Silver Mediated Thio-Acetoxylation and TFA Triggered Cyclization of Amino Disulfides with Unactivated Alkenes: Synthesis of 3-Aryl/Alkyl-1,4-benzothiazines

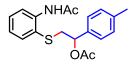
Ch. Durga Prasad, Ajay Verma, Moh. Sattar, Sangit Kumar*

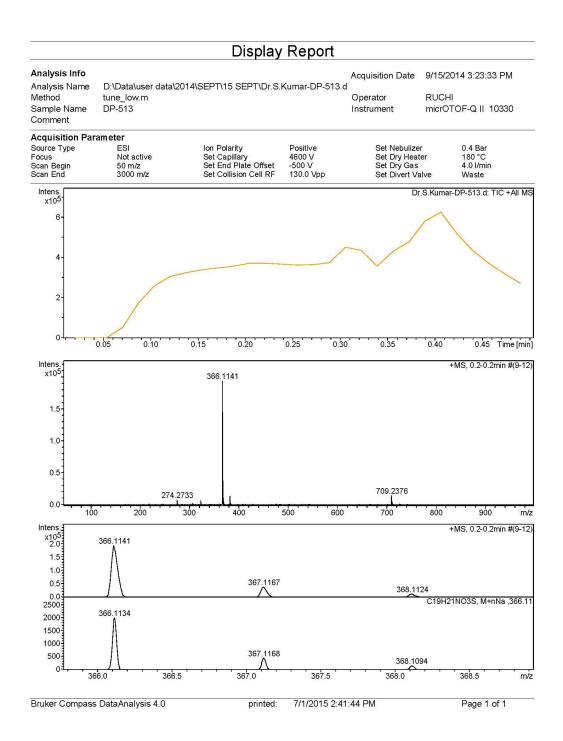
Content

HRMS of synthesized compounds

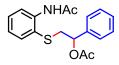
S2-S27

HRMS spectra of compound 1a





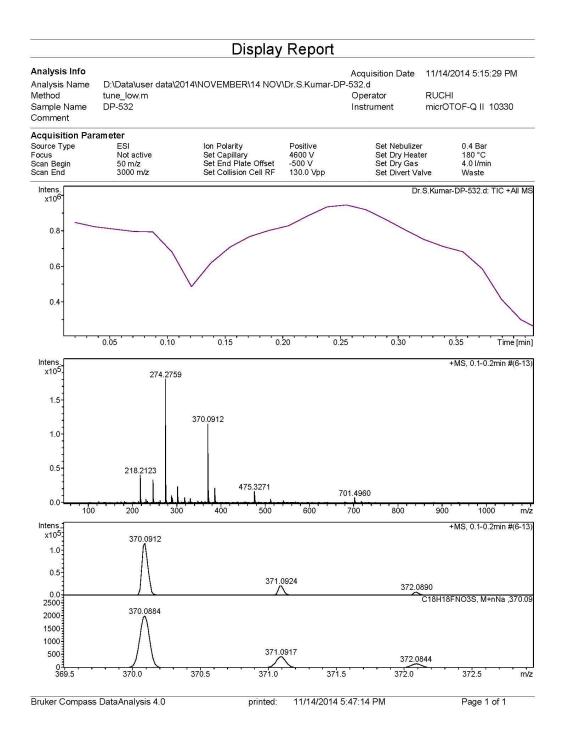
HRMS spectra of compound 1b



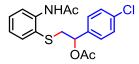
| | | | Report | | | |
|---|--|--|---|--|---------------|---------------------------------------|
| Analysis Info Analysis Name Method Sample Name Comment | D:\Data\user data\20 tune_low.m DP-535 | 14\NOVEMBER\17 NO\ | /\Dr.S.Kumar-DP-5 | Acquisition Date 335.d Operator Instrument | RUCHI | 4:25:10 AM Q II 10330 |
| Acquisition Par | rameter | | | | | |
| Source Type Focus Scan Begin Scan End | ESI Not active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | Positive 4600 V -500 V 130.0 Vpp | Set Nebulize Set Dry Heat Set Dry Gas Set Divert Ve | ter 18 4.0 | 4 Bar 30 °C 0 I/min ′aste |
| Intens. x10 ⁵ | | | | Dr | S.Kumar-DP- | 535.d: TIC +All N |
| x100 | | | | | | |
| 6- | | | \sim | | | |
| | | | \vee \ | | | |
| 4- | | | | | | |
| 1 | | | | N N | | |
| 2- | | | | | | |
| | | | | | | |
| مــــــ | | | | | | |
| | 0.1 | 0.2 0.3 | 3 0.4 | 4 0 | .5 | Time [mi |
| Intens x10 ⁵ | 25 | 2.1003 | | | +MS, 0 |).3-0.4min #(18-2 |
| | 33. | 2.1003 | | | | |
| - | | | | | | |
| 1.5- | | | | | | |
| 1.5- | | | | | | |
| 1.5- | 274.2762 | | | | | |
| | 274.2762 | | | | | |
| | 274.2762 | | | | | |
| 1.0 | 274.2762 | 475.3259 | 701 4932 | | | |
| 1.0 | 274.2762 | 475.3259 | 701.4932 | 800 | 1000 | , m |
| 1.0 0.5 0.0 | | Alexander Street | | 800 · | | , .3-0.4min #(18-2: |
| 1.0- 0.5- 0.0- | | Alexander Street | | 800 | | |
| 1.0- 0.5- 0.0- Intens. 2.0- 1.5- | | Alexander Street | | | | |
| 1.0- 0.5- 0.0- | | Alexander Street | 600 | | | |
| 1.0 0.5 0.0 Intens. x10 ⁵ 2.0 1.5 1.0 0.5 | | 400 | 600 | 800 · | +MS, 0 |).3-0.4min #(18-2 |
| 1.0- 0.5- 0.0- Intens. 2.0- 1.5- 1.0- 0.5- | | 400 | 600 | | +MS, 0 |).3-0.4min #(18-2 |
| 1.0 0.5 0.0 intens. x10 ⁵ 2.0 1.5 1.0 0.5 0.0 2500 2000 1500 | 200 352.1003 | 400 | 600 | | +MS, 0 |).3-0.4min #(18-2 |
| 1.0 0.5 0.0 1.5 1.0 0.5 0.0 2500 2500 1500 1500 1000 | 200 352.1003 | 400 | 354 | 0989 | +MS, 0 |).3-0.4min #(18-2 |
| 1.0 0.5 0.0 intens. x10 ⁵ 2.0 1.5 1.0 0.5 0.0 2500 2000 1500 | 200 352.1003 | 353.1028 353.1011 | 354 | 0989 | +MS, 0 | 0.3-0.4min #(18-2 3S, M+nNa ,352.1 |

HRMS spectra of compound 1c



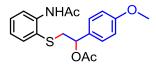


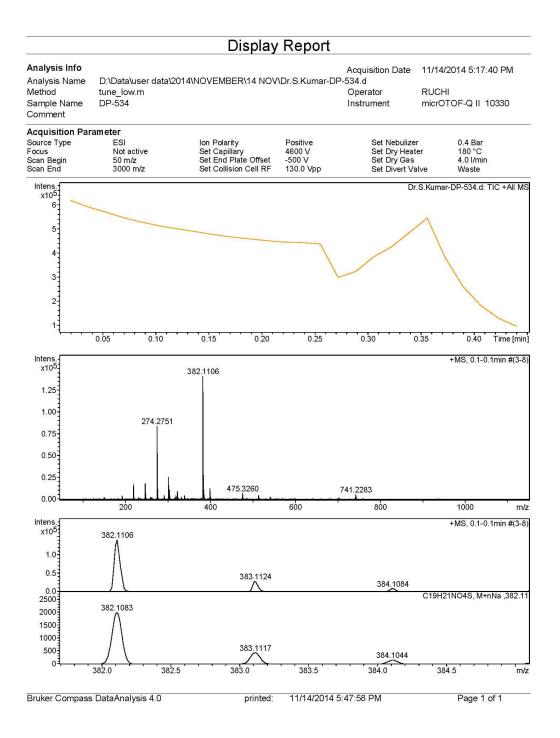
HRMS spectra of compound 1d



| | | Displa | y Report | | | |
|---|---|--|------------------|--|-------------------------------------|-----------------------------------|
| Analysis Info Analysis Name Method Sample Name Comment | D:\Data\user data\ HRLCMS-20 Sept. Dr.S.Kumar-DP-51 | | Kumar-DP-515_1-/ | Acquisition Date A,6_01_60.d Operator Instrument | 9/12/2014 2: RUCHI micrOTOF-C | |
| Acquisition Par Source Type Focus Scan Begin Scan End | ameter ESI Active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | | Set Nebulize Set Dry Heat Set Dry Gas Set Divert Va | er 200 7.0 | °C I/min |
| Intens x10 ⁶ 1.00 0.75 0.50 0.25 | | | | Dr.S.Kumar-DP- | 515_1-A,6_01_6 | 30.d: TIC +All M |
| Intens. [mAU] x10 ⁵ 2 1 1 | | M | Dr.S.Kumar-DF | 2-515_1-A,6_01_60.d | : UV Chromatog | ram, 200-400 n |
| · · · · · · | 1 | 2 | 3 | 4 | 5 | Time [mi |
| 200 Intens- [mAU] 1000 500 | 220 240 | 260 280 | 300 321 | 0 <u>340</u> | 360 UV, 2.6-2.7m | Wavelength [nn in #(1504-1597) |
| Intens x10 ⁵ 1.0 0.5 0.0 100 | 166.0324 | 304.0569 386.0602 300 400 | 500 600 | 749.12 | | .7min #(153-16 900 m |
| Intens. | | | | | +MS, 2.6-2 | .7min #(153-16 |
| 0.0 | 66.0602 | 387.0616 A | 388.0562 | | 9.0586 C18H18CINO38 | 6, M+nNa ,386.(|
| 2000 - So 1000 - | | 387.0621 A | 388.0560 A | 38 | 9.0592 | |
| ₀ 1, , , , , , , , , , , , , , , , , , , | 36.0 386.5 | 387.0 387.5 | 388.0 | 388.5 388 | 9.0 389 |).5 m |

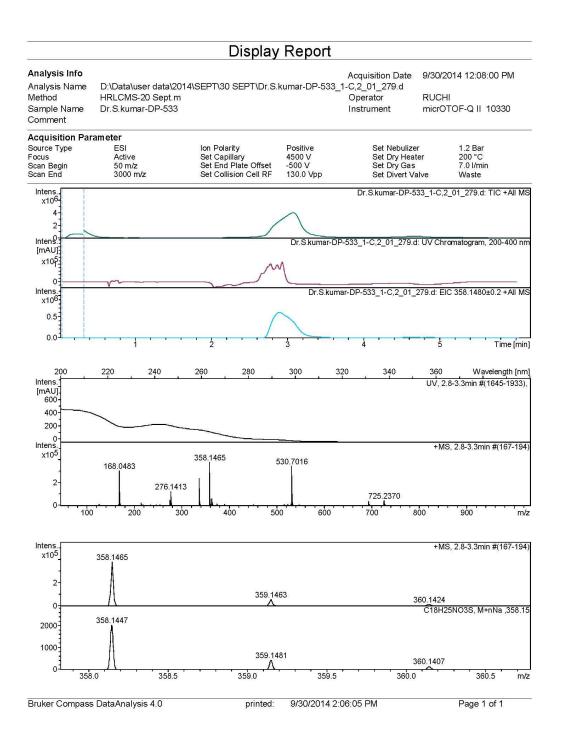
HRMS spectra of compound 1e



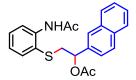


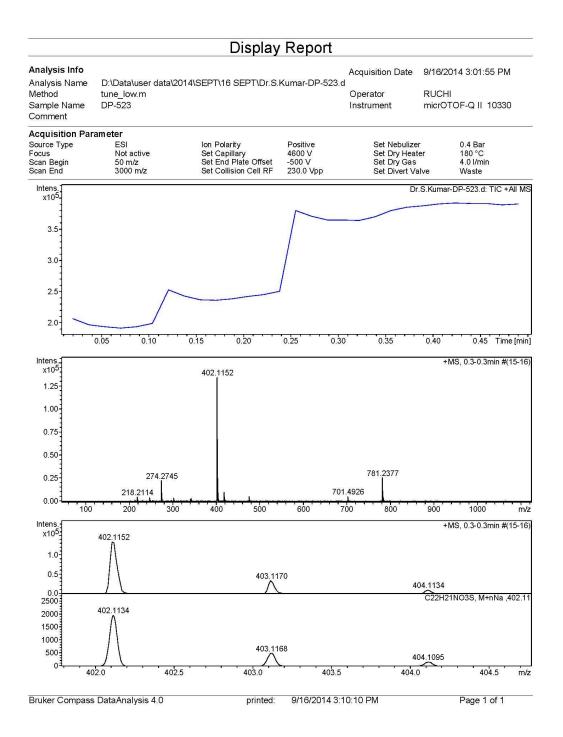
HRMS spectra of compound 1f



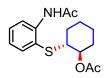


HRMS spectra of compound 1g

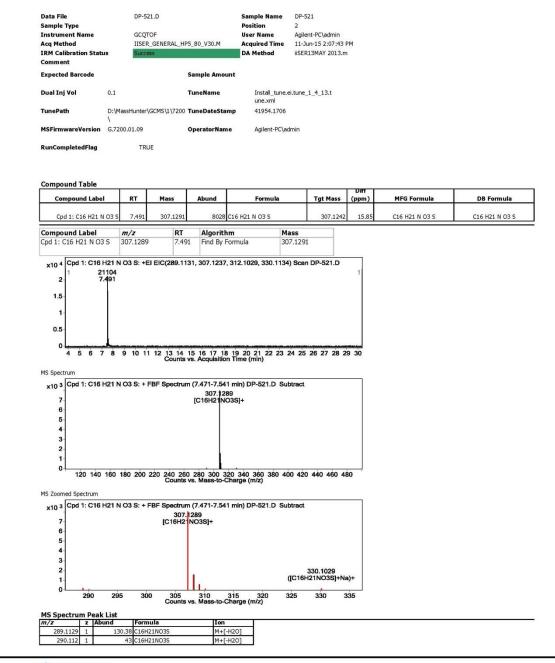




HRMS spectra of compound 1h



Qualitative Compound Report

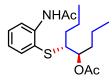


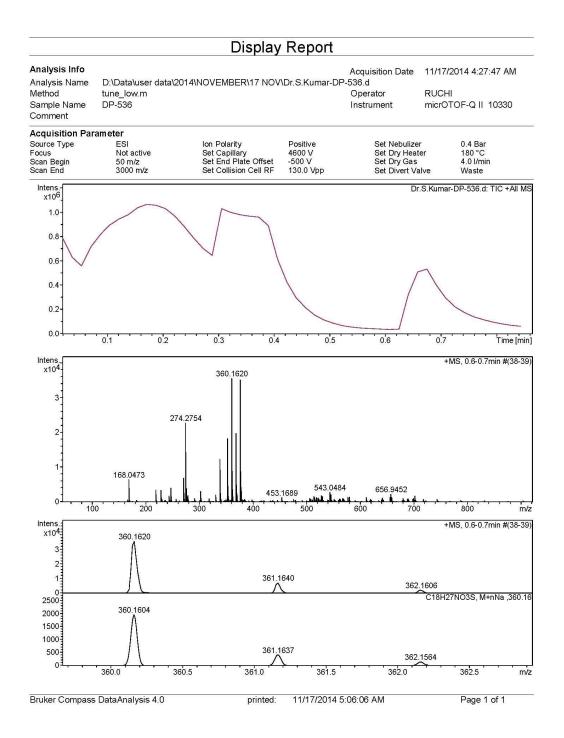
Agilent Technologies

Page 1 of 2

Printed at: 3:37 PM on:11-06-15

HRMS spectra of compound 1i





HRMS spectra of compound 1j



| | | | Displa | y Report | | | | |
|---|---|---------------|--|---|---|------------|---|--------------------|
| Analysis Info Analysis Name Method Sample Name Comment | D:∖Data∖user o tune_low.m DP-540 | data\2014\NO\ | /EMBER\17 NO | V\Dr.S.Kumar-D | Acquisition Date P-540.d Operator Instrument | RUCH | /2014 4:30:38 / HI)TOF-Q II 1033 | |
| Acquisition Par Source Type Focus Scan Begin Scan End | a meter ESI Not active 50 m/z 3000 m/z | Sel | Polarity t Capillary t End Plate Offset t Collision Cell RF | Positive 4600 V -500 V 230.0 Vpp | Set Nebuli Set Dry He Set Dry Ga Set Divert | ater Is | 0.4 Bar 180 °C 4.0 I/min Waste | |
| Intens. x106 1.1 1.0 1.0 | | | | | | Dr.S.Kuma | ar-DP-540.d: TIC - | -AII M |
| 0.9 Intens. x10 ⁵ | 0.05 0.2 | 10 0.15 | in and the second s | 0.25 | 0.30 0.3 | 35 | 0.40 Tin +MS, 0.0r | ne [mir nin #(2 |
| 2.5 2.0 1.5 1.0 0.5 | 100 · · · · | 150 20 | 218.2117 | L., L., | 350 400 | 428.1306 | 475.3251 512 50 500 | .5035 m/ |
| Intens. x10 ⁵ 0.75 0.50 0.25 0.00 | 428.1306 | | 429.1331 | | 430.1307 | | +MS, 0.0r | |
| 2500 | 428.1291 A | | | | | C24H2 | 23NO3S, M+nNa | ,428.1 |
| 2000 1500 1000 500 | 428.0 | 428.5 | 429.1324 | 429.5 | 430.1252 | 0.5 | 431. <u>1</u> 283 431.0 | |

HRMS spectra of compound 1k



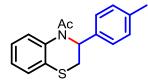
| | | Display | Report | | |
|--|---|--|---|--|---|
| Analysis Info Analysis Name Aethod Sample Name Comment | D:\Data\user data\20 HRLCMS-20 Sept.m Dr.S.Kumar-DP-549 | 015\JUNE-2015\10-JUNE า | | nar-DP-549_1-A,5_01_2 Operator RU | 10/2015 2:49:30 PM /744.d JCHI crOTOF-Q II 10330 |
| Acquisition Par Source Type Focus Scan Begin Scan End | rameter ESI Active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | Positive 4500 V -500 V 130.0 Vpp | Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve | 1.2 Bar 200 °C 7.0 I/min Waste |
| Intens x10 ⁶ 1.00 0.75 0.50 0.25 | | ~~~ | \bigwedge | Dr.S.Kumar-DP-549_1- | A,5_01_2744.d: TIC +AII N |
| Intens [mAU] x10 ⁵ 0.50 0.25 0.00 | v | | Dr.S.Kumar-DP | -549_1-A,5_01_2744.d: UV | ' Chromatogram, 200-400 r |
| 1 | 1 2 | 3 | 4 | 5 6 | 7 Time [m |
| 200 Intens. [mAU] 500 | 220 240 | 260 280 | 300 3 | 1 7 1 1 | 360 Wavelength [ni V, 4.3-4.4min #(2559-2621 |
| 0 Intens. x10 ⁵ 2 | 230.0632 | 398.1786 | | | +MS, 4.3-4.4min #(258-26 |
| | 0 200 | | 500 | 600 700 | 817.3325 800 m |
| | | | | | |
| Intens x10 ⁵ 2 | 398.1786 | | | | +MS, 4.3-4.4min #(258-26 |
| x105 2 1 | \bigwedge | 399.1802 A | | 400 <u>.1</u> 781 | |
| x10 ⁵ 2 1 0 | 398.1786 398.1784 | 399.1802 399.1818 | | | +MS, 4.3-4.4min #(258-26 |

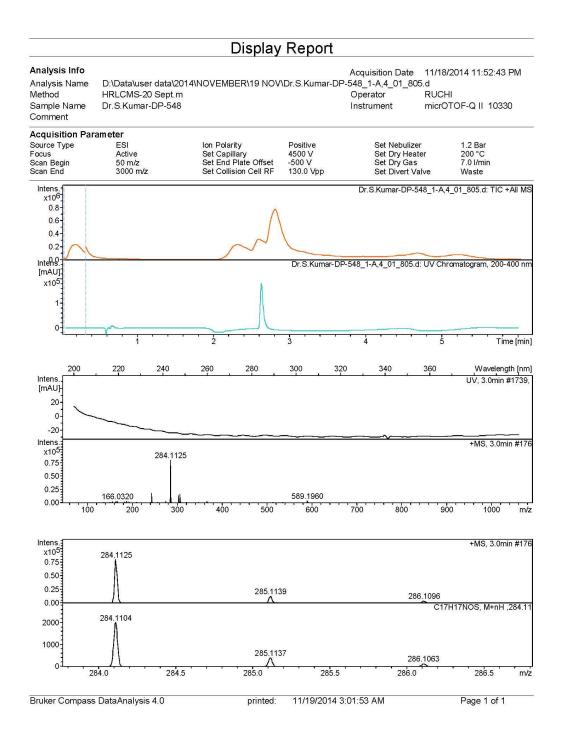
HRMS spectra of compound 1m



| | | Display | / Report | t | | |
|--|--|--|---|---|--------------------------------------|--|
| Analysis Info Analysis Name Method Sample Name Comment | D:\Data\user data HRLCMS-20 Sept Dr.S.Kumar-DP-5 | | .Kumar-DP-5 | Acquisition Date 25_1-A,5_01_180.d Operator Instrument | 9/22/2014 1:1 RUCHI micrOTOF-Q | |
| Acquisition Para Source Type Focus Scan Begin Scan End | ameter ESI Active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | Positive 4500 V -500 V 130.0 Vpp | Set Nebuliz Set Dry He Set Dry Ga Set Divert 1 | ater 200 Is 7.0 I | °C /min |
| Intens. x10 ⁶ | | | | Dr.S.Kumar-DP | -525_1-A,5_01_18 | 0.d: TIC +All MS |
| Intens. [mAU] x102 | | Л | Dr.S.Kumar | -DP-525_1-A,5_01_180 | l.d: UV Chromatogr | am, 200-400 nm |
| 0 Intens x10 ⁵ 2 1 | | \wedge | Dr.S.K | umar-DP-525_1-A,5_01 | _180.d: EIC 334.1 | 528±0.2 +All MS |
| 200 Intens. [mAU]- | 220 240 | 2 260 280 | 300 | 320 340 | 1 1 1 | Time [min] Wavelength [nm] n #(1561-1615), |
| 400 200- Intens x10 ⁵ | 274.12 | 76 | | | +MS, 2.6-2. | 7min #(157-162) |
| 2 1 0 | | 334.1483 | 600 | 700 800 | 900 | 1000 m/z |
| 1.0 | 34.1483 | | | | +MS, 2.6-2. | 7min #(157-162) |
| 2000- | 34.1471 | 335. | 1490 | | 336,1457 C18H23NO35 | 8, M+nH ,334.15 |
| 1000- 0- 334.00 | 334.25 334.5 | | 1505 \ 335.25 3 | 35.50 335.75 | 336.1431 336.00 336.25 | 5 m/z |
| Bruker Compass | DataAnalysis 4.0 | printed: | 9/22/2014 | 1:43:15 PM | Pag | e 1 of 1 |

HRMS spectra of compound 2a



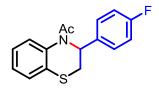


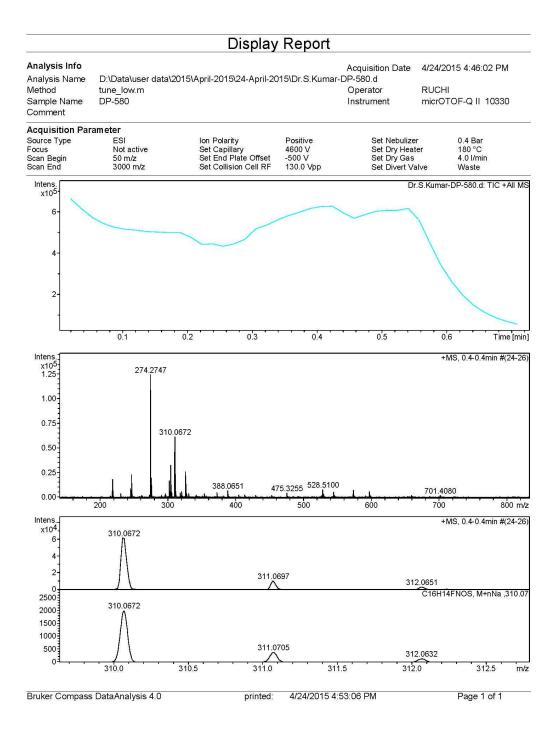
HRMS spectra of compound 2b



| | | Display | Report | | | |
|--|--|--|---|--|------------------|--|
| Analysis Info Analysis Name Aethod Sample Name Comment | D:\Data\user data\2 tune_low.m DP-535-E | 2015\JUNE-2015\04-june-2 | 2015\Dr.S.Kumai | Acquisition Date r-DP-535-E.d Operator Instrument | RUCHI | 5 10:39:53 AM OF-Q II 10330 |
| acquisition Par cource Type ocus can Begin can End | rameter ESI Not active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | Positive 4600 V -500 V 130.0 Vpp | Set Nebulize Set Dry Heat Set Dry Gas Set Divert Va | er | 0.4 Bar 180 °C 4.0 I/min Source |
| Intens. x10 ⁵ 6- | | | $\overline{}$ | | | |
| 4- 2- | | | | | | |
| о <mark>]</mark> [тіс | 0.1 0.2 | 0.3 0.4 | 0.5 0. | 6 0.7 | 0.8 | 0.9 Time [mi |
| Intens. | | | | | +N | 1S, 0.5-0.6min #(32-3 |
| x10 ⁴ 1.25- | | 414.1521 | | | | |
| 1.00 0.75 0.50 | 27 | 4.2750 374.1597 | | | | |
| - | 24.0219 | | 506.5324 | 614.7231 701.49 | 40 e | 305.3089 |
| 0.00 | <u>مار با از جمع میں از _</u> | والمجد الكركان والدربال فراجه المغاب الكركان الكراك | فطيعه كالقريف واللبيان | · · · · · · · · · · · · · · · · · · · | | ╴╷╸┥╺╻╸ |
| 0.00 - 10 10 | <u>مار با از جمع میں از _</u> | 300 400 | 500 | 600 700 | + N | |
| 0.00 10 10 Intens. | <u>مار با از جمع میں از _</u> | | | 600 700 | +N | |
| 10.00 10 ntens. 2000 1000 | <u>, ing an ing an</u> | 271.096 | | 600 700 | 272.0958 | 1S, 0.5-0.6min #(32-3 |
| 10.00 100 1000 1000 1000 2500 | <u>, ing an ing an</u> | | 32 | 600 700 | 272.0958 С16Н | 1S, 0.5-0.6min #(32-3 |
| 1 0.00 100 1000 22000 2000 2000 2000 200 | 70.0953 70.0947 | 271.09 | 32 | | 272.0958 | 1S, 0.5-0.6min #(32-3 |

HRMS spectra of compound 2c



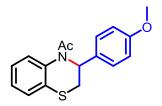


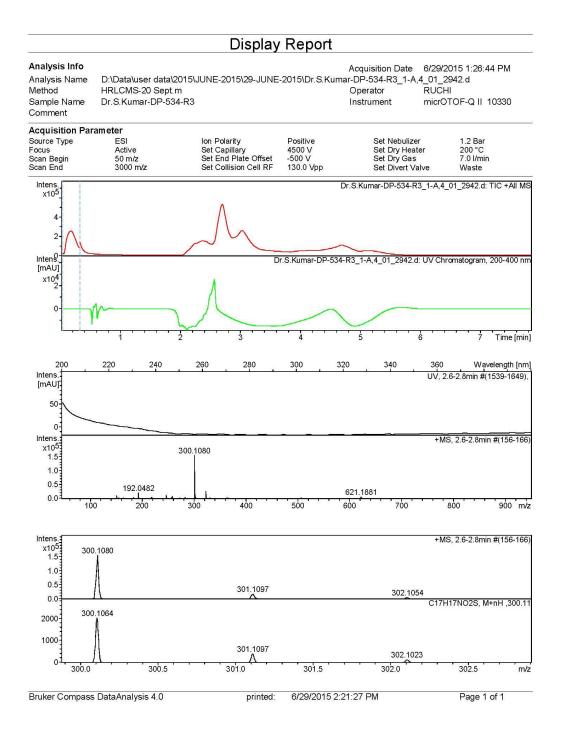
HRMS spectra of compound 2d



| | | Display | Report | | | | |
|--|--|--|---|--|--------------|---|-------------------|
| Analysis Info Analysis Name Method Sample Name Comment | D:\Data\user data' tune_low.m DP-556 | 2015\April-2015\24-April-2(| 015\Dr.S.Kumar- | Acquisition Date DP-556.d Operator Instrument | RUCHI | 15 4:32:26 PN OF-Q II 1033 | |
| Acquisition Par Source Type Focus Scan Begin Scan End | am eter ESI Not active 50 m/z 3000 m/z | Ion Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | Positive 4600 V -500 V 130.0 Vpp | Set Nebuli Set Dry He Set Dry Ga Set Divert | eater as | 0.4 Bar 180 °C 4.0 I/min Waste | |
| Intens. x105 5 4 4 3 4 2 2 | 0.1 | | 0.4 | 0.5 | Dr.S.Kumar-I | DP-556.d: TIC + | AII MS |
| Intens. x10 ⁴ - | | | | | | +MS, 0.3mi | |
| - | 286.143 I | 31 | 344.0499 | | | | |
| 1.0- - 0.8- | | | | | | | |
| 0.6- | | | | | | | |
| 0.4- | 274.2753 | | 7 | 360.0295 | | | |
| 0.2- | | 296.1401 | | 2 | 386.0608 | 3 | |
| 0.0 262. | 0464 | 304.0579 10.0.10.00 300 320 | | 376 | .0190 | 402.035141 400 | 3.2664 m/z |
| Intens. | | | | | | +MS, 0.3mi | n #(17) |
| 800- 304.057 | | | | | | | |
| 600- 400- | 304.2619 N | | 306.0571 | | | | |
| 200- | A | | 308.0571 A | | | | |
| 2500 | | <u></u> | <u> </u> | ~ | C16H14 | CINOS, M+nH | 304.06 |
| 2000 304.055 | 57 | | | | | 8 | |
| 1500 | | | | | | | |
| 1000 | | | 306.0528 | | | | |
| 500 | | 305.0591 | <u> </u> | | 307.0561 | | |
| 304.0 | 304.5 | 305.0 305.5 | 306.0 | 306.5 | 307.0 | 307.5 | m/z |
| Bruker Compass | DataAnalysis 4.0 | printed: | 4/24/2015 4: | 52:13 PM | | Page 1 of 1 | |

HRMS spectra of compound 2e

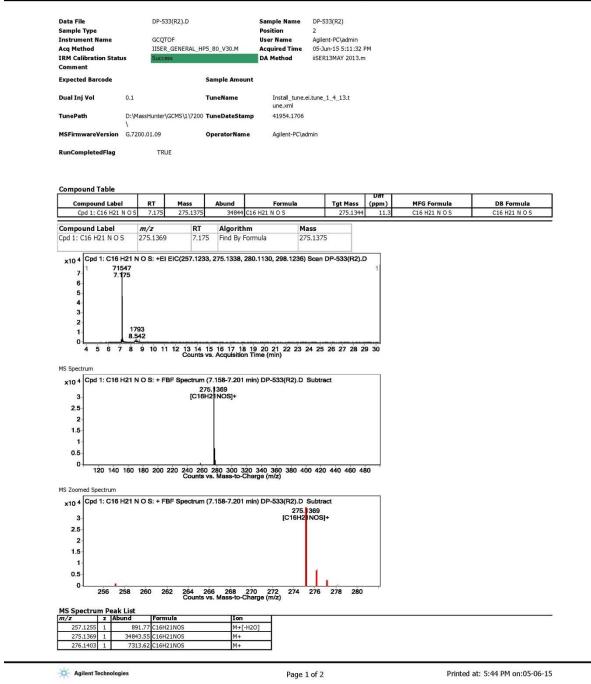




HRMS spectra of compound 2f

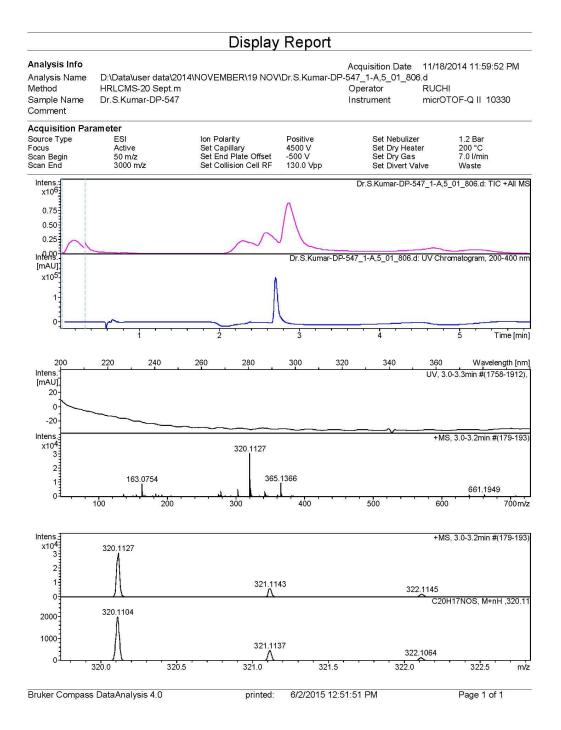


Qualitative Compound Report

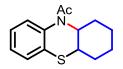


HRMS spectra of compound 2g





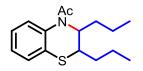
HRMS spectra of compound 2h

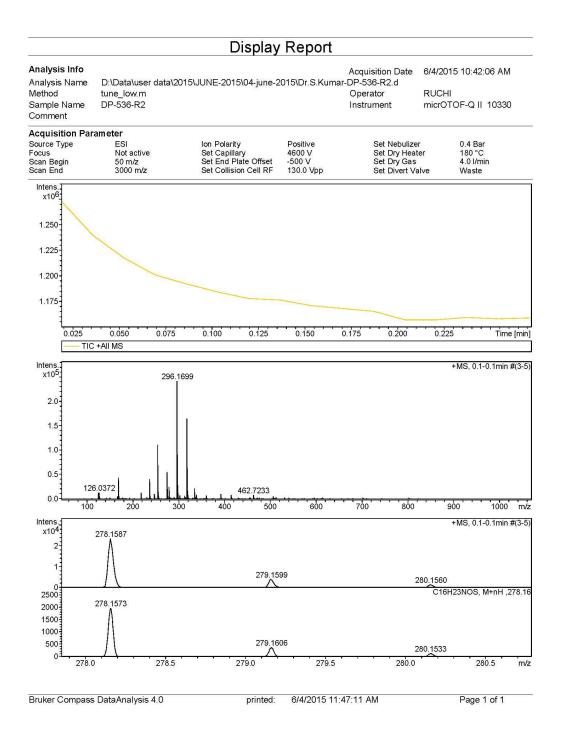


| | | Display | Report | | |
|---|--|--|---|--|---|
| Analysis Info Analysis Name Method Sample Name Comment | D:\Data\user data\/ tune_low.m DP-564 | 2015\JUNE-2015\02-JUNE | -2015\Dr.S.Kumar (| Acquisition Date -DP-564.d Operator Instrument | 6/2/2015 4:42:50 PM RUCHI micrOTOF-Q II 10330 |
| Acquisition Par Source Type Focus Scan Begin Scan End | ra meter ESI Not active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | Positive 4600 V -500 V 130.0 Vpp | Set Nebulize Set Dry Heat Set Dry Gas Set Divert Va | er 180 °C 4.0 l/min |
| Intens. x10 ⁶ 1.0- 0.8- 0.6- 0.4- 0.2- | | \bigwedge | | Dr | S.Kumar-DP-564.d: TIC +All N |
| 0.0 | 0.2 | 0.4 0.6 116 288.1046 | 0.8 | 1.0 | 1.2 Time [m +MS, 0.4-0.6min #(22-3 |
| 0.5 | 124.0215 00 200 | 41 | 7.6530 475.3247 0 500 | 600 | 683.1749 • • • • • • • • • • • • • • • • • • • |
| Intens. x104 0.75 0.50 | 248.1102 | | | | +MS, 0.4-0.6min #(22-3 |
| 0.25 0.00 2500 | | 249,1284 | | 250.1119 | C14H17NOS, M+nH ,248. |
| 2000 1500 1000 | 248.1104 | | | | |

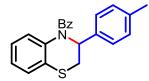
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HRMS spectra of compound 2i





HRMS spectra of compound 2j

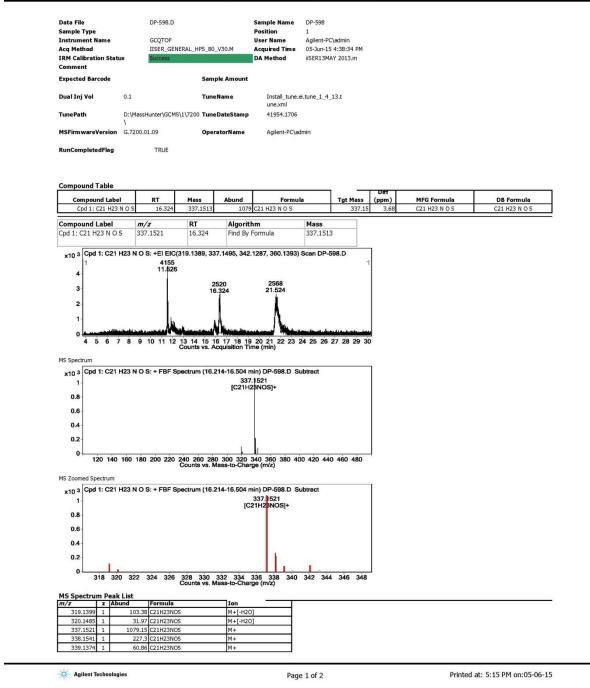


| | | Dis | play Re | port | | | |
|---|--|---|--------------|-------------------|---|-------------------------------------|--------------------------------|
| Analysis Info Analysis Name Method Sample Name Comment | D:\Data\user data\ tune_wide.m DP-554-1 | 2015\JUNE-2015\0 | 1-JUNE-2015\ | Dr.S.Kumar-D O | equisition Date)P-554-1.d perator strument | 6/1/2015 5:0 RUCHI micrOTOF-G | |
| Acquisition Par Source Type Focus Scan Begin Scan End | am eter ESI Not active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Set Collision (| | V | Set Nebulizer Set Dry Heat Set Dry Gas Set Divert Va | er 180 4.0 | °C /min |
| Intens x106 2.0 1.5 1.0 0.5 | | | | | Dr.S | Kumar-DP-554 | 1.d: TIC +AII MS |
| 0.0 | · · · · · · · · · · · · · · · · · · · | | 75.3273 | | 713.2266 | 873.6223 | MS, 0.1min #(7 |
| 100 Intens. x105 3 2 1 | 368.1090 | 300 400 | 369.1110 | 600 | 700 800 | | ' 1000' m/; ∙MS, 0.1min #(7 |
| 0 2500 1500 1000 500 | 368.1080 | | 369.1113 | | 370. | C22H19NOS | , M+nNa ,368.11 |
| | 368.0 | 368.5 | 369.0 | 369.5 | 370.0 | 37 | 0.5 m/z |

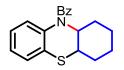
HRMS spectra of compound 2k



Qualitative Compound Report



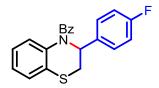
HRMS spectra of compound 21

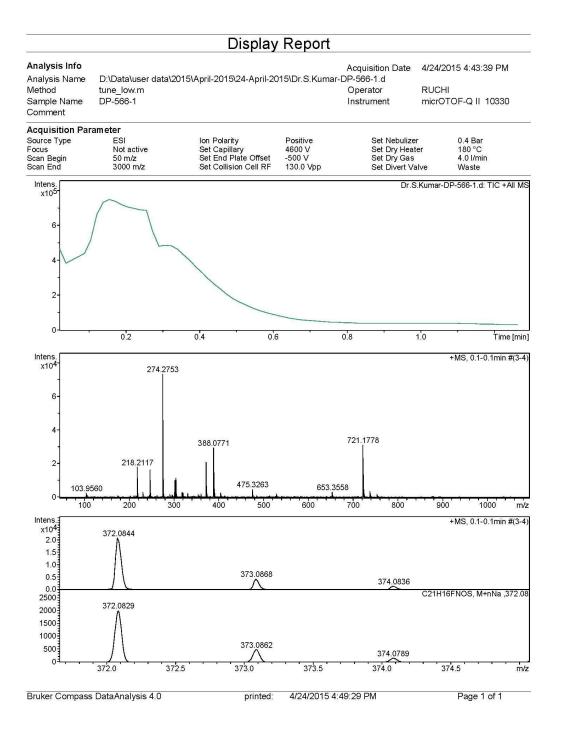


| | | Display | Report | | | |
|--|--|--|---|--|---|---|
| Analysis Info Analysis Name Method Sample Name Comment | D:\Data\user dat tune_low.m DP-562-R | a\2015\JUNE-2015\02-JUNE | -2015\Dr.S.Kumar- (| Acquisition Date DP-562-R.d Dperator nstrument | RUCHI | 94:45:48 PM DF-Q II 10330 |
| Acquisition Par Source Type Focus Scan Begin Scan End | rameter ESI Not active 50 m/z 3000 m/z | lon Polarity Set Capillary Set End Plate Offset Set Collision Cell RF | Positive 4600 V -500 V 130.0 Vpp | Set Nebulize Set Dry Heat Set Dry Gas Set Divert Va | ter | 0.4 Bar 180 °C 4.0 I/min Waste |
| Intens. x106 0.8- 0.6- 0.4- 0.2- 0.0 | | | · · · · · · · · · · · | | | 562-R.d: TIC +AI |
| | | | | 0.5 | 0 | .6 Time [n |
| Intens. | 0.1 | 0.2 0.3 | 0.4 | 0.5 | | IS, 0.1-0.2min #(7- |
| Intens. x104- 6- 4- 2- | 228.0484 | 0.2 0.3 | 679.510 | 86 | | |
| Intens. x104- 6- 4- 2- 0 | 228.0484 | 328.1382 | | 5 773.2290 ⁸⁶¹ | +M 9.2096 | IS, 0.1-0.2min #(7- |
| Intens. x104 6 4 2 0 100 Intens. x104 2 1 0 2500 2500 2000 1500 | 228.0484 | 328.1382 | 679.510 | 5 773.2290 ⁸⁶³ | 9.2096 → , , , , , , , , , , , , , , , , , , , | IS, 0.1-0.2min #(7- |
| Intens. x104 6 4 2 0 100 Intens. x104 310 2 500 2000 310 | 228.0484 | | 679.510 600 700 | 5 773.2290 ⁸⁶³ 0 800 3 | 9.2096 → , , , , , , , , , , , , , , , , , , , | IS, 0.1-0.2min #(7- |

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HRMS spectra of compound 3a





HRMS spectra of compound 3b



