Electronic Supplementary Information

Hydroquinone and Benzoquinone-Catalyzed Aqueous Knoevenagel Condensation

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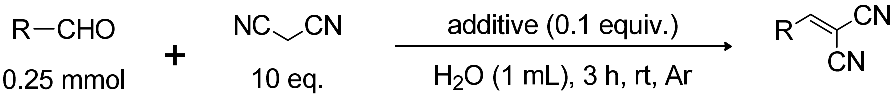
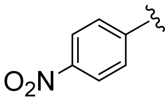
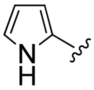
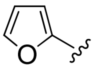
1. General information

All reactions were performed under argon. H_2O, hexane, and THF, MeOH, isopropanol, DMF, CH_2Cl_2 as solvents were purchased from a commercial source and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 μm spherical, neutral). ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL 400, ECZ 400 and ECA 500 spectrometer at room temperature in $CDCl_3$ or DMSO-d_6 as a solvent and internal standard (^{1}H NMR: δ= 7.26 for $CDCl_3$, ^{1}H NMR: δ= 2.50 for DMSO-d_6; ^{13}C NMR: δ= 77.0 for $CDCl_3$, ^{13}C NMR: δ= 39.5 for DMSO-d_6) with tetramethylsilane as an internal standard. IR spectra were recorded by a Brucker FT-IR ALPHA. ESI high resolution mass spectra (HRMS) were measured by a Shimadzu hybrid IT-TOF mass spectrometer. Aldehydes (**1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g** ,**1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1q**, **1r**, **1s**, **1t**, **1u**, and **1v**) and reagents (hydroquinone, benzoquinone, 2-methoxy-p-hydroquinone, 2-chloro-p-hydroquinone, resorcinol, catechol, phenol and 1,4-dimethoxybenzene) were purchased from a commercial source. Aldehydes (**1p**, **1w**, and **1x**) and reagent (2-methoxy-p-benzoquinone and 2-chloro-p-benzoquinone) were prepared according to reference 1, 2, 3, and 4, respectively.

2. Addition effect of hydroquinone and benzoquinone

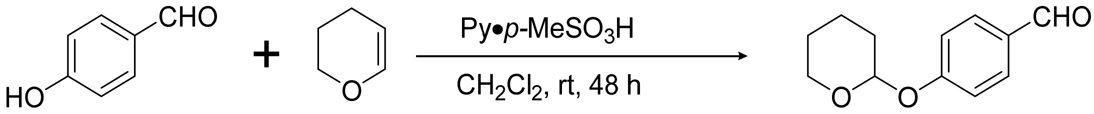


entry	R	additive	Yield (%)[a]	
			SM	Product
1		HQ and BQ	5	73
2		—	0	47
3		HQ and BQ	0	82
4		—	51	30
5		HQ and BQ	0	Quant.
6		—	0	87

Knoevenagel condensation of aromatic aldehydes in water in the absence of catalyst has been reported.[5] Therefore, we compared the additive effect of HQ and BQ using some aromatic aldehydes. Consequently, evert reaction efficiencies were also improved to give corresponding products in good to high yields.

3. Preparation of substrates

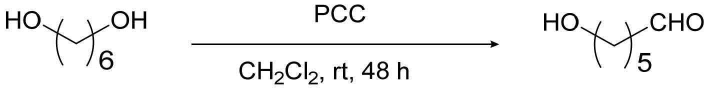
Preparation of 4-(tetrahydropyran-2-yloxy)benzaldehyde (1p)



To the solution *p*-hydroxybenzaldehyde (611 mg, 5.00 mmol) and pyridinium *p*-toluenesulfonate (62.8 mg 0.25 mmol) in CH_2Cl_2 (20 mL) was added 3,4-dihydro-2*H*-pyran (635 µL, 7.50 mmol) under argon. The reaction mixture was stirred at room temperature for 48 h. The crude reaction mixture was washed with saturated $NaHCO_3$ aq. and brine. The organic layer was dried with Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The resultant crude material was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1 to 6/1) to give **1p** (883 mg, 4.28 mmol) in 86% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.83 (d, *J* = 9.3 Hz, 2H), 7.16 (d, *J* = 9.3 Hz, 2H), 5.55 (dd, *J* = 3.0, 3.0 Hz 1H), 3.85 (ddd, *J* = 10.5, 10.5, 3.0 Hz, 1H), 3.66-3.62 (m, 1H), 2.05-2.00 (m, 1H), 1.91-1.88 (m, 2H), 1.77-1.68 (m, 2H), 1.64-1.56 (m, 1H). Spectroscopic data of ^{1}H NMR of **1p** was identical to that of reference 1.

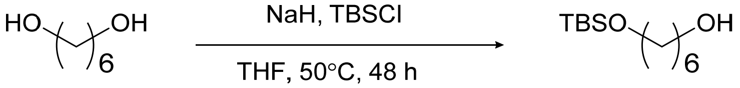
Preparation of 6-hydroxyhexanal (1w)



To a solution of hexane-1,6-diol (1.77 g, 15.0 mmol) in chloroform (25 mL) were added PCC (1.61 g, 7.50 mmol) and celite (2 g) at room temperature under argon atmosphere and the reaction mixture was stirred for 20 h. The reaction mixture was filtered, and the filtrate was concentrated under reduced pressure. The resultant crude material was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 2/1) to give 6-hydroxyhexanal (331 mg, 2.80 mmol) in 18% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (s, 1H), 3.68-3.65 (m, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.69-1.65 (m, 2H), 1.62-1.57 (m, 2H), 1.45-1.40 (m, 2H), 1.25 (brs, 1H). Spectroscopic data of ^{1}H NMR of **1y** was identical to that of reference 2.

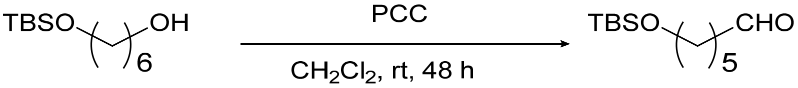
Preparation of 6-[(tert-butyldimethylsilyl)oxy]-hexanol



Hexan-1,6-diol (2.36 g, 20.0 mmol) was dissolved in dry THF (40 mL). Sodium hydride (960 mg, 24.0 mmol) and *tert*-butyldimethylsilyl chloride (3.61 g, 24.0 mmol) were added, and the mixture was stirred at room temperature overnight. After dilution with Et_2O (20 mL), the solution was washed with Na_2CO_3 and brine (4 × 20 mL). The organic layer was dried with Na_2SO_4 and filtered. The filtrate was concentrated in vacuo. The resultant crude material was purified by silica gel column chromatography (*n*-hexane/EtOAc = 1/1) to give 6-[(*tert*-butyldimethylsilyl)oxy]-hexan-ol (1.59 g, 6.84 mmol) in 34% yield.

^{1}H NMR (400 MHz, CDCl$_3$): δ 3.64-3.59 (m, 4H), 1.58-1.51 (m, 4H), 1.37-1.36 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H). Spectroscopic data of ^{1}H NMR of 6-[(tert-butyldimethylsilyl)oxy]-hexan-ol was identical to that of reference 3.

Preparation of 6-[(tert-butyldimethylsilyl)oxy]hexanal (1x)



The corresponding alcohol (1.59 g, 6.84 mmol) was added dropwise at 0 °C for 10 min to a suspension of PCC (2.18 g, 10.1 mmol) in dry CH$_2$Cl$_2$ (25 mL). After 5h, the dark suspension was filtered twice through a silica gel pad and washed with Et$_2$O. The solvent was evaporated in vacuo. The resultant crude material was purified by silica gel column chromatography (*n*-hexane/EtOAc = 25/1) to give **1z** (915 mg, 3.97 mmol) in 59% yield.

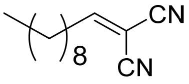
^{1}H NMR (400 MHz, CDCl$_3$): δ 9.77 (t, J = 2.0 Hz, 1H), 3.61 (t, J = 6.6 Hz, 2H), 2.44 (td, J = 7.2, 2.0 Hz, 2H), 1.67-1.64 (m, 2H) 1.55-1.52 (m, 2H), 1.40-1.36 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). Spectroscopic data of ^{1}H NMR of **1z** was identical to that of reference 4.

4. General procedure

Malononitrile (165 mg, 2.50 mmol, 10 eq.), hydroquinone (2.75 mg, 0.025 mmol, 10 mol%), benzoquinone (2.70 mg, 0.025 mmol, 10 mol%) and H_2O (1 mL) were placed in a flask, and then the test tube was sealed with a septum. The inside air was replaced with argon (balloon). The aldehyde (**1**; 0.25 mmol) was added to the reaction mixture and stirred at room temperature for 3 h. The reaction mixture was extracted with diethyl ether (8.0 mL x 5). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the corresponding knoevenagel product (**2**).

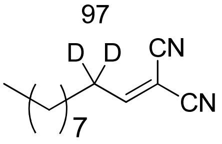
5. Spectroscopic data of the synthesized products

2-Decylidenemalononitrile (2a)



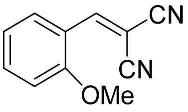
Yellow liquid; IR (ATR) cm^{-1}: 2924, 2854, 2237, 1606, 1464, 1377, 1020. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.33 (t, *J* = 8.0 Hz, 1H), 2.60 (dt, *J* = 8.0, 8.0 Hz, 2 H), 1.58-1.52 (m, 2 H), 1.35-1.27 (m, 12 H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 169.8, 112.1, 110.5, 89.8, 32.8, 31.7, 29.2, 29.2, 29.1, 29.0, 27.5, 22.6, 14.0. ESI-HRMS m/z: 243.1247 ([M+K$^+$]). Calcd for C$_{13}$H$_{20}$N$_2$K: 243.1258.

2-Decylidenemalononitrile-*d*$_2$ (2a-*d*$_2$)



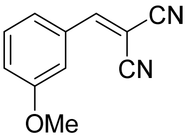
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.33 (t, *J* = 8.0 Hz, 1H), 2.57 (m, 0.05H), 1.55 (t, *J* = 7.6 Hz, 2H) 1.34-1.27 (m, 12H), 0.88 (t, *J* = 7.6 Hz, 3H). ^{2}H NMR (77 MHz, CHCl$_3$): δ 2.57 (s).

2-(2-Methoxybenzylidene)malononitrile (2b)



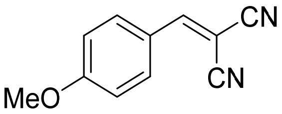
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.31 (s, 1H), 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.4, 8.0, 1.6 Hz, 1H), 7. 07 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.92 (s, 3H).
Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 6.

2-(3-Methoxybenzylidene)malononitrile (2c)



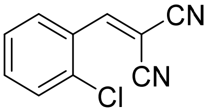
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 (s, 1H), 7.49-7.40 (m, 3H), 7.19-7.16 (m, 1H), 3.86 (s, 3H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 6.

2-(4-Methoxyphenylmethylene)malononitrile (2d)



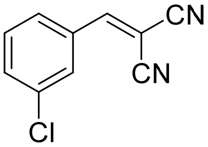
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.65 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$): *δ* 164.8, 158.9, 133.4, 123.9, 115.1, 114.4, 113.3, 78.5, 55.7. Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 6.

***o*-Chlorobenzylidene malononitrile (2e)**



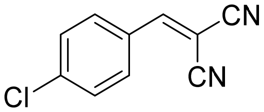
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.27 (s, 1H), 8.18 (d, *J* = 8.0, 1H), 7.58-7.53 (m, 2H), 7.48-7.42 (m, 1H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 7.

2-(3-Chlorobenzylidene)malononitrile (2f)



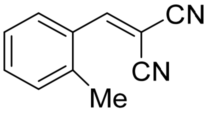
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.89-7.84 (m, 2H), 7.74 (s, 1H), 7.61-7.59 (m, 1H), 7.54-7.45 (m, 1H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 7.

2-(4-Chlorobenzylidene)malononitrile (2g)



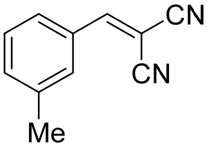
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.74 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 2H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 8.

2-(2-Methylbenzylidene)malononitrile (2h)



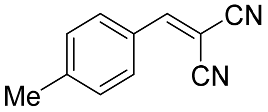
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (s, 1H), 8.08 (d, *J* = 7.6 Hz, 2H), 7.52-7.48 (m, 1H), 7.37-7.32 (m, 1H), 2.45 (s, 3H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 9 and 10.

2-(3-methylbenzylidene)malononitrile (2i)



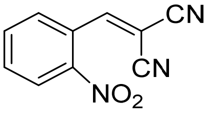
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74-7.73 (m, 2H), 7.69 (s, 1H), 7.46-7.41 (m, 2H), 2.43 (s, 3H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 11.

2-(4-Methylphenylmethylene)malononitrile (2j)



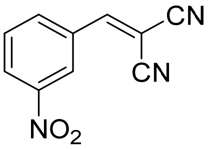
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 12.

2-(2-Nitrobenzylidene)malononitrile (2k)



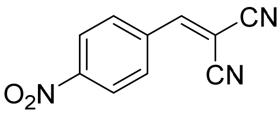
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.45 (s, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.91-7.79 (m, 3H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 13.

2-(3-Nitrobenzylidene)malononitrile (2l)



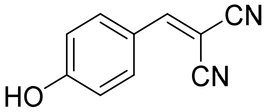
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.67 (s, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.80 (t, *J* = 8.0 Hz, 1H). Spectroscopic data of ^{1}H NMR of the product was identical to those of the reference 13.

2-(4-Nitrobenzylidene)malononitrile (2m)



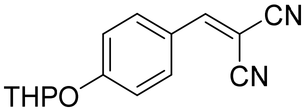
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.8 Hz, 2H) 7.90 (s, 1H). Spectroscopic data of ^{1}H NMR was identical to those of the reference 13.

2-(4-Hydroxybenzylidene)malononitrile (2n)



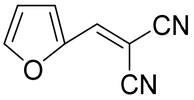
^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 11.02 (brs, 1H), 8.31 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H). Spectroscopic data of ^{1}H NMR was identical to those of the reference 14.

2-[[4-(Oxan-2-yloxy)phenyl]methylidene]propanedinitrile (2o)



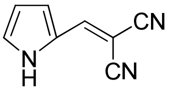
Yellow solid; M. p. 89-92 °C. IR (ATR) cm^{-1}: 2944, 2218, 1585, 1556, 1504, 1425, 1362, 1309, 1253, 1199, 1173, 1109, 1047, 1021. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.89 (d, *J* = 8.8 Hz, 2H), 7.66 (s, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 5.56 (t, *J* = 2.8 Hz, 1H), 3.81 (m, 1H), 3.65 (m, 1H), 2.11-1.95 (m, 1H), 1.98-1.89 (m, 2H) 1.81-1.68 (m, 2H), 1.64-1.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.3, 158.9, 133.2, 124.3, 117.1, 114.3, 113.2, 96.1, 78.5, 62.0, 29.7, 24.8, 18.1. ESI-HRMS m/z: 277.0928. ([M+Na$^+$]). Calcd for $C_{54}H_{14}N_2O_2Na$: 277.0947.

2-(Furan-2-ylmethylene)malononitrile (2p)



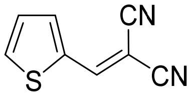
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 1.6 Hz, 1H), 7.52 (s, 1H), 7.37 (d, *J* = 4.0 Hz, 1H), 6.72 (dd, *J* = 1.6, 4.0 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those of the reference 15.

1,1-Dicyano-2-(2-pyrrolyl)ethene (2q)



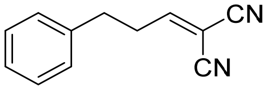
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (brs, 1H), 7.51 (s, 1H), 7.31 (m, 1H), 7.02 (m, 1H), 6.49 (t, *J* = 1.6 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those of the reference 16.

2-(Thiophen-2-ylmethylene)malononitrile (2r)



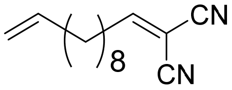
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90-7.89 (m, 2H), 7.82 (d, *J* = 4.0 Hz, 1H), 7.28 (t, *J* = 4.0 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those of the reference 15.

2-(3-Phenylpropylidene)malononitrile (2s)



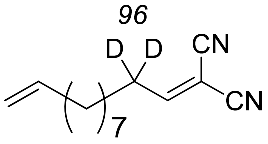
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 (t, *J* = 7.5 Hz, 2H), 7.30-7.25 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 2H), 2.94-2.86 (s, 4H). Spectroscopic data of ^{1}H NMR was identical to those of the reference 17.

2-(10-Undecenylidene)malononitrile (2t)



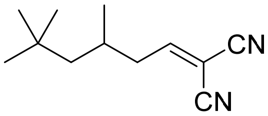
Yellow liquid; IR (ATR) cm^{-1}: 2926, 2855, 2237, 1736, 1640, 1606, 1463, 1372, 1239, 1097, 1045. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (td, *J* = 7.6, 2.4 Hz, 1H), 5.86-5.76 (m, 1H), 5.02-4.92 (m, 2H), 2.61 (dt, *J* = 7.6, 7.6 Hz, 2H), 2.07-2.01 (m, 2H), 1.60-1.52 (m, 2H), 1.43-1.23 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 139.0, 114.2, 112.0, 110.4, 89.8, 33.6, 32.8, 29.1, 29.0, 28.9, 28.7, 27.5. ESI-HRMS m/z: 239.1517 ([M+Na$^+$]). Calcd for $C_{14}H_{20}N_2Na$: 239.1519.

2-(10-Undecenylidene)malononitrile-*d*$_2$ (2t-*d*$_2$)



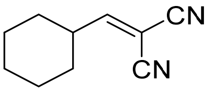
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 5.84-5.77 (m, 1H), 5.02-4.92 (m, 2H), 2.60-2.56 (m, 0.08 H), 2.06-2.01 (m, 2H), 1.56-1.53 (m, 2H), 1.38-1.25 (m, 10H). ^{2}H NMR (61 MHz, $CHCl_3$): δ 2.57 (s).

2-(3,5,5-Trimethylhexylidene)propanedinitrile (2u)



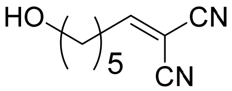
Yellow liquid; IR (ATR) cm^{-1}:2956, 2236, 1736, 1605, 1468, 1366, 1242, 1045. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.35 (t, *J* = 8.0 Hz, 1H), 2.61-2.56 (m, 1H), 2.51-2.43 (m, 1H), 1.92-1.81 (m, 1H), 1.26-1.16 (m, 2H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.92 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 169.0, 112.0, 110.6, 90.4, 50.3, 42.0, 31.0, 29.7, 29.3, 22.4. ESI-HRMS m/z: 213.1346 ([M+Na$^+$]). Calcd for $C_{12}H_{18}N_2Na$: 213.1362.

1,1-Dicyano-2-cyclohexylethene (2v)



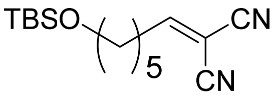
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 10.8 Hz, 1H), 2.77-2.69 (m, 1H), 1.83-1.72 (m, 4H), 1.42-1.20 (m, 6H). Spectroscopic data of ^{1}H NMR was identical to those of the reference 7.

2-(6-Hydroxyhexylidene)malononitrile (2w)



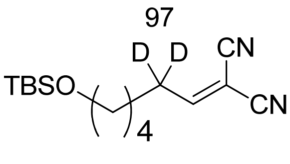
Yellow liquid; IR (ATR) cm^{-1}: 3362, 2936, 2864, 2238, 1725, 1606, 1513, 1461, 1373, 1246, 1044. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (t, J = 8.0 Hz, 1H), 3.66 (t, J = 6.0 Hz, 2H), 2.32 (dt, J = 8.0, 7.5 Hz, 2H) 1.63-1.57 (m, 4H), 1.48-1.44 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 112.1, 110.6, 90.1, 64.4 32.8, 32.1, 27.4, 25.4. ESI-HRMS m/z: 187.0864 ([M+Na$^+$]). Calcd for $C_9H_{12}N_2ONa$: 187.0842.

2-[6-[(tert-Butyldimethylsilyl)oxy]hexylidene]malononitrile (2x)



Yellow liquid; IR (ATR) cm^{-1}: 2929, 2857, 2237, 1606, 1462, 1388, 1360, 1253, 1097, 1006; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, J = 8.0 Hz, 1H), 3.61 (t, J = 6.0, Hz, 2H), 2.60 (dt, J = 8.0, 7.2 Hz, 2H), 1.64-1.51 (m, 4H), 1.45-1.38 (m, 2H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 112.0, 110.4, 89.9, 62.5, 32.8, 32.1, 27.3, 25.9, 25.4, 18.3, 5.3; ESI-HRMS m/z: 317.1451 ([M+K$^+$]). Calcd for $C_{15}H_{26}N_2SiK$: 317.1446.

2-[6-[(tert-Butyldimethylsilyl)oxy]hexylidene]malononitrile-d_2 (2x-d_2)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 3.61 (t, J = 6.0, Hz, 2H), 2.58 (m, 0.06 H), 1.59-1.51 (m, 4H), 1.45-1.40 (m, 2H), 0.89 (s, 9H), 0.04 (s, 6H). ^{2}H NMR (61 MHz, $CHCl_3$): δ 2.61 (s).

6. Reference

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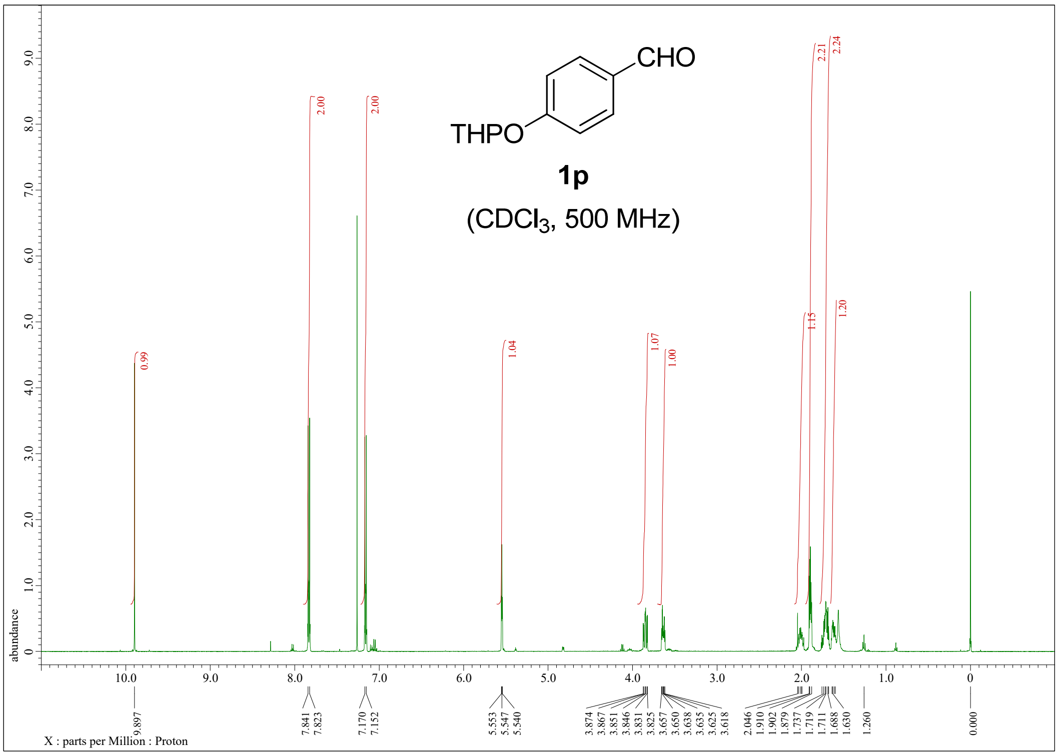
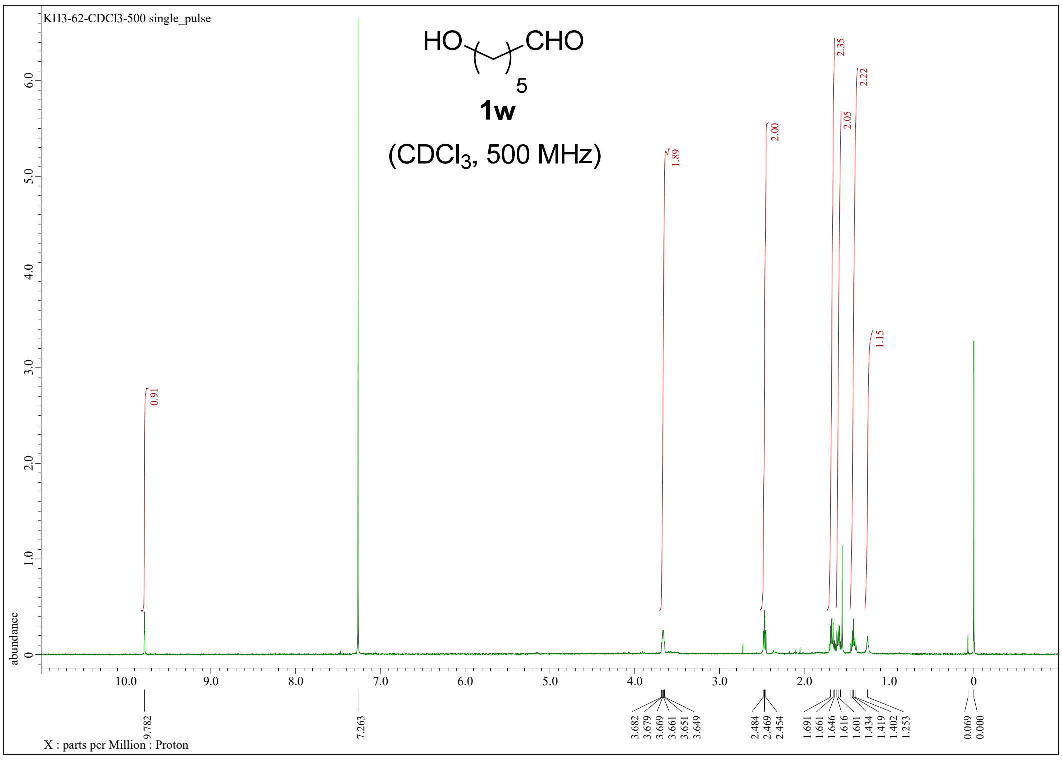
7. ^{1}H NMR spectra of substrates

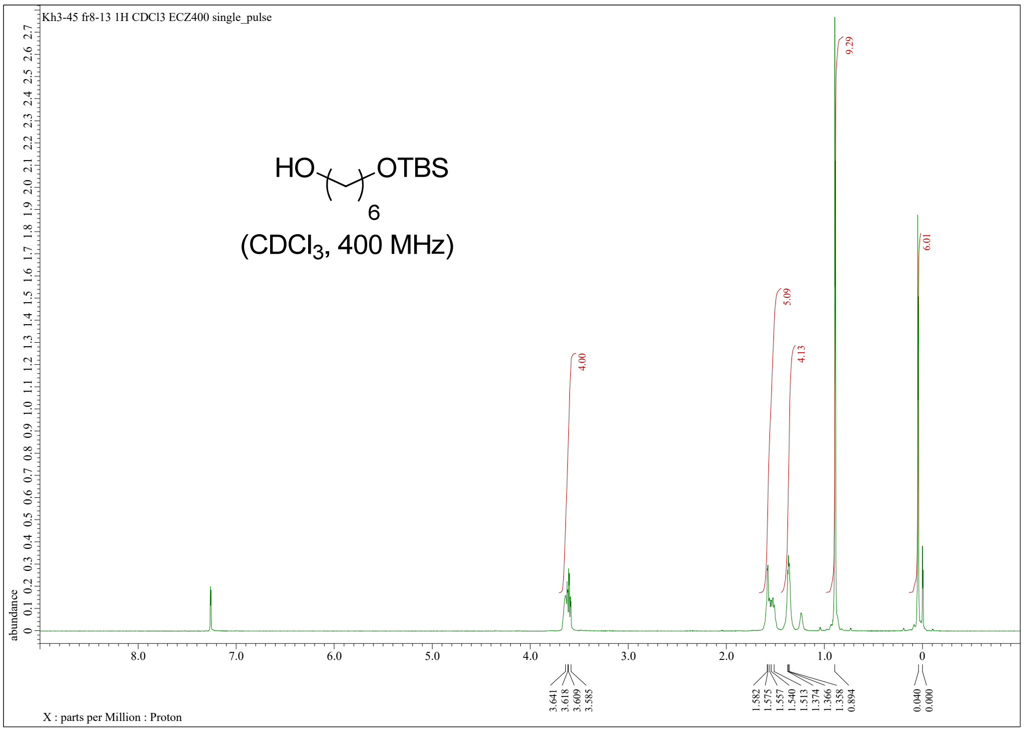
^{1}H NMR of 4-(tetrahydropyran-2-yloxy)benzaldehyde (1p)



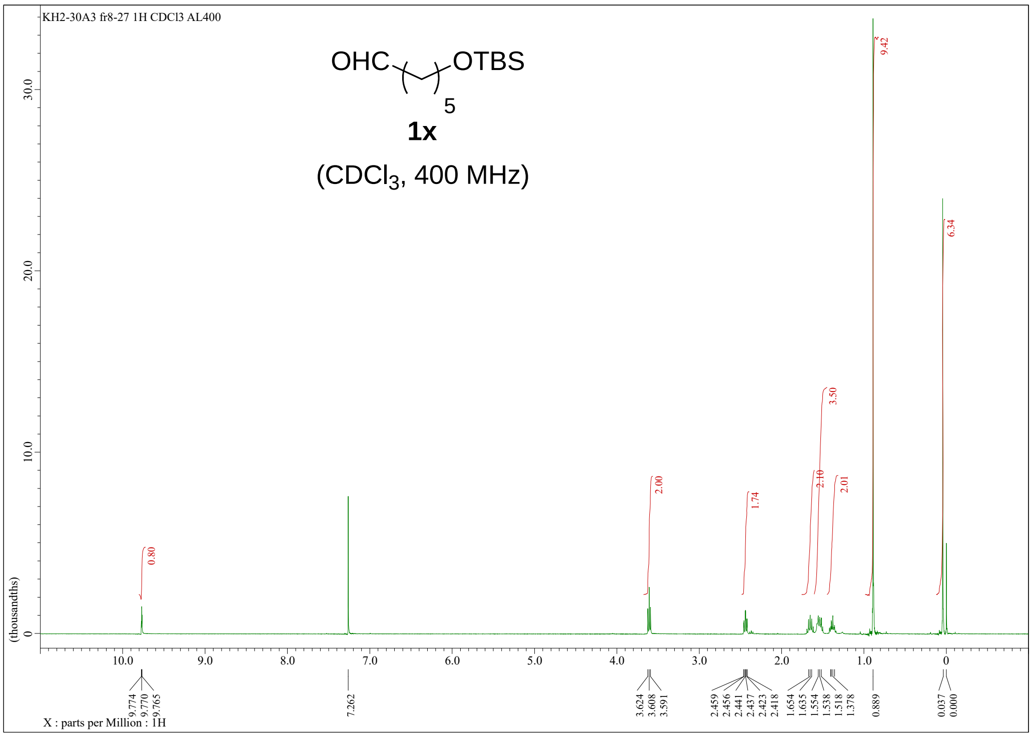
^{1}H NMR of 6-hydroxyhexanal (1y)



^{1}H NMR of 6-[(tert-butyldimethylsilyl)oxy]-hexanol

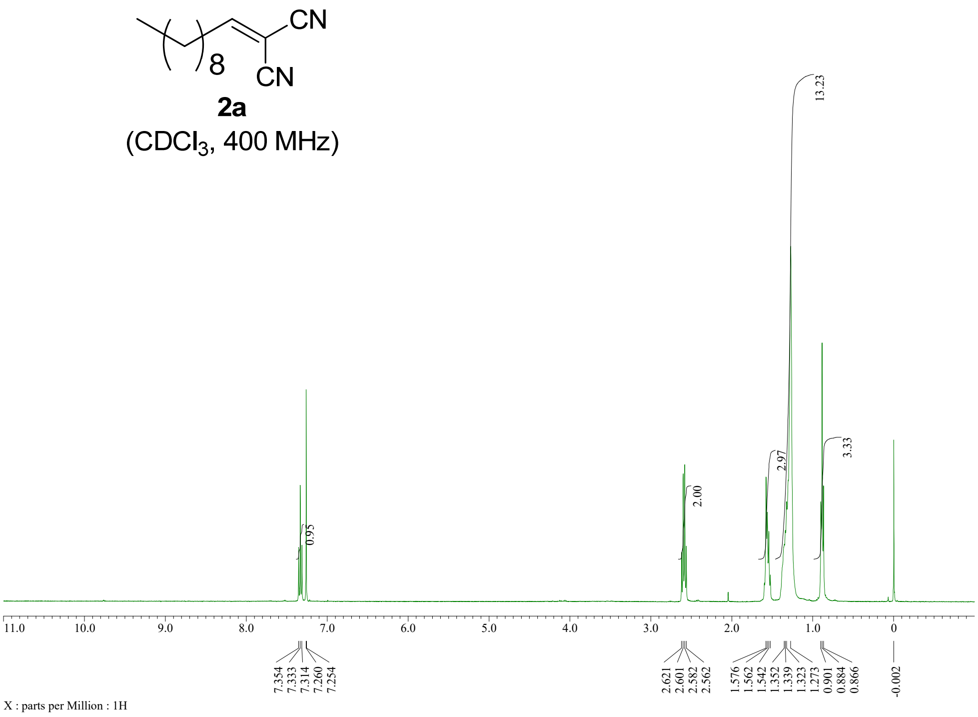


^{1}H NMR of 6-[(tert-butyldimethylsilyl)oxy]hexanal (1z)

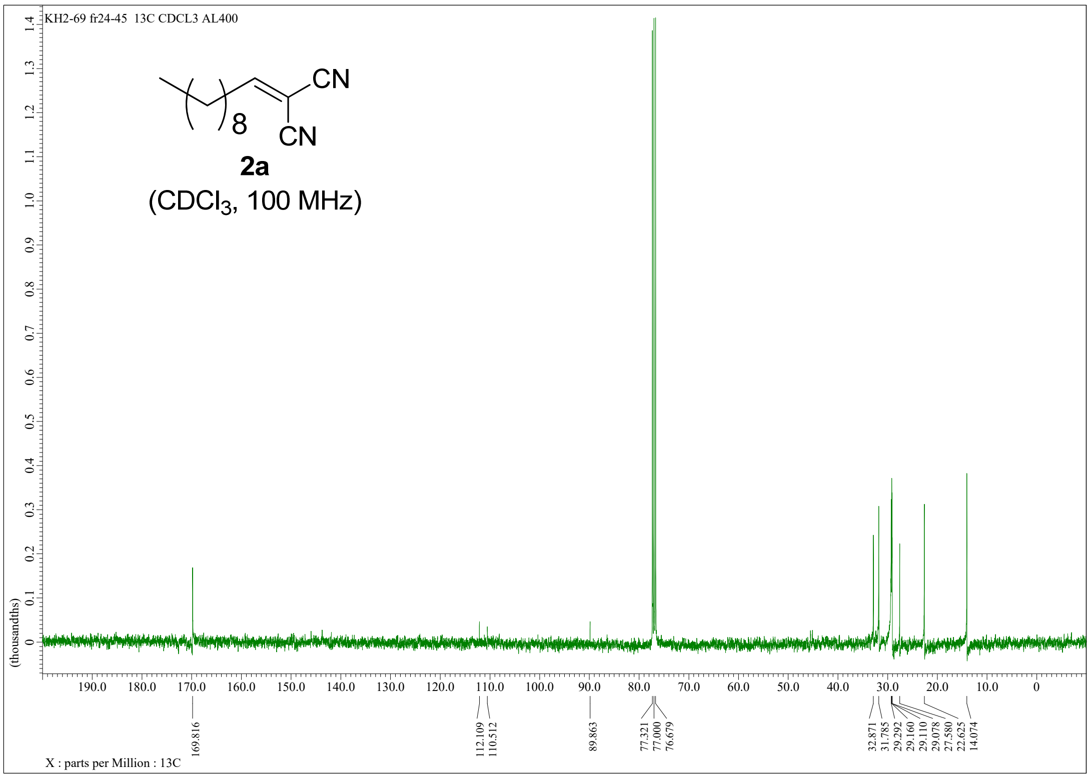


8. ^{1}H, ^{13}C and ^{2}H NMR spectra of products

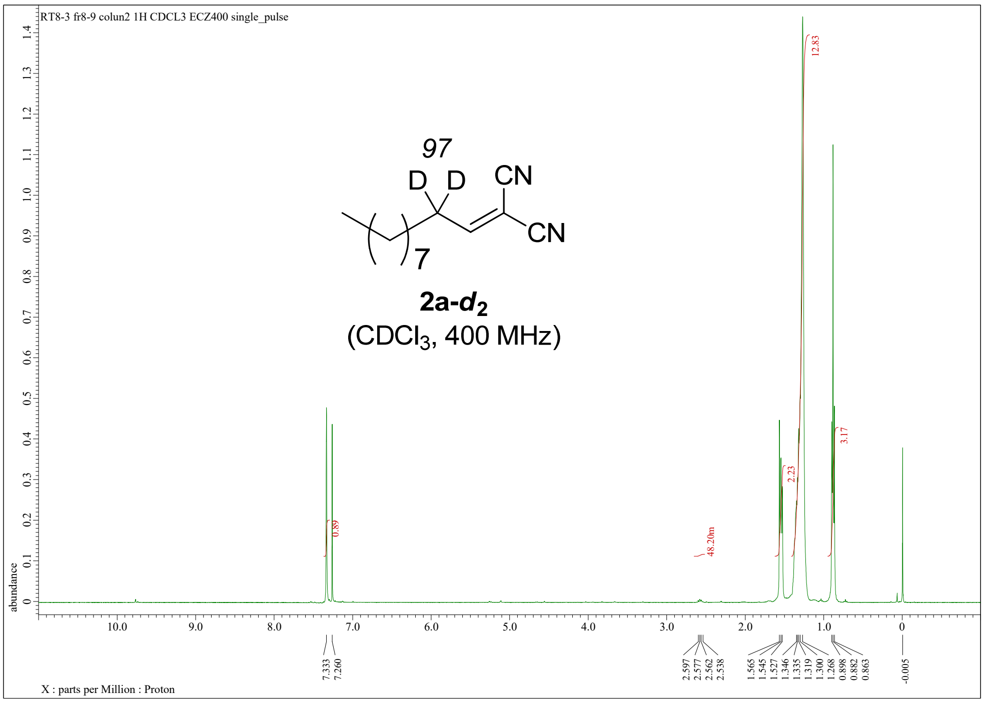
^{1}H NMR of 2-decylidenemalononitrile (2a)



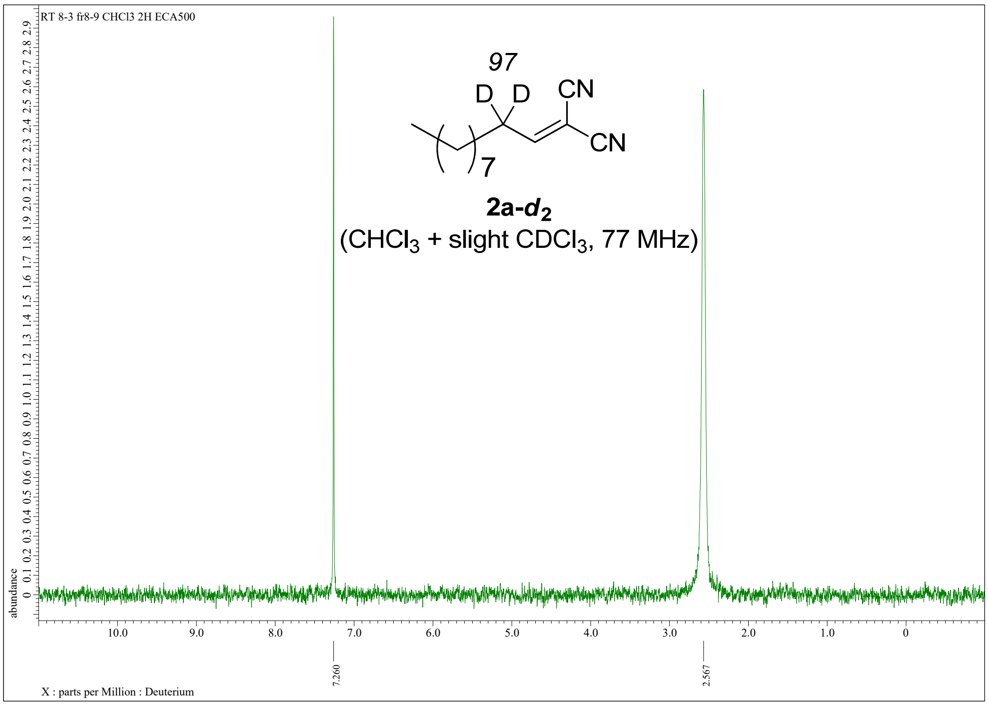
^{13}C NMR of 2-decylidenemalononitrile (2a)



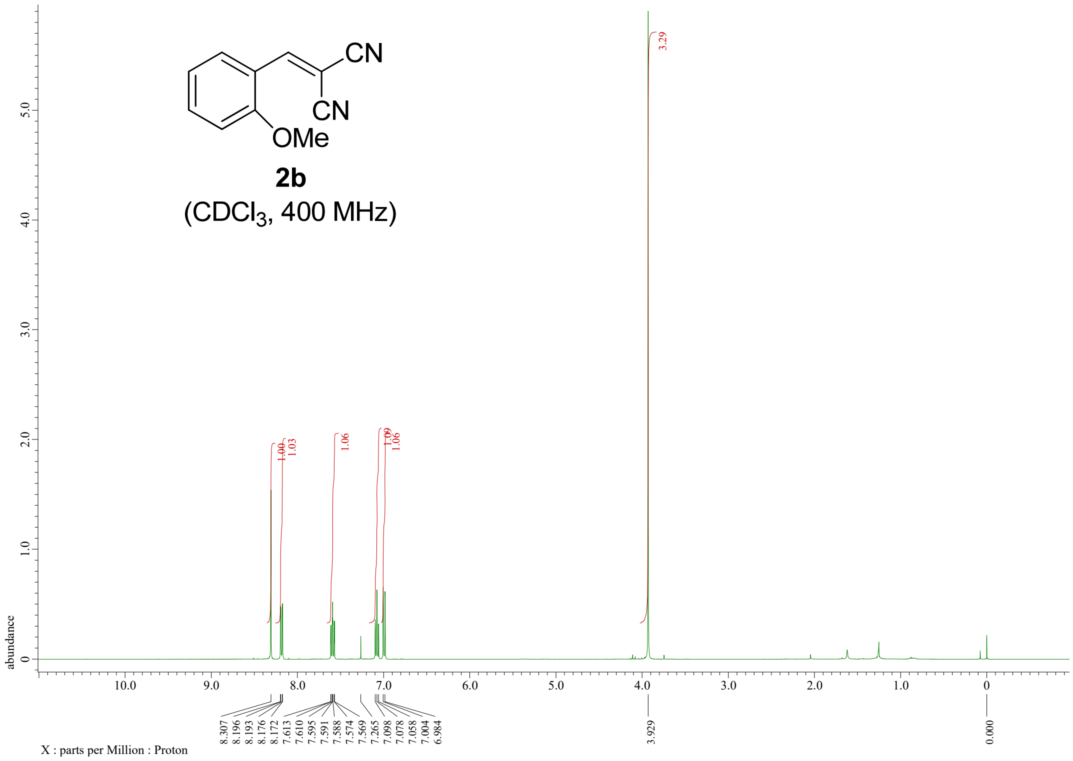
^{1}H NMR of 2-decylidenemalononitrile-d_2 (2a-d_2)



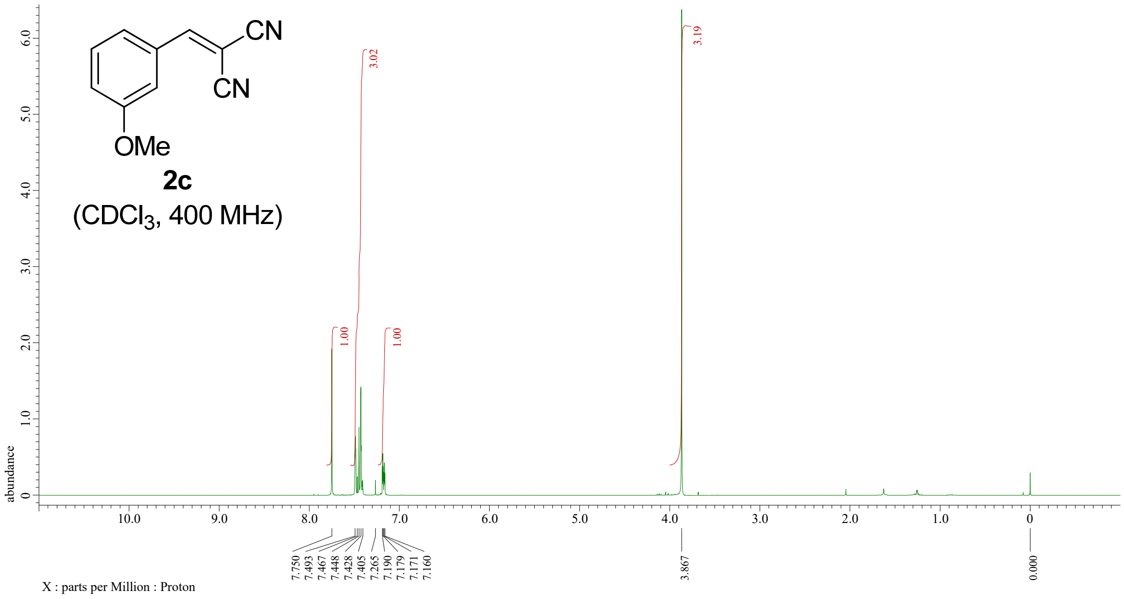
^{2}H NMR of 2-decylidenemalononitrile-d_2 (2a-d_2)



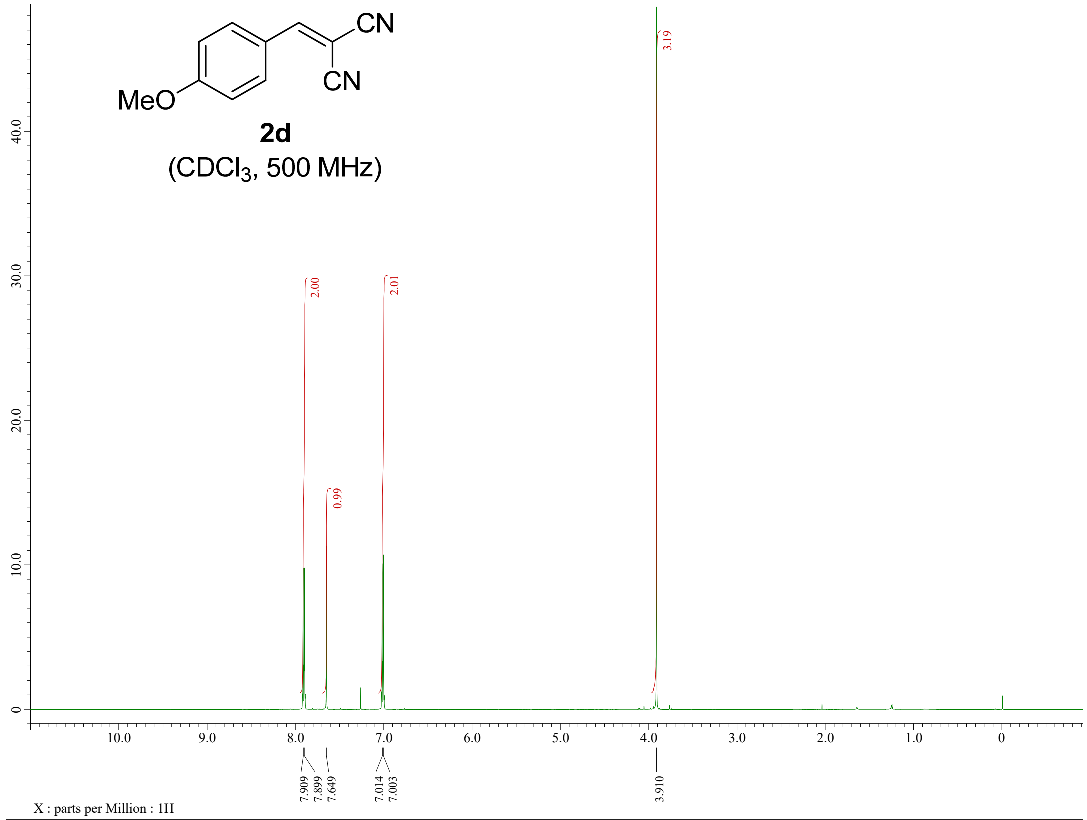
^{1}H NMR of 2-(2-methoxybenzylidene)malononitrile (2b)



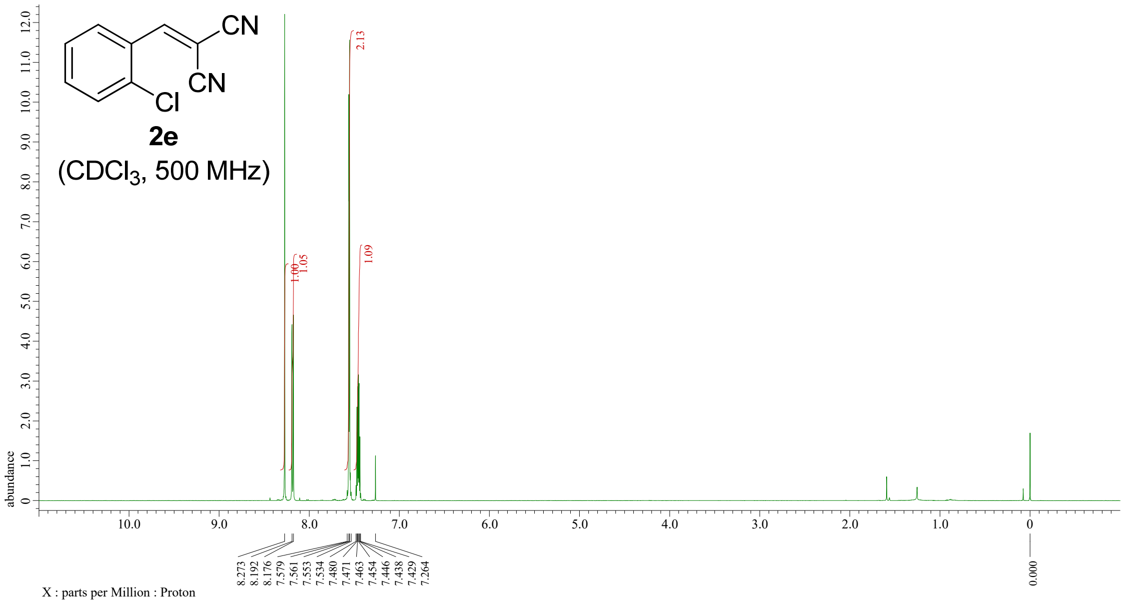
^{1}H NMR of 2-(3-methoxybenzylidene)malononitrile (2c)



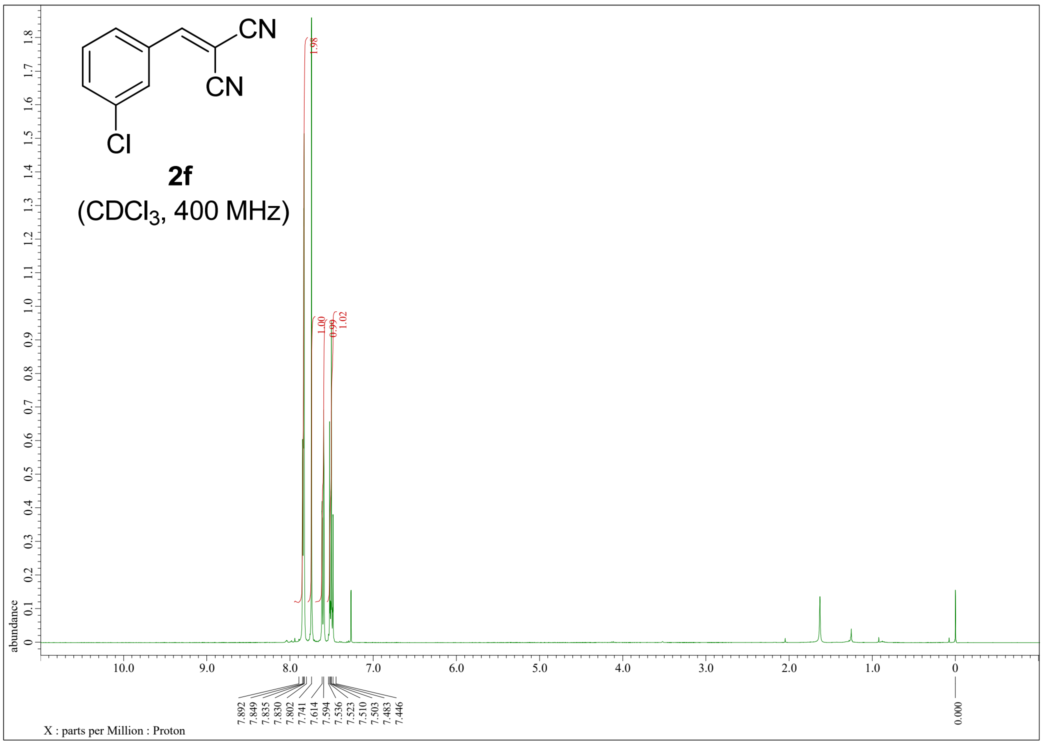
^{1}H NMR of 2-(4-Methoxyphenylmethylene)malononitrile (2d)



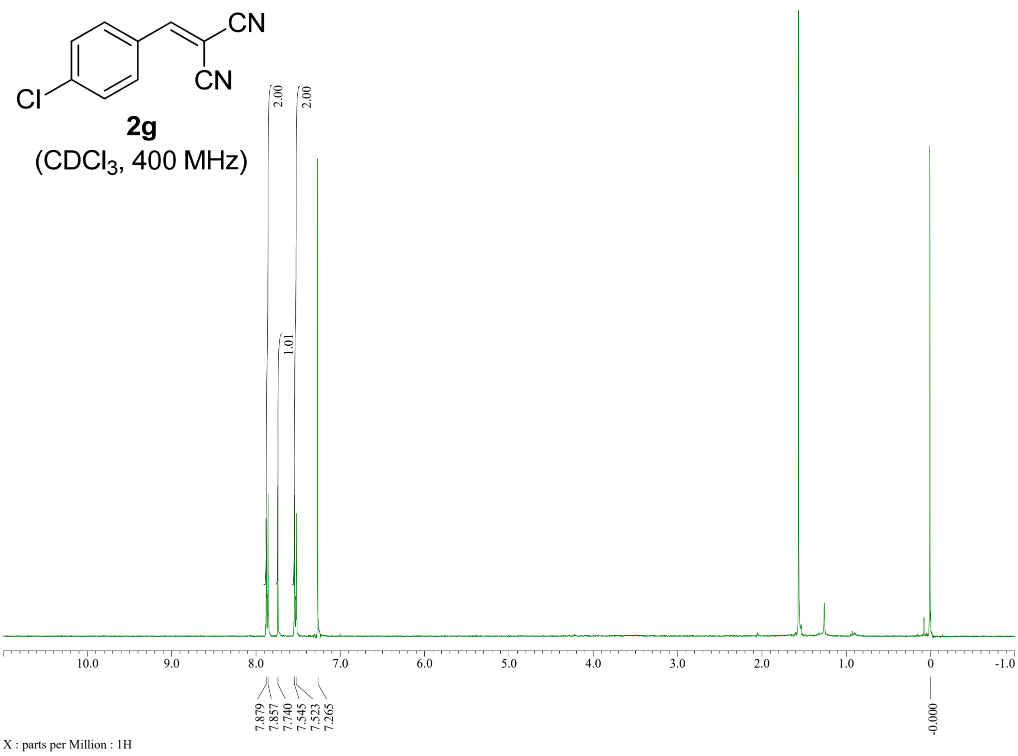
^{1}H NMR of o-chlorobenzylidene malononitrile (2e)



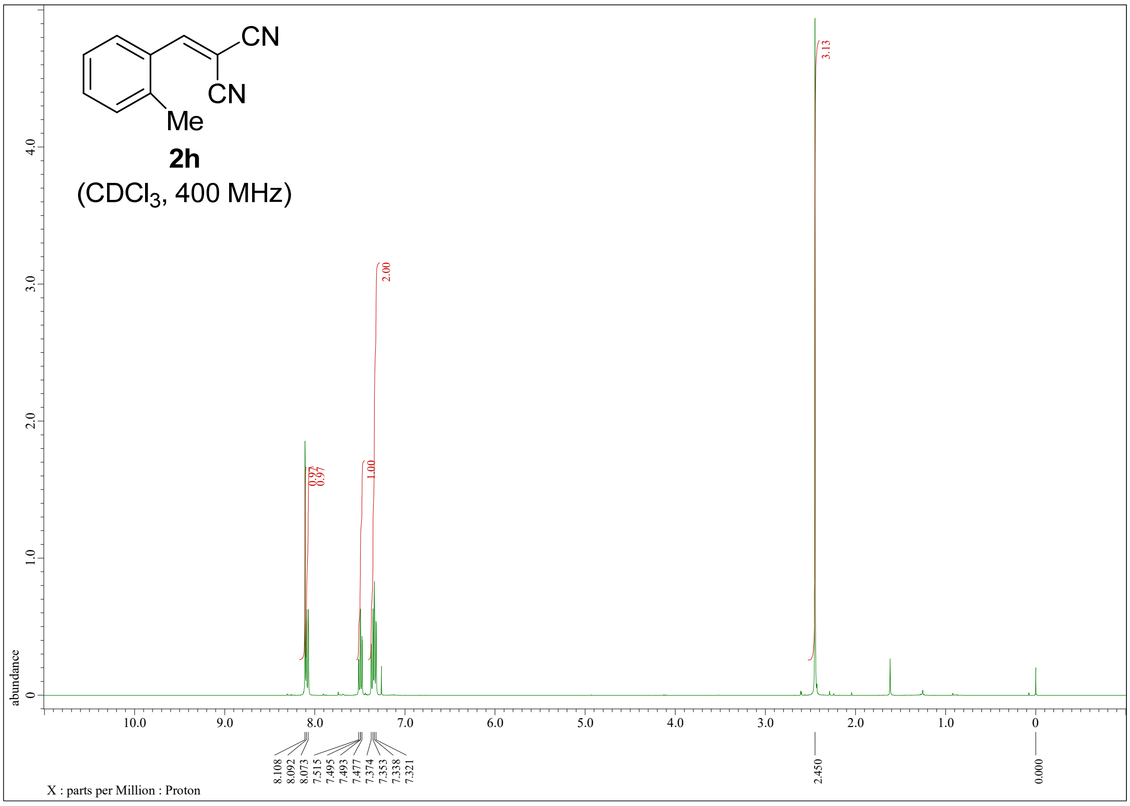
^{1}H NMR of 2-(3-chlorobenzylidene)malononitrile (2f)



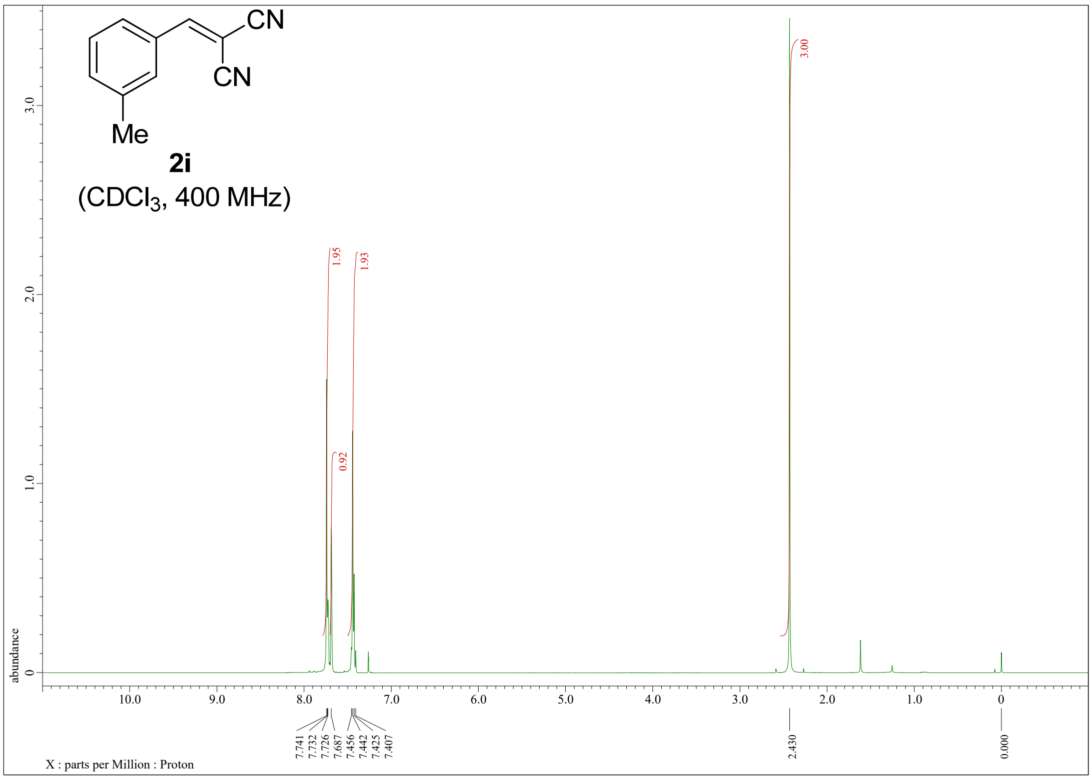
^{1}H NMR of 2-(4-chlorobenzylidene)malononitrile (2g)



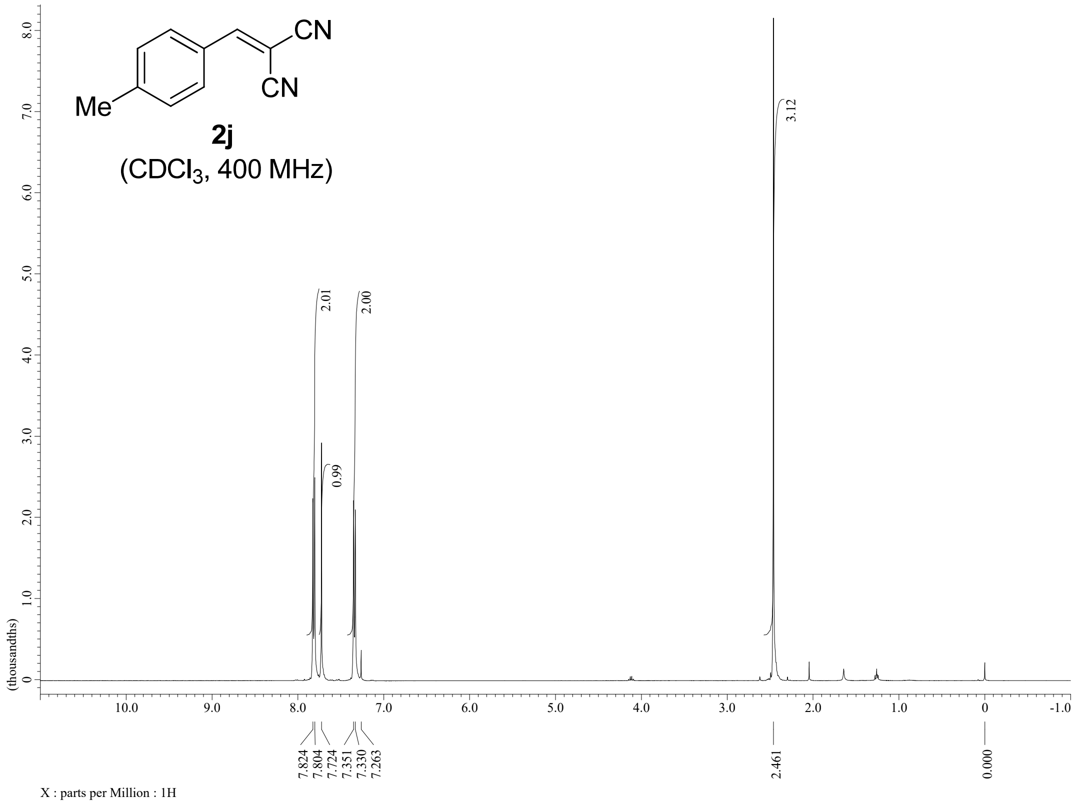
^{1}H NMR of 2-(2-methylbenzylidene)malononitrile (2h)



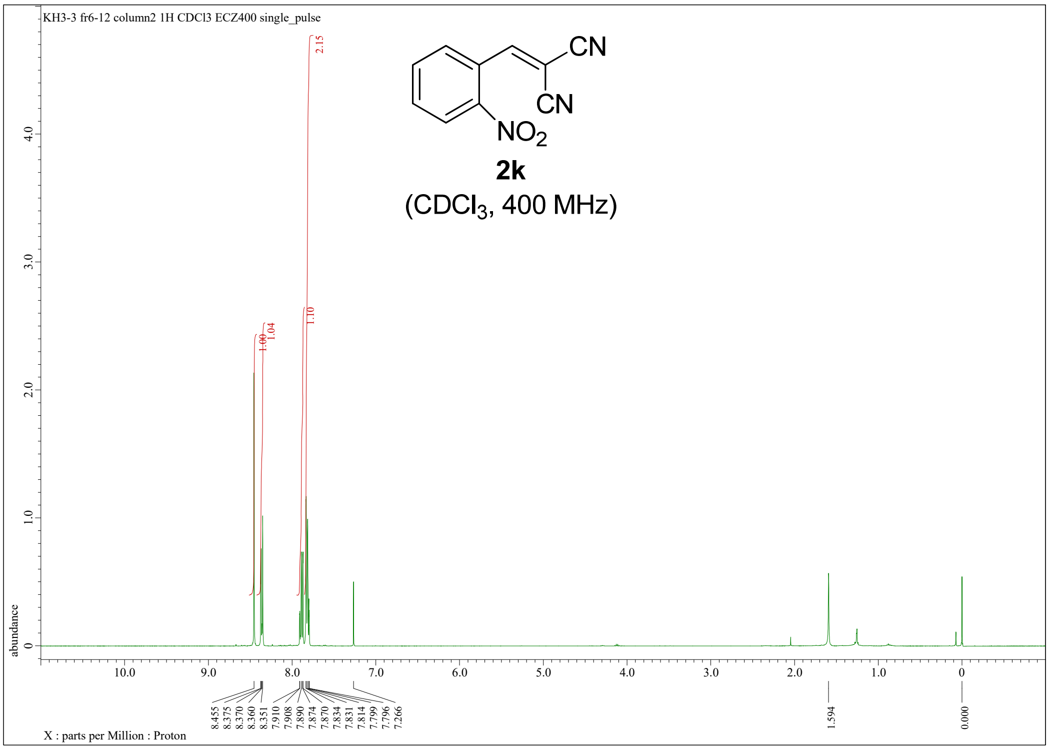
^{1}H NMR of 2-(3-methylbenzylidene)malononitrile (2i)



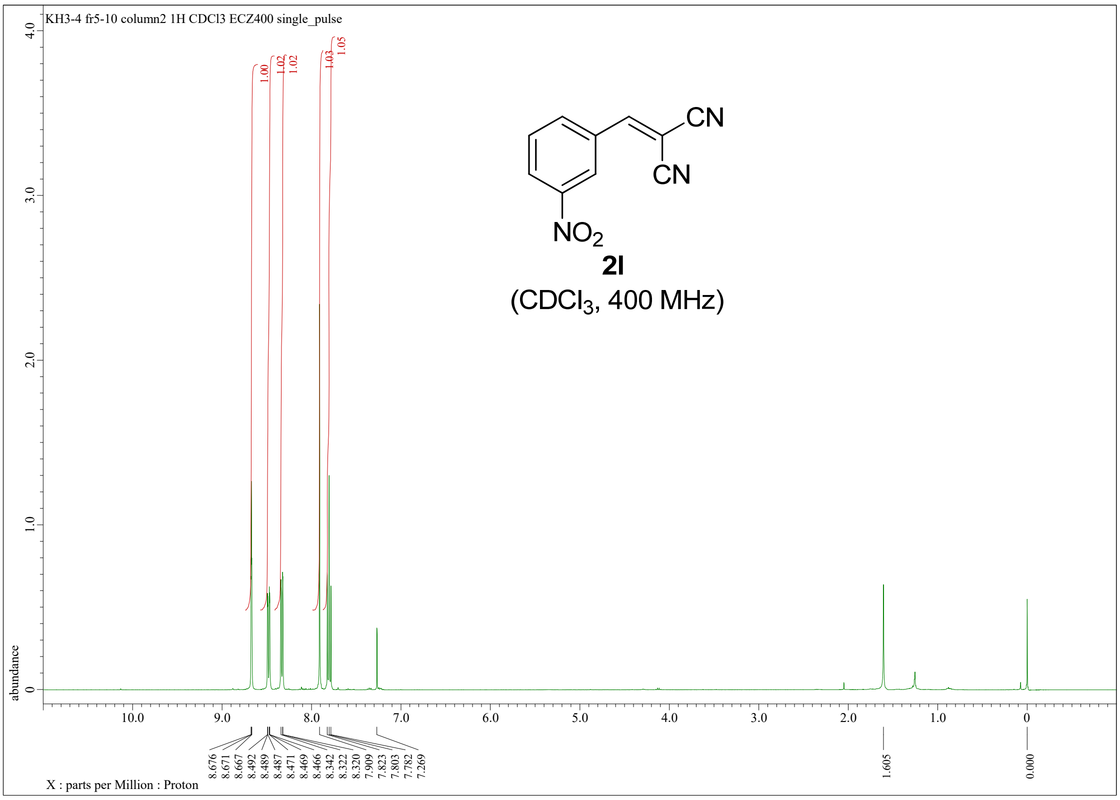
^{1}H NMR of 2-(4-Methylphenylmethylene)malononitrile (2j)



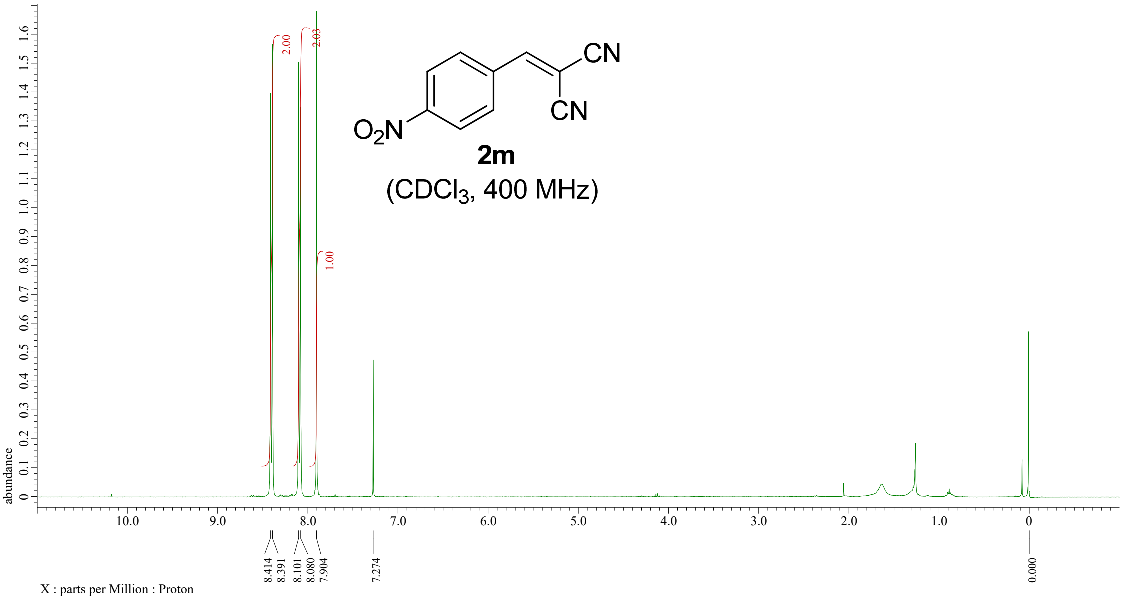
^{1}H NMR of 2-(2-nitrobenzylidene)malononitrile (2k)



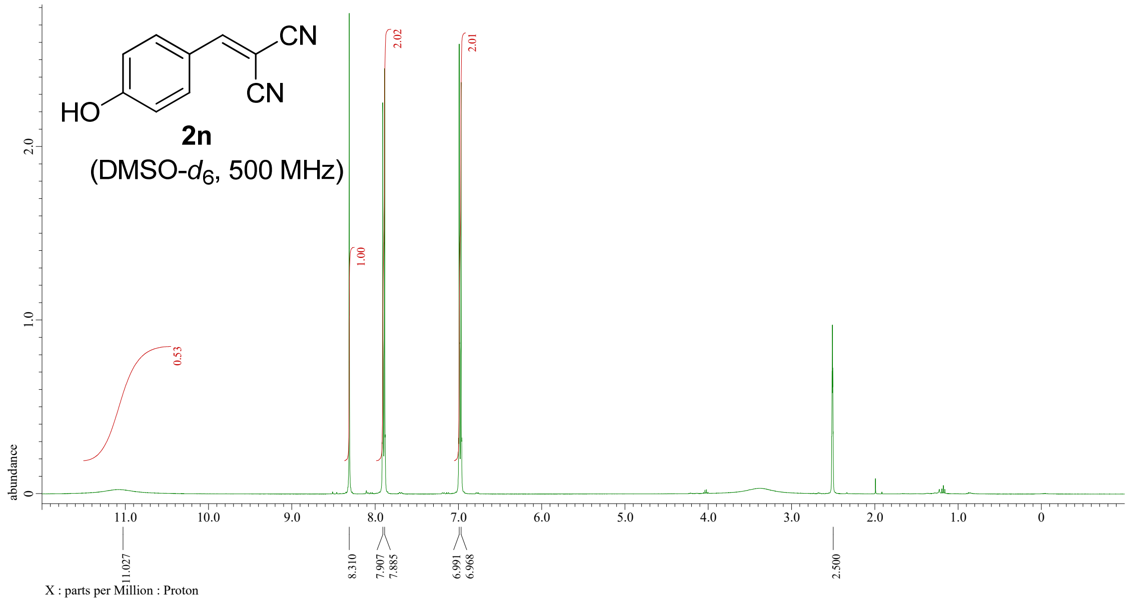
^{1}H NMR of 2-(3-nitrobenzylidene)malononitrile (2l)



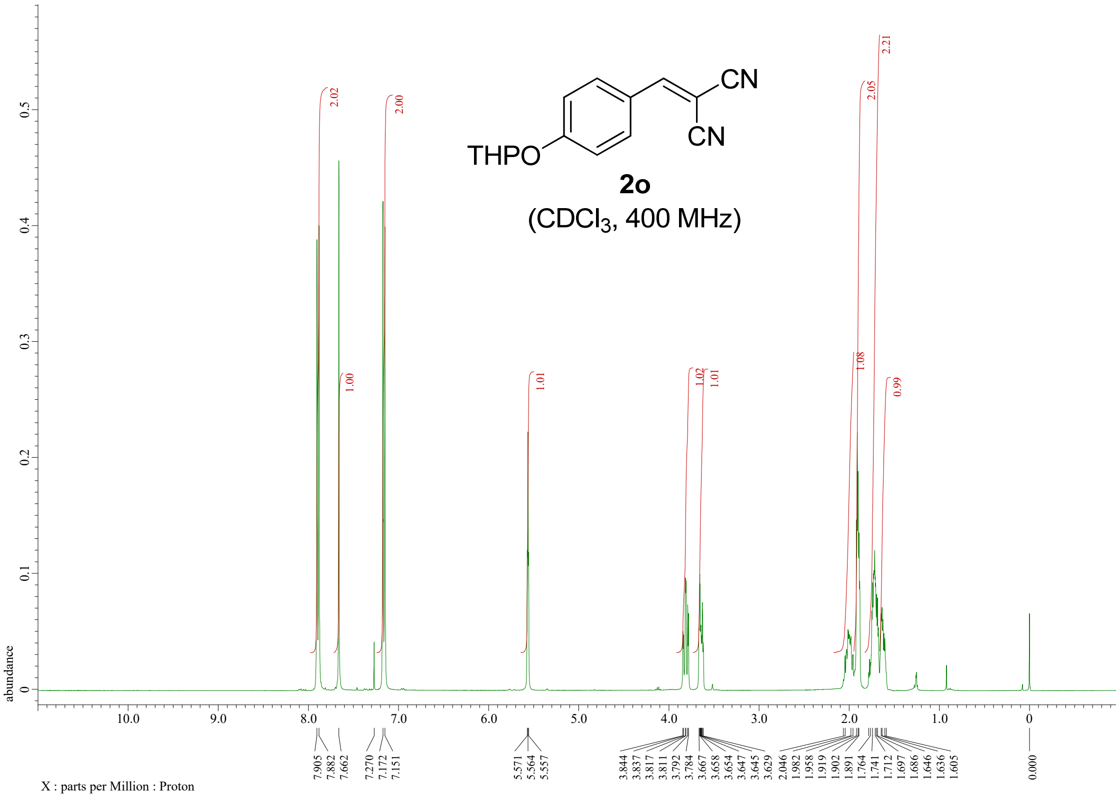
^{1}H NMR of 2-(4-nitrobenzylidene)malononitrile (2m)



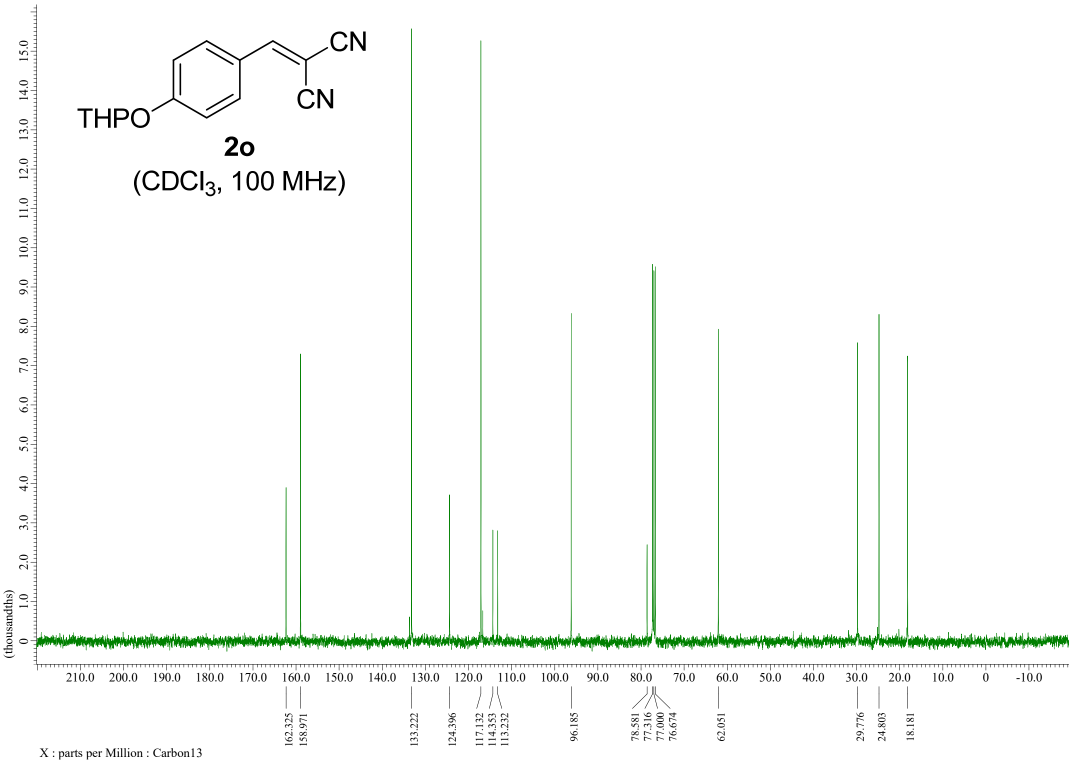
^{1}H NMR of 2-(4-hydroxybenzylidene)malononitrile (2n)



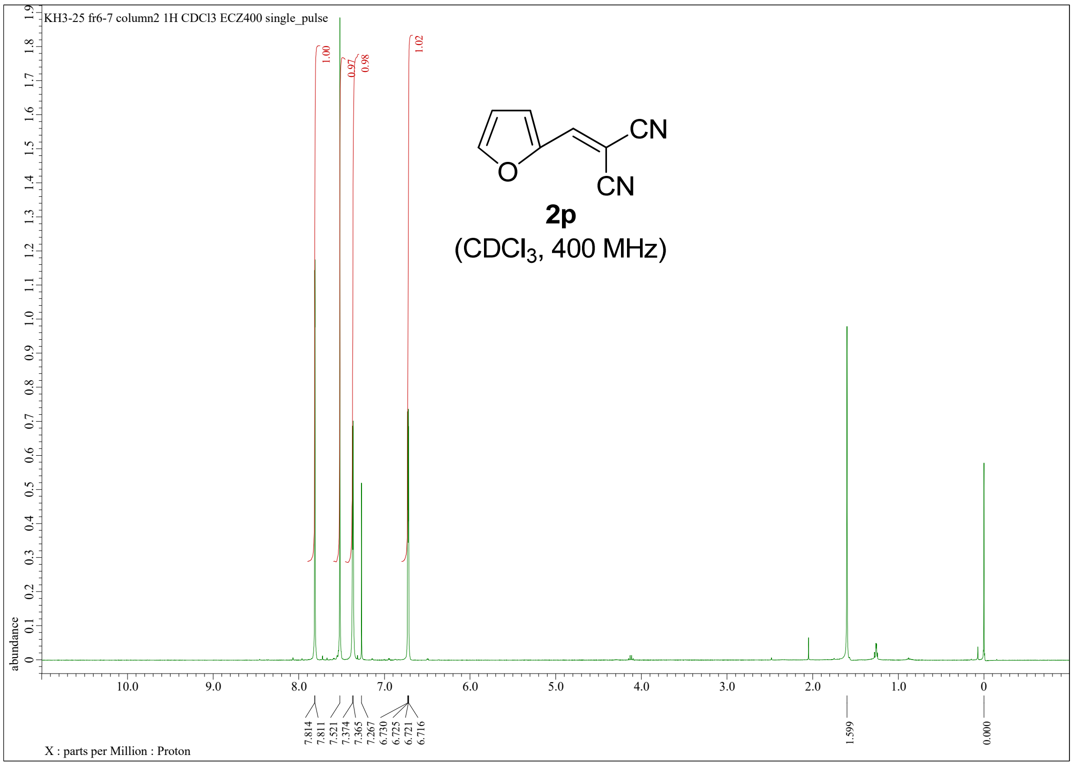
^{1}H NMR of 2-[[4-(oxan-2-yloxy)phenyl]methylidene]propanedinitrile (2o)



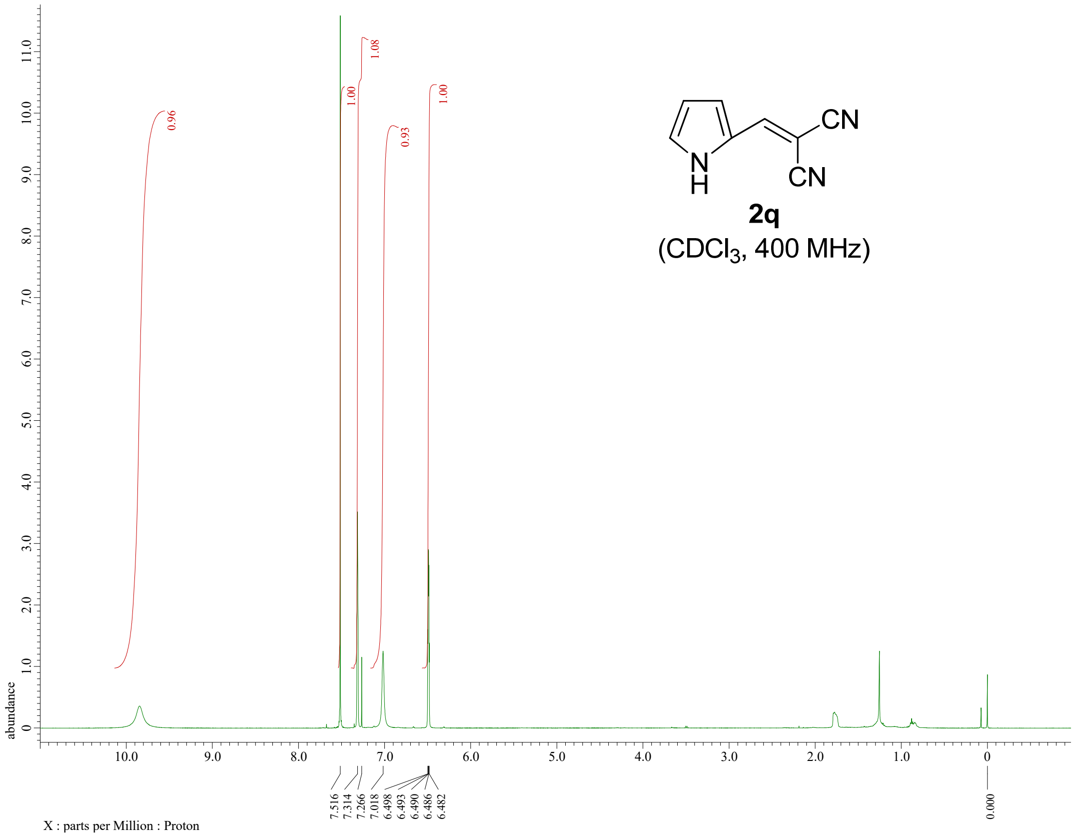
^{13}C NMR of 2-[[4-(oxan-2-yloxy)phenyl]methylidene]propanedinitrile (2o)



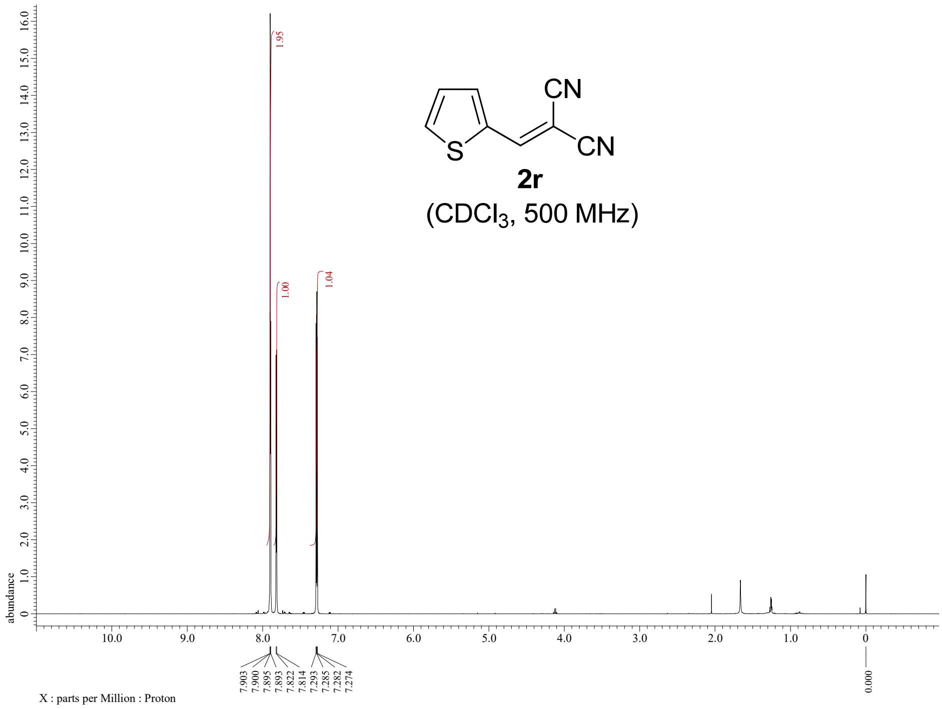
^{1}H NMR of 2-(Furan-2-ylmethylene)malononitrile (2p)



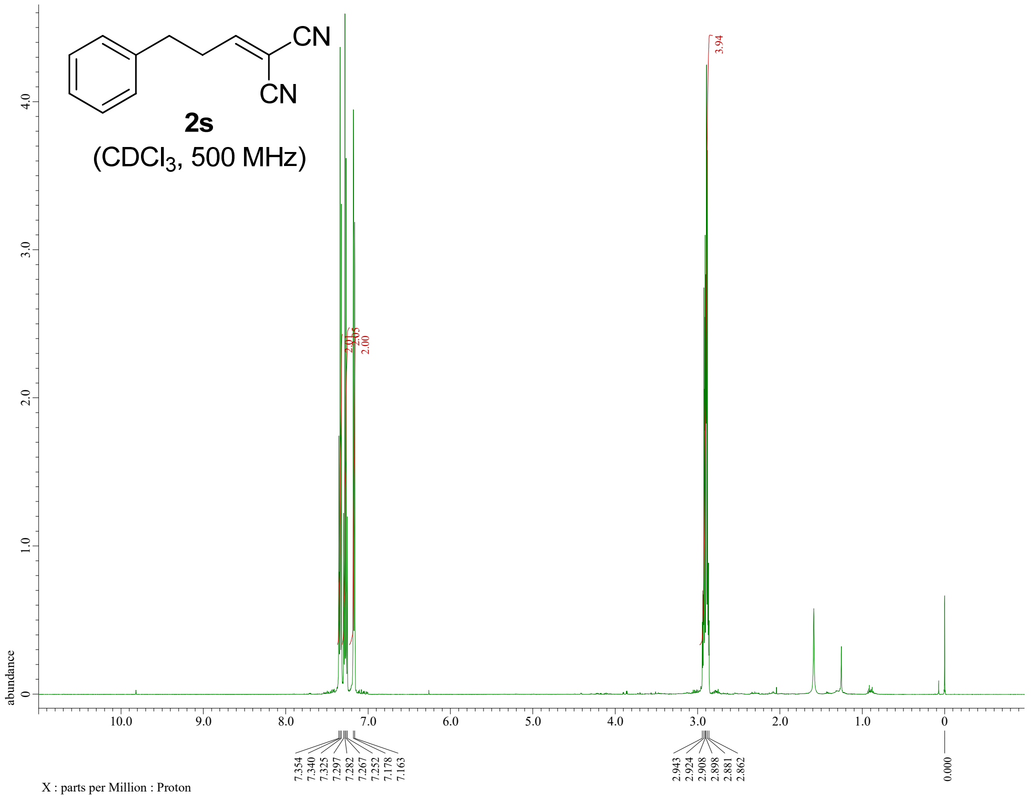
^{1}H NMR of 1,1-dicyano-2-(2-pyrrolyl)ethene (2q)



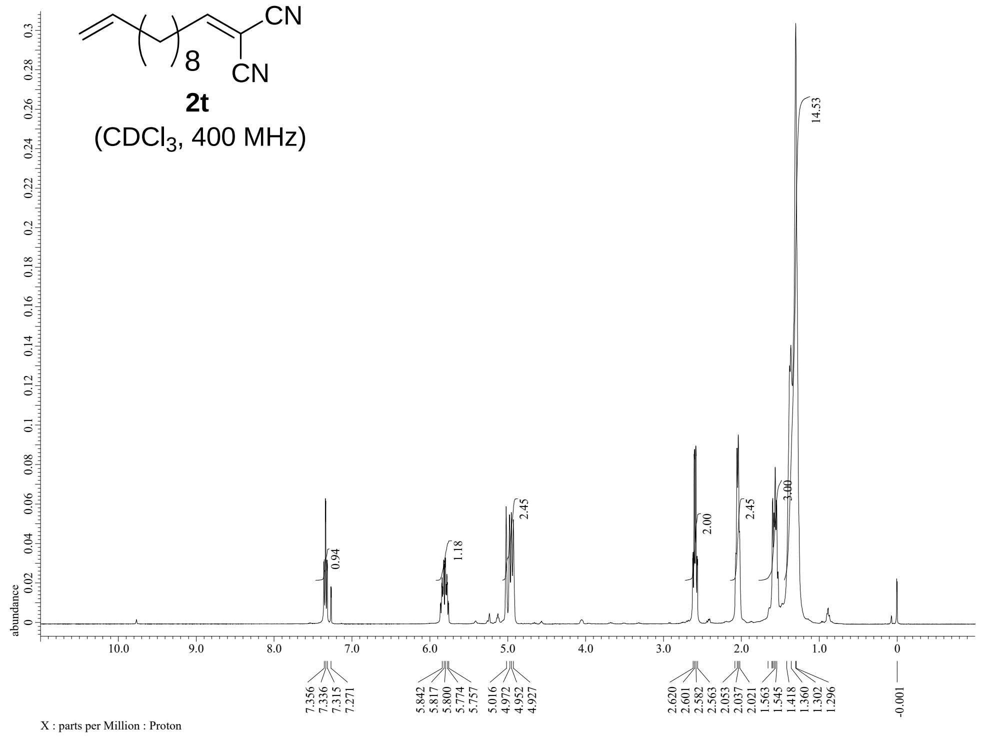
^{1}H NMR of 2-(Thiophen-2-ylmethylene)malononitrile (2r)



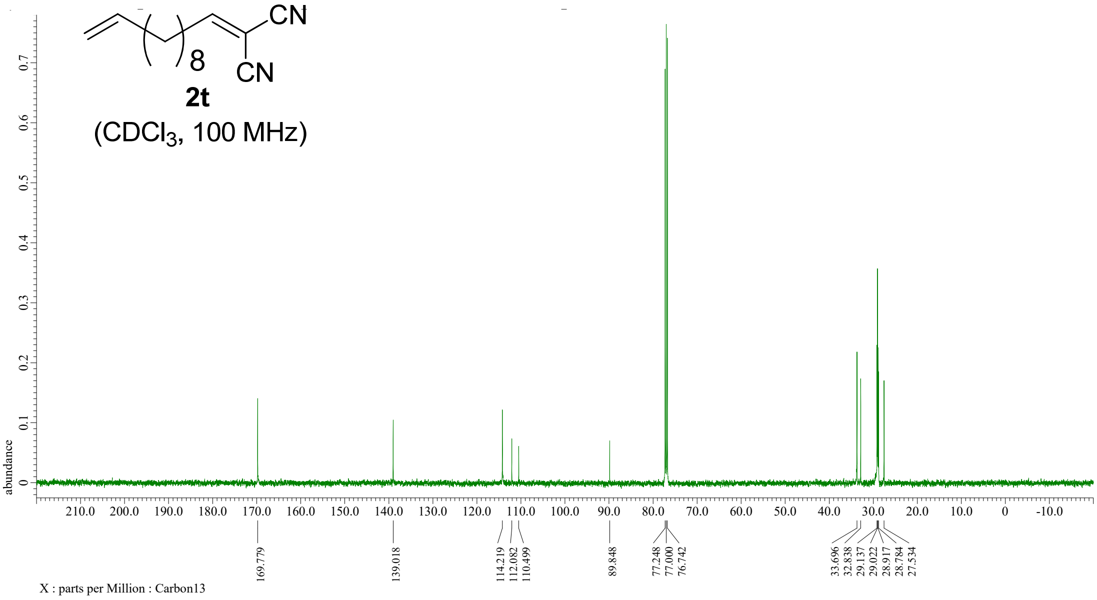
^{1}H NMR of 2-(3-phenylpropylidene)malononitrile (2s)



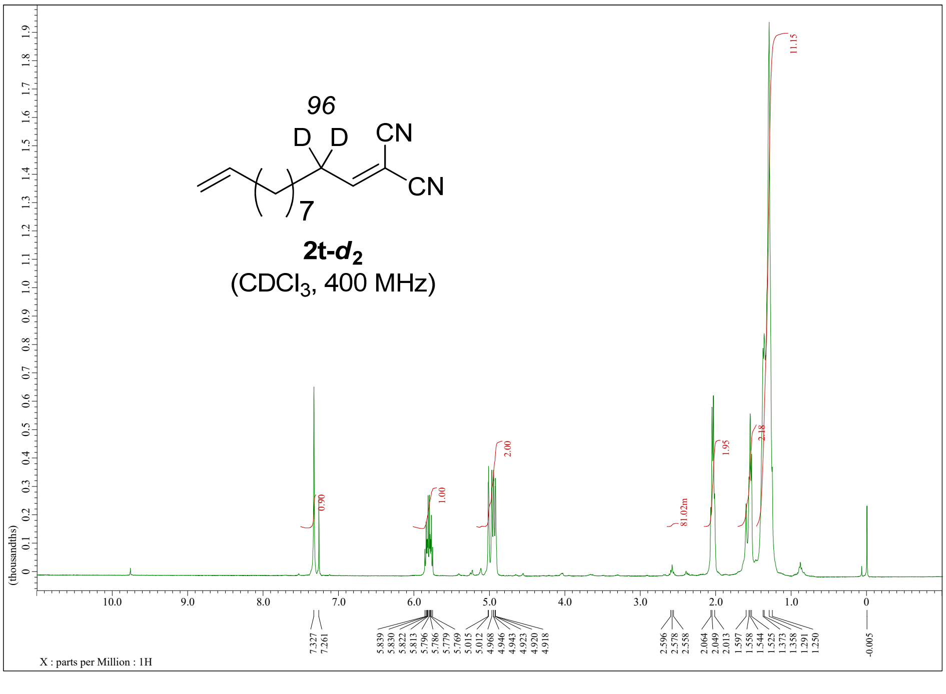
^{1}H NMR of 2-(10-undecenylidene)malononitrile (2t)



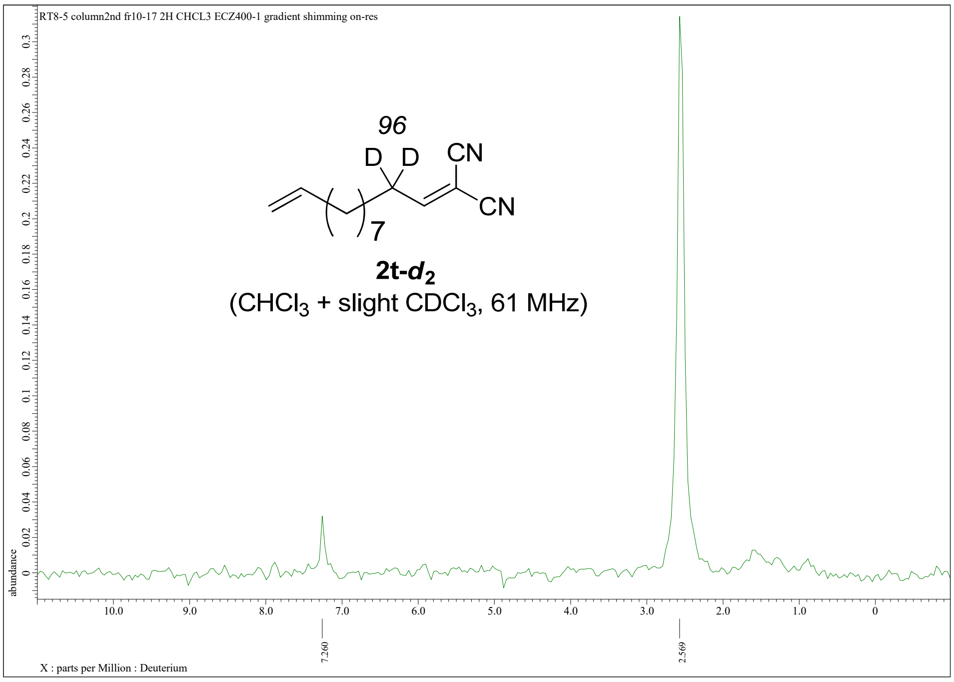
^{13}C NMR of 2-(10-undecenylidene)malononitrile (2t)



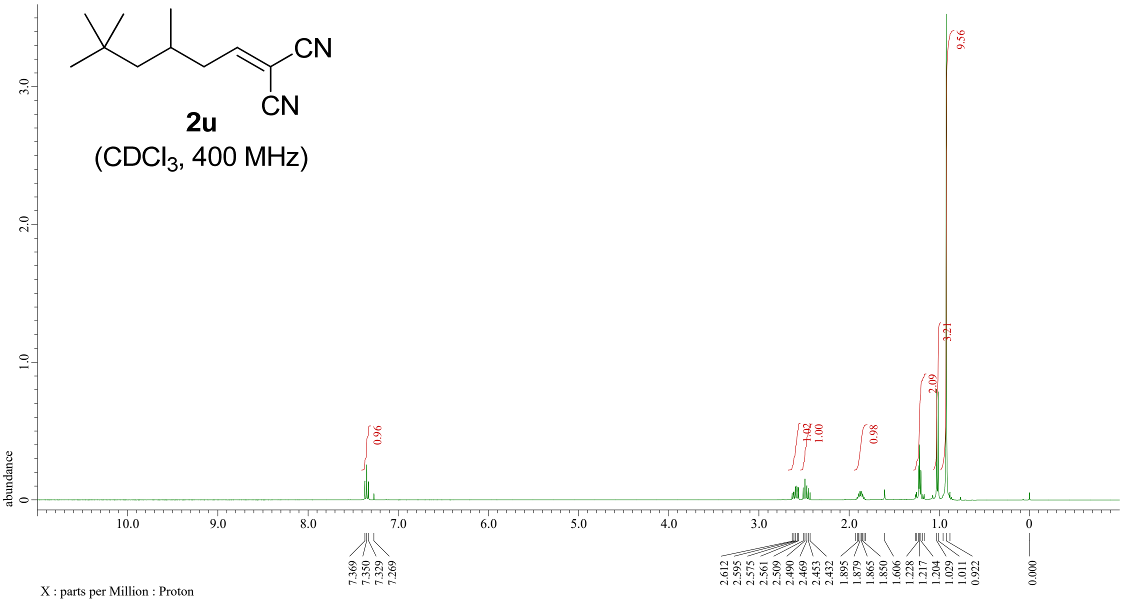
^{1}H NMR of 2-(10-undecenylidene)malononitrile-d_2 (2t-d_2)



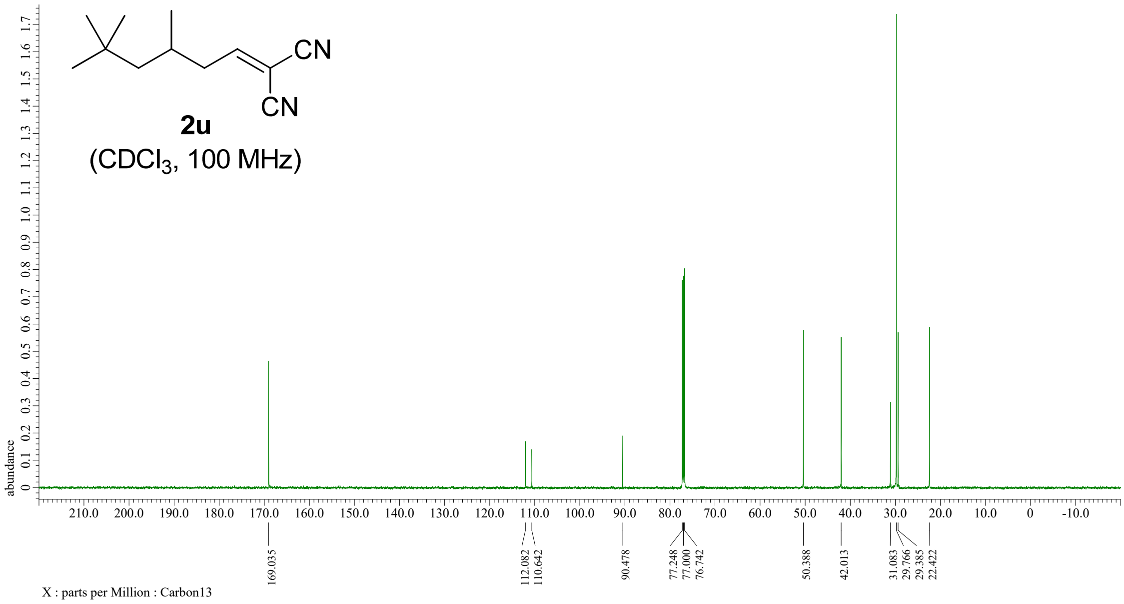
^{2}H NMR of 2-(10-undecenylidene)malononitrile-d_2 (2t-d_2)



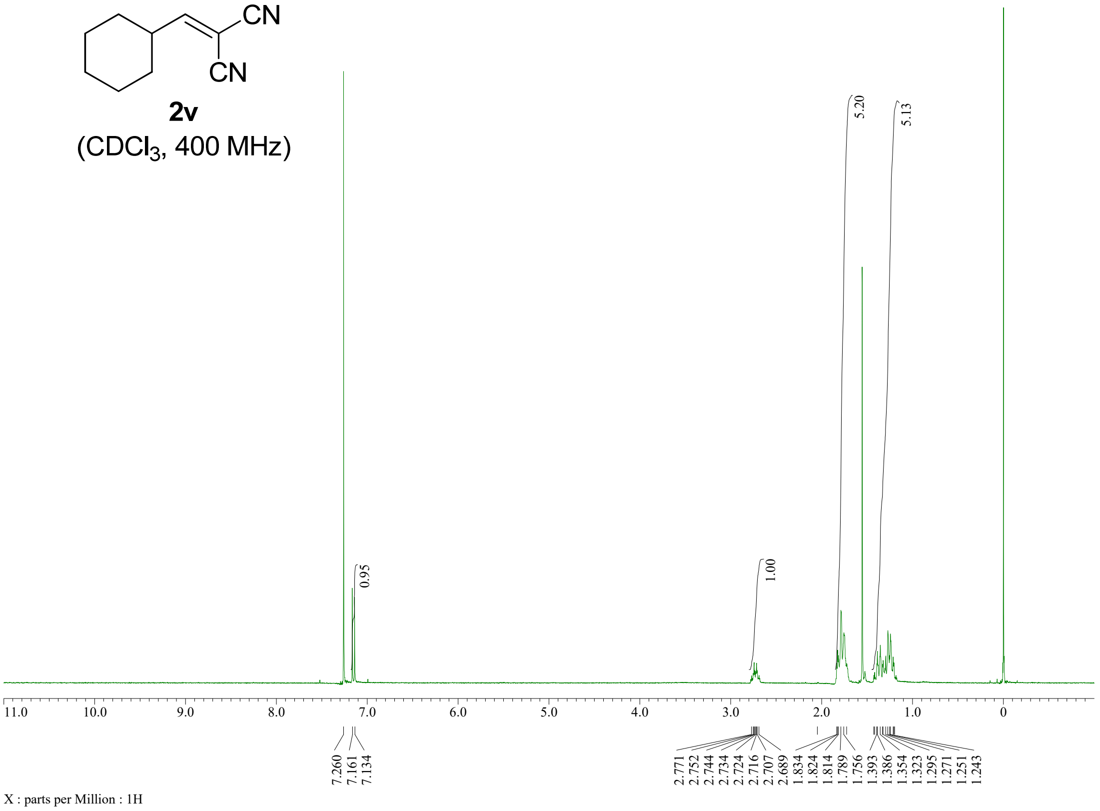
^{1}H NMR of 2-(3,5,5-trimethylhexylidene)propanedinitrile (2u)



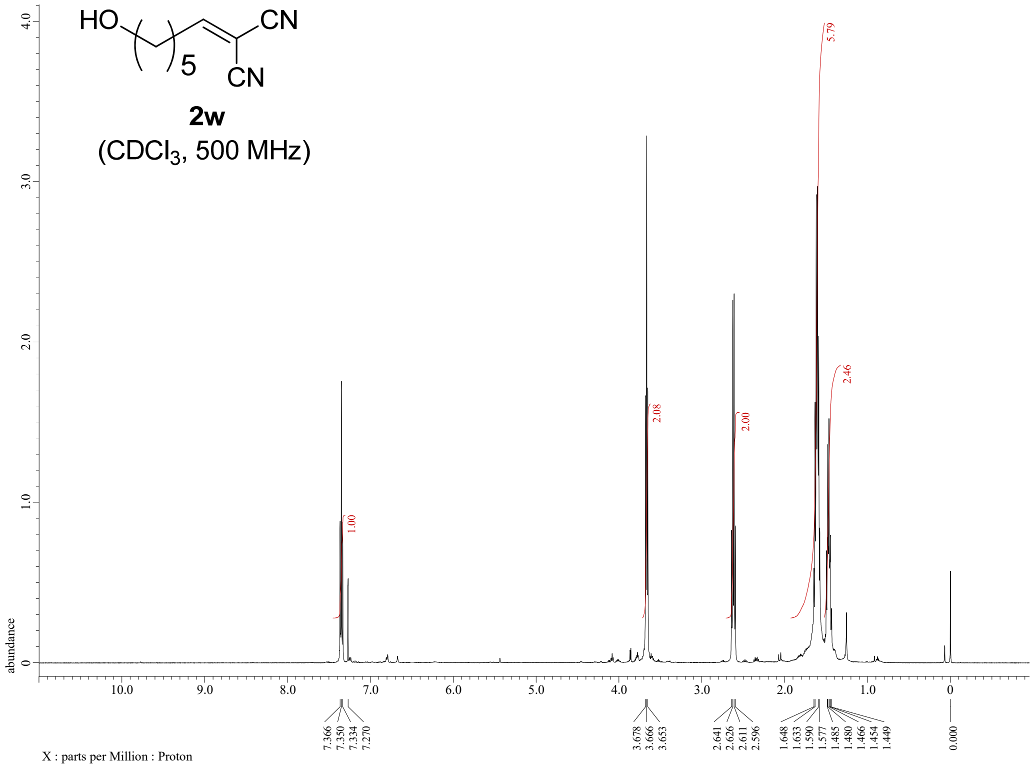
^{13}C NMR of 2-(3,5,5-trimethylhexylidene)propanedinitrile (2u)



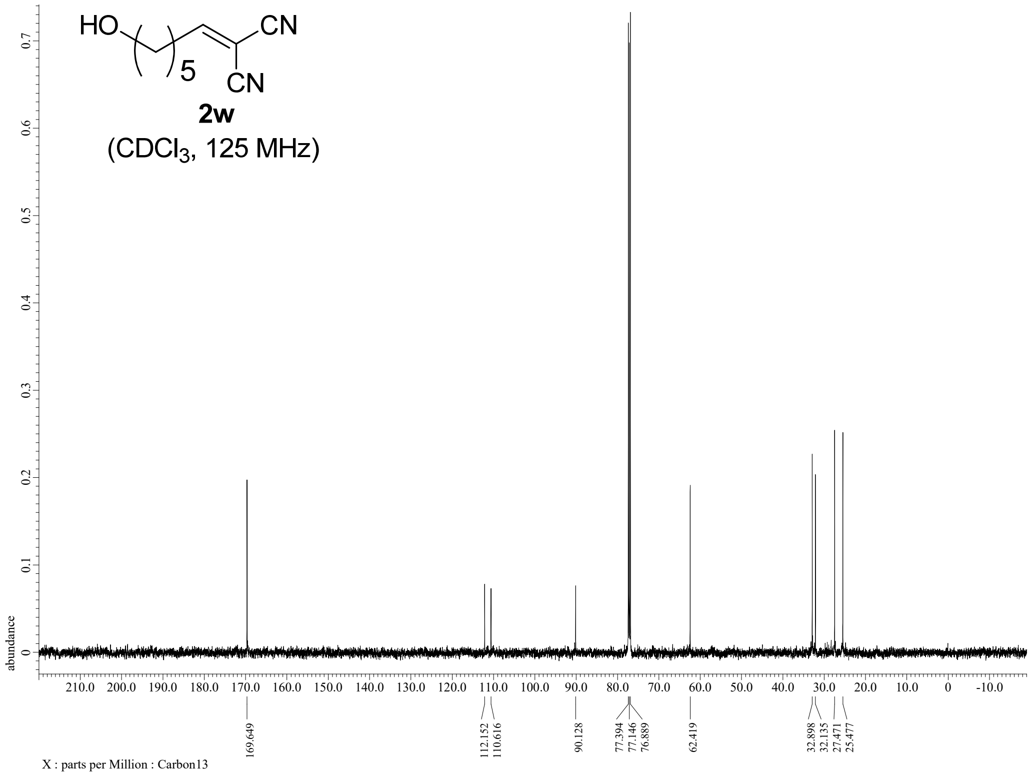
^{1}H NMR of 1,1-dicyano-2-cyclohexylethene (2v)



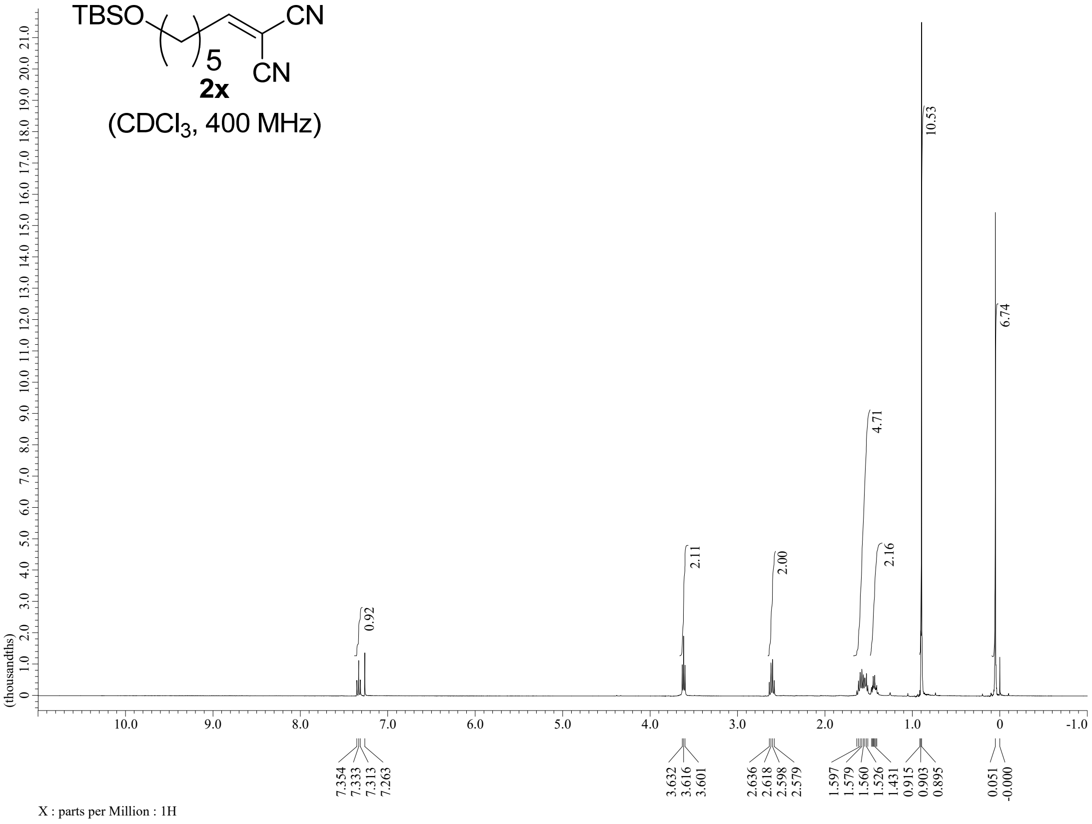
^{1}H NMR of 2-(6-hydroxyhexylidene)malononitrile (2w)



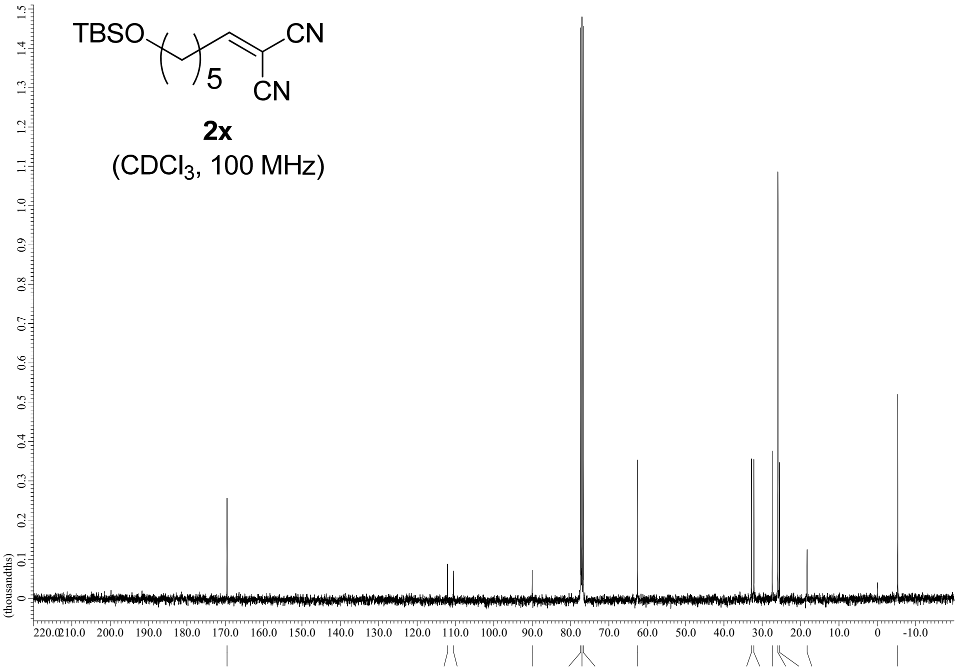
^{13}C NMR of 2-(6-hydroxyhexylidene)malononitrile (2w)



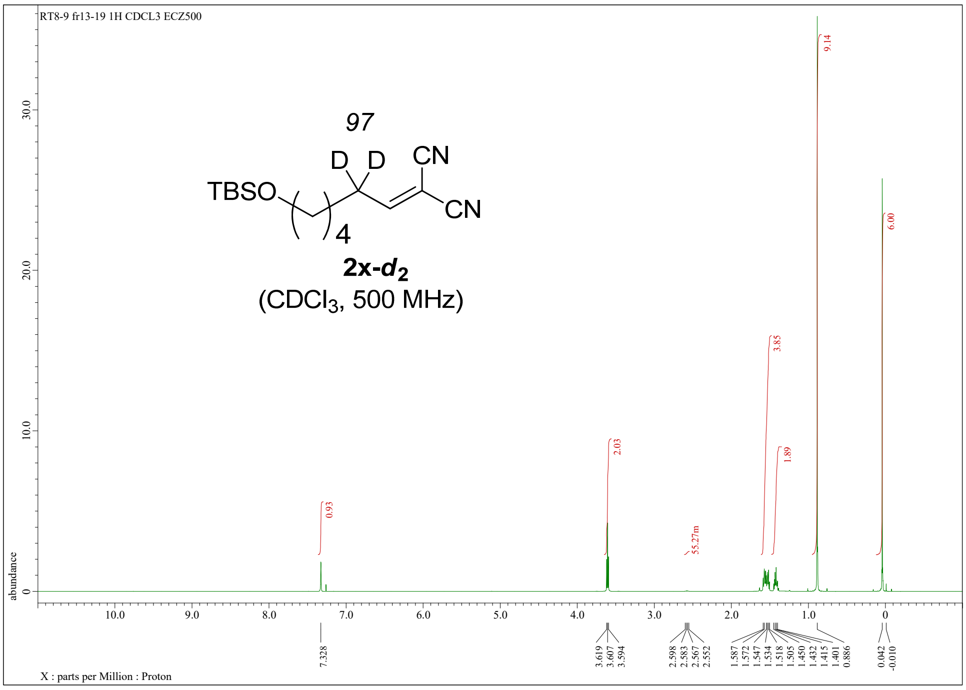
^{1}H NMR of 2-[6-[(tert-butyldimethylsilyl)oxy]hexylidene]malononitrile (2x)



^{13}C NMR of 2-[6-[(tert-butyldimethylsilyl)oxy]hexylidene]malononitrile (2x)



^{1}H NMR of 2-[6-[(tert-butyldimethylsilyl)oxy]hexylidene]malononitrile-d_2 (2x-d_2)



^{2}H NMR of 2-[6-[(tert-butyldimethylsilyl)oxy]hexylidene]malononitrile-d_2 (2x-d_2)