Enantioselective Synthesis of Atropisomeric Benzamides through Peptide-Catalyzed Bromination

Supporting Information (Part II)

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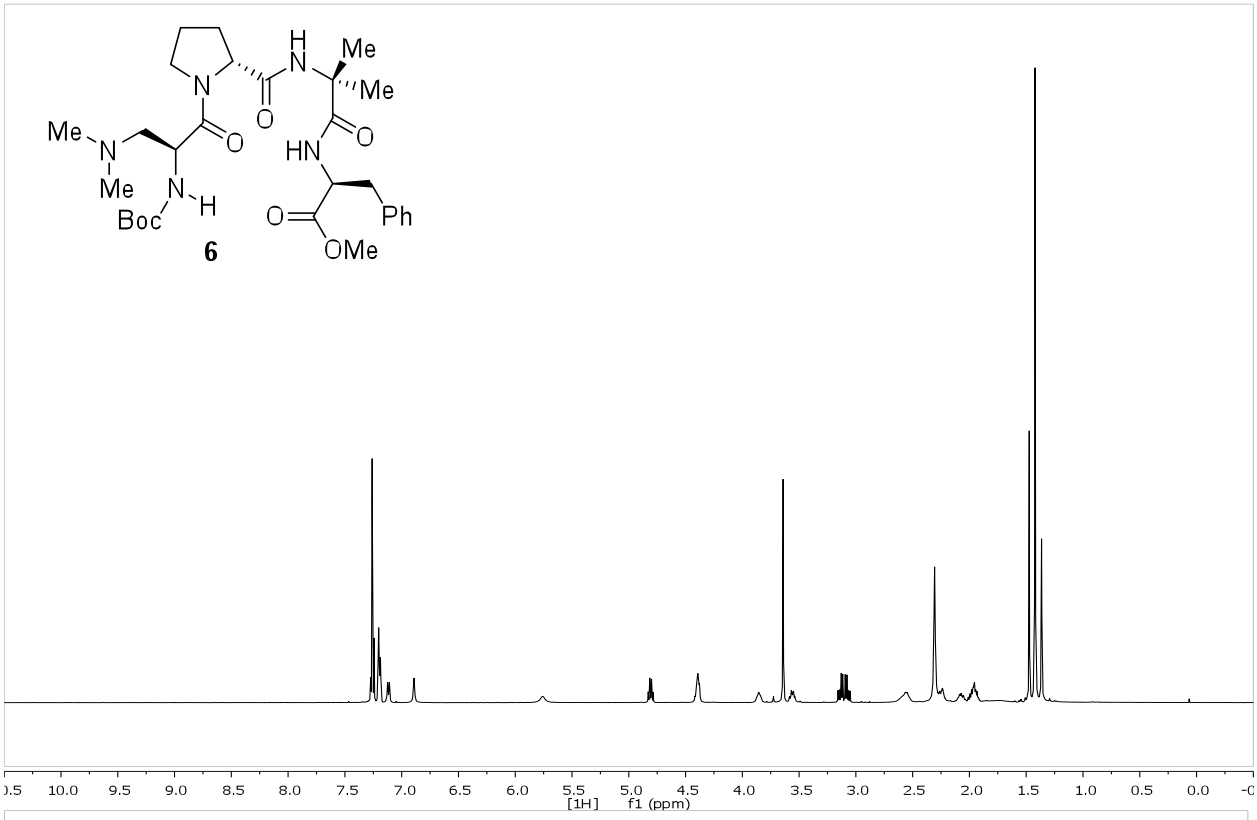
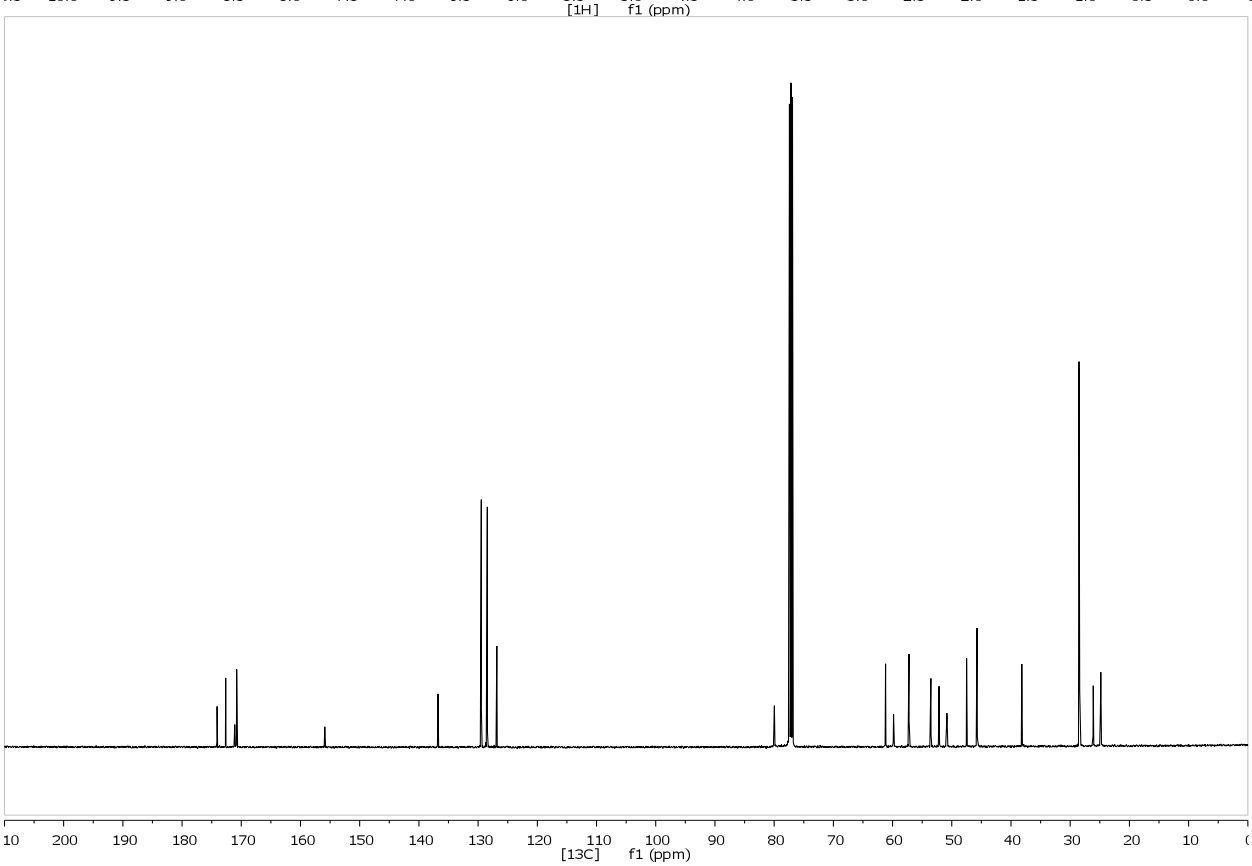
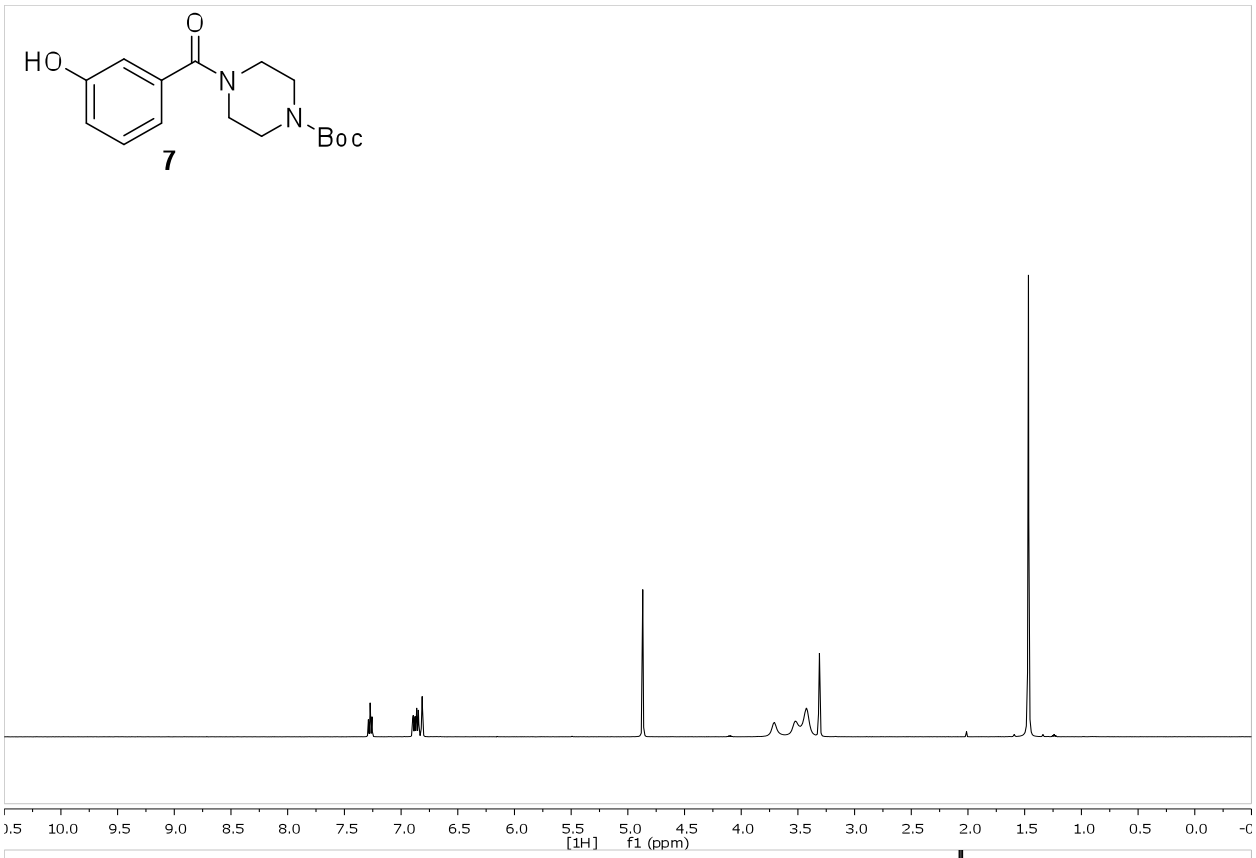
Table of Contents

X. ^{1}H and ^{13}C Spectra For Catalyst, Substrates, and Products



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O
N
N
Boc
7
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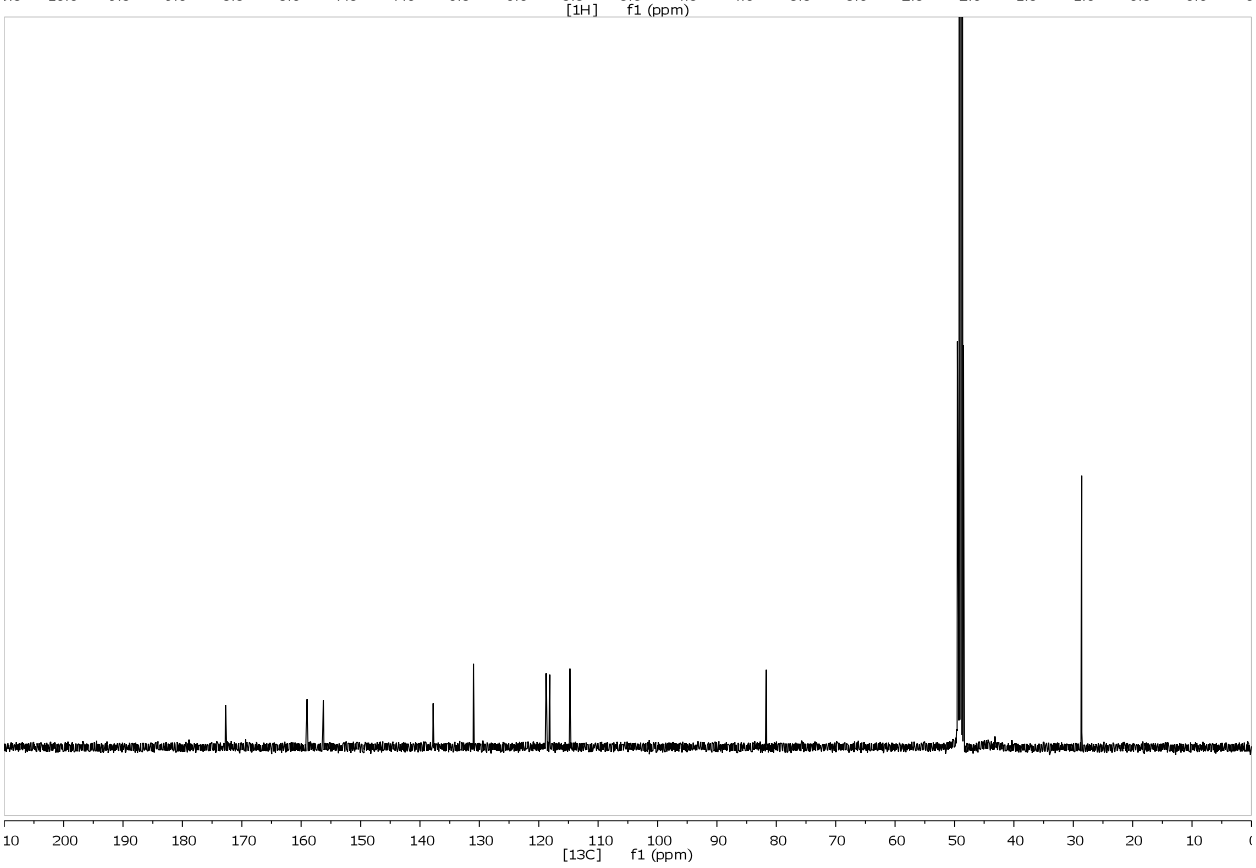
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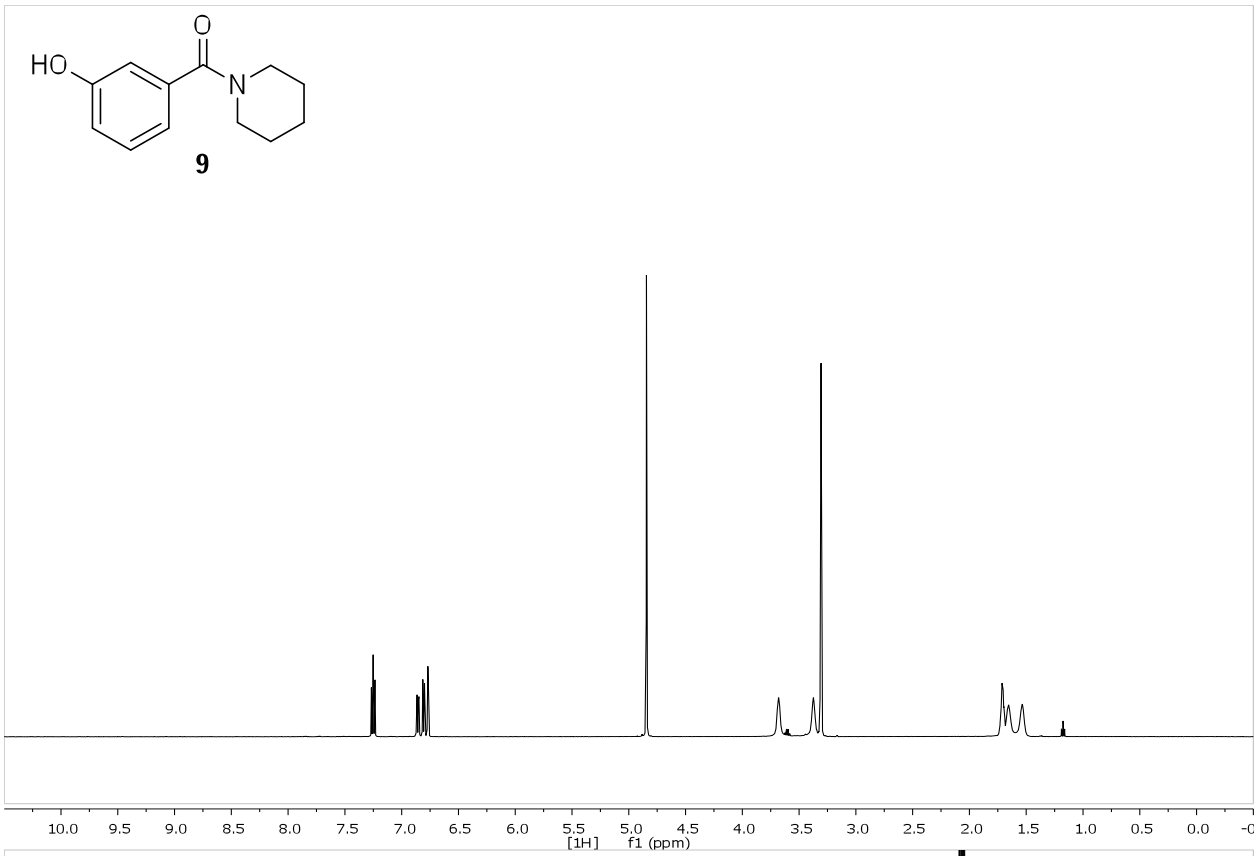
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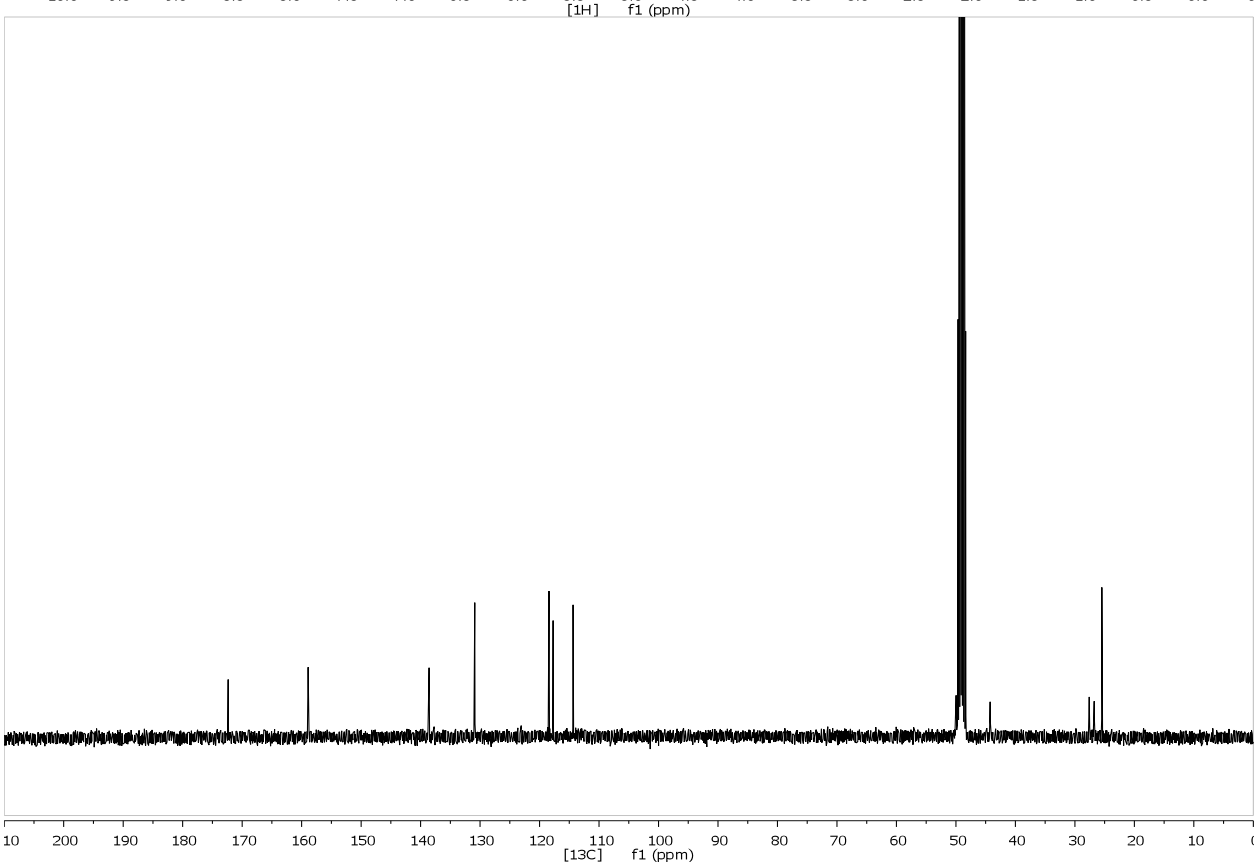
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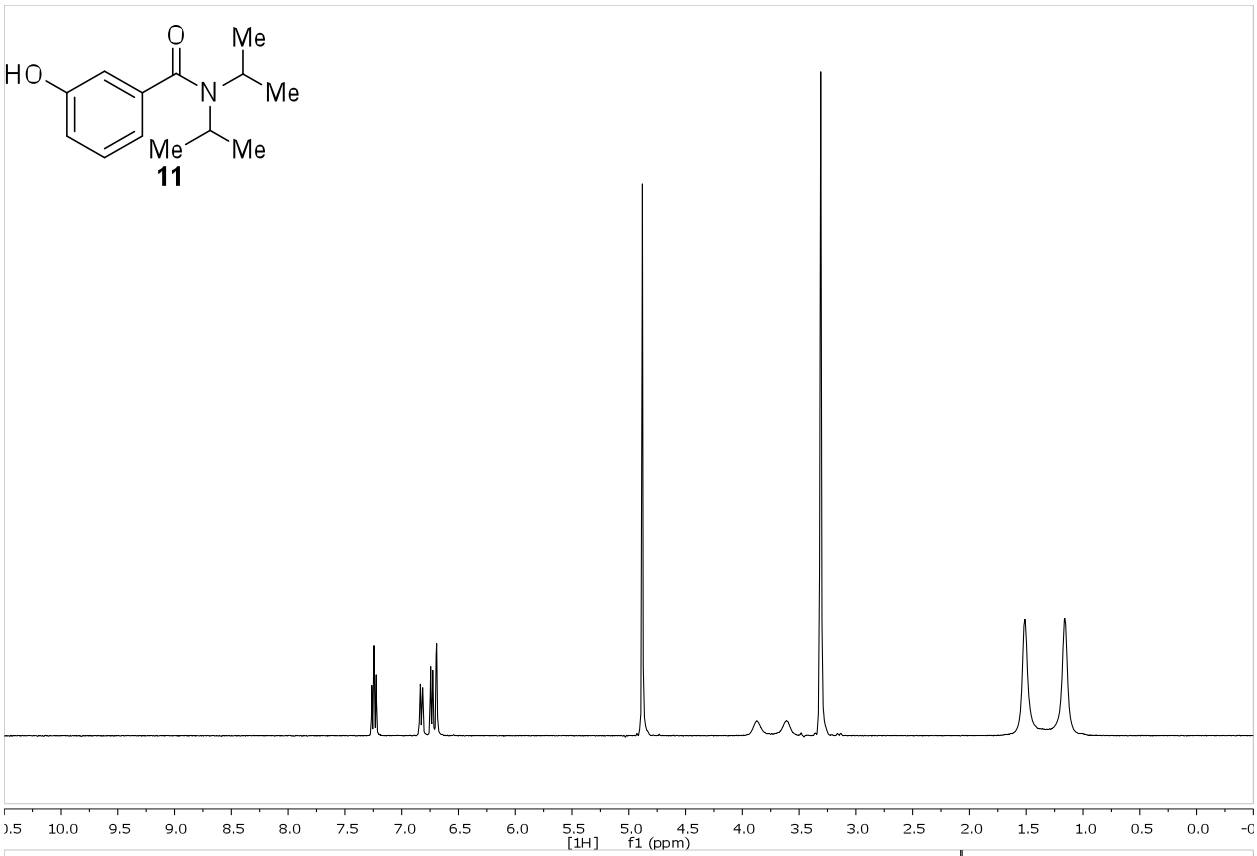
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O
N
Me
Me
Me
Me
11
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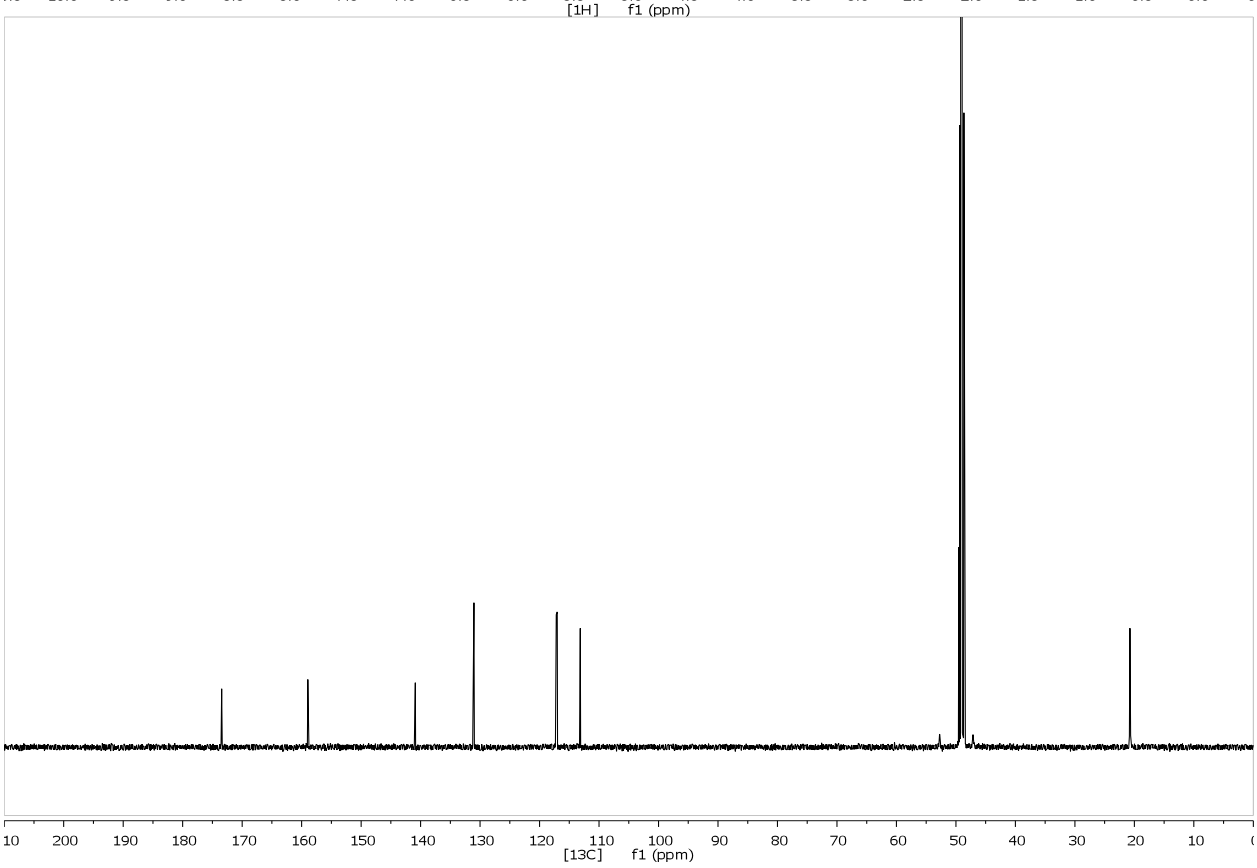
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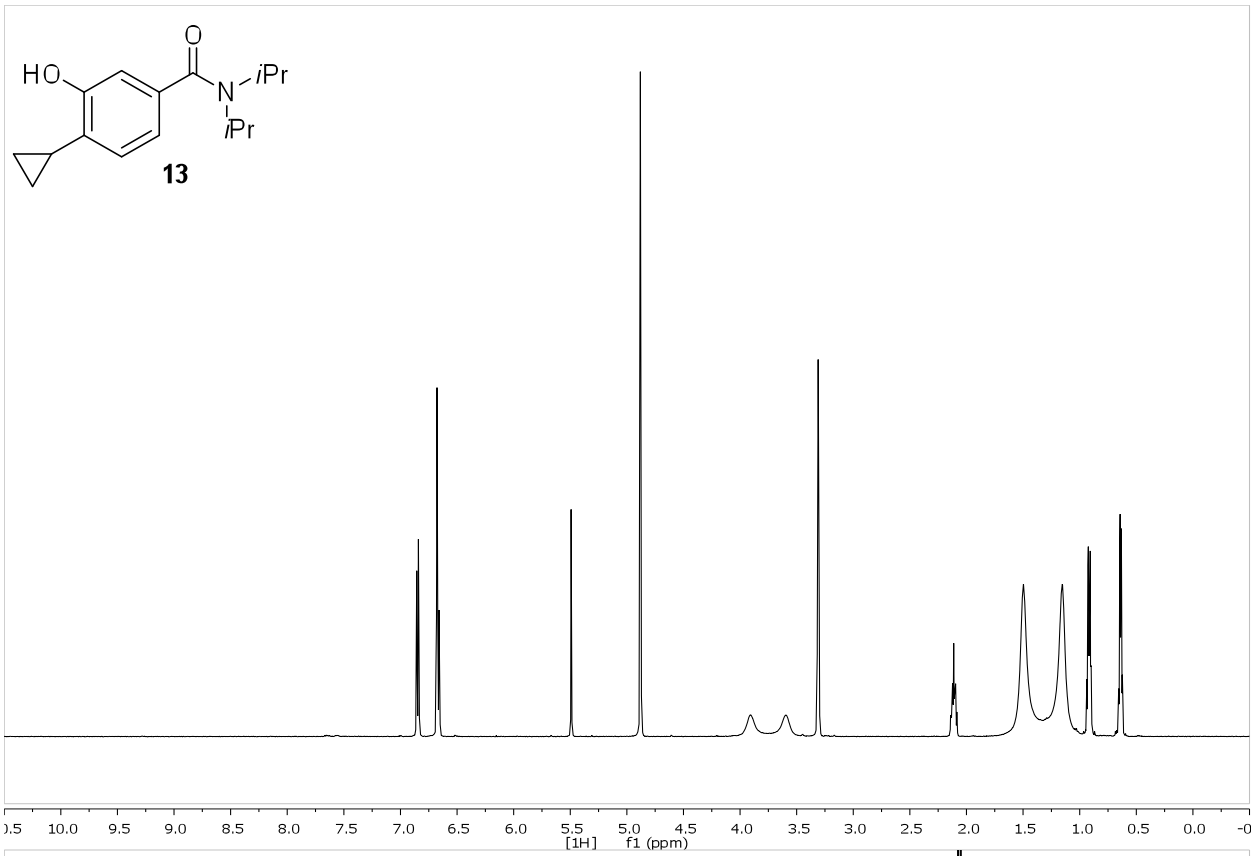
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O
N
iPr
iPr
13
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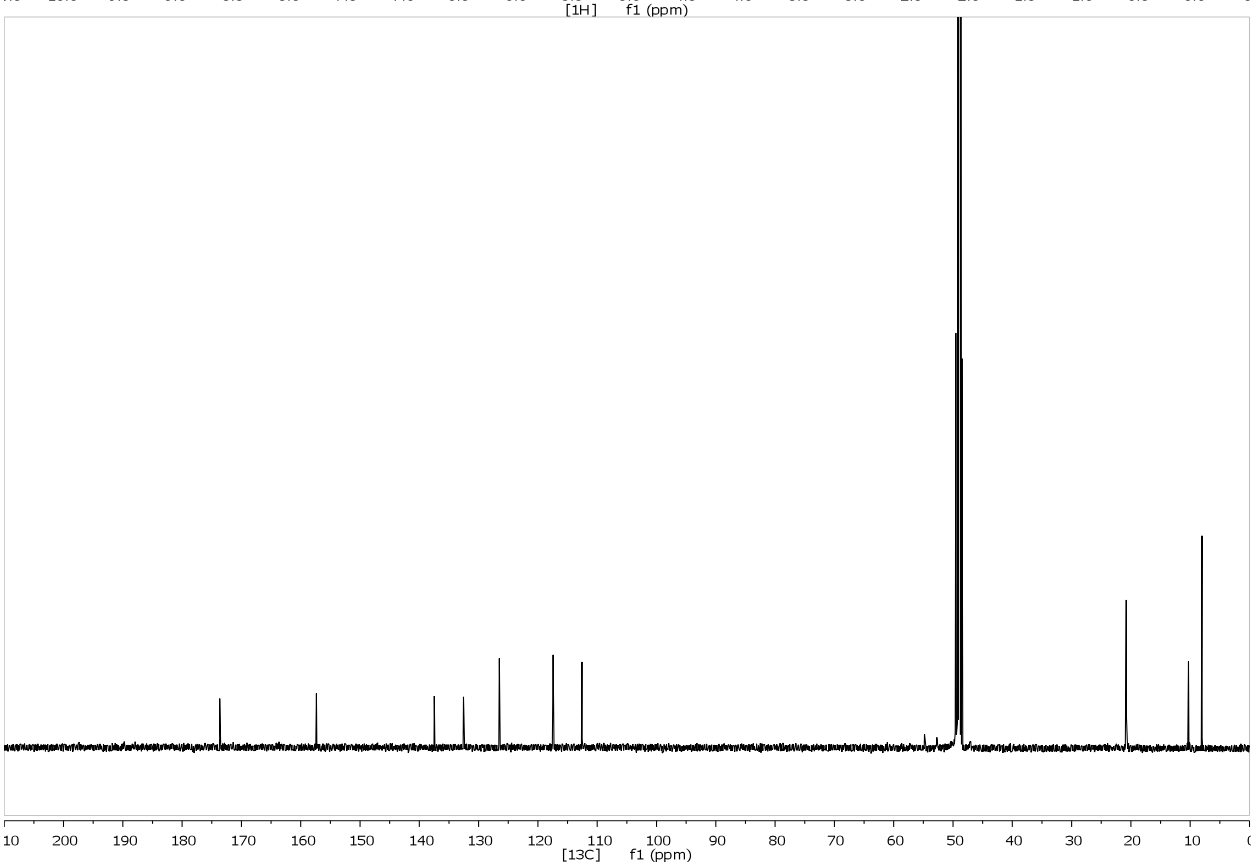
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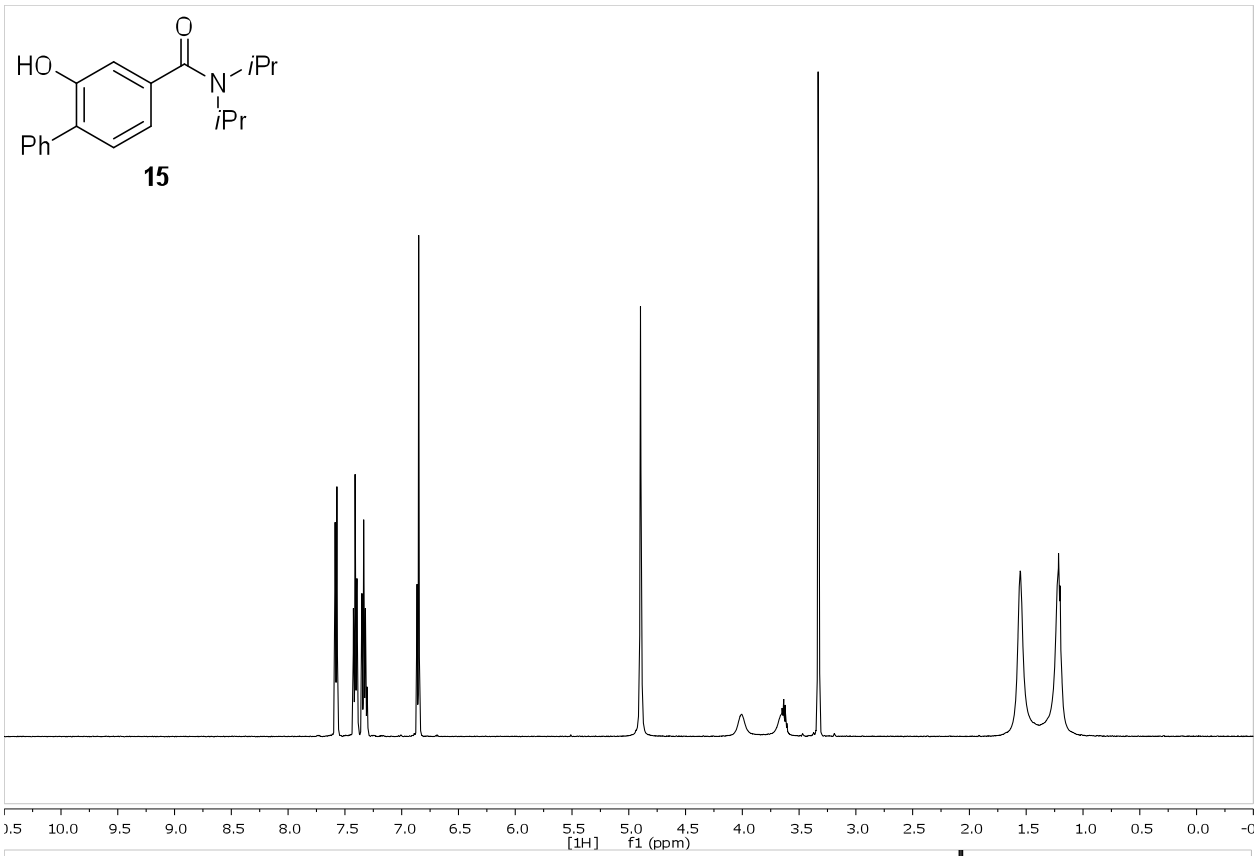
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N
iPr
iPr
Ph
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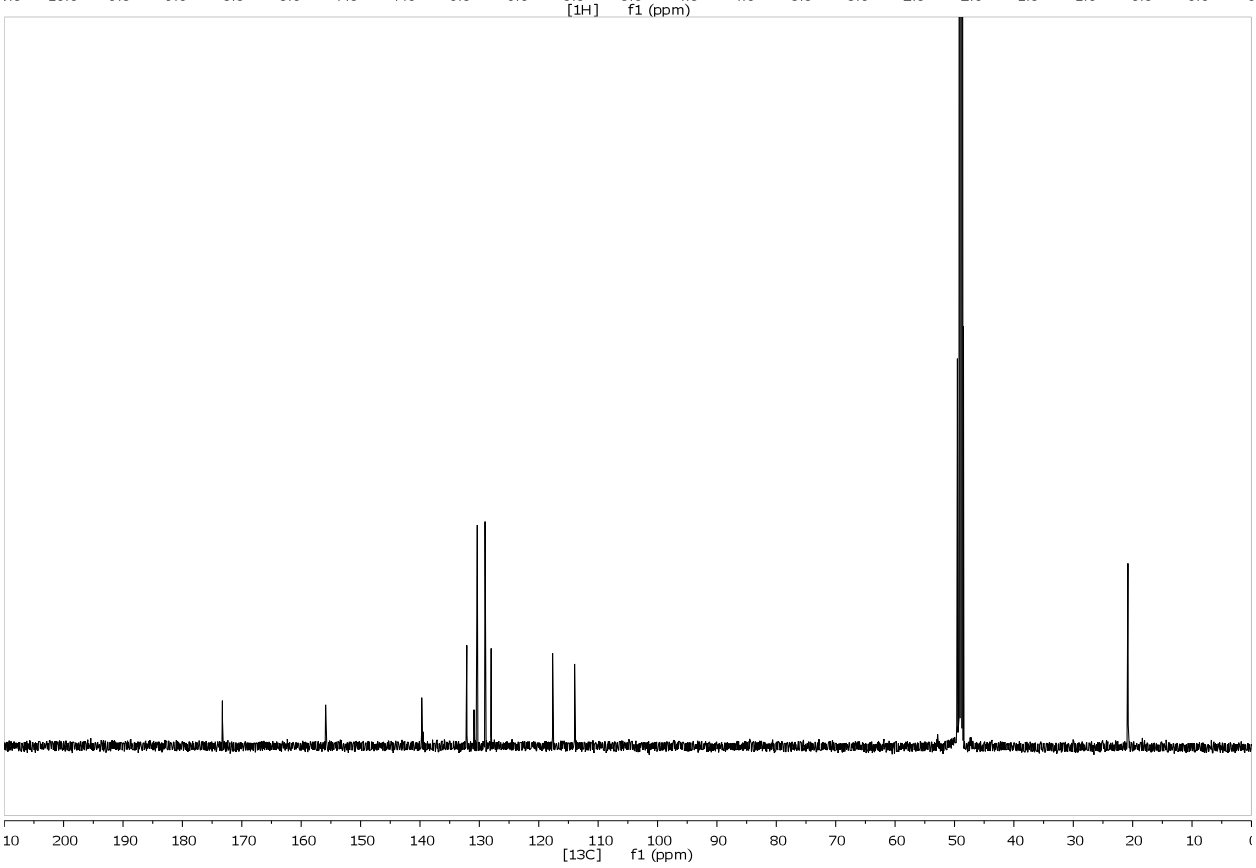
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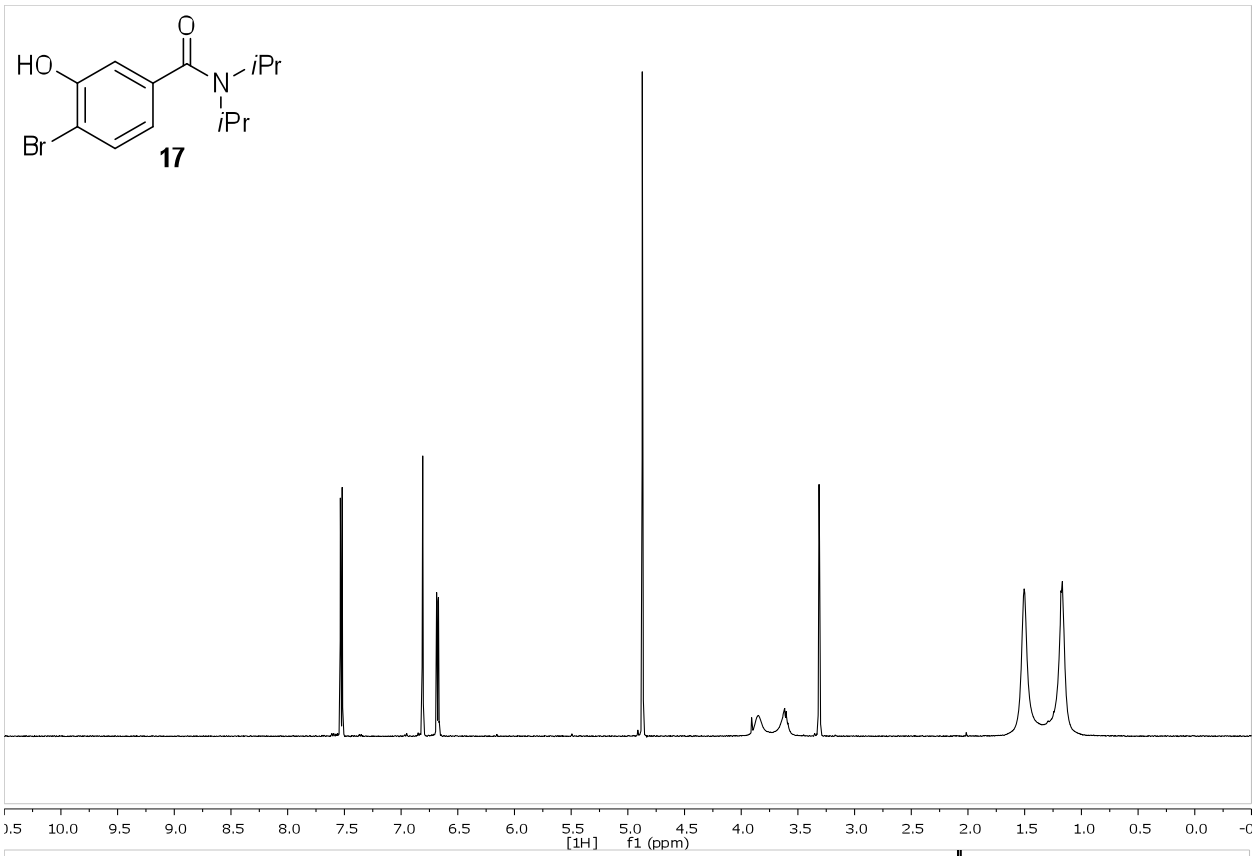
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O
N
iPr
iPr
Br
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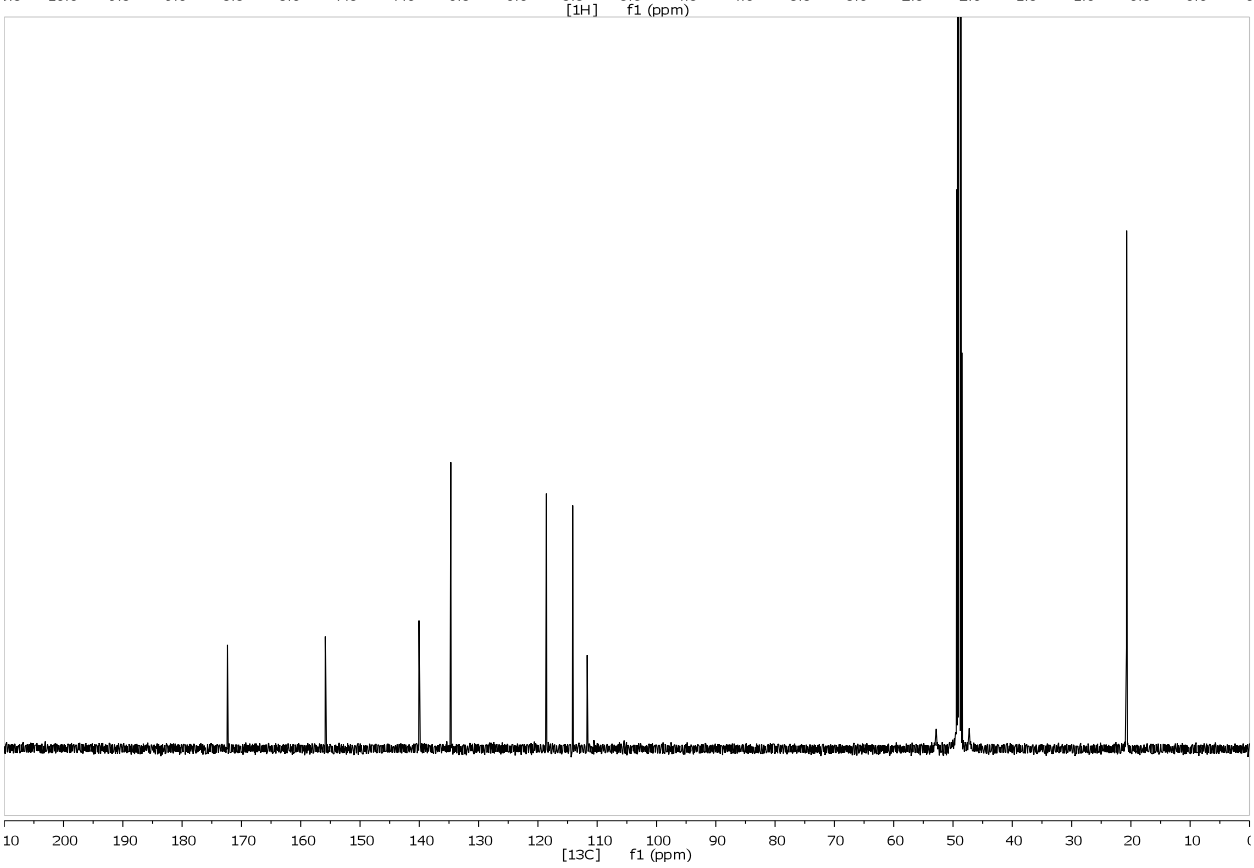
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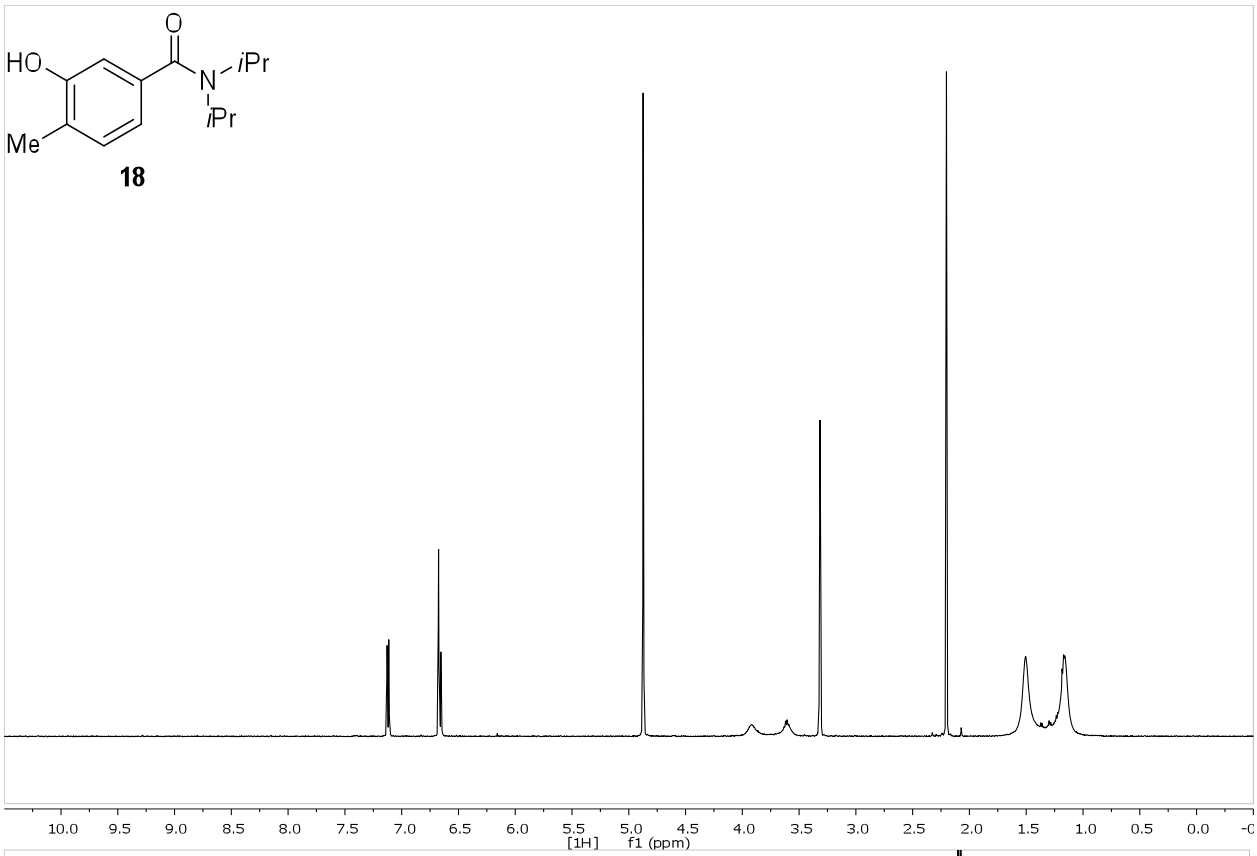
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N
iPr
iPr
Me
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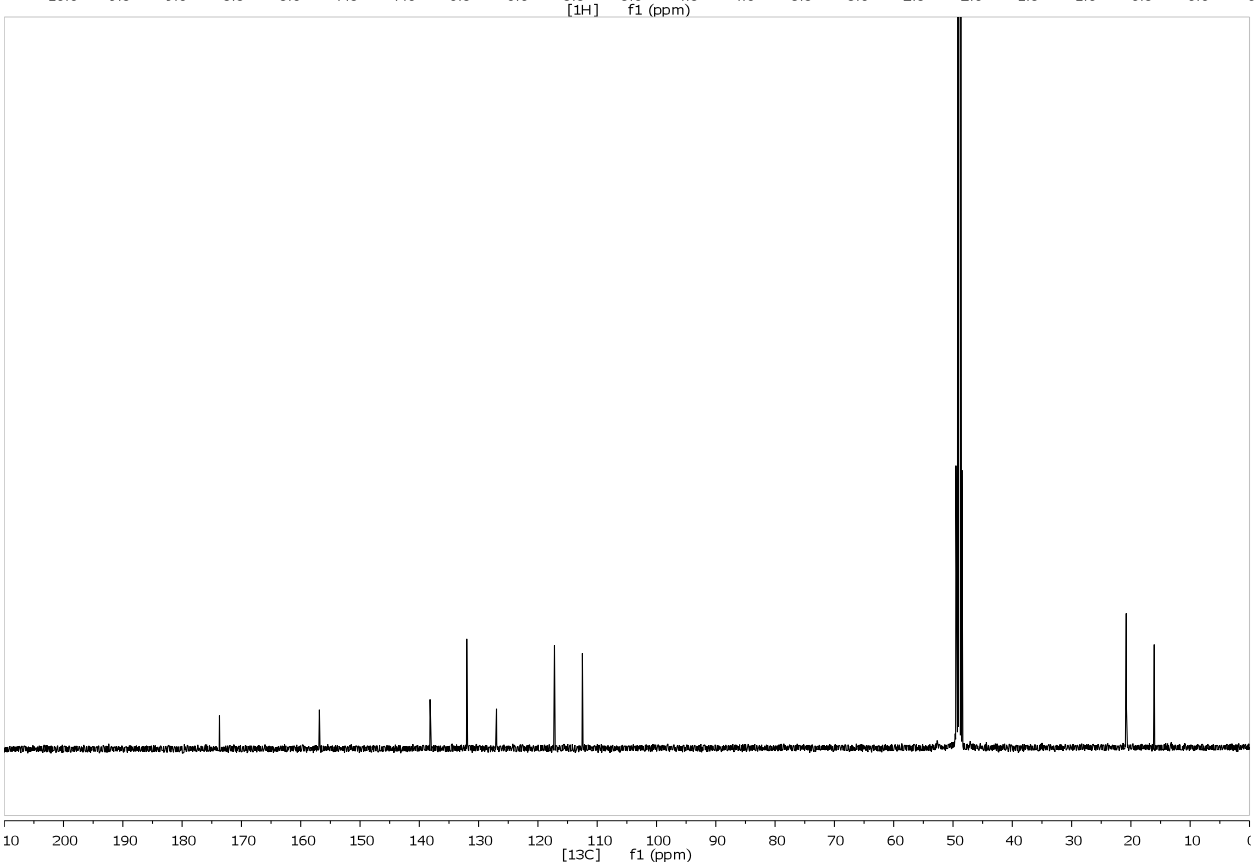
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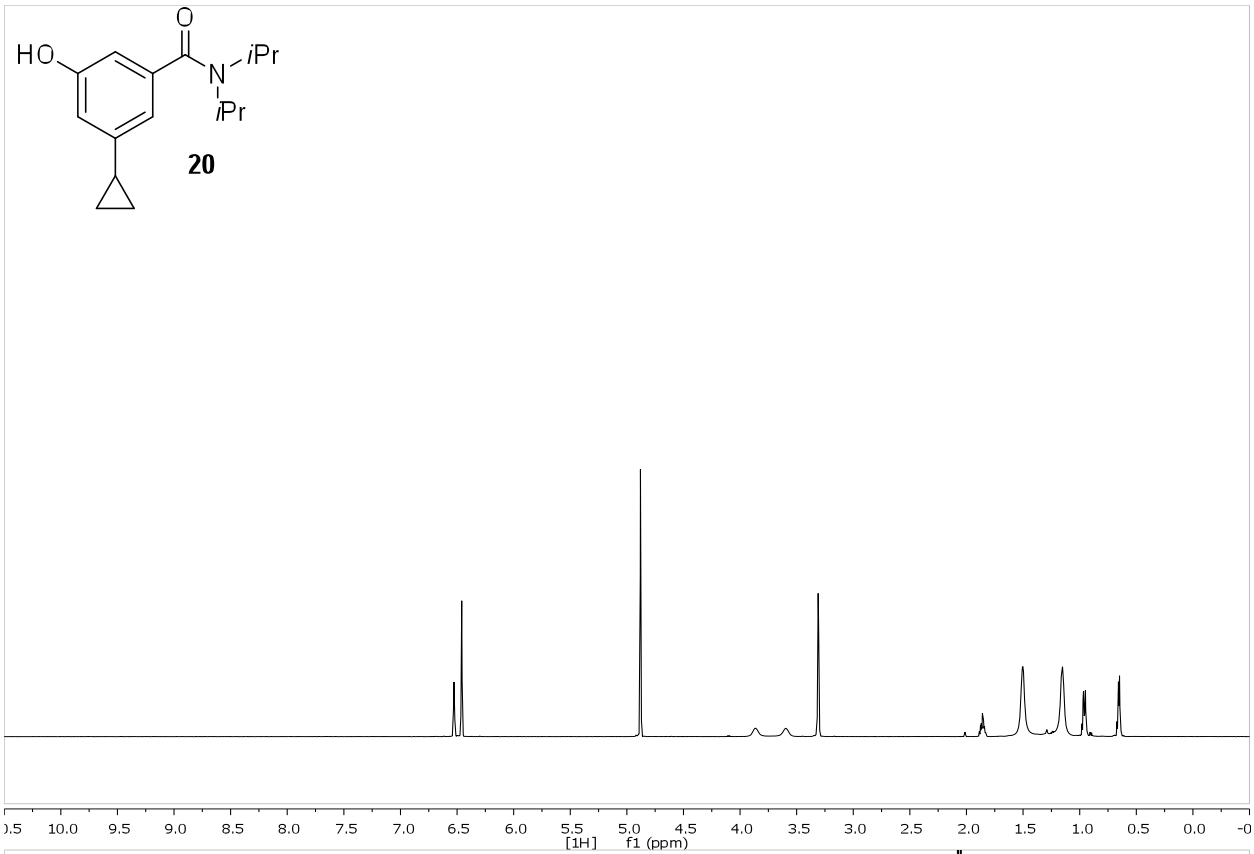
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O
N
iPr
iPr
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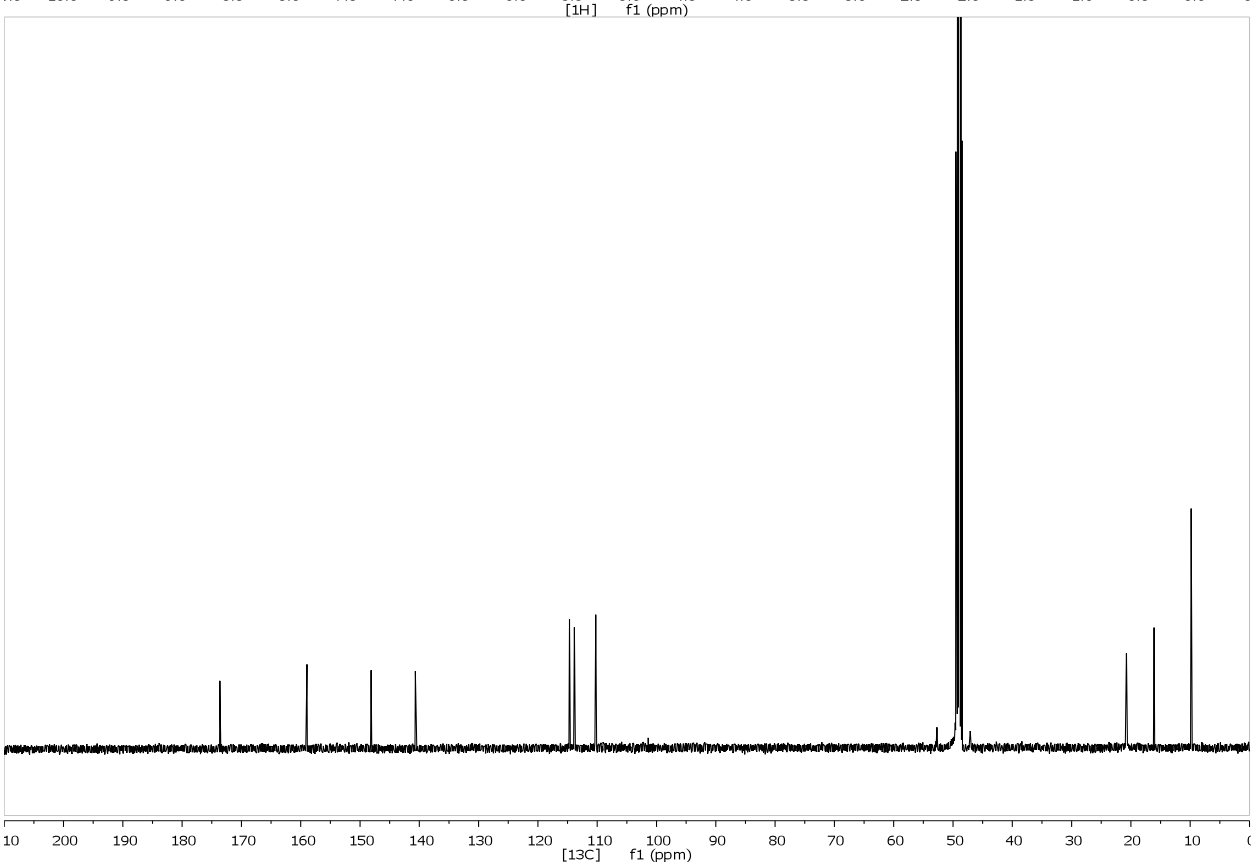
[1H] f1 (ppm)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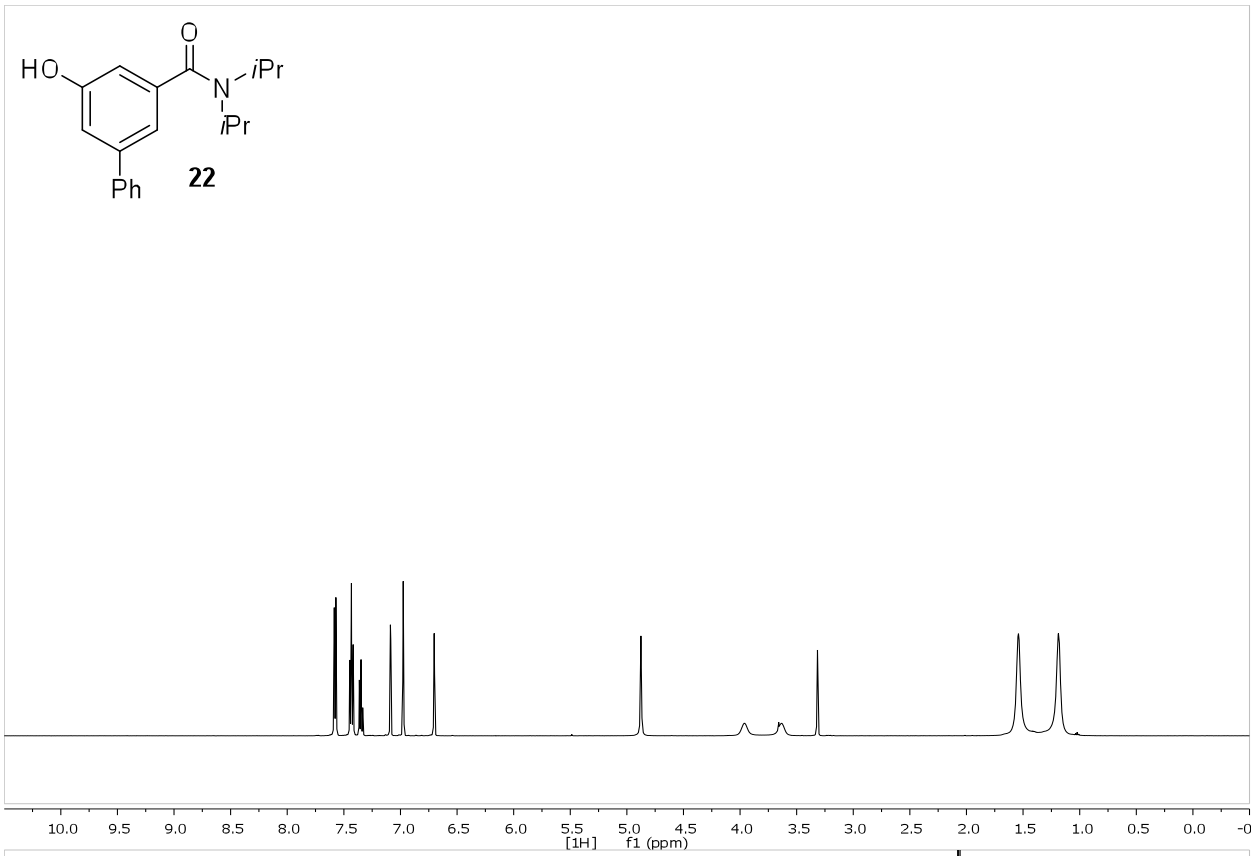
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O
N
iPr
iPr
Ph
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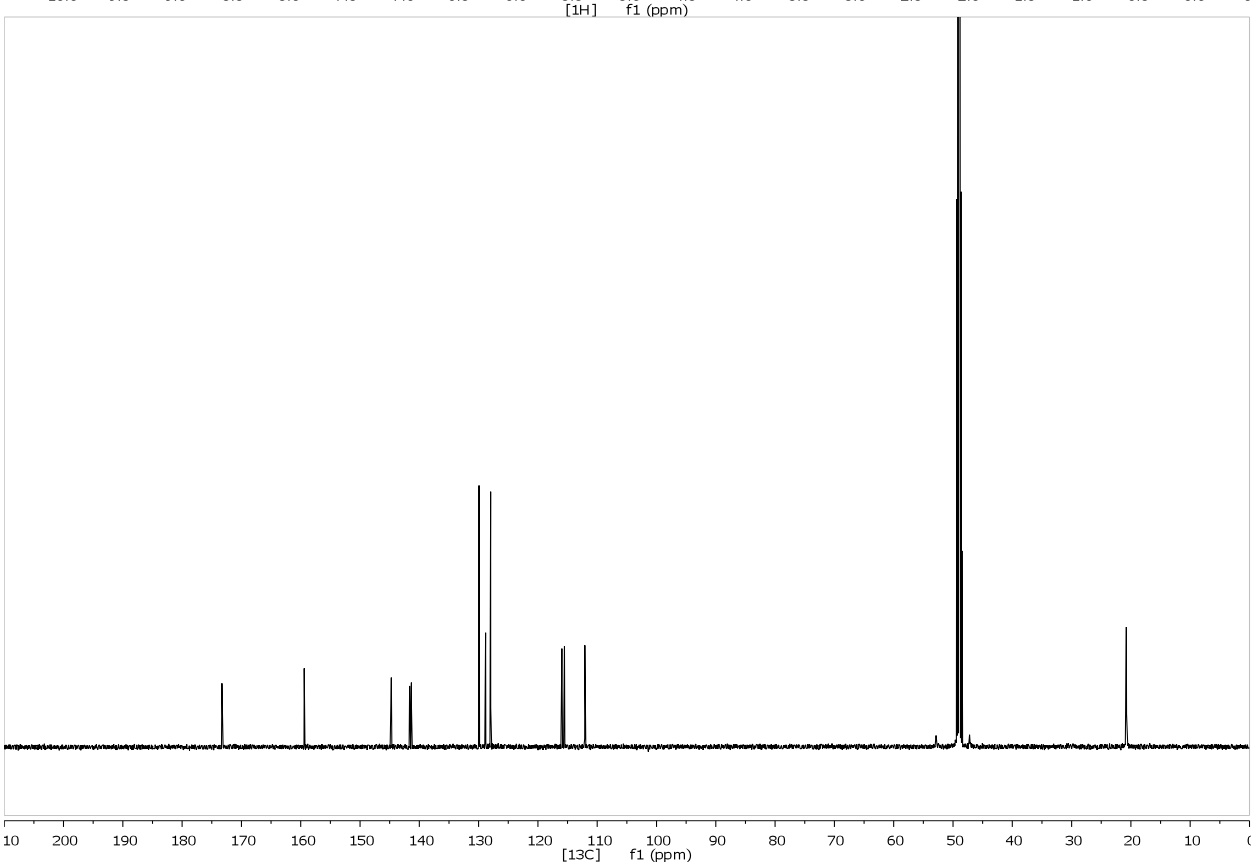
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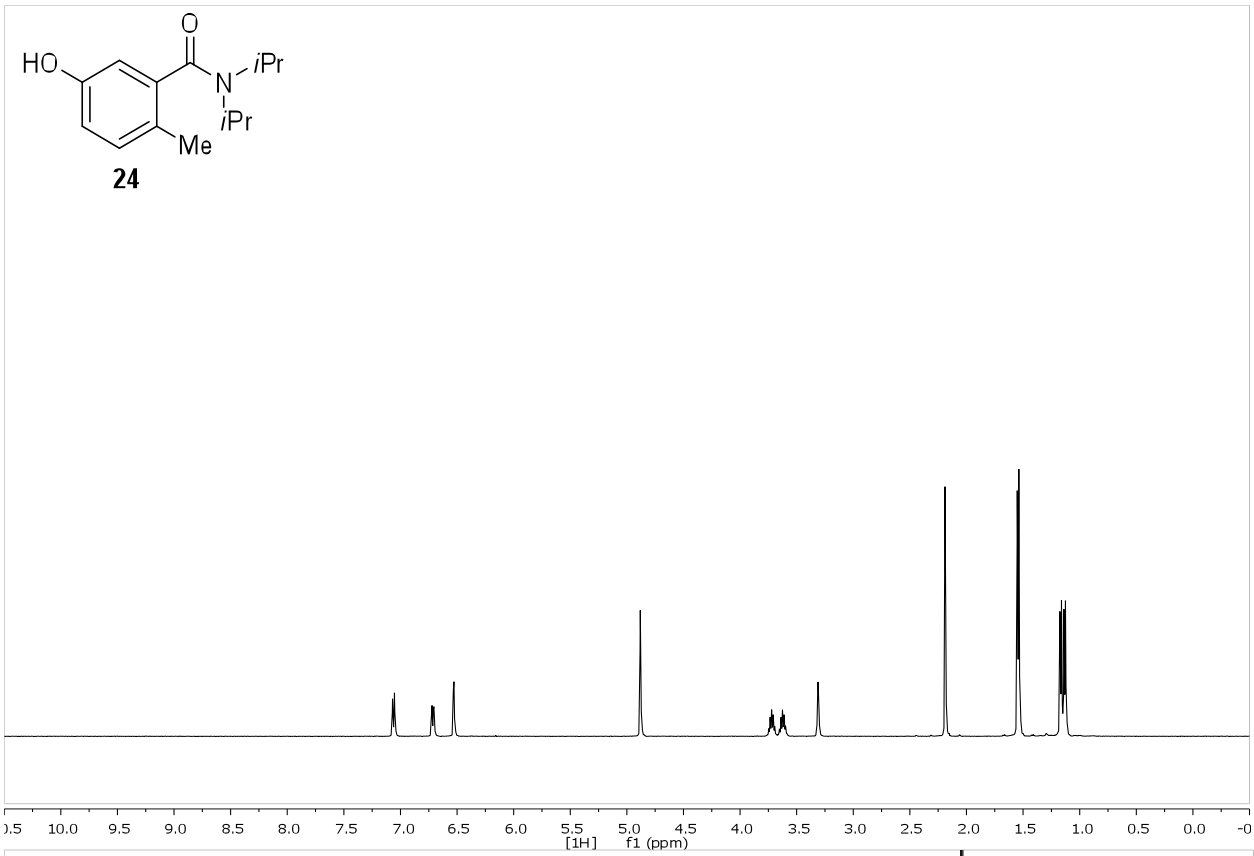
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O
N
iPr
iPr
Me
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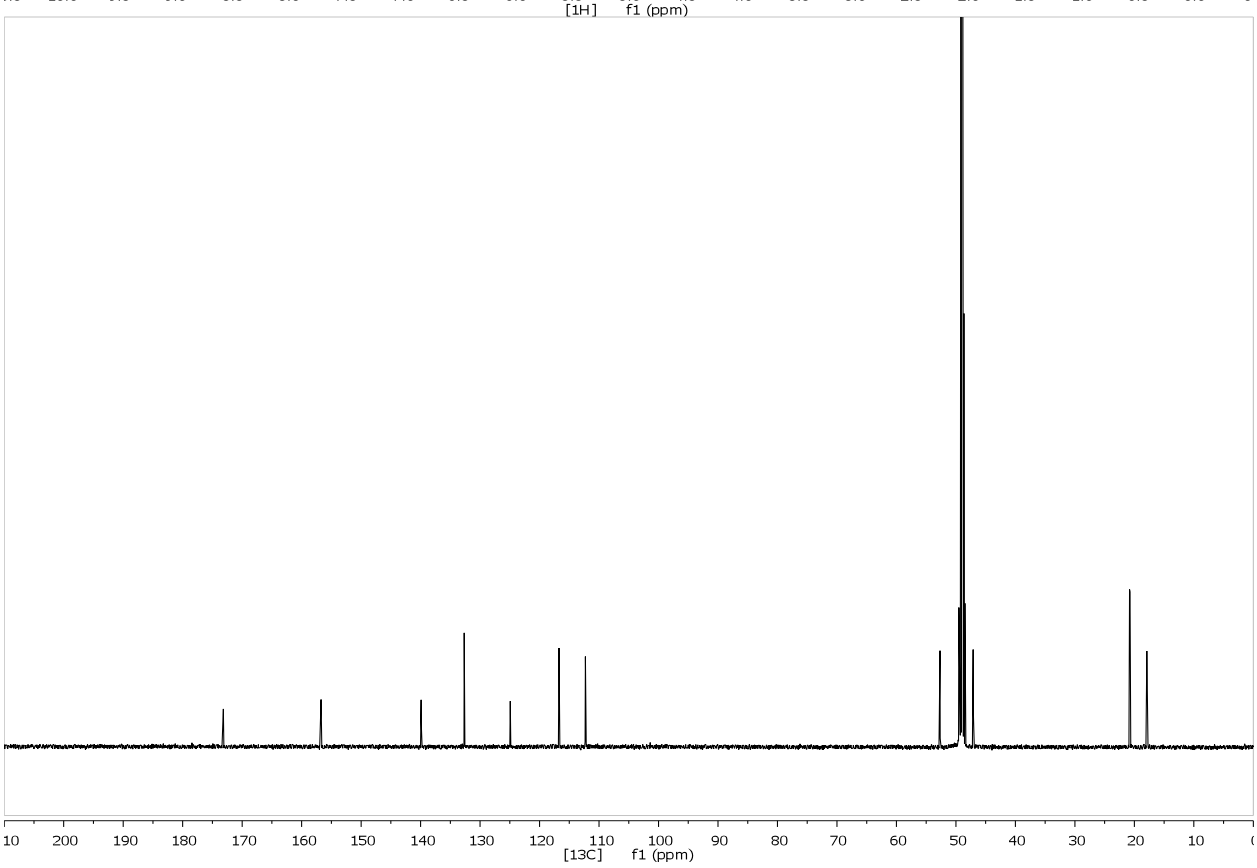
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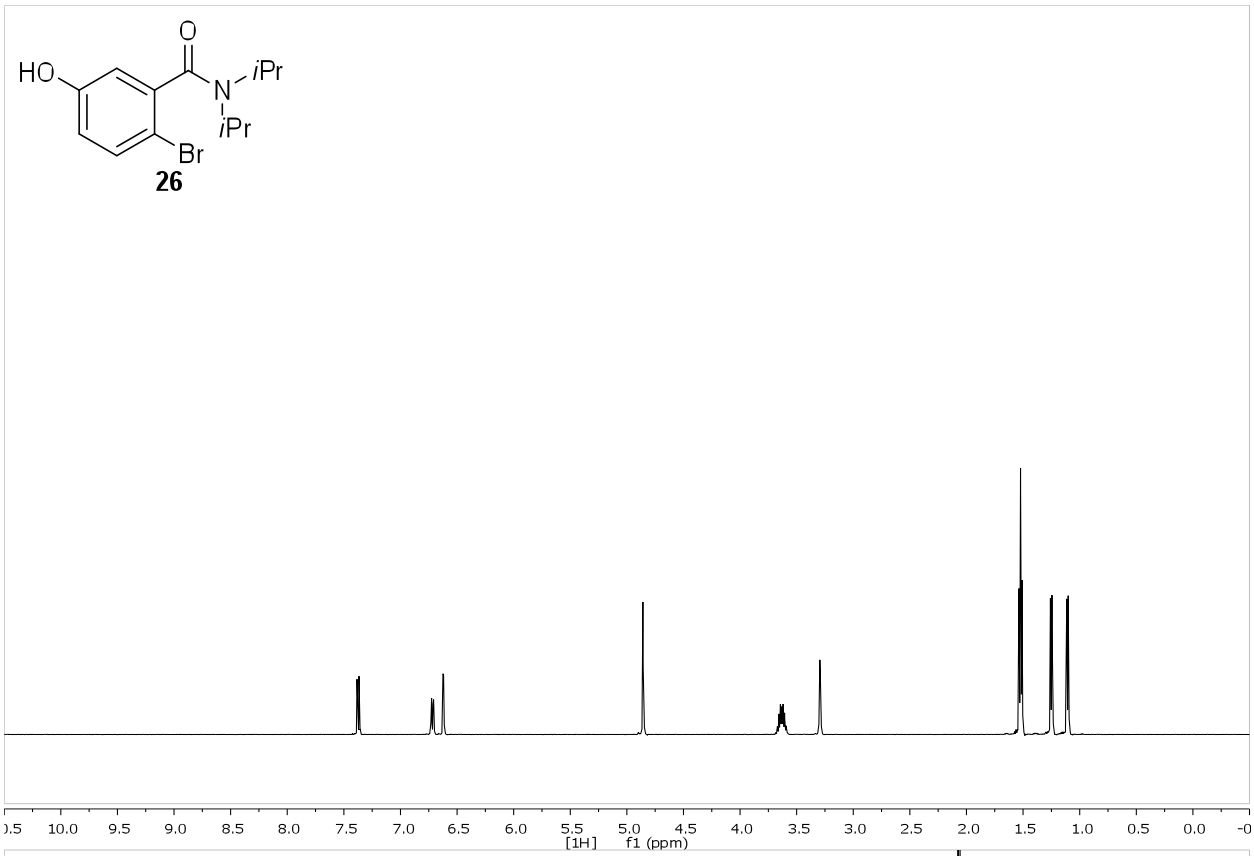
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N
iPr
iPr
Br
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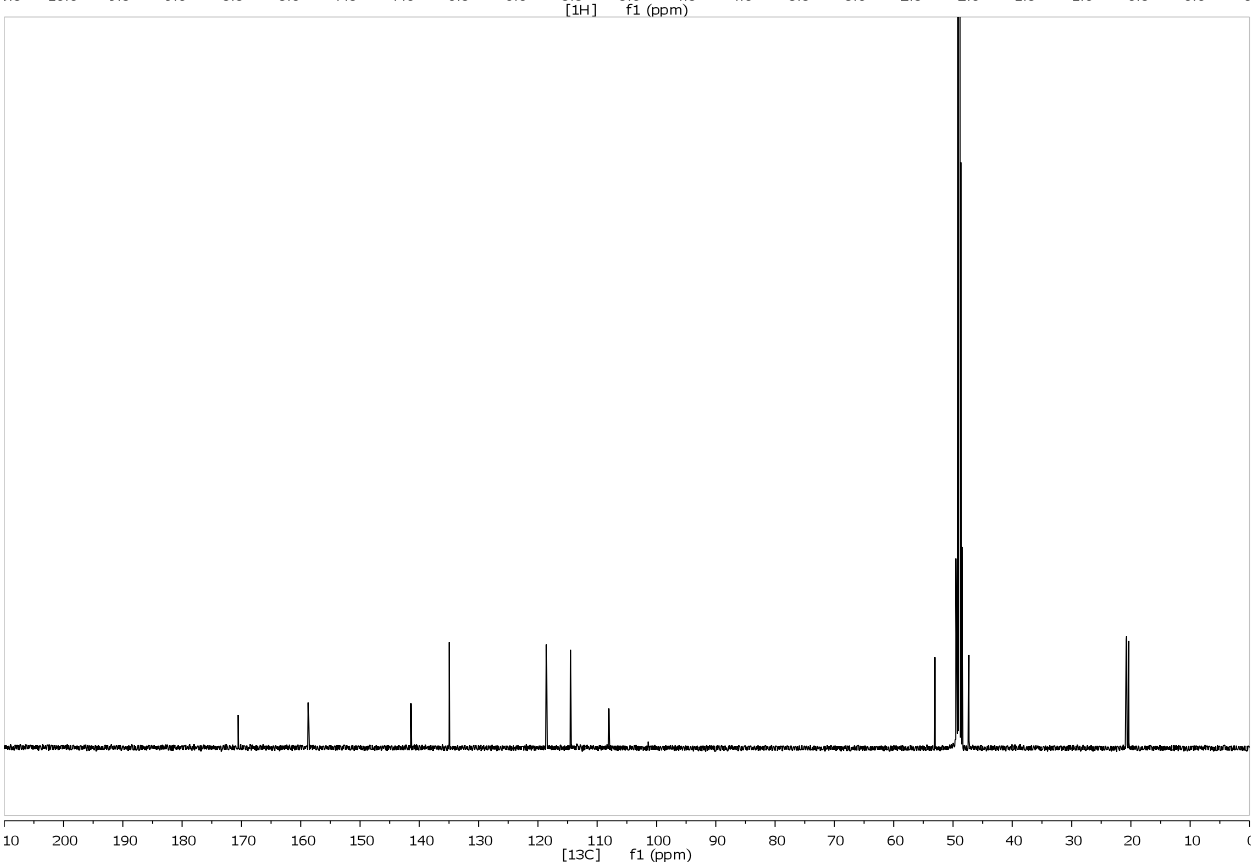
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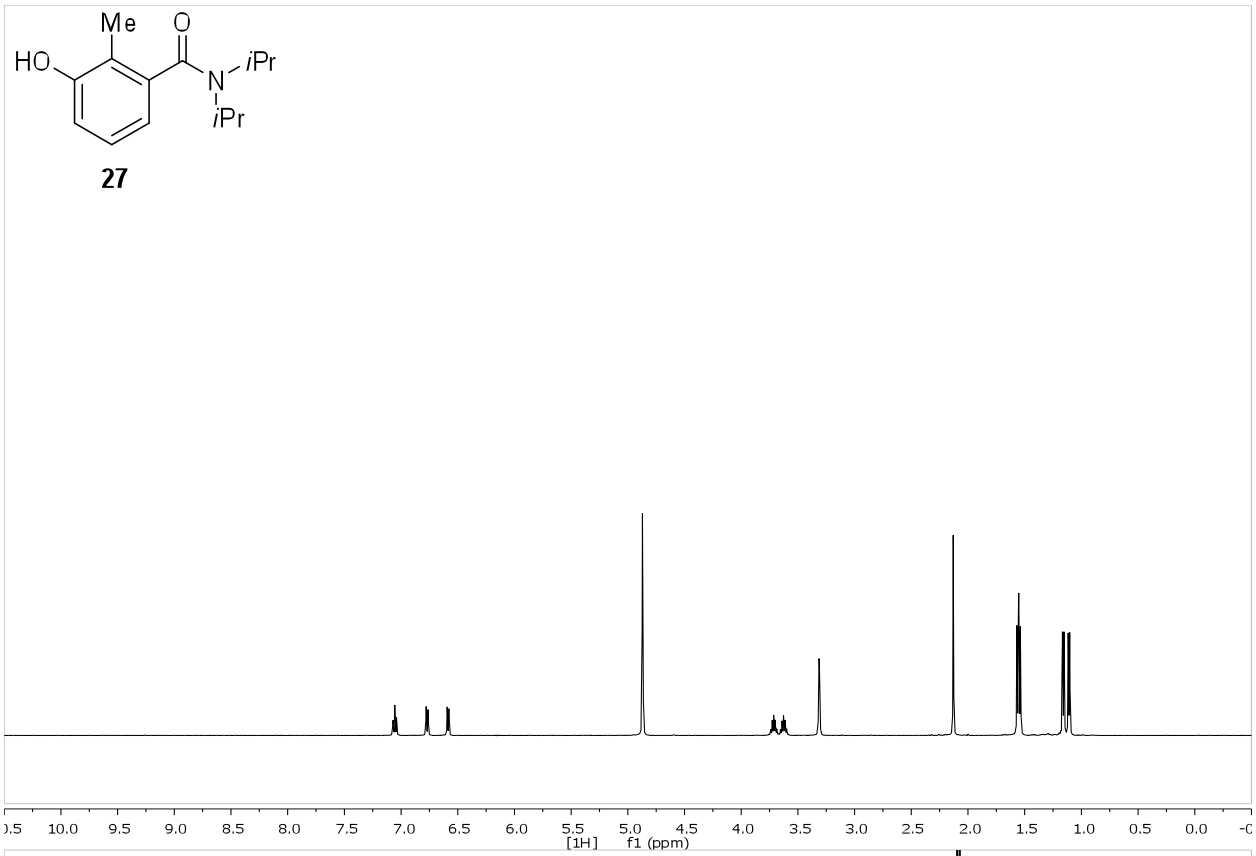
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O
HO
N
iPr
iPr
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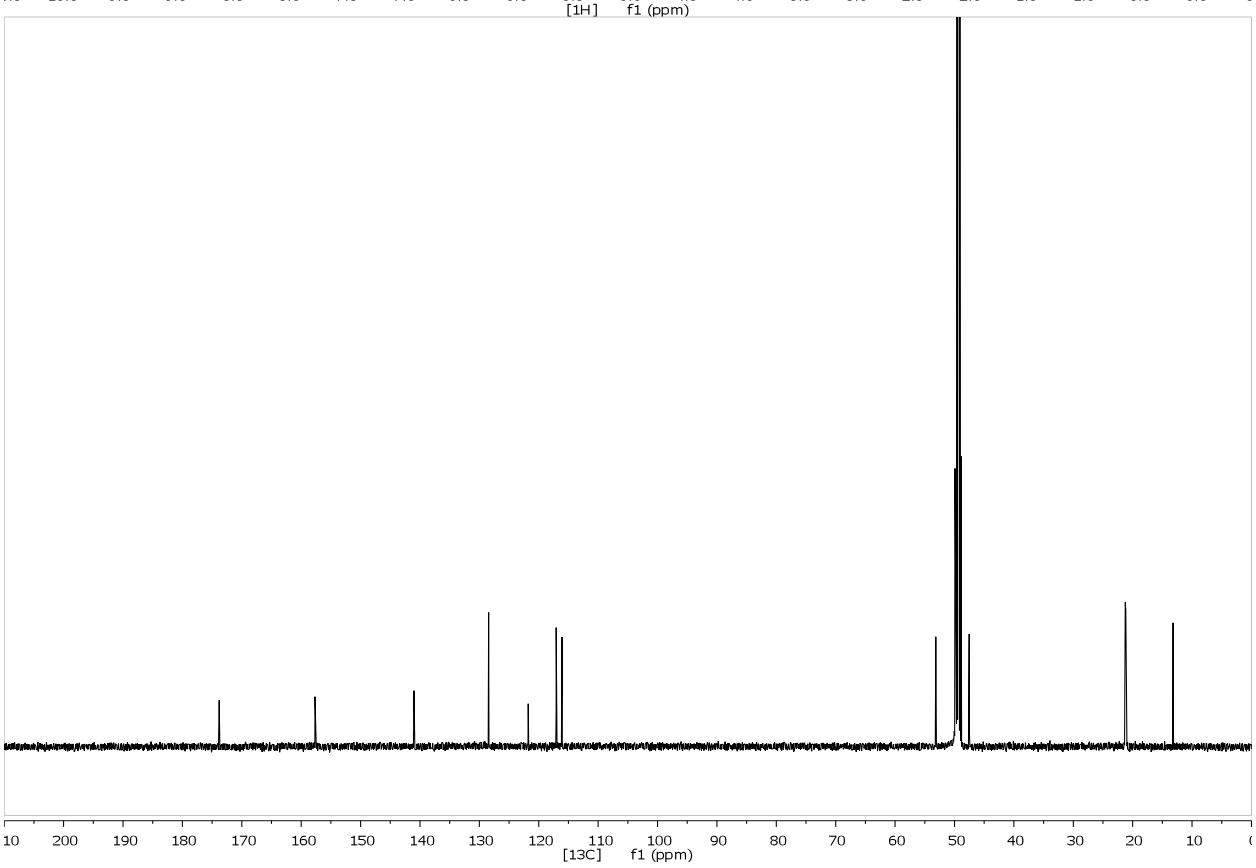
[1H] f1 (ppm)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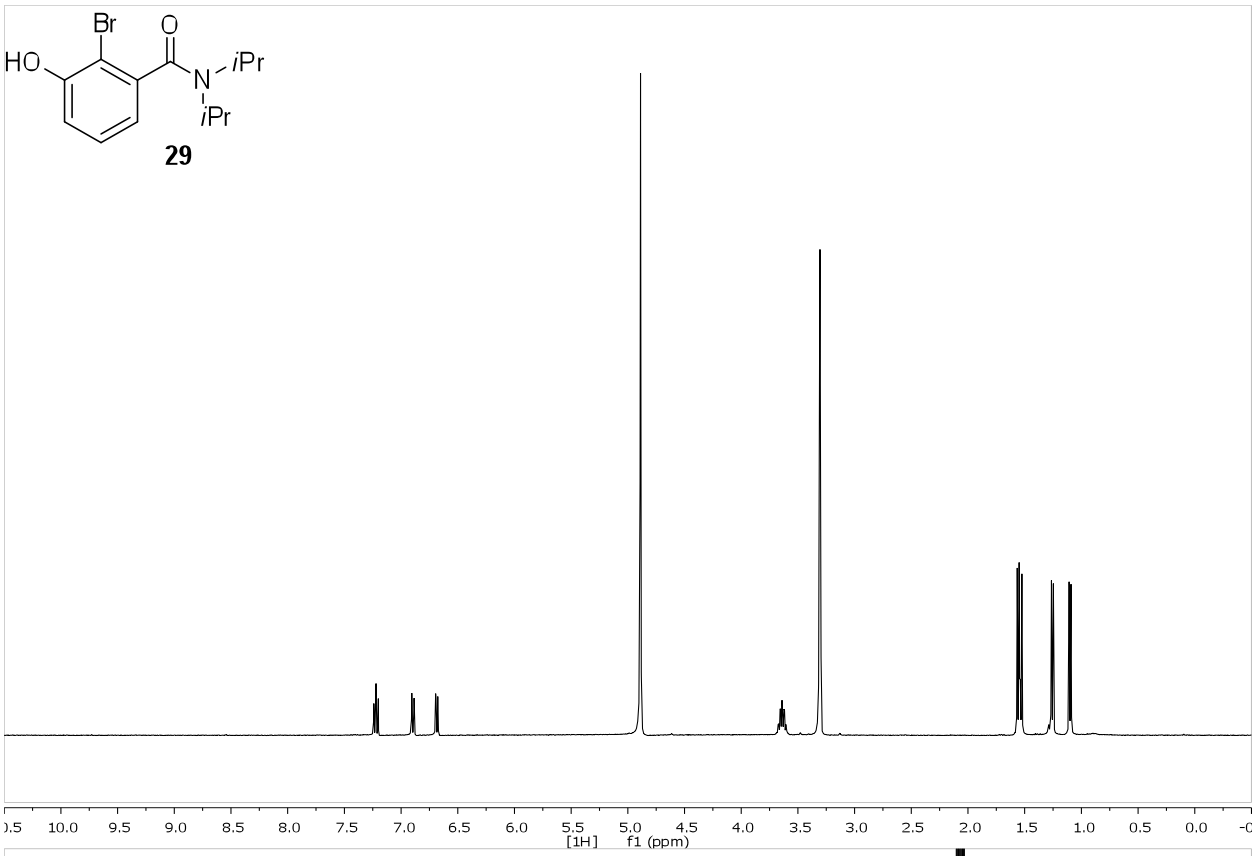
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O
HO
N
iPr
iPr
29
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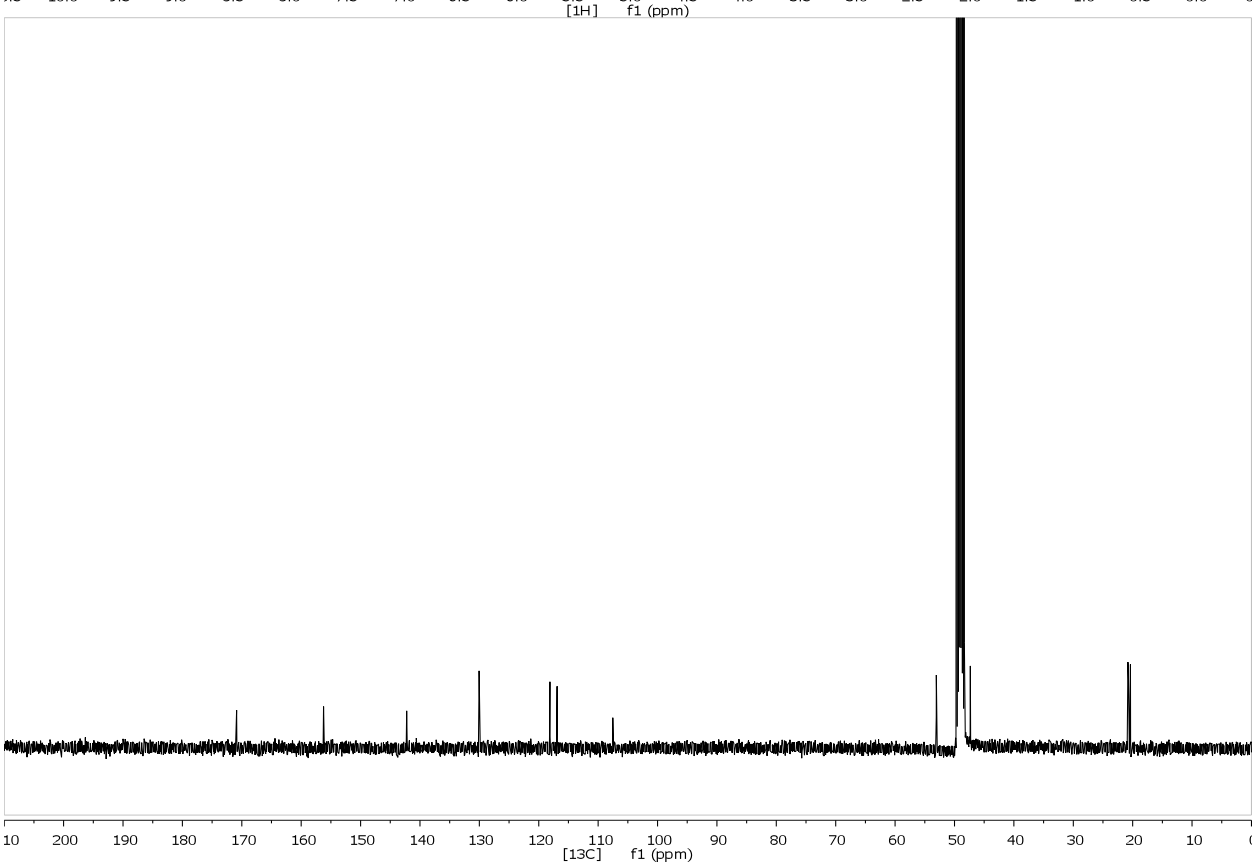
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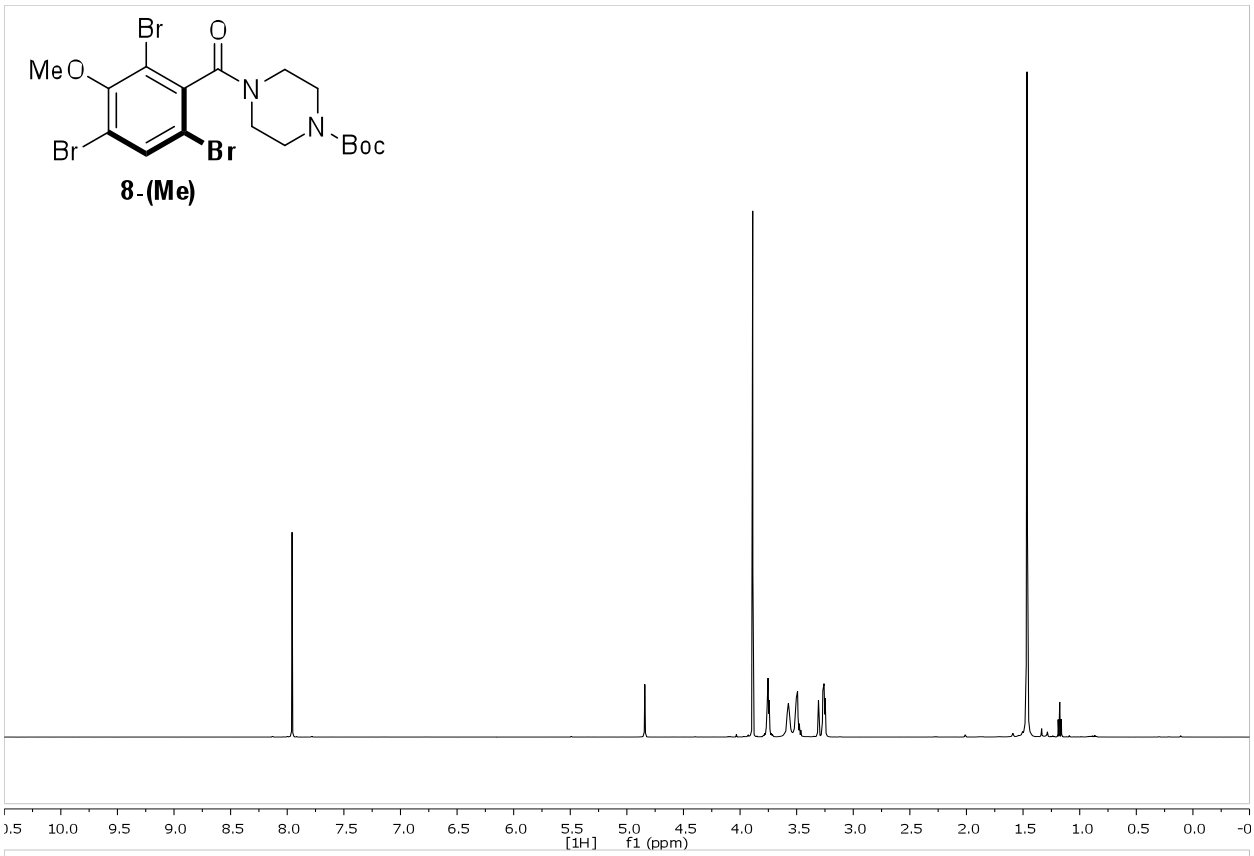
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MeO
N
N
Boc
Br
Br
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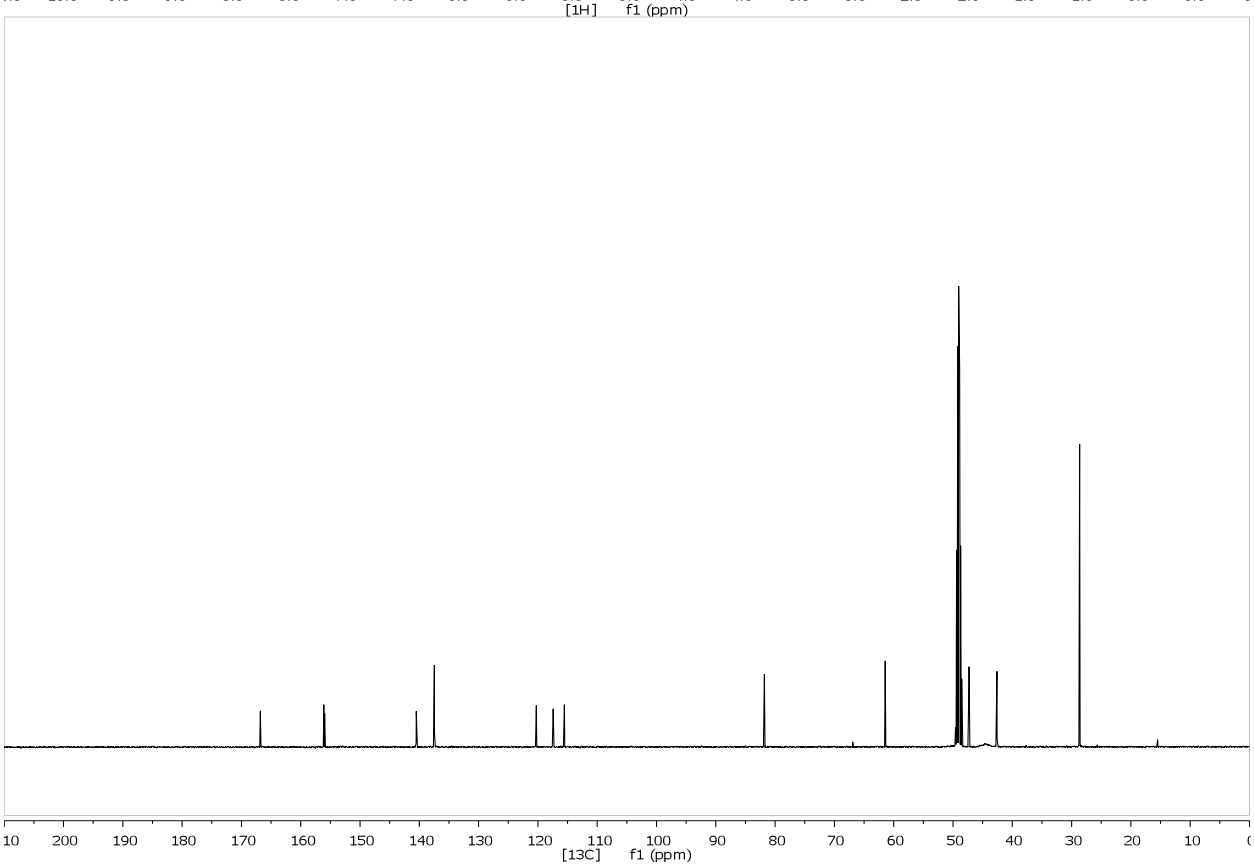
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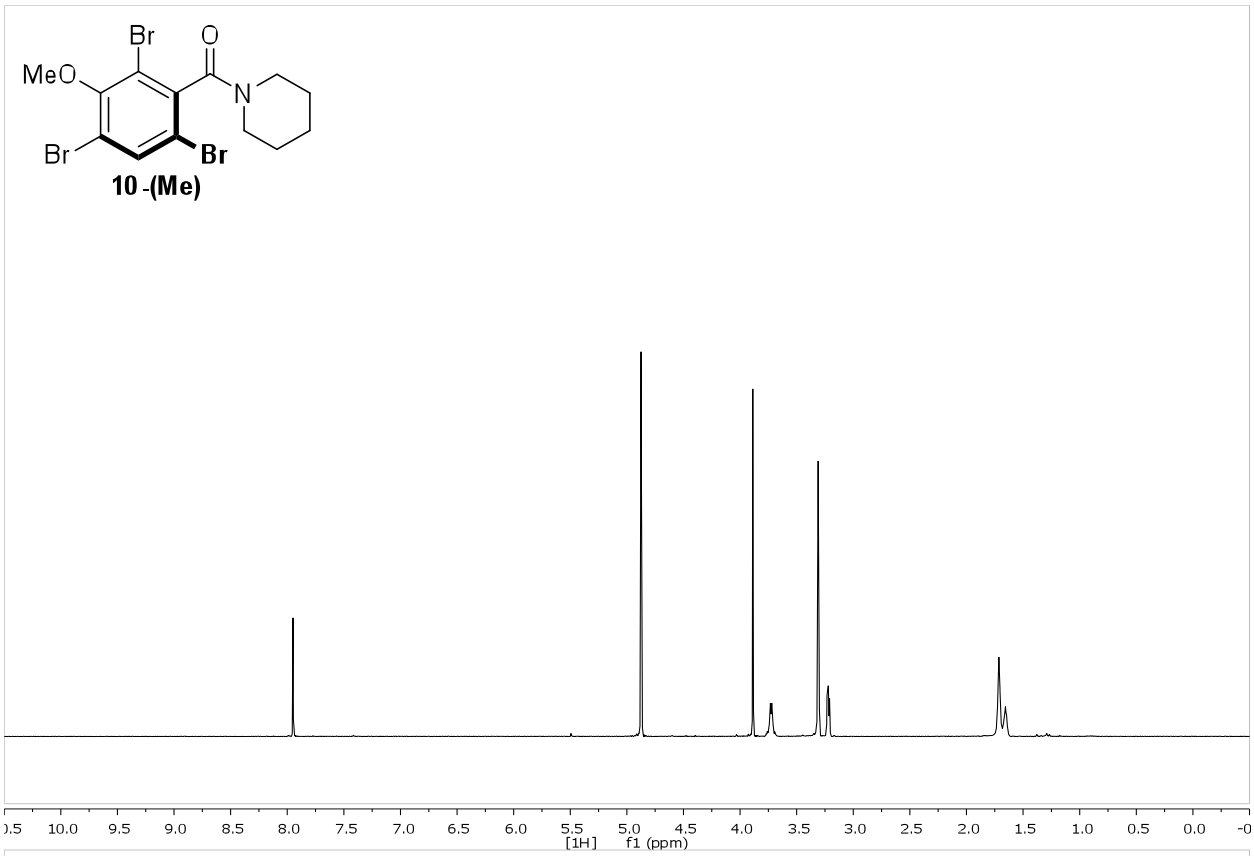
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MeO
N
Br
Br
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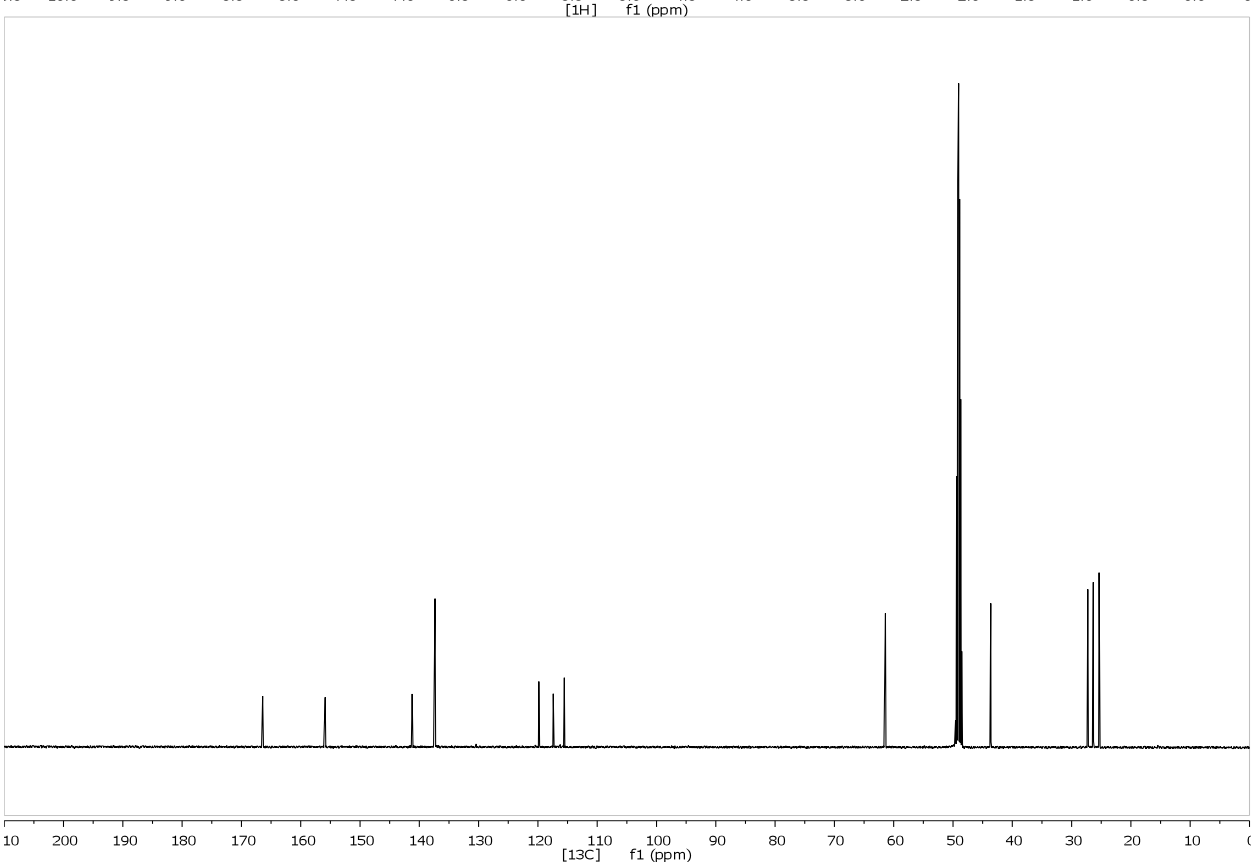
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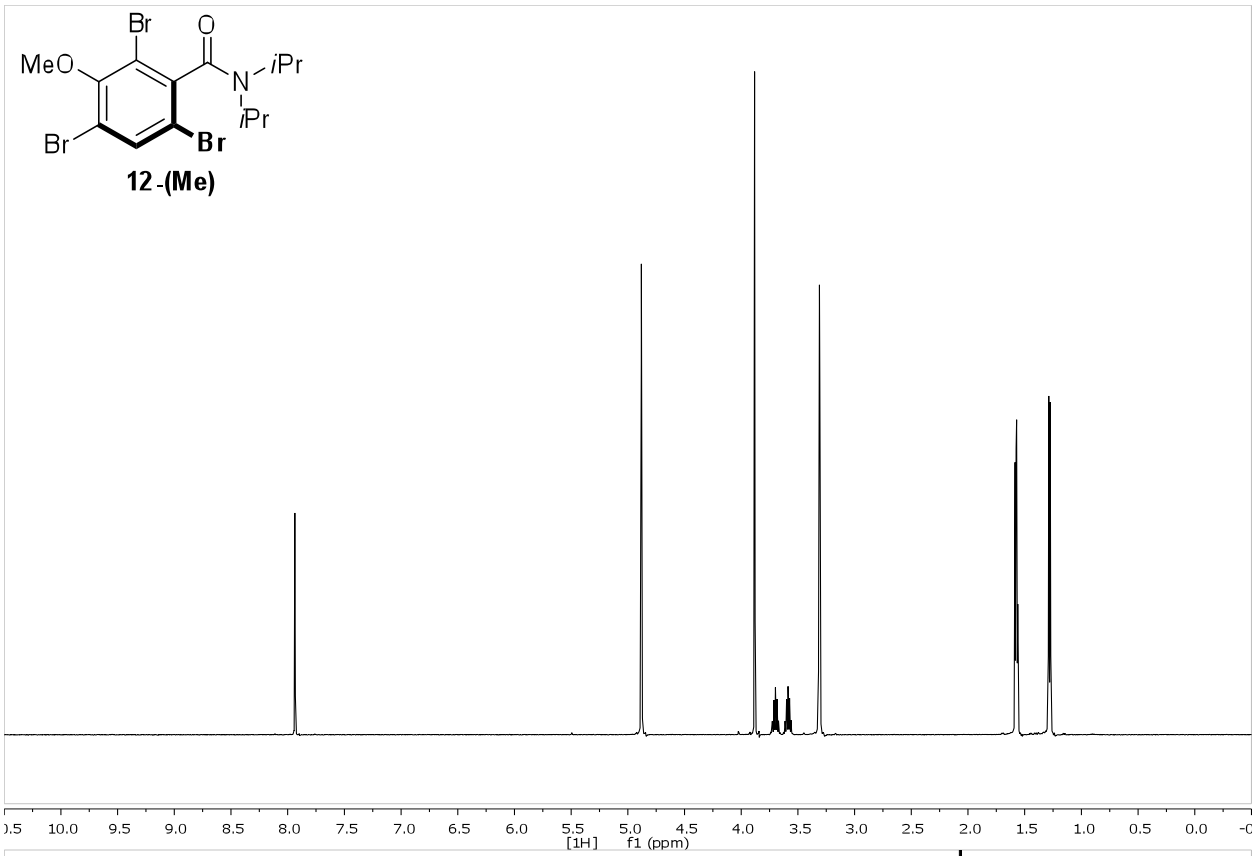
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MeO
N
iPr
iPr
Br
Br
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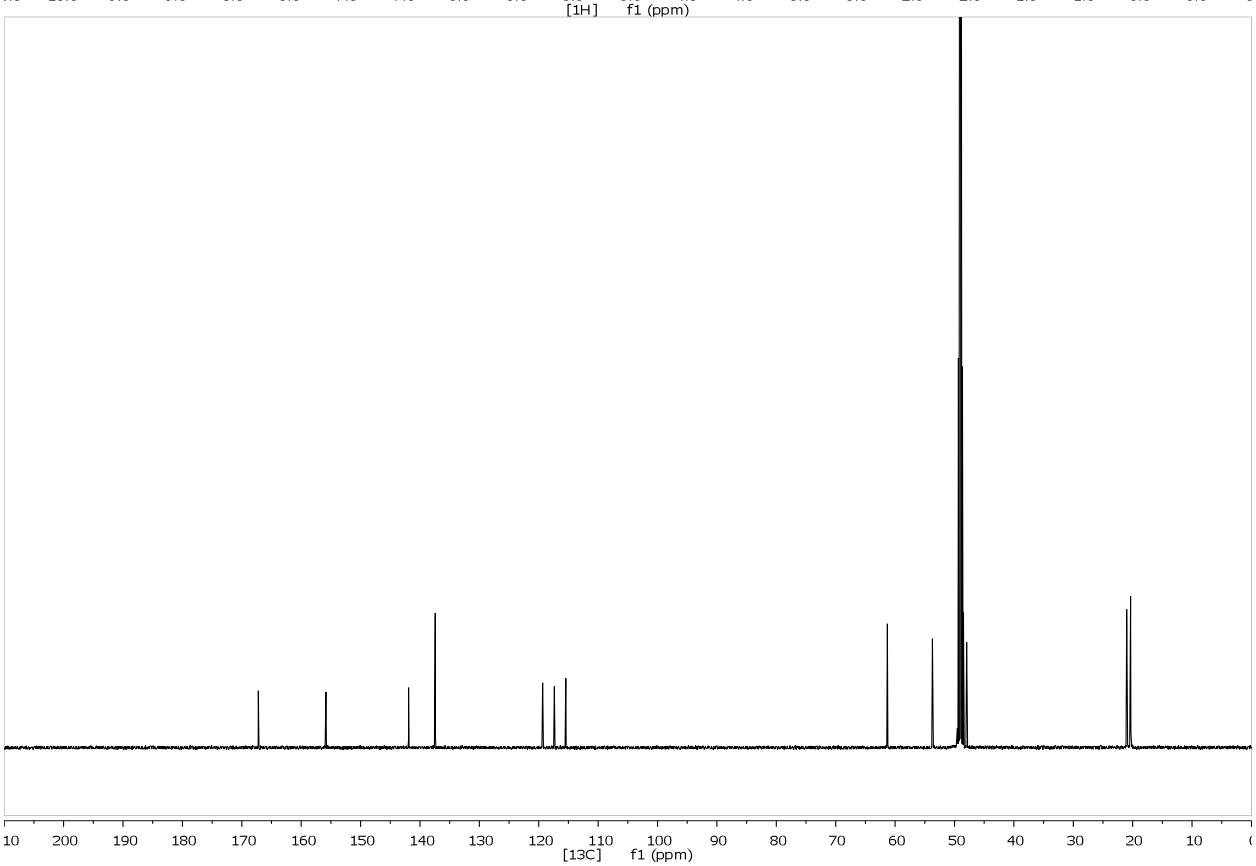
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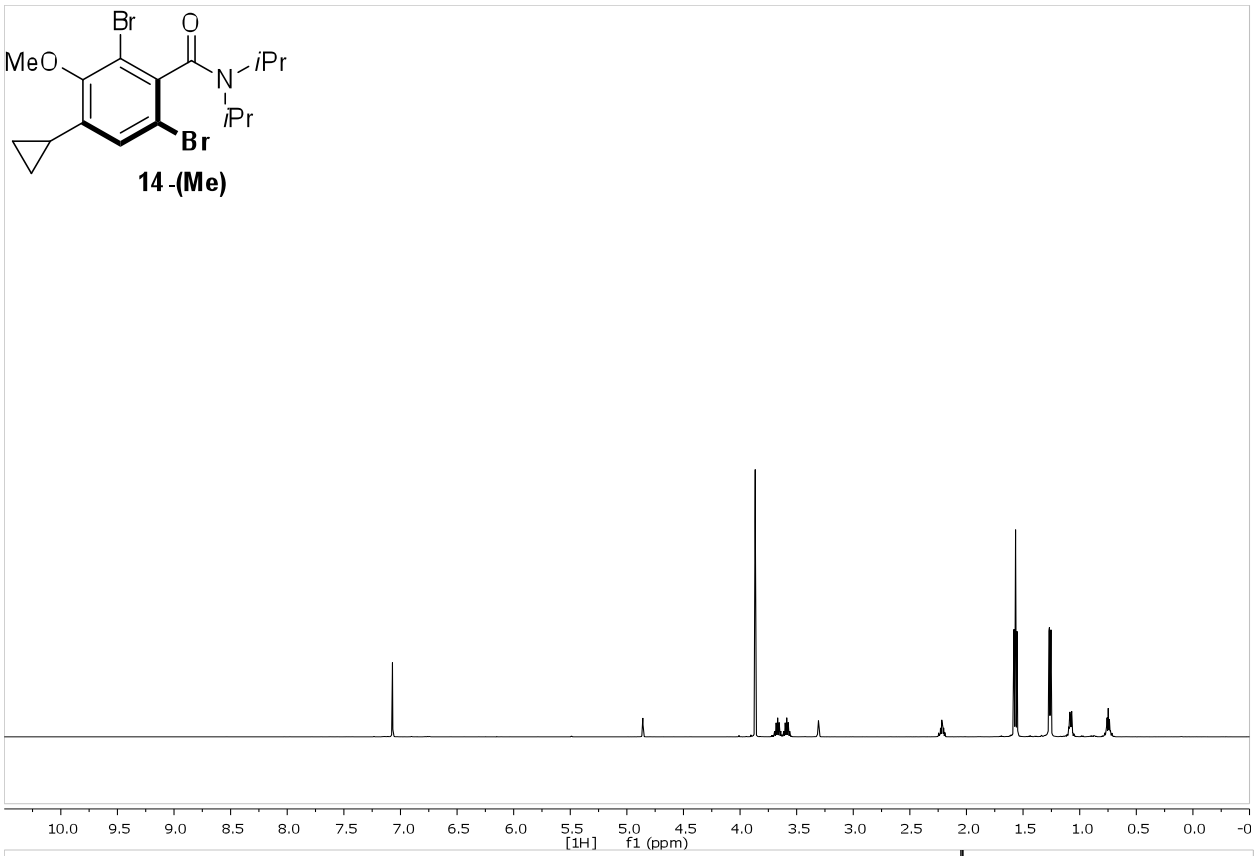
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N
iPr
iPr
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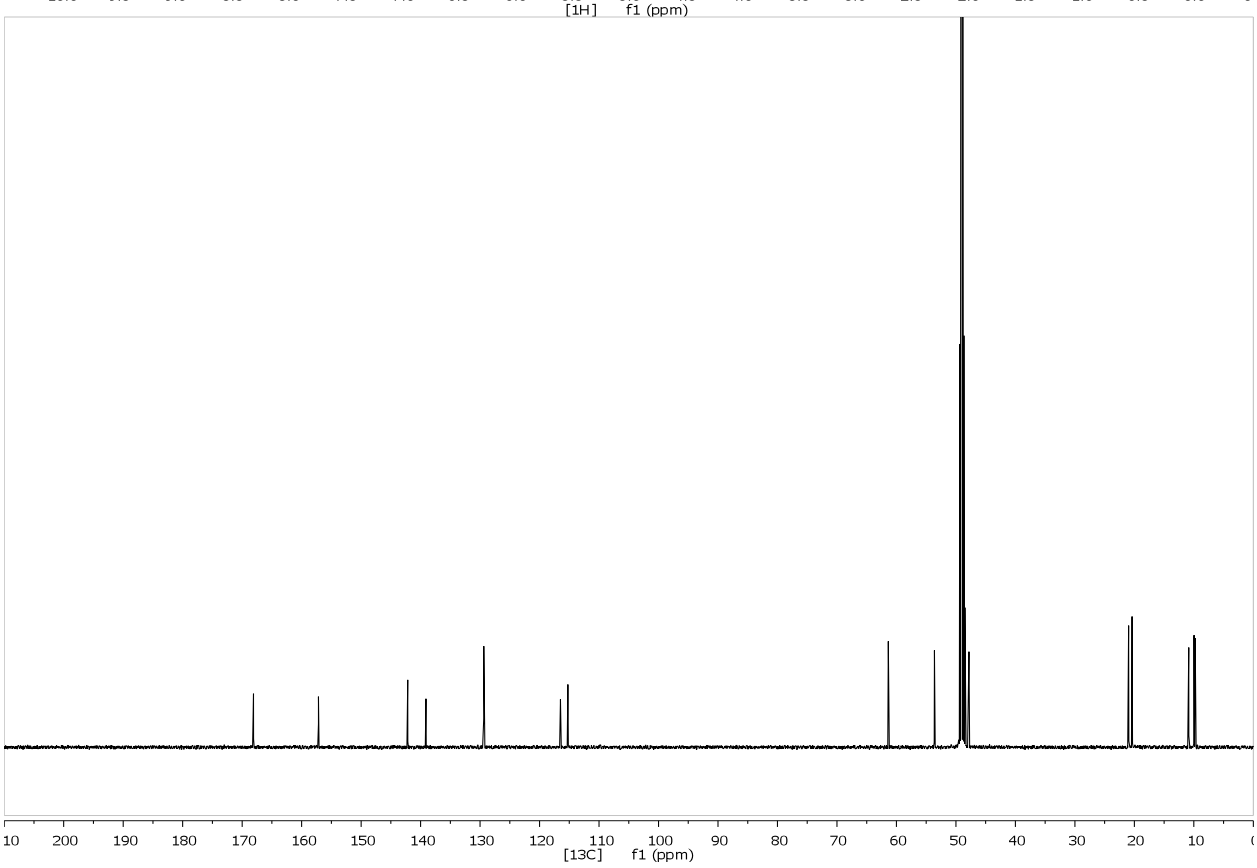
[1H] f1 (ppm)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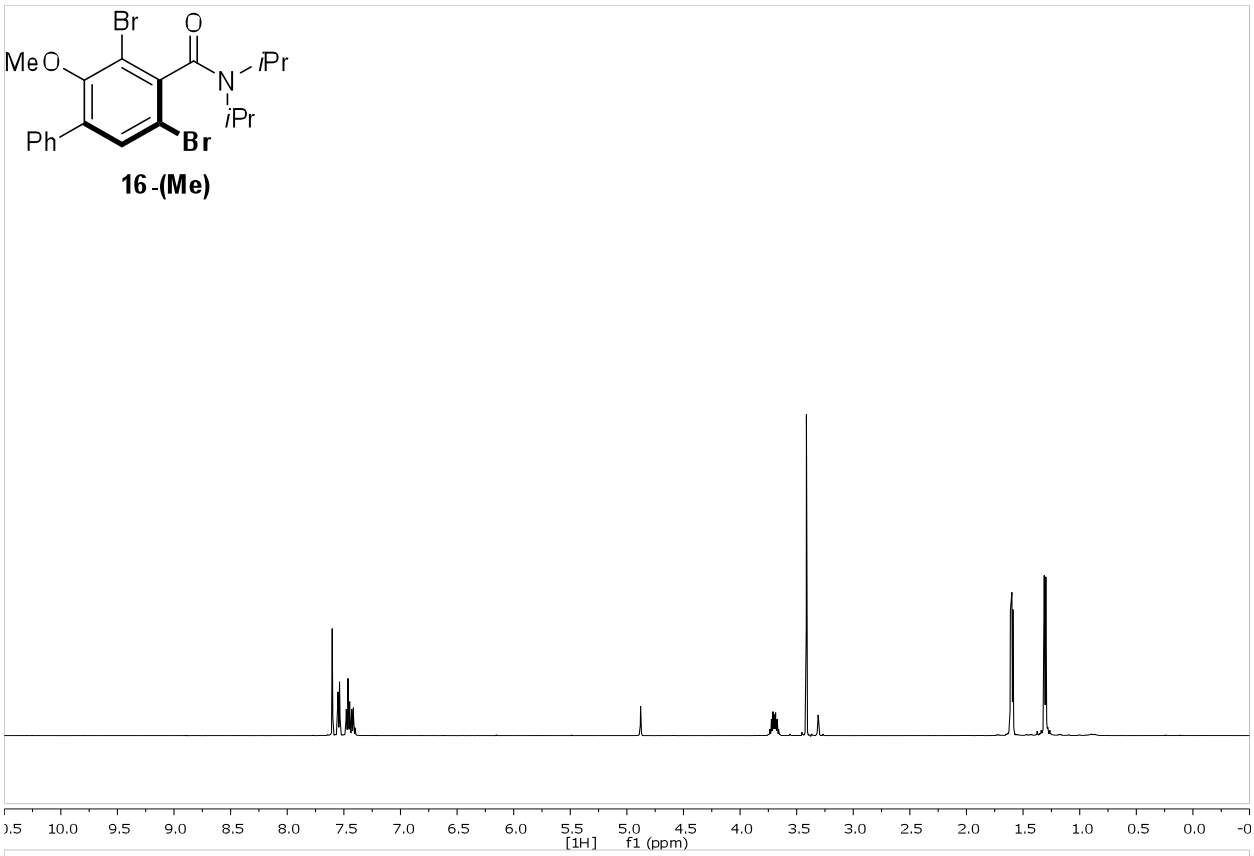
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MeO
N
iPr
iPr
Ph
Br
16-(Me)
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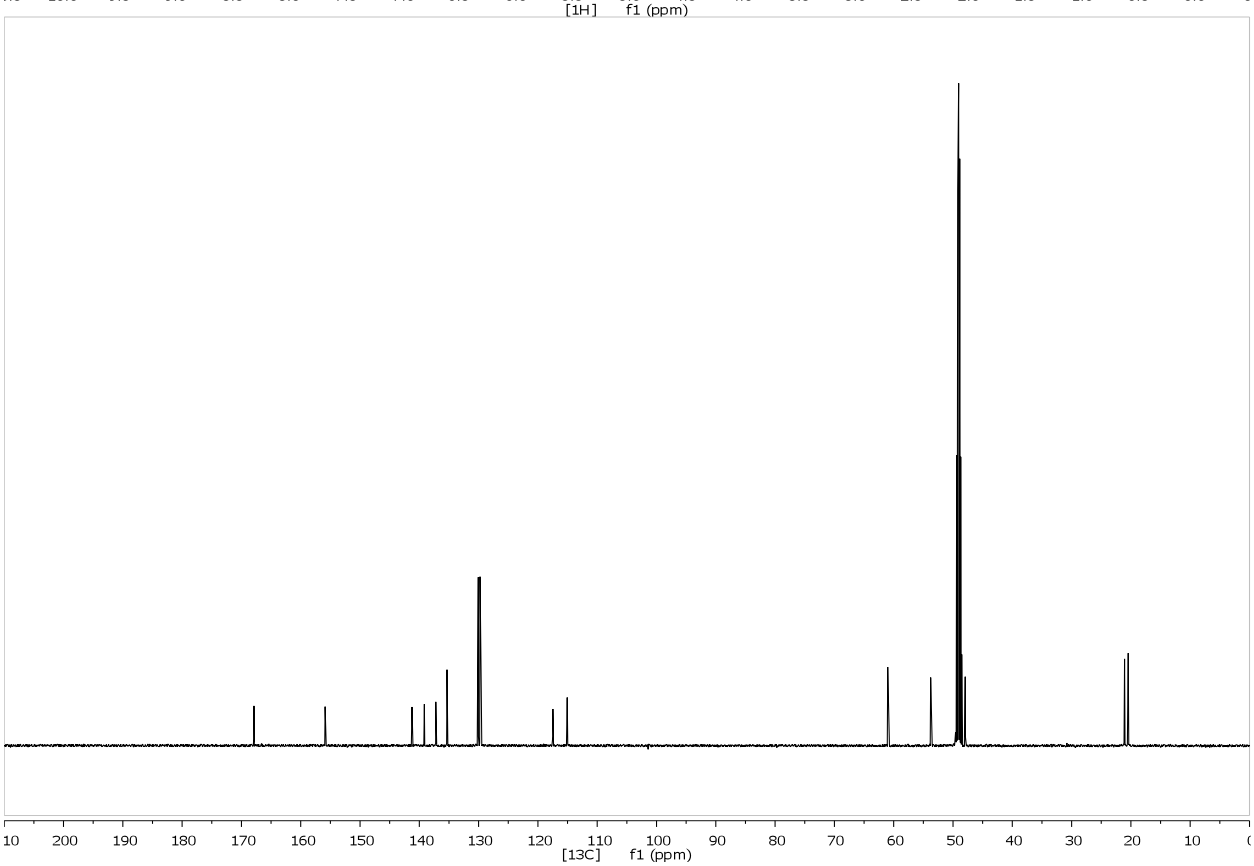
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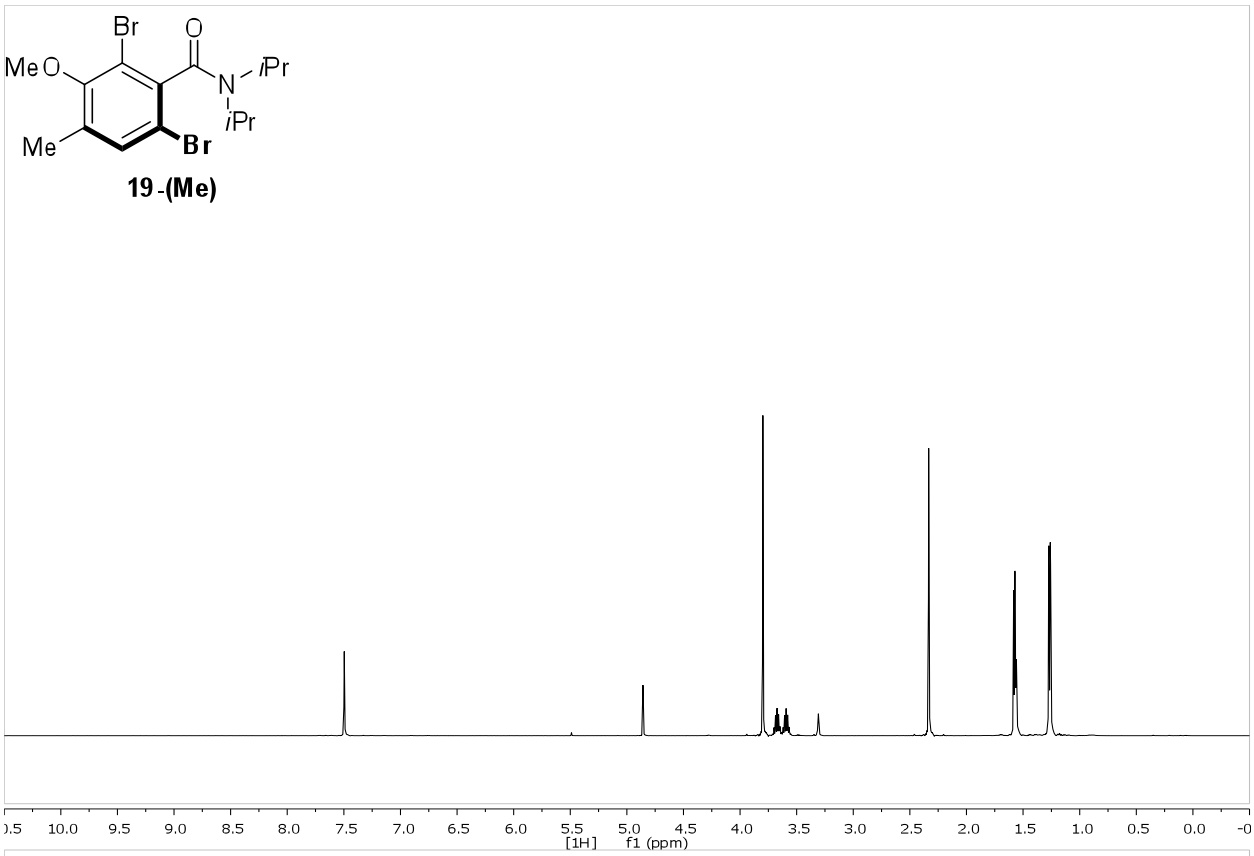
Br
O
Me O
N
iPr
iPr
Me
Br
19-(Me)
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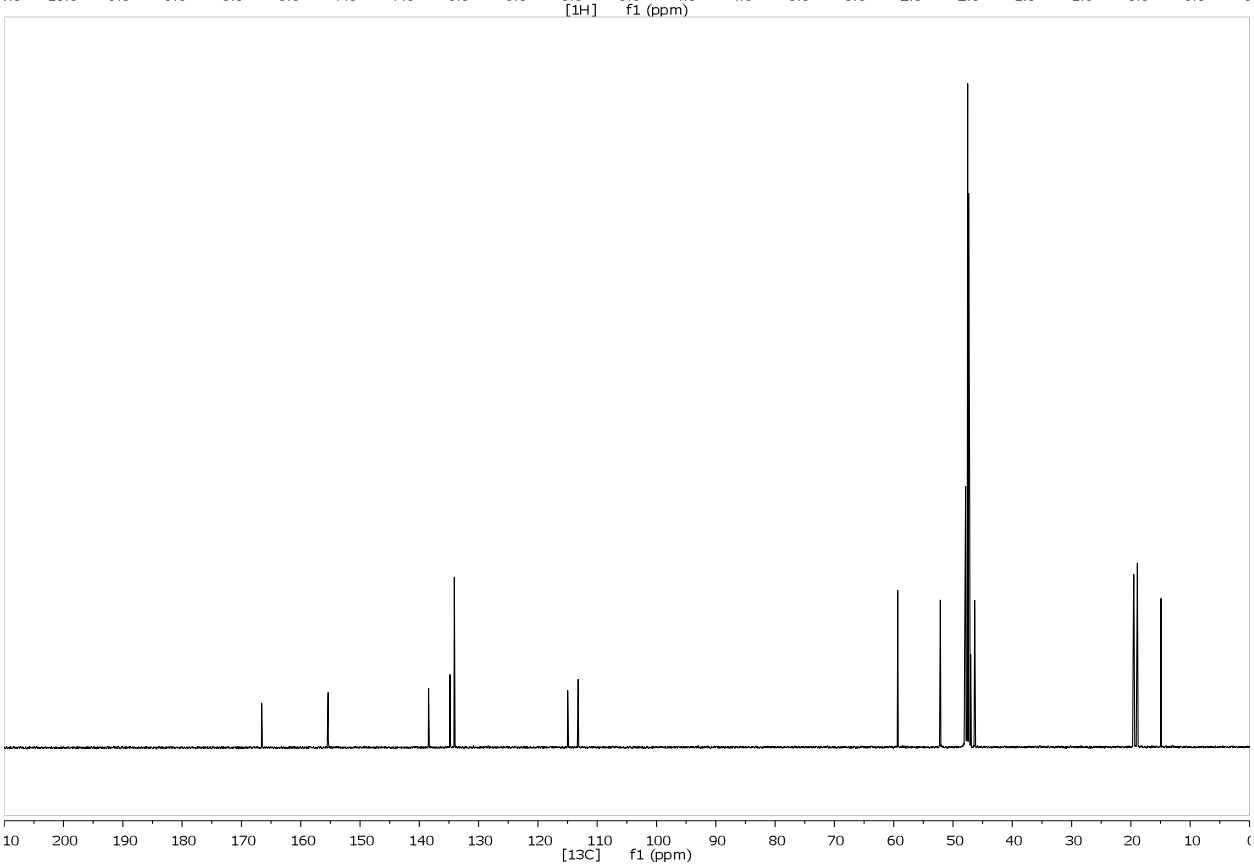
[1H] f1 (ppm)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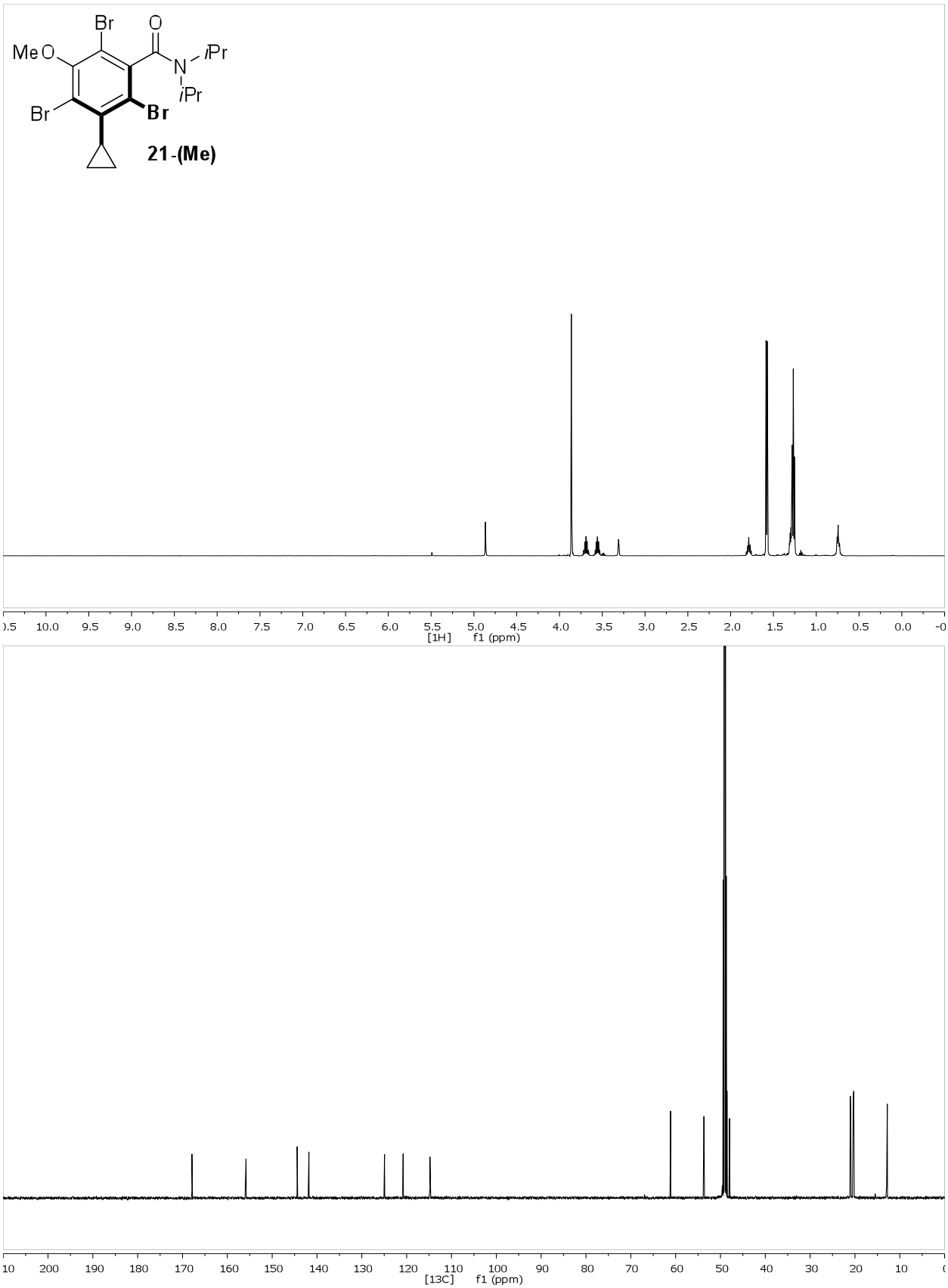
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N
iPr
iPr
Br
Br
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[1H] f1 (ppm)
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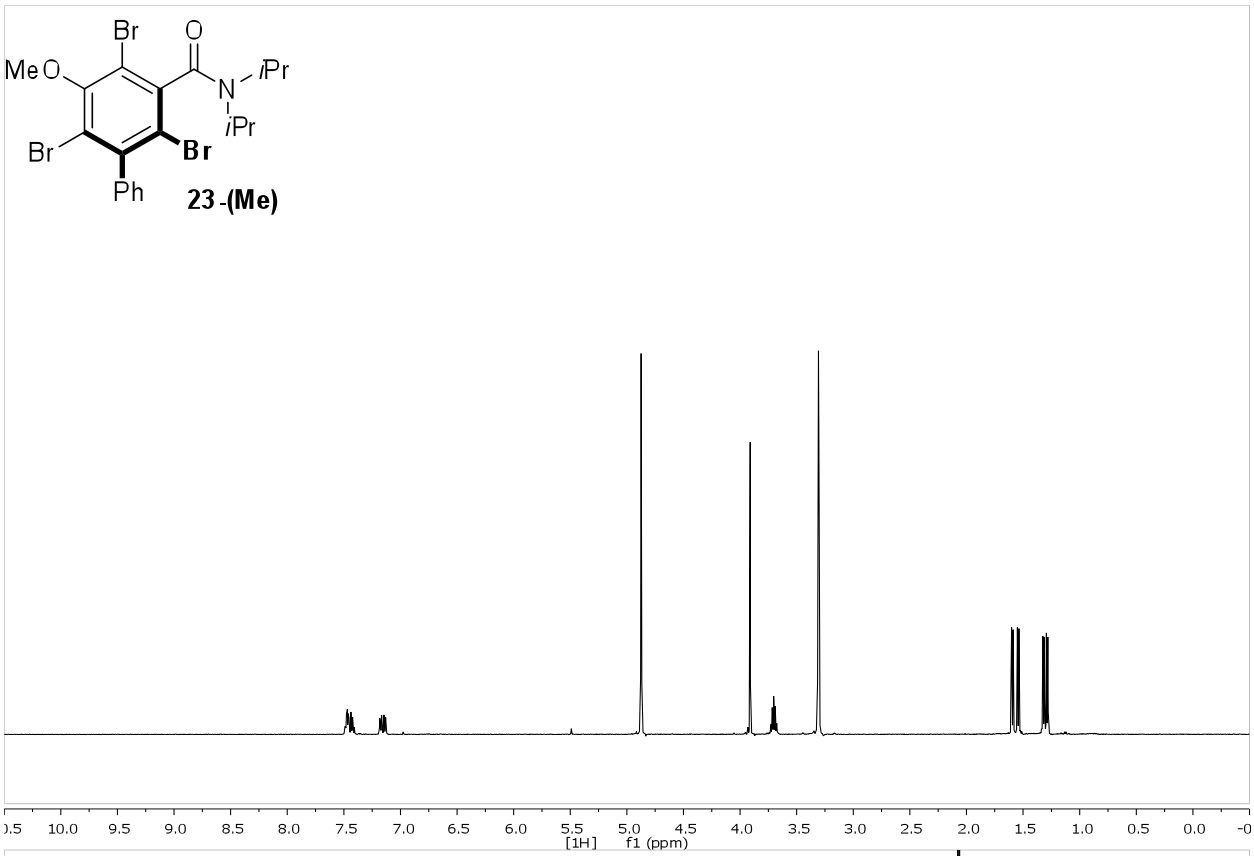
[13C] f1 (ppm)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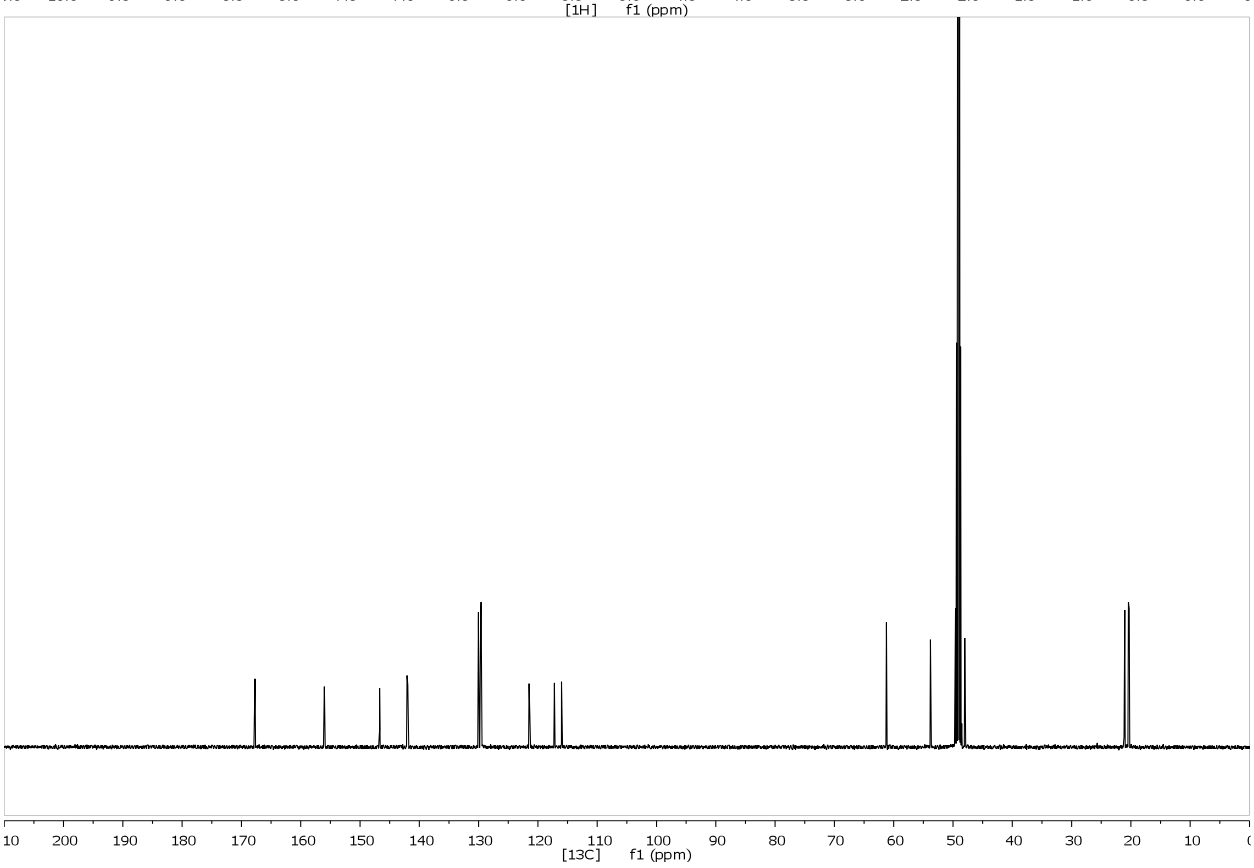
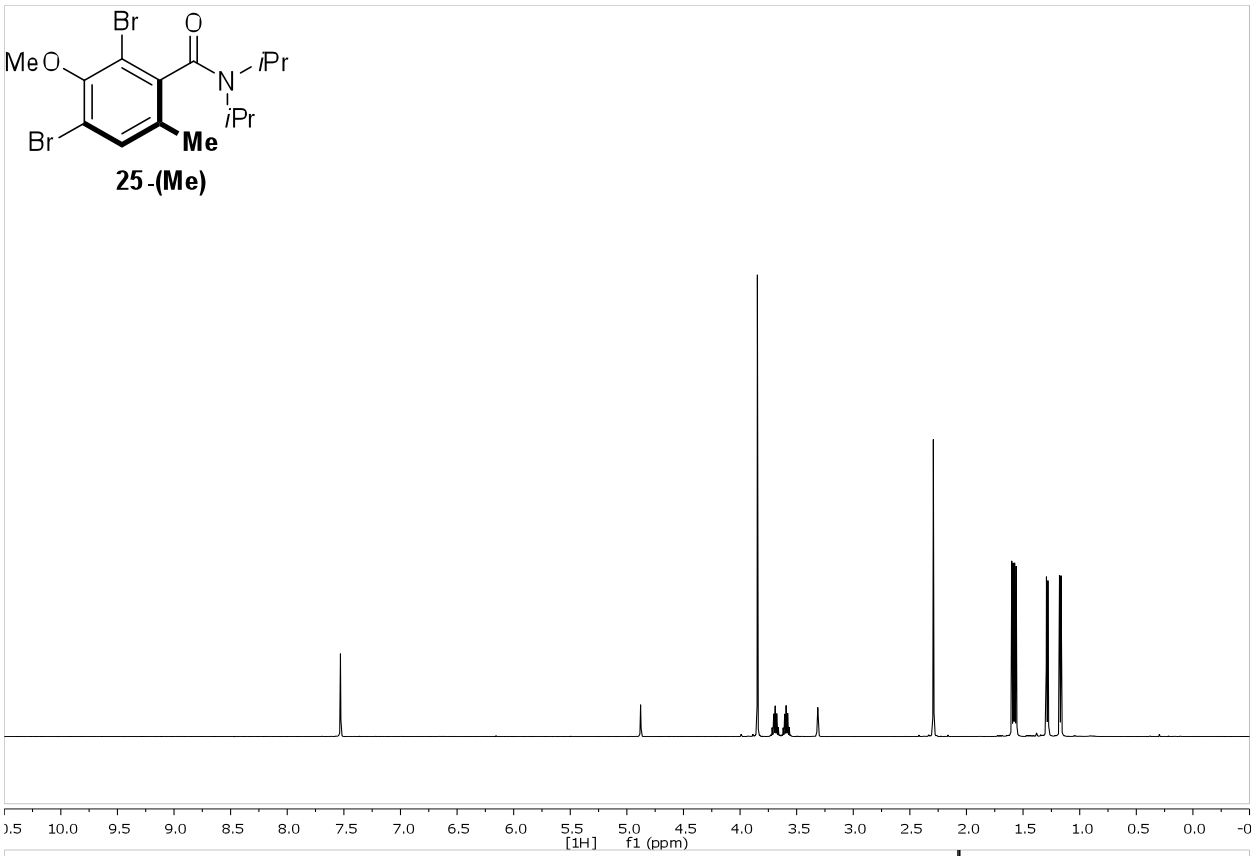
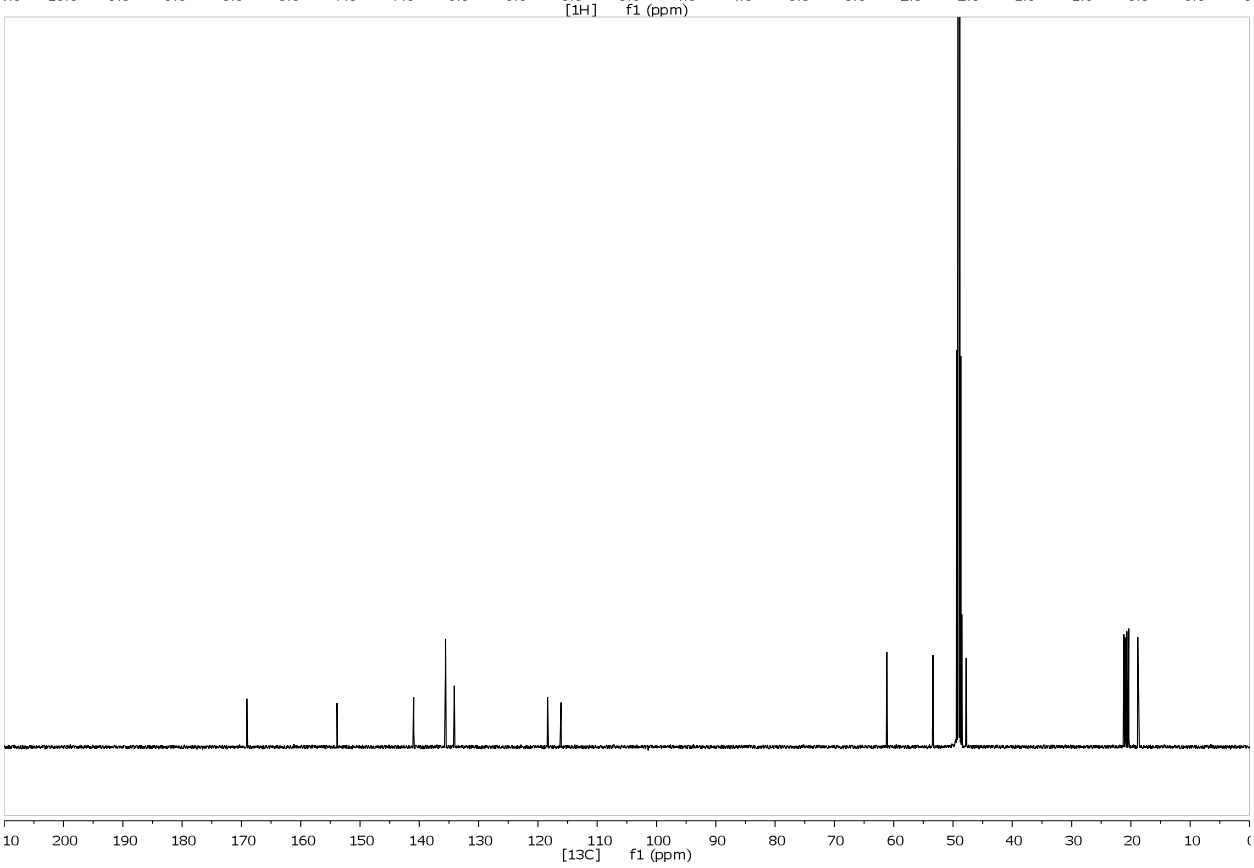
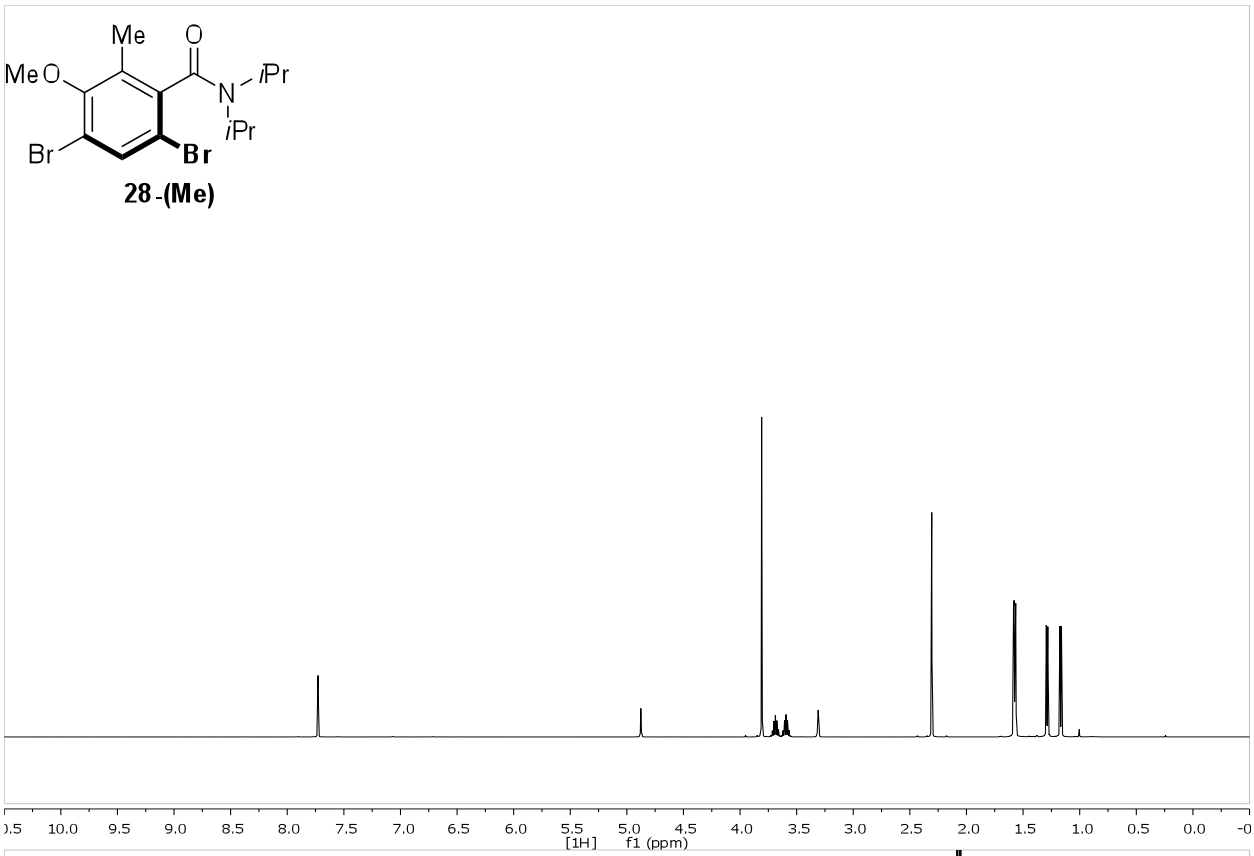
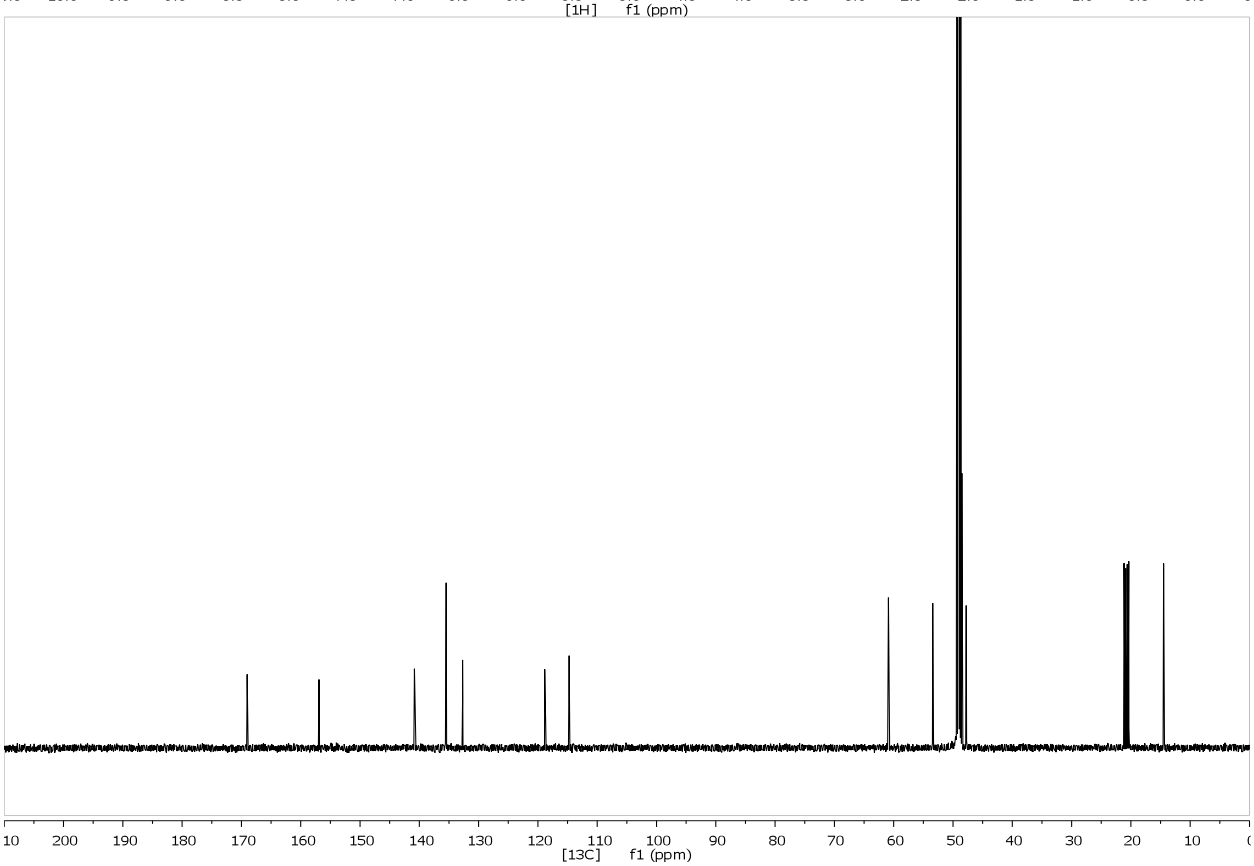
O
MeO
N
iPr
iPr
Br
Br
Ph
23-(Me)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
[1H] f1 (ppm)

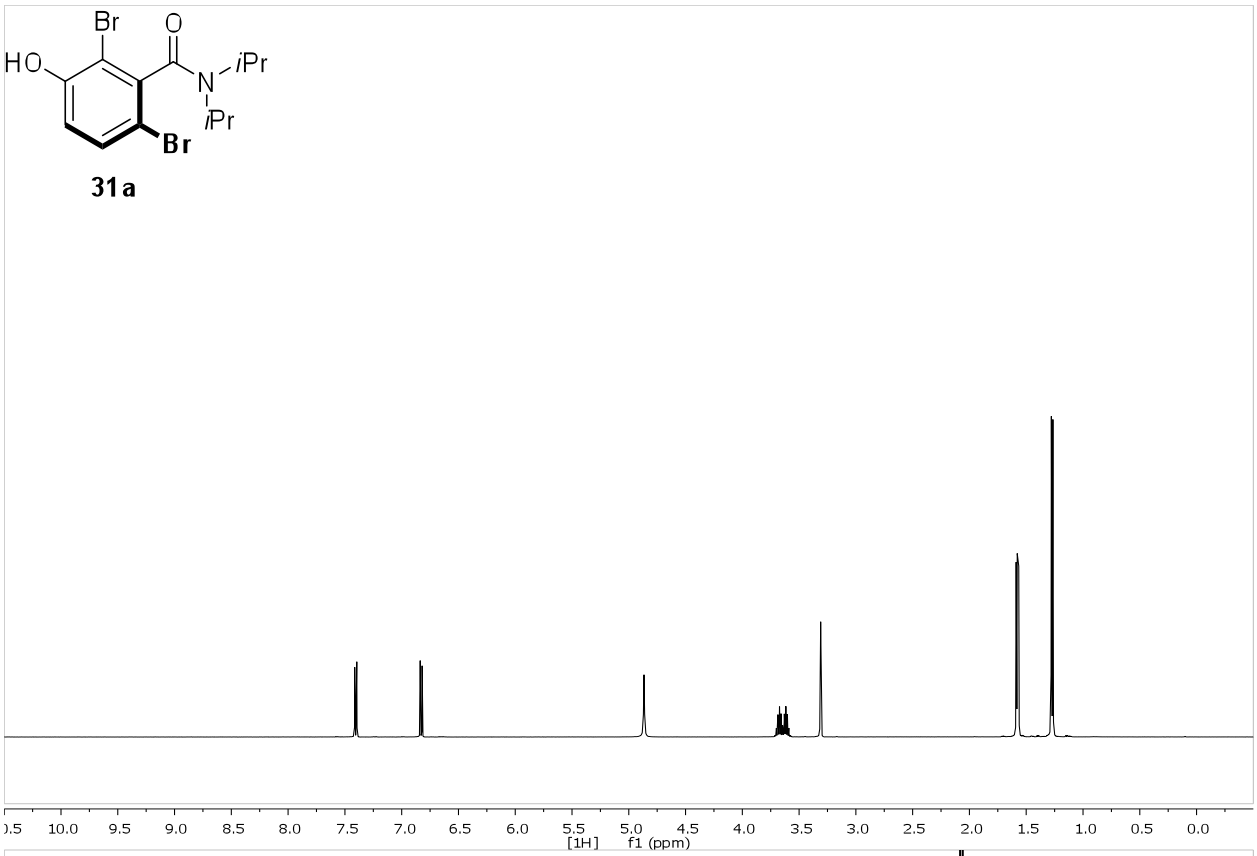

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
[13C] f1 (ppm)

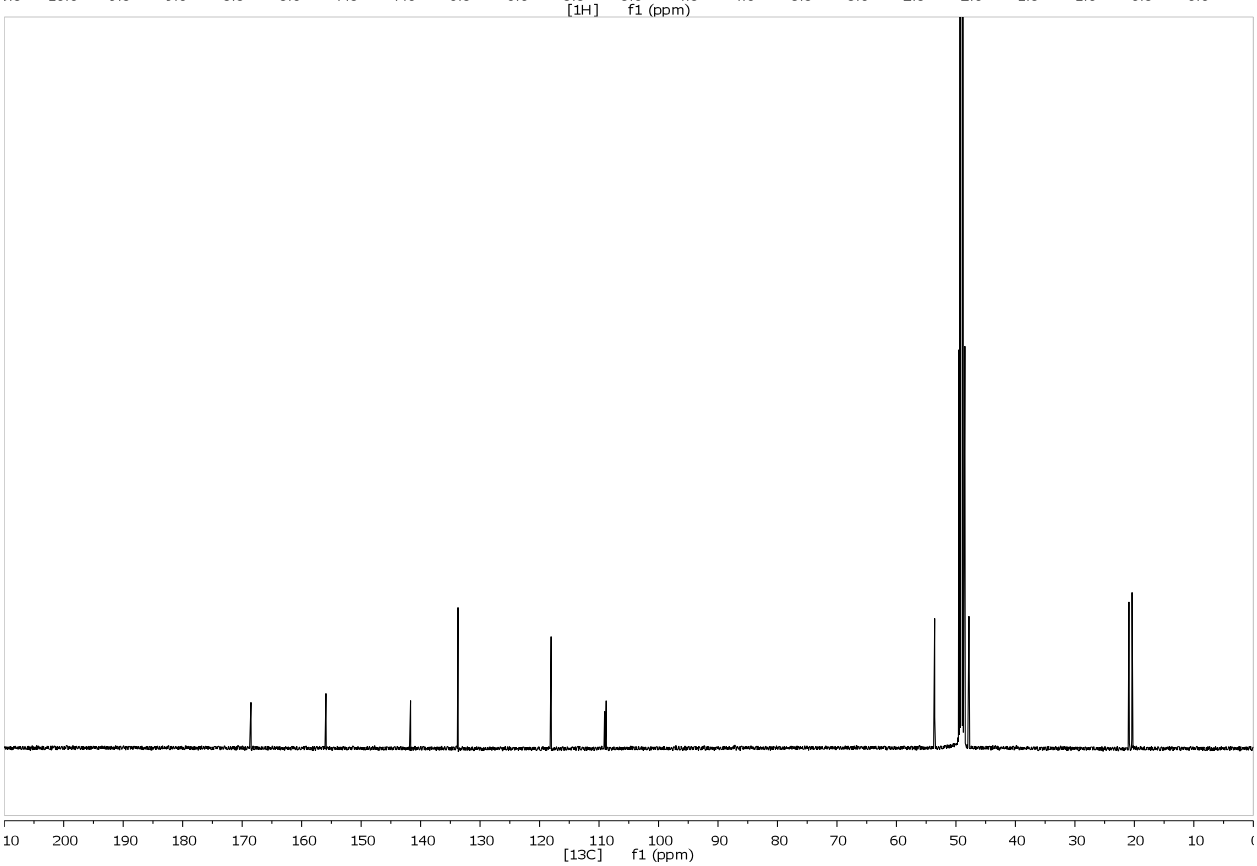

Br
O
MeO
N
iPr
iPr
Br
Me
25-(Me)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
[1H] f1 (ppm)

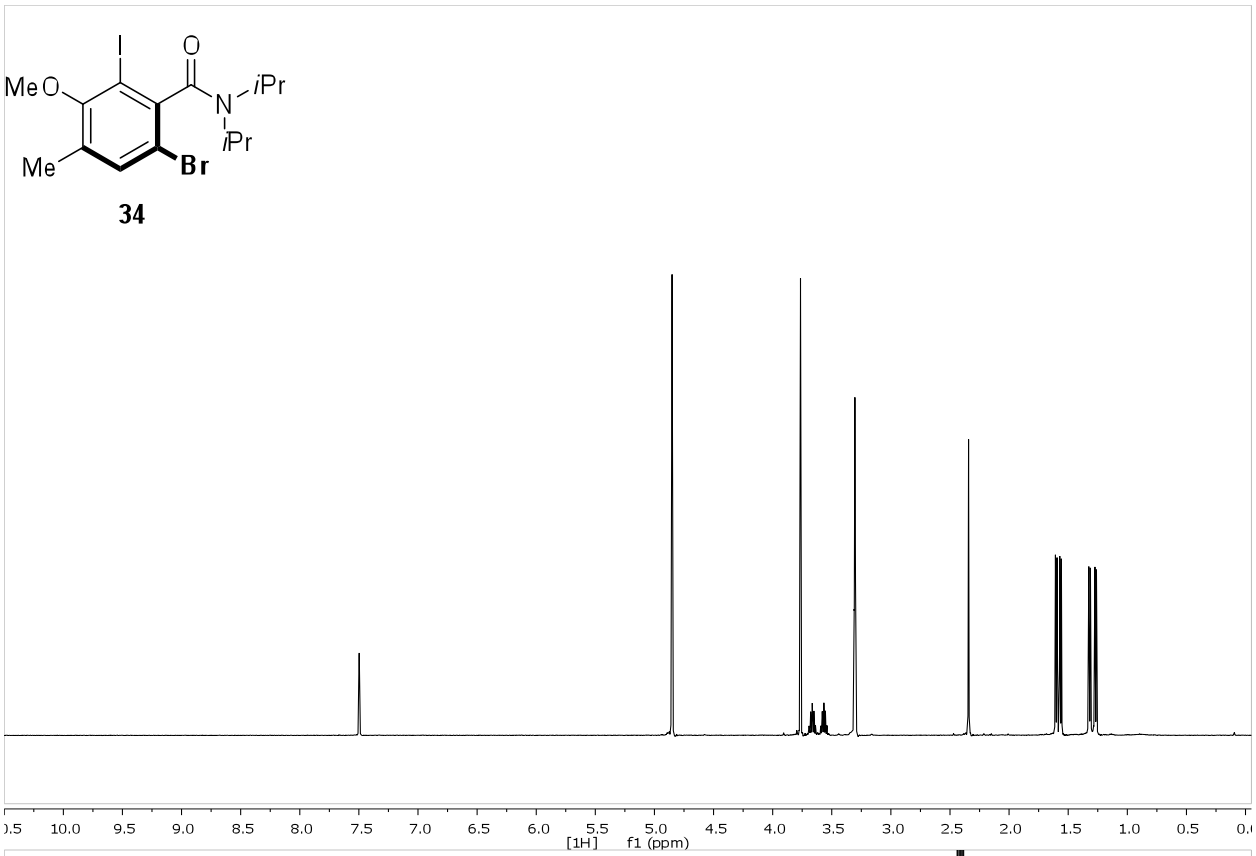

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
[13C] f1 (ppm)

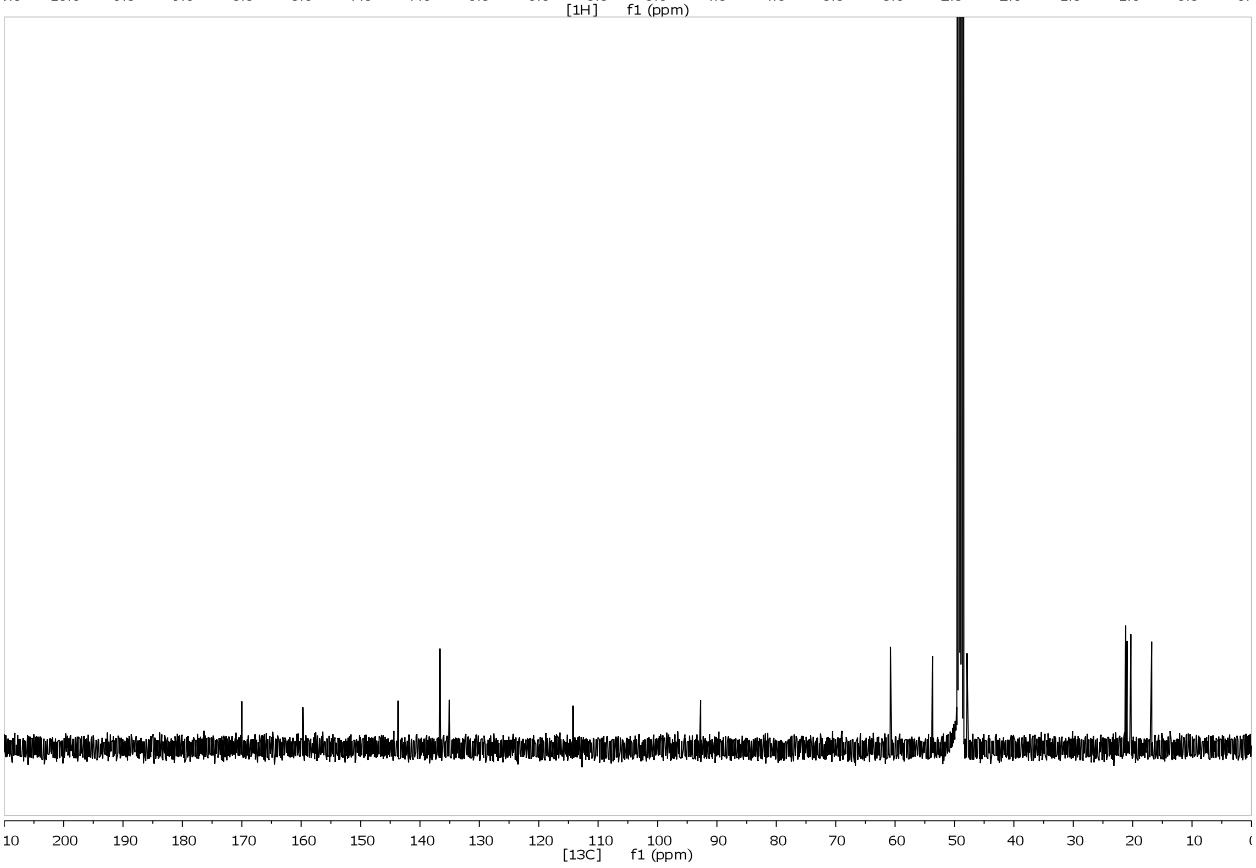

Me
O
MeO
N
iPr
iPr
Br
Br
28-(Me)
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
[1H] f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
[13C] f1 (ppm)

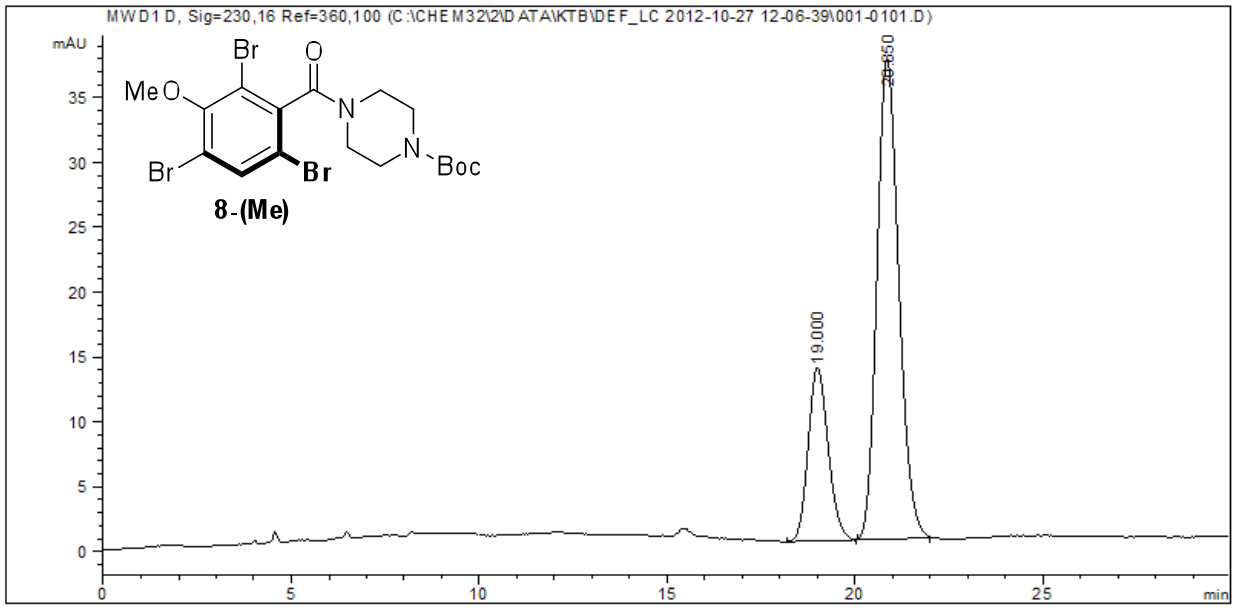

Br
O
HO
N
iPr
iPr
Br
31a
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
[1H] f1 (ppm)


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
[13C] f1 (ppm)


I
O
MeO
N
iPr
iPr
Me
Br
34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
[1H] f1 (ppm)

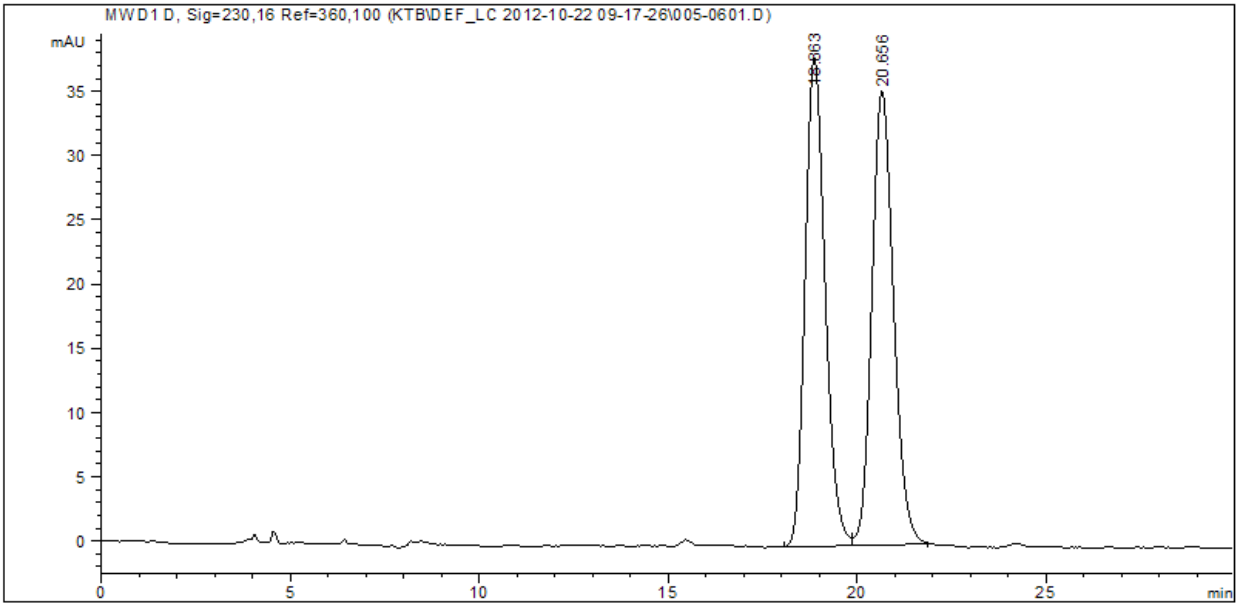

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
[13C] f1 (ppm)

XI. HPLC Traces



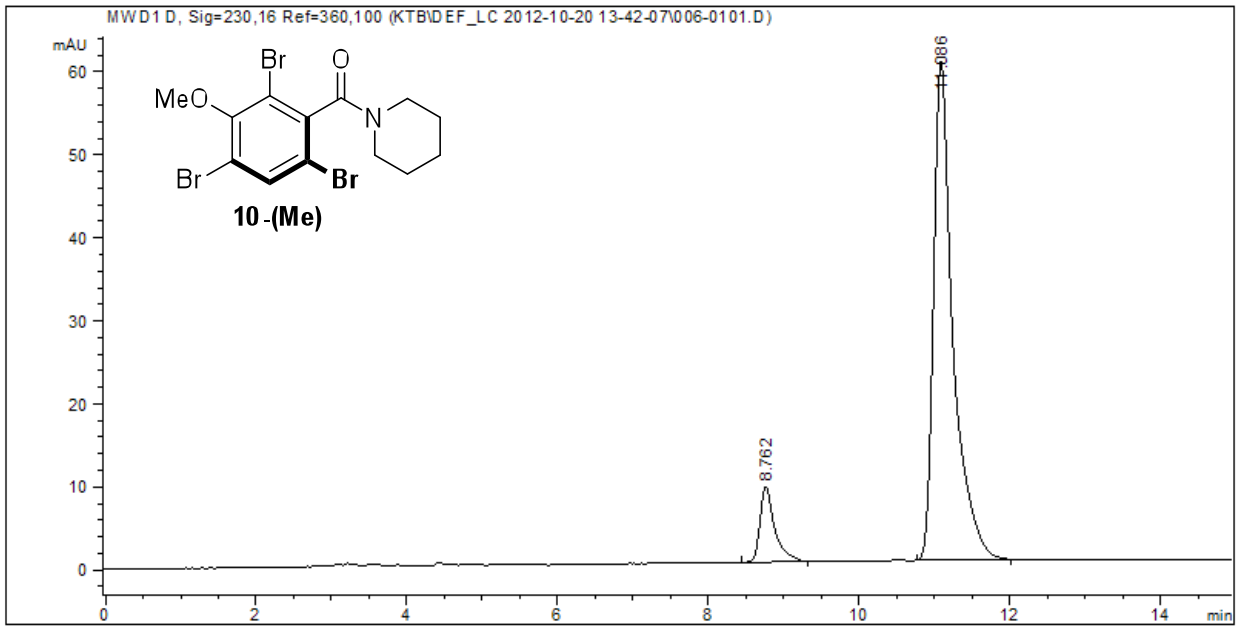
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.000	BB	0.5577	494.70578	13.36997	24.8670
2	20.850	BB	0.6172	1494.70178	37.00478	75.1330



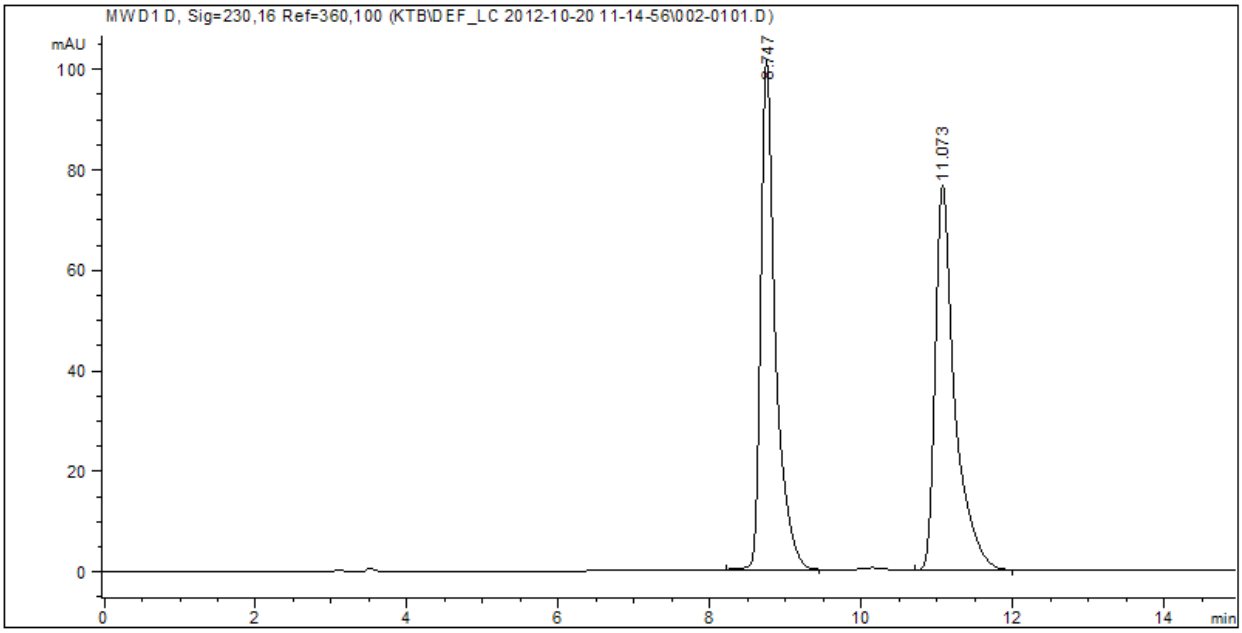
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.863	BV	0.5629	1405.74597	38.05801	49.9246
2	20.656	VB	0.6216	1409.98987	35.32849	50.0754



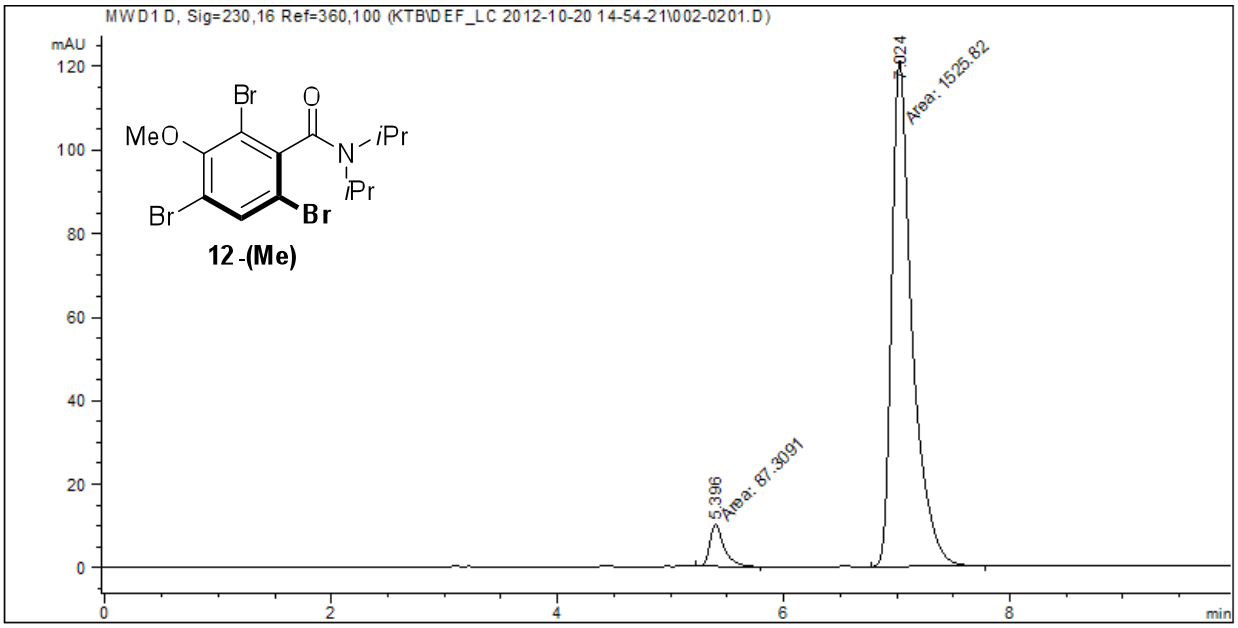
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.762	BB	0.1993	124.62751	9.12481	10.3872
2	11.086	BB	0.2606	1075.18506	60.13776	89.6128



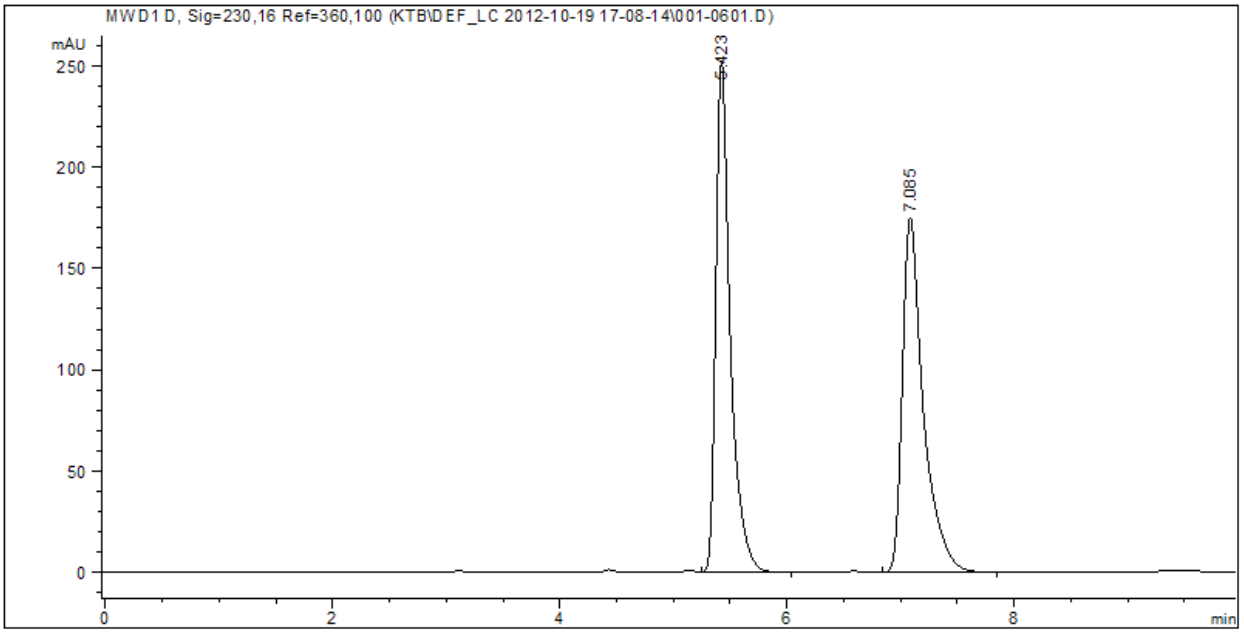
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.747	BB	0.1983	1376.40186	101.44308	49.9979
2	11.073	BB	0.2616	1376.51709	76.62478	50.0021



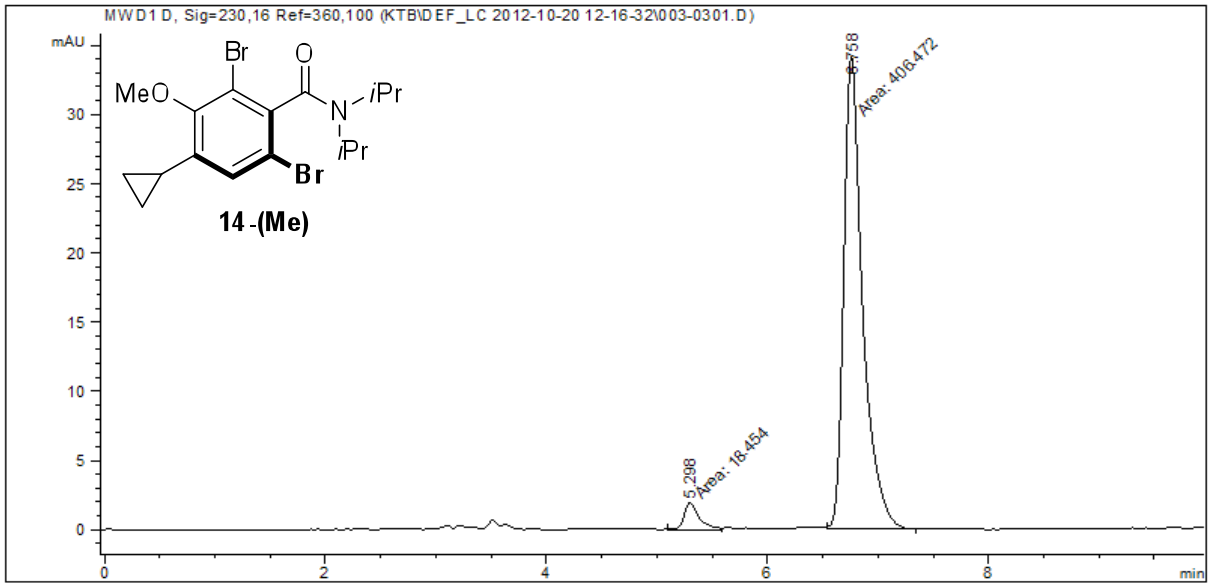
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.396	MM	0.1443	87.30910	10.08416	5.4124
2	7.024	MM	0.2098	1525.82312	121.20348	94.5876



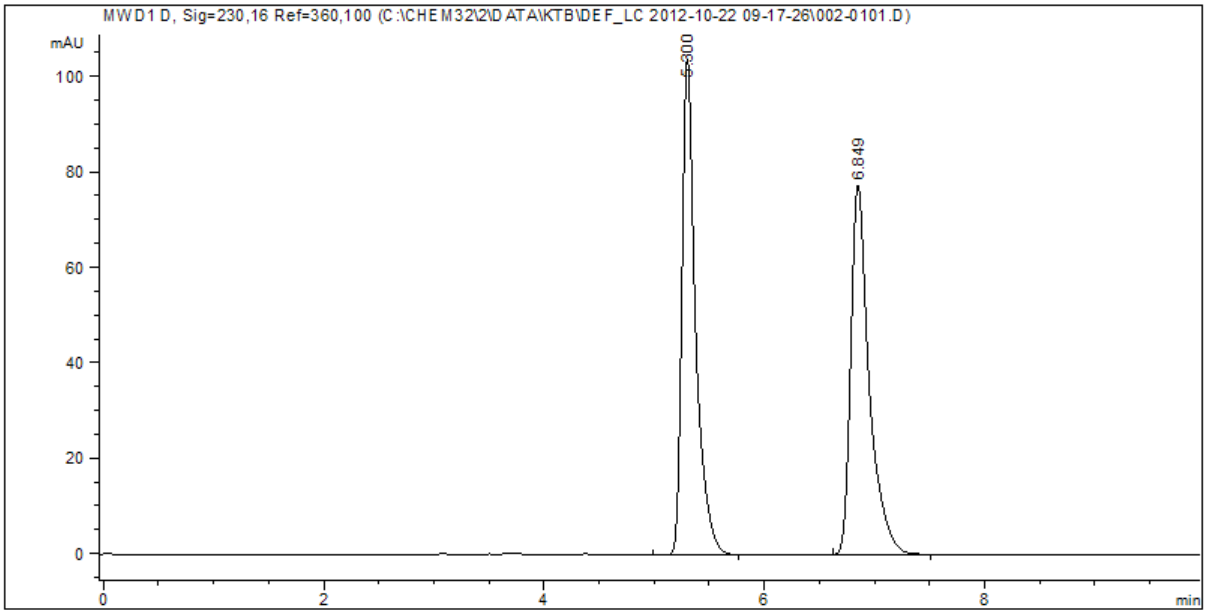
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.423	VV	0.1291	2237.37622	253.06039	49.9343
2	7.085	VB	0.1873	2243.26733	175.25504	50.0657



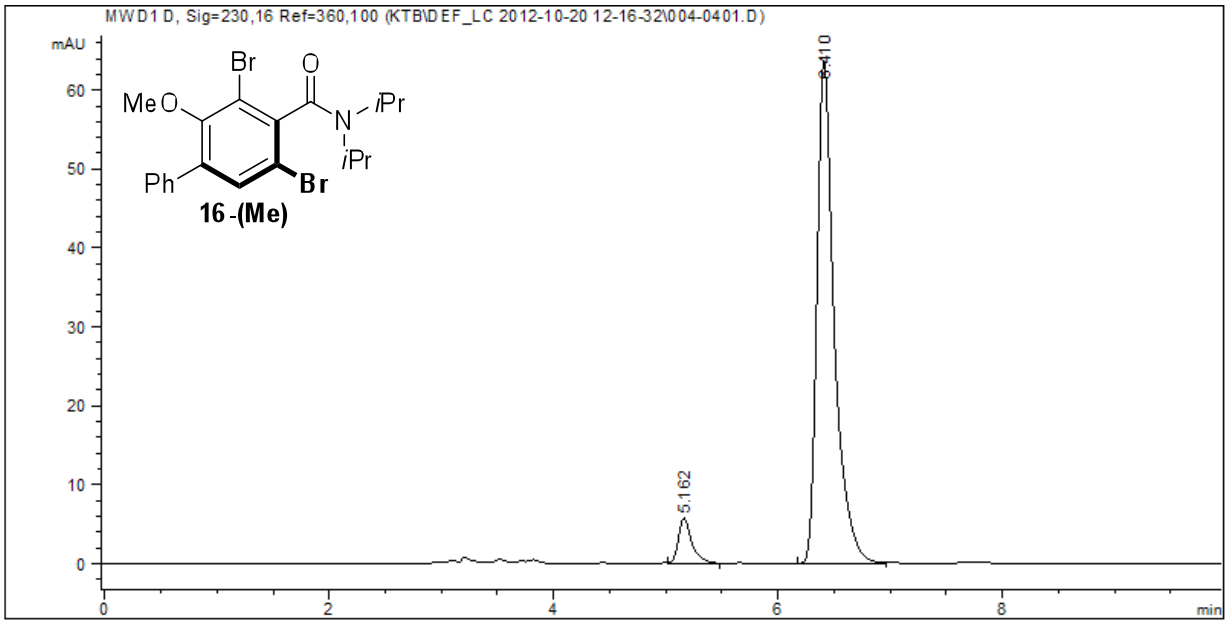
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.298	MM	0.1572	18.45400	1.95622	4.3429
2	6.758	MM	0.1984	406.47180	34.14426	95.6571



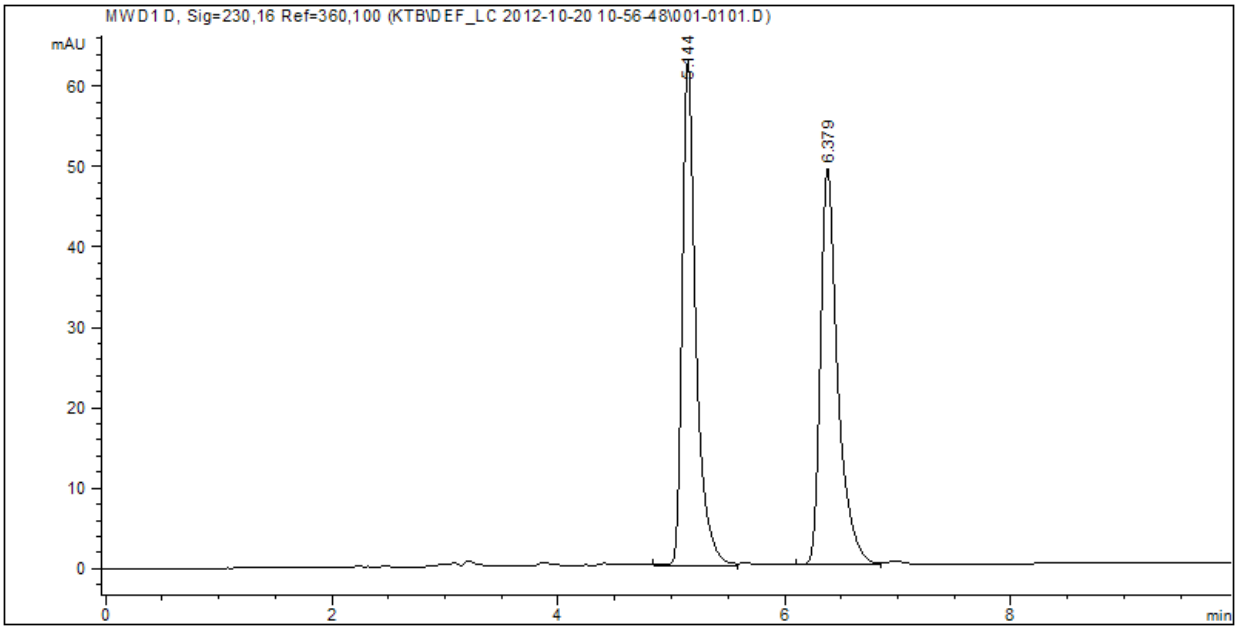
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.300	VB	0.1264	897.62671	104.26949	49.9250
2	6.849	BB	0.1715	900.32269	77.54530	50.0750



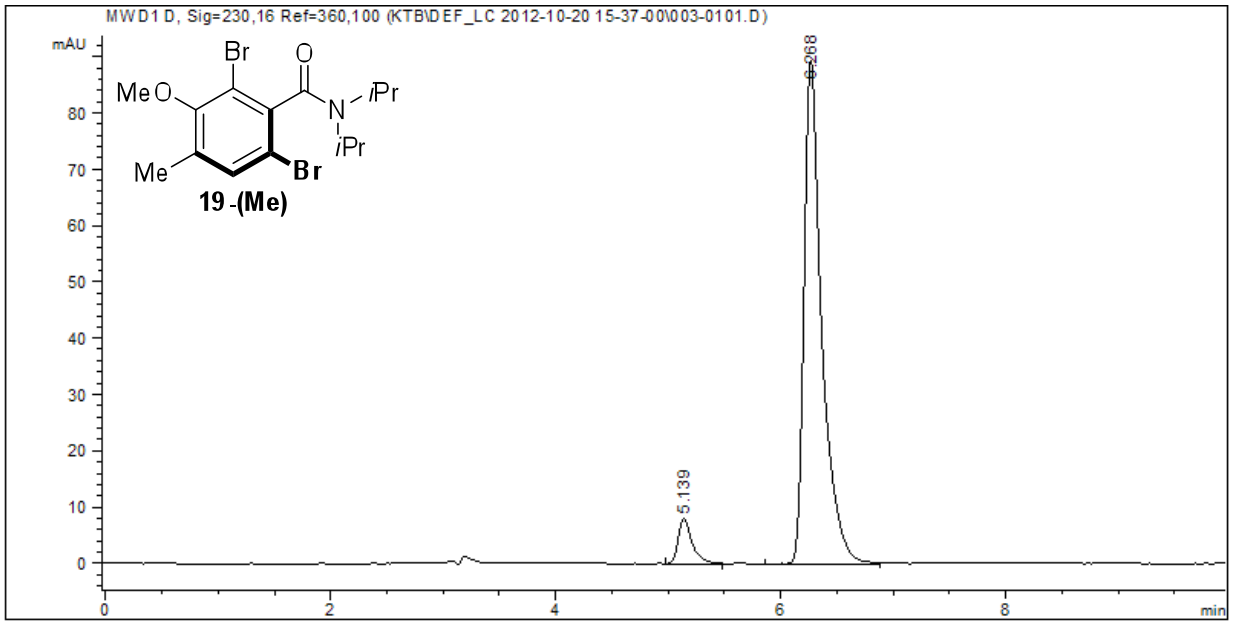
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.162	BB	0.1251	48.97157	5.76291	6.6709
2	6.410	VB	0.1592	685.13568	63.85630	93.3291



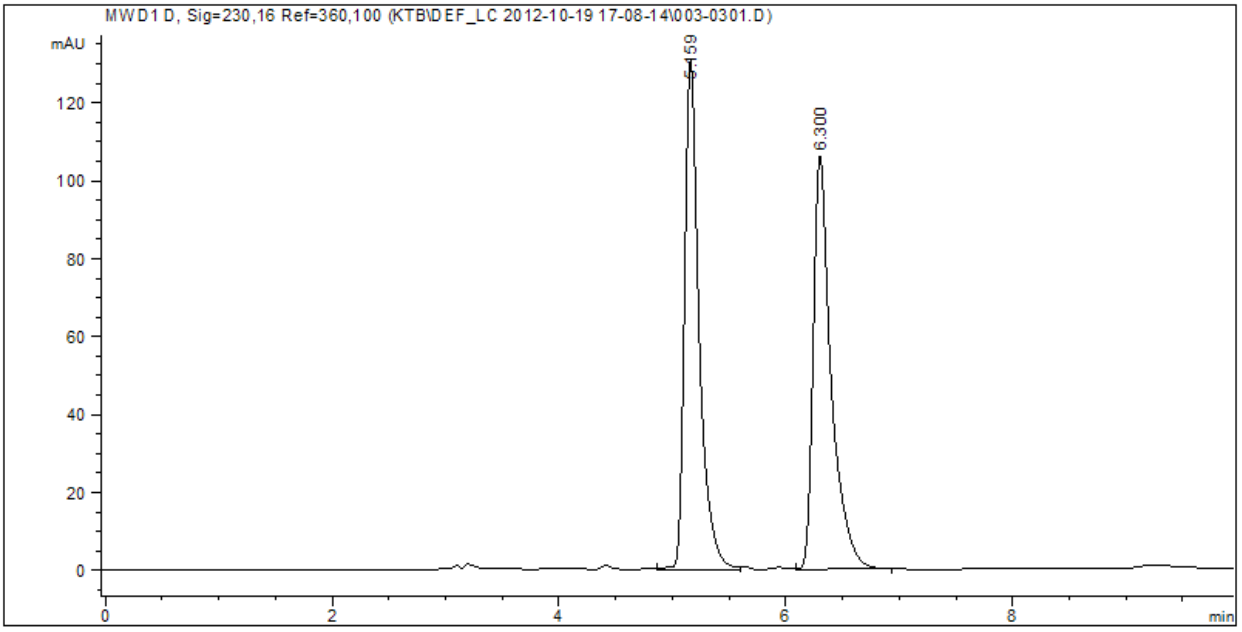
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.144	VV	0.1242	529.32434	62.90157	50.2217
2	6.379	BV	0.1580	524.65015	49.35864	49.7783



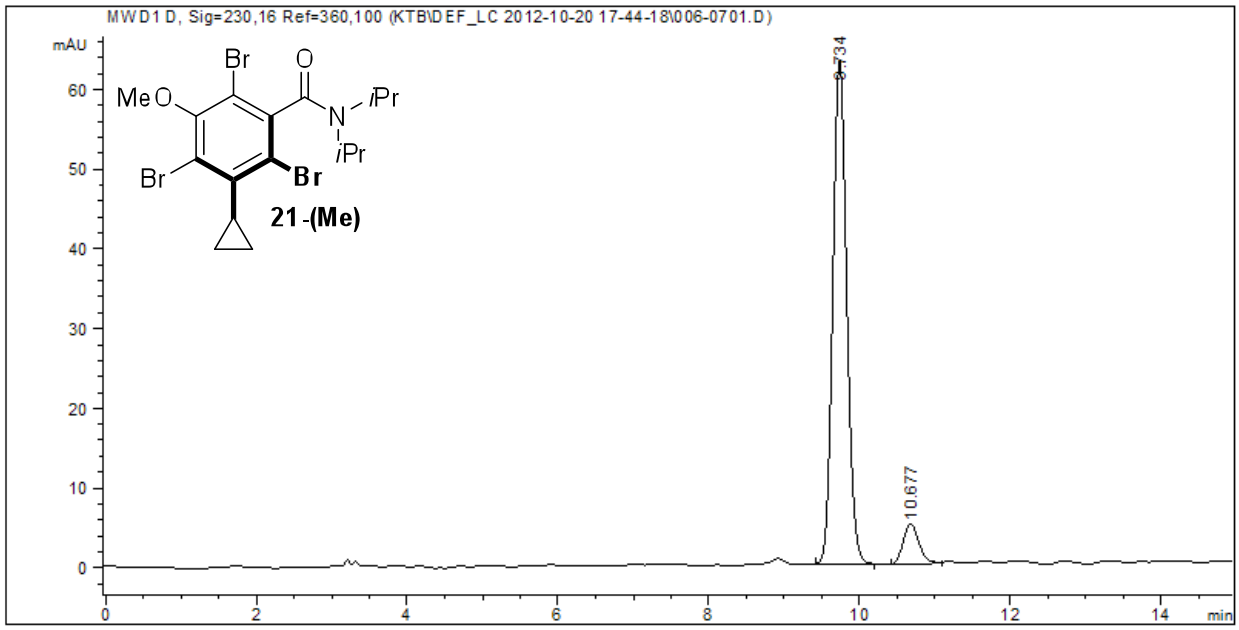
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.139	VB	0.1296	73.10352	8.23524	6.9122
2	6.268	VB	0.1602	984.49261	89.56736	93.0878



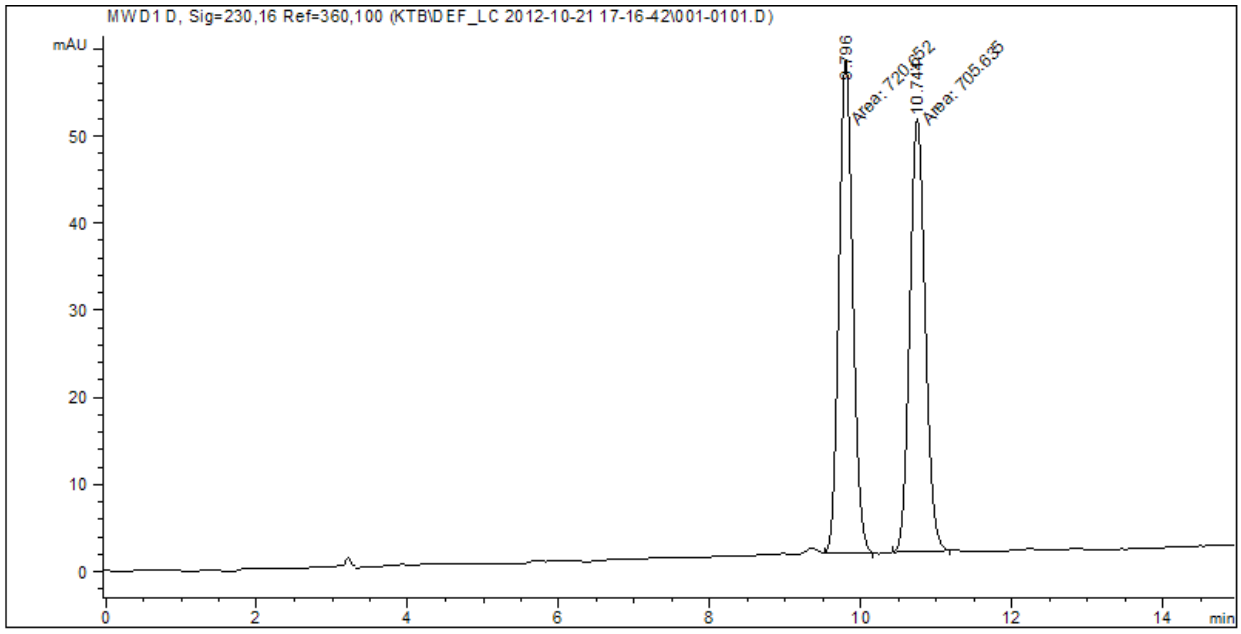
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.159	VV	0.1347	1174.46655	130.88486	50.2333
2	6.300	VB	0.1599	1163.55908	106.13003	49.7667



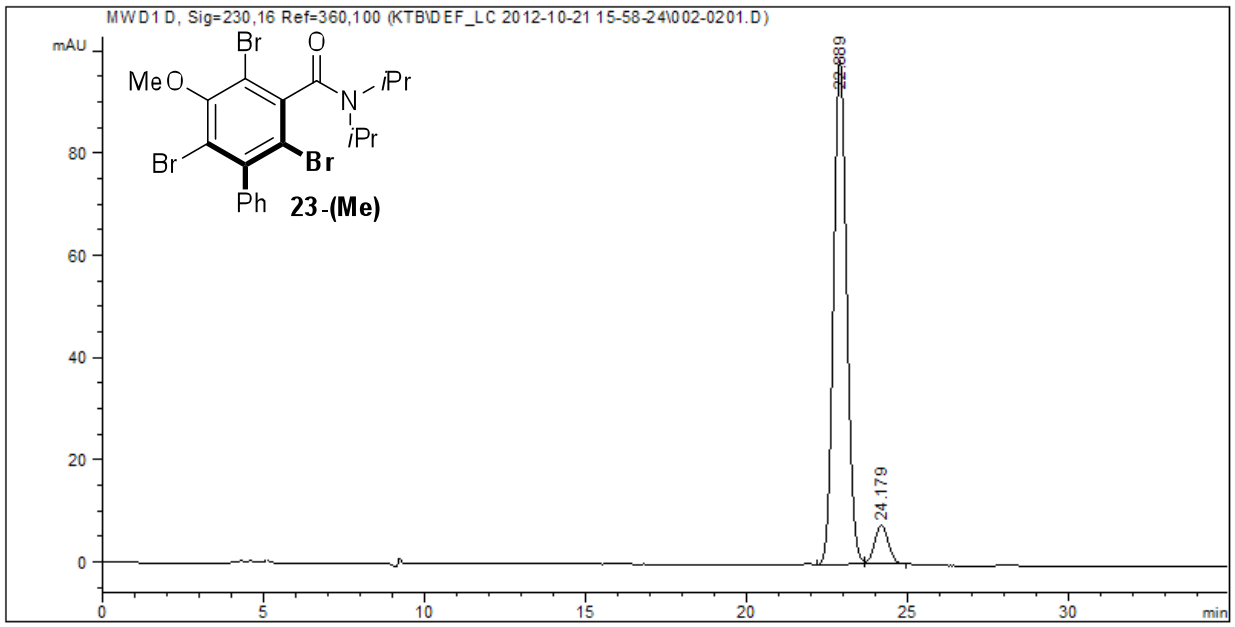
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.734	BB	0.1975	809.90277	63.19147	91.6800
2	10.677	BB	0.2238	73.49915	5.05075	8.3200



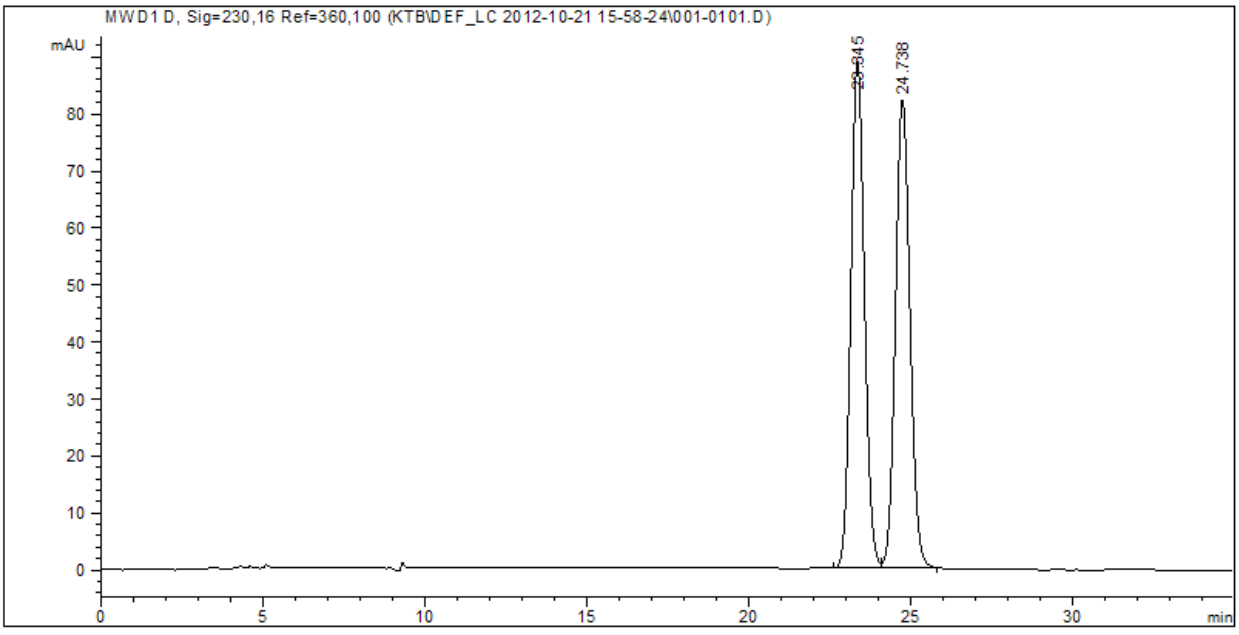
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.796	MM	0.2127	720.65228	56.46532	50.5264
2	10.744	MM	0.2372	705.63513	49.57956	49.4736



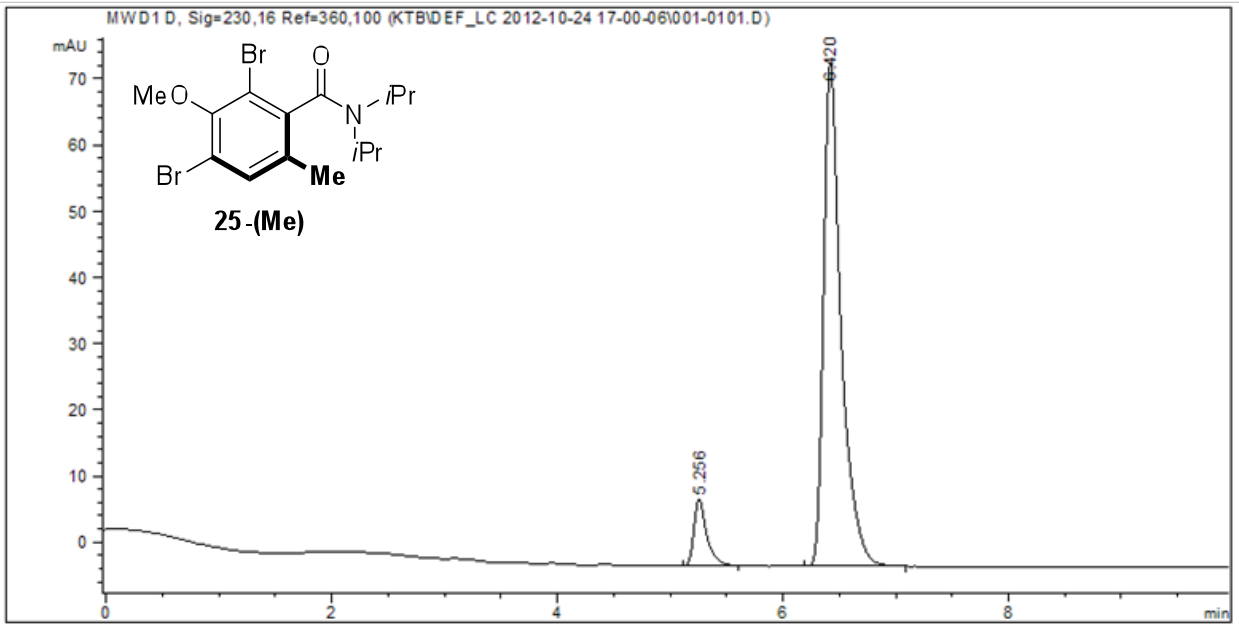
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.889	VV	0.4421	2803.92163	98.49827	92.6111
2	24.179	VB	0.4537	223.70955	7.59310	7.3889



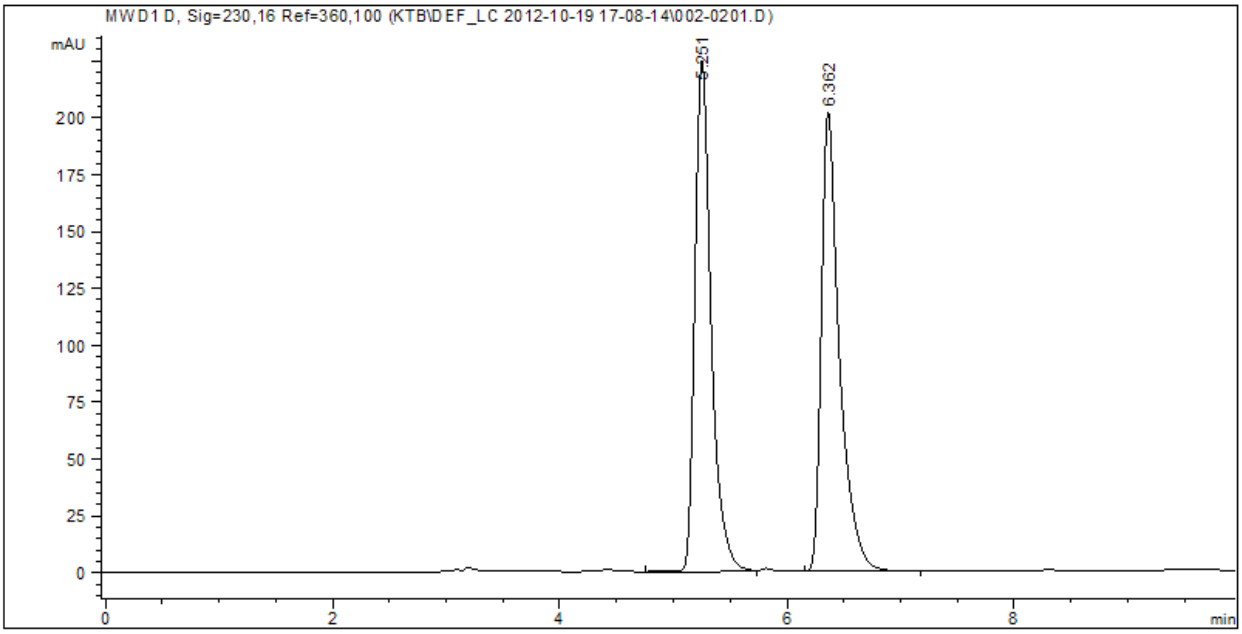
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.345	BV	0.4546	2595.51001	88.91248	50.2995
2	24.738	VB	0.4840	2564.59814	82.20853	49.7005



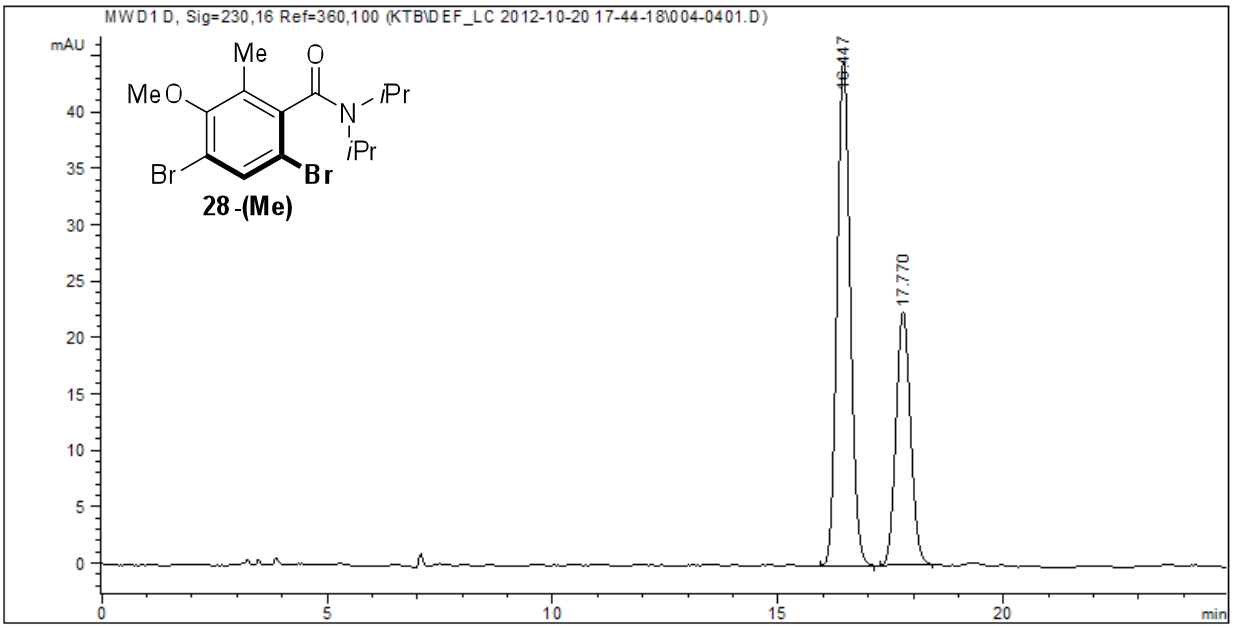
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.256	BB	0.1155	78.79140	10.04616	8.7212
2	6.420	BB	0.1601	824.65228	76.28735	91.2788



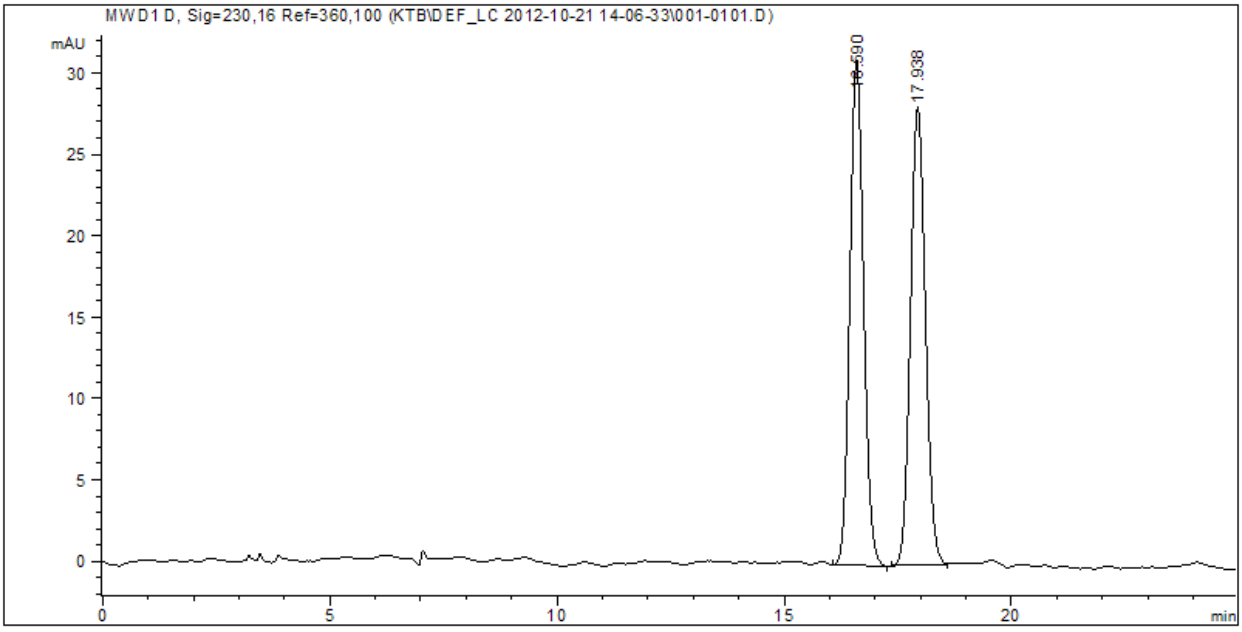
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.251	BV	0.1527	2246.77490	224.62238	50.0090
2	6.362	BB	0.1617	2245.96362	202.00563	49.9910



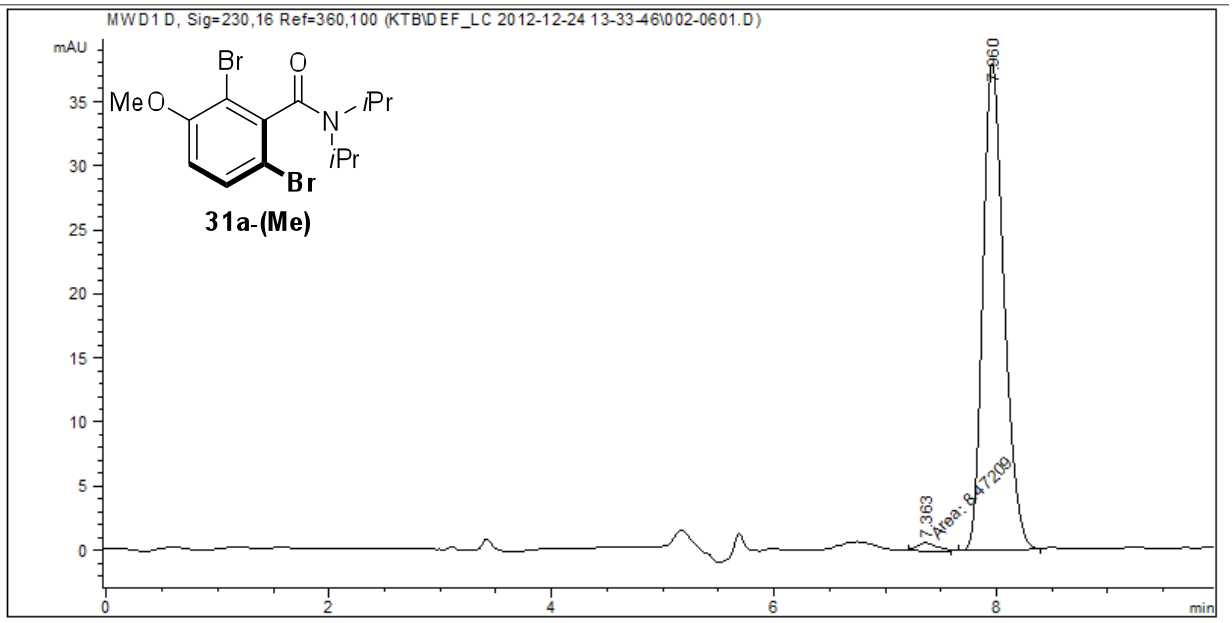
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.447	BB	0.3168	916.99475	44.79425	64.5055
2	17.770	BB	0.3499	504.58212	22.48139	35.4945



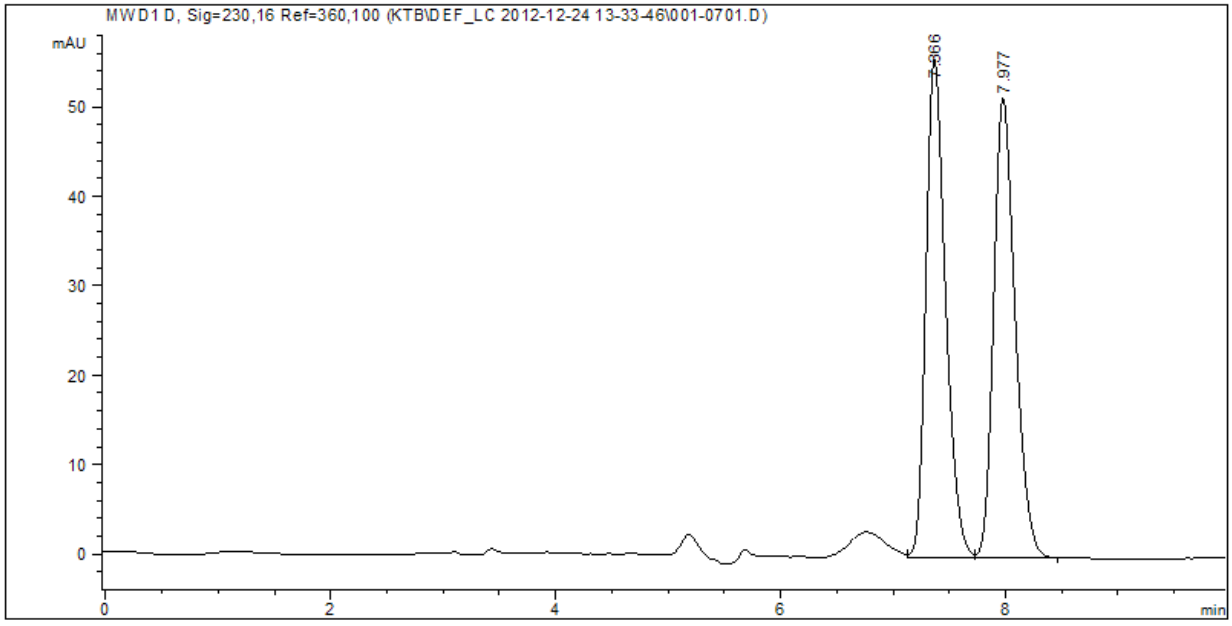
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.590	VB	0.3238	654.71490	31.07128	50.3963
2	17.938	BB	0.3534	644.41864	28.11579	49.6037



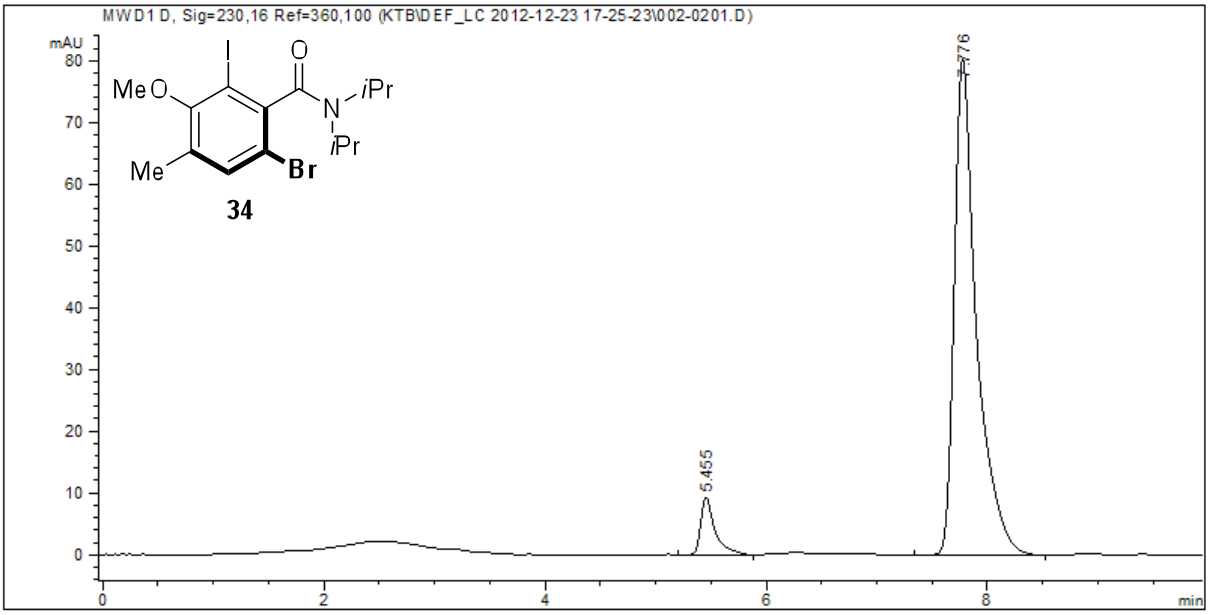
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.363	MM	0.2232	8.47209	6.32626e-1	1.6585
2	7.960	VV	0.2023	502.36096	37.98979	98.3415



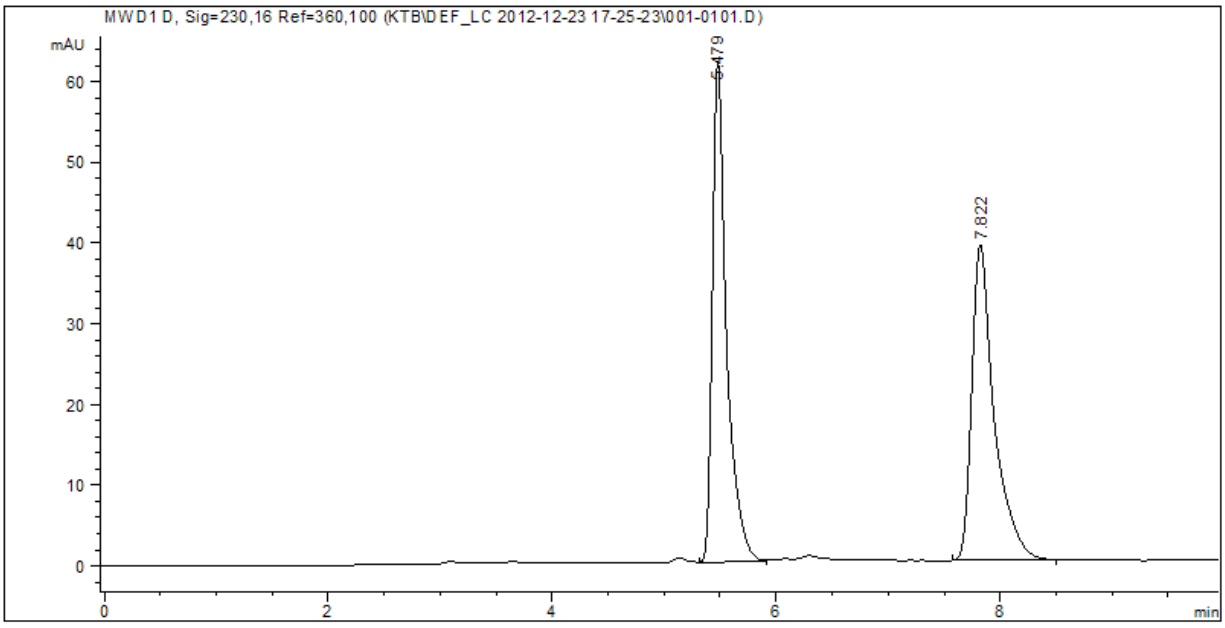
Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.366	VV	0.1841	680.60284	55.87001	49.8744
2	7.977	VB	0.2010	684.03009	51.49565	50.1256



Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.455	VV	0.1324	85.46181	9.37270	7.0314
2	7.776	BB	0.2039	1129.96472	80.44437	92.9686



Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.479	VB	0.1285	545.76984	62.14253	50.0943
2	7.822	BB	0.2021	543.71503	39.13185	49.9057

XII. Crystallographic Data for Compound 11

Experimental

Data Collection

A colorless prism crystal of $C_{14}H_{19}Br_3NO_2$ having approximate dimensions of 0.20 x 0.20 x 0.20 mm was mounted on a glass fiber. All measurements were made on a Rigaku Mercury275R CCD (SCX mini) diffractometer using graphite monochromated Mo-Kα radiation. The crystal-to-detector distance was 49.90 mm. Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions: a = 7.6495(14) Å, b = 9.4852(18) Å, c = 24.586(4) Å, and V = 1783.9(6) $Å^3$.

For Z = 4 and F.W. = 472.01, the calculated density is 1.757 g/cm^3. The reflection conditions of: h00: h = 2n, 0k0: k = 2n, 00l: l = 2n uniquely determine the space group to be: $P2_12_12_1$ (#19).

The data were collected at a temperature of -50 ± 1ºC to a maximum 2θ value of 48.7º. A total of 360 oscillation images were collected. A sweep of data was done using ω scans from -120.0 to 60.0º in 1.0º step, at χ=54.0º and ϕ= 0.0º. The exposure rate was 50.0 [sec/º]. The detector swing angle was -28.40º. A second sweep was performed using ω scans from -120.0 to 60.0º in 1.0º step, at χ=54.0º and ϕ = 120.0º. The exposure rate was 50.0 [sec/º]. The detector swing angle was -28.40º. The crystal-to-detector distance was 49.90 mm. Readout was performed in the 0.146 mm pixel mode.

Data Reduction

Of the 8639 reflections that were collected, 2895 were unique (R_{int} = 0.0374). Data were collected and processed using CrystalClear (Rigaku).[1] The linear absorption coefficient, μ, for Mo-Kα radiation is 68.047 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.142 to 0.256. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. **A rigid group restraint was applied to C1-C6 atoms resulting in a regular hexagon.** Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 2895 observed reflections and 181 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o| = 0.0462$$

$$wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma \, w(F_o^2)^2]^{1/2} = 0.1059$$

The standard deviation of an observation of unit weight[4] was 1.04. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.79 and -0.86 $e^-/Å^3$, respectively. The absolute structure was deduced based on Flack parameter, 0.03(2), using 1196 Friedel pairs.[5]

Neutral atom scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in Fcalc;[7] the values for Δf' and Δf'' were those of Creagh and McAuley.[8] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[9] All calculations were performed using the CrystalStructure[10] crystallographic software package except for refinement, which was performed using SHELXL-97.[11]

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$Br_3O_2NC_{14}H_{18}$
Formula Weight	472.01
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 7.6495(14) Å b = 9.4852(18) Å c = 24.586(4) Å V = 1783.9(6) $Å^3$
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.757 g/cm^3
F_{000}	920.00
m(MoKa)	68.047 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku Mercury275R CCD (SCX mini)
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-50.0ºC
Detector Aperture	75 mm (diameter)
Data Images	360 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	-120.0 - 60.0º
Exposure Rate	50.0 sec/º
Detector Swing Angle	-28.40º
ω oscillation Range (χ=54.0, ϕ=120.0)	-120.0 - 60.0º

Exposure Rate	50.0 sec/º
Detector Swing Angle	-28.40º
Detector Position	49.90 mm
Pixel Size	0.146 mm
$2\theta_{max}$	48.7º
No. of Reflections Measured	Total: 8639
	Unique: 2895 (R_{int} = 0.0374)
	Friedel pairs: 1196
Corrections	Lorentz-polarization
	Absorption (trans. factors: 0.142 - 0.256)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1/\ [\ \Sigma^2(F_o^2) + (0.0416 \cdot P)^2$
	$+ 2.4104 \cdot P\ ]$
	where $P = (Max(F_o^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	48.7º
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2895
No. Variables	181
Reflection/Parameter Ratio	15.99
Residuals: R1 (I>2.00σ(I))	0.0462
Residuals: R (All reflections)	0.0628
Residuals: wR2 (All reflections)	0.1059
Goodness of Fit Indicator	1.036
Flack Parameter	0.03(2)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.79 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.86 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	Beq
Br(1)	0.66770(15)	0.17931(9)	0.52766(4)	7.15(3)
Br(2)	0.78254(12)	-0.36470(11)	0.44101(4)	7.59(3)
Br(3)	0.78814(16)	-0.28733(9)	0.66861(4)	7.48(3)
O(1)	0.7071(7)	-0.0457(6)	0.4425(2)	6.11(13)
O(2)	0.5301(7)	0.0282(6)	0.6537(2)	6.00(13)
N(1)	0.8102(6)	0.0992(5)	0.66620(18)	3.26(9)
C(1)	0.7695(9)	-0.2072(7)	0.5978(3)	4.29(14)
C(2)	0.7873(9)	-0.2969(7)	0.5536(3)	5.07(15)
C(3)	0.7651(9)	-0.2429(8)	0.5017(3)	4.89(15)
C(4)	0.7351(8)	-0.1009(8)	0.4936(3)	4.38(14)
C(5)	0.7179(9)	-0.0145(7)	0.5388(3)	4.00(13)
C(6)	0.7332(8)	-0.0643(6)	0.5923(3)	3.51(12)
C(7)	0.6836(9)	0.0251(7)	0.6402(3)	3.79(13)
C(8)	0.9968(9)	0.0896(8)	0.6506(3)	4.72(16)
C(9)	1.0701(13)	0.2300(11)	0.6326(4)	8.7(3)
C(10)	1.1072(10)	0.0268(11)	0.6960(4)	6.9(2)
C(11)	0.7635(10)	0.1905(7)	0.7133(3)	4.72(15)
C(12)	0.6990(13)	0.1067(10)	0.7616(3)	7.4(2)
C(13)	0.6379(14)	0.3056(10)	0.6974(4)	8.2(3)
C(14)	0.8680(13)	-0.0069(11)	0.4148(3)	7.3(2)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	Biso		atom	x	y	z	Biso
H(2)	0.8140	-0.393	0.5588	6.08		H(12A)	0.7296	0.0082	0.7569	8.85
H(8)	1.0045	0.0247	0.6192	5.66		H(12B)	0.5730	0.1157	0.7644	8.85
H(9A)	1.0043	0.2642	0.6015	10.44		H(12C)	0.7530	0.1424	0.7946	8.85
H(9B)	1.1918	0.2186	0.6224	10.44		H(13A)	0.6901	0.3636	0.6693	9.86
H(9C)	1.0611	0.2972	0.6622	10.44		H(13B)	0.6119	0.3635	0.7289	9.86
H(10A)	1.0973	0.0852	0.7283	8.32		H(13C)	0.5307	0.2639	0.6838	9.86
H(10B)	1.2284	0.0228	0.6846	8.32		H(14A)	0.9283	0.0649	0.4358	8.73
H(10C)	1.0661	-0.068	0.7042	8.32		H(14B)	0.8407	0.0297	0.3790	8.73
H(11)	0.8727	0.2377	0.7249	5.66		H(14C)	0.9423	-0.089	0.4113	8.73

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(1)	0.1337(9)	0.0744(5)	0.0634(5)	0.0415(5)	-0.0186(5)	-0.0036(4)
Br(2)	0.0672(5)	0.1151(7)	0.1061(7)	0.0123(5)	-0.0111(5)	-0.0733(6)
Br(3)	0.1339(9)	0.0690(5)	0.0812(6)	-0.0123(6)	0.0057(6)	0.0199(5)
O(1)	0.062(3)	0.119(4)	0.051(3)	0.029(3)	-0.023(3)	-0.017(3)
O(2)	0.042(3)	0.105(4)	0.081(4)	-0.010(3)	0.013(3)	-0.039(3)
N(1)	0.033(3)	0.053(3)	0.038(3)	-0.006(2)	0.000(2)	-0.003(2)
C(1)	0.037(4)	0.065(4)	0.061(4)	-0.007(3)	0.006(3)	-0.002(4)
C(2)	0.050(4)	0.051(4)	0.092(6)	-0.001(4)	0.003(4)	-0.018(4)
C(3)	0.047(4)	0.077(5)	0.062(4)	0.004(4)	0.002(4)	-0.034(4)
C(4)	0.033(4)	0.081(5)	0.053(4)	0.013(3)	-0.012(3)	-0.017(4)
C(5)	0.051(4)	0.055(4)	0.046(4)	0.011(3)	-0.006(3)	-0.013(3)
C(6)	0.033(4)	0.049(3)	0.051(4)	-0.003(3)	-0.001(3)	-0.014(3)
C(7)	0.033(4)	0.069(4)	0.043(4)	-0.001(3)	0.001(3)	-0.013(3)
C(8)	0.044(4)	0.087(5)	0.048(4)	-0.019(4)	0.012(3)	-0.026(4)
C(9)	0.091(7)	0.142(9)	0.098(7)	-0.053(7)	0.023(6)	0.015(7)
C(10)	0.044(5)	0.133(8)	0.087(6)	0.013(5)	-0.011(4)	-0.014(6)
C(11)	0.058(5)	0.073(4)	0.048(4)	-0.007(4)	0.006(3)	-0.026(4)
C(12)	0.103(7)	0.125(7)	0.052(5)	-0.036(7)	0.031(5)	-0.030(5)
C(13)	0.114(8)	0.086(6)	0.113(8)	0.024(6)	-0.022(6)	-0.046(6)
C(14)	0.096(8)	0.118(8)	0.063(6)	0.021(6)	-0.008(5)	0.000(6)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

atom	atom	distance		atom	atom	distance
Br(1)	C(5)	1.898(6)		Br(2)	C(3)	1.893(8)
Br(3)	C(1)	1.904(7)		O(1)	C(4)	1.378(9)
O(1)	C(14)	1.453(11)		O(2)	C(7)	1.220(8)
N(1)	C(7)	1.357(8)		N(1)	C(8)	1.481(8)
N(1)	C(11)	1.489(8)		C(1)	C(2)	1.387(10)
C(1)	C(6)	1.390(9)		C(2)	C(3)	1.386(11)
C(3)	C(4)	1.381(11)		C(4)	C(5)	1.388(9)
C(5)	C(6)	1.401(9)		C(6)	C(7)	1.501(9)
C(8)	C(9)	1.511(13)		C(8)	C(10)	1.521(11)
C(11)	C(12)	1.513(11)		C(11)	C(13)	1.506(12)

Table 5. Bond angles (°)

atom	atom	atom	angle		atom	atom	atom	angle
C(4)	O(1)	C(14)	113.0(6)		C(7)	N(1)	C(8)	122.3(5)
C(7)	N(1)	C(11)	119.8(5)		C(8)	N(1)	C(11)	117.9(5)
Br(3)	C(1)	C(2)	117.6(5)		Br(3)	C(1)	C(6)	119.6(5)
C(2)	C(1)	C(6)	122.7(6)		C(1)	C(2)	C(3)	118.9(7)
Br(2)	C(3)	C(2)	119.5(6)		Br(2)	C(3)	C(4)	119.5(6)
C(2)	C(3)	C(4)	121.0(7)		O(1)	C(4)	C(3)	121.9(7)
O(1)	C(4)	C(5)	119.5(6)		C(3)	C(4)	C(5)	118.4(6)
Br(1)	C(5)	C(4)	118.4(5)		Br(1)	C(5)	C(6)	118.6(5)
C(4)	C(5)	C(6)	123.0(6)		C(1)	C(6)	C(5)	116.0(6)
C(1)	C(6)	C(7)	121.6(6)		C(5)	C(6)	C(7)	121.7(5)
O(2)	C(7)	N(1)	123.1(6)		O(2)	C(7)	C(6)	118.1(6)
N(1)	C(7)	C(6)	118.8(5)		N(1)	C(8)	C(9)	112.3(6)
N(1)	C(8)	C(10)	111.6(6)		C(9)	C(8)	C(10)	110.8(7)
N(1)	C(11)	C(12)	112.6(6)		N(1)	C(11)	C(13)	111.9(6)
C(12)	C(11)	C(13)	112.1(7)					

Table 6. Torsion Angles(°)
(Those having bond angles > 160 degrees are excluded.)

atom1	atom2	atom3	atom4	angle		atom1	atom2	atom3	atom4	angle
C(14)	O(1)	C(4)	C(3)	-87.7(8)		C(14)	O(1)	C(4)	C(5)	98.1(7)
C(7)	N(1)	C(8)	C(9)	119.1(6)		C(7)	N(1)	C(8)	C(10)	-115.8(6)
C(8)	N(1)	C(7)	C(6)	-3.1(8)		C(7)	N(1)	C(11)	C(12)	66.0(7)
C(7)	N(1)	C(11)	C(13)	-61.3(7)		C(11)	N(1)	C(7)	O(2)	-0.5(9)
C(8)	N(1)	C(11)	C(12)	-112.0(6)		C(8)	N(1)	C(11)	C(13)	120.7(6)
C(11)	N(1)	C(8)	C(9)	-62.9(6)		C(11)	N(1)	C(8)	C(10)	62.2(7)
Br(3)	C(1)	C(6)	C(7)	-8.7(8)		C(2)	C(1)	C(6)	C(5)	-0.9(9)
C(6)	C(1)	C(2)	C(3)	-1.2(10)		C(1)	C(2)	C(3)	C(4)	3.5(10)
Br(2)	C(3)	C(4)	O(1)	3.9(8)		C(2)	C(3)	C(4)	C(5)	-3.6(10)
O(1)	C(4)	C(5)	Br(1)	-3.2(8)		C(3)	C(4)	C(5)	C(6)	1.4(9)
Br(1)	C(5)	C(6)	C(7)	9.8(8)		C(4)	C(5)	C(6)	C(1)	0.7(9)
C(1)	C(6)	C(7)	O(2)	-85.6(8)		C(1)	C(6)	C(7)	N(1)	94.9(7)
C(5)	C(6)	C(7)	O(2)	83.8(8)		C(5)	C(6)	C(7)	N(1)	-95.7(7)

Table 7. Intramolecular contacts less than 3.60 Å

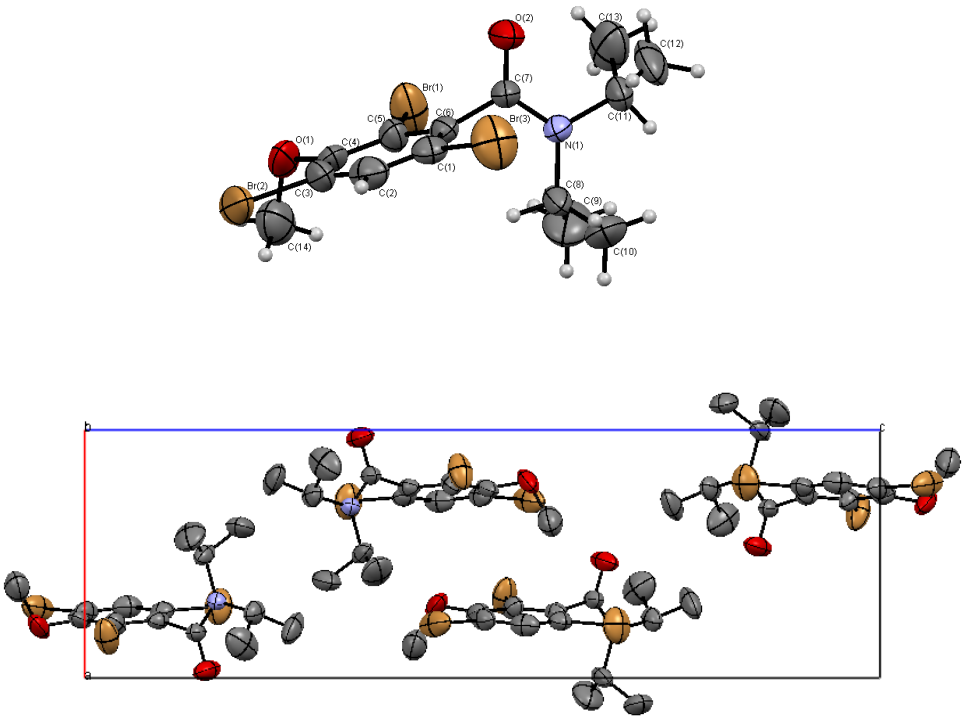
atom	atom	distance		atom	atom	distance
Br(1)	O(1)	3.006(6)		Br(1)	O(2)	3.573(6)
Br(1)	C(7)	3.132(6)		Br(2)	O(1)	3.080(6)
Br(2)	C(14)	3.516(10)		Br(3)	C(7)	3.148(7)
O(2)	C(1)	3.197(9)		O(2)	C(5)	3.195(8)
O(2)	C(11)	2.776(9)		O(2)	C(12)	3.044(10)
O(2)	C(13)	2.959(11)		N(1)	C(1)	3.372(8)
N(1)	C(5)	3.387(8)		C(1)	C(4)	2.767(10)
C(1)	C(8)	3.554(10)		C(2)	C(5)	2.755(9)
C(3)	C(6)	2.807(10)		C(3)	C(14)	3.193(12)
C(5)	C(14)	3.258(11)		C(6)	C(8)	2.873(9)
C(7)	C(9)	3.543(12)		C(7)	C(10)	3.519(10)
C(7)	C(12)	3.087(10)		C(7)	C(13)	3.030(12)
C(8)	C(12)	3.559(11)		C(9)	C(11)	3.095(12)
C(10)	C(11)	3.083(11)		C(10)	C(12)	3.595(13)

Table 8. Intermolecular contacts less than 3.60 Å

atom	atom	distance		atom	atom	distance
Br(2)	$O(2)^{1}$	3.378(5)		Br(2)	$C(5)^{1}$	3.557(7)
O(1)	$C(2)^{2}$	3.543(9)		O(2)	$Br(2)^{2}$	3.378(5)
O(2)	$C(10)^{3}$	3.399(9)		C(2)	$O(1)^{1}$	3.543(9)
C(5)	$Br(2)^{2}$	3.557(7)		C(10)	$O(2)^{4}$	3.399(9)

Symmetry Operators:

(1) X+1/2,-Y+1/2-1,-Z+1
(2) X+1/2-1,-Y+1/2-1,-Z+1
(3) X-1,Y,Z
(4) X+1,Y,Z



View of packing along b (H Atoms omitted)

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(1) CrystalClear: Rigaku Corporation, 1999. CrystalClear Software User's Guide, Molecular Structure Corporation, (c) 2000.J.W.Pflugrath (1999) Acta Cryst. D55, 1718-1725.

(2) SIR92: Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M., Polidori, G., and Camalli, M. (1994) J. Appl. Cryst., 27, 435.

(3) Least Squares function minimized: (SHELXL97)

$$\Sigma w(F_o^2 - F_c^2)^2$$ where w = Least Squares weights.

(4) Standard deviation of an observation of unit weight:

$$[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$$

where N_o = number of observations

N_v = number of variables

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