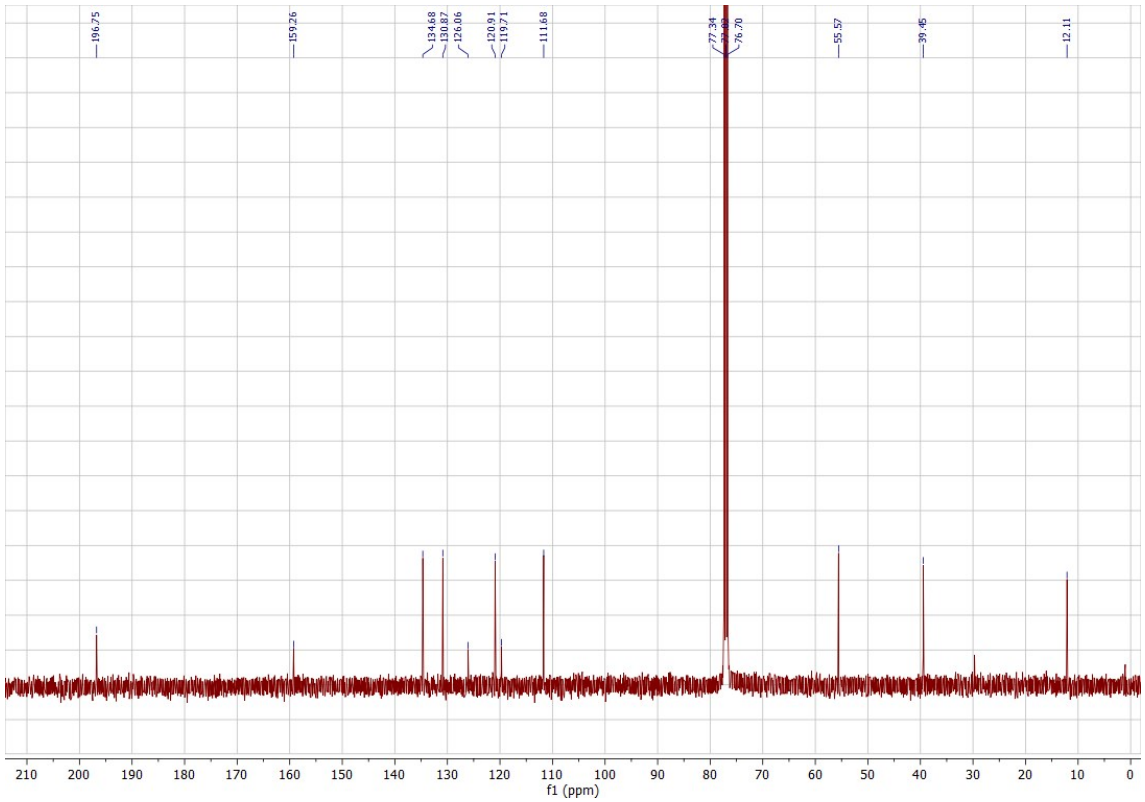
Characterization data matching data reported in the literature.[10,13]

^{1}H NMR spectrum ($CDCl_3$)



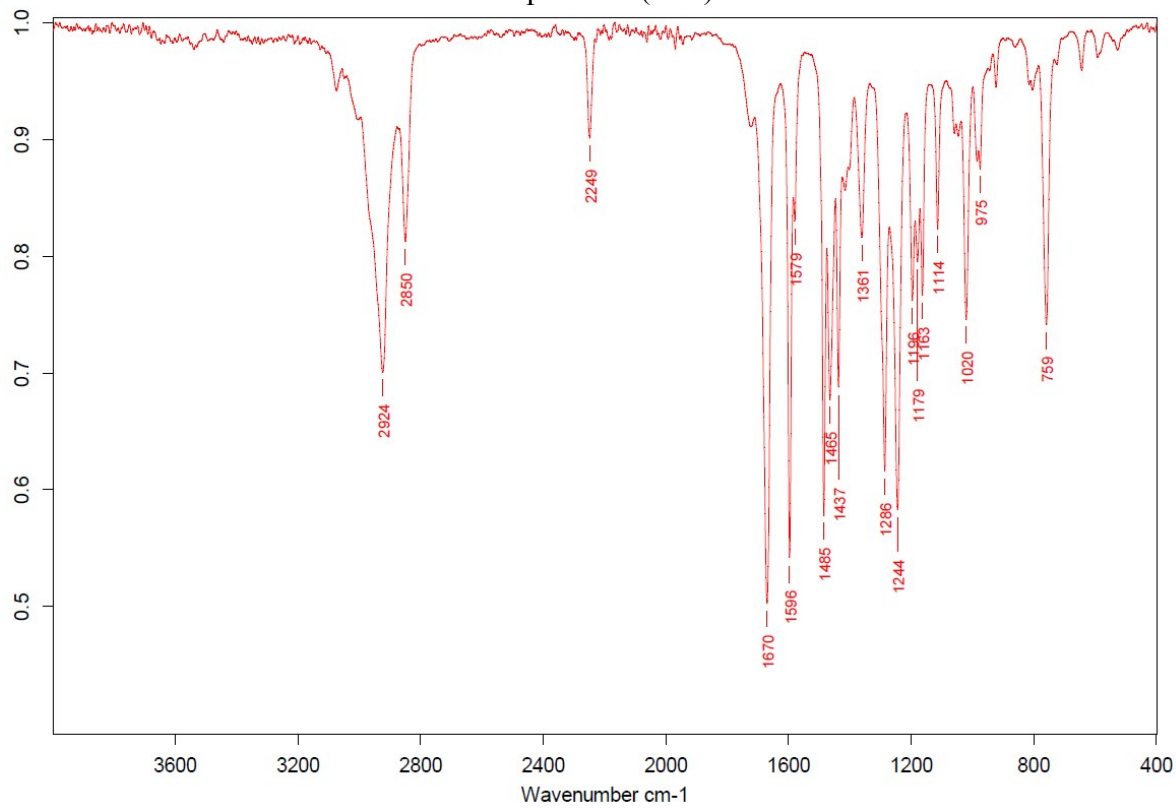
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (dd, *J* = 8.0 Hz, 1H), 7.57-7.52 (m, 1H), 7.08-7.01 (m, 2H), 3.97 (s, 3H), 3.43 (t, *J* = 8.0 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H).

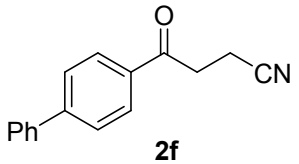
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 196.75, 159.26, 134.68, 130.87, 126.06, 120.91, 119.71, 111.68, 55.57, 39.45, 12.11.

IR spectrum (neat)



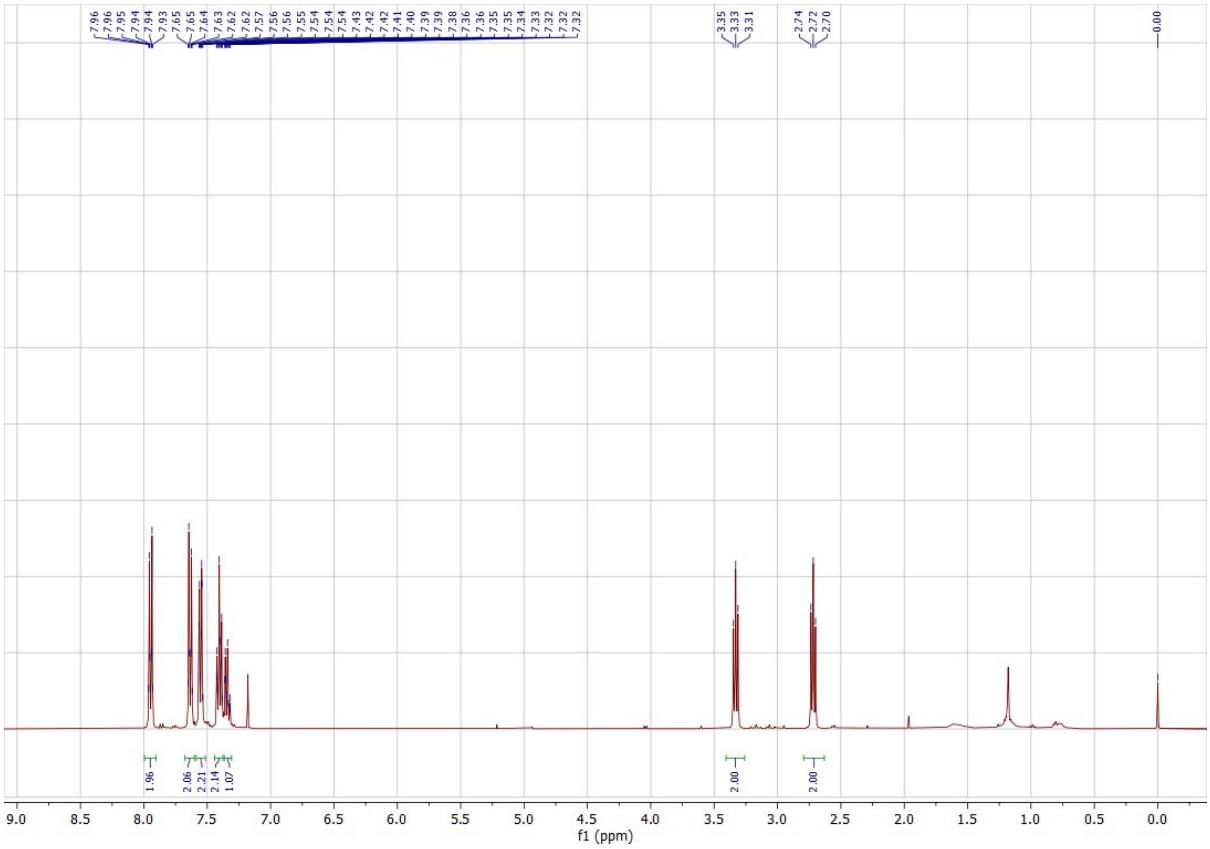


2f

The product was isolated as a white solid. Yield: 80%

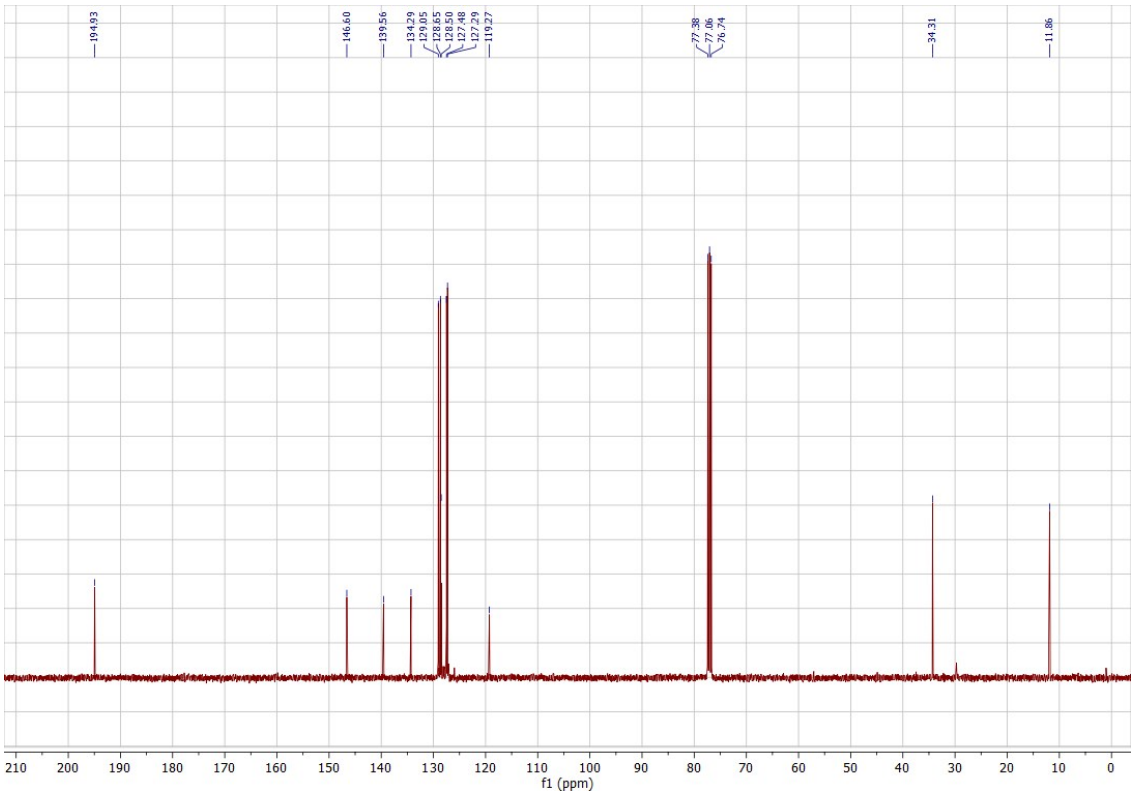
Characterization data matching data reported in the literature.[6,13]

^{1}H NMR spectrum ($CDCl_3$)



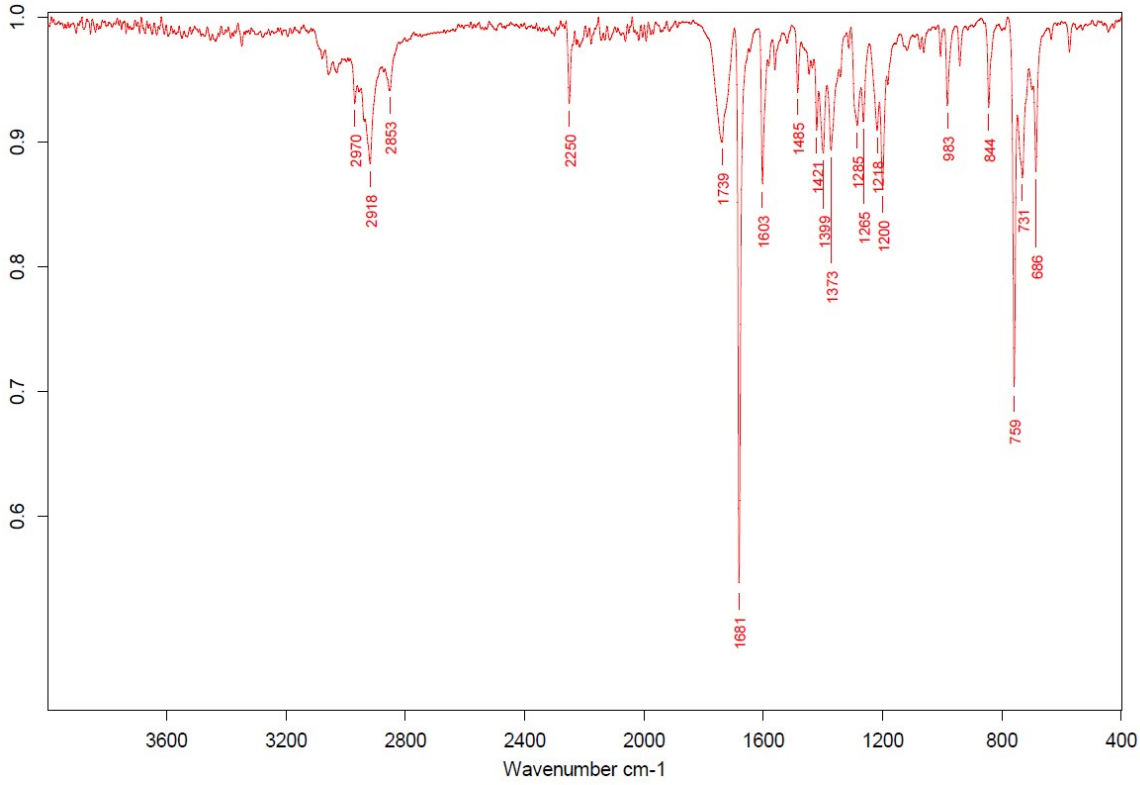
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.65-7.62 (m, 2H), 7.57-7.54 (m, 2H), 7.43-7.38 (m, 1H), 7.36-7.32 (m, 1H), 3.33 (t, J = 8.0 Hz, 2H), 2.72 (t, J = 8.0 Hz, 2H).

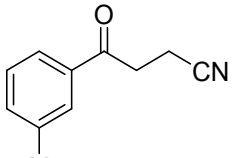
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 194.93, 146.60, 139.56, 134.29, 129.05, 128.65, 128.50, 127.48, 127.29, 119.27, 34.31, 11.86.

IR spectrum (neat)





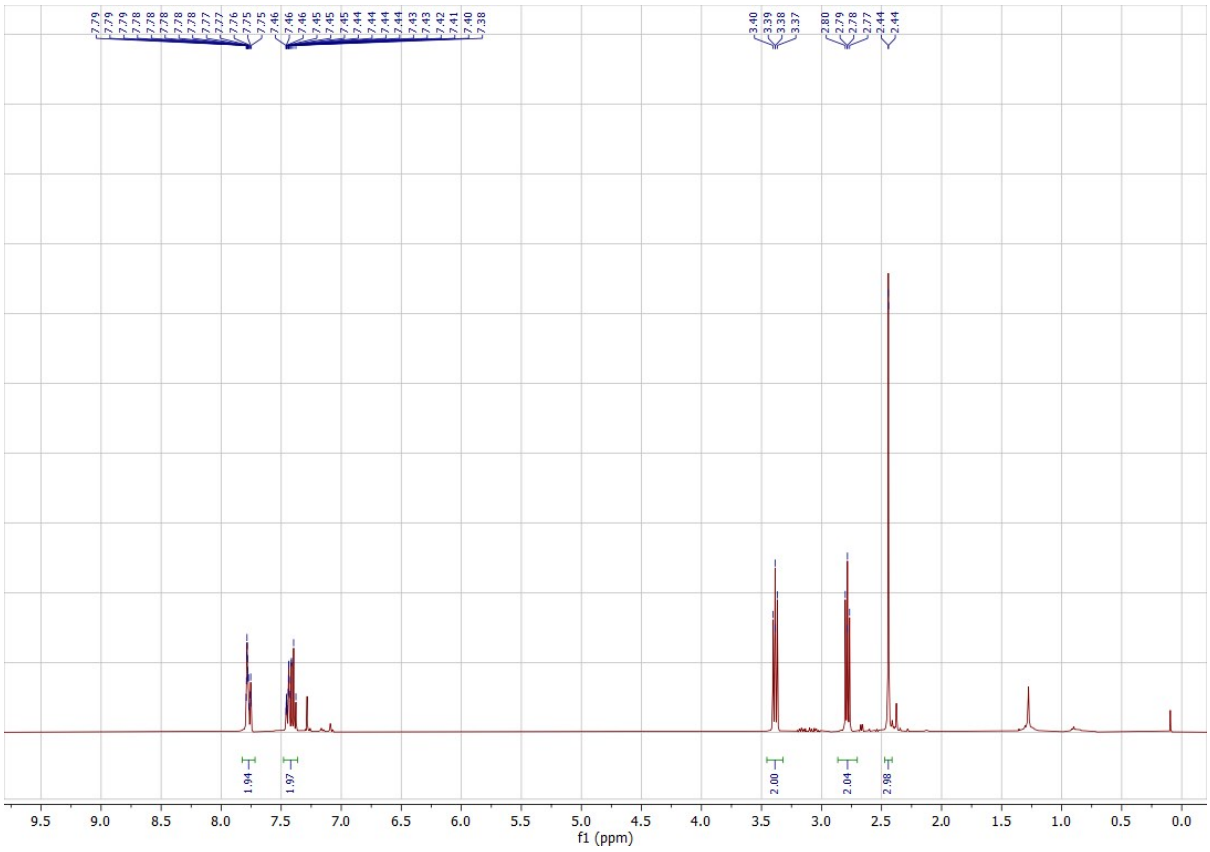
2g

The product was isolated as a white solid. Yield: 76%

PLEASE NOTE: the product was purified several times by column chromatography without changing (virtually) the outcome. The main impurity is ascribed to the dicyanated product such as **4** (see main text).

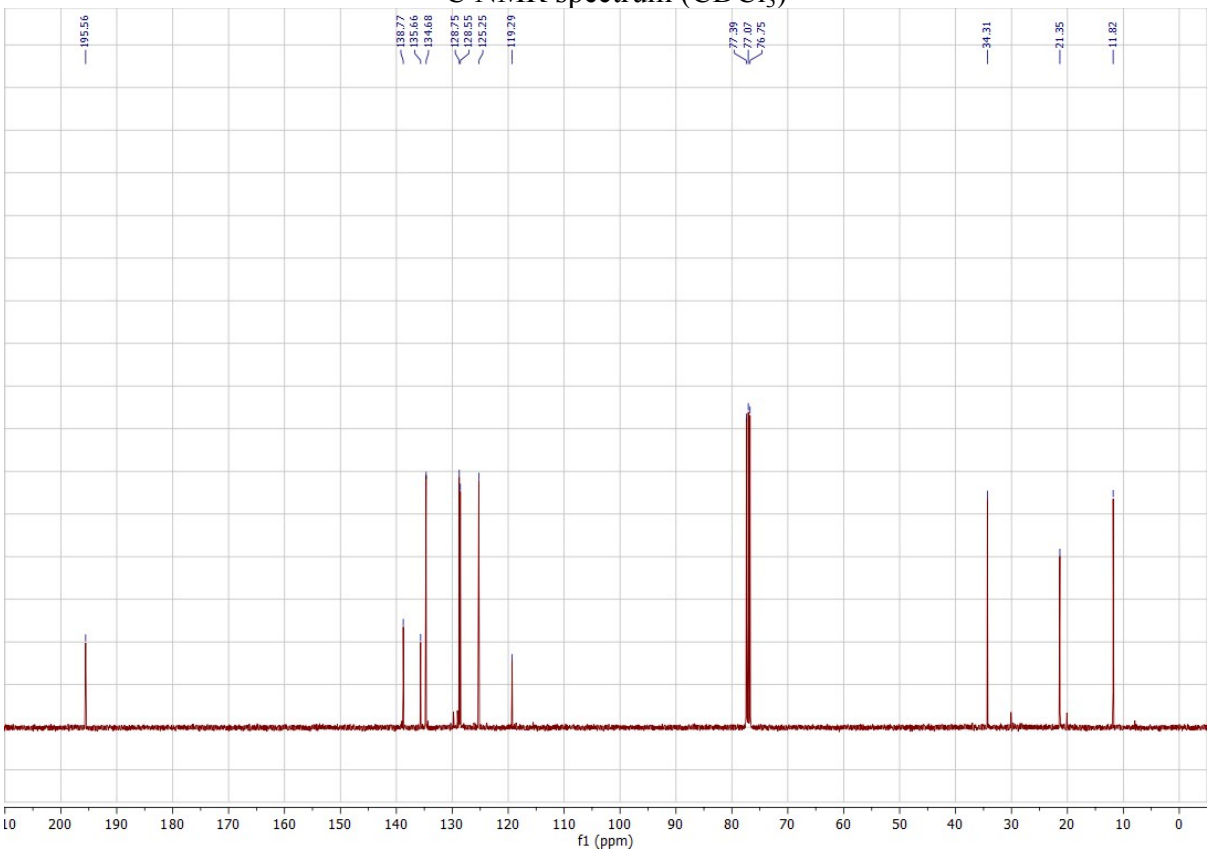
Characterization data matching data reported in the literature.[10]

^{1}H NMR spectrum ($CDCl_3$)



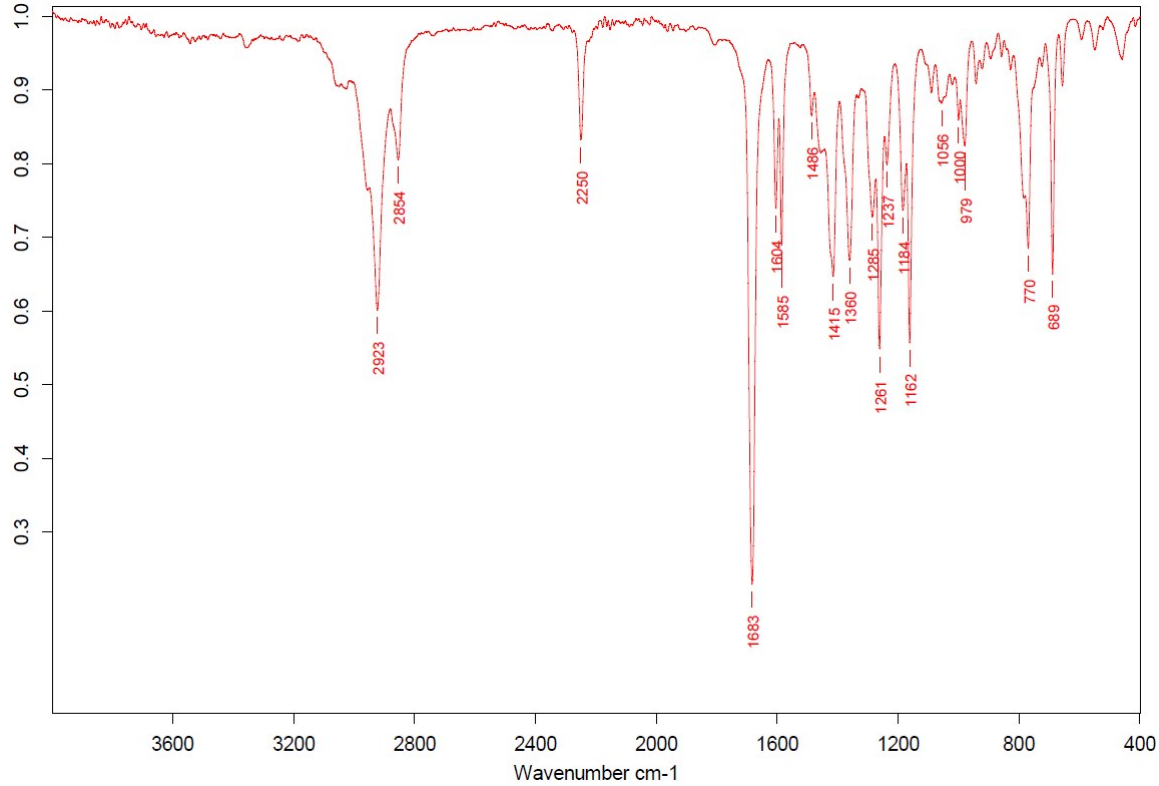
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.46-7.38 (m, 2H), 3.39 (t, J = 8.0 Hz, 2H), 2.78 (t, J = 8.0 Hz, 2H), 2.44 (s, 3H).

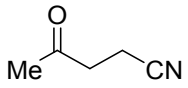
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 195.56, 138.77, 135.66, 134.68, 128.75, 128.55, 125.25, 119.29, 34.31, 21.35, 11.82.

IR spectrum (neat)





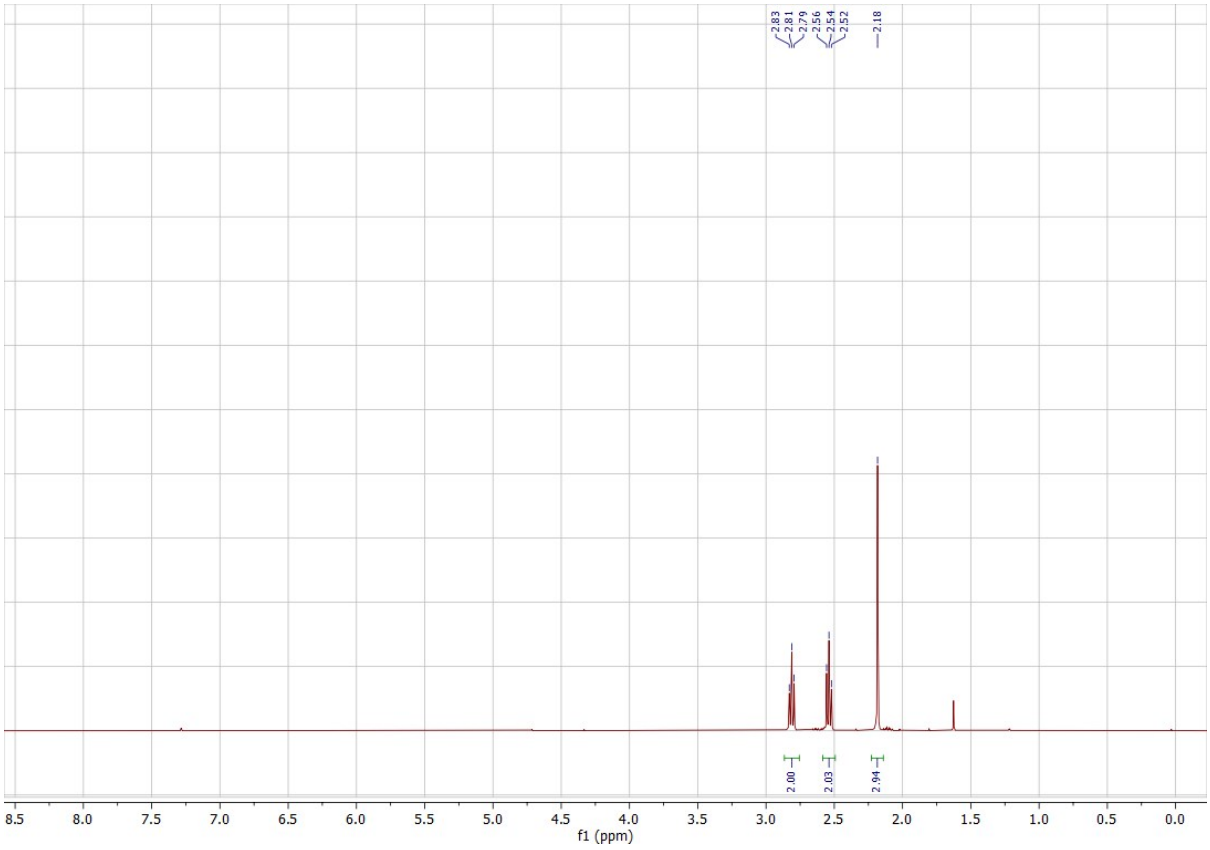
2h

The product was isolated as a white solid. Yield: 25%.

Note that the isolated yield is likely low due to the volatile nature of the product which complicated to some extent the separation from the solvent used in the column purification.

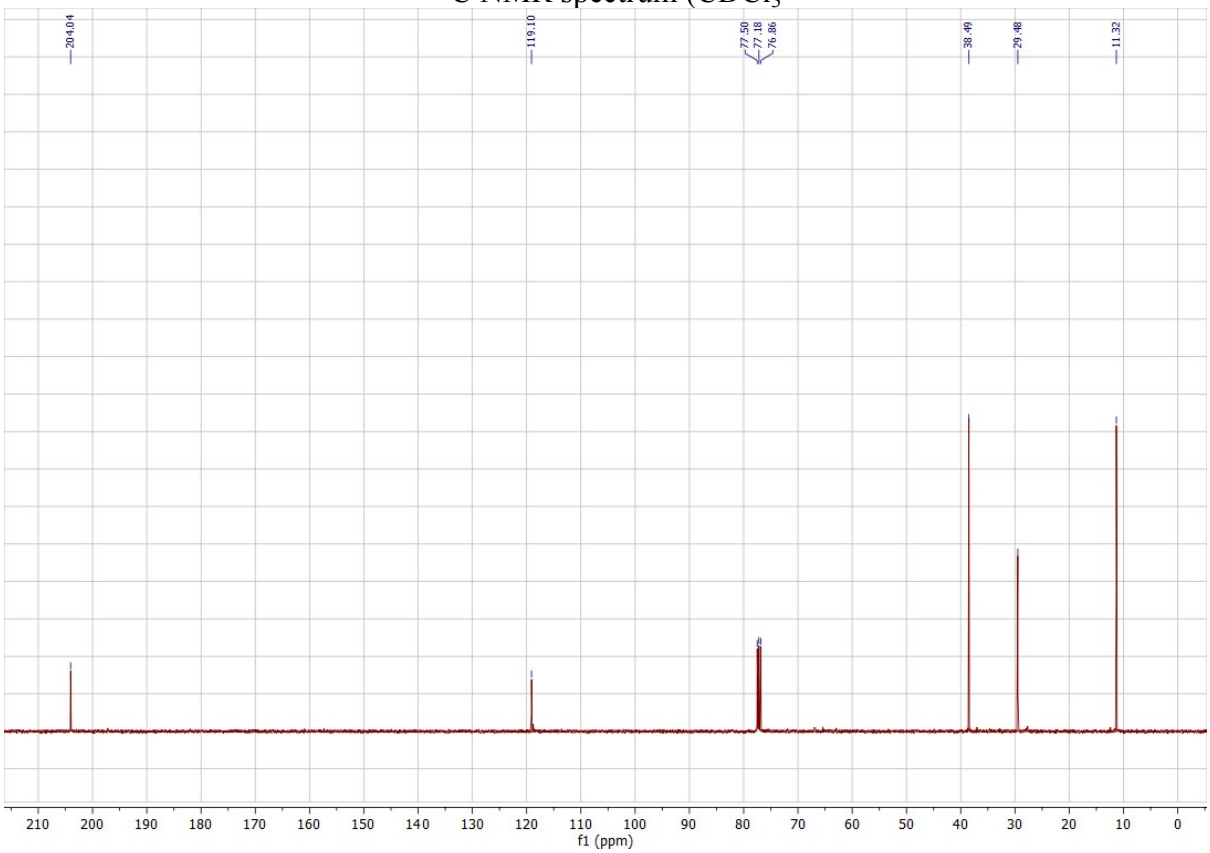
Characterization data matching data reported in the literature.[14]

^{1}H NMR spectrum ($CDCl_3$)



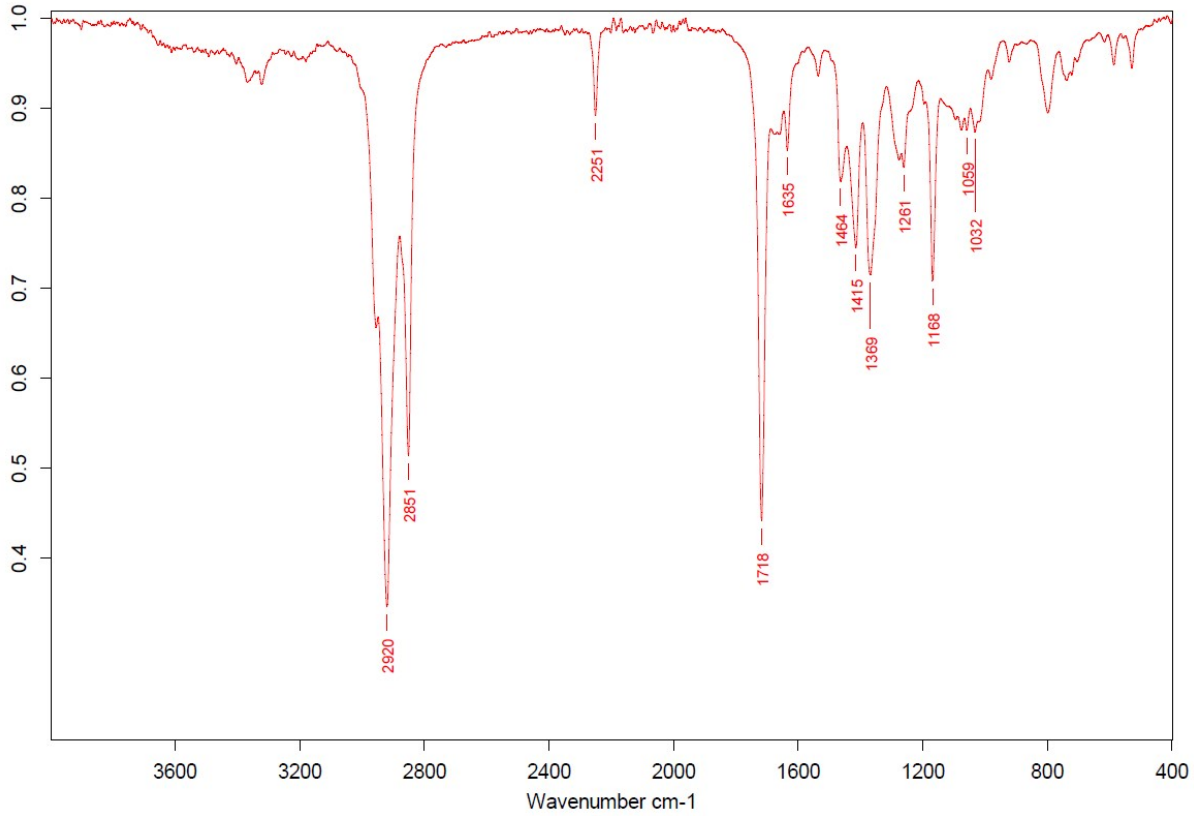
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (t, J = 8.0 Hz, 2H), 2.54 (t, J = 8.0 Hz, 2H), 2.18 (s, 3H).

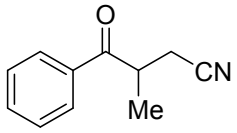
^{13}C NMR spectrum ($CDCl_3$



^{13}C NMR (101 MHz, $CDCl_3$) δ 204.04, 119.10, 38.49, 29.48, 11.32.

IR spectrum (neat)





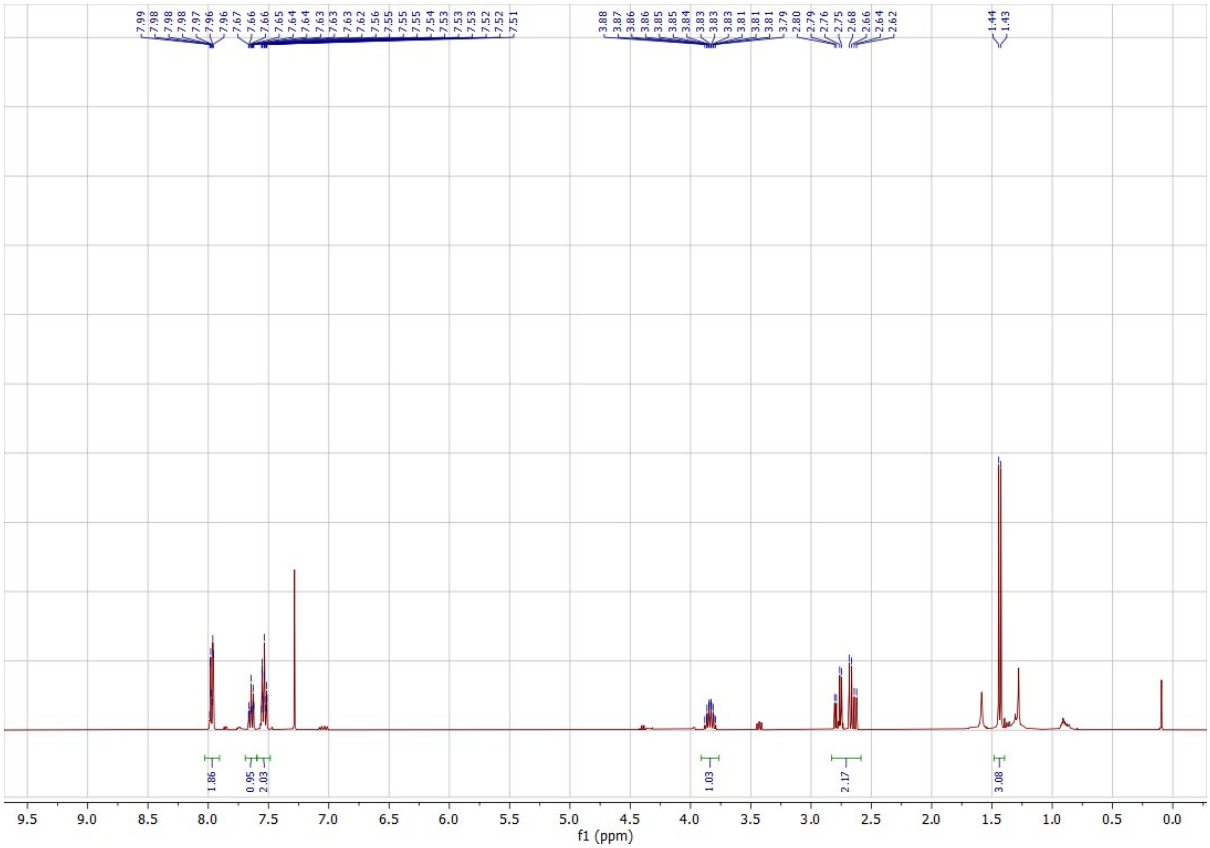
2i

The product was isolated as a white solid. Yield: 30%

PLEASE NOTE: the product was purified several times by column chromatography without changing (virtually) the outcome. The main impurity(ies) is/are ascribed to the dicyanated product such as **4** (see main text) and some solvent (impurity) arising from the eluent used in the column purification step.

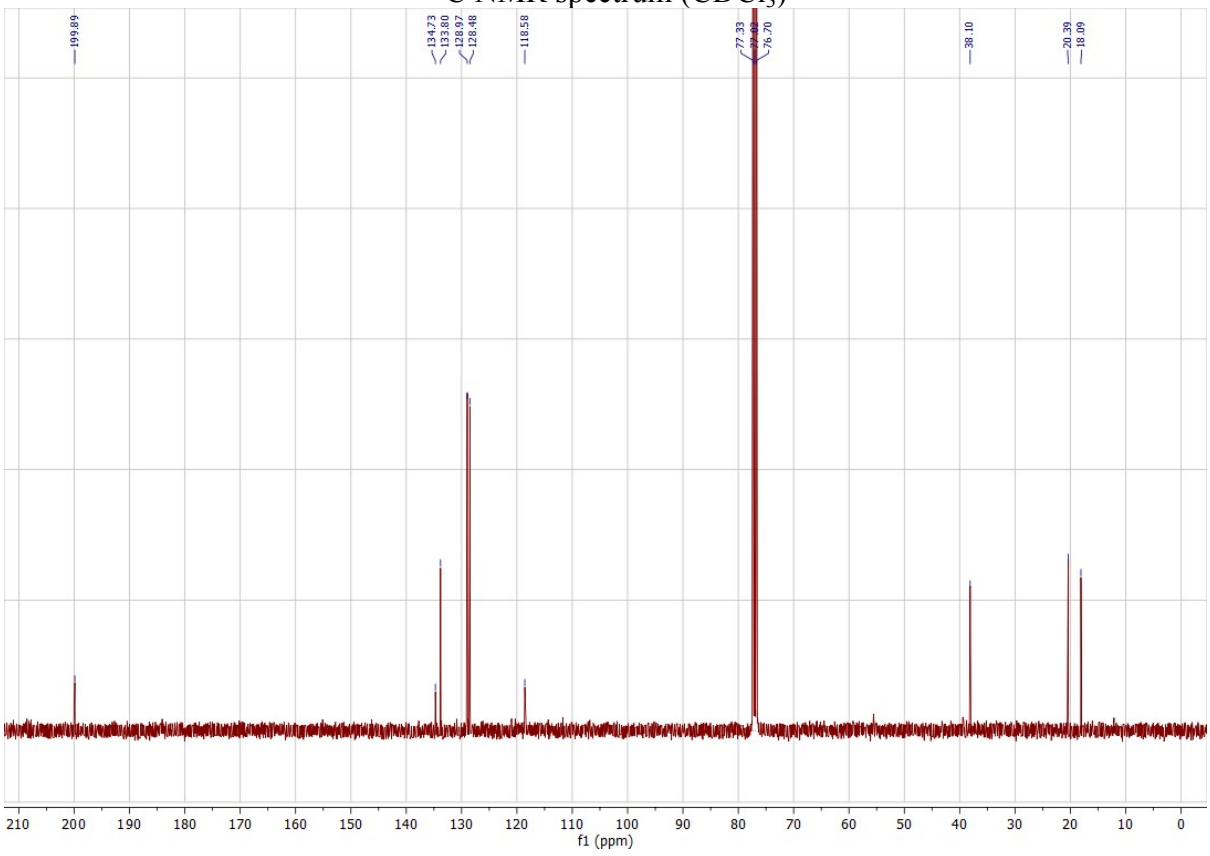
Characterization data matching data reported in the literature.[4]

^{1}H NMR spectrum ($CDCl_3$)



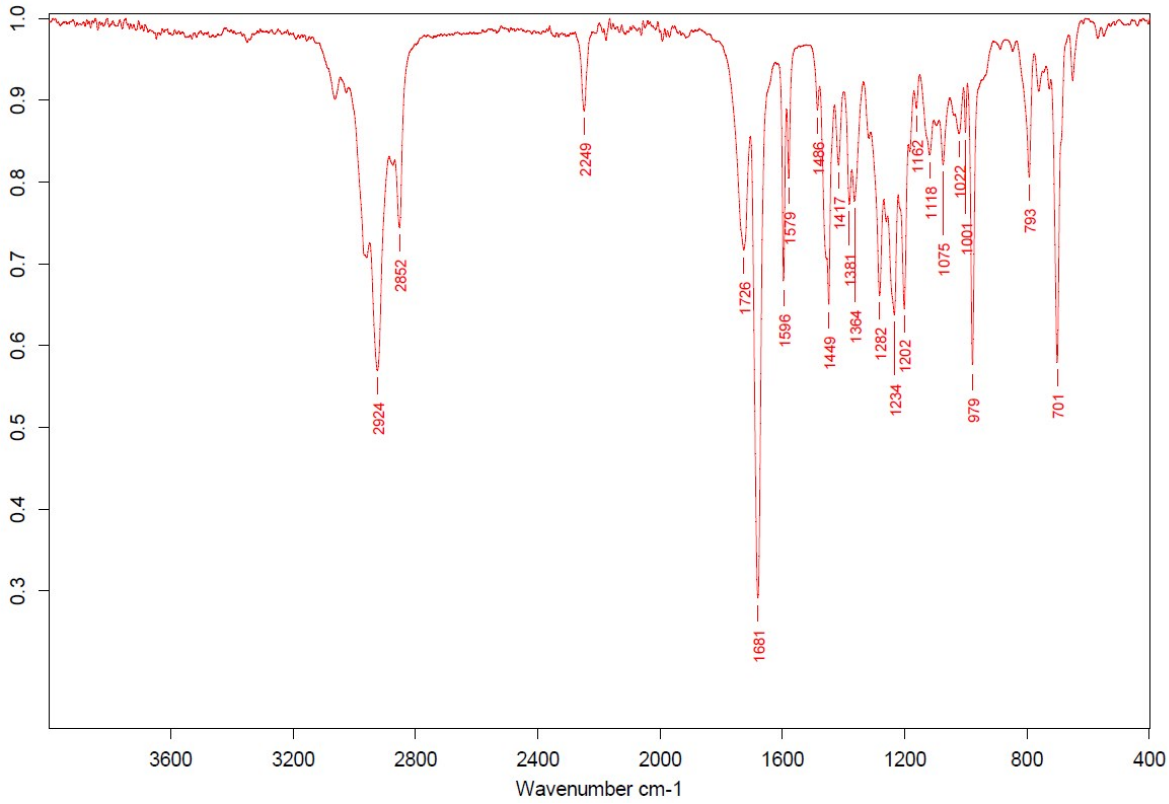
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.96 (m, 2H), 7.67-7.62 (m, 1H), 7.56-7.51 (m, 2H), 3.88-3.79 (m, 1H), 2.80-2.62 (m, 2H), 1.44-1.43 (d, J = 4.0 Hz, 3H).

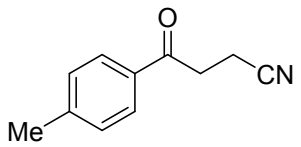
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 199.89, 134.73, 133.80, 128.97, 128.48, 118.58, 38.10, 20.39, 18.09.

IR spectrum (neat)



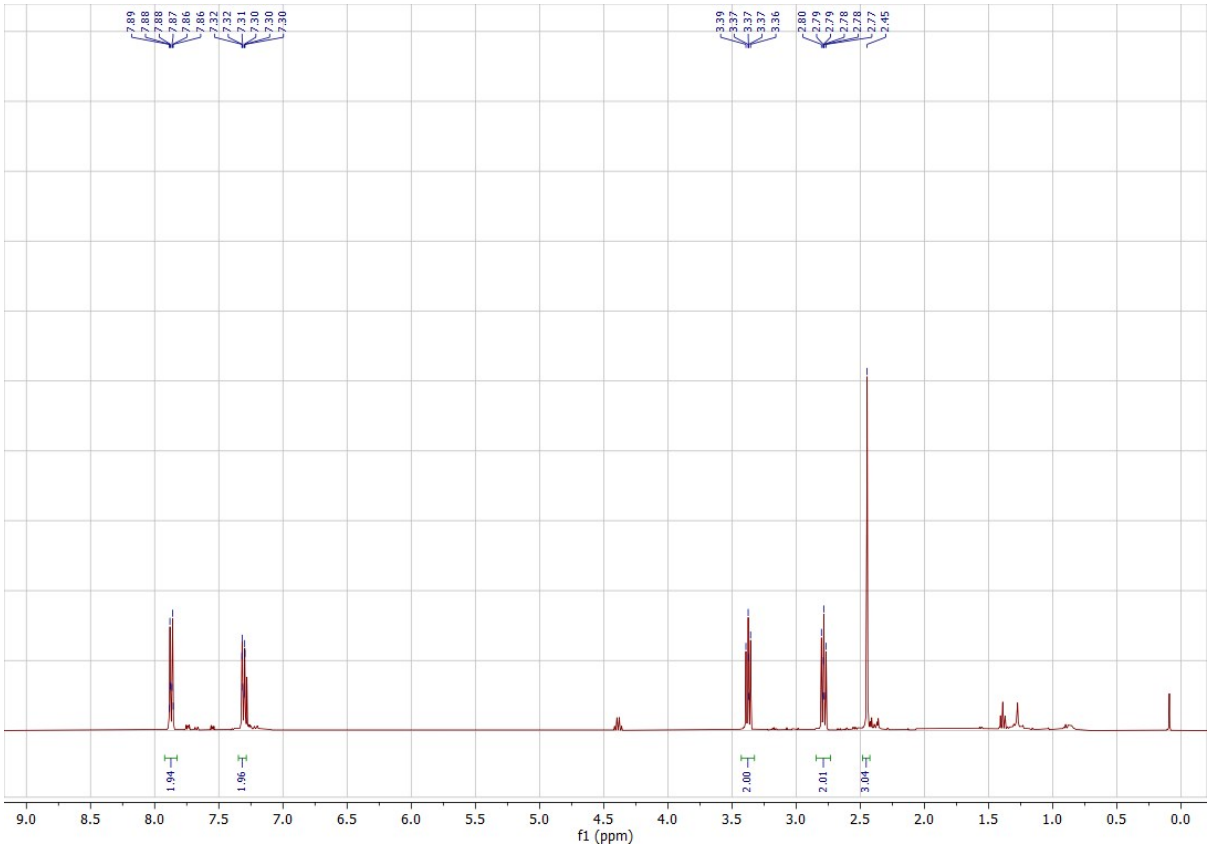


2j

The product was isolated as a white solid. Yield: 75%

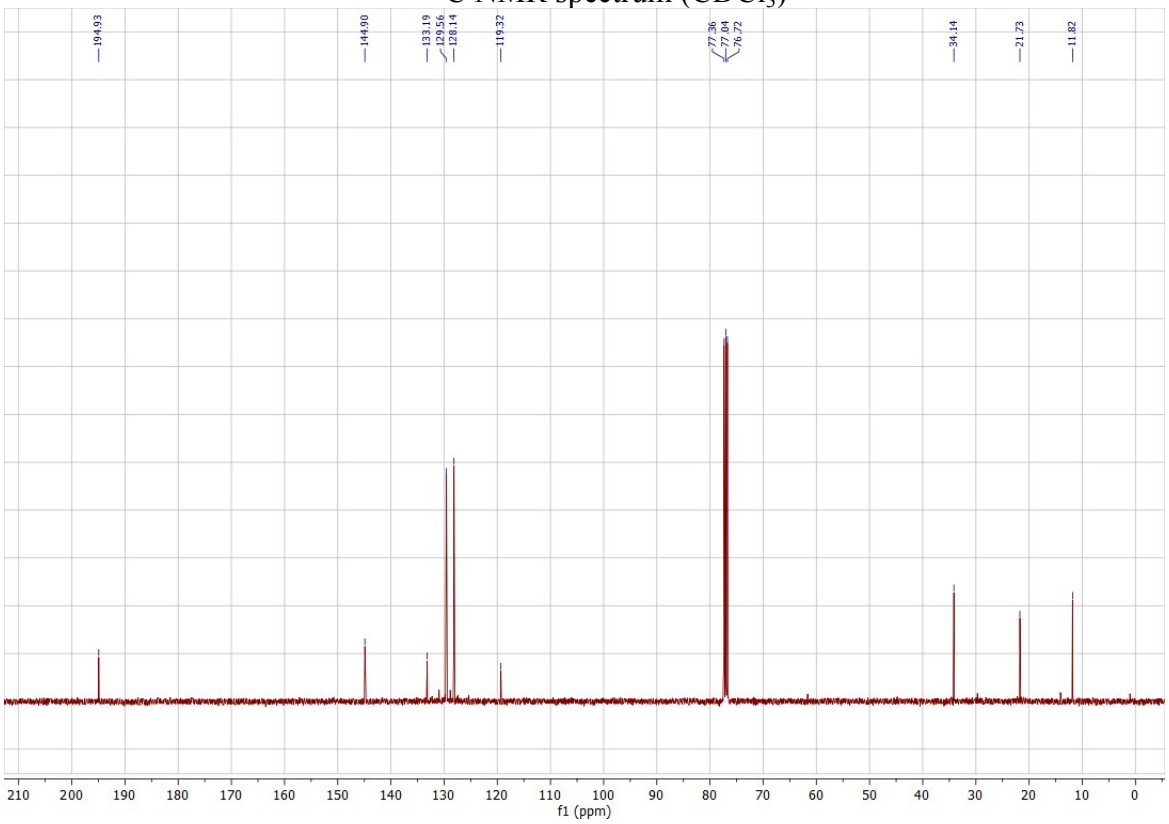
Characterization data matching data reported in the literature.[6,10,13]

^{1}H NMR spectrum ($CDCl_3$)



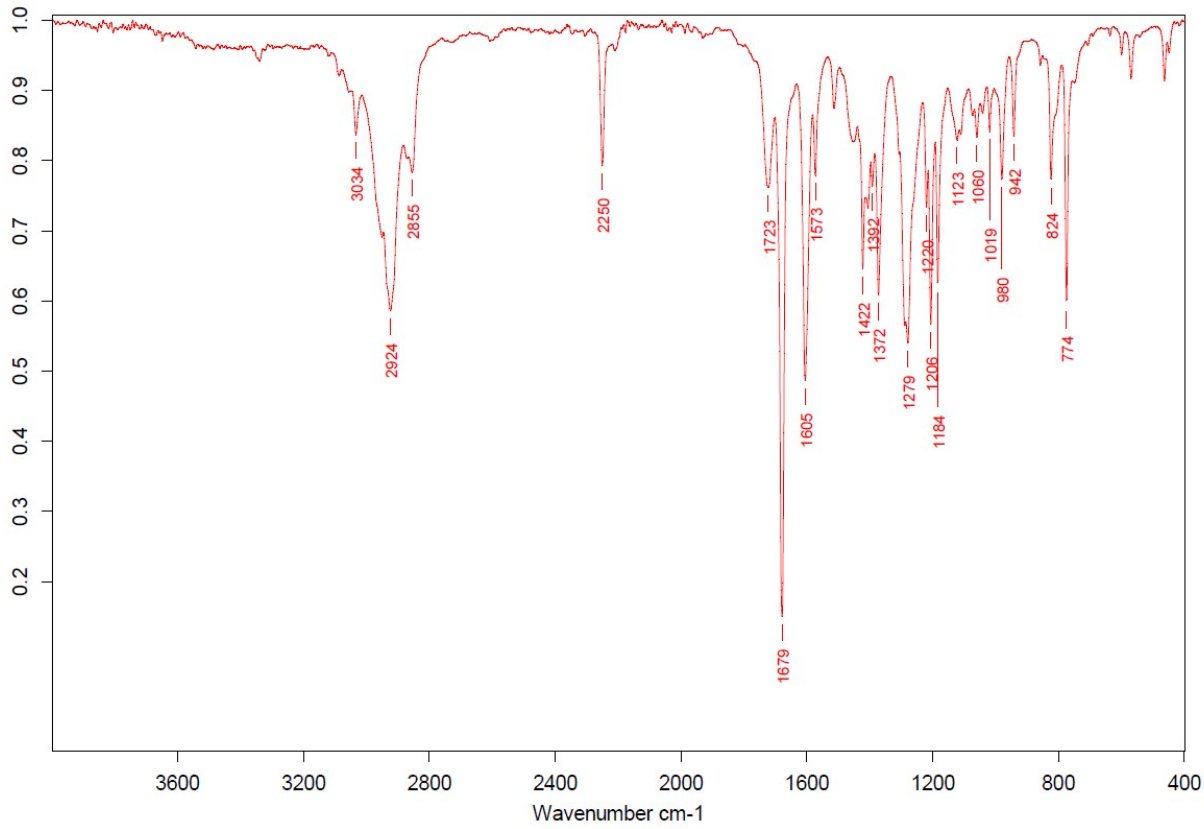
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 2H), 7.32-7.30 (m, 2H), 3.37 (t, J = 8.0 Hz, 2H), 2.78 (t, J = 8.0 Hz, 2H), 2.45 (s, 3H).

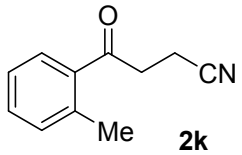
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 194.93, 144.90, 133.19, 129.56, 128.14, 119.32, 34.14, 21.73, 11.82.

IR spectrum (neat)



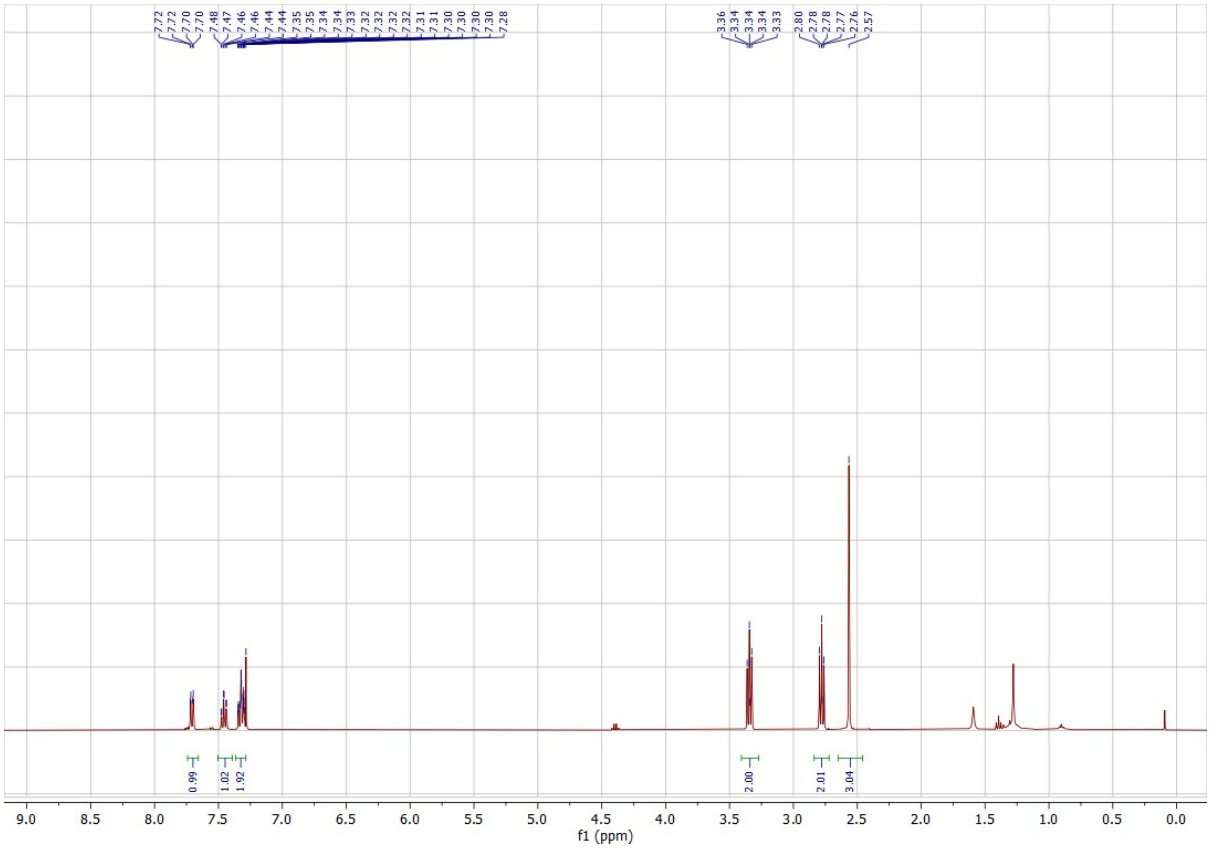


2k

The product was isolated as a yellowish oil. Yield: 45%

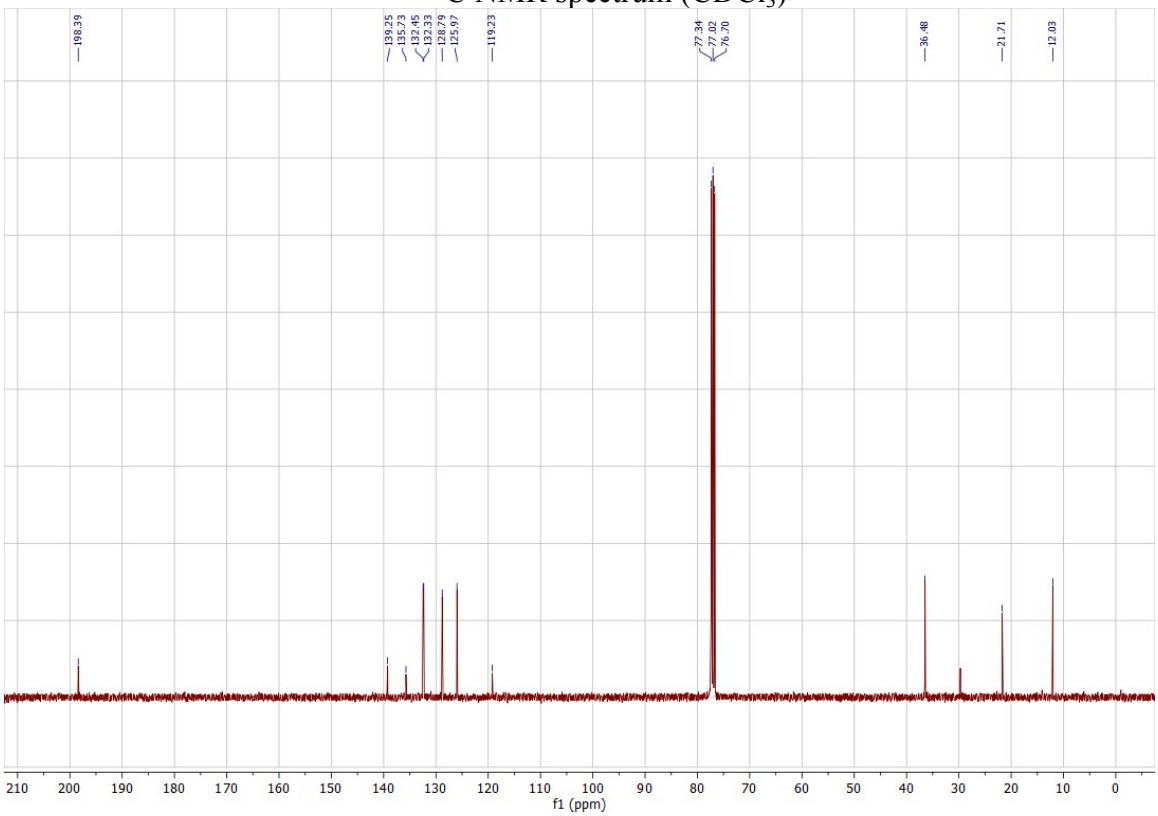
Characterization data matching data reported in the literature.[6,9,10]

^{1}H NMR spectrum ($CDCl_3$)



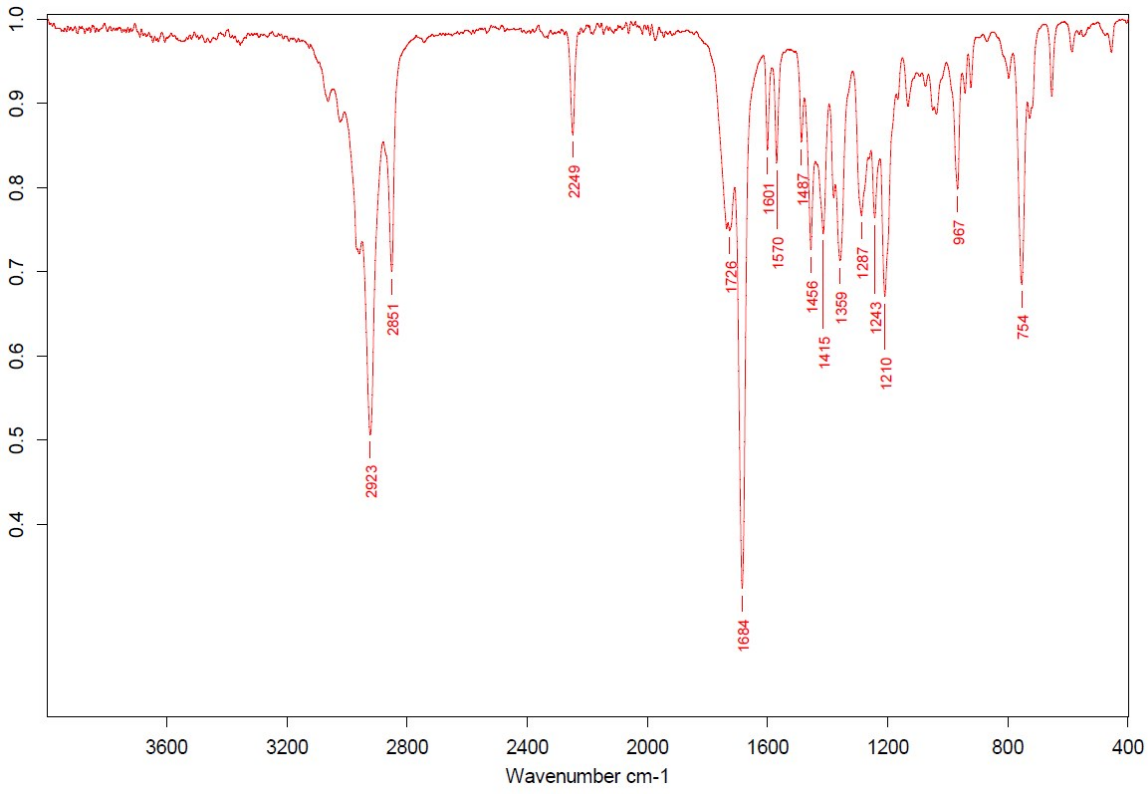
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.48-7.44 (m, 1H), 7.35-7.28 (m, 2H), 3.34 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.57 (s, 3H).

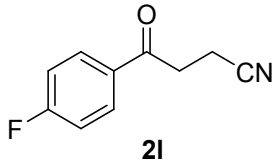
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 198.39, 139.25, 135.73, 132.45, 132.33, 128.79, 125.97, 119.23, 36.48, 21.71, 12.03.

IR spectrum (neat)



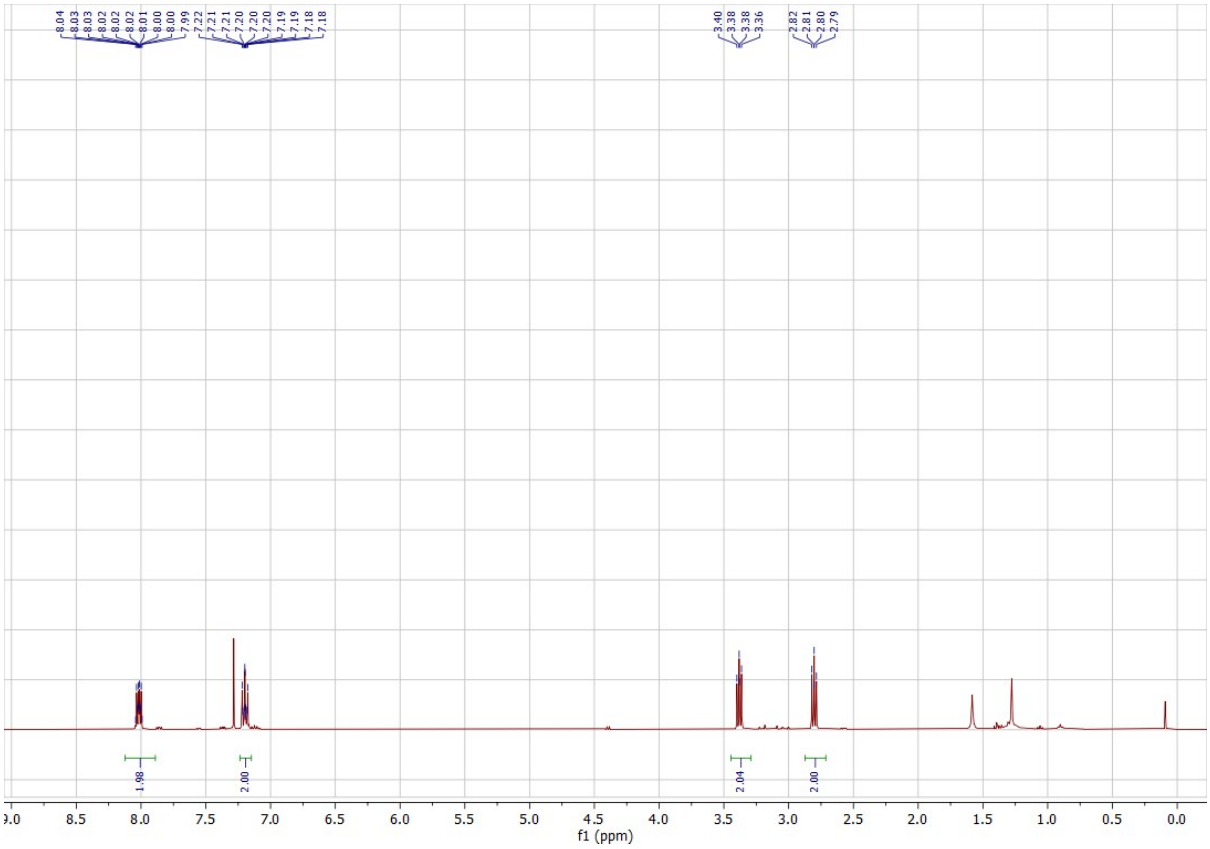


2l

The product was isolated as a white solid. Yield: 66%

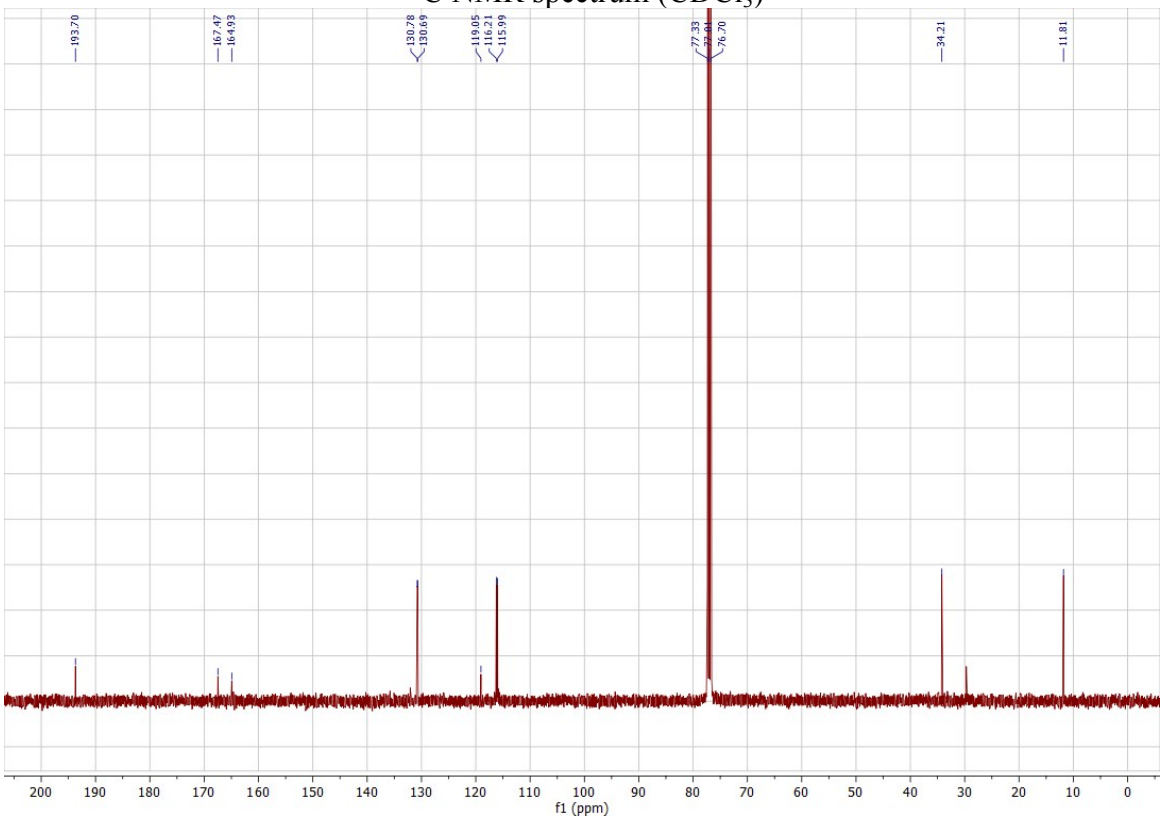
Characterization data matching data reported in the literature.[6,9,10,13]

^{1}H NMR spectrum ($CDCl_3$)



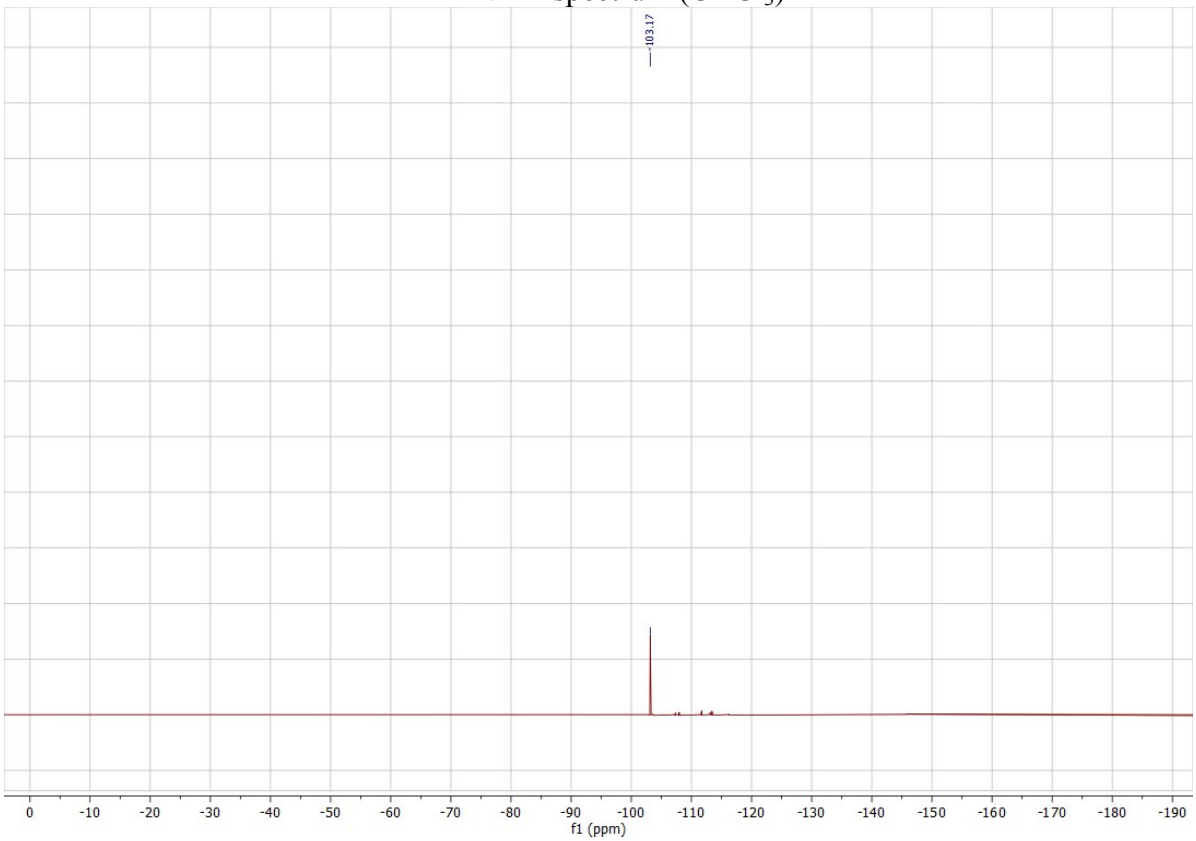
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 2H), 7.22-7.18 (m, 2H), 3.38 (t, *J* = 8.0 Hz, 2H), 2.80 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)



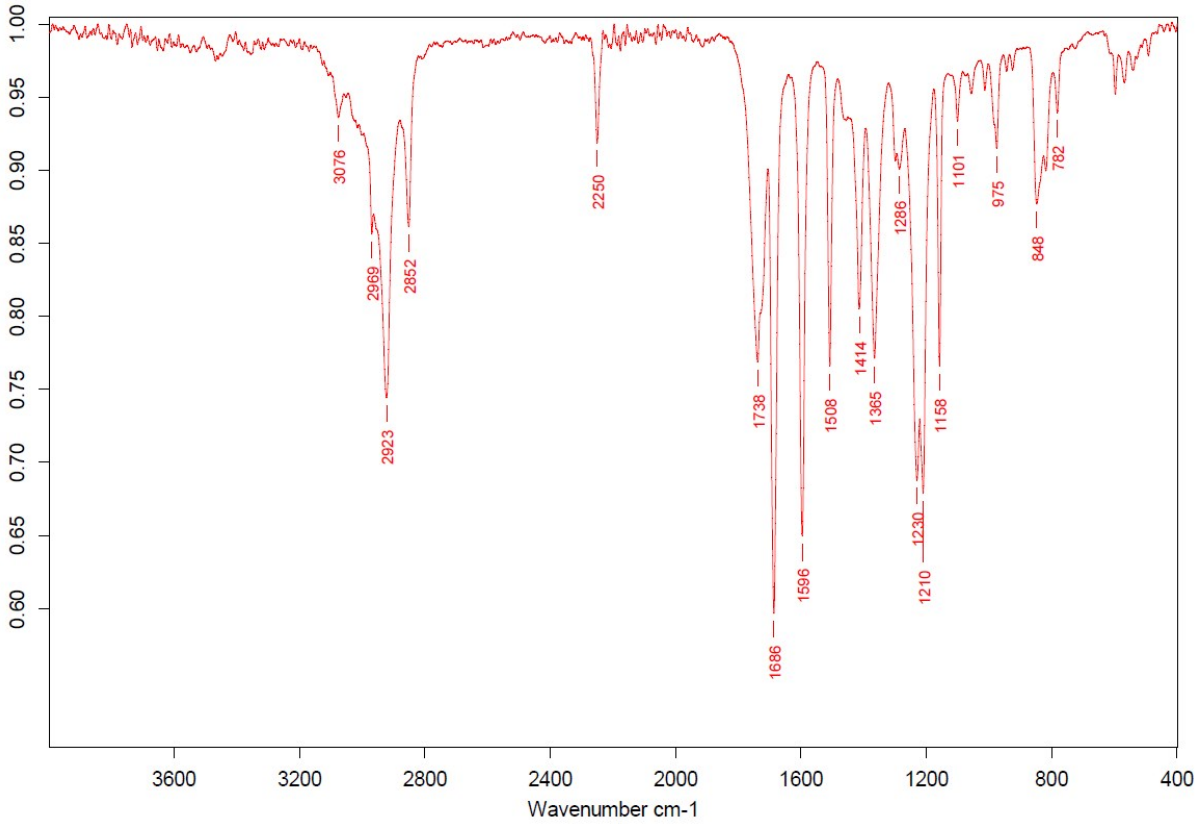
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.70, 166.20 (d, J = 256.5 Hz), 130.74 (d, J = 9.1 Hz), 119.05, 115.90 (d, J = 22.2 Hz), 34.21, 11.81.

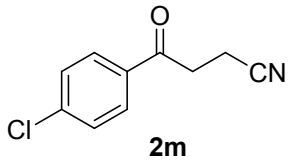
^{19}F NMR spectrum ($CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$) δ -103.17.

IR spectrum (neat)



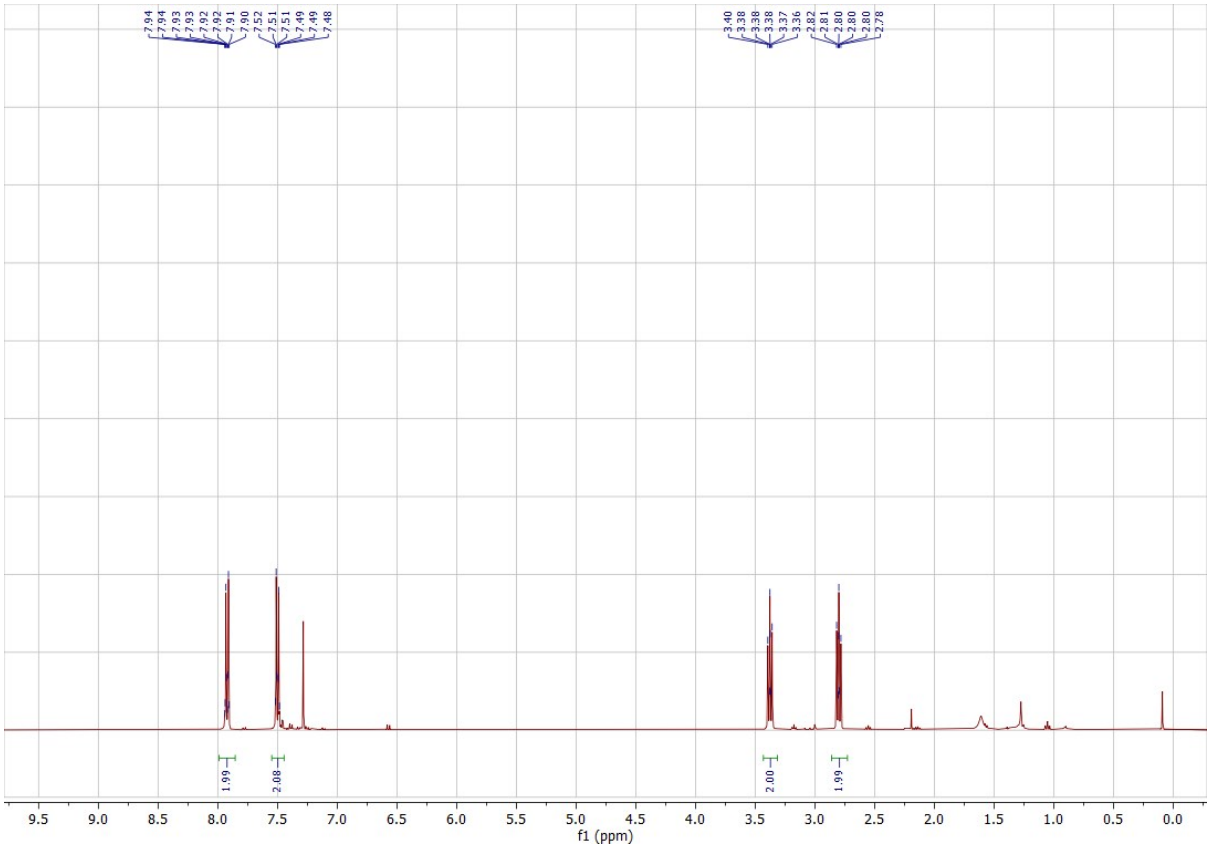


2m

The product was isolated as a white solid. Yield: 50%

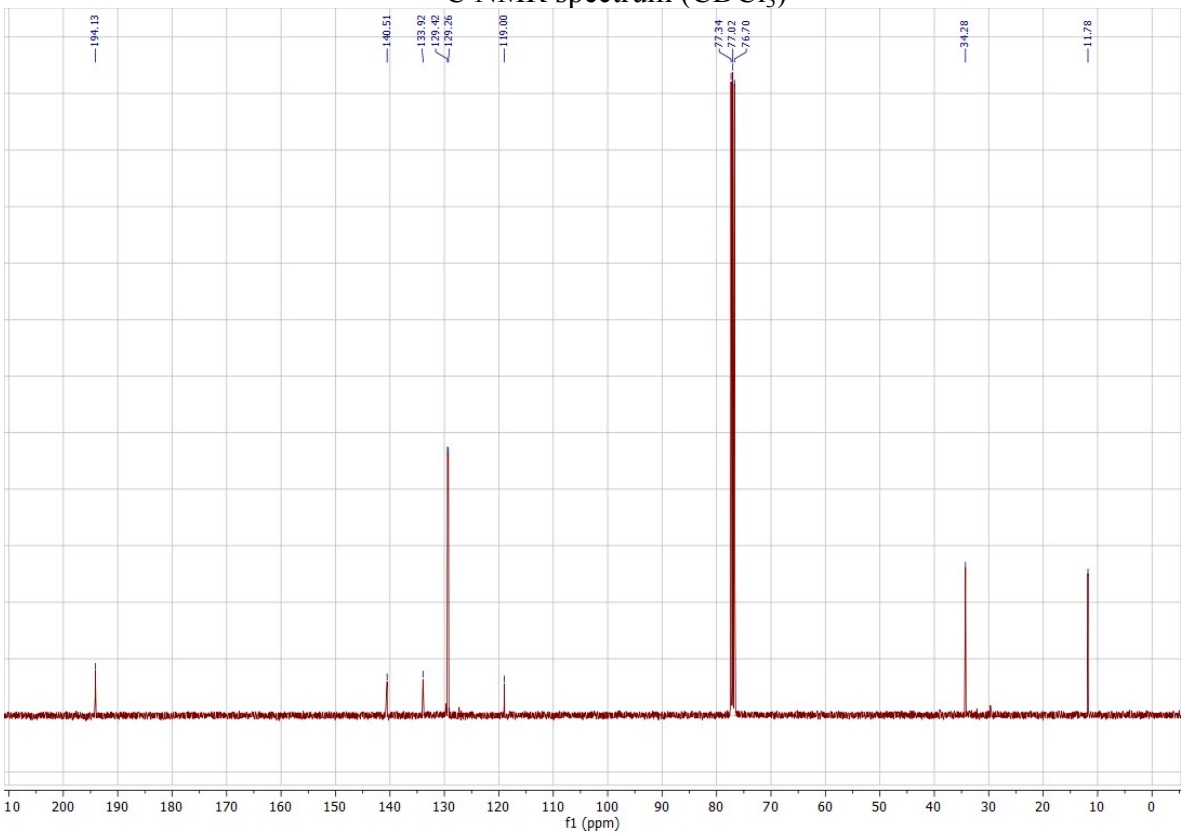
Characterization data matching data reported in the literature.[6,9,10,13]

^{1}H NMR spectrum ($CDCl_3$)



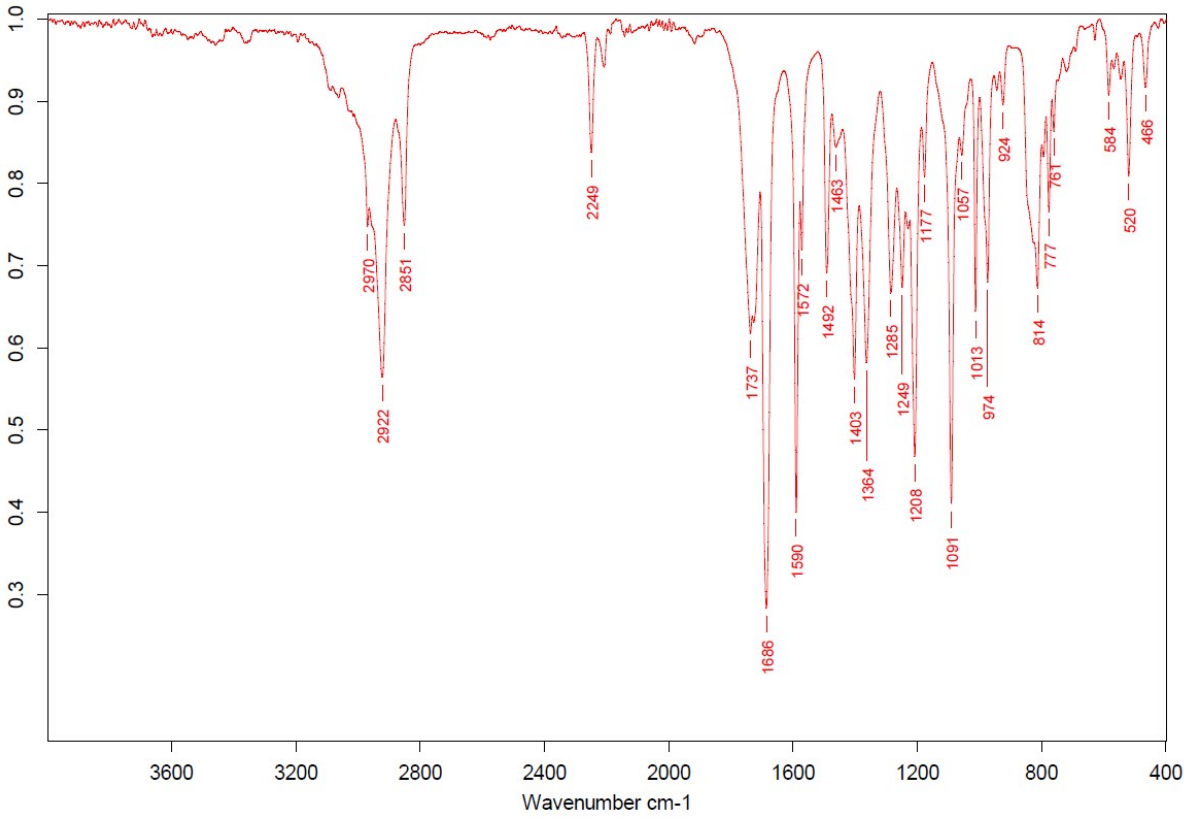
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.90 (m, 2H), 7.52-7.48 (m, 2H), 3.38 (t, J = 8.0 Hz, 2H), 2.80 (t, J = 8.0 Hz, 2H).

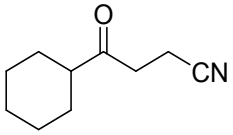
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 194.13, 140.51, 133.92, 129.42, 129.26, 119.00, 34.28, 11.78.

IR spectrum (neat)



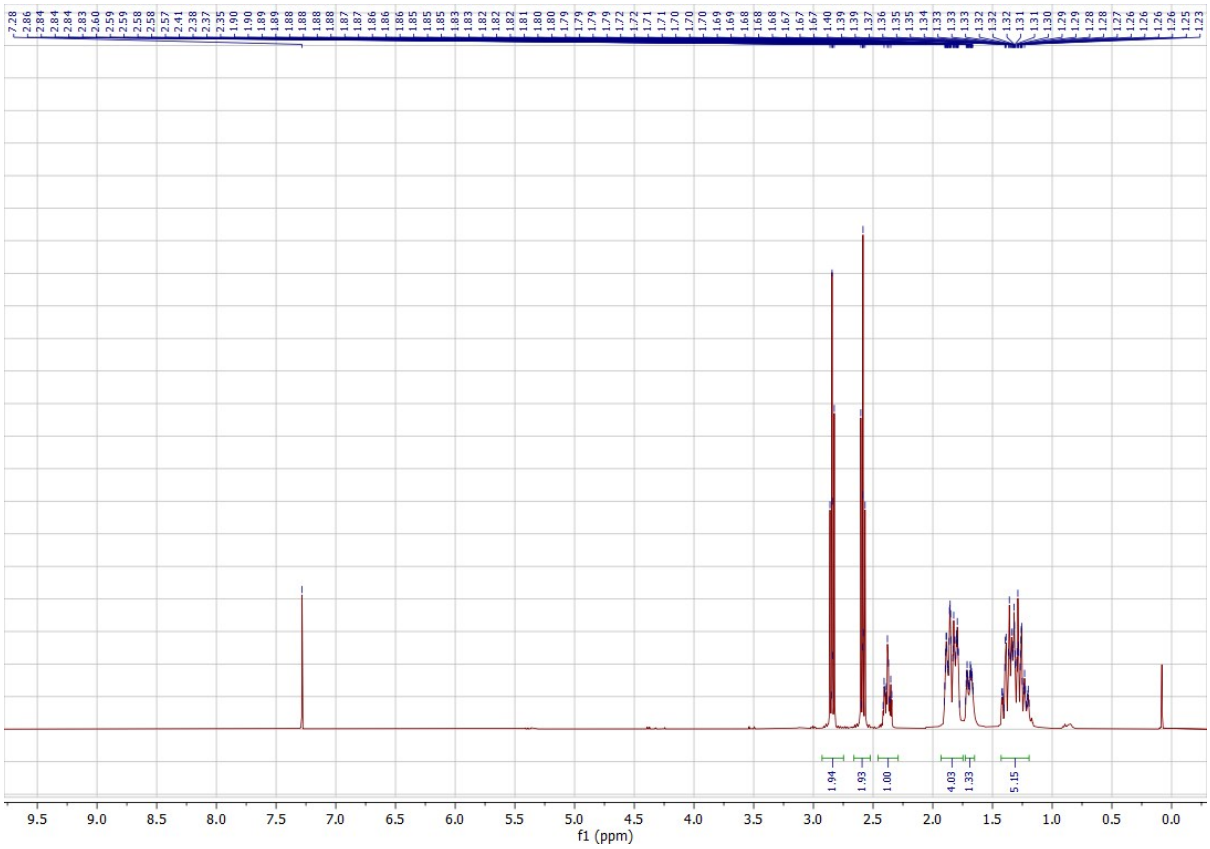


2n

The product was isolated as a colorless oil. Yield: 51%

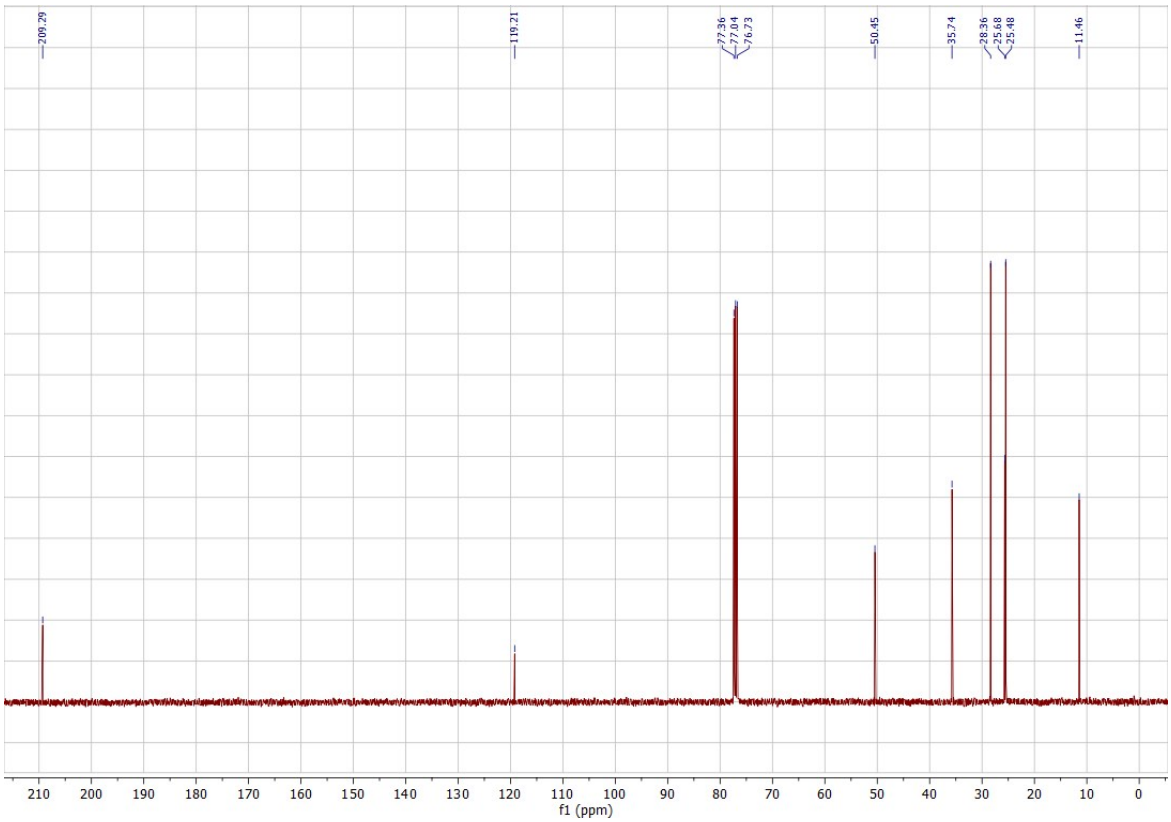
Characterization data matching data reported in the literature.[8]

^{1}H NMR spectrum ($CDCl_3$)



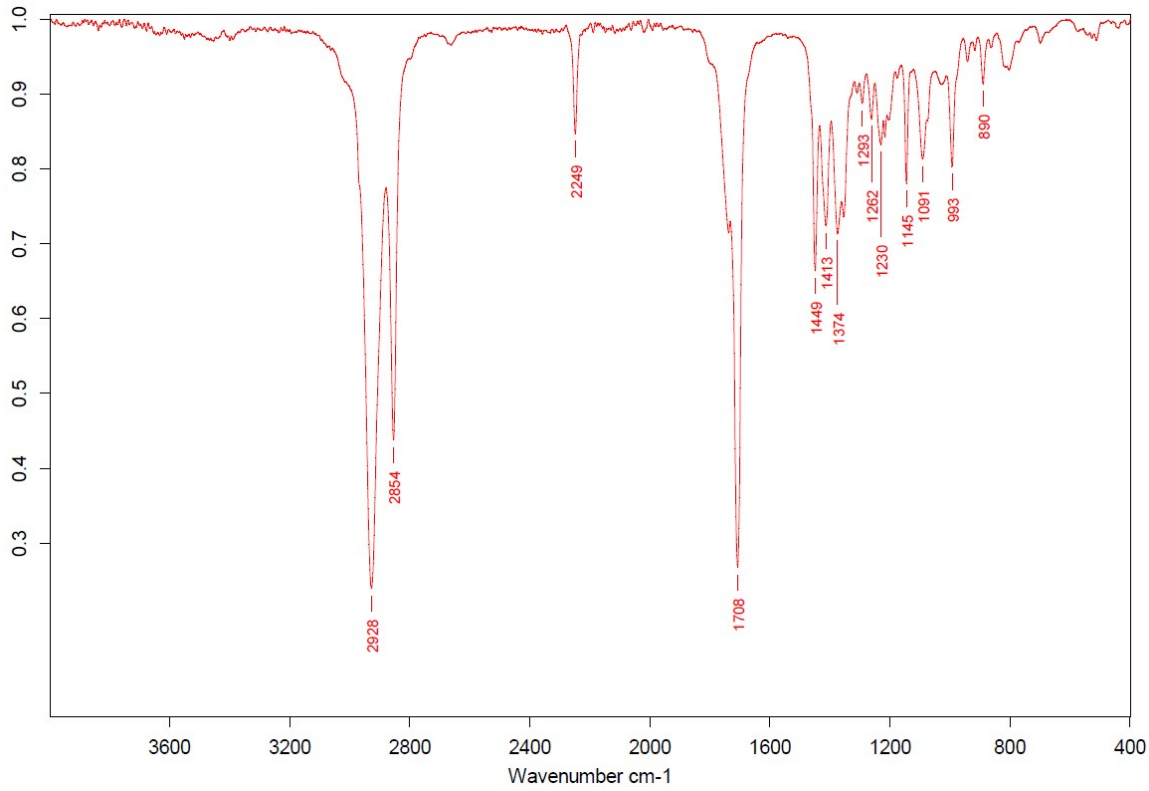
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.84 (t, *J* = 8.0 Hz, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.42-2.34 (m, 1H), 1.90-1.78 (m, 4H), 1.73-1.66 (m, 1H), 1.42-1.19 (m, 5H).

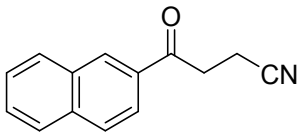
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 209.29, 119.21, 50.45, 35.74, 28.36, 25.68, 25.48, 11.46.

IR spectrum (neat)



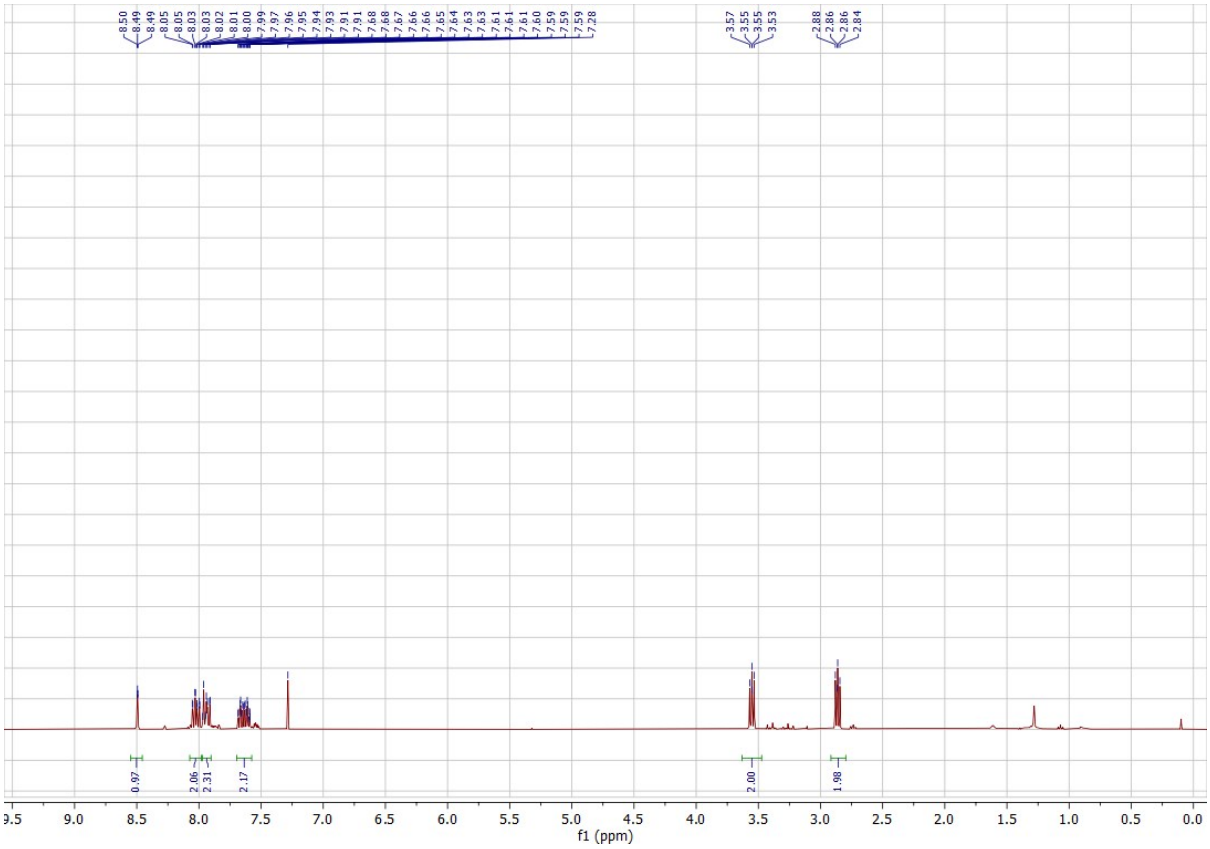


2o

The product was isolated as a white solid. Yield: 69%

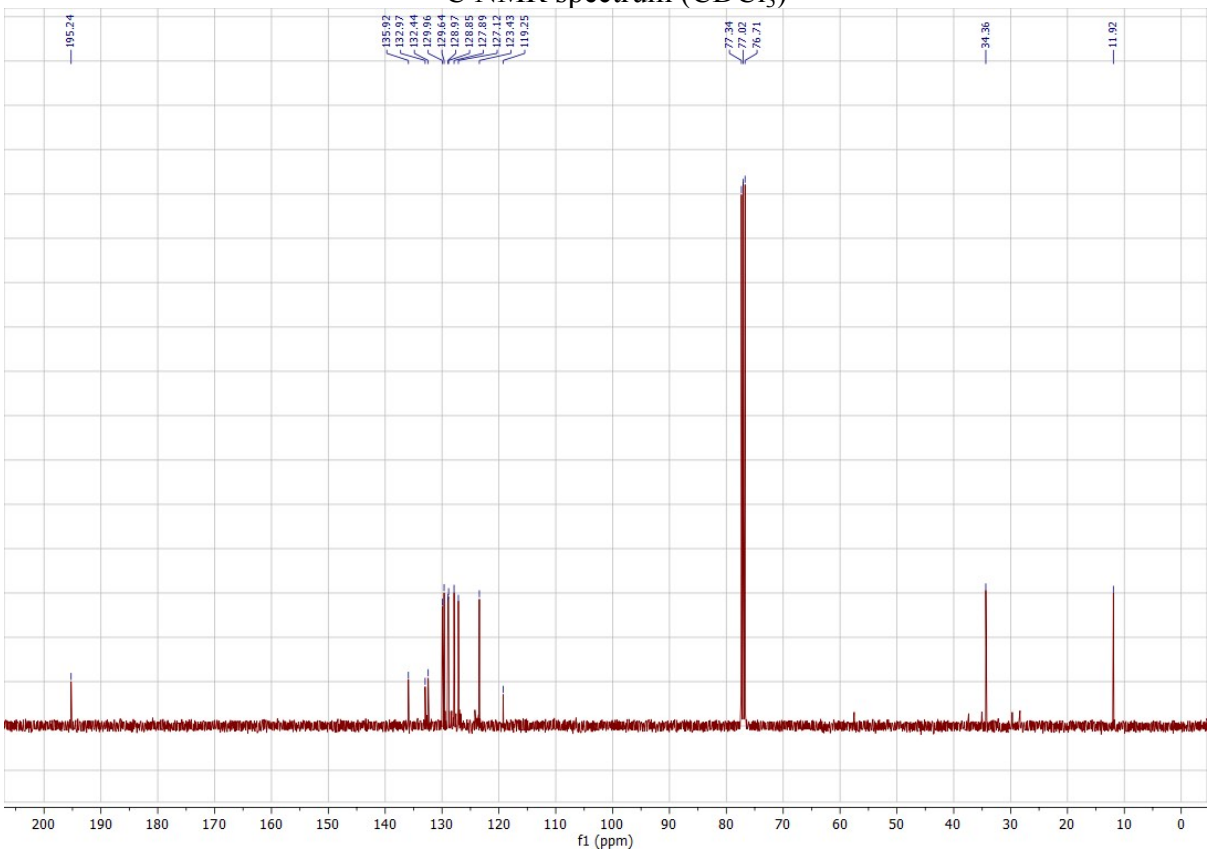
Characterization data matching data reported in the literature.[11,13]

^{1}H NMR spectrum ($CDCl_3$)



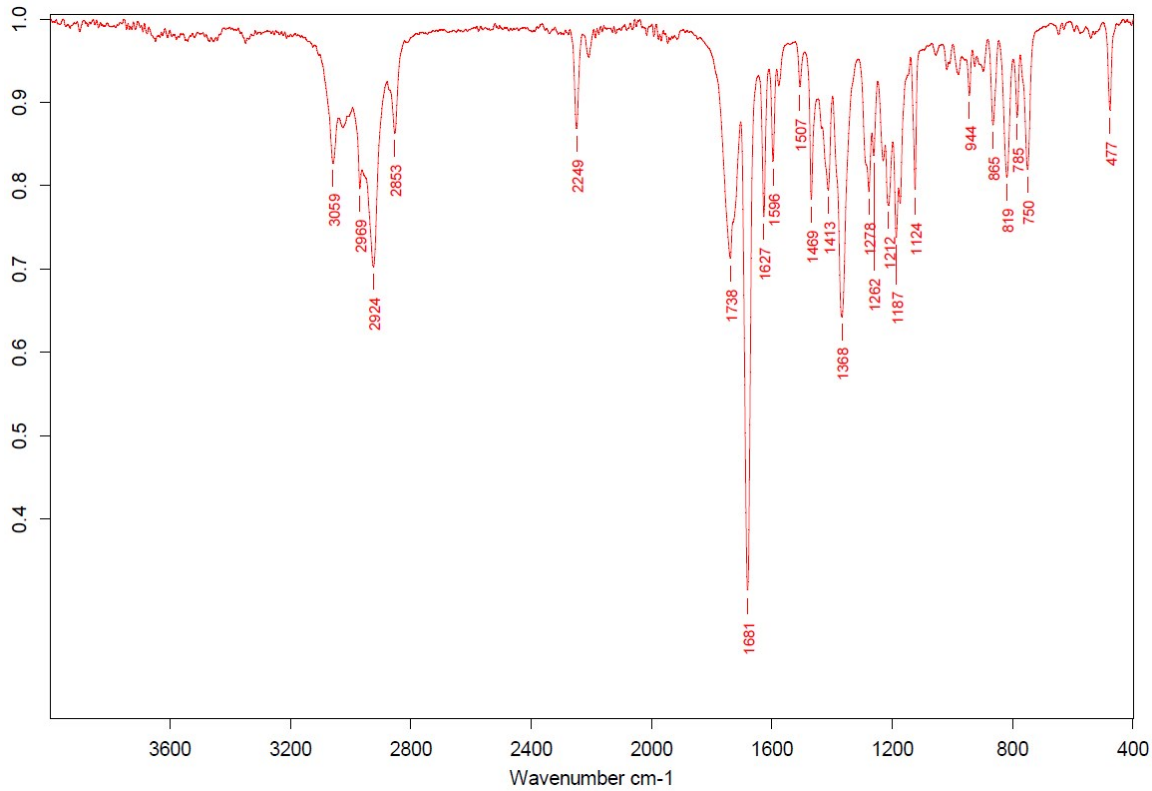
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50-8.49 (m, 1H), 8.05-7.99 (m, 2H), 7.97-7.91 (m, 2H), 7.68-7.59 (m, 2H), 3.55 (t, *J* = 8.0 Hz, 2H), 2.86 (t, *J* = 8.0 Hz, 2H).

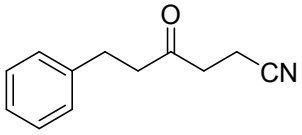
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 195.24, 135.92, 132.97, 132.44, 129.96, 129.64, 128.97, 128.85, 127.89, 127.12, 123.43, 119.25, 34.36, 11.92.

IR spectrum (neat)



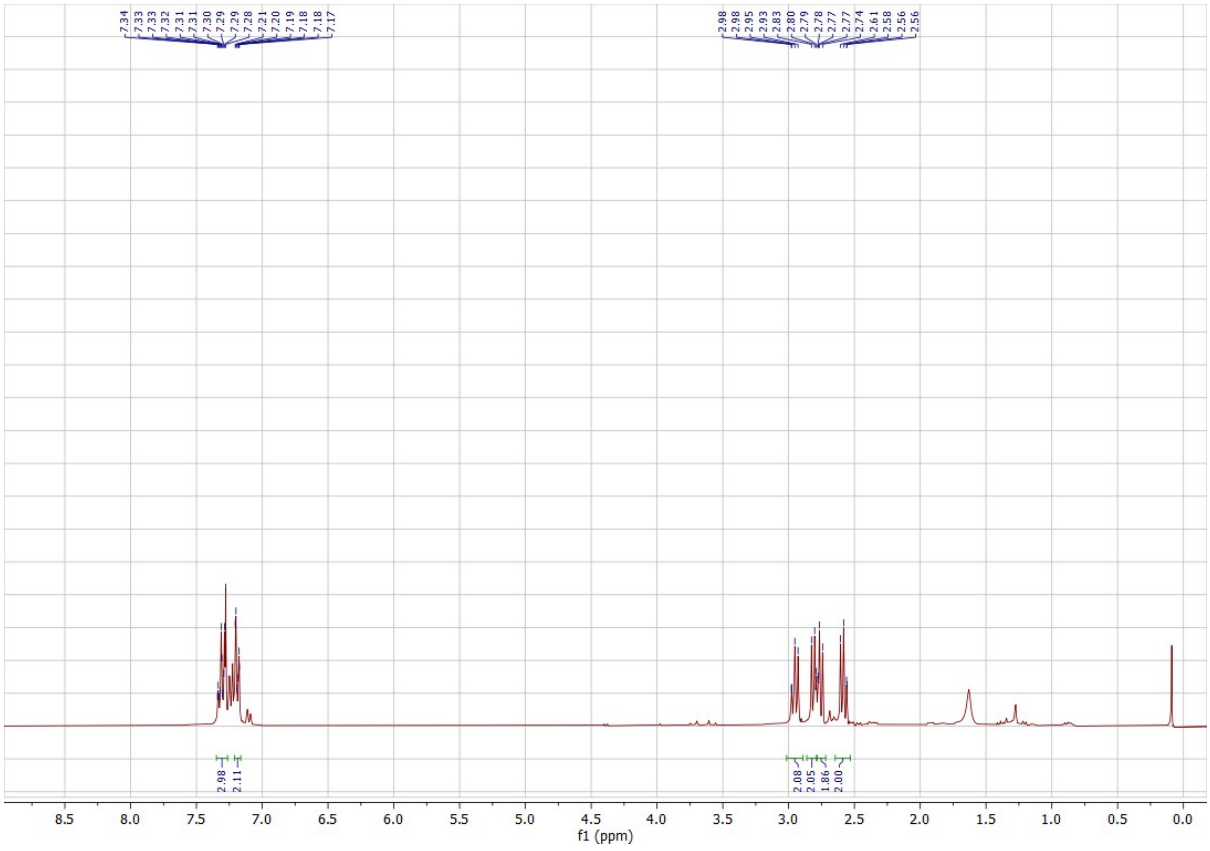


2p

The product was isolated as a white solid. Yield: 70%

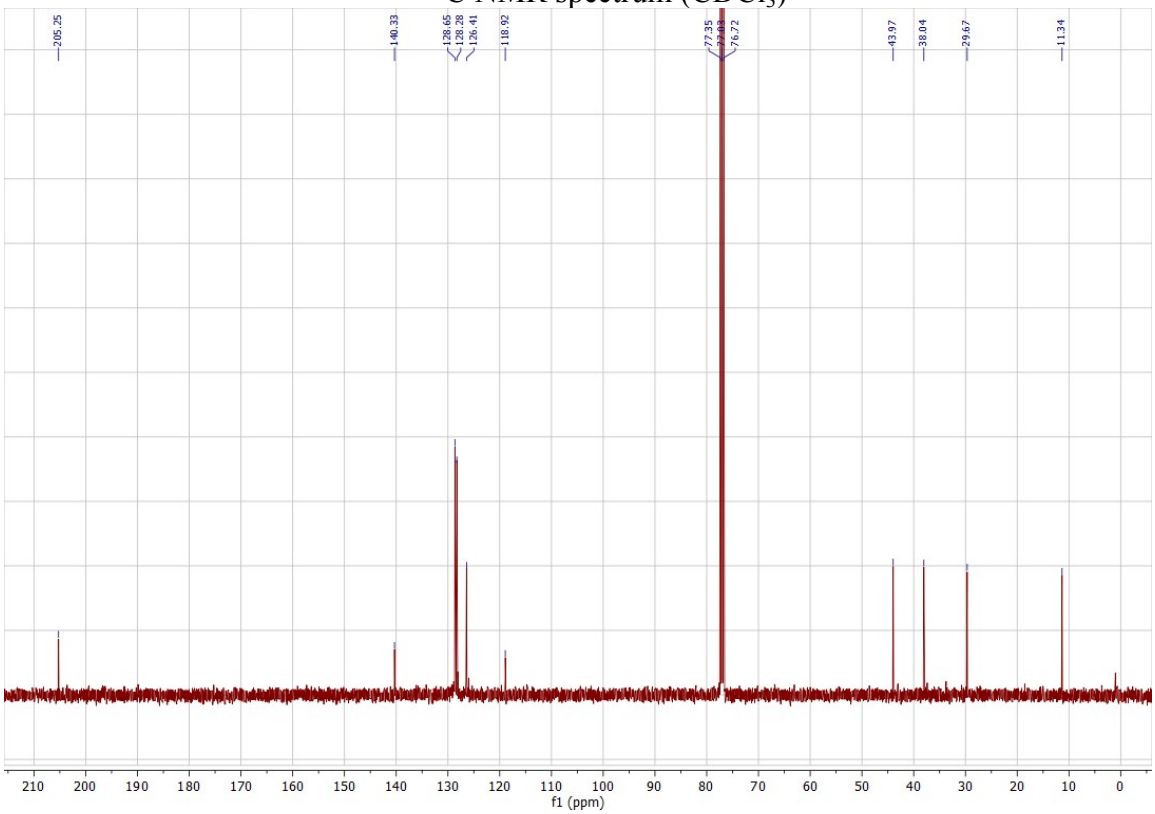
Characterization data matching data reported in the literature.[12]

^{1}H NMR spectrum ($CDCl_3$)



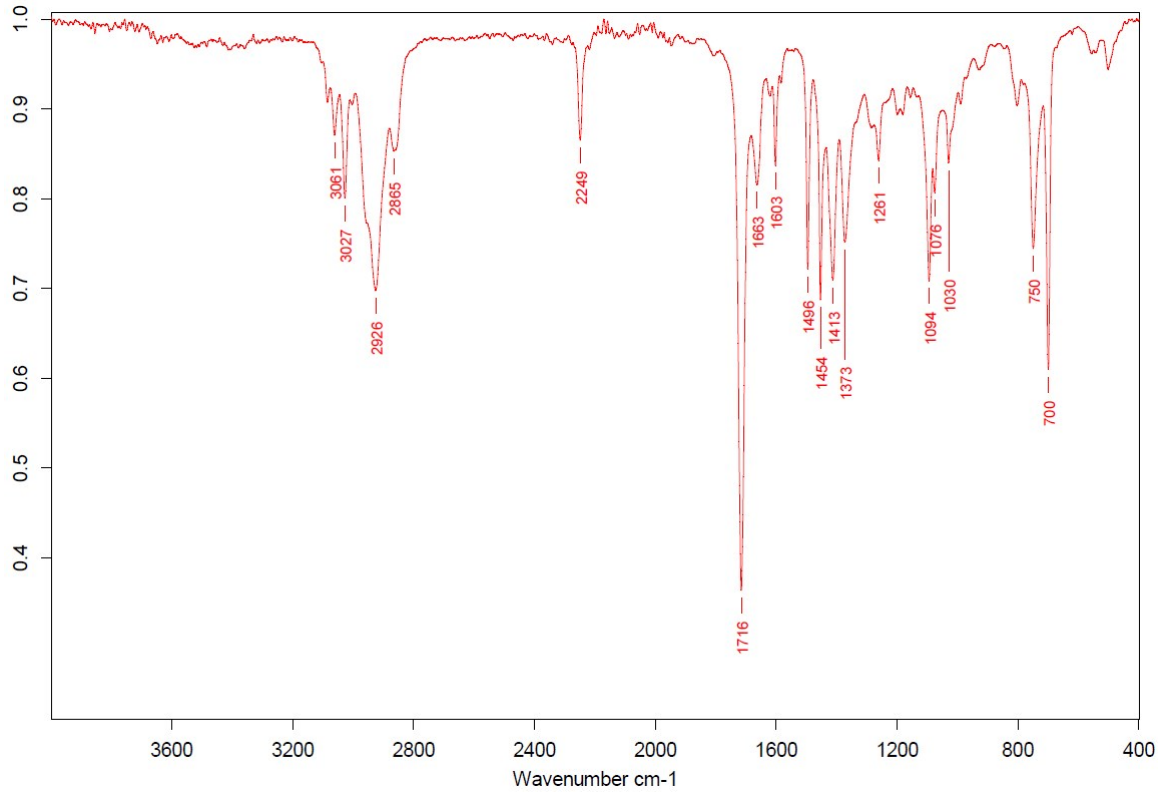
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 3H), 7.21-7.17 (m, 2H), 2.98-2.93 (m, 2H), 2.83-2.79 (m, 2H), 2.78-2.74 (m, 2H), 2.61-2.56 (m, 2H).

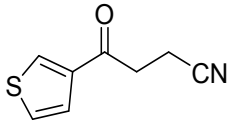
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 205.25, 140.33, 128.65, 128.28, 126.41, 118.92, 43.97, 38.04, 29.67, 11.34.

IR spectrum (neat)

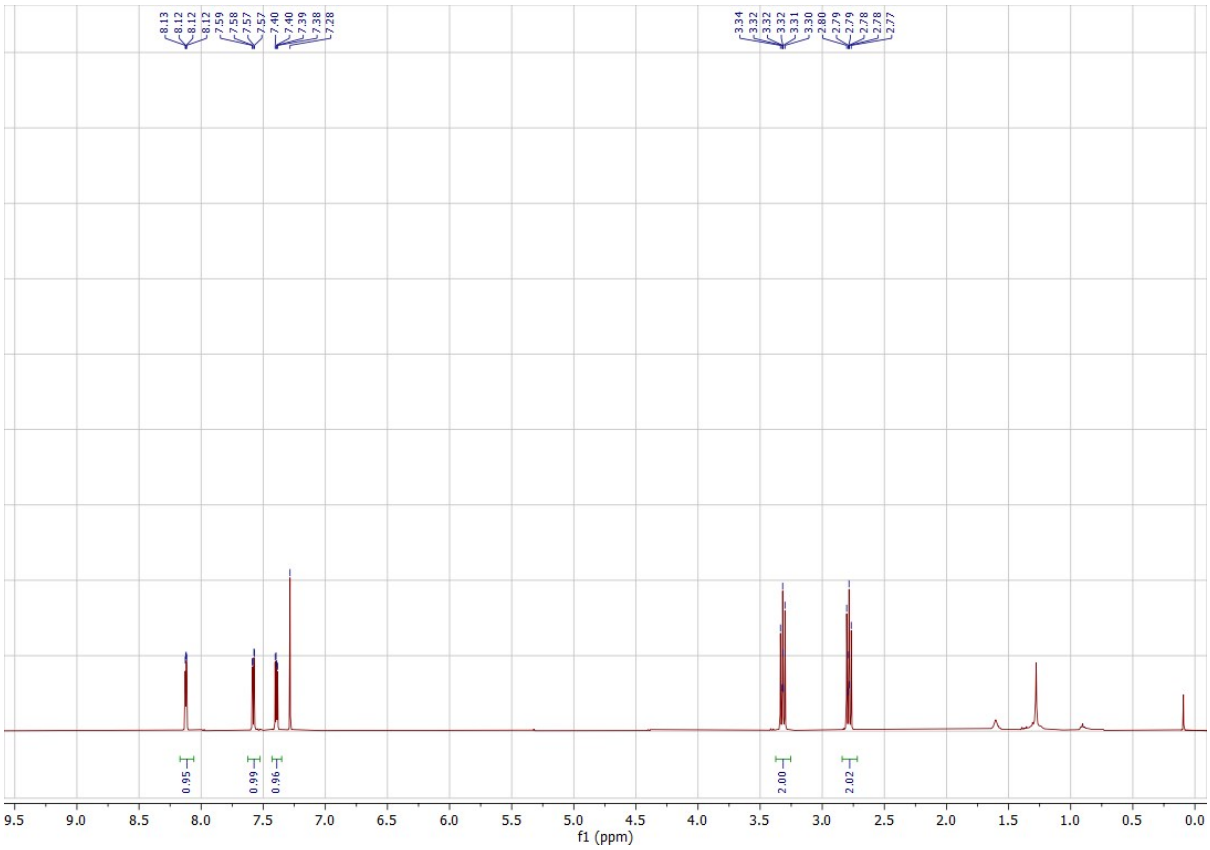




2q

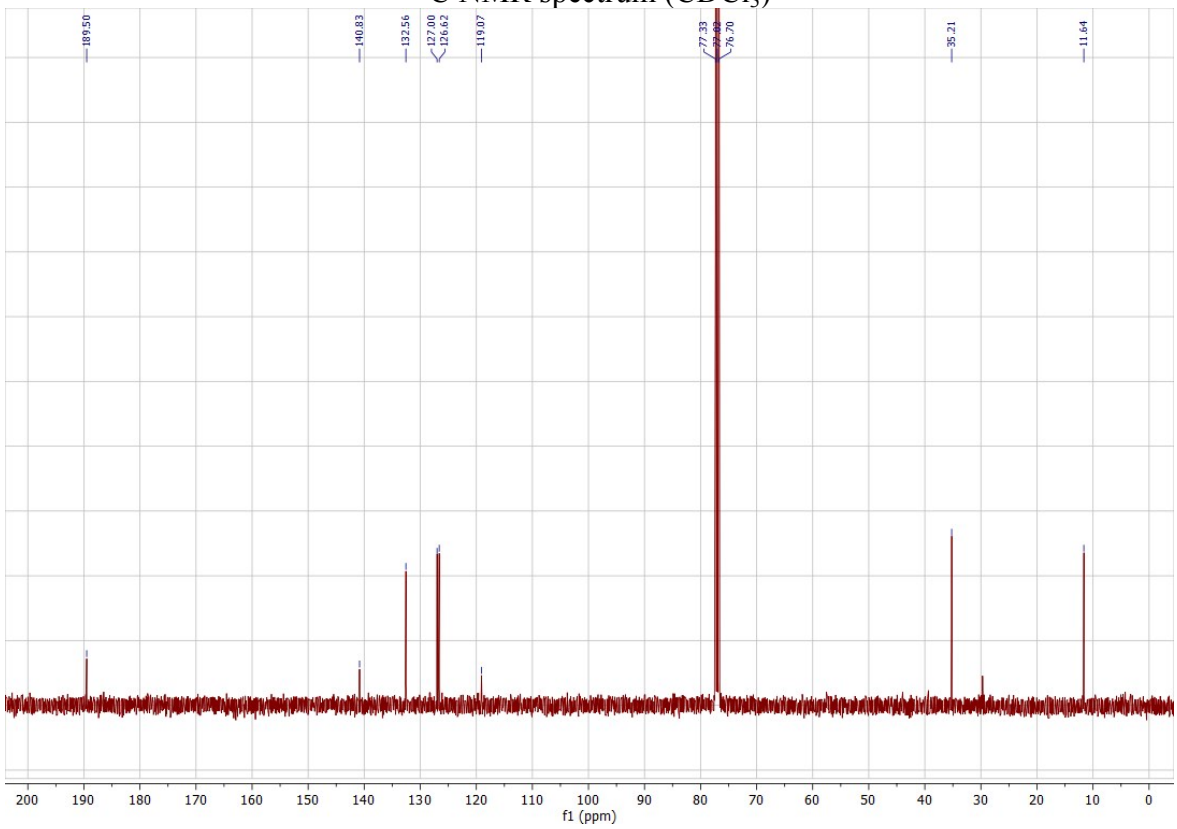
The product was isolated as a white solid. Yield: 25%

^{1}H NMR spectrum ($CDCl_3$)



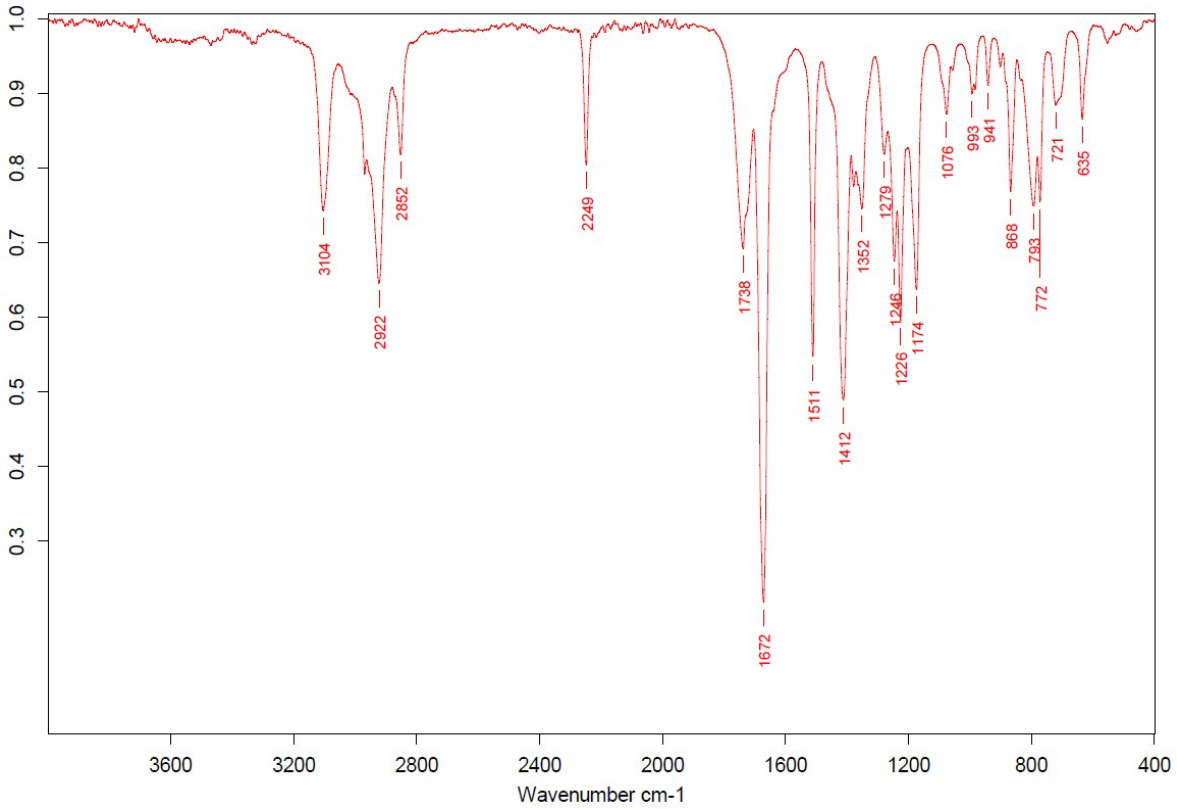
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13-8.12 (m, 1H), 7.59-7.57 (m, 1H), 7.40-7.38 (m, 1H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.78 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)

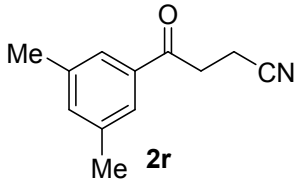


^{13}C NMR (101 MHz, $CDCl_3$) δ 189.50, 140.83, 132.56, 127.00, 126.62, 119.07, 35.21, 11.64.

IR spectrum (neat)



HRMS (ESI+, MeOH): *m/z* calcd. 188.0140 $(M + Na)^+$, found: 188.0137.

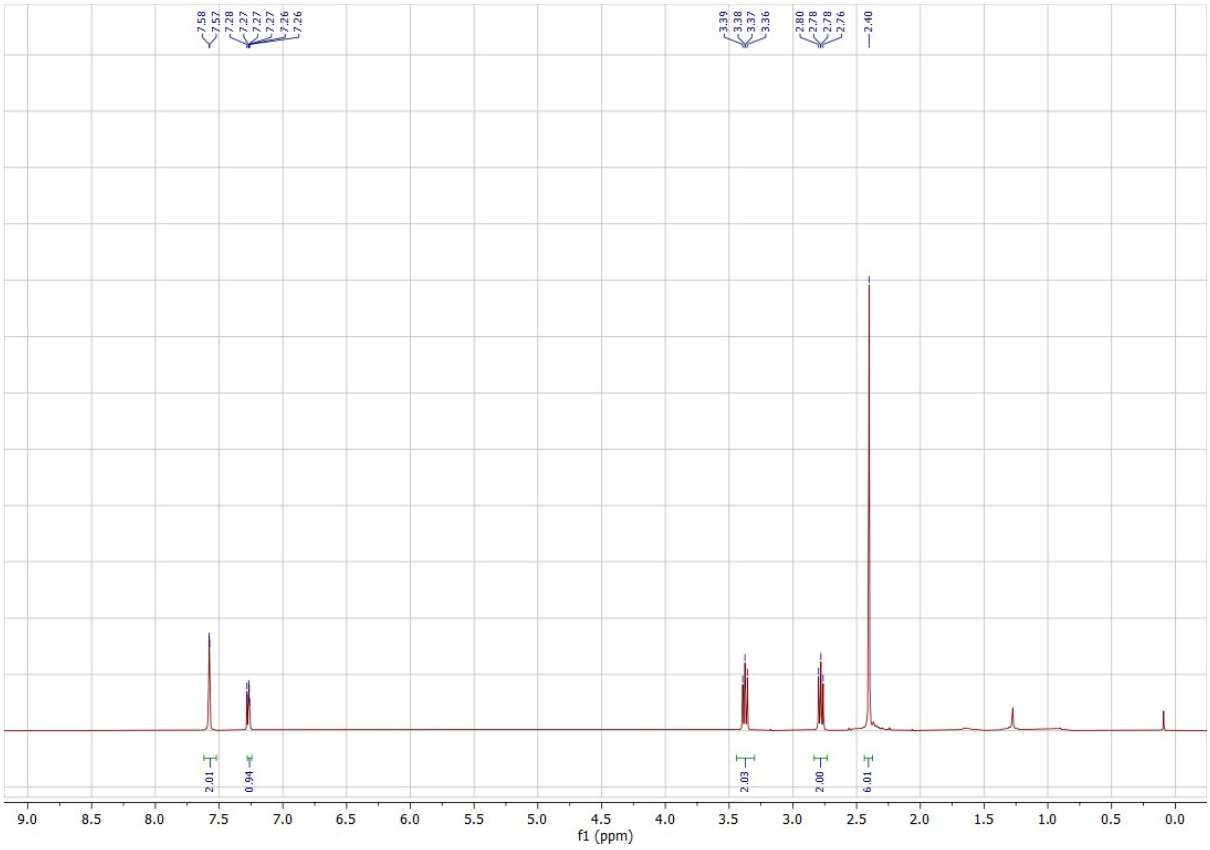


2r

The product was isolated as a white solid. Yield: 49%

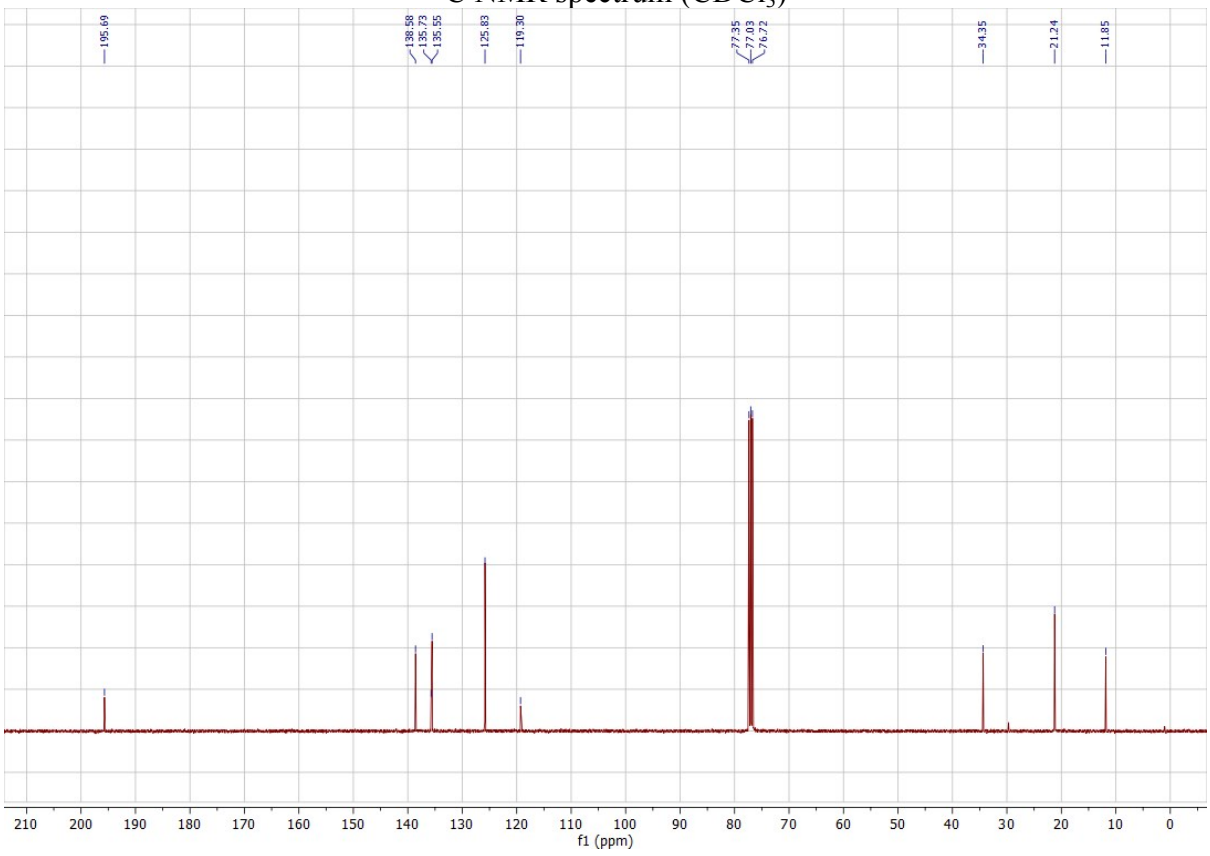
Characterization data matching data reported in the literature.[15]

^{1}H NMR spectrum ($CDCl_3$)



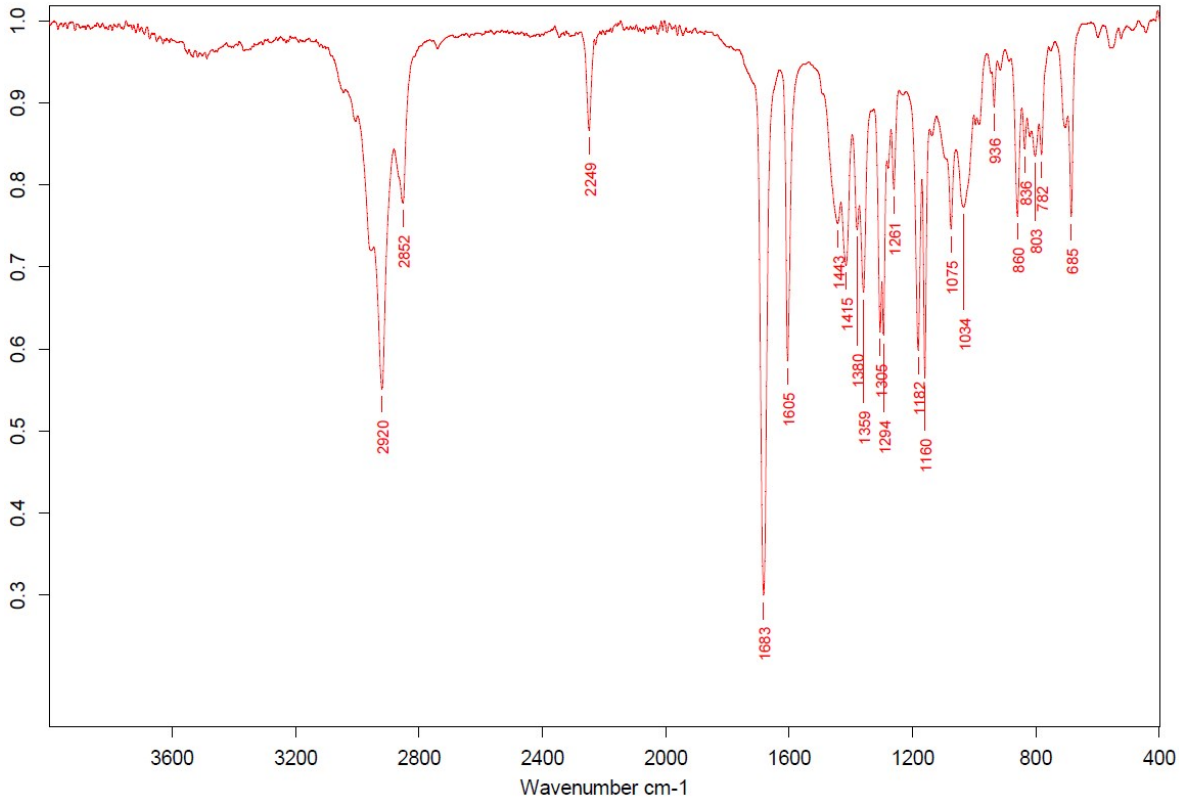
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 1H), 7.45-7.44 (d, *J* = 4.0 Hz, 1H), 6.91-6.89 (d, *J* = 8.0 Hz, 1H), 6.09 (s, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H).

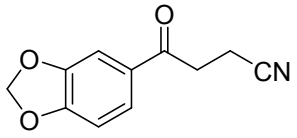
^{13}C NMR spectrum ($CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$) δ 193.31, 152.46, 148.46, 130.49, 124.46, 119.27, 108.10, 107.73, 102.08, 34.01, 11.93.

IR spectrum (neat)



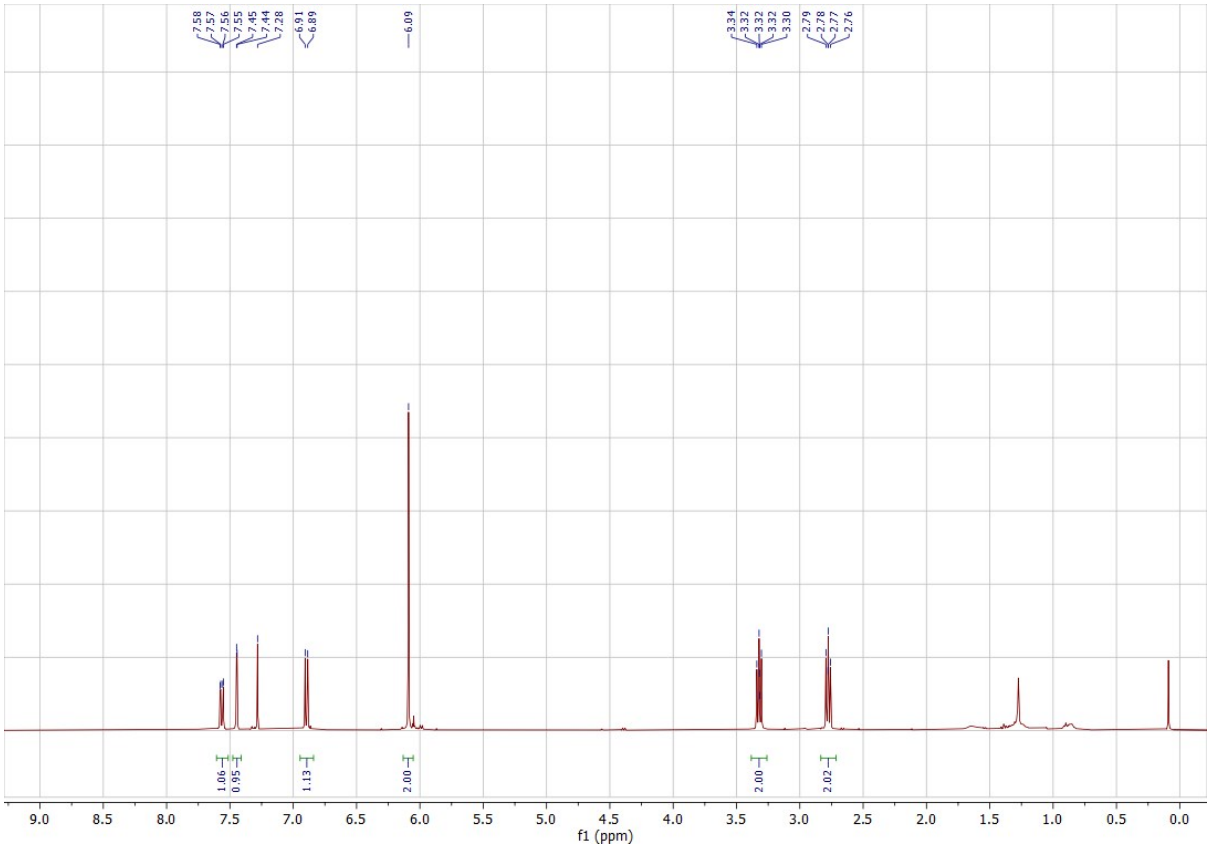


2s

The product was isolated as a white solid. Yield: 40%

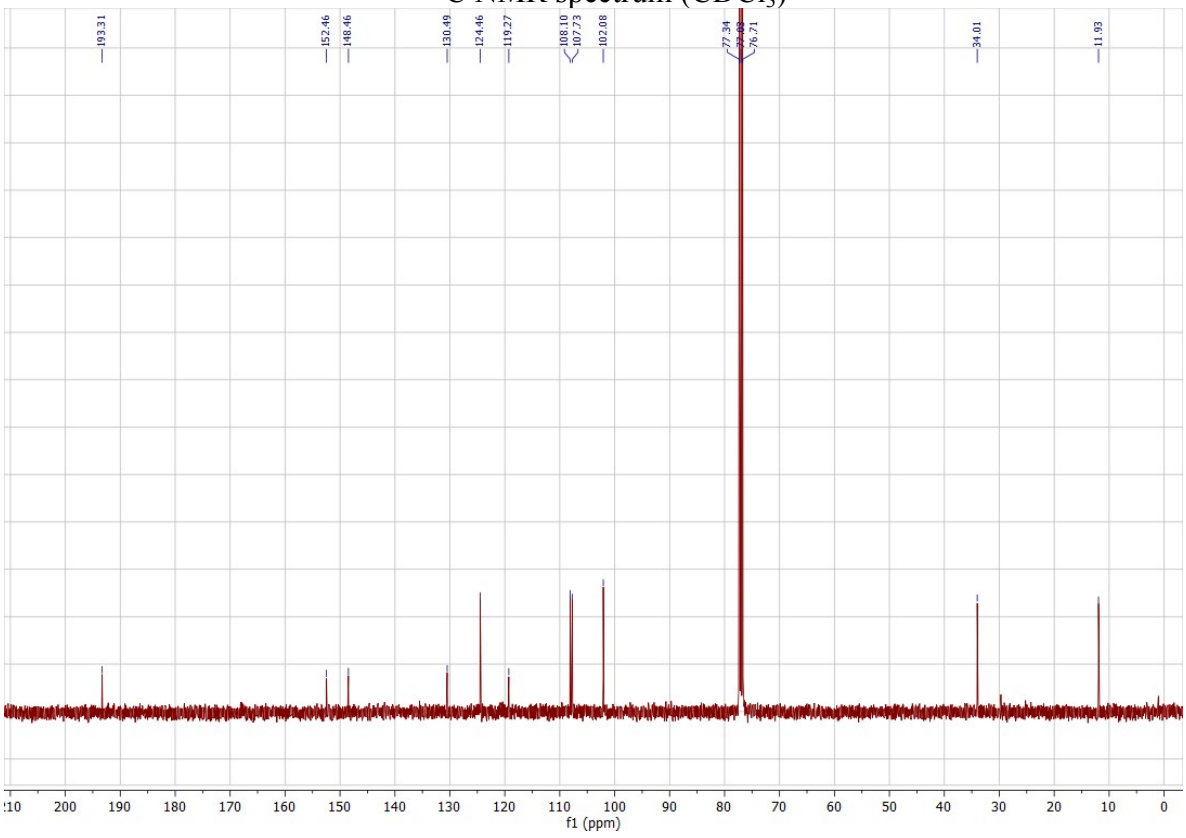
Characterization data matching data reported in the literature.[11]

^{1}H NMR spectrum ($CDCl_3$)



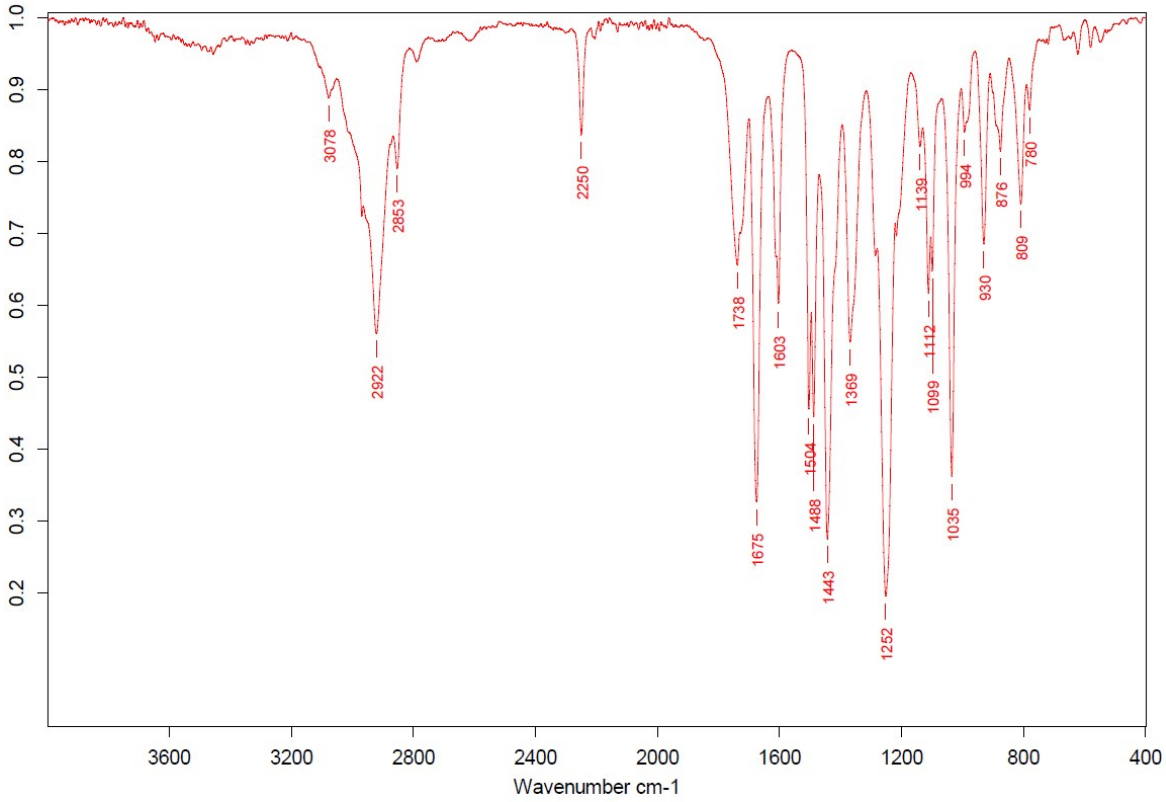
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 1H), 7.45-7.44 (d, *J* = 4.0 Hz, 1H), 6.91-6.89 (d, *J* = 8.0 Hz, 1H), 6.09 (s, 2H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H).

^{13}C NMR spectrum ($CDCl_3$)



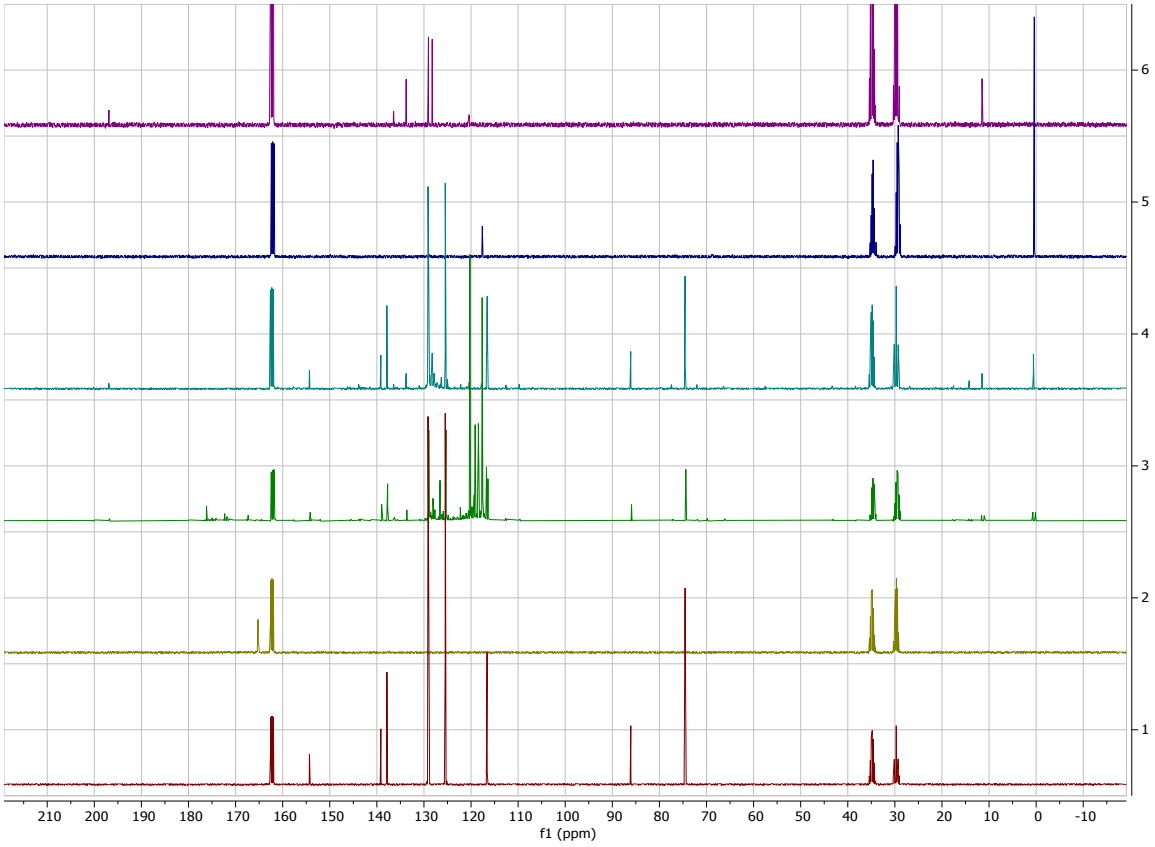
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.31, 152.46, 148.46, 130.49, 124.46, 119.27, 108.10, 107.73, 102.08, 34.01, 11.93.

IR spectrum (neat)

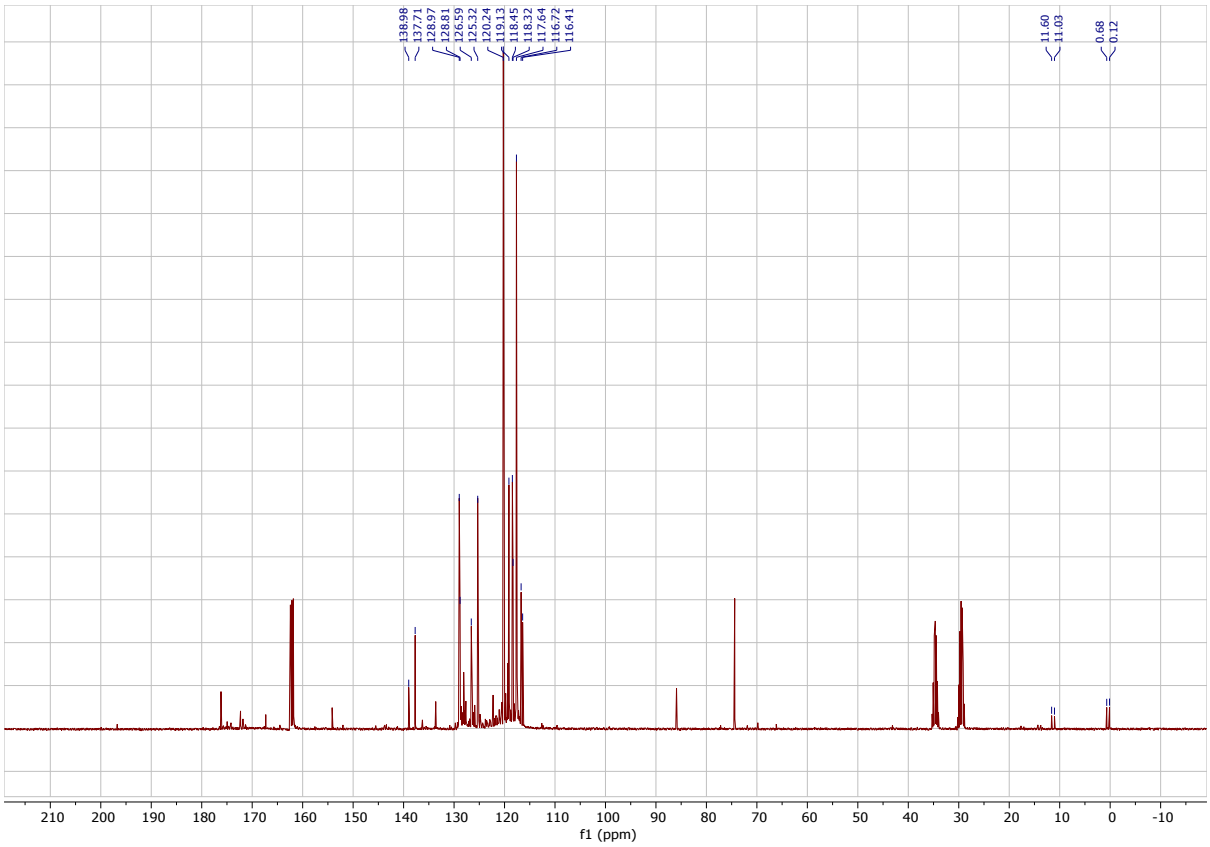


S46. Full ^{13}C NMR spectral comparison

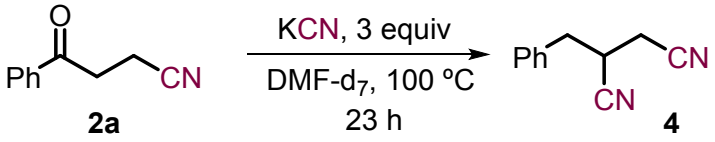
Relates to **Figure 2** in the main text, all spectra were recorded in DMF-d_7 at 100 MHz:



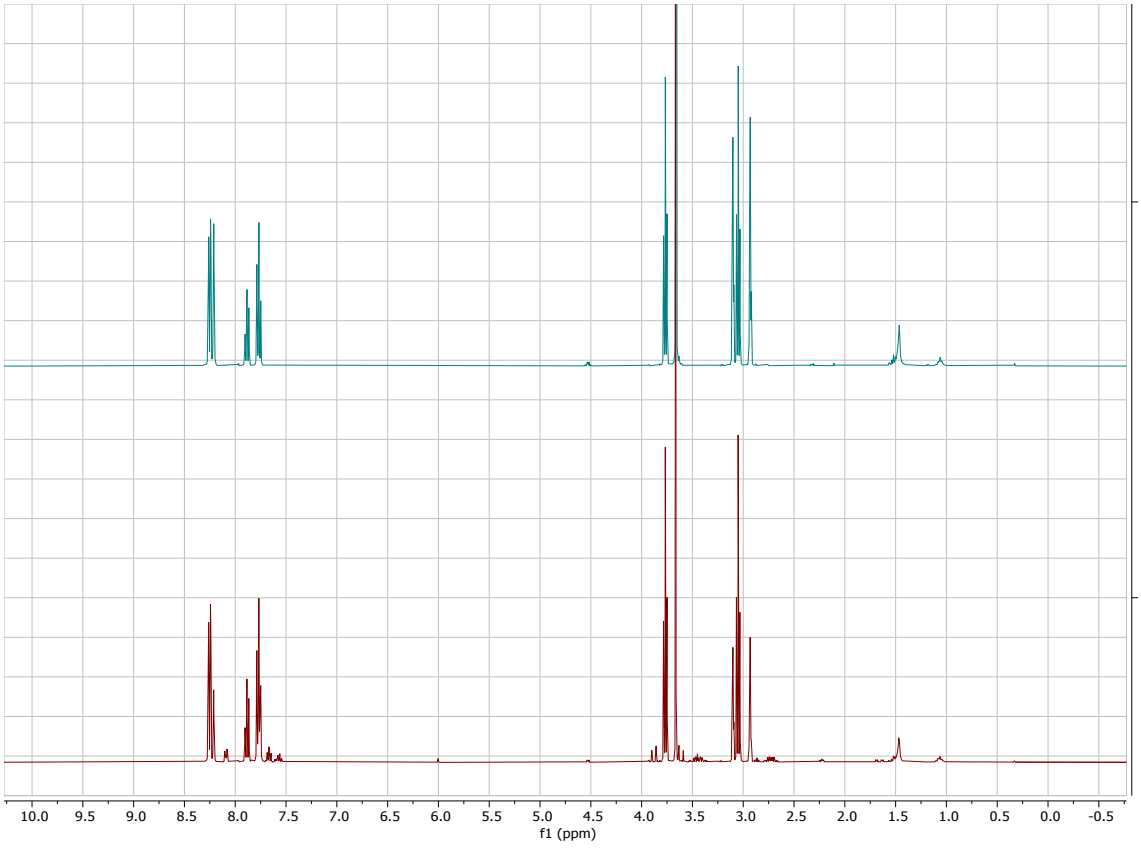
The full spectrum of the reaction mixture after 48 h using **K^{13}CN** as reagent:



S48. Control experiment regarding the formation of byproduct 4

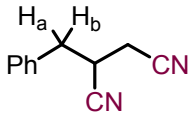


To a solution of 30 mg of **2a** (0.19 mmol) in DMF-d_7 (0.5 mL) was added KCN (3 molar equiv) and the mixture was kept, while stirring, at 100 ºC under Ar. Then, the mixture was transferred to an NMR tube following ^{1}H NMR analysis. The spectrum was compared to the one from isolated and column-purified **2a**.

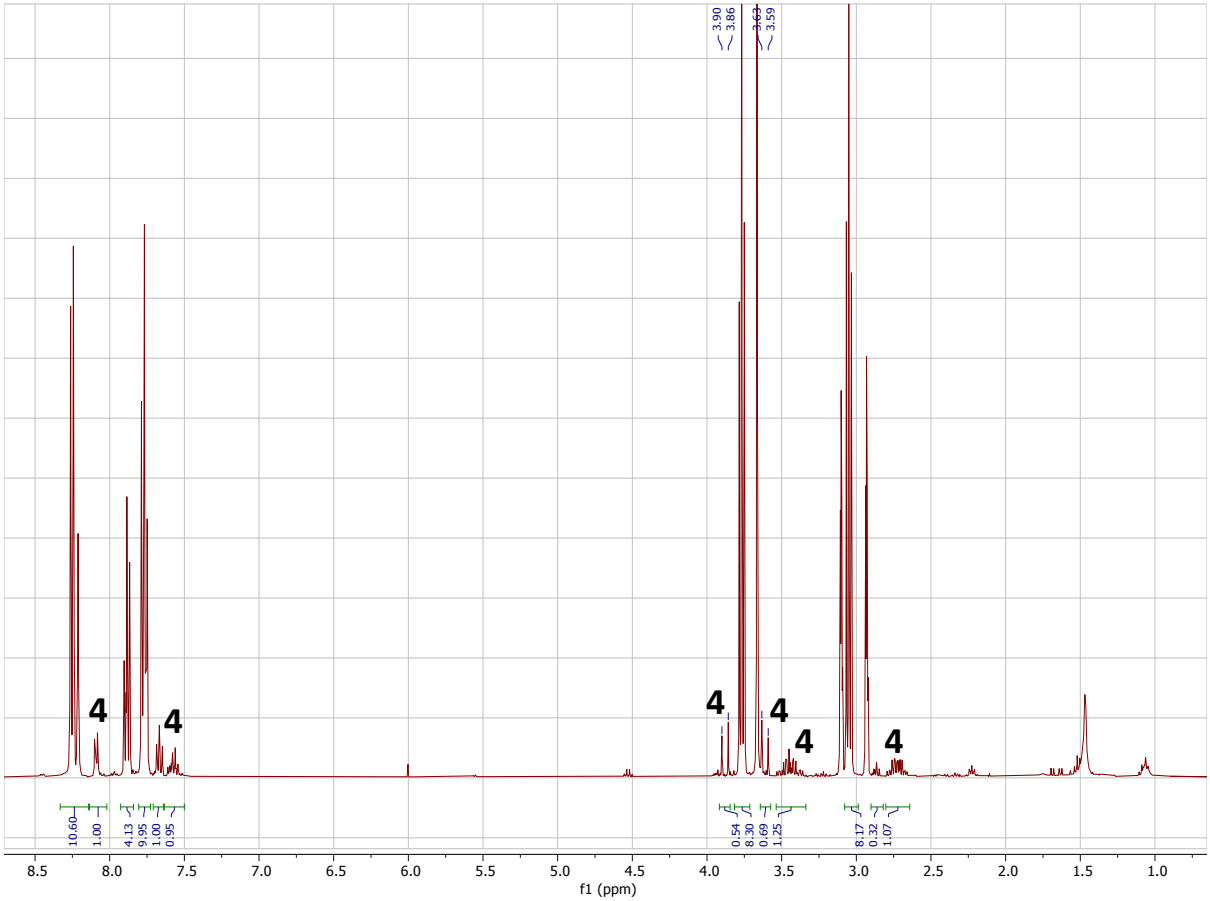


^{1}H (DMF-d_7) comparison between isolated/pure **2a** (top) and post-treated **2a** (below) in the presence of KCN. There are several peaks that emerged during this KCN-treatment which are ascribed to the formation of byproduct **4**.

Comparative integration (**2a** versus **4**) reveals that the ratio between the two compounds after heating for 23 h at 100 ºC is 88:12, meaning that about 12% of **4** is formed under these conditions. A characteristic ^{2}J (H_a,H_b) of around 16 Hz is present in the spectrum below for the benzylic H´s located at 3.88 and 3.61 ppm.



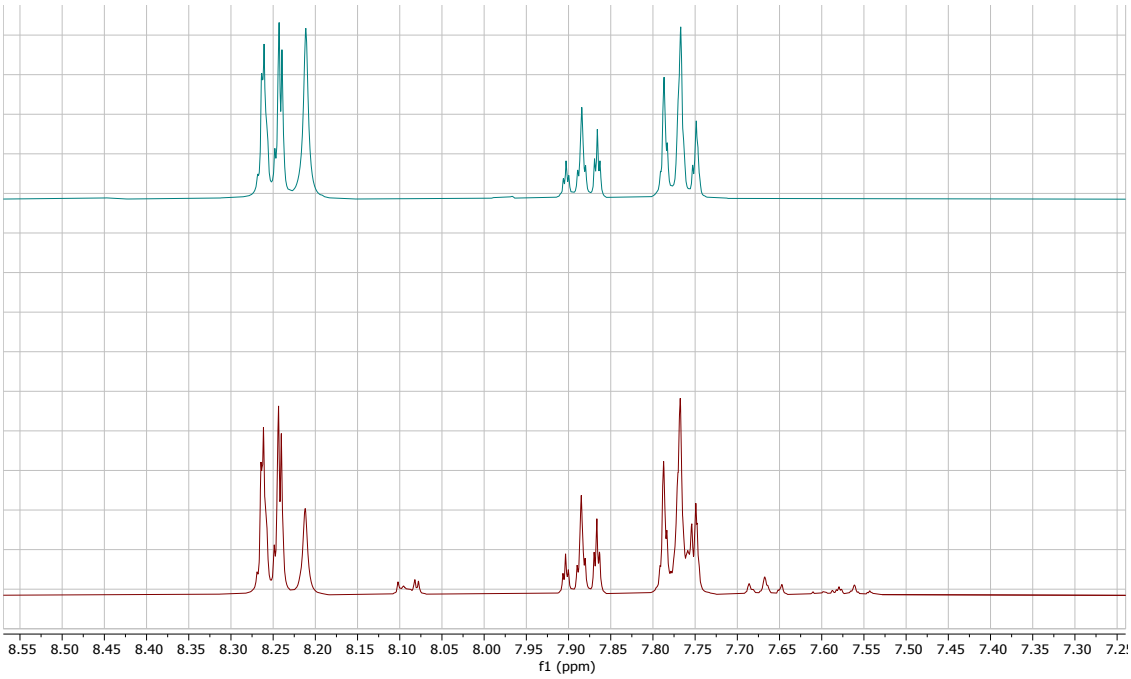
4

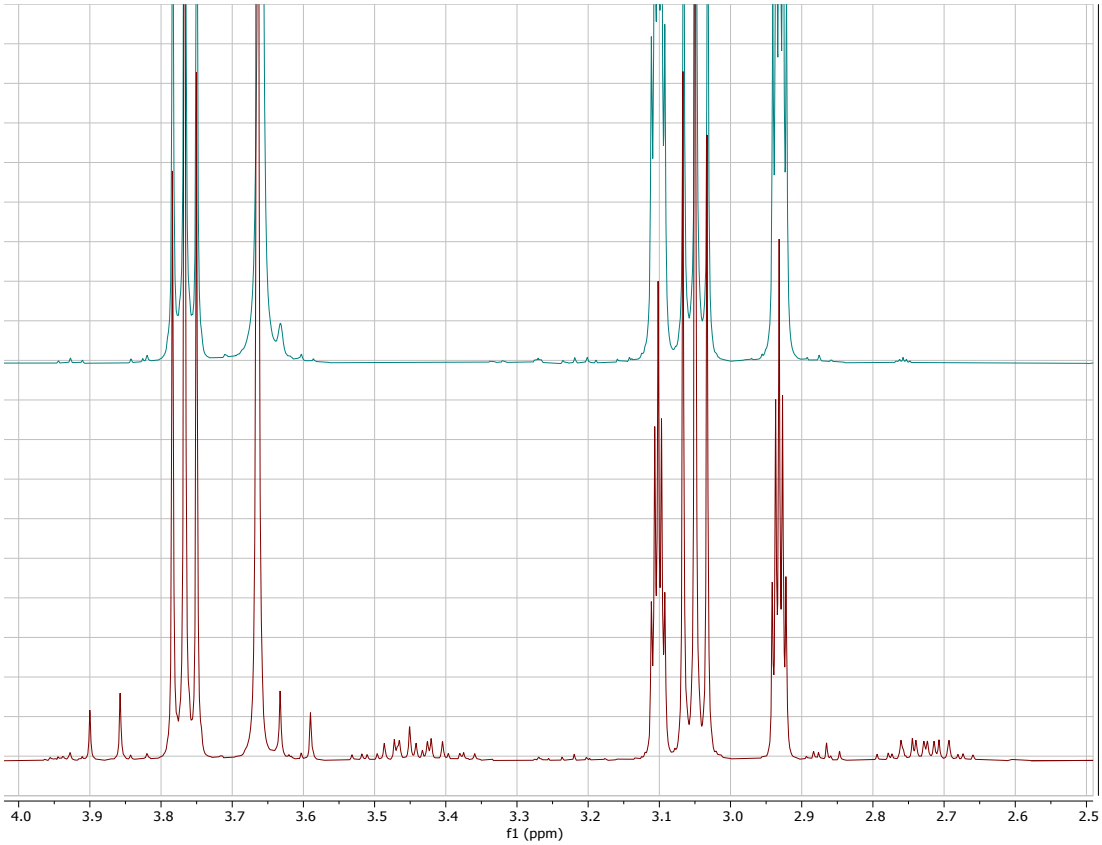


Compound **4** has been reported before, see:

B. Giese and Gebhard Thoma, Dimeric Metal Complexes as Mediators for Radical C-C Bond-Forming Reactions, *Helv. Chim. Acta*, 1991, **74**, 1135-1142.

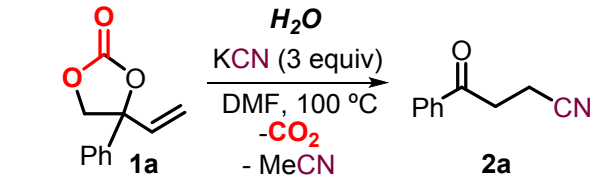
Below displayed are the zoomed area between 7.2-8.5 ppm and 2.5-4.0 ppm.





S51. Influence of amount of water on the yield of 2a

The reactions were performed as described in the main text using the optimized protocol while varying the molar amount of water.

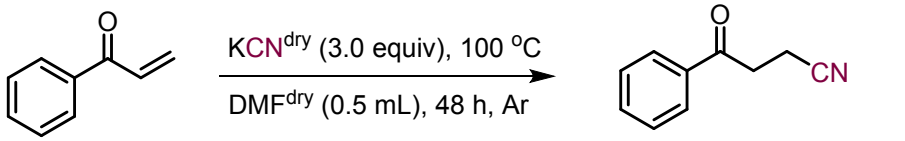


Entry	[H_2O] [mol%]	Conv.[a] [%]	Yield of **2a** [%][b]	Yield of **3** [%][b]	Yield of **4** [%][b]
1	1	81%	64%	10%	1%
2	10	80%	62%	11%	2%
3	100	80%	57%	11%	1%
4[c]	–	81%	64%	12%	1%

[a]Determined by ^{1}H NMR ($CDCl_3$) spectroscopy of the crude product. [b]Determined by ^{1}H NMR ($CDCl_3$) using mesitylene as internal standard. [c]Dry DMF was used.

S52. Control experiment using an α,β-unsaturated ketone as substrate

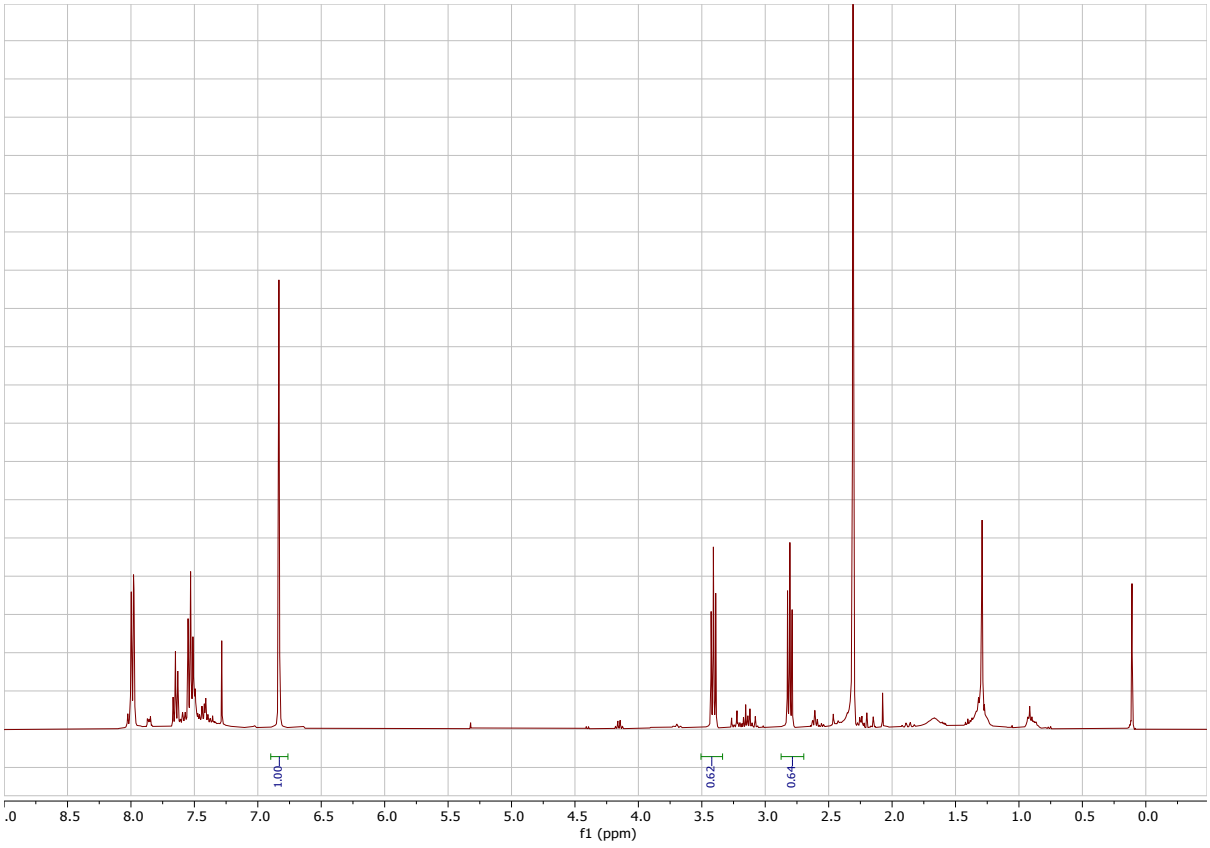
To credit the idea that the formation of product **2a** can indeed arise from an α,β-unsaturated ketone intermediate, a control experiment was carried out (see below).



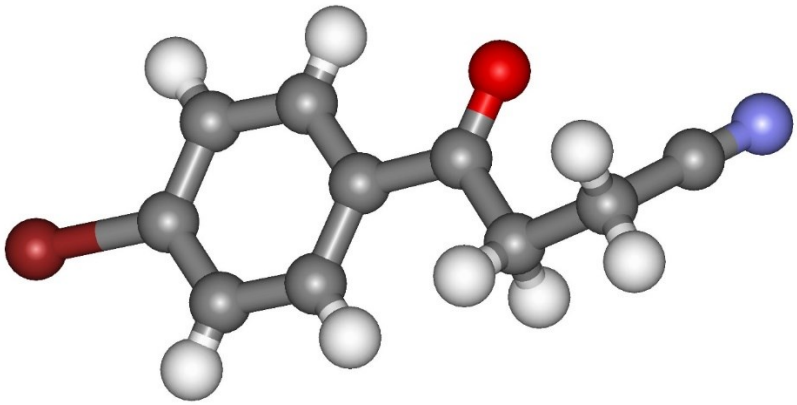
2a: NMR Yield: 73.4%

In an N_2-filled glovebox, to a Schlenk tube equipped with a magnetic stirring bar, the respective α,β-unsaturated ketone (40 mg, 0.30 mmol, 1.0 equiv), KCN (59 mg, 0.90 mmol, 3.0 equiv), and dry DMF (0.5 mL) were added. The resulting mixture was stirred at 100 ºC for 48 h, and then the reaction mixture was cooled to room temperature, the product was extracted with EtOAc, and the organic phase washed with H_2O (3 times to remove DMF). The organic phase was dried with Na_2SO_4, filtered, and concentrated, after which to the product was added mesitylene (28 mg, 0.233 mol) to calculate the NMR yield of the β-cyano ketone product **2a**.

The corresponding ^1H NMR spectrum ($CDCl_3$) is provided below (IS = 6.8 ppm, 100%, 3H, 0.233 mmol, **2a** = 3.48 + 2.82 ppm, 0.63, 2H, 0.220 mmol = 73.4 %):



S53. X-ray molecular structure of compound 2b



Further details are provided in **CCDC-2081268**.

S54. References

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