Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Visible Light-Mediated, Decarboxylative, Desulfonylative Smiles Rearrangement For General Arylethylamine Syntheses

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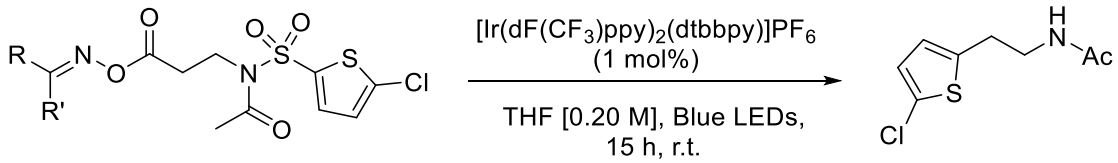
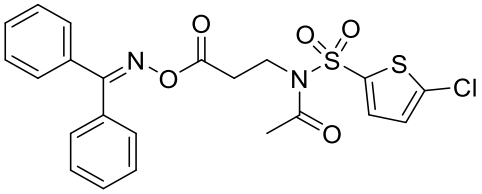
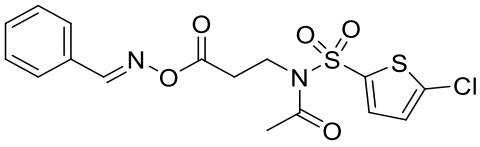
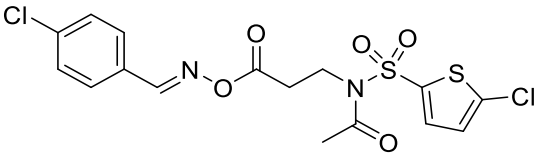
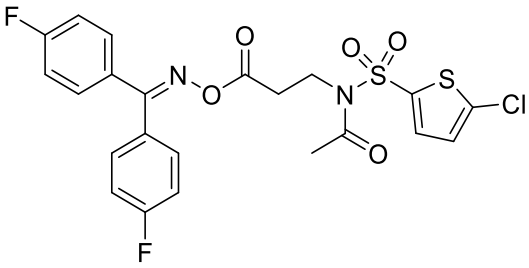
General Remarks

^{1}H–NMR, ^{13}C{1H}–NMR and were recorded at 500/400 MHz, 126/101 MHz, on a Bruker 400 spectrometers. All spectra are referenced to $CDCl_3$ residual $CHCl_3$ peak (1H NMR δ = 7.26 ppm; 13C{1H} NMR δ = 77.16 ppm) or to acetone-d6 residual acetone peak (1H NMR δ = 2.05 ppm; 13C{1H} NMR δ = 29.84 ppm). All chemical shifts are quoted in parts per million (ppm), measured from the centre of the signal except in the case of multiplets, which are quoted as a range. Coupling constants are quoted to the nearest 0.1 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin.), septet (sept.), multiplet (m), and combinations thereof. High resolution mass spectrometry was measured using an Agilent 6200 series TOF LC/MS system. Melting points were determined using a Büchi Melting Point B-540 and are uncorrected. Thin layer chromatography (TLC) was performed using pre–coated Merck 60F254 silica plates. Visualization was performed using either UV light or treatment with acidified potassium permanganate solution. Flash chromatography was performed using Merck silica gel 60 (0.040 – 0.063 mm). Light mediated reactions were irradiated by a A360WE Tuna Blue aquarium light (http://www.kessil.com/aquarium/Saltwater_A360.php). UV reactions were irradiated with an Omnicure S2000 UV Curing System fitted with a 365 nm filter. Chiral HPLC was conducted using a Shimadzu UFLC LC20AD system. $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ was purchased from Strem Chemicals.

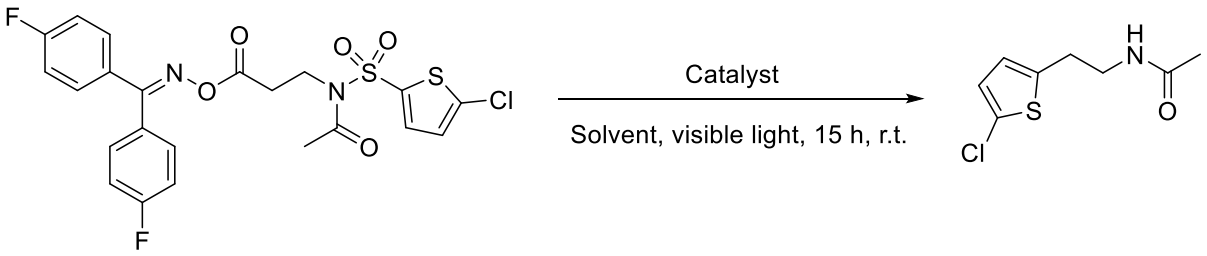
Optimisation

Oxime Variation (0.05 mmol scale)



	Substrate	Conversion (%)
Oxime variant A		41
Oxime variant B		50
Oxime variant C		45
SM 11a		63

Reaction conditions optimization



Entry	Catalyst	Solvent	Irradiation	Conc. [M]	Loading (%)	NMR Yield (%)
1	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	Blue LEDs	0.20	1	63
2	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	HFIP	Blue LEDs	0.20	1	14
3	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DCM	Blue LEDs	0.20	1	14
4	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	Dioxane	Blue LEDs	0.20	1	56
5	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DMSO	Blue LEDs	0.20	1	30
6	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	Me-THF	Blue LEDs	0.20	1	45
7	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	IPA	Blue LEDs	0.20	1	57
8	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	$CHCl_3$	Blue LEDs	0.20	1	24
9	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	Ethyl acetate	Blue LEDs	0.20	1	36
10	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	Toluene	Blue LEDs	0.20	1	41
11	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	DMF	Blue LEDs	0.20	1	-
12	$Ru(bpy)_3Cl_2.6H_2O$	THF	Blue LEDs	0.20	1	-
13	$[Ir(ppy)_2(dtbbpy)]PF_6$	THF	Blue LEDs	0.20	1	-
14	$Cu(dmp)(BINAP)BF_4$	THF	Blue LEDs	0.20	1	-
15	$[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$	THF	Blue LEDs	0.20	1	51
16	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	White LEDs	0.20	1	48
17[a]	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	Blue LEDs	0.20	1	53
18	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	Blue LEDs	0.50	1	45
19	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	Blue LEDs	0.08	1	63
20	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	Blue LEDs	0.04	1	57
21	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	Blue LEDs	0.08	0.25	56
22	-	THF	Blue LEDs	0.08	-	20
23	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$	THF	-	0.08	1	0
24	**$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$**	**THF**	**Blue LEDs**	**0.08**	**1**	**56[b]**

Yields determined using a 1, 3, 5 trimethoxybenzene NMR standard. [a] Heated to 60°C in an oil bath. [b] Isolated yield.

Experimental Procedures

General Procedure 1a: Starting Material Synthesis

β-amino acid (2.0 mmol, 1.0 eq), was dissolved in aqueous NaOH solution (0.5 M, 8 mL) and THF (8 mL). Aryl sulfonyl chloride (2.0 mmol, 1.0 eq) was added portionwise and stirred at room temperature for 15 h. Concentrated hydrochloric acid was added to the solution dropwise to pH 1 then the mixture was extracted with ethyl acetate. The combined extracts were dried with $MgSO_4$ and evaporated under reduced pressure. The resulting sulfonamide crude product could be carried forward without further purification in all cases.

The crude product (1.0 eq) was suspended in anhydrous DCM (0.1 M), to which DMAP (0.10 eq) was added, followed by the respective oxime (1.0 eq). EDC.HCl (2.5 eq) was added portionwise and stirred overnight at room temperature under Ar. Water was added to the reaction mixture and extracted three times with DCM, dried with $MgSO_4$ and evaporated under reduced pressure to give the crude oxime ester. The resulting sulfonamide crude product could be carried forward without further purification in all cases. (Adapted from Glorius *et. al.*[1]).

The crude product (1.0 eq) was dissolved in anhydrous DCM (0.1 M), to which DMAP (0.10 eq) was added with stirring. Under Ar, at 0 °C, Et_3N (2.0 eq) was added slowly, followed by AcCl (4.0 eq) dropwise. The reaction was stirred to r.t. overnight. Saturated NH_4Cl solution was added and the reaction mixture extracted three times with DCM, dried with $MgSO_4$ and evaporated to dryness. The resulting crude product was then purified with flash column chromatography (20:80 ethyl acetate:hexane).

General Procedure 1b:

β-amino acid (2.0 mmol, 1.0 eq), was dissolved in aqueous NaOMe solution (0.5 M, 8 mL) and THF (8 mL). Aryl sulfonyl chloride (2.0 mmol, 1.0 eq) was added portionwise and stirred at room temperature for 15 h. Concentrated hydrochloric acid was added to the solution dropwise to pH 1 then the mixture was extracted with ethyl acetate. The combined extracts were dried with $MgSO_4$ and evaporated under reduced pressure. The resulting sulfonamide crude product could be carried forward without further purification in all cases.

The crude product (1.0 eq) was suspended in anhydrous DCM (0.1 M), to which DMAP (0.10 eq) was added, followed by the respective oxime (1.0 eq). EDC.HCl (2.5 eq) was added portionwise and stirred overnight at room temperature under Ar. Water was added to the reaction mixture and extracted three times with DCM, dried with $MgSO_4$ and evaporated under reduced pressure to give the crude oxime ester. The resulting sulfonamide crude product could be carried forward without further purification in all cases. (adapted from Glorius *et. al.*[1])

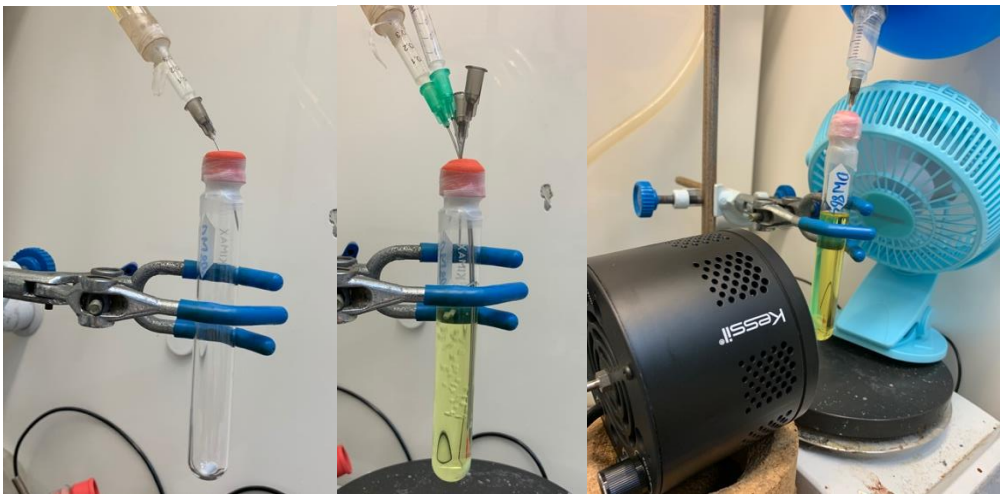
The crude product (1.0 eq) was dissolved in anhydrous DCM (0.1 M), to which DMAP (0.10 eq) was added with stirring. Under Ar, at 0 °C, Et_3N (2.0 eq) was added slowly, followed by AcCl (4.0 eq) dropwise. The reaction was stirred to r.t. overnight. Saturated NH_4Cl solution was added and the reaction mixture extracted three times with DCM, dried with $MgSO_4$ and evaporated to dryness. The resulting crude product was then purified with flash column chromatography (20:80 ethyl acetate:hexane).

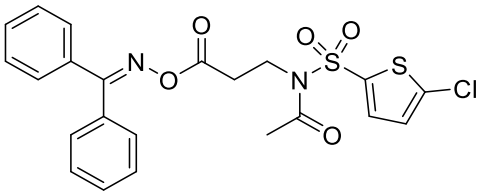
General Procedure 2a: Visible light-mediated Smiles rearrangement

$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (2.2 mg, 1 mol %) and the respective starting material (0.2 mmol) were dissolved in anhydrous THF (2.5 mL) in a colourless specimen vial with a septum fitted. The mixture was then vigorously purged with Ar whilst stirring for 10 minutes. The septum was then replaced with a screw-top lid and secured with Parafilm. The reaction mixture was stirred in front of blue LED light whilst cooled to room temperature with a desk fan for 15 h. The reaction mixture was purified directly with flash column chromatography to give the pure products.

General Procedure 2b: Visible light-mediated Smiles rearrangement (1 mmol)

A specimen vial fitted with septum (secured with Parafilm) and stirrer bar underwent three vacuum/argon cycles. **SM 16d** (527 mg, 1.0 mmol) and $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (11.2 mg) were added in THF solution (12.5 mL). The mixture was then vigorously purged with Ar whilst stirring, for 20 minutes. The reaction mixture was stirred in front of blue LED light under an N_2 balloon whilst cooled to room temperature with a desk fan for 15 h. The reaction mixture was purified directly with flash column chromatography to give the **Product 17d** as an orange oil (79 mg, 47% yield).





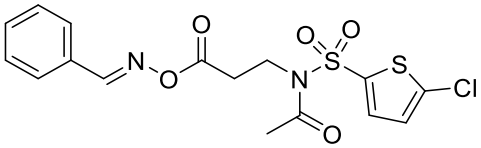
Oxime variant A *N*-((5-chlorothiophen-2-yl)sulfonyl)-*N*-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)acetamide

Synthesised according to General Procedure 1a. Isolated as a colourless oil (108 mg, 11% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.53 (d, J = 4.1 Hz, 1H), 7.50 – 7.43 (m, 4H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 6.96 (d, J = 4.1 Hz, 1H), 4.02 – 3.95 (m, 2H), 2.86 – 2.79 (m, 2H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.8, 165.3, 139.8, 137.0, 134.7, 133.9, 132.5, 131.2, 129.9, 129.2, 128.9, 128.6, 128.4, 127.0, 42.6, 33.1, 25.2.

HRMS (ESI) Calculated 491.0497 $[M+H]^+$; found 491.0492.



Oxime variant B (*E*)-*N*-(3-((benzylideneamino)oxy)-3-oxopropyl)-*N*-((5-chlorothiophen-2-yl)sulfonyl)acetamide

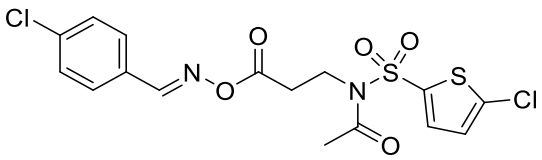
Synthesised according to General Procedure 1a. Isolated as a colourless solid (357 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.76 – 7.71 (m, 2H), 7.59 (d, J = 4.1 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.46 – 7.41 (m, 2H), 6.98 (d, J = 4.1 Hz, 1H), 4.14 – 4.08 (m, 2H), 3.00 – 2.93 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 169.0, 156.6, 139.9, 137.0, 134.0, 132.0, 130.0, 129.1, 128.6, 127.0, 42.8, 33.0, 25.2.

HRMS (ESI) Calculated 415.0184 $[M+H]^+$; found 415.0180.

mp 109 – 110 °C ($CHCl_3$).



Oxime variant C (*E*)-N-(3-(((4-chlorobenzylidene)amino)oxy)-3-oxopropyl)-N-((5-chlorothiophen-2-yl)sulfonyl)acetamide

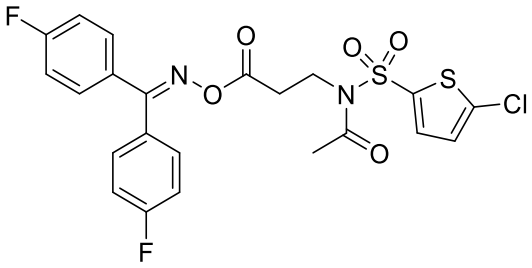
Synthesised according to General Procedure 1a. Isolated as a colourless solid (198 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 4.1 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 4.1 Hz, 1H), 4.13 – 4.07 (m, 2H), 2.99 – 2.93 (m, 2H), 2.48 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 169.0, 156.6, 139.9, 137.0, 134.0, 132.0, 130.0, 129.1, 128.6, 127.0, 42.8, 33.0, 25.2.

HRMS (ESI) Calculated 448.9794 $[M+H]^+$; found 448.9792.

m.p. 152 – 155 °C ($CHCl_3$).



SM 16a N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((5-chlorothiophen-2-yl)sulfonyl)acetamide

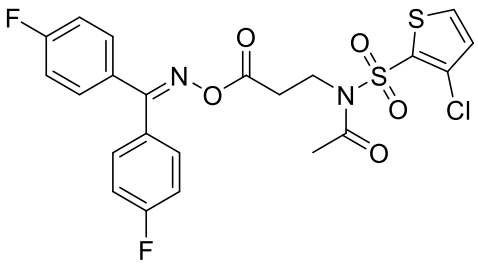
Synthesised according to General Procedure 1a (6.0 mmol scale). Isolated as a colourless solid (1.35 g, 43 % yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.54 (d, *J* = 4.1 Hz, 1H), 7.33 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 7.07 (dd, *J* = 8.9, 8.3 Hz, 2H), 6.98 (d, *J* = 4.1 Hz, 1H), 4.03 – 3.95 (m, 2H), 2.87 – 2.79 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) 169.9, 168.7, 164.8 (d, *J* = 252.5 Hz), 163.5 (d, *J* = 251.0 Hz), 163.3, 139.9, 137.0, 133.8, 131.3 (d, *J* = 7.9 Hz), 131.3 (d, *J* = 8.3 Hz), 130.7 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 3.7 Hz), 127.0, 115.9 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.8 Hz), 42.6, 33.1, 25.2.

HRMS (ESI)**:** Calculated 549.0128 $[M+Na]^+$; found 549.0123.

m.p. 120 – 123 °C ($CHCl_3$).



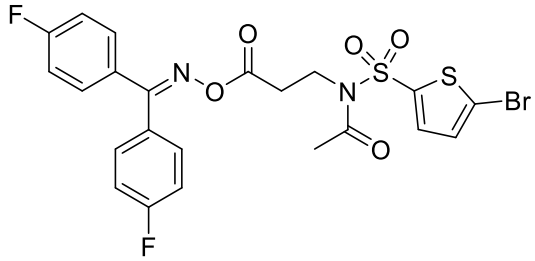
SM 16b N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((3-chlorothiophen-2-yl)sulfonyl)acetamide

Synthesised according to general procedure 1a (1.59 mmol scale). Isolated as a colourless viscous oil (354 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 5.3 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.32 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.11 – 7.02 (m, 3H), 4.12 – 4.04 (m, 2H), 2.86 – 2.78 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 168.5, 164.6 (d, *J* = 252.4 Hz), 163.4 (d, *J* = 250.8 Hz), 163.1, 132.9, 132.1, 131.2 (d, *J* = 8.6 Hz), 131.1 (d, *J* = 8.5 Hz), 130.6 (d, *J* = 3.2 Hz), 130.3, 129.8, 128.0 (d, *J* = 3.6 Hz), 115.7 (d, *J* = 22.0 Hz), 115.7 (d, *J* = 21.8 Hz), 42.7, 32.7, 25.3.

HRMS (ESI): Calculated 527.0308 $[M+H]^+$; found 527.0305.



SM 16c N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((5-bromothiophen-2-yl)sulfonyl)acetamide

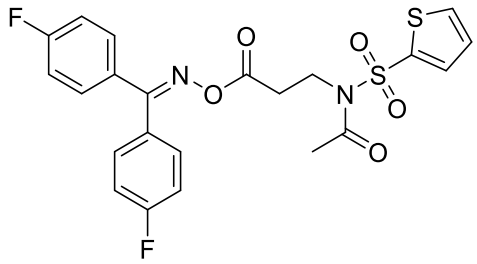
Synthesised according to General Procedure 1a (1.2 mmol scale). Isolated as a colourless solid (287 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.49 (d, *J* = 4.1 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.20 – 7.14 (m, 2H), 7.11 (d, *J* = 4.0 Hz, 1H), 7.10 – 7.04 (m, 2H), 4.02 – 3.96 (m, 2H), 2.86 – 2.80 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.7, 164.8 (d, *J* = 252.5 Hz), 163.5 (d, *J* = 251.0 Hz), 163.3, 139.8, 134.5, 131.3 (d, *J* = 8.7 Hz), 131.3 (d, *J* = 8.3 Hz), 130.7 (d, *J* = 3.2 Hz), 130.7, 128.1 (d, *J* = 3.6 Hz), 122.6, 115.9 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.7 Hz), 42.6, 33.1, 25.2.

HRMS (ESI) Calculated 570.9803 $[M+H]^+$; found 570.9802.

mp 120 - 121 °C ($CHCl_3$).



SM 16d N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-(thiophen-2-ylsulfonyl)acetamide

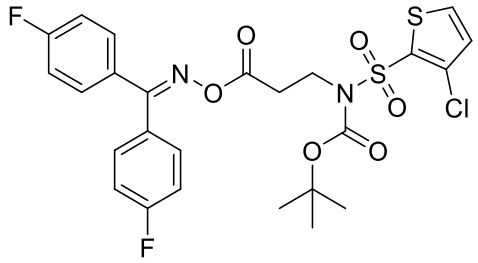
Synthesised according to General Procedure 1a. Isolated as a colourless solid (438 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.60 – 7.53 (m, 2H), 7.36 – 7.30 (m, 2H), 7.20 – 7.12 (m, 3H), 7.10 – 7.03 (m, 2H), 4.05 – 3.96 (m, 2H), 2.88 – 2.79 (m, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.7, 164.7 (d, *J* = 252.3 Hz), 163.5 (d, *J* = 250.8 Hz), 163.1, 139.4, 134.2, 134.0, 131.3 (d, *J* = 8.7 Hz), 131.3 (d, *J* = 8.5 Hz), 130.7 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 3.6 Hz), 127.8, 115.8 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.8 Hz), 42.5, 33.1, 25.3.

HRMS calculated 515.0517 $[M+Na]^+$; found 515.0517.

mp 101 - 103 °C ($CHCl_3$).



SM 16e *tert*-butyl (3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)((3-chlorothiophen-2-yl)sulfonyl)carbamate

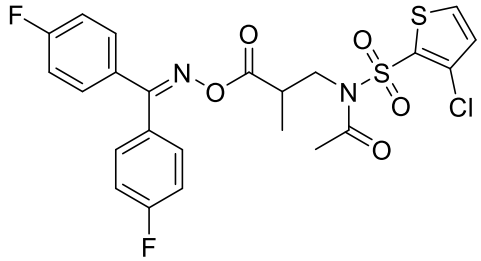
Synthesised according to General Procedure 1a. Isolated as a colourless solid (362 mg, 31% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.53 (m, 3H), 7.38 – 7.30 (m, 2H), 7.21 – 7.15 (m, 2H), 7.10 – 7.04 (m, 2H), 7.01 (d, *J* = 5.3 Hz, 1H), 4.23 – 4.17 (m, 2H), 2.92 – 2.86 (m, 2H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 164.7 (d, *J* = 252.3 Hz), 163.5 (d, *J* = 250.8 Hz), 163.2, 150.3, 134.4, 131.3 (d, *J* = 8.8 Hz), 131.3 (d, *J* = 8.5 Hz), 131.2, 130.8 (d, *J* = 3.2 Hz), 129.6, 128.8, 128.2 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.6 Hz), 115.8 (d, *J* = 21.9 Hz), 85.6, 43.9, 33.8, 28.0.

HRMS (ESI) calculated 607.0546 $[M+Na]^+$; found 607.0544.

mp 109 - 111 °C ($CHCl_3$)



SM 16f N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-2-methyl-3-oxopropyl)-N-((3-chlorothiophen-2-yl)sulfonyl)acetamide

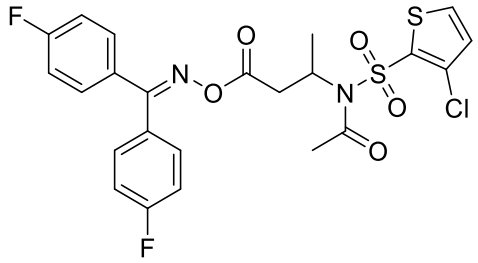
Synthesised according to General Procedure 1a. Isolated as colourless solid (410 mg, 38% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 5.4 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.38 – 7.30 (m, 2H), 7.20 – 7.11 (m, 2H), 7.09 – 7.00 (m, 3H), 4.08 (dd, *J* = 14.5, 7.0 Hz, 1H), 3.95 (dd, *J* = 14.5, 7.2 Hz, 1H), 2.98 (q, *J* = 7.1 Hz, 1H), 2.37 (s, 3H), 1.17 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 170.1, 164.7 (d, *J* = 252.3 Hz), 163.6, 163.4 (d, *J* = 250.8 Hz), 133.4, 132.2, 131.3 (d, *J* = 8.7 Hz), 131.3 (d, *J* = 8.6 Hz), 130.7 (d, *J* = 3.2 Hz), 130.2, 128.2 (d, *J* = 3.6 Hz), 129.6, 115.7 (d, *J* = 21.9 Hz), 115.7 (d, *J* = 21.8 Hz), 49.4, 38.7, 25.1, 14.9.

HRMS: (ESI) Calculated 541.0464 $[M+H]^+$; found 541.0465.

mp 94 - 98 °C ($CHCl_3$).



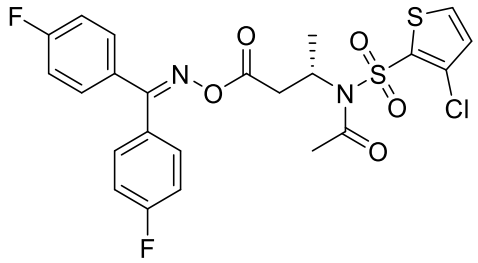
SM 16g N-(4-(((bis(4-fluorophenyl)methylene)amino)oxy)-4-oxobutan-2-yl)-N-((3-chlorothiophen-2-yl)sulfonyl)acetamide

Synthesised according to General Procedure 1a. Isolated as a colourless oil (154 mg, 14% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 5.3 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.35 – 7.25 (m, 2H), 7.22 – 7.12 (m, 2H), 7.11 – 7.01 (m, 3H), 4.61 (dqd, *J* = 9.2, 6.7, 3.7 Hz, 1H), 3.14 (dd, *J* = 16.8, 9.3 Hz, 1H), 2.70 (dd, *J* = 16.8, 3.8 Hz, 1H), 2.52 (s, 3H), 1.39 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 168.7, 164.7 (d, *J* = 252.3 Hz), 163.4 (d, *J* = 251.0 Hz), 163.2, 132.9, 132.4, 131.3 (d, *J* = 7.5 Hz), 131.2 (d, *J* = 7.3 Hz), 130.7 (d, *J* = 3.2 Hz), 130.3, 129.8, 128.0 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.9 Hz), 53.4, 38.2, 27.3, 18.5.

HRMS Calculated 563.0284 $[M+Na]^+$; found 563.0284.



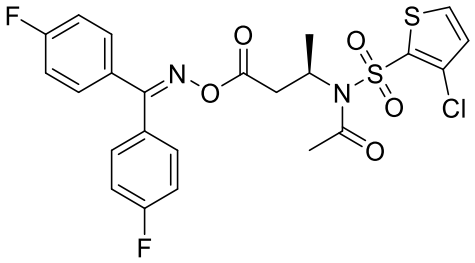
SM *S*-16g (*S*)-N-(4-(((bis(4-fluorophenyl)methylene)amino)oxy)-4-oxobutan-2-yl)-N-((3-chlorothiophen-2-yl)sulfonyl)acetamide

Synthesised according to General Procedure 1a. Isolated as a colourless oil (237 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 5.3 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.34 – 7.25 (m, 2H), 7.22 – 7.12 (m, 2H), 7.11 – 7.00 (m, 3H), 4.61 (dqd, *J* = 9.2, 6.7, 3.8 Hz, 1H), 3.14 (dd, *J* = 16.8, 9.3 Hz, 1H), 2.69 (dd, *J* = 16.8, 3.8 Hz, 1H), 2.51 (s, 3H), 1.39 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 168.7, 164.7 (d, *J* = 252.4 Hz), 163.5 (d, *J* = 251.1 Hz), 163.2, 132.9, 132.4, 131.3 (d, *J* = 8.1 Hz), 131.2 (d, *J* = 8.1 Hz), 130.7 (d, *J* = 3.3 Hz), 130.3, 129.8, 128.0 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.8 Hz), 115.8 (d, *J* = 21.8 Hz), 53.4, 38.2, 27.3, 18.5.

HRMS (ESI) Calculated 563.0284 $[M+Na]^+$; found 563.0284.



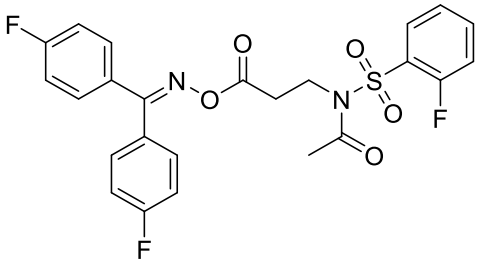
SM *R*-16g (*R*)-N-(4-(((bis(4-fluorophenyl)methylene)amino)oxy)-4-oxobutan-2-yl)-N-((3-chlorothiophen-2-yl)sulfonyl)acetamide

Synthesised according to General Procedure 1a. Isolated as a colourless oil (209 mg, 19% yield).

^{1}H NMR (400 MHz, $CDCl_3$ δ 7.66 (d, *J* = 5.3 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.34 – 7.25 (m, 2H), 7.22 – 7.12 (m, 2H), 7.11 – 7.00 (m, 3H), 4.61 (dt, *J* = 13.4, 6.7, 3.7, 3.3 Hz, 1H), 3.14 (dd, *J* = 16.8, 9.3 Hz, 1H), 2.69 (dd, *J* = 16.8, 3.8 Hz, 1H), 2.51 (s, 3H), 1.39 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 168.7, 164.7 (d, *J* = 252.4 Hz), 163.5 (d, *J* = 251.1 Hz) 163.2, 132.9, 132.4, 131.3 (d, *J* = 8.2 Hz), 131.2 (d, *J* = 8.1 Hz), 130.7 (d, *J* = 3.4 Hz), 130.3, 129.8, 128.0 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.8 Hz), 115.8 (d, *J* = 21.8 Hz), 53.4, 38.2, 27.3, 18.5.

HRMS (ESI) Calculated 541.0465 $[M+H]^+$; found 541.0460.



SM 16h N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((2-fluorophenyl)sulfonyl)acetamide

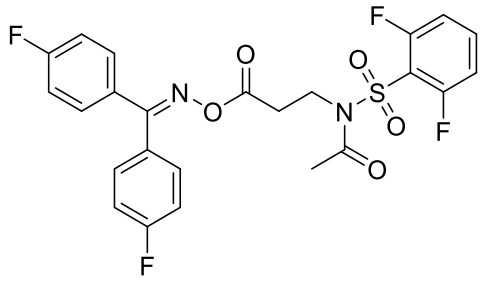
Synthesised according to General Procedure 1a. Isolated as colourless solid (456 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (ddd, *J* = 8.0, 7.1, 1.8 Hz, 1H), 7.68 (dddd, *J* = 8.3, 7.5, 5.0, 1.8 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.38 – 7.30 (m, 3H), 7.27 – 7.22 (m, 1H), 7.20 – 7.11 (m, 2H), 7.10 – 7.01 (m, 2H), 4.04 – 3.96 (m, 2H), 2.87 – 2.79 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 168.7, 164.6 (d, *J* = 252.3 Hz), 163.4 (d, *J* = 250.8 Hz), 163.1, 158.9 (d, *J* = 256.8 Hz), 136.7 (d, *J* = 8.8 Hz), 131.3 (d, *J* = 2.6 Hz), 131.2 (d, *J* = 2.3 Hz), 131.0, 130.7 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 3.6 Hz), 126.7 (d, *J* = 13.4 Hz), 124.9 (d, *J* = 3.9 Hz), 117.7 (d, *J* = 20.9 Hz), 115.8 (d, *J* = 21.9 Hz), 115.7 (d, *J* = 21.8 Hz), 42.1, 32.9, 25.1.

HRMS (ESI) Calculated 527.0859 $[M+Na]^+$; found 527.0857.

mp 85 - 88 °C ($CHCl_3$).



SM 16i N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((2,6-difluorophenyl)sulfonyl)acetamide

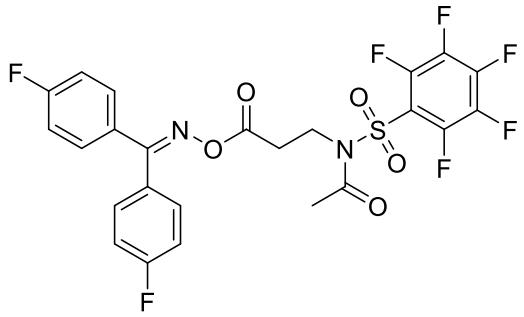
Synthesised according to General Procedure 1a. Isolated as a colourless solid (377 mg, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$ δ 7.68 – 7.56 (m, 1H), 7.55 (dd, *J* = 4.9, 1.7 Hz, 2H), 7.37 – 7.28 (m, 2H), 7.21 – 7.10 (m, 2H), 7.12 – 7.03 (m, 4H), 4.09 – 4.01 (m, 2H), 2.89 – 2.81 (m, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 168.6, 164.7 (d, *J* = 252.4 Hz), 163.5 (d, *J* = 250.8 Hz), 163.2, 159.6 (dd, *J* = 260.8, 3.3 Hz), 136.2 (t, *J* = 11.2 Hz), 131.3 (d, *J* = 8.7 Hz), 131.2 (d, *J* = 8.5 Hz), 130.7 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 3.6 Hz), 117.3 (t, *J* = 15.1 Hz), 115.8 (d, *J* = 21.9 Hz), 115.7 (d, *J* = 21.9 Hz), 114.0 – 113.2 (m), 42.4, 33.0, 24.9.

HRMS (ESI) Calculated 545.0765 $[M+Na]^+$; found 545.0765.

mp 121 - 122 °C ($CHCl_3$).



SM 16j N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((perfluorophenyl)sulfonyl)acetamide

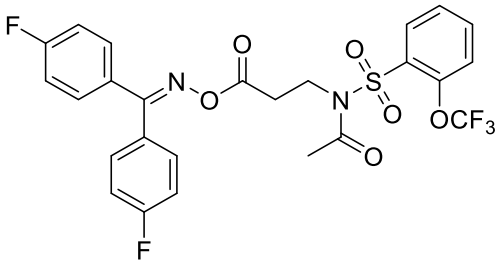
Synthesised according to General Procedure 1a. Isolated as a colourless solid (252 mg, 22% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.35 – 7.30 (m, 2H), 7.20 – 7.14 (m, 2H), 7.10 – 7.04 (m, 2H), 4.12 – 4.03 (m, 2H), 2.91 – 2.83 (m, 2H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.5, 164.8 (d, *J* = 252.9 Hz), 163.5 (d, *J* = 251.1 Hz), 163.5, 146.6 – 146.1 (m), 143.9 – 143.5 (m), 139.6 – 139.1 (m), 137.1 – 136.6 (m), 131.3 (d, *J* = 8.7 Hz), 131.2 (d, *J* = 8.5 Hz), 130.6 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 3.6 Hz), 115.5 – 115.2 (m), 115.9 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.9 Hz), 115.6 – 115.1 (m), 42.9, 33.1, 24.7.

HRMS (ESI) Calculated 577.0663 $[M+H]^+$; found 577.0663.

mp 44 – 46 °C ($CHCl_3$).



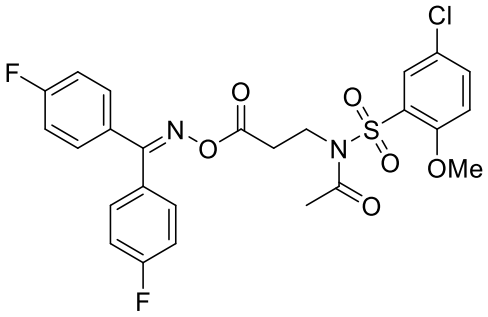
SM 16k N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((2-(trifluoromethoxy)phenyl)sulfonyl)acetamide

Synthesised according to General Procedure 1a. Isolated as a colourless oil (353 mg, 31% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.52 – 7.41 (m, 2H), 7.37 – 7.29 (m, 2H), 7.20 – 7.11 (m, 2H), 7.11 – 7.02 (m, 2H), 4.05 – 3.97 (m, 2H), 2.87 – 2.79 (m, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.6, 164.6 (d, *J* = 252.2 Hz), 163.4 (d, *J* = 250.8 Hz), 163.1, 146.2 – 146.1 (m), 136.0, 132.1, 131.3 (d, *J* = 1.8 Hz), 131.2 (d, *J* = 1.5 Hz), 130.6 (d, *J* = 3.2 Hz), 130.2, 127.9 (d, *J* = 3.6 Hz), 126.6, 120.2 (q, *J* = 262.4 Hz), 120.0 (q, *J* = 2.2 Hz), 115.8 (d, *J* = 7.4 Hz), 115.6 (d, *J* = 7.4 Hz), 42.1, 32.9, 24.9.

HRMS (ESI) Calculated $[M+H]^+$ 571.0957; found 571.0950.



SM 16l N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((5-chloro-2-methoxyphenyl)sulfonyl)acetamide

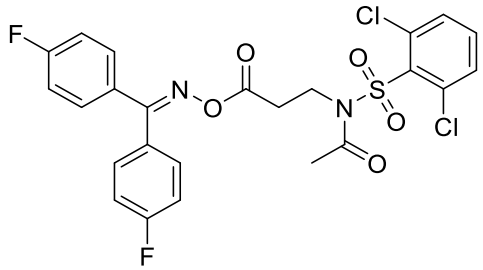
Synthesised according to General Procedure 1a. Isolated as a colourless solid (419 mg, 38% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 2.7 Hz, 1H), 7.61 – 7.51 (m, 3H), 7.36 – 7.28 (m, 2H), 7.20 – 7.11 (m, 2H), 7.11 – 7.02 (m, 2H), 6.99 (d, *J* = 8.9 Hz, 1H), 3.99 – 3.92 (m, 2H), 3.90 (s, 3H), 2.84 – 2.75 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.0, 164.7 (d, *J* = 252.2 Hz), 163.4 (d, *J* = 250.9 Hz), 163.0, 155.4, 135.9, 131.3 (d, *J* = 8.3 Hz), 131.2 (d, *J* = 8.3 Hz), 130.9, 130.8 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 3.7 Hz), 127.4, 126.1, 115.8 (d, *J* = 21.9 Hz), 115.7 (d, *J* = 21.8 Hz), 114.0, 56.7, 42.0, 32.7, 25.3.

HRMS (ESI) Calculated 551.0849 $[M+H]^+$; found 551.0850.

mp 156 – 158 °C ($CHCl_3$).



SM 16m N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-((2,6-dichlorophenyl)sulfonyl)acetamide

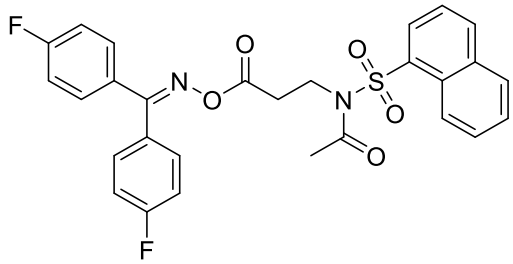
Synthesised according to General Procedure 1a. Isolated as a colourless solid (303 mg, 27% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.52 – 7.48 (m, 2H), 7.42 (dd, *J* = 8.9, 7.0 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.19 – 7.13 (m, 2H), 7.10 – 7.03 (m, 2H), 4.11 – 4.03 (m, 2H), 2.91 – 2.82 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.6, 164.8 (d, *J* = 252.3 Hz), 163.5 (d, *J* = 251.0 Hz), 163.3, 135.7, 134.7, 133.8, 132.0, 131.3 (d, *J* = 8.8 Hz), 131.3 (d, *J* = 8.5 Hz), 130.7 (d, *J* = 3.2 Hz), 128.1 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 22.0 Hz), 42.6, 32.8, 24.8.

HRMS (ESI) Calculated 577.0177 $[M+Na]^+$; found 577.0174.

mp 50 – 52 °C ($CHCl_3$).



SM 16n *N*-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-*N*-(naphthalen-1-ylsulfonyl)acetamide

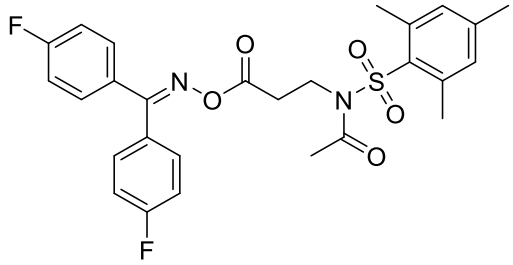
Synthesised according to General Procedure 1a. Isolated as a colourless solid (226 mg, 11% yield),

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 – 8.37 (m, 1H), 8.15 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 2H), 8.01 – 7.97 (m, 1H), 7.72 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.65 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.35 – 7.29 (m, 2H), 7.19 – 7.11 (m, 2H), 7.10 – 7.03 (m, 2H), 4.18 – 4.08 (m, 2H), 2.88 – 2.80 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 168.8, 164.8 (d, *J* = 252.3 Hz), 163.5 (d, *J* = 251.0 Hz), 163.2, 135.7, 134.6, 134.1, 131.3 (d, *J* = 8.7 Hz), 131.3 (d, *J* = 8.4 Hz), 130.8 (d, *J* = 3.2 Hz), 129.7, 129.5, 129.2, 128.2, 128.1 (d, *J* = 3.6 Hz), 127.6, 124.2, 123.8, 115.8 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.9 Hz), 42.4, 32.8, 25.5.

HRMS (ESI) calculated 559.1110 $[M+Na]^+$; found 559.1117.

mp 45 – 47 °C ($CHCl_3$).



SM 16o N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-(mesitylsulfonyl)acetamide

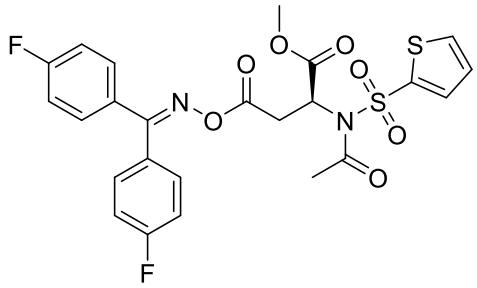
Synthesised according to General Procedure 1a. Isolated as a colourless solid (308 mg, 29% yield),

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.35 – 7.29 (m, 2H), 7.20 – 7.13 (m, 2H), 7.10 – 7.04 (m, 2H), 6.99 (s, 2H), 4.02 – 3.96 (m, 2H), 2.83 – 2.77 (m, 2H), 2.55 (s, 6H), 2.32 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 168.8, 164.8 (d, *J* = 252.4 Hz), 163.2, 163.5 (d, *J* = 251.0 Hz), 144.2, 140.0, 133.4, 132.6, 131.3 (d, *J* = 8.6 Hz), 131.3 (d, *J* = 8.5 Hz), 130.8 (d, *J* = 3.3 Hz), 128.1 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.9 Hz), 41.4, 32.5, 24.7, 22.6, 21.2.

HRMS (ESI): Calculated 551.1420 $[M+Na]^+$; found 551.1420.

mp 127 – 128 °C ($CHCl_3$).



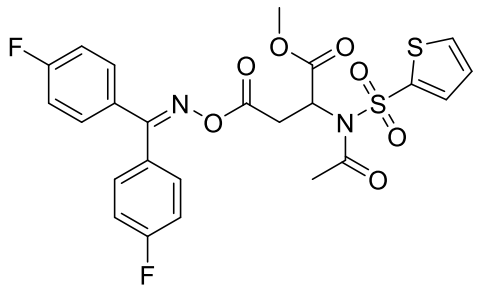
SM 16p methyl (S)-4-(((bis(4-fluorophenyl)methylene)amino)oxy)-4-oxo-2-(N-(thiophen-2-ylsulfonyl)acetamido)butanoate

Synthesised according to General Procedure 1b. Isolated as a colourless oil (171 mg, 8% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.76 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.61 – 7.50 (m, 2H), 7.38 – 7.28 (m, 2H), 7.21 – 7.11 (m, 3H), 7.11 – 7.01 (m, 2H), 5.35 (dd, *J* = 8.7, 4.1 Hz, 1H), 3.64 (s, 3H), 3.49 (dd, *J* = 16.9, 8.7 Hz, 1H), 2.67 (dd, *J* = 16.9, 4.2 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, CDCl3,) δ 170.2, 168.6, 168.1, 165.3 (d, *J* = 125.0 Hz), 163.3, 162.8 (d, *J* = 123.9 Hz), 138.7, 135.3, 134.7, 131.4 (d, *J* = 2.2 Hz), 131.3 (d, *J* = 1.9 Hz), 130.7 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 3.7 Hz), 127.8, 115.9 (d, *J* = 4.4 Hz), 115.7 (d, *J* = 4.3 Hz), 56.2, 53.1, 35.0, 25.2.

HRMS (ESI): Calculated 551.0753 $[M+H]^+$; found 551.0756.



SM *rac*-16p methyl 4-(((bis(4-fluorophenyl)methylene)amino)oxy)-4-oxo-2-(N-(thiophen-2-ylsulfonyl)acetamido)butanoate

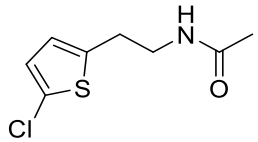
Synthesised according to General Procedure 1b. Isolated as a colourless solid (194 mg, 9% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 3.9, 1.4 Hz, 1H), 7.76 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.38 – 7.30 (m, 2H), 7.22 – 7.12 (m, 3H), 7.11 – 7.02 (m, 2H), 5.36 (dd, *J* = 8.7, 4.2 Hz, 1H), 3.64 (s, 3H), 3.50 (d d, *J* = 17.0, 8.7 Hz, 1H), 2.67 (dd, *J* = 16.9, 4.2 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 168.6, 168.2, 164.7 (d, *J* = 252.3 Hz), 163.5 (d, *J* = 250.8 Hz), 163.3, 138.7, 135.3, 134.7, 131.3 (d, *J* = 8.9 Hz), 131.3 (d, *J* = 8.5 Hz), 130.7 (d, *J* = 3.3 Hz), 128.0 (d, *J* = 3.7 Hz), 127.8, 115.8 (d, *J* = 21.9 Hz), 115.8 (d, *J* = 21.8 Hz), 56.2, 53.1, 35.0, 25.2.

HRMS (ESI) Calculated 573.0573 $[M+Na]^+$; found 573.0572.

mp 52 – 56 °C ($CHCl_3$)**.**



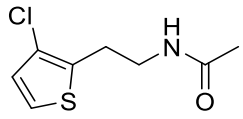
17a *N*-(2-(5-chlorothiophen-2-yl)ethyl)acetamide

Synthesised according to General Procedure 2a. Isolated as an orange oil (23 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 3.7 Hz, 1H), 6.59 (dt, *J* = 3.7, 1.0 Hz, 1H), 5.77 (bs, 1H), 3.46 (dd, *J* = 6.5, 6.5 Hz, 2H), 2.92 (td, *J* = 6.7, 1.0 Hz, 2H), 1.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 140.4, 127.9, 126.1, 124.9, 40.7, 30.4, 23.4.

HRMS (ESI) Calculated 204.0244 $[M+H]^+$; found 204.0240.



17b *N*-(2-(3-chlorothiophen-2-yl)ethyl)acetamide

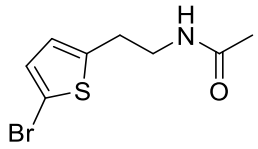
Synthesised according to General Procedure 2a. Isolated as a yellow oil (33 mg, 81% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.13 (d, *J* = 5.4 Hz, 1H), 6.87 (d, *J* = 5.4 Hz, 1H), 5.96 (bs, 1H), 3.48 (q, *J* = 6.4 Hz, 2H), 3.00 (t, *J* = 6.6 Hz, 2H), 1.96 (s, 3H).

^{13}C NMR 13C NMR (101 MHz, CDCl3) δ 170.9, 133.6, 127.8, 123.3, 123.2, 40.2, 27.6, 23.2.

HRMS (ESI) Calculated 204.0244 [M+H]+ ; found 204.0242.

17b also synthesised with thioxanthone catalyst (10 mol%), giving 41% NMR yield using 1, 3, 5-trimethoxybenzene as an internal standard.



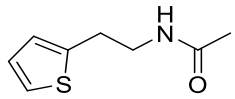
17c *N*-(2-(5-bromothiophen-2-yl)ethyl)acetamide

Synthesised according to General Procedure 2a. As an orange oil in (26 mg, 52% yield).

^{1}H NMR ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 3.7 Hz, 1H), 6.61 – 6.57 (m, 1H), 5.69 (bs, 1H), 3.47 (dd, *J* = 6.4, 6.4 Hz, 2H), 2.95 (td, *J* = 6.6, 1.0 Hz, 2H), 1.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 143.3, 129.9, 126.0, 110.0, 40.7, 30.4, 23.4.

HRMS (ESI) Calculated 269.9559 $[M+Na]^+$; found 269.9554.



17d *N*-(2-(thiophen-2-yl)ethyl)acetamide

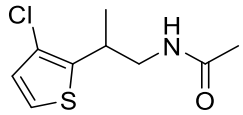
Synthesised according to general procedure 2a. Isolated as a yellow oil (20 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.88 – 6.78 (m, 1H), 3.51 (q, *J* = 6.4 Hz, 2H), 3.03 (td, *J* = 6.7, 0.9 Hz, 2H), 1.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 141.2, 127.2, 125.5, 124.1, 41.2, 29.8, 23.1.

HRMS (ESI) Calculated 170.0634 $[M+H]^+$; found 170.0634.

17d was also synthesised according to general procedure 2b. Isolated as a yellow oil (79 mg, 47% yield).



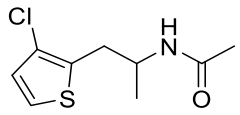
17f *N*-(2-(3-chlorothiophen-2-yl)propyl)acetamide

Synthesised according to general procedure 2a. Isolated as a yellow oil (41 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.4, 0.6 Hz, 1H), 6.86 (d, *J* = 5.3 Hz, 1H), 5.72 (bs, 1H), 3.62 (ddd, *J* = 13.3, 6.8, 5.7 Hz, 1H), 3.52 – 3.41 (m, 1H), 3.19 (ddd, *J* = 13.5, 8.4, 5.3 Hz, 1H), 1.91 (s, 3H), 1.29 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 140.3, 127.8, 122.9, 122.4, 46.2, 33.6, 23.3, 19.5.

HRMS (ESI) Calculated 218.0401 [$M+H^+$]; found 218.0398.



17g *N*-(1-(3-chlorothiophen-2-yl)propan-2-yl)acetamide

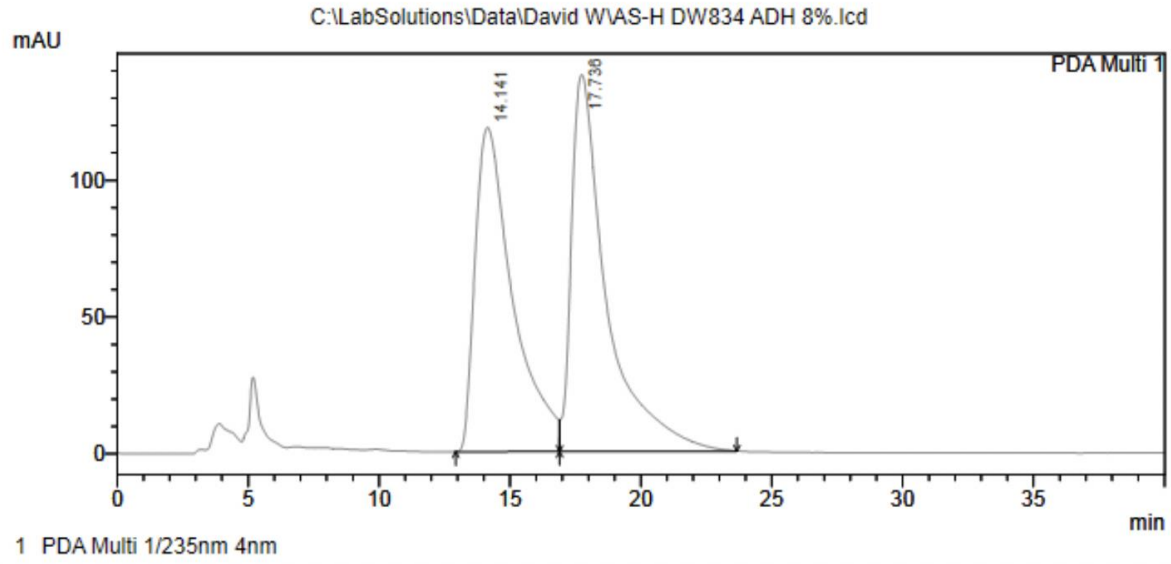
Synthesised according to General Procedure 2a. Isolated as a yellow oil (37 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 5.3 Hz, 1H), 6.87 (d, *J* = 5.4 Hz, 1H), 5.61 (bd, *J* = 8.3 Hz, 1H), 4.32 – 4.18 (m, 1H), 3.02 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.94 (dd, *J* = 14.7, 6.2 Hz, 1H), 1.94 (s, 3H), 1.15 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 132.7, 127.6, 123.8, 123.5, 46.1, 33.7, 23.6, 20.0.

HRMS (ESI) Calculated 218.0401 $[M+H]^+$; found 218.0404.

Chiral HPLC CHIRALPAK AS-H column, 20:80 *i*PrOH:Hexane, 1.0 mL/min, 20 °C, 235 nm, 14.141 min (*L* isomer, 48%) and 17.736 min (*D* isomer, 52%).



PeakTable

PDA Ch1 235nm 4nm

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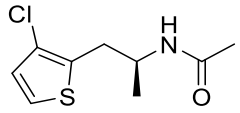
Total		24720700	256306	100.000	100.000



S-17g (*S*)-*N*-(2-(3-chlorothiophen-2-yl)propyl)acetamide

Synthesised according to General Procedure 2a. Isolated as a yellow solid (34 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 5.4 Hz, 1H), 6.86 (d, *J* = 5.4 Hz, 1H), 5.69 (bd, *J* = 6.5 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.01 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.93 (dd, *J* = 14.7, 6.2 Hz, 1H), 1.93 (s, 3H), 1.14 (d, *J* = 6.8 Hz, 3H).

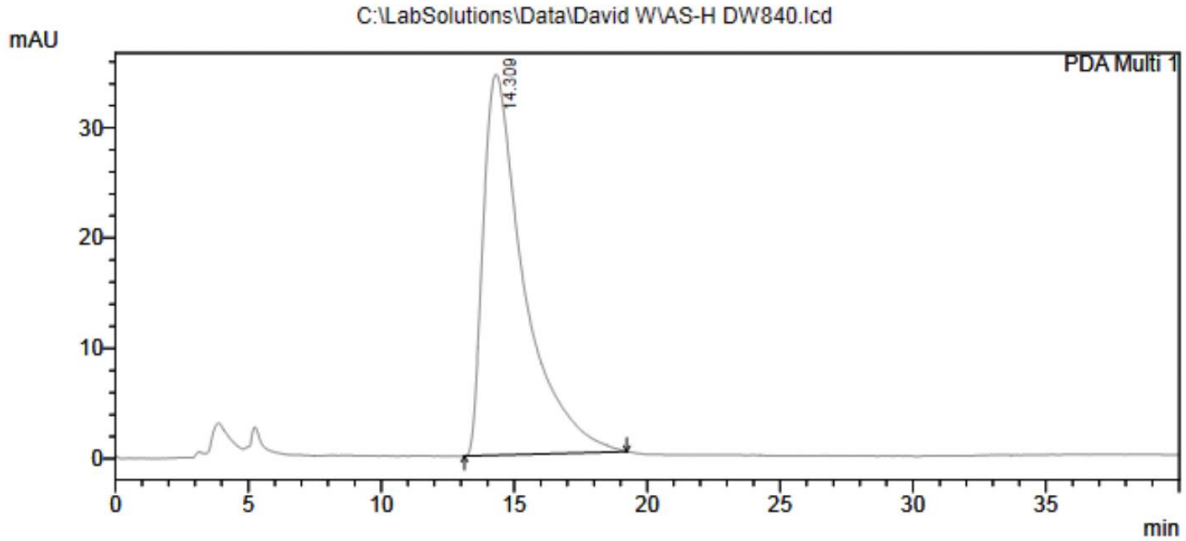
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 132.7, 127.5, 123.8, 123.5, 46.1, 33.7, 23.6, 20.0.

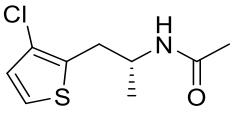
HRMS (ESI) calculated 218.0401 $[M+H]^+$; found 218.0403.

mp 72 – 75 °C ($CHCl_3$).

Specific rotation: $[\alpha]_D^{23}$ -32.9 (c = 0.30, $CHCl_3$).

Chiral HPLC CHIRALPAK AS-H column, 20:80 *i*PrOH:Hexane, 1.0 mL/min, 20 °C, 235 nm, 14.309 min





***R*-17g** (*R*)-*N*-(1-(3-chlorothiophen-2-yl)propan-2-yl)acetamide

Synthesised according to General Procedure 2a. Isolated as a yellow solid (36 mg, 83% yield).

^{1}H NMR ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 5.4 Hz, 1H), 6.87 (d, *J* = 5.4 Hz, 1H), 5.63 (bd, *J* = 8.3 Hz, 1H), 4.30 – 4.19 (m, 1H), 3.01 (dd, *J* = 14.7, 5.9 Hz, 1H), 2.93 (dd, *J* = 14.7, 6.2 Hz, 1H), 1.94 (s, 3H), 1.15 (d, *J* = 6.8 Hz, 3H).

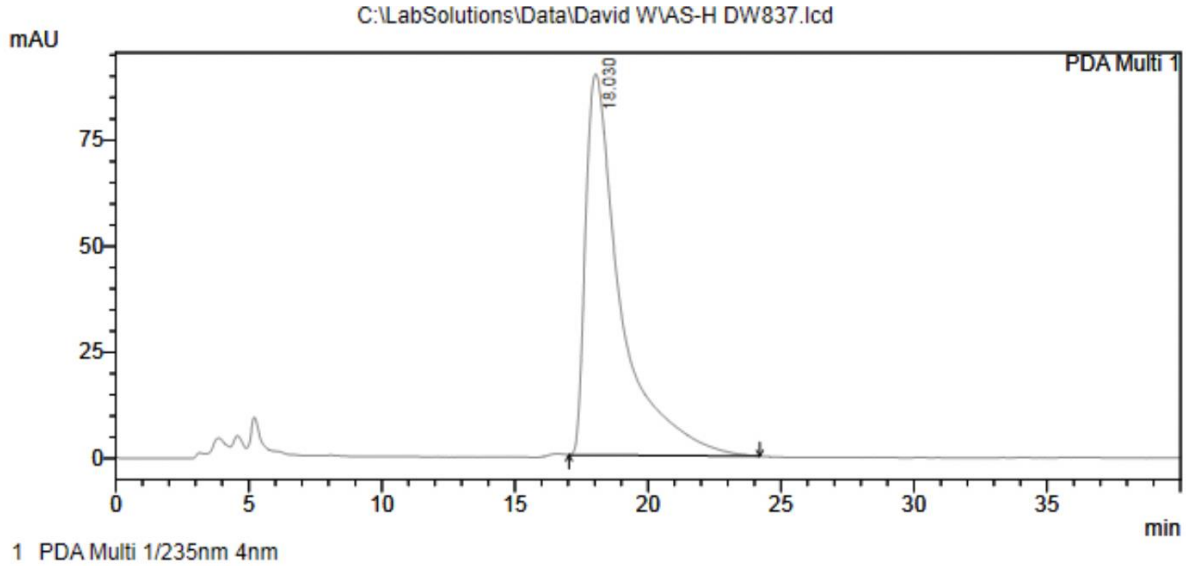
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 132.7, 127.6, 123.8, 123.5, 46.1, 33.7, 23.6, 20.0.

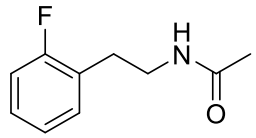
HRMS Calculated 218.0401 $[M+H]^+$; found 218.0403

mp 71 – 74 ℃.

Specific rotation: $[\alpha]_D^{22}$ +27.6 (c = 0.30, $CHCl_3$).

Chiral HPLC CHIRALPAK AS-H column, 20:80 *i*PrOH:Hexane, 1.0 mL/min, 20 °C, 235 nm, 18.030 min





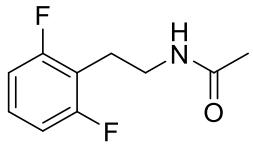
17h *N*-(2-fluorophenethyl)acetamide

Synthesised according to General Procedure 2a. Isolated as a yellow oil (14 mg, 39% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 7.11 – 6.99 (m, 2H), 5.63 (bs, 1H), 3.49 (q, *J* = 6.7 Hz, 2H), 2.85 (td, *J* = 6.9, 1.2 Hz, 2H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.33, 161.37 (d, *J* = 244.8 Hz), 131.24 (d, *J* = 4.9 Hz), 128.47 (d, *J* = 8.1 Hz), 125.90 (d, *J* = 15.9 Hz), 124.35 (d, *J* = 3.6 Hz), 115.48 (d, *J* = 22.0 Hz), 39.75, 29.23 (d, *J* = 1.7 Hz), 23.43.

HRMS (ESI) Calculated 182.0976 $[M+H]^+$; found 182.0976.



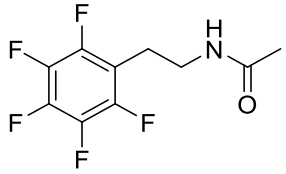
17i *N*-(2,6-difluorophenethyl)acetamide

Synthesised according to General Procedure 2a. Isolated as an orange oil (33 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.10 (m, 1H), 6.85 (ddd, *J* = 8.0, 6.7, 1.1 Hz, 2H), 5.74 (bs, 1H), 3.46 (q, *J* = 6.5 Hz, 2H), 2.93 – 2.84 (m, 2H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.39, 161.81 (dd, *J* = 246.7, 8.7 Hz), 128.31 (t, *J* = 10.3 Hz), 114.76 (t, *J* = 20.3 Hz), 111.99 – 110.74 (m), 39.12, 23.27, 22.93 – 22.40 (m).

HRMS (ESI) calculated 200.0881 $[M+H]^+$; found 200.0881.



17j *N*-(2-(perfluorophenyl)ethyl)acetamide

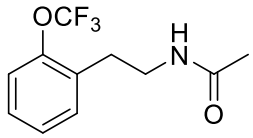
Synthesised according to General Procedure 2a. Isolated as a yellow solid (26 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (bs, 1H), 3.49 (q, *J* = 6.5 Hz, 2H), 2.93 (tt, *J* = 6.6, 1.7 Hz, 2H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 147.0 – 146.3 (m), 144.4 – 143.9 (m), 141.6 – 141.1 (m), 139.1 – 138.5 (m), 136.5 – 136.0 (m), 112.3 (td, *J* = 18.8, 3.9 Hz), 38.7, 23.3, 23.0.

HRMS (ESI) Calculated 254.0599 $[M+H]^+$; 254.0600.

mp 88 – 91 °C ($CHCl_3$).



17k *N*-(2-(trifluoromethoxy)phenethyl)acetamide

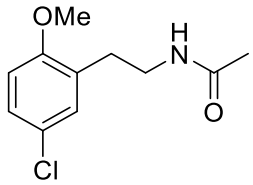
Synthesised according to General Procedure 2a. Isolated as a yellow solid (30 mg, 61% yield)

^{1}H NMR (400 MHz, Acetone- d_6) δ 7.43 – 7.28 (m, 4H), 3.45 – 3.37 (m, 2H), 2.87 (dd, *J* = 8.0, 6.7 Hz, 2H), 1.84 (s, 3H).

^{13}C NMR (101 MHz, Acetone-d_6) δ 169.9, 148.4 (d, *J* = 1.6 Hz), 133.1, 132.3, 128.9, 128.1, 121.7 – 121.0 (m), 121.5 (q, *J* = 256.5 Hz), 39.9, 30.5, 22.8.

HRMS (ESI) calculated 248.0893 $[M+H]^+$; found 248.0896.

mp 88 – 91 °C ($CHCl_3$).



17l *N*-(5-chloro-2-methoxyphenethyl)acetamide

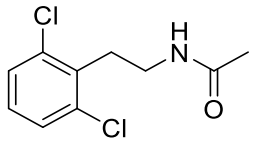
Synthesised according to general procedure 2a. Isolated as a yellow solid (35 mg, 77% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.08 (d, *J* = 2.7 Hz, 1H), 6.76 (d, *J* = 8.8 Hz, 1H), 5.75 (bs, 1H), 3.80 (s, 3H), 3.48 – 3.39 (m, 2H), 2.77 (t, *J* = 6.8 Hz, 2H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 156.2, 130.4, 129.3, 127.5, 125.4, 111.6, 55.7, 39.6, 30.17, 23.4.

HRMS (ESI) calculated 250.0605 $[M+Na]^+$; found 250.0602.

mp 90 – 93 °C ($CHCl_3$).



17m *N*-(2,6-dichlorophenethyl)acetamide

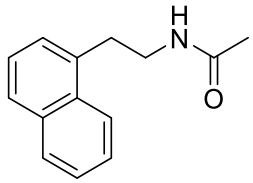
Synthesised according to general procedure 2a. Isolated as a light yellow solid (40 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.10 (dd, *J* = 8.5, 7.6 Hz, 1H), 5.70 (bs, 1H), 3.53 (q, *J* = 6.6 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 135.9, 135.1, 128.5, 38.2, 31.1, 23.4.

HRMS (ESI) Calculated 232.0920 $[M+H]^+$; found 232.0289.

mp 109 – 111°C ($CHCl_3$).



17n *N*-(2-(naphthalen-1-yl)ethyl)acetamide

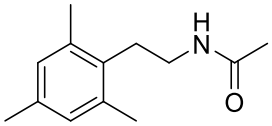
Synthesised according to General Procedure 2a. Isolated as a yellow solid in (23 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.05 (m, 1H), 7.85 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.39 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.31 (dd, *J* = 7.0, 1.3 Hz, 1H), 6.48 (bs, 1H), 3.63 (dd, *J* = 6.6, 6.6 Hz, 2H), 3.30 (t, *J* = 7.1 Hz, 2H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 134.7, 134.0, 132.0, 129.0, 127.6, 126.9, 126.3, 125.9, 125.6, 123.6, 41.0, 32.6, 22.4.

HRMS (ESI) Calculated 214.1226 $[M+H]^+$; found 214.1225.

mp 68 – 71°C ($CHCl_3$).



17o *N*-(2,4,6-trimethylphenethyl)acetamide

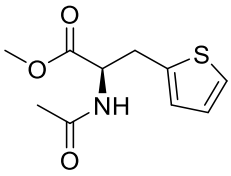
Synthesised according to General Procedure 2a. As a yellow solid (22 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 5.66 (bs, 1H), 3.39 – 3.30 (m, 2H), 2.87 – 2.79 (m, 2H), 2.31 (s, 6H), 2.25 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 136.7, 135.9, 132.4, 129.2, 38.9, 29.5, 23.5, 20.9, 19.9.

HRMS (ESI) Calculated 228.1359 $[M+Na]^+$; found 228.1358.

mp 116 – 119 °C ($CHCl_3$).



17p methyl (*S*)-2-acetamido-3-(thiophen-2-yl)propanoate

Synthesised according to General Procedure 2a. Isolated as a pale yellow solid (31 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.92 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.76 (dd, *J* = 3.5, 1.1 Hz, 1H), 6.17 (bd, *J* = 7.6 Hz, 1H), 4.87 (dt, *J* = 7.7, 4.9 Hz, 1H), 3.75 (s, 3H), 3.37 (ddd, *J* = 4.9, 2.5, 0.8 Hz, 2H), 2.02 (s, 3H).

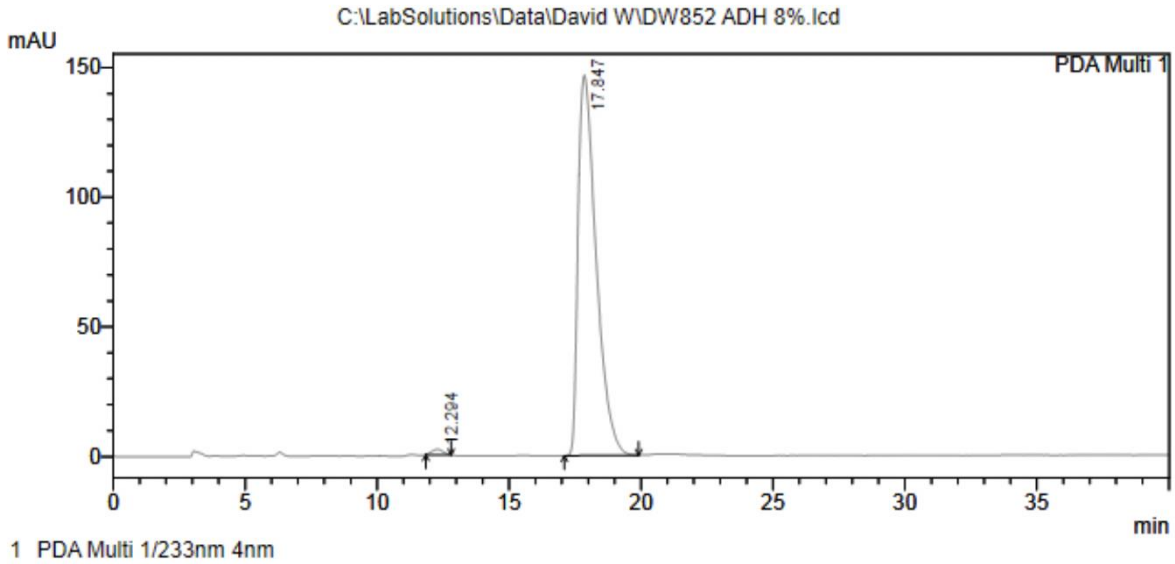
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 169.8, 137.3, 127.1, 126.8, 125.0, 53.1, 52.7, 32.0, 23.3.

HRMS (ESI) Calculated 250.0508 $[M+Na]^+$; found 250.0506.

mp 108 – 110 °C ($CHCl_3$).

Specific rotation: $[\alpha]_D^{23}$ +66.4 (c = 0.30, $CHCl_3$).

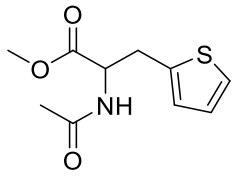
Chiral HPLC CHIRALPAK AD-H column, 8:92 *i*PrOH:Hexane, 1.0 mL/min, 20 °C, 233 nm, 12.294 min (*D* isomer, 0.898%) and 17.847 min (*L* isomer, 99.102%) giving 98% e.e.



PeakTable

PDA Ch1 233nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.294	63369	2082	0.898	1.399
2	17.847	6993775	146722	99.102	98.601
Total		7057144	148804	100.000	100.000



***rac*-17p** methyl 2-acetamido-3-(thiophen-2-yl)propanoate

Synthesised according to general procedure 2a. Isolated as a yellow solid (31 mg, 68% yield).

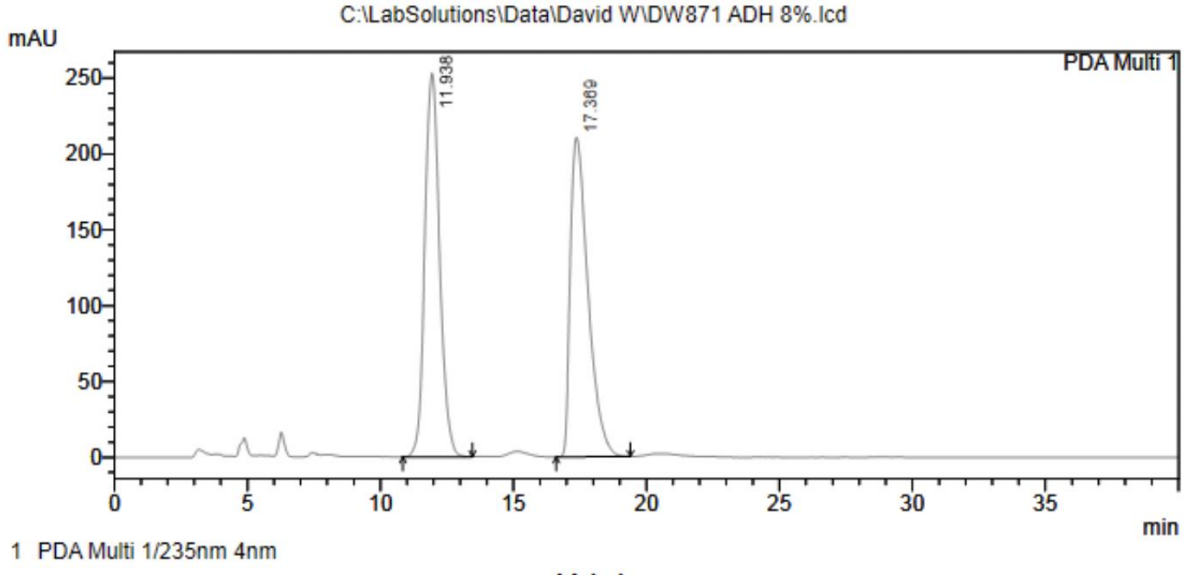
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.76 (dd, *J* = 3.5, 1.1 Hz, 1H), 6.15 (bd, *J* = 7.7 Hz, 1H), 4.87 (dt, *J* = 7.6, 4.9 Hz, 1H), 3.76 (s, 3H), 3.37 (ddd, *J* = 4.9, 2.3, 0.8 Hz, 2H), 2.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 169.8, 137.3, 127.2, 126.8, 125.0, 53.1, 52.7, 32.0, 23.3.

HRMS (ESI) Calculated 250.0508 $[M+Na]^+$; found 250.0506.

mp 85 – 87 °C ($CHCl_3$).

Chiral HPLC CHIRALPAK AD-H column, 8:92 *i*PrOH:Hexane, 1.0 mL/min, 20 °C, 235 nm, 11.938 min (*D* isomer, 50.047%) and 17.369 min (*L* isomer, 49.953%).



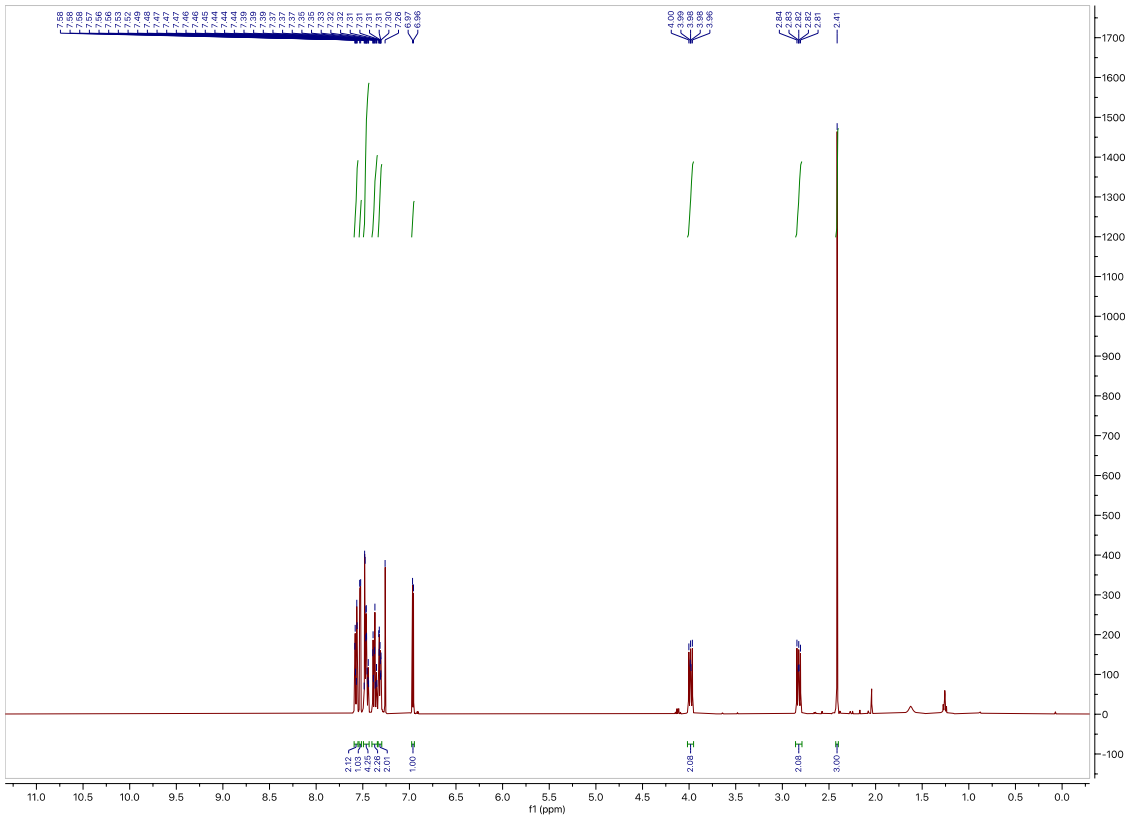
PeakTable

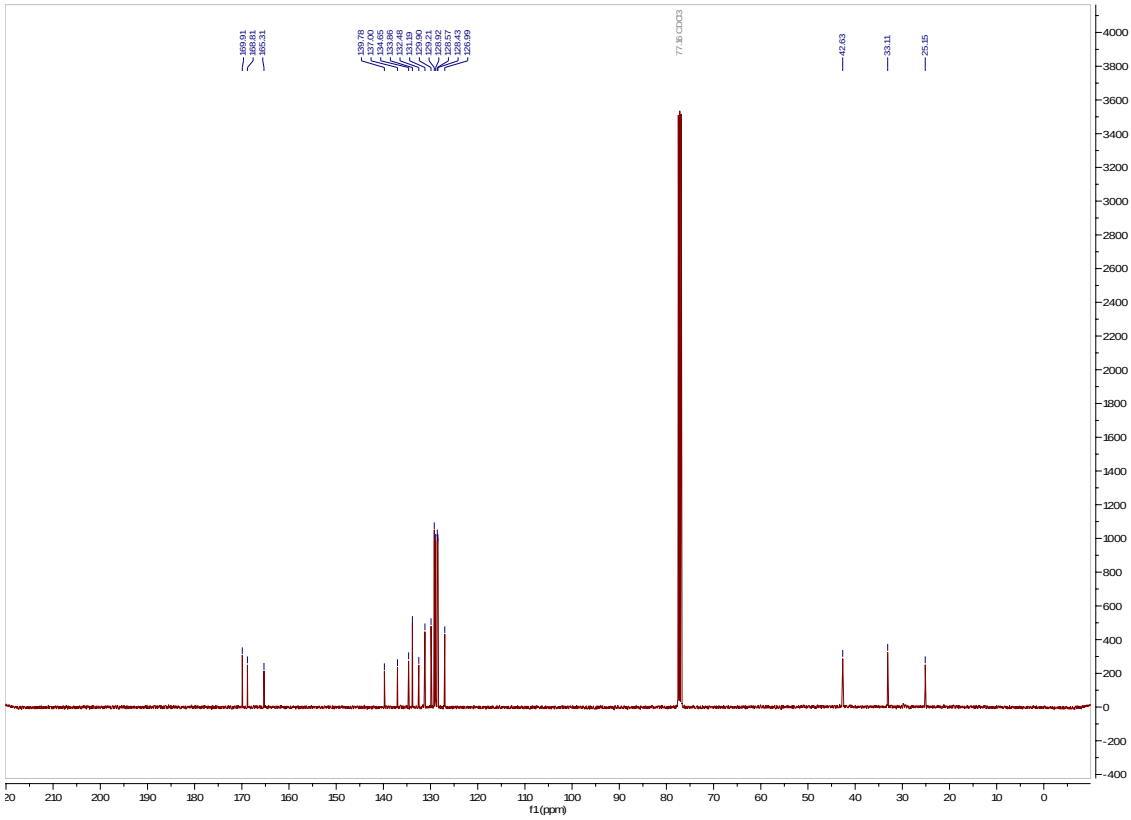
PDA Ch1 235nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.938	9796625	252970	50.047	54.570
2	17.369	9778162	210597	49.953	45.430
Total		19574786	463567	100.000	100.000

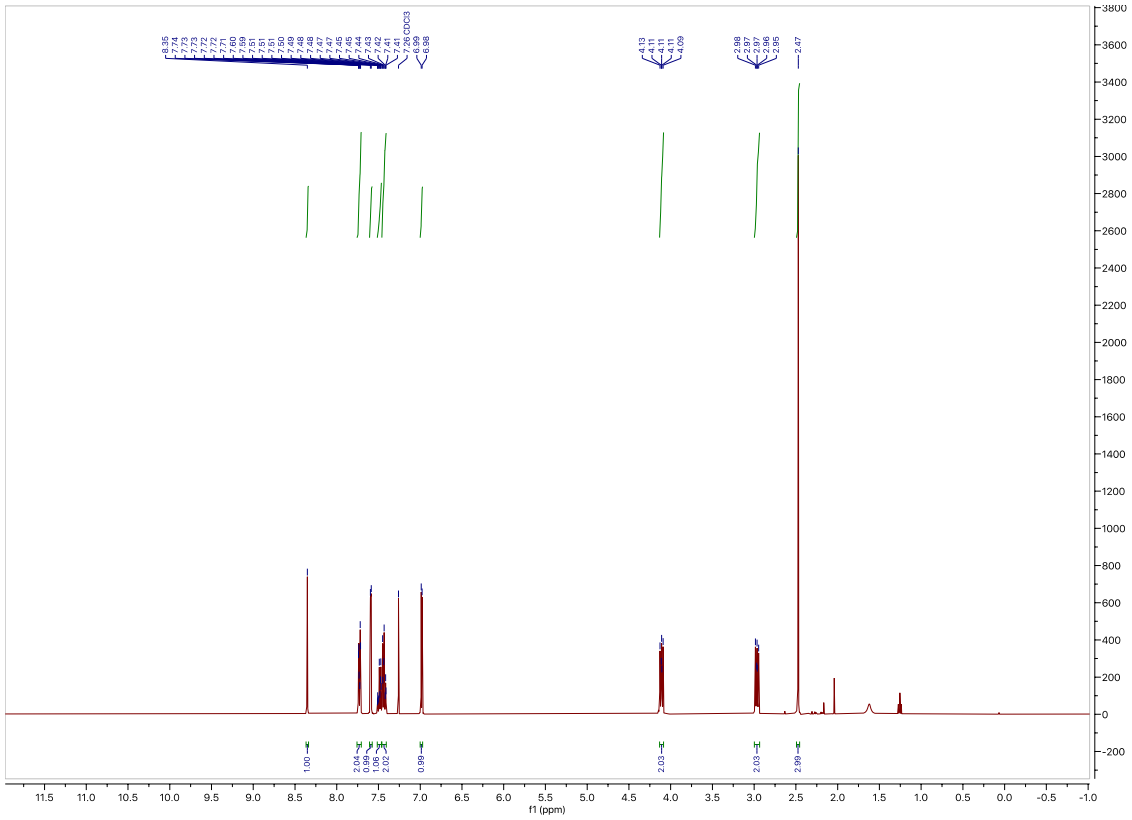
Spectral Data

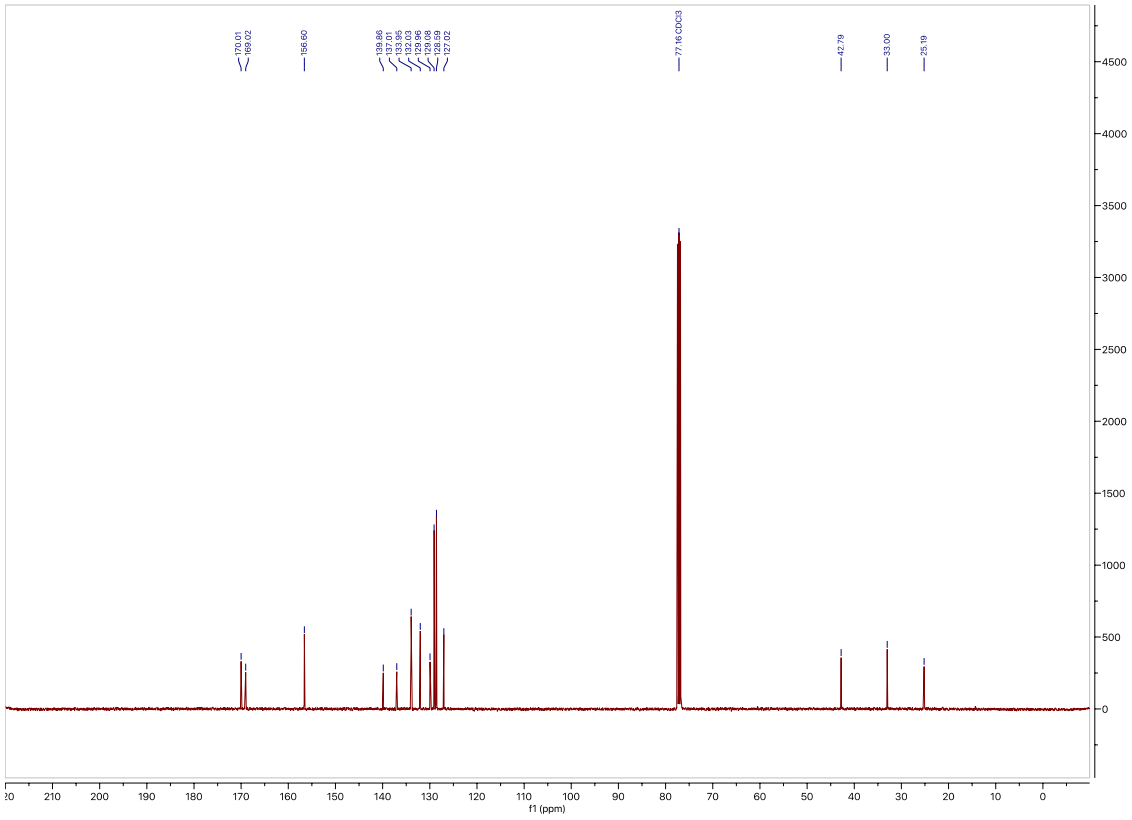
Oxime variant A



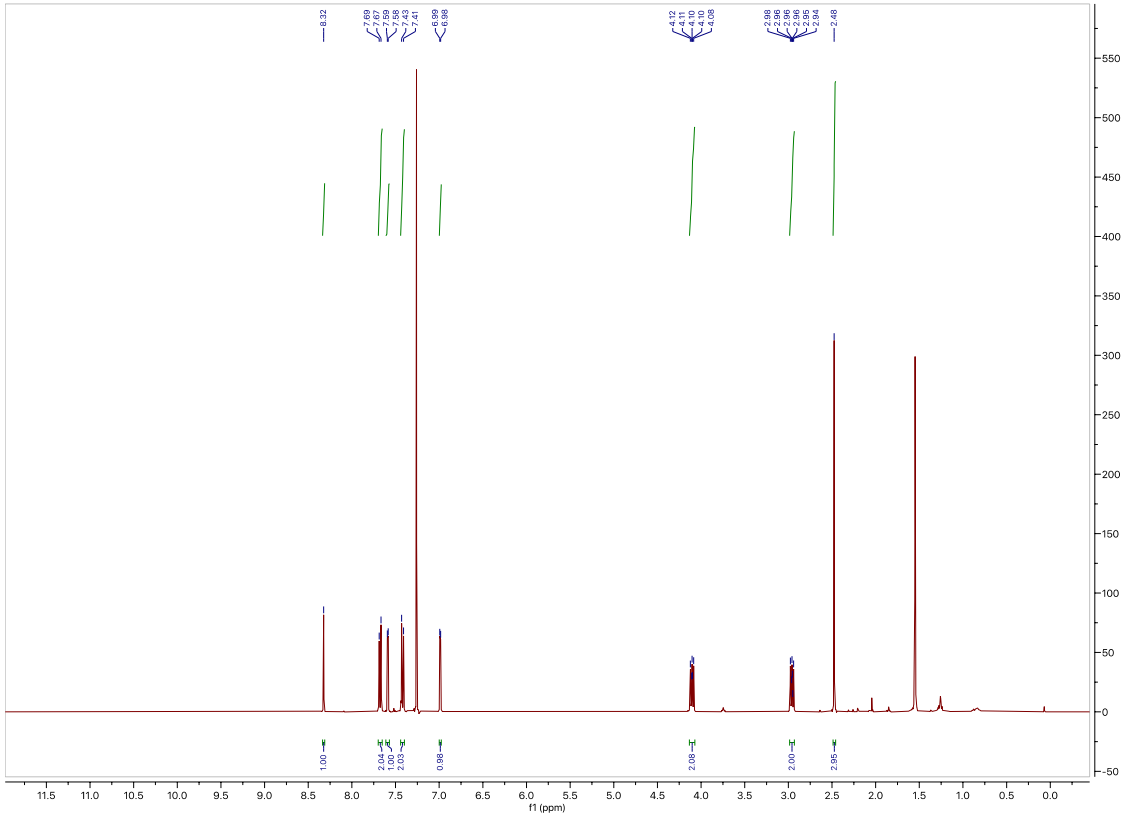


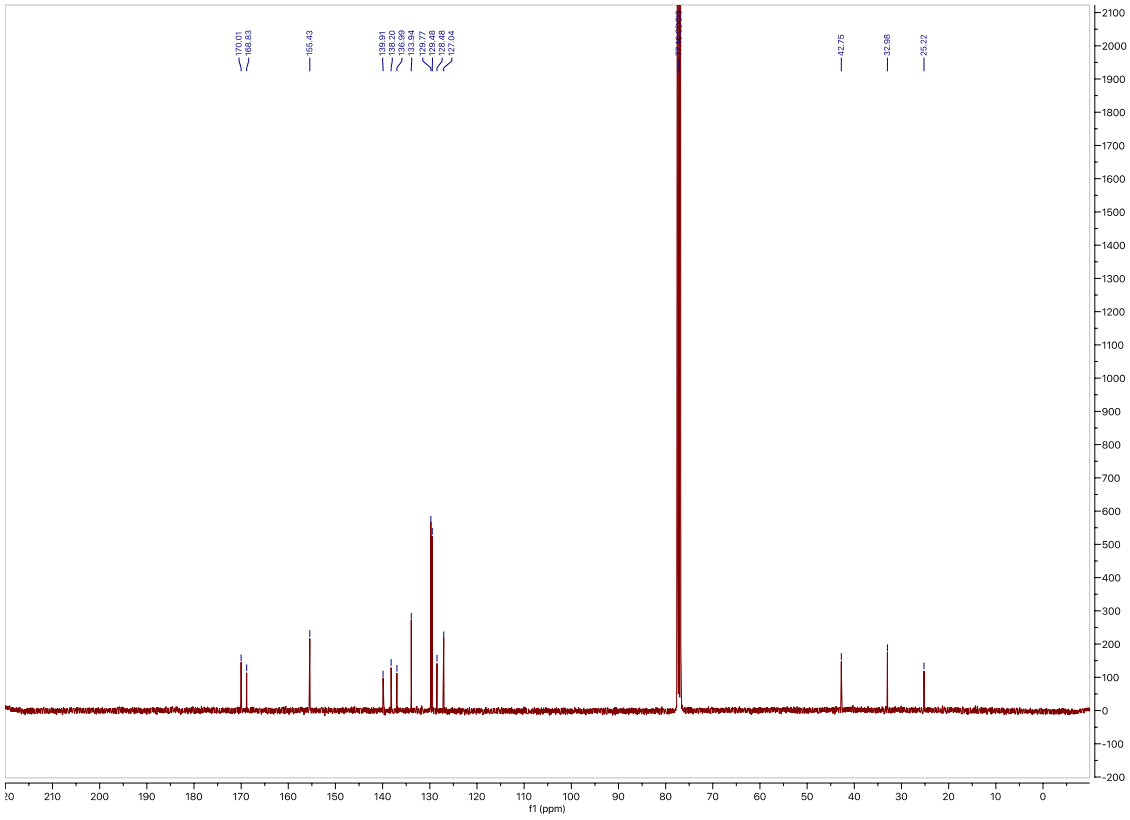
Oxime variant B



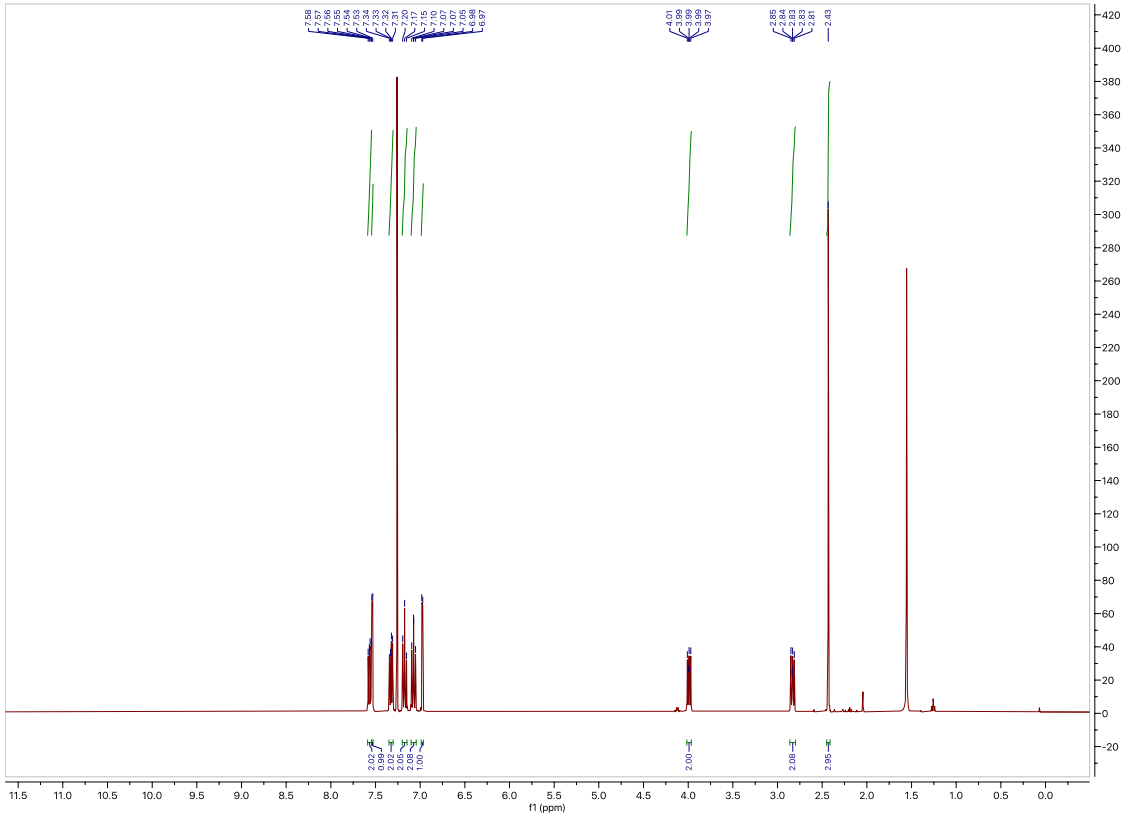


Oxime variant C





SM 16a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7.55
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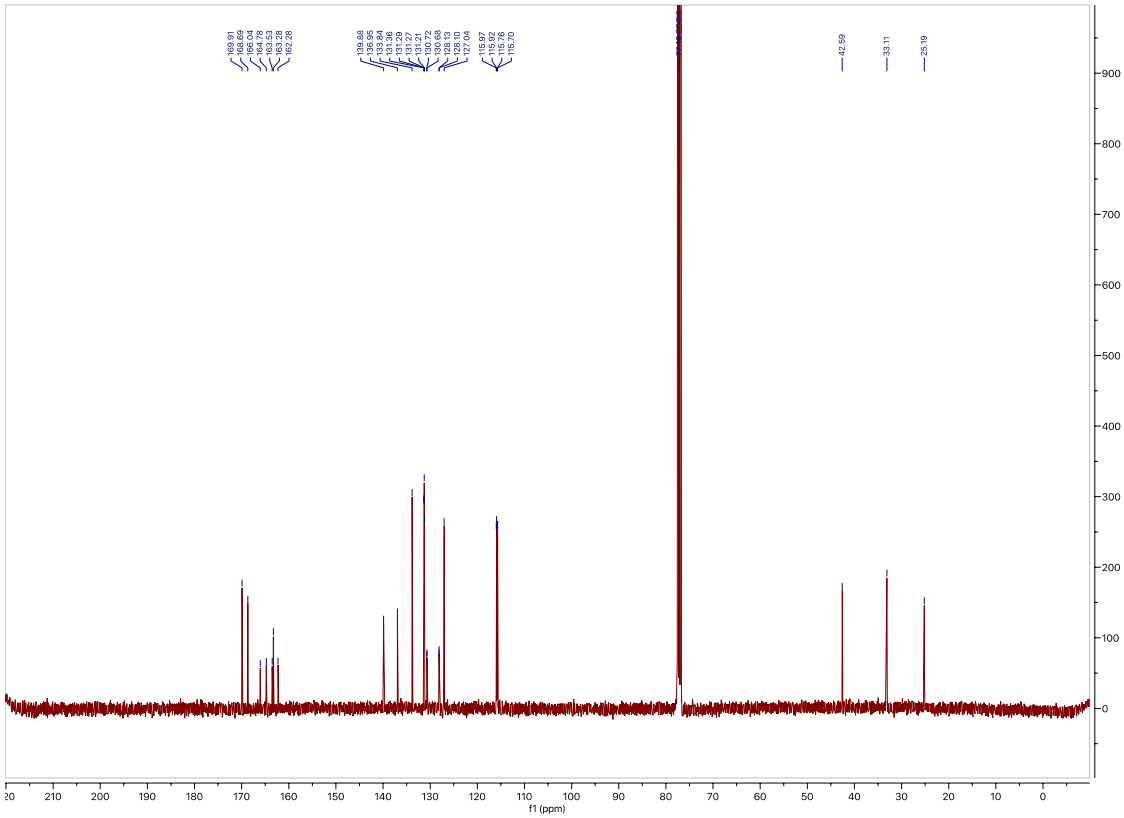
7.53
7.34
7.33
7.32
7.31
7.20
7.17
7.15
7.10
7.07
7.07
7.05
6.98
6.97
4.01
3.99
3.98
3.99
3.97
2.85
2.84
2.83
2.83
2.81
2.43
2.02
0.99
2.02
2.05
2.08
1.00
2.00
2.08
2.95
f1 (ppm)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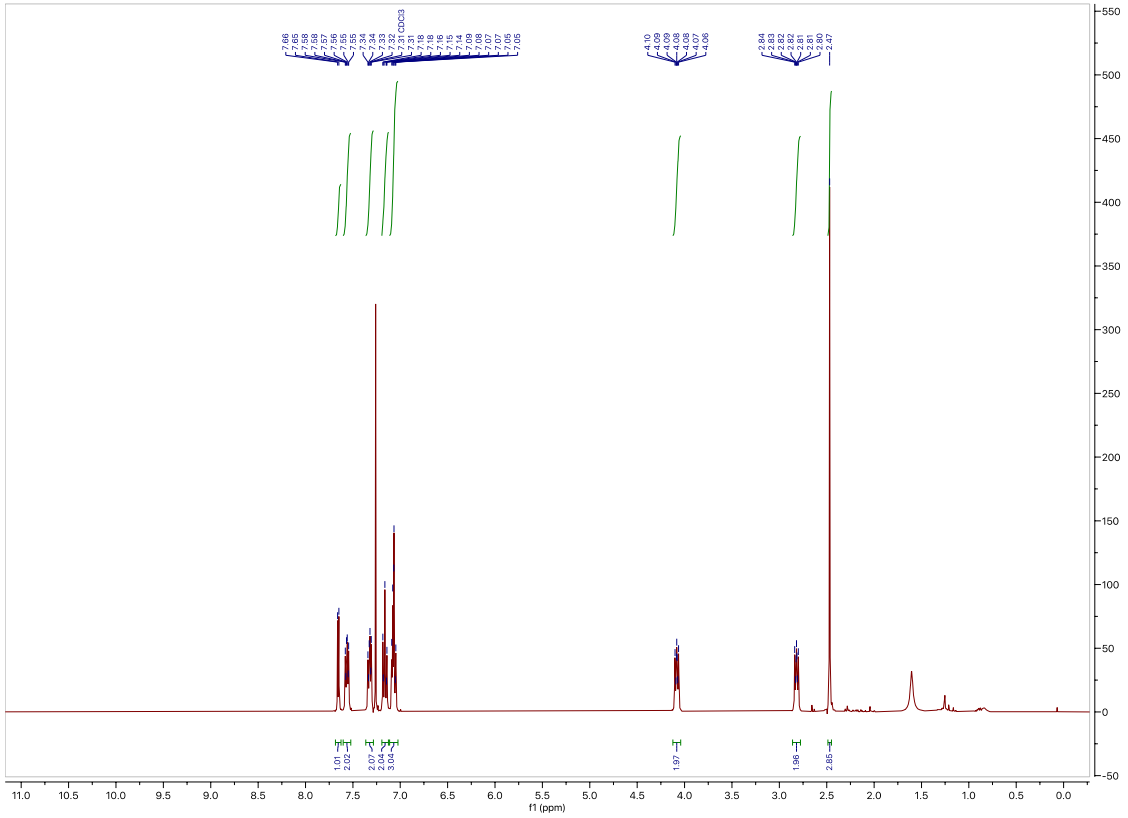
168.68
166.04
164.78
163.53
163.28
162.28
139.88
138.95
135.84
131.36
131.29
131.27
131.21
130.72
130.68
128.13
128.10
127.04
115.97
115.92
115.76
115.70
42.59
33.11
25.19
f1 (ppm)

SM 16b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7.55
7.55
7.34
7.34
7.33
7.32
7.31 CDCl3
7.31
7.18
7.18
7.16
7.15
7.15
7.14
7.09
7.09
7.07
7.07
7.07
7.06
7.05
4.10
4.09
4.09
4.08
4.08
4.07
4.06
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2.83
2.82
2.82
2.81
2.81
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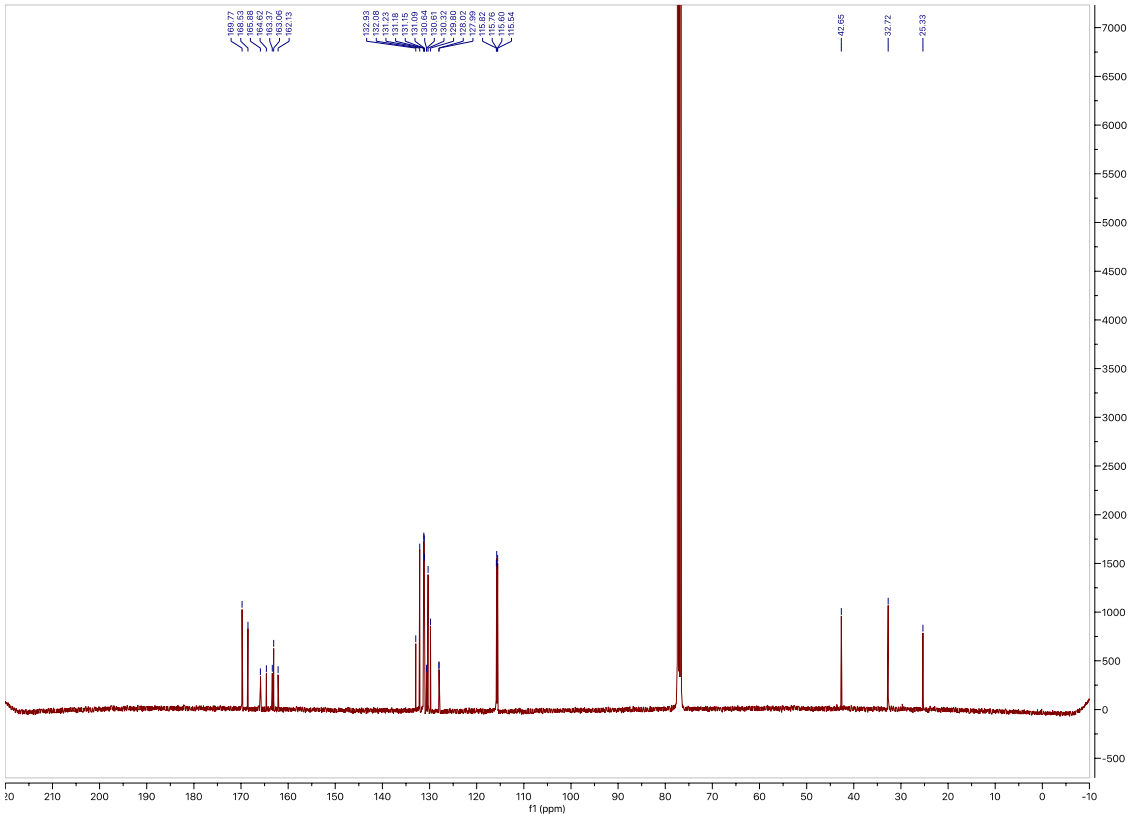
1.01
2.02
2.07
2.44
3.04
1.97
1.96
2.65
f1 (ppm)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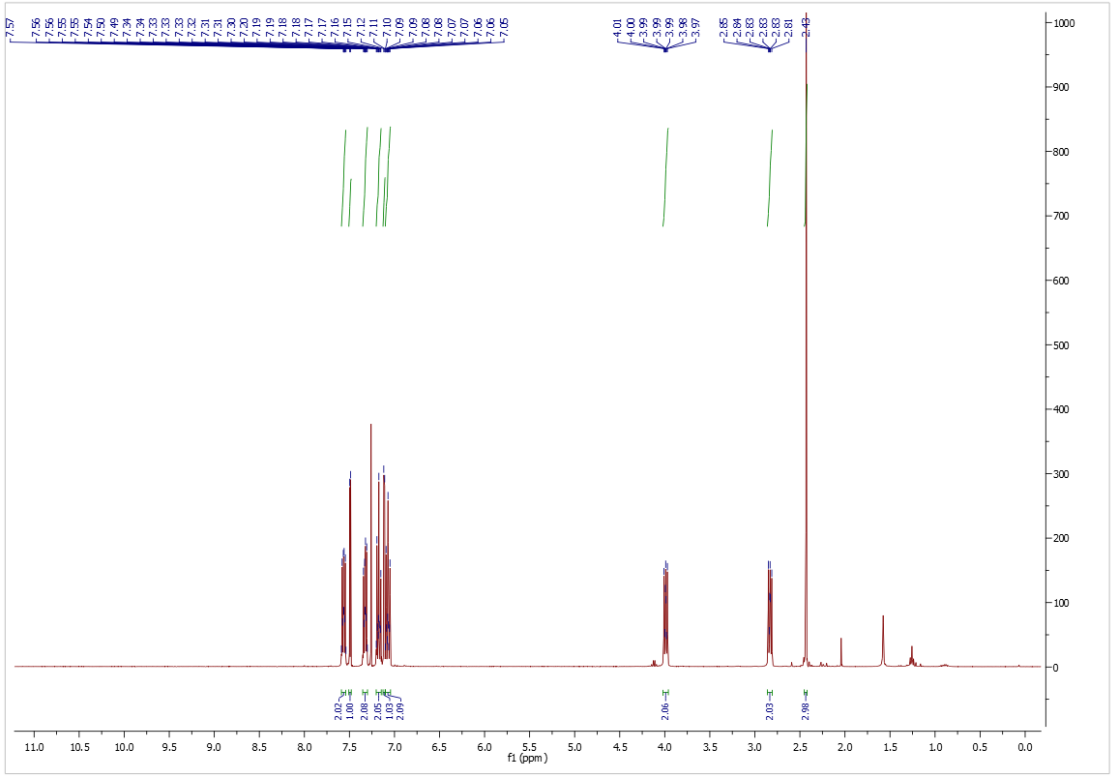
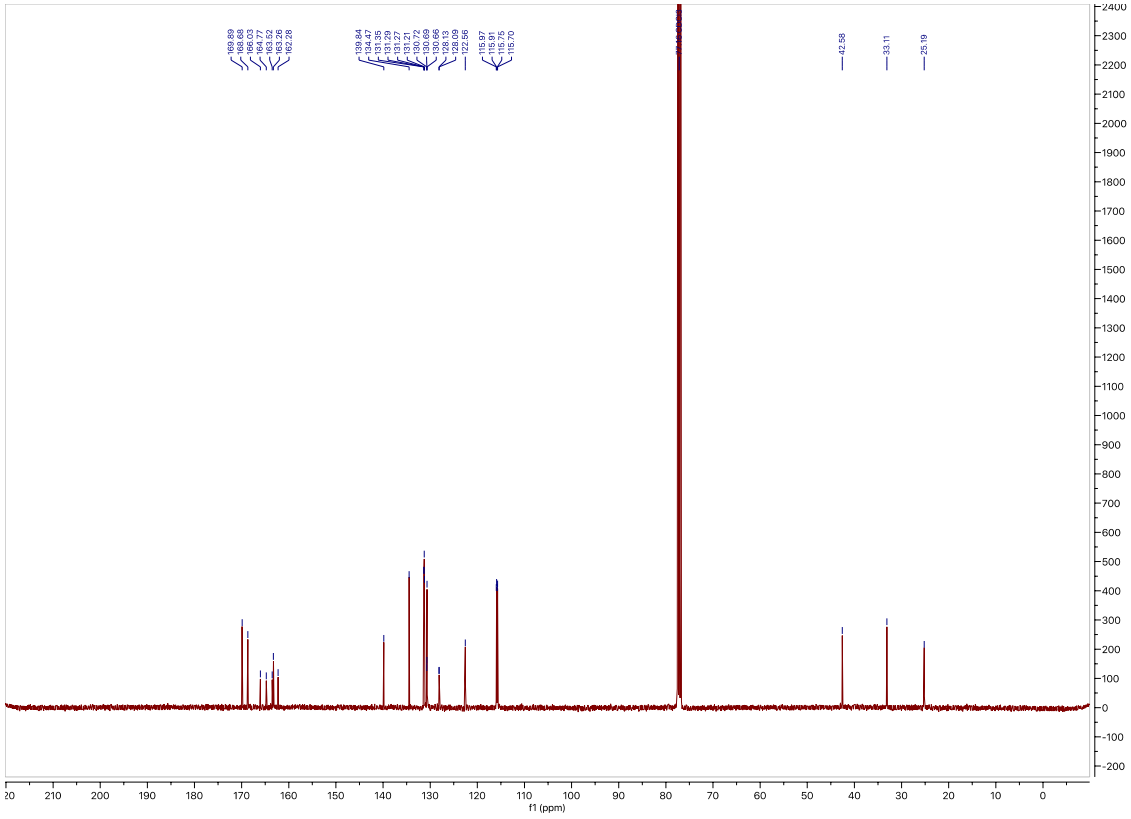
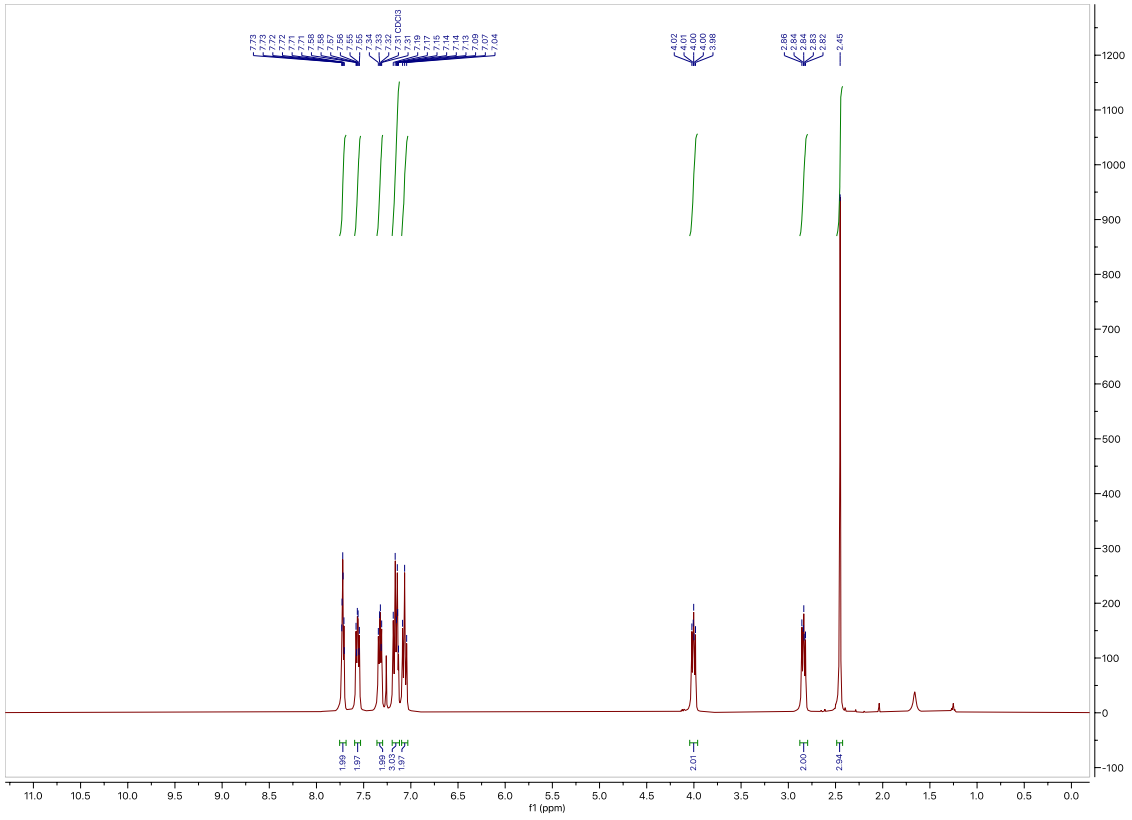
168.93
165.88
164.62
163.77
163.06
162.13
132.93
132.08
131.23
131.16
131.15
131.09
130.64
130.61
130.32
129.80
129.62
127.99
115.82
115.75
115.60
115.54
42.65
32.72
25.33
f1 (ppm)

SM 16c





SM 16d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7.56
7.55
7.34
7.33
7.31 CDCl3
7.19
7.17
7.15
7.14
7.13
7.09
7.07
7.04
4.02
4.01
4.00
4.00
3.99
2.86
2.84
2.84
2.83
2.82
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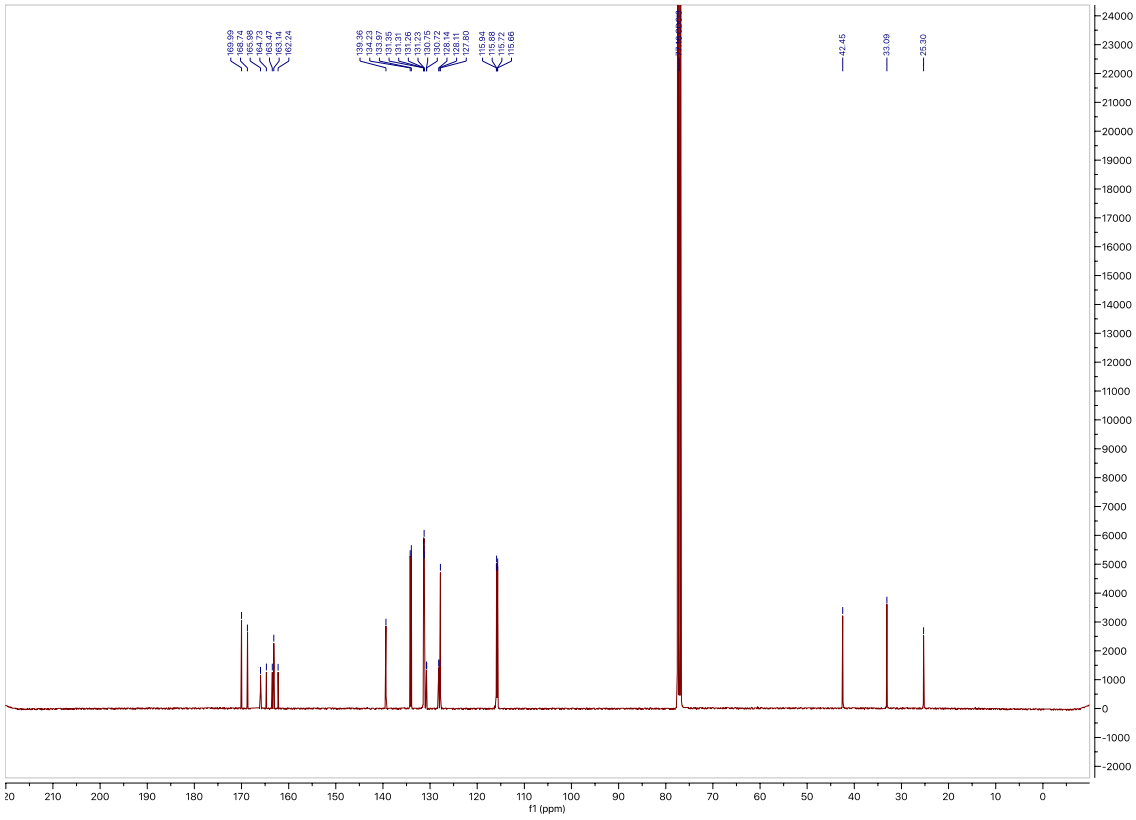
1.99
3.03
1.97
2.01
2.00
2.94
f1 (ppm)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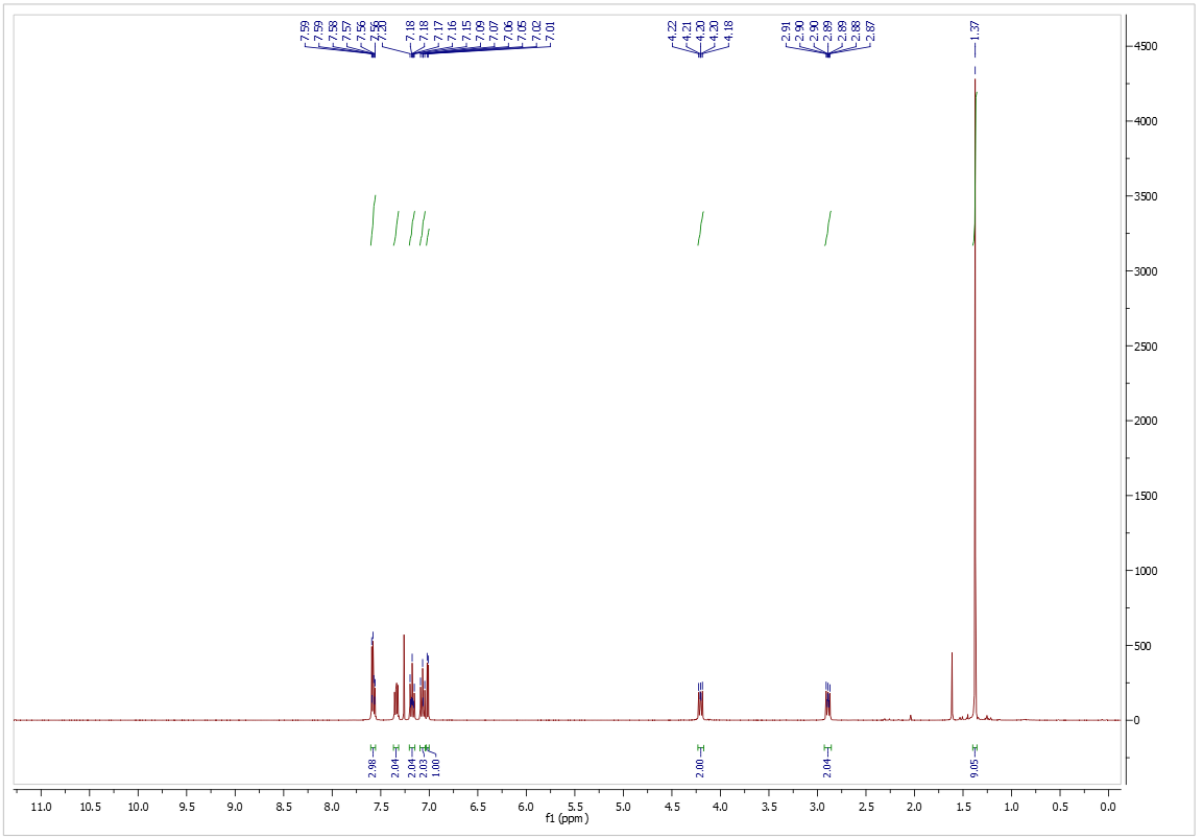
131.35
131.31
131.26
131.23
130.75
130.72
128.14
128.11
127.80
115.94
115.88
115.72
115.66
42.45
33.09
25.30
f1 (ppm)

SM 16e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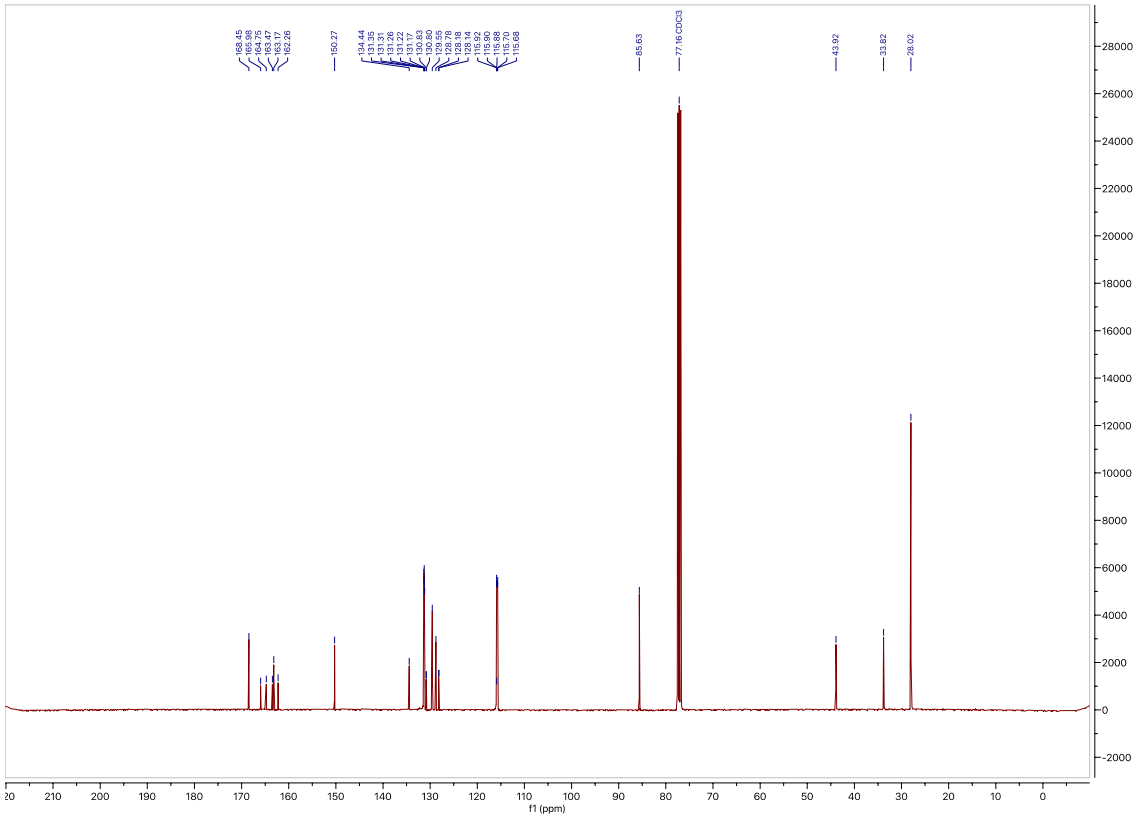
7.15
7.09
7.07
7.06
7.05
7.05
7.02
7.01
4.22
4.21
4.21
4.20
4.20
4.18
2.91
2.90
2.90
2.89
2.89
2.88
2.87
1.37
2.98
2.04
2.04
2.03
1.00
2.00
2.04
9.05
f1 (ppm)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160.27
134.44
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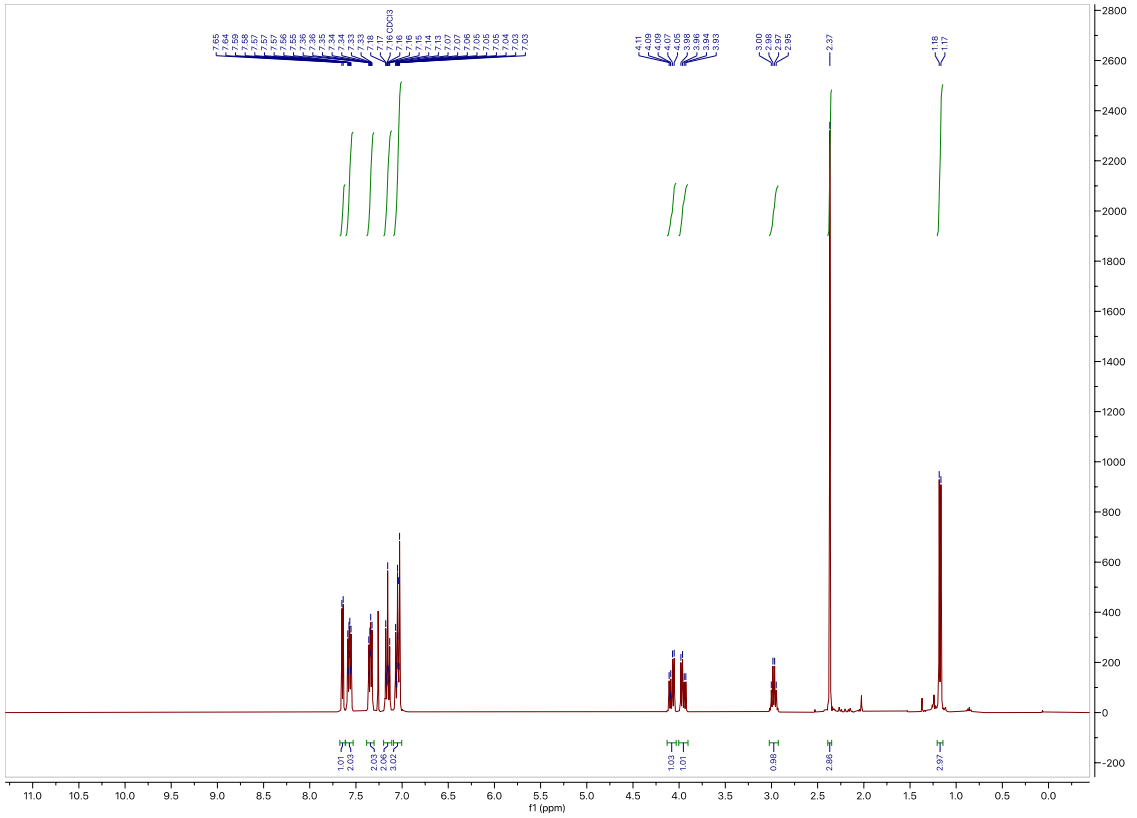
131.31
131.26
131.22
131.17
130.83
130.80
129.95
129.88
128.18
128.14
116.00
115.90
115.88
115.80
115.68
85.63
77.16 CDCl3
43.92
33.82
29.02
f1 (ppm)

SM 16f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7.34
7.34
7.33
7.33
7.18
7.17
7.16 CDCl3
7.16
7.15
7.14
7.13
7.07
7.07
7.06
7.06
7.05
7.05
7.04
7.04
7.03
7.03
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4.09
4.07
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3.98
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2.97
2.95
2.37
1.18
1.17
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2.03
2.06
2.02
1.03
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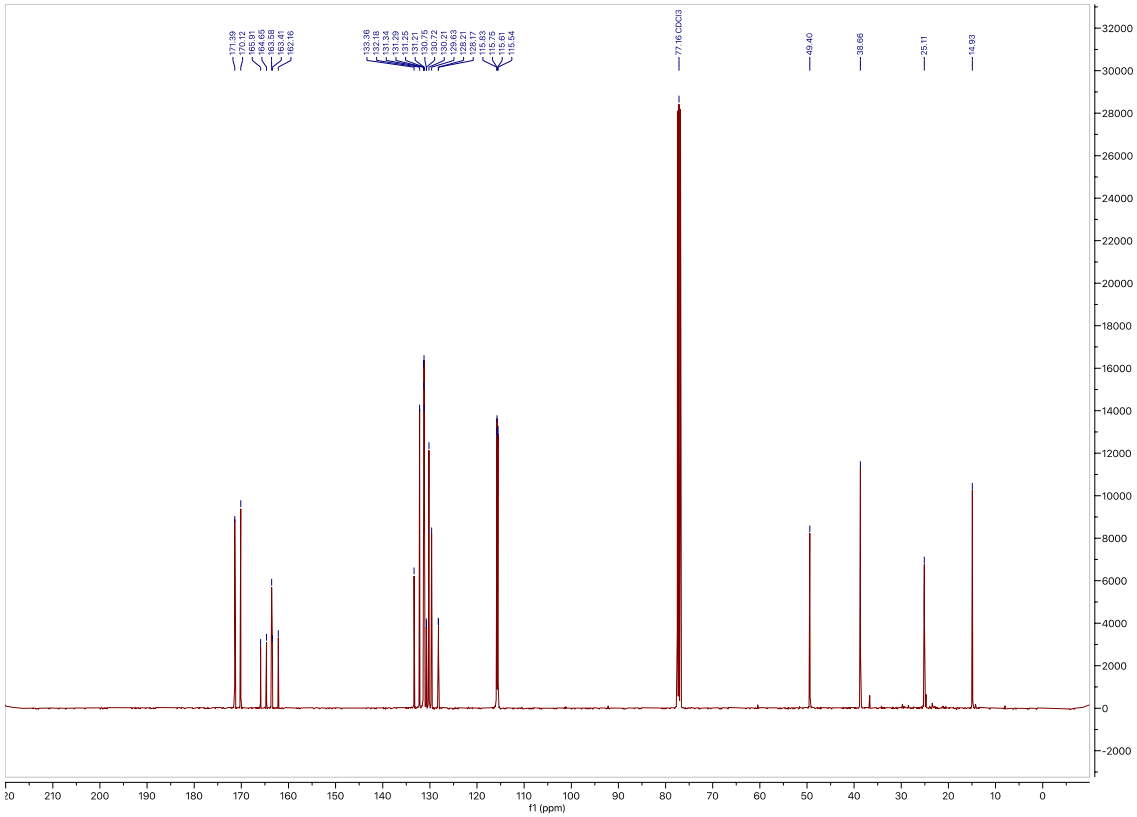
2.97
f1 (ppm)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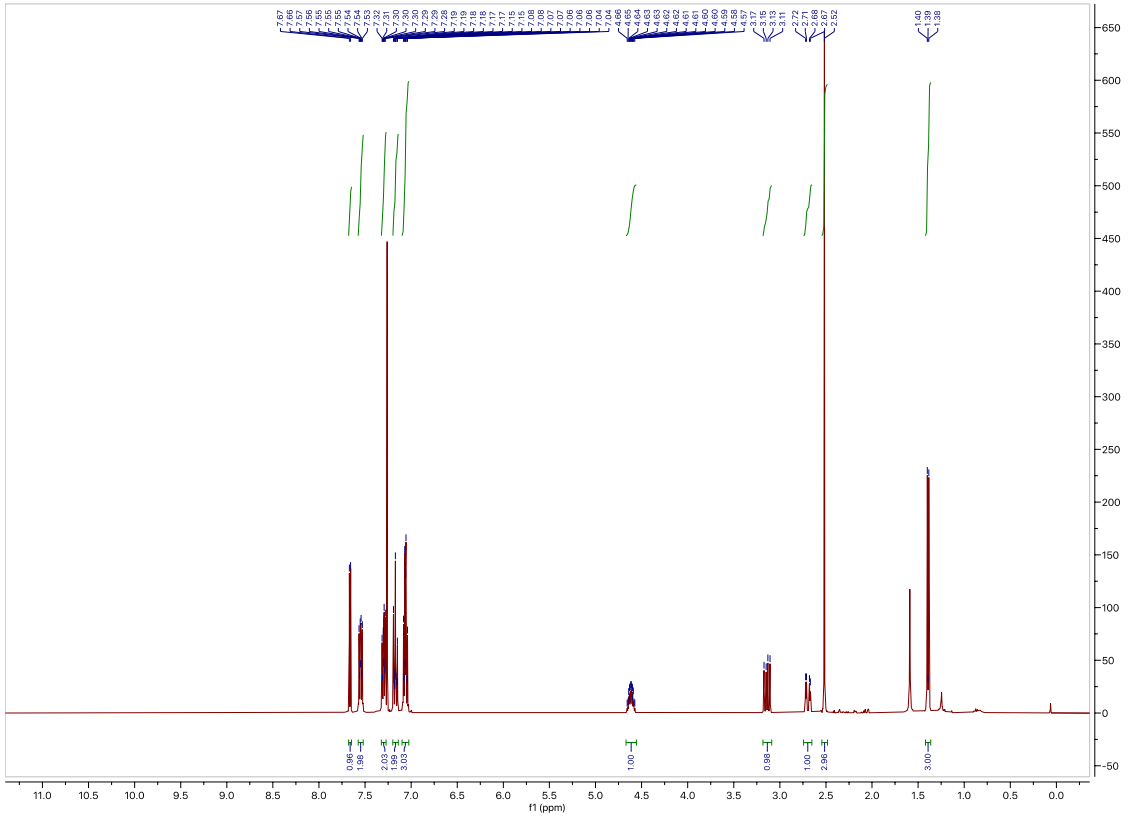
131.29
131.25
131.21
130.75
130.72
130.21
129.60
129.27
128.17
115.83
115.75
115.61
115.54
77.16 CDCl3
49.40
38.66
25.11
14.93
f1 (ppm)

SM 16g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3.15
3.13
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2.69
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2.67
2.52
1.40
1.39
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3.03
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1.00
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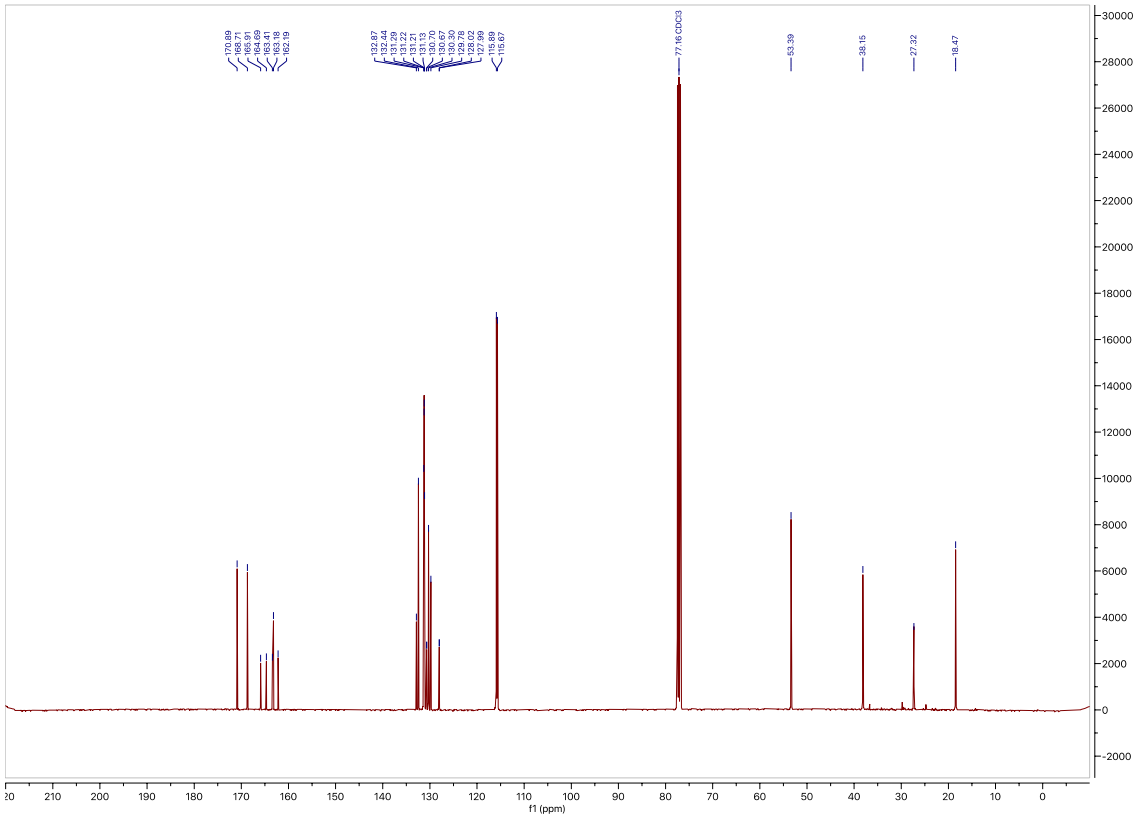
3.00
f1 (ppm)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131.13
131.13
130.70
130.67
130.30
129.78
128.02
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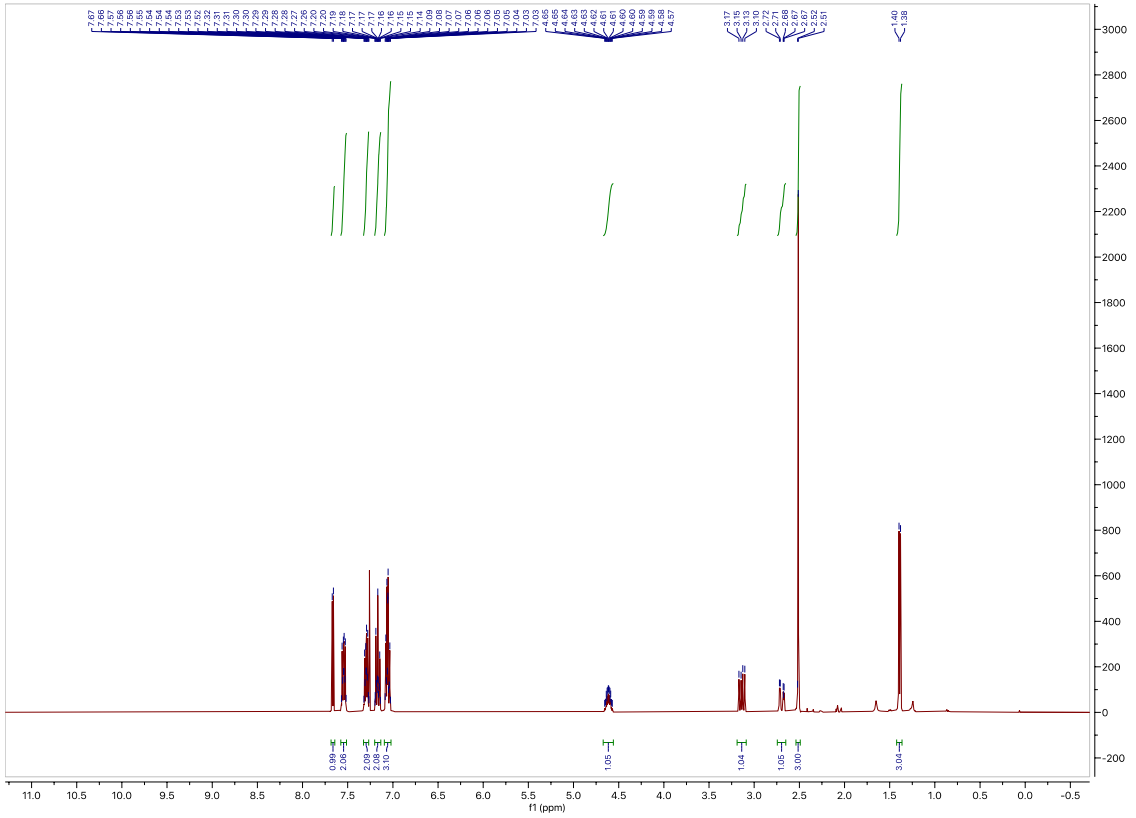
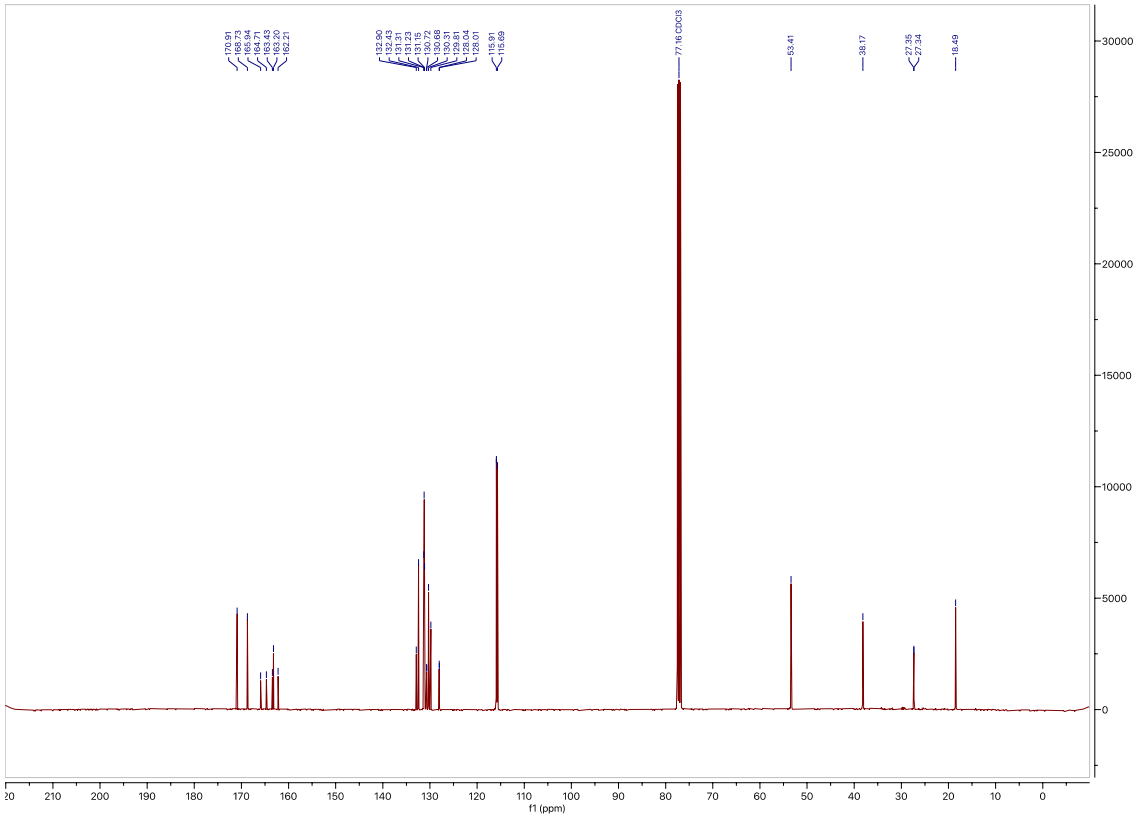
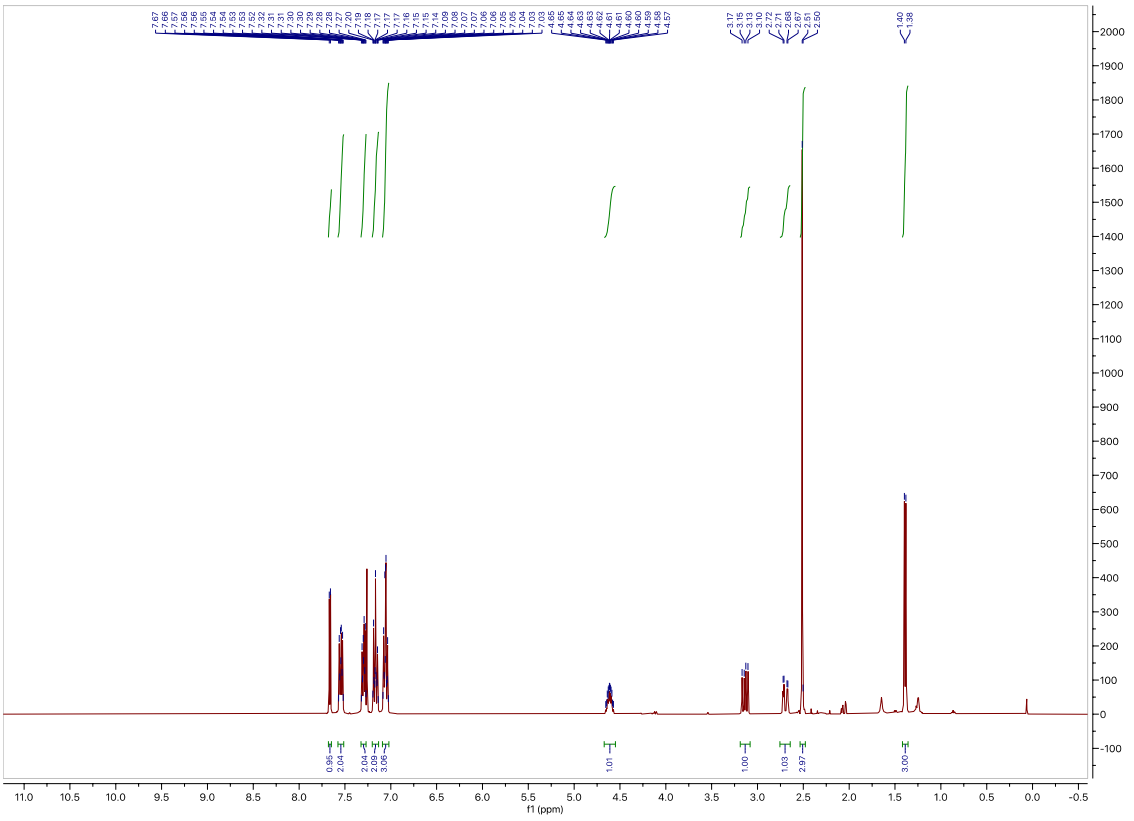
115.67
77.16 CDCl3
53.39
38.15
27.32
18.47
f1 (ppm)

SM *S*-16g





SM *R*-16g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7.15
7.14
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7.07
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3.17
3.15
3.13
3.10
2.72
2.71
2.68
2.67
2.51
2.50
1.40
1.38
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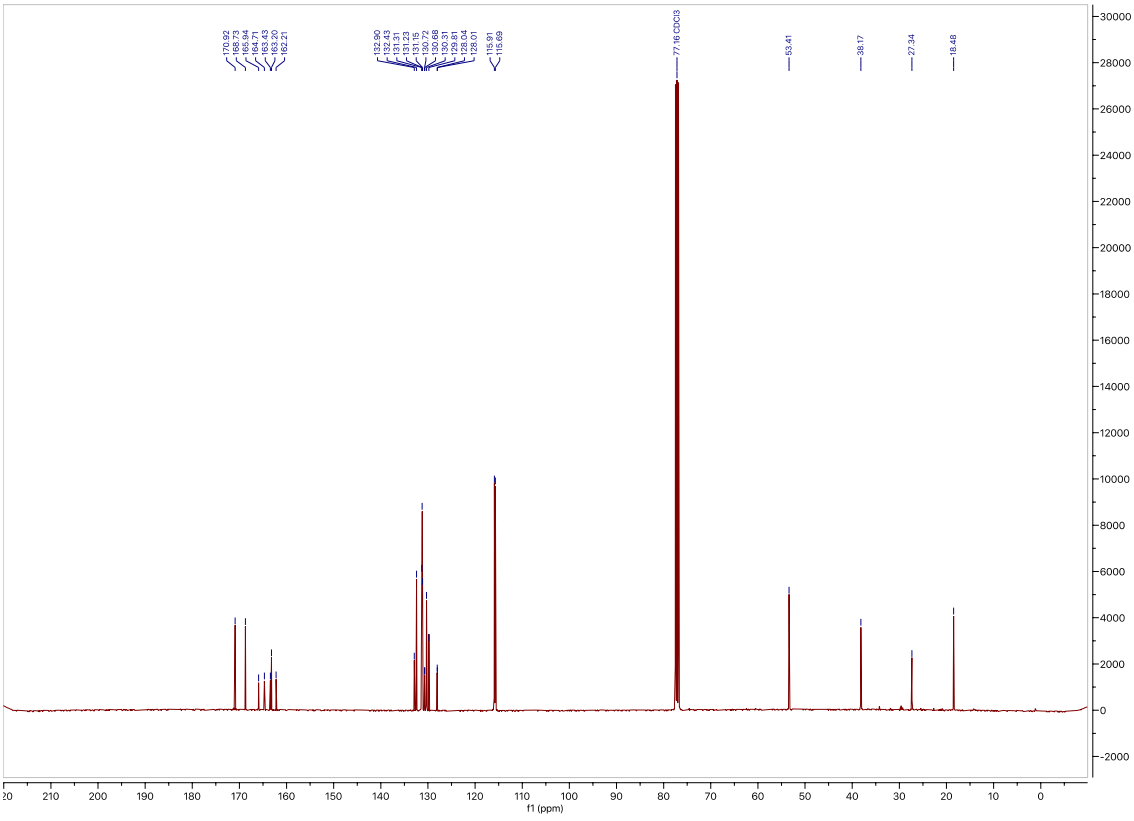
2.04
2.09
3.06
1.01
1.00
1.03
2.97
3.00
f1 (ppm)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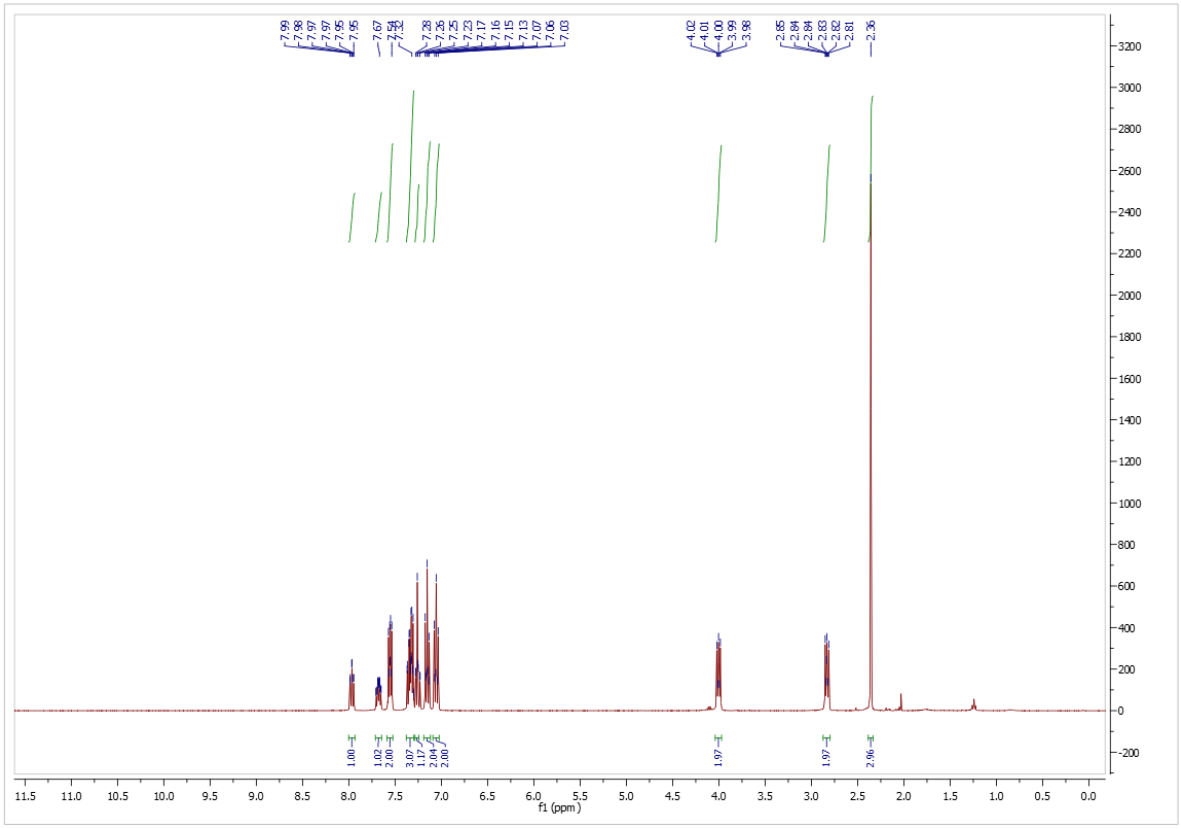
131.15
130.72
130.68
130.31
129.81
129.64
128.01
115.91
115.69
77.16 CDCl3
53.41
38.17
27.34
18.48
f1 (ppm)

SM 16h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7.23
7.17
7.16
7.15
7.13
7.07
7.06
7.03
4.02
4.01
4.00
3.99
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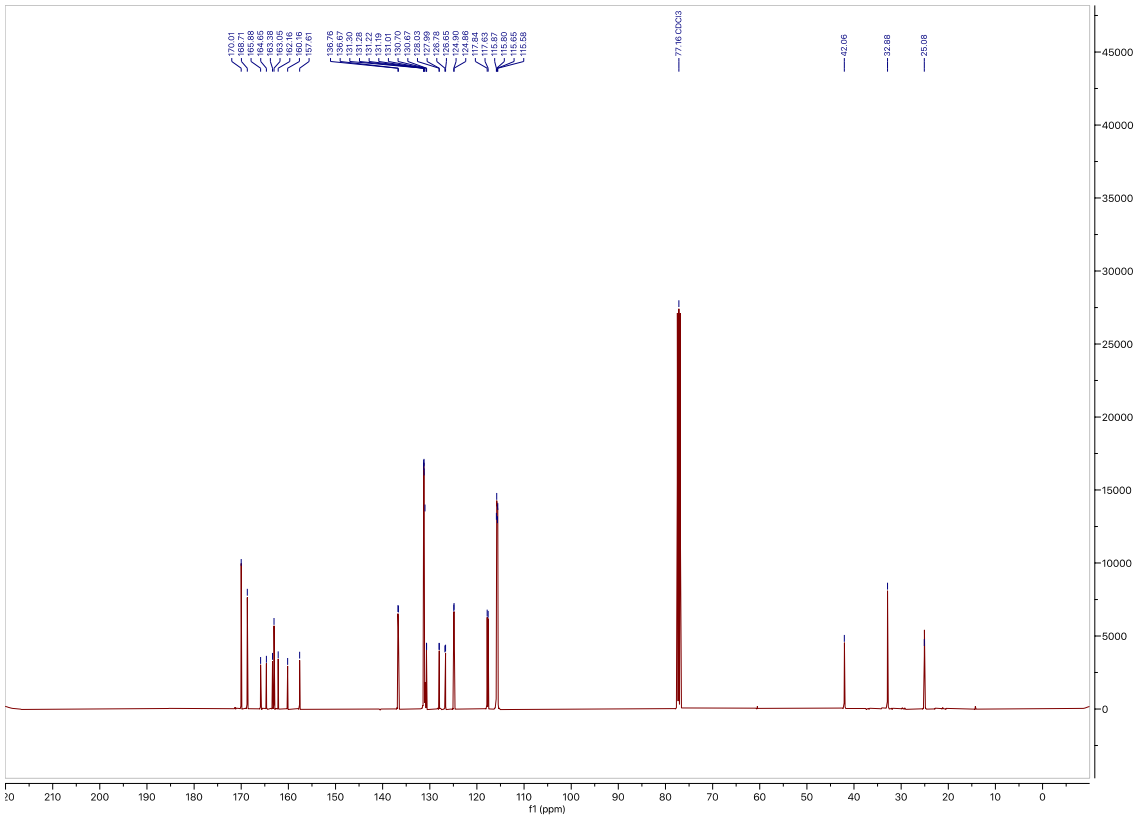
2.00
1.97
1.97
2.96
f1 (ppm)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157.61
136.76
136.67
131.30
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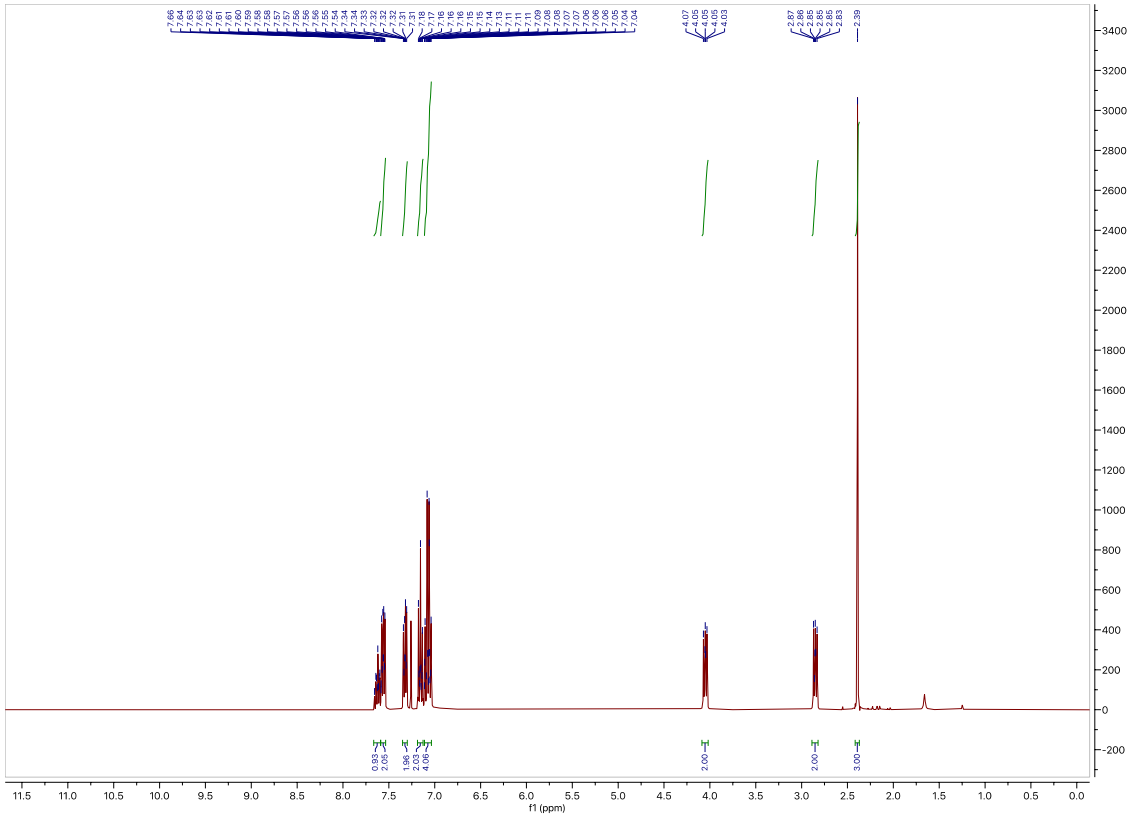
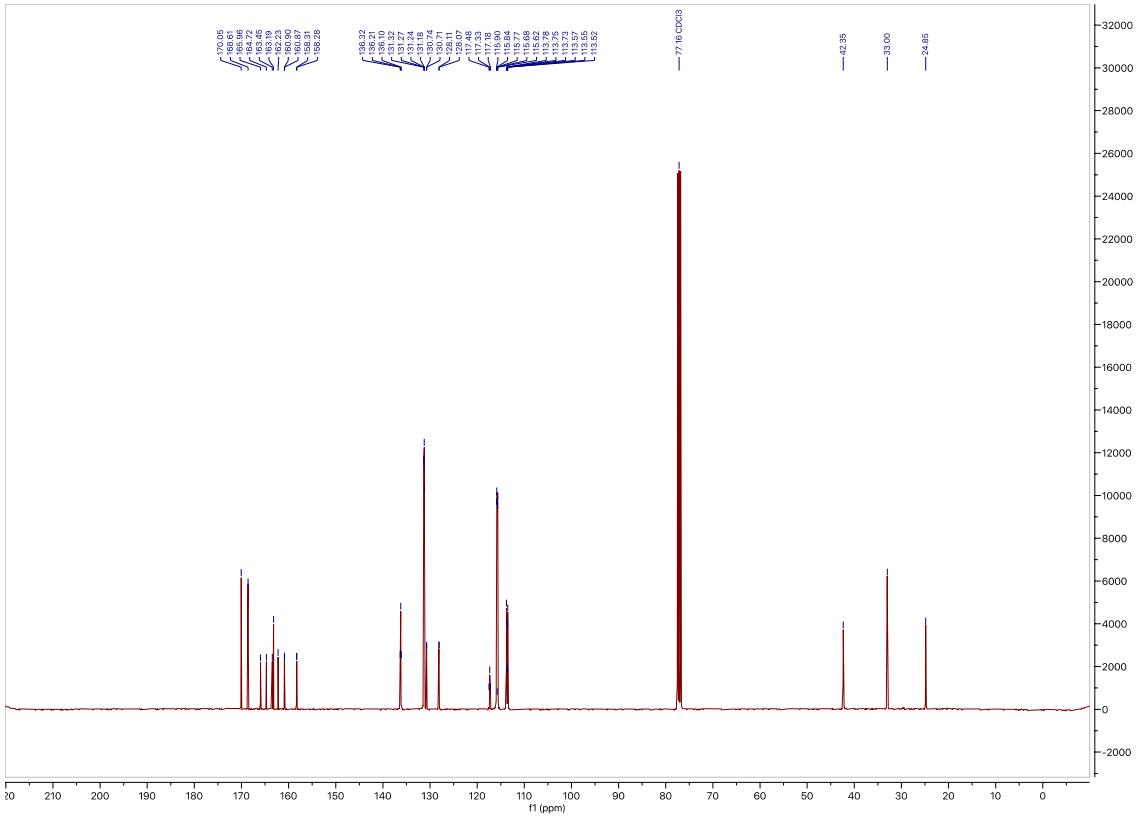
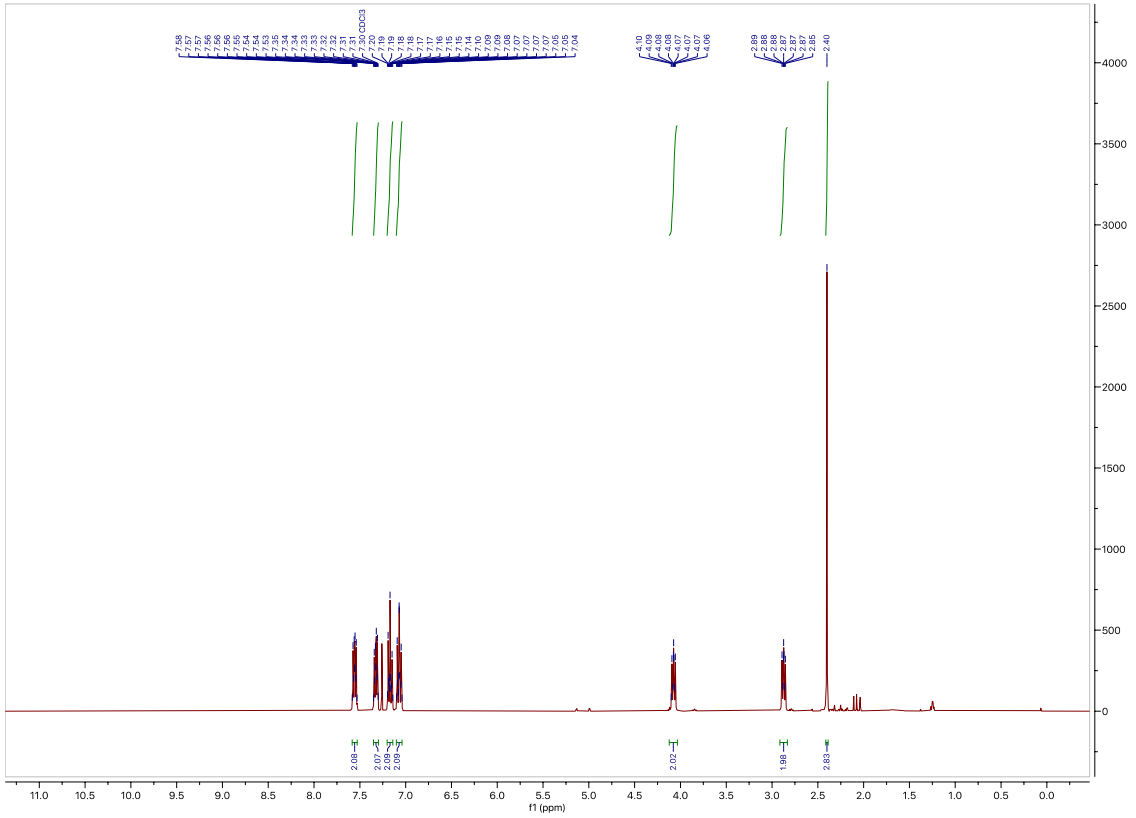
131.22
131.19
131.01
130.70
130.67
128.03
127.99
126.78
126.65
124.90
124.86
117.84
117.63
115.87
115.80
115.65
115.58
77.16 CDCl3
42.06
32.88
25.08
f1 (ppm)

SM 16i





SM 16j


7.58
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7.54
7.53
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.30 CDCl3
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.10
7.09
7.09
7.08
7.08
7.07
7.07
7.07
7.07
7.05
7.05
7.04
4.10
4.09
4.08
4.08
4.07
4.07
4.07
4.06
2.89
2.88
2.88
2.87
2.87
2.87
2.86
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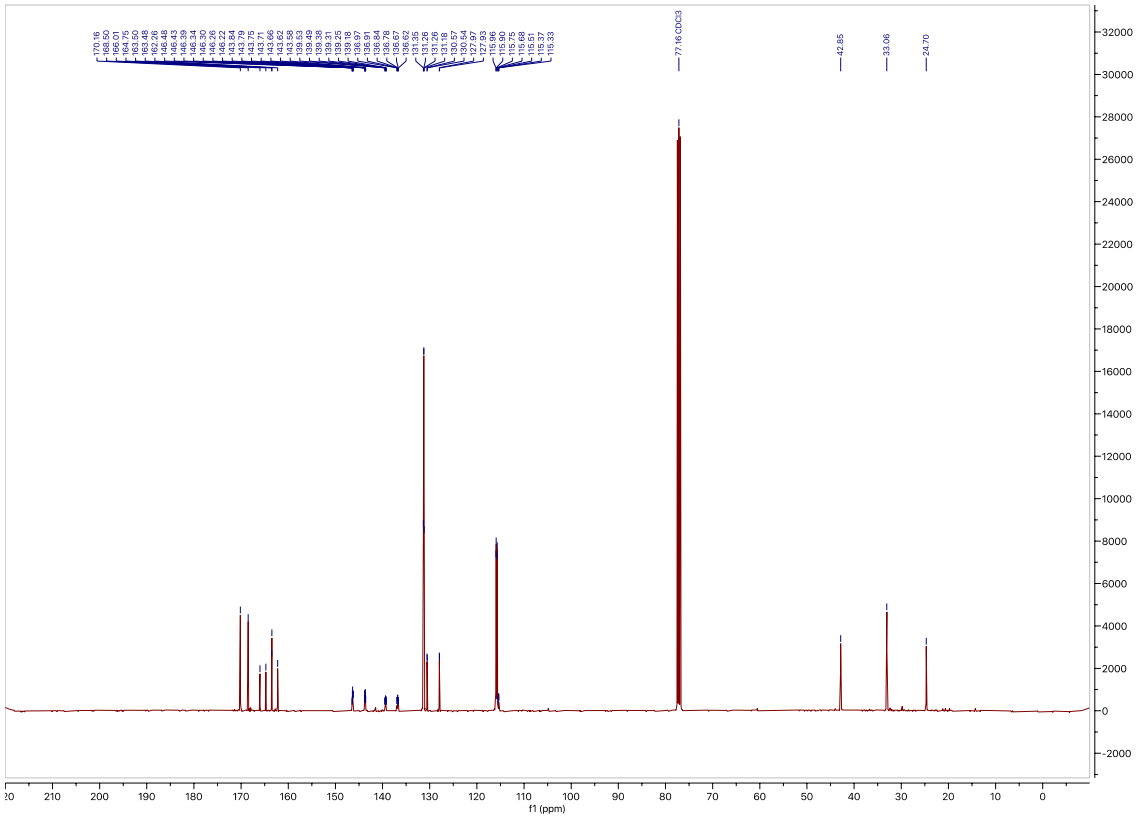
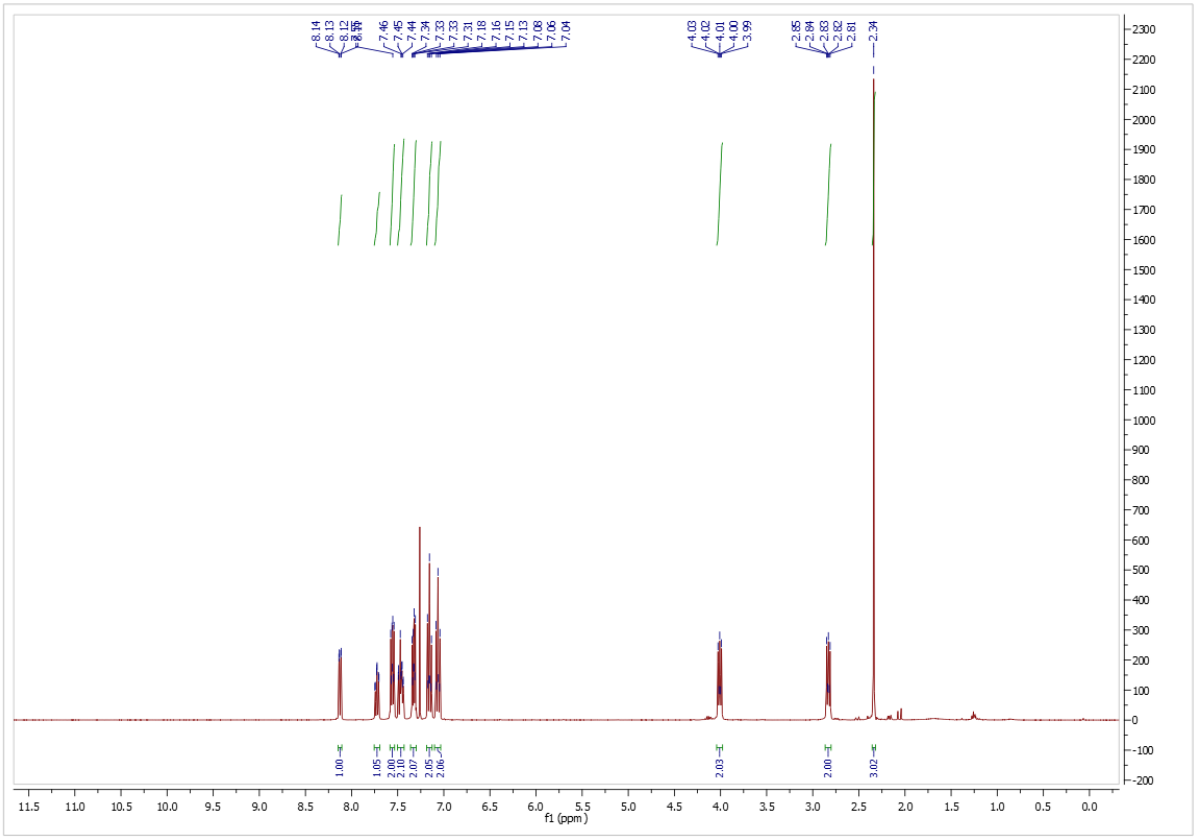
2.40
2.08
2.07
2.09
2.09
2.02
1.98
2.83
f1 (ppm)


170.16
168.50
166.01
164.75
163.50
162.48
162.48
146.48
146.43
146.39
146.34
146.30
146.26
146.22
143.84
143.79
143.75
143.71
143.66
143.62
143.58
139.43
139.40
139.38
139.31
139.25
139.18
136.97
136.91
136.84
136.78
136.67
136.62
131.35
131.26
131.18
131.09
130.57
130.54
127.93
127.88
115.96
115.90
115.75
115.68
115.51
115.37
115.33
77.16 CDCl3
42.85
33.06
24.70
f1 (ppm)

SM 16k


8.14
8.13
8.12
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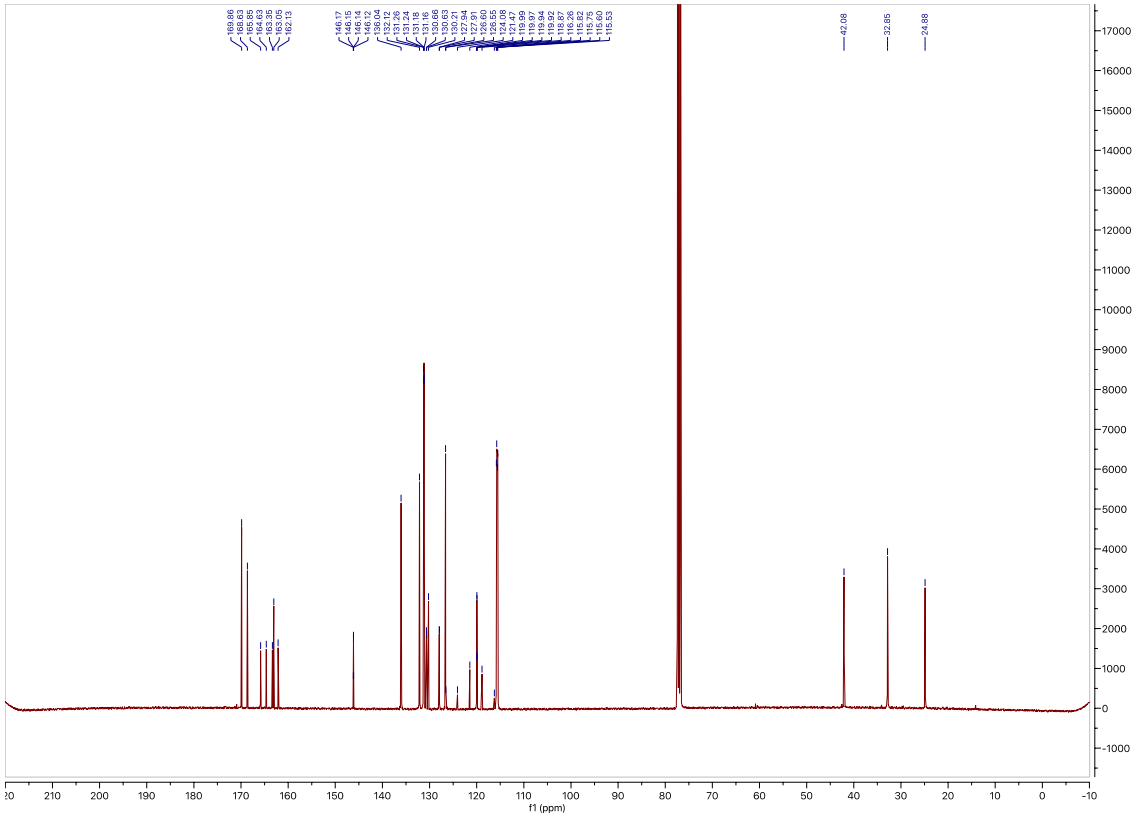
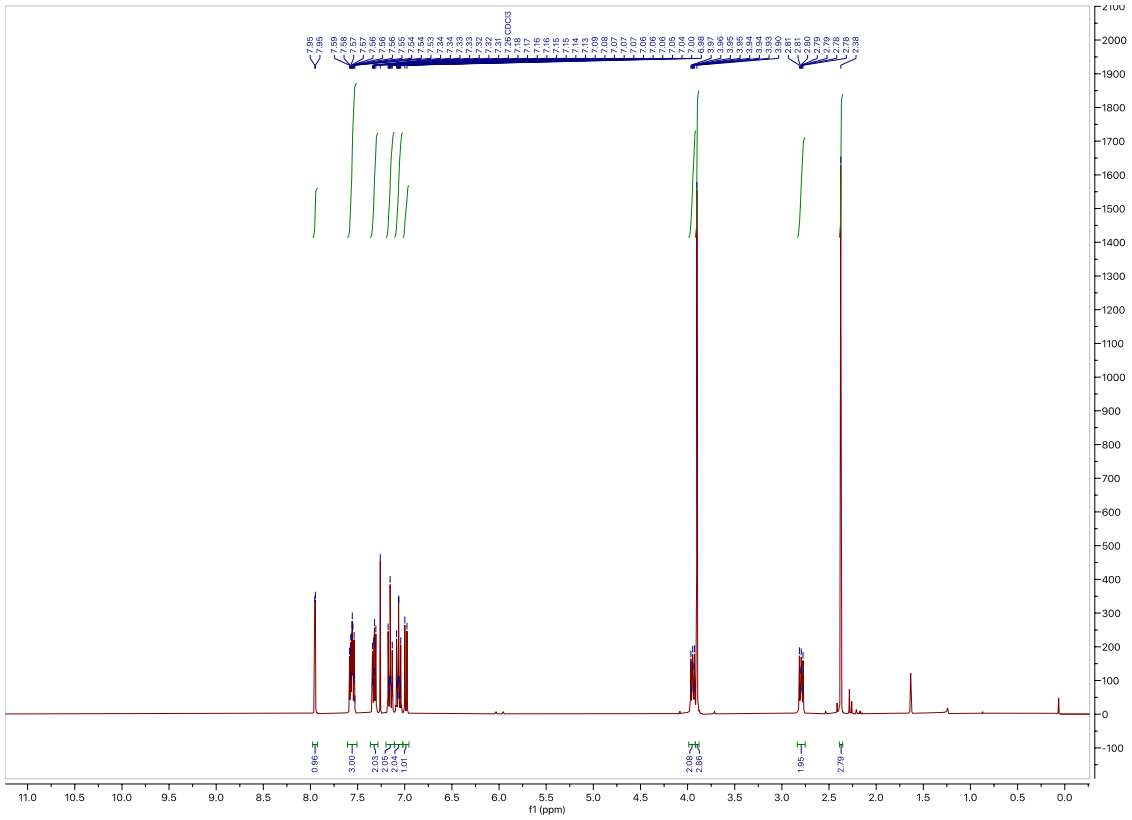
7.45
7.44
7.34
7.33
7.31
7.18
7.16
7.15
7.13
7.08
7.06
7.04
4.03
4.02
4.01
4.00
3.99
2.85
2.84
2.83
2.82
2.81
2.34
1.00
1.05
2.00
2.10
2.07
2.05
2.06
2.03
2.00
3.02
f1 (ppm)


169.86
166.63
166.86
164.63
163.35
163.05
162.13
146.77
146.15
146.14
146.07
138.04
132.12
131.26
131.24
131.16
130.68
130.63
130.21
127.94
127.91
126.60
125.55
124.08
121.47
119.99
119.97
119.94
119.92
118.62
118.26
115.82
115.79
115.60
115.53
42.08
32.85
24.88
f1 (ppm)

SM 16l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7.56
7.55
7.54
7.54
7.53
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.28 CDCl3
7.18
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.09
7.09
7.08
7.07
7.07
7.07
7.07
7.06
7.06
7.06
7.05
7.04
7.00
6.99
3.97
3.96
3.95
3.95
3.94
3.94
3.93
3.90
2.81
2.81
2.80
2.79
2.79
2.78
2.78
2.68
0.96
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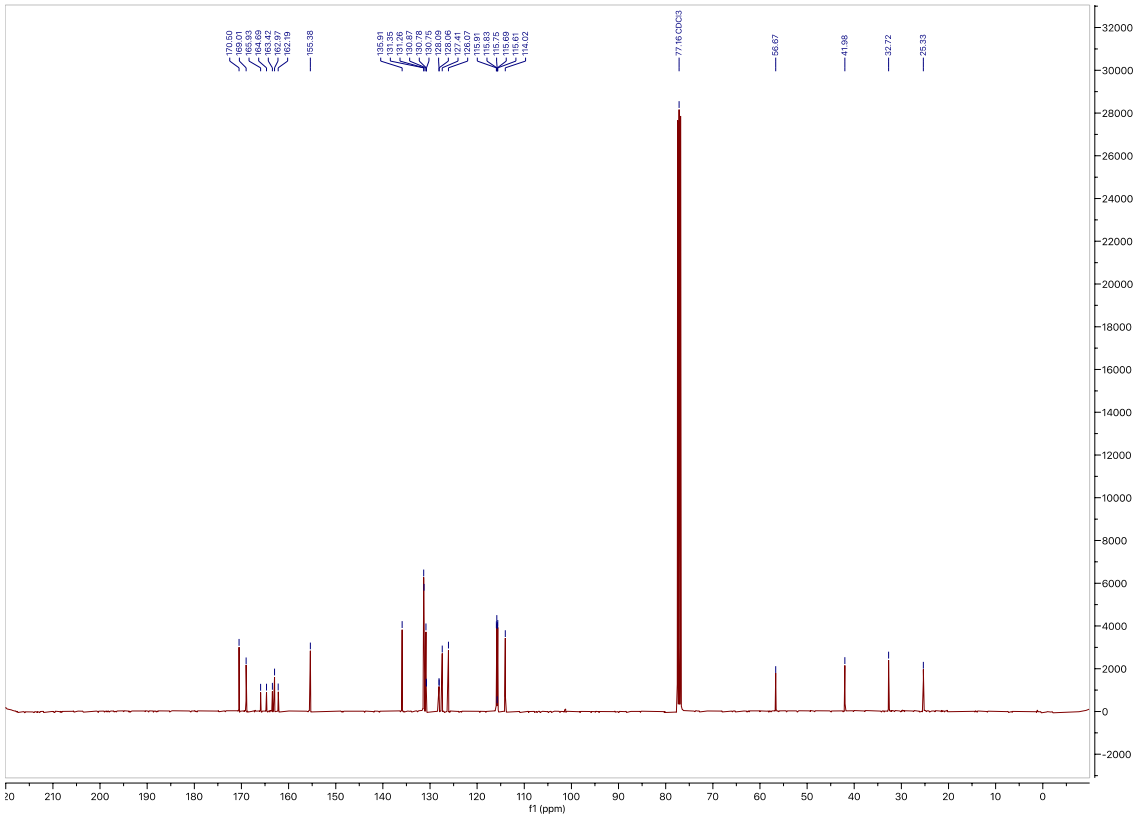
2.03
2.05
2.04
1.01
2.08
2.86
1.95
2.79
f1 (ppm)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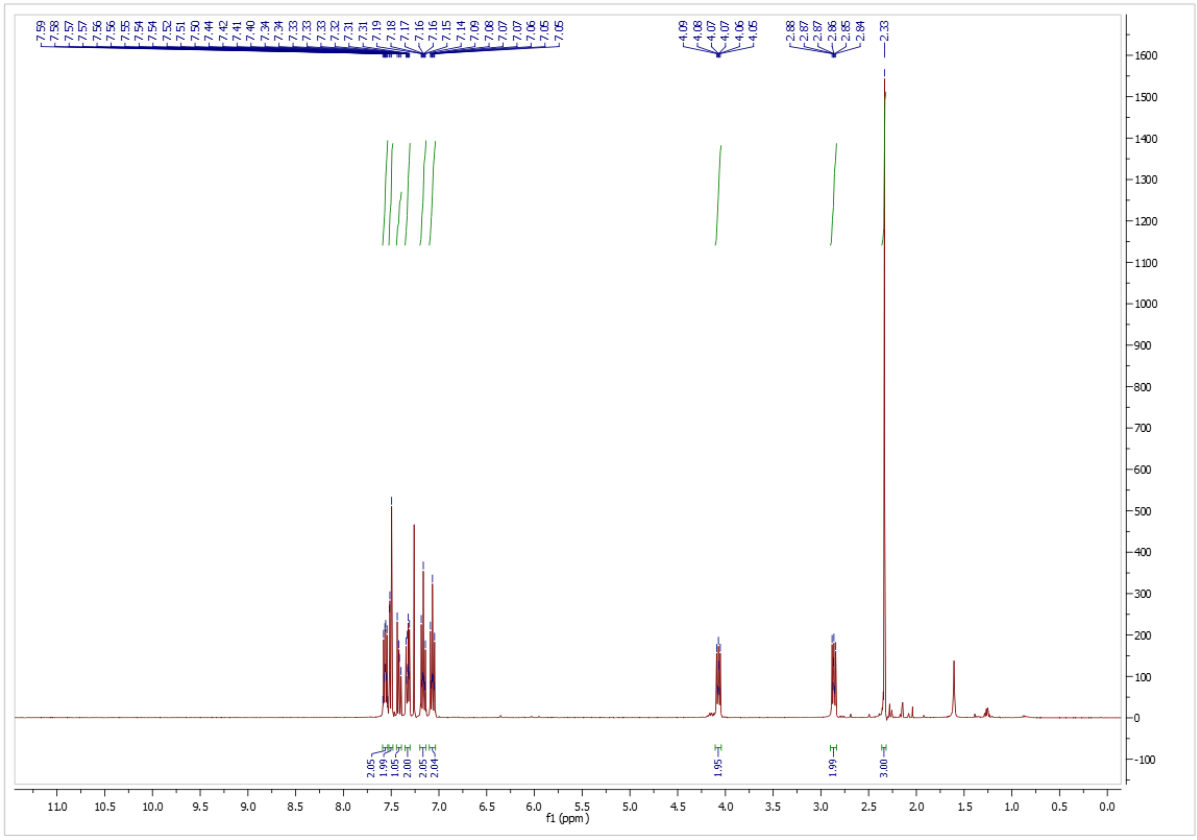
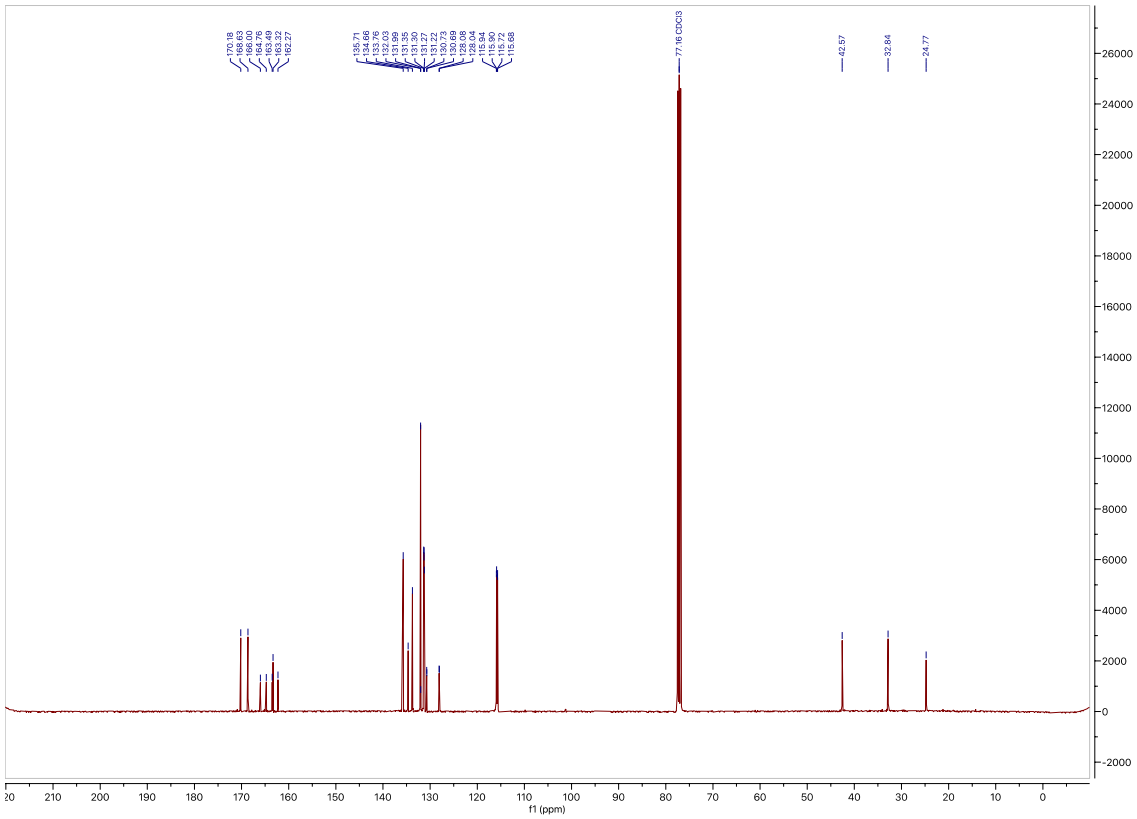
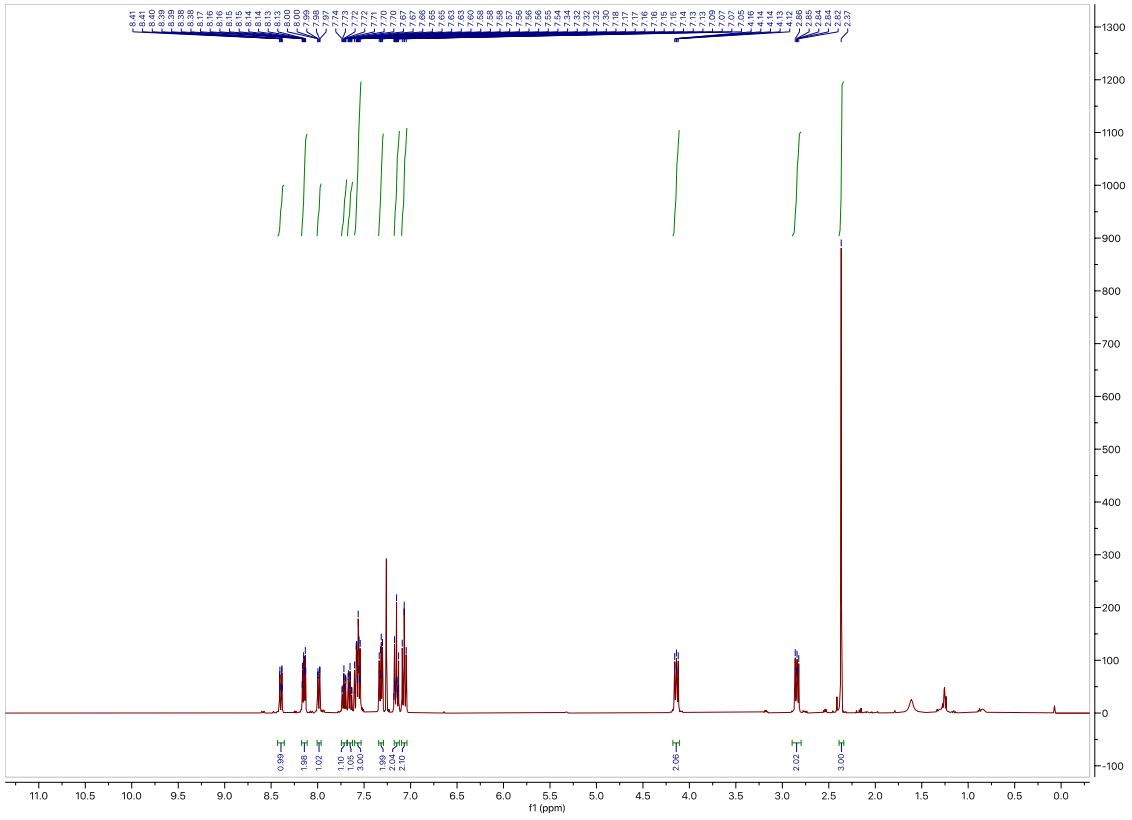
163.47
162.97
162.19
155.38
135.91
131.35
131.26
130.87
130.78
130.75
128.09
128.08
127.41
126.07
115.91
115.83
115.75
115.69
115.61
114.02
77.16 CDCl3
56.67
41.98
32.72
25.33
f1 (ppm)

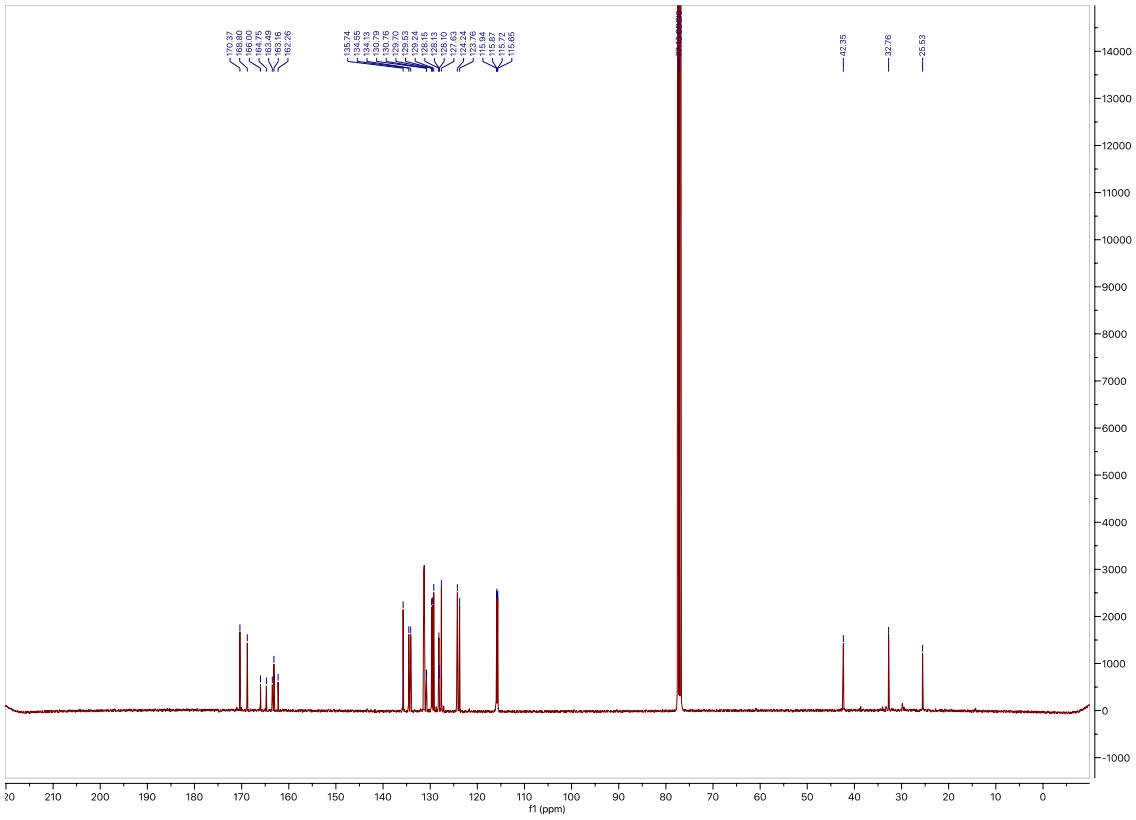
SM 16m



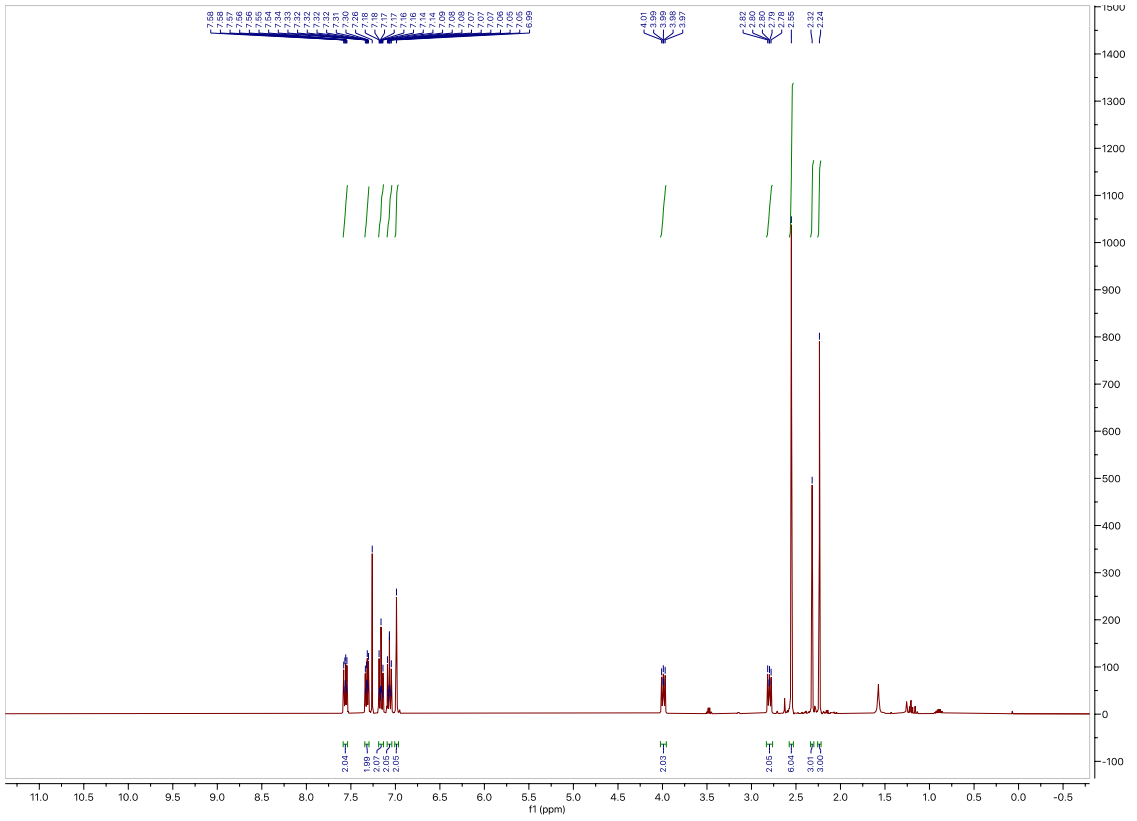


SM 16n





SM 16o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7.33
7.32
7.32
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7.31
7.30
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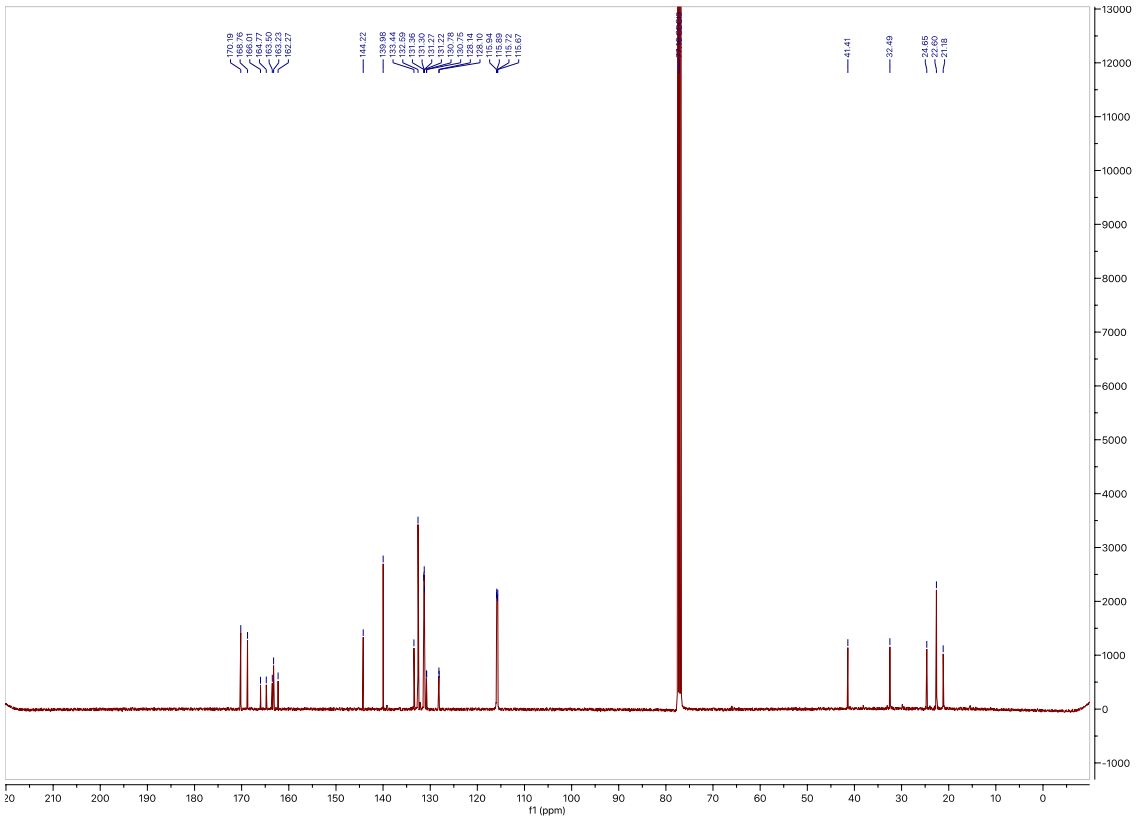
7.18
7.18
7.17
7.17
7.16
7.16
7.14
7.09
7.08
7.08
7.07
7.07
7.07
7.06
7.05
7.05
7.05
6.99
4.01
3.99
3.99
3.98
3.97
2.82
2.80
2.80
2.79
2.78
2.55
2.32
2.24
2.04
1.99
2.07
2.05
2.05
2.03
2.05
6.04
3.01
3.00
f1 (ppm)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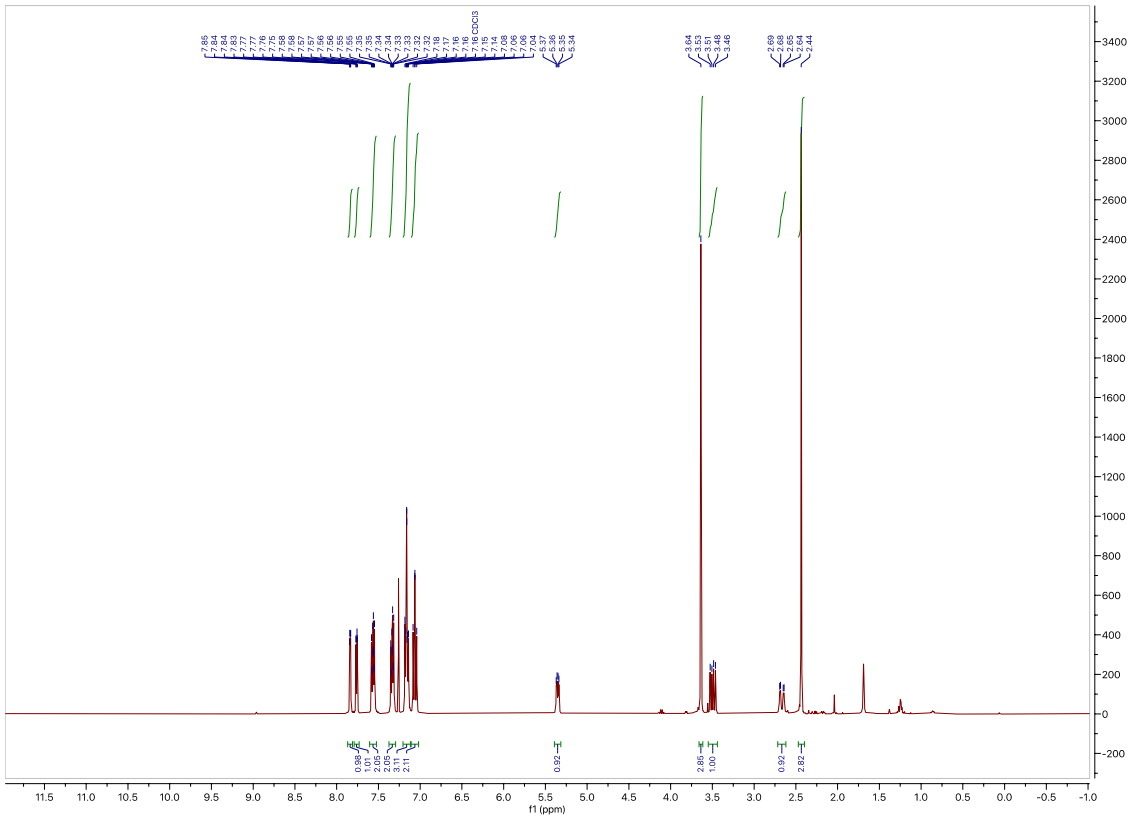
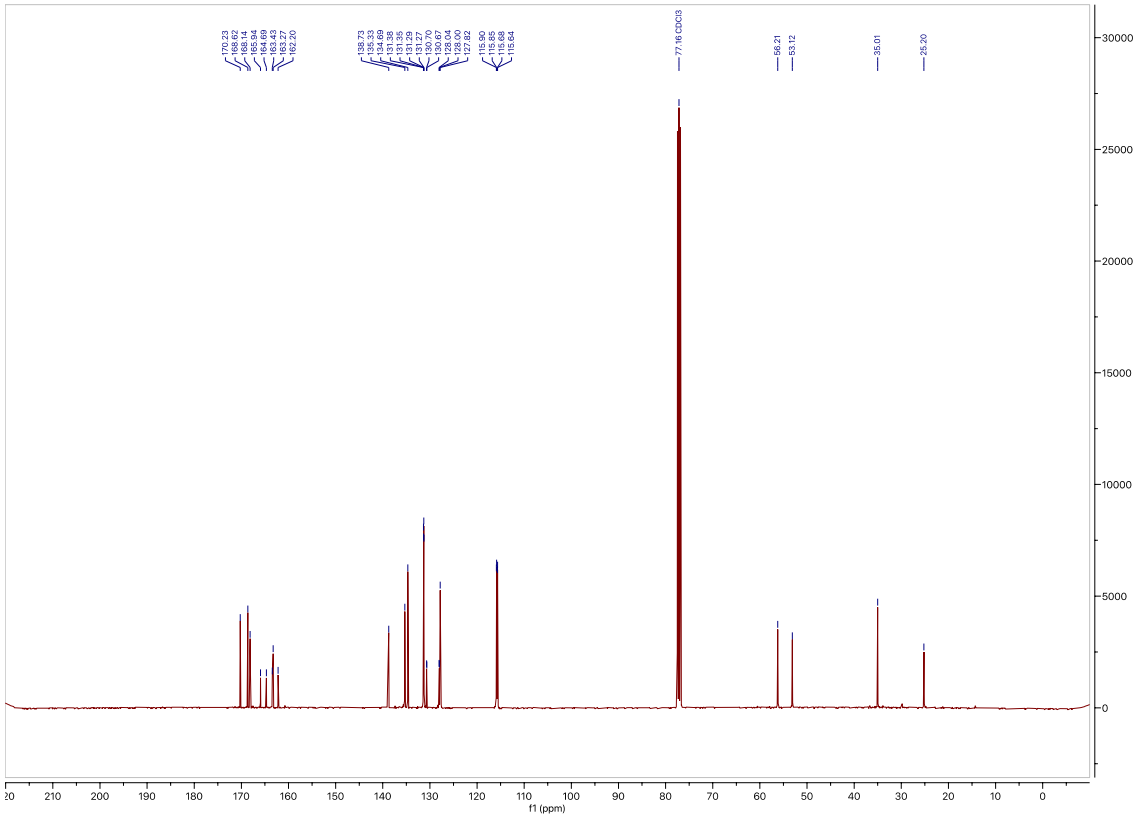
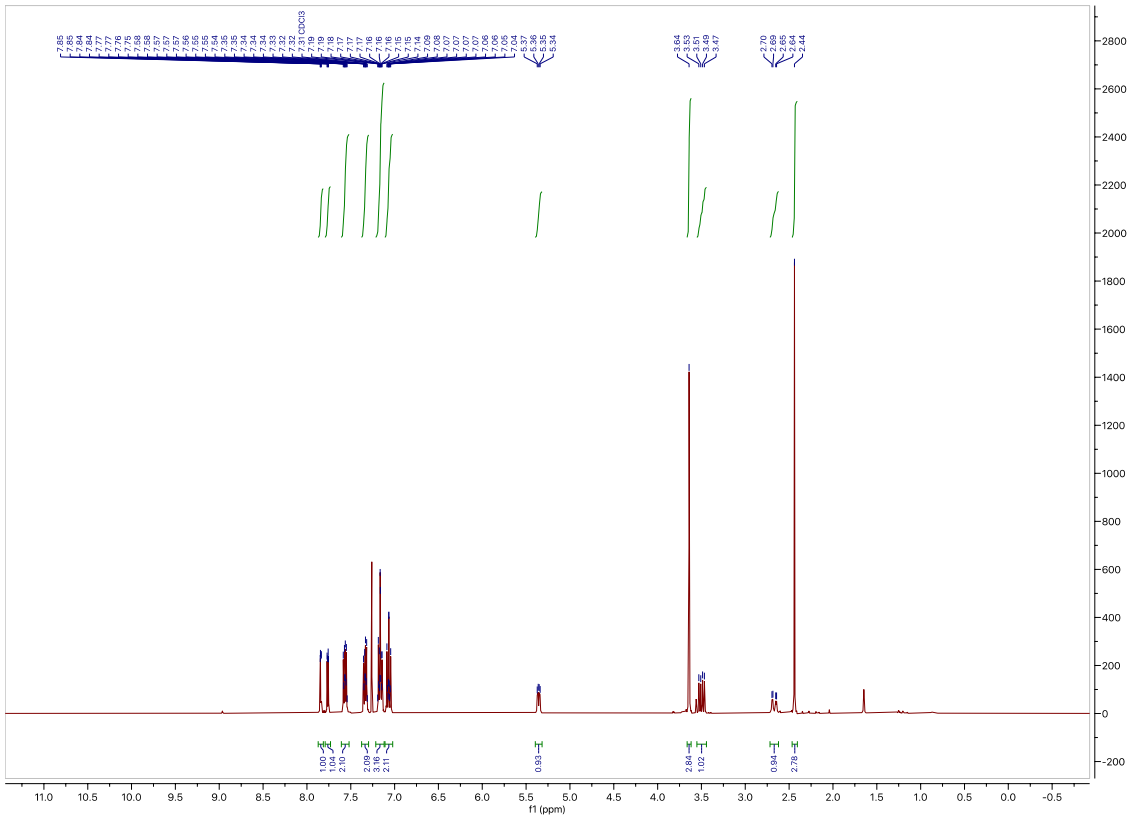
163.23
162.27
144.22
139.98
133.44
132.59
131.36
131.30
131.27
131.22
130.78
130.75
128.14
126.10
116.94
115.89
115.72
115.67
77.16
41.41
32.49
24.65
22.60
21.18
f1 (ppm)

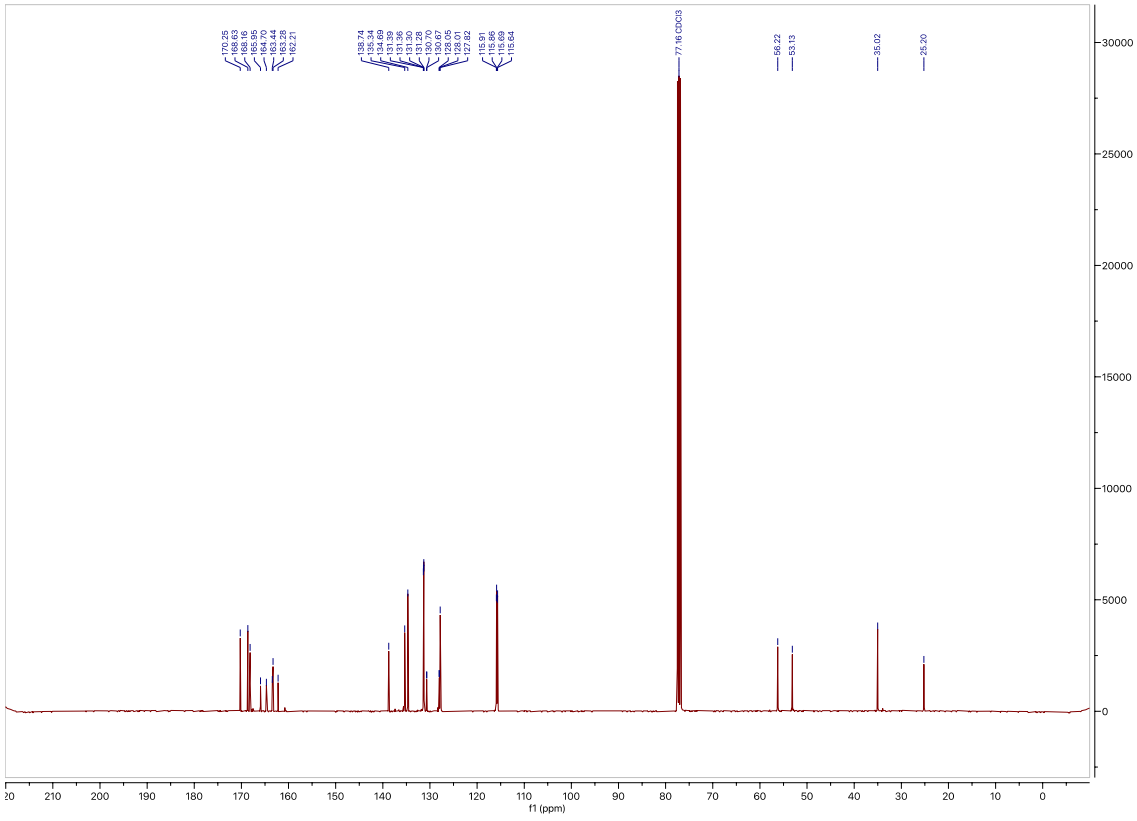
SM 16p


7.85
7.84
7.84
7.83
7.77
7.77
7.76
7.75
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.19
7.17
7.16
7.16
7.16 CDCl3
7.15
7.14
7.08
7.06
7.06
7.04
5.37
5.36
5.35
5.34
3.64
3.53
3.51
3.48
3.46
2.69
2.68
2.65
2.64
2.44
0.88
1.77
2.05
2.05
3.11
2.11
0.92
2.85
1.00
0.92
2.82
f1 (ppm)


170.23
168.62
168.14
165.84
164.69
163.43
163.27
162.20
138.73
135.33
134.89
131.38
131.35
131.29
131.27
130.70
130.67
130.64
128.00
127.82
115.90
115.85
115.68
115.64
77.16 CDCl3
56.21
53.12
35.01
25.20
f1 (ppm)

SM *rac*-16p


7.85
7.85
7.84
7.84
7.77
7.77
7.76
7.75
7.58
7.57
7.57
7.57
7.56
7.55
7.54
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31 CDCl3
7.19
7.18
7.17
7.17
7.17
7.16
7.16
7.16
7.15
7.15
7.14
7.09
7.08
7.07
7.07
7.07
7.07
7.06
7.06
7.06
7.05
7.04
5.37
5.36
5.35
5.34
3.64
3.63
3.51
3.49
3.47
2.70
2.68
2.66
2.65
2.64
2.44
1.00
1.04
2.10
2.09
3.16
2.11
0.93
2.64
1.02
0.94
2.78
f1 (ppm)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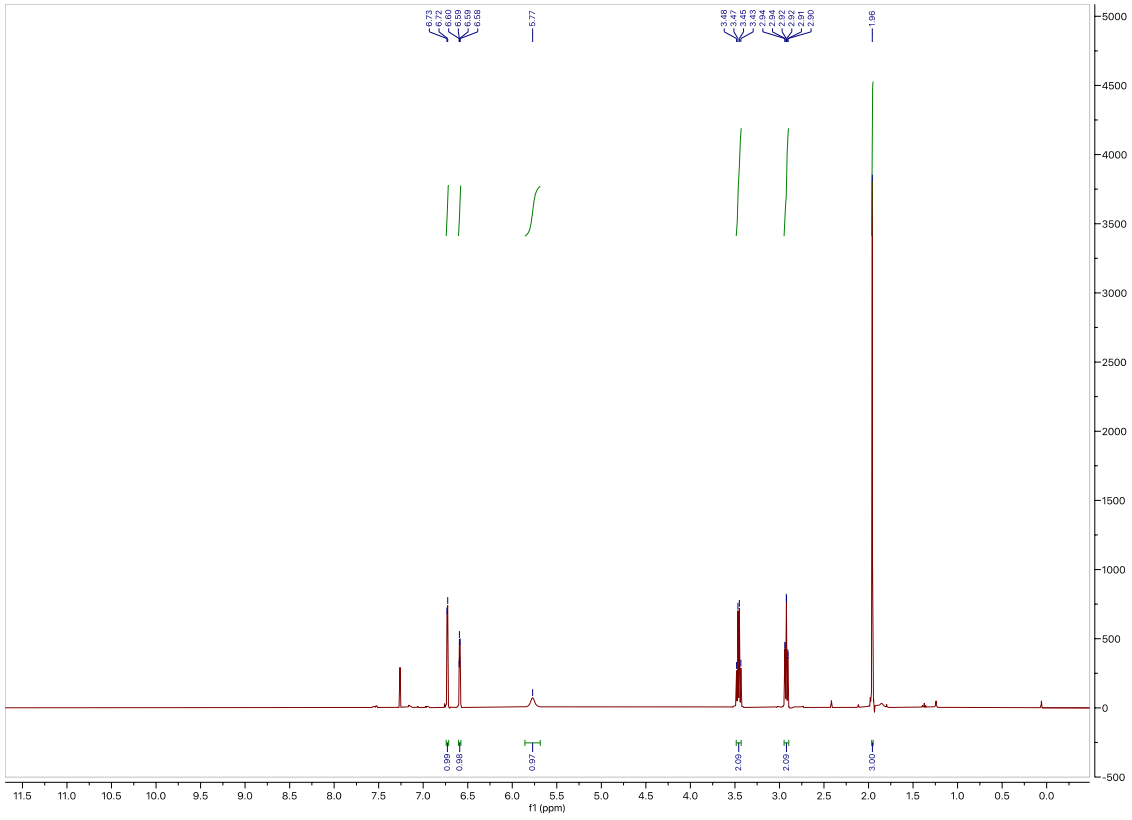
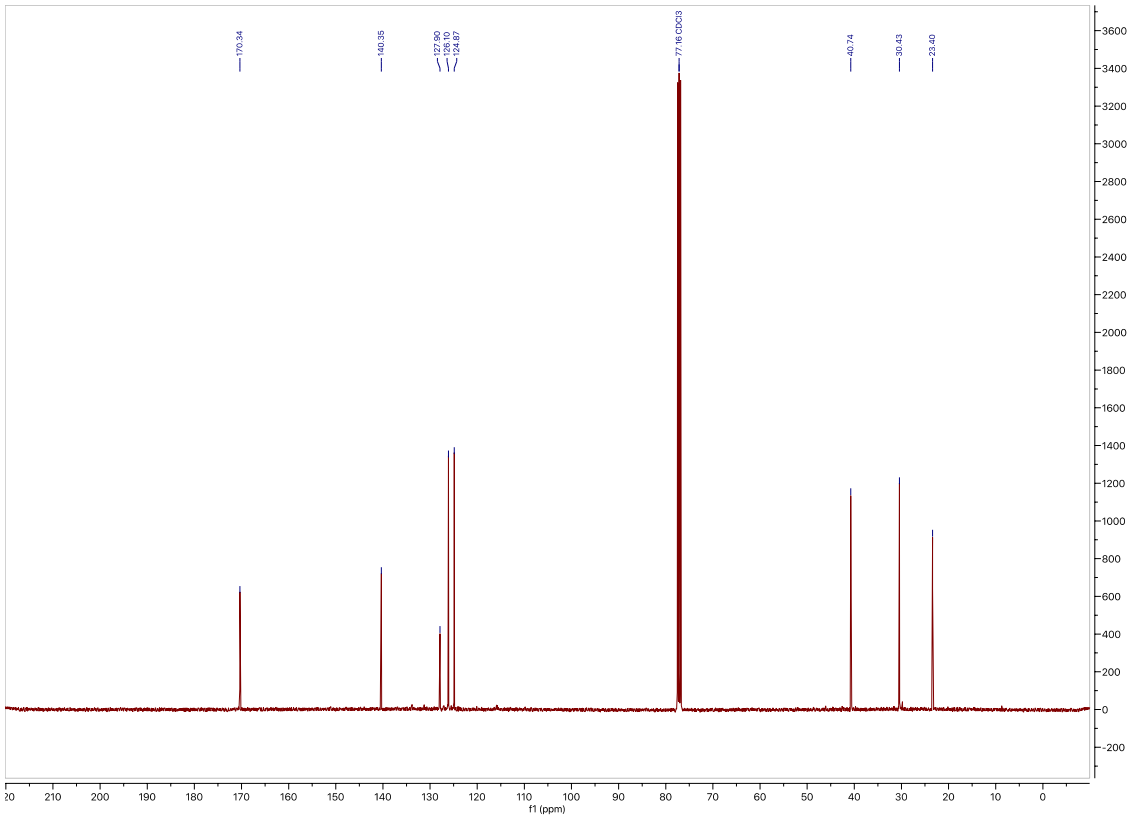
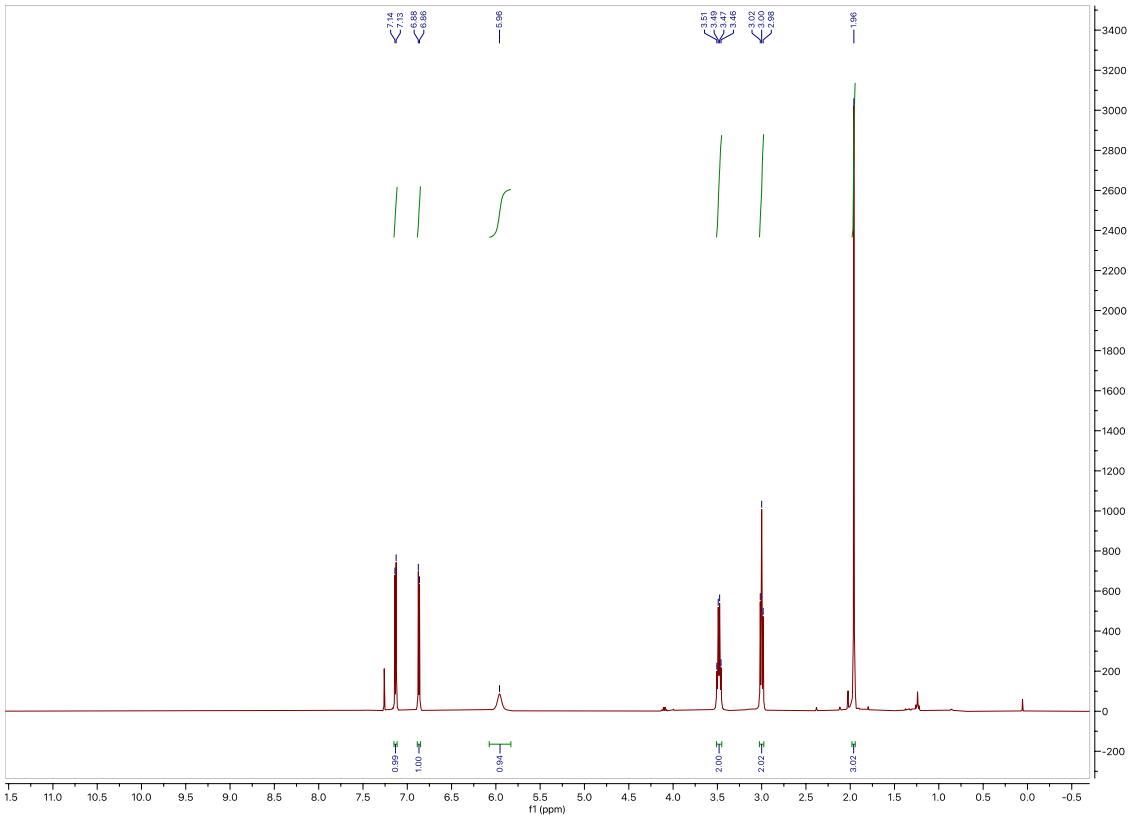
168.63
168.16
165.85
164.70
163.44
163.28
162.21
138.74
135.34
134.69
131.39
131.36
131.33
131.28
130.70
130.67
130.65
128.01
127.82
115.91
115.86
115.69
115.64
77.16 CDCl3
66.22
53.13
35.02
25.20
f1 (ppm)

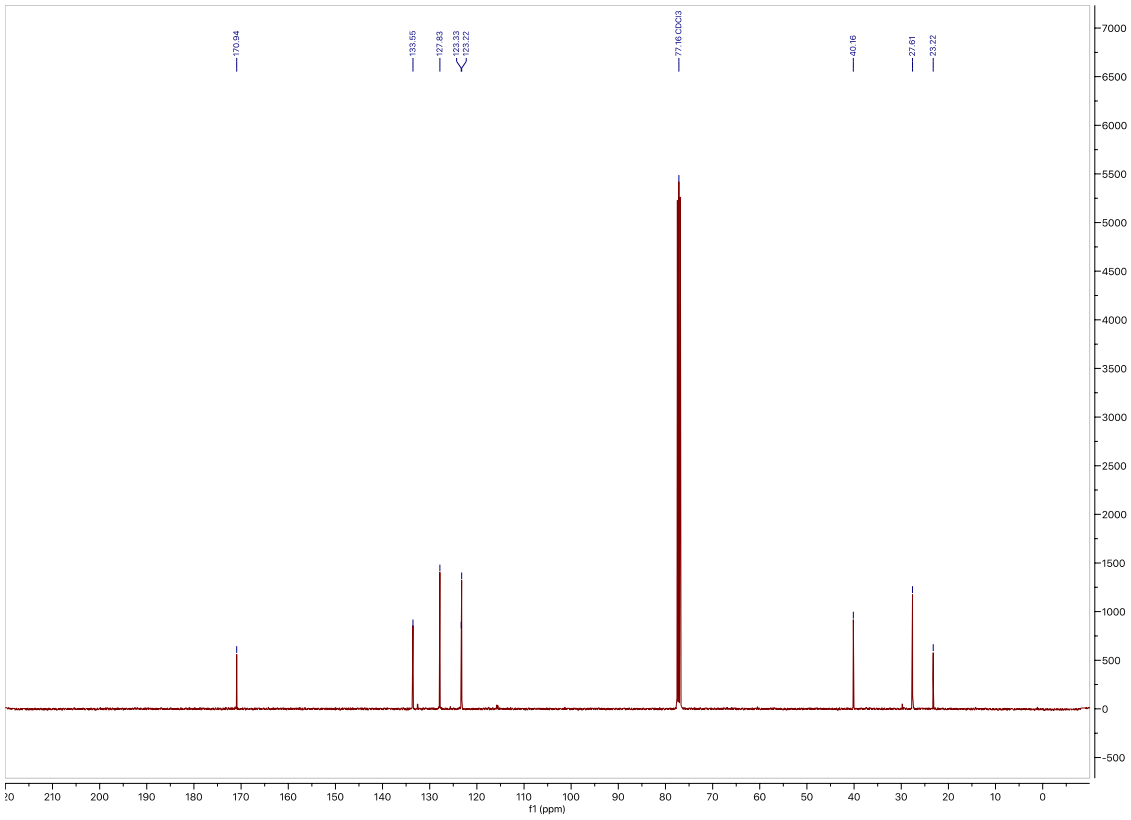
Product 17a


6.73
6.72
6.60
6.59
6.59
6.58
5.77
3.48
3.47
3.45
3.43
2.94
2.94
2.92
2.92
2.91
2.90
1.96
0.99
0.98
0.97
2.09
2.09
3.00
f1 (ppm)

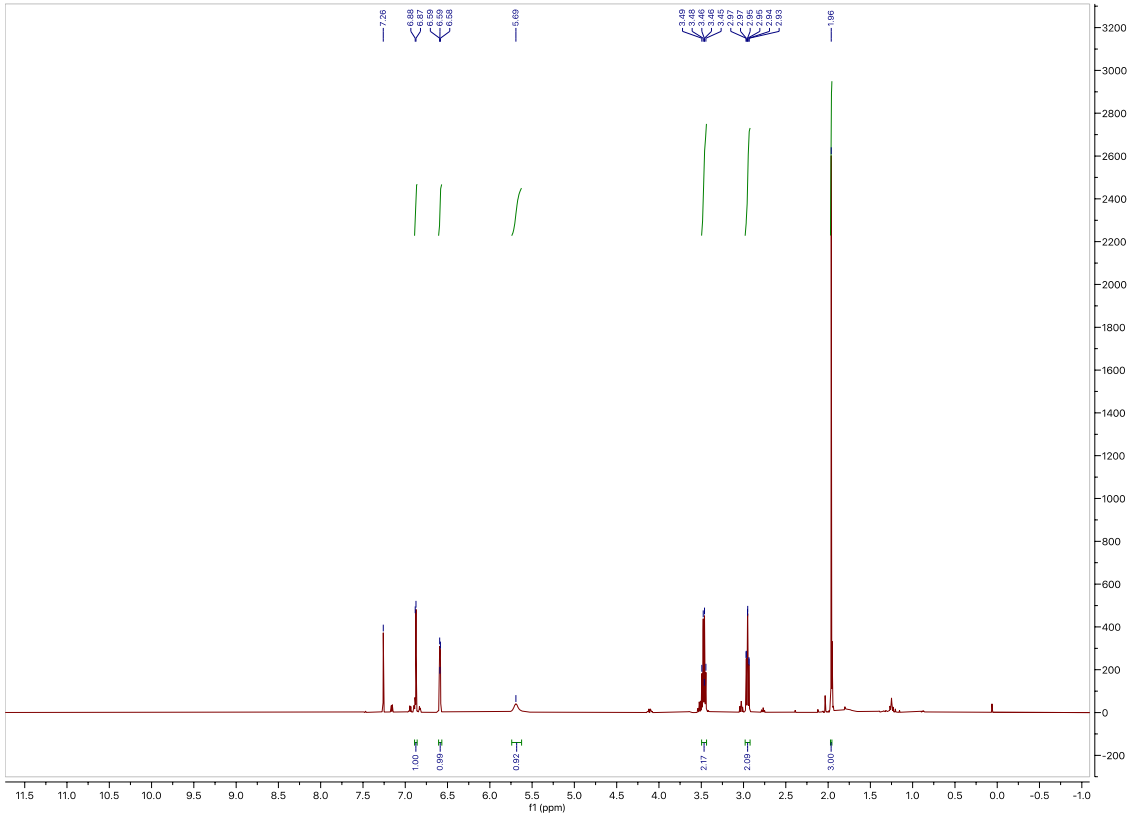

170.34
140.35
127.90
126.10
124.87
77.16 CDCl3
40.74
30.43
23.40
f1 (ppm)

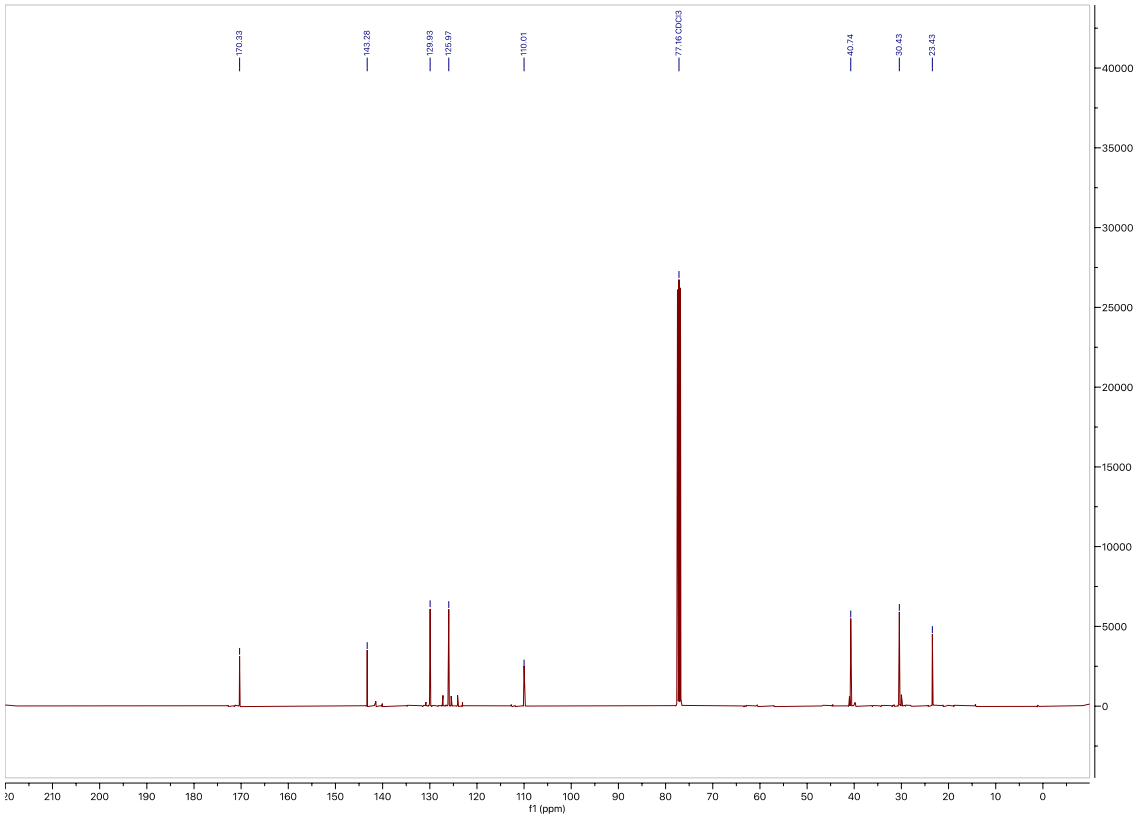
Product 17b


7.14
7.13
6.88
6.86
5.96
3.51
3.49
3.47
3.46
3.02
3.00
2.98
1.96
0.99
1.00
0.94
2.00
2.02
3.02
f1 (ppm)

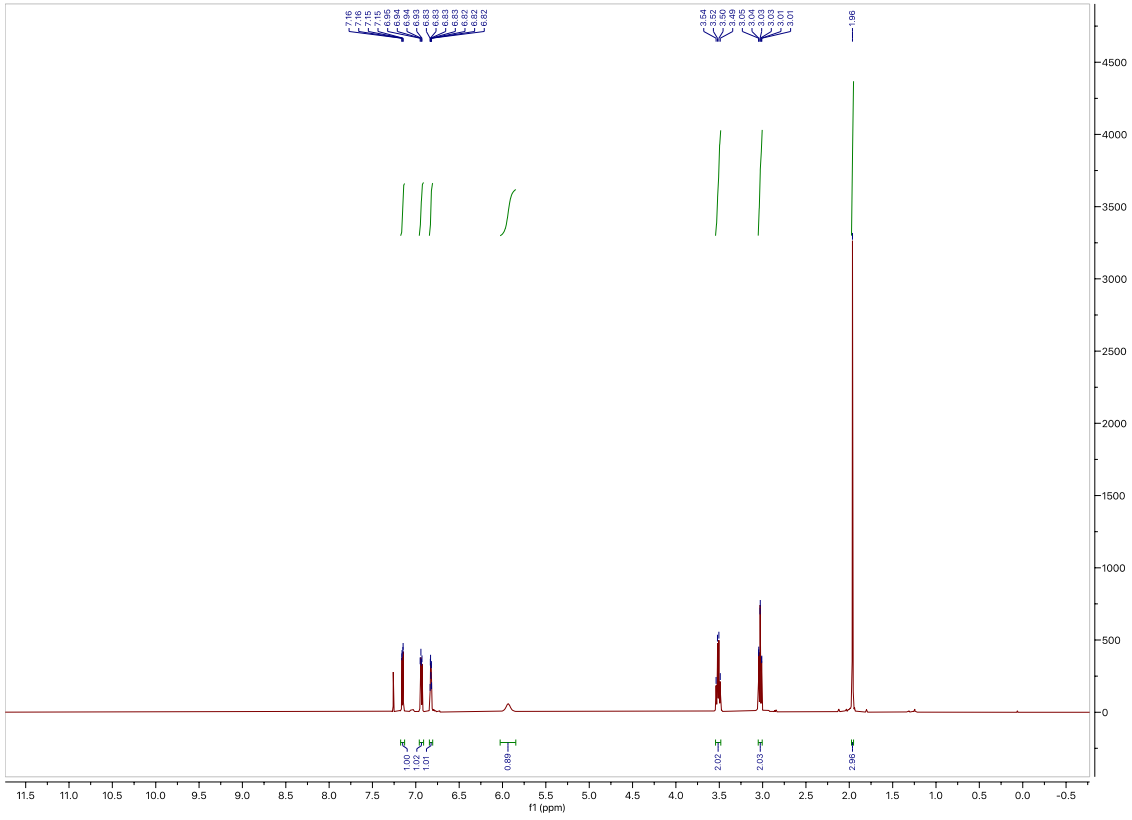

170.94
133.55
127.83
123.33
123.22
77.16 CDCl3
40.16
27.61
23.22
f1 (ppm)

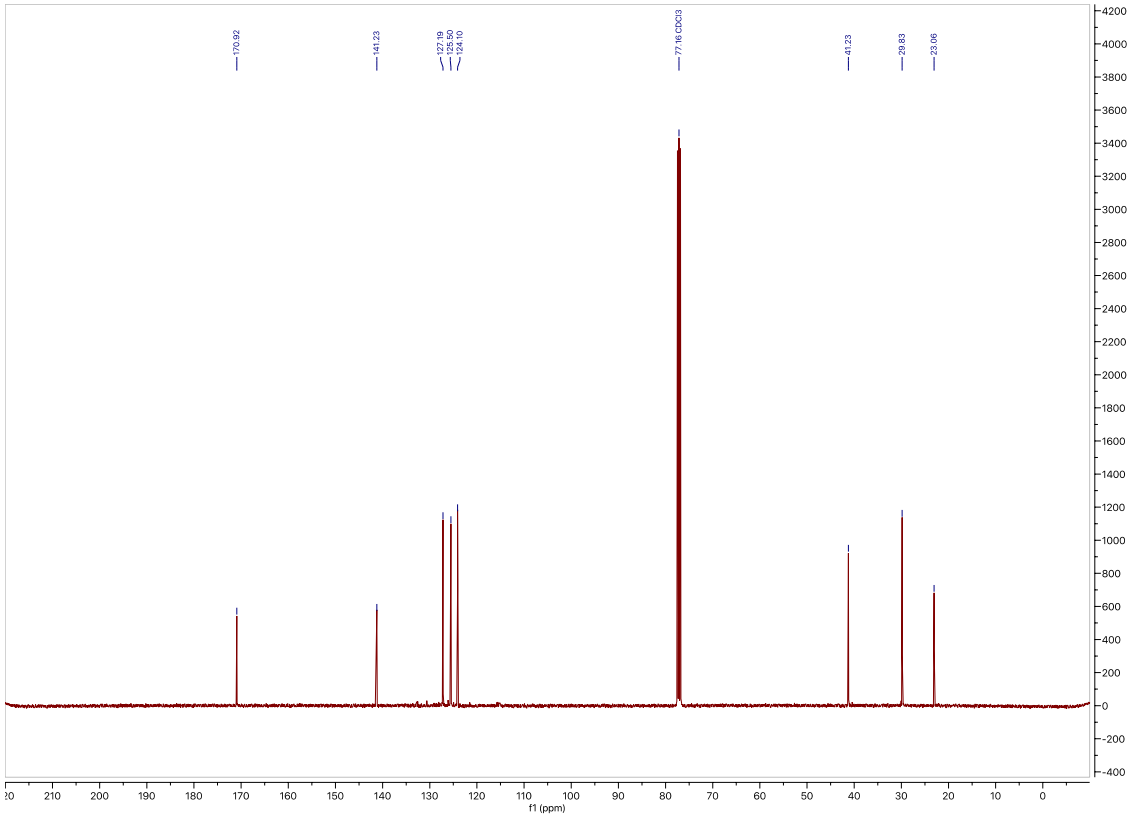
Product 17c


7.26
6.88
6.87
6.59
6.59
6.58
5.69
3.49
3.48
3.47
3.46
3.45
3.37
2.97
2.95
2.95
2.94
2.93
1.96
1.00
0.99
0.92
2.17
2.09
3.00
f1 (ppm)

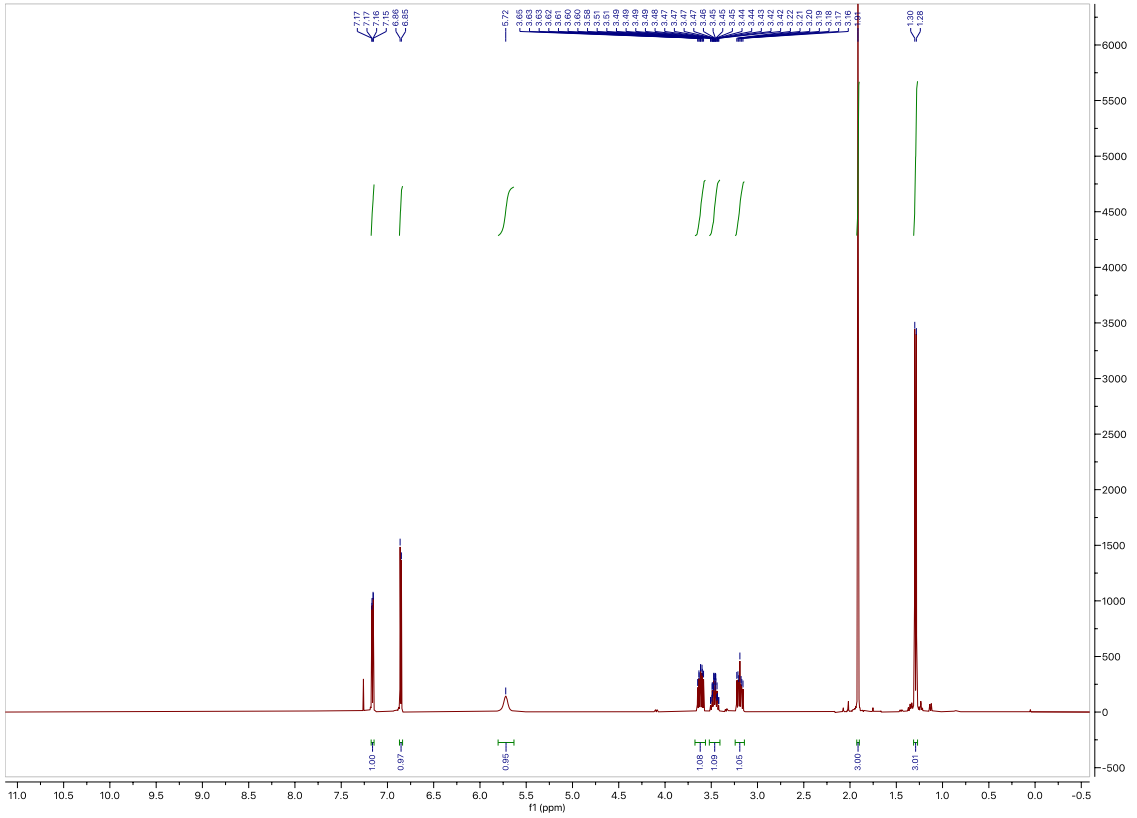

170.33
143.28
129.93
125.97
110.01
77.16 CDCl3
40.74
30.43
23.43
f1 (ppm)

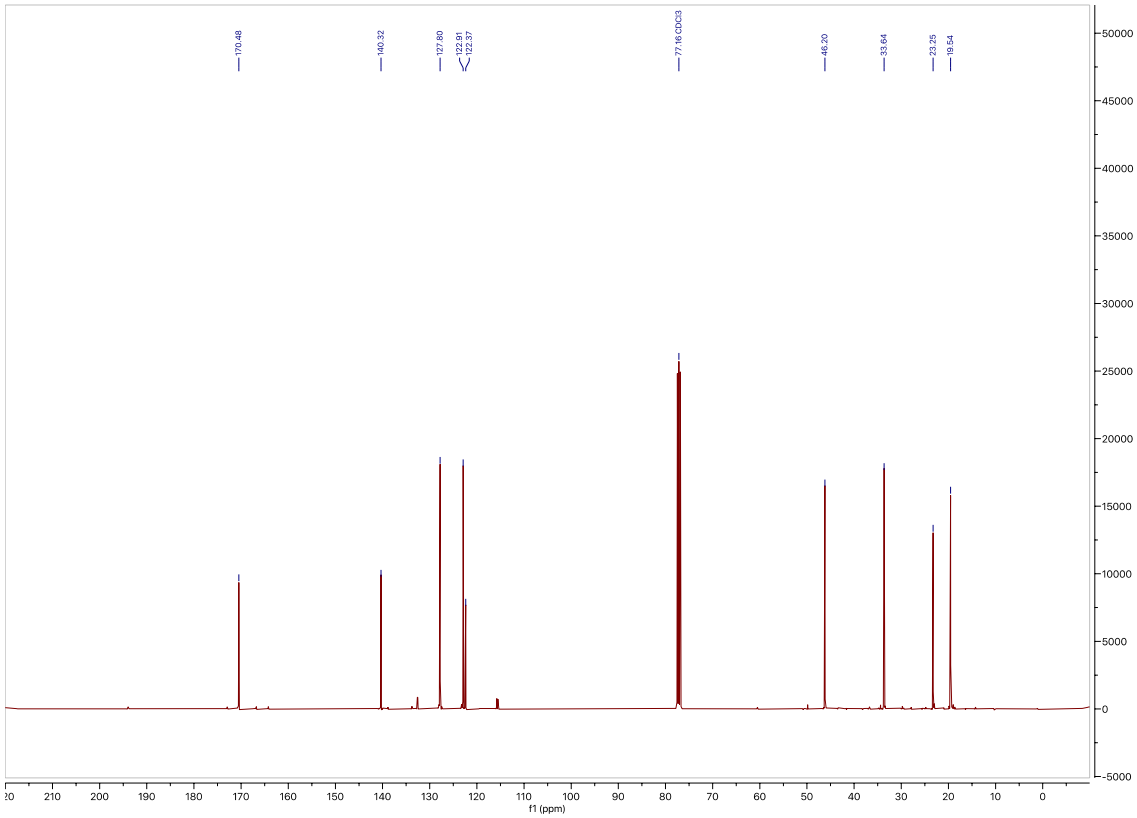
Product 17d


7.16
7.16
7.15
7.15
7.15
6.96
6.94
6.94
6.93
6.83
6.83
6.83
6.83
6.82
6.82
6.82
3.54
3.52
3.50
3.49
3.05
3.04
3.03
3.03
3.01
3.01
1.96
1.00
1.02
1.01
0.89
2.02
2.03
2.96
f1 (ppm)

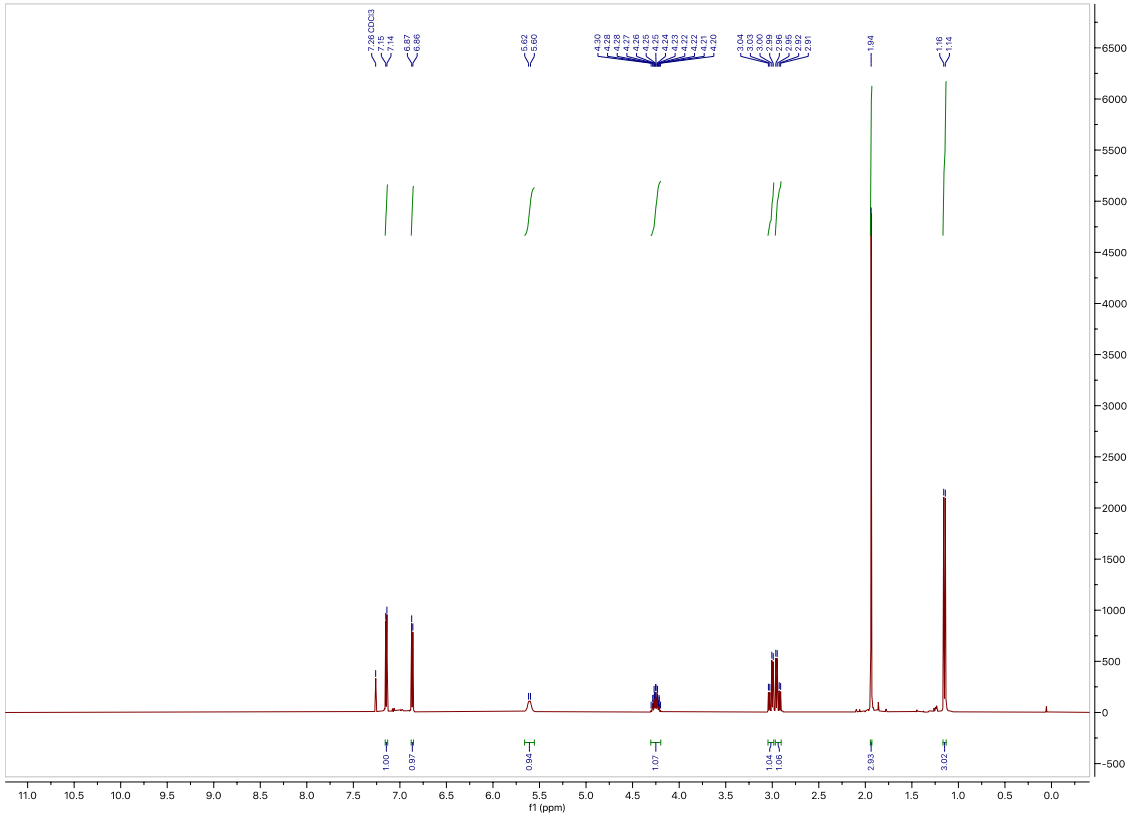

170.92
141.23
127.19
125.50
124.10
77.16 CDCl3
41.23
29.83
23.06
f1 (ppm)

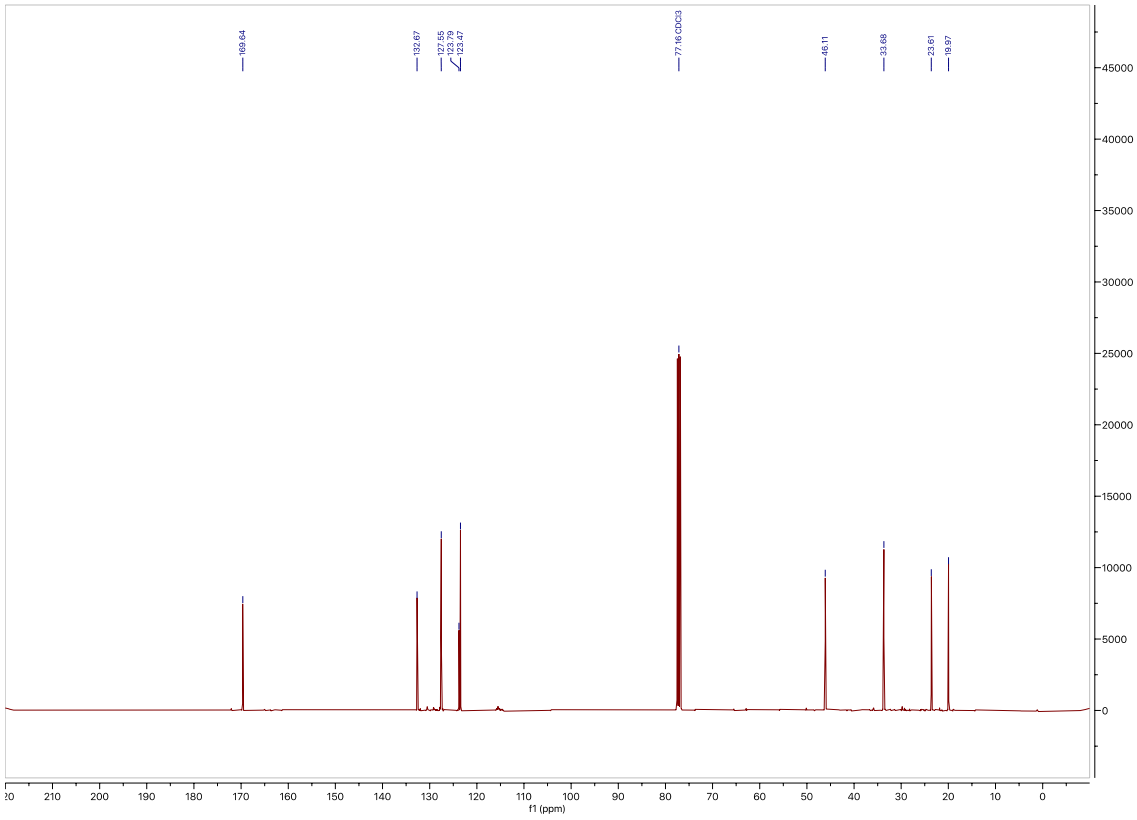
Product 17f



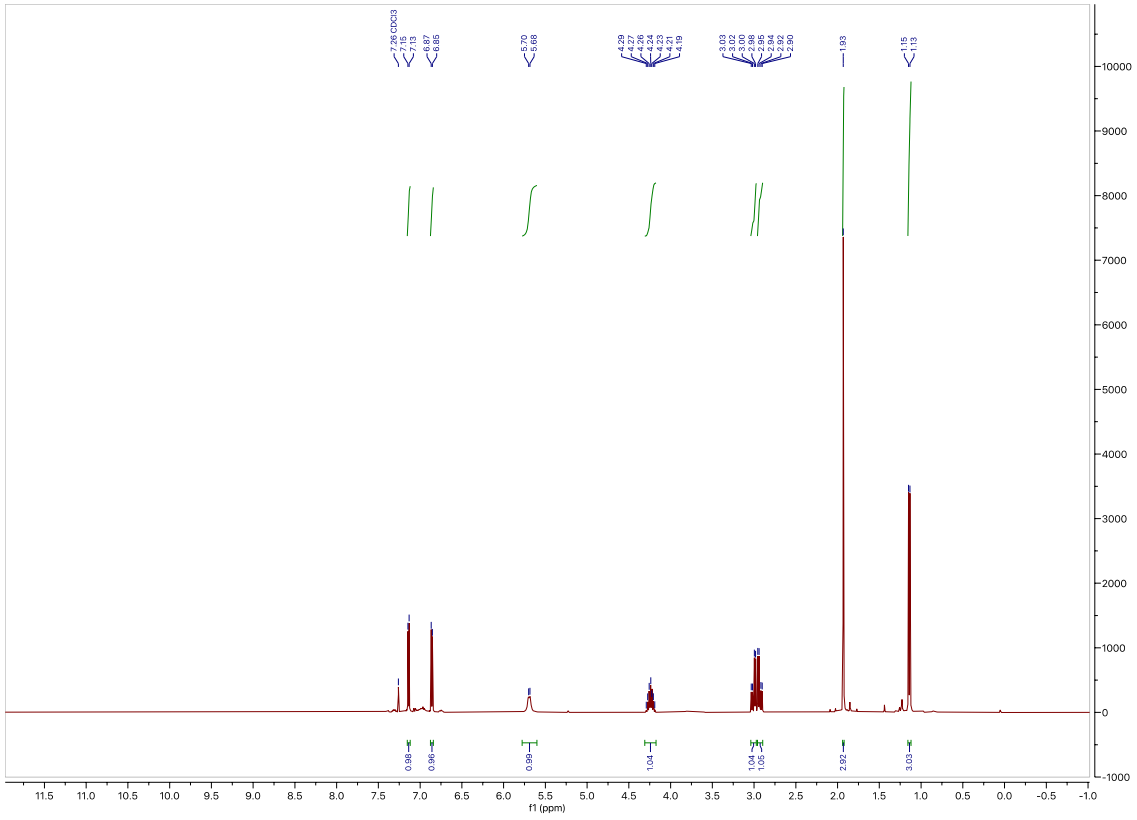


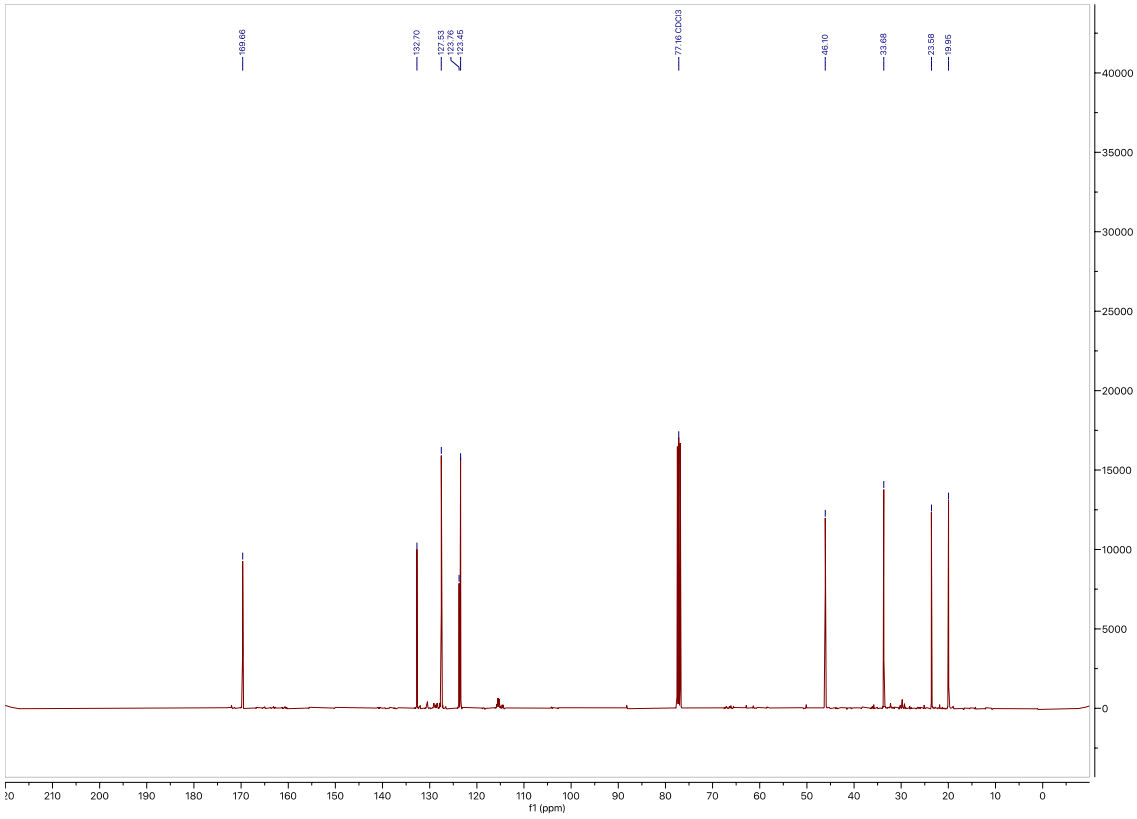
Product 17g


7.28 CDCl3
7.15
7.14
6.87
6.86
5.62
5.60
4.30
4.28
4.28
4.27
4.26
4.25
4.25
4.24
4.23
4.22
4.22
4.21
4.20
3.04
3.03
3.00
2.99
2.96
2.95
2.92
2.91
1.94
1.16
1.14
1.00
0.97
0.94
1.07
1.04
1.06
2.93
3.02
f1 (ppm)

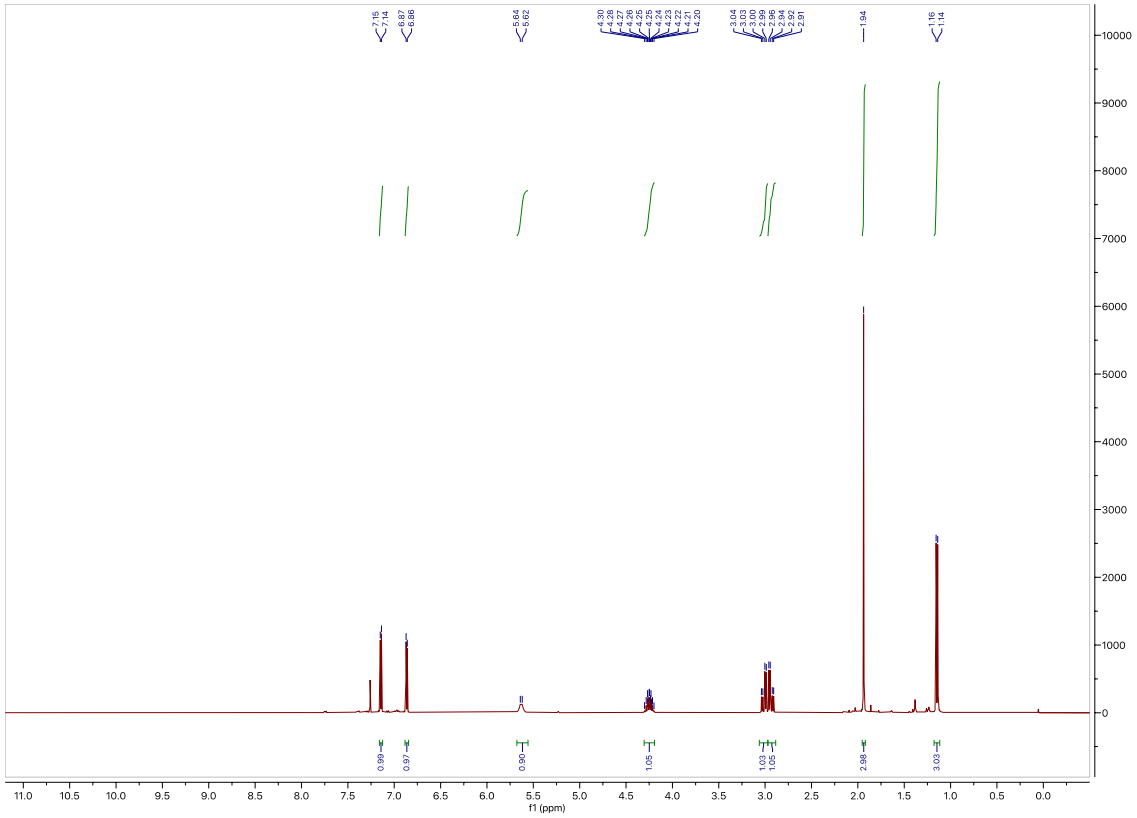

169.64
132.67
127.55
123.79
123.47
77.16 CDCl3
46.11
33.68
23.61
19.97
f1 (ppm)

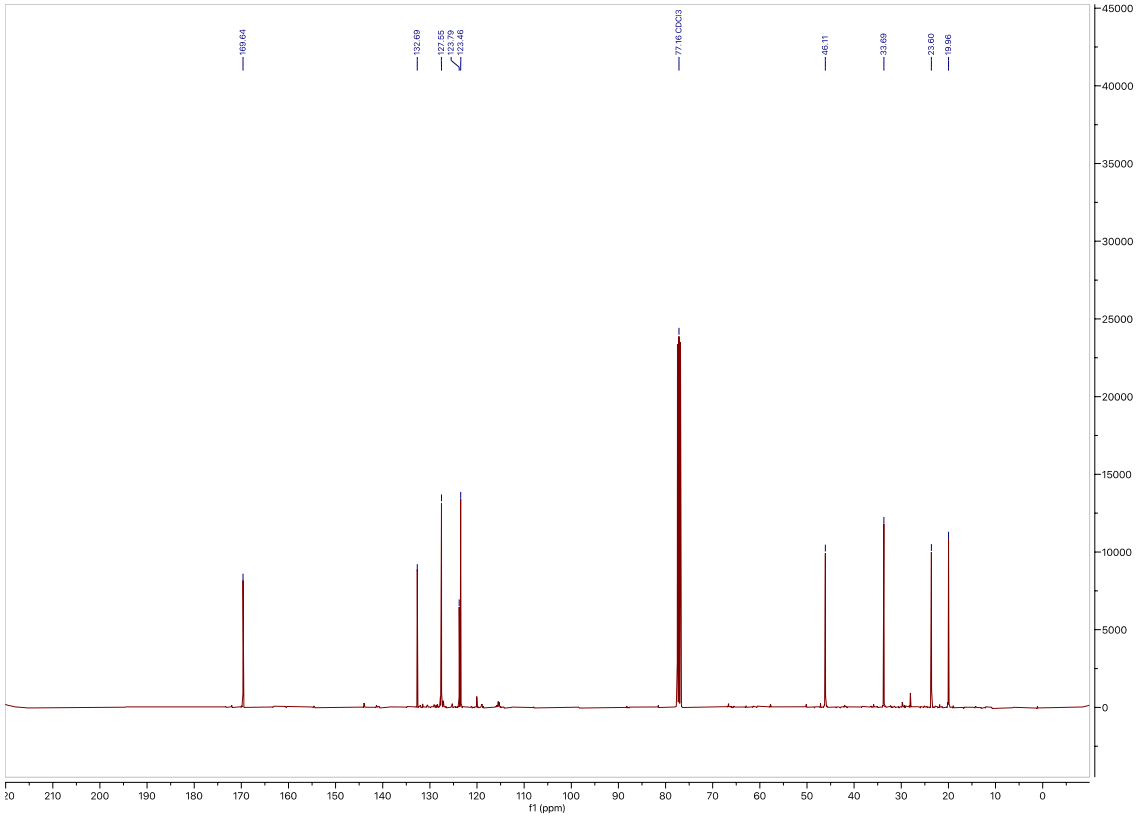
Product *S*-17g



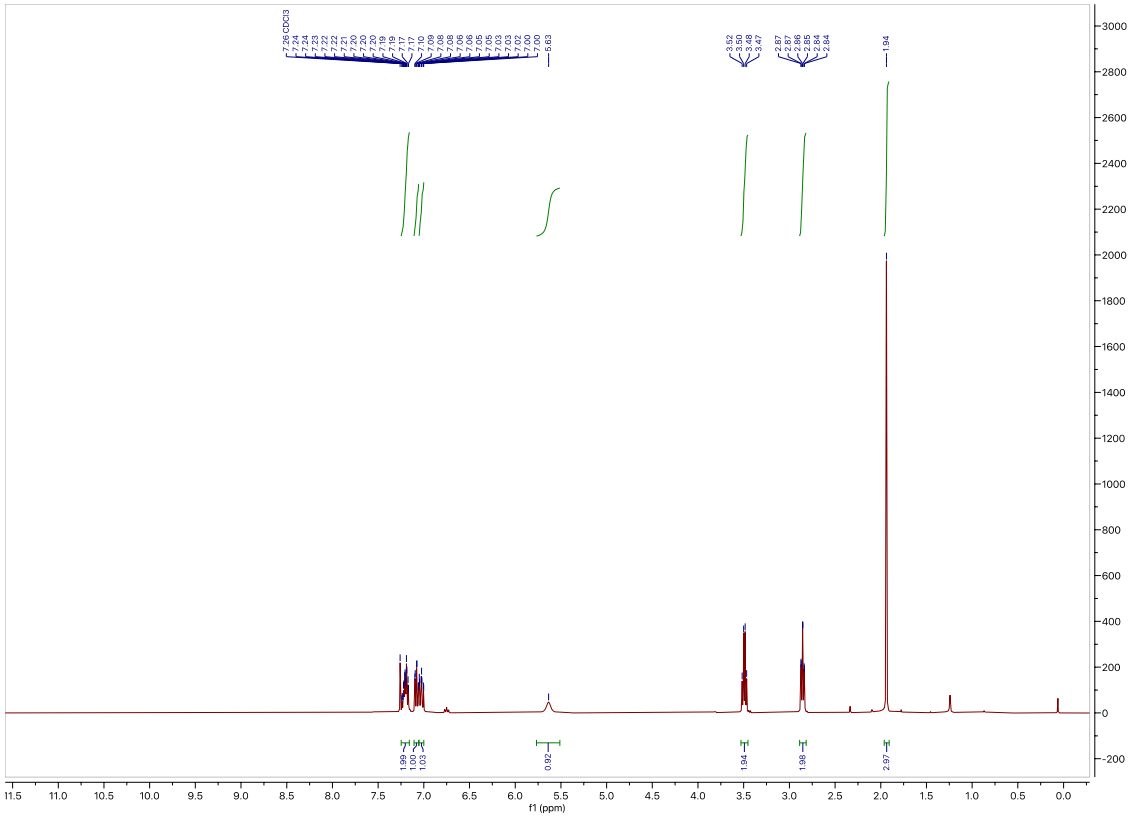


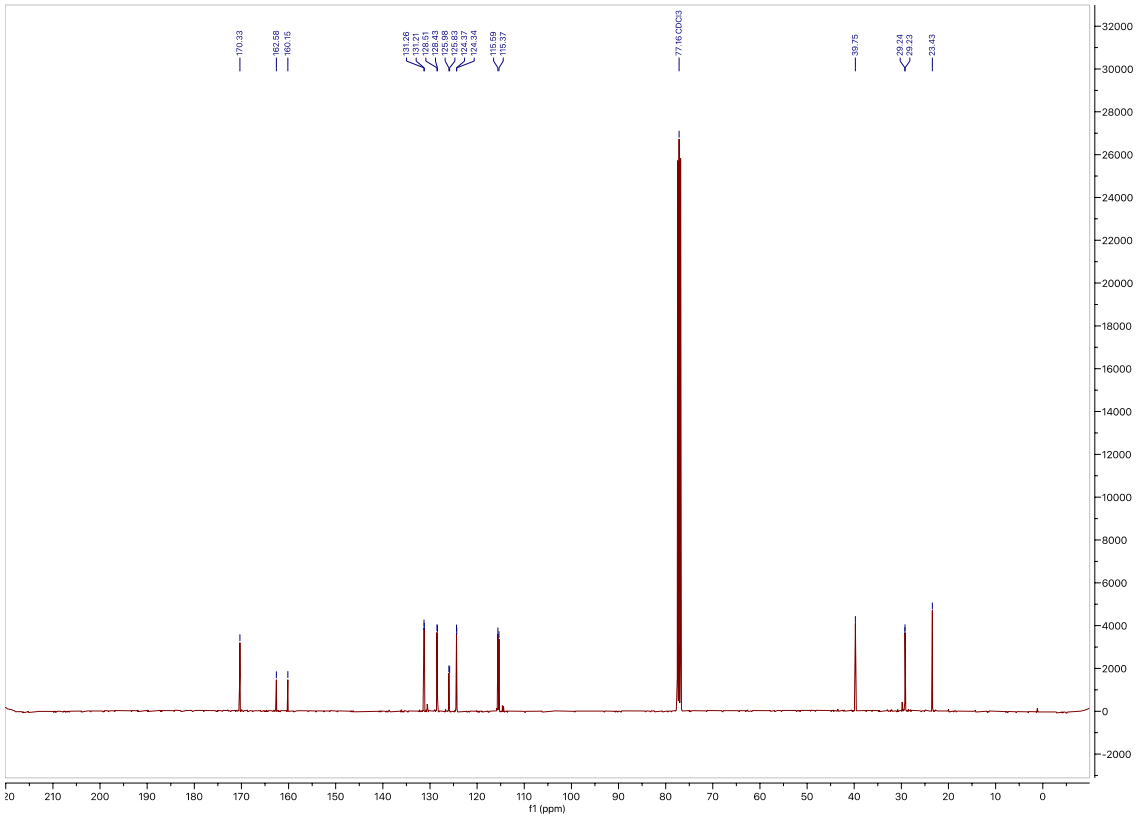
Product *R*-17g



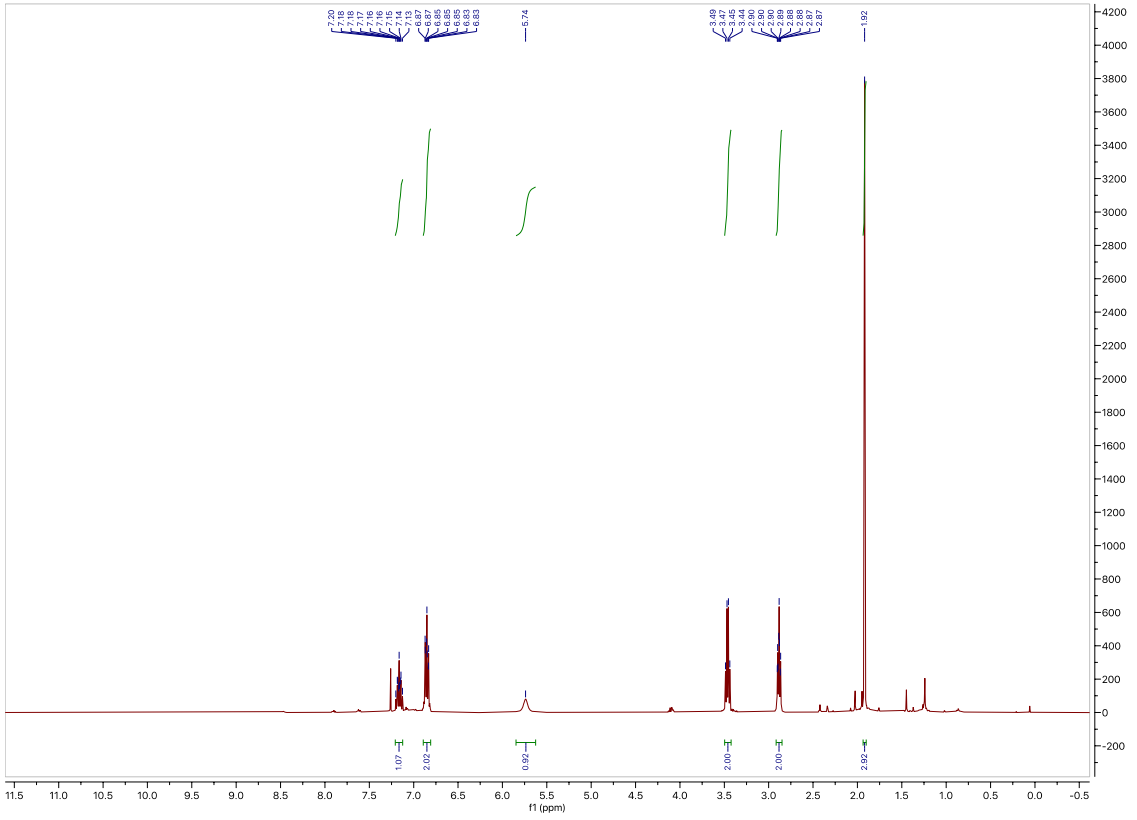


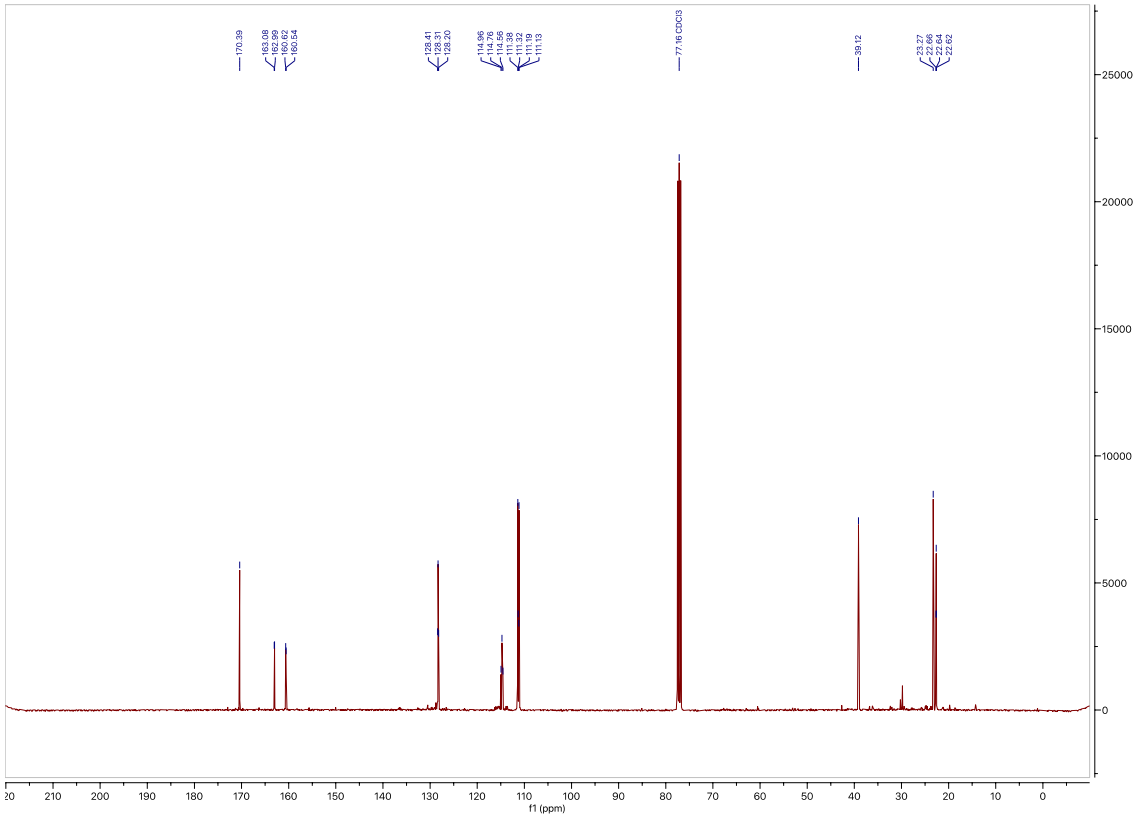
Product 17h


7.26 CDCl3
7.24
7.23
7.22
7.21
7.20
7.20
7.20
7.19
7.18
7.17
7.17
7.10
7.09
7.08
7.08
7.06
7.06
7.05
7.05
7.03
7.03
7.02
7.00
7.00
5.63
3.52
3.50
3.48
3.47
2.87
2.87
2.86
2.85
2.84
2.84
1.94
1.99
1.00
1.03
0.92
1.94
1.98
2.97
f1 (ppm)

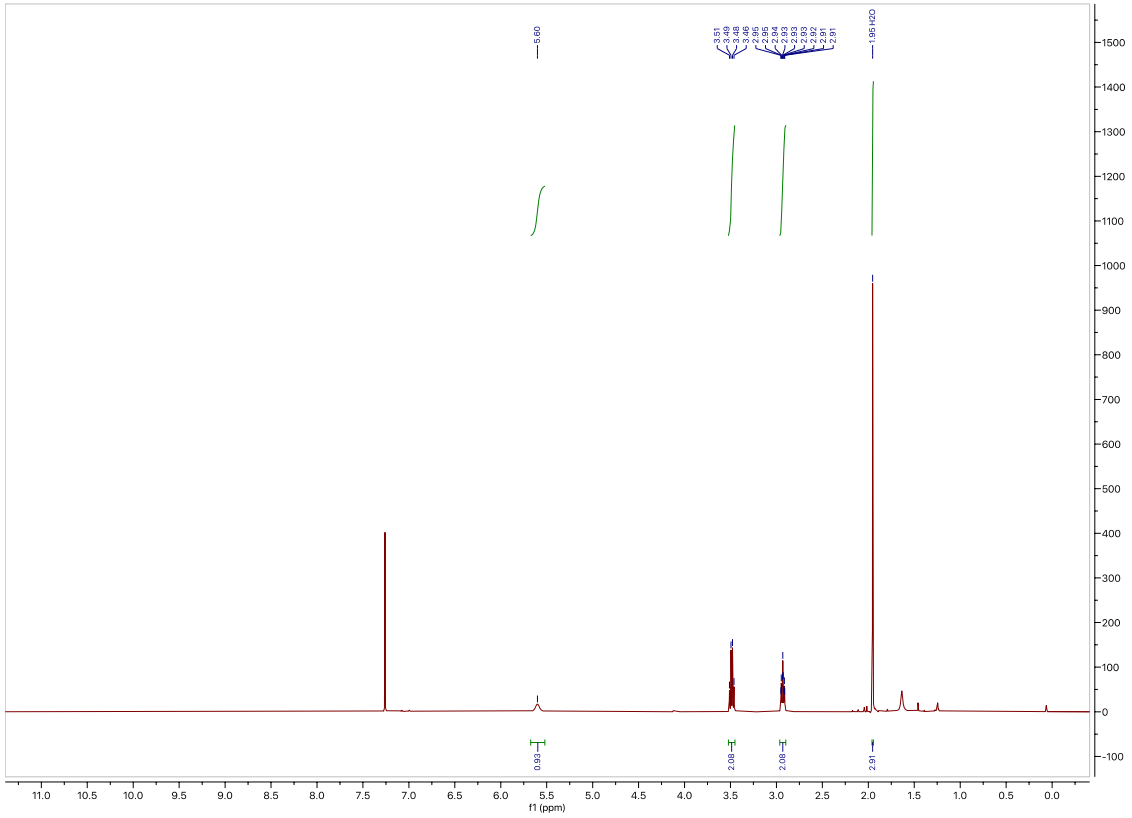

170.33
162.58
160.15
131.26
131.21
128.61
128.43
125.98
125.83
124.37
124.34
115.59
115.37
77.16 CDCl3
39.75
29.24
29.23
23.43
f1 (ppm)

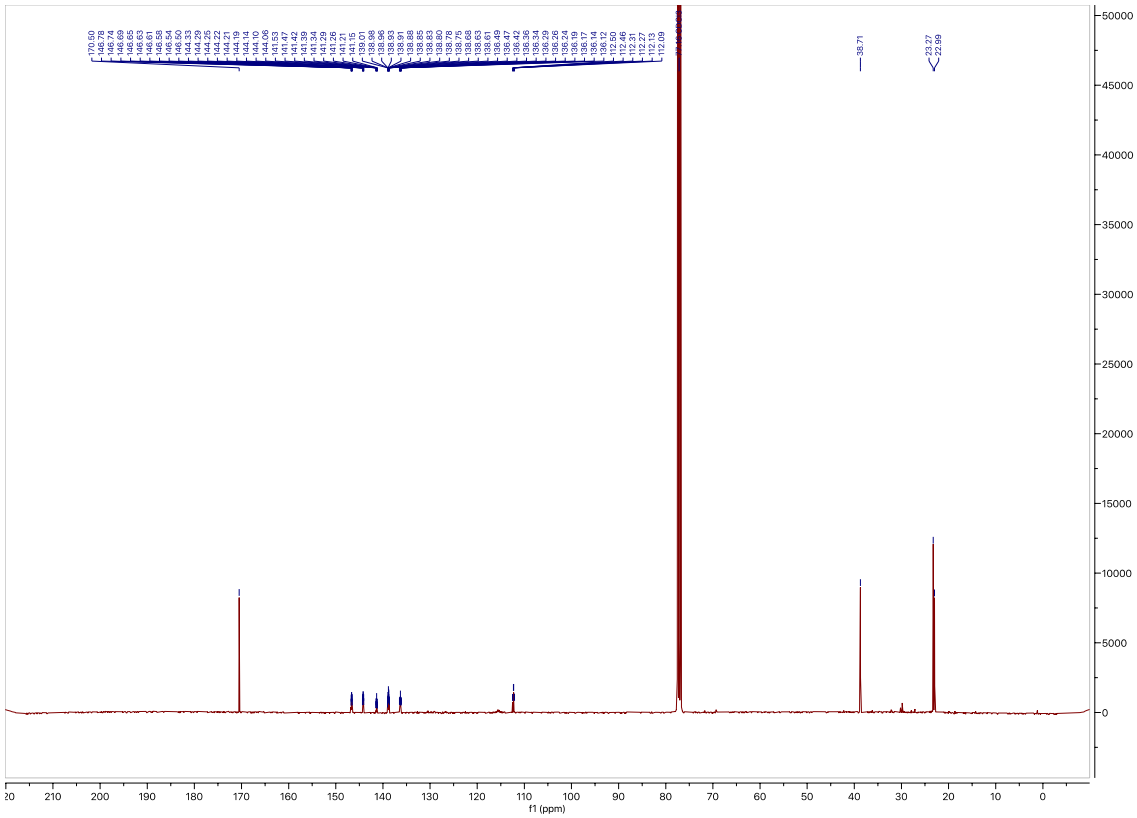
Product 17i


7.20
7.18
7.17
7.16
7.16
7.15
7.14
7.13
6.87
6.87
6.85
6.85
6.85
6.83
6.83
5.74
3.49
3.47
3.45
3.44
2.90
2.90
2.89
2.88
2.88
2.87
2.87
1.92
1.07
2.02
0.92
2.00
2.00
2.92
f1 (ppm)

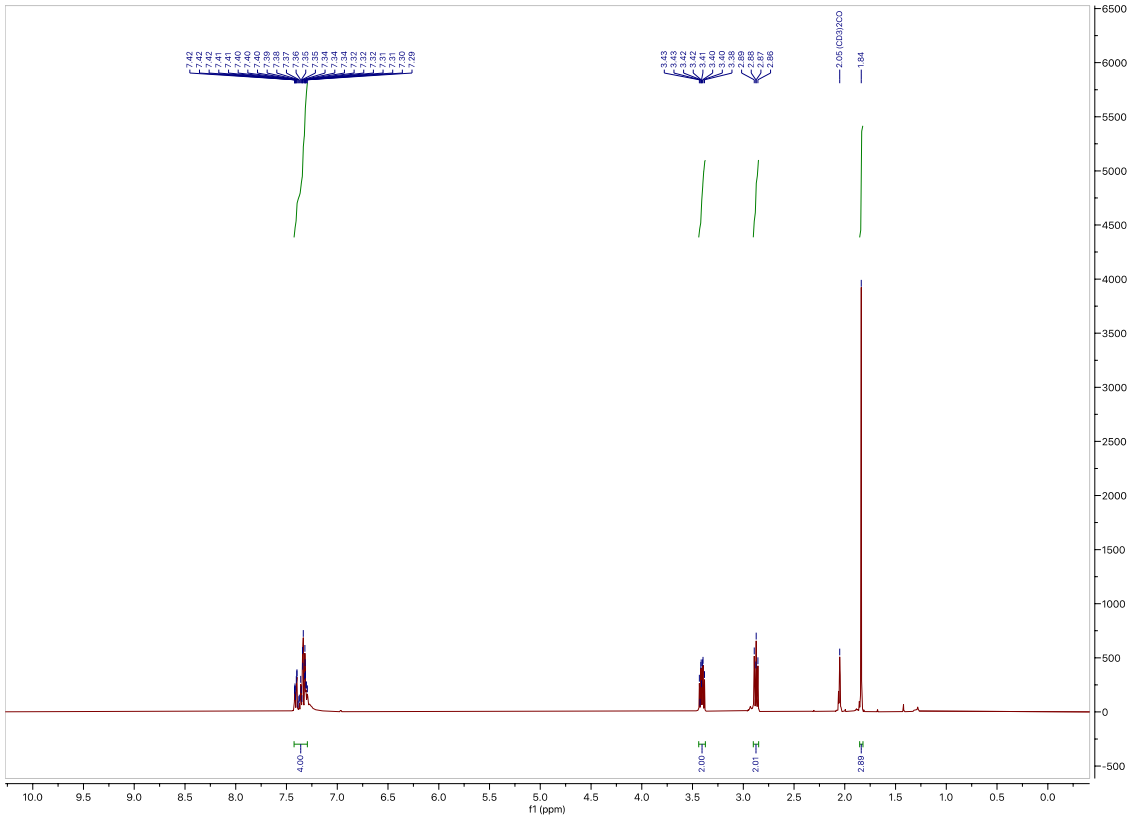

170.39
163.08
162.99
160.62
160.54
128.41
128.31
128.20
114.96
114.96
114.56
111.38
111.32
111.19
111.13
77.16 CDCl3
39.12
23.27
22.66
22.64
22.62
f1 (ppm)

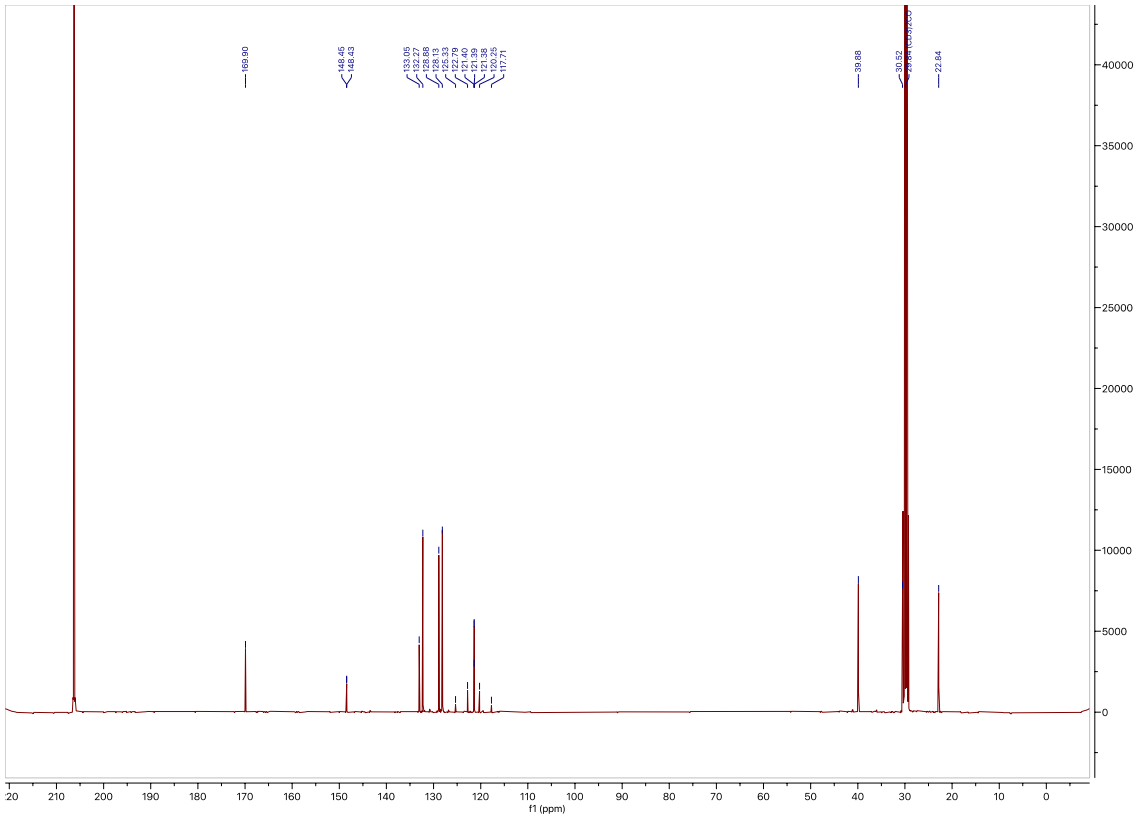
Product 17j


5.60
3.51
3.49
3.48
3.46
2.96
2.95
2.94
2.93
2.93
2.92
2.91
1.95 H2O
0.93
2.08
2.08
2.91
f1 (ppm)

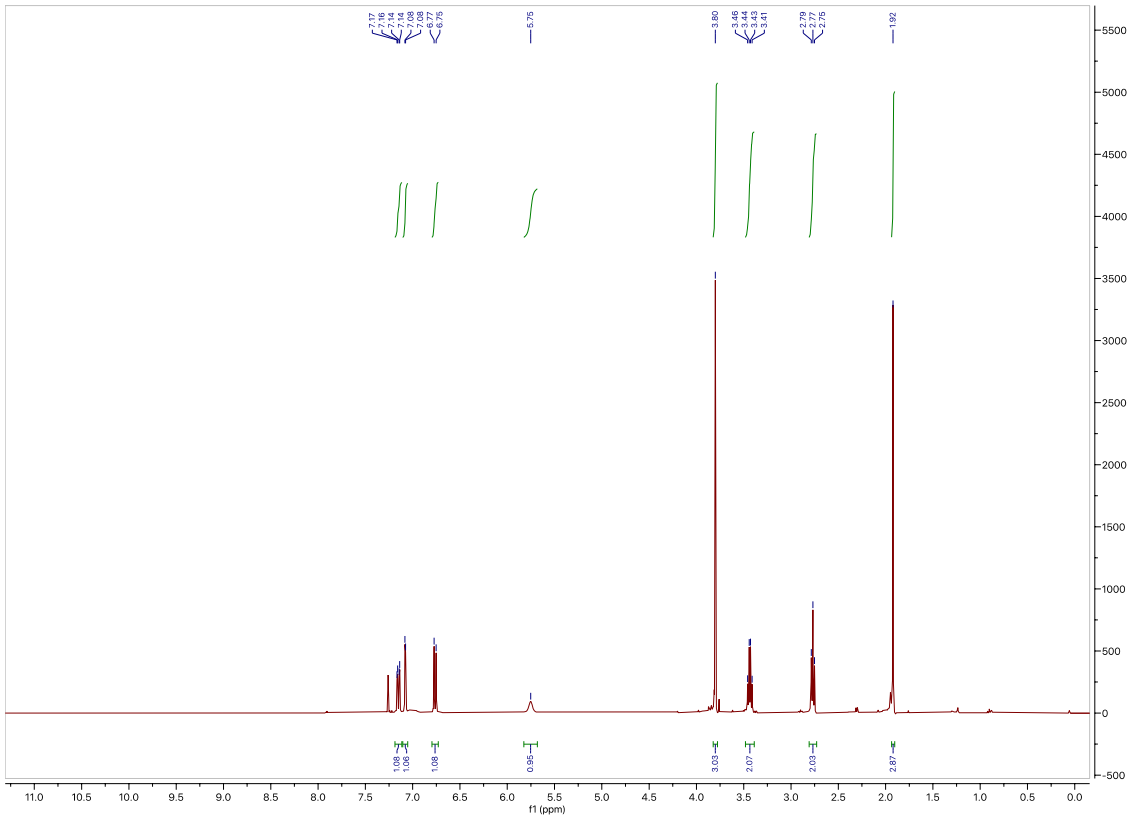

38.71
23.27
22.99
f1 (ppm)

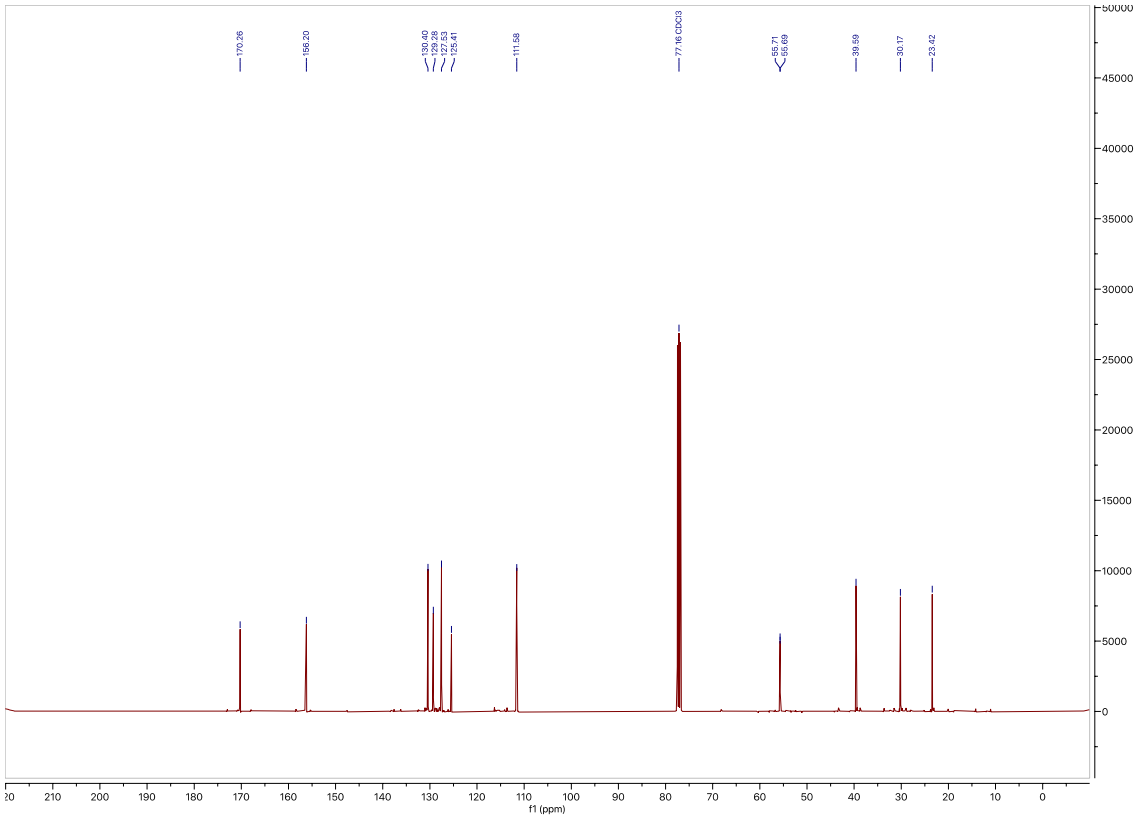
Product 17k


7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.40
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.30
7.29
3.43
3.42
3.42
3.42
3.41
3.40
3.40
3.39
3.38
2.89
2.88
2.87
2.86
2.05 (CD3)2CO
1.84
4.00
2.00
2.01
2.89
f1 (ppm)

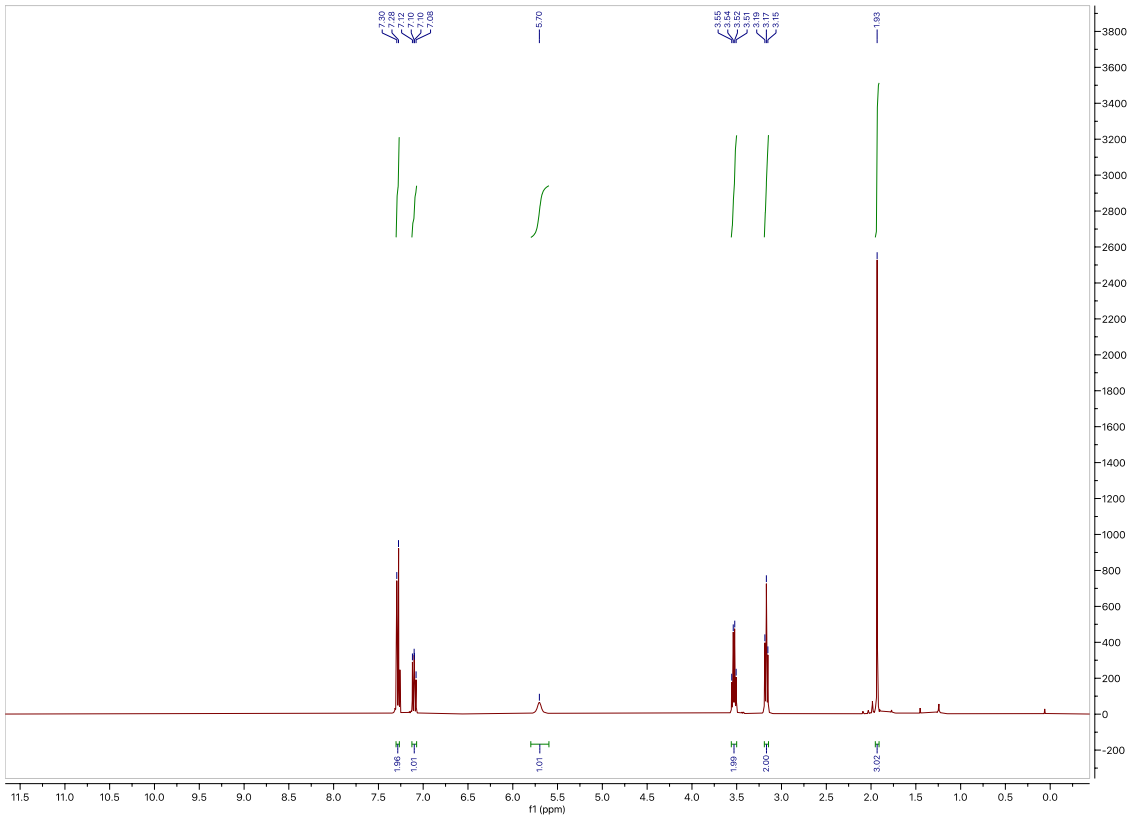

169.90
148.45
148.43
133.05
132.27
128.88
128.51
125.33
122.79
121.46
121.39
120.25
117.71
39.88
30.52
29.84 (CD3)2CO
22.84
f1 (ppm)

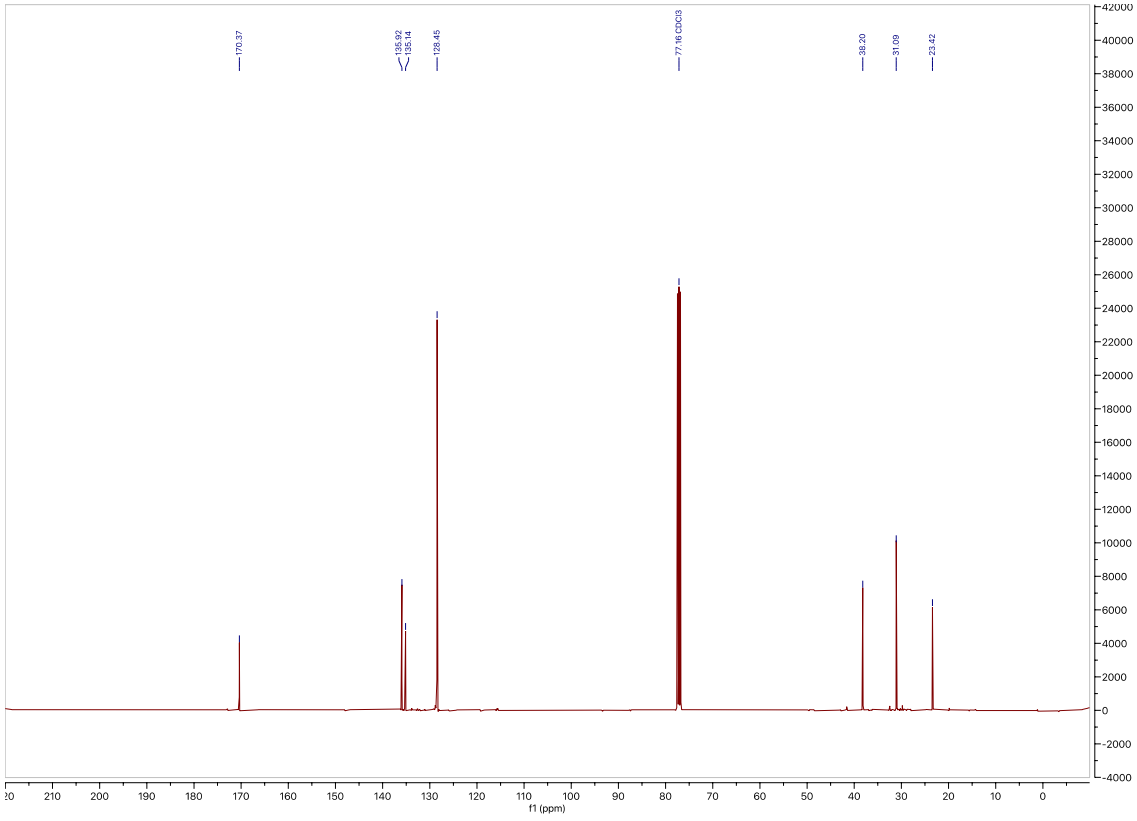
Product 17l


7.17
7.16
7.14
7.08
7.08
6.77
6.75
5.75
3.80
3.46
3.44
3.43
3.41
2.79
2.77
2.75
1.92
1.08
1.08
1.08
0.95
3.03
2.07
2.03
2.87
f1 (ppm)

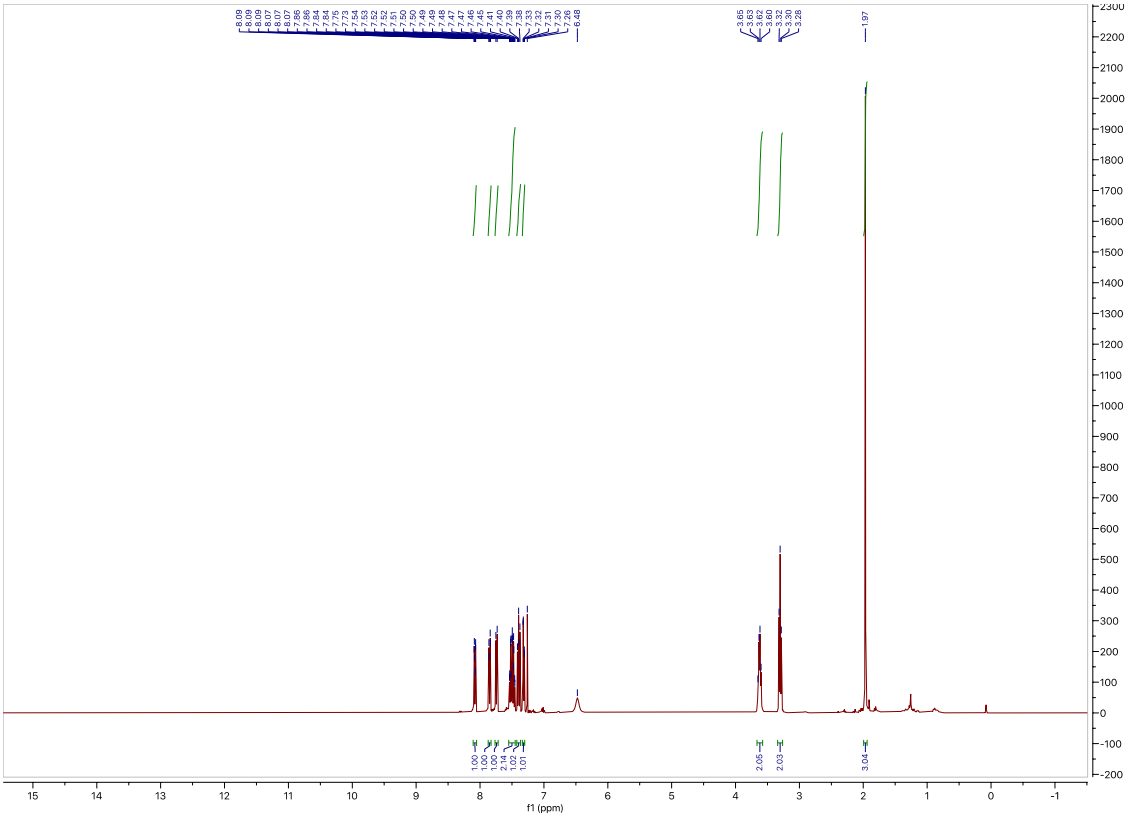

170.26
156.20
130.49
129.28
127.53
125.41
111.58
77.16 CDCl3
65.71
64.69
39.59
30.17
23.42
f1 (ppm)

Product 17m


7.30
7.29
7.12
7.10
7.09
7.08
5.70
3.55
3.54
3.52
3.51
3.19
3.17
3.15
1.93
1.96
1.01
1.01
1.99
2.00
3.02
f1 (ppm)


170.37
135.92
135.14
128.45
77.16 CDCl3
38.20
31.09
23.42
f1 (ppm)

Product 17n


8.09
8.09
8.09
8.08
8.07
8.07
7.86
7.86
7.84
7.84
7.76
7.73
7.54
7.53
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.41
7.40
7.39
7.38
7.33
7.32
7.31
7.30
7.26
6.48
3.65
3.63
3.62
3.60
3.32
3.30
3.28
1.97
1.00
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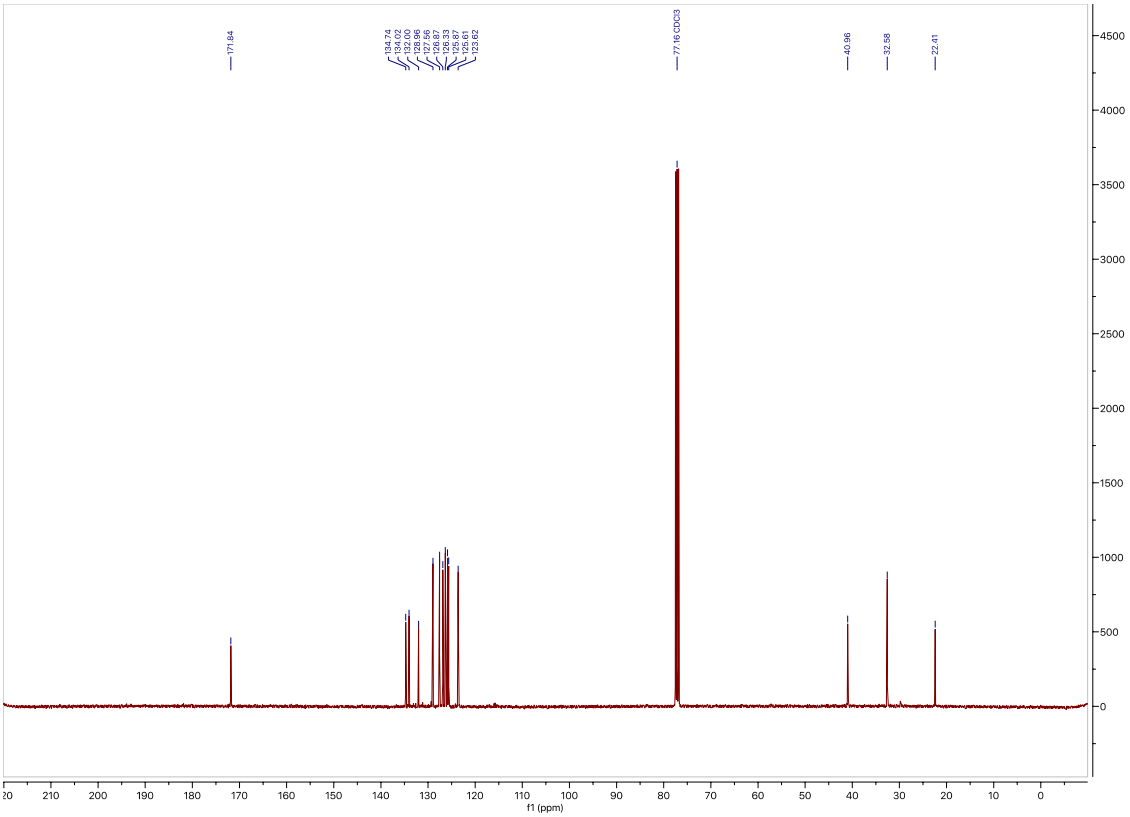
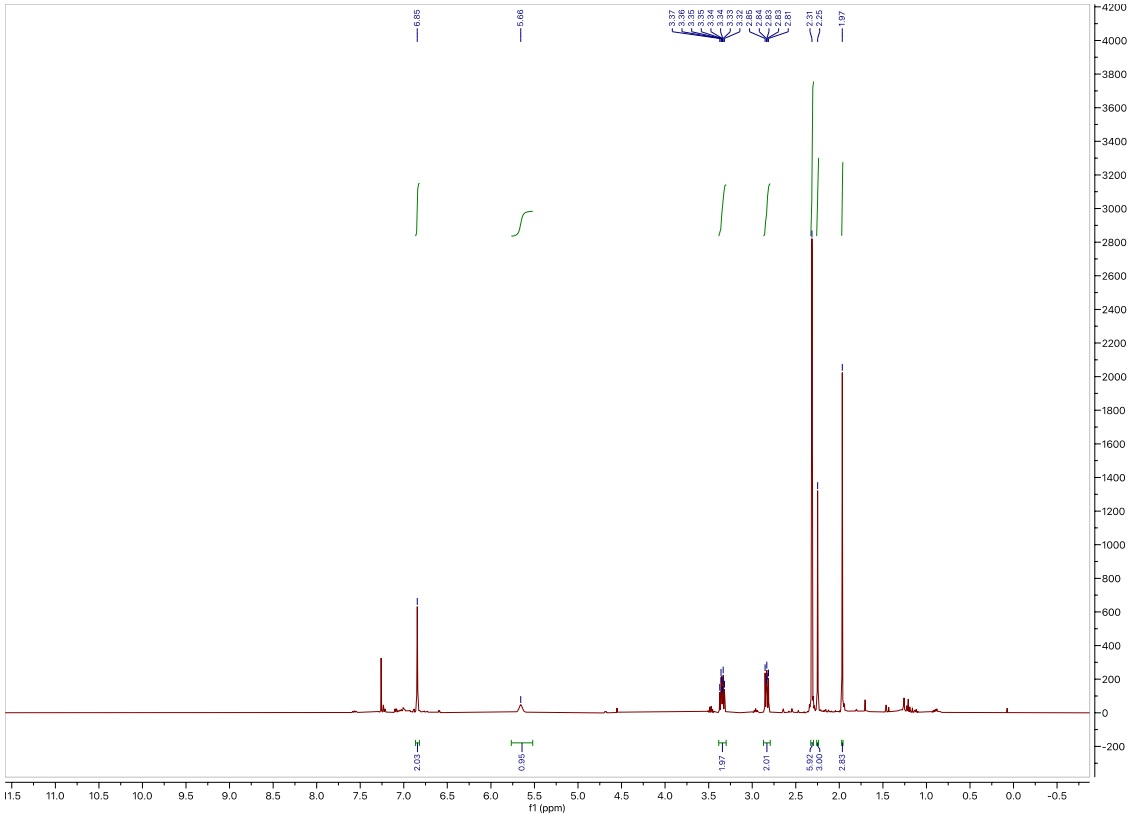
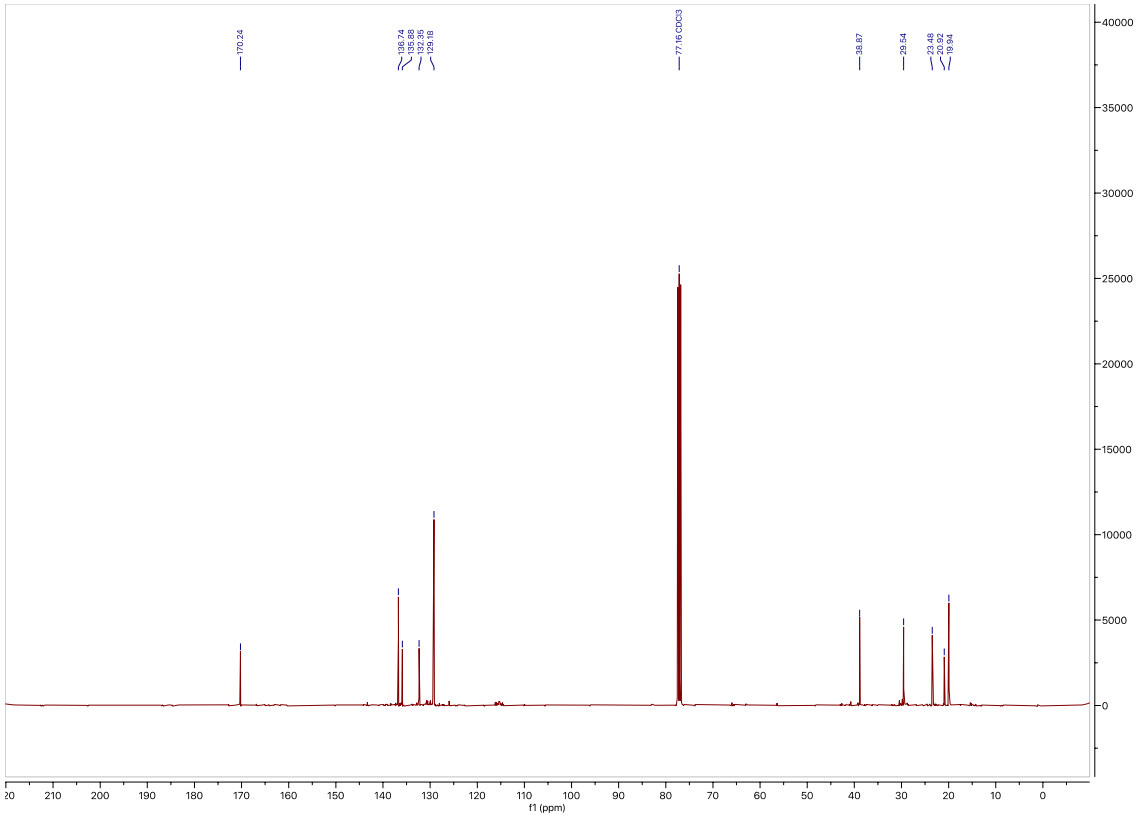
1.00
1.00
2.14
1.02
1.01
2.05
2.03
3.04
f1 (ppm)

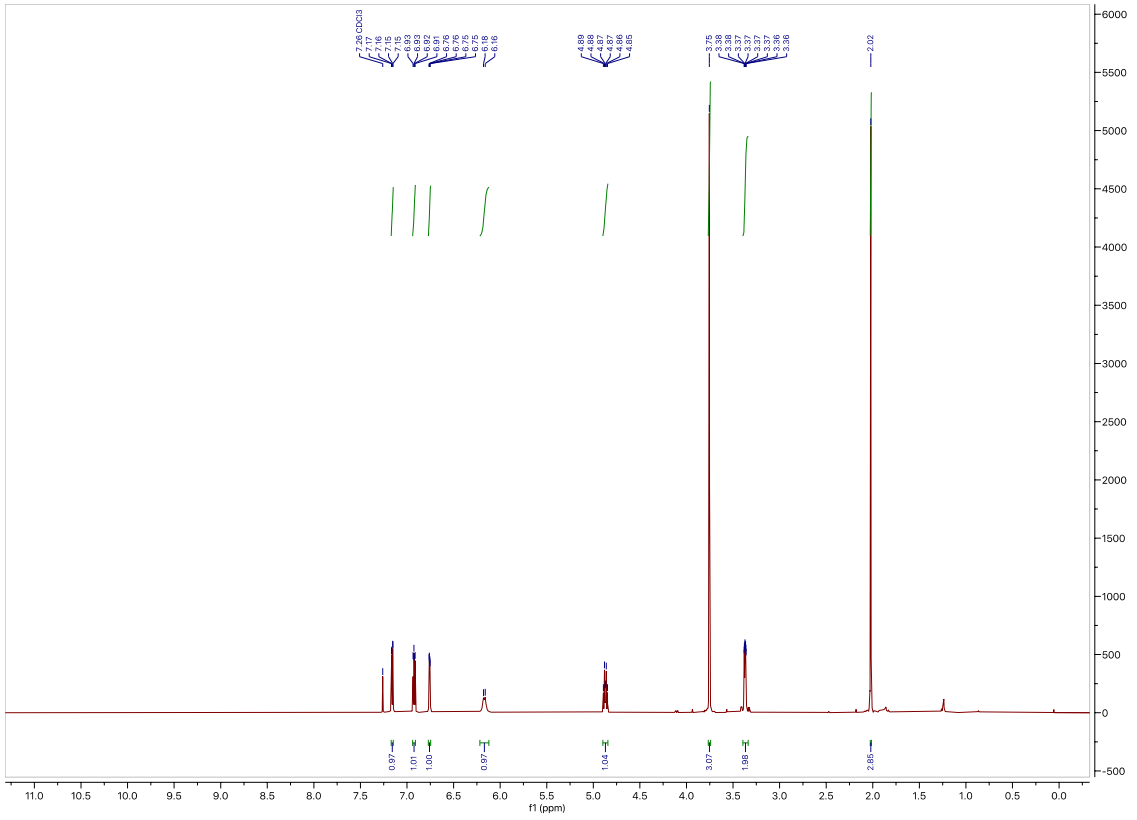

171.84
134.74
134.02
133.00
128.96
127.56
126.93
126.83
125.87
125.61
125.02
77.16 CDCl3
40.96
32.58
22.41
f1 (ppm)

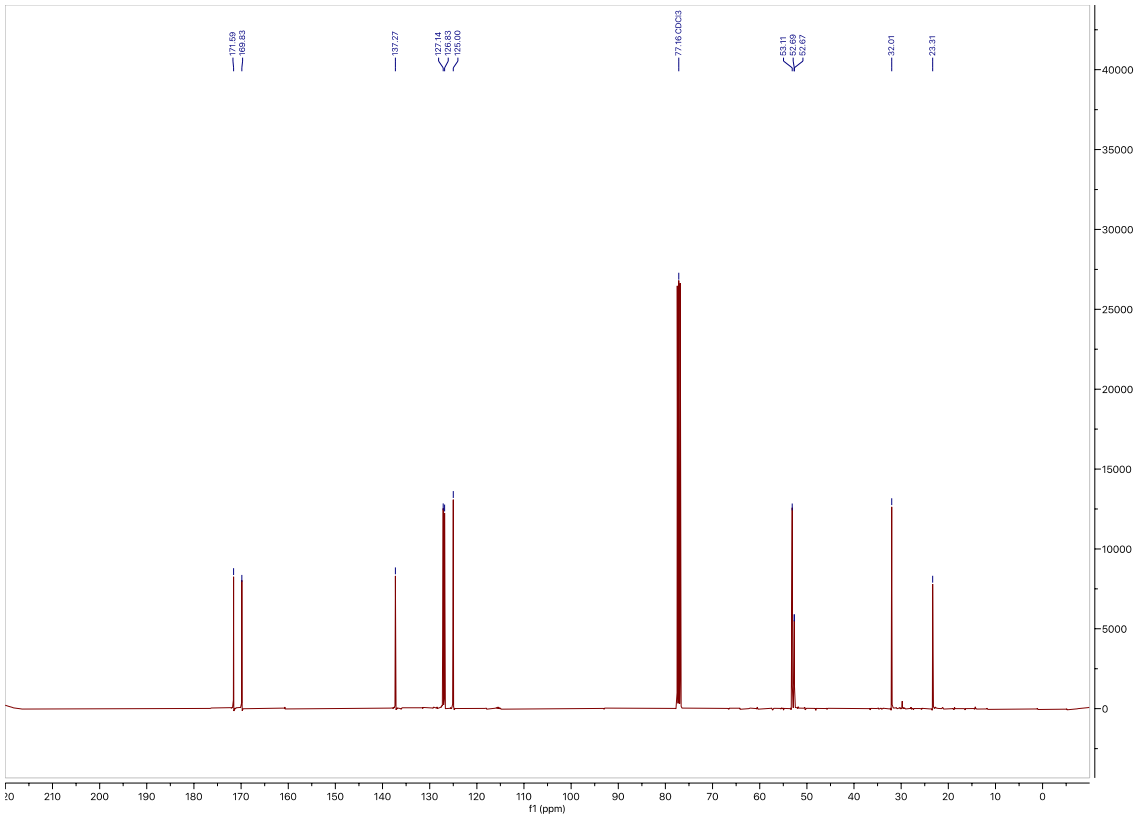
Product 17o


6.85
5.68
3.37
3.36
3.35
3.35
3.34
3.34
3.33
3.32
2.85
2.84
2.83
2.83
2.81
2.31
2.25
1.97
2.03
0.95
1.97
2.01
5.92
3.00
2.83
f1 (ppm)

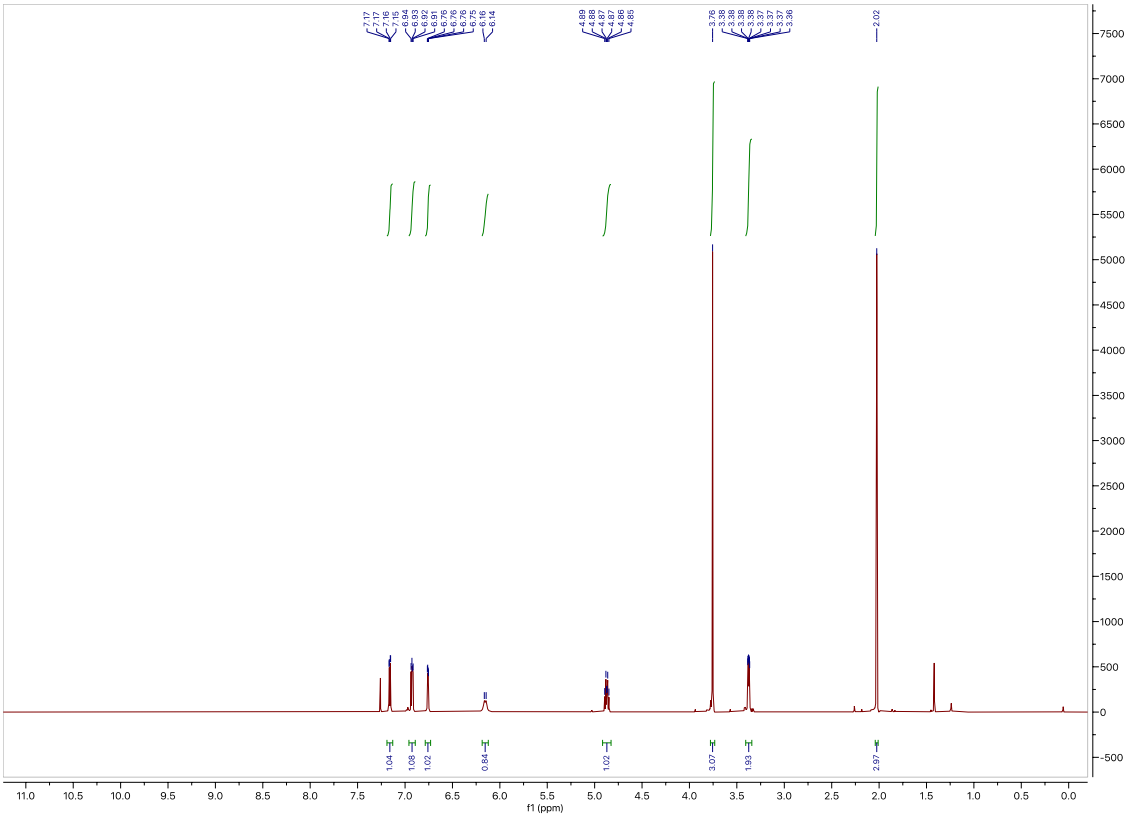

170.24
136.74
135.88
132.45
129.18
77.16 CDCl3
38.87
29.54
23.48
20.92
19.94
f1 (ppm)

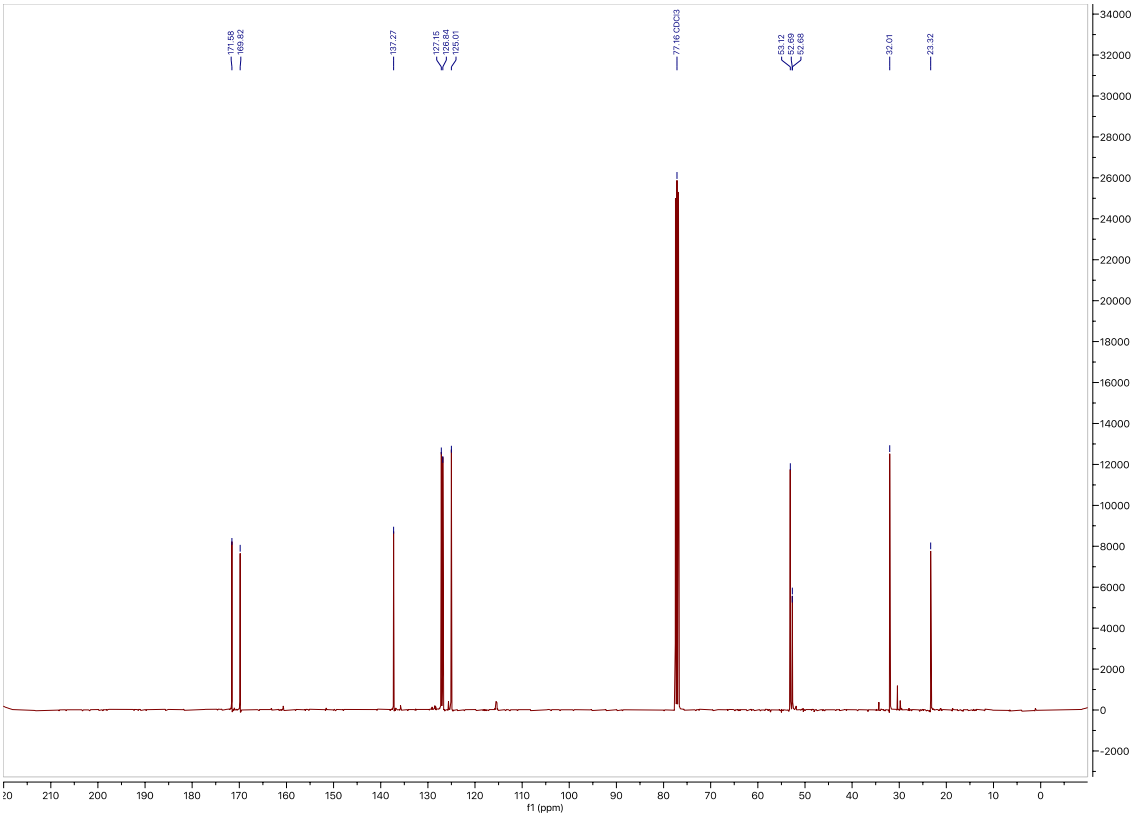
Product 17p


7.26 CDCl3
7.17
7.16
7.15
6.93
6.92
6.91
6.76
6.75
6.75
6.18
6.16
4.89
4.88
4.87
4.87
4.86
4.85
3.75
3.38
3.38
3.37
3.37
3.37
3.36
3.36
2.02
0.97
1.01
1.00
0.97
1.04
3.07
1.98
2.65
f1 (ppm)


171.59
169.83
137.27
127.14
126.83
125.00
77.16 CDCl3
53.11
52.69
52.67
32.01
23.31
f1 (ppm)

Product *rac*-17p





References

1. T. Patra, S. Mukherjee, J. Ma, F. Strieth-Kalthoff, F. Glorius, *Angew. Chem. Int. Ed.* **2019**, *58*, 10514 – 10520.