

Supporting information

NH₄I-promoted oxidative formation of benzothiazoles and thiazoles from arylacetic acids and phenylalanines with elemental sulfur

Yujia Xia,^a Huawen Huang,^{*,a} Wei Hu, Guo-Jun Deng,^{*,a,b}

^a Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China

E-mail: hwhuang@xtu.edu.cn; gjdeng@xtu.edu.cn

^b Beijing National Laboratory for Molecular Sciences, Chinese Academy of Sciences (CAS), Beijing 100190, China.

Table of Contents

General information	S2
General procedure for the thiophene formation	S2
Characterization data of products	S3-S12
References	S13
Copies of ¹H and ¹³C NMR spectra of products	S14-S51

General information

All reactions were carried out under an atmosphere of air. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400, 100 and 376 MHz, respectively) instrument internally referenced to tetramethyl silane (TMS) or chloroform signals. Mass spectra were measured on Agilent 5977 GC-MS instrument (EI). High-resolution mass spectra (HRMS) were performed on Agilent 6230 TOF LC/MS. The structures of known compounds were further corroborated by comparing their ^1H NMR, ^{13}C NMR data and MS data with those of literature. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Starting materials were obtained from commercial suppliers and used without further purification.

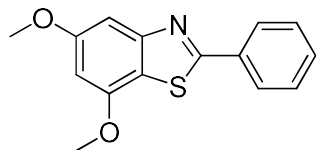
General procedure for the thiazole formation:

Benzothiazoles: A 10 mL reaction vessel was charged with NH_4I (0.04 mmol, 0.2 equiv), K_3PO_4 (0.2 mmol, 1.0 equiv), arylamine (**1**, 0.2 mmol, 1.0 equiv), aryl acetic acid (**2**, 0.3 mmol, 1.5 equiv), sulfur (1.0 mmol, 5.0 equiv). DMSO (0.25 mL) and chlorobenzene (0.75 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 120 °C for 16 h. The mixture was then allowed to cool down to room temperature and flushed through a short column of silica gel with ethyl acetate. After rotary evaporation, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) to give **3**.

2,5-Disubstituted thiazoles: A 10 mL reaction vessel was charged with NH_4I (0.04 mmol, 0.2 equiv), K_3PO_4 (0.1 mmol, 0.5 equiv), phenylalanine (**4**, 0.4 mmol, 2.0 equiv), sulfur (1.0 mmol, 5.0 equiv). DMSO (1.0 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 120 °C for 16 h. The mixture was then allowed to cool down to room temperature and flushed through a short column of silica gel with ethyl acetate. After rotary evaporation, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc = 20:1) to give **5**.

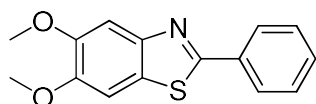
Characterization data of products

5,7-dimethoxy-2-phenylbenzo[d]thiazole (3a)^[1]



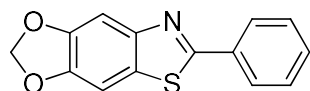
White solid, 91% yield. MP = 109 – 112 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.01 (m, 2H), 7.50 – 7.43 (m, 3H), 7.18 (d, *J* = 1.9 Hz, 1H), 6.48 (d, *J* = 1.9 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.2, 160.3, 155.7, 154.2, 133.6, 130.7, 128.9, 127.2, 116.1, 97.4, 96.8, 77.3, 77.0, 76.7, 55.8, 55.7.

5,6-dimethoxy-2-phenylbenzo[d]thiazole (3b)^[1]



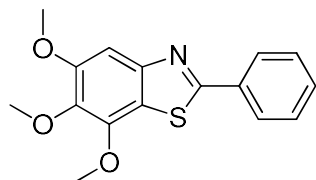
White solid, 83% yield. MP = 142 – 144 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.07 – 7.94 (m, 2H), 7.54 (s, 1H), 7.51 – 7.41 (m, 3H), 7.27 (d, *J* = 2.1 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.1, 149.3, 148.4, 148.4, 133.7, 130.3, 128.9, 126.9, 126.9, 104.5, 102.3, 56.2, 56.0.

6-phenyl-[1,3]dioxolo[4',5':4,5]benzo[1,2-d]thiazole (3c)



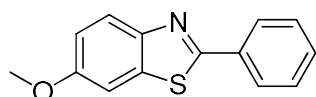
White solid, 88% yield. MP = 150 – 153 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.96 (m, 2H), 7.47 – 7.42 (m, 4H), 7.21 (s, 1H), 6.03 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 149.1, 147.9, 146.8, 133.7, 130.3, 128.9, 128.1, 126.9, 102.6, 101.7, 100.1. HRMS calcd. for: C₁₄H₁₀NO₂S⁺ [M+H]⁺ 256.0427, found 256.0440.

5,6,7-trimethoxy-2-phenylbenzo[d]thiazole (3d)^[1]



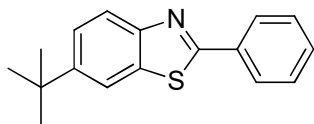
Yellow solid, 85% yield. MP = 67 – 71 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.50 – 7.47 (m, 3H), 7.38 (s, 1H), 4.11 (s, 3H), 3.97 (s, 3H), 3.95 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 153.9, 150.4, 146.7, 139.7, 133.5, 130.7, 128.9, 127.1, 100.7, 61.4, 60.5, 56.2.

6-methoxy-2-phenylbenzo[d]thiazole (3e)^[1]



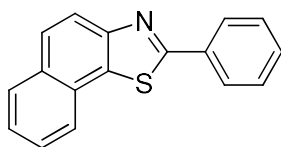
White solid, 78% yield. MP = 108 – 110 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.04 (m, 2H), 7.99 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.46 (m, 3H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.5, 157.7, 148.6, 136.4, 133.7, 130.5, 128.9, 127.2, 123.6, 115.6, 104.1, 55.7.

6-(tert-butyl)-2-phenylbenzo[d]thiazole (3f)^[1]



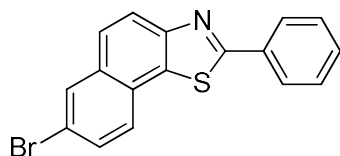
White solid, 67% yield. MP = 111 – 114 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.06 (m, 2H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 1.8 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.55 – 7.42 (m, 3H), 1.41 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 167.4, 152.1, 148.7, 135.1, 133.8, 130.7, 128.9, 127.4, 124.5, 122.5, 117.7, 35.0, 31.5.

2-phenylnaphtho[2,1-d]thiazole (3g)^[1]



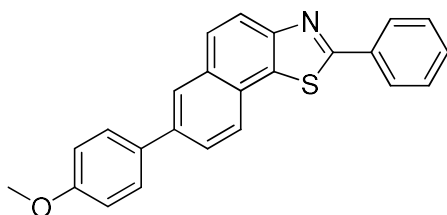
White solid, 97% yield. MP = 107 – 110 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.02 (m, 3H), 7.99 – 7.87 (m, 2H), 7.83 (t, *J* = 8.6 Hz, 1H), 7.60 – 7.41 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 152.1, 133.6, 132.1, 130.9, 130.6, 129.0, 128.9, 128.0, 127.3, 127.2, 126.9, 125.9, 125.1, 121.6.

7-bromo-2-phenylnaphtho[2,1-d]thiazole (3h)^[2]



White solid, 73% yield. MP = 179 – 182 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.03 (m, 4H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.47 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 152.4, 133.4, 132.2, 131.0, 130.9, 130.2, 129.1, 127.3, 126.7, 126.5, 126.4, 122.8, 119.7.

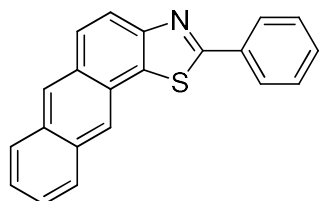
7-(4-methoxyphenyl)-2-phenylnaphtho[2,1-d]thiazole (3i)



White solid, 78% yield. MP = 175 – 178 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16 – 8.04 (m, 4H),

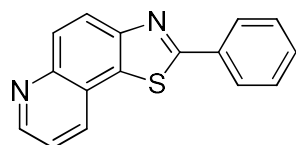
7.99 (d, $J = 8.4$ Hz, 1H), 7.87 (d, $J = 8.8$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 5.1$ Hz, 3H), 7.01 (d, $J = 8.4$ Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 159.3, 152.1, 138.3, 133.6, 133.0, 132.1, 131.4, 130.7, 129.0, 128.3, 127.6, 127.3, 126.7, 126.3, 126.0, 125.6, 122.0, 114.3, 55.3. HRMS calcd. for: $\text{C}_{24}\text{H}_{18}\text{NOS}^+$ $[\text{M}+\text{Na}]^+$ 368.1104, found 368.1120.

2-phenylanthra[2,1-d]thiazole (3j)^[1]



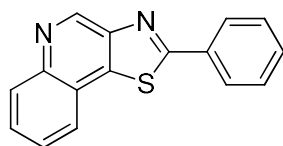
White solid, 74% yield. MP = 181 – 183 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.55 (s, 1H), 8.51 (s, 1H), 8.19 – 8.13 (m, 2H), 8.08 – 7.97 (m, 4H), 7.57 – 7.49 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 151.9, 133.7, 132.0, 131.8, 131.5, 130.6, 129.5, 129.1, 128.3, 128.0, 127.8, 127.8, 127.2, 126.4, 126.3, 125.7, 123.2, 121.8.

2-phenylthiazolo[5,4-f]quinoline (3k)^[3]



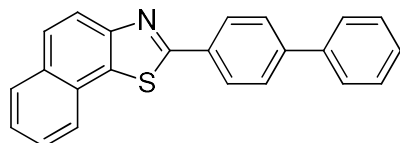
Yellow solid, 46% yield. MP = 155 – 160 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.99 – 8.91 (m, 1H), 8.30 (d, $J = 9.0$ Hz, 2H), 8.16 – 8.08 (m, 3H), 7.54 – 7.46 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 152.2, 149.8, 146.4, 133.3, 133.1, 131.5, 131.0, 129.1, 128.8, 127.3, 125.1, 123.3, 121.5.

2-phenylthiazolo[4,5-c]quinoline (3l)^[3]



Yellow solid, 23% yield. MP = 159 – 162 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.55 (s, 1H), 8.27 (d, $J = 8.4$ Hz, 1H), 8.19 – 8.13 (m, 2H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.77 (t, $J = 7.7$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.56 (t, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 148.7, 146.2, 144.3, 140.3, 133.0, 131.5, 130.6, 129.3, 129.0, 127.6, 125.0, 123.4.

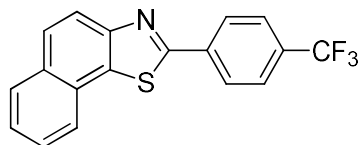
2-([1,1'-biphenyl]-4-yl)naphtho[2,1-d]thiazole (3m)



White solid, 88% yield. MP = 174 – 176 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 7.6$ Hz, 2H), 8.08 (d, $J = 8.9$ Hz, 1H), 7.97 (d, $J = 7.9$ Hz, 1H), 7.91 (d, $J = 7.9$ Hz, 1H), 7.83 (d, $J = 8.8$

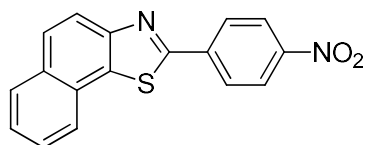
Hz, 1H), 7.68 (d, $J = 7.5$ Hz, 2H), 7.62 (d, $J = 7.4$ Hz, 2H), 7.57 – 7.48 (m, 2H), 7.44 (t, $J = 7.3$ Hz, 2H), 7.41 – 7.34 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 152.2, 143.3, 139.9, 132.5, 132.1, 131.0, 128.9, 128.9, 128.0, 127.9, 127.7, 127.6, 127.4, 127.0, 127.0, 125.9, 125.1, 121.6. HRMS calcd. for: $\text{C}_{23}\text{H}_{16}\text{NS}^+$ $[\text{M}+\text{H}]^+$ 338.0998, found 338.1011.

2-(4-(Trifluoromethyl)phenyl)naphtho[2,1-d]thiazole (3n)^[4]



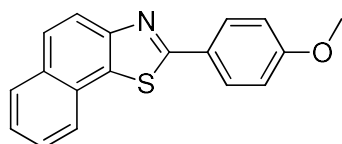
White solid, 55% yield. MP = 169 – 172 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.1$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 1H), 7.98 (d, $J = 7.9$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.72 (d, $J = 8.1$ Hz, 2H), 7.62 – 7.50 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.0, 152.2, 136.7, 132.6, 132.1 (q, $J = 32.5$ Hz), 131.2, 129.0, 127.9, 127.8, 127.4, 127.2, 126.3, 125.9 (q, $J = 3.8$ Hz), 125.1, 123.8 (q, $J = 268.6$ Hz), 121.7.

2-(4-nitrophenyl)naphtho[2,1-d]thiazole (3o)^[3]



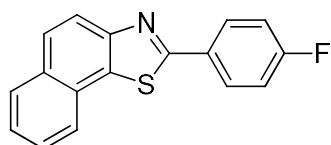
White solid, 44% yield. MP = 151 – 153 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.48 – 8.24 (m, 4H), 8.13 (d, $J = 8.6$ Hz, 1H), 8.08 (d, $J = 7.7$ Hz, 1H), 8.01 (d, $J = 7.3$ Hz, 1H), 7.94 (d, $J = 9.2$ Hz, 1H), 7.69 – 7.55 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 184.4, 152.4, 148.7, 139.2, 135.0, 133.2, 131.4, 129.1, 128.2, 127.9, 127.4, 126.7, 125.3, 124.4, 121.8.

2-(4-methoxyphenyl)naphtho[2,1-d]thiazole (3p)^[1]



White solid, 86% yield. MP = 118 – 121 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 7.98 (m, 3H), 7.99 – 7.88 (m, 2H), 7.82 (d, $J = 8.8$ Hz, 1H), 7.58 – 7.47 (m, 2H), 6.97 (d, $J = 7.8$ Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.0, 161.6, 152.1, 131.6, 130.8, 128.9, 128.8, 128.0, 127.2, 126.9, 126.4, 125.7, 125.0, 121.4, 114.3, 55.4.

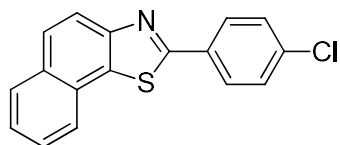
2-(4-fluorophenyl)naphtho[2,1-d]thiazole (3q)^[3]



White solid, 81% yield. MP = 141 – 143 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.09 – 7.99 (m, 3H), 7.91 (t, $J = 9.0$ Hz, 2H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.56 – 7.46 (m, 2H), 7.24 – 7.06 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.7, 164.19 (d, $J = 251.5$ Hz), 152.1, 132.1, 130.9, 129.9 (d, $J = 3.4$

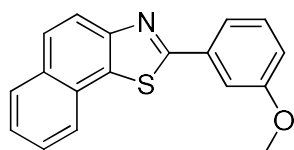
Hz), 129.1 (d, $J = 8.6$ Hz), 128.9, 127.9, 127.4, 127.0, 125.9, 125.0, 121.5, 116.1 (d, $J = 22.0$ Hz).

2-(4-chlorophenyl)naphtho[2,1-d]thiazole (3r)^[1]



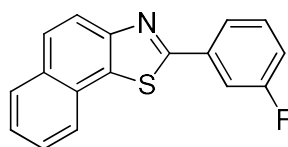
White solid, 50% yield. MP = 148 – 150 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.16 – 7.89 (m, 5H), 7.86 (d, $J = 8.8$ Hz, 1H), 7.60 – 7.52 (m, 2H), 7.45 (d, $J = 7.9$ Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 165.7, 152.1, 136.7, 132.2, 132.1, 131.1, 129.3, 129.0, 128.4, 128.0, 127.6, 127.1, 126.1, 125.1, 121.6.

2-(3-methoxyphenyl)naphtho[2,1-d]thiazole (3s)^[1]



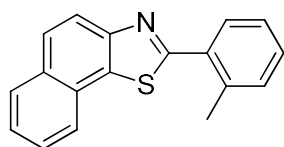
White solid, 75% yield. MP = 126 – 138 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, $J = 8.8$ Hz, 1H), 8.03 (d, $J = 8.1$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.76 – 7.66 (m, 2H), 7.64 – 7.51 (m, 2H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 1H), 3.94 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 160.1, 152.1, 134.9, 132.2, 131.0, 130.1, 129.0, 128.0, 127.4, 127.0, 126.0, 125.2, 121.7, 120.0, 117.1, 111.7, 55.5.

2-(3-fluorophenyl)naphtho[2,1-d]thiazole (3t)^[1]



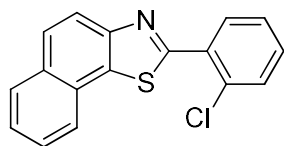
White solid, 79% yield. MP = 121 – 123 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, $J = 8.8$ Hz, 1H), 8.01 – 7.90 (m, 2H), 7.95 – 7.78 (m, 3H), 7.60 – 7.50 (m, 2H), 7.49 – 7.39 (m, 1H), 7.16 (t, $J = 8.2$ Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.4, 163.0 (d, $J = 247.0$ Hz), 152.0, 135.7 (d, $J = 8.0$ Hz), 132.3, 131.1, 130.6 (d, $J = 8.1$ Hz), 129.0, 127.9, 127.6, 127.1, 126.2, 125.1, 122.9 (d, $J = 2.9$ Hz), 121.7, 117.5 (d, $J = 21.7$ Hz), 113.9 (d, $J = 23.5$ Hz).

2-(o-tolyl)naphtho[2,1-d]thiazole (3u)^[1]



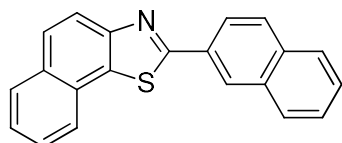
White solid, 45% yield. MP = 88 – 90 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, $J = 8.8$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.90 – 7.82 (m, 2H), 7.62 – 7.52 (m, 2H), 7.40 – 7.30 (m, 3H), 2.71 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.0, 151.8, 137.1, 133.1, 132.7, 131.6, 131.0, 130.5, 129.9, 128.9, 128.0, 127.2, 127.0, 126.1, 126.0, 125.3, 121.8, 21.5.

2-(2-chlorophenyl)naphtho[2,1-d]thiazole (3v)^[1]



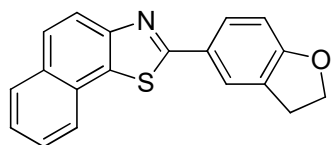
White solid, 77% yield. MP = 145 – 147 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.35 – 8.29 (m, 1H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.43 – 7.35 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.8, 150.6, 133.4, 132.4, 132.1, 131.5, 131.0, 130.9, 130.8, 128.9, 127.9, 127.4, 127.1, 127.0, 126.1, 125.1, 121.7.

2-(naphthalen-2-yl)naphtho[2,1-d]thiazole (3w)^[1]



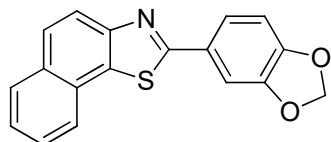
White solid, 82% yield. MP = 153 – 155 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.85 – 7.80 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.43 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.1, 152.2, 134.4, 133.1, 132.2, 131.0, 130.9, 128.9, 128.8, 128.7, 128.0, 127.8, 127.4, 127.2, 127.0, 126.9, 126.8, 125.9, 125.1, 124.2, 121.6.

2-(2,3-dihydrobenzofuran-5-yl)naphtho[2,1-d]thiazole (3x)



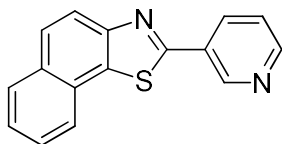
White solid, 51% yield. MP = 198 – 201 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 9.9 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.65 (t, *J* = 8.7 Hz, 2H), 3.28 (t, *J* = 8.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 162.5, 152.2, 131.5, 130.8, 128.9, 128.2, 128.2, 128.1, 127.2, 126.9, 126.6, 125.7, 125.0, 124.0, 121.4, 109.7, 71.9, 29.2. HRMS calcd. for: C₁₉H₁₄NOS⁺ [M+H]⁺ 304.0791, found 304.0780.

2-(benzo[d][1,3]dioxol-5-yl)naphtho[2,1-d]thiazole (3y)^[3]



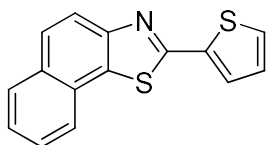
White solid, 85% yield. MP = 167 – 170 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.98 – 7.88 (m, 2H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.62 – 7.47 (m, 4H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.01 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 152.0, 149.8, 148.3, 131.7, 130.9, 128.9, 128.0, 128.0, 127.3, 126.9, 125.7, 125.0, 122.1, 121.5, 108.6, 107.2, 101.6.

2-(pyridin-3-yl)naphtho[2,1-d]thiazole (3z)^[1]



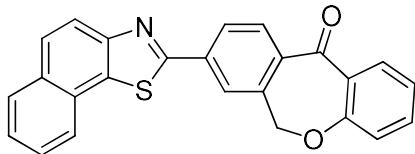
White solid, 84% yield. MP = 130 – 133 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.29 (s, 1H), 8.68 (d, *J* = 4.5 Hz, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 8.9 Hz, 1H), 7.98 – 7.90 (m, 2H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.65 – 7.48 (m, 2H), 7.42 – 7.37 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 152.0, 151.2, 148.2, 134.1, 132.2, 131.1, 129.6, 128.9, 127.8, 127.7, 127.1, 126.2, 125.1, 123.7, 121.5.

2-(thiophen-2-yl)naphtho[2,1-d]thiazole (3aa) ^[1]



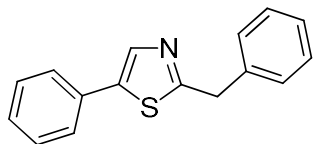
White solid, 48% yield. MP = 141 – 144 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.95 (t, *J* = 7.0 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 3.6 Hz, 1H), 7.60 – 7.47 (m, 3H), 7.14 (t, *J* = 4.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 151.7, 137.4, 131.6, 131.0, 129.0, 128.9, 128.1, 128.1, 127.9, 127.5, 127.0, 126.0, 125.0, 121.4.

9-(naphtho[2,1-d]thiazol-2-yl)dibenzo[b,e]oxepin-11(6H)-one (3ab)



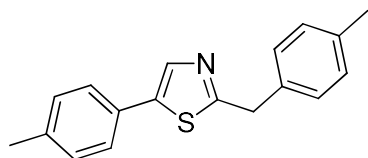
White solid, 53% yield. MP = 219 – 221 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.92 (s, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 8.13 – 8.01 (m, 2H), 7.99 – 7.85 (m, 3H), 7.65 – 7.50 (m, 4H), 7.44 – 7.37 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 5.28 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 190.6, 166.0, 163.0, 152.1, 140.5, 135.0, 133.5, 133.1, 132.2, 131.6, 131.1, 129.6, 129.5, 129.1, 128.1, 128.0, 127.6, 127.2, 126.1, 125.4, 125.2, 121.9, 121.6, 73.7. HRMS calcd. for: C₂₅H₁₅NNaO₂S⁺ [M+Na]⁺ 416.0716, found 416.0733.

2-benzyl-5-phenylthiazole (5a) ^[5]



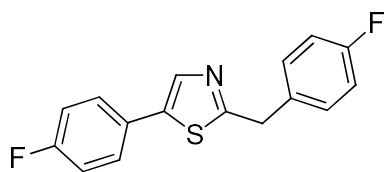
Yellow oil, 58% yield. MP = 151 – 153 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.50 – 7.46 (m, 2H), 7.38 – 7.33 (m, 6H), 7.32 – 7.27 (m, 2H), 4.33 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 139.4, 137.8, 131.4, 129.0, 129.0, 128.8, 128.0, 127.2, 127.1, 126.5, 39.9.

2-(4-methylbenzyl)-5-(p-tolyl)thiazole (5b)



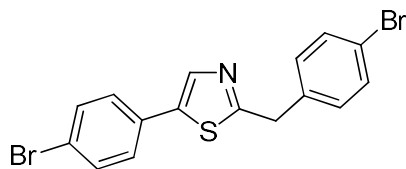
Yellow solid, 49% yield. MP = 169 – 171 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.09 (m, 4H), 4.28 (s, 2H), 2.34 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 169.7, 139.5, 138.0, 137.2, 136.8, 134.8, 129.6, 129.5, 128.9, 128.6, 126.4, 39.5, 21.2, 21.1. HRMS calcd. for: C₁₈H₁₇NNaS⁺ [M+Na]⁺ 302.0974, found 302.1009.

2-(4-fluorobenzyl)-5-(4-fluorophenyl)thiazole (5c)



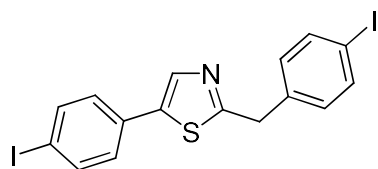
White solid, 44% yield. MP = 160 – 162 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (s, 1H), 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 2H), 7.05 (q, *J* = 8.6 Hz, 4H), 4.29 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 162.5 (d, *J* = 248.2 Hz), 162.0 (d, *J* = 245.7 Hz), 138.4, 137.8, 133.4 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 8.1 Hz), 128.3 (d, *J* = 8.2 Hz), 127.5 (d, *J* = 3.5 Hz), 116.0 (d, *J* = 21.7 Hz), 115.7 (d, *J* = 21.5 Hz), 39.0. HRMS calcd. for: C₁₆H₁₂F₂NS⁺ [M+H]⁺ 288.0653, found 288.0637.

2-(4-bromobenzyl)-5-(4-bromophenyl)thiazole (5d)



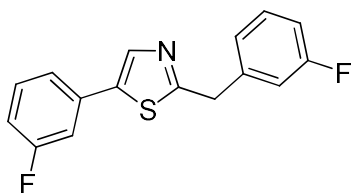
Yellow solid, 57% yield. MP = 85 – 87 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.51 – 7.44 (m, 4H), 7.37 – 7.31 (m, 2H), 7.25 – 7.18 (m, 2H), 4.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 138.4, 138.2, 136.5, 132.1, 131.9, 130.7, 130.2, 127.9, 122.1, 121.3, 39.2. HRMS calcd. for: C₁₆H₁₁Br₂NNaS⁺ [M+Na]⁺ 429.8871, found 429.8898.

2-(4-iodobenzyl)-5-(4-iodophenyl)thiazole (5e)



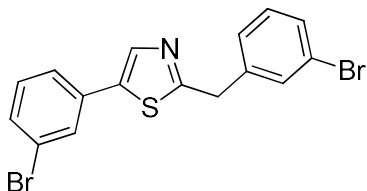
Yellow solid, 56% yield. MP = 153 – 155 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (s, 1H), 7.72 – 7.65 (m, 4H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 4.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.2, 138.6, 138.1, 138.0, 137.1, 131.0, 130.8, 128.7, 128.1, 93.6, 92.8, 39.3. HRMS calcd. for: C₁₆H₁₁I₂NNaS⁺ [M+Na]⁺ 525.8594, found 525.8637.

2-(3-fluorobenzyl)-5-(3-fluorophenyl)thiazole (5f)



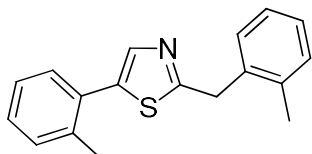
Yellow solid, 51% yield. MP = 135 – 137 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (s, 1H), 7.36 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.29 – 7.10 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 9.6 Hz, 1H), 7.03 – 6.95 (m, 2H), 4.32 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 169.1, 162.8 (d, *J* = 245.4 Hz), 162.7 (d, *J* = 245.0 Hz), 139.8 (d, *J* = 7.4 Hz), 138.6, 138.3 (d, *J* = 2.7 Hz), 133.3 (d, *J* = 8.5 Hz), 130.6 (d, *J* = 8.4 Hz), 130.3 (d, *J* = 8.2 Hz), 124.6 (d, *J* = 2.9 Hz), 122.3 (d, *J* = 2.9 Hz), 115.9 (d, *J* = 21.8 Hz), 115.0 (d, *J* = 21.2 Hz), 114.2 (d, *J* = 20.9 Hz), 113.4 (d, *J* = 23.2 Hz), 39.4. HRMS calcd. for: C₁₆H₁₂F₂NS⁺ [M+H]⁺ 288.0653, found 288.0648.

2-(3-bromobenzyl)-5-(3-bromophenyl)thiazole (5g)



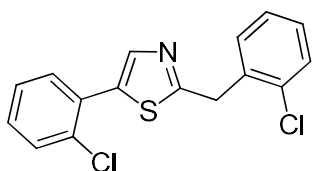
Yellow oil, 52% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.64 (t, *J* = 1.7 Hz, 1H), 7.50 (s, 1H), 7.45 – 7.39 (m, 3H), 7.30 – 7.19 (m, 3H), 4.30 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.1, 139.7, 138.6, 138.0, 133.3, 132.0, 131.1, 130.5, 130.4, 130.4, 129.4, 127.6, 125.2, 123.0, 122.8, 39.3. HRMS calcd. for: C₁₆H₁₁Br₂NNa⁺ [M+Na]⁺ 429.8871, found 429.8844.

2-(2-methylbenzyl)-5-(o-tolyl)thiazole (5h)



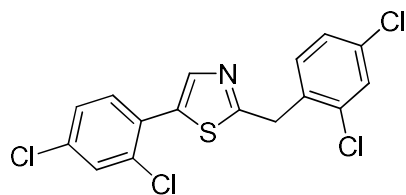
Yellow solid, 55% yield. MP = 133 – 135 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.31 – 7.28 (m, 2H), 7.26 – 7.18 (m, 6H), 4.35 (s, 2H), 2.36 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 140.5, 137.4, 136.7, 136.2, 130.7, 130.7, 130.6, 130.5, 130.0, 128.3, 127.5, 126.4, 126.0, 126.0, 37.6, 21.1, 19.6. HRMS calcd. for: C₁₈H₁₈NS⁺ [M+Na]⁺ 280.1154, found 280.1188.

2-(2-chlorobenzyl)-5-(2-chlorophenyl)thiazole (5i)



Yellow solid, 50% yield. MP = 129 – 131 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.50 – 7.40 (m, 4H), 7.30 – 7.23 (m, 4H), 4.50 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.3, 141.7, 135.5, 135.1, 134.1, 132.5, 131.3, 131.3, 130.4, 130.1, 129.8, 129.3, 128.8, 127.2, 127.0, 37.2. HRMS calcd. for: C₁₆H₁₂Cl₂NS⁺ [M+H]⁺ 320.0062, found 320.0039.

2-(2,4-dichlorobenzyl)-5-(2,4-dichlorophenyl)thiazole (5j)

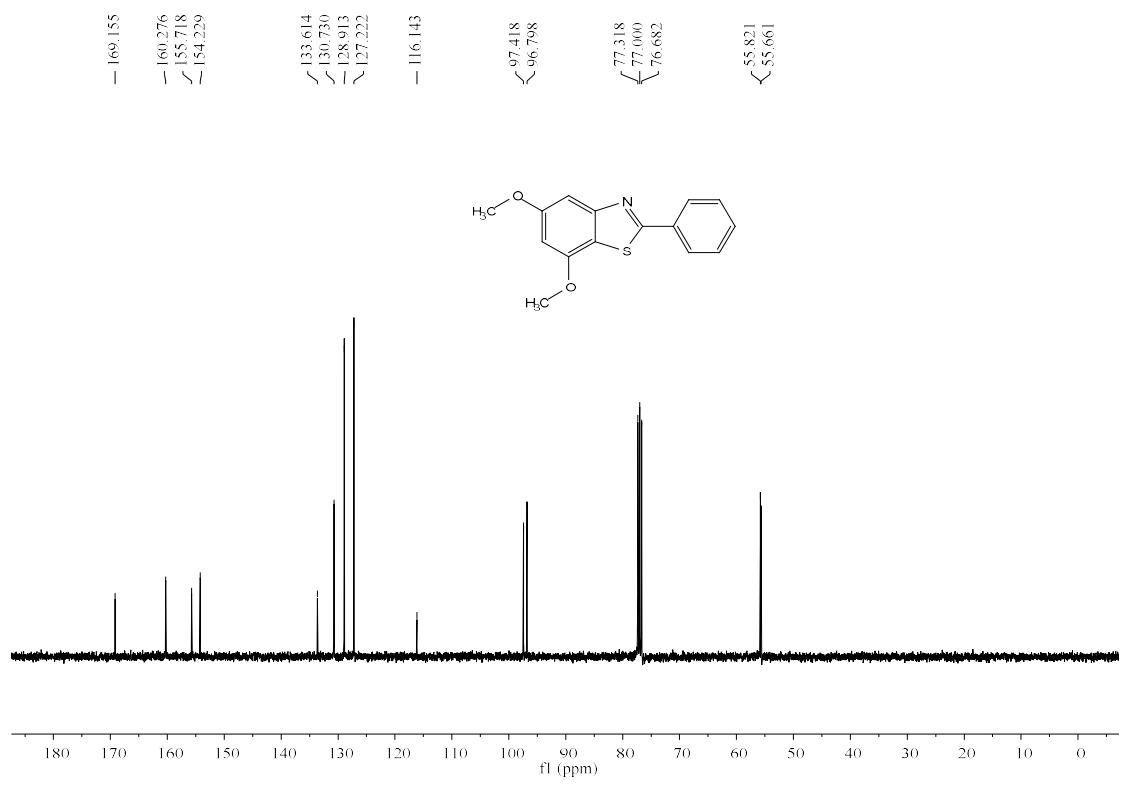
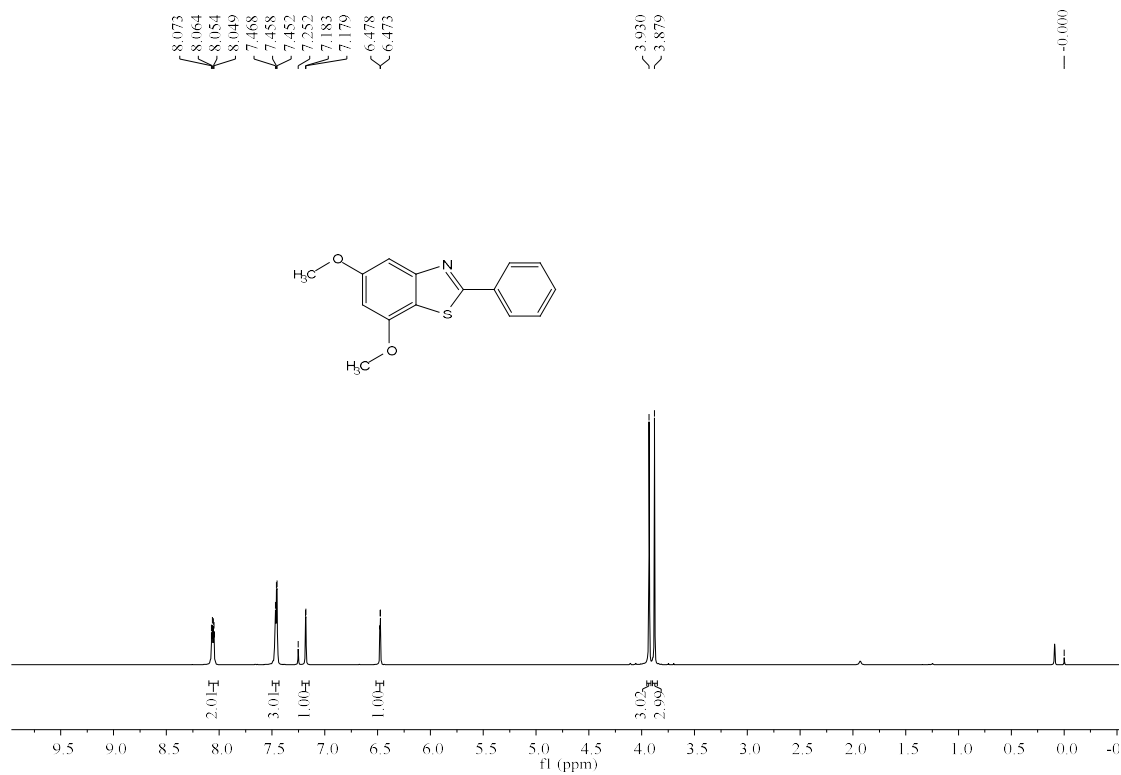


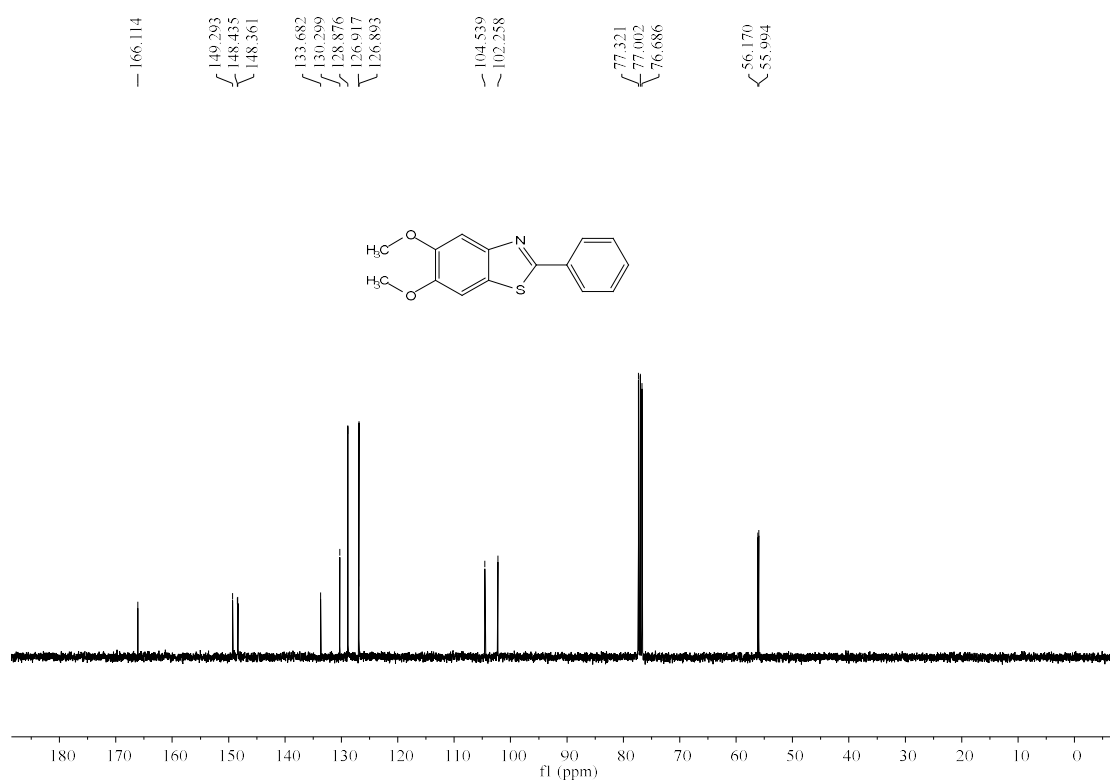
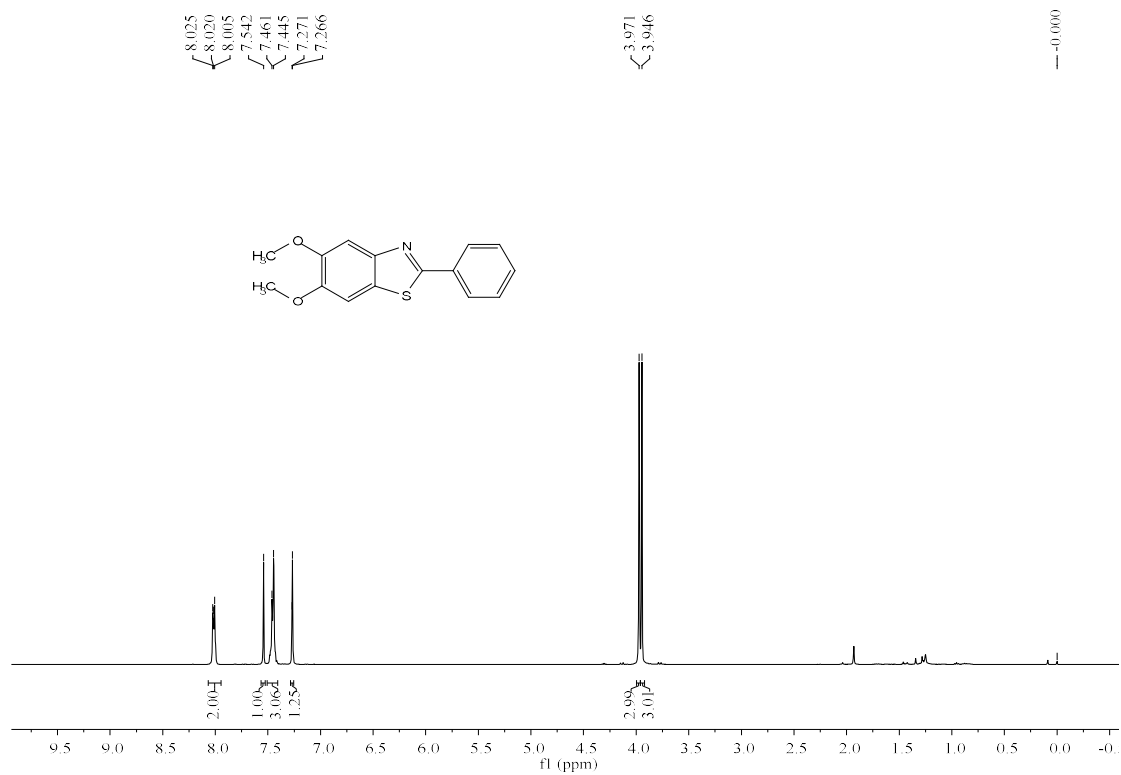
Yellow oil, 48% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.51 – 7.43 (m, 2H), 7.43 – 7.34 (m, 2H), 7.29 – 7.24 (m, 2H), 4.46 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.9, 141.9, 134.8, 134.7, 134.2, 134.0, 133.9, 133.2, 132.0, 131.9, 130.3, 129.6, 128.6, 127.6, 127.5, 36.6. HRMS calcd. for: $\text{C}_{16}\text{H}_9\text{Cl}_4\text{NNaS}^+$ $[\text{M}+\text{Na}]^+$ 409.9102, found 409.9157.

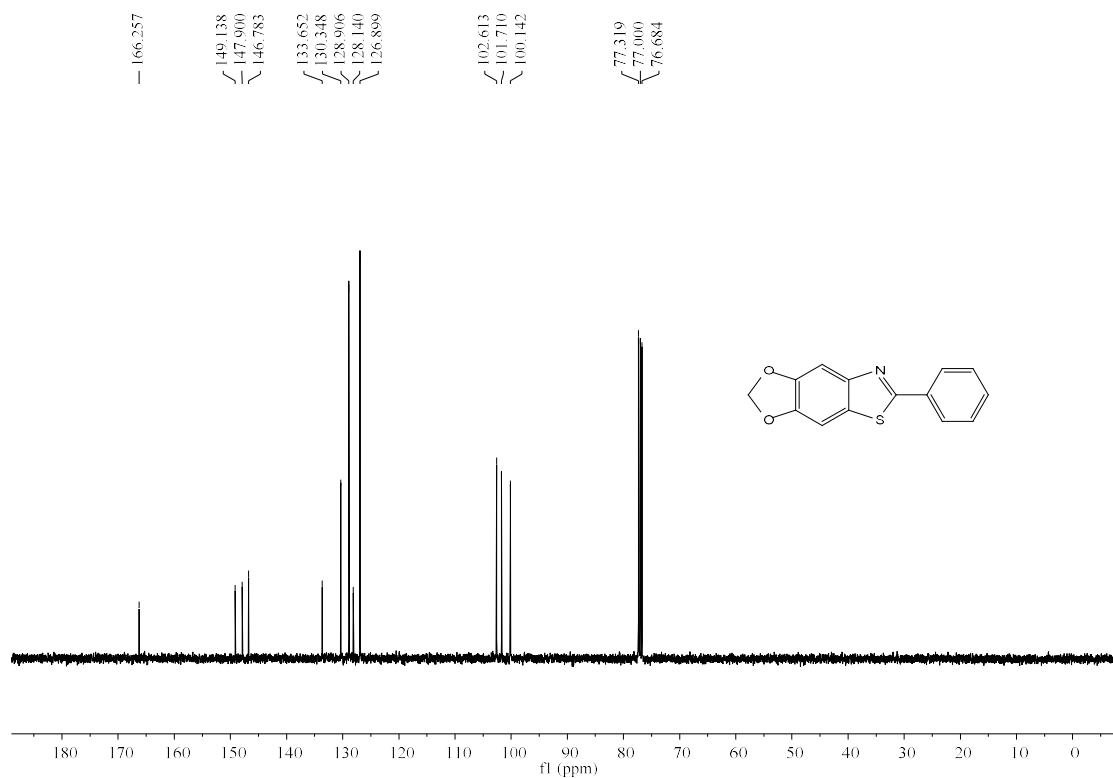
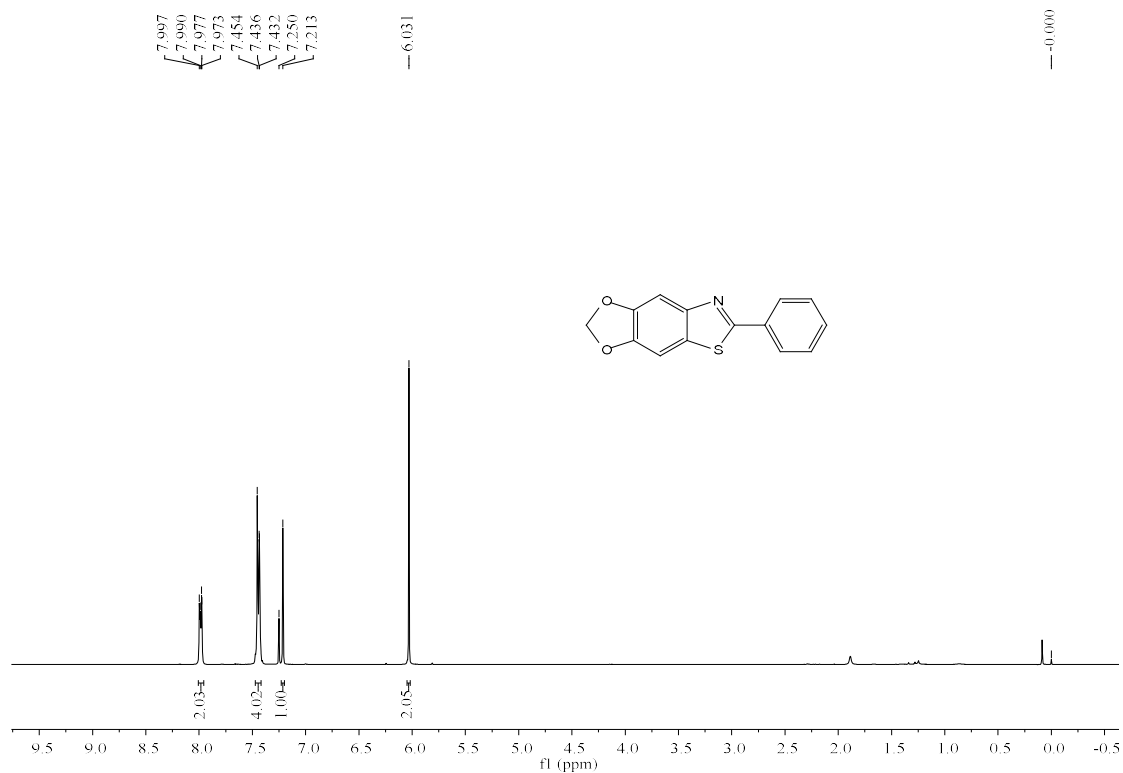
References

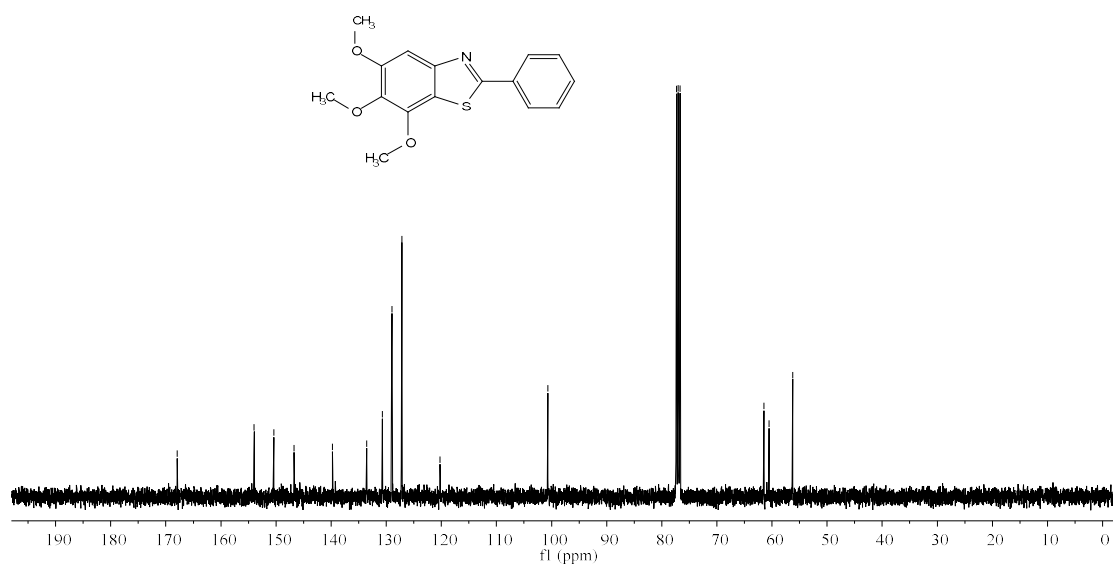
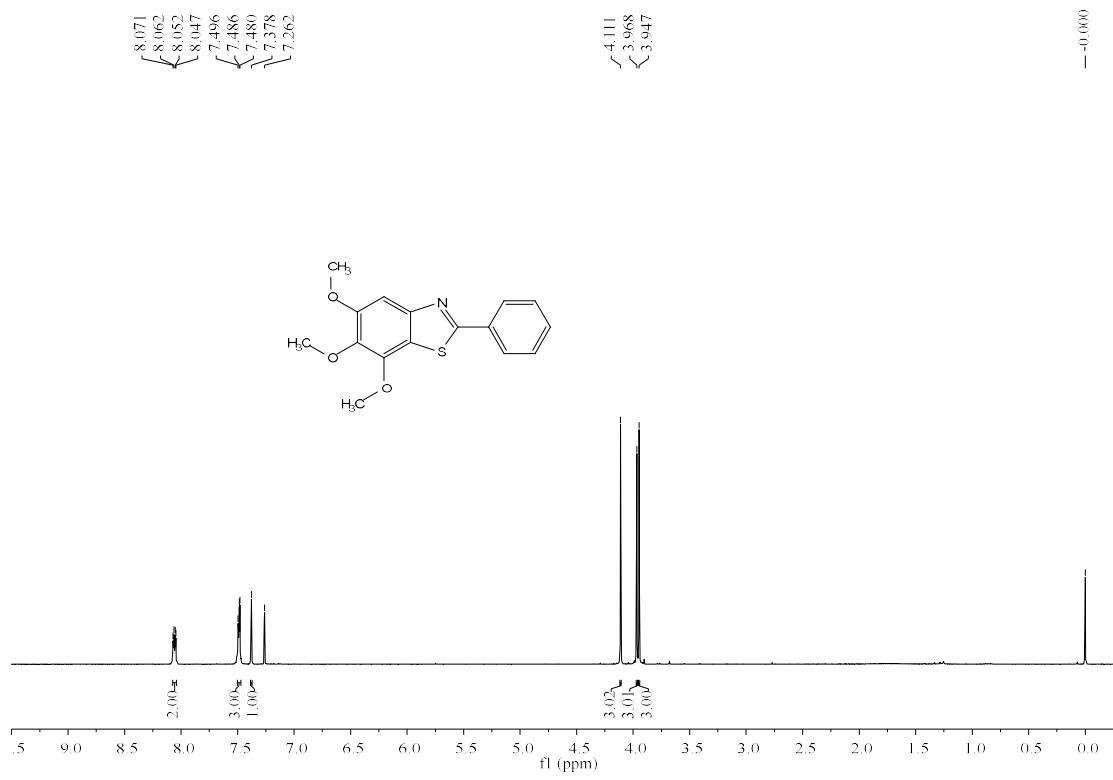
- [1] Che, Xingzong; Jiang, Jingjing; Xiao, Fuhong; Huang, Huawen; Deng, Guo-Jun. *Org. Lett.* **2017**, *19*, 4576–4579.
- [2] Hengyang Normal University; Zhu Xiaoming; Zhang Fuxing; Feng Yonglan; Wang Chengyong; Wang Zhiqiang; Yu Jiangxi. *CN111909113*, **2020**, A.
- [3] Kim, Jihyeon; Oh, Kyungsoo. *Adv. Synth. Catal.* **2020**, *362*, 3576–3582.
- [4] Zhu, Xiaoming; Yang, Yuzhong; Xiao, Genhua; Song, Jianxin; Liang, Yun; Deng, Guobo. *Chem. Commun.* **2017**, *53*, 11917–11920.
- [5] Cheng, Yan; Xiang, Jia-Chen; Wang, Zi-Xuan; Ma, Jin-Tian; Wang, Miao; Tang, Bo-Cheng; Wu, Yan-Dong; Zhu, Yan-Ping; Wu, An-Xin. *Adv. Synth. Catal.* **2018**, *360*, 550–555.

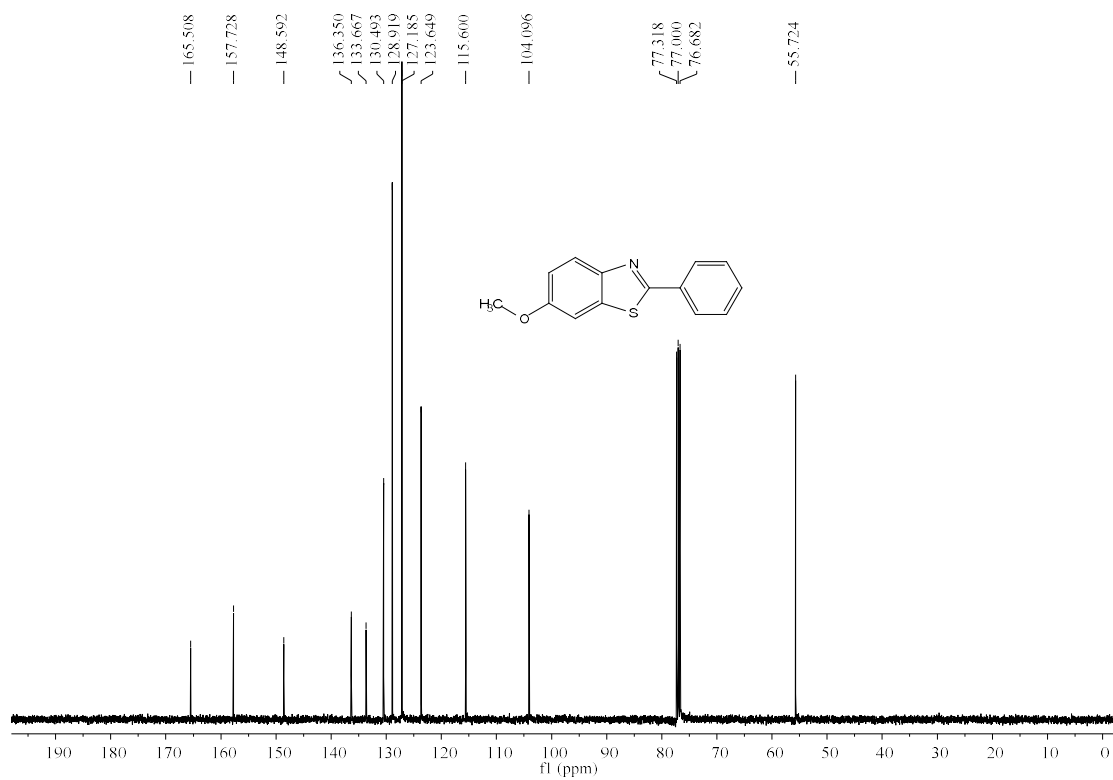
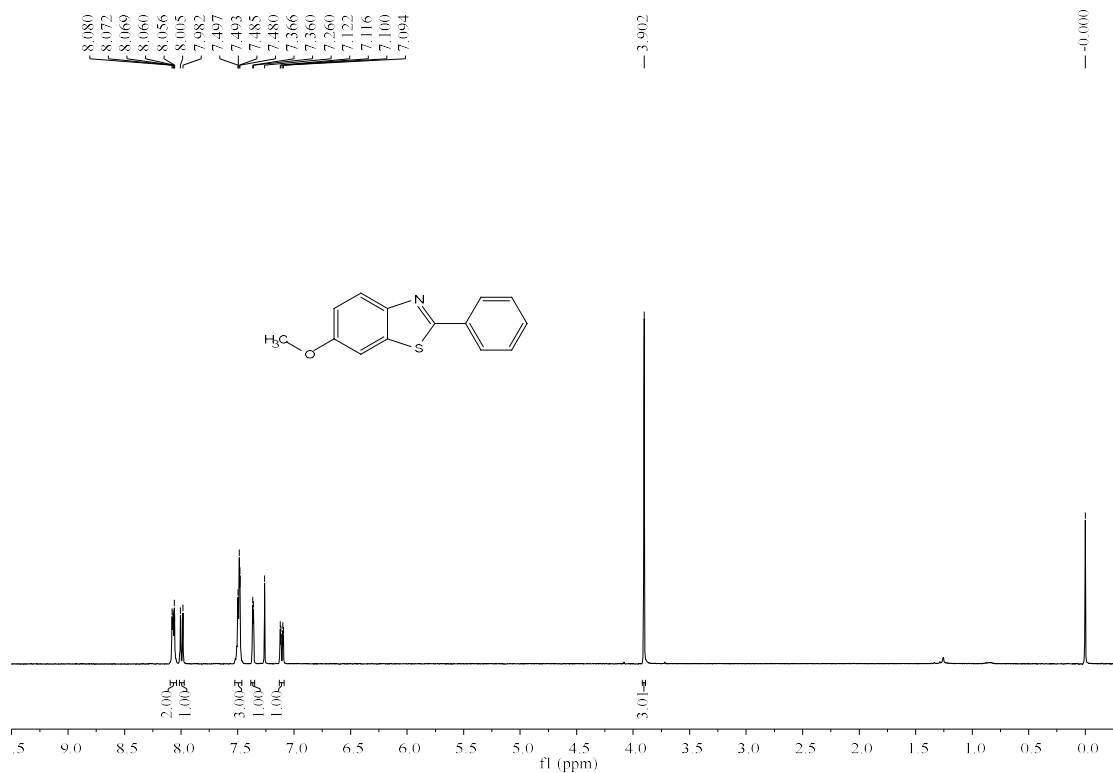
Copies of ^1H and ^{13}C NMR spectra of products

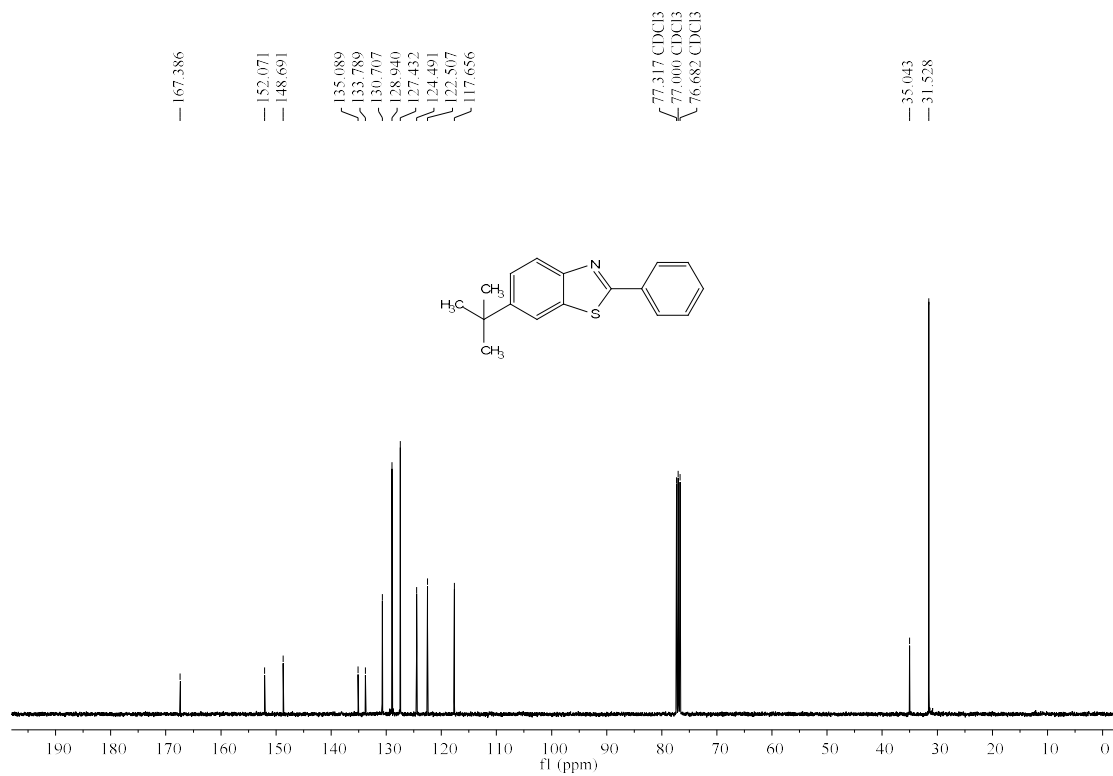
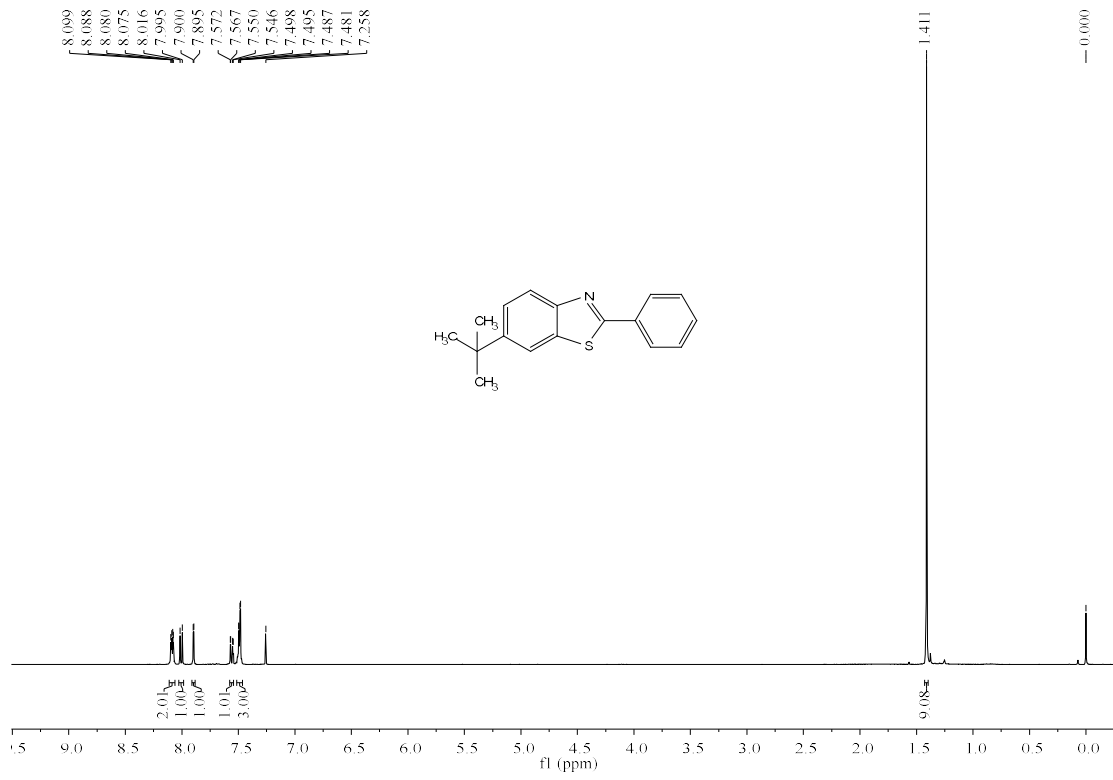


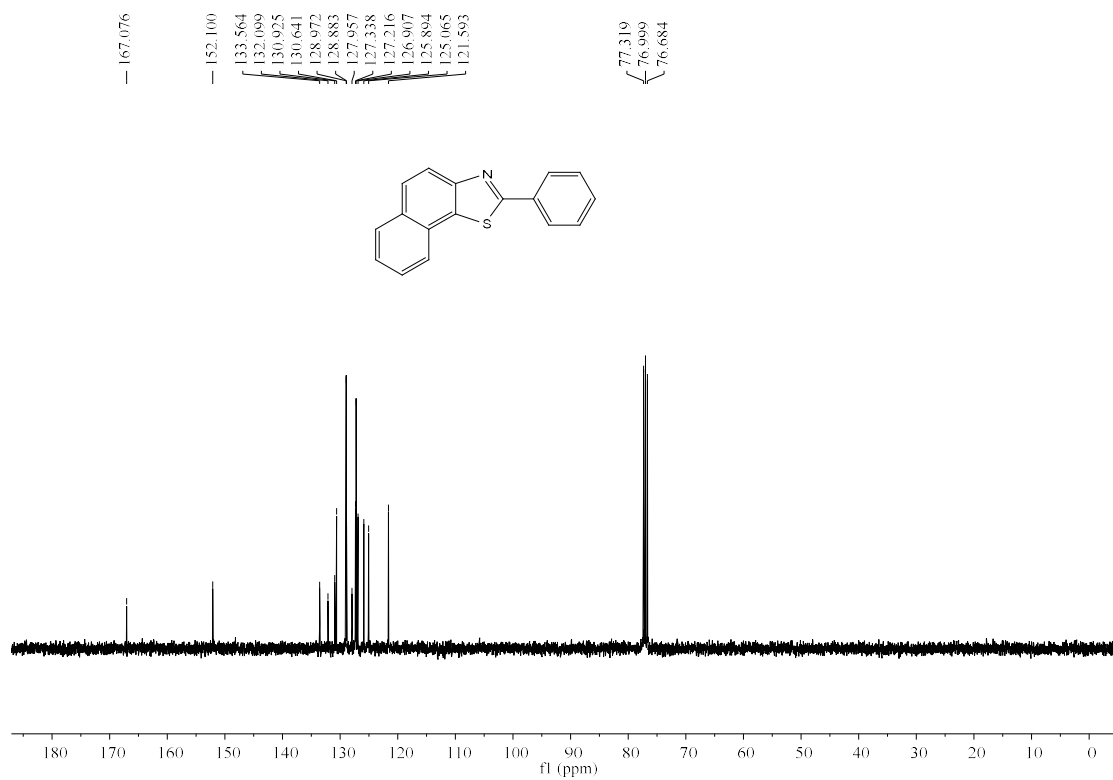
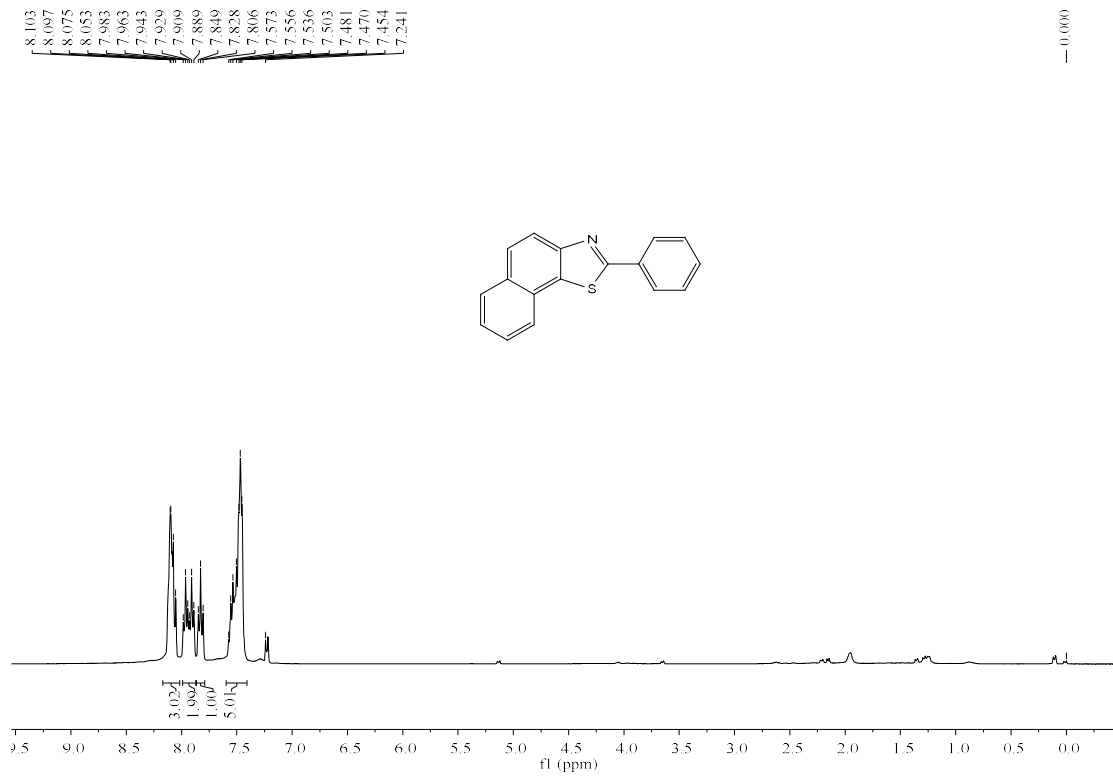


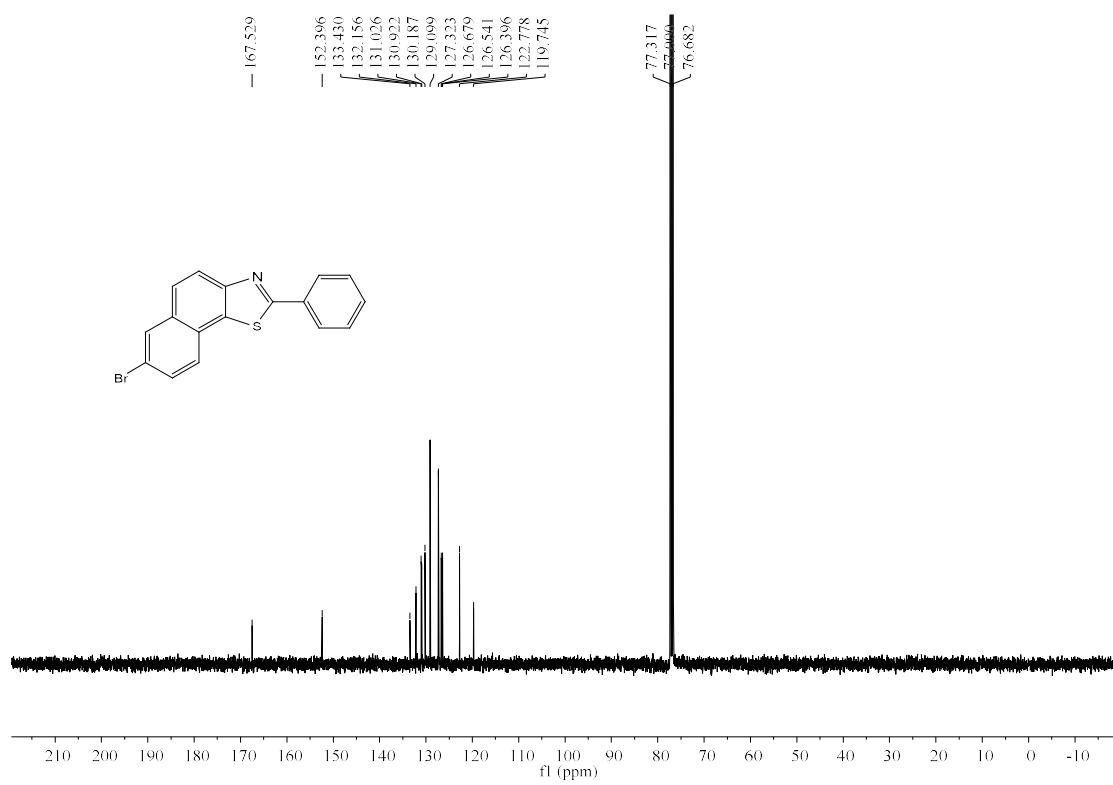
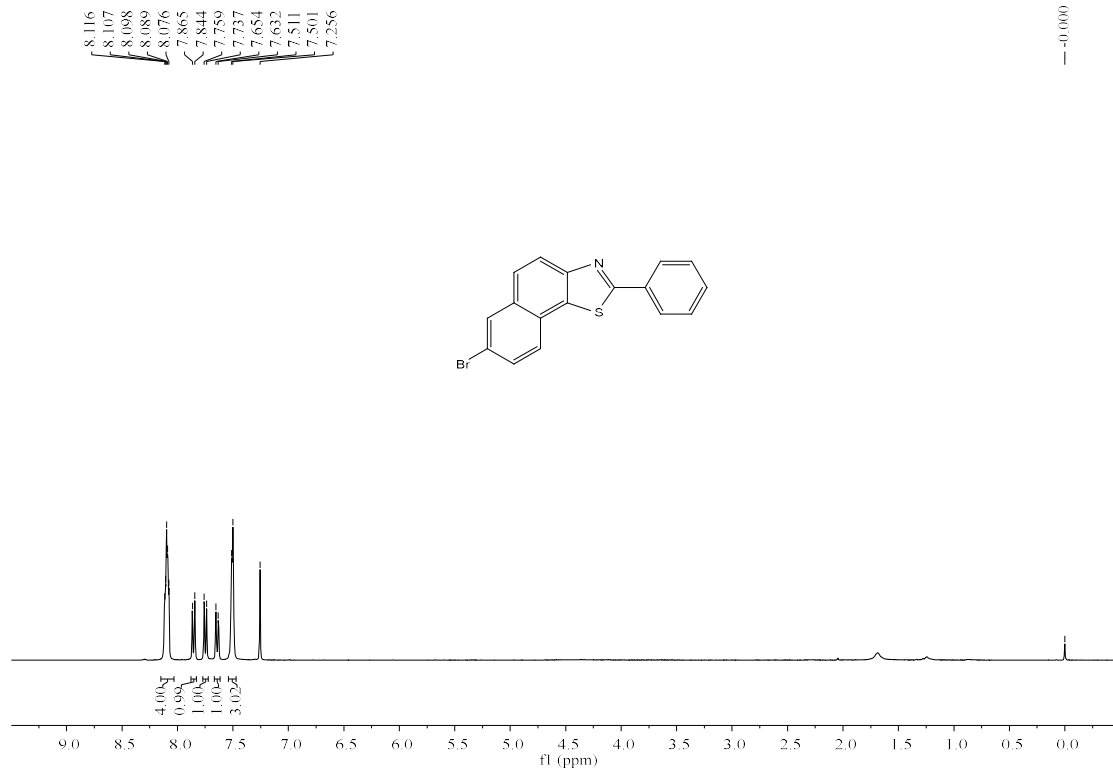




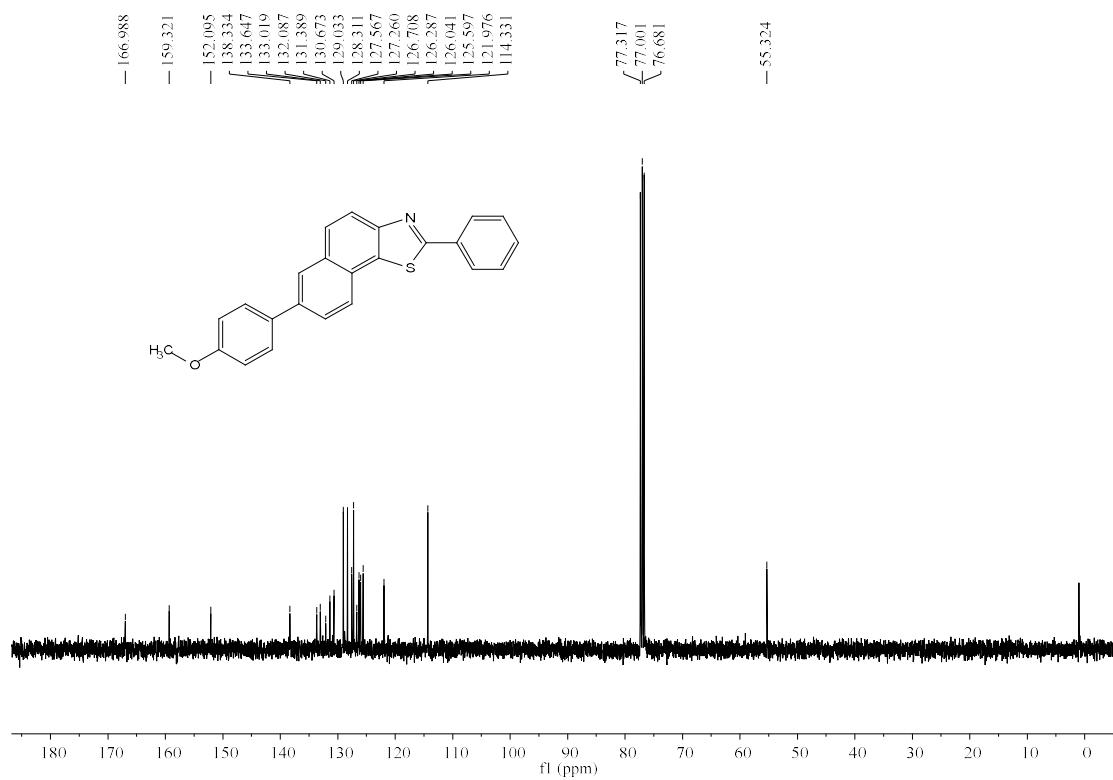
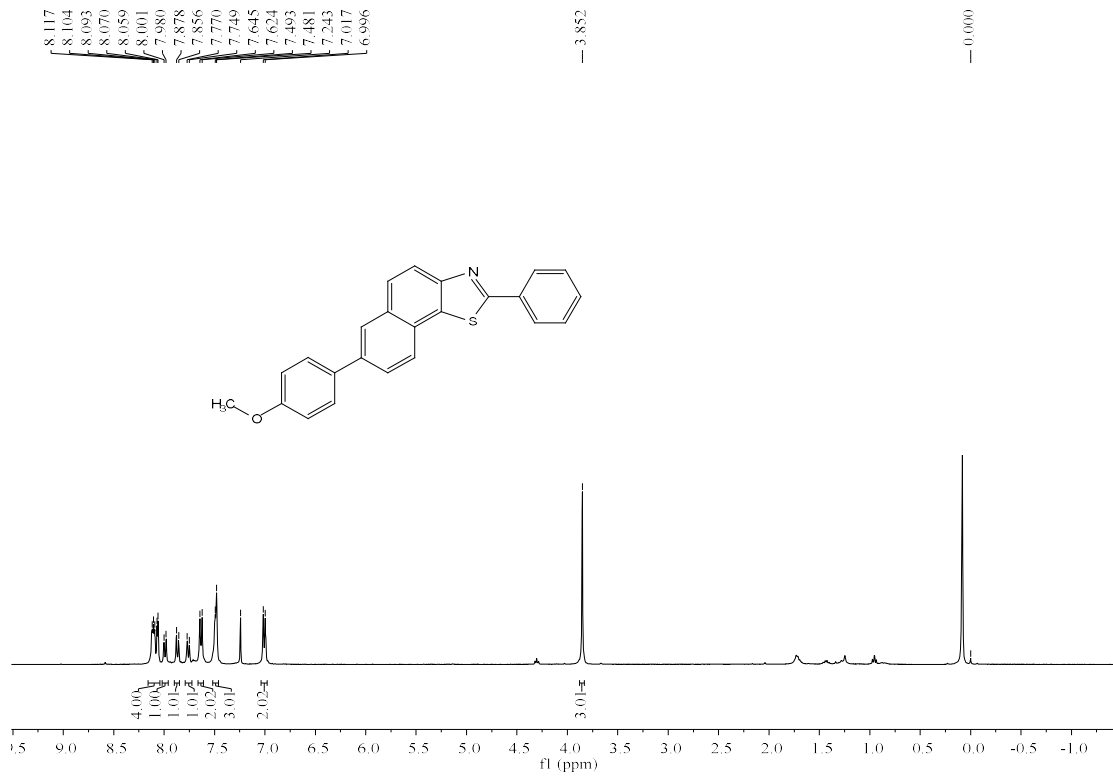


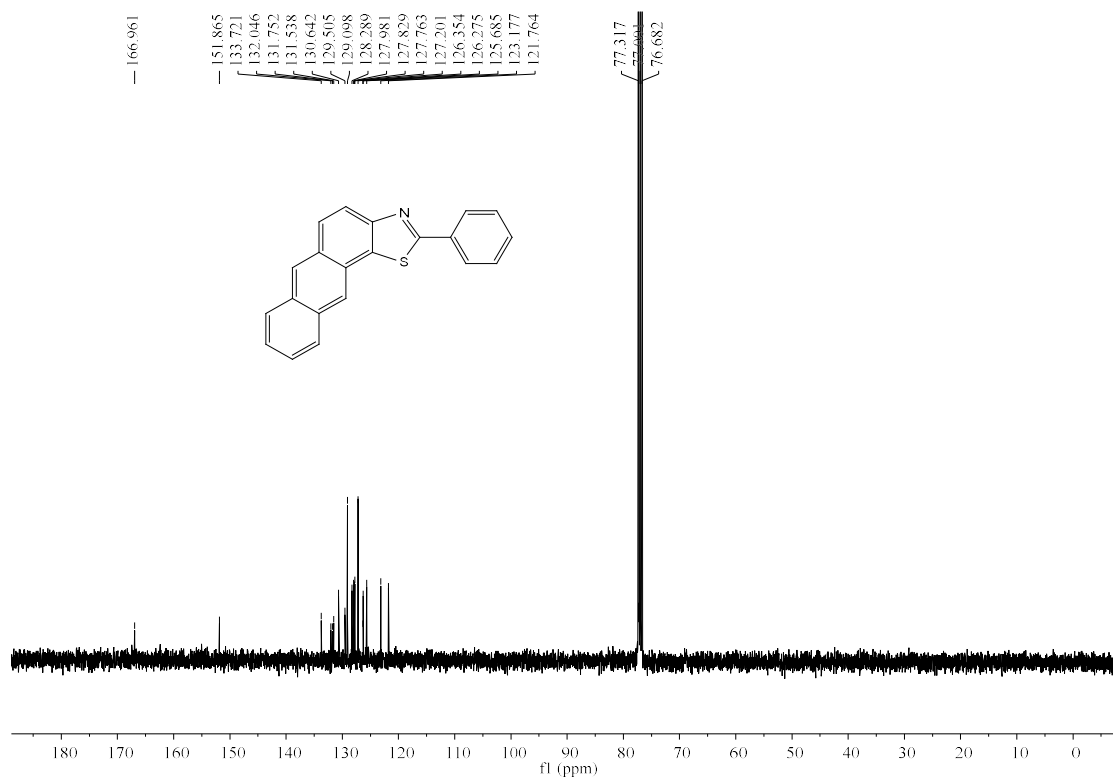
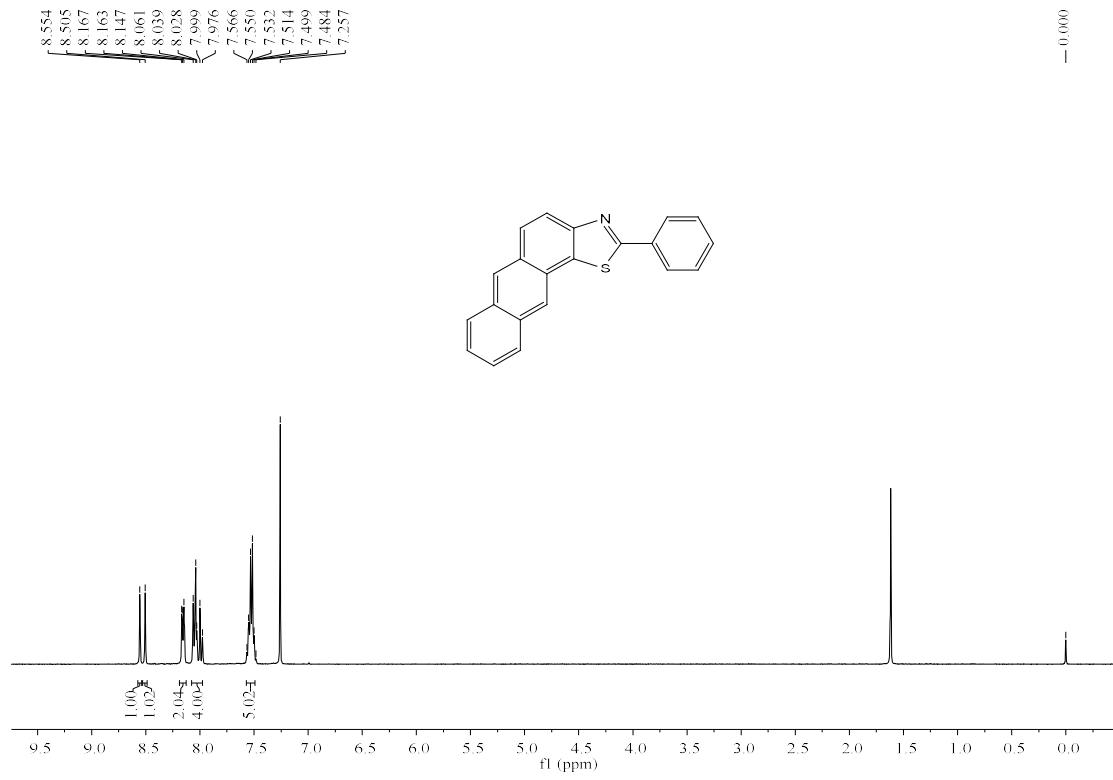


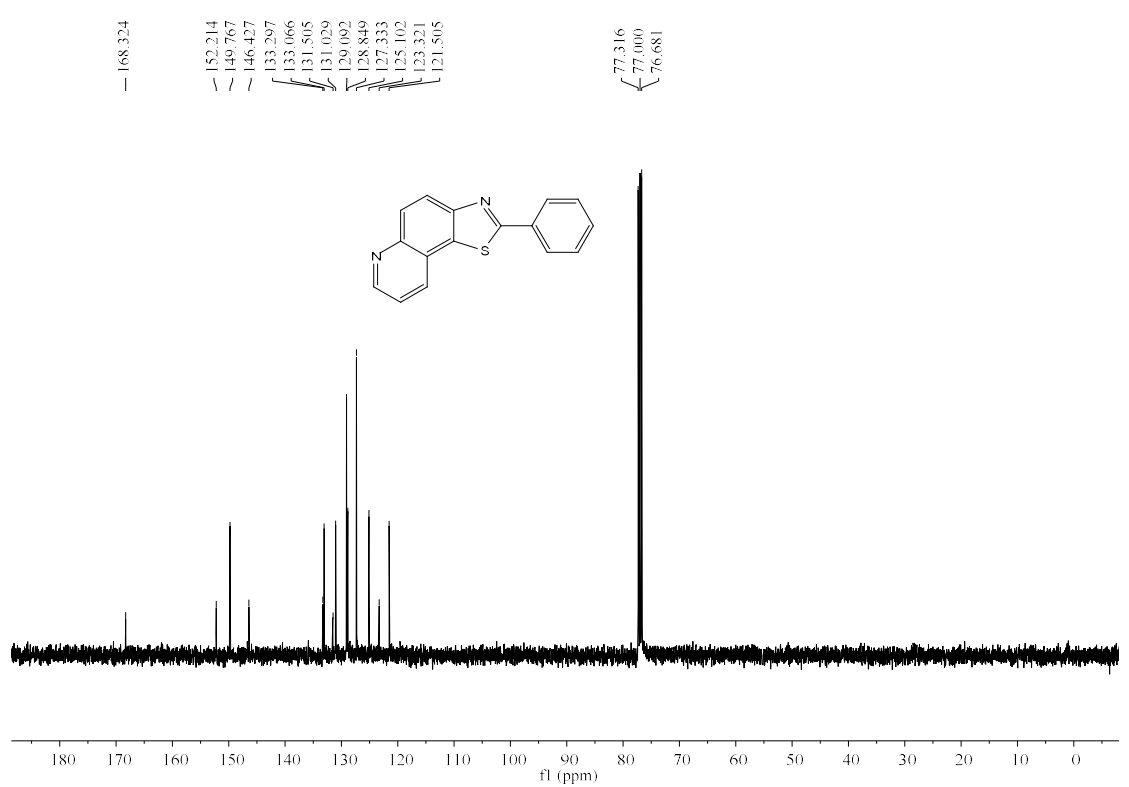
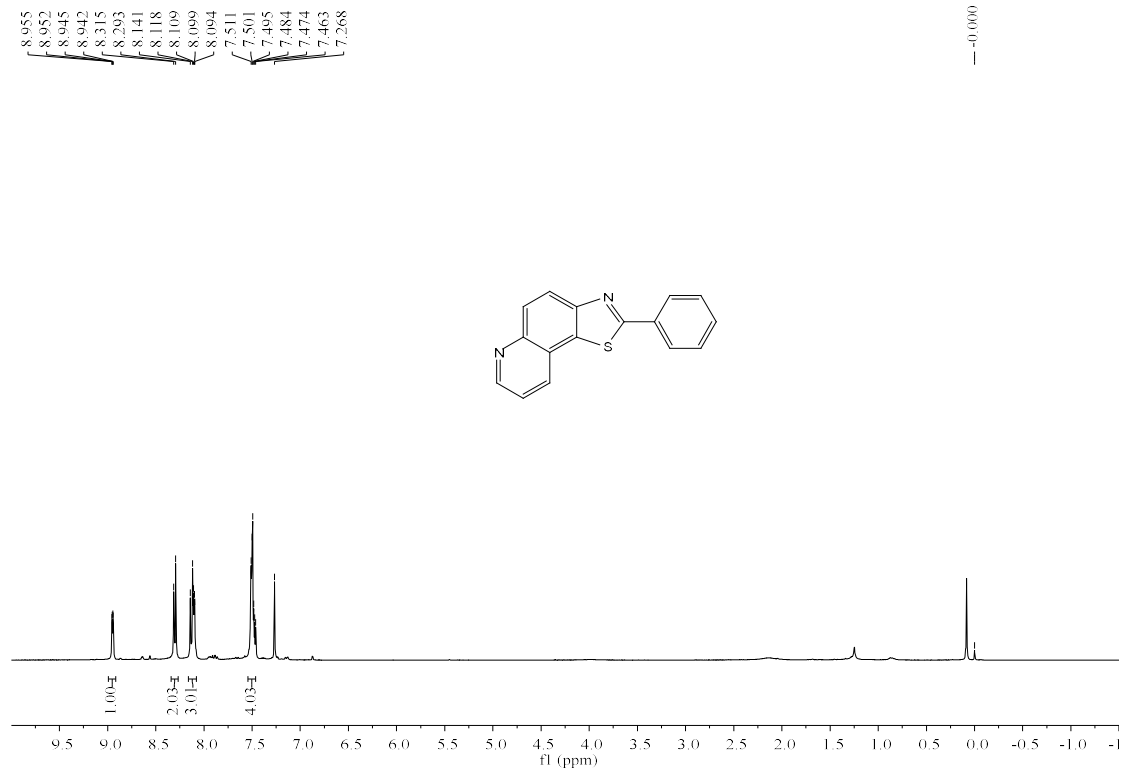


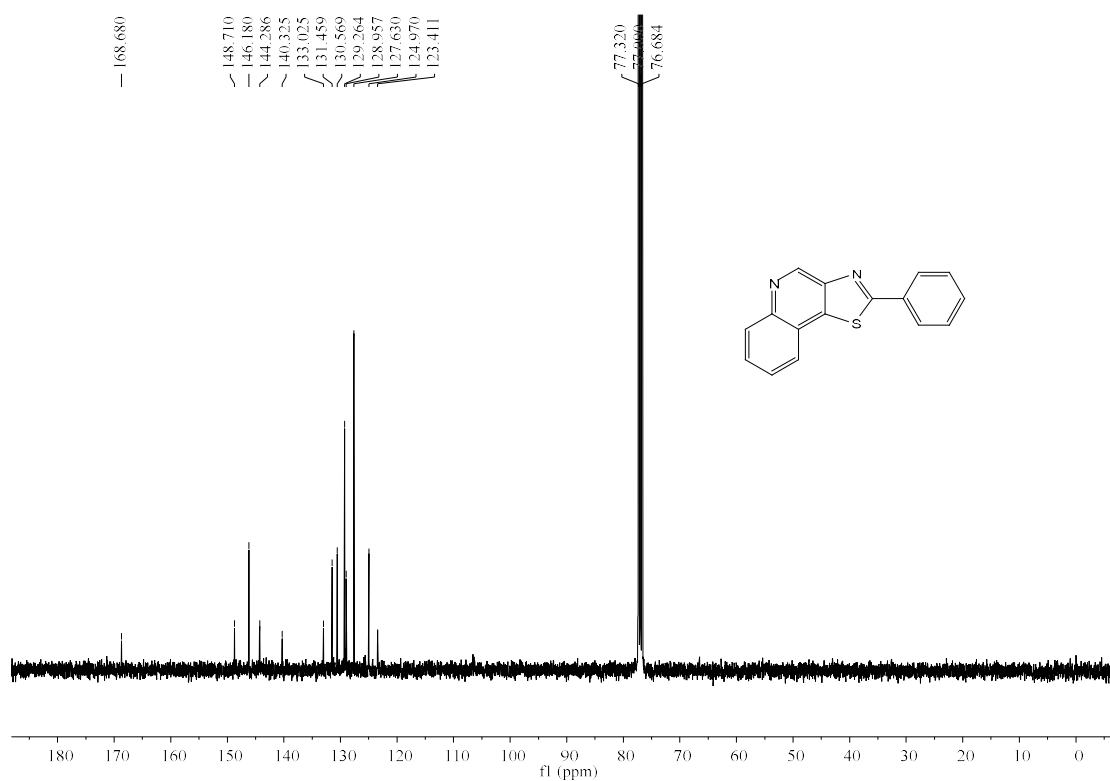
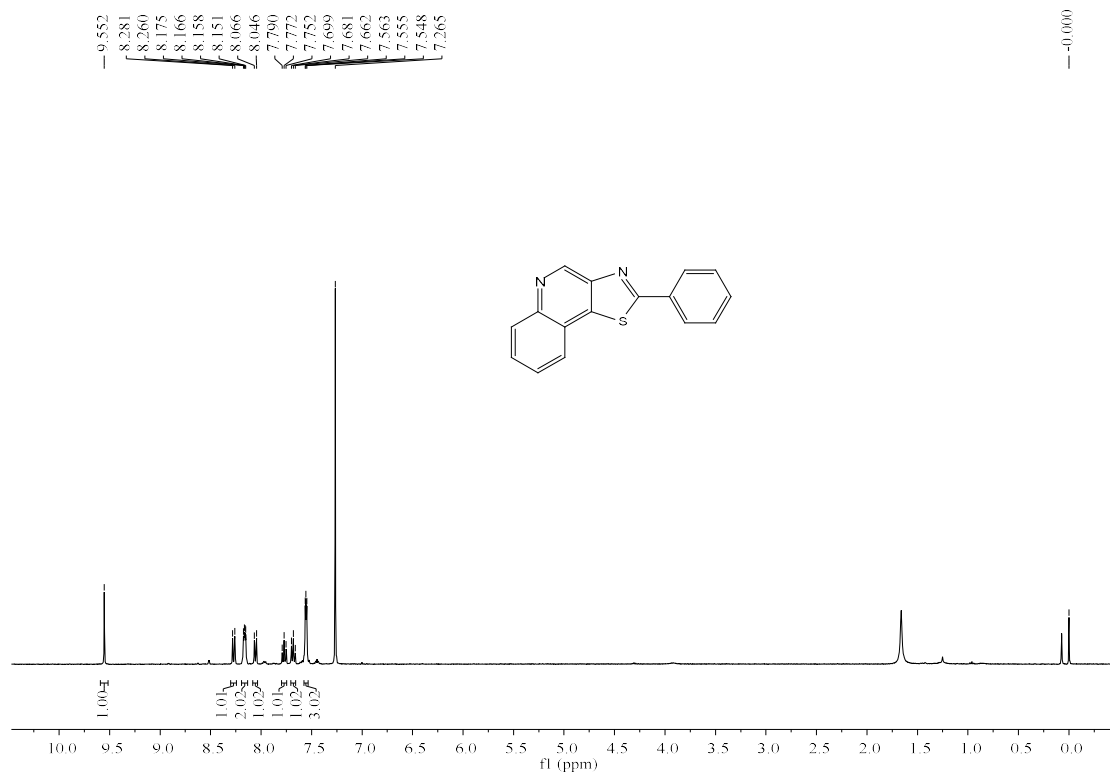


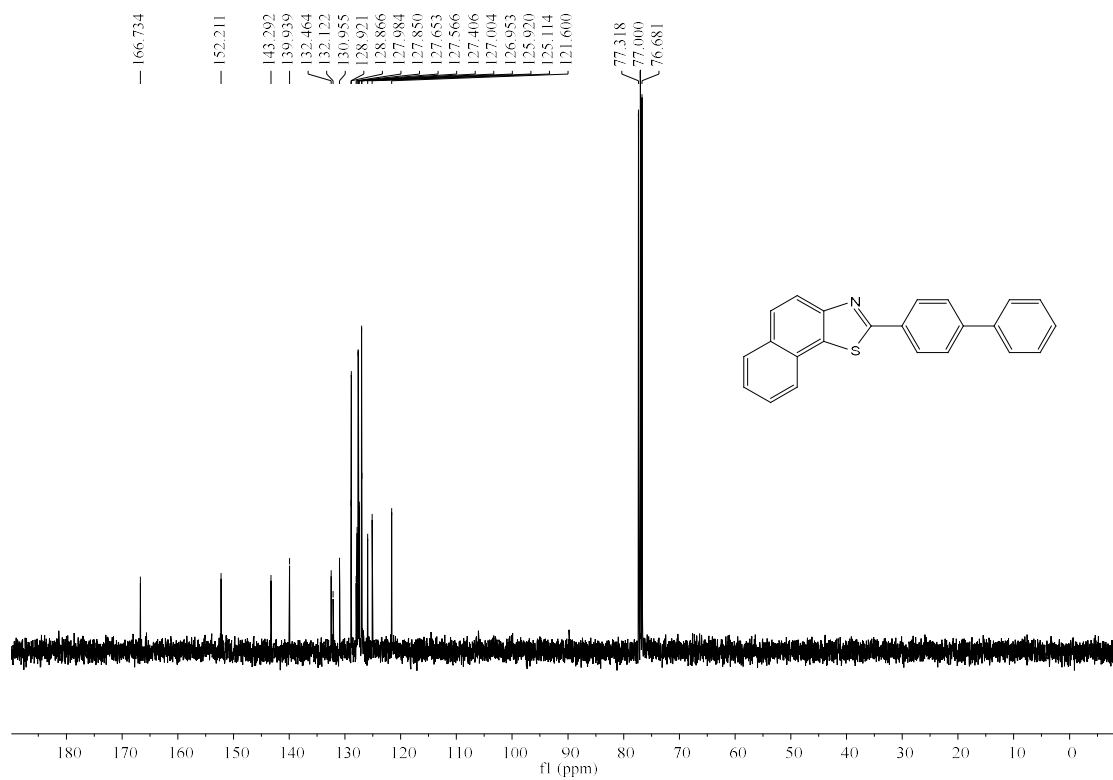
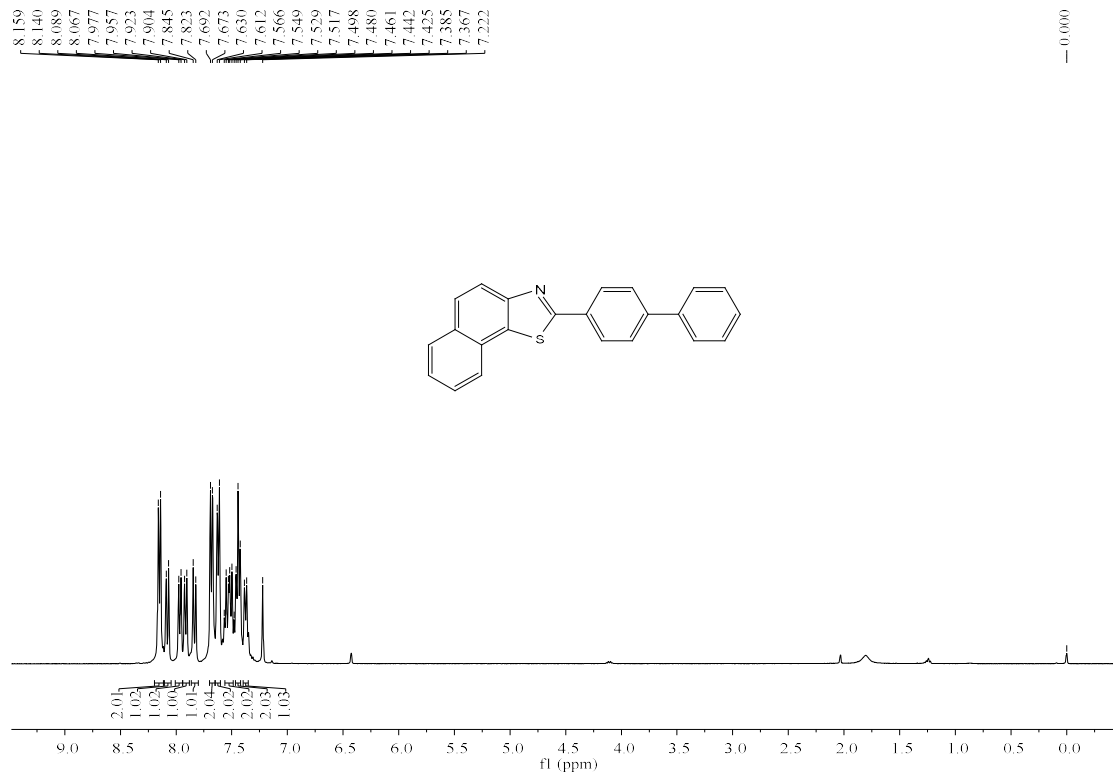
-0.000

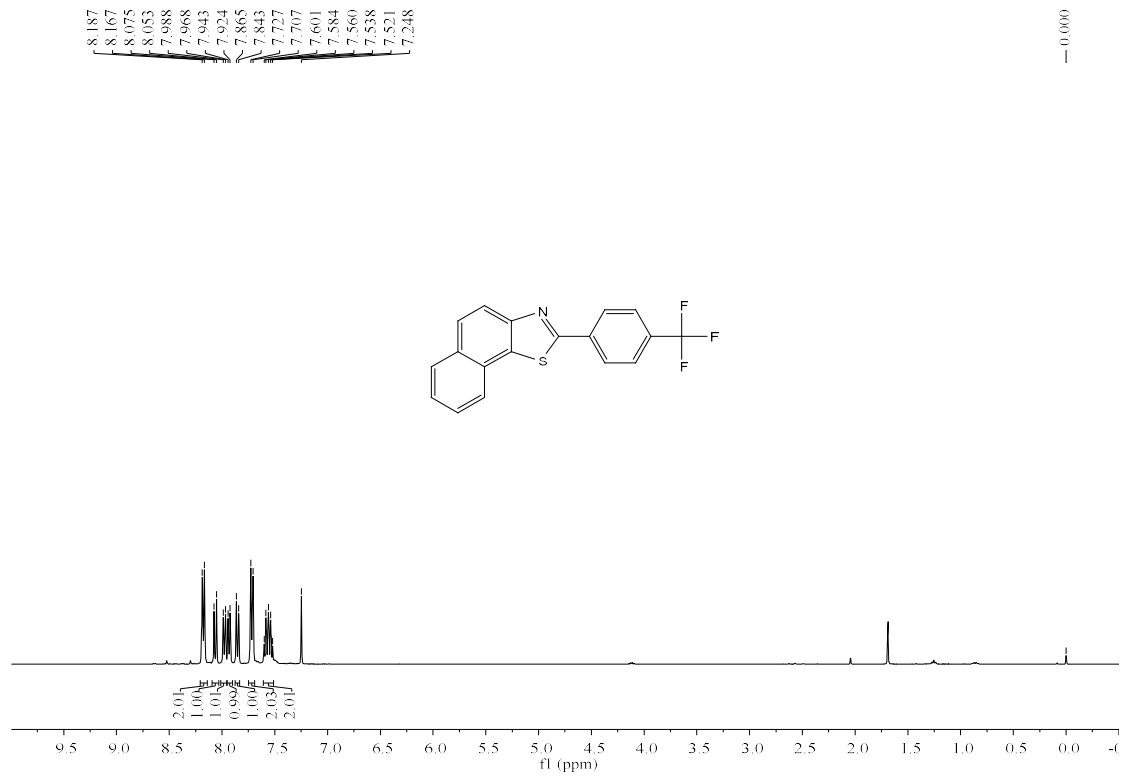












0.000

