Supporting Information

Transition-metal-free synthesis of thiazolidin-2-ones and 1,3-thiazinan-2-ones from arylamines, elemental sulfur and CO_2

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1 General Information

Unless otherwise noted, all reactions were set up using standard Schlenk techniques and carried out under carbon dioxide atmosphere with dry solvents. Sodium *tert*-butoxide (NaO^{t}Bu) was purchased from Energy Chemical and lithium *tert*-butoxide (LiO^{t}Bu) was purchased from Adamas. Anhydrous 1,4-dioxane was purchased from J&K Chem Co., Ltd. and stored over molecular sieves under nitrogen. Commercially available chemicals were obtained from Adamas-beta®, Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR and TCI Shanghai and used as received unless otherwise stated. The substituted arylamines were synthesized according to the literature procedure.[1.2.]

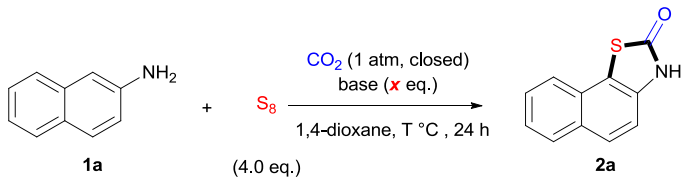
Reactions were monitored by thin-layer chromatography (TLC) or HPLC. TLC was performed using commercially Precoated silica gel plates (GF254, 100-400 mesh), and visualized by UV light 254 nm or iodine in silica gel. Organic solutions were concentrated under reduced pressure on EYELA rotary evaporator. Flash column chromatography was performed on Silica Gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., Ltd.

GC-MS was obtained using electron ionization (Agilent Technologies 7890B/GC-System and 5977A/MSD, controled by Masshunter software). HRMS analysis was performed on a Shimadzu LCMS IT-TOF Mass Spectrometer. ESI-mass data were acquired using a Thermo LTQ Instrument equipped with an ESI source and controlled by Xcalibur software.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS (δ= 0.00 ppm), The residual solvent signals were used as references (DMSO: 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, b = broad.

2 Optimization of the Reaction Conditions

Table S1 Screening of the Reaction Conditions[a]



1a 2a

entry	base	x	T /°C	yield (%)[b]	entry	base	x	T /°C	yield (%)[b]
1	LiO^{t}Bu	5	140	44	10[c]	NaO^{t}Bu	6	140	35
2	KO^{t}Bu	5	140	62	11[d]	NaO^{t}Bu	6	140	74
3	NaO^{t}Bu	5	140	78	12[e]	NaO^{t}Bu	6	140	22
4	Cs_2CO_3	5	140	8	13[f]	NaO^{t}Bu	6	140	35
5	NaO^{t}Bu	3	140	24	14[g]	NaO^{t}Bu	6	140	12
6	NaO^{t}Bu	4	140	40	15[h]	NaO^{t}Bu	6	140	36
7	**NaO^{t}Bu**	**6**	**140**	**87**	16[i]	NaO^{t}Bu	6	140	68
8	NaO^{t}Bu	6	120	n.d.	17[j]	NaO^{t}Bu	6	140	n.d.
9	NaO^{t}Bu	6	130	34	18[k]	NaO^{t}Bu	6	140	n.d.

[a]Reaction Conditions: **1a** (0.2 mmol), S_8 (32 g/mol, 0.8 mmol, 25.6 mg), CO_2 (1 atm, closed), 1 mL of 1,4-dioxane, 24 h. [b]Isolated yields. [c]S_8 (32 g/mol, 0.4 mmol, 12.8 mg). [d]S_8 (32 g/mol, 0.6 mmol, 19.2 mg) [e]diglyme (1.0 mL). [f]*N*,*N*-Dimethylformamide (1.0 mL). [g]*N*,*N*-Dimethylacetamide (1.0 mL). [h]Dimethyl sulfoxide (1.0 mL). [i]1,4-dioxane (2.0 mL). [j]without S_8. [k]Under the atmospheric of N_2 instead of CO_2. n.d. = not detected.

3 Experimental procedures and characterization data

3.1 General Procedure for naphthylamine

To an oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was added arylamine substrate **1** (0.20 mmol, 1.0 equiv for solid substrates) and elemental sulfur (32 g/mol, 0.8 mmol, 25.6 mg). Then the tube was moved into a glovebox. NaO^{t}Bu (1.2 mmol, 6.0 equiv) was added to the tube before transferring out of the glovebox and placing under an atmosphere of nitrogen. Then the Schlenk tube was evacuated and back-filled with CO_2. Arylamine substrate **1** (0.20 mmol, 1.0 equiv for liquid substrates), anhydrous 1,4-dioxane (1 mL) was added via syringe under CO_2 atmosphere. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for 24 h at 140 °C. Then, the mixture was diluted with water (2.0 mL) and extracted by ethyl acetate (3 mL x 5). The combined organic phase was concentrated *in vacuo* and purified by flash column chromatography (silica: 200–300 mesh, typical eluent: petroleum ether/ethyl acetate = 10:1-5:1) to give the desired product.

Tips:

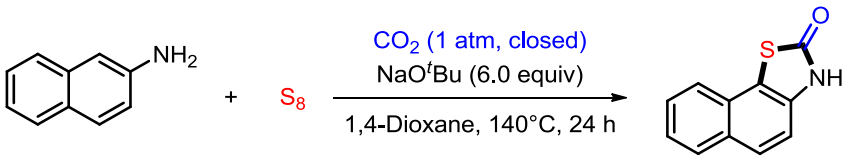
1. The solvent should cover the substrates and the substrates should not be shaken onto the reaction tube.
2. For substrates are not completely converted, pickling (2 N HCl) can be used to remove the unreacted substrates.

3.2 General Procedure for aniline

To an oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was added arylamine substrate **7** (0.20 mmol, 1.0 equiv for solid substrates) and elemental sulfur (32 g/mmol, 0.5 mmol, 16 mg). Then the tube was moved into a glovebox. LiO^tBu (1.3 mmol, 6.5 equiv) and NaI (0.2 mmol, 1.0 equiv) was added to the tube before transferring out of the glovebox and placing under an atmosphere of nitrogen. Then the Schlenk tube was evacuated and back-filled with CO_2. Arylamine substrate **7** (0.20 mmol, 1.0 equiv for liquid substrates), anhydrous DMF (0.5 mL) was added via syringe under CO_2 atmosphere. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for 24 h at 140 °C. Then, the mixture was diluted with water (2.0 mL) and extracted by ethyl acetate (3 mL x 5). The combined organic phase was concentrated *in vacuo* and purified by flash column chromatography (silica: 200–300 mesh, typical eluent: petroleum ether/ethyl acetate = 10:1-5:1) to give the desired product.

3.3 Synthesis of **2a** in gram scale

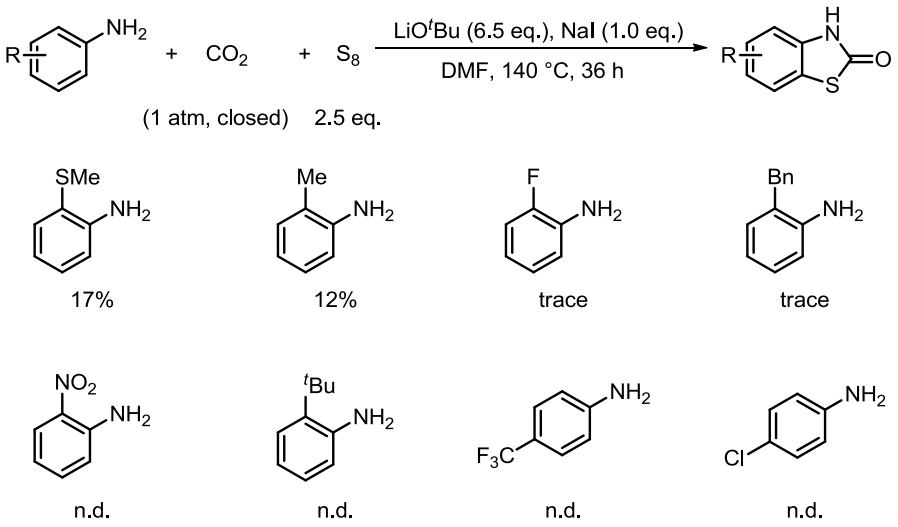
Gram scale:



1a, 8 mmol (4.0 eq.) **2a**, 1.22 g, 76%

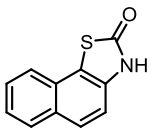
To an oven-dried Schlenk tube (350 mL) equipped with a magnetic stir bar was added naphthalen-2-amine (**1a**, 8 mmol, 1.14 g, 1.0 equiv) and elemental sulfur (1.02 g, 32 mmol, 4.0 equiv, 32 mg/mmol). Then the tube was moved into a glovebox. NaO^tBu (48 mmol, 4.61g, 6.0 equiv) was added to the tube before transferring out of the glovebox and placing under an atmosphere of nitrogen. Then the Schlenk tube was evacuated and back-filled with CO_2. Anhydrous 1,4-dioxane (40 mL) was added via syringe under CO_2 atmosphere. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for 24 h at 140 °C. Then, the mixture was diluted with water (50 mL) and extracted by ethyl acetate (40 mL x 5). The combined organic phase was concentrated and purified by flash column chromatography to give the desired product **2a** (1.22 g, 76%, white solid).

3.4 Some unsuccessful examples



3.5 Characterization data

Naphtho[2,1-*d*]thiazol-2(3*H*)-one (**2a**)

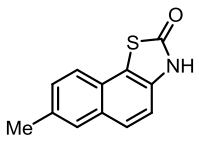


35.0 mg, 87% isolated yield, yellowish solid, Mp: 234-236 °C;

R_f (PE:EA=5:1): 0.4;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.16 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.48, 133.93, 129.64, 129.52, 127.98, 127.76, 127.43, 125.05, 123.01, 117.48, 112.85. **IR**(KBr) 3439, 3122, 3024, 2860, 1714, 1622, 1585, 1517, 1348, 1245, 1213, 1130, 798, 735, 656, 594. **HRMS (ESI-)** calcd. for $C_{11}H_7NOS^-$ [M-H]$^-$: 200.0176, found: 200.0178.

7-methylnaphtho[2,1-*d*]thiazol-2(3*H*)-one (**2b**)

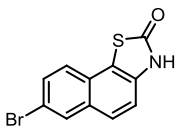


33.5 mg, 78% isolated yield, yellowish solid, Mp: 237-239 °C;

R_f (PE:EA=3:1): 0.43;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (s, 1H), 7.74 – 7.64 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.35 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.41, 134.25, 133.25, 130.01, 129.87, 128.35, 126.74, 125.99, 122.89, 117.47, 112.80, 21.47. **IR** (KBr) 3130, 3057, 2912, 2849, 1674, 1595, 1517, 1467, 1344, 1253, 1205, 1041, 875, 800, 648, 576, 538, 507. **HRMS (ESI-)** calcd. for $C_{12}H_9NOS^-$ [M-H]$^-$: 214.0332, found: 214.0338.

7-bromonaphtho[2,1-*d*]thiazol-2(3*H*)-one (**2c**)



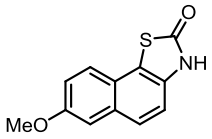
35.4 mg, 63% isolated yield, yellowish solid, Mp: 242-244 °C;

R_f (PE:EA=3:1): 0.49;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.23 (s, 1H), 8.24 (d, *J* = 1.9 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.66 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.25, 134.44, 131.31, 130.87, 130.72, 126.67,

126.32, 125.26, 117.83, 117.78, 113.93. **IR** (KBr) 3130, 3008, 2989, 2850, 1674,1610, 1577, 1506, 1346, 1244, 1213, 1136, 1041, 982, 825, 733, 673, 602, 528. **HRMS (ESI-)** calcd. for $C_{11}H_6BrNOS^-$ $[M-H]^-$: 277.9281, found: 277.9281.

7-methoxynaphtho[2,1-*d*]thiazol-2(3*H*)-one (**2d**)

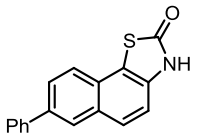


34.2 mg, 74% isolated yield, yellowish solid, Mp: 232-234 °C;

R_f (PE:EA=3:1): 0.42;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.03 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.40 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.23 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.29, 156.71, 132.16, 130.97, 126.23, 124.53, 122.99, 120.25, 117.89, 113.13, 108.10, 55.68. **IR** (KBr) 3134, 3020, 2914, 2846, 1670, 1626, 1595, 1519,1479, 1213, 1236, 1213, 1164, 1126, 1029, 820, 719, 656, 600, 553, 511. **HRMS (ESI-)** calcd. for $C_{12}H_9NO_2S^-$ $[M-H]^-$: 230.0281, found: 230.0284.

7-phenylnaphtho[2,1-*d*]thiazol-2(3*H*)-one (**2e**)

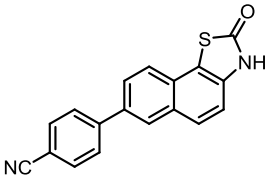


38.2 mg, 69% isolated yield, yellowish solid, Mp: 243-245 °C;

R_f (PE:EA=3:1): 0.40;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.20 (s, 1H), 8.27 (s, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.89 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.39 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.48, 139.99, 136.63, 134.13, 130.06, 129.48, 128.00, 127.93, 127.25, 127.06, 127.00, 126.96, 123.82, 117.43, 113.31. **IR** (KBr) 3446, 3126, 3057, 2920, 2850, 1674, 1599, 1502, 1377, 1338, 1253, 1207, 806, 686, 626, 546. **HRMS (ESI-)** calcd. for $C_{17}H_{11}NOS^-$ $[M-H]^-$: 276.0489, found: 276.0487.

4-(2-oxo-2,3-dihydronaphtho[2,1-*d*]thiazol-7-yl)benzonitrile (**2f**)

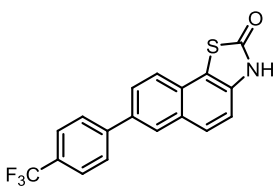


37.5 mg, 62% isolated yield, yellowish solid, Mp: 247-249 °C;

R_f (PE:EA=3:1): 0.35;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.23 (s, 1H), 8.36 (s, 1H), 8.00 – 7.85 (m, 6H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.44, 144.44, 134.67, 134.51, 133.32, 129.86, 128.22, 128.07, 128.00, 127.51, 126.69, 124.07, 119.32, 117.45, 113.54, 110.40. **IR** (KBr) 3408, 3126, 3062, 2918, 2848, 1674, 1492, 1463,1338, 1253, 1251, 1089, 1006, 881, 802, 680, 623, 500, 457. **HRMS (ESI-)** calcd. for $C_{18}H_9N_2OS^-$ $[M-H]^-$: 301.0441, found:.301.0446.

7-(4-(trifluoromethyl)phenyl)naphtho[2,1-*d*]thiazol-2(3*H*)-one (**2g**)



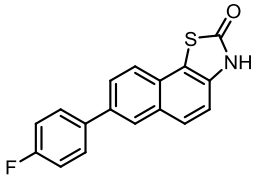
42.0 mg, 61% isolated yield, white solid, Mp: 253-255 °C;

R_f (PE:EA=3:1): 0.35;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.18 (s, 1H), 8.24 (s, 1H), 7.87 (m, 3H), 7.76 (m, 3H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.47, 143.86, 134.76, 134.46, 129.83, 128.74 (d, *J* = 13.8 Hz), 127.81, 127.85 (q, *J* = 33.3 Hz), 127.33, 126.65, 126.15 (q, *J* = 4.0 Hz), 124.81 (q, *J* = 285.8 Hz). 123.89, 117.43, 113.38, 110.02. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -60.96. **IR** (KBr) 3429, 3138, 3070, 2922, 2850, 1670, 1514, 1409, 1326, 1253, 1192,

1107, 1068, 1015, 974, 848, 812, 671, 615, 509. **HRMS (ESI-)** calcd. for $C_{18}H_9F_3NOS^-$ [M-H]$^-$: 344.0362, found: 344.0368.

7-(4-fluorophenyl)naphtho[2,1-*d*]thiazol-2(3*H*)-one (**2h**)

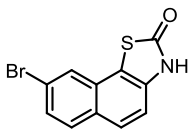


34.2 mg, 58% isolated yield, white solid, Mp: 243-245 °C;

R_f (PE:EA=3:1): 0.58;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.16 (s, 1H), 8.18 (d, J = 1.5 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.39 – 7.21 (m, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.45, 162.34 (d, *J* = 244.6 Hz), 136.45 (d, *J* = 3.0 Hz), 135.53, 134.09, 129.98, 129.17 (d, *J* = 8.2 Hz), 127.83, 126.88, 126.86, 123.76, 117.42, 116.21 (d, *J* = 21.3 Hz), 113.29. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -115.31. **IR** (KBr) 3361, 3132, 3067, 2922, 2852, 1732, 1651, 1601, 1508, 1380, 1340, 1240, 1155, 1095, 814, 748, 644, 517. **HRMS (ESI-)** calcd. for $C_{17}H_9FNOS^-$ [M-H]$^-$: 294.0394, found: 294.0394.

8-bromonaphtho[2,1-*d*]thiazol-2(3*H*)-one (**2i**)



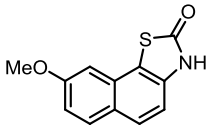
37.9 mg, 68% isolated yield, yellowish solid, Mp: 242-244 °C;

R_f (PE:EA=3:1): 0.36;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.26 (s, 1H), 7.99 – 7.81 (m, 3H), 7.58 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.39, 134.93, 131.77, 128.90, 128.19, 128.03, 127.53, 124.91, 121.44, 116.65, 113.38. **IR** (KBr) 3151, 3068, 2918, 2847, 1672, 1508, 1469, 1407, 1196, 889, 833, 758, 694, 661, 567. **HRMS (ESI-)** calcd. for $C_{11}H_6BrNOS^-$ [M-H]$^-$: 277.9281, found: 277.9282.

8-methoxynaphtho[2,1-*d*]thiazol-2(3*H*)-one (**2j**)

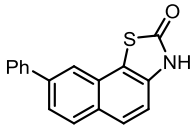
38.4 mg, 83% isolated yield, yellowish solid, Mp: 246-247 °C;



R_f (PE:EA=3:1): 0.39;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.01 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.19 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.29, 156.69, 132.16, 130.96, 126.24, 124.55, 122.98, 120.28, 117.88, 113.14, 108.06, 55.68. **IR** (KBr) 3120, 3018, 2926, 2908, 2860, 1664, 1510, 1456, 1350, 1249, 1213, 1130, 804, 740, 660, 594, 536. **HRMS (ESI-)** calcd. for $C_{12}H_9NO_2S^-$ [M-H]$^-$:230.0281, found: 230.0285.

8-phenylnaphtho[2,1-*d*]thiazol-2(3*H*)-one (**2k**)

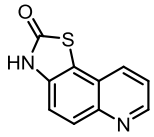


31.0 mg, 56% isolated yield, white solid, Mp: 249-251 °C;

R_f (PE:EA=3:1): 0.52;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.16 (s, 1H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.79 – 7.69 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.29 (m, 2H) **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.56, 139.91, 139.56, 134.37, 130.29, 129.46, 128.85, 128.32, 128.14, 127.60, 127.16, 124.23, 120.30, 117.81, 112.88. IR (KBr) 3134, 3070, 2922, 2850, 2702, 1730, 1591, 1497, 1422, 1342, 1251, 1215, 889, 806, 752, 694, 659, 605, 518. **HRMS (ESI-)** calcd. for $C_{17}H_{11}NOS^-$ [M-H]$^-$: 276.0489, found: 276.0487.

Thiazolo[5,4-*f*]quinolin-2(3*H*)-one (**2l**)

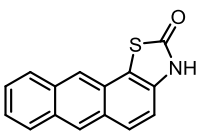


26.7 mg, 66% isolated yield, yellowish solid, Mp: 257-259 °C;

R_f (PE:EA=1:1): 0.45;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.27 (s, 1H), 8.81 (s, 1H), 8.13 – 8.07 (m, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.45 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.52, 149.38, 144.61, 134.16, 131.48, 128.52, 123.31, 122.66, 117.48, 116.04. **IR** (KBr) 3354, 3122, 3068, 2922, 2852, 1672, 1562, 1460, 1367, 1203, 1033, 893, 800, 696, 631, 544, 492. **HRMS (ESI+)** calcd. for $C_{11}H_6N_2OS^+$ $[M+H]^+$: 201.0128, found: 201.0133.

Anthra[2,1-*d*]thiazol-2(3*H*)-one (**4**)

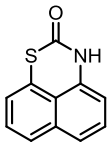


26.1 mg, 52% isolated yield, yellowish solid, Mp: 246-248 °C;

R_f (PE:EA=3:1): 0.37;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.24 (s, 1H), 8.65 (s, 1H), 8.29 (s, 1H), 8.15 – 8.03 (m, 3H), 7.59 – 7.47 (m, 2H), 7.41 (d, J = 8.9 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.67, 133.19, 132.40, 130.59, 128.67, 128.62, 128.37, 128.19, 128.02, 126.93, 126.03, 125.73, 120.53, 115.84, 113.81. **IR** (KBr) 3396, 3047, 2920, 2852, 1710, 1666, 1544, 1458, 1411, 1303, 1201, 864, 770, 735, 632, 540, 466. **HRMS (ESI-)** calcd. for $C_{15}H_9NOS^-$ $[M-H]^-$: 250.0332, found: 250.0342.

Naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (**6a**)

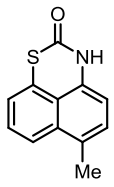


27.0 mg, 67% isolated yield, white solid, Mp: 229-231 °C;

R_f (PE:EA=3:1): 0.39;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.59 (s, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.66 (m, 2H), 7.59 – 7.52 (m, 1H), 7.49 (m, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.64, 131.99, 131.61, 129.03, 127.08, 126.26, 123.10, 122.20, 120.74, 120.54, 118.63. **IR** (KBr) 3429, 3143, 3060, 2918, 2846, 1662, 1514, 1463, 1398, 1200, 1083, 1046, 955, 829, 766, 694, 590, 550. **HRMS (ESI-)** calcd. for $C_{11}H_7NOS^-$ $[M-H]^-$: 200.0176, found: 200.0180.

6-methylnaphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (**6b**)

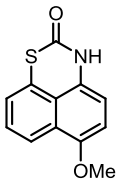


27.5 mg, 64% isolated yield, yellowish solid, Mp: 229-232 °C;

R_f (PE:EA=3:1): 0.51;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.25 – 8.17 (m, 1H), 8.02 – 7.93 (m, 1H), 7.64 – 7.42 (m, 3H), 2.57 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.10, 130.54, 129.84, 128.94, 126.43, 125.80, 125.06, 122.29, 120.35, 120.31, 117.83, 18.94. **IR** (KBr) 3404, 3149, 3072, 2918, 2848, 1672, 1512, 1473, 1436, 1373, 1197, 1093, 887, 835, 760, 694, 663, 569, 499. **HRMS (ESI-)** calcd. for $C_{12}H_9NOS^-$ $[M-H]^-$: 214.0332, found: 214.0334.

6-methoxynaphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (**6c**)



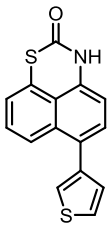
31.9 mg, 69% isolated yield, yellowish solid, Mp: 251-252 °C;

R_f (PE:EA=3:1): 0.45;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.08 (s, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.07 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H). 3.86 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.51, 158.95, 134.47, 131.27, 129.16, 127.25, 124.82, 117.42, 116.27, 110.30, 101.77, 55.87. **IR** (KBr) 3141, 3060, 2958, 2923, 2854,

1659, 1512, 1365, 1201, 1109, 1020, 837, 765, 694, 669, 599, 528. **HRMS (ESI-)** calcd. for $C_{12}H_9NO_2S^-$ [M-H]$^-$: 230.0281, found: 230.0287.

6-(thiophen-3-yl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (**6d**)

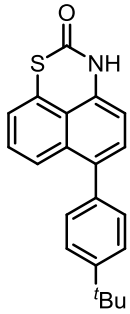


36.2 mg, 64% isolated yield, yellowish solid, Mp: 247-249 °C;

R_f (PE:EA=3:1): 0.53;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.82 – 7.39 (m, 5H), 7.34 – 7.22 (m, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.65, 140.12, 131.47, 130.10, 129.94, 129.82, 127.06, 126.80, 126.62, 124.65, 122.68, 121.46, 120.72, 118.50. **IR** (KBr) 3143, 3074, 2922, 2851, 1666, 1614, 1571, 1512, 1465, 1409, 1325, 1169, 1109, 1064, 1014, 839, 760, 694, 656, 611, 545. **HRMS (ESI-)** calcd. for $C_{15}H_8NOS_2^-$ [M-H]$^-$:282.0053, found: 282.0050.

6-(4-(tert-butyl)phenyl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (**6e**)

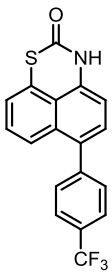


37.4 mg, 56% isolated yield, yellowish solid, Mp: 228-230 °C;

R_f (PE:EA=3:1): 0.53;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 8.29 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.35 – 7.29 (m, 2H), 1.30 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.65, 150.19, 136.91, 134.97, 131.32, 130.04, 130.00, 126.99, 126.75, 126.47, 125.66, 122.67, 121.33, 120.74, 118.54, 34.75, 31.57. **IR** (KBr) 3404, 3149, 3072, 2918, 2848, 1672, 1512, 1473, 1436, 1373, 1197, 1093, 887, 835, 760, 694, 663, 569, 499. **HRMS (ESI-)** calcd. for $C_{21}H_{19}NOS^-$ [M-H]$^-$: 332.1115, found: 332.1121.

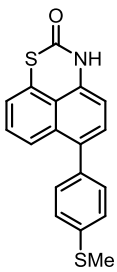
6-(4-(trifluoromethyl)phenyl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (**6f**)



39.4mg, 57% isolated yield, c yellowish solid, Mp: 263-265 °C;

R_f (PE:EA=3:1): 0.53;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.74 (s, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.76 – 7.60 (m, 5H), 7.51 (m, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.65 , 144.11, 133.34, 132.08, 131.24, 129.58, 128.40 (q, *J* = 31.3 Hz), 127.21 , 126.92 , 126.27, 124.76 (q, *J* = 273.71 Hz), 125.78 (q, *J* = 3.7 Hz), 122.82, 121.82, 120.66, 118.51. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -60.89. IR (KBr) 3394, 2958, 2922, 2852, 1730, 1653, 1595, 1498, 1461, 1379, 1340, 1256, 1090, 887, 806, 754, 656, 609. **HRMS (ESI-)** calcd. for $C_{18}H_9NOS^-$ [M-H]$^-$: 344.0362, found: 344.0366.



6-(4-(methylthio)phenyl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (**6g**)

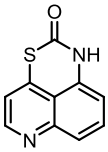
44.0 mg, 68% isolated yield, yellowish solid, Mp: 263-265 °C;

R_f (PE:EA=3:1): 0.43;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.65 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.55 (t, 2H), 7.44 (t, 1H), 7.33 (t, 4H), 2.48 (d, *J* = 9.5 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 171.66, 137.95, 136.24, 134.44, 131.45, 130.84, 129.93, 127.02, 126.59, 126.53, 126.20, 122.72, 121.35, 120.75, 118.55, 15.03. IR (KBr) 3147, 3064,

2918, 2846, 1672, 1510, 1469, 1406, 1329, 1196, 1028, 887, 833, 758, 692, 663, 569, 496. **HRMS (ESI-)** calcd. for $C_{18}H_{12}NOS_2^-$ $[M-H]^-$: 322.0366, found: 332.0368.

[1,3]thiazino[6,5,4-*de*]quinolin-2(1*H*)-one (**6h**)

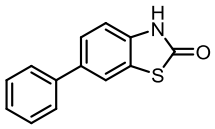


21.0 mg, 52% isolated yield, yellowish solid, Mp: 257-259 °C;

R_f (PE:EA=1:1): 0.32;

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.26 (s, 1H), 7.99 – 7.81 (m, 3H), 7.58 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.52, 149.38, 144.61, 134.16, 131.48, 128.52, 123.31, 122.66, 117.48, 116.04. **IR** (KBr) 3338, 3112, 3069, 2934, 1674, 1562, 1460, 1367, 1203, 1033, 893, 800, 706, 631, 544, 499. **HRMS (ESI+)** calcd. for $C_{11}H_6N_2OS^+$ $[M+H]^+$: 201.0128, found: 201.0125.

6-phenylbenzo[*d*]thiazol-2(3*H*)-one (**8a**)

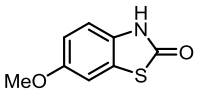


20.8 mg, 46% isolated yield, yellowish solid;

R_f (PE:EA=3:1): 0.42;

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.97 (s, 1H), 7.91 (d, *J* = 1.8 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.58 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.45 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.51, 139.96, 136.20, 135.34, 129.38, 127.64, 126.86, 125.52, 124.64, 121.26, 112.23. **HRMS (ESI-)** calcd. for $C_{13}H_9NOS^-$ $[M-H]^-$: 226.0332, found: 226.0329.

6-methoxybenzo[*d*]thiazol-2(3*H*)-one (**8b**)

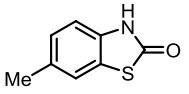


13.1 mg, 36% isolated yield, yellowish solid;

R_f (PE:EA=5:1): 0.42;

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H), 7.23 (d, *J* = 2.6 Hz, 1H), 7.01 (d, *J* = 8.7 Hz, 1H), 6.86 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.19, 155.63, 130.29, 124.75, 113.65, 112.54, 108.14, 56.00. **HRMS (ESI-)** calcd. for $C_8H_7NO_2S^-$ $[M-H]^-$: 181.0197, found: 181.0202.

6-methylbenzo[*d*]thiazol-2(3*H*)-one (**8c**)

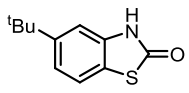


12.8 mg, 39% isolated yield, yellowish solid;

R_f (PE:EA=5:1): 0.42;

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.76 (s, 1H), 7.36 (s, 1H), 7.08 (ddd, *J* = 8.1, 1.7, 0.6 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 2.29 (s,3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.36, 134.38, 132.24, 127.55, 123.66, 123.09, 111.64, 21.07. **HRMS (ESI-)** calcd. for $C_8H_7NOS^-$ $[M-H]^-$: 164.0176, found:164.0180.

5-(*tert*-butyl)benzo[*d*]thiazol-2(3*H*)-one (**8d**)



20.7 mg, 50% isolated yield, yellowish solid;

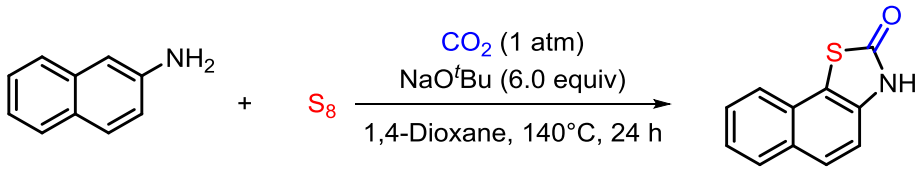
R_f (PE:EA=5:1): 0.42;

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.13 (d, *J* = 10.1 Hz, 1H), 7.04 (s, 1H), 1.23 (s, 9H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.74, 149.85, 136.62, 122.65, 120.54, 120.44, 108.60, 34.88, 31.52. **HRMS (ESI-)** calcd. for $C_8H_7NO_2S^-$ $[M-H]^-$: 206.0645, found:206.0649.

4 Mechanistic Studies or Investigation of the Mechanism

4.1 Control Experiments

Table S2 Control Experiments[a]

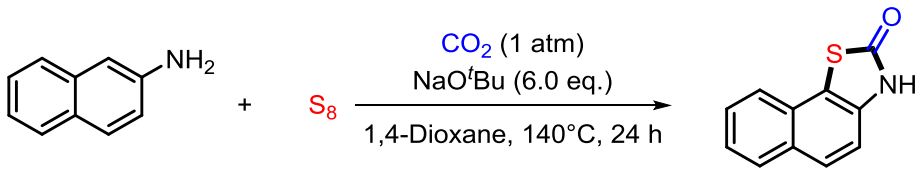


1a, 0.2 mmol (4.0 eq.) 32 mg/mmol **2a**

entry	variation from the standard conditions	yield (%)[b]
1	None	87%
2	without S_8	N.D.
3	Under N_2	N.D.
4	2.0 eq NaO^{t}Bu	N.D.

[a]**1a** (0.2 mmol), **S_8** (25.6 mg, 0.8 mmol, 4.0 eq, 32 mg/mmol), NaO^{t}Bu (1.2 mmol, 6.0 eq), 1 atm of CO_2, 1.0 mL of 1,4-dioxane (0.2 M) at 140 °C for 24 h. isolated yields. N.D. = Not detected.

4.2 Radical Inhibition Experiment

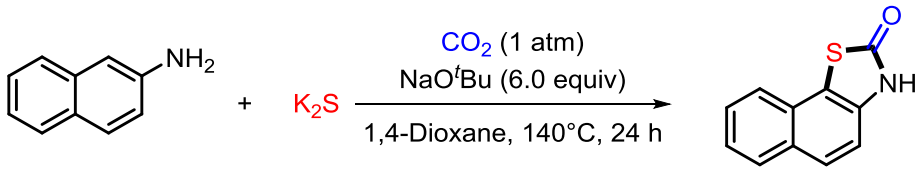


1a, 0.2 mmol (4.0 eq.) 32 mg/mmol **2a**

entry	variation from the standard conditions	yield (%)[b]
1	None[a]	87
2	Adding TEMPO 4.0 eq.	82
6	Adding PhSeSePh 4.0 eq.	80

[a]**1a** (0.2 mmol), **S_8** (25.6 mg, 0.8 mmol, 4.0 eq, 32 mg/mmol), NaO^{t}Bu (1.2 mmol, 6.0 eq), additive (0.8 mmol, 4.0 eq), 1 atm of CO_2, 1.0 mL of 1,4-dioxane (0.2 M) at 140 °C for 24 h. isolated yields.

4.3 Control Experiment with K_2S Instead of S_8



1a, 0.2 mmol (4.0 equiv) **2a,** N.D.

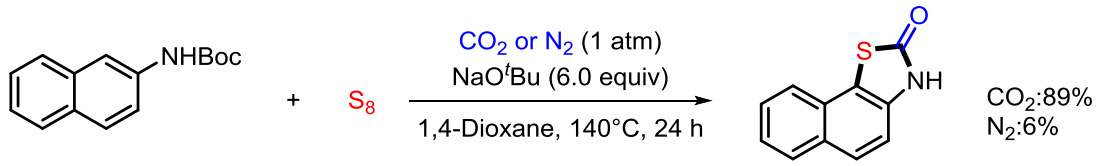
To an oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was added arylamine substrate **1a** (0.20 mmol) and K_2S (0.8 mmol, 4.0 equiv). Then the tube was moved into a

glovebox. NaO^tBu (1.2 mmol, 6.0 equiv) was added to the tube before transferring out of the glovebox and placing under an atmosphere of nitrogen. Then the Schlenk tube was evacuated and back-filled with CO_2. Anhydrous 1,4-dioxane (1 mL) was added via syringe under CO_2 atmosphere. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for 24 h at 140 °C. Then, the mixture was diluted with water (2.0 mL) and detected by ESI-MS.

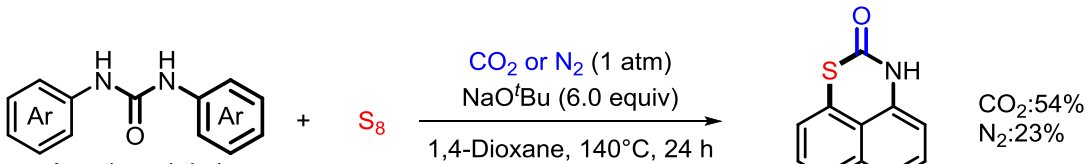
The target product not detected by ESI-MS, the sulfur anion should not be the reaction intermediate.

4.4 Control Experiments with Arylamine Derivatives

To an oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was added arylamine derivative **9, 10, 11 or 12** (0.20 mmol, 1.0 equiv) and elemental sulfur (25.6 mg, 0.8 mmol, 4.0 equiv, 32 mg/mmol). Then the tube was moved into a glovebox. NaO^tBu (1.3 mmol, 6.5 equiv) was added to the tube before transferring out of the glovebox and placing under an atmosphere of nitrogen. Then the Schlenk tube was evacuated and back-filled with CO_2. Anhydrous 1,4-dioxane (1.0 mL) was added via syringe under CO_2 atmosphere or N_2 atmosphere. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for 24 h at 140 °C. Then, the mixture was diluted with water (2.0 mL) and extracted by ethyl acetate (3 mL x 5). The combined organic phase was concentrated *in vacuo* and purified by flash column chromatography (silica: 200–300 mesh, typical eluent: petroleum ether / ethyl acetate = 10:1-5:1) to give the desired product.

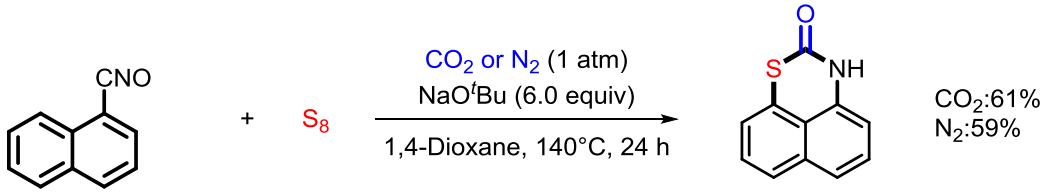


9, 0.2 mmol (4.0 eq.), 32 mg/mmol **2a**

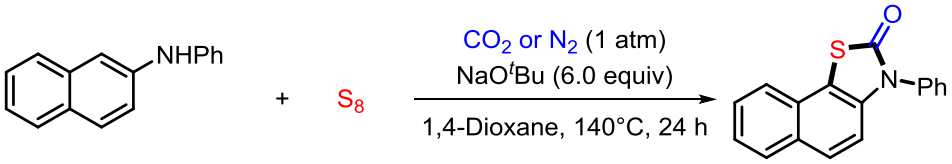


Ar = 1-naphthyl

10, 0.2 mmol (4.0 eq.), 32 mg/mmol **6a**



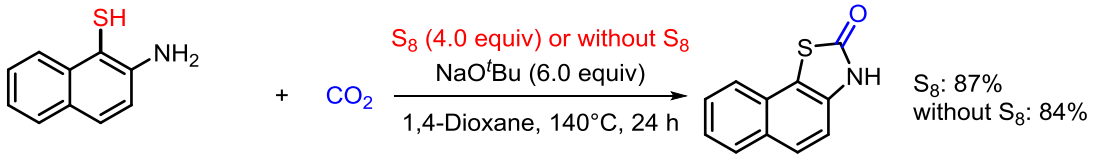
11, 0.2 mmol (4.0 eq.), 32 mg/mmol **6a**



12, 0.2 mmol (4.0 eq.), 32 mg/mmol **13,** N.D.

4.5 Control Experiment with 2-Aminobenzenethiol

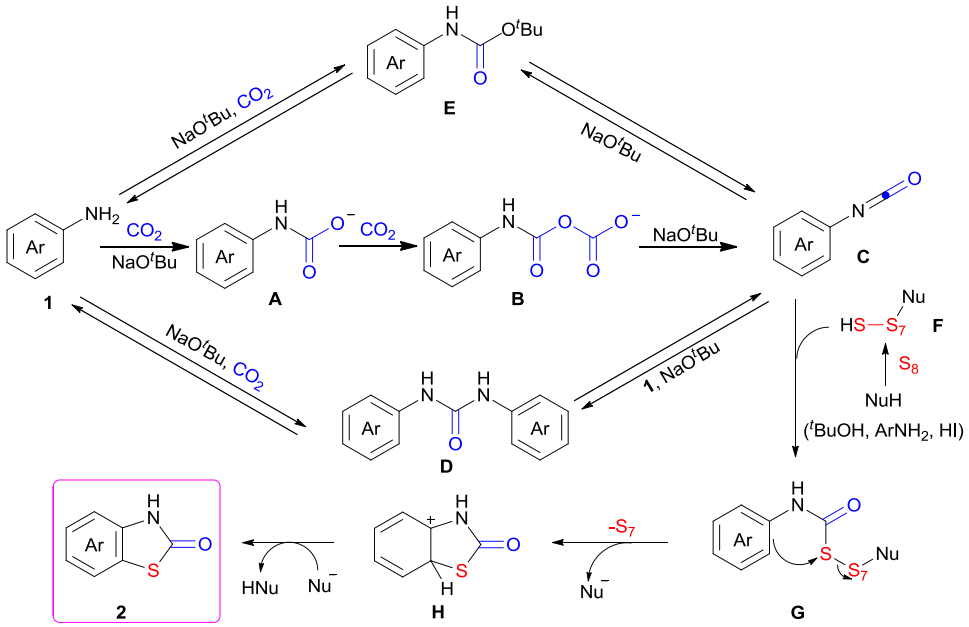
To an oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was added arylamine substrate **14** (0.20 mmol, 1.0 equiv) and S_8 (25.6 mg, 0.8 mmol, 4.0 equiv, 32 mg/mmol) or without S_8. Then the tube was moved into a glovebox. NaO^{t}Bu (1.3 mmol, 6.5 equiv) was added to the tube before transferring out of the glovebox and placing under an atmosphere of nitrogen. Then the Schlenk tube was evacuated and back-filled with CO_2. Anhydrous 1,4-dioxane (1.0 mL) was added via syringe under CO_2 atmosphere or N_2 atmosphere. Once added, the Schlenk tube was sealed at atmospheric pressure of CO_2 (1 atm). The resulting mixture was stirred for 24 h at 140 °C. Then, the mixture was diluted with water (2.0 mL) and extracted by ethyl acetate (3 mL x 5). The combined organic phase was concentrated *in vacuo* and purified by flash column chromatography (silica: 200–300 mesh, typical eluent: petroleum ether / ethyl acetate = 10:1-5:1) to give the desired product.

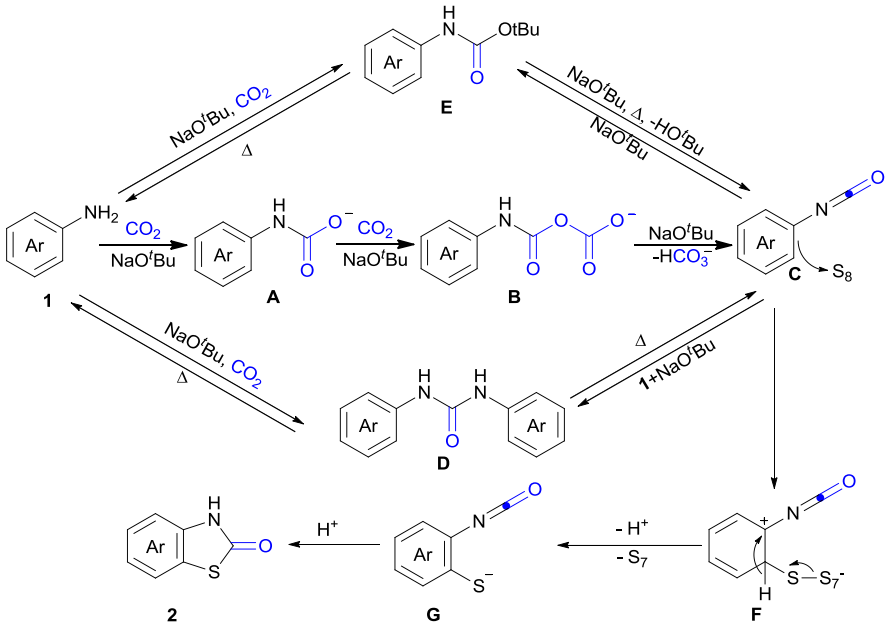


14, 0.2 mmol (1 atm, closed) **2a**

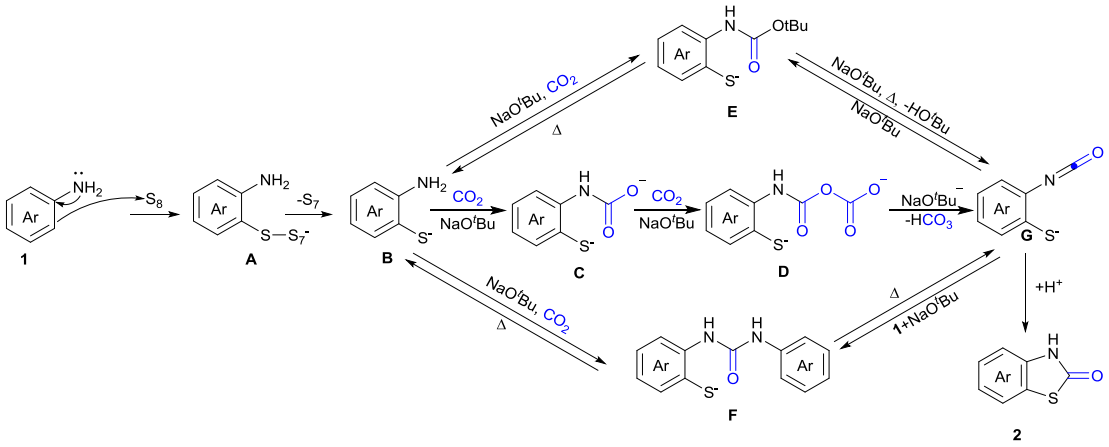
4.6 Proposed mechanism

Based on the results, we proposed there possible pathways. Further mechanistic studies and investigation will be going on in our lab. One possible path is the construct of isocyanate intermediate as the starting step[3].





another possible path is the construction of 2-aminobenzenethiol intermediate as the starting step[4].


Ar
NH2
S8
-S7
S—S7-
1
A
B
CO2
NaO'Bu
C
D
NaO'Bu
-HCO3
G
+H+
2
E
OtBu
NaO'Bu, Δ, -HO'Bu
NaO'Bu, CO2
Δ
F
1+NaO'Bu

5 References

(1) Y. Liang, J. Ji, X. Zhang, Q. Jiang, J. Luo and X. Zhao, *Angew. Chem. Int. Ed*. 2020, **59**, 4959-4964.

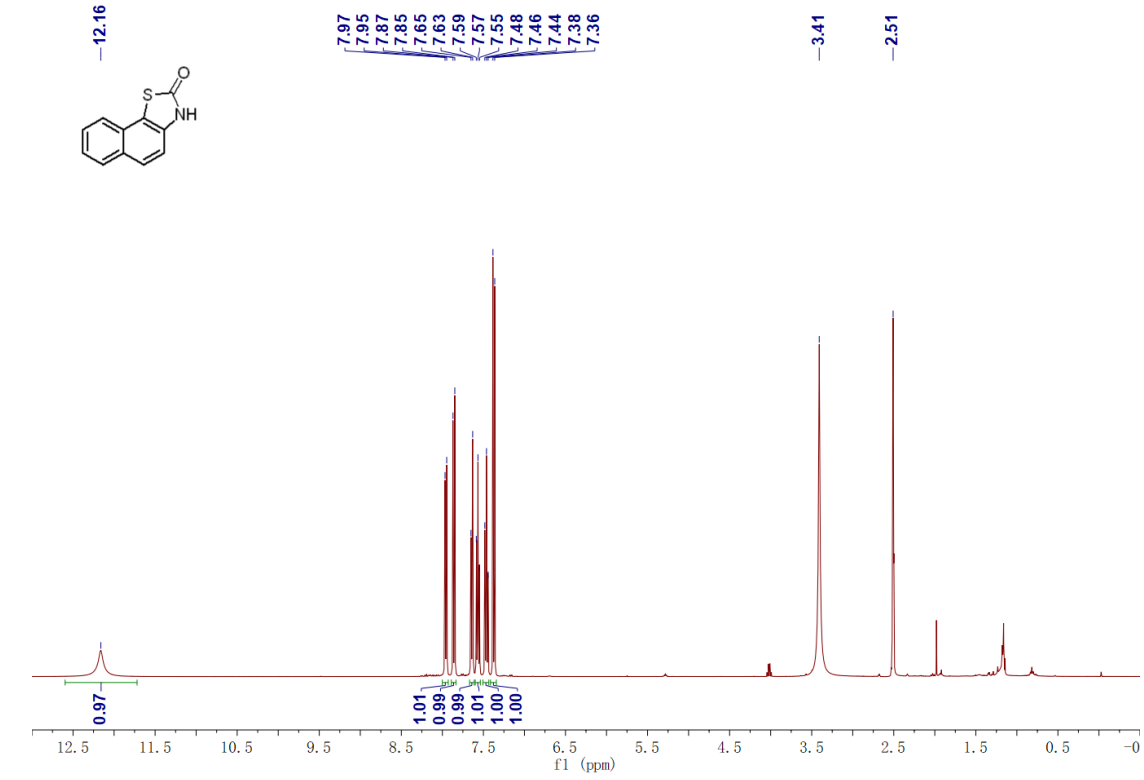
(2) B. Saikia，P. R. Boruah, A. A. Ali and D. Sarma, *Tetrahedron Lett.* 2015, **56**, 633-635.

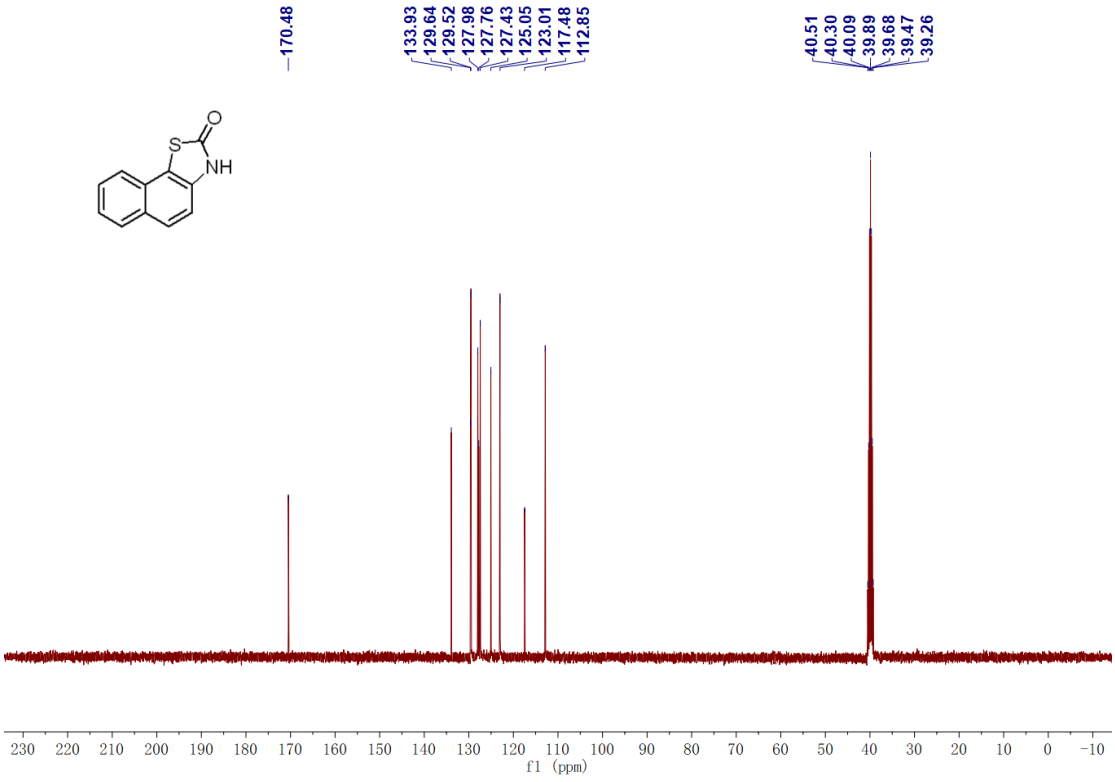
(3) Z. Zhang, L.-L. Liao, S.-S. Yan, L. Wang, Y.-Q. He, J.-H. Ye, J. Li, Y.-G. Zhi and D.-G. Yu, *Angew. Chem. Int. Ed.* 2016, **55**, 7068-7072.

(4) (a) L. Meng, T. Fujikawa, M. Kuwayama, Y. Segawa and K. Itami, *J. Am. Chem. Soc.* 2016, **138**, 10351−10355. (b) X. Ma, X. Yu, H. Huang, Y. Zhou and Q. Song, *Org. Lett*. 2020, **22**, 5284-8288.

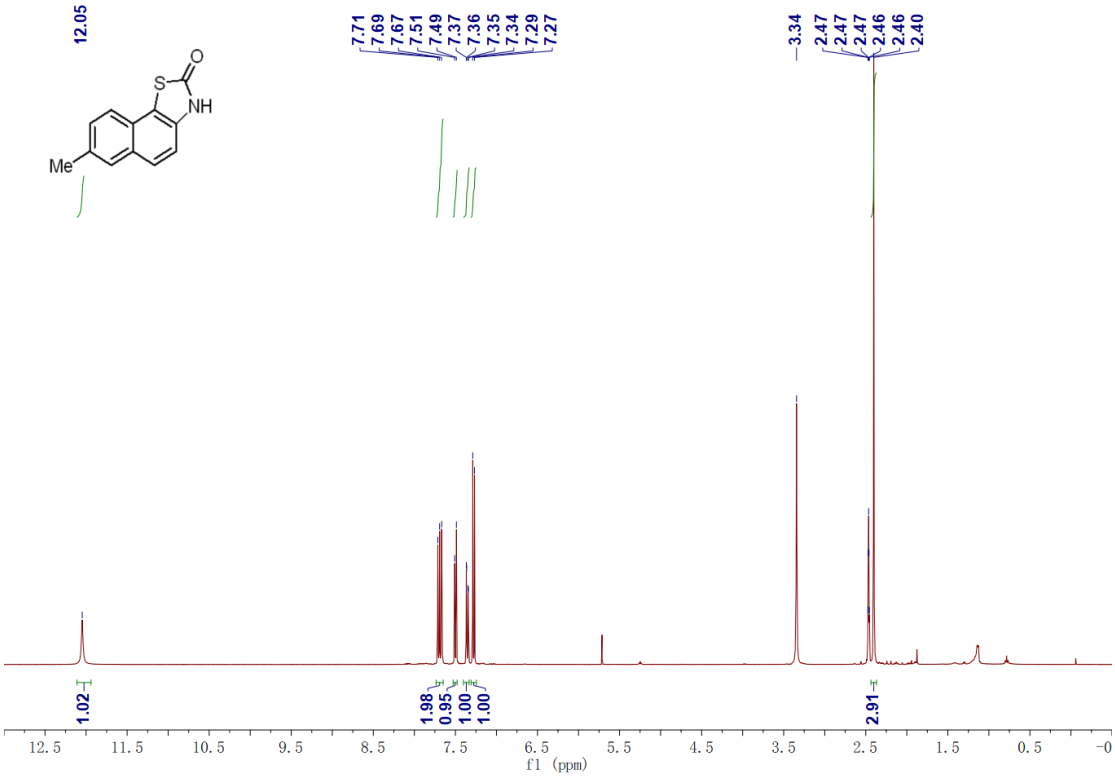
6 NMR Spectra

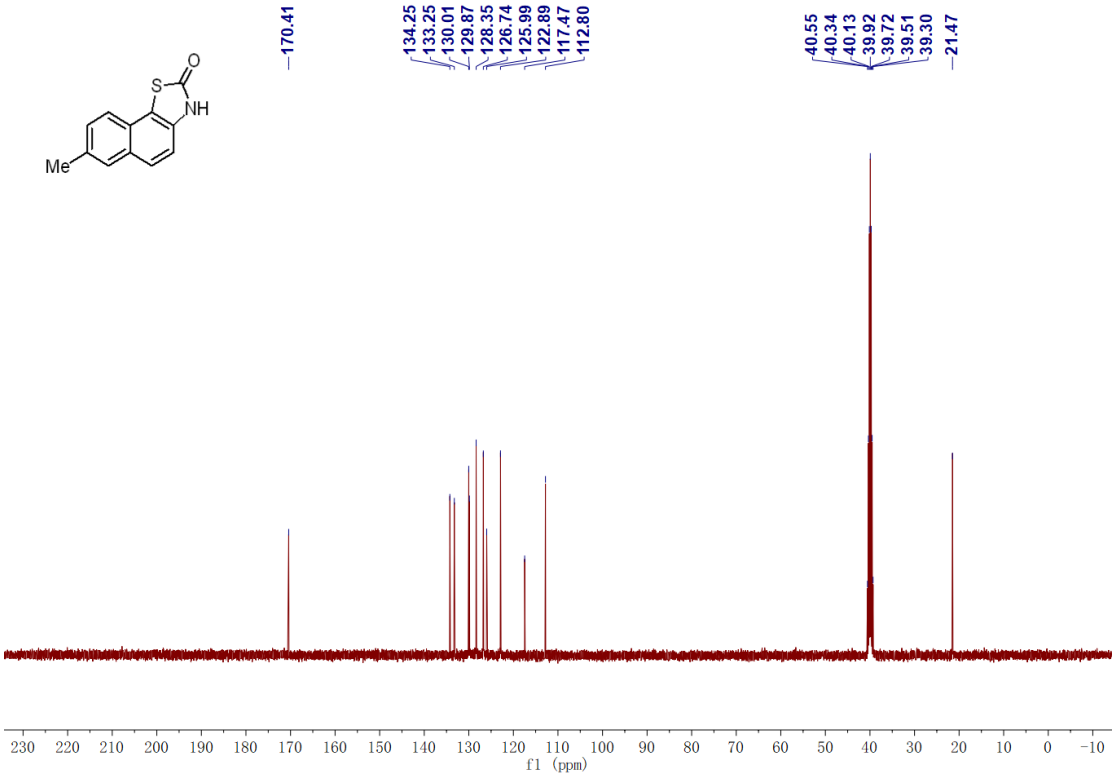
Naphtho[2,1-*d*]thiazol-2(3*H*)-one (2a)



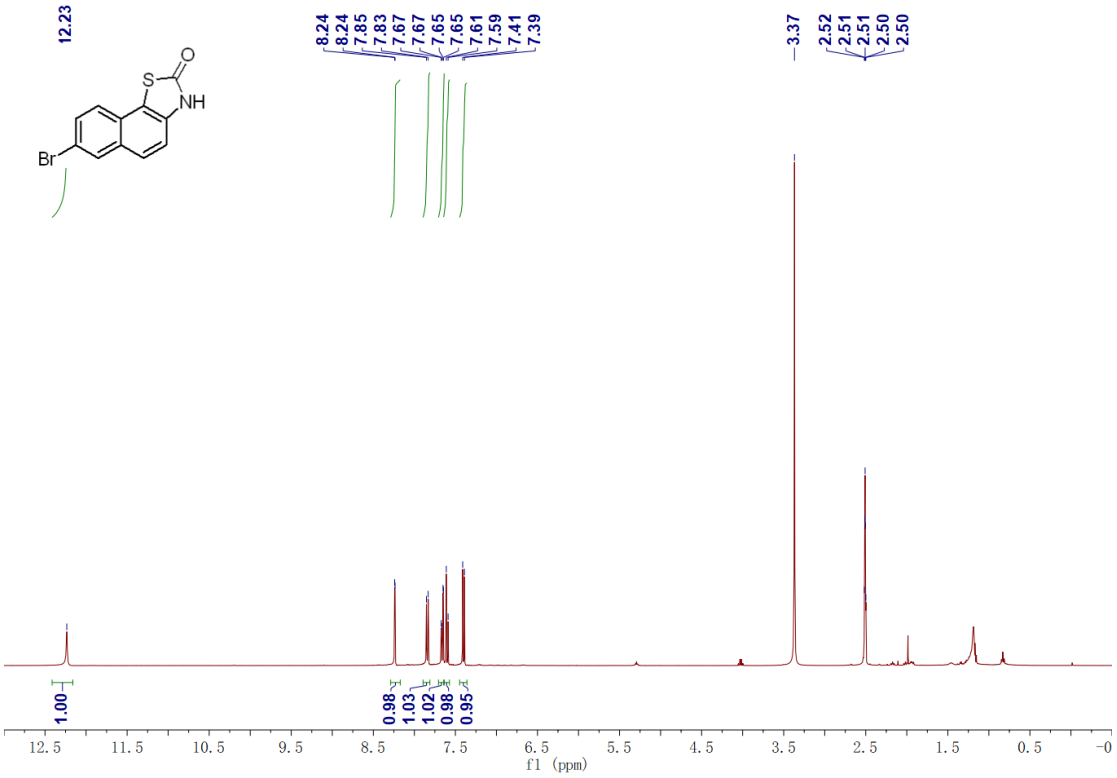


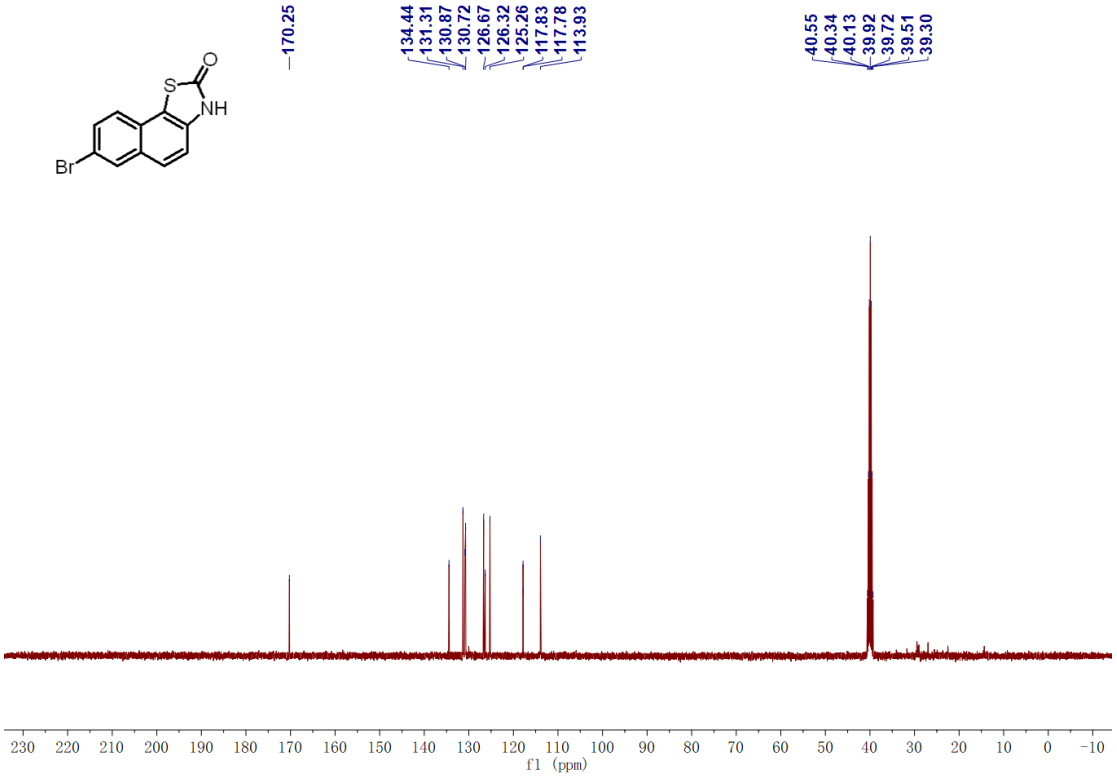
7-methylnaphtho[2,1-*d*]thiazol-2(3*H*)-one (2b)



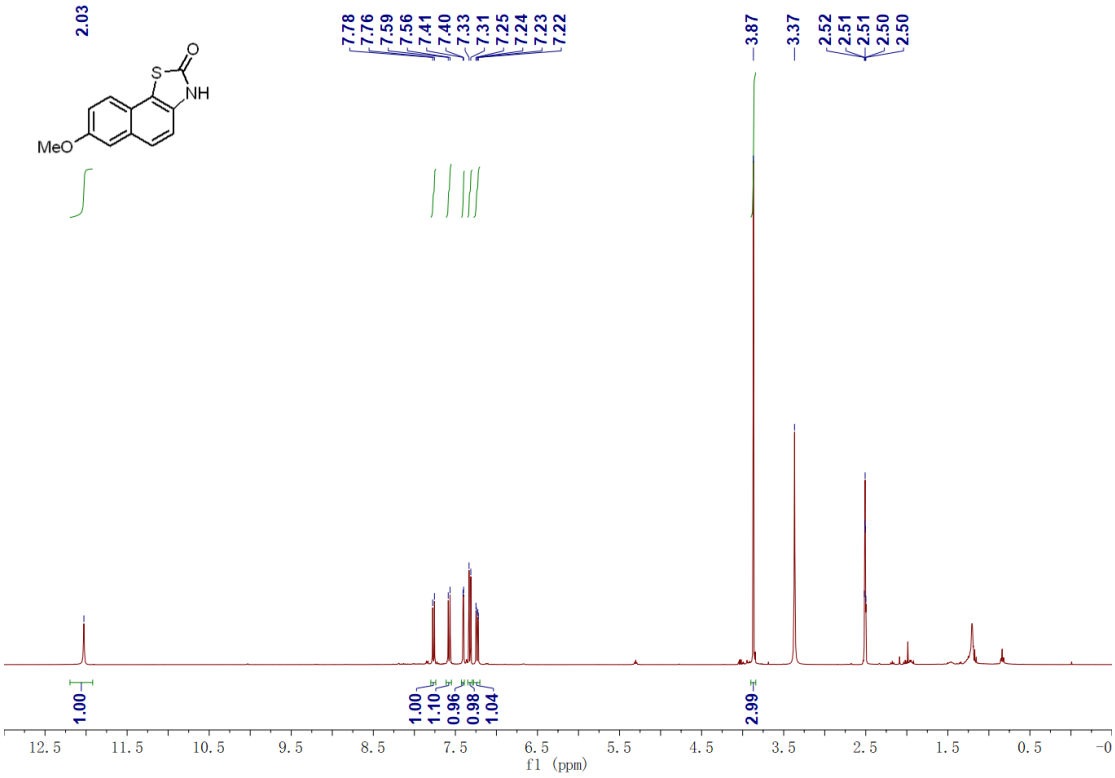


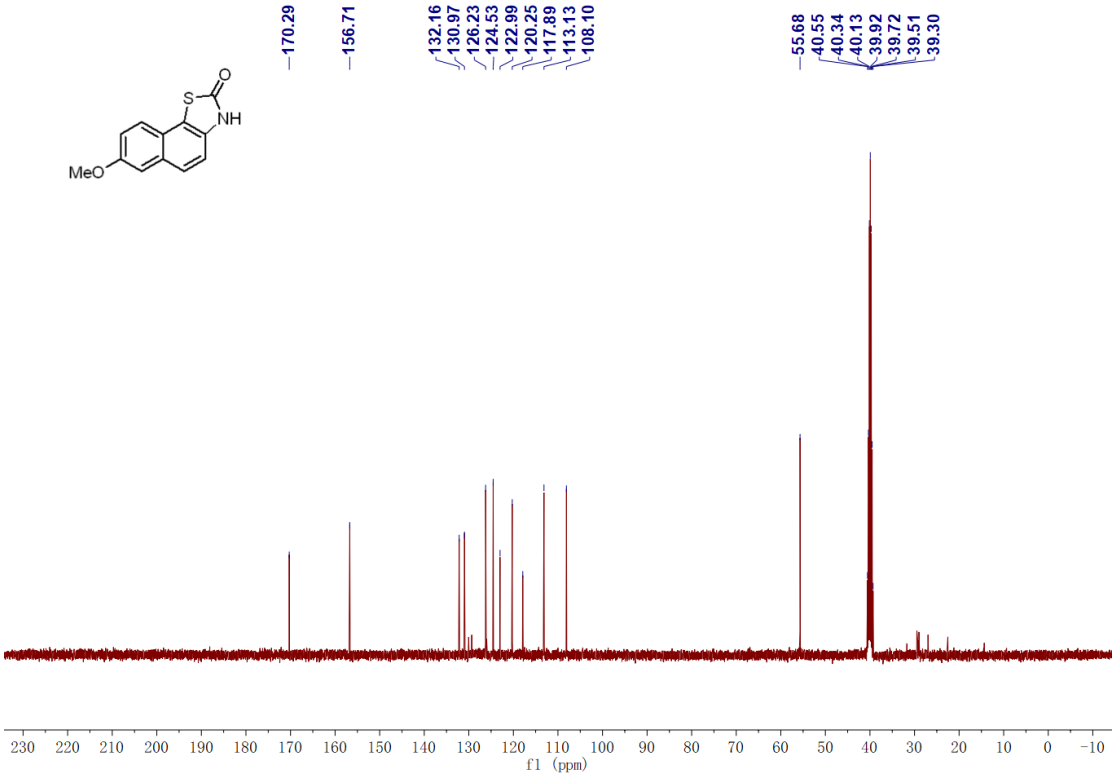
7-bromonaphtho[2,1-*d*]thiazol-2(3*H*)-one (2c)



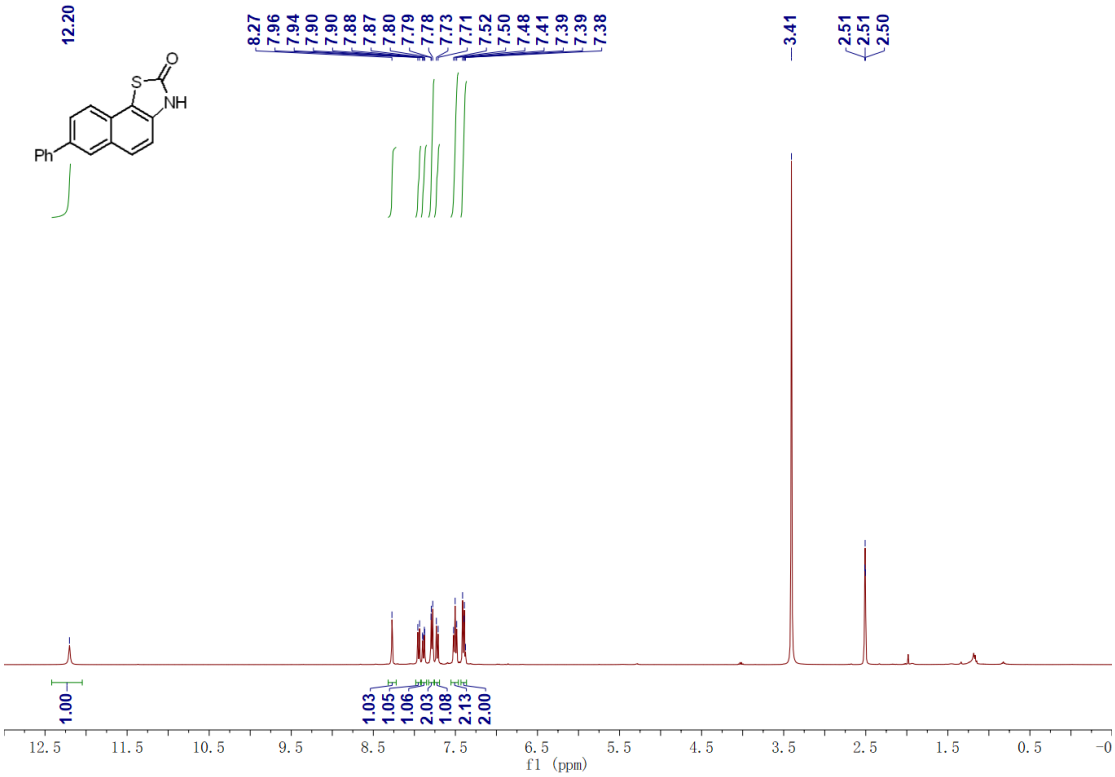


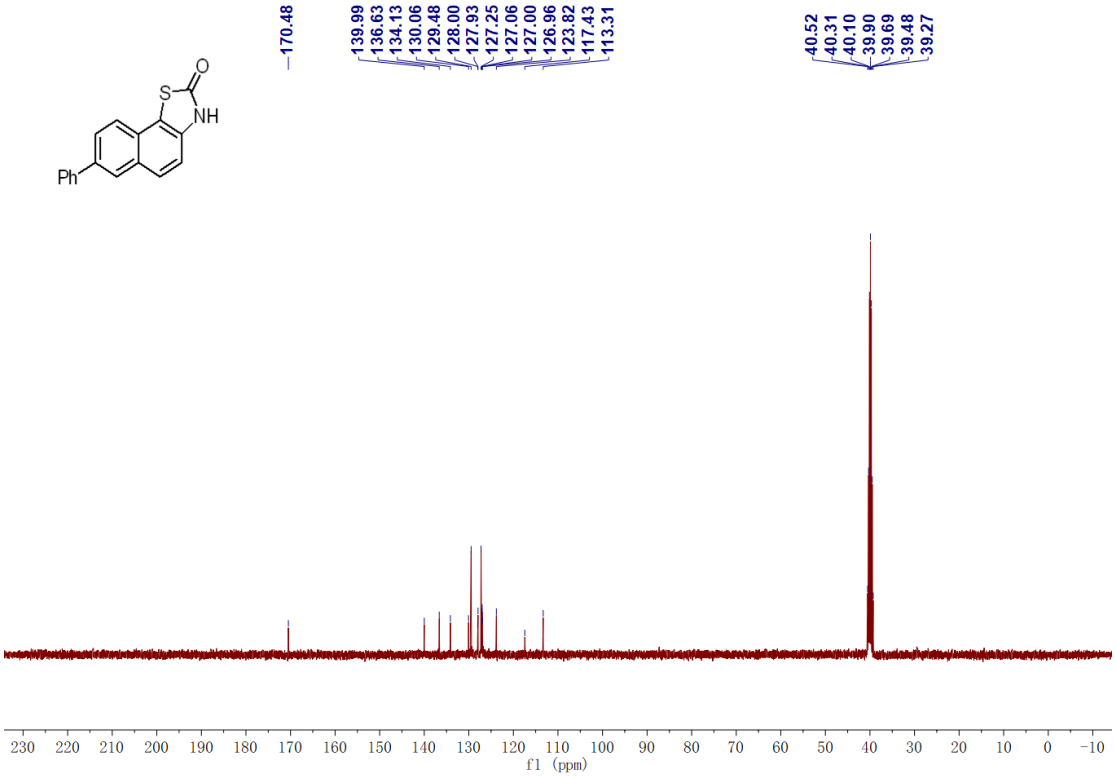
7-methoxynaphtho[2,1-*d*]thiazol-2(3*H*)-one (2d)



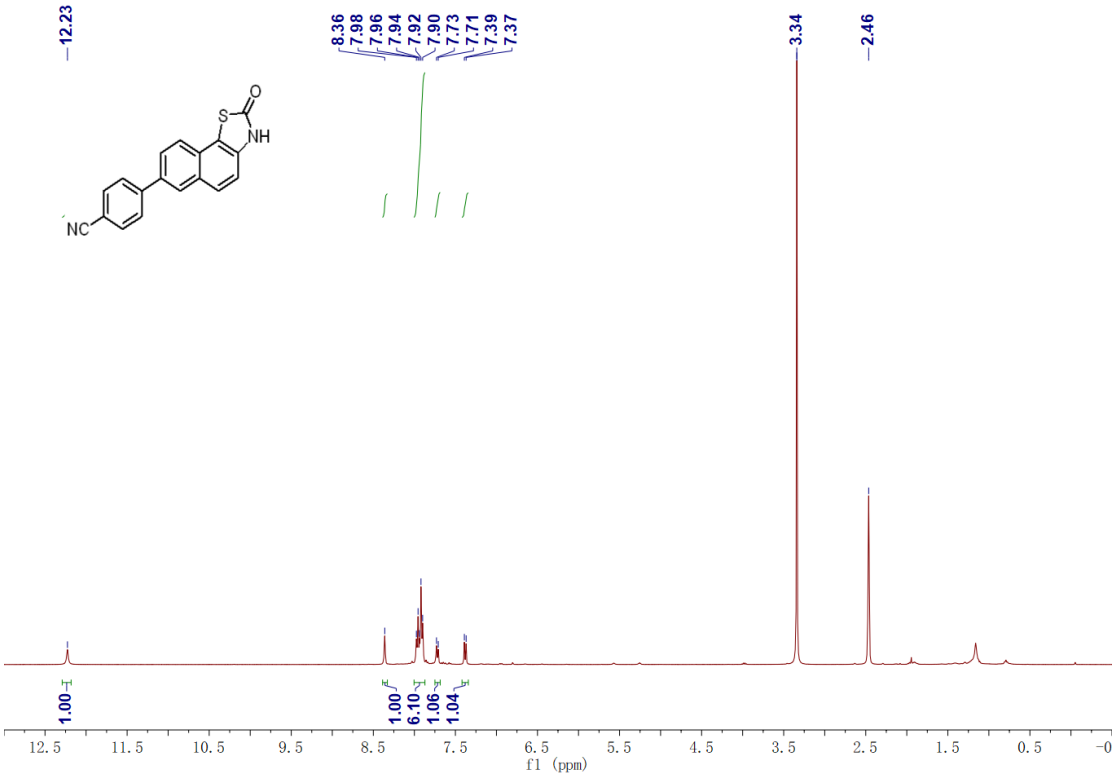


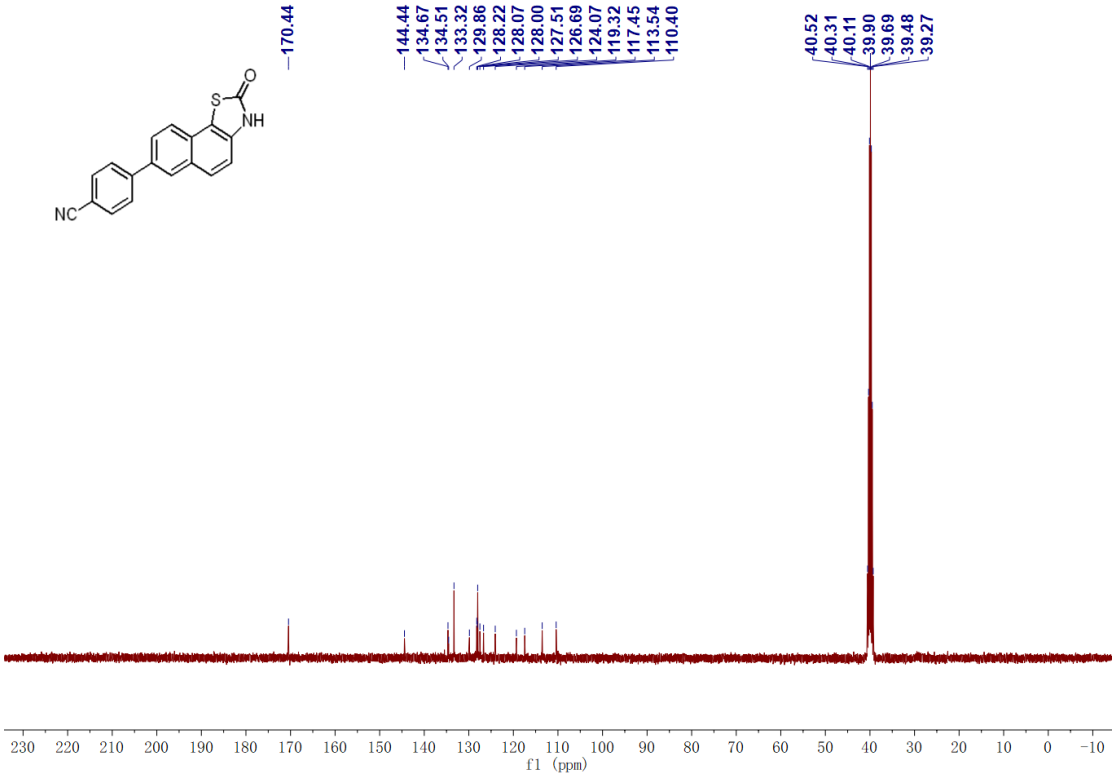
7-phenylnaphtho[2,1-*d*]thiazol-2(3*H*)-one (2e)



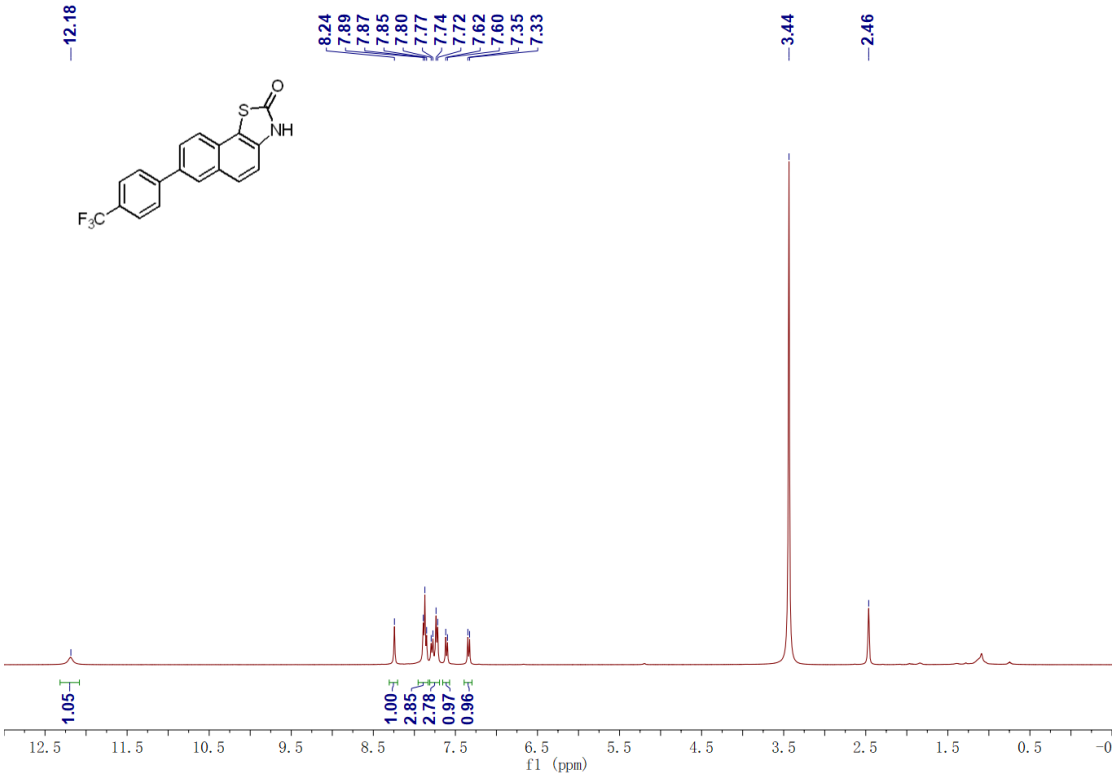


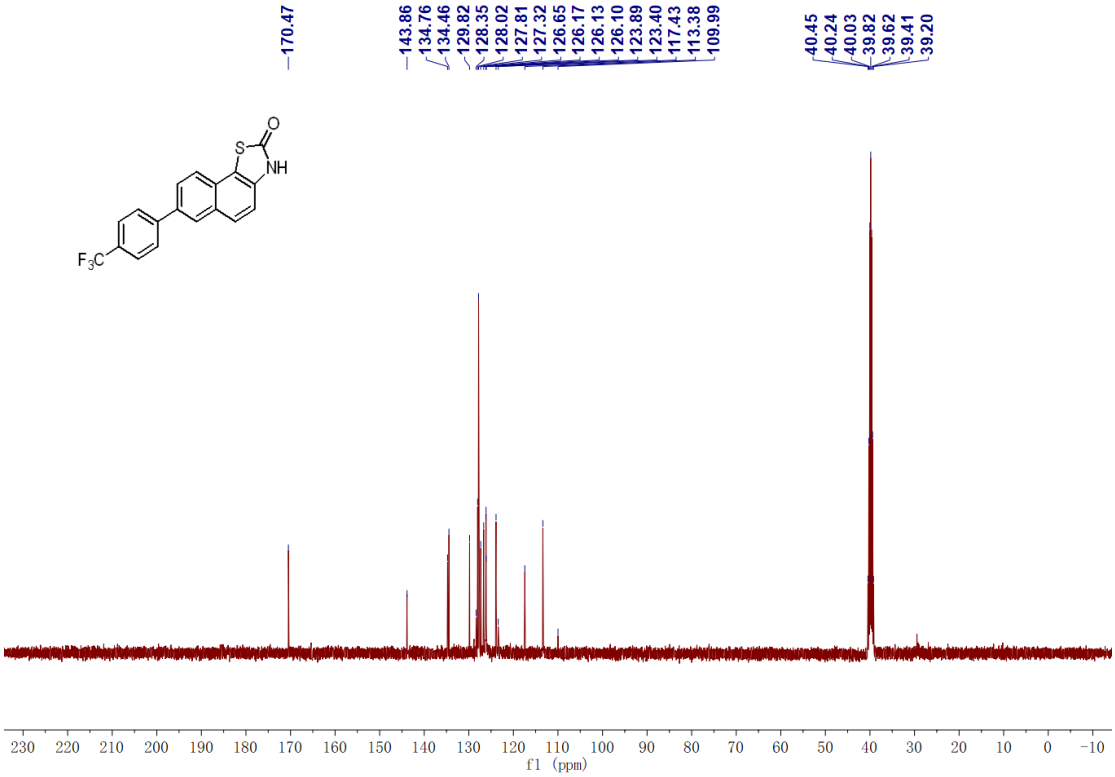
4-(2-oxo-2,3-dihydronaphtho[2,1-*d*]thiazol-7-yl)benzonitrile (2f)

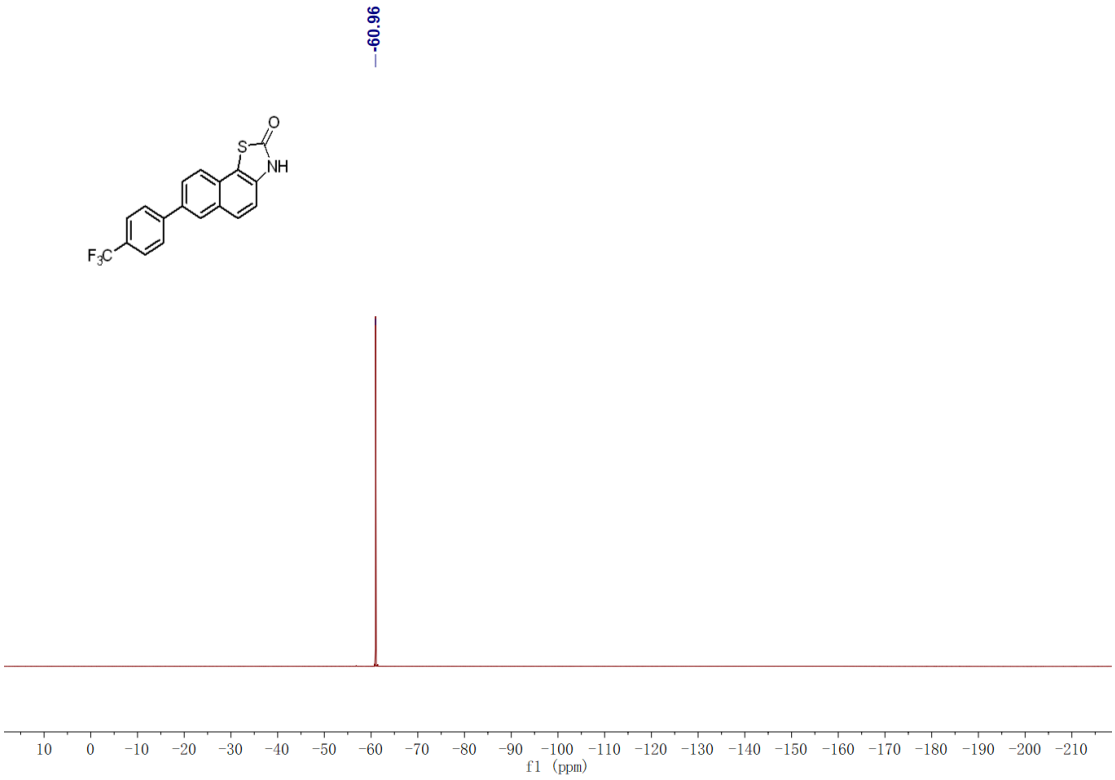




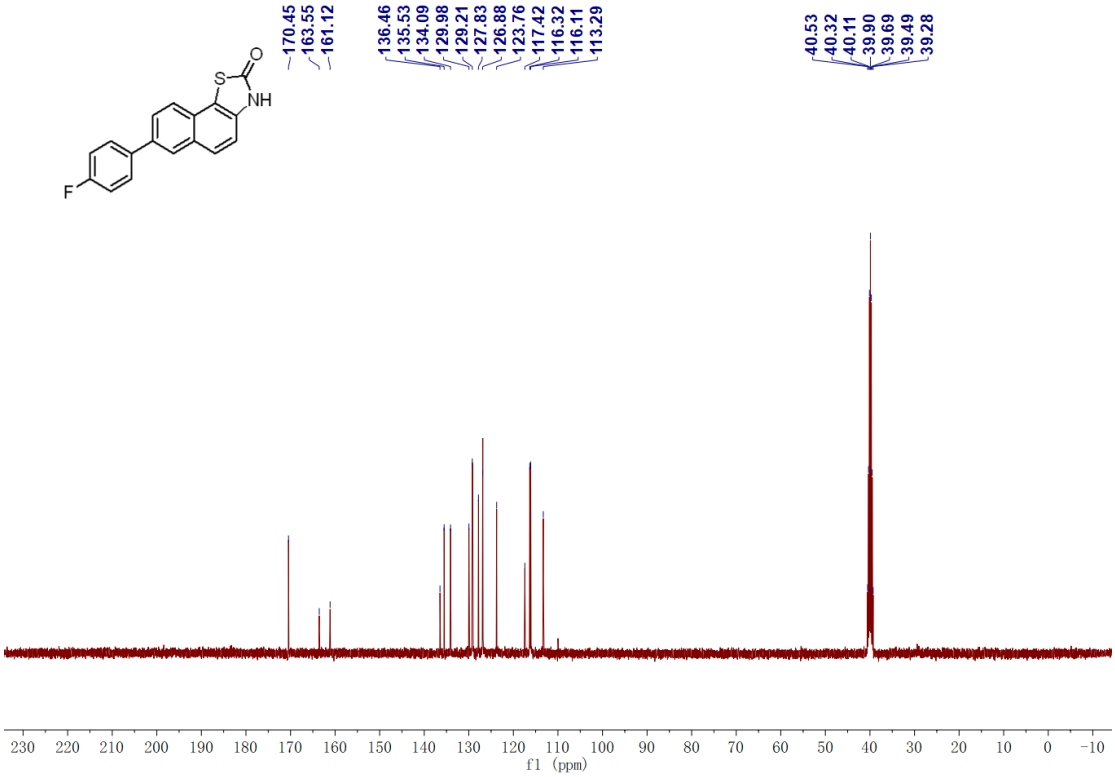
7-(4-(trifluoromethyl)phenyl)naphtho[2,1-*d*]thiazol-2(3*H*)-one (2g)

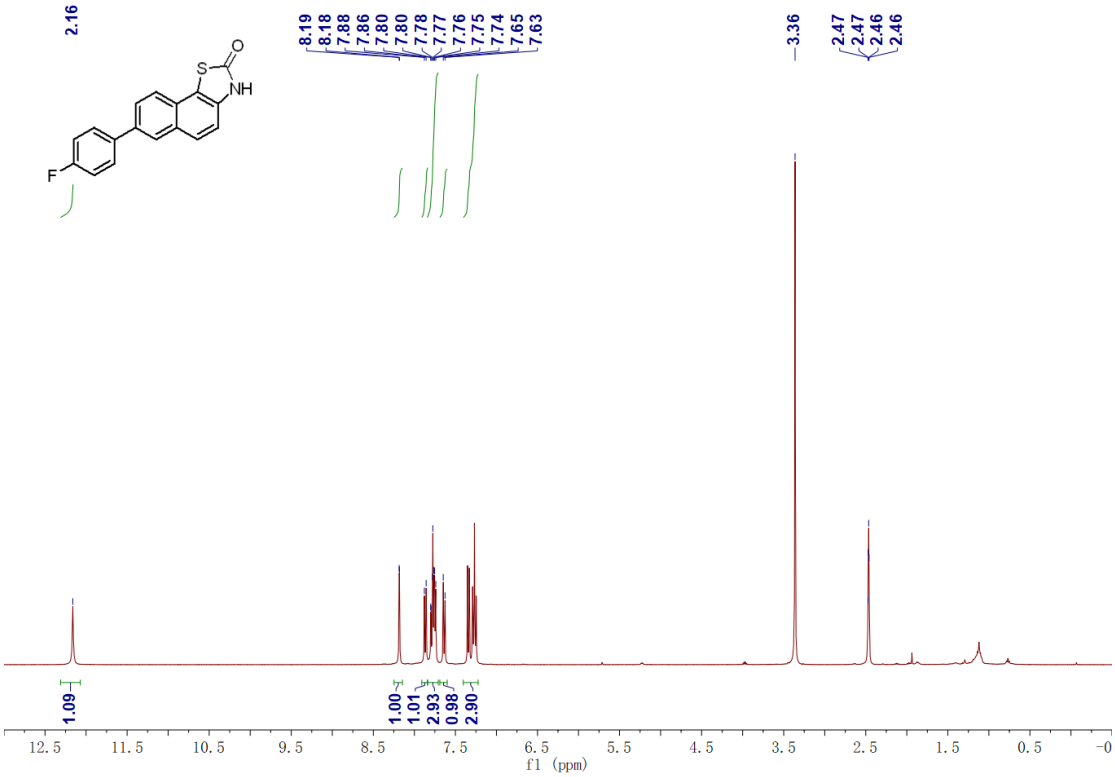


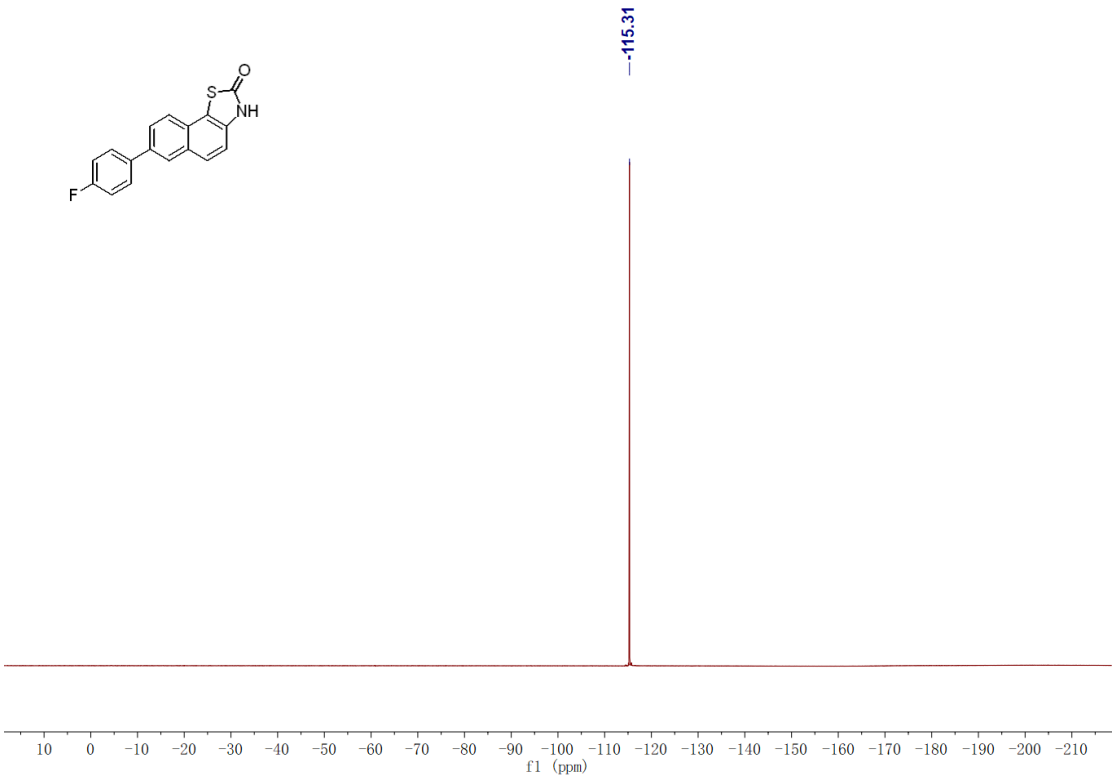



-60.99
O
S
NH
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

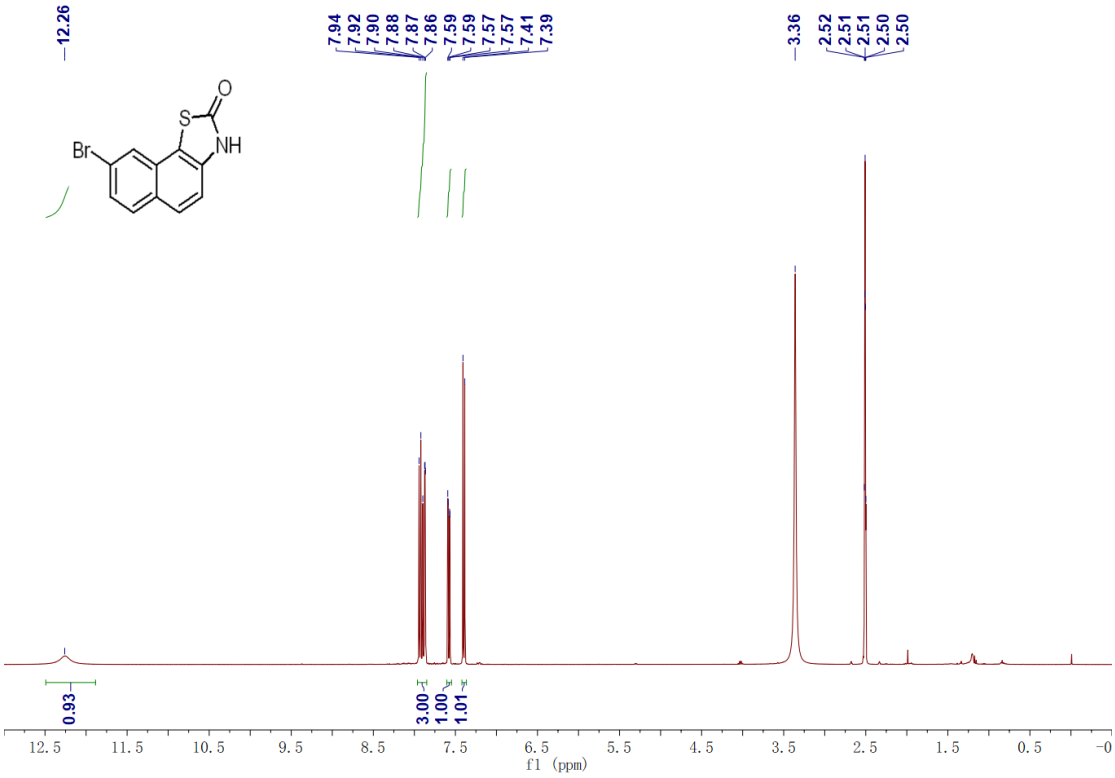
7-(4-fluorophenyl)naphtho[2,1-*d*]thiazol-2(3*H*)-one (2h)

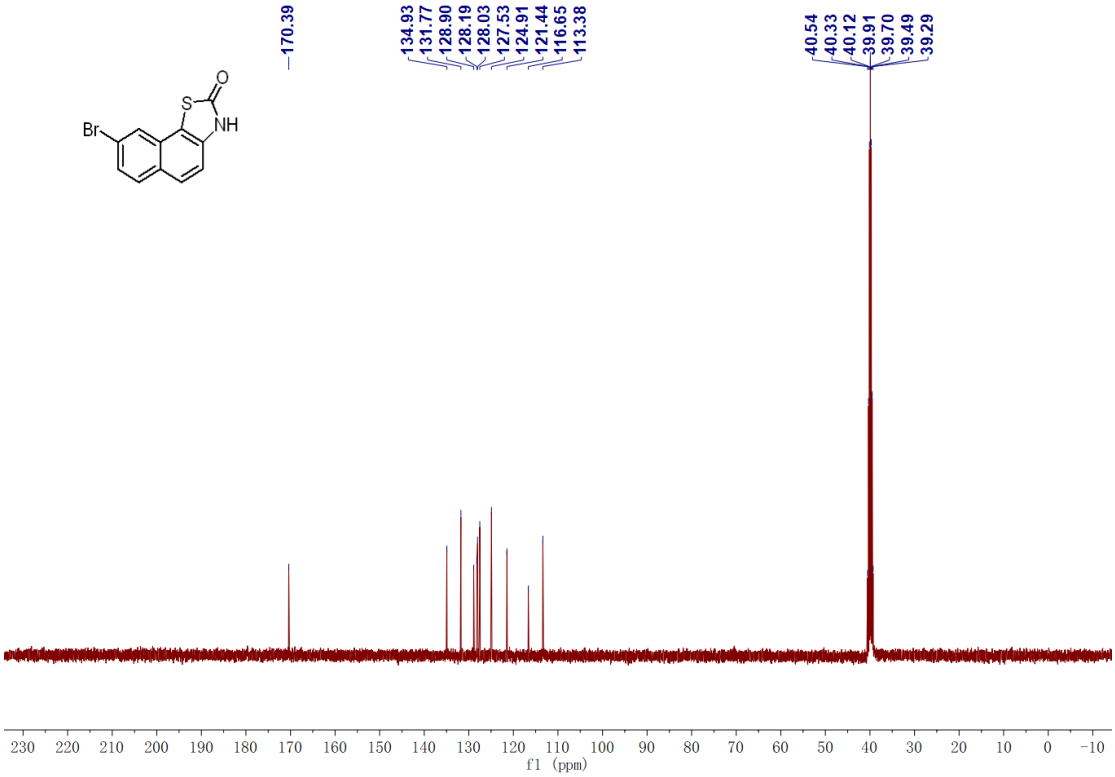




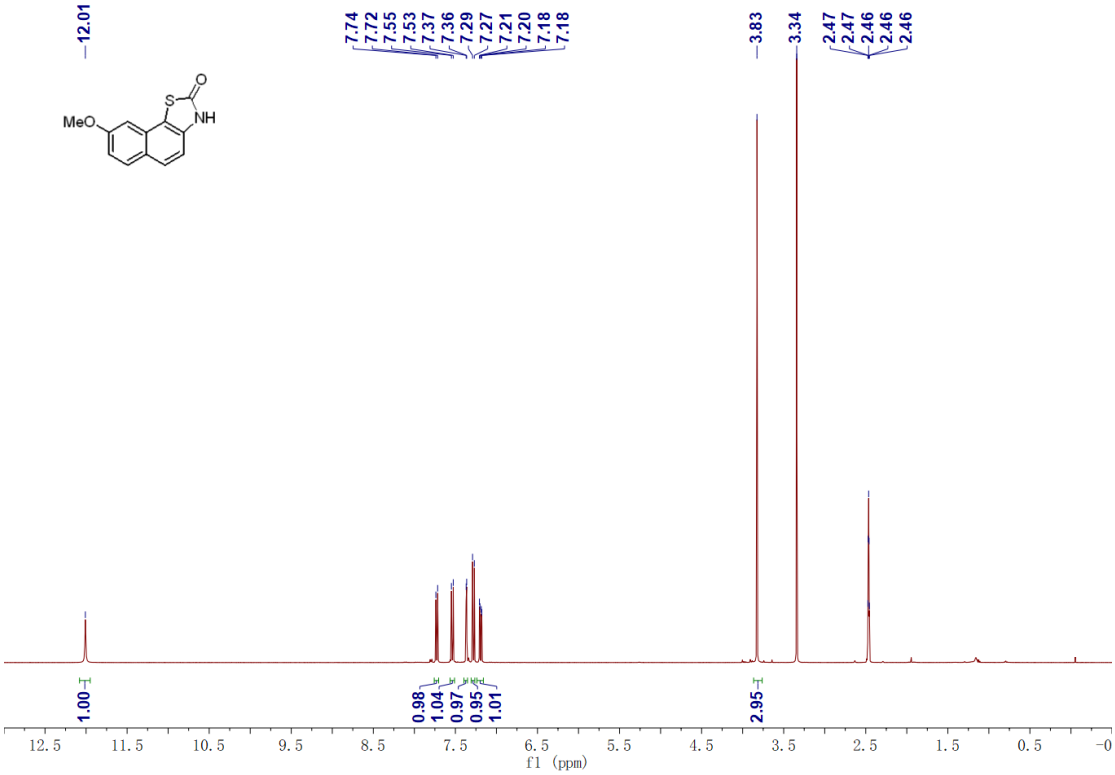

-115.31
O
S
NH
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

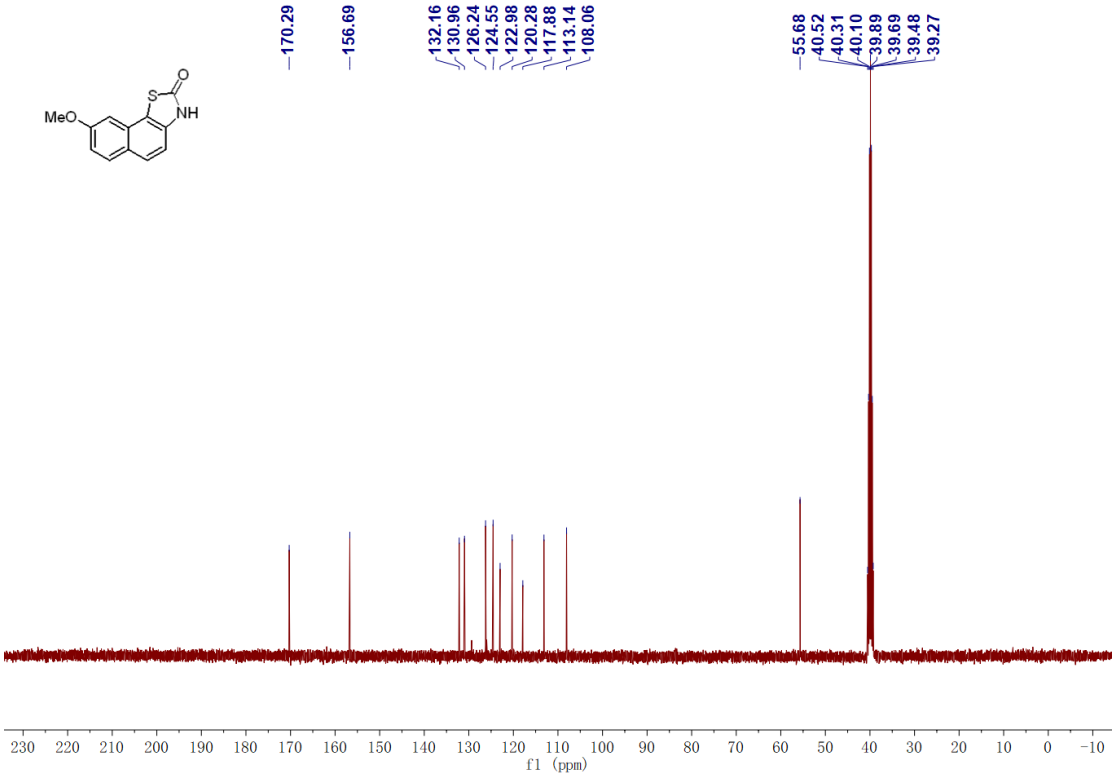
8-bromonaphtho[2,1-*d*]thiazol-2(3*H*)-one (2i)



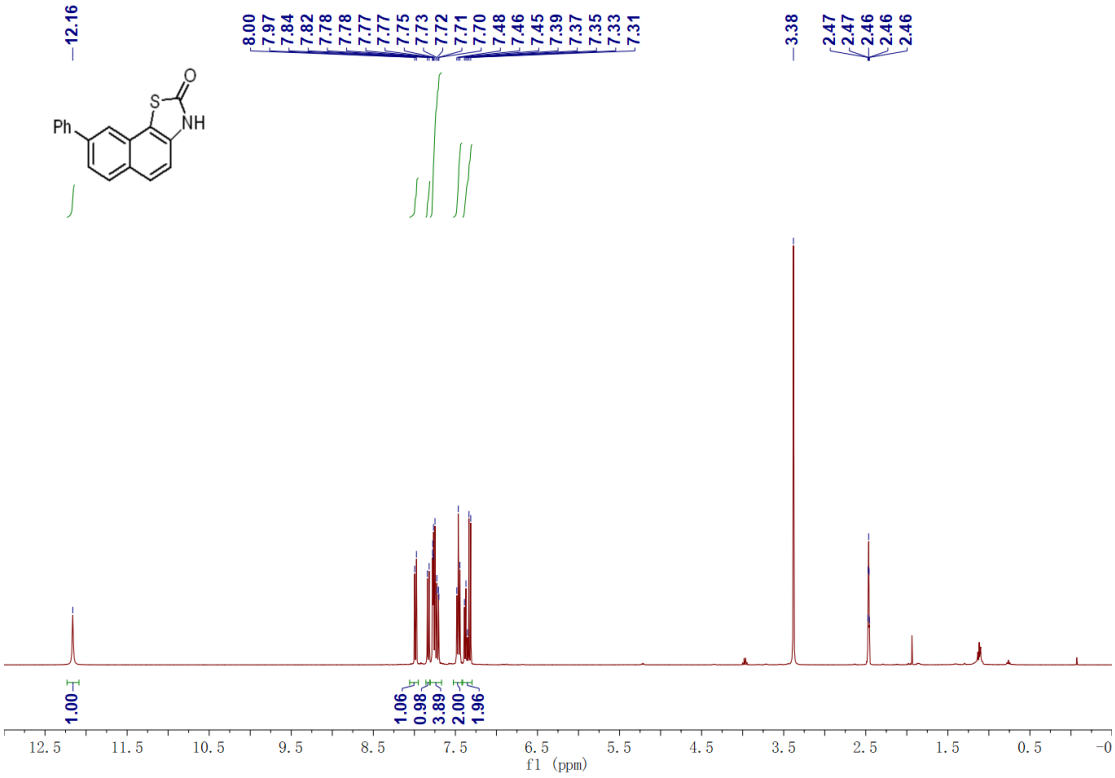


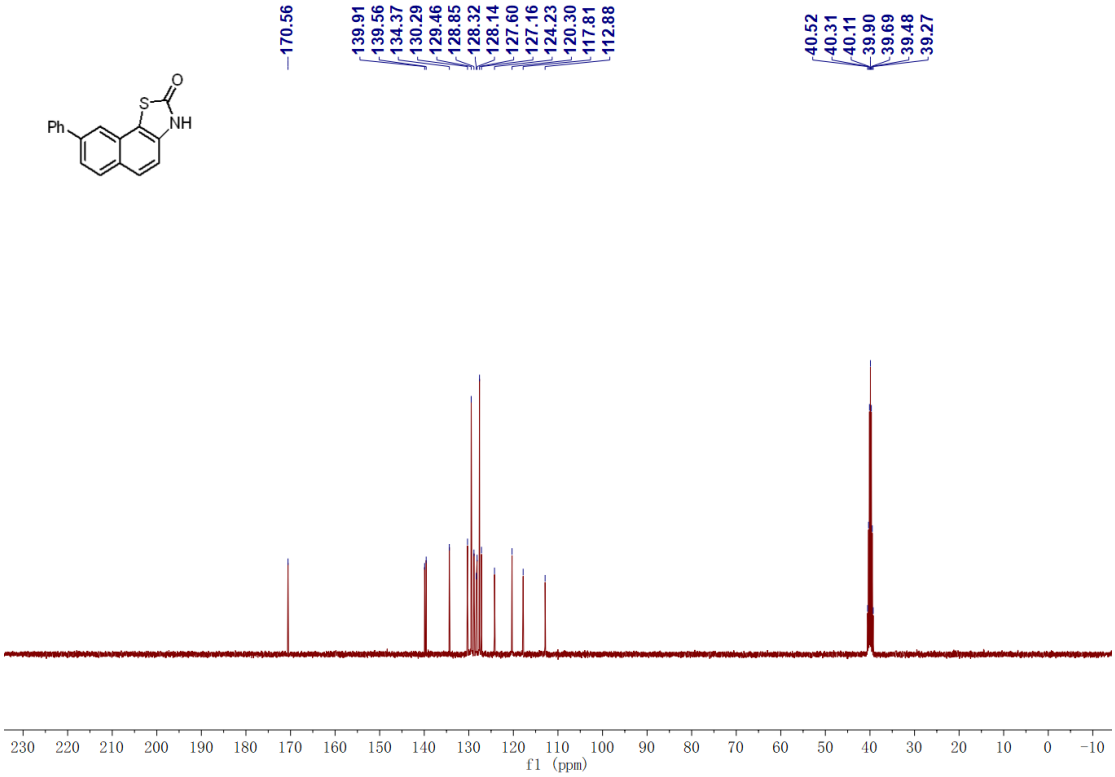
8-methoxynaphtho[2,1-*d*]thiazol-2(3*H*)-one (2j)



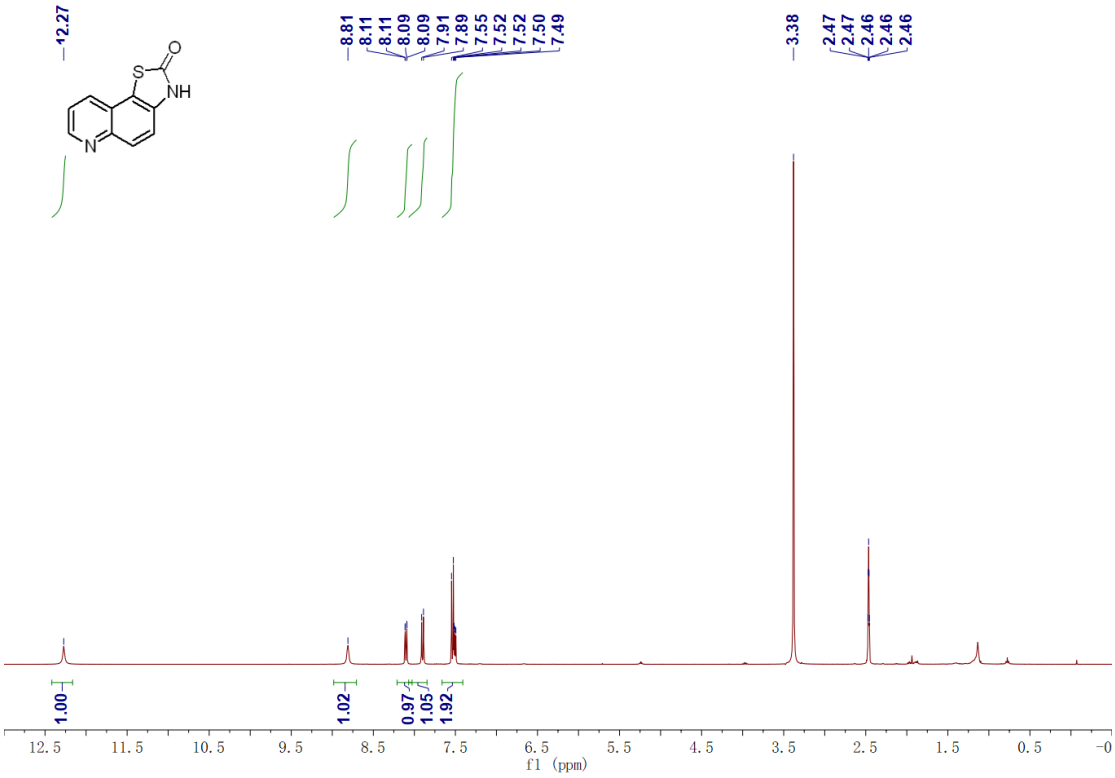


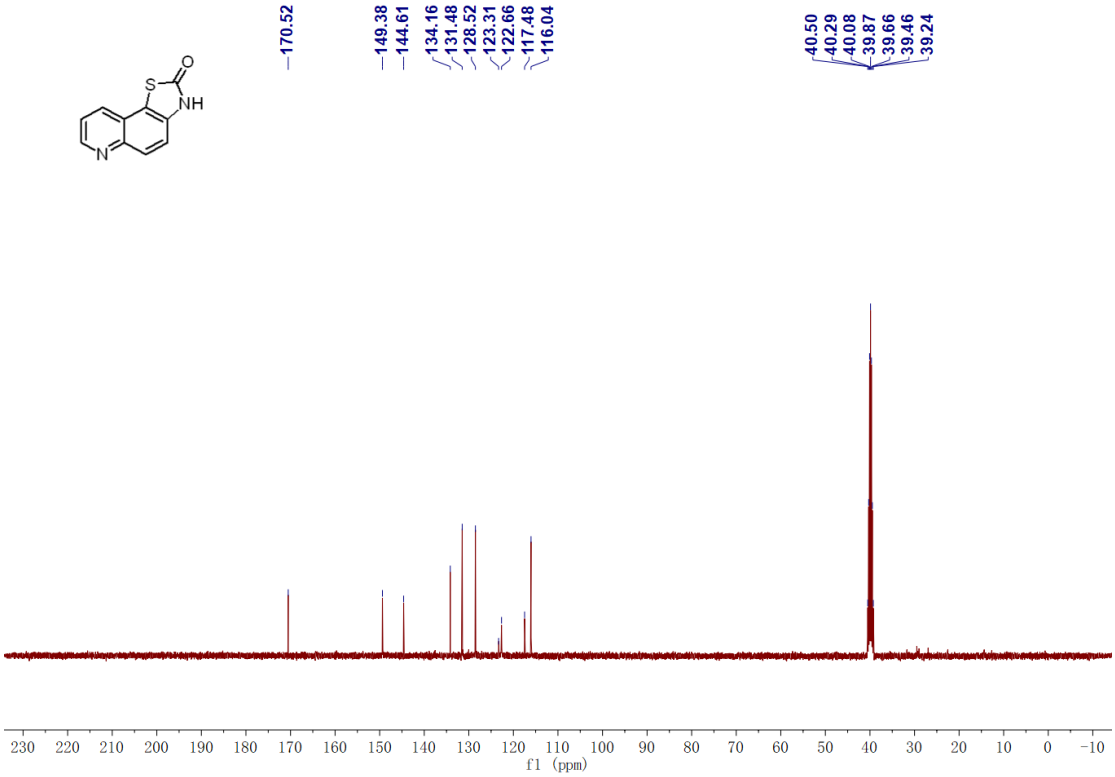
8-phenylnaphtho[2,1-*d*]thiazol-2(3*H*)-one (2k)



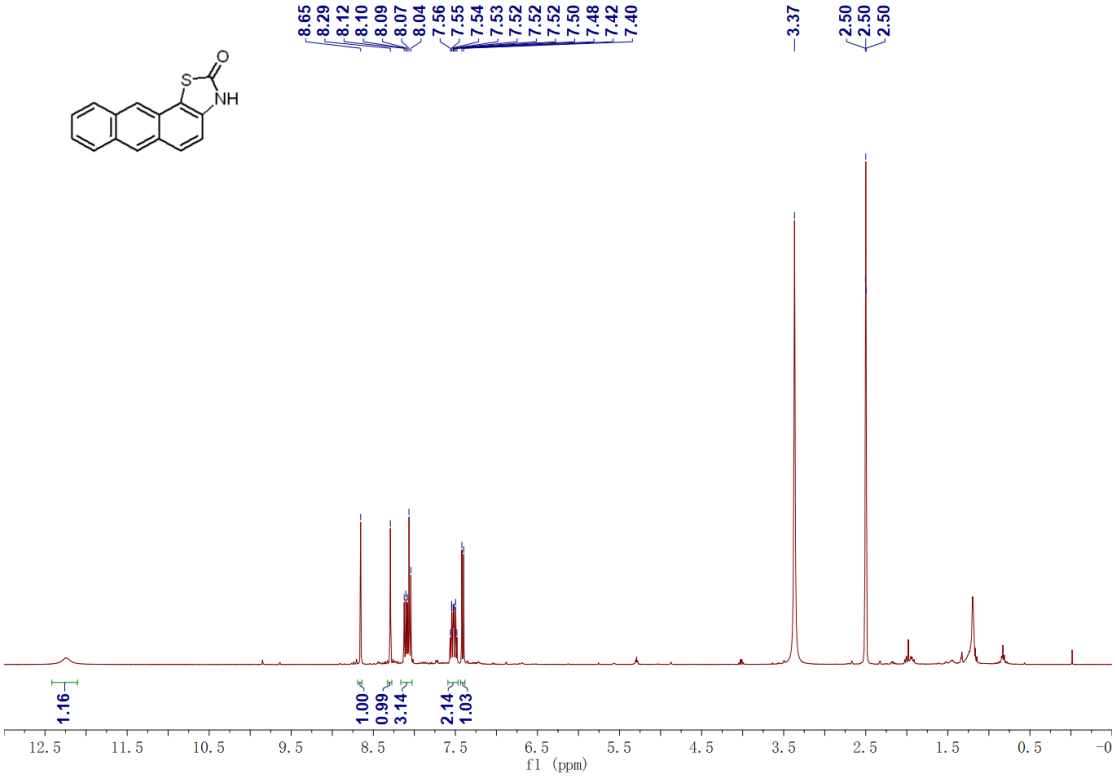


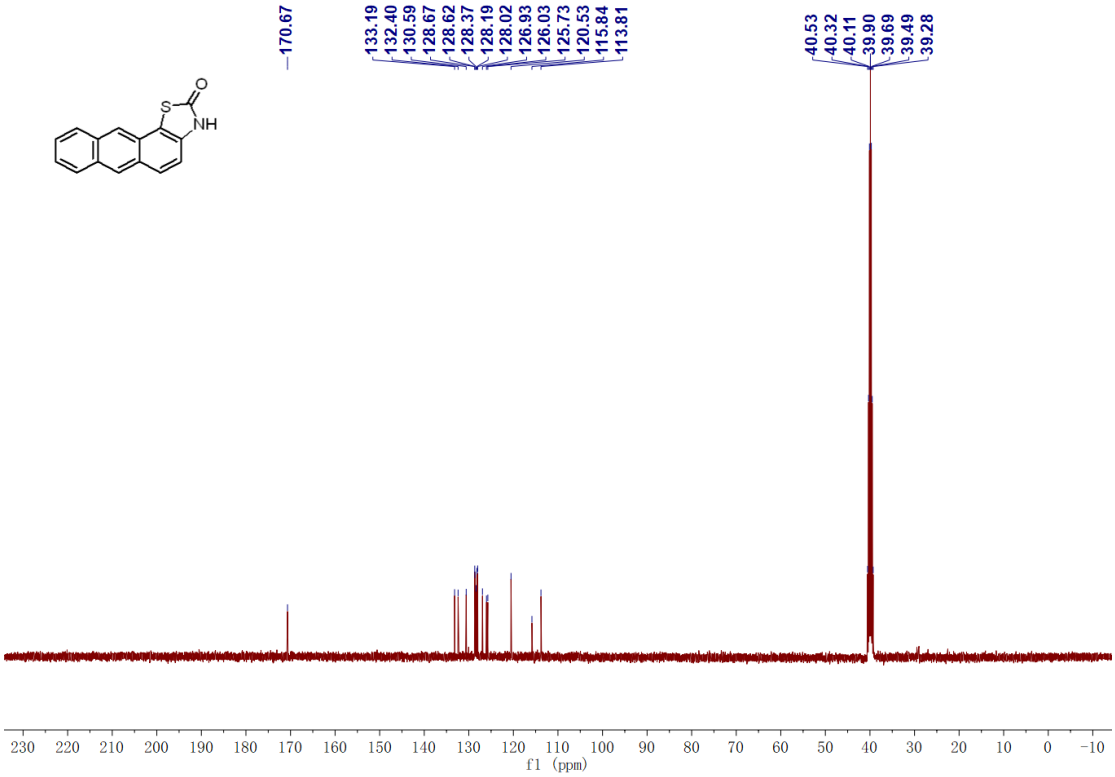
Thiazolo[5,4-*f*]quinolin-2(3*H*)-one (2l)



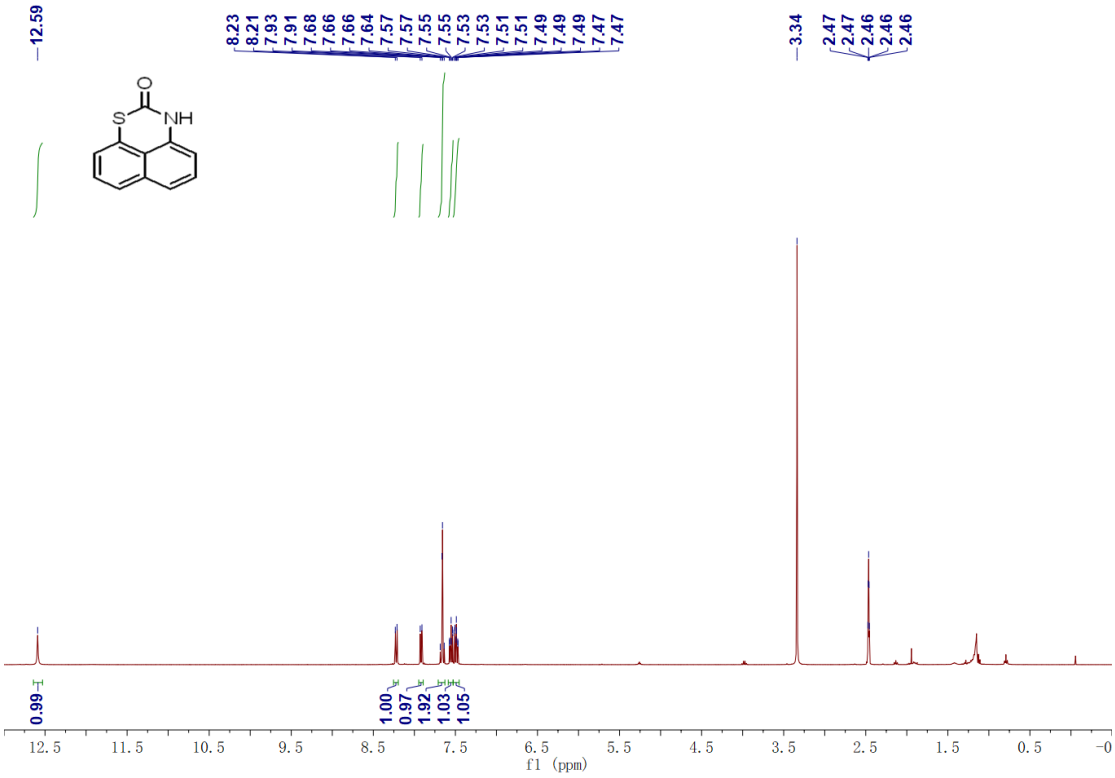


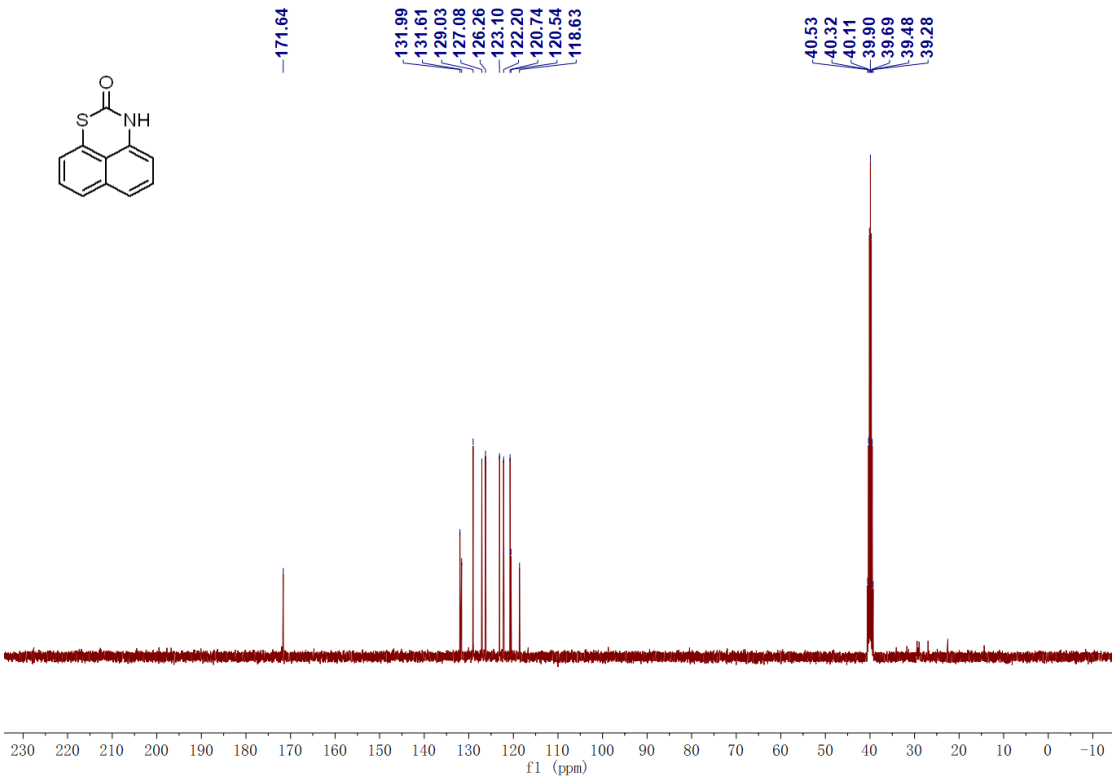
Anthra[2,1-*d*]thiazol-2(3*H*)-one (4)



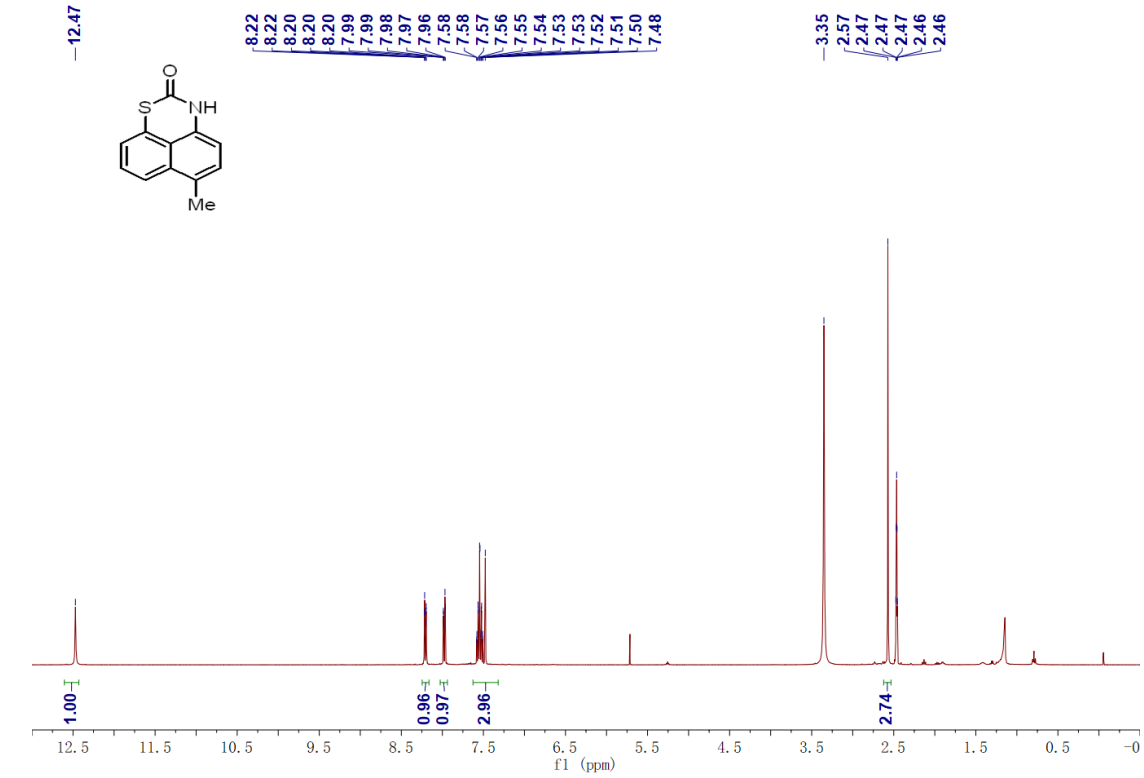


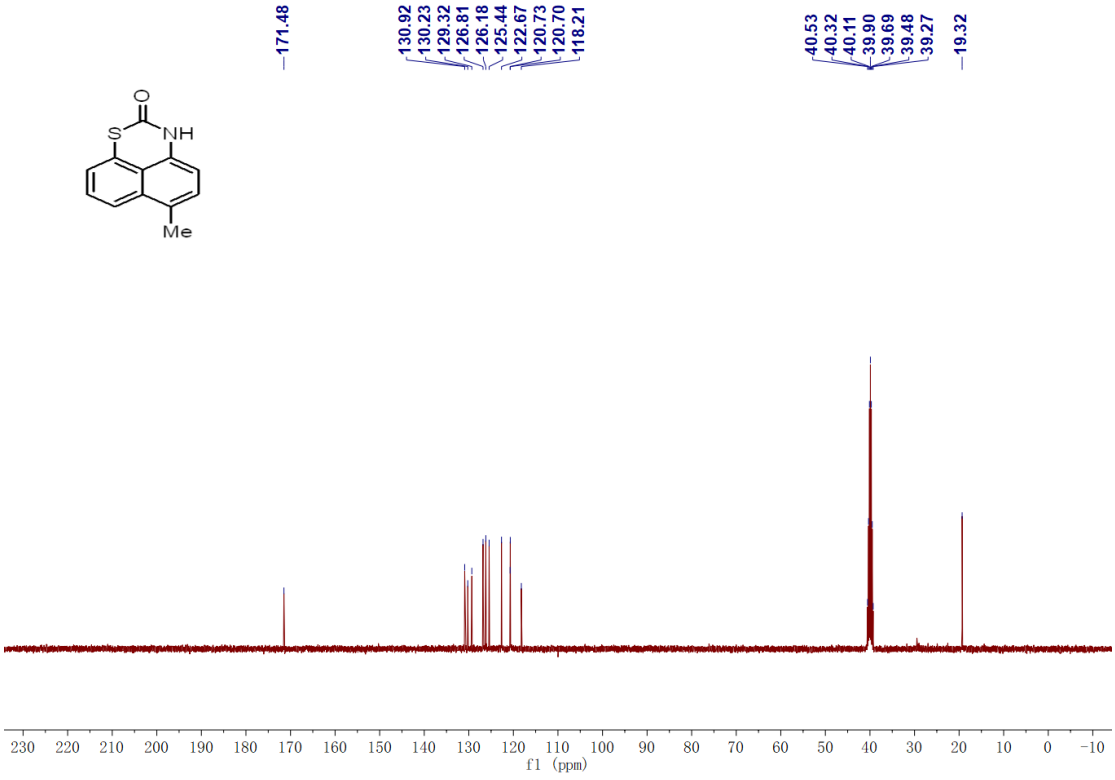
Naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (6a)



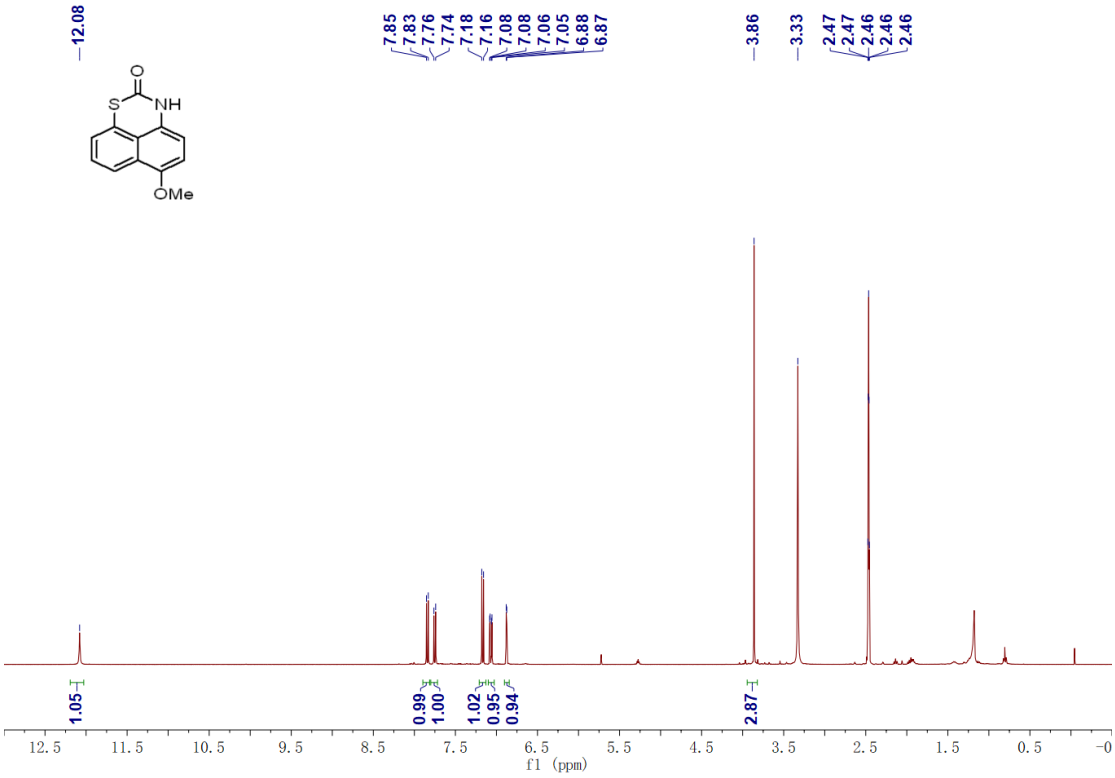


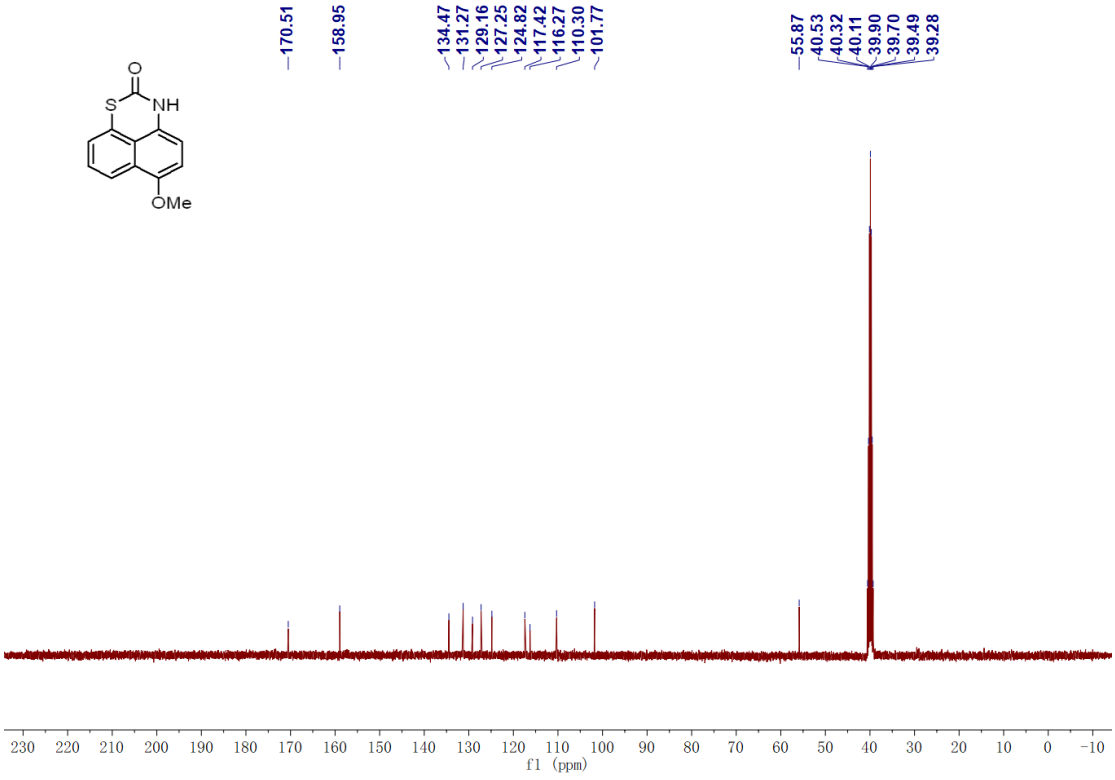
6-methylnaphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (6b)



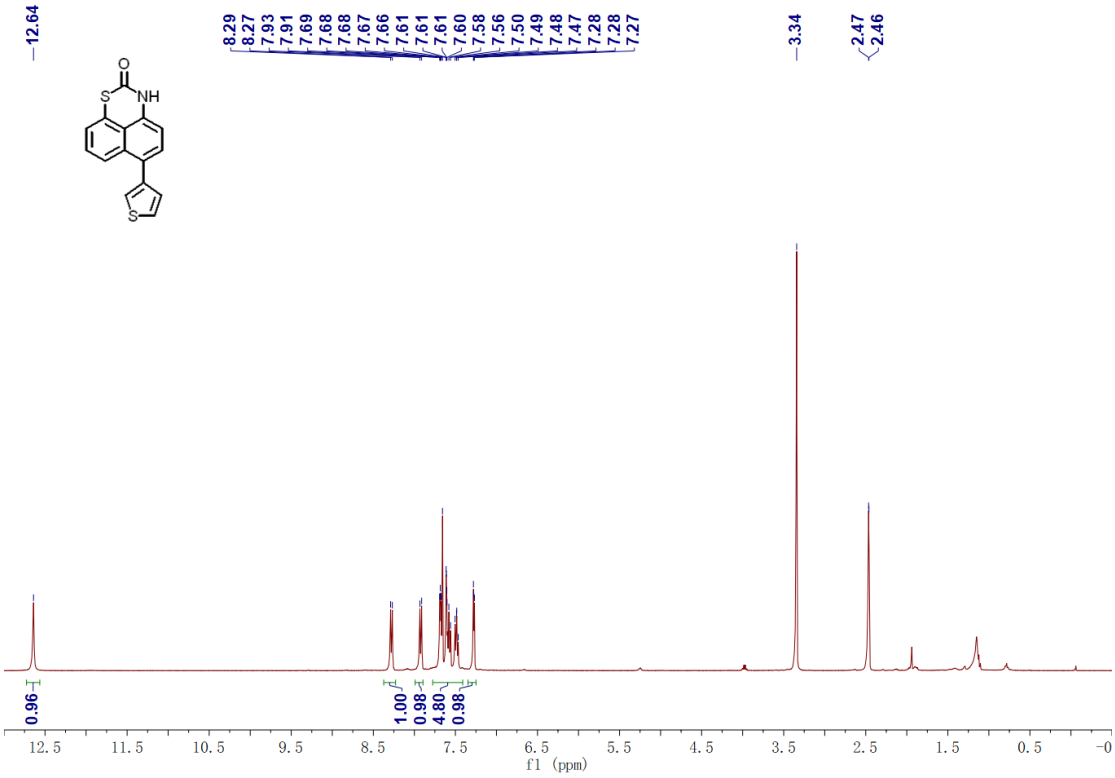


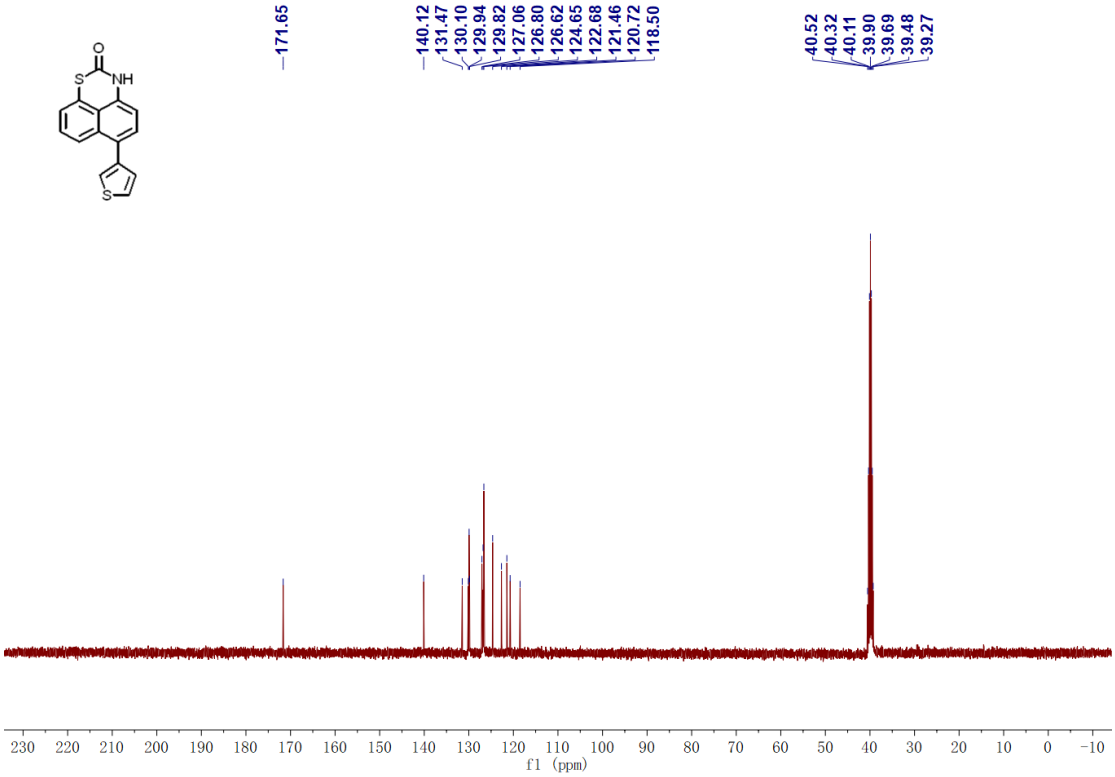
6-methoxynaphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (6c)



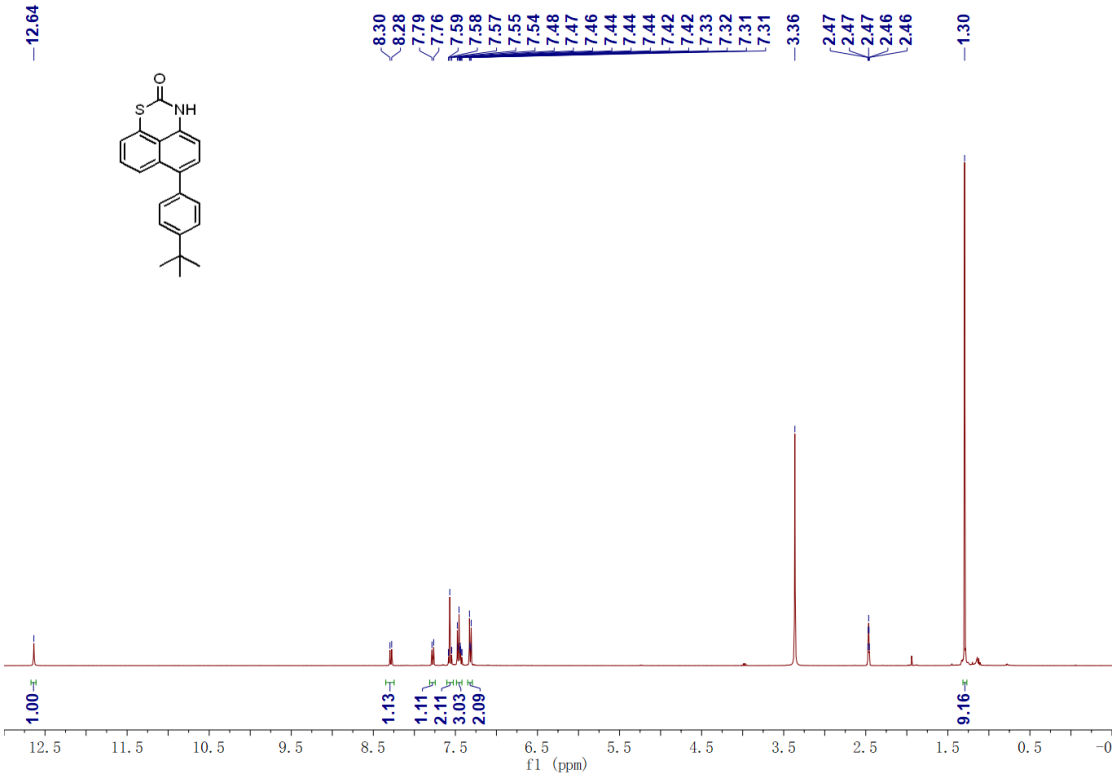


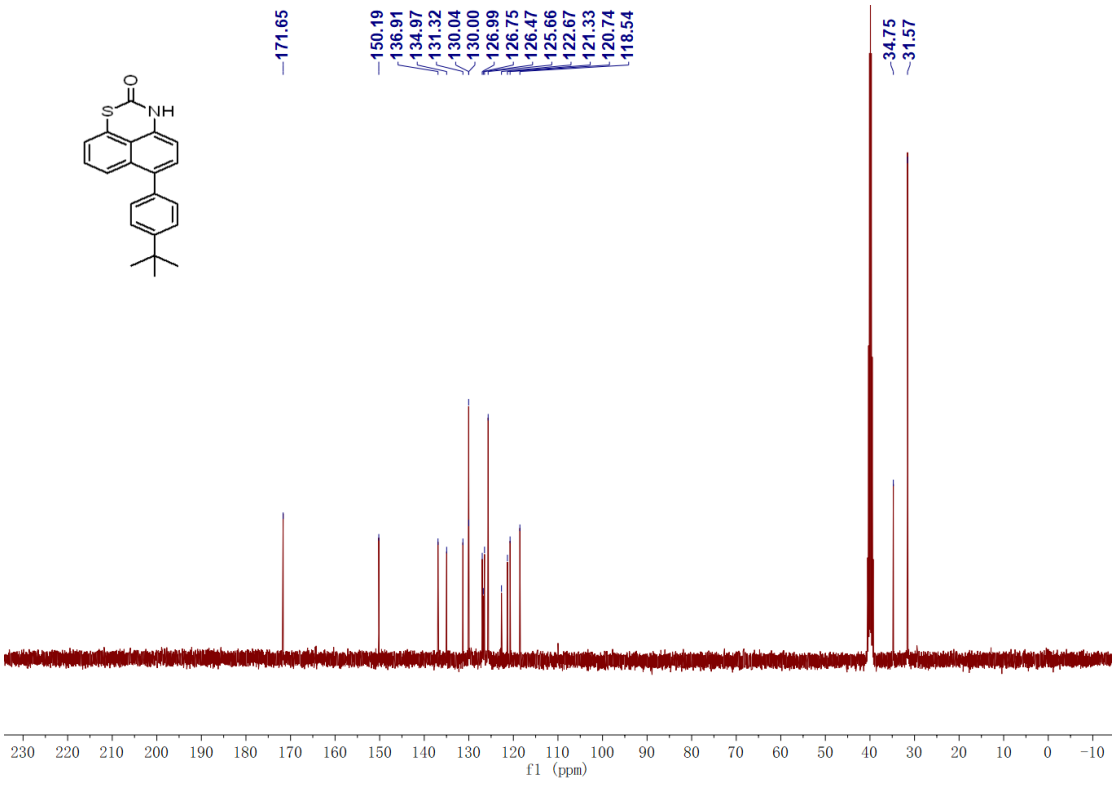
6-(thiophen-3-yl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (6d)



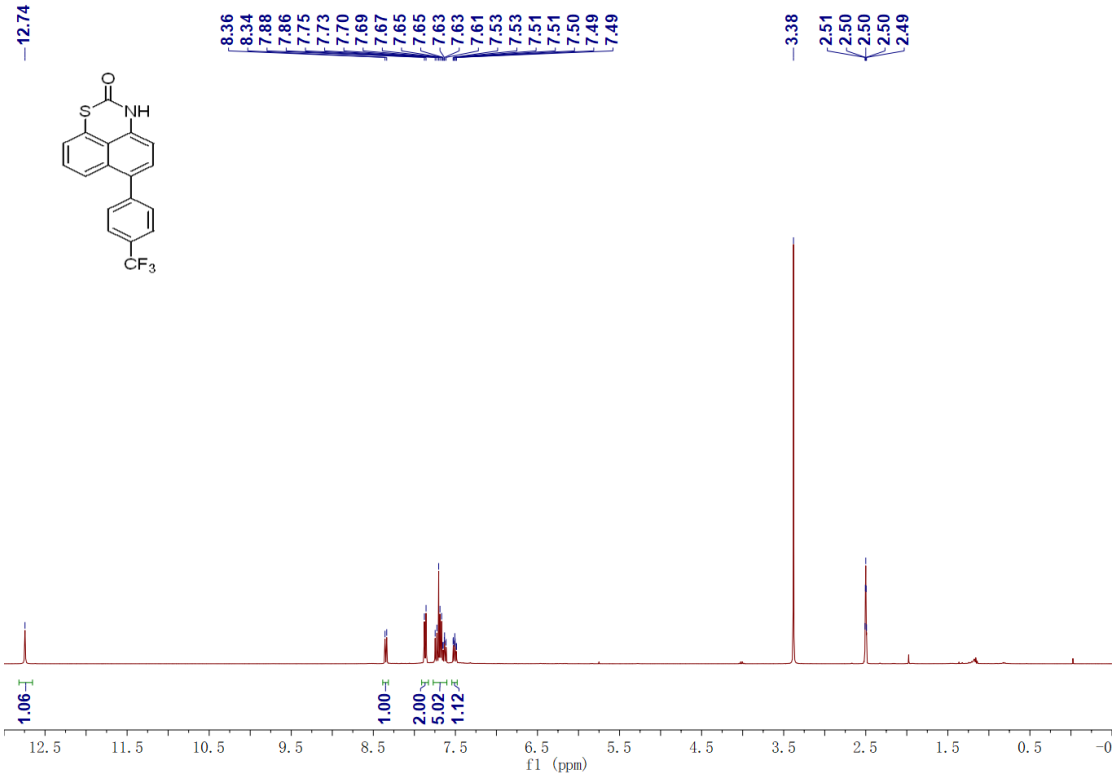


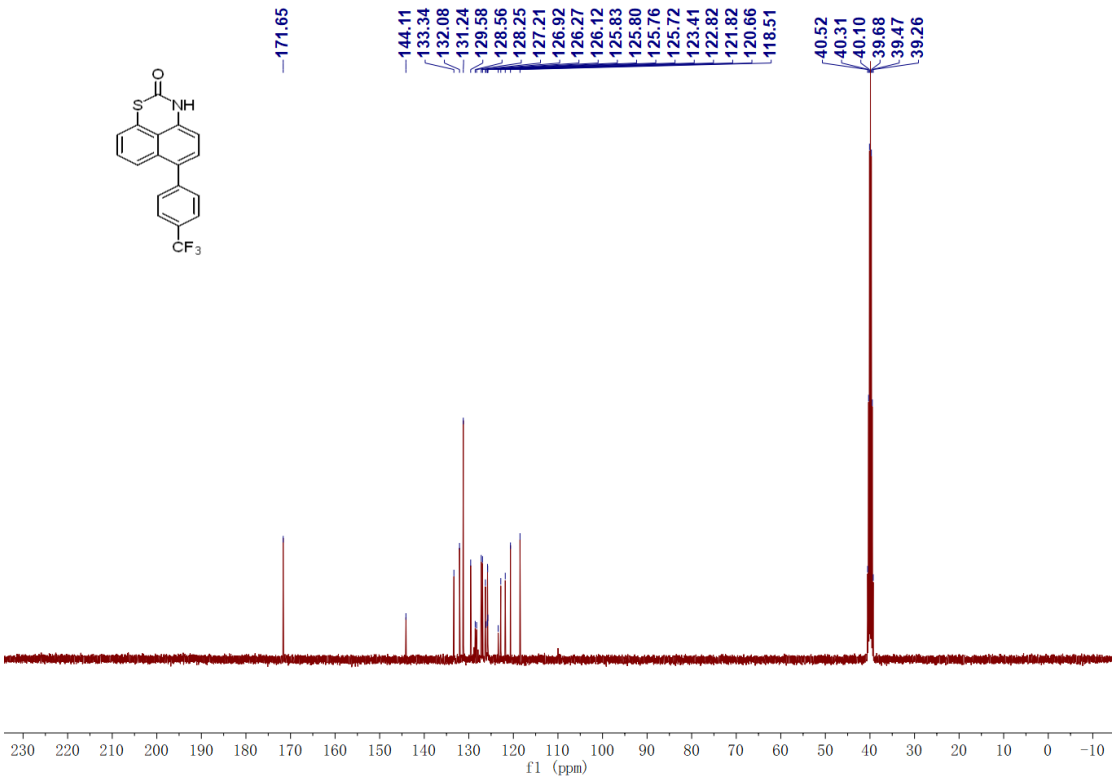
6-(4-(tert-butyl)phenyl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (6e)

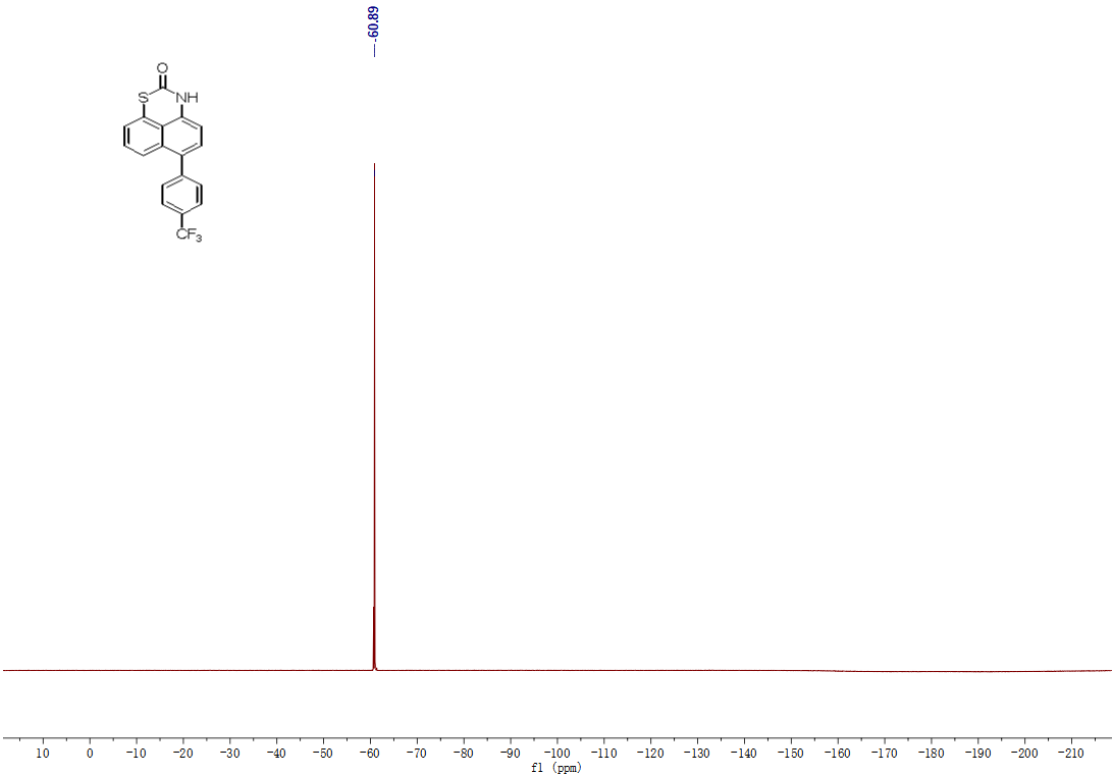




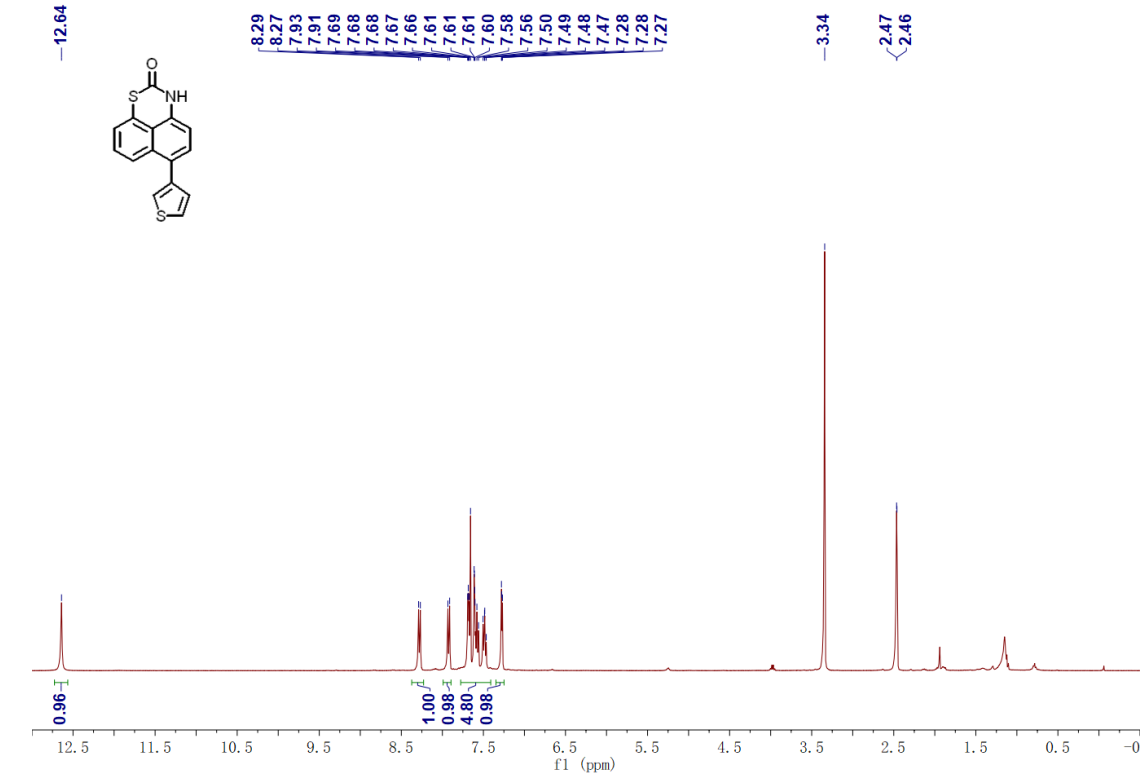
6-(4-(trifluoromethyl)phenyl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (6f)

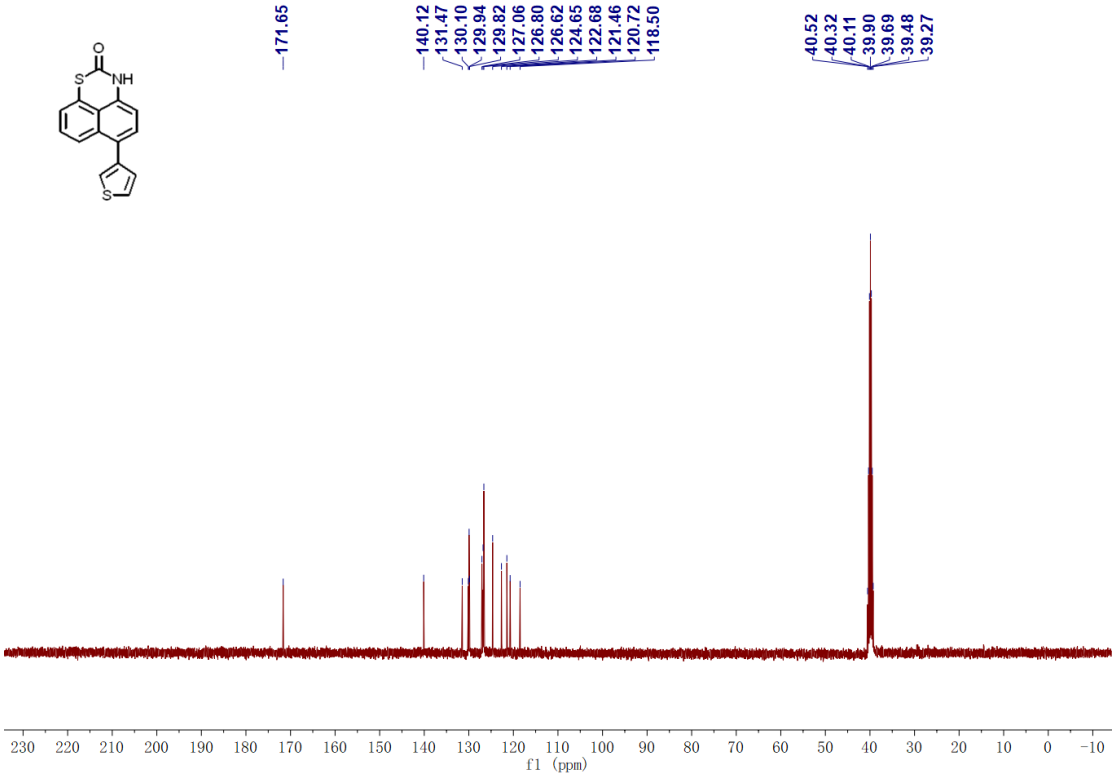




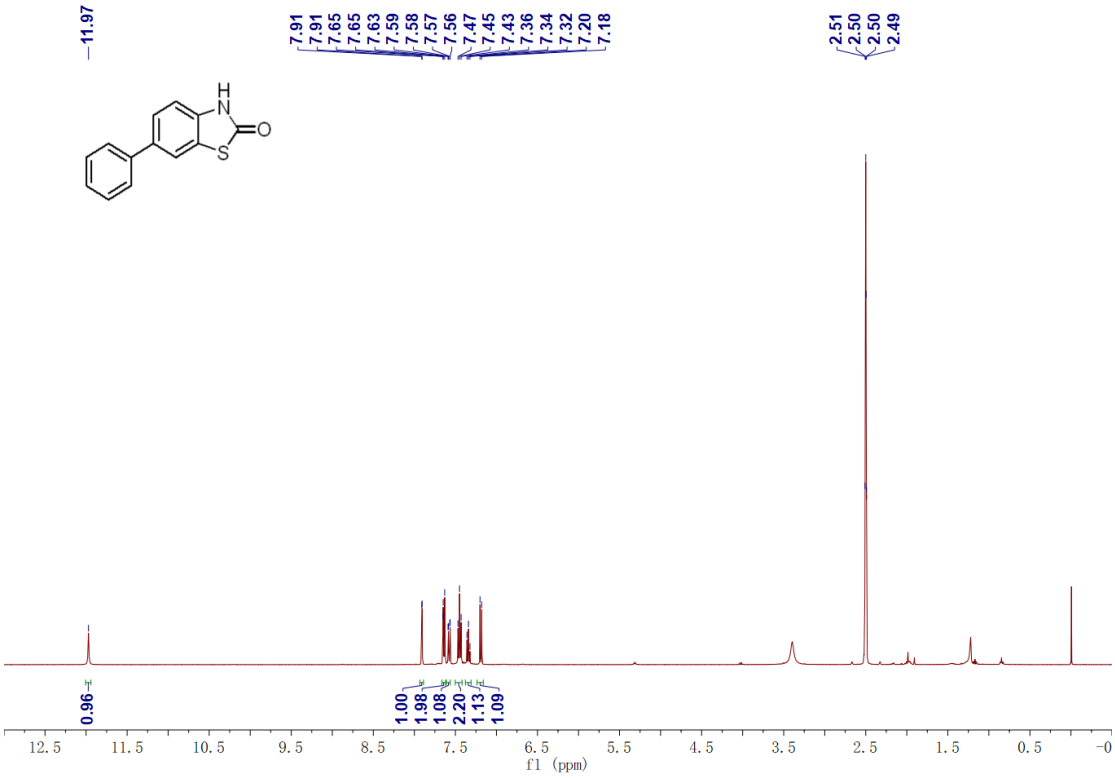

-60.89
O
S
NH
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

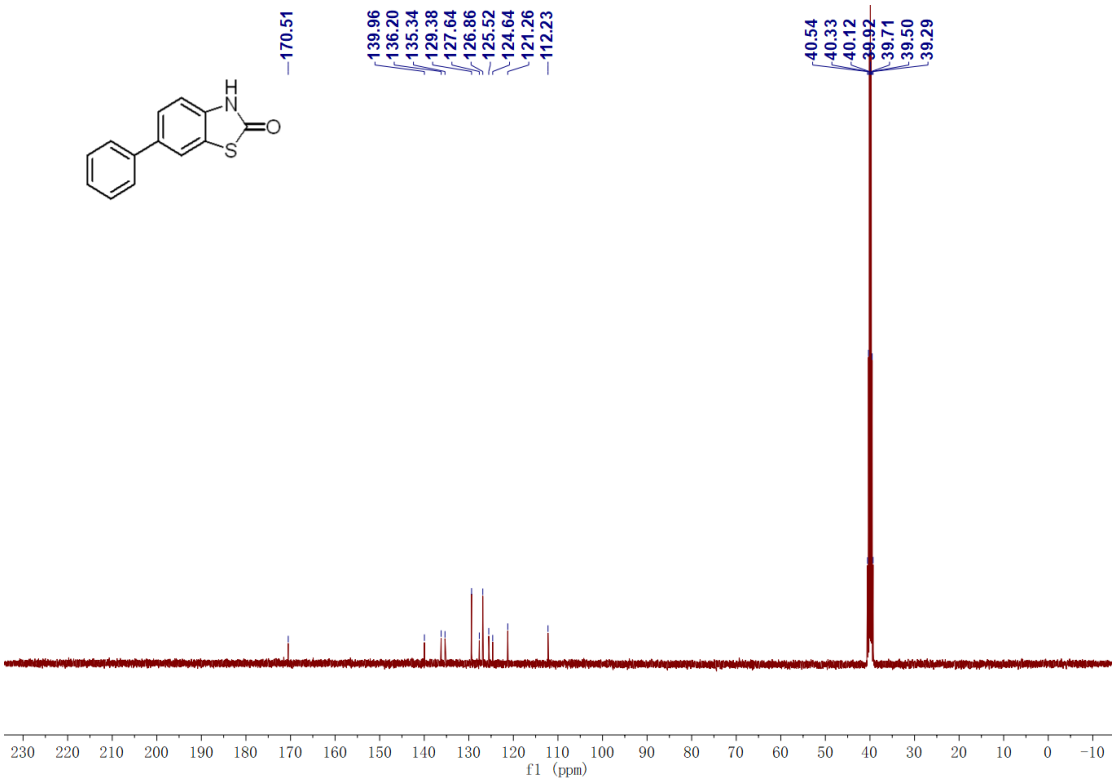
6-(4-(methylthio)phenyl)naphtho[1,8-*de*][1,3]thiazin-2(3*H*)-one (6g)



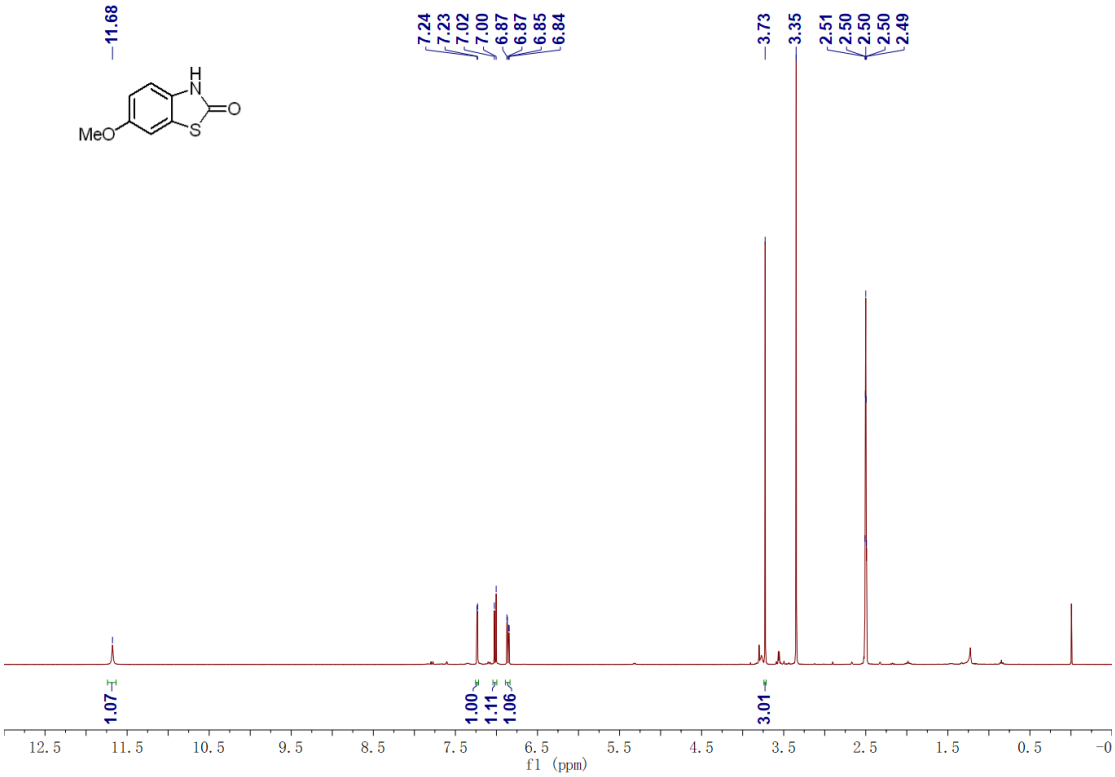


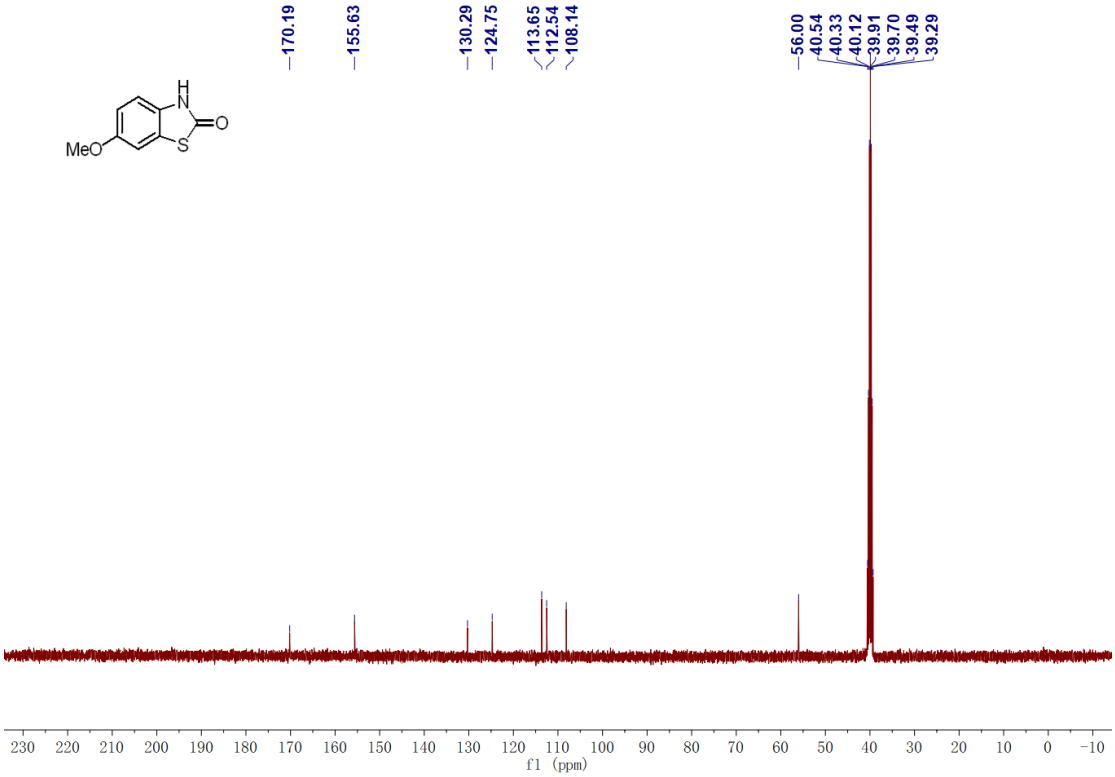
6-phenylbenzo[*d*]thiazol-2(3*H*)-one (8a)



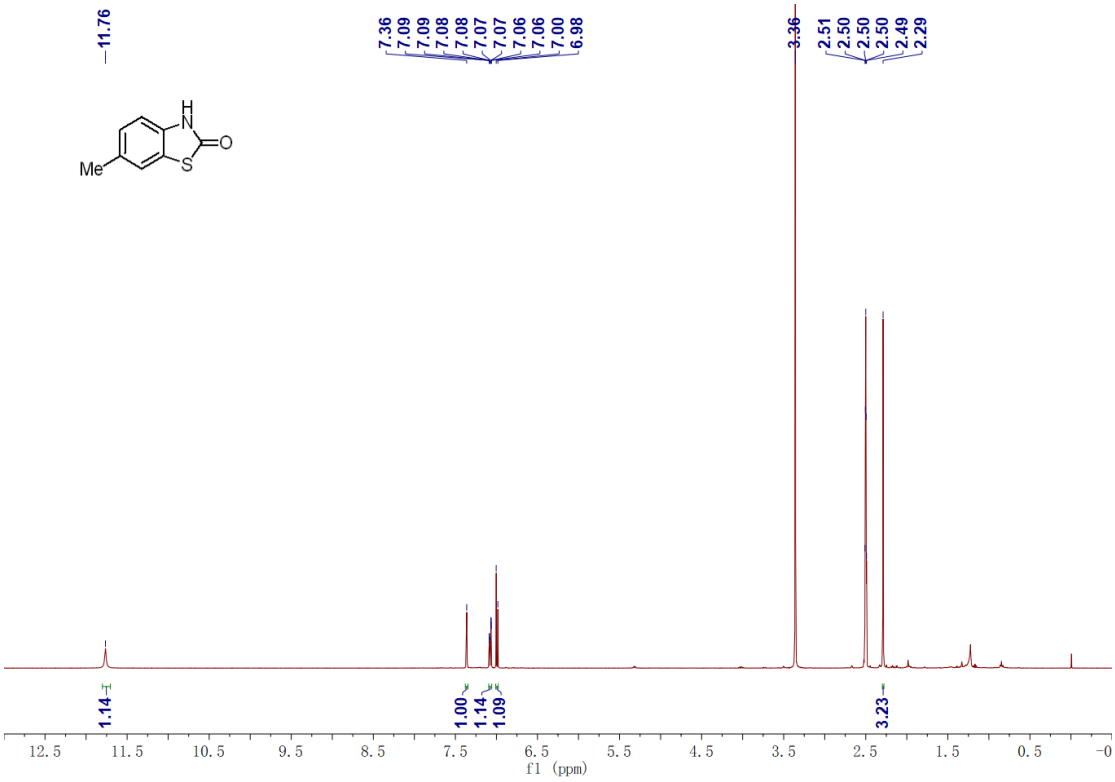


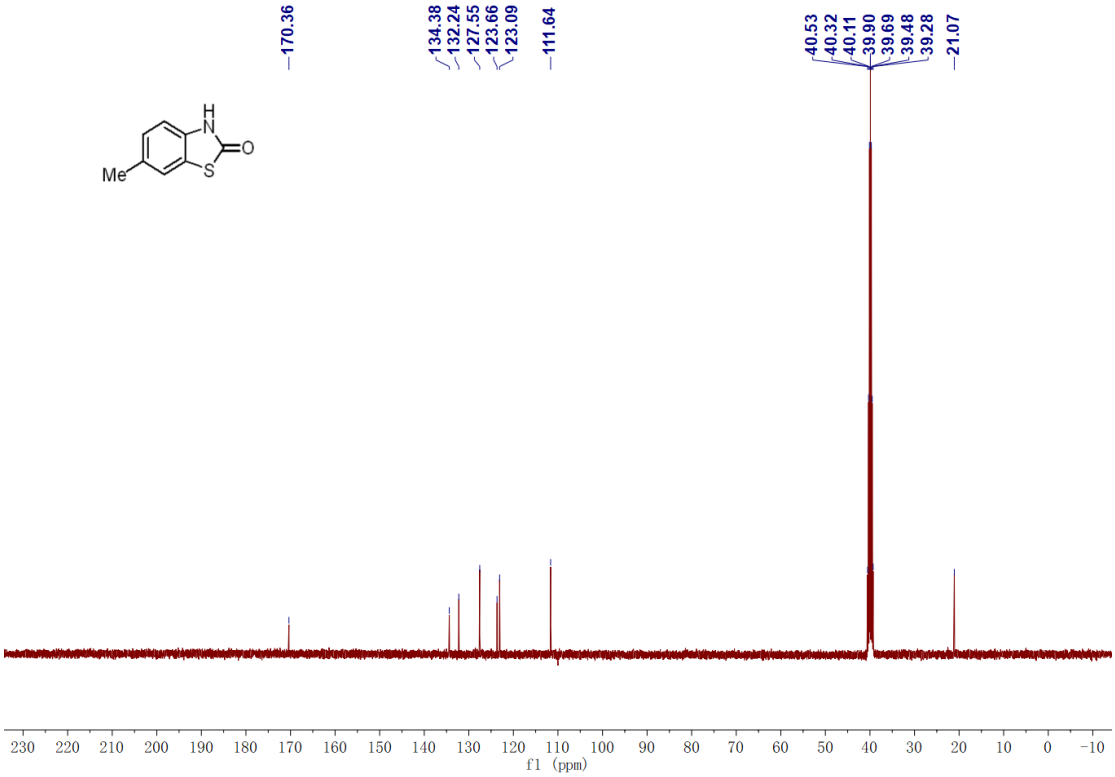
6-methoxybenzo[*d*]thiazol-2(3*H*)-one (8b)



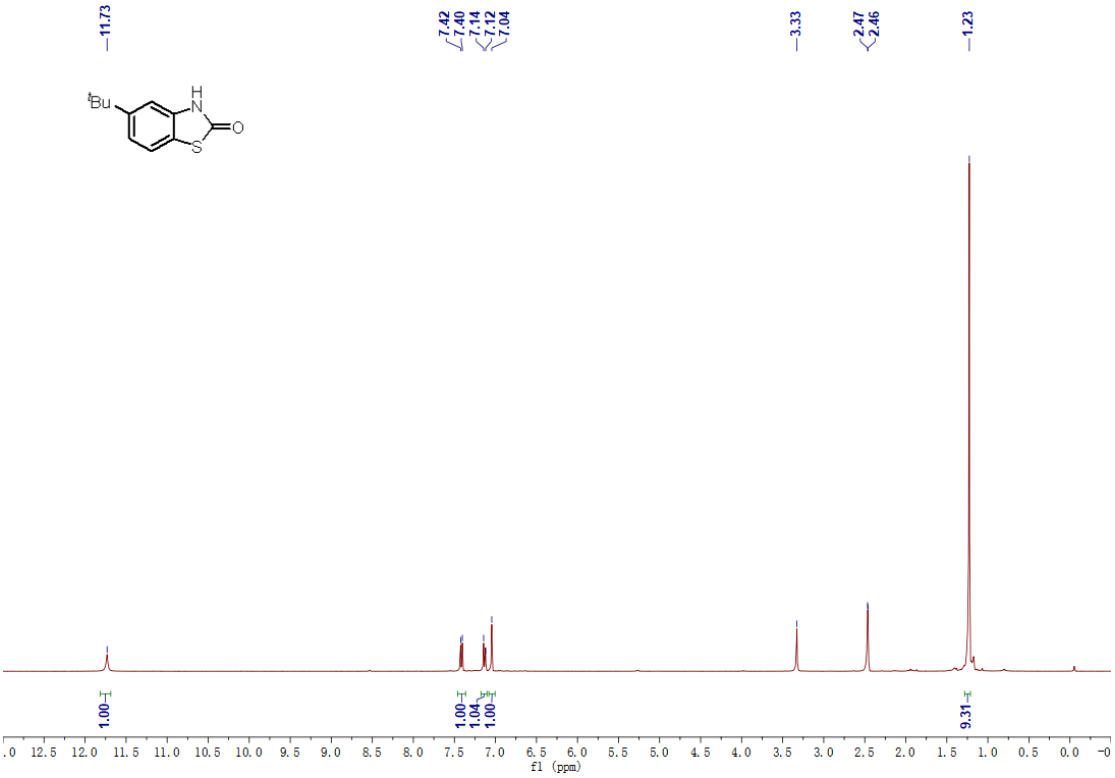


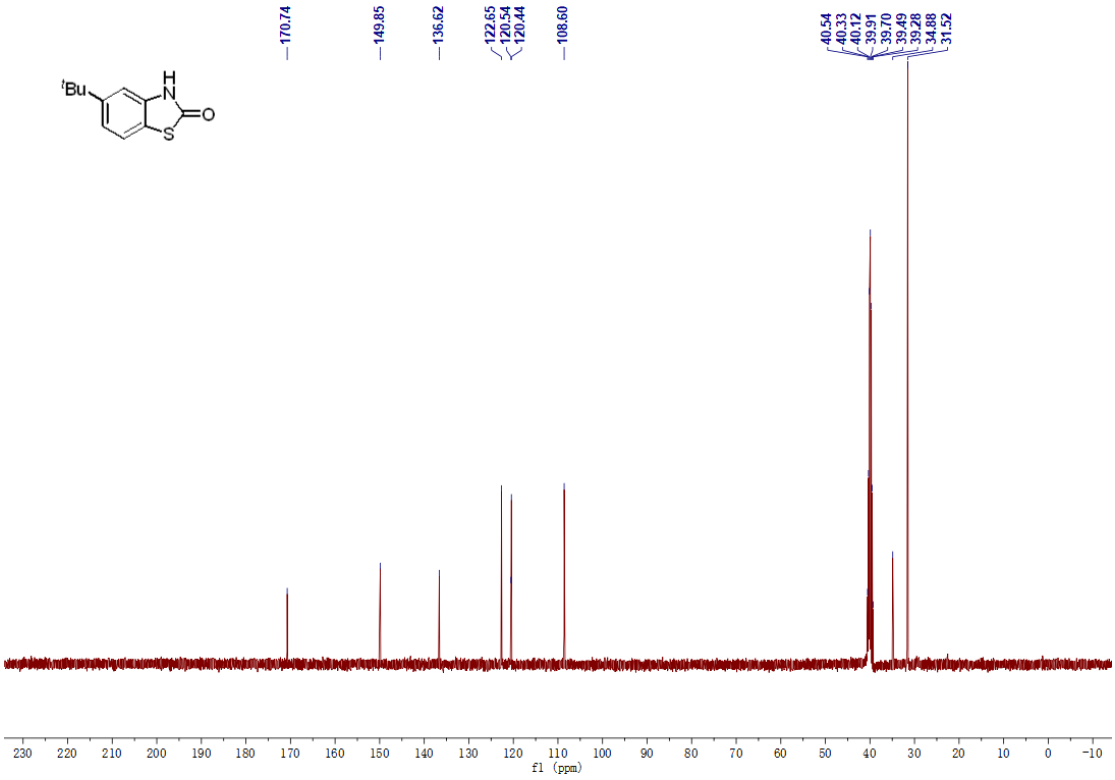
6-methylbenzo[*d*]thiazol-2(3*H*)-one (8c)





5-(tert-butyl)benzo[*d*]thiazol-2(3*H*)-one (4d)





[1,3]thiazino[6,5,4-*de*]quinolin-2(1*H*)-one (6h)