Supporting Information

Synthesis of *β*-hydroxysulfides *via* visible-light-driven and EDA complex-promoted hydroxysulfenylation of styrenes with heterocyclic thiols in EtOH under photocatalyst-free conditions

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1. General information

General. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Inova-400 or Bruker-400 (400 MHz, 100 MHz and 376 MHz, respectively) spectrometer. ^{1}H and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0, DMSO-d_6 (δ(^{1}H), 2.50 ppm; δ(^{13}C), 39.52 ppm) or $CDCl_3$ (δ(^{1}H), 7.26 ppm; δ(^{13}C), 77.16 ppm). Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The HRMS analysis was obtained on a Bruker SolariX-70FT-MS mass spectrometer. X-ray single crystal diffraction data were collected on a Bruker D8 Venture. EPR spectra were recorded on a Bruker EMXPLUS spectrometer. The melting point was recorded on BÜCHI (M-560) and uncorrected. Optical absorption spectra were recorded on a Thermo Nanodrop 2000c UV/Vis spectrometer. The photocatalytic reactions were performed on WATTECS Parallel Light Reactor (WP-TEC-1020L). Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60 F254 plates and viewed by UV light (254 nm). Column chromatographic purification was performed using 200-300 mesh silica gel.

Materials. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Starting materials **2b-u**,[1] **2w**[2] are known compounds and synthesized according to the reported method.

The Light Source. Manufacturer： Xi'an WATTECS experimental equipment co. LTD

Figure S1. Light Reactor.

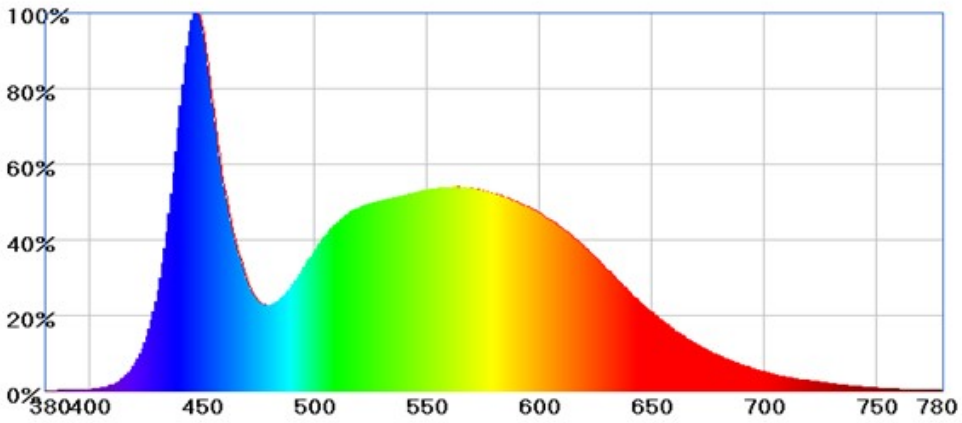
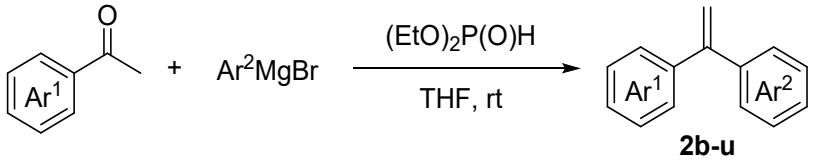


Figure S2. Emission spectrum of white LED light (6000-6500 K).

2. Experimental procedures

2.1 General procedure for synthesis of substrates

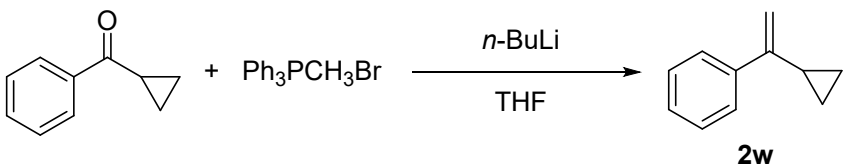
2.1.1 A typical procedure for the synthesis of 2b-u:



2b-u

Under a nitrogen atmosphere, a solution of Grignard reagents (8.8 mL, 1.0 M in THF, 8.8 mmol) was added dropwise to a solution of carbonyl compounds (4.0 mmol) in dry THF (15 mL) at room temperature. After 0.5 h stirring, diethylphosphite (0.62 mL, 4.8 mmol) was added. The reaction mixture was stirred and monitored by TLC analysis. After the reaction finished, the reaction was quenched with water and extracted with EtOAc (3×20 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered, and all the volatiles were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography.

2.1.2 A typical procedure for the synthesis of 2w:

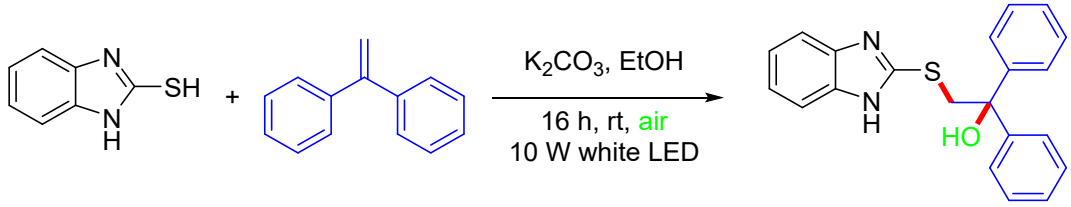


2w

To a flask charged with methyltriphenylphosphonium bromide (3.57 g, 10 mmol,

2 equiv.) and 30 mL of anhydrous THF at 0 °C was added *n*-butyllithium (4 mL, 2.5 M in hexanes, 10 mmol, 2 equiv.). The reaction was allowed to warm to room temperature spontaneously and then stirred for 1 h. Cyclopropyl(phenyl)methanone (5 mmol, 1 equiv.) in anhydrous THF (3 mL) was added dropwise, and the reaction was stirred for 12 h at 40 °C. After the reaction finished, the reaction was quenched with brine and extracted with EtOAc (3×20 mL). The combined organic layers were washed with water three times, dried (anhydrous $MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography to afford the desired product.

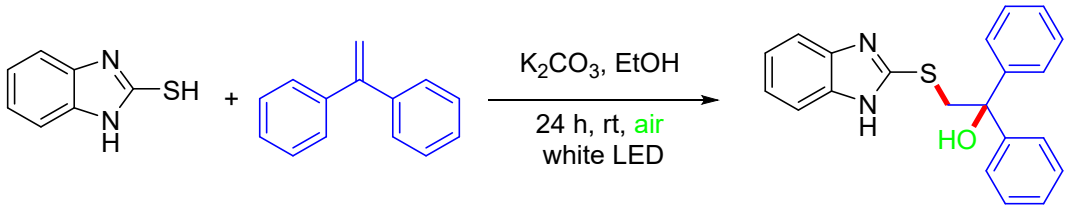
2.2 General procedure for the synthesis of products (taking 3a as an example)



1a **2a** **3a**

Under air, a mixture of 2-mercaptobenzoimidazole **1a** (90.1 mg, 0.6 mmol), 1,1-diphenylethylene **2a** (53 μL, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol) and C_2H_5OH (1.0 mL) were added to a 15 mL quartz tube. The reaction mixture was stirred and irradiated using 10 W white LED for 16 h. After the reaction finished, the resulting mixture were evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: DCM/CH_3OH = 250 : 1, v/v) to afford the desired product **3a** in 94% yield.

3. Gram-scale reaction



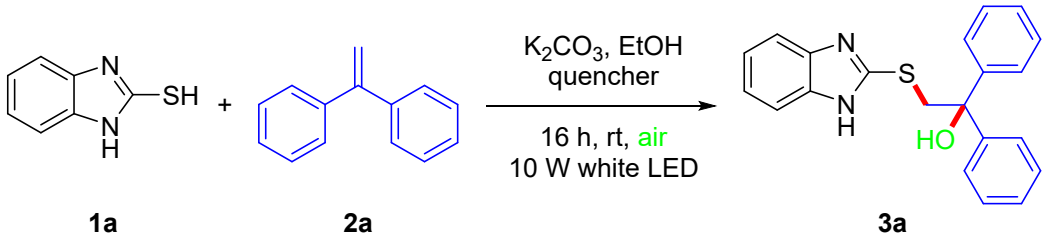
1a **2a** **3a** (90% yield with 1.9 g)

To a 100 mL round bottom flask with magnetic stirrer, 2-mercaptobenzoimidazole **1a** (1.80 g, 12 mmol), 1,1-diphenylethylene **2a** (1.06 mL, 6 mmol) and K_2CO_3 (414.63 mg, 3 mmol) were dissolved in C_2H_5OH (20 mL), and then the round bottom flask was stirred under the irradiation of white LED strip in open air at room temperature for 24

h. After the reaction finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: DCM/CH_3OH = 250 : 1, v/v) to afford the desired product **3a** in 90% yield.

4. Mechanistic studies

4.1 Radical trapping experiments



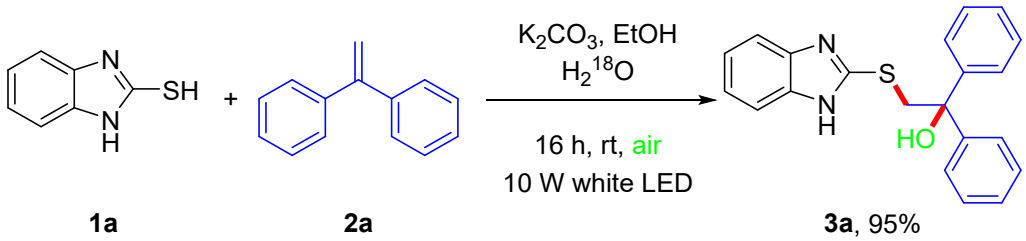
1a **2a** **3a**

Entry	Quencher	Yield of **3a** (%)	Conclusions
1	TEMPO (4 equiv.)	51	radical
2	BHT (4 equiv.)	44	radical
3	benzoquinone (2 equiv.)	0	superoxide radical

Under air, a mixture of 2-mercaptobenzoimidazole **1a** (90.1 mg, 0.6 mmol), 1,1-diphenylethylene **2a** (53 μL, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol), radical scavengers (4.0 equiv. or 2.0 equiv.) and C_2H_5OH (1.0 mL) were added to a 15 mL quartz tube. The reaction mixture was stirred and irradiated using 10 W white LED for 16 h. After the reaction finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: DCM/CH_3OH = 250 : 1, v/v) to afford the desired product **3a**.

4.2 Isotope labeling experiments

4.2.1 Isotope labeling experiment with $H_2{}^{18}O$



1a **2a** **3a**, 95%

Under air, a mixture of 2-mercaptobenzoimidazole **1a** (90.1 mg, 0.6 mmol), 1,1-diphenylethylene **2a** (53 μL, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol), $H_2{}^{18}O$ (10 equiv.) and C_2H_5OH (1.0 mL) were added to a 15 mL quartz tube. The reaction mixture

was stirred and irradiated using 10 W white LED for 16 h. After the reaction finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: DCM/CH_3OH = 250 : 1, v/v) to afford the desired product **3a** in 95% yield. Then the product was analyzed by HRMS.

HRMS of **3a**: calcd. for $C_{21}H_{19}N_2OS$ $[M+H]^+$: 347.1213; found 347.1219.

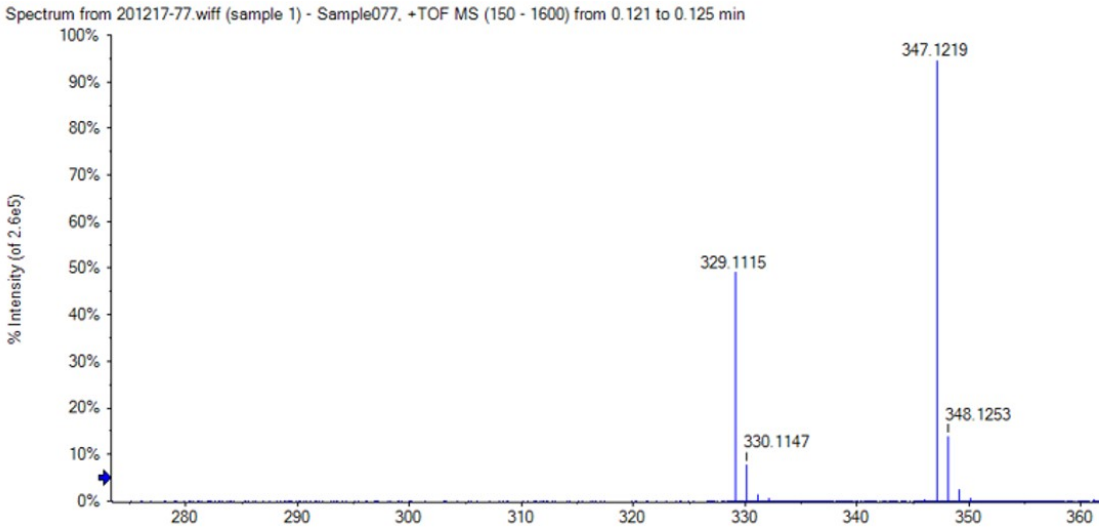
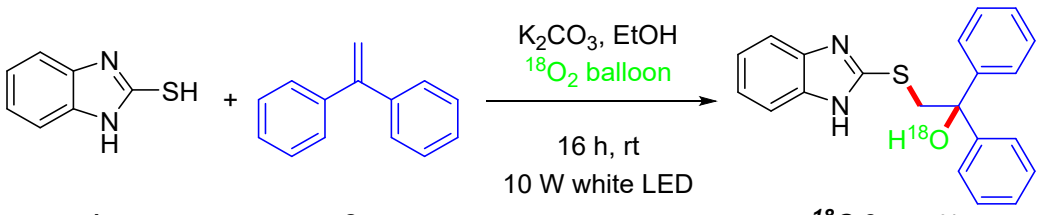


Figure S3. HRMS of **3a**.

4.2.2 Isotope labeling experiment with $^{18}O_2$



1a **2a** ***^{18}O*-3a**, 94%

A mixture of 2-mercaptobenzoimidazole **1a** (90.1 mg, 0.6 mmol), 1,1-diphenylethylene **2a** (53 μL, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol) and C_2H_5OH (1.0 mL) were added to a 15 mL quartz tube. Then the reaction tube was equipped with a $^{18}O_2$ balloon. The reaction mixture was stirred and irradiated using 10 W white LED for 16 h. After the reaction finished, the resulting mixture was evaporated under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: DCM/CH_3OH = 250 : 1, v/v) to afford the desired product ***^{18}O*-3a** in 94% yield. Then the product was analyzed by HRMS.

HRMS of ***^{18}O*-3a**: calcd. for $C_{21}H_{19}N_2{}^{18}OS$ $[M+H]^+$: 349.1255; found 349.1262.

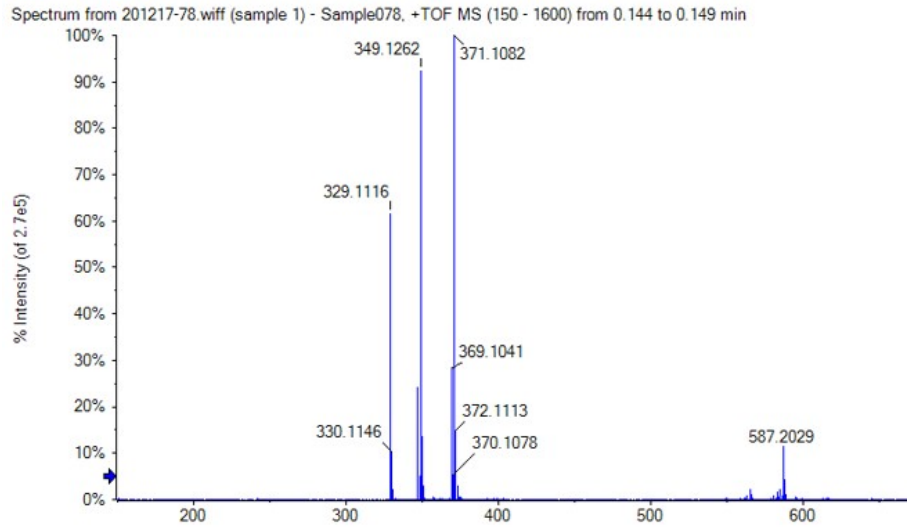


Figure S4. HRMS of ***[18]O*-3a**.

4.3 UV−vis spectroscopic measurements

The UV/vis absorption spectra of 2-mercaptobenzoimidazole **1a** (0.06 M), 1,1-diphenylethylene **2a** (0.03 M) with and K_2CO_3 (0.015 M) in EtOH were recorded in 1 cm path quartz cuvettes by using a Thermo Nanodrop 2000c UV/Vis spectrophotometer, respectively (Figure S5).

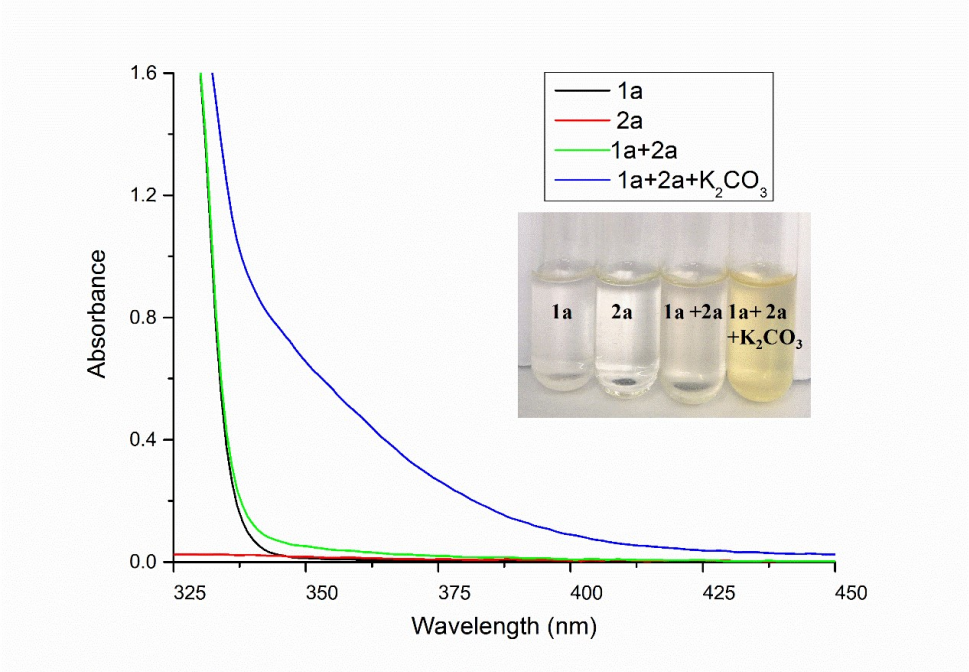


Figure S5. UV−vis spectroscopic measurements on various combinations of **1a**, **2a**, and K_2CO_3 in EtOH.

4.4 ^{1}H NMR experiments

^{1}H NMR experiments were performed by the preparation of DMSO-d_6 solutions containing 2-mercaptobenzimidazole (**1a**), 1,1-diphenylethylene (**2a**) and K_2CO_3 in different ratios, keeping constant the amount of 1,1-diphenylethylene (0.15 mol/L) and increasing the amount of **1a** and K_2CO_3 (**1a** : K_2CO_3 : **2a** = 0 : 0 : 1, 1 : 1 : 1, 2 : 2 : 1, 3 : 3 : 1, 4 : 4 : 1 and 5 : 5 : 1). The figure S6 shows the full spectras collected. The evidence of interaction between **1a** and **2a** is highlighted in figure S7, where is possible to observe the change in the chemical shifts of 1,1-diphenylethylene **2a** shifted upfield with increasing amounts of **1a** and K_2CO_3.

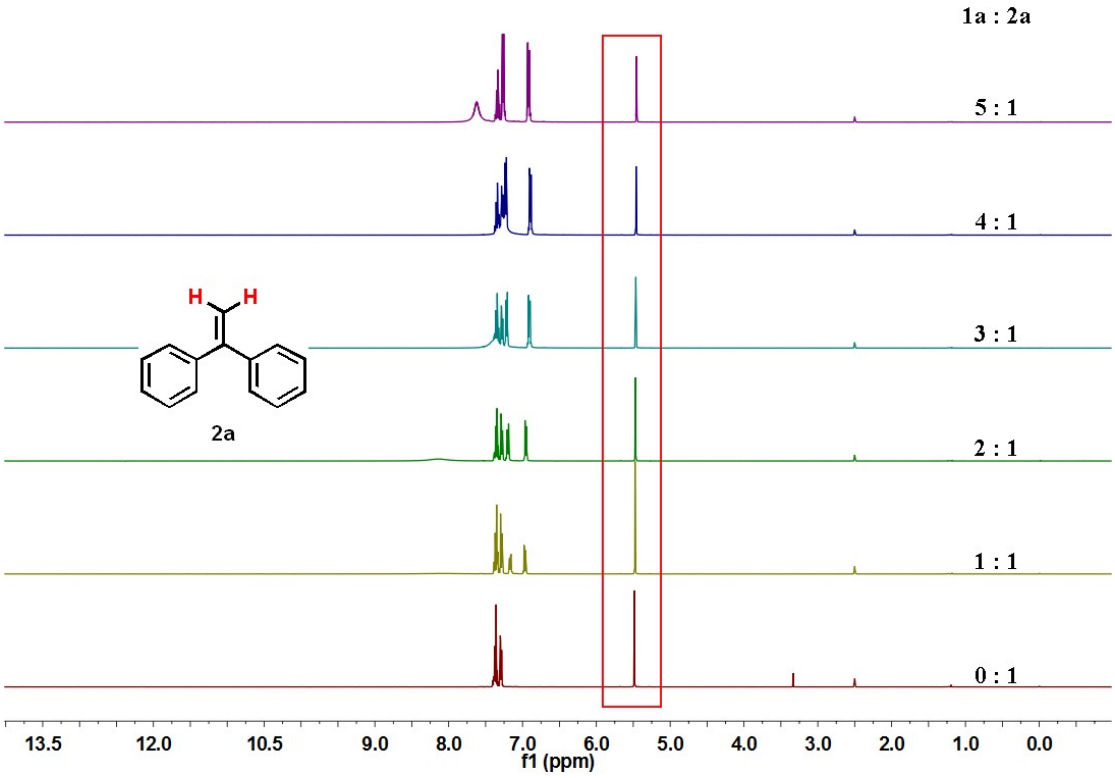


Figure S6. Solutions of **1a** and **2a** examined by the ^{1}H NMR.

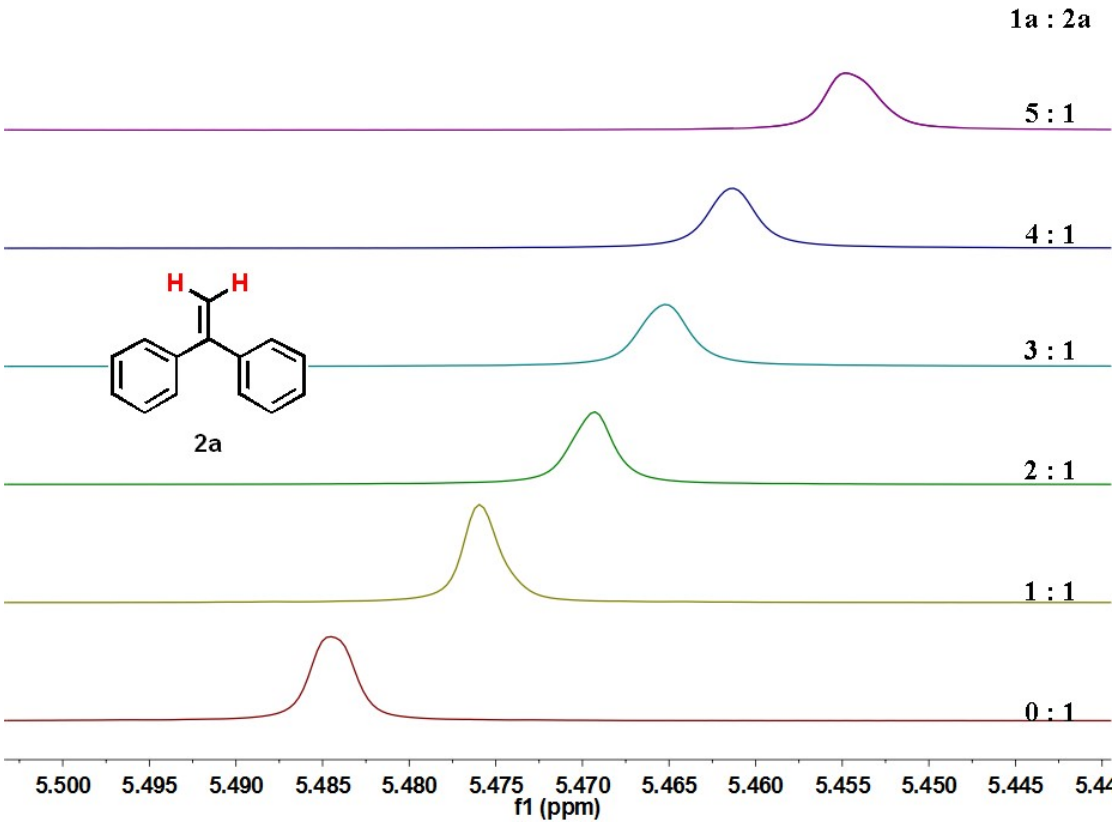


Figure S7. Evidence for the formation of EDA complex through ^{1}H NMR.

4.5 EPR experiments

(A) Standard conditions: A mixture of 2-mercaptobenzoimidazole **1a** (90.1 mg, 0.6 mmol), 1,1-diphenylethylene **2a** (53 μL, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol), C_2H_5OH (1.0 mL) and DMPO (12 μL) was open to air and stirred under the irradiation of 10 W white LED at room temperature for 30 min. Afterwards, this mixture was analyzed by EPR.

(B) Without visible-light irration: A mixture of 2-mercaptobenzoimidazole **1a** (90.1 mg, 0.6 mmol), 1,1-diphenylethylene **2a** (53 μL, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol), C_2H_5OH (1.0 mL) and DMPO (12 μL) was open to air and stirred at room temperature for 30 min. Afterwards, this mixture was analyzed by EPR.

(C) N_2 atmosphere: Under N_2, a mixture of 2-mercaptobenzoimidazole **1a** (90.1 mg, 0.6 mmol), 1,1-diphenylethylene **2a** (53 μL, 0.3 mmol), K_2CO_3 (20.7 mg, 0.15 mmol), C_2H_5OH (1.0 mL) and DMPO (12 μL) was stirred under the irradiation of 10 W white LED at room temperature for 30 min. Afterwards, this mixture was analyzed by EPR.

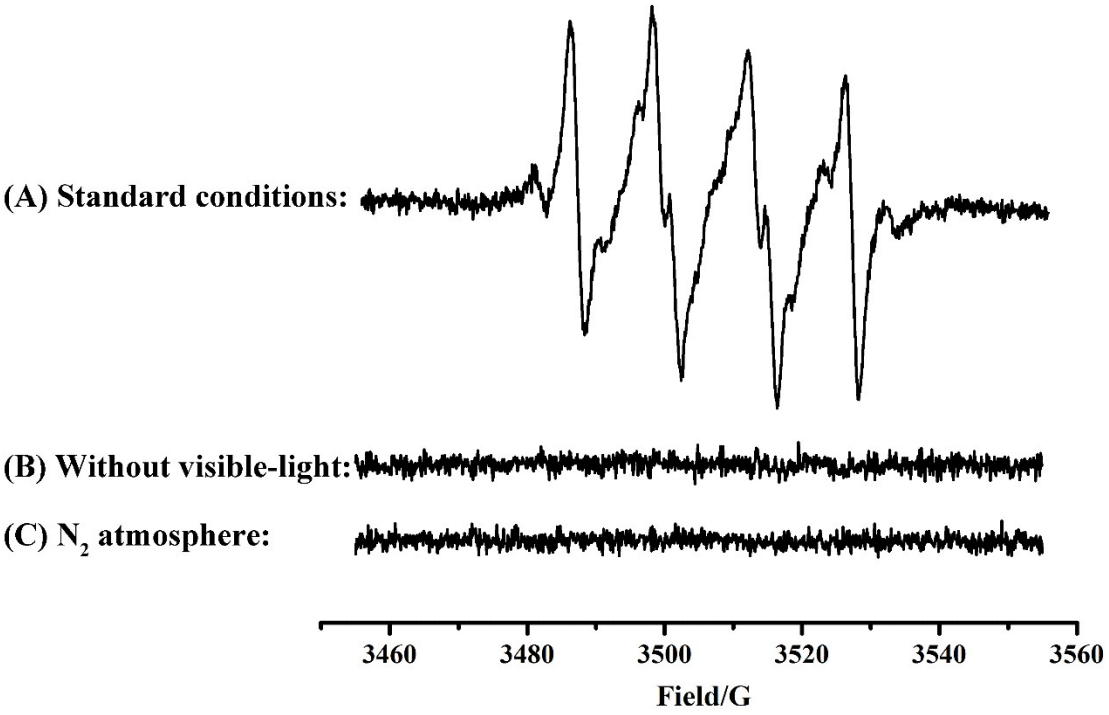
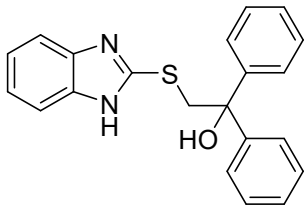
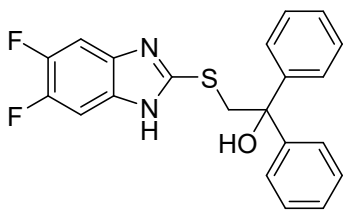


Figure S8. EPR experiments.

5. Characterization of Products

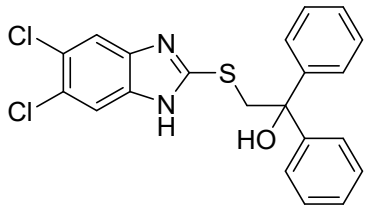


2-((*1H*-benzo[*d*]imidazol-2-yl)thio)-1,1-diphenylethan-1-ol (3a): 97.9 mg, 94% yield. White solid. m.p.: 292.7-293.2 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.49 (s, 1H), 7.56-7.54 (m, 4H), 7.42 (s, 2H), 7.31 (t, J = 7.4 Hz, 4H), 7.20 (t, J = 7.3 Hz, 2H), 7.13-7.09 (m, 2H), 6.64 (s, 1H), 4.34 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.6, 146.7, 127.9(8), 126.7, 125.9, 121.4, 76.5, 43.8. **HRMS** (ESI) m/z Calcd for $C_{21}H_{19}N_2OS$ $[M+H]^+$: 347.1213; Found: 347.1209.

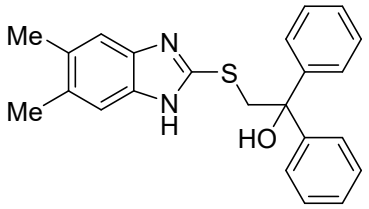


2-((5,6-difluoro-1*H*-benzo[*d*]imidazol-2-yl)thio)-1,1-diphenylethan-1-ol (3b):

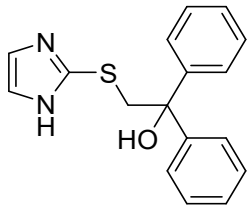
103.4 mg, 90% yield. Light yellow solid. m.p.: 177.5-178.8 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.70 (s, 1H), 7.62-7.57 (m, 1H), 7.54 (d, J = 7.9 Hz, 4H), 7.44-7.40 (m, 1H), 7.31 (t, J = 7.4 Hz, 4H), 7.21 (t, J = 7.2 Hz, 2H), 6.49 (s, 1H), 4.35 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.5, 146.5, 146.2 (dd, J = 235.0, 14.0 Hz), 138.9 (d, J = 9.0 Hz), 130.7 (d, J = 13.0 Hz), 127.9(8), 126.8, 125.8, 104.7 (d, J = 21.0 Hz), 98.5 (d, J = 22.0 Hz), 76.3, 43.9(5). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -145.18 (d, J = 23.3 Hz), -146.27 (d, J = 23.3 Hz). **HRMS** (ESI) m/z Calcd for $C_{21}H_{17}F_2N_2OS$ $[M+H]^+$: 383.1024; Found: 383.1028.



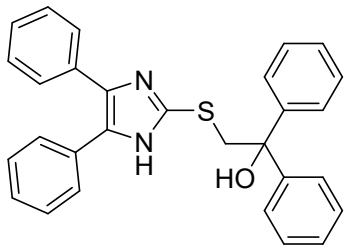
2-((5,6-dichloro-1*H*-benzo[*d*]imidazol-2-yl)thio)-1,1-diphenylethan-1-ol (3c): 120.5 mg, 97% yield. White solid. m.p.: 147.9-149.8 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.77 (s, 1H), 7.68 (s, 2H), 7.54-7.51 (m, 4H), 7.33-7.29 (m, 4H), 7.23-7.18 (m, 2H), 6.42 (s, 1H), 4.35 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 155.0, 146.5, 128.1, 126.8, 125.9, 123.8, 76.3, 43.9. **HRMS** (ESI) m/z Calcd for $C_{21}H_{17}Cl_2N_2OS$ $[M+H]^+$: 415.0433; Found: 415.0447.



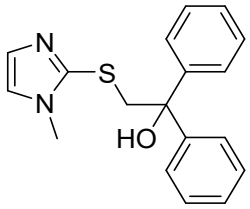
2-((5,6-dimethyl-1*H*-benzo[*d*]imidazol-2-yl)thio)-1,1-diphenylethan-1-ol (3d): 106.7 mg, 95% yield. White solid. m.p.:160.9-163.3 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.24 (s, 1H), 7.56-7.54 (m, 4H), 7.30 (t, J = 7.4 Hz, 5H), 7.21-7.17 (m, 2H), 7.11 (s, 1H), 6.75 (s, 1H), 4.29 (s, 2H), 2.27 (s, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.2, 146.8, 127.9, 126.7, 125.9, 76.6, 43.9, 19.9. **HRMS** (ESI) m/z Calcd for $C_{23}H_{23}N_2OS$ $[M+H]^+$: 375.1526; Found: 375.1516.



2-((1*H*-imidazol-2-yl)thio)-1,1-diphenylethan-1-ol (3e): 66.0 mg, 74% yield. White solid. m.p.: 156.4-158.3 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.20 (s, 1H), 7.52 (d, J = 7.4 Hz, 4H), 7.28 (t, J = 7.4 Hz, 4H), 7.18 (t, J = 7.3 Hz, 2H), 7.03 (s, 2H), 4.05 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.0, 140.9, 127.9, 126.5, 125.9, 76.8, 45.1. **HRMS** (ESI) m/z Calcd for $C_{17}H_{17}N_2OS$ $[M+H]^+$: 297.1056; Found:297.1067.

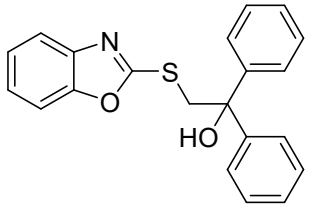


2-((4,5-diphenyl-1*H*-imidazol-2-yl)thio)-1,1-diphenylethan-1-ol (3f): 127.6 mg, 95% yield. White solid. m.p.: 90.3-92.6 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.46 (s, 1H), 7.56-7.53 (m, 4H), 7.48-7.45 (m, 2H), 7.38-7.36 (m, 4H), 7.33-7.28 (m, 7H), 7.24-7.17 (m, 3H), 6.88 (s, 1H), 4.17 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 146.9, 141.8, 136.5, 134.7, 130.7, 128.7, 128.3, 128.2, 127.9, 127.8, 127.6, 126.9, 126.7, 126.6, 125.9(8), 76.8, 44.8. **HRMS** (ESI) m/z Calcd for $C_{29}H_{25}N_2OS$ $[M+H]^+$: 449.1682; Found: 449.1680.

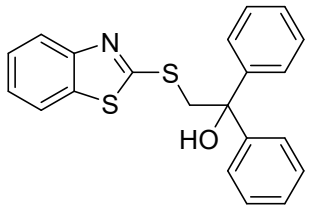


2-((1-methyl-1*H*-imidazol-2-yl)thio)-1,1-diphenylethan-1-ol (3g): 49.6 mg, 53% yield. White solid. m.p.: 161.8-163.7 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.50-7.47 (m, 4H), 7.29-7.25 (m, 4H), 7.20-7.15 (m, 3H), 6.92 (d, J = 1.2 Hz, 1H), 6.79 (s, 1H), 4.02 (s, 2H), 3.39 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 146.9, 141.9, 127.8(4), 127.8(0), 126.5, 125.9, 122.9, 76.8, 46.0, 32.8. **HRMS** (ESI) m/z Calcd for

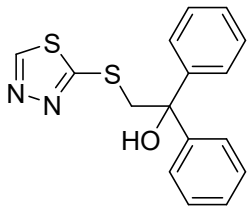
$C_{18}H_{19}N_2OS$ $[M+H]^+$: 311.1213; Found: 311.1214.



2-(benzo[*d*]oxazol-2-ylthio)-1,1-diphenylethan-1-ol (3h): 87.4 mg, 84% yield. White solid. m.p.: 113.7-115.1 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.64-7.59 (m, 2H), 7.56-7.53 (m, 4H), 7.35-7.29 (m, 6H), 7.24-7.19 (m, 2H), 6.43 (s, 1H), 4.42 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 165.1, 151.2, 146.0, 141.3, 128.1, 126.9, 125.8, 124.5, 124.1, 118.1, 110.1, 75.9(9), 44.8. **HRMS** (ESI) m/z Calcd for $C_{21}H_{17}NO_2SNa$ $[M+Na]^+$: 370.0872; Found: 370.0871.

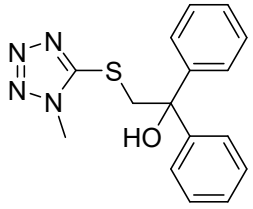


2-(benzo[*d*]thiazol-2-ylthio)-1,1-diphenylethan-1-ol (3i): 65.9 mg, 60% yield. White solid. m.p.: 105.8-108.0 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.97 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 7.5 Hz, 4H), 7.47-7.43 (m, 1H), 7.36-7.30 (m 5H), 7.22 (t, J = 7.4 Hz, 2H), 6.40 (s, 1H), 4.43 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 167.5, 152.6, 146.2, 134.5, 128.0, 126.9, 126.3, 125.8, 124.3, 121.7, 120.9(5), 76.2, 45.6. **HRMS** (ESI) m/z Calcd for $C_{21}H_{18}NOS_2$ $[M+H]^+$: 364.0824; Found: 364.0825.

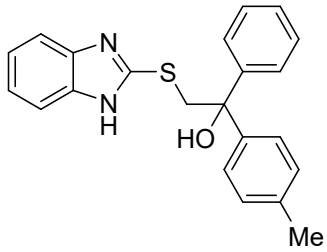


2-((1,3,4-thiadiazol-2-yl)thio)-1,1-diphenylethan-1-ol (3j): 69.5 mg, 74% yield. White solid. m.p.: 170.5-172.6 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.45 (s, 1H), 7.53-7.50 (m, 4H), 7.33-7.29 (m, 4H), 7.23-7.19 (m, 2H), 6.36 (s, 1H), 4.37 (s, 2H). **^{13}C**

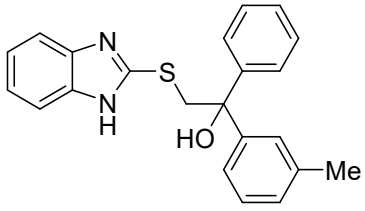
NMR (100 MHz, DMSO-d_6) δ 166.5, 153.6, 146.1, 128.0, 126.9, 125.8, 76.2, 46.7. **HRMS** (ESI) m/z Calcd for $C_{16}H_{15}N_2OS_2$ $[M+H]^+$: 315.0621; Found: 315.0627.



2-((2-methyl-2*H*-tetrazol-5-yl)thio)-1,1-diphenylethan-1-ol (3k): 74.1 mg, 79% yield. White solid. m.p.: 106.9-109.2 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.51-7.48 (m, 4H), 7.32-7.27 (m, 4H), 7.23-7.18 (m, 2H), 6.32 (s, 1H), 4.31 (s, 2H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 154.3, 145.9, 128.0, 126.9, 125.8, 76.1, 46.2, 33.5. **HRMS** (ESI) m/z Calcd for $C_{16}H_{16}N_4OSNa$ $[M+Na]^+$: 335.0943; Found: 335.0942.

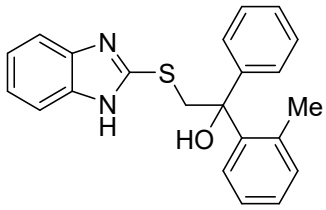


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-phenyl-1-(*p*-tolyl)ethan-1-ol (4a): 92.3 mg, 85% yield. White solid. m.p.: 144.4-146.0 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 7.54-7.50 (m, 3H), 7.42 (d, J = 8.2 Hz, 2H), 7.34-7.28 (m, 3H), 7.21-7.17 (m, 1H), 7.13-7.08 (m, 4H), 6.54 (s, 1H), 4.30 (s, 2H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.7, 146.9, 143.8, 135.8, 128.5, 127.9(5), 126.7, 125.8, 121.4, 117.1, 110.3, 76.4, 43.9(5), 20.6. **HRMS** (ESI) m/z Calcd for $C_{22}H_{21}N_2OS$ $[M+H]^+$: 361.1369; Found: 361.1364.

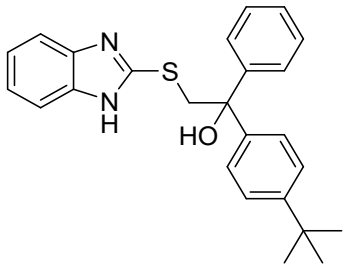


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-phenyl-1-(*m*-tolyl)ethan-1-ol (4b): 94.6 mg, 88% yield. White solid. m.p.: 152.3-153.4 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.43 (s, 1H), 7.55-7.50 (m, 3H), 7.37 (s, 1H), 7.34-7.28 (m, 4H), 7.21-7.16 (m, 2H),

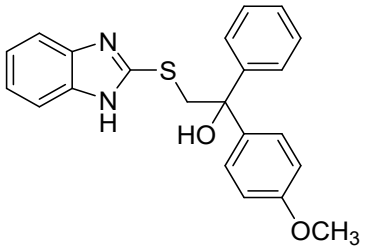
7.13-7.08 (m, 2H), 7.01 (d, J = 7.4 Hz, 1H), 6.54 (s, 1H), 4.31 (s, 2H), 2.26 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.6, 146.7, 146.6, 143.4, 136.9, 135.4, 127.9, 127.8(5), 127.3, 126.6, 126.4, 125.8, 122.9(8), 121.5, 121.2, 117.1, 110.2, 76.4, 43.9, 21.3. **HRMS** (ESI) m/z Calcd for $C_{22}H_{21}N_2OS$ $[M+H]^+$: 361.1369; Found: 361.1364.



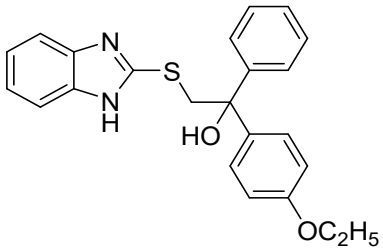
2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-phenyl-1-(*o*-tolyl)ethan-1-ol (4c): 103.0 mg, 95% yield. White solid. m.p.: 143.3-145.1 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.46 (s, 1H), 7.74 (dd, J = 7.8, 1.3 Hz, 1H), 7.50 (s, 1H), 7.37-7.32 (m, 3H), 7.30-7.23 (m, 3H), 7.22-7.17 (m, 2H), 7.12-7.06 (m, 3H), 6.44 (s, 1H), 4.36 (d, J = 12.6 Hz, 1H), 4.21 (d, J = 12.5 Hz, 1H), 2.02 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.5, 145.7, 143.3, 137.1, 132.2, 127.6, 127.4, 126.6, 126.3, 126.1, 125.1, 121.3, 76.9, 45.3, 21.3. **HRMS** (ESI) m/z Calcd for $C_{22}H_{20}N_2OSNa$ $[M+Na]^+$: 383.1189; Found: 383.1188.



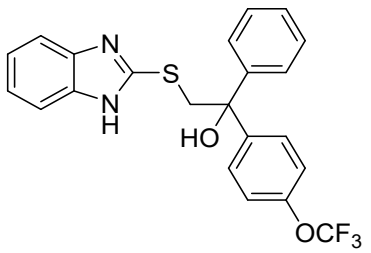
2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-(*tert*-butyl)phenyl)-1-phenylethan-1-ol (4d): 116.4 mg, 96% yield. White solid. m.p.: 177.1-179.0 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 7.56-7.50 (m, 3H), 7.47-7.44 (m, 2H), 7.34-7.28 (m, 5H), 7.21-7.17 (m, 1H), 7.13-7.08 (m, 2H), 6.53 (s, 1H), 4.31 (s, 2H), 1.24 (s, 9H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.6, 148.9, 146.7, 143.8, 135.4, 127.9, 126.6, 125.8, 125.5, 124.7, 121.3, 116.9, 110.2, 76.3, 43.9, 34.1, 31.1. **HRMS** (ESI) m/z Calcd for $C_{25}H_{27}N_2OS$ $[M+H]^+$: 403.1839; Found: 403.1834.



2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-methoxyphenyl)-1-phenylethan-1-ol (4e): 99.6 mg, 88% yield. White solid. m.p.: 155.8-157.6 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 7.54-7.51 (m, 3H), 7.46-7.42 (m, 2H), 7.32-7.28 (m, 3H), 7.22-7.17 (m, 1H), 7.13-7.08 (m, 2H), 6.88-6.84 (m, 2H), 6.51 (s, 1H), 4.29 (s, 2H), 3.71 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 157.9(5), 151.6, 146.9(5), 138.7, 127.9, 127.1, 126.6, 125.8, 121.3, 113.2, 76.2, 55.0, 44.0. **HRMS** (ESI) m/z Calcd for $C_{22}H_{20}N_2O_2SNa$ $[M+Na]^+$: 399.1138; Found: 399.1141.

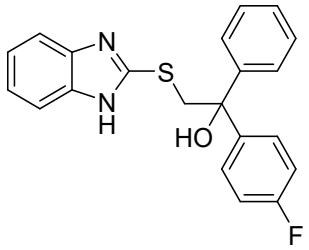


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-ethoxyphenyl)-1-phenylethan-1-ol (4f): 102.3 mg, 87% yield. White solid. m.p.: 61.0-62.3 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.51 (s, 1H), 7.57-7.54 (m, 2H), 7.47-7.44 (m, 4H), 7.33-7.29 (m, 2H), 7.22-7.18 (m, 1H), 7.15-7.10 (m, 2H), 6.87-6.84 (m, 2H), 6.56 (s, 1H), 4.33 (s, 2H), 3.97 (q, J = 7.0 Hz, 2H), 1.29 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 157.3, 151.7, 146.9(9), 138.6, 127.9, 127.2, 126.6, 125.9, 121.4, 113.7, 76.3, 62.9, 44.1, 14.7. **HRMS** (ESI) m/z Calcd for $C_{23}H_{23}N_2O_2S$ $[M+H]^+$: 391.1475; Found: 391.1496.

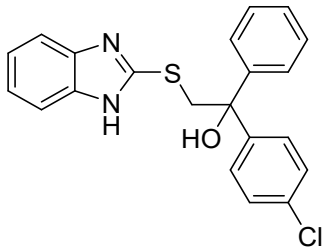


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-phenyl-1-(4-

(trifluoromethoxy)phenyl)ethan-1-ol (4g): 126.9 mg, 98% yield. White solid. m.p.: 75.3-77.1 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.49 (s, 1H), 7.69-7.65 (m, 2H), 7.58-7.51 (m, 3H), 7.35-7.29 (m, 5H), 7.25-7.21 (m, 1H), 7.14-7.09 (m, 2H), 6.83 (s, 1H), 4.38 (d, J = 13.0 Hz, 1H), 4.33 (d, J = 13.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.4, 147.1, 146.3, 146.1, 128.2, 127.9(6), 127.0, 125.9, 121.5, 121.4, 120.5, 118.9, 76.3, 43.7. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -56.80 (s). **HRMS** (ESI) m/z Calcd for $C_{22}H_{18}F_3N_2O_2S$ $[M+H]^+$: 431.1036; Found: 431.1035.

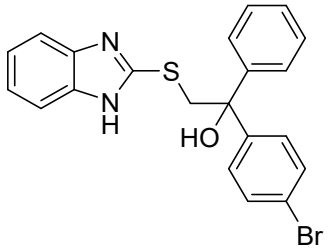


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-fluorophenyl)-1-phenylethan-1-ol (4h): 105.3 mg, 96% yield. White solid. m.p.: 158.7-160.3 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 7.60-7.51 (m, 5H), 7.34-7.30 (m, 3H), 7.24-7.19 (m, 1H), 7.15-7.09 (m, 4H), 6.72 (s, 1H), 4.35 (d, J = 13.0 Hz, 1H), 4.30 (d, J = 13.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 161.0 (d, J = 242.0 Hz), 151.4, 146.6, 142.9 (d, J = 3.0 Hz), 128.1, 128.0 (d, J = 9.0 Hz), 126.9, 125.9, 121.4, 114.6 (d, J = 21.0 Hz), 76.3, 43.9. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -116.32 (s). **HRMS** (ESI) m/z Calcd for $C_{21}H_{18}FN_2OS$ $[M+H]^+$: 365.1119; Found: 365.1097.

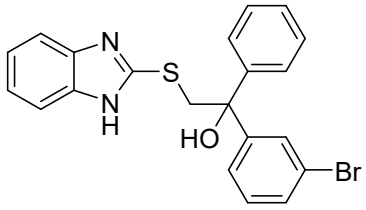


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-chlorophenyl)-1-phenylethan-1-ol (4i): 110.0 mg, 96% yield. White solid. m.p.: 141.8-143.1 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 7.57-7.51 (m, 5H), 7.37-7.30 (m, 5H), 7.22 (t, J = 7.3 Hz, 1H), 7.13-7.09 (m, 2H), 6.78 (s, 1H), 4.36 (d, J = 13.0 Hz, 1H), 4.30 (d, J = 13.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.4, 146.4, 145.7, 143.3, 135.5, 131.5, 128.2,

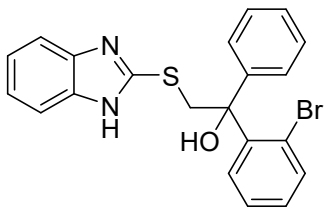
127.9(5), 126.9(8), 125.9, 121.7, 121.3, 117.2, 110.3, 76.3, 43.7. **HRMS** (ESI) m/z Calcd for $C_{21}H_{18}ClN_2OS$ $[M+H]^+$: 381.0823; Found: 381.0825.



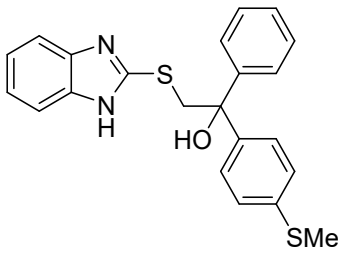
2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-bromophenyl)-1-phenylethan-1-ol (4j): 120.8 mg, 95% yield. White solid. m.p.: 140.1-141.3 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 7.55-7.50 (m, 7H), 7.34-7.30 (m, 3H), 7.24-7.20 (m, 1H), 7.13-7.09 (m, 2H), 6.78 (s, 1H), 4.35 (d, J = 13.0 Hz, 1H), 4.29 (d, J = 13.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.4, 146.3, 146.1, 143.3, 135.4, 130.9, 128.3, 128.2, 126.9(8), 125.8, 121.7, 121.3, 120.1, 117.2, 110.3, 76.3, 43.6. **HRMS** (ESI) m/z Calcd for $C_{21}H_{18}BrN_2OS$ $[M+H]^+$: 425.0318; Found: 425.0324.



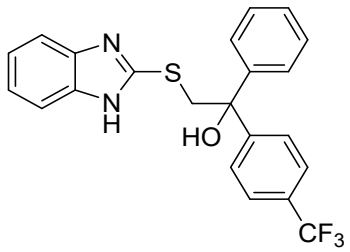
2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(3-bromophenyl)-1-phenylethan-1-ol (4k): 121.5 mg, 95% yield. White solid. m.p.: 144.6-145.6 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 7.74 (s, 1H), 7.57-7.51 (m, 4H), 7.40 (d, J = 7.9 Hz, 1H), 7.35-7.21 (m, 5H), 7.13-7.09 (m, 2H), 6.84 (s, 1H), 4.37 (d, J = 13.1 Hz, 1H), 4.30 (d, J = 13.0 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.3, 149.4, 146.1, 143.3, 135.4, 130.2, 129.6, 128.7, 128.1, 126.9(9), 125.8, 125.0, 121.6, 121.5(5), 121.2, 117.1, 110.3, 76.3, 43.5. **HRMS** (ESI) m/z Calcd for $C_{21}H_{18}BrN_2OS$ $[M+H]^+$: 425.0318; Found: 425.0312.



2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(2-bromophenyl)-1-phenylethan-1-ol (4l): 119.4 mg, 94% yield. White solid. m.p.: 172.1-172.6 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.06 (dd, J = 7.9, 1.7 Hz, 1H), 7.52-7.45 (m, 3H), 7.37-7.29 (m, 5H), 7.27-7.19 (m, 2H), 7.13-7.09 (m, 2H), 6.80 (s, 1H), 4.72 (d, J = 12.7 Hz, 1H), 4.43 (d, J = 12.7 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.3, 144.9, 143.7, 143.4, 135.4, 134.7, 129.6, 129.4, 127.8, 127.2, 127.1, 126.9(8), 121.7, 121.4, 121.3, 117.2, 110.3, 76.9(9), 42.0. **HRMS** (ESI) m/z Calcd for $C_{21}H_{18}BrN_2OS$ $[M+H]^+$: 425.0318; Found: 425.0317.

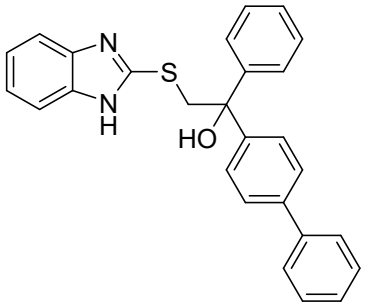


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-(methylthio)phenyl)-1-phenylethan-1-ol (4m): 103.2 mg, 88% yield. White solid. m.p.: 120.0-121.9 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 7.54-7.46 (m, 5H), 7.34-7.29 (m, 3H), 7.22-7.18 (m, 3H), 7.13-7.08 (m, 2H), 6.61 (s, 1H), 4.33 (d, J = 12.9 Hz, 1H), 4.28 (d, J = 12.9 Hz, 1H), 2.43 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.5, 146.7, 143.3, 136.4, 135.4, 127.9(7), 126.7, 126.5, 125.8, 125.5, 121.6, 121.2, 117.1, 110.2, 76.3, 43.8, 14.7. **HRMS** (ESI) m/z Calcd for $C_{22}H_{19}N_2OS_2$ $[M-H]^-$: 391.0944; Found: 391.0946.

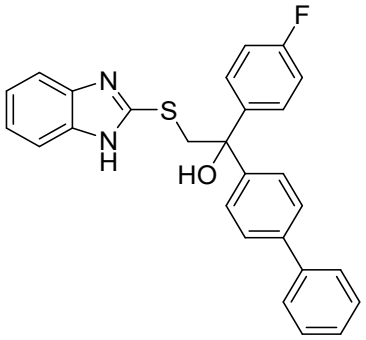


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-phenyl-1-(4-(trifluoromethyl)phenyl)ethan-1-ol (4n): 113.6 mg, 91% yield. White solid. m.p.: 143.1-145.0 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.58-7.52 (m, 3H), 7.34 (t, J = 7.8 Hz, 3H), 7.23 (t, J = 7.4 Hz, 1H), 7.14-7.09 (m, 2H), 6.92 (s, 1H), 4.42 (d, J = 13.1 Hz, 1H), 4.35 (d, J =

13.1 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.2(0), 151.1(5), 146.1, 143.3, 135.4, 128.2, 127.4 (q, J = 31.0 Hz), 127.1, 126.8, 125.9, 124.90 (q, J = 3.0 Hz), 124.3 (q, J = 270.0 Hz), 121.6, 121.3, 117.1, 110.3, 76.5, 43.5. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -60.88 (s). **HRMS** (ESI) m/z Calcd for $C_{22}H_{18}F_3N_2OS$ $[M+H]^+$: 415.1087; Found: 415.1083.

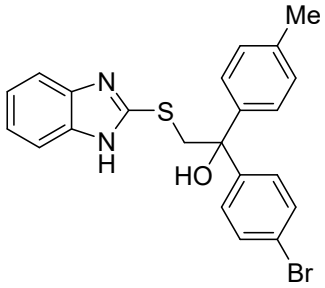


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-ol (4o): 121.6 mg, 96% yield. White solid. m.p.: 140.1-141.9 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.48 (s, 1H), 7.65-7.58 (m, 8H), 7.54-7.52 (m, 1H), 7.46-7.42 (m, 2H), 7.36-7.31 (m, 4H), 7.24-7.20 (m, 1H), 7.13-7.09 (m, 2H), 6.69 (s, 1H), 4.40 (d, J = 13.0 Hz, 1H), 4.36 (d, J = 12.9 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.5, 146.7, 145.9, 139.8, 138.6, 128.9, 128.0, 127.4, 126.8, 126.6, 126.5, 126.3, 125.8, 121.4, 76.4, 43.8. **HRMS** (ESI) m/z Calcd for $C_{27}H_{23}N_2OS$ $[M+H]^+$: 423.1526; Found: 423.1525.

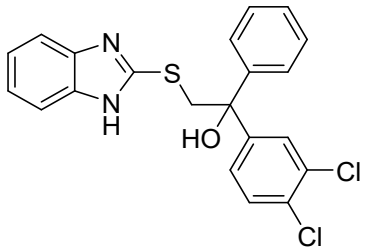


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-([1,1'-biphenyl]-4-yl)-1-(4-fluorophenyl)ethan-1-ol (4p): 129.8 mg, 98% yield. White solid. m.p.: 187.7-188.9 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.50 (s, 1H), 7.64-7.60 (m, 8H), 7.46-7.32 (m, 5H), 7.17-7.09 (m, 4H), 6.80 (s, 1H), 4.37 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 161.1 (d, J = 242.0 Hz), 151.4, 145.8, 142.8 (d, J = 3.0 Hz), 139.8, 138.7, 128.9(8), 128.0(5) (d, J = 8.0 Hz), 127.5, 126.7, 126.5, 126.4, 121.5, 114.7 (d, J = 21.0 Hz), 76.2,

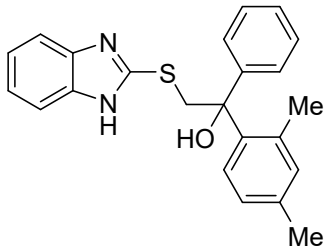
43.9. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -116.21 (s). **HRMS** (ESI) m/z Calcd for $C_{27}H_{22}FN_2OS$ $[M+H]^+$: 441.1431; Found: 441.1434.



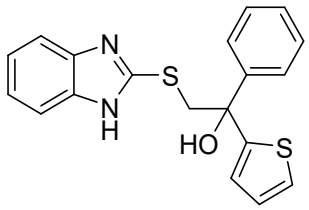
2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(4-bromophenyl)-1-(*p*-tolyl)ethan-1-ol (4q): 123.6 mg, 94% yield. White solid. m.p.: 147.0-148.4 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 7.52-7.45 (m, 5H), 7.40 (d, J = 8.2 Hz, 2H), 7.34-7.32 (m, 1H), 7.13-7.09 (m, 4H), 6.69 (s, 1H), 4.31 (d, J = 13.0 Hz, 1H), 4.26 (d, J = 13.0 Hz, 1H), 2.25 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.4, 146.3, 143.3(9), 143.3(3), 136.1, 135.4, 130.8, 128.7, 128.3, 125.8, 121.7, 121.3, 120.0, 117.1, 110.3, 76.2, 43.7, 20.6. **HRMS** (ESI) m/z Calcd for $C_{22}H_{20}BrN_2OS$ $[M+H]^+$: 439.0474; Found: 439.0474.



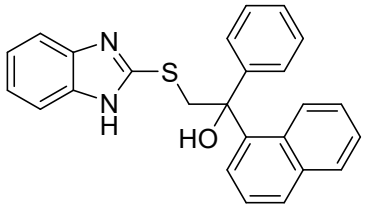
2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(3,4-dichlorophenyl)-1-phenylethan-1-ol (4r): 115.0 mg, 92% yield. White solid. m.p.: 82.4-84.5 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.50 (s, 1H), 7.79 (d, J = 1.8 Hz, 1H), 7.58-7.50 (m, 5H), 7.36-7.33 (m, 3H), 7.26-7.23 (m, 1H), 7.14-7.10 (m, 2H), 6.99 (s, 1H), 4.41 (d, J = 13.2 Hz, 1H), 4.29 (d, J = 13.2 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.1, 147.7, 145.9, 143.3, 135.4, 130.8, 130.2, 129.5, 128.3, 128.0, 127.2, 126.5, 125.8, 121.7, 121.3, 117.2, 110.4, 76.2, 43.3. **HRMS** (ESI) m/z Calcd for $C_{21}H_{17}Cl_2N_2OS$ $[M+H]^+$: 415.0433; Found: 415.0438.



2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(2,4-dimethylphenyl)-1-phenylethan-1-ol (4s): 107.5 mg, 96% yield. White solid. m.p.: 93.5-95.7 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.51-7.48 (m, 1H), 7.35-7.26 (m, 5H), 7.21 -7.17 (m, 1H), 7.12-7.07 (m, 2H), 7.04 (d, J = 7.8 Hz, 1H), 6.88 (s, 1H), 6.34 (s, 1H), 4.33 (d, J = 12.5 Hz, 1H), 4.17 (d, J = 12.5 Hz, 1H), 2.25 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.7, 145.9(7), 143.4, 140.6, 136.9, 136.4, 135.5, 133.0, 127.7, 126.6, 126.3, 126.1, 125.6, 121.6, 121.2, 117.1, 110.2, 76.7, 45.4, 21.2, 20.5. **HRMS** (ESI) m/z Calcd for $C_{23}H_{23}N_2OS$ $[M+H]^+$: 375.1526; Found: 375.1528.

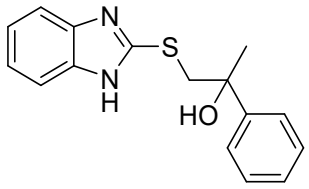


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-phenyl-1-(thiophen-2-yl)ethan-1-ol (4t): 89.0 mg, 84% yield. White solid. m.p.: 162.0-163.3 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.53 (s, 1H), 7.61 (d, J = 7.4 Hz, 2H), 7.43-7.30 (m, 5H), 7.25-7.21 (m, 2H), 7.15-7.10 (m, 3H), 6.96 (dd, J = 5.0, 3.6 Hz, 1H), 4.34 (d, J = 13.3 Hz, 1H), 4.29 (d, J = 13.2 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 152.7, 151.4, 145.9, 127.9(6), 127.0, 126.8, 125.6, 125.0, 123.6, 121.5, 75.7, 44.7. **HRMS** (ESI) m/z Calcd for $C_{19}H_{17}N_2OS_2$ $[M+H]^+$: 353.0777; Found: 353.0793.

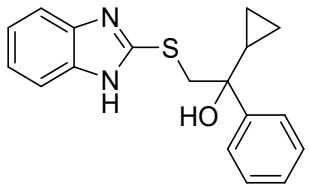


2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-(naphthalen-1-yl)-1-phenylethan-1-ol (4u): 104.2 mg, 88% yield. White solid. m.p.: 112.8-114.4 °C. **^{1}H NMR** (400 MHz,

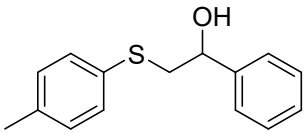
DMSO-d_6) δ 12.45 (s, 1H), 8.24 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 7.2 Hz, 1H), 7.87 (dd, J = 11.9, 8.2 Hz, 2H), 7.56 (t, J = 7.9 Hz 1H), 7.50-7.44 (m, 3H), 7.38-7.32 (m, 2H), 7.28-7.21 (m, 3H), 7.16 (t, J = 7.3 Hz, 1H), 7.12-7.08 (m, 2H), 6.86 (s, 1H), 4.49 (d, J = 12.5 Hz, 1H), 4.34 (d, J = 12.5 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.5, 146.5, 143.4, 140.7, 135.4, 134.5, 130.7, 128.7, 128.5, 127.9, 127.6, 126.7, 125.8, 125.1, 124.9, 124.6, 124.3, 121.5, 121.2, 117.1, 110.2, 77.3, 45.9(5). **HRMS** (ESI) m/z Calcd for $C_{25}H_{21}N_2OS$ $[M+H]^+$: 397.1369; Found: 397.1368.



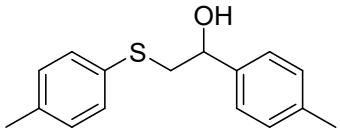
1-((1*H*-benzo[*d*]imidazol-2-yl)thio)-2-phenylpropan-2-ol (4v): 81.4 mg, 95% yield. White solid. m.p.: 152.7-154.1 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.43 (s, 1H), 7.55-7.53 (m, 2H), 7.48 (s, 1H), 7.35-7.31 (m, 3H), 7.22 (t, J = 7.3 Hz, 1H), 7.12-7.07 (m, 2H), 5.85 (s, 1H), 3.80 (d, J = 12.9 Hz, 1H), 3.71 (d, J = 12.9 Hz, 1H), 1.59 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.5, 147.6, 143.4, 135.5, 127.9, 126.5, 125.1, 121.3, 117.1, 110.1, 72.8, 45.3, 29.2. **HRMS** (ESI) m/z Calcd for $C_{16}H_{17}N_2OS$ $[M+H]^+$: 285.1056; Found: 285.1054.



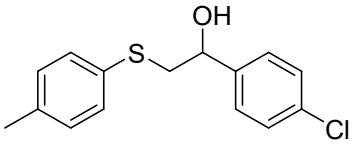
2-((1*H*-benzo[*d*]imidazol-2-yl)thio)-1-cyclopropyl-1-phenylethan-1-ol (4w): 66.2 mg, 71% yield. White solid. m.p.: 63.0-65.4 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.45 (s, 1H), 7.56-7.54 (m, 2H), 7.51-7.49 (m, 1H), 7.31 (t, J = 7.8 Hz, 3H), 7.21 (t, J = 7.3 Hz, 1H), 7.12-7.08 (m, 2H), 5.77 (s, 1H), 3.93 (d, J = 13.1 Hz, 1H), 3.85 (d, J = 13.1 Hz, 1H), 1.45-1.38 (m, 1H), 0.67-0.61 (m, 1H), 0.44-0.37 (m, 1H), 0.32-0.26 (m, 1H), 0.23-0.16 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.8, 146.5, 143.2, 135.4, 127.7, 126.5, 125.6, 121.6, 121.2, 117.0, 110.2, 73.1, 44.5, 21.5, 1.6, 0.2. **HRMS** (ESI) m/z Calcd for $C_{18}H_{17}N_2OS$ $[M-H]^-$: 309.1067; Found: 309.1069.



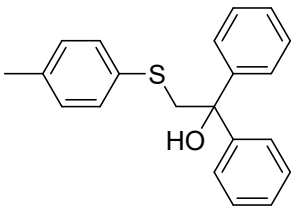
1-phenyl-2-(*p*-tolylthio)ethan-1-ol (5a)[3]: 52.6 mg, 72% yield. Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 7H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.66 (dd, J = 9.5, 3.3 Hz, 1H), 3.25 (dd, *J* = 13.8, 3.4 Hz, 1H), 3.02 (dd, *J* = 13.8, 9.6 Hz, 1H), 2.95 (s, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 137.2, 131.1, 131.1, 130.1, 128.6, 128.0, 126.0, 71.6, 44.9, 21.2.



1-(*p*-tolyl)-2-(*p*-tolylthio)ethan-1-ol (5b)[4]: 35.2 mg, 45% yield. Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.7 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.8 Hz, 4H), 4.64 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.24 (dd, *J* = 13.7, 2.9 Hz, 1H), 3.02 (dd, *J* = 13.5, 9.7 Hz, 1H), 2.87 (s, 1H), 2.33 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.4, 137.7, 137.1, 131.2, 131.1, 130.0, 129.3, 125.9, 71.5, 44.8, 21.3, 21.2.

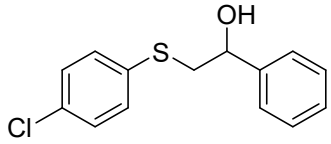


1-(4-chlorophenyl)-2-(*p*-tolylthio)ethan-1-ol (5c)[5]: 40.7 mg, 49% yield. Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 6H), 7.12 (d, *J* = 7.4 Hz, 2H), 4.62 (d, *J* = 8.8 Hz, 1H), 3.21 (dd, *J* = 13.8, 1.1 Hz, 1H), 3.00-2.93 (m, 2H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.8, 137.5, 133.7, 131.4, 130.7, 130.1, 128.8, 127.4, 70.9, 45.0, 21.2.

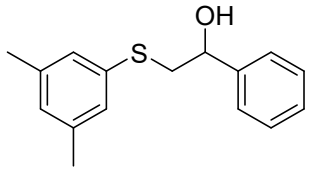


1,1-diphenyl-2-(*p*-tolylthio)ethan-1-ol (5d)[4]: 40.7 mg, 49% yield. Light yellow solid, mp 68.7-70.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 4H), 7.30-

7.25 (m, 8H), 7.03 (d, *J* = 7.7 Hz, 2H), 3.81 (s, 2H), 3.60 (s, 1H), 2.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.4, 136.9, 132.9, 131.0, 129.9, 128.3, 127.4, 126.3, 77.8, 49.8, 21.1.



2-((4-chlorophenyl)thio)-1-phenylethan-1-ol (5e)[3]: 60.8 mg, 77% yield. Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 9H), 4.70 (dd, *J* = 9.0, 3.5 Hz, 1H), 3.25 (dd, *J* = 13.7, 3.7 Hz, 1H), 3.09 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.83 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.1, 133.8, 132.9, 131.5, 129.3, 128.7, 128.2, 125.9, 71.9, 44.1.



2-((3,5-dimethylphenyl)thio)-1-phenylethan-1-ol (5f)[3]: 58.5 mg, 75% yield. Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 7.02 (s, 2H), 6.85 (s, 1H), 4.70 (dd, *J* = 9.3, 2.9 Hz, 1H), 3.28 (dd, *J* = 13.7, 2.9 Hz, 1H), 3.04 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.95 (s, 1H), 2.28 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 138.8, 134.4, 128.8, 128.6, 128.0, 126.0, 71.7, 44.1, 21.3.

6. References

[1] (a) T. Wang, Y. Hu and S. Zhang, *Org. Biomol. Chem.*, 2010, **8**, 2312; (b) Z. Cheng, W. Jin and C. Liu, *Org. Chem. Front.*, 2019, **6**, 841.

[2] J. Li, J. Chen, W. Jiao, G. Wang, Y. Li, X. Cheng and G. Li, *J. Org. Chem.*, 2016, **81**, 9992.

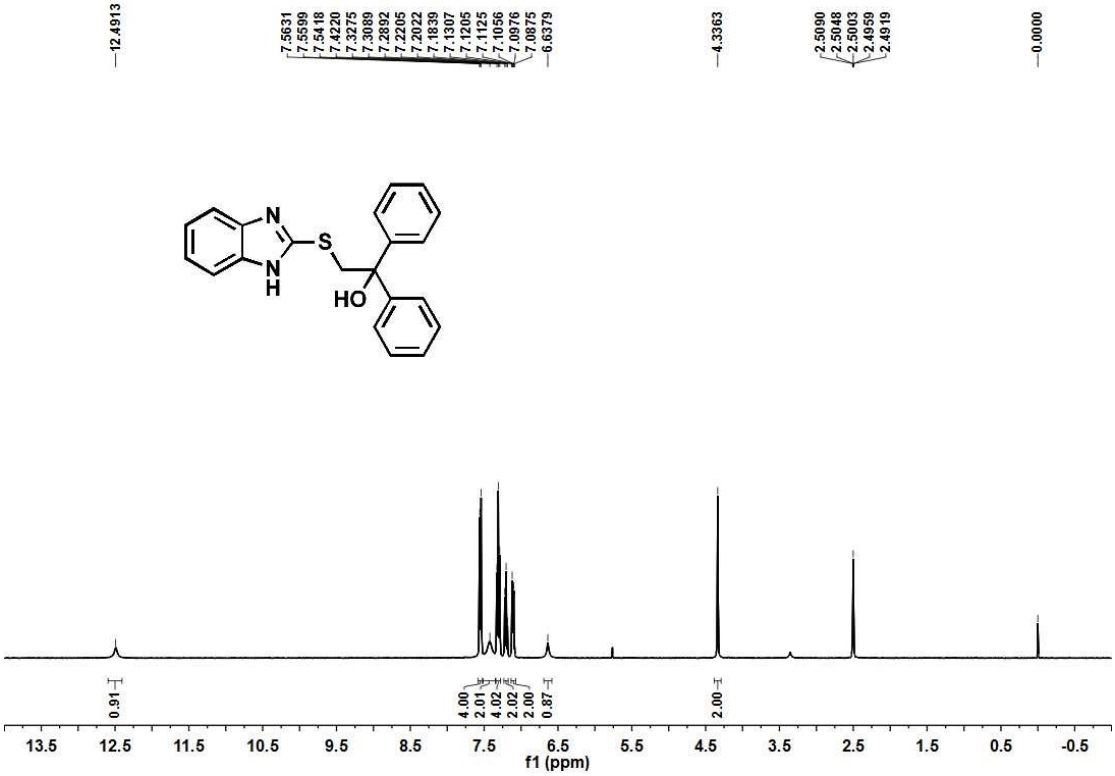
[3] J. Shi, X.-W. Gao, Q.-X. Tong and J.-J. Zhong, *J. Org. Chem.*, 2021, **86**, 12922.

[4] H. Xi, B. Deng, Z. Zong, S. Lu and Z. Li, *Org. Lett.*, 2015, **17**, 1180.

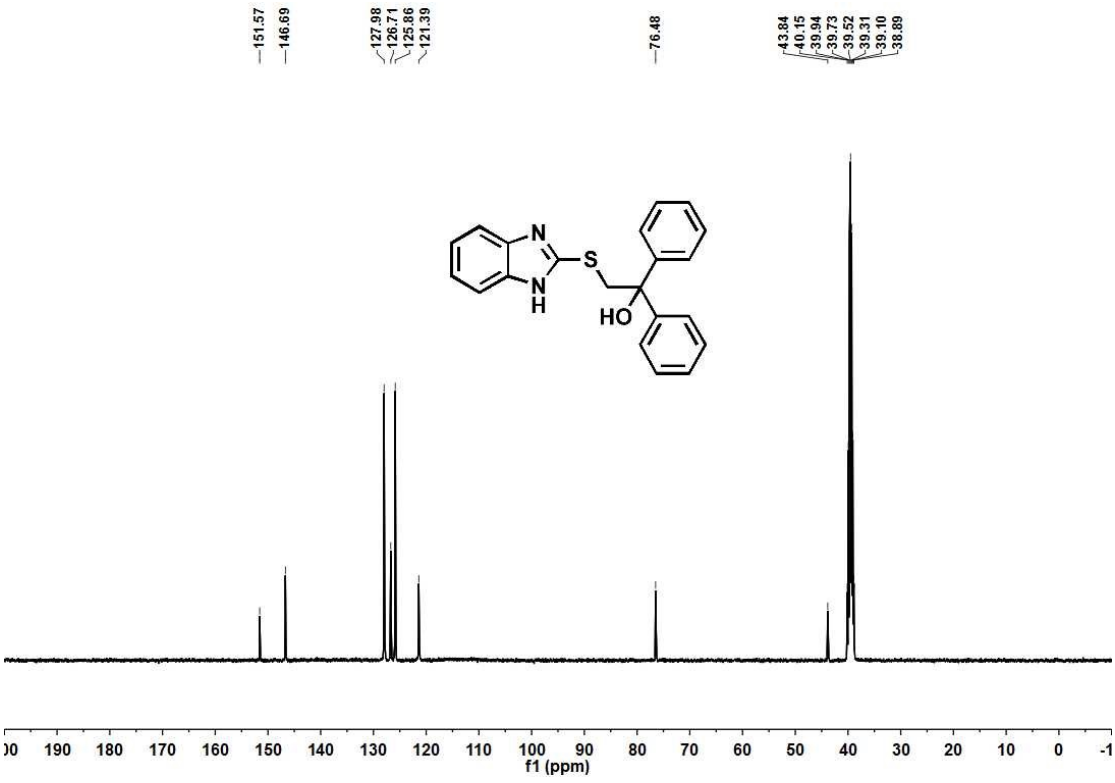
[5] B. Zhang, T. Liu, Y. Bian, T. Lu and J. Feng, *ACS Sustainable Chem. Eng.*, 2018, **6**, 2651.

7. Copies of NMR spectra

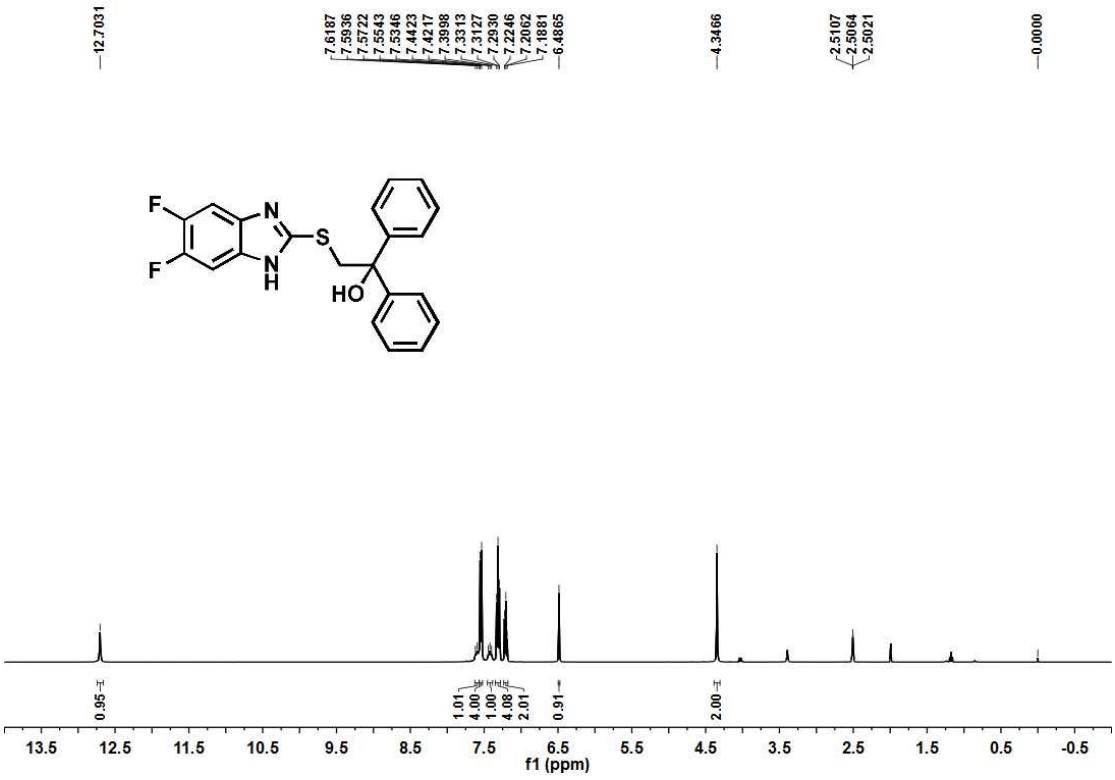
^{1}H NMR of product 3a in DMSO-d_6 (400 MHz)



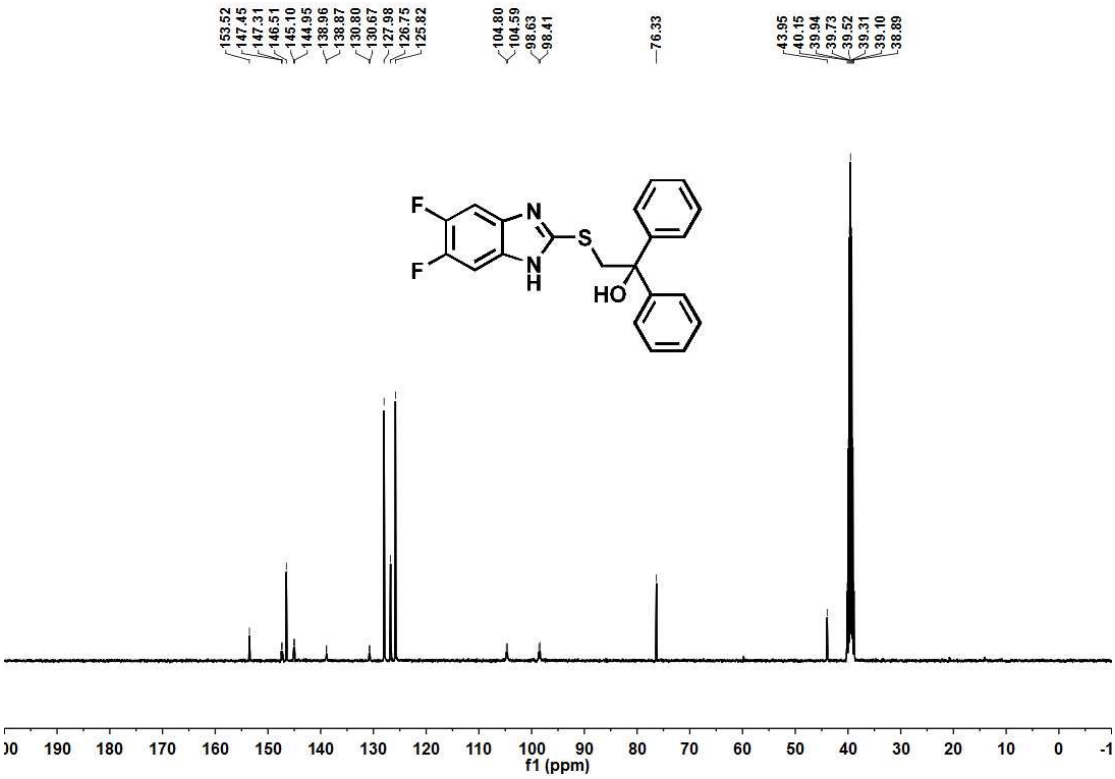
^{13}C NMR of product 3a in DMSO-d_6 (100 MHz)



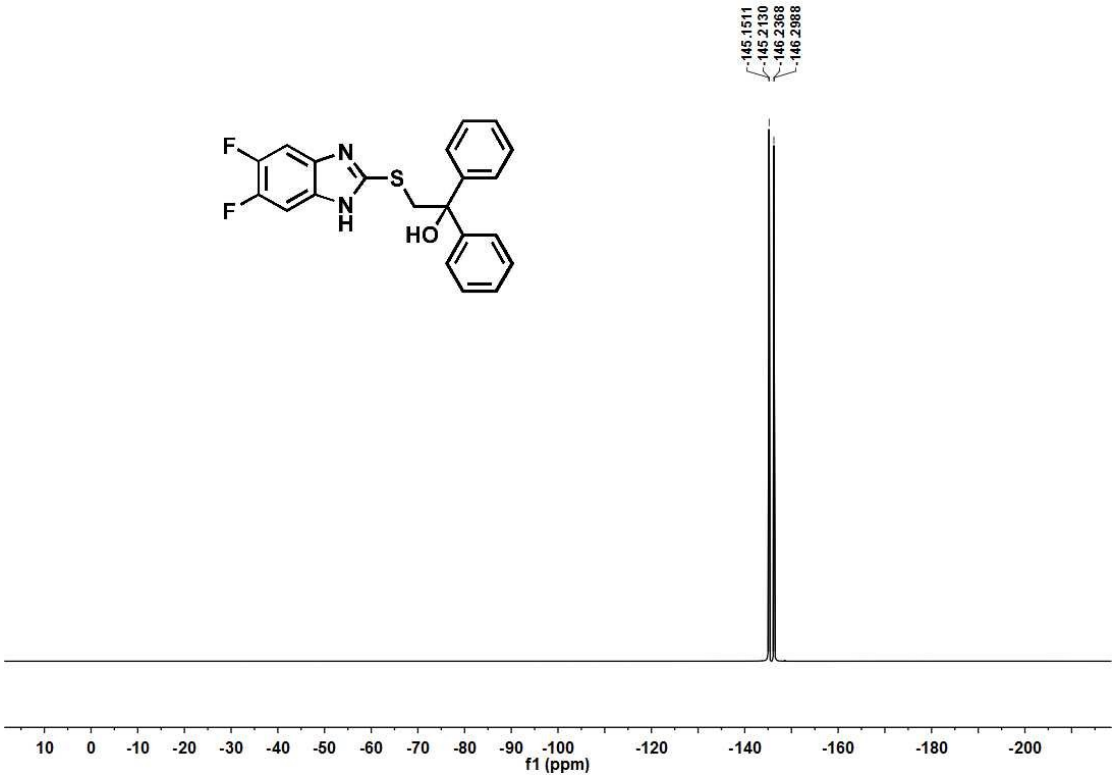
^{1}H NMR of product 3b in DMSO-d_6 (400 MHz)



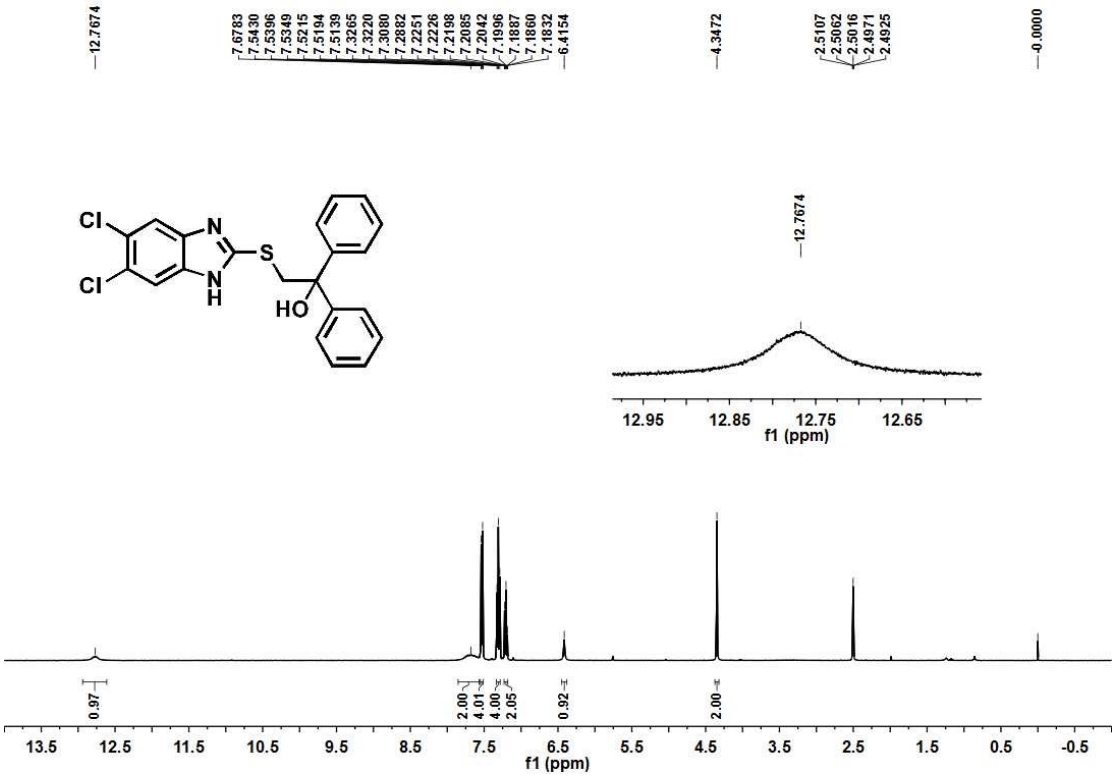
^{13}C NMR of product 3b in DMSO-d_6 (100 MHz)



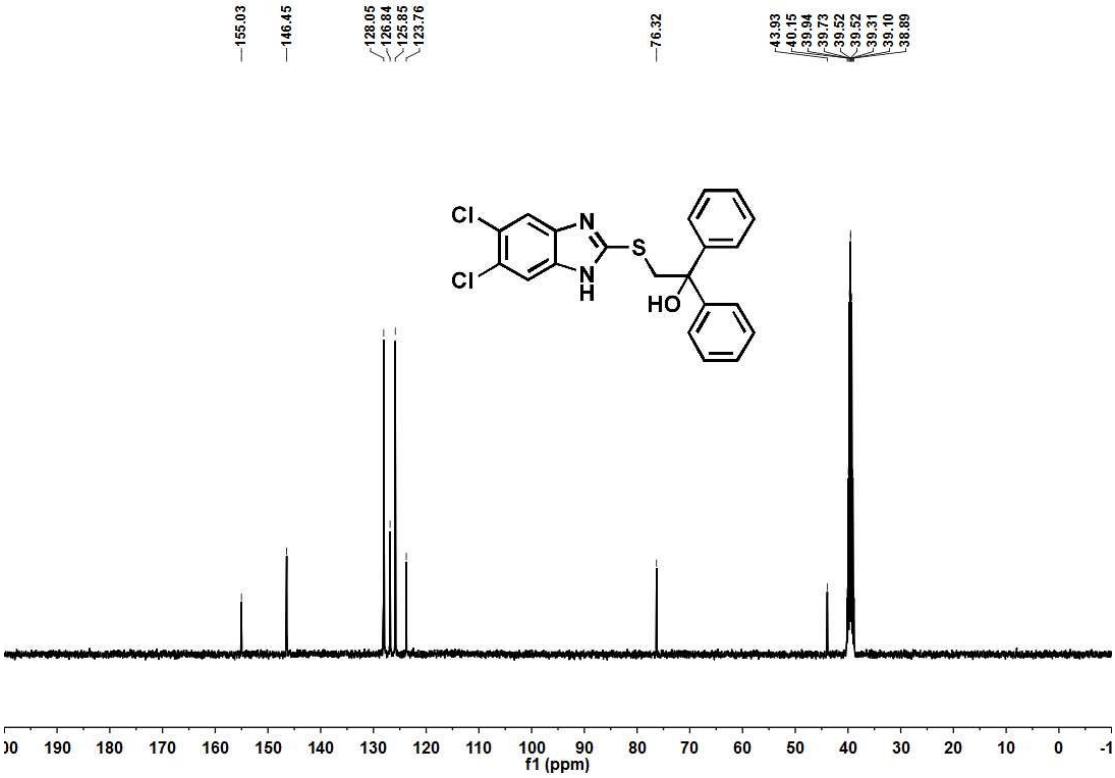
^{19}F NMR of product 3b in DMSO-d_6 (376 MHz)



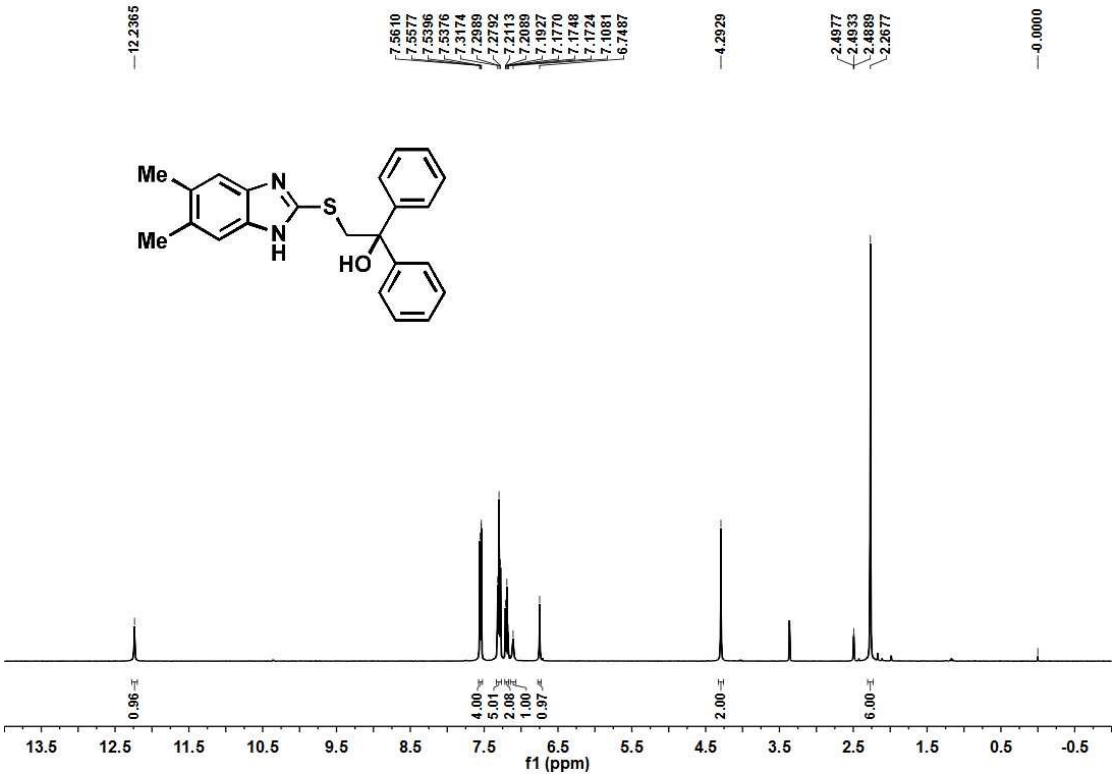
^{1}H NMR of product 3c in DMSO-d_6 (400 MHz)



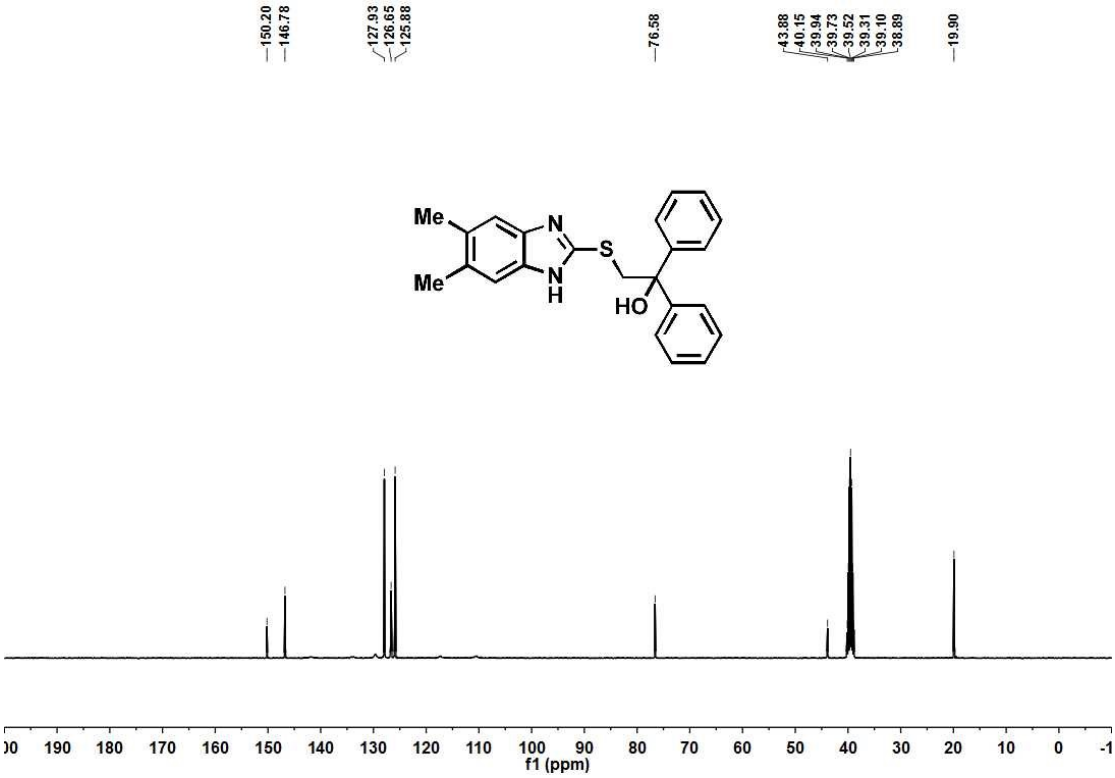
^{13}C NMR of product 3c in DMSO-d_6 (100 MHz)



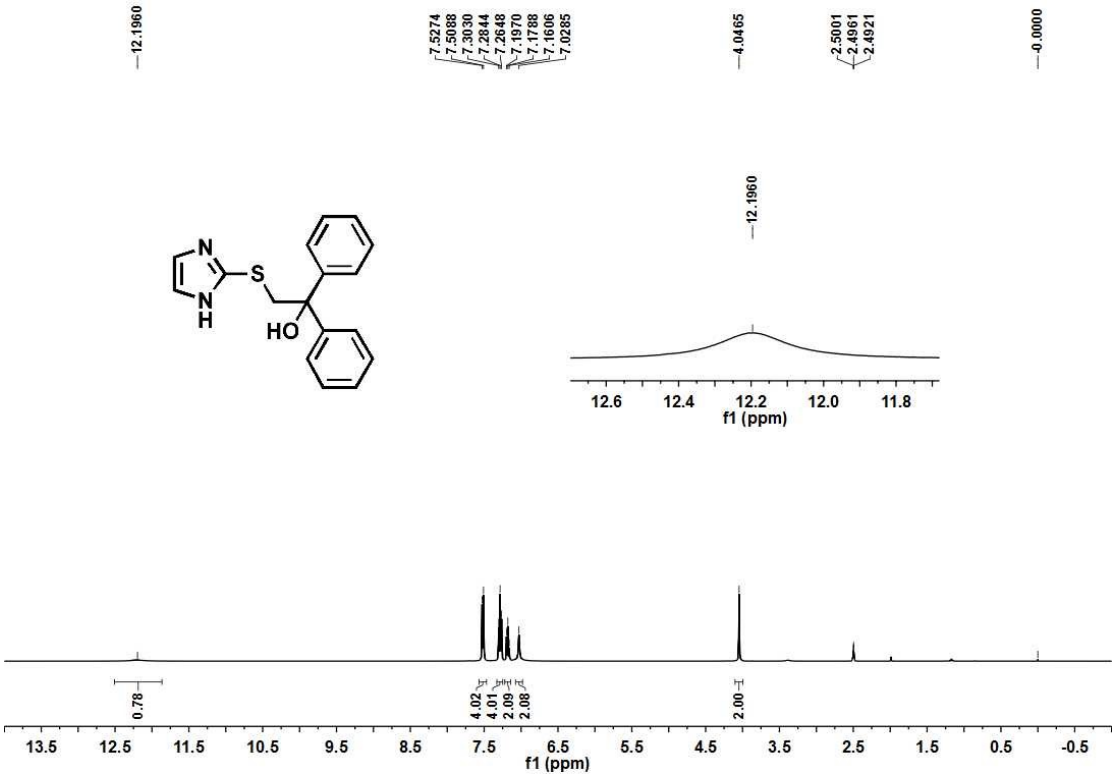
^{1}H NMR of product 3d in DMSO-d_6 (400 MHz)



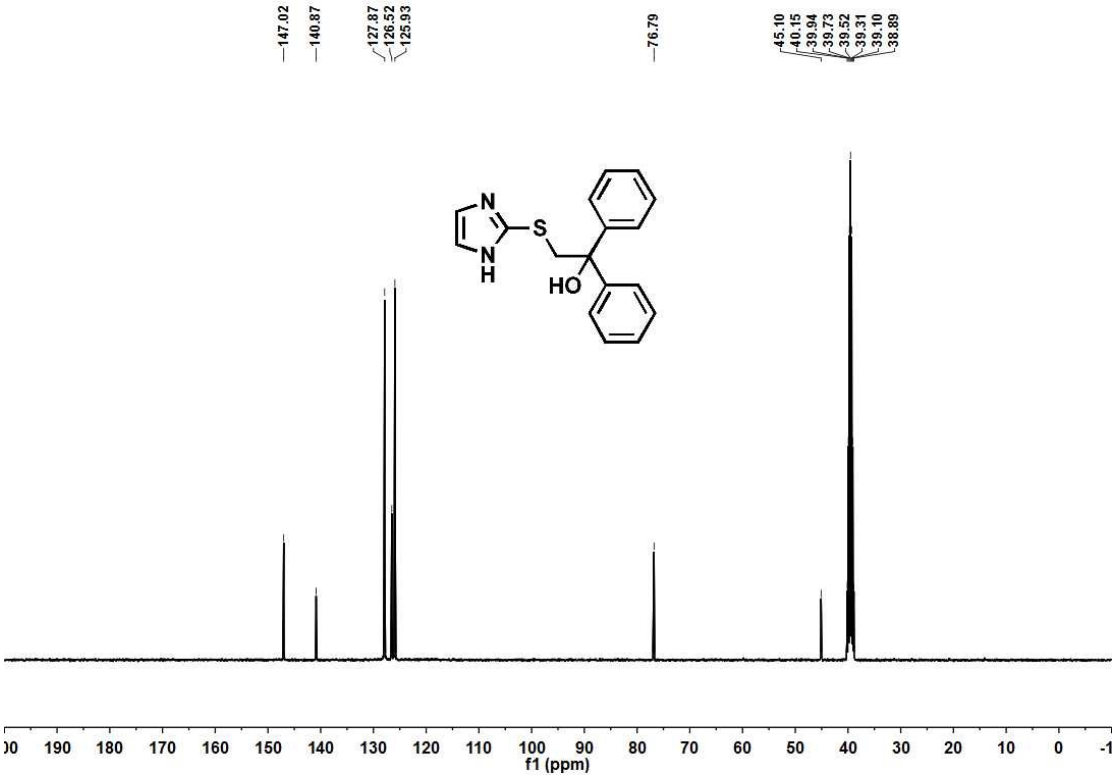
^{13}C NMR of product 3d in DMSO-d_6 (100 MHz)



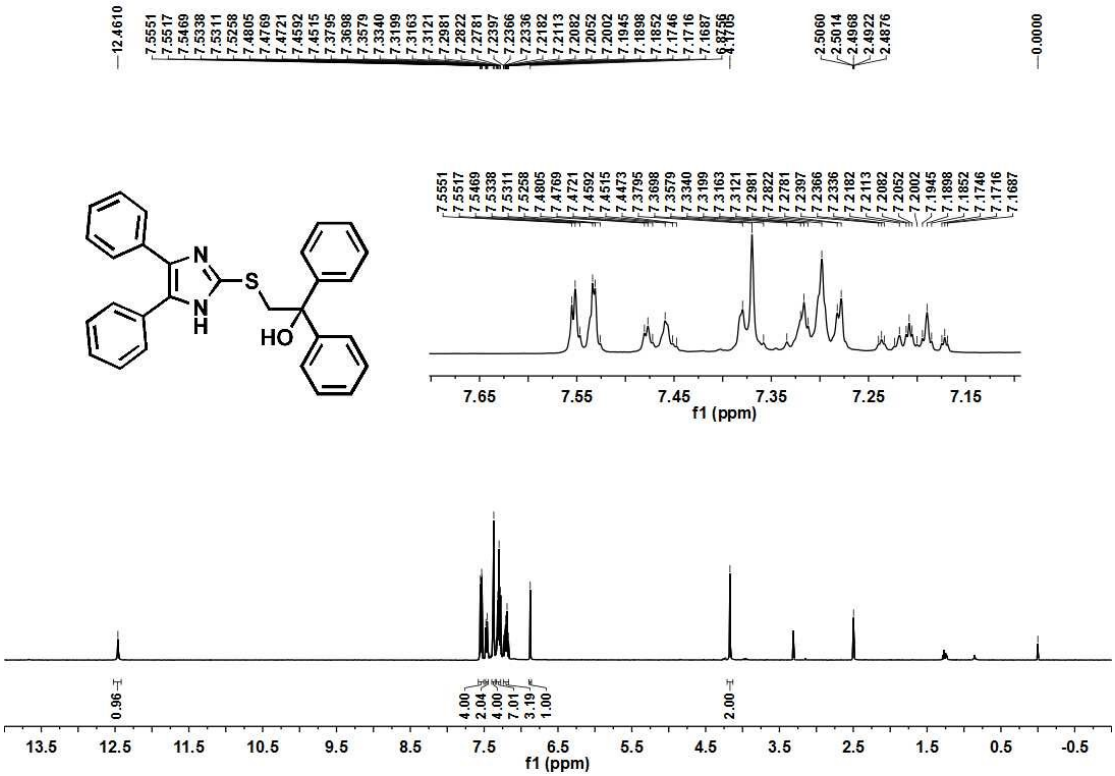
^{1}H NMR of product 3e in DMSO-d_6 (400 MHz)



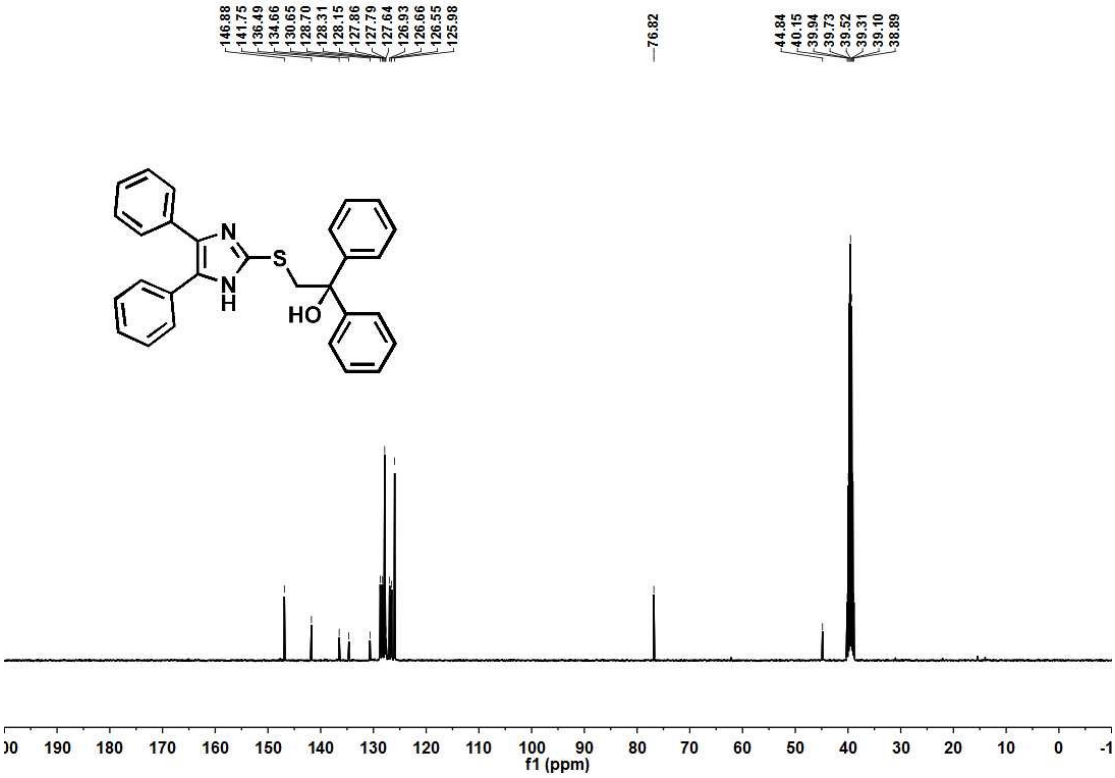
^{13}C NMR of product 3e in DMSO-d_6 (100 MHz)



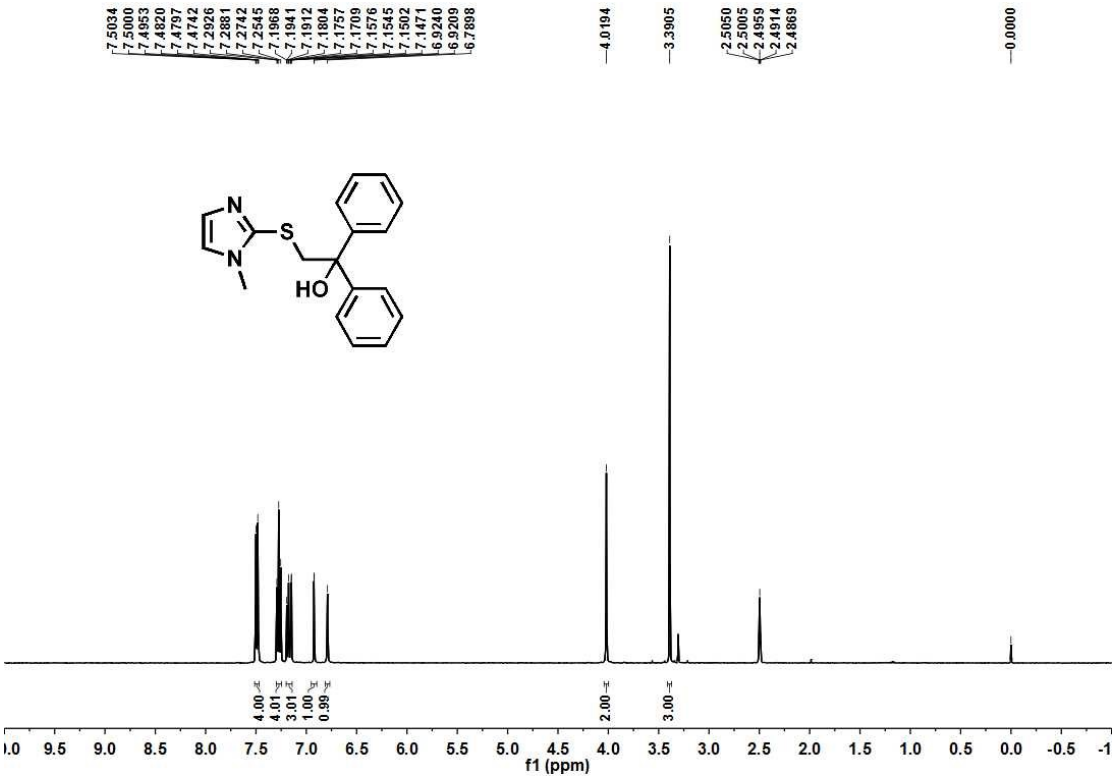
^{1}H NMR of product 3f in DMSO-d_6 (400 MHz)



^{13}C NMR of product 3f in DMSO-d_6 (100 MHz)



^{1}H NMR of product 3g in DMSO-d_6 (400 MHz)



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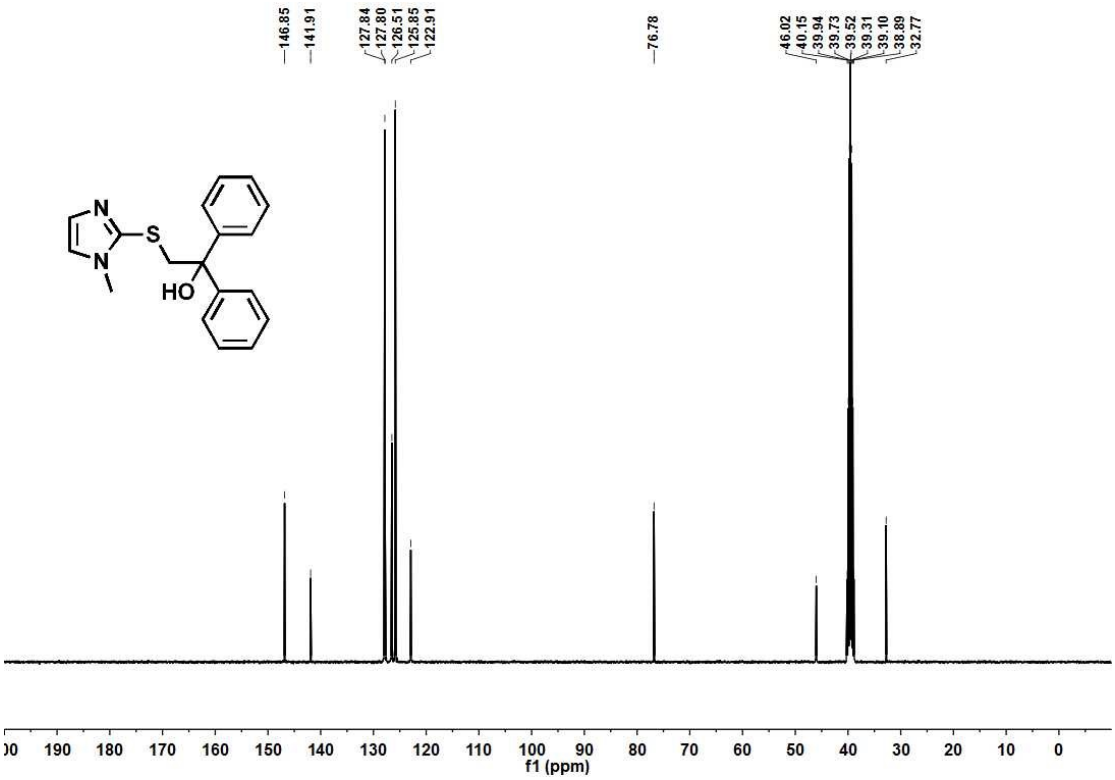
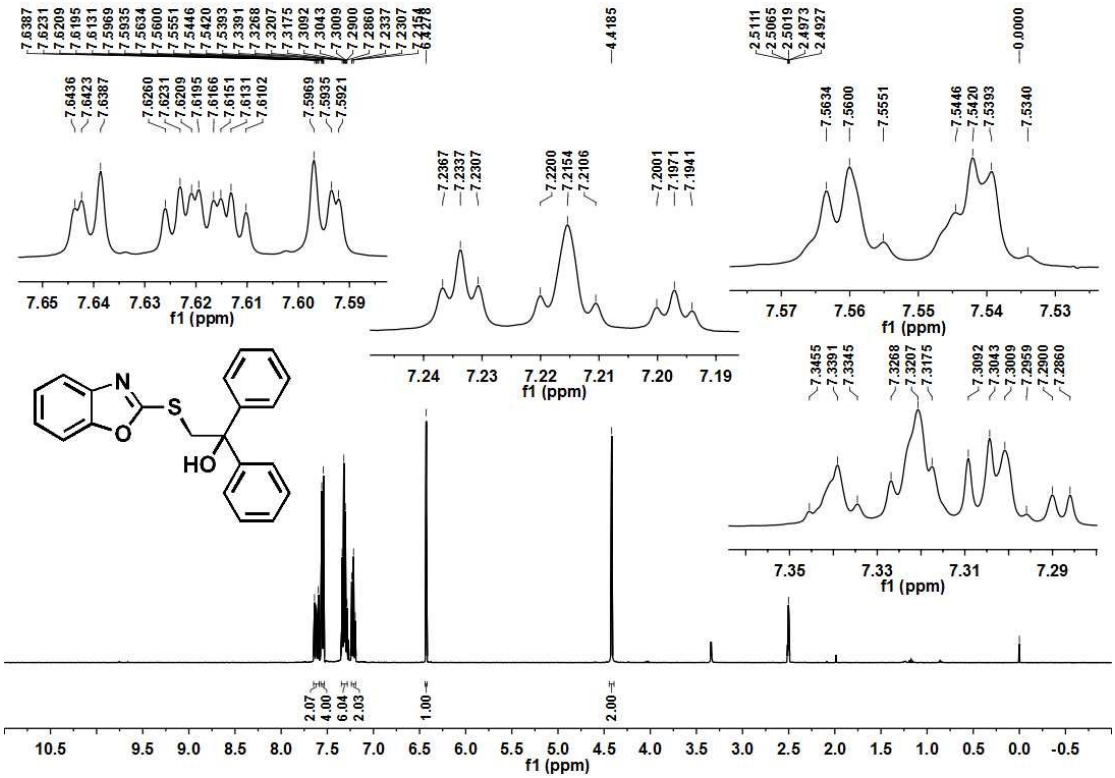
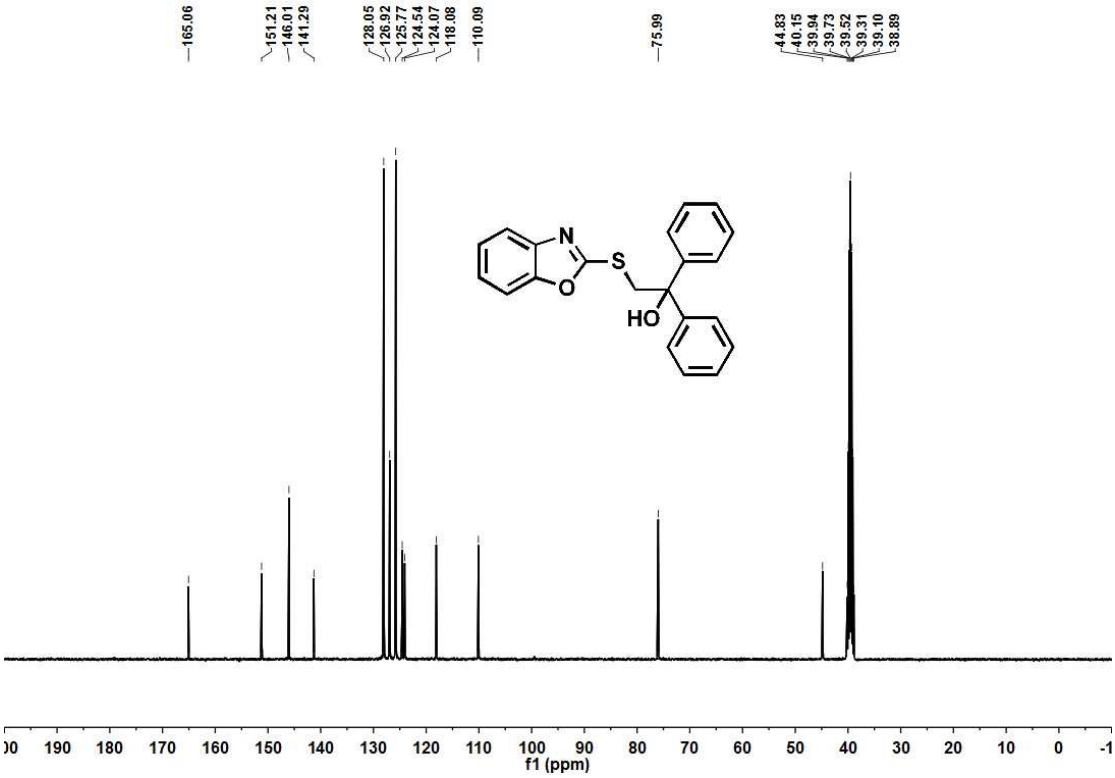


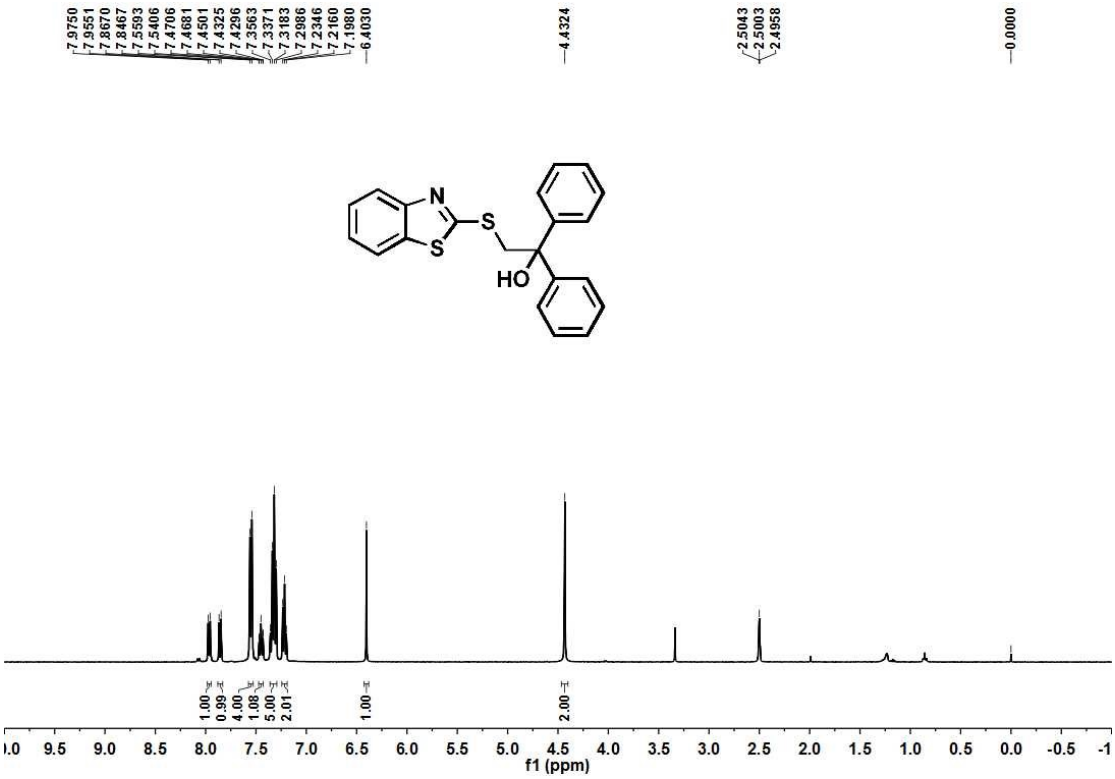
^{1}H NMR of product 3h in DMSO-d_6 (400 MHz)



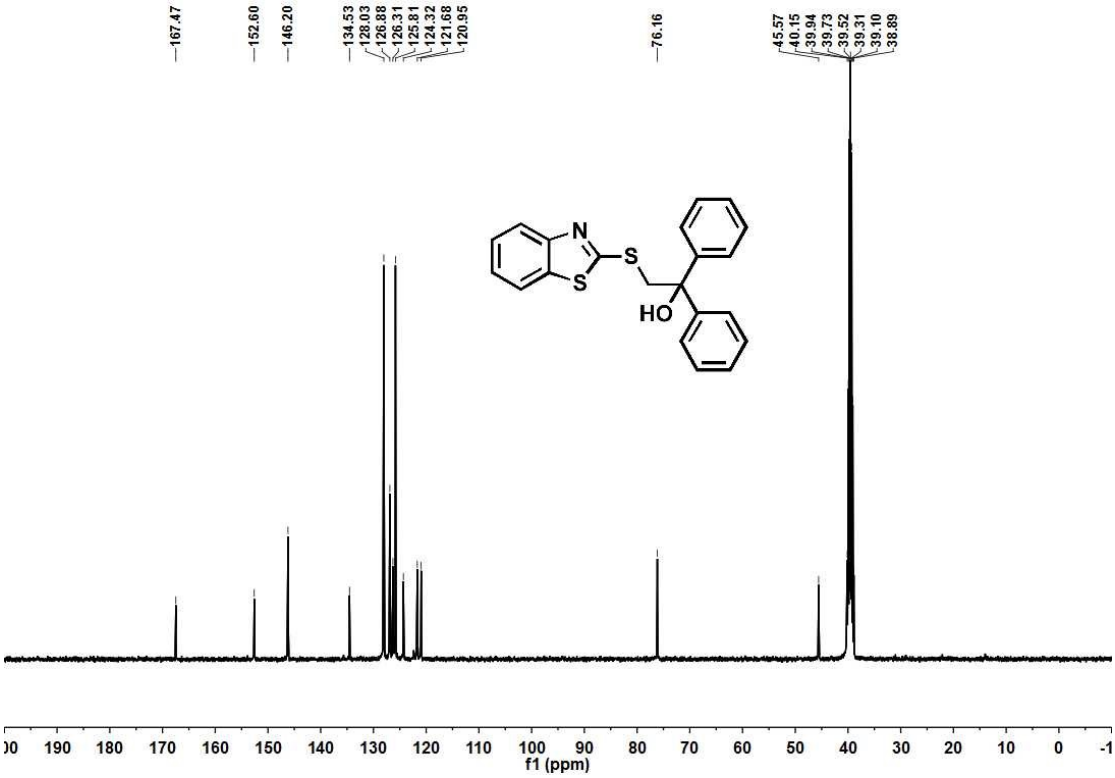
^{13}C NMR of product 3h in DMSO-d_6 (100 MHz)



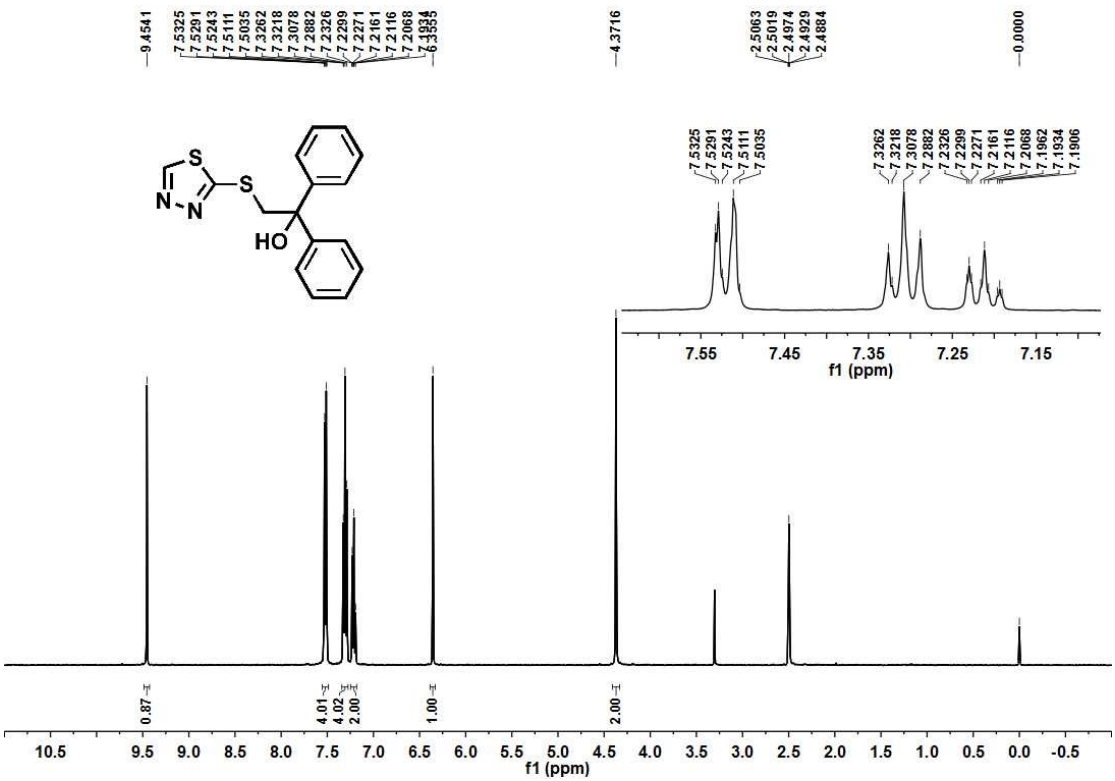
^{1}H NMR of product 3i in DMSO-d_6 (400 MHz)



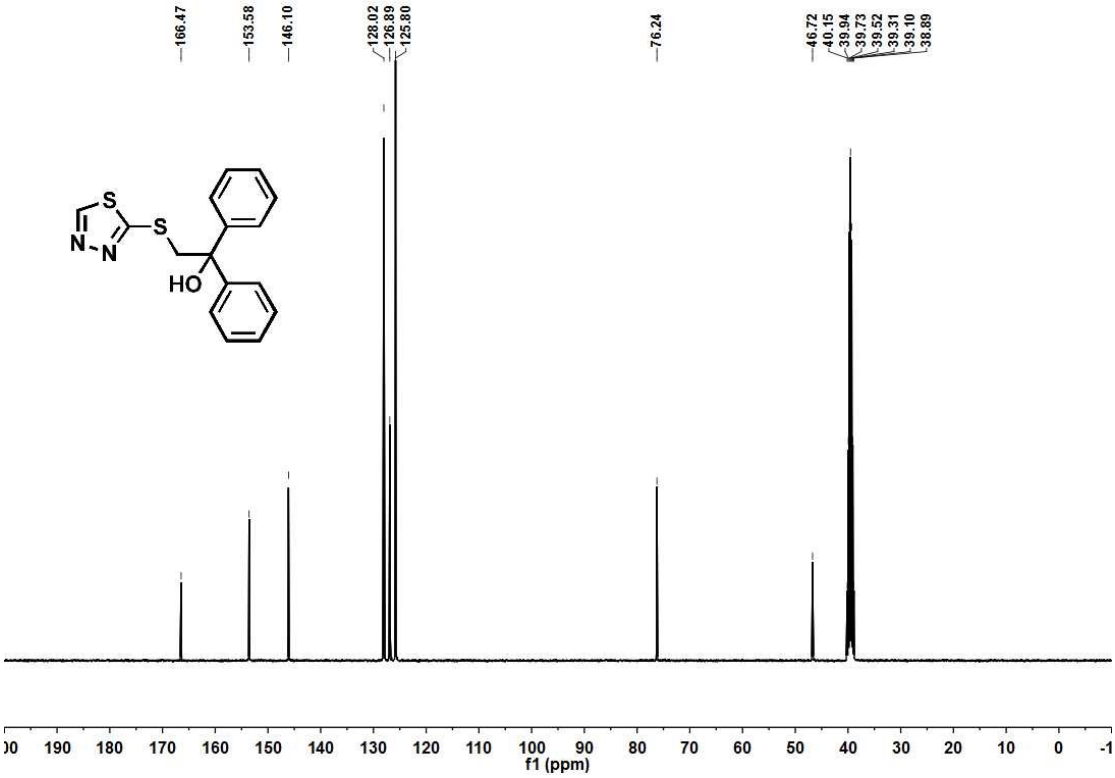
^{13}C NMR of product 3i in DMSO-d_6 (100 MHz)



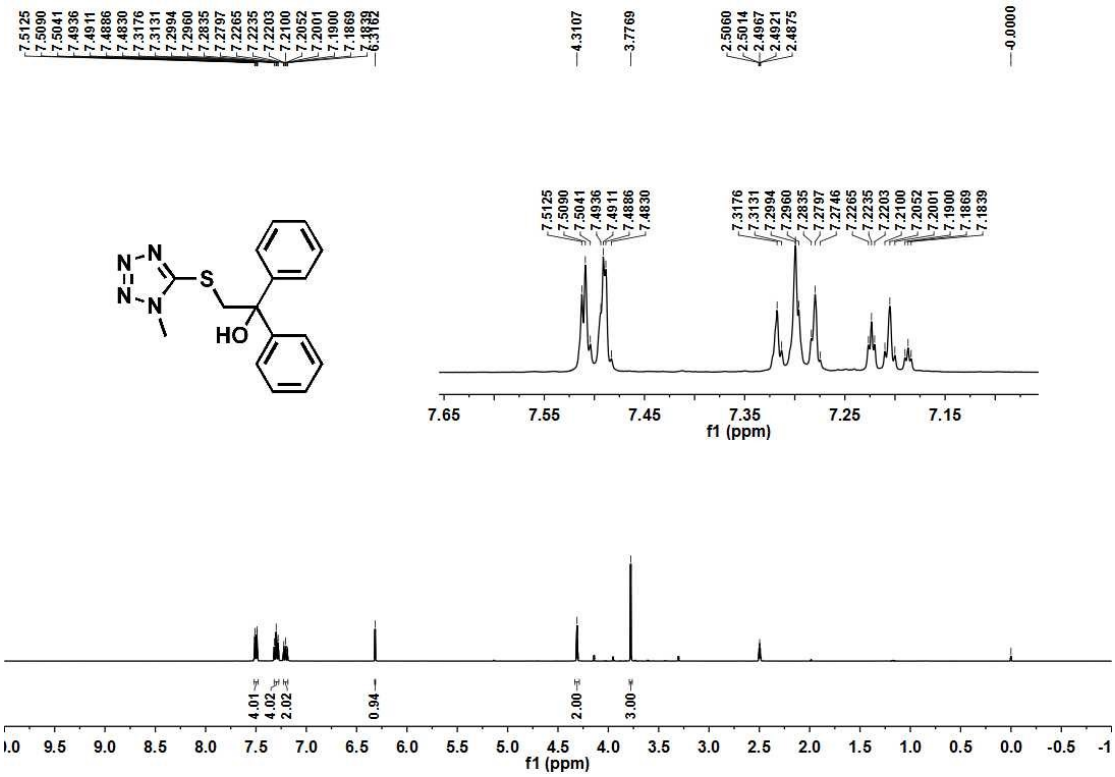
^{1}H NMR of product 3j in DMSO-d_6 (400 MHz)



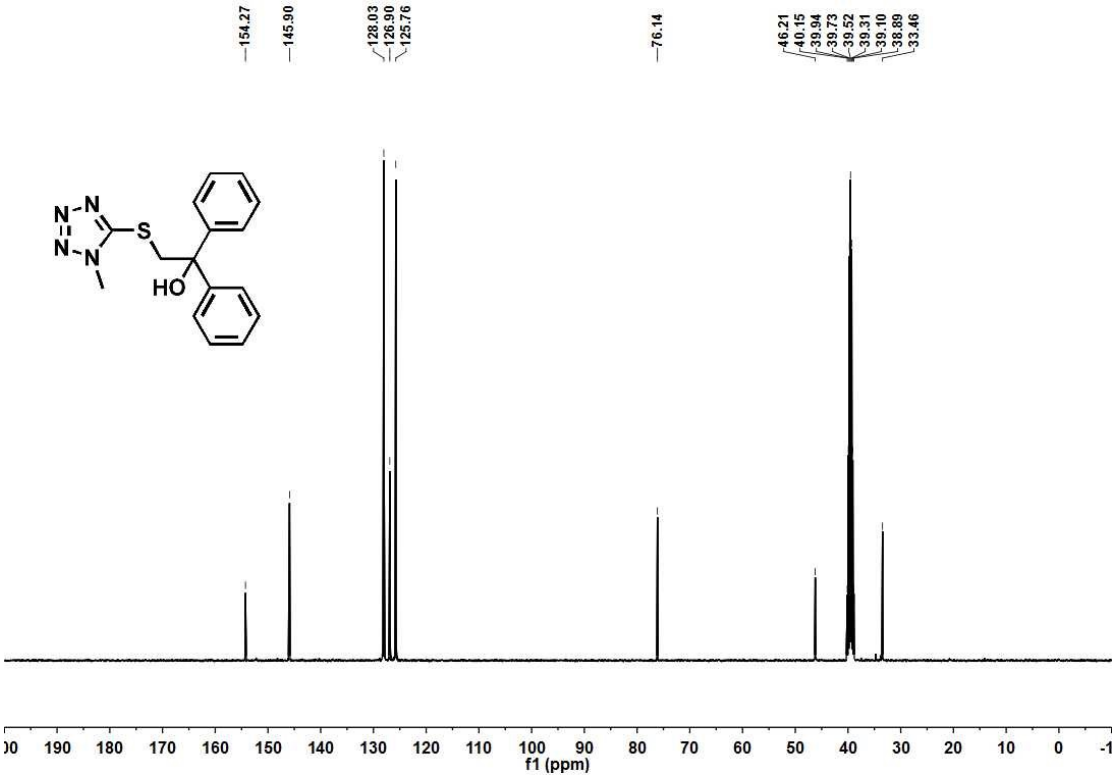
^{13}C NMR of product 3j in DMSO-d_6 (100 MHz)



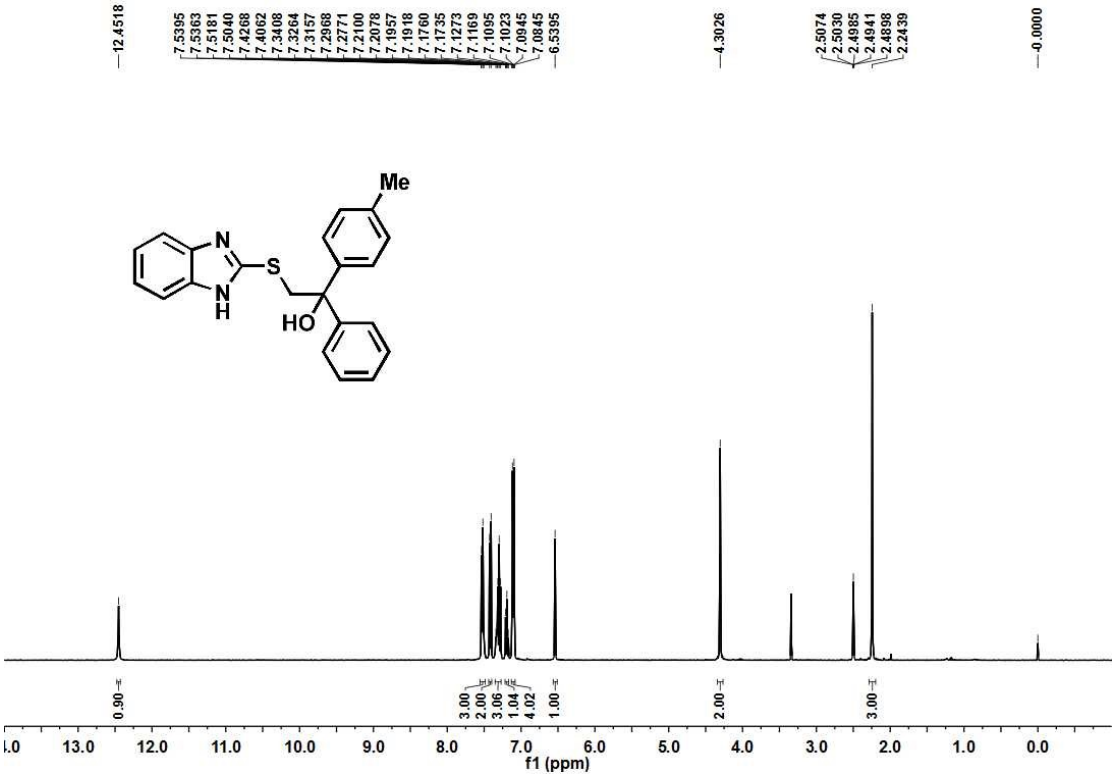
^{1}H NMR of product 3k in DMSO-d_6 (400 MHz)



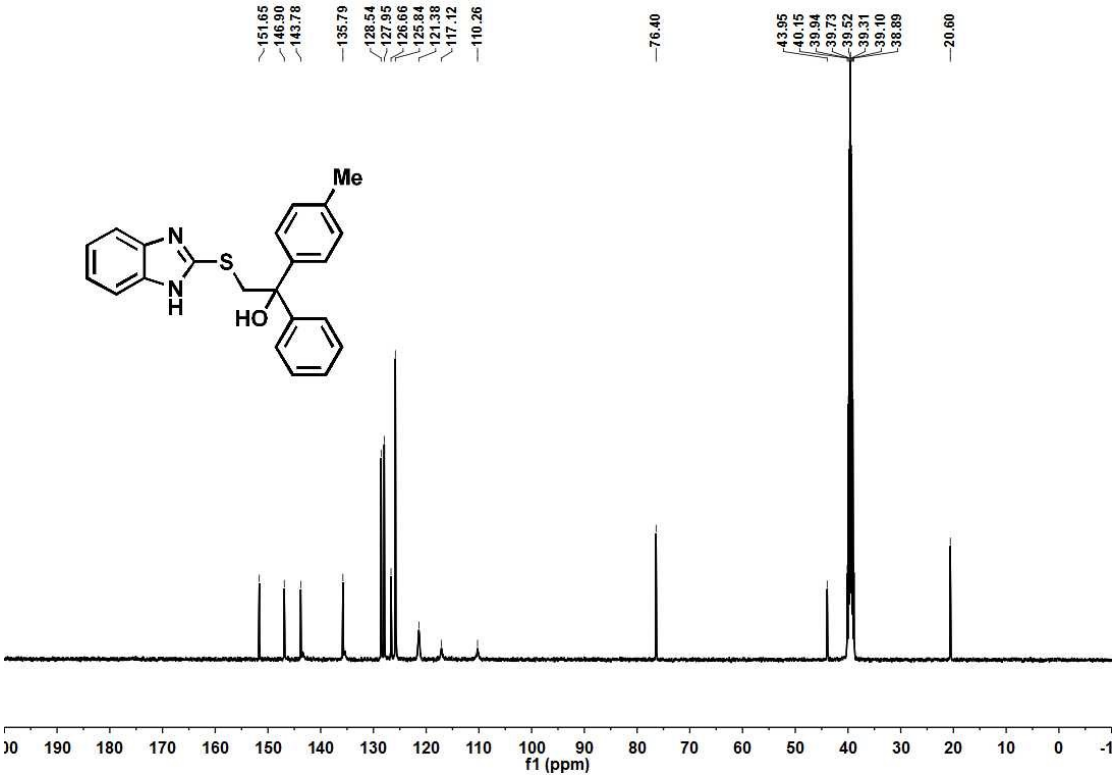
^{13}C NMR of product 3k in DMSO-d_6 (100 MHz)



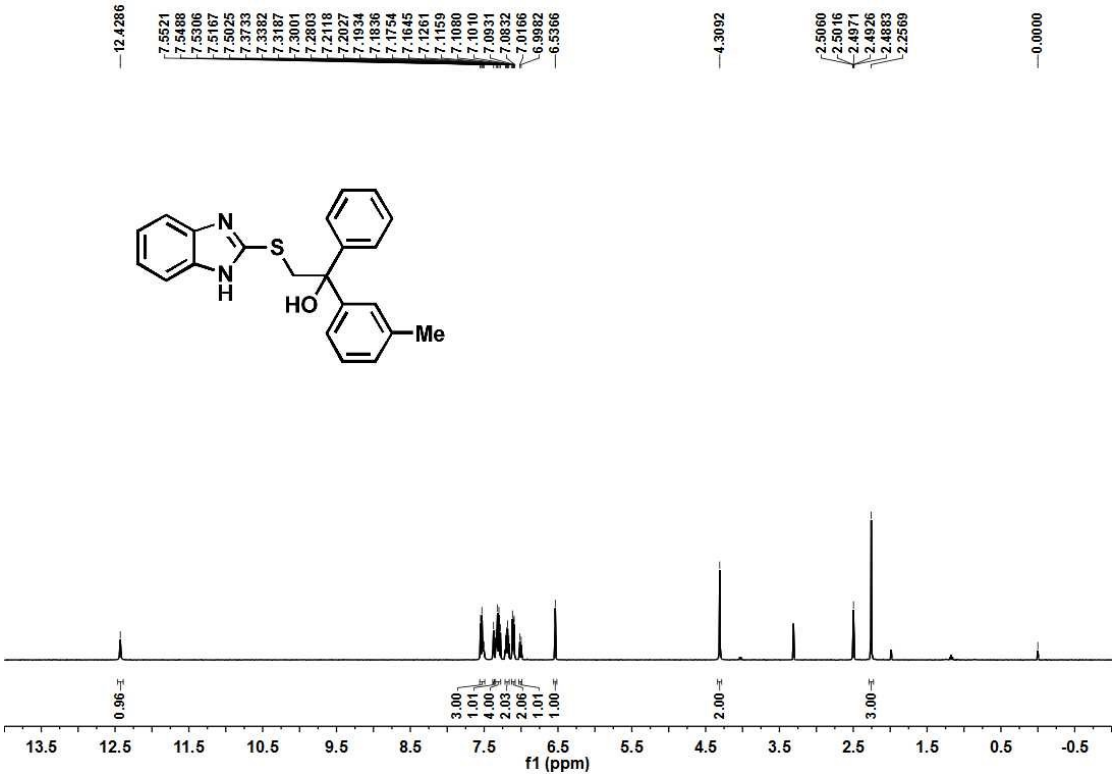
^{1}H NMR of product 4a in DMSO-d_6 (400 MHz)



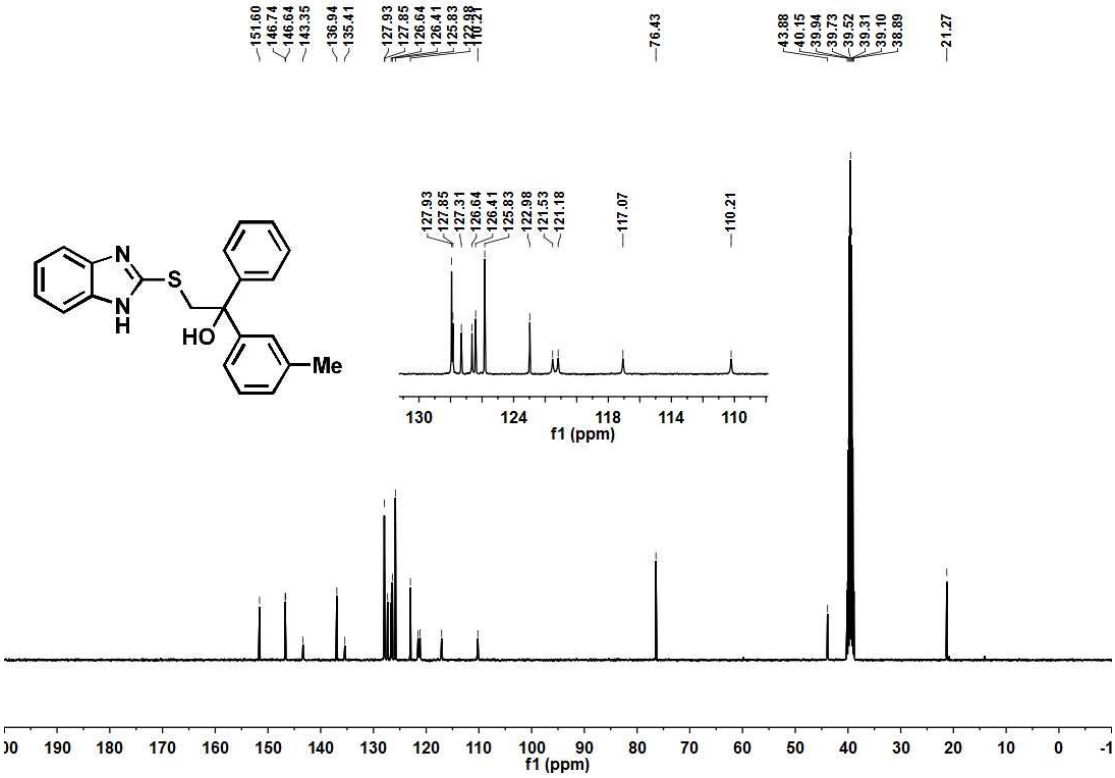
^{13}C NMR of product 4a in DMSO-d_6 (100 MHz)



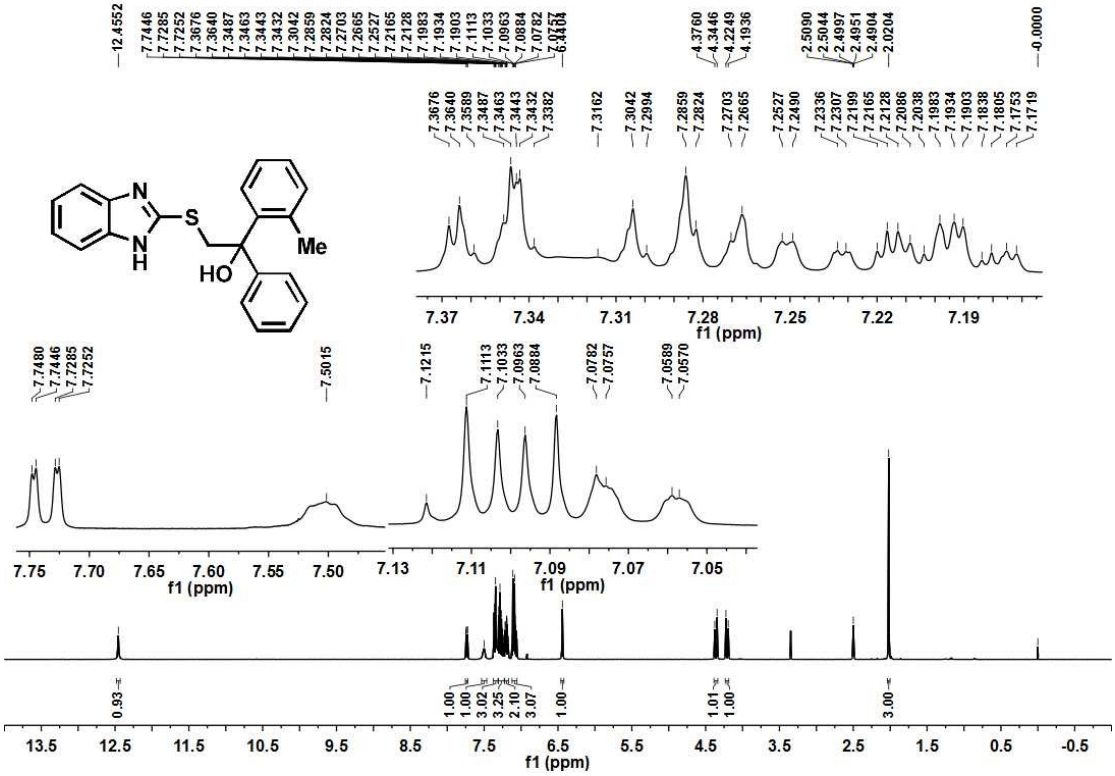
^{1}H NMR of product 4b in DMSO-d_6 (400 MHz)



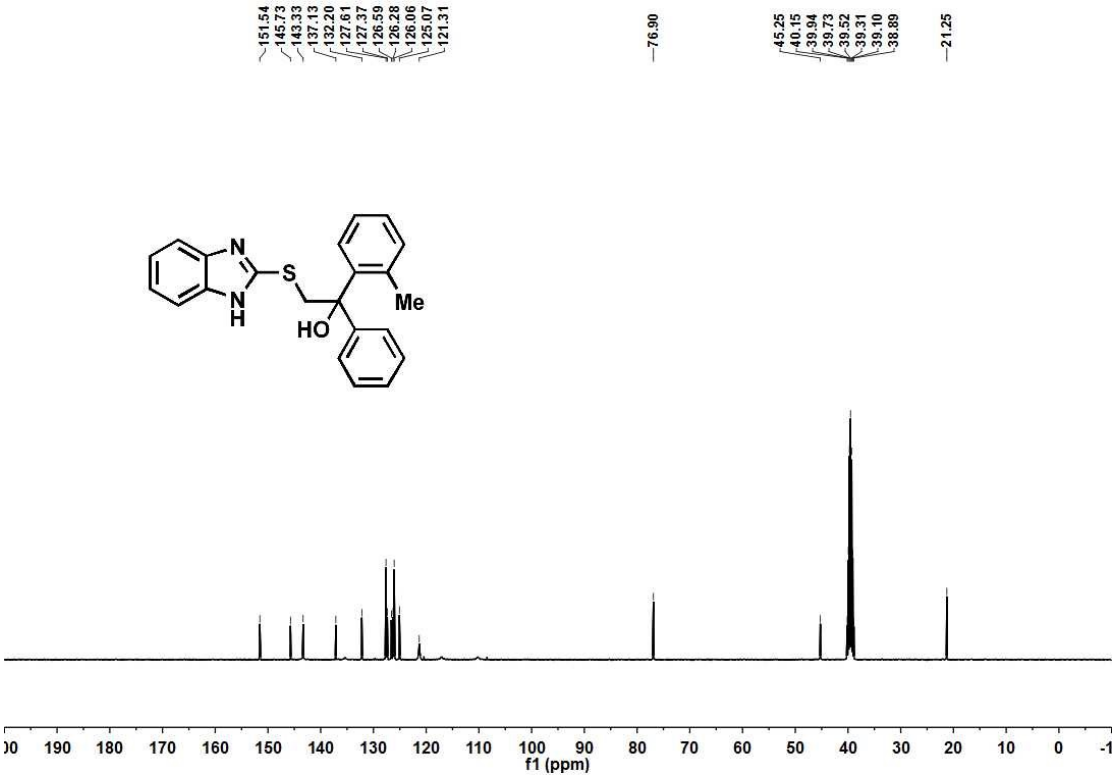
^{13}C NMR of product 4b in DMSO-d_6 (100 MHz)



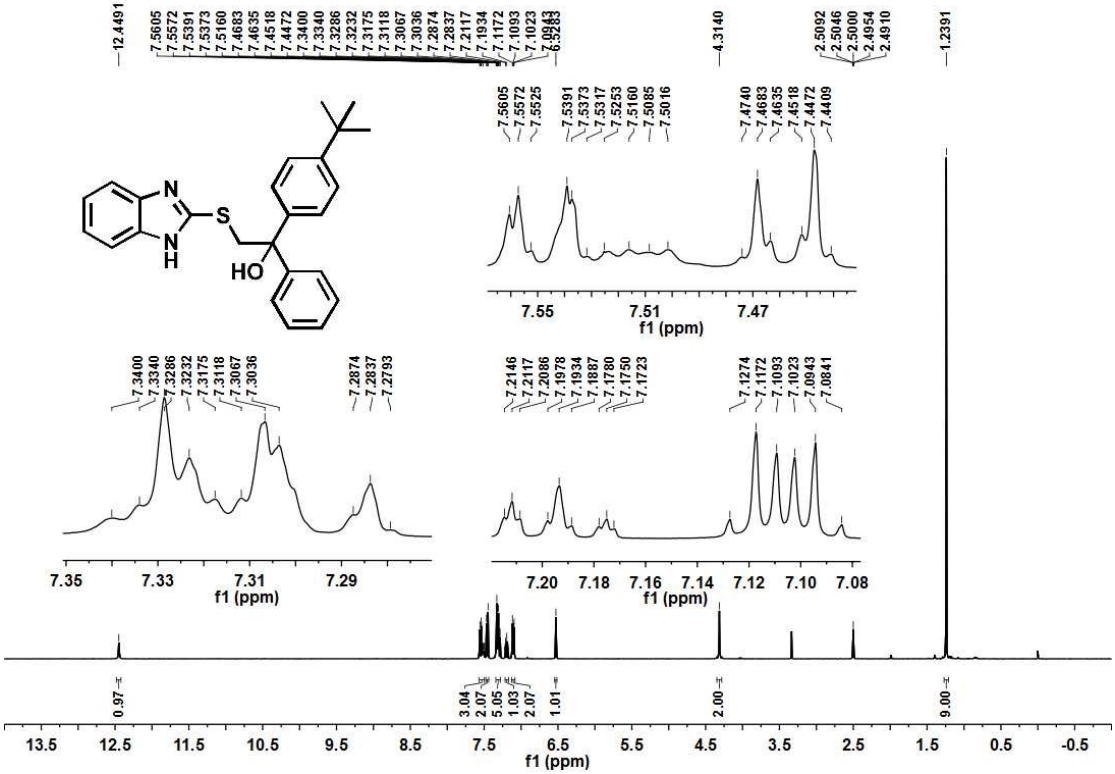
^{1}H NMR of product 4c in DMSO-d_6 (400 MHz)



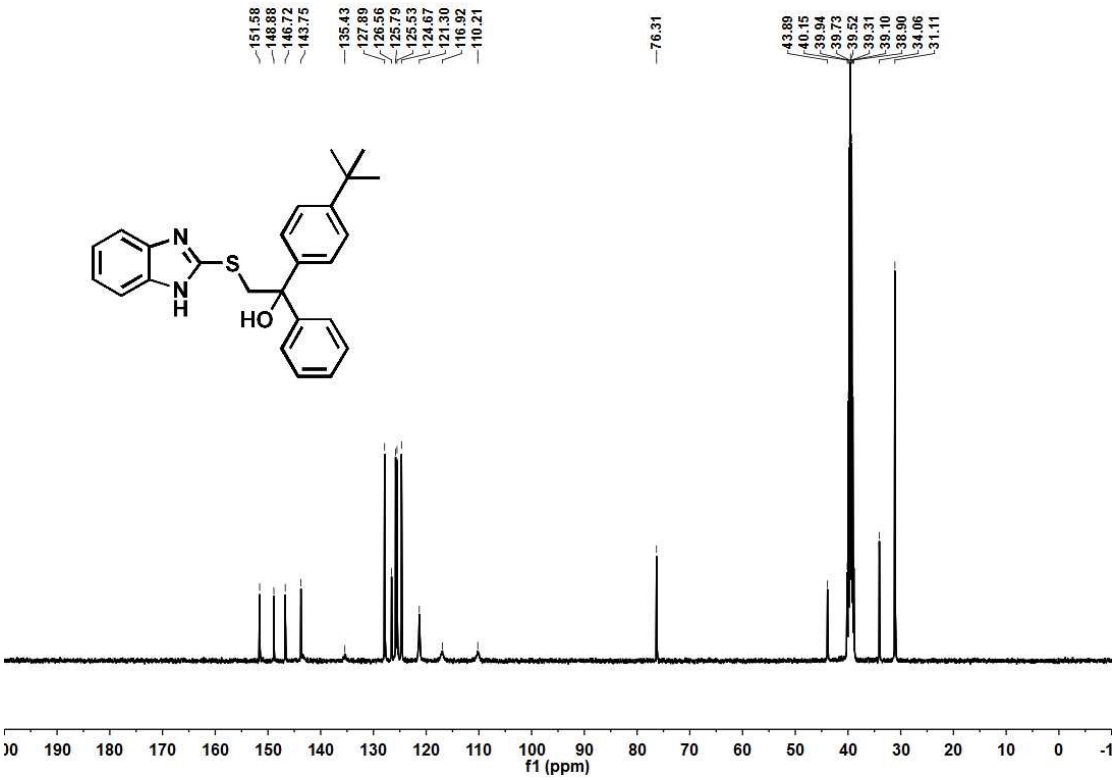
^{13}C NMR of product 4c in DMSO-d_6 (100 MHz)



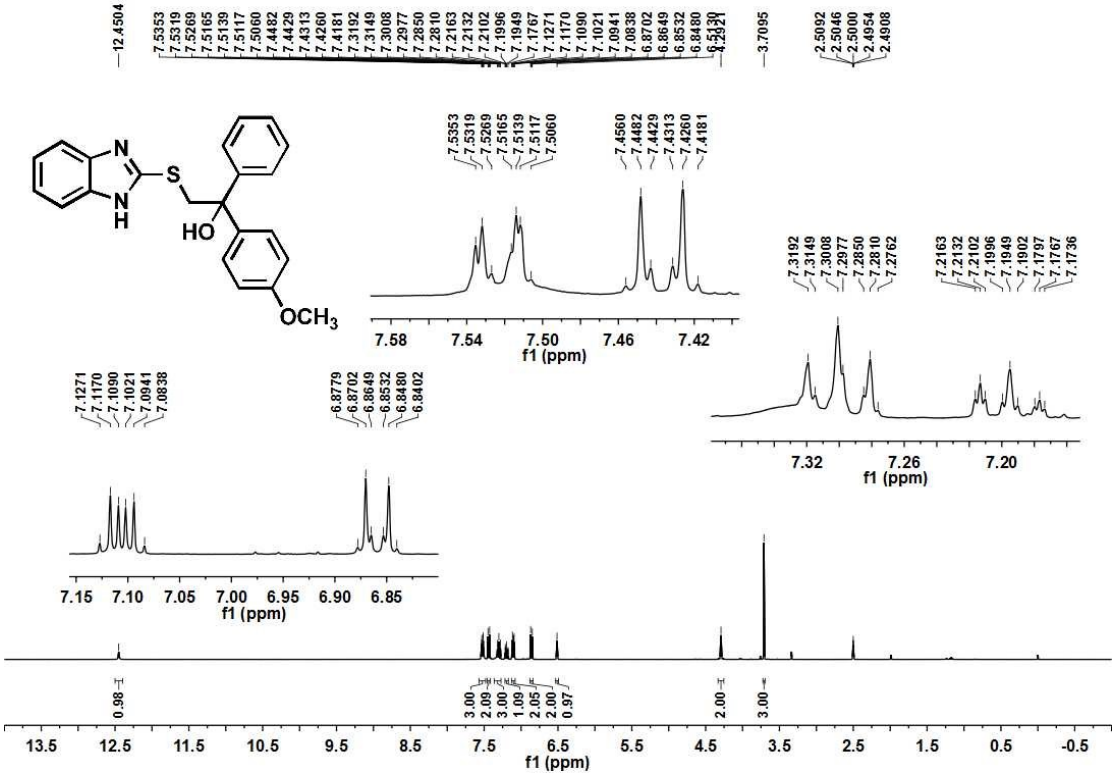
^{1}H NMR of product 4d in DMSO-d_6 (400 MHz)



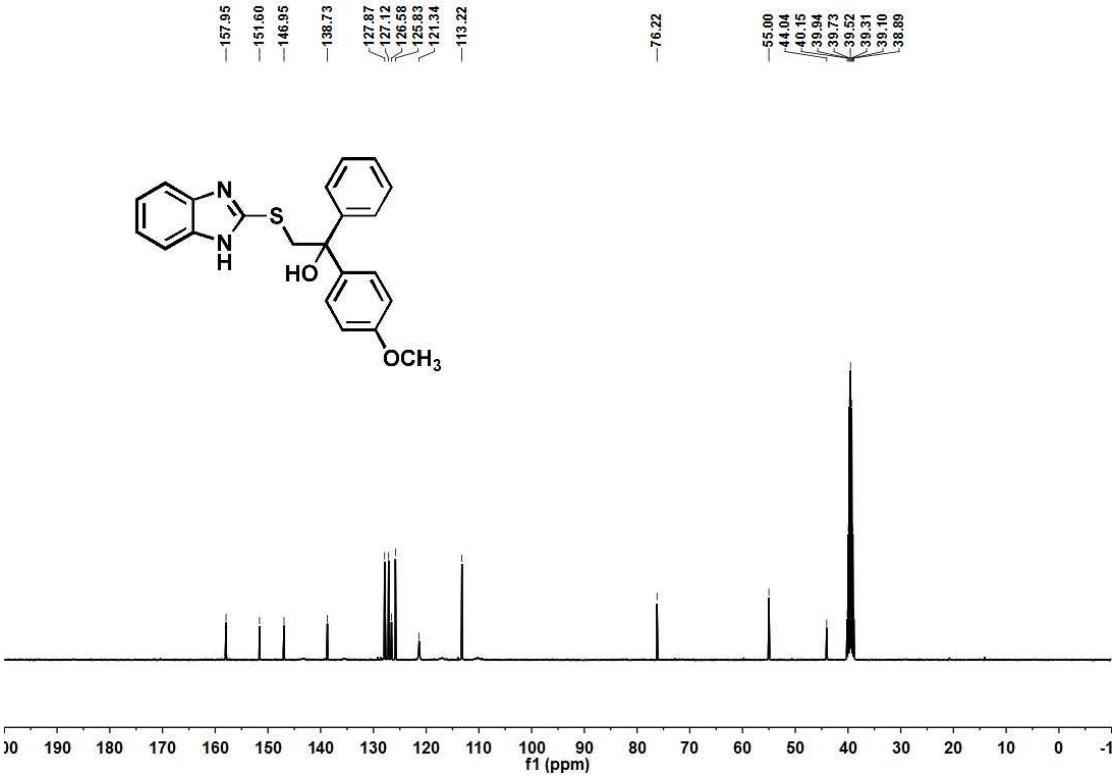
^{13}C NMR of product 4d in DMSO-d_6 (100 MHz)



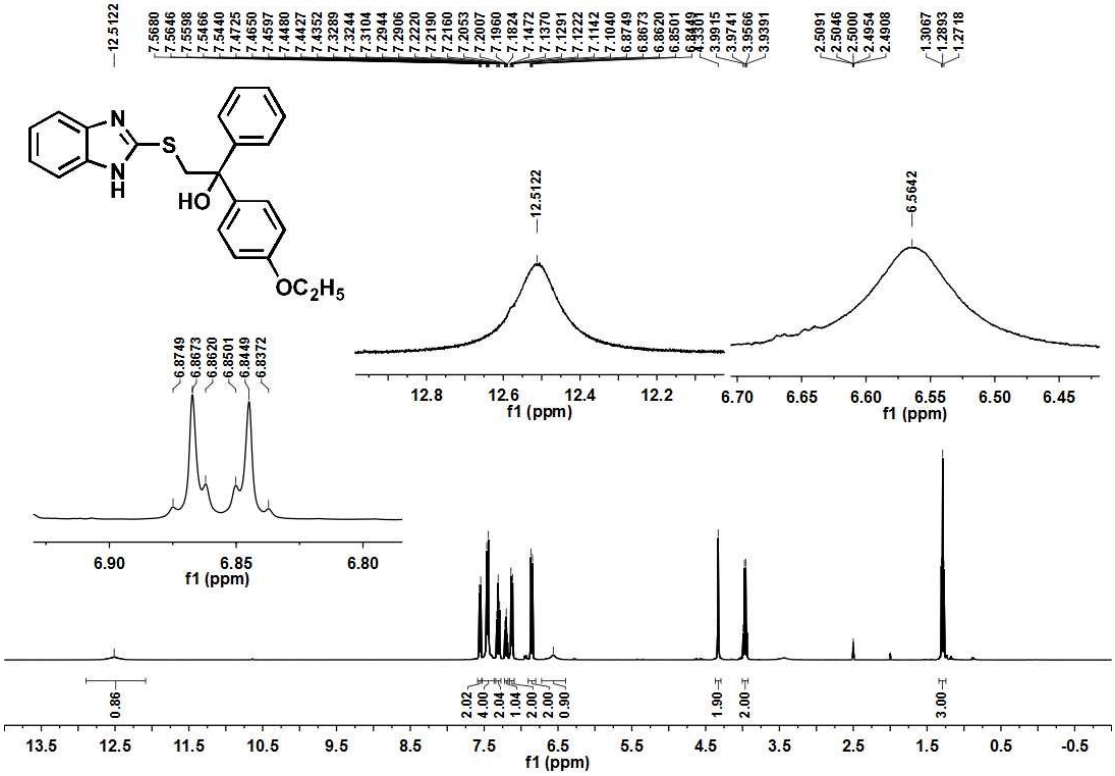
^{1}H NMR of product 4e in DMSO-d_6 (400 MHz)



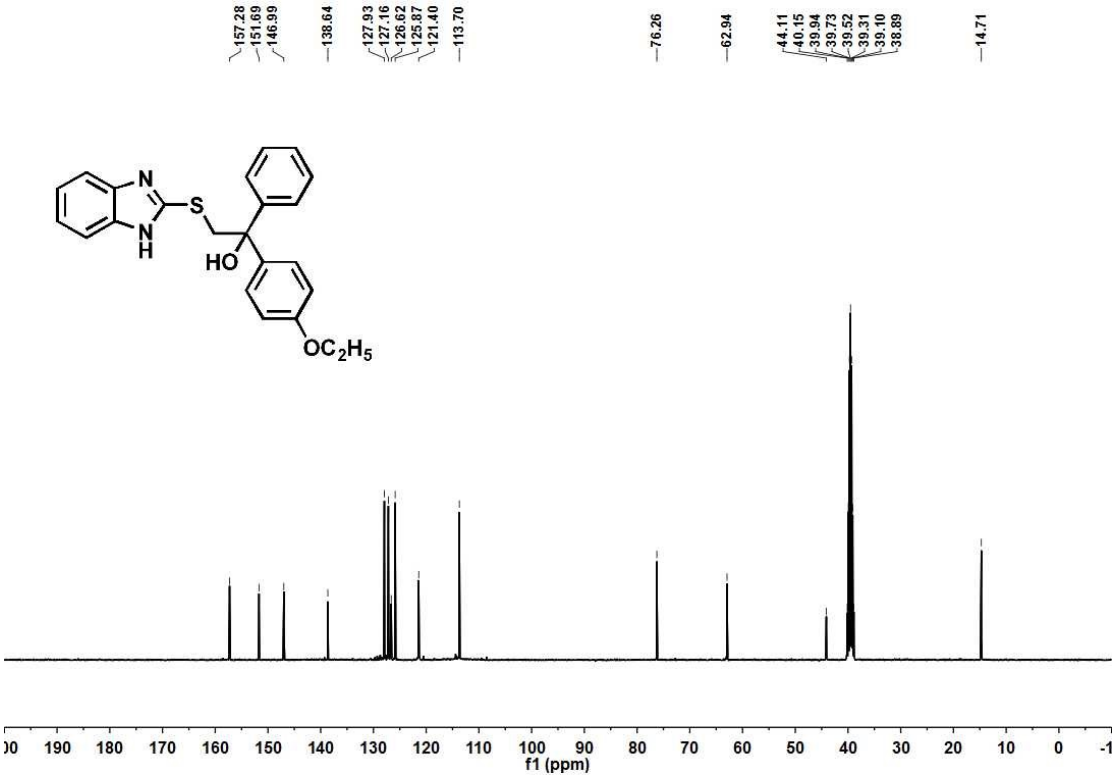
^{13}C NMR of product 4e in DMSO-d_6 (100 MHz)



^{1}H NMR of product 4f in DMSO-d_6 (400 MHz)



^{13}C NMR of product 4f in DMSO-d_6 (100 MHz)



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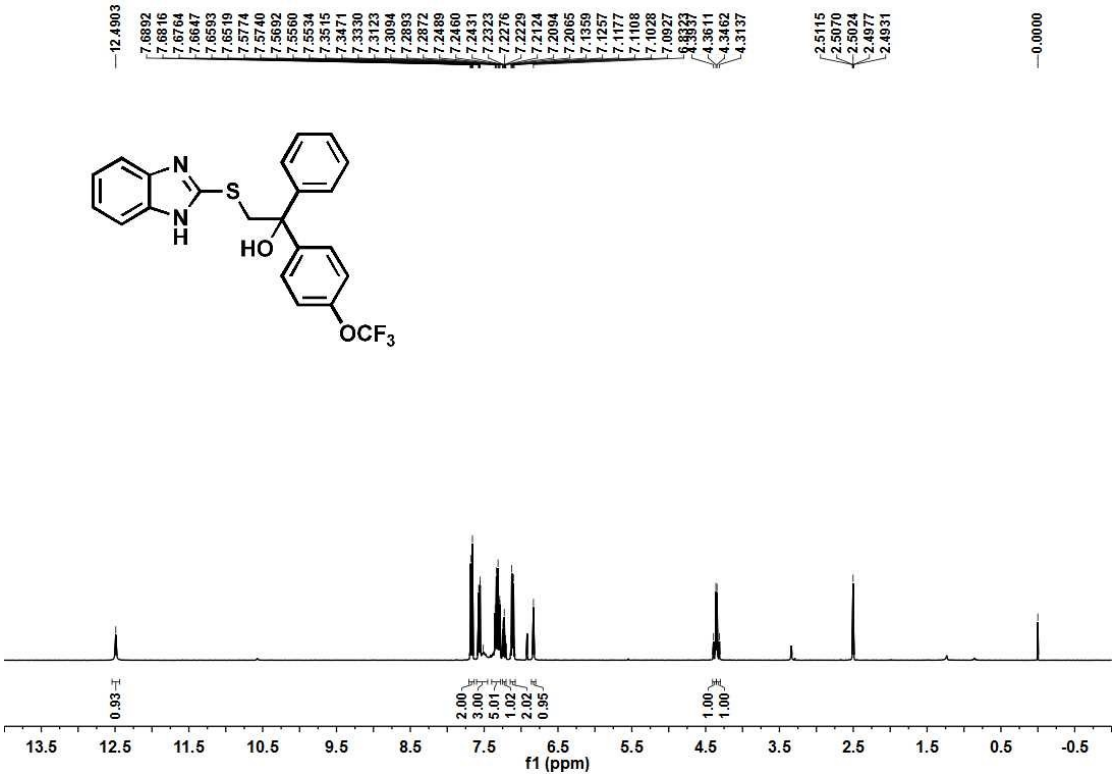
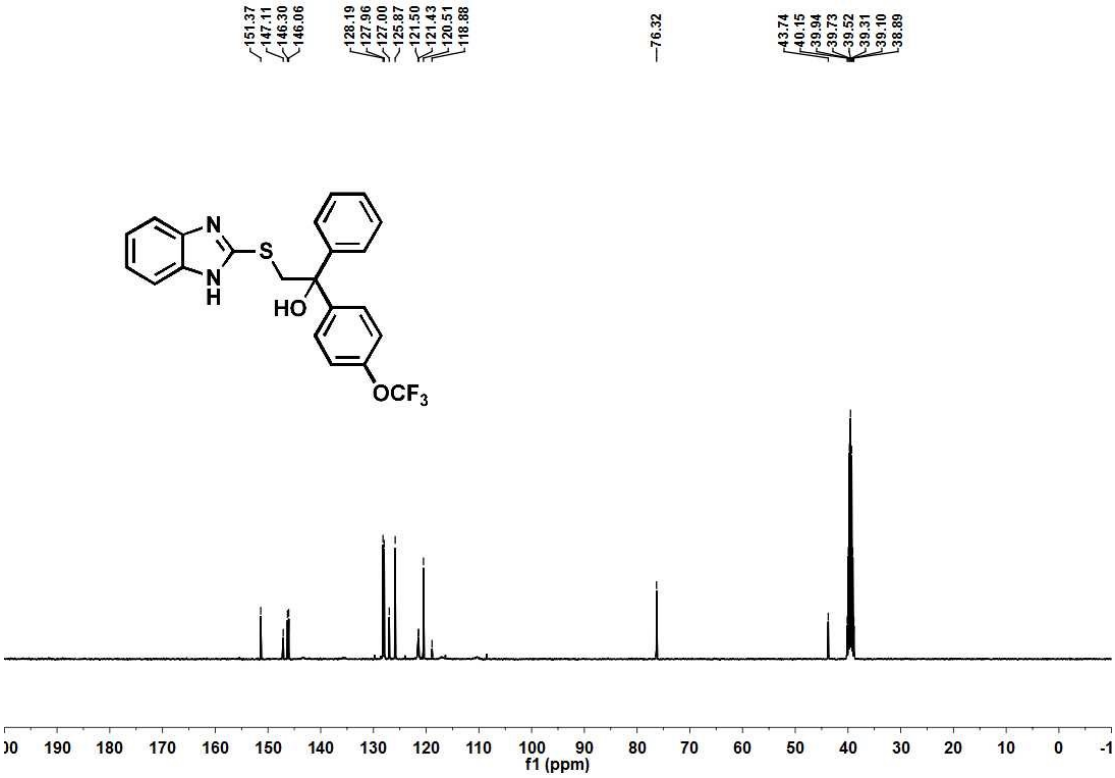
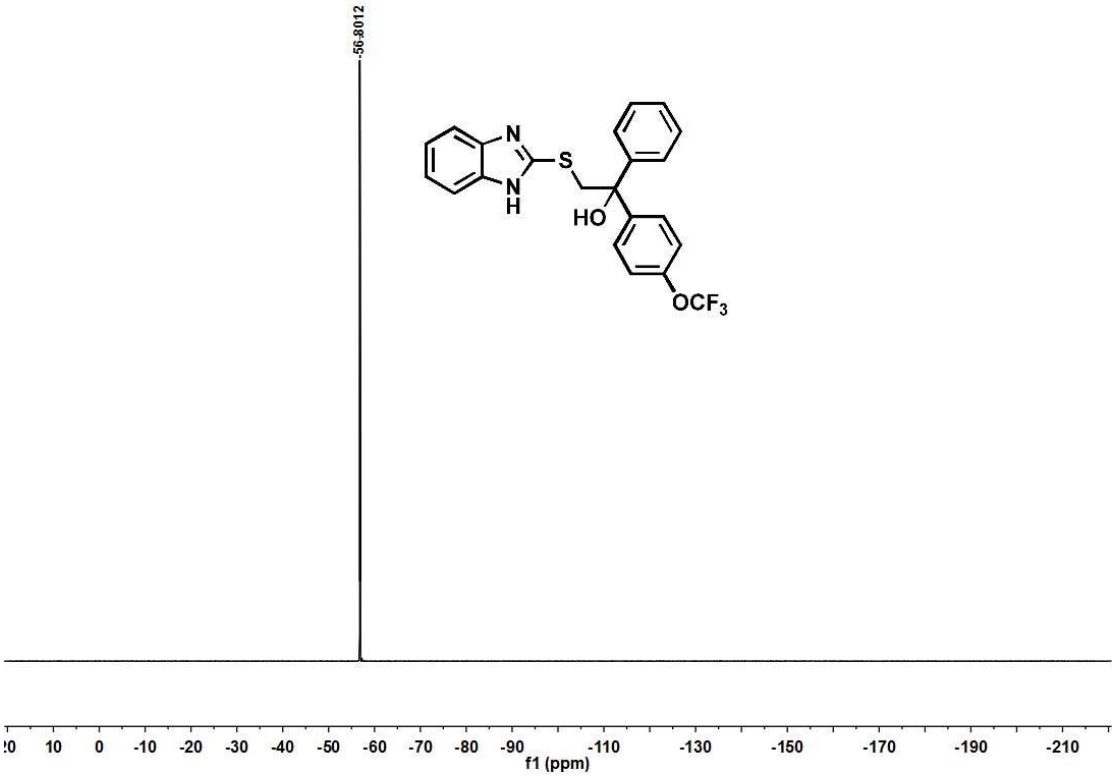


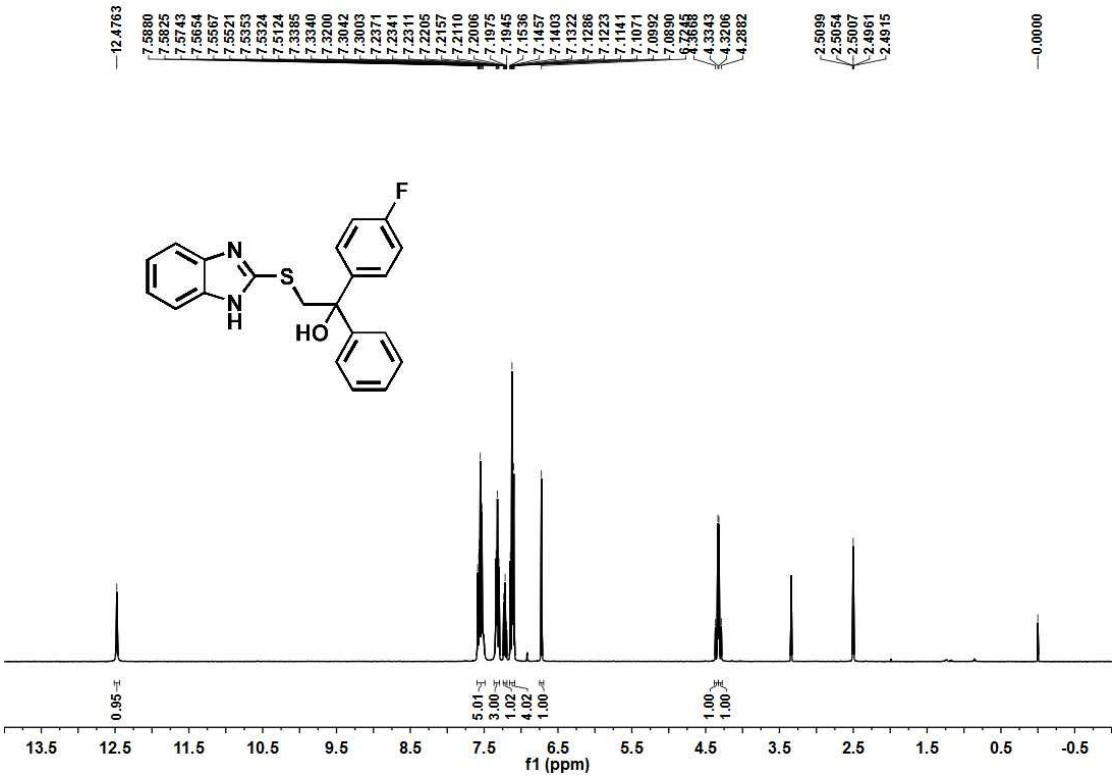
^{13}C NMR of product 4g in DMSO-d_6 (100 MHz)



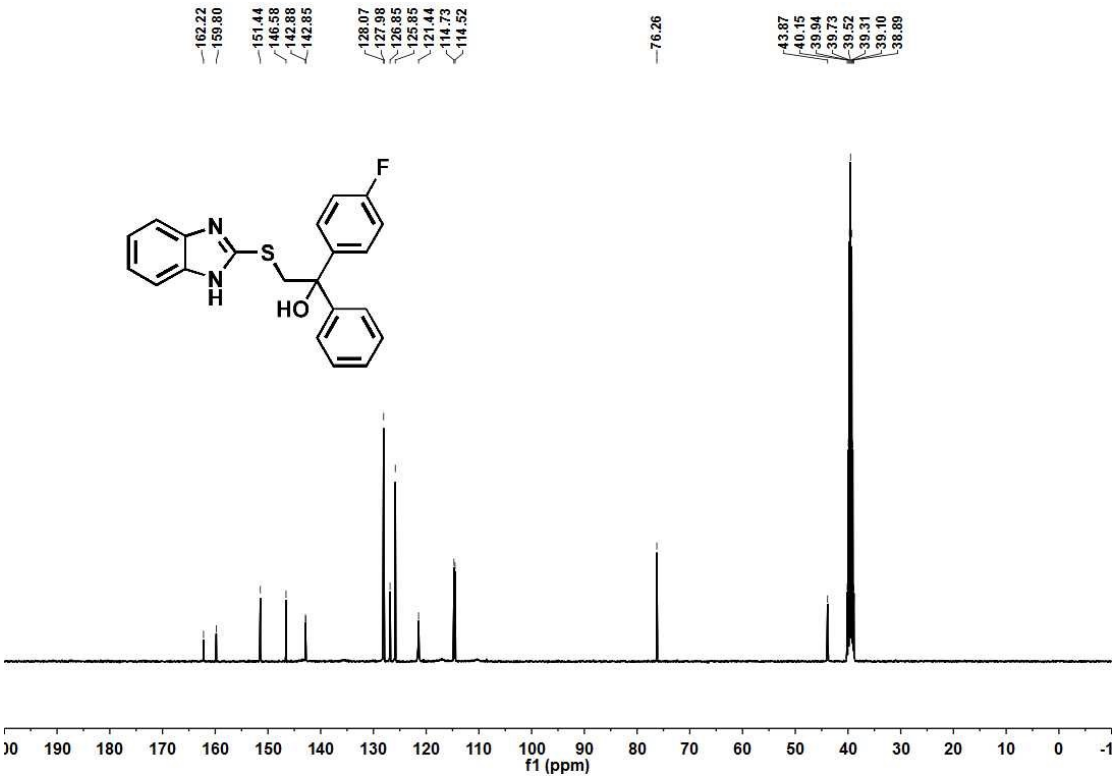
^{19}F NMR of product 4g in DMSO-d_6 (376 MHz)



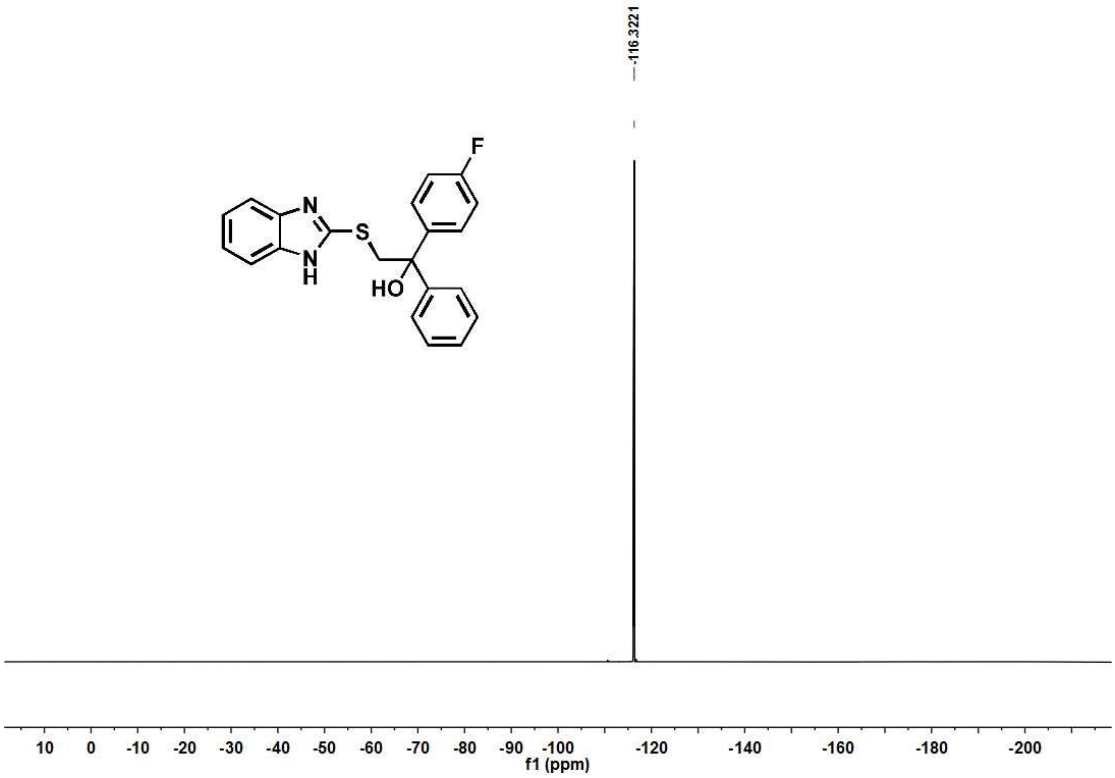
^{1}H NMR of product 4h in DMSO-d_6 (400 MHz)



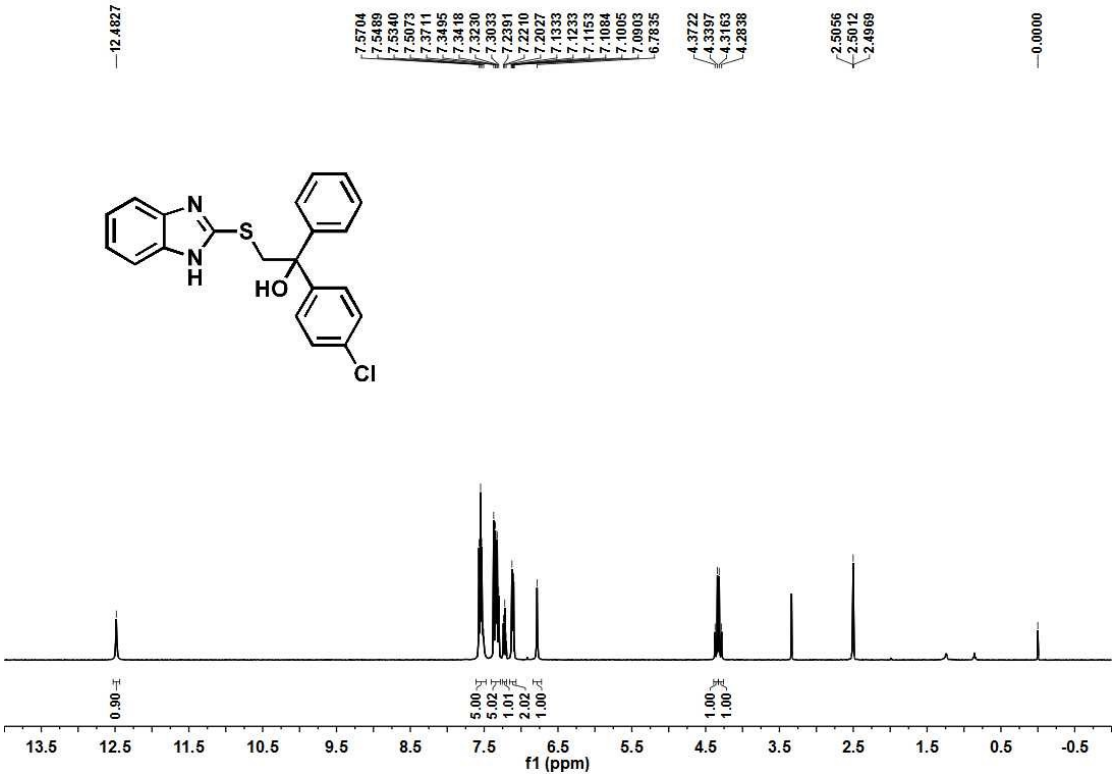
^{13}C NMR of product 4h in DMSO-d_6 (100 MHz)



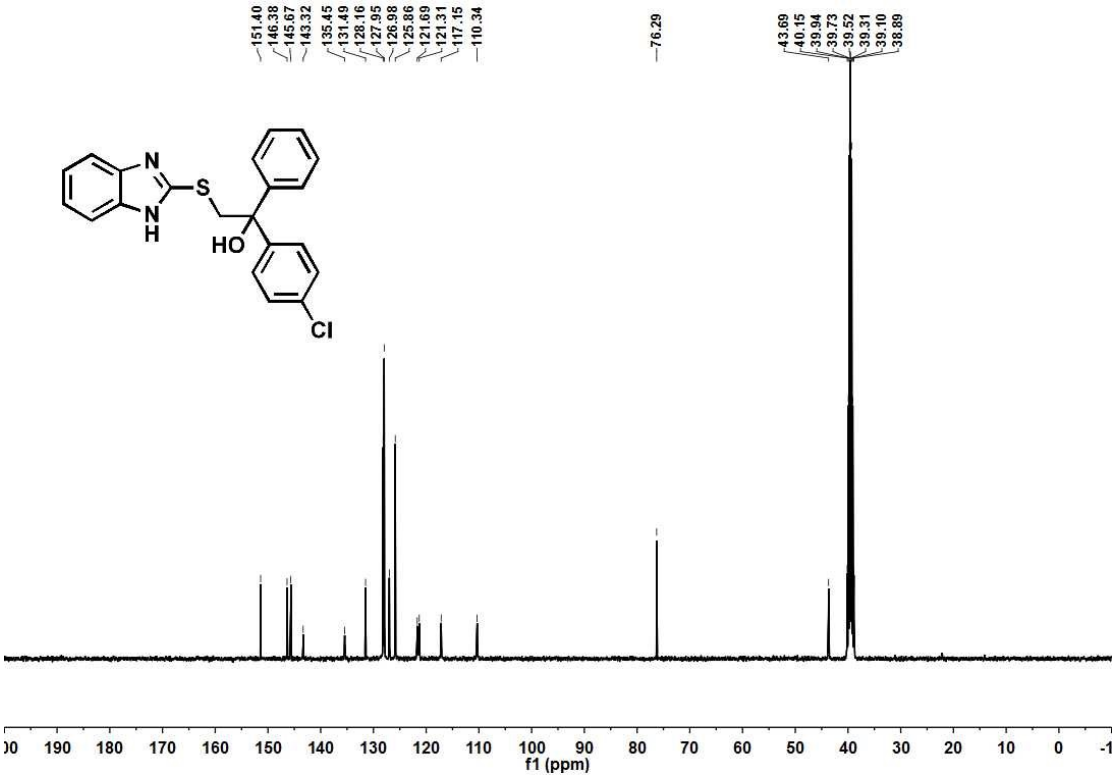
^{19}F NMR of product 4h in DMSO-d_6 (376 MHz)



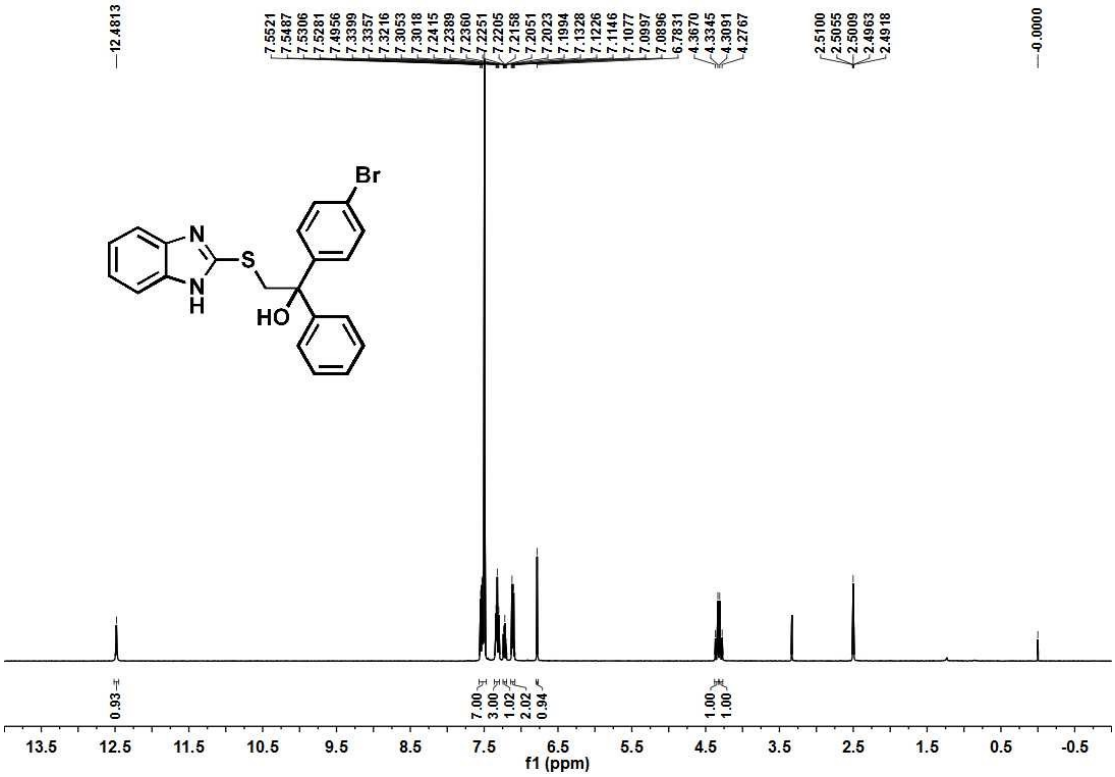
^{1}H NMR of product 4i in DMSO-d_6 (400 MHz)



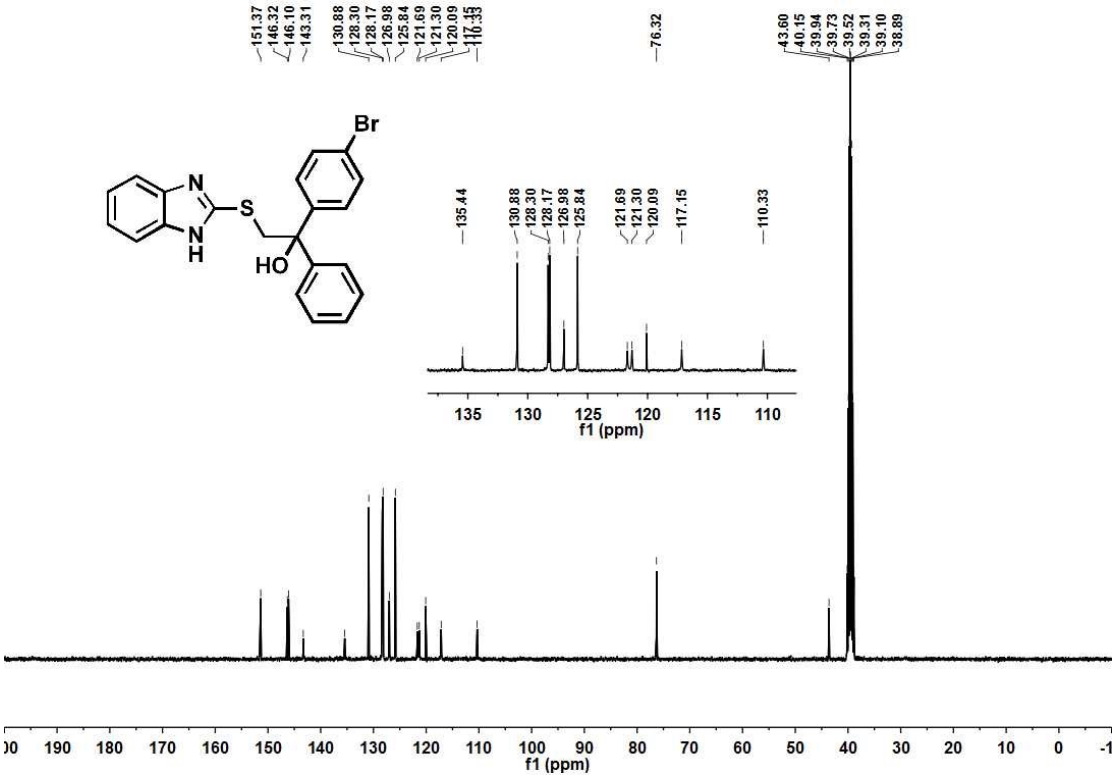
^{13}C NMR of product 4i in DMSO-d_6 (100 MHz)



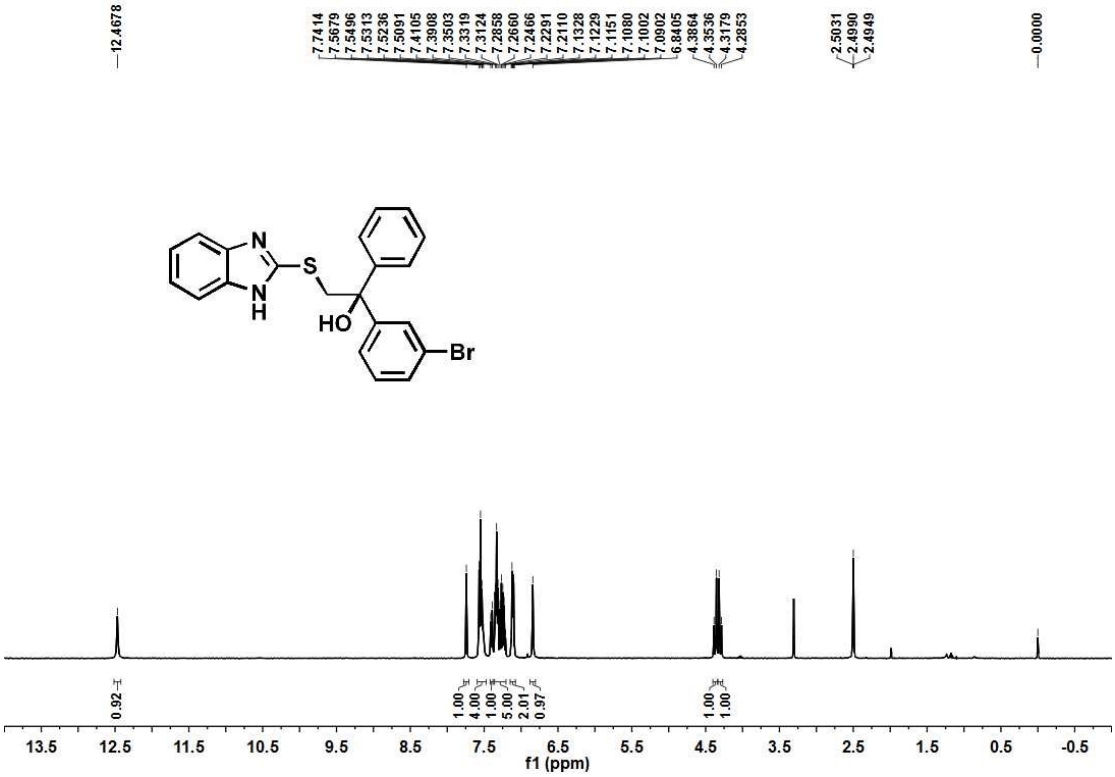
^{1}H NMR of product 4j in DMSO-d_6 (400 MHz)



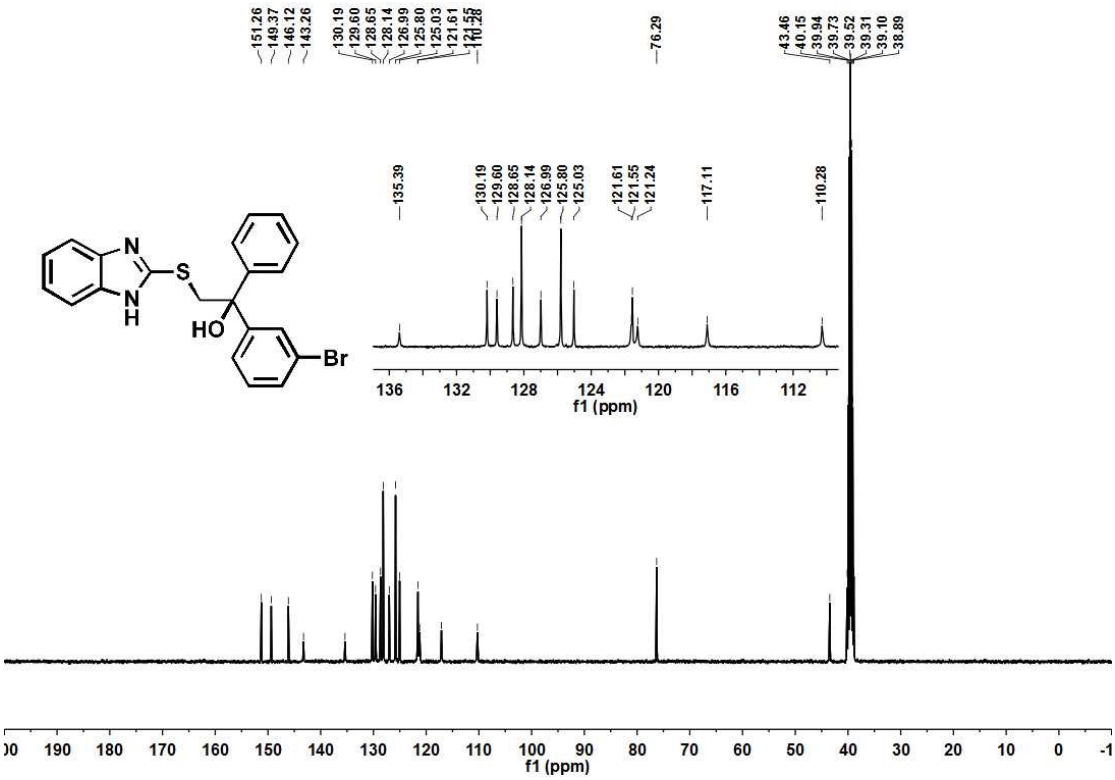
^{13}C NMR of product 4j in DMSO-d_6 (100 MHz)



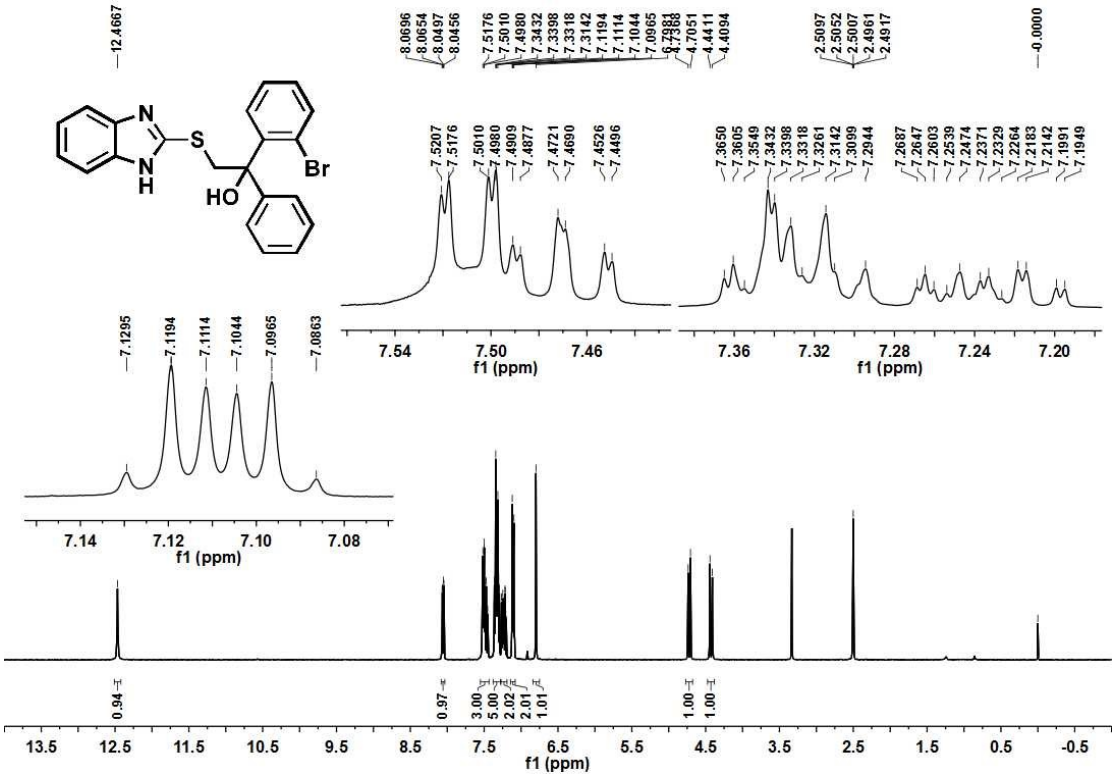
^{1}H NMR of product 4k in DMSO-d_6 (400 MHz)



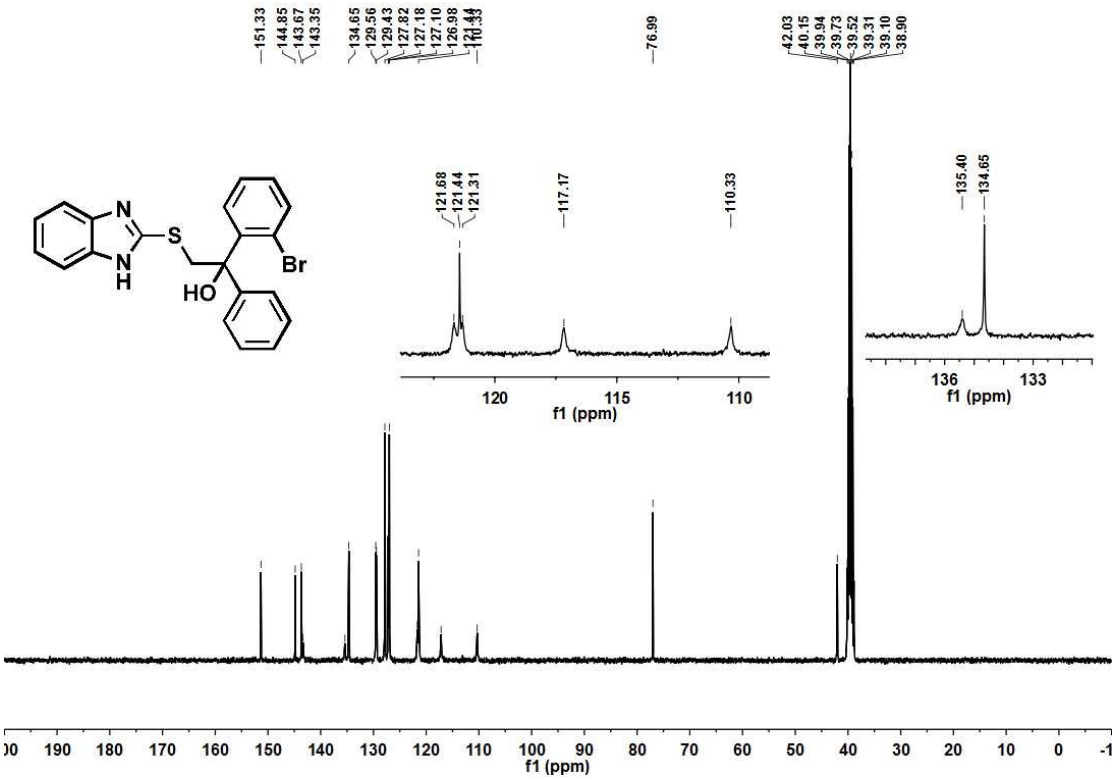
^{13}C NMR of product 4k in DMSO-d_6 (100 MHz)



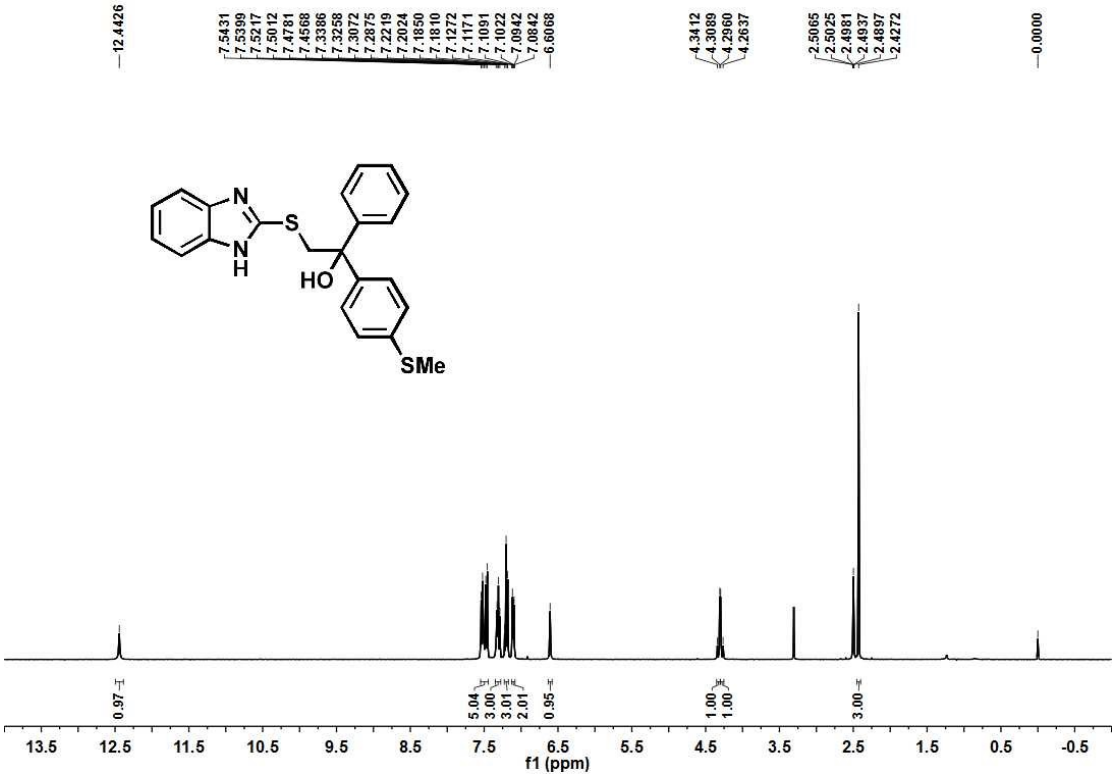
^{1}H NMR of product 4l in DMSO-d_6 (400 MHz)



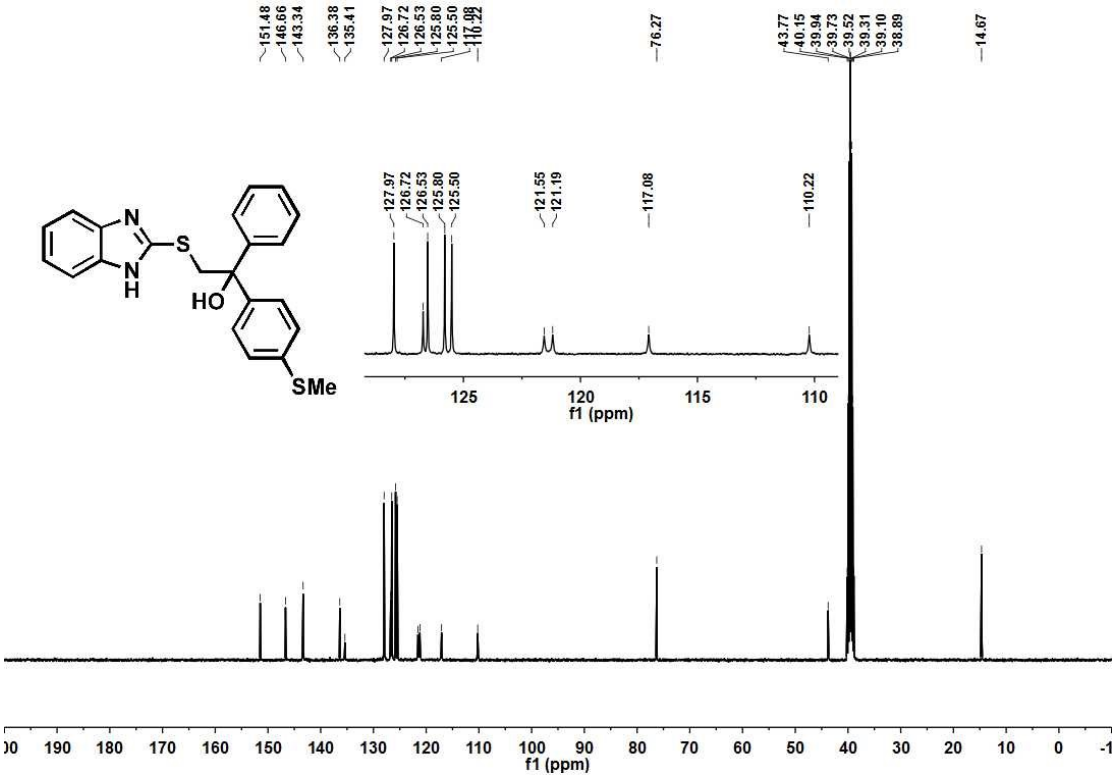
^{13}C NMR of product 4l in DMSO-d_6 (100 MHz)



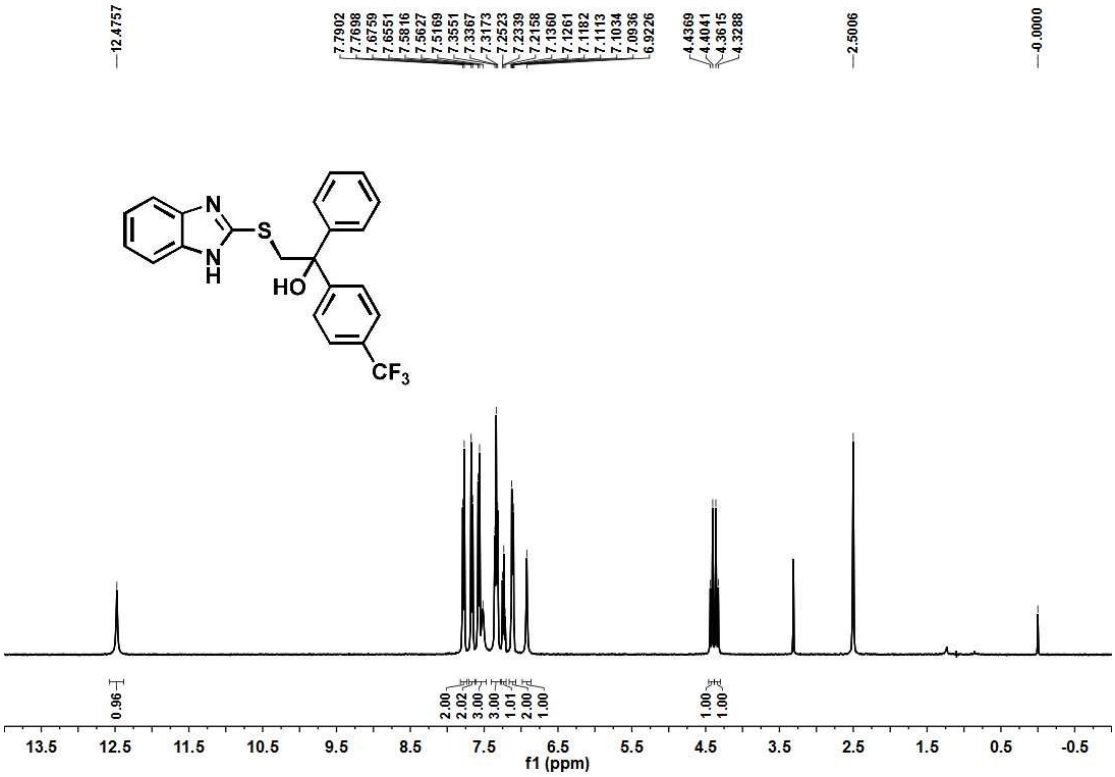
^{1}H NMR of product 4m in DMSO-d_6 (400 MHz)



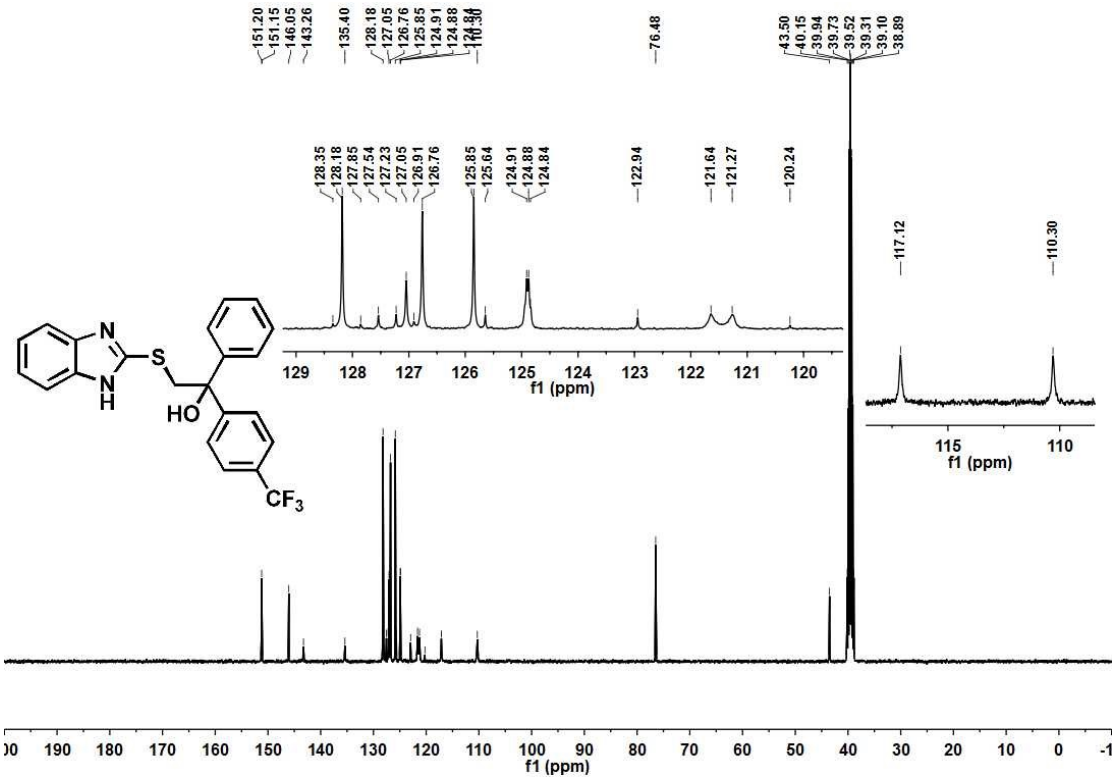
^{13}C NMR of product 4m in DMSO-d_6 (100 MHz)



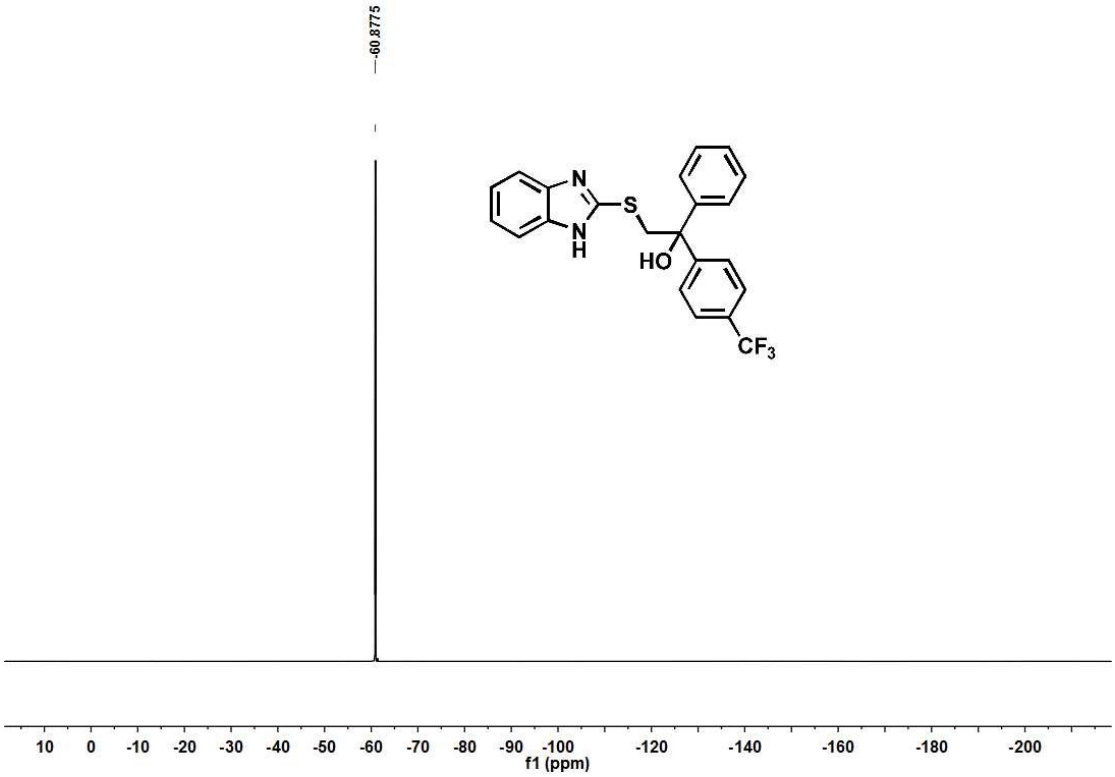
^{1}H NMR of product 4n in DMSO-d_6 (400 MHz)



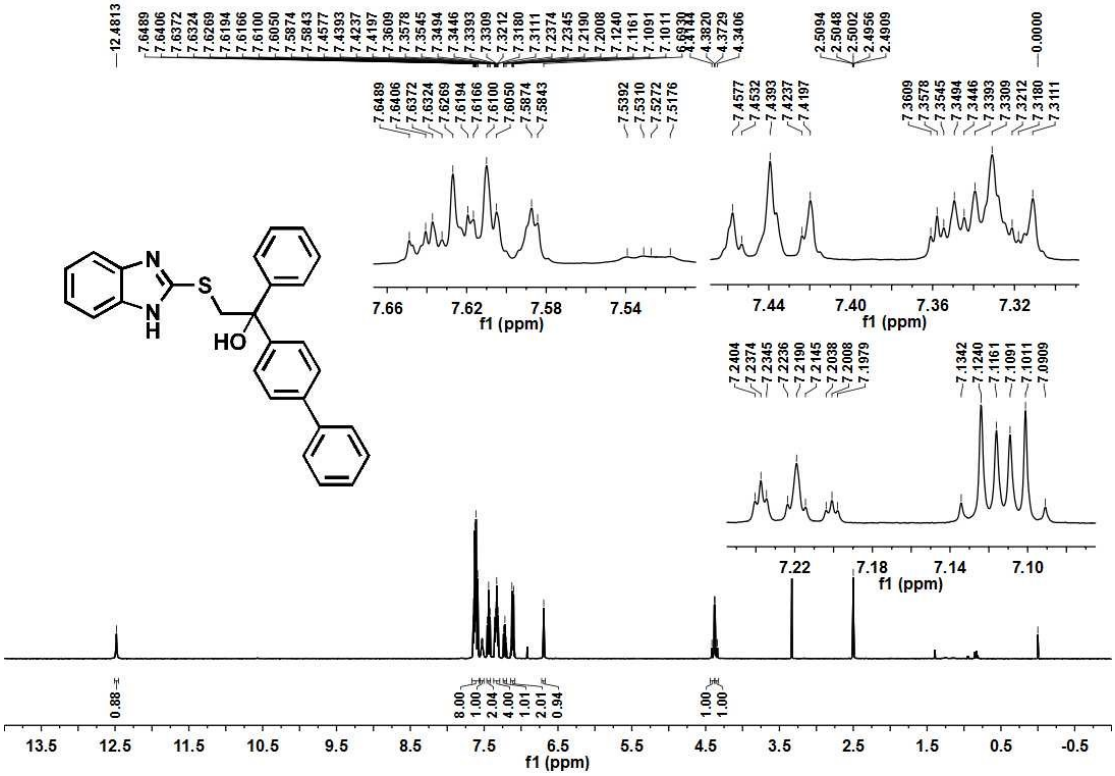
^{13}C NMR of product 4n in DMSO-d_6 (100 MHz)



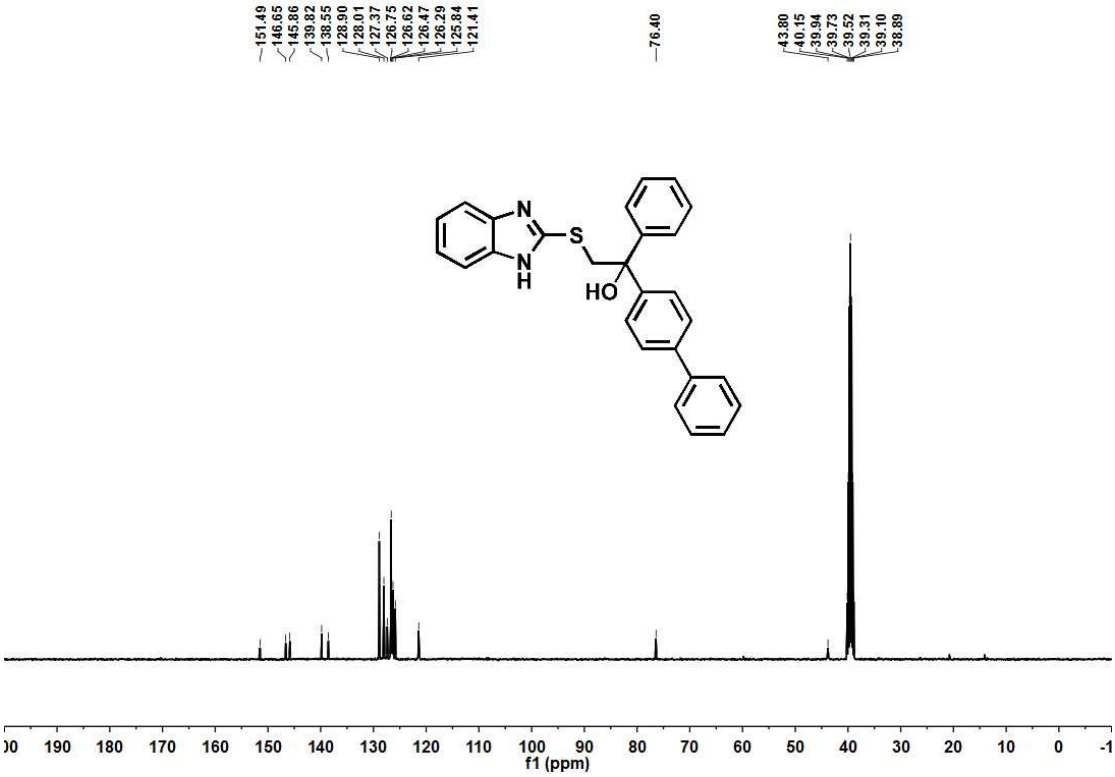
^{19}F NMR of product 4n in DMSO-d_6 (376 MHz)



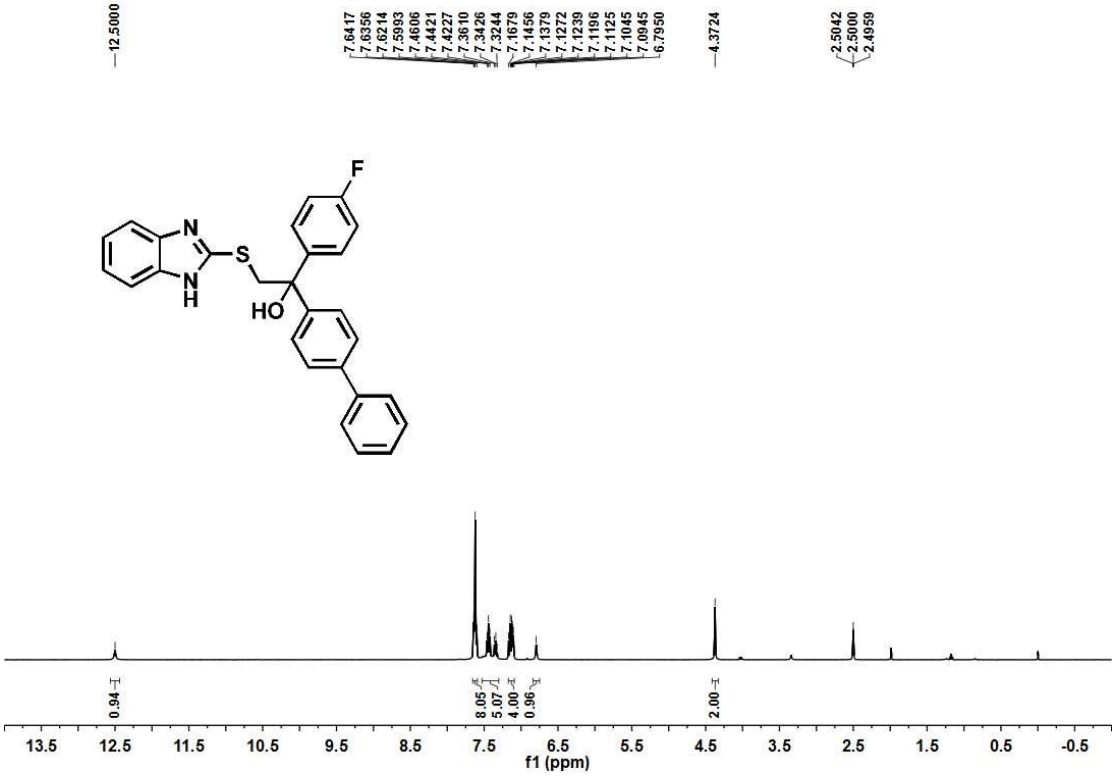
^{1}H NMR of product 4o in DMSO-d_6 (400 MHz)



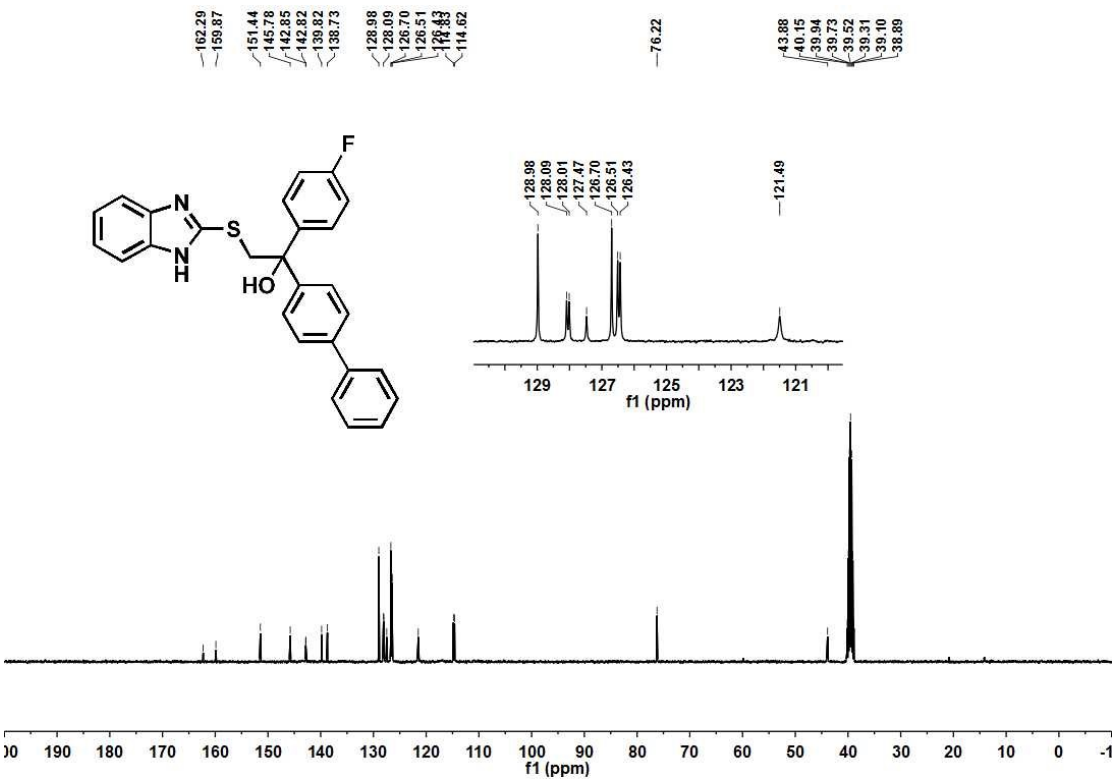
^{13}C NMR of product 4o in DMSO-d_6 (100 MHz)



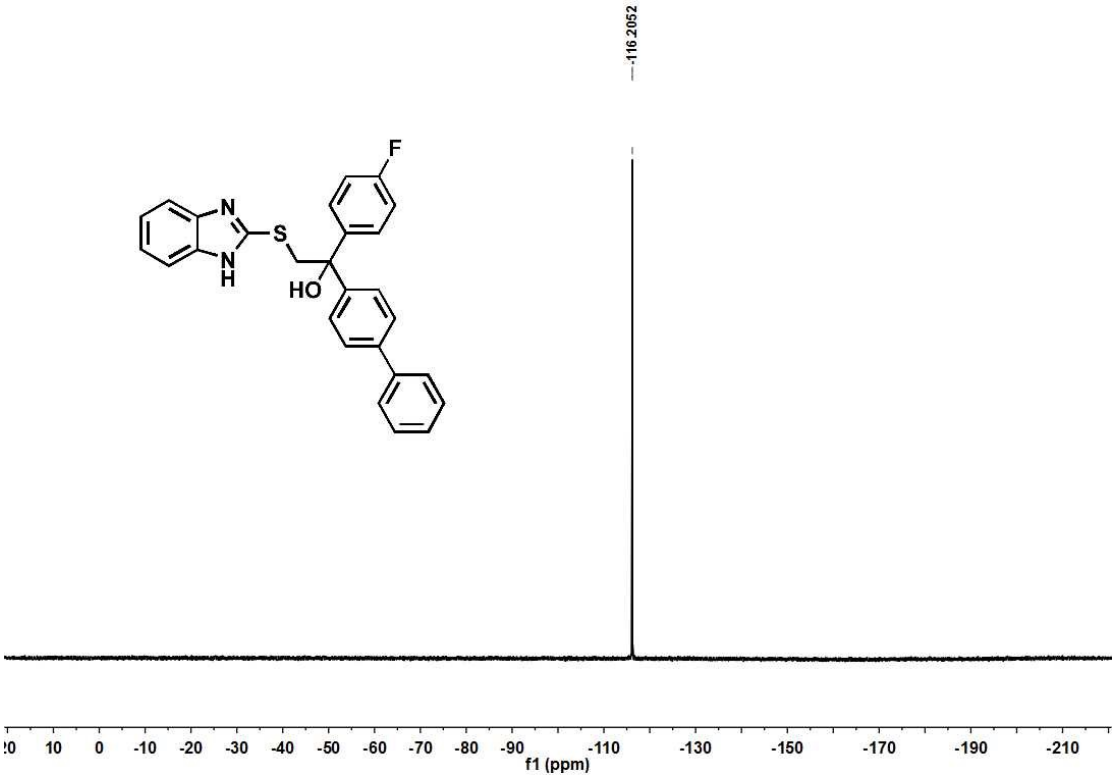
^{1}H NMR of product 4p in DMSO-d_6 (400 MHz)



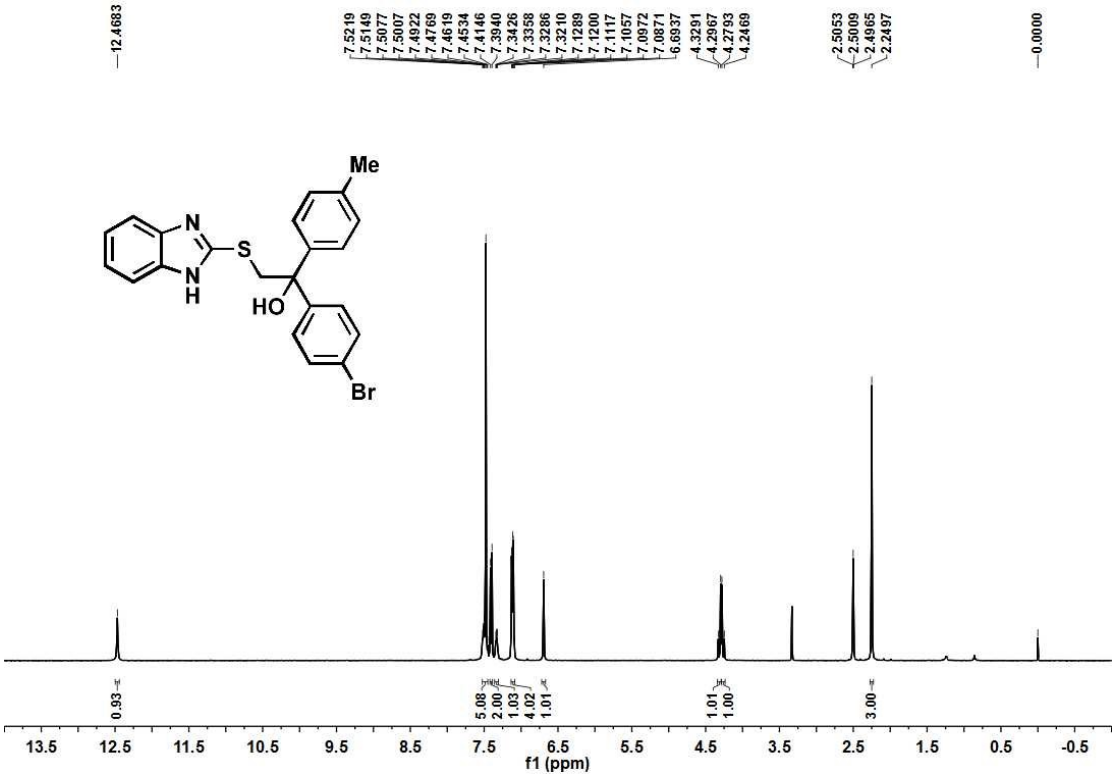
^{13}C NMR of product 4p in DMSO-d_6 (100 MHz)



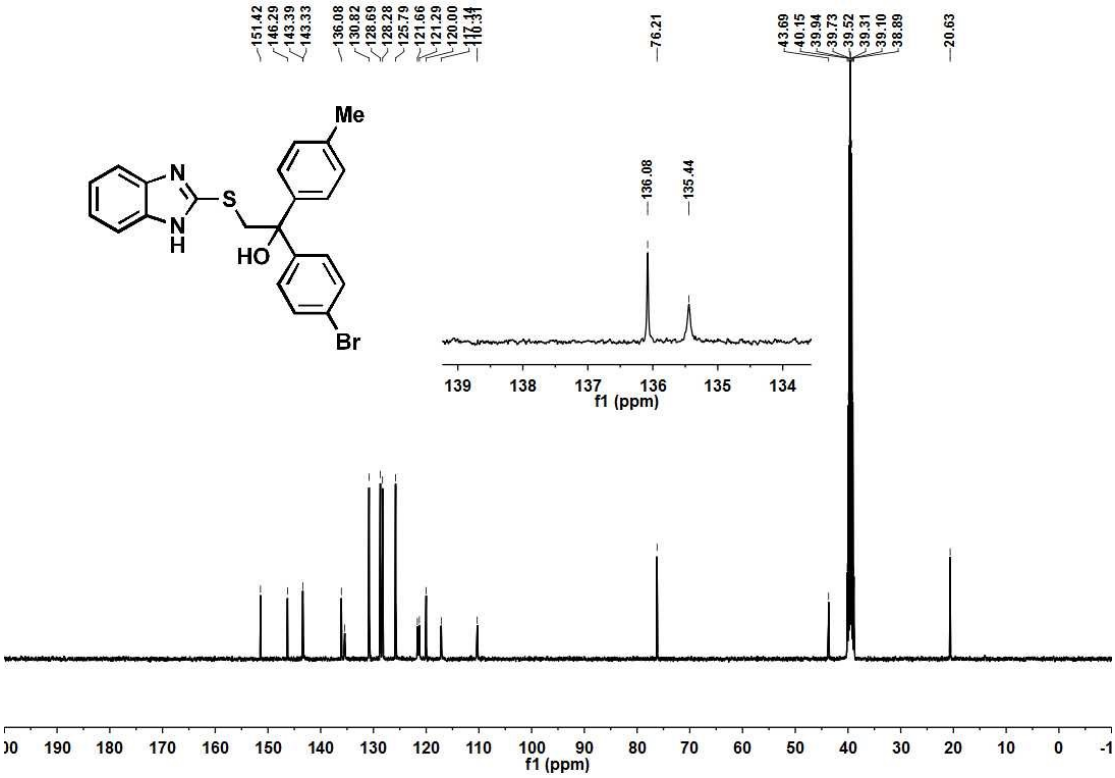
^{19}F NMR of product 4p in DMSO-d_6 (376 MHz)



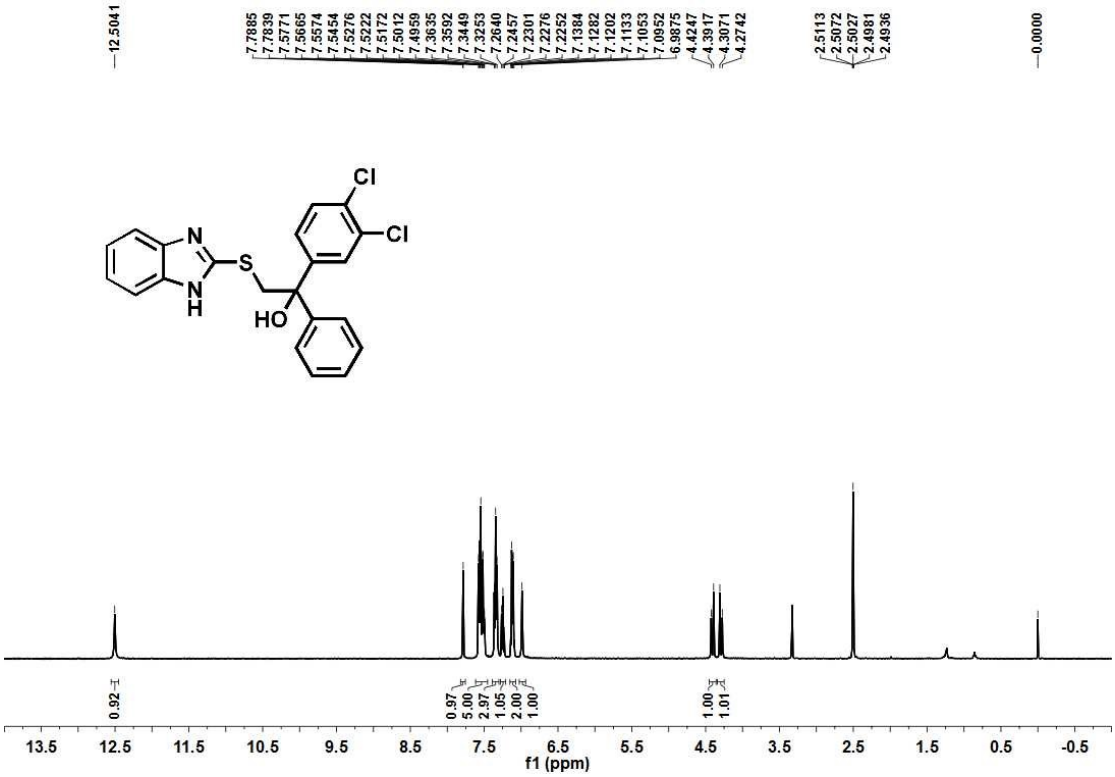
^{1}H NMR of product 4q in DMSO-d_6 (400 MHz)



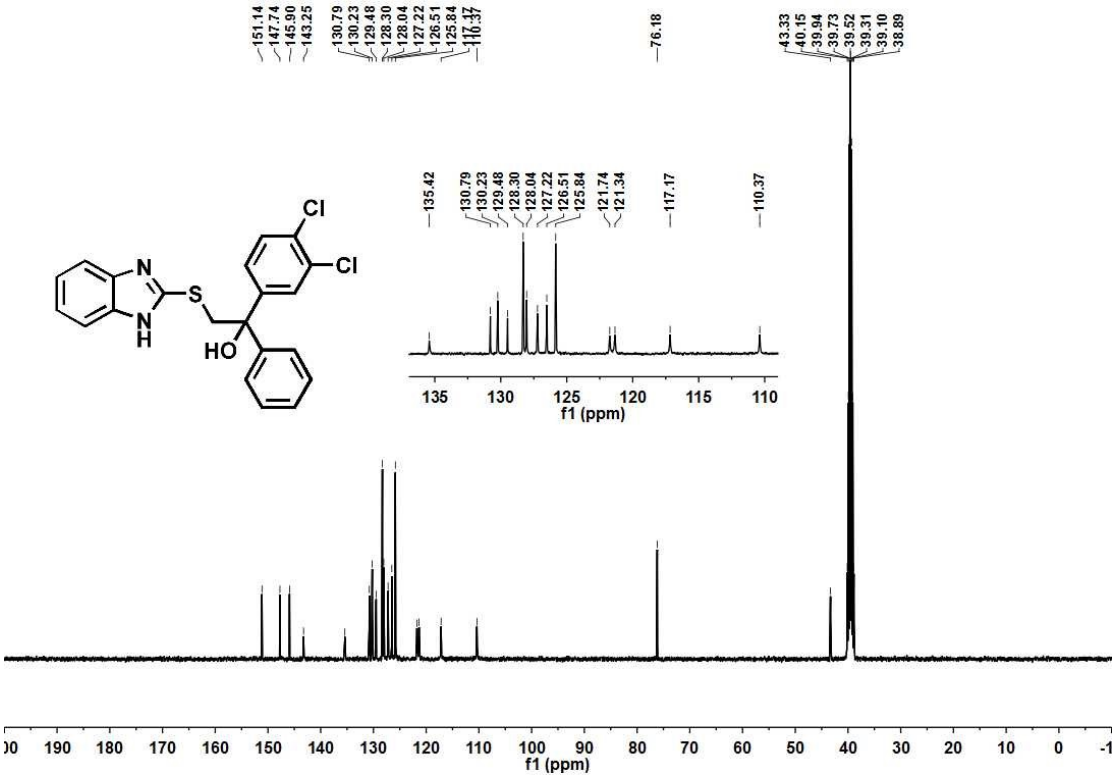
^{13}C NMR of product 4q in DMSO-d_6 (100 MHz)



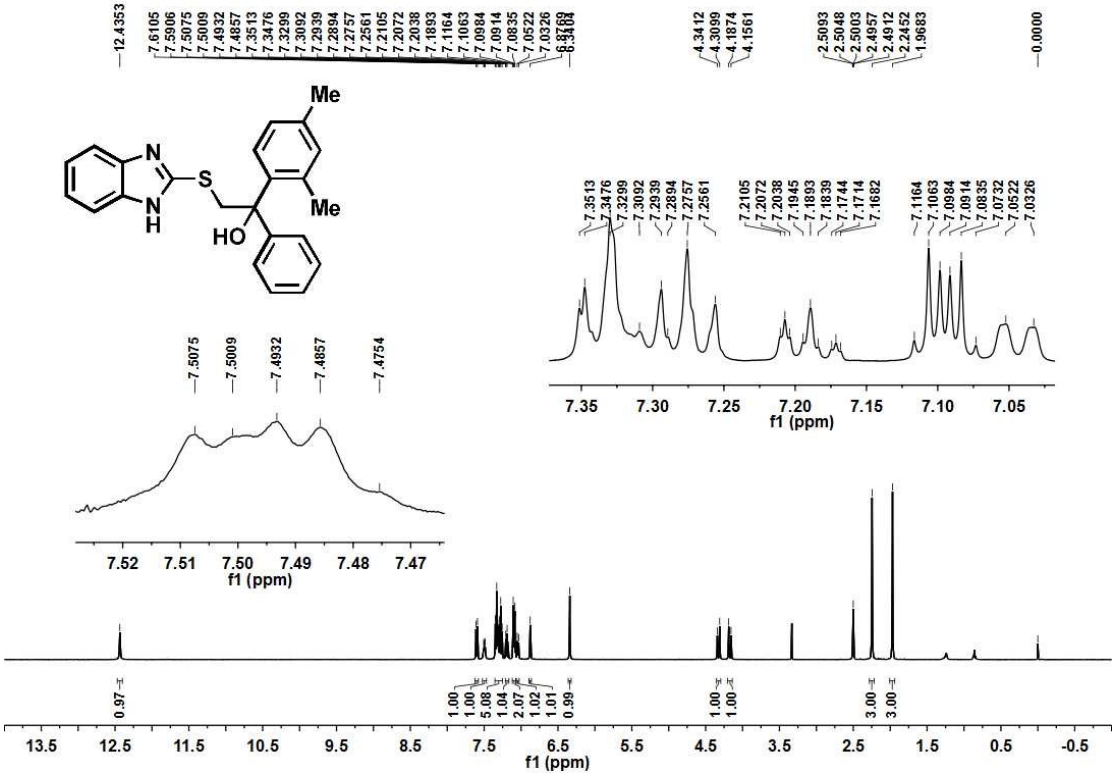
^{1}H NMR of product 4r in DMSO-d_6 (400 MHz)



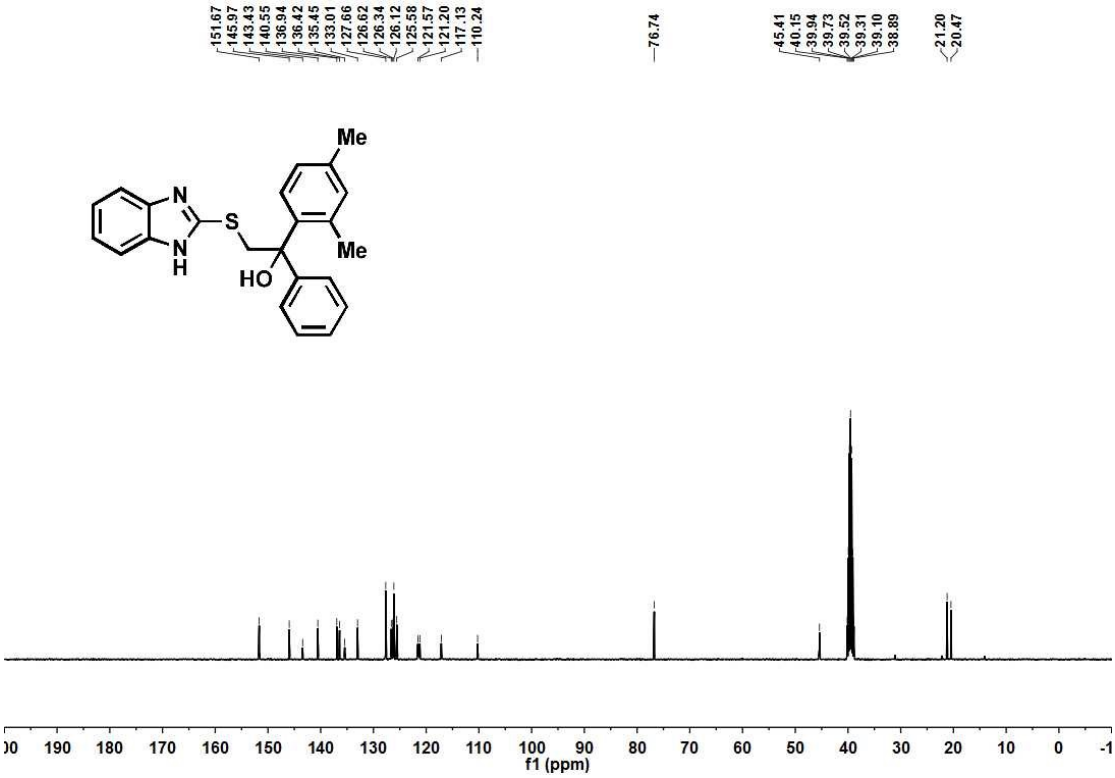
^{13}C NMR of product 4r in DMSO-d_6 (100 MHz)



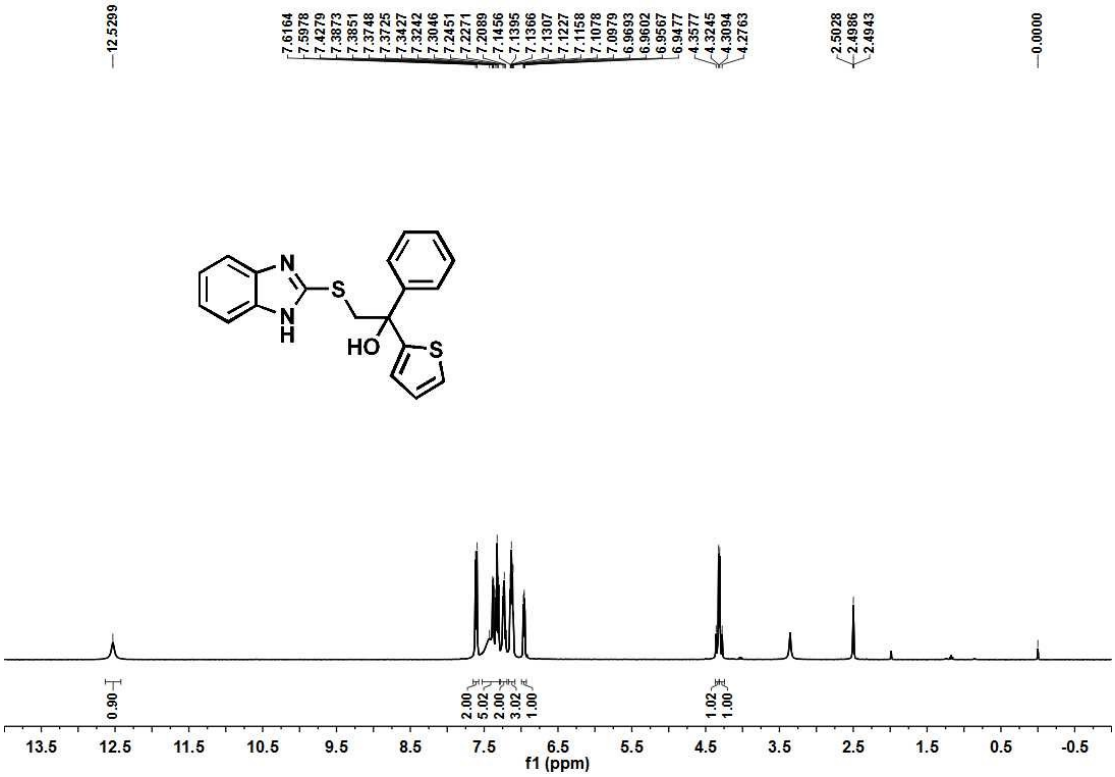
^{1}H NMR of product 4s in DMSO-d_6 (400 MHz)



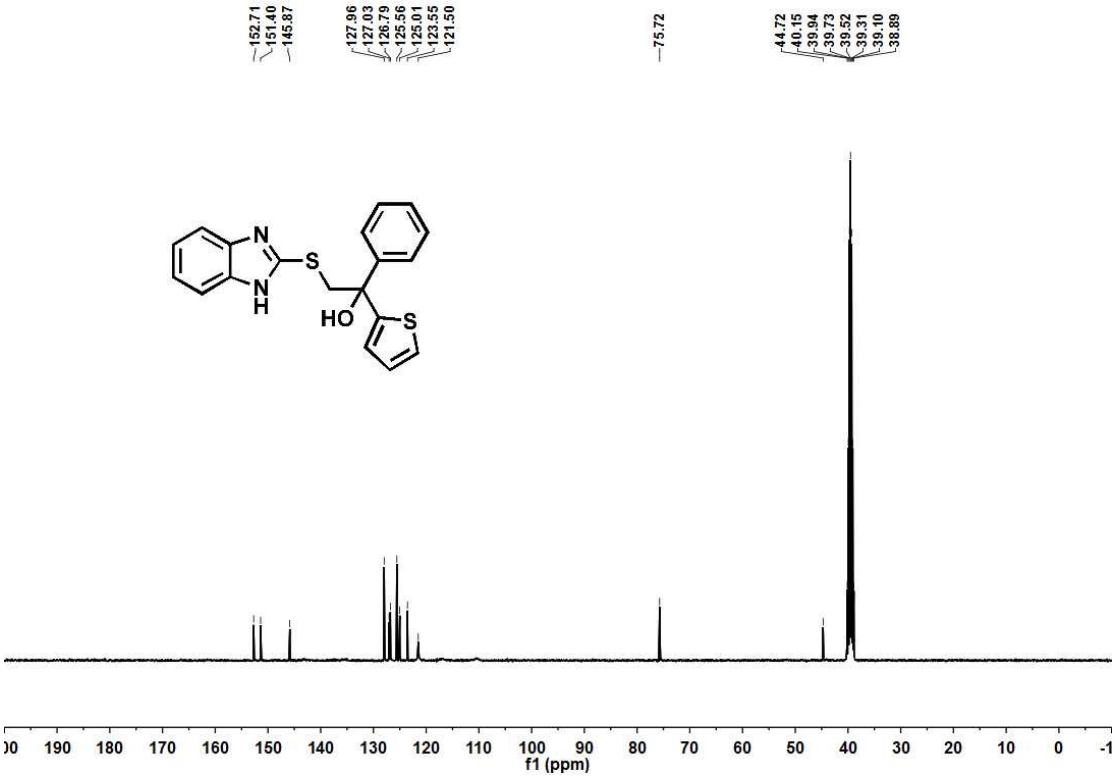
^{13}C NMR of product 4s in DMSO-d_6 (100 MHz)



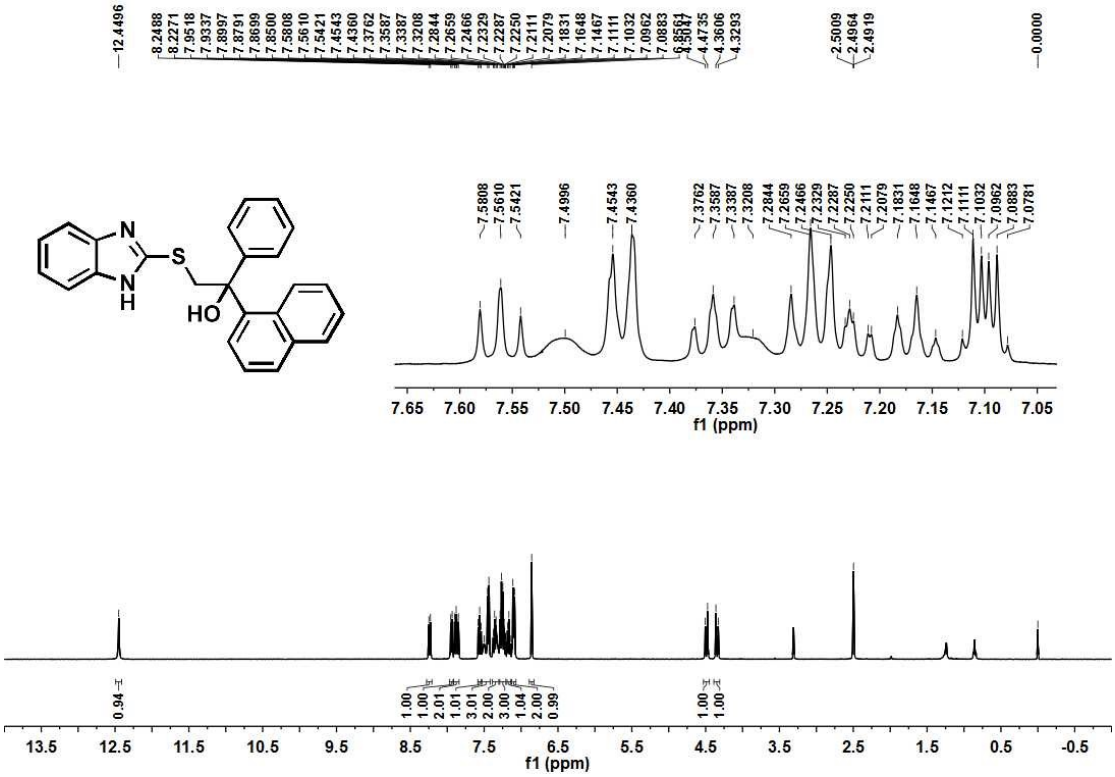
^{1}H NMR of product 4t in DMSO-d_6 (400 MHz)



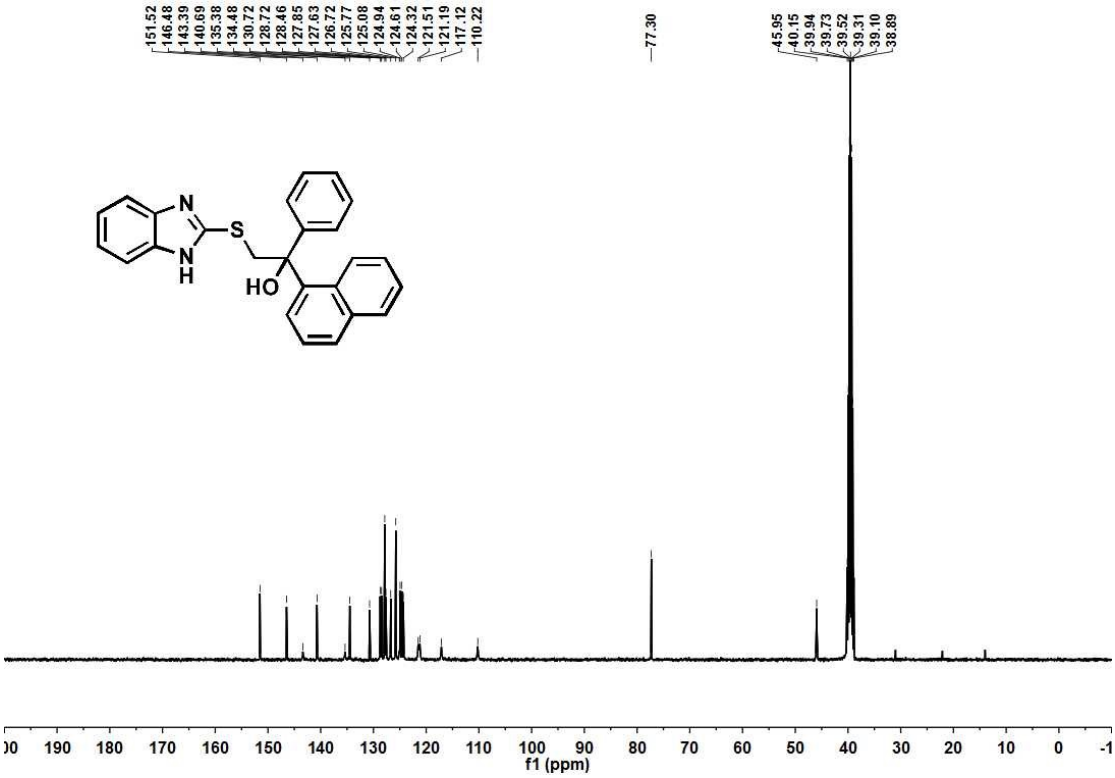
^{13}C NMR of product 4t in DMSO-d_6 (100 MHz)



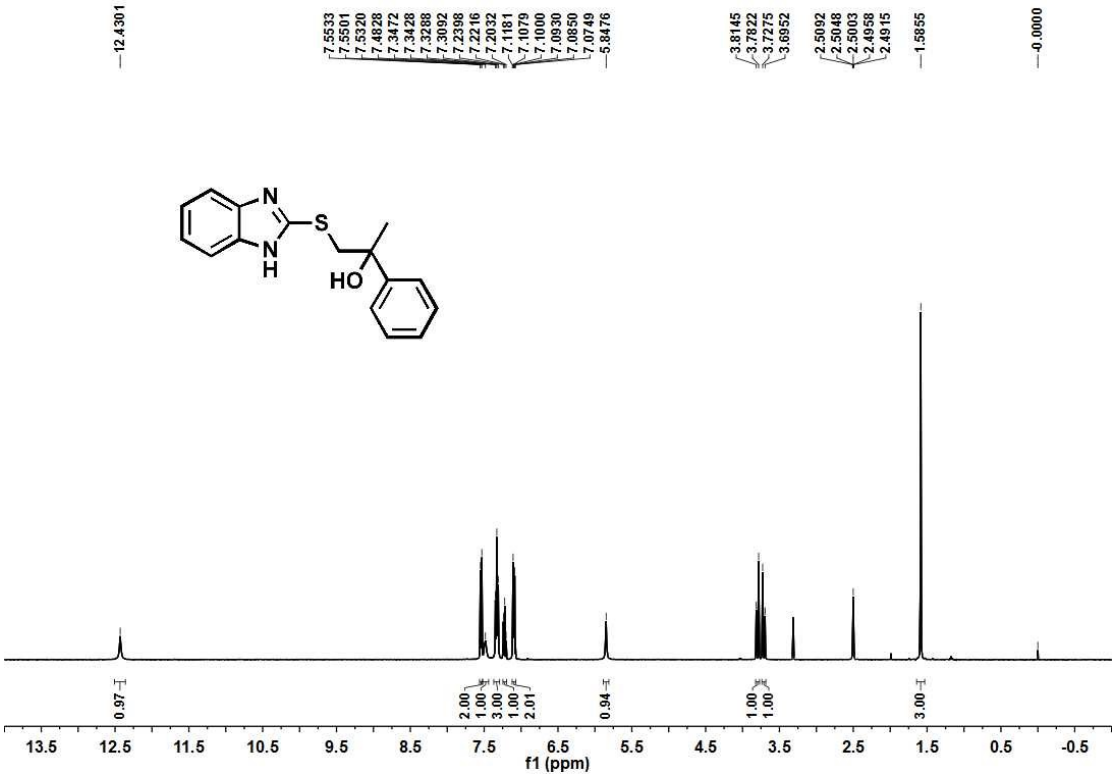
^{1}H NMR of product 4u in DMSO-d_6 (400 MHz)



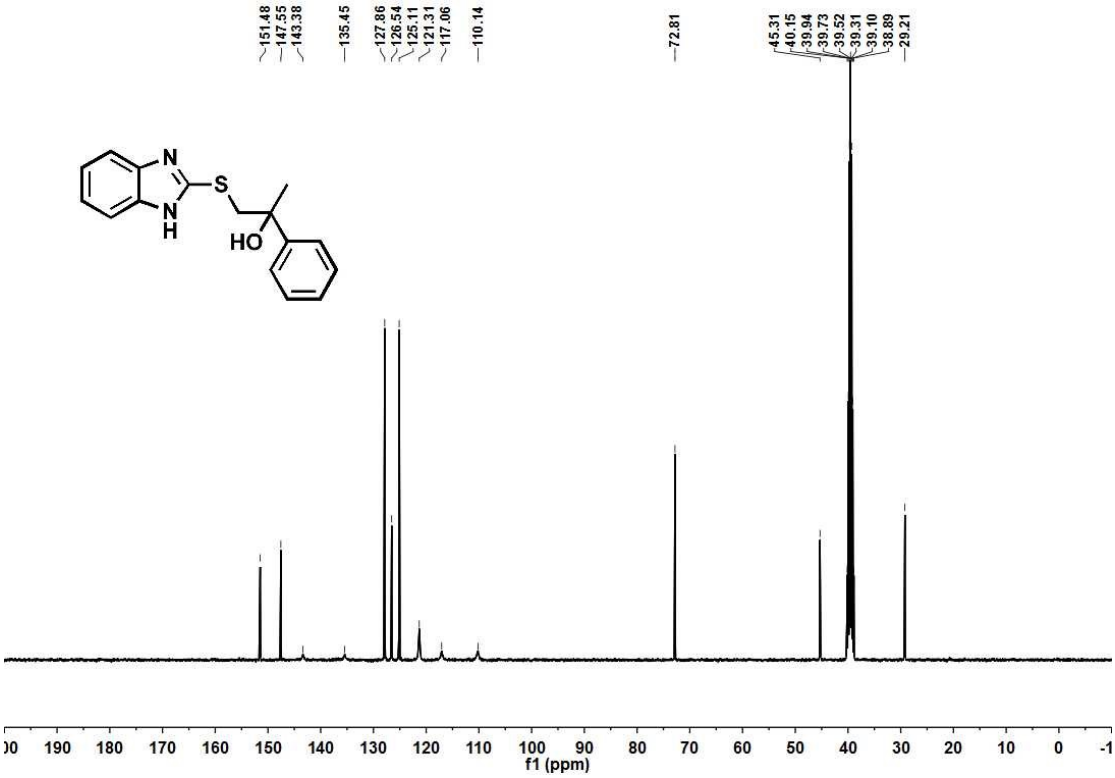
^{13}C NMR of product 4u in DMSO-d_6 (100 MHz)



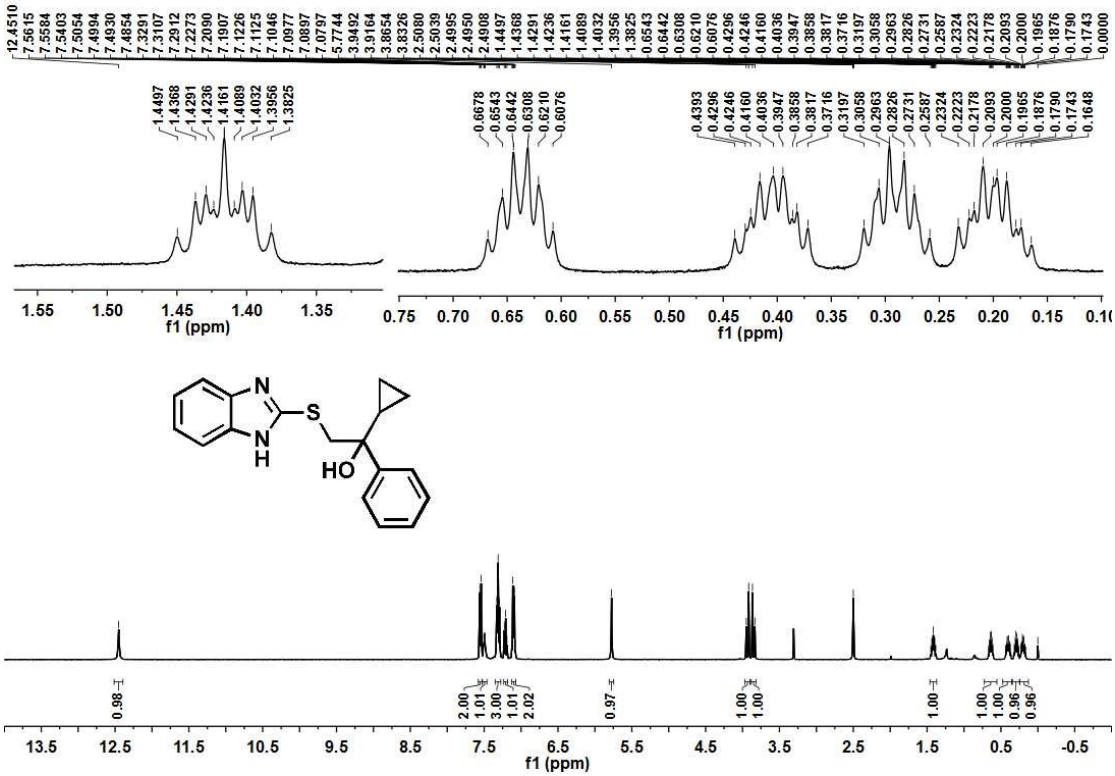
^{1}H NMR of product 4v in DMSO-d_6 (400 MHz)



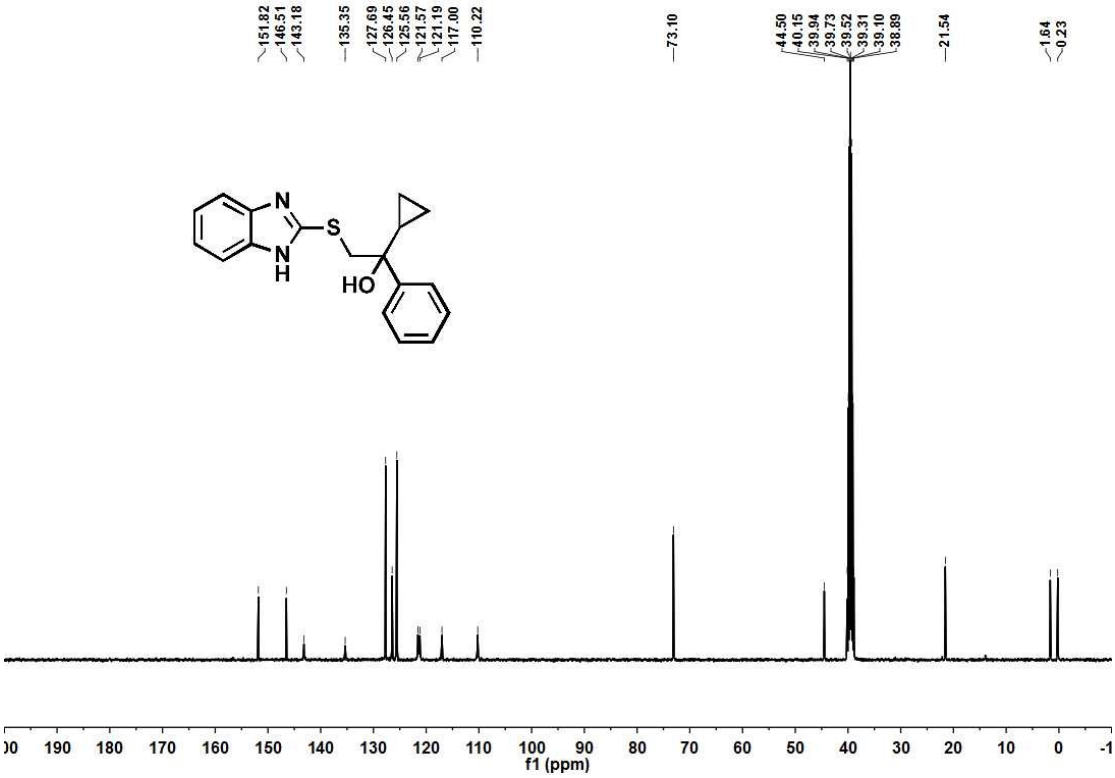
^{13}C NMR of product 4v in DMSO-d_6 (100 MHz)



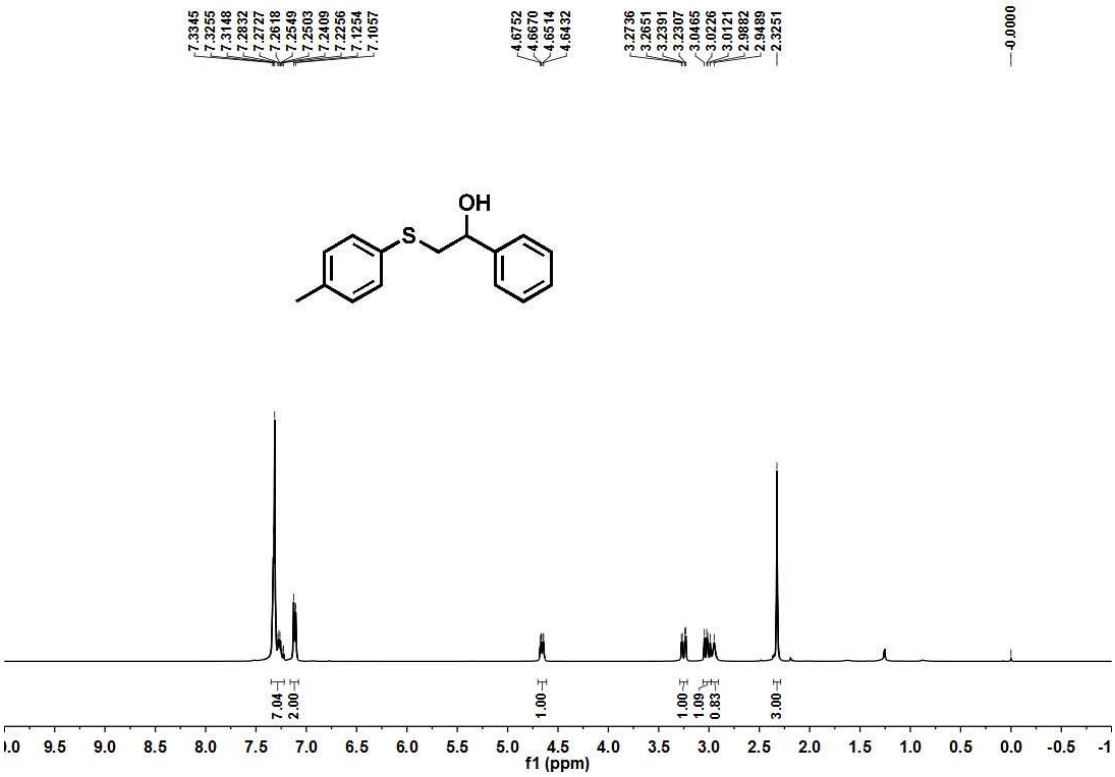
^{1}H NMR of product 4w in DMSO-d_6 (400 MHz)



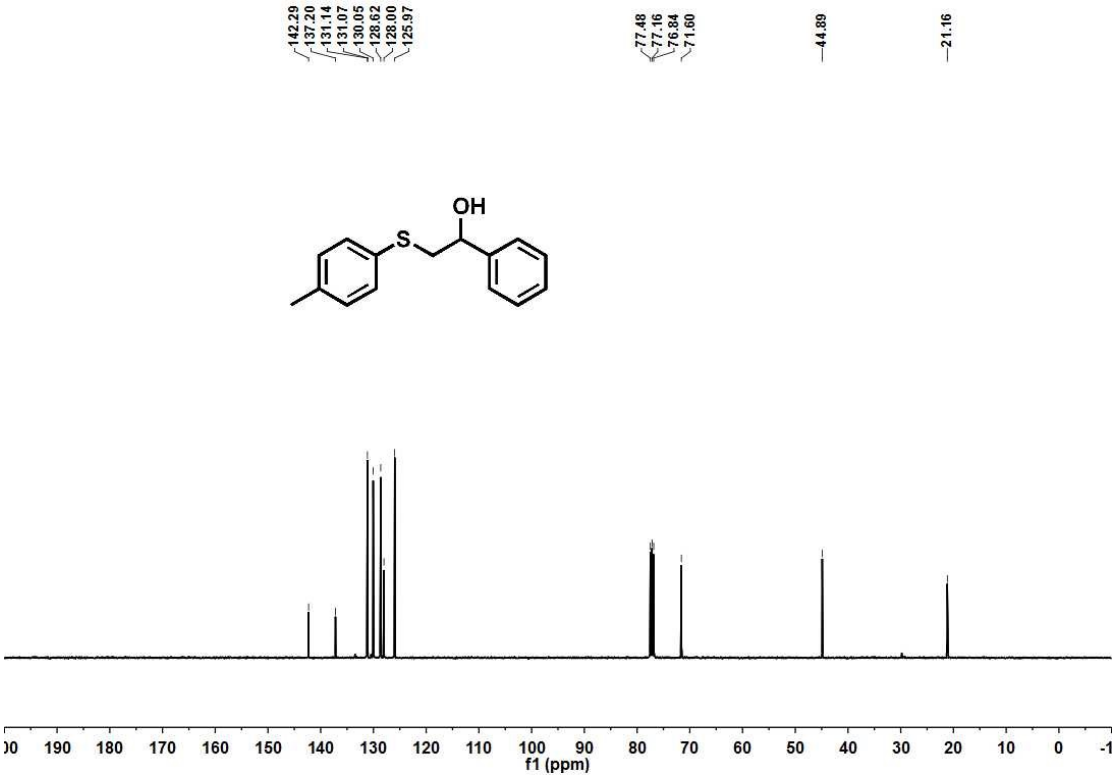
^{13}C NMR of product 4w in DMSO-d_6 (100 MHz)



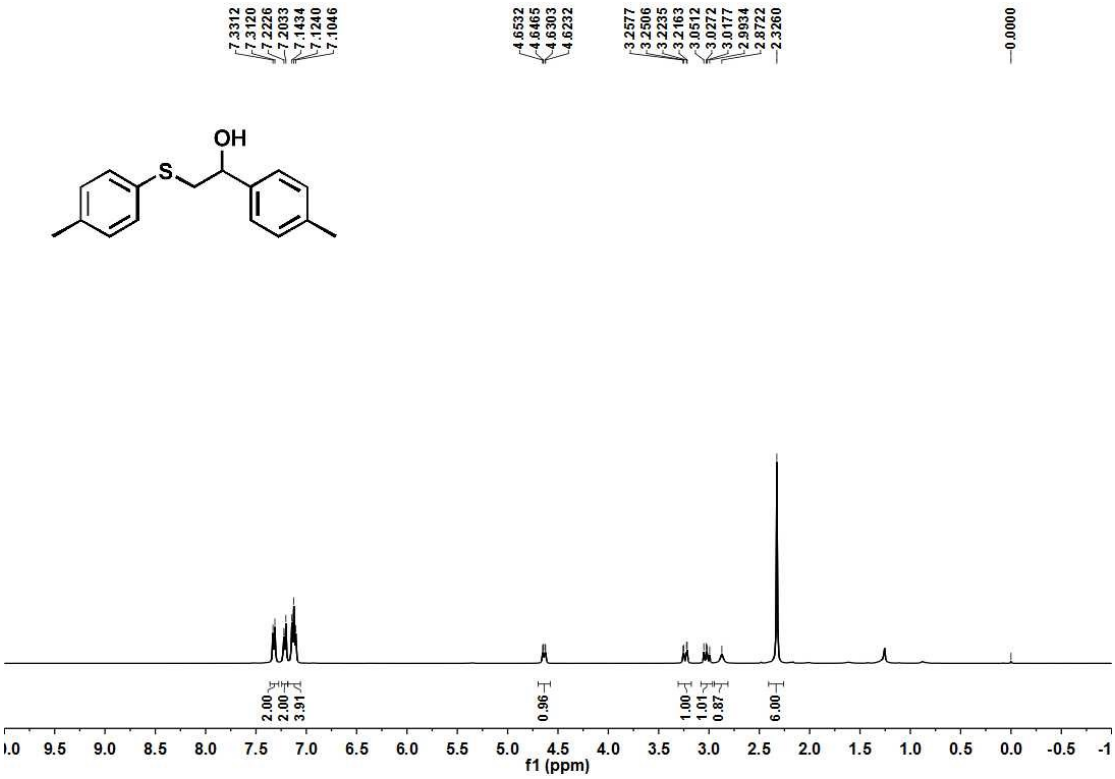
^{1}H NMR of product 5a in $CDCl_3$ (400 MHz)



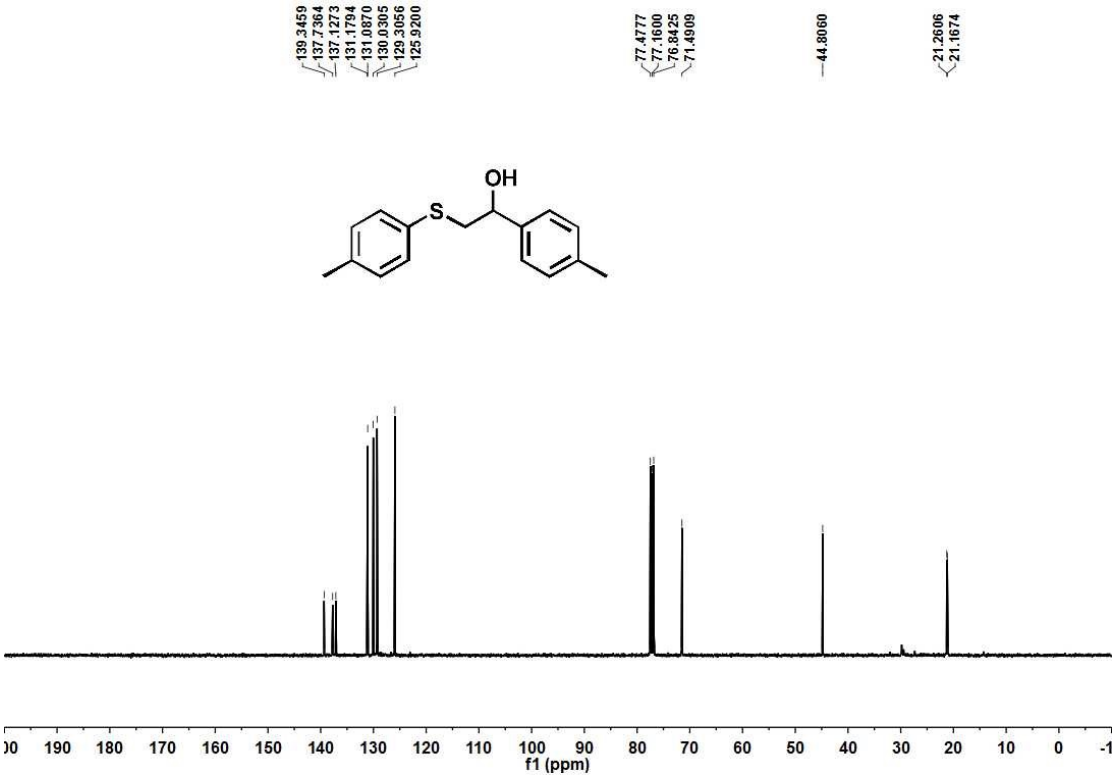
^{13}C NMR of product 5a in $CDCl_3$ (100 MHz)



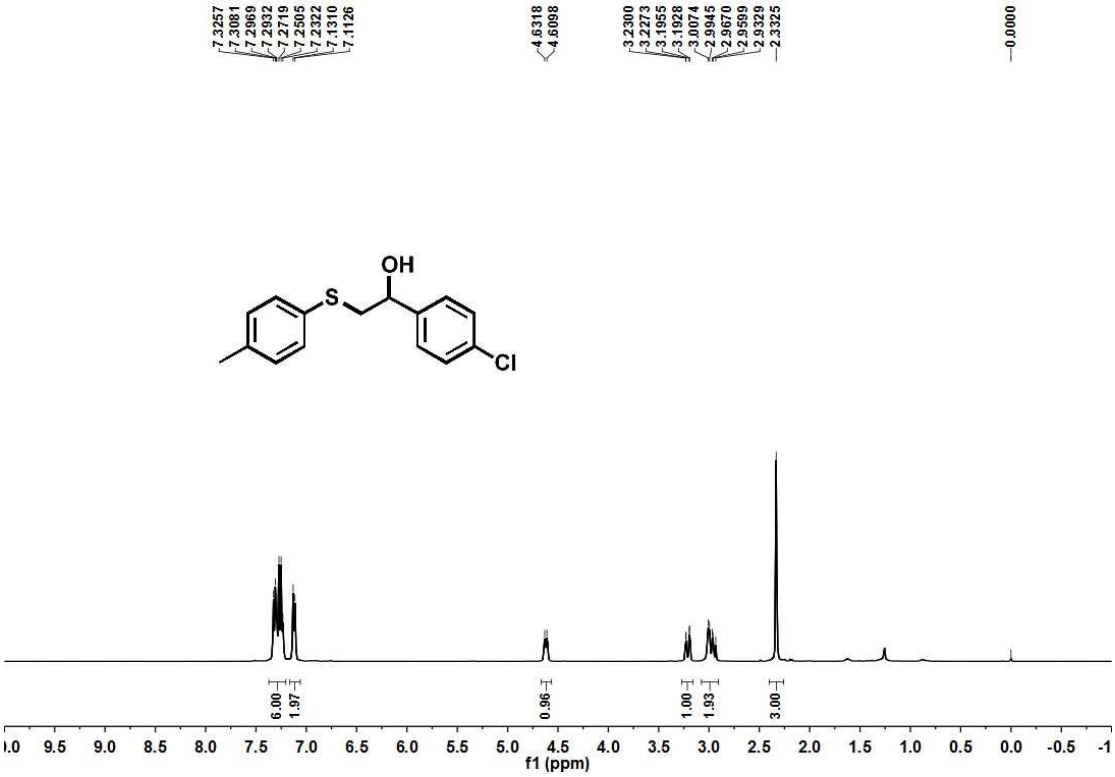
^{1}H NMR of product 5b in $CDCl_3$ (400 MHz)



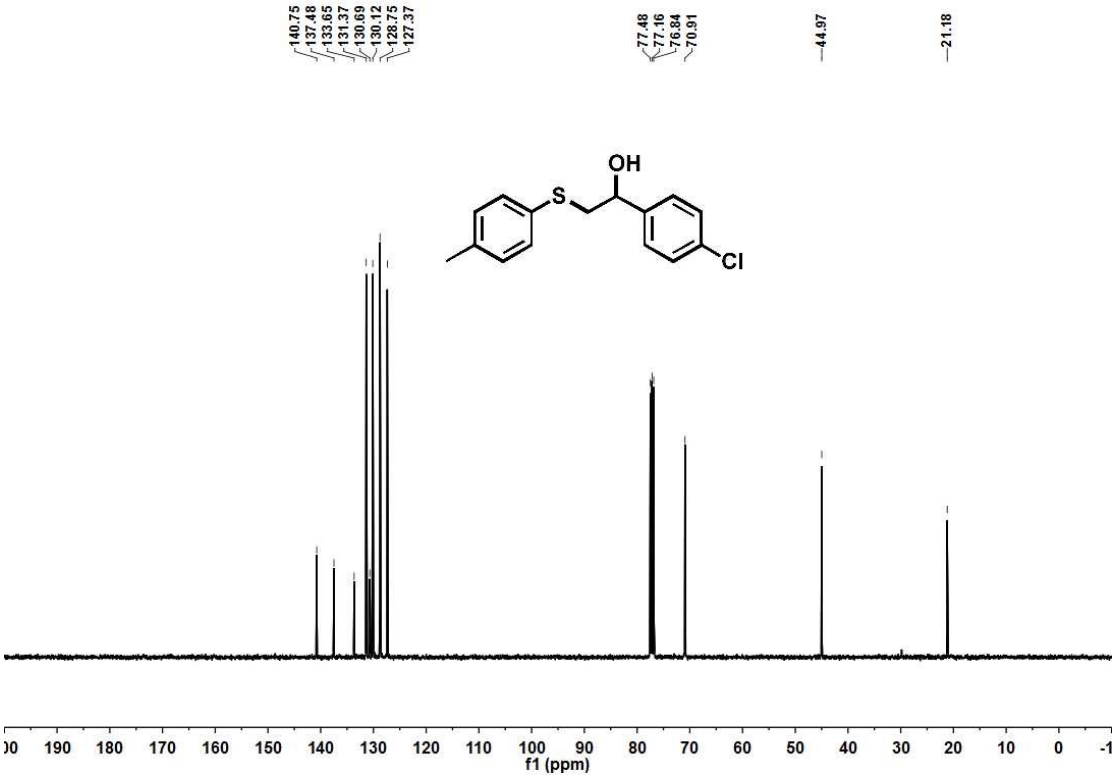
^{13}C NMR of product 5b in $CDCl_3$ (100 MHz)



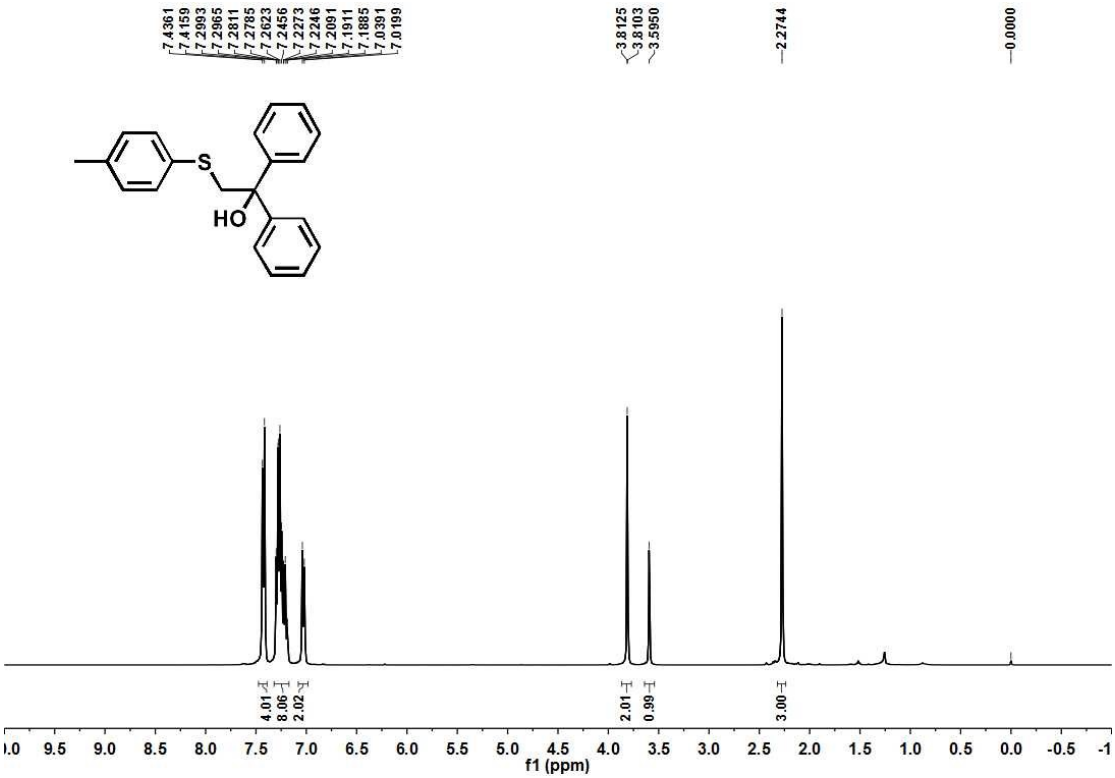
^{1}H NMR of product 5c in $CDCl_3$ (400 MHz)



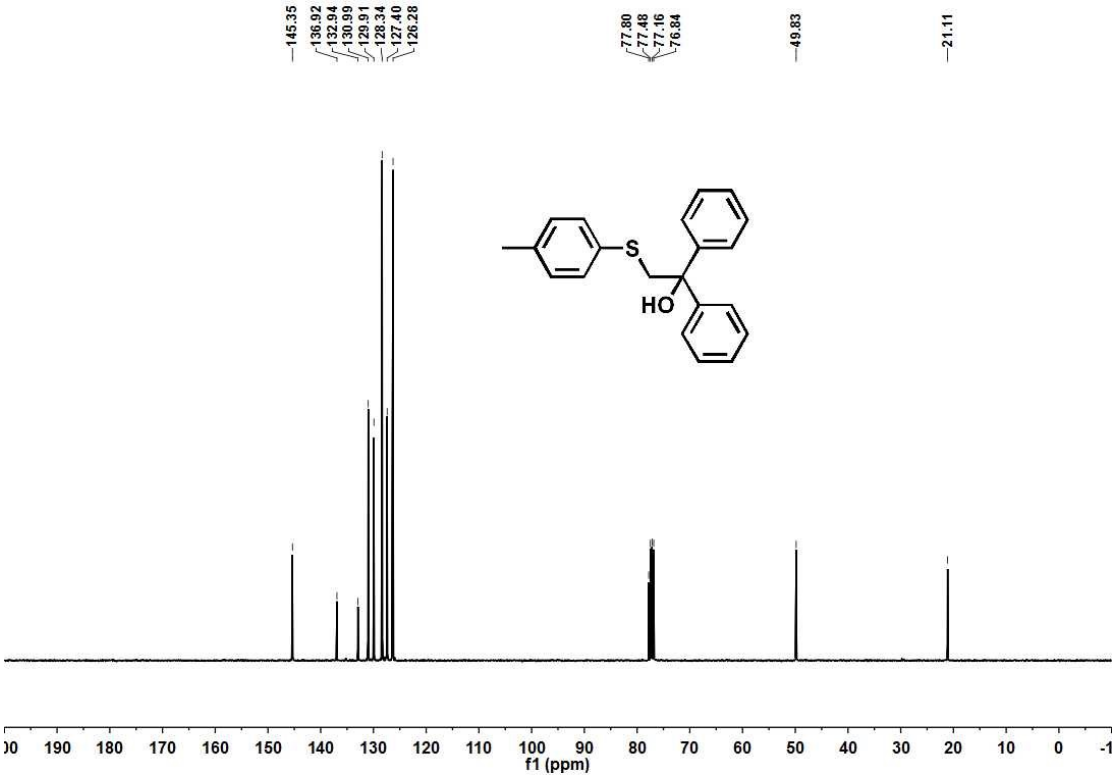
^{13}C NMR of product 5c in $CDCl_3$ (100 MHz)



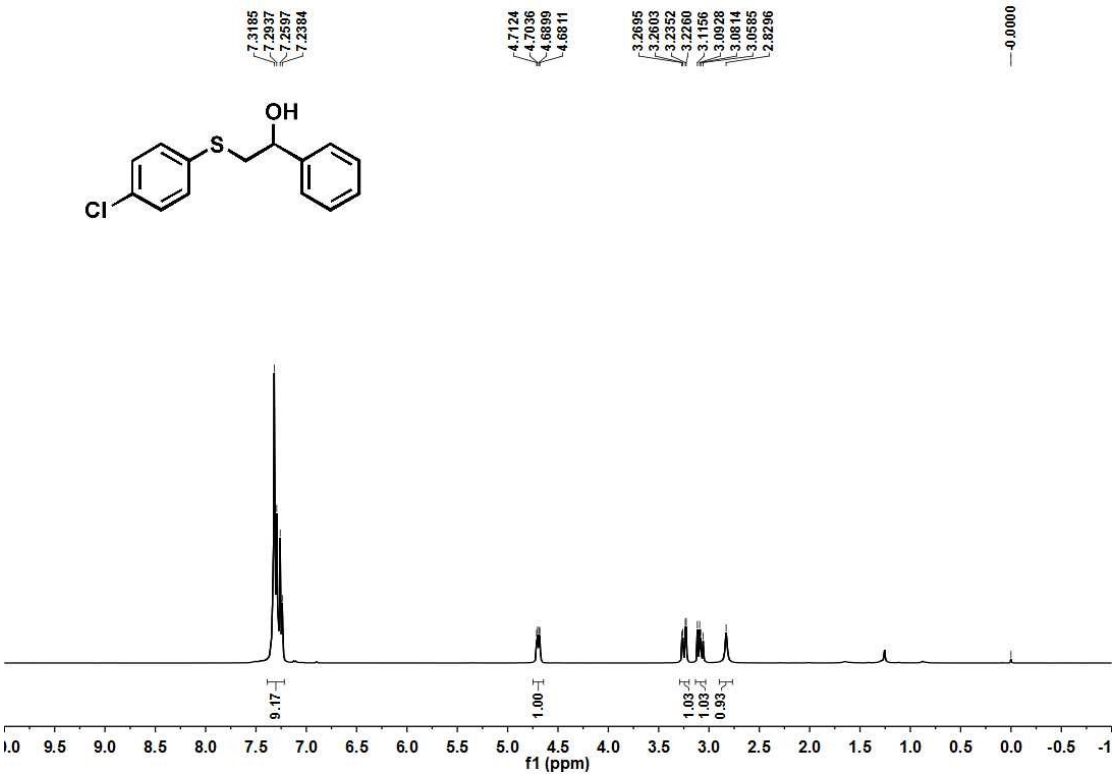
^{1}H NMR of product 5d in $CDCl_3$ (400 MHz)



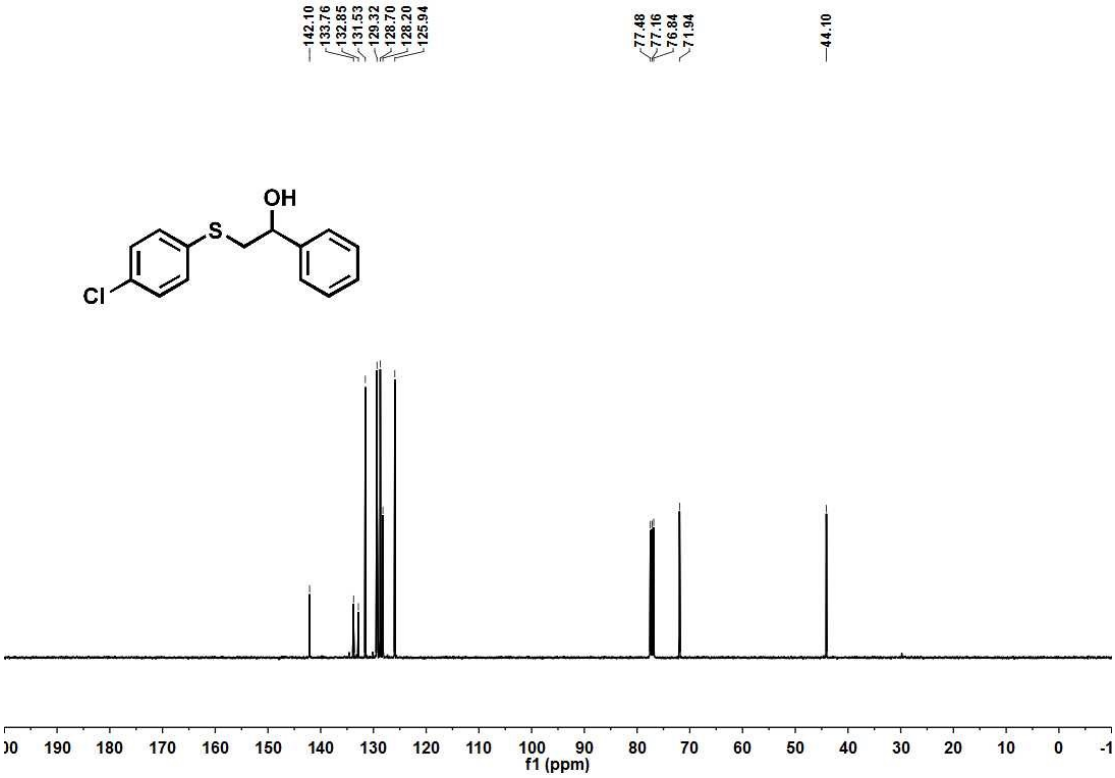
^{13}C NMR of product 5d in $CDCl_3$ (100 MHz)



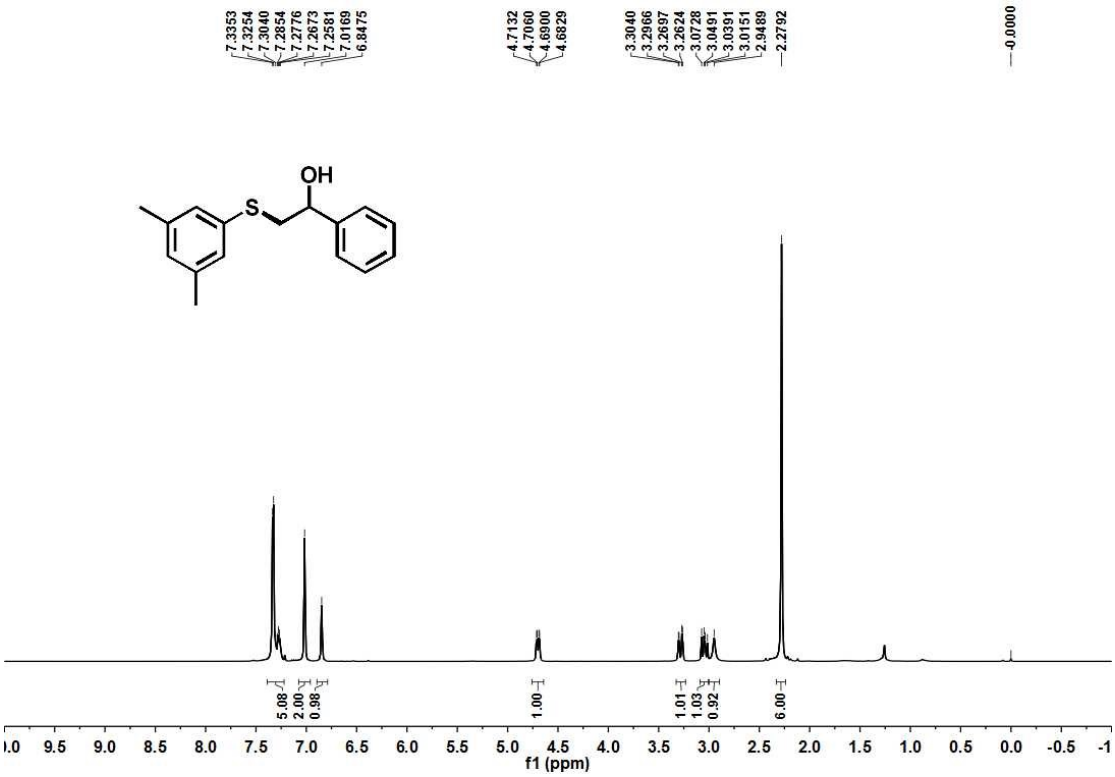
^{1}H NMR of product 5e in $CDCl_3$ (400 MHz)



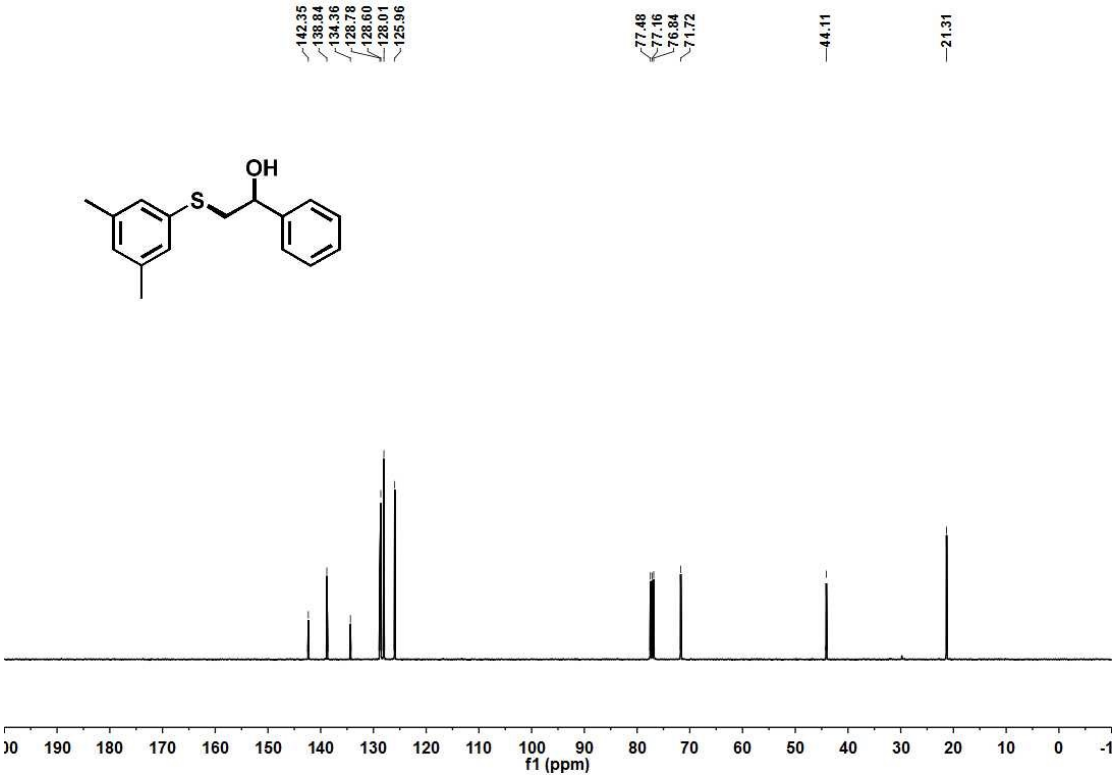
^{13}C NMR of product 5e in $CDCl_3$ (100 MHz)



^{1}H NMR of product 5f in $CDCl_3$ (400 MHz)



^{13}C NMR of product 5f in $CDCl_3$ (100 MHz)



8. X-Ray crystallography data of 3a and 3c

The suitable crystals were selected on a **XtaLAB Synergy**, **Dualflex**, **HyPix** diffractometer. The crystals were kept at 100.03(10) K during data collection. Using Olex2[1], the structures were solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation.

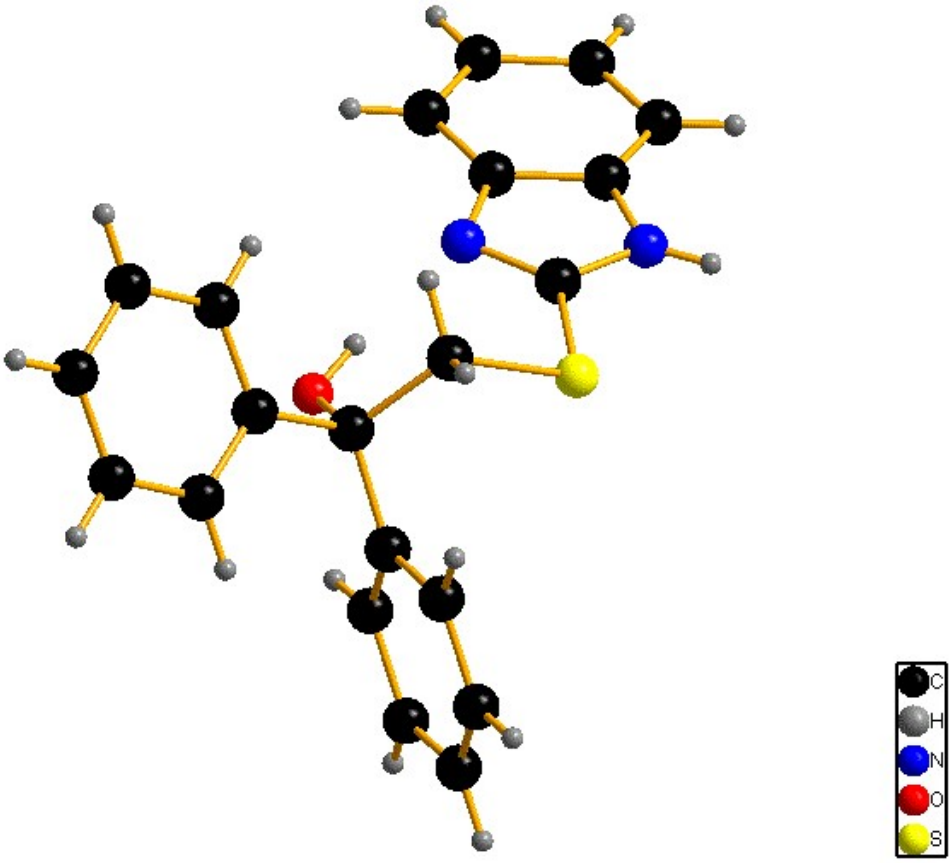
[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

[2] Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.

[3] Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Single-crystals suitable for X-ray diffraction analysis were grown from the recrystallization in chloroform and *n*-hexane (1/1, v/v) at 25 ^{o}C. Thermal ellipsoids of the crystal structures of **3a** and **3c** was set at 50%.

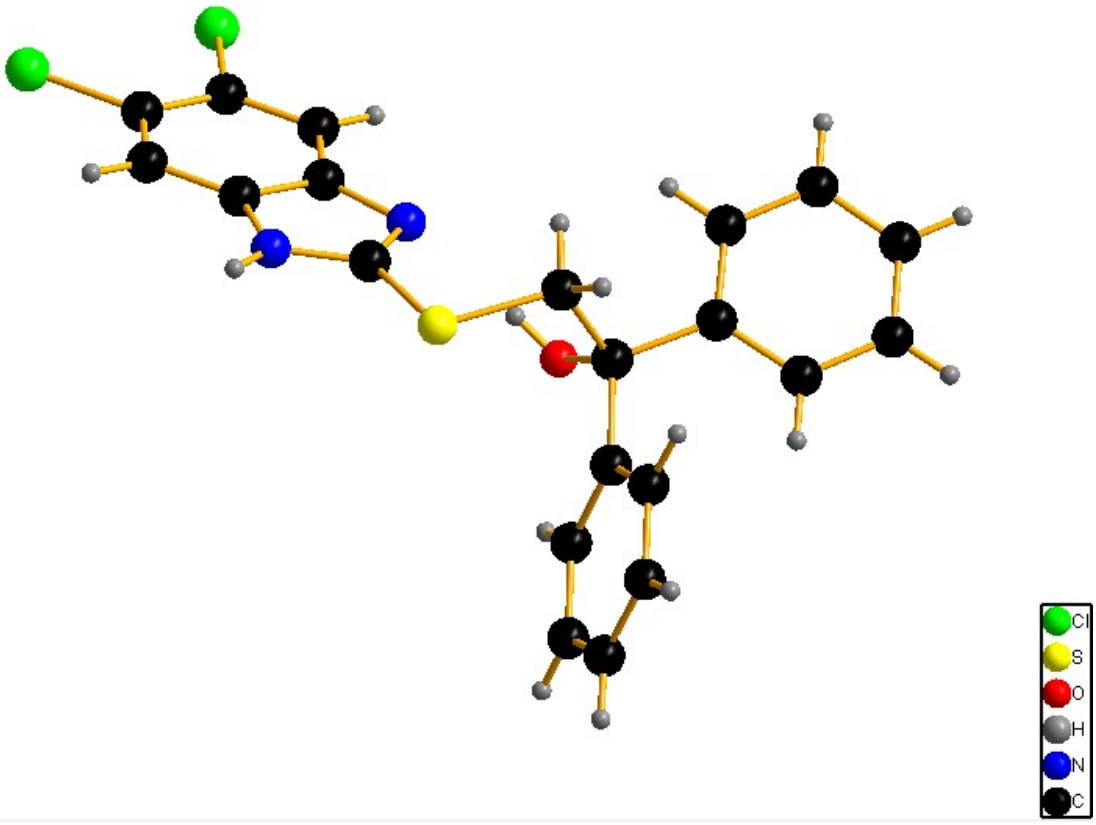
8.1 X-Ray crystallography data of 3a (CCDC 2080027)



Identification code	CCDC 2080027
Empirical formula	$C_{21}H_{18}N_2OS$
Formula weight	346.44
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	11.9441(16)
b/Å	12.2012(17)
c/Å	13.4500(19)
α/°	76.259(2)
β/°	72.322(2)
γ/°	79.906(2)
Volume/Å^3	1802.8(4)
Z	2
ρ_{calc}g/cm^3	1.276
μ/mm^{-1}	0.190
F(000)	728.0
Crystal size/mm^3	0.28 × 0.26 × 0.24
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	6.02 to 55.316
Index ranges	$-14 \leq h \leq 15, -13 \leq k \leq 15, -17 \leq l \leq 17$
Reflections collected	11040
Independent reflections	7932 [R_{int} = 0.0155, R_{sigma} = 0.0335]
Data/restraints/parameters	7932/0/467
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.1007
Final R indexes [all data]	R_1 = 0.0628, wR_2 = 0.1137
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.28

8.2 X-Ray crystallography data of 3c (CCDC 2080030)



Identification code	CCDC 2080030
Empirical formula	$C_{21}H_{16}Cl_2N_2OS$
Formula weight	415.33
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	24.764(5)
b/Å	12.538(3)
c/Å	13.430(3)
α/°	90
β/°	91.148(3)
γ/°	90

Volume/Å^3	4168.9(14)
Z	2
ρ_{calc}g/cm^3	1.358
μ/mm^{-1}	0.426
F(000)	1762.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.624 to 55.502
Index ranges	-32 ≤ h ≤ 26, -15 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	25147
Independent reflections	9475 [R_{int} = 0.0313, R_{sigma} = 0.0398]
Data/restraints/parameters	9475/3/517
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0494, wR_2 = 0.1375
Final R indexes [all data]	R_1 = 0.0807, wR_2 = 0.1564
Largest diff. peak/hole / e Å^{-3}	0.67/-0.34