Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Metal-free and Selectfluor-mediated diverse transformations of 2-alkylthiobenzamides to access 2,3-dihydrobenzothiazin-4-ones, benzoisothiazol-3-ones and 2-alkylthiobenzonitriles

Shengfei Dai, Ke Yang*, Yanqi Luo, Ziyuan Xu, Zhi Li, Zhengyi Li, Bijin Li* and Xiaoqiang Sun*

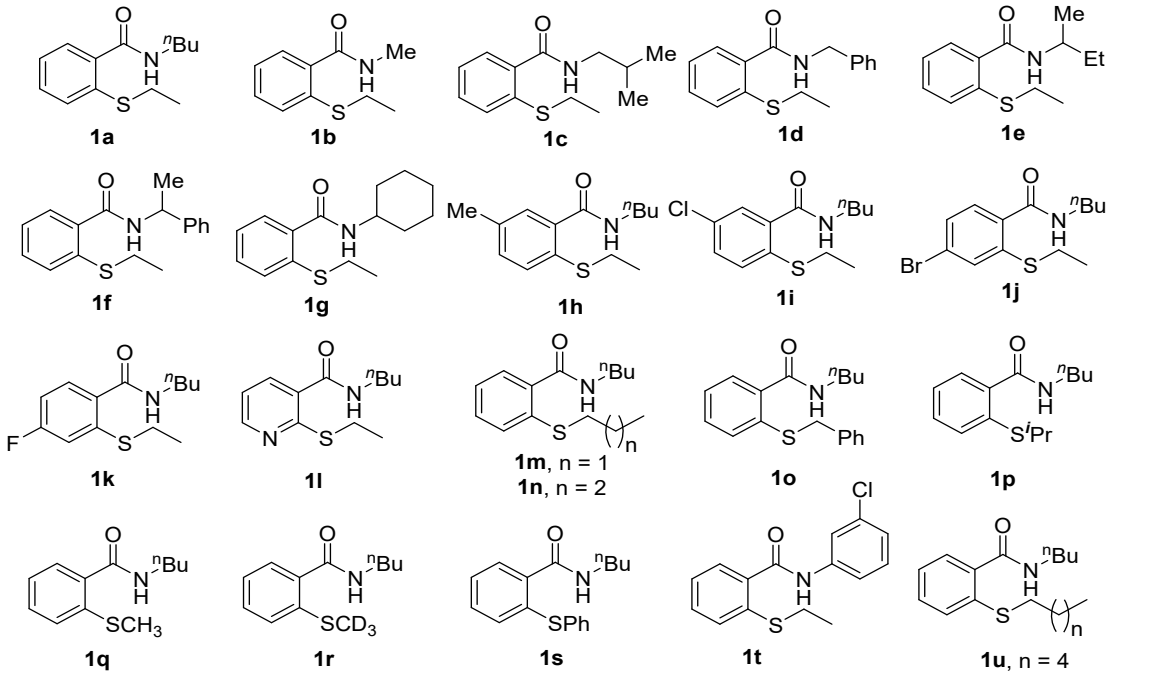
Table of contents

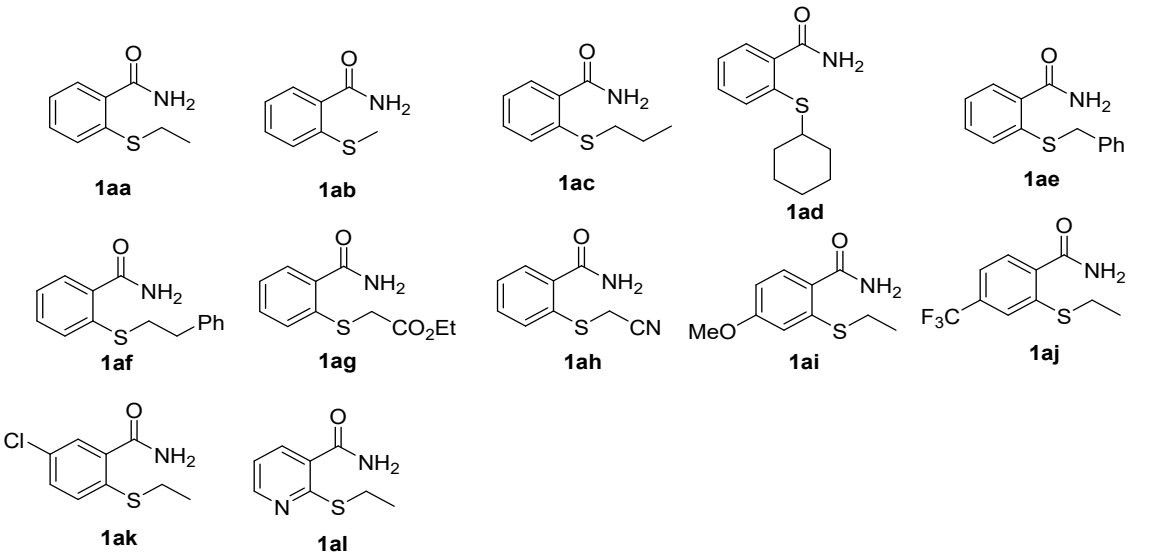
I. General Information

All the solvents and commercially available reagents were purchased and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light. Column chromatography was performed on EMD Silica Gel 60 (200–300 Mesh) using a forced flow of 0.5–1.0 bar. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AVANCE III–300 or 400 spectrometer. ^{1}H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Mass (HRMS) analysis was obtained using Agilent 6200 Accurate-Mass TOF LC/MS system with Electrospray Ionization (ESI). Melting points were measured by an X4-A microscopic melting point apparatus.

II. Experimental Section

1. Starting materials:





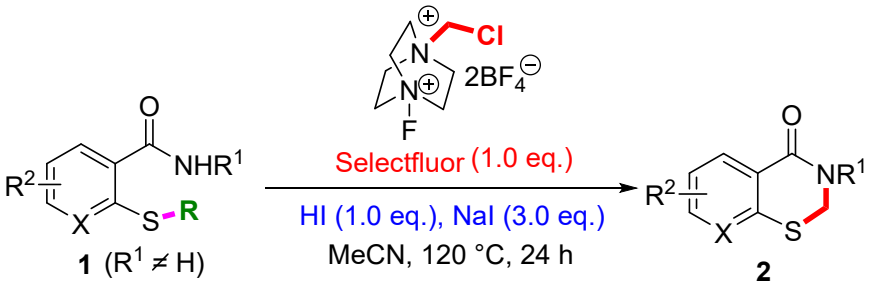
Scheme S1. 2-Alkylthiobenzamide **1**

2-Alkylthiobenzamides (**1a-u**) were prepared from commercial 2-(methylthio)benzoic acid (2.0 mmol) and the corresponding amines (3.0 mmol) in DCM at room temperature according to the reported procedure.[1] 2-Alkylthiobenzamides (**1aa-al**) were prepared from commercial 2-(methylthio)benzoic acid (2.0 mmol) and the corresponding ammonium hydroxide (1.5 mL) according to the reported procedure.[2]

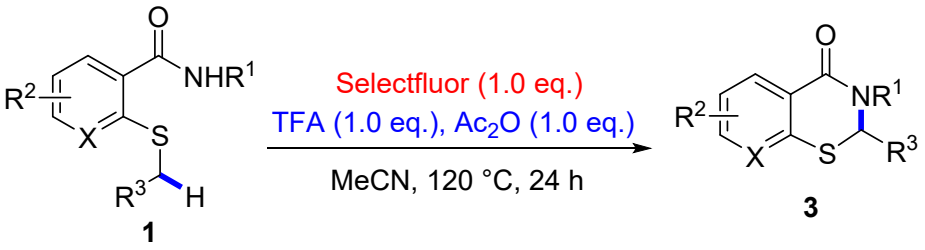
2. Optimization of the reaction conditions

A 30 mL Schlenk tube was charged with *N*-butyl-2-(ethylthio)benzamide **1a** (0.2 mmol), Selectfluor (0 ~ 0.3 mmol), additives (0.2 ~ 0.8 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **2a, 3a** and **4a**.

3. General procedure for the scope study

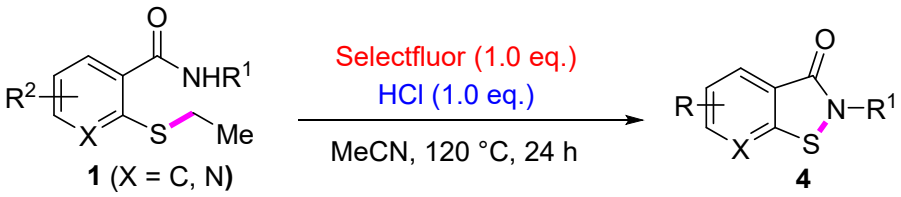


A 30 mL Schlenk tube was charged with *N*-substituted 2-(alkylthio)benzamides **1** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HI (55% in water, 0.2 mmol, 27.0 μL), NaI (0.6 mmol, 89.9 mg) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **2**.



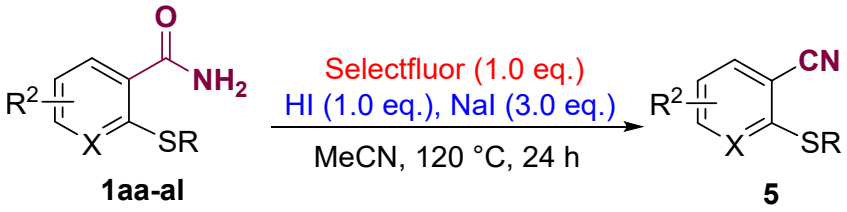
1 **3**

A 30 mL Schlenk tube was charged with *N*-substituted 2-(alkylthio)benzamides **1** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), TFA (0.2 mmol, 15.0 μL), Ac_2O (0.2 mmol, 19.0 μL) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **3**.



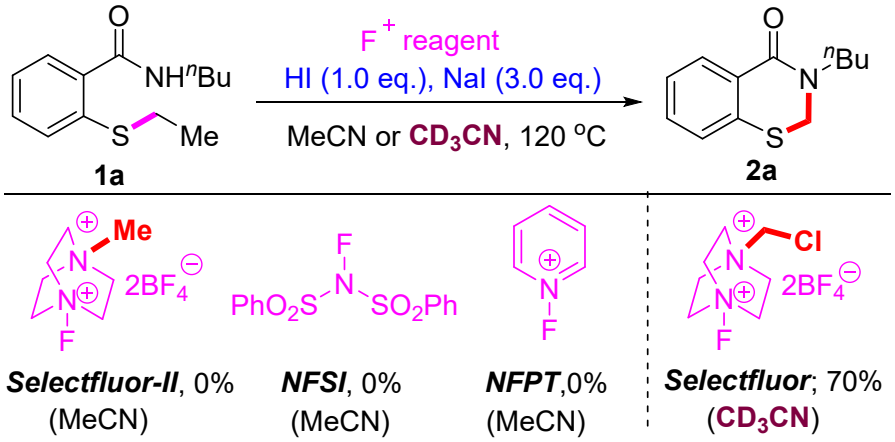
1 (X = C, N) **4**

A 30 mL Schlenk tube was charged with *N*-substituted 2-(alkylthio)benzamides **1** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HCl (37% in water, 0.2 mmol, 19.7 μL) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **4**.



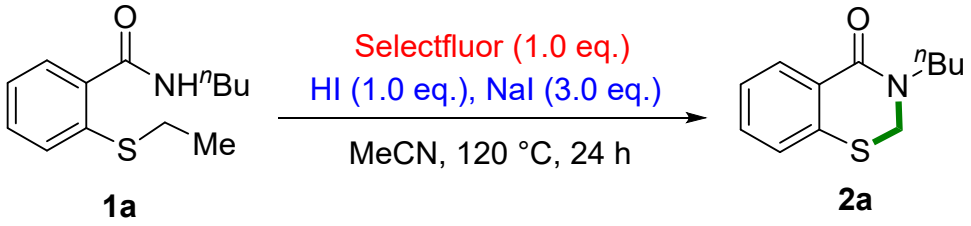
A 30 mL Schlenk tube was charged with 2-(alkylthio)benzamides **1aa-al** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HI (55% in water, 0.2 mmol, 27.0 μL), NaI (0.6 mmol, 89.9 mg) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **5**.

4. Investigation of F^+ reagents and solvents



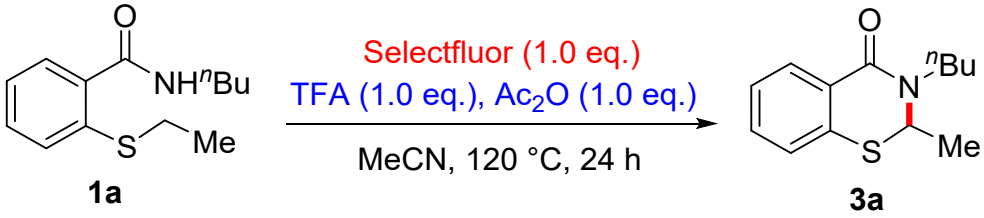
A 30 mL Schlenk tube was charged with *N*-butyl-2-(ethylthio)benzamide **1a** (0.2 mmol, 47.5 mg), F^+ reagents (0.2 mmol), HI (55% in water, 0.2 mmol, 27.0 μL), NaI (0.6 mmol, 89.9 mg) and MeCN or CD_3CN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **3a**.

5. The gram-scale reaction



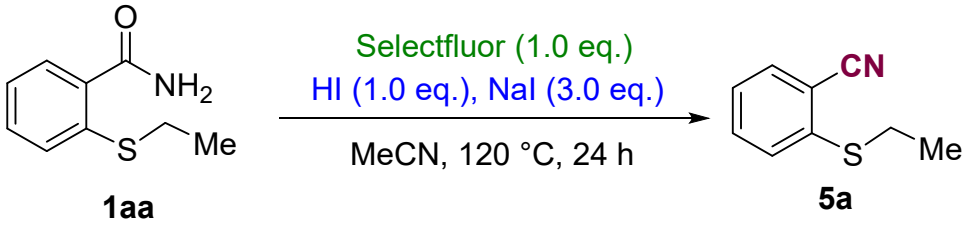
1a **2a**

A 150 mL Schlenk tube was charged with *N*-butyl-2-(ethylthio)benzamide **1a** (4.5 mmol, 1.07 g), Selectfluor (4.5 mmol, 1.6 g), HI (55% in water, 4.5 mmol, 608.0 μL), NaI (13.5 mmol, 2.02 g) and MeCN (20.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **2a** (0.77 g, 77%).



1a **3a**

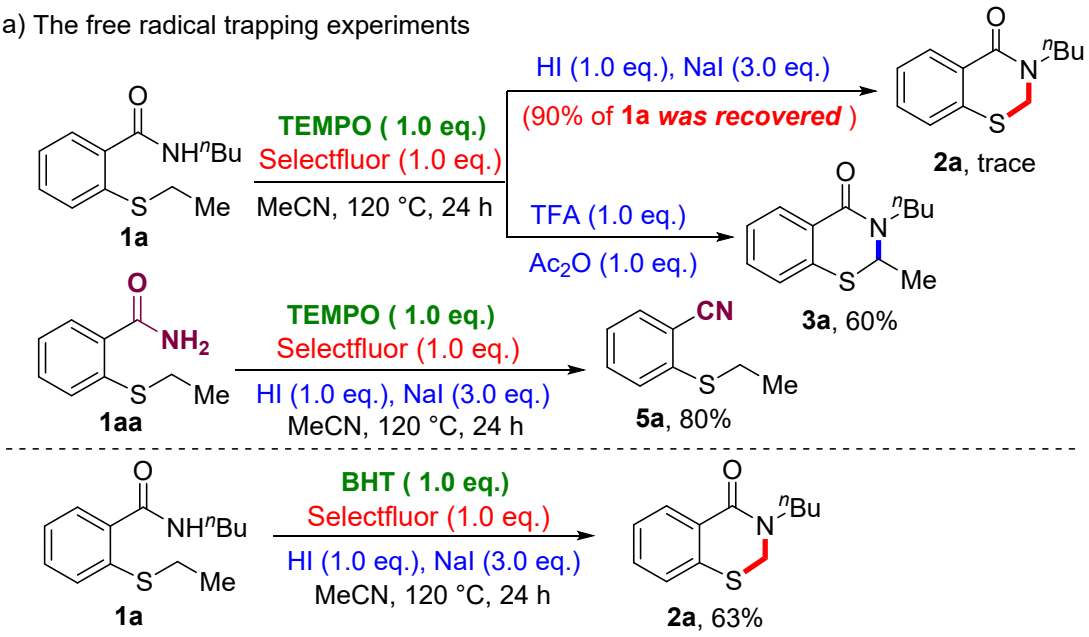
A 150 mL Schlenk tube was charged with *N*-butyl-2-(ethylthio)benzamide **1a** (4.5 mmol, 1.07 g), Selectfluor (4.5 mmol, 1.6 g), TFA (4.5 mmol, 338.0 μL), Ac_2O (4.5 mmol, 428.0 μL), and MeCN (20.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **3a** (0.64 g, 60%).



A 150 mL Schlenk tube was charged with 2-(ethylthio)benzamide **1aa** (6.0 mmol, 1.09 g), Selectfluor (6.0 mmol, 2.13 g), HI (55% in water, 6.0 mmol, 810.0 μL), NaI (18 mmol, 2.70 g) and MeCN (20.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired products **5a** (0.81 g, 83%).

6. Mechanistic studies

a) The free radical trapping experiments

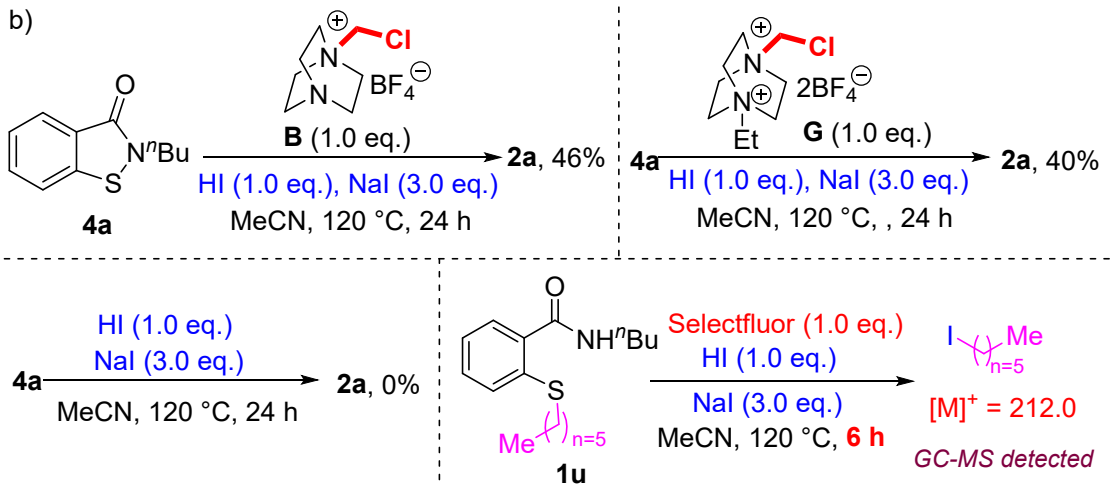


A 30 mL Schlenk tube was charged with *N*-butyl-2-(ethylthio)benzamide **1a** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HI (0.2 mmol), NaI (0.6 mmol), MeCN (2.0 mL) and **TEMPO** or **BHT** (0.2 mmol). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture

was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel. Using **TEMPO** (0.2 mmol) as the inhibitor, only trace product of **2a** was detected and 90% (42.7 mg) of **1a** was recovered. However, using **BHT** (0.2 mmol) as the inhibitor, 63% (27.9 mg) of **3a** was isolated.

A 30 mL Schlenk tube was charged with *N*-butyl-2-(ethylthio)benzamide **1a** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), TFA (0.2 mmol), Ac_2O (0.2 mmol), **TEMPO** (0.2 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **3a** (28.2 mg, 60%).

A 30 mL Schlenk tube was charged with 2-(ethylthio)benzamide **1aa** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HI (0.2 mmol), NaI (0.6 mmol), MeCN (2.0 mL) and **TEMPO** (0.2 mmol). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **5a** (26.1 mg, 80%).

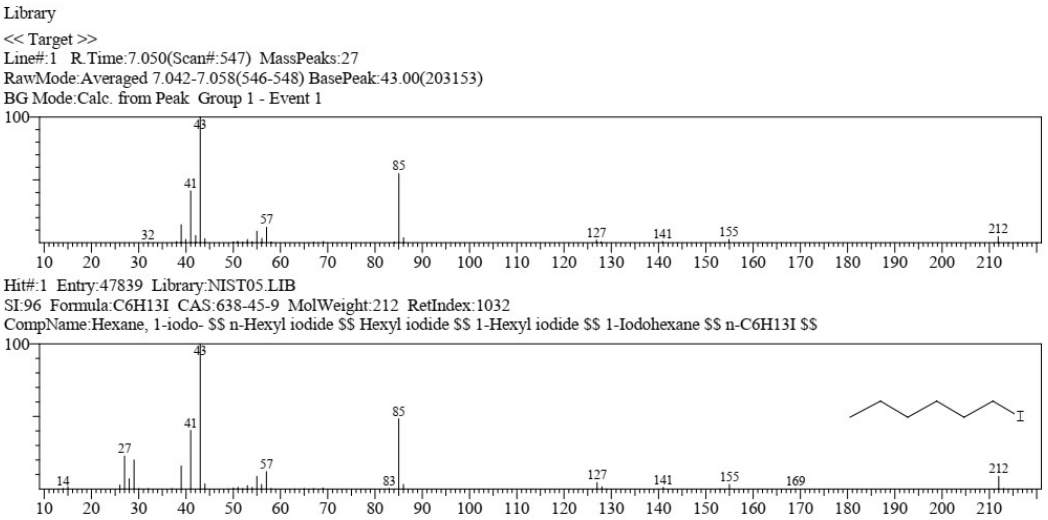


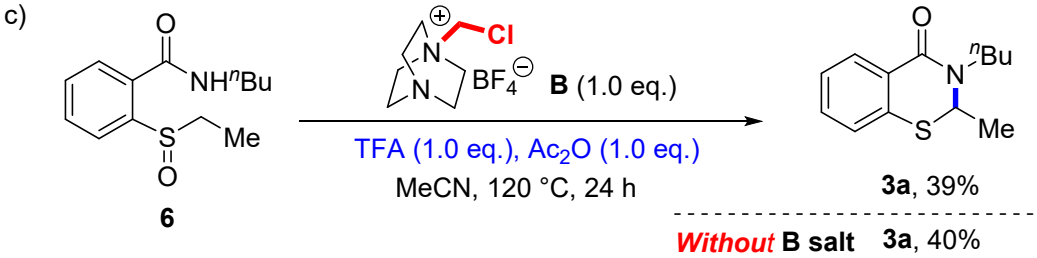
A 30 mL Schlenk tube was charged with **4a** [1] (0.2 mmol), HI (0.2 mmol), NaI (0.6 mmol), MeCN (2.0 mL) and **B** [1] (0.2 mmol). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **2a** (20.3 mg, 46%).

A 30 mL Schlenk tube was charged with **4a** (0.2 mmol), HI (0.2 mmol), NaI (0.6 mmol), MeCN (2.0 mL) and **G** [1] (with 20% of **B**) (0.2 mmol). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **2a** (17.7 mg, 40%).

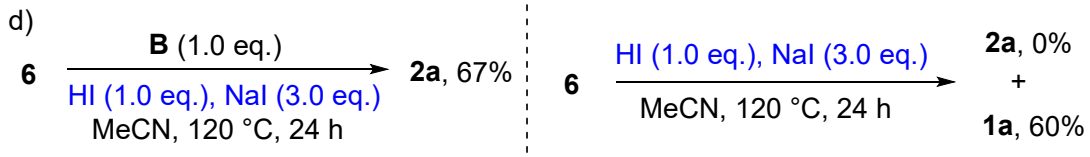
A 30 mL Schlenk tube was charged with **4a** (0.2 mmol), HI (0.2 mmol), NaI (0.6 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. No desired product **2a** was isolated.

A 30 mL Schlenk tube was charged with **1u** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), NaI (0.6 mmol), HI (0.2 mmol), and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 6 h. After cooling to room temperature, the reaction mixture was detected by GC-MS and hexyliodide was found in MS.



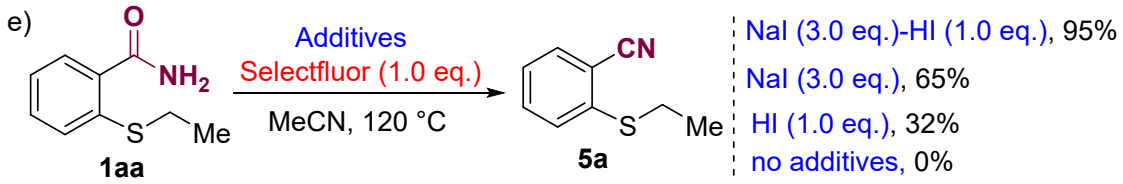


A 30 mL Schlenk tube was charged with sulfoxide **6** (0.2 mmol), TFA (0.2 mmol), Ac_2O (0.2 mmol), MeCN (2.0 mL) and **B** salt (0 or 0.2 mmol). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **3a** [with **B** salt (39%, 18.4 mg); without **B** salt (40%, 18.8 mg)].



A 30 mL Schlenk tube was charged with sulfoxide **6** (0.2 mmol), HI (0.2 mmol), NaI (0.6 mmol), MeCN (2.0 mL) and **B** salt (0 or 0.2 mmol). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **2a** (67%, 29.7 mg).

A 30 mL Schlenk tube was charged with sulfoxide **6** (0.2 mmol), HI (0.2 mmol) NaI (0.6 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the product **1a** (60%, 28.5 mg) and no desired product **2a** was isolated.



A 30 mL Schlenk tube was charged with **1aa** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HI (0.2 mmol), NaI (0.6 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **5a** (31.0 mg, 95%).

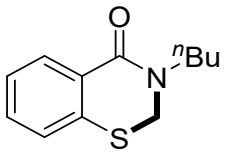
A 30 mL Schlenk tube was charged with **1aa** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), NaI (0.6 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **5a** (21.2 mg, 65%).

A 30 mL Schlenk tube was charged with **1aa** (0.2 mmol), Selectfluor (0.2 mmol, 70.9 mg), HI (0.2 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction

mixture was then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to yield the desired product **5a** (10.4 mg, 32%).

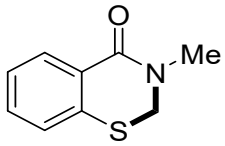
A 30 mL Schlenk tube was charged with **1aa** (0.2 mmol), HI (0.2 mmol), NaI (0.6 mmol) and MeCN (2.0 mL). The tube was sealed and the reaction was then stirred vigorously at 120 ˚C for 24 h. After cooling to room temperature, the reaction mixture was then concentrated in vacuo. No desired product **5a** was isolated.

7. Data of compounds



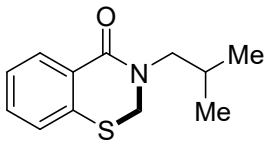
2a

Yellow oil, 37.6 mg, yield: 85% (known compound[3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 1H), 7.30 – 7.25 (m, 1H), 7.21 – 7.16 (m, 2H), 4.49 (s, 2H), 3.59 – 3.54 (m, 2H), 1.63 – 1.53 (m, 2H), 1.40 – 1.28 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.70, 137.02, 131.45, 130.69, 129.64, 127.08, 126.11, 48.58, 48.13, 30.19, 20.19, 13.86.



2b

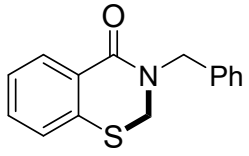
Yellow oil, 27.0 mg, yield: 74% (known compound[4]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 1H), 7.31 – 7.26 (m, 1H), 7.22 – 7.17 (m, 2H), 4.52 (s, 2H), 3.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.18, 136.84, 131.57, 130.62, 129.27, 127.11, 126.17, 50.10, 35.75.



2c

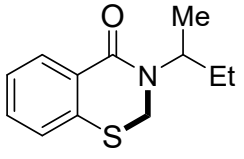
Yellow oil, 26.5 mg, yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 1H), 7.31 – 7.25 (m, 1H), 7.22 – 7.16 (m, 2H), 4.50 (s, 2H), 3.38 (d, J = 7.4 Hz, 2H), 2.05

– 1.91 (m, 1H), 0.93 (d, J = 6.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.94, 137.08, 131.45, 130.77, 129.66, 127.10, 126.12, 55.95, 49.28, 27.67, 20.24. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{15}NOS$ $[M+H]^+$: 222.0947, found: 222.0947.



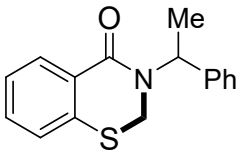
2d

Yellow oil, 29.6 mg, yield:58% (known compound[3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 1H), 7.33 – 7.19 (m, 8H), 4.80 (s, 2H), 4.43 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.05, 137.08, 136.36, 131.74, 130.95, 129.28, 128.84, 128.08, 127.83, 127.19, 126.19, 51.08, 47.76.



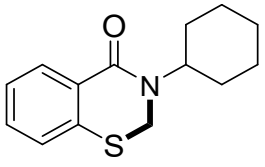
2e

Yellow oil, 30.9 mg, yield: 70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 1H), 7.31 – 7.17 (m, 3H), 4.78 – 4.71 (m, 1H), 4.38 (q, J = 13.1 Hz, 2H), 1.56 – 1.46 (m, 2H), 1.16 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.82, 137.10, 131.40, 130.96, 129.96, 127.04, 126.04, 51.22, 42.63, 27.30, 18.33, 11.18. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{15}NOS$ $[M+H]^+$: 222.0947, found: 222.0947.



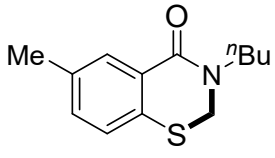
2f

Yellow oil, 28.5 mg, yield: 53% (known compound[3]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.11 (m, 1H), 7.38 – 7.19 (m, 8H), 6.12 (q, *J* = 7.1 Hz, 1H), 4.39 – 4.35 (m, 1H), 4.13 – 4.09 (m,1H), 1.57 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.72, 138.67, 136.18, 130.60, 129.94, 128.52, 127.65, 126.74, 126.40, 126.08, 125.04, 50.84, 42.65, 15.33.



2g

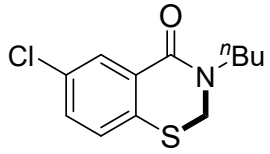
Yellow oil, 33.1 mg, yield: 67% (known compound[5]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 1H), 7.30 – 7.16 (m, 3H), 4.58 – 4.55 (m, 1H), 4.44 (s, 2H), 1.79 – 1.62 (m, 5H), 1.46 – 1.31 (m, 4H), 1.11 – 1.03 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.39, 137.20, 131.34, 130.94, 130.02, 127.03, 126.02, 53.40, 43.53, 30.56, 25.63, 25.51.



2h

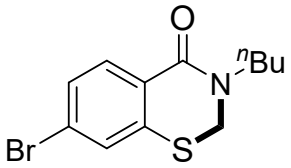
Yellow oil, 29.1 mg, yield: 62%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.09 – 7.09 (m, 2H), 4.47 (s, 2H), 3.56 (t, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 1.60 – 1.52 (m, 2H),

1.37 – 1.30 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.91, 136.06, 133.48, 132.39, 131.08, 129.41, 126.96, 48.68, 48.09, 30.20, 20.98, 20.18, 13.85. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{17}NOS$ $[M+H]^+$: 236.1104, found: 236.1103.



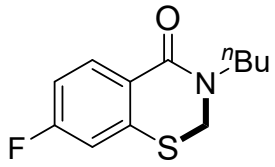
2i

Yellow oil, 32.2 mg, yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 8.01 (m, 1H), 7.26 – 7.23 (m, 1H), 7.15 – 7.13 (m, 1H), 4.49 (s, 2H), 3.56 (t, J = 7.3 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.40 – 1.27 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.59, 134.32, 131.16, 130.43, 129.85, 129.52, 127.27, 47.49, 47.18, 29.05, 19.10, 12.77. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{14}NClOS$ $[M+H]^+$: 256.0557, found: 256.0555.



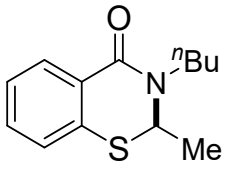
2j

Yellow oil, 35.9 mg, yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.87 (m, 1H), 7.37 – 7.29 (m, 2H), 4.49 (s, 2H), 3.55 (t, J = 7.3 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.39 – 1.27 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.12, 139.02, 132.14, 129.60, 129.43, 128.40, 126.15, 48.58, 48.19, 30.12, 20.17, 13.83. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{14}BrNOS$ $[M+H]^+$: 300.0052, found: 300.0050.



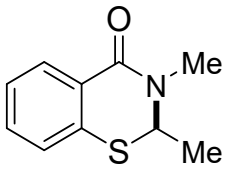
2k

Yellow oil, 24.4 mg, yield: 51%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 1H), 6.93 – 6.84 (m, 2H), 4.51 (s, 2H), 3.55 (t, *J* = 7.3 Hz, 2H), 1.62 – 1.55 (m, 2H), 1.37 – 1.30 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.00 (d, *J* = 254.7 Hz), 163.06, 139.62 (d, *J* = 9.5 Hz), 133.30 (d, *J* = 9.7 Hz), 125.98, 113.89 (d, *J* = 12.2 Hz), 113.59 (d, *J* = 10.0 Hz), 48.70, 48.12, 30.17, 20.18, 13.83. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{14}FNOS$ $[M+H]^+$: 240.0853, found: 240.0851.



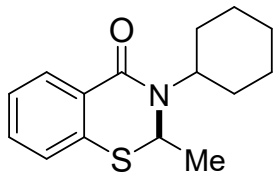
3a

Red oil, 35.3 mg, yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 1H), 7.31 – 7.26 (m, 1H), 7.20 – 7.15 (m, 2H), 4.56 – 4.49 (m, 1H), 4.05 – 3.96 (q, *J* = 6.7 Hz, 1H), 3.07 – 2.98 (m, 1H), 1.62 – 1.52 (m, 5H), 1.38 – 1.31 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.58, 133.81, 131.80, 130.15, 128.85, 127.96, 125.93, 56.04, 47.50, 30.65, 22.20, 20.14, 13.88. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{17}NOS$ $[M+H]^+$: 236.1104, found: 236.1103.



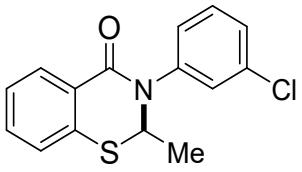
3b

Yellow oil, 27.0 mg, yield: 70%.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 1H), 7.33 – 7.16 (m, 3H), 4.52 (q, *J* = 6.8 Hz, 1H), 3.15 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.10, 133.79, 131.94, 130.19, 128.41, 127.89, 125.98, 57.95, 34.86, 21.14. HRMS (ESI, *m/z*): calcd. for $C_{10}H_{11}NOS$ $[M+H]^+$: 194.0634, found:194.0634.



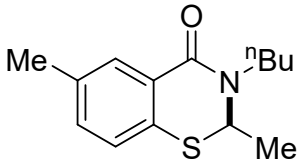
3c

White solid, 35.0 mg, yield: 67%, m.p. 122 – 123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 8.01 (m, 1H), 7.32 – 7.16 (m, 3H), 4.73 – 4.58 (m, 2H), 1.81 – 1.34 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.34, 133.80, 131.68, 130.36, 129.54, 128.06, 125.90, 54.23, 51.04, 31.47, 30.66, 25.82, 25.51, 24.45. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{19}NOS$ $[M+H]^+$: 262.1260, found: 262.1262.



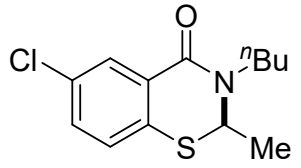
3d

Yellow oil, 33.5 mg, yield: 58%.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 – 8.08 (m, 1H), 7.37 – 7.19 (m, 7H), 4.95 (q, *J* = 6.8 Hz, 1H), 1.66 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.84, 142.81, 134.84, 134.52, 132.51, 130.79, 130.36, 128.55, 128.12, 127.86, 127.52, 126.29, 125.41, 59.35, 22.37. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{12}NClOS$ $[M+H]^+$: 290.0401, found: 290.0399.



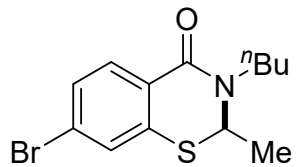
3e

Yellow oil, 29.9 mg, yield: 60%.^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.14 – 7.05 (m, 2H), 4.51 (q, *J* = 6.8 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.08 – 2.98 (m, 1H), 2.28 (s, 3H), 1.66 – 1.51 (m, 5H), 1.39 – 1.31 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 162.79, 135.88, 132.74, 130.60, 130.18, 128.63, 127.88, 56.02, 47.48, 30.67, 22.12, 21.01, 20.14, 13.88. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{19}NOS$ $[M+H]^+$: 250.1260, found: 250.1260.



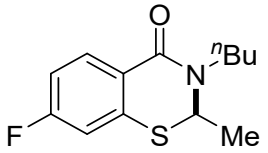
3f

Yellow oil, 29.6 mg, yield: 55%.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 8.02 (m, 1H), 7.29 – 7.26 (m, 1H), 7.14 – 7.11 (m, 1H), 4.54 (q, *J* = 6.8 Hz, 1H), 4.02 – 3.98 (m, 1H), 3.09 – 2.99 (m, 1H), 1.59 – 1.52 (m, 5H), 1.36 – 1.33 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.55, 132.22, 132.02, 131.86, 130.11, 129.24, 56.11, 47.62, 30.58, 22.22, 20.11, 13.85. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{16}ClNOS$ $[M+H]^+$: 270.0714, found: 270.0713.



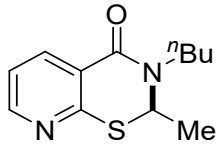
3g

Yellow oil, 35.7 mg, yield: 57%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 1H), 7.35 – 7.29 (m, 2H), 4.53 (q, *J* = 6.8 Hz, 1H), 4.04 – 3.94 (m, 1H), 3.07 – 3.00 (m, 1H), 1.61 – 1.53 (m, 5H), 1.39 – 1.30 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.00, 135.96, 131.69, 130.39, 129.27, 127.64, 126.42, 56.28, 47.57, 30.59, 22.34, 20.13, 13.86. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{16}BrNOS$ $[M+Na]^+$: 314.0209, found: 314.0204.



3h

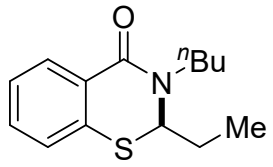
Yellow oil, 25.3 mg, yield: 50%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 1H), 6.91 – 6.83 (m, 2H), 4.54 (q, *J* = 6.8 Hz, 1H), 4.05 – 3.95 (m, 1H), 3.07 – 2.98 (m, 1H), 1.64 – 1.54 (m, 5H), 1.41 – 1.31 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.40 (d, *J* = 254.5 Hz), 161.92, 136.52 (d, *J* = 9.5 Hz), 132.82 (d, *J* = 9.7 Hz), 125.18 (d, *J* = 3.0 Hz), 114.57 (d, *J* = 24.1 Hz), 113.45 (d, *J* = 21.8 Hz).56.34, 47.49, 30.63, 22.32, 20.13, 13.86. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{16}FNOS$ $[M+Na]^+$: 254.1009, found: 254.1010.



3i

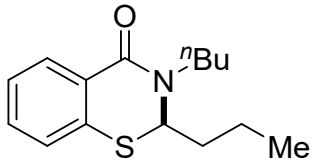
Yellow oil, 30.7 mg, yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 – 8.46 (m, 1H), 8.31 – 8.28 (m, 1H), 7.17 – 7.12 (m, 1H), 4.62 (q, *J* = 6.8 Hz, 1H), 4.05 – 4.01 (m, 1H), 3.10 – 3.00 (m, 1H), 1.63 – 1.55 (m, 5H), 1.39 – 1.31 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.00, 156.16, 151.17, 136.72, 124.21, 119.89, 54.90, 46.40,

29.50, 22.01, 19.04, 12.78. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{16}N_2OS$ $[M+H]^+$: 237.1056, found: 237.1069.



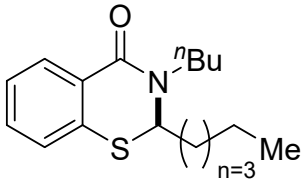
3j

Yellow oil, 35.4 mg, yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 1H), 7.30 – 7.15 (m, 3H), 4.20 – 4.11 (m, 2H), 2.97 – 2.88 (m, 1H), 1.82 – 1.77 (m, 2H), 1.63 – 1.58 (m, 2H), 1.39 – 1.32 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.65, 133.78, 131.71, 130.04, 129.28, 127.83, 125.91, 62.88, 48.47, 30.63, 28.13, 20.19, 13.89, 11.59. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{19}NOS$ $[M+H]^+$: 250.1260, found: 250.1260.



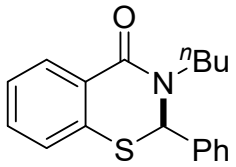
3k

Yellow oil, 31.6 mg, yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 1H), 7.30 – 7.15 (m, 3H), 4.28 – 4.11 (m, 2H), 2.95 – 2.86 (m, 1H), 1.79 – 1.58 (m, 4H), 1.40 – 1.30 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.70, 133.85, 131.72, 130.06, 129.25, 127.83, 125.91, 60.89, 48.39, 37.04, 30.62, 20.20, 20.09, 13.88, 13.34. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{21}NOS$ $[M+H]^+$: 264.1417, found: 264.1416.



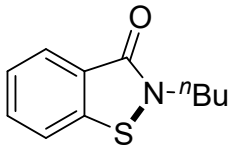
3l

Yellow oil, 30.3 mg, yield: 52%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 1H), 7.31 – 7.26 (m, 1H), 7.26 – 7.15 (m, 2H), 4.26 – 4.11 (m, 2H), 2.95 – 2.86 (m, 1H), 1.81 – 1.73 (m, 2H), 1.66 – 1.56 (m, 4H), 1.41 – 1.12 (m, 6H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.78 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.69, 133.84, 131.72, 130.05, 129.25, 127.84, 125.91, 61.19, 48.41, 34.93, 31.00, 30.63, 26.58, 22.49, 20.20, 13.92, 13.89. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{25}NOS$ $[M+H]^+$: 292.1730, found: 292.1729.



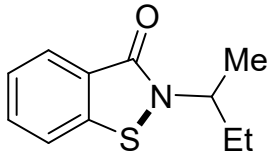
3m

Yellow oil, 35.1 mg, yield: 59%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 – 8.06 (m, 1H), 7.19 – 6.99 (m, 8H), 5.58 (s, 1H), 4.27 – 4.17 (m, 1H), 2.99 – 2.89 (m, 1H), 1.64 – 1.56 (m, 2H), 1.38 – 1.31 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.92, 139.10, 132.76, 131.92, 129.93, 129.25, 128.45, 128.20, 127.45, 126.27, 126.22, 61.82, 48.56, 30.50, 20.21, 13.86. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{19}NOS$ $[M+H]^+$: 298.1260, found: 298.1260.



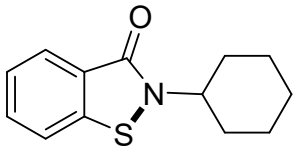
4a

Yellow oil, 35.7 mg, yield: 86% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 3.83 (t, *J* = 7.2 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.40 – 1.27 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.40, 140.13, 131.64, 126.63, 125.43, 124.85, 120.31, 43.67, 31.59, 19.82, 13.69.



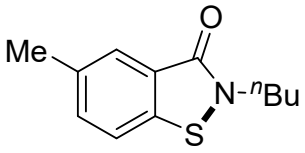
4b

Yellow oil, 33.2 mg, yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.33 – 7.28 (m, 1H), 4.76 – 4.65 (m, 1H), 1.71 – 1.61 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.32, 139.11, 130.47, 125.55, 124.35, 124.30, 119.38, 50.47, 28.69, 19.51, 9.90. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{14}NOS$ $[M+H]^+$: 208.0791, found: 208.0795.



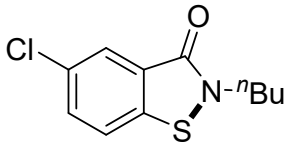
4c

Yellow oil, 35.9 mg, yield: 77% (known compound[1]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.33 – 7.28 (m, 1H), 4.56 – 4.47 (m, 1H), 1.97 (d, *J* = 10.3 Hz, 2H), 1.80 (d, *J* = 12.0 Hz, 2H), 1.65 (d, *J* = 13.1 Hz, 1H), 1.54 – 1.33 (m, 4H), 1.20 – 1.11 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.75, 139.22, 130.37, 125.43, 124.41, 124.24, 119.30, 52.10, 31.87, 24.56, 24.19.



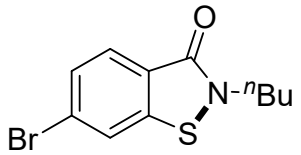
4d

Yellow oil, 32.3 mg, yield: 73%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.42 (s, 2H), 3.88 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.75 – 1.70 (m, 2H), 1.43 – 1.35 (m, 2H), 0.95 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.33, 137.16, 135.56, 133.17, 126.47, 124.95, 119.99, 43.68, 31.59, 21.12, 19.82, 13.69. HRMS (ESI, *m/z*): calcd. for $C_{12}H_{16}NOS$ $[M+H]^+$: 222.0947, found: 222.0950.



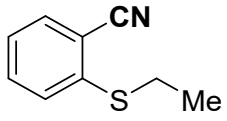
4e

White solid, 41.1 mg, yield: 85%, m.p. 75 – 76 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.9 Hz, 1H), 7.58 – 7.47 (m, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.46 – 1.34 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.19, 138.21, 132.08, 131.85, 126.36, 126.25, 121.54, 43.90, 31.54, 19.81, 13.66. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{13}ClNOS$ $[M+H]^+$: 242.0401, found: 242.0410.



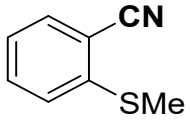
4f

White solid, 40.1 mg, yield: 70%, m.p. 105 – 106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 1.2 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 3.89 (t, *J* = 7.1 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.46 – 1.34 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.91, 141.63, 129.14, 127.75, 126.43, 124.08, 123.07, 43.75, 31.57, 19.81, 13.67. HRMS (ESI, *m/z*): calcd. for $C_{11}H_{13}BrNOS$ $[M+H]^+$: 285.9896, found: 285.9903.



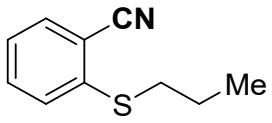
5a

Yellow oil, 31.0 mg, yield: 95% (known compound[6]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 1H), 7.47 – 7.41 (m, 1H), 7.35 – 7.33 (m, 1H), 7.20 – 7.15 (m, 1H), 2.98 (q, *J* = 7.4 Hz, 2H), 1.28 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.80, 133.67, 132.83, 128.77, 125.87, 117.21, 113.39, 27.63, 14.01.



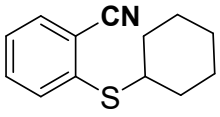
5b

Yellow oil, 26.8 mg, yield: 90% (known compound[6]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 2H), 7.26 – 7.17 (m, 1H), 7.17 – 7.12 (m, 1H), 2.49 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.60, 132.46, 131.90, 125.14, 124.07, 115.93, 110.57, 14.73.



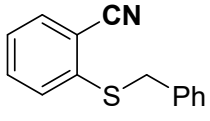
5c

Yellow oil, 29.0 mg, yield: 82% (known compound[7]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 1H), 7.46 – 7.40 (m, 1H), 7.35 – 7.32 (m, 1H), 7.19 – 7.14 (m, 1H), 2.93 (t, *J* = 7.4 Hz, 2H), 1.70 – 1.58 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.15, 133.67, 132.78, 128.78, 125.78, 117.23, 113.43, 35.53, 22.26, 13.40.



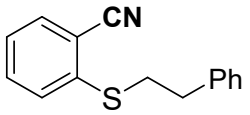
5d

Yellow oil, 31.3 mg, yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.55 (m, 1H), 7.46 – 7.39 (m, 2H), 7.27 – 7.19 (m, 1H), 3.27 – 3.17 (m, 1H), 1.95 – 1.88 (m, 2H), 1.76 – 1.69 (m, 2H), 1.59 – 1.53 (m, 1H), 1.41 – 1.18 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.10, 132.68, 131.59, 131.20, 125.74, 116.49, 114.87, 46.07, 32.06, 24.85, 24.56. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{15}NS$ $[M+H]^+$: 218.0998, found: 218.1004.



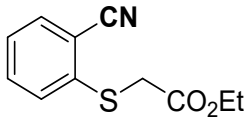
5e

Yellow oil, 27.0 mg, yield: 60% (known compound[6]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 1H), 7.36 – 7.16 (m, 8H), 4.14 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.65, 134.93, 132.60, 131.71, 129.56, 127.84, 127.59, 126.54, 125.60, 116.10, 113.39, 37.71.



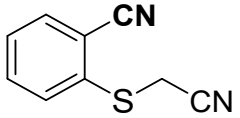
5f

Yellow oil, 33.5 mg, yield: 70% (known compound[8]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 1H), 7.45 – 7.40 (m, 1H), 7.36 – 7.33 (m, 1H), 7.25 – 7.12 (m, 6H), 3.22 – 3.17 (m, 2H), 2.92 – 2.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.52, 139.49, 133.78, 132.87, 129.16, 128.67, 128.53, 126.75, 126.14, 117.20, 113.76, 35.43, 35.07.



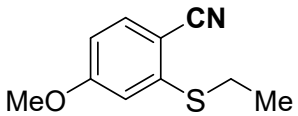
5g

Yellow oil, 33.1 mg, yield: 75% (known compound[9]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.44 (m, 3H), 7.30 – 7.20 (m, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.66 (s, 2H), 1.16 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.80, 139.38, 133.79, 133.10, 131.01, 127.40, 116.91, 114.72, 61.93, 36.18, 14.05.



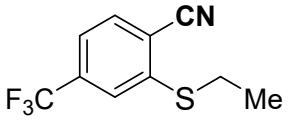
5h

Yellow oil, 29.9 mg, yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.62 – 7.57 (m, 1H), 7.48 – 7.42 (m, 1H), 3.68 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.39, 134.34, 134.13, 133.73, 129.64, 116.87, 116.58, 115.48, 20.65. HRMS (ESI, *m/z*): calcd. for $C_9H_6N_2S$ $[M+H]^+$: 175.0324, found: 175.0331.



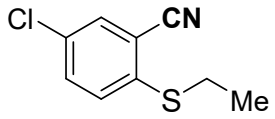
5i

Yellow oil, 26.3 mg, yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 1H), 6.82 – 6.81 (m, 1H), 6.69 – 6.65 (m, 1H), 3.79 (s, 3H), 2.96 (q, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.78, 143.68, 135.26, 117.59, 114.57, 111.35, 105.08, 55.65, 27.54, 13.91. HRMS (ESI, *m/z*): calcd. for $C_{10}H_{11}NOS$ $[M+H]^+$: 194.0634, found: 194.0633.



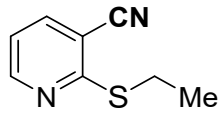
5j

Yellow oil, 26.3 mg, yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 1H), 7.51 (s, 1H), 7.42 – 7.39 (m, 1H), 3.04 (q, *J* = 7.4 Hz, 2H), 1.34 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.17, 134.62 (q, *J* = 33.1 Hz), 134.11, 124.22 (q, *J* = 3.9 Hz), 122.96 (q, *J* = 273.5 Hz), 122.15 (q, *J* = 3.7 Hz), 115.89, 115.81, 27.32, 13.62. HRMS (ESI, *m/z*): calcd. for $C_{10}H_{11}F_3NS$ $[M+H]^+$: 232.0402, found: 232.0399.



5k

Yellow oil, 31.5 mg, yield: 80% (known compound[10]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 1H), 7.26 – 7.25 (m, 1H), 7.15 – 7.12 (m, 1H), 2.99 (q, *J* = 7.4 Hz, 2H), 1.32 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.39, 139.58, 134.51, 127.59, 125.93, 116.39, 110.84, 27.32, 13.71.



5l

Yellow oil, 21.3 mg, yield: 65% (known compound[11]). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 – 8.49 (m, 1H), 7.73 – 7.70 (m, 1H), 7.01 – 6.97 (m, 1H), 3.20 (q, *J* = 7.4 Hz, 2H), 1.33 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.28, 151.08, 139.49, 117.30, 114.58, 106.41, 23.66, 13.32.

III. References and notes:

(1) K. Yang, H. Zhang, B. Niu, T. Tang and H. Ge, Benzisothiazol-3-ones through a metal-free intramolecular N–S bond formation, *Eur. J. Org. Chem.*, 2018, **2018**, 5520-5523.

(2) G. Hallas and A. D. Towns, Dyes derived from aminothiophenes. Part 7: Synthesis and properties of some benzo[*b*]thiophene-based azo disperse dyes. *Dyes Pigm.*, 1997, **35**, 219-237.

(3) K. Yang, B. Niu, Z. Ma, H. Wang, B. Lawrence and H. Ge, Silver-promoted site-selective intramolecular cyclization of 2-methylthiobenzamide through α-C(sp^3)−H functionalization, *J. Org. Chem.*, 2019, **84**, 14045-14052.

(4) Y. Kita, O. Tamura, N. Shibata and T. Miki, Chemistry of *O*-silylated ketene acetals :a novel intramolecular Pummerer-type reaction of ω-carbamoylsulfoxide leading to α-thiolactams, *Chem. Pharm. Bull.*, 1990, **38**, 1473-1478.

(5) J. Xiong, G. Zhong and Y. Liu, Domino reactions initiated by copper-catalyzed aryl–I bond thiolation for the switchable synthesis of 2,3-dihydrobenzothiazinones and benzoisothiazolones, *Adv. Synth. Catal.*, 2019, **361**, 550-555.

(6) R. Beugelmans, M. Bois-Choussy and B. Boudet, Etude des reactions de$_{srn}$1—partie 10: Action de sulfanions sur les halogenures d'aryle fonctionnalises. synthese directe de benzothiophenes et thienopyridines, *Tetrahedron*, 1983, **39**, 4153-4161.

(7) X. Wang, Y. Tang, C. Long, W. Dong, C. Li, X. Xu, W. Zhao and X. Wang, Nucleophilic amination and etherification of aryl alkyl thioethers. *Org. Lett.*, 2018, **20**, 4749-4753.

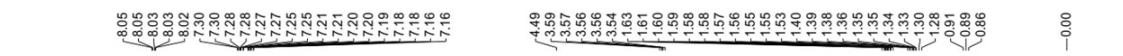
(8) Y. Zhou, Y. Wang, Y. Lou and Q. Song, Facile synthesis of 1,2-thiobenzonitriles *via* Cu-catalyzed denitrogenative radical coupling reaction. *Chem. Commun.*, 2019, **55**, 10265-10268.

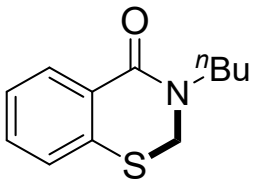
(9) Y. Seo, S. Bhuniya, S. Tapadar, J. Yi and B. Kim, Expanded fluorescent nucleoside analog as hybridization probe. *Bull. Korean Chem. Soc.*, 2007, **28**, 1923-1924.

(10) T. Murata, S. Niizuma, S. Hara, H. Kawada, K. Hada, H. Shimada, H. Tanaka and Y. Nakanishi, Quinazolinone and isoquinolinone derivatives, PCT Int. Appl., 2015060373.

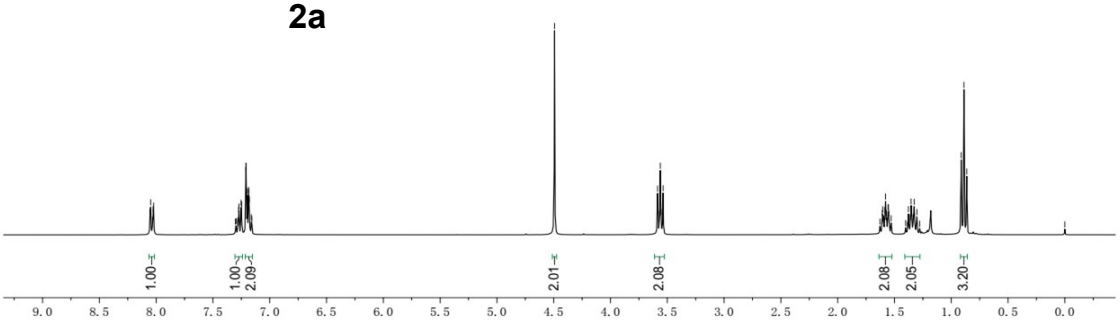
(11) A. Sokolov, A. Mikhaylov, N. Baleeva and M. Baranov, Xanthates as thiol surrogates for nucleophilic substitution with aryl halides. *Eur. J. Org. Chem.*, 2021, **2021**, 4350-4357.

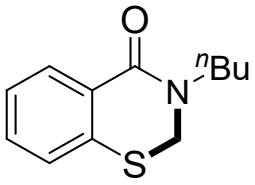
IV. ^{1}H and ^{13}C NMR



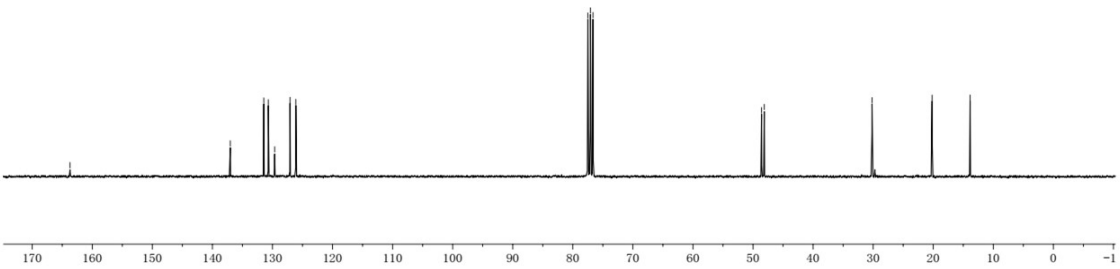


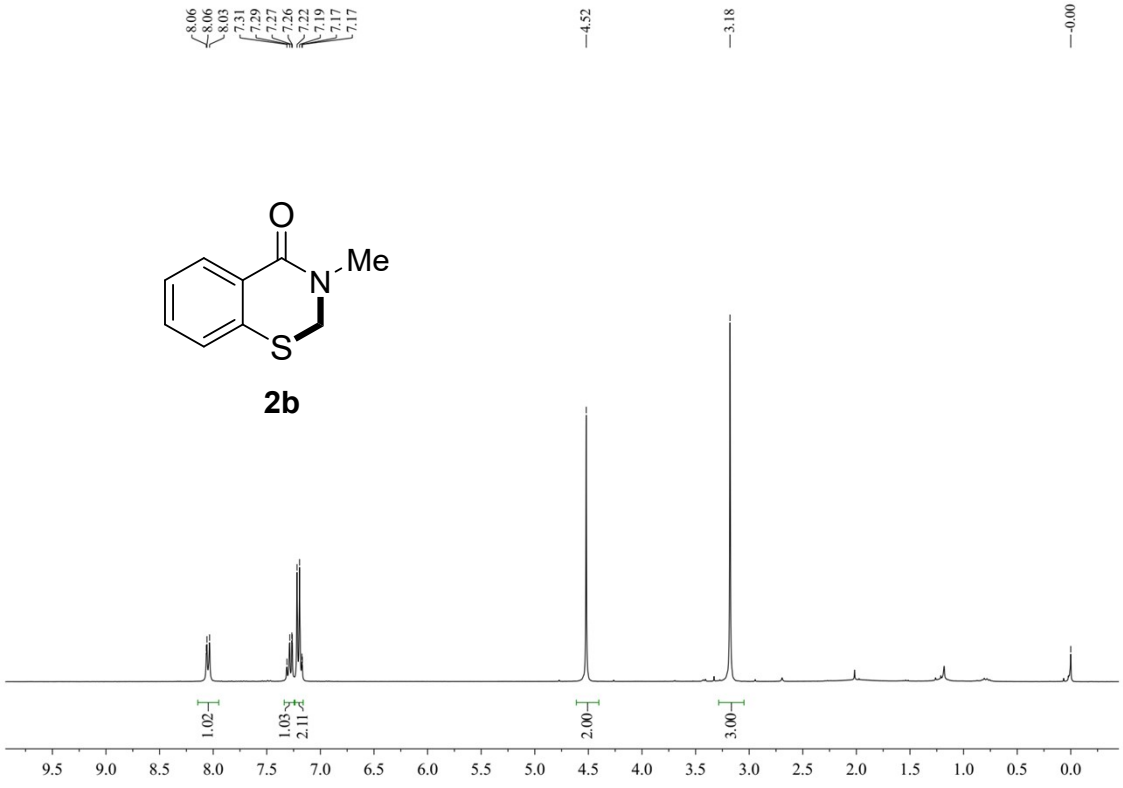
2a



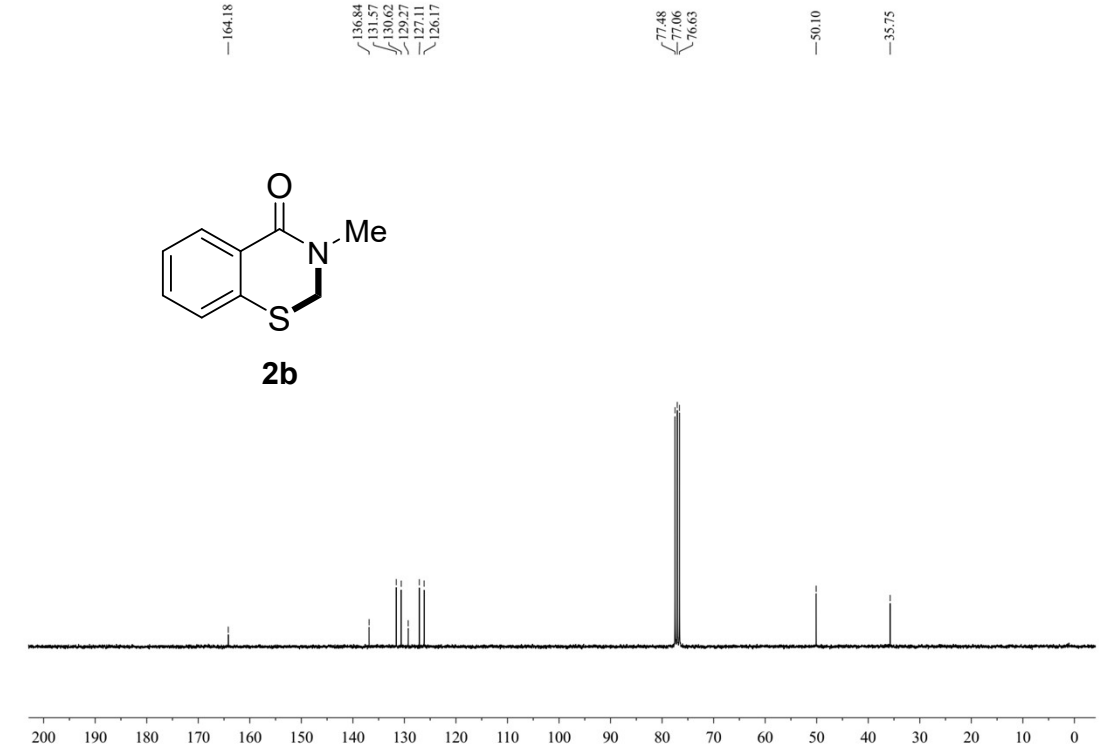


2a



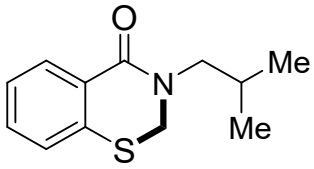

8.06
8.06
8.03
7.31
7.29
7.27
7.26
7.22
7.19
7.17
7.17
4.52
3.18
0.00
O
N
Me
S
1.02
1.03
2.11
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

2b

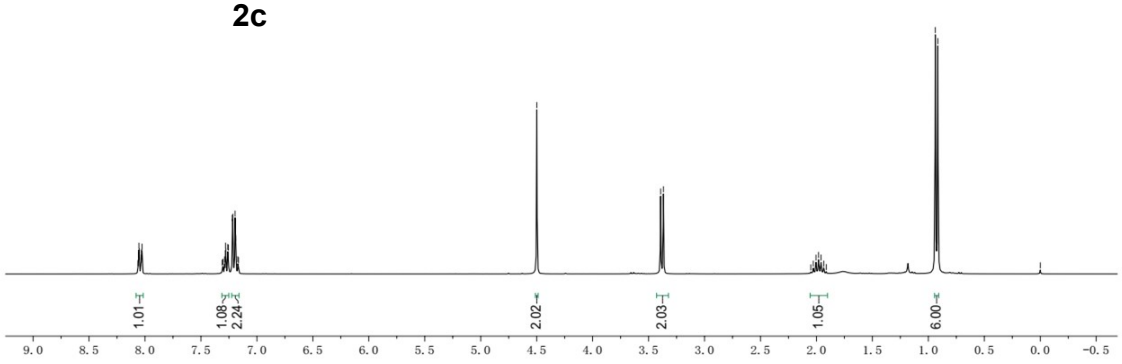

164.18
136.84
131.57
130.62
129.27
127.11
126.17
77.48
77.06
76.63
50.10
35.75
O
N
Me
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

2b

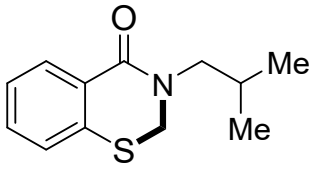

8.06
8.06
8.05
8.05
8.04
8.03
8.03
7.31
7.30
7.29
7.28
7.28
7.26
7.25
7.22
7.22
7.20
7.19
7.17
7.16
4.50
3.39
3.37
2.05
2.03
2.00
1.98
1.96
1.93
1.91
0.94
0.92
0.00


O
N
S
Me
Me

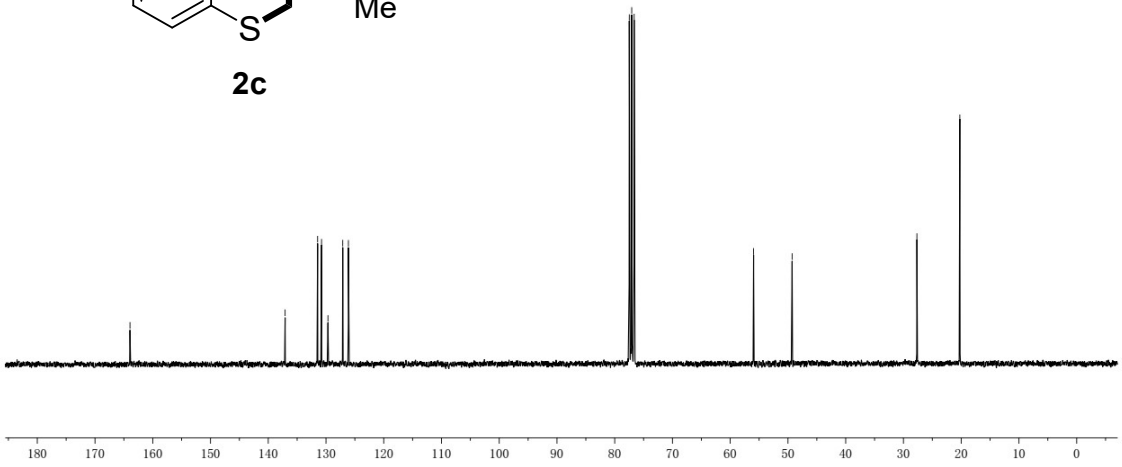
2c

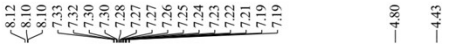

1.01
1.08
2.24
2.02
2.03
1.05
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

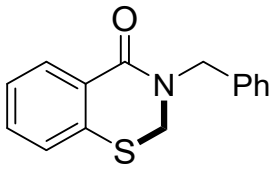

163.94
137.08
131.45
130.77
129.66
127.10
126.12
77.48
77.06
76.63
55.95
49.28
27.67
20.24


O
N
S
Me
Me

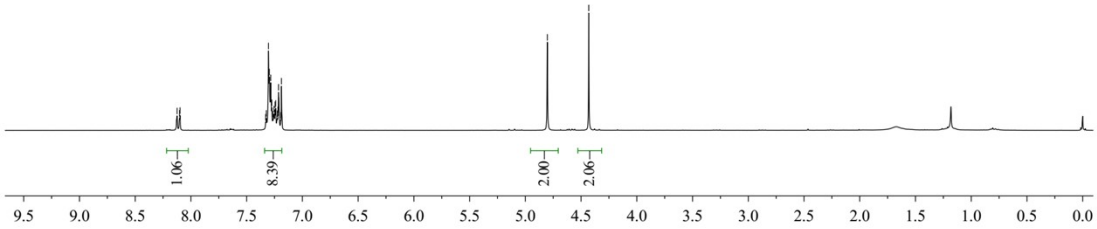
2c


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

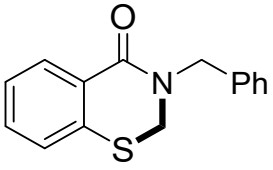

8.12
8.10
8.10
7.33
7.32
7.30
7.30
7.28
7.27
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.19
7.19
4.80
4.43


O
N
Ph
S

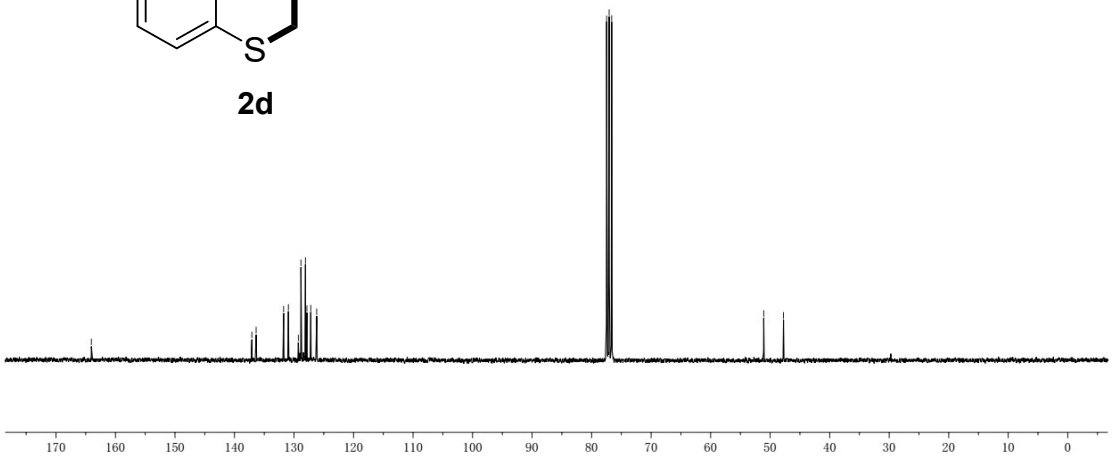
2d

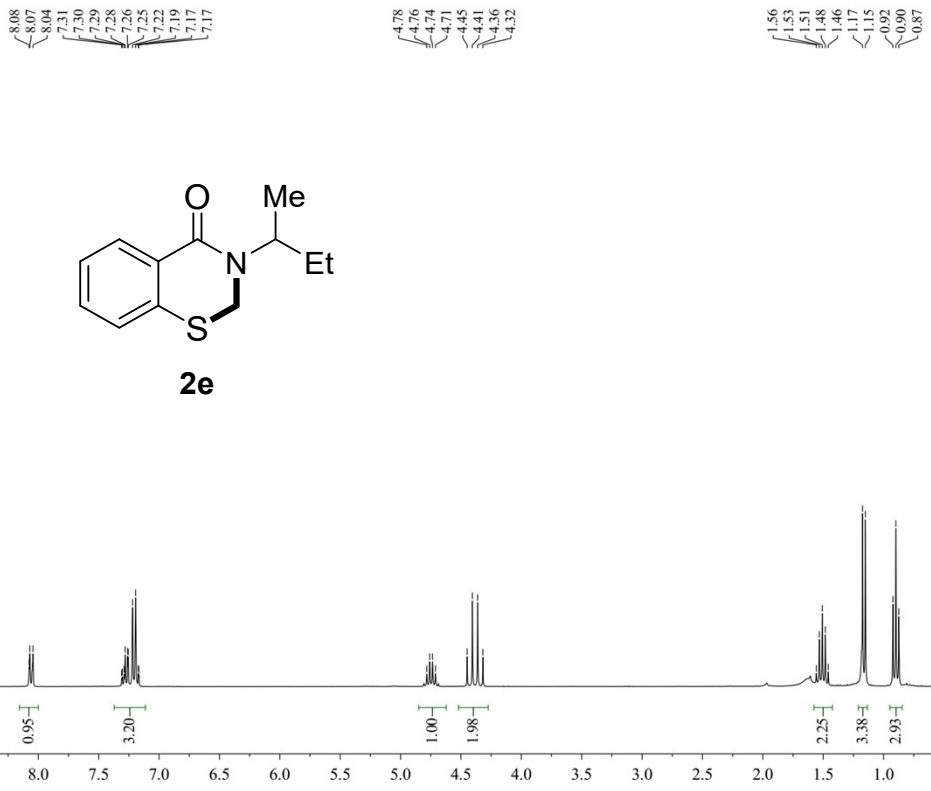

1.06
8.39
2.00
2.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

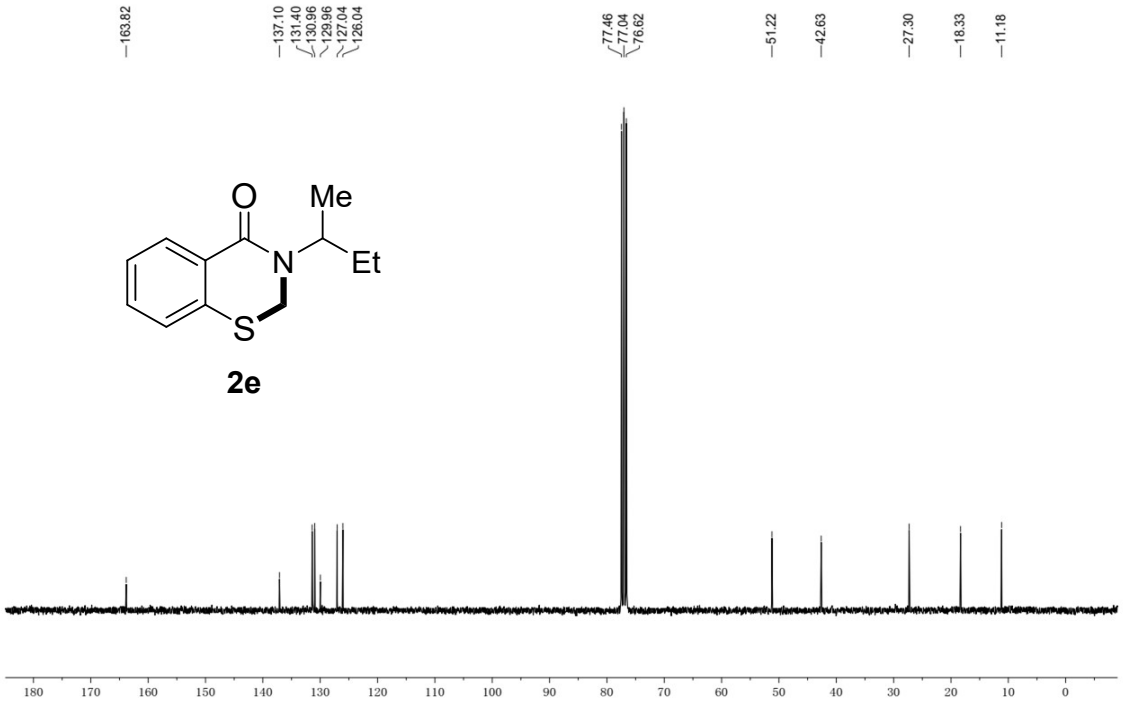

164.05
137.08
136.36
131.74
130.95
129.28
128.84
128.08
127.83
127.19
126.19
77.47
77.05
76.63
51.08
47.76

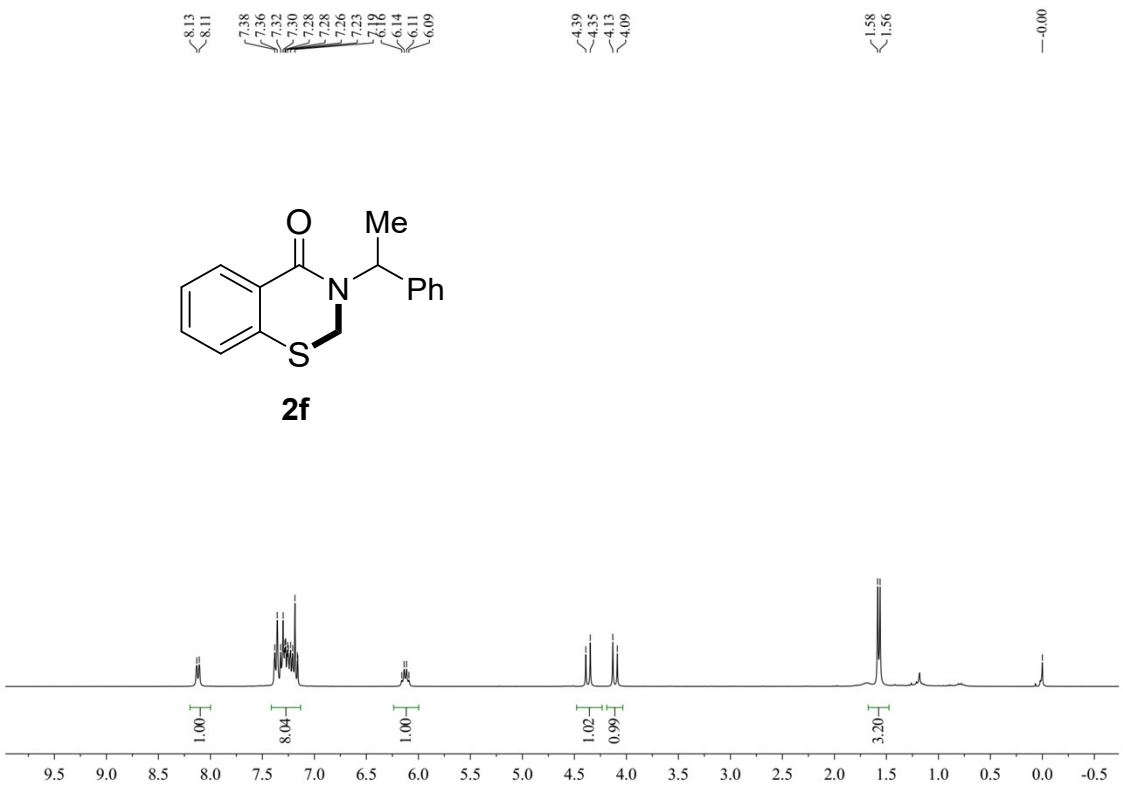

O
N
Ph
S

2d

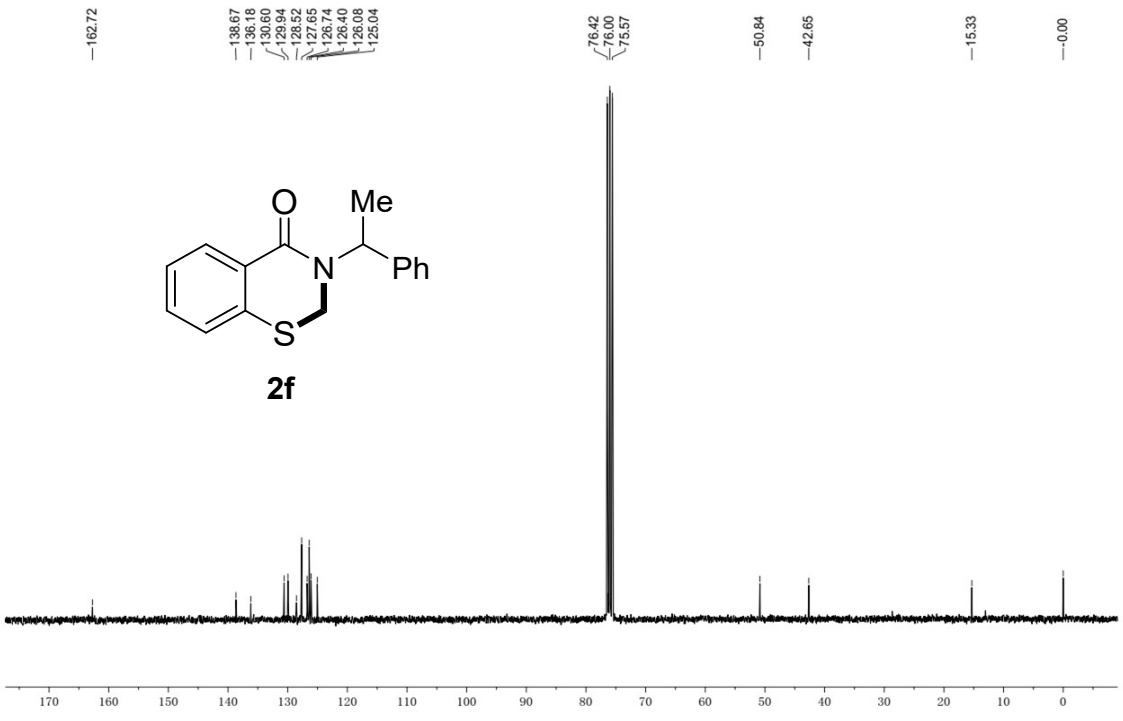

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.08
8.07
8.04
7.31
7.30
7.29
7.28
7.26
7.25
7.22
7.19
7.17
7.17
4.78
4.76
4.74
4.71
4.45
4.41
4.36
4.32
1.56
1.53
1.51
1.48
1.46
1.17
1.15
0.92
0.90
0.87
O
Me
N
Et
S
2e
0.95
3.20
1.00
1.98
2.25
3.38
2.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

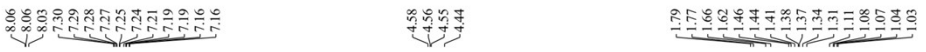

163.82
137.10
131.40
130.96
129.96
127.04
126.04
77.46
77.04
76.62
51.22
42.63
27.30
18.33
11.18
O
Me
N
Et
S
2e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

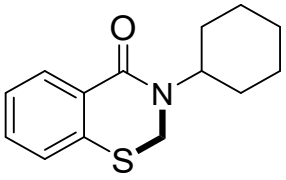

8.13
8.11
7.38
7.36
7.32
7.30
7.28
7.28
7.26
7.23
7.19
6.18
6.14
6.11
6.09
4.39
4.35
4.13
4.09
1.58
1.56
0.00
O
Me
N
Ph
S
1.00
8.04
1.00
1.02
0.99
3.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

2f

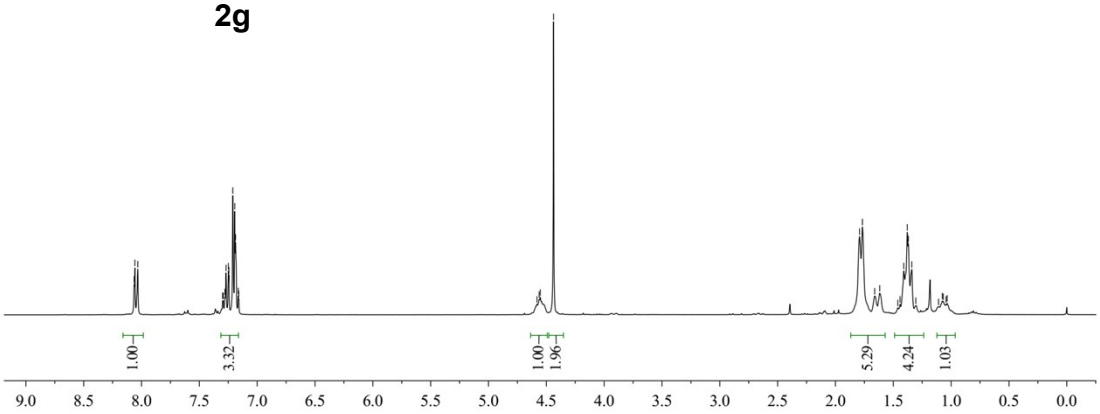

162.72
138.67
136.18
130.60
129.94
128.52
127.65
126.74
126.40
126.08
125.04
76.42
76.00
75.57
50.84
42.65
15.33
0.00
O
Me
N
Ph
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

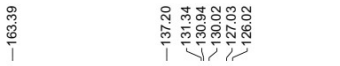
2f

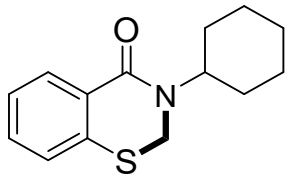

8.06
8.06
8.03
7.30
7.29
7.28
7.27
7.25
7.24
7.21
7.19
7.19
7.16
7.16
4.58
4.56
4.55
4.44
1.79
1.77
1.66
1.62
1.46
1.44
1.41
1.38
1.37
1.34
1.31
1.11
1.08
1.07
1.04
1.03


O
N
S

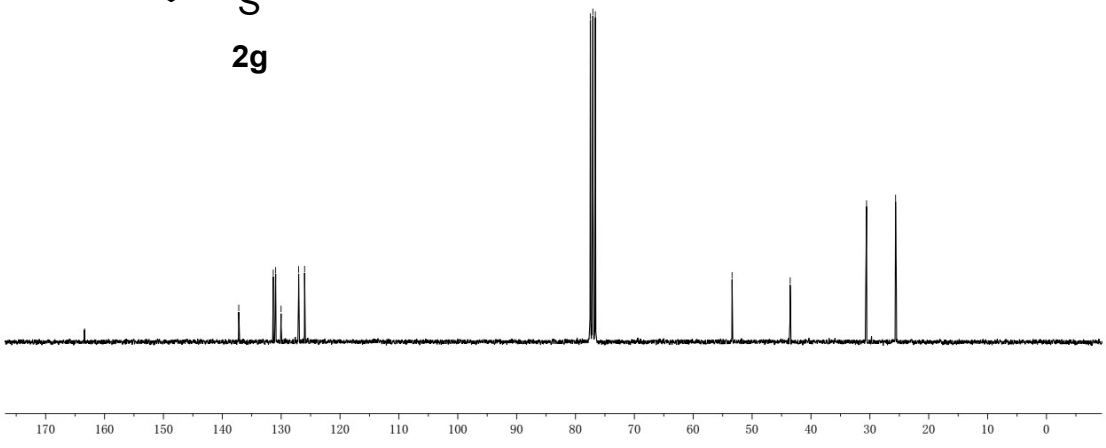
2g

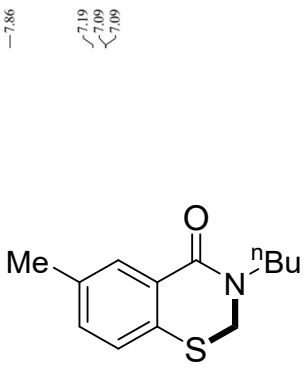

1.00
3.32
1.00
1.96
5.29
4.24
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


163.39
137.20
131.34
130.94
130.02
127.03
126.02
77.48
77.05
76.83
53.40
43.53
30.56
25.63
25.51

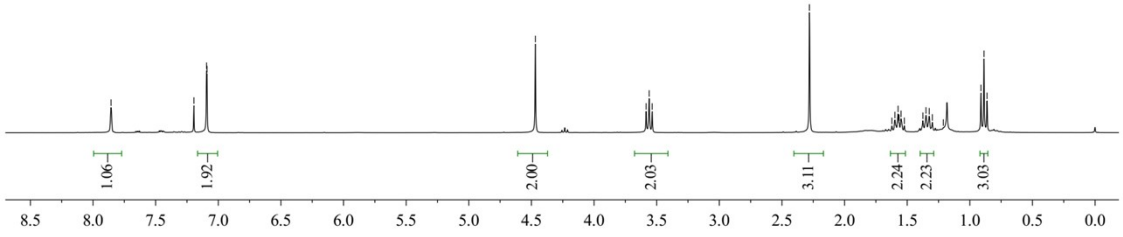

O
N
S

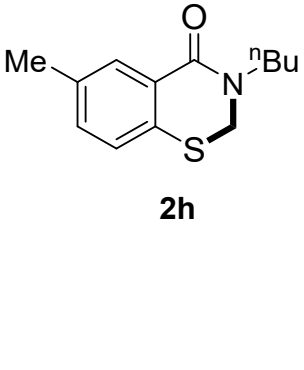
2g


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

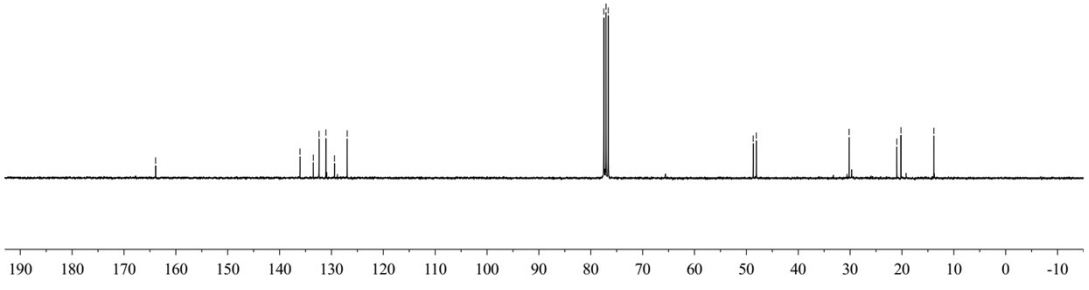

Me
O
N
nBu
S

2h

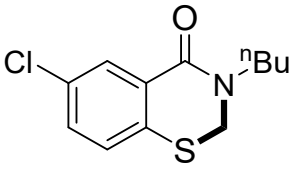

1.06
1.92
2.00
2.03
3.11
2.24
2.23
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Me
O
N
nBu
S

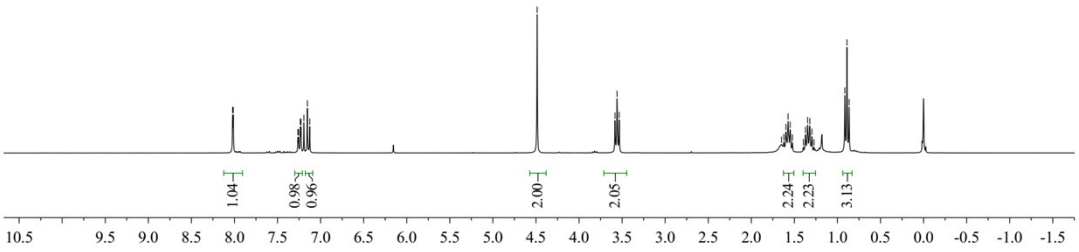
2h


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

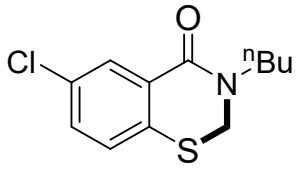

8.02
8.01
7.26
7.26
7.24
7.23
7.19
7.15
7.13
4.49
3.58
3.56
3.53
1.65
1.62
1.60
1.57
1.55
1.52
1.40
1.37
1.35
1.32
1.30
1.27
0.91
0.89
0.86


O
Cl
nBu
N
S

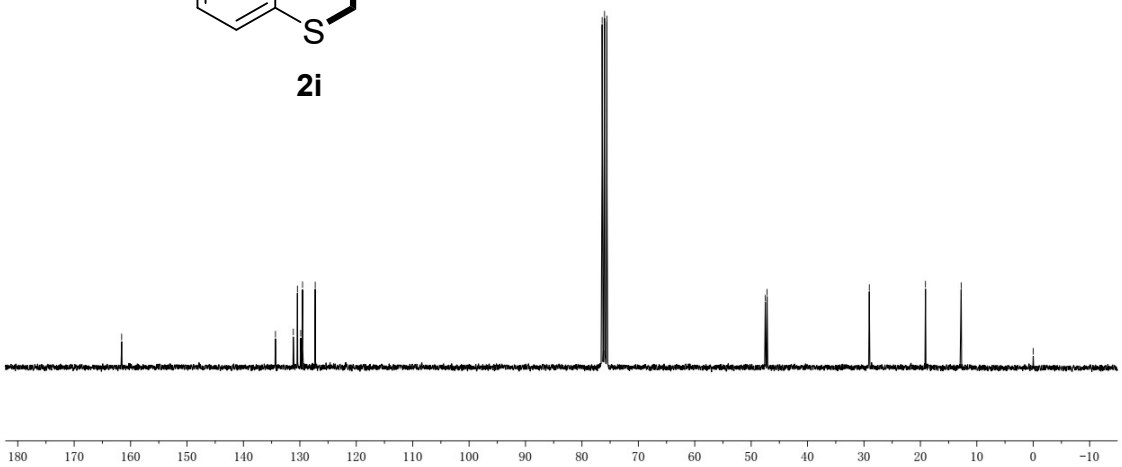
2i


1.04
0.98
0.96
2.00
2.05
2.24
2.23
3.13
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

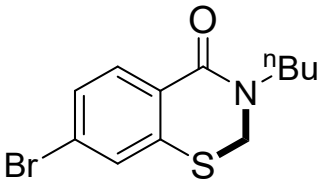

161.59
134.32
131.16
130.43
129.85
129.52
127.27
76.41
75.99
75.57
47.49
47.18
29.05
19.10
12.77
0.00


O
Cl
nBu
N
S

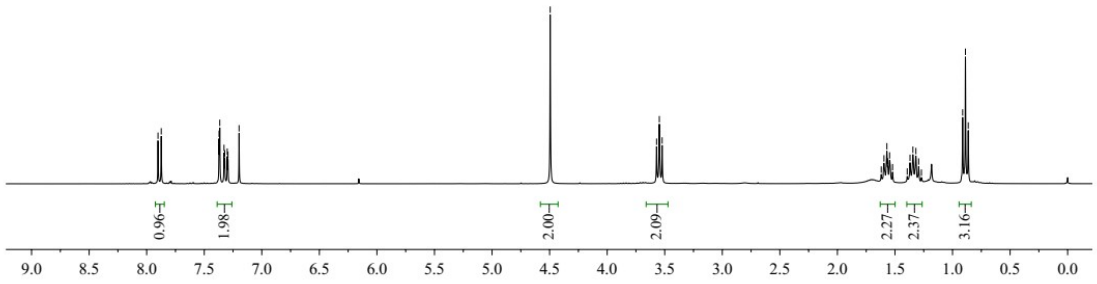
2i


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

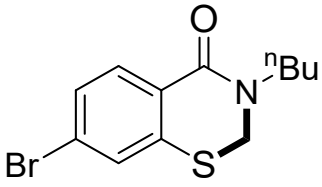

7.90
7.87
7.37
7.37
7.33
7.32
7.30
7.29
7.20
4.49
3.57
3.55
3.52
1.62
1.60
1.57
1.56
1.55
1.52
1.39
1.37
1.34
1.32
1.29
1.27
0.91
0.89
0.86


O
nBu
N
Br
S

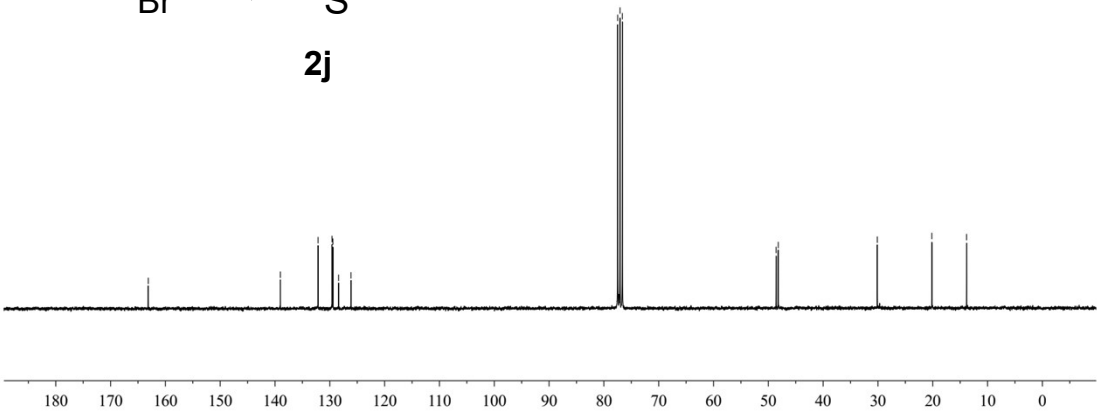
2j

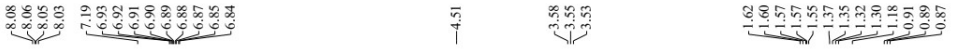

0.96
1.98
2.00
2.09
2.27
2.37
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

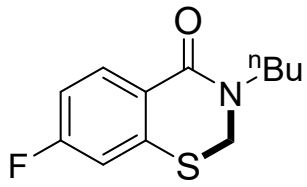

163.12
139.02
132.14
129.60
129.43
128.40
126.15
77.48
77.06
76.63
48.58
48.19
30.12
20.17
13.83


O
nBu
N
Br
S

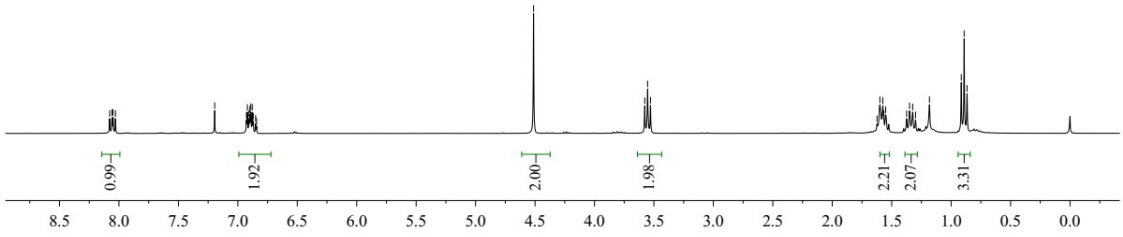
2j

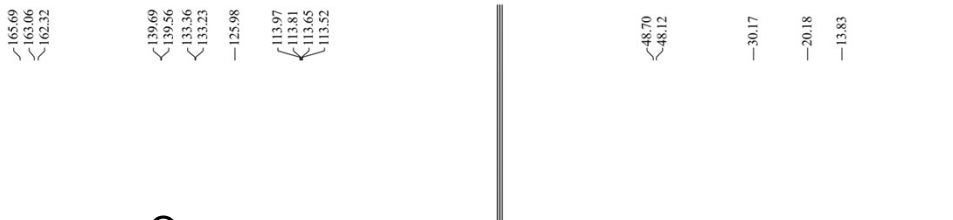

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

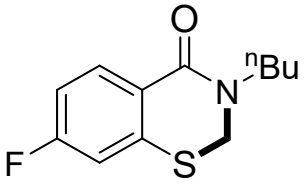

8.08
8.06
8.05
8.03
7.19
6.93
6.92
6.91
6.90
6.89
6.88
6.87
6.85
6.84
4.51
3.58
3.55
3.53
1.62
1.60
1.57
1.57
1.55
1.37
1.35
1.32
1.30
1.18
0.91
0.89
0.87


O
nBu
N
F
S

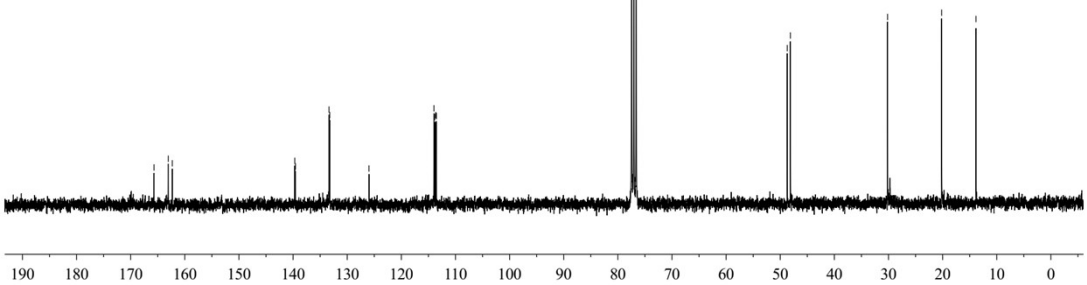
2k

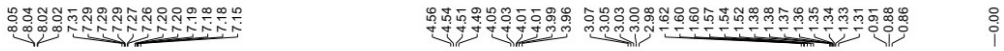

0.99
1.92
2.00
1.98
2.21
2.07
3.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

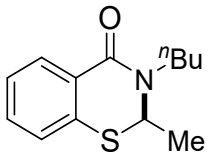

165.69
163.06
162.32
139.69
139.56
133.36
133.23
125.98
113.97
113.81
113.65
113.52
48.70
48.12
30.17
20.18
13.83


O
nBu
N
F
S

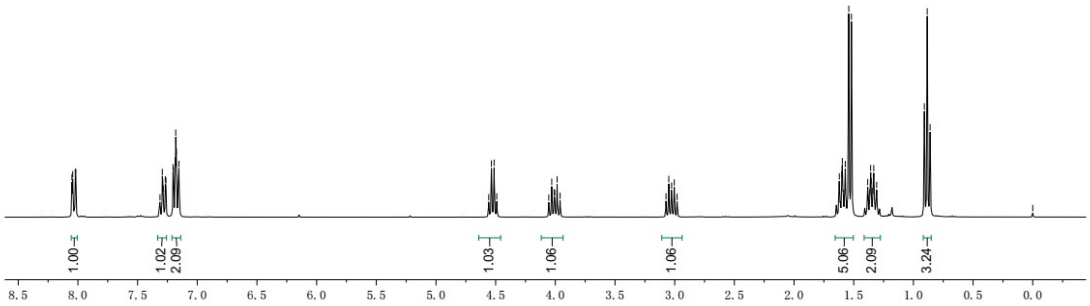
2k


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

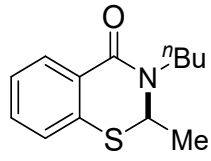

8.05
8.04
8.02
8.02
7.31
7.29
7.29
7.29
7.27
7.26
7.20
7.20
7.19
7.18
7.18
7.15
4.56
4.54
4.51
4.49
4.05
4.03
4.01
4.01
3.99
3.96
3.07
3.05
3.03
3.00
2.98
1.62
1.60
1.60
1.57
1.54
1.52
1.38
1.37
1.36
1.35
1.34
1.33
1.31
0.91
0.88
0.86
0.00


O
nBu
N
S
Me

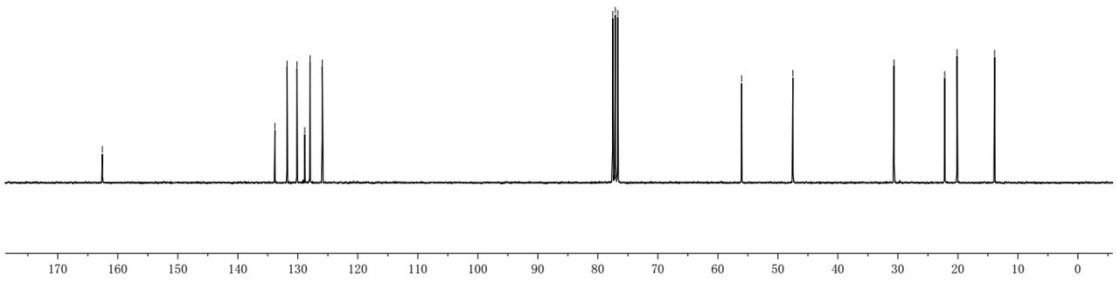
3a

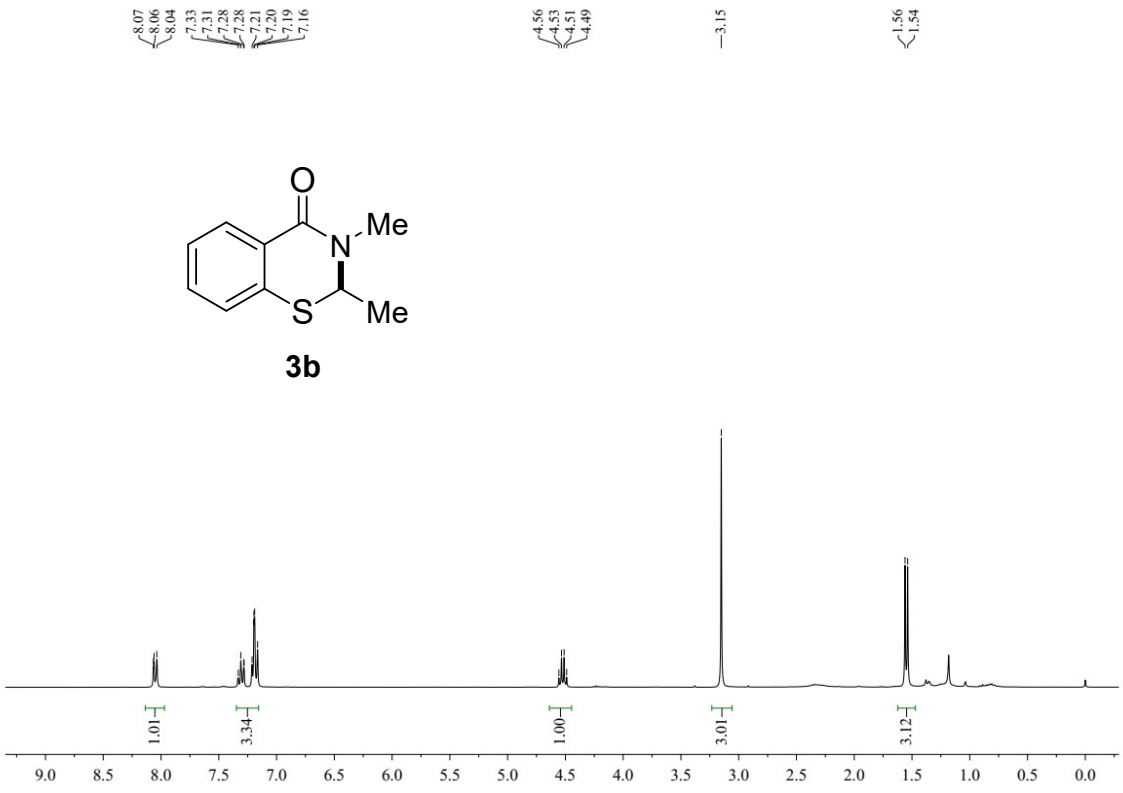

1.00
1.02
2.09
1.03
1.06
1.06
5.06
2.09
3.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


162.58
133.81
131.80
130.15
128.85
127.96
125.93
77.52
77.10
76.67
56.04
47.50
30.65
22.20
20.14
13.88

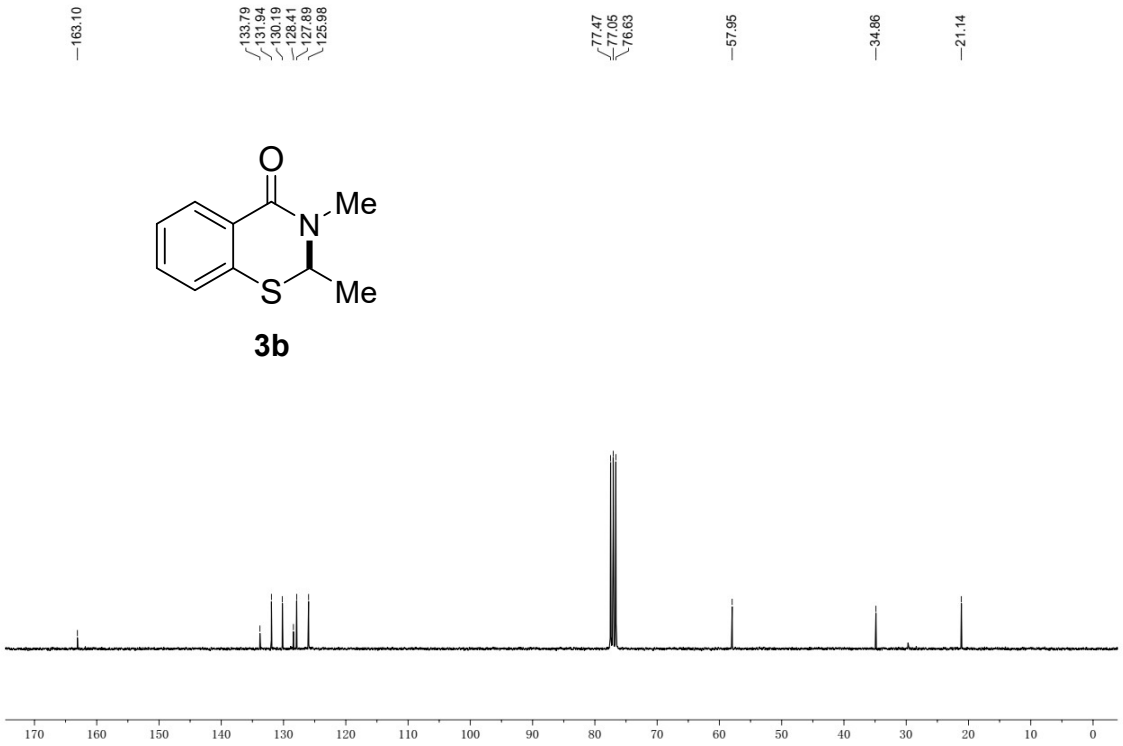

O
nBu
N
S
Me

3a

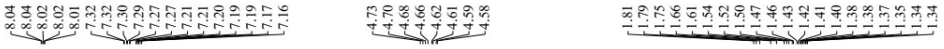

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

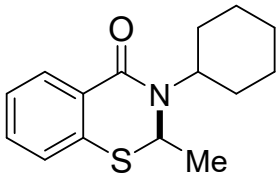

8.07
8.06
8.04
7.33
7.31
7.28
7.28
7.21
7.20
7.19
7.16
4.56
4.53
4.51
4.49
3.15
1.56
1.54
O
N
Me
S
Me
1.01
3.34
1.00
3.01
3.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

3b

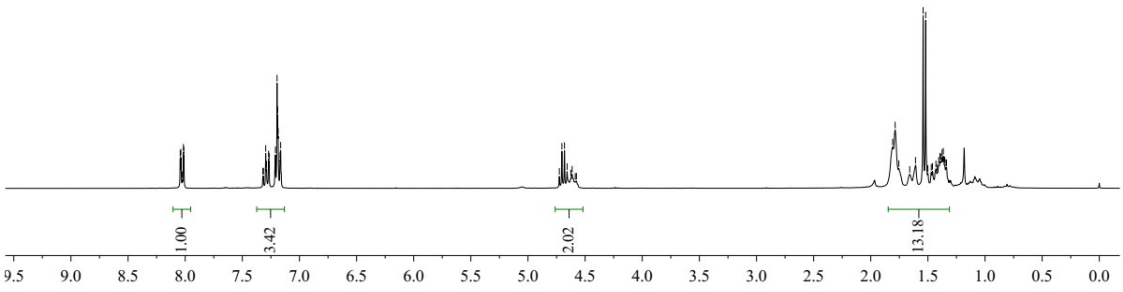

163.10
133.79
131.94
130.19
128.41
127.89
125.98
77.47
77.05
76.63
57.95
34.86
21.14
O
N
Me
S
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

3b

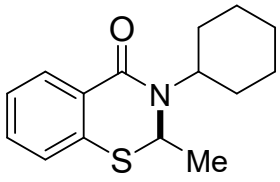

8.04
8.04
8.02
8.02
8.01
7.32
7.32
7.30
7.29
7.27
7.27
7.21
7.21
7.20
7.19
7.19
7.17
7.16
4.73
4.70
4.68
4.66
4.62
4.61
4.59
4.58
1.81
1.79
1.75
1.66
1.61
1.54
1.52
1.50
1.47
1.46
1.43
1.42
1.41
1.40
1.38
1.38
1.37
1.35
1.34
1.34


O
N
S
Me

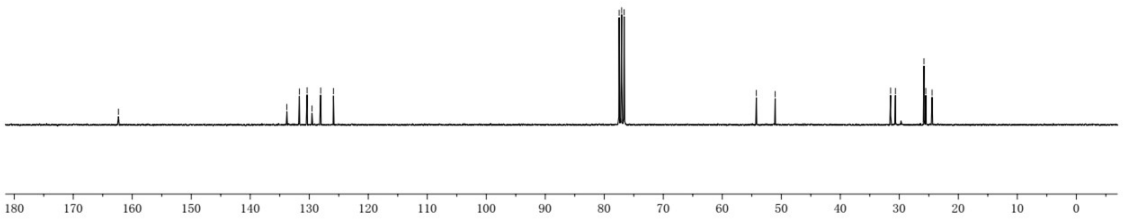
3c


1.00
3.42
2.02
13.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

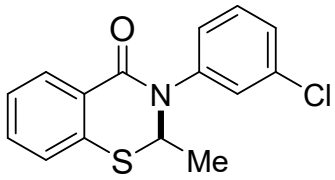

162.34
133.80
131.68
130.36
129.54
128.06
125.90
77.48
77.05
76.63
54.23
51.04
31.47
30.66
25.82
25.51
24.45


O
N
S
Me

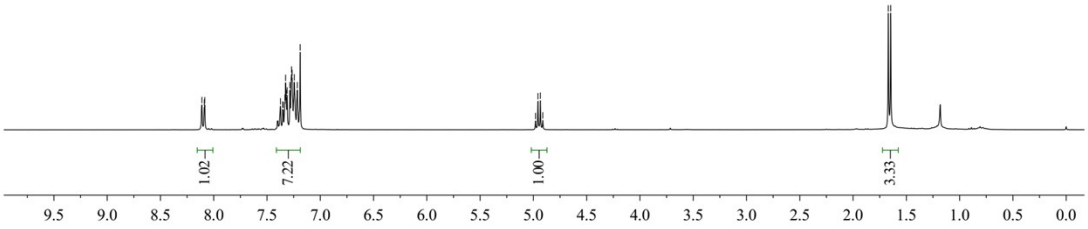
3c


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

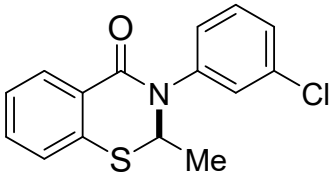

8.11
8.09
8.08
7.37
7.35
7.35
7.33
7.33
7.32
7.31
7.29
7.27
7.26
7.24
7.22
7.19
4.98
4.96
4.93
4.91
1.67
1.65


O
N
Cl
S
Me

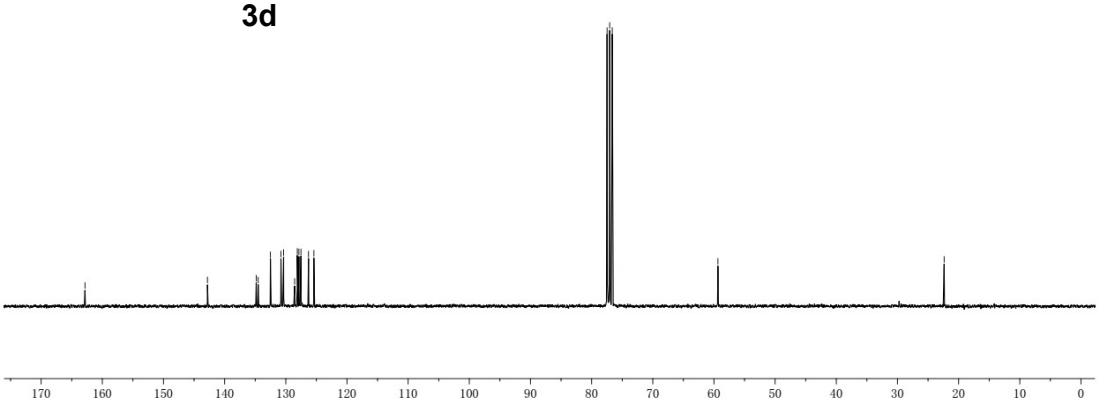
3d

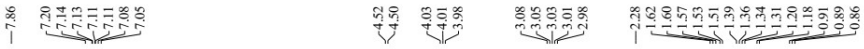

1.02
7.22
1.00
3.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

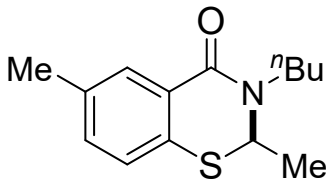

162.84
142.81
134.84
134.52
132.51
130.79
130.36
128.55
128.12
127.86
127.52
126.29
125.41
77.47
77.05
76.63
59.35
22.37


O
N
Cl
S
Me

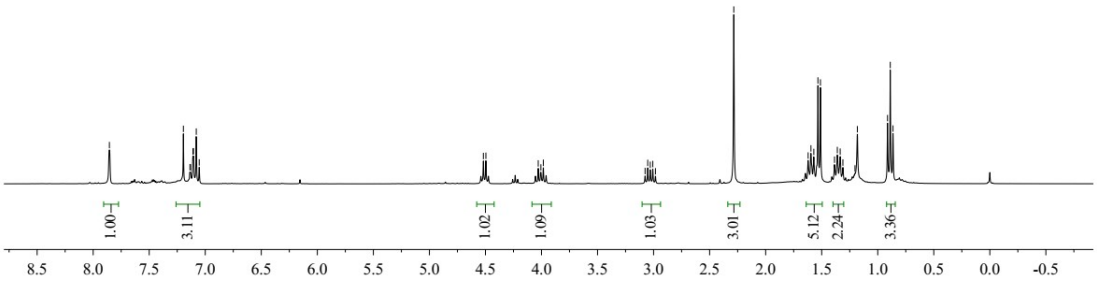
3d


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

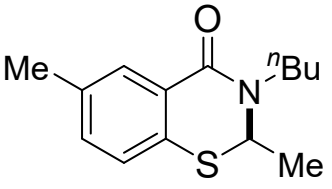

7.86
7.20
7.14
7.13
7.11
7.11
7.08
7.05
4.52
4.50
4.03
4.01
3.98
3.08
3.05
3.03
3.01
2.98
2.28
1.62
1.60
1.57
1.53
1.51
1.39
1.36
1.34
1.31
1.20
1.18
0.91
0.89
0.86


O
Me
nBu
N
S
Me

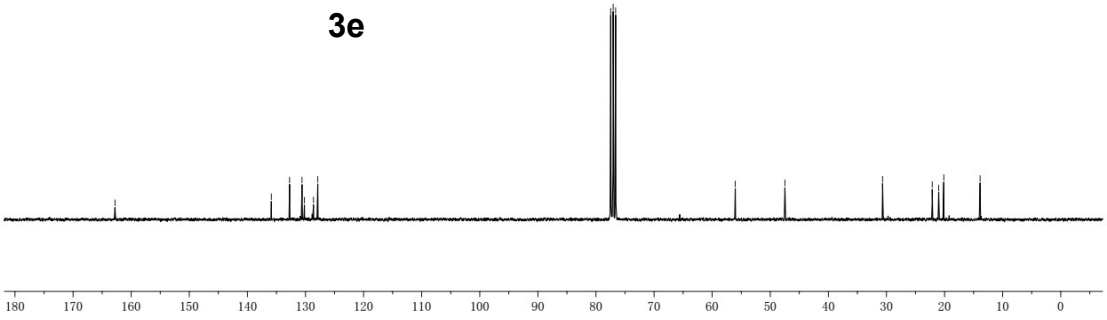
3e

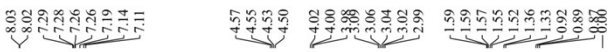

1.00
3.11
1.02
1.09
1.03
3.01
5.12
2.24
3.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

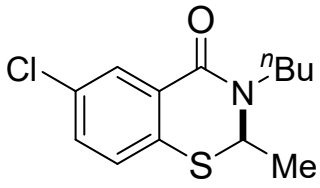

162.79
135.88
132.74
130.60
130.18
128.63
127.88
77.46
77.04
76.62
56.02
47.48
30.67
22.12
21.01
20.14
13.88


O
Me
nBu
N
S
Me

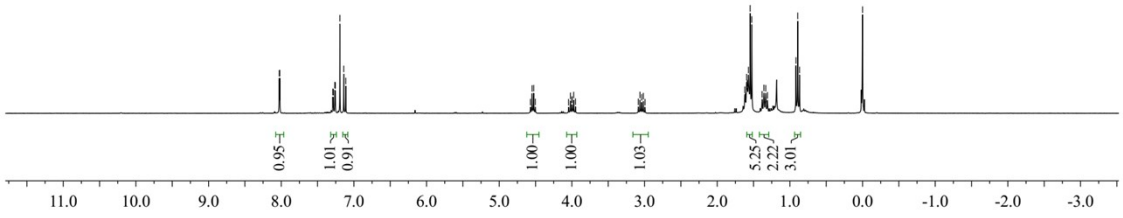
3e

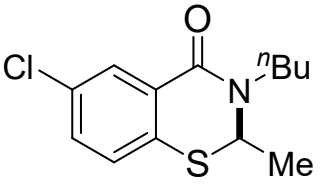

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



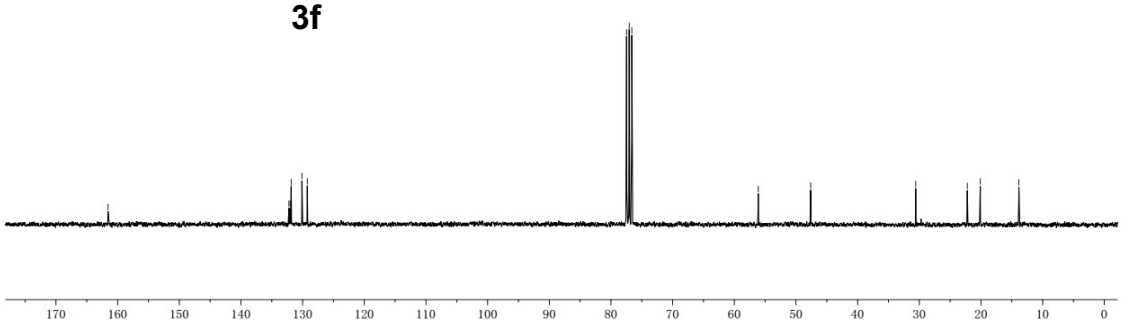


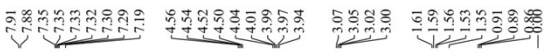
3f

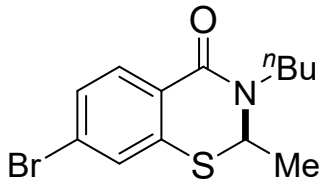




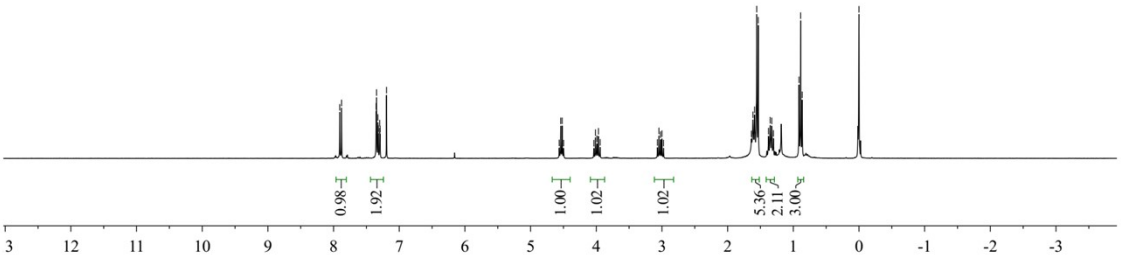
3f



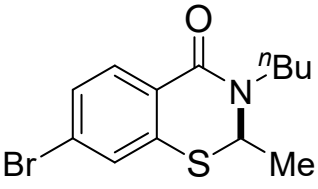

7.91
7.88
7.35
7.35
7.33
7.32
7.30
7.29
7.19
4.56
4.54
4.52
4.50
4.04
4.01
3.99
3.97
3.94
3.07
3.05
3.02
3.00
1.61
1.59
1.56
1.53
1.35
0.91
0.89
0.86
0.86


O
nBu
N
Br
S
Me

3g

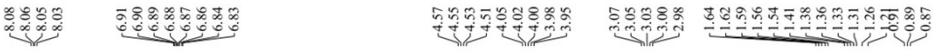

0.98
1.92
1.00
1.02
1.02
5.36
2.11
3.00
3
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3

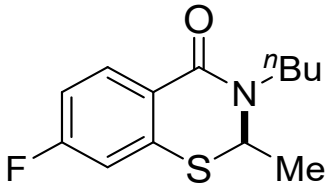

162.00
135.96
131.69
130.39
129.27
127.64
126.42
77.46
77.04
76.62
56.28
47.57
30.59
22.34
20.13
13.86


O
nBu
N
Br
S
Me

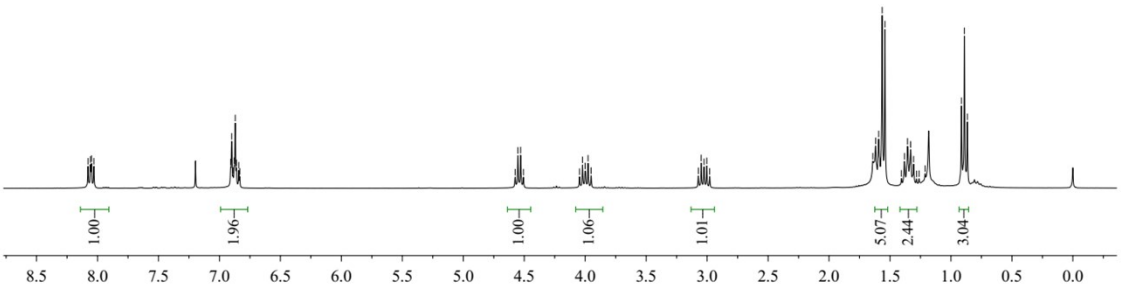
3g

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1

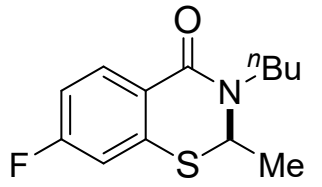

8.08
8.06
8.05
8.03
6.91
6.90
6.89
6.88
6.87
6.86
6.84
6.83
4.57
4.55
4.53
4.51
4.05
4.02
4.00
3.98
3.95
3.07
3.05
3.03
3.00
2.98
1.64
1.62
1.59
1.56
1.54
1.41
1.38
1.36
1.33
1.31
1.26
0.91
0.89
0.87


O
N
nBu
F
S
Me

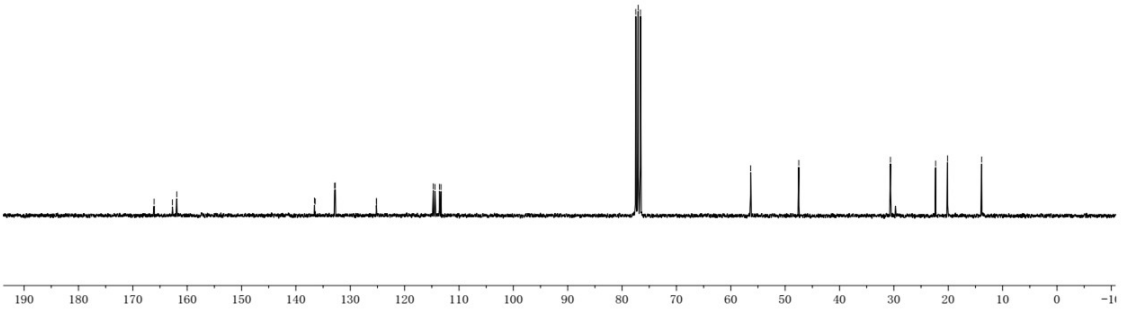
3h

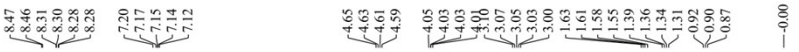

1.00
1.96
1.00
1.06
1.01
5.07
2.44
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

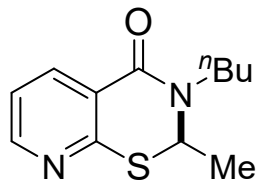

166.09
162.72
161.92
136.59
136.46
132.88
132.75
125.20
125.16
114.73
114.41
113.60
113.31
77.47
77.04
76.62
56.34
47.49
30.63
22.32
20.13
13.86


O
N
nBu
F
S
Me

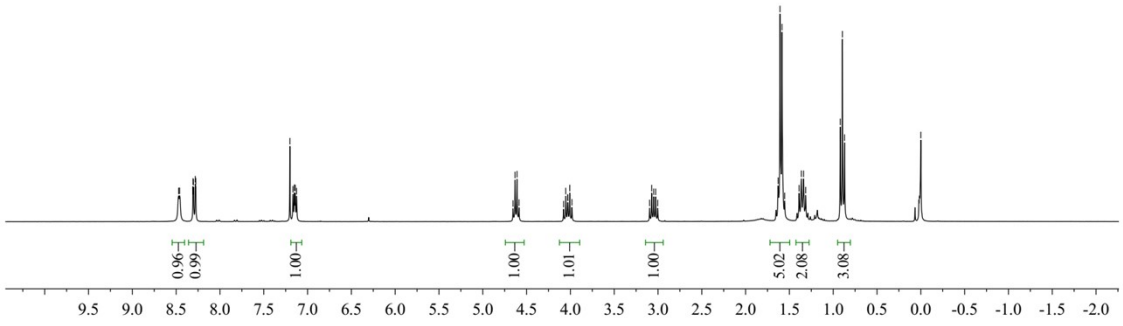
3h

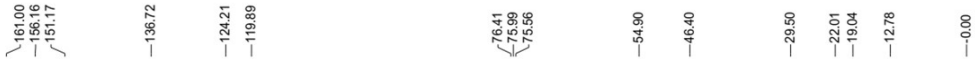

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

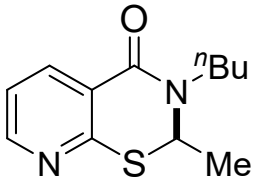

8.47
8.46
8.31
8.30
8.28
8.28
7.20
7.17
7.15
7.14
7.12
4.65
4.63
4.61
4.59
4.05
4.03
4.03
4.01
3.10
3.07
3.05
3.03
3.00
1.63
1.61
1.58
1.55
1.39
1.36
1.34
1.31
0.92
0.90
0.87
0.00


O
nBu
N
N
S
Me

3i


0.96
0.99
1.00
1.00
1.01
1.00
5.02
2.08
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0

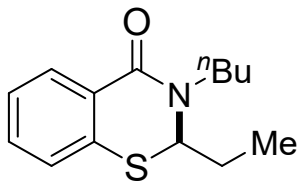

161.00
156.16
151.17
136.72
124.21
119.89
76.41
75.99
75.56
54.90
46.40
29.50
22.01
19.04
12.78
0.00


O
nBu
N
N
S
Me

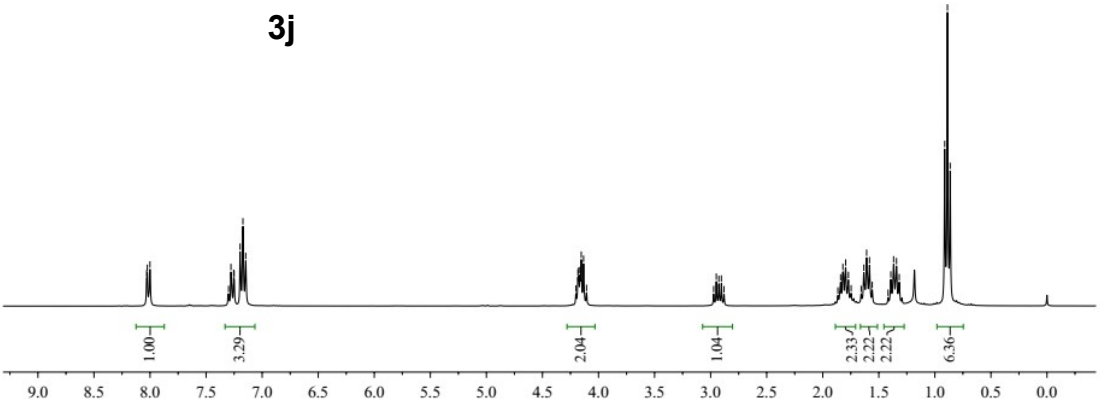
3i

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

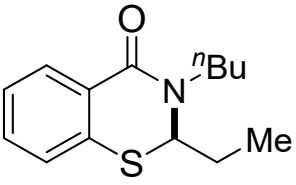

8.03
8.02
8.00
7.30
7.28
7.25
7.25
7.20
7.17
7.15
4.20
4.18
4.18
4.17
4.15
4.13
4.11
2.97
2.95
2.93
2.90
2.88
1.82
1.80
1.77
1.63
1.61
1.58
1.39
1.37
1.34
0.91
0.89
0.86


O
nBu
N
Me
S

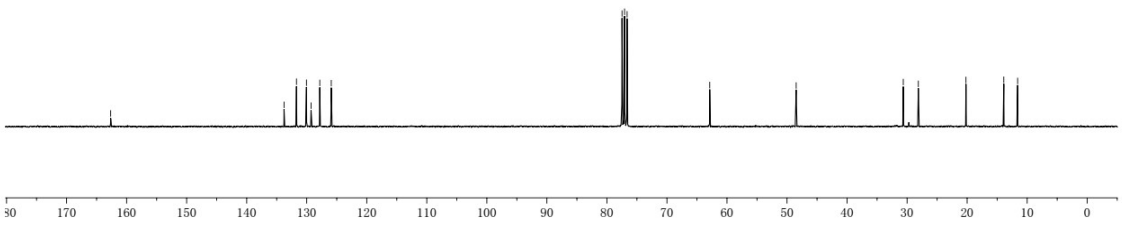
3j

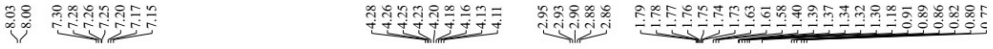

1.00
3.29
2.04
1.04
2.33
2.22
2.22
6.36
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

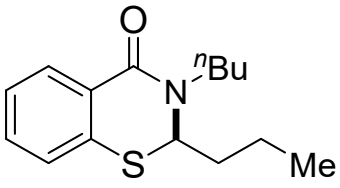

162.65
133.78
131.71
130.04
129.28
127.83
125.91
77.48
77.06
76.64
62.88
48.47
30.63
28.13
20.19
13.89
11.59


O
nBu
N
Me
S

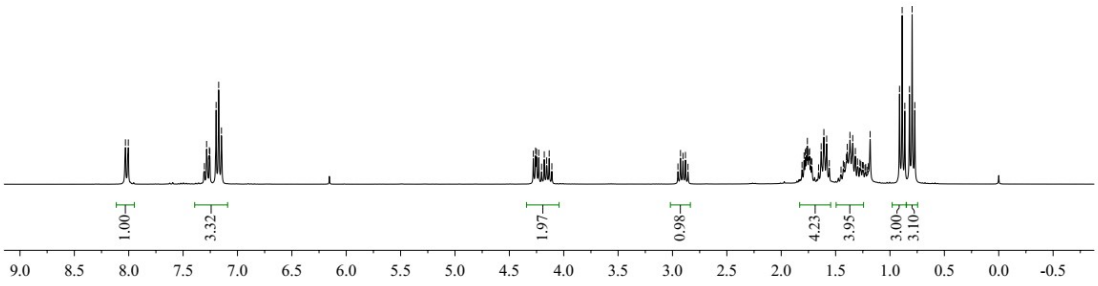
3j

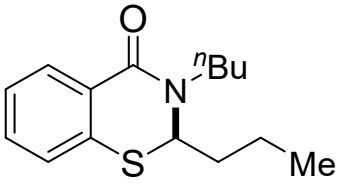

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



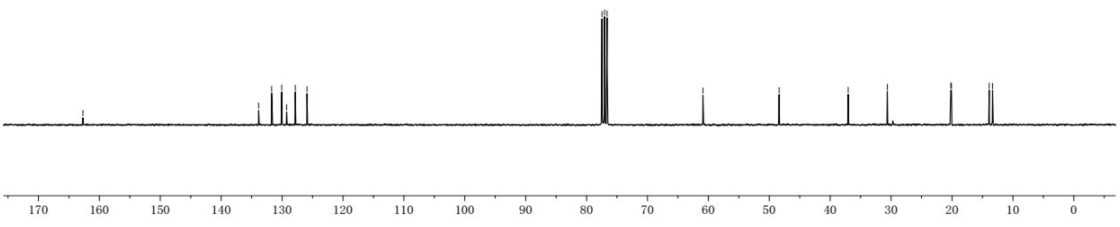


3k

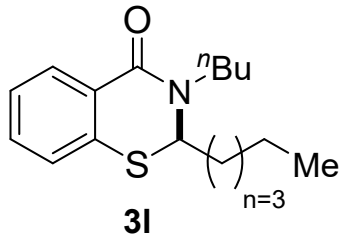




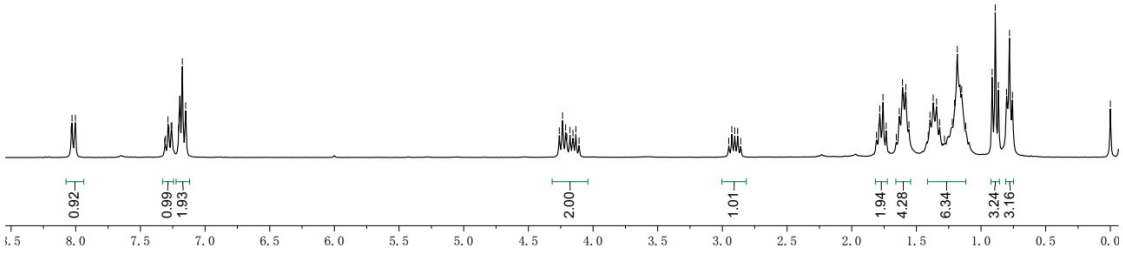
3k



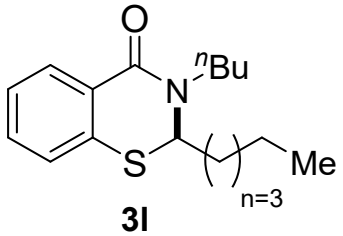

8.03
8.03
8.00
7.31
7.31
7.29
7.28
7.26
7.26
7.21
7.20
7.18
7.15
4.26
4.24
4.21
4.20
4.18
4.16
4.13
4.11
2.95
2.93
2.90
2.88
2.86
1.81
1.79
1.78
1.76
1.73
1.66
1.63
1.61
1.60
1.58
1.56
1.41
1.39
1.37
1.34
1.32
1.28
1.22
1.21
1.18
1.15
1.12
0.91
0.89
0.87
0.80
0.78
0.76
0.00


O
nBu
N
S
Me
n=3

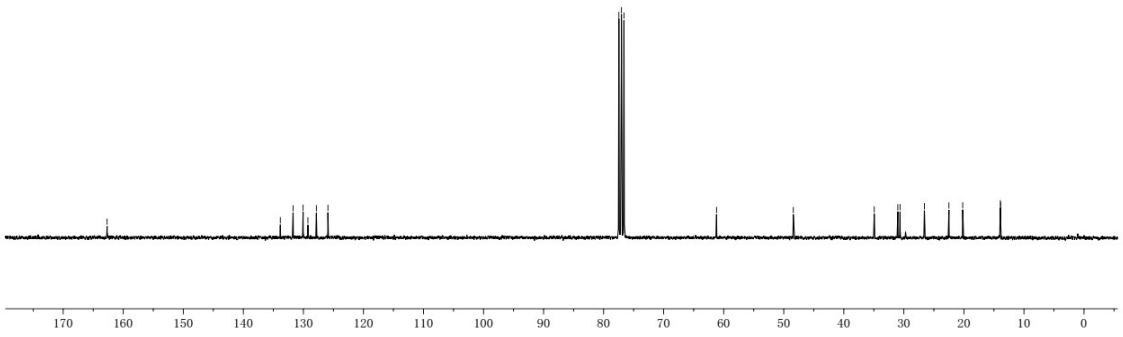
3l

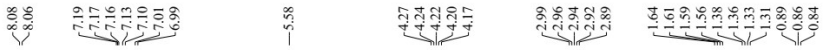

0.92
0.99
1.93
2.00
1.01
1.94
4.28
6.34
3.24
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

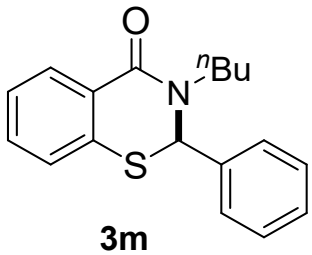

162.69
133.84
131.72
130.05
129.25
127.84
125.91
77.46
77.04
76.61
61.19
48.41
34.93
31.00
30.63
26.58
22.49
20.20
13.92
13.89


O
nBu
N
S
Me
n=3

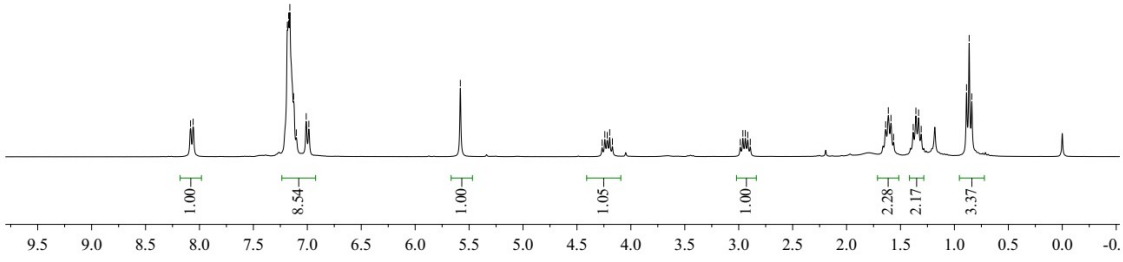
3l

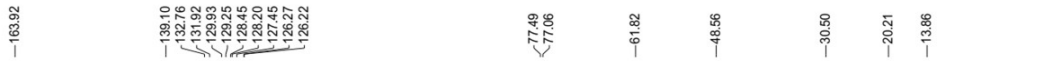

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

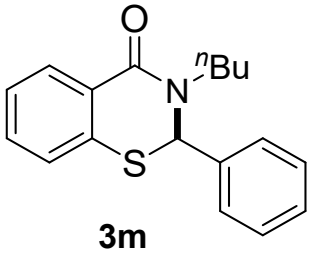

8.08
8.06
7.19
7.17
7.16
7.13
7.10
7.01
6.99
5.58
4.27
4.24
4.22
4.20
4.17
2.99
2.96
2.94
2.92
2.89
1.64
1.61
1.59
1.56
1.38
1.36
1.33
1.31
0.89
0.86
0.84


O
nBu
N
S

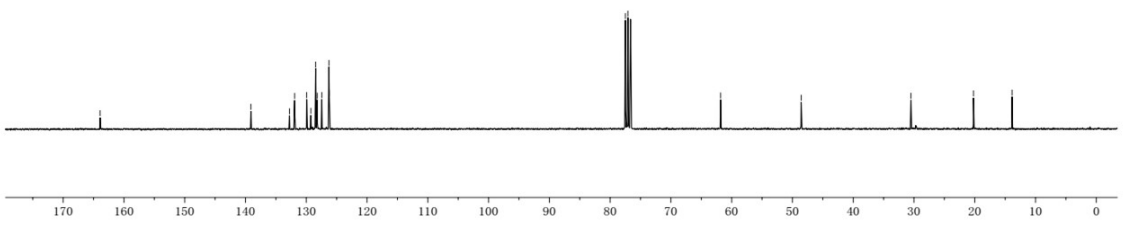
3m


1.00
8.54
1.00
1.05
1.00
2.28
2.17
3.37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

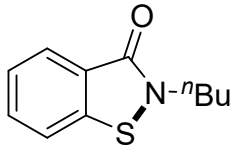

163.92
139.10
132.76
131.92
129.93
129.25
128.45
128.20
127.45
126.27
126.22
77.49
77.06
61.82
48.56
30.50
20.21
13.86


O
nBu
N
S

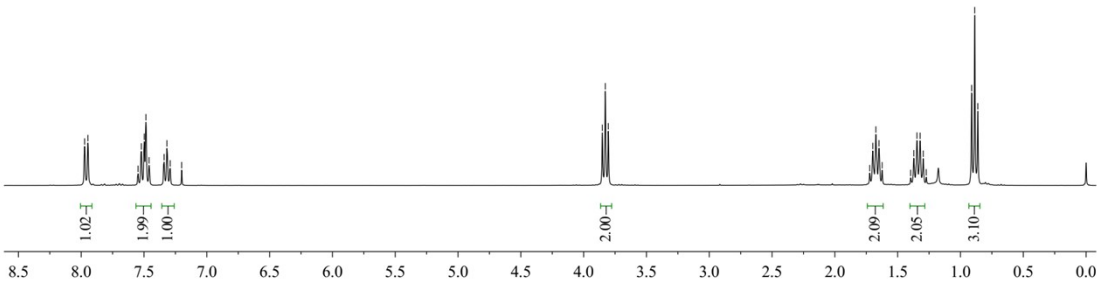
3m


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

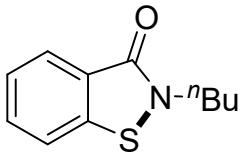

7.97
7.95
7.55
7.52
7.50
7.48
7.46
7.34
7.32
7.29
7.20
3.85
3.83
3.80
1.72
1.70
1.67
1.65
1.62
1.40
1.37
1.35
1.32
1.30
1.27
0.91
0.89
0.86


O
N-nBu
S

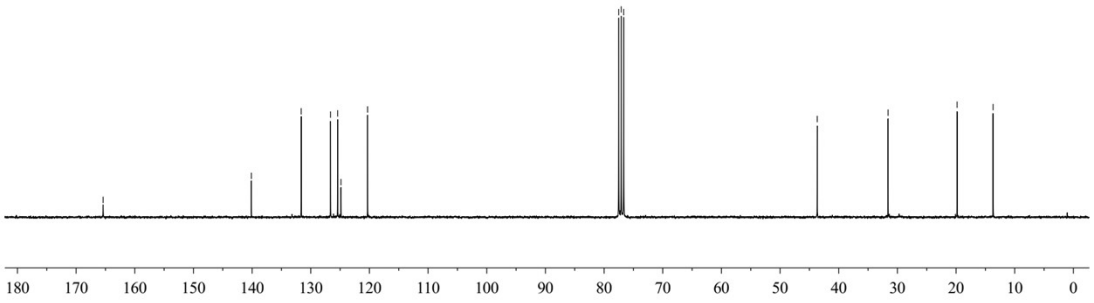
4a

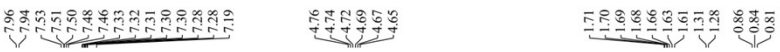

1.02
1.99
1.00
2.00
2.09
2.05
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

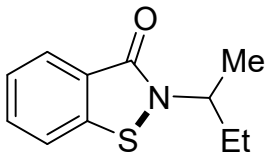

165.40
140.13
131.64
126.63
125.43
124.85
120.31
77.51
77.08
76.66
43.67
31.59
19.82
13.69


O
N-nBu
S

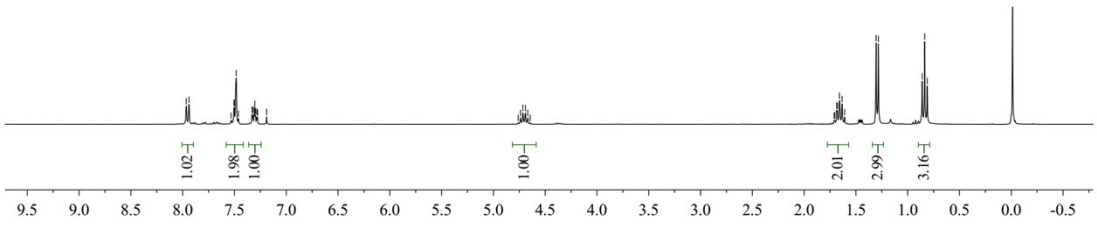
4a

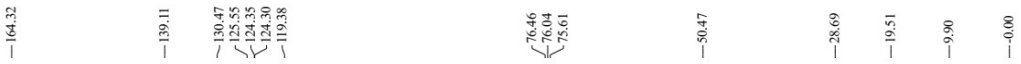

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

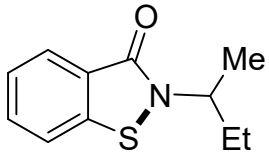

7.96
7.94
7.53
7.51
7.50
7.48
7.46
7.33
7.32
7.31
7.30
7.30
7.28
7.28
7.19
4.76
4.74
4.72
4.69
4.67
4.65
1.71
1.70
1.69
1.68
1.66
1.63
1.61
1.31
1.28
0.86
0.84
0.81


O
Me
N
S
Et

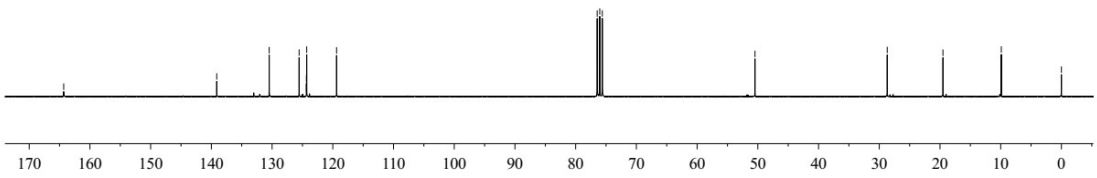
4b


1.02
1.98
1.00
1.00
2.01
2.99
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

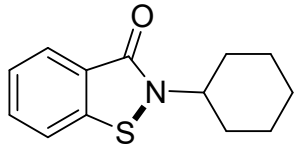

164.32
139.11
130.47
125.55
124.35
124.30
119.38
76.46
76.04
75.61
50.47
28.69
19.51
9.90
-0.00


O
Me
N
S
Et

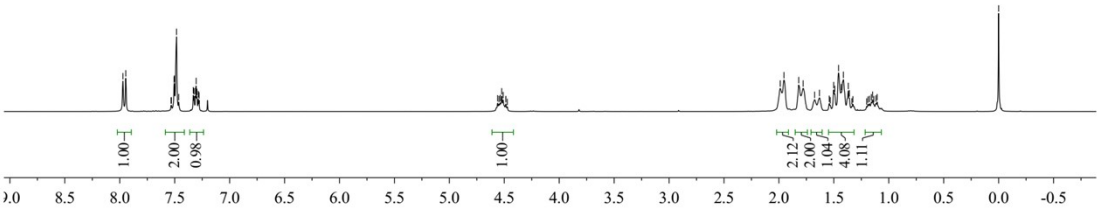
4b


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

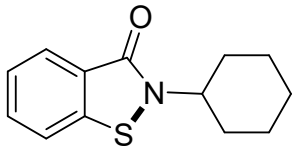

7.97
7.95
7.53
7.53
7.51
7.50
7.48
7.46
7.33
7.32
7.31
7.30
7.30
7.29
7.28
4.56
4.55
4.54
4.52
4.51
4.49
4.47
1.99
1.95
1.82
1.78
1.67
1.63
1.54
1.53
1.50
1.49
1.46
1.43
1.41
1.37
1.36
1.34
1.33
1.20
1.19
1.18
1.16
1.15
1.14
1.12
1.11
0.00



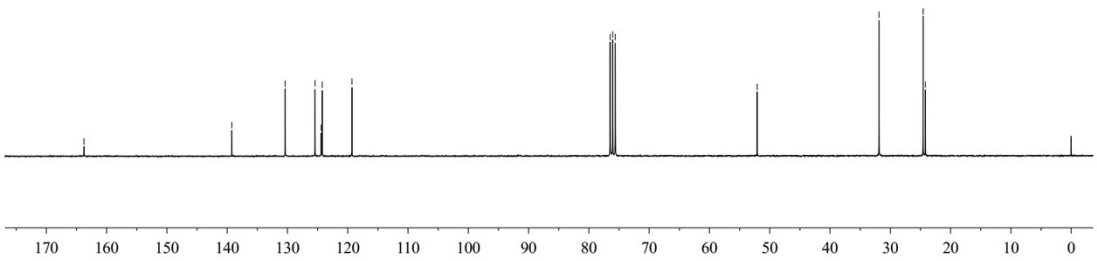
4c

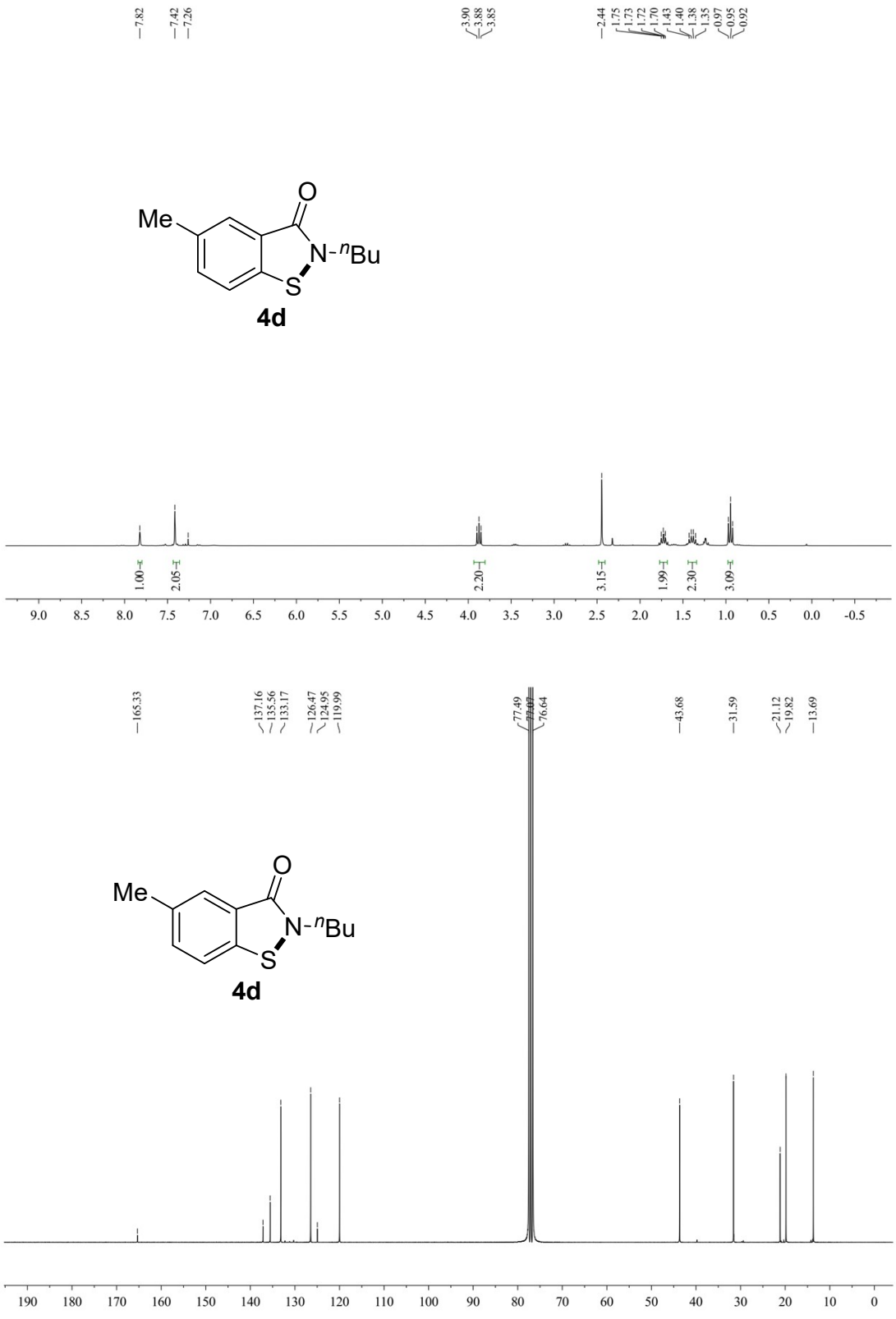

1.00
2.00
0.98
1.00
2.12
2.00
1.04
4.08
1.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


163.75
139.22
130.37
125.43
124.41
124.24
119.30
76.47
76.05
75.62
52.10
31.87
24.56
24.19

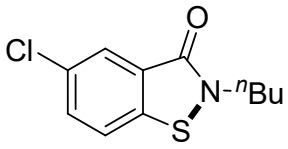


4c

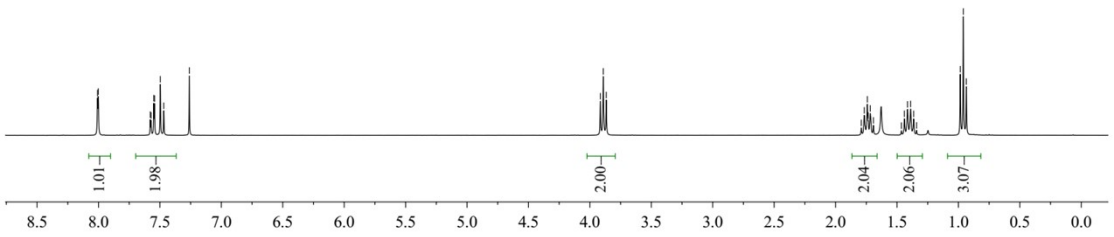

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.82
7.42
7.26
3.90
3.88
3.85
2.44
1.75
1.73
1.72
1.70
1.43
1.40
1.38
1.35
0.97
0.95
0.92
O
Me
N-nBu
S
4d
1.00
2.05
2.20
3.15
1.99
2.30
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
165.33
137.16
135.56
133.17
126.47
124.95
119.99
77.49
77.07
76.64
43.68
31.59
21.12
19.82
13.69
O
Me
N-nBu
S
4d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

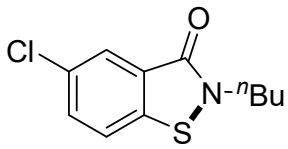

8.01
8.00
7.58
7.57
7.55
7.54
7.50
7.47
7.26
3.91
3.89
3.87
1.79
1.77
1.74
1.73
1.72
1.69
1.46
1.44
1.41
1.39
1.36
1.34
0.98
0.96
0.94


O
Cl
N-nBu
S

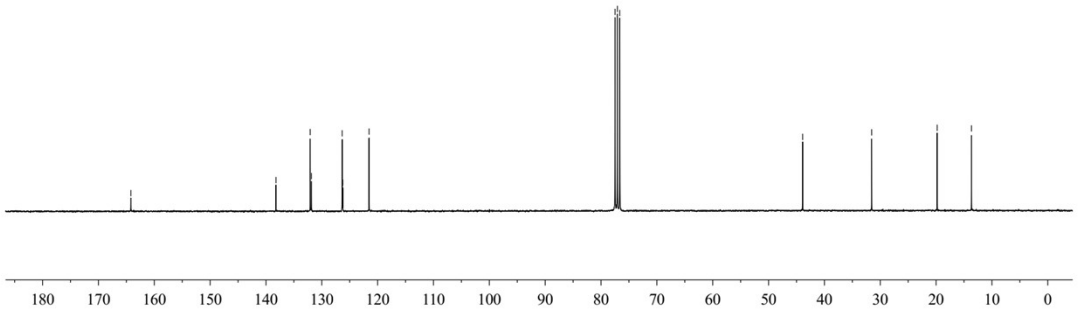
4e

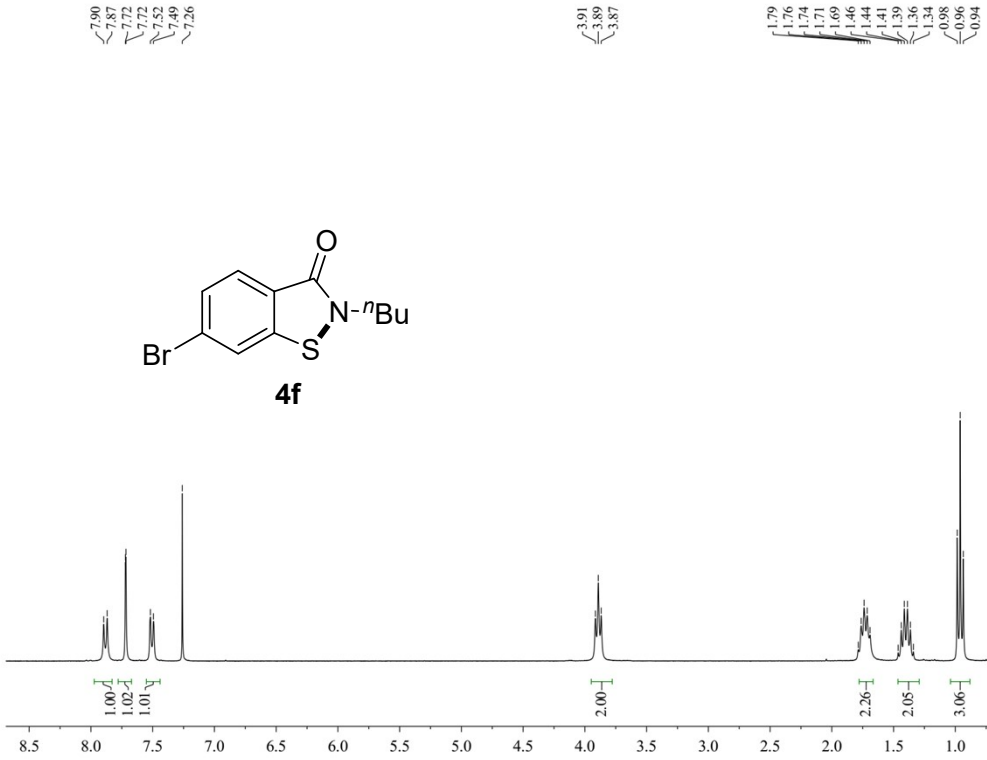

1.01
1.98
2.00
2.04
2.06
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

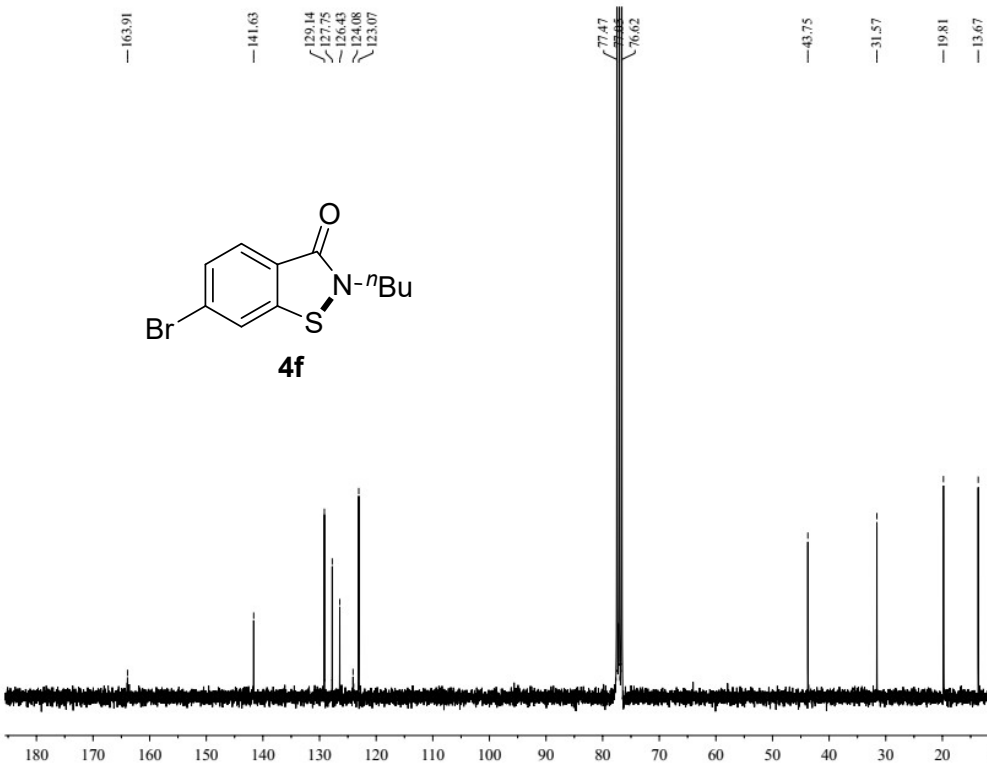

164.19
138.21
132.08
131.85
126.36
126.25
121.54
77.49
77.07
76.64
43.90
31.54
19.81
13.66


O
Cl
N-nBu
S

4e


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

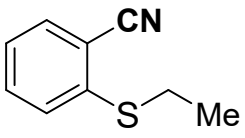

7.90
7.87
7.72
7.72
7.72
7.52
7.49
7.26
3.91
3.89
3.87
1.79
1.76
1.74
1.71
1.69
1.46
1.44
1.41
1.39
1.36
1.34
0.98
0.96
0.94
O
N-nBu
S
Br
4f
1.00
1.02
1.01
2.00
2.26
2.05
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


163.91
141.63
129.14
127.75
126.43
124.08
123.07
77.47
77.05
76.62
43.75
31.57
19.81
13.67
O
N-nBu
S
Br
4f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

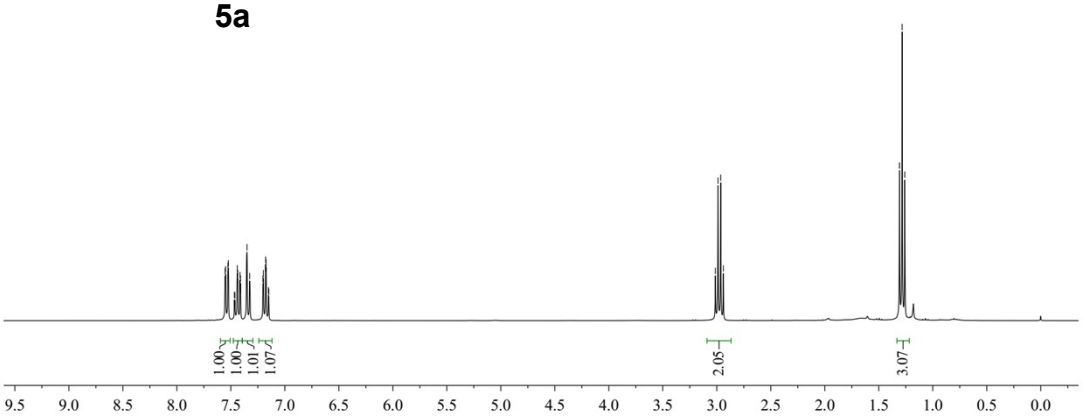

7.55
7.55
7.53
7.52
7.47
7.46
7.44
7.44
7.44
7.42
7.41
7.35
7.33
7.20
7.20
7.18
7.17
7.15
7.15


3.01
2.99
2.96
2.94

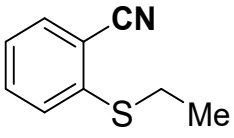

1.31
1.28
1.26


CN
S
Me

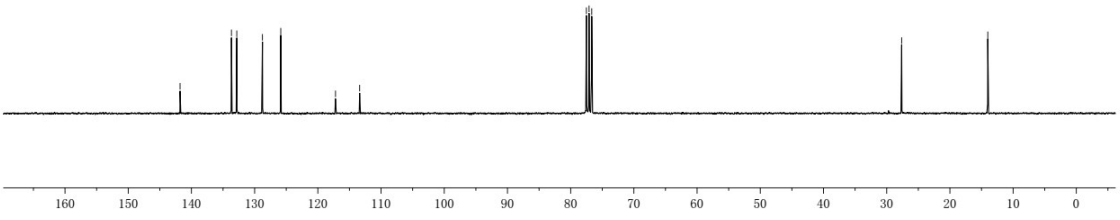
5a


1.00
1.00
1.01
1.07
2.05
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


141.80
133.67
132.83
128.77
125.87
117.21
113.39
77.51
77.09
76.66
27.63
14.01

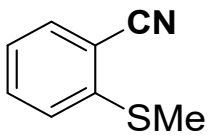

CN
S
Me

5a

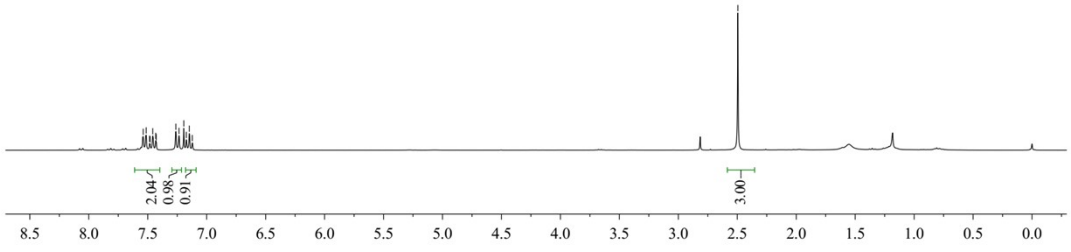

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.54
7.51
7.48
7.48
7.46
7.43
7.43
7.26
7.23
7.19
7.17
7.15
7.12

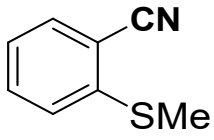
2.49


CN
SMe

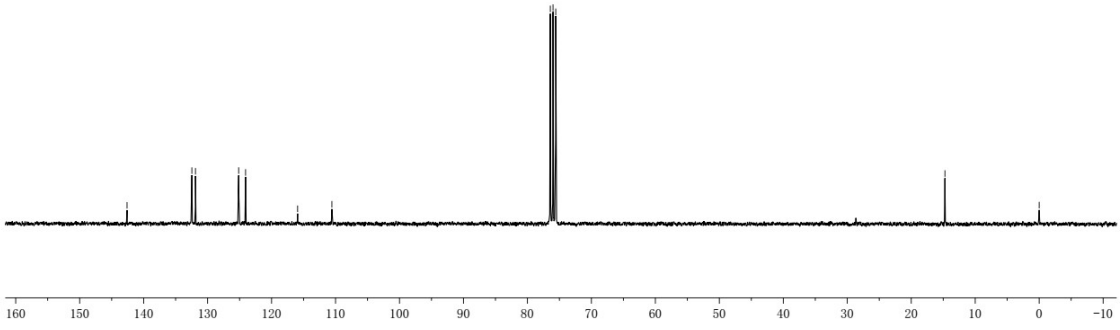
5b

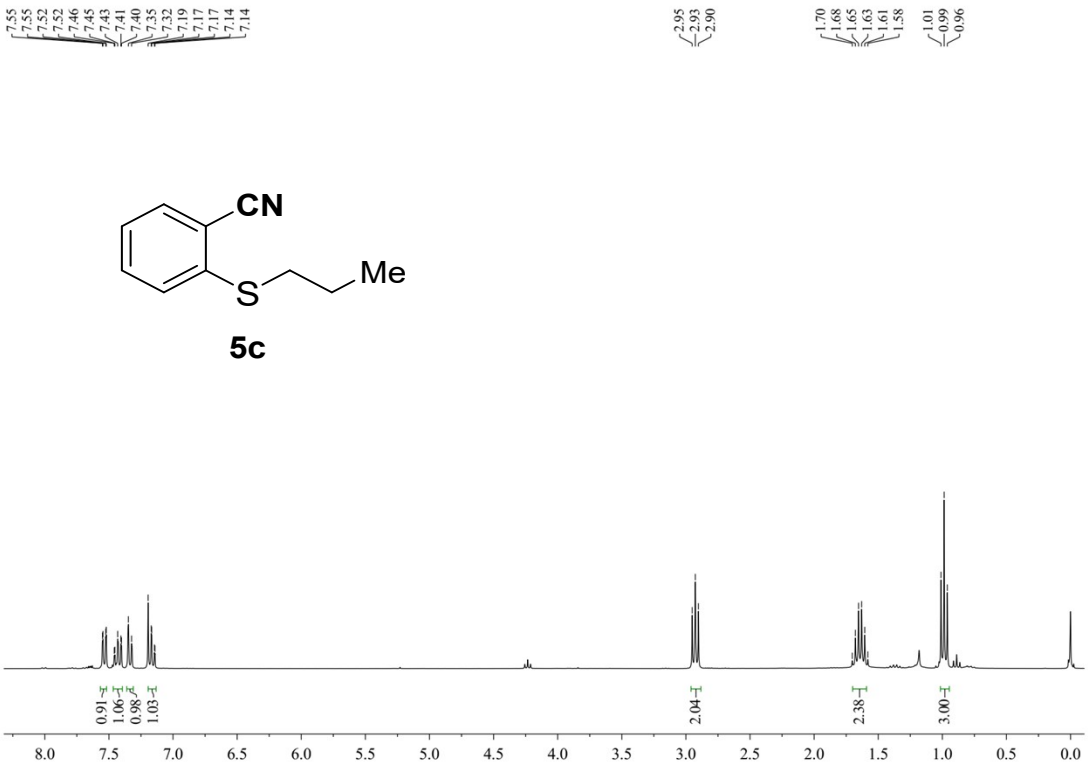

2.04
0.98
0.91
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

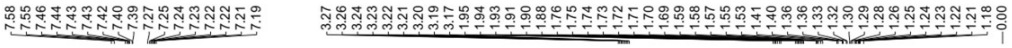

142.60
132.46
131.90
125.14
124.07
115.93
110.57
76.42
76.00
75.58
14.73
0.00

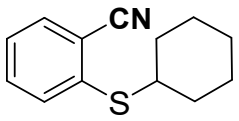

CN
SMe

5b

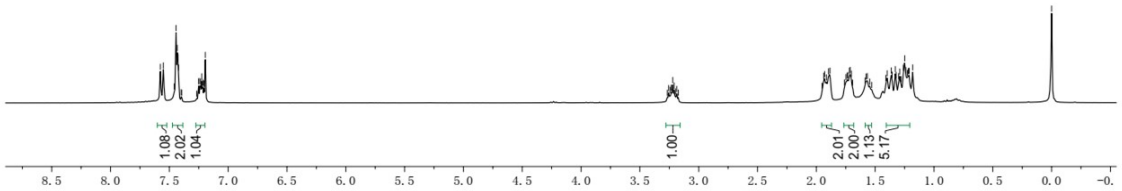

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

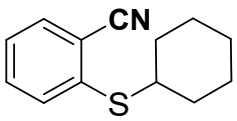

7.55
7.55
7.52
7.52
7.46
7.45
7.43
7.41
7.40
7.35
7.32
7.19
7.17
7.17
7.14
7.14
2.95
2.93
2.90
1.70
1.68
1.65
1.63
1.61
1.58
1.01
0.99
0.96
CN
S
Me
5c
0.91
1.06
0.98
1.03
2.04
2.38
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
142.15
133.67
132.78
128.78
125.78
117.23
113.43
77.48
77.06
76.64
35.53
22.26
13.40
CN
S
Me
5c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



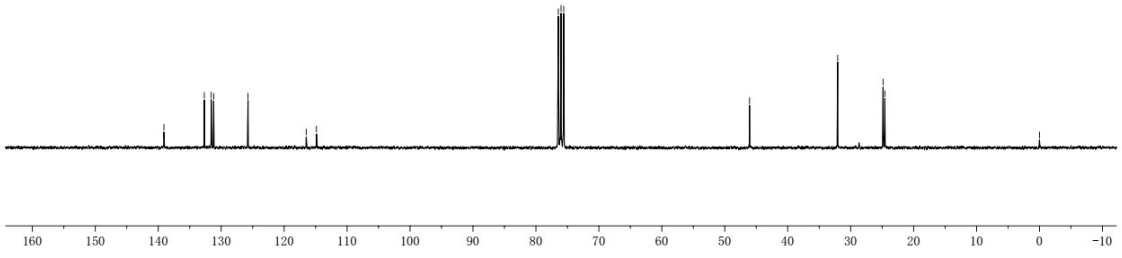


5d

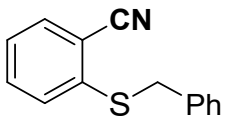




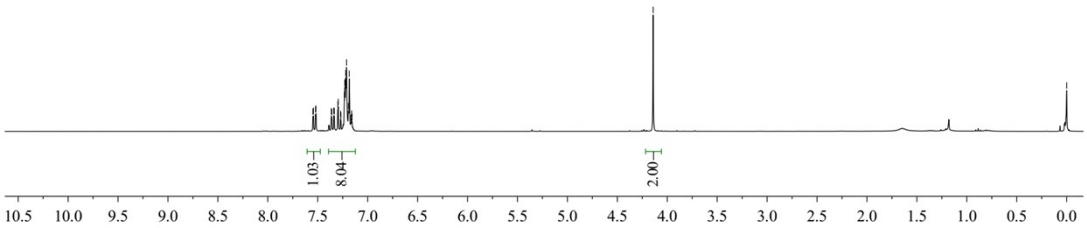
5d

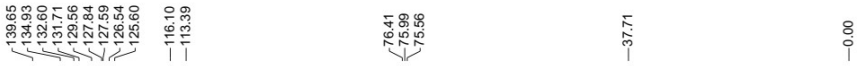


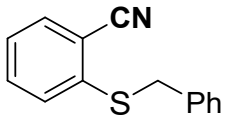

7.55
7.54
7.52
7.52
7.52
7.36
7.36
7.34
7.33
7.30
7.30
7.27
7.27
7.23
7.23
7.23
7.22
7.21
7.19
7.18
7.17
7.16
7.16
4.14
0.00


CN
S
Ph

5e

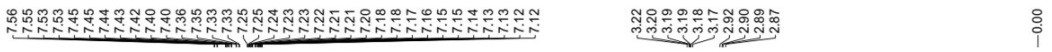

1.03
8.04
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

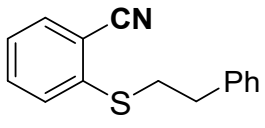

139.65
134.93
132.60
131.71
129.56
127.84
127.59
126.54
125.60
116.10
113.39
76.41
75.99
75.56
37.71
0.00


CN
S
Ph

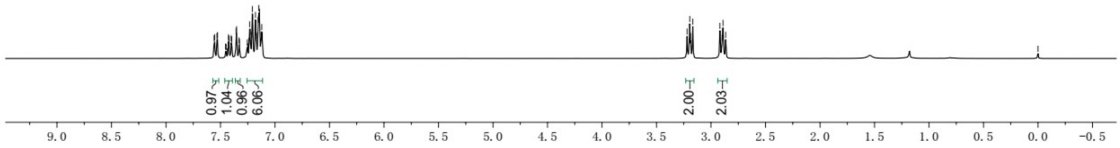
5e

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

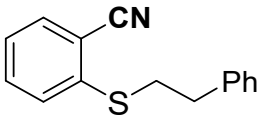

7.56
7.55
7.53
7.53
7.45
7.45
7.44
7.43
7.42
7.40
7.40
7.36
7.35
7.33
7.33
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.18
7.18
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.12
7.12
3.22
3.20
3.19
3.19
3.18
3.17
2.92
2.90
2.89
2.87
0.00


CN
S
Ph

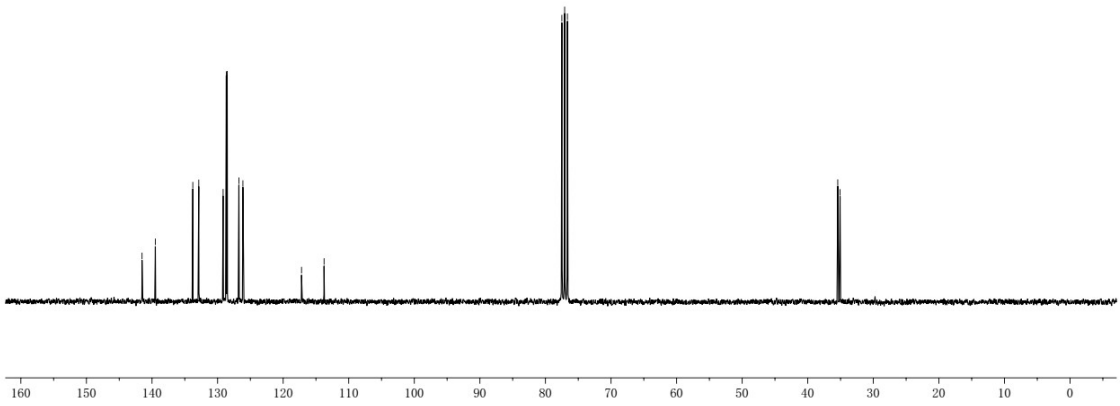
5f


0.97
1.04
0.96
6.06
2.00
2.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

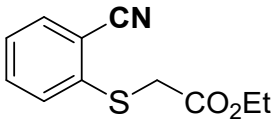

141.52
139.49
133.78
132.87
129.16
128.67
128.53
126.75
126.14
117.20
113.76
77.50
77.08
76.65
35.43
35.07


CN
S
Ph

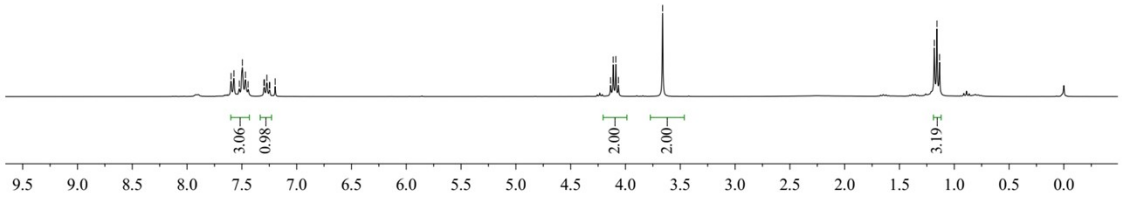
5f


160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

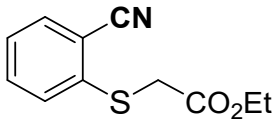

7.60
7.57
7.52
7.50
7.47
7.44
7.30
7.29
7.27
7.25
7.25
7.20
4.14
4.11
4.09
4.06
3.66
1.18
1.16
1.13


CN
S
CO2Et

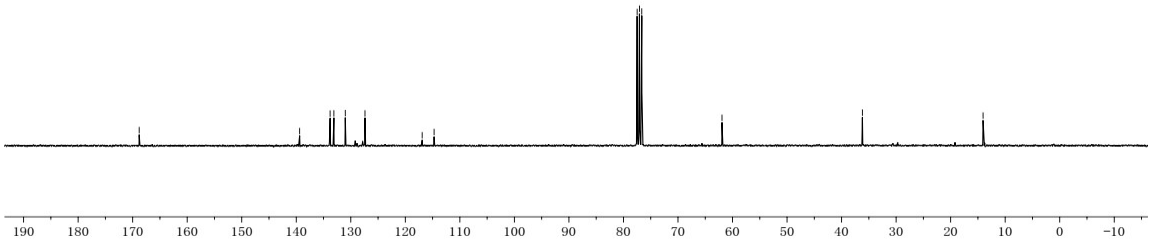
5g


3.06
0.98
2.00
2.00
3.19
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

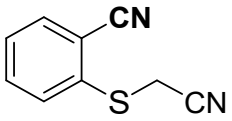

168.80
139.38
133.79
133.10
131.01
127.40
116.91
114.72
77.49
77.06
76.64
61.93
36.18
14.05


CN
S
CO2Et

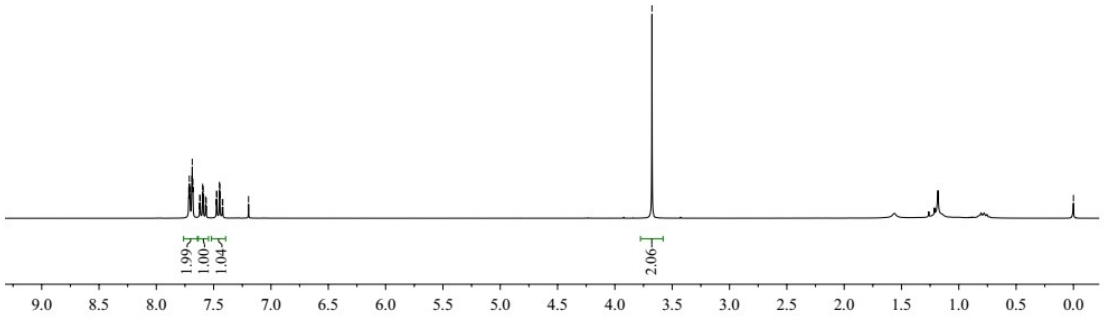
5g


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

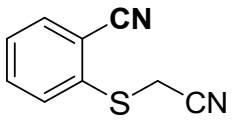

7.72
7.71
7.71
7.69
7.69
7.68
7.62
7.62
7.60
7.59
7.57
7.57
7.48
7.47
7.45
7.45
7.42
7.42
7.20
3.68
0.00


CN
S
CN

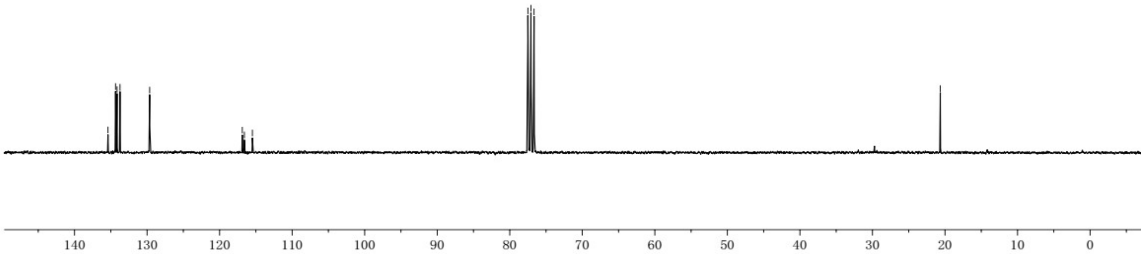
5h


1.99
1.00
1.04
2.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

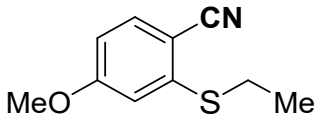

135.39
134.34
134.13
133.73
129.64
116.87
116.58
115.48
77.50
77.08
76.65
20.65


CN
S
CN

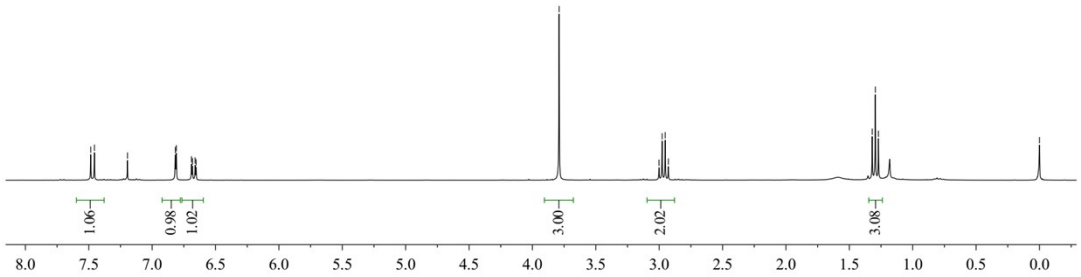
5h


140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

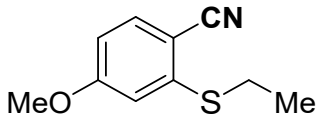

7.48
7.46
7.19
6.82
6.81
6.69
6.68
6.66
6.65
3.79
3.00
2.98
2.95
2.93
1.32
1.29
1.27
0.00


CN
MeO
S
Me

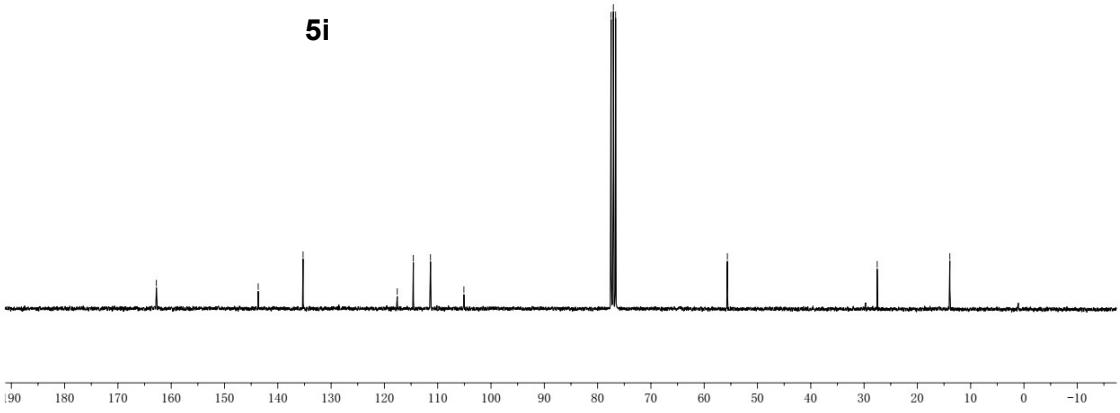
5i

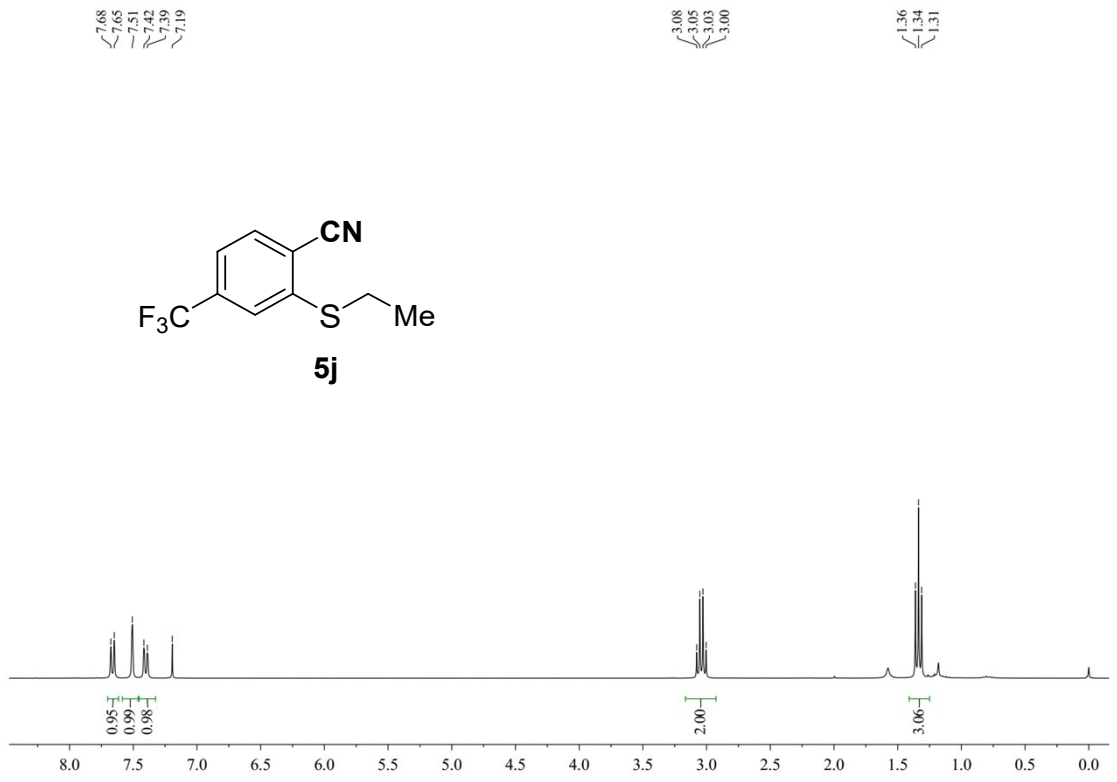

1.06
0.98
1.02
3.00
2.02
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

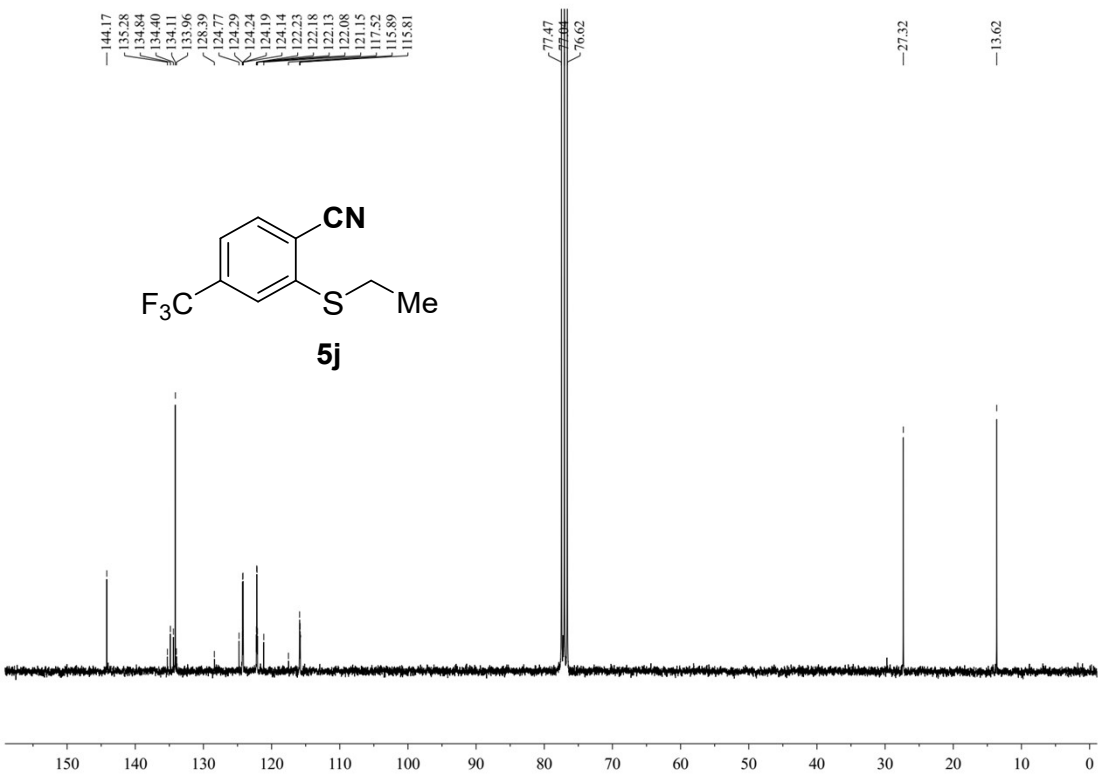

162.78
143.68
135.26
117.59
114.57
111.35
105.08
77.47
77.05
76.62
55.65
27.54
13.91

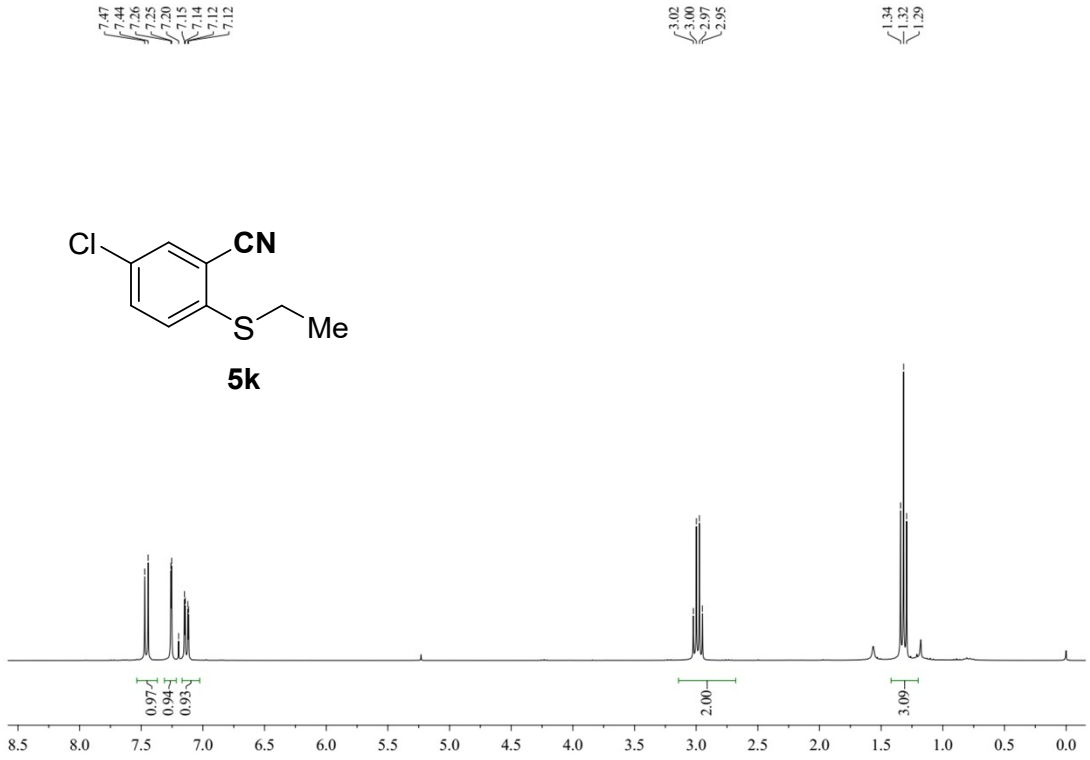

CN
MeO
S
Me

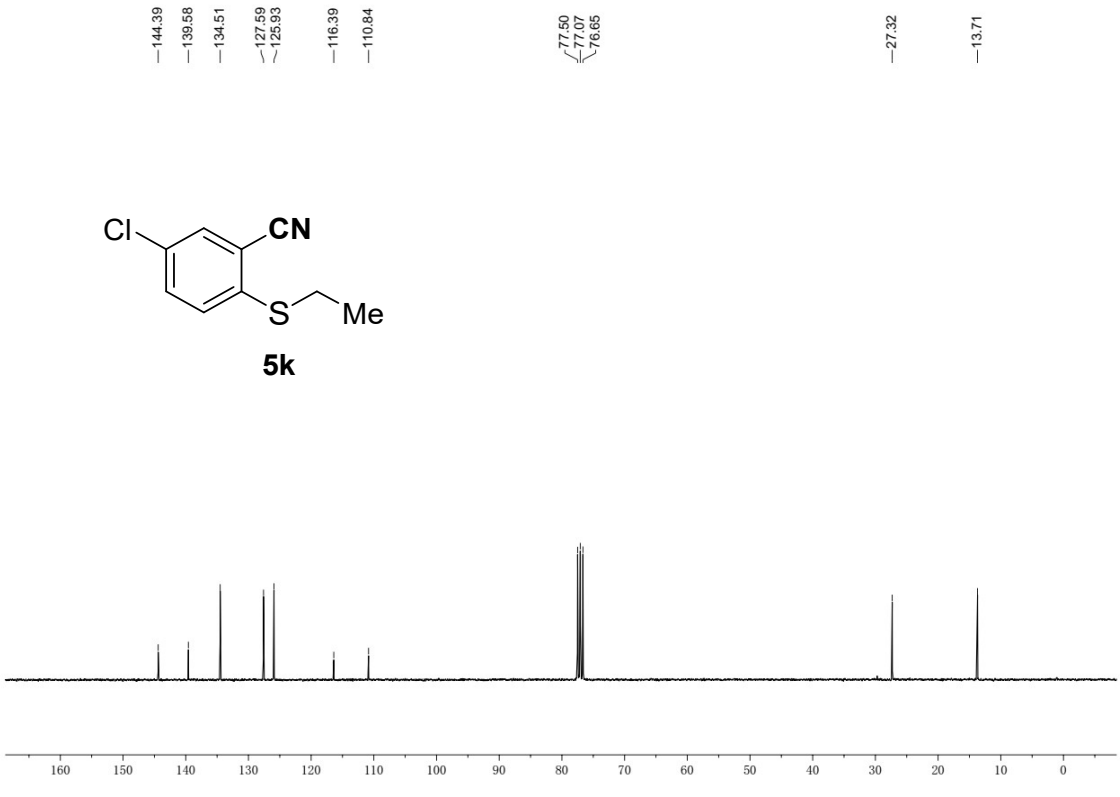
5i


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

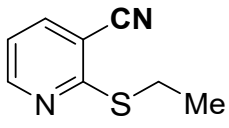

7.68
7.65
7.51
7.42
7.39
7.19
3.08
3.05
3.03
3.00
1.36
1.34
1.31
CN
F3C
S
Me
5j
0.95
0.99
0.98
2.00
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


144.17
135.28
134.84
134.40
134.11
133.96
128.39
124.77
124.29
124.24
124.19
124.14
122.23
122.18
122.13
122.08
121.15
117.52
115.89
115.81
77.47
77.04
76.62
27.32
13.62
CN
F3C
S
Me
5j
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

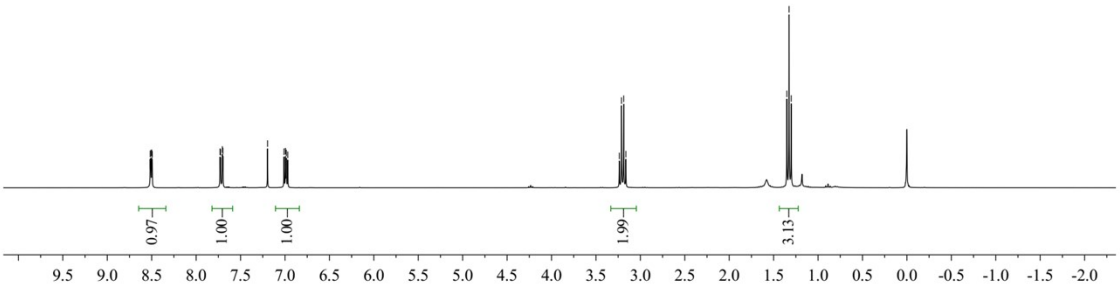

7.47
7.44
7.26
7.25
7.20
7.15
7.14
7.12
7.12
3.02
3.00
2.97
2.95
1.34
1.32
1.29
Cl
CN
S
Me
5k
0.97
0.94
0.93
2.00
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

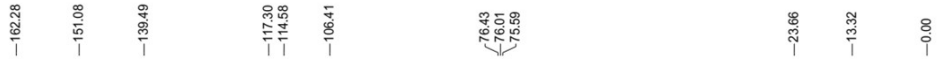

144.39
139.58
134.51
127.59
125.93
116.39
110.84
77.50
77.07
76.65
27.32
13.71
Cl
CN
S
Me
5k
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

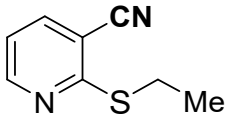

8.52
8.51
8.50
8.49
7.73
7.70
7.28
7.01
6.99
6.98
6.97
3.24
3.21
3.19
3.16
1.35
1.33
1.30


CN
N
S
Me

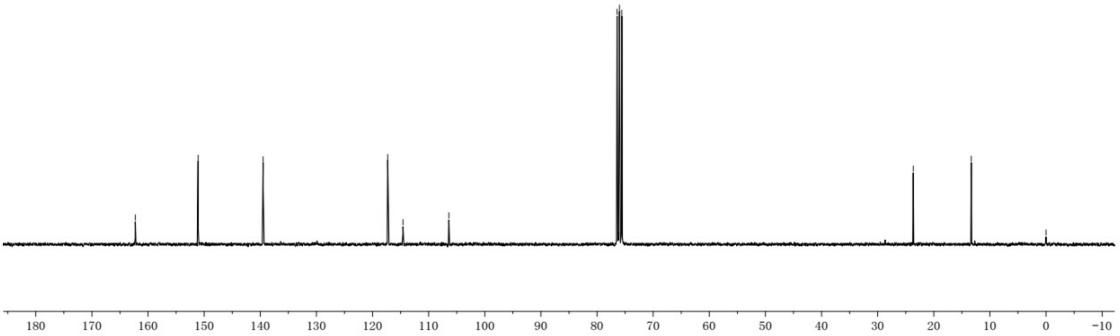
5l


0.97
1.00
1.00
1.99
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0


162.28
151.08
139.49
117.30
114.58
106.41
76.43
76.01
75.59
23.66
13.32
0.00


CN
N
S
Me

5l


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10