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Supporting Information

Transborylation Enabled, Borane-Catalysed Reductive Cyanation of Enones.

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General Information

Reaction Setup: All reactions were carried out in oven (185 °C) dried glassware, which had been cleaned using base (KOH, ^{i}PrOH) and acid ($HCl_{(aq)}$) baths. All air and moisture sensitive reactions were carried out using an argon atmosphere glovebox or a Schleck line (nitrogen). All reported reaction temperatures correspond to external bath temperatures. All glassware was cleaned using base (KOH, ^{i}PrOH) and acid ($HCl_{(aq)}$) baths. Room temperature was approximately 20 °C. "Brine" refers to a saturated solution of sodium chloride in H_2O.

NMR Spectroscopy: ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on Bruker Avance III 400 and 500 MHz; Bruker Avance I 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C NMR spectra were referenced to the residual solvent peak ($CHCl_3$: 7.26 ppm, 77.00 ppm CH_2Cl_2: 5.32 ppm, 54.00 ppm; THF: 1.73 ppm, 25.37; CH_3CN: 1.94 ppm, 1.39 ppm). Multiplicities are shows as s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext. (sextet), sept. (septet), non. (nonet), ap. (apparent). Coupling constants, J, are reported in Hertz and are rounded to the nearest 0.1 Hz. Integration of peaks is provided with the assignments indicated where appropriate.

Infrared Spectroscopy: Infra-red (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR, or Shimadzu IRAffinity-1 spectrometer (serial no. A213749) spectrometer. Peaks are reported in cm-1 with indicated relative intensities: s (strong, 0-33% T), m (medium, 34-66% T), w (weak, 67- 100% T), and br (broad).

Chromatography: Column chromatography was carried out on a Teledyne ISCO CombiFlash NextGen 300+ using RediSep R_f normal phase silica flash columns (12, 25, 40, or 80 g; 20-40 microns). Substrates were purified using 40/60 petroleum ether and EtOAc on a gradient of 100:0 to 0:100 with flow rates of 10-110 mL min-1 depending on the size of column and ΔRf.

Mass Spectrometry: Mass spectrometry (MS) was performed by the University of Edinburgh, School of Chemistry, Mass Spectrometry Laboratory. High-resolution mass spectra were recorded on a VG autospec, or Thermo/Finnigan MAT 900, mass spectrometer. Electron Impact (EI^+) spectra were performed at 70 eV using methane as the carrier gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyzer. Chemical Ionization (CI^+) spectra were performed with methane reagent gas, with either a double focusing sector field (DFSF) or time-of-flight (TOF) mass analyser. Electrospray Ionisation (ESI^+) spectra were

performed using a time-of-flight (TOF) mass analyser. Data are reported in the form of m/z (intensity relative to the base peak = 100).

Melting Points: Melting points were determined using a Stuart Scientific SMP10, or Griffin Gallankamp and are uncorrected.

Chemicals: All reagents were purchased from Sigma Aldrich, Acros Organics or Alfa Aesar and were used as received, or were synthesised in the laboratory.

Solvents: All solvents for air- and moisture- sensitive techniques were obtained from an anhydrous solvent system (Innovative Technology). Reaction solvents tetrahydrofuran (THF) (Fisher, HPLC grade), ether (Et_2O) (Fisher, BHT stabilized ACS grade), and dichloromethane (CH_2Cl_2) (Fisher, unstabilised HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Toluene (ACS grade) was dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant (supported copper catalyst for scavenging oxygen) under a positive pressure of argon. Solvents for filtration, transfers, chromatography, and recrystallization were dichloromethane (CH_2Cl_2) (ACS grade), ether (Et_2O) (Fisher, BHT stabilised ACS grade), ethyl acetate (EtOAc) (Fisher, ACS grade), hexane (Optima), methanol (MeOH) (ACS grade), pentane (ACS grade), and petroleum ether (40–60 °C, ACS grade).

Purification Conditions:

Aryl Enones:

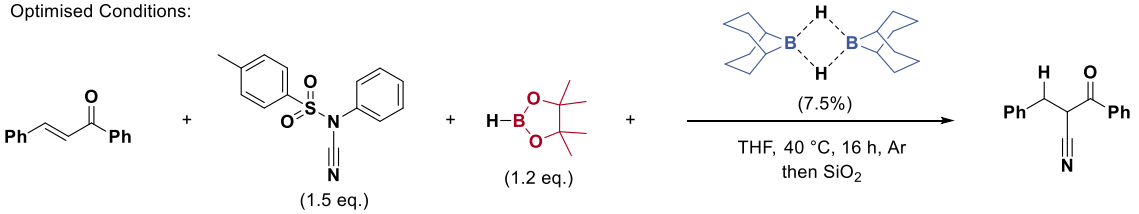
Purification by flash column chromatography, chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø. Using a CombiFlash Isco NextGen300+ petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes.

Alkyl Enones:

Purification by flash column chromatography, chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø. Using a CombiFlash Isco NextGen300+. petroleum ether/ethyl acetate gradient elution 10/90 over 50 minutes, 10/90 to 100/0 over 10 minutes.

Optimisation of Reaction Conditions

Optimised Conditions:

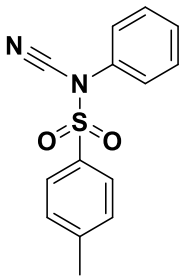


Entry	Catalyst	Catalyst Loading (%)	Temperature (°C)	Reaction Time (hours)	Solvent	Conversion (%)
1	[H-*B*-9-BBN]$_2$	15	40	16	THF	>95
2	[H-*B*-9-BBN]$_2$	7.5	40	16	THF	>95
3	[H-*B*-9-BBN]$_2$	5	40	16	THF	66
4	[H-*B*-9-BBN]$_2$	2.5	40	16	THF	62
5	[H-*B*-9-BBN]$_2$	1	40	16	THF	24
6	[H-*B*-9-BBN]$_2$	7.5	40	16	Hexane	24
7	[H-*B*-9-BBN]$_2$	7.5	40	16	Toluene	68
8	[H-*B*-9-BBN]$_2$	7.5	40	16	Ethyl Acetate	78
9	[H-*B*-9-BBN]$_2$	7.5	40	16	Diethyl Ether	74
10	[H-*B*-9-BBN]$_2$	7.5	40	16	Dichloromethane	72
11[a]	[H-*B*-9-BBN]$_2$	7.5	40	16	THF	68
12[b]	[H-*B*-9-BBN]$_2$	7.5	40	16	THF	12
13	[H-*B*-9-BBN]$_2$	7.5	70	2	THF	13
14	[H-*B*-9-BBN]$_2$	7.5	70	4	THF	33
15	Catecholborane	15	40	16	THF	0
16	Dicyclohexylborane	15	40	16	THF	38
17	Borane	15	40	16	THF	0
18	None	-	40	16	THF	Trace

Table S1: Reaction optimisation for boron-catalysed hydrocyanation of enones. [a] 0.5 mmol (1 equiv) of NCTS used as cyanide source. [b] 0.75 mmol (1.5 equiv) of TsCN used as cyanide source.

Preparation of Electrophilic Cyanation Reagent

N-Cyano-*N*-phenyl-*p*-toluenesulfonamide (NCTS)



According to the procedure of Kurzer[1] *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide was prepared by dropwise addition of *p*-toluenesulfonyl chloride (52.8 g, 27.7 mmol) to a solution of phenylurea (10.9 g, 80.1 mmol) and pyridine (54 mL). The reaction mixture was stirred for 15 minutes) and added to ice-cooled water (400 mL). The precipitate was collected by vacuum filtration and recrystallised from ethanol gave *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide as a microcrystalline colourless solid (17.86 g, 65.66 mmol, 82%).

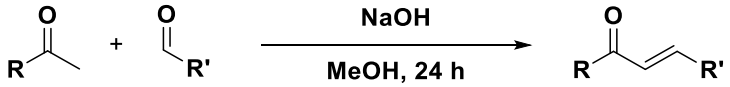
m.p. 86-87 °C (ethanol), Lit; 85-86 (ethanol).[2]

^{1}H NMR (500 MHz, $CDCl_3$) 7.64-7.60 (m, 2H), 7.43-7.32 (m, 5H), 7.20-7.16 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) 146.9, 134.7, 132.4, 130.3, 130.0, 129.9, 128.5, 126.5, 108.8, 21.9.

Data were in accordance with those previously reported.[1]

General Procedure A: Preparation of Enones

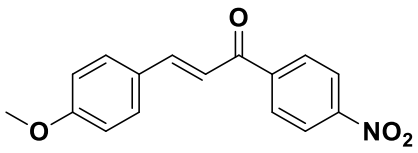


Scheme S1: Claisen condensation to generate enone substrates.

To a solution of sodium hydroxide in methanol (2.5 M, 20 mL), aldehyde (20 mmol) and ketone (20 mmol) were added and stirred for 24 hours. Upon precipitation, the solid was collected by vacuum filtration and recrystallised from petroleum ether and CH_2Cl_2.

Synthesis of Enones

4'-Methoxy-4-nitrochalcone, **2c**



4'-Methoxy-4-nitrochalcone was prepared according to general procedure A. 4-Nitrobenzaldehyde (3.02 g, 20.0 mmol), 1-(4-methoxyphenyl)ethanone (3.00 g, 20.0 mmol), and sodium hydroxide (2.0 g) in methanol (20 mL) were reacted. Purification by recrystallisation from petroleum ether and CH_2Cl_2 gave the enone as a pale orange microcrystalline solid (2.04 g, 7.20 mmol, 36%).

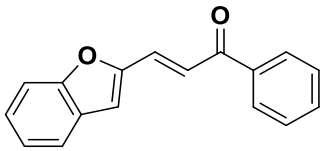
m.p. 168-170 °C (petroleum ether/CH_2Cl_2), Lit; 172-174.[3]

^{1}H NMR (500 MHz, $CDCl_3$) 8.30 (d, *J* = 8.9 Hz, 2H), 8.08 (d, *J* = 9.1 Hz, 2H), 7.82-7.76 (t, J = 15.6 3H), 7.67 (d, *J* = 15.6 Hz, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) 187.9, 164.0, 148.6, 141.5, 140.8, 131.1, 130.6, 129.0, 125.8, 124.3, 114.2, 55.7.

Data were in accordance with those previously reported.[3]

(*E)*-3-(Benzofuran-2-yl)-1-phenylprop-2-en-1-one, **3q**



(*E)*-3-(Benzofuran-2-yl)-1-phenylprop-2-en-1-one was prepared according to general procedure A. 2-Formylbenzofuran (2.92 g, 20.0 mmol), acetophenone (2.40 g, 20.0 mmol), and sodium hydroxide (2.0 g) in methanol (20 mL) were reacted. Purification by recrystallisation from petroleum ether and CH_2Cl_2 gave the enone as a pale yellow amorphous solid (2.46 g, 10.0 mmol, 50%).

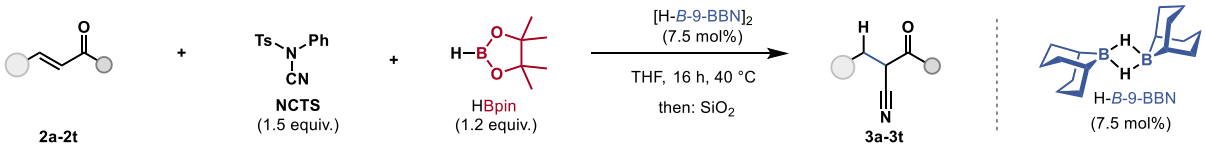
m.p. 89-91 °C (petroleum ether/CH_2Cl_2), Lit; 92 °C (methanol).[4]

^{1}H NMR (500 MHz, $CDCl_3$) 8.10-8.07 (m, 2H), 7.72 (d, *J* = 1.1 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.54-7.49 (m, 3H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 1.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.7, 155.8, 153.2, 138.1, 133.1, 131.0, 128.8, 128.7, 126.9, 123.6, 122.1, 122.0, 122.0, 112.6, 111.5.

Data were in accordance with those previously reported.[4]

General Procedure B: Reductive Cyanation of Enones

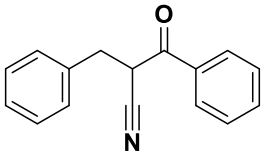


Scheme S2: H-*B*-9-BBN catalysed cyanation with NCTS.

Enone (0.50 mmol), NCTS (0.75 mmol), H-*B*-9-BBN (150 µL, 0.5 M, THF, 0.0075 mmol), and pinacolborane (87 µL, 0.6 mmol) were reacted in THF (1 mL) under an inert (Ar or N_2) atmosphere. The mixture was heated to 40 °C for 16 h. The reactions were quenched with SiO_2 (0.3 g, excess) filtered and concentrated *in vacuo*. The product was purified by flash column chromatography using a CombiFlash Isco NextGen300+ (see general experimental information – column conditions).

H-*B*-9-BBN Catalysed Reductive Cyanation of Enones

2-Benzyl-3-oxo-3-phenylpropanenitrile, **3a**



2-Benzyl-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure B. (*E)*-Chalcone (104 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø, using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the α-cyanoketone as a pale yellow microcrystalline solid (100 mg, 0.44 mmol, 87%).

m.p. 83-84 °C (petroleum ether/ethyl acetate), Lit; 85 °C.[5]

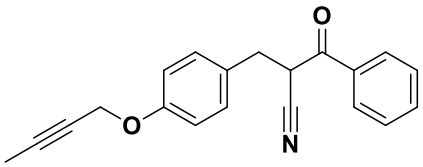
^{1}H NMR (500 MHz, $CDCl_3$) 7.97 (d, *J* = 7.5 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.40-7.25 (m, 5H), 4.54 (dd, *J* = 8.8 Hz, 5.6 Hz, 1H), 3.39 (dd, *J* = 14.1 Hz, 5.6 Hz, 1H), 3.28 (dd, *J* = 14.1 Hz, 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.9, 135.9, 134.6, 134.1, 129.1, 129.0, 128.9, 128.8, 127.7, 116.9, 41.8, 35.5.

IR V_{max} (neat) 2238 (w), 1697 (s) cm^{-1}.

Data were in accordance with those previously reported.[5]

2-(4-(2-Butynyloxy)phenylmethyl)-3-oxo-3-phenylpropanenitrile, **3b**



2-(4-(2-Butynyloxy)phenylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure B. (*E*)-3-(4-(2-Butynyloxy)phenyl)-1-phenylprop-2-en-1-one (139 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a colourless microcrystalline solid (105 mg, 0.35 mmol, 69%), contains 15% NCTS as an inseparable impurity.

m.p. 109-111 °C (ethyl acetate).

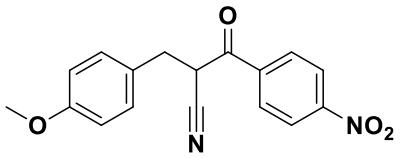
^{1}H NMR (500 MHz, $CDCl_3$) 8.02 – 7.94 (m, 2H), 7.68 – 7.64 (m, 1H), 7.58 – 7.47 (m, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 4.65 (d, *J* = 2.4 Hz, 2H), 4.51 (dd, *J* = 8.8, 5.8 Hz, 1H), 3.37 – 3.20 (m, 2H), 1.89 (t, *J* = 2.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) 190.1, 157.4, 134.6, 130.1, 129.1, 128.8, 127.3, 121.8, 117.1, 115.3, 83.9, 73.9, 56.5, 42.1, 34.8, 3.7.

IR V_{max} (neat) 3065 (w), 2246 (w), 1671 (m), 1510 (m) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{20}H_{17}O_2N$ 303.1254; found 303.1256.

2-(4-Methoxyphenylmethyl)-3-oxo-3-(4-nitrophenyl)propanenitrile, **3c**



2-(4-Methoxyphenyl)-3-(4-nitrophenyl)-3-oxopropanenitrile was prepared according to General Procedure B. (2*E*)-1-Phenyl-3-(1H-pyrrol-2-yl)prop-2-en-1-one (99 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a dark orange microcrystalline solid (95 mg, 0.31 mmol, 62%).

m.p. 143-145 °C (petroleum ether/ethyl acetate).

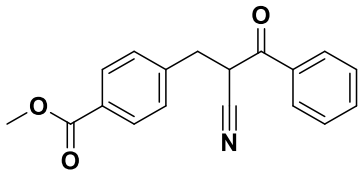
^{1}H NMR (500 MHz, $CDCl_3$) 8.23 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 4.49 (dd, *J* =8.5 Hz, 6.2 Hz, 1H), 3.93 (s, 3H), 3.50 (dd, *J* = 14.1 Hz, 6.2 Hz, , 1H), 3.39 (dd, *J* = 14.1 Hz, 8.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 187.1, 165.1, 147.7, 143.7, 131.5, 130.3, 126.8, 124.2, 116.8, 114.7, 55.9, 40.4, 34.8.

IR V_{max} (neat) 2249 (w), 1664 (s), 1518 (s) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{17}H_{14}O_4N_2$ 310.0948; found 310.0955.

Methyl-4-(2-cyano-3-phenylpropanoyl)benzoate, **3d**



(E)-Methyl 4-(2-cyano-3-phenylpropanoyl)benzoate was prepared according to General Procedure C. (*E)*-Methyl-4-(3-oxo-3-phenylprop-1-en-1-yl)benzoate (133 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a yellow microcrystalline solid (77 mg, 0.27 mmol, 53%).

m.p. 81-83 °C (petroleum ether/ethyl acetate).

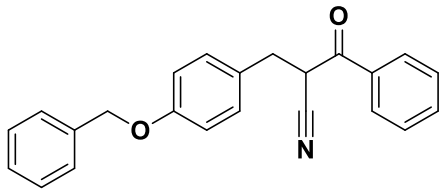
^{1}H NMR (500 MHz, $CDCl_3$) 8.03 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 4.56 (dd, *J* = 8.5 Hz, 6.0 Hz, 1H), 3.93 (s, 3H), 3.43 (dd, *J* = 14.1 Hz, 6.0 Hz, 1H), 3.33 (dd, *J* = 14.1 Hz, 8.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.4, 166.7, 141.1, 134.7, 134.0, 130.2, 129.7, 129.2 (d, *J* = 5.6 Hz), 128.8, 116.2, 52.1, 41.2, 35.1.

IR V_{max} (neat) 2249 (w), 1716 (s), 1686 (m) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{18}H_{15}O_3N$ requires 293.1047; found 293.1045.

2-(4-Benzoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile, **3e**



2-(4-Benzoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure C. (*E*)-3-(4-(Benzyloxy)phenyl)-1-phenylprop-2-en-1-one (157 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a yellow microcrystalline solid (128 mg, 0.38 mmol, 75%).

m.p. 95-97 °C (petroleum ether/ethyl acetate).

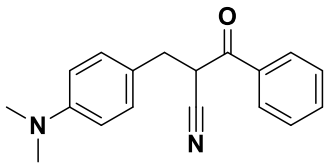
^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.71 – 7.63 (m, 1H), 7.57 – 7.51 (m, 2H), 7.48 – 7.39 (m, 4H), 7.38 – 7.33 (m, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.07 (s, 2H), 4.50 (dd, *J* = 8.7, 5.8 Hz, 1H), 3.38 – 3.17 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) 190.1, 158.2, 136.7, 134.4, 134.1, 130.1, 129.0, 128.7, 128.5, 128.1, 127.9, 127.4, 116.9, 115.2, 70.0, 42.0, 34.8.

IR V_{max} 3036 (w), 2249 (w), 1675 (m), 1512 (m), 1256 (m), 1241 (s).

HRMS (EI^+) m/z: Cald for $C_{23}H_{19}O_2N$ requires 341.1410; found 341.1409

2-(4-Dimethylaminophenylmethyl)-3-oxo-3-phenylpropanenitrile, **3f**



2-(4-Dimethylaminophenylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure B. 4-Dimethylamino-chalcone (123 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol) and pinacolborane (87 µL, 0.6 mmol) were reacted in THF (1 mL). Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a black amorphous solid (119 mg, 0.415 mmol, 83%).

m.p. 69-71 °C (petroleum ether/ethyl acetate).

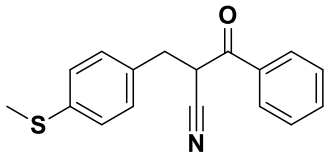
^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (d, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 4.50 (dd, *J* = 8.5 Hz, 5.5 Hz, 1H), 3.30 (dd, *J* = 14.1 Hz, 5.5 Hz, 1H), 3.19 (dd, *J* = 14.1 Hz, 8.5 Hz, 1H), 2.96 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) 190.5, 149.9, 134.4, 134.2, 131.2, 129.8, 129.1, 128.8, 128.3, 127.8, 117.3, 43.9, 42.5, 35.0, 24.9, 24.6.

IR V_{max} (neat) 2261 (w), 1680 (s), 1522 (s) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{18}H_{18}ON_2$ 278.1414; found 278.1409.

2-(4-Methylthiophenylmethyl)-3-oxo-3-phenylpropanenitrile, **3g**



2-(4-Methylthiophenylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure C. 3-(4-(Methylthio)phenyl)-1-phenylprop-2-en-1-one (127 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as an off white amorphous solid (88 mg, 0.32 mmol, 64%).

m.p. 44-46 °C (petroleum ether/ethyl acetate).

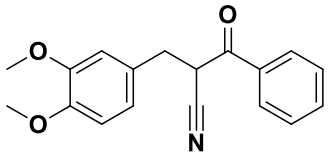
^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (d, *J* = 8.5 Hz, 2H), 7.68 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 8.1 Hz, 2H), 7.24 (app. s, 4H), 4.51 (dd, *J* = 8.5 Hz, 6.0 Hz, 1H), 3.35 (dd, *J* = 14.1 Hz, 6.0 Hz, 1H), 3.24 (dd, *J* =14.1 Hz, 8.5 Hz, 1H), 2.49 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.8, 138.1, 134.6, 134.1, 129.5, 129.2, 128.8, 127.0, 116.9, 41.8, 35.0, 15.8.

IR V_{max} (neat) 2252 (w), 1686 (s) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{17}H_{15}ONS$ 281.0869; found 281.0864.

2-(3,4-Dimethoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile, **3h**



2-(3,4-Dimethoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure C. 3,4-Dimethoxychalcone (134 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a yellow amorphous solid (118 mg, 0.41 mmol, 81%).

m.p. 97-99 °C (petroleum ether/ethyl acetate).

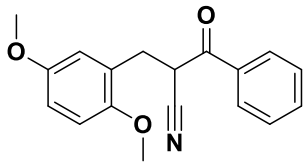
^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.55 (t, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 11.3 Hz, 3H), 4.52 (dd, *J* = 8.5 Hz, 6.0 Hz, 1H), 3.89 (s, 6H), 3.32 (dd, *J* = 14.1 Hz, 6.0 Hz, 1H), 3.24 (dd, *J* = 14.1 Hz, 8.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 190.2, 149.2, 148.6, 134.6, 134.2, 129.1, 128.8, 128.4, 121.2, 117.1, 112.3, 111.5, 55.9, 42.1, 35.3.

IR V_{max} (neat) 2252 (w), 1680 (s) 1238 (s) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{18}H_{17}O_3N$ 295.1203; found 295.1196.

2-(2,5-Dimethoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile, **3i**



2-(2,5-Dimethoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure B. 3-(2,5-Dimethoxyphenyl)-1-phenyl-2-propenone (132 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a yellow microcrystalline solid (102 mg, 0.36 mmol, 72%).

m.p. 108-110 °C (petroleum ether/ethyl acetate).

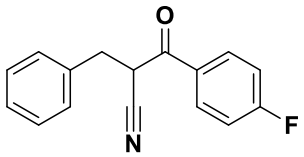
^{1}H NMR (500 MHz, $CDCl_3$) 8.05 (d, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 8.3 Hz, 2H), 6.84 (m, 5H), 4.83 (dd, *J* = 5.7 Hz, 9.8 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.45 (dd, *J* = 5.4 Hz, 13.5 Hz, 1H), 3.08 (dd, *J* = 9.5 Hz, 13.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 190.8, 153.6, 151.4, 134.3, 134.2, 130.0, 128.9, 125.0, 117.4, 117.2, 113.6, 111.2, 55.8, 55.7, 40.0, 32.2.

IR V_{max} (neat) 2246 (w), 1692 (s), 1229 (s) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{18}H_{17}O_3N$ 295.1203; Found 295.1196.

2-Benzyl-3-oxo-3-(4-fluorophenyl)propanenitrile, **3j**



2-Benzyl-3-(4-fluorophenyl)-3-oxopropanenitrile was prepared according to General Procedure B. (*E)*-1-(4-Fluorophenyl)-3- phenylprop-2-en-1-one (111 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the α-cyanoketone as a pale yellow amorphous solid (88 mg, 0.35 mmol, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) 8.09-7.98 (m, 2H), 7.42-7.15 (m, 7H), 4.50 (dd, *J* = 8.7 Hz, 6.0 Hz, 1H), 3.38 (dd, *J* = 14.3 Hz, 6.0 Hz, 1H), 3.28 (dd, *J* = 14.3 Hz, 8.6 Hz, 1H).

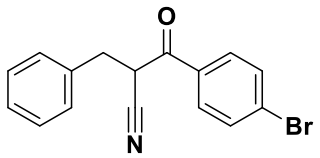
^{13}C NMR (126 MHz, $CDCl_3$) 188.5, 166.5 (d, $^{4}J_{CF}$ = 258.0 Hz), 135.8, 131.7 (d, $^{3}J_{CF}$ = 10.1 Hz), 130.6 (d, $^{1}J_{CF}$ = 3.1 Hz), 129 (d, ^{2}J = 7.0 Hz), 127.8, 116.5, 116.9, 41.7, 35.5.

^{19}F NMR (470 MHz, $CDCl_3$) -101.83.

IR V_{max} (neat) 2245 (w), 1696 (s), 1239 (s) cm^{-1}.

Data were in accordance with those previously reported.[6]

2-Benzyl-3-oxo-3-(4-bromophenyl)propanenitrile, **3k**



2-Benzyl-3-(4-bromophenyl)-3-oxopropanenitrile was prepared according to General Procedure B. (*E)*-1-(4-Bromophenyl)-3- phenylprop-2-en-1-one (141 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the α-cyanoketone as a pale yellow microcrystalline solid (113 mg, 0.37 mmol, 73%).

m.p. 102-103 °C (petroleum ether/ethyl acetate).

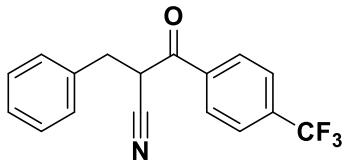
^{1}H NMR (500 MHz, $CDCl_3$) 8.00 (d, *J* = 8.5 Hz, 2H), 7.71 (t, 7.3 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 4.53 (dd, *J* = 8.5 Hz, 6.0 Hz, 1H), 3.46 (dd, *J* = 14.0 Hz, 6.0 Hz, 1H), 3.35 (dd, *J* = 14.0 Hz, 8.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.2, 135.9, 133.0, 132.7, 130.3, 129.2, 127.9, 116.8, 41.9, 35.6.

IR V_{max} (neat) 2225 (w), 1699 (s), 687 (s) cm^{-1}.

Data were in accordance with those previously reported.[6]

2-Benzyl-3-oxo-3-(4-(trifluoromethyl)phenyl)propanenitrile, **3l**



2-Benzyl-3-oxo-3-(4-(trifluoromethyl)phenyl)propanenitrile was prepared according to General Procedure B. (*E)*-3-Phenyl-1- (4-(trifluoromethyl)phenyl)prop-2-en-1-one (161 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the α-cyanoketone as a light yellow crystalline solid (80 mg, 0.26 mmol, 53%).

m.p. 86-87 °C (petroleum ether/ethyl acetate), Lit; 88.6-89.5.[6]

^{1}H NMR (500 MHz, $CDCl_3$) 8.05 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.36-7.26 (m, 5H), 4.50 (dd, J = 8.5 Hz, 6.0 Hz, 1H), 3.38 (dd, J = 14.0 Hz, 6.0 Hz, 1H), 3.28 (dd, J = 14.0 Hz, 8.1 Hz, 1H).

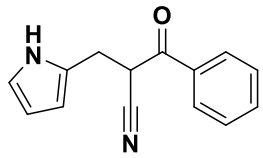
^{13}C NMR (126 MHz, $CDCl_3$) 189.45, 136.97, 135.68, 129.32, 129.19 (d, $^2J_{CF}$ = 4.0 Hz), 128.02, 126.35 (q, $^1J_{CF}$ = 3.8 Hz), 42.25, 35.49.

^{19}F NMR (470 MHz, $CDCl_3$) −63.39.

IR V_{max} (neat) 2249 (w), 1695 (s) cm^{-1}.

Data were in accordance with those previously reported.[6]

2-(2-Pyrrolmethyl)-3-oxo-3-phenylpropanenitrile, **3m**



2-(2-Pyrrolmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure C. (2*E*)-1-Phenyl-3-(1H-pyrrol-2-yl)prop-2-en-1-one (99 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a dark brown oil (64 mg, 0.29 mmol, 58%).

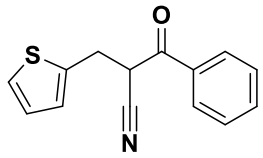
^{1}H NMR (500 MHz, $CDCl_3$) 8.00 (d, *J* = 8.5 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 6.75-6.71 (m, 1H), 6.17-6.06 (m, 2H), 4.51 (dd, *J* = 7.1 Hz, 6.0 Hz, 1H), 3.47 (dd, *J* = 14.8 Hz, 7.1 Hz, 1H), 3.34 (dd, *J* =14.8 Hz, 6.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 190.4, 134.8, 134.0, 129.2, 128.9, 126.1, 118.2, 117.1, 108.6, 108.0, 40.6, 27.4.

IR V_{max} (neat) 3386 (bw), 2253 (w), 1686 (s) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{14}H_{12}ON_2$ 224.0944; found 224.0948.

2-(2-Thienylmethyl)-3-oxo-3-phenylpropanenitrile, **3n**



2-(2-Thienylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure B. 3-(2'-Thienyl)acrylphenone (105 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø, using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a dark brown amorphous solid (101 mg, 0.42 mmol, 84%).

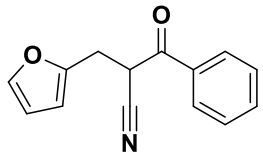
^{1}H NMR (500 MHz, $CDCl_3$) 7.99 (d, *J* = 8.5 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 5.1 Hz, 1H), 7.02 (d, *J* = 5.1 Hz, 1H), 6.97 (dd, *J* = 5.1 Hz, 3.5 Hz, 1H), 4.60 (dd, *J* = 8.1 Hz, 6.1 Hz, 1H), 3.62 (dd, *J* = 15.0 Hz, 6.1 Hz, 1H), 3.53 (dd, 15.1 Hz, 8.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.5, 137.6, 134.7, 134.0, 129.2, 128.9, 127.3, 127.2, 125.2, 116.7, 41.8, 29.5.

IR V_{max} (neat) 2252 (w), 1683 (s) cm^{-1}.

MS (HRMS-ESI$^+$) Found 241.0556 ($C_{14}H_{11}ONS$), requires 241.0556.

2-(2-Furylmethyl)-3-oxo-3-phenylpropanenitrile, **3o**



2-(2-Furylmethyl)-3-oxo-3-phenylpropanenitrile was prepared according to General Procedure B. (*E)*-3-(2-Furyl)-1-phenylprop-2- en-1-one (97 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø, using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the α-cyanoketone as a dark orange oil (99 mg, 0.44 mmol, 88%).

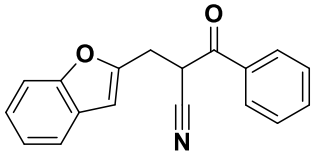
^{1}H NMR (500 MHz, $CDCl_3$) 8.01 (d, *J* = 8.5 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 8.5 Hz, 2H), 7.37 (d, 2.0 Hz, 1H) 6.33 (dd, *J* = 3.3 Hz, 2.0 Hz, 1H), 6.27 (d, *J* = 3.3 Hz, 1H), 4.71 (dd, *J* = 8.5 Hz, 6.1 Hz, 1H), 3.44 (dd, *J* = 15.4 Hz, 6.1 Hz, 1H), 3.35 (dd, *J* = 15.4 Hz, 8.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.5, 149.3, 142.4, 134.7, 134.0 129.2, 128.9, 116.6, 110.7, 108.5, 38.7, 28.2.

IR V_{max} (neat) 2244 (w), 1690 (s), 1259 (m) cm^{-1}.

Data were in accordance with those previously reported.[6]

2-(Benzofuran-2-ylmethyl)-3-oxo-3-phenylpropanenitrile, **3p**



2-(Benzofuran-2-ylmethyl)-3-phenyl-3-oxopropanenitrile was prepared according to General Procedure B. (2E)-1-Phenyl-3-(1H-pyrrol-2-yl)prop-2-en-1-one (99 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1,5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 100/0 to 70/30 over 35 minutes, 30/70 to 100/0 over 15 minutes) gave the *α-cyanoketone* as a pale yellow oil (90 mg, 0.34 mmol, 67%).

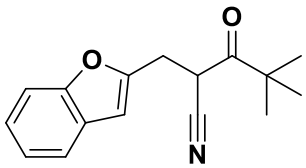
^{1}H NMR (500 MHz, $CDCl_3$) 8.05 (d, *J* = 8.5 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 3H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.28-7.20 (m, 2H), 6.68 (s, 1H), 4.85 (dd, *J* = 8.5 Hz, 6.1 Hz, 1H), 3.60 (dd, *J* = 15.6 Hz, 6.1 Hz, 1H), 3.48 (dd, *J* = 15.6 Hz, 8.5 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) 189.2, 155.1, 152.3, 134.9, 134.0, 129.3, 129.1, 128.4, 124.4, 123.1, 121.1, 116.6, 111.1, 105.7, 38.4, 28.7.

IR V_{max} (neat) 2241(w), 1697 (s), 1252 (m) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{18}H_{13}O_2N$ 275.0941; found 275.0933.

2-(Benzofuran-2-ylmethyl)-4,4-dimethyl -3-oxopentanenitrile, **3q**



2-(Benzofuran-2-ylmethyl)-4,4-dimethyl -3-oxopentanenitrile was prepared according to General Procedure B. (*E)*-1-(Benzofuran-2-yl)-4,4-dimethylpent-1-en-3-one (114 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 10/90 over 50 minutes, 10/90 to 100/0 over 10 minutes) gave the *α-cyanoketone* as a light yellow oil (75 mg, 0.30 mmol, 59%).

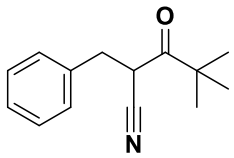
^{1}H NMR (500 MHz, $CDCl_3$) 7.53 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.30-7.22 (m, 2H), 6.59 (q, 0.8 Hz, 1H), 4.36 (dd, *J* = 7.7 Hz, 7.2 Hz, 1H), 3.44 (ddd, *J* = 15 Hz, 7.7 Hz, 0.8 Hz, 1H), 3.35 (ddd, *J* = 15.0 Hz, 7.2 Hz, 0.8 Hz), 1.21 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) 204.3, 155.0, 152.4, 128.3, 124.5, 123.2, 121.2, 116.6, 111.0, 105.6, 45.9, 35.7, 29.1, 26.0.

IR V_{max} (neat) 2242 (w), 1720 (s), 1251 (m) cm^{-1}.

HRMS (EI^+) m/z: Calcd for $C_{16}H_{17}O_2N$ 255.12538; found 255.12593.

2-Benzyl-4,4-dimethyl-3-oxopentanenitrile, **3r**



2-Benzyl-4,4-dimethyl-3-oxopentanenitrile was prepared according to General Procedure C. (*E)*-Benzylidenepinacolone (94 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 10/90 over 50 minutes, 10/90 to 100/0 over 10 minutes) gave the α-cyanoketone as a colourless oil (51 mg, 0.24 mmol, 48%).

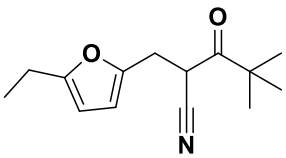
^{1}H NMR (500 MHz, $CDCl_3$) 7.36-7.26 (m, 3H), 7.23 (d, *J* = 7.4 Hz, 2H), 4.03 (t, *J* = 7.6, 1H), 3.23 (dd, *J* = 13.7 Hz, 7.3 Hz, 1H), 3.16 (dd, *J* = 13.7 Hz, 7.3 Hz, 1H), 1.12 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) 204.8, 136.3, 129.1, 128.9, 127.6, 117.0, 45.5, 38.8, 36.0, 25.8.

IR V_{max} (neat) 2359 (w), 1717 (m) cm^{-1}.

Data were in accordance with those previously reported.[6]

2-(2-(5-Ethylfuryl)methyl)-4,4-dimethyl-3-oxopentanenitrile, **3s**



2-(2-(5-Ethylfuryl)methyl)-4,4-dimethyl-3-oxopentanenitrile was prepared according to General Procedure C. (*E)*-1-(5-ethyl-2-yl)-4,4-dimethylpent-1-en-3-one (94 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 10/90 over 50 minutes, 10/90 to 100/0 over 10 minutes) gave the α-cyanoketone as a colourless oil (91 mg, 0.39 mmol, 78%).

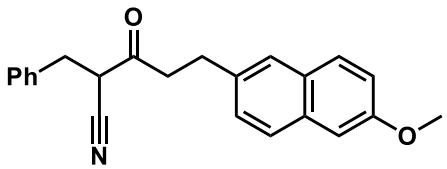
^{1}H NMR (400 MHz, $CDCl_3$) 6.06 – 6.00 (m, 1H), 5.87 (dt, *J* = 3.1, 1.0 Hz, 1H), 4.20 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.30 – 3.20 (m, 1H), 3.15 (ddd, *J* = 14.8, 6.7, 0.7 Hz, 1H), 2.59 (qd, *J* = 7.6, 1.0 Hz, 2H), 1.32 – 1.18 (m, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) 204.6, 157.7, 147.4, 116.8, 108.9, 104.8, 45.7, 35.9, 28.8, 25.6, 21.3, 12.2.

IR V_{max} (neat) 2974 (w), 2243 (w), 1721 (s), 1566 (w).

HRMS (EI^+) m/z: Calcd for $C_{14}H_{19}O_2N$ 233.1410; found 233.1406.

2-Benzyl-5-(2-methoxynapthyl)-3-oxopentanenitrile, **3t**



2-Benzyl-5-(2-methoxynapthyl)-3-oxopentanenitrilewas prepared according to General Procedure C. (*E*)-5-(2-Methoxynapthyl)-1-phenylpenta-1-en-3-one (94 mg, 0.5 mmol), H-*B*-9-BBN solution in THF (150 µL, 0.5 M, 0.075 mmol), *N*-cyano-*N*-phenyl-*p*-toluenesulfonamide (204 mg, 0.75 mmol), pinacolborane (87 µL, 0.6 mmol) and THF (1 mL) were reacted. Purification by flash column chromatography (chromatography column: Teledyne catalogue number #692203347, 40 g SiO_2, 1.5 cm Ø. Using a CombiFlash Isco NextGen300+ Petroleum ether/ethyl acetate gradient elution 10/90 over 50 minutes, 10/90 to 100/0 over 10 minutes) gave the *α-cyanoketone* as a microcrystalline solid (51 mg, 0.24 mmol, 48%).

m.p. 115-116 °C (petroleum ether/ethyl acetate).

^{1}H NMR (500 MHz, $CDCl_3$) 7.69 (d, *J* = 8.6 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.33 – 7.29 (m, 3H), 7.25 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.21 – 7.14 (m, 3H), 7.13 (d, *J* = 2.6 Hz, 1H), 3.94 (s, 3H), 3.60 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.26 – 2.97 (m, 6H).

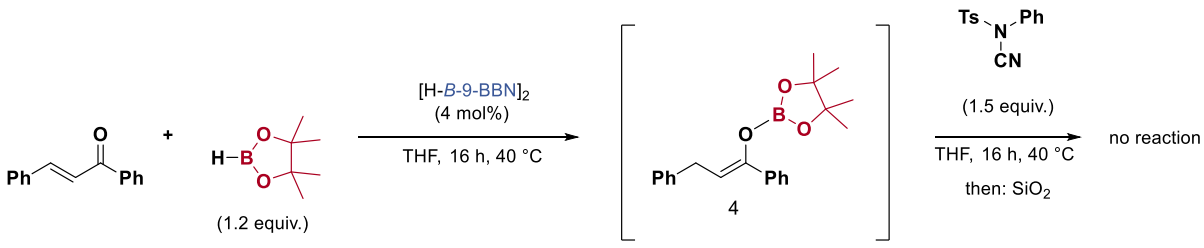
^{13}C NMR (126 MHz, $CDCl_3$) 199.8, 157.5, 135.5, 134.9, 129.0, 129.0, 128.9, 127.7, 127.3, 127.2, 126.5, 119.0, 117.1, 105.7, 55.3, 45.9, 43.5, 34.9, 29.3.

3 x ^{13}C resonances are overlapping therefore 19 resonances are reported rather than the expected 21

IR V_{max} 2951 (w), 2241 (w), 1671 (m), 1509 (m).

HRMS (EI^+) m/z: Calcd for $C_{23}H_{21}O_2N$ 343.1567; found 343.1559.

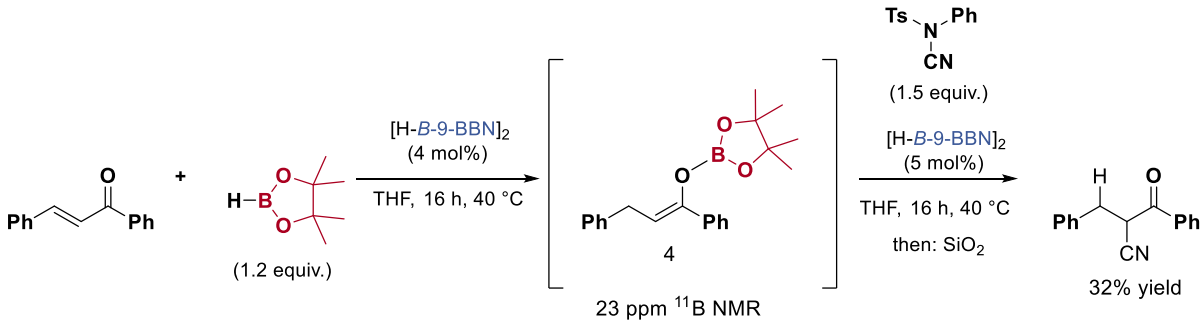
Preparation and Reaction of Bpin enolate 4



Scheme S3) Reaction of Bpin enolate 4 in electrophilic cyanation.

Chalcone (0.104 g, 0.5 mmol), H-*B*-9-BBN (0.005 g, 0.02 mmol) and HBpin (90 µL, 0.6 mmol) were reacted for 16 hours in THF (1 mL) at 40 °C in an argon atmsophere. After 16 hours NCTS (204 mg, 1.5 mmol) was added, the solution was allowed to stir for a further 16 hours at 40 °C. The reaction mixture was quenched with SiO_2 (0.1 g, excess). ^{1}H NMR yield was measured using 1,3,5-trimethoxybenzene as an internal standard. Cyanation product was not observed and the saturated ketone, dihydrochalcone was recovered.

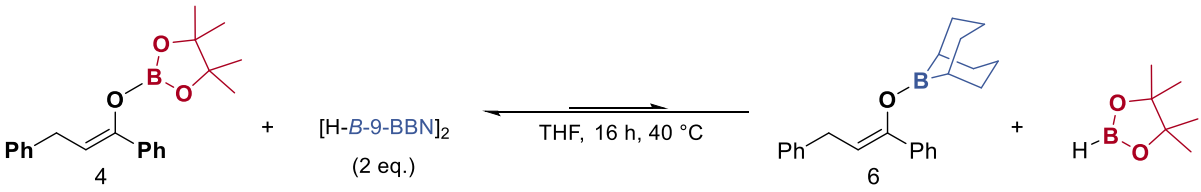
Attempted reaction of Bpin enolate 4 with NCTS catalysed by H-*B*-9-BBN



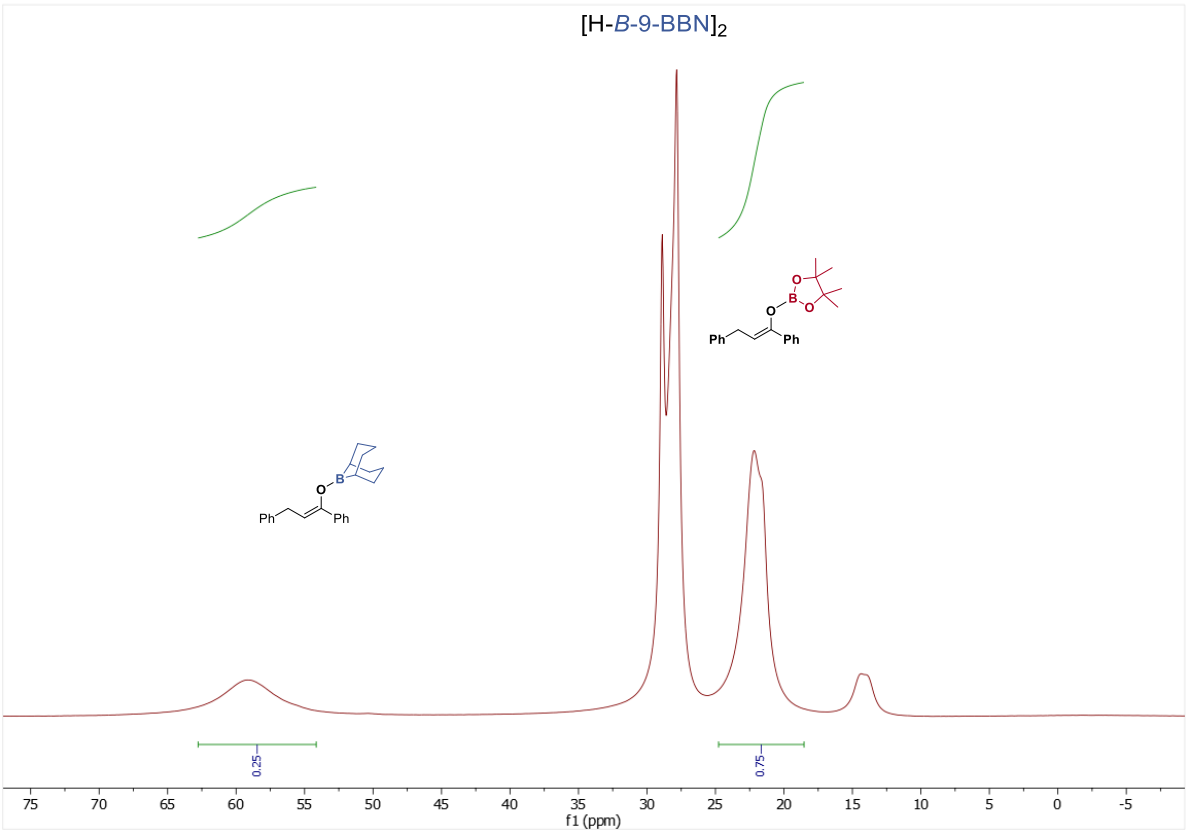
A similar experiment was conducted where an additional 5 mol% of H-*B*-9-BBN (0.003 g, 0.0125 mmol) was added to the O-Bpin enolate before reaction with NCTS:

Chalcone (0.052 g, 0.25 mmol), H-*B*-9-BBN (0.0025 g, 0.01 mmol) and HBpin (45 µL, 0.3 mmol) were reacted for 16 hours in THF (0.5 mL) at 40 °C in an argon atmsophere. The conversion to the O-Bpin enolate was confirmed through ^{11}B NMR (23 ppm). After 16 hours NCTS (68 mg, 0.25 mmol) and H-*B*-9-BBN (0.003 g, 0.0125 mmol) were added, the solution was allowed to stir for a further 16 hours at 40 °C. The reaction mixture was quenched with SiO_2 (0.1 g, excess). ^{1}H NMR yield (32%) was measured using 1,3,5-trimethoxybenzene as an internal standard.

Investigation of enolate equilibrium

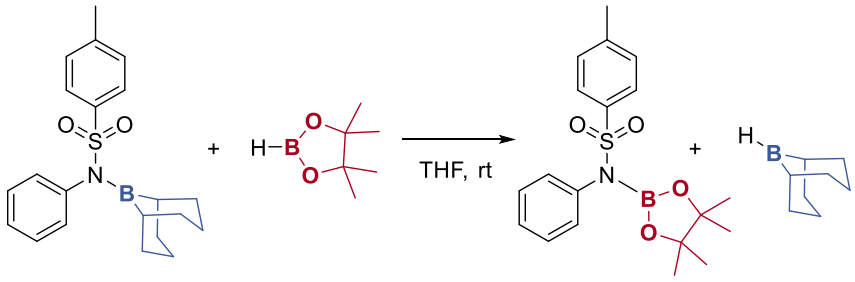


In a glovebox with a purified argon atmosphere, to a solution of OBpin enolate 4 (0.25 mmol, 0.5 M THF) was added H-*B*-9-BBN (0.122 g, 0.5 mmol) and reacted for 16 hours at 40 °C. The ratio of O-Bpin enolate: O-BBN enolate was measured by ^{11}B NMR to be 3:1.

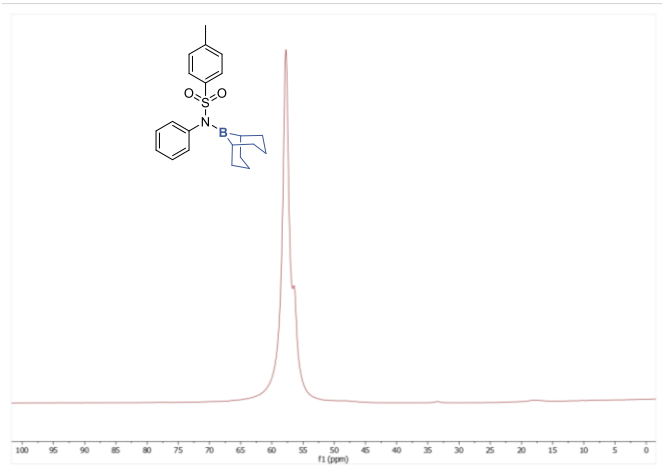


^{11}B NMR (160 MHz)

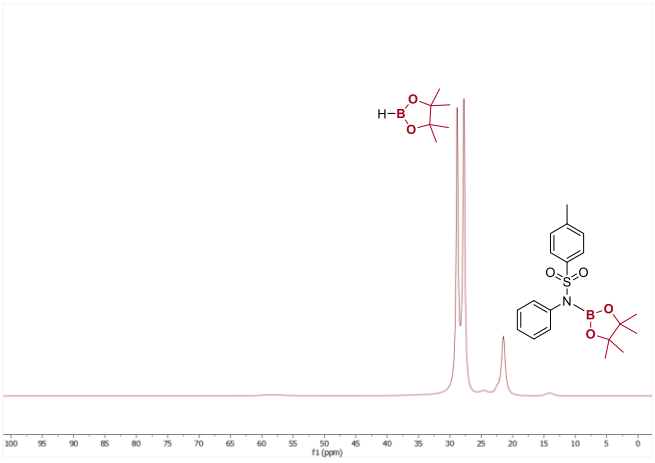
Investigation into B–N transborylation



In a glovebox with a purified argon atmosphere, to a solution of amino-9-BBN, (0.25 mmol, 0.5 M in THF) (^{11}B NMR: 58 ppm) was added HBpin (175 µL, 1.2 mmol) and reacted for 16 hours at 40 °C to give full conversion to amino-Bpin product (^{11}B NMR: 22 ppm). To this solution was added H-*B*-9-BBN (244 mg, 1 mmol, 4 eq.), however, this resulted in no reaction of the amino-Bpin (^{11}B NMR: 22 ppm) with HBpin.

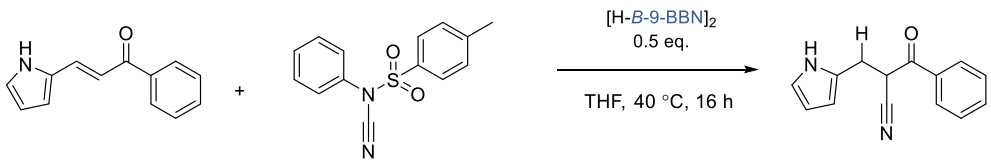


^{11}B NMR (160 MHz) of amino-BBN prior to addition of HBpin

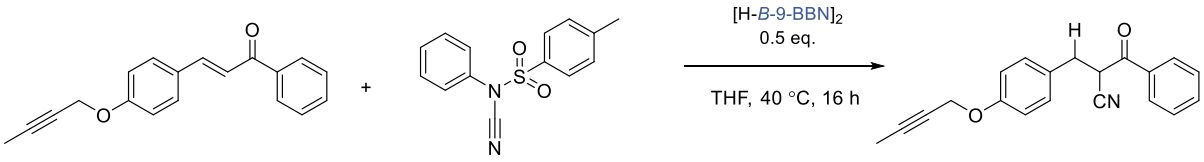


^{11}B NMR (160 MHz) after reaction with HBpin to give amino-Bpin

Stoichiometric 1,4-hydroboration-cyanation of enones

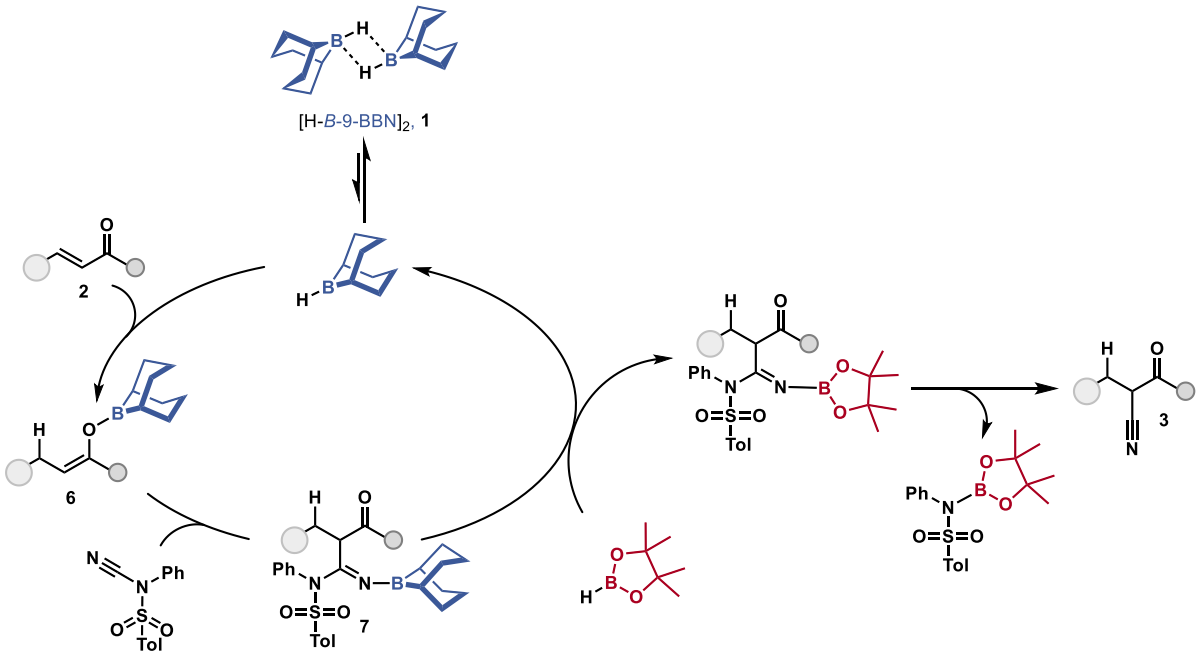


In a glovebox with a purified argon atmosphere, [H-*B*-9-BBN]$_2$ (64 mg, 0.263 mmol), (2*E*)-1-phenyl-3-(1H-pyrrol-2-yl)prop-2-en-1-one (99 mg, 0.5 mmol) and NCTS (136 mg, 0.5 mmol) were reacted in THF (1 mL) at 40 °C for 16 hours. The reactions were quenched with SiO_2 and the ^{1}H NMR yield (53%) was measured using 1,3,5-trimethoxybenzene as an internal standard.



In a glovebox with a purified argon atmosphere, [H-*B*-9-BBN]$_2$ (64 mg, 0.263 mmol), (*E*)-3-(4-(2-butynyloxy)phenyl)-1-phenylprop-2-en-1-one (139 mg, 0.5 mmol) and NCTS (136 mg, 0.5 mmol) were reacted in THF (1 mL) at 40 °C for 16 hours. The reactions were quenched with SiO_2 and the ^{1}H NMR yield (26%) was measured using 1,3,5-trimethoxybenzene as an internal standard.

Alternative Reaction Mechanism



Scheme S1: Alternative mechanism for the reductive cyanation of enones.

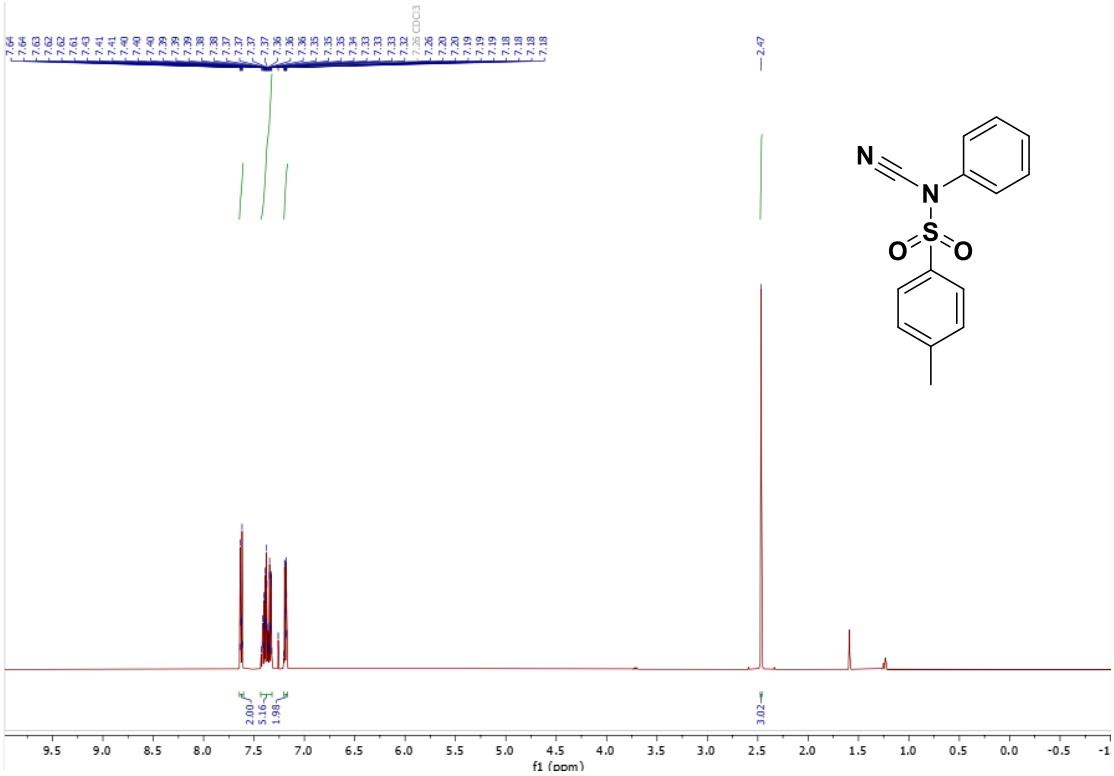
References

1. F. Kurzer, *J. Chem. Soc.*, 1949, 1034-1038.
2. C. Wang, Y. Qu, X. Liu, Z. Ma, B. Yang, Z. Liu, X. Chen, and Y. Chen, *J. Org. Chem.*, 2021, **86**, 3546-3554.
3. Revathi A. Gupta, S. G. Kaskhedikar, *Med. Chem. Res.,* 2013, **22**, 3863-3880.
4. M. S. Altowyan, A. Barakat, A. M. Al-Majid, and H.A. Al-Ghulikah, Molecules, 2020, **24**, 2342.
5. Y. Ji, W. C. Trenkle, J. V. Vowles, *Org. Lett.*, 2006, **8**, 1161-1163.
6. K. Kiyokawa, T. Nagata, S. Minakata, *Angew. Chem. Int. Ed.*, 2016, **55**, 10458-10462.

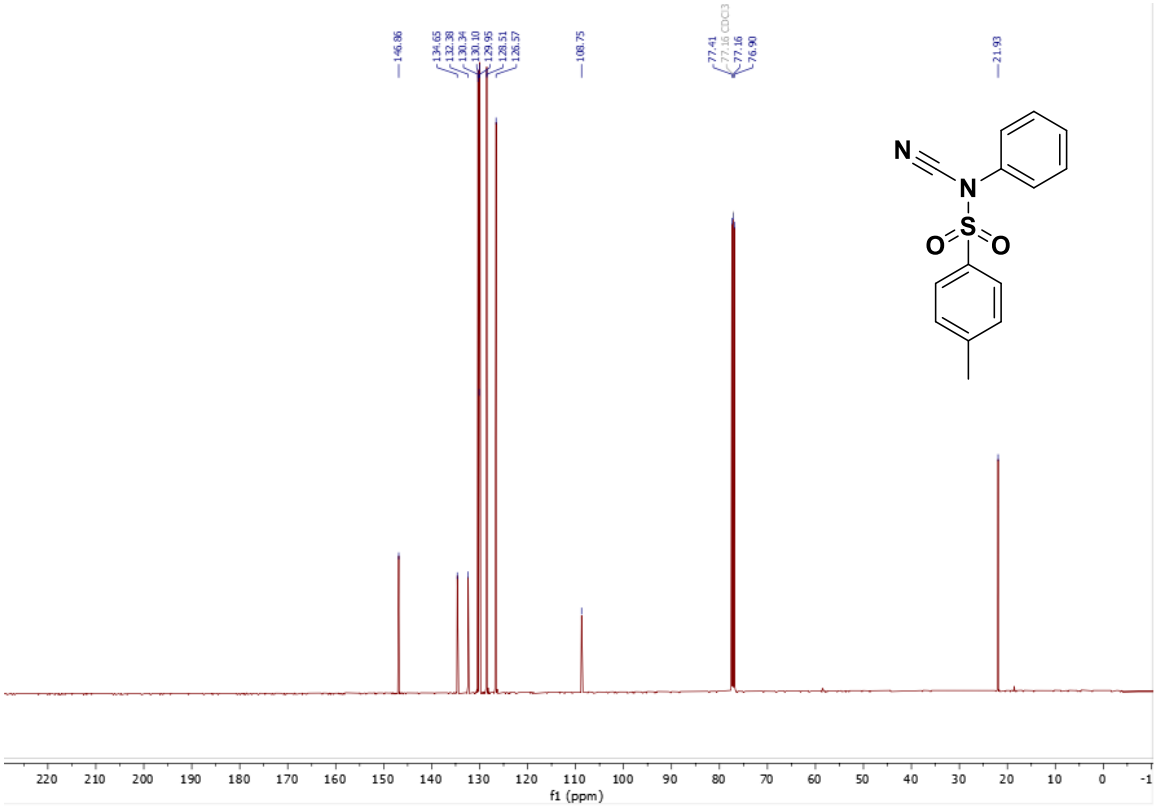
NMR Spectra of Isolated Compounds

N-cyano-*N*-phenyl-*p*-toluenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$)

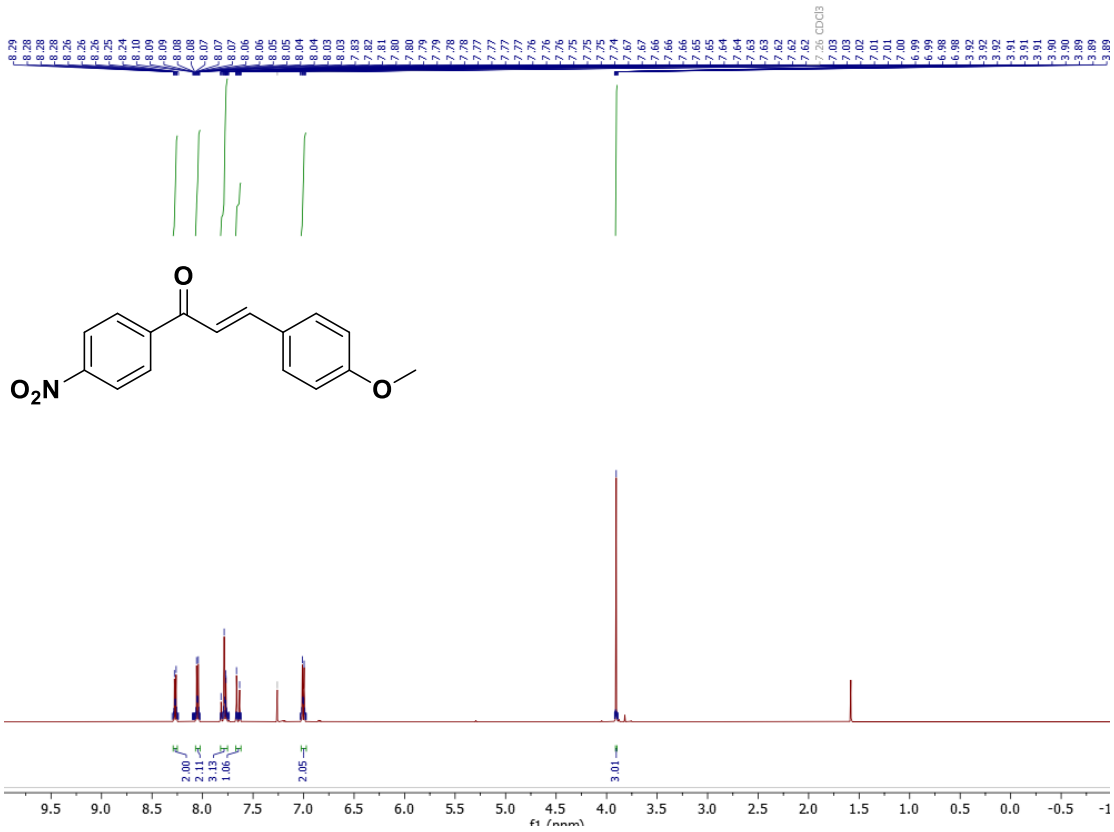


^{13}C NMR (126 MHz, $CDCl_3$)

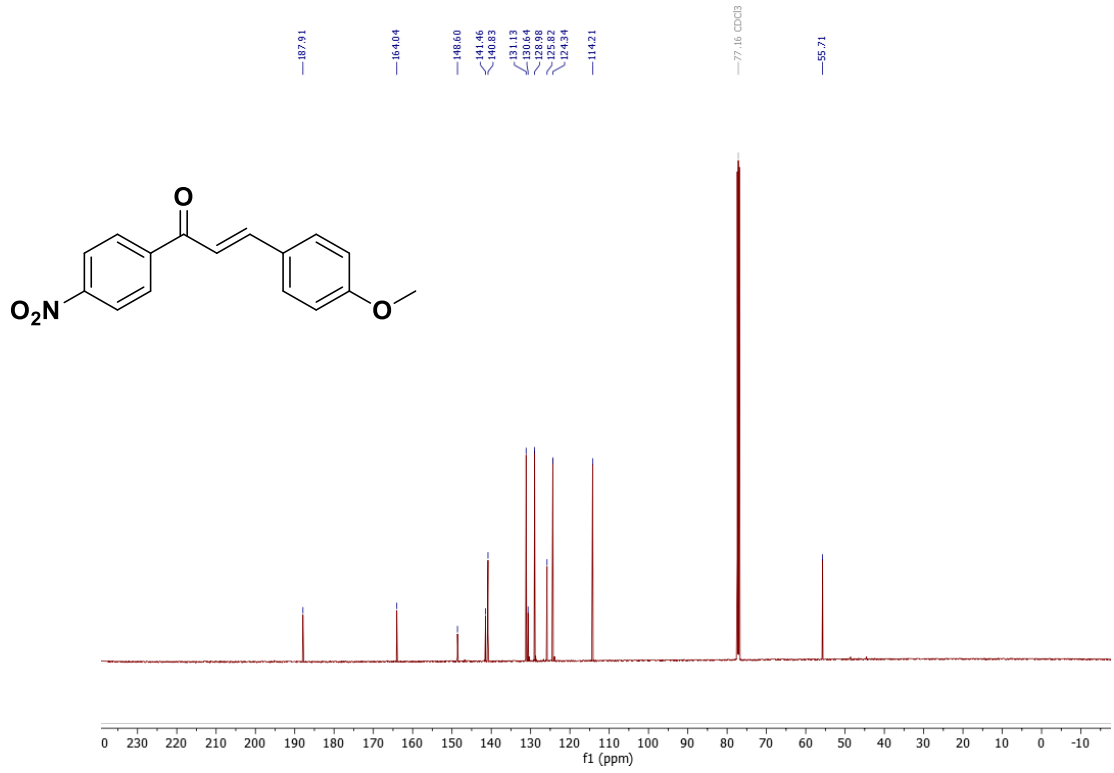


4'-Methoxy-4-nitrochalcone

^{1}H NMR (500 MHz, $CDCl_3$)

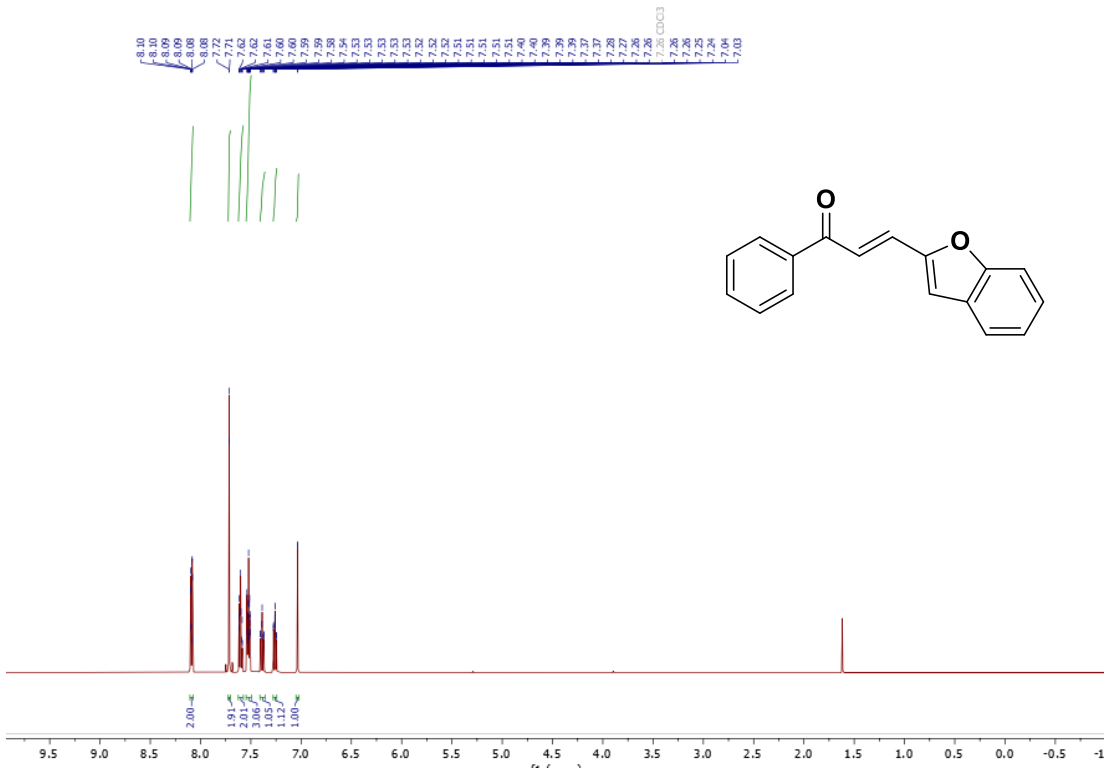


^{13}C NMR (126 MHz, $CDCl_3$)



(*E*)-3-(Benzofuran-2-yl)-1-phenylprop-2-en-1-one

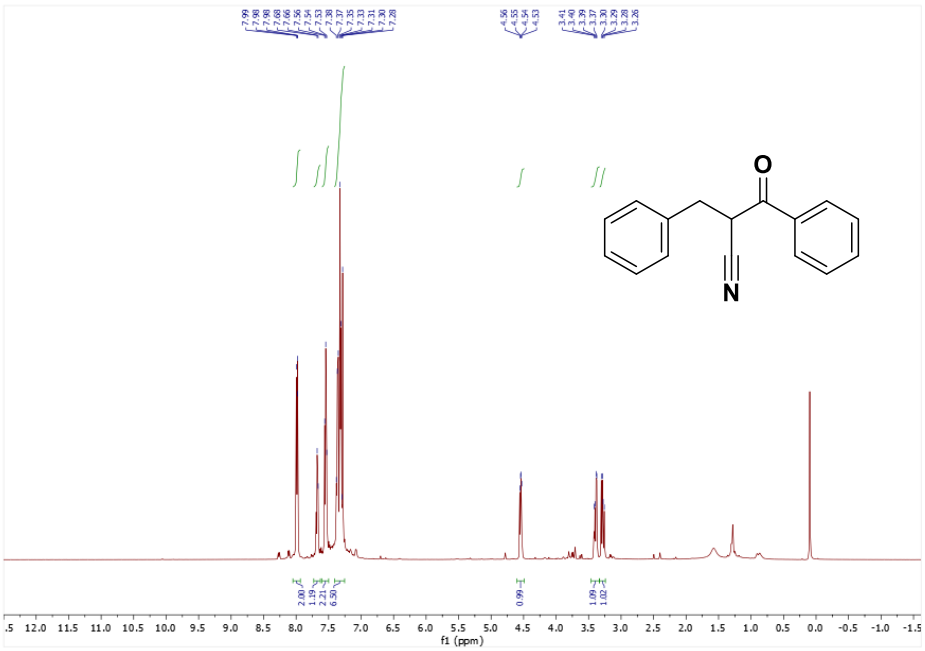
^{1}H NMR (500 MHz, $CDCl_3$)



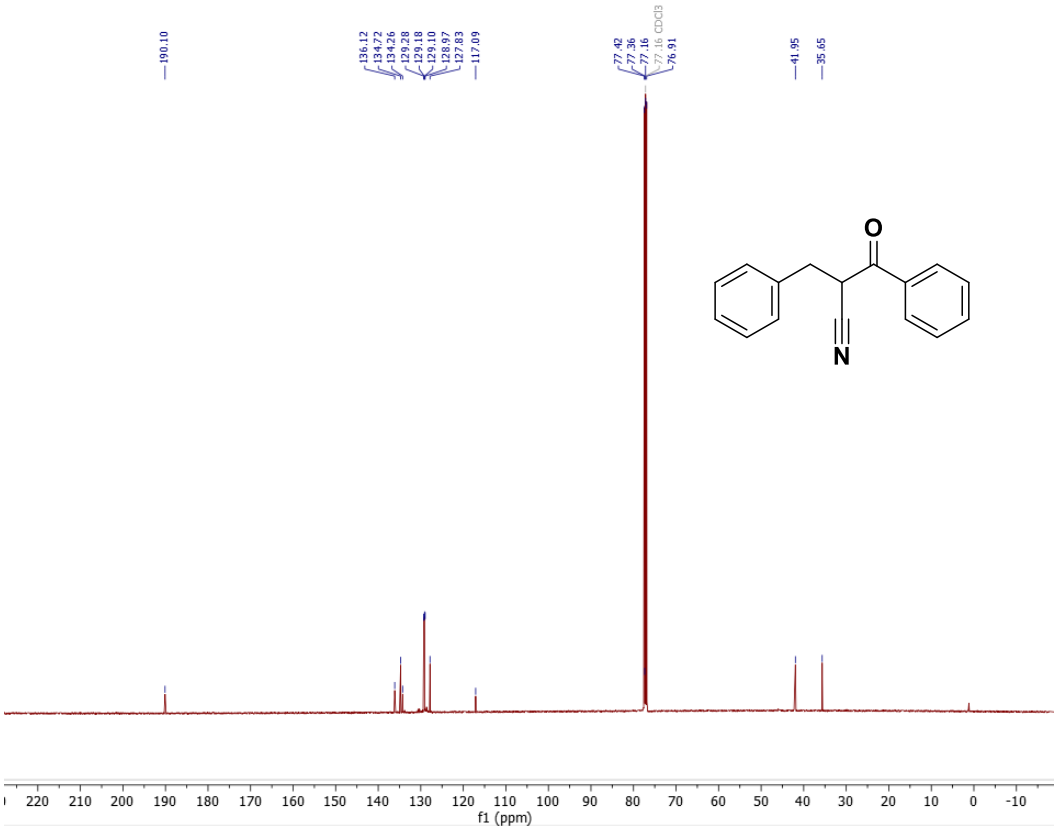
^{13}C NMR (126 MHz, $CDCl_3$)

2-Benzyl-3-oxo-3-phenylpropanenitrile (**3a**)

^{1}H NMR (500 MHz, $CDCl_3$)

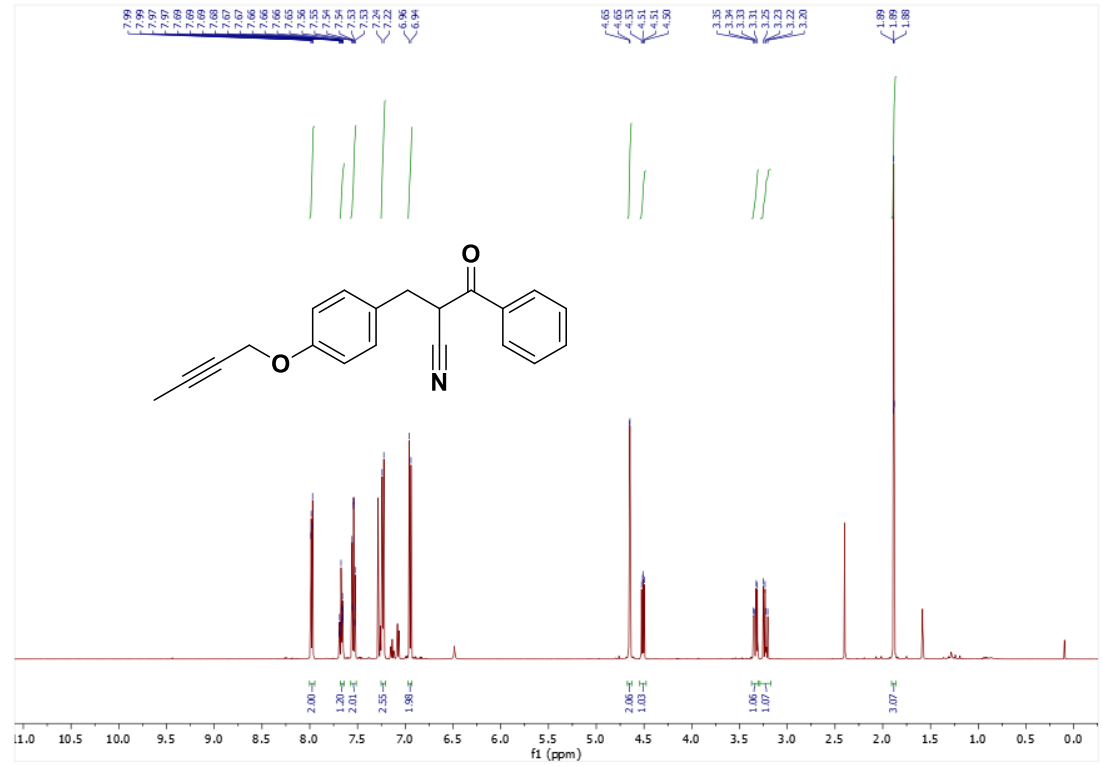


^{13}C NMR (126 MHz, $CDCl_3$)

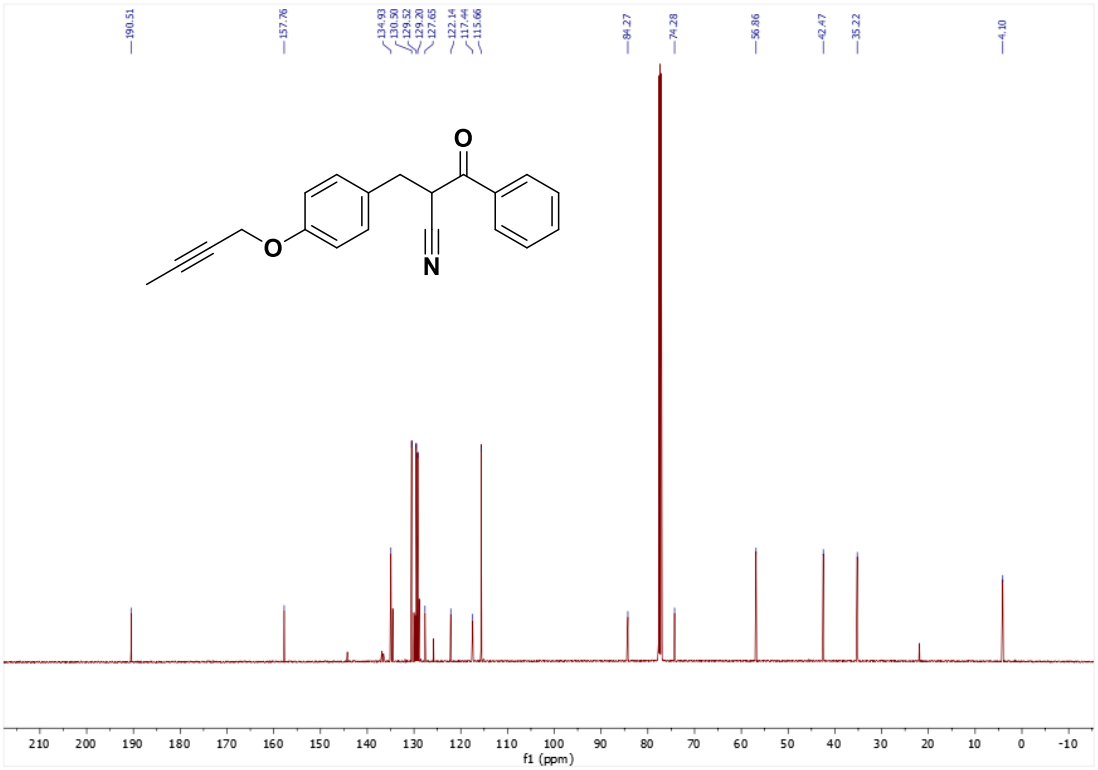


2-(4-(2-Butynyloxy)phenylmethyl)-3-oxo-3-phenylpropanenitrile, **3b**

^{1}H NMR (500 MHz, $CDCl_3$)

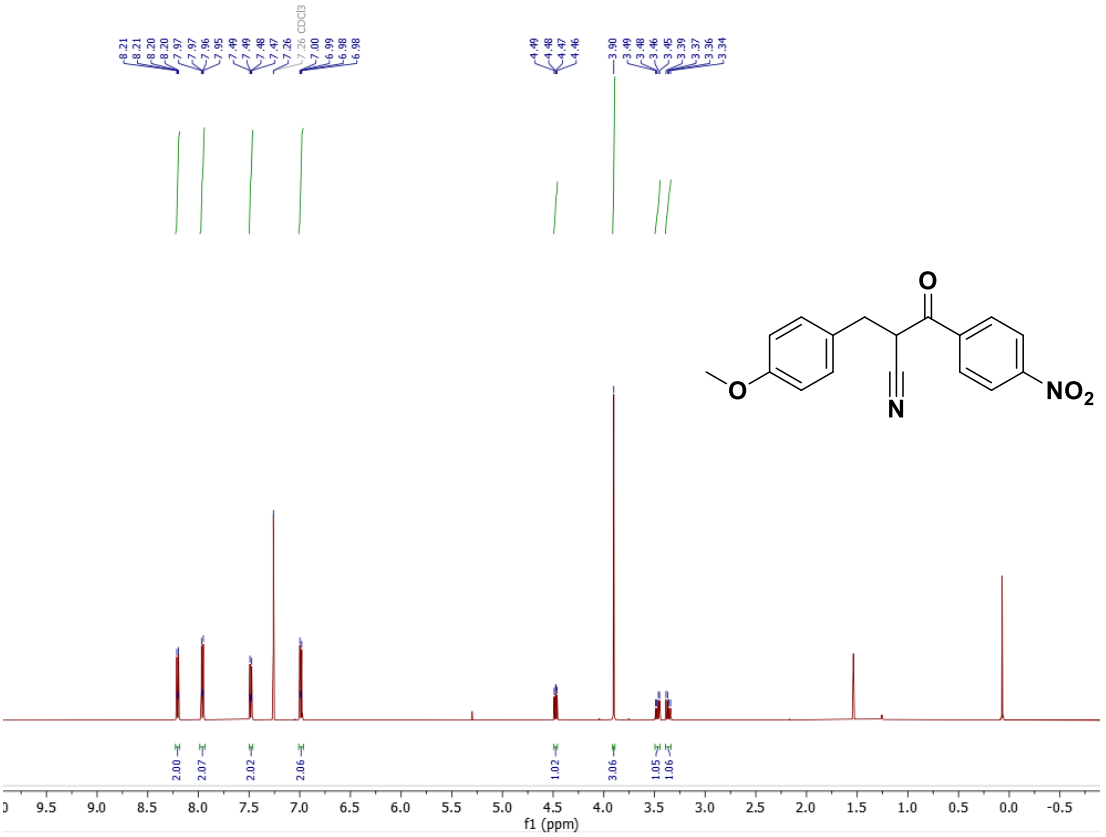


^{13}C NMR (126 MHz, $CDCl_3$)

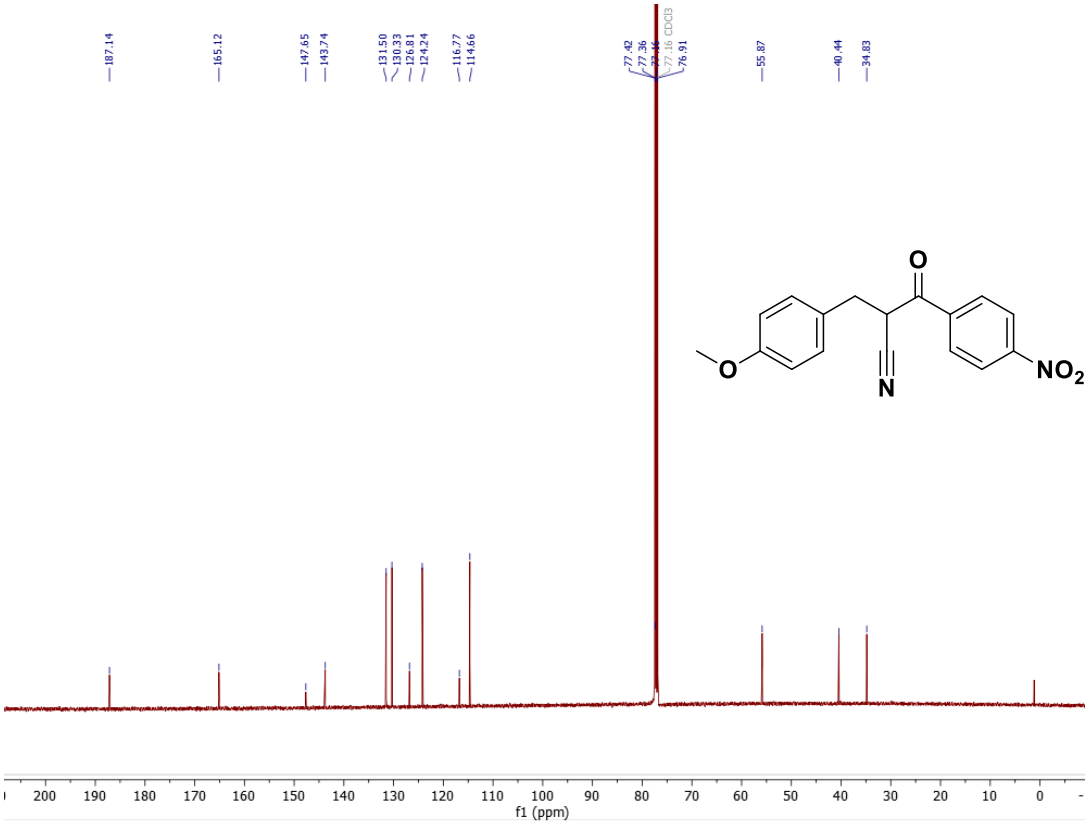


2-(4-Methoxyphenyl)-3-(4-nitrophenyl)-3-oxopropanenitrile **(3c)**

^{1}H NMR (500 MHz, $CDCl_3$)

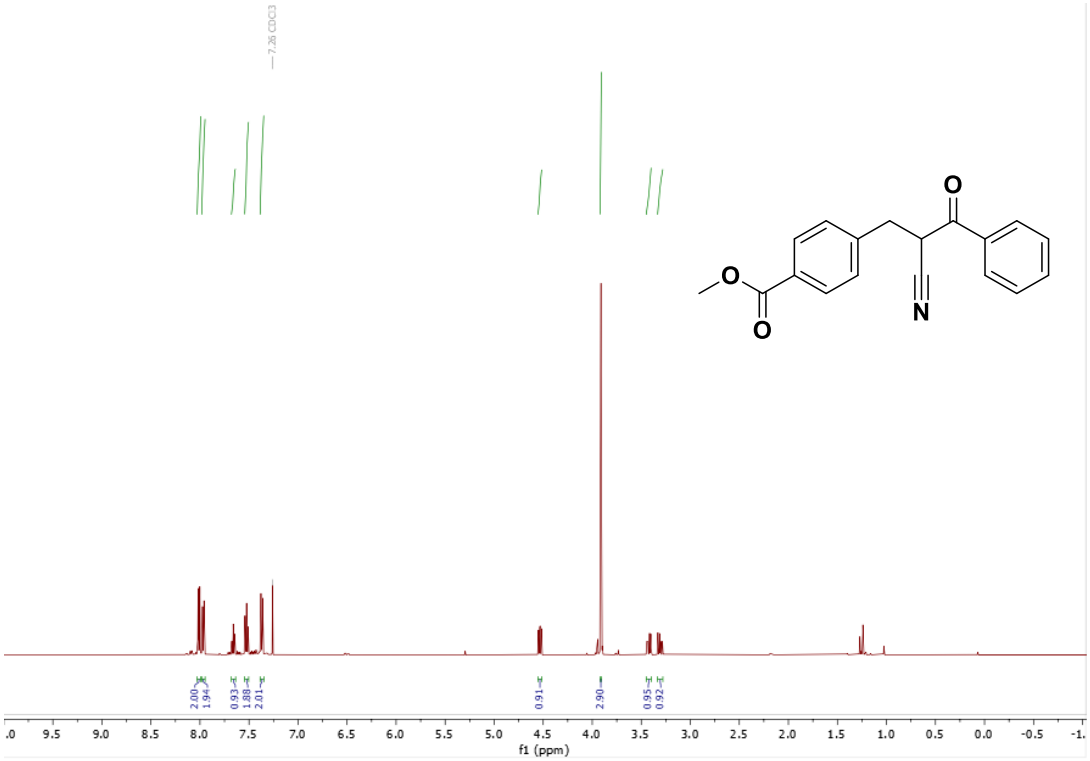


^{13}C NMR (126 MHz, $CDCl_3$)

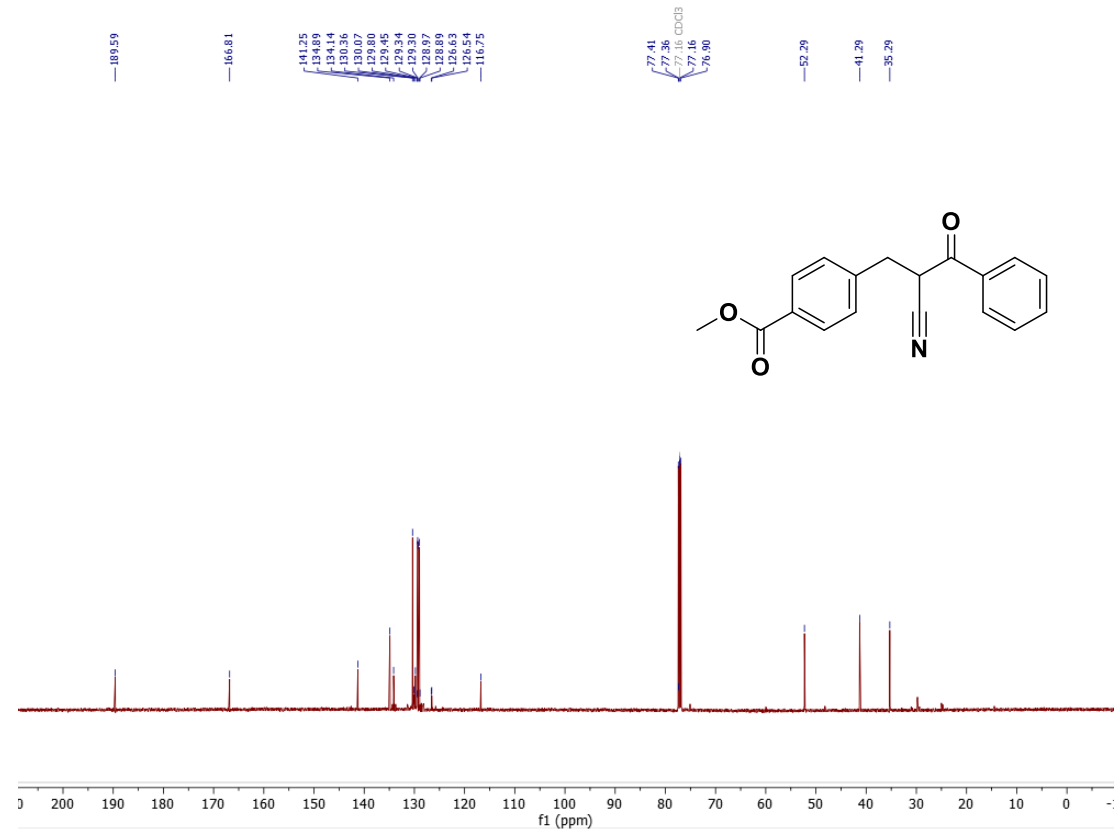


(*E*)-Methyl 4-(2-cyano-3-phenylpropanoyl)benzoate **(3d)**

^{1}H NMR (500 MHz, $CDCl_3$)

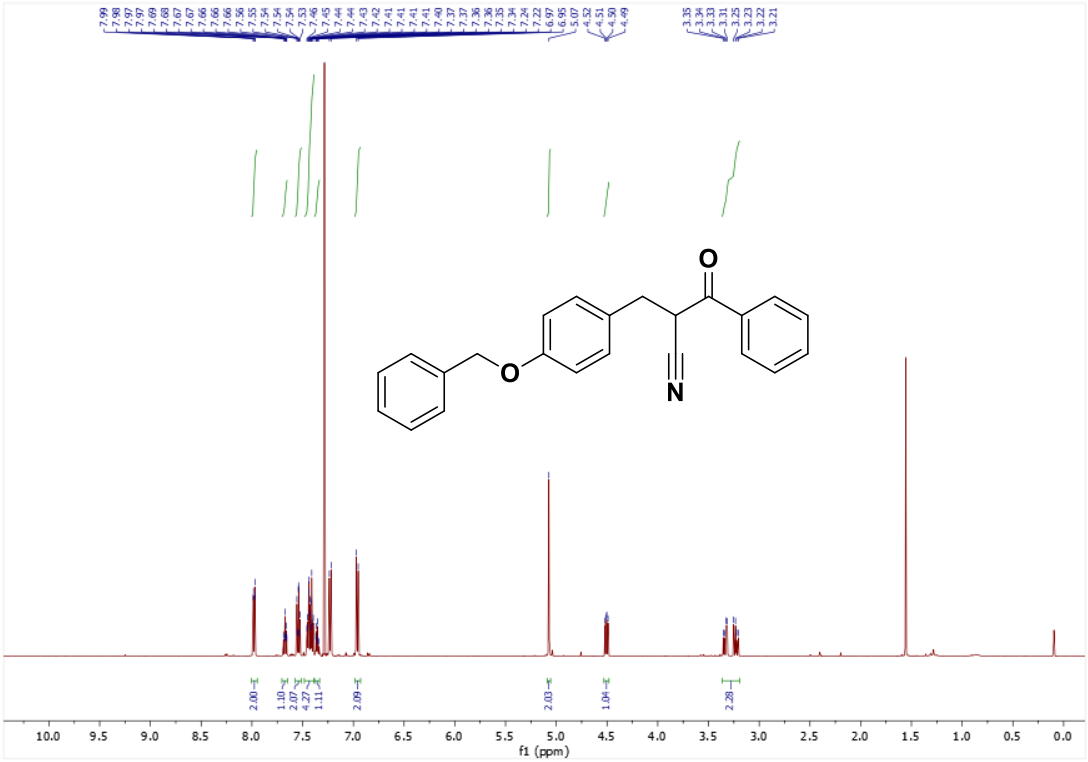


^{13}C NMR (126 MHz, $CDCl_3$)

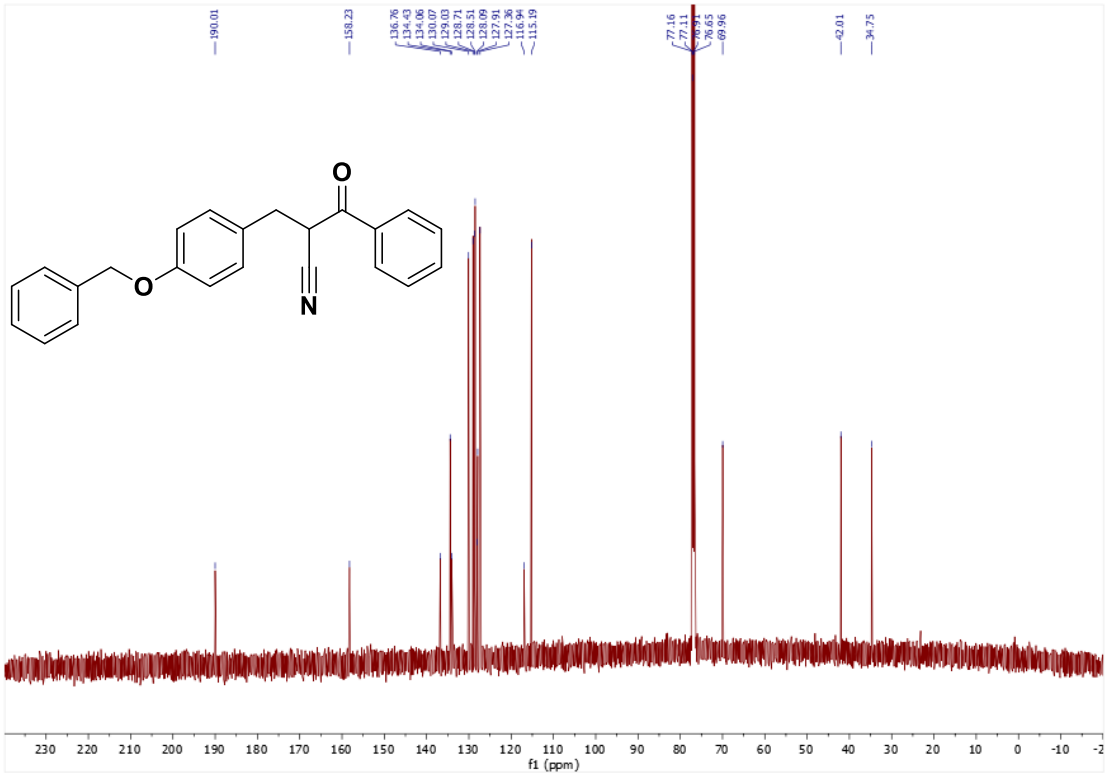


2-(4-Benzoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile, **3e**

^{1}H NMR (500 MHz, $CDCl_3$)

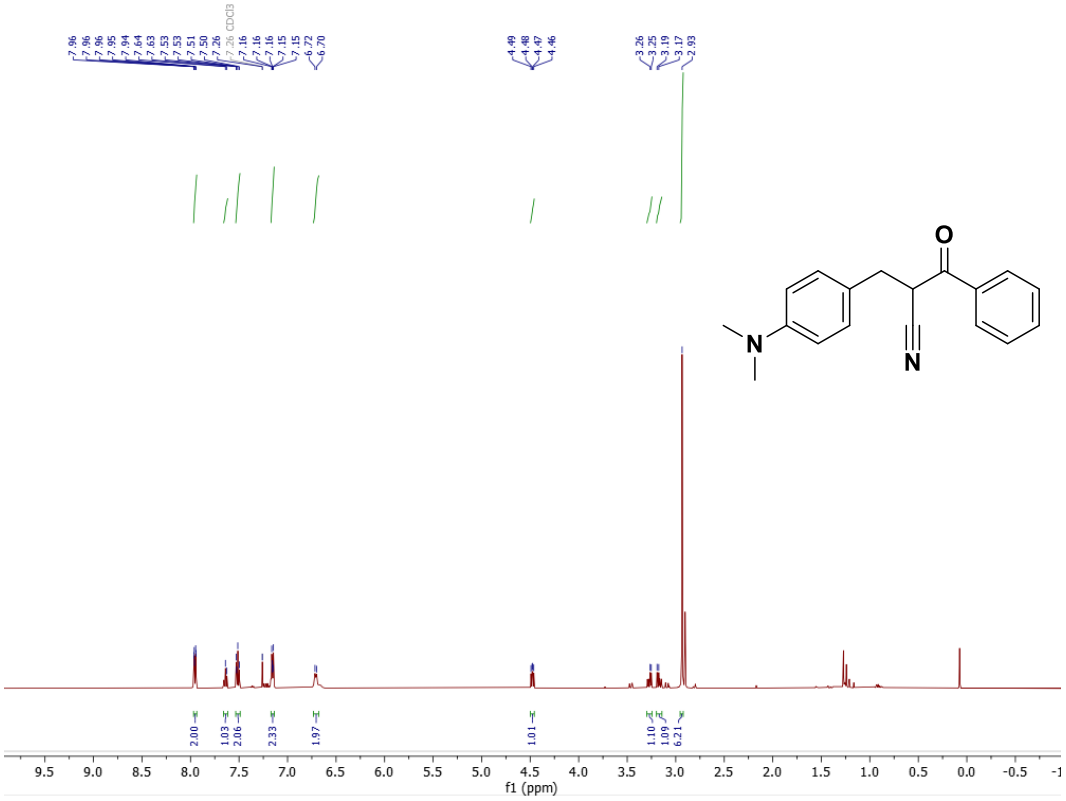


^{13}C NMR (126 MHz, $CDCl_3$)

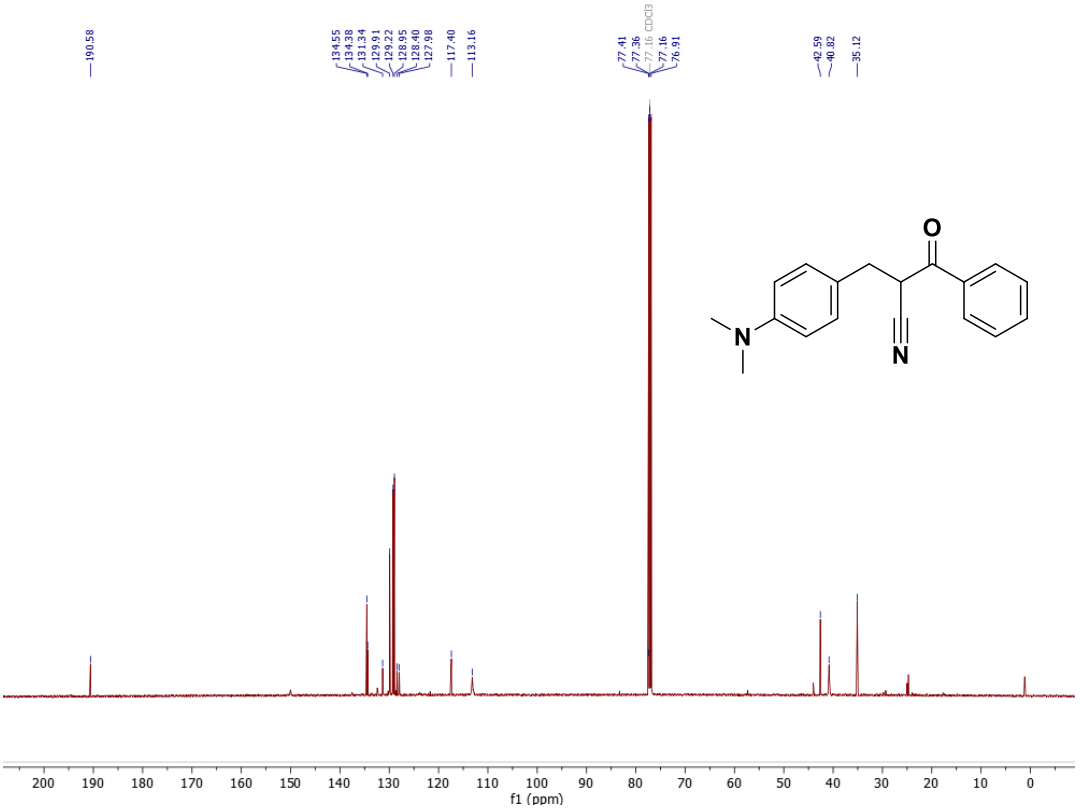


2-(4-Dimethylaminophenylmethyl)-3-oxo-3-phenylpropanenitrile **(3f)**

^{1}H NMR (500 MHz, $CDCl_3$)

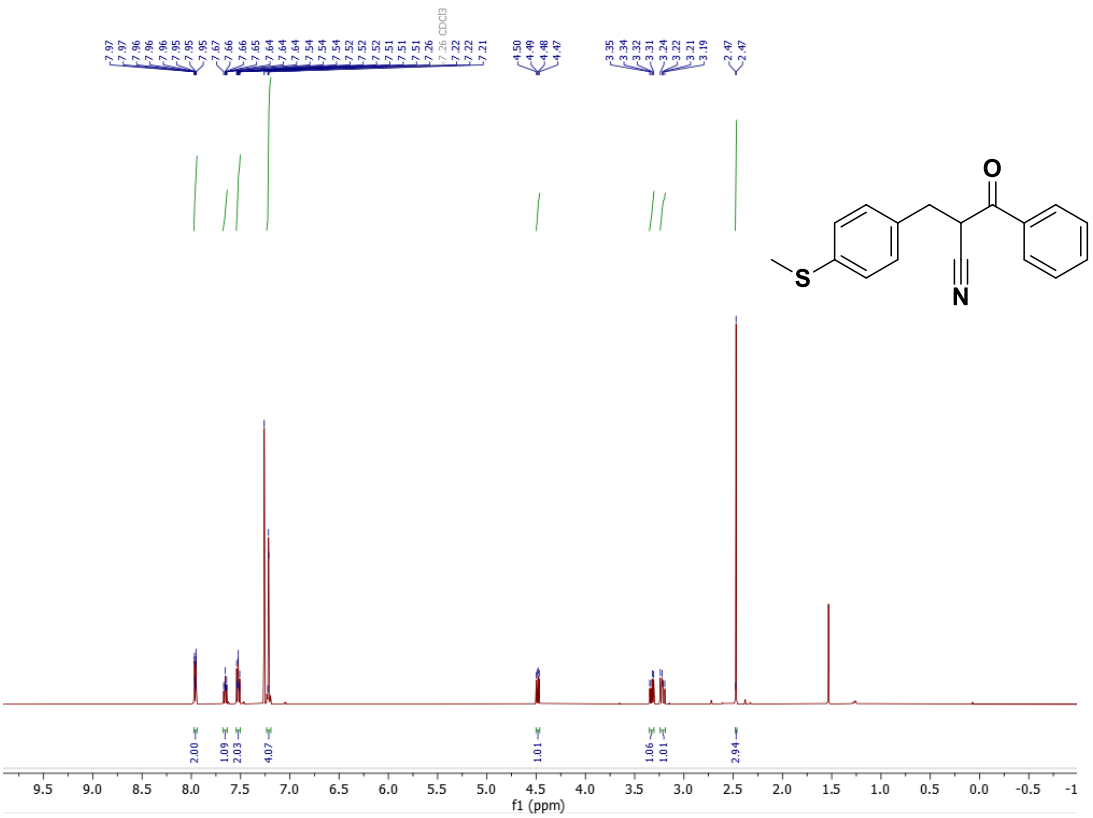


^{13}C NMR (126 MHz, $CDCl_3$)

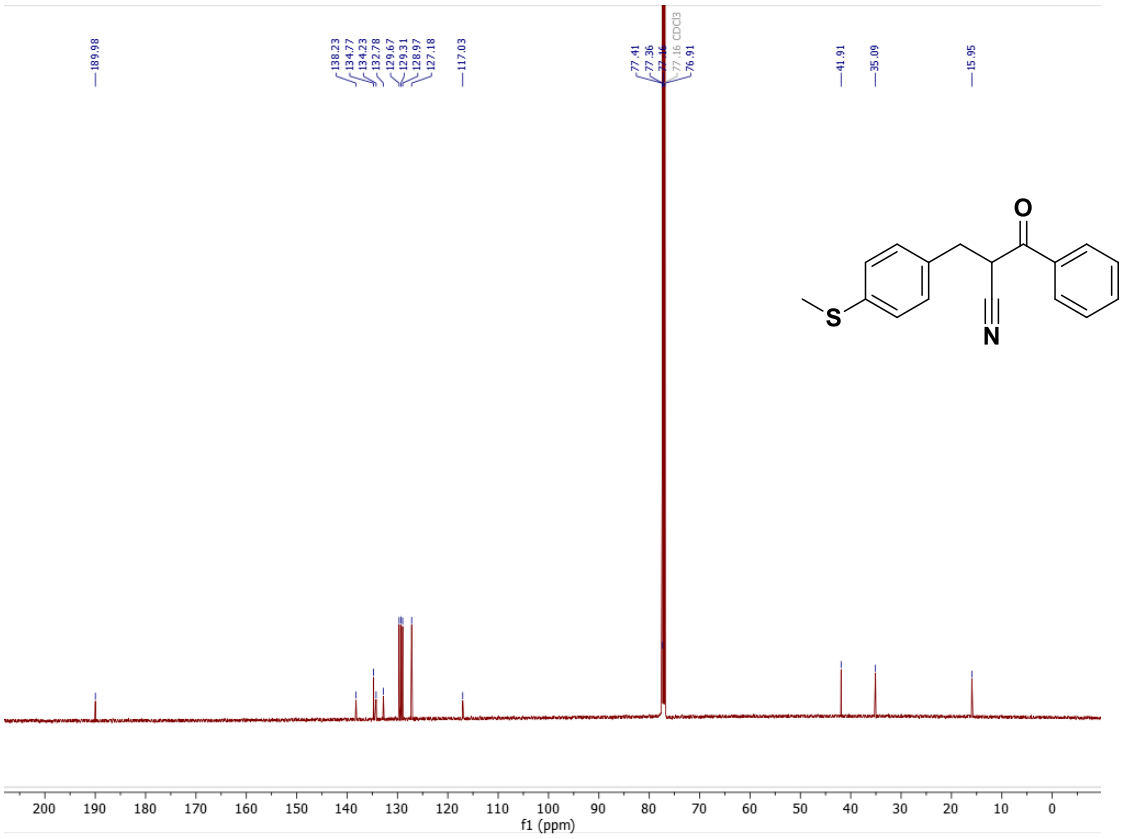


2-(4-Methylthiophenylmethyl)-3-oxo-3-phenylpropanenitrile **(3g)**

^{1}H NMR (500 MHz, $CDCl_3$)

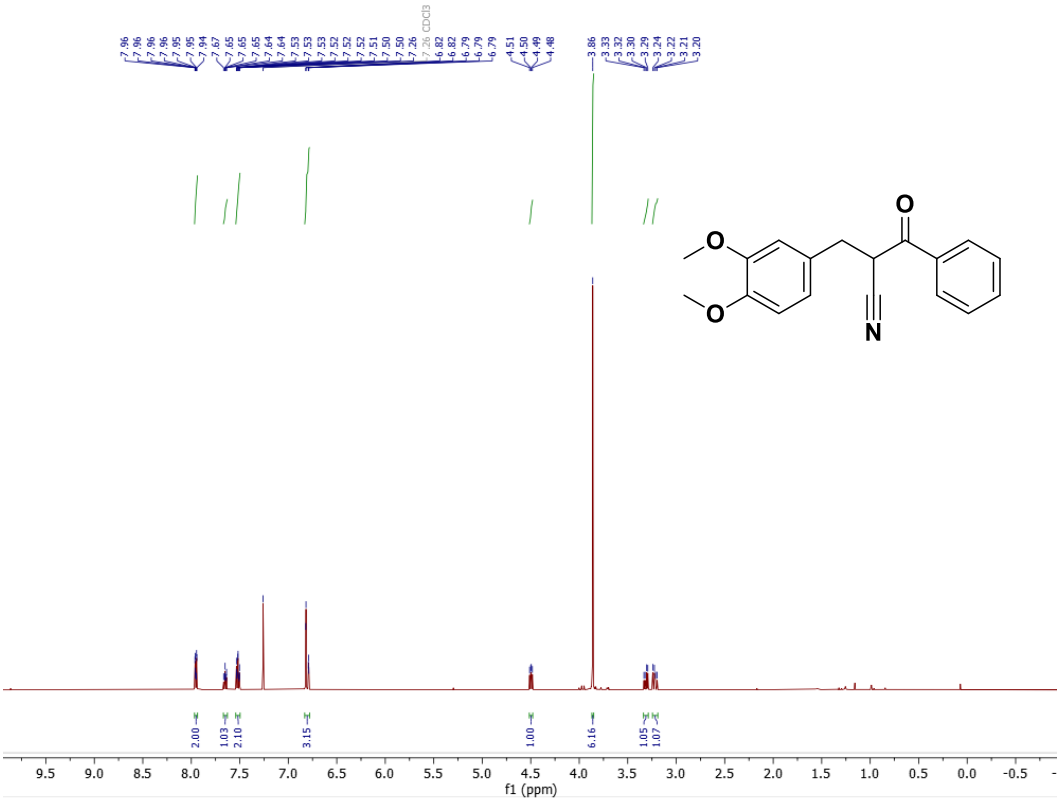


^{13}C NMR (126 MHz, $CDCl_3$)

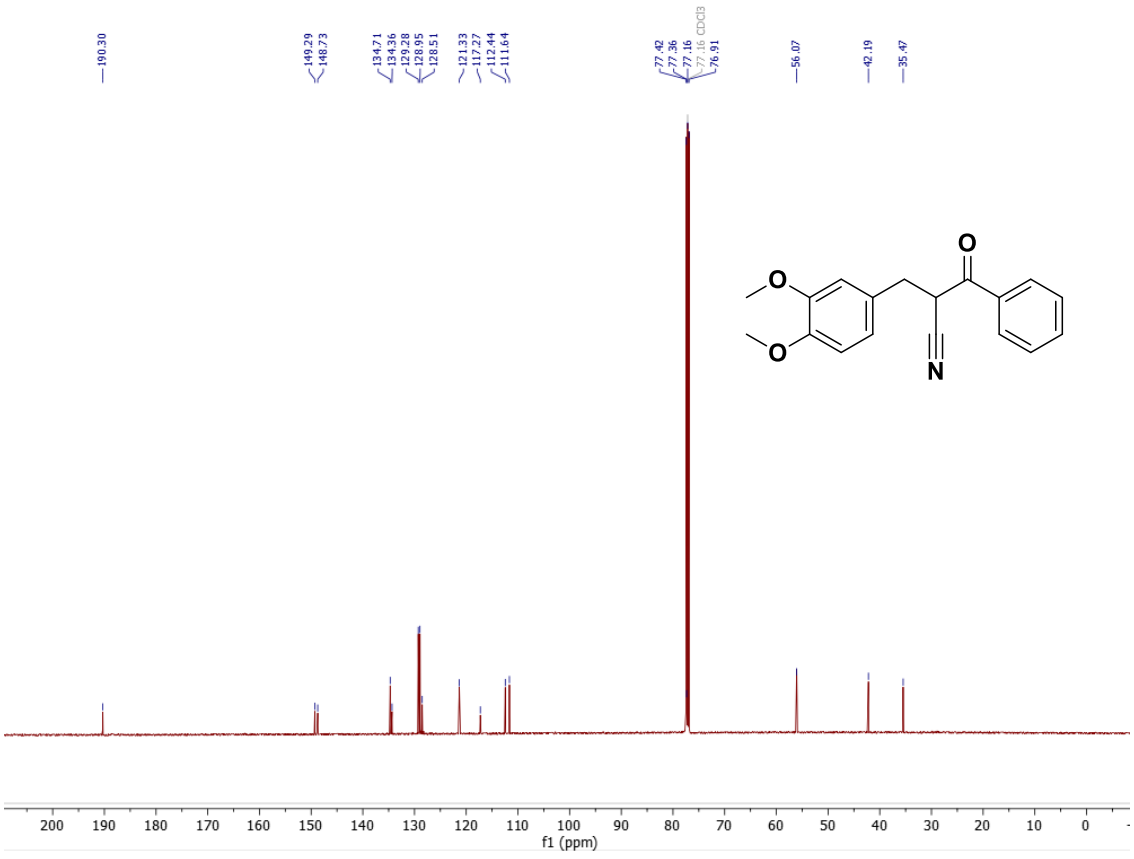


2-(3,4-Dimethoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile **(3h)**

^{1}H NMR (500 MHz, $CDCl_3$)

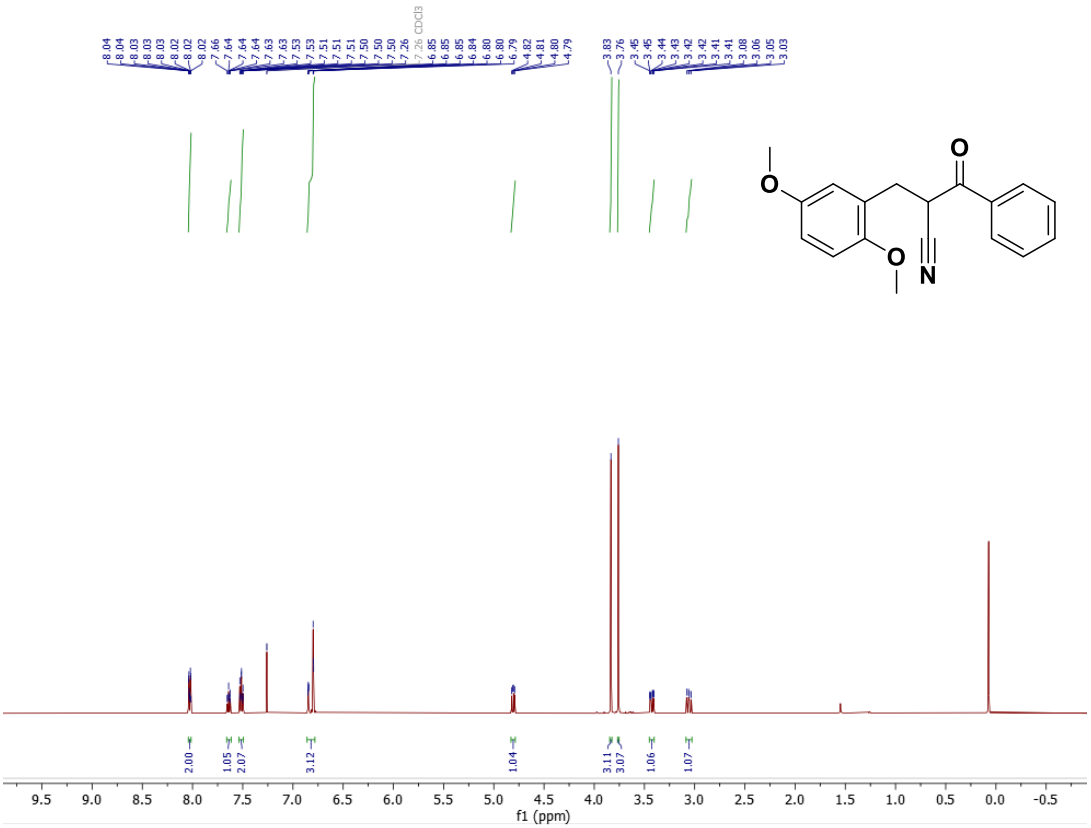


^{13}C NMR (126 MHz, $CDCl_3$)

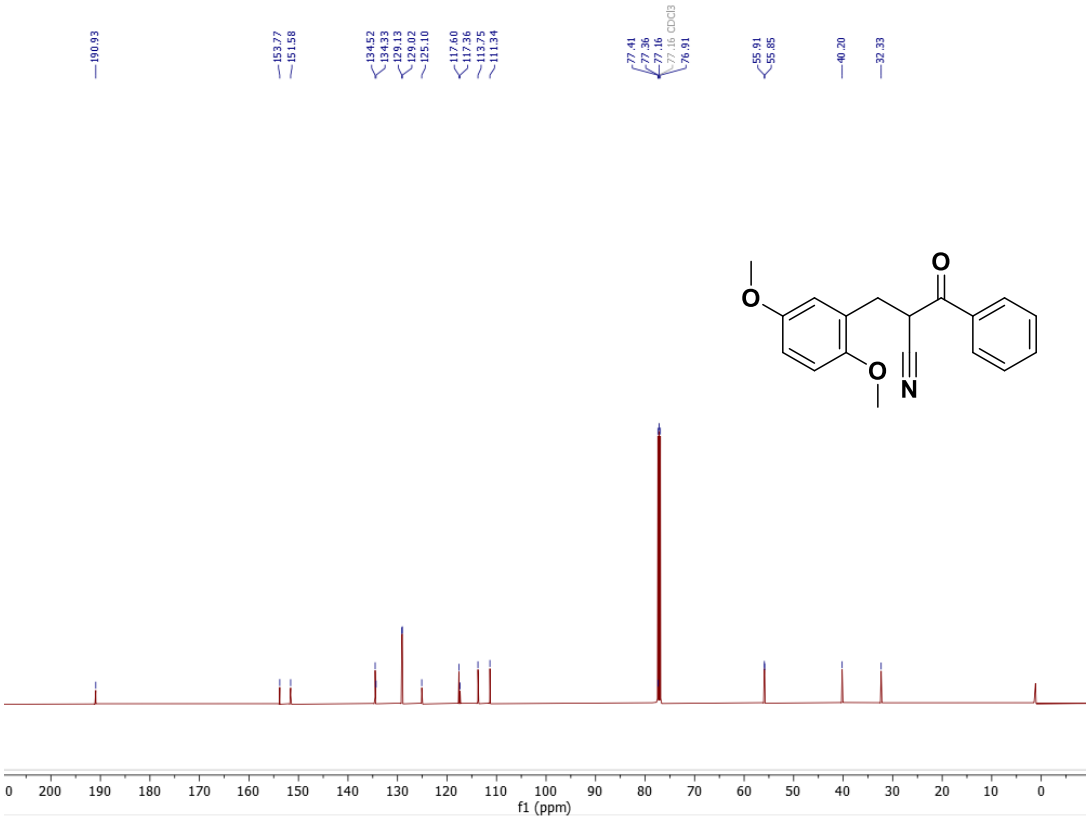


2-(2,5-Dimethoxyphenylmethyl)-3-oxo-3-phenylpropanenitrile **(3i)**

^{1}H NMR (500 MHz, $CDCl_3$)

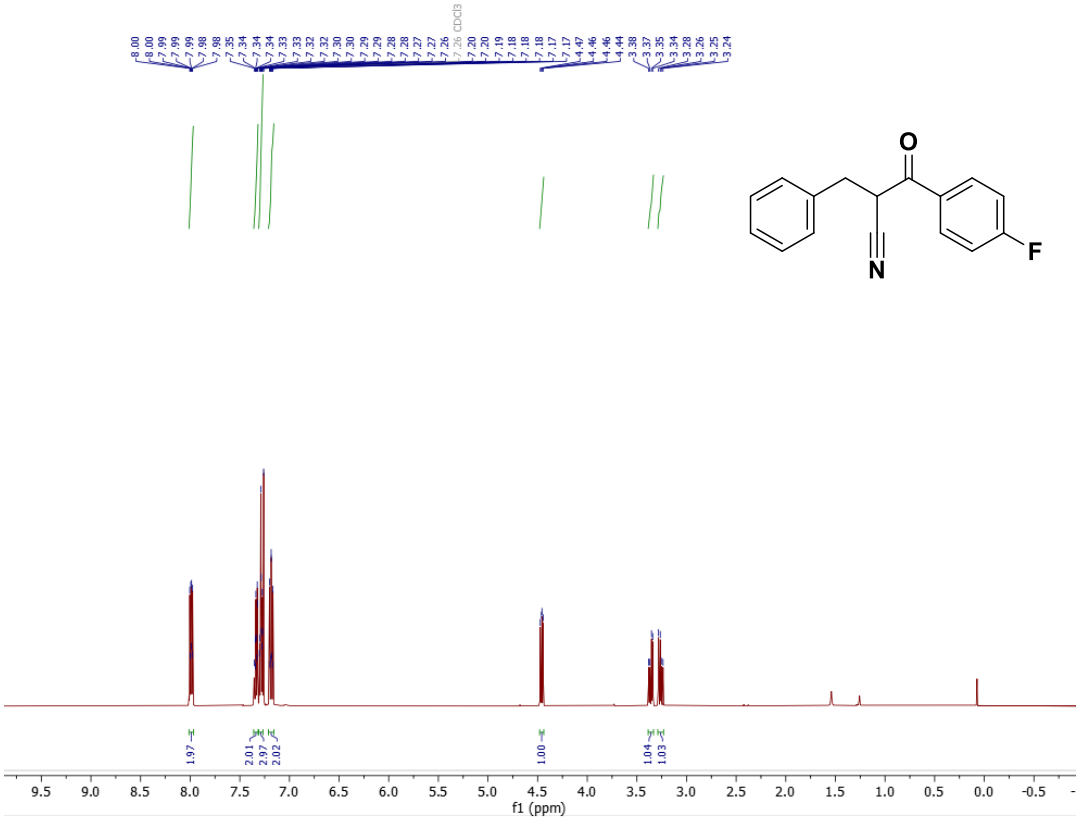


^{13}C NMR (126 MHz, $CDCl_3$)

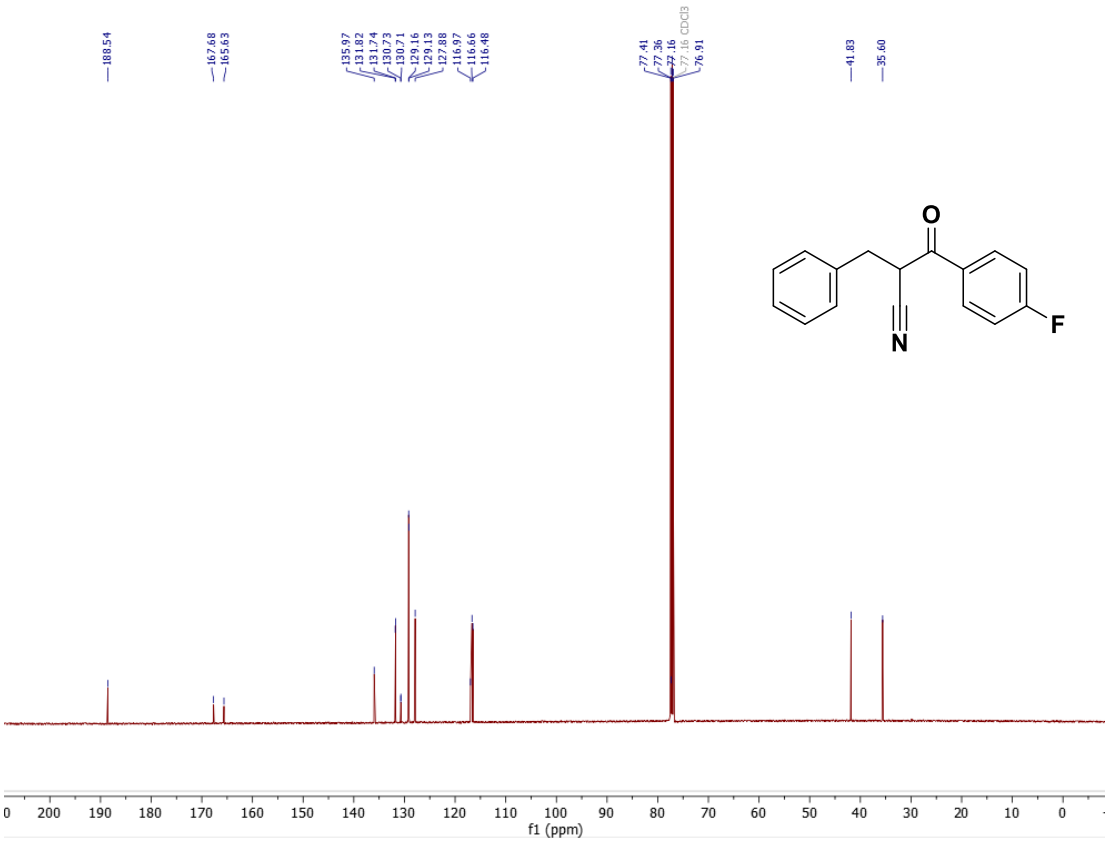


2-Benzyl-3-(4-fluorophenyl)-3-oxopropanenitrile (**3j**)

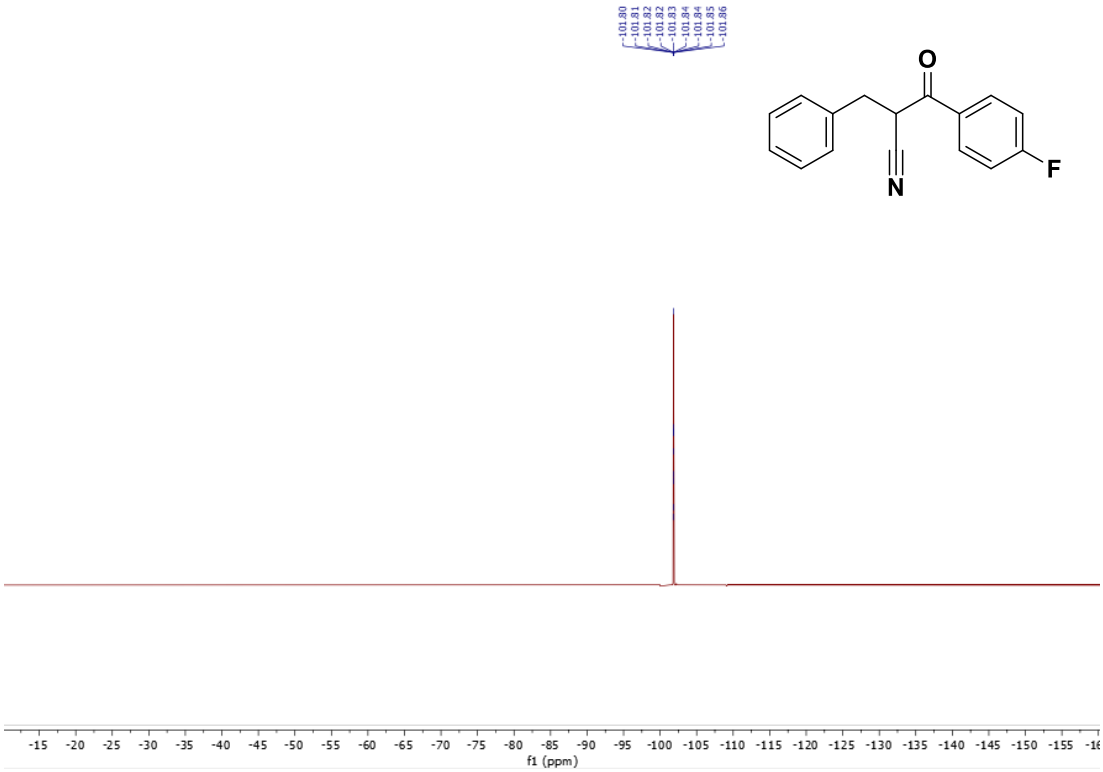
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

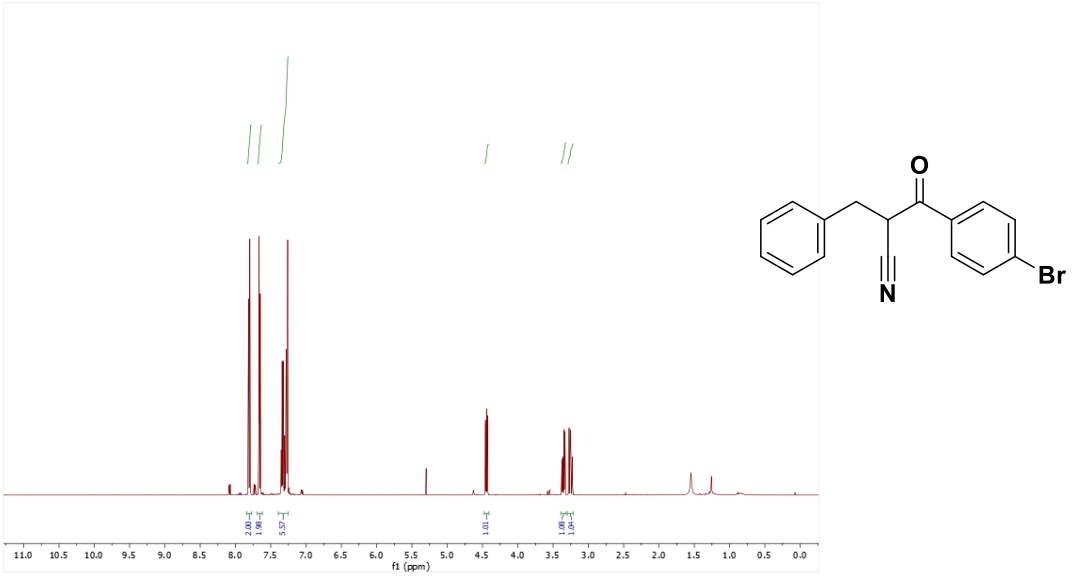


^{19}F NMR (470 MHz, $CDCl_3$)

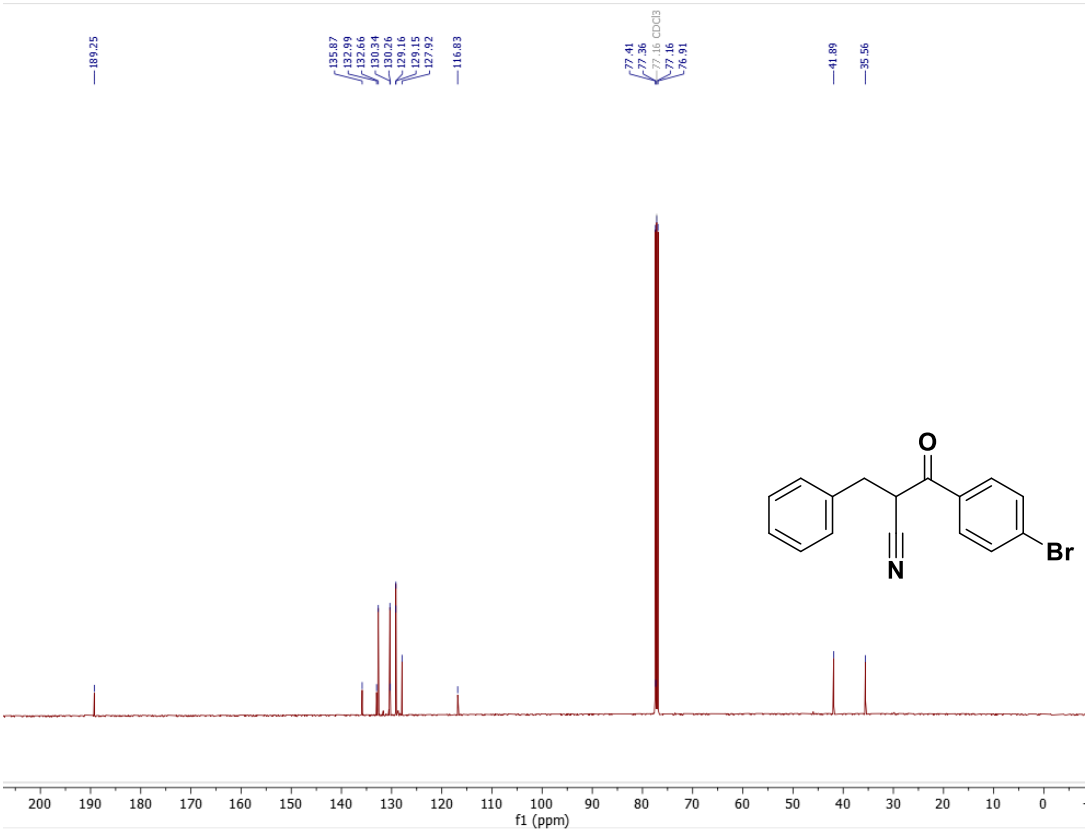


2-Benzyl-3-(4-bromophenyl)-3-oxopropanenitrile (**3k**)

^{1}H NMR (500 MHz, $CDCl_3$)

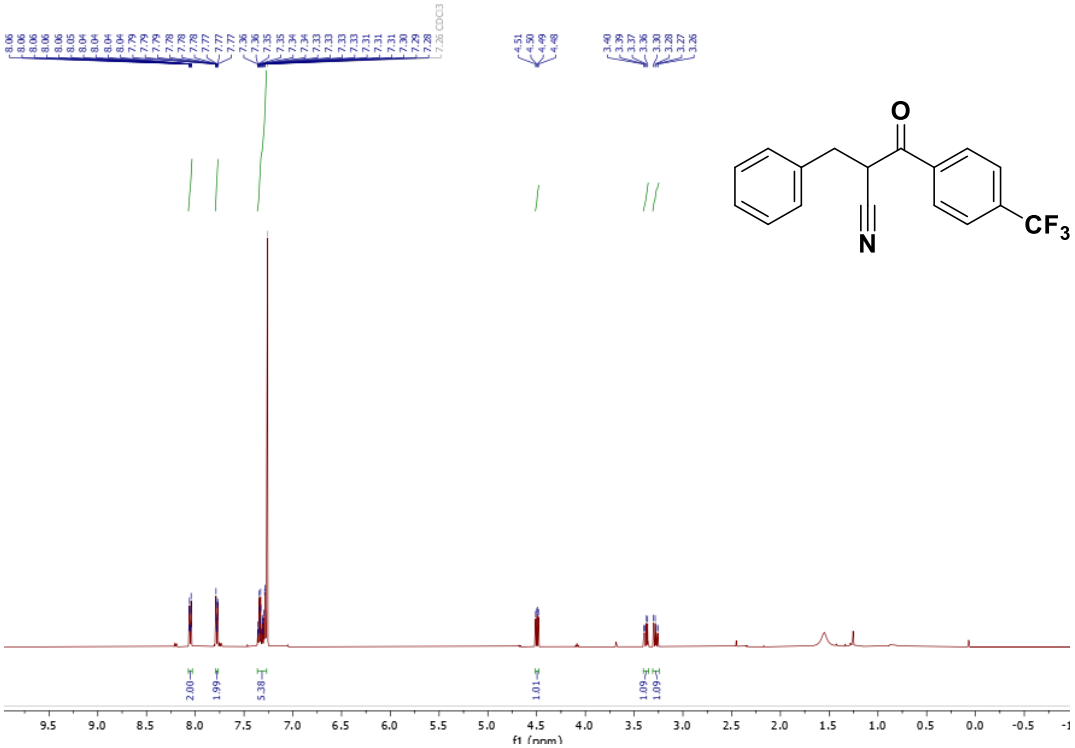


^{13}C NMR (126 MHz, $CDCl_3$)

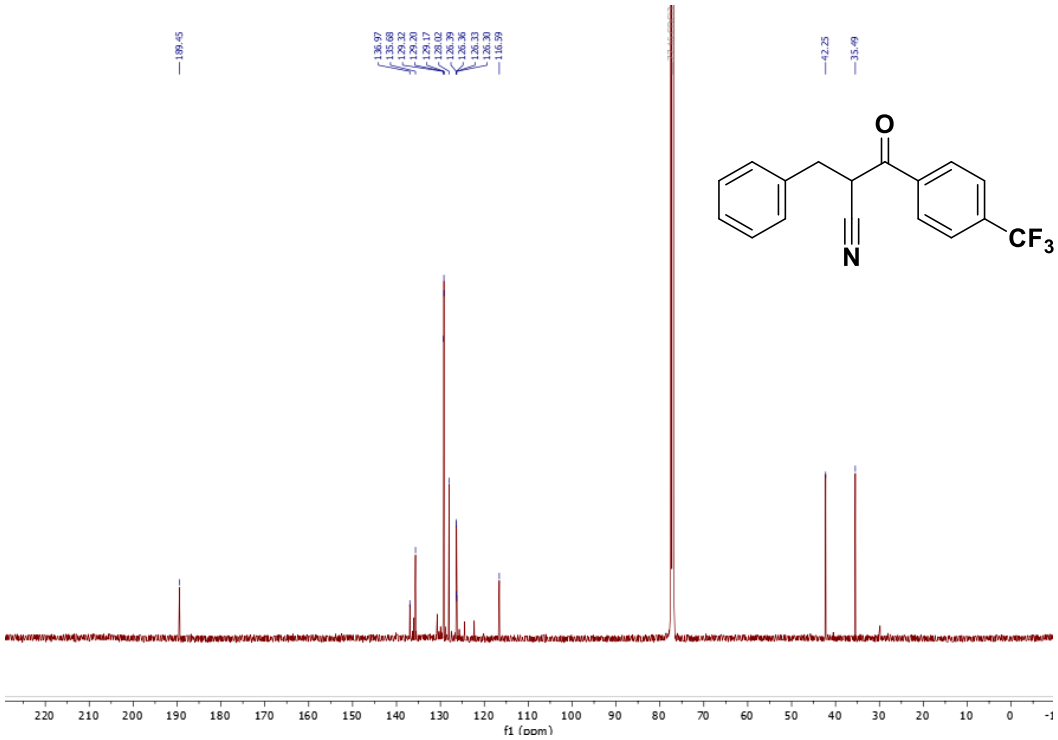


2-Benzyl-3-oxo-3-(4-(trifluoromethyl)phenyl)propanenitrile (**3l**)

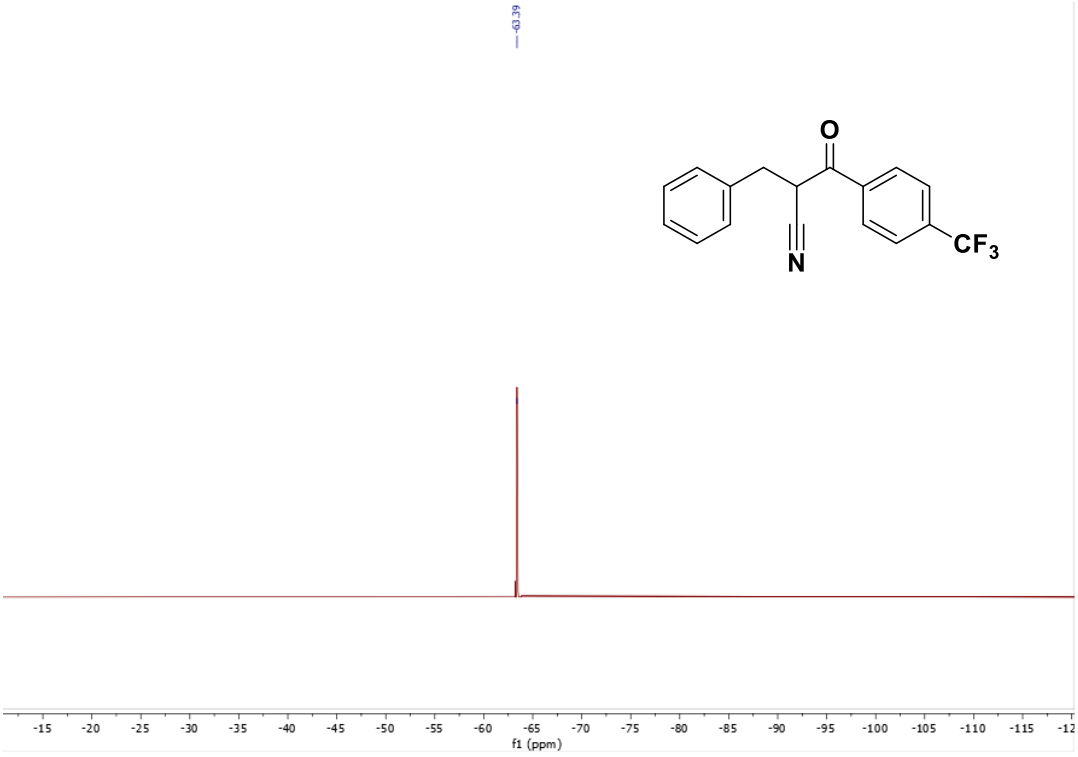
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

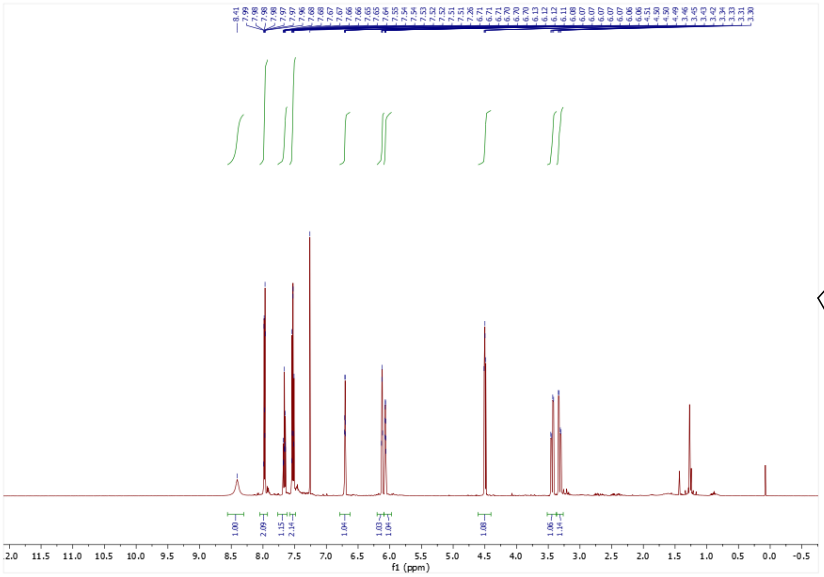


^{19}F NMR (470 MHz, $CDCl_3$)



2-(2-Pyrrolmethyl)-3-oxo-3-phenylpropanenitrile **(3m)**

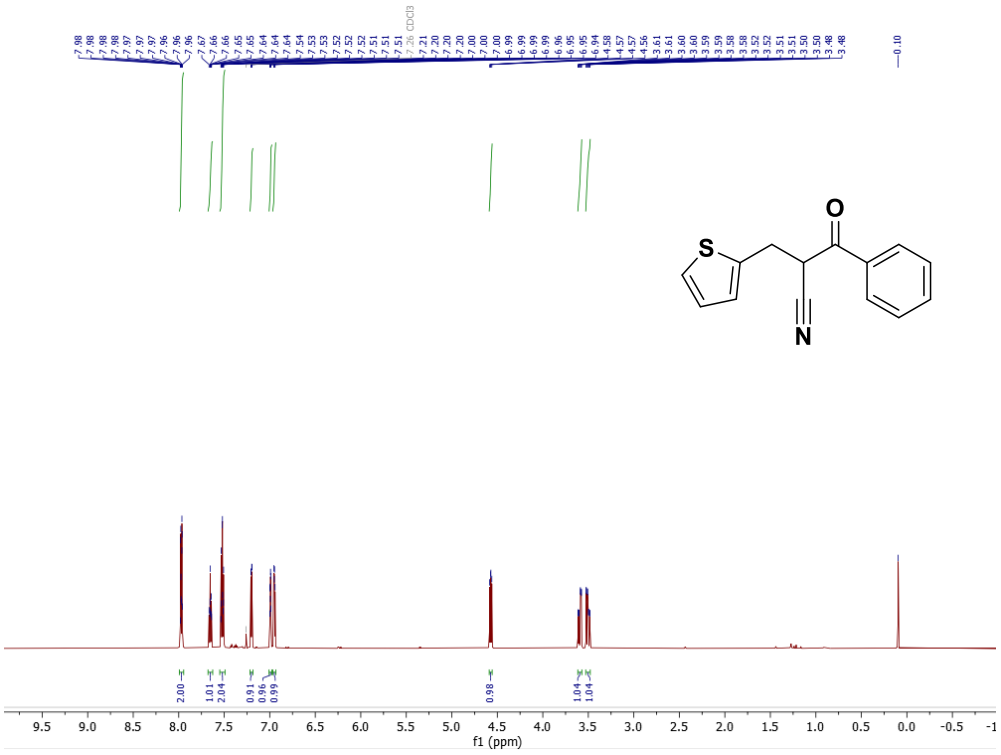
^{1}H NMR (500 MHz, $CDCl_3$)



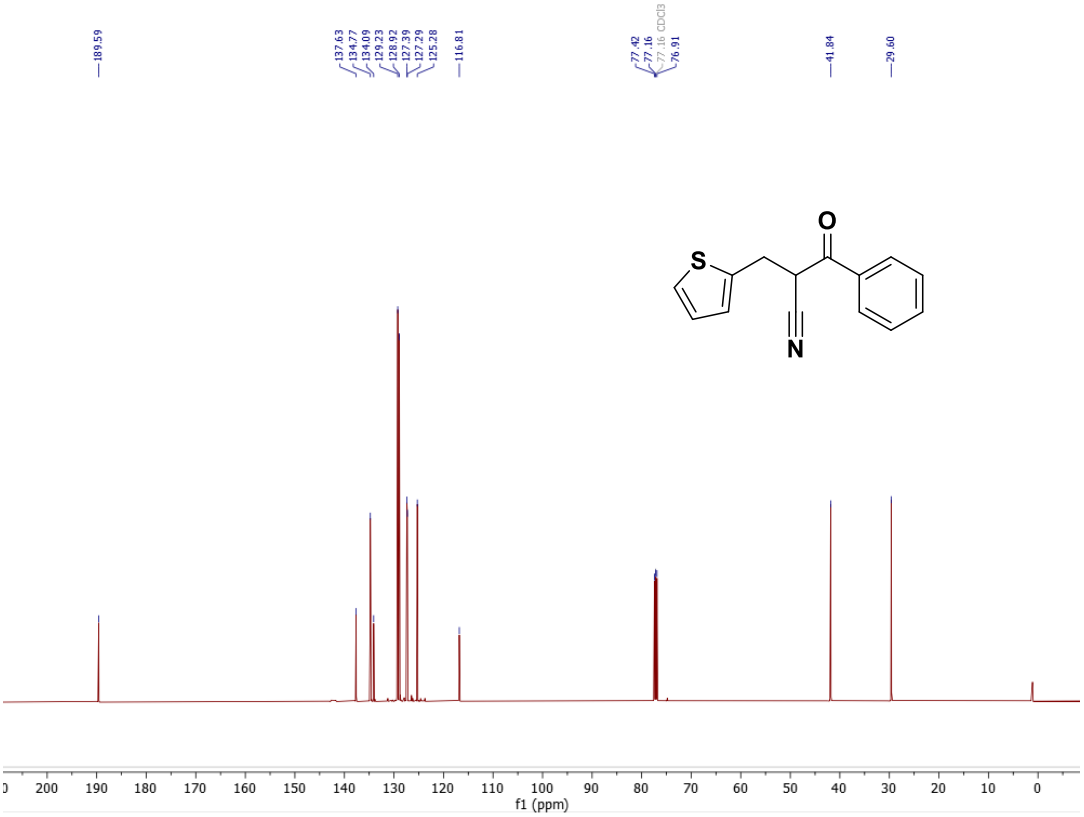
^{13}C NMR (126 MHz, $CDCl_3$)

2-(2-Thienylmethyl)-3-oxo-3-phenylpropanenitrile (**3n**)

^{1}H NMR (500 MHz, $CDCl_3$)

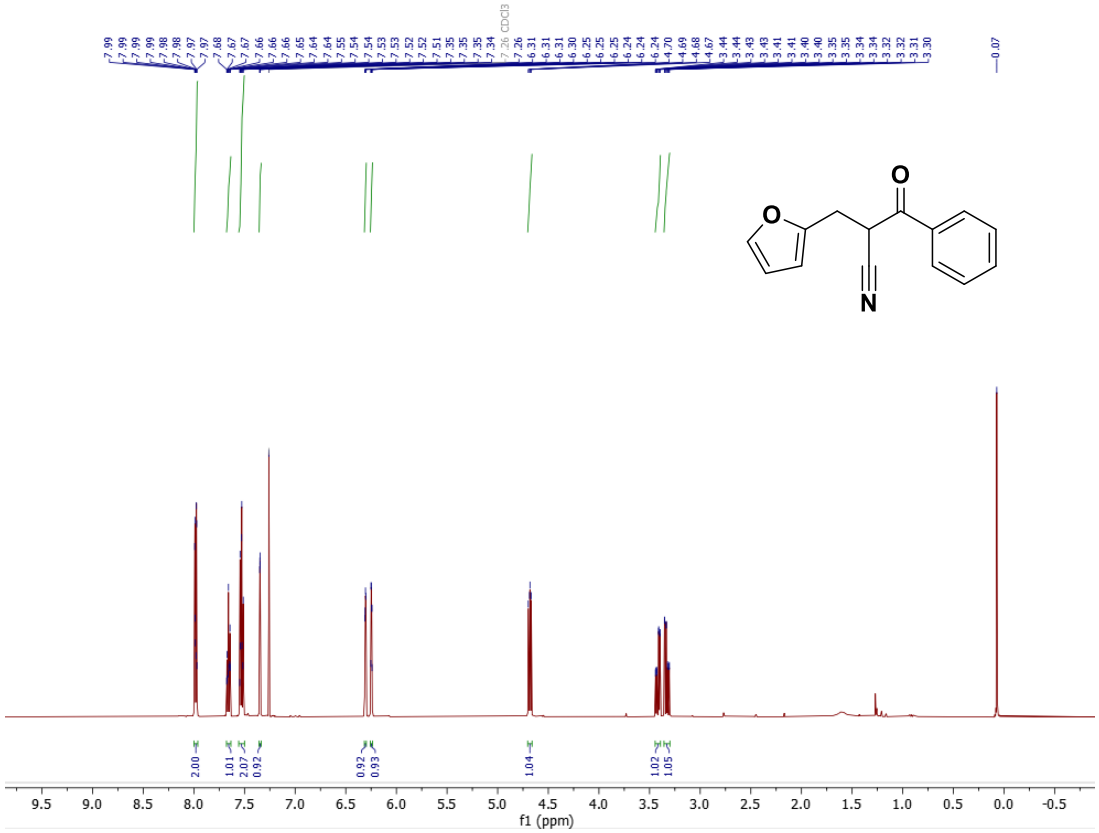


^{13}C NMR (126 MHz, $CDCl_3$)

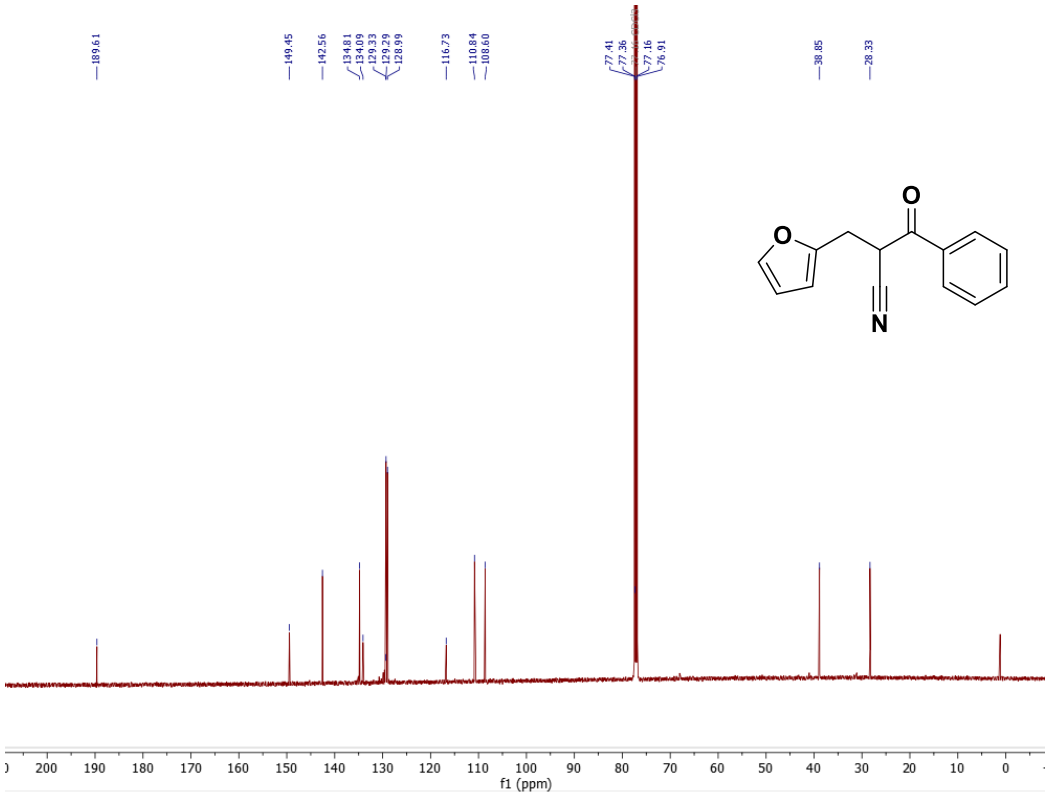


2-(2-Furylmethyl)-3-oxo-3-phenylpropanenitrile (**3o**)

^{1}H NMR (500 MHz, $CDCl_3$)

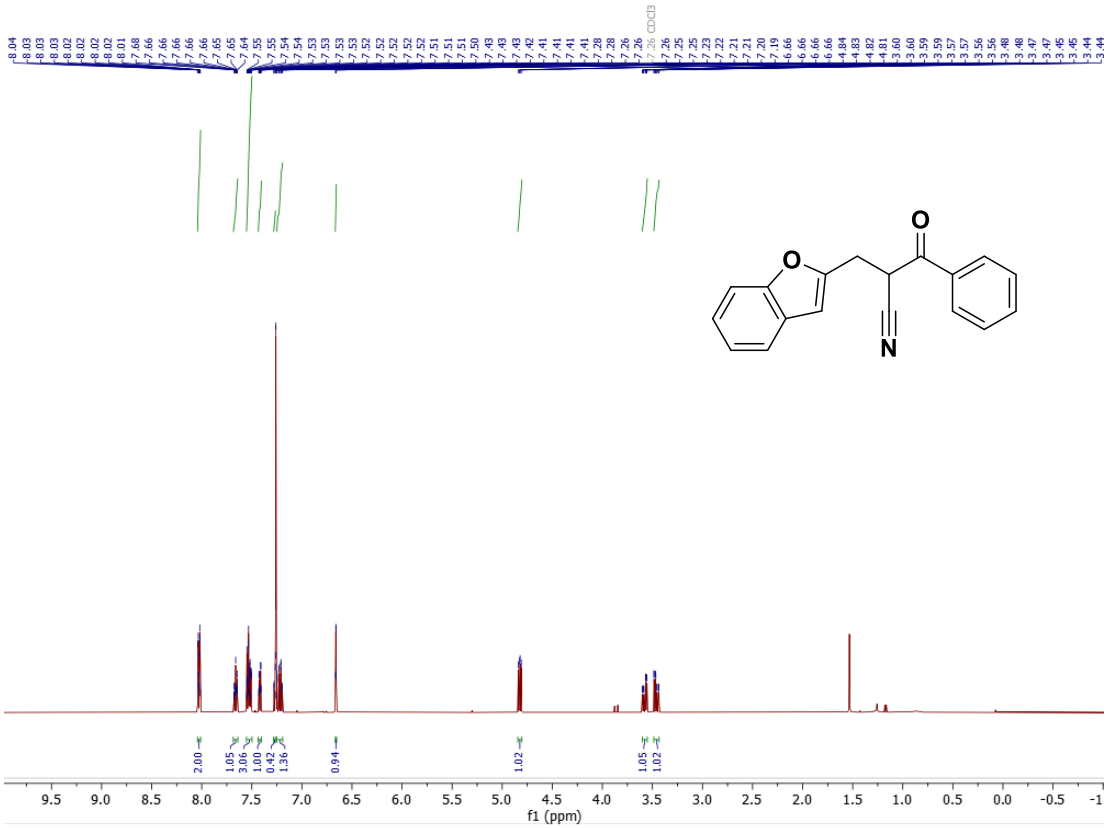


^{13}C NMR (126 MHz, $CDCl_3$)

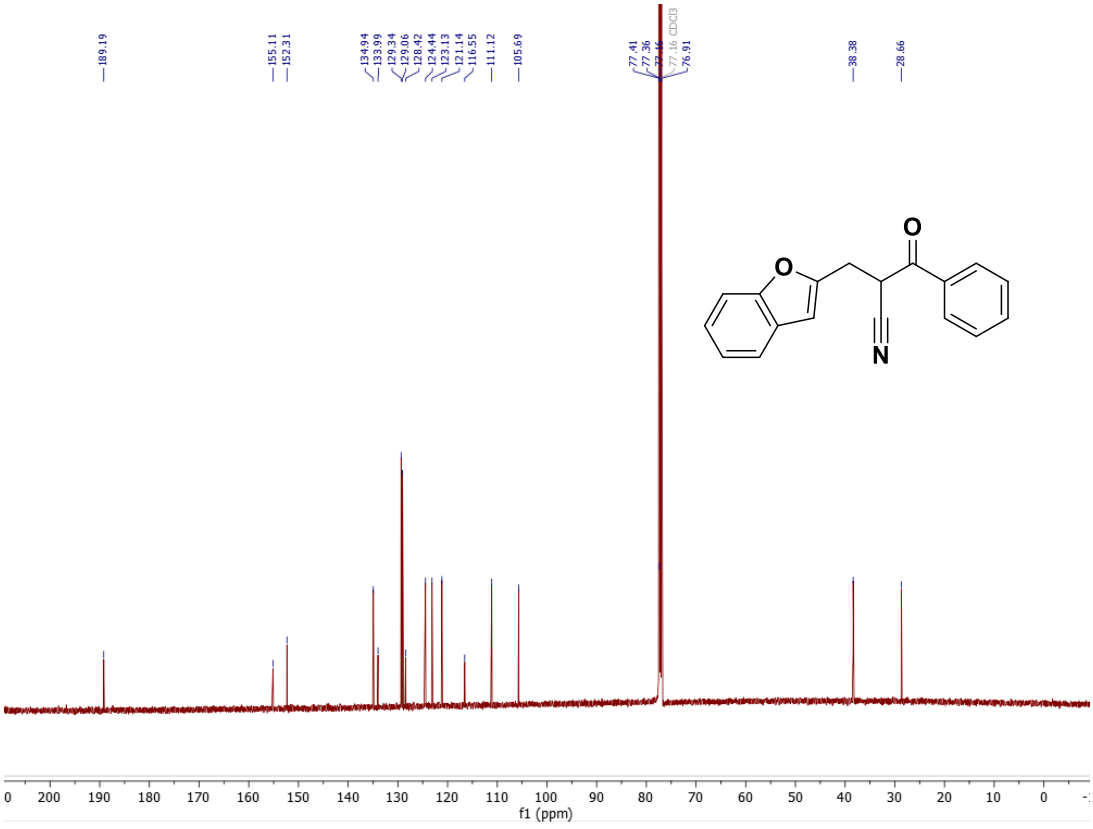


2-(Benzofuran-2-ylmethyl)-3-phenyl-3-oxopropanenitrile **(3p)**

^{1}H NMR (500 MHz, $CDCl_3$)

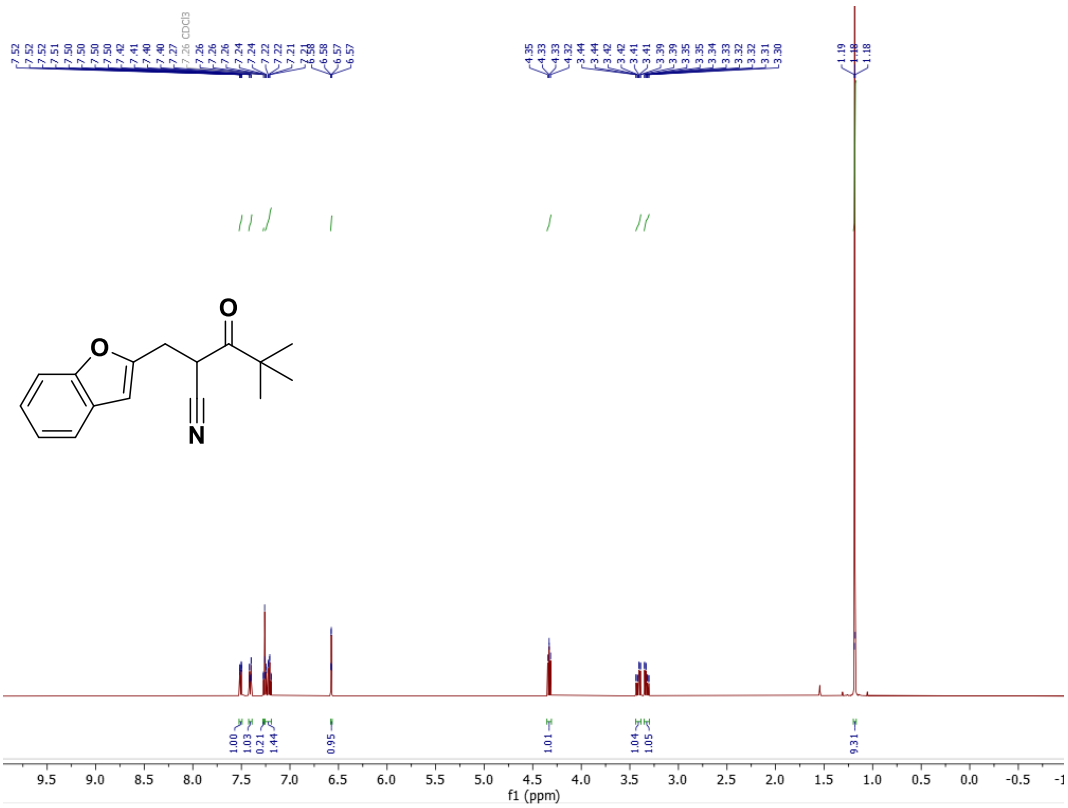


^{13}C NMR (126 MHz, $CDCl_3$)

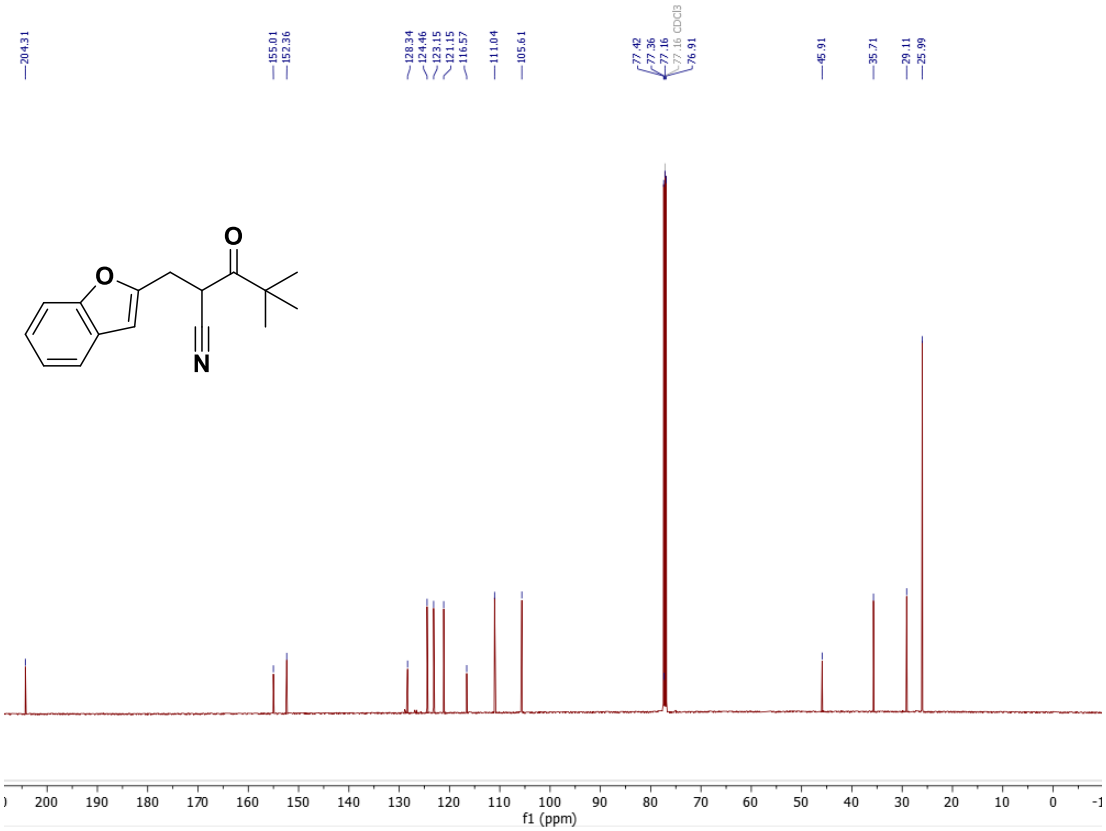


2-(Benzofuran-2-ylmethyl)-4,4-dimethyl -3-oxopentanenitrile **(3q)**

^{1}H NMR (500 MHz, $CDCl_3$)

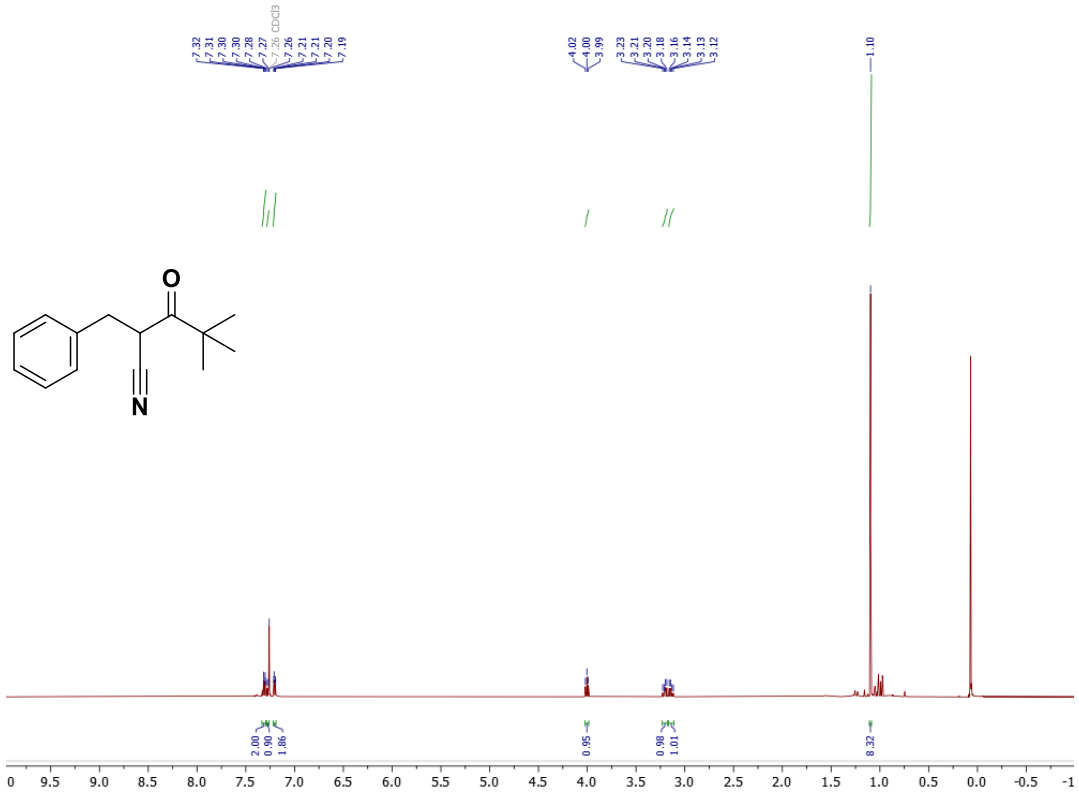


^{13}C NMR (126 MHz, $CDCl_3$)

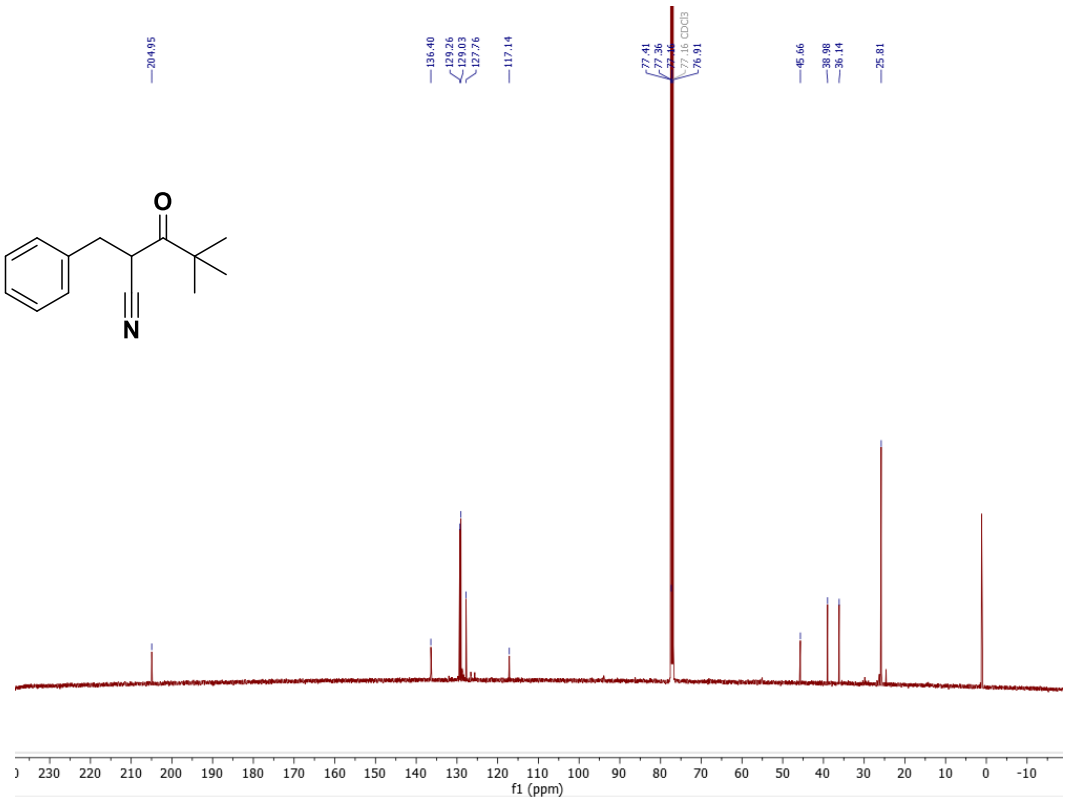


2-Benzyl-4,4-dimethyl-3-oxopentanenitrile **(3r)**

^{1}H NMR (500 MHz, $CDCl_3$)

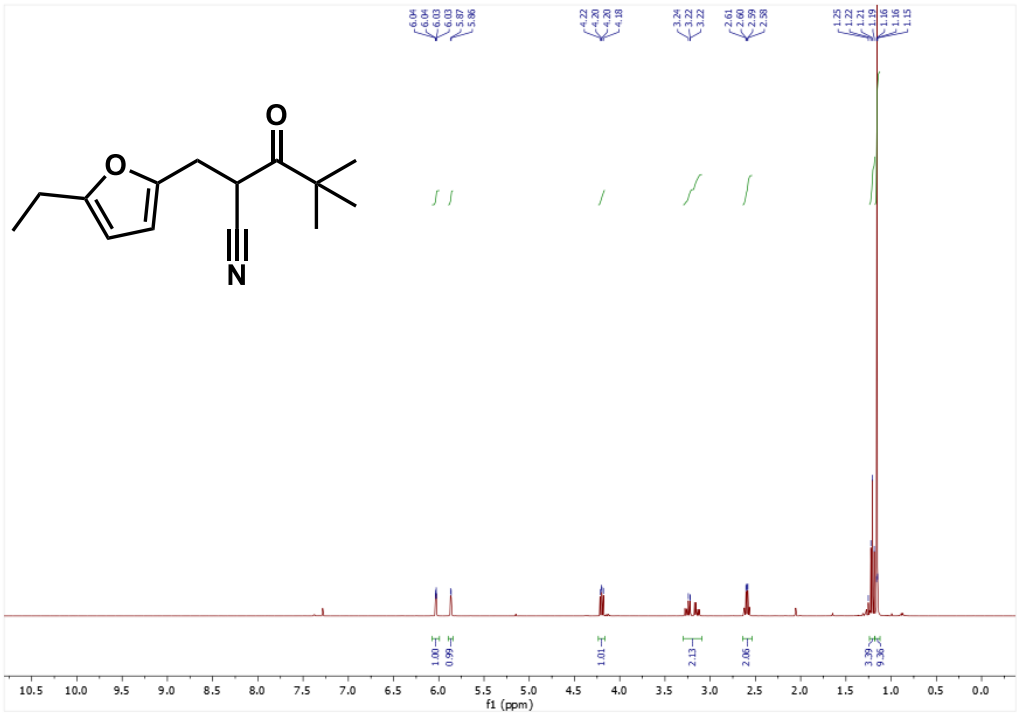


^{13}C NMR (126 MHz, $CDCl_3$)

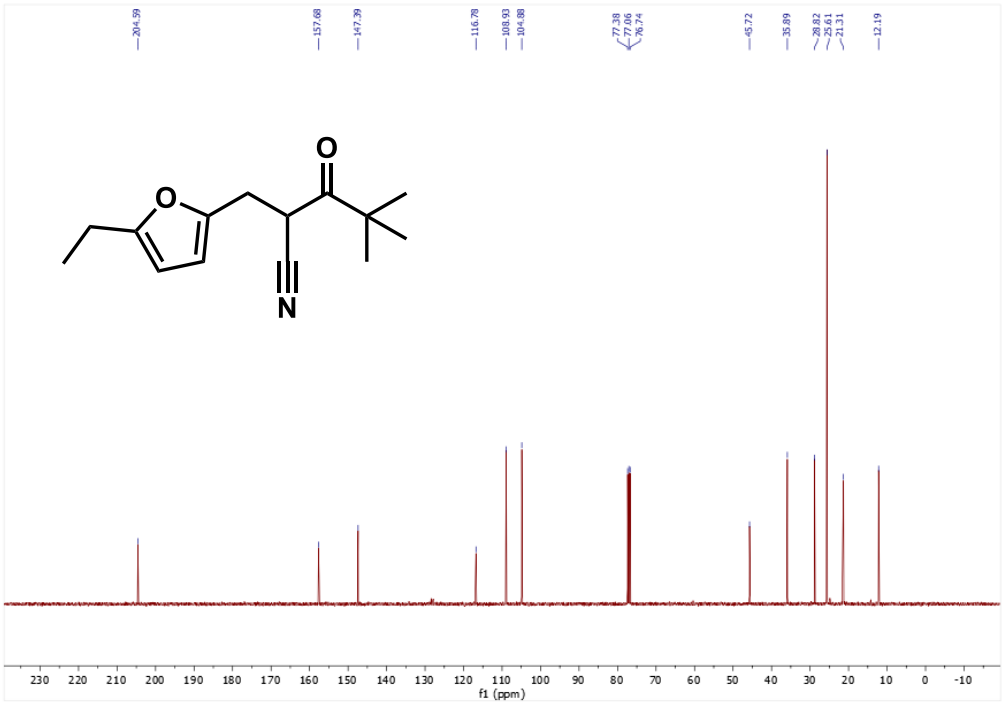


2-(2-(5-Ethylfuryl)methyl)-4,4-dimethyl-3-oxopentanenitrile, **3s**

^{1}H NMR (400 MHz, $CDCl_3$)

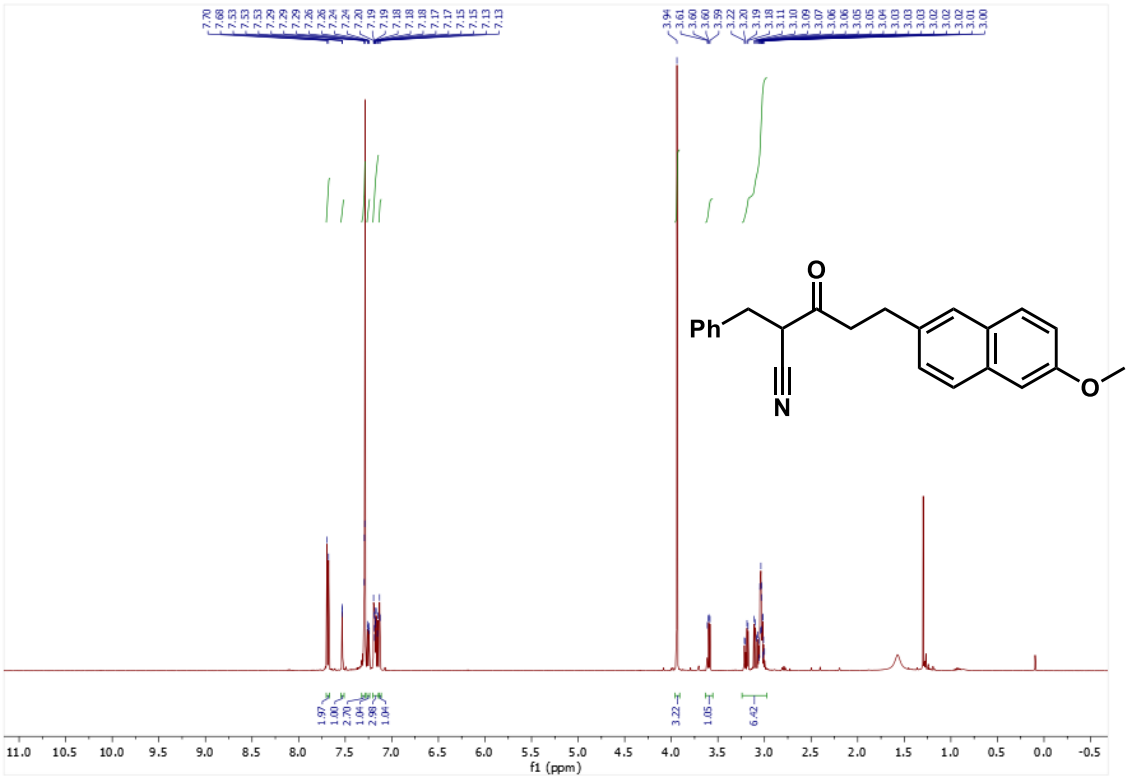


^{13}C NMR (101 MHz, $CDCl_3$)



2-Benzyl-5-(2-methoxynapthyl)-3-oxopentanenitrile, **3t**

H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)