Supporting Information

Visible Light Uranyl Photocatalysis: Direct C-H to C-C Bond Conversion

Luca Capaldo, Daniele Merli, Maurizio Fagnoni, Davide Ravelli*

PhotoGreen Lab, Department of Chemistry, University of Pavia

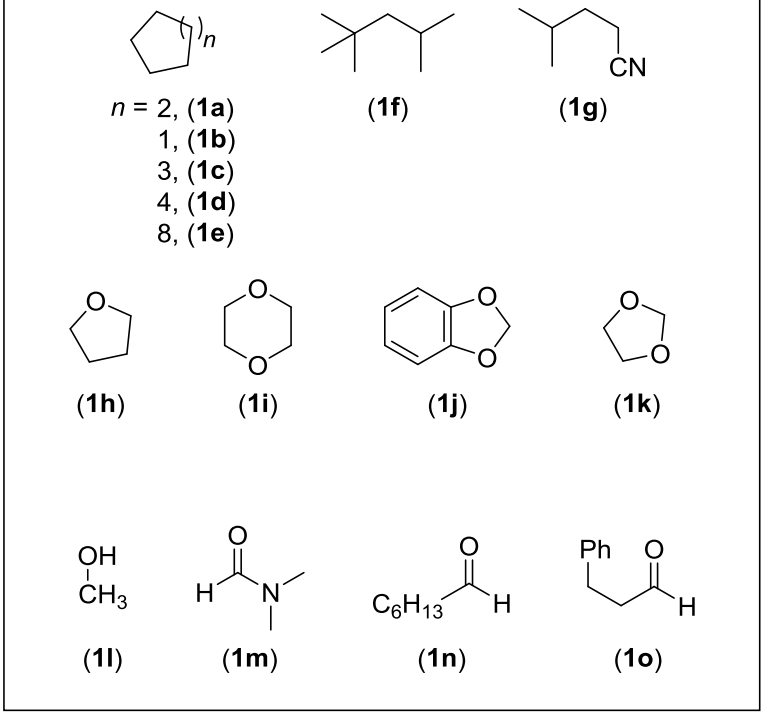
Viale Taramelli 12, 27100 Pavia, Italy

Fax: +39 0382 987323; Tel: +39 0382 987198. E-mail: davide.ravelli@unipv.it

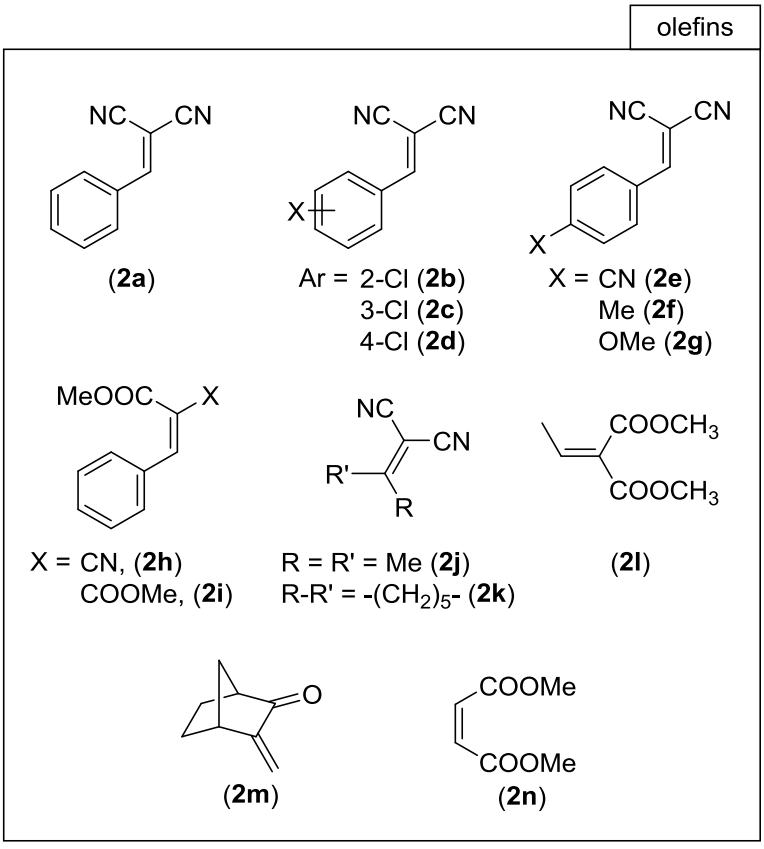
CONTENT (60 pages)

1. Starting materials chart

H-donors

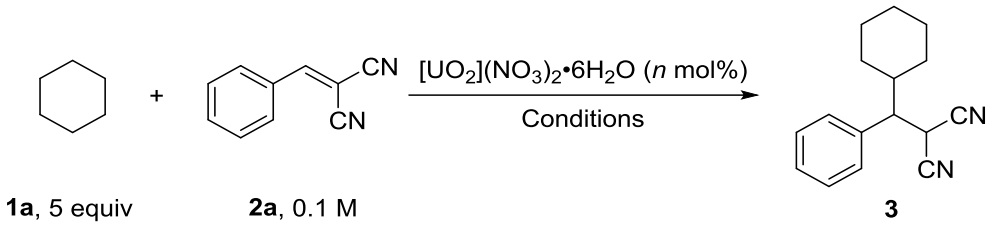


olefins



2. Optimization of reaction conditions

The optimization of reaction conditions was carried out on the photocatalyzed addition of cyclohexane **1a** onto 2-benzylidenemalononitrile **2a** to give 2-(cyclohexyl(phenyl)methyl)malononitrile (**3**) in 1 mL of the chosen solvent on a 0.1 mmol scale (see Scheme S1 and Tables S1-S3).



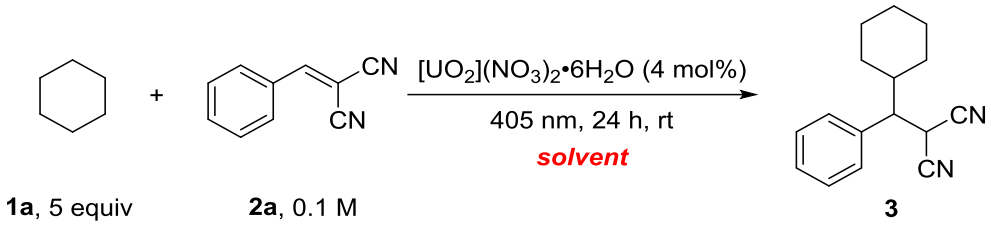
Scheme S1. Reaction studied for the optimization of conditions.

Reaction conditions: **2a** (0.1 M), **1a** (5 equiv, 0.5 M), uranyl nitrate hexahydrate $[UO_2](NO_3)_2 \cdot 6H_2O$ (*n* mol%) in 1 mL of the chosen solvent under air-equilibrated conditions. After irradiation, dodecane (1 μl/mL) was added as external standard and the mixture was filtered through a short SiO_2 plug to remove U-based species. The resulting solution was then analyzed via GC-FID analysis and yields were calculated by means of calibration curves with authentic samples.

The reaction was optimized in terms of solvent, catalyst loading, light source and irradiation time (see below).

Solvent optimization

Table S1. Solvent optimization.



1a, 5 equiv **2a**, 0.1 M **3**

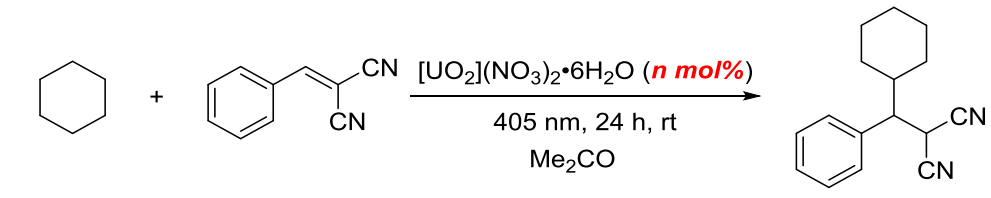
Entry	Solvent	Consumption of **2a** (%)	Yield of **3** (%)[a]
1	CH_2Cl_2	28	5
2	$CHCl_3$	46	3
3	$PhCF_3$	20	3
4	TFE	68	65
5	DMC	33	10
6	EtOAc	39	15
7	MeCN	40	36
8	MeCN/H_2O 9:1	46	37
9	DMSO	57	8
10	**Me_2CO**	**72**	**70**
11	Me_2CO/H_2O 9:1	45	44

[a] Absolute yields determined by means of calibration curves with authentic samples. TFE: 2,2,2-trifluoroethanol; DMC: dimethyl carbonate; EtOAc: ethyl acetate; DMSO: dimethyl sulfoxide.

Neat acetone was chosen as the best solvent.

Photocatalyst loading optimization

Table S2. Photocatalyst loading optimization.



1a, 5 equiv **2a**, 0.1 M **3**

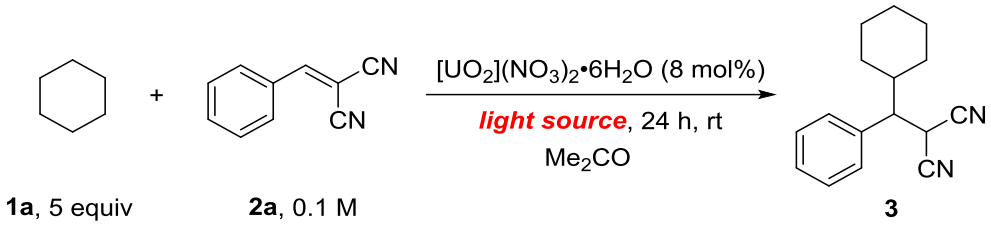
Entry	Loading (n mol%)	Consumption of **2a** (%)	Yield of **3** (%)[a]
1	1	27	26
2	2	36	36
3	4	72	70
4	4 [$UO_2(OAc)_2$•$2H_2O$]	-	n.d.
5	6	93	93
6	**8**	**100**	**95**

[a] Absolute yields determined by means of calibration curves with authentic samples. n.d.: not detected.

8 mol% was chosen as the optimal loading.

Irradiation wavelength optimization

Table S3. Irradiation wavelength optimization.



1a, 5 equiv **2a**, 0.1 M **3**

Entry	Light source (nm)	Consumption of **2a** (%)	Yield of **3** (%)[a]
1	310[b]	29	7
2	366[c]	17	3
3	405[d]	100	95
4	**456**[d]	**100**	**95**
5	505[d]	26	15

[a] Absolute yields determined by means of calibration curves with authentic samples. [b] Multi-lamp apparatus fitted with 10×15 W phosphor-coated lamps (emission centered at 310 nm); [c] Multi-lamp apparatus fitted with 10×15 W phosphor-coated lamps (emission centered at 366 nm); [d] 1 W LED.

456 nm was chosen as the optimal wavelength of irradiation.

Reaction time optimization

The kinetic profile of the reaction reported in Scheme S1 under optimized conditions (Table S3, *entry 4*) was monitored. Results are reported in Figure S1. Small aliquots were subtracted from the reaction mixture at 1, 3, 4, 6, 12 and 24 hours, then analysed via GC-FID and consumptions/yields were calculated by means of calibration curves with authentic samples (external standard: dodecane).

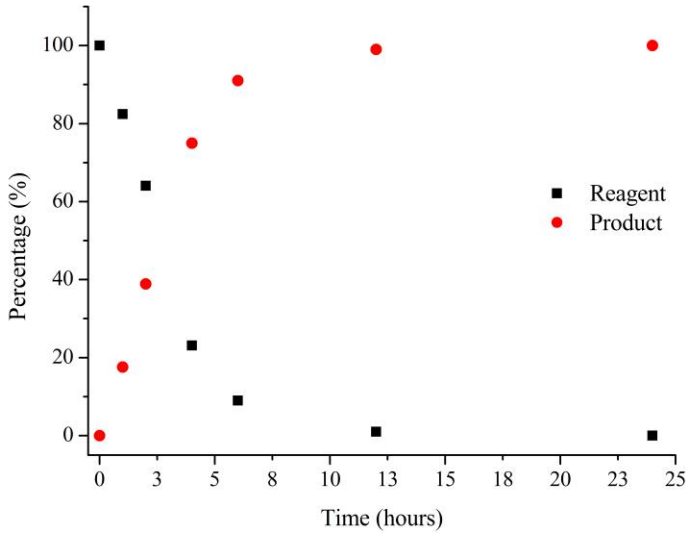
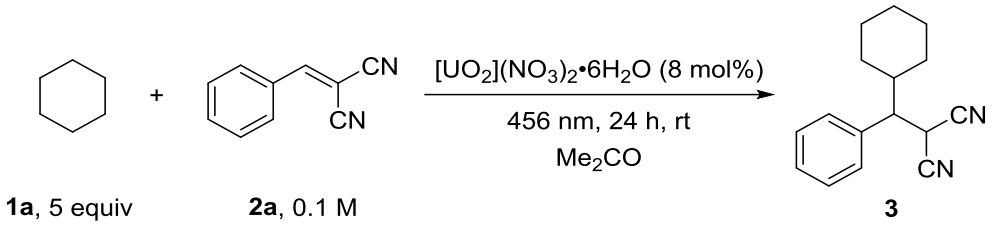


Figure S1. Time profile for the consumption of **2a** and formation of **3**.

24 hours are required for complete conversion of olefin **2a**.

Further experiments

Table S4. Control and additional experiments.



1a, 5 equiv **2a**, 0.1 M **3**

Entry	Variation from optimized conditions	Consumption of **2a** (%)	Yield of **3** (%)[a]
1	No light	<5	n.d.
2	No light, 60 °C (refluxing acetone)	<5	n.d.
3	No photocatalyst	<5	n.d.
4	N_2 sparged solution (3 min)	100	95
5	In the presence of TEMPO (1.0 equiv)	<5	n.d.

[a] Absolute yields determined by means of calibration curves with authentic samples. n.d.: not detected.

3. Spectroscopic Data

UV-Vis spectra were recorded with a double beam spectrophotometer equipped with Deuterium lamp (190-350 nm) and Halogen lamp (330-900 nm) and a Photomultiplier R928.

Absorption spectroscopy:	quartz cuvette (optical path: 1 cm)
	range scanned: 250-600 nm
	solvent cut-off: 330 nm (acetone)
	bandwidth: 1.0 nm
	speed: 400 nm/min
	data pitch: 1.0 nm
Emission spectroscopy:	quartz cuvette (optical path: 1 cm)
	range scanned: 450-600 nm
	excitation wavelength: 430 nm
	excitation slits: 10.0 nm
	emission slits: 5.0 nm
	speed: 300 nm/min
	each spectrum is an average of 6 acquisitions

Absorption and emission spectra

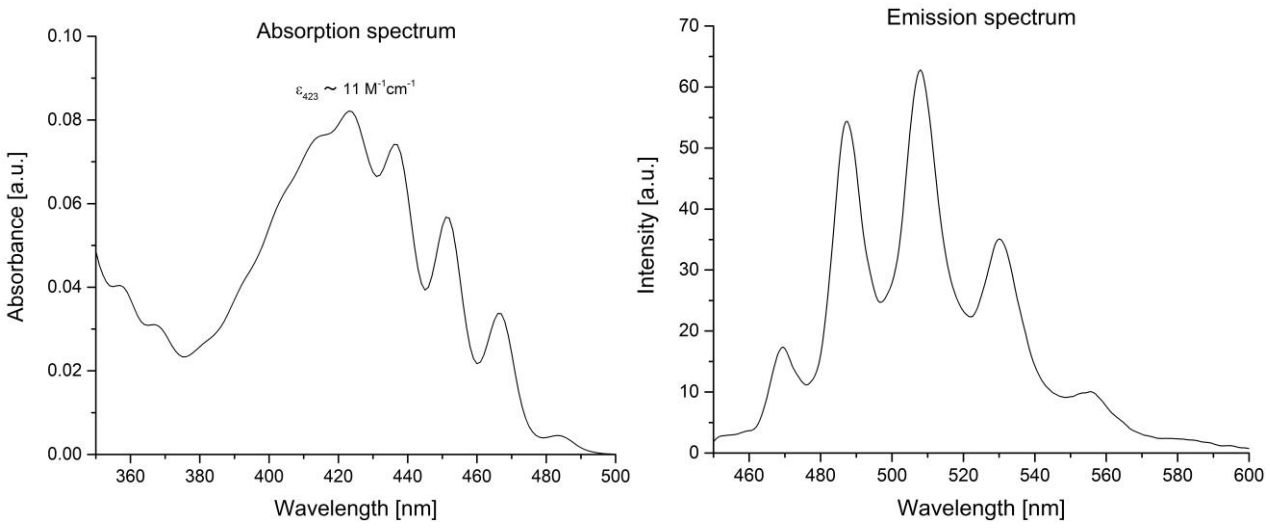


Figure S2. Absorption and emission spectra of an acetone solution of $[UO_2](NO_3)_2 \cdot 6H_2O$ ($7.97 \cdot 10^{-3}$ M).

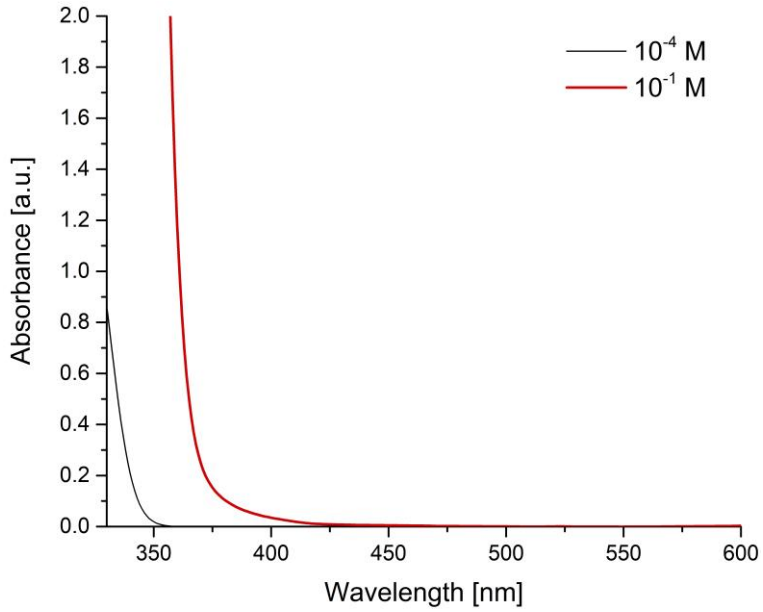


Figure S3. Absorption spectrum of an acetone solution of 2-benzylidenemalononitrile (**2a**).

Emission quenching experiments

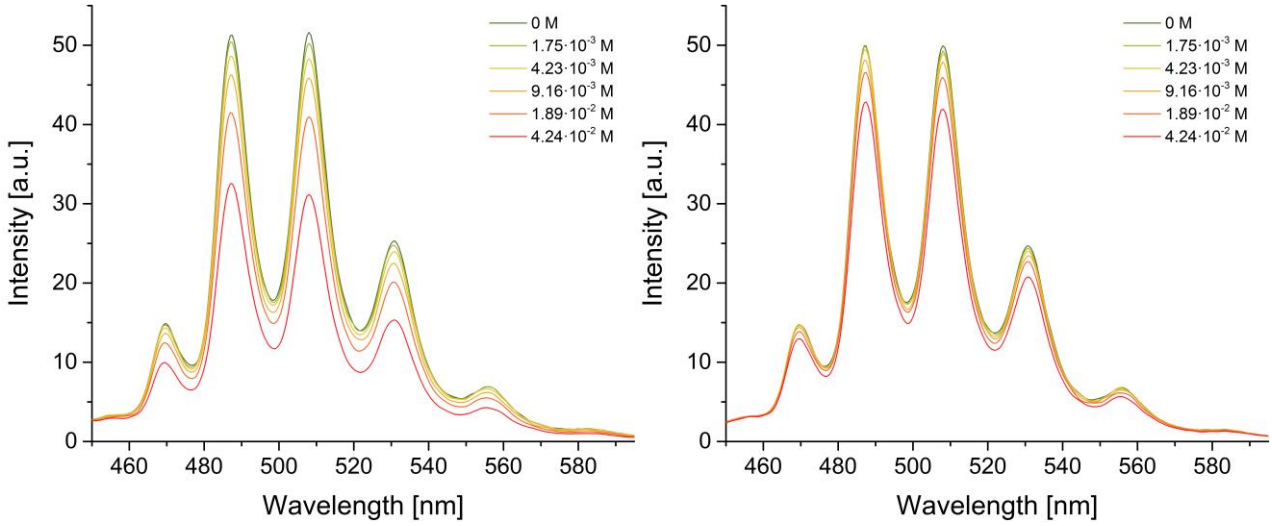


Figure S4. Emission of an acetone solution of $[UO_2(NO_3)_2 \cdot 6H_2O$ ($7.97 \cdot 10^{-3}$ M) recorded at increasing amounts of protiated cyclohexane (C_6H_{12}, left) and deuterated cyclohexane (C_6D_{12}, right).

Stern-Volmer plot

By monitoring the emission intensity profile at 508 nm in Figure S4, Stern-Volmer plots were obtained and reported in Figure S5.

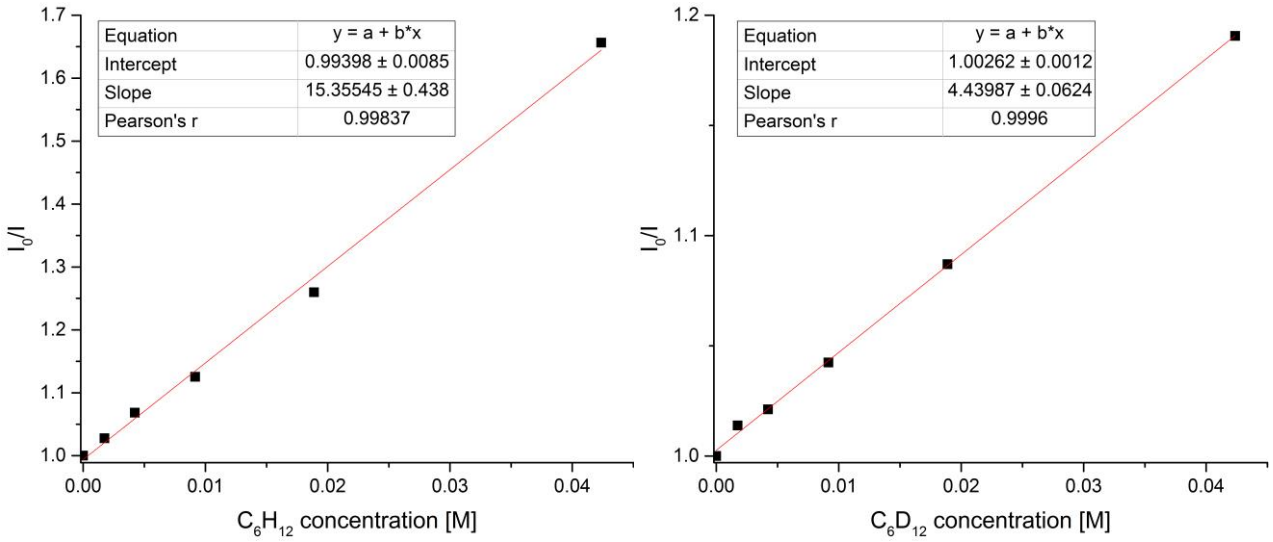


Figure S5. Stern-Volmer plots resulting from $[UO_2](NO_3)_2 \cdot 6H_2O$ emission quenching by protiated cyclohexane (C_6H_{12}, left) and deuterated cyclohexane (C_6D_{12}, right) followed at 508 nm.

Table S5. Stern-Volmer constants (k_{SV}) for the experiments reported in Figure S5.

Entry	Quencher	k_{SV} [M^{-1}]
1	C_6H_{12}	15.3
2	C_6D_{12}	4.4

Kinetic Isotope Effect (KIE) can be calculated as the ratio between k_{SV} reported in Table S5, *entry 1* and *entry 2*.

Accordingly, KIE = 3.5.

4. Electrochemical data

The electrochemical measurements were carried out by a BASi computer-controlled electrochemical analyzer. Electrochemical measurements (cyclic voltammetry) were performed in a three-electrode cell (volume 10 mL; acetonitrile for **2** and acetone for the photocatalyst were used as solvents, $LiClO_4$ 0.1 M as the supporting electrolyte, 2 mM concentration of the tested compound) at glassy carbon (diameter 2 mm, BASi) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (3 M NaCl) as the reference electrode. Scan speed was 100 mV/s.

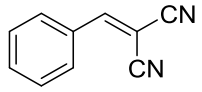
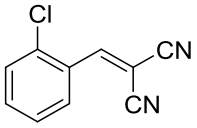
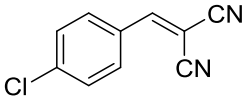
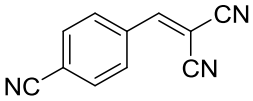
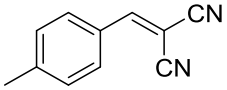
The potentials measured were then referred to SCE by applying the equation:

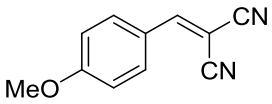
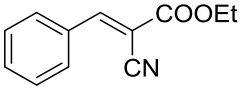
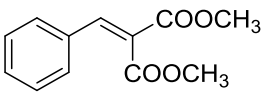
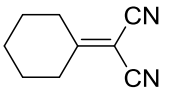
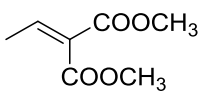
$$E \text{ (V vs SCE)} = E \text{ (V vs Ag/AgCl; 3 M NaCl)} - 35 \text{ mV}$$

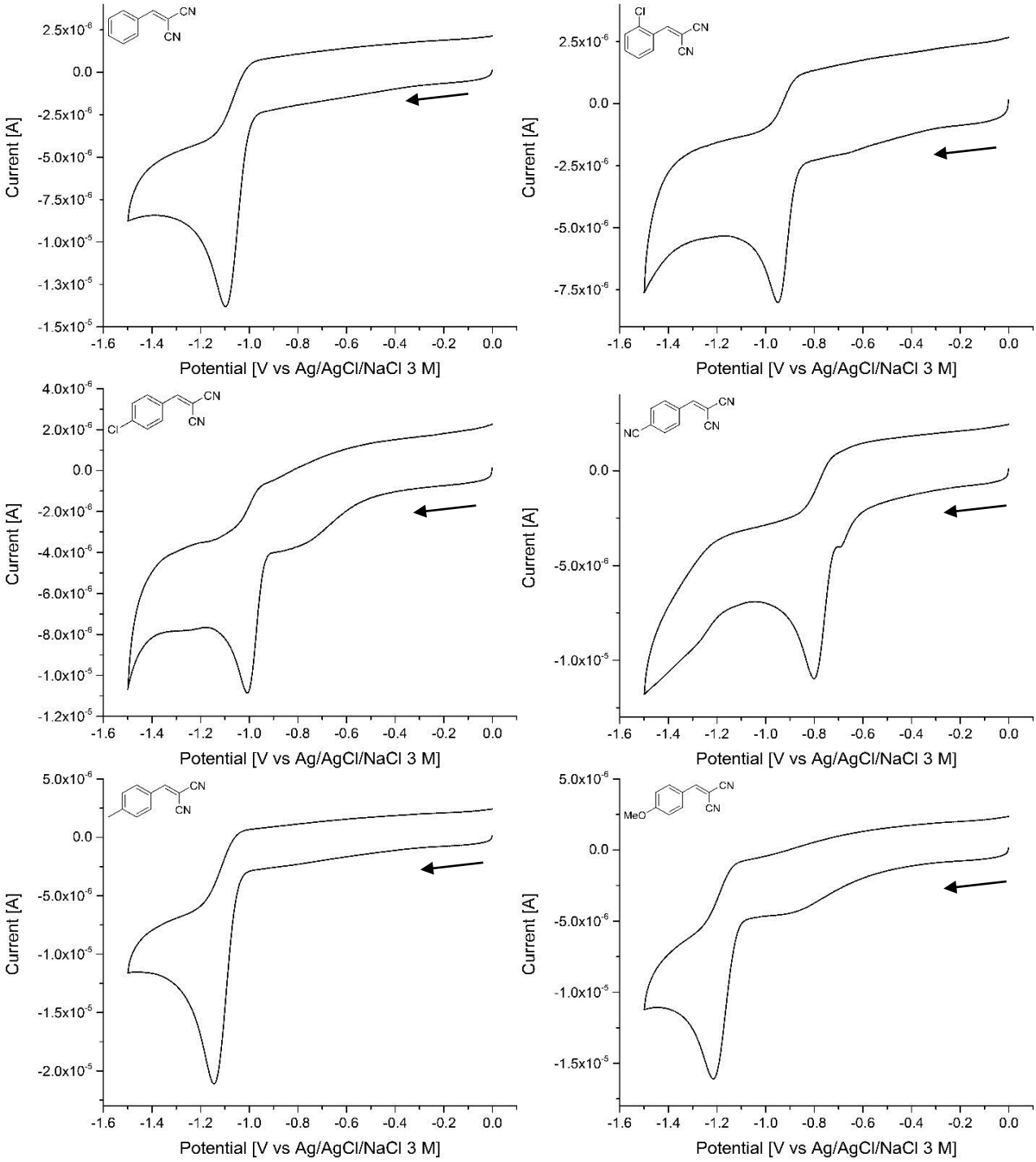
All the electron-poor olefins used in this work showed a reversible behavior with an EC mechanism.[S1]

Redox potentials of olefins

Table S6. Redox potentials of representative electron-poor olefins used in this work, reported against saturated calomel electrode (SCE). The potential refers to the reduction of the title compound to the radical anion.

2a	**2b**	**2d**	**2e**	**2f**
				
-1.08 V vs SCE	-0.95 V vs SCE	-1.02 V vs SCE	-0.80 V vs SCE	-1.14 V vs SCE

2g	**2h**	**2i**	**2k**	**2l**
				
-1.21 V vs SCE	-1.18 V vs SCE	-1.29 V vs SCE	-1.69 V vs SCE	-1.57 V vs SCE


Current [A]
Potential [V vs Ag/AgCl/NaCl 3 M]
CN
CN
Cl
NC
MeO

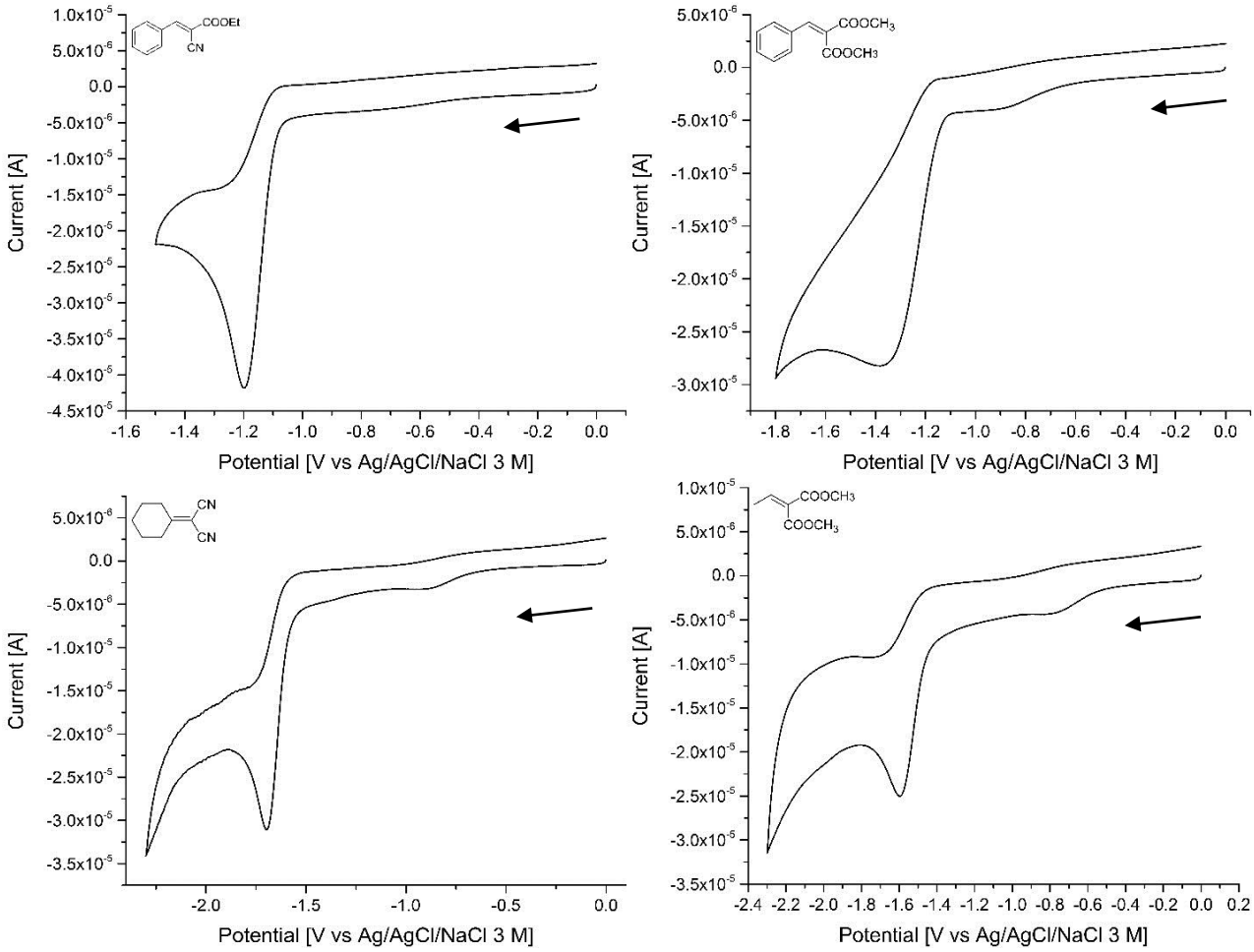
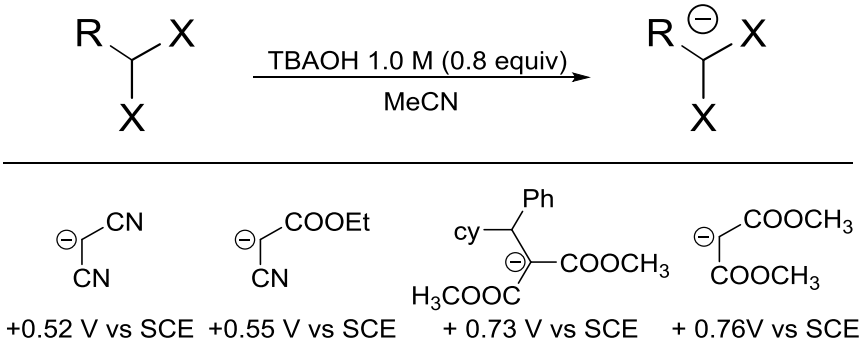


Figure S6. CV of representative electron-poor olefins used in this work, reported against Ag/AgCl/NaCl 3M. Scan range: from 0.0 V to -1.5 or -2.3 V, depending on the substrate. Scan speed: 100 mV/s. Initial potential: 0.0 V. The arrow in the figure indicates the direction of the scan.

Redox potentials of anions

Table S7. Redox potentials of carbanions generated *in-situ* by utilizing $(n\text{Bu})_4\text{N}^+\text{OH}^-$ (TBAOH; 0.8 equiv) from malononitrile, ethyl cyanoacetate, product **25** and dimethyl malonate. The potential refers to the oxidation of the carbanion to the neutral radical.



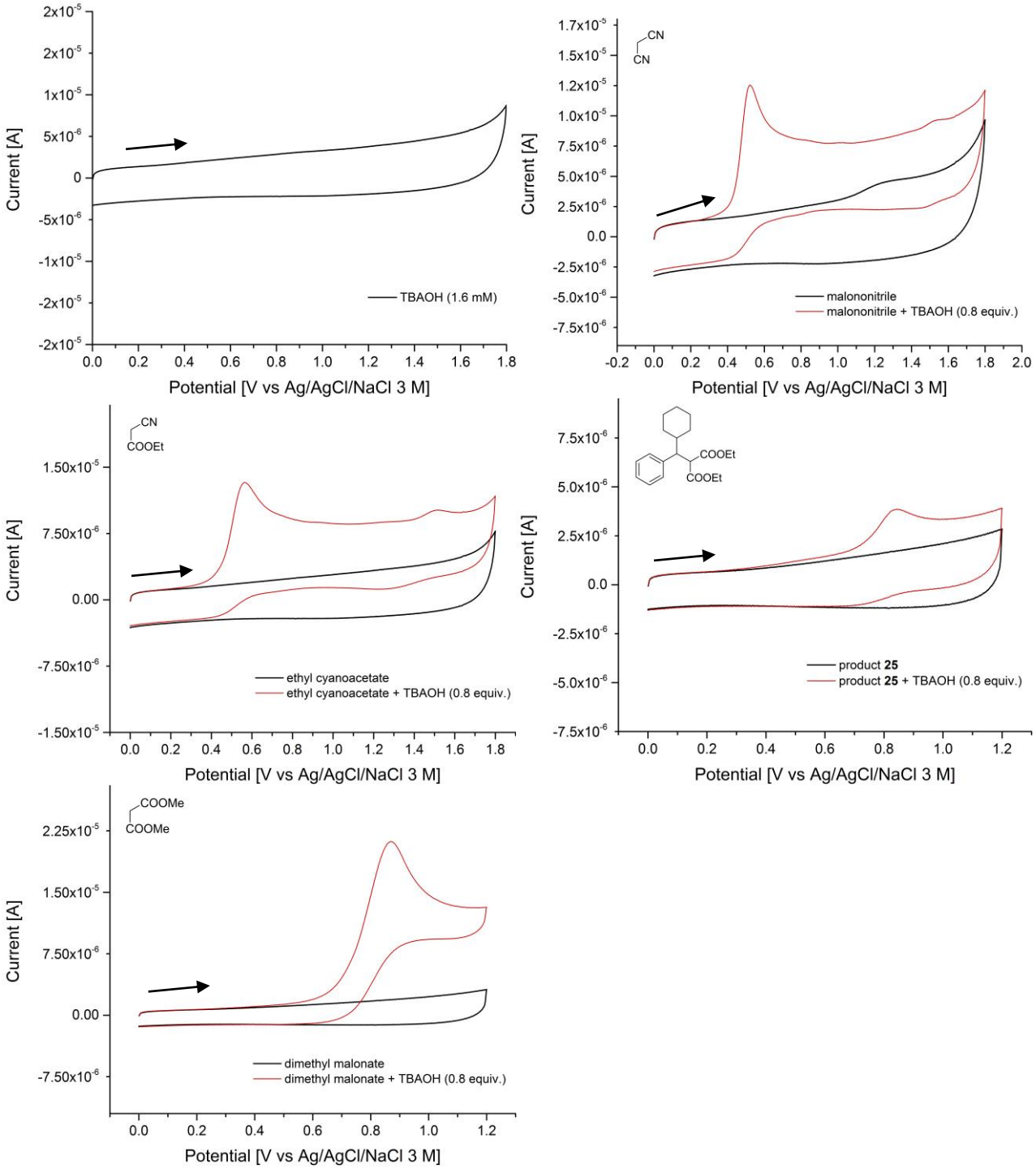


Figure S7. CV of malononitrile, ethyl cyanoacetate, product **25** and dimethyl malonate against Ag/AgCl/NaCl 3M. Scan range: from 0.0 V to +1.2 or +1.8 V depending on the substrate. Scan speed: 100 mV/s. Initial potential: 0.0 V. The arrow in the figure indicates the direction of the scan. The first CV refers to a blank experiment with TBAOH (1.6 mM).

Redox potential of uranyl nitrate hexahydrate

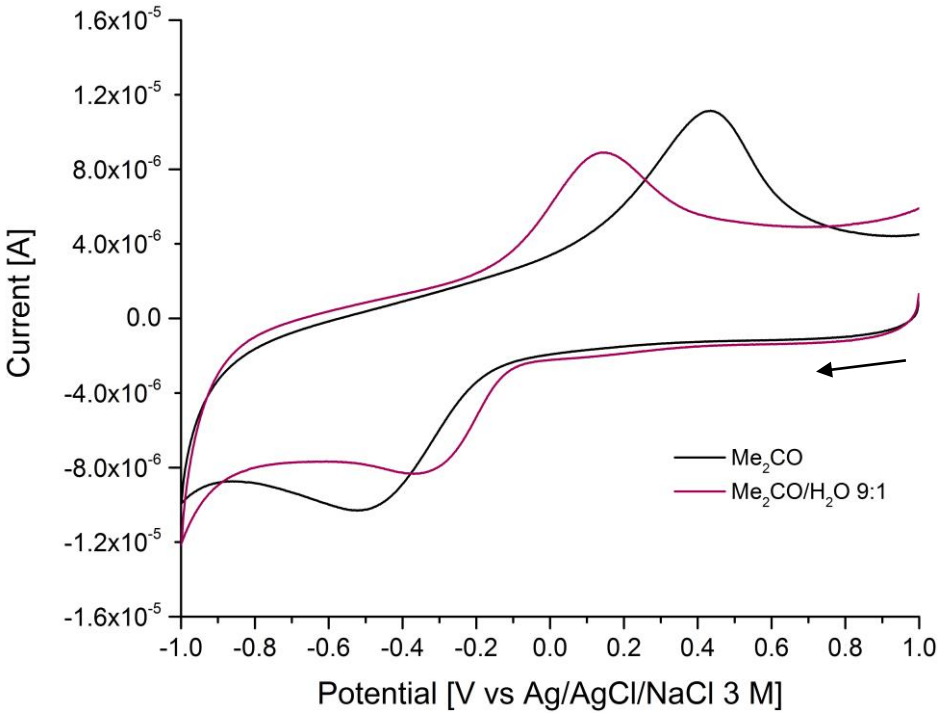


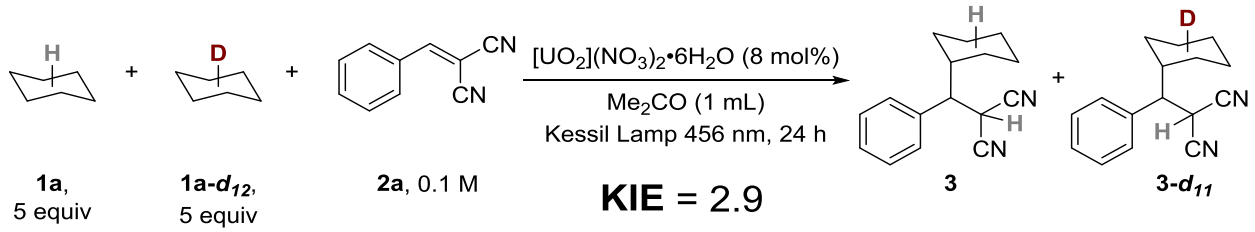
Figure S8. CV of uranyl nitrate hexahydrate against Ag/AgCl/NaCl 3M in acetone and acetone:water 9:1. Scan range: from +1.0 V to –1.0 V. Scan speed: 100 mV/s. Initial potential: +1.0 V. The arrow in the figure indicates the direction of the scan.

According to our results and literature data,[S2,S3] the observed peaks in Figure S8 are attributed to the reduction of U^{VI} to U^{V} ($E_{1/2}$ = –0.43 V vs SCE in Me_2CO and $E_{1/2}$ = –0.18 V vs SCE in Me_2CO/H_2O 9:1) and re-oxidation of U^{V} to U^{VI} ($E_{1/2}$ = +0.32 V vs SCE in Me_2CO and $E_{1/2}$ = +0.10 V vs SCE in Me_2CO/H_2O 9:1).

5. Deuterium labeling experiment

Deuteration of the H-Donor

An experiment under the optimized conditions (Table S3, *entry 4*) was carried out in the presence of a mixture of protiated **1a** (5.0 equiv) and deuterated cyclohexane **1a-*d*$_{12}$** (5.0 equiv, see Scheme S2 and Figure S9). After irradiation, the reaction mixture was filtered through a short silica plug in a pasteur pipette. Finally, the resulting solution was analyzed via GC/MS (see Experimental Section).



Scheme S2. Deuteration experiment to determine KIE.

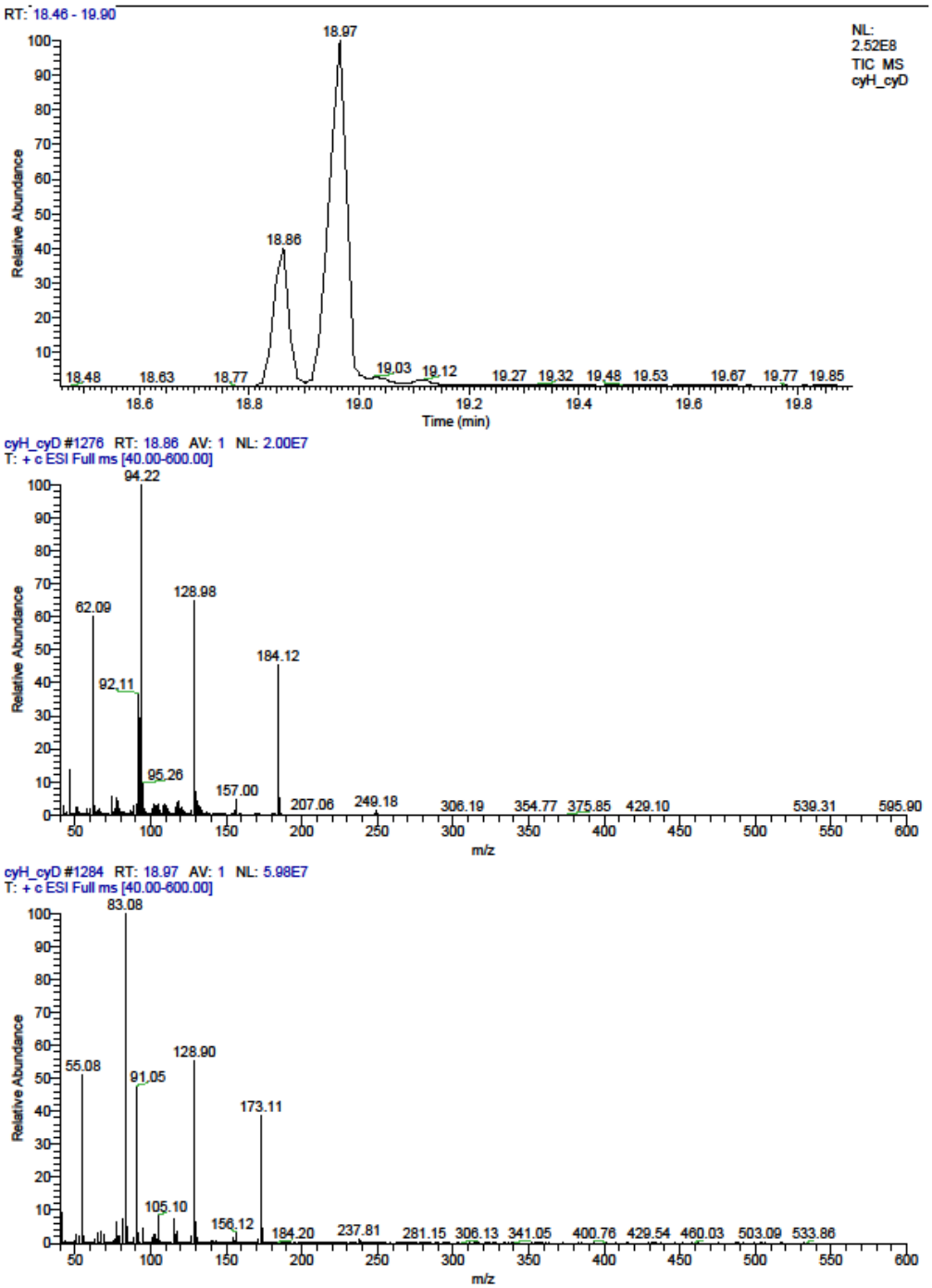


Figure S9. GC/MS analysis results for the reaction reported in Scheme S2: chromatogram (top), mass spectrum for peak at 18.86 min (middle), mass spectrum for peak at 18.97 (bottom).

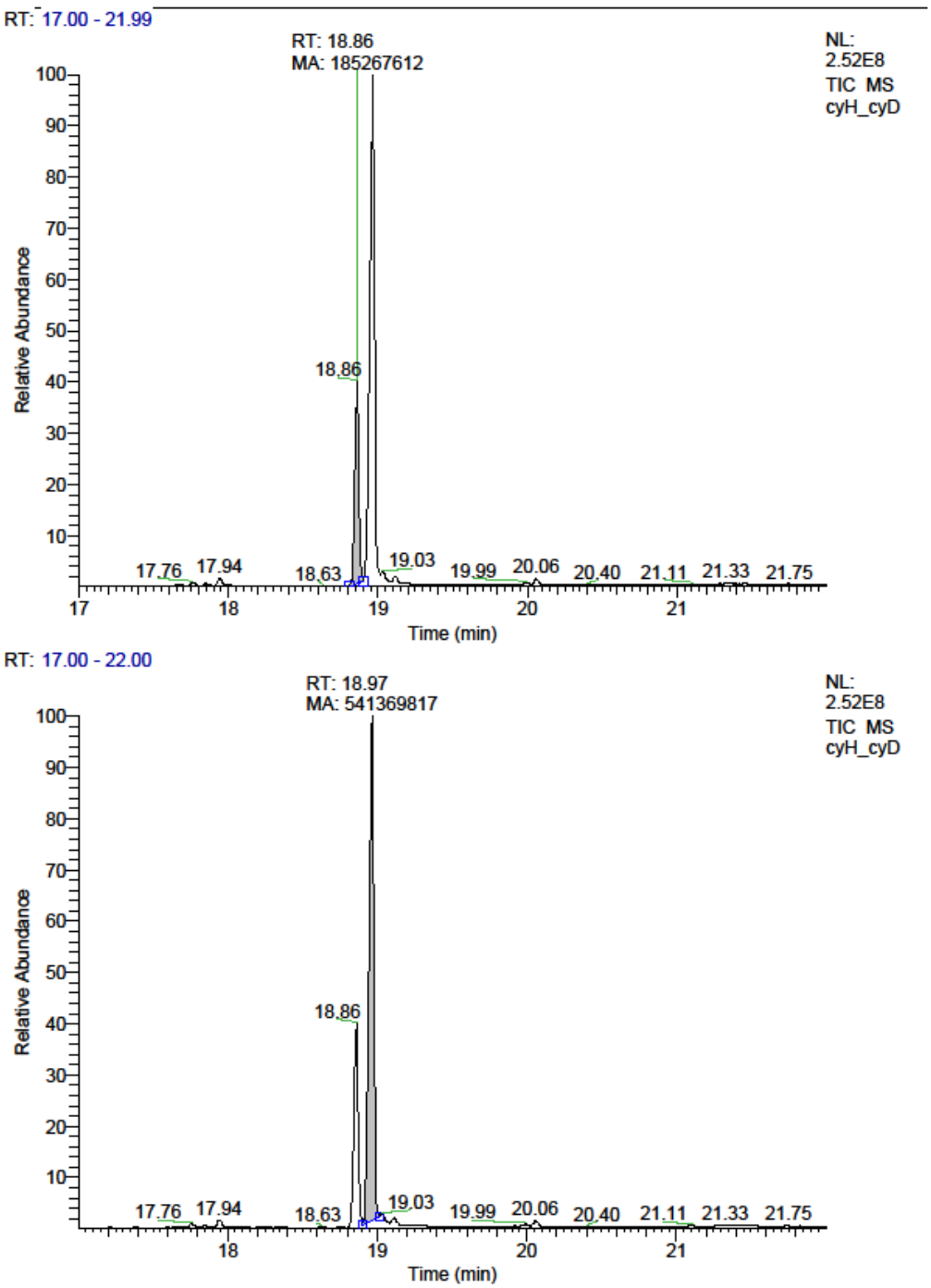
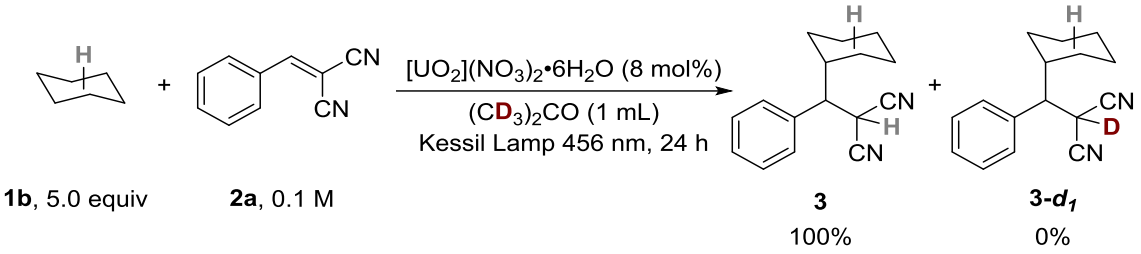


Figure S10. GC/MS analysis results for reaction reported in Scheme S2, details of the chromatogram with peak areas displayed.

- From Figure S9 it can be concluded that peaks at 18.86 min and 18.97 min correspond to **3** and **3-*d*$_{11}$**, respectively;
- From Figure S10 the KIE value can be calculated as the ratio between the area of **3** and **3-*d*$_{11}$** (KIE = 2.9).

Deuteration of the reaction medium

An experiment under the optimized conditions (Table S3, *entry 4*) was carried out in deuterated acetone as the solvent (see Scheme S3 and Figure S11). After irradiation, the reaction mixture was filtered through a short silica plug in a Pasteur pipette. Finally, the crude mixture was analyzed via GC/MS (see Experimental Section).



Scheme S3. Reaction carried out in deuterated acetone as the solvent.

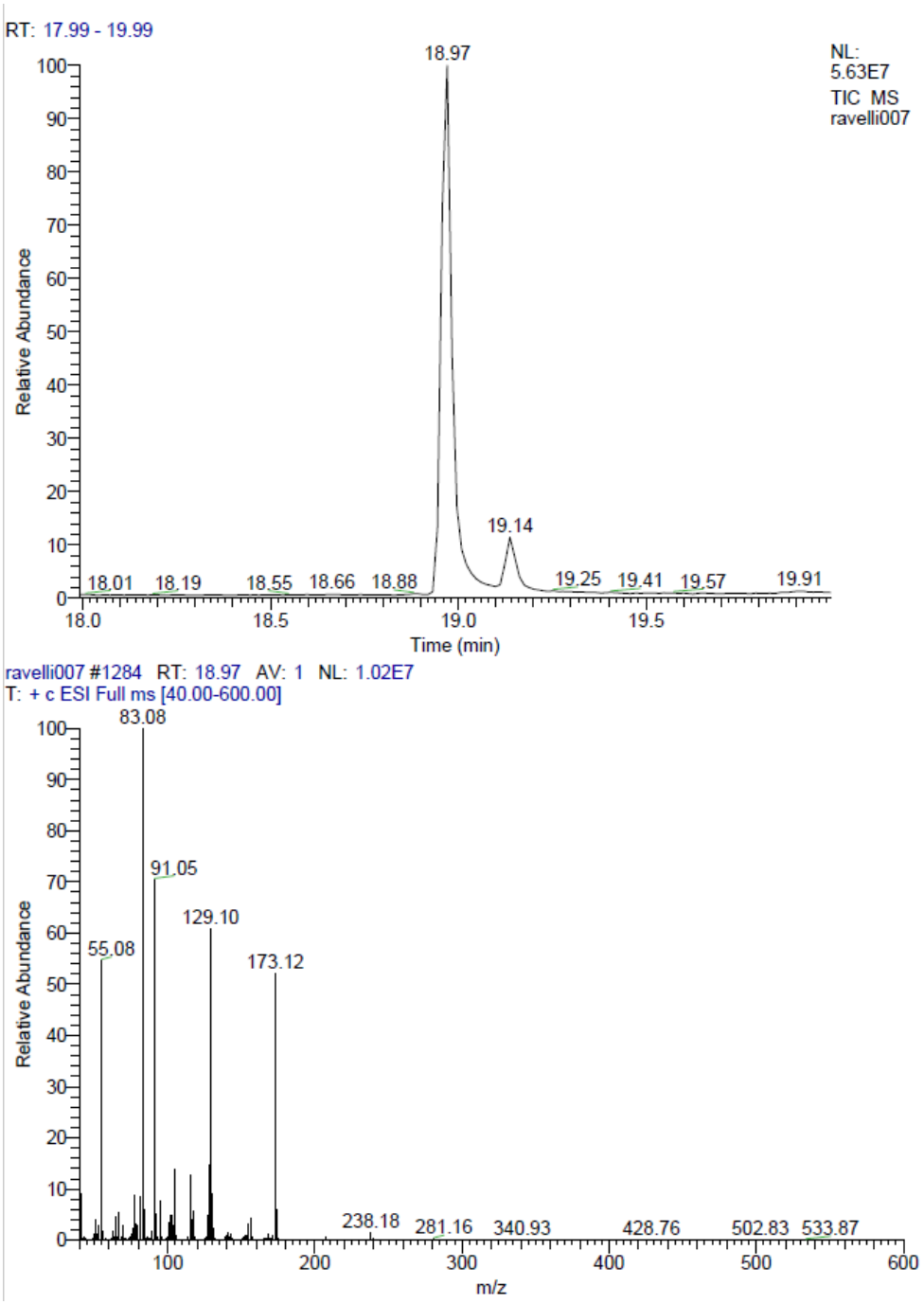


Figure S11. GC/MS analysis results for reaction reported in Scheme S3.

Figure S11 shows that no deuterium atoms from the solvent are incorporated in the product.

6. Experimental section

H-donors **1** and olefins **2j**, **2l-2n** were commercially available and used as received. Oxygenated H-donors **1h-i,1k** and aldehydes **1n, 1o** were freshly distilled prior to use. Solvents were at least of 99.5% purity grade and used as received. NMR spectra were recorded on a 300 (for ^{1}H) or 75 (for ^{13}C) MHz spectrometer; the attributions were based on ^{1}H and ^{13}C NMR chemical shift. Data for ^{1}H NMR are reported as follows: chemical shift referred to TMS (δ ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sext = sextuplet, sept = septuplet, m = multiplet), coupling constant (*J*, Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift. Thin-layer chromatography (TLC) was performed on silica gel 60 F-254 plates. Visualization of the developed plates was performed by fluorescence quenching, 2,4-dinitrophenylhydrazine or $KMnO_4$ staining.
GC/MS analyses were carried out on a Thermo Scientific DSQII single quadrupole GC/MS system. The injection in the GC/MS system was performed at 250 °C split mode. The initial oven temperature of 80 °C was maintained for 5 min, increased by 10 °C/min to 250 °C and held for 5 min. A Restek Rxi-5Sil MS 30 m x 0.25 mm x 0.25 µm film thickness capillary column was used with helium as the carrier gas at a constant flow rate of 1.0 mL/min. The transfer line temperature was 270 °C and the ion source temperature was 250 °C. Electron ionization mode was used with 70 eV and the ions were registered in full scan mode in a mass range of m/z 40-600 amu. The chromatogram acquisition, detection of mass spectral peaks and their waveform processing were performed using Xcalibur MS Software Version 2.1 (Thermo Scientific Inc.). Assignment of chemical structures to chromatographic peaks was based on the comparison with the databases for GC-MS NIST Mass Spectral Library (NIST 08) and Wiley Registry of Mass Spectral Data (8th Edition). The percentage content of each component was directly computed from the peak areas in the GC/MS chromatogram.
GC-FID analyses were performed on an Agilent 7820A. The injection was performed at 250 °C split mode. The initial oven temperature of 80 °C was maintained for 2 min, increased by 10 °C/min to 250 °C and held for 5 min. An Agilent HP5 30 m x 0.32 mm x 0.25 µm film thickness capillary column was used with nitrogen as the carrier gas at a constant flow rate of 6.0 mL/min.
Chromatographic purification of products was accomplished using ISOLERA flash chromatography system by Biotage (cartridges: direct phase – SiO_2, Biotage ULTRA SNAP 10 g, speed: 36 mL/min).

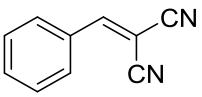
ICP-MS analyses were performed on Perkin Elmer ICP-MSDRCe (inductively coupled plasma equipped with mass spectrometric detector and direct reaction cell), following the standard procedures suggested by the manufacturer. For the analysis of the samples, the compounds (ca. 10 mg) were sonicated in a test tube for 30 min at 70°C with 1 mL ultrapure 65% nitric acid, and then diluted to 5 mL with Milli-Q water. The solutions were filtered with a 0.45 µm Nylon filter and analyzed by ICP-MS. Ultrapure 65% nitric acid (Merck Sigma Aldrich, Merck KGaA, Darmstadt, Germany) was used.

General procedure for the synthesis of electron-poor olefins 2a-i, 2k

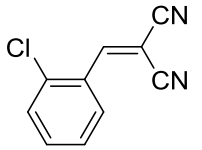
Electron-poor styrenes **2a-h** used in this work were prepared on a 3.0 mmol scale following a procedure previously reported in the literature.[S4] In particular, the chosen aromatic aldehyde (1.0 equiv, 1.0 M) was reacted with the active methylene (1.0 equiv, 1.0 M) in the presence of 10 mol% of 1,4-diazabicyclo[2.2.2]octane (DABCO). Solvent: water (3 mL); temperature: 20 °C. Reaction was monitored via TLC. The product precipitated upon formation, and the obtained solid was filtered and recrystallized from cyclohexane.

Dimethyl 2-benzylidenemalonate (**2i**) was prepared on a 3.0 mmol scale according to a different procedure reported in the literature.[S5] In particular, a round-bottom flask was charged with benzaldehyde (1 equiv, 0.12 M), followed by benzene (25 mL), dimethyl malonate (1.1 equiv, 0.13 M), piperidine (10 mol%) and acetic acid (10 mol%). The mixture was refluxed with a Dean-Stark trap overnight. Upon completion of the reaction (as determined by TLC analysis), evaporation of the solvent gave the crude product, which was purified by silica gel column chromatography.[S5]

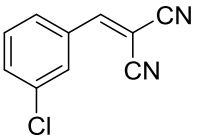
2-Cyclohexylidenemalononitrile (**2k**) was prepared with the same procedure adopted for **2a-h**.[S4]



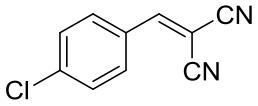
2-benzylidenemalononitrile (2a). Reaction time: 5 min. White solid, yield: 60%. mp: 83-85° C (lit.[S4] 83-84 °C). Spectroscopic data of compound **2a** were in accordance with the literature.[S4]



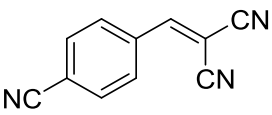
2-(2-chlorobenzylidene)malononitrile (2b). Reaction time: 2 min. White solid, yield: 99%. mp: 94-96 °C (lit.[S6] 95 °C). Spectroscopic data of compound **2b** were in accordance with the literature.[S6]



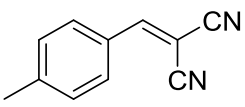
2-(3-chlorobenzylidene)malononitrile (2c). Reaction time: 2 min. White solid, yield: 90%. mp: 115-117 °C (lit.[S7] 116-117 °C) Spectroscopic data of compound **2c** were in accordance with the literature.[S6]



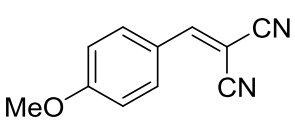
2-(4-chlorobenzylidene)malononitrile (2d). Reaction time: 2 min. White solid, yield: 80%. mp: 163-165 °C (lit.[S4] 164-165 °C). Spectroscopic data of compound **2d** were in accordance with the literature.[S4]



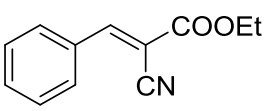
2-(4-cyanobenzylidene)malononitrile (2e). Reaction time: 2 min. White solid, yield: 88%. mp: 153-156 °C (lit.[S8] 157 °C). Spectroscopic data of compound **2e** were in accordance with the literature.[S9]



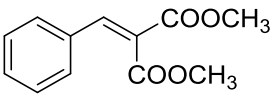
2-(4-methylbenzylidene)malononitrile (2f). Reaction time: 3 min. White solid, yield: 88%. mp: 132-134 °C (lit.[S4] 133-134 °C). Spectroscopic data of compound **2f** were in accordance with the literature.[S4]



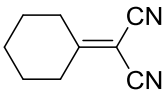
2-(4-methoxybenzylidene)malononitrile (2g). Reaction time: 10 min. White solid, yield: 88%. mp: 118-119 °C (lit.[S6] 116-118 °C). Spectroscopic data of compound **2g** were in accordance with the literature.[S6]



ethyl (E)-2-cyano-3-phenylacrylate (2h). Reaction time: 3 h White solid, yield: 85%. mp: 48-49 °C (lit. 48-49 °C).[S4] Spectroscopic data of compound **2h** were in accordance with the literature.[S4]



dimethyl 2-benzylidenemalonate (2i). Colorless oil. Spectroscopic data of compound **2i** were in accordance with the literature.[S10,S11]



2-cyclohexylidenemalononitrile (2k). Reaction time: 5 min. yellowish liquid, yield: 80%. Spectroscopic data of compound **2k** were in accordance with the literature.[S4]

General procedure for the uranyl cation photocatalyzed C-H to C-C bond conversion.

Note: main risks deriving from the use of uranium salts are associated with chemical toxicity. Thus, a judicious use of PPE (Personal Protection Equipment) makes most common uranium compounds, such as uranyl nitrate or uranyl acetate, no more noxious than any other heavy metal complex.

Explorative experiments: the olefin (**2a-n**, 0.1 mmol, 0.1 M), the H-donor (**1a-o**, 0.1-2.0 mmol, 0.1-2.0 M, 1-20 equiv, see below) and uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$; $8 \cdot 10^{-3}$ mmol, $8 \cdot 10^{-3}$ M, 8 mol%) were dissolved in acetone (1 mL) in a borosilicate glass vial (see Figure S12,S13, left). After irradiation for the indicated time by using an EvoluChem apparatus equipped with a Kessil lamp (456 nm), the reaction mixture was filtered through a short silica plug in a pasteur pipette to remove the grey precipitate formed during the irradiation, which was rinsed with 2x2mL of dichloromethane. External standard was added (dodecane; 1 μL/mL) and finally the resulting solution was analyzed via GC-FID analysis.

Preparative experiments: the olefin (**2a-n**, 1.0 mmol, 0.1 M), the H-donor (**1a-o**, 1-20 equiv, see below) and uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$, 8 mol%) were dissolved in acetone (10 mL) in a borosilicate glass vessel (see Figure S12,S13, right). After irradiation for the indicated time by using a 40 W Kessil lamp (456 nm) positioned at 5 cm away from the reaction vessel, the reaction mixture was filtered through filter paper to remove the grey precipitate formed during the irradiation, checked via GC-FID analysis and purified via flash chromatography.

Figure S12. Picture of vessels used in this work: a 3 mL borosilicate glass vial was used for explorative experiments (left), while a 20 mL vessel was used for preparative experiments (right).

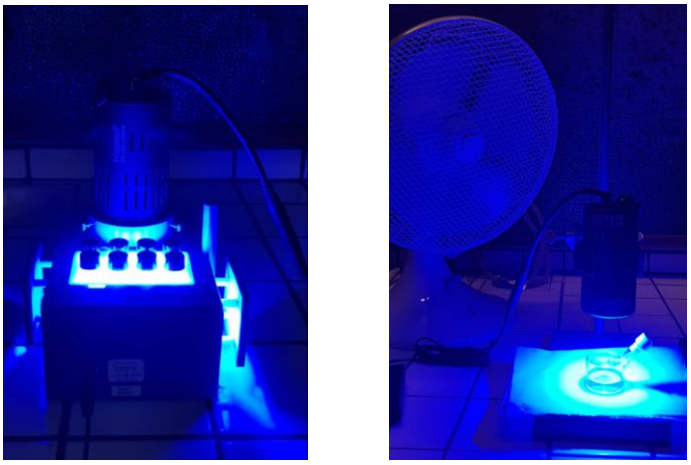
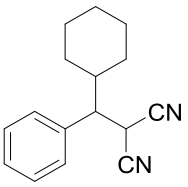


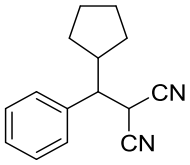
Figure S13. Irradiation setups for explorative (left) and preparative experiments (right) at 456 nm.

Deviations, if any, from general procedures are reported for each case.

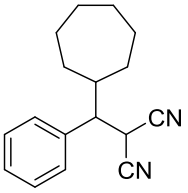
Scope of the H-donor



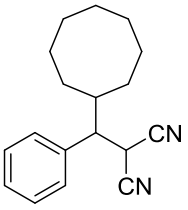
2-(Cyclohexyl(phenyl)methyl)malononitrile (3). From cyclohexane **1a** (0.5 M, 5.0 equiv, 540 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **3** as a colorless oil (229 mg, 96% yield). Characterization data for **3** are in accordance with the literature.[S12] The residual uranium content in isolated **3** was determined by an ICP-MS analysis to be < 20 μg/kg.



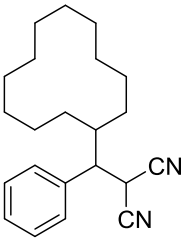
2-(Cyclopentyl(phenyl)methyl)malononitrile (4). From cyclopentane **1b** (0.5 M, 5.0 equiv, 467 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **4** as a colorless oil (150 mg, 67% yield). Characterization data for **4** are in accordance with those reported in the literature.[S12]



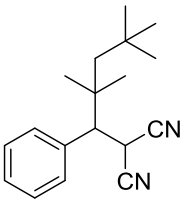
2-(Cycloheptyl(phenyl)methyl)malononitrile (5). From cycloheptane **1c** (0.5 M, 5.0 equiv, 605 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **5** as a colorless oil (192 mg, 76% yield). Characterization data for **5** are in accordance with the literature.[S12]



2-(Cyclooctyl(phenyl)methyl)malononitrile (6). From cyclooctane **1d** (0.5 M, 5.0 equiv, 673 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **6** as a colorless oil (208 mg, 78% yield). Characterization data for **6** are in accordance with the literature.[S12]

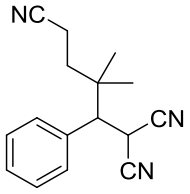


2-(Cyclododecyl(phenyl)methyl)malononitrile (7). From cyclododecane **1e** (0.5 M, 5.0 equiv, 842 mg) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **7** as a white solid (136 mg, 42% yield). m.p.:106-107 °C. Spectroscopic data for **7** are in accordance with the literature.[S12]



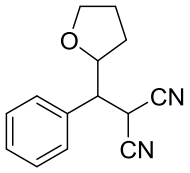
2-(2,2,4,4-Tetramethyl-1-phenylpentyl)malononitrile (8). From 2,2,4-trimethylpentane **1f** (2.0 M, 20 equiv, 3.31 mL) and **2a** (0.1 M, 1.0 equiv, 154 mg). 15 mol% uranyl nitrate hexahydrate was used. The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 98:2) to afford **8** as a colorless oil (182 mg, 68% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.36 (m, 5H), 4.29 (d, *J* = 5 Hz, 1H), 3.06 (d, *J* = 5 Hz, 1H), 1.47 (s, 2H), 1.23 (s, 3H), 1.14 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.2, 129.9, 128.8, 128.7, 113.5, 113.3, 58.3, 52.2, 39.4, 32.6, 32.2, 27.3, 26.5, 24.9. Anal. Calcd. for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44. Found: C, 80.5; H, 9.0; N, 10.4.

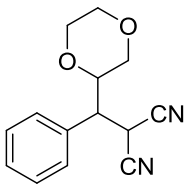


3,3-Dimethyl-2-phenylpentane-1,1,5-tricarbonitrile (9). From isocapronitrile **1g** (1.0 M, 10.0 equiv, 1.21 mL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **9** as a colorless oil (171 mg, 68% yield).

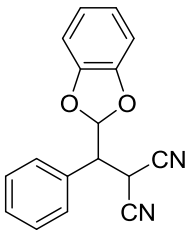
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.28 (m, 5H), 4.27 (d, *J* = 6 Hz, 1H), 3.05 (d, *J* = 6 Hz, 1H), 2.38-2.11 (m, 2H), 1.78-1.66 (m, 2H), 1.16 (s, 3H), 1.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 129.4, 129.2, 129.1, 119.7, 113.1, 112.9, 55.3, 37.3, 36.1, 25.0, 25.0, 23.8, 12.3. Anal. Calcd. for $C_{16}H_{17}N_3$: C, 76.46; H, 6.82; N, 16.72. Found: C, 74.5; H, 6.8; N, 16.7.



2-(Phenyl(tetrahydrofuran-2-yl)methyl)malononitrile (10). From freshly distilled tetrahydrofuran **1h** (0.5 M, 5.0 equiv, 406 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **10** as a mixture of diastereomers (ratio 1:1) as a yellowish oil (136 mg, 60% yield). Characterization data for **10** are in accordance with the literature.[S13]

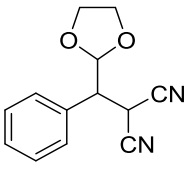


2-((1,4-Dioxan-2-yl)(phenyl)methyl)malononitrile (11). From freshly distilled 1,4-dioxane **1i** (0.5 M, 5.0 equiv, 428 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 95:5) to afford **11** as a mixture of diastereomers (ratio 1:1) as a colorless liquid (170 mg, 70% yield). Characterization data for **11** are in accordance with the literature.[S13]



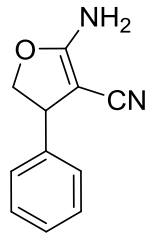
2-(1,3-Benzodioxol-2-yl(phenyl)methyl)malononitrile (12). From 1,3-benzodioxole **1j** (0.11 M, 1.1 equiv, 127 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **12** as a colorless oil (160 mg, 58% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.45 (m, 5H), 6.97-6.81 (m, 4H), 6.54 (d, *J* = 4 Hz, 1H), 4.44 (d, *J* = 6 Hz, 1H), 3.78 (dd, J_1 = 6 Hz, J_2 = 5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 146.5, 131.6, 130.0, 129.6, 129.1, 122.8, 122.7, 111.4, 111.2, 109.4, 109.4, 109.0, 50.0, 24.6. Anal. Calcd. for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.9; H, 4.4; N, 10.1.



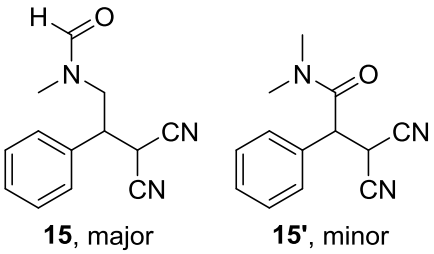
2-((1,3-Dioxolan-2-yl)(phenyl)methyl)malononitrile (13). From freshly distilled 1,3-dioxolane **1k** (0.5 M, 5.0 equiv, 349 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **13** as a yellowish oil (136 mg, 68% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.39 (m, 5H), 5.25 (d, *J* = 3 Hz, 1H), 4.30 (d, *J* = 7 Hz, 1H), 4.25-3.83 (m, 4H), 3.52 (dd, J_1 = 7 Hz, J_2 = 3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.3, 129.5, 129.4, 129.1, 112.1, 111.9, 103.0, 66.1, 65.2, 49.4, 24.4. Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.3; H, 5.4; N, 12.2.



2-Amino-4-phenyl-4,5-dihydrofuran-3-carbonitrile (14). From methanol **1l** (0.5 M, 5 equiv, 202 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **14** as a red oil (140 mg, 75% yield). Cyclization of the product to dihydrofuran **14** occurred upon purification.[S13] Characterization data for **14** are in accordance with the literature.[S13]

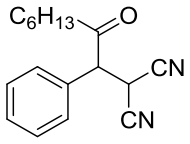
^{1}H NMR (300 MHz, CD_3COCD_3) δ 7.50-7.01 (m, 5H), 6.43 (bs, 2H), 4.78 (t, J = 9 Hz, 1H), 4.34 (dd, J_1 = 9 Hz, J_2 = 6 Hz, 1H), 4.19 (dd, J_1 = 9 Hz, J_2 = 6 Hz, 1H). ^{13}C NMR (75 MHz, CD_3COCD_3) δ 169.4, 144.1, 129.5, 128.0, 128.0, 119.0, 78.9, 56.6, 48.5. Anal. Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04; Found: C, 70.9; H, 5.4; N, 15.1.



Reaction between DMF and 2a. From *N*,*N*-dimethylformamide **1m** (0.4 M, 4.0 equiv, 310 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford 150 mg of *N*-(3,3-dicyano-2-phenylpropyl)-*N*-methylformamide (**15**; 66% yield) and 77 mg of 3,3-dicyano-*N*,*N*-dimethyl-2-phenylpropanamide (**15'**; 33% yield) as colorless oil and a white solid (m.p. 137-139 °C),[S14] respectively. Thus, the two constitutional isomers have been obtained in a **15**:**15'** = 2:1 ratio.

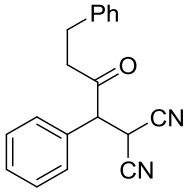
Characterization data for **15**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (major, s, 1H), 7.98 (minor, s, 1H), 7.50 – 7.32 (m, 10H), 4.28 (major, d, J = 6 Hz, 1H), 4.25 (minor, d, J = 6 Hz, 1H), 4.11 (major, dd, J_1 = 13 Hz, J_2 = 7 Hz, 1H), 3.89 (minor, dd, J_1 = 14 Hz, J_2 = 7 Hz, 1H), 3.81 – 3.49 (m, 4H), 2.86 (minor, s, 3H), 2.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 162.8, 134.6, 133.8, 129.9, 129.8, 129.5, 129.5, 128.1, 127.9, 112.0, 111.6, 111.6, 111.4, 51.4, 47.3, 44.3, 44.0, 35.8, 30.3, 27.8, 27.2.

Characterization data for **15'**[S14] are in accordance with the literature.



2-(2-Oxo-1-phenyloctyl)malononitrile (16). From freshly distilled heptanal **1n** (0.1 M, 1.0 equiv, 141 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **16** as a colorless oil (250 mg, 93% yield).

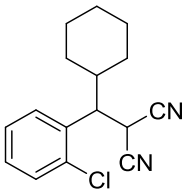
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.36 (m, 3H), 7.34-7.03 (m, 2H), 4.42 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 4.29 (d, J = 9 Hz, 1H), 2.43 (t, J = 7 Hz, 2H), 1.68-1.46 (m, 2H), 1.30-1.05 (m, 6H), 0.85 (t, J = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.2, 131.3, 130.1, 130.1, 128.8, 112.1, 111.6, 58.3, 41.1, 31.4, 28.5, 25.6, 23.6, 22.4, 14.0. Anal. Calcd. for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found: C, 76.1; H, 7.5; N, 10.4.



2-(2-Oxo-1,4-diphenylbutyl)malononitrile (17). From freshly distilled hydrocynnamaldehyde **1o** (0.1 M, 1.0 equiv, 130 μL) and **2a** (0.1 M, 1.0 equiv, 154 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **17** as a colorless oil (202 mg, 70% yield).

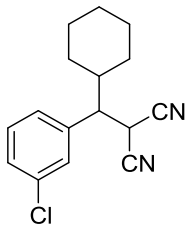
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.37 (m, 3H), 7.37-7.22 (m, 3H), 7.22-7.14 (m, 2H), 7.15-6.97 (m, 2H), 4.36 (d, *J* = 8 Hz, 1H), 4.17 (d, *J* = 8 Hz, 1H), 3.04-2.80 (m, 2H), 2.81-2.68 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.1, 139.8, 130.9, 130.1, 128.8, 128.7, 128.3, 126.6, 112.0, 111.4, 58.5, 42.5, 29.7, 25.5. Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 79.14; H, 5.59; N, 9.72. Found: C, 79.1; H, 5.7; N, 9.7.

Scope of the olefins



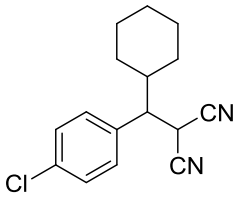
2-((2-Chlorophenyl)(cyclohexyl)methyl)malononitrile (18). From **1a** (0.5 M, 5.0 equiv, 540 μL) and 2-(2-chlorobenzylidene)malononitrile **2b** (0.1 M, 1.0 equiv, 189 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **18** as an orange oil (224 mg, 82% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 8 Hz, 1H), 7.49 (dd, J_1 = 8 Hz, J_2 = 1 Hz, 1H), 7.42-7.28 (m, 2H), 4.19 (d, J = 5 Hz, 1H), 3.81 (dd, J_1 = 10 Hz, J_2 = 5 Hz, 1H), 2.11-1.98 (m, 2H), 1.96-1.83 (m, 1H), 1.80-1.59 (m, 2H), 1.49-1.33 (m, 2H), 1.27-1.08 (m, 3H), 1.06-0.85 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 135.1, 130.6, 129.2, 128.6, 126.5, 112.0, 111.7, 52.0, 39.3, 31.2, 30.7, 27.0, 25.9, 25.8, 25.8. Anal. Calcd. for $C_{16}H_{17}ClN_2$: C, 70.45; H, 6.28; N, 10.27. Found: C, 70.4; H, 6.3; N, 10.3.

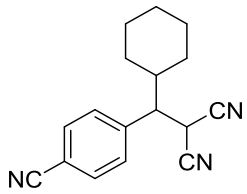


2-((3-Chlorophenyl)(cyclohexyl)methyl)malononitrile (19). From **1a** (0.5 M, 5.0 equiv, 540 μL) and 2-(3-chlorobenzylidene)malononitrile **2c** (0.1 M, 1.0 equiv, 189 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 8:2) to afford **19** as a yellowish oil (199 mg, 73% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 5.0 Hz, 2H), 7.33 (s, 1H), 7.29-7.22 (m, 1H), 4.22 (d, J = 6 Hz, 1H), 2.88 (dd, J_1 = 10 Hz, J_2 = 6 Hz, 1H), 2.11-1.79 (m, 3H), 1.76-1.60 (m, 2H), 1.55-0.96 (m, 5H), 0.97-0.75 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 135.1, 130.6, 129.2, 128.6, 126.5, 112.0, 111.7, 52.0, 39.3, 31.2, 30.7, 27.0, 25.87, 25.84, 25.76. Anal. Calcd. for $C_{16}H_{17}ClN_2$: C, 70.45; H, 6.28; N, 10.27. Found: C, 70.4; H, 6.4; N, 10.2

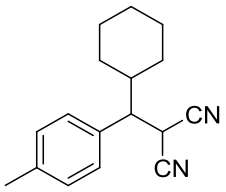


2-((4-Chlorophenyl)(cyclohexyl)methyl)malononitrile (20). From **1a** (0.5 M, 5.0 equiv, 540 μL) and 2-(4-chlorobenzylidene)malononitrile **2d** (0.1 M, 1.0 equiv, 189 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **20** as a yellowish oil (172 mg, 63% yield). Characterization data for **20** are in accordance with the literature.[S15]



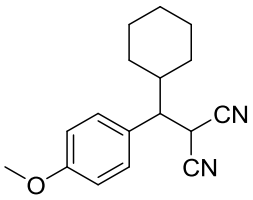
2-((4-cyanophenyl)(cyclohexyl)methyl)malononitrile (21). From **1a** (0.5 M, 5.0 equiv, 540 μL) and 2-(4-cyanobenzylidene)malononitrile **2e** (0.1 M, 1.0 equiv, 179 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **21** as a yellowish oil (174 mg, 66% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8 Hz, 2H), 7.47 (d, J = 8 Hz, 2H), 4.24 (d, J = 5 Hz, 1H), 2.94 (dd, J_1 = 10, J_2 = 5 Hz, 1H), 2.12-1.80 (m, 3H), 1.77-1.53 (m, 2H), 1.50-0.98 (m, 5H), 0.93-0.69 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 133.0, 129.4, 118.3, 113.1, 111.8, 111.4, 52.3, 39.1, 31.0, 30.8, 26.7, 25.8, 25.8, 25.7. Anal. Calcd. for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.5; H, 6.5; N, 16.0.



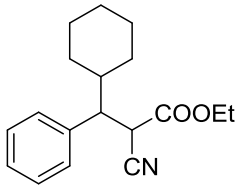
2-(Cyclohexyl(p-tolyl)methyl)malononitrile (22). From **1a** (0.5 M, 5 equiv, 540 μL) and 2-(4-methylbenzylidene)malononitrile **2f** (0.1 M, 1.0 equiv, 168 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **22** as a yellowish oil (151 mg, 60% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 4H), 4.16 (d, J = 5 Hz, 1H), 2.85 (dd, J_1 = 10 Hz, J_2 = 6 Hz, 1H), 2.36 (s, 3H), 2.09-1.74 (m, 3H), 1.72-1.62 (m, 2H), 1.59-0.97 (m, 5H), 0.93-0.71 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 133.8, 129.9, 128.3, 112.5, 112.1, 52.2, 39.4, 31.4, 30.7, 27.3, 26.0, 26.0, 25.9, 21.2. Anal. Calcd. for $C_{17}H_{20}N_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 81.1; H, 8.2; N, 11.0.



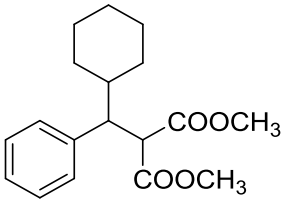
2-(Cyclohexyl(4-methoxyphenyl)methyl)malononitrile (23). From **1a** (0.5 M, 5 equiv, 540 μL) and 2-(4-methoxybenzylidene)malononitrile **2g** (0.1 M, 1.0 equiv, 184 mg). Reaction time: 96 hours. The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **23** as a yellowish oil (177 mg, 66% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 9 Hz, 2H), 6.92 (d, J = 9 Hz, 2H), 4.17 (d, J = 5 Hz, 1H), 3.82 (s, 3H), 2.84 (dd, J_1 = 10 Hz, J_2 = 5.4 Hz, 1H), 2.14-1.75 (m, 3H), 1.74-1.61 (m, 2H), 1.52-0.95 (m, 5H), 0.89-0.71 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 129.5, 128.7, 114.5, 112.5, 112.1, 55.4, 51.8, 39.3, 31.3, 30.7, 27.5, 26.0, 25.9, 25.9. Anal. Calcd. for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.51; N, 10.44. Found: C, 76.1; H, 7.5; N, 10.4.

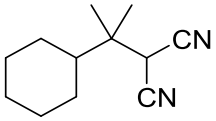


Ethyl 2-cyano-3-cyclohexyl-3-phenylpropanoate (24). From **1a** (0.5 M, 5.0 equiv, 540 μL) and ethyl 2-cyano-3-phenylacrylate **2h** (0.1 M, 1.0 equiv, 201 mg). Reaction time: 30 hours. The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **24** as a mixture of inseparable diastereomers (ratio 2:1) as a yellowish oil (220 mg, 77% yield).

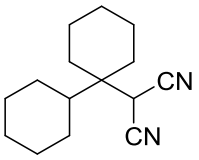
^{1}H NMR (300 MHz, $CDCl_3$, from the mixture of two diastereomers) δ 7.43-7.13 (m, 10H), 4.12 (q, J = 7 Hz, 1H), 4.11 (q, J = 7 Hz, 1H), 4.03 (d, J = 6 Hz, 1H), 3.96 (q, J = 7 Hz, 1H), 3.95 (q, J = 7 Hz, 1H), 3.81 (d, J = 6 Hz, 1H), 3.20 (dd, J_1 = 8 Hz, J_2 = 6 Hz, 1H), 2.96 (dd, J_1 = 10 Hz, J_2 = 6 Hz, 1H), 2.07-1.90 (m, 3H), 1.88-1.47 (m, 8H), 1.46-1.30 (m, 4H), 1.26-1.01 (m, 7H), 0.97 (t, J = 7.1 Hz, 4H), 0.91-0.69 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, from the mixture of two diastereomers) δ 166.0, 165.8, 139.2, 138.2, 128.7, 128.7, 128.5, 127.9, 127.7, 116.3, 115.8, 62.8, 62.5, 52.0, 51.7, 42.2, 41.7, 40.3, 39.6, 31.5, 31.3, 31.2, 30.0, 26.3, 26.2, 26.2, 26.2, 26.1, 26.0, 13.9, 13.8.



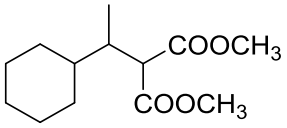
Dimethyl 2-(cyclohexyl(phenyl)methyl)malonate (25). From **1a** (0.5 M, 5.0 equiv, 540 μL) and dimethyl 2-benzylidenemalonate **2i** (0.1 M, 1.0 equiv, 220 mg). Reaction time: 65 hours. The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **25** as a yellowish oil (225 mg, 74% yield). Characterization data for **25** are in accordance with the literature.[S15]



2-(2-Phenylpropan-2-yl)malononitrile (26). From **1a** (0.5 M, 5.0 equiv, 540 μL) and 2-(propan-2-ylidene)malononitrile **2j** (0.1 M, 1.0 equiv, 106 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **26** as a yellowish oil (103 mg, 54% yield). Characterization data for **26** are in accordance with the literature.[S16]

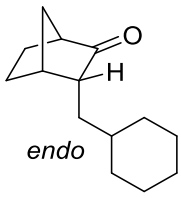


2-([1,1'-bi(Cyclohexan)]-1-yl)malononitrile (27). From **1a** (0.5 M, 5.0 equiv, 540 μL) and 2-cyclohexylidenemalononitrile **2k** (0.1 M, 1.0 equiv, 146 mg). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **27** as a yellowish oil (113 mg, 49% yield, 82% based on 60% consumption of **2k**). Characterization data for **27** are in accordance with the literature.[S17]

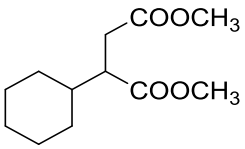


Dimethyl 2-(1-cyclohexylethyl)malonate (28). From **1a** (0.5 M, 5.0 equiv, 540 μL) and dimethyl 2-ethylidenemalonate **2l** (0.1 M, 1.0 equiv, 142 μL). The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **27** as a yellowish oil (199 mg, 82% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.70 (s, 3H), 3.42 (d, *J* = 9 Hz, 1H), 2.33-2.06 (m, 1H), 1.82-1.48 (m, 5H), 1.28-1.01 (m, 5H), 1.01-0.90 (m, 1H), 0.87 (d, *J* = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 169.3, 55.3, 52.2, 52.1, 40.2, 38.5, 31.3, 27.3, 26.6, 26.4, 26.3, 12.8. Anal. Calcd. for $C_{13}H_{22}O_4$: C, 64.44; H, 9.15. Found: C, 64.4; H, 9.2.



3-(Cyclohexylmethyl)bicyclo[2.2.1]heptan-2-one (29). From **1a** (0.5 M, 5.0 equiv, 540 μL) and 3-methylene-2-norbornanone **2m** (0.1 M, 1.0 equiv, 122 μL). Reaction time: 16 hours. The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford exclusively *endo*-**29** as a yellowish oil (142 mg, 69% yield). Characterization data for **29** are in accordance with the literature.[S18]



Dimethyl 2-cyclohexylsuccinate (30). From **1a** (0.5 M, 5.0 equiv, 540 μL) and dimethyl maleate **2n** (0.1 M, 1.0 equiv, 125 μL) in a Me_2CO:H_2O 8:2 medium. The crude mixture was purified through column chromatography (SiO_2: cyclohexane/ethyl acetate 9:1) to afford **30** as a colorless oil (137 mg, 60% yield). Characterization data for **29** are in accordance with the literature.[S19]

7. References

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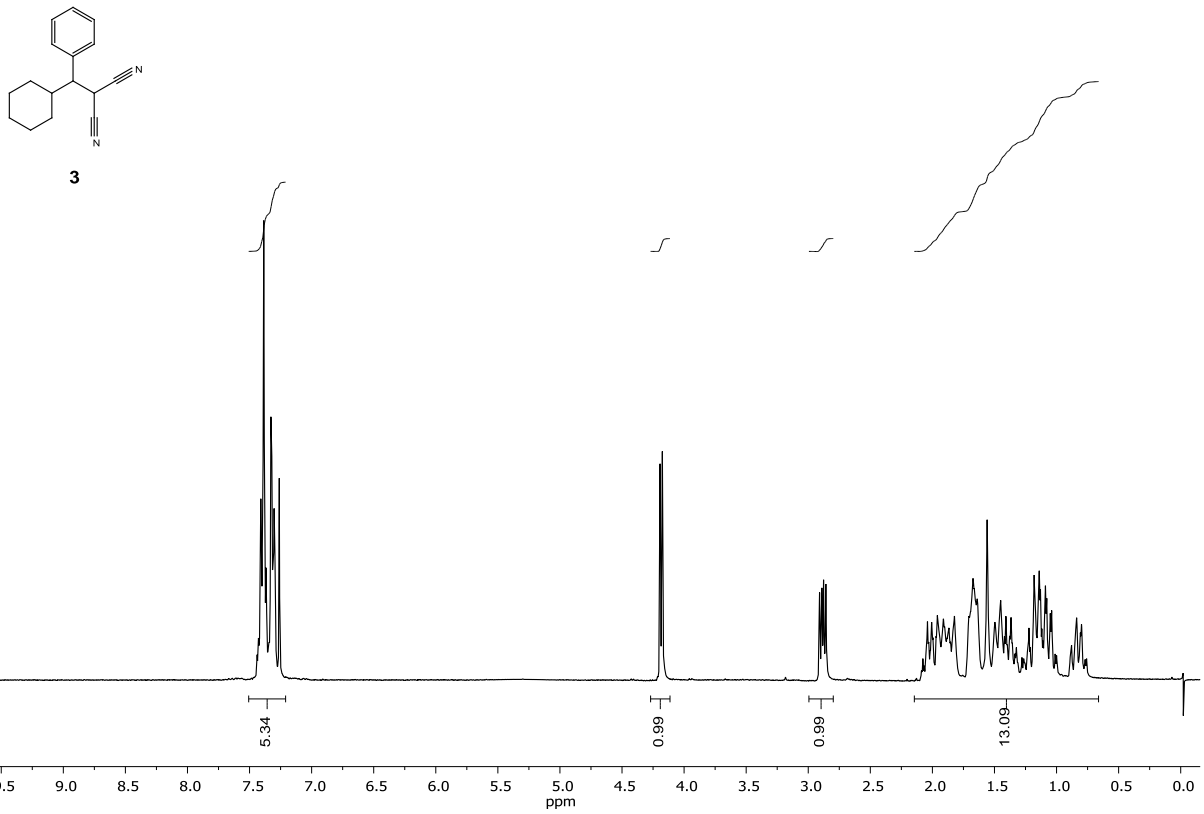
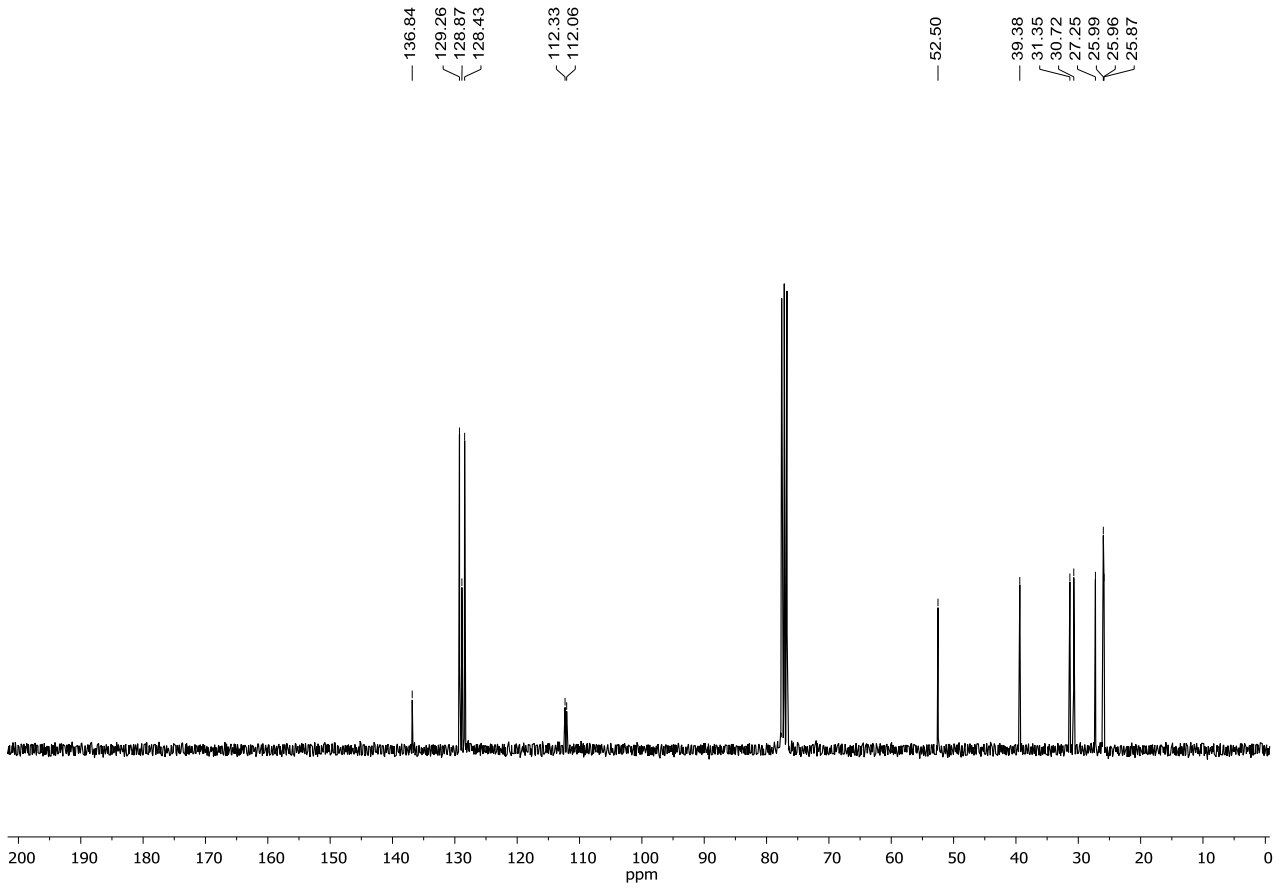
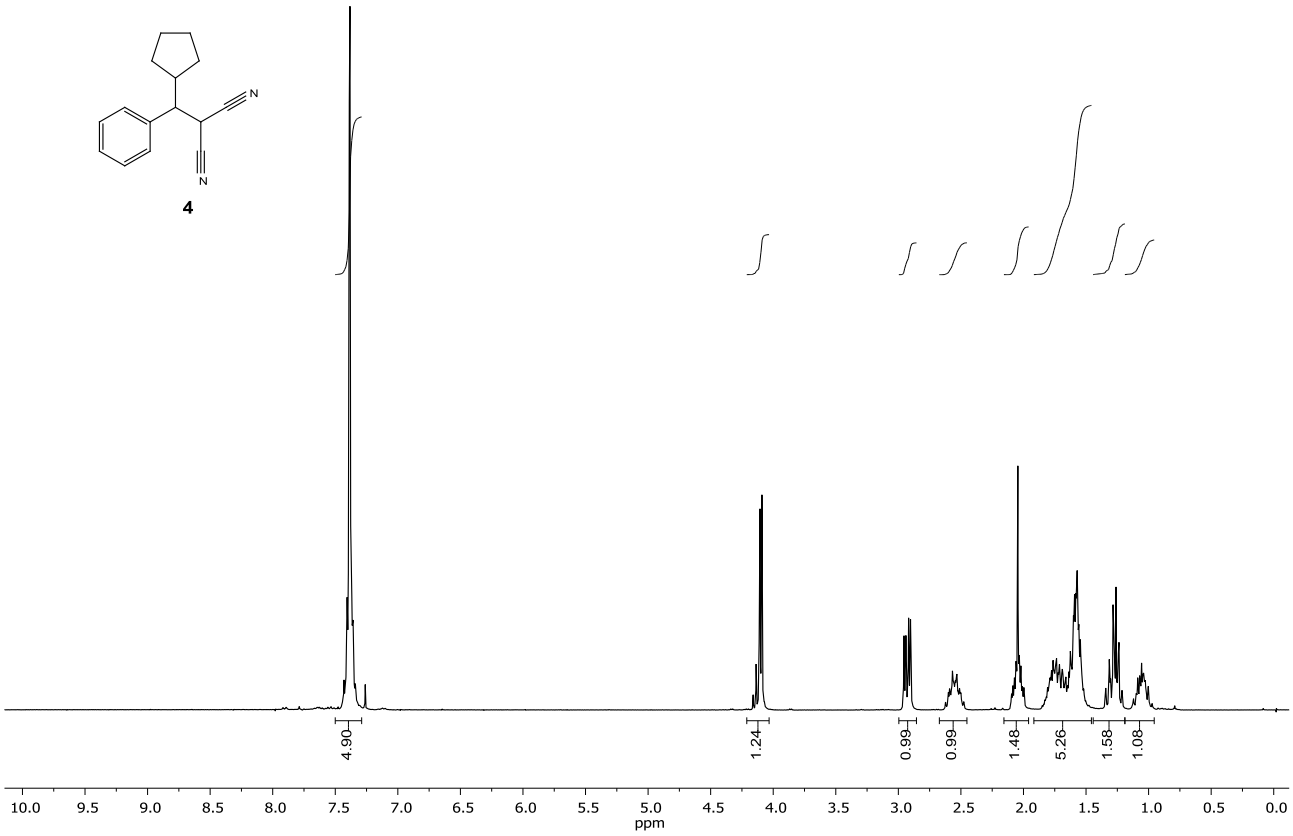
8. Copy of ^{1}H and ^{13}C NMR of synthesized compounds



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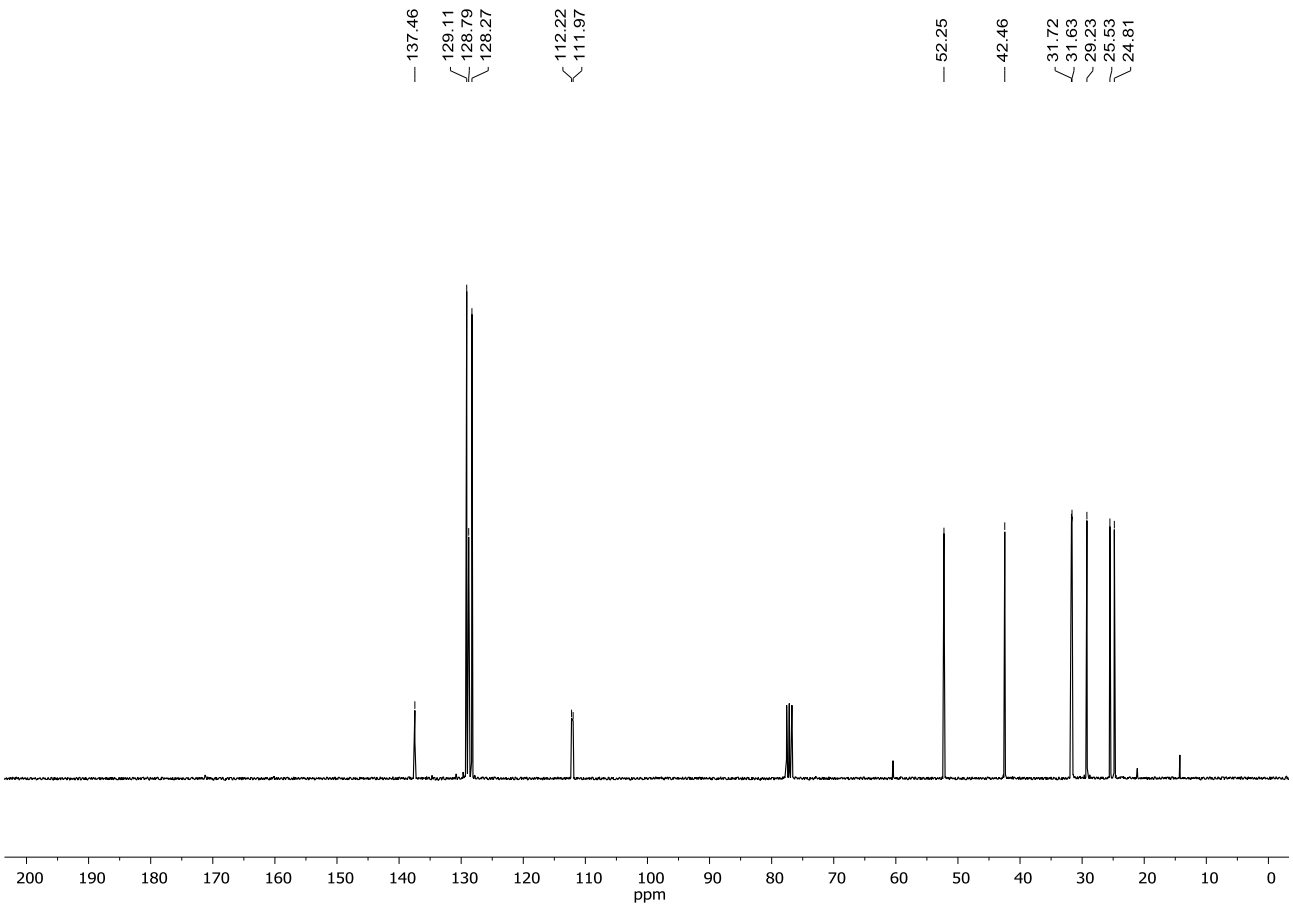
0.99
0.99
1.48
5.26
1.58
1.08
ppm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128.79
128.27
112.22
111.97
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42.46
31.72
31.63
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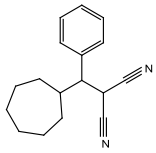
25.53
24.81
ppm



5

5.48
0.99
0.98
0.96
1.03
13.72
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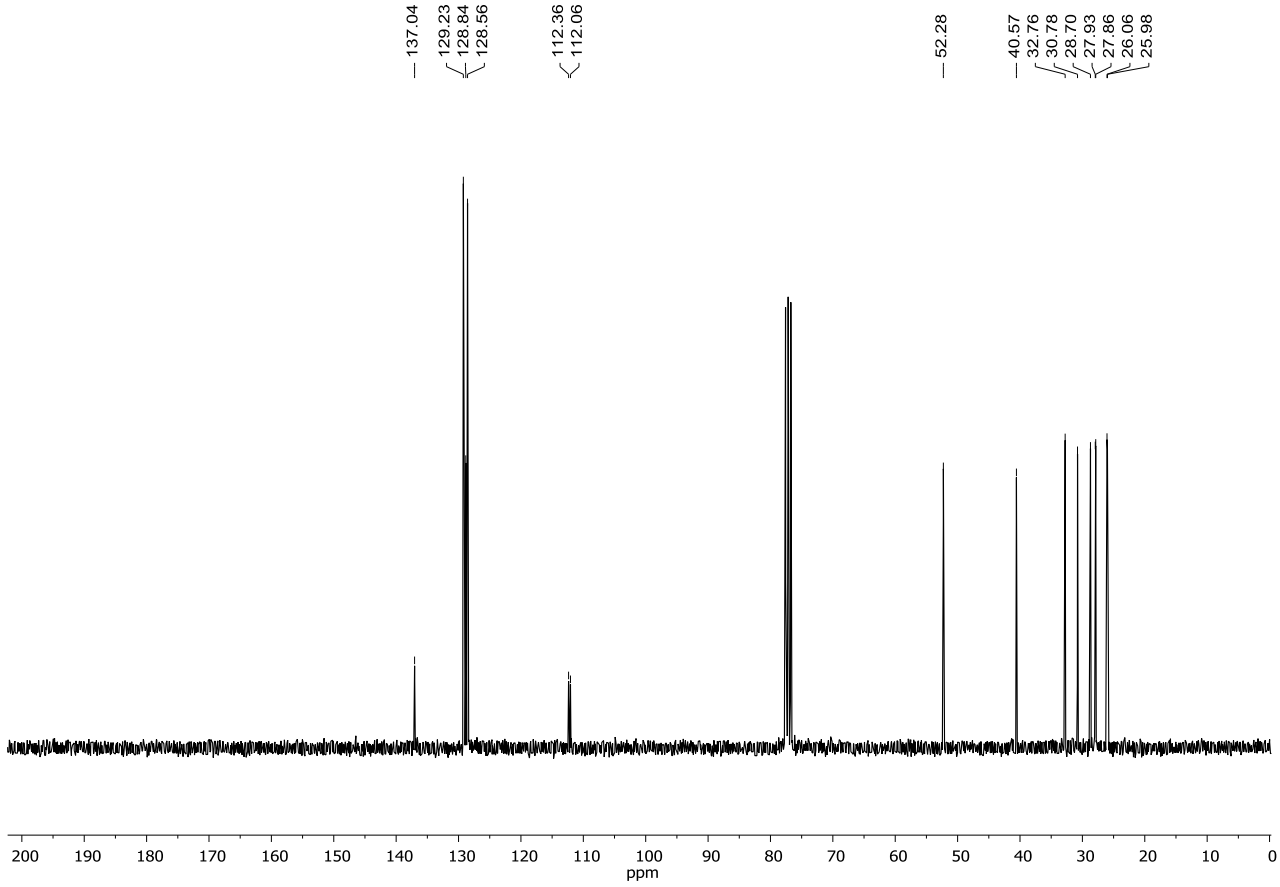
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129.23
128.84
128.56
112.36
112.06
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40.57
32.76
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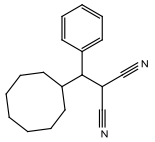
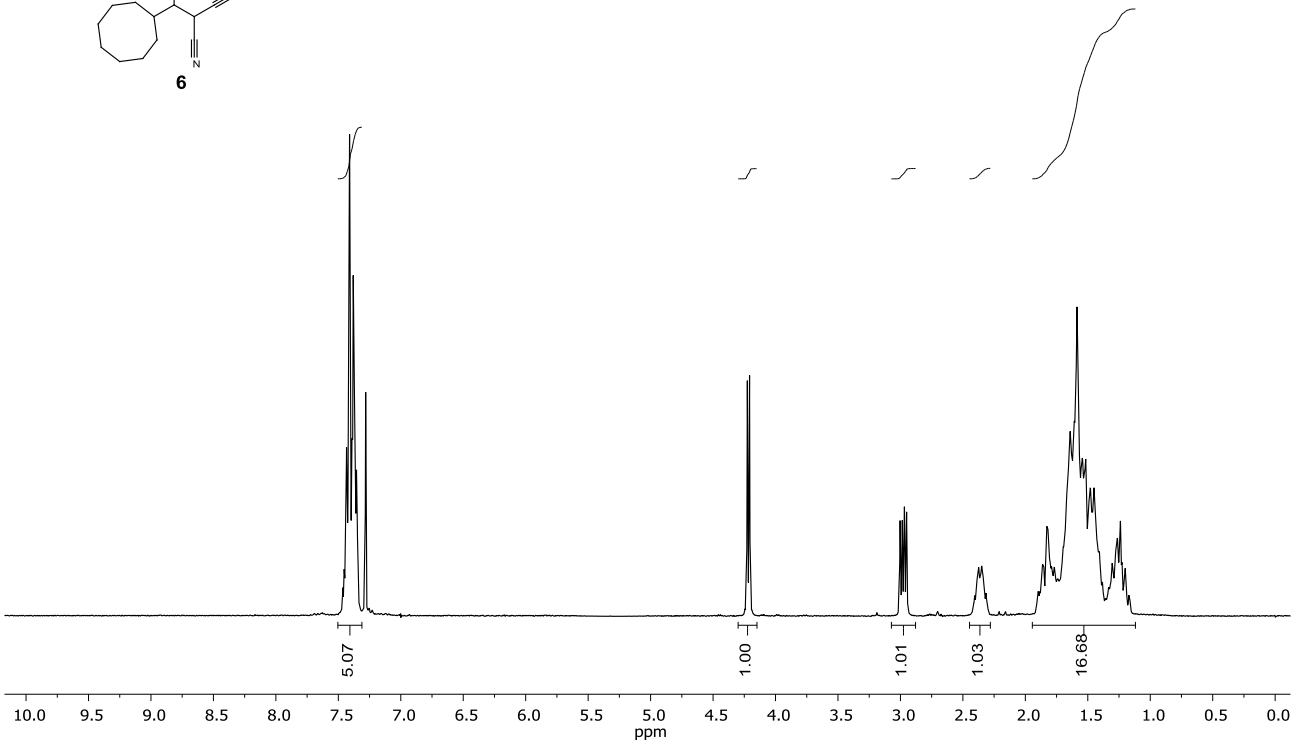
27.86
26.06
25.98
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N
N

6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1.00
1.01
1.03
16.68
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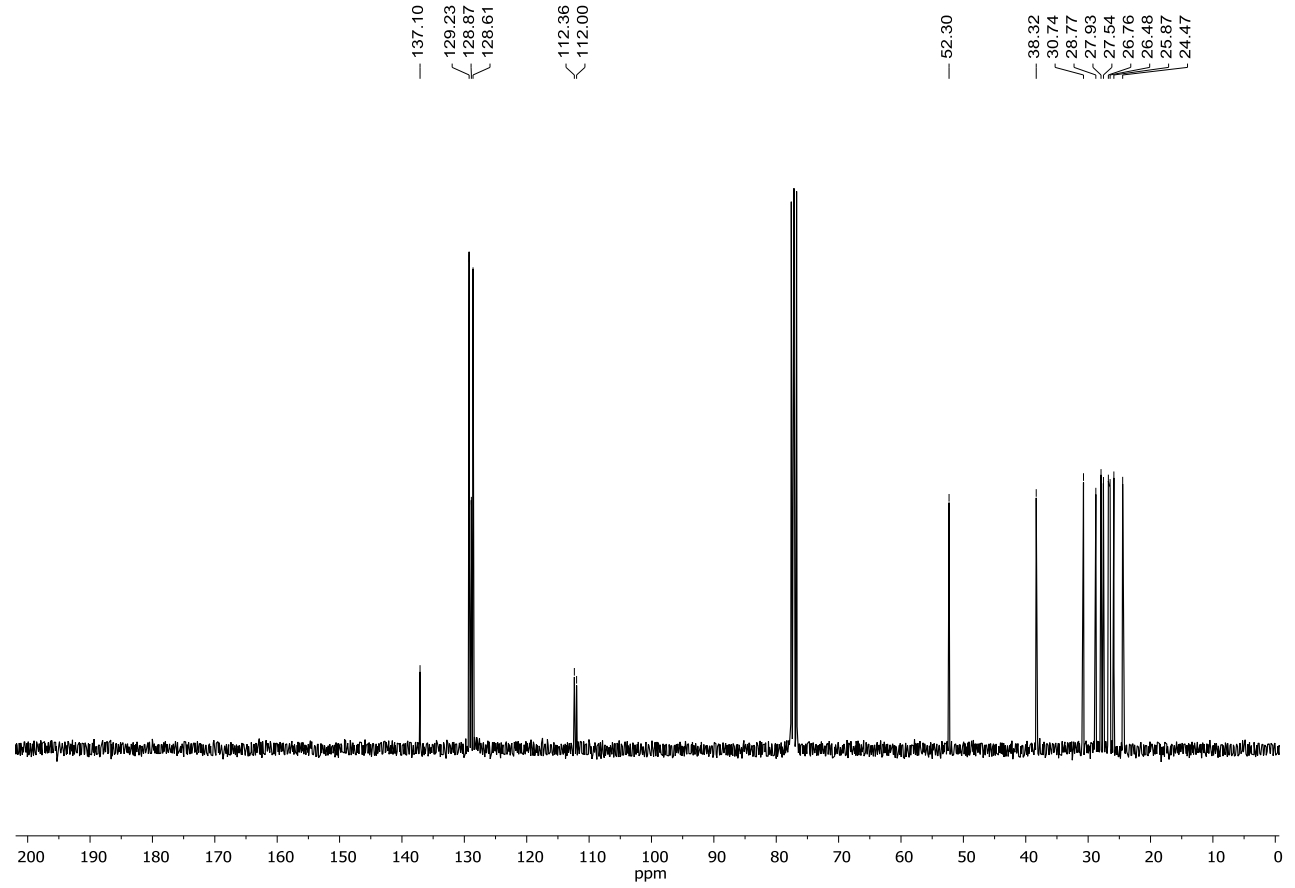
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128.61
112.36
112.00
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38.32
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25.87
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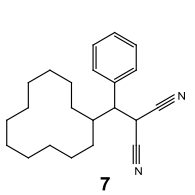
ppm


N
N

7

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1.00
1.00
1.04
23.45
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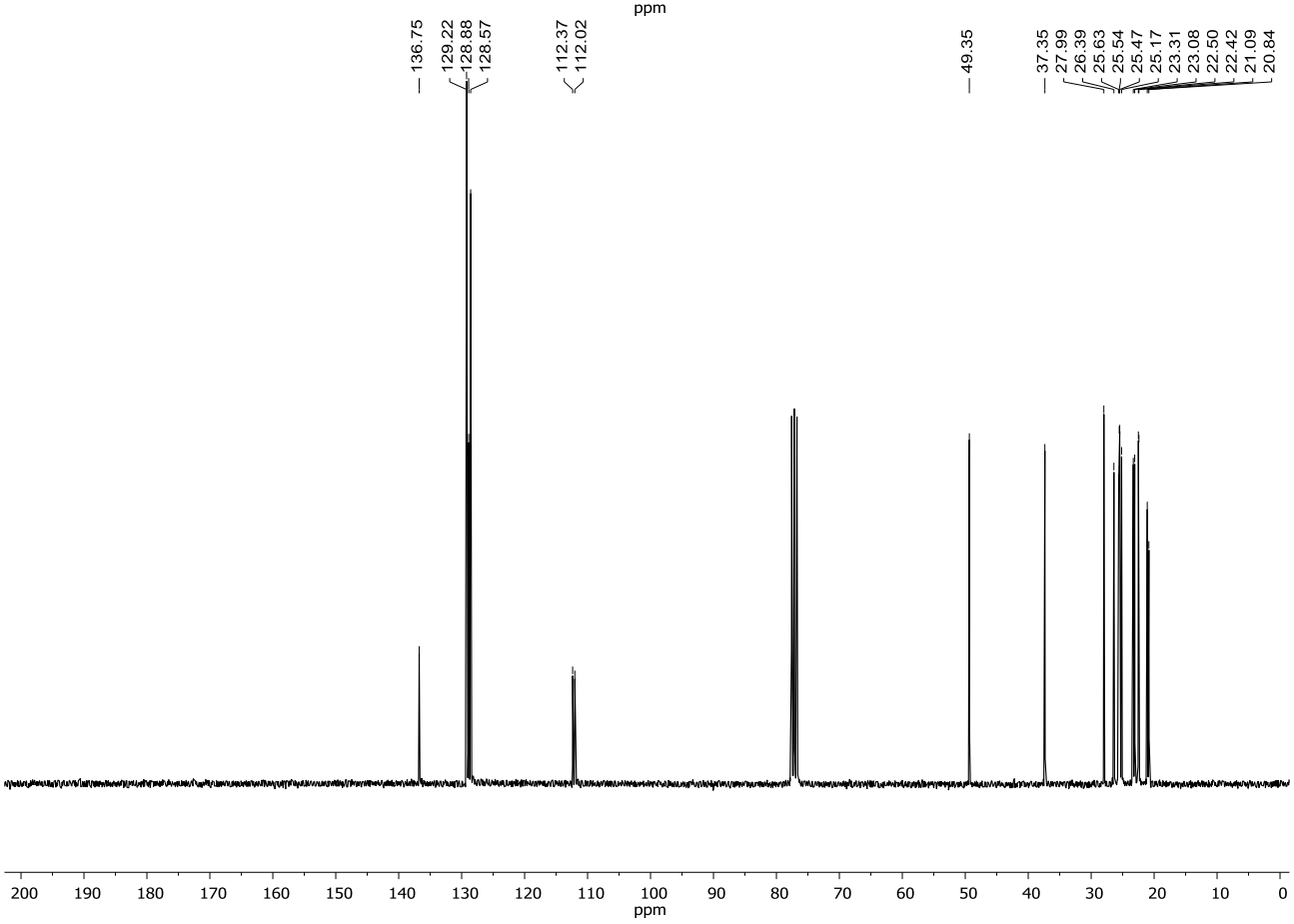
ppm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112.02
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37.35
27.99
26.39
25.63
25.54
25.47
25.17
23.31
23.08
22.50
22.42
21.09
20.84
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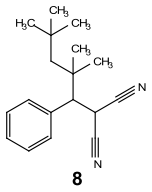
ppm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H3C
CH3
CH3
CH3
N
N

8

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1.00
1.03
2.11
3.36
3.55
9.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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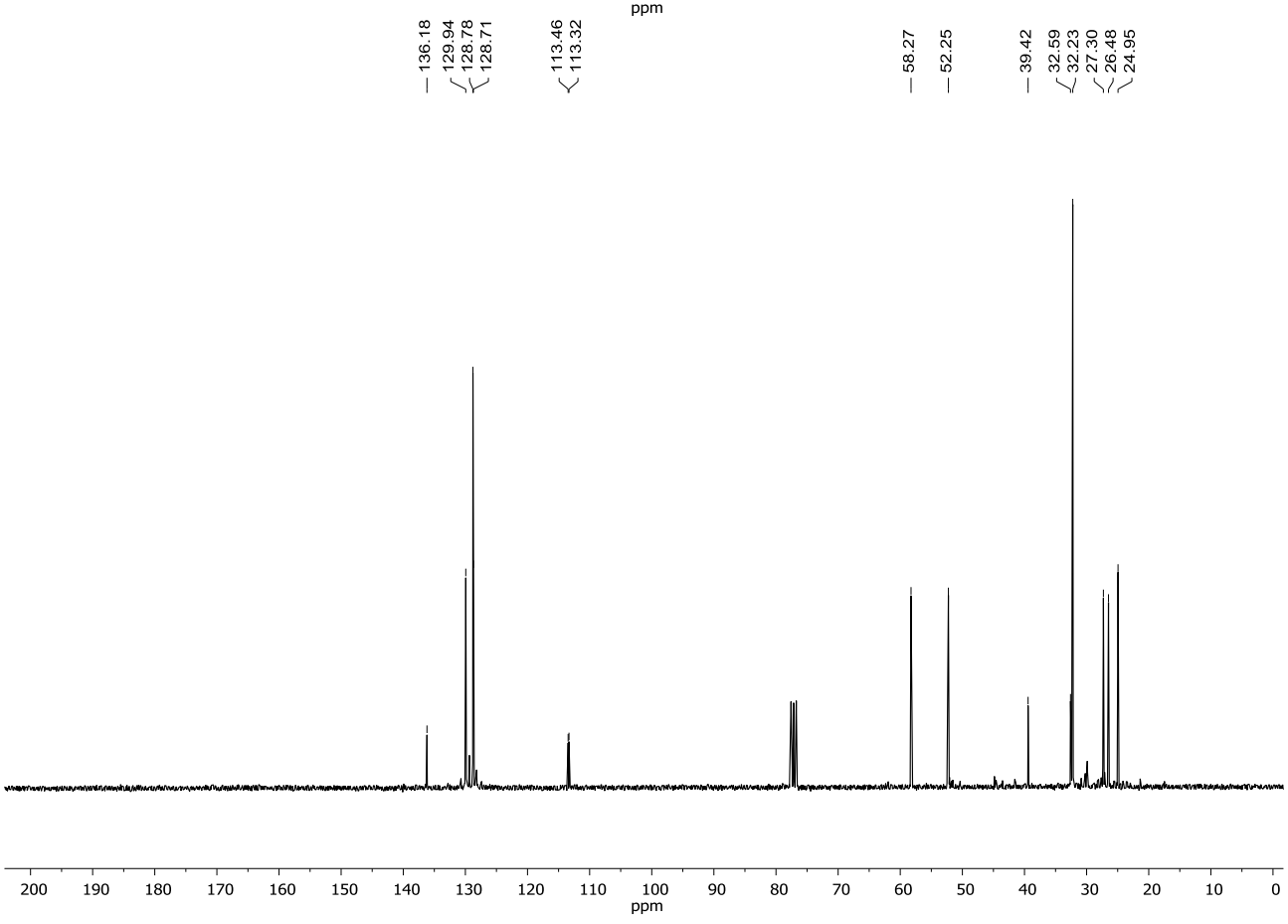
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58.27
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39.42
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32.23
27.30
26.48
24.95
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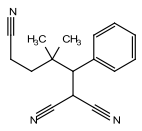
ppm


N
H3C
CH3
N
N

9

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1.00
1.01
2.18
2.08
6.16
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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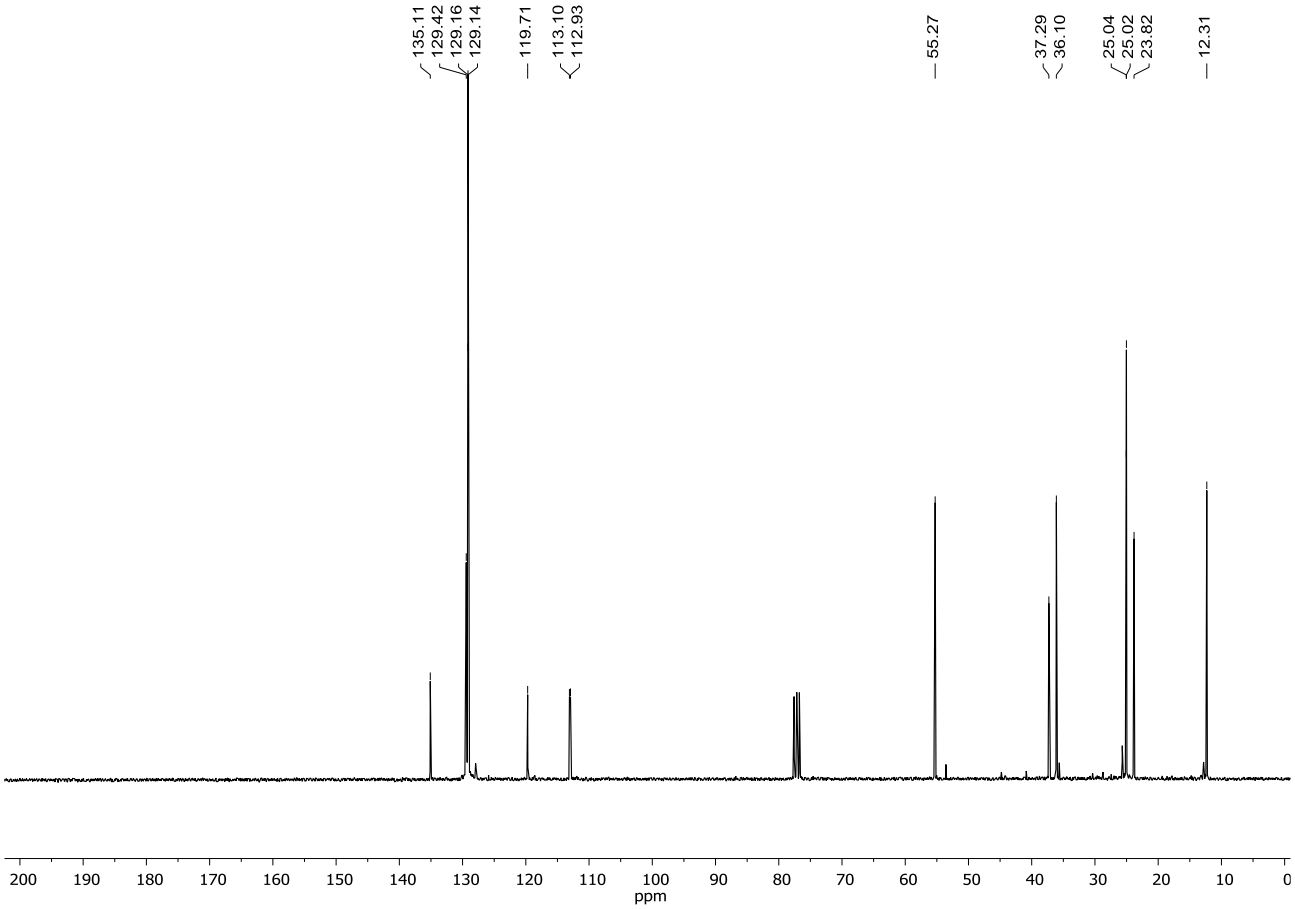
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55.27
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23.82
12.31
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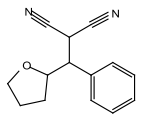
ppm



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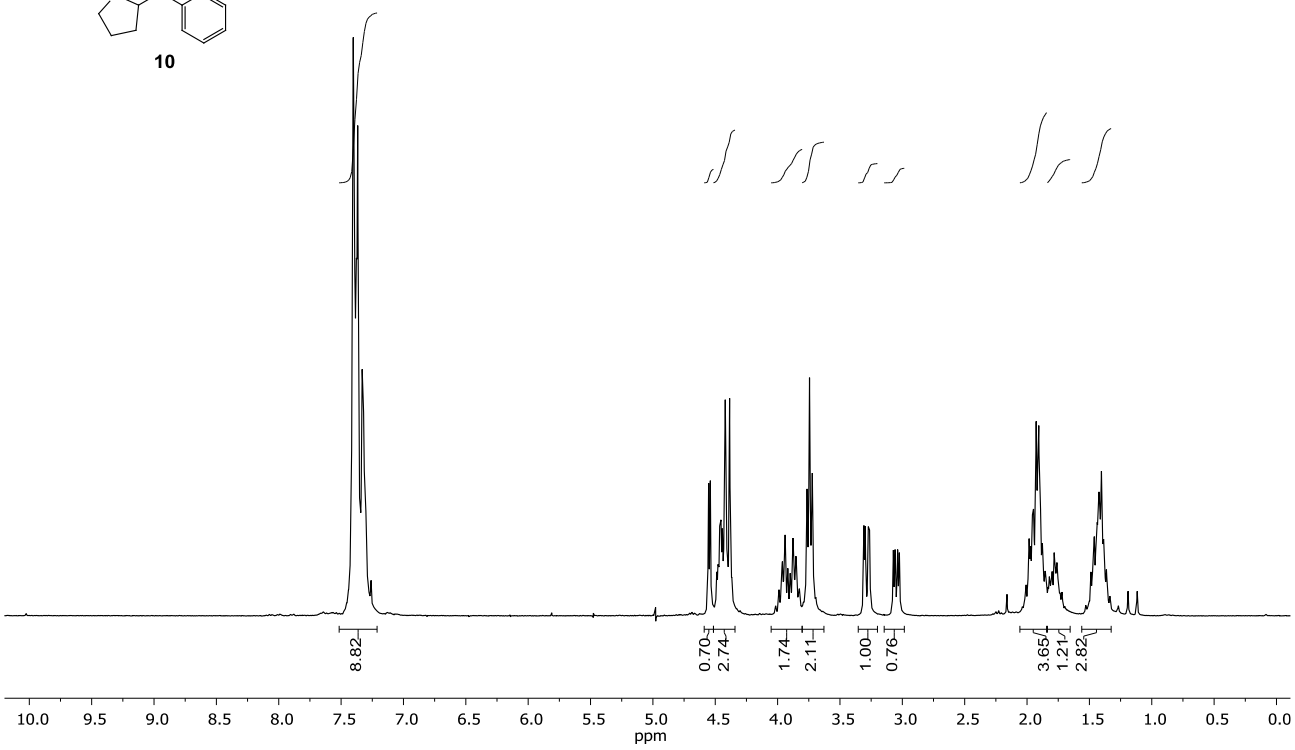
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1.00
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2.82
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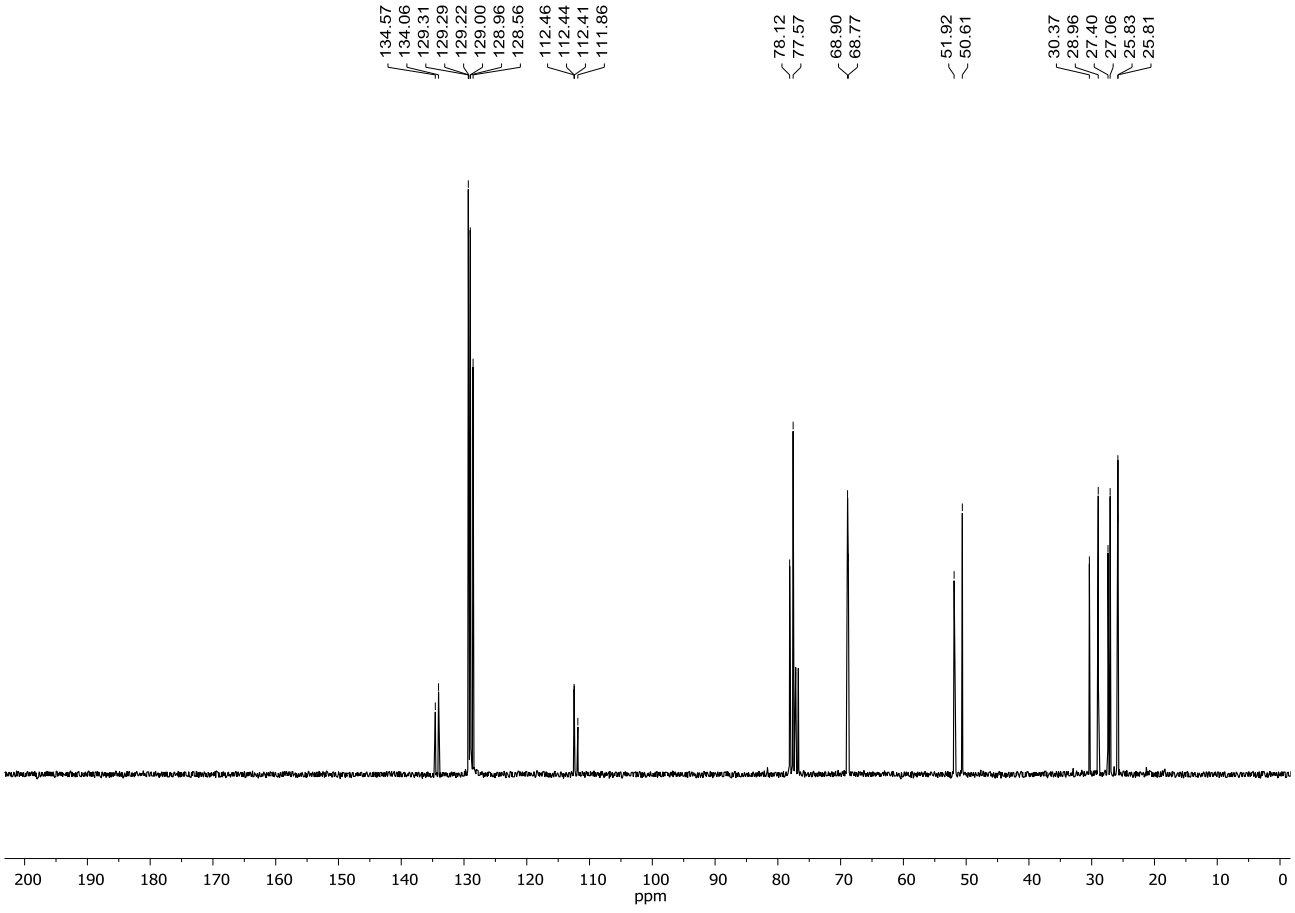
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68.77
51.92
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30.37
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27.40
27.06
25.83
25.81
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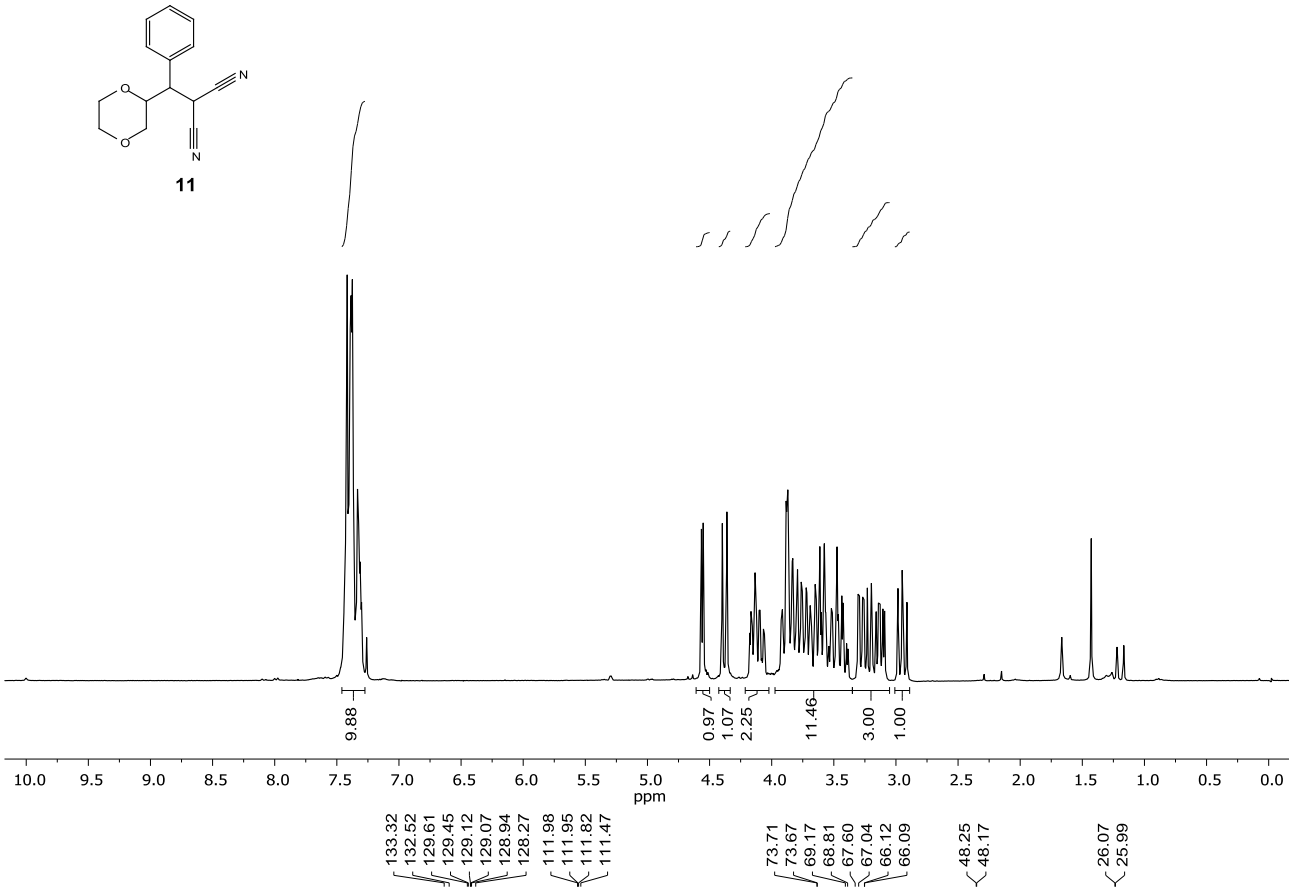
ppm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11.46
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1.00
ppm
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132.52
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128.27
111.98
111.95
111.82
111.47
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68.81
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67.04
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66.09
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48.17
26.07
25.99
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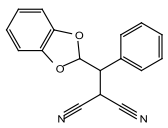

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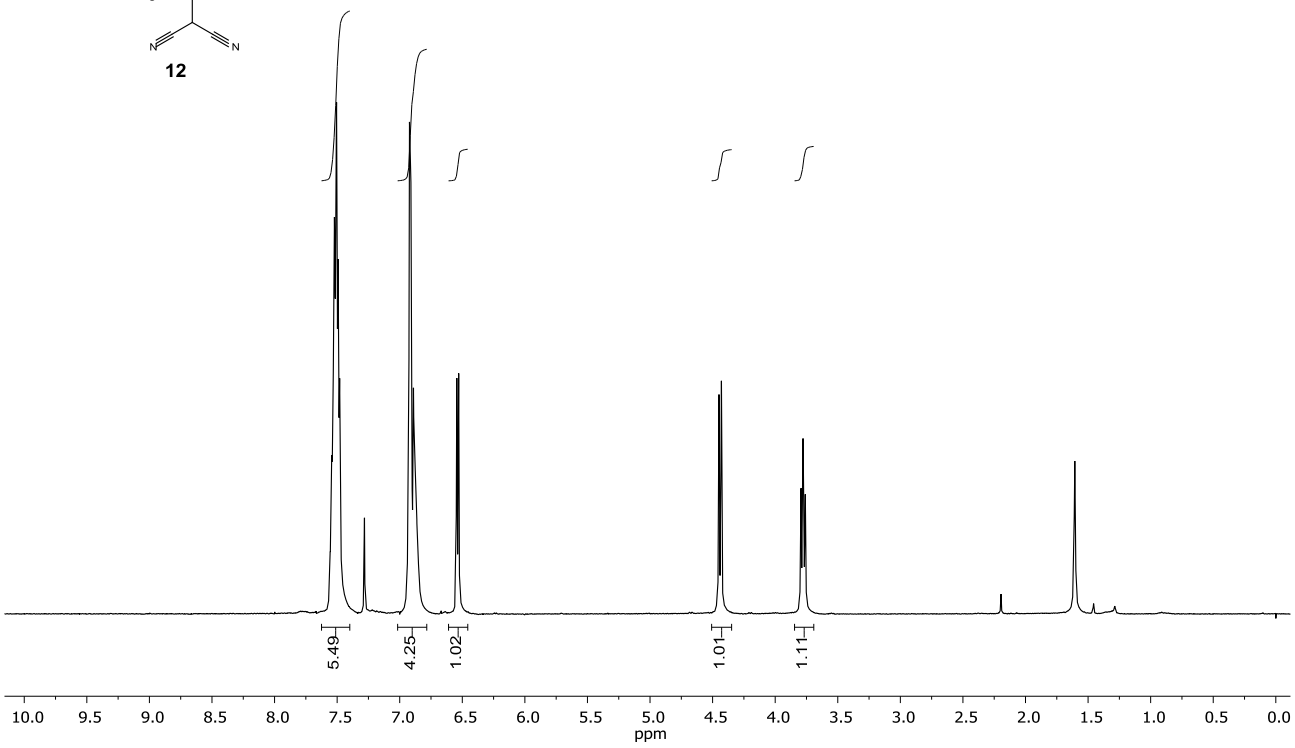
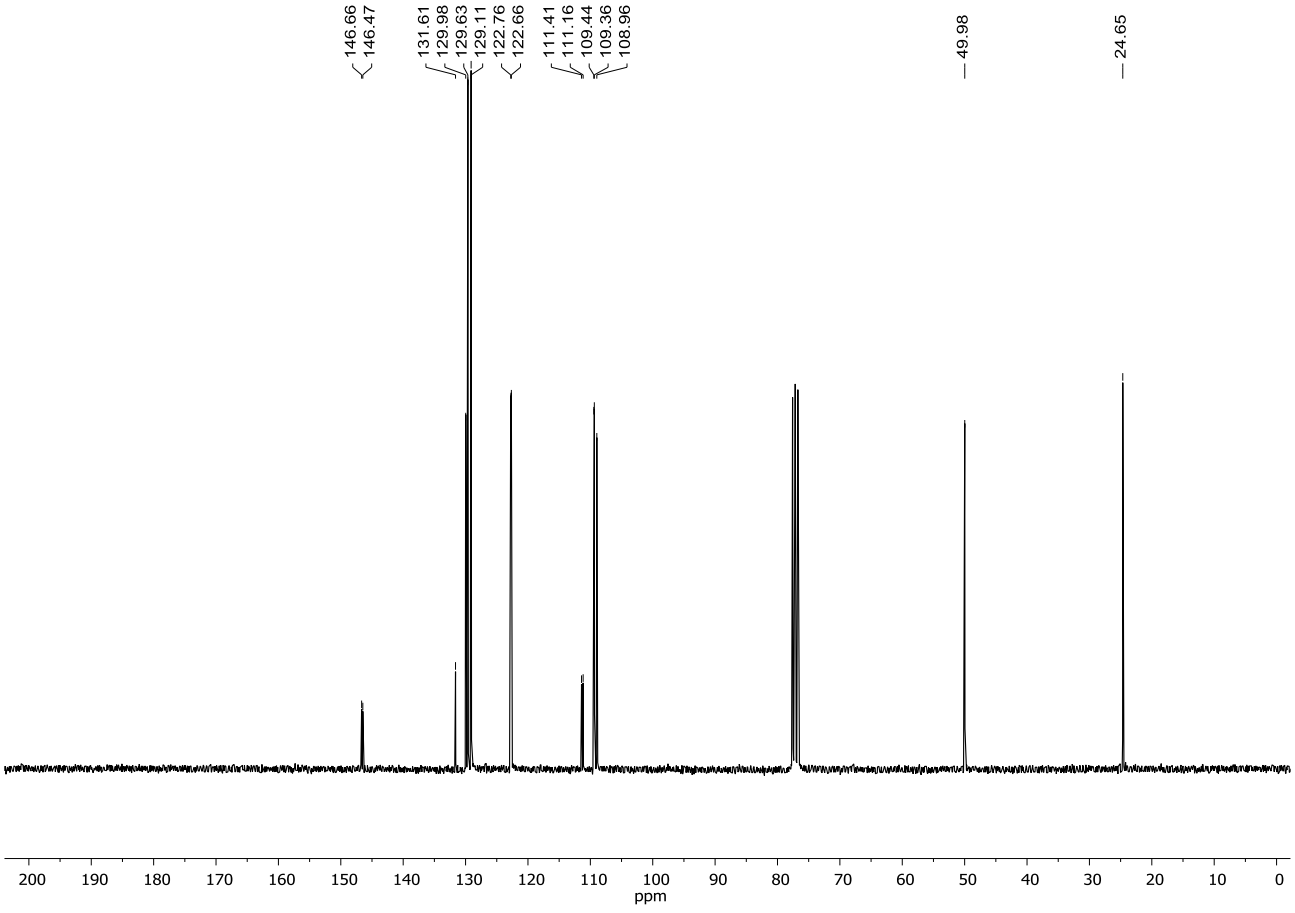

5.49
4.25
1.02
1.01
1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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129.63
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122.66
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49.98
24.65
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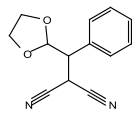

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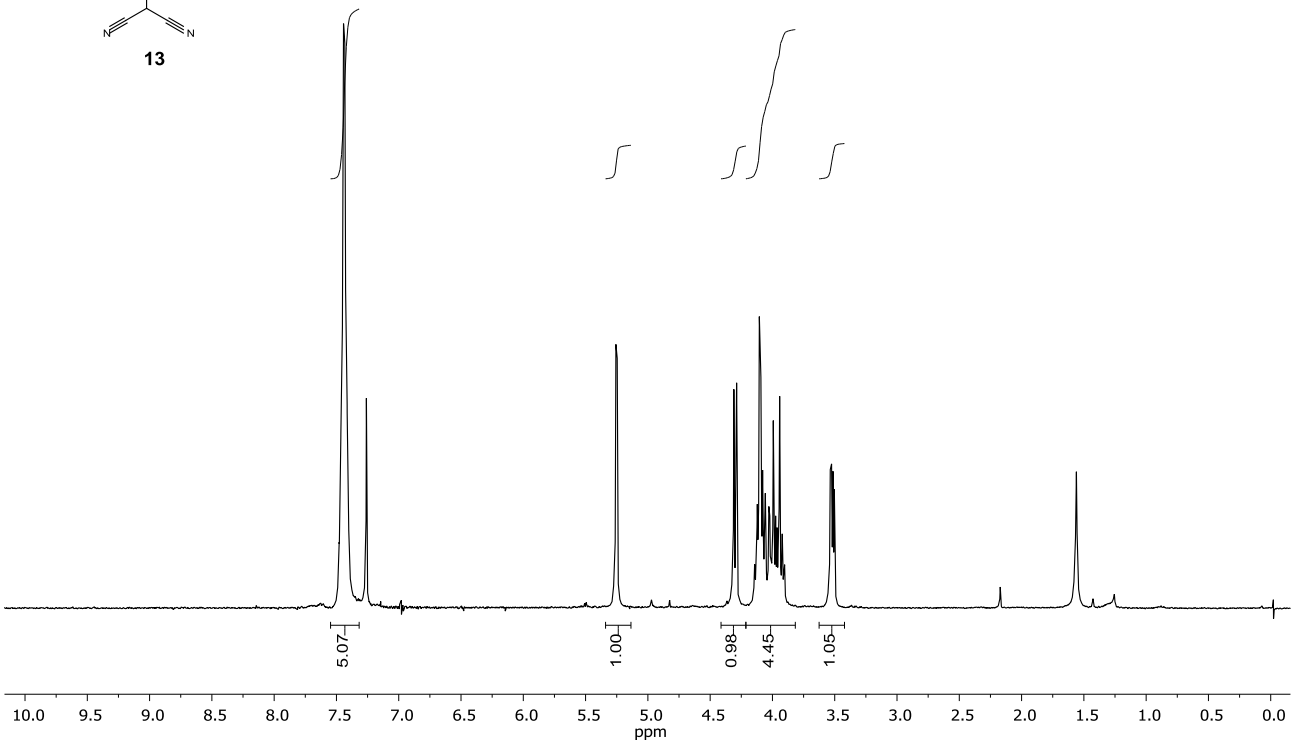
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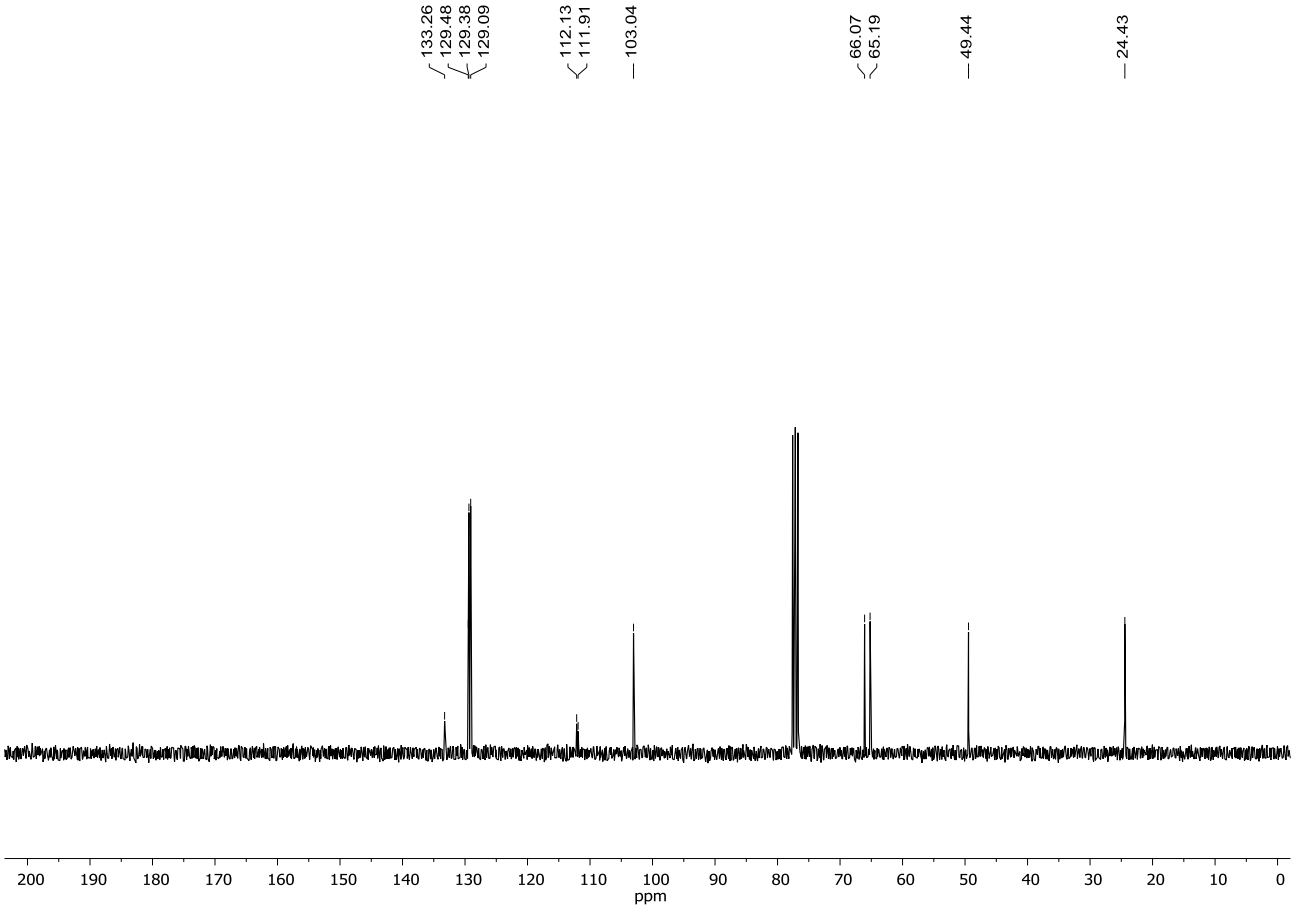
1.00
0.98
4.45
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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65.19
49.44
24.43
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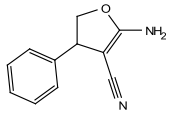
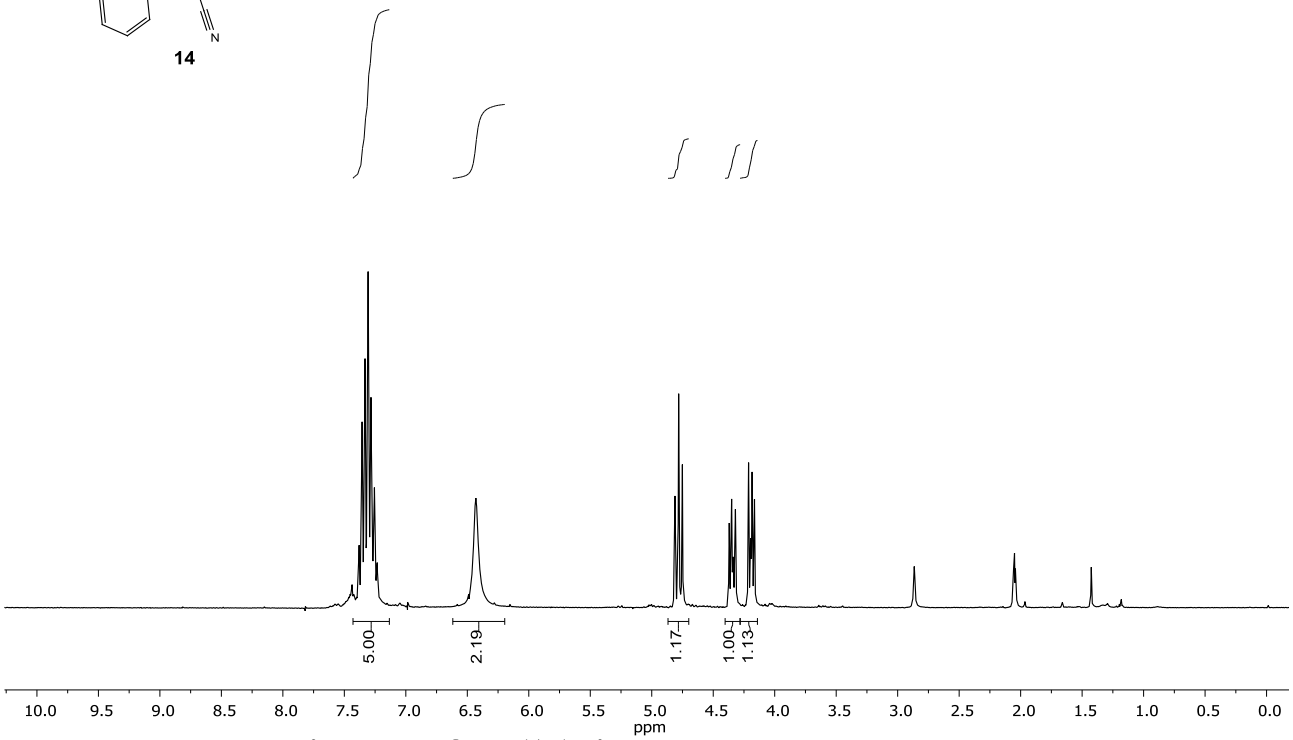
ppm


O
NH2
N

14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1.13
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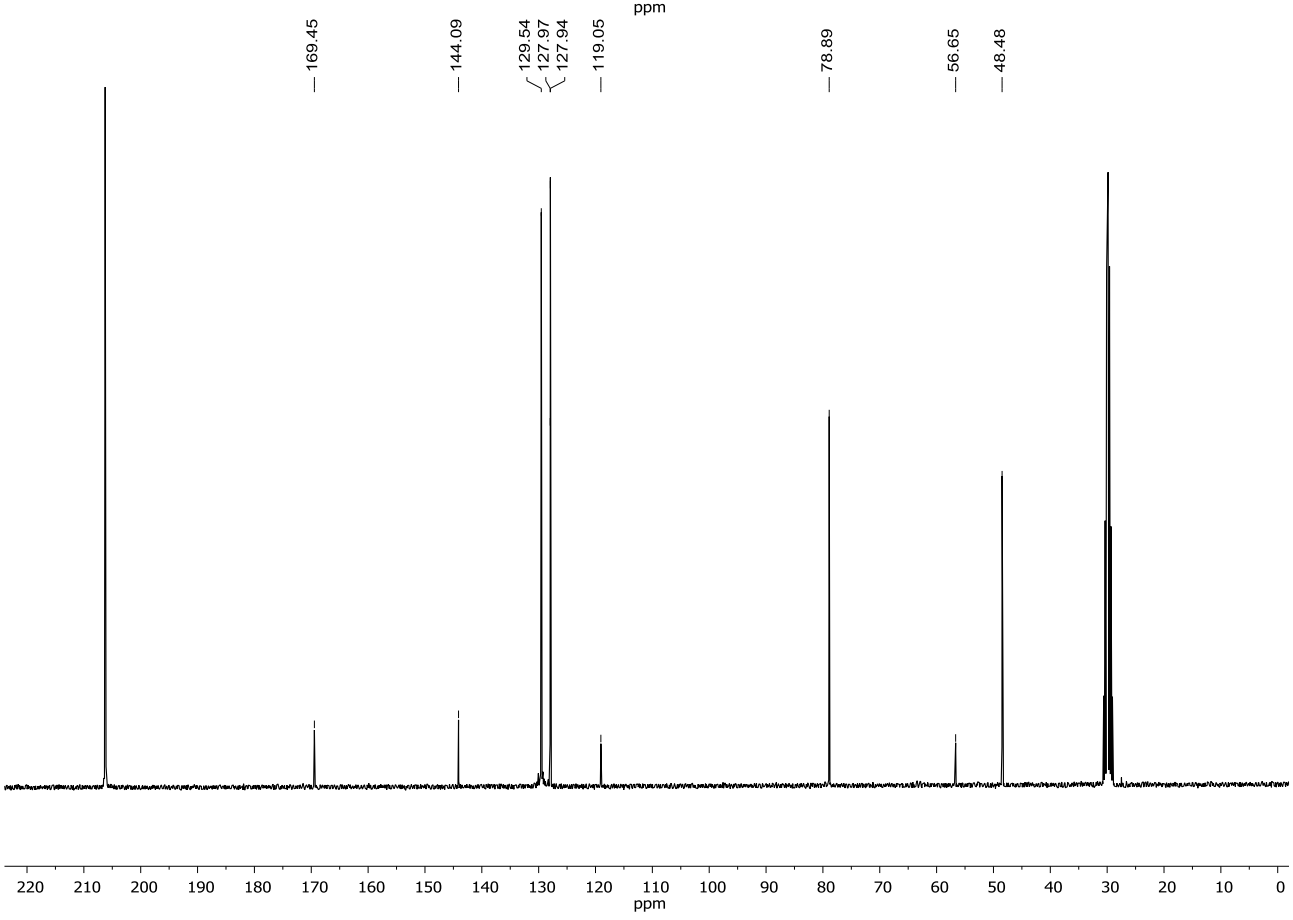
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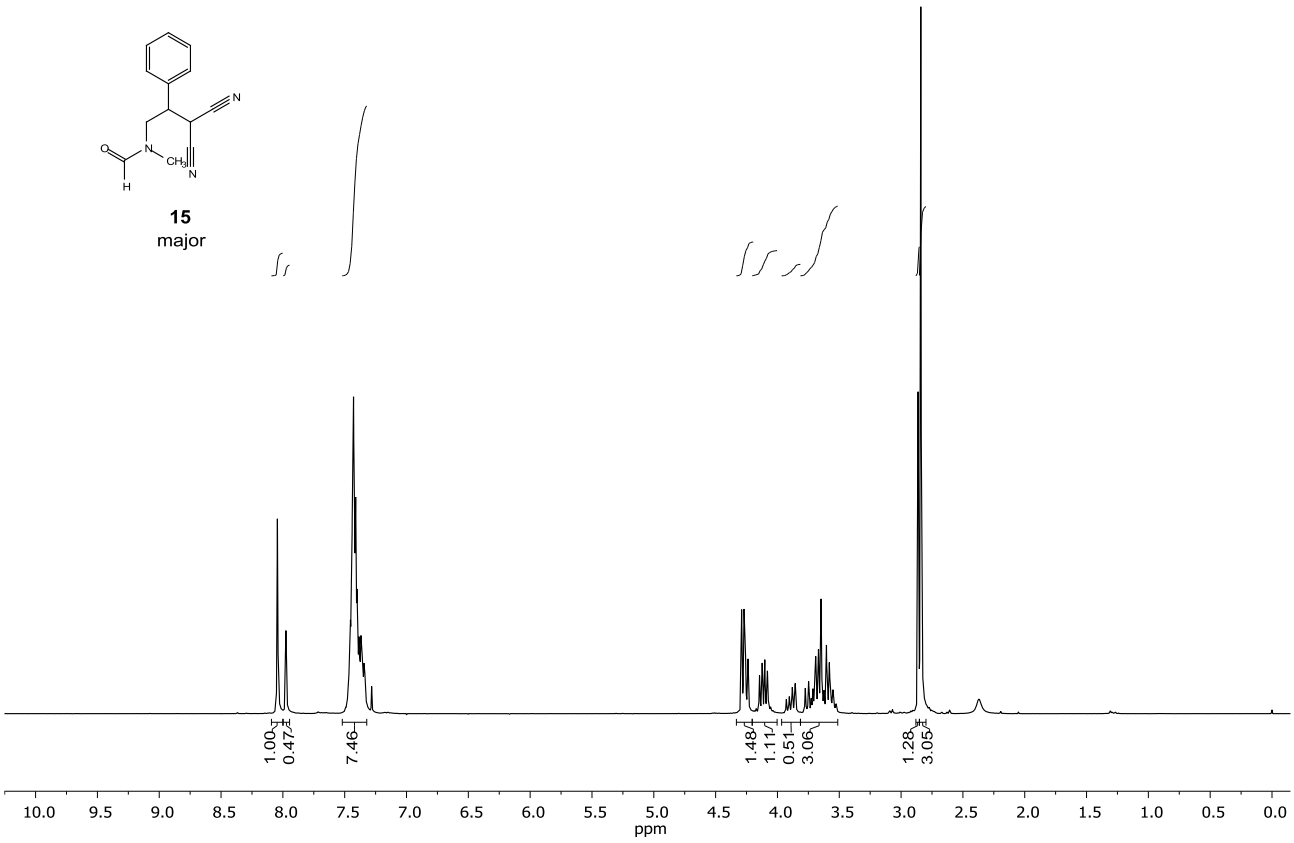
ppm


15
major
1.00
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1.48
1.11
0.51
3.06
1.28
3.05
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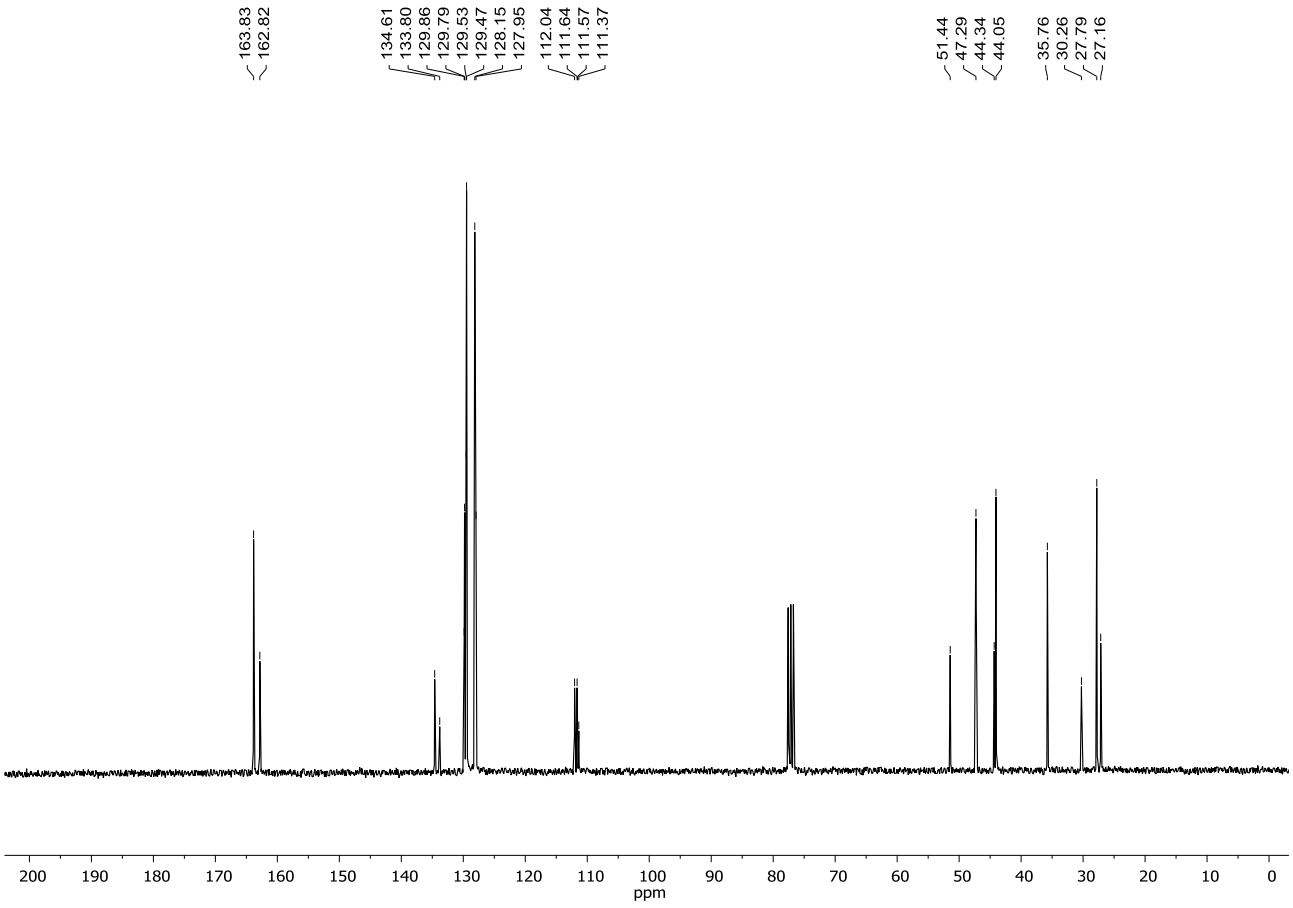
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127.95
112.04
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51.44
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35.76
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27.79
27.16
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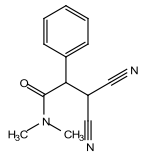
ppm



15'
minor

5.16
0.94
1.00
3.21
3.14
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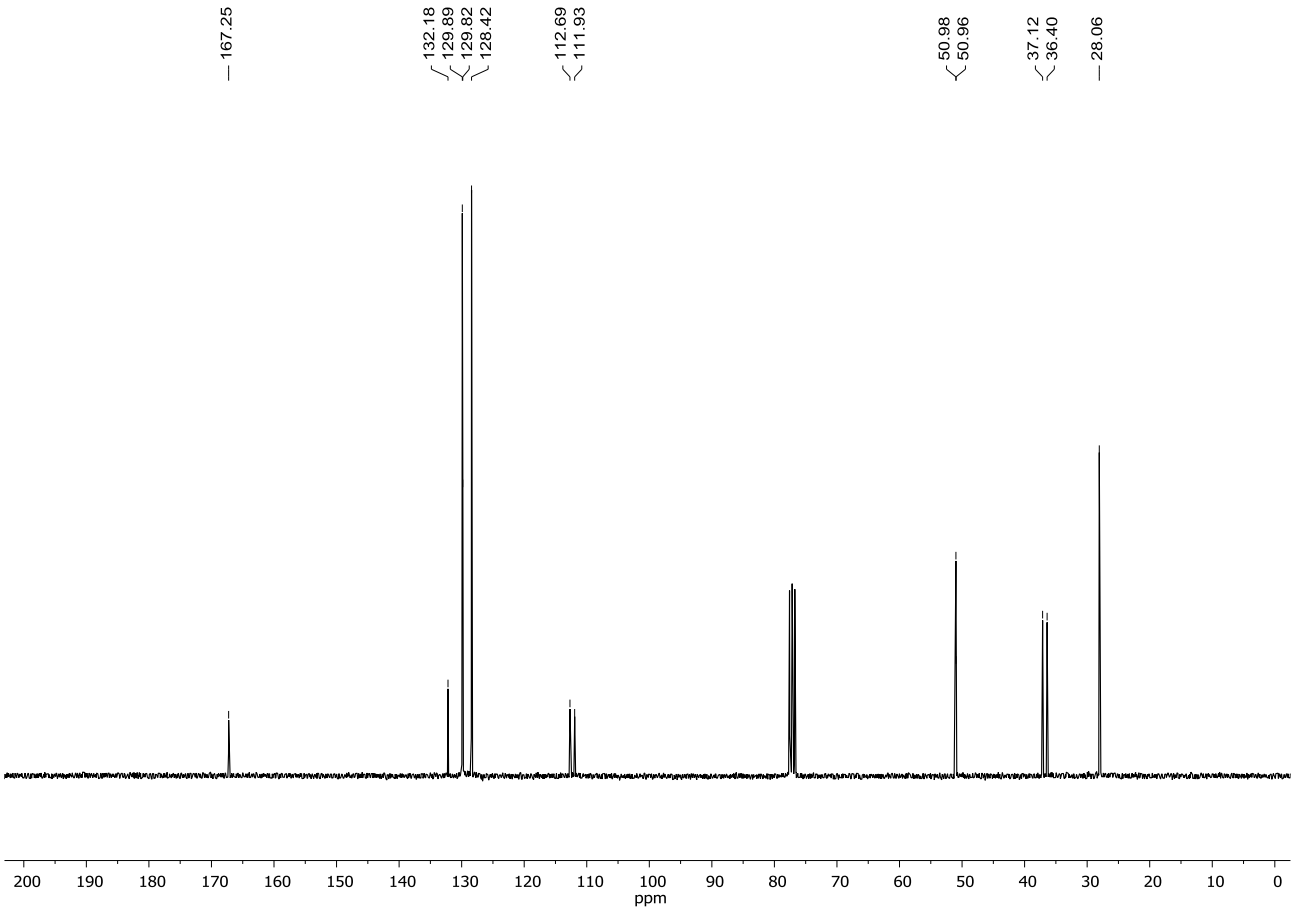
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128.42
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50.98
50.96
37.12
36.40
28.06
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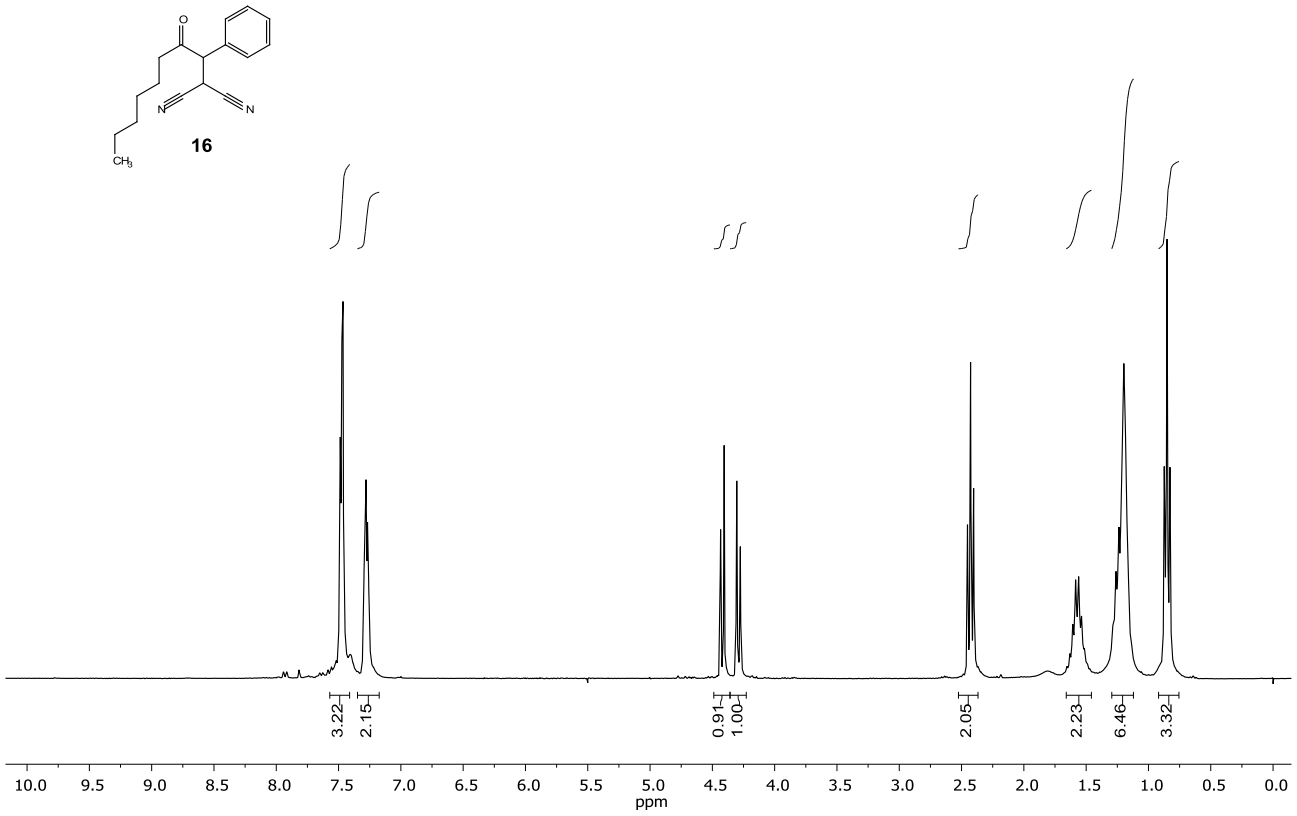
ppm


O
N
N
CH3
16
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0.91
1.00
2.05
2.23
6.46
3.32
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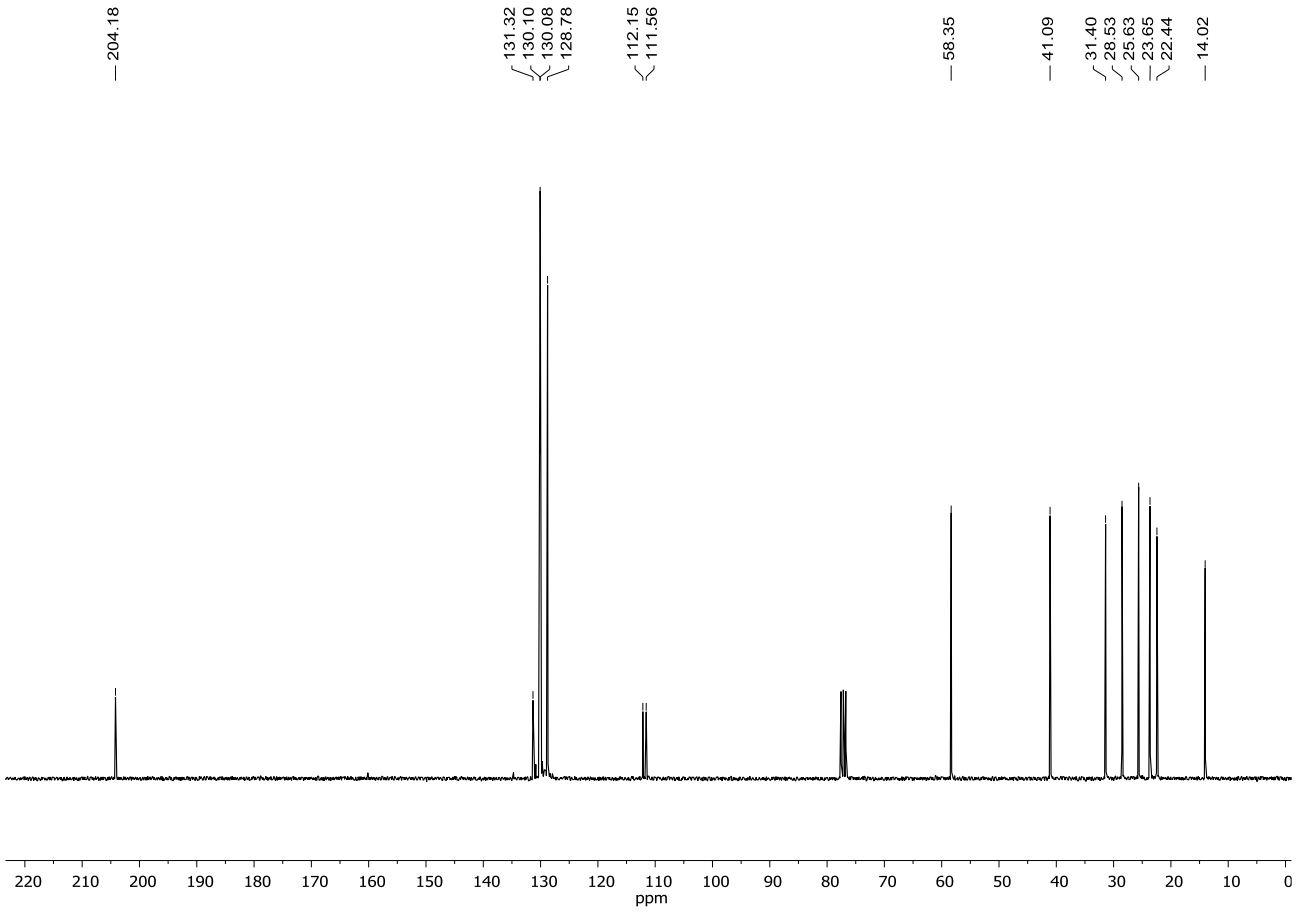
ppm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128.78
112.15
111.56
58.35
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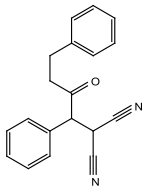
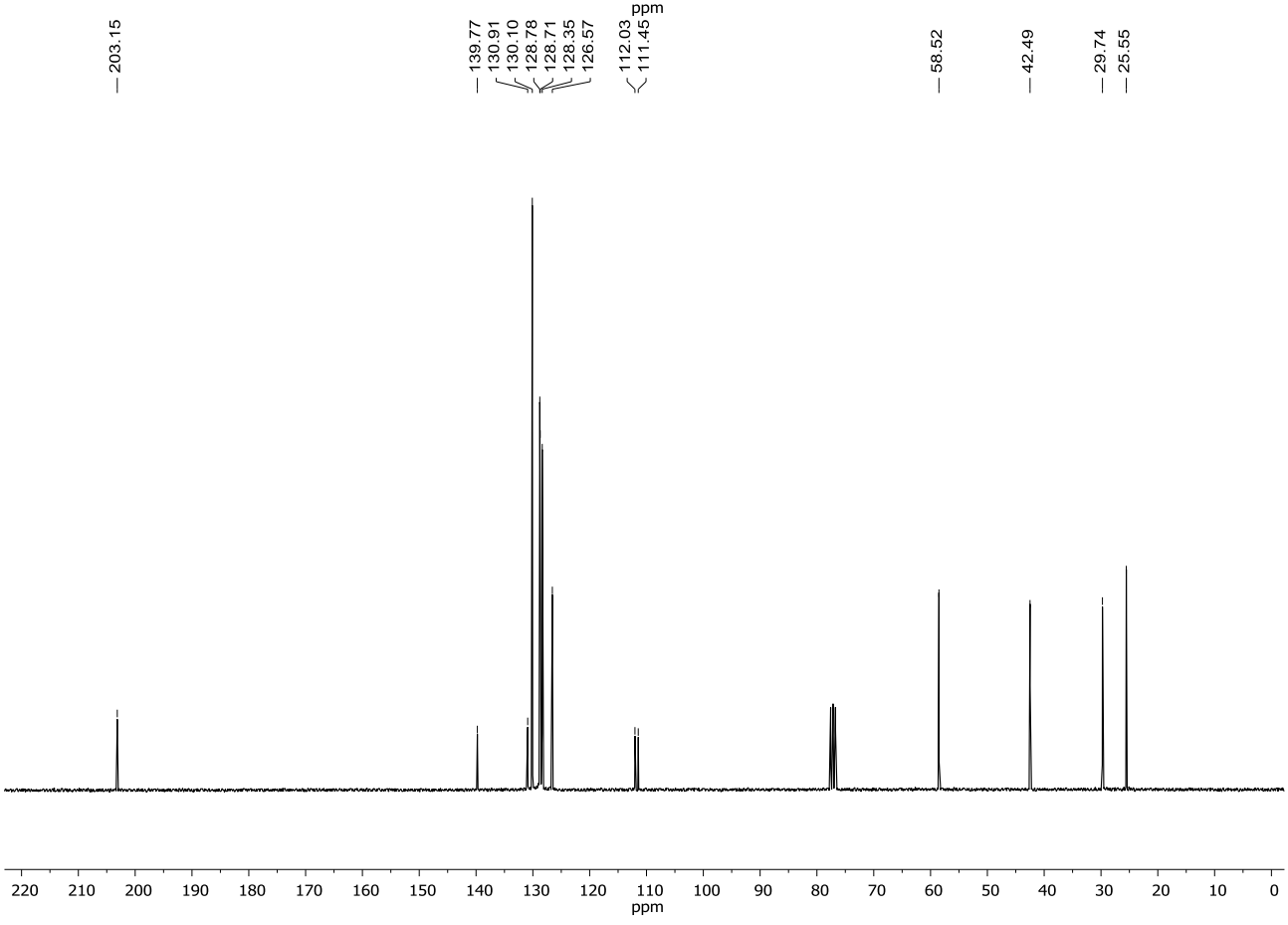
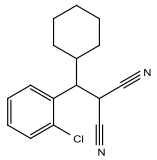
31.40
28.53
25.63
23.65
22.44
14.02
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
N
N

17

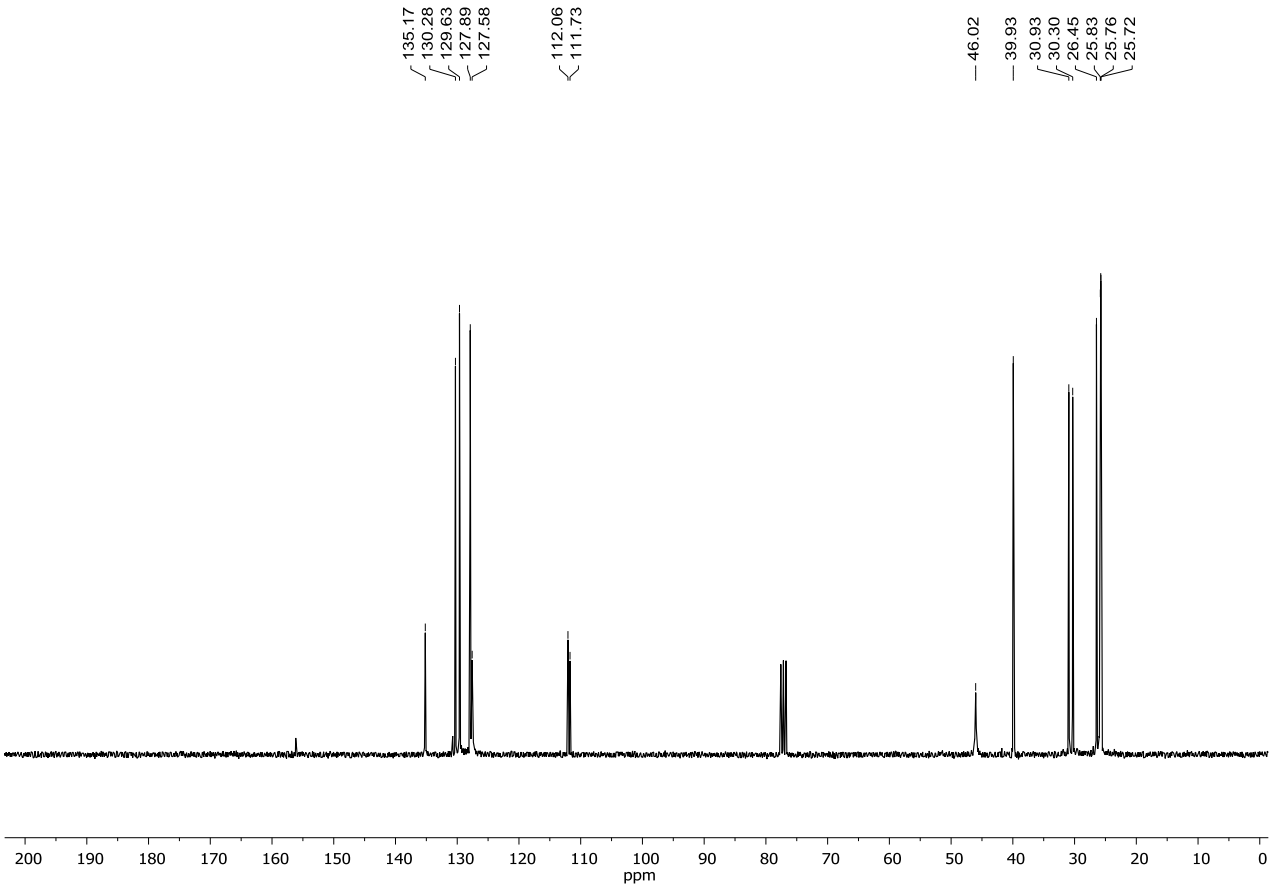
11.28
1.00
1.14
2.53
2.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

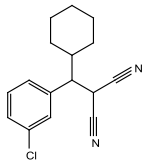

203.15
139.77
130.91
130.10
128.78
128.71
128.35
126.57
112.03
111.45
58.52
42.49
29.74
25.55
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N
Cl
N

18

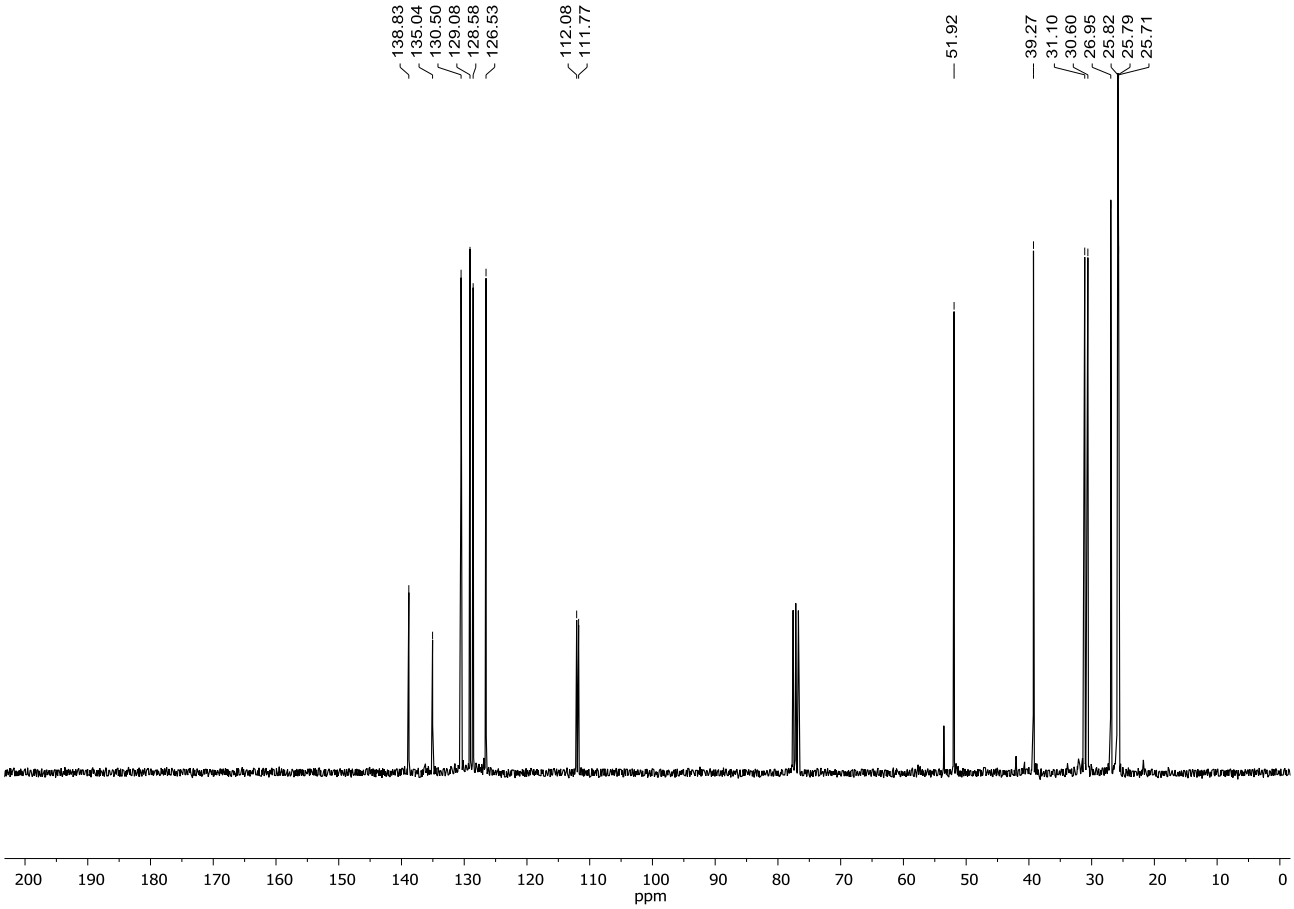
1.13
0.99
2.16
1.00
0.96
12.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

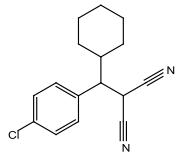

135.17
130.28
129.63
127.89
127.58
112.06
111.73
46.02
39.93
30.93
30.30
26.45
25.83
25.76
25.72
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


N
N
Cl

19

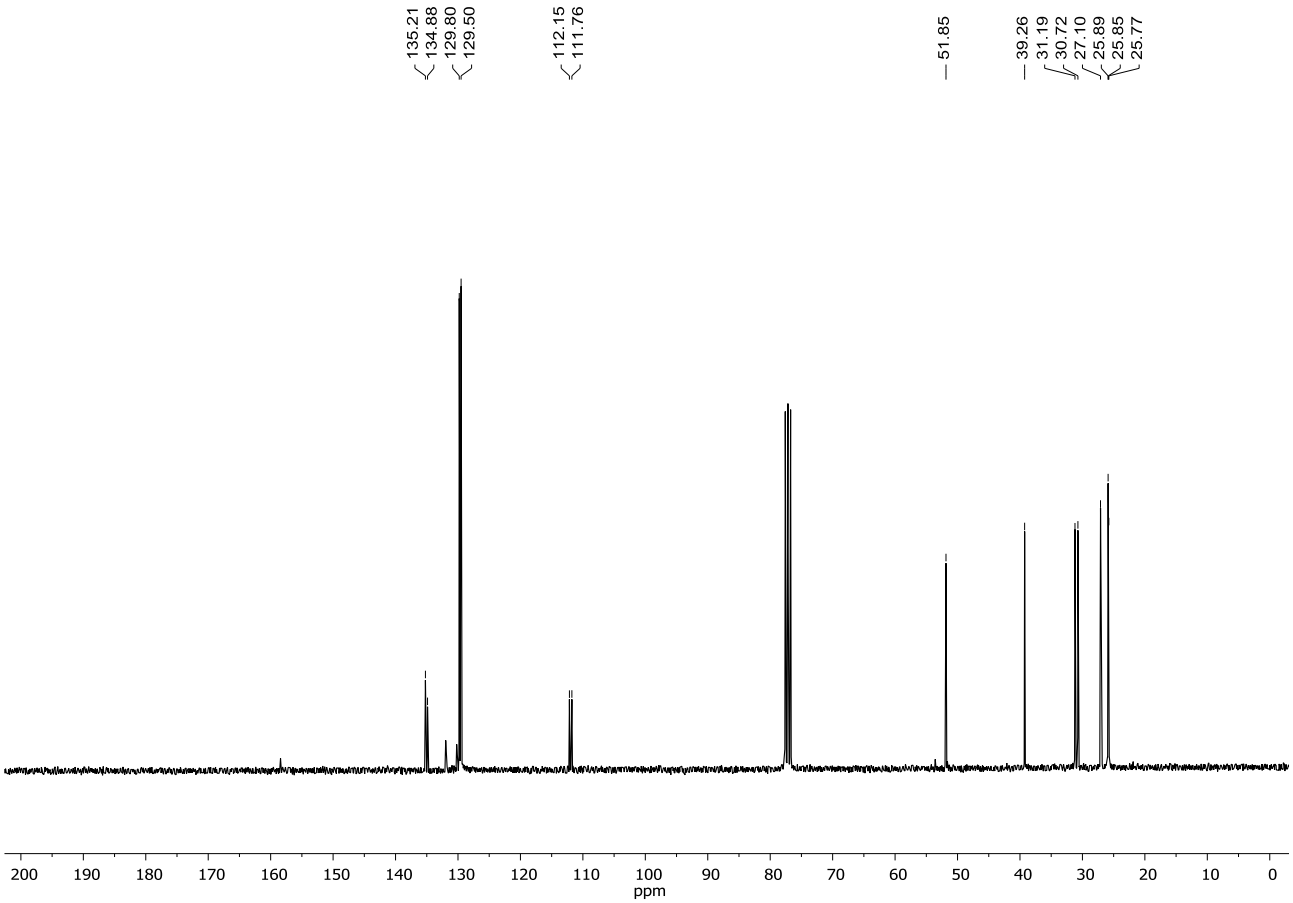
4.51
1.00
1.02
3.91
3.12
6.31
1.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

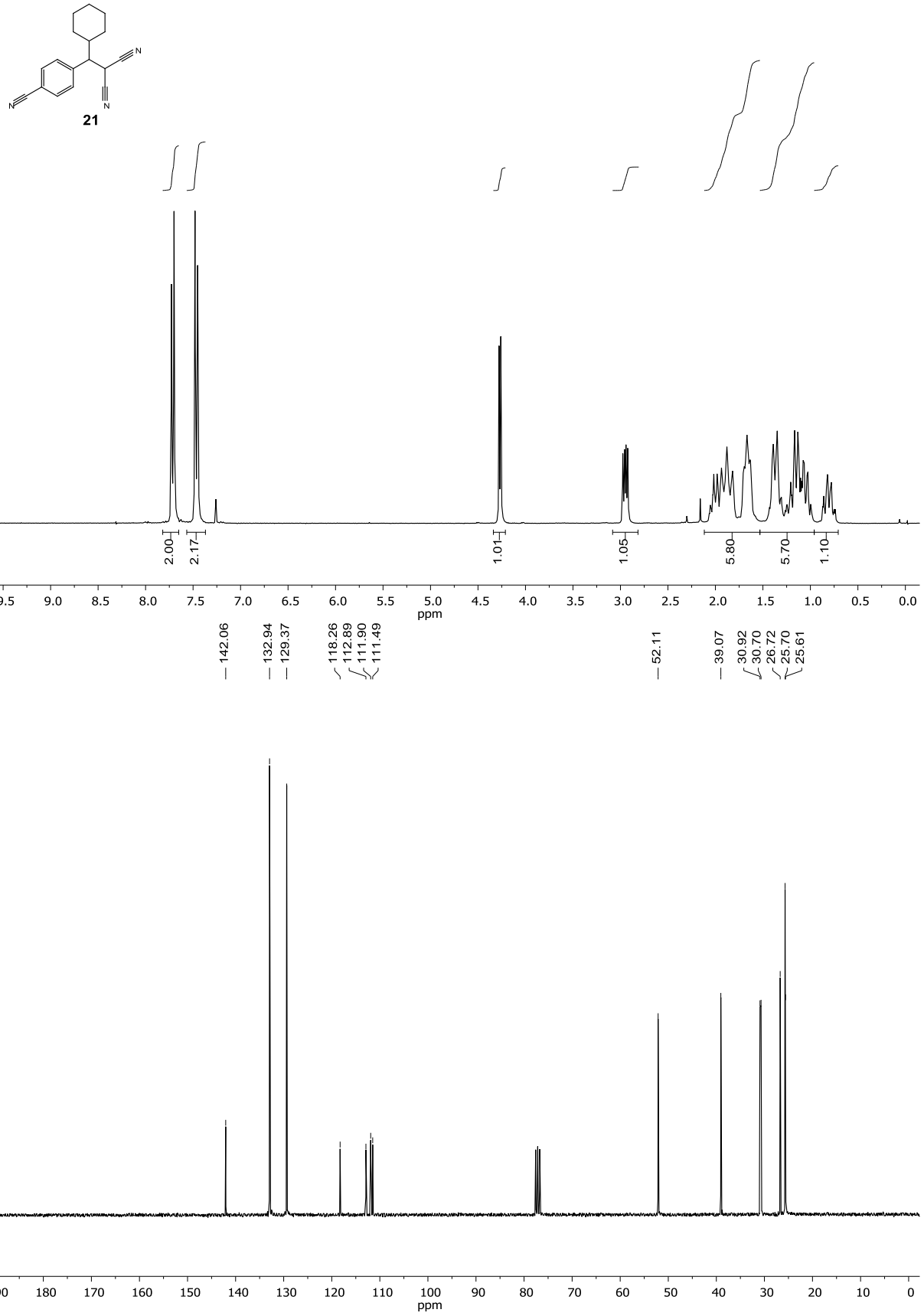

138.83
135.04
130.50
129.08
128.58
126.53
112.08
111.77
51.92
39.27
31.10
30.60
26.95
25.82
25.79
25.71
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

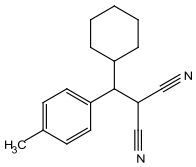

Cl
N
N

20

2.17
2.32
1.00
1.00
13.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

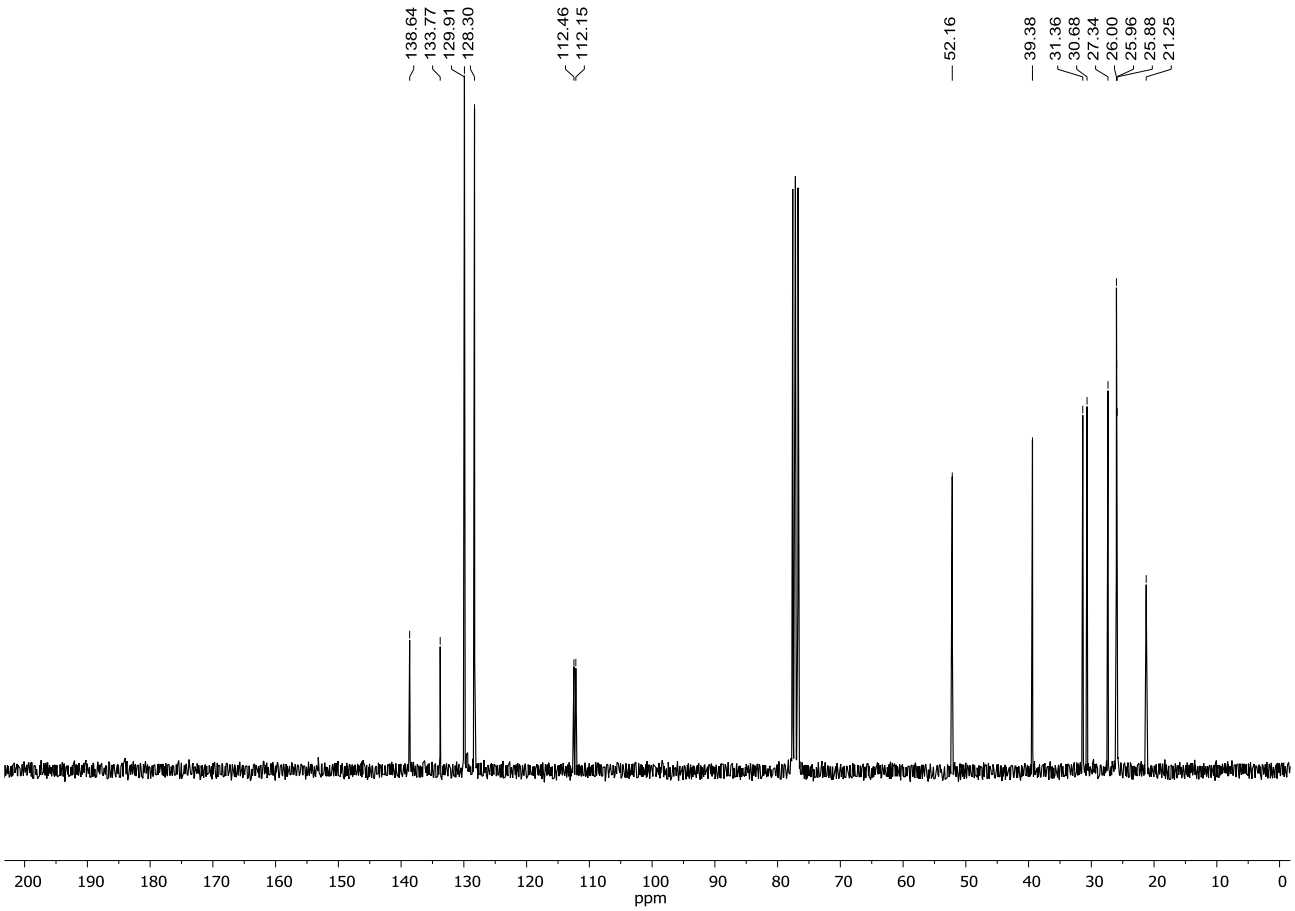

135.21
134.88
129.80
129.50
112.15
111.76
51.85
39.26
31.19
30.72
27.10
25.89
25.85
25.77
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

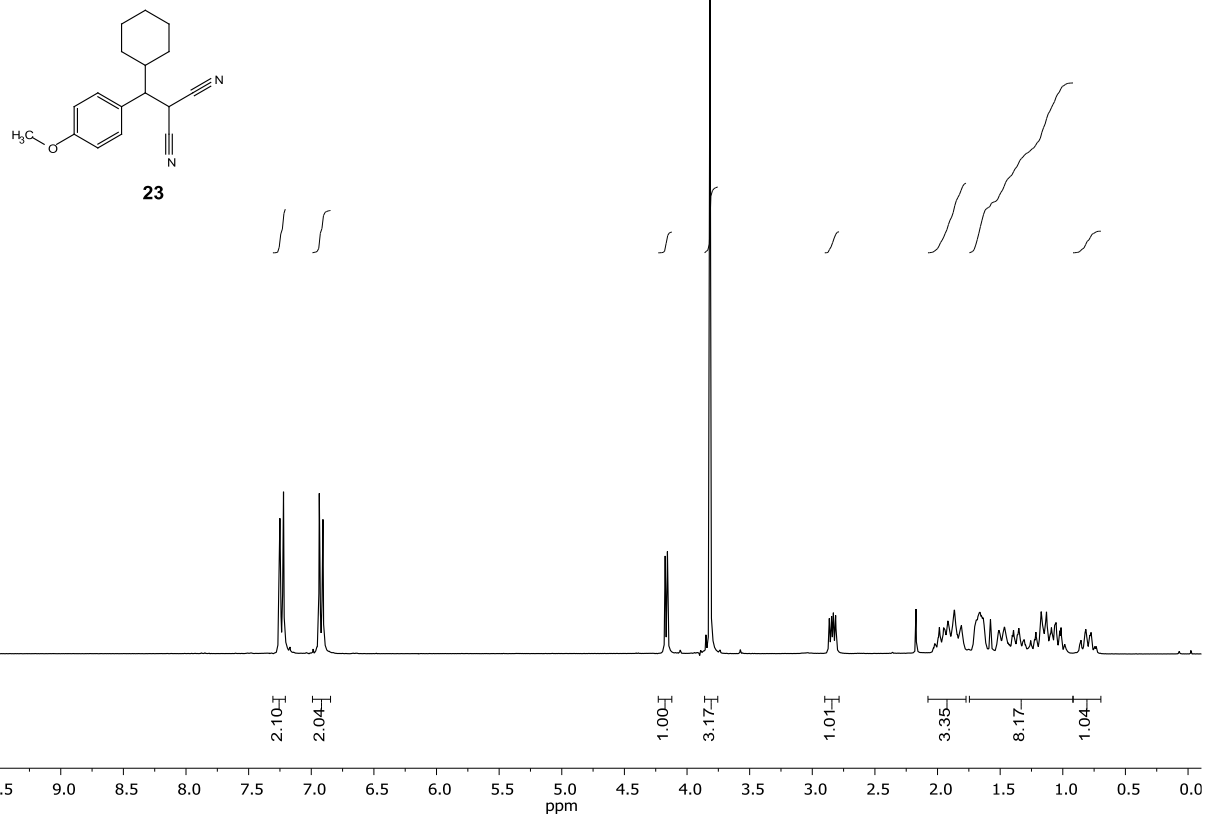

21
2.00
2.17
1.01
1.05
5.80
5.70
1.10
ppm
142.06
132.94
129.37
118.26
112.89
111.90
111.49
52.11
39.07
30.92
30.70
26.72
25.70
25.61
ppm


N
N
H3C

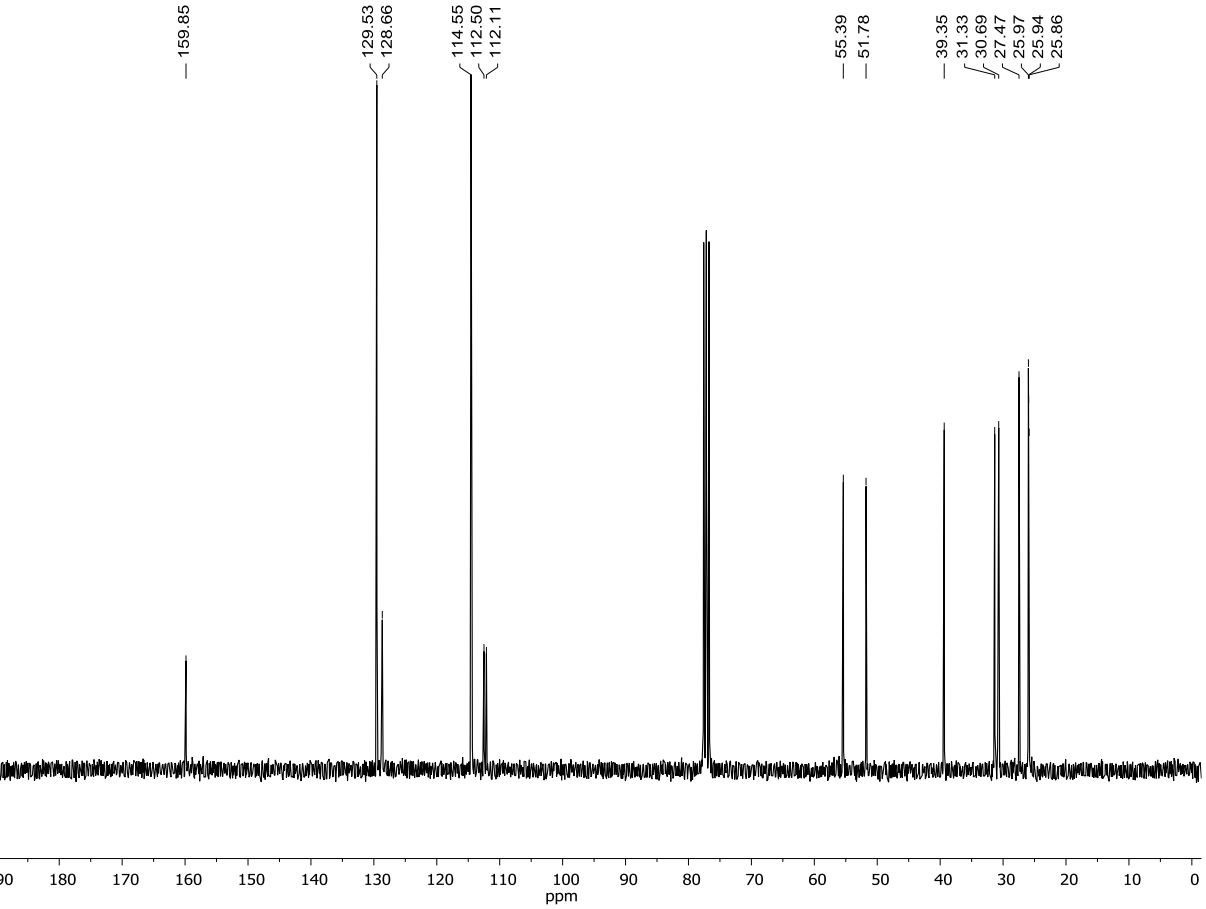
22

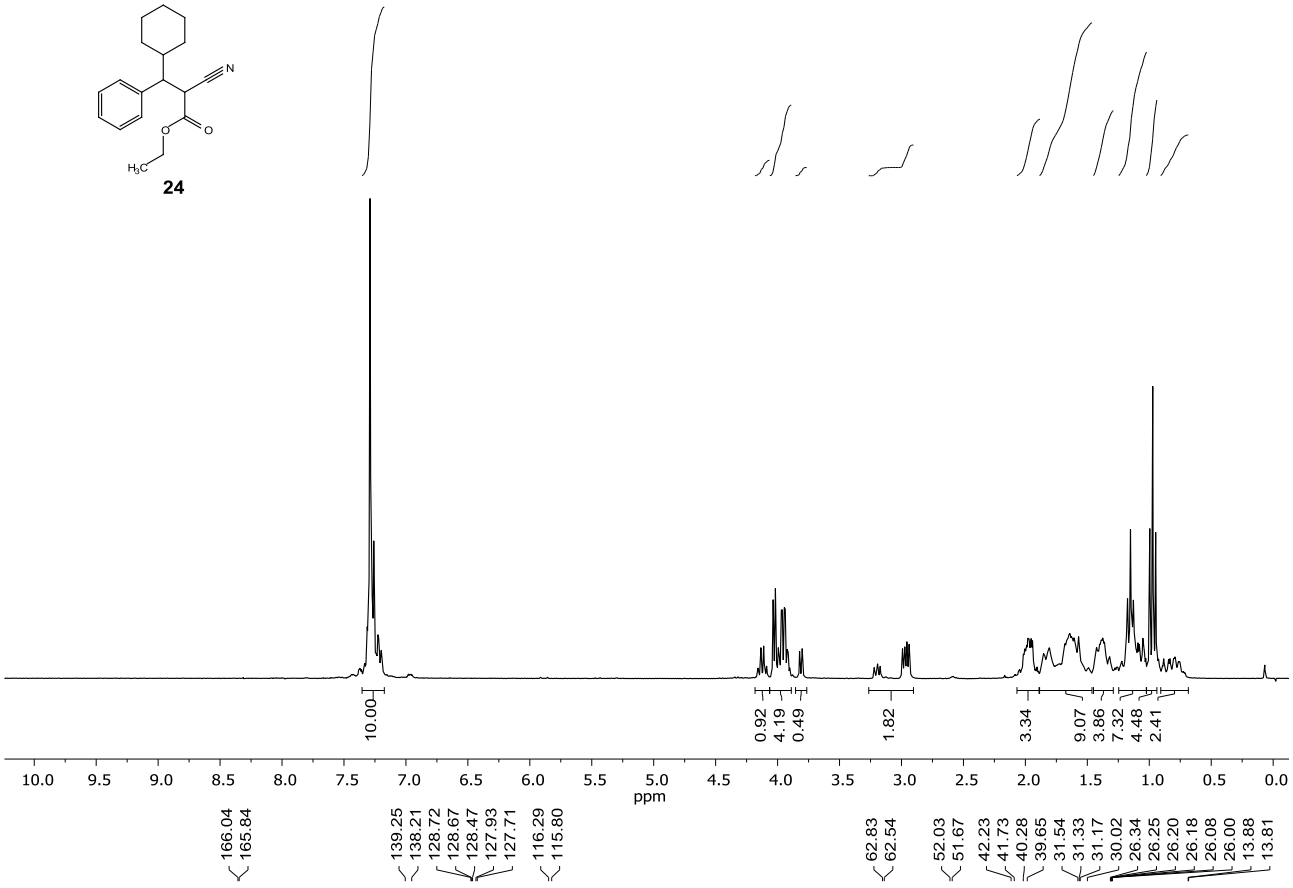
3.80
1.00
1.05
3.37
3.58
2.46
6.74
1.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

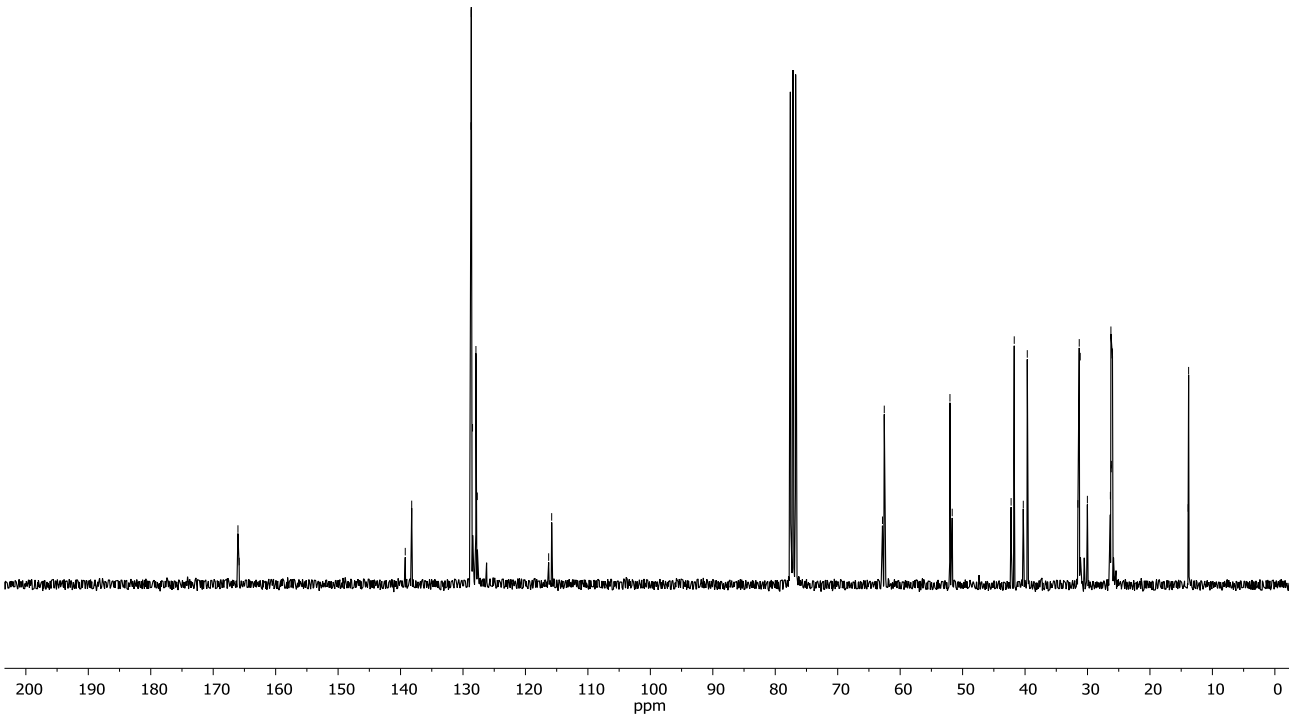

138.64
133.77
129.91
128.30
112.46
112.15
52.16
39.38
31.36
30.68
27.34
26.00
25.96
25.88
21.25
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

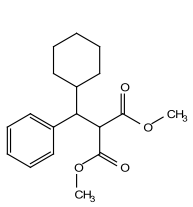

2.10
2.04
1.00
3.17
1.01
3.35
8.17
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

23


159.85
129.53
128.66
114.55
112.50
112.11
55.39
51.78
39.35
31.33
30.69
27.47
25.97
25.94
25.86
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

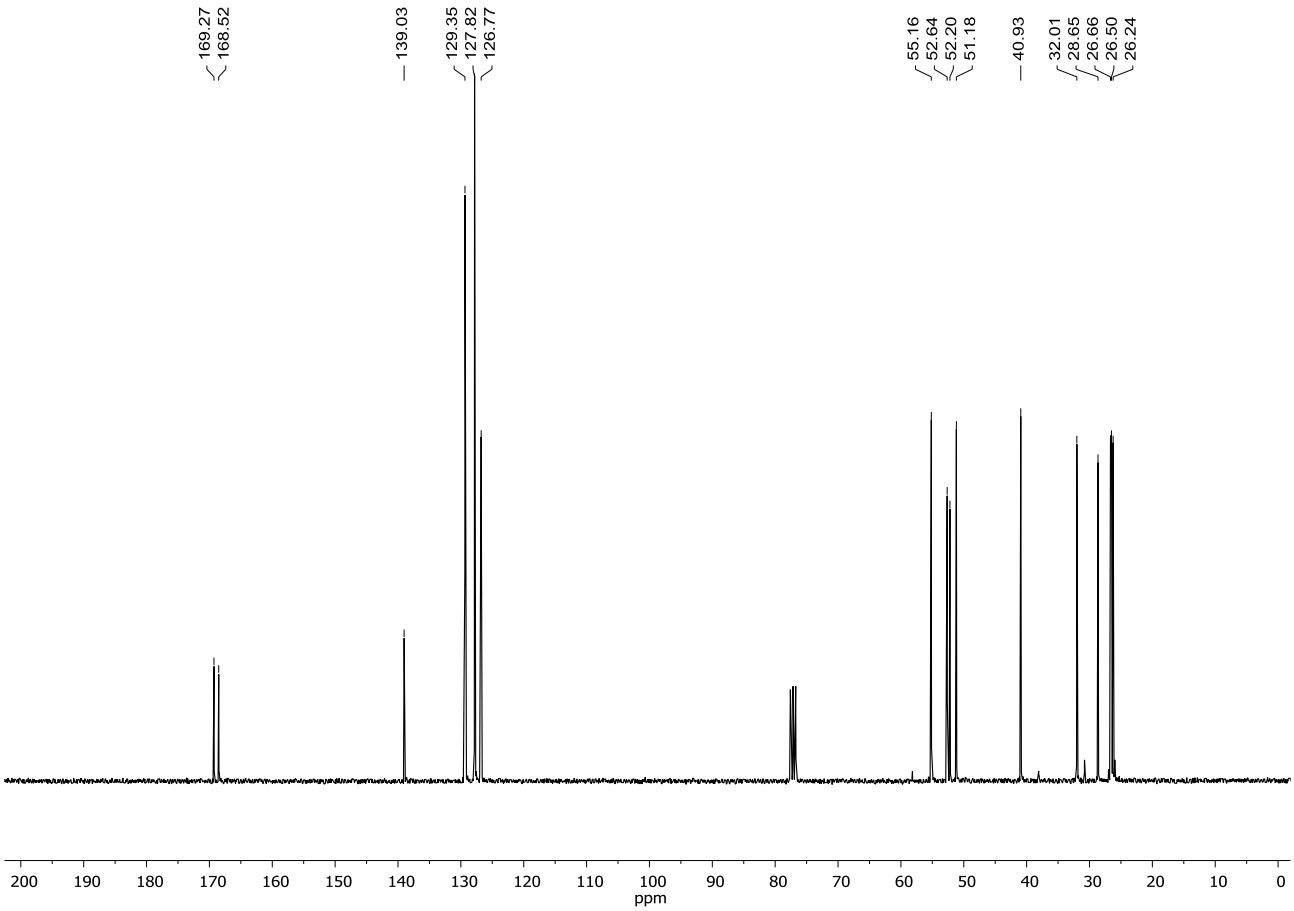

N
O
O
H3C
24
10.00
0.92
4.19
0.49
1.82
3.34
9.07
3.86
7.32
4.48
2.41
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
166.04
165.84
139.25
138.21
128.72
128.67
128.47
127.93
127.71
116.29
115.80
62.83
62.54
52.03
51.67
42.23
41.73
40.28
39.65
31.54
31.33
31.17
30.02
26.34
26.25
26.20
26.18
26.08
26.00
13.88
13.81

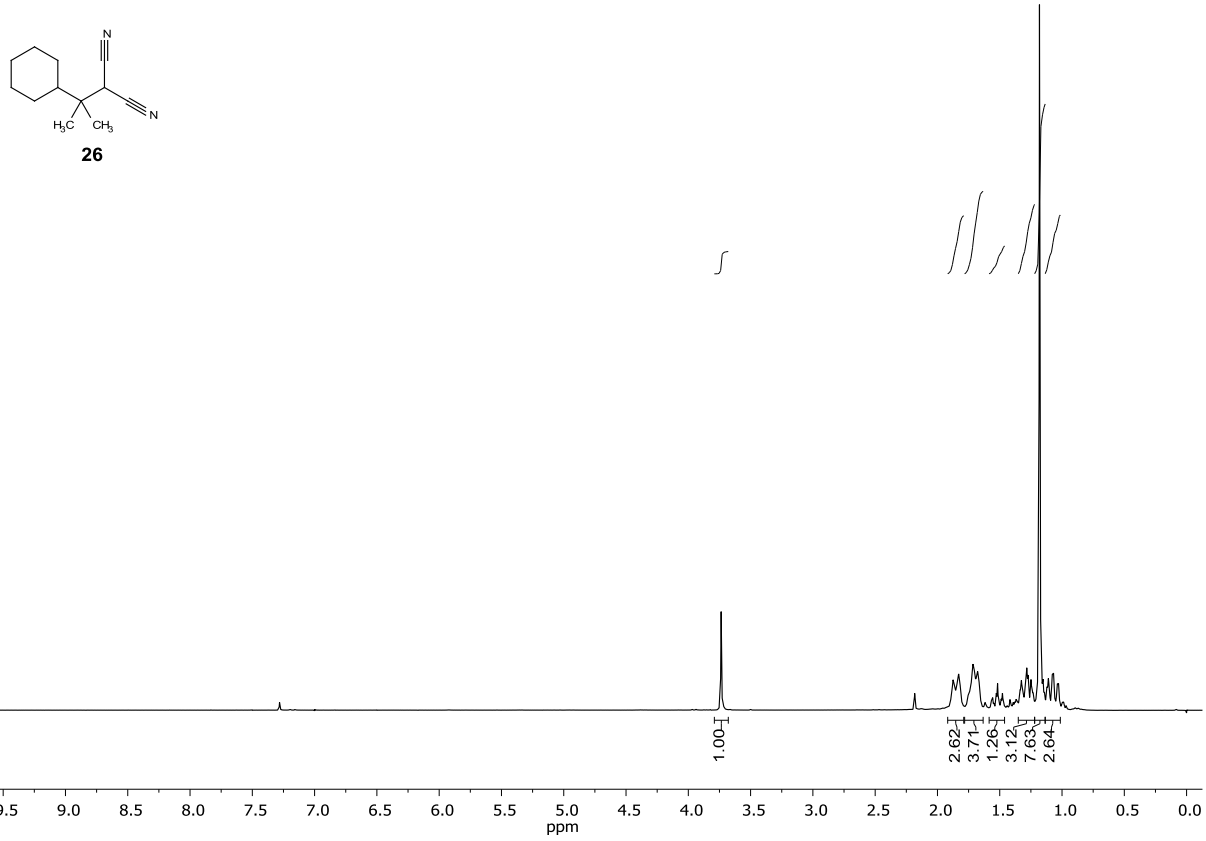

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



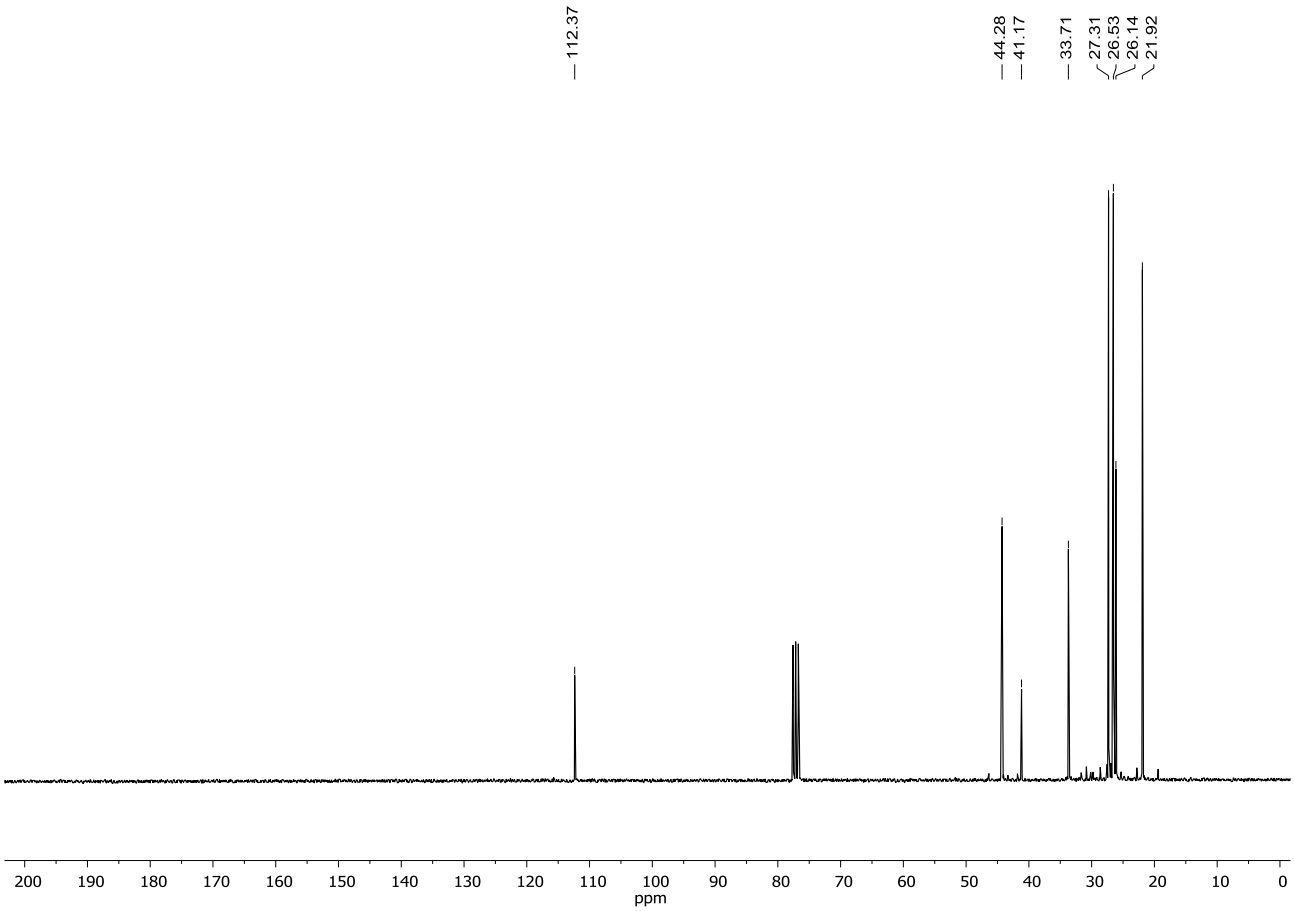
25

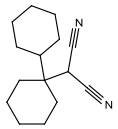
4.97
1.00
3.13
3.86
6.42
4.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


169.27
168.52
139.03
129.35
127.82
126.77
55.16
52.64
52.20
51.18
40.93
32.01
28.65
26.66
26.50
26.24
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

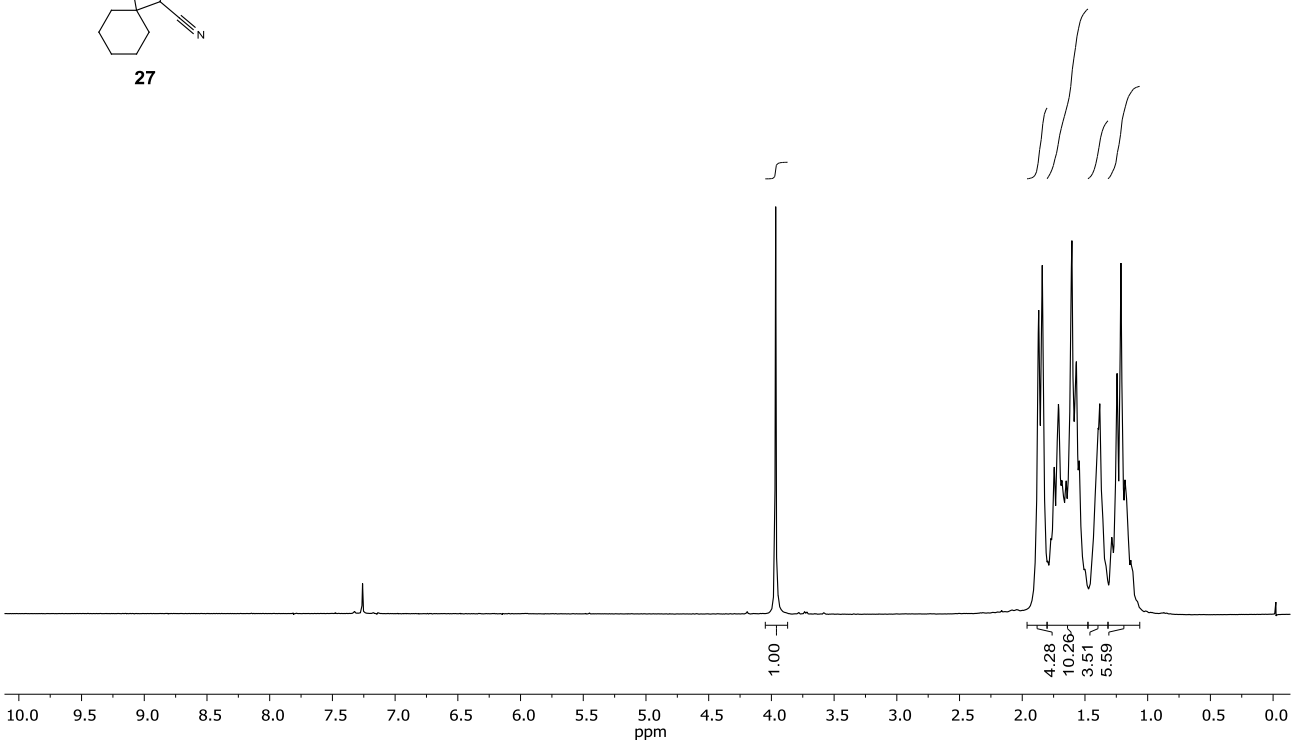

N
N
H3C
CH3
1.00
2.62
3.71
1.26
3.12
7.63
2.64
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

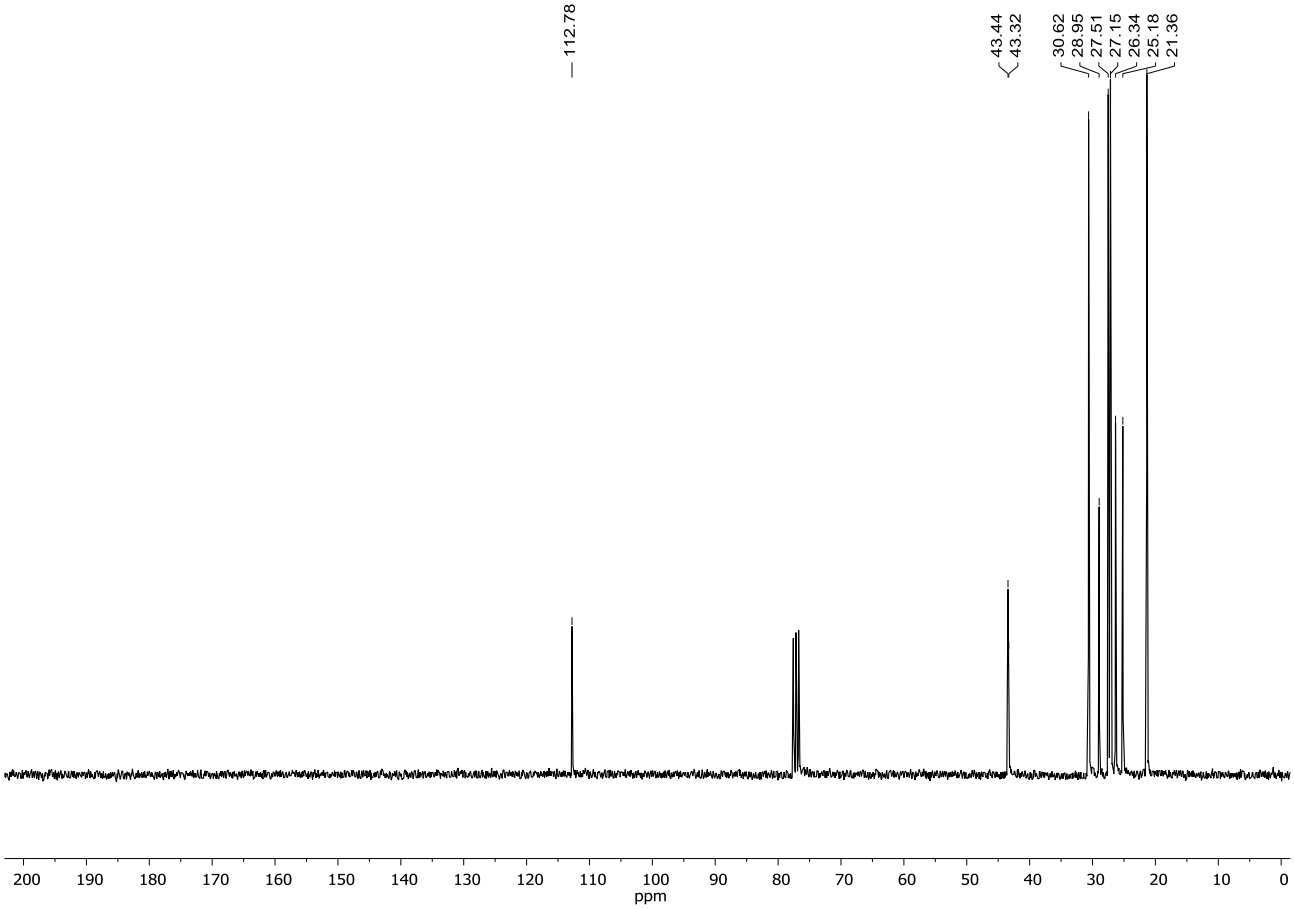
26

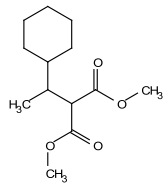

112.37
44.28
41.17
33.71
27.31
26.53
26.14
21.92
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


N
N

27

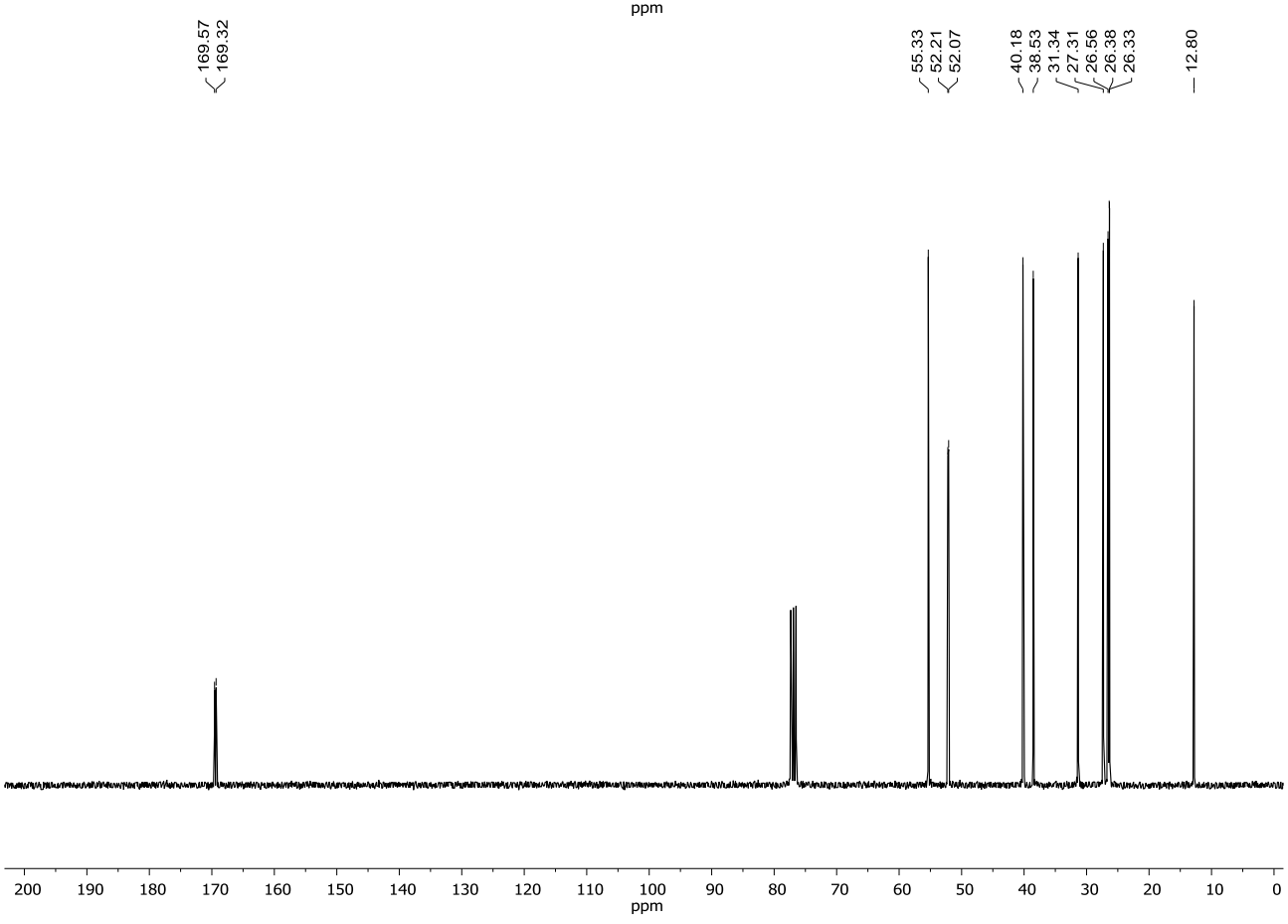

1.00
4.28
10.26
3.51
5.59
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

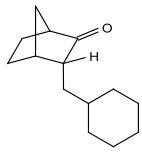

112.78
43.44
43.32
30.62
28.95
27.51
27.15
26.34
25.18
21.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



28

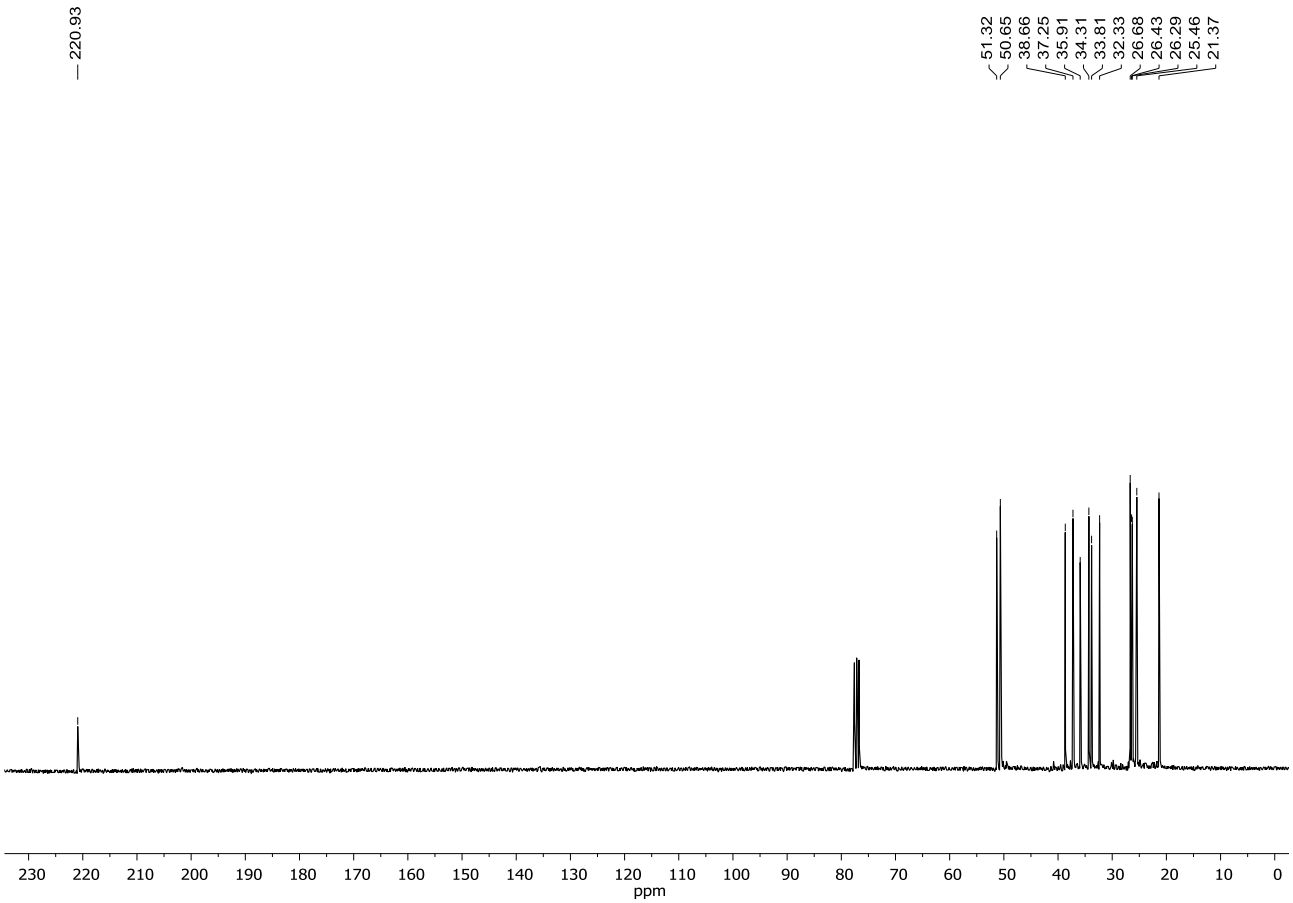
6.39
1.00
1.14
5.93
5.75
4.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

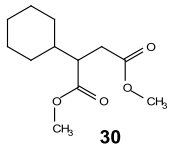

169.57
169.32
55.33
52.21
52.07
40.18
38.53
31.34
27.31
26.56
26.38
26.33
12.80
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
H

29, *endo*

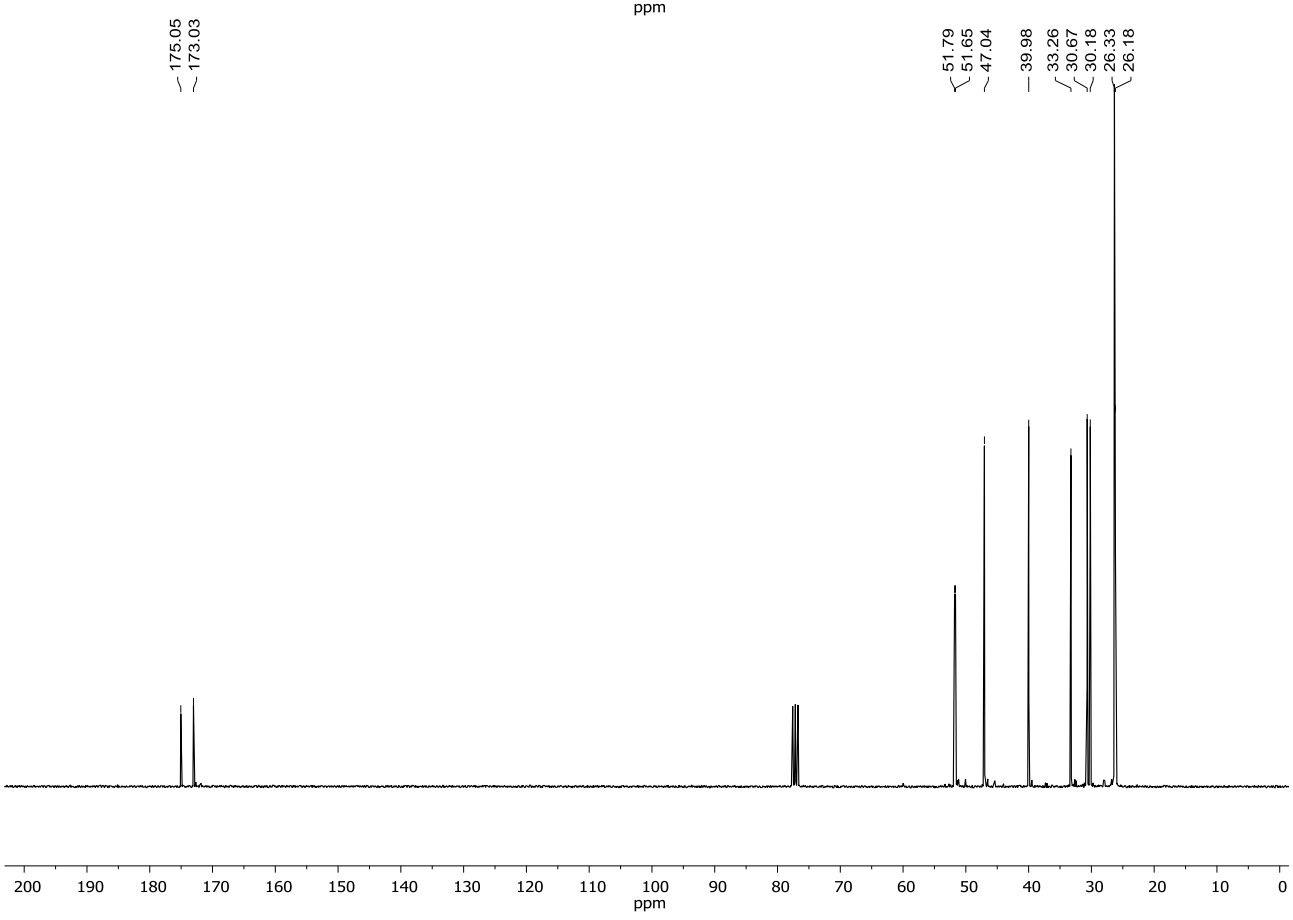
1.00
0.60
12.70
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


220.93
51.32
50.65
38.66
37.25
35.91
34.31
33.81
32.33
26.68
26.43
26.29
25.46
21.37
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



30

2.91
2.90
2.00
1.03
6.50
5.53
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


175.05
173.03
51.79
51.65
47.04
39.98
33.26
30.67
30.18
26.33
26.18
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm