Supporting Information

Metal- and Base-Free Domino Protocol for the Synthesis of 1,3-Benzoselenazines, 1,3-Benzothiazines and Related Scaffolds

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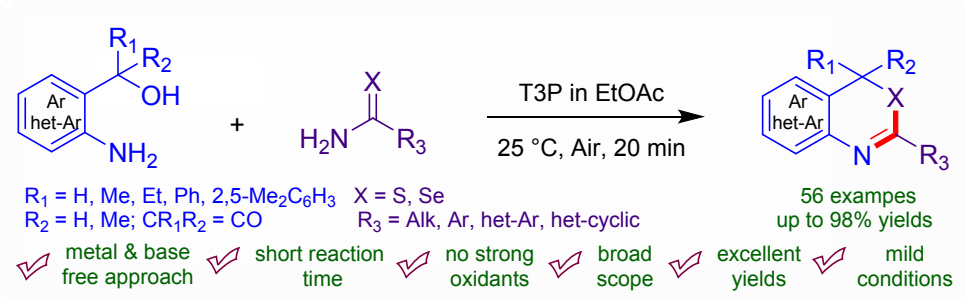


1. General methods

All starting materials were purchased from commercial suppliers (Sigma-Aldrich, Alfa-Aesar, SD fine chemicals, Merck, HI Media) and were used without further purification unless otherwise indicated. All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. The reactions were performed in pressure tube purchased from Sigma-Aldrich glassware. Solvents used in extraction and purification were distilled prior to use. Thin-layer chromatography (TLC) was performed on TLC plates purchase from Merck. Compounds were visualized with UV light (λ = 254 nm) and/or by immersion in $KMnO_4$ staining solution followed by heating. Products were purified by column chromatography on

silica gel, 100 - 200 mesh. ^{1}H (^{13}C) NMR spectra were recorded at 400 (100) MHz on a Brucker spectrometer using $CDCl_3$ and DMSO-d_6 as a solvent. The ^{1}H and ^{13}C chemical shifts were referenced to residual solvent signals at $\delta_{H/C}$ 7.26 /77.28 ($CDCl_3$) and $\delta_{H/C}$ 2.51 /39.50 (DMSO-d_6) relative to TMS as internal standards. Coupling constants J [Hz] were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), overlapped and br (broad).

2. General experimental procedure for the synthesis of 1,3-benzoselenazines (3aa-ah, 3ba-la) and 1,3-benzothiazines (5aa-as, 5ba-oa, 5pt)

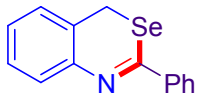
A 10 mL reaction vial was charged with aryl/htero-aryl alkyl alcohols **1a**-p (1.0 mmol), selenocarboxamide **2a-h** (1.0 mmol) or thiocarboxamides **4a**-s (1.0 mmol), T3P anhydride solution ≥50 wt. % in ethyl acetate (1.1 mmol). The reaction mixture was then stirred at 25 °C for 20 minutes in an open vial. After completion of the reaction (progress was monitored by TLC; SiO_2, Hexane/EtOAc = 95:5), the mixture was diluted with ethyl acetate (15 mL) and water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the remaining residue was purified by column chromatography over silica gel using hexane / ethyl acetate = 95:5 as an eluent to obtain the desired 1,3-benzoselenazines (**3aa-ah**, **3ba-la**) and 1,3-benzothiazines (**5aa-as**, **5ba-oa**, **5pt**) in high yields.

3. General experimental procedure for the synthesis of 2-aryl thiazin-4-ones (7aa-ca) and diaryl[*b*,*f*]1,5]diazocine-6,12(*5H*,*11H*)-diones (8aa-cc)

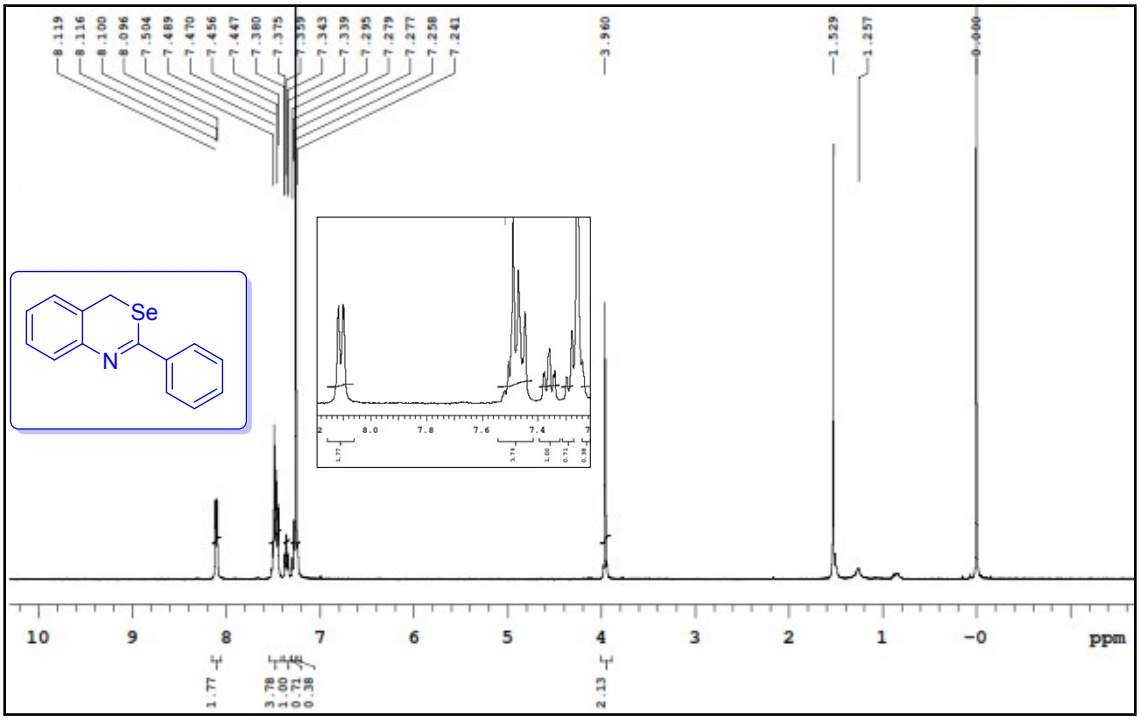
A 10 mL reaction vial was charged with anthranilic acids **6a-c** (1.0 mmol), thiobenzamide **4a** (1.0 mmol), T3P anhydride solution ≥50 wt. % in ethyl acetate (1.1 mmol). The reaction mixture was then stirred at 25 °C for 12 hours in an open vial. After completion of the reaction (progress was monitored by TLC; SiO_2, Hexane/EtOAc = 3:1), the mixture was diluted with ethyl acetate (15 mL) and water (20 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (3 × 10 mL) and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the remaining residue was purified by column chromatography over silica gel using hexane / ethyl acetate = 95:5 as an eluent to obtain the desired 2-aryl thiazin-4-ones (**7aa-ca**) and diaryl[*b*,*f*]1,5]diazocine-6,12(*5H*,*11H*)-diones (**8aa-cc**) in good yields.

4. Experimental procedures and analytical data of synthesized 1,3-benzoselenazines (3aa-ah, 3ba-la)

Synthesis of 2-phenyl-4H-benzo[d][1,3]selenazine (3aa); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-phenyl-4H-benzo[d][1,3]selenazine **3aa** in 97% (265 mg) yield as pale yellow solid.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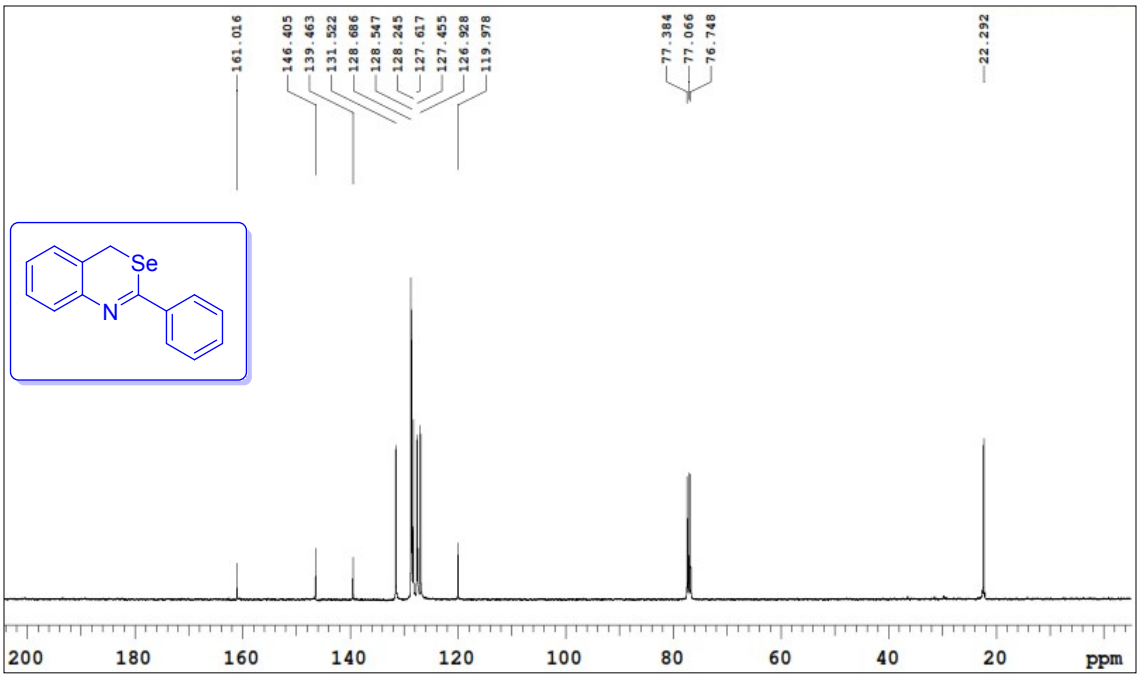
7.339
7.295
7.279
7.277
7.258
7.241
3.960
1.529
1.257
0.000
Se
N
10
9
8
7
6
5
4
3
2
1
−0
ppm
1.77
3.78
1.00
0.71
0.38
2.13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131.522
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128.547
128.245
127.617
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126.928
119.978
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22.292
Se
N
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140
120
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80
60
40
20
ppm

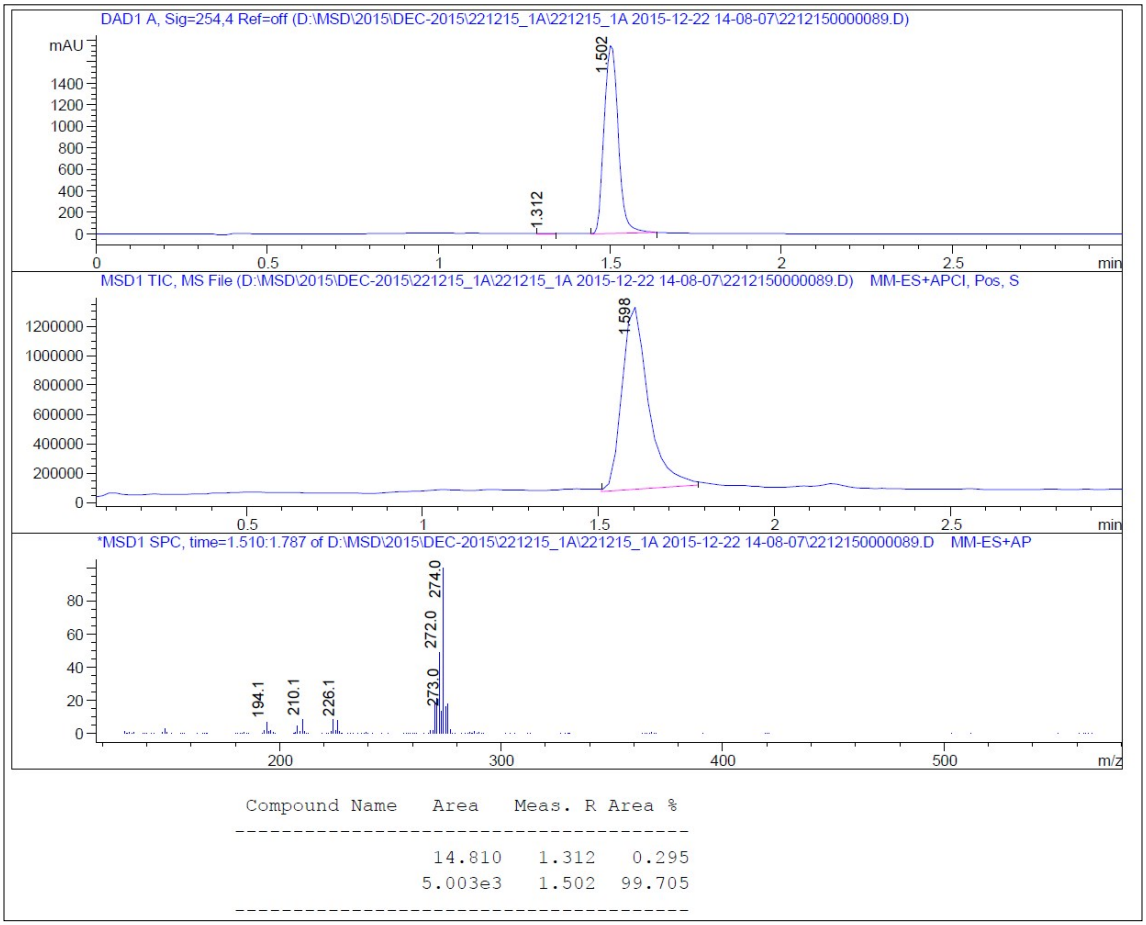
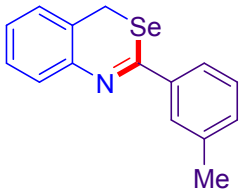


Figure 1. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3aa** in $CDCl_3$ and LC-MS in Acetonitrile.

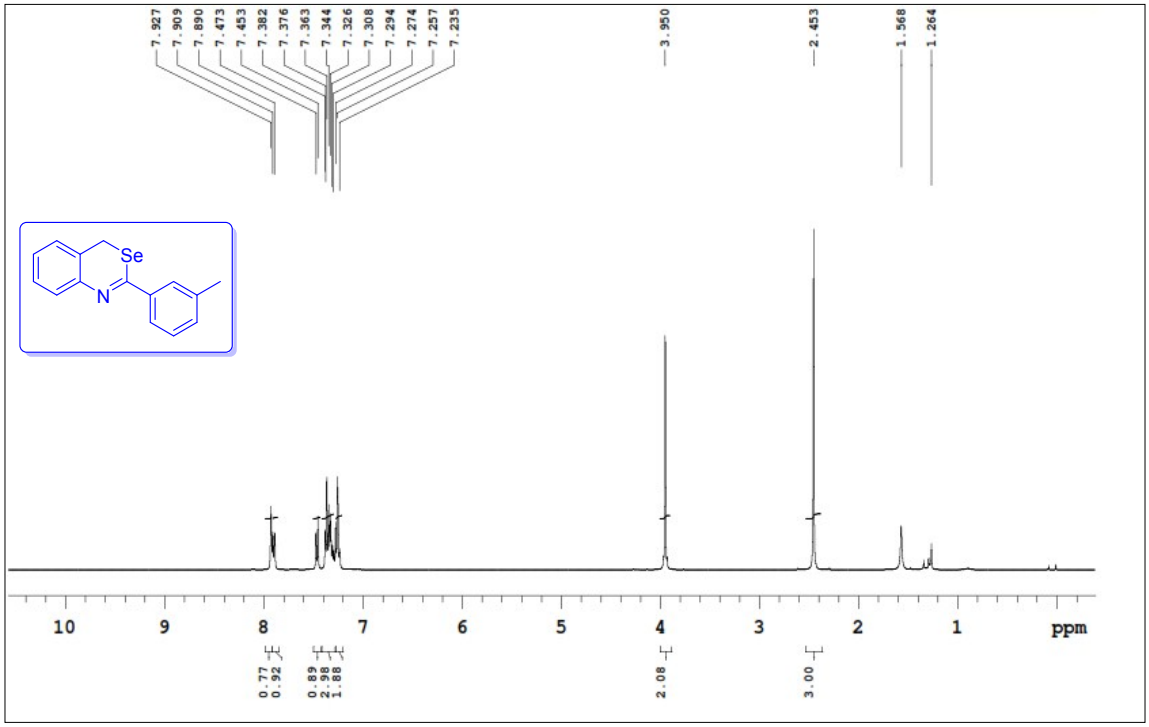
Pale yellow solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.10 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.51 – 7.44 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.24 (m, 2H), 3.96 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.0, 146.4, 139.4, 131.5, 128.6, 128.5, 128.2, 127.6, 127.4, 126.9, 119.9, 22.2 ppm; **MS** (APCI): $[M + 1]^+$ = 274.0 (99.70%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{12}NSe$: 274.0134; found: 274.0130.

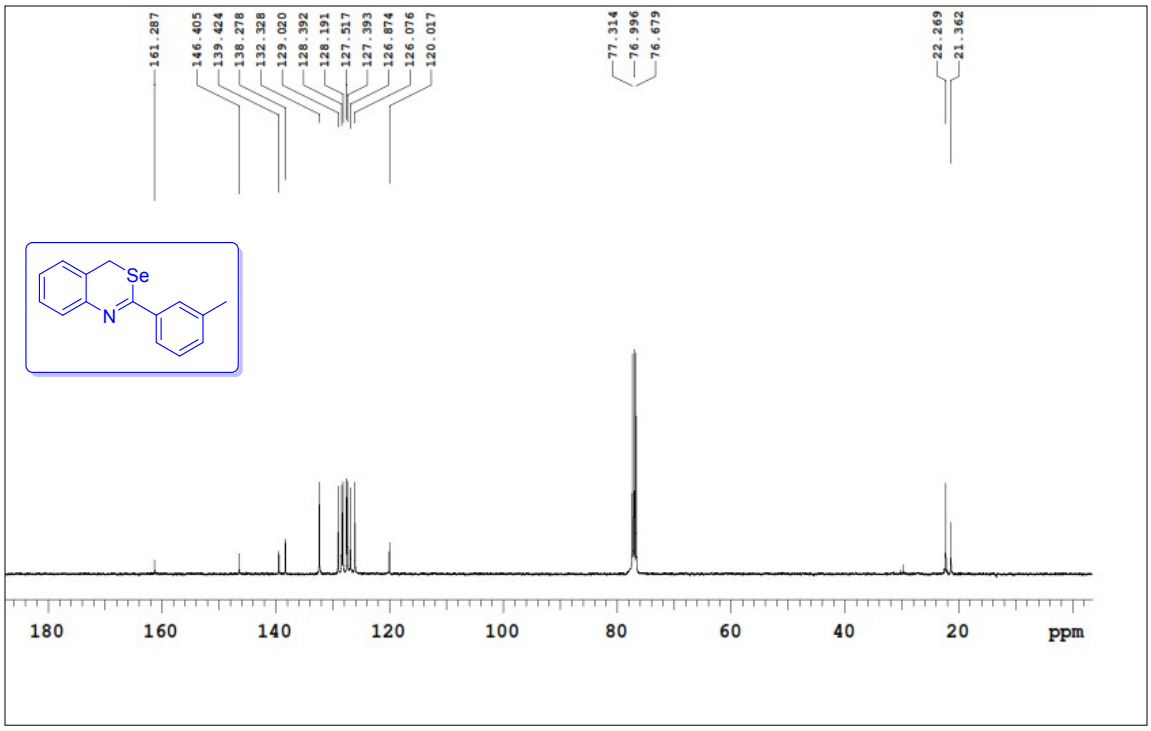
Synthesis of 2-(m-tolyl)-4H-benzo[d][1,3]selenazine (3ab); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 3-methylbenzoselenoamide **2b** (1.0 mmol, 198 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 2-(m-tolyl)-4H-benzo[d][1,3]selenazine **3ab** in 95% (272 mg) yield as green solid.

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77.314
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22.269
21.362
Se
N
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160
140
120
100
80
60
40
20
ppm

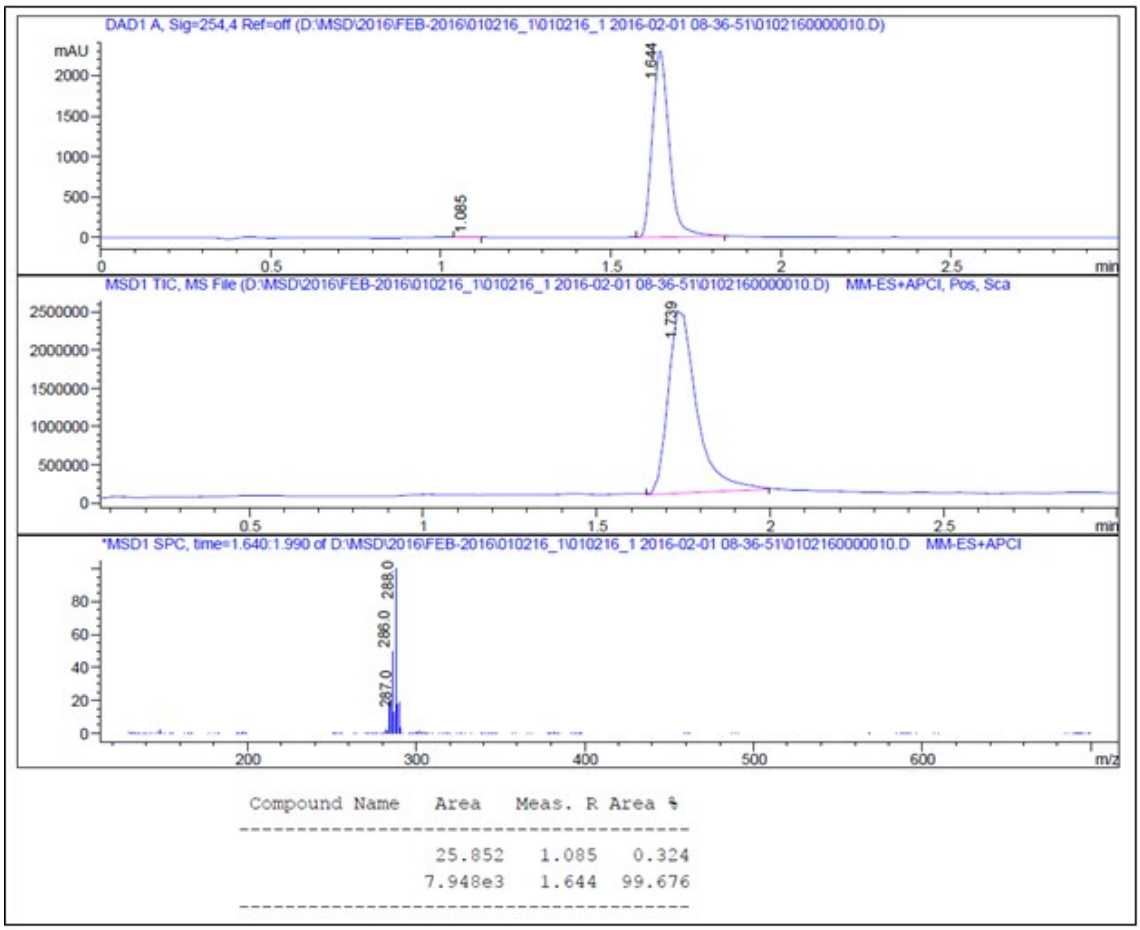
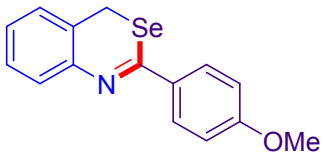


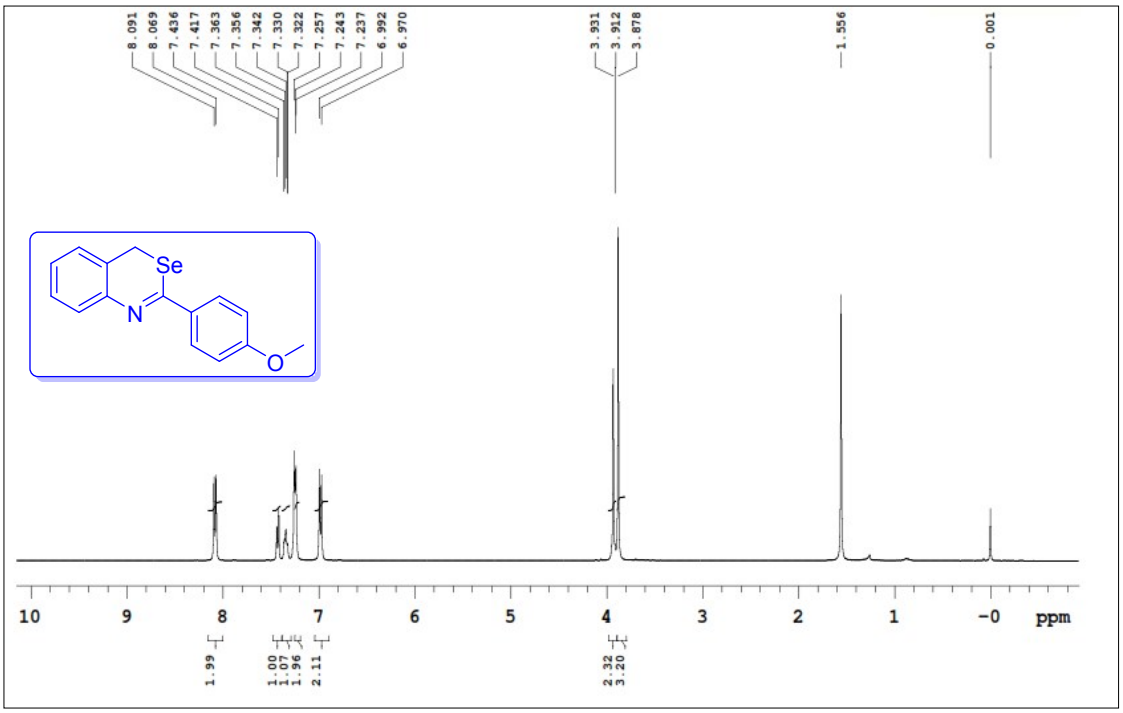
Figure 2. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ab** in $CDCl_3$ and LC-MS in Acetonitrile.

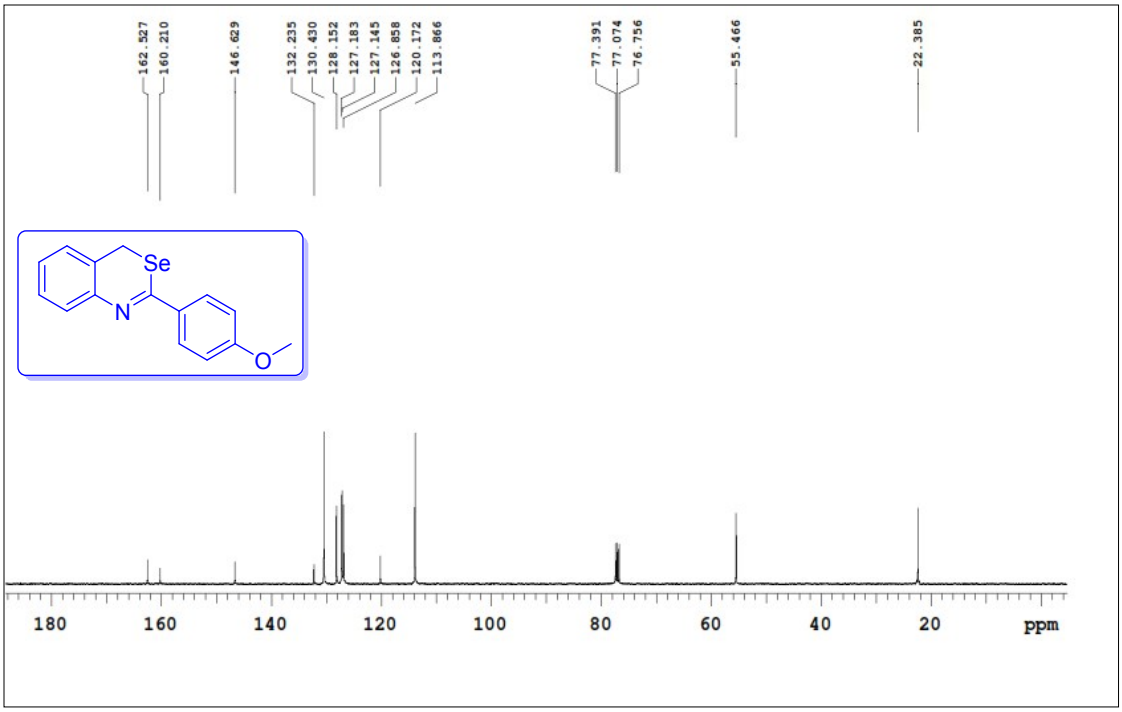
Green solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.92 – 7.89 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.38 - 7.29 (m, 3H), 7.27 – 7.23 (m, 2H), 3.95 (s, 2H), 2.45 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.2, 146.4, 139.4, 138.2, 132.3, 129.0, 128.3, 128.1, 127.5, 127.3, 126.8, 126.0, 120.0, 22.2, 21.3 ppm; **MS** (APCI): $[M + 1]^+$ = 288.0 (99.67%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NSe$: 288.0291; found: 288.0289.

Synthesis of 2-(4-methoxyphenyl)-4H-benzo[d][1,3]selenazine (3ac); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-methoxybenzoselenoamide **2c** (1.0 mmol, 214 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(4-methoxyphenyl)-4H-benzo[d][1,3]selenazine **3ac** in 92% (278 mg) yield as off-white solid.

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160
140
120
100
80
60
40
20
ppm

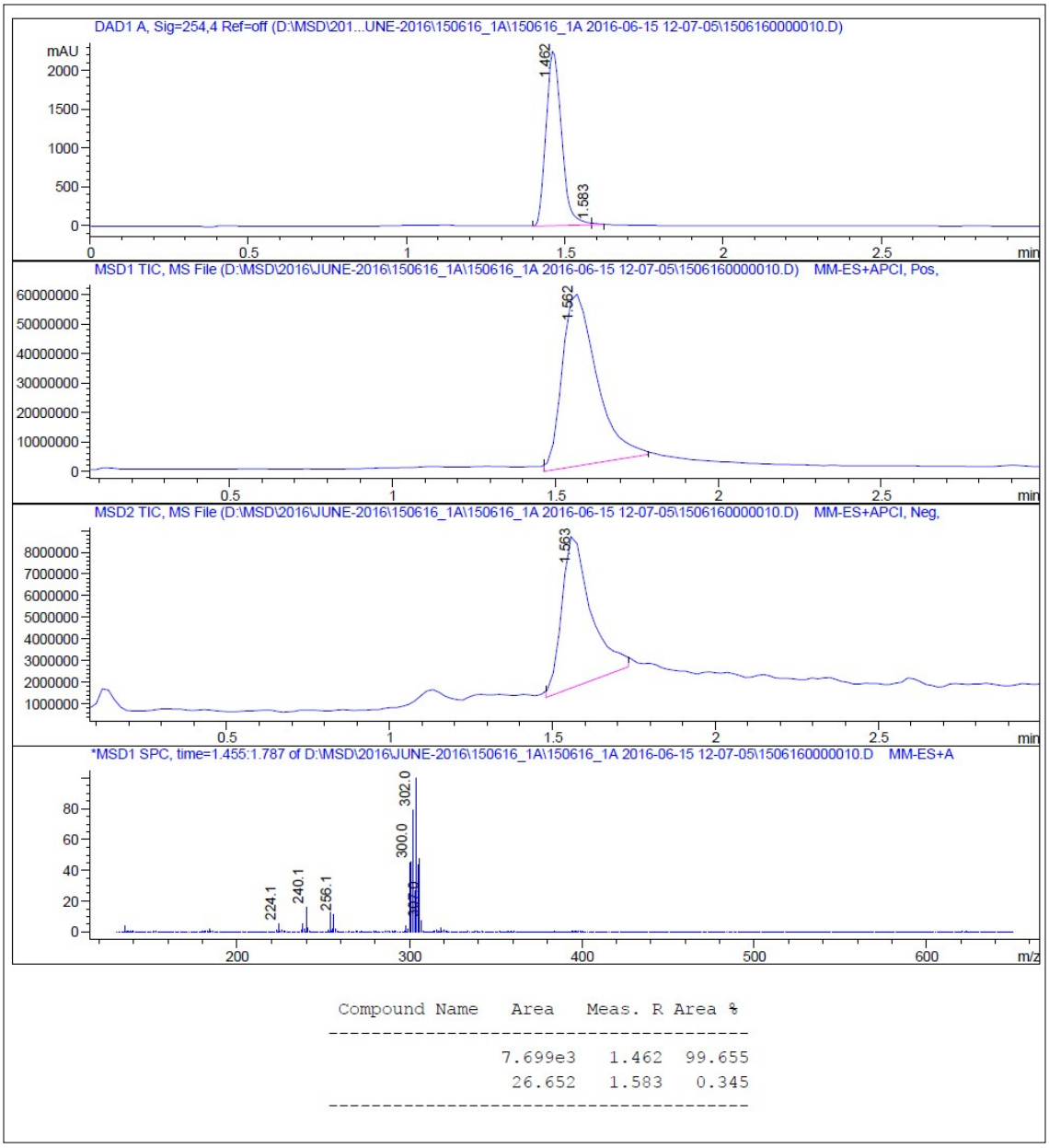
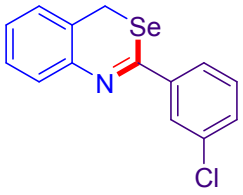


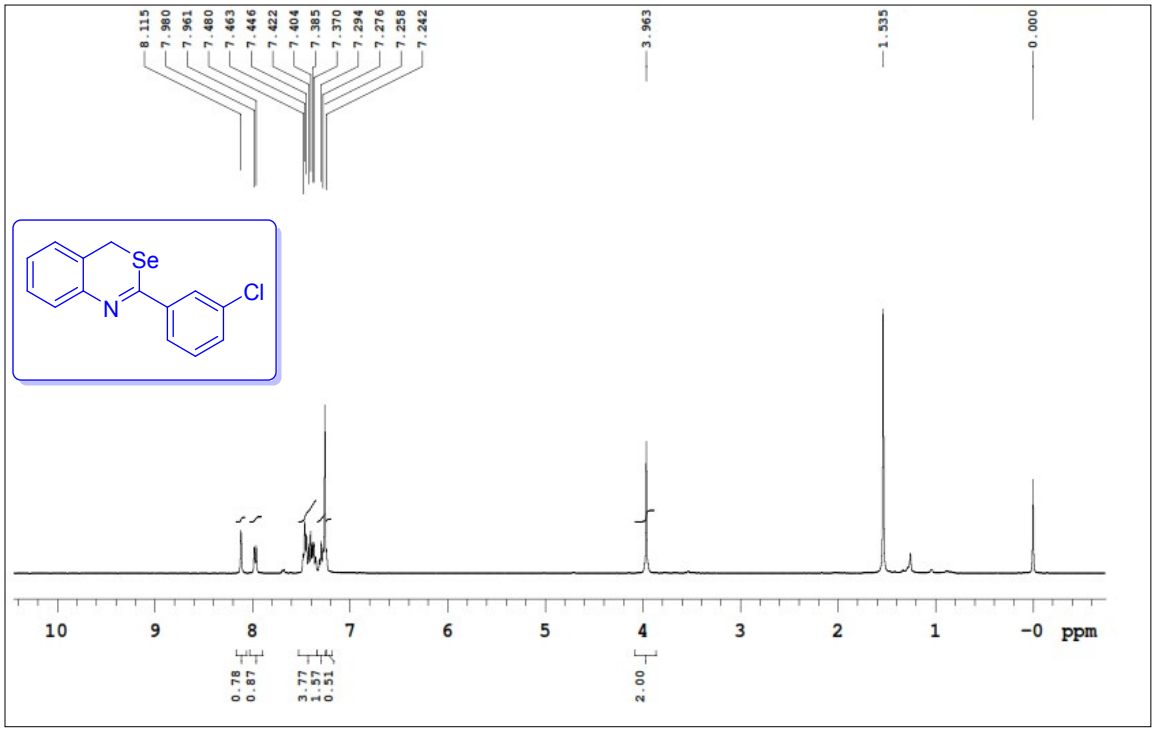
Figure 3. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ac** in $CDCl_3$ and LC-MS in Acetonitrile.

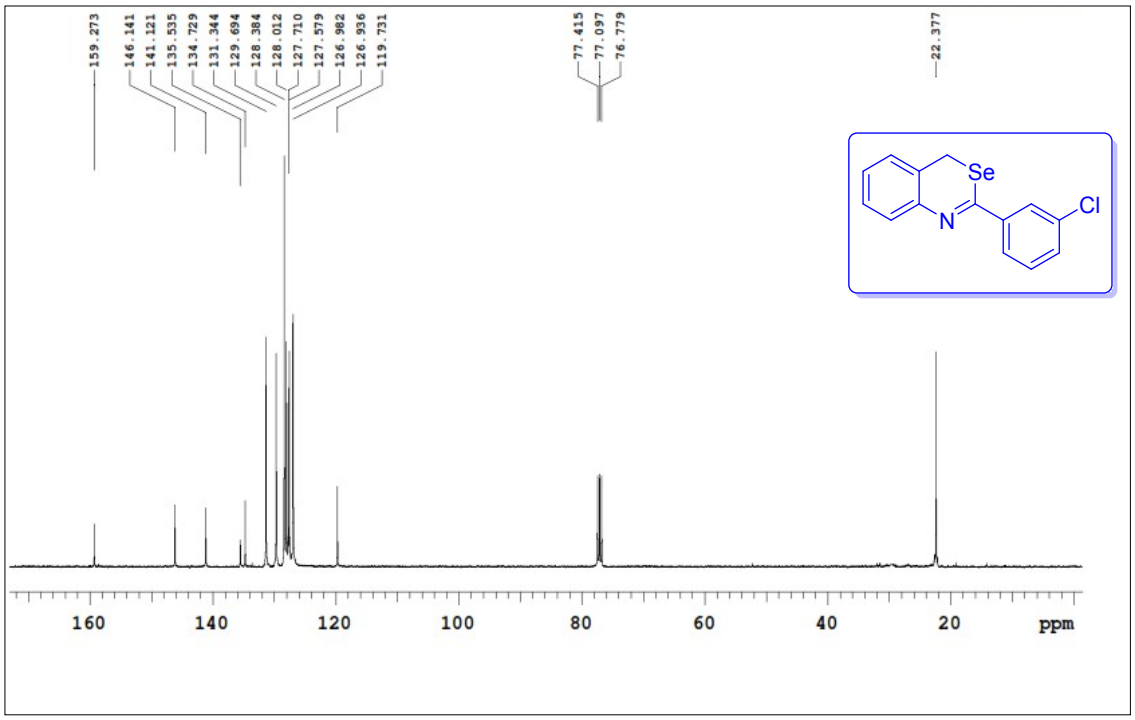
Off-white solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.36 - 7.32 (m, 1H), 7.25 – 7.23 (m, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.5, 160.2, 146.6, 132.2, 130.4, 128.1, 127.1, 127.1, 126.8, 120.1, 113.8, 55.4, 22.3 ppm; **MS** (APCI): $[M + 1]^+$ = 302.0 (99.65%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NOSe$: 304.0240; found: 304.0241.

Synthesis of 2-(3-chlorophenyl)-4H-benzo[d][1,3]selenazine (3ad); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 3-chlorobenzoselenoamide **2d** (1.0 mmol, 218.5 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(3-chlorophenyl)-4H-benzo[d][1,3]selenazine **3ad** in 90% (276 mg) yield as off-white solid.

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140
120
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80
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40
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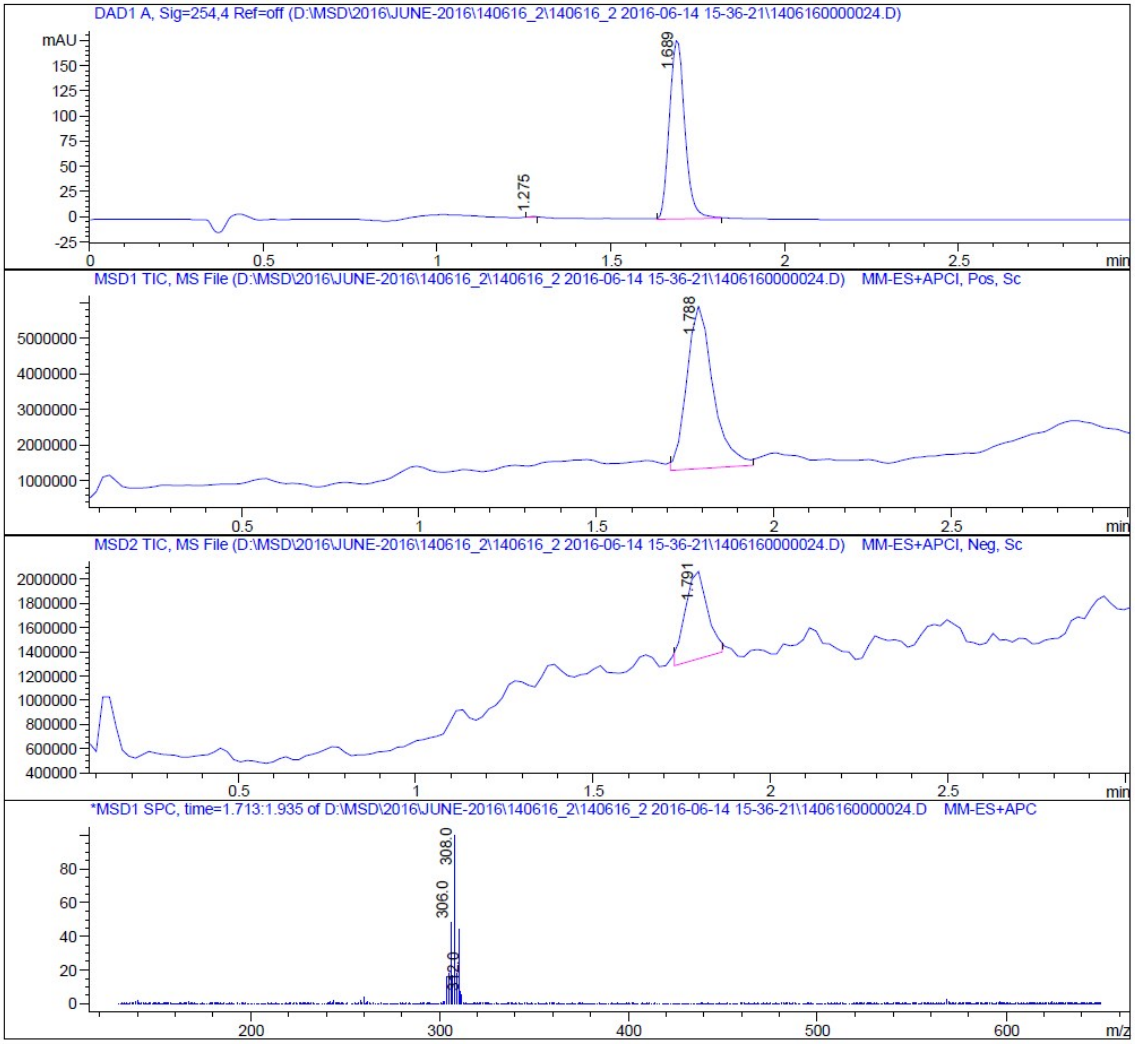
ppm

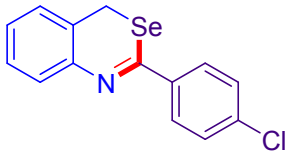


Compound Name	Area	Meas. R	Area %
	0.382	1.275	0.070
	547.715	1.689	99.930

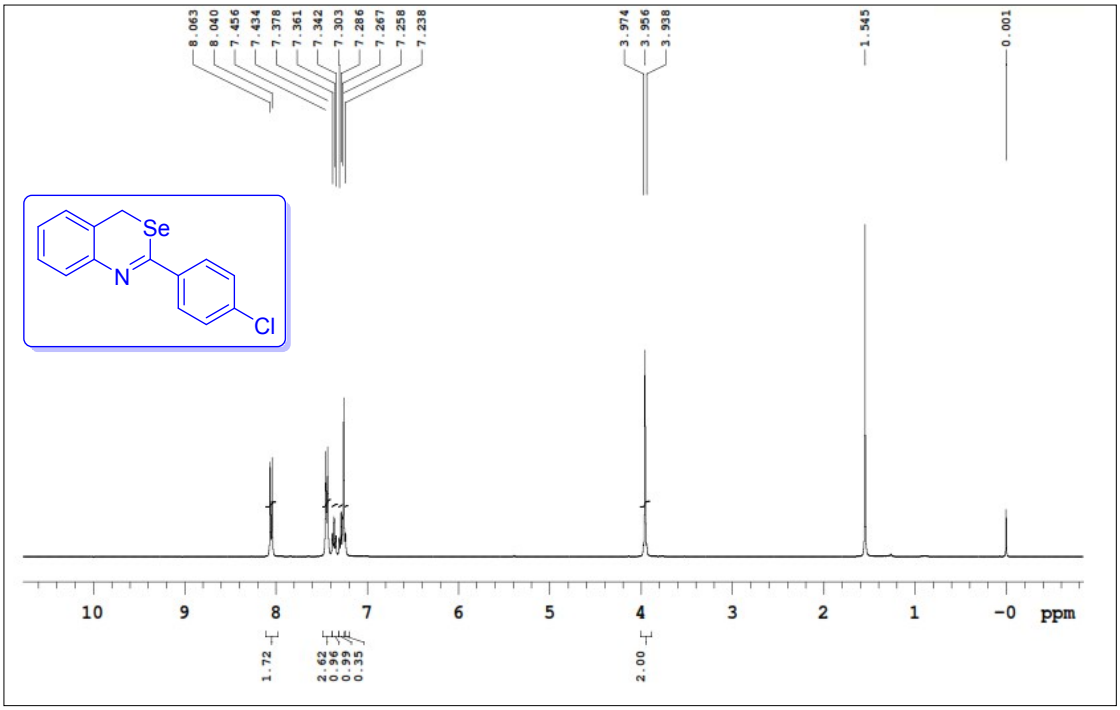
Figure 4. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ad** in $CDCl_3$ and LC-MS in Acetonitrile.

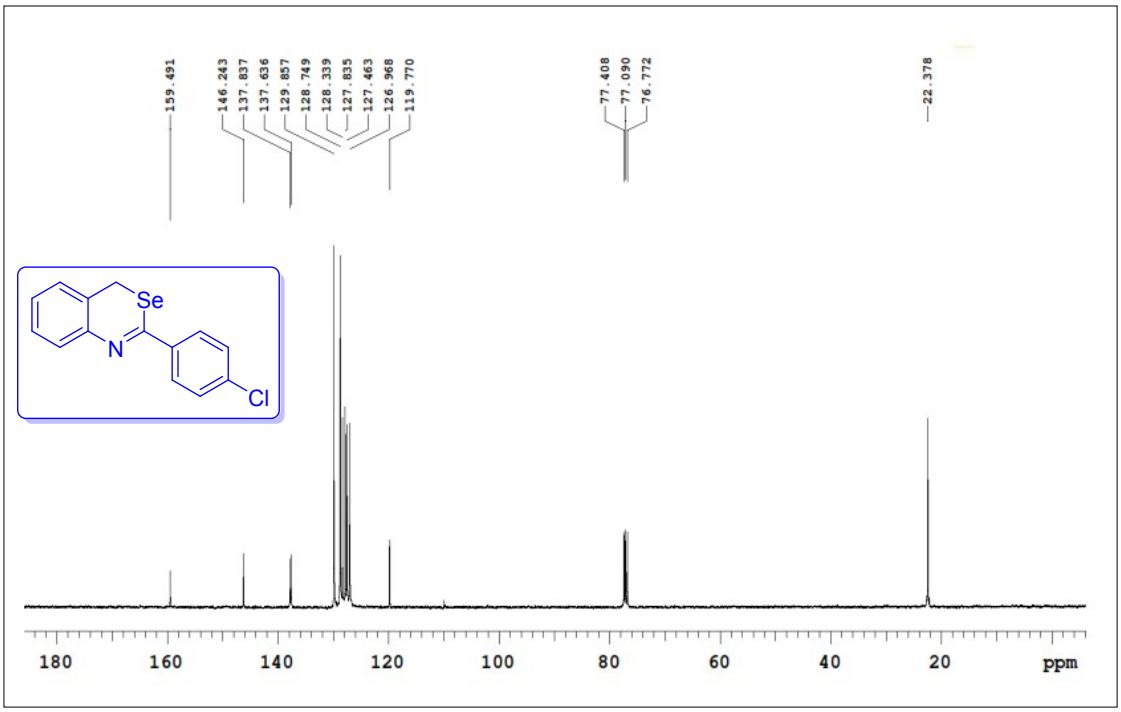
Off-white solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.48 - 7.35 (m, 4H), 7.31 – 7.24 (m, 2H), 3.96 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.2, 146.1, 141.1, 135.5, 134.7, 131.3, 129.6, 128.3, 128.0, 127.7, 127.5, 126.9, 126.9, 119.7, 29.7, 26.8, 22.3 ppm; **MS** (APCI): $[M + 1]^+$ = 308.0 (99.93%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}ClNSe$: 307.9745; found: 307.9741.

Synthesis of 2-(4-chlorophenyl)-4H-benzo[d][1,3]selenazine (3ae); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-chlorobenzoselenoamide **2e** (1.0 mmol, 218.5 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(4-chlorophenyl)-4H-benzo[d][1,3]selenazine **3ae** in 91% (280 mg) yield as off-white solid.

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22.378
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140
120
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60
40
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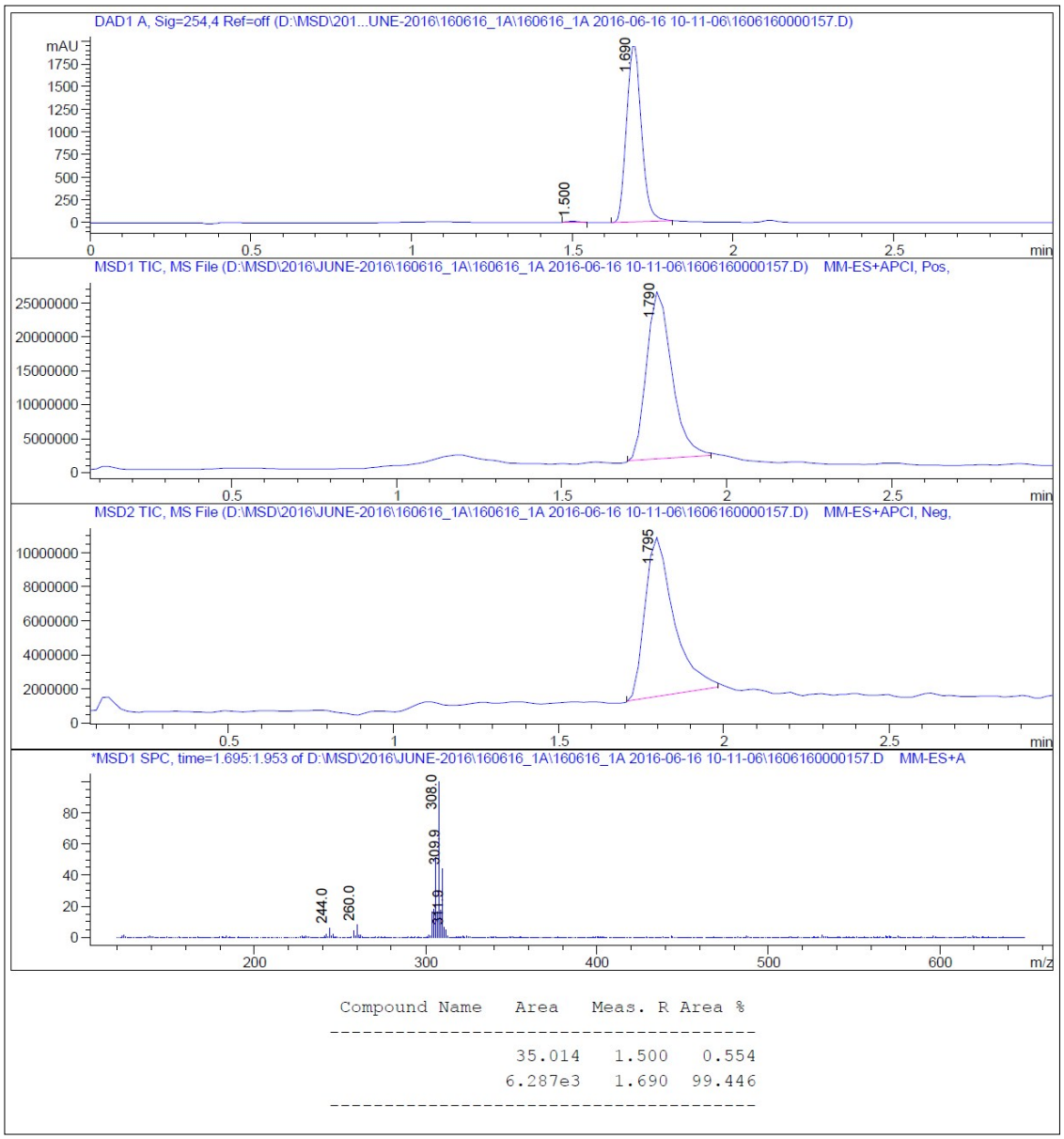
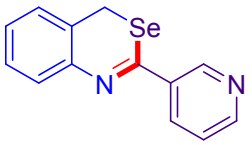


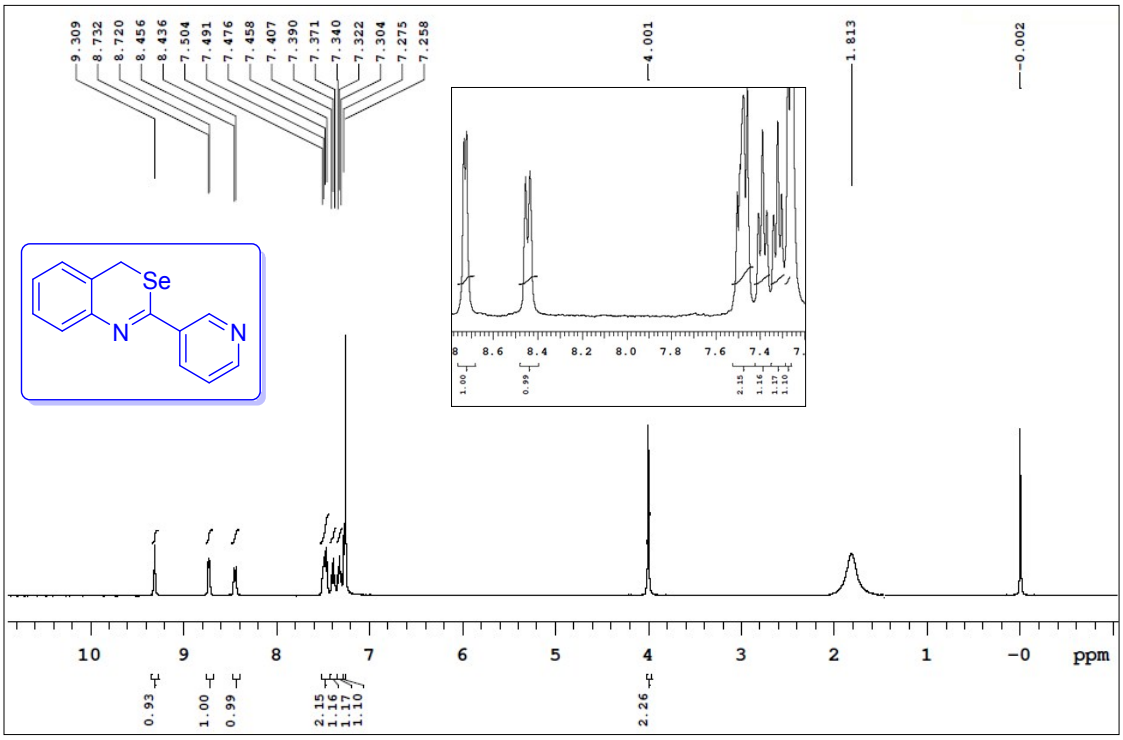
Figure 5. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ae** in $CDCl_3$ and LC-MS in Acetonitrile.

Off-white solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 9.2 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.23 (m, 2H), 3.95 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.4, 146.2, 137.8, 137.6, 129.8, 128.7, 128.3, 127.8, 127.4, 126.9, 119.7, 22.3 ppm; **MS** (APCI): $[M + 1]^+$ = 308.0 (99.44%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}ClNSe$: 307.9745; found: 307.9742.

Synthesis of 2-(pyridin-3-yl)-4H-benzo[d][1,3]selenazine (3af); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), pyridine-2-carboselenoamide **2f** (1.0 mmol, 185 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(pyridin-3-yl)-4H-benzo[d][1,3]selenazine **3af** in 89% (243 mg) yield as pale yellow solid.



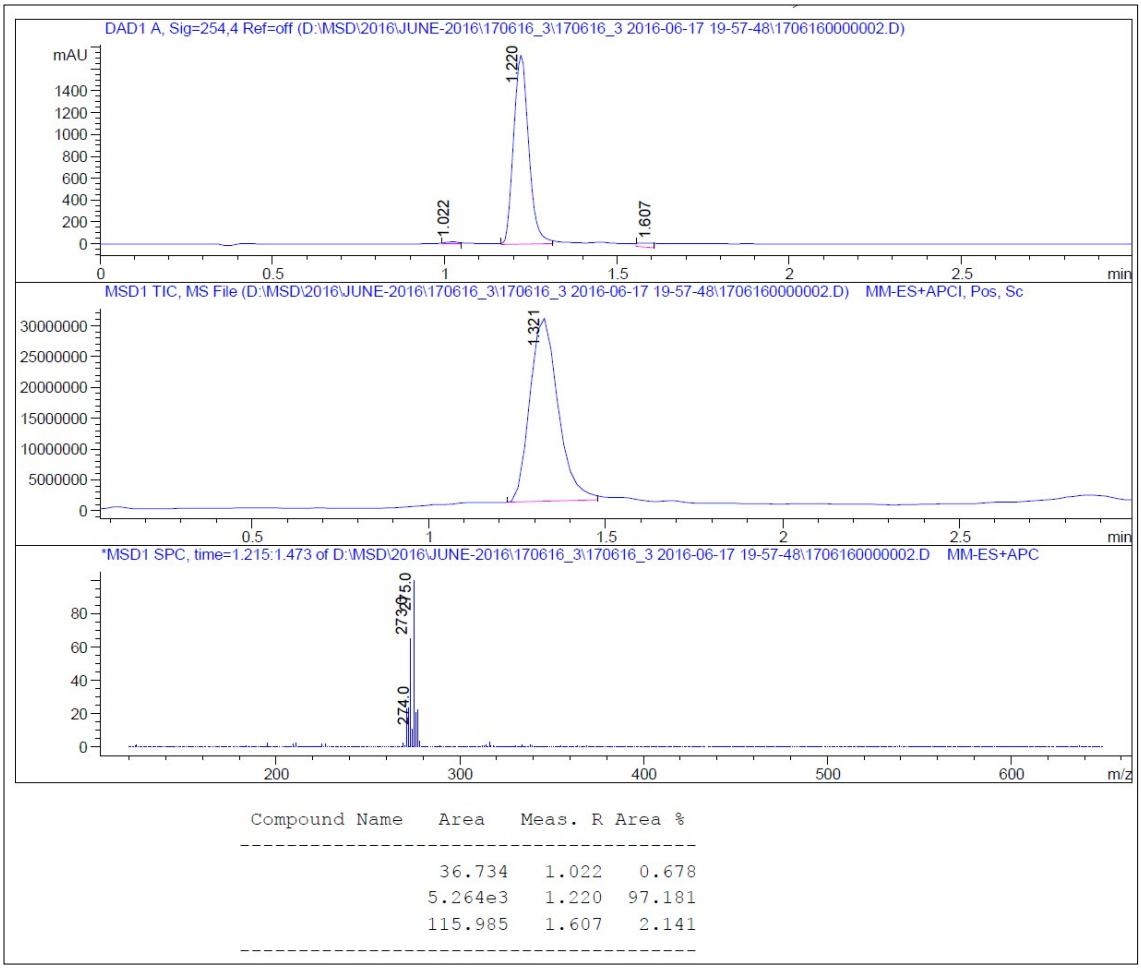
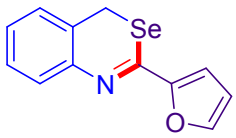


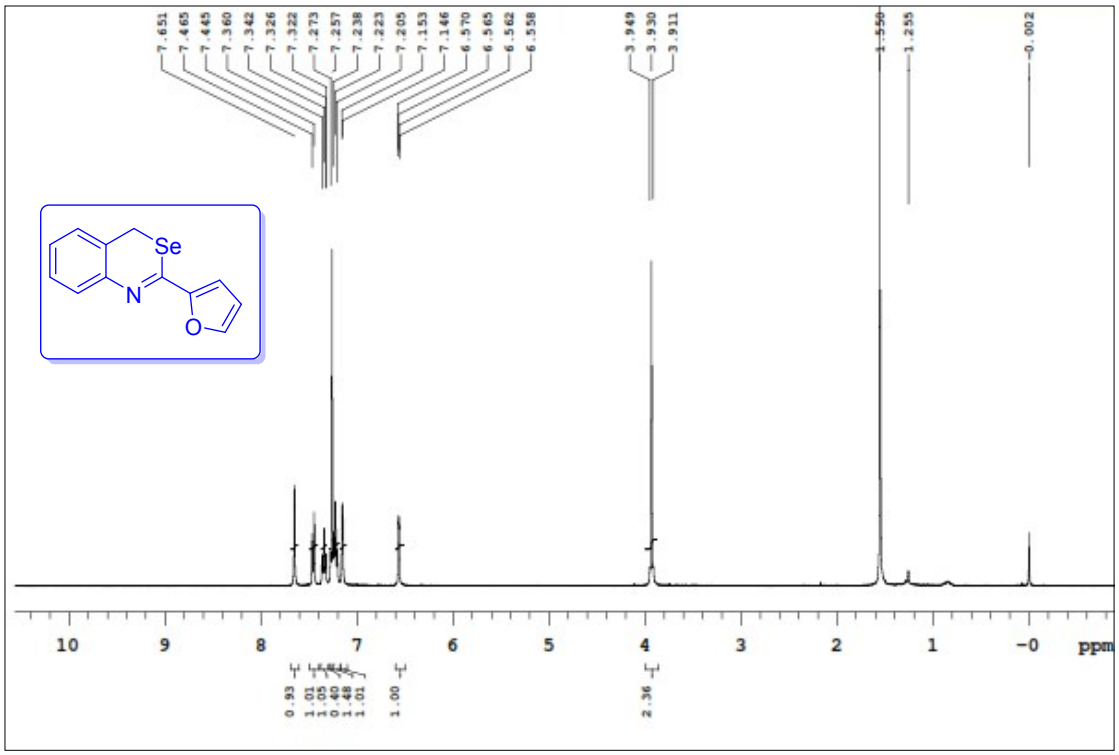
Figure 6. ^{1}H (400 MHz) NMR spectra of **3af** in $CDCl_3$ and LC-MS in Acetonitrile.

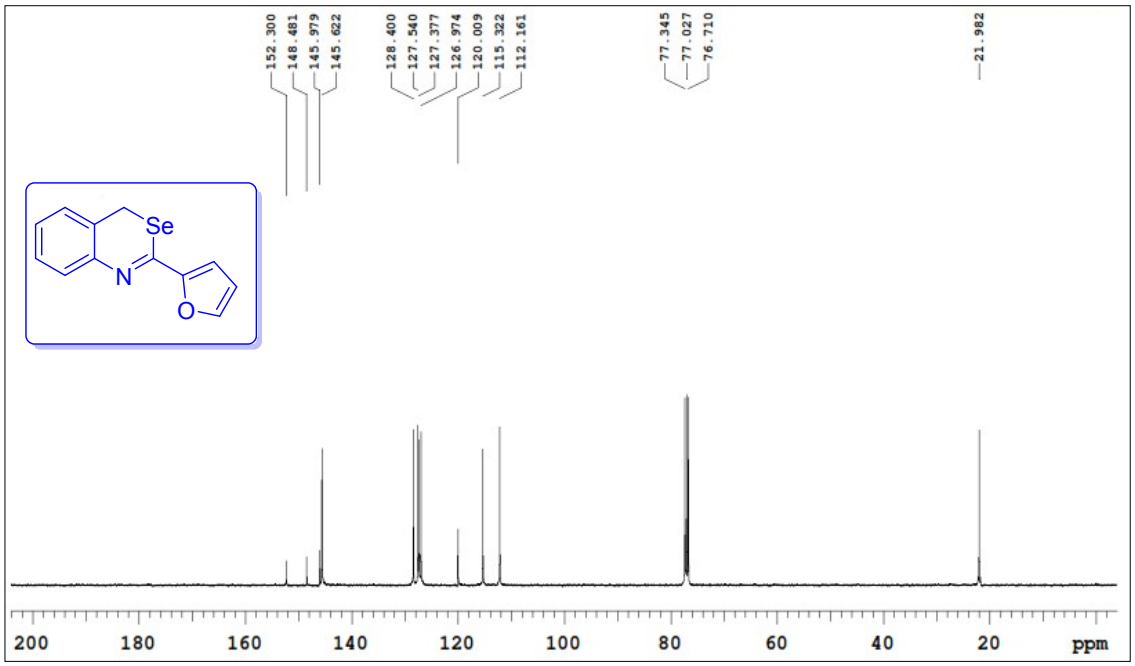
Pale yellow solid; $\mathbf{R_f}$ = 0.50 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.30 (s, 1H), 8.72 (d, *J* = 4.8 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 4.00 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.2, 152.2, 151.5, 146.0, 139.9, 131.7, 131.3, 128.5, 128.4, 128.0, 127.4, 120.5, 22.8 ppm; **MS** (APCI): $[M + 1]^+$ = 275.0 (99.65%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{13}H_{11}N_2Se$: 275.0087; found: 275.0084.

Synthesis of 2-(furan-2-yl)-4H-benzo[d][1,3]selenazine (3ag); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), furan-2-carboselenoamide **2g** (1.0 mmol, 174 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(furan-2-yl)-4H-benzo[d][1,3]selenazine **3ag** in 95% (249 mg) yield as brown semisolid.


7.651
7.465
7.445
7.360
7.342
7.326
7.322
7.273
7.257
7.238
7.223
7.205
7.153
7.146
6.570
6.565
6.562
6.558
3.949
3.930
3.911
1.550
1.255
0.002
Se
N
O
10
9
8
7
6
5
4
3
2
1
−0
ppm
0.93
1.01
1.05
0.40
0.48
1.01
1.00
2.36


152.300
148.481
145.979
145.622
128.400
127.540
127.377
126.974
120.009
115.322
112.161
77.345
77.027
76.710
21.982
Se
N
O
200
180
160
140
120
100
80
60
40
20
ppm

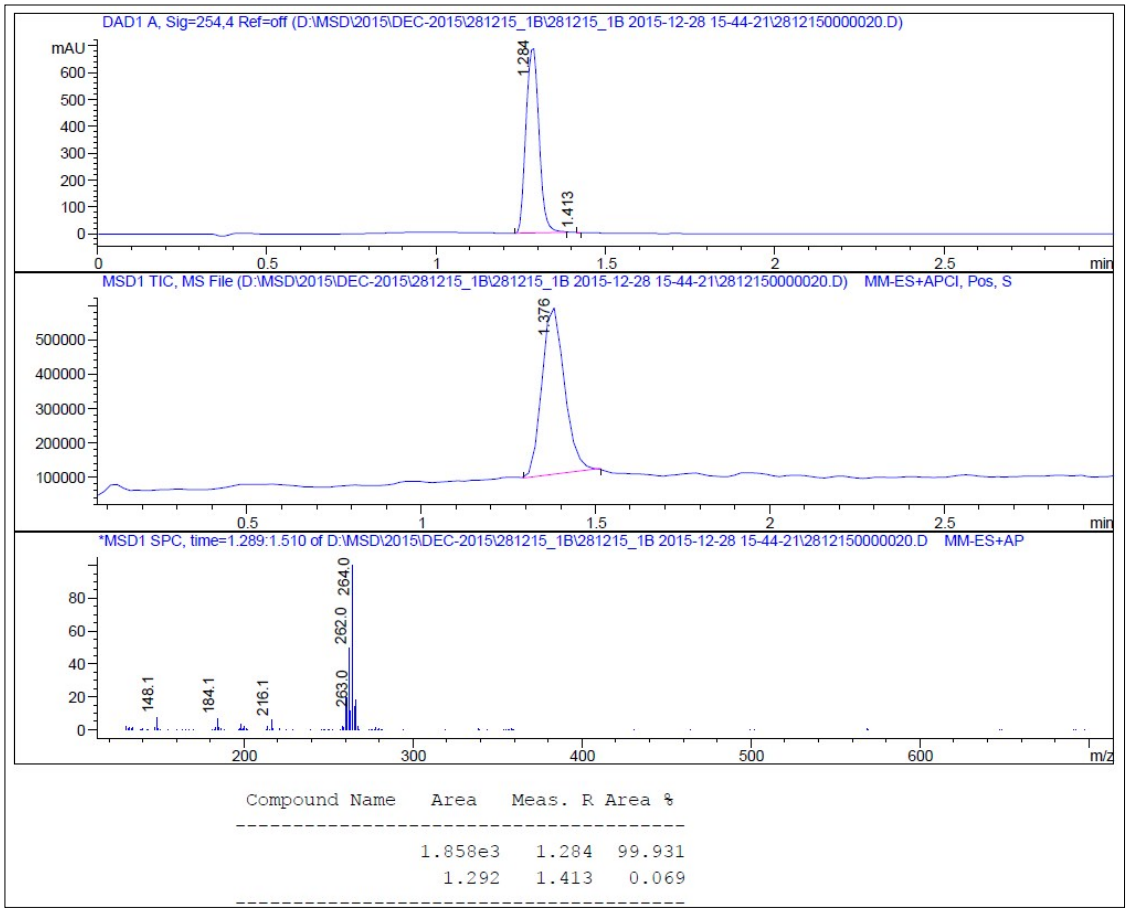
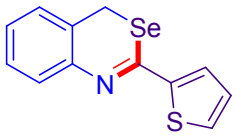


Figure 7. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ag** in $CDCl_3$ and LC-MS in Acetonitrile.

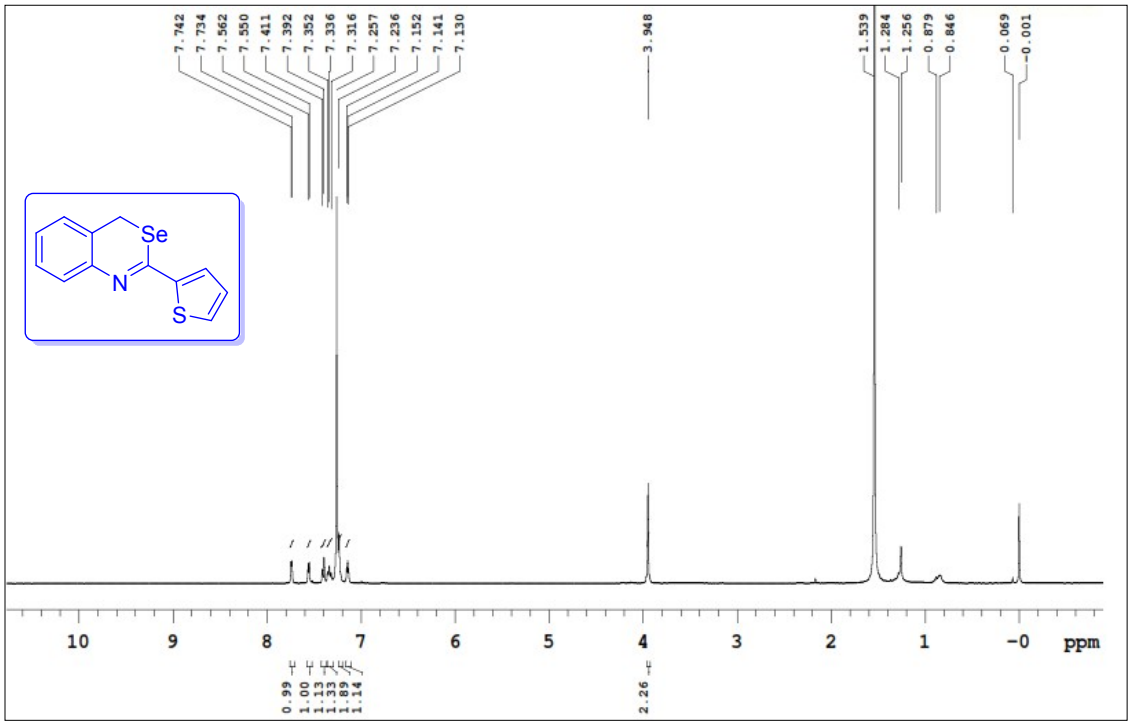
Brown semisolid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.65 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 6.4 Hz, 1H), 7.27 - 7.20 (m, 2H), 7.14 (d, *J* = 2.8 Hz, 1H), 6.66 (q, *J* = 2, 3.2 Hz, 1H), 3.93 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 152.3, 148.4, 145.9, 145.6, 128.4, 127.5, 127.3, 126.9, 120.0, 115.3, 112.1, 21.9 ppm; **MS** (APCI): $[M + 1]^+$ = 264.0 (99.93%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{12}H_{10}NOSe$: 263.9927; found: 263.9926.

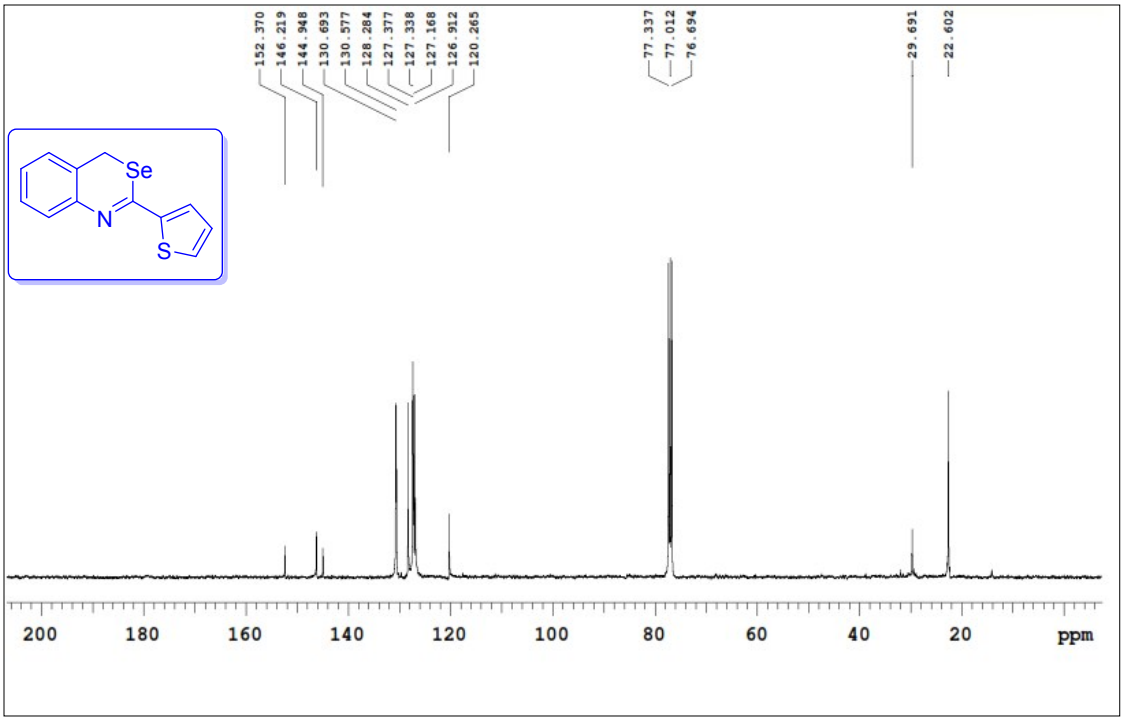
Synthesis of 2-(thiophen-2-yl)-4H-benzo[d][1,3]selenazine (3ah); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), thiophene-2-carboselenoamide **2h** (1.0 mmol, 190 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 2-(thiophen-2-yl)-4H-benzo[d][1,3]selenazine **3ah** in 93% (259 mg) yield as yellow semisolid.




152.370
146.219
144.948
130.693
130.577
128.284
127.377
127.338
127.168
126.912
120.265
77.337
77.012
76.694
29.691
22.602
Se
N
S
200
180
160
140
120
100
80
60
40
20
ppm

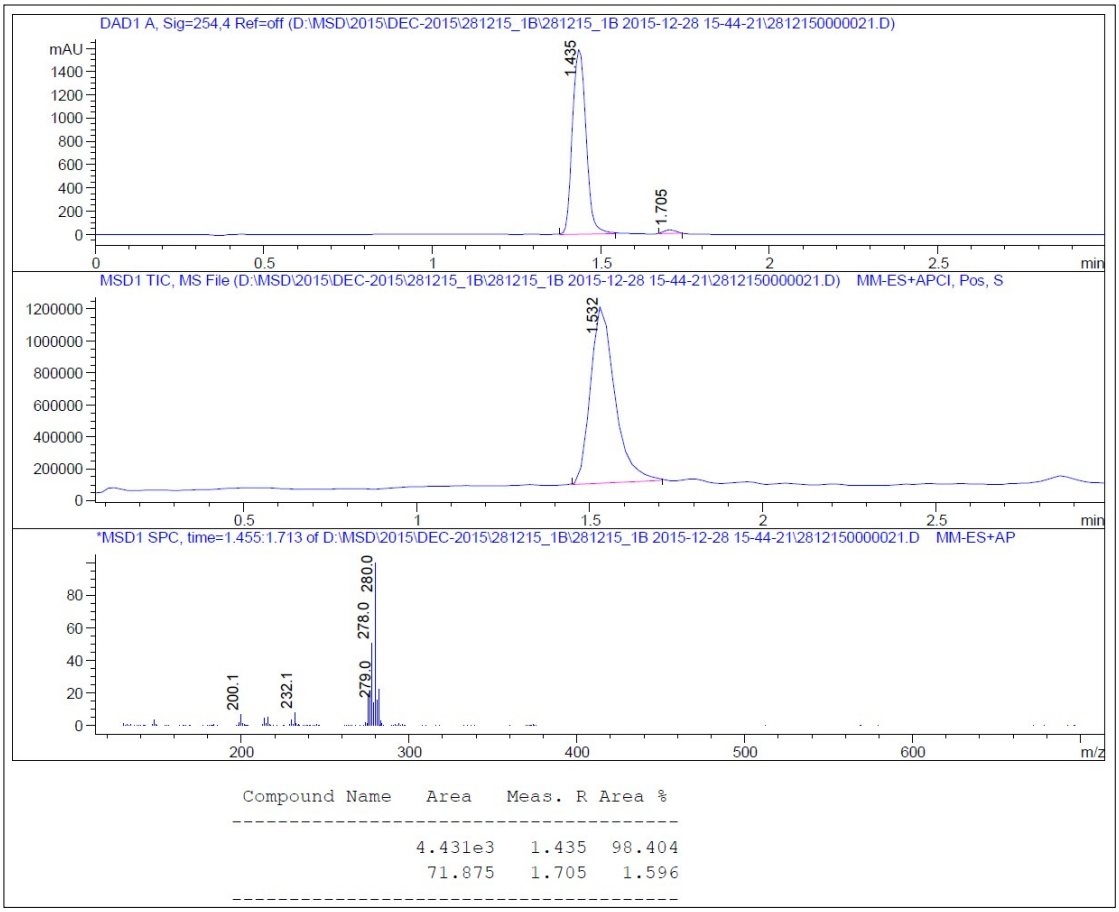
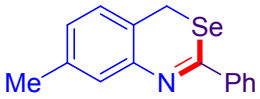


Figure 8. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ah** in $CDCl_3$ and LC-MS in Acetonitrile.

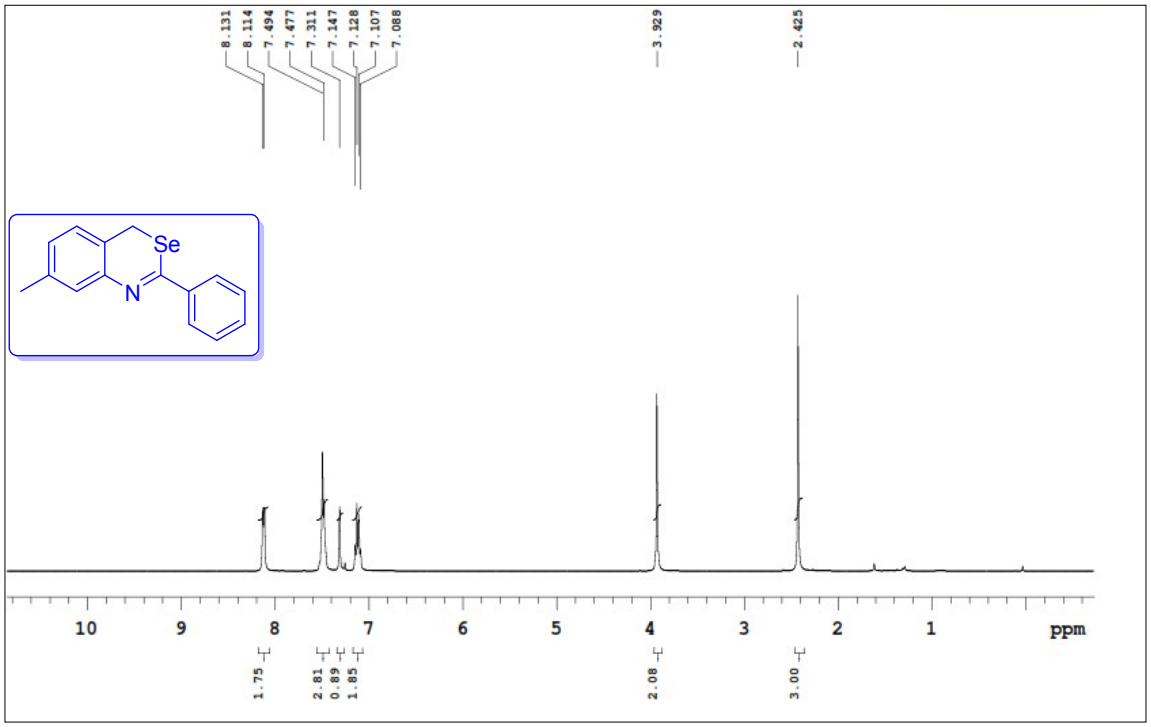
Yellow semisolid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 3.2 Hz, 1H), 7.55 (d, *J* = 4.8 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 6.4 Hz, 1H), 7.25 – 7.23 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 3.94 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 152.3, 146.2, 144.9, 130.6, 130.5, 128.2, 127.3, 127.3, 127.1, 126.9, 120.2, 29.6, 22.6 ppm; **MS** (APCI): $[M + 1]^+$ = 280.0 (98.40%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{12}H_{10}NSSe$: 279.9699; found: 279.9701.

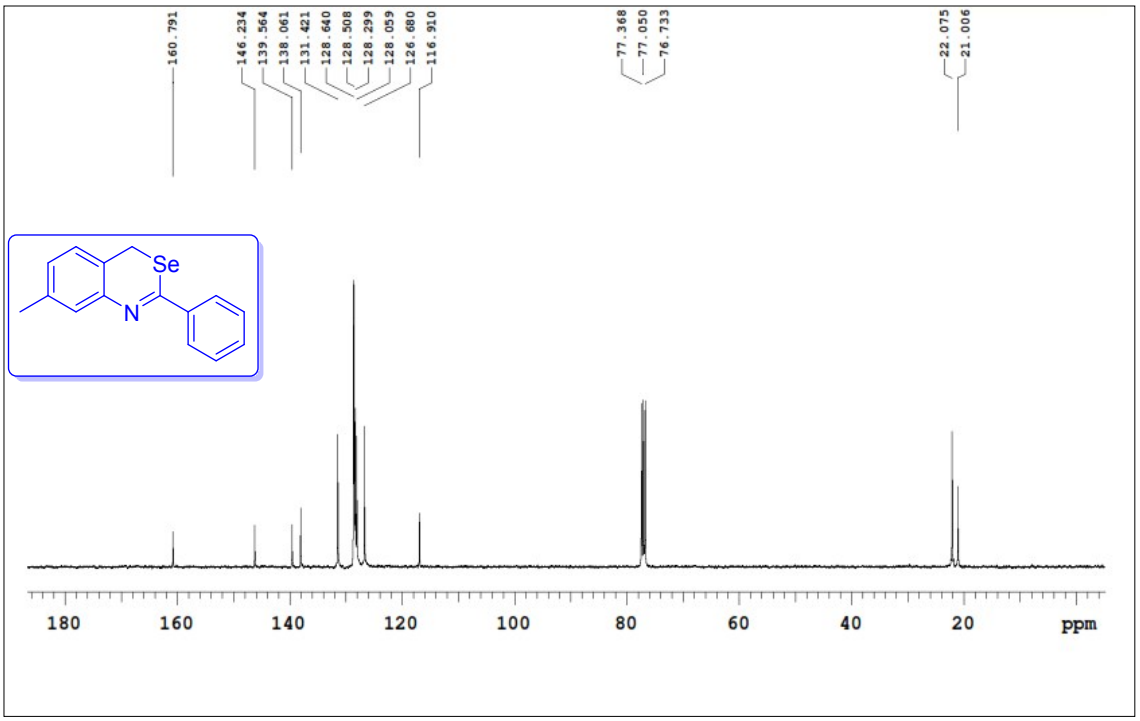
Synthesis of 7-methyl-2-phenyl-4H-benzo[d][1,3]selenazine (3ba); new compound



According to the general procedure, reactions between 2-amino-4-methylbenzyl alcohol **1b** (1.0 mmol, 137 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 7-methyl-2-phenyl-4H-benzo[d][1,3]selenazine **3ba** in 92% (263 mg) yield as brown solid.




160.791
146.234
139.564
138.061
131.421
128.640
128.508
128.299
128.059
126.680
116.910
77.368
77.050
76.733
22.075
21.006
Se
N
180
160
140
120
100
80
60
40
20
ppm

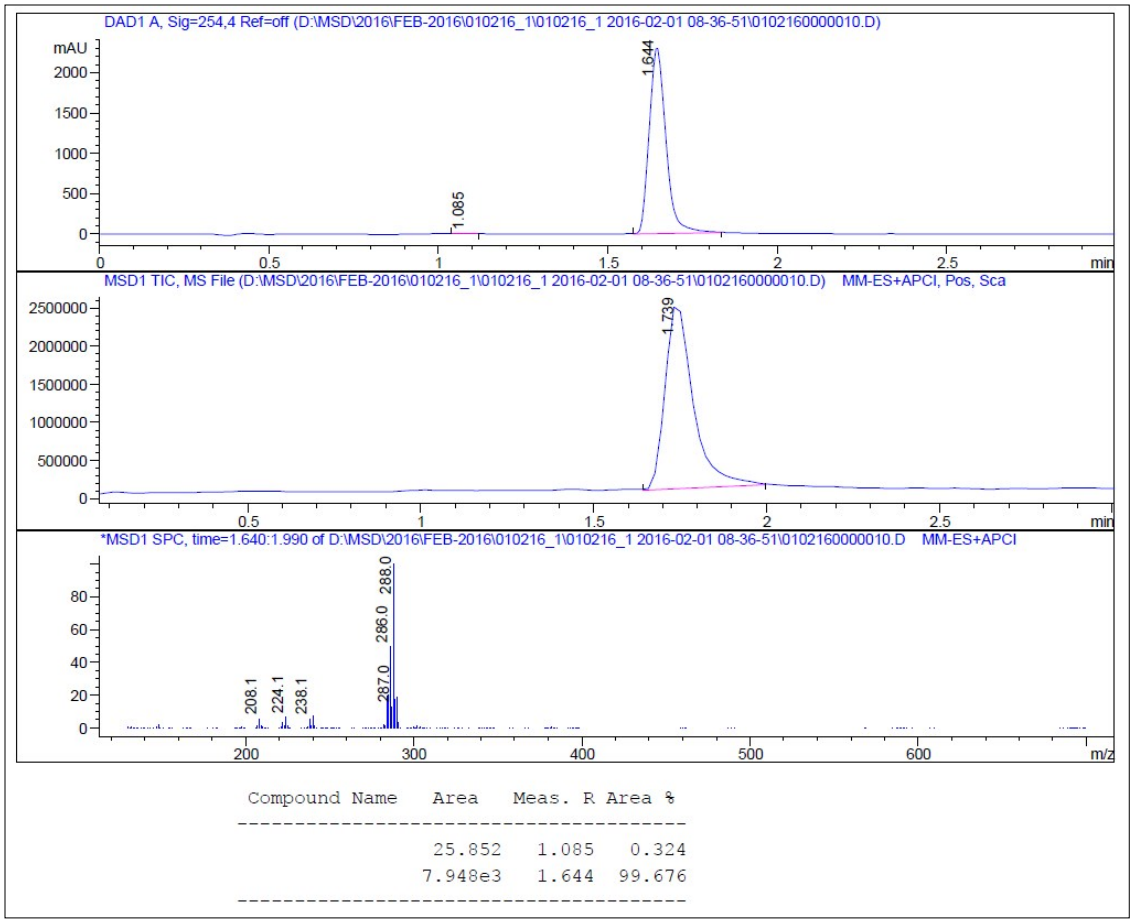
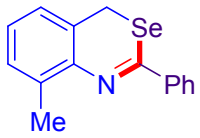


Figure 9. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ba** in $CDCl_3$ and LC-MS in Acetonitrile.

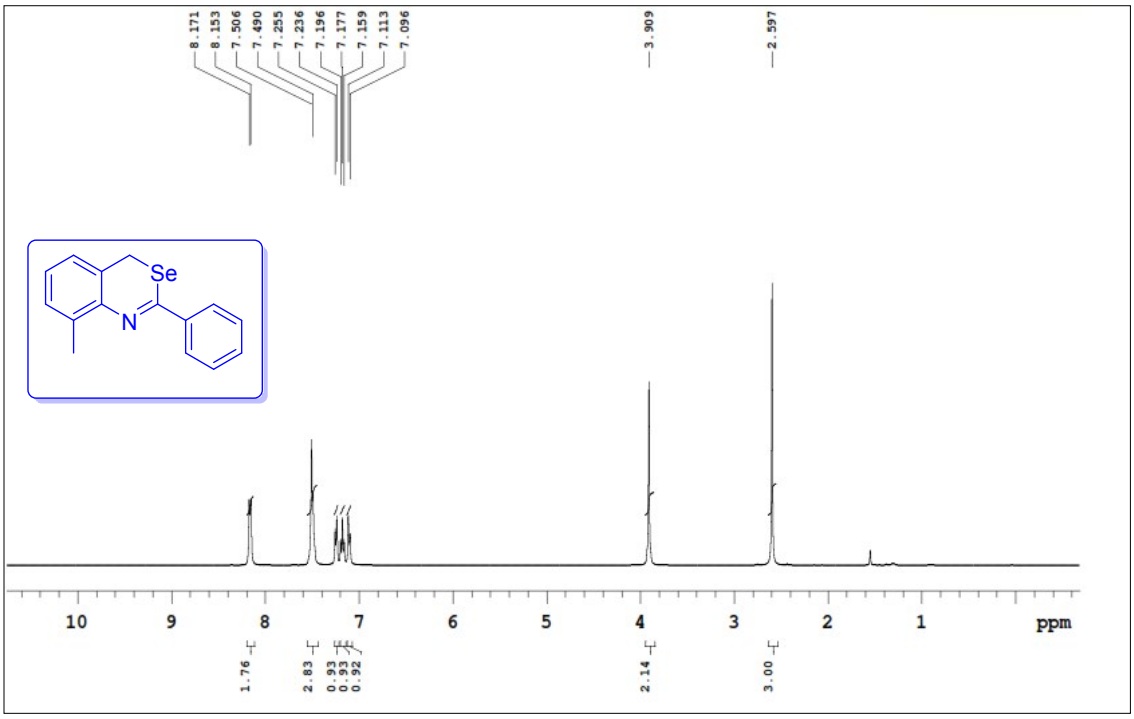
Brown solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 6.8 Hz, 2H), 7.49 – 7.47 (m, 3H), 7.31 (s, 1H), 7.14 – 7.08 (m, 2H), 3.92 (s, 2H), 2.42 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 160.7, 146.2, 139.5, 138.0, 131.4, 128.6, 128.5, 128.2, 128.0, 126.6, 116.9, 22.0, 21.0 ppm; **MS** (APCI): $[M + 1]^+$ = 288.0 (99.67%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NSe$: 288.0291; found: 288.0293.

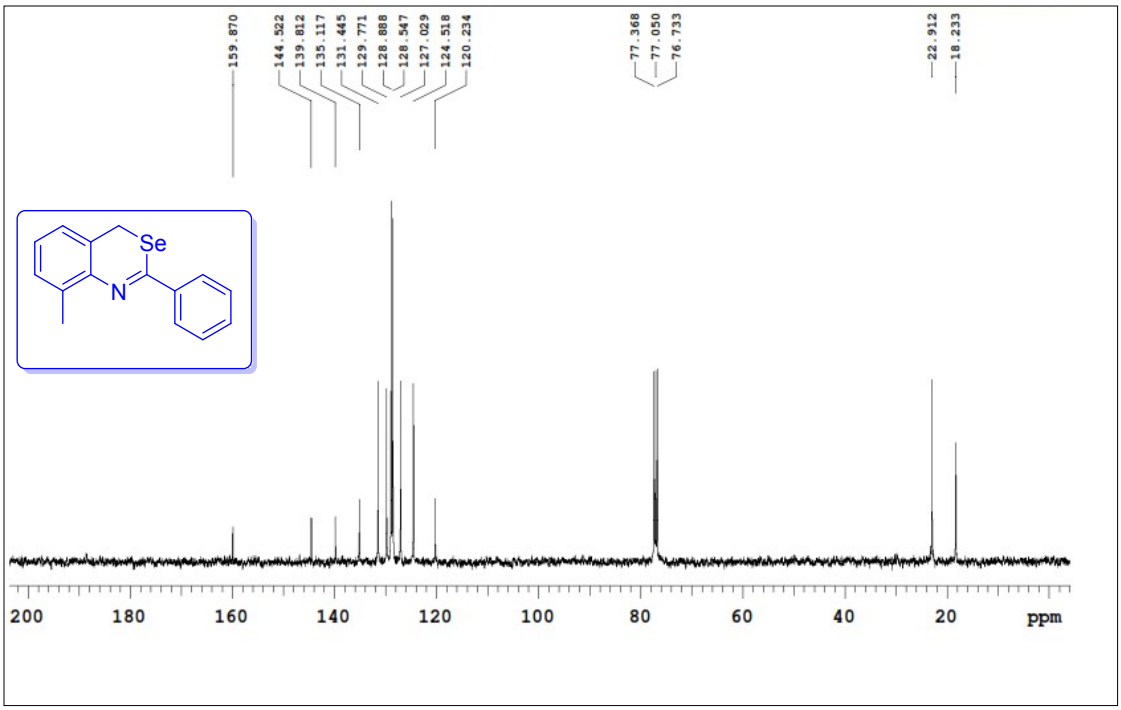
Synthesis of 8-methyl-2-phenyl-4H-benzo[d][1,3]selenazine (3ca); new compound



According to the general procedure, reactions between 2-amino-3-methylbenzyl alcohol **1c** (1.0 mmol, 137 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 8-methyl-2-phenyl-4H-benzo[d][1,3]selenazine **3ca** in 91% (260 mg) yield as pale yellow solid.




159.870
144.522
139.812
135.117
131.445
129.771
128.888
128.547
127.029
124.518
120.234
77.368
77.050
76.733
22.912
18.233
Se
N
200
180
160
140
120
100
80
60
40
20
ppm

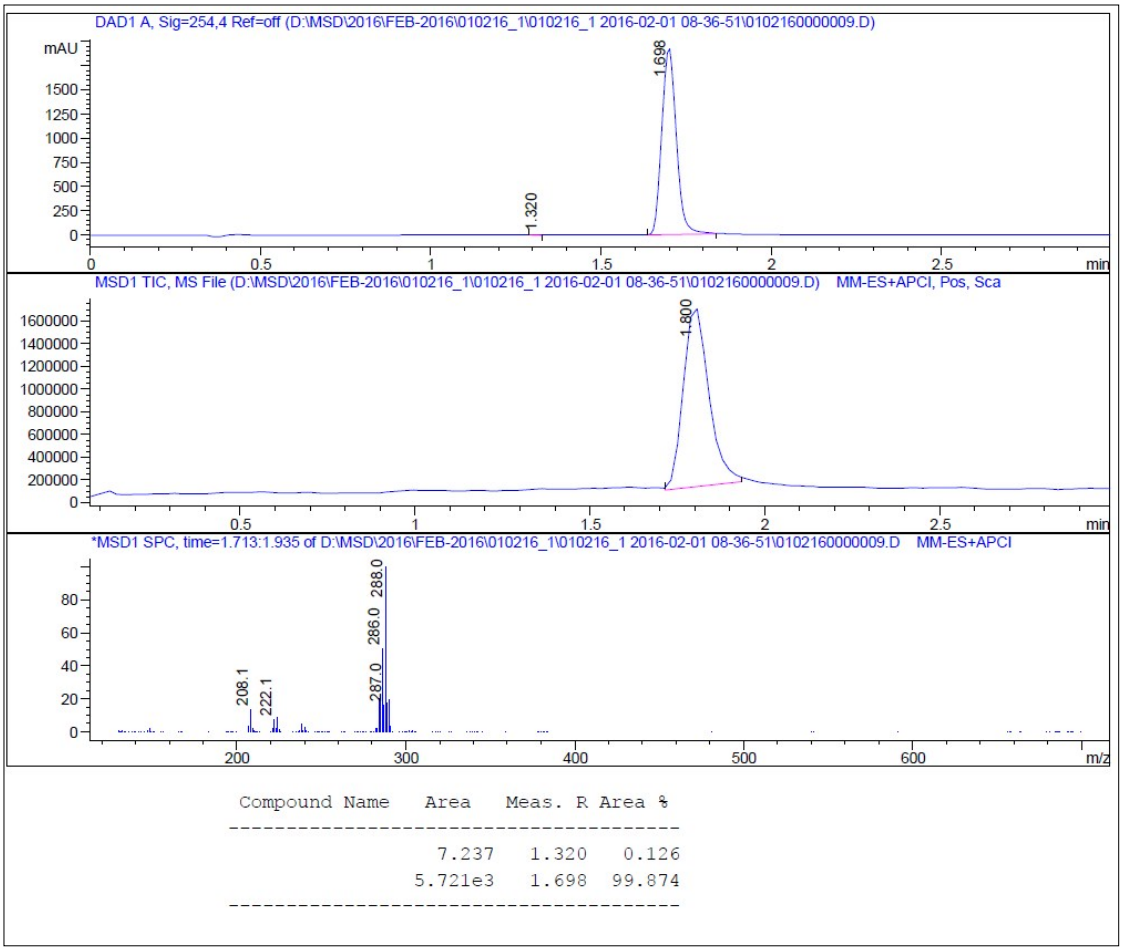
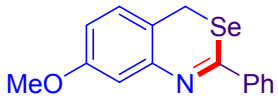


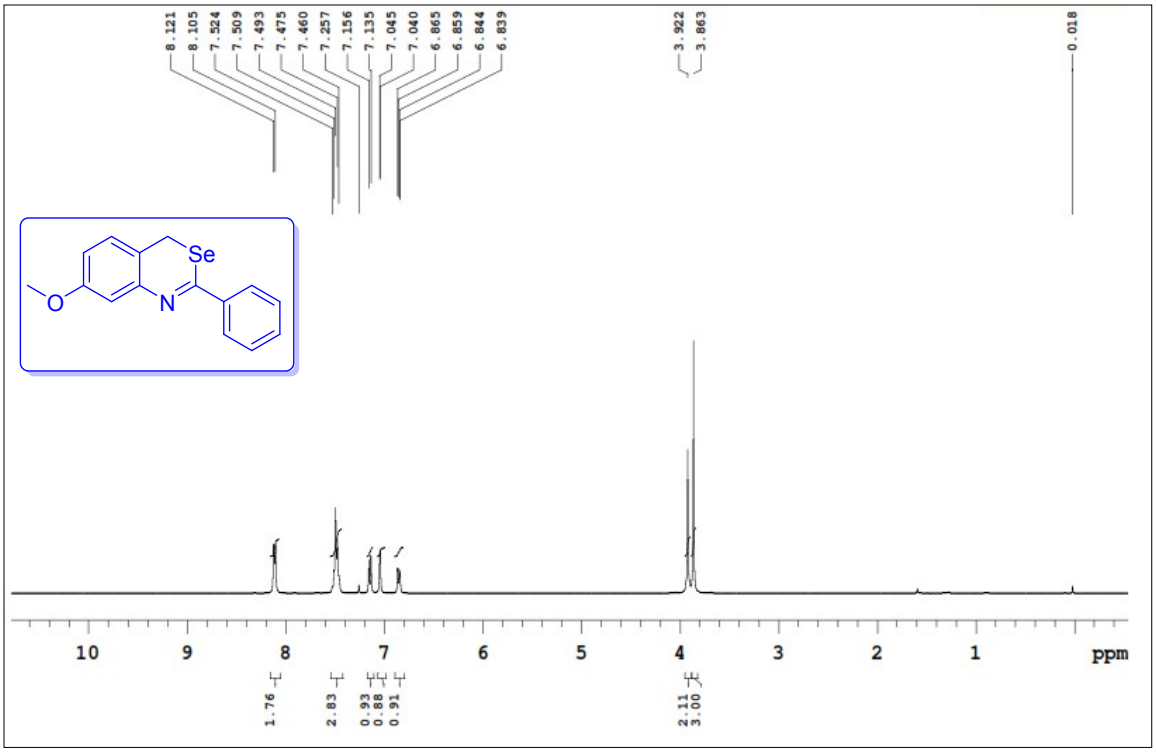
Figure 10. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ca** in $CDCl_3$ and LC-MS in Acetonitrile.

Pale yellow solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.49 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 6.8 Hz, 1H), 3.90 (s, 2H), 2.59 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.8, 144.5, 139.8, 135.1, 131.4, 129.7, 128.8, 128.5, 127.0, 124.5, 120.2, 22.9, 18.2 ppm; **MS** (APCI): $[M + 1]^+$ = 288.0 (99.87%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NSe$: 288.0291; found: 288.0293.

Synthesis of 7-methoxy-2-phenyl-4H-benzo[d][1,3]selenazine (3da); new compound



According to the general procedure, reactions between 2-amino-4-methoxybenzyl alcohol **1d** (1.0 mmol, 153 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-methoxy-2-phenyl-4H-benzo[d][1,3]selenazine **3da** in 96% (290 mg) yield as pale yellow solid.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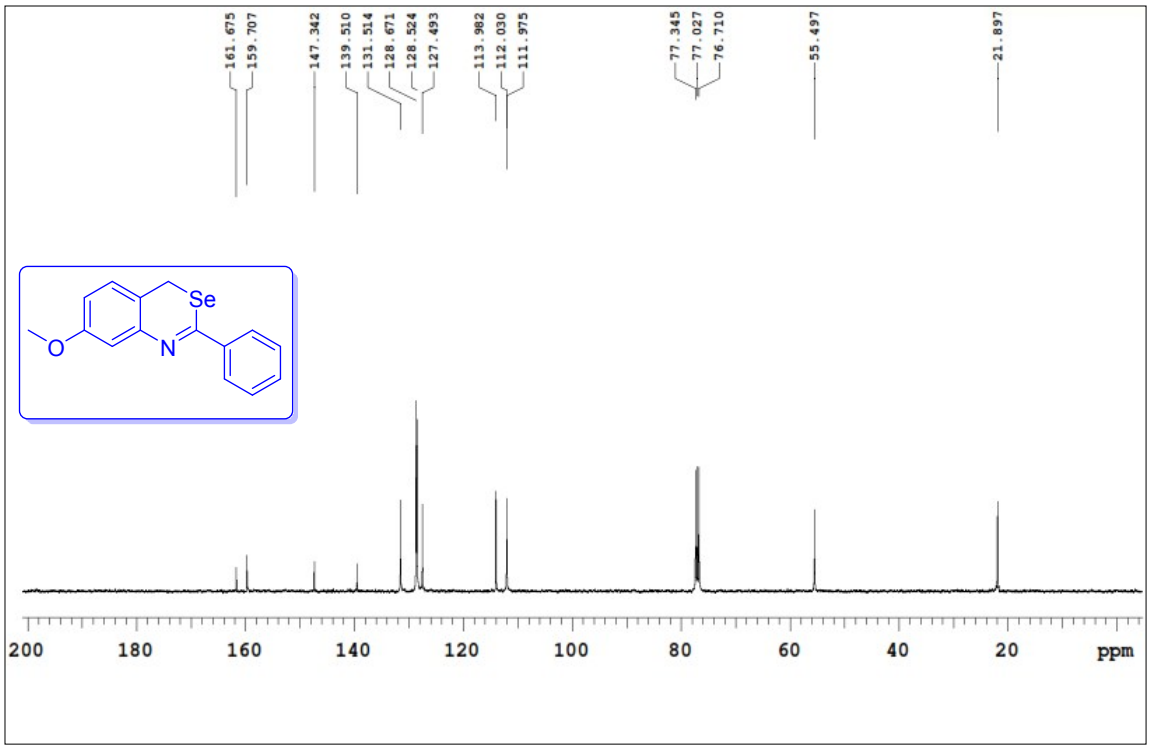
7.524
7.509
7.493
7.475
7.460
7.257
7.156
7.135
7.045
7.040
6.865
6.859
6.844
6.839
3.922
3.863
0.018
Se
O
N
10
9
8
7
6
5
4
3
2
1
ppm
1.76
2.83
0.93
0.88
0.91
2.11
3.00


161.675
159.707
147.342
139.510
131.514
128.671
128.524
127.493
113.982
112.030
111.975
77.345
77.027
76.710
55.497
21.897
Se
O
N
200
180
160
140
120
100
80
60
40
20
ppm

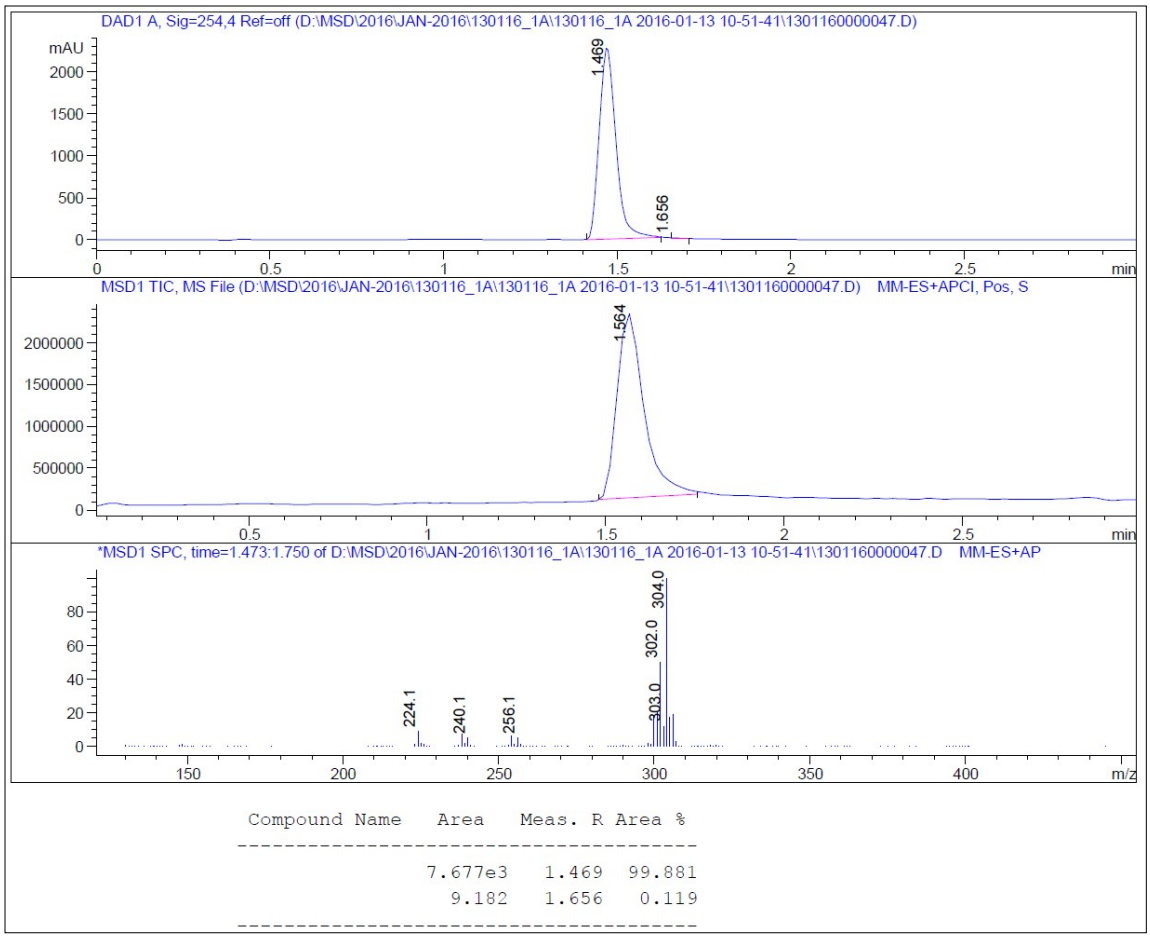
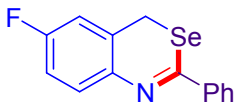


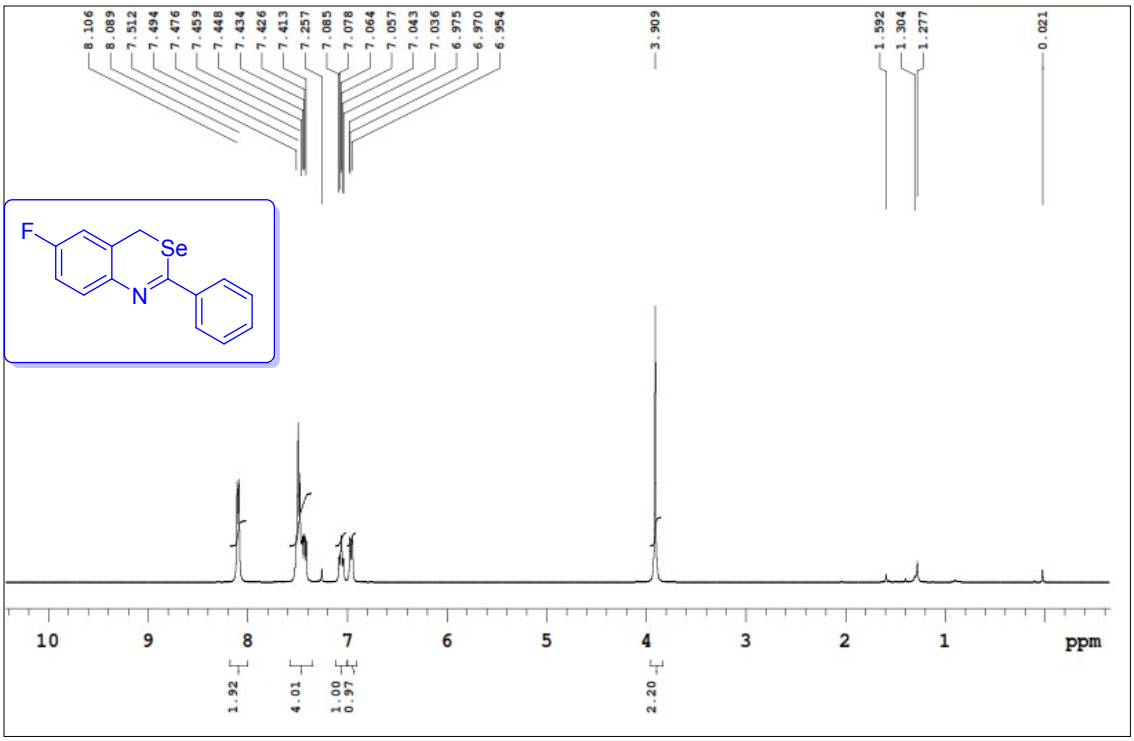
Figure 11. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3da** in $CDCl_3$ and LC-MS in Acetonitrile.

Pale yellow solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 6.4 Hz, 2H), 7.52 - 7.46 (m, 3H), 7.14 (t, *J* = 8.4 Hz, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.84 (dd, J = 8.4 Hz, 1H), 3.92 (s, 2H), 3.86 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.6, 159.7, 147.3, 139.5, 131.5, 128.6, 128.5, 127.4, 113.9, 112.0, 111.9, 55.4, 21.8 ppm; **MS** (APCI): $[M + 1]^+$ = 304.0 (99.88%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NOSe$: 304.0240; found: 304.0241.

Synthesis of 6-fluoro-2-phenyl-4H-benzo[d][1,3]selenazine (3ea); new compound



According to the general procedure, reactions between 2-amino-5-fluorobenzyl alcohol **1e** (1.0 mmol, 141 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 6-fluoro-2-phenyl-4H-benzo[d][1,3]selenazine **3ea** in 92% (267 mg) yield as off-white solid.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8.089
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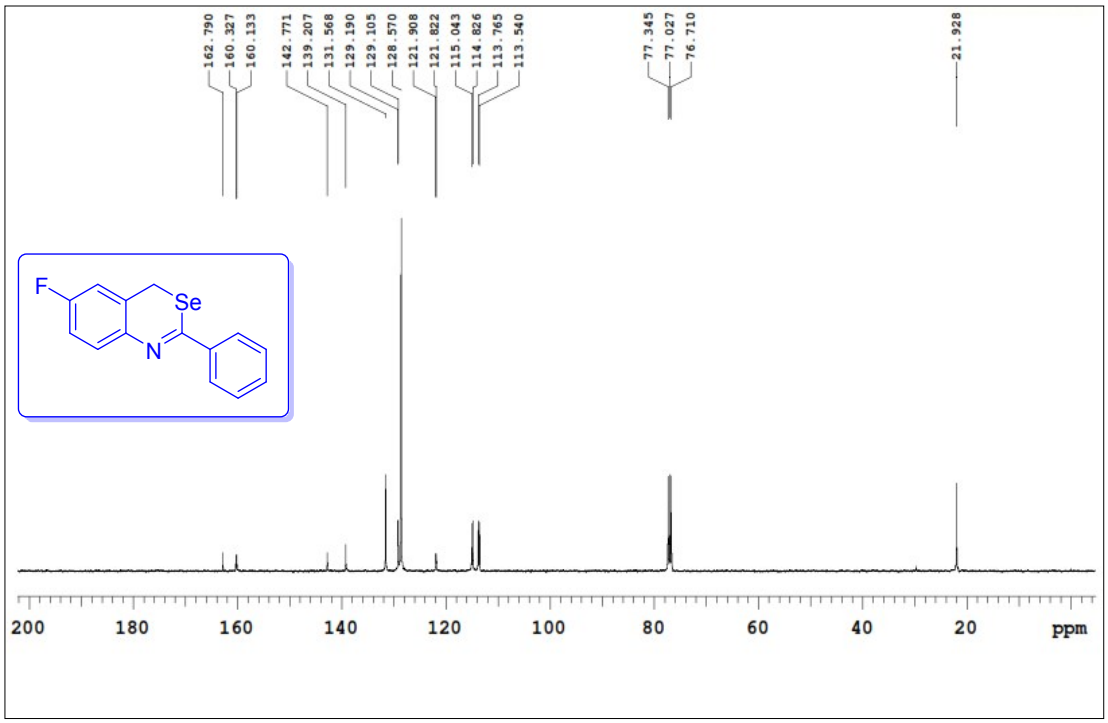
7.494
7.476
7.459
7.448
7.434
7.426
7.413
7.257
7.085
7.078
7.064
7.057
7.043
7.036
6.975
6.970
6.954
3.909
1.592
1.304
1.277
0.021
F
Se
N
10
9
8
7
6
5
4
3
2
1
ppm
1.92
4.01
1.00
0.97
2.20


162.790
160.327
160.133
142.771
139.207
131.568
129.190
129.105
128.570
121.908
121.822
115.043
114.826
113.765
113.540
77.345
77.027
76.710
21.928
F
Se
N
200
180
160
140
120
100
80
60
40
20
ppm

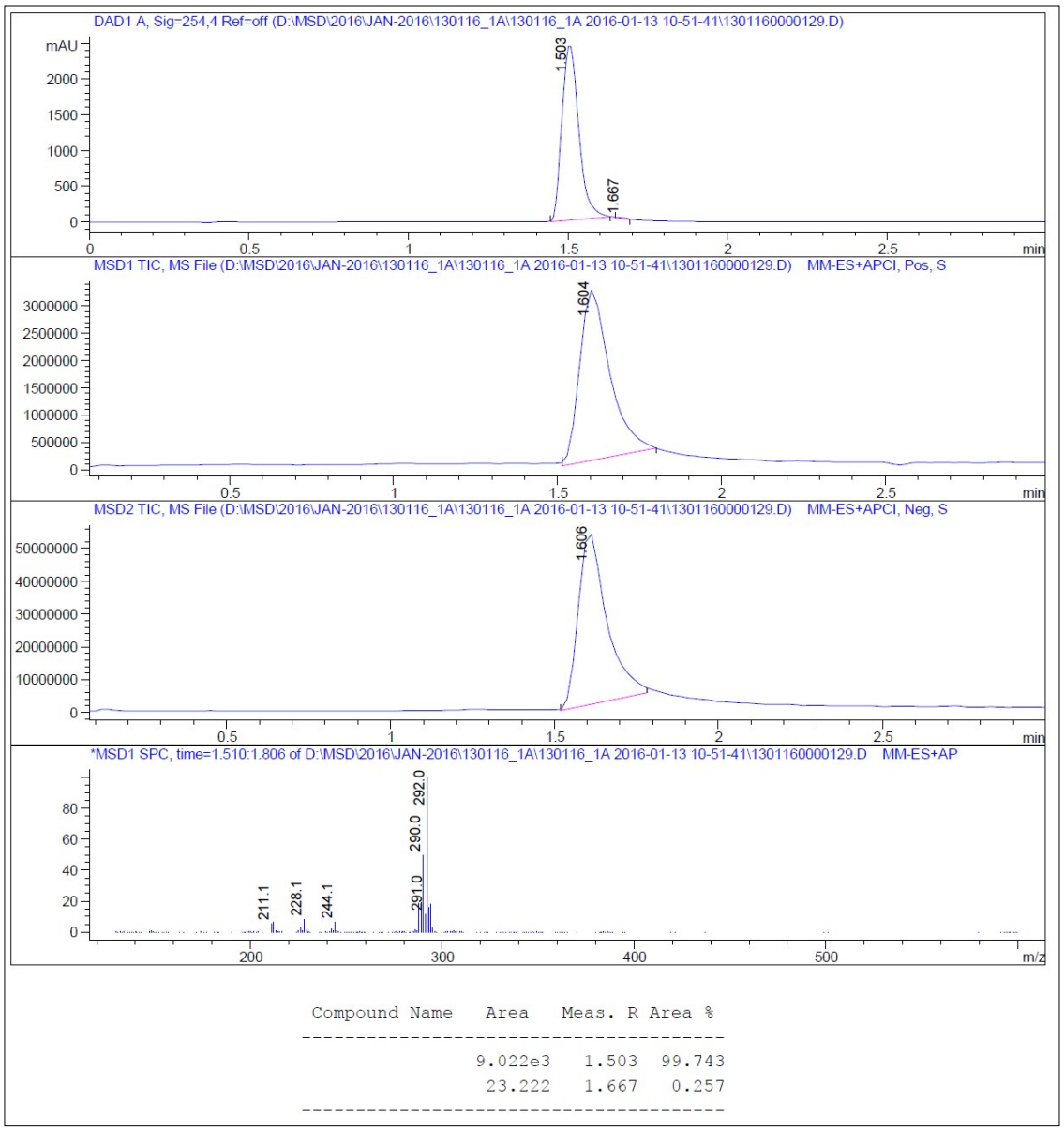
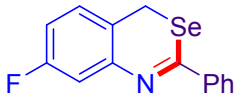


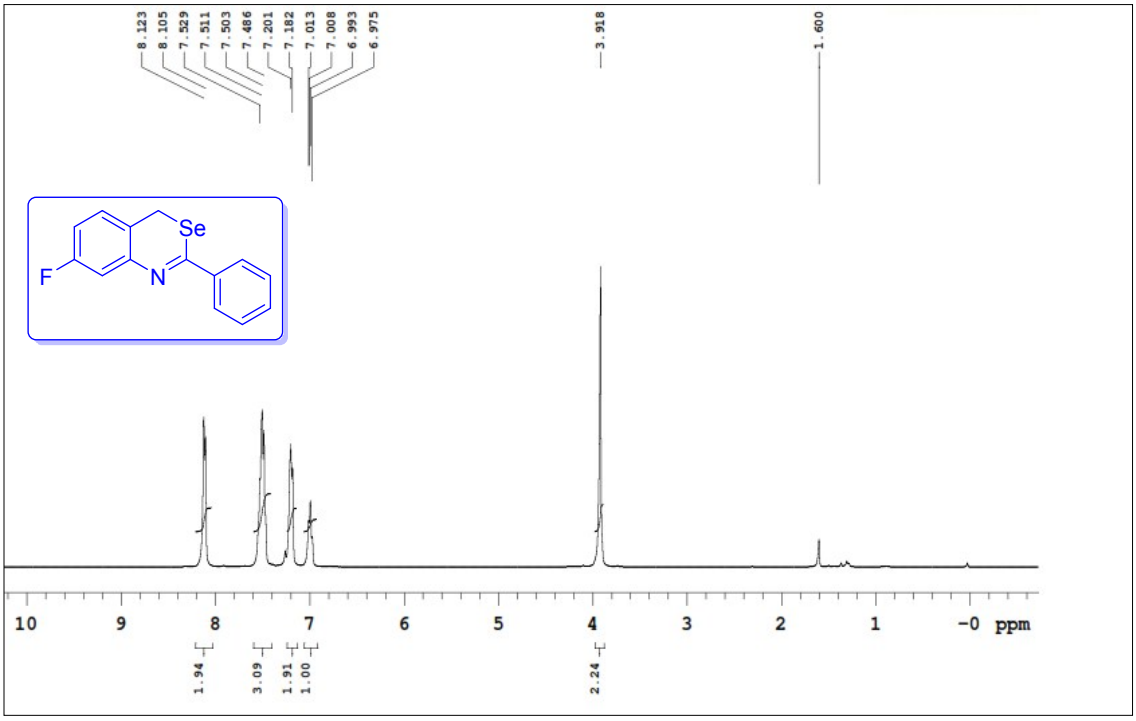
Figure 12. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ea** in $CDCl_3$ and LC-MS in Acetonitrile.

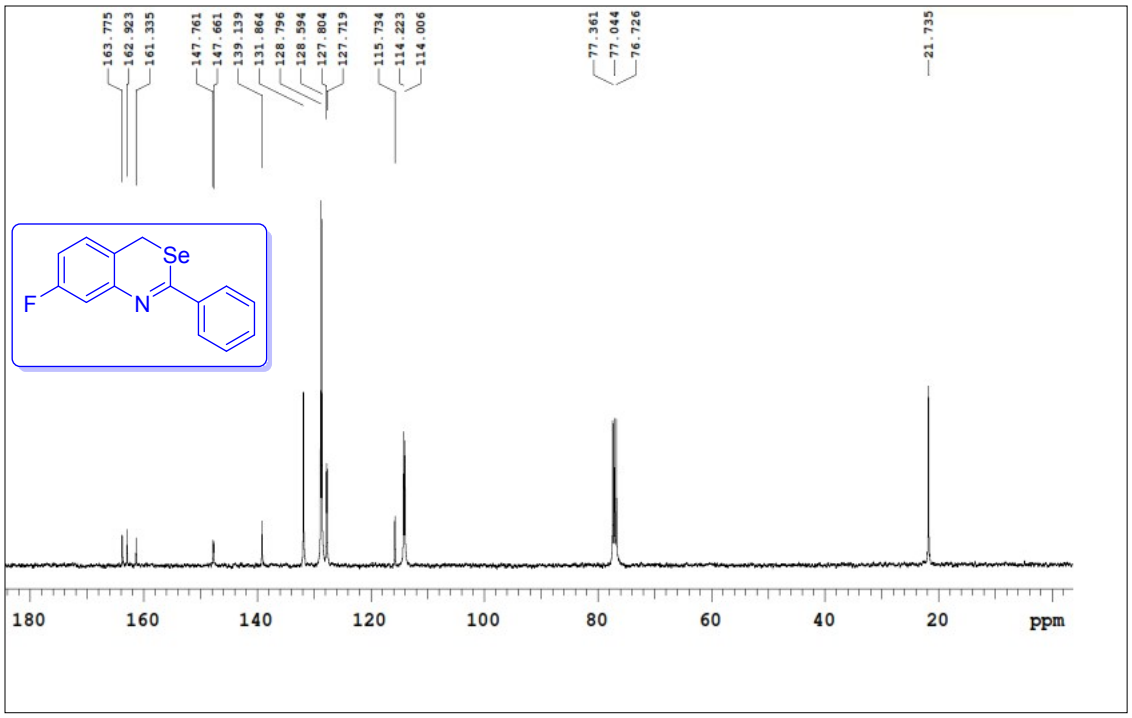
Off-white solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 6.8 Hz, 2H), 7.51 - 7.41 (m, 4H), 7.05 (dt, *J* = 8.4, 2.4 Hz, 1H), 6.96 (dd, *J* = 2.0, 8.4 Hz, 1H), 3.90 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.5 (d, *J* = 249.0 Hz), 160.1, 142.7, 139.2, 131.5, 129.1, 129.1, 128.5, 121.9, 121.8, 115.0, 114.8, 113.7, 113.5, 21.9 ppm; **MS** (APCI): $[M + 1]^+$ = 292.01 (99.74%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNSe$: 292.0040; found: 292.0038.

Synthesis of 7-fluoro-2-phenyl-4H-benzo[d][1,3]selenazine (3fa); new compound



According to the general procedure, reactions between 2-amino-4-fluorobenzyl alcohol **1f** (1.0 mmol, 141 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-fluoro-2-phenyl-4H-benzo[d][1,3]selenazine **3fa** in 92% (267 mg) yield as brown solid.




163.775
162.923
161.335
147.761
147.661
139.139
131.864
128.796
128.594
127.804
127.719
115.734
114.223
114.006
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180
160
140
120
100
80
60
40
20
ppm

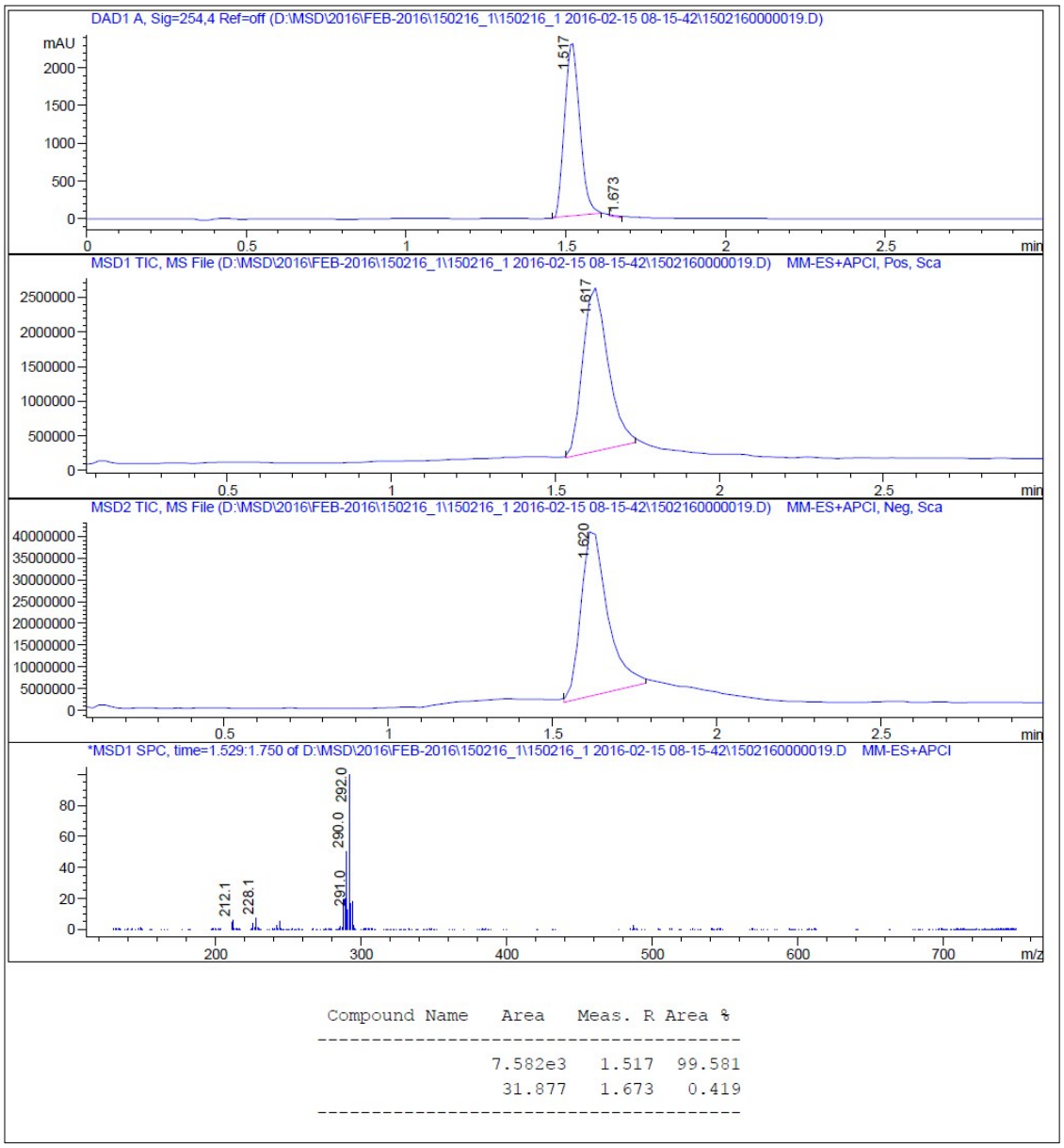
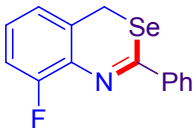


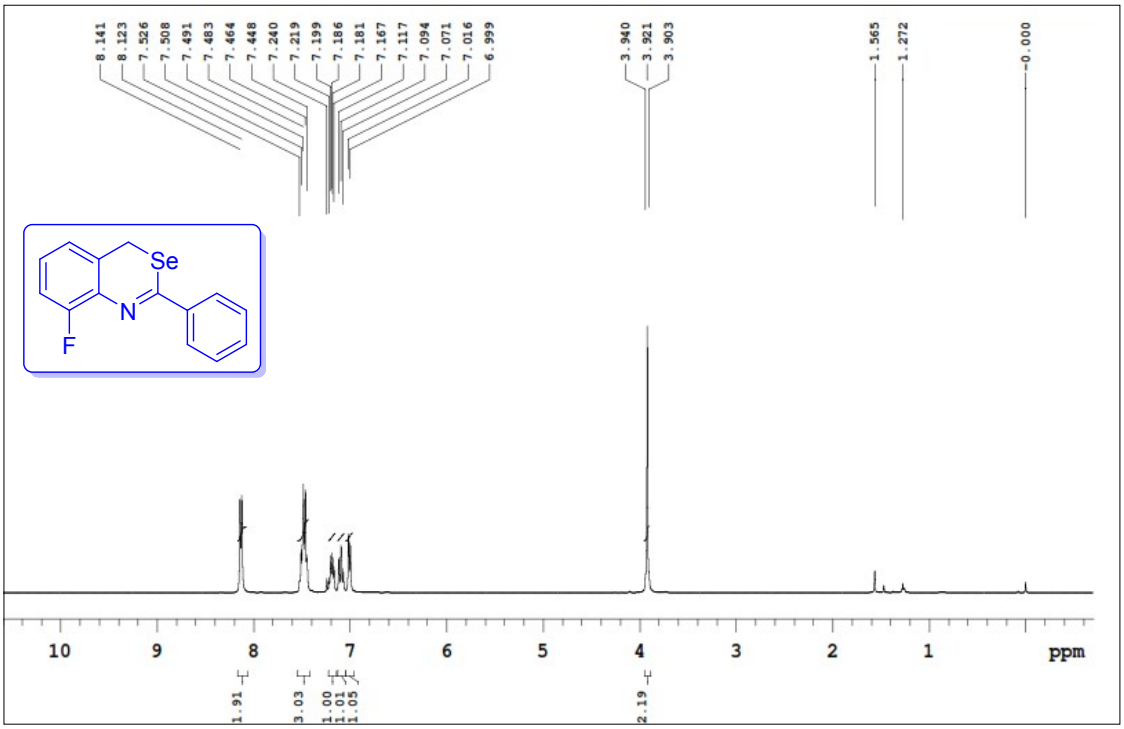
Figure 13. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3fa** in $CDCl_3$ and LC-MS in Acetonitrile.

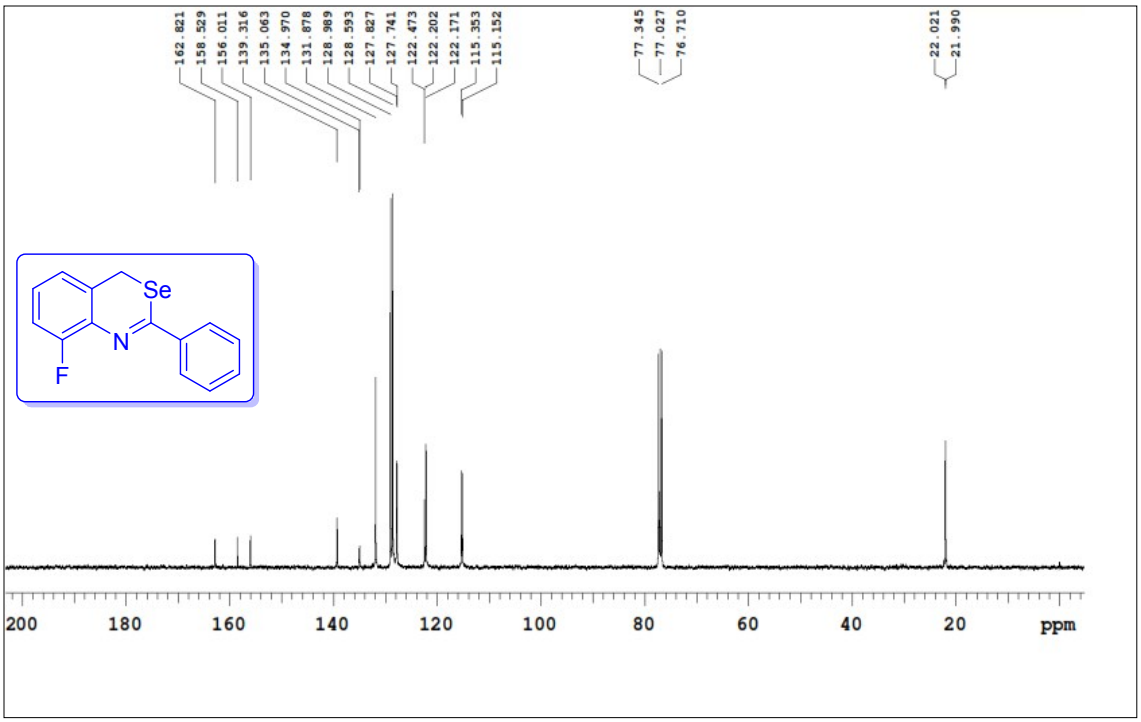
Brown solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.48 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 3.91 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.9, 162.5 (d, *J* = 244.5 Hz), 147.7, 147.6, 139.1, 131.8, 128.7, 128.5, 127.8, 127.7, 115.7, 114.2, 114.0, 21.7 ppm; **MS** (APCI): $[M + 1]^+$ = 292.0 (99.58%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNSe$: 292.0040; found: 292.0038.

Synthesis of 8-fluoro-2-phenyl-4H-benzo[d][1,3]selenazine (3ga); new compound



According to the general procedure, reactions between 2-amino-3-fluorobenzyl alcohol **1g** (1.0 mmol, 141 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 8-fluoro-2-phenyl-4H-benzo[d][1,3]selenazine **3ga** in 90% (261 mg) yield as pale yellow solid.




162.821
158.529
156.011
139.316
135.063
134.970
131.878
128.989
128.593
127.827
127.741
122.473
122.202
122.171
115.353
115.152
77.345
77.027
76.710
22.021
21.990
Se
N
F
200
180
160
140
120
100
80
60
40
20
ppm

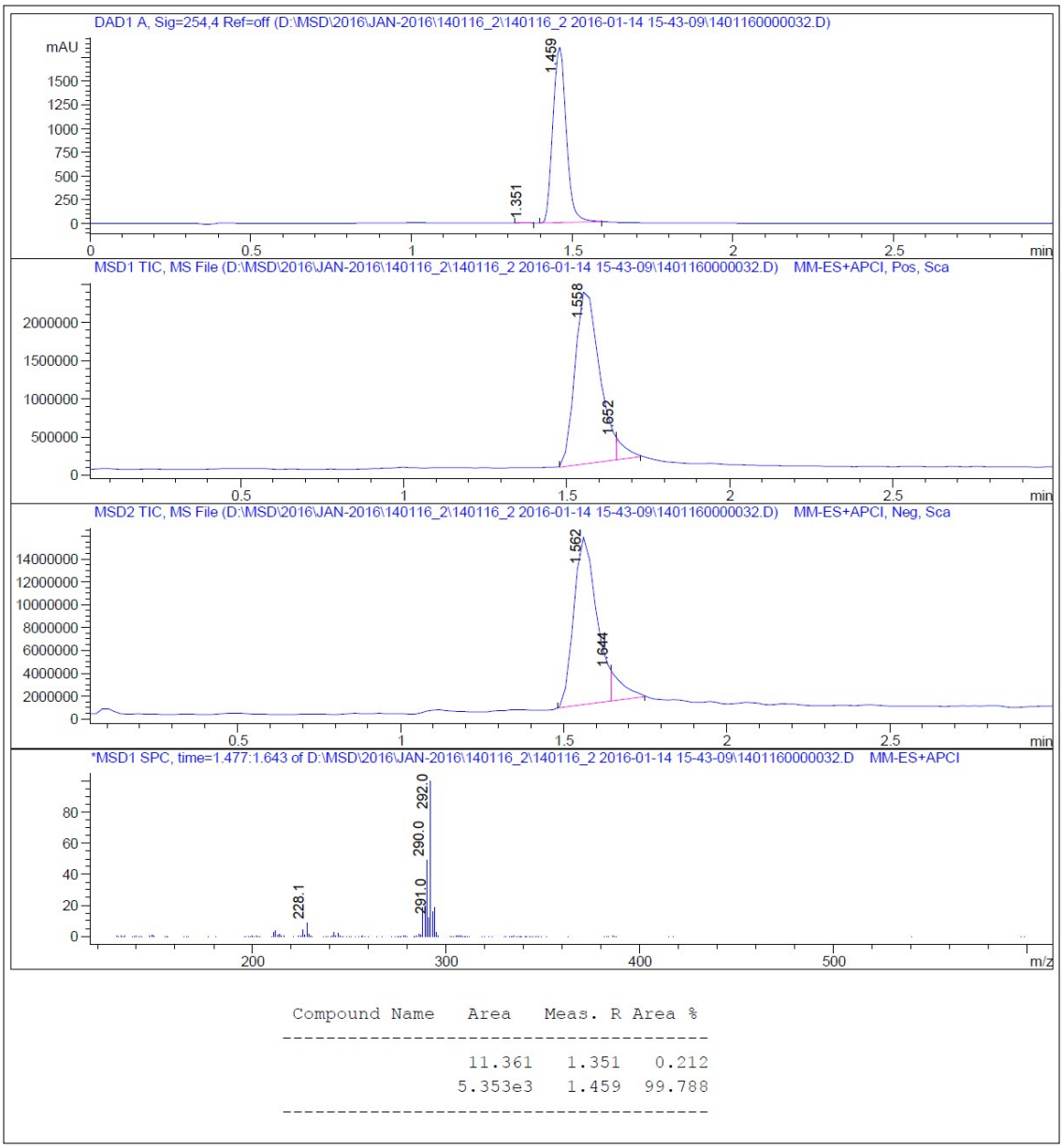
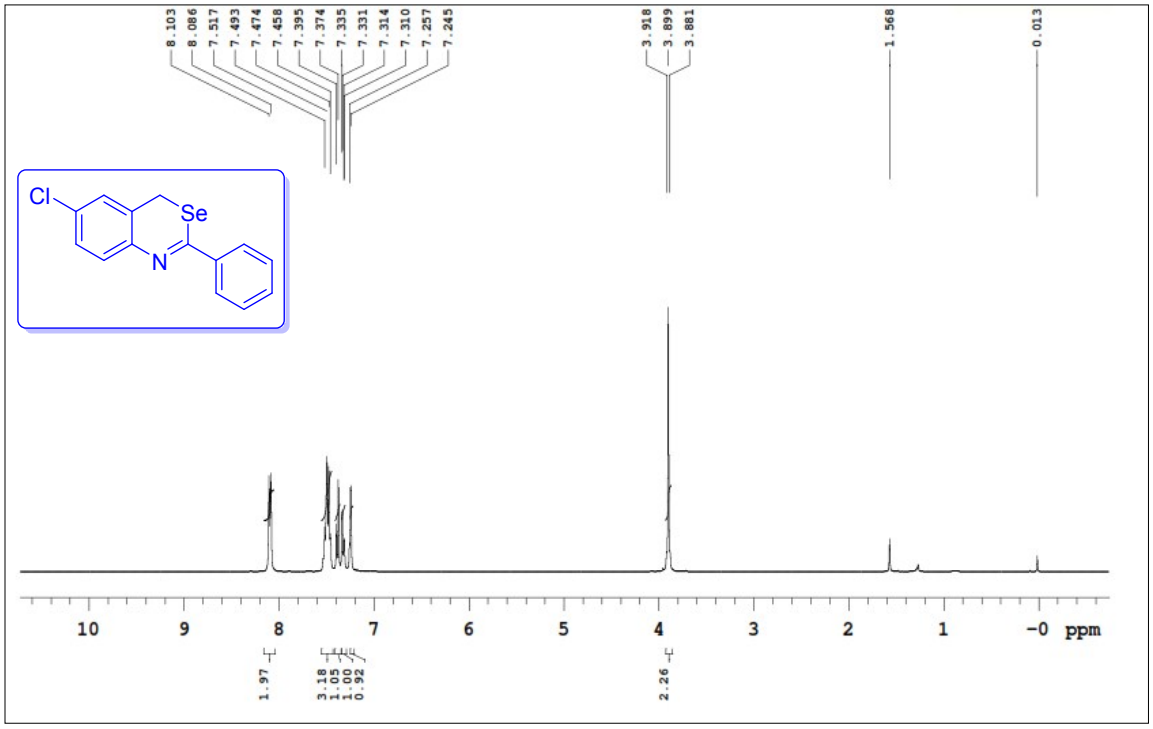


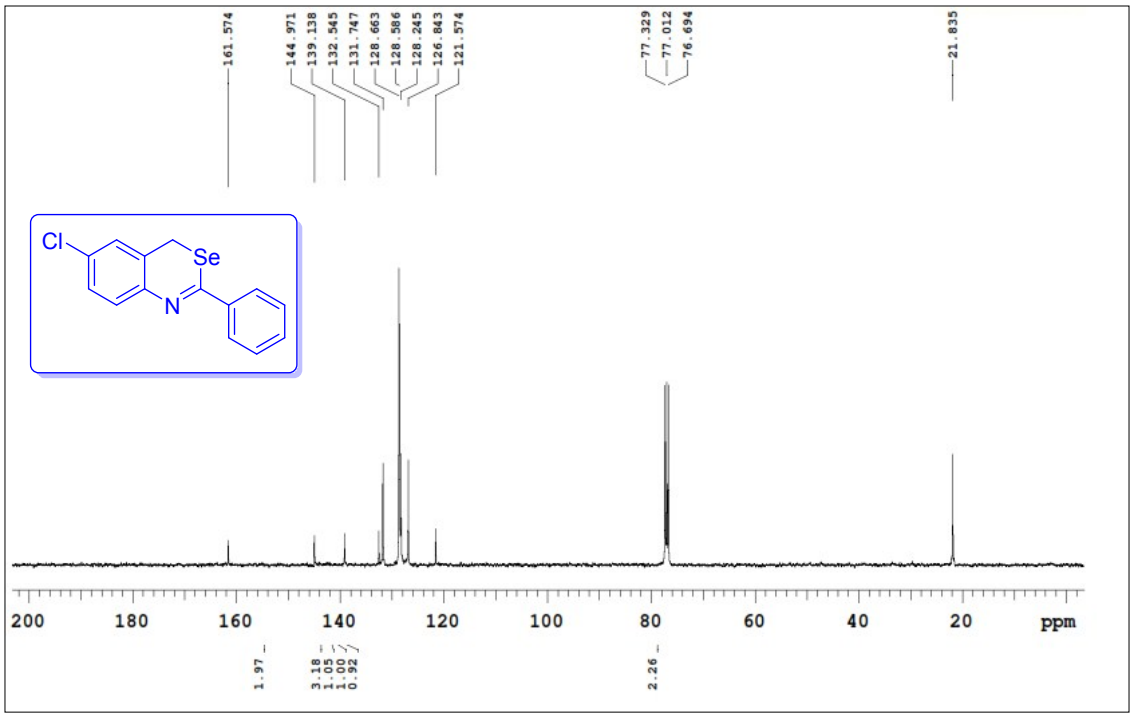
Figure 14. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ga** in $CDCl_3$ and LC-MS in Acetonitrile.

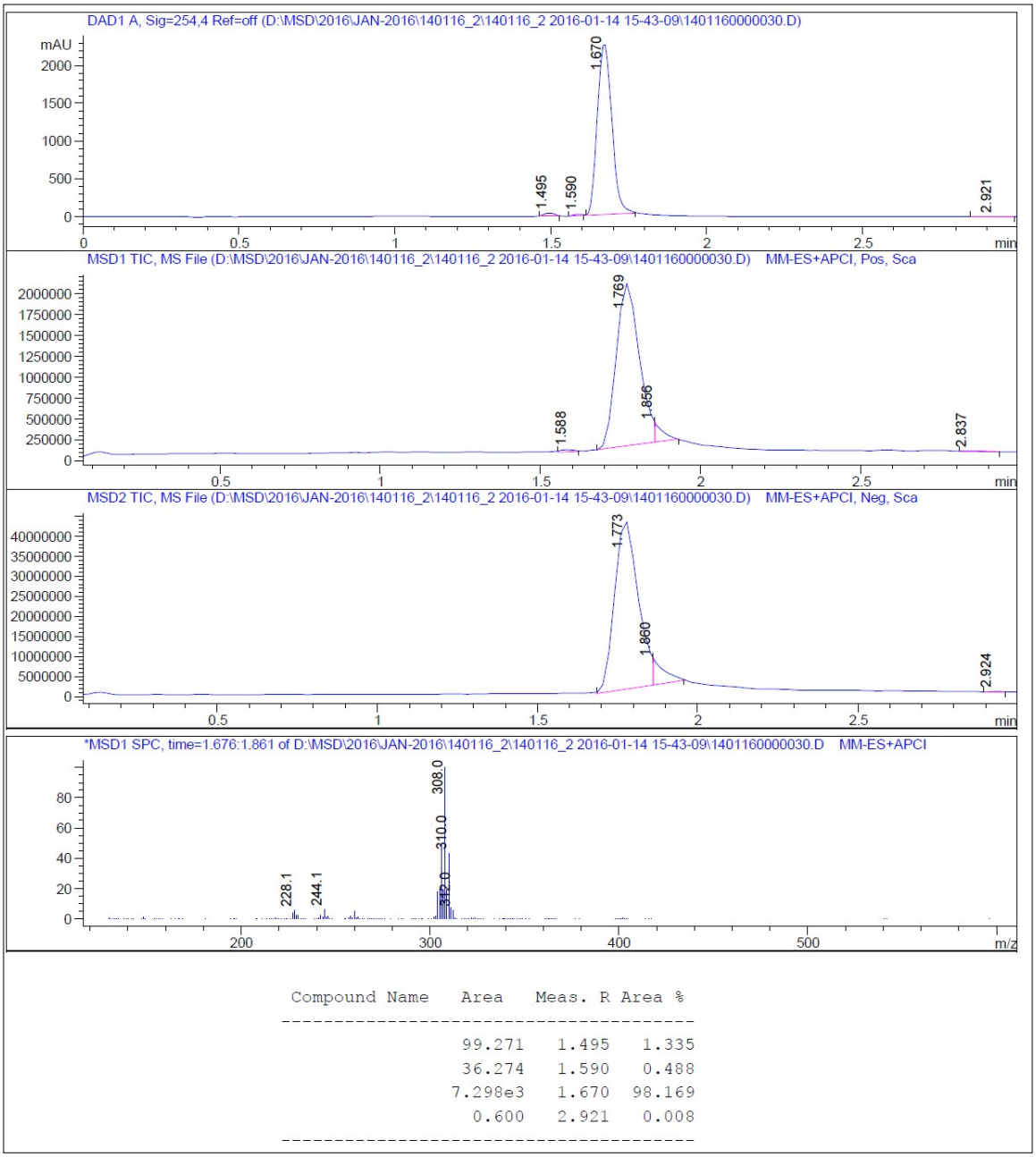
Pale yellow solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.2 Hz, 2H), 7.52 – 7.44 (m, 3H), 7.21 – 7.18 (m, 1H), 7.11 (t, *J* = 9.2 Hz, 1H), 7.00 (d, *J* = 6.8 Hz, 1H), 3.92 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.8, 157.2 (d, *J* = 252.9 Hz), 139.3, 135.0, 134.9, 131.8, 128.9, 128.5, 127.8, 127.7, 122.4, 122.2, 122.1, 115.3, 115.1, 22.0, 21.9 ppm; **MS** (APCI): $[M + 1]^+$ = 292.01 (99.78%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNSe$: 292.0040; found: 292.0041.

Synthesis of 6-chloro-2-phenyl-4H-benzo[d][1,3]selenazine (3ha); new compound

According to the general procedure, reactions between 2-amino-5-chlorobenzyl alcohol **1h** (1.0 mmol, 158 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 6-chloro-2-phenyl-4H-benzo[d][1,3]selenazine **3ha** in 93% (285 mg) yield as pale yellow solid.




161.574
144.971
139.138
132.545
131.747
128.663
128.586
128.245
126.843
121.574
77.329
77.012
76.694
21.835
Cl
Se
N
200
180
160
140
120
100
80
60
40
20
ppm
1.97
3.18
1.05
1.00
0.92
2.26

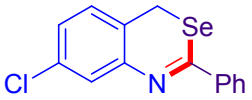


Compound Name	Area	Meas. R	Area %
	99.271	1.495	1.335
	36.274	1.590	0.488
	7.298e3	1.670	98.169
	0.600	2.921	0.008

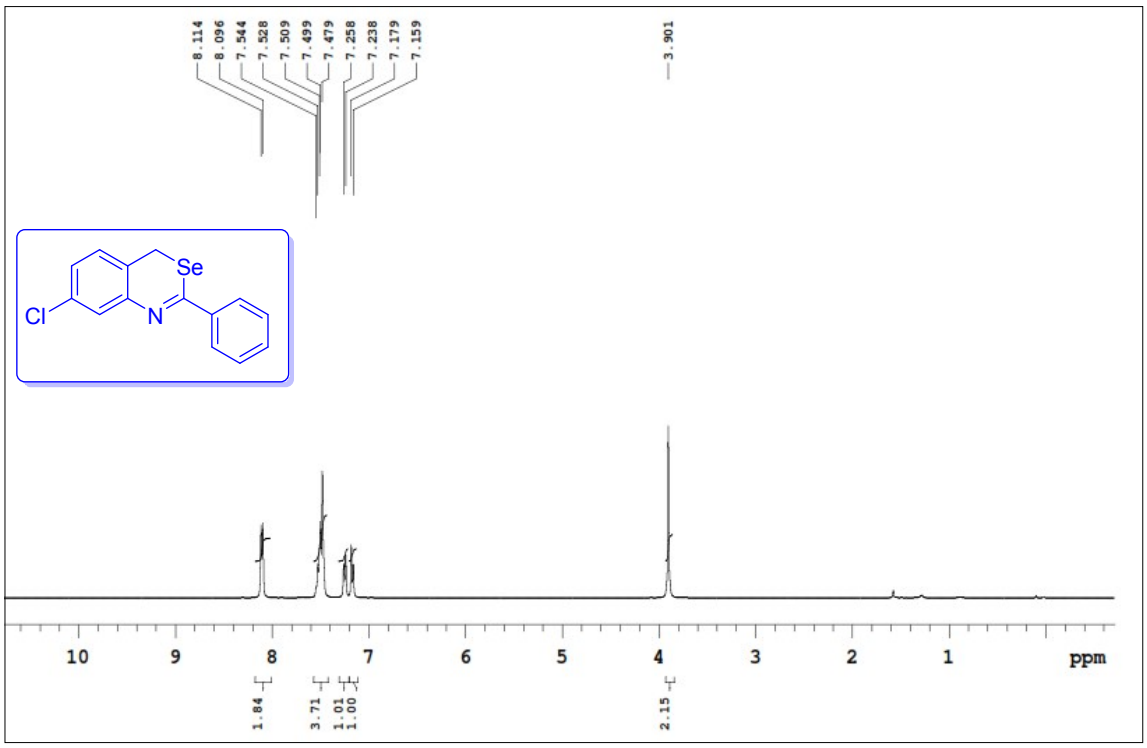
Figure 15. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ha** in $CDCl_3$ and LC-MS in Acetonitrile.

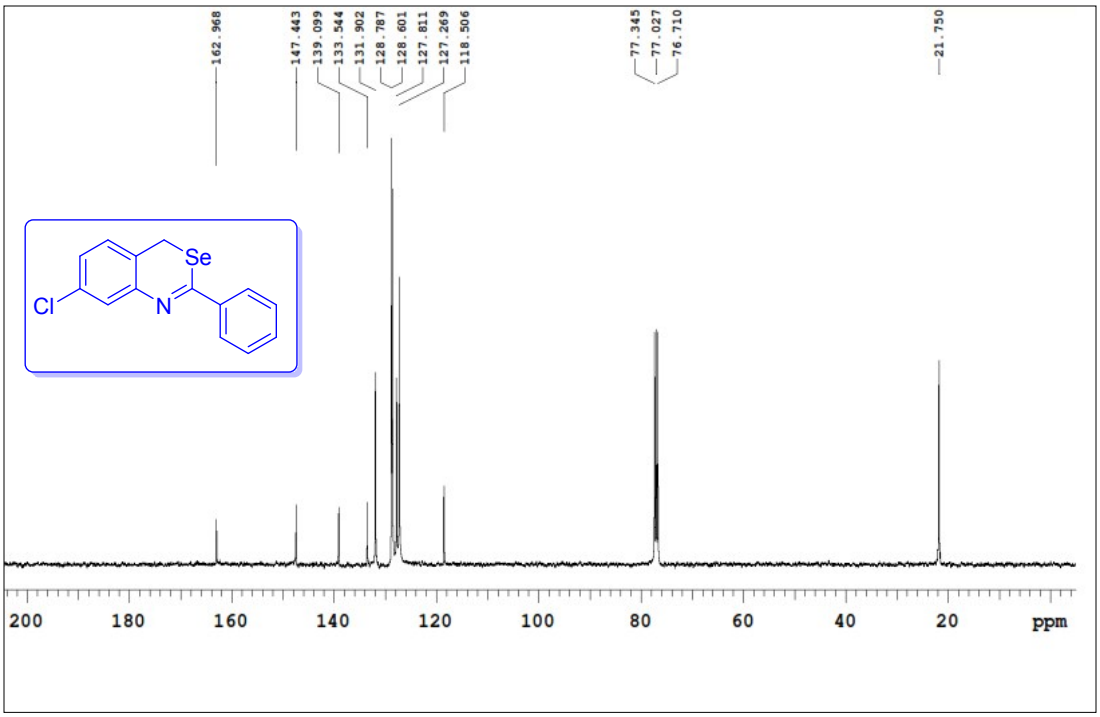
Pale yellow solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 6.8 Hz, 2H), 7.53 – 7.45 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.32 (dd, *J* = 8.4 Hz, 1H), 7.24 (s, 1H), 3.89 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.5, 144.9, 139.1, 132.5, 131.7, 128.6, 128.5, 128.2, 126.8, 121.5, 21.8 ppm; **MS** (APCI): $[M + 1]^+$ = 308.0 (98.16%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}ClNSe$: 307.9745; found: 307.9744.

Synthesis of 7-chloro-2-phenyl-4H-benzo[d][1,3]selenazine (3ia); new compound



According to the general procedure, reactions between 2-amino-4-chlorobenzyl alcohol **1i** (1.0 mmol, 158 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-chloro-2-phenyl-4H-benzo[d][1,3]selenazine **3ia** in 95% (291 mg) yield as pale yellow solid.




162.968
147.443
139.099
133.544
131.902
128.787
128.601
127.811
127.269
118.506
77.345
77.027
76.710
21.750
Se
Cl
N
200
180
160
140
120
100
80
60
40
20
ppm

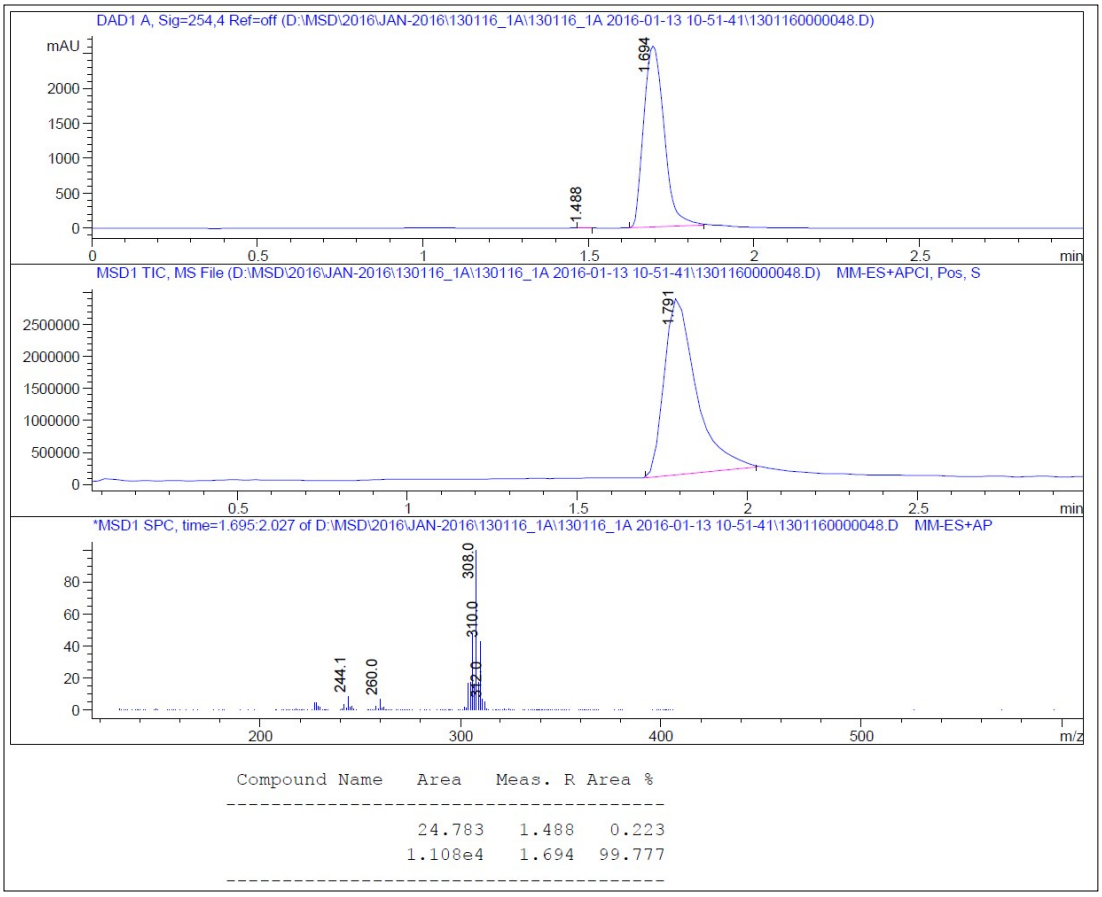
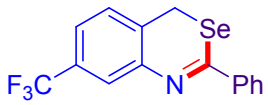


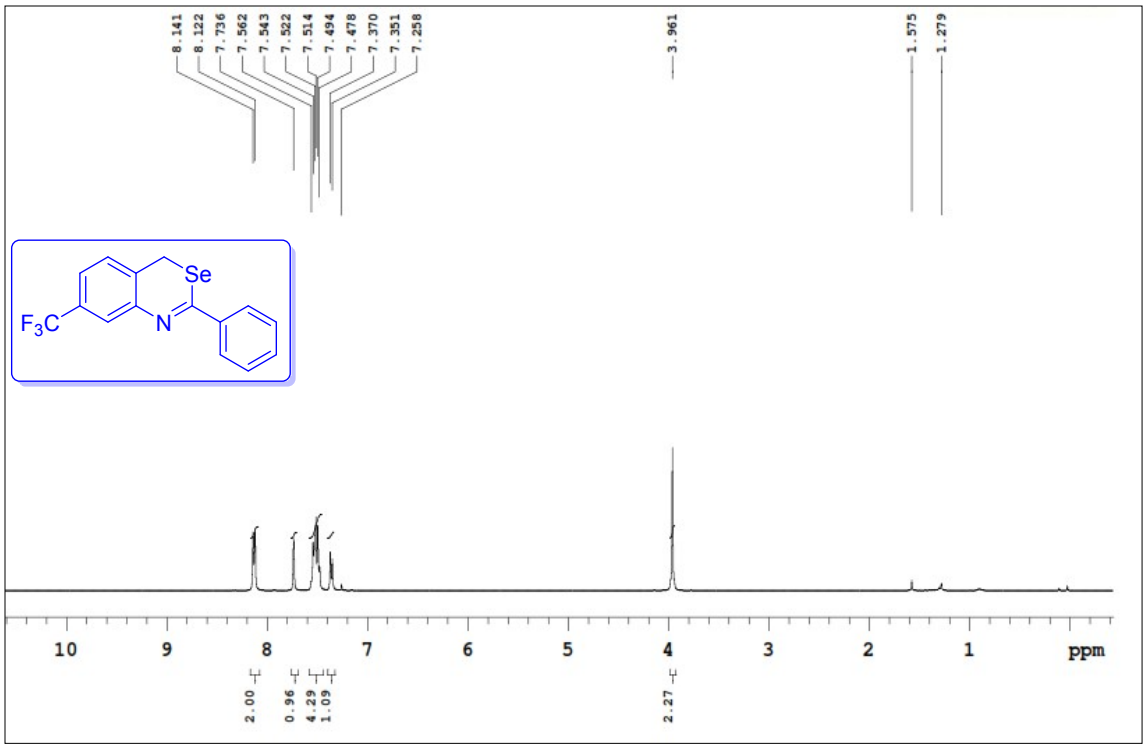
Figure 16. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ia** in $CDCl_3$ and LC-MS in Acetonitrile.

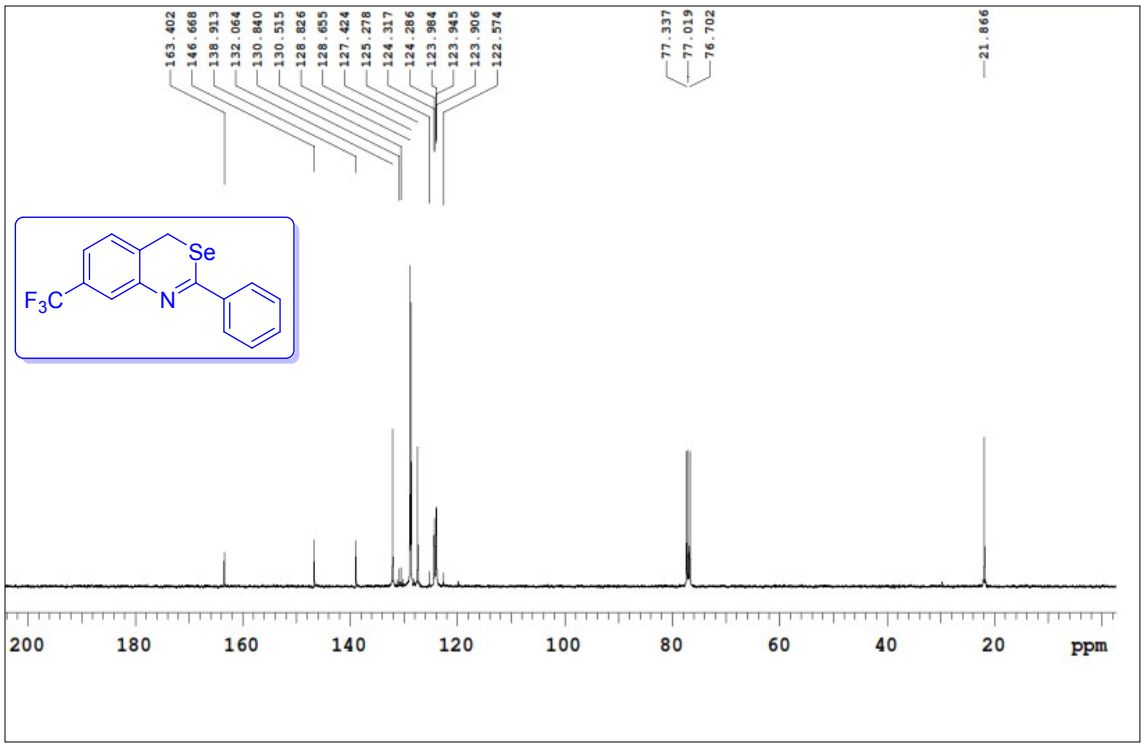
Pale yellow solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 7.2 Hz, 2H), 7.54 - 7.47 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.9, 147.4, 139.0, 133.5, 131.9, 128.7, 128.6, 127.8, 127.2, 118.5, 21.7 ppm; **MS** (APCI): $[M + 1]^+$ = 308.0 (99.77%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}ClNSe$: 307.9745; found: 307.9743.

Synthesis of 2-phenyl-7-(trifluoromethyl)-4H-benzo[d][1,3]selenazine (3ja); new compound



According to the general procedure, reactions between 2-amino-4-trifluoromethylbenzyl alcohol **1j** (1.0 mmol, 191 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-phenyl-7-(trifluoromethyl)-4H-benzo[d][1,3]selenazine **3ja** in 94% (320 mg) yield as off-white solid.


8.141
8.122
7.736
7.562
7.543
7.522
7.514
7.494
7.478
7.370
7.351
7.258
3.961
1.575
1.279
Se
F3C
N
10
9
8
7
6
5
4
3
2
1
ppm
2.00
0.96
4.29
1.09
2.27


163.402
146.668
138.913
132.064
130.840
130.515
128.826
128.655
127.424
125.278
124.317
124.286
123.984
123.945
123.906
122.574
77.337
77.019
76.702
21.866
Se
F3C
N
200
180
160
140
120
100
80
60
40
20
ppm

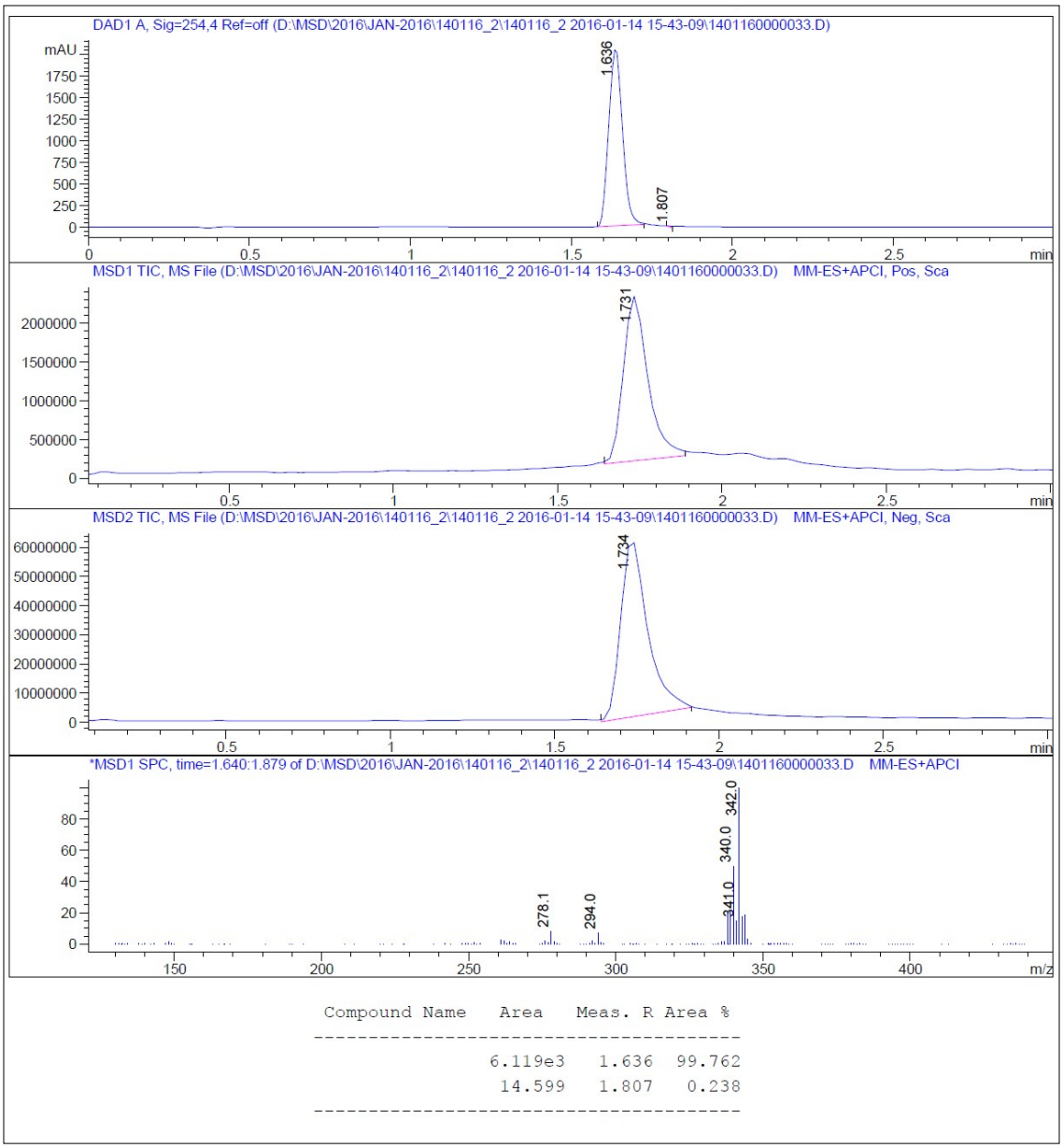
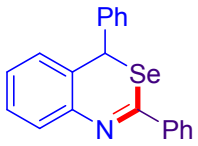


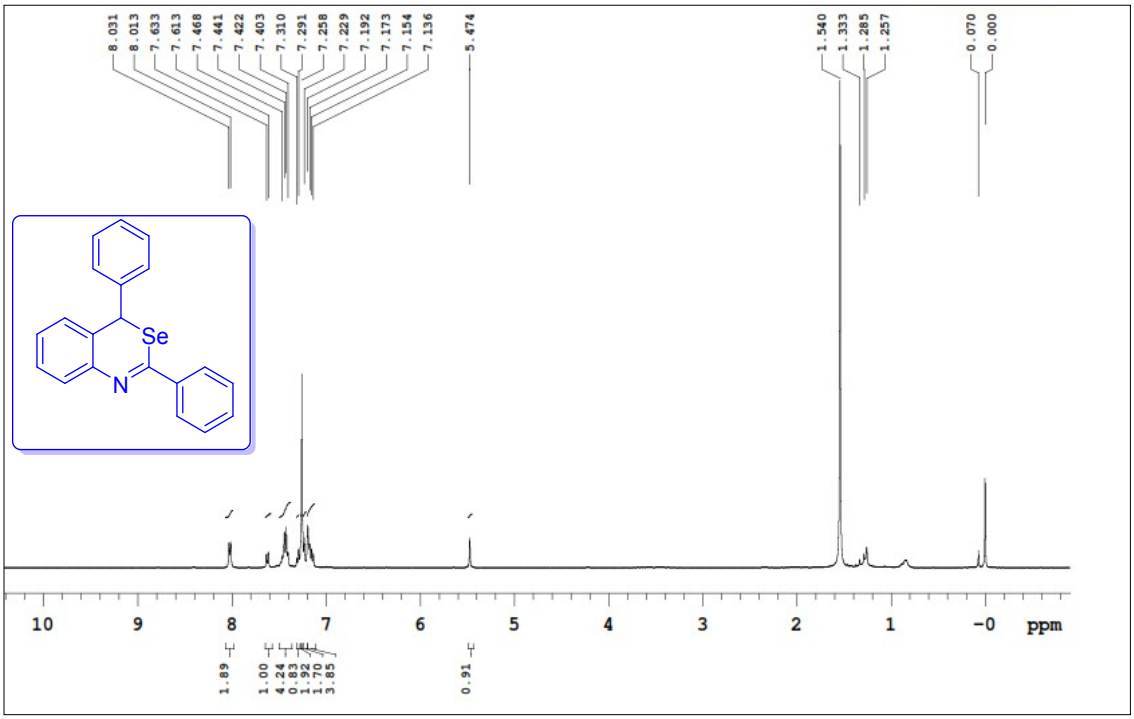
Figure 17. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ja** in $CDCl_3$ and LC-MS in Acetonitrile.

Off-white solid; $\mathbf{R_f}$ = 0.67 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.6 Hz, 2H), 7.73 (s, 1H), 7.56 – 7.47 (m, 4H), 7.36 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.4, 146.6, 138.9, 132.0, 130.6 (q, *J* = 32.8 Hz), 128.8, 128.6, 127.4, 124.3, 124.2, 123.98, 123.94, 123.92 (q, *J* = 274.6 Hz), 123.90, 21.8 ppm; **MS** (APCI): $[M + 1]^+$ = 342.0 (99.76%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{11}F_3NSe$: 342.0008; found: 342.0005.

Synthesis of 2,4-diphenyl-4H-benzo[d][1,3]selenazine (3ka); new compound



According to the general procedure, reactions between 2-aminobenzhydrol **1k** (1.0 mmol, 199 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2,4-diphenyl-4H-benzo[d][1,3]selenazine **3ka** in 89% (310 mg) yield as pale yellow solid.



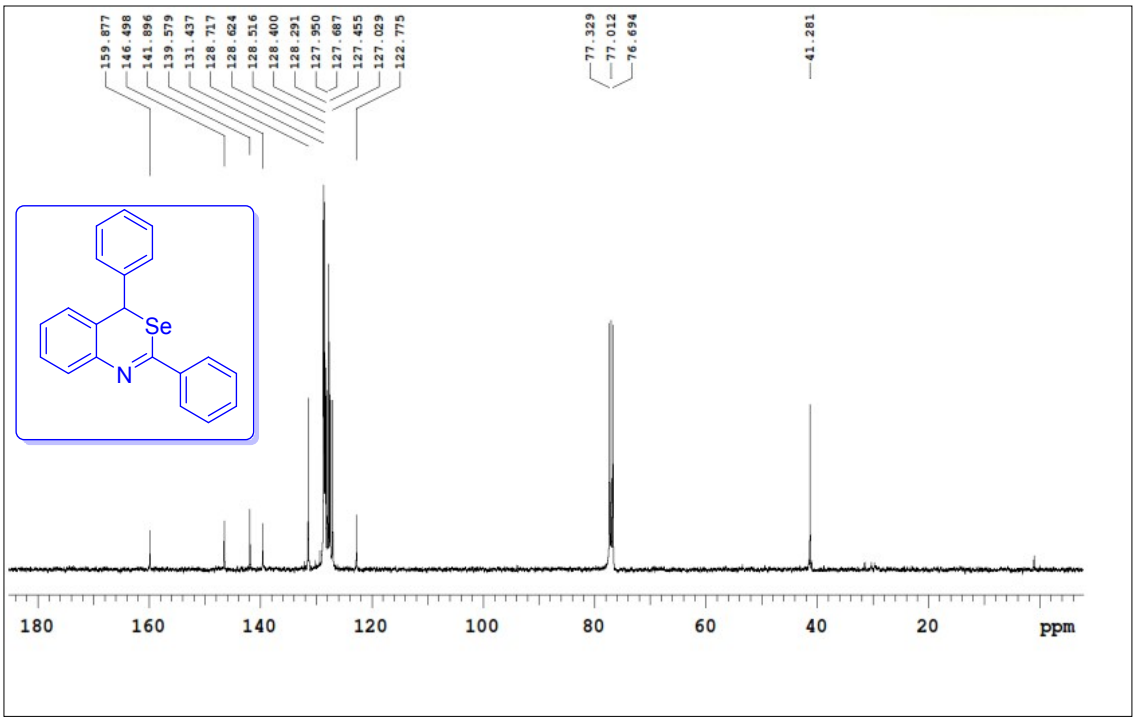
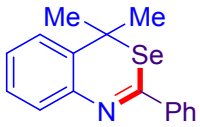


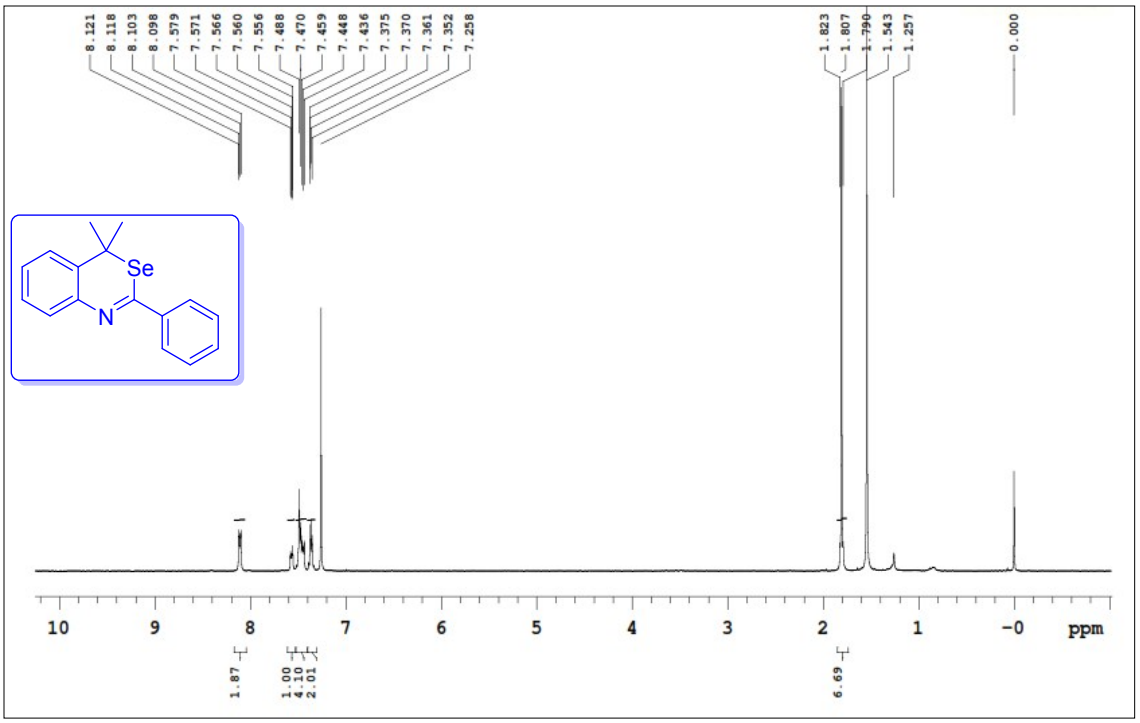
Figure 18. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3ka** in $CDCl_3$.

Pale yellow solid; $\mathbf{R_f}$ = 0.67 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.51 - 7.40 (m, 4H), 7.31 – 7.29 (m, 3H), 5.47 (s, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.8, 146.4, 141.8, 139.5, 131.4, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.6, 127.4, 127.0, 122.7, 41.2 ppm; **MS** (APCI): $[M + 1]^+$ = 350.0 (99.25%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{20}H_{16}NSe$: 350.0447; found: 350.0445.

Synthesis of 4,4-dimethyl-2-phenyl-4H-benzo[d][1,3]selenazine (3la); new compound



According to the general procedure, reactions between 2-(2-aminophenyl)propan-2-ol **1l** (1.0 mmol, 151 mg), benzoselenoamide **2a** (1.0 mmol, 184 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 4,4-dimethyl-2-phenyl-4H-benzo[d][1,3]selenazine **3la** in 86% (258 mg) yield as white solid.


8.121
8.118
8.103
8.098
7.579
7.571
7.566
7.560
7.556
7.488
7.470
7.459
7.448
7.436
7.375
7.370
7.361
7.352
7.258
1.823
1.807
1.790
1.543
1.257
0.000
Se
N
10
9
8
7
6
5
4
3
2
1
−0
ppm
1.87
1.00
4.10
2.01
6.69

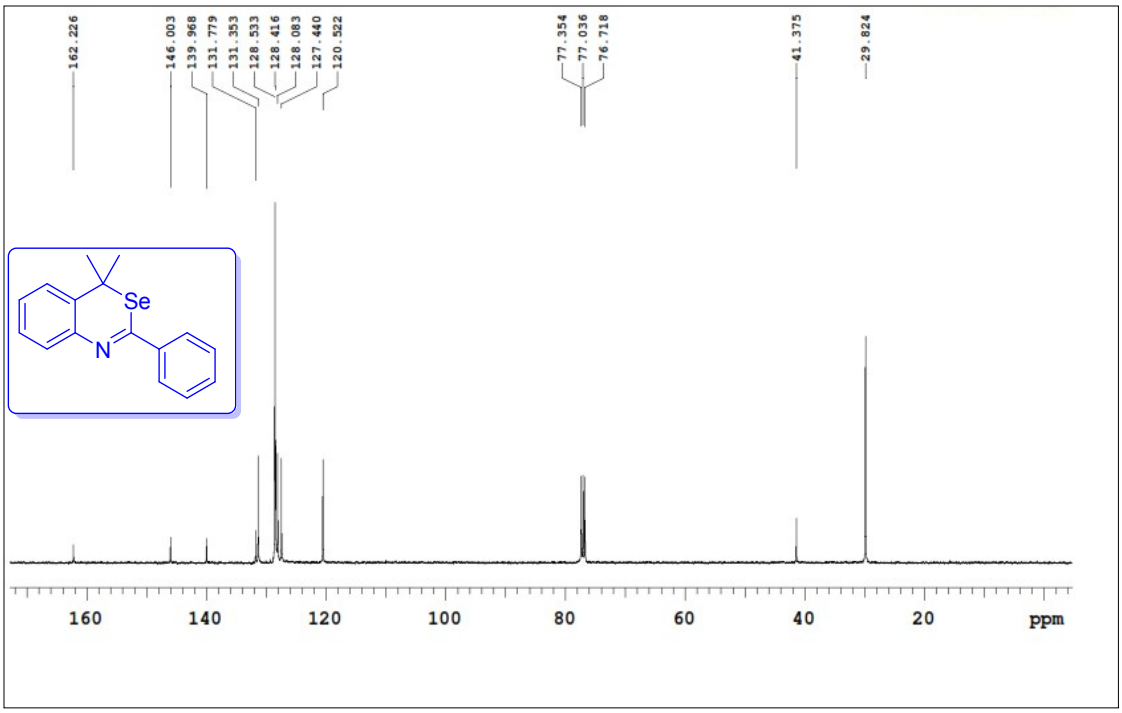
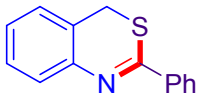

162.226
146.003
139.968
131.779
131.353
128.533
128.416
128.083
127.440
120.522
77.354
77.036
76.718
41.375
29.824
Se
N
160
140
120
100
80
60
40
20
ppm

Figure 19. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **3la** in $CDCl_3$ and LC-MS in Acetonitrile.

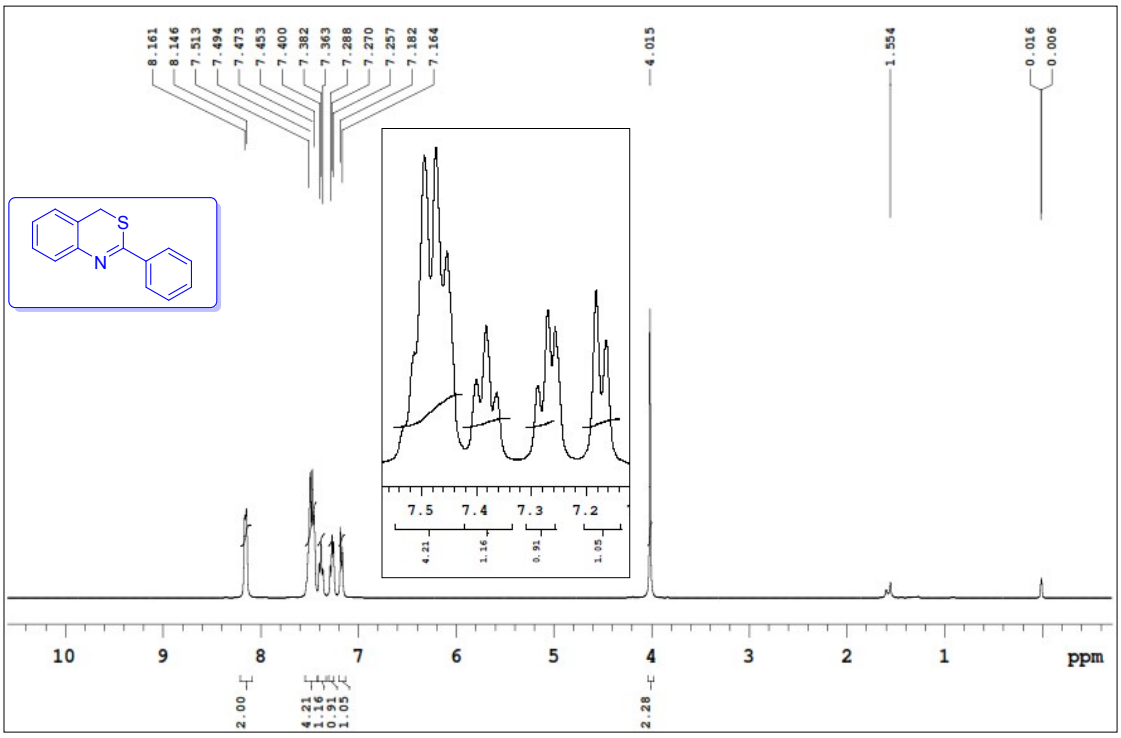
White solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.11 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.57 – 7.55 (m, 1H), 7.48 – 7.43 (m, 4H), 7.38 - 7.33 (m, 2H), 1.80 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.2, 146.0, 139.9, 131.7, 131.3, 128.5, 128.4, 128.0, 127.4, 120.5, 41.3, 29.8 ppm; **MS** (APCI): $[M + 1]^+$ = 302.0 (99.65%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{16}H_{16}NSe$: 302.0447; found: 302.0443.

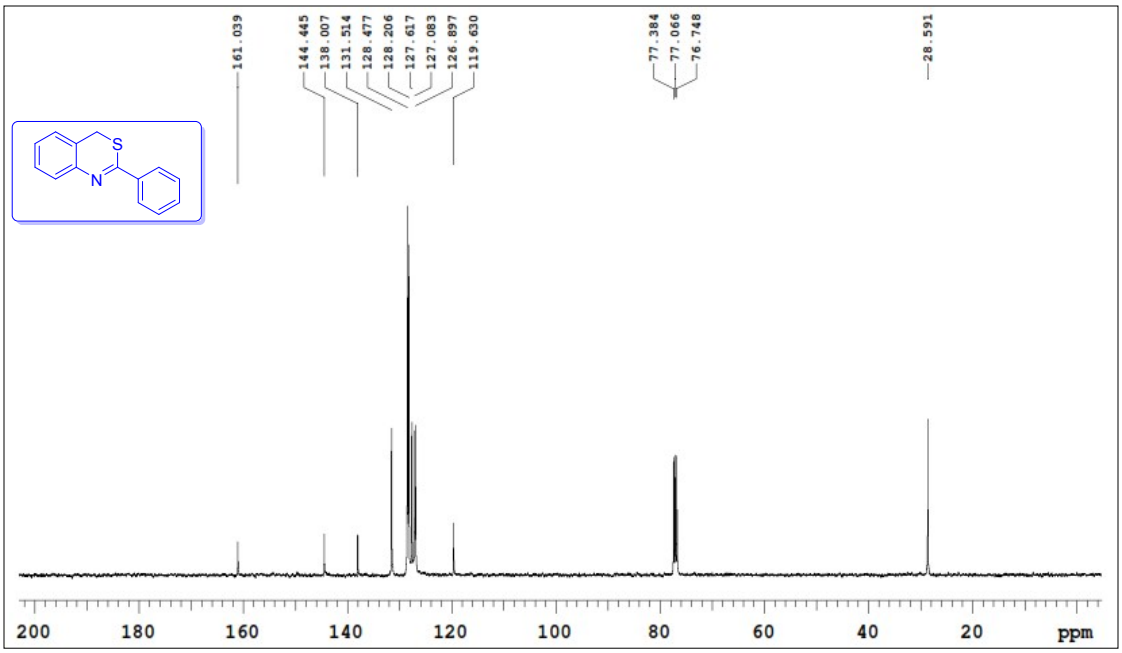
5. Experimental procedures and analytical data of synthesized 1,3-benzothiazines (5aa-as, 5ba-oa, 5pt)

Synthesis of 2-phenyl-4H-benzo[d][1,3]thiazine (5aa); known compound[1]



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-phenyl-4H-benzo[d][1,3]thiazine **5aa** in 98% (221 mg) yield as white solid.




161.039
144.445
138.007
131.514
128.477
128.206
127.617
127.083
126.897
119.630
77.384
77.066
76.748
28.591
S
N
200
180
160
140
120
100
80
60
40
20
ppm

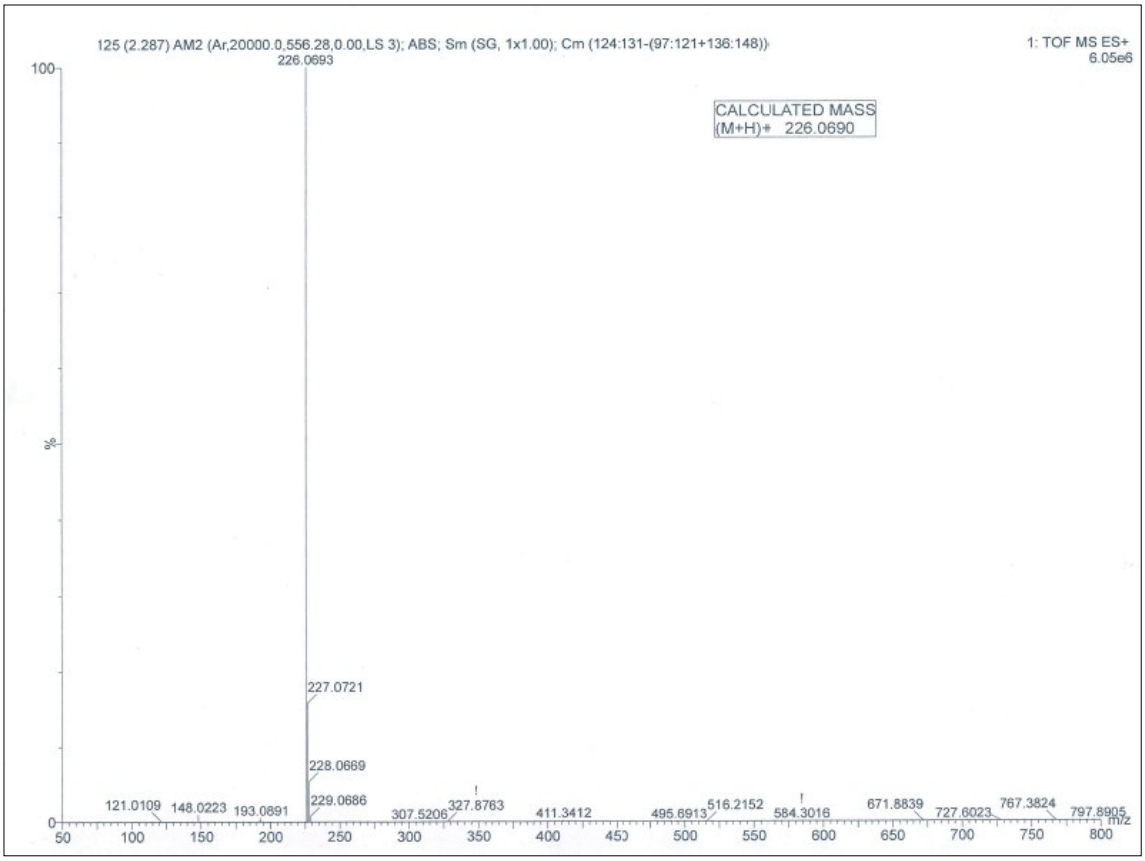
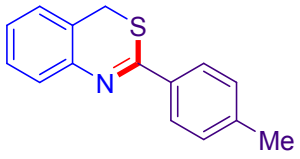


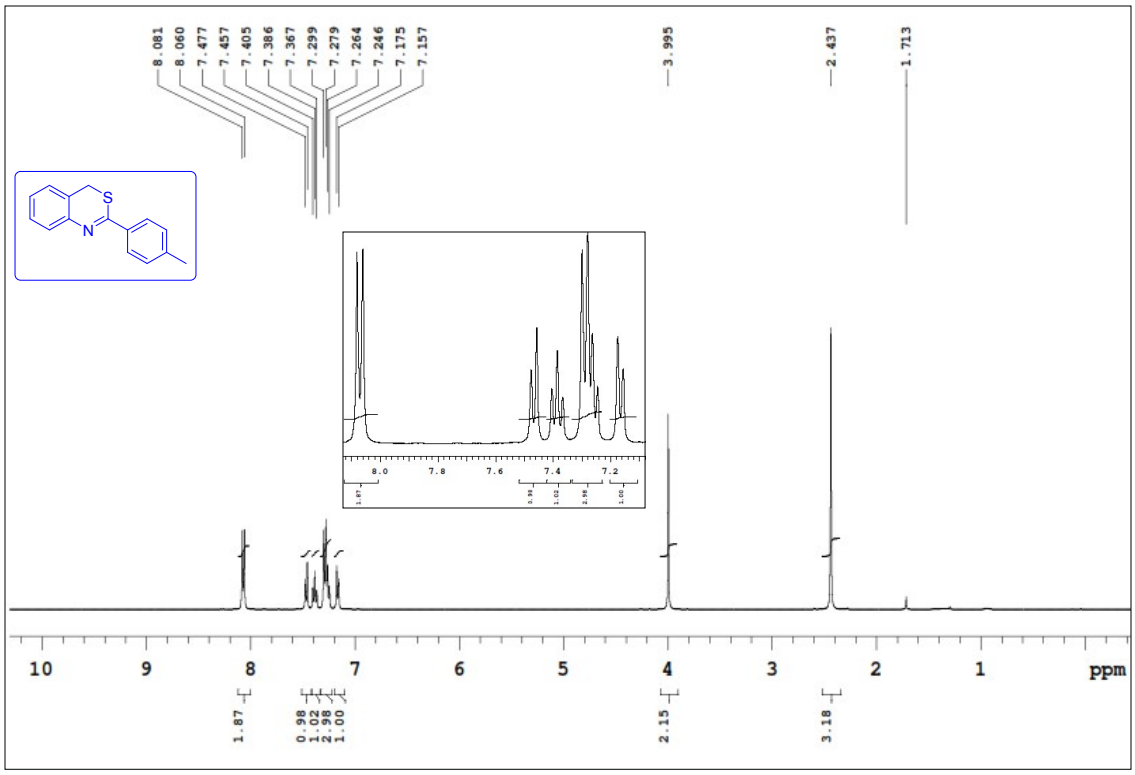
Figure 20. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5aa** in $CDCl_3$ and HRMS in Acetonitrile.

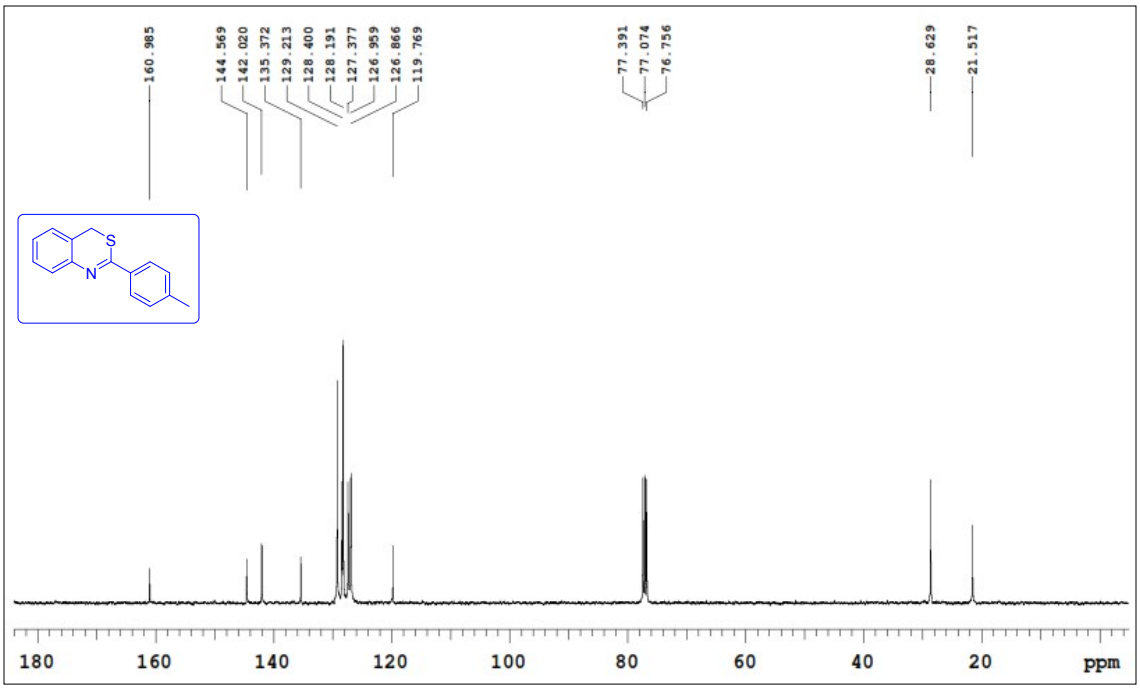
White solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 55 - 56 °C (Lit[1] 55 - 58 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 6.0 Hz, 2H), 7.51 - 7.45 (m, 4H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.00 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) = δ 161.0, 144.4, 138.0, 131.5, 128.4, 128.2, 127.6, 127.0, 126.8, 119.6, 28.5 ppm; **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{12}NS$: 226.0690; found: 226.0693.

Synthesis of 2-(p-tolyl)-4H-benzo[d][1,3]thiazine (5ab); known compound[2]



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-methylbenzothioamide **4b** (1.0 mmol, 151 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(p-tolyl)-4H-benzo[d][1,3]thiazine **5ab** in 92% (220 mg) yield as white solid.


8.081
8.060
7.477
7.457
7.405
7.386
7.367
7.299
7.279
7.264
7.246
7.175
7.157
3.995
2.437
1.713
S
N
10
9
8
7
6
5
4
3
2
1
ppm
1.87
0.98
1.02
2.98
1.00
2.15
3.18


160.985
144.569
142.020
135.372
129.213
128.400
128.191
127.377
126.959
126.866
119.769
77.391
77.074
76.756
28.629
21.517
S
N
180
160
140
120
100
80
60
40
20
ppm

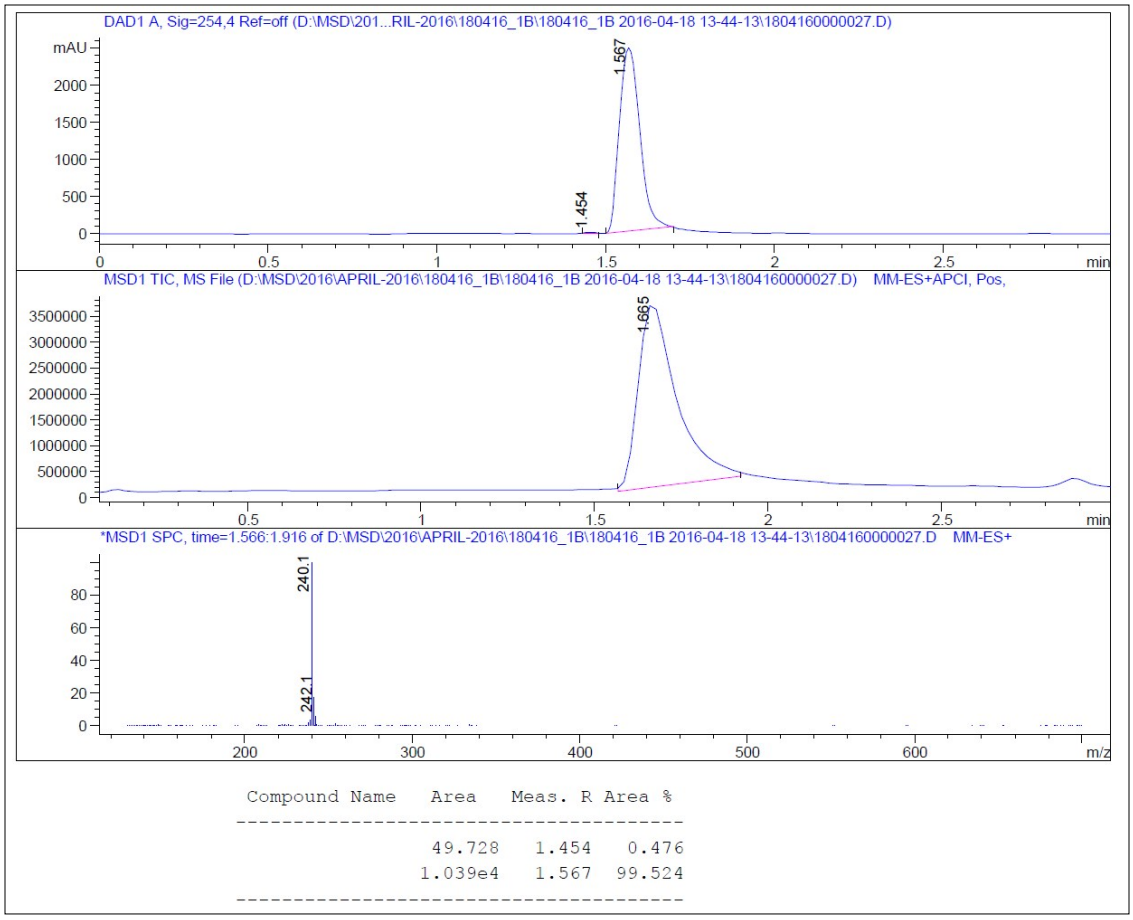
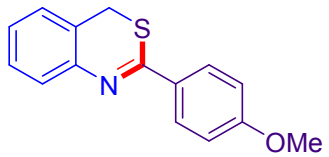


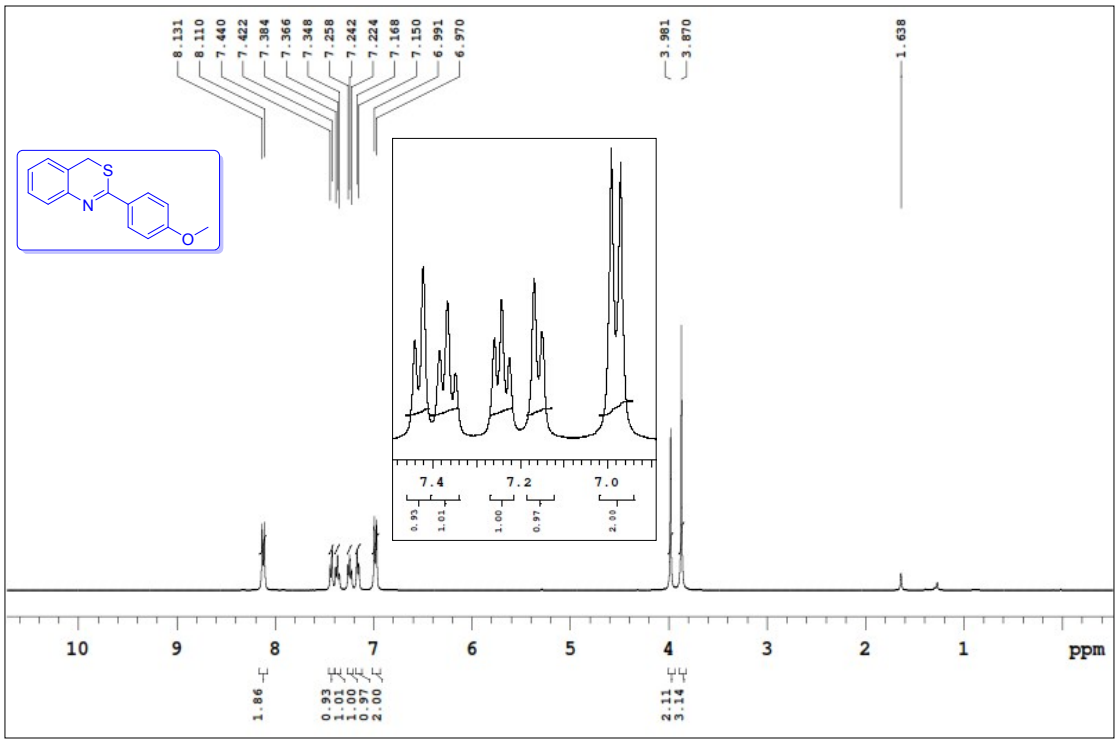
Figure 21. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ab** in $CDCl_3$ and LC-MS in Acetonitrile.

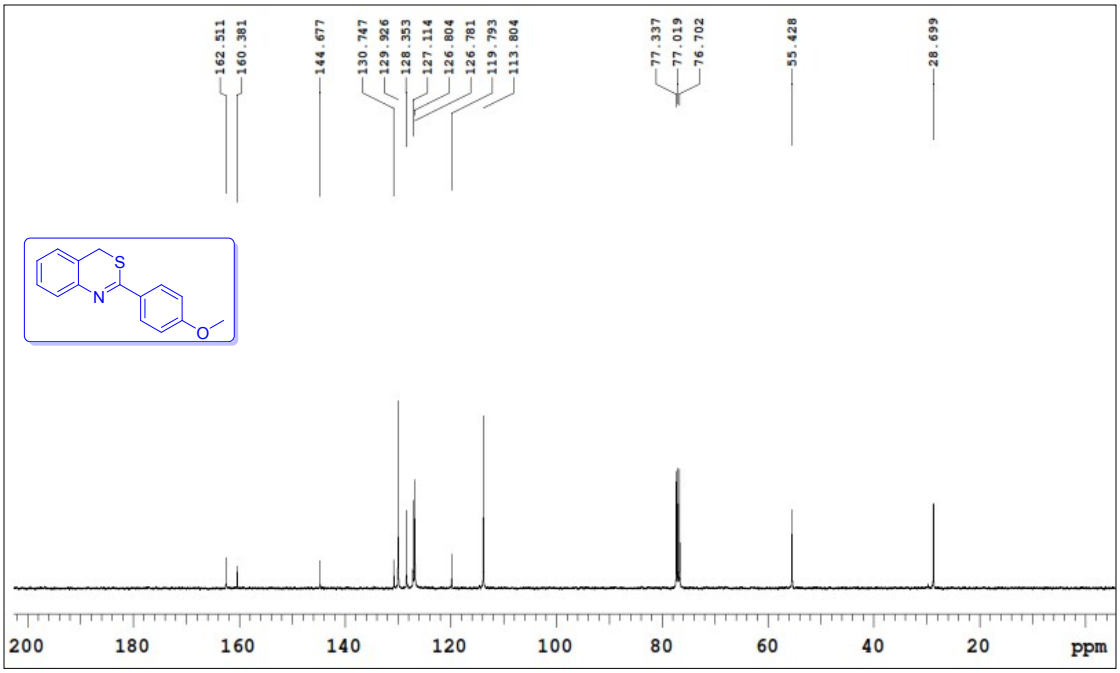
White solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 103 - 105 °C (Lit[2] 104 – 106 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 - 7.24 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 3.99 (s, 2H), 2.43 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 160.9, 144.5, 142.0, 135.3, 129.2, 128.4, 128.1, 127.3, 126.9, 126.8, 119.7, 28.6, 21.5 ppm; **MS** (APCI): $[M + 1]^+$ = 240.1 (99.52%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NS$: 240.0846; found: 240.0843.

Synthesis of 2-(4-methoxyphenyl)-4H-benzo[d][1,3]thiazine (5ac); known compound[2]



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-methoxybenzothioamide **4c** (1.0 mmol, 167 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(4-methoxyphenyl)-4H-benzo[d][1,3]thiazine **5ac** in 95% (242 mg) yield as off-white solid.


8.131
8.110
7.440
7.422
7.384
7.366
7.348
7.258
7.242
7.224
7.168
7.150
6.991
6.970
3.981
3.870
1.638
S
N
O
7.4
7.2
7.0
0.93
1.01
1.00
0.97
2.00
10
9
8
7
6
5
4
3
2
1
ppm
1.86
0.93
1.01
1.00
0.97
2.00
2.11
3.14


162.511
160.381
144.677
130.747
129.926
128.353
127.114
126.804
126.781
119.793
113.804
77.337
77.019
76.702
55.428
28.699
S
N
O
200
180
160
140
120
100
80
60
40
20
ppm

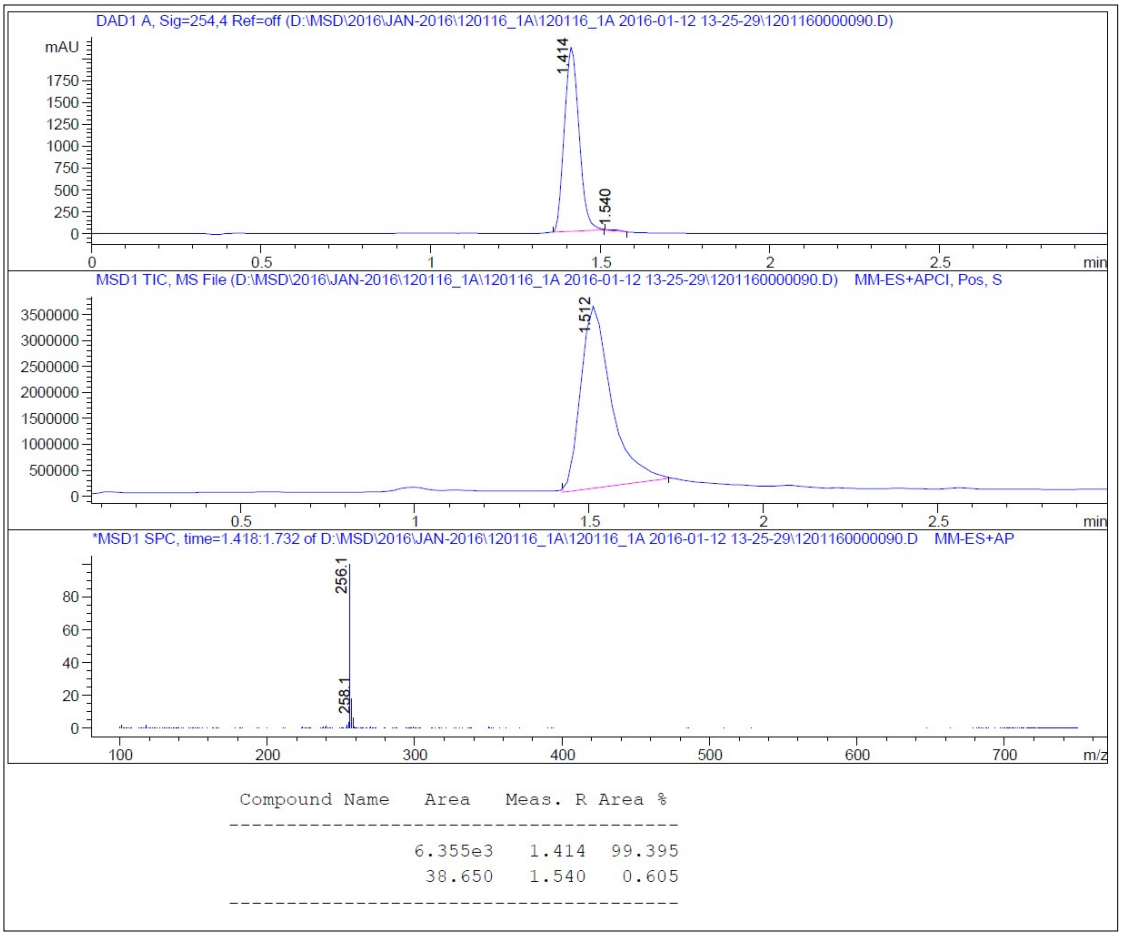
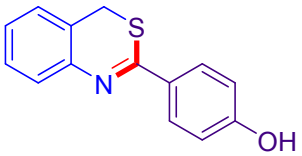


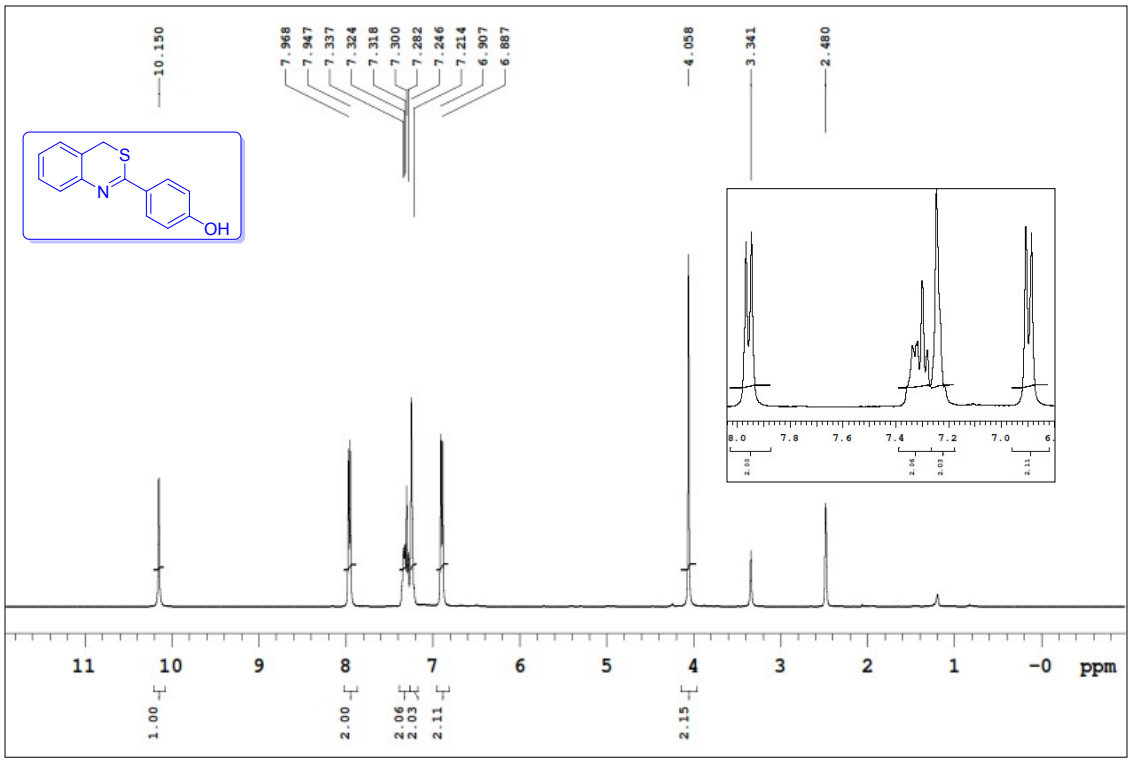
Figure 22. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ac** in $CDCl_3$ and LC-MS in Acetonitrile.

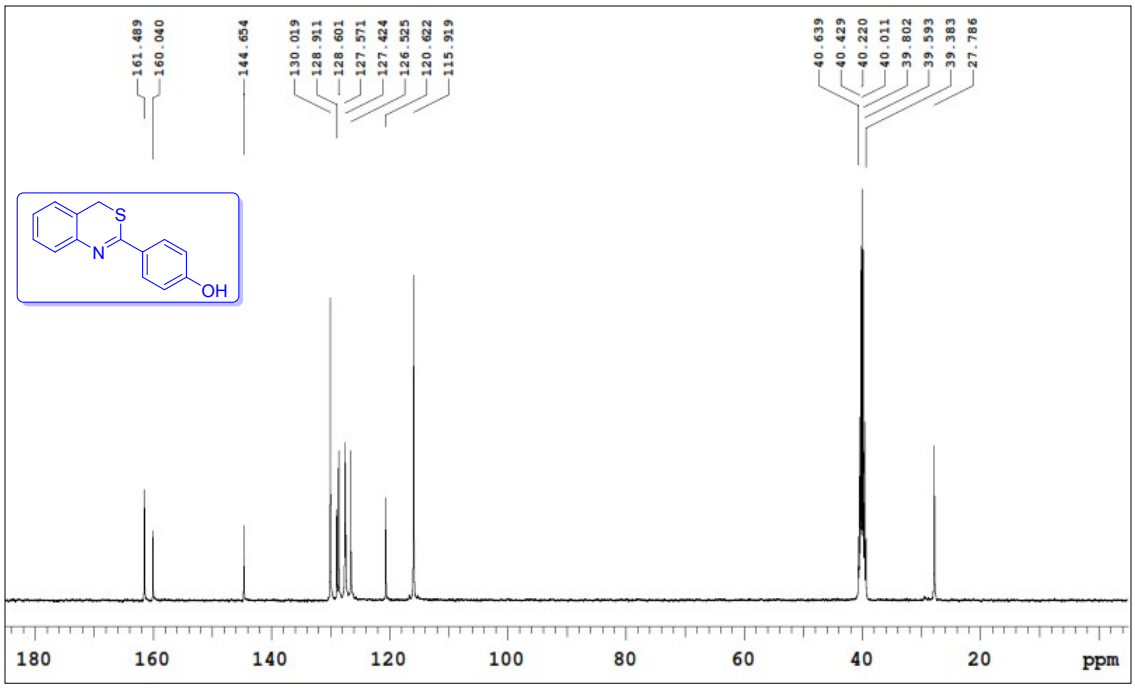
Off-White solid; $\mathbf{R_f}$ = 0.66 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 123 - 124 °C (Lit[2] 122 - 123 °C);**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 6.4 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.98 (s, 2H), 3.87 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.5, 160.3, 144.6, 130.7, 129.9, 128.3, 127.1, 126.8, 126.7, 119.7, 113.8, 55.4, 28.6 ppm; **MS** (APCI): $[M + 1]^+$ = 256.1 (99.39%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NOS$: 256.0796; found: 256.0793.

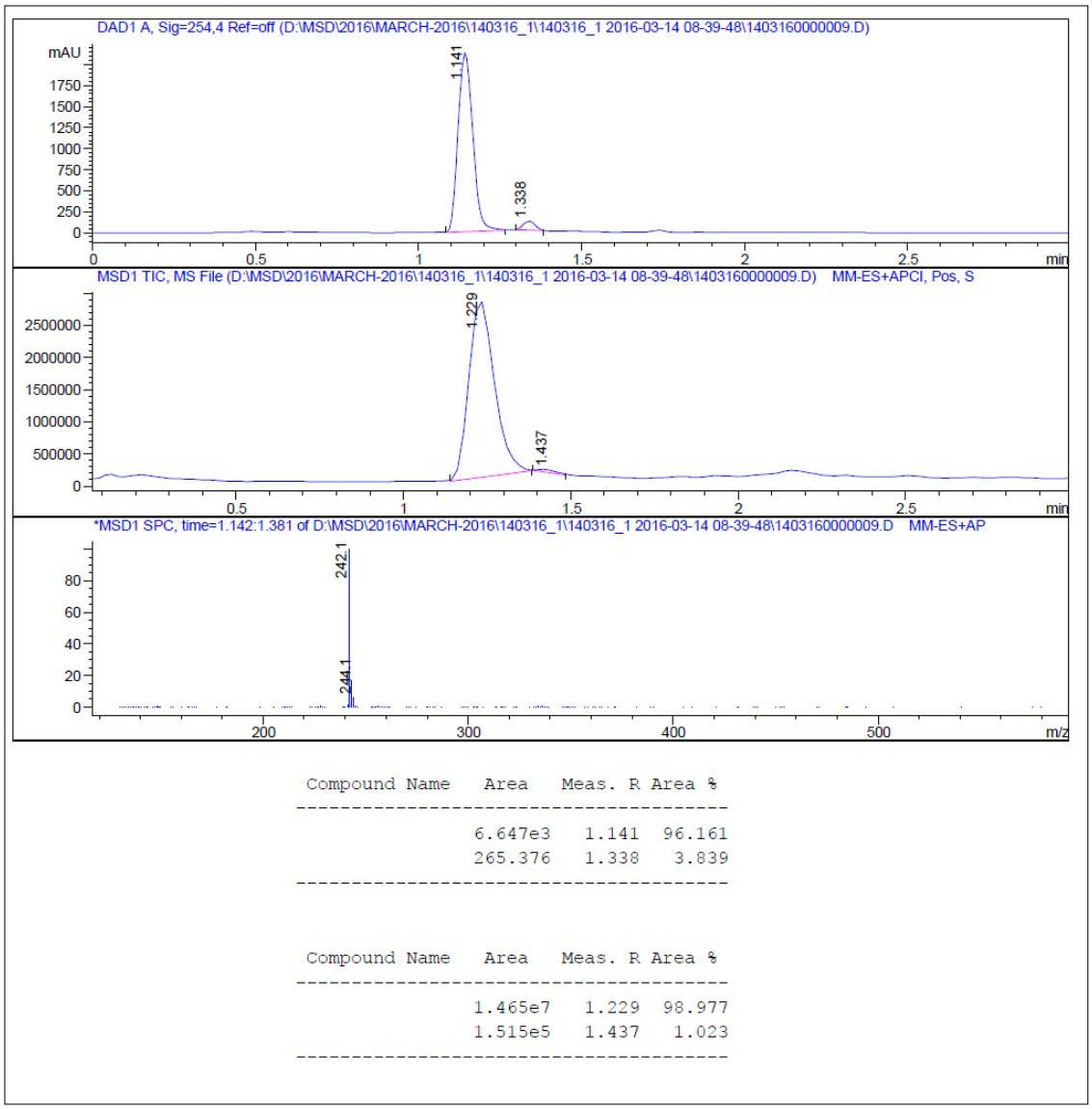
Synthesis of 4-(4H-benzo[d][1,3]thiazin-2-yl)phenol (5ad); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-hydroxybenzothioamide **4d** (1.0 mmol, 153 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 4-(4H-benzo[d][1,3]thiazin-2-yl)phenol **5ad** in 92% (222 mg) yield as off-white solid.


10.150
7.968
7.947
7.337
7.324
7.318
7.300
7.282
7.246
7.214
6.907
6.887
4.058
3.341
2.480
S
N
OH
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
2.00
2.06
2.03
2.11
2.15


161.489
160.040
144.654
130.019
128.911
128.601
127.571
127.424
126.525
120.622
115.919
40.639
40.429
40.220
40.011
39.802
39.593
39.383
27.786
S
N
OH
180
160
140
120
100
80
60
40
20
ppm



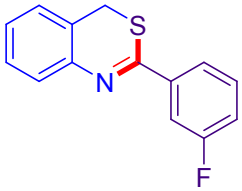
Compound Name	Area	Meas. R	Area %
	6.647e3	1.141	96.161
	265.376	1.338	3.839

Compound Name	Area	Meas. R	Area %
	1.465e7	1.229	98.977
	1.515e5	1.437	1.023

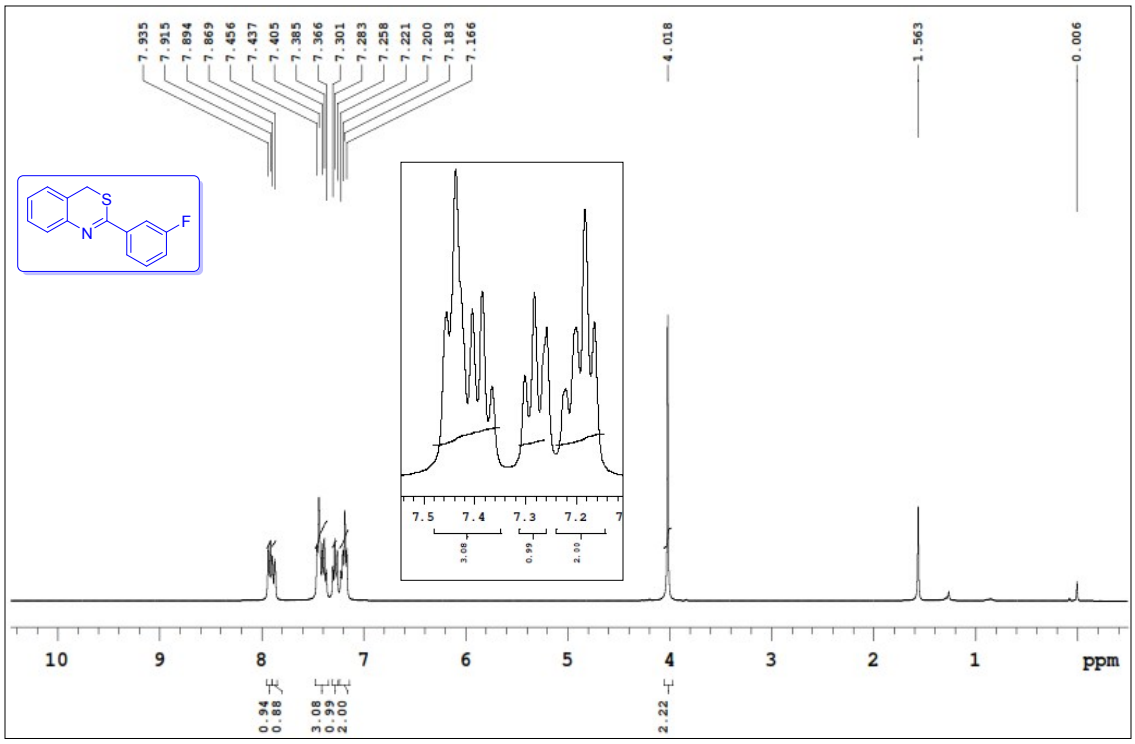
Figure 23. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ad** in DMSO-d_6 and LC-MS in Acetonitrile.

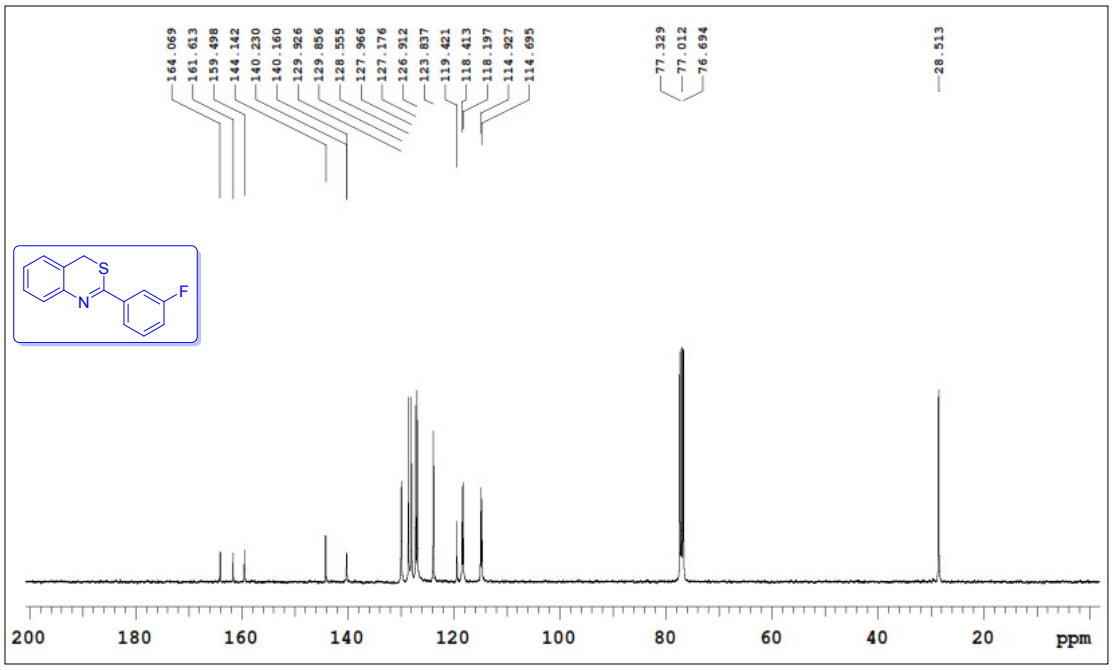
Off-white solid; $\mathbf{R_f}$ = 0.45 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 183 - 184 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 10.15 (s, 1H), 7.95 (d, J = 7.6 Hz, 2H), 7.33 - 7.21 (m, 4H), 6.89 (d, J = 8.0 Hz, 2H), 4.05 (s, 2H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 161.4, 160.0, 144.6, 130.0, 128.9, 128.6, 127.5, 127.4, 126.5, 120.6, 115.9, 27.7 ppm; **MS** (APCI): $[M + 1]^+$ = 242.1 (96.16%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{12}NOS$: 242.0639; found: 242.0641.

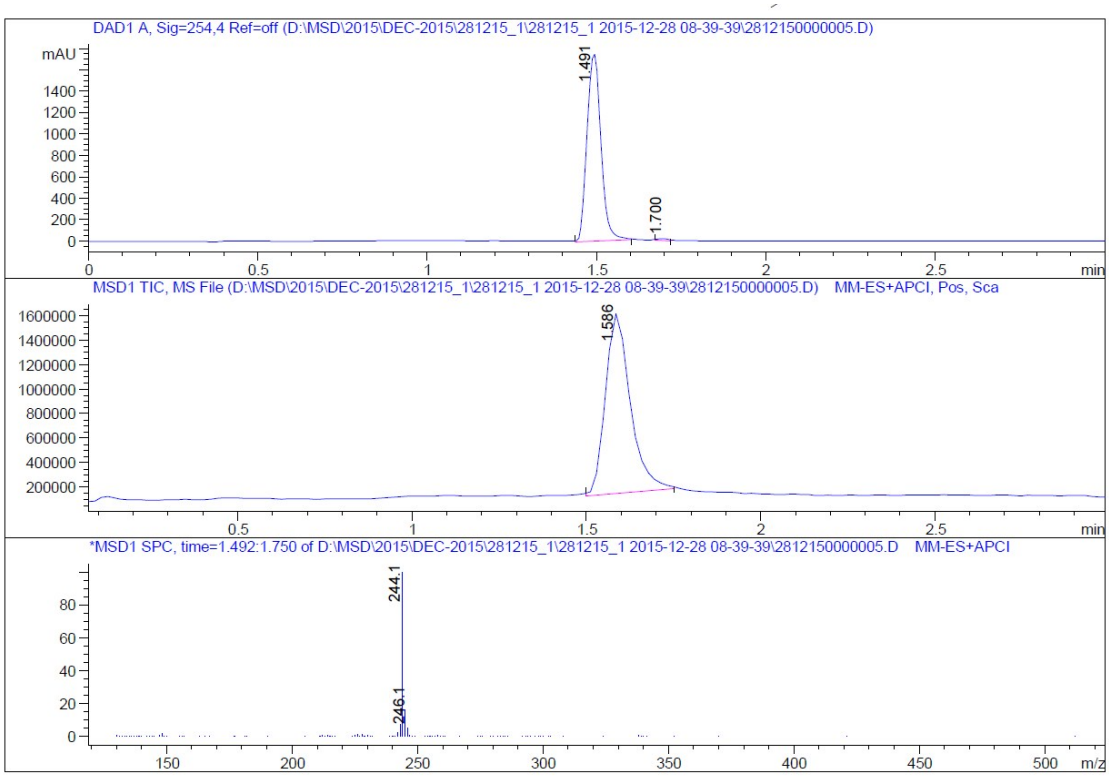
Synthesis of 2-(3-fluorophenyl)-4H-benzo[d][1,3]thiazine (5ae); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 3-fluorobenzothioamide **4e** (1.0 mmol, 155 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(3-fluorophenyl)-4H-benzo[d][1,3]thiazine **5ae** in 95% (231 mg) yield as off-white solid.




164.069
161.613
159.498
144.142
140.230
140.160
129.926
129.856
128.555
127.966
127.176
126.912
123.837
119.421
118.413
118.197
114.927
114.695
77.329
77.012
76.694
28.513
S
N
F
200
180
160
140
120
100
80
60
40
20
ppm

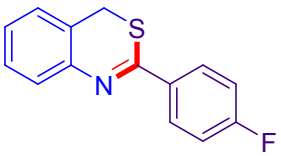


Compound Name	Area	Meas. R	Area %
	5.004e3	1.491	99.161
	42.348	1.700	0.839

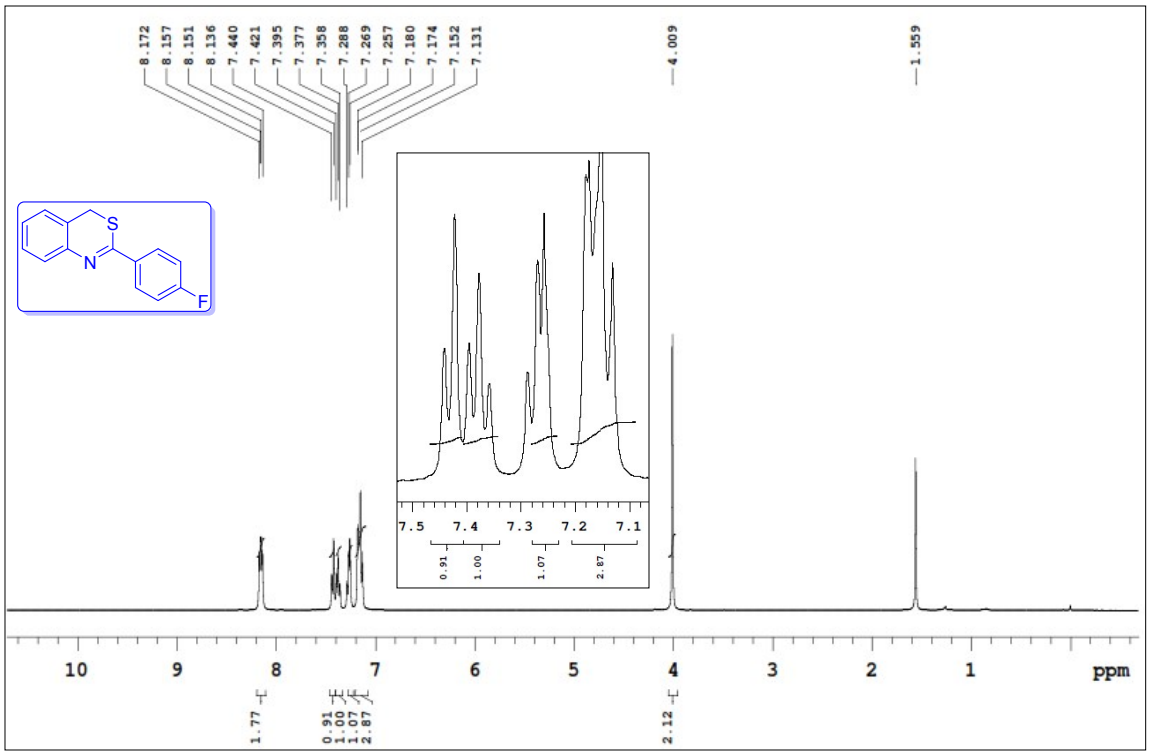
Figure 24. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ae** in DMSO-d_6 and LC-MS in Acetonitrile.

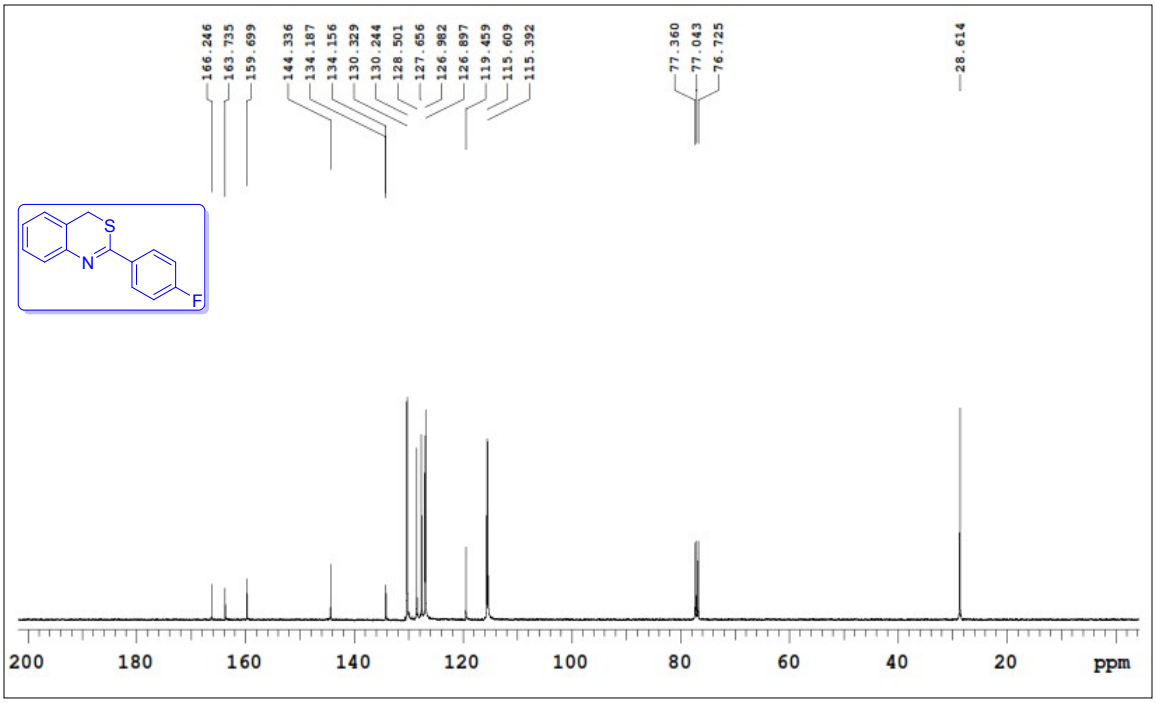
Off-white solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 65 - 67 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 7.89 - 7.86 (m, 2H), 7.45 - 7.36 (m, 3H), 7.28 (t, J = 7.2 Hz, 1H), 7.22 - 7.16 (m, 2H), 4.01 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ = 162.8 (d, J = 246.0 Hz), 159.4, 144.1, 140.2, 140.1, 129.9, 129.8, 128.5, 127.9, 127.1, 126.9, 123.8, 119.4, 118.4, 118.1, 114.9, 114.6, 28.5 ppm; **MS** (APCI): $[M + 1]^+$ = 244.1 (99.16%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNS$: 244.0596; found: 244.0594.

Synthesis of 2-(4-fluorophenyl)-4H-benzo[d][1,3]thiazine (5af); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-fluorobenzothioamide **4f** (1.0 mmol, 155 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(4-fluorophenyl)-4H-benzo[d][1,3]thiazine **5af** in 95% (231 mg) yield as off-white solid.


8.172
8.157
8.151
8.136
7.440
7.421
7.395
7.377
7.358
7.288
7.269
7.257
7.180
7.174
7.152
7.131
4.009
1.559
S
N
F
7.5
7.4
7.3
7.2
7.1
0.91
1.00
1.07
2.87
10
9
8
7
6
5
4
3
2
1
ppm
1.77
0.91
1.00
1.07
2.87
2.12


166.246
163.735
159.699
144.336
134.187
134.156
130.329
130.244
128.501
127.656
126.982
126.897
119.459
115.609
115.392
77.360
77.043
76.725
28.614
S
N
F
200
180
160
140
120
100
80
60
40
20
ppm

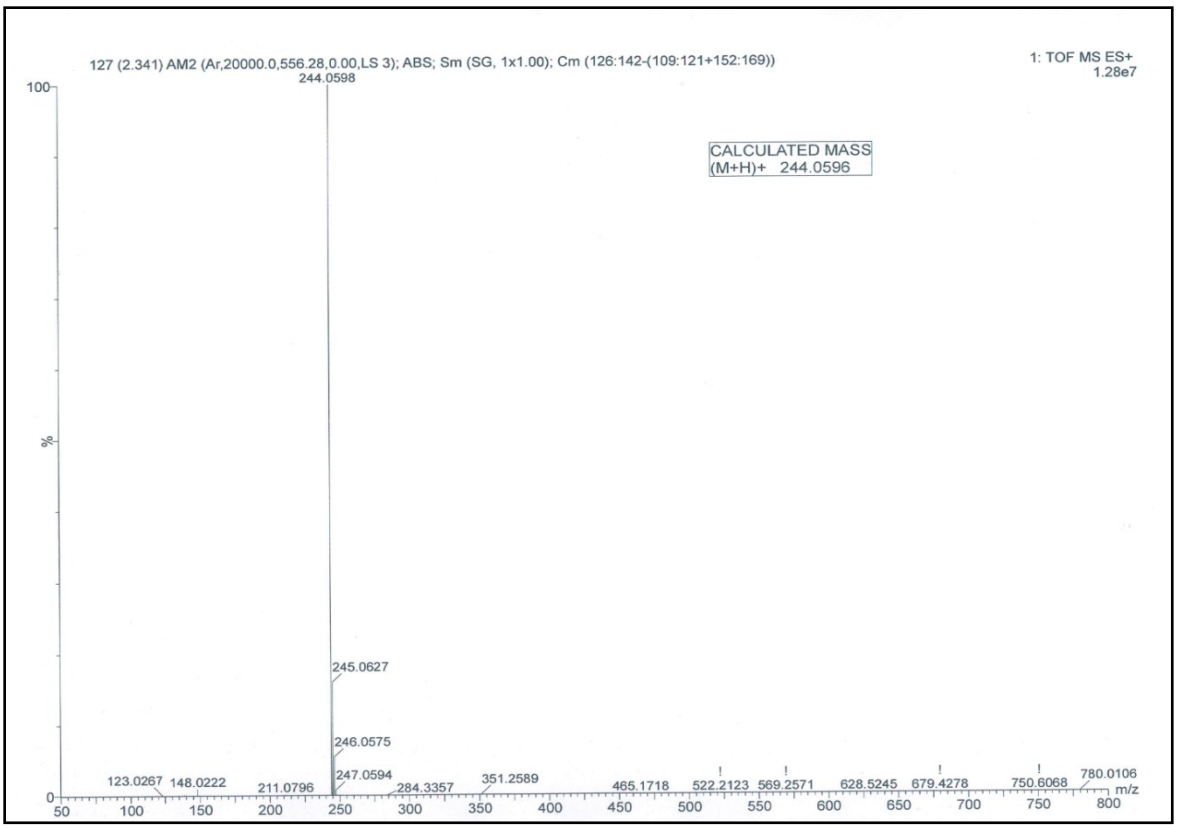
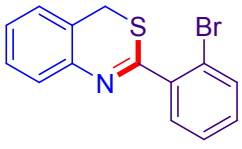


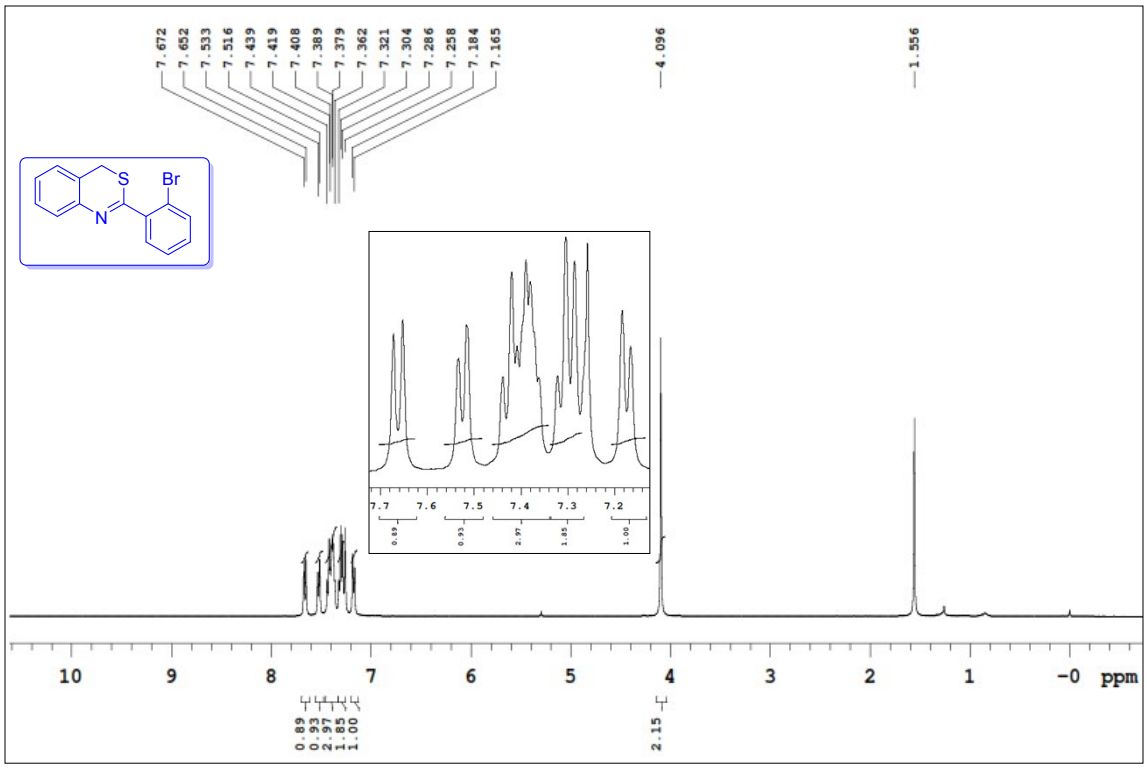
Figure 25. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5af** in DMSO-d_6 and HRMS in Acetonitrile

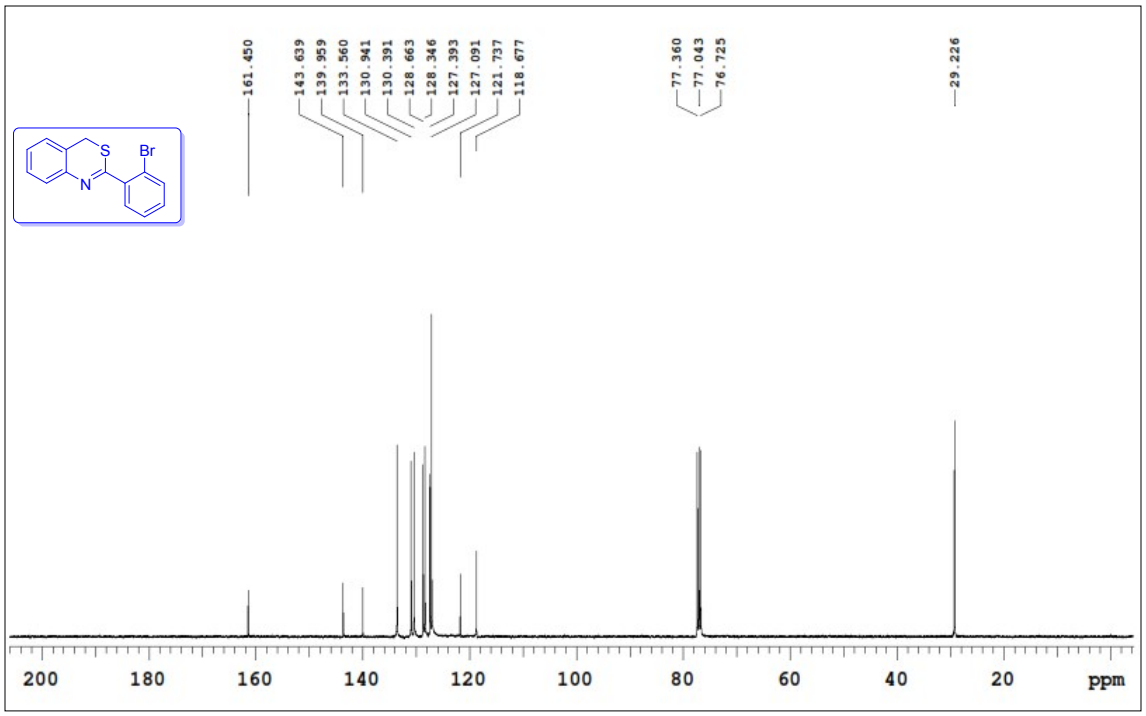
Off-white solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 114 - 115 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 8.15 (t, J = 6.8 Hz, 2H), 7.43 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.28 - 7.25 (m, 1H), 7.18 - 7.13 (m, 3H), 4.00 (s, 2H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 164.9 (d, J = 252.4 Hz), 159.6, 144.3, 134.1, 134.1, 130.3, 130.2, 128.5, 127.6, 126.9, 126.8, 119.4, 115.6, 115.3, 28.6 ppm; **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNS$: 244.0596; found: 240.0598.

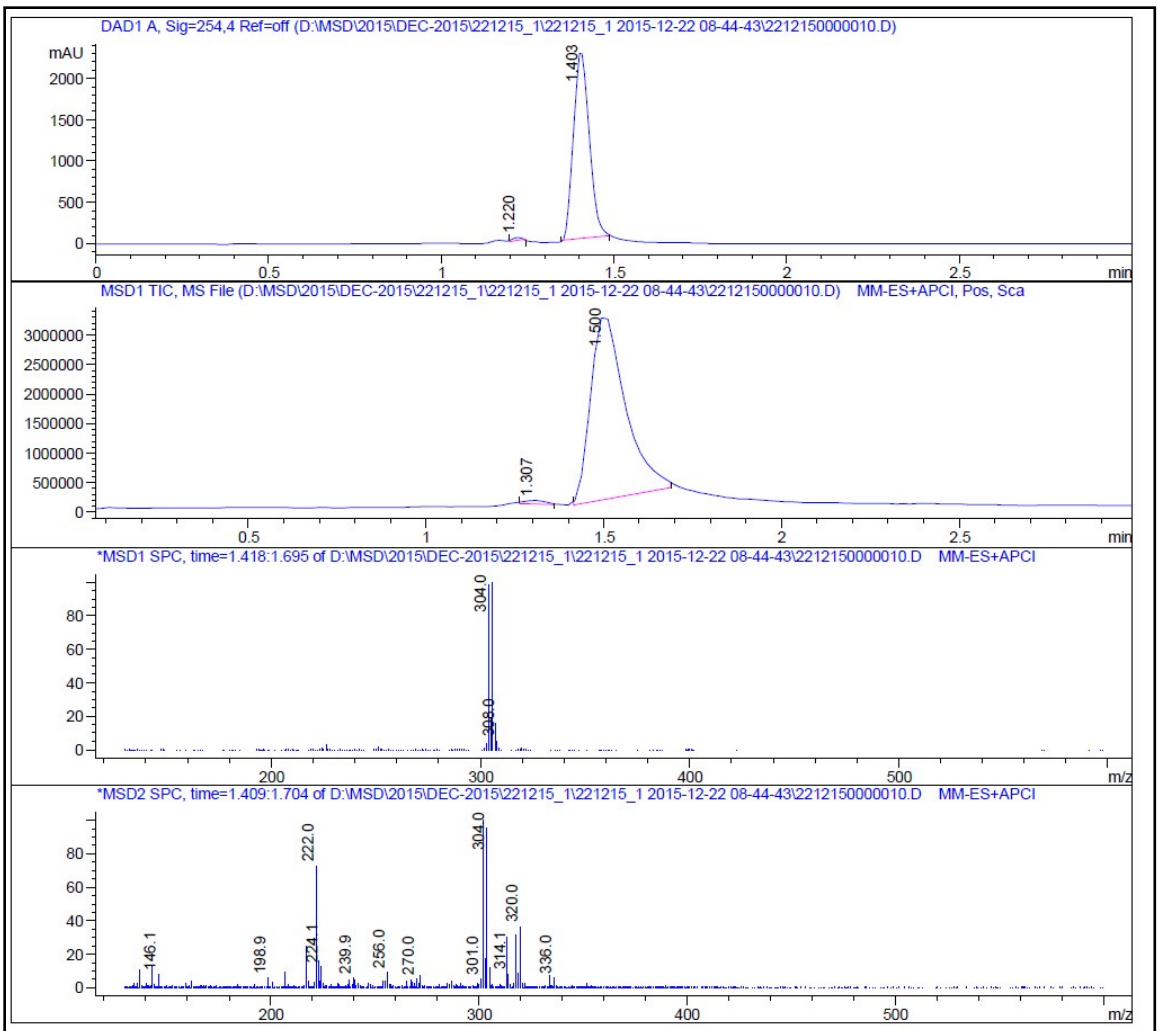
Synthesis of 2-(2-bromophenyl)-4H-benzo[d][1,3]thiazine (5ag); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 2-bromobenzothioamide **4g** (1.0 mmol, 216 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(2-bromophenyl)-4H-benzo[d][1,3]thiazine **5ag** in 94% (286 mg) yield as orange liquid.


7.672
7.652
7.533
7.516
7.439
7.419
7.408
7.389
7.379
7.362
7.321
7.304
7.286
7.258
7.184
7.165
4.096
1.556
S
N
Br
7.7
7.6
7.5
7.4
7.3
7.2
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.89
0.93
2.97
1.85
1.00
2.15


161.450
143.639
139.959
133.560
130.941
130.391
128.663
128.346
127.393
127.091
121.737
118.677
77.360
77.043
76.725
29.226
S
N
Br
200
180
160
140
120
100
80
60
40
20
ppm



Compound Name	Area	Meas. R	Area %
	57.539	1.220	0.796
	7.171e3	1.403	99.204

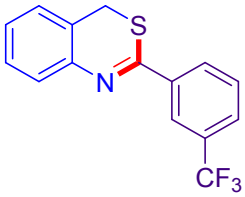
Compound Name	Area	Meas. R	Area %
	2.410e5	1.307	1.120
	2.127e7	1.500	98.880

Compound Name	Area	Meas. R	Area %
	2.411e7	1.304	35.518
	4.377e7	1.505	64.482

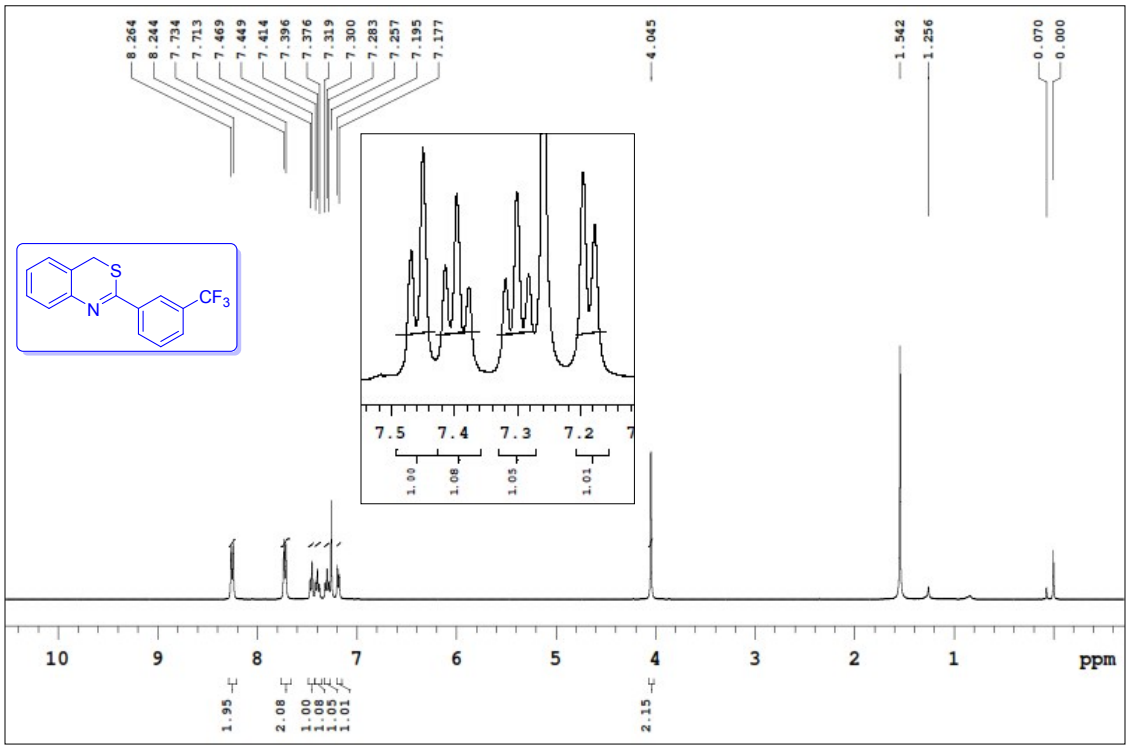
Figure 26. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ag** in $CDCl_3$ and LC-MS in Acetonitrile.

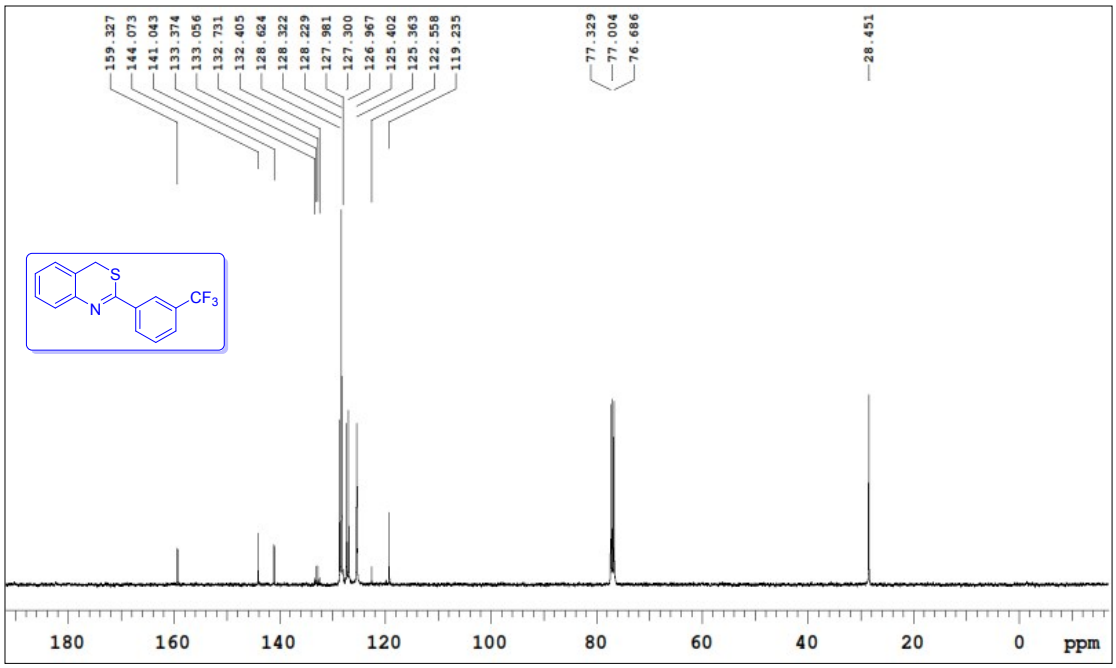
Orange liquid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.44 - 7.36 (m, 3H), 7.30 (t, *J* = 6.8 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 1H), 4.09 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 143.6, 139.9, 133.5, 130.9, 130.3, 128.6, 128.3, 127.3, 127.0, 121.7, 118.6, 29.2 ppm; **MS** (APCI): $[M]^+$, $[M + 2]^+$ = 302, 304 (99.20%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}BrNS$: 303.9795; found: 303.9790.

Synthesis of 2-(3-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]thiazine (5ah); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 3-(trifluoromethyl)benzothioamide **4h** (1.0 mmol, 205 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(3-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]thiazine **5ah** in 90% (264 mg) yield as off-white solid.




159.327
144.073
141.043
133.374
133.056
132.731
132.405
128.624
128.322
128.229
127.981
127.300
126.967
125.402
125.363
122.558
119.235
77.329
77.004
76.686
28.451
S
N
CF3
180
160
140
120
100
80
60
40
20
0
ppm

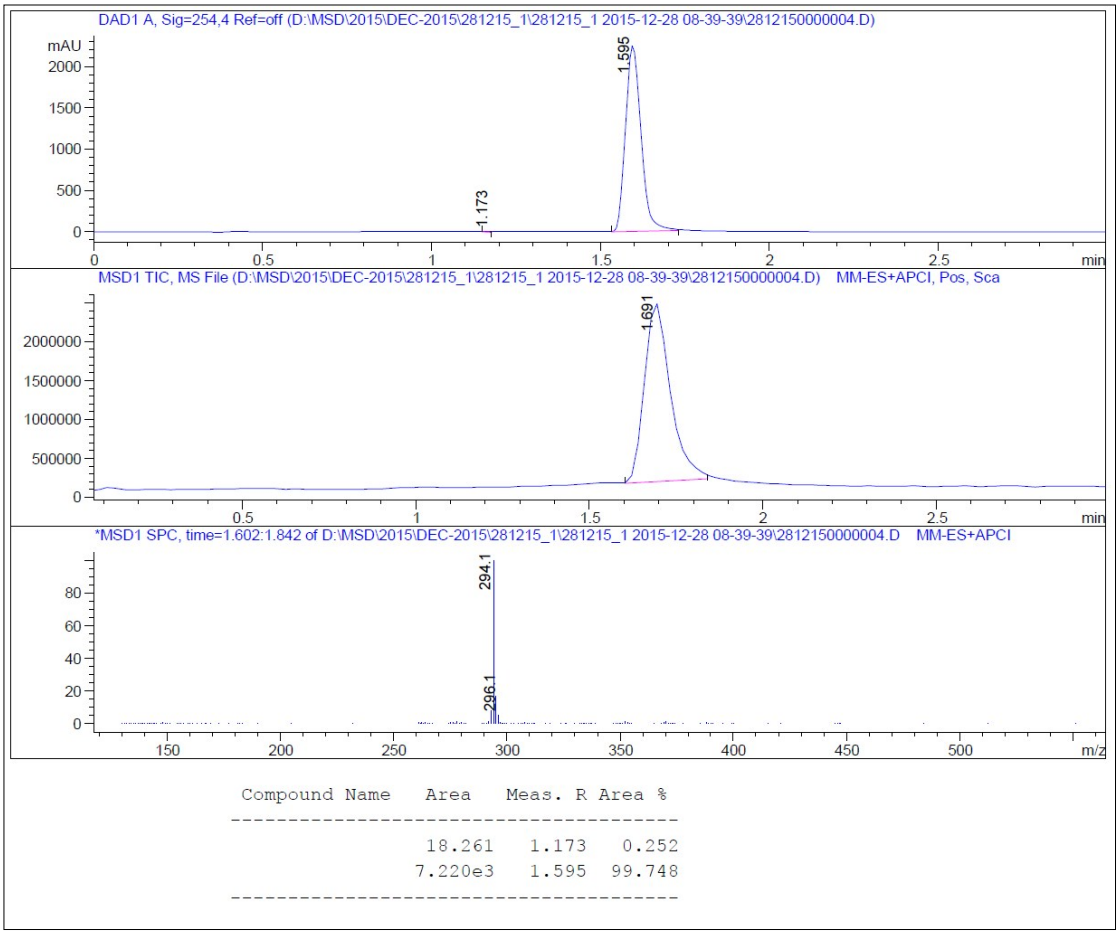
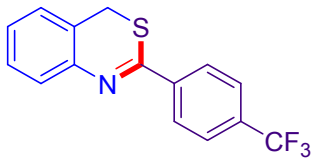


Figure 27. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ah** in DMSO-d_6 and LC-MS in Acetonitrile.

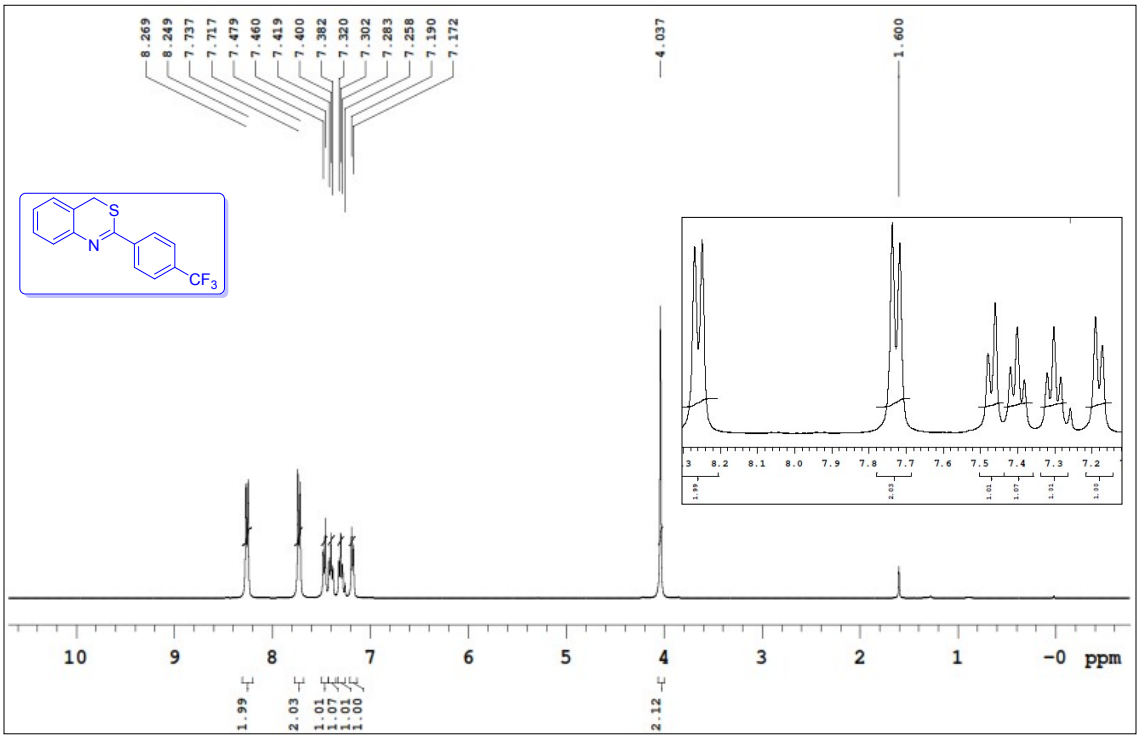
Off-white solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 160 - 161 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ= 8.25 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 4.04 (s, 2H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 159.3, 144.0, 141.0, 132.8 (q, J = 32.3 Hz), 128.6, 128.3, 128.2, 127.3, 126.9, 125.4, 125.3, 123.8 (q, J = 270.07 Hz), 119.2, 28.4 ppm; **MS** (APCI): $[M + 1]^+$ = 294.1 (99.74%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{11}F_3NS$: 294.0564; found: 294.0560.

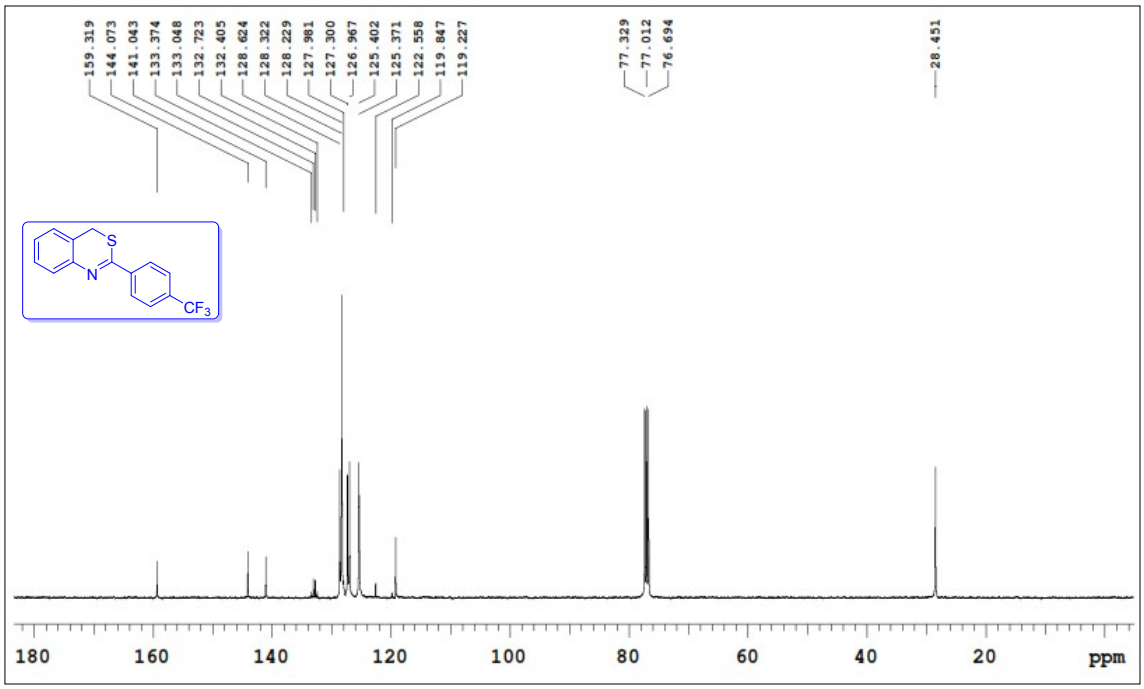
Synthesis of 2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]thiazine (5ai); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-(trifluoromethyl)benzothioamide **4i** (1.0 mmol, 205 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 2-(4-(trifluoromethyl)phenyl)-4H-benzo[d][1,3]thiazine **5ai** in 94% (276 mg) yield as off-white solid.




159.319
144.073
141.043
133.374
133.048
132.723
132.405
128.624
128.322
128.229
127.981
127.300
126.967
125.402
125.371
122.558
119.847
119.227
77.329
77.012
76.694
28.451
S
N
CF3
180
160
140
120
100
80
60
40
20
ppm

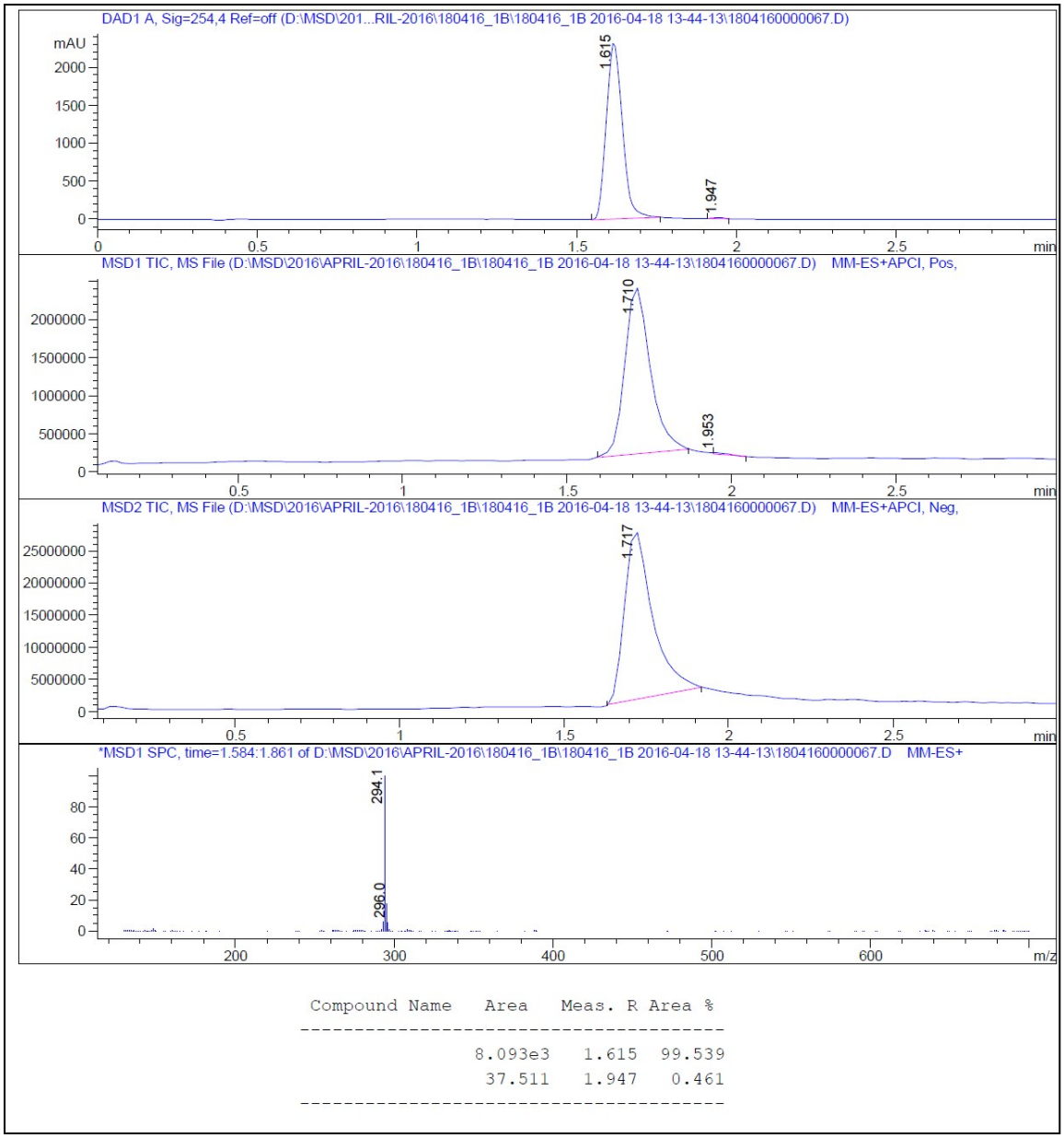
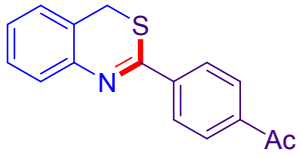


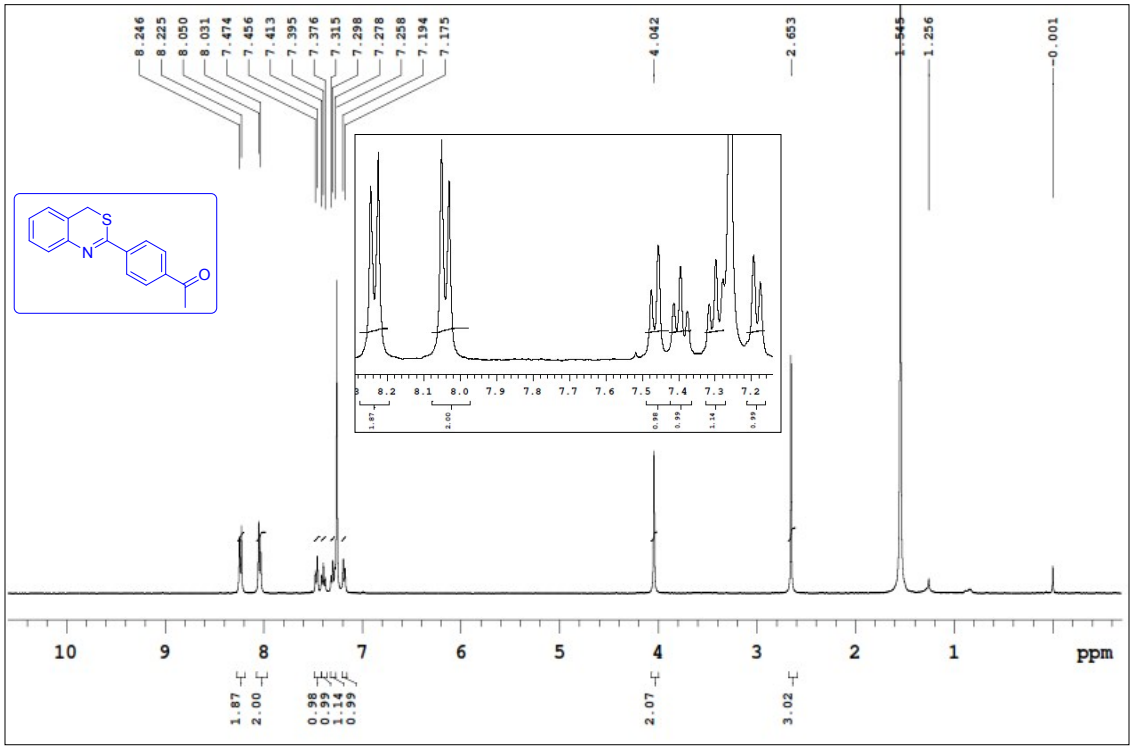
Figure 28. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ai** in DMSO-d_6 and LC-MS in Acetonitrile.

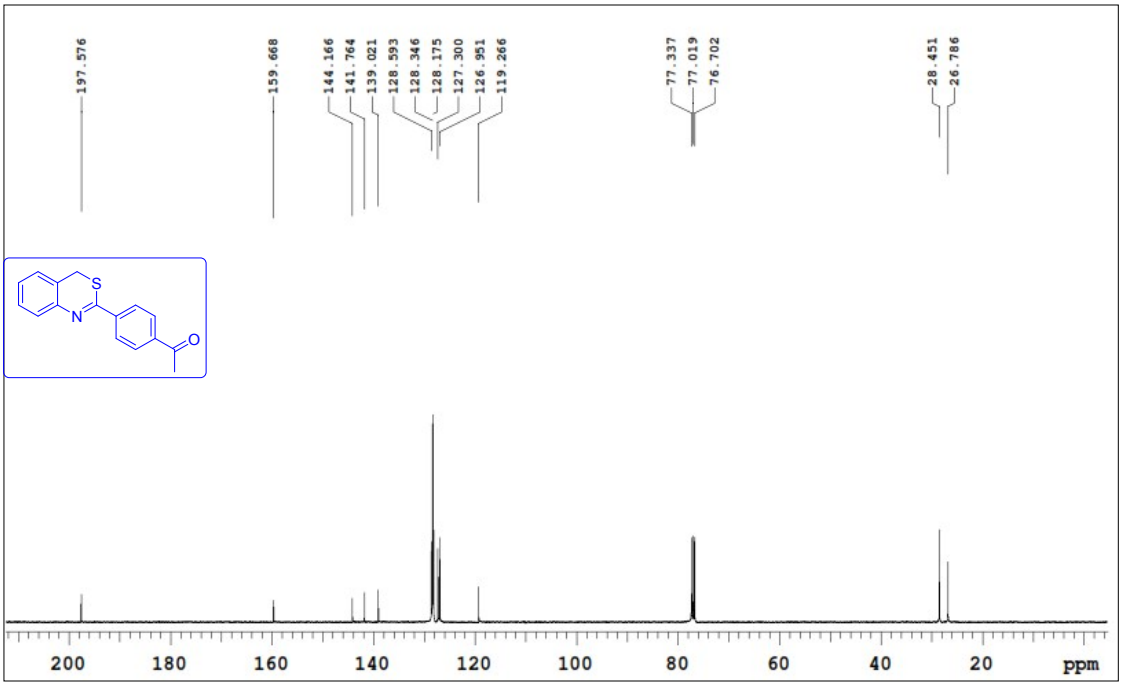
Off-white solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 159 - 160 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 8.25 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 7.2 Hz, 1H), 7.40 (t, J =7.6 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.18 (d, J = 7.2 Hz, 1H), 4.03 (s, 2H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 159.3, 144.0, 141.0, 132.8 (q, J = 32.5 Hz), 128.6, 128.3, 128.2, 127.9, 127.3, 126.9, 125.4, 125.3, 122.5, 119.8, 119.2, 28.4 ppm; **MS** (APCI): $[M + 1]^+$ = 294.1 (99.53%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{11}F_3NS$: 294.0564; found: 294.0560.

Synthesis of 1-(4-(4H-benzo[d][1,3]thiazin-2-yl)phenyl)ethan-1-one (5aj); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 4-acetylbenzothioamide **4j** (1.0 mmol, 179 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 1-(4-(4H-benzo[d][1,3]thiazin-2-yl)phenyl)ethan-1-one **5aj** in 87% (232 mg) yield as pale yellow solid.




197.576
159.668
144.166
141.764
139.021
128.593
128.346
128.175
127.300
126.951
119.266
77.337
77.019
76.702
28.451
26.786
S
N
O
200
180
160
140
120
100
80
60
40
20
ppm

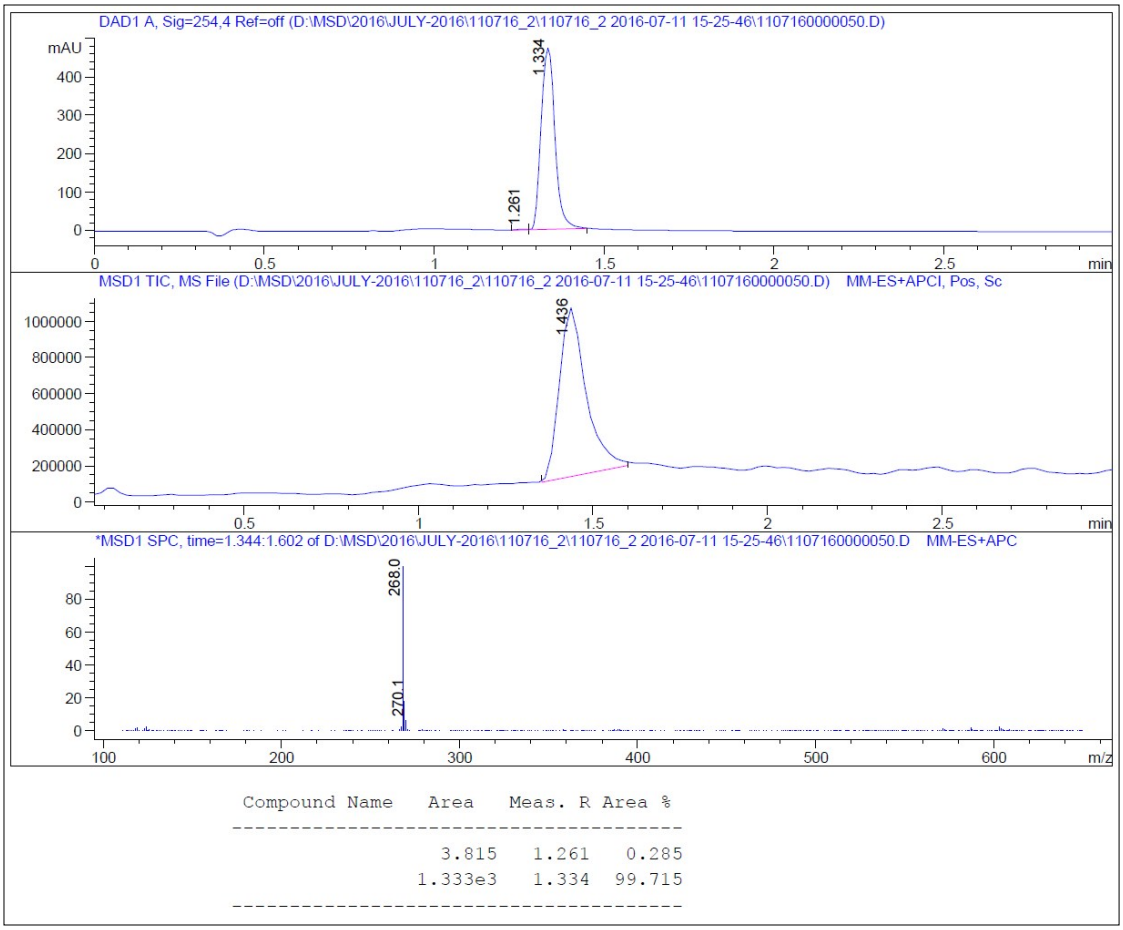
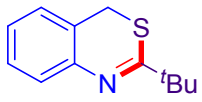


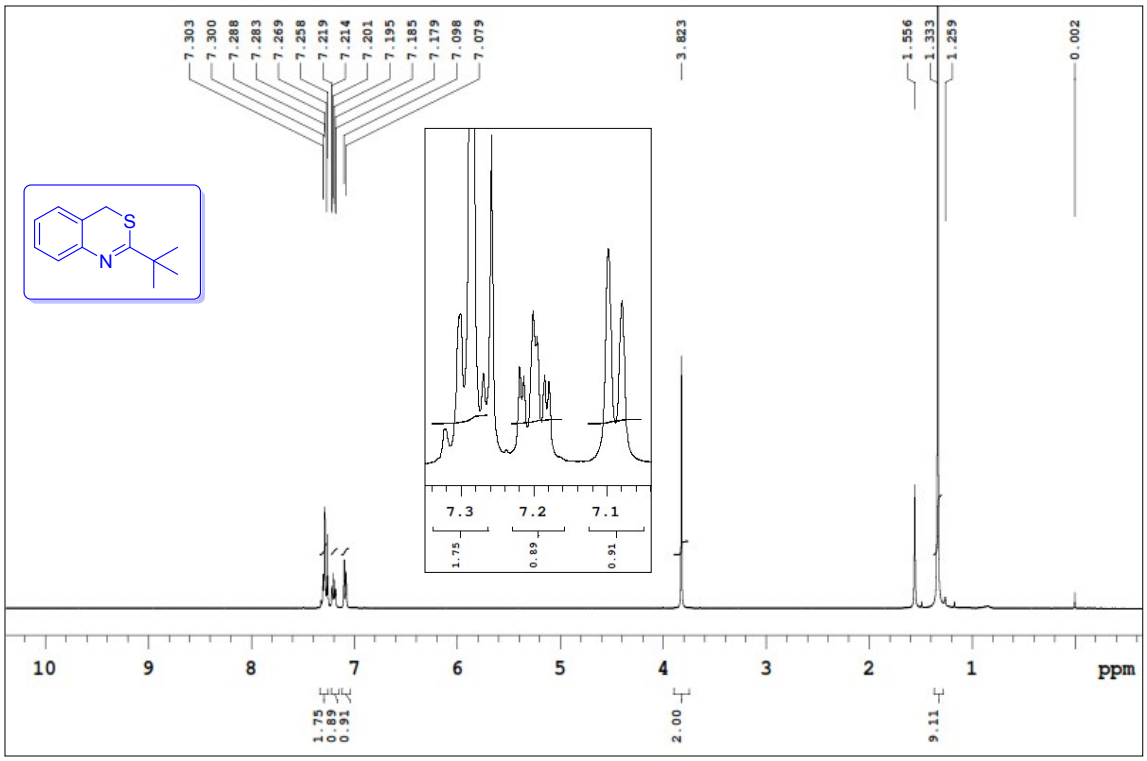
Figure 29. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5aj** in $CDCl_3$ and LC-MS in Acetonitrile.

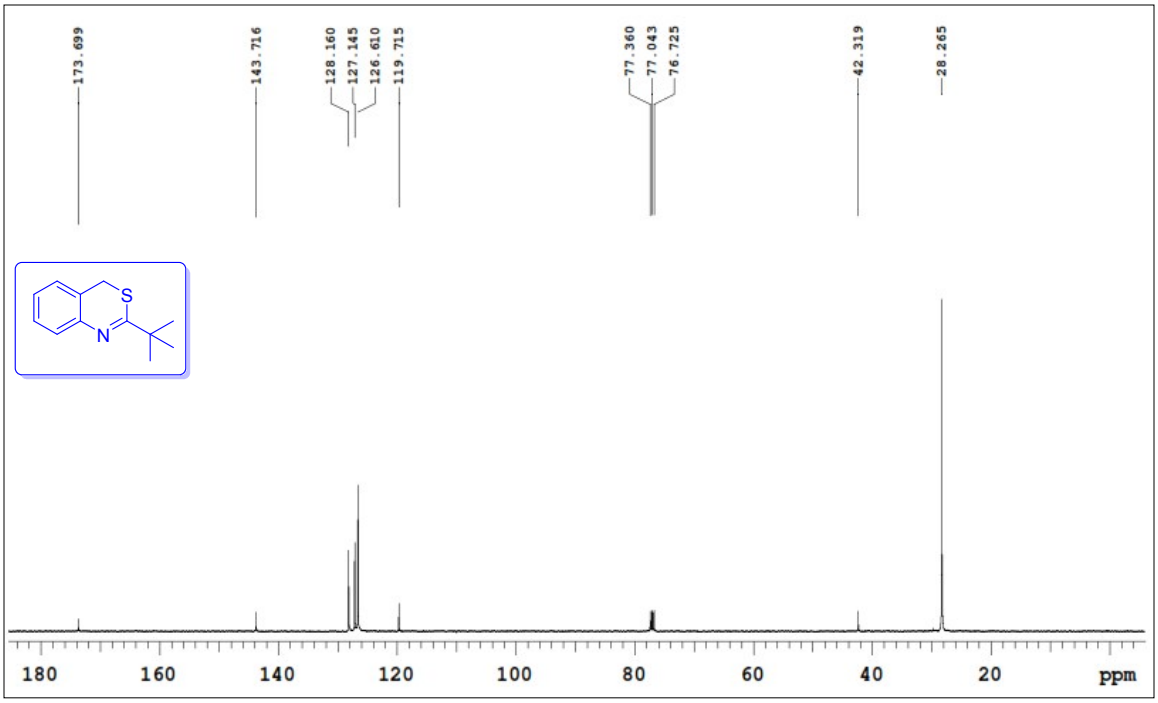
Pale yellow solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 131 - 132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 6.8 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 4.04 (s, 2H), 2.65 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 197.5, 159.6, 144.1, 141.7, 139.0, 128.5, 128.3, 128.1, 127.3, 126.9, 119.2, 28.4, 26.7 ppm; **MS** (APCI): $[M + 1]^+$ = 268.0 (99.71%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{16}H_{14}NOS$: 268.0796; found: 268.0793.

Synthesis of 2-(*tert*-butyl)-4H-benzo[d][1,3]thiazine (5ak); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), 2,2-dimethylpropanethioamide **4k** (1.0 mmol, 117 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(*tert*-butyl)-4H-benzo[d][1,3]thiazine **5ak** in 95% (195 mg) yield as off-white solid.


7.303
7.300
7.288
7.283
7.269
7.258
7.219
7.214
7.201
7.195
7.185
7.179
7.098
7.079
3.823
1.556
1.333
1.259
0.002
S
N
7.3
7.2
7.1
1.75
0.89
0.91
10
9
8
7
6
5
4
3
2
1
ppm
1.75
0.89
0.91
2.00
9.11


173.699
143.716
128.160
127.145
126.610
119.715
77.360
77.043
76.725
42.319
28.265
S
N
180
160
140
120
100
80
60
40
20
ppm

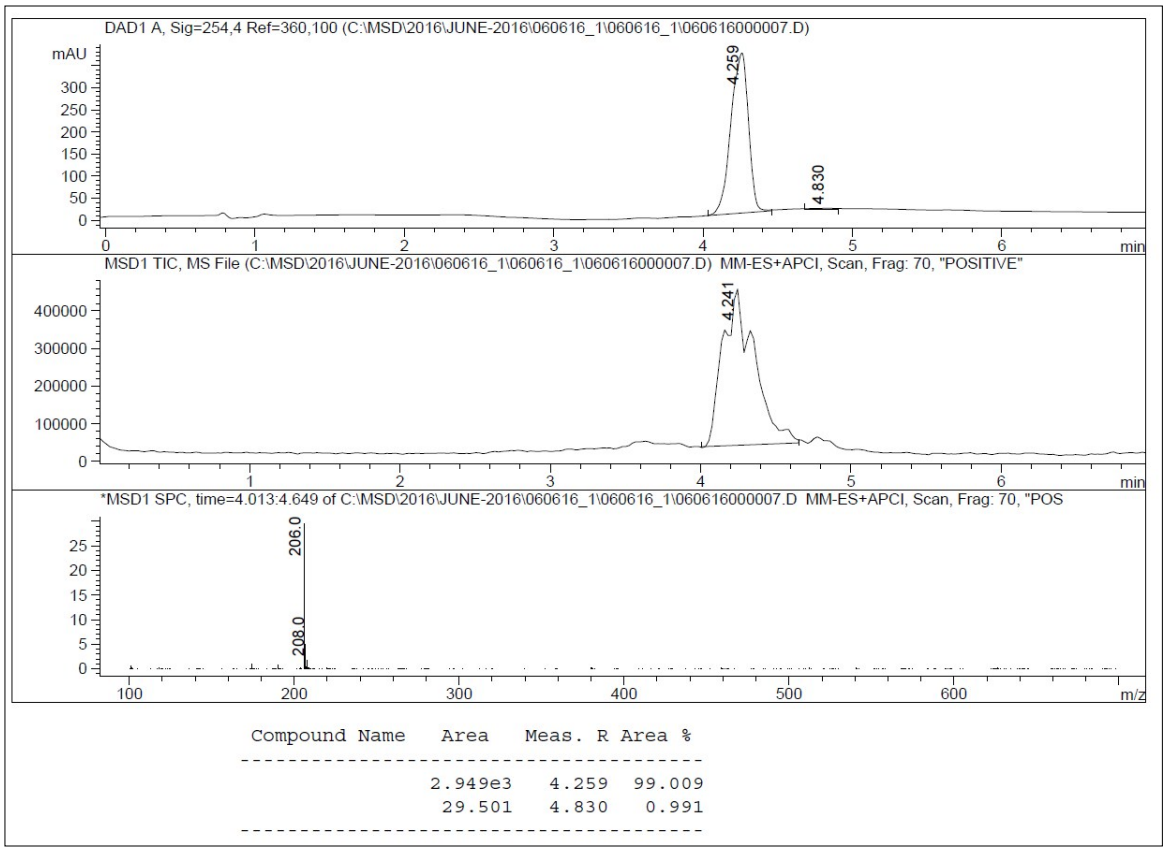
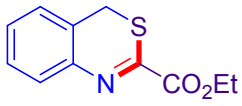


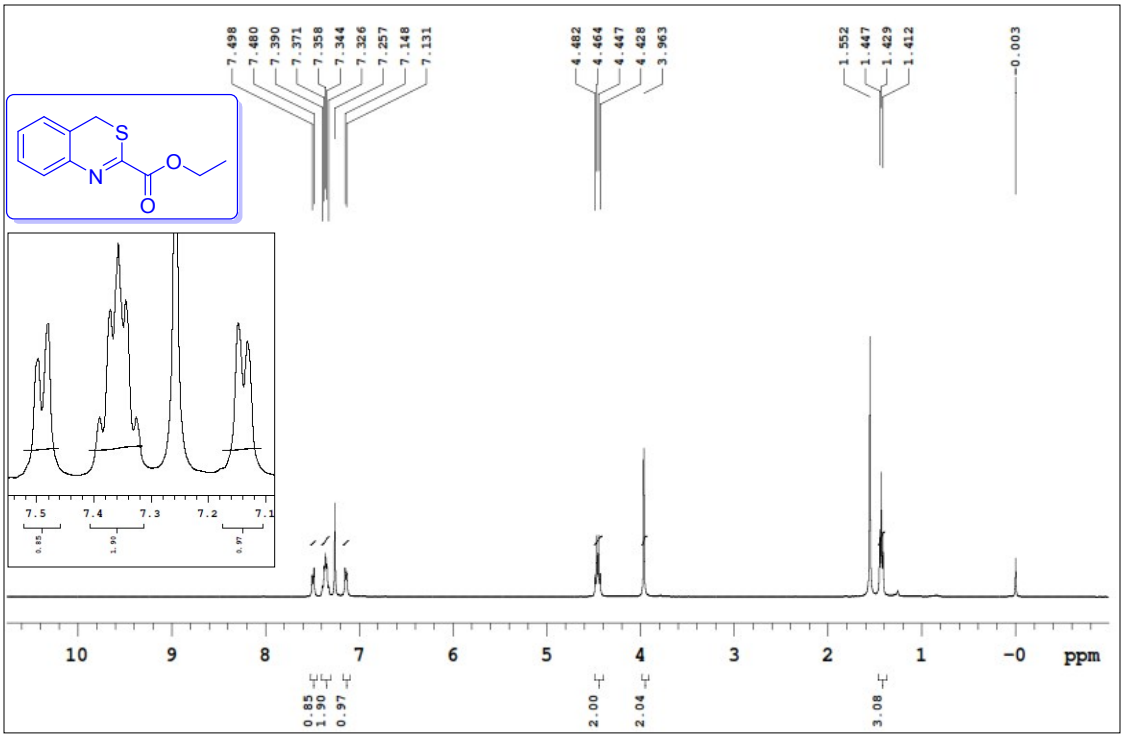
Figure 30. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ak** in $CDCl_3$ and LC-MS in Acetonitrile.

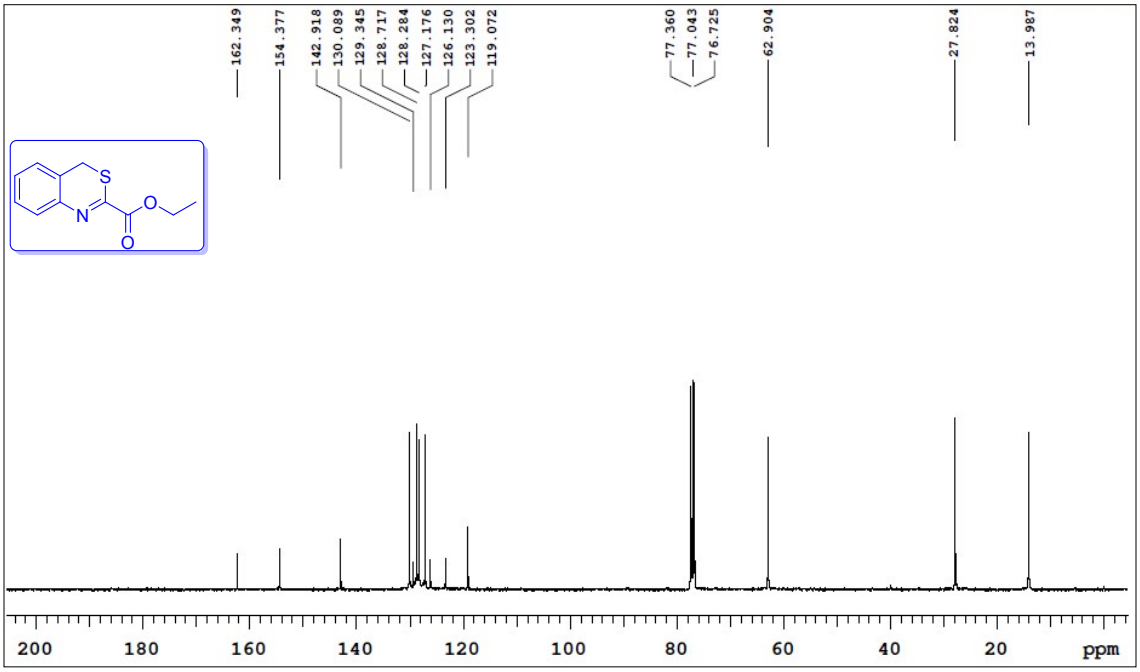
Off-white solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 51 - 53 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32 - 7.25 (m, 2H), 7.19 (dt, *J* = 2.0 Hz, 9.2 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 2H), 1.33 (s, 9H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 173.6, 143.7, 128.1, 127.1, 126.6, 119.7, 42.3, 28.2 ppm; **MS** (APCI): $[M + 1]^+$ = 206.0 (99.00%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{12}H_{16}NS$: 206.1003; found: 206.1002.

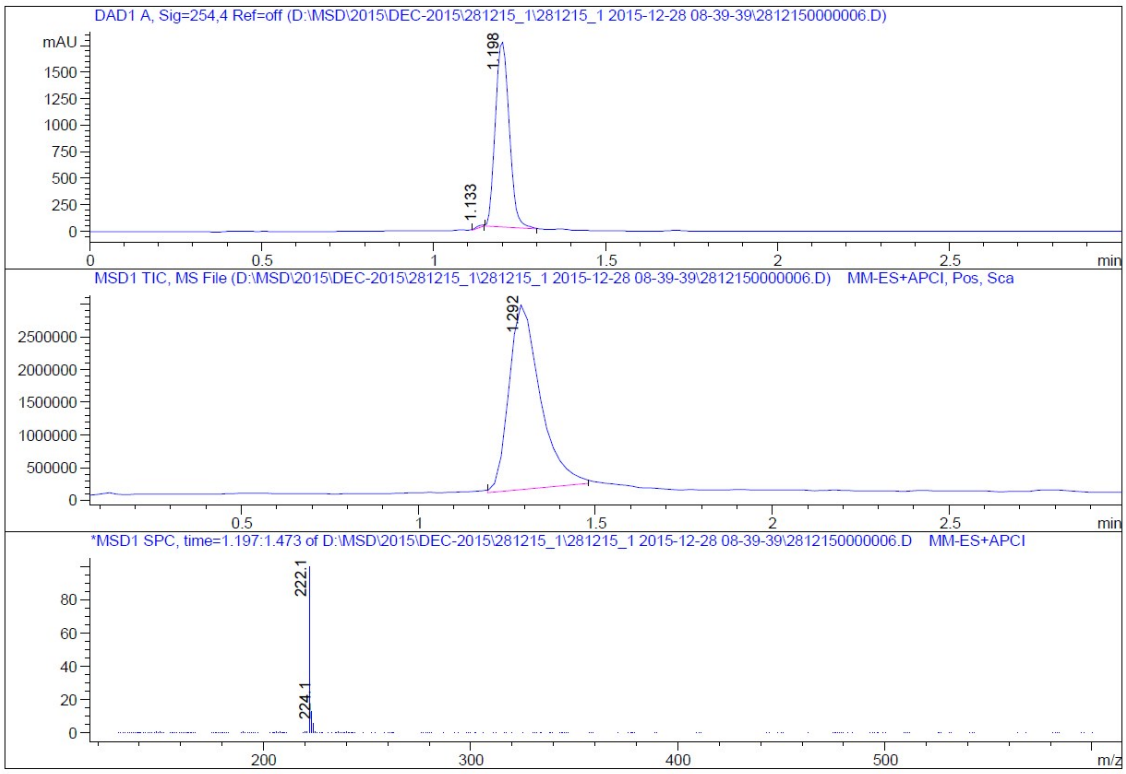
Synthesis of Ethyl 4H-benzo[d][1,3]thiazine-2-carboxylate (5al); known compound[3]



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), ethyl thiooxamate **4l** (1.0 mmol, 133 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired ethyl 4h-benzo[d][1,3]thiazine-2-carboxylate **5al** in 90% (199 mg) yield as orange liquid.


7.498
7.480
7.390
7.371
7.358
7.344
7.326
7.257
7.148
7.131
4.482
4.464
4.447
4.428
3.963
1.552
1.447
1.429
1.412
0.003
S
N
O
O
7.5
7.4
7.3
7.2
7.1
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.85
1.90
0.97
2.00
2.04
3.08


162.349
154.377
142.918
130.089
129.345
128.717
128.284
127.176
126.130
123.302
119.072
77.360
77.043
76.725
62.904
27.824
13.987
S
N
O
O
200
180
160
140
120
100
80
60
40
20
ppm

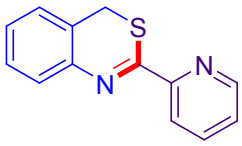


Compound Name	Area	Meas. R	Area %
	24.234	1.133	0.493
	4.894e3	1.198	99.507

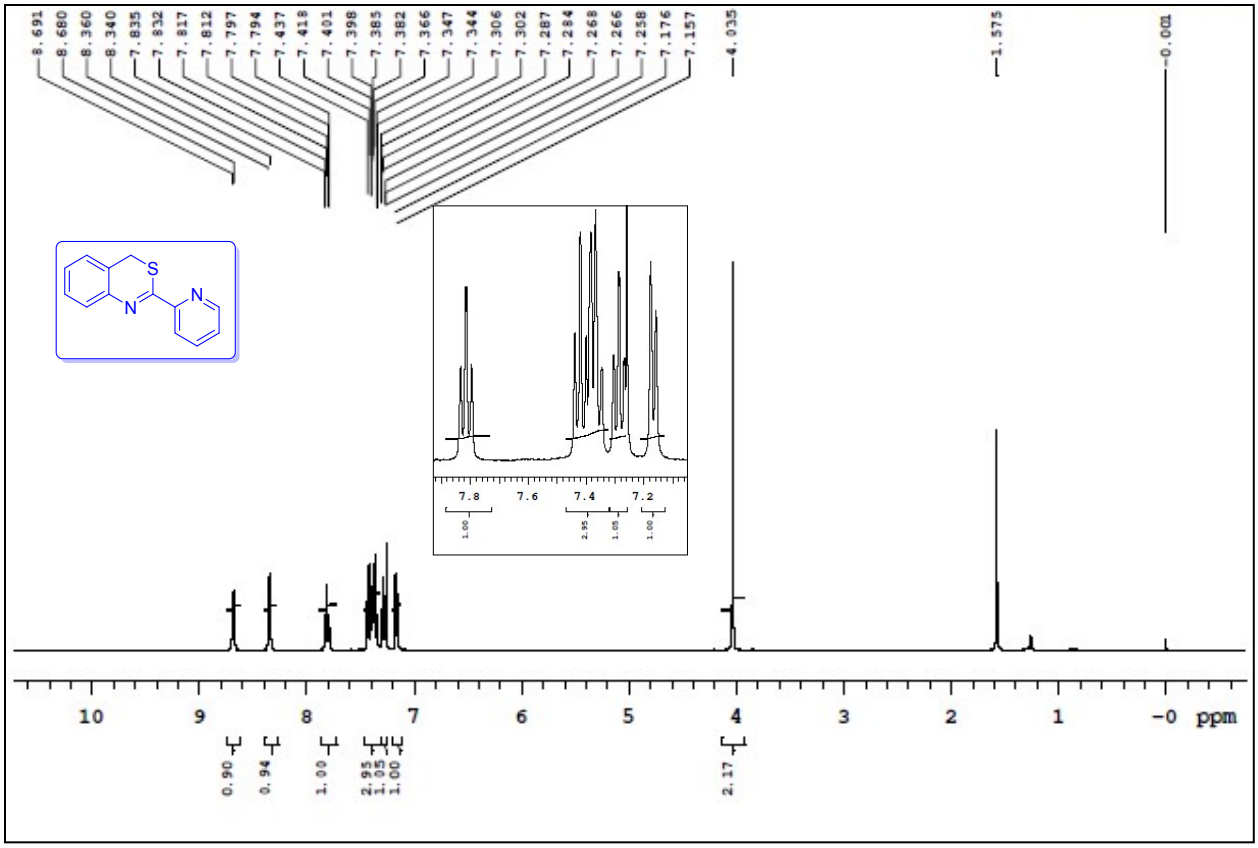
Figure 31. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5al** in $CDCl_3$ and LC-MS in Acetonitrile.

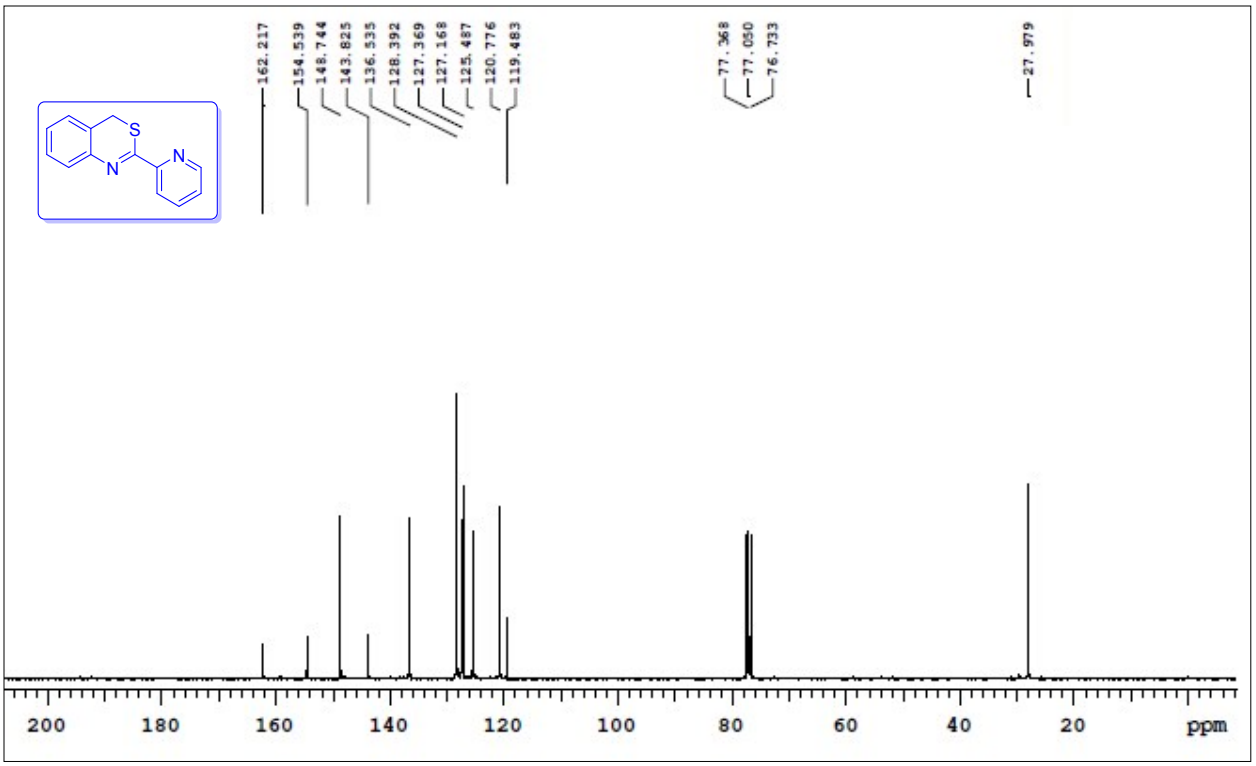
Orange liquid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **b.p** = 148 - 150 °C (Lit[3] 150 °C); **^{1}H NMR** (400 MHz $CDCl_3$) δ = 7.49 (d, *J* = 7.2 Hz, 1H), 7.32 - 7.39 (m, 2H), 7.13 (d, *J* = 6.8 Hz, 1H), 4.45 (q, *J* = 7.2, 6.8 Hz, 2H), 3.96 (s, 2H), 1.42 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.3, 154.3, 142.9, 130.0, 129.3, 128.7, 128.2, 127.1, 126.1, 123.3, 119.0, 62.9, 27.8, 13.9 ppm; **MS** (APCI): $[M + 1]^+$ = 222.1 (99.50%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{11}H_{12}NO_2S$: 222.0588; found: 222.0583.

Synthesis of 2-(pyridin-2-yl)-4H-benzo[d][1,3]thiazine (5am); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), pyridine-2-carbothioamide **4m** (1.0 mmol, 138 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(pyridin-2-yl)-4H-benzo[d][1,3]thiazine **5am** in 88% (199 mg) yield as pale yellow solid.


8.691
8.680
8.360
8.340
7.835
7.832
7.817
7.812
7.797
7.794
7.437
7.418
7.401
7.398
7.385
7.382
7.366
7.347
7.344
7.306
7.302
7.287
7.284
7.268
7.266
7.258
7.176
7.157
4.035
1.575
0.001
S
N
N
7.8
7.6
7.4
7.2
10
9
8
7
6
5
4
3
2
1
0
ppm
0.90
0.94
1.00
2.95
1.05
1.00
2.17


162.217
154.539
148.744
143.825
136.535
128.392
127.369
127.168
125.487
120.776
119.483
77.368
77.050
76.733
27.979
200
180
160
140
120
100
80
60
40
20
ppm

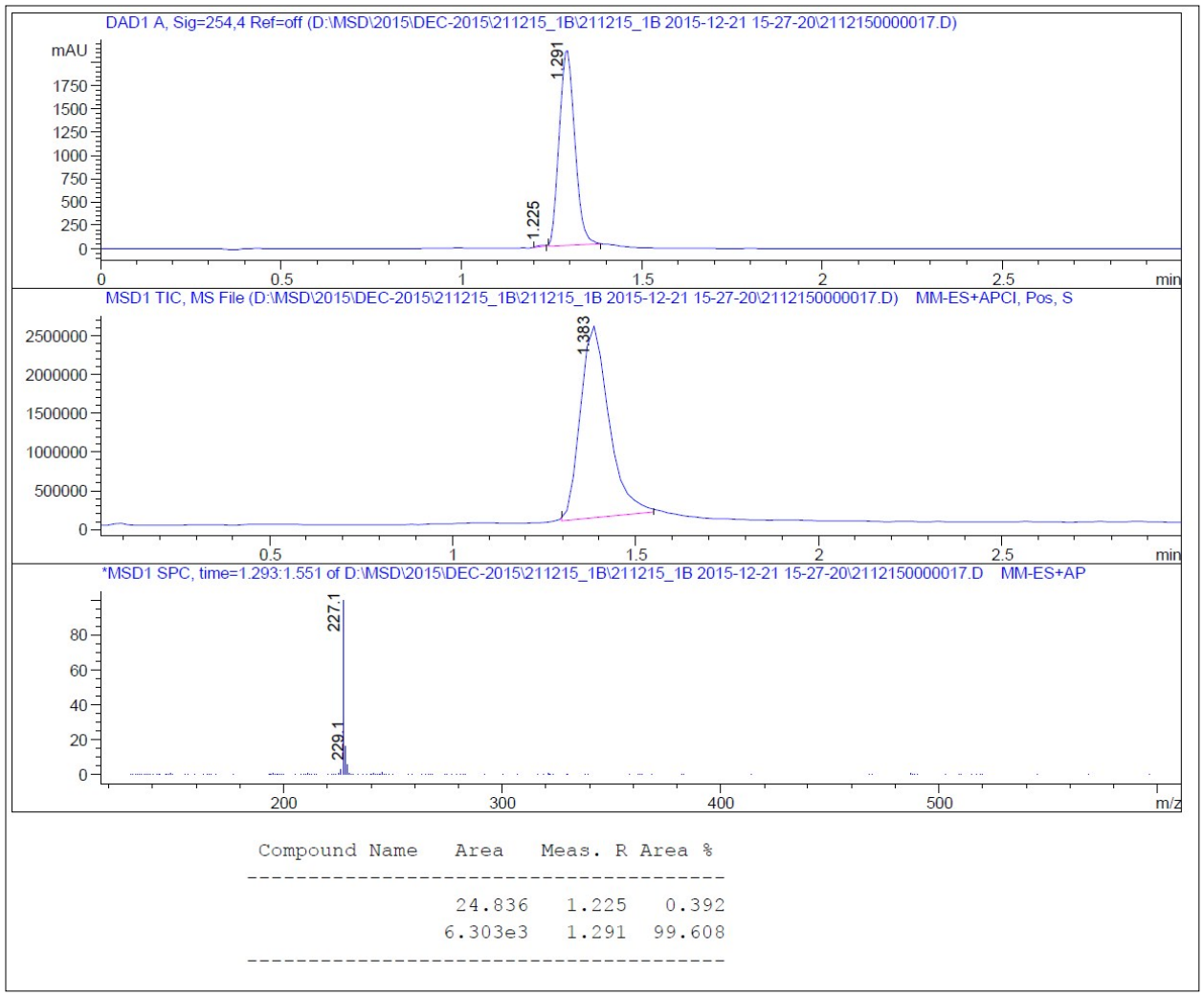
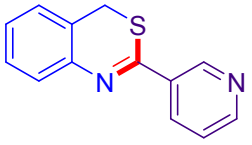


Figure 32. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5am** in $CDCl_3$ and LC-MS in Acetonitrile.

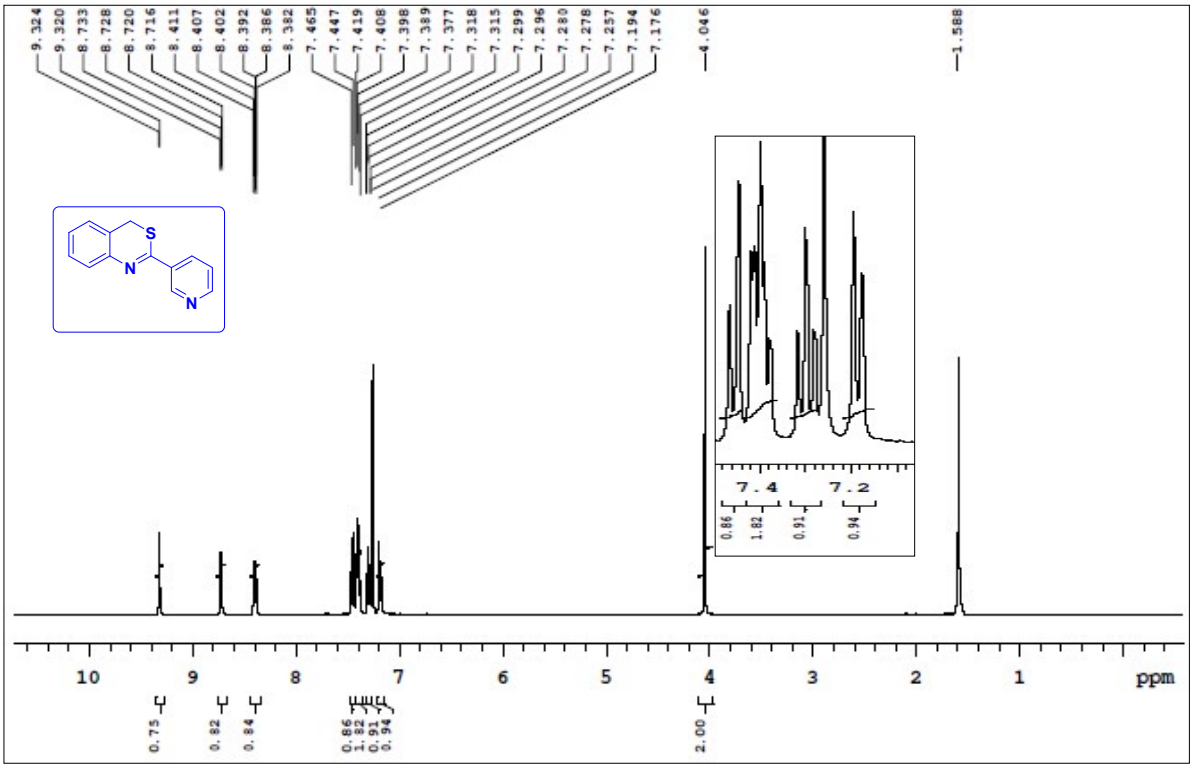
Pale yellow solid; $\mathbf{R_f}$ = 0.45 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 97 - 98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.69 (d, *J* = 4.4 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.81 (dt, *J* = 7.2, 2.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.39 - 7.34 (m, 2H), 7.28 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 4.03 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.2, 154.5. 148.7, 143.8, 136.5, 128.3, 127.3, 127.1, 125.4, 120.7, 119.4, 27.9 ppm; **MS** (APCI): $[M + 1]^+$ = 227.1 (99.6%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{13}H_{11}N_2S$: 227.0642; found: 227.0644.

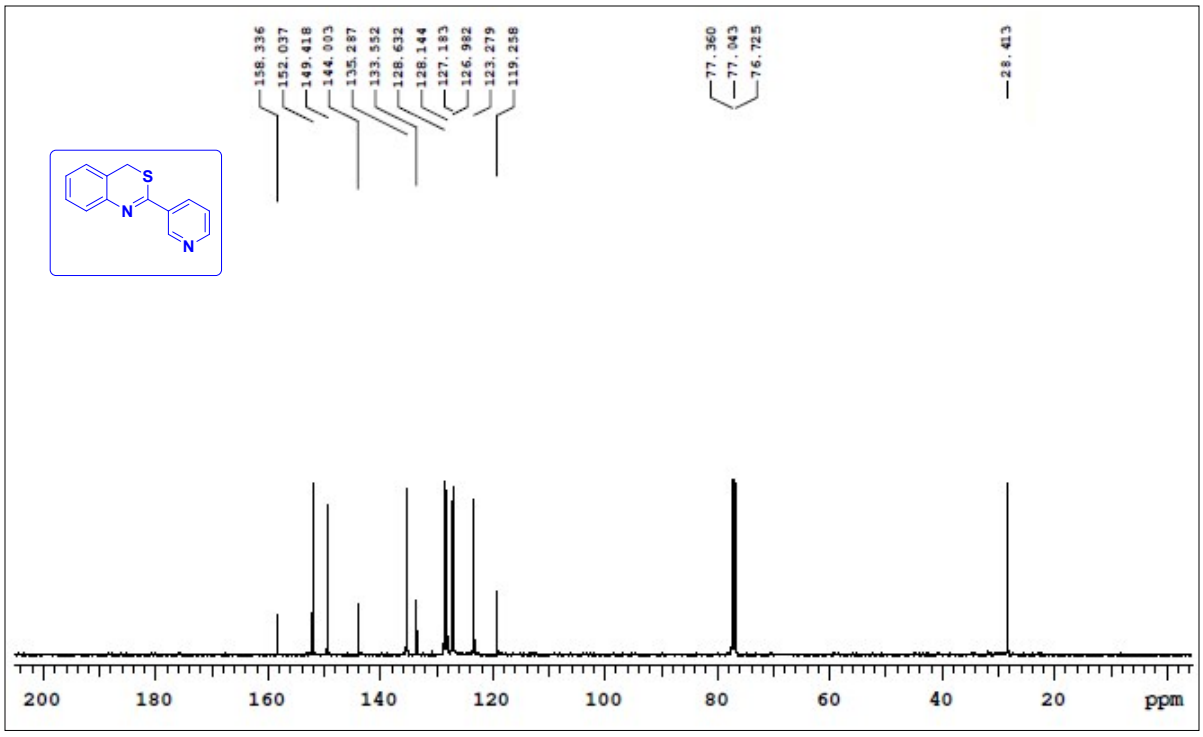
Synthesis of 2-(pyridin-3-yl)-4H-benzo[d][1,3]thiazine (5an); known compound[1]



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), pyridine-3-carbothioamide **4n** (1.0 mmol, 138 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 2-(pyridin-3-yl)-4H-benzo[d][1,3]thiazine **5an** in 90% (203 mg) yield as pale yellow solid.




158.336
152.037
149.418
144.003
135.287
133.552
128.632
128.144
127.183
126.982
123.279
119.258
77.360
77.043
76.725
28.413
S
N
N
200
180
160
140
120
100
80
60
40
20
ppm

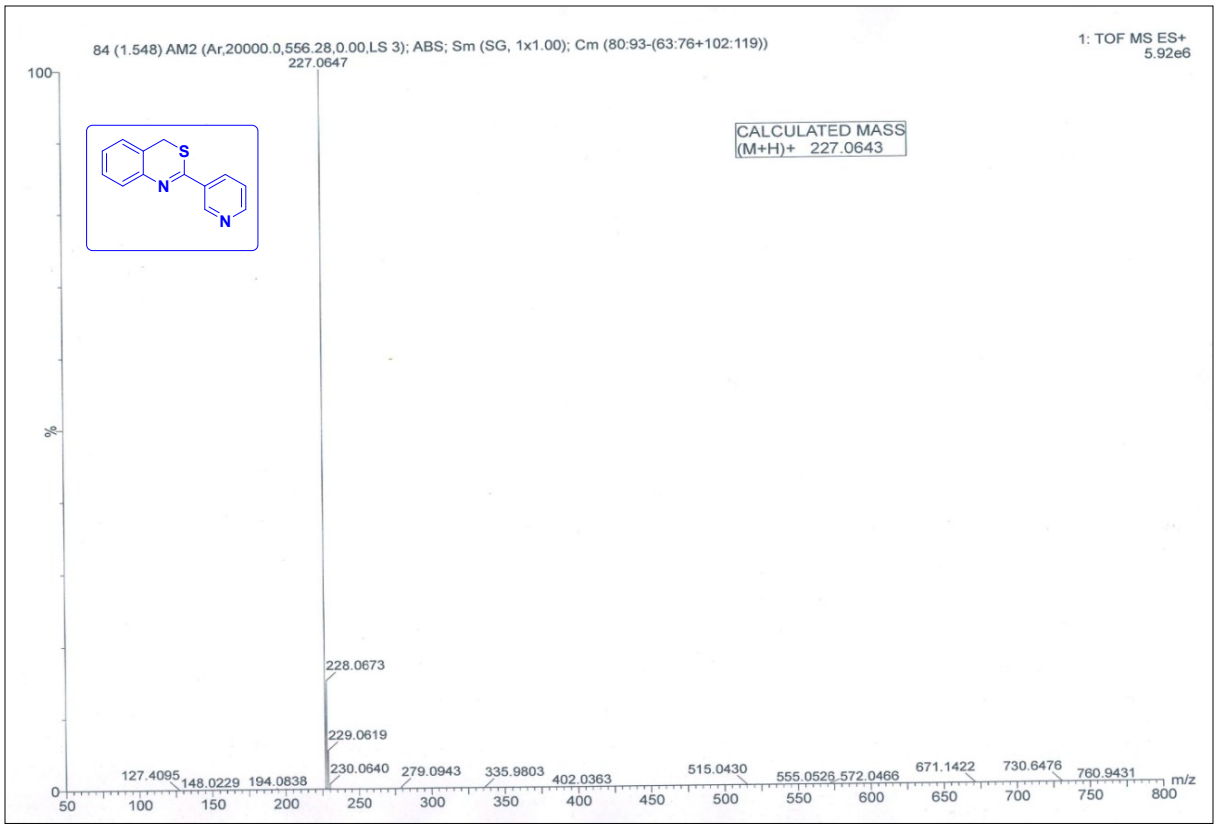
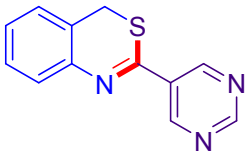


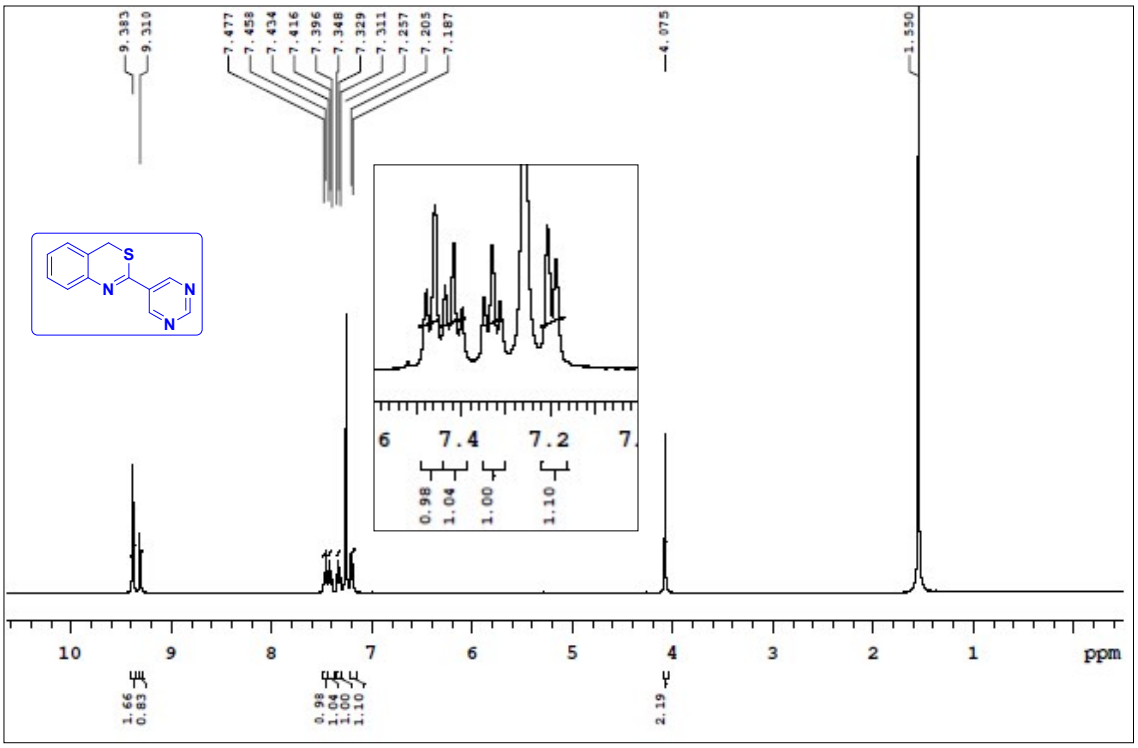
Figure 33. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5an** in $CDCl_3$ and HRMS in Acetonitrile.

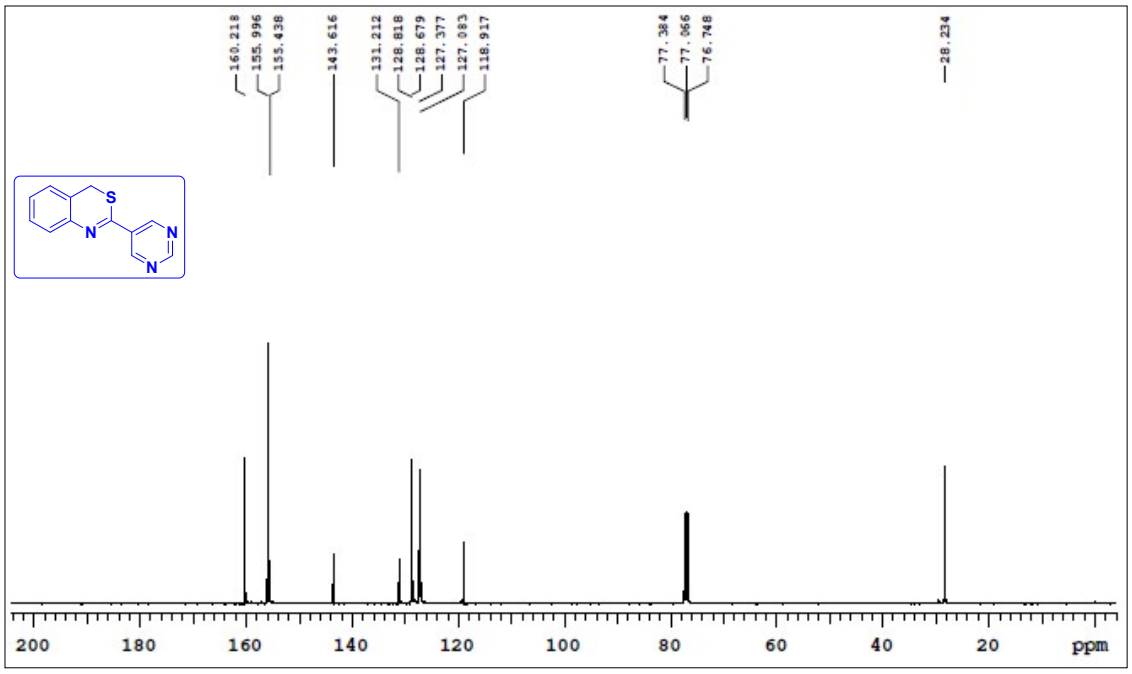
Pale yellow solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 181 - 182 °C (Lit[1] 182 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.32 (d, *J* = 1.6 Hz, 1H), 8.72 (dd, *J* = 5.2, 2.0 Hz, 1H), 8.40 (td, *J* = 8.4, 1.6 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.41 - 7.37 (m, 2H), 7.31 – 7.27 (m, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 4.04 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 158.33, 152.03, 149.41, 144.0, 135.28, 133.55, 128.63, 128.14, 127.18, 126.98, 123.27, 119.25, 28.41 ppm; **HRMS** (ESI, $[M + H]^+$): calculated for $C_{13}H_{11}N_2S$: 227.0642; found: 227.0647.

Synthesis of 2-(pyrimidin-5-yl)-4H-benzo[d][1,3]thiazine (5ao); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), pyrimidine-5-carbothioamide **4o** (1.0 mmol, 139 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(pyrimidin-5-yl)-4H-benzo[d][1,3]thiazine **5ao** in 92% (209 mg) yield as pale yellow solid.


9.383
9.310
7.477
7.458
7.434
7.416
7.396
7.348
7.329
7.311
7.257
7.205
7.187
4.075
1.550
S
N
N
N
6
7.4
7.2
7.
0.98
1.04
1.00
1.10
10
9
8
7
6
5
4
3
2
1
ppm
1.66
0.83
0.98
1.04
1.00
1.10
2.19


160.218
155.996
155.438
143.616
131.212
128.818
128.679
127.377
127.083
118.917
77.384
77.066
76.748
28.234
S
N
N
N
200
180
160
140
120
100
80
60
40
20
ppm

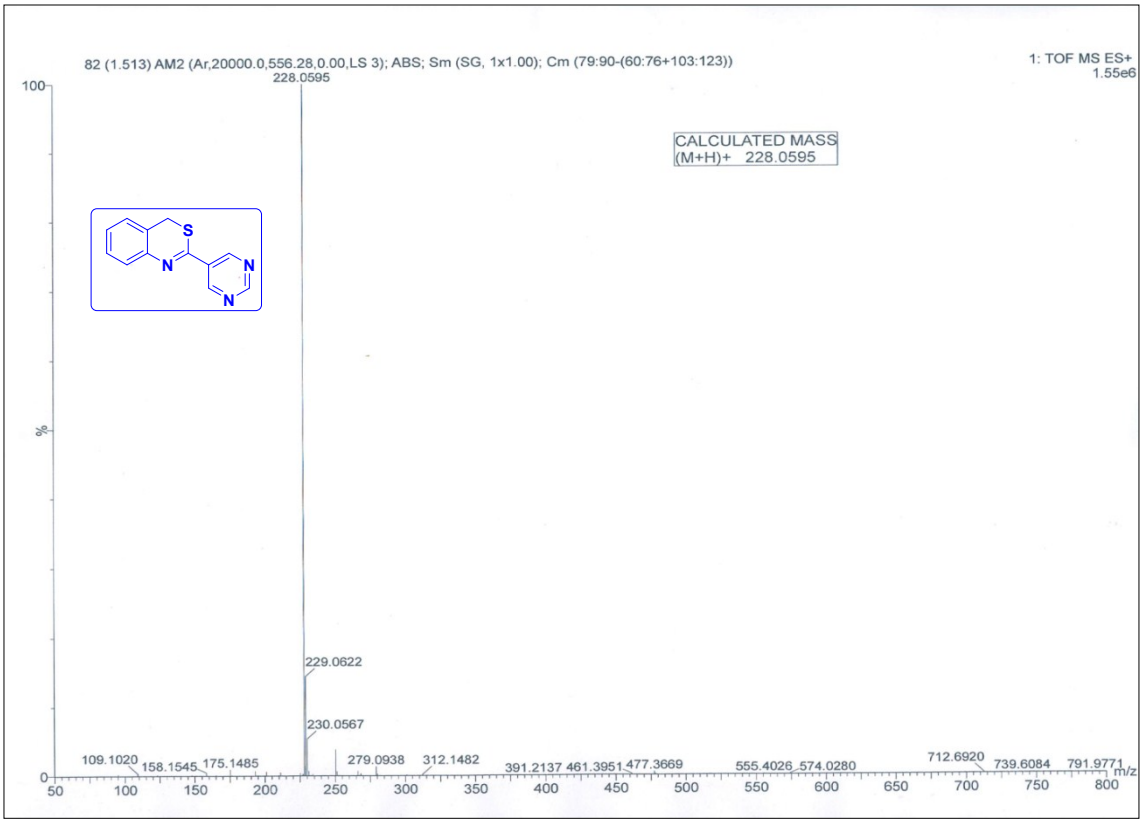
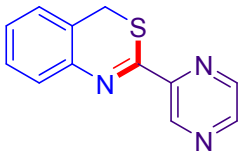


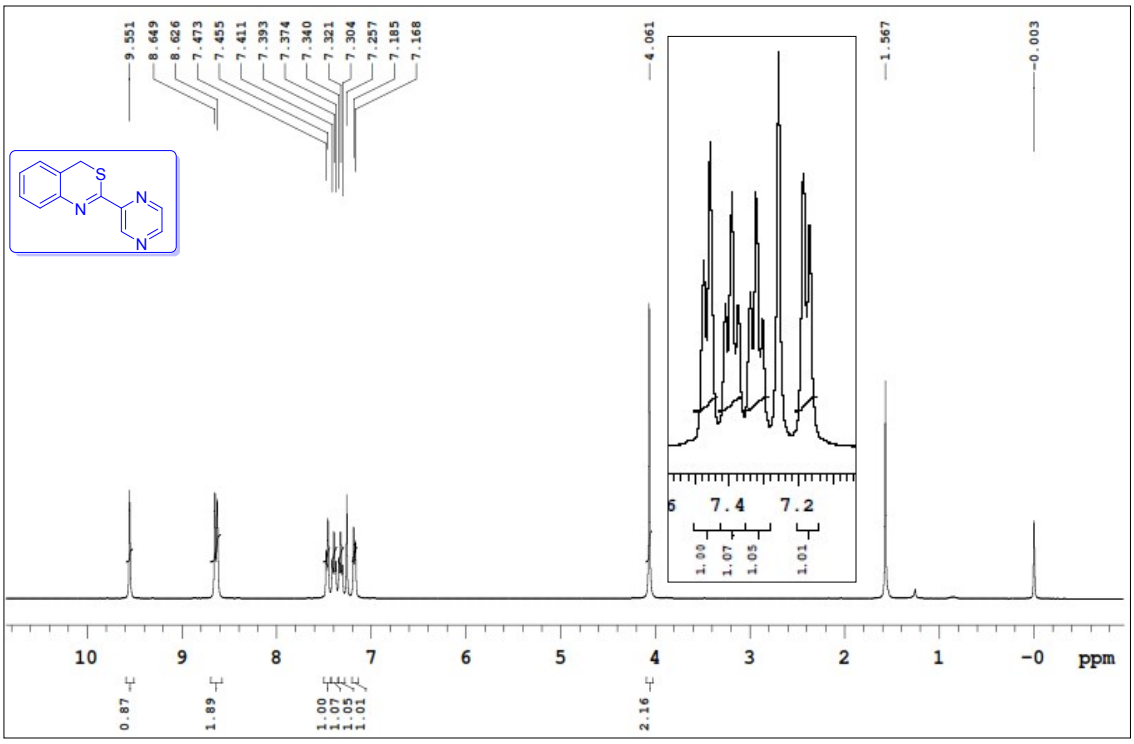
Figure 34. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ao** in $CDCl_3$ and HRMS in Acetonitrile.

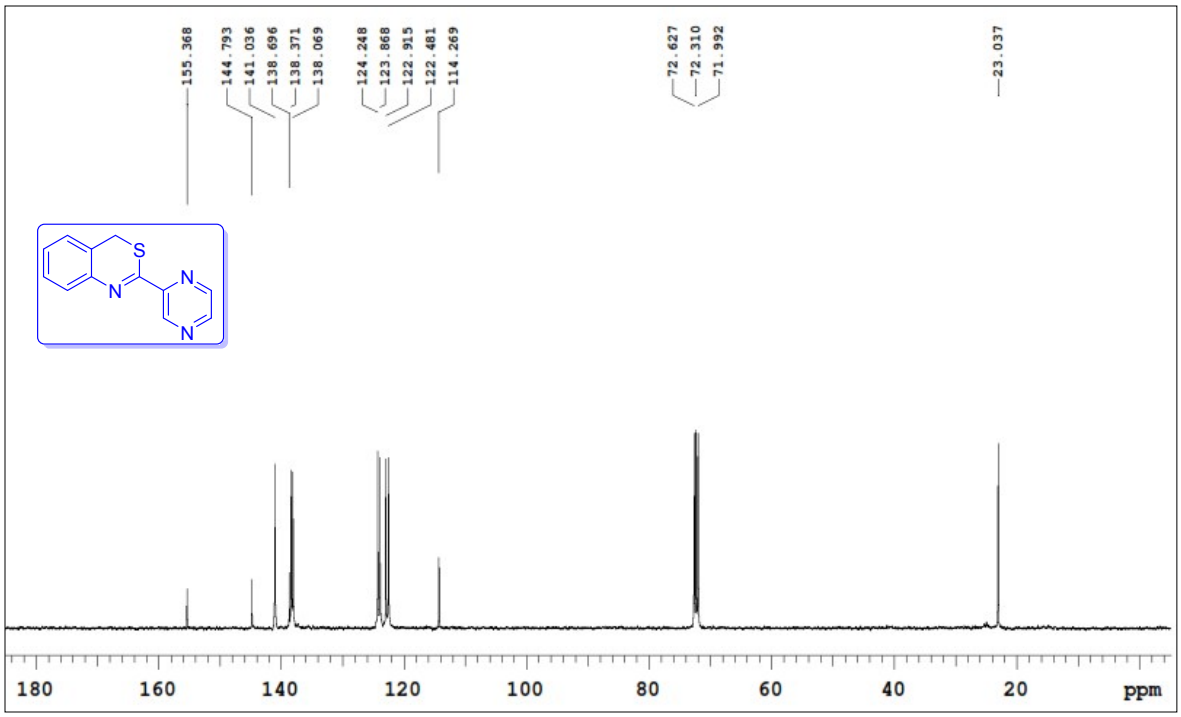
Pale yellow solid; $\mathbf{R_f}$ = 0.45 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.38 (s, 2H), 9.31 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 4.04 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2, 155.9, 155.4, 143.6, 131.2, 128.8, 128.6, 127.3, 127.0, 118.9, 28.2 ppm; **HRMS** (ESI, $[M + H]^+$): calculated for $C_{12}H_{10}N_3S$: 228.0595; found: 228.0595.

Synthesis of 2-(pyrazin-2-yl)-4H-benzo[d][1,3]thiazine (5ap); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), pyrazine-2-carbothioamide **4p** (1.0 mmol, 139 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(pyrazin-2-yl)-4H-benzo[d][1,3]thiazine **5ap** in 93% (211 mg) yield as pale yellow solid.


9.551
8.649
8.626
7.473
7.455
7.411
7.393
7.374
7.340
7.321
7.304
7.257
7.185
7.168
4.061
1.567
0.003
7.4
7.2
1.00
1.07
1.05
1.01
10
9
8
7
6
5
4
3
2
1
−0
ppm
0.87
1.89
2.16


155.368
144.793
141.036
138.696
138.371
138.069
124.248
123.868
122.915
122.481
114.269
72.627
72.310
71.992
23.037
S
N
N
N
180
160
140
120
100
80
60
40
20
ppm

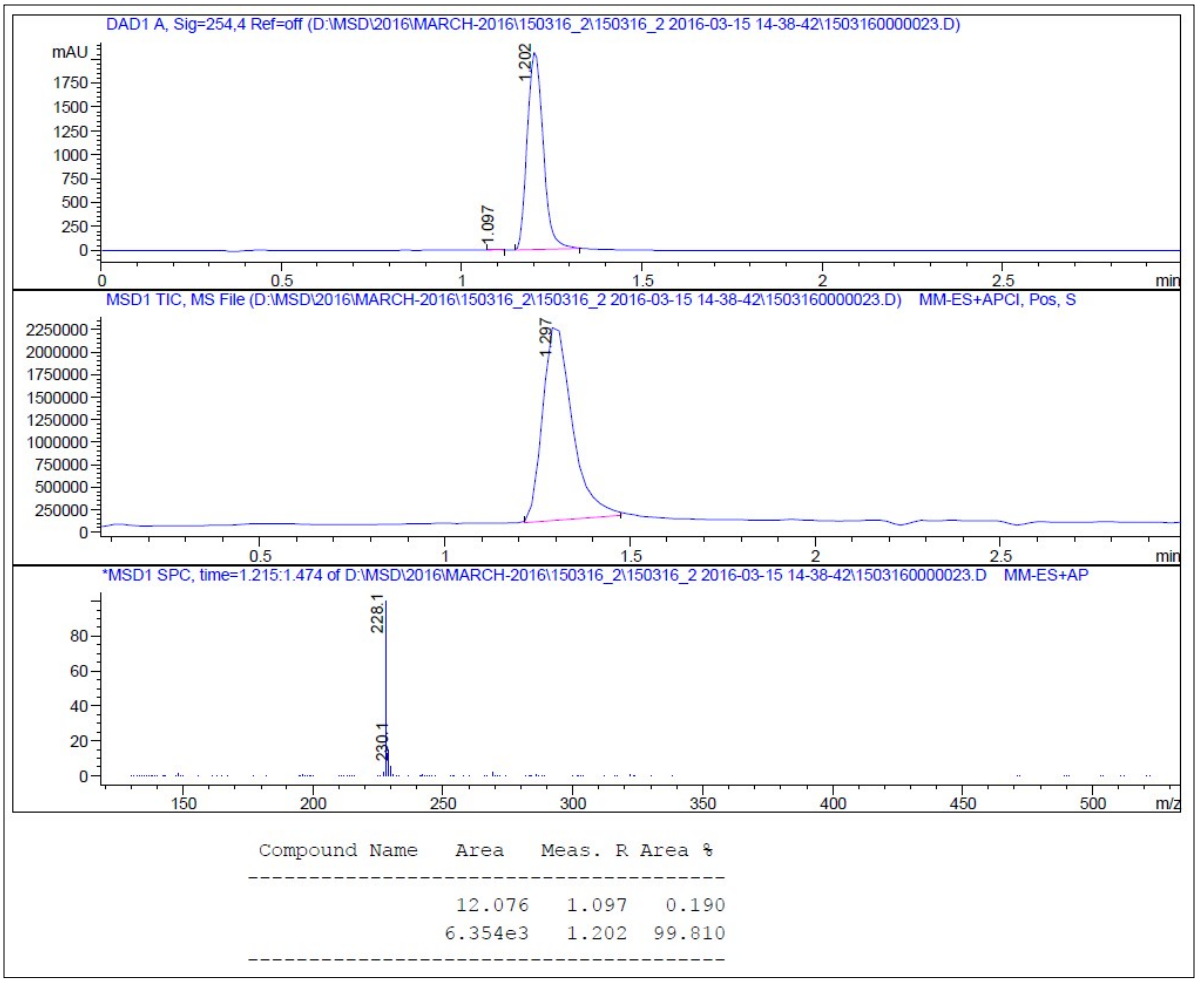
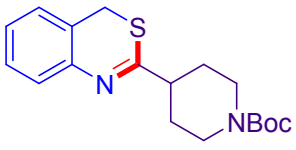


Figure 35. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ap** in $CDCl_3$ and LC-MS in Acetonitrile.

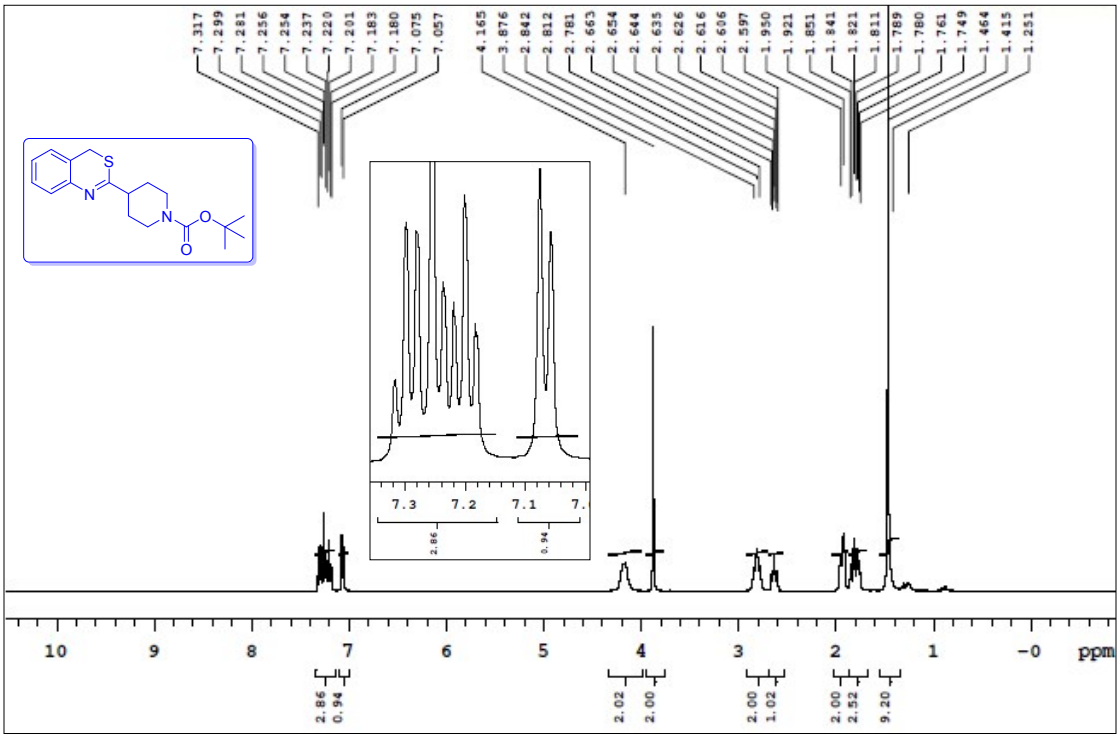
Pale yellow solid; $\mathbf{R_f}$ = 0.40 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 97 - 98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 9.55 (s, 1H), 8.63 (d, *J* = 9.2 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 6.8 Hz, 1H), 4.06 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 155.3, 144.7, 141.0, 138.6, 138.3, 138.0, 124.2, 123.8, 122.9, 122.4, 114.2, 23.0 ppm; **MS** (APCI): $[M + 1]^+$ = 228.1 (99.81%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{12}H_{10}N_3S$: 228.0595; found: 228.0593.

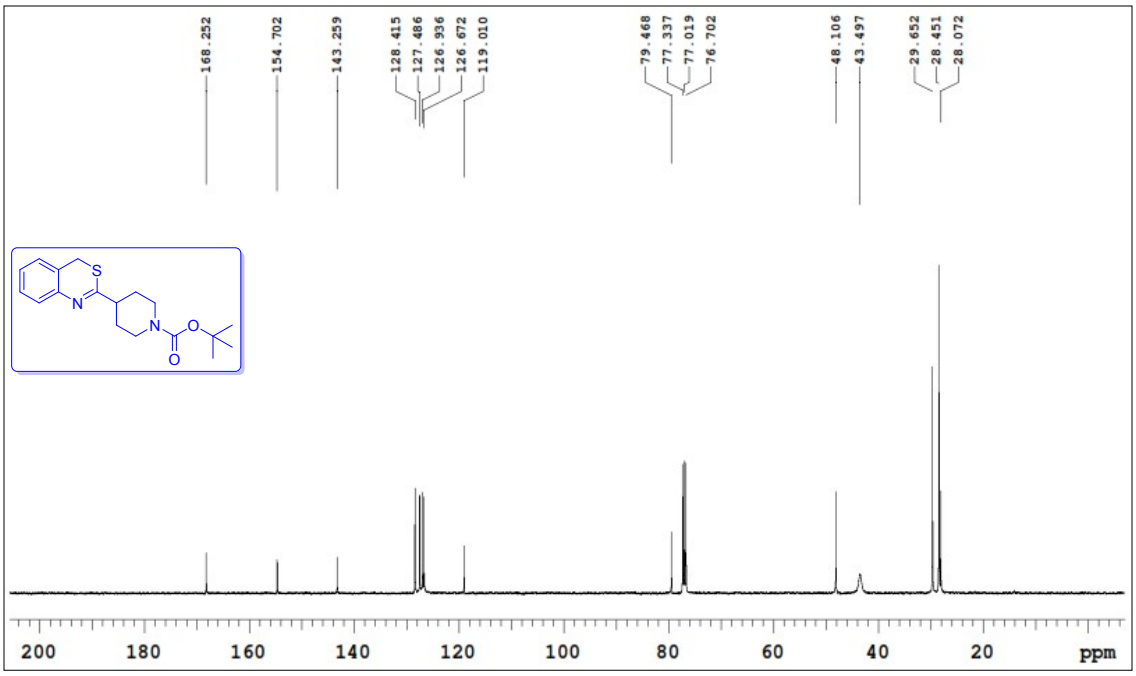
Synthesis of *tert*-butyl 4-(4H-benzo[d][1,3]thiazin-2-yl)piperidine-1-carboxylate (5aq); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), *tert*-butyl 4-carbamothioylpiperidine-1-carboxylate **4q** (1.0 mmol, 244 mg), T3P (1.1

mmol, 349.8 mg) were performed to obtain the desired *tert*-butyl 4-(4H-benzo[d][1,3]thiazin-2-yl)piperidine-1-carboxylate **5aq** in 95% (316 mg) yield as orange semisolid.




168.252
154.702
143.259
128.415
127.486
126.936
126.672
119.010
79.468
77.337
77.019
76.702
48.106
43.497
29.652
28.451
28.072
S
N
N
O
O
200
180
160
140
120
100
80
60
40
20
ppm

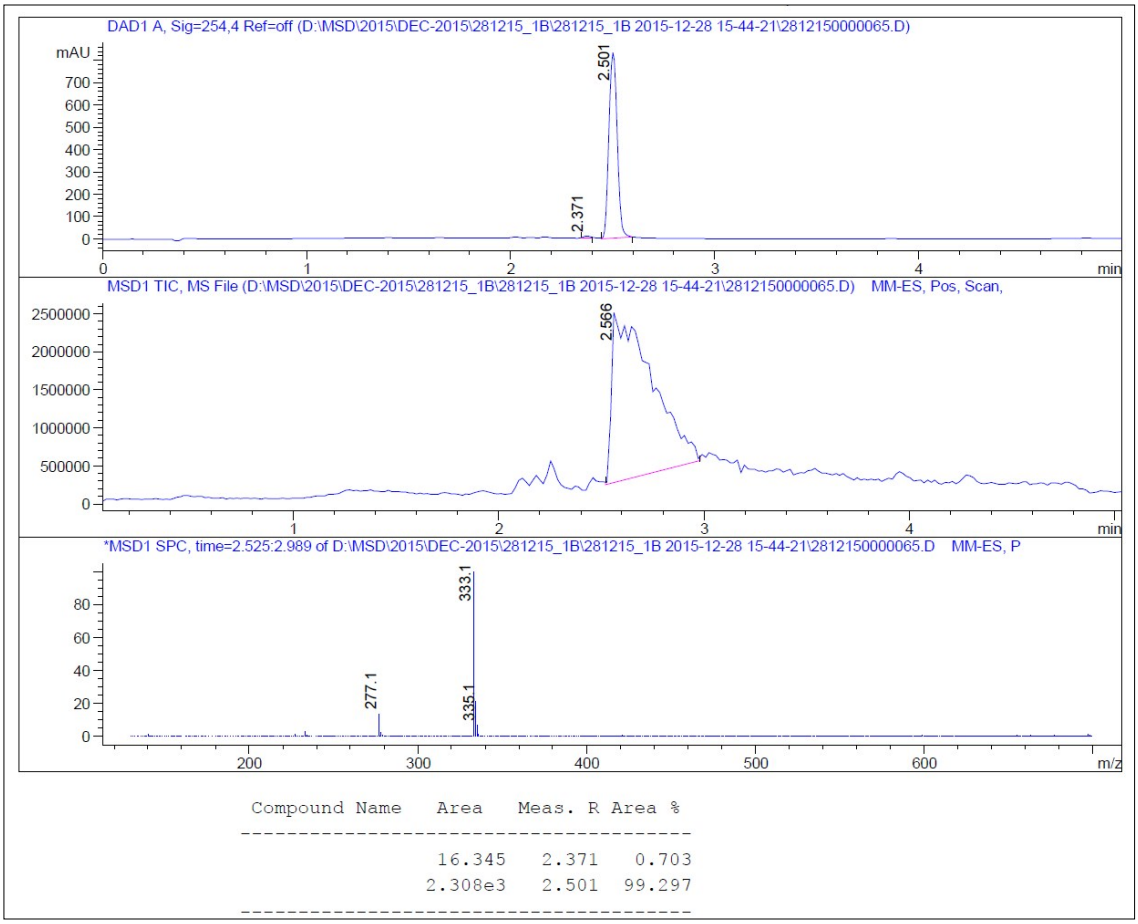
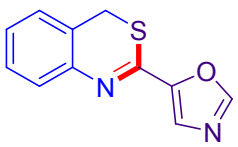


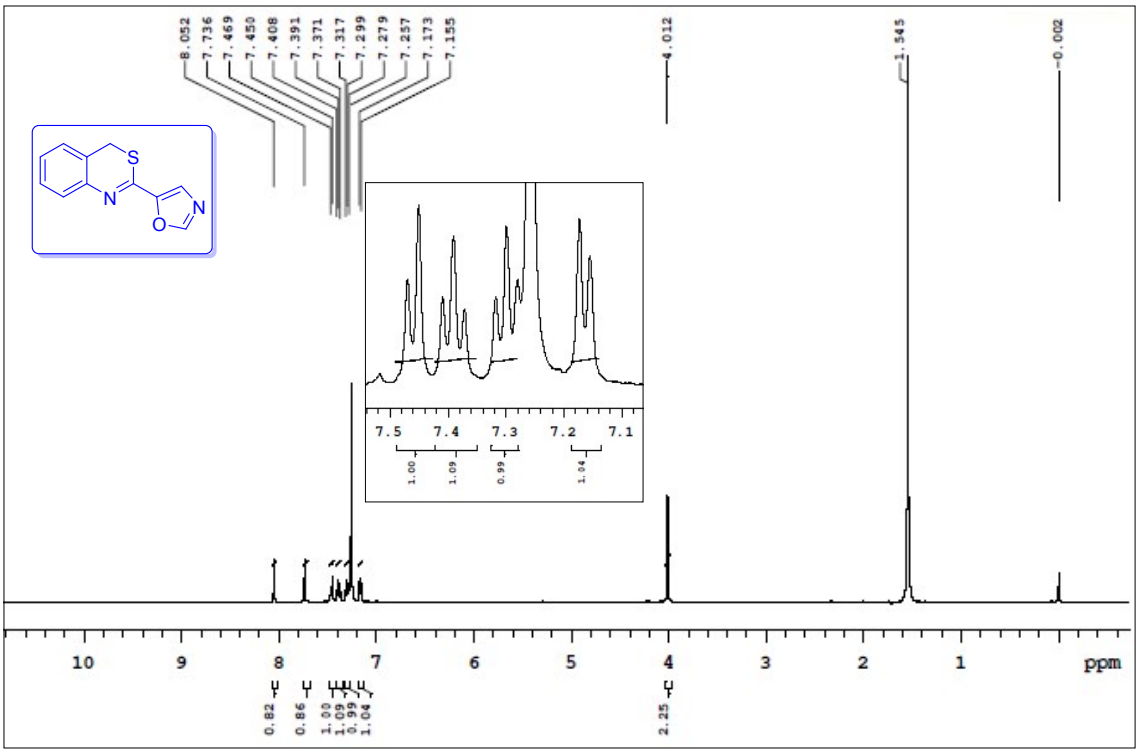
Figure 36. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5aq** in $CDCl_3$ and LC-MS in Acetonitrile.

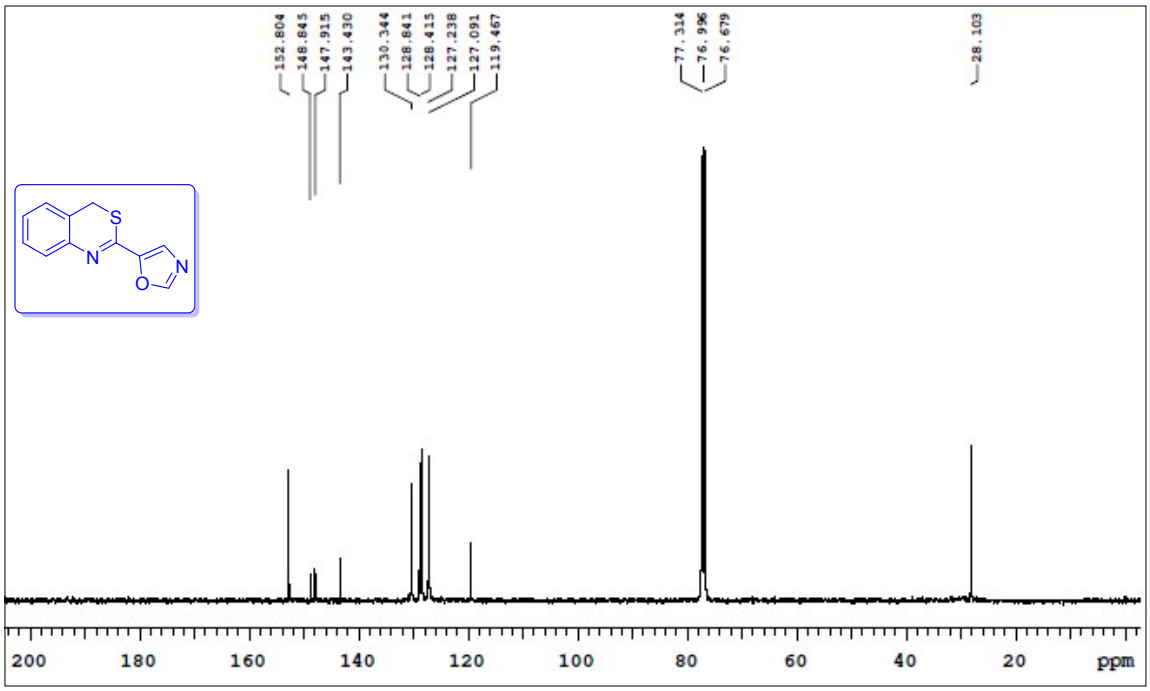
Orange semisolid; $\mathbf{R_f}$ = 0.40 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 73 - 75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.31 - 7.18 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 4.16 (bs, 2H), 3.87 (s, 2H), 2.81 (t, *J* = 12 Hz, 2H), 2.78 - 2.59 (m, 1H), 1.93 (d, *J* = 11.6 Hz, 2H), 1.85 - 1.76 (m, 2H), 1.46 (s, 9H) ppm; **^{13}C NMR** (100 MHz $CDCl_3$) δ = 168.2, 154.7, 143.2, 128.4, 127.4, 126.9, 126.6, 119.0, 79.4, 48.1, 43.4, 29.6, 28.4, 28.0 ppm; **MS** (APCI): $[M + 1]^+$ = 333.1 (99.29%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{18}H_{25}N_2O_2S$: 333.1636; found: 333.1630.

Synthesis of 5-(4H-benzo[d][1,3]thiazin-2-yl)oxazole (5ar); new compound



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), oxazole-5-carbothioamide **4r** (1.0 mmol, 128 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 5-(4H-benzo[d][1,3]thiazin-2-yl)oxazole **5ar** in 89% (192 mg) yield as pale yellow solid.


8.052
7.736
7.469
7.450
7.408
7.391
7.371
7.317
7.299
7.279
7.257
7.173
7.155
4.012
1.545
0.002
S
N
O
N
7.5
7.4
7.3
7.2
7.1
1.00
1.09
0.99
1.04
10
9
8
7
6
5
4
3
2
1
ppm
0.82
0.86
1.00
1.09
0.99
1.04
2.25


152.804
148.845
147.915
143.430
130.344
128.841
128.415
127.238
127.091
119.467
77.314
76.996
76.679
28.103
S
N
O
N
200
180
160
140
120
100
80
60
40
20
ppm

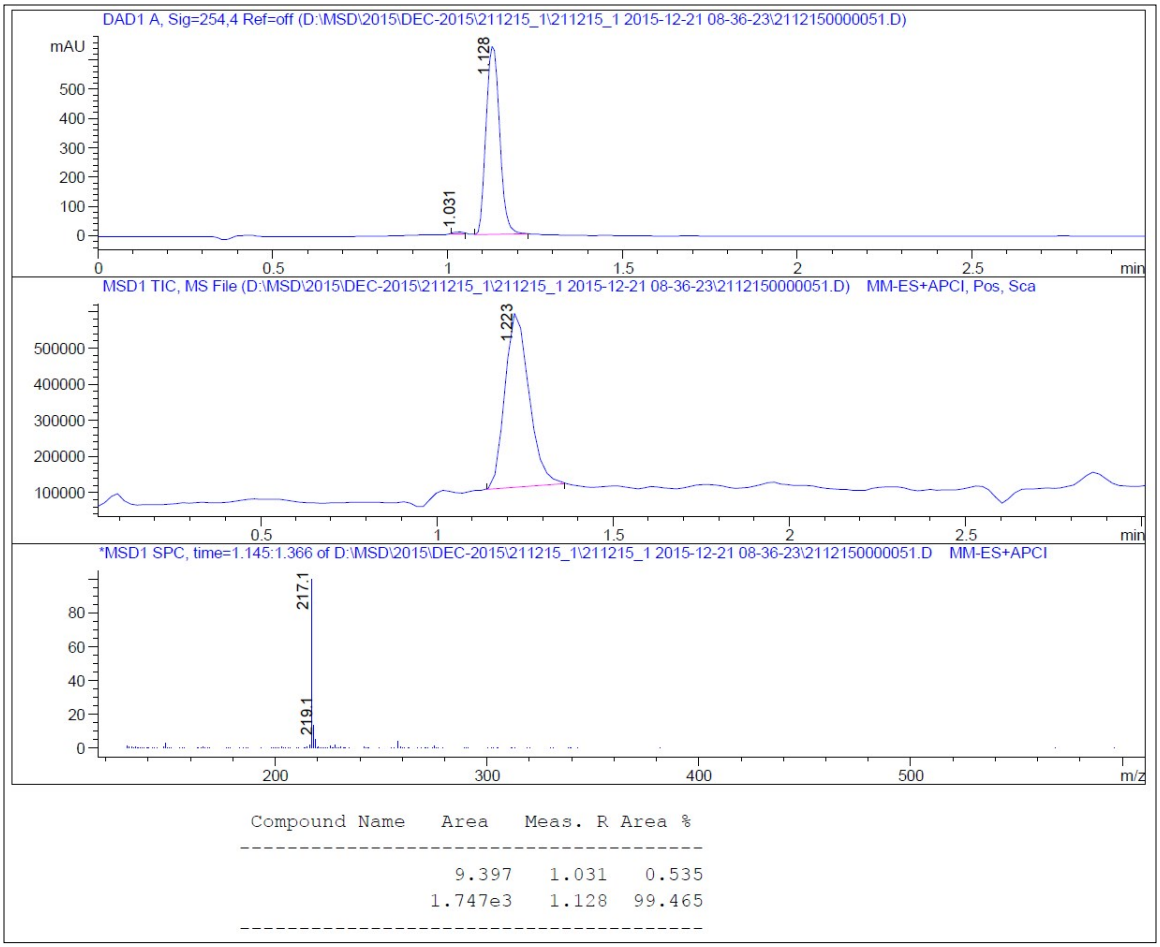
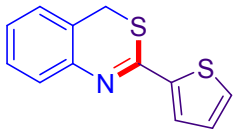


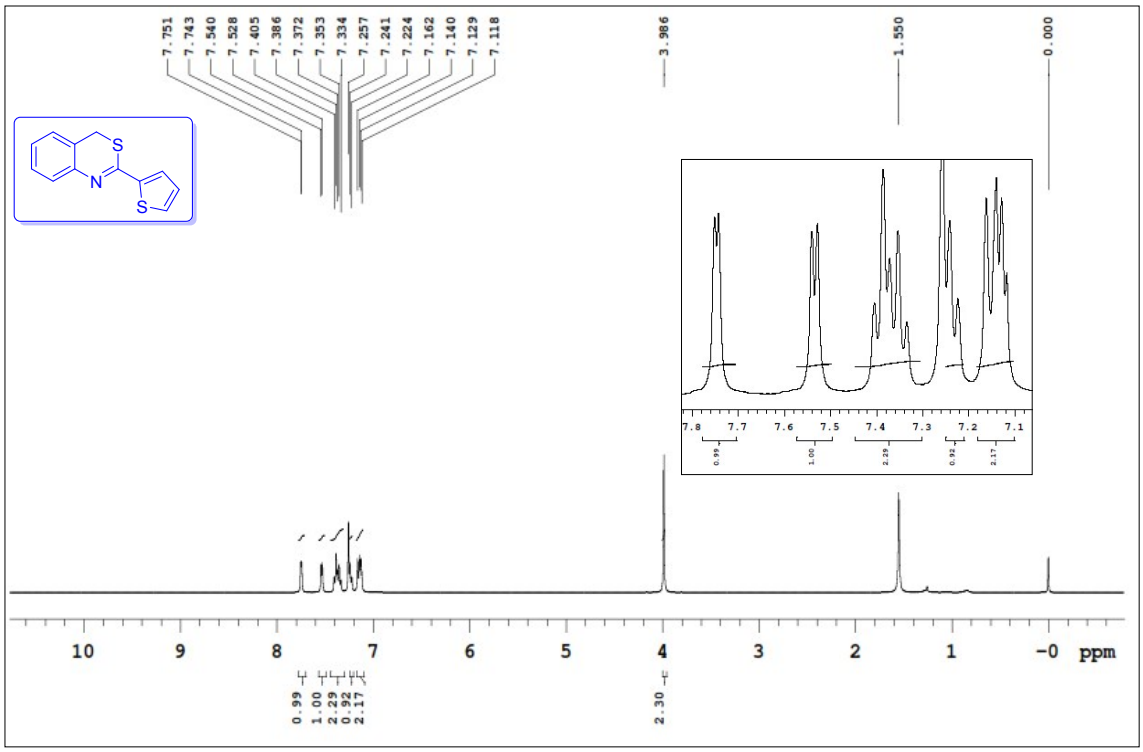
Figure 37. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ar** in $CDCl_3$ and LC-MS in Acetonitrile.

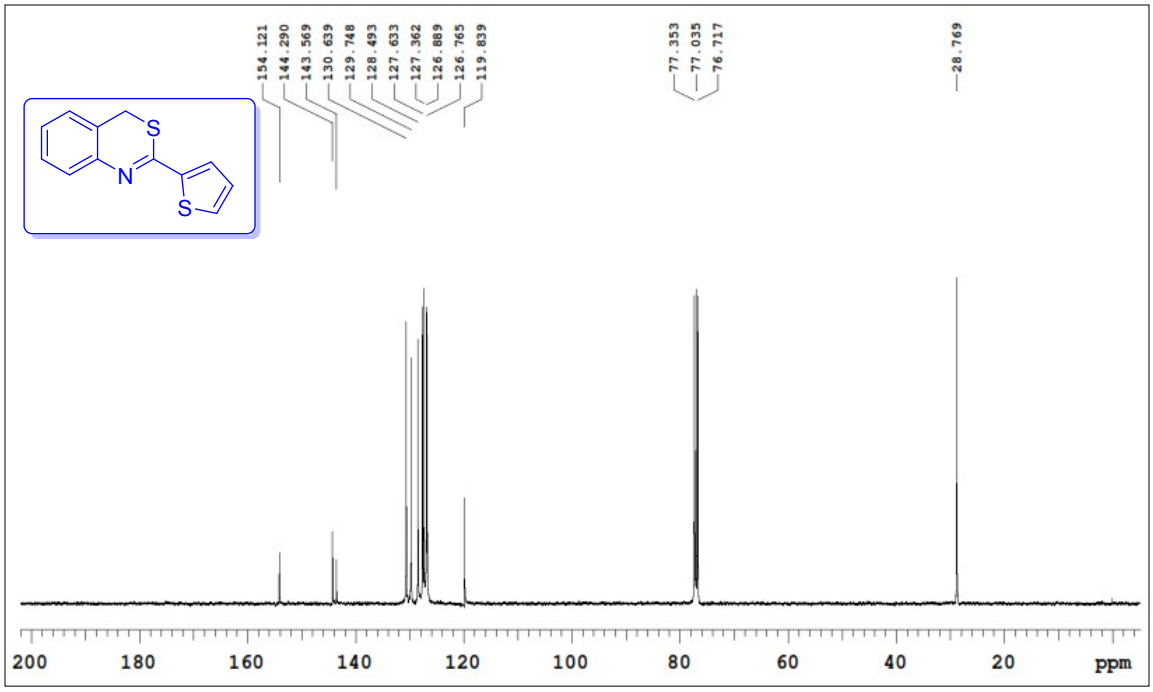
Pale Yellow solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.05 (s, 1H), 7.73 (s, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 4.01 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 152.8, 148.84, 147.91, 143.43, 130.34, 128.84, 128.41, 127.23, 127.0, 119.46, 28.1 ppm; **MS** (APCI): $[M + 1]^+$ = 217.1 (99.46%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{11}H_9N_2OS$: 217.0435; found: 217.0433.

Synthesis of 2-(thiophen-2-yl)-4H-benzo[d][1,3]thiazine (5as); known compound[4]



According to the general procedure, reactions between 2-aminobenzyl alcohol **1a** (1.0 mmol, 123 mg), thiophene-2-carbothioamide **4s** (1.0 mmol, 143 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-(thiophen-2-yl)-4H-benzo[d][1,3]thiazine **5as** in 89% (206 mg) yield as light brown solid.


7.751
7.743
7.540
7.528
7.405
7.386
7.372
7.353
7.334
7.257
7.241
7.224
7.162
7.140
7.129
7.118
3.986
1.550
0.000
S
N
S
10
9
8
7
6
5
4
3
2
1
−0
ppm
0.99
1.00
2.29
0.92
2.17
2.30


154.121
144.290
143.569
130.639
129.748
128.493
127.633
127.362
126.889
126.765
119.839
77.353
77.035
76.717
28.769
S
N
S
200
180
160
140
120
100
80
60
40
20
ppm

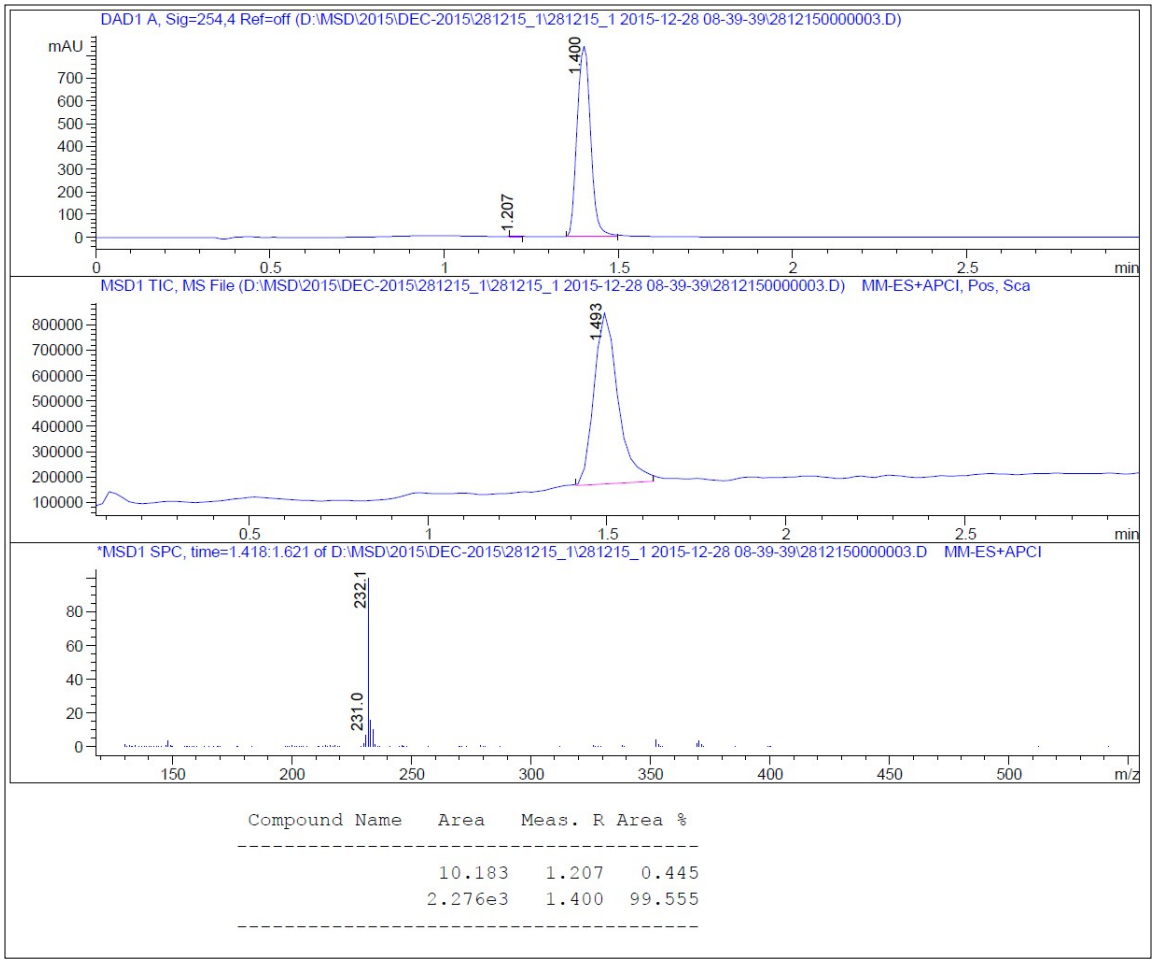
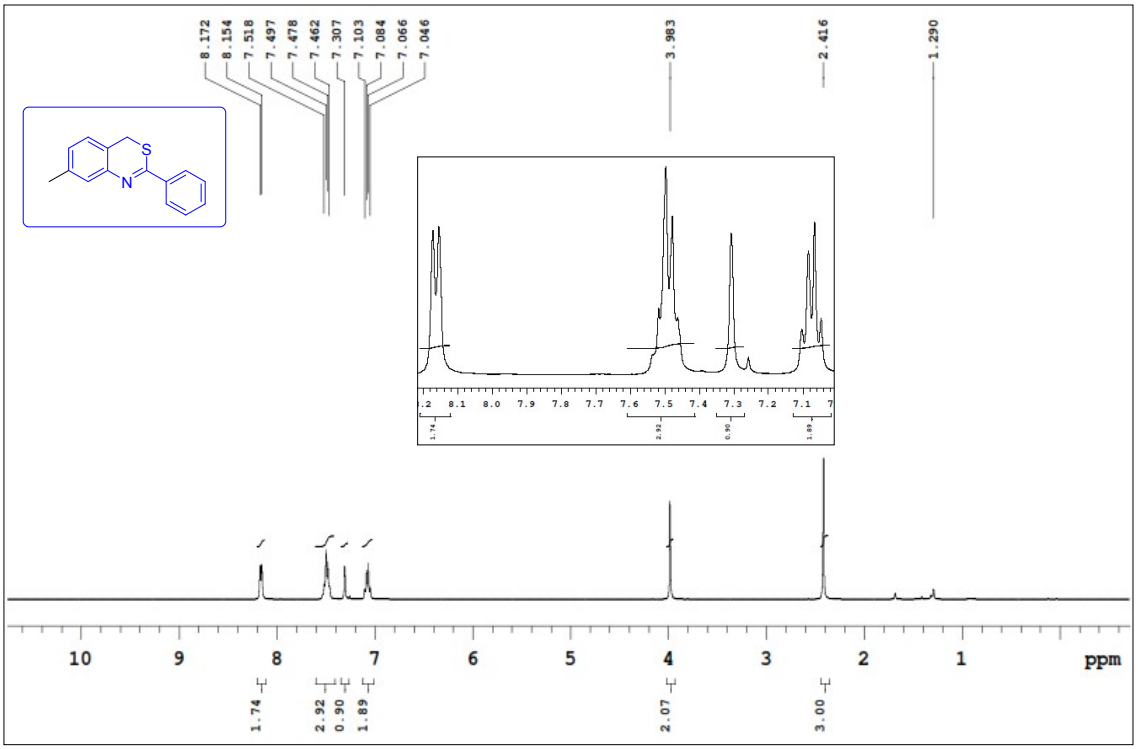


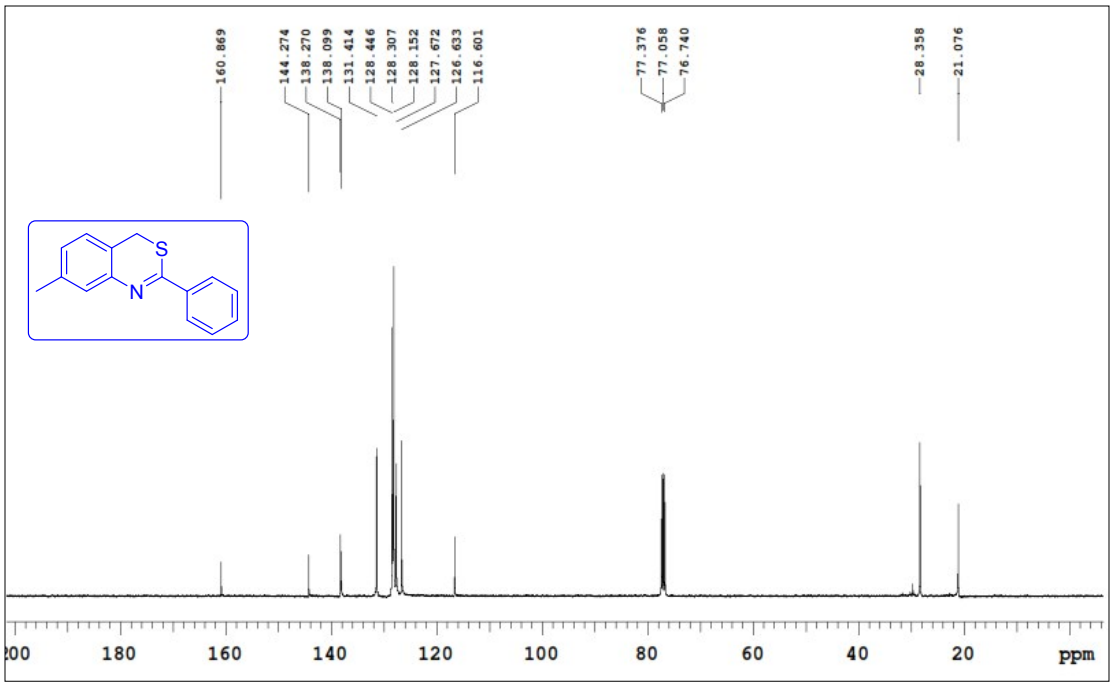
Figure 38. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5as** in $CDCl_3$ and LC-MS in Acetonitrile.

Light brown solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 208 - 211 °C (Lit[4] 210 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 3.2 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.46 - 7.33 (m, 2H), 7.24 - 7.22 (m, 1H), 7.16 - 7.11 (m, 2H), 3.98 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 154.1, 144.2, 143.5, 130.6, 129.7, 128.4, 127.6, 127.3, 126.8, 126.7, 119.8, 28.7 ppm; **MS** (APCI): $[M + 1]^+$ = 232.1 (99.55%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{12}H_{10}NS_2$: 232.0254; found: 232.0250.

Synthesis of 7-methyl-2-phenyl-4H-benzo[d][1,3]thiazine (5ba); new compound

According to the general procedure, reactions between 2-amino-4-methylbenzyl alcohol **1b** (1.0 mmol, 137 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-methyl-2-phenyl-4H-benzo[d][1,3]thiazine **5ba** in 92% (220 mg) yield as white solid.


8.172
8.154
7.518
7.497
7.478
7.462
7.307
7.103
7.084
7.066
7.046
3.983
2.416
1.290
S
N
10
9
8
7
6
5
4
3
2
1
ppm
1.74
2.92
0.90
1.89
2.07
3.00


160.869
144.274
138.270
138.099
131.414
128.446
128.307
128.152
127.672
126.633
116.601
77.376
77.058
76.740
28.358
21.076
S
N
200
180
160
140
120
100
80
60
40
20
ppm

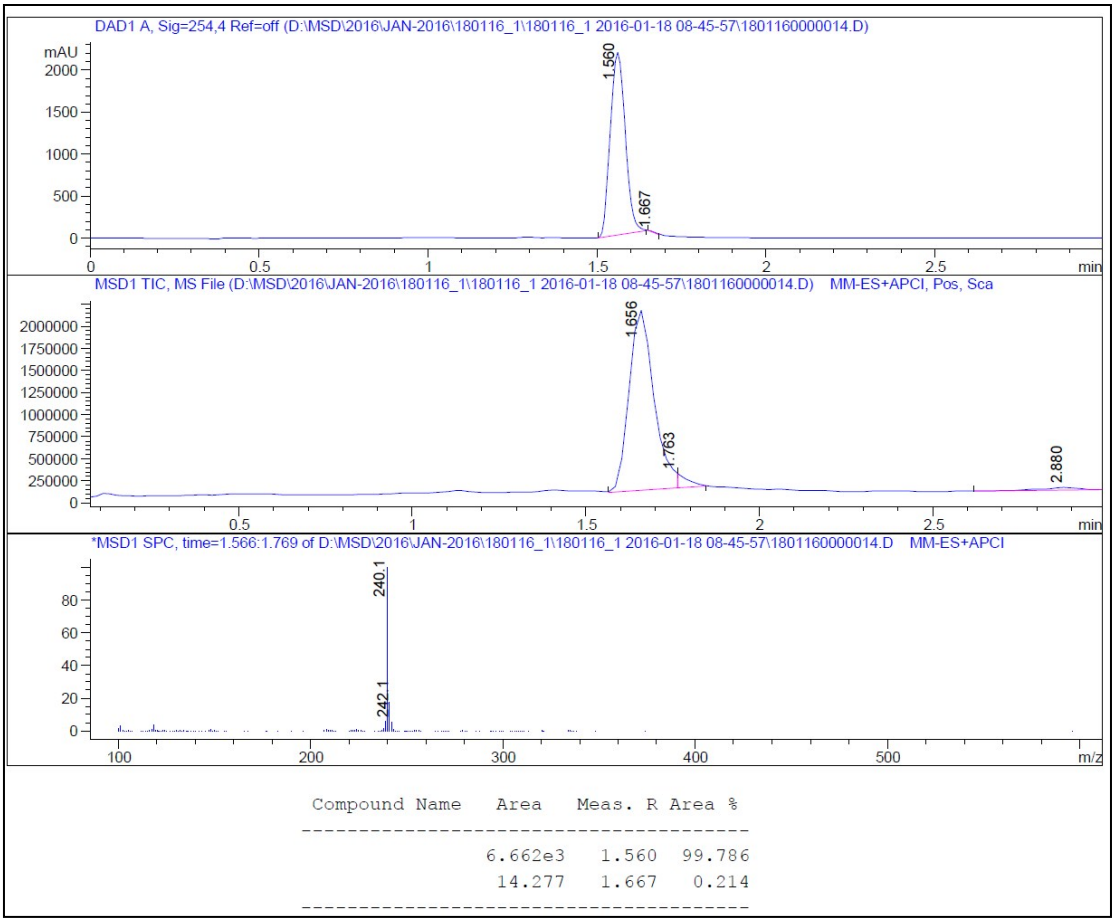
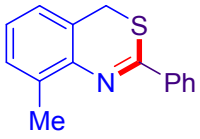


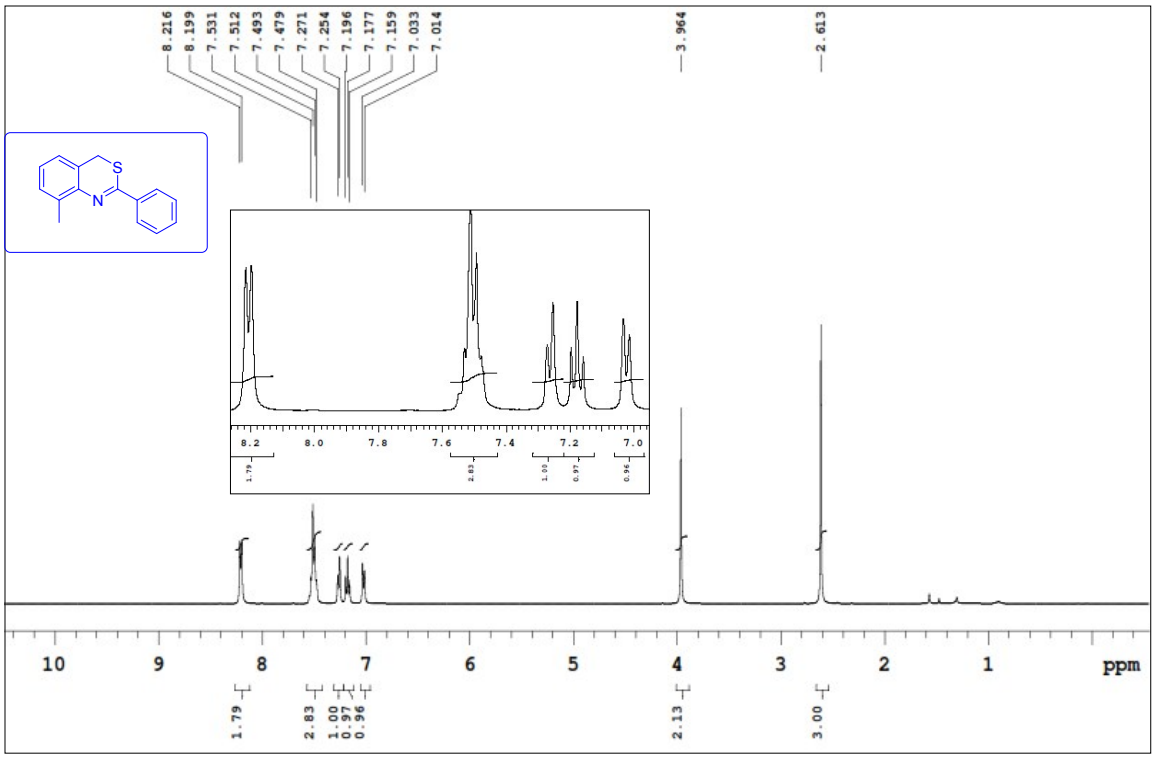
Figure 39. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ba** in $CDCl_3$ and LC-MS in Acetonitrile.

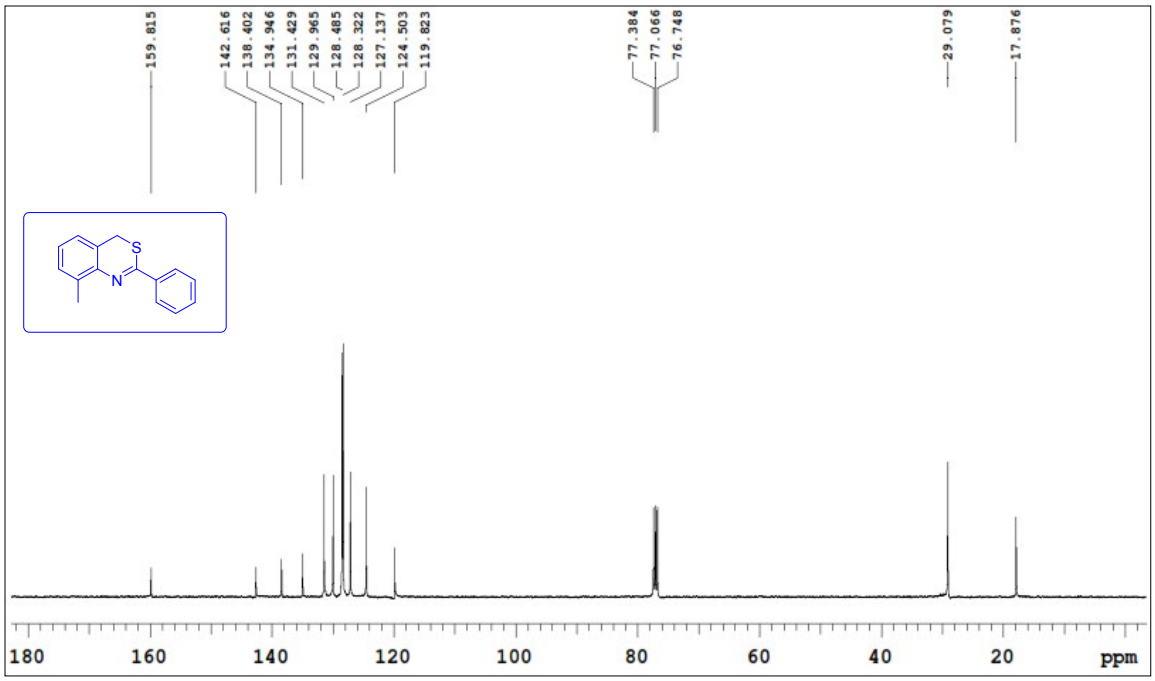
White solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 100 - 101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 6.8 Hz, 2H), 7.51 - 7.46 (m, 3H), 7.30 (s, 1H), 7.10 - 7.04 (m, 1H), 3.98 (s, 2H), 2.41 (s, 3H) ppm; **^{13}C NMR** (100 MHz $CDCl_3$) δ = 160.8, 144.2, 138.2, 138.0, 131.4, 128.4, 128.3, 128.1, 127.6, 126.6, 116.6, 28.3, 21.0 ppm; **MS** (APCI): $[M + 1]^+$ = 240.1 (99.78%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NS$: 240.0846; found: 240.0845.

Synthesis of 8-methyl-2-phenyl-4H-benzo[d][1,3]thiazine (5ca); new compound



According to the general procedure, reactions between 2-amino-3-methylbenzyl alcohol **1c** (1.0 mmol, 137 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 8-methyl-2-phenyl-4H-benzo[d][1,3]thiazine **5ca** in 90% (215 mg) yield as off-white solid.


8.216
8.199
7.531
7.512
7.493
7.479
7.271
7.254
7.196
7.177
7.159
7.033
7.014
3.964
2.613
S
N
8.2
8.0
7.8
7.6
7.4
7.2
7.0
10
9
8
7
6
5
4
3
2
1
ppm
1.79
2.83
1.00
0.97
0.96
2.13
3.00


159.815
142.616
138.402
134.946
131.429
129.965
128.485
128.322
127.137
124.503
119.823
77.384
77.066
76.748
29.079
17.876
S
N
180
160
140
120
100
80
60
40
20
ppm

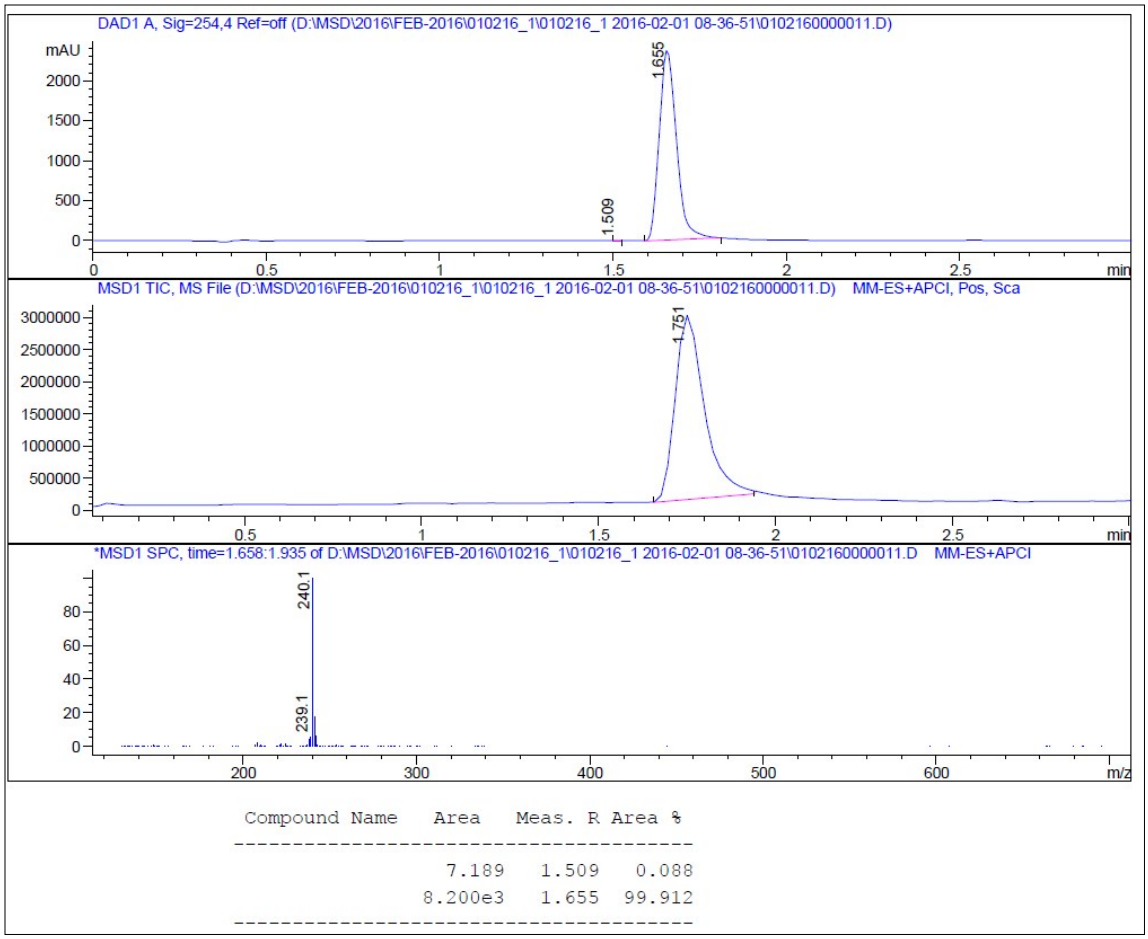
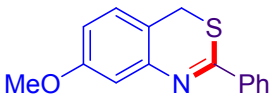


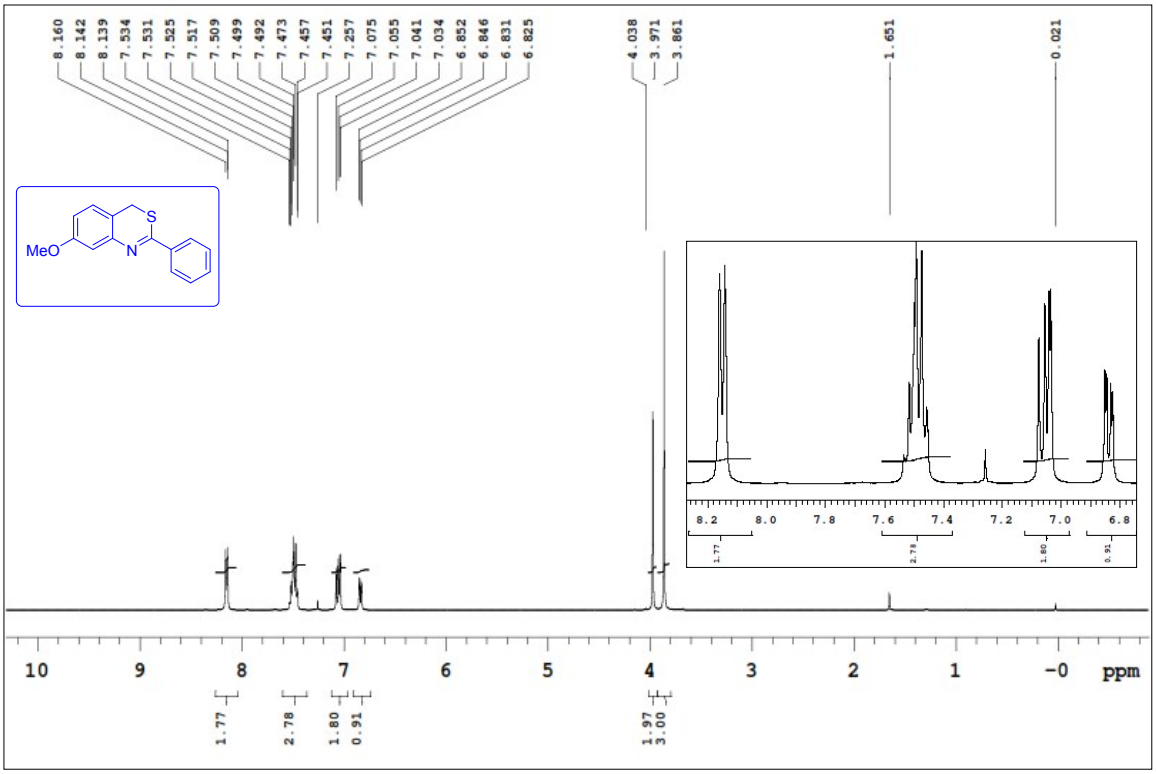
Figure 40. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ca** in $CDCl_3$ and LC-MS in Acetonitrile.

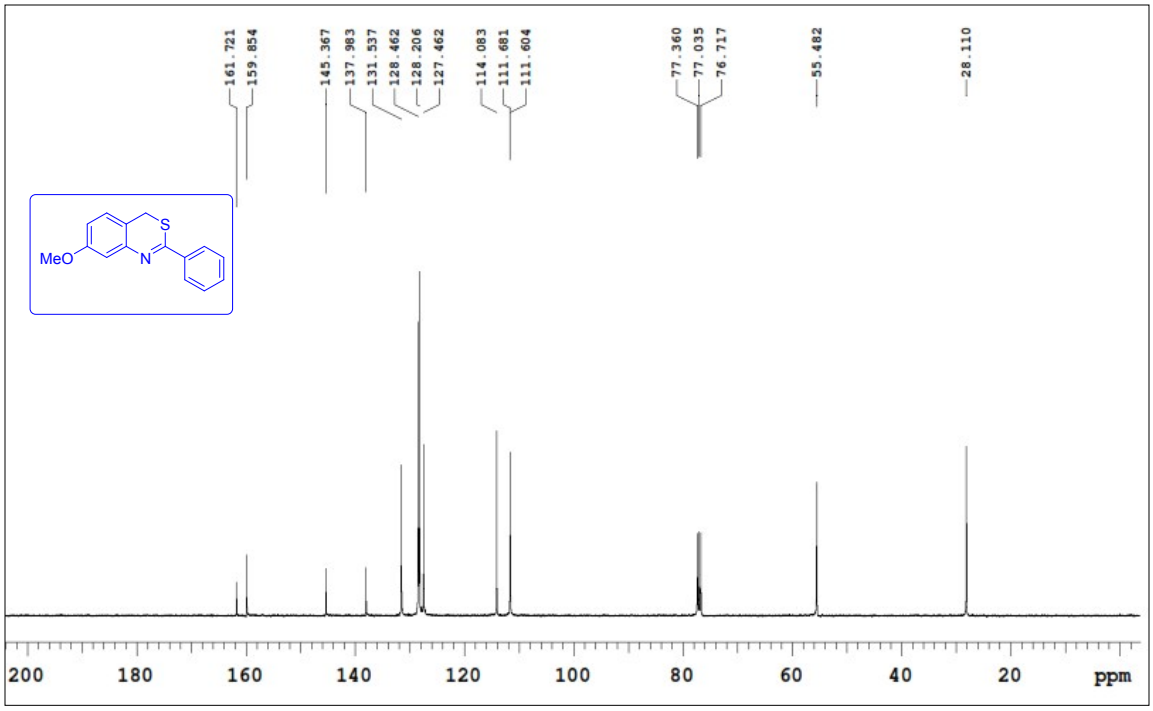
Off-white solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 86 - 87 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 6.8 Hz, 2H), 7.54 - 7.47 (m, 3H), 7.26 (t, *J* = 6.8 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 2H), 2.61 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.8, 142.6, 138.4, 134.9, 131.4, 129.9, 128.4, 128.3, 127.1, 124.5, 119.8, 29.0, 17.8 ppm; **MS** (APCI): $[M + 1]^+$ = 240.1 (99.91); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NS$: 240.0846; found: 240.0845.

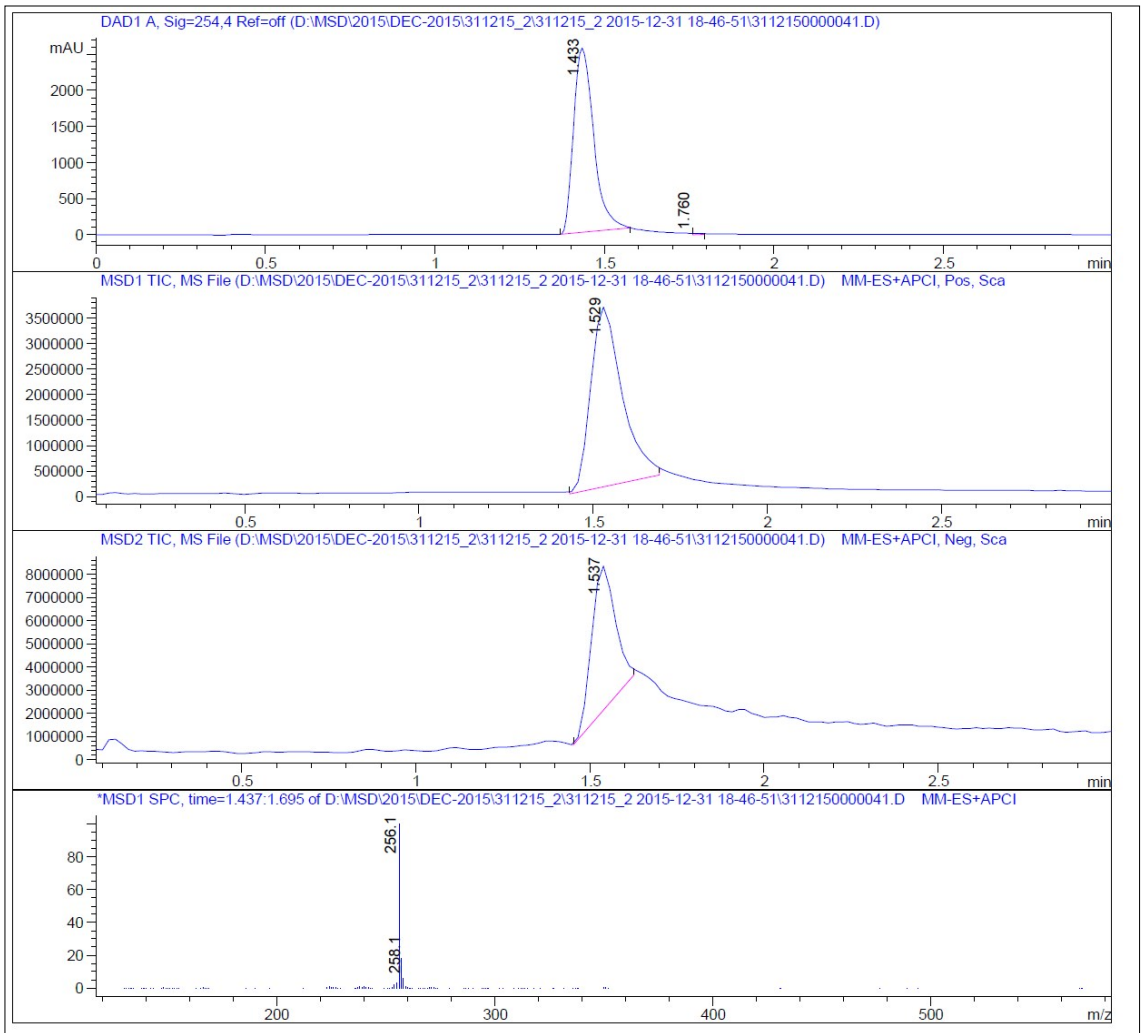
Synthesis of 7-methoxy-2-phenyl-4H-benzo[d][1,3]thiazine (5da); new compound



According to the general procedure, reactions between 2-amino-4-methoxybenzyl alcohol **1d** (1.0 mmol, 153 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-methoxy-2-phenyl-4H-benzo[d][1,3]thiazine **5da** in 92% (235 mg) yield as off-white solid.


8.160
8.142
8.139
7.534
7.531
7.525
7.517
7.509
7.499
7.492
7.473
7.457
7.451
7.257
7.075
7.055
7.041
7.034
6.852
6.846
6.831
6.825
4.038
3.971
3.861
1.651
0.021
MeO
S
N
10
9
8
7
6
5
4
3
2
1
−0
ppm
1.77
2.78
1.80
0.91
1.97
3.00


161.721
159.854
145.367
137.983
131.537
128.462
128.206
127.462
114.083
111.681
111.604
77.360
77.035
76.717
55.482
28.110
MeO
S
N
200
180
160
140
120
100
80
60
40
20
ppm



Compound Name	Area	Meas. R	Area %
	1.056e4	1.433	99.754
	26.049	1.760	0.246

Compound Name	Area	Meas. R	Area %
	2.216e7	1.529	100.000

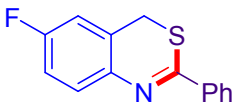
Compound Name	Area	Meas. R	Area %
	2.960e7	1.537	100.000

Figure 41. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5da** in $CDCl_3$ and LC-MS in Acetonitrile.

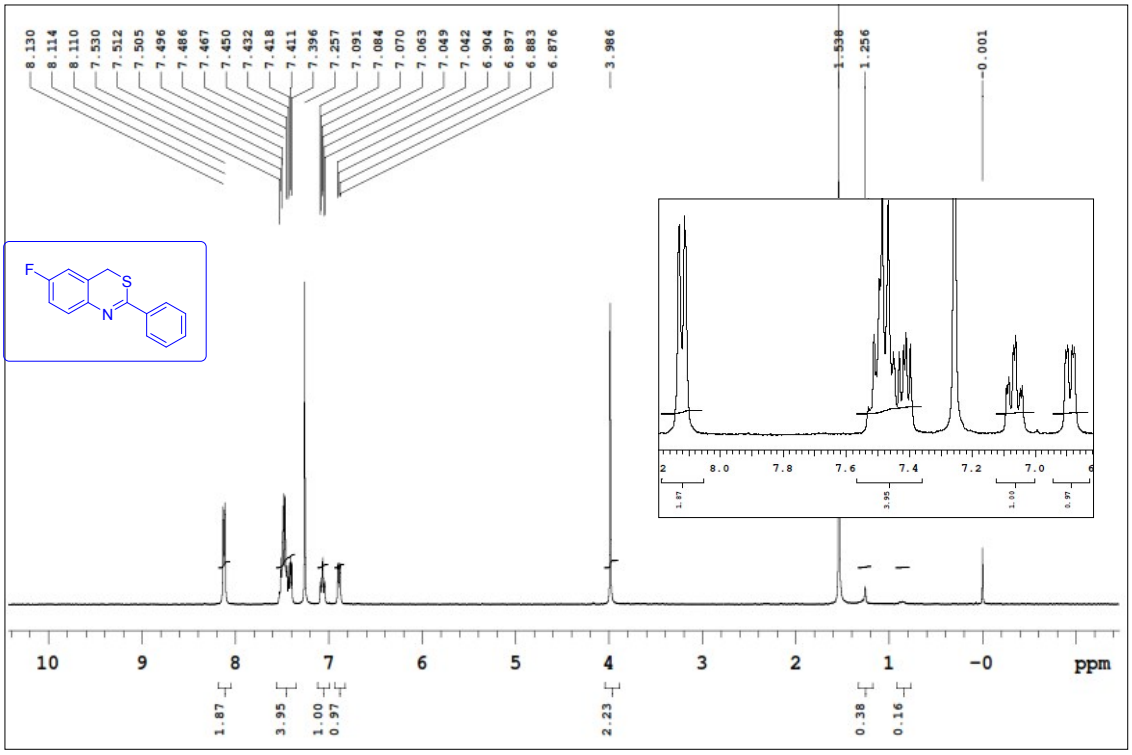
Off-white solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 93 - 94 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 7.2 Hz, 2H), 7.53 - 7.45 (m, 3H), 7.07 - 7.03 (m, 2H), 6.84 (dd, *J* =

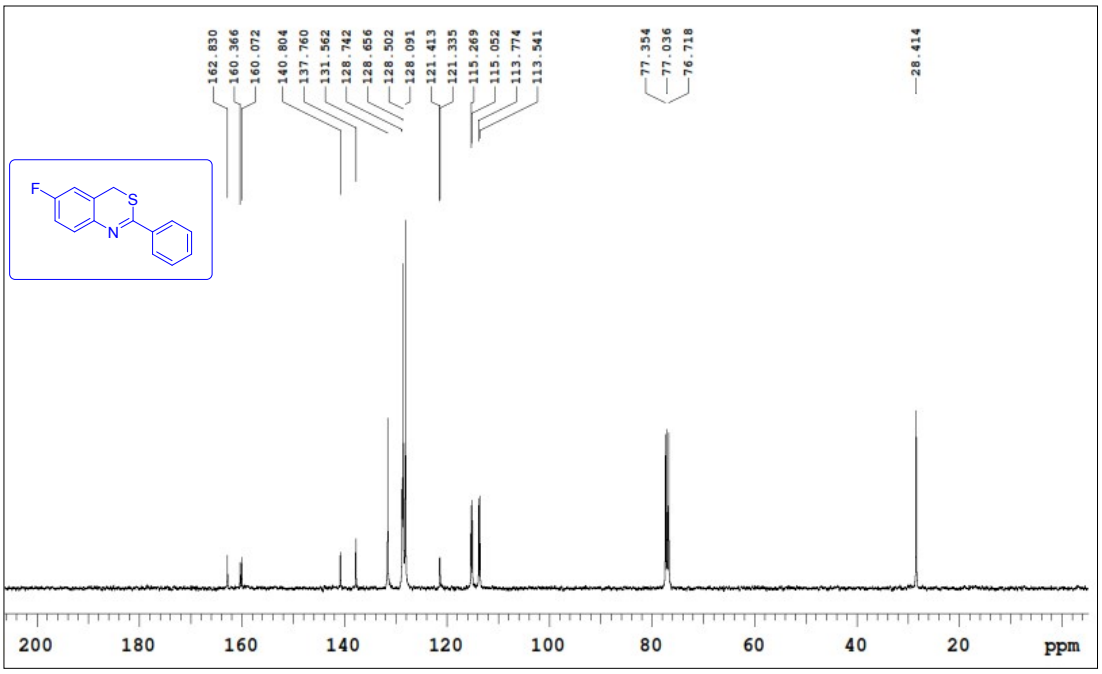
8.4, 2.4 Hz, 1H), 3.97 (s, 2H), 3.86 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.7, 159.8, 137.9, 131.5, 128.4, 128.2, 127.4, 114.0, 111.6, 111.6, 55.4, 28.1 ppm; **MS** (APCI): $[M + 1]^+$ = 256.1 (99.75%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{14}NOS$: 256.0796; found: 256.0794.

Synthesis of 6-fluoro-2-phenyl-4H-benzo[d][1,3]thiazine (5ea); new compound



According to the general procedure, reactions between 2-amino-5-fluorobenzyl alcohol **1e** (1.0 mmol, 141 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 6-fluoro-2-phenyl-4H-benzo[d][1,3]thiazine **5ea** in 95% (231 mg) yield as white solid.




162.830
160.366
160.072
140.804
137.760
131.562
128.742
128.656
128.502
128.091
121.413
121.335
115.269
115.052
113.774
113.541
77.354
77.036
76.718
28.414
F
S
N
200
180
160
140
120
100
80
60
40
20
ppm

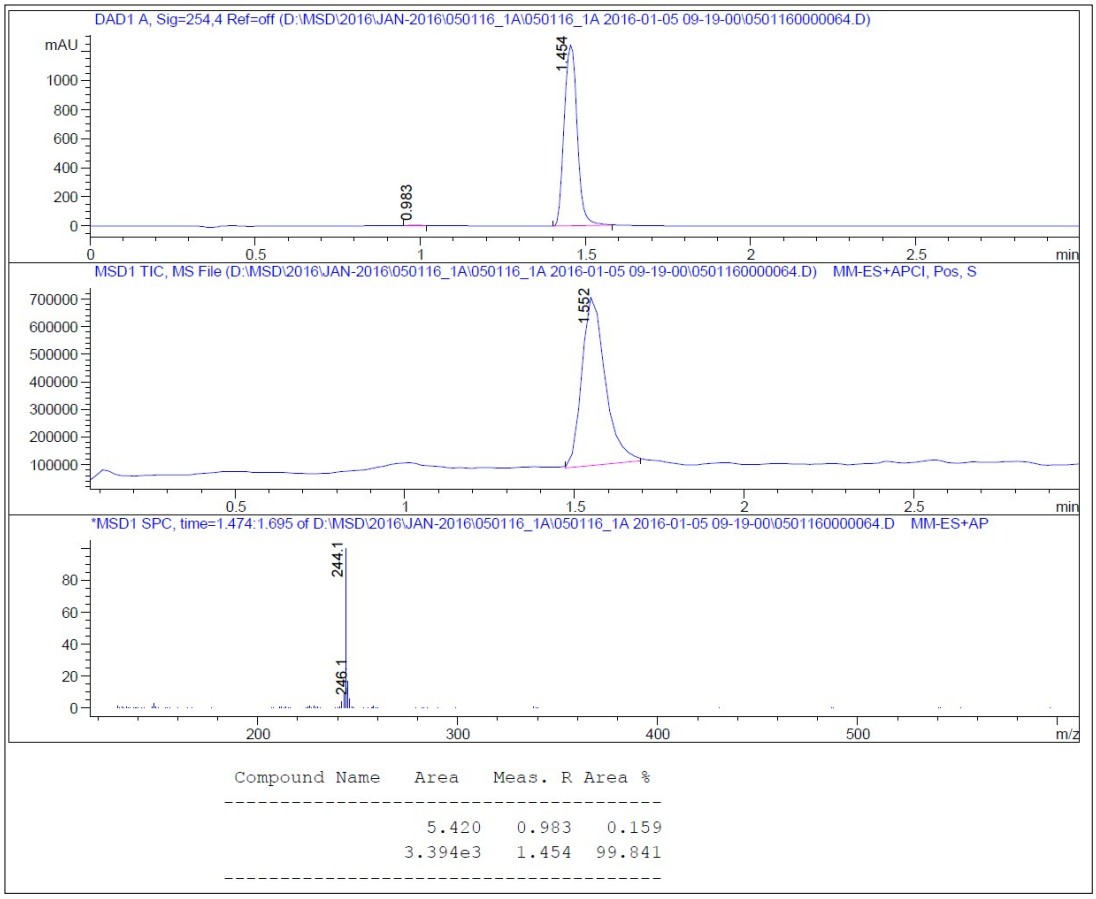
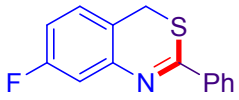


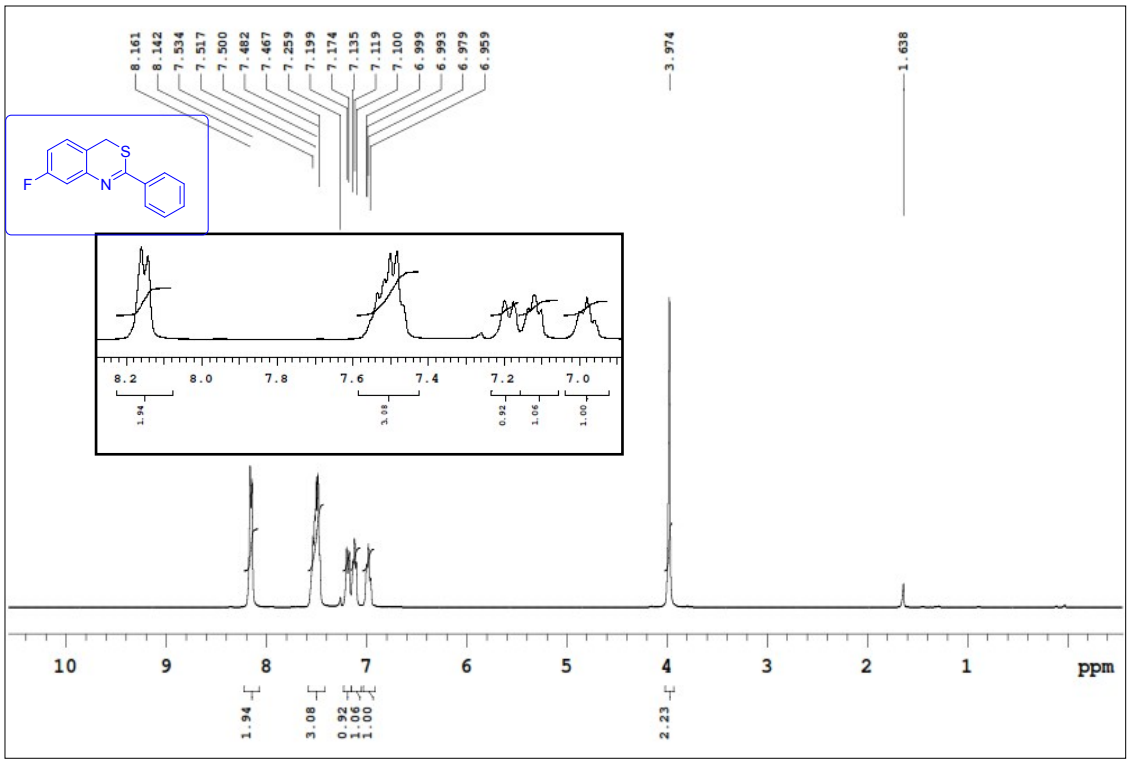
Figure 42. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ea** in DMSO-d_6 and LC-MS in Acetonitrile.

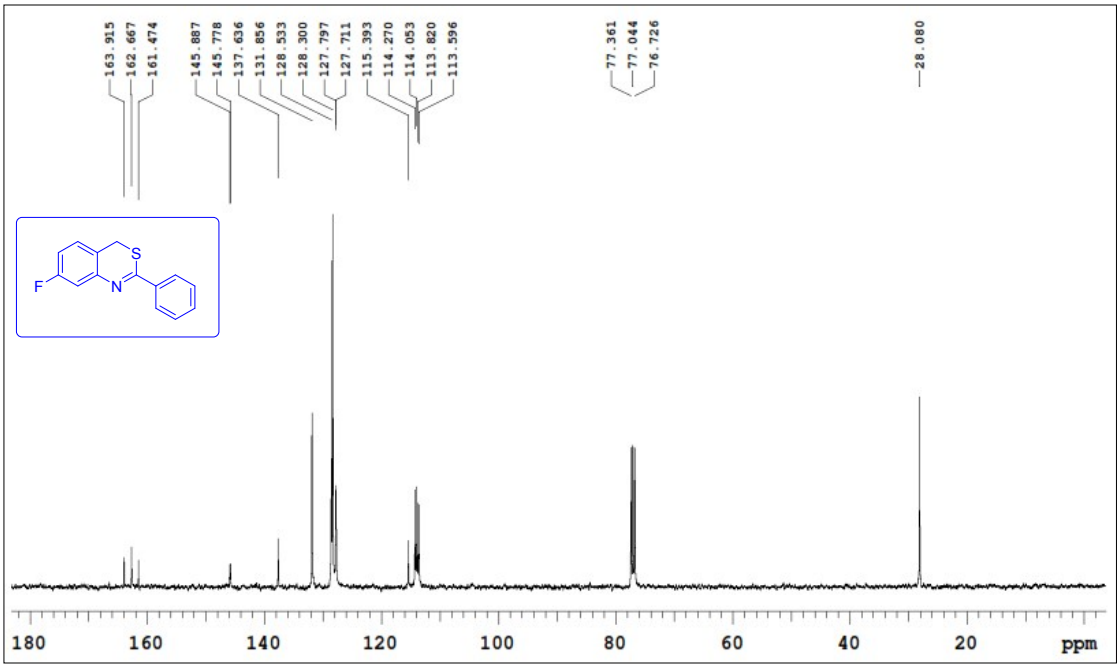
White solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 84 - 85 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 8.12 (d, J = 8.0 Hz, 2H), 7.53 - 7.39 (m, 4H), 7.07 (dt, J = 8.4, 2.4 Hz, 1H), 6.89 (dd, J = 8.4, 2.4 Hz, 1H), 3.98 (s, 2H) ppm; **^{13}C NMR** (100 MHz, DMSO-d_6) δ = 161.5 (d, J = 247.5 Hz), 160.0, 140.8, 137.7, 131.5, 128.7, 128.6, 128.5, 128.0, 121.4, 121.3, 115.2, 115.0, 113.7, 113.5, 28.4 ppm; **MS** (APCI): $[M + 1]^+$ = 244.1 (99.84%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNS$: 244.0596; found: 244.0595.

Synthesis of 7-fluoro-2-phenyl-4H-benzo[d][1,3]thiazine (5fa); new compound



According to the general procedure, reactions between 2-amino-4-fluorobenzyl alcohol **1f** (1.0 mmol, 141 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-fluoro-2-phenyl-4H-benzo[d][1,3]thiazine **5fa** in 92% (224 mg) yield as white solid.


8.161
8.142
7.534
7.517
7.500
7.482
7.467
7.259
7.199
7.174
7.135
7.119
7.100
6.999
6.993
6.979
6.959
3.974
1.638
F
S
N
8.2
8.0
7.8
7.6
7.4
7.2
7.0
1.94
3.08
0.92
1.06
1.00
10
9
8
7
6
5
4
3
2
1
ppm
1.94
3.08
0.92
1.06
1.00
2.23


163.915
162.667
161.474
145.887
145.778
137.636
131.856
128.533
128.300
127.797
127.711
115.393
114.270
114.053
113.820
113.596
77.361
77.044
76.726
28.080
F
S
N
180
160
140
120
100
80
60
40
20
ppm

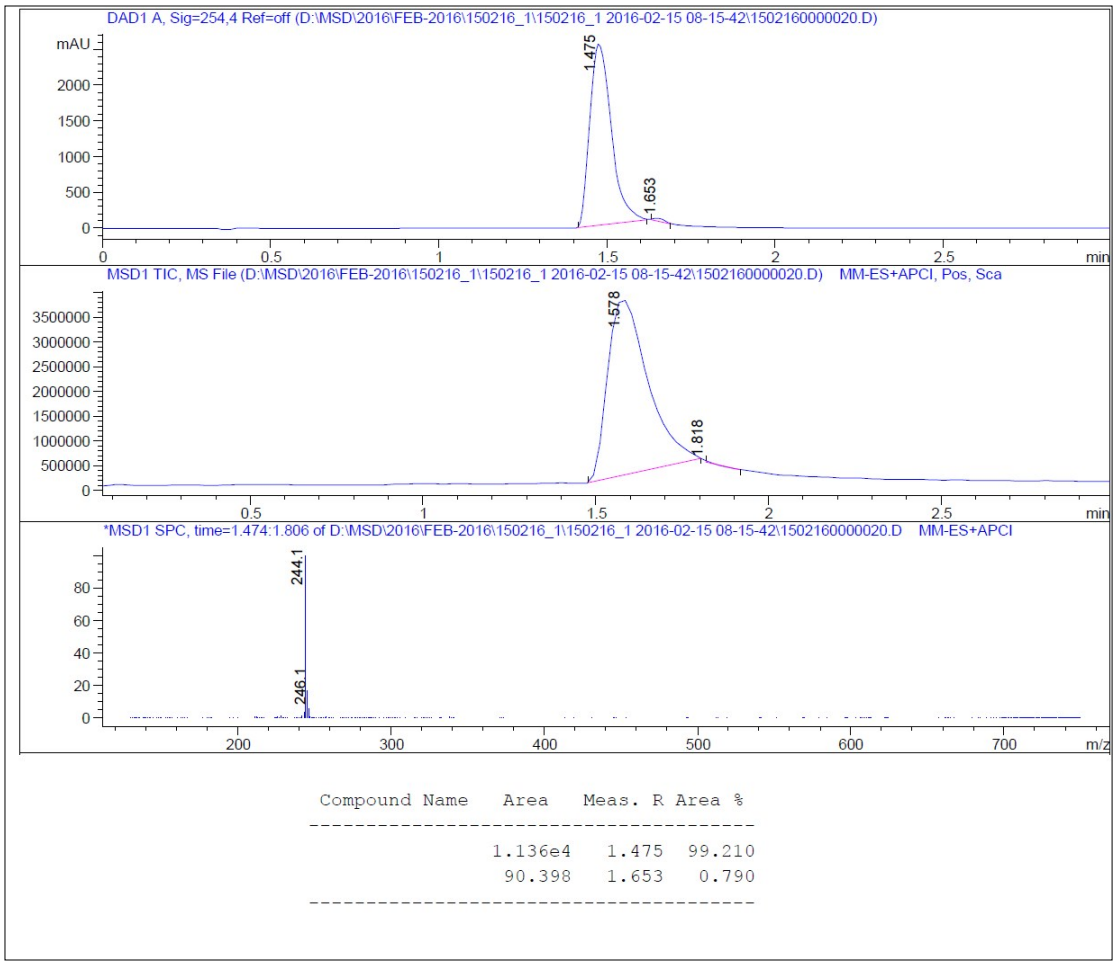
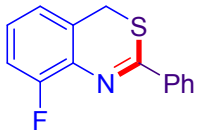


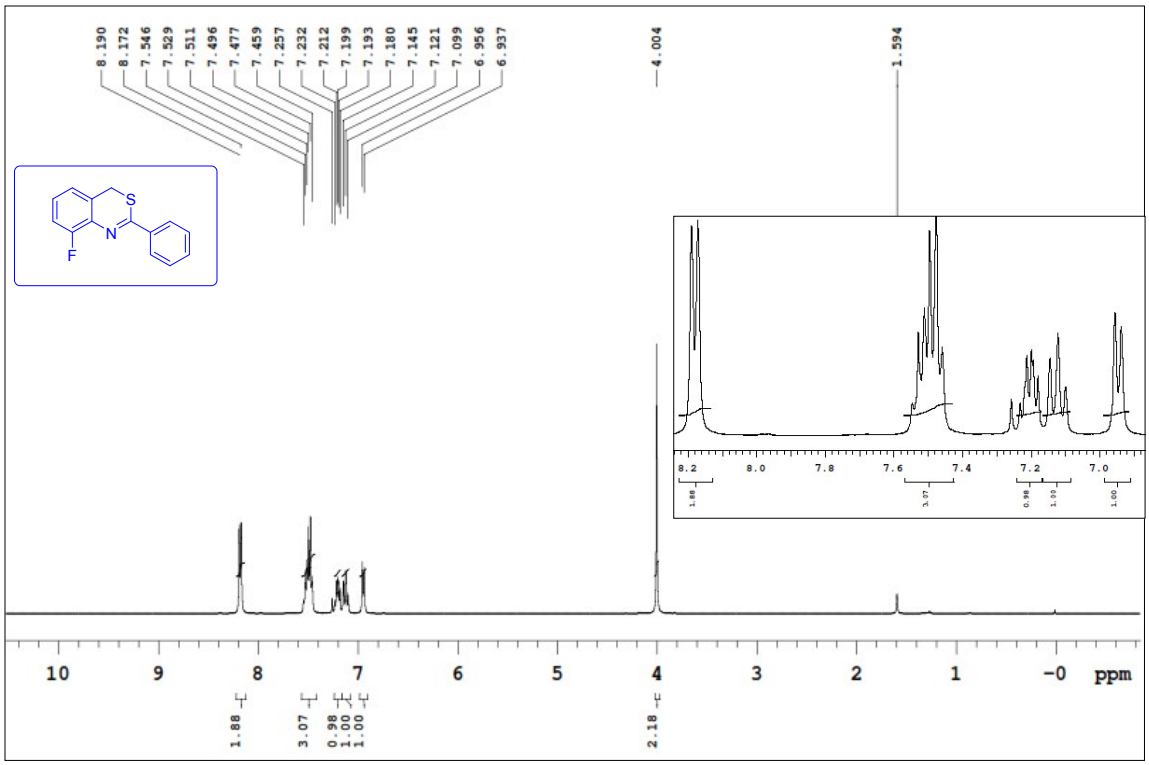
Figure 43. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5fa** in $CDCl_3$ and LC-MS in Acetonitrile.

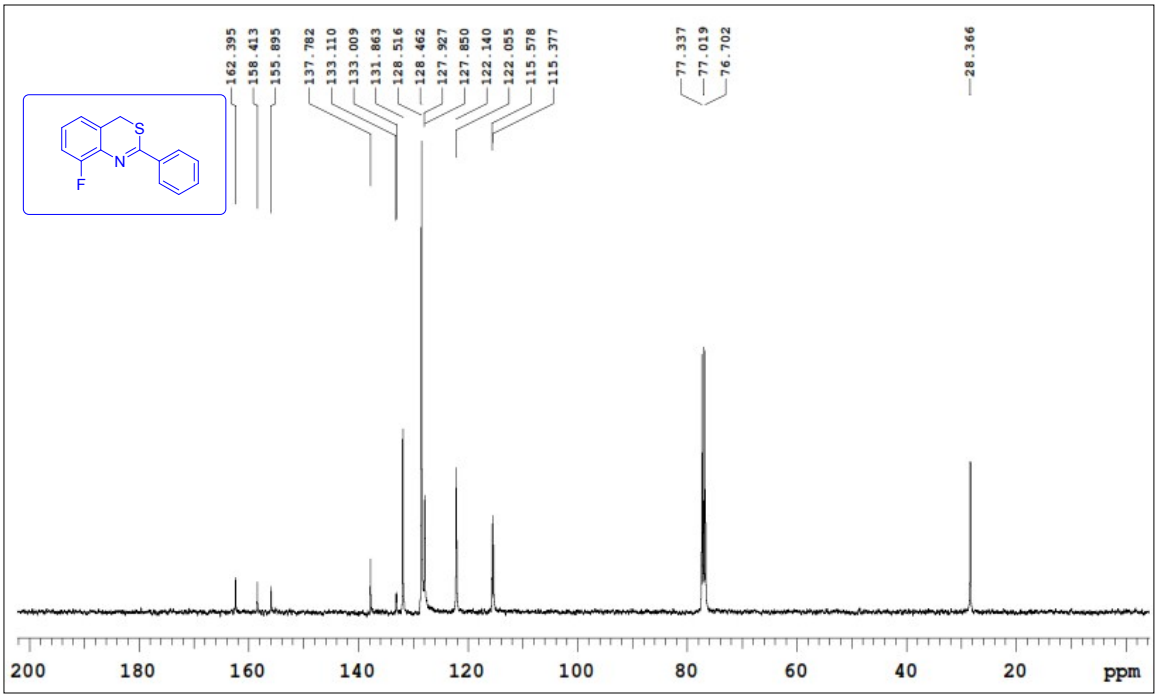
White solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 71 - 72 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 7.6 Hz, 2H), 7.53 - 7.46 (m, 3H), 7.19 - 7.17 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.99 - 6.95 (m, 1H), 3.97 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.69 (d, *J* = 244.5 Hz), 162.66, 145.8, 145.7, 137.6, 131.8, 128.5, 128.3, 127.7, 127.7, 115.3, 114.2, 114.0, 113.8, 113.5, 28.0 ppm; **MS** (APCI): $[M + 1]^+$ = 244.1 (99.21%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNS$: 244.0596; found: 244.0595.

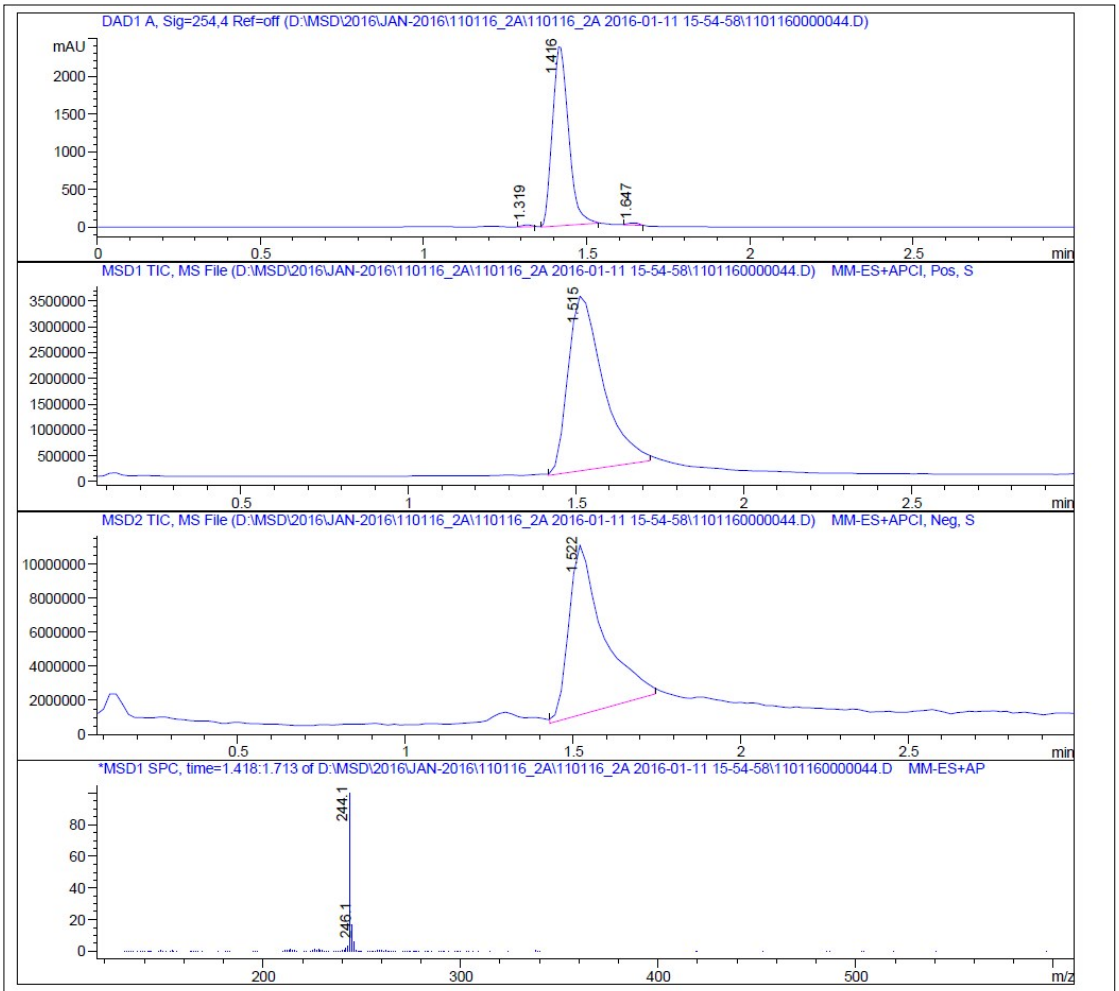
Synthesis of 8-fluoro-2-phenyl-4H-benzo[d][1,3]thiazine (5ga); new compound



According to the general procedure, reactions between 2-amino-3-fluorobenzyl alcohol **1g** (1.0 mmol, 141 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 8-fluoro-2-phenyl-4H-benzo[d][1,3]thiazine **5ga** in 90% (219 mg) yield as off-white solid.


8.190
8.172
7.546
7.529
7.511
7.496
7.477
7.459
7.257
7.232
7.212
7.199
7.193
7.180
7.145
7.121
7.099
6.956
6.937
4.004
1.594
S
N
F
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.88
3.07
0.98
1.00
1.00
2.18


162.395
158.413
155.895
137.782
133.110
133.009
131.863
128.516
128.462
127.927
127.850
122.140
122.055
115.578
115.377
77.337
77.019
76.702
28.366
S
N
F
200
180
160
140
120
100
80
60
40
20
ppm



Compound Name	Area	Meas. R	Area %
	54.828	1.319	0.661
	8.182e3	1.416	98.588
	62.363	1.647	0.751

Compound Name	Area	Meas. R	Area %
	2.457e7	1.515	100.000

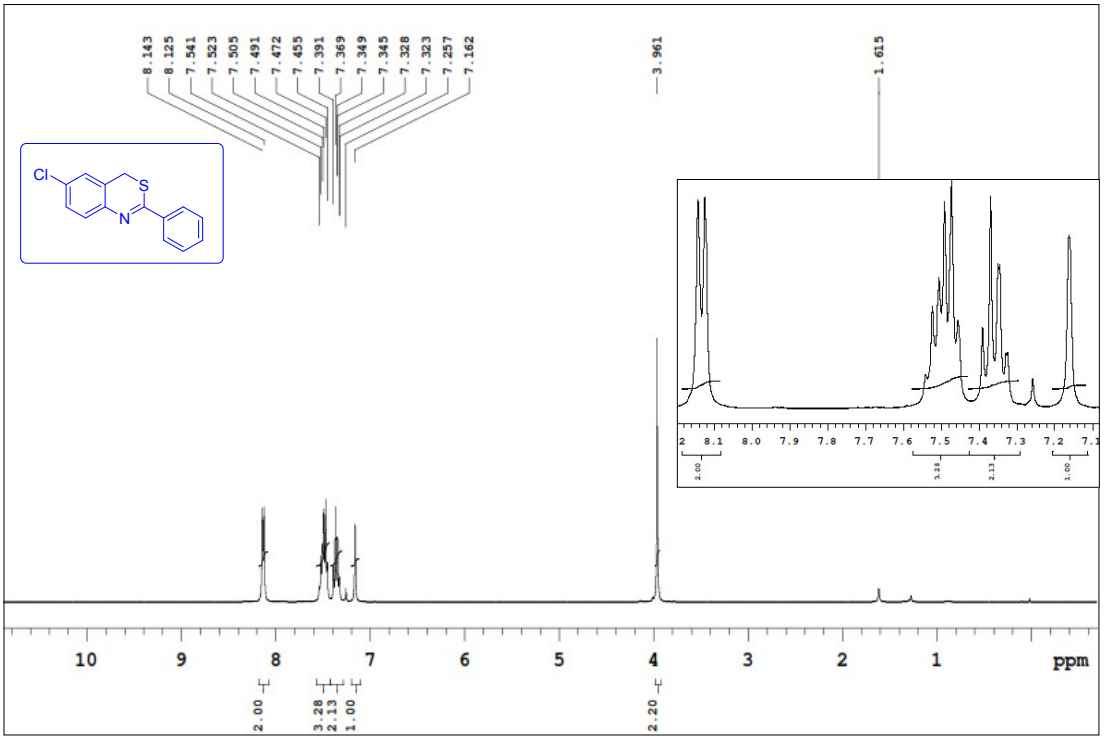
Compound Name	Area	Meas. R	Area %
	7.105e7	1.522	100.000

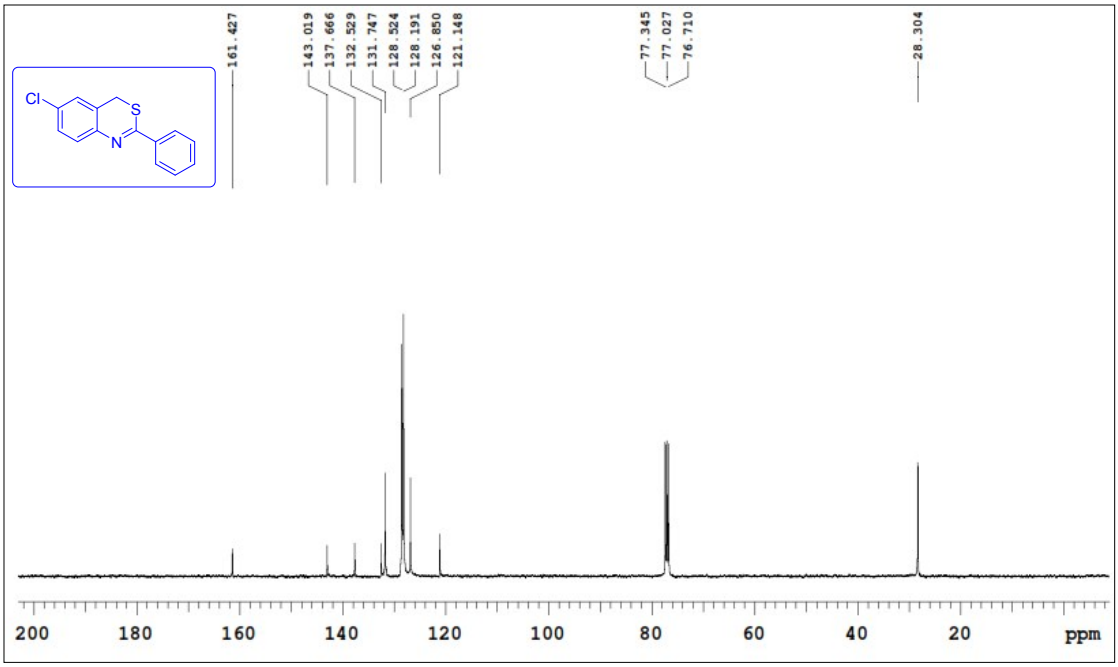
Figure 44. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ga** in $CDCl_3$ and LC-MS in Acetonitrile.

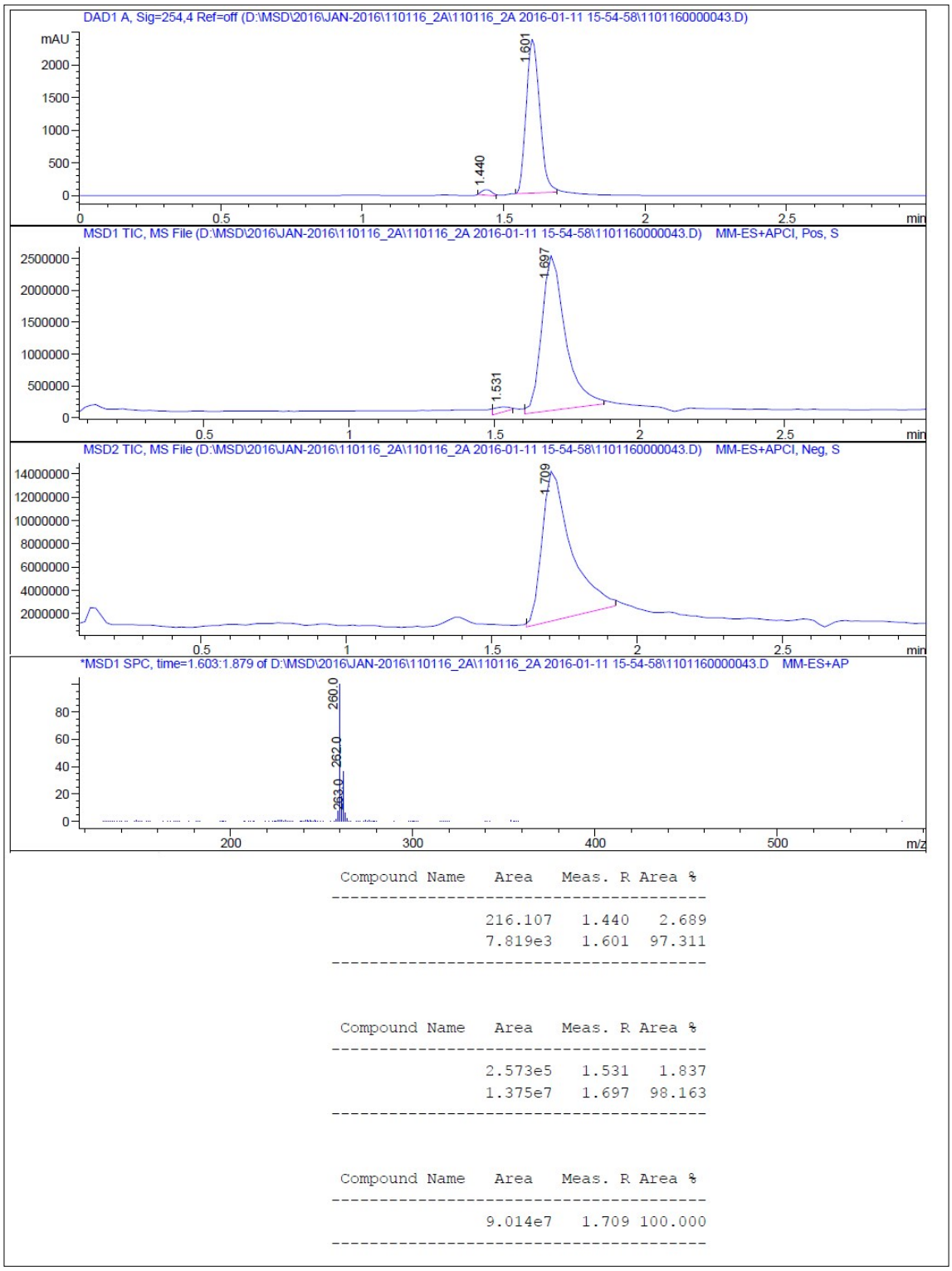
Off-white solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 64 - 66 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.18 (d, *J* = 7.2 Hz, 2H), 7.54 - 7.45 (m, 3H), 7.25 - 7.18 (m, 1H), 7.12 (t, *J* = 9.6 Hz, 1H), 6.94 (d, *J* = 7.6Hz, 1H), 4.00 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.3, 157.1 (d, *J* = 253.5 Hz), 137.7, 133.1, 133.0, 131.8, 128.5, 128.4, 127.9, 127.8, 122.1, 122.0, 115.5, 115.3, 28.3 ppm; **MS** (APCI): $[M + 1]^+$ = 244.1 (98.58%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}FNS$: 244.0596; found: 244.0595.

Synthesis of 6-chloro-2-phenyl-4H-benzo[d][1,3]thiazine (5ha); new compound

According to the general procedure, reactions between 2-amino-5-chlorobenzyl alcohol **1h** (1.0 mmol, 158 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 6-chloro-2-phenyl-4H-benzo[d][1,3]thiazine **5ha** in 90% (234 mg) yield as white solid.




161.427
143.019
137.666
132.529
131.747
128.524
128.191
126.850
121.148
77.345
77.027
76.710
28.304
Cl
S
N
200
180
160
140
120
100
80
60
40
20
ppm



Compound Name	Area	Meas. R	Area %
	216.107	1.440	2.689
	7.819e3	1.601	97.311

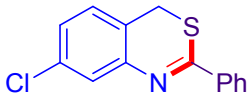
Compound Name	Area	Meas. R	Area %
	2.573e5	1.531	1.837
	1.375e7	1.697	98.163

Compound Name	Area	Meas. R	Area %
	9.014e7	1.709	100.000

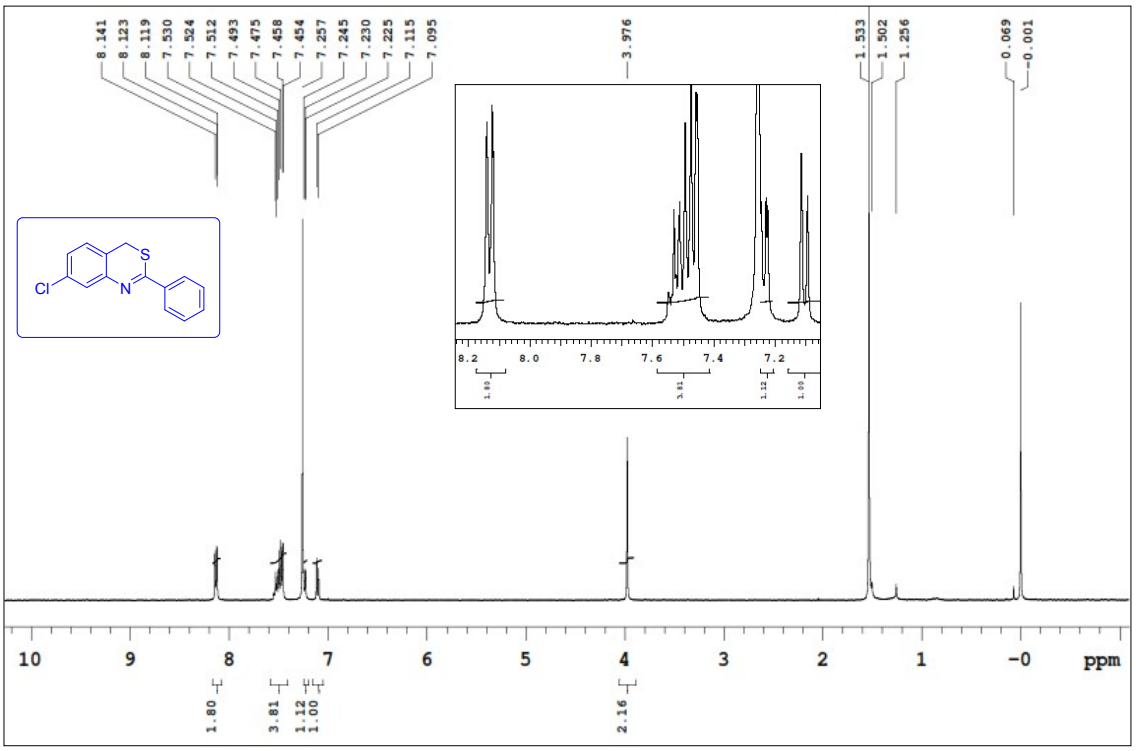
Figure 45. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ha** in $CDCl_3$ and LC-MS in Acetonitrile.

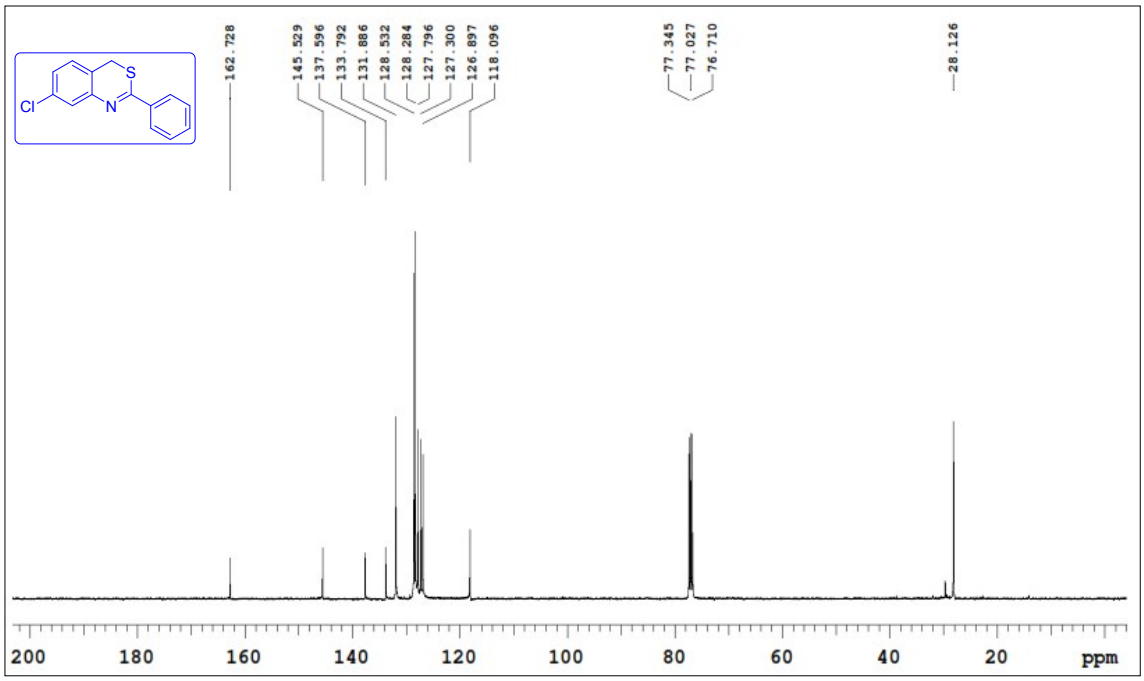
White solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 104 - 108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.2 Hz, 2H), 7.54 - 7.45 (m, 3H), 7.39 - 7.32 (m, 2H), 7.16 (s, 1H), 3.96 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.4, 143.0, 137.6, 132.5, 131.7, 128.5, 128.1, 126.8, 121.1, 28.3 ppm; **MS** (APCI): $[M + 1]^+$ = 260.0 (97.31%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}ClNS$: 260.0300; found: 260.0302.

Synthesis of 7-chloro-2-phenyl-4H-benzo[d][1,3]thiazine (5ia); new compound



According to the general procedure, reactions between 2-amino-4-chlorobenzyl alcohol **1i** (1.0 mmol, 158 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-chloro-2-phenyl-4H-benzo[d][1,3]thiazine **5ia** in 96% (250 mg) yield as off-white solid.




Cl
S
N
162.728
145.529
137.596
133.792
131.886
128.532
128.284
127.796
127.300
126.897
118.096
77.345
77.027
76.710
28.126
200
180
160
140
120
100
80
60
40
20
ppm

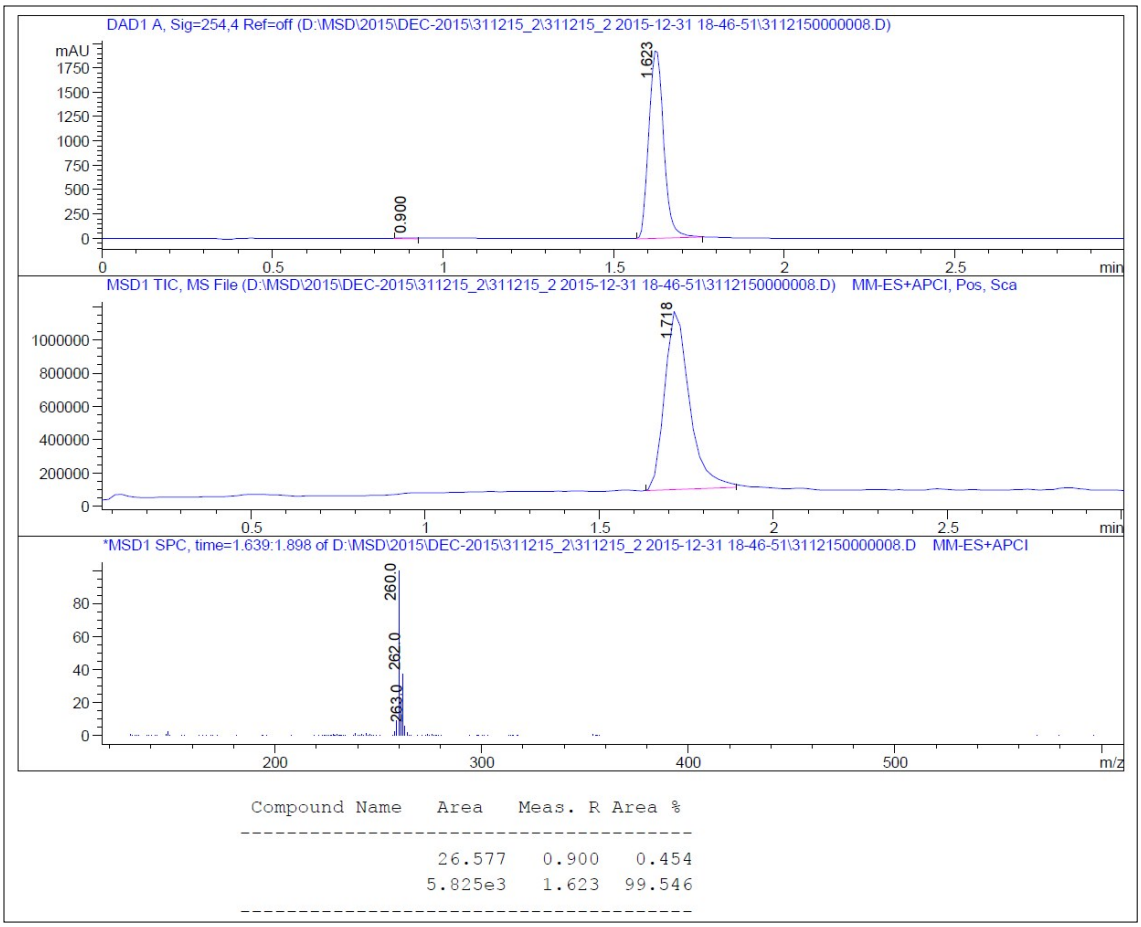
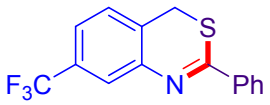


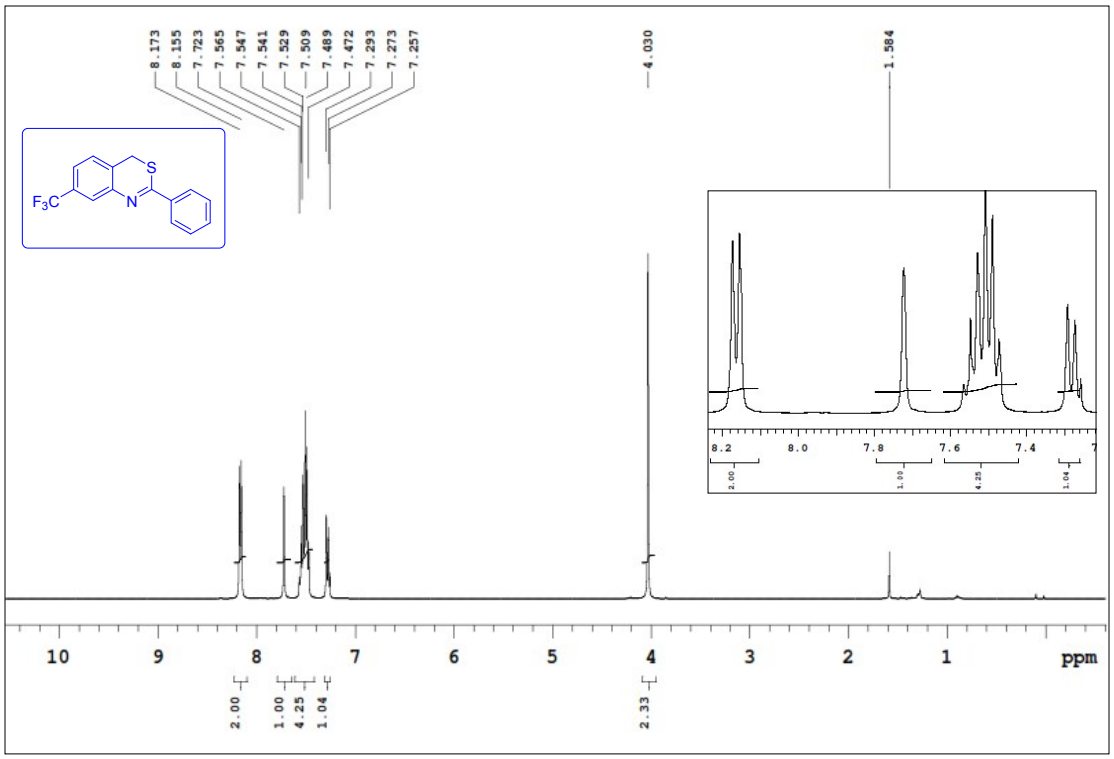
Figure 46. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ia** in $CDCl_3$ and LC-MS in Acetonitrile.

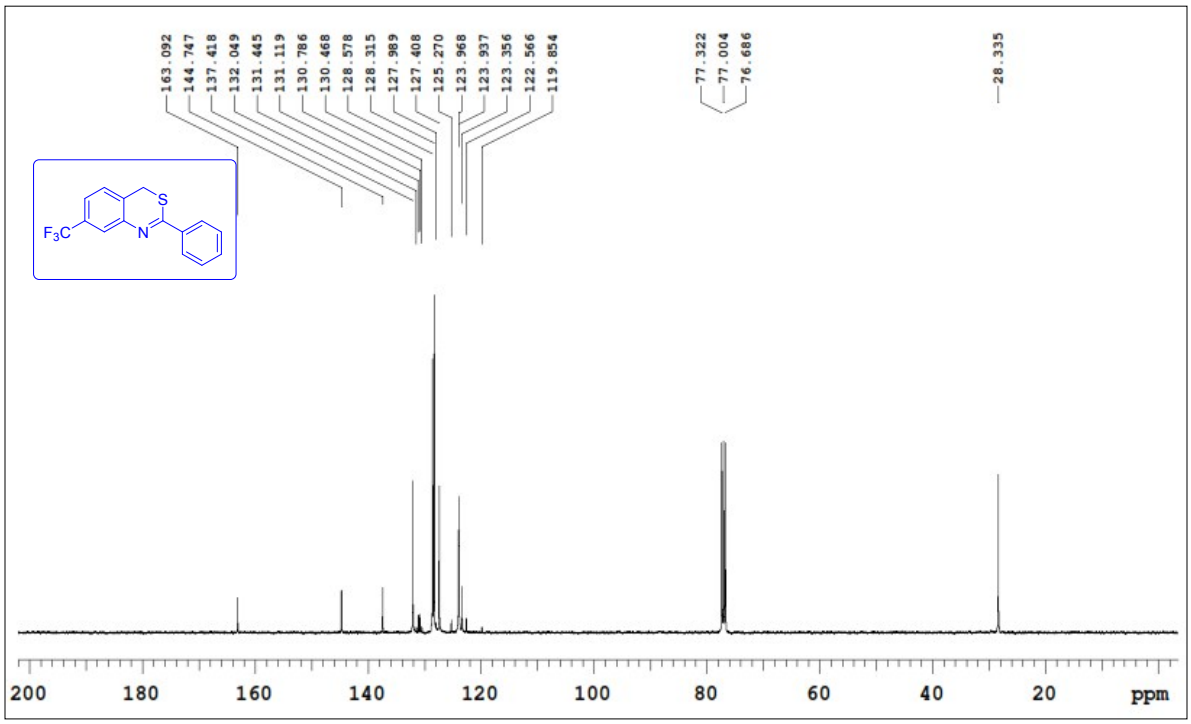
Off-white solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 105 - 106 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.2 Hz, 2H), 7.54 - 7.45 (m, 4H), 7.24 (dd, *J* = 6.0, 8.0 Hz, 1H), 7.10 (d, *J* = 8 Hz, 1H), 3.97 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 162.7, 145.5, 137.5, 133.7, 131.8, 128.5, 128.2, 127.7, 127.3, 126.8, 118.0, 28.1 ppm; **MS** (APCI): $[M + 1]^+$ = 260.0 (99.54%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{11}ClNS$: 260.0300; found: 260.0302.

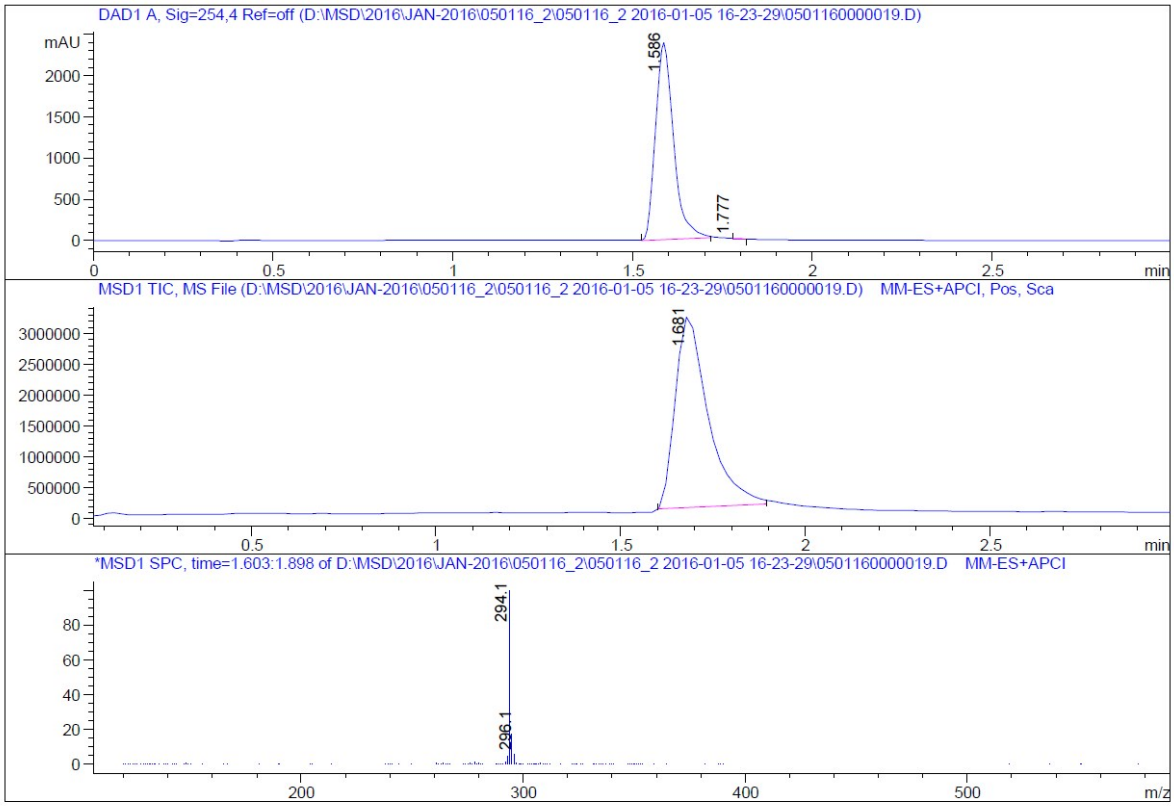
Synthesis of 2-phenyl-7-(trifluoromethyl)-4H-benzo[d][1,3]thiazine (5ja); new compound



According to the general procedure, reactions between (2-amino-4-(trifluoromethyl)benzyl alcohol **1i** (1.0 mmol, 191 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-phenyl-7-(trifluoromethyl)-4H-benzo[d][1,3]thiazine **5ja** in 94% (276 mg) yield as white solid.


8.173
8.155
7.723
7.565
7.547
7.541
7.529
7.509
7.489
7.472
7.293
7.273
7.257
4.030
1.584
F3C
S
N
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.00
4.25
1.04
2.33


163.092
144.747
137.418
132.049
131.445
131.119
130.786
130.468
128.578
128.315
127.989
127.408
125.270
123.968
123.937
123.356
122.566
119.854
77.322
77.004
76.686
28.335
F3C
S
N
200
180
160
140
120
100
80
60
40
20
ppm

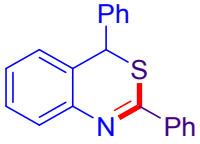


Compound Name	Area	Meas. R	Area %
	8.357e3	1.586	99.854
	12.181	1.777	0.146

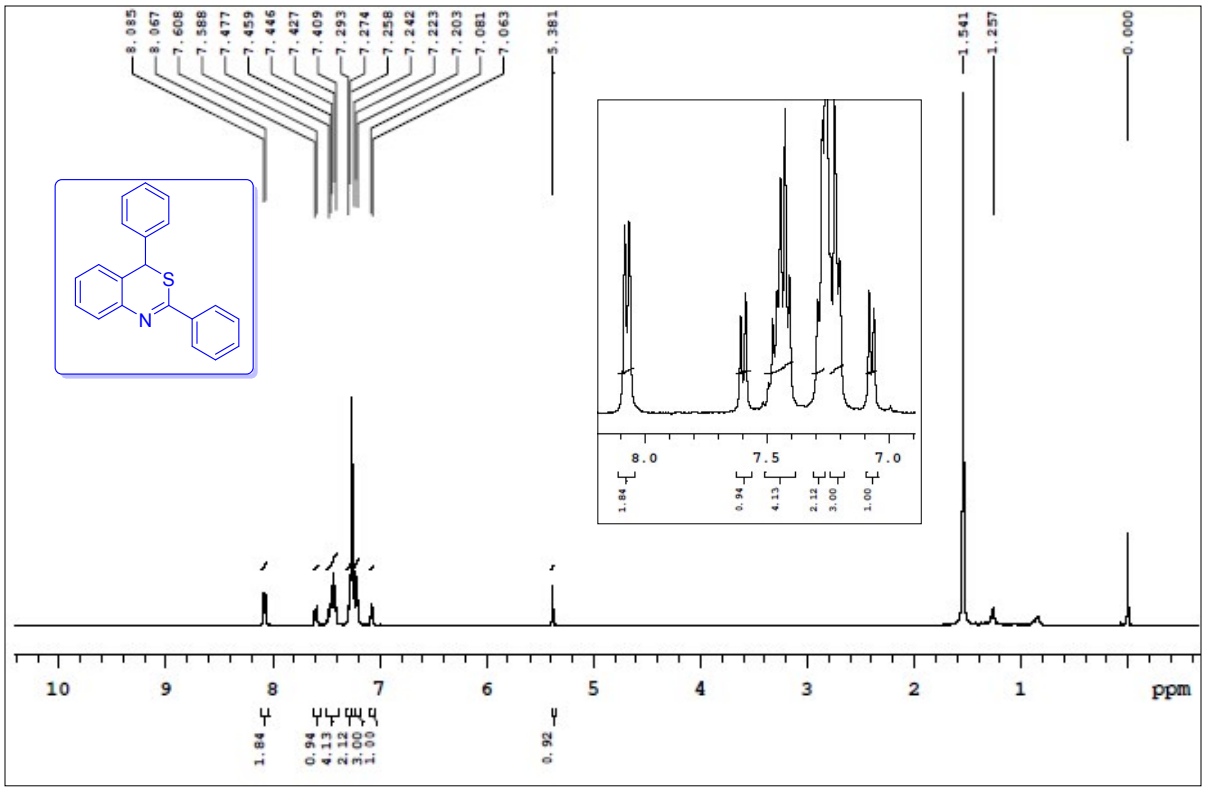
Figure 47. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ja** in $CDCl_3$ and LC-MS in Acetonitrile.

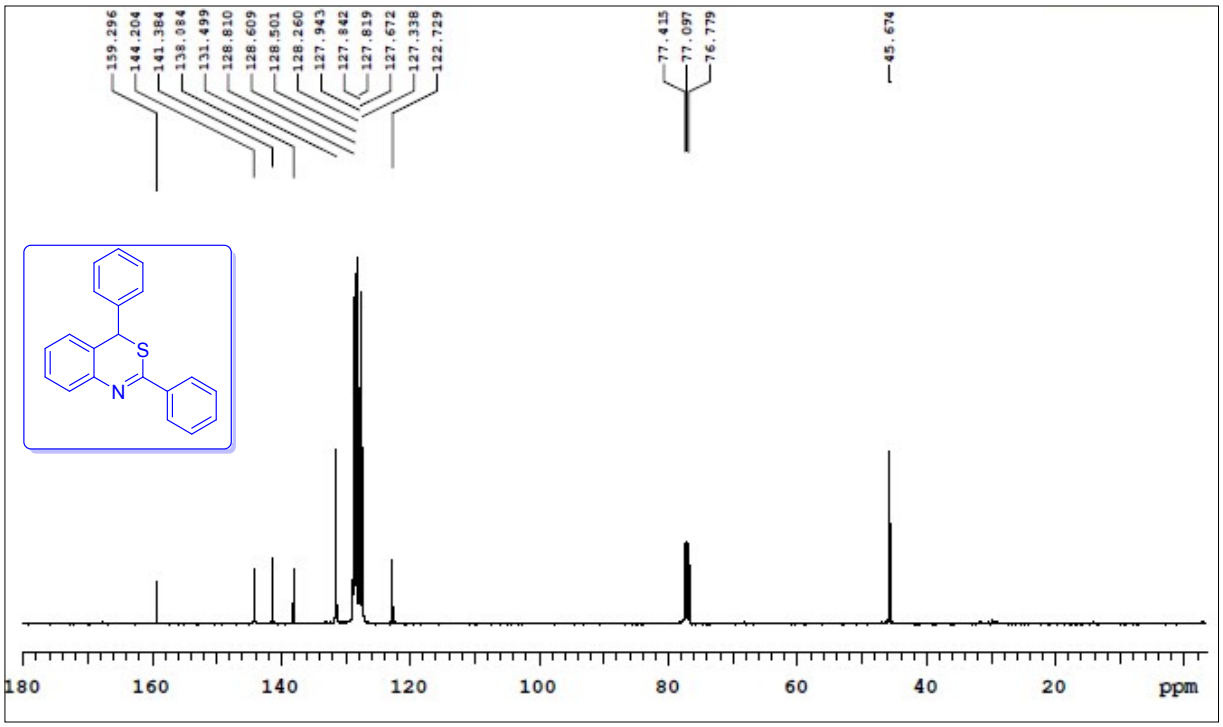
White solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 114 - 115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.72 (s, 1H), 7.56 - 7.47 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 163.0, 144.7, 137.4, 132.0, 130.9 (q, *J* = 32.7 Hz), 128.5, 128.3, 127.4, 123.96, 123.93, 123.92 (q, *J* = 271.6 Hz), 123.3, 28.3 ppm; **MS** (APCI): $[M + 1]^+$ = 294.1 (99.85%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{11}F_3NS$: 294.0564; found: 294.0560.

Synthesis of 2,4-diphenyl-4H-benzo[d][1,3]thiazine (5ka); new compound



According to the general procedure, reactions between 2-aminobenzhydrol **1k** (1.0 mmol, 199 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2,4-diphenyl-4H-benzo[d][1,3]thiazine **5ka** in 92% (277 mg) yield as off-white solid.


8.085
8.067
7.608
7.588
7.477
7.459
7.446
7.427
7.409
7.293
7.274
7.258
7.242
7.223
7.203
7.081
7.063
5.381
1.541
1.257
0.000
S
N
8.0
7.5
7.0
1.84
0.94
4.13
2.12
3.00
1.00
10
9
8
7
6
5
4
3
2
1
ppm
1.84
0.94
4.13
2.12
3.00
1.00
0.92


159.296
144.204
141.384
138.084
131.499
128.810
128.609
128.501
128.260
127.943
127.842
127.819
127.672
127.338
122.729
77.415
77.097
76.779
45.674
S
N
180
160
140
120
100
80
60
40
20
ppm

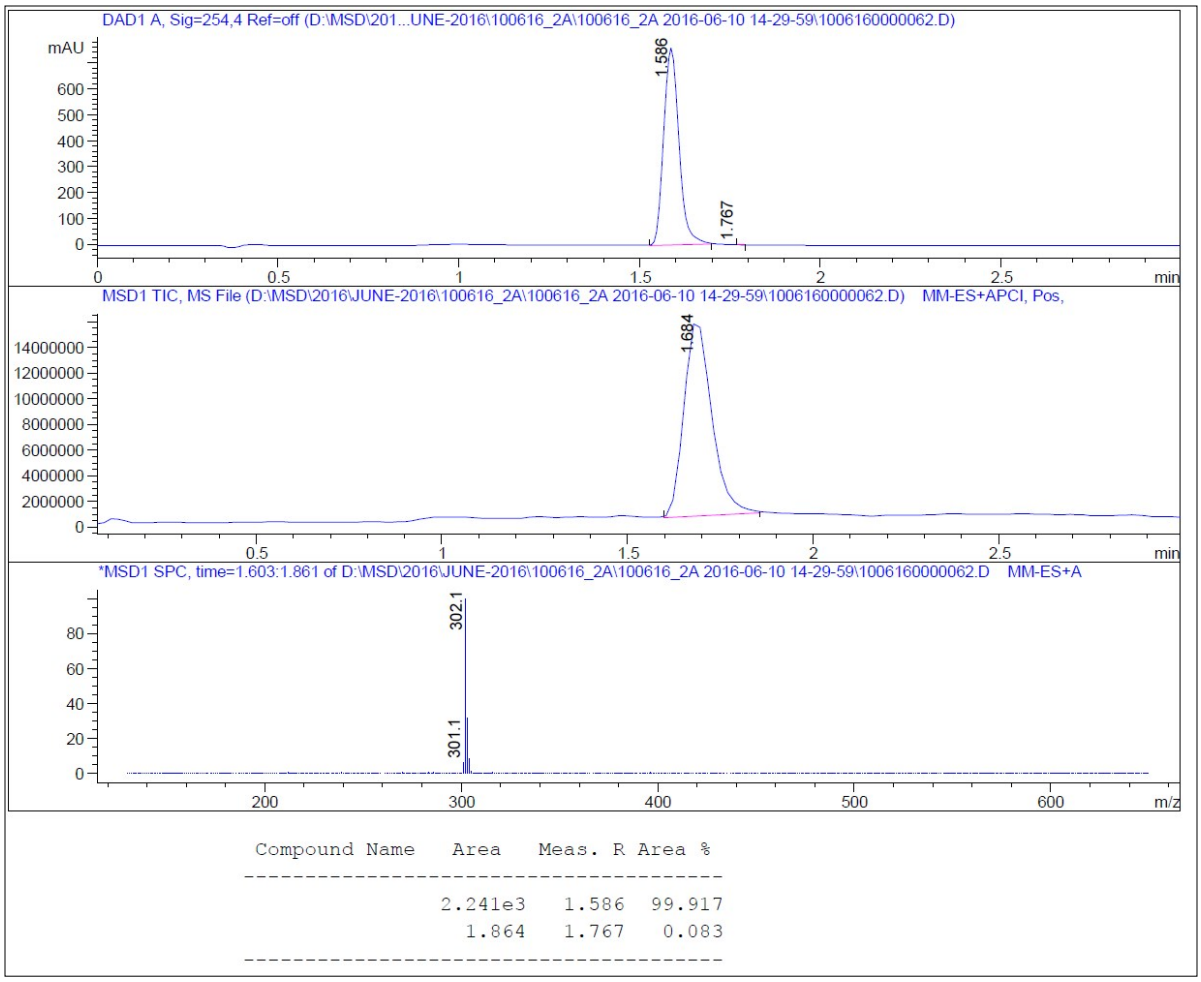
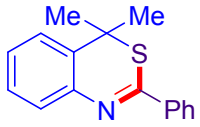


Figure 48. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ka** in $CDCl_3$ and LC-MS in Acetonitrile.

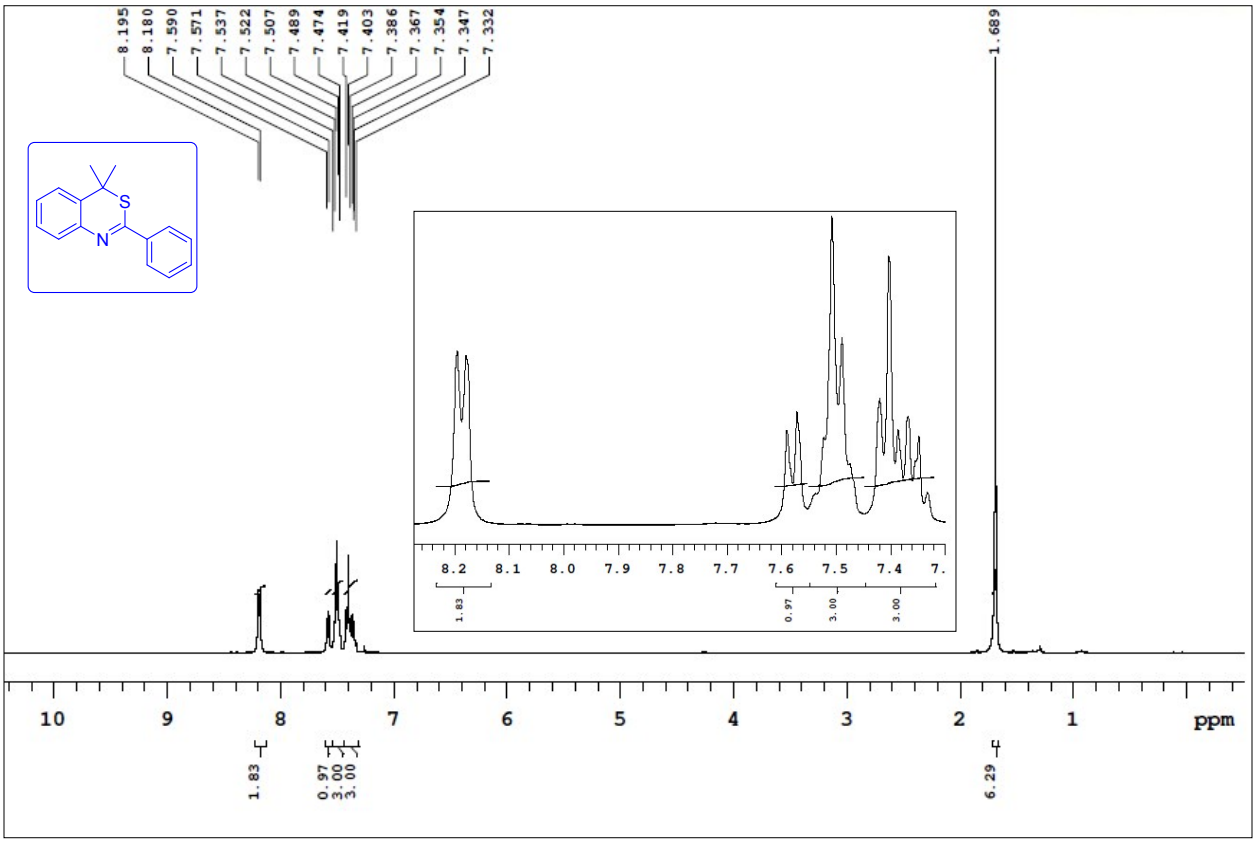
Off-white solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 83 - 85 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.40 (m, 4H), 7.29 - 7.20 (m, 6H), 7.07 (d, *J* = 7.2 Hz, 1H), 5.38 (s, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.2, 144.2, 141.3, 138.0, 131.4, 128.8, 128.6, 128.5, 128.2, 127.9, 127.84, 127.81, 127.6, 127.3, 122.7, 45.6 ppm; **MS** (APCI): $[M + 1]^+$ = 302.1 (99.91%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{20}H_{16}NS$: 302.1003; found: 302.1000.

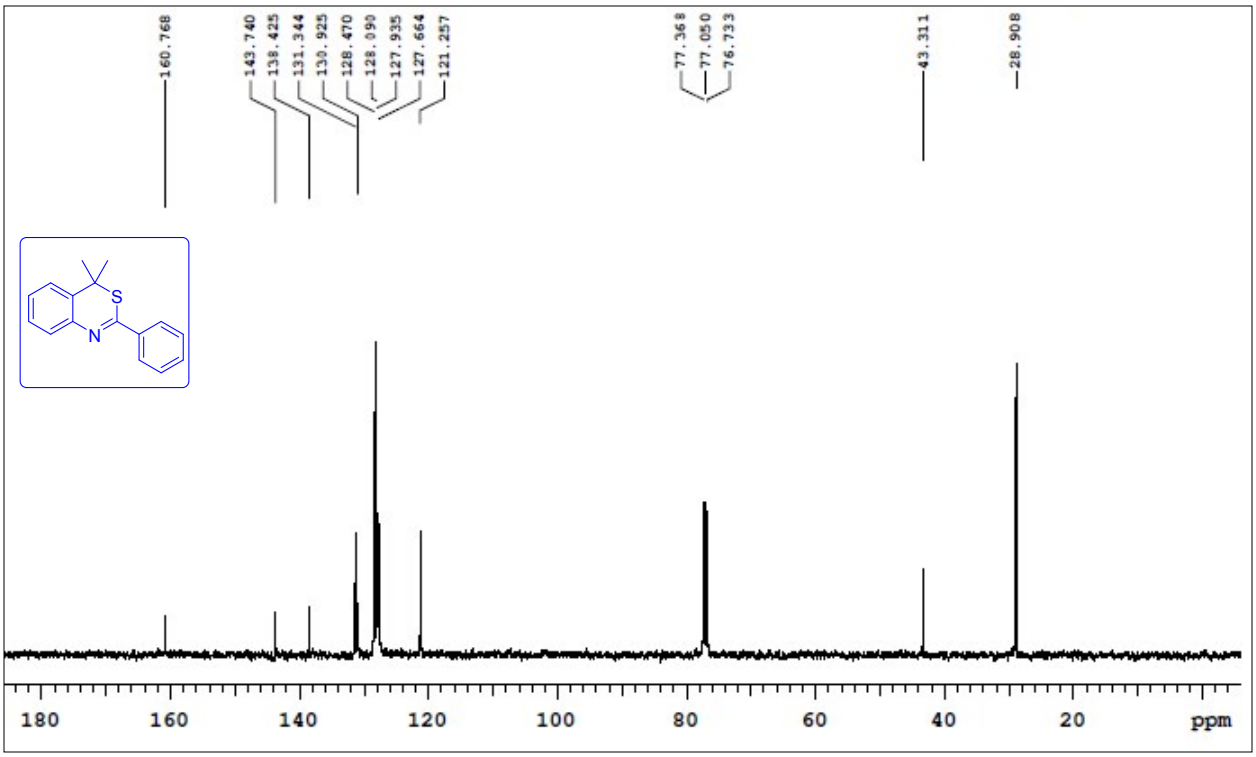
Synthesis of 4,4-dimethyl-2-phenyl-4H-benzo[d][1,3]thiazine (5la); new compound

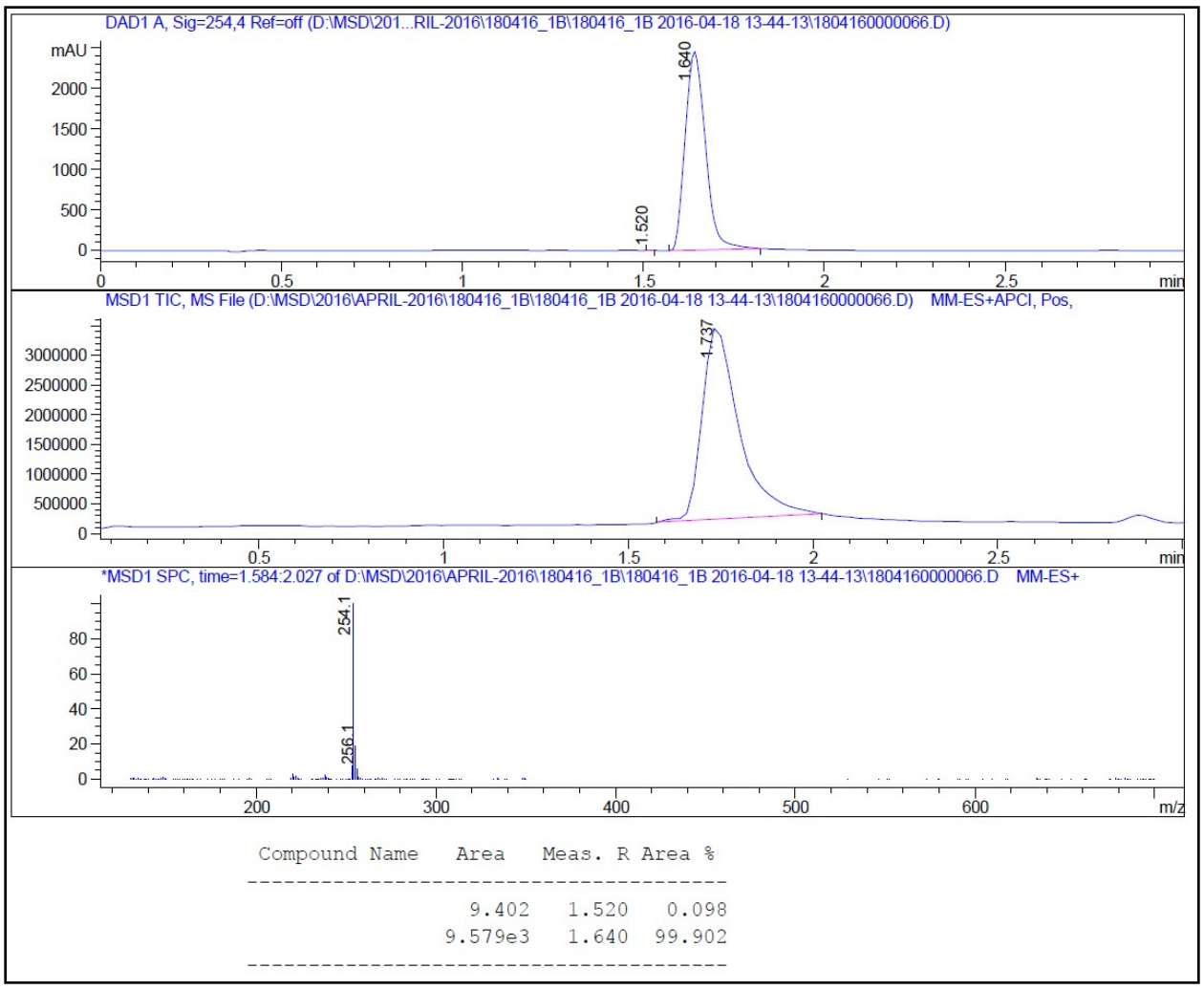


According to the general procedure, reactions between 2-(2-aminophenyl)propan-2-ol **1l** (1.0 mmol, 151 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 4,4-dimethyl-2-phenyl-4H-benzo[d][1,3]thiazine **5la** in 89% (225 mg) yield as colorless viscous solid




160.768
143.740
138.425
131.344
130.925
128.470
128.090
127.935
127.664
121.257
77.368
77.050
76.733
43.311
28.908
S
N
180
160
140
120
100
80
60
40
20
ppm

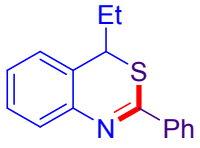


Compound Name	Area	Meas. R Area	%
	9.402	1.520	0.098
	9.579e3	1.640	99.902

Figure 49. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5la** in $CDCl_3$ and LC-MS in Acetonitrile.

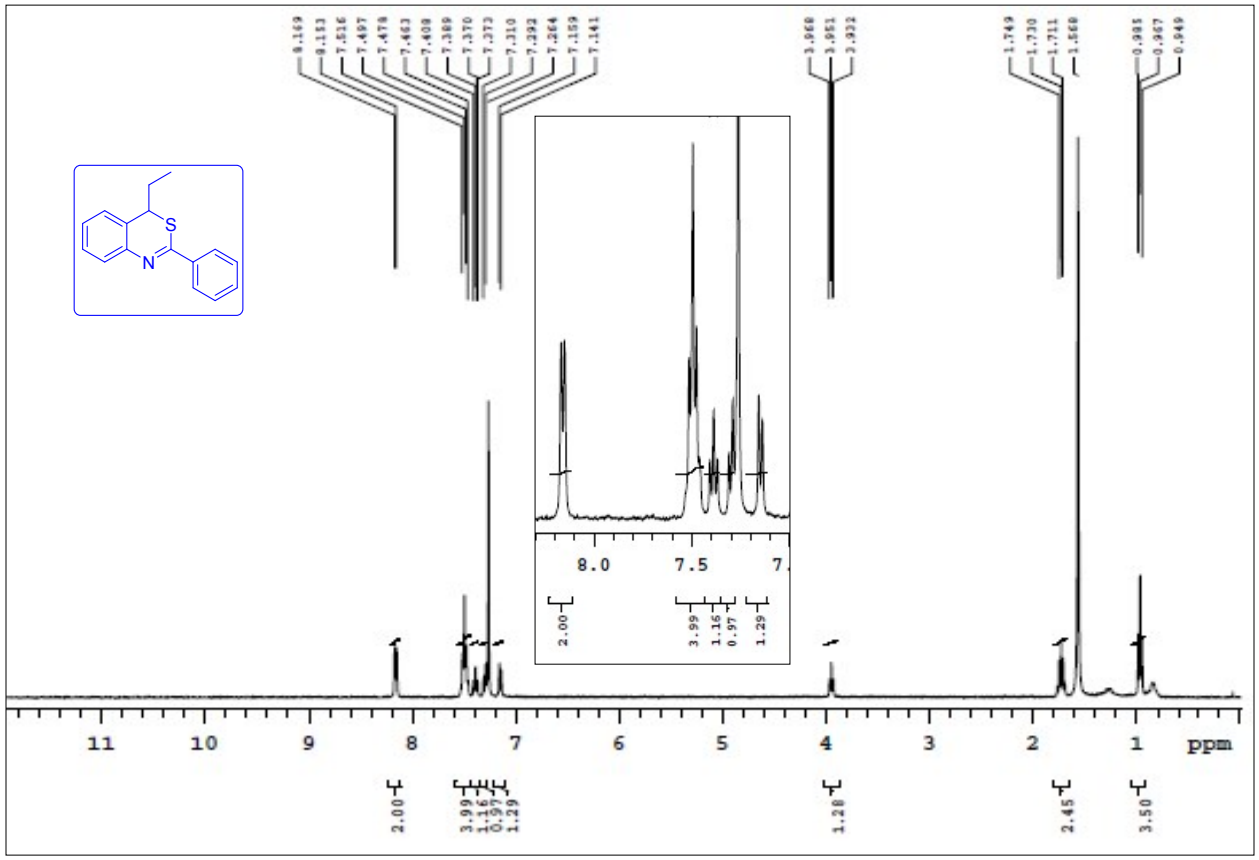
Colorless viscous solid; $\mathbf{R_f}$ = 0.60 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.18 (d, *J* = 6.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.53 - 7.47 (m, 3H), 7.41 - 7.33 (m, 3H), 1.68 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 160.7, 143.7, 138.4, 131.3, 130.92, 128.4, 128.0, 127.9, 127.6, 121.2, 43.3, 28.9 ppm; **MS** (APCI): $[M + 1]^+$ = 254.1 (99.9%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{16}H_{16}NS$: 254.1003; found: 254.1001.

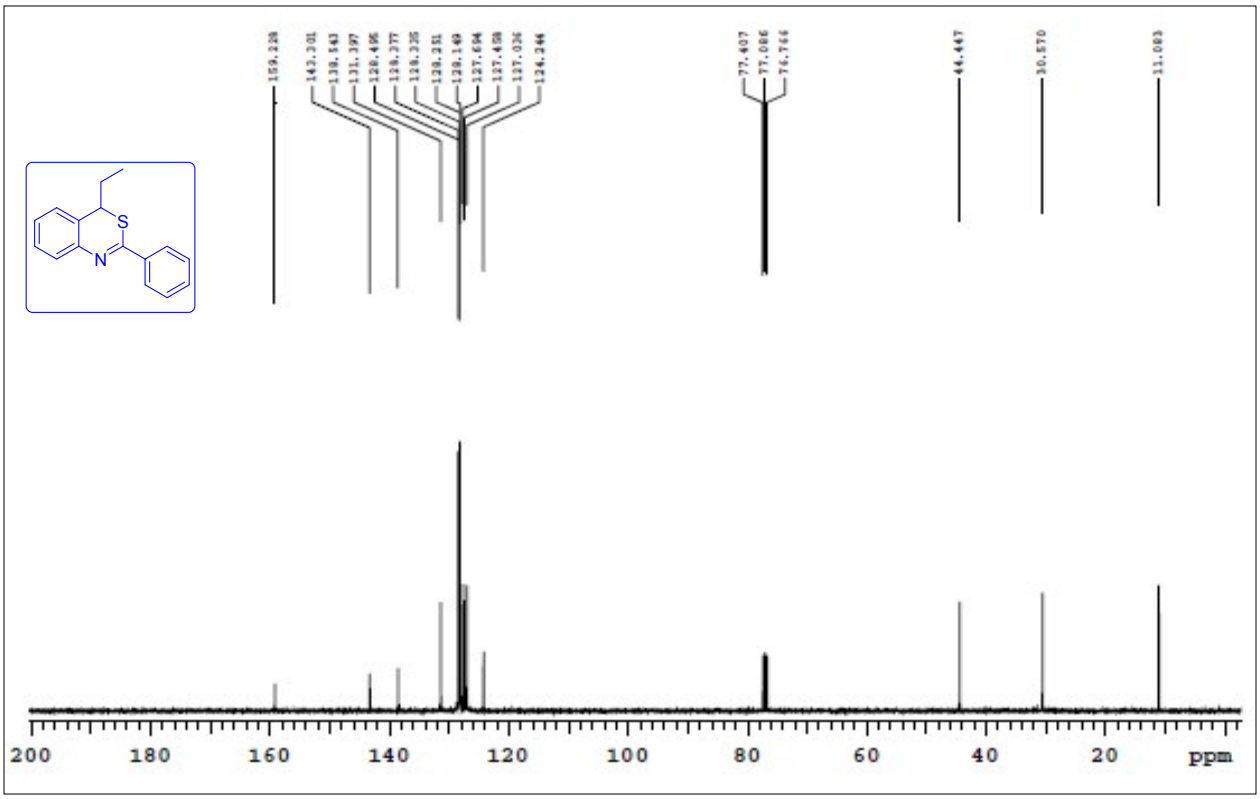
Synthesis of 4-ethyl-2-phenyl-4H-benzo[d][1,3]thiazine (5ma); new compound



According to the general procedure, reactions between 1-(2-aminophenyl)propan-1-ol **1m** (1.0 mmol, 151 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were

performed to obtain the desired 4-ethyl-2-phenyl-4H-benzo[d][1,3]thiazine **5ma** in 91% (230 mg) yield as colorless viscous solid.




159.228
143.301
138.543
131.397
128.406
128.377
128.305
128.251
128.149
127.694
127.458
127.026
124.244
77.407
77.088
76.766
44.447
30.570
11.083
S
N
200
180
160
140
120
100
80
60
40
20
ppm

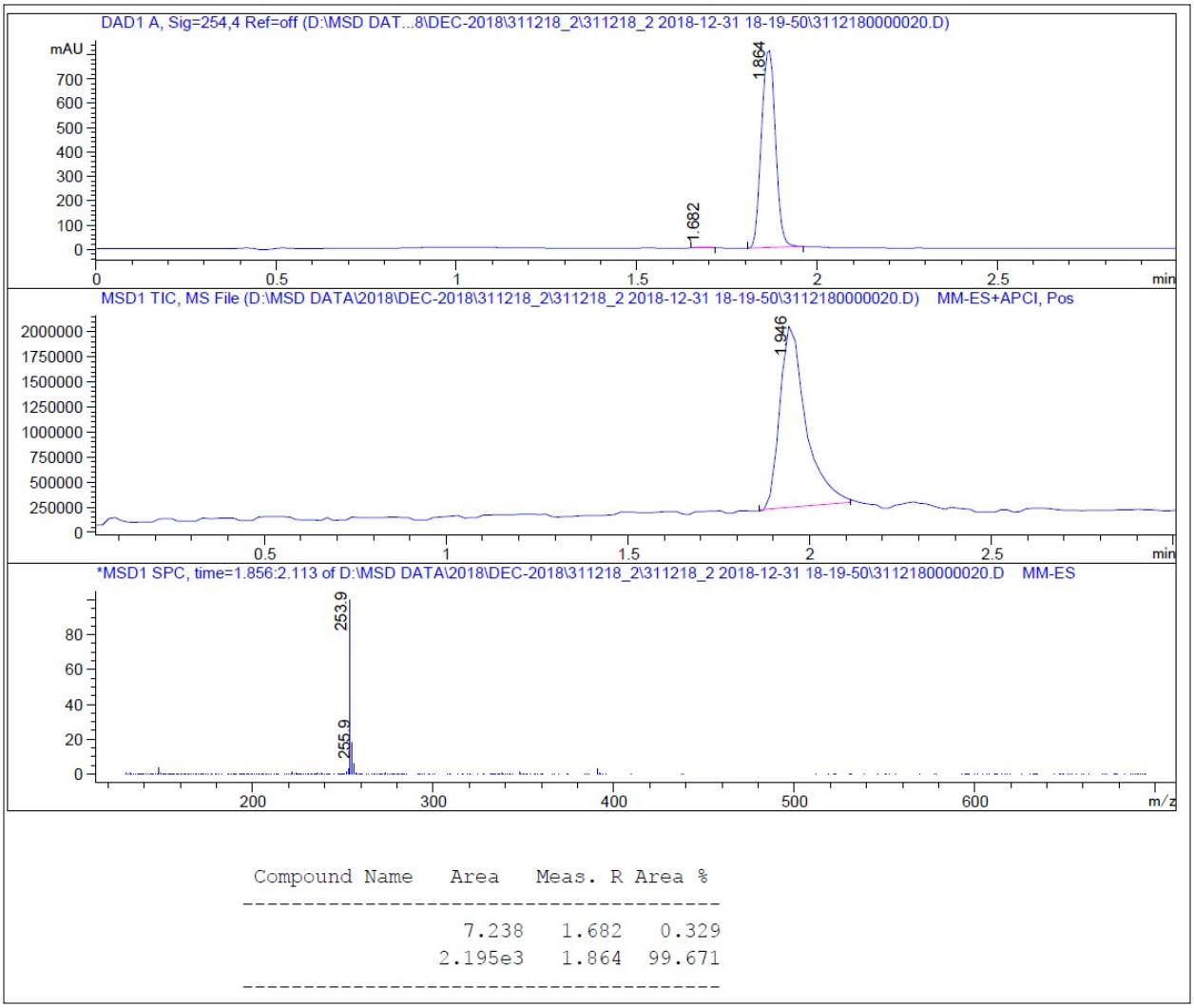
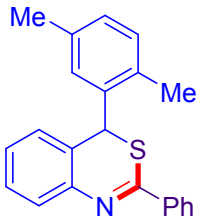


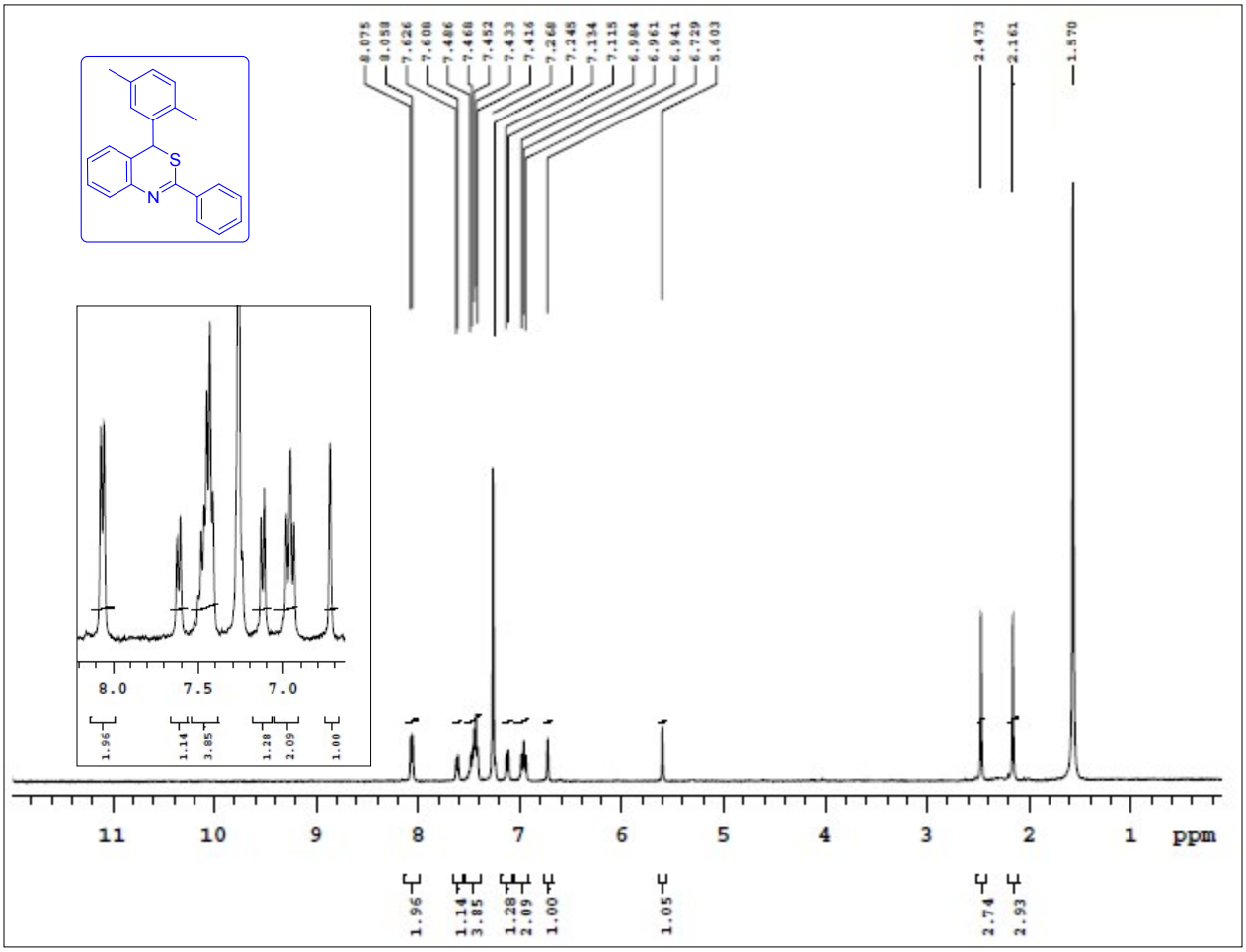
Figure 50. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5ma** in $CDCl_3$ and LC-MS in Acetonitrile.

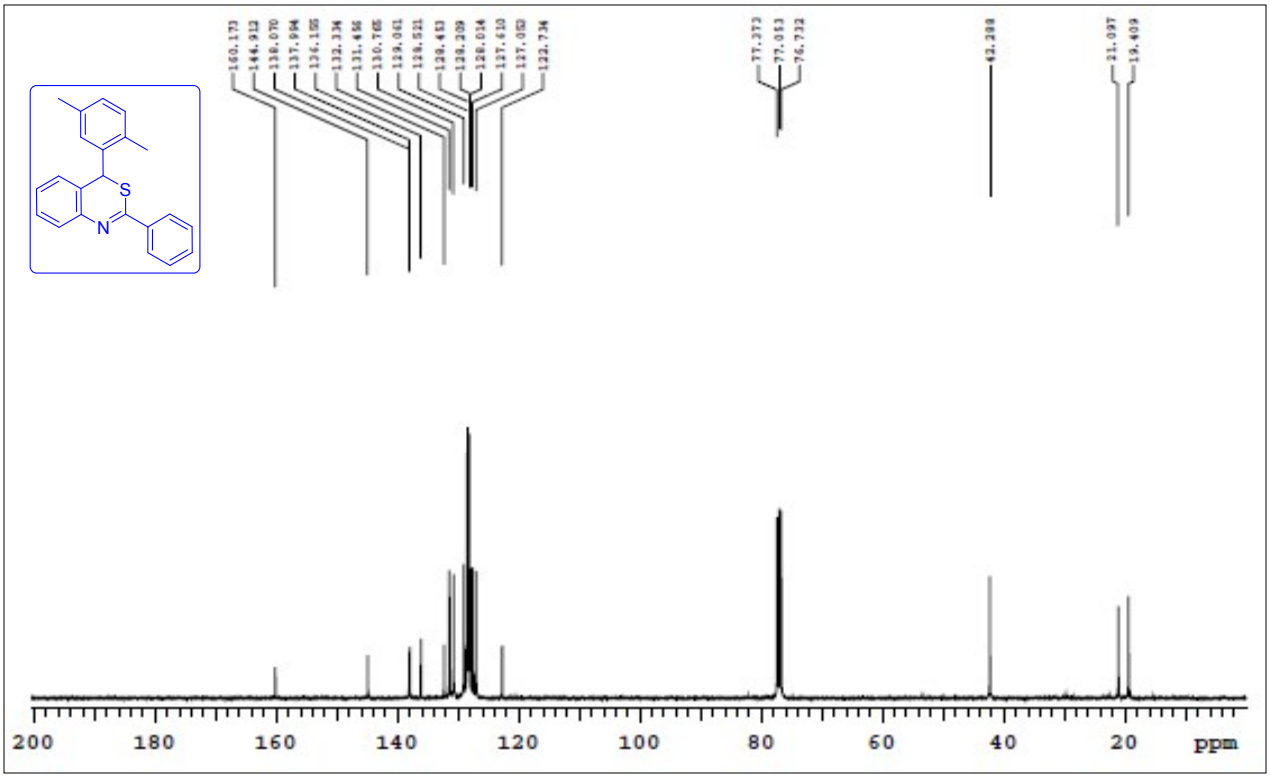
Colorless viscous solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 111 - 112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 6.4 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 3.95 (t, *J* = 6.8 Hz, 1H), 1.73 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 159.2, 143.3, 138.5, 131.3, 128.4, 128.37, 128.33, 128.2, 128.1, 127.6, 127.4, 127.0, 124.2, 44.4, 30.5, 11.08 ppm; **MS** (APCI): $[M + 1]^+$ = 253.9 (99.67%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{16}H_{16}NS$: 254.1003; found: 254.1000.

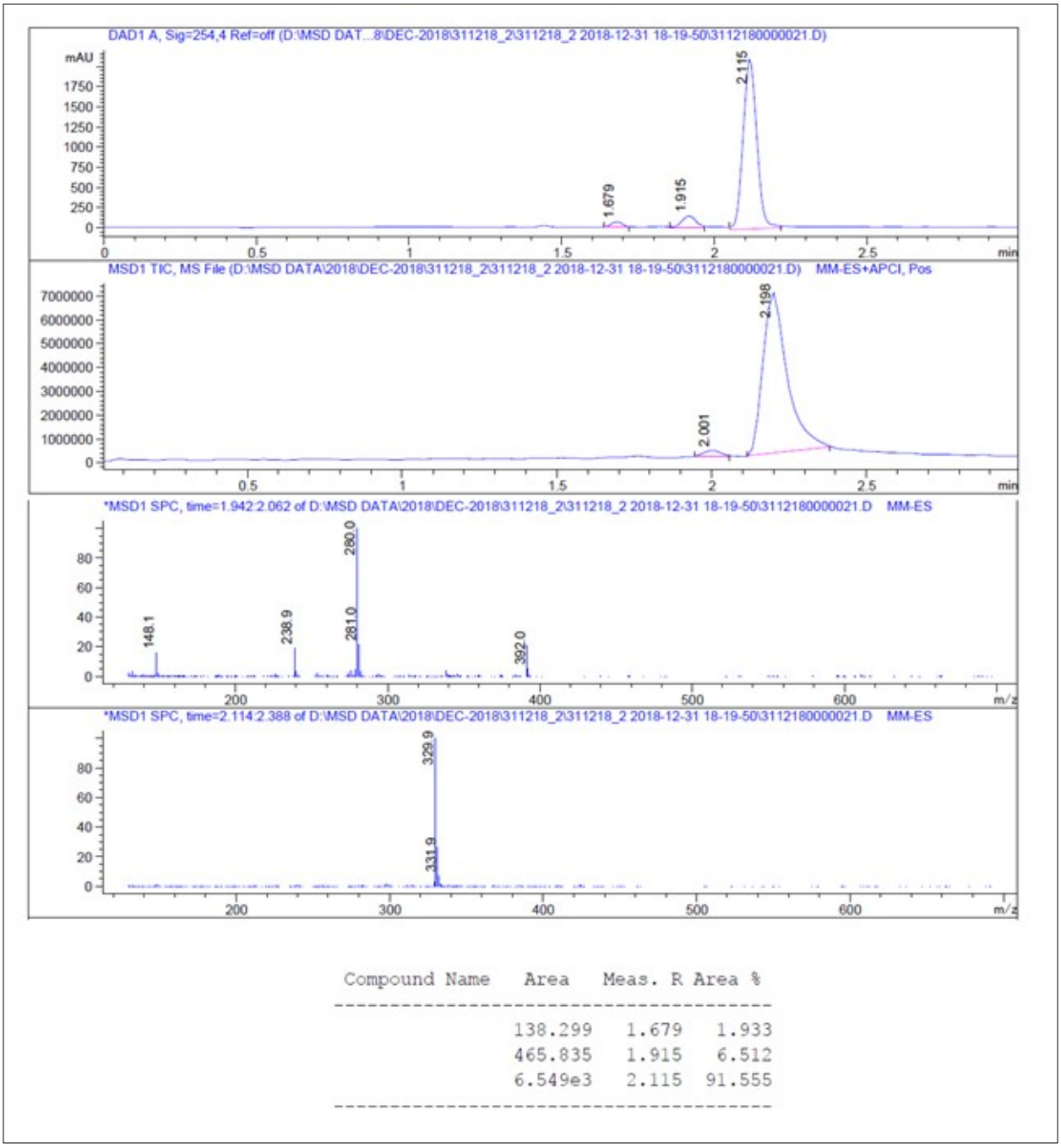
Synthesis of 4-(2,5-dimethylphenyl)-2-phenyl-4H-benzo[d][1,3]thiazine (5na); new compound



According to the general procedure, reactions between (2-aminophenyl)(2,5-dimethylphenyl)methanol **1n** (1.0 mmol, 227 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 4-(2,5-dimethylphenyl)-2-phenyl-4H-benzo[d][1,3]thiazine **5na** in 95% (313 mg) yield as colorless viscous solid.




160.173
144.913
136.070
137.994
134.155
132.334
131.456
130.765
129.061
128.521
128.453
128.209
128.034
127.610
127.052
122.734
77.272
77.053
76.732
42.288
21.097
19.409
S
N
200
180
160
140
120
100
80
60
40
20
ppm



Compound Name	Area	Meas. R	Area %
	138.299	1.679	1.933
	465.835	1.915	6.512
	6.549e3	2.115	91.555

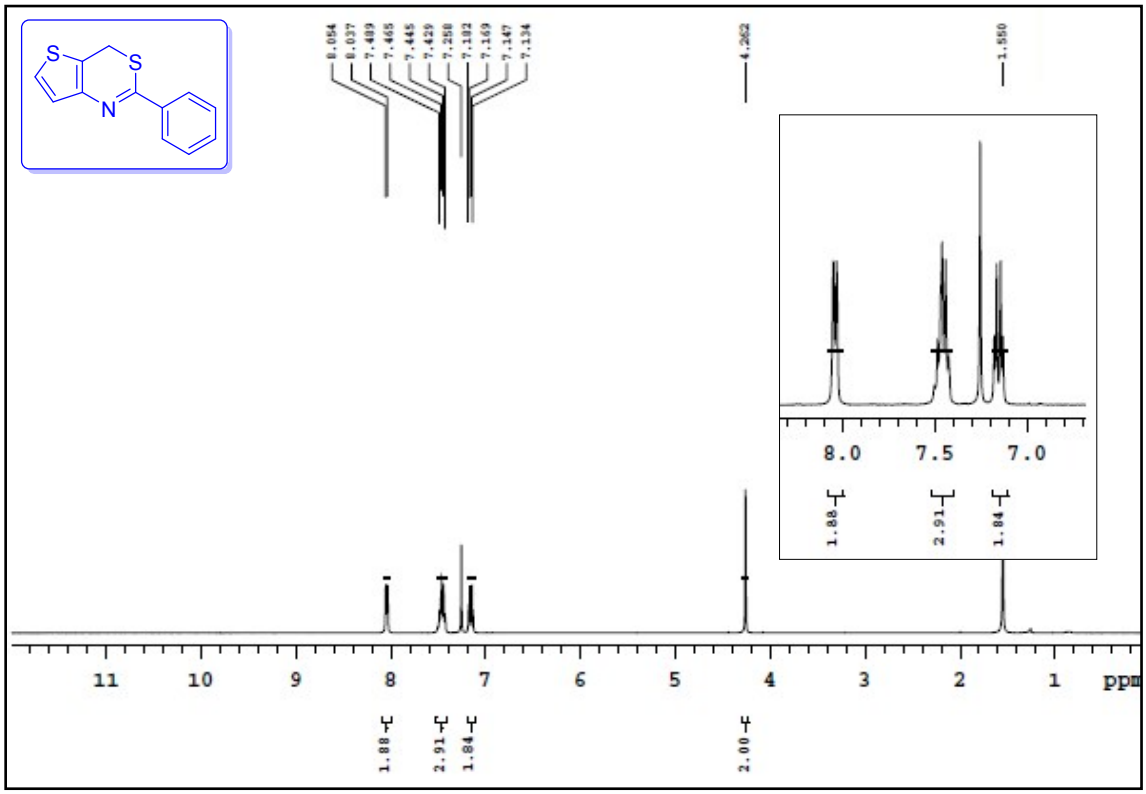
Figure 51. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5na** in $CDCl_3$ and LC-MS in Acetonitrile.

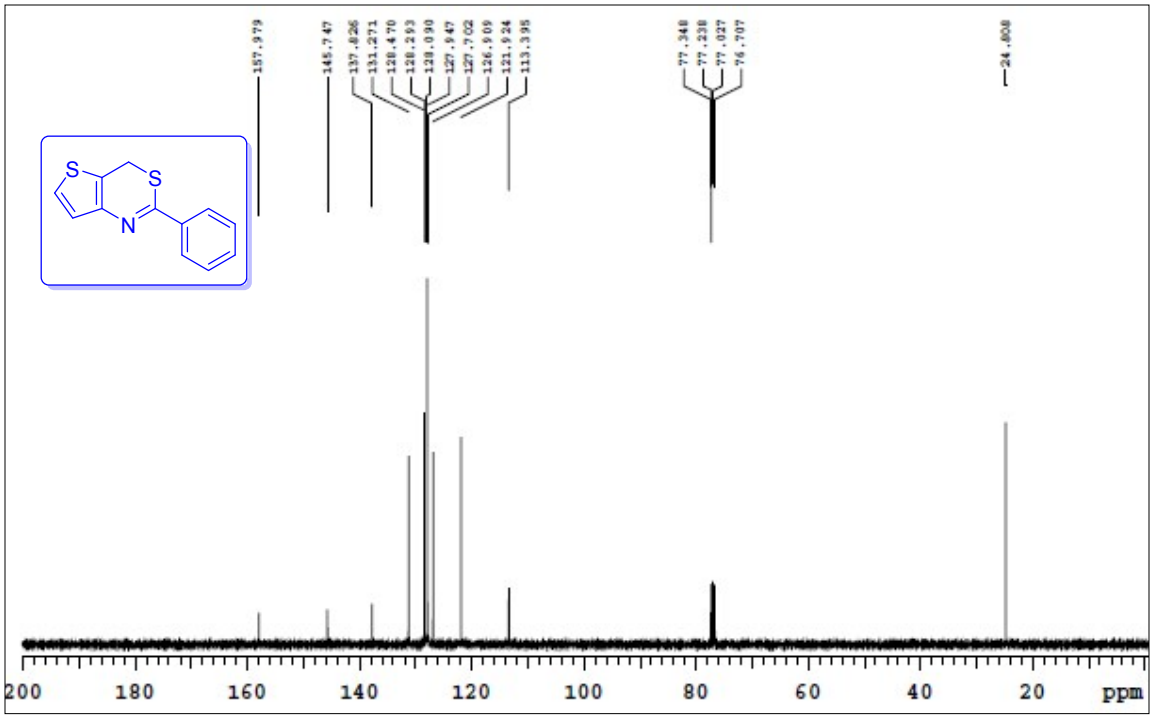
Colorless viscous solid; $\mathbf{R_f}$ = 0.50 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 6.8 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.48-7.41 m, 4H), 7.24 (overlapped, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.96 (t, *J* = 8.4 Hz, 2H), 6.72 (s, 1H), 5.60 (s, 1H), 2.47 (s, 3H), 2.16 (s, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 160.1, 144.9, 138.0, 137.9, 136.1, 132.3, 131.4, 130.7, 129.0, 128.5, 128.4, 128.2, 128.0, 127.6, 127.0, 122.7, 42.2, 21.0, 19.4 ppm; **MS** (APCI):

$[M + 1]^+$ = 329.9 (91.55%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{22}H_{20}NS$: 330.1316; found: 330.1312.

Synthesis of 2-phenyl-4H-thieno[3,2-d][1,3]thiazine (5oa); new compound

According to the general procedure, reactions between (3-aminothiophen-2-yl)methanol **1o** (1.0 mmol, 129 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-phenyl-4H-thieno[3,2-d][1,3]thiazine **5oa** in 93% (215 mg) yield as off-white solid.




157.979
145.747
137.826
131.271
128.470
128.293
128.090
127.947
127.702
126.909
121.924
113.395
77.348
77.238
77.027
76.707
24.608
S
S
N
200
180
160
140
120
100
80
60
40
20
ppm

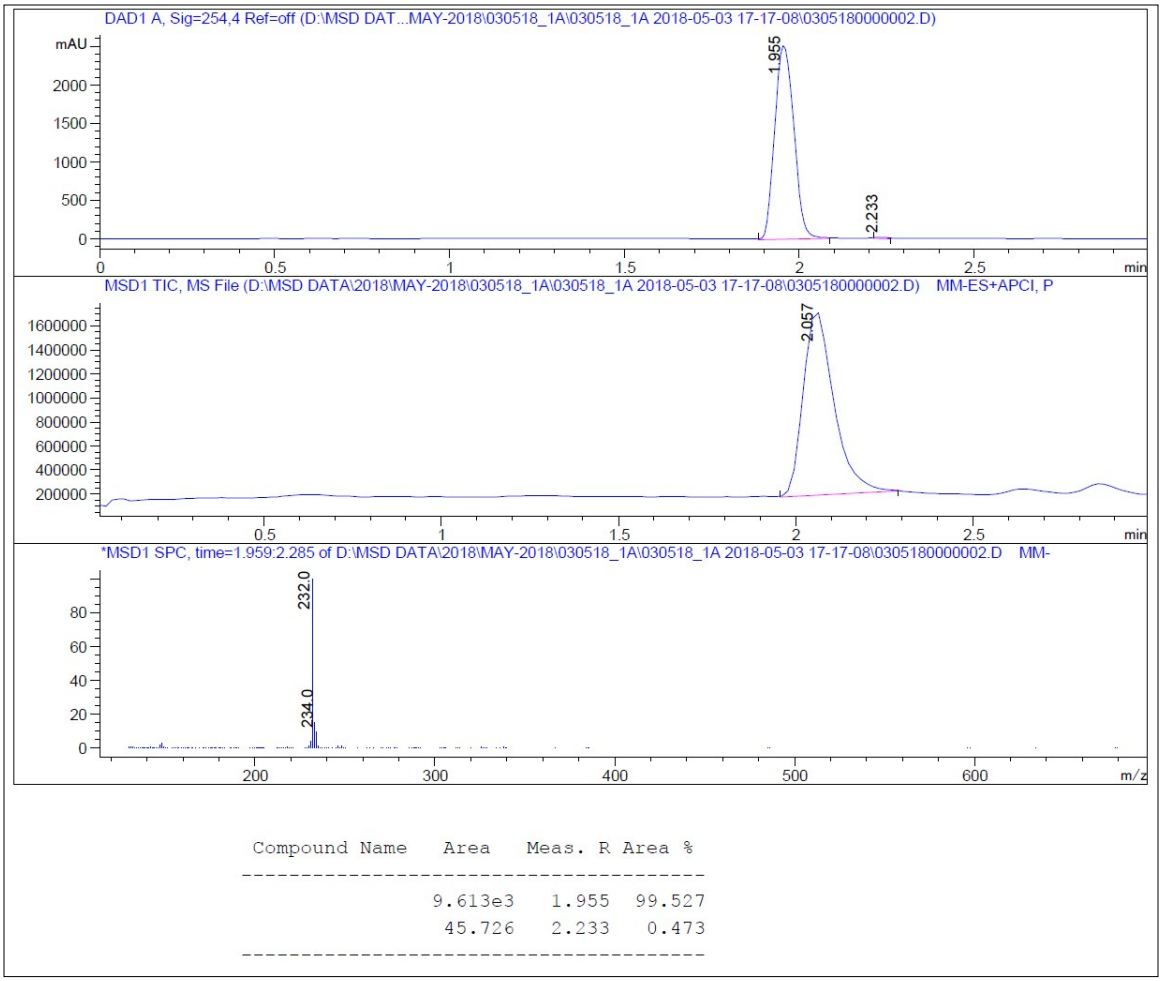
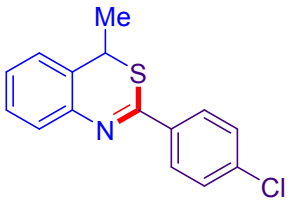


Figure 52. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **50a** in $CDCl_3$ and LC-MS in Acetonitrile.

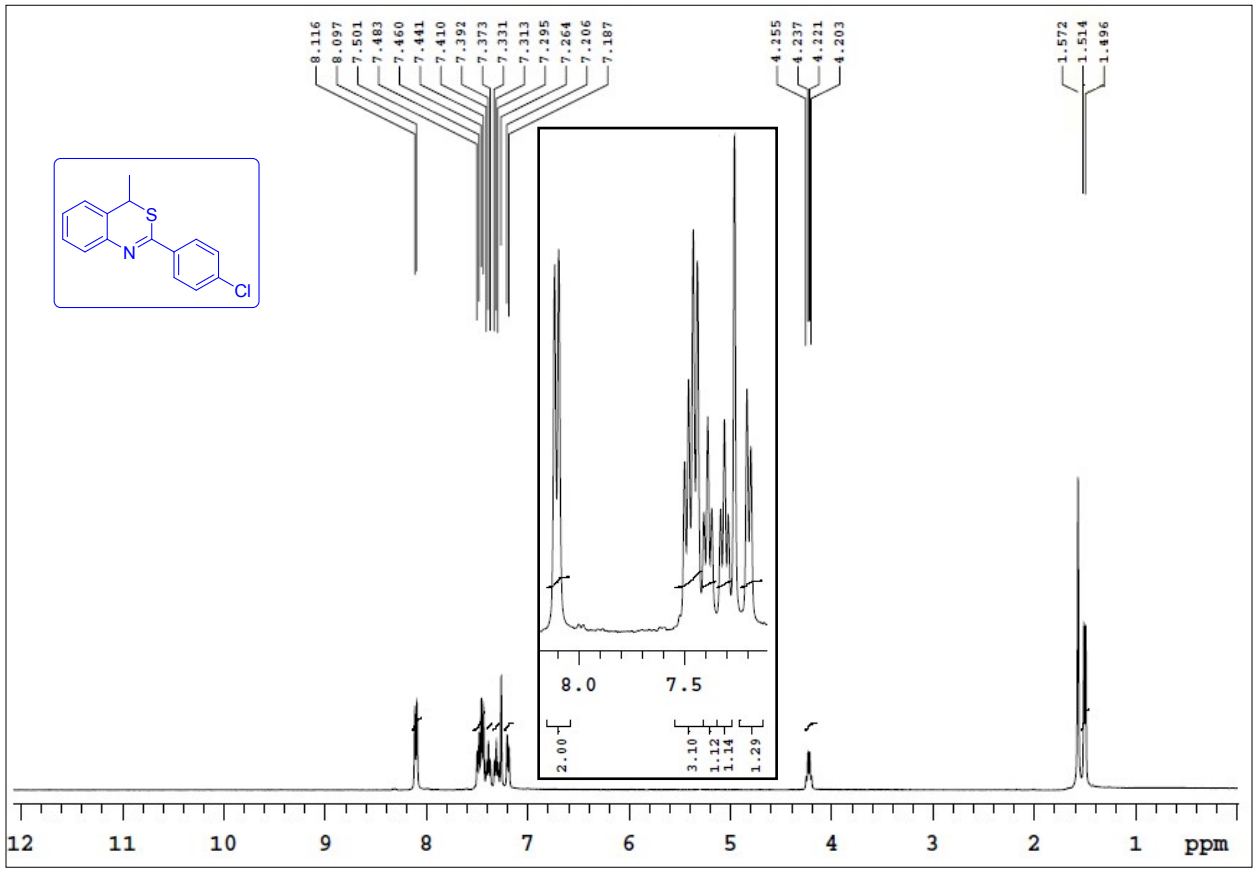
Off-white solid; $\mathbf{R_f}$ = 0.50 (SiO_2, Hexane/EtOAc = 95:5); **m.p** = 111 - 112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 6.8 Hz, 2H), 7.50 - 7.42 (m, 3H), 7.16 - 7.13 (m, 2H), 4.26 (s, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 157.9, 145.7, 137.8, 131.2, 128.4, 128.2, 128.0, 128.9, 128.7, 126.9, 121.9, 113.3, 24.8 ppm; **MS** (APCI): $[M + 1]^+$ = 232.0 (99.52%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{12}H_{10}NS_2$: 232.0254; found: 232.0250.

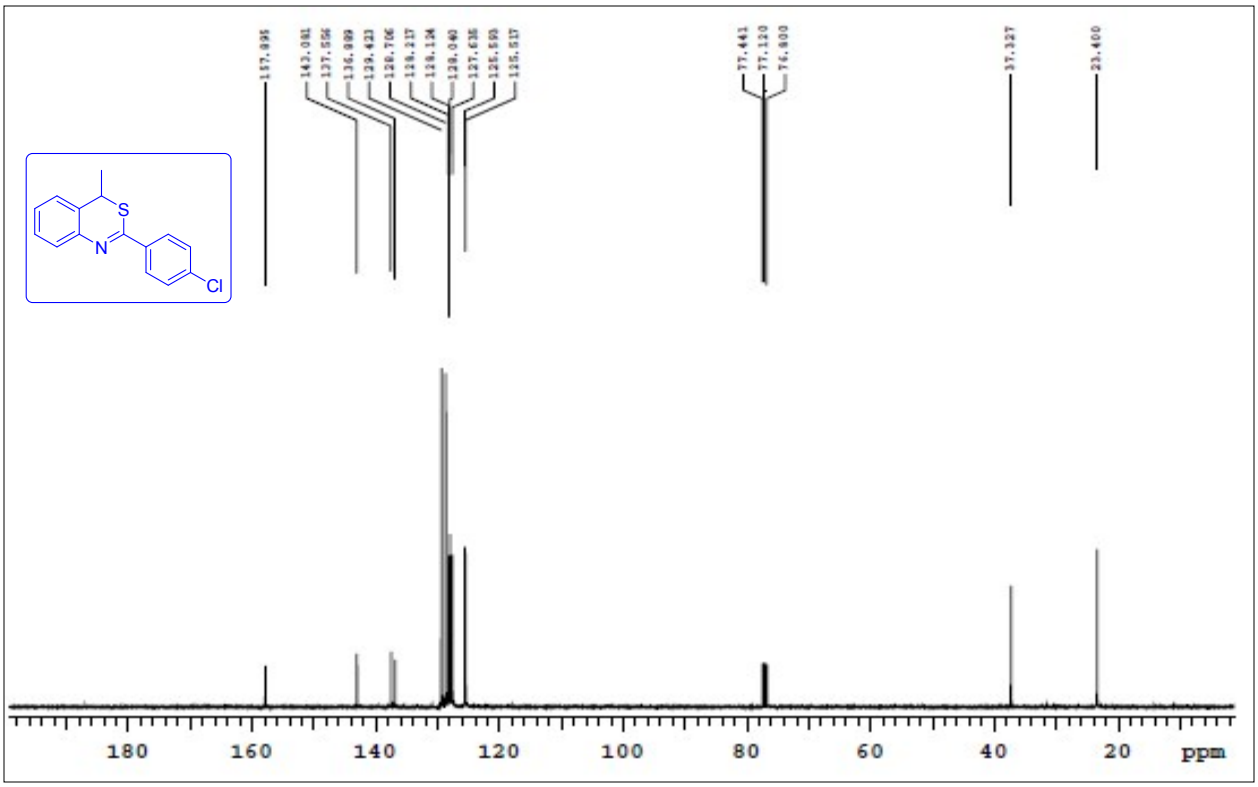
Synthesis of 2-(4-chlorophenyl)-4-methyl-4H-benzo[d][1,3]thiazine (5pt); new compound

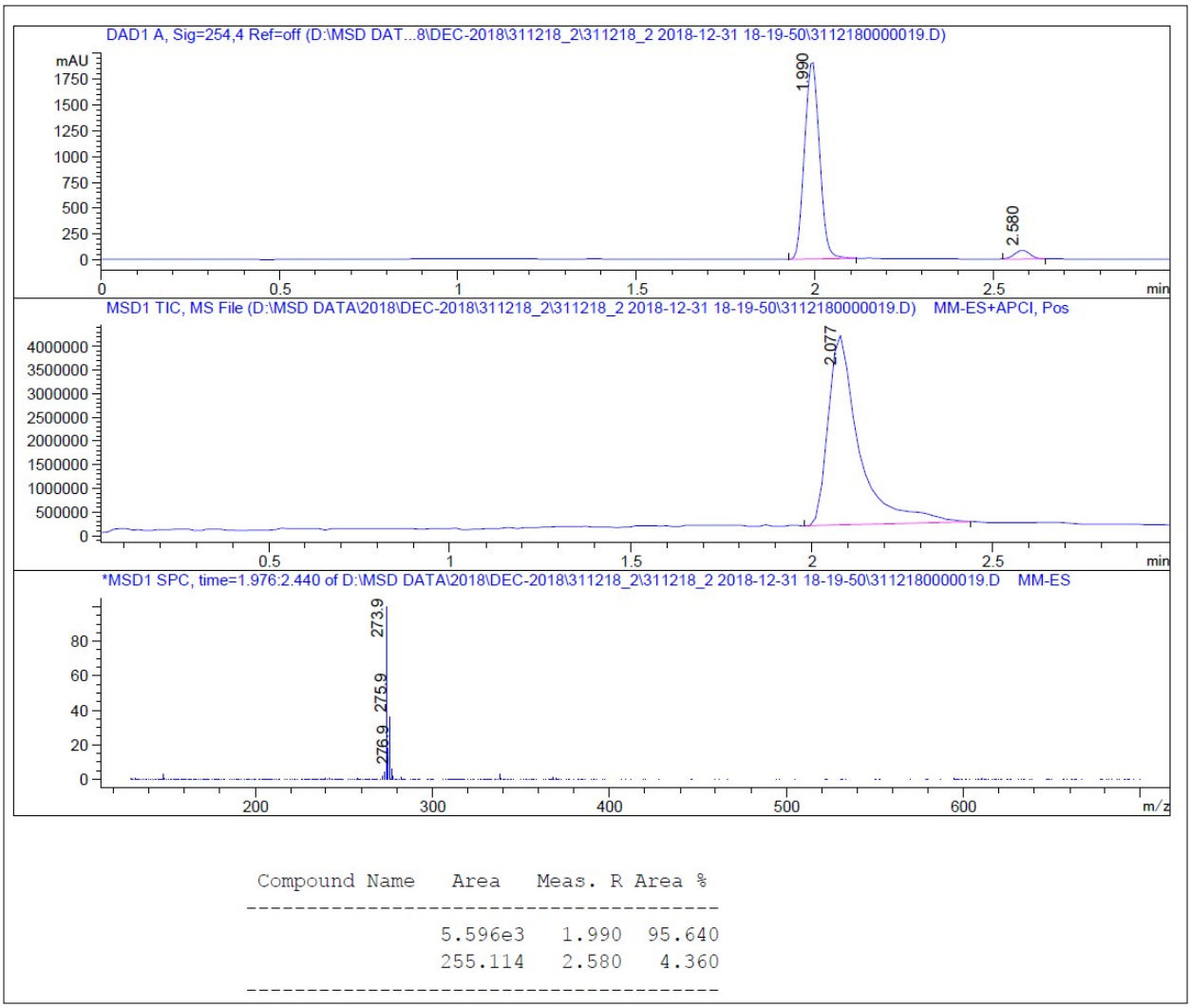


According to the general procedure, reactions between 1-(2-aminophenyl)ethan-1-ol **1p** (1.0 mmol, 137 mg), 4-chlorobenzothioamide **4t** (1.0 mmol, 171.6 mg), T3P (1.1 mmol, 349.8 mg)

were performed to obtain the desired 2-(4-chlorophenyl)-4-methyl-4H-benzo[d][1,3]thiazine **5pt** in 91% (248 mg) yield as colorless viscous solid




157.995
143.081
137.556
136.989
130.423
128.706
128.217
128.134
128.040
127.638
125.593
125.517
77.441
77.110
76.800
37.327
23.400
S
N
Cl
180
160
140
120
100
80
60
40
20
ppm



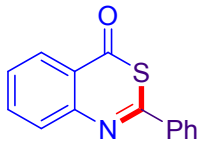
Compound Name	Area	Meas. R	Area %
	5.596e3	1.990	95.640
	255.114	2.580	4.360

Figure 53. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **5pt** in $CDCl_3$ and LC-MS in Acetonitrile.

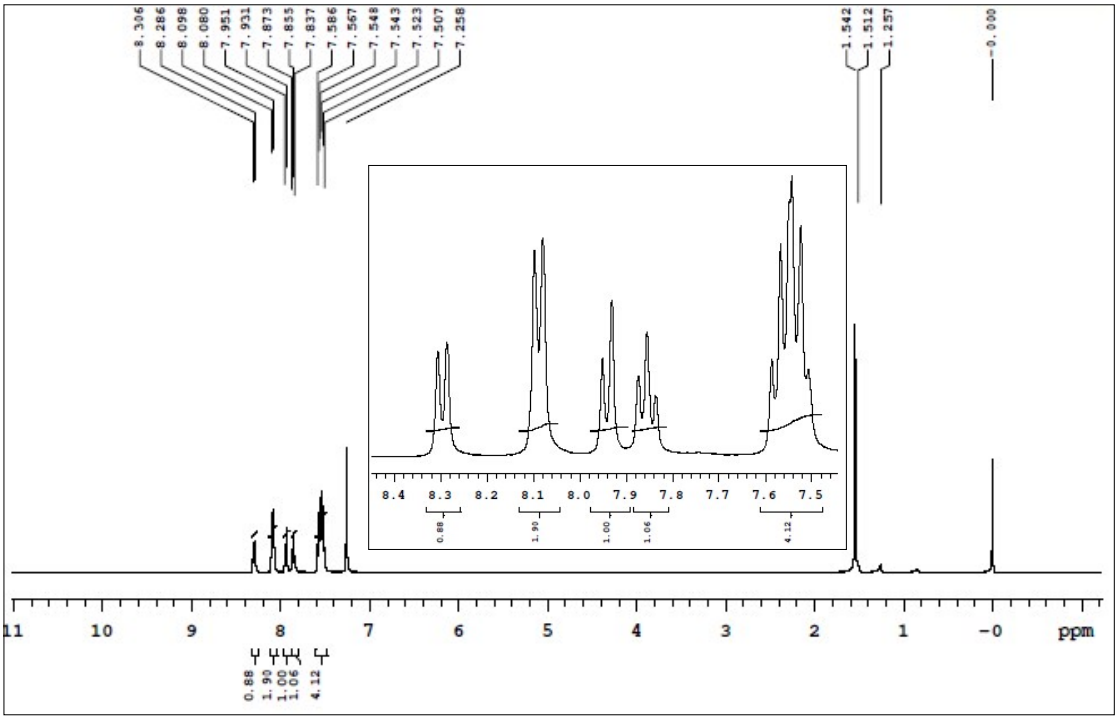
Colorless viscous solid; $\mathbf{R_f}$ = 0.65 (SiO_2, Hexane/EtOAc = 95:5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 157.8, 143.0, 137.5, 136.8, 129.4, 128.7, 128.2, 128.1, 128.0, 127.6, 125.59, 125.51, 37.3, 23.4 ppm; **MS** (APCI): $[M + 1]^+$ = 273.9 (95.6%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{13}ClNS$: 274.0457; found: 274.0454.

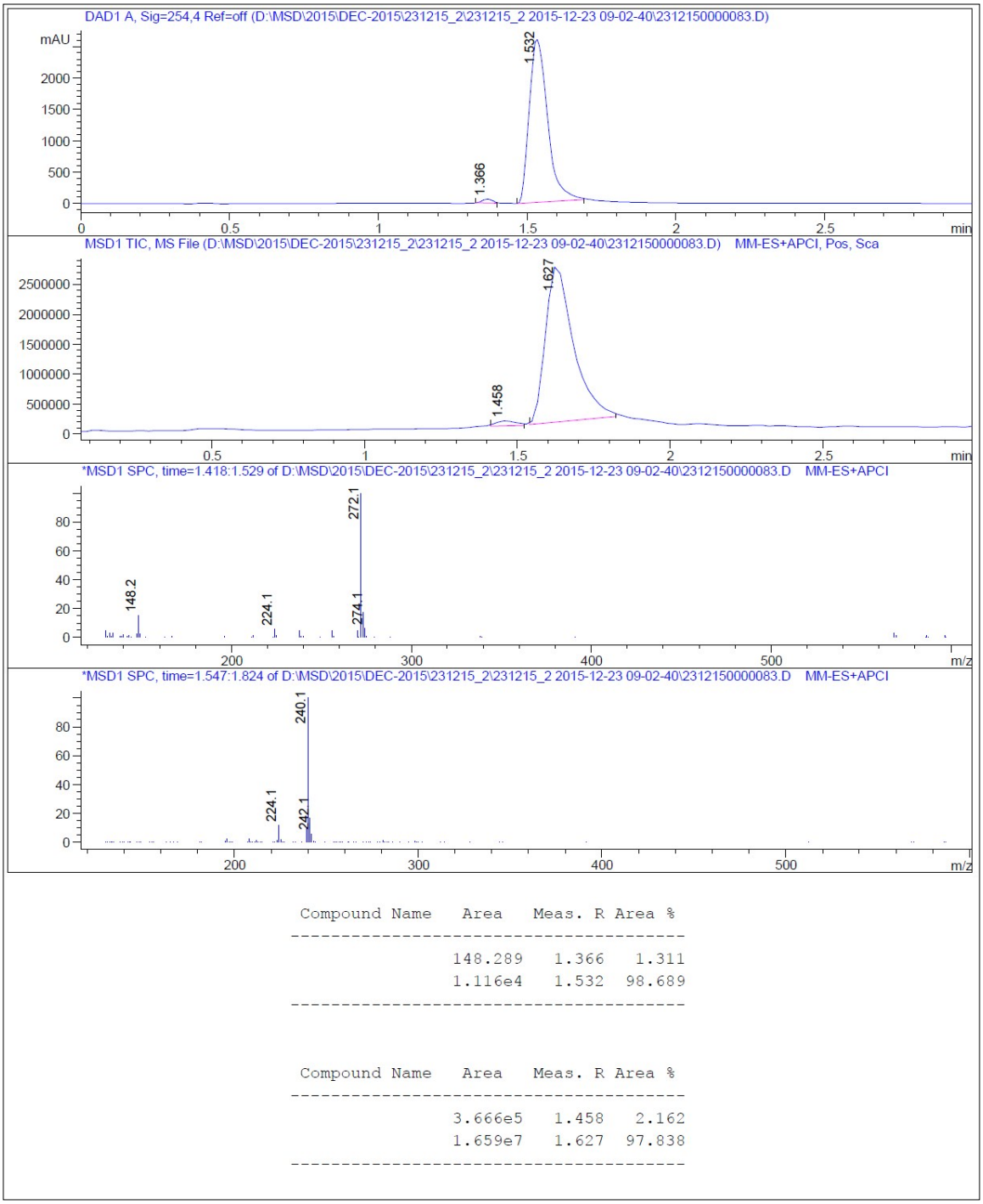
6. Experimental procedures and analytical data of synthesized 2-aryl thiazin-4-ones (7aa-ca)

Synthesis of 2-phenyl-4H-benzo[d][1,3]thiazin-4-one (7aa); known compound[5]



According to the general procedure, reactions between anthranilic acid **6a** (1.0 mmol, 137 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 2-phenyl-4H-benzo[d][1,3]thiazin-4-one **7aa** in 70% (167 mg) yield as white solid.





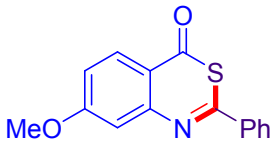
Compound Name	Area	Meas. R	Area %
	148.289	1.366	1.311
	1.116e4	1.532	98.689

Compound Name	Area	Meas. R	Area %
	3.666e5	1.458	2.162
	1.659e7	1.627	97.838

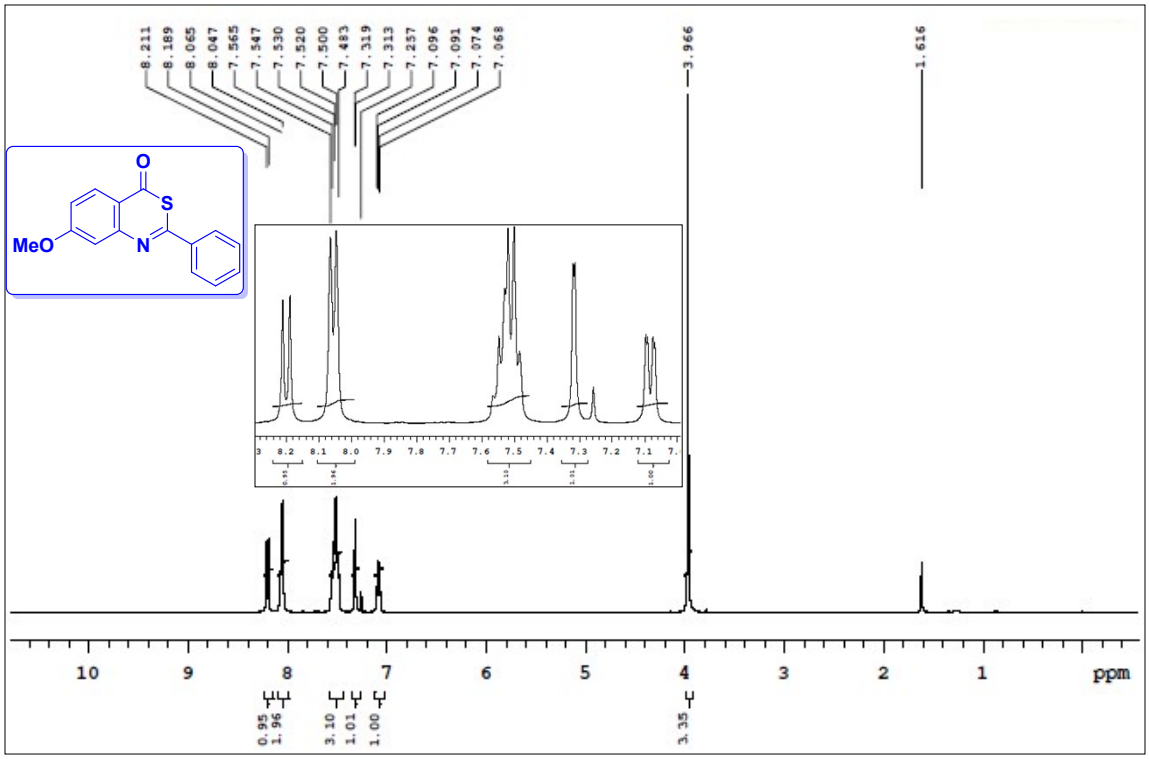
Figure 54. ^{1}H (400 MHz) NMR spectra of **7aa** in $CDCl_3$ and LC-MS in Acetonitrile.

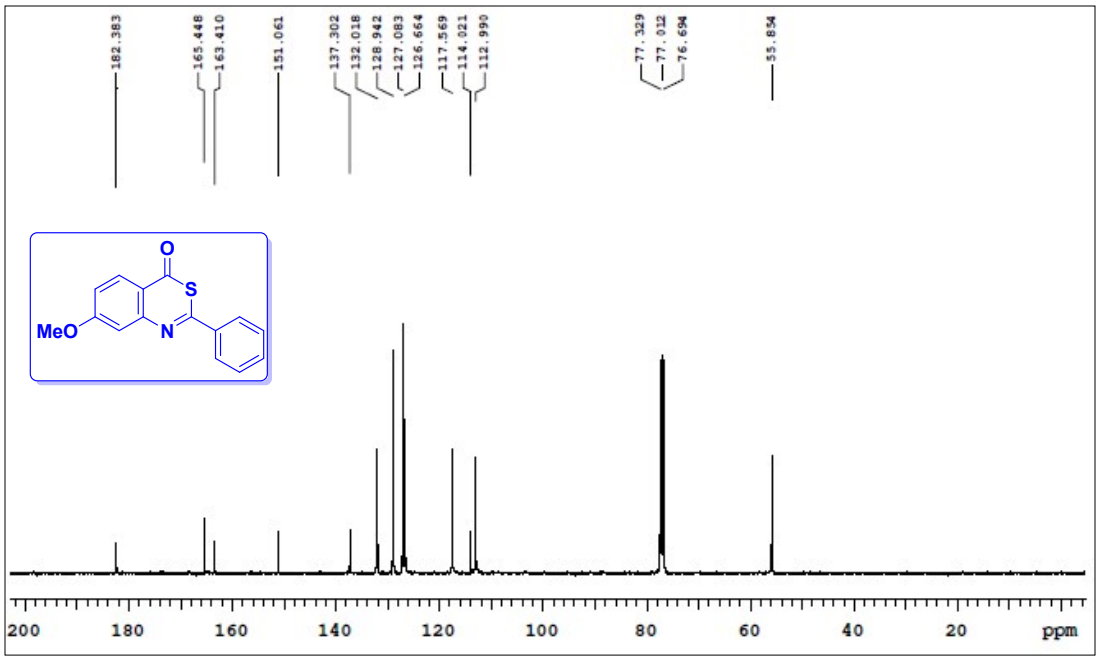
White solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 3:1); **m.p** = 114 - 116 °C (Lit[5] 116 °C); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 7.2 Hz, 1H), 7.58 - 7.50 (m, 4H) ppm; **MS** (APCI): $[M + 1]^+$ = 240.1 (98.68%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_{10}NOS$: 240.0483; found: 240.0480.

Synthesis of 7-methoxy-2-phenyl-4H-benzo[d][1,3]thiazin-4-one (7ba); new compound



According to the general procedure, reactions between 4-methoxyanthranilic acid **6b** (1.0 mmol, 167 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-methoxy-2-phenyl-4H-benzo[d][1,3]thiazin-4-one **7ba** in 72% (194 mg) yield as off-white solid.




182.383
165.448
163.410
151.061
137.302
132.018
128.942
127.083
126.664
117.569
114.021
112.990
77.329
77.012
76.694
55.854
O
S
MeO
N
200
180
160
140
120
100
80
60
40
20
ppm

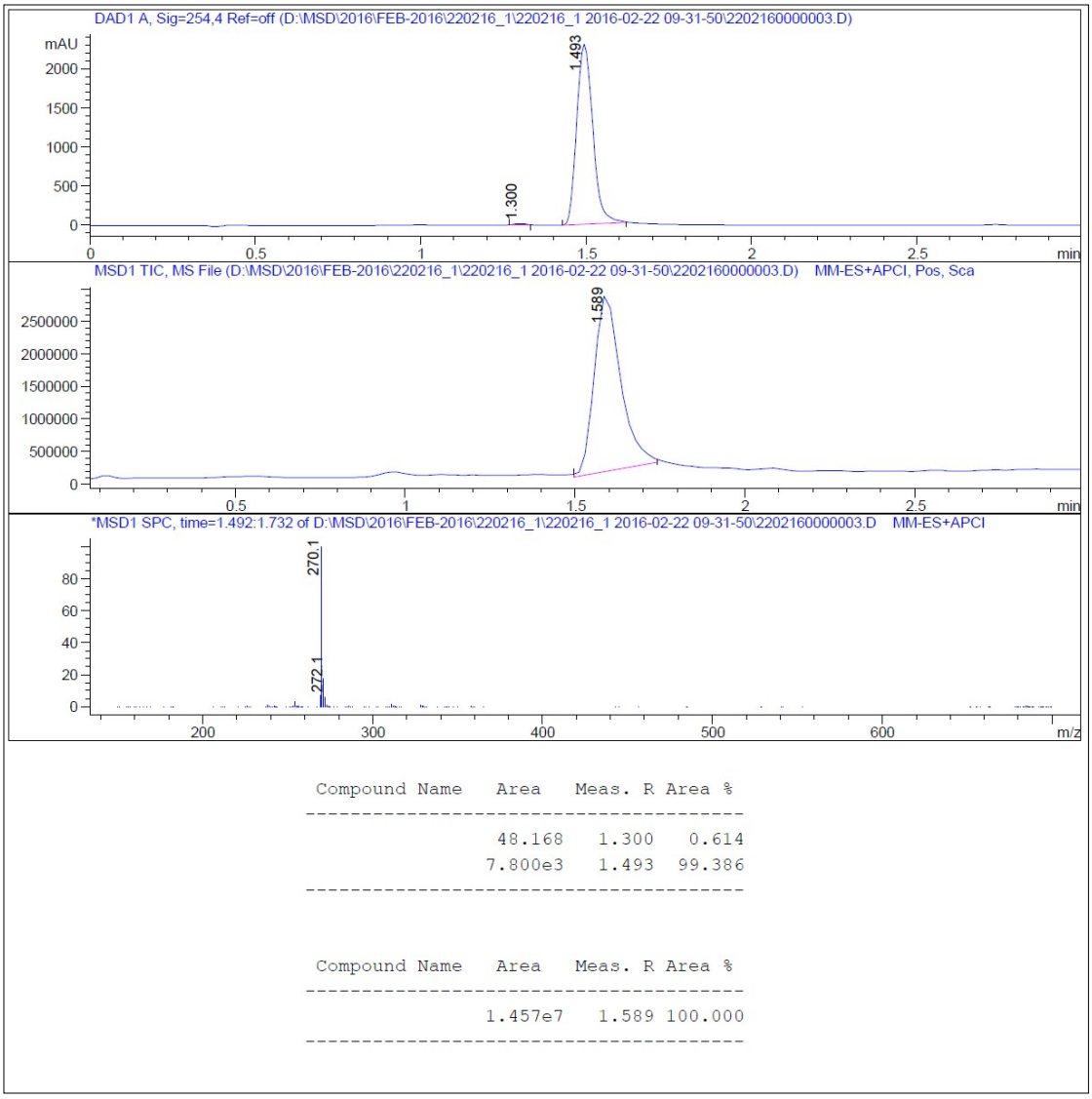
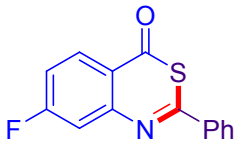


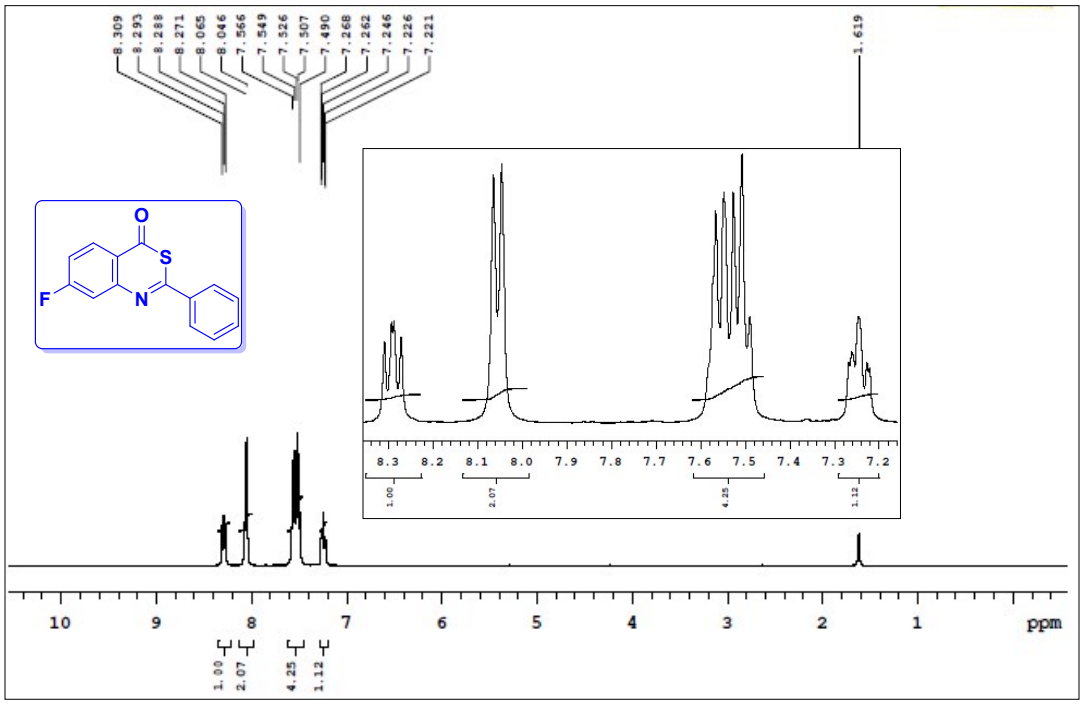
Figure 55. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **7ba** in $CDCl_3$ and LC-MS in Acetonitrile.

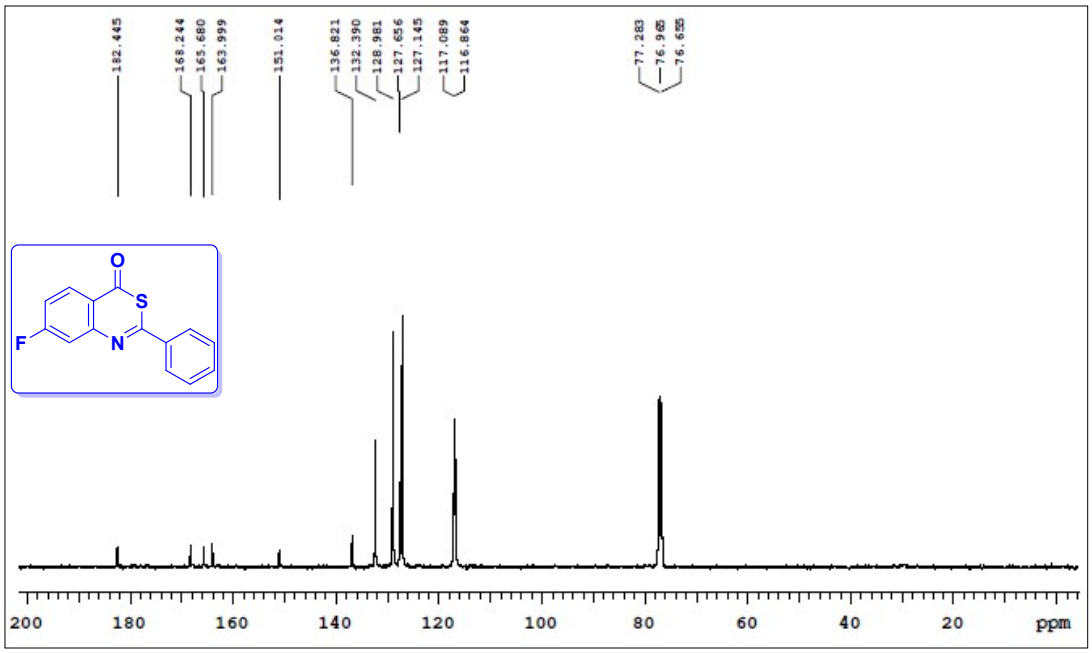
Off-white solid; $\mathbf{R_f}$ = 0.50 (SiO_2, Hexane/EtOAc = 3:1); **m.p** = 156 - 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 2H), 7.56 - 7.48 (m, 3H), 7.31 (d, *J* = 2.4 Hz, 1H), 7.08 (dd, *J* = 2.0 Hz, 7.2 Hz, 1H), 3.96 (s, 3H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ = 182.3, 165.4, 163.4, 151.0, 137.3, 132.0, 128.9, 127.0, 126.6, 117.5, 114.0, 112.9, 55.8 ppm; **MS** (APCI): $[M + 1]^+$ = 270.1 (99.38%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{15}H_{12}NO_2S$: 270.0588; found: 270.0585.

Synthesis of 7-fluoro-2-phenyl-4H-benzo[d][1,3]thiazin-4-one (7ca); new compound



According to the general procedure, reactions between 4-fluoroanthranilic acid **6c** (1.0 mmol, 155 mg), thiobenzamide **4a** (1.0 mmol, 137 mg), T3P (1.1 mmol, 349.8 mg) were performed to obtain the desired 7-fluoro-2-phenyl-4H-benzo[d][1,3]thiazin-4-one **7ca** in 60% (154 mg) yield as off-white solid.




182.445
168.244
165.680
163.999
151.014
136.821
132.390
128.981
127.656
127.145
117.089
116.864
77.283
76.965
76.655
O
S
N
F
200
180
160
140
120
100
80
60
40
20
ppm

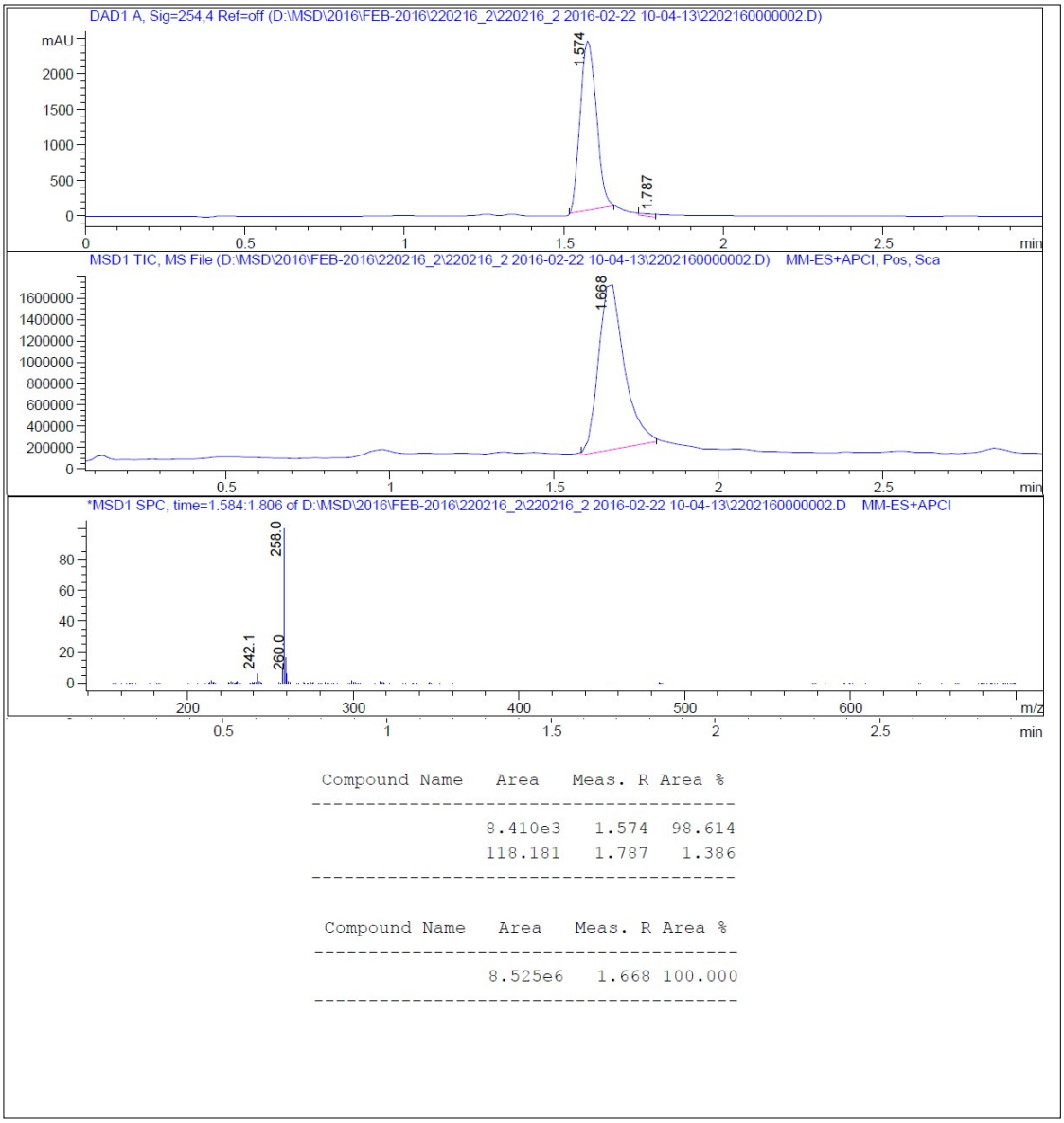


Figure 56. ^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra of **7ca** in $CDCl_3$ and LC-MS in Acetonitrile.

Off-white solid; $\mathbf{R_f}$ = 0.55 (SiO_2, Hexane/EtOAc = 3:1); **m.p** = 163 - 165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.28 (dt, *J* = 6.8 Hz, 2.0 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 6.8 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.26 - 7.22 (m, 1H) ppm; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ = 182.4, 166.9 (d, *J* = 256.40 Hz), 163.9, 151.0 (d, *J* = 13.24 Hz), 136.8, 132.3, 128.9, 127.6, 127.1, 116.9 (d, *J* = 22.5 Hz) ppm; **MS** (APCI): $[M + 1]^+$ = 258.0 (98.61%); **HRMS** (ESI, $[M + H]^+$): calculated for $C_{14}H_9FNOS$: 258.0388; found: 258.0385.

7. References

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(2) Csomós, P.; Fodor, L.; Csámpai, A.; Sohár, P. *Tetrahedron* **2010**, *66*, 3207.

(3) Sorkin, E.; Hinden, W. *Helv. Chim. Acta* **1949**, *32*, 63.

(4) Nishio, T.; Sekiguchi, H. *Heterocycles* **2002**, *58,* 203.

(5) Clausen, K.; Lawesson, S.-O. *Bull. Soc. Chim. Belg*. **2010**, *88*, 305.