Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

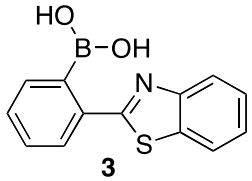
Click with a Boronic Acid Handle: A Neighboring Group-assisted Click Reaction that Allows Ready Secondary Functionalization

Alexander Draganov, Ke Wang, Jalisa Holmes, Krishna Damera, Danzhu Wang, Chaofeng Dai, Binghe Wang
Department of Chemistry and Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, GA 30302-3965 USA

Materials and Methods

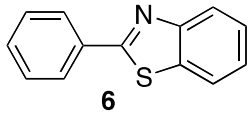
All reagents and solvents were of reagent grade. All formylphenylboronic acids were provided by Frontier Scientific Inc.; 2-aminobezothiol and 2-amino-4-(trifluoromethyl)thiophenol were purchased from Alpha Aeser; and 2-amino-4-chlorothiophenol was purchased from Sigma-Aldrich. Column chromatography was carried out on flash silica gel (Sorbent 230–400 mesh). TLC analysis was conducted on silica gel plates (Sorbent Silica G UV254). NMR spectra were recorded at 400 MHz for ^{1}H and100 MHz for ^{13}C on a Bruker instrument. Chemical shifts (δ values) and coupling constants (*J* values) are given in ppm and hertz, respectively, using the appropriate deuterated solvents as references.

General procedure for the preparation of compounds **3**-**22**.



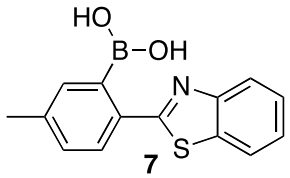
3

*Compound **3**, (2-(benzo[d]thiazol-2-yl)phenyl)boronic acid:*
2-Formylphenylboronic acid (120 mg, 0.8 mmol) was dissolved in 4 ml methanol. 2-Aminobenzothiol (100 mg, 85.5 µL, 0.8 mmol) was added and the reaction was stirred at room temperature open to air. Full consumption of the starting materials was achieved within 5 min (confirmed by TLC, DCM: EtOAc = 9:1) of stirring. The organic solvent was then evaporated and the yellow oily residue was purified via gradient silica gel flash column chromatography (eluent DCM: EtOAc = 100:1 and DCM: MeOH= 200:1; 100:1; 50:1). 170 mg off-white solid was collected as pure product **3** (85% isolated yield). ^{1}H NMR (CD_3OD): δ 8.00 (t, *J* = 6.8 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.55–7.42 (m, 6H); ^{13}C NMR (CD_3OD): δ 170.6, 149.9, 135.0, 134.6, 131.1, 130.8, 128.6, 126.9, 126.3, 125.8, 125.6, 122.3, 121.2. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{13}H_{10}BNO_2S$ 256.0598, found 256.0600.



6

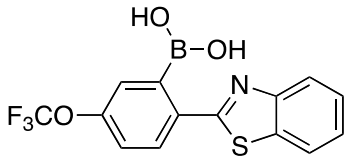
*Compound **6**, 2-phenylbenzo[d]thiazole:*
Spectroscopic data matches that of literature report.[1]



7

Compound 7, (2-(benzo[d]thiazol-2-yl)-5-methylphenyl)boronic acid:

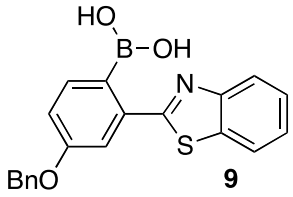
Isolated yield 95%. ^{1}H NMR (CD_3OD): δ 7.98 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.29 (s, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 2.38 (s, 1H); ^{13}C NMR (CD_3OD): δ 170.7, 149.8, 141.8, 134.5, 132.5, 131.5, 129.2, 126.8, 125.8, 125.4, 122.3, 121.0, 20.4. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{14}H_{12}BNO_2S$ 270.0755, found 270.0757.



8

*Compound **8**, (2-(benzo[d]thiazol-2-yl)-5-(trifluoromethoxy)phenyl)boronic acid:*

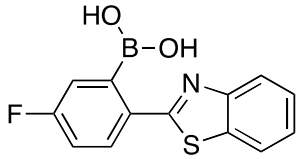
Isolated yield 97%. ^{1}H NMR (CD_3OD): δ 8.01 (d, *J* = 8 Hz, 1H), 7.96 (d, *J* = 8 Hz, 1H), 7.86 (d, *J* = 8 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.29 (m, 2H); ^{13}C NMR (CD_3OD): δ 170.5, 152.7, 136.1, 134.9, 130.2, 128.7, 128.5, 127.2, 124.1, 123.8, 123.1, 122.5, 122.0, 120.5. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{14}H_9BF_3NO_3S$ 340.0421, found 340.0423.



9

*Compound **9**, (2-(benzo[d]thiazol-2-yl)-4-(benzyloxy)phenyl)boronic acid:*

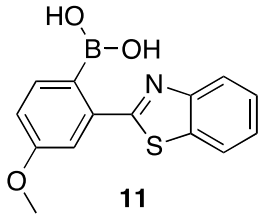
Isolated yield 60%. ^{1}H NMR (DMSO-*d*6): 8.13 (d, *J* = 8.0 Hz, 1H), 8.07 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.57- 7.52 (m, 2H), 7.50-7.46 (m, 3H), 7.45-7.39 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 5.23 (s, 2H). ^{13}C NMR (DMSO-*d*6): 169.7, 158.9, 153.3, 137.5, 137.3, 135.4, 135.3, 129.0, 128.4, 128.1, 127.0, 125.9, 123.1, 122.7, 116.8, 115.4, 69.7, 48.4, 48.2, 48.0, HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{20}H_{16}BNO_3S$ 362.1017, found 362.1009.



10

*Compound **10**, (2-(benzo[d]thiazol-2-yl)-5-fluorophenyl)boronic acid:*

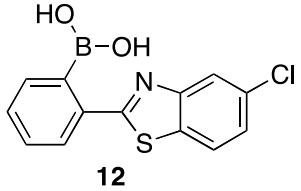
Isolated yield 78%. ^{1}H NMR (CD_3OD): δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.91-7.87 (m, 1H), 7.59 (t, *J* = 7.2 Hz, 1H) 7.48 (t, *J* = 7.6 Hz, 1H), 7.24-7.16 (m, 2H); ^{13}C NMR (CD_3OD): δ 170.2, 163.9, 148.4, 134.5, 131.1, 127.7, 127.3, 125.8, 122.6, 120.7, 117.6, 117.4, 115.5, 115.2. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{13}H_9BFNO_2S$ 274.0504, found 274.0507.



11

*Compound **11**, (2-(benzo[d]thiazol-2-yl)-4-methoxyphenyl)boronic acid:*

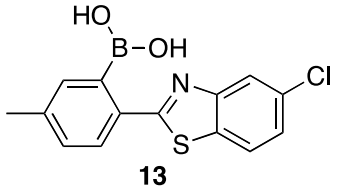
Isolated yield 95%. ^{1}H NMR (CD_3OD): δ 8.00 (t, J = 3.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.46–7.38 (m, 3H), 7.11 (d, J = 7.6 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (CD_3OD): δ 169.9, 160.3, 150.7, 136.5, 134.7, 132.1, 126.7, 126.3, 125.5, 122.1, 121.6, 116.4, 111.8, 54.5. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{14}H_{12}BNO_3S$ 286.0704, found 286.0706.



12

*Compound **12**, (2-(5-chlorobenzo[d]thiazol-2-yl)phenyl)boronic acid:*

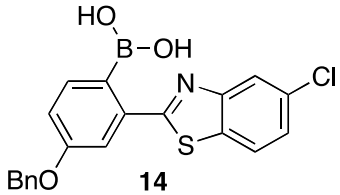
Isolated yield 84%. ^{1}H NMR (CD_3OD): δ 7.96-7.94 (m, 2H), 7.84 (d, J = 7.2 Hz, 2H), 7.54-7.39 (m, 4H); ^{13}C NMR (CD_3OD): δ 171.9, 152.3, 134.8, 133.2, 132.6, 131.1, 131.0, 128.7, 126.7, 125.7, 123.2, 121.3. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{13}H_9BClNO_2S$ 290.0251, found 290.0215.



13

*Compound **13**, (2-(5-chlorobenzo[d]thiazol-2-yl)-5-methylphenyl)boronic acid:*

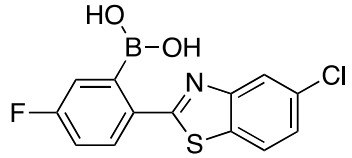
Isolated yield 75%. ^{1}H NMR (CD_3OD): δ 8.00-7.95 (m, 2H), 7.78 (d, J = 8 Hz, 1H), 7.44 (d, J = 8 Hz, 1H), 7.33-7.30 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (CD_3OD): δ 172.0, 152.3, 142.0, 133.1, 132.6, 132.3, 131.7, 129.4, 127.1, 126.6, 125.5, 123.2, 121.1, 20.3. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for 304.0387, found 304.0370.



14

*Compound **14**, (4-(Benzyloxy)-2-(5-chlorobenzo[d]thiazol-2-yl)phenyl)boronic acid:*

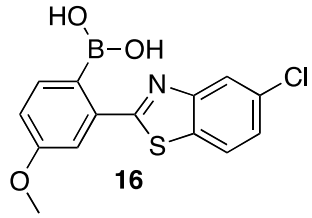
Isolated yield 77%. ^{1}H NMR (CD_3OD): δ 8.00 (d, J = 32.0 Hz, 2H), 7.50-7.31 (m, 8H), 7.22 (d, 1H), 5.19 (s, 2H); ^{13}C NMR (CD_3OD): δ 171.5, 159.4, 152.7, 136.9, 136.3, 133.3, 132.5, 132.4, 128.2, 127.6, 127.2, 125.6, 123.1, 121.4, 117.5, 113.4, 69.8; HRMS (ESI-TOF) *m/z*: $[M + 1]^+$ calcd for $C_{20}H_{15}BClNO_3S$ 396.0622, found: 396.0632.



15

*Compound **15**, (2-(5-Chlorobenzo[d]thiazol-2-yl)-4-fluorophenyl)boronic acid:*

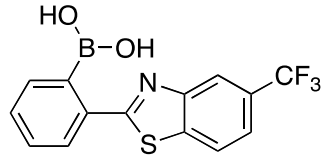
Isolated yield 52%. ^{1}H NMR (CD_3OD): δ 8.04 (d, *J* = 22.0 Hz, 2H), 7.97 (dd, *J* = 13.0, 22.0 Hz, 1H), 7.49 (dd, *J* = 5.0, 22.0 Hz, 1H), 7.26-7.22 (m, 2H); ^{13}C NMR (CD_3OD): δ 171.1, 151.2, 133.2, 132.9, 131.0, 128.6, 125.8, 123.3, 120.9, 117.9, 117.7, 115.7, 115.4; HRMS (ESI-TOF) *m/z*: $[M + 1]^+$ calcd for $C_{13}H_8BClFNO_2S$ 308.0115, found: 308.0118.



16

*Compound **16**, (2-(5-chlorobenzo[d]thiazol-2-yl)-4-methoxyphenyl)boronic acid:*

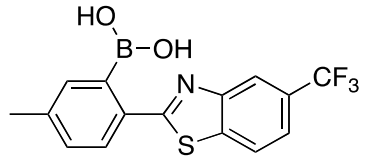
Isolated yield 74%. ^{1}H NMR (CD_3OD) δ 8.01 (s, *J* = 8.8 Hz, 1 H), 7.97 (s, 1 H), 7.46 (dd, *J* = 8.8, 2.0 Hz, 1 H), 7.41 (s, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.15 (dd, *J* = 8.4, 2.4 Hz, 1 H), 3.90 (s, 3 H); ^{13}C NMR (CD_3OD) δ 173.0, 161.8, 154.1, 137.7, 134.7, 133.9, 133.8, 127.0, 125.7, 124.5, 122.8, 117.9, 113.7, 55.9; HRMS (ESI-TOF) *m/z*: $[M + 1]^+$ calcd for $C_{20}H_{15}BClNO_3S$ 320.0241, found: 320.0303.



17

*Compound **17**, (2-(5-(trifluoromethyl)benzo[d]thiazol-2-yl)phenyl)boronic acid:*

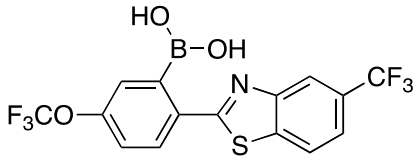
Isolated yield 56%. ^{1}H NMR (CD_3OD): δ 8.24 (d, 1 H), 8.22 (s, 1 H), 7.93 (d, 1 H), 7.71 (d, 1 H), 7.60-7.48 (m, 3 H); ^{13}C NMR (CD_3OD): δ 173.4, 153.2, 140.0, 136.0, 132.6, 132.5, 130.5, 130.2, 128.5, 124.6, 122.8, 122.8, 120.1, 120.0; HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{14}H_9BF_3NO_2S$ 324.0399, found 324.0474.



18

*Compound **18**, (5-methyl-2-(5-(trifluoromethyl)benzo[d]thiazol-2-yl)phenyl)boronic acid:*

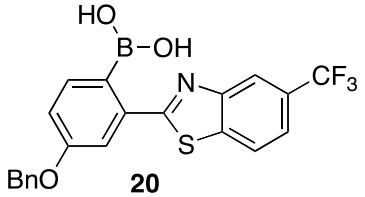
Isolated yield 56%. ^{1}H NMR (CD_3OD): δ 8.21 (s, 1H), 8.19 (s, 1H), 7.80 (d, *J* = 8 Hz), 7.69 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8 Hz, 1H), 7.309 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (CD_3OD): δ 172.0, 142.5, 138.7, 132.0, 131.9, 129.7, 128.5, 127.3, 123.1, 122.7, 121.3, 118.8, 20.2. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{15}H_{11}BF_3NO_2S$ 338.1245, found 338.0632.



19

*Compound **19**, (5-(trifluoromethoxy)-2-(5-(trifluoromethyl)benzo[d]thiazol-2-yl)phenyl)boronic acid:*

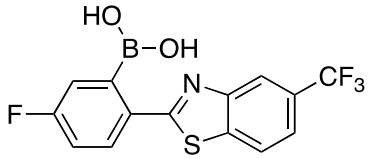
Isolated yield 58%. ^{1}H NMR (CD_3OD): δ 8.27 (d, 1 H), 8.24 (s, 1 H), 8.06 (d, 1 H), 7.75, (d, 1 H), 7.44 (d, 1 H), 7.38 (s, 1 H); ^{13}C NMR (CD_3OD): δ 171.9, 152.8, 140.2, 134.76, 132.3, 130.8, 130.5, 130.3, 126.9, 124.8, 124.6, 124.2, 123.1, 122.3, 120.5, 120.1, 120.0; HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{15}H_8BF_6NO_3S$ 408.0301, found 408.0302.



20

*Compound **20**, (4-(benzyloxy)-2-(5-(trifluoromethyl)benzo[d]thiazol-2-yl)phenyl)boronic acid:*

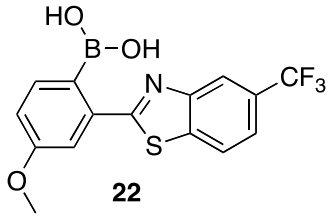
Isolated yield 74%. ^{1}H NMR (CD_3OD): δ 8.20 (s, 1 H), 8.19 (d, 1 H), 7.69 (d, 1 H), 7.47 (d, 3 H), 7.386 (t, 3 H), 7.32 (d, 1 H), 7.20 (d, 1 H), 5.184 (s, 2 H); ^{13}C NMR (CD_3OD): δ 173.0, 160.8, 153.4, 140.0, 138.2, 137.5, 133.9, 130.5, 130.1, 129.6, 129.5, 129.0, 128.6, 128.6, 124.5, 124.2, 122.8, 122.7, 120.2, 120.2, 118.9, 115.2, 71.2; HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{21}H_{15}BF_3NO_3S$ 430.0818, found 430.0895.



21

*Compound **21**, (5-fluoro-2-(5-(trifluoromethyl)benzo[d]thiazol-2-yl)phenyl)boronic acid:*

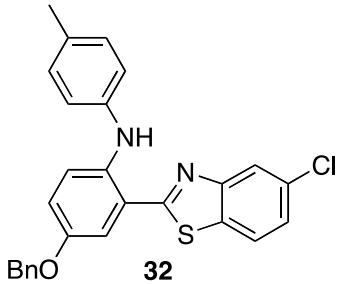
Isolated yield 68%. ^{1}H NMR (CD_3OD): δ 8.24 (d, 1 H), 8.22 (s, 1 H), 7.98-7.95 (m, 1 H), 7.71 (d, 1 H), 7.26-7.22 (m, 2 H); ^{13}C NMR (CD_3OD): δ 171.1, 138.6, 130.9, 129.3, 123.3, 121.5, 118.4, 118.0, 117.8, 115.7, 115.5; HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{14}H_8BF_4NO_2S$ 342.0305, found 342.0378.



22

*Compound **22**, (4-methoxy-2-(5-(trifluoromethyl)benzo[d]thiazol-2-yl)phenyl)boronic acid:*

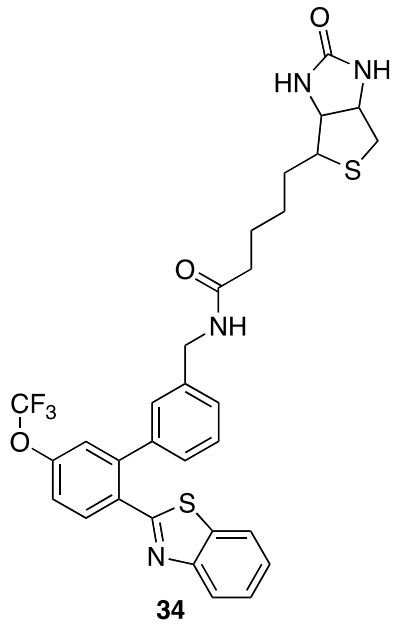
Isolated yield 94%. ^{1}H NMR (CD_3OD): δ 8.24 (d, 1 H), 8.22 (s, 1 H), 7.72 (d, 1 H), 7.45 s, 1 H), 7.41 (d, 1 H), 7.165 (d, 1 H), 4.85 (s, 3 H); ^{13}C NMR (CD_3OD): δ 172.1, 159.6, 152.6, 139.3, 136.6, 134.9, 127.6, 127.3, 123.9, 123.0, 119.4, 119.3, 116.0, 114.1, 55.4; HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{15}H_{11}BF_3NO_3S$ 354.0584, found 354.0586.



32

Compound **32,** 4-(benzyloxy)-2-(5-chlorobenzo[d]thiazol-2-yl)-N-(p-tolyl)aniline:

A 10 mL vial containing arylboronic acid **14** (20 mg, 0.0506 mmol), *p*-toluidine (6.5 mg, 0.0607 mmol), $NiCl_2.6H_2O$ (1.3 mg, 0.0101 mmol), 2,2'-bipyridyl (1.5 mg, 0.0101 mmol), DBU (15.3 mg, 0.101 mmol) and acetonitrile (2 mL) was stirred at room temperature under atmospheric conditions. The progress of the reaction was monitored by TLC using EtOAc and n-hexane as eluent. After completion, the reaction mixture was treated with EtOAc (5 mL) and water (5 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic phase was washed with water (2 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated to yield a residue, which was purified by silica gel column chromatography using hexane/ethyl acetate to yield a pale yellow oil (13 mg, 56%). 1H NMR (CDCl3): δ 10.1 (s, 1H), 7.99 (d, 1H, *J* = 5.0 Hz), 7.81 (d, 1H, *J* = 21 Hz), 7.50 (d, 2H, *J* = 18 Hz), 7.43 (t, 2H, *J* = 18 Hz), 7.38-7.35 (m, 3H), 7.32 (d, 1H, *J* = 21 Hz), 7.25-7.19 (m, 4H), 7.03 (dd, 1H, *J* = 7.0, 23.0 Hz), 5.11 (s, 2H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 170.2, 154.3, 150.7, 139.2, 137.0, 132.4, 132.2, 131.7, 129.9, 128.6, 128.1, 127.6, 125.5, 122.3, 121.9, 121.7, 121.6, 120.4, 116.8, 115.8, 71.0, 20.8; HRMS (ESI-TOF) *m/z*: $[M + 1]^+$ calcd for $C_{27}H_{21}ClN_2OS$ 457.1163, found: 457.1141.



34

*Compound **34**, N-((2'-(benzo[d]thiazol-2-yl)-5'-(trifluoromethoxy)-[1,1'-biphenyl]-3-yl)methyl)-5-(2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)pentanamide:*

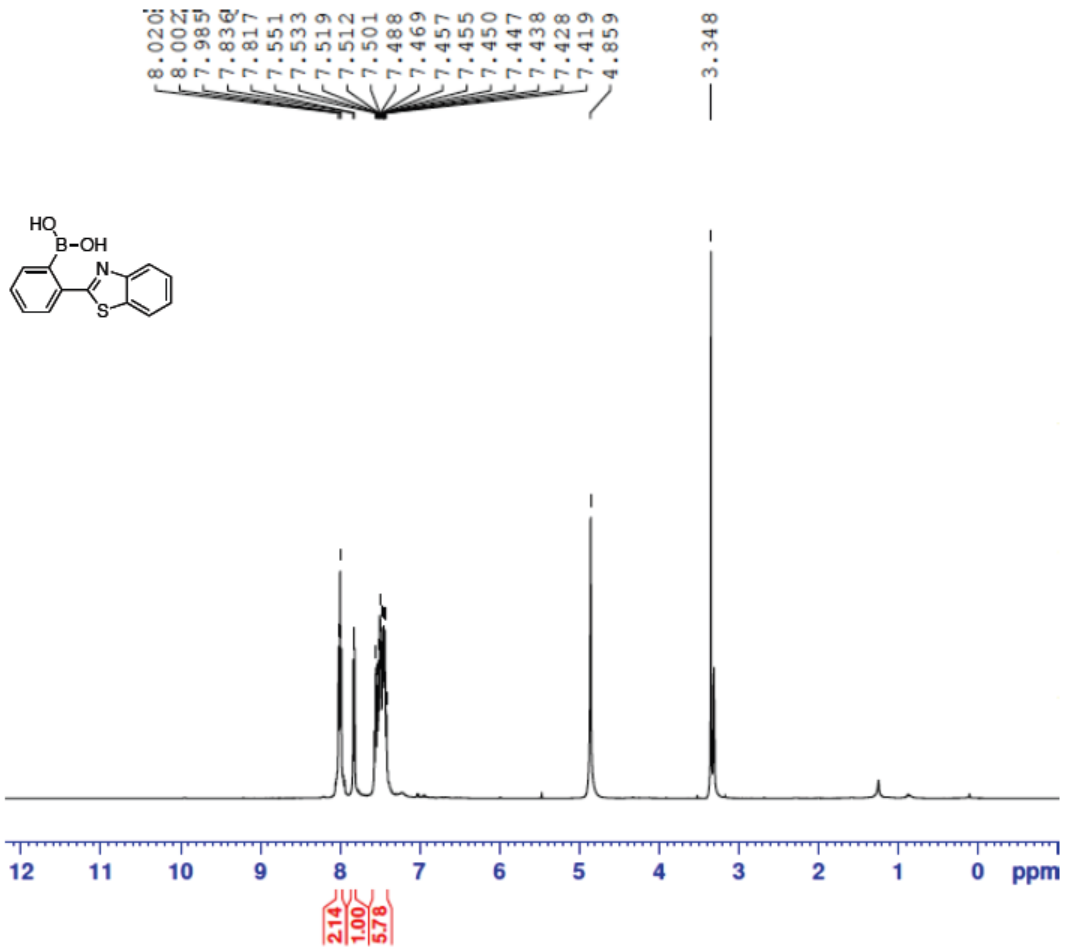
A flame-dried, two-neck round bottom flask was charged with compound **8** (50 mg, 0.147 mmol), aryl halide **33** (45 mg, 0.11 mmol), flame-dried CsF (49 mg, 0.323 mmol), and $Pd(PPh_3)_4$ (8.5 mg, 7.3×10^{-3} mmol) under argon atmosphere. Distilled DME (8 ml) was added and after immediate evacuation of the gas atmosphere in the flask via a vacuum pump, the reaction mixture was stirred overnight at reflux temperature under argon. After stirring overnight, TLC (DCM:MeOH = 20:1) showed full consumption of the starting materials. The reaction mixture was cooled to room temperature and diluted with water (15 mL). The residue was extracted with ethyl acetate (2 × 50 mL) and the organic layers were combined and washed with water (1 × 20 mL), 1N NaOH solution (1 × 5 mL), water (1 × 30 mL), and brine (1 × 20 mL). The organic layer was then dried over Na_2SO_4 and evaporated *in vaccuo*. The brown/yellow residue was purified via silica gel flash column chromatography (eluent DCM: MeOH= 200:1; 100:1; 50:1; 30:1) to give 55 mg of an off-white solid (85% yield). ^{1}H NMR (CD_3OD): δ 8.13 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 8 Hz, 1H), 7.82(d, J = 8 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.27 (s, 1H), 7.21 – 7.18 (m, 1H), 4.44 (dd, J_1 = 4.4 Hz, J_2 = 4.8 Hz, 1H), 4.33 (d, J = 2.4 Hz, 2H), 4.22 (dd, J_1 = 4.4 Hz, J_2 = 4.4 Hz, 1H), 3.12 – 3.07 (m, Hz, 1H), 2.87 (dd, J_1 = 5.2 Hz, J_2 = 4.8 Hz, 1H), 2.67 (d, J = 12.4 Hz, 1H), 2.08 (t, J = 7.6 Hz, 2H),1.69 – 1.53 (m, 5H), 1.39 – 1.31 (m, 2H); ^{13}C NMR (CD_3OD): δ 174.4, 166.6, 164.6, 152.2, 150.1, 143.9, 139.5, 138.9, 136.2, 132.1, 131.1, 128.6, 128.5, 128.1, 127.5, 126.2, 125.3, 122.6, 122.5, 121.8, 121.3, 119.7, 61.9, 60.2, 55.5, 42.3, 39.6, 35.2, 28.3, 28.0, 25.3. HRMS (ESI-TOF) m/z $[M+1]^+$ calcd. for $C_{31}H_{29}F_3N_4O_3S_2$ $[M+H]^+$ 627.1704, found 627.1710.

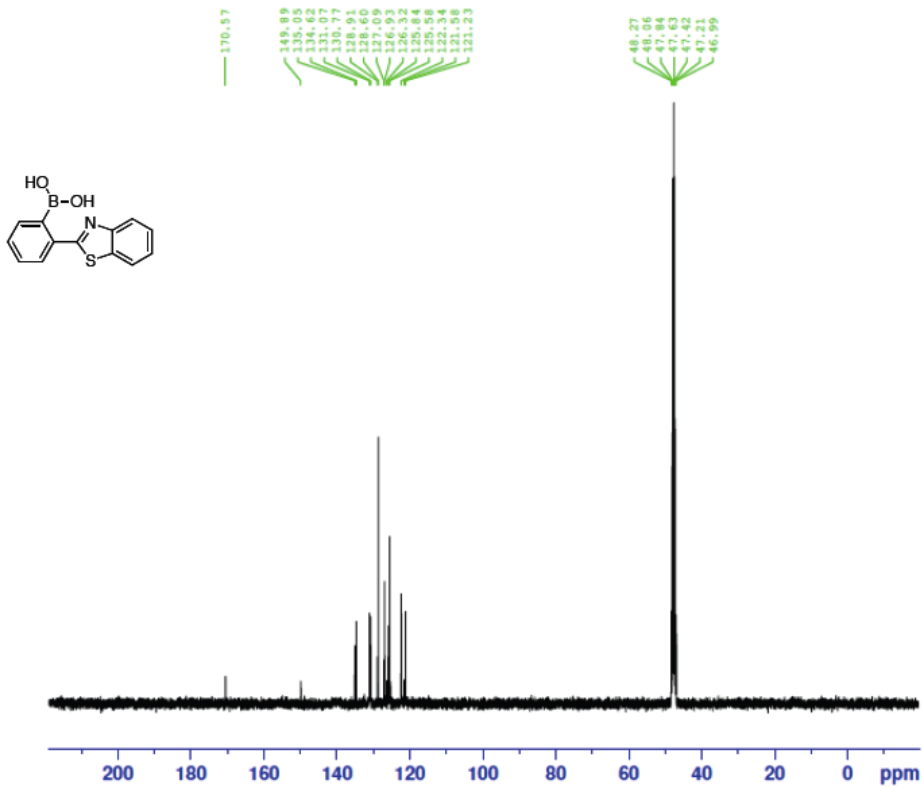
References

1. Y. Tong, Q. Pan, Z. Jiang, D. Miao, X. Shi and S. Han, *Tetrahedron Lett.*, 2014, **55**, 5499-5503.

2.

NMR and MS Data

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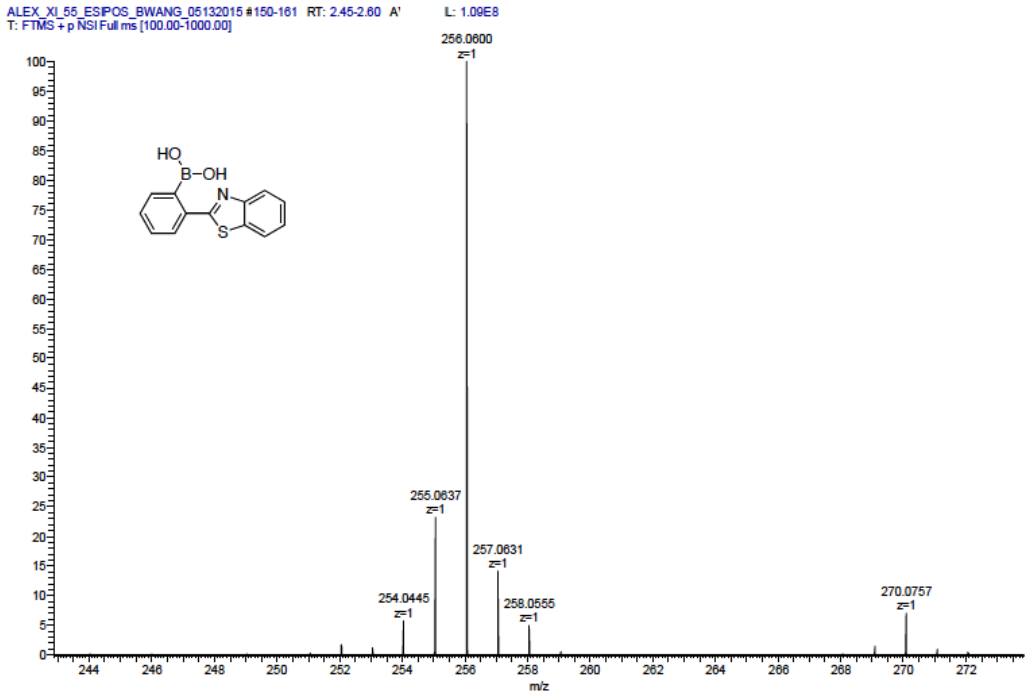
149.89
135.05
134.62
131.07
130.77
128.91
128.60
127.09
126.93
126.32
125.84
125.58
122.34
121.58
121.23
48.27
48.06
47.84
47.63
47.42
47.21
46.99
HO
B-OH
N
S
200
180
160
140
120
100
80
60
40
20
0
ppm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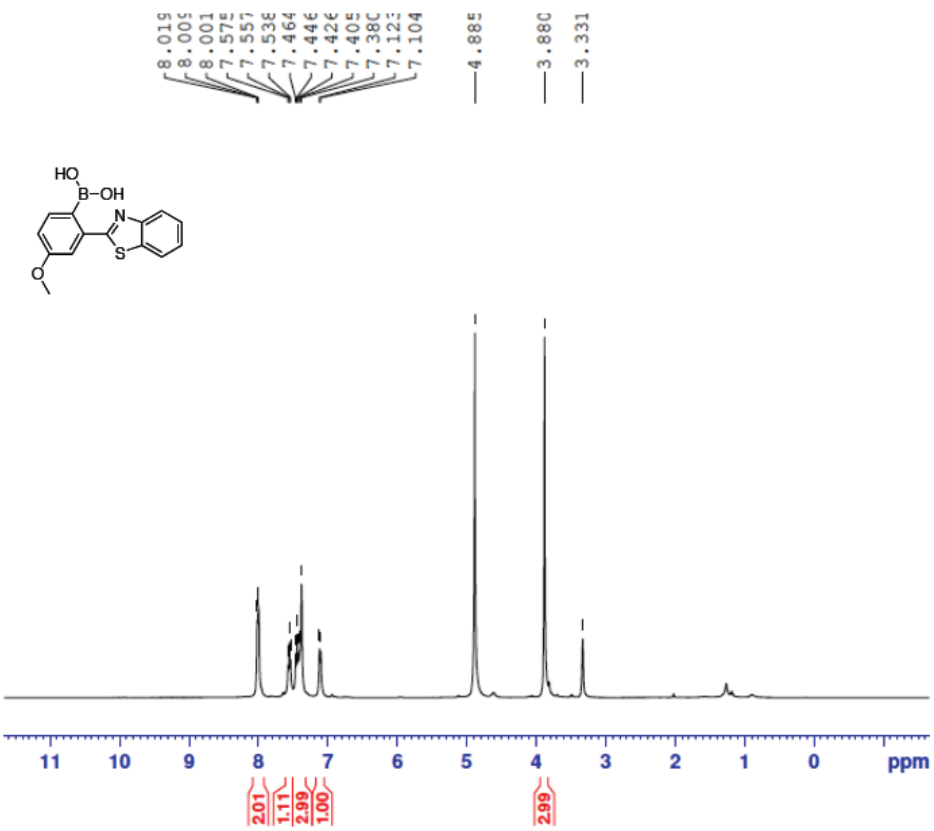
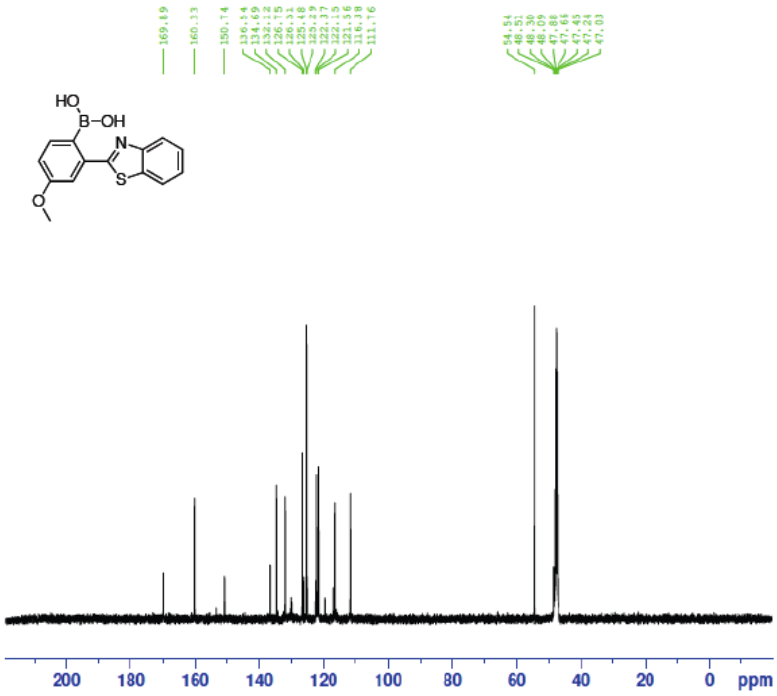
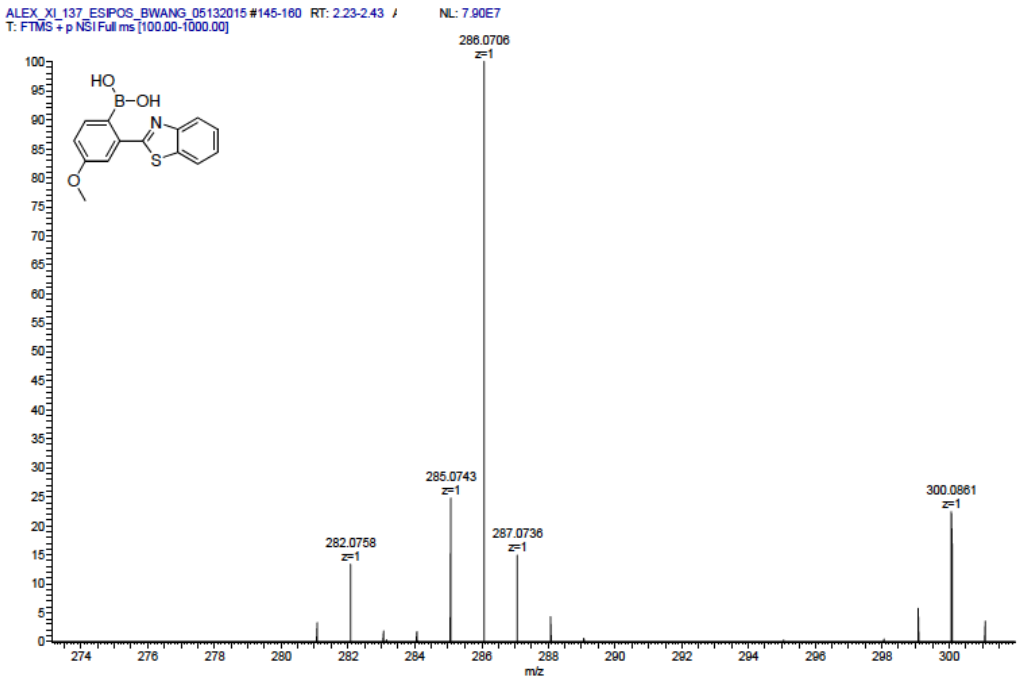
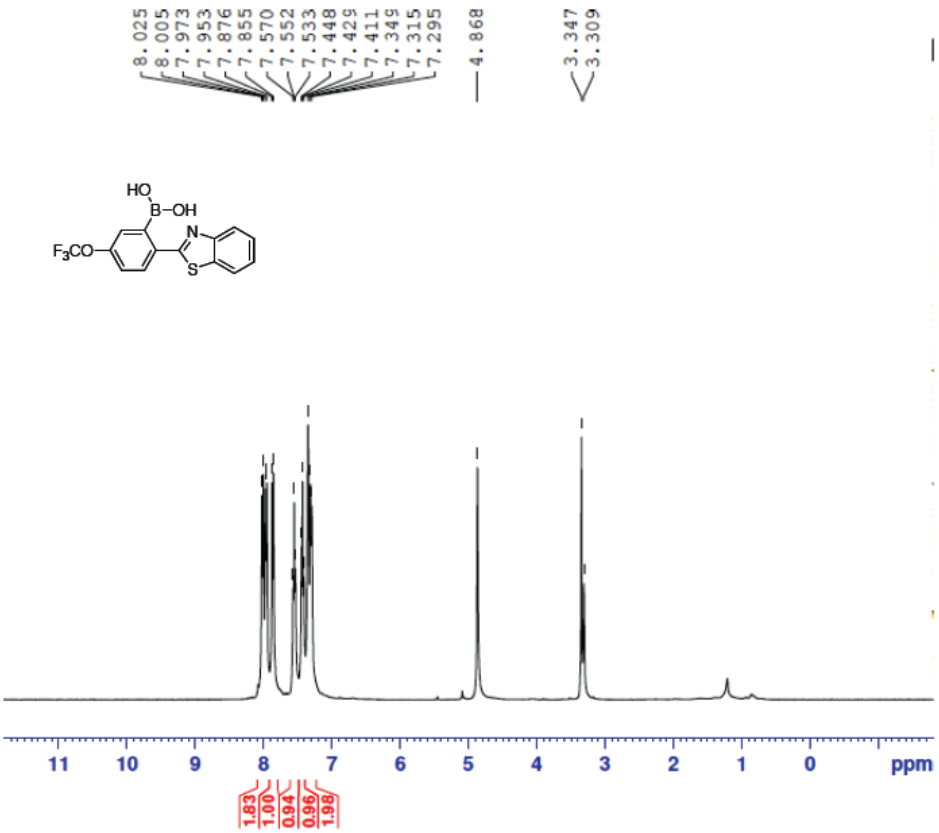
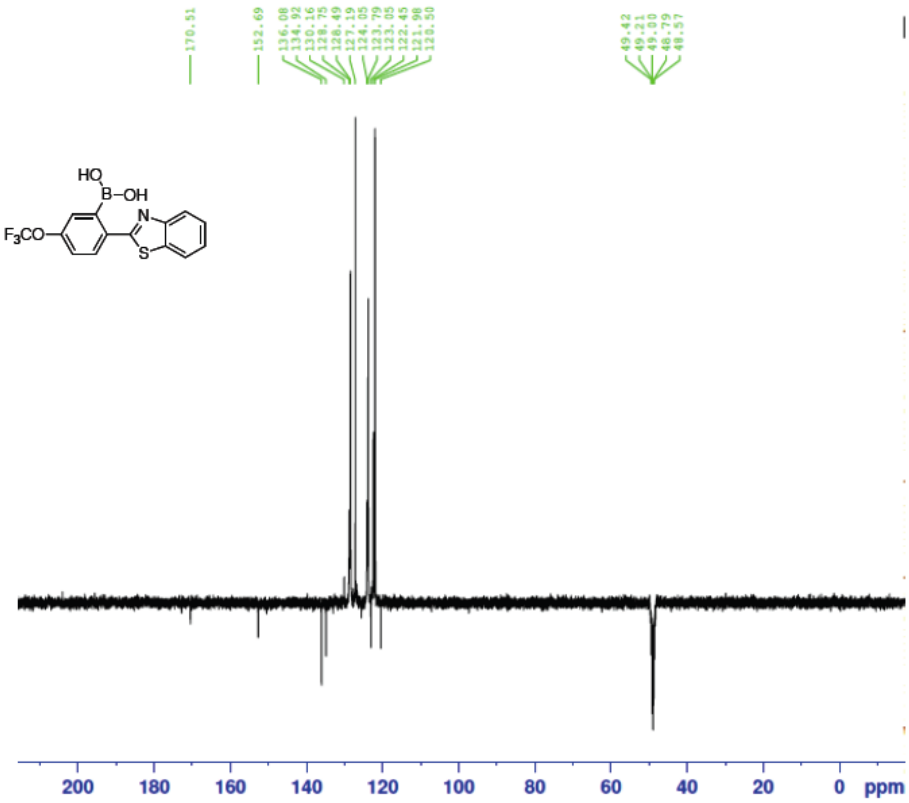
T: FTMS + p NSI Full ms [100.00-1000.00]
256.0600
z=1
255.0637
z=1
257.0631
z=1
254.0445
z=1
258.0555
z=1
270.0757
z=1
HO
B–OH
N
S
m/z

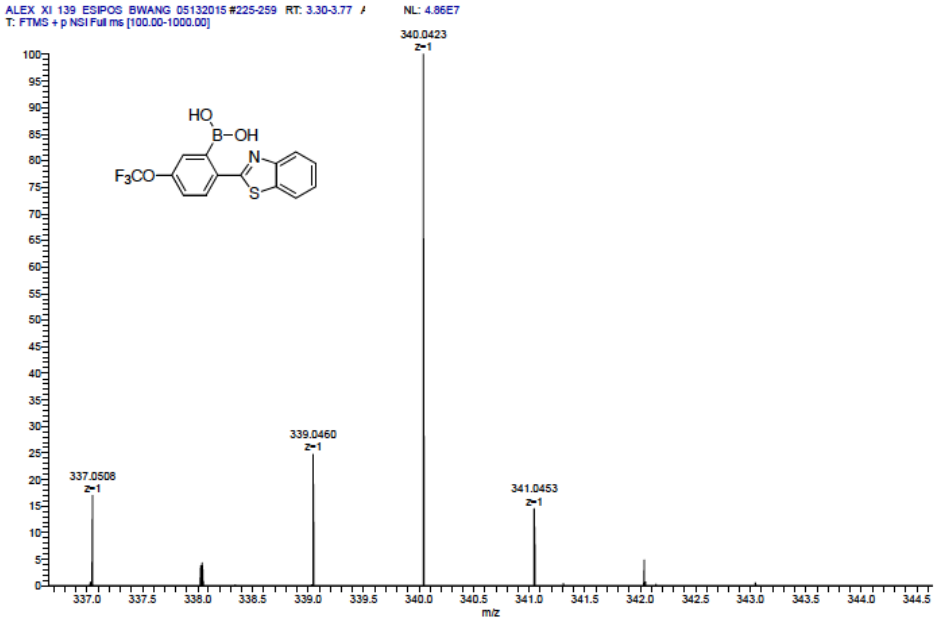

8.019
8.005
8.001
7.575
7.557
7.538
7.464
7.446
7.426
7.405
7.380
7.123
7.104
4.885
3.880
3.331
HO
B–OH
N
S
O
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.11
2.99
1.00
2.99

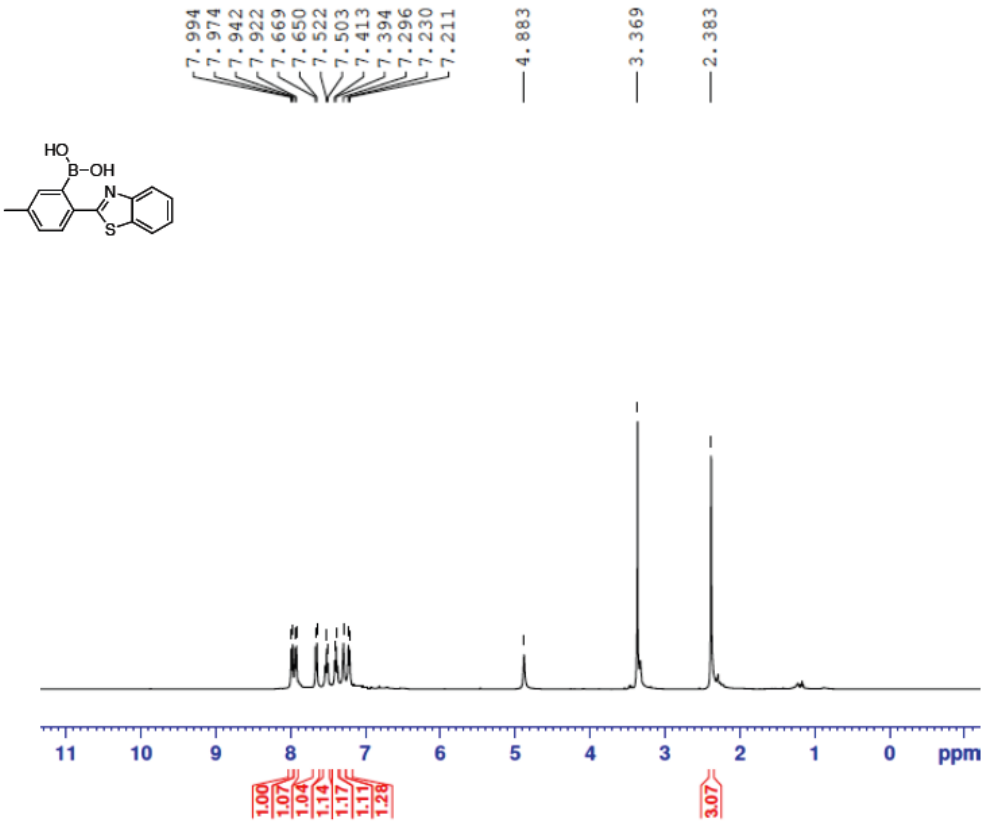

169.89
160.33
150.74
136.14
134.69
132.12
126.15
126.31
125.48
125.29
122.37
122.15
121.36
115.38
111.76
54.54
48.51
48.30
48.09
47.88
47.65
47.45
47.24
47.03
HO
B–OH
N
S
O
200
180
160
140
120
100
80
60
40
20
0
ppm

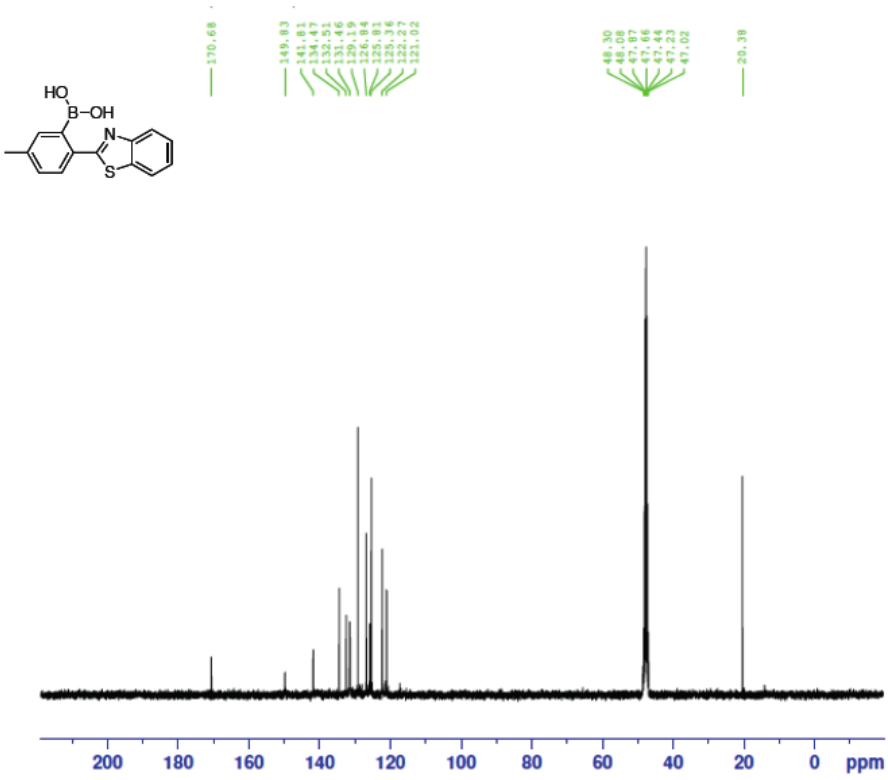

ALEX_XI_137_ESIPOS_BWANG_05132015 #145-160 RT: 2.23-2.43
NL: 7.90E7
T: FTMS + p NSI Full ms [100.00-1000.00]
286.0706
z=1
285.0743
z=1
282.0758
z=1
287.0736
z=1
300.0861
z=1
HO
B–OH
N
S
O
m/z

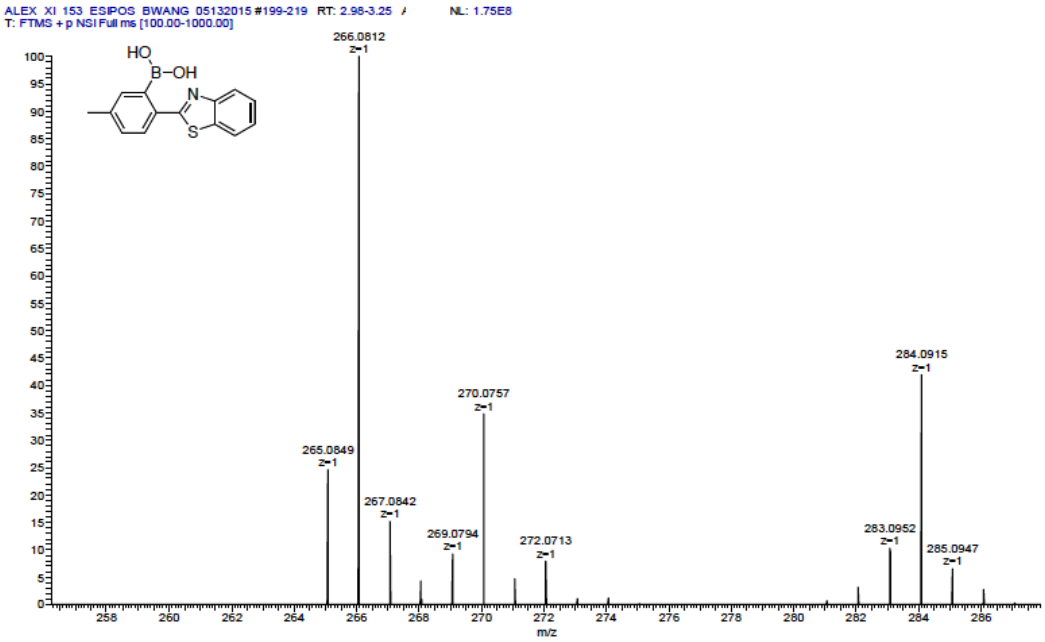

8.025
8.005
7.973
7.953
7.876
7.855
7.570
7.552
7.533
7.448
7.429
7.411
7.349
7.315
7.295
4.868
3.347
3.309
HO
B–OH
N
S
F3CO
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.83
1.00
0.94
0.96
1.98

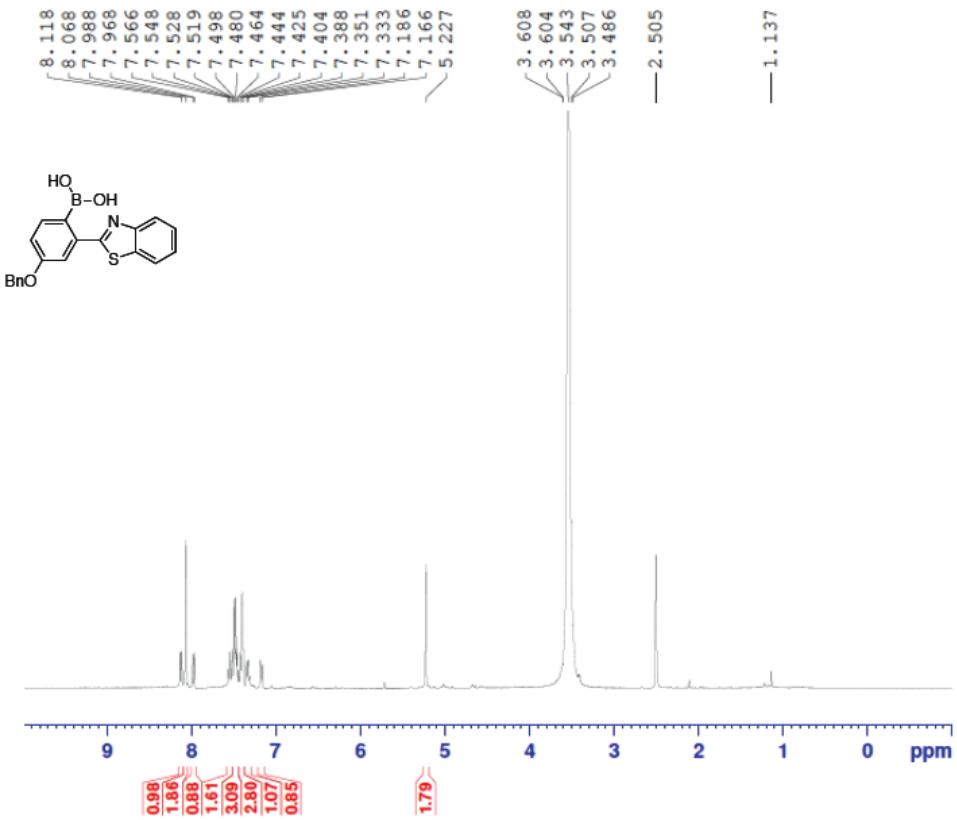

170.51
152.69
136.08
134.92
130.16
128.75
126.49
125.19
124.05
123.79
123.05
122.45
121.98
120.50
49.42
49.21
49.10
48.79
48.57
HO
B–OH
N
S
F3CO
200
180
160
140
120
100
80
60
40
20
0
ppm

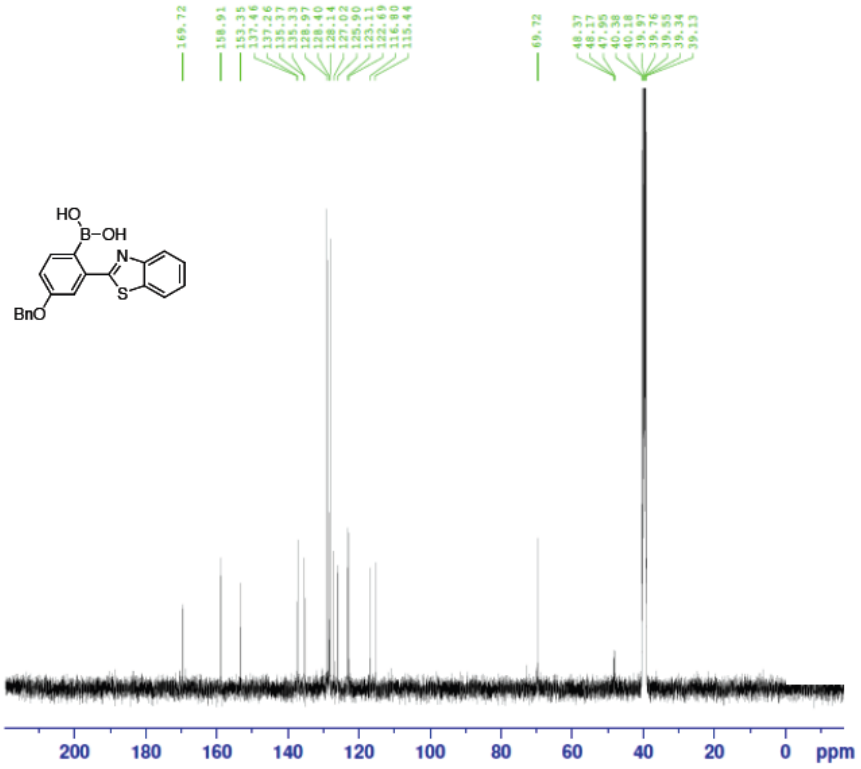

ALEX XI 139 ESIPOS BWANG 05132015 #225-259 RT: 3.30-3.77
T: FTMS + p NSI Full ms [100.00-1000.00]
NL: 4.86E7
340.0423
z=1
339.0460
z=1
337.0508
z=1
341.0453
z=1
HO
B–OH
N
S
F3CO
m/z

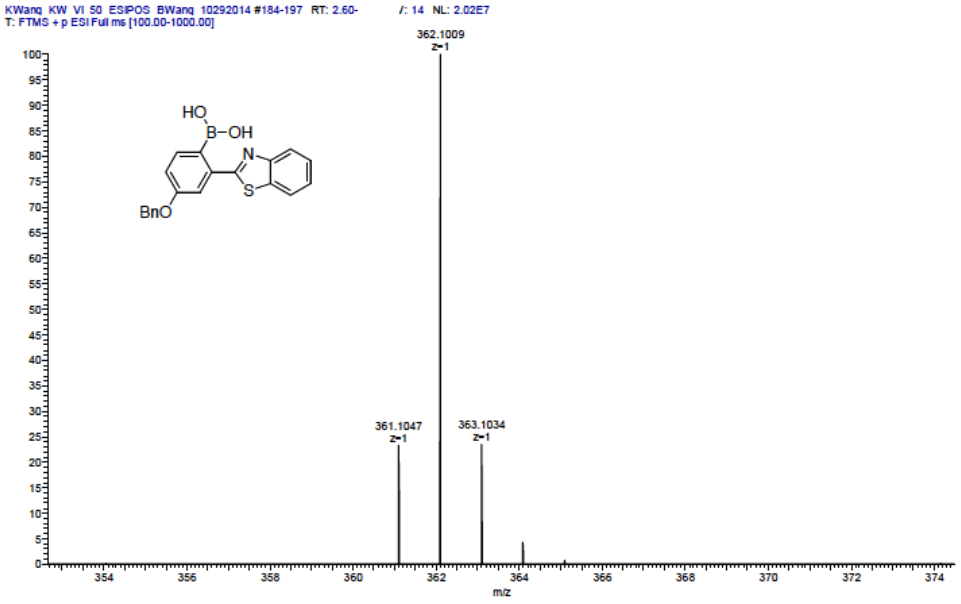

7.994
7.974
7.942
7.922
7.669
7.650
7.522
7.503
7.413
7.394
7.296
7.230
7.211
4.883
3.369
2.383
HO
B–OH
N
S
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.07
1.04
1.14
1.17
1.11
1.28
3.07

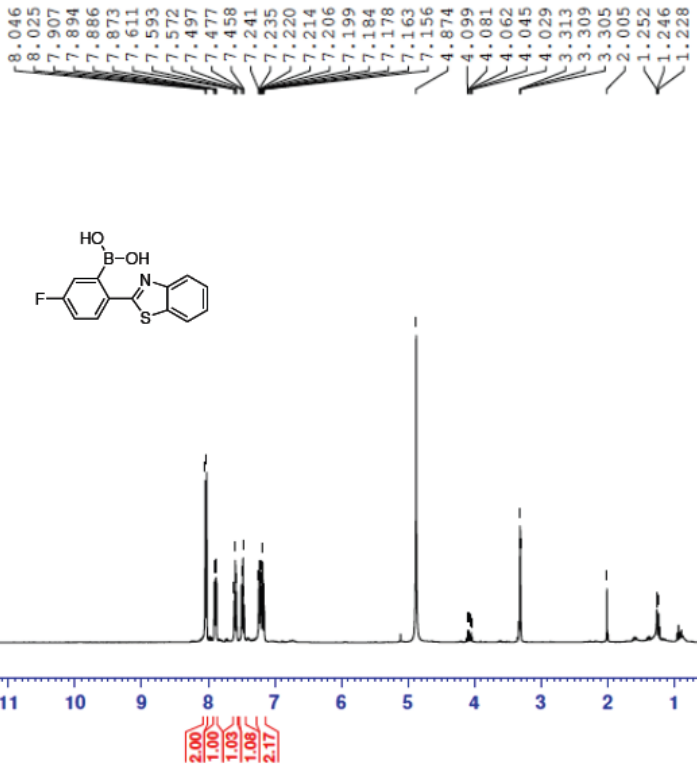

HO
B–OH
N
S
170.68
149.83
141.81
134.47
132.51
131.46
129.19
126.84
125.91
125.36
122.27
121.02
48.30
48.08
47.87
47.66
47.44
47.23
47.02
20.38
200
180
160
140
120
100
80
60
40
20
0
ppm

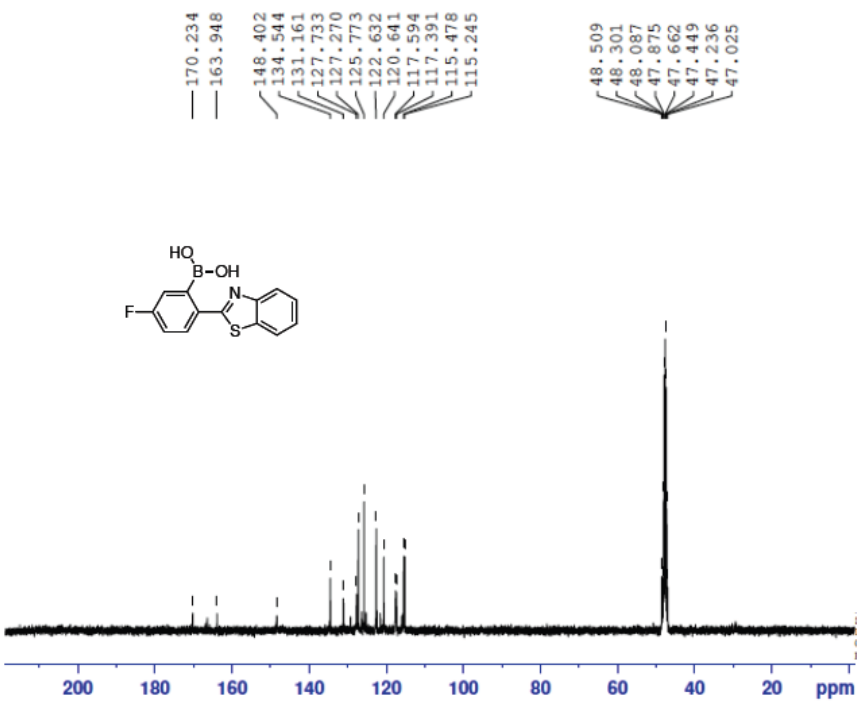

ALEX XI 153 ESIPOS BWANG 05132015 #199-219 RT: 2.98-3.25
NL: 1.75E8
T: FTMS + p NSI Full ms [100.00-1000.00]
HO
B–OH
N
S
266.0812
z=1
284.0915
z=1
270.0757
z=1
265.0849
z=1
267.0842
z=1
269.0794
z=1
272.0713
z=1
283.0952
z=1
285.0947
z=1
m/z

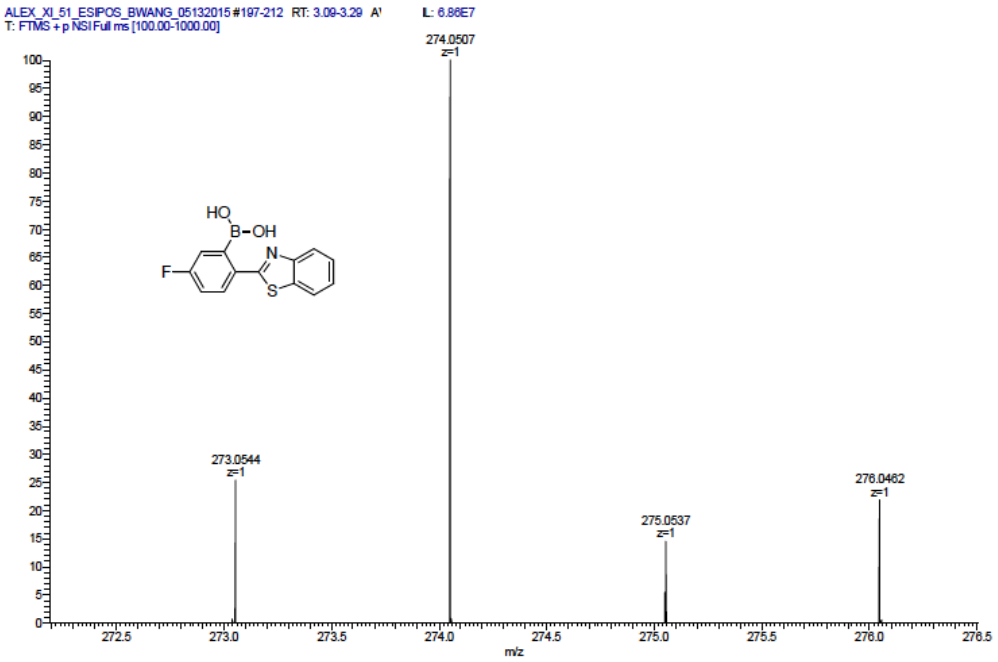

8.118
8.068
7.988
7.968
7.566
7.548
7.528
7.519
7.498
7.480
7.464
7.444
7.425
7.404
7.388
7.351
7.333
7.186
7.166
5.227
3.608
3.604
3.543
3.507
3.486
2.505
1.137
HO
B–OH
N
S
BnO
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.86
0.88
1.61
3.09
2.80
1.07
0.85
1.79


169.72
158.91
153.35
137.46
137.26
135.37
135.33
128.87
128.40
128.14
127.02
125.90
123.11
122.69
116.80
115.44
69.72
48.37
48.17
47.95
40.38
40.18
39.97
39.76
39.55
39.34
39.13
HO
B–OH
N
S
BnO
200
180
160
140
120
100
80
60
40
20
0
ppm


KWang KW VI 50 ESIPOS BWang 10292014 #184-197 RT: 2.60-
T: FTMS + p ESI Full ms [100.00-1000.00]
/: 14 NL: 2.02E7
362.1009
z=1
361.1047
z=1
363.1034
z=1
HO
B–OH
N
S
BnO
m/z


8.046
8.025
7.907
7.894
7.886
7.873
7.611
7.593
7.572
7.497
7.477
7.458
7.241
7.235
7.220
7.214
7.206
7.199
7.184
7.178
7.163
7.156
4.874
4.099
4.081
4.062
4.045
4.029
3.313
3.309
3.305
2.005
1.252
1.246
1.228
HO
B–OH
N
F
S
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
1.03
1.08
2.17


170.234
163.948
148.402
134.544
131.161
127.733
127.270
125.773
122.632
120.641
117.594
117.391
115.478
115.245
48.509
48.301
48.087
47.875
47.662
47.449
47.236
47.025
HO
B-OH
F
N
S
200
180
160
140
120
100
80
60
40
20
ppm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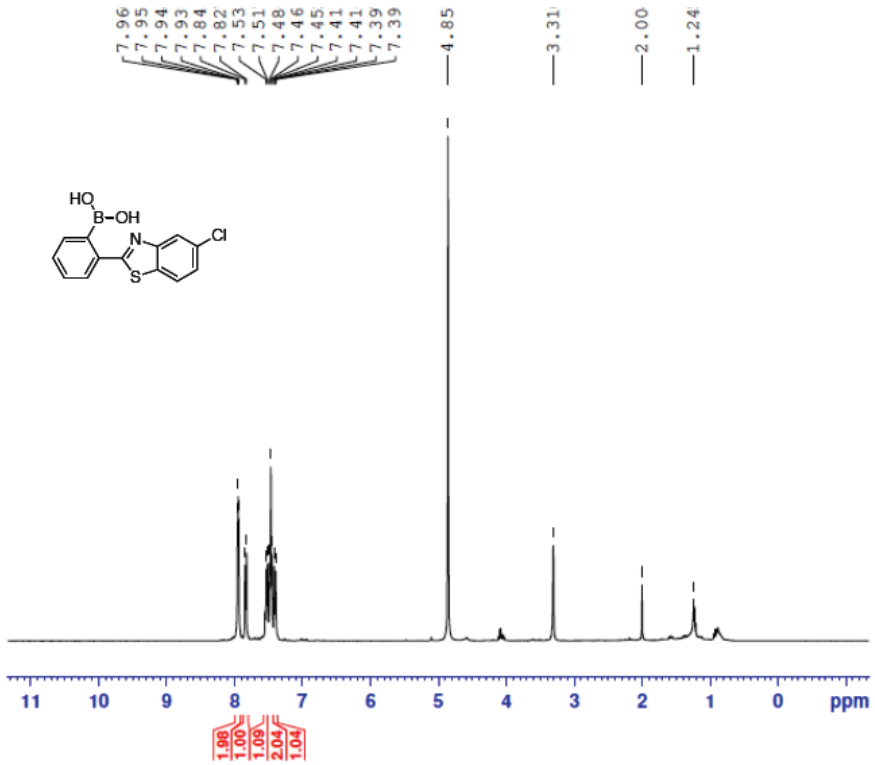
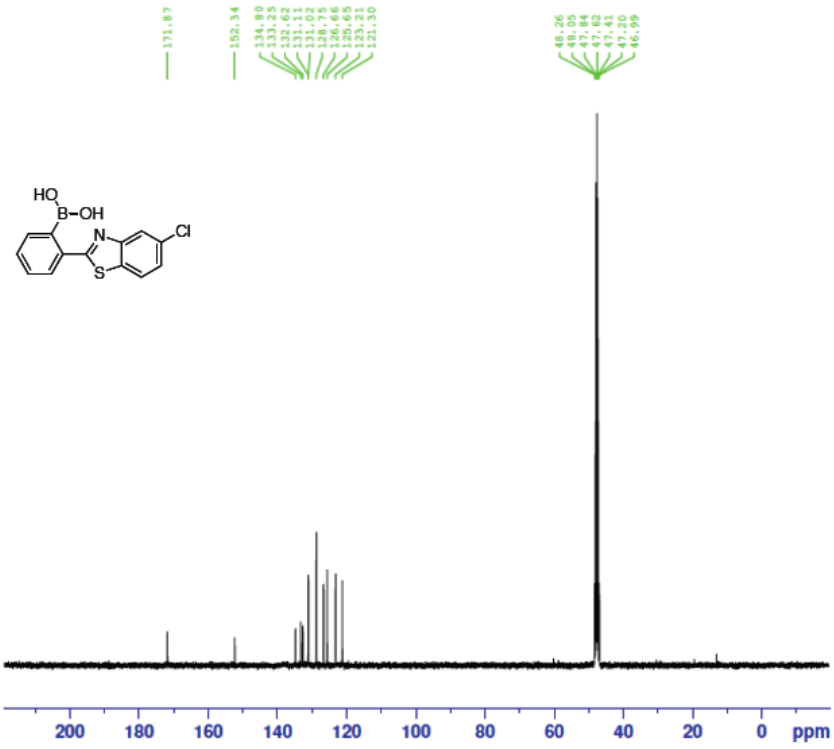
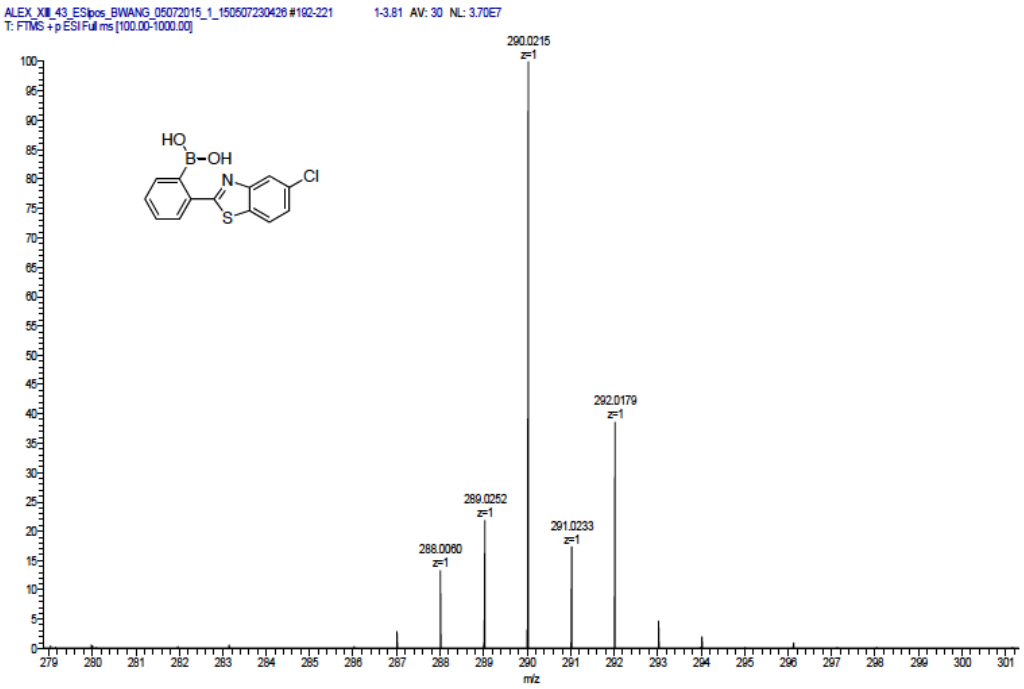
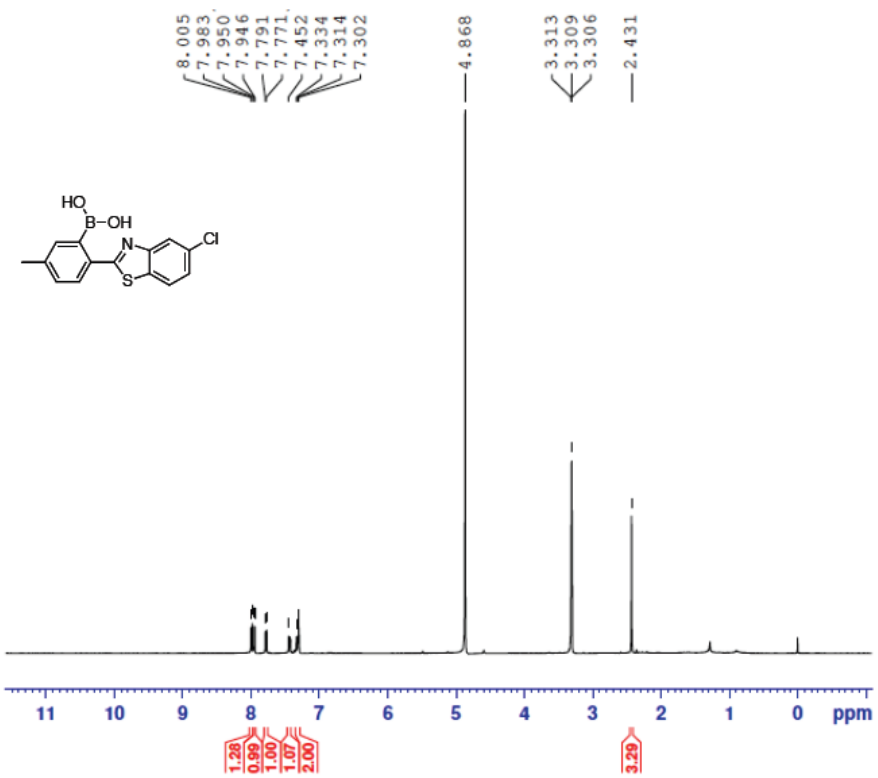
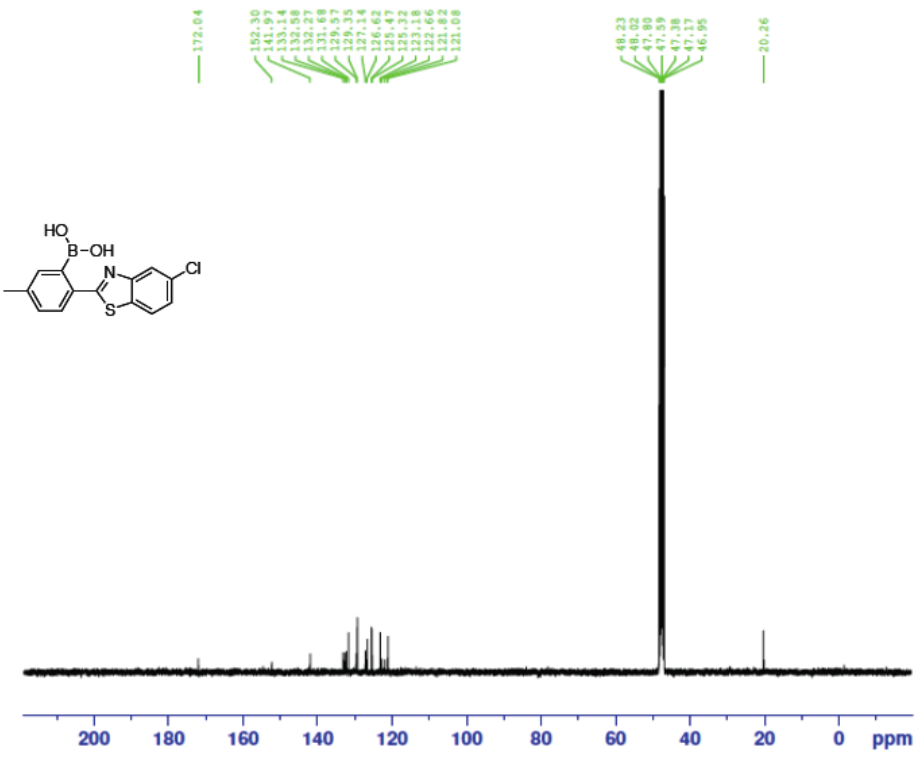
T: FTMS + p NSI Full ms [100.00-1000.00]
IL: 6.86E7
274.0507
z=1
273.0544
z=1
275.0537
z=1
276.0462
z=1
HO
B-OH
N
F
S
m/z

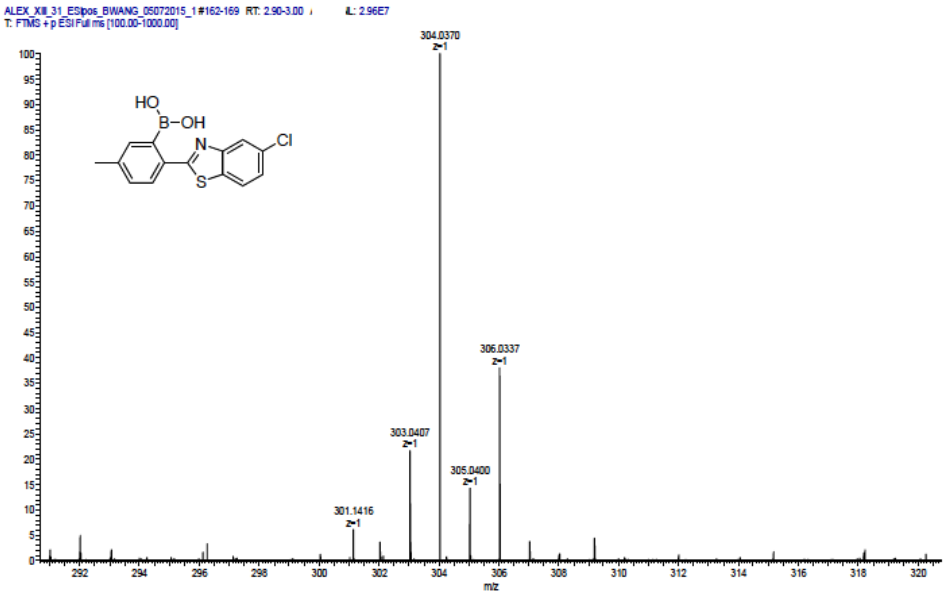

7.96
7.95
7.94
7.93
7.84
7.82
7.53
7.51
7.48
7.46
7.45
7.41
7.41
7.39
7.39
4.85
3.31
2.00
1.24
HO
B–OH
N
S
Cl
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
1.00
1.09
2.04
1.04

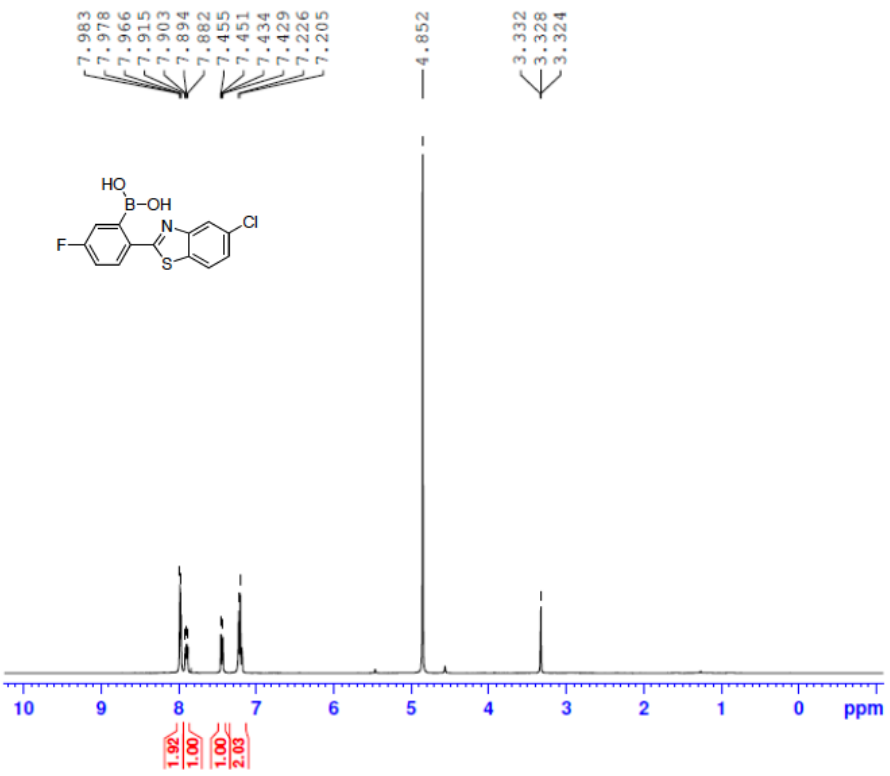

171.87
152.34
134.80
133.25
132.62
131.11
131.02
126.75
126.66
125.65
123.21
121.30
48.26
48.05
47.84
47.62
47.41
47.20
46.99
HO
B–OH
N
S
Cl
200
180
160
140
120
100
80
60
40
20
0
ppm

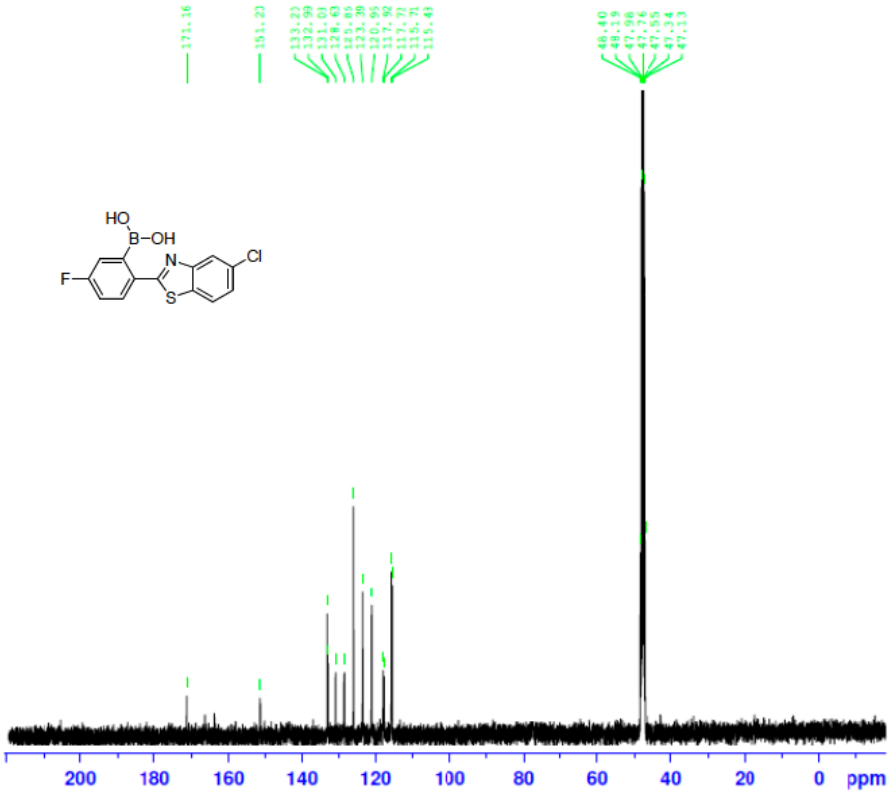

ALEX_XIII_43_ESIpos_BWANG_05072015_1_150507230426 #192-221
1-3.81 AV: 30 NL: 3.70E7
T: FTMS + p ESI Full ms [100.00-1000.00]
290.0215
z=1
292.0179
z=1
289.0252
z=1
291.0233
z=1
288.0060
z=1
HO
B–OH
N
S
Cl
m/z

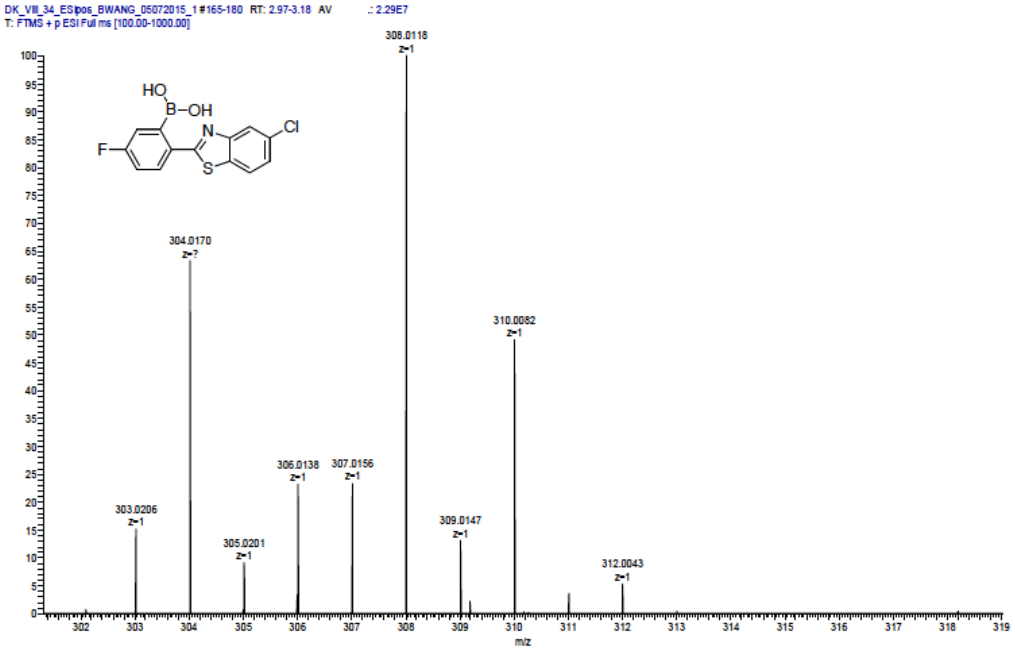

8.005
7.983
7.950
7.946
7.791
7.771
7.452
7.334
7.314
7.302
4.868
3.313
3.309
3.306
2.431
HO
B–OH
N
S
Cl
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.28
0.99
1.00
1.07
2.00
3.29

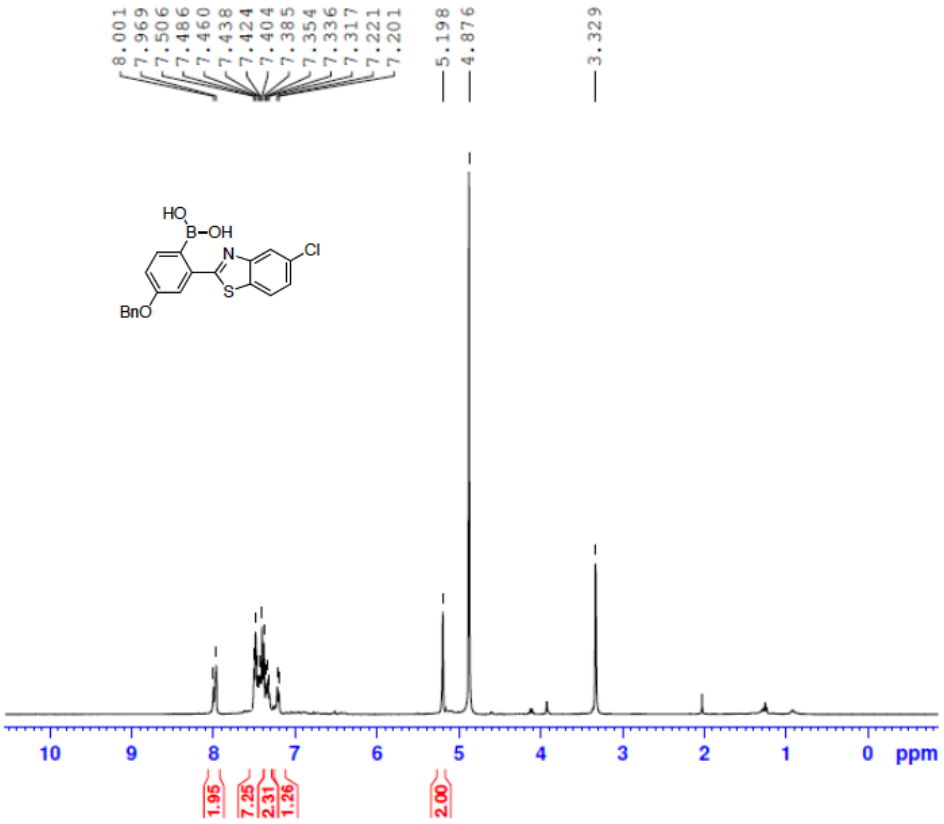

172.04
152.30
141.97
133.14
132.89
132.29
131.68
129.57
129.35
127.14
126.62
125.47
125.32
123.18
122.66
121.82
121.08
48.23
48.02
47.80
47.59
47.38
47.17
46.95
20.26
HO
B–OH
N
S
Cl
200
180
160
140
120
100
80
60
40
20
0
ppm

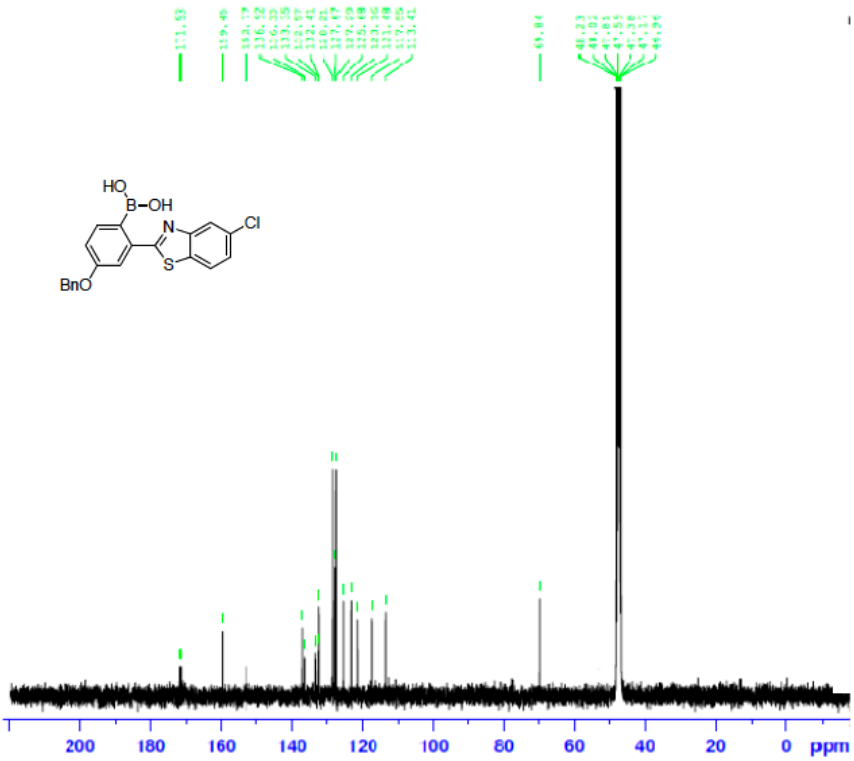

ALEX_XIII_31_ESIpos_BWANG_05072015_1 #162-169 RT: 2.90-3.00
T: FTMS + p ESI Full ms [100.00-1000.00]
304.0370
z=1
306.0337
z=1
303.0407
z=1
305.0400
z=1
301.1416
z=1
HO
B–OH
N
S
Cl
m/z

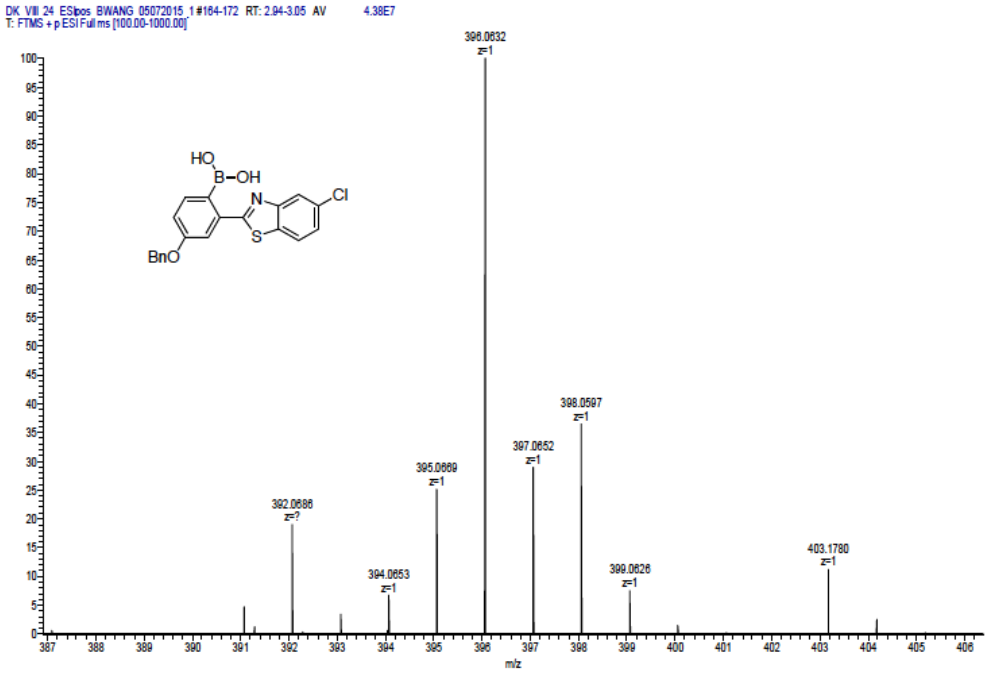

7.983
7.978
7.966
7.915
7.903
7.894
7.882
7.455
7.451
7.434
7.429
7.226
7.205
4.852
3.332
3.328
3.324
HO
B–OH
N
S
F
Cl
10
9
8
7
6
5
4
3
2
1
0
ppm
1.92
1.00
1.00
2.03

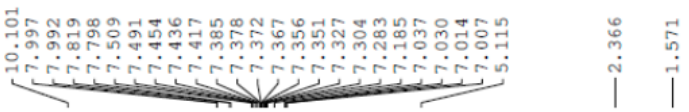

171.16
151.23
133.23
132.99
132.03
131.63
128.80
125.39
120.95
117.92
117.72
115.71
115.49
48.40
48.19
47.98
47.76
47.55
47.34
47.13
HO
B–OH
N
F
Cl
S
200
180
160
140
120
100
80
60
40
20
0
ppm

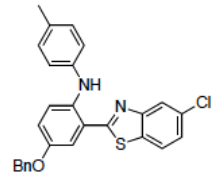

DK_VIII_34_ESIpos_BWANG_05072015_1 #165-180 RT: 2.97-3.18 AV .: 2.29E7
T: FTMS + p ESI Full ms [100.00-1000.00]
HO
B–OH
N
F
Cl
S
308.0118
z=1
304.0170
z=?
310.0082
z=1
306.0138
z=1
307.0156
z=1
303.0206
z=1
309.0147
z=1
305.0201
z=1
312.0043
z=1
m/z

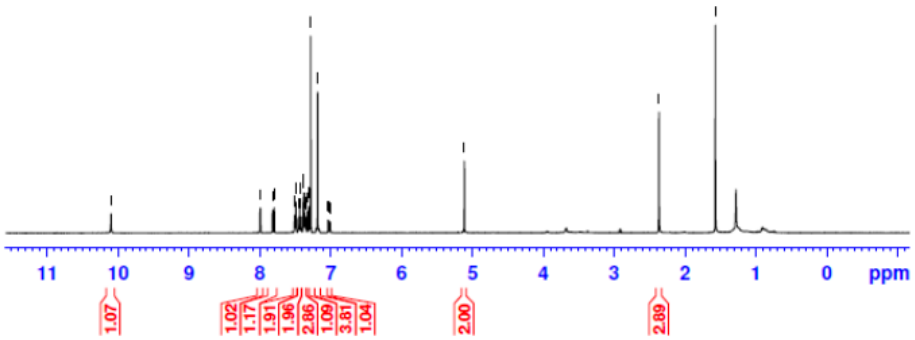

8.001
7.969
7.506
7.486
7.460
7.438
7.424
7.404
7.385
7.354
7.336
7.317
7.221
7.201
5.198
4.876
3.329
HO
B–OH
N
S
Cl
BnO
10
9
8
7
6
5
4
3
2
1
0
ppm
1.95
7.25
2.31
1.26
2.00

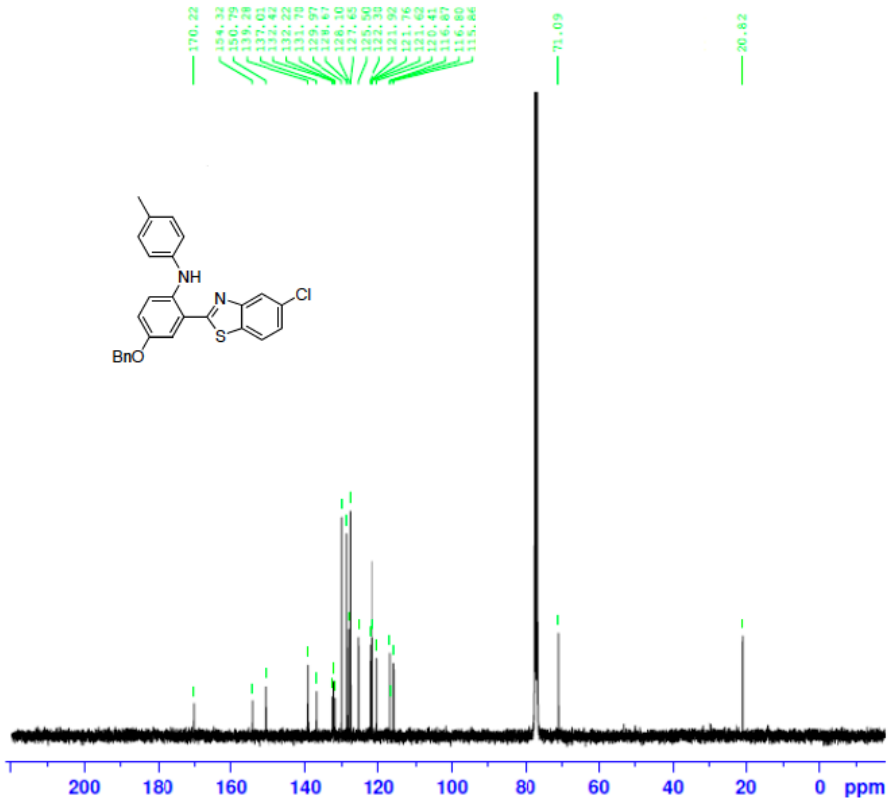

HO
B–OH
N
S
Cl
BnO
200
180
160
140
120
100
80
60
40
20
0
ppm

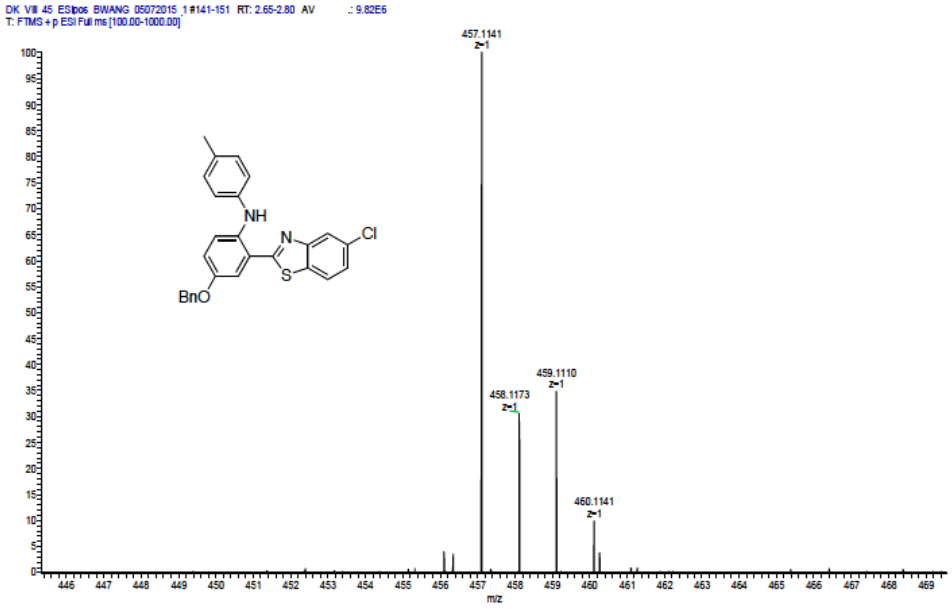

DK_VIII_24_ESIpos_BWANG_05072015_1 #164-172 RT: 2.94-3.05 AV 4.38E7
T: FTMS + p ESI Full ms [100.00-1000.00]
396.0632
z=1
398.0597
z=1
397.0652
z=1
395.0669
z=1
392.0686
z=?
403.1780
z=1
394.0653
z=1
399.0626
z=1
HO
B–OH
N
Cl
S
BnO
m/z

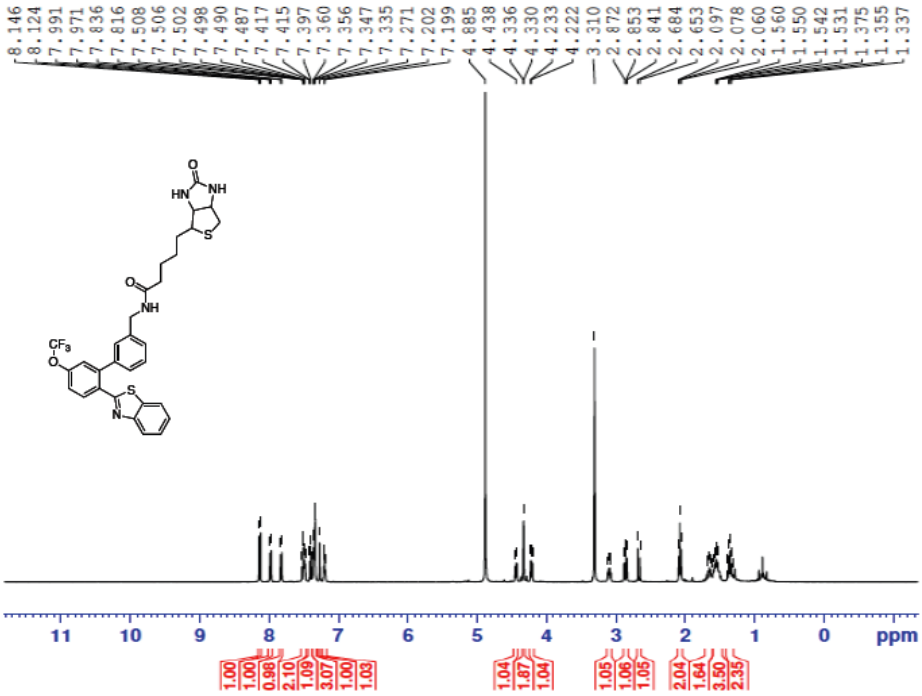

10.101
7.997
7.992
7.819
7.798
7.509
7.491
7.454
7.436
7.417
7.385
7.378
7.372
7.367
7.356
7.351
7.327
7.304
7.283
7.185
7.037
7.030
7.014
7.007
5.115
2.366
1.571

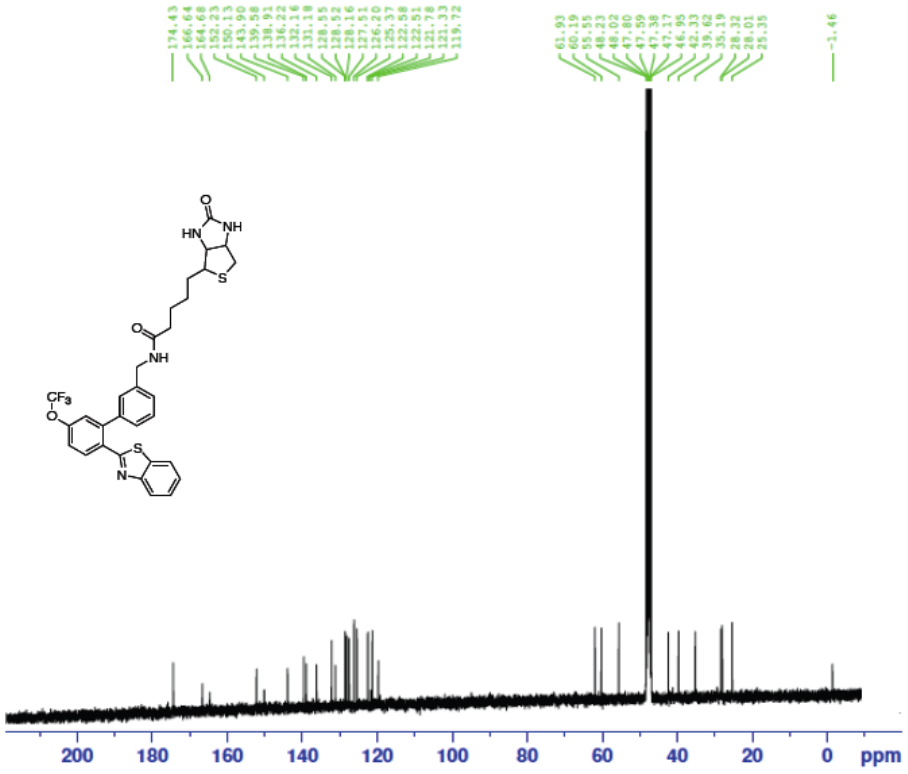

NH
N
S
Cl
BnO

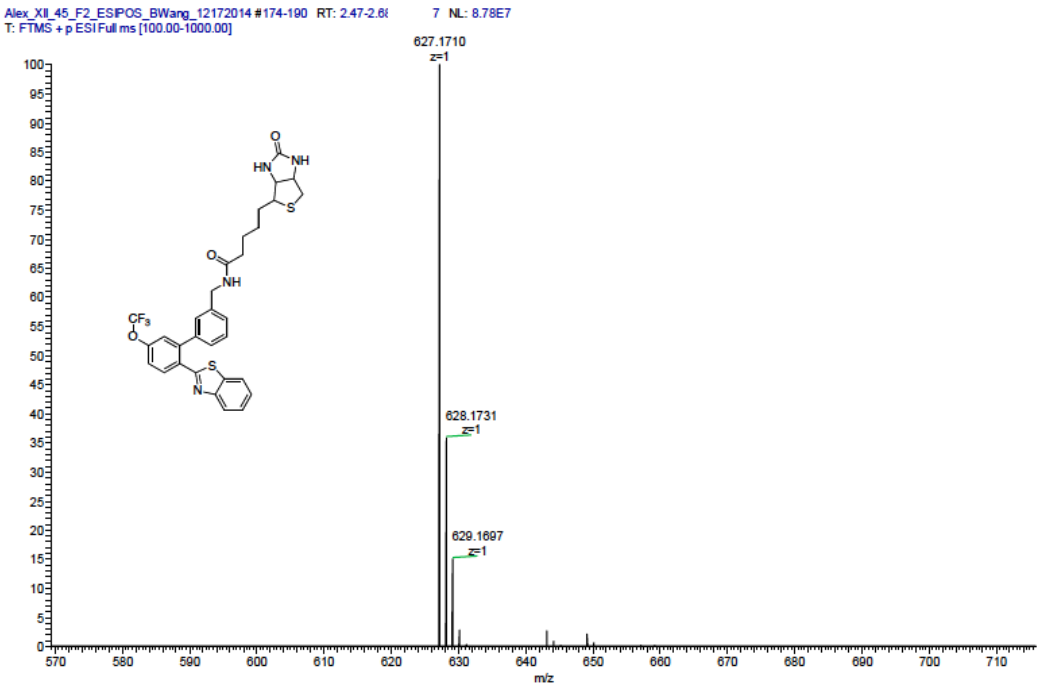

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.07
1.02
1.17
1.91
1.96
2.86
1.09
3.81
1.04
2.00
2.89

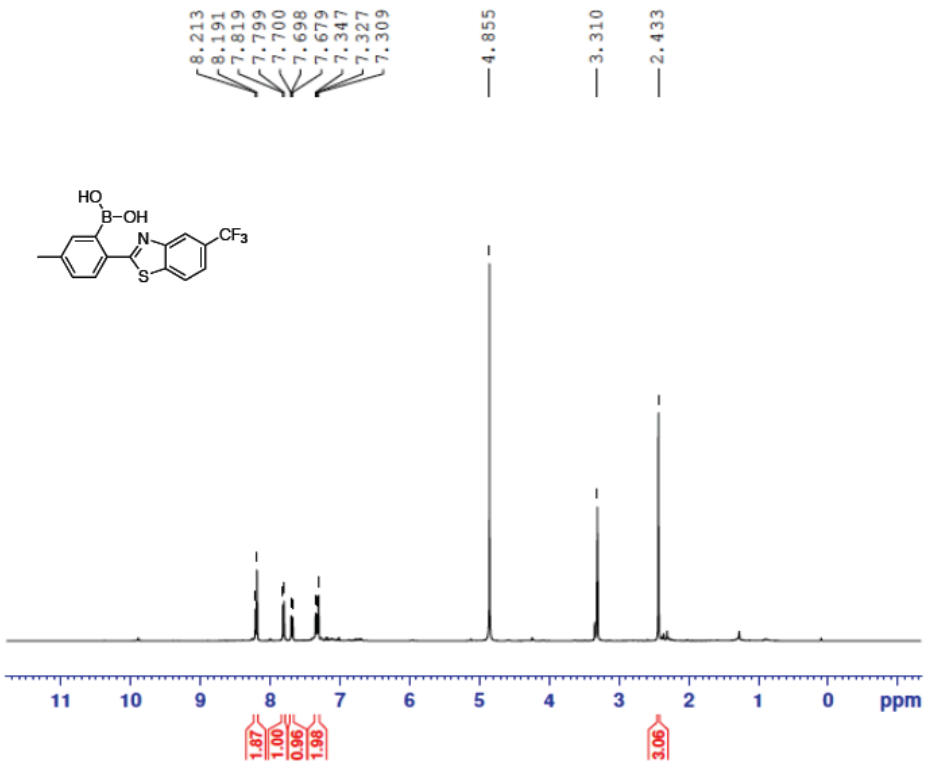

170.22
154.32
150.79
139.28
137.01
132.42
132.22
131.78
129.97
129.67
128.10
127.65
125.90
122.33
121.92
121.76
121.62
120.41
116.87
116.80
115.86
71.09
20.82
NH
N
S
Cl
BnO
200
180
160
140
120
100
80
60
40
20
0
ppm

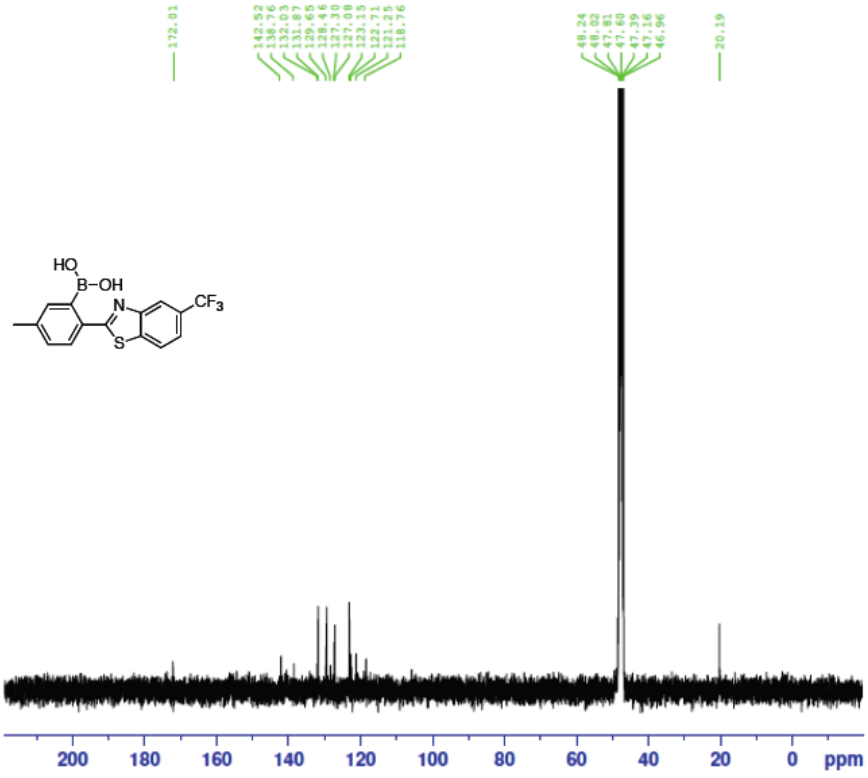

DK VIII 45 ESIpos BWANG 05072015 1 #141-151 RT: 2.65-2.80 AV
T: FTMS + p ESI Full ms [100.00-1000.00]
457.1141
z=1
459.1110
z=1
458.1173
z=1
460.1141
z=1
NH
N
S
Cl
BnO
m/z

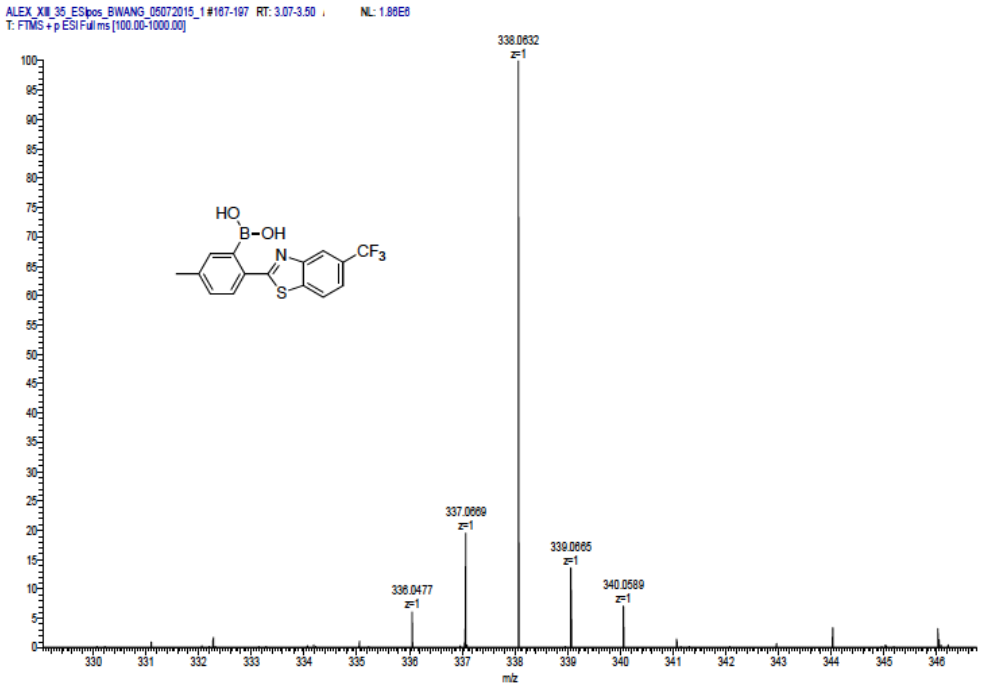

8.146
8.124
7.991
7.971
7.836
7.616
7.508
7.506
7.502
7.498
7.490
7.487
7.417
7.415
7.397
7.360
7.356
7.347
7.335
7.271
7.202
7.199
4.885
4.438
4.336
4.330
4.233
4.222
3.310
2.872
2.853
2.841
2.684
2.653
2.097
2.078
2.060
1.560
1.550
1.542
1.531
1.375
1.355
1.337
HN
NH
O
S
NH
O
CF3
O
S
N
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
0.98
2.10
1.09
3.07
1.00
1.03
1.04
1.87
1.04
1.05
1.06
1.05
2.04
1.64
3.50
2.35

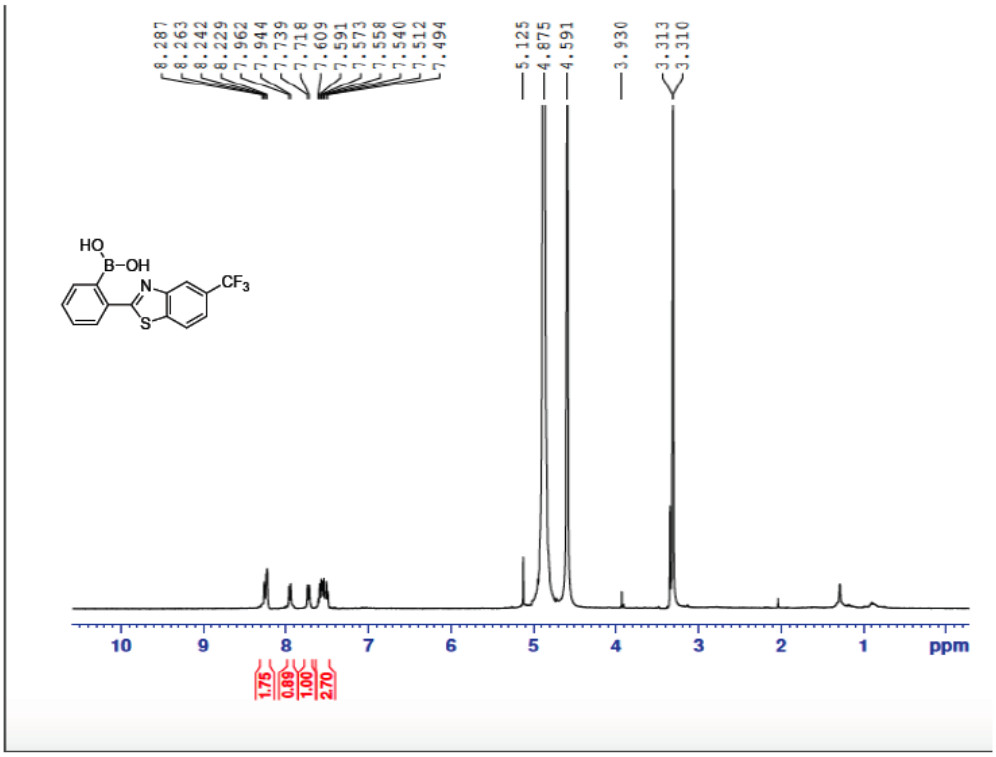

174.43
166.64
164.68
152.23
150.13
143.90
139.58
138.91
136.22
132.16
131.19
128.55
128.52
128.16
127.51
126.20
125.37
122.58
122.51
121.78
121.33
119.72
61.93
60.19
55.55
48.23
48.02
47.80
47.59
47.38
47.17
46.96
42.33
39.62
35.19
28.32
28.01
25.35
-1.46
HN
NH
O
S
NH
O
CF3
O
S
N
200
180
160
140
120
100
80
60
40
20
0
ppm

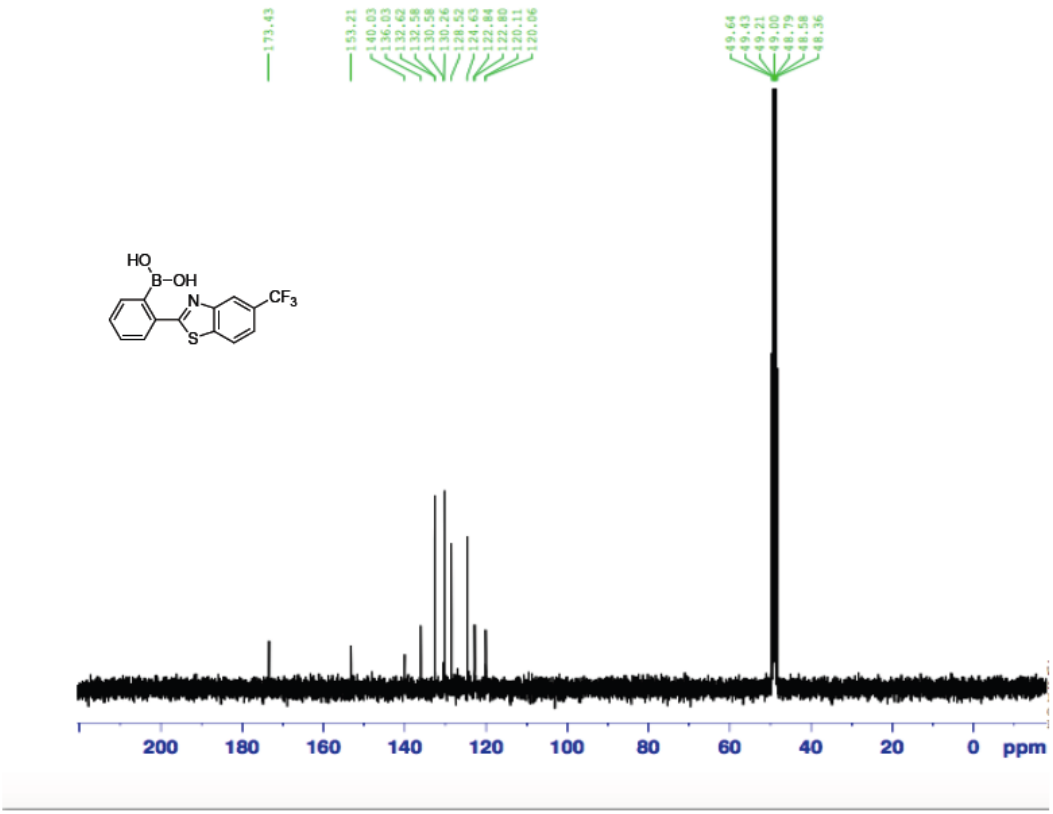

Alex_XII_45_F2_ESIPOS_BWang_12172014 #174-190 RT: 2.47-2.6
7 NL: 8.78E7
T: FTMS + p ESI Full ms [100.00-1000.00]
627.1710
z=1
628.1731
z=1
629.1697
z=1
m/z

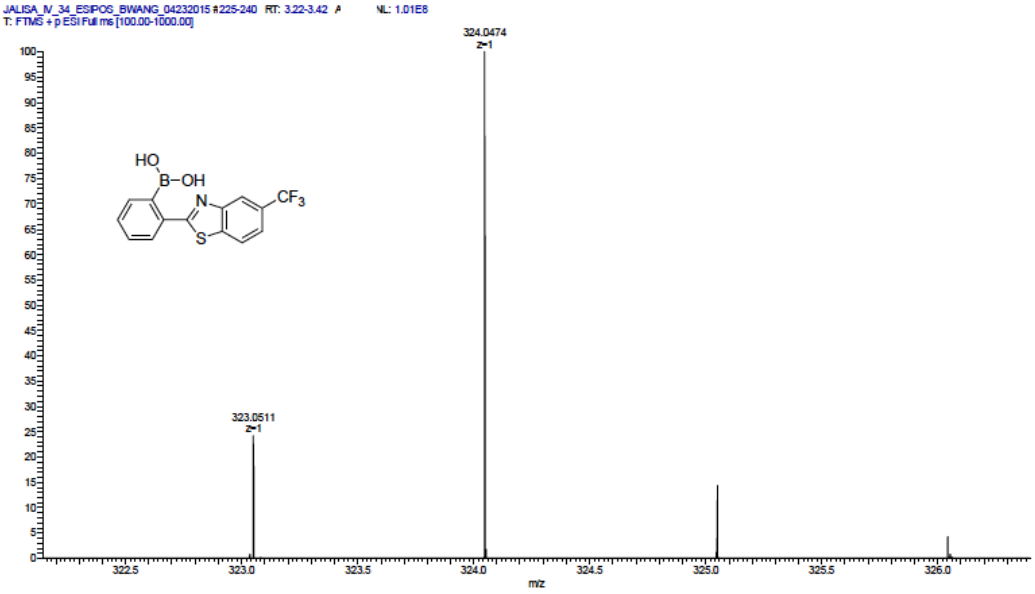

8.213
8.191
7.819
7.799
7.700
7.698
7.679
7.347
7.327
7.309
4.855
3.310
2.433
HO
B–OH
N
S
CF3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.87
1.00
0.96
1.98
3.06

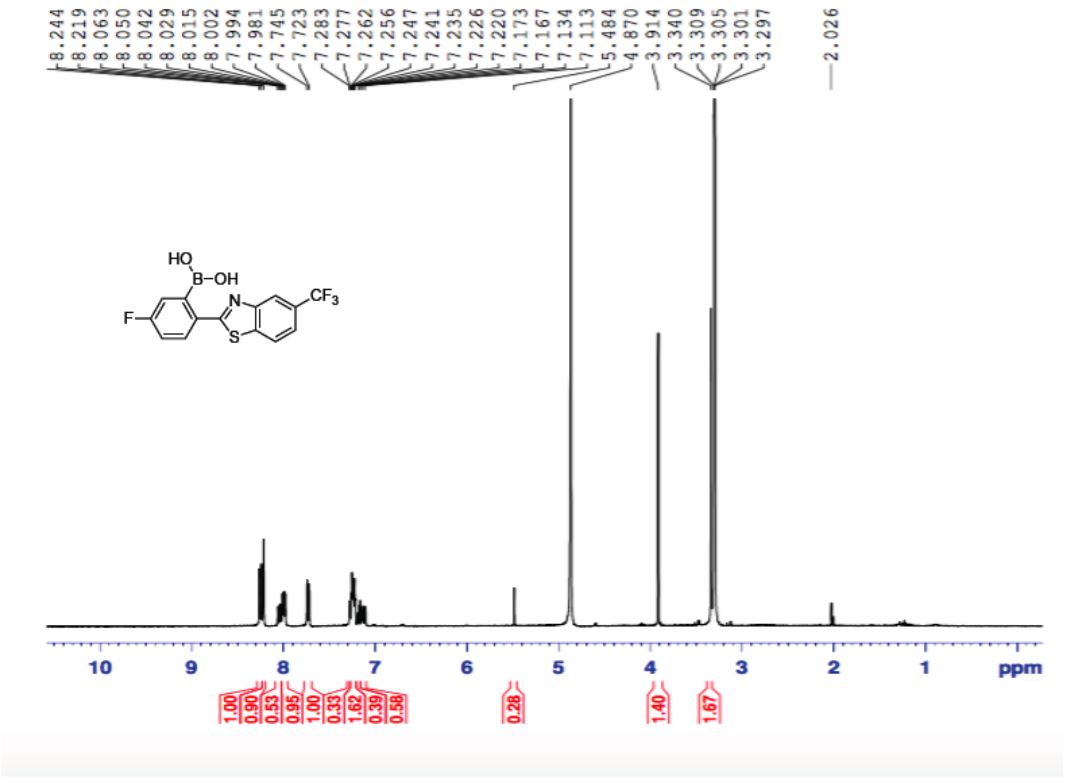

172.01
142.52
138.76
132.03
131.27
126.65
124.46
123.15
122.71
121.25
118.76
48.24
48.02
47.81
47.60
47.39
47.16
46.96
20.19
HO
B–OH
N
S
CF3
200
180
160
140
120
100
80
60
40
20
0
ppm

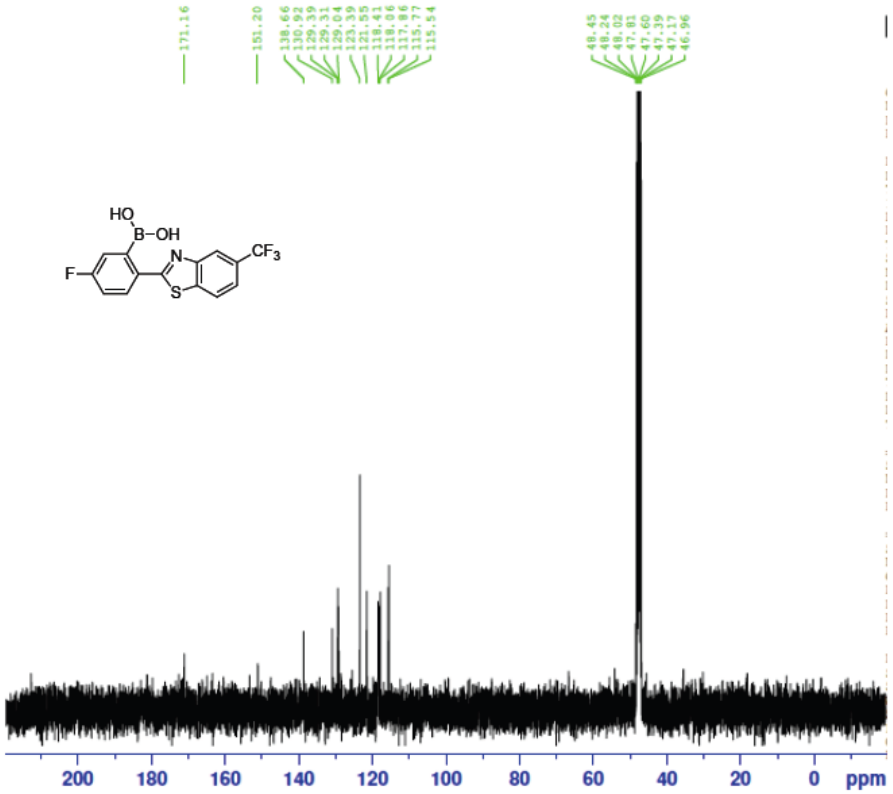

ALEX_XIII_35_ESIpos_BWANG_05072015_1 #167-197 RT: 3.07-3.50
NL: 1.86E6
T: FTMS + p ESI Full ms [100.00-1000.00]
338.0632
z=1
337.0669
z=1
339.0665
z=1
340.0589
z=1
336.0477
z=1
HO
B-OH
N
S
CF3
m/z

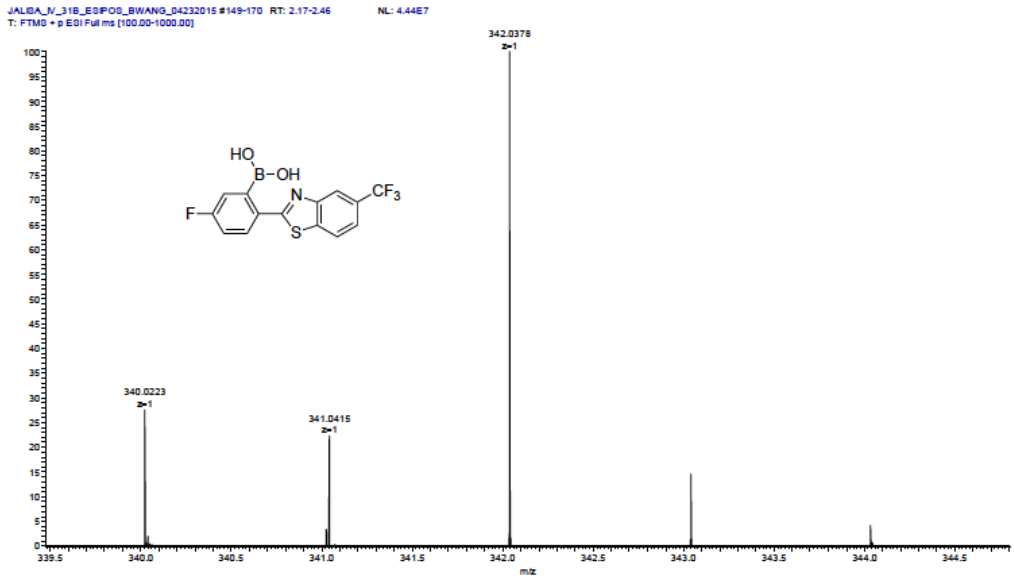

8.287
8.263
8.242
8.229
7.962
7.944
7.739
7.718
7.609
7.591
7.573
7.558
7.540
7.512
7.494
5.125
4.875
4.591
3.930
3.313
3.310
HO
B–OH
N
S
CF3
10
9
8
7
6
5
4
3
2
1
ppm
1.75
0.89
1.00
2.70

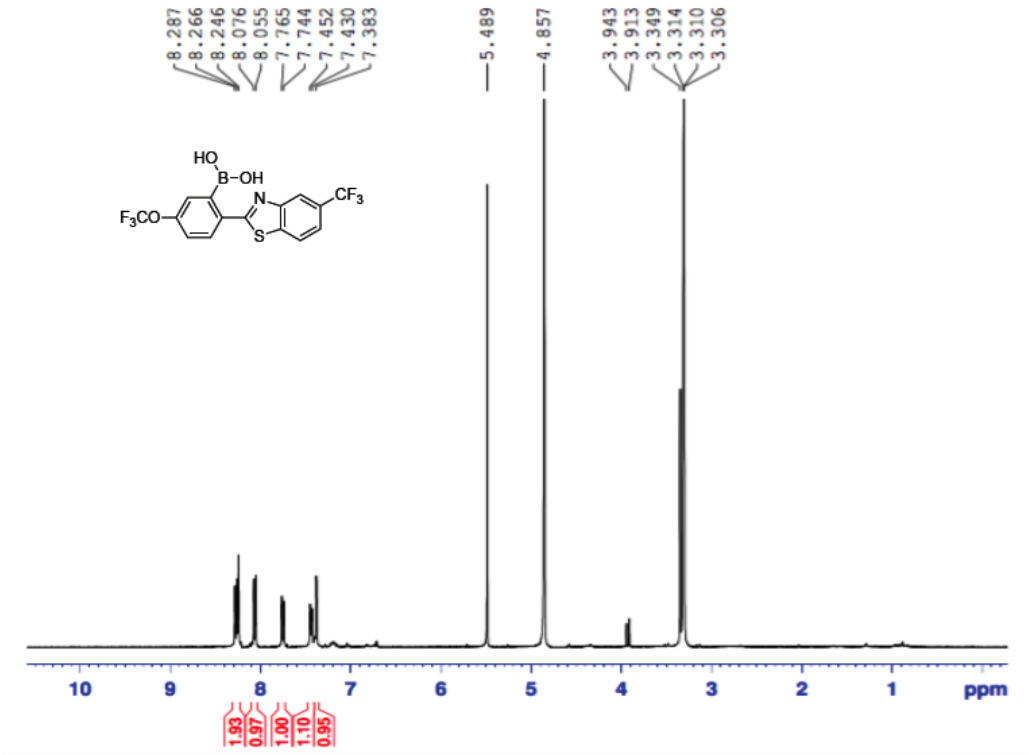

173.43
153.21
140.03
136.03
132.62
132.58
130.58
130.26
128.52
124.63
122.84
122.80
120.11
120.06
49.64
49.43
49.21
49.00
48.79
48.58
48.36
HO
B–OH
N
S
CF3
200
180
160
140
120
100
80
60
40
20
0
ppm

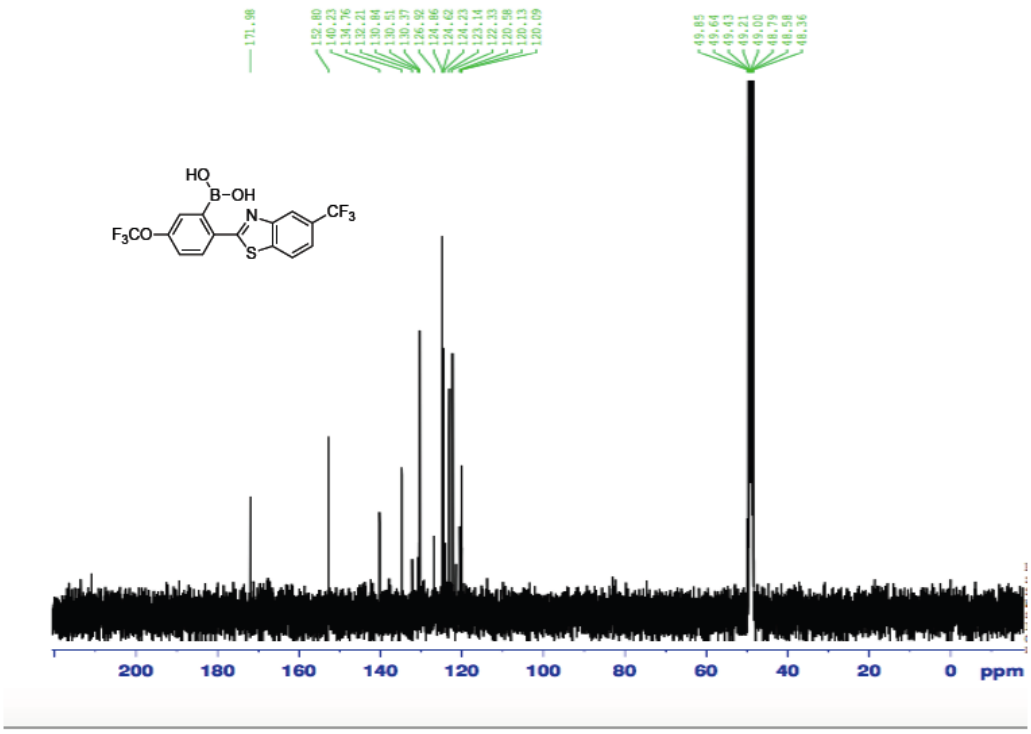

JALISA_IV_34_ESIPOS_BWANG_04232015 #225-240 RT: 3.22-3.42 A NL: 1.01E8
T: FTMS + p ESI Full ms [100.00-1000.00]
324.0474
z=1
323.0511
z=1
HO
B–OH
N
S
CF3
m/z

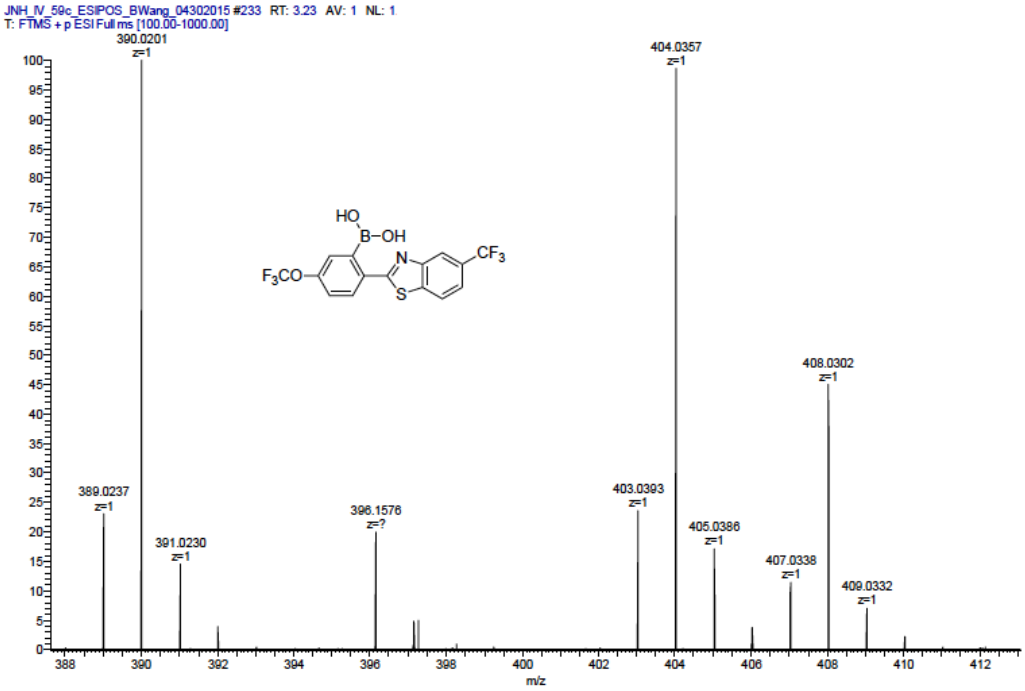

8.244
8.219
8.063
8.050
8.042
8.029
8.015
8.002
7.994
7.981
7.745
7.723
7.283
7.277
7.262
7.256
7.247
7.241
7.235
7.226
7.220
7.173
7.167
7.134
7.113
5.484
4.870
3.914
3.340
3.309
3.305
3.301
3.297
2.026
HO
B–OH
N
S
F
CF3
10
9
8
7
6
5
4
3
2
1
ppm
1.00
0.90
0.53
0.95
1.00
0.33
1.62
0.39
0.58
0.28
1.40
1.67

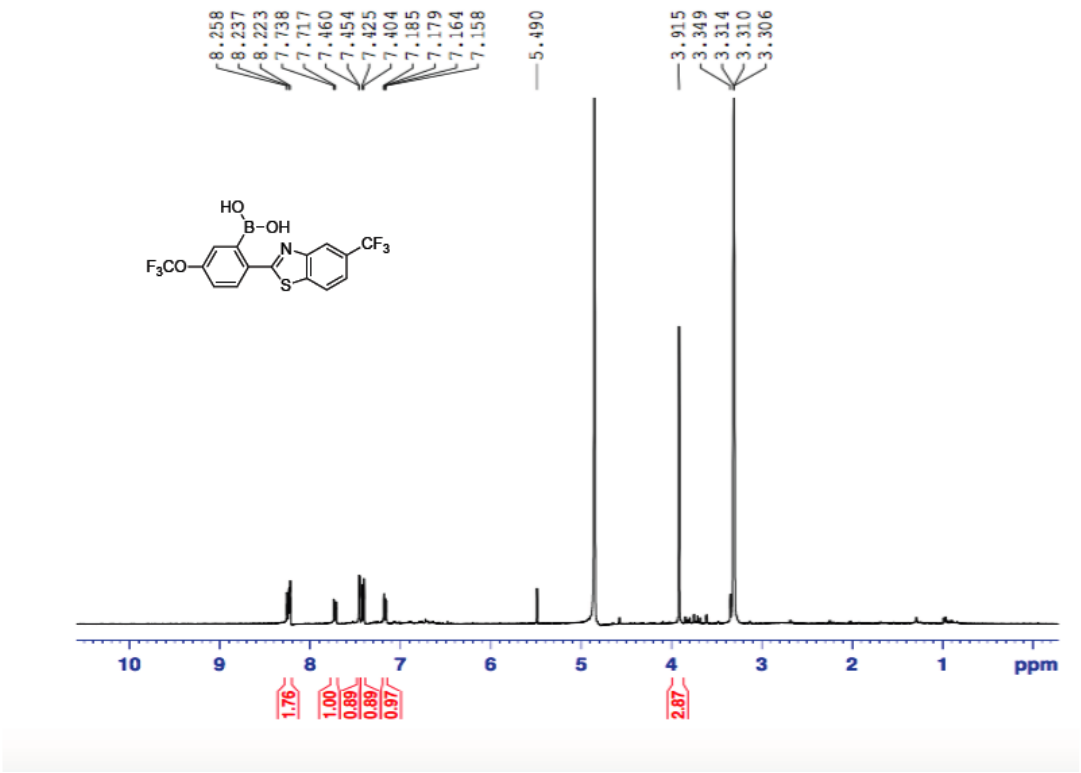

171.16
151.20
138.66
130.92
129.38
129.31
129.04
123.39
121.55
118.41
118.06
117.86
115.77
115.54
49.45
48.24
48.02
47.81
47.60
47.39
47.17
46.96
HO
B–OH
N
S
F
CF3
200
180
160
140
120
100
80
60
40
20
0
ppm

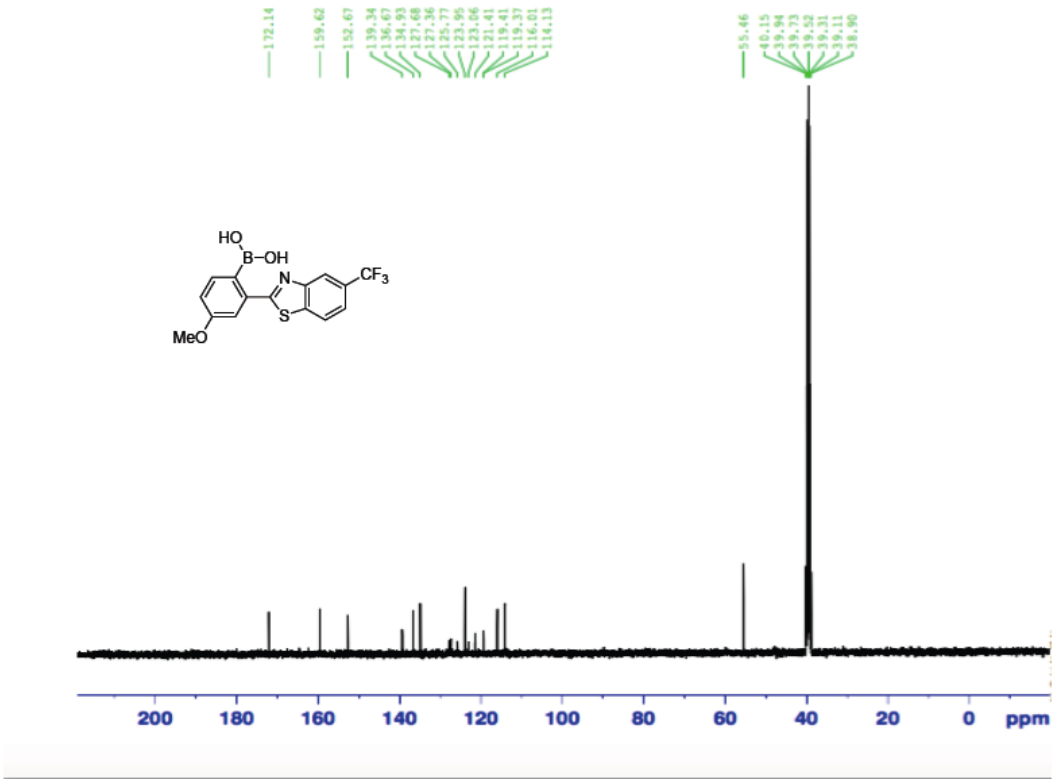

JALIGA_IV_31B_ESIPOS_BWANG_04232015 #149-170 RT: 2.17-2.46 NL: 4.44E7
T: FTMS + p ESI Full ms [100.00-1000.00]
342.0378
z=1
340.0223
z=1
341.0415
z=1
HO
B–OH
N
S
F
CF3
m/z

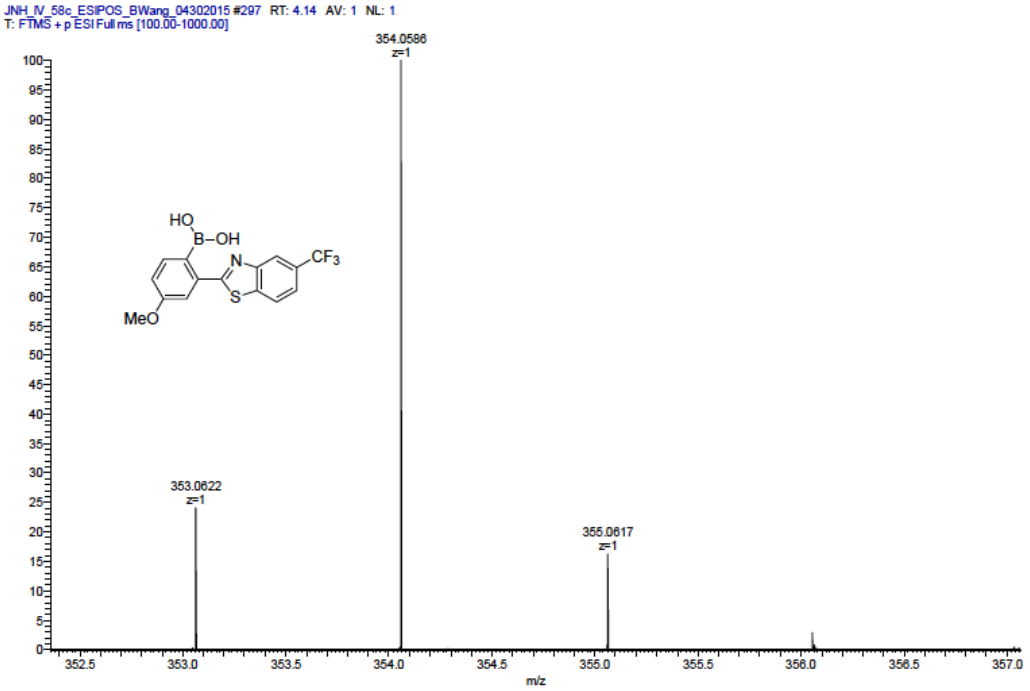

8.287
8.266
8.246
8.076
8.055
7.765
7.744
7.452
7.430
7.383
5.489
4.857
3.943
3.913
3.349
3.314
3.310
3.306
HO
B–OH
N
S
F3CO
CF3
10
9
8
7
6
5
4
3
2
1
ppm
1.93
0.97
1.00
1.10
0.95

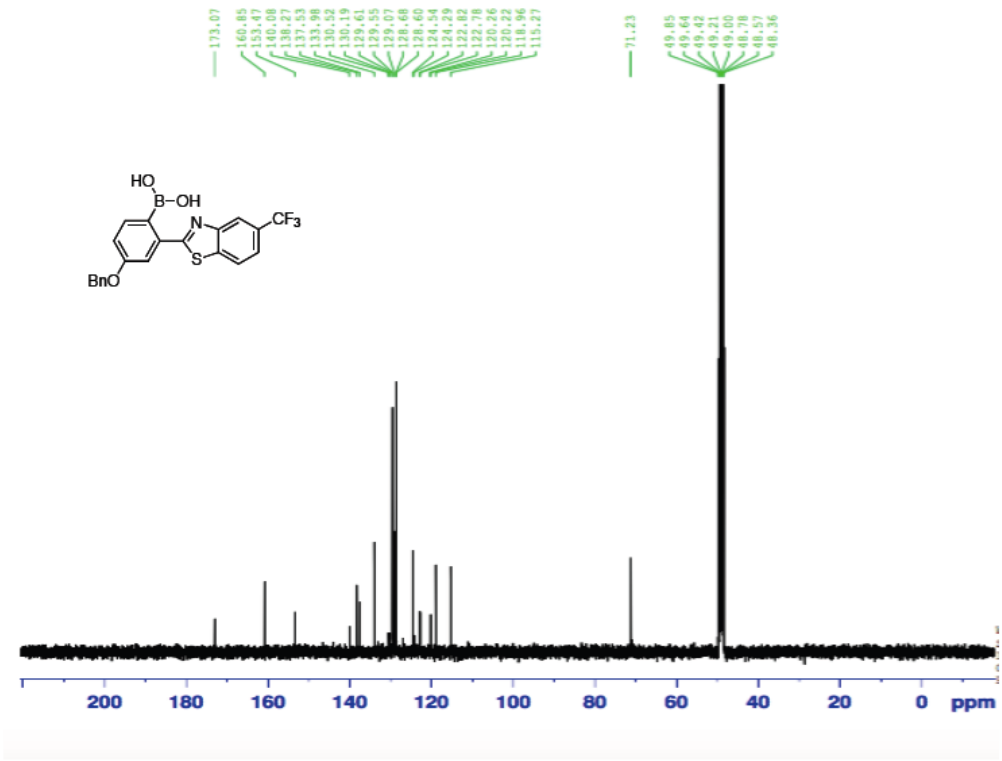

171.98
152.80
140.23
134.76
132.21
130.84
130.51
130.37
126.92
124.86
124.62
124.23
123.14
122.33
120.58
120.13
120.09
49.85
49.64
49.43
49.21
49.00
48.79
48.58
48.36
HO
B–OH
N
S
CF3
F3CO
200
180
160
140
120
100
80
60
40
20
0
ppm

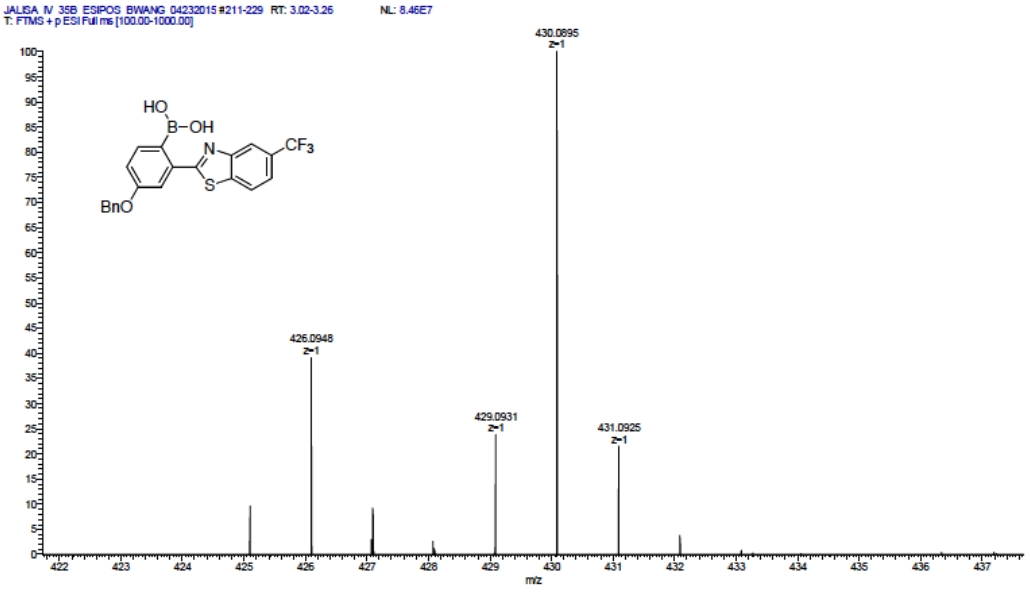

JNH_IV_59c_ESIPOS_BWang_04302015 #233 RT: 3.23 AV: 1 NL: 1
T: FTMS + p ESI Full ms [100.00-1000.00]
390.0201
z=1
404.0357
z=1
408.0302
z=1
389.0237
z=1
391.0230
z=1
396.1576
z=?
403.0393
z=1
405.0386
z=1
407.0338
z=1
409.0332
z=1
HO
B–OH
N
S
CF3
F3CO
m/z

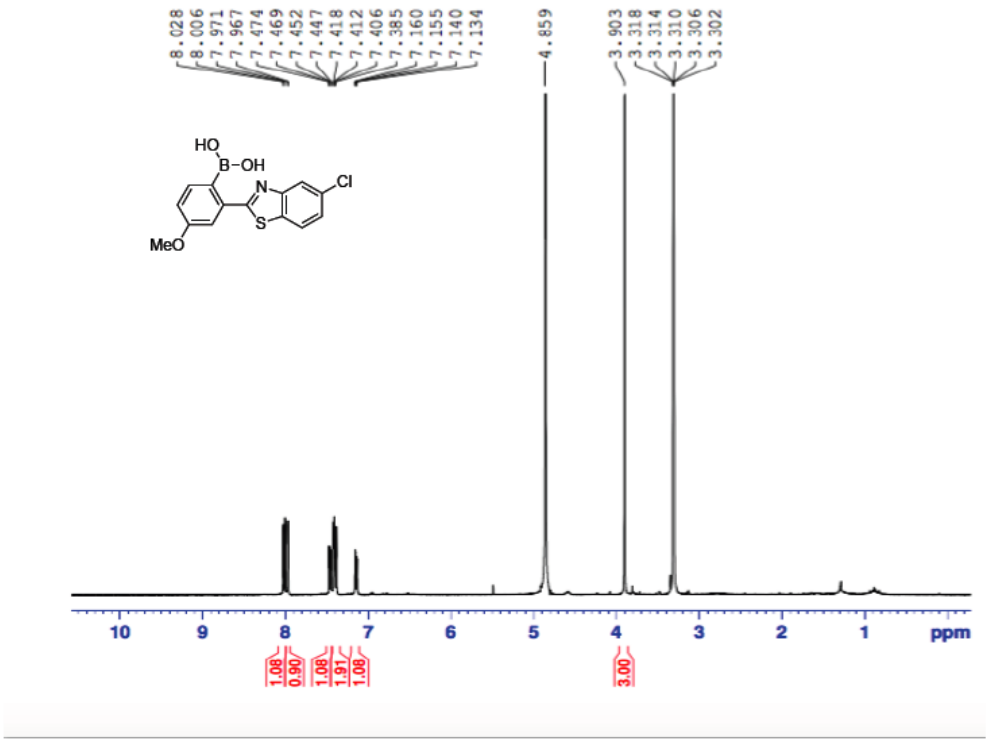

8.258
8.237
8.223
7.738
7.717
7.460
7.454
7.425
7.404
7.185
7.179
7.164
7.158
5.490
3.915
3.349
3.314
3.310
3.306
HO
B–OH
N
S
F3CO
CF3
10
9
8
7
6
5
4
3
2
1
ppm
1.76
1.00
0.89
0.89
0.97
2.87

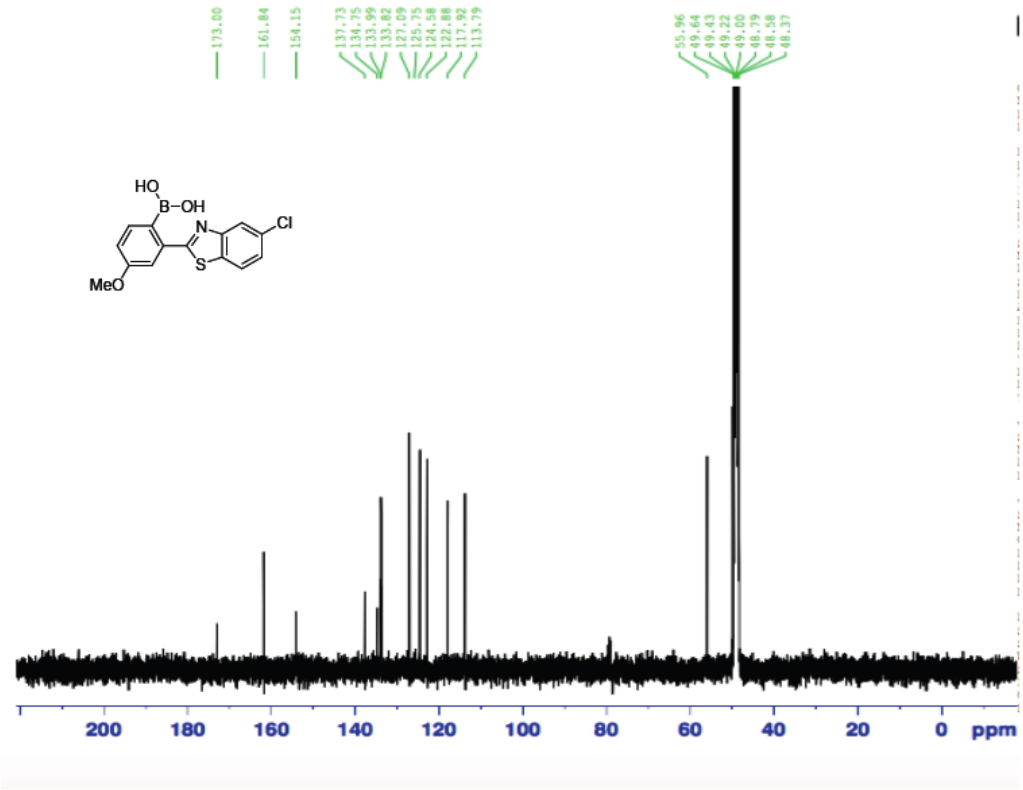

172.14
159.62
152.67
139.34
136.67
134.93
127.68
127.36
125.77
123.95
123.06
121.41
119.41
119.37
116.01
114.13
55.46
40.15
39.94
39.73
39.52
39.31
39.11
38.90
HO
B–OH
N
S
CF3
MeO
200
180
160
140
120
100
80
60
40
20
0
ppm

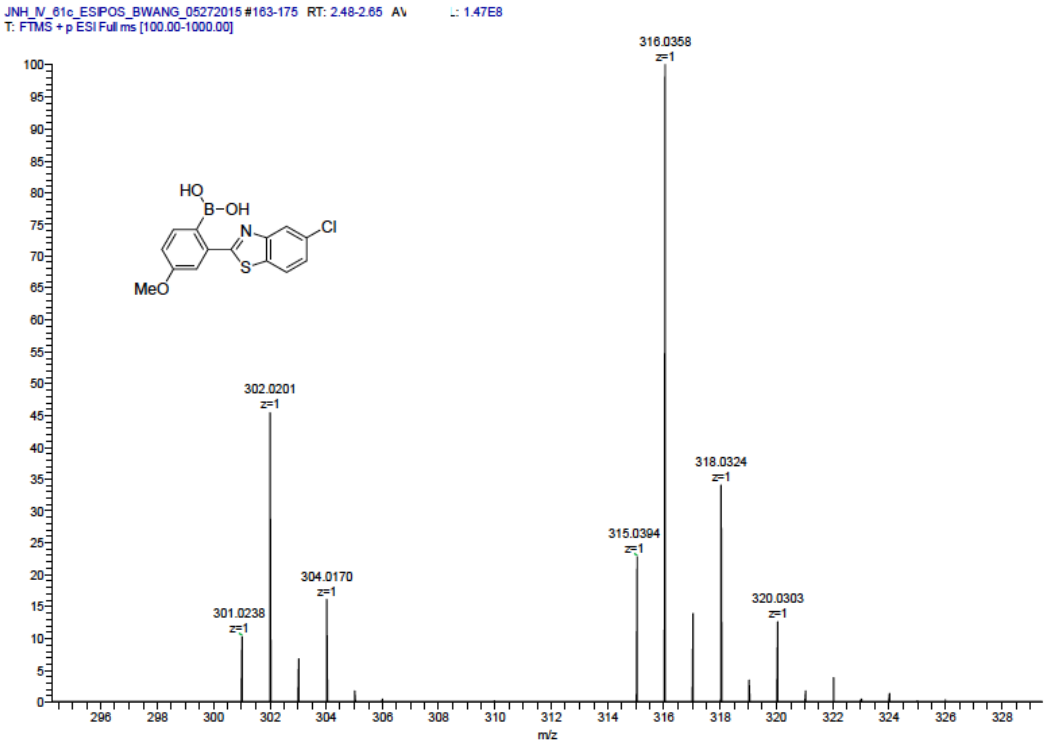

JNH_IV_58c_ESIPOS_BWang_04302015 #297 RT: 4.14 AV: 1 NL: 1
T: FTMS + p ESI Full ms [100.00-1000.00]
354.0586
z=1
353.0622
z=1
355.0617
z=1
HO
B–OH
N
S
CF3
MeO
m/z


HO
B–OH
N
S
CF3
BnO
200
180
160
140
120
100
80
60
40
20
0
ppm


JALIDA IV 35B ESIPOS BWANG 04232015 #211-229 RT: 3.02-3.26 NL: 8.46E7
T: FTMS + p ESI Full ms [100.00-1000.00]
430.0895
z=1
426.0948
z=1
429.0931
z=1
431.0925
z=1
HO
B–OH
N
S
CF3
BnO
m/z


8.028
8.006
7.971
7.967
7.474
7.469
7.452
7.447
7.418
7.412
7.406
7.385
7.160
7.155
7.140
7.134
4.859
3.903
3.318
3.314
3.310
3.306
3.302
HO
B–OH
N
S
Cl
MeO
10
9
8
7
6
5
4
3
2
1
ppm
1.08
0.90
1.08
1.91
1.08
3.00


173.00
161.84
154.15
137.73
134.75
133.99
133.82
127.09
125.75
124.58
122.88
117.92
113.79
55.96
49.64
49.43
49.22
49.00
48.79
48.58
48.37
HO
B–OH
N
Cl
S
MeO
200
180
160
140
120
100
80
60
40
20
0
ppm


JNH_IV_61c_ESIPOS_BWANG_05272015 #163-175 RT: 2.48-2.65 AV
T: FTMS + p ESI Full ms [100.00-1000.00]
316.0358
z=1
302.0201
z=1
318.0324
z=1
315.0394
z=1
304.0170
z=1
320.0303
z=1
301.0238
z=1
HO
B–OH
N
Cl
S
MeO
m/z