Solar photo-thermochemical reaction and supercritical CO_2 work up for a fully green process of preparation of pure *p*-nitrobenzyl bromide

Milan Dinda, Supratim Chakraborty, Supravat Samanta, Chitrangi Bhatt, Subarna Maiti, Sandip Roy, Yogesh Kadam, and Pushpito K. Ghosh

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General procedure for isolation of *p*-nitrobenzyl bromide by Sc-CO_2 extraction

This separation process was carried out in 0.5 L. SCFE set up. As shown in Figure S1, the SCFE plant comprised the following equipments: 1) Extractor 2) Separator 3) CO_2 pump 4) Condenser 5) Pre-heater 6) High Pressure Control Valve 7) CO_2 gas flow meter.

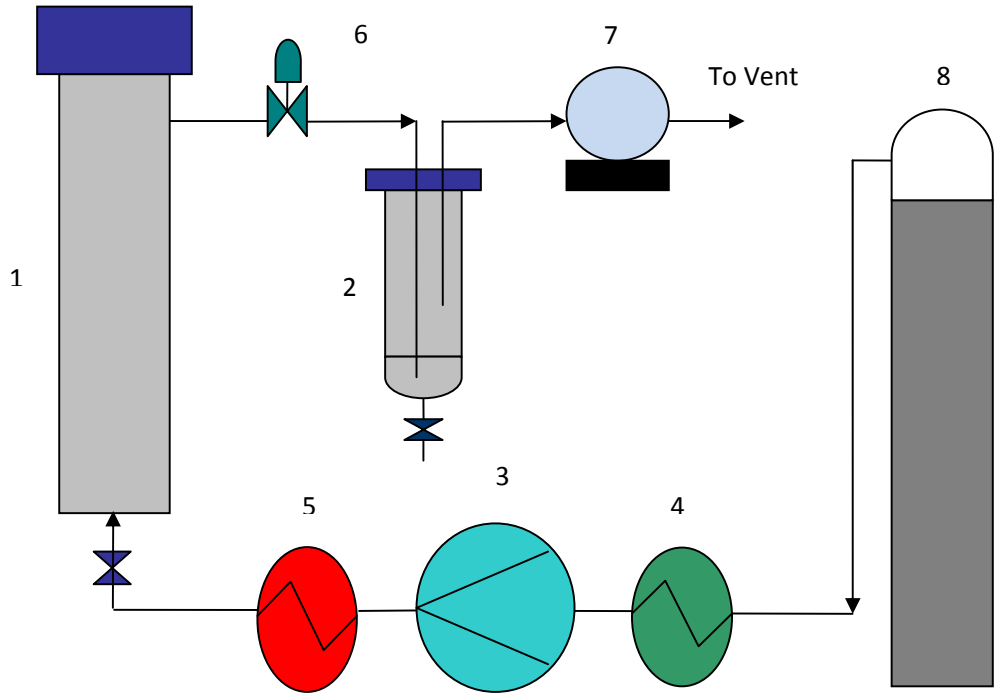

Figure S1. Schematic of SCFE Apparatus [1) Extractor; 2) Separator; 3) CO_2 pump; 4) Condenser; 5) Pre-heater; 6) High Pressure Control Valve; 7) CO_2 gas flow meter; 8) CO_2 Cylinder]

Process Description: The mixture of compounds to be separated was fed to the extractor. The carbon dioxide gas from the cylinder was first liquefied & then pressurized to the required pressure necessary for separation. The liquefied CO_2 was then heated above the critical temperature of CO_2 as per the requirement. The Sc-CO_2 then entered the extractor where the compounds to be separated were fed. The separation was achieved on the basis of set pressure & temperature. The PNT, along with some amount of PNBBr, were dissolved in Sc-CO_2 & finally exited to the separator maintained at atmospheric pressure. The volume of CO_2 leaving the separator is measured by passing it through a CO_2 gas flow meter. Although not collected in the present study, the extracted fraction may be recycled in subsequent preparation of PNBBr. The residue remaining after Sc-CO_2 extraction was analyzed by GC-MS for estimation of PNBBr purity.

GCMS data of PNT bromination in SPTR-1 (Entry 1, Table 1)

Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\SPTR -1_BP 5_140313_06.qgd

Sample Information

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Analyzed	: 3/14/2013 12:42:46 PM
Sample ID	: SPTR -1
Vial #	: 1
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Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
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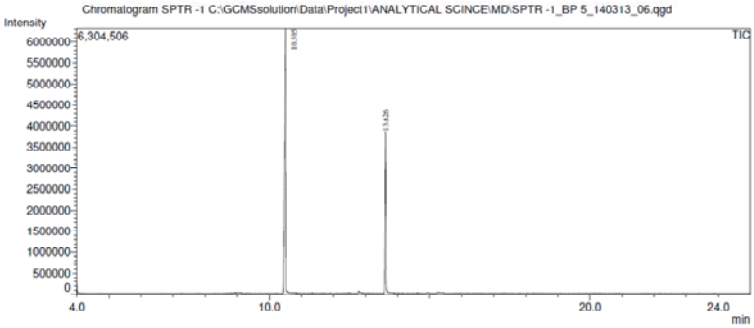

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.505	15580539	69.22	6271329	61.98	Benzene, 1-methyl-4-nitro-
2	13.626	6927586	30.78	3846242	38.02	Benzene, 1-(bromomethyl)-4-nitro-
		22508125	100.00	10117571	100.00	

Spectrum

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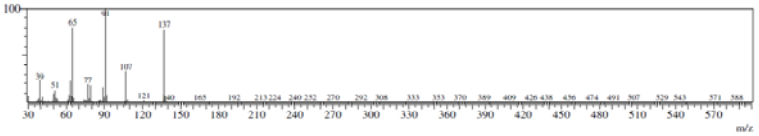

Line#:2 R.Time:13.6(Scan#:1156)
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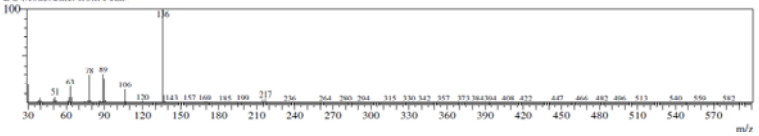
BG Mode:Calc. from Peak



1 / 1

GCMS data of PNT bromination in SPTR-1 (Entry 2, Table 1)

Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\SPTR-2_BP 5_140313_05.qgd

Sample Information

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Sample ID	: MD SPTR-2
Vial #	: 1
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Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
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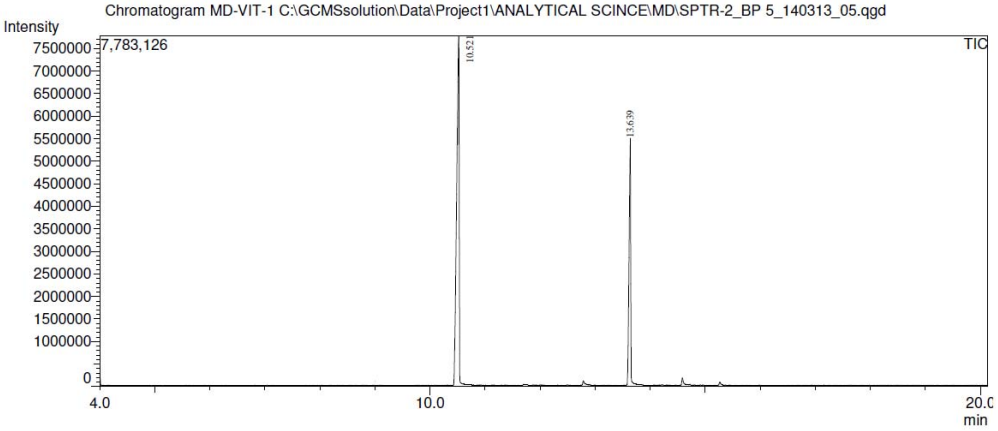

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.521	24736798	68.48	7753267	58.61	Benzene, 1-methyl-4-nitro-
2	13.639	11385853	31.52	5475051	41.39	Benzene, 1-(bromomethyl)-4-nitro-
		36122651	100.00	13228318	100.00	

Spectrum

Line#:1 R.Time:10.5(Scan#:784)
MassPeaks:334
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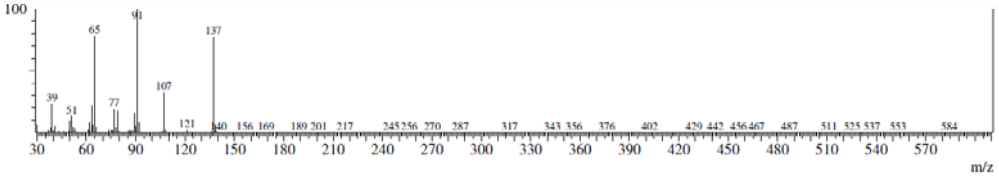
BG Mode:Calc. from Peak



Line#:2 R.Time:13.6(Scan#:1158)
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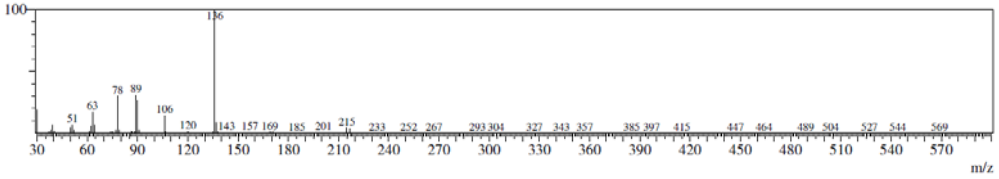

1 / 1

GCMS spectra of PNT bromination in SPTR-1 in black painted RB flask (Entry 3, Table 1)

Central Salt and Marine Chemicals Research Institute 3/20/2013 12:31

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Sample Name	:SPTR-3
Sample ID	: SPTR-3
Vial #	: 1
Injection Volume	: 0.200
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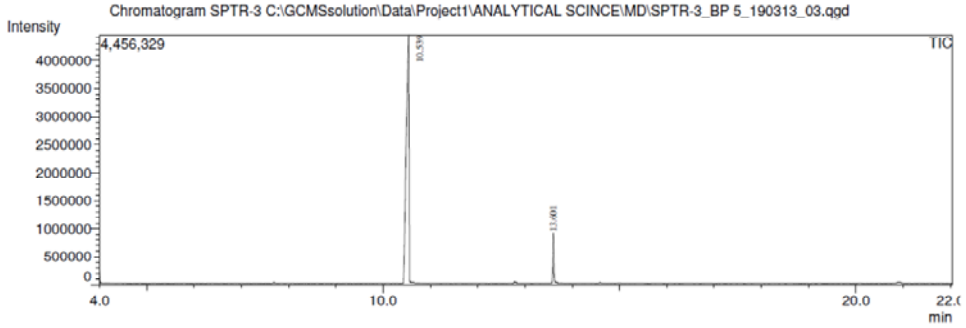

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name	Base m/z
1	10.539	17978704	93.07	4431479	83.13	Benzene, 1-methyl-4-nitro-	91.05
2	13.601	1339593	6.93	899128	16.87	Benzene, 1-(bromomethyl)-4-nitro-	136.05
		19318297	100.00	5330607	100.00		

Spectrum

Line#:1 R.Time:10.5(Scan#:786)
MassPeaks:345
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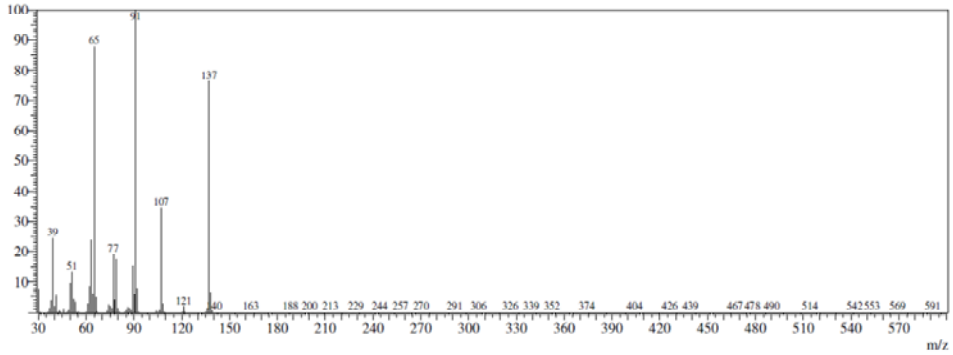

GCMS data of PNT bromination in SPTR-2 (Entry 1, Table 2)

Central Salt and Marine Chemicals Research Institute 3/20/2013 12:32

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Sample Information

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Sample Type	: Unknown
Sample Name	:MD-SOLAR-3
Sample ID	: MD-SOLAR-3
Vial #	: 1
Injection Volume	: 0.200
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD-SOLAR-3_BP 5_190313_04.qgd
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\tuning_190313_EI.qgt

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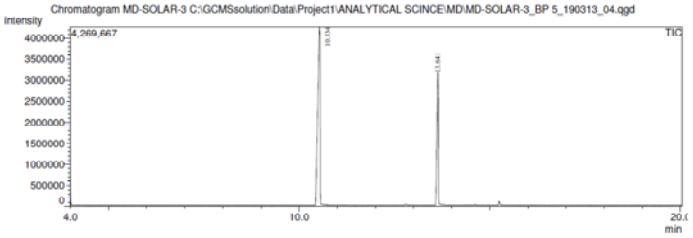

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name	Base m/z
1	10.534	18669657	69.62	4248714	57.42	Benzene, 1-methyl-4-nitro-	91.10
2	13.641	8146679	30.38	3150793	42.58	Benzene, 1-(bromomethyl)-4-nitro-	136.10
		26816336	100.00	7399507	100.00		

Spectrum

Line#:1 R.Time:10.5(Scan#:785)
MassPeaks:358
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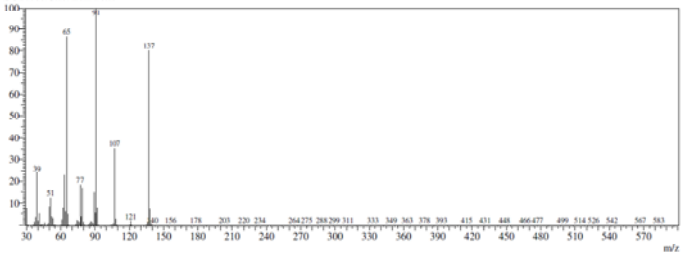
BG Mode:Calc. from Peak



1 / 2

GCMS data of PNT bromination in SPTR-2 (Entry 2, Table 2)

Sample Information

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Sample ID	: MD-SOLAR-5
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Report File	:
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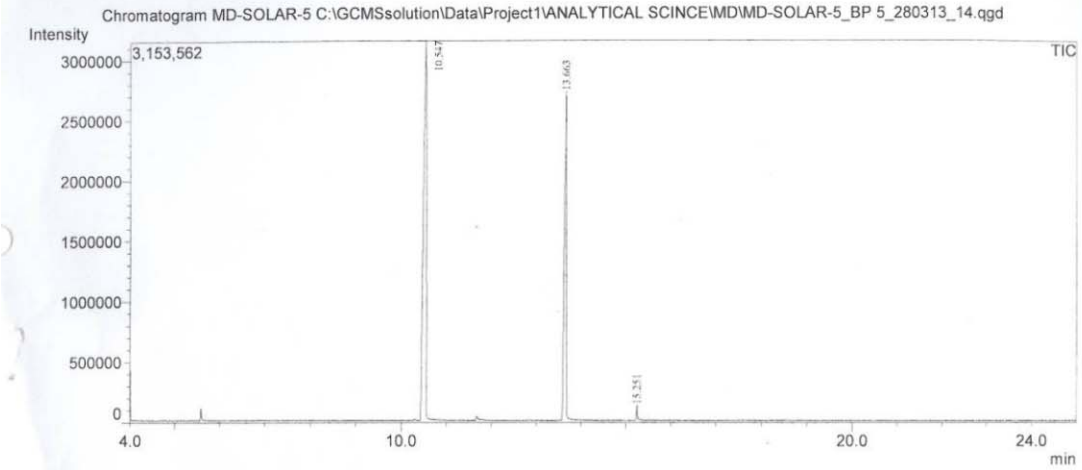
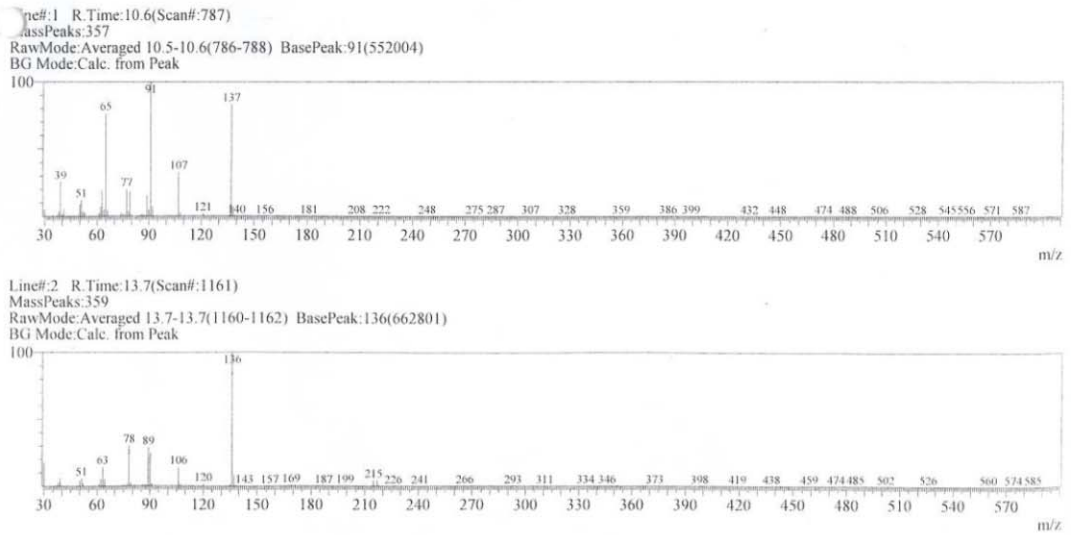


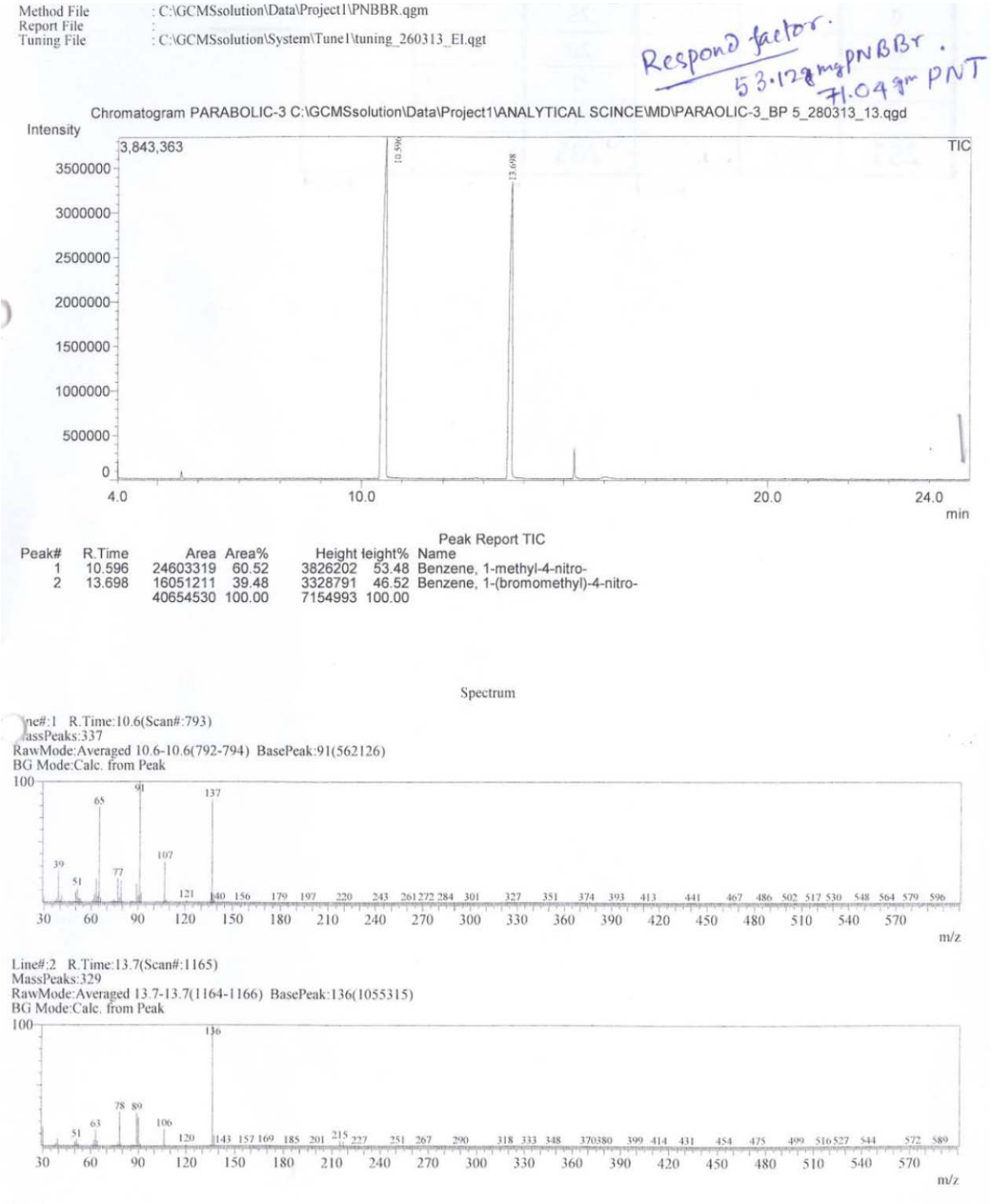
Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.547	14072782	60.75	3134224	52.46	Benzene, 1-methyl-4-nitro-
2	13.663	8892588	38.39	2716851	45.47	Benzene, 1-(bromomethyl)-4-nitro-
3	15.251	199816	0.86	123897	2.07	
		23165186	100.00	5974972	100.00	

Spectrum



Response factor comptation for GC-MS data presented in Table 2 and Tables S1-S4 (similar methodology was followed for GC yield computations in Table 1).



GCMS data of PNT bromination reaction mass before Sc CO_2 extraction.

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD-41-EDC_RTX 5_150212-01.qgd

Sample Information

Analyzed by	: Admin
Analyzed	: 2/15/2012 9:34:23 AM
Sample Type	: Unknown
Sample Name	:MD-41
Sample ID	: MD-41
Vial #	: 1
Injection Volume	: 0.600
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Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\tuning_191010_EI.qgt

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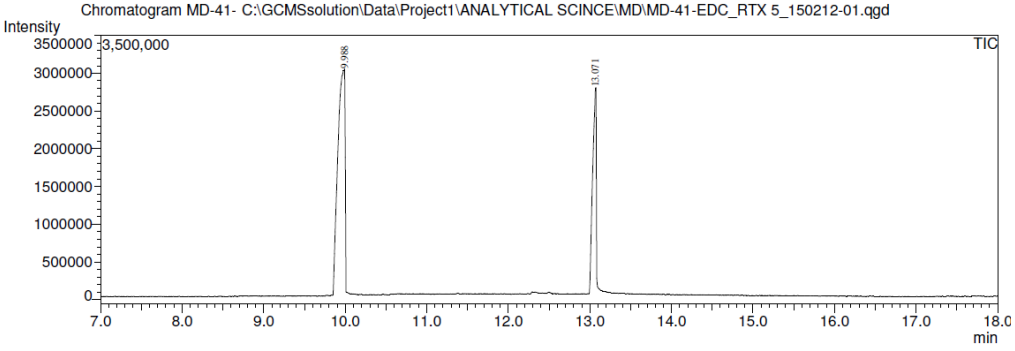

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name	Base m/z
1	9.988	18537838	68.53	2996524	52.34	Benzene, 1-methyl-4-nitro-	91.00
2	13.071	8514560	31.47	2728775	47.66	Benzene, 1-(bromomethyl)-4-nitro-	136.05
		27052398	100.00	5725299	100.00		

Spectrum

Line#:1 R.Time:10.0(Scan#:720)
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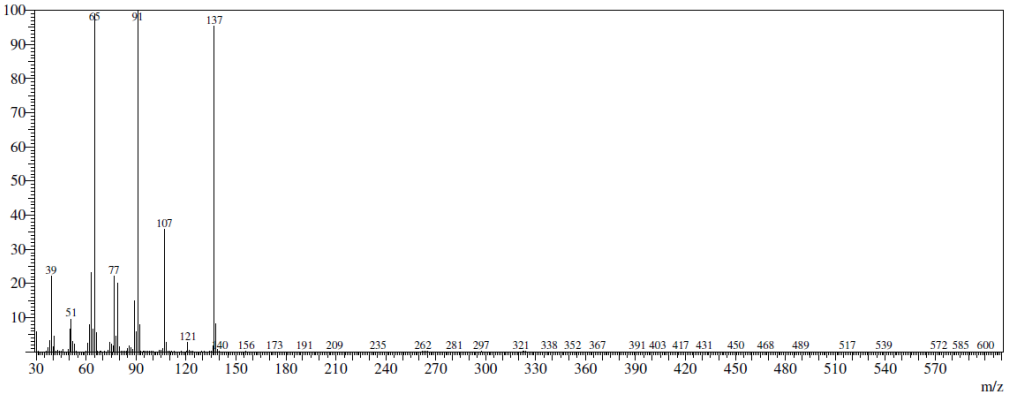

GCMS data of PNT bromination reaction mass after Sc CO_2 extraction under optimised condition (Entry 4, Table 3).

Central Salt and Marine Chemicals Research Institute

Sample Information

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Sample ID	: MD-SC-2M
Vial #	: 1
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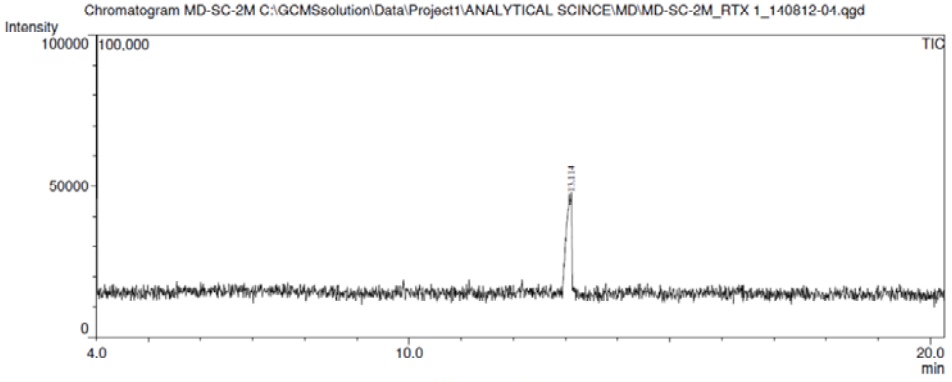
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\tuning_140812_ELqgt

Chromatogram MD-SC-2M C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD-SC-2M_RTX 1_140812-04.qgd



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	13.114	256605	100.00	34759	100.00	Benzene, 1-(bromomethyl)-4-nitro-
		256605	100.00	34759	100.00	

Spectrum

Line#:1 R.Time:13.1(Scan#:1095)
MassPeaks:322
RawMode:Averaged 13.1-13.1(1094-1096) BasePeak:136(9594)
BG Mode:Calc. from Peak

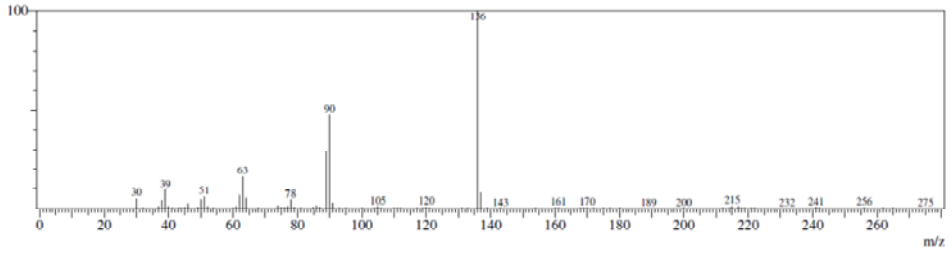


Table S1. Solar photo-thermochemical synthesis of PNBBr from PNT using liquid bromine[a]

Entry	Temperature of reaction (^{o}C)	Time/h	Yield of PNBBr on based on Br in liquid bromine (%)
1	61-67	1.5	58

[a] 9 mmol PNT; 1.5 mmol liquid Br_2 (3 mmol total Br).

Table S2. Synthesis of PNBBr from PNT at 1:1 and 3:1 substrate to reagent (2:1 Br^-:BrO_3^-) ratio and LED lamp as light source[a]

Entry	Temperature of reaction(^{o}C)	Unreacted PNT (%)	Yield of PNBBr (%) on reagent basis.	Yield of α,α-dibromo impurity on reagent basis (%)
1[a]	65	24	68	7
2[b]	65	212	88	0

[a] 9 mmol PNT; 9 mmol total Br as 2:1 Br^-:BrO_3^-; 9 mmol $KHSO_4$; [b] 9 mmol PNT; 3 mmol total Br as 2:1 Br^-:BrO_3^-; 3 mmol $KHSO_4$.

Table S3. Synthesis of PNBBr from PNT at different temperatures using LED lamp as light source[a]

Entry	Temperature of reaction (^{o}C)	Time/h	Yield of PNBBr on reagent basis (%)	Yield of side product benzyl alcohol formed upon hydrolysis of PNBBr (%)
1	60	2	88	0
2	80	2	91	0
3	100	2	90	5
4	110	2	71	21

[a] 9 mmol PNT; 3 mmol total Br as 2:1 Br^-:BrO_3^-; 3 mmol $KHSO_4$.

Table S4. Synthesis of *p*-nitrobenzylbromide (PNBBr) from *p*-nitrotoluene (PNT) using artificial light sources[a]

Entry	Light source (Watt)	Temperature of reaction (^{o}C)	Time/h	Yield of PNBBr on Br basis (%)
1	LED lamp (25)	65	2	88
2	UV lamp (25)	65	2	86
3	CFL lamp (25)	65	2	89

[a] 9 mmol PNT; 3 mmol total Br as 2:1 Br^-:BrO_3^-; 3 mmol $KHSO_4$.

Bromination of PNT using liq. Bromine (Table S1, Entry 1)

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C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 359_050713_07.QGD

Sample Information

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Analyzed	: 7/5/2013 3:14:24 PM
Sample ID	: MD 359
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Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
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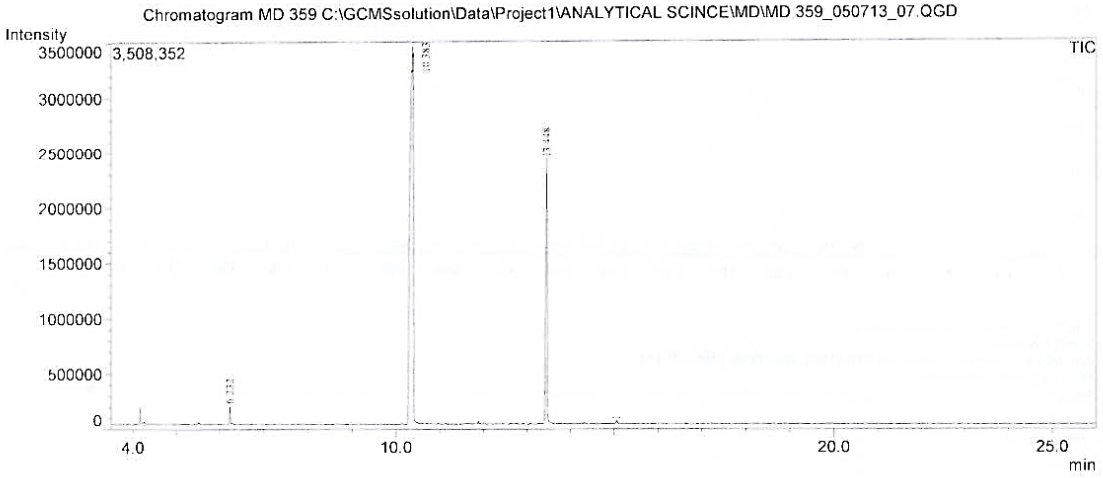

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	6.232	292699	1.44	180772	2.98	
2	10.383	18744996	75.87	3463189	57.10	Benzene, 1-methyl-4-nitro-
3	13.448	5606450	22.69	2395060	39.49	Benzene, 1-methyl-4-nitro- → 58

Bromination of PNT using 1:1 substrate to reagent (Table S2, Entry 1)

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C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 358_050713_09.QGD

Sample Information

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Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

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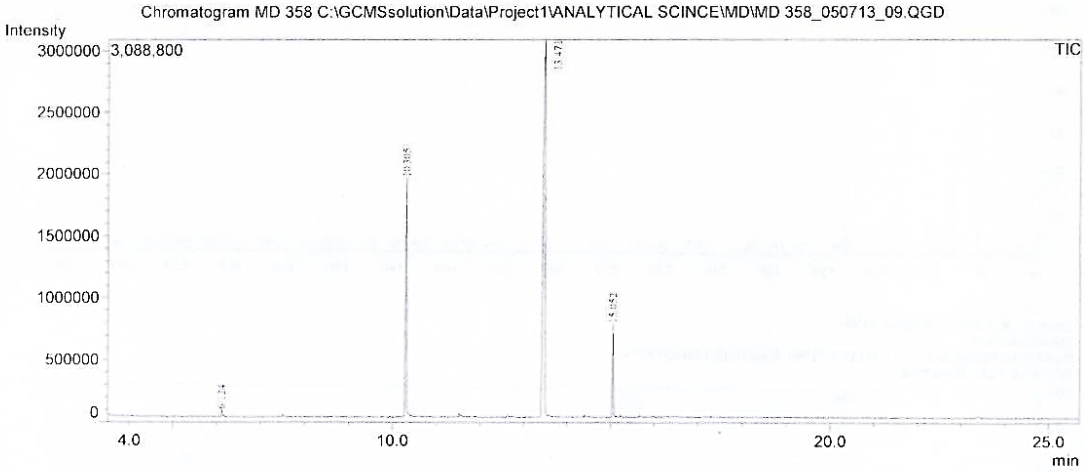

Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	6.124	95119	0.62	53373	0.92	
2	10.305	3723030	24.17	1924315	33.33	Benzene, 1-methyl-4-nitro-
3	13.471	10480548	68.04	3043713	52.72	Benzene, 1-(bromomethyl)-4-nitro-
4	15.052	1105651	7.18	752228	13.03	Benzene, 1,1-(dibromethyl)-4-nitro
		15404348	100.00	5773629	100.00	

PNT Reaction at 60°C (Table S3, Entry 1)

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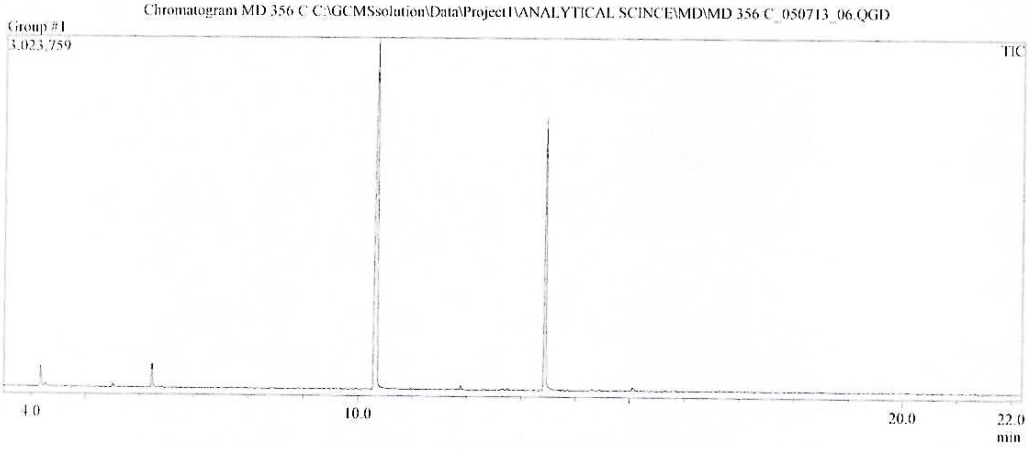
C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356 C_050713_06.QGD

Sample Information

Analyzed by	: Admin
Analyzed	: 7/5/2013 2:44:17 PM
Sample Type	: Unknown
Sample Name	: MD 356 C
Sample ID	: MD 356 C
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356 C_050713_06.QGD
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

Chromatogram MD 356 C C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356 C_050713_06.QGD



Peak Report TIC

Peak#	R.Time	Area	Area%	Name
1	10.338	9377401	65.50	Benzene, 1-methyl-4-nitro-
2	13.446	4938442	34.50	Benzene, 1-(bromomethyl)-4-nitro-
		14315843	100.00	

Spectrum

PNT Reaction at 80°C (Table S3, Entry 2)

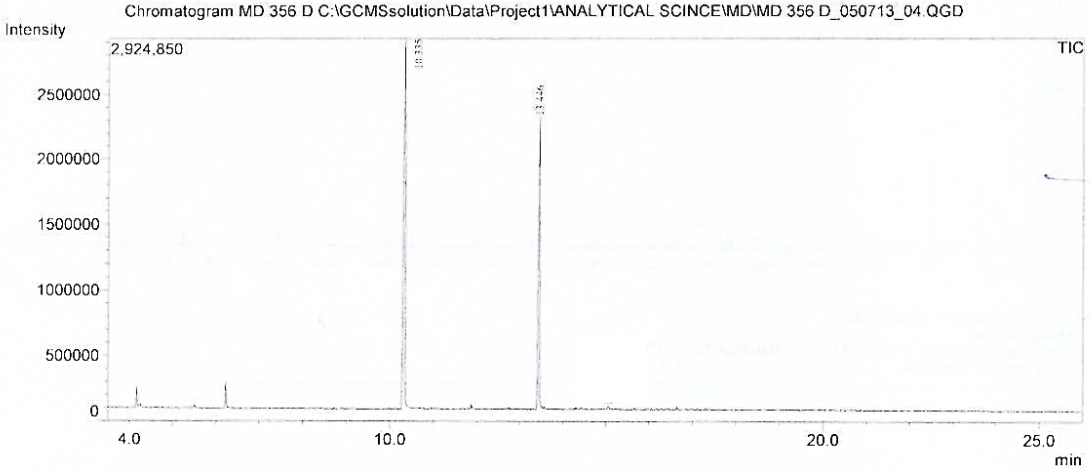
Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356 D_050713_04.QGD

Sample Information

Analyzed by	: Admin
Analyzed	: 7/5/2013 1:07:53 PM
Sample ID	: MD 356 D
Vial #	: 1
Injection Volume	: 0.200
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356 D_050713_04.QGD
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

Chromatogram MD 356 D C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356 D_050713_04.QGD



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.335	8800344	64.60	2830448	55.47	Benzene, 1-methyl-4-nitro-
2	13.446	4860689	35.40	2245699	44.01	Benzene, 1-methyl-4-nitro-

90

PNT Reaction at 100°C (Table S3, Entry 3)

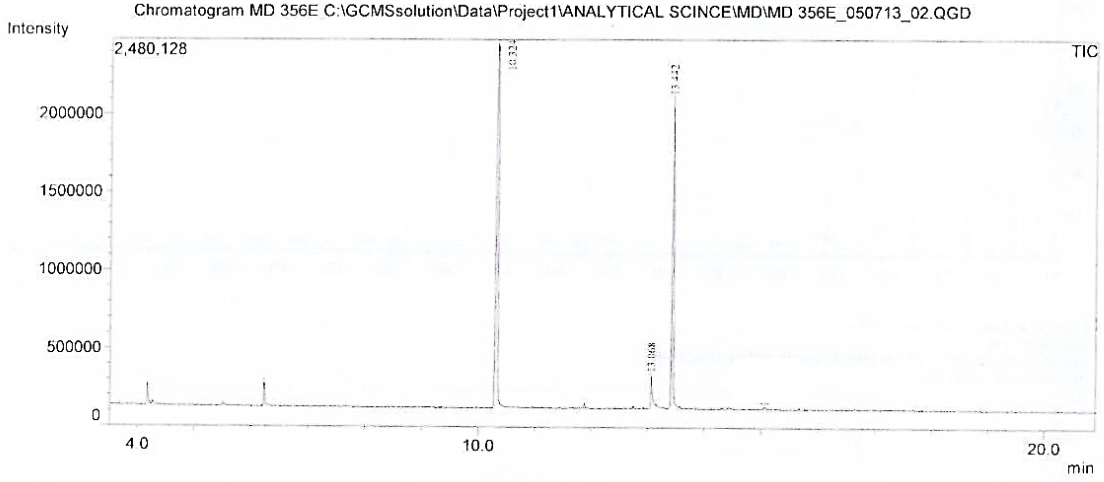
Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356E_050713_02.QGD

Sample Information

Analyzed by	: Admin
Analyzed	: 7/5/2013 12:08:36 PM
Sample ID	: MD 356E
Vial #	: 1
Injection Volume	: 0.200
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356E_050713_02.QGD
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

Chromatogram MD 356E C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356E_050713_02.QGD



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.324	6694989	59.00	2357706	51.18	Benzene, 1-methyl-4-nitro-
2	13.068	577561	5.79	230256	5.00	Benzenemethanol, 3-nitro-
3	13.442	3992338	35.21	2000053	43.42	Benzene, 1-(bromomethyl)-4-nitro-

5%
90%

PNT Reaction at 110°C (Table S3, Entry 4)

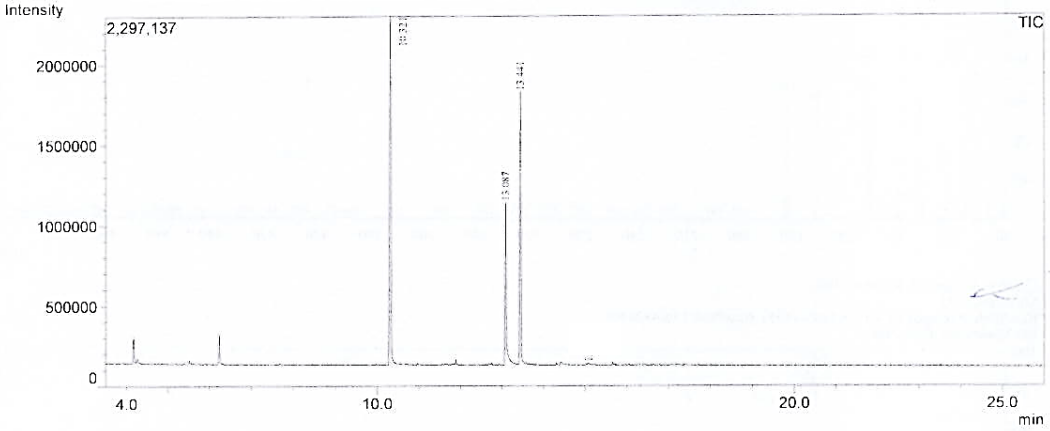
Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356F_050713_01.qgd

Sample Information

Analyzed by	: Admin
Analyzed	: 7/5/2013 11:33:50 AM
Sample ID	: MD 356F
Vial #	: 1
Injection Volume	: 0.200
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356F_050713_01.qgd
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

Chromatogram MD 356F C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 356F_050713_01.qgd



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.321	5743948	49.94	2166978	44.31	2-Bromo-5-methylbenzoic acid
2	13.087	2503996	21.77	1019539	20.85	Benzenemethano 4-nitro- → 21.71
3	13.441	3233327	28.28	1692565	34.61	Benzenemethanol, 3-nitro- → 71

PNT Reaction using LED lamp (Table S4, Entry 1)

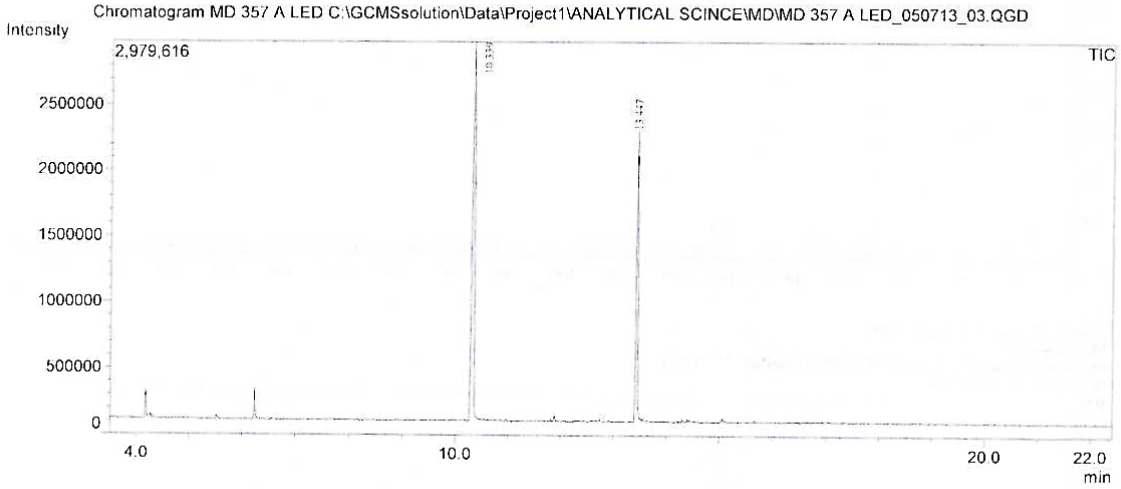
Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 A LED_050713_03.QGD

Sample Information

Analyzed by	: Admin
Analyzed	: 7/5/2013 12:37:27 PM
Sample ID	: MD 357 A LED
Vial #	: 1
Injection Volume	: 0.200
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 A LED_050713_03.QGD
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

Chromatogram MD 357 A LED C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 A LED_050713_03.QGD



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.339	9416805	65.15	2869951	56.15	Benzene, 1-methyl-4-nitro-
2	13.447	5083591	34.85	2212234	43.28	Benzene, 1-methyl-4-nitro-

89

Reaction using UV lamp (Table S4, Entry 2)

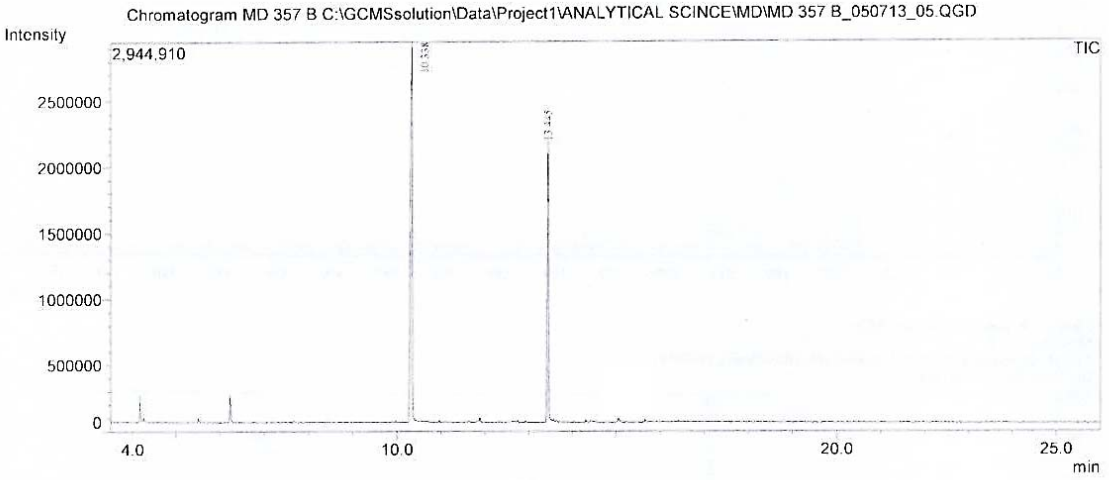
Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 B_050713_05.QGD

Sample Information

Analyzed by	: Admin
Analyzed	: 7/5/2013 2:09:44 PM
Sample ID	: MD 357 B
Vial #	: 1
Injection Volume	: 0.200
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 B_050713_05.QGD
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	:
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

Chromatogram MD 357 B C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 B_050713_05.QGD



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name
1	10.338	8928453	66.40	2874840	57.29	Benzene, 1-methyl-4-nitro-
2	13.445	4550463	33.60	2118060	42.21	Benzene, 1-methyl-4-nitro-

86

Reaction using Fluorescent lamp ((Table S4, Entry 3)

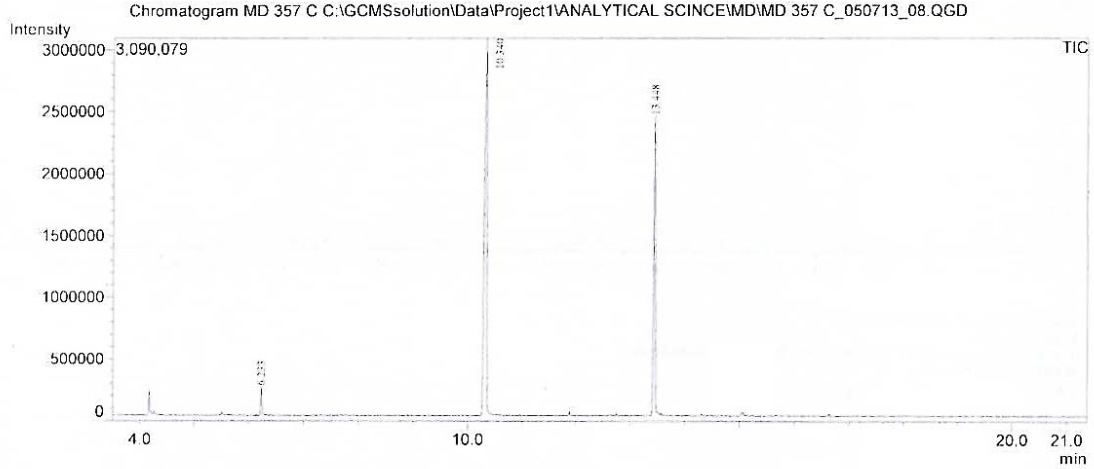
Central Salt and Marine Chemicals Research Institute

C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 C_050713_08.QGD

Sample Information

Analyzed by	: Admin
Analyzed	: 7/5/2013 3:19:13 PM
Sample ID	: MD 357 C
Vial #	: 1
Injection Volume	: 0.200
Data File	: C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 C_050713_08.QGD
Method File	: C:\GCMSsolution\Data\Project1\PNBBR.qgm
Report File	
Tuning File	: C:\GCMSsolution\System\Tune1\050713.qgt

Chromatogram MD 357 C C:\GCMSsolution\Data\Project1\ANALYTICAL SCINCE\MD\MD 357 C_050713_08.QGD



Peak Report TIC

Peak#	R Time	Area	Area%	Height	Height%	Name
1	6.233	377122	3.10	234984	4.09	
2	10.340	10214528	62.65	3044774	52.95	Benzene, 1-methyl-4-nitro-
3	13.448	5583945	34.25	2420871	42.10	Benzene, 1-methyl-4-nitro-

→ 88

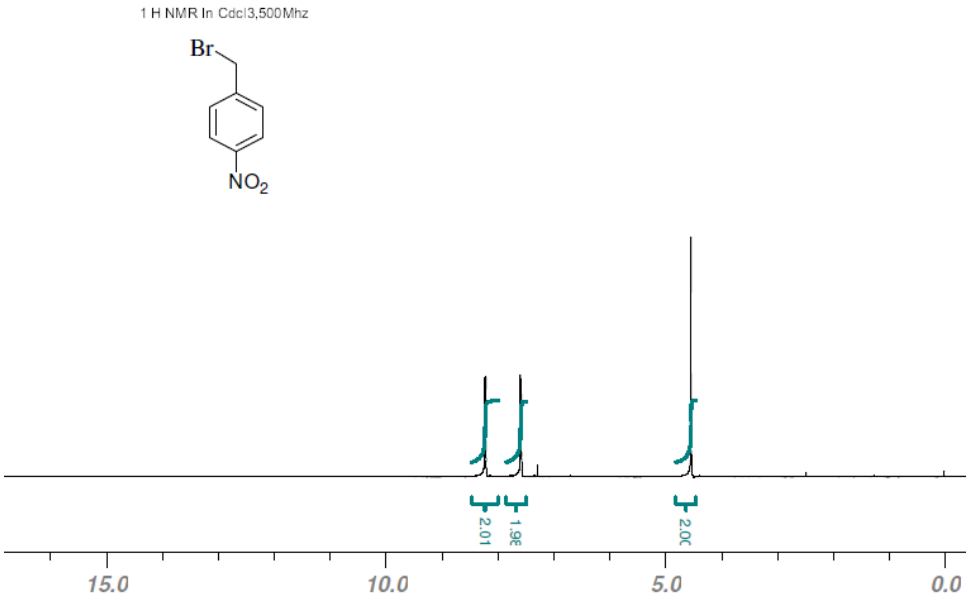
***p*-Nitrobenzyl bromide (PNBBr)**

NMR data

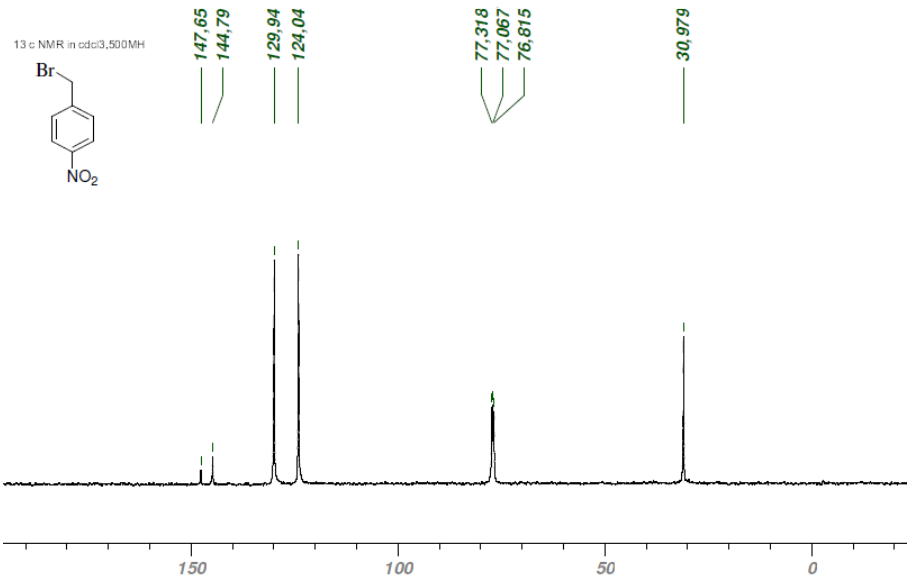
^{1}H NMR ($CDCl_3$-500 MHz): δ 8.21-8.23 (2H, d, J=8.5); 7.58-7.6 (2H, d, J=8.5); 4.55 (2H, S).

^{13}C NMR ($CDCl_3$-500 MHz): δ 147.7, 144.8, 129.9 (2C), 124.0 (2C), 31.0

^{1}H NMR



C^{13} NMR



IR data

V_{max} (KBr): 3051, 2840, 2378, 1604, 1534, 1344, 1224, 1099, 1011, 874, 798, 692, 592 cm^{-1}

Melting point (product of Entry 4, Table 3)

Observed: 97-100^0 C, Reported: 96-99^0 C (Sigma Aldrich electronic database)

Table S5. Bromination of toluene derivatives:

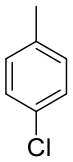
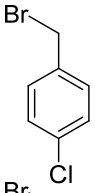
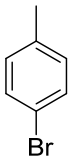
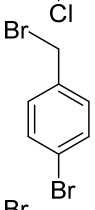
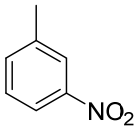
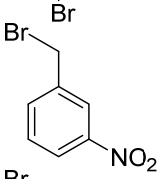
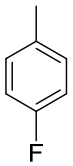
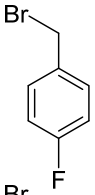
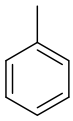
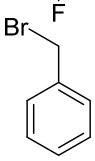
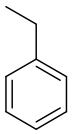
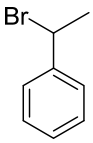
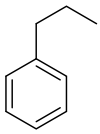
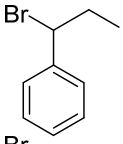
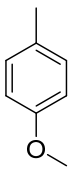
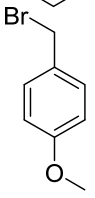
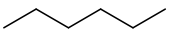
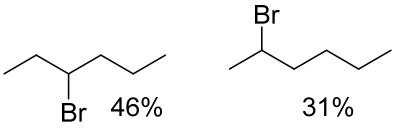
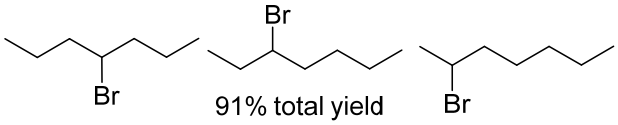
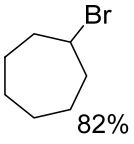
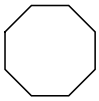
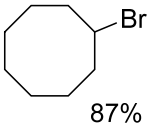
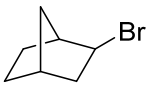
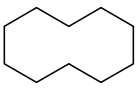
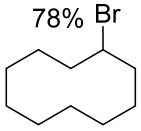
Entry	Substrate	g/mmol	Desired Product	Time min	Average reaction temp.(oC)	Conversion by GCa (%)
1		1.14/9.0		120	58	98
2		1.59/9.3		135	72	97
3		11.17/81.5		110	63	98
4		0.99/9.0		40	72	97
5		4.71/51.1		90	57	99
6		1.93/18.2		50	72	87
7		1.09/9.1		90	55	88
8		1.09/9.02		120	52	91

Table S6. Bromination of cyclic alkanes and linear alkanes:

Entry	Substrate	Time min(h)	Average reaction temp.(°C)	product/yield[a]
1		1.5	57	
2		1.0	55	
3		1.0	61	
4		1.5	60	
5		1.5	63	
6		2.0	67	

[a] indicated isolated yield except entry 6. [b] indicated GC yield

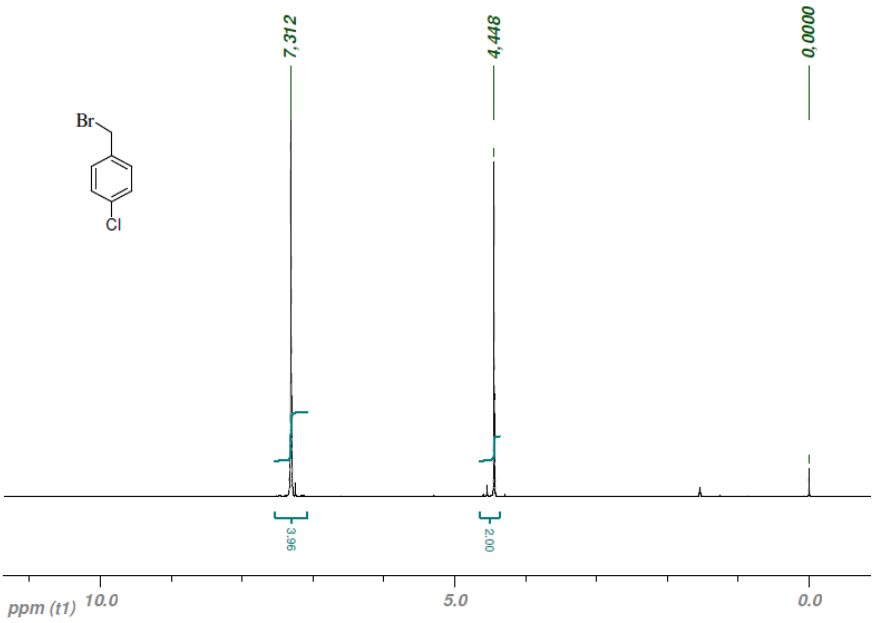
General procedure for bromination in SPTR-1 for the reactions shown in Table S5 and S6

For the reactions of Entries 1, 2, 4 and 7 of Table S5, the typical procedure was as follows: 9 mmol (two-fold excess) of p-chlorotoluene and 3 mmol (active bromine) of aq. brominating reagent (2:1 NaBr, $NaBrO_3$) were taken in RB flask without any organic solvent and placed in SPTR-1 during high sunshine hours. 3.3 mmol aqueous $KHSO_4$ was added drop-wise. The average reaction temperature was 58^oC over the duration of the reaction (3 h). The organic phase was dissolved in EDC and a small portion was taken for GC-MS (98% GC conversion reagent basis) while the remaining was separated on column to isolate the pure product whose NMR was recorded. The reactions of Entries 3, 5 and 7 were conducted at somewhat larger scales, i.e., 81.5, 51.1 and 18.2 mmol substrate, respectively. For the bromination reactions of alkanes (Table S6), all reactions were carried out with 9 mmol substrate and 3 mmol (active bromine) of aq. brominating reagent (2:1 NaBr, $NaBrO_3$). EDC was used as solvent and 10 mol % (with respect to active bromine) MnO_2 (LOBA Chemie) as catalyst.

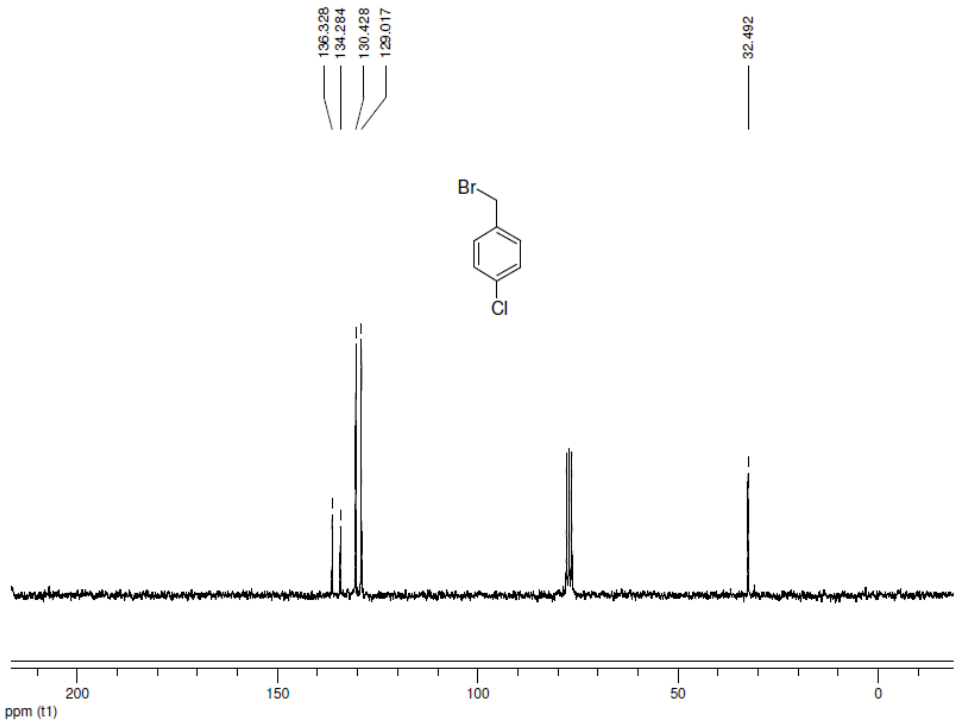
H^1 NMR

<u>Entry 1, Table S5 (*p*-Chlorobenzyl bromide)</u>

H^1 NMR

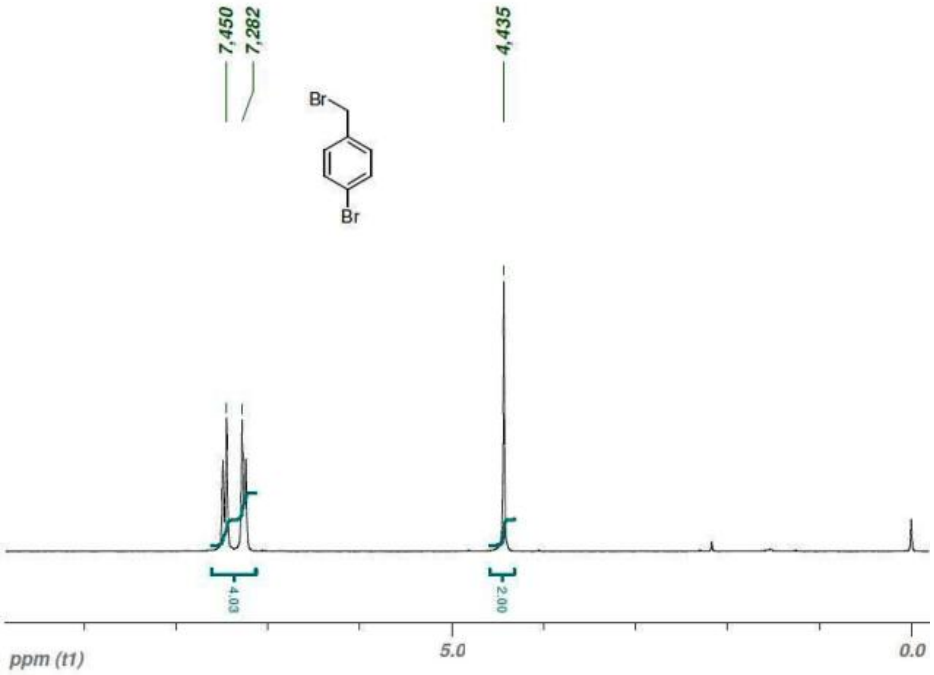


C^{13} NMR

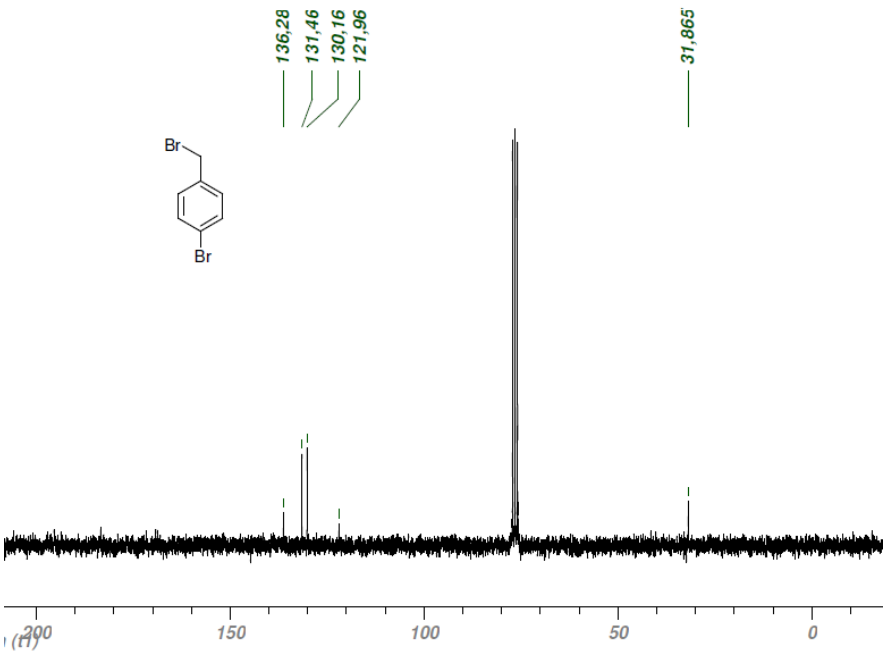


Entry 2, Table S5 (*p*-Bromobenzyl bromide)

H^1 NMR

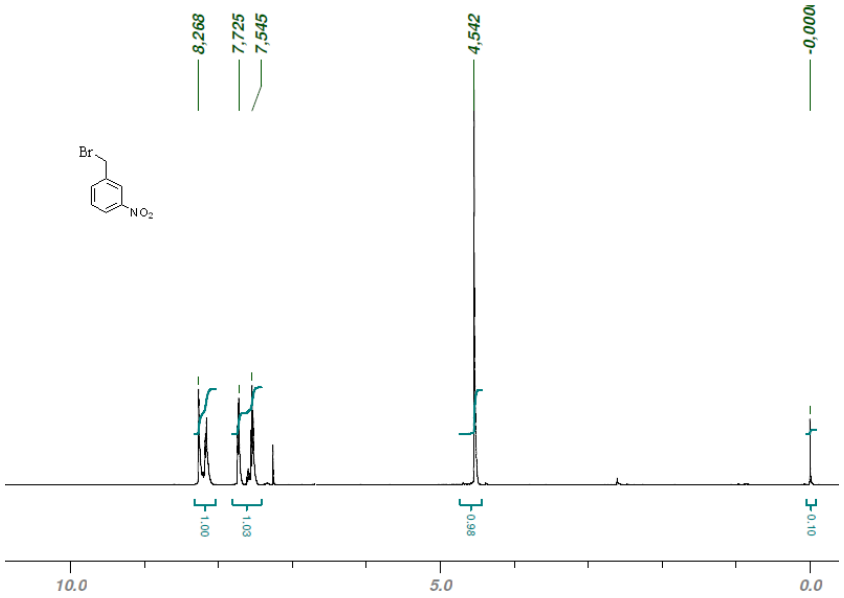


C^{13} NMR

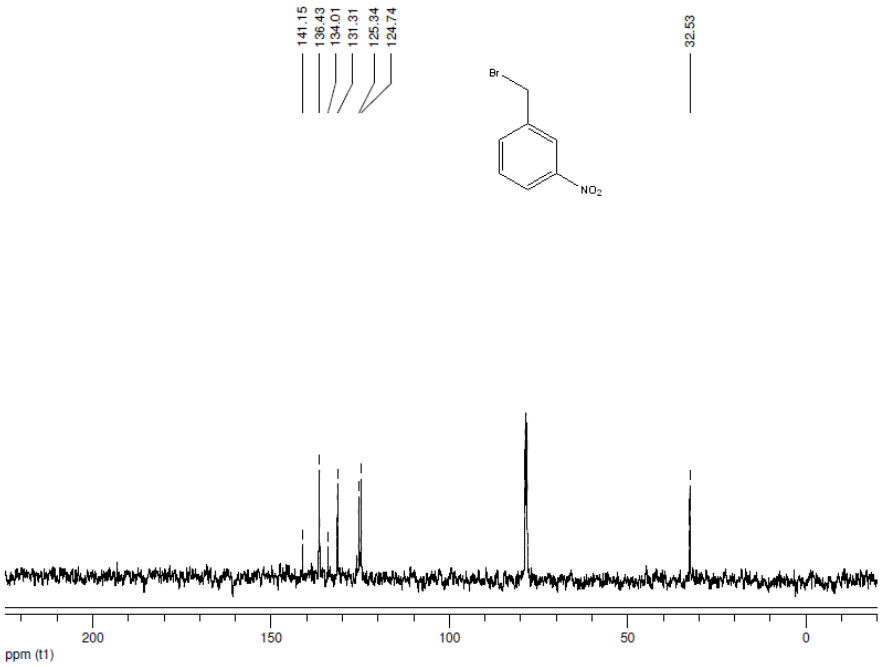


Entry 3, Table S5 (*m*-Nitrobenzyl bromide)

H^1 NMR

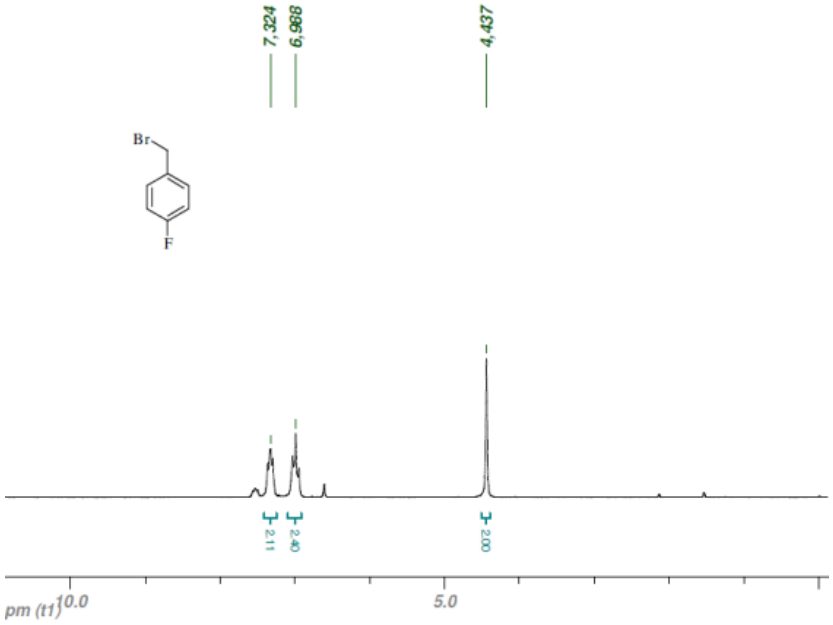


C^{13} NMR

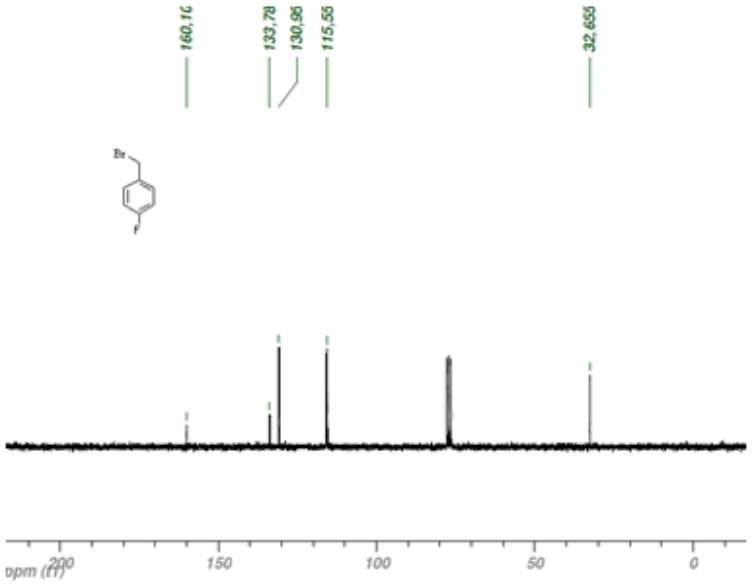


Entry 4, Table S5 (*p*-fluorobenzyl bromide)

H^1 NMR

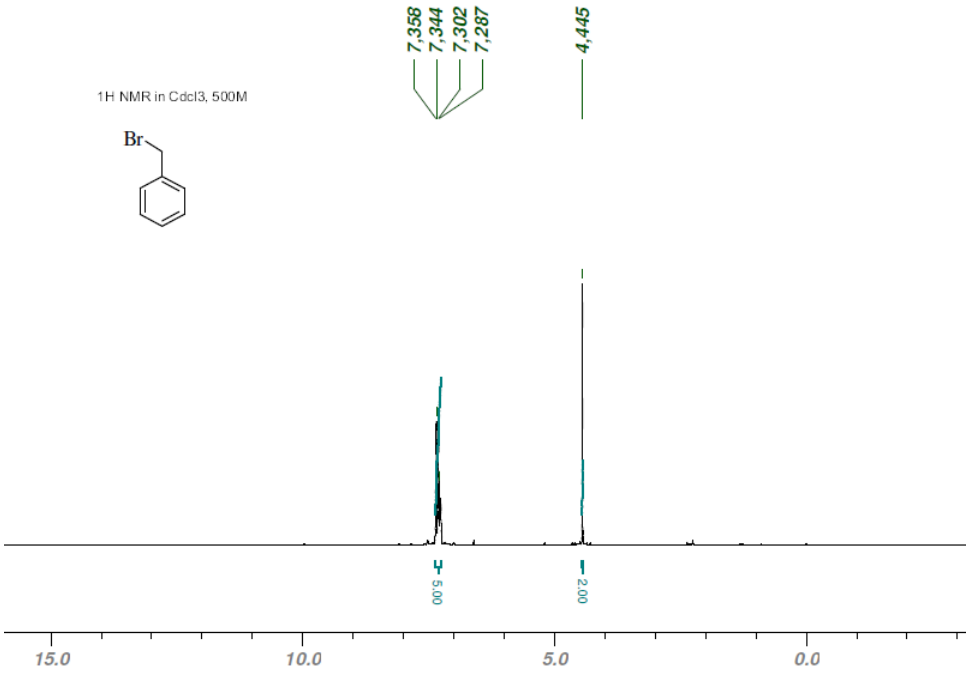


C^{13} NMR

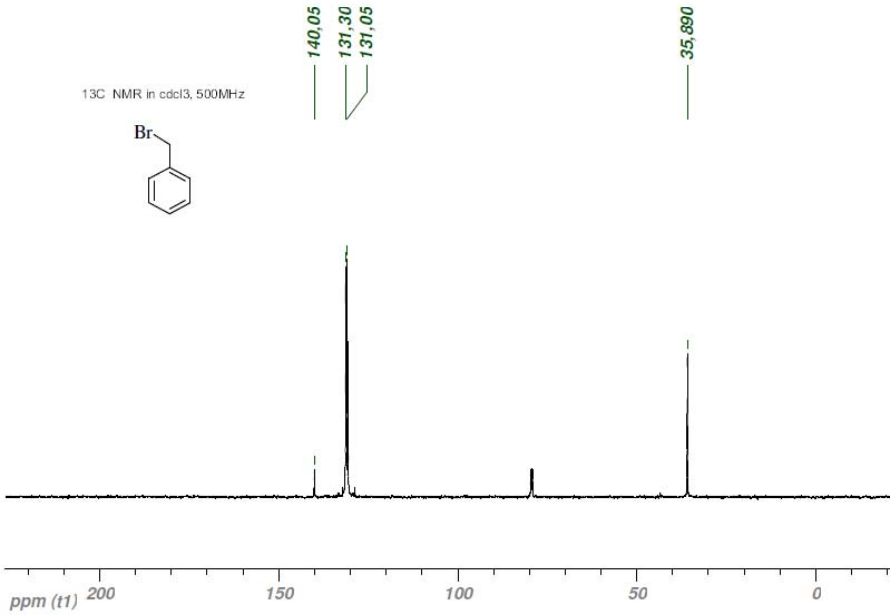


Entry 5, Table S5 (Benzyl bromide)

H^1 NMR

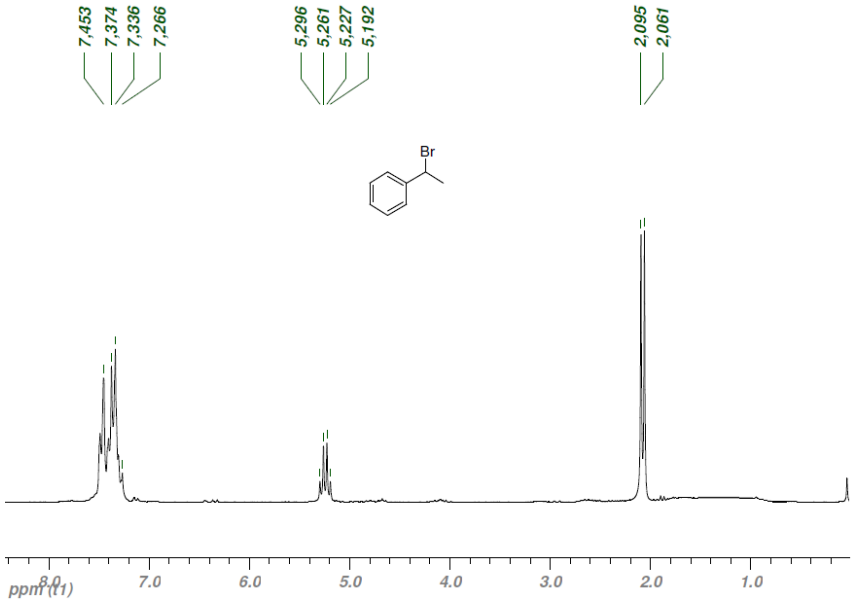


C^{13} NMR

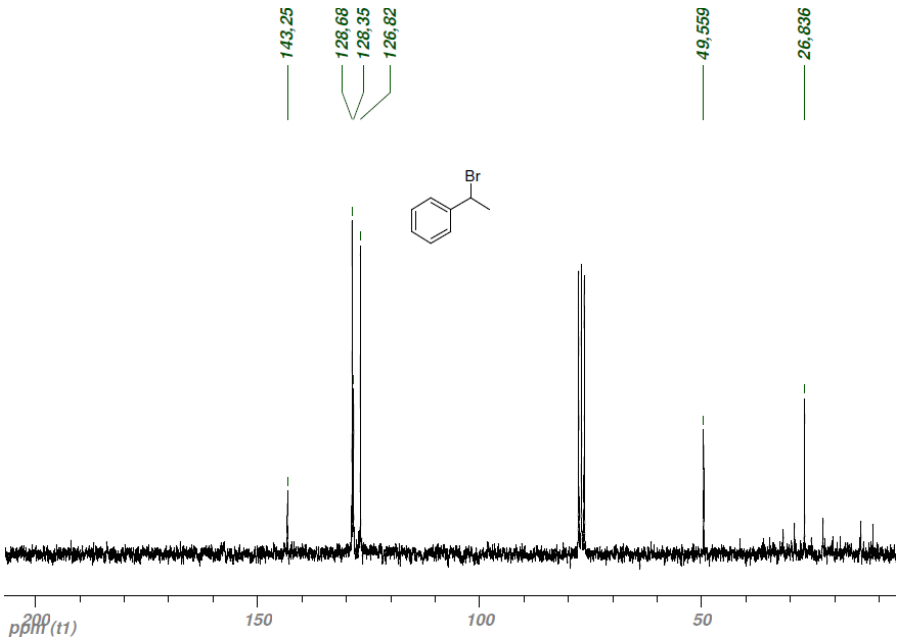


Entry 6, Table S5 (1-bromo-1-phenyl ethane)

H^1 NMR

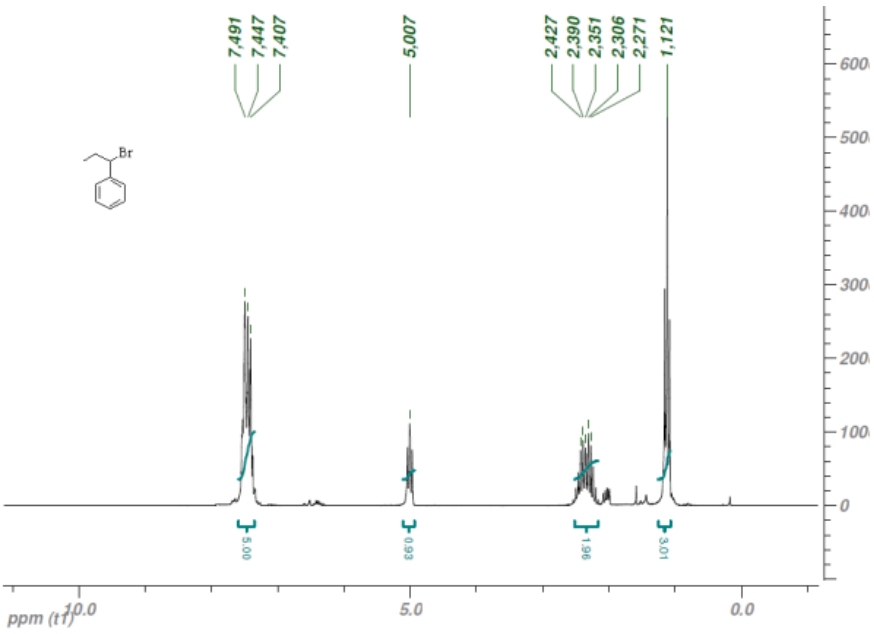


C^{13} NMR

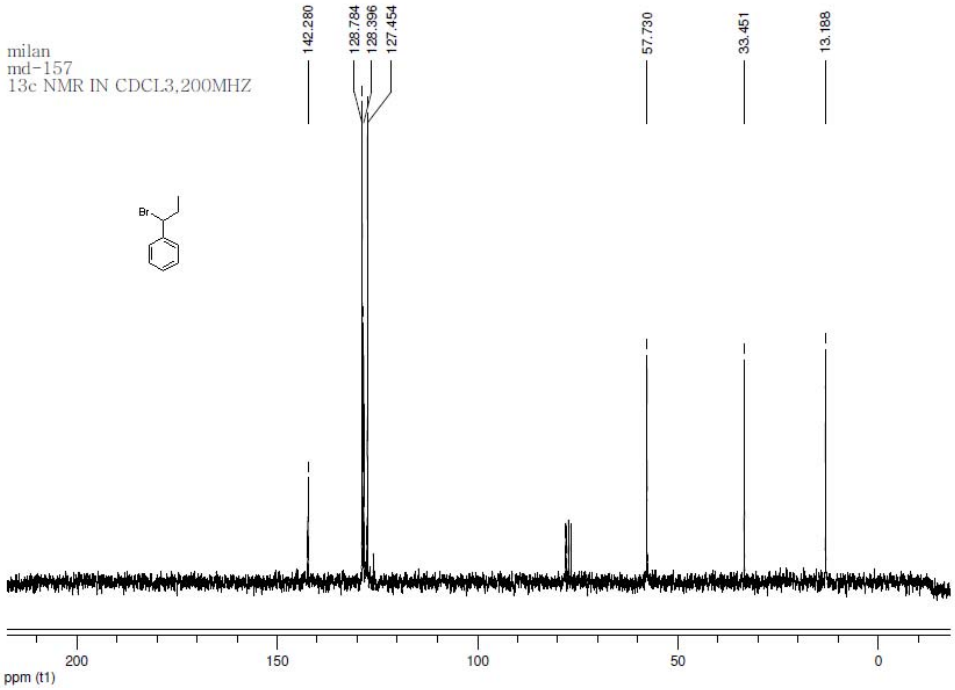


Entry 7, Table S5 (1-bromo-1-phenyl propane)

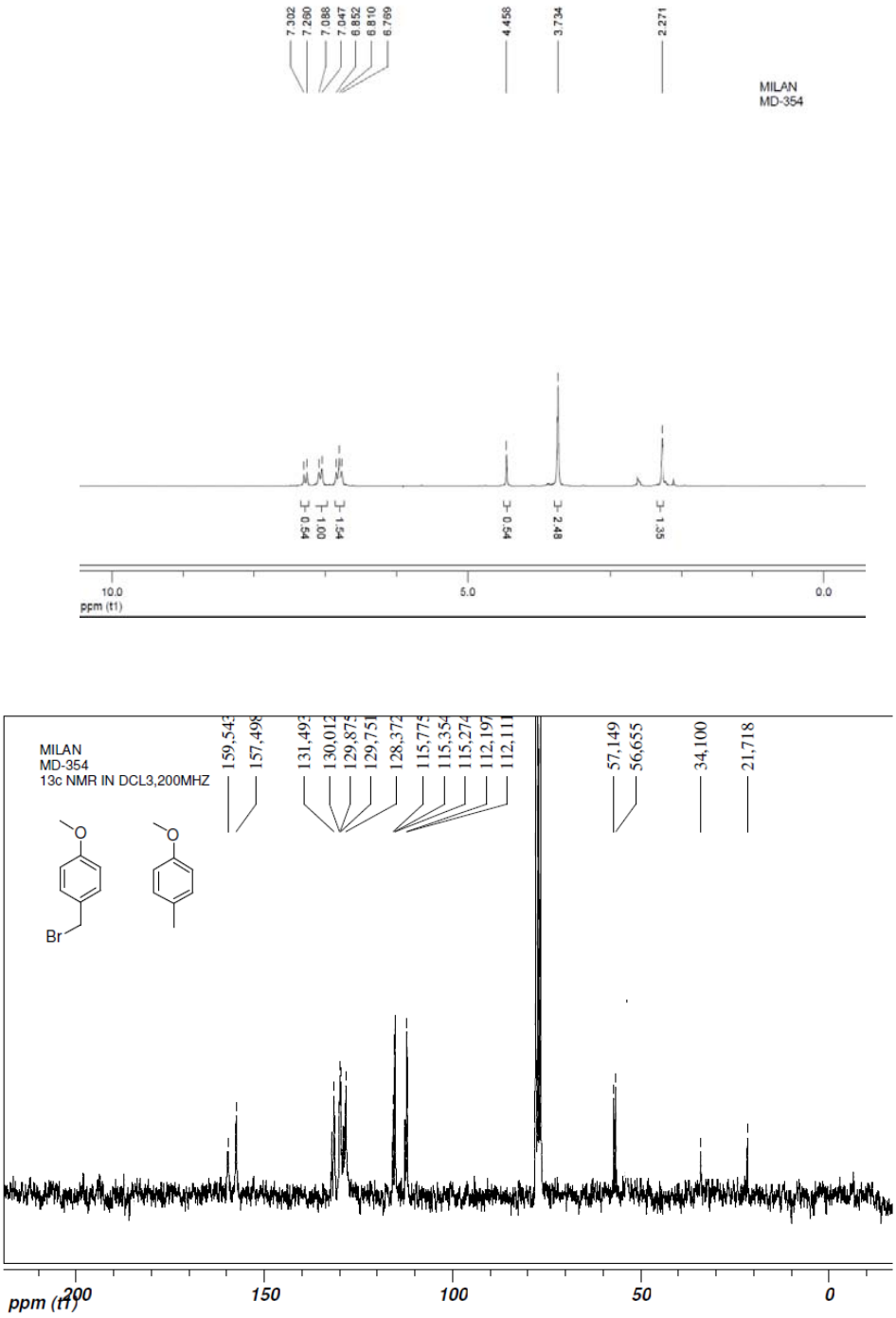
H^1 NMR



C^{13} NMR

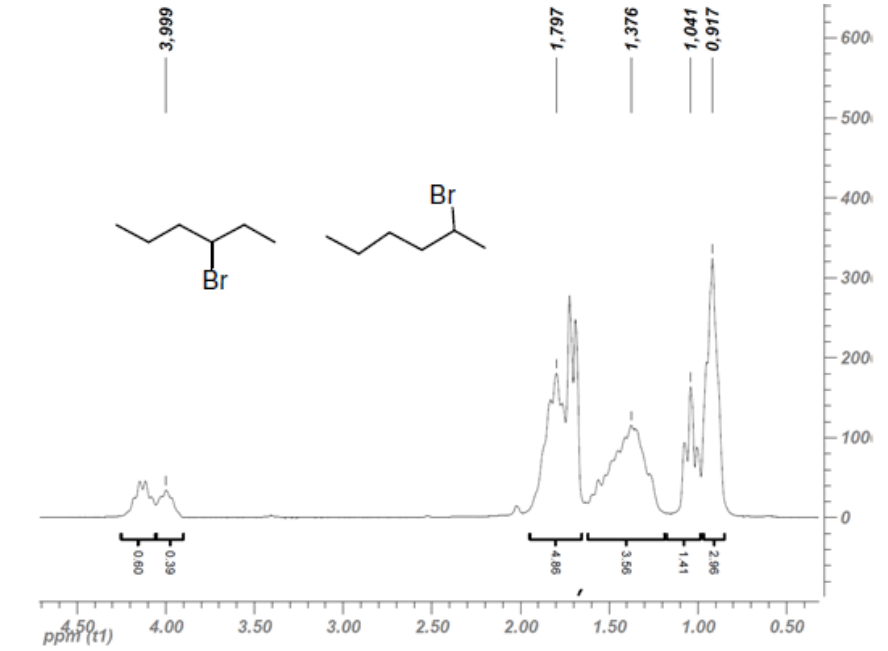


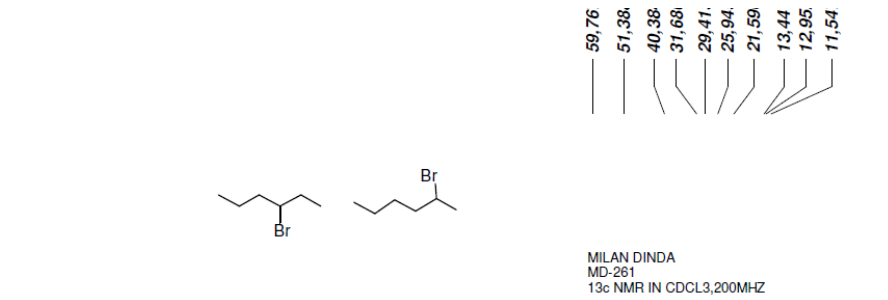
Entry 8, Table S5 (Reaction mixture containing twofold excess 4-Methoxy toluene and 4-Methoxy Benzyl bromide)



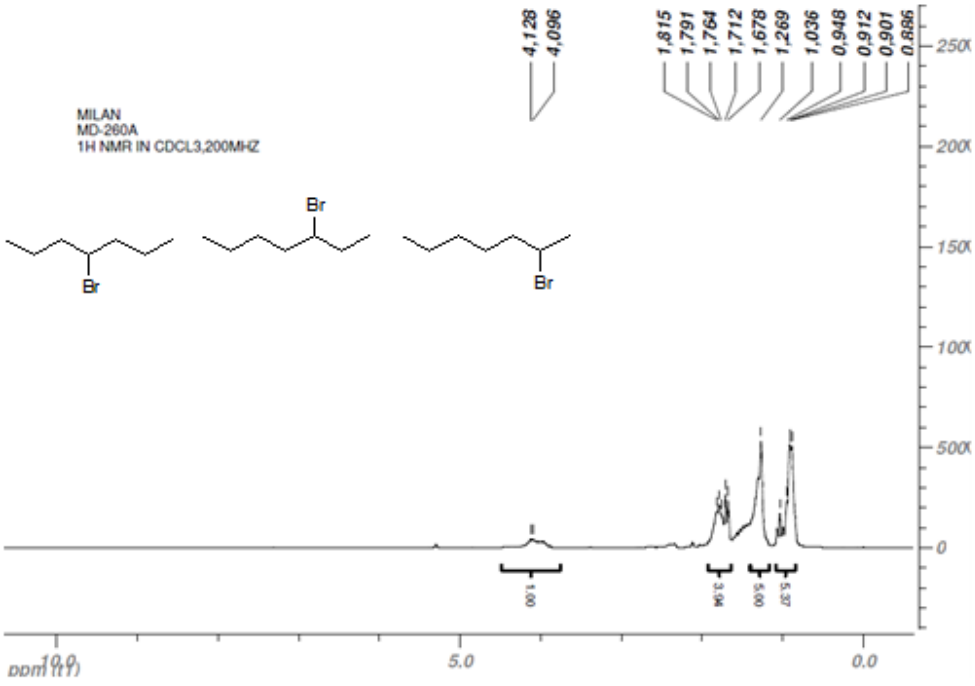
NMR of Bromoalkane

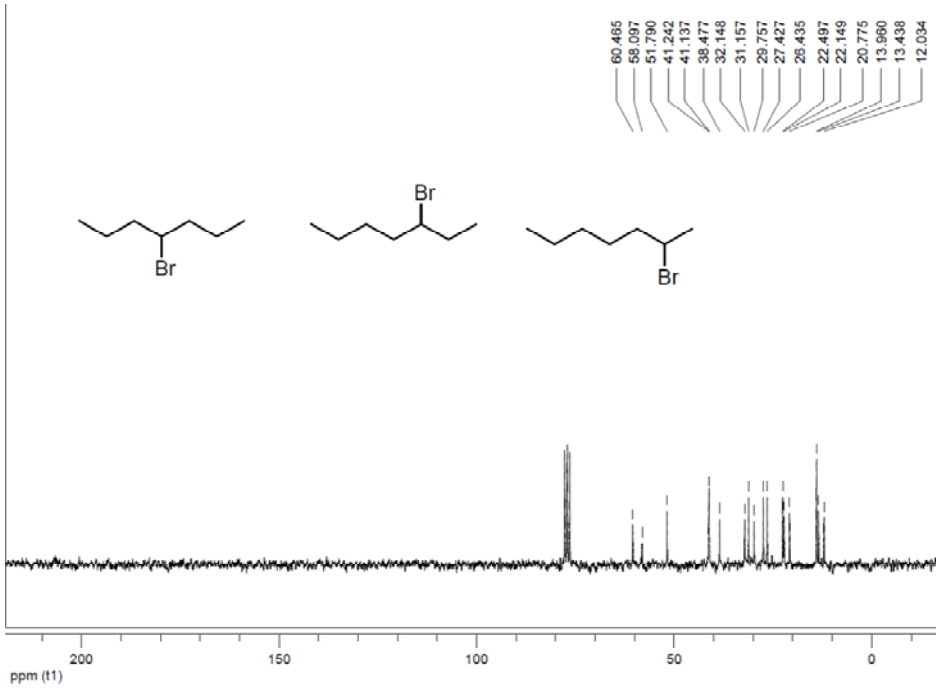
Entry 1, Table S6 (mixture of 2 bromo and 3 bromo hexane)



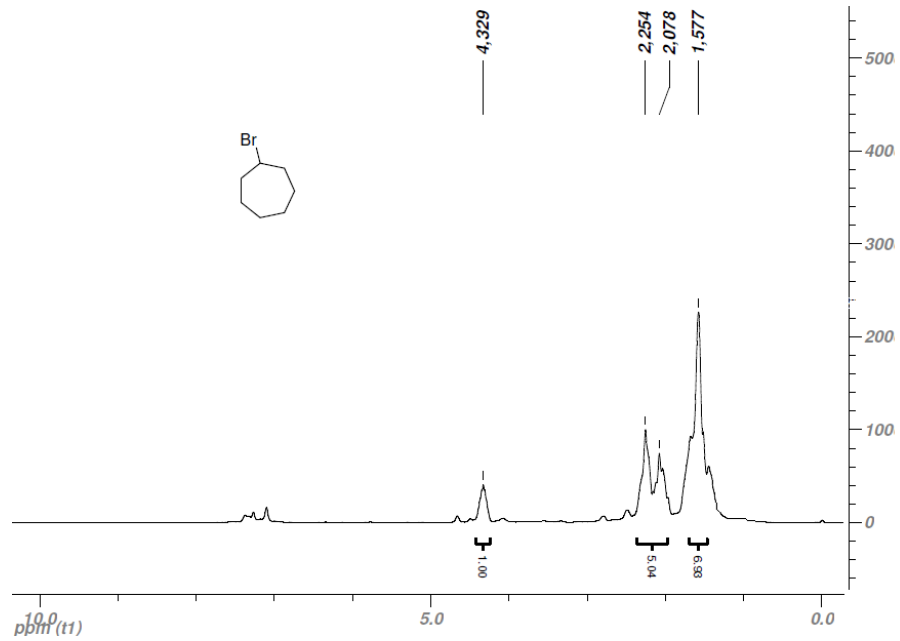


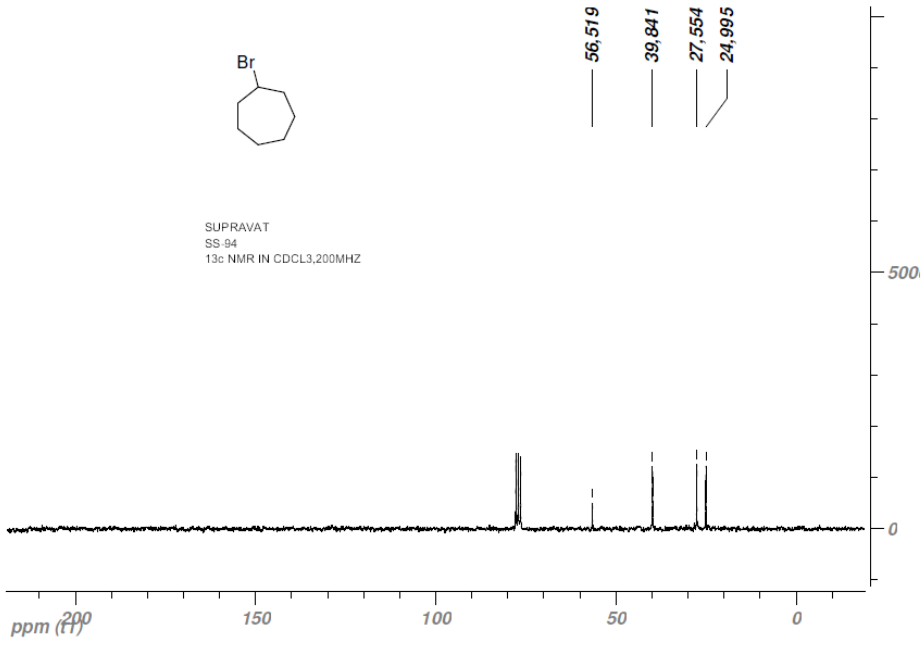
Entry 2, Table S6 (mixture of 2bromo, 3bromo and 4 bromo heptane)



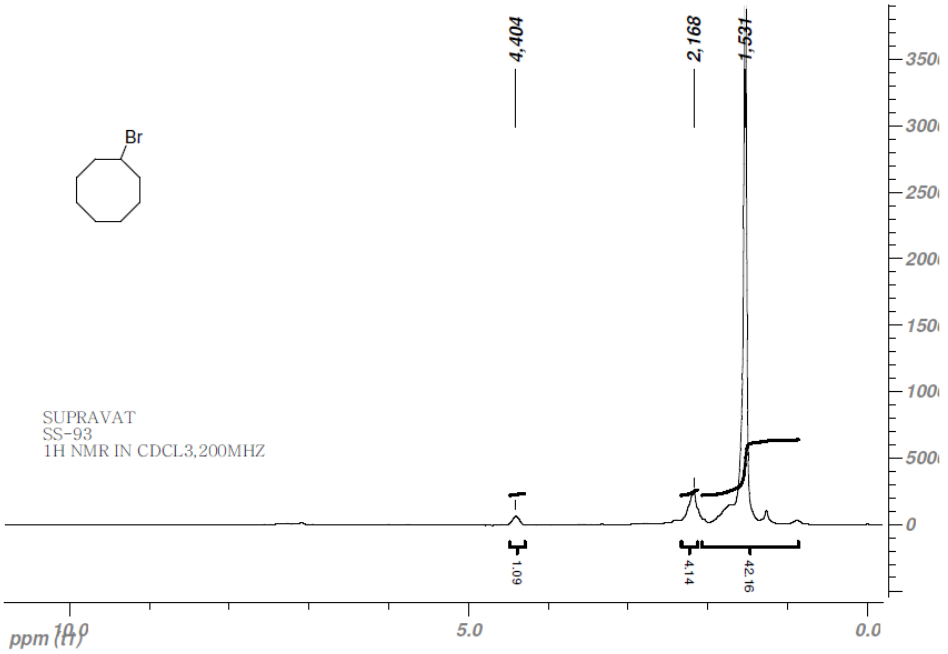


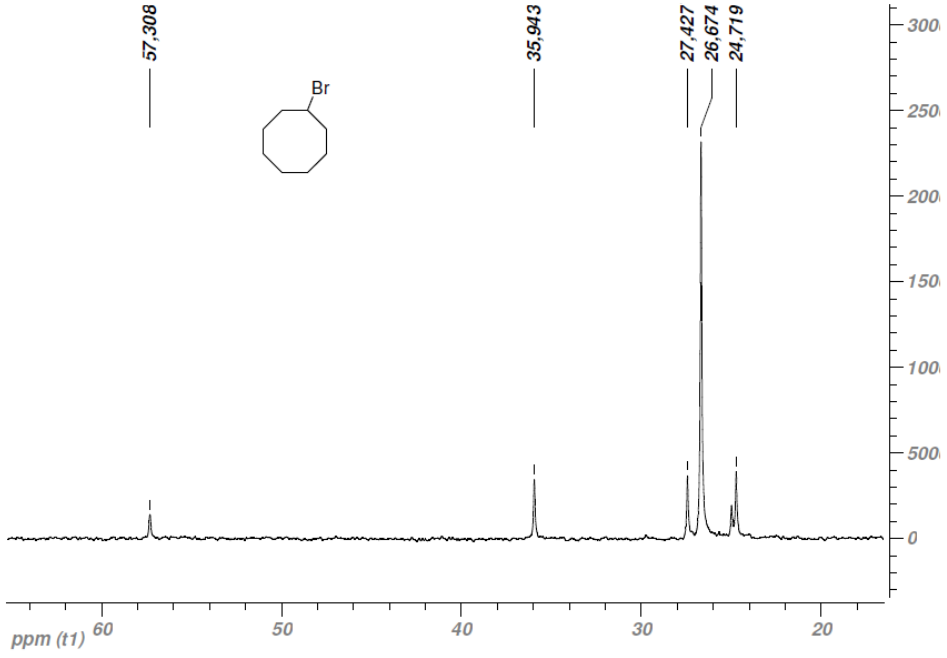
Entry 3, Table S6 (1 Bromo cycloheptane)



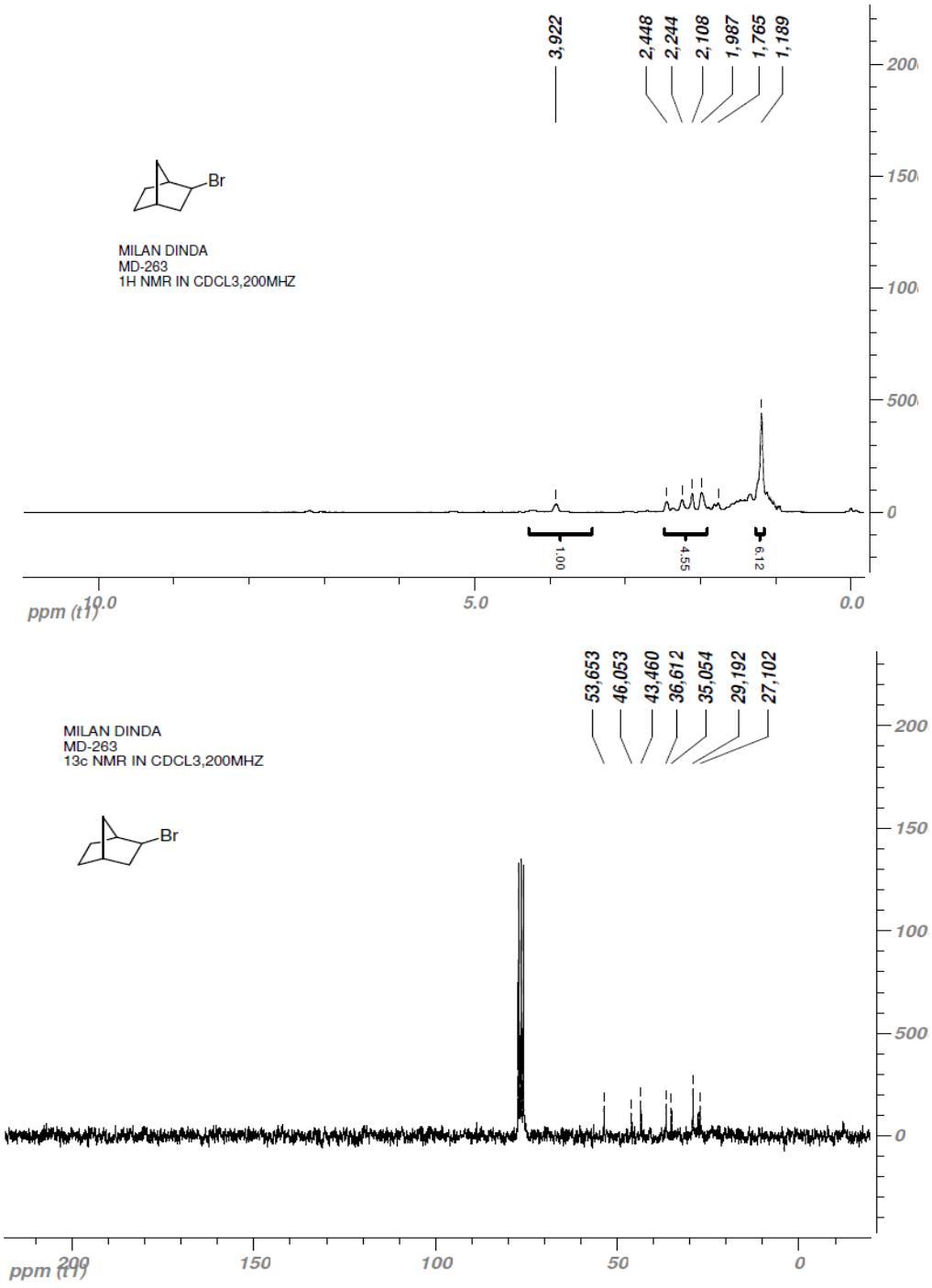


Entry 4, Table S6, (1-Bromo cyclooctane)





Entry 5, Table S6 (2-Bromo norbornane)



Entry 6, Table S6 (1 Bromo cyclodecane)