Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Acyl radicals generated from aldehydes with NHPI as electrocatalyst: Aldehydes and alcohols as carbon-centered radical precursors

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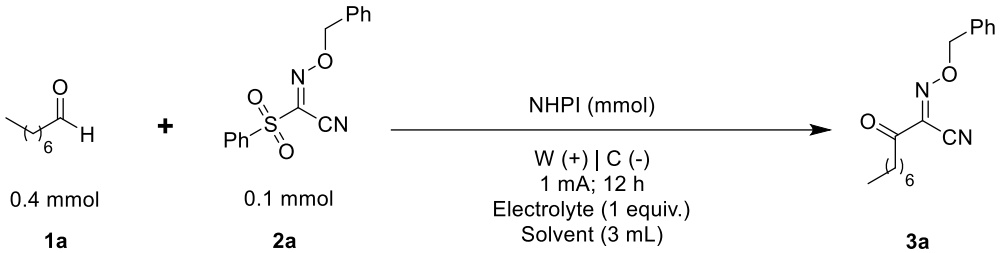
1. General methods and starting materials.

The starting materials except for the oximes used in the first part of the study, as well as the solvents used for the reactions, were acquired from commercial suppliers and used without further purification (The acetonitrile used as solvent was CHROMASOLV™ Gradient for HPLC, gradient grade ≥99,9%; water was distilled water, tetrahydrofuran was inhibitor free). The oximes where synthesised following a procedure reported in literature.[1] For the thin layer chromatography (TLC) silica gel sheets containing a fluorescent indicator (254 nm) were used and compounds were visualized by irradiation with 254 nm light and/or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Flash column chromatography was performed using Geduran® Silica Gel 60 (0.040-0.063 nm)**.** Cyclohexane, ethyl acetate for flash chromatography were acquired from commercial sources and were used without previous purification. NMR spectra were acquired on a *Bruker AVANCE 300 MHz spectrometer*, running at 300 MHz, 75 MHz and 282 MHz for ^{1}H, ^{13}C and ^{9}F, respectively or in a or in *Bruker AVANCE NEO 500 spectrometer* (500 MHz for ^{1}H and 126 MHz for ^{13}C). Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H-NMR and 77.16 ppm for ^{13}C-NMR). ^{13}C-NMR was acquired on a broad band decoupled mode. The following abbreviations are used to describe peak patterns: s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), tt (triplet of triplets, ddt (doublet of doublet of triplets), ttd (triplet of triplet of doublets). The exact mass of the products was measured with an *Agilent Technologies 6120 Quadrupole LC/MS* mass spectrometer. MS (ESI) (Electrospray ionization mass spectroscopy) was the technique of choice for the ionisation of the samples. *MassWorks software ver. 4.0.0.0 (Cerno Bioscience*) was used for the identification of the molecules. *MassWorks* is a MS calibration software which calibrates for isotope profile as well as for mass accuracy, allowing highly accurate comparisons between calibrated and theoretical spectra.[1]

All the electrodes and equipment (ElectraSyn 2.0) used for the electrochemical experiments were acquired from IKA.
GRC electrode: Graphite SK-50 (https://www.ika.com/es/Productos-LabEq/Kit-de-electroquimica-pg516/Graphite-SK-50,-Set-of-12-40002858/)
Ni foam: Nickel foam, (https://www.ika.com/es/Productos-LabEq/Kit-de-electroquimica-pg516/Nickel-foam,-Set-of-12-40002861/)

2. Optimisation Tables.

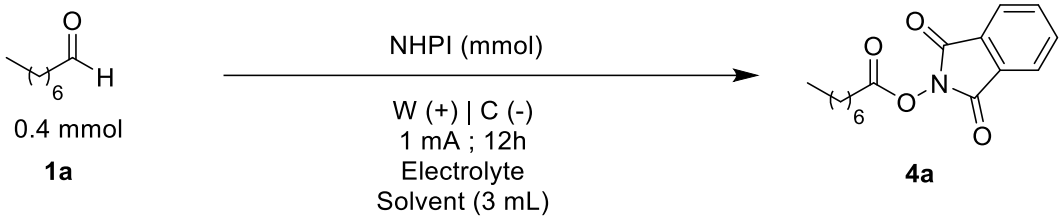
Table S1. Optimisation table of the addition of acyl radicals to oximes.[a]



Entry	*Solvent (3 mL)*	*NHPI (equiv.)*	*Electrolyte*	*W (+) / C (-)*	*Yield (%)[b]*
1[c]	MeCN:H_2O 2:1	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	28
2	MeCN:H_2O 2:1	0.5	$TBABF_4$	GRC (+) | Pt (-)	8
3	MeCN:H_2O 2:1	0.5	$TBABF_4$	GRC (+) | Zn (-)	3
4	MeCN:H_2O 2:1	0.5	$TBABF_4$	GRC (+) | GRC (+)	7
5	MeCN	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	34
6	MeCN:H_2O 2:1	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	67
7	DMF	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	0
8	Acetone	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	33
9	Acetone:H_2O 2:1	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	5
10	H_2O	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	6
11	MeCN:H_2O 1:2	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	8
12	MeCN:H_2O 1:1	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	10
13	MeCN:H_2O 3:1	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	69
14	MeCN:H_2O 4:1	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	46
15	MeCN:H_2O 5:1	0.5	$TBABF_4$	GRC (+) | Ni_{foam} (-)	62
16	MeCN:H_2O 3:1	0.5	$TBAPF_6$	GRC (+) | Ni_{foam} (-)	15
17	MeCN:H_2O 3:1	0.5	NH_4BF_4	GRC (+) | Ni_{foam} (-)	32
18	MeCN:H_2O 3:1	0.5	$LiClO_4$	GRC (+) | Ni_{foam} (-)	48
19	MeCN:H_2O 3:1	0.5	TBABr	GRC (+) | Ni_{foam} (-)	37
20	MeCN:H_2O 3:1	0.5	NH_4PF_6	GRC (+) | Ni_{foam} (-)	48
21	MeCN:H_2O 3:1	0.5	KCl	GRC (+) | Ni_{foam} (-)	72
22	MeCN:H_2O 3:1	0.5	NaCl	GRC (+) | Ni_{foam} (-)	59
23	MeCN:H_2O 3:1	0.1	KCl	GRC (+) | Ni_{foam} (-)	33
24	MeCN:H_2O 3:1	0.2	KCl	GRC (+) | Ni_{foam} (-)	53
25	MeCN:H_2O 3:1	0.2	KCl	GRC (+) | Ni_{foam} (-)	48
26	MeCN:H_2O 3:1	0.4	KCl	GRC (+) | Ni_{foam} (-)	55
27[d]	MeCN:H_2O 3:1	0.5	KCl	GRC (+) | Ni_{foam} (-)	55
28[e]	MeCN:H_2O 3:1	0.5	KCl	GRC (+) | Ni_{foam} (-)	15
29	MeCN:H_2O 3:1	-	KCl	GRC (+) | Ni_{foam} (-)	n.r.

[a] Standard reaction conditions: 0.1 mmol of N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide and 0.4 mmol of octanal in 3 mL MeCN:H_2O 2:1 with TBABF4 (0.1 mmol), under air atmosphere, were set at constant current of 1 mA for 12h at room temperature. [b] Yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c] 2.5 mA, 3h instead of 1 mA, 12h d 0.2 mmol of octanal instead of 0.4 mmol. [e] 5 mA, 12h instead of 1 mA, 12h.

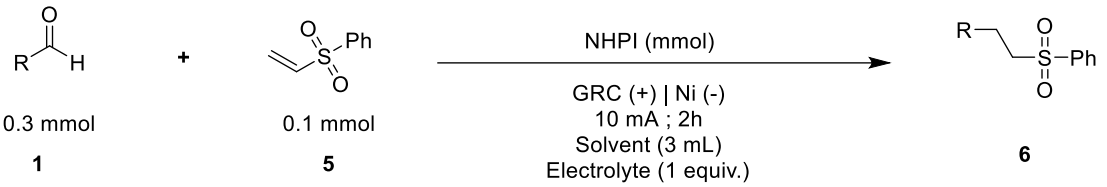
Table S2. Optimisation table towards RAE preparation.[a]



Entry	*Solvent*	*1a (mmol)*	*NHPI (mmol)*	*Electrolyte*	*W (+) / C (-)*	*Yield (%)[b]*
1	MeCN:H_2O 3:1	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	65
2	Acetone	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	38
3	DCM	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	20
4	DMF	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	6
5	H_2O	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	3
6	MeCN	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	20
7	MeCN:H_2O 1:1	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	59
8	MeCN:H_2O 2:1	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	65
9	MeCN:H_2O 1:2	0.4	0.05	$LiClO_4$	GRC (+) | Ni_{foam} (-)	14
10	MeCN:H_2O 3:1	0.1	0.1	$LiClO_4$	GRC (+) | Ni_{foam} (-)	21
11	MeCN:H_2O 3:1	0.05	0.1	$LiClO_4$	GRC (+) | Ni_{foam} (-)	15
12	MeCN:H_2O 3:1	0.1	0.2	$LiClO_4$	GRC (+) | Ni_{foam} (-)	27
13	MeCN:H_2O 3:1	0.1	0.3	$LiClO_4$	GRC (+) | Ni_{foam} (-)	24
14	MeCN:H_2O 3:1	0.1	0.4	$LiClO_4$	GRC (+) | Ni_{foam} (-)	27
15	MeCN:H_2O 3:1	0.1	0.2	$LiClO_4$	GRC (+) | Ni_{foam} (-)	7
16[c]	MeCN:H_2O 3:1	0.1	0.2	$LiClO_4$	GRC (+) | Ni_{foam} (-)	22
17[d]	MeCN:H_2O 3:1	0.1	0.2	$LiClO_4$	GRC (+) | Ni_{foam} (-)	25
18[e]	MeCN:H_2O 3:1	0.1	0.2	$LiClO_4$	GRC (+) | Ni_{foam} (-)	24
19[f]	MeCN:H_2O 3:1	0.1	0.2	$LiClO_4$	GRC (+) | Ni_{foam} (-)	50
20	MeCN:H_2O 3:1	0.4	0.05	$TBAPF_6$	GRC (+) | Ni_{foam} (-)	62
21	MeCN:H_2O 3:1	0.4	0.05	NH_4BF_4	GRC (+) | Ni_{foam} (-)	65
22	MeCN:H_2O 3:1	0.4	0.05	NH_4PF_6	GRC (+) | Ni_{foam} (-)	61
23	MeCN:H_2O 3:1	0.4	0.05	TBABr	GRC (+) | Ni_{foam} (-)	56
24	MeCN:H_2O 3:1	0.4	0.05	KCl	GRC (+) | Ni_{foam} (-)	75
25	MeCN:H_2O 3:1	0.4	0.05	KCl	GRC (+) | GRC (+)	60
26	MeCN:H_2O 3:1	0.4	0.05	KCl	GRC (+) | RVC (-)	28
27	MeCN:H_2O 3:1	0.4	0.05	KCl	GRC (+) | Pt (-)	67
28	MeCN:H_2O 3:1	0.4	0.05	KCl	GRC (+) | SS (-)	44
29	MeCN:H_2O 3:1	0.4	0.05	KCl	GRC (+) | Zn (-)	4

[a] Standard reaction conditions: 0.05 mmol of N-hydroxyphthalimide and 0.4 mmol of octanal in 3 mL MeCN:H_2O 3:1 with $LiClO_4$ (0.1 mmol), under air atmosphere, were set at constant current of 1 mA for 12h at room temperature. [b] Yields determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c] 2.5 mA, 12h instead of 1 mA, 12h. [d] 2.5 mA, 2h instead of 1 mA, 12h. [e] 5 mA, 2h instead of 1 mA, 12h. [f] 10 mA, 2h instead of 1 mA, 12h.

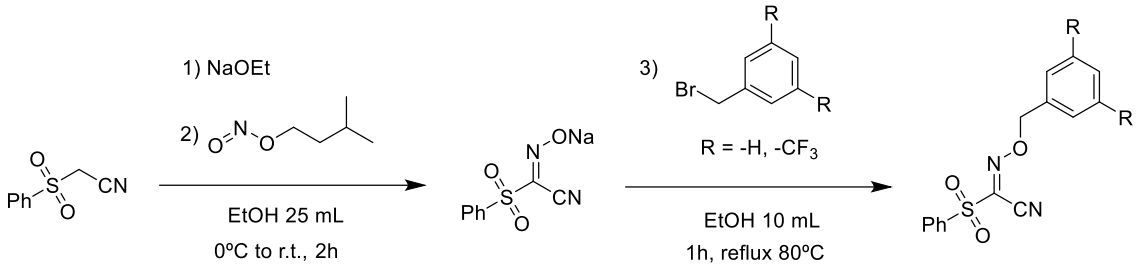
Table S3. Optimisation table of Giese type addition.[a]



Entry	*Solvent*	*1a (mmol)*	*NHPI (mmol)*	*Electrolyte*	*W (+) / C (-)*	*Yield (%)[b]*
1	MeCN:H_2O 3:1	0.3	0.1	$LiClO_4$	GRC (+) | GRC (-)	32
2	MeCN:H_2O 3:1	0.3	0.1	$LiClO_4$	GRC (+) | Ni (-)	43
3	MeCN:H_2O 3:1	0.3	0.1	$LiClO_4$	GRC (+) | Zn (-)	25
4	MeCN:H_2O 3:1	0.3	0.1	$LiClO_4$	GRC (+) | Pt (-)	46
5	MeCN:H_2O 3:1	0.3	0.1	$LiClO_4$	RVC (+) | Ni_{foam} (-)	16
6	MeCN:H_2O 3:1	0.3	0.1	$LiClO_4$	GC (+) | Ni_{foam} (-)	50
7	MeCN:H_2O 3:1	0.3	0.1	$LiClO_4$	Ni_{foam} (+) | Ni_{foam} (-)	32
8	MeCN:H_2O 3:1	0.3	0.1	KCl	GRC (+) | Ni_{foam} (-)	26
9	MeCN:H_2O 3:1	0.3	0.1	$TBAPF_6$	GRC (+) | Ni_{foam} (-)	35
10	MeCN:H_2O 3:1	0.3	0.1	NH_4BF_4	GRC (+) | Ni_{foam} (-)	48
11	MeCN:H_2O 3:1	0.3	0.1	TBPCl	GRC (+) | Ni_{foam} (-)	37
12	MeCN:H_2O 3:1	0.3	0.1	$NaClO_4$	GRC (+) | Ni_{foam} (-)	43
13	MeCN:H_2O 3:1	0.3	0.1	NaOAc	GRC (+) | Ni_{foam} (-)	33
14	MeCN:H_2O 3:1	0.3	0.1	$TBABF_4$	GRC (+) | Ni_{foam} (-)	41
15	MeCN:H_2O 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	50
16[c]	MeCN:H_2O 3:1	0.3	0.1	NH_4Cl	GRC (+) | Ni_{foam} (-)	32
17[d]	MeCN:H_2O 3:1	0.3	0.1	NH_4BF_4	GRC (+) | Ni_{foam} (-)	31
18[e]	DCM:H_2O 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	0
19[f]	DMF:H_2O 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	25
20	MeCN:MeOH 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	0
21	MeCN:DMF 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	0
22	DMSO:DMF 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	3
23	THF:DMF 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	6
24	MeCN:H_2O 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	7
25	MeCN:H_2O 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	31
26	MeCN:H_2O 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	44
27	MeCN:H_2O 3:1	0.3	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	50
28	MeCN:H_2O 3:1	0.1	0.3	NH_4PF_6	GRC (+) | Ni_{foam} (-)	28
29	MeCN:H_2O 3:1	0.6	0.1	NH_4PF_6	GRC (+) | Ni_{foam} (-)	34

[a] Standard reaction conditions: 0.3 mmol of cyclohexanecarbaldehyde and 0.1 mmol of (vinylsulfonyl)benzene in the presence of 0.2 mmol of N-hydroxyphthalimide in 3 mL MeCN:H_2O 3:1 with $LiClO_4$ (0.1 mmol), under air atmosphere, were set at constant current of 10 mA for 2h at room temperature. [b] Yields determined by 1H-NMR using 1,3,5-trimethoxybenzene as internal standard. [c] 1 mA, 12h instead of 10 mA, 2h. d 5 mA, 2h instead of 10 mA, 2h. [e] 15 mA, 2h instead of 10 mA, 2h. [f] 10 mA, 4h instead of 10 mA, 2h.

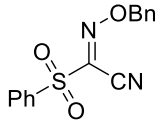
3. General procedure A: Synthesis of the starting materials. Oximes



The oximes used as starting materials were synthesized following a procedure described in the literature.[2] A sodium ethoxide solution was prepared from sodium (790 mg, 34.3 mmol, 1.2 equiv), and 18 mL of ethanol. This solution was added on a suspension of phenylsufonylacetonitrile (5290.0 mg, 28.6 mmol, 1 equiv) in 7 mL of ethanol after cooling it in an ice bath. After that, isoamyl nitrite (4.8 mL, 34.3 mmol, 1.2 equiv) was added to the resulting solution and the mixture was allowed to react at r.t. for 2 hours. Then, the crude was cooled down to 0ºC again, and the suspension was filtered to obtain the solid. The solid was washed with cold ethanol and dried under vacuum to obtain the desired salt, N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide as a yellow solid (76% yield). This salt was used for the next reaction step without further purification.

A mixture of N-hydroxy-1-(phenylsulfonyl)methanimidoyl cyanide (1000 mg, 4.3 mmol, 1 equiv) and the corresponding benzylic bromide (5.2 mmol, 1.2 equiv) in 10 mL of ethanol was heated under reflux for 1 hour. After that, the mixture was cooled down to r.t. and the solvent was removed under reduced pressure. The crude was purified by flash chromatography using cyclohexane:ethyl acetate as eluents to obtain the desired products.

N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (2a)

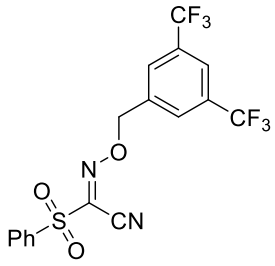


Following the general procedure A: 2-(phenylsulfonyl)acetonitrile (1000 mg, 4.4 mmol) and benzyl bromide (0.63 mL, 5.2 mmol) gave product **2a** (80% yield) as a white solid. Elution: Cyclohexane:ethyl acetate 100:0 to 85:15.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 8.03 – 7.86 (m, 2H), 7.82 – 7.70 (m, 1H), 7.68 – 7.56 (m, 2H), 7.53 – 7.25 (m, 5H), 5.44 (s, 2H).

Spectra data is in accordance with those reported in the literature.[2]

N-((3,5-bis(trifluoromethyl)benzyl)oxy)-1-(phenylsulfonyl)methanimidoyl cyanide (2b)



Following the general procedure A: 2-(phenylsulfonyl)acetonitrile (1000 mg, 4.4 mmol) and 1-(bromomethyl)-3,5-bis(trifluoromethyl)benzene (1600 mg, 5.2 mmol) gave product **2b** (78% yield) as a white solid. Elution: Cyclohexane: ethyl acetate 100:0 to 85:5.

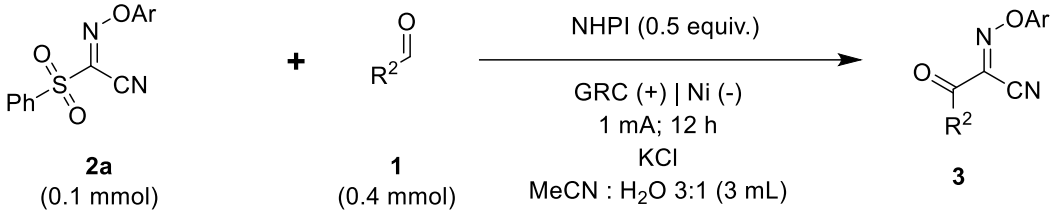
^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 2H), 7.92 – 7.88 (m, 1H), 7.82 – 7.73 (m, 3H), 7.67 – 7.59 (m, 2H), 5.52 (s, 2H).

^{13}C-NMR: (126 MHz, Chloroform-*d*) δ 136.4, 136.3, 136.0, 132.8, 132.5 (q, *J* = 33.8 Hz) 132.3, 130.1, 129.4, 123.5, 123.0 (q, *J* = 272.8 Hz), 105.5, 79.2.

^{19}F-NMR: δ -62.93**.**

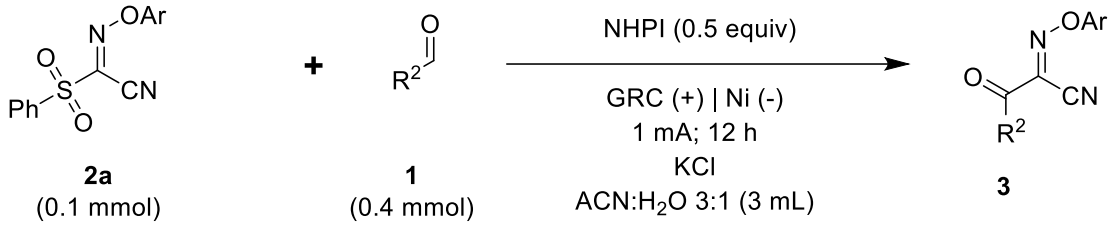
HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{17}H_{14}F_6N_3O_3S^+$: 454.3674, found: 454.0655.

4. General procedure B: Electrochemical acylation of oximes



The corresponding oxime (0.1 mmol, 1 equiv), N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 0.5 equiv), potassium chloride (7.5 mg, 0.1 mmol, 1 equiv) and a stirring bar were added into a Electrasyn 5 mL vial, followed by 2.25 mL acetonitrile and 0.75 mL H_2O as solvent. Finally, the corresponding aldehyde (0.4 mmol, 4 equiv) was added. The vial was closed, a graphite carbon electrode was used as anode and a nickel foam electrode was used as cathode. The mixture underwent electrolysis under constant current conditions (1 mA, 12h) and stirring (400 rpm). Upon completion, the crude was diluted in ethyl acetate and transferred to a round-bottom flask. The solvent was removed using a rotavapor. Then, the residue was dissolved with diethyl ether and filtered through cotton. The solvent was removed under reduced pressure and the crude was purified by flash chromatography using cyclohexane:ethyl acetate as eluent.

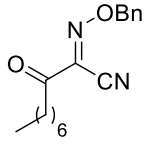
5. General procedure C: Electrochemical acylation of oximes



2a (0.1 mmol) + **1** (0.4 mmol) → **3**

The corresponding oxime (0.1 mmol, 1 equiv), N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 0.5 equiv), potassium chloride (7.5 mg, 0.1 mmol, 1 equiv) and a stirring bar were added into a Electrasyn 5 mL vial, followed by 2.25 mL acetonitrile and 0.75 mL H_2O as solvent. Finally, the corresponding aldehyde (0.4 mmol, 4 equiv) was added. The vial was closed, a graphite carbon electrode was used as anode and a nickel foam electrode was used as cathode. The mixture underwent electrolysis under constant current conditions (1 mA, 12h) and stirring (400 rpm). Upon completion, the crude was diluted with ethyl acetate and treated with a saturated aqueous solution of sodium bisulphite (15 mL) and stirred vigorously for approximately 30 seconds.[3] The resulting suspension was diluted with water (10 mL) and extracted with cyclohexane:ethyl acetate 9:1 (3x10 mL). The organic layers were washed with water (10 mL), then dried with anhydrous sodium sulphate and filtered through cotton. The solvent was removed under reduced pressure and the crude was purified by flash chromatography using cyclohexane:ethyl acetate as eluent.

N-(Benzyloxy)-2-oxononanimidoyl cyanide (3a)



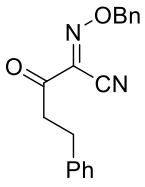
Following the general procedure B: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and octanal (62.5 µL, 0.4 mmol, 4 equiv) gave product **3a** (53% yield) as a colourless oil. Eluent: Isocratic cyclohexane: ethyl acetate 97:3.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.40 (s, 5H), 5.47 (s, 2H); 2.77 (t, *J* = 7.4 Hz, 2H), 1.61 (t, *J* = 7.3 Hz, 2H), 1.27 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 2H)

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 192.6, 134.6, 132.5, 129.4, 129.1, 129.0, 107.5, 80.8, 38.0, 31.7, 29.2, 29.1, 23.9, 22.7, 14.2

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{17}H_{26}N_3O_2^+$ 304.4140, found 304.2020

N-(Benzyloxy)-2-oxo-4-phenylbutanimidoyl cyanide (3b)



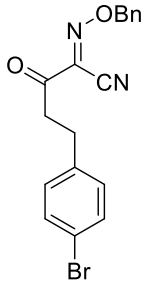
Following a modified version of the general procedure B: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and 3-phenylpropanal (53.7 µL, 0.4 mmol, 4 equiv) gave product **3b** (50% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.46 (s, 5H), δ 7.39 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 7.26 – 7.21 (m, 2H), 5.51 (s,2H), 3.18 (t, *J* = 7.4 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H)

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 191.5, 140.1, 134.5, 132.4, 129.4, 129.1, 129.0, 128.8, 128.5, 126.6, 107.4, 80.9, 39.6, 29.7

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{18}H_{20}N_3O_2^+$ 310.3770, found 310.1550.

N-(Benzyloxy)-4-(4-bromophenyl)-2-oxobutanimidoyl cyanide (3c)



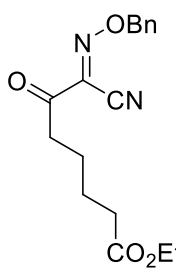
Following the general procedure C: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and 3-(4-bromophenyl)propanal (85.2 mg, 0.4 mmol, 4 equiv) gave product **3c** (46% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 95:5 to 91:9.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.44-7.35 (m, 7H), 7.04 (dt, *J* = 11.8, 2.5, 2.0 Hz, 2H), 5.45 (s, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.90 (t, *J* = 7.2 Hz, 2H).

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 191.2, 139.1, 134.5, 132.4, 131.8, 130.3, 129.5, 129.1, 129.0, 120.4, 107.3, 80.9, 39.3, 29.0.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{18}H_{19}BrN_3O_2^+$ 389.2730, found 390.0574.

Ethyl 7-((benzyloxy)imino)-7-cyano-6-oxoheptanoate (3d)



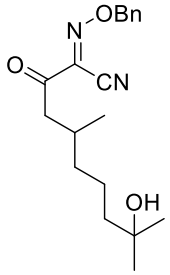
Following the general procedure C: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and ethyl 6-oxohexanoate (63.28 mg, 0.4 mmol, 4 equiv) gave product **3d** (59% yield) as a pale yellow oil. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.40 (s, 5H), 5.47 (s, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.80 (t, *J* = 7.0 Hz, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.83 – 1.49 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 192.0, 173.3, 134.5, 132.4, 129.4, 129.11, 129.0, 107.4, 80.8, 60.5, 37.5, 34.0, 24.4, 23.1, 14.4.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{17}H_{24}N_3O_4^+$ 334.3960, found 334.1761.

N-(Benzyloxy)-8-hydroxy-4,8-dimethyl-2-oxononanimidoyl cyanide (3e)



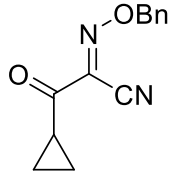
Following the general procedure C: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and 7-hydroxy-3,7-dimethyloctanal (68.9 mg, 0.4 mmol, 4 equiv) gave product **3e** (68% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 90:10 to 80:20

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.40 (s, 5H), 5.47 (s, 2H), 2.76 (dd, *J* = 15.9, 5.9 Hz, 1H) 2.61 (dd, *J* = 15.9, 7.8 Hz, 1H), 2.03 (dq, *J* = 13.1, 6.6 Hz, 1H), 1.46 – 1.24 (m, 7H), 1.21 (s, 6H), 0.90 (d, *J* = 6.7 Hz, 3H).

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 192.2, 134.5, 132.7, 129.3, 128.9, 128.9, 107.4, 80.7, 70.9, 44.9, 43.8, 37.3, 29.6, 29.4, 29.3, 21.6, 19.8.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{19}H_{30}N_3O_3^+$ 348.4670, found 348.2282.

N-(Benzyloxy)-2-cyclopropyl-2-oxoacetimidoyl cyanide (3f)



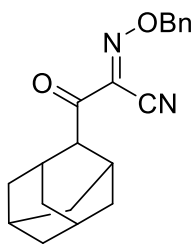
Following the general procedure B: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and cyclopropanecarbaldehyde (29.9 µL, 0.4 mmol, 4 equiv) gave product **3f** (45% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.42 (s, 5H), 5.51 (s, 2H), 2.70 (ttd, *J* = 7.9, 4.6, 1.0 Hz, 1H), 1.32 – 1.20 (m, 2H), 1.09 (ddt, *J* = 7.3, 4.0, 3.0 Hz, 2H)

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 192.0, 134.7, 133.1, 129.3, 129.0, 129.0, 107.6, 80.8, 16.7, 13.1.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{13}H_{16}N_3O_2^+$ 246.2900, found 246.0873.

2-(Adamantan-2-yl)-N-(benzyloxy)-2-oxoacetimidoyl cyanide (3g)



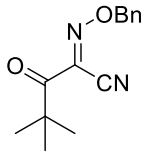
Following the general procedure C: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and adamantane-2-carbaldehyde (65.7 mg, 0.4 mmol, 4 equiv) gave product **3g** (46% yield) as a colourless oil . Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.40 (s, 5H), 5.44 (s, 2H), 2.06-1.96 (m, 3H), 1.95-1.87 (s, 6H), 1.80-1.60 (m, 7H).

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 196.4, 135.02, 129.4, 129.4, 128.9, 80.2, 47.5, 38.3, 36.6, 28.0.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{20}H_{26}N_3O_2^+$ 340.4470 found 340.2020.

N-(Benzyloxy)-3,3-dimethyl-2-oxobutanimidoyl cyanide (3h)



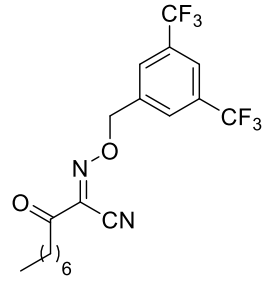
Following the general procedure C: N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (30 mg, 0.1 mmol, 1 equiv) and pivalaldehyde (44.2 µL, 0.4 mmol, 4 equiv) gave product **3h** (16 % yield) as a colourless oil . Eluent: Cyclohexane: ethyl acetate from 97:3 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 5H), 5.23 (s, 2H), 1.23 (s, 9H).

^{13}C-NMR: (300 MHz, Chloroform-*d*) δ 196.9, 134.7, 129.2, 129.1, 129.0, 107.8, 80.3, 44.5, 26.8.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{14}H_{20}N_3O_2^+$ 262.3330, found 262.1550.

N-[(3,5-Bis(trifluoromethyl)benzyl)oxy]-2-oxononanimidoyl cyanide (3i)



Following the general procedure C: N-((3,5 bis(trifluoromethyl)benzyl)oxy)-1-(phenylsulfonyl)methanimidoyl cyanide (43.6 mg, 0.1 mmol, 1 equiv) and octanal (62.5 µL, 0.4 mmol, 4 equiv) gave product **3i** (30% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 99:1 to 90:10. A second flash chromatography purification was required using cyclohexane: dichloromethane 65:35.

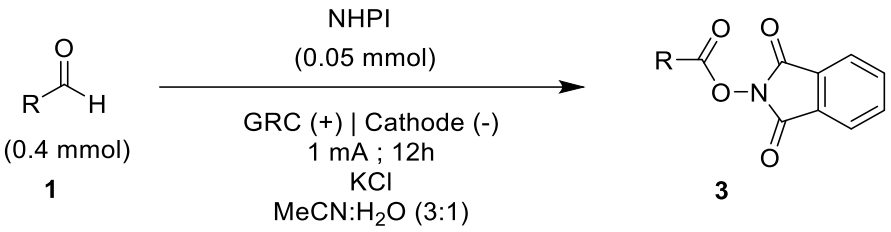
^{1}H NMR: (300 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.87 (s, 2H), 5.56 (s, 2H), 2.76 (t, *J* = 7.4 Hz, 2H), 1.62 (t, *J* = 7.2 Hz, 2H), 1.26 (m, 8H), 0.94 – 0.82 (m, 3H).

^{13}C NMR: (75 MHz, Chloroform-*d*) δ 191.9, 137.0, 133.5, 134.1 (q, *J* = 33.7 Hz), 123.4 (m), 123.1 (q, *J* = 272.3 Hz), 121.3, 107.2, 78.5, 38.1, 31.7, 29.1, 29.0, 23.7, 22.7, 14.2.

^{19}F-NMR: (282 MHz, Chloroform-*d*) δ -62.95.

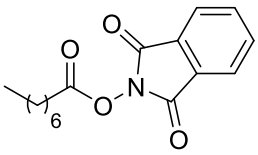
HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{19}H_{24}F_6N_3O_2^+$: 440.4032, found 440.1841.

6. General procedure D: RAE formation



N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 1 equiv), potassium chloride (7.5 mg, 0.1 mmol, 2 equiv) and a stirring bar were added into a Electrasyn 5 mL vial, followed by 2.25 mL acetonitrile and 0.75 mL H_2O as solvent. Finally, the corresponding aldehyde (0.4 mmol, 8 equiv) was added. The vial was closed, a graphite carbon electrode was used as anode and a nickel foam electrode was used as cathode. The mixture underwent electrolysis under constant current conditions (1 mA, 12h) and stirring (400 rpm). Upon completion, the crude was diluted with ethyl acetate and transferred to a round-bottom flask. The solvent was removed under reduced pressure, the residue was dissolved in diethyl ether and filtered through cotton. After removing the solvent again using a rotovap the crude was purified by flash chromatography using cyclohexane:ethyl acetate as eluent.

1,3-Dioxoisoindolin-2-yl octanoate (4a)

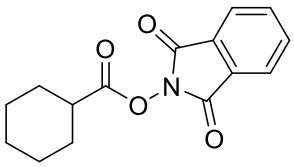


Following the general procedure D: Octanal (62.5 µL, 0.4 mmol, 4 equiv) and N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 1 equiv) gave product **4a** (34 % yield) as a white solid. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 2H), 7.83 – 7.74 (m, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.79 (p, *J* = 7.5 Hz, 2H), 1.39 – 1.21 (m, 8H), 0.93 – 0.87 (m, 3H).

Spectra data is in accordance with those reported in the literature.[4]

1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (4b)

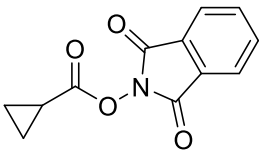


Following the general procedure D: Cyclohexanecarbaldehyde (48.4 µL, 0.4 mmol, 8 equiv) and N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 1 equiv) gave product **4b** (56 % yield) as a white solid. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.93 – 7.84 (m, 2H), 7.82 – 7.74 (m, 2H), 2.74 (tt, *J* = 10.9, 3.7 Hz, 1H), 2.18 – 2.04 (m, 2H), 1.91 – 1.77 (m, 2H), 1.74 – 1.62 (m, 3H), 1.46 – 1.28 (m, 3H).

Spectra data is in accordance with those reported in the literature.[4]

1,3-Dioxoisoindolin-2-yl cyclopropanecarboxylate (4c)

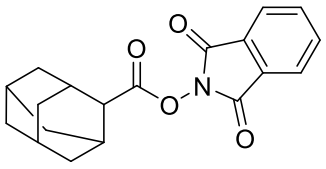


Following the general procedure D: Cyclopropanecarbaldehyde (29.9 µL, 0.4 mmol, 4 equiv) and N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 1 equiv) gave product **4c** (29 % yield) as a white solid. Eluent: Cyclohexane: ethyl acetate from 97:3 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 2H), 7.82-7.73 (m, 2H), 1.97 (tt, *J* = 7.9, 4.7 Hz, 1H), 1.33 – 1.23 (m, 2H), 1.23 – 1.11 (m, 2H).

Spectra data is in accordance with those reported in the literature.[4]

1,3-Dioxoisoindolin-2-yl adamantane-2-carboxylate (4d)



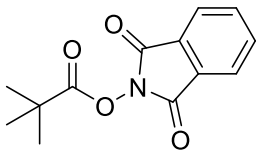
Following the general procedure D: adamantane-2-carbaldehyde (65.7 mg, 0.4 mmol, 4 equiv) and N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 1 equiv) gave **4d** product (39 % yield) as a white solid. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 2H), 7.83 – 7.73 (m, 2H), 2.16 – 2.13 (m, 6H), 2.12 – 2.08 (m, 3H), 1.78 (t, *J* = 3.0 Hz, 6H).

^{13}C-NMR: (75 MHz, Chloroform-*d*) δ 173.41, 162.31, 134.75, 129.28, 123.99, 40.69, 38.62, 36.37, 27.82.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{19}H_{23}N_2O_4^+$ 343.4030, found 343.1781.

1,3-Dioxoisoindolin-2-yl pivalate (4e)

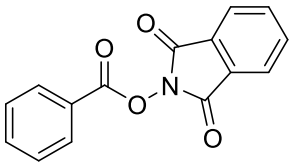


Following the general procedure D: pivalaldehyde (44.2 µL, 0.4 mmol, 4 equiv) and N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 1 equiv) gave product **4e** (31 % yield) as a white solid. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10

^{1}H-NMR: δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 1.44 (s, 9H).

Spectra data is in accordance with those reported in the literature.[4]

1,3-Dioxoisoindolin-2-yl benzoate (4f)

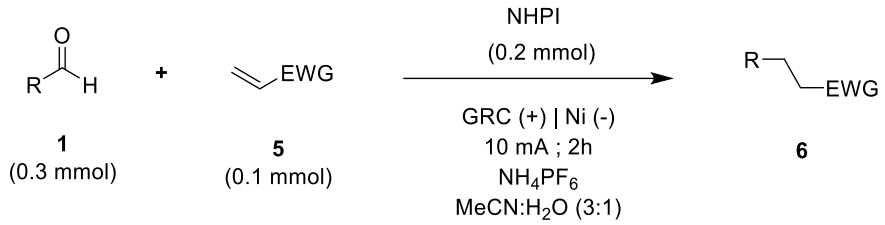


Following the general procedure D: Benzaldehyde (40.8 µL) and N-hydroxyphthalimide (8.2 mg, 0.05 mmol, 1 equiv) gave product 4f (43% yield) as a white solid. Eluent: Cyclohexane: ethyl acetate from 100:0 to 90:10.

^{1}H NMR: (300 MHz, Chloroform-*d*) δ 8.26 – 8.10 (m, 2H), 7.92 (m, 2H), 7.81 (m, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 2H).

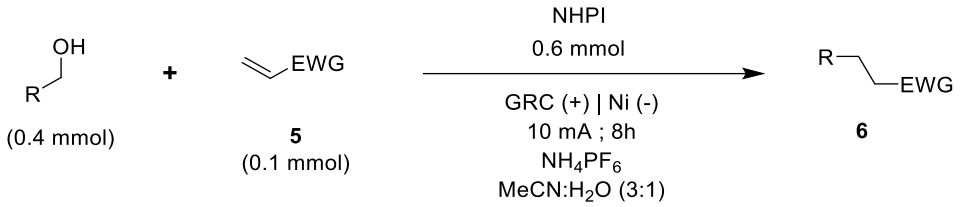
Spectra data is in accordance with those reported in the literature.[5]

7. General procedure E: Giese-type alkylation from aldehydes



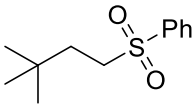
N-hydroxyphthalimide (32.6 mg, 0.2 mmol, 2 equiv), ammonium hexafluorophosphate (16.3 mg, 0.1 mmol, 2 equiv), an electron-poor alkene (**5**) (0.1 mmol, 1 equiv) and a stirring bar were added into a Electrasyn 5 mL vial, followed by 2.25 mL acetonitrile and 0.75 mL H_2O as solvent. Then, the aldehyde was added (0.3 mmol) to the mixture. The vial was closed, a graphite carbon electrode was used as anode and a nickel foam electrode was used as cathode. The mixture underwent electrolysis under constant current conditions (10 mA, 2h) and stirring (400 rpm). Upon completion, the crude was diluted with ethyl acetate and transferred to a round-bottom flask. The solvent was removed under reduced pressure, the residue was dissolved in diethyl ether and filtered through cotton. After removing the solvent again using a rotavapor the crude was purified by flash chromatography using cyclohexane:ethyl acetate as eluent.

8. General procedure F: Giese-type alkylation from alcohols



N-hydroxyphthalimide (97.9 mg, 0.6 mmol, 6 equiv), ammonium hexafluorophosphate (16.3 mg, 0.1 mmol, 1 equiv), a Michael acceptor (0.1 mmol, 1 equiv) and a stirring bar were added into a Electrasyn 5 mL vial, followed by 2.25 mL acetonitrile and 0.75 mL H_2O as solvent. The alcohol of choice was then added to the mixture (0.4 mmol) The vial was closed, a graphite carbon electrode was used as anode and a nickel foam electrode was used as cathode. The mixture underwent electrolysis under constant current conditions (10 mA, 8h) and stirring (400 rpm). Upon completion, the crude was diluted with ethyl acetate and transferred to a round-bottom flask. The solvent was removed under reduced pressure, the residue was dissolved in diethyl ether and filtered through cotton. After removing the solvent again using a rotavapor the crude was purified by flash chromatography using cyclohexane:ethyl acetate or cyclohexane:dichloromethane as eluent.

[(3,3-Dimethylbutyl)sulfonyl]benzene (6a)



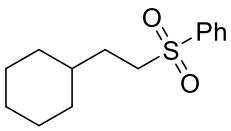
Following the general procedure E: pivalaldehyde (33.1 µL, 0.3 mmol, 3 equiv) and (vinylsulfonyl)benzene (16.8 mg, 0.1 mmol, 1 equiv) gave product **6a** (70% yield) as a yellow solid. Eluent: Cyclohexane: ethyl acetate from 95:5 to 90:10.

Following the general procedure F: 2,2-dimethylpropan-1-ol (35.3 mg, 0.4 mmol, 4 equiv), $LiClO_4$ (10.6 mg, 0.1 mmol, 1 equiv) instead of ammonium hexafluorophosphate and (vinylsulfonyl)benzene (16.8 mg, 0.1 mmol, 1 equiv), after reacting for 10 hours gave product **6a** (50% yield) as a yellow solid. Eluent: Cyclohexane: ethyl acetate from 97:3 to 85:15.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.96 – 7.86 (m, 2H), 7.72 – 7.60 (m, 1H), 7.61-7.52 (m, 2H), 3.11 – 2.99 (m, 2H), 1.65 – 1.54 (m, 2H), 0.86 (d, *J* = 0.8 Hz, 9H).

Spectra data is in accordance with those reported in the literature.[6]

[(2-Cyclohexylethyl)sulfonyl]benzene (6b)



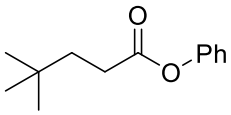
Following the general procedure E: Cyclohexanecarbaaldehyde (36.3 µL, 0.3 mmol, 3 equiv) and (vinylsulfonyl)benzene (16.8 mg, 0.1 mmol, 1 equiv) gave product **6b** (39% yield) as a yellow solid. Eluent: Cyclohexane:ethyl acetate from 95:5 to 90:10.

Following the general procedure F: Cyclohexylmethanol (48.9 µL, 0.4 mmol, 4 equiv) and (vinylsulfonyl)benzene (16.8 mg, 0.1 mmol, 1 equiv) gave product **6b** (35% yield) as a yellow solid. Eluent: Cyclohexane:dichloromethane from 60:40 to 50:50.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.61 (m, 3H), 3.15 – 3.03 (m, 2H), 1.63 (m, 7H), 1.18 (m, 4H), 0.96 – 0.76 (m, 2H).

Spectra data is in accordance with those reported in the literature. [6]

Phenyl 4,4-dimethylpentanoate (6c)

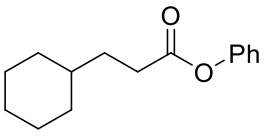


Following the general procedure E: Pivalaldehyde (36.3 µL, 0.3 mmol, 3 equiv) and phenyl acrylate (13.7 µL, 0.1 mmol, 1 equiv) gave product **6c** (30% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 100:0 to 95:5.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 2H), 7.25 – 7.18 (m, 1H), 7.11 – 7.05 (m, 2H), 2.59 – 2.48 (m, 2H), 1.75 – 1.64 (m, 2H), 0.96 (s, 9H).

Spectra data is in accordance with those reported in the literature.[7]

Phenyl 3-cyclohexylpropanoate (6d)

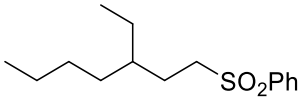


Following the general procedure E: Cyclohexanecarbaldehyde (36.3 µL, 0.3 mmol, 3 equiv) and phenyl acrylate (13.7 µL, 0.1 mmol, 1 equiv) gave product **6d** (25% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 100:0 to 95:5.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.45 – 7.31 (m, 2H), 7.28 – 7.16 (m, 1H), 7.13 – 7.03 (m, 2H), 2.62 – 2.51 (t, *J* = 7.8 Hz, 2H), 1.83 – 1.61 (m, 7H), 1.37 – 1.17 (m, 4H), 1.03 – 0.87 (m, 2H).

Spectra data is in accordance with those reported in the literature.[8]

[(3-Ethylheptyl)sulfonyl]benzene (6e)



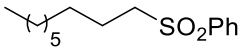
Following the general procedure F: 2-ethylhexan-1-ol (62.5 µL, 0.4 mmol, 4 equiv) and (vinylsulfonyl)benzene (16.8 mg, 0.1 mmol, 1 equiv) gave product **6e** (25% yield) as a colourless oil. Eluent: Cyclohexane: ethyl acetate from 99:1 to 96:4.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.95 – 7.89 (m, 2H), 7.70 – 7.62 (m, 1H), 7.62 – 7.53 (m, 2H), 3.11 – 2.99 (m, 2H), 1.72 – 1.61 (m, 2H), 1.31 – 1.11 (m, 9H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.78 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR: (126 MHz, Chloroform-*d*) δ 139.4, 133.7, 129.4, 128.2, 54.2, 38.0, 32.5, 28.8, 25.6 (2C) , 23.0, 14.2, 10.7.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{15}H_{28}NO_2S^+$ 268.4540 found: 286.1835.

(Nonylsulfonyl)benzene (6f)

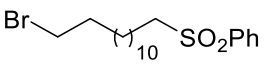


Following the general procedure F: Octanal (62.8 µL, 0.4 mmol, 4 equiv) and (vinylsulfonyl)benzene (16.8 mg, 0.1 mmol, 1 equiv) gave product **6f** (35% yield) as a colourless solid. Eluent: Cyclohexane: ethyl acetate from 99:1 to 96:4.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 2H), 7.70 – 7.62 (m, 1H), 7.62 – 7.52 (m, 2H), 3.16 – 2.98 (m, 2H), 1.78 – 1.63 (m, 2H), 1.24 (m, 12H), 0.91 – 0.82 (t, *J* = 6.8 Hz, 3H).

Spectra data is in accordance with those reported in the literature.[9]

[(13-Bromotridecyl)sulfonyl]benzene (6g)



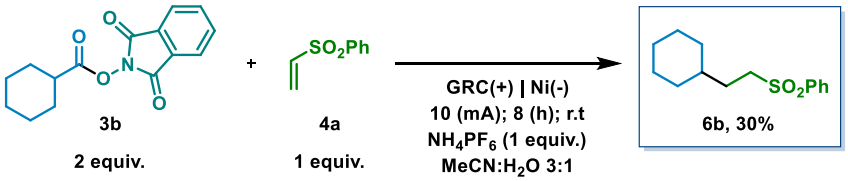
Following the general procedure F: 12-Bromo-1-dodecanol (µL, 0.4 mmol, 4 equiv) and (vinylsulfonyl)benzene (16.8 mg, 0.1 mmol, 1 equiv) gave product **6g** (30 % yield) as a colourles oil. Eluent: Cyclohexane: ethyl acetate from 99:1 to 96:4.

^{1}H-NMR: (300 MHz, Chloroform-*d*) δ 7.95 – 7.88 (m, 2H), 7.69 – 7.62 (m, 1H), 7.61 – 7.53 (m, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 3.12 – 3.03 (m, 2H), 1.85 (p, *J* = 7.0 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.37 – 1.14 (m, 18H).

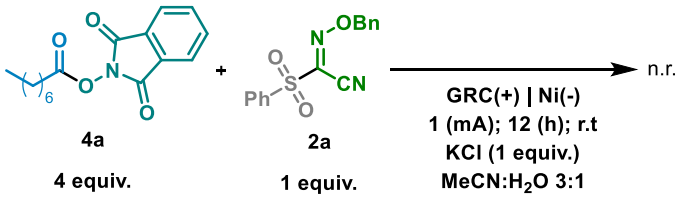
^{13}C-NMR: (126 MHz, Chloroform-*d*) δ 139.4, 133.7, 129.4, 128.2, 56.5, 34.2, 33.0, 29.6, 29.6, 29.6, 29.5, 29.3, 29.1, 28.9, 28.4, 28.3, 22.8.

HRMS (ESI): $[M\text{-}NH_4]^+$ calculated for $C_{19}H_{35}BrNO_2S^+$ 421.4580, found 421.1526.

9. Mechanistic investigations



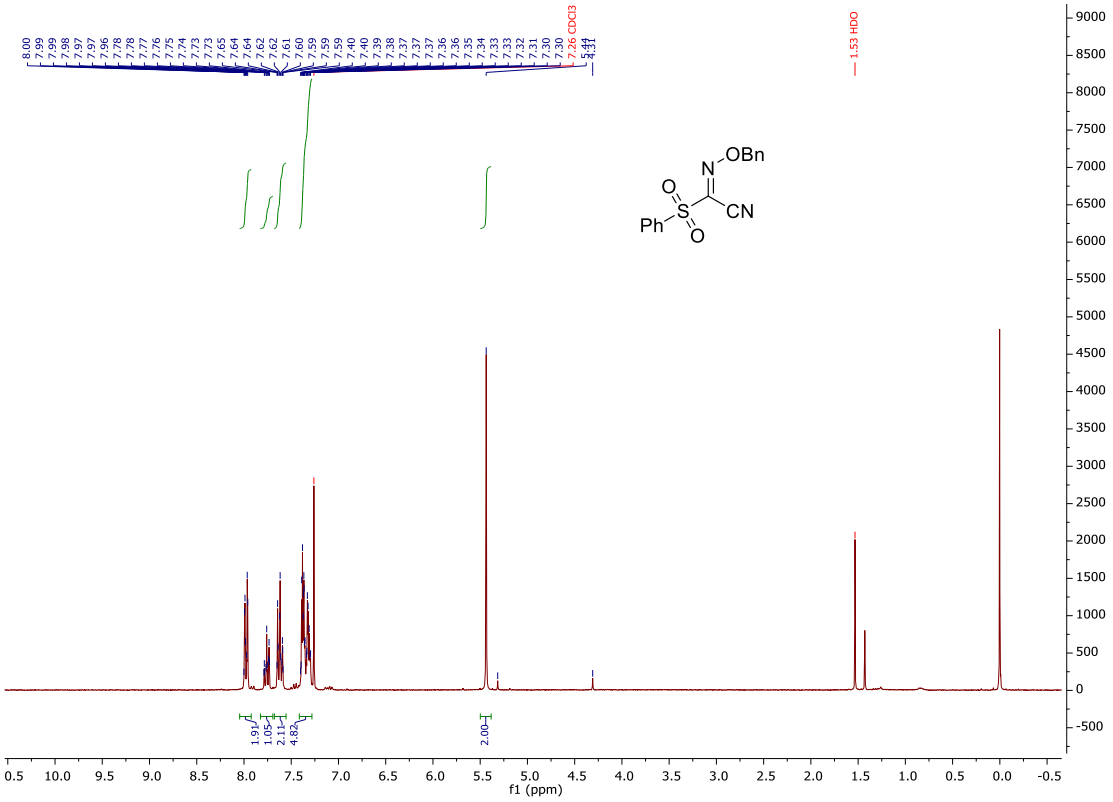
3b (54,66 mg, 0.2 mmol, 2 equiv), ammonium hexafluorophosphate (16.3 mg, 0.1 mmol, 1 equiv), vinyl sulfone **4a** (16.8 mg, 0.1 mmol, 1 equiv) and a stirring bar were added into a Electrasyn 5 mL vial, followed by 2.25 mL acetonitrile and 0.75 mL H_2O as solvent. The vial was closed, a graphite carbon electrode was used as anode and a nickel foam electrode was used as cathode. The mixture underwent electrolysis under constant current conditions (10 mA, 8h) and stirring (400 rpm). Upon completion, the crude was diluted with ethyl acetate and transferred to a round-bottom flask. The solvent was removed under reduced pressure, the residue was dissolved in diethyl ether and filtered through cotton. After removing the solvent again using a rotavapor the crude was purified by flash chromatography using cyclohexane:ethyl acetate from 95:5 to 90:10 as eluent. **6b** (30% yield) was obtained as a yellow solid.



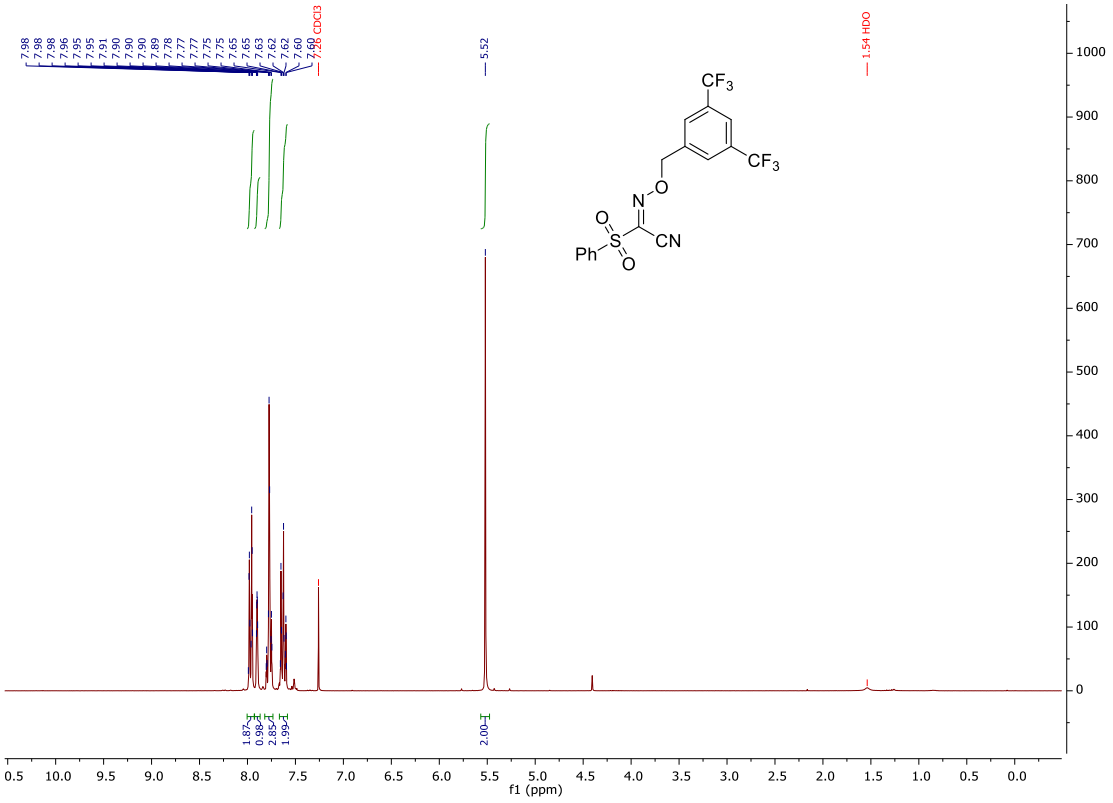
4a (115.7 mg, 0.4 mmol, 4 equiv), potassium chloride (7.5 mg, 0.1 mmol, 1 equiv), oxime **2a** (0.1 mmol, 1 equiv) and a stirring bar were added into a Electrasyn 5 mL vial, followed by 2.25 mL acetonitrile and 0.75 mL H_2O as solvent. The vial was closed, a graphite carbon electrode was used as anode and a nickel foam electrode was used as cathode. The mixture underwent electrolysis under constant current conditions (1 mA, 12h) and stirring (400 rpm). Upon completion, the crude was diluted with ethyl acetate and transferred to a round-bottom flask. The solvent was removed under reduced pressure, the residue was dissolved in diethyl ether and filtered through cotton. There was no reaction and oxime **2a** was recovered untouched.

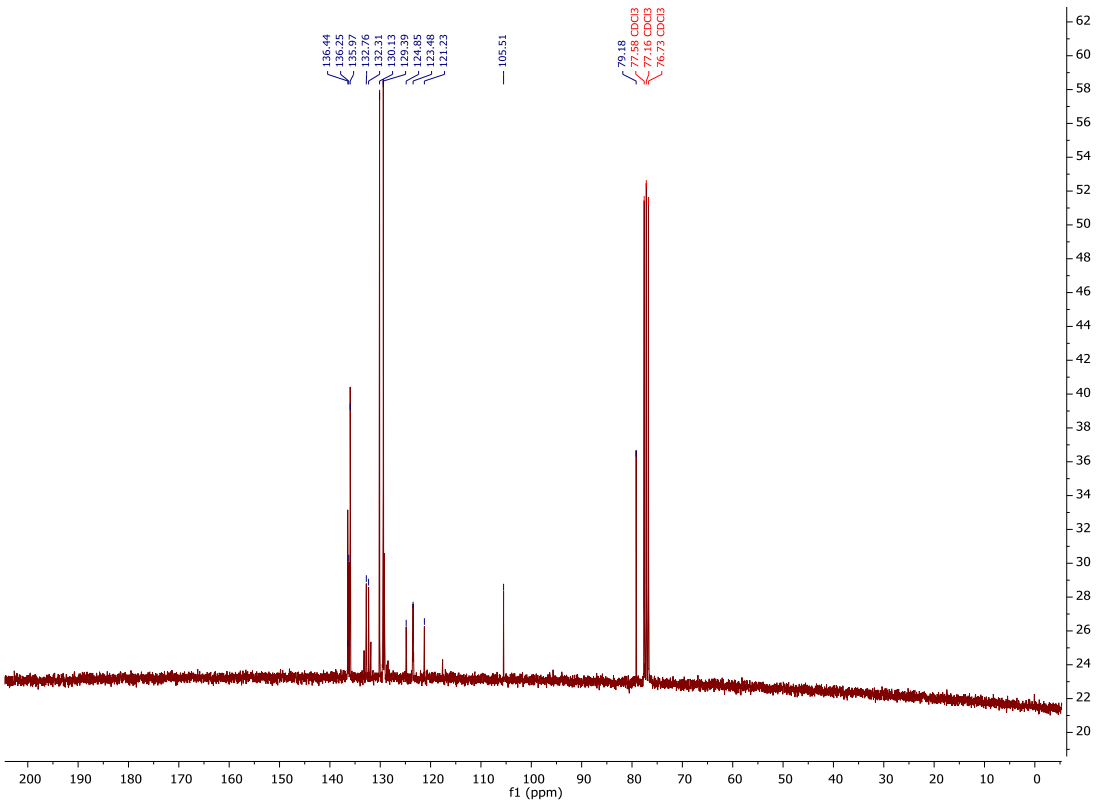
10. NMR spectra

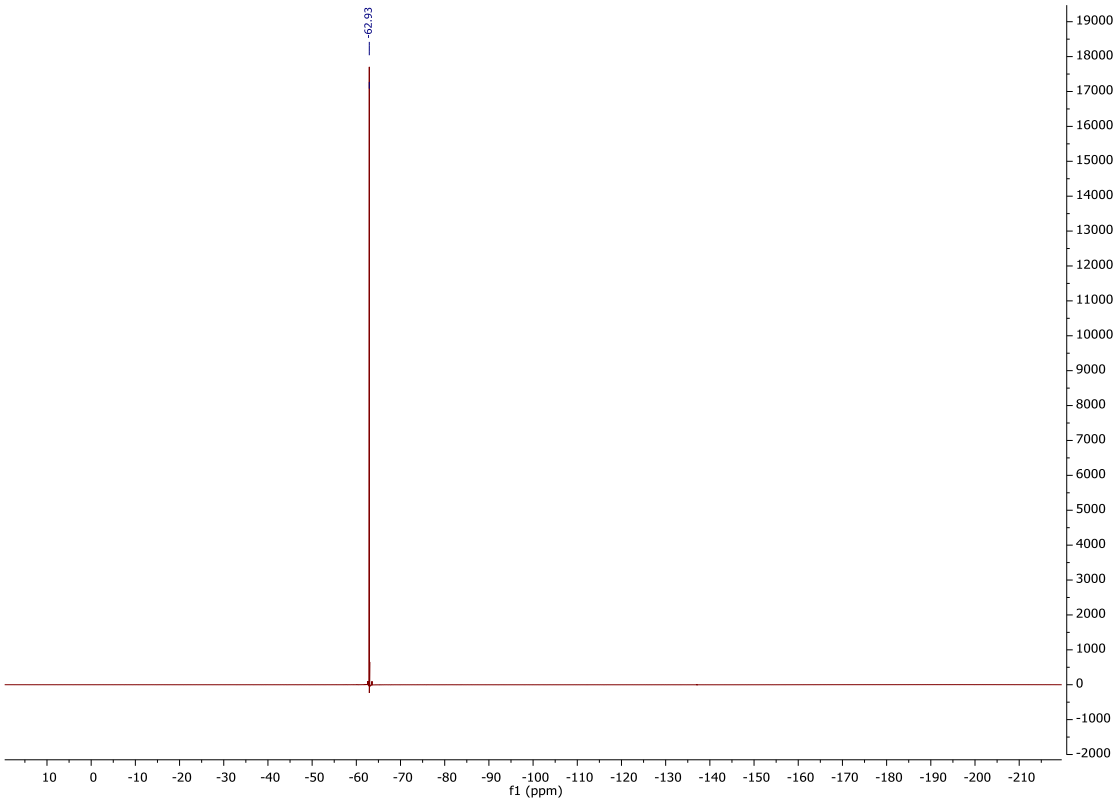
N-(benzyloxy)-1-(phenylsulfonyl)methanimidoyl cyanide (2a)



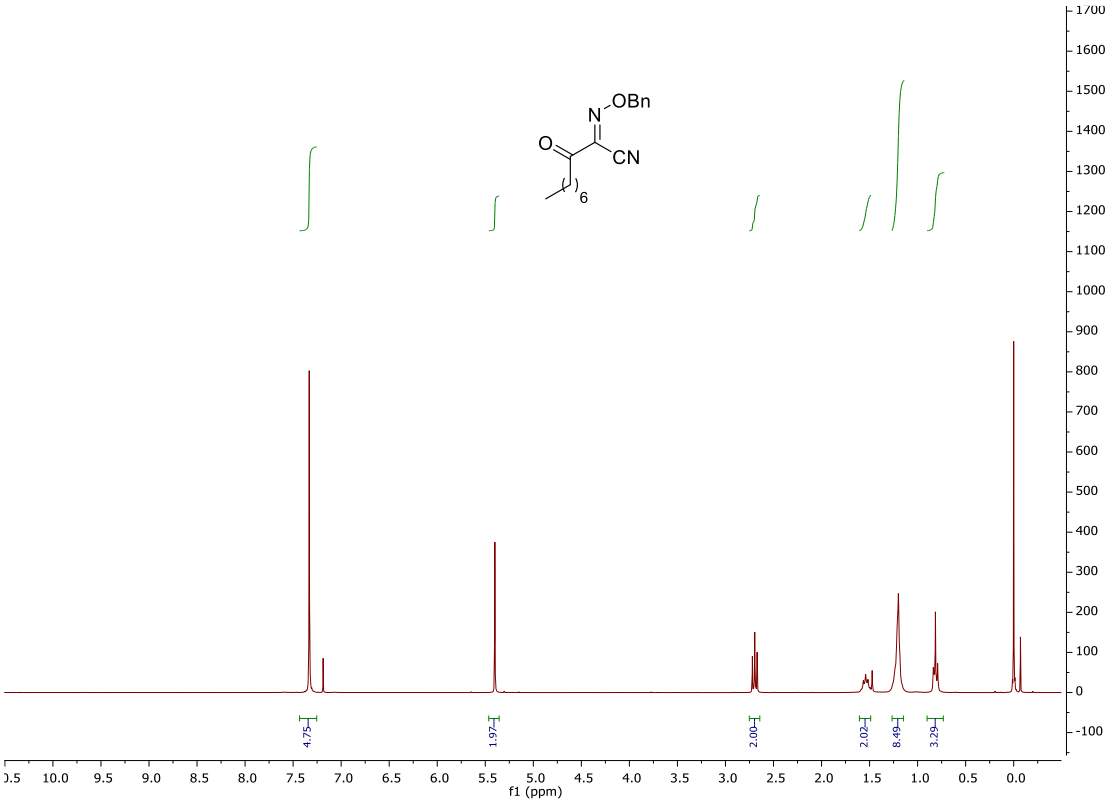
N-((3,5-bis(trifluoromethyl)benzyl)oxy)-1-(phenylsulfonyl)methanimidoyl cyanide (2b)

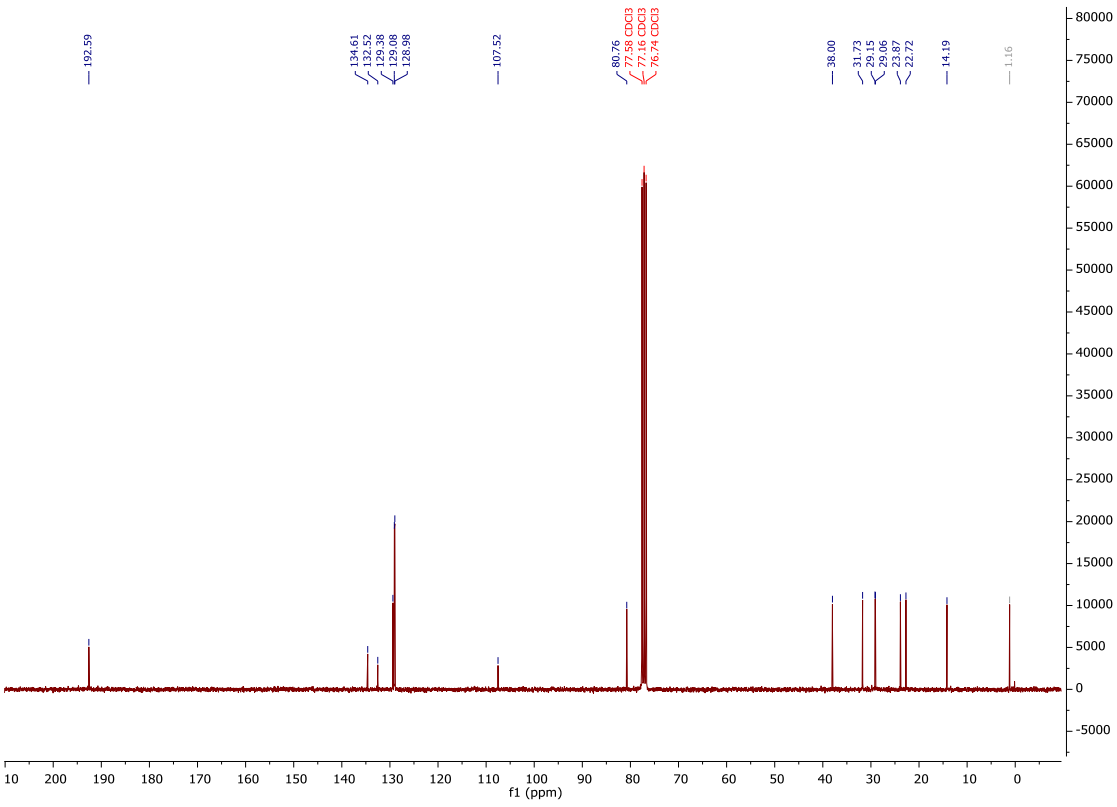




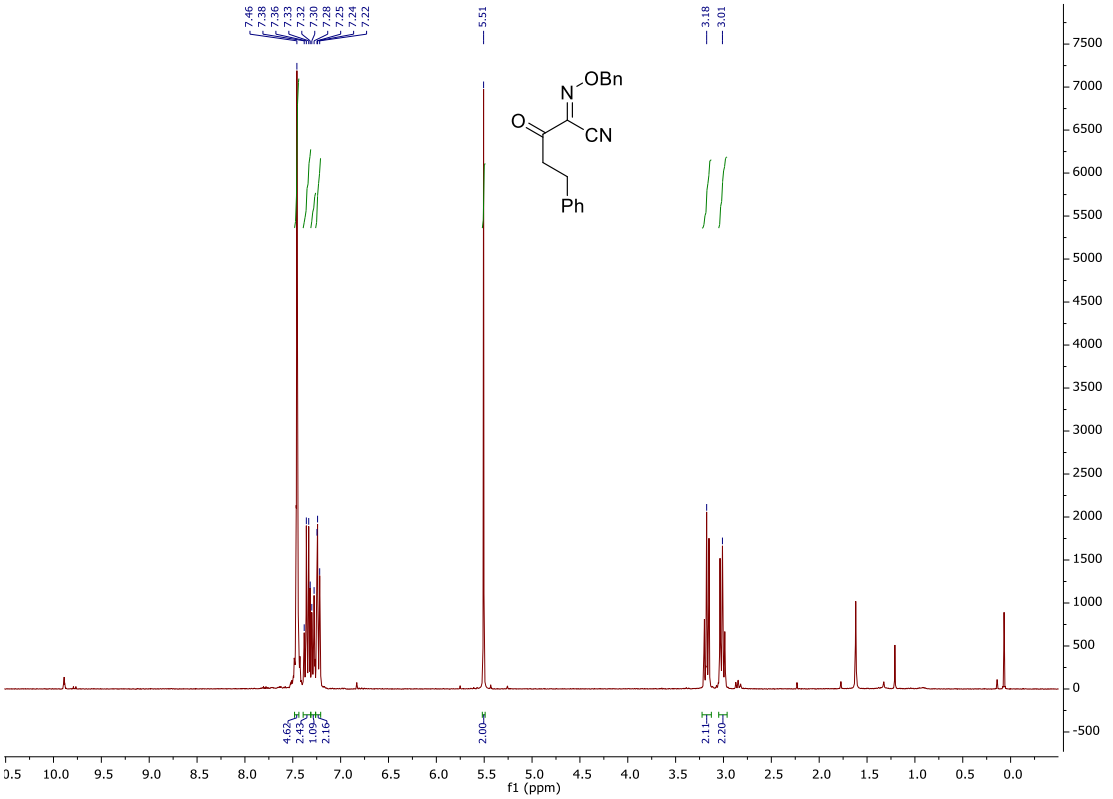

-62.93
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

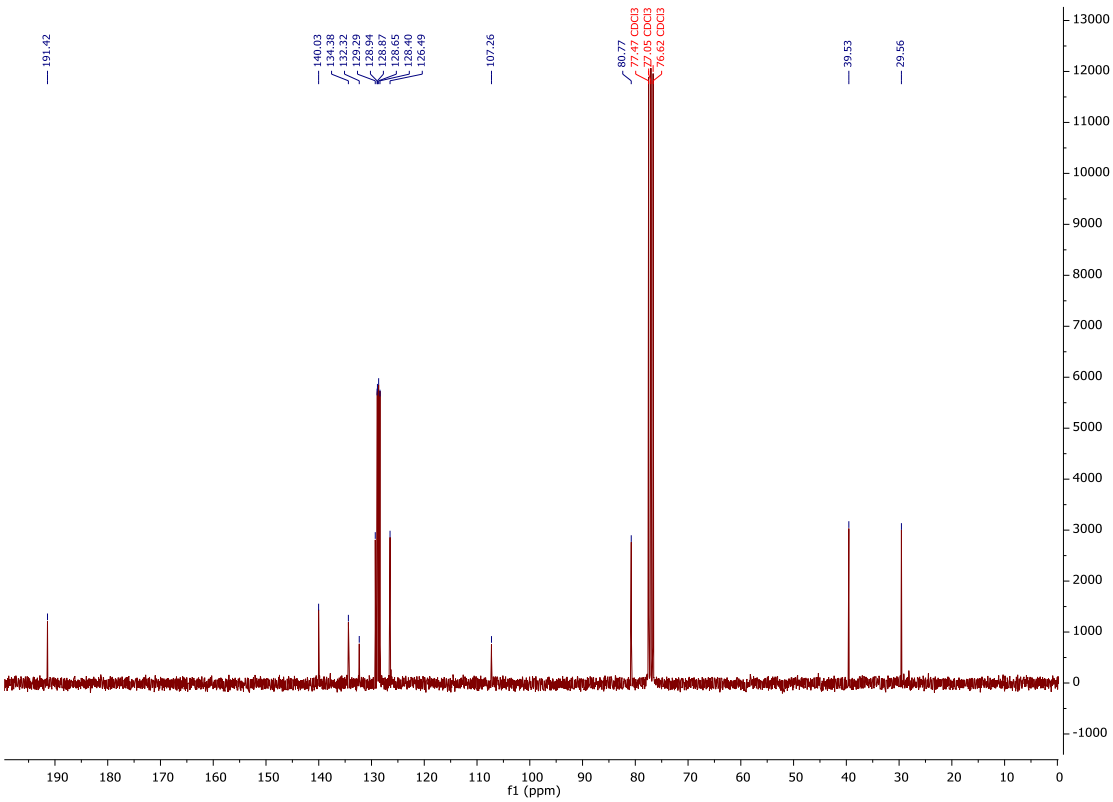
N-(benzyloxy)-2-oxononanimidoyl cyanide (3a)



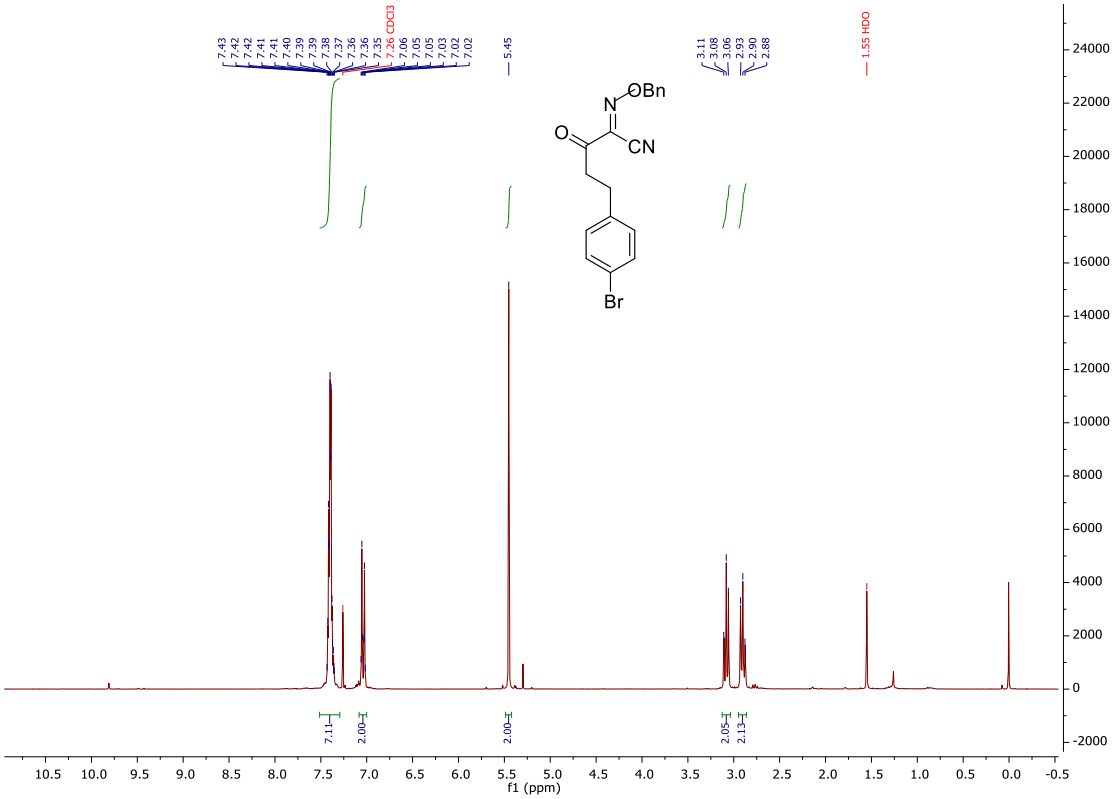


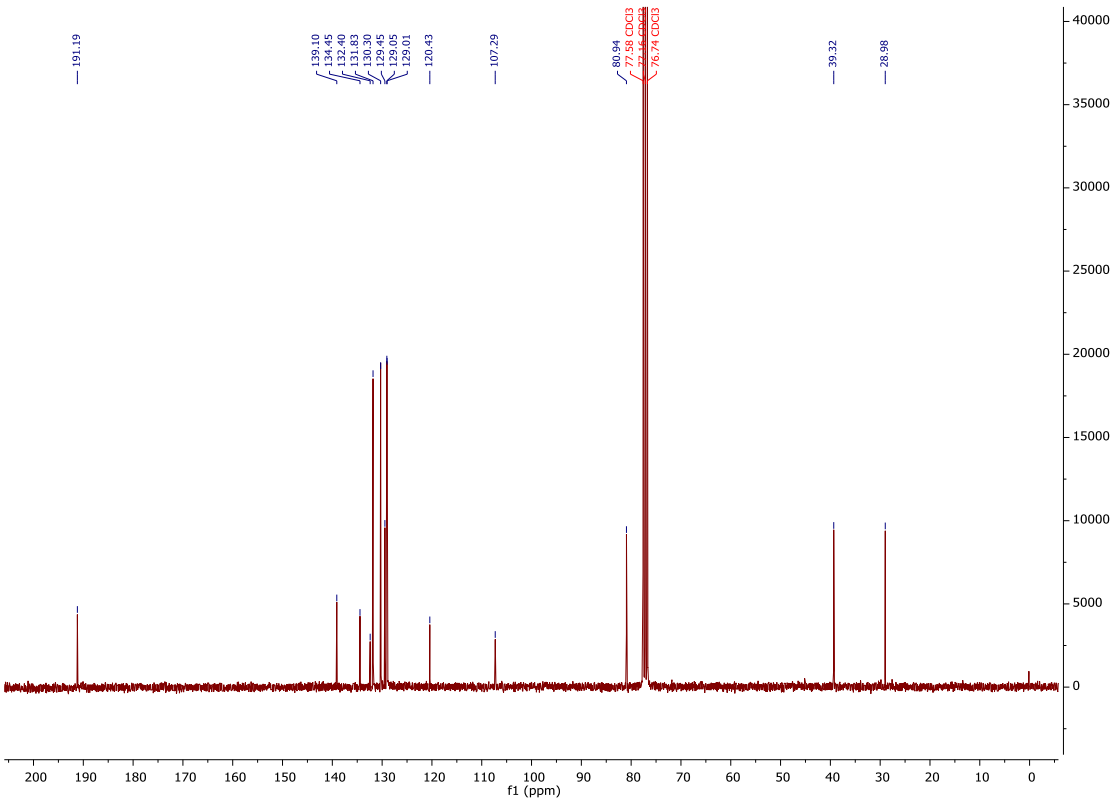
N-(benzyloxy)-2-oxo-4-phenylbutanimidoyl cyanide (3b)



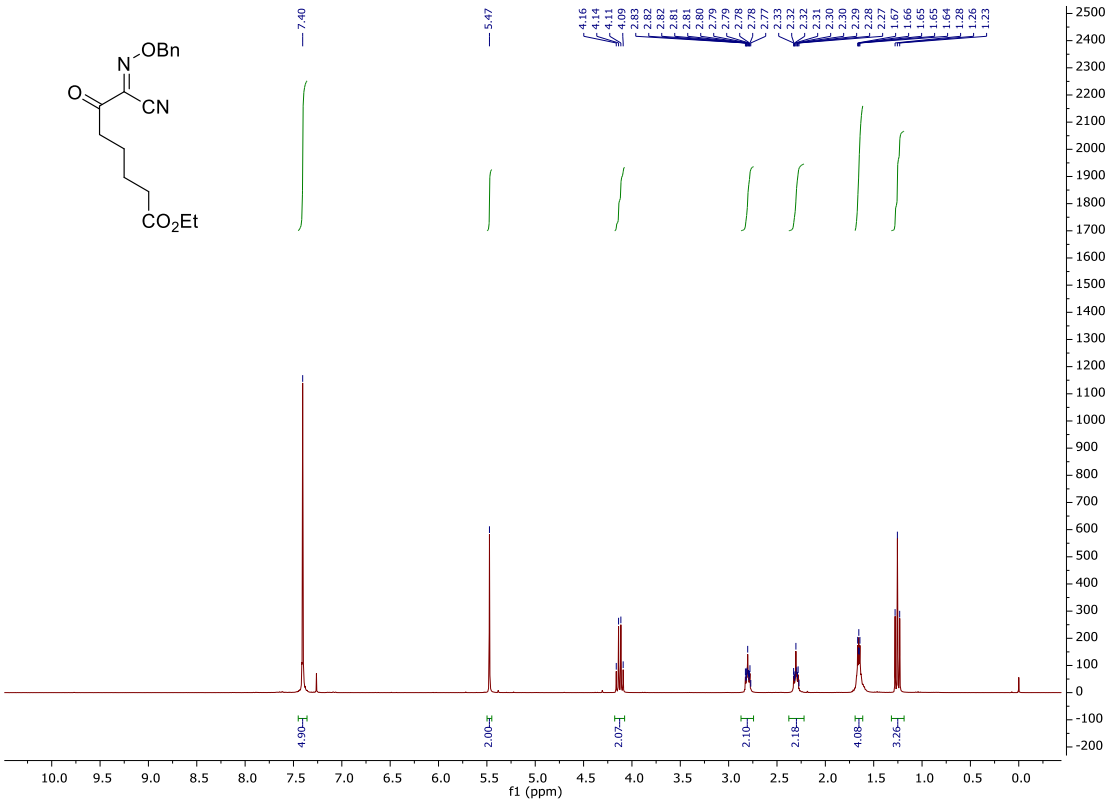


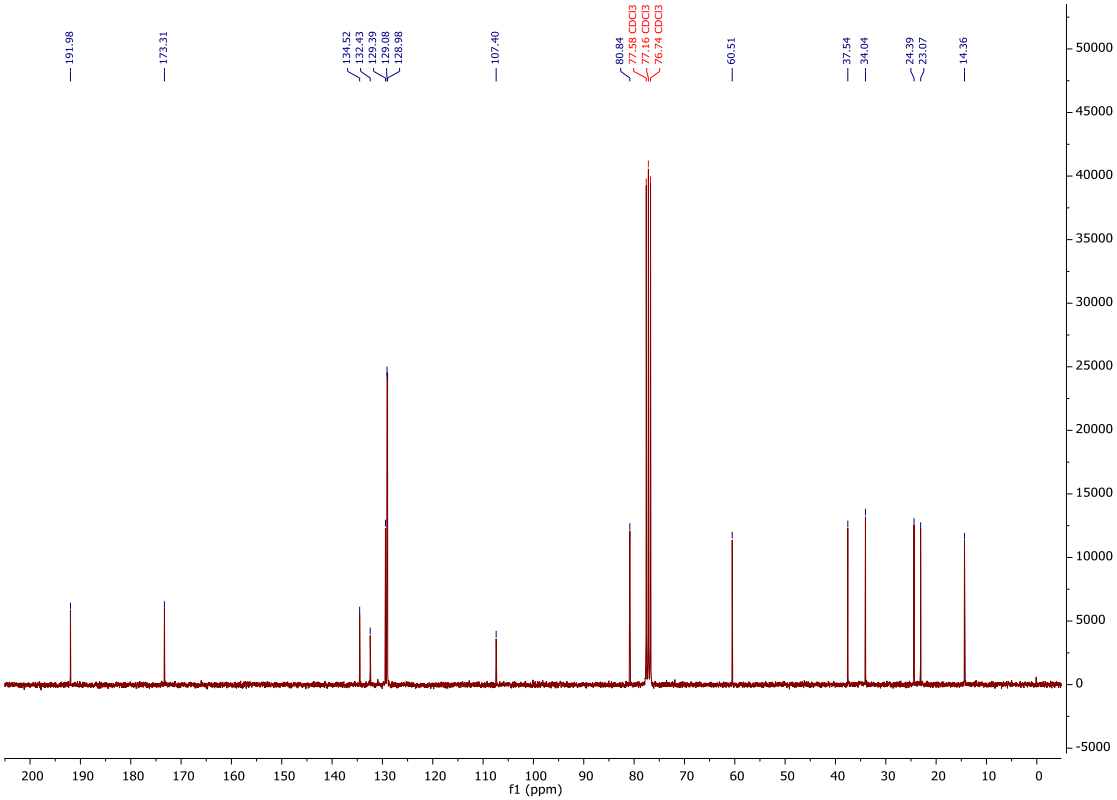
N-(benzyloxy)-4-(4-bromophenyl)-2-oxobutanimidoyl cyanide (3c)



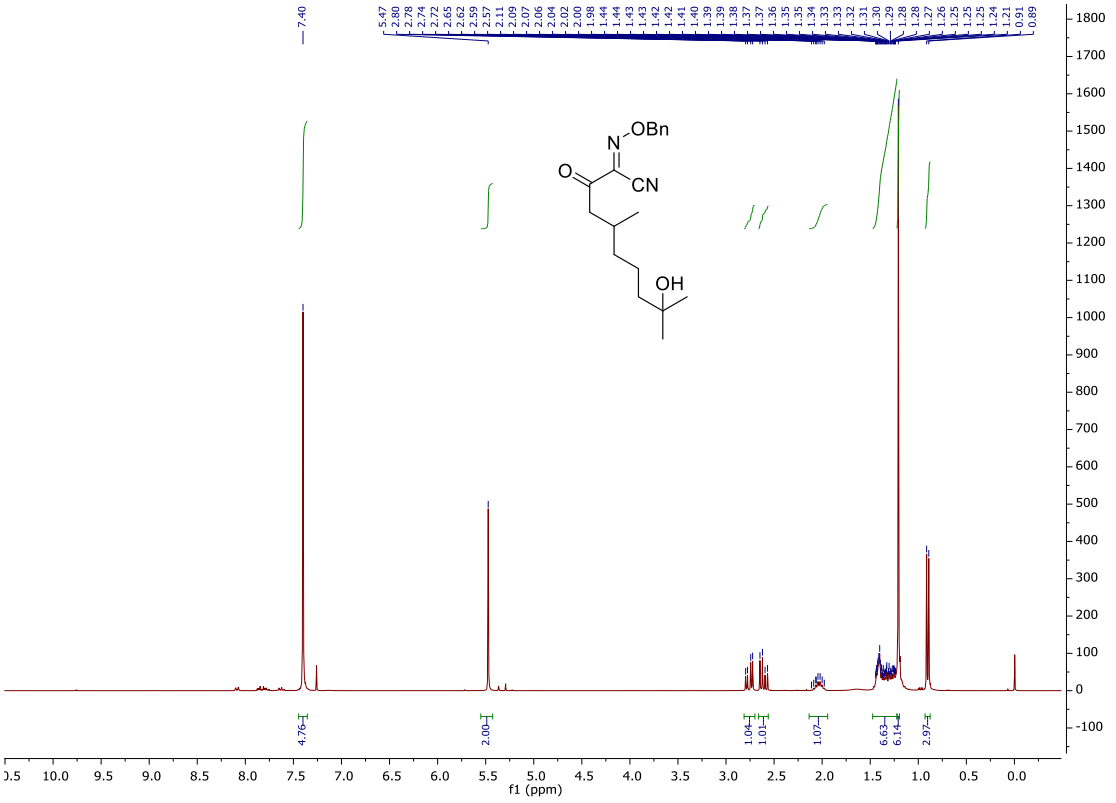


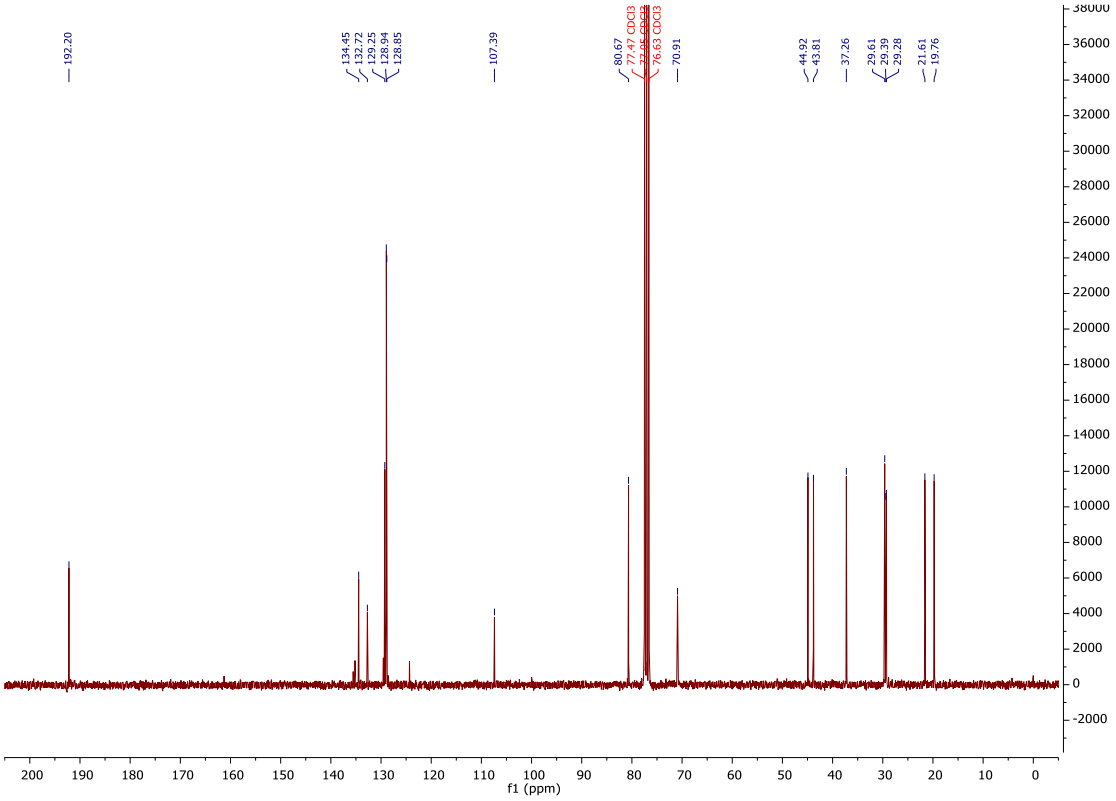
Ethyl 7-((benzyloxy)imino)-7-cyano-6-oxoheptanoate (3d)



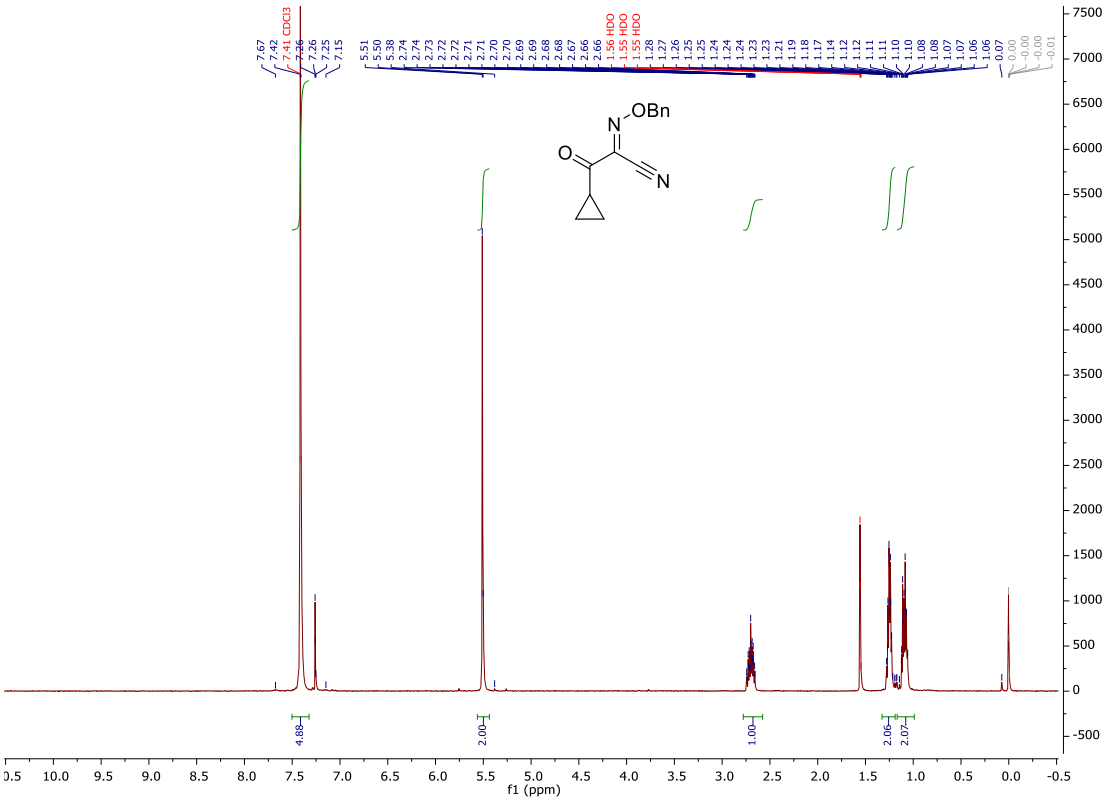


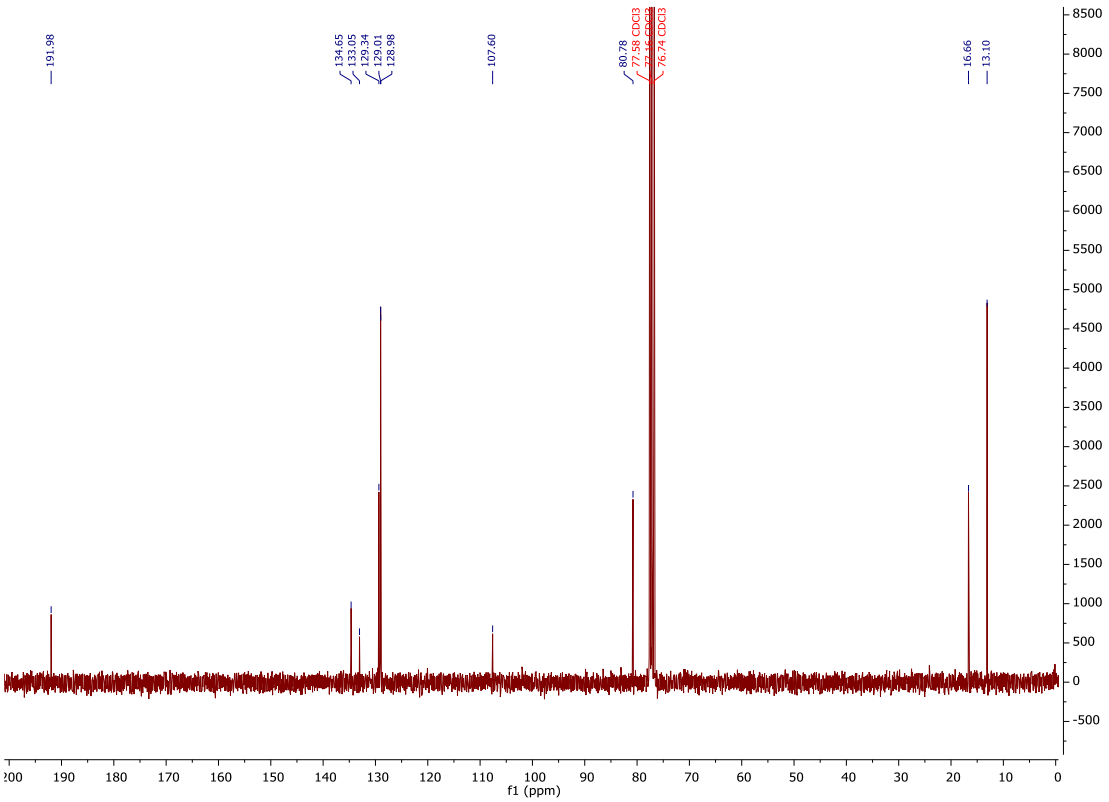
N-(benzyloxy)-8-hydroxy-4,8-dimethyl-2-oxononanimidoyl cyanide (3e)



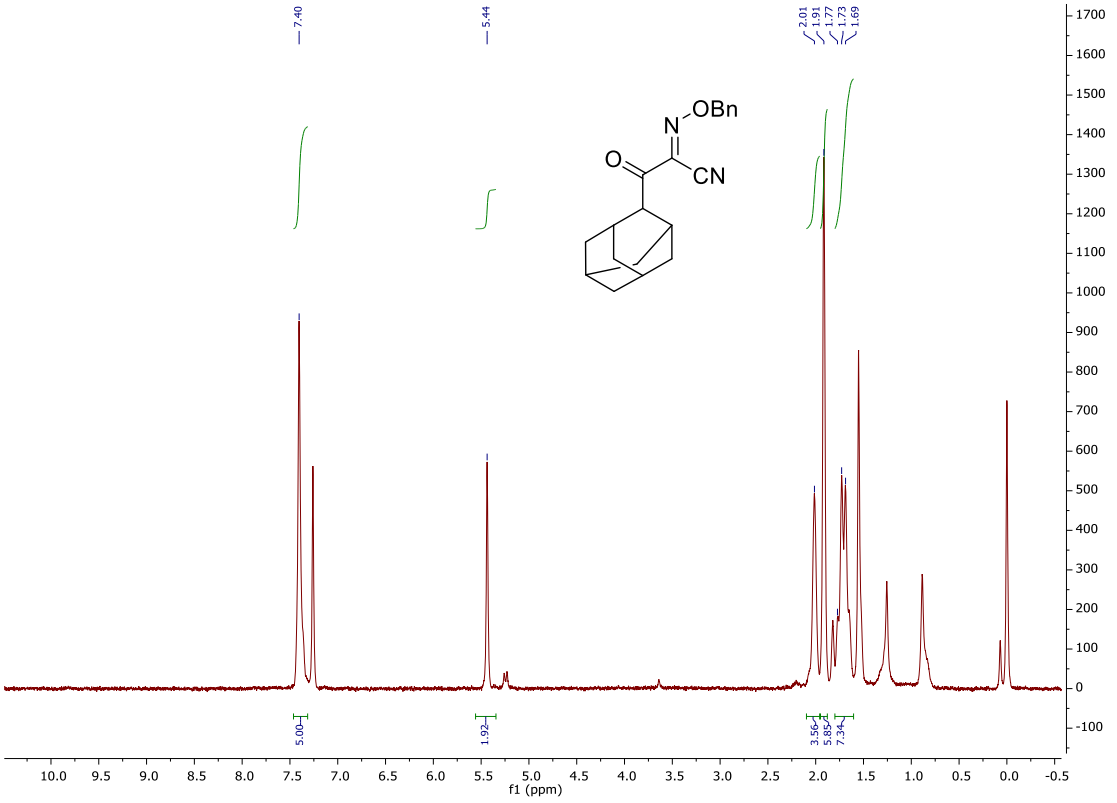


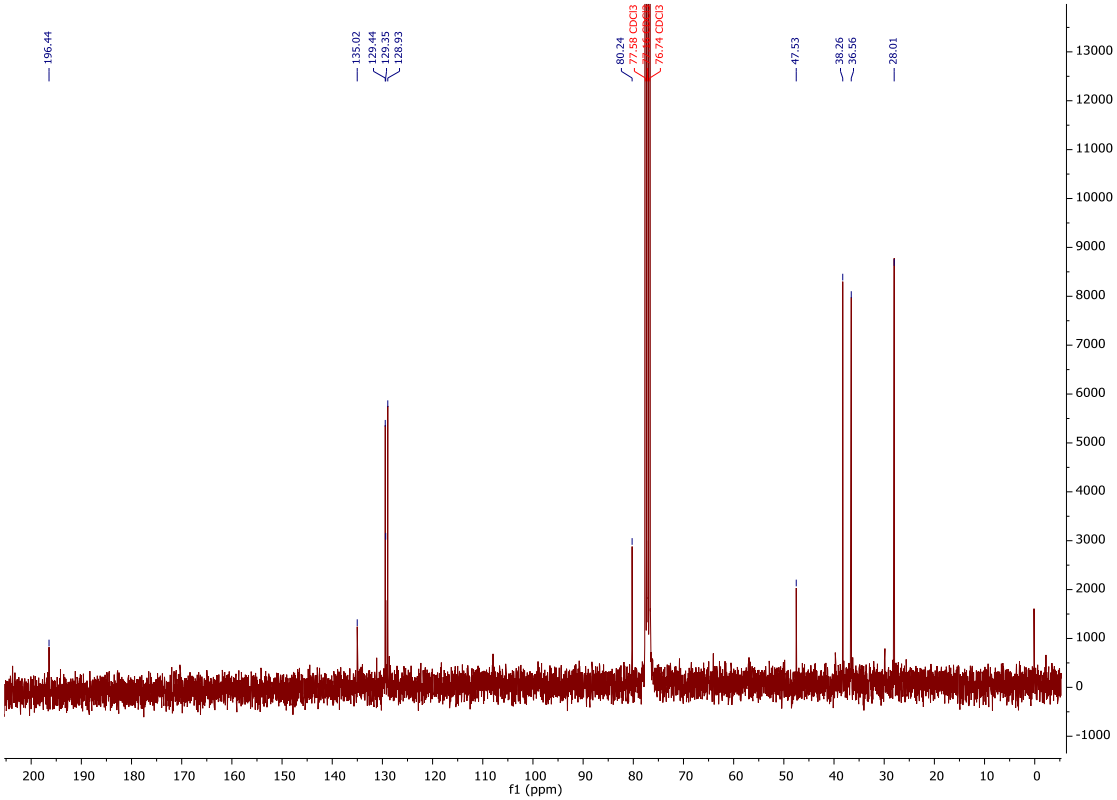
N-(benzyloxy)-2-cyclopropyl-2-oxoacetimidoyl cyanide (3f)



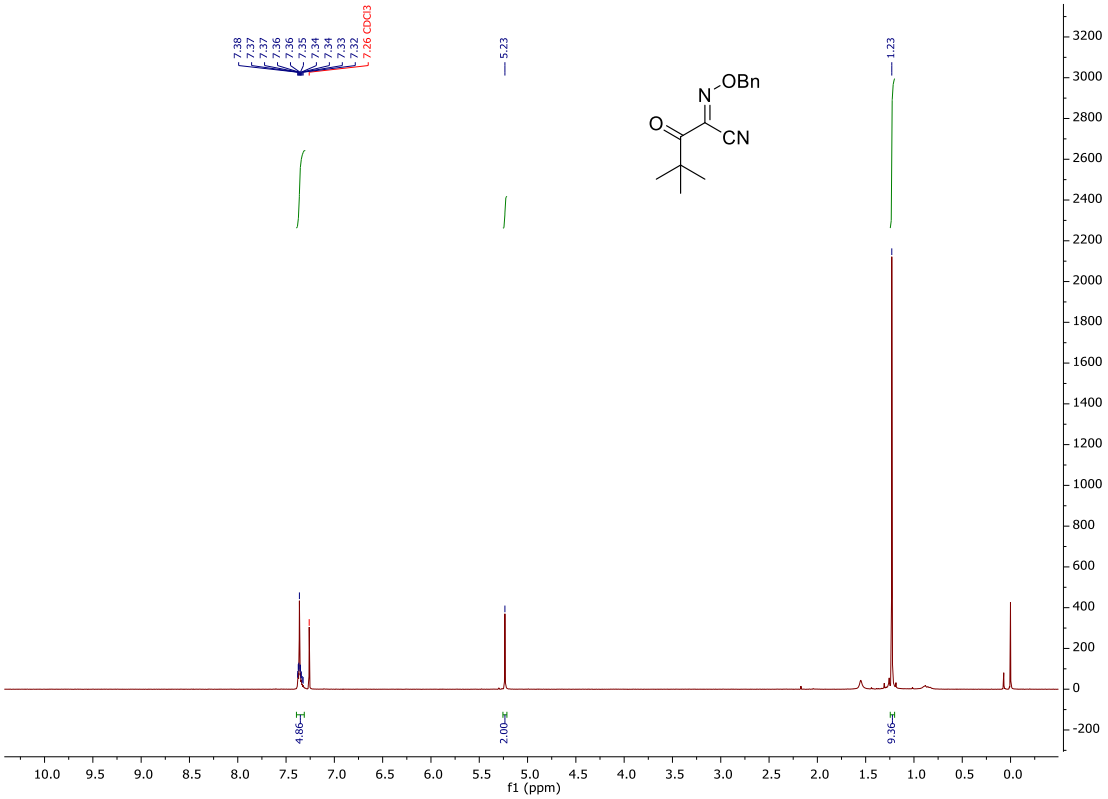


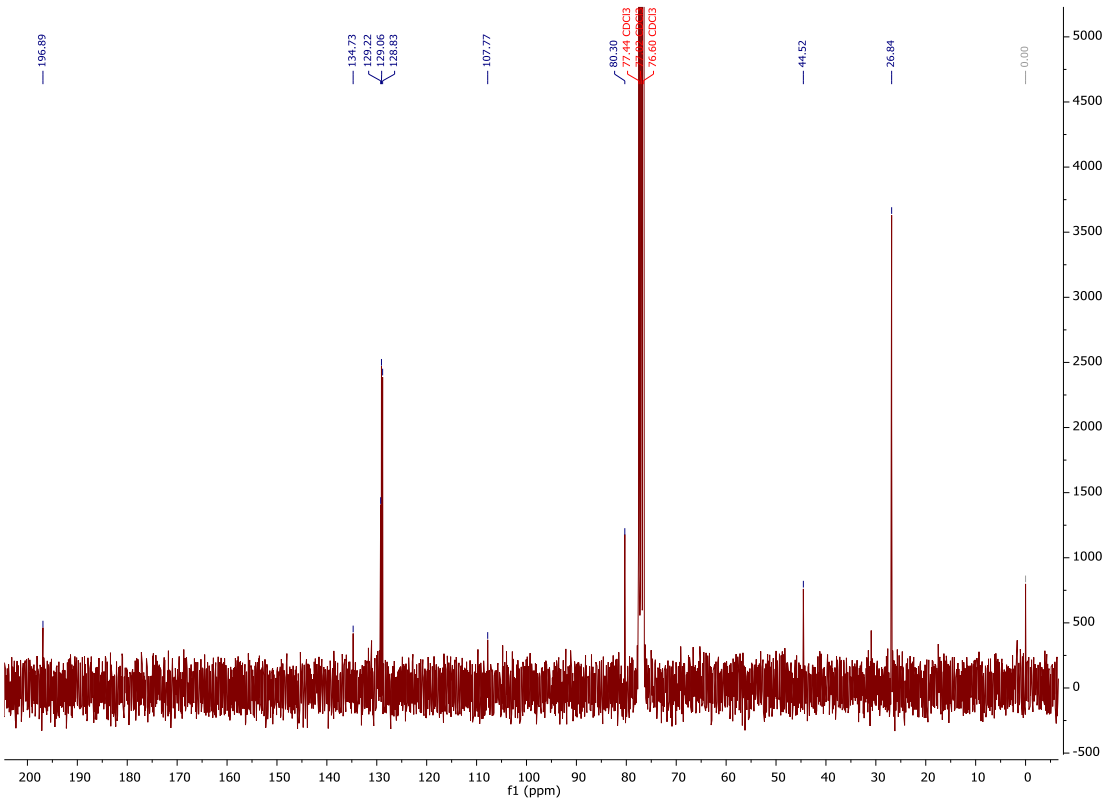
2-(adamantan-2-yl)-N-(benzyloxy)-2-oxoacetimidoyl cyanide (3g)



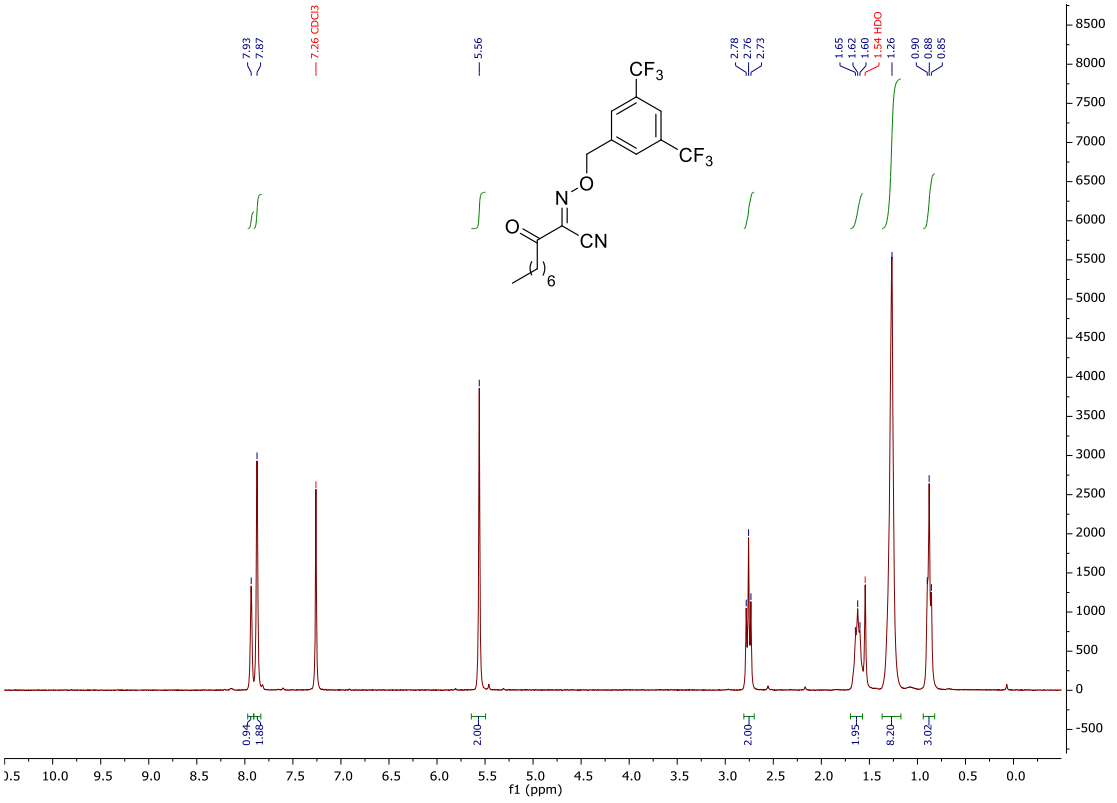


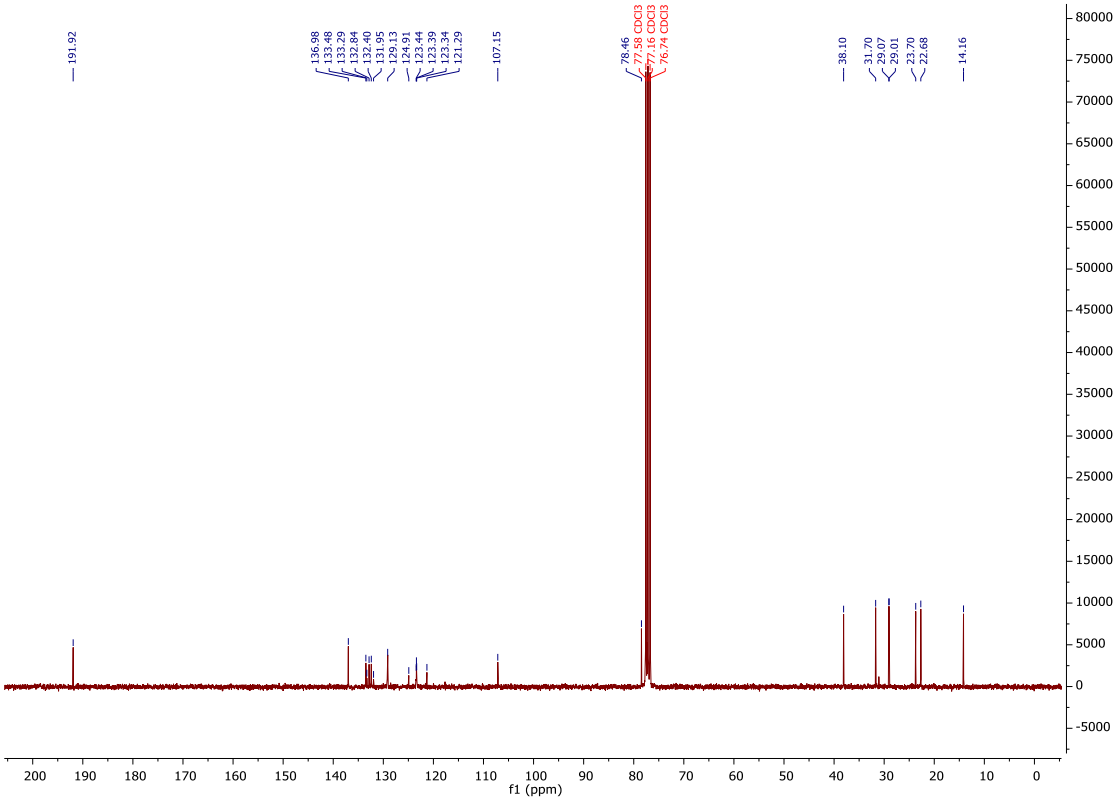
N-(benzyloxy)-3,3-dimethyl-2-oxobutanimidoyl cyanide (3h)

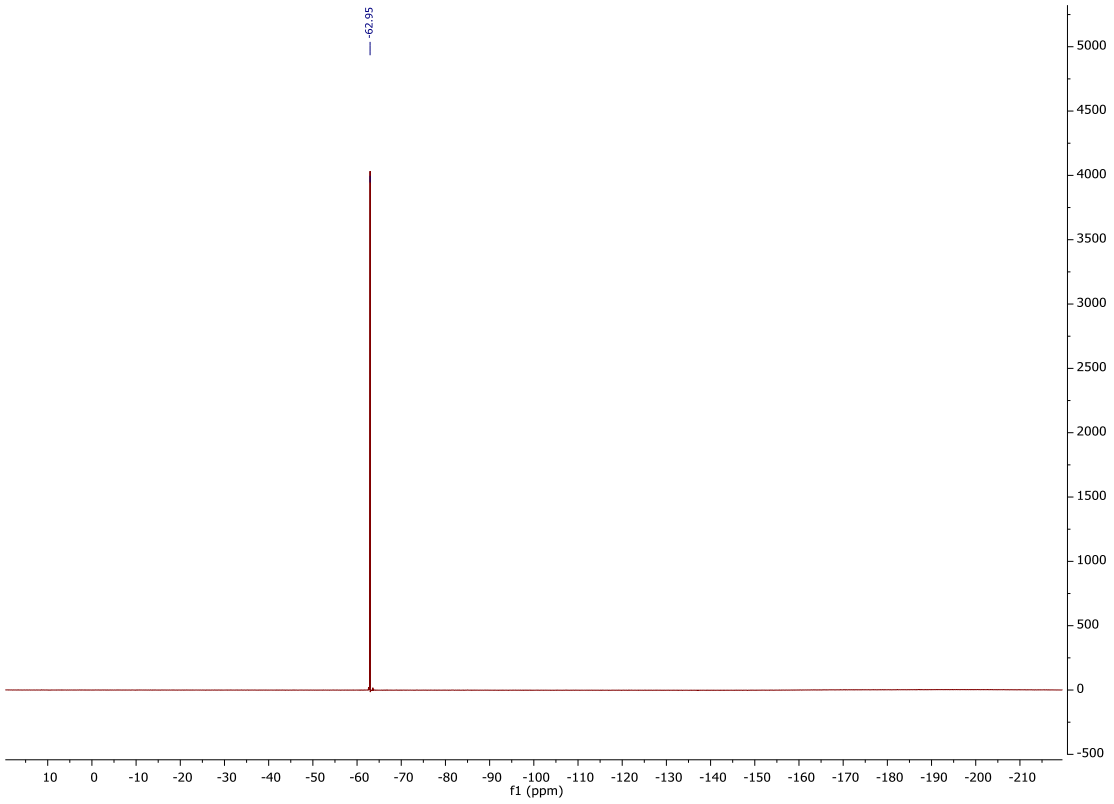




N-((3,5-bis(trifluoromethyl)benzyl)oxy)-2-oxononanimidoyl cyanide (3i)






-62.95
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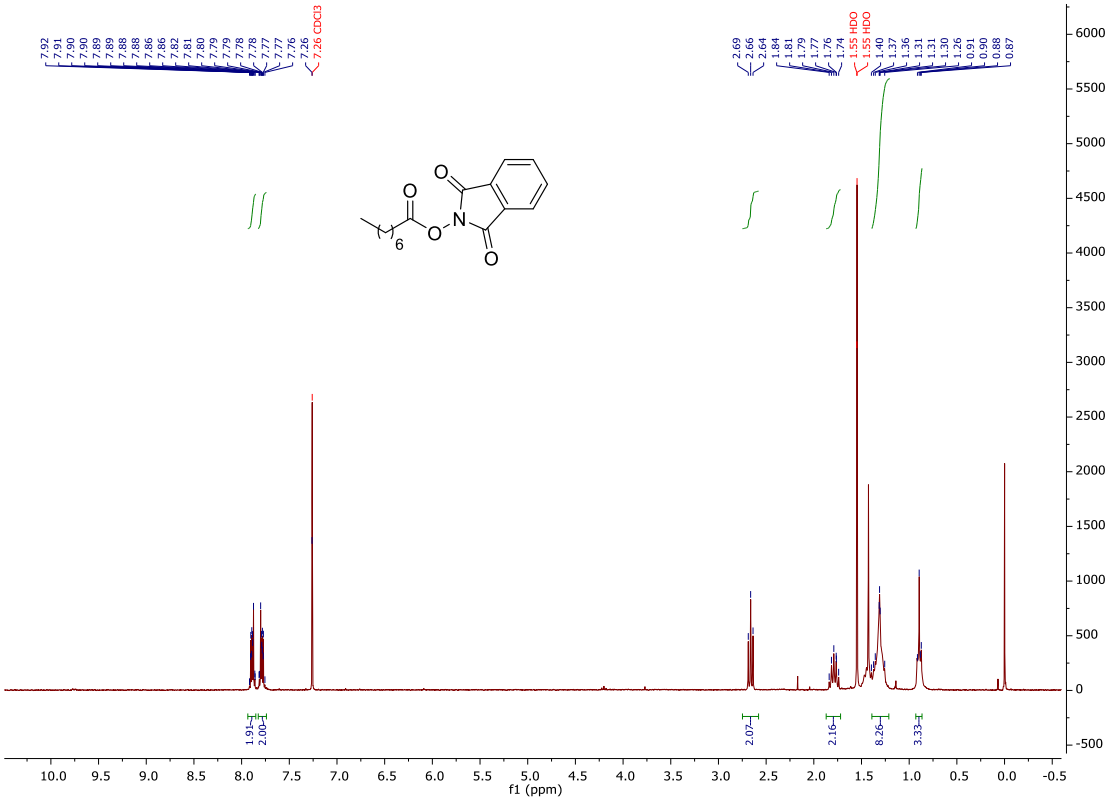
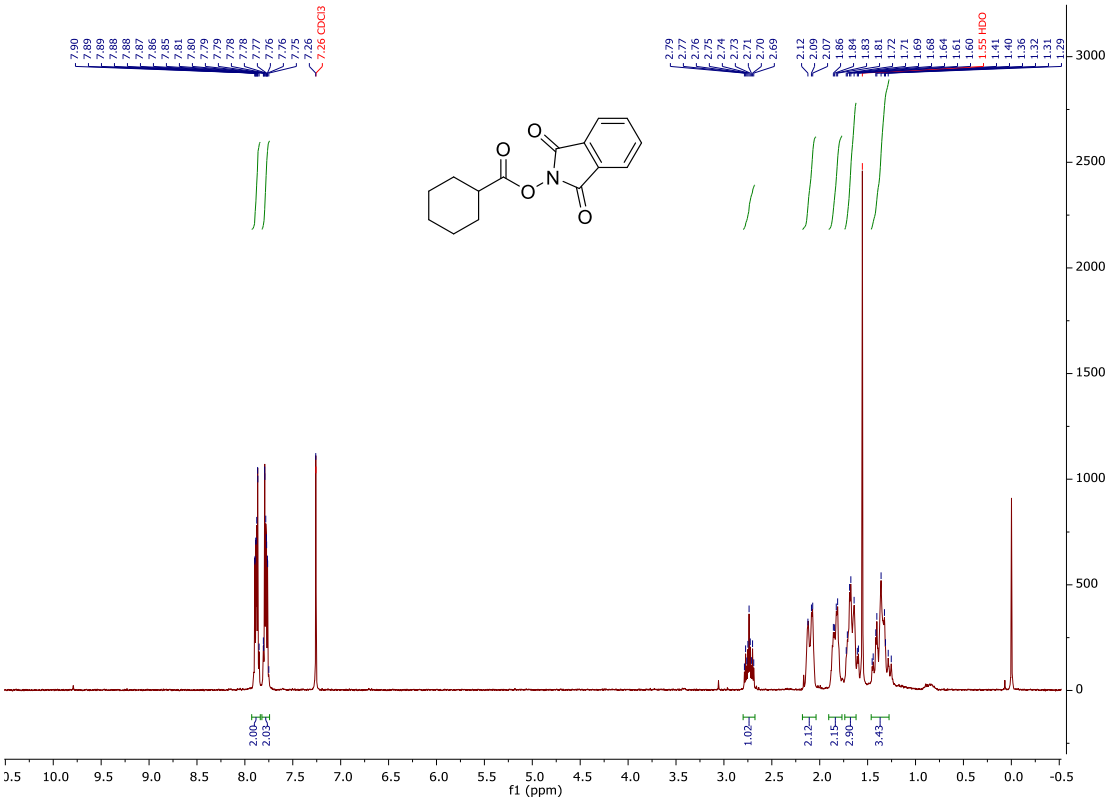
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

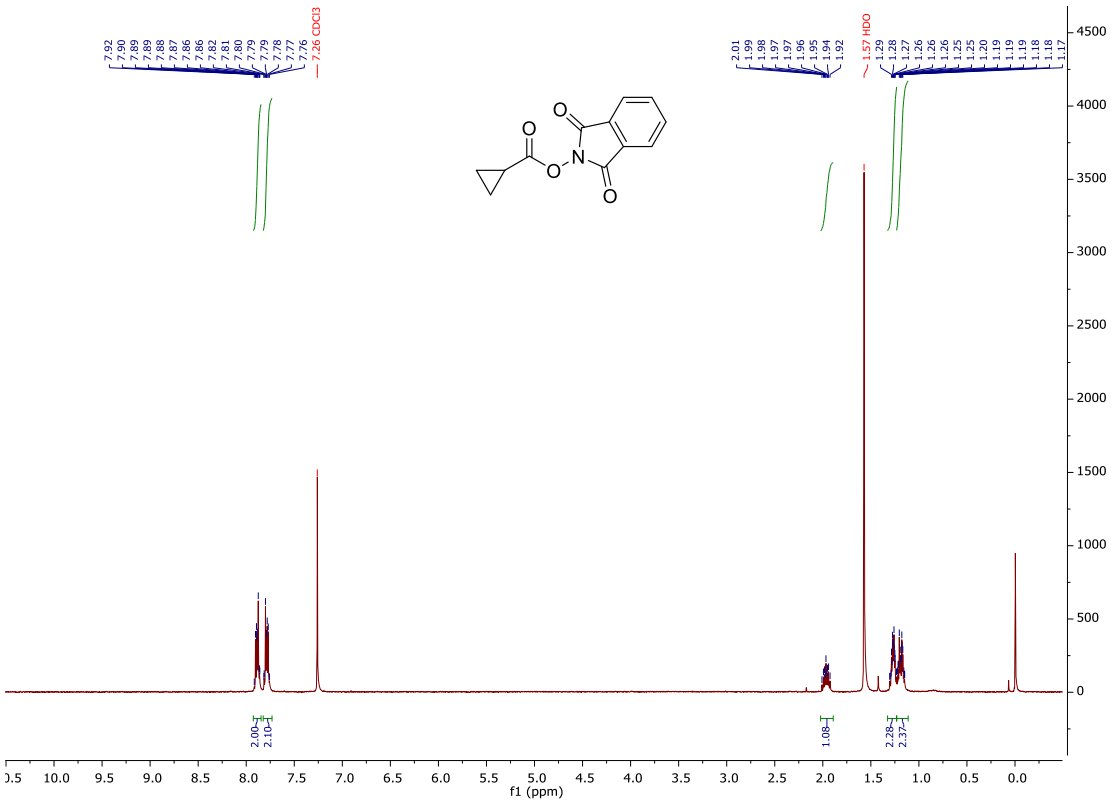
1,3-dioxoisoindolin-2-yl octanoate (4a)



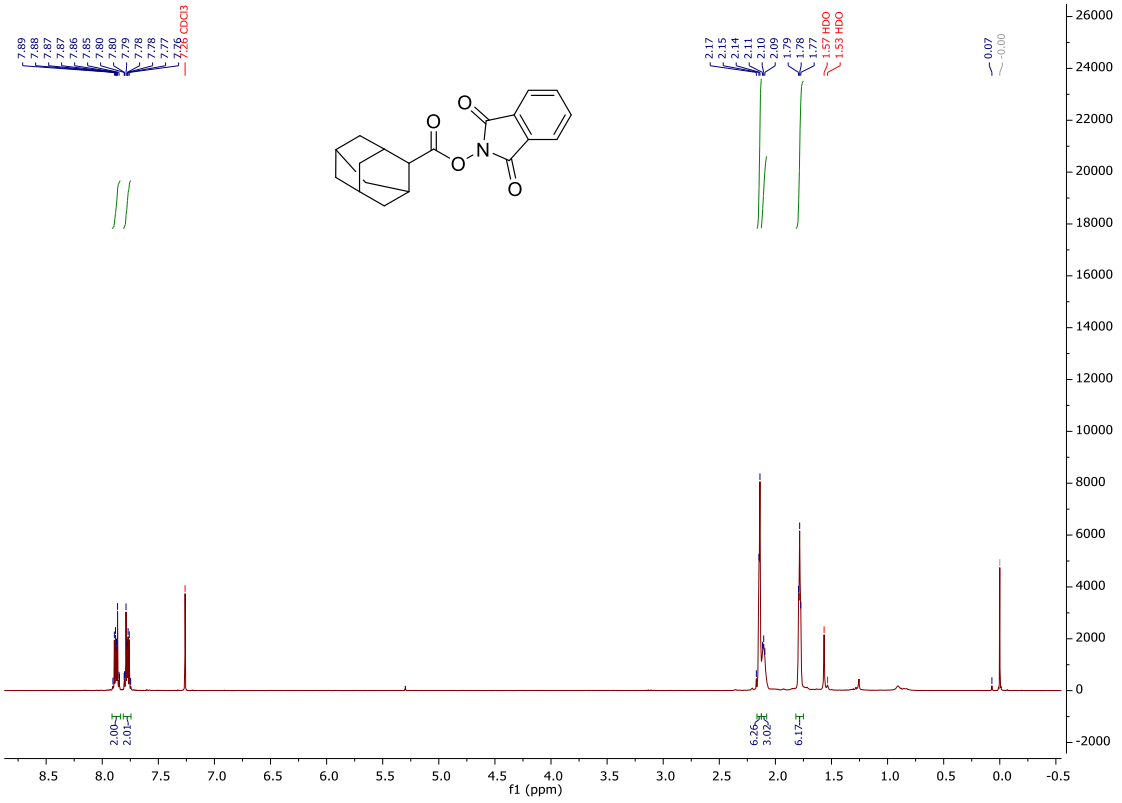
1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (4b)

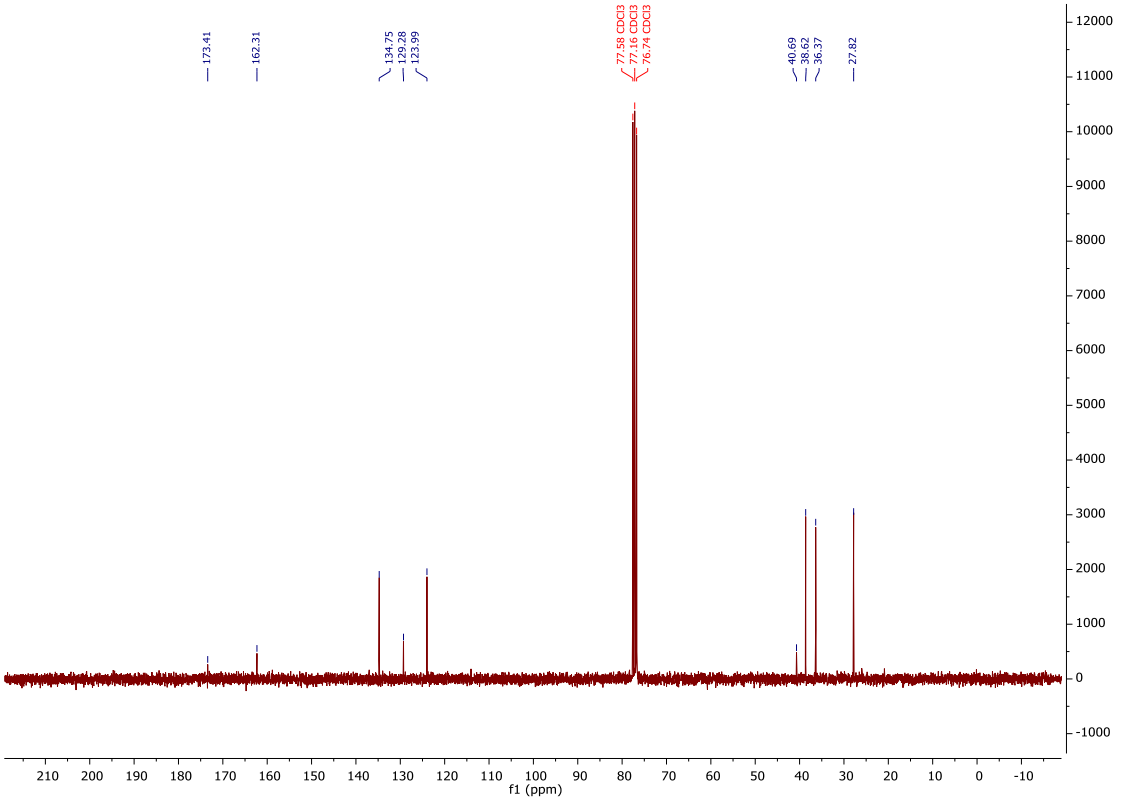


1,3-dioxoisoindolin-2-yl cyclopropanecarboxylate (4c)

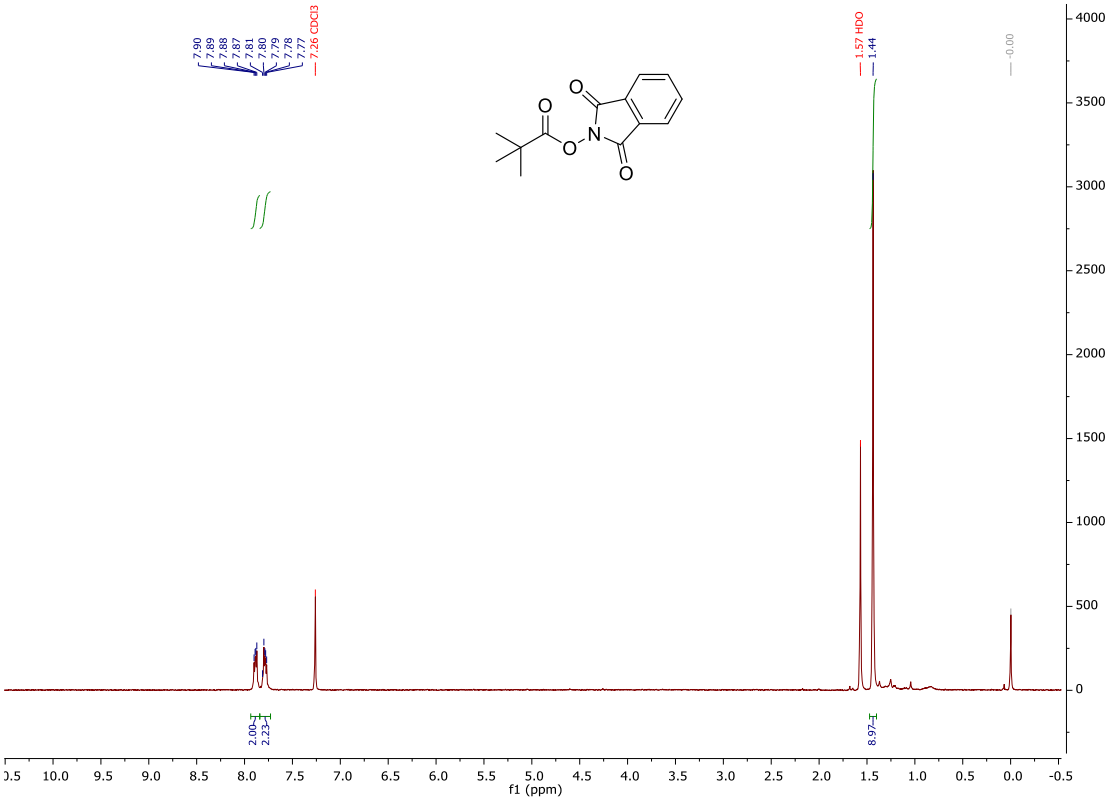


1,3-dioxoisoindolin-2-yl adamantane-2-carboxylate (4d)

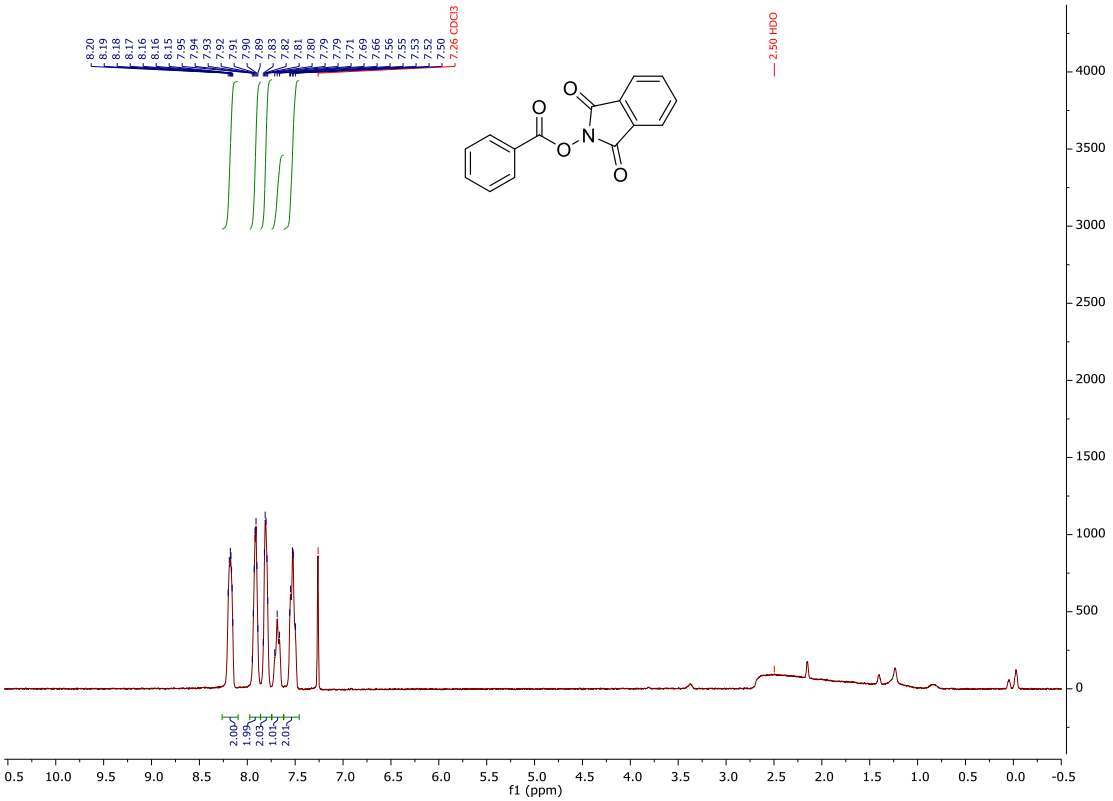




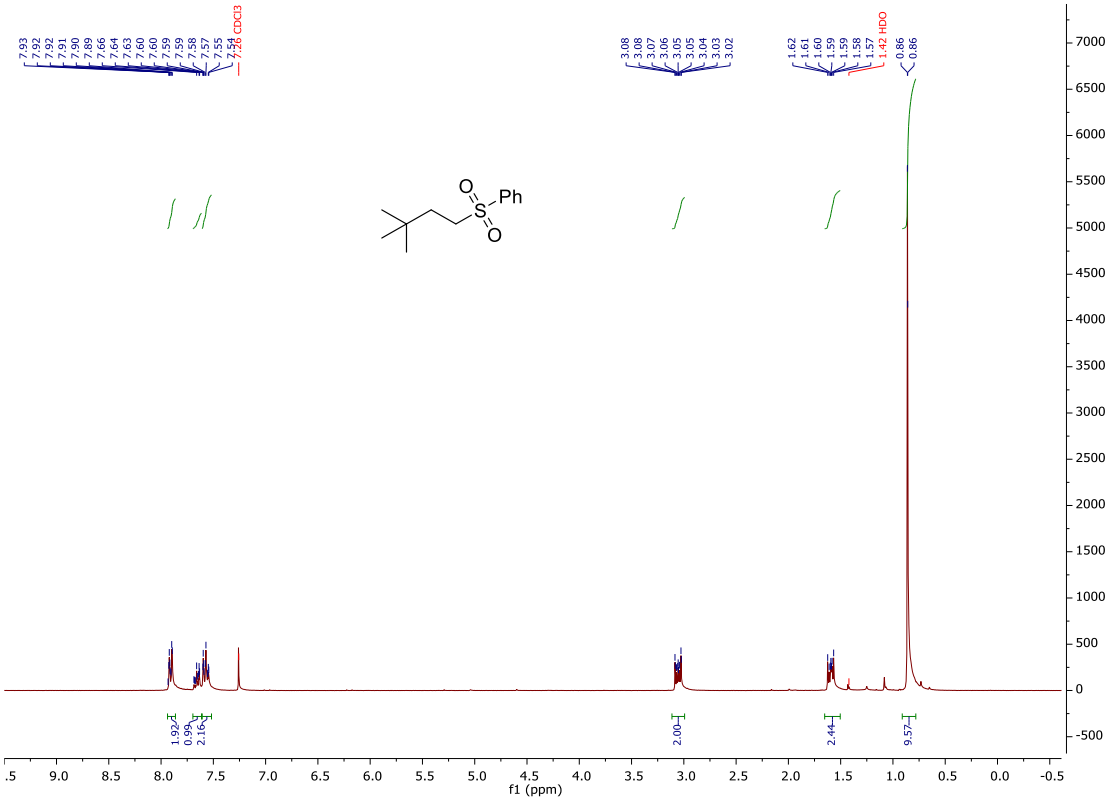
1,3-dioxoisoindolin-2-yl pivalate (4e)



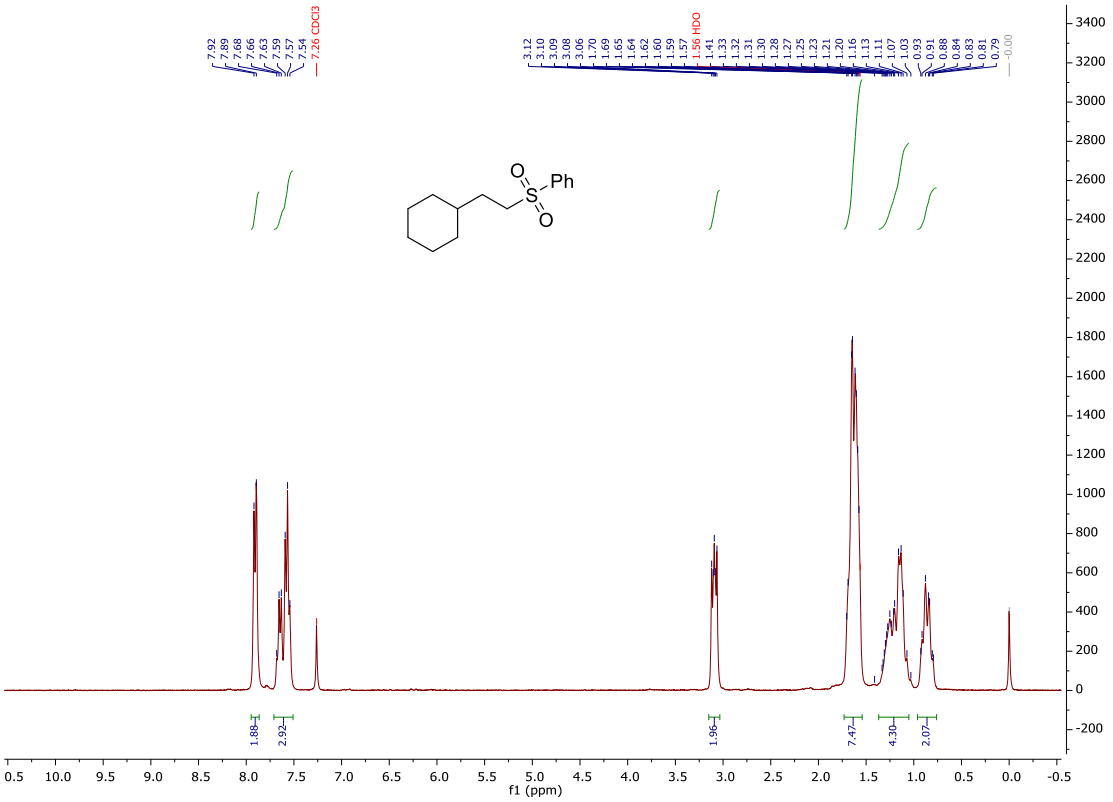
1,3-dioxoisoindolin-2-yl benzoate (4f)



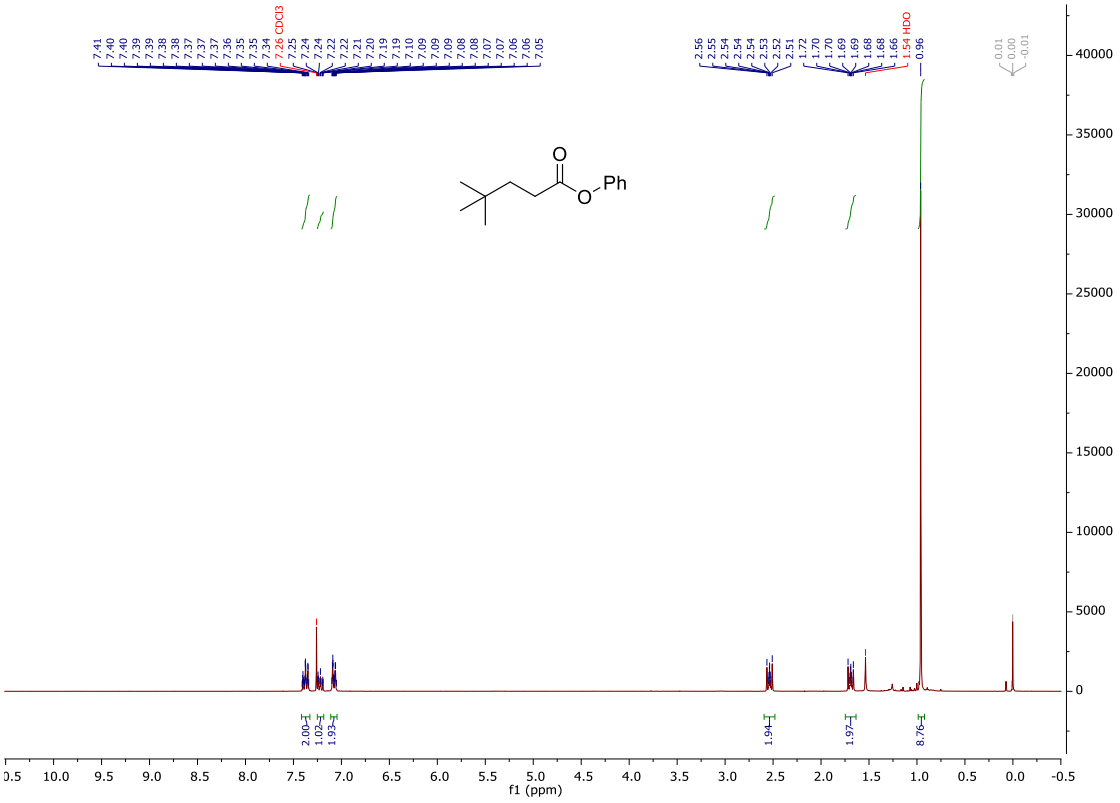
((3,3-dimethylbutyl)sulfonyl)benzene (6a)



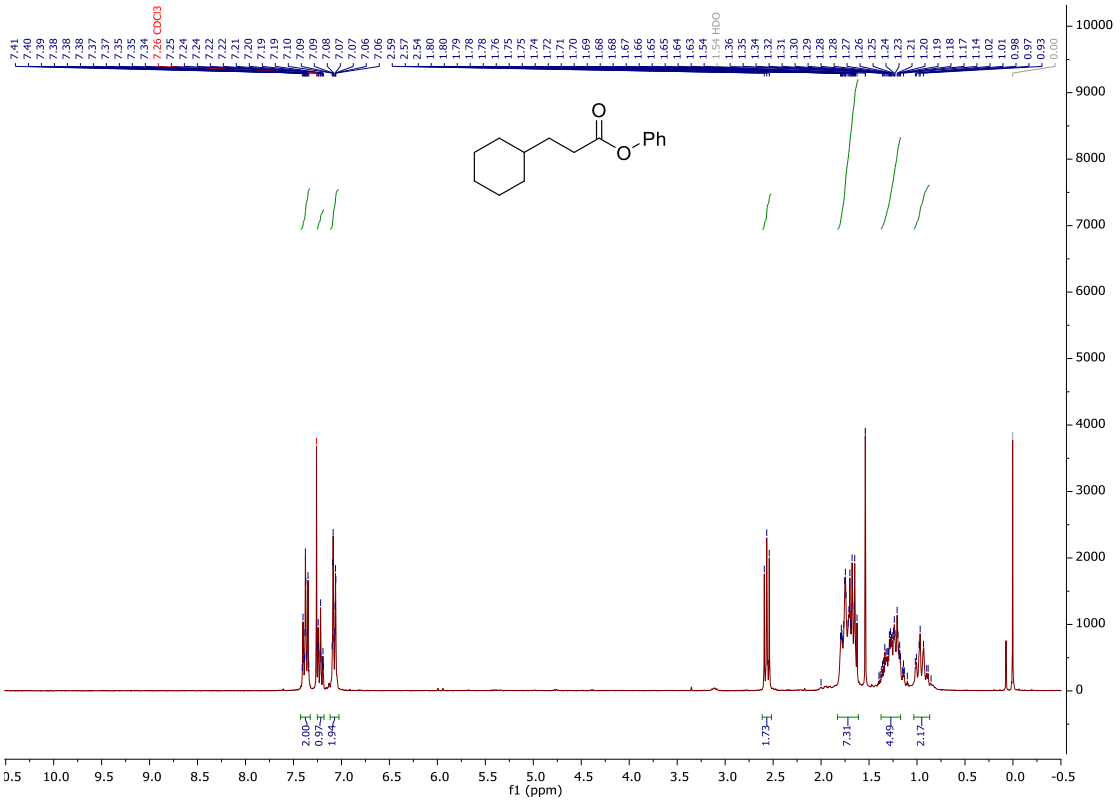
((2-cyclohexylethyl)sulfonyl)benzene (6b)



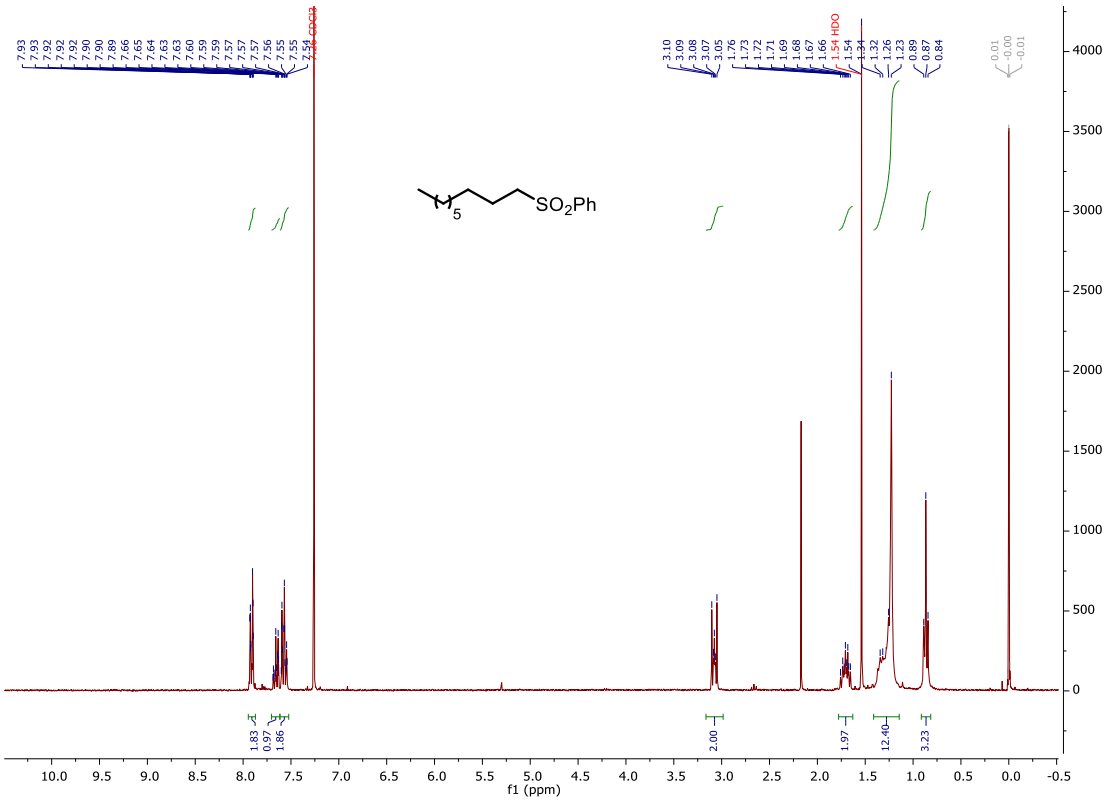
Phenyl 4,4-dimethylpentanoate (6c)



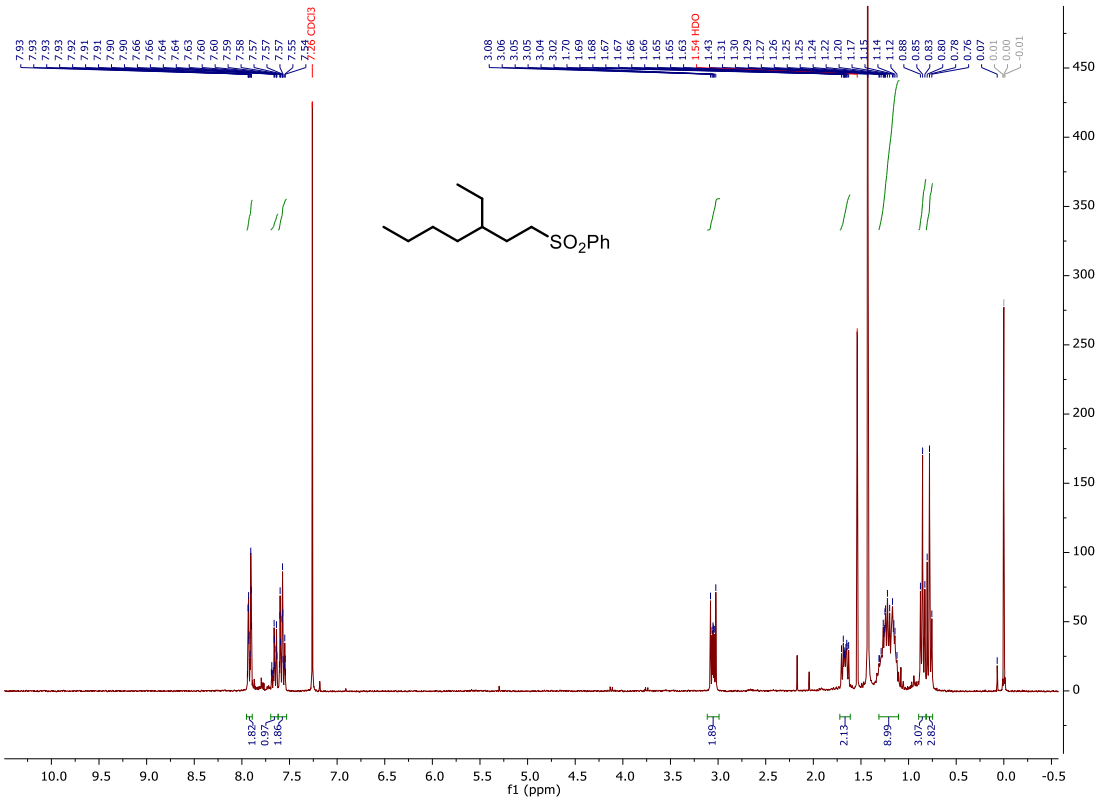
Phenyl 3-cyclohexylpropanoate (6d)

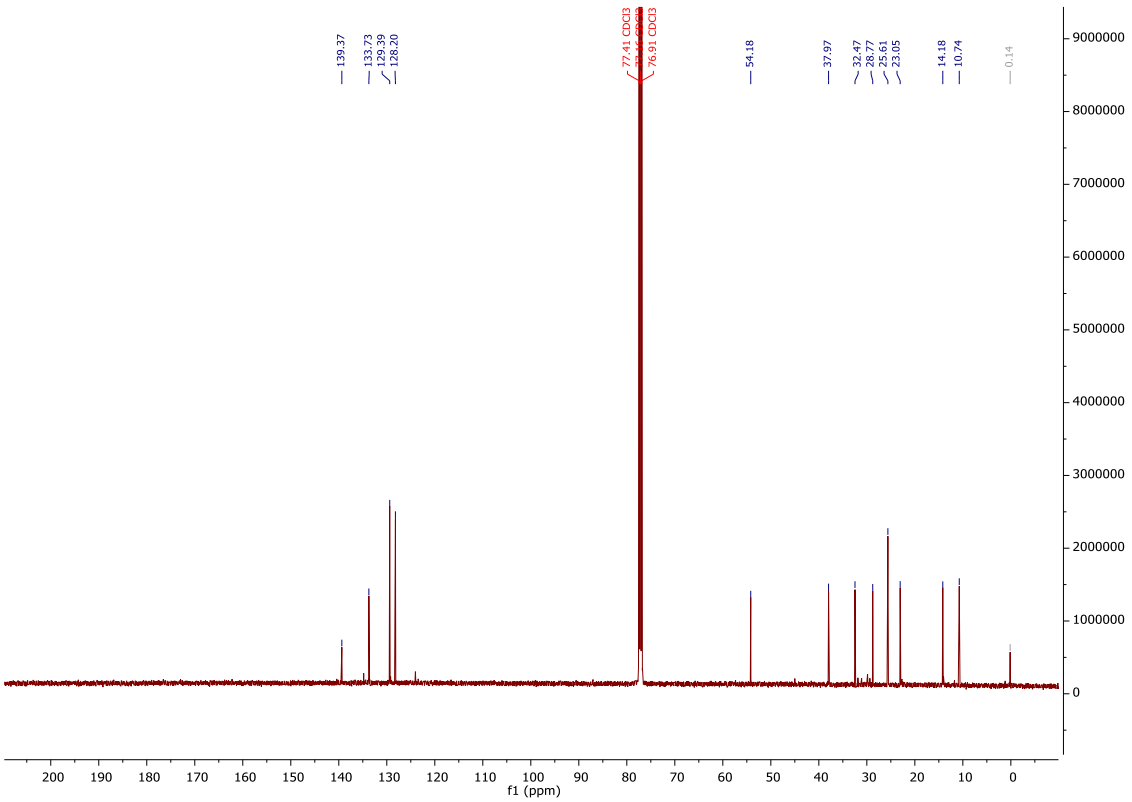


(Nonylsulfonyl)benzene (6e)

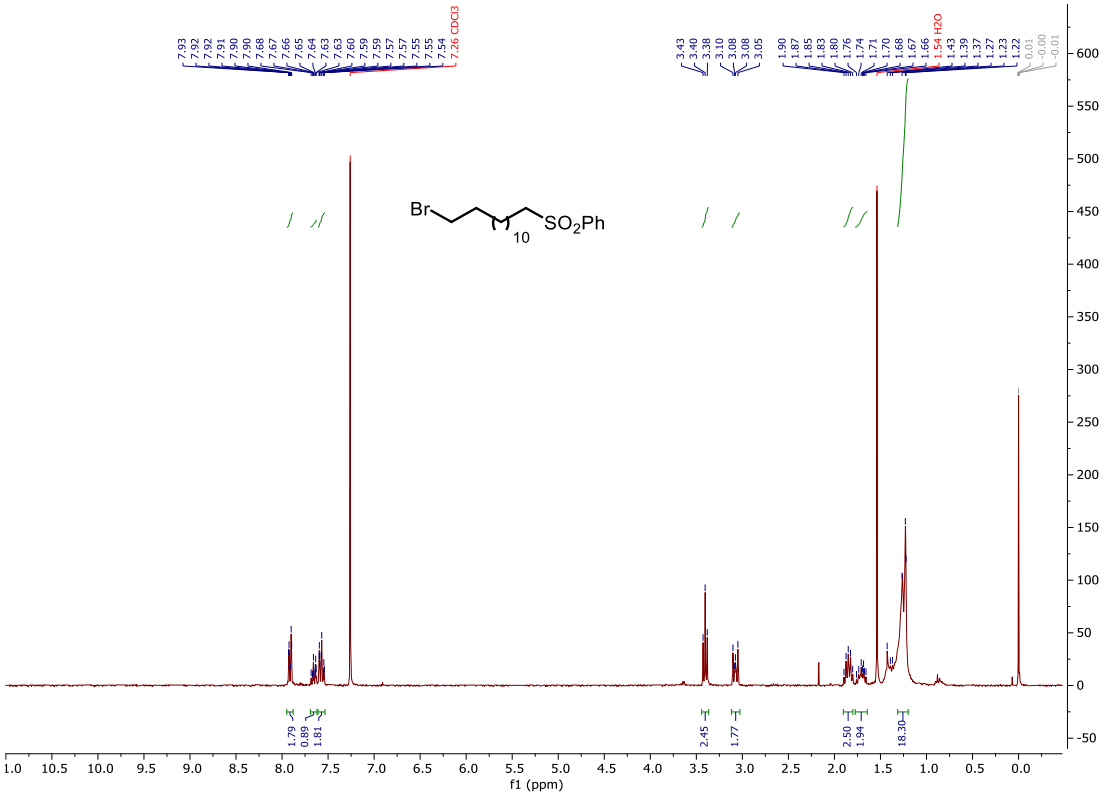


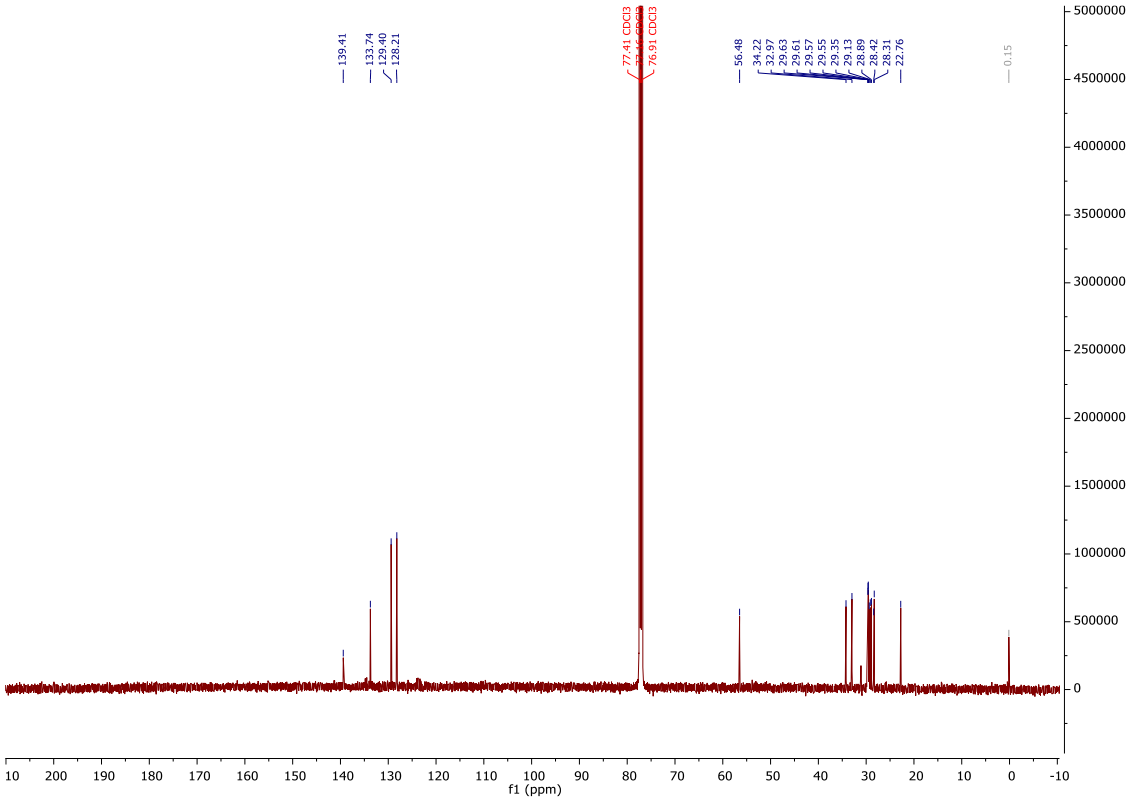
((3-ethylheptyl)sulfonyl)benzene (6f)





((13-bromotridecyl)sulfonyl)benzene (6g)





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