Supporting information for

Direct Catalytic Asymmetric Reductive Amination of Simple Aromatic Ketones

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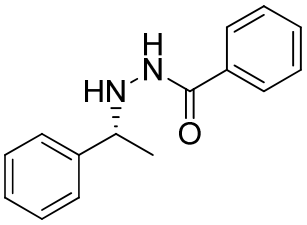
CONTENTS

I. General remarks

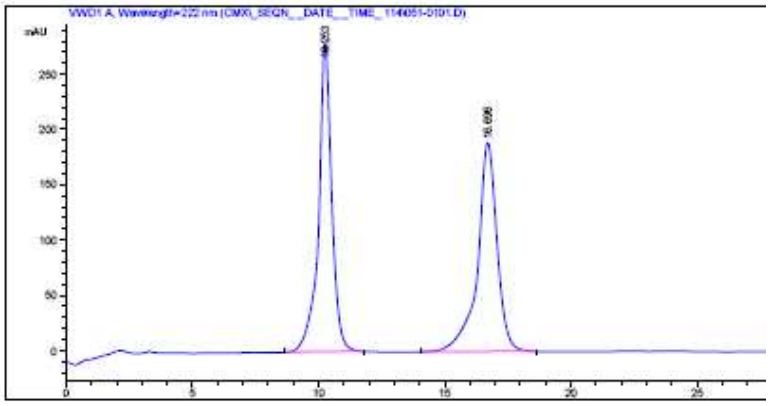
All reactions were performed in the nitrogen-filled glovebox or under nitrogen using standard Schlenk techniques unless otherwise noted. Column chromatography was performed using Sorbent silica gel 60 (230 – 450 mesh). ^{1}H NMR, and ^{13}C NMR spectral data were obtaineded from Bruker 400 MHz spectrometers. Chemical shifts are reported in ppm. Enantiomeric excess values were determined by chiral HPLC on an Agilent 1200 Series instrument. All new products were further characterized by HRMS. A positive ion mass spectrum of sample was acquired on a Micromass 70-VSE mass spectrometer with an electron ionization source..

II. General Procedure for Asymmetric Hydrogenation.

Typical reductive amination procedure: In a nitrogen-filled glovebox, ketone (0.22 mmol), 4Å molecular sieves (0.2 g), p-toluenesulfonic acid (0.02 mmol) and phenylhydrazide (0.20 mmol) were stirred in anhydrous CH_2Cl_2 (0.5 mL) and MeOH (0.5 mL) for 10 min in a vial. Then [Ir(COD)f-Binaphane]Cl (0.002 mmol) in situ generated (from $[Ir(COD)Cl]_2$ and f-Binaphane stirred in CH_2Cl_2 for 15 min) was added to this vial, followed by I_2 (5.1 mg, 0.02 mmol). The total solution was made to 2.0 mL at a MeOH / CH_2Cl_2 ratio of 1:1. The resulting vial was transferred to an autoclave, which was charged with 50 atm of H_2, and stirred at room temperature for 24 h. The hydrogen gas was released slowly and the solution was concentrated and passed through a short column of silica gel to remove the metal complex and molecular sieve. The product was then analyzed by chiral HPLC to determine the enantiomeric excesses.



(*R*)- *N*'-(1-phenylethyl)benzohydrazide (3a): [1] white solid (95% yield, 94 % ee). $[\alpha]^{20}_{D}$ +167.2 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.76 (m, 11H), 4.22 (q, *J*=6.6 Hz, 1H), 1.41 (d, *J*=6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 143.1, 133.0, 131.8, 128.6, 127.6, 127.3, 126.8, 60.1, 22.7. Enantiomeric excess was determined by HPLCusing Chiralcel OJ-H column, Hex/IPA=90:10, 1 mL/min.



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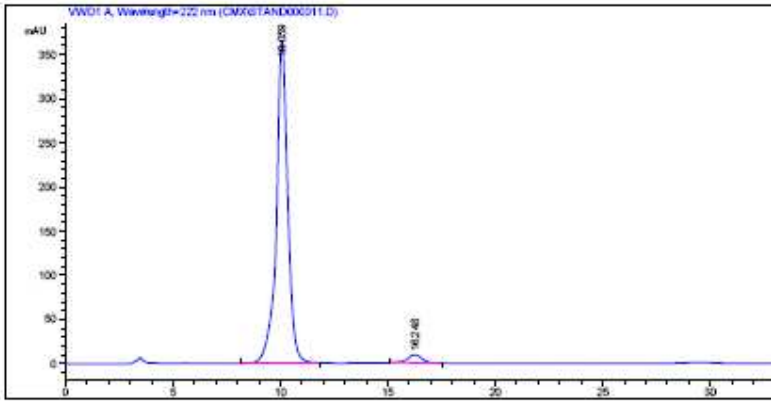
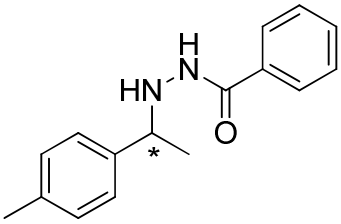
2	16.696	BB	0.7892	1.01421e4	188.97099	49.9292

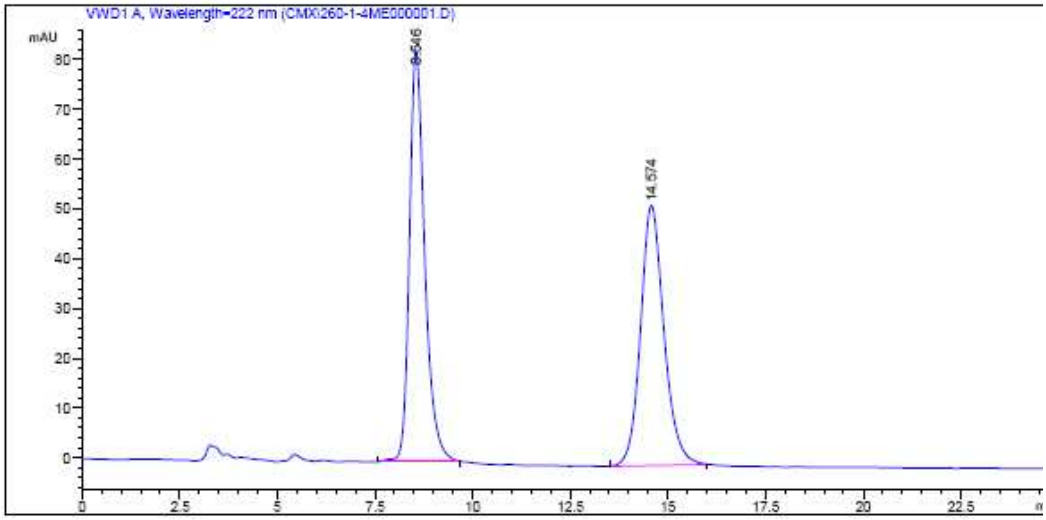


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.059	BB	0.5424	1.34713e4	365.25116	96.7570
2	16.248	BB	0.6978	451.52301	9.43965	3.2430



(+)- *N*'-(1-(p-tolyl)ethyl)benzohydrazide (3b): white solid (94% yield, 96 % ee). $[\alpha]^{20}_{D}$ +164.6 (c = 0.25 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J*=7.2 Hz, 2H), 7.38-7.53 (m, 4H), 7.28 (d, *J*=8 Hz, 2H), 7.10 (d, *J*=7.2 Hz, 2H), 4.18 (q, *J*=6.6 Hz, 1H), 2.33 (s, 3H), 1.41 (d, *J*=6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 140.1, 137.2, 133.0, 131.7, 129.3,128.6, 127.1, 126.8, 59.8, 21.2, 21.1. EI-HRMS: 255.1499 (Calculated for $C_{16}H_{19}N_2O^+$([M+H]$^+$): 255.1497). Enantiomer ratio was determine by HPLC

using a Chiralcel OJ-H column, Hex/IPA=90:10, 1 mL/min.



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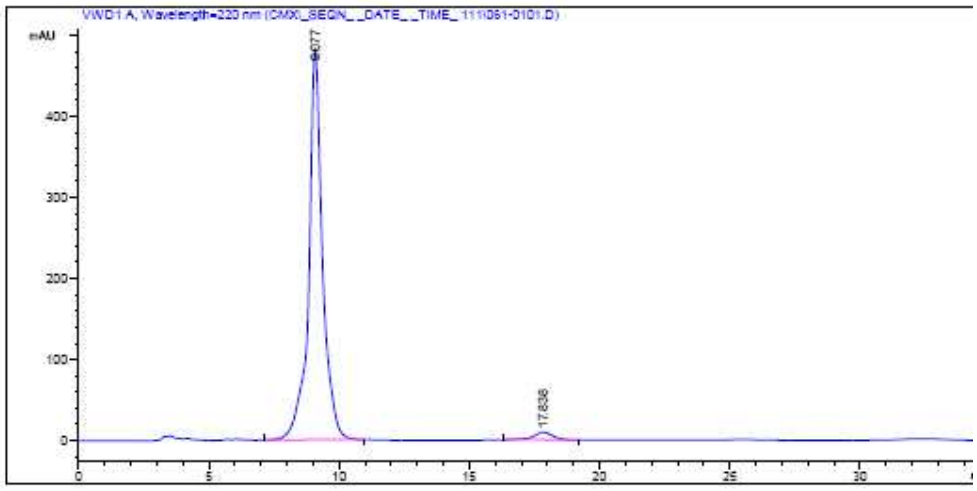
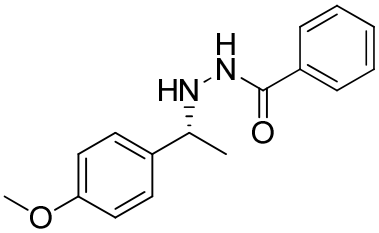
1	10.155	BB	0.4585	3539.85278	115.50782	51.0672
2	15.587	VB	0.6289	3391.89819	80.90830	48.9328
Totals :				6931.75098	196.41612	

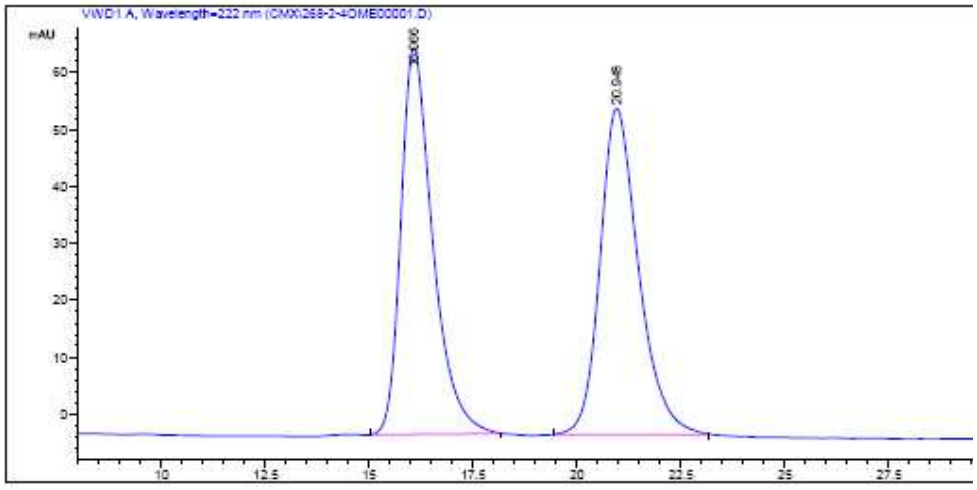


Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.077	BB	0.5291	1.77891e4	482.58063	97.2582
2	17.838	BB	0.7942	501.46392	9.42298	2.7418
Totals :				1.82906e4	492.00361	



(*R*)- *N*'-(1-(4-methoxyphenyl)ethyl)benzohydrazide (3c): [1] light yellow oil (92% yield, 98 % ee). $[\alpha]^{20}_{D}$ +148.3 (c = 1 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$)δ 7.61 (d, *J*=7.2 Hz, 2H), 7.40 (m, 1H), 7.32 (m, 2H), 7.28 (d, *J*=7.2 Hz, 2H), 6.82 (d, *J*=7.2 Hz, 2H), 4.18 (q, *J*=6.6 Hz, 1H), 3.79 (s, 3H), 1.40 (d, *J*=6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 158.1, 134.0, 132.0, 130.7, 128.0, 127.8, 125.8, 113.0, 58.4, 54.3, 20.2. Enantiomer ratio was determine by HPLC using a Chiralcel OJ-H column, Hex/IPA=90:10, 1 mL/min.



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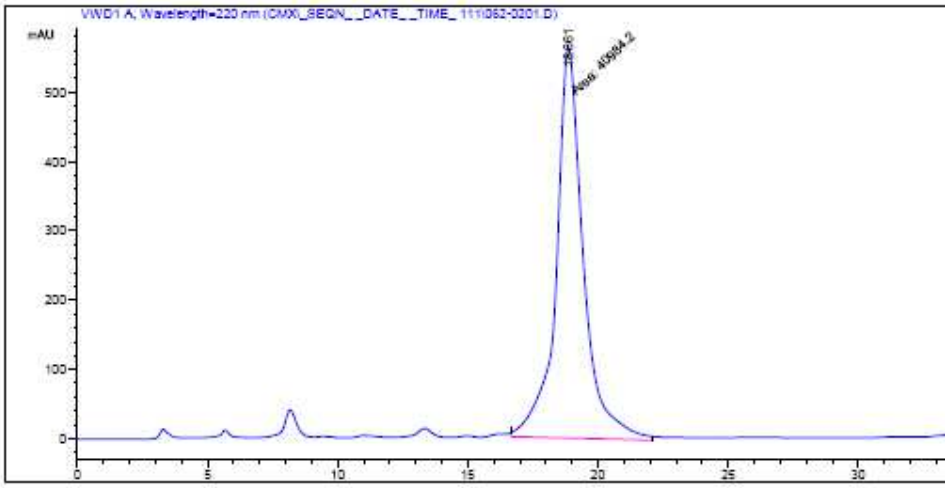
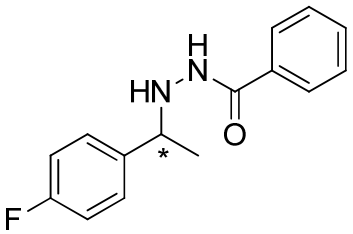
1	16.066	BB	0.8071	3630.83691	67.92702	49.5182
2	20.948	BB	0.9761	3701.48486	57.32062	50.4818
Totals :				7332.32178	125.24764	

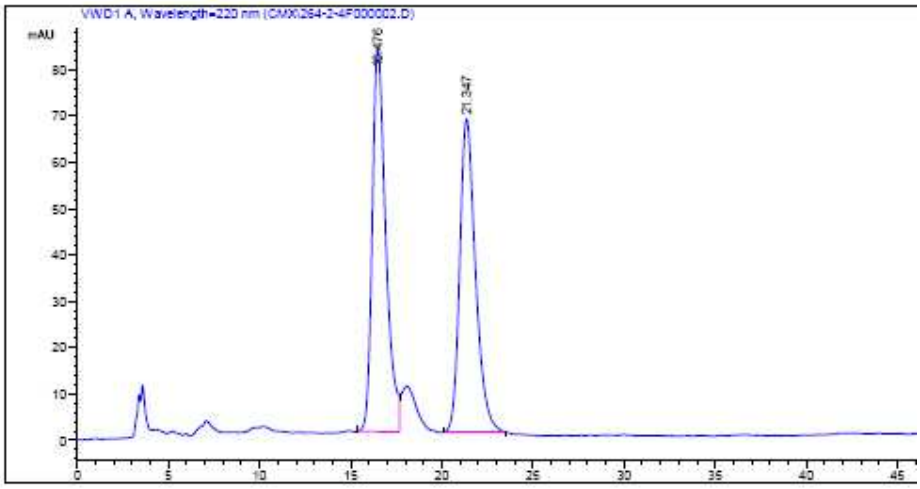


Signal 1: VWD1 A, Wavelength=220 nm

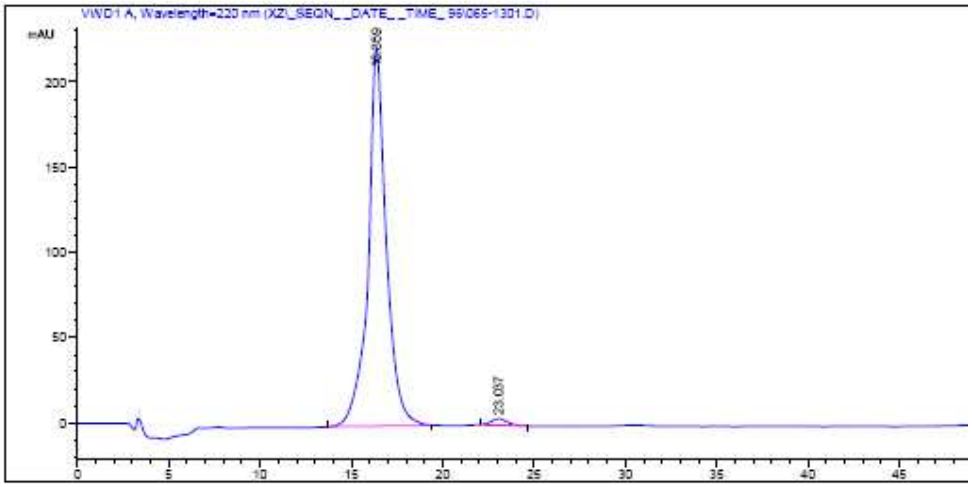
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.861	MM	1.2126	4.09842e4	563.30292	100.0000
Totals :				4.09842e4	563.30292	



(+)-*N*'-(1-(4-fluorophenyl)ethyl)benzohydrazide (3d): white solid (86% yield, 96 % ee). $[\alpha]^{20}_{D}$ +177.6 (c = 0.5 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.72 (m, 2H), 7.54 (m, 2H), 7.32 (m, 4H), 6.98 (m, 2H), 5.02 (s, br,1H), 4.24 (q, *J*=6.6 Hz,1H), 1.30 (d, *J*=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ167.4, 163.5, 161.0, 138.9, 132.8, 131.9, 128.8, 128.7, 126.8, 115.5, 115.3, 59.3, 29.7, 21.3. EI-HRMS: 259.1253 (Calculated for $C_{15}H_{16}N_2OF^+$([M+H]$^+$): 259.1247). Enantiomer ratio was determine by HPLC using a Chiralcel OJ-H column, Hex/IPA=94:6, 1 mL/min.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.476	BV	0.7844	4272.50342	82.94896	51.1642
2	21.347	BB	0.8982	4078.06885	67.66426	48.8358
Totals :				8350.57227	150.61322	



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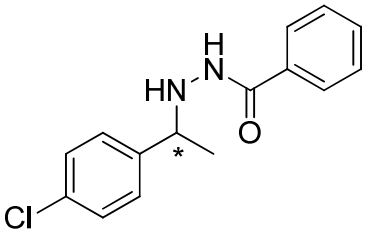
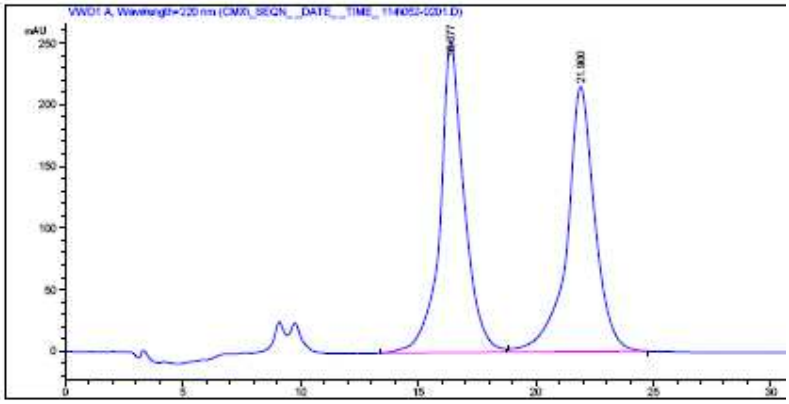
1	16.359	BB	0.9863	1.53404e4	222.11655	98.3365
2	23.037	BB	0.8852	259.50607	3.96877	1.6635
Totals :				1.55999e4	226.08532	



(+)-*N*'-(1-(4-chlorophenyl)ethyl)benzohydrazide (3e): white solid (92% yield, 97 % ee). $[\alpha]^{20}_{D}$ +159.3 (c = 0.5 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$)δ 7.62 (d, *J*=7.2 Hz, 2H), 7.48 (m, 1H), 7.28-7.44 (m, 7H), 4.24 (q, *J*=6.6 Hz, 1H), 1.42 (d, *J*=6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ167.4, 141.8, 133.3, 132.7, 131.9, 128.8, 128.7, 128.6, 126.8, 59.4, 21.3. EI-HRMS: 275.0946 (Calculated for $C_{15}H_{16}N_2OCl^+$([M+H]$^+$): 275.0951). Enantiomer ratio was determine by HPLC using a Chiralcel OJ-H column, Hex/IPA=94:6, 1 mL/min.



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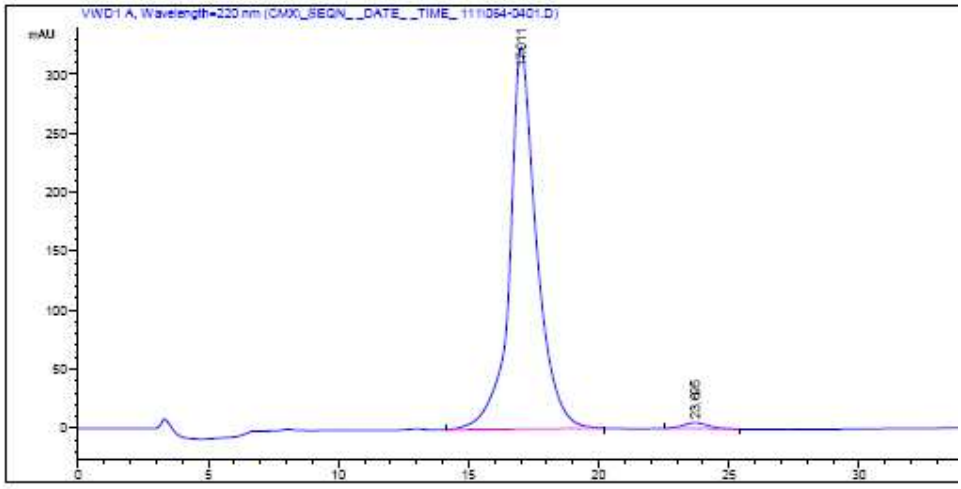
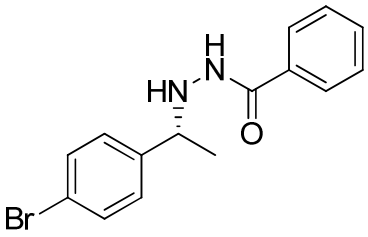
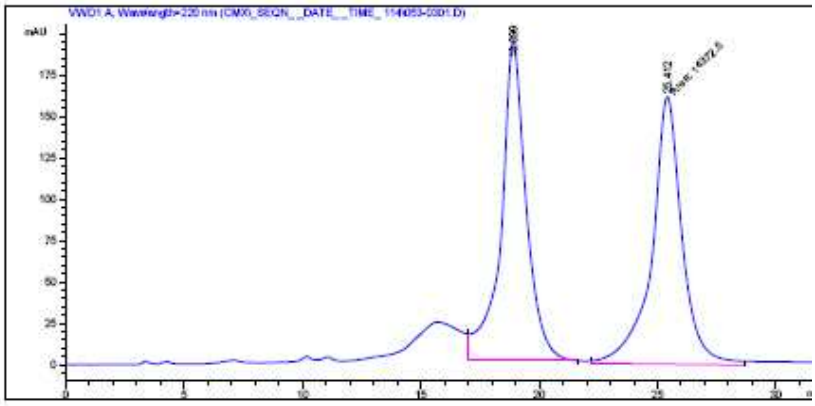
1	16.377	BB	1.0110	1.80677e4	252.93231	50.3942
2	21.900	BB	1.2007	1.77851e4	214.72481	49.6058



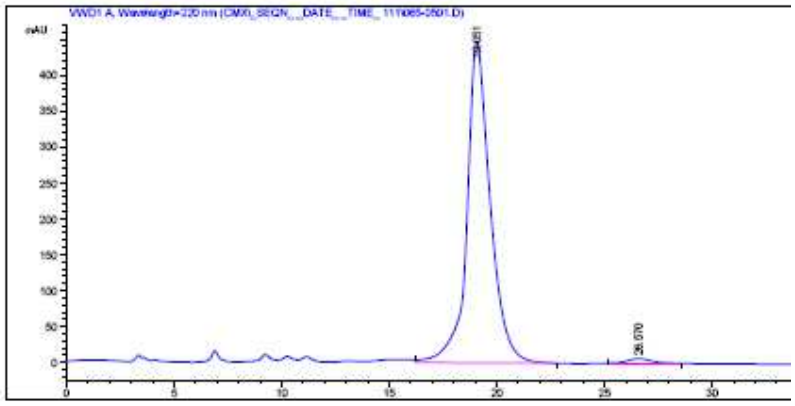
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.011	BB	1.0430	2.33829e4	323.95868	98.5793
2	23.695	BB	0.9193	336.99341	4.98761	1.4207
Totals :				2.37199e4	328.94629	



(*R*)-*N*'-(1-(4-bromophenyl)ethyl)benzohydrazide (3f):[1] white solid (95% yield, 97 % ee). $[\alpha]^{20}_{D}$ +144.3 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.68 (d, *J*=7.2 Hz, 2H), 7.20-7.50 (m, 8H), 4.24 (q, *J*=6.6 Hz, 1H), 1.42 (d, *J*=6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ167.4, 142.3, 132.7, 131.9, 131.7, 129.0, 128.7, 126.8, 121.4, 59.5, 21.3. Enantiomer ratio was determine by HPLC using a Chiralcel OJ-H column, Hex/IPA=94:6, 1 mL/min.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.899	VB	1.0670	1.4366344	192.88112	49.9892
2	25.412	MM	1.4815	1.4372544	161.69095	50.0108



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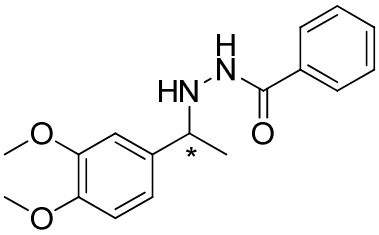
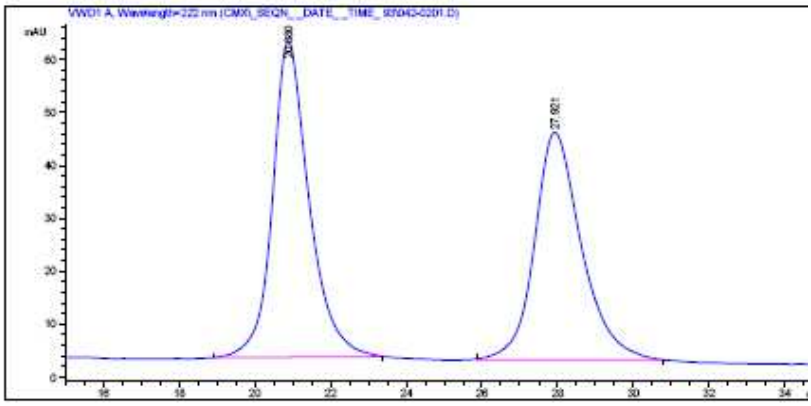
1	19.051	VB	1.1054	3.38809e4	448.56287	98.5447
2	26.570	BB	1.0525	500.35195	6.53088	1.4553
Totals :				3.43813e4	455.09374	

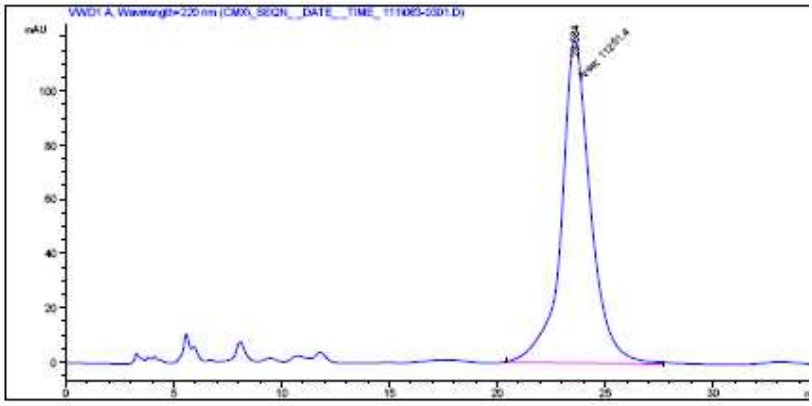


(+)-*N*'-(1-(3,4-dimethoxyphenyl)ethyl)benzohydrazide (3g): white solid (90% yield, >99 % ee). $[\alpha]^{20}_{D}$ +143.9 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.64 (d, *J*=7.2 Hz, 2H), 7.50 (m, 1H), 7.40 (m, 2H), 7.04 (m, 1H), 6.88-7.00 (m, 2H), 6.84 (d, *J*=7.2 Hz,1H), 4.26 (q, *J*=6.6 Hz, 1H), 3.90 (m, 2H), 1.46 (d, *J*=6.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ167.2, 149.2, 148.6, 135.0, 132.7, 131.9, 128.7, 126.9, 119.6, 111.2, 110.2, 60.0, 55.9, 20.9. EI-HRMS: 301.1560 (Calculated for $C_{17}H_{21}N_2O_3^+$([M+H]$^+$): 301.1552). Enantiomer ratio was determine by HPLC using a Chiralcel OJ-H column, Hex/IPA=90:10, 1 mL/min.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.880	BB	0.9989	4031.50244	59.70547	52.1144
2	27.921	BB	1.2644	3704.36255	42.99308	47.8856

Totals : 7735.86499 102.69854



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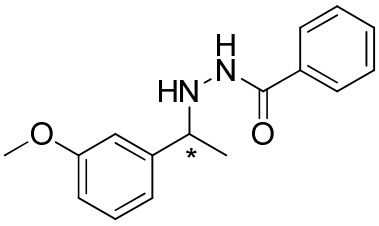
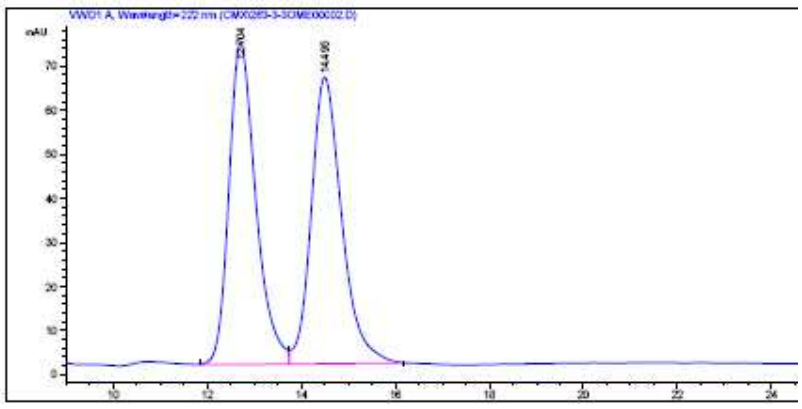
1	23.584	MM	1.5761	1.12514e4	118.97861	100.0000

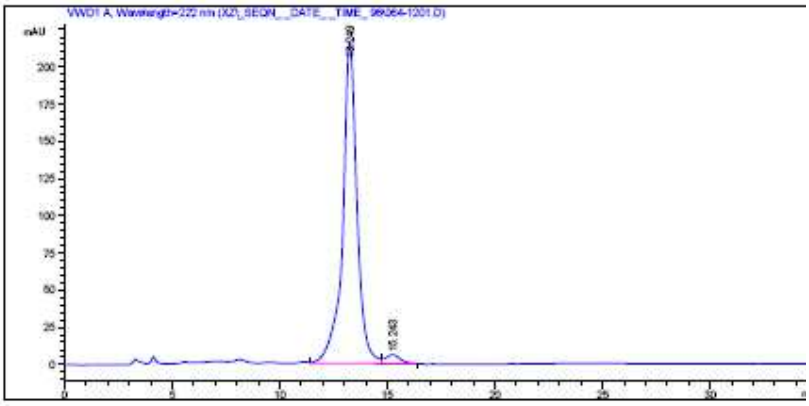
Totals : 1.12514e4 118.97861



(+)-*N*'-(1-(3-methoxyphenyl)ethyl)benzohydrazide (3h): white solid (92% yield, 94 % ee). $[\alpha]^{20}_{D}$ +176.5 (c = 0.25 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.62 (d, *J*=7.2 Hz, 2H), 7.24-7.52 (m, 5H), 7.00 (m, 2H), 6.82 (m, 1H), 6.76 (d, *J*=6.6 Hz, 1H), 4.24 (q, *J*=6.6 Hz, 1H), 3.80 (s, 3H), 1.42 (d, *J*=6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ167.3, 159.9, 144.9, 132.9, 131.8, 129.6, 128.7, 126.8, 119.6, 113.0, 112.6, 60.1, 55.2, 21.4. EI-HRMS: 271.1457 (Calculated for $C_{16}H_{19}N_2O_2^+$([M+H]$^+$): 271.1447). Enantiomeric excess was determined by HPLC using Chiralcel OJ-H column, Hex/IPA=90:10, 1 mL/min.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.704	BV	0.6079	2920.99634	73.01730	49.8686
2	14.495	VB	0.6837	2936.38818	65.07520	50.1314
Totals :				5857.38452	138.09249	



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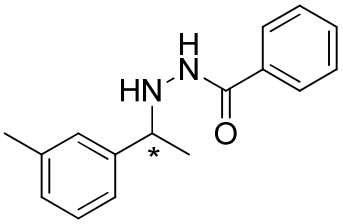
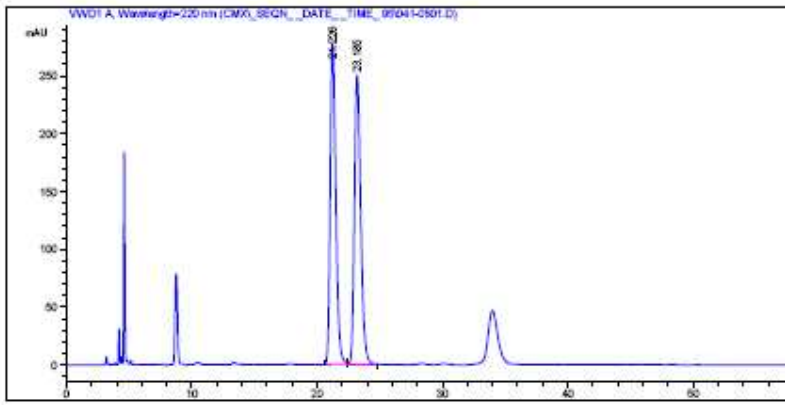
1	13.249	VB	0.6742	9986.36621	216.24530	97.1287
2	15.243	BB	0.7097	295.21869	6.13749	2.8713

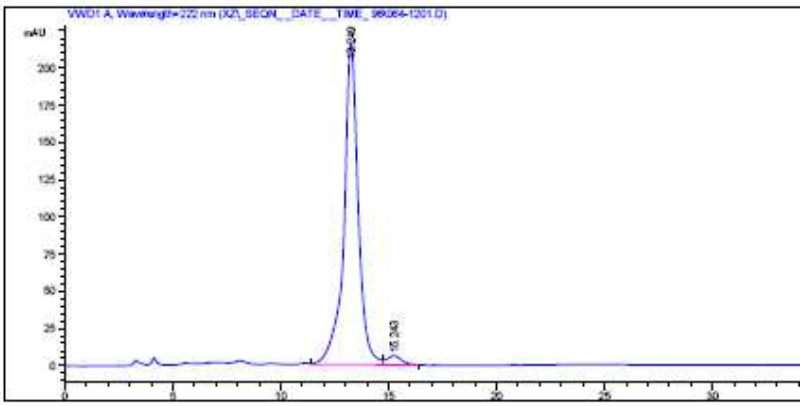


(+)-*N*'-(1-(m-tolyl)ethyl)benzohydrazide (3i): colorless liquid (93% yield, 97 % ee). $[\alpha]^{20}_{D}$ +156.6 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.60 (m, 3H), 7.40 (m, 1H), 7.30 (m, 2H), 7.16 (m, 3H), 7.00 (d, *J*=7.2 Hz,1H), 4.12 (q, *J*=6.6 Hz, 1H), 1.32 (q, *J*=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 143.0, 138.2, 133.0, 131.7, 131.5, 128.6, 128.5, 128.4,

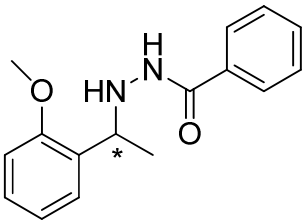
128.0, 126.9, 124.3. EI-HRMS: 255.1503 (Calculated for $C_{16}H_{19}N_2O^+$([M+H]$^+$): 255.1497). Enantiomeric excess was determined by HPLC using Chiralpak AD-H column, Hex/IPA=96:4, 1 mL/min.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.226	BV	0.4815	8715.61426	278.57104	49.9132
2	23.185	VB	0.5373	8745.94238	250.26825	50.0868

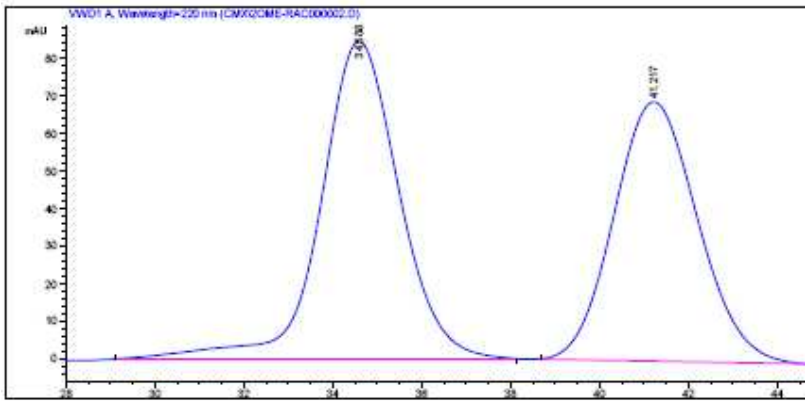


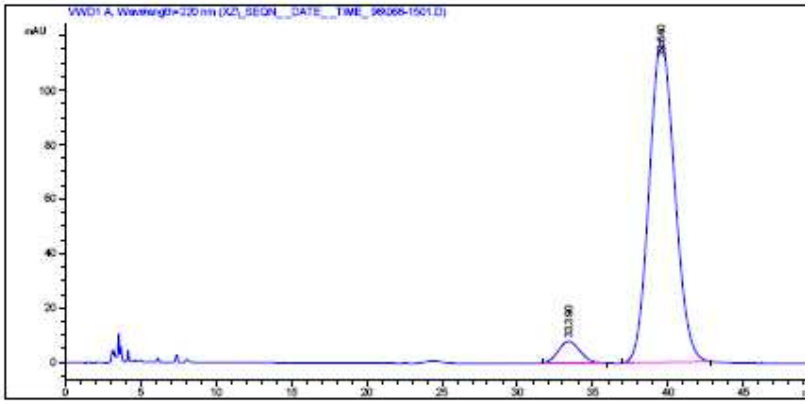
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.706	BB	0.5119	2.55642e4	768.49353	96.4148
2	20.701	BB	0.5731	950.61884	24.84542	3.5852
Totals :				2.65148e4	793.33895	



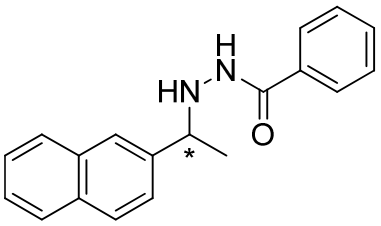
(+)- *N*'-(1-(2-methoxyphenyl)ethyl)benzohydrazide (3j): white solid (86% yield, 89 % ee). $[\alpha]^{20}_D$ +87.2 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.62 (m, 2H), 7.32-7.48 (m,

5H), 7.22 (m, 1H), 6.94 (m, 1H), 6.82 (d, *J*=7.2 Hz,1H), 4.58 (q, *J*=6.6 Hz, 1H), 3.73 (s, 3H),1.36 (q, *J*=6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 157.4, 133.2, 131.6, 131.1, 128.6, 128.3, 126.9, 126.8, 120.7, 110.7, 55.4, 53.9, 19.6. EI-HRMS: 269.1292 (Calculated for $C_{16}H_{17}N_2O_2^+$([M+H]$^+$): 269.1290). Enantiomeric excess was determined by HPLC using Chiralpak AS-H column, Hex/IPA=75:25, 1 mL/min.



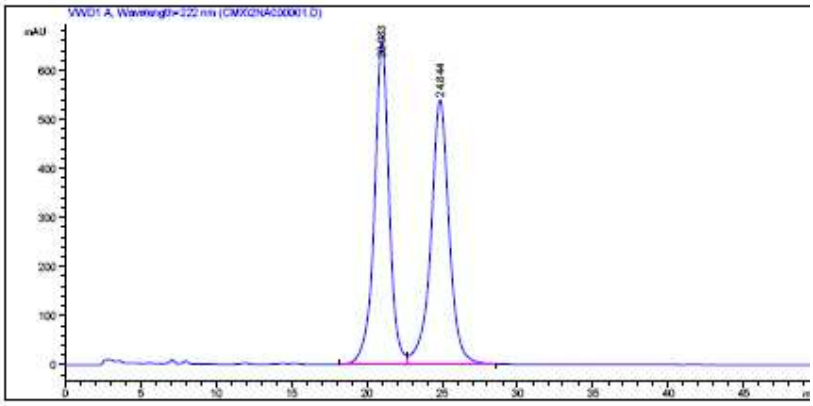


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.390	BB	1.2528	800.03418	7.95877	5.4370
2	39.540	BB	1.8211	1.39146e4	118.26759	94.5630
Totals :				1.47146e4	126.22637	

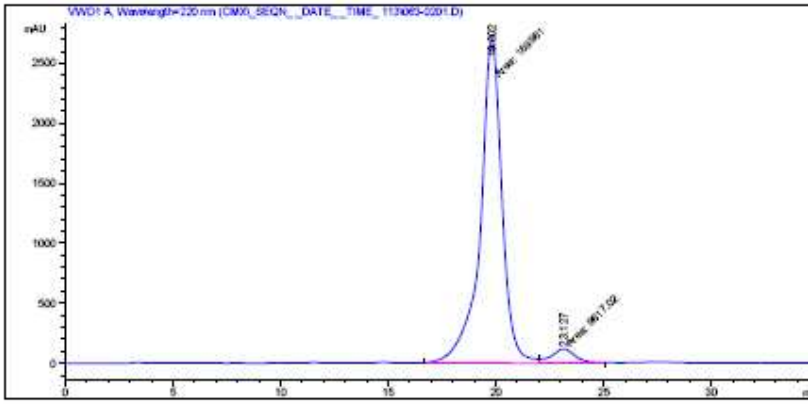


(*R*)- *N*'-(1-(naphthalen-2-yl)ethyl)benzohydrazide (3k):[1] white solid (91% yield, 90 % ee). $[\alpha]^{20}_D$ +195.9 (c = 1 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.76 (m, 4H), 7.54 (m, 4H), 7.40 (m, 3H), 7.30 (m, 2H), 6.70-6.78 (m, 3H), 4.40 (q, *J*=6.6 Hz, 1H), 1.42 (q, *J*=6.6 Hz,

3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4,140.6, 133.5, 133.1, 132.9, 131.8, 128.6, 128.4, 127.9, 127.7, 127.2, 126.9, 126.1, 126.1, 125.8, 125.2, 60.2, 21.3. Enantiomeric excess was determined by HPLC using Chiralcel OJ-H column, Hex/IPA=85:15, 1 mL/min.

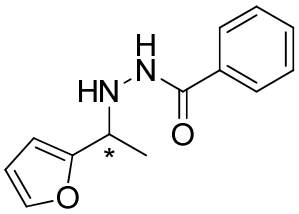


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.983	BV	1.0233	4.50181e4	657.24530	49.8347
2	24.844	VB	1.2536	4.53168e4	537.93628	50.1653



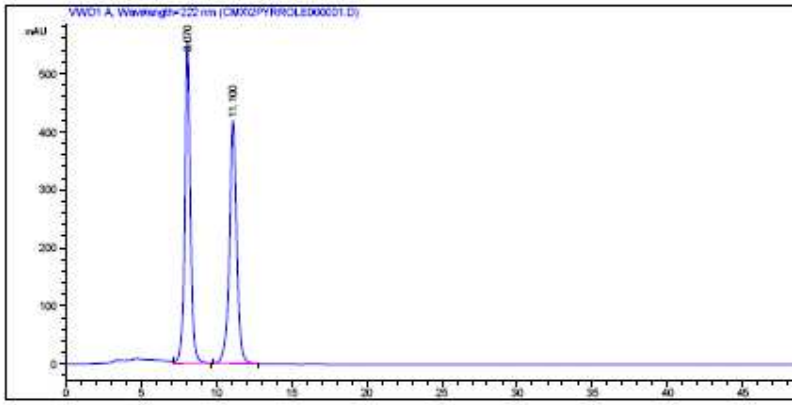
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.802	MF	1.1752	1.89981e5	2694.23364	95.1818
2	23.127	FM	1.3408	9617.02344	119.54082	4.8182

Totals : 1.99598e5 2813.77447

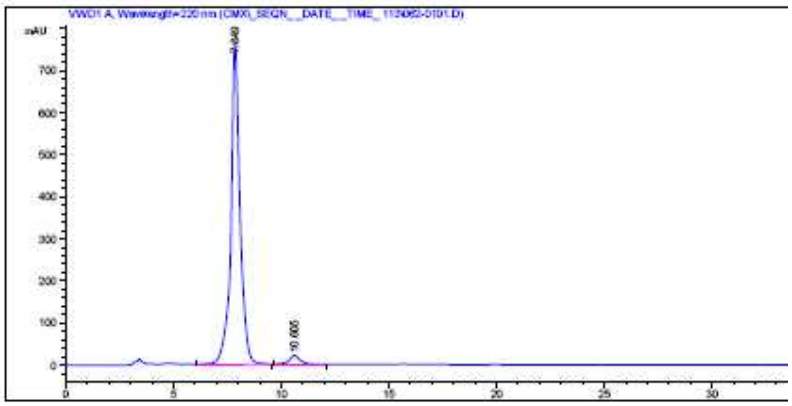


(+)-*N*'-(1-(furan-2-yl)ethyl)benzohydrazide (3l): yellow oil (91% yield, 89 % ee). $[\alpha]^{20}_{D}$ +105.1 (c = 0.25 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.70 (m, 2H), 7.62 (s, 1H), 7.50

(m, 1H), 7.42 (m, 3H), 6.32 (m, 1H), 6.20 (m, 1H), 4.32 (q, *J*=6.6 Hz, 1H), 1.48 (q, *J*=6.6 Hz, 3H).. ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 155.5, 142.1, 132.9, 131.9, 128.7, 126.9, 110.1, 106.7, 53.6, 17.6. EI-HRMS: 231.1138 (Calculated for $C_{13}H_{15}N_2O_2^+$([M+H]$^+$): 231.1134). Enantiomeric excess was determined by HPLC using Chiralcel OJ-H column, Hex/IPA=85:15, 1 mL/min.

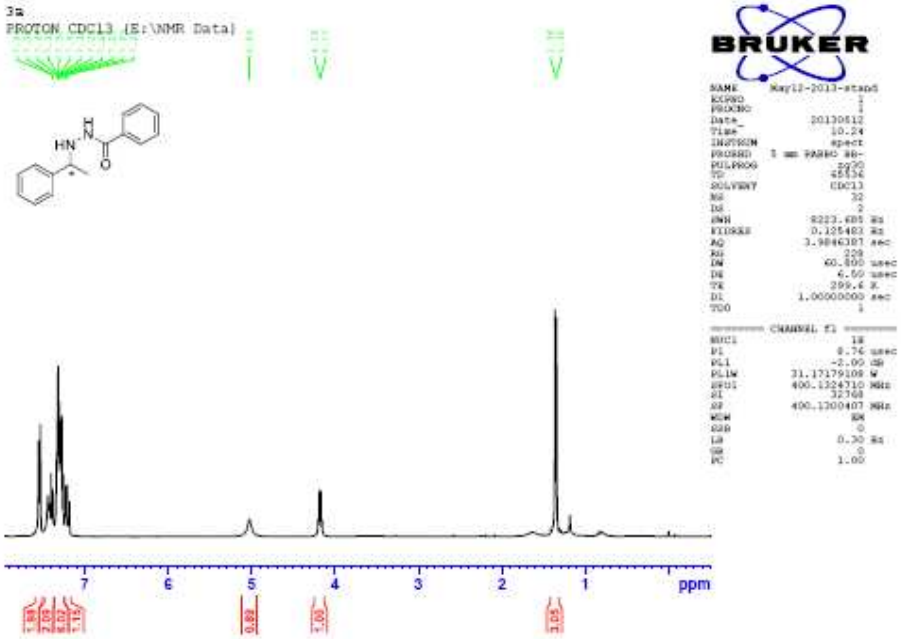


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.070	VB	0.3809	1.43682e4	554.59888	50.4716
2	11.100	BB	0.5018	1.40997e4	417.44537	49.5284

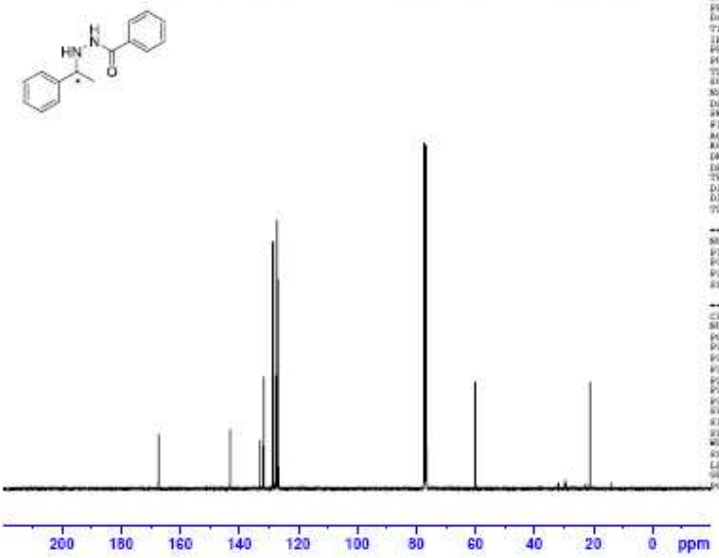


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.849	VB	0.4217	2.27594e4	767.37189	96.3948
2	10.605	BB	0.5572	851.19940	21.67142	3.6052
Totals :				2.36106e4	789.04331	

V. NMR & HRMS Spectra



3a
C13CPD CDCl3 (E:\NMR Data) mc 42



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PROCNO                1
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Time                 14.59
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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
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FIDRES        0.366798 Hz
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RG                  2050
DW                 20.800 usec
DE                  6.50 usec
TE                 302.6 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.50 usec
PL1               1.00 dB
PL1W        75.02196584 W
SFO1       100.6228296 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             80.00 usec
PL2               -2.00 dB
PL12              18.23 dB
PL13              19.00 dB
PL2W        31.17179108 W
PL12W        0.29562937 W
PL13W        0.24760634 W
SFO2       400.1316005 MHz
SI                 32768
SF         100.6127690 MHz
WDW                  EM
SSB                   0
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GB                    0
PC                 1.40
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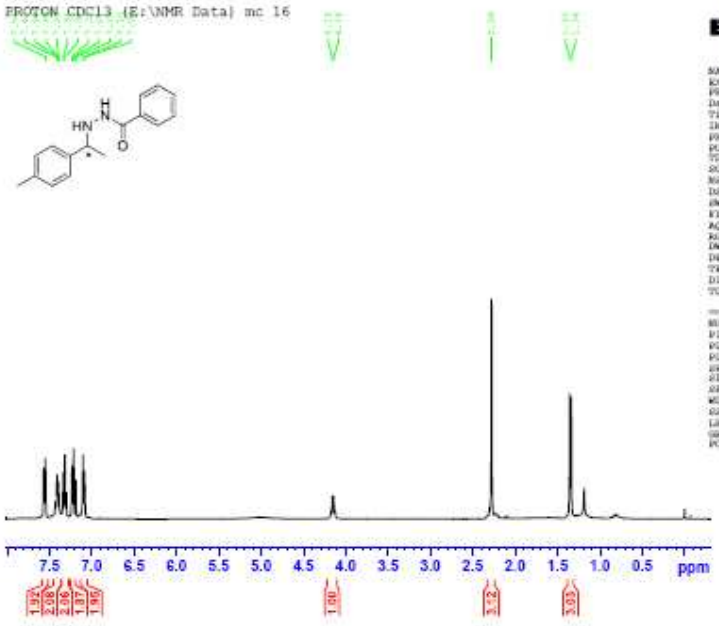
3b
PROTON CDCl3 (E:\NMR Data) mc 16



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PROCNO                1
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PULPROG           zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH           8223.685 Hz
FIDRES        0.125463 Hz
AQ            3.9846307 sec
RG                   362
DW                 60.800 usec
DE                  6.50 usec
TE                 299.5 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.76 usec
PL1               -2.00 dB
PL1W        31.17179108 W
SFO1       400.1324710 MHz
SI                 32768
SF         400.1300394 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
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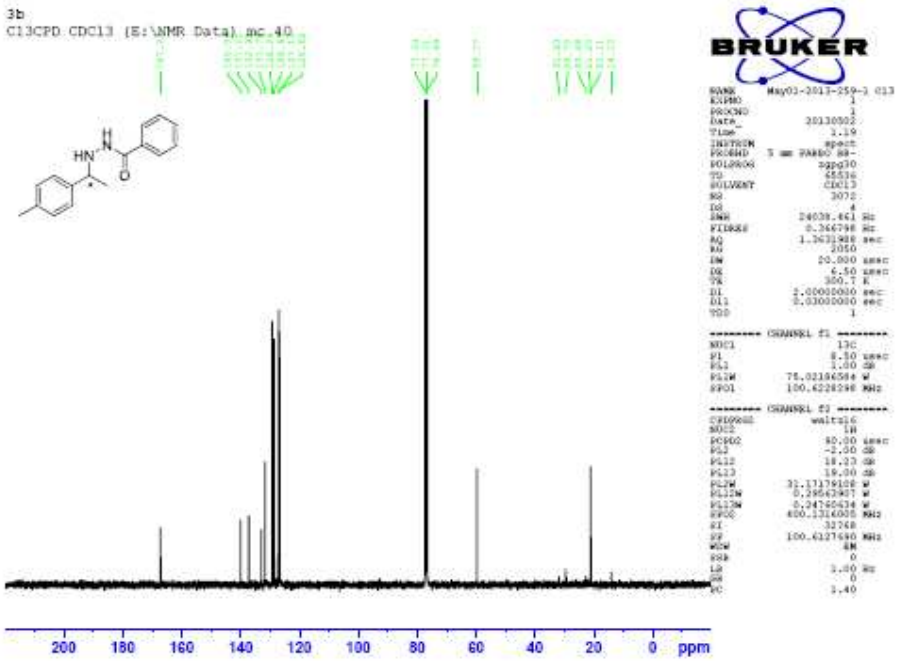


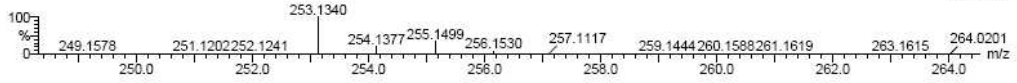
HRMS for (+)- *N*'-(1-(p-tolyl)ethyl)benzohydrazide (3b):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
73 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-130 H: 0-250 N: 0-4 O: 0-3

Mingxin ChangCMX-RA-1-4Me University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_47462 30 (2.245) AM (Cen,3, 80.00, Ar,15000.0,558.36,0.70,LS 3); Sm (SG, 2x3.00); Cm (29:30) 1: TOF MS ES+
2.13e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	600.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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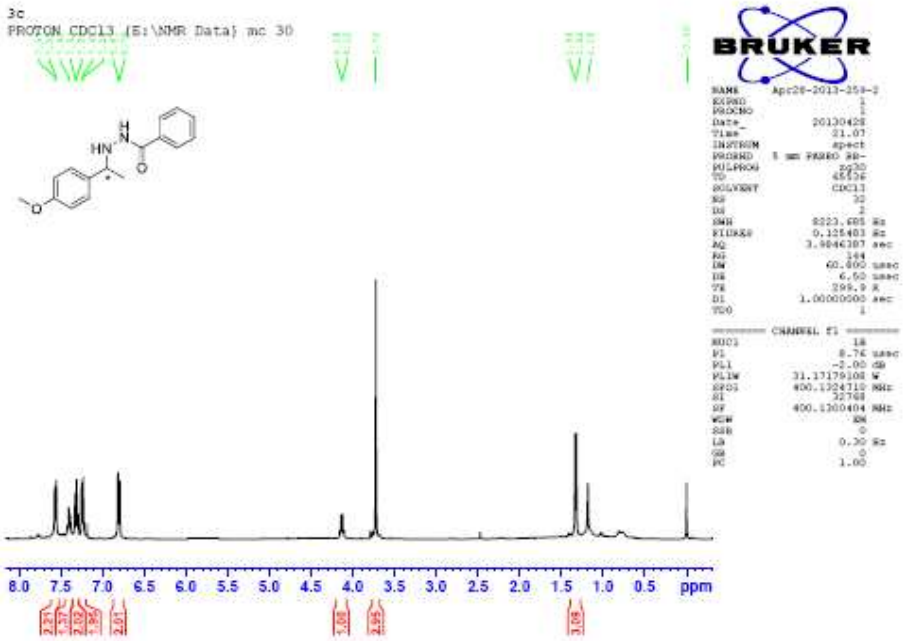
3c
PROTON CDCl3 (E:\NMR Data) mc 30
HN
O
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.01
2.07
2.02
1.96
2.07
1.00
2.05
3.06
BRUKER
NAME Apr28-2013-259-2
EXPNO 1
PROCNO 1
Date_ 20130428
Time 21.07
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.125403 Hz
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RG 144
DW 60.800 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
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PL1 -2.00 dB
PLW1 31.17179108 W
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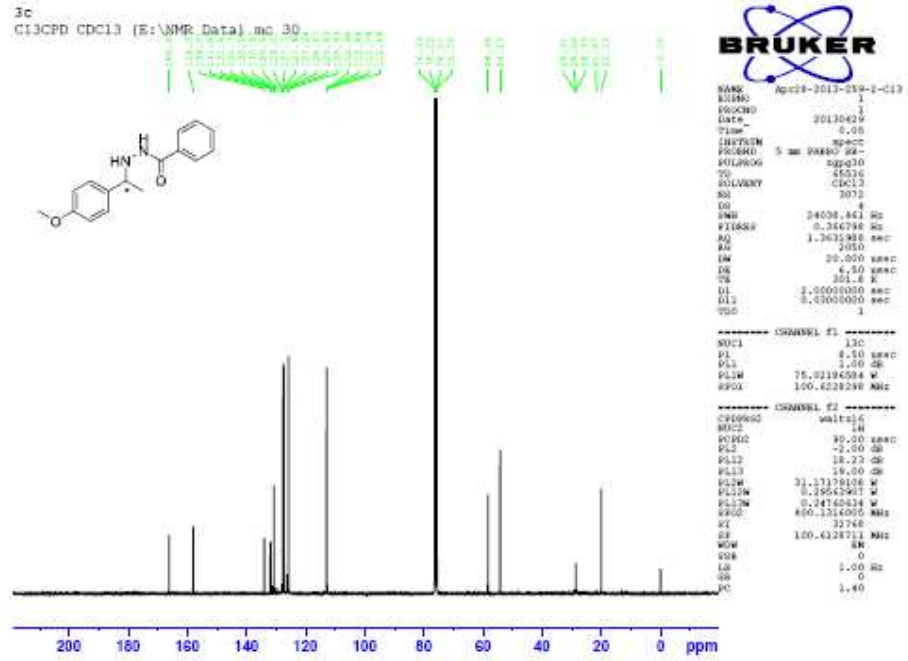
SSB 0
LB 0.30 Hz
GB 0
PC 1.00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O
O
200 180 160 140 120 100 80 60 40 20 0 ppm
BRUKER
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EXPNO 1
PROCNO 1
Date_ 20130429
Time 0.05
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2072
DS 4
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FIDRES 0.366796 Hz
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DE 6.50 usec
TE 301.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
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NUC1 13C
P1 8.50 usec
PL1 1.00 dB
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SFO1 100.6228298 MHz
CHANNEL f2
CPDPRG2 waltz16
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PCPD2 90.00 usec
PL2 -2.00 dB
PL12 18.23 dB
PL13 19.00 dB
PLW2 31.17179108 W
PLW12 0.39562907 W
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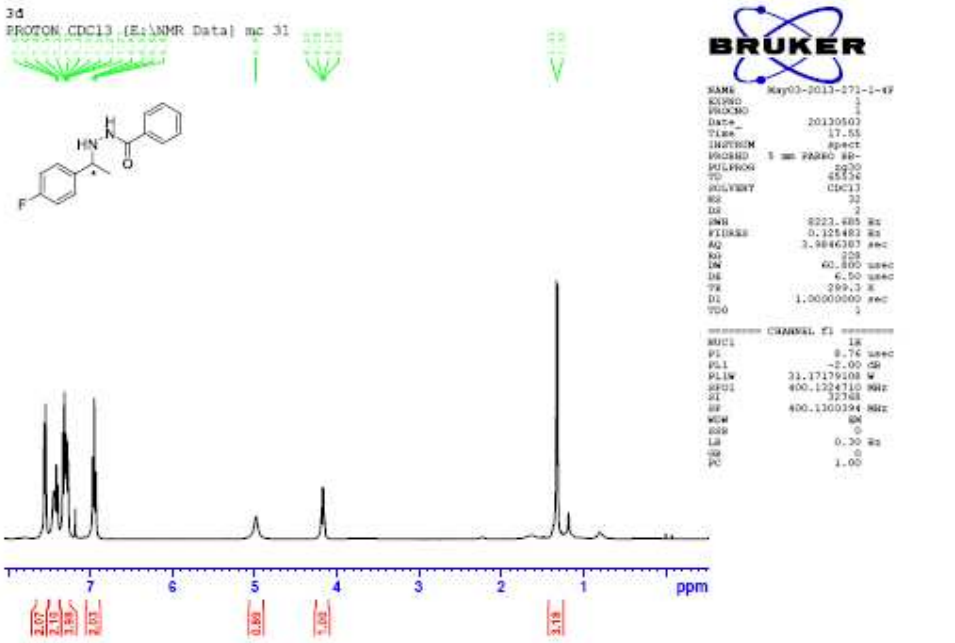
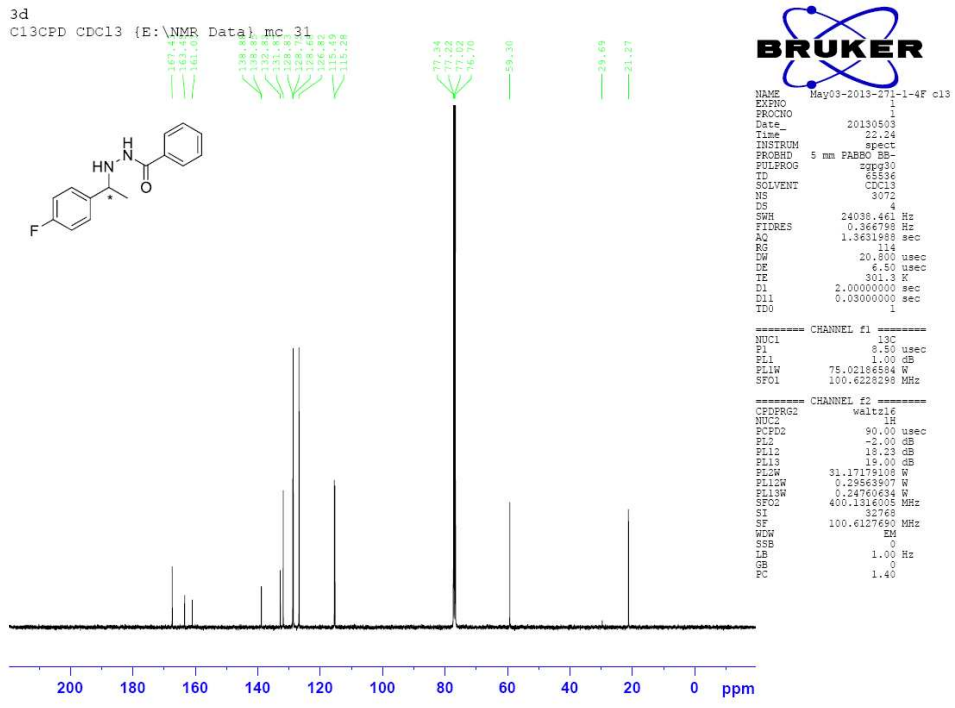




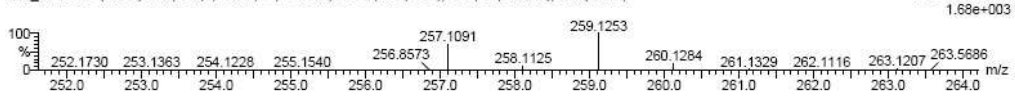
HRMS for (+)-*N*'-(1-(4-fluorophenyl)ethyl)benzohydrazide (3d):

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
66 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-130 H: 0-250 N: 0-4 O: 0-3 F: 1-1

Mingxin ChangCMX-RA-2-4F University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_47463 23 (1.723) AM (Cen,3, 80.00, Ar,15000.0,558.36,0.70,LS 3); Sm (SG, 2x3.00); Cm (22:23) 1: TOF MS ES+
1.68e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	600.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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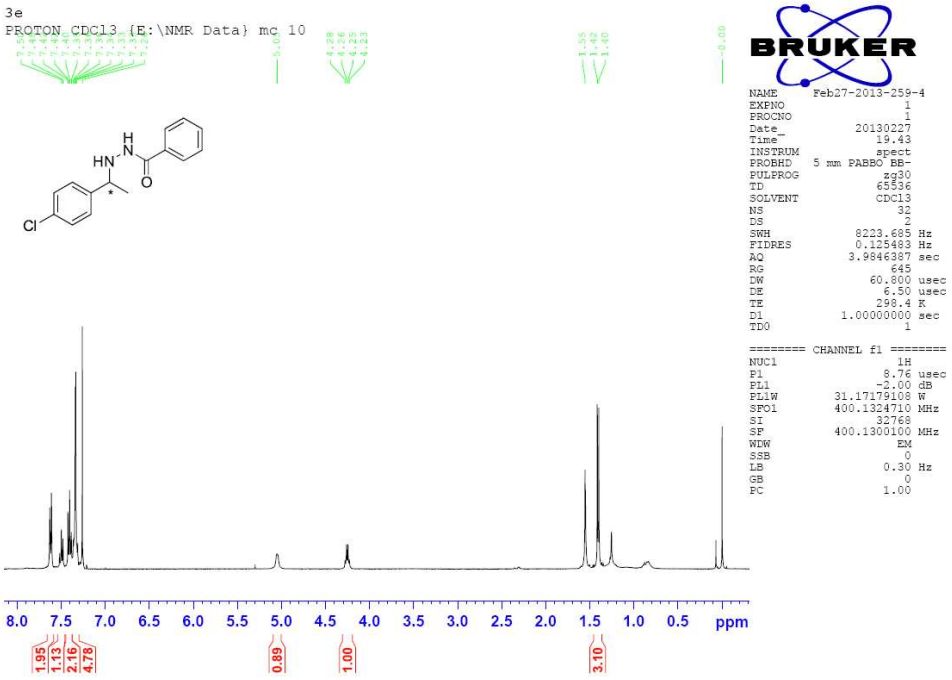
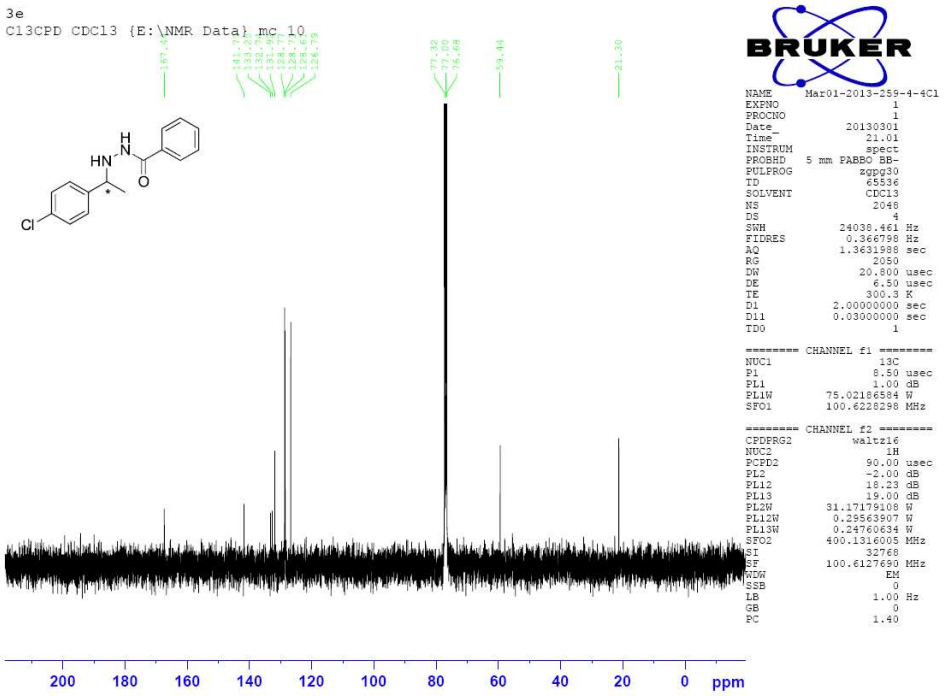




HRMS for (+)-*N*'-(1-(4-chlorophenyl)ethyl)benzohydrazide (3e):

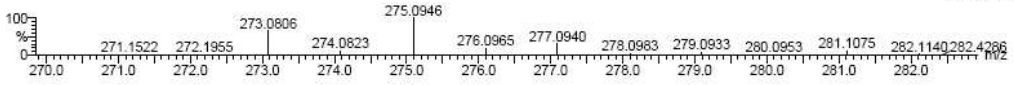
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
141 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-130 H: 0-250 N: 0-4 O: 0-3 Cl: 0-1

Mingxin ChangCMX-RA-3-4Cl University of Illnois, SCS, Mass Spectrometry Lab
Qtof_47464 24 (1.798) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (22:24)

Q-tof UE521
1: TOF MS ES+
6.97e+002



Minimum:				-1.5		
Maximum:		5.0	10.0	600.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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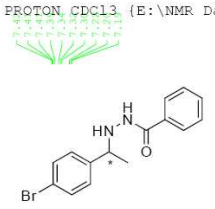
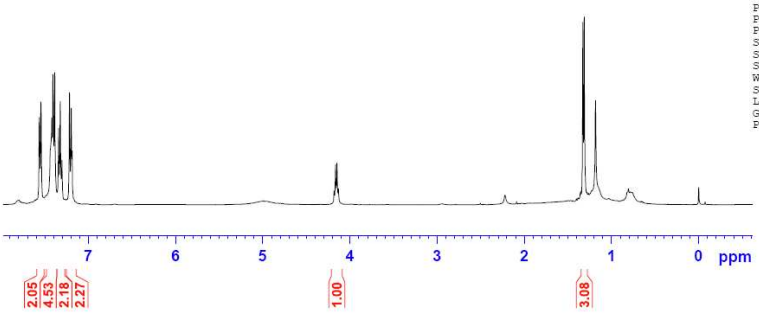
	275.0933	1.3	4.7	13.5	91.3	C16 H11 N4 O

3f
PROTON CDCl3 {E:\NMR Data} mc 50



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PROCNO                     1
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Time_                 17.13
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TD                    65536
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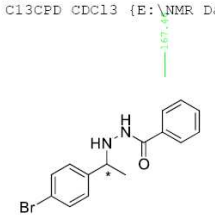
FIDRES             0.125483 Hz
AQ                 3.9846387 sec
RG                      256
DW                   60.800 usec
DE                    6.50 usec
TE                   299.7 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     8.76 usec
PL1                   -2.00 dB
PL1W           31.17179108 W
SFO1          400.1324710 MHz
SI                     32768
SF            400.1300392 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                      1.00
```

3f
C13CPD CDCl3 {E:\NMR Data} mc 11

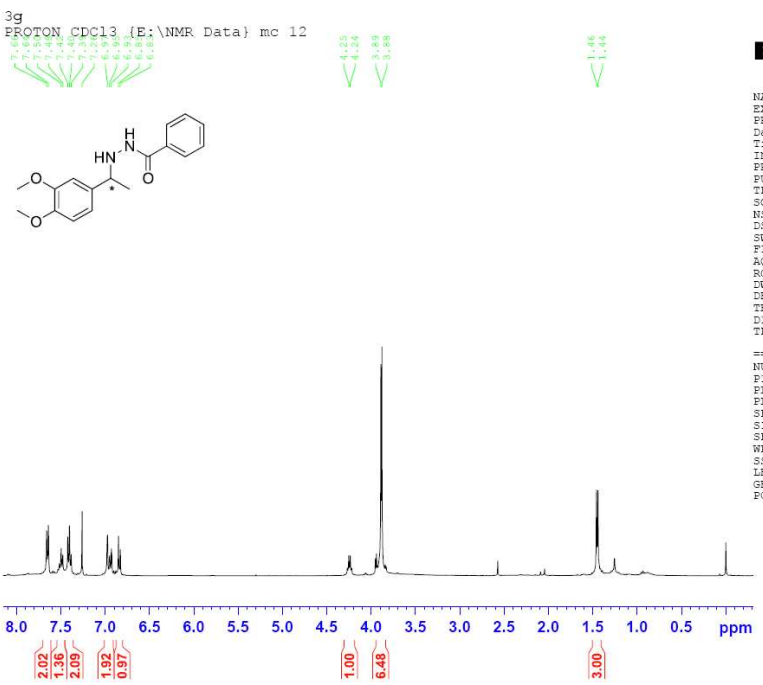



```
NAME          Mar01-2013-259-5
EXPNO                      1
PROCNO                     1
Date_               20130301
Time_                 23.03
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2048
DS                        4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                      2050
DW                   20.800 usec
DE                    6.50 usec
TE                   300.3 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                     8.50 usec
PL1                    1.00 dB
PL1W           75.02186584 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                   -2.00 dB
PL12                  18.23 dB
PL13                  19.00 dB
PL2W           31.17179108 W
PL12W           0.29563907 W
PL13W           0.24760634 W
SFO2          400.1316005 MHz
SI                     32768
SF            100.6127690 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                      1.40
```

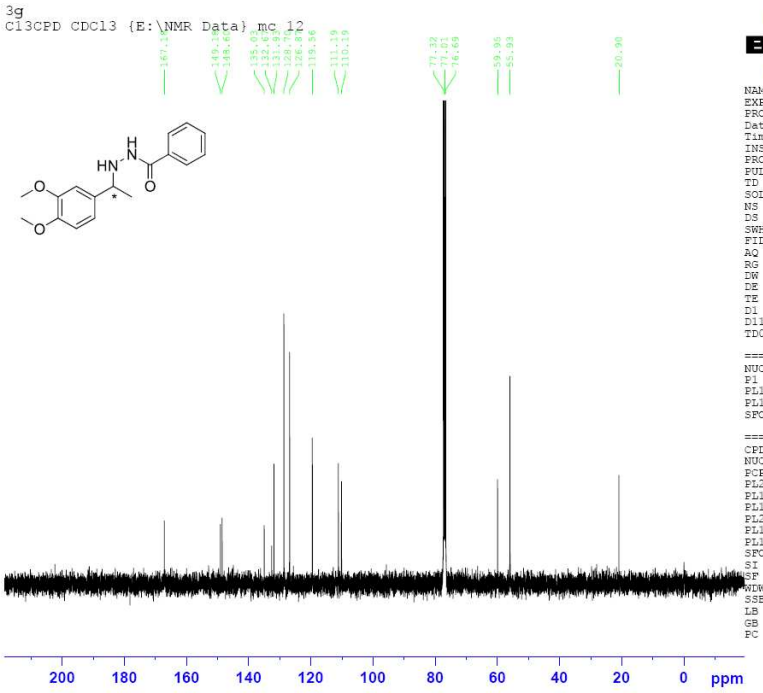
3g
PROTON CDCl3 {E:\NMR Data} mc 12



BRUKER

NAME	Mar01-2013-259-7-H
EXPNO	1
PROCNO	1
Date_	20130301
Time	18.10
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	456
DW	60.800 usec
DE	6.50 usec
TE	298.4 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	8.76 usec
PL1	-2.00 dB
PL1W	31.17179108 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1300091 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

3g
C13CPD CDCl3 {E:\NMR Data} mc 12



BRUKER

NAME	Mar01-2013-259-7
EXPNO	1
PROCNO	1
Date_	20130302
Time	1.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	2048
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	2050
DW	20.800 usec
DE	6.50 usec
TE	300.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	1.00 dB
PL1W	75.02186584 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	18.23 dB
PL13	19.00 dB
PL2W	31.17179108 W
PL12W	0.29563907 W
PL13W	0.24760634 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

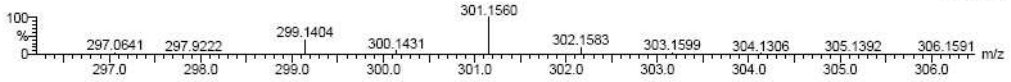
HRMS for (+)-*N*'-(1-(3,4-dimethoxyphenyl)ethyl)benzohydrazide (3g):

Elemental Composition Report **Page 1**

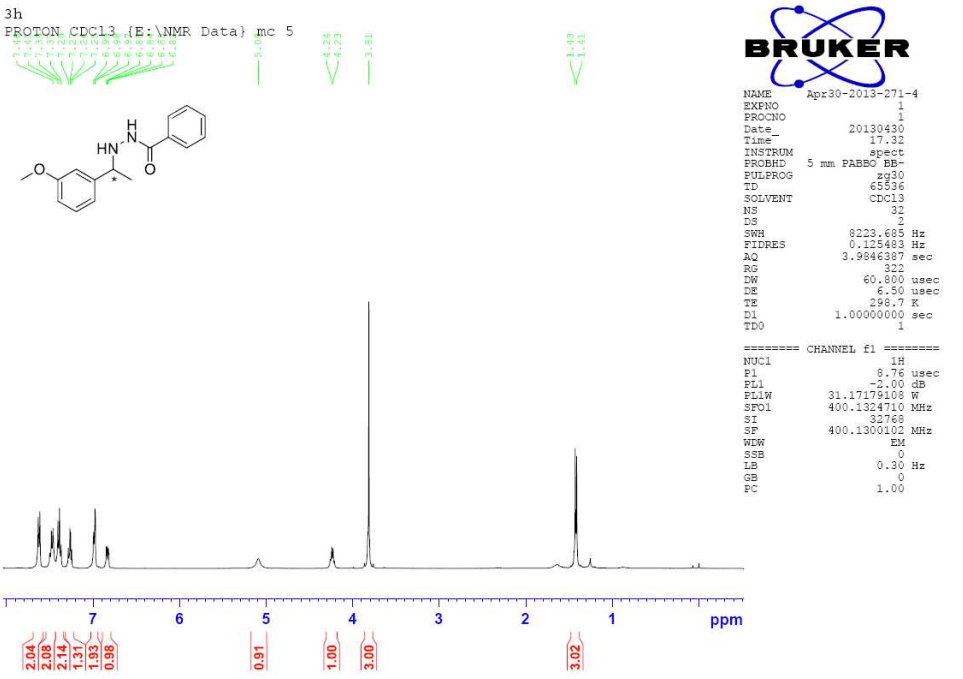
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

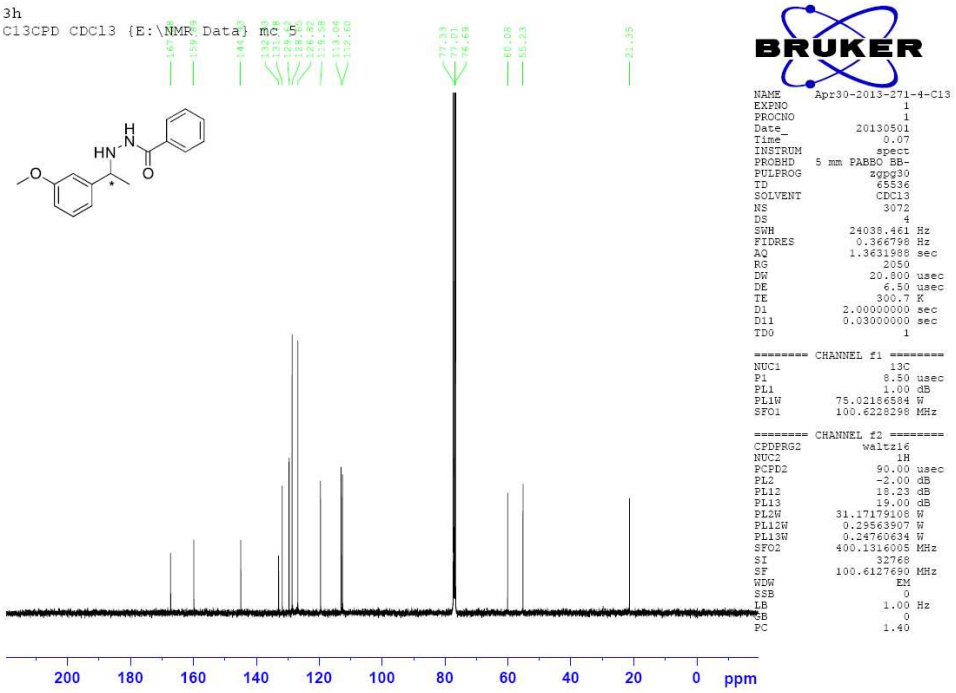
Monoisotopic Mass, Even Electron Ions
154 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-130 H: 0-250 N: 0-4 O: 0-3 Cl: 0-1

Mingxin ChangCMX-RA-4-34OMe University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_47465 22 (1.648) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (20:22) 1: TOF MS ES+
6.20e+002



Minimum:		5.0	10.0	-1.5		
Maximum:				600.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
301.1560	301.1552	0.8	2.7	8.5	1.4	C17 H21 N2 O3
	301.1570	-1.0	-3.3	3.5	216.0	C16 H26 O3 Cl





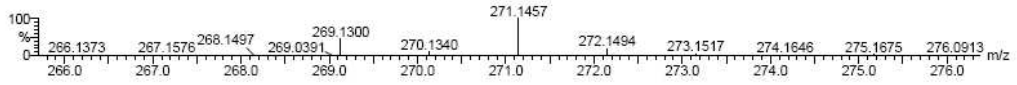
HRMS for (+)-*N*'-(1-(3-methoxyphenyl)ethyl)benzohydrazide (3h):

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

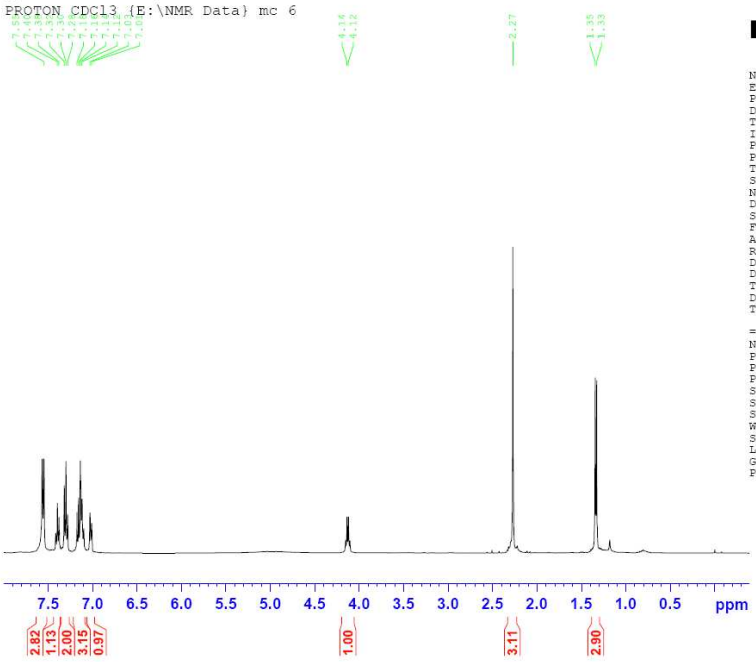
Monoisotopic Mass, Even Electron Ions
75 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-130 H: 0-250 N: 0-4 O: 0-3

Mingxin ChangCMX-RA-5-3OMe University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_47466 37 (2.767) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (37:40) 1: TOF MS ES+
3.52e+003



Minimum:				-1.5		
Maximum:		5.0	10.0	600.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
271.1457	271.1447	1.0	3.7	8.5	4.8	C16 H19 N2 O2

3i
PROTON CDCl3 {E:\NMR Data} mc 6

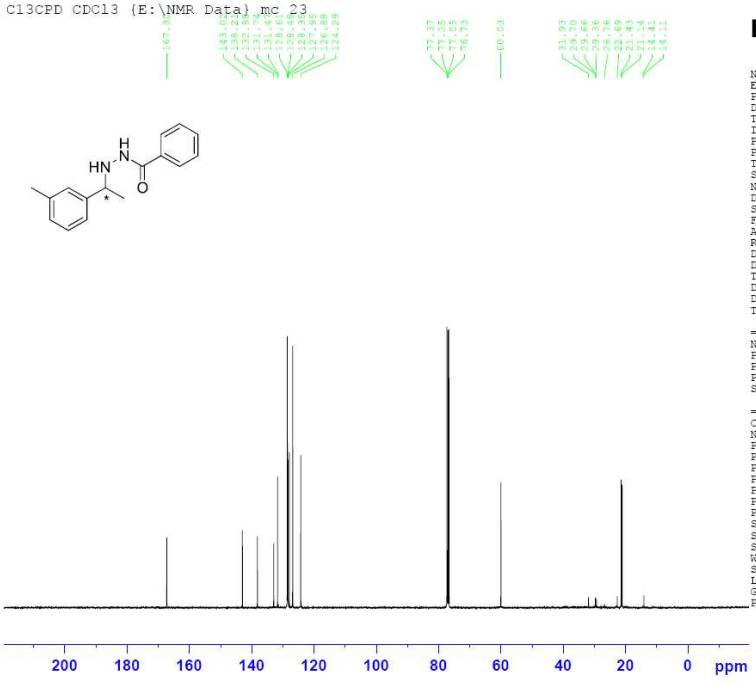


BRUKER

```
NAME          May12-2013-3mE
EXPNO                      1
PROCNO                     1
Date_               20130512
Time_                  15.04
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      144
DW                 60.800 usec
DE                  6.50 usec
TE                  299.6 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     8.76 usec
PL1                   -2.00 dB
PL1W           31.17179108 W
SFO1           400.1324710 MHz
SI                      32768
SF             400.1300432 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

3i
C13CPD CDCl3 {E:\NMR Data} mc 23



BRUKER

```
NAME          May08-2013-282-3 c13
EXPNO                      1
PROCNO                     1
Date_               20130509
Time_                  22.13
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     3072
DS                        4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      2050
DW                 20.800 usec
DE                  6.50 usec
TE                  301.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.50 usec
PL1                    1.00 dB
PL1W          75.02186584 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                90.00 usec
PL2                   -2.00 dB
PL12                  18.23 dB
PL13                  19.00 dB
PL2W          31.17179108 W
PL12W          0.29563907 W
PL13W          0.24760634 W
SFO2          400.1316005 MHz
SI                      32768
SF            100.6127690 MHz
WDW                       EM
SSB                        0
LB                      1.00 Hz
GB                         0
PC                      1.40
```

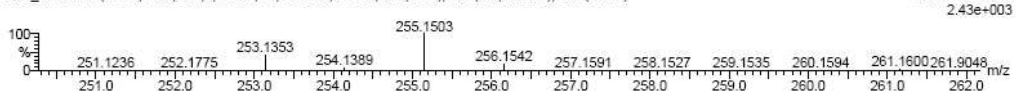
HRMS for (+)-*N*'-(1-(m-tolyl)ethyl)benzohydrazide (3i):

Elemental Composition Report **Page 1**

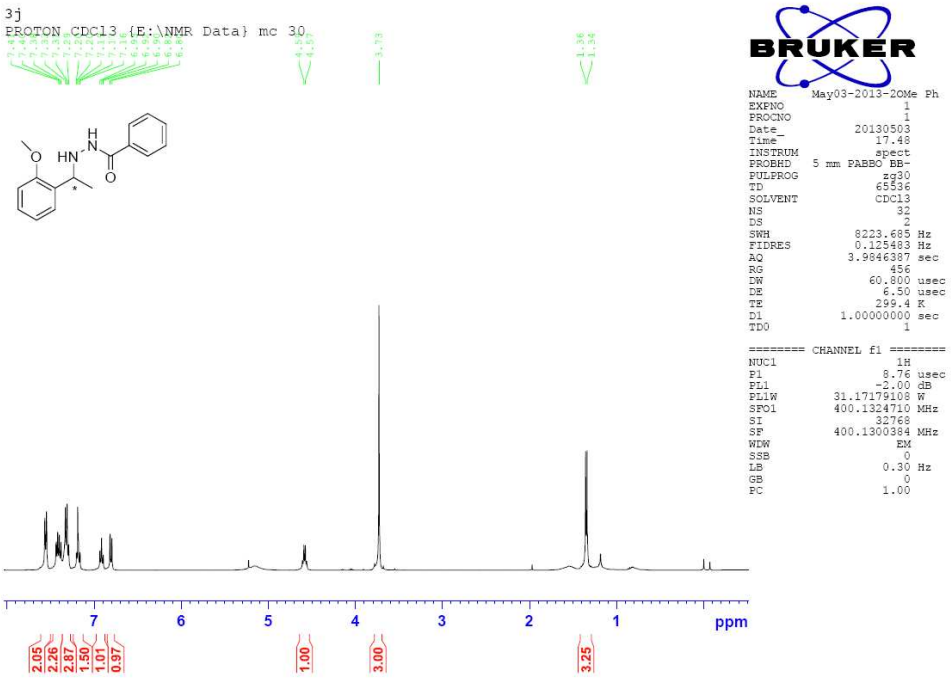
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

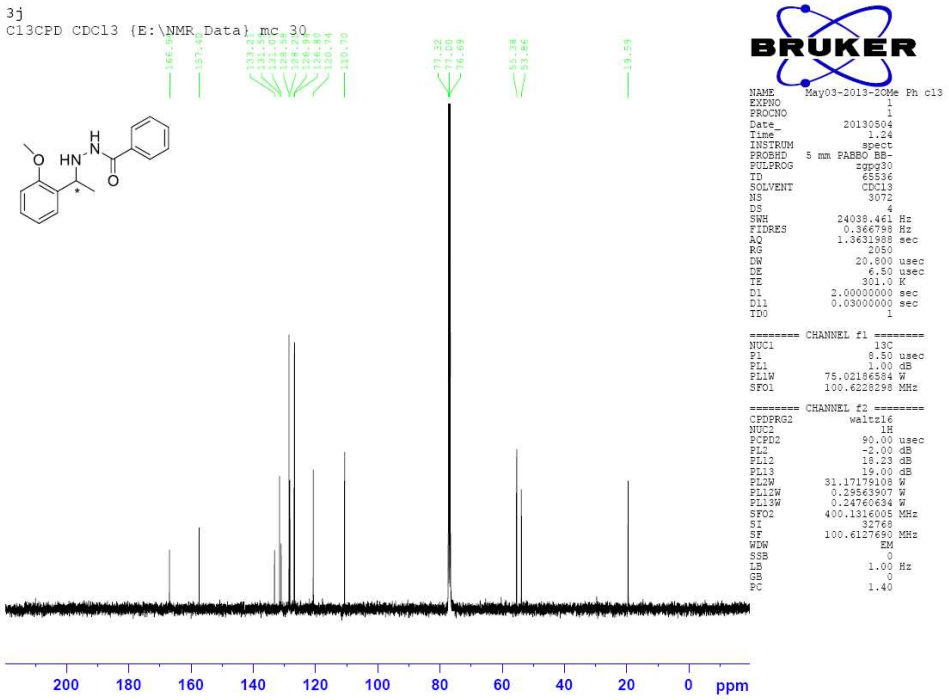
Monoisotopic Mass, Even Electron Ions
73 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-130 H: 0-250 N: 0-4 O: 0-3

Mingxin ChangCMX-RA-6-3Me University of Illnois, SCS, Mass Spectrometry Lab Q-tof UE521
Qtof_47467 22 (1.649) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (21:22) 1: TOF MS ES+
2.43e+003

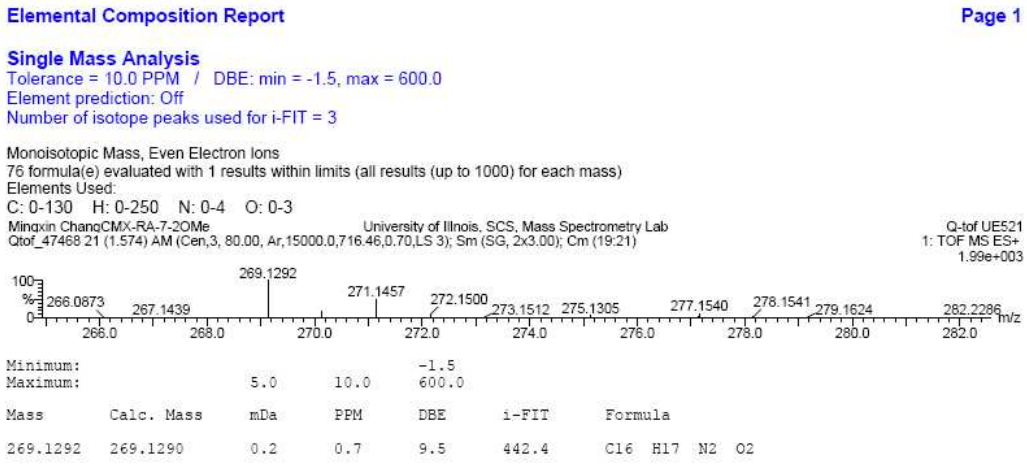


Minimum:				-1.5		
Maximum:		5.0	10.0	600.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
255.1503	255.1497	0.6	2.4	8.5	0.3	C16 H19 N2 O

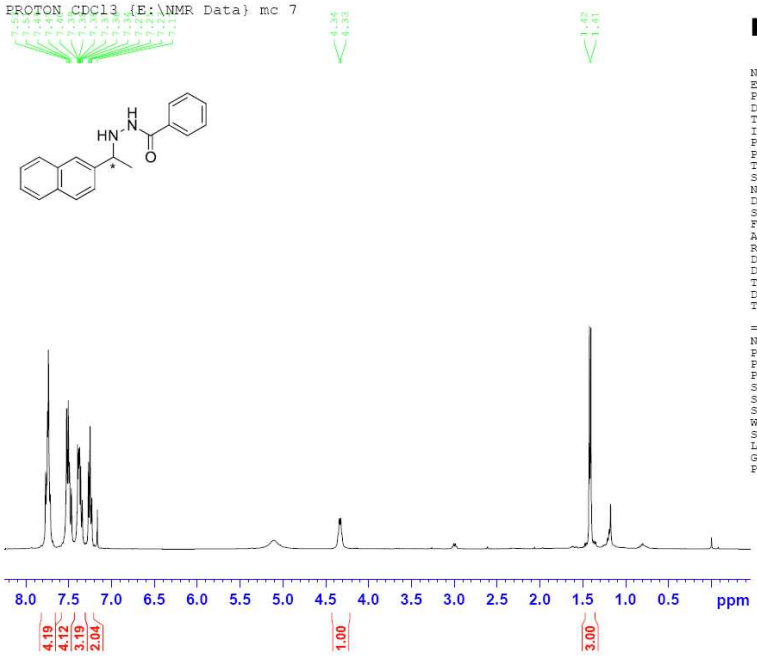




HRMS for (+)- *N*'-(1-(2-methoxyphenyl)ethyl)benzohydrazide (3j):



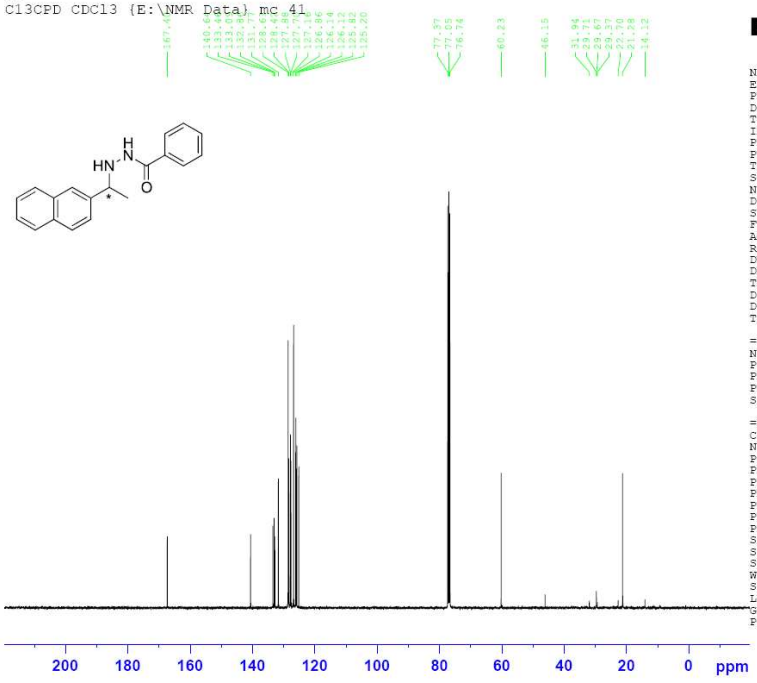
3k
PROTON CDCl3 {E:\NMR Data} mc 7




```
NAME          May12-2013-2NA
EXPNO                      1
PROCNO                     1
Date_               20130512
Time_                 15.11
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                3.9846387 sec
RG                      161
DW                 60.800 usec
DE                  6.50 usec
TE                  299.6 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     8.76 usec
PL1                   -2.00 dB
PL1W           31.17179108 W
SFO1          400.1324710 MHz
SI                     32768
SF            400.1300471 MHz
WDW                       EM
SSB                        0
LB                    0.30 Hz
GB                         0
PC                    1.00
```

3k
C13CPD CDCl3 {E:\NMR Data} mc 41

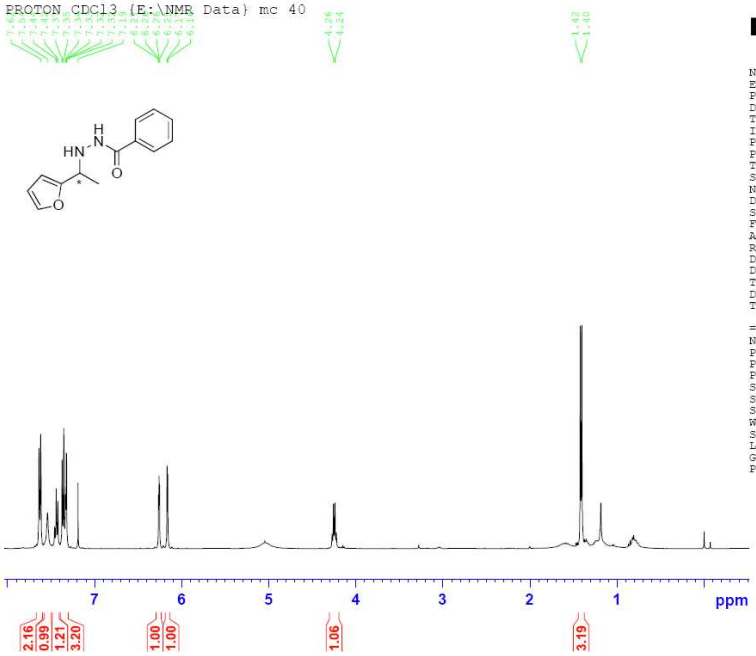



```
NAME          May09-2013-2Na-C13
EXPNO                      1
PROCNO                     1
Date_               20130510
Time_                  4.30
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      3072
DS                         4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      2050
DW                 20.800 usec
DE                  6.50 usec
TE                  301.4 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      13C
P1                     8.50 usec
PL1                    1.00 dB
PL1W           75.02186584 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                   -2.00 dB
PL12                  18.23 dB
PL13                  19.00 dB
PL2W           31.17179108 W
PL12W           0.29563907 W
PL13W           0.24760634 W
SFO2          400.1316005 MHz
SI                     32768
SF            100.6127690 MHz
WDW                       EM
SSB                        0
LB                    1.00 Hz
GB                         0
PC                    1.40
```

31
PROTON CDCl3 {E:\NMR Data} mc 40

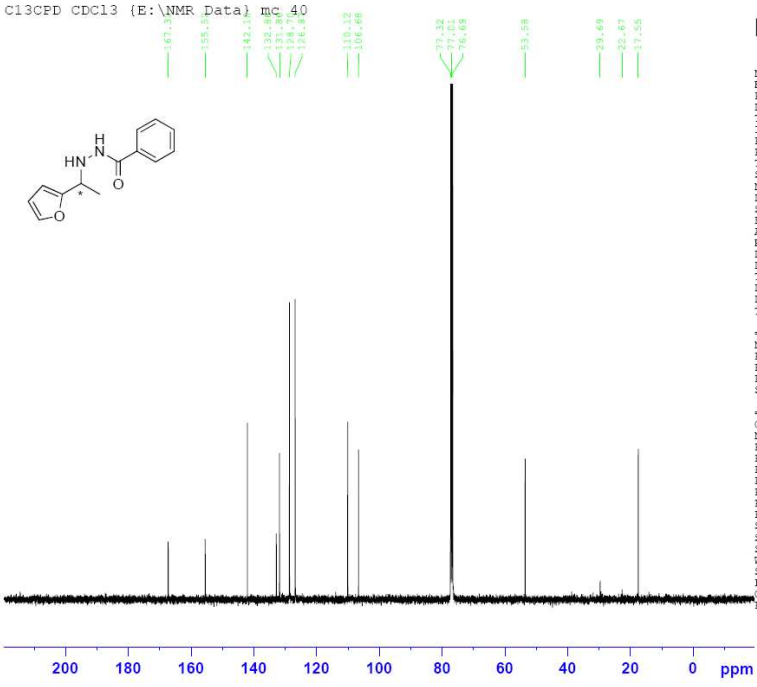


BRUKER

```
NAME          May09-2013-furan-H1
EXPNO                           1
PROCNO                          1
Date_                    20130509
Time_                       22.28
INSTRUM                     spect
PROBHD   5 mm PABBO BB-
PULPROG                     zg30
TD                         65536
SOLVENT                    CDCl3
NS                            32
DS                             2
SWH                     8223.685 Hz
FIDRES                  0.125483 Hz
AQ                      3.9846387 sec
RG                           362
DW                        60.800 usec
DE                         6.50 usec
TE                        300.0 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                          1H
P1                         8.76 usec
PL1                       -2.00 dB
PL1W                31.17179108 W
SFO1               400.1324710 MHz
SI                         32768
SF                 400.1300381 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

31
C13CPD CDCl3 {E:\NMR Data} mc 40



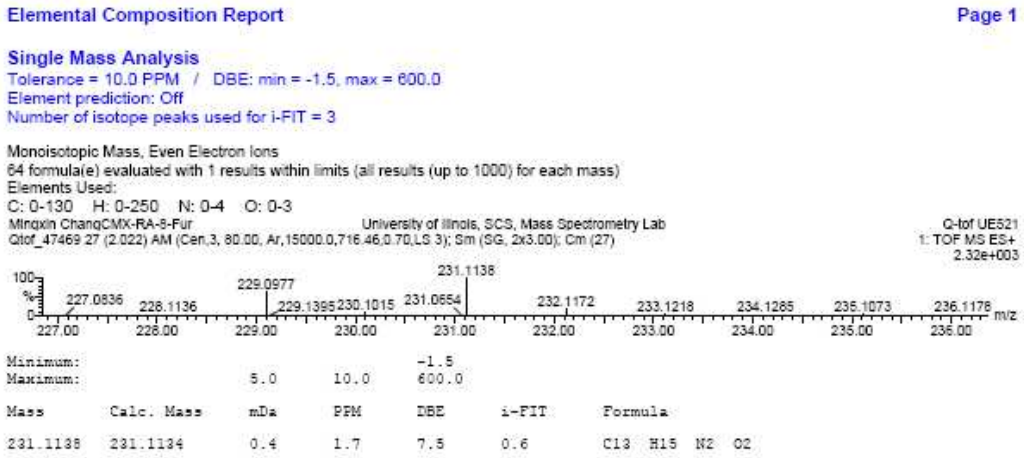
BRUKER

```
NAME          May09-2013-furan-c13
EXPNO                           1
PROCNO                          1
Date_                    20130510
Time_                       1.25
INSTRUM                     spect
PROBHD   5 mm PABBO BB-
PULPROG                  zgpg30
TD                         65536
SOLVENT                    CDCl3
NS                          3072
DS                             4
SWH                    24038.461 Hz
FIDRES                  0.366798 Hz
AQ                      1.3631988 sec
RG                          2050
DW                        20.800 usec
DE                         6.50 usec
TE                        301.6 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                         8.50 usec
PL1                        1.00 dB
PL1W                75.02186584 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                  waltz16
NUC2                          1H
PCPD2                     90.00 usec
PL2                       -2.00 dB
PL12                      18.23 dB
PL13                      19.00 dB
PL2W                31.17179108 W
PL12W                0.29563907 W
PL13W                0.24760634 W
SFO2               400.1316005 MHz
SI                         32768
SF                 100.6127690 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

HRMS for (+)-*N*'-(1-(furan-2-yl)ethyl)benzohydrazide (3l):



Elemental Composition Report — Page 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 600.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
64 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-130 H: 0-250 N: 0-4 O: 0-3

Mingxin ChangCMX-RA-8-Fur — University of Illinois, SCS, Mass Spectrometry Lab — Q-tof UE521
Qtof_47469 27 (2.022) AM (Cen,3, 80.00, Ar,15000.0,716.46,0.70,LS 3); Sm (SG, 2x3.00); Cm (27) — 1: TOF MS ES+ 2.32e+003

Minimum:		5.0	10.0	-1.5		
Maximum:				600.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
231.1138	231.1134	0.4	1.7	7.5	0.6	C13 H15 N2 O2

III. References

[1] M. J. Burk, J. E. Feaster, *J. Am. Chem. Soc.* **1992**, *114*, 6267.