

离子液体 **BmmimOAc** 催化 **2-芳氨基乙醇**与**二硫化碳**一步缩合合成**3-芳基-2-噻唑硫酮**

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BmmimOAc-Catalyzed Direct Condensation of 2-(Arylamino) Alcohols to Synthesize 3-Arylthiazolidine-2-thiones

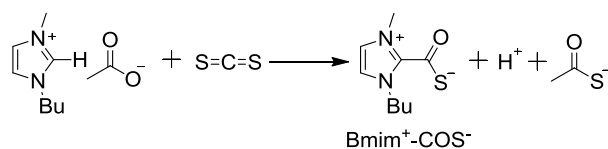
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S1 The reaction of ionic liquid BmimOAc with CS₂

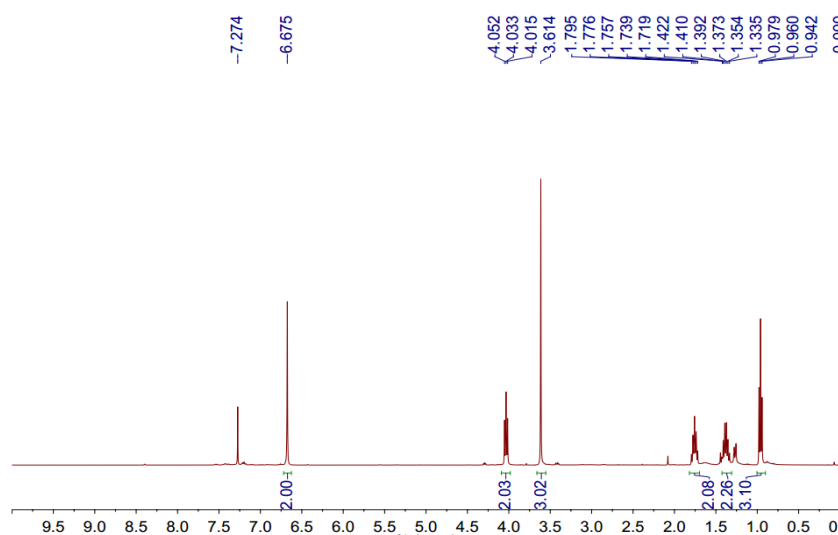


S2 ¹H and ¹³C NMR data of Bmim⁺-COS⁻

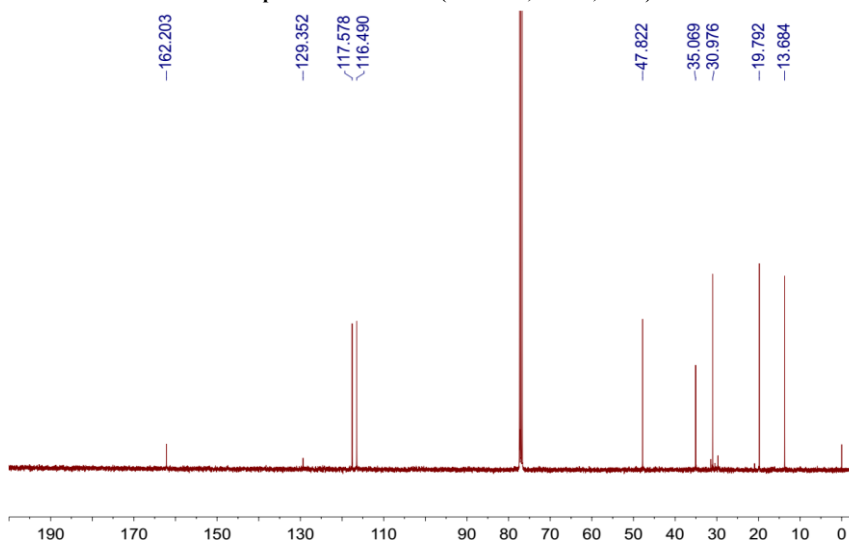
¹H NMR (400 MHz, CDCl₃, TMS) δ 6.68 (s, 2H), 4.03 (t, *J* = 7.4 Hz, 2H), 3.61 (s, 3H), 1.72–1.80 (m, 2H), 1.34–1.42 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 162.20, 129.35, 117.58, 116.49, 47.82, 35.07, 30.98, 19.79, 13.68.

S3 ¹H and ¹³C NMR spectra of Bmim⁺-COS⁻

Compound Bmim⁺-COS⁻ (¹H NMR, CDCl₃, TMS)



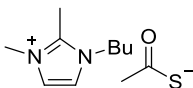
Compound Bmim⁺-COS⁻ (¹³C NMR, CDCl₃, TMS)



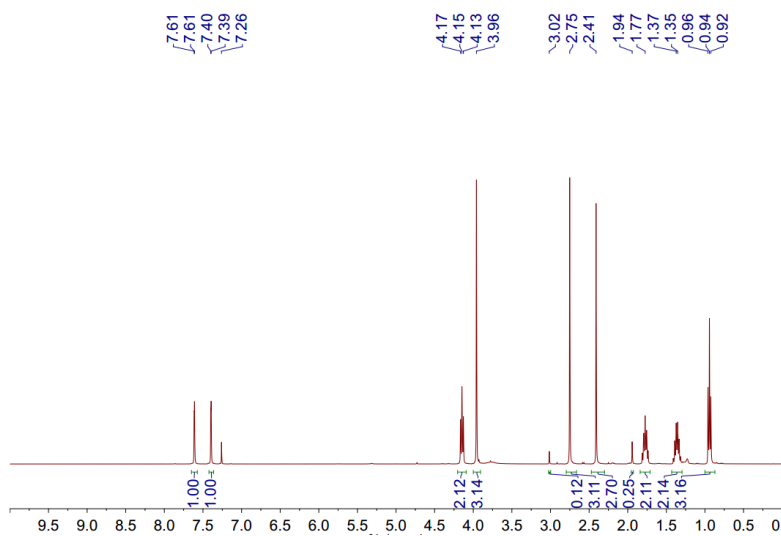
S4 The procedure for synthesis of ionic liquid BmmimCOS

BmmimOAc (4 mmol) in 100 mL round bottomed flask, CS₂ (200 mmol) was added. The mixture was stirred for 6 h under reflux conditions. The desired ionic liquid BmmimCOS was obtained after the residual CS₂ and generated product OCS were removed under reduced pressure distillation and structurally characterized by NMR spectroscopy and mass spectrometry.

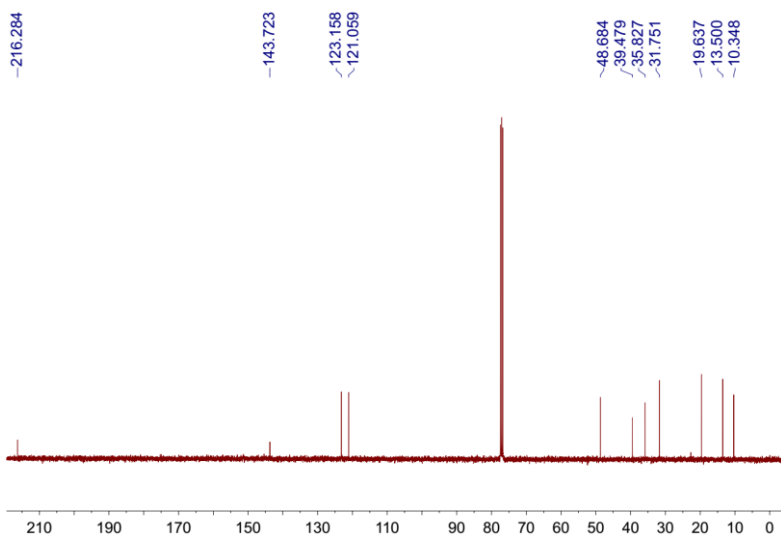
S5 ¹H and ¹³C NMR spectra of ionic liquid BmmimCOS



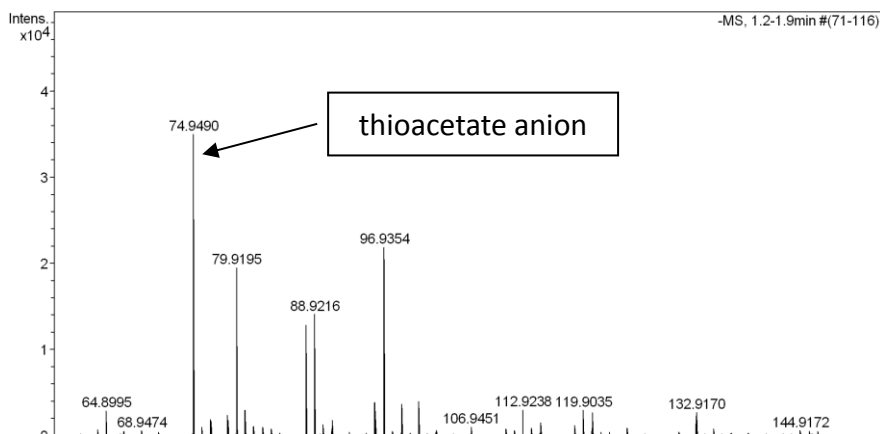
BmmimCOS (¹H NMR, CDCl₃, TMS)



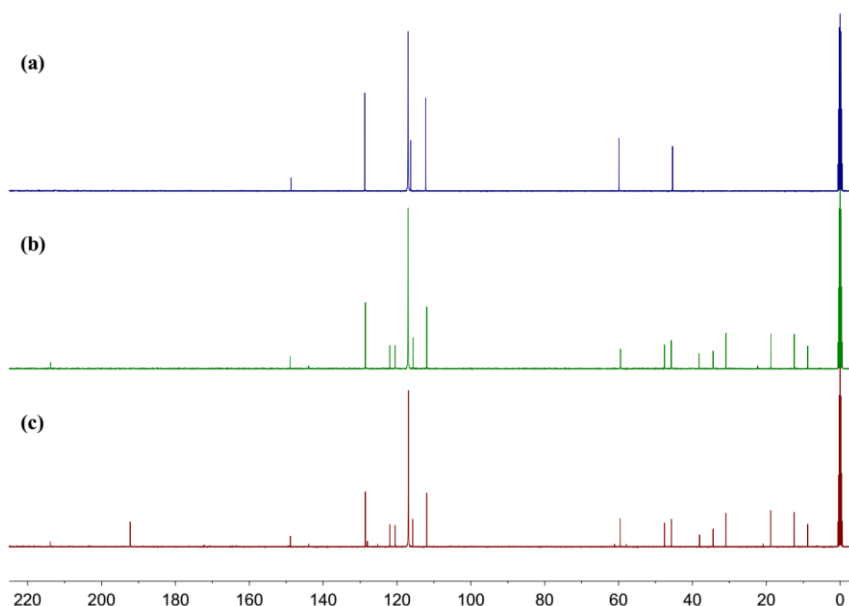
BmmimCOS (¹³C NMR, CDCl₃, TMS)



S6 Mass spectrum of thioacetate anion



S7 Chemical shift in the ¹³C NMR spectra of 2-(phenylamino) ethanol



Solvent: CD₃CN. (a) 2-(phenylamino) ethanol; (b) BmmimCOS : 2-(phenylamino) ethanol = 1 : 1; (c) CS₂ : BmmimCOS : 2-(phenylamino) ethanol = 5 : 1 : 1 (molar fraction).

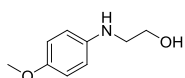
S8 General procedure for synthesis of (2-arylamino) alcohols

The synthetic approaches of 2-(arylamino) alcohols by using aryl amines with ethylene carbonate (EC) were reported^{1,2}; herein we use the ionic liquid 1-butyl-3-methylimidazolium bromide (BmimBr) as catalyst.

Aryl amines (60 mmol) in 50 mL round bottomed flask, EC (30 mmol), BmimBr (3 mmol, 5%, molar fraction) were added. The mixture was stirred at 130 °C for 3 h under nitrogen atmosphere. The reaction mixture was analyzed by a gas chromatograph. The pure compounds were isolated by chromatography on silica gel.

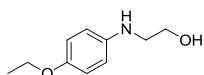
S9 ¹H NMR data of 2-(arylamino) alcohols

1. 2-(4-Methoxyphenylamino) ethanol



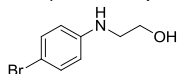
¹H NMR (400 MHz, CDCl₃, TMS) δ 6.79 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 2H), 3.79–3.81 (m, 2H), 3.75 (s, 3H), 3.24 (s, 2H).

2. 2-(4-Ethoxyphenylamino) ethanol



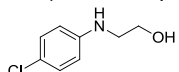
$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 6.79 (d, $J = 8.0$ Hz, 2H), 6.63 (d, $J = 8.0$ Hz, 2H), 3.94–3.99 (m, 2H), 3.81 (t, $J = 4.0$ Hz, 2H), 3.25 (t, $J = 4.0$ Hz, 2H), 1.38 (t, $J = 4.0$ Hz, 3H).

3. 2-(4-Bromophenylamino) ethanol



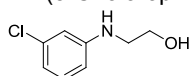
$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.25–7.29 (m, 2H), 6.52–6.56 (m, 2H), 3.83 (t, $J = 4.0$ Hz, 2H), 3.26 (t, $J = 4.0$ Hz, 2H).

4. 2-(4-Chlorophenylamino) ethanol



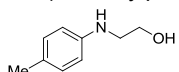
$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.12–7.14 (m, 2H), 6.57–6.59 (m, 2H), 3.82–3.85 (m, 2H), 3.26–3.28 (m, 2H).

5. 2-(3-Chlorophenylamino) ethanol



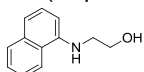
$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.08 (t, $J = 8.0$ Hz, 1H), 6.69 (d, $J = 8.0$ Hz, 1H), 6.62 (s, 1H), 6.50–6.53 (m, 1H), 3.83 (t, $J = 4.0$ Hz, 2H), 3.27 (t, $J = 4.0$ Hz, 2H).

6. 2-(4-Methylphenylamino) ethanol



$^1\text{H NMR}$ (400 MHz; CDCl_3) δ 7.00 (d, $J = 8.0$ Hz, 2H), 6.57 (d, $J = 8.0$ Hz, 2H), 3.77 (t, $J = 4.0$ Hz, 2H), 3.23 (t, $J = 4.0$ Hz, 2H), 2.24 (s, 3H).

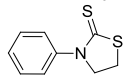
7. 2-(Naphthalene-4-ylamino) ethanol



$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.50–7.47 (m, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.31 (t, $J = 8.0$ Hz, 2H), 6.69 (d, $J = 8.0$ Hz, 1H), 4.0 (t, $J = 4.0$ Hz, 2H), 3.49 (t, $J = 4.0$ Hz, 2H).

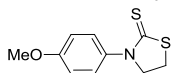
S10 ^1H and ^{13}C NMR data of 3-arylthiazolidine-2-thiones

1. 3-Phenylthiazolidine-2-thione (1a)



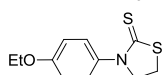
$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.41–7.48 (m, 4H), 7.35 (t, $J = 8.0$ Hz, 1H), 4.47 (t, $J = 8.0$ Hz, 2H), 3.46 (t, $J = 8.0$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , TMS) δ 198.06, 140.33, 129.30, 128.00, 125.77, 60.51, 28.45.

2. 3-(4-Methoxyphenyl)-thiazolidine-2-thione (1b)



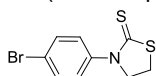
$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.33 (d, $J = 12.0$ Hz, 2H), 6.97 (d, $J = 12.0$ Hz, 2H), 4.42 (t, $J = 8.0$ Hz, 2H), 3.82 (s, 3H), 3.44 (t, $J = 8.0$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , TMS) δ 198.25, 159.19, 133.31, 127.36, 114.80, 60.98, 55.70, 28.49.

3. 3-(4-Ethoxyphenyl)-thiazolidine-2-thione (1c)



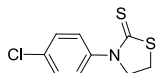
$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.31 (d, $J = 8.0$ Hz, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 4.42 (t, $J = 8.0$ Hz, 2H), 4.03 (t, $J = 8.0$ Hz, 2H), 3.43 (t, $J = 8.0$ Hz, 2H), 1.41 (t, $J = 8.0$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , TMS) δ 197.98, 158.42, 132.93, 127.12, 115.08, 63.75, 60.80, 28.29, 14.79.

4. 3-(4-Bromophenyl)-thiazolidine-2-thione (1d)



$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.60 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.46 (t, $J = 8.0$ Hz, 2H), 3.48 (t, $J = 8.0$ Hz, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3 , TMS) δ 198.42, 139.33, 132.51, 127.46, 121.60, 60.26, 28.50.

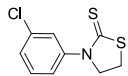
5. 3-(4-Chlorophenyl)-thiazolidine-2-thione (1e)



$^1\text{H NMR}$ (400 MHz, CDCl_3 , TMS) δ 7.36–7.43 (m, 4H), 4.45 (t, $J = 8.0$ Hz, 2H), 3.46 (t, $J = 8.0$ Hz, 2H); ^{13}C

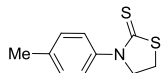
NMR (100 MHz, CDCl₃, TMS) δ 198.35, 138.67, 133.50, 129.42, 127.04, 60.16, 28.34.

6. 3-(3-Chlorophenyl)-thiazolidine-2-thione (1f)



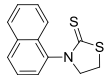
¹H NMR (CDCl₃; TMS) δ 7.31–7.44 (m, 4H), 4.45 (t, *J* = 6.0 Hz, 2H), 3.47 (t, *J* = 6.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 198.65, 141.47, 134.91, 130.37, 128.26, 126.19, 124.26, 60.35, 28.66.

7. 3-(4-Methylphenyl)-thiazolidine-2-thione (1g)



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.24–7.30 (m, 4H), 4.44 (t, *J* = 8.0 Hz, 2H), 3.45 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 198.07, 138.24, 137.92, 130.12, 125.72, 60.74, 28.51, 21.32.

8. 3-(Naphthalen-1-yl)-thiazolidine-2-thione (1h)



¹H NMR (400 MHz, CDCl₃, TMS) δ 7.70–7.86 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.38–7.48 (m, 4H), 4.31–4.42 (m, 2H), 3.56–3.63 (m, 1H), 3.43–3.49 (m, 1H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 198.91, 137.16, 134.66, 129.42, 128.90, 127.39, 126.77, 125.77, 125.43, 122.31, 60.73, 29.26.

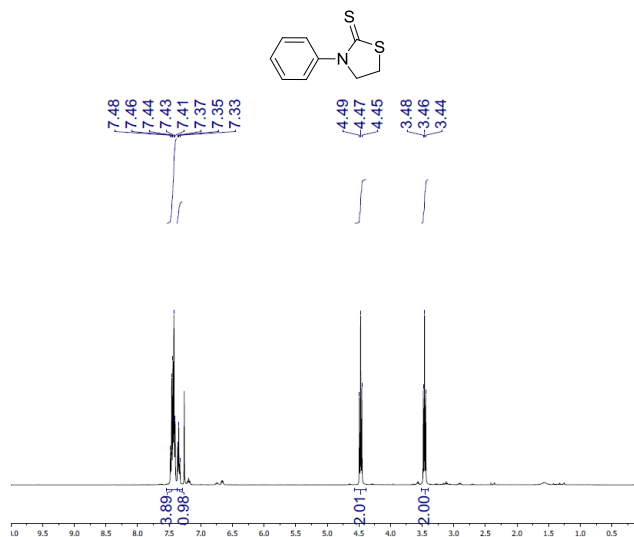
9. Thiazolidine-2-thione (1i)



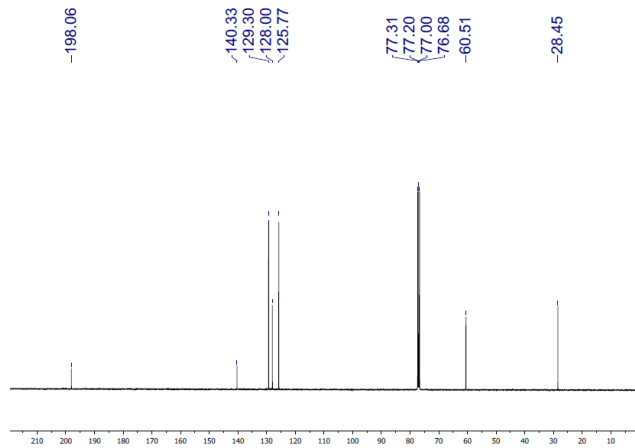
¹H NMR (CDCl₃; CDCl₃, TMS) δ 8.20 (s, 1H), 4.01 (t, *J* = 8.0 Hz, 2H), 3.58 (t, *J* = 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃, TMS) δ 201.94, 51.32, 33.73.

S11 ¹H and ¹³C NMR spectra of 3-arylthiazolidine-2-thiones

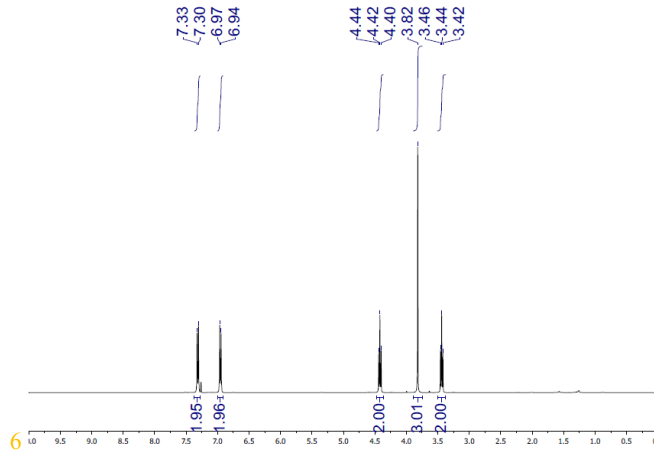
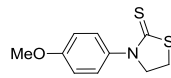
Compound 1a (¹H NMR, CDCl₃, TMS)



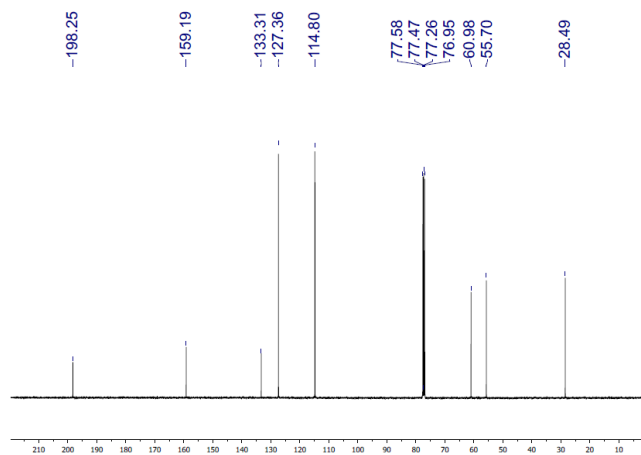
Compound 1a (¹³C NMR, CDCl₃, TMS)



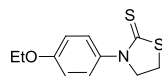
Compound 1b (¹H NMR, CDCl₃, TMS)

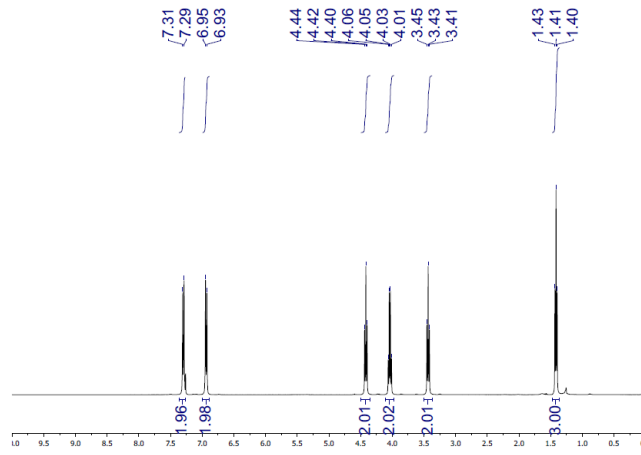


Compound 1b (¹³C NMR, CDCl₃, TMS)



Compound 1c (¹H NMR, CDCl₃, TMS)

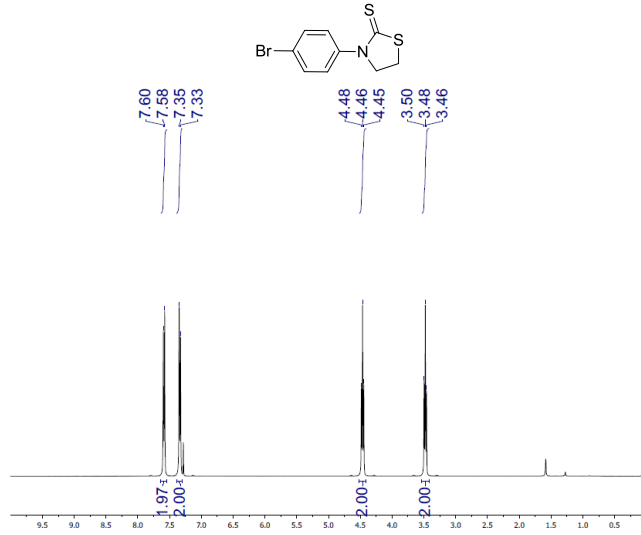




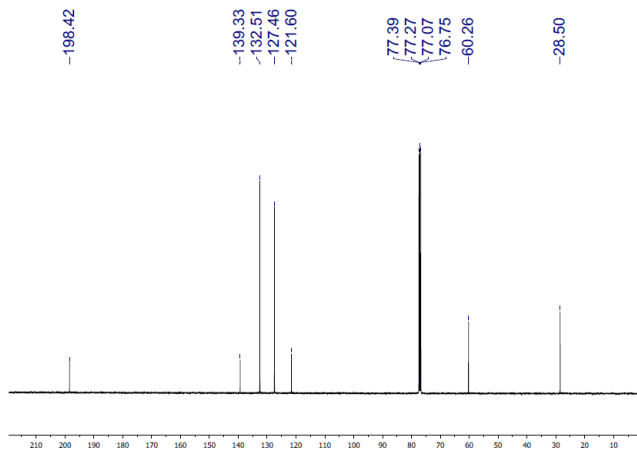
Compound 1c (^{13}C NMR, CDCl_3 , TMS)



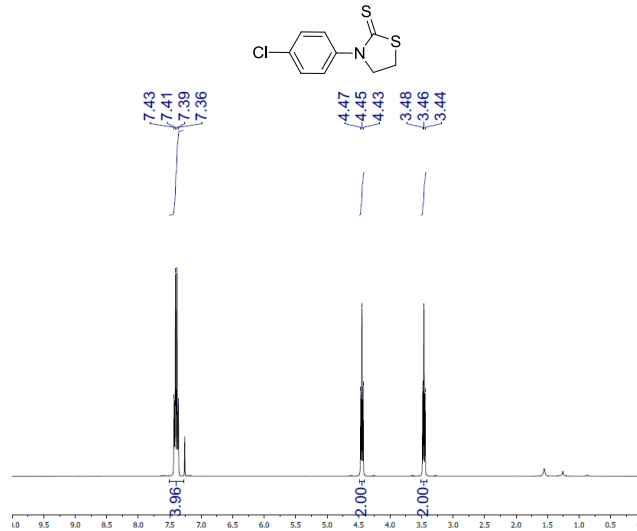
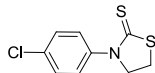
Compound 1d (^1H NMR, CDCl_3 , TMS)



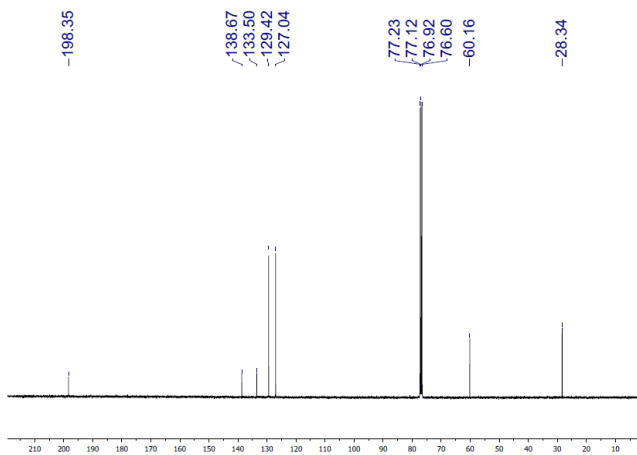
Compound 1d (¹³C NMR, CDCl₃, TMS)



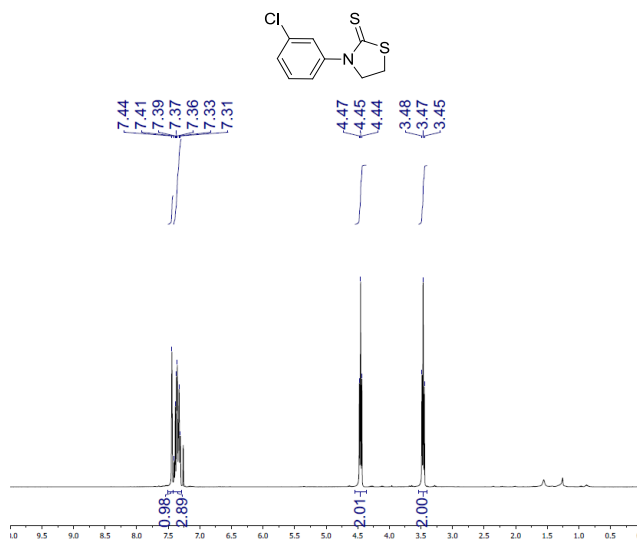
Compound 1e (¹H NMR, CDCl₃, TMS)



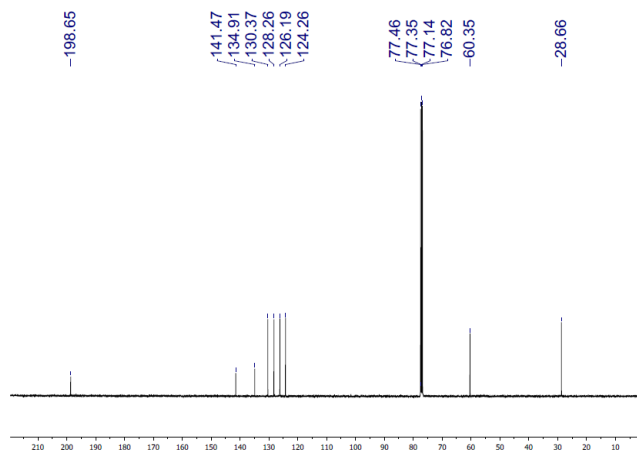
Compound 1e (¹³C NMR, CDCl₃, TMS)



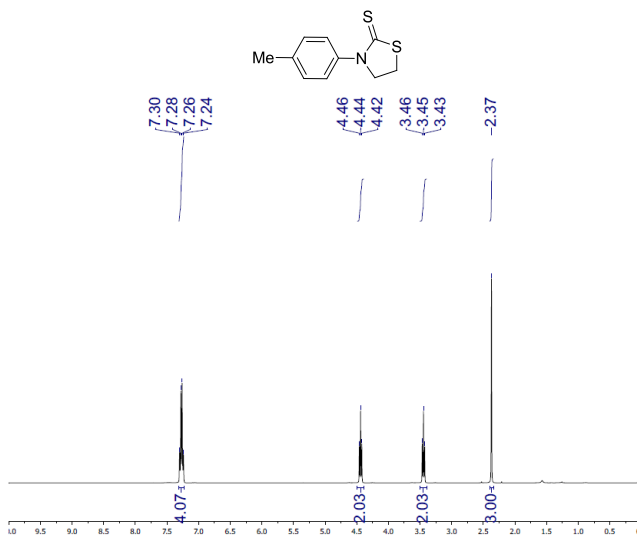
Compound 1f (¹H NMR, CDCl₃, TMS)



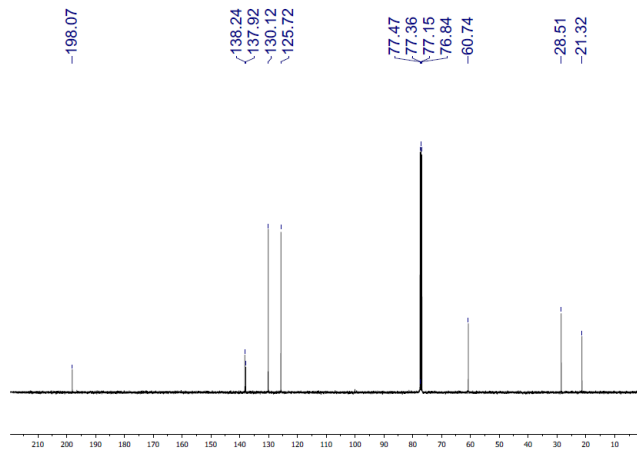
Compound 1f (¹³C NMR, CDCl₃, TMS)



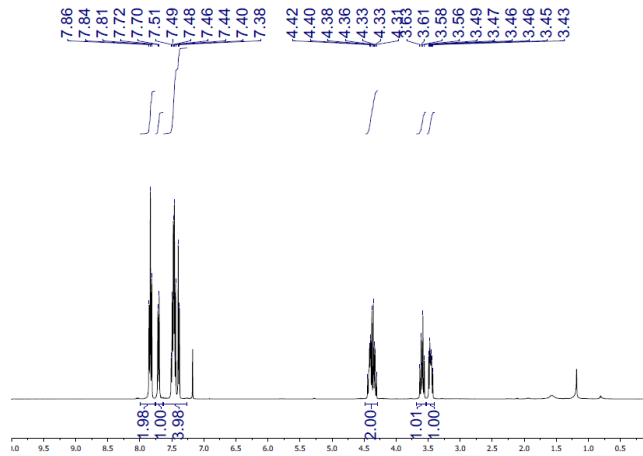
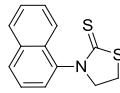
Compound 1g (¹H NMR, CDCl₃, TMS)



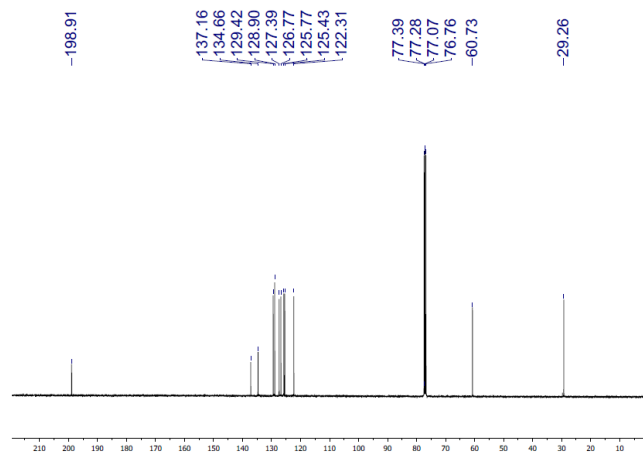
Compound 1g (¹³C NMR, CDCl₃, TMS)



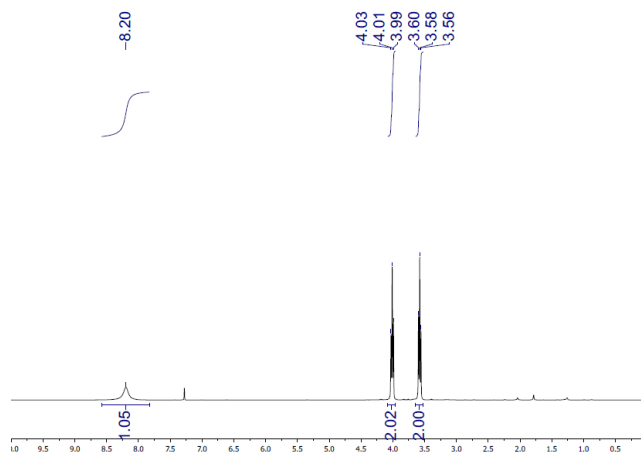
Compound 1h (¹H NMR, CDCl₃, TMS)



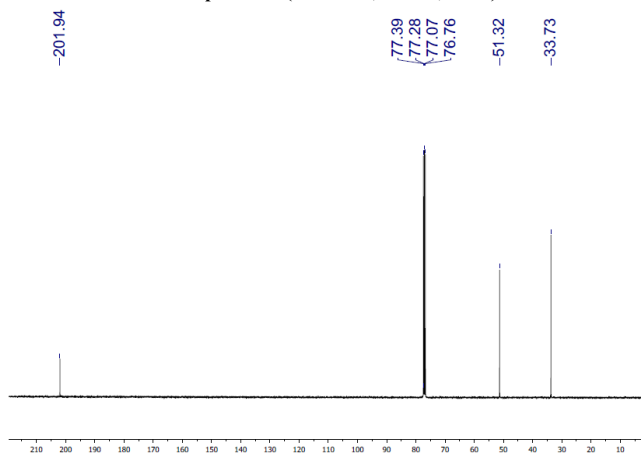
Compound 1h (¹³C NMR, CDCl₃, TMS)



Compound 1i (¹H NMR, CDCl₃, TMS)



Compound 1i (¹³C NMR, CDCl₃, TMS)



S12 References

- (1) Selva, M.; Perosa, A.; Fabris, M. *Green Chem.* **2008**, *10*, 1068. doi: 10.1039/B805436C
- (2) Liu, S.; Xie, J.; Li, W.; Kong, W.; Wang, L.; Zhou, Q. *Org. Lett.* **2009**, *11*, 4994. doi: 10.1021/ol901605a