New synthesis of 2-aroylbenzothiazoles via metal-free domino transformations of anilines, acetophenones, and elemental sulfur

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Supporting information

Materials and instrumentation

All reagents and starting materials were obtained commercially from Sigma-Aldrich, Acros and Merck, and were used as received without any further purification unless otherwise noted. Gas chromatographic (GC) analyses were performed using a Shimadzu GC 2010-Plus equipped with a flame ionization detector (FID) and an SPB-5 column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC analysis held samples at 100 ^{o}C for 1 min; heated them from

100 to 280 °C at 40 °C/min; held them at 280 °C for 4.5 min. Inlet and detector temperatures were set constant at 280 °C. The GC yield was calculated using diphenyl ether as the internal standard. GC-MS analyses were analyzed on a Shimadzu GCMS-QP2010Ultra with a ZB-5MS column (length = 30 m, inner diameter = 0.25 mm, and film thickness = 0.25 μm). The temperature program for GC-MS analysis held samples at 50 °C for 2 min; heated samples from 50 to 280°C at 10 °C/min and held them at 280 °C for 10 min. Inlet temperature was set constant at 280 °C. MS spectra were compared with the spectra gathered in the NIST library. The ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV 500 spectrometers using residual solvent peak as a reference. FT-IR spectra were recorded on a Bruker Tensor 27 and samples were prepared as KBr plates. HR-MS spectra were recorded by an Agilent HPLC 1200 Series coupled to Bruker micrOTOF-QII.

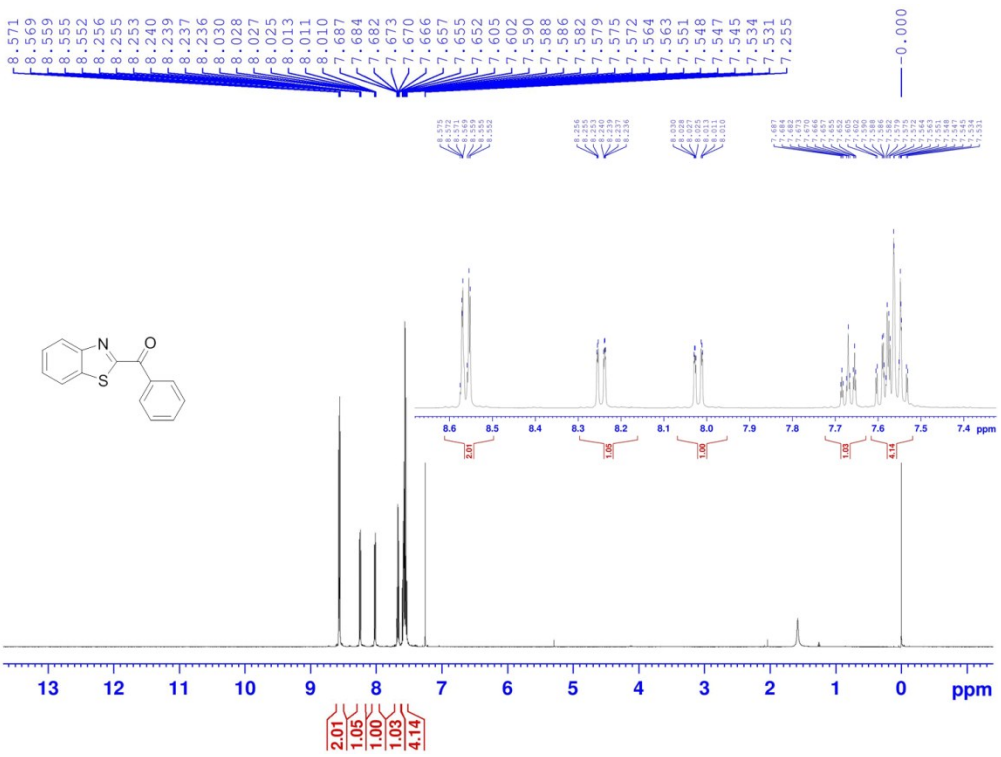

Fig.S1. ^{1}H-NMR spectra of benzo[*d*]thiazol-2-yl(phenyl)methanone.

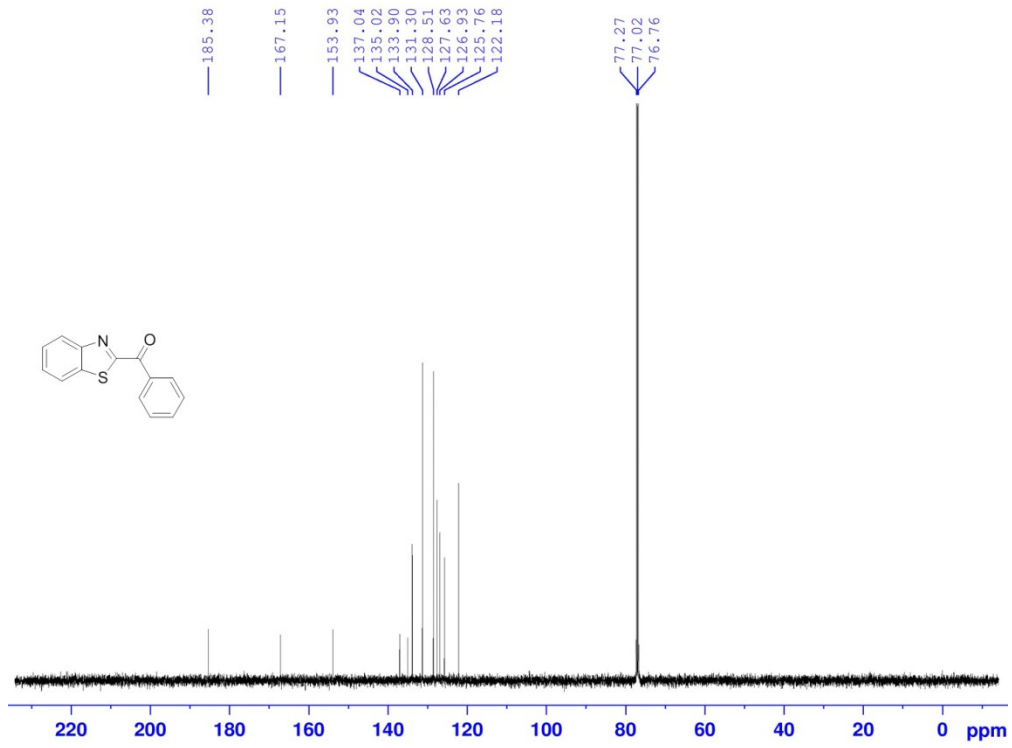

Fig.S2. ^{13}C-NMR spectra of benzo[*d*]thiazol-2-yl(phenyl)methanone.

Characterization data for benzo[*d*]thiazol-2-yl(phenyl)methanone (3aa)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 78 % yield (37.3 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.53 – 7.60 (m, 4H), 7.65 – 7.68 (m, 1H), 8.01 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 8.23 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 8.55 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.1, 125.7, 126.9, 127.6, 128.5, 131.3, 133.9, 135.0, 137.0, 153.9, 167.1, 185.3.

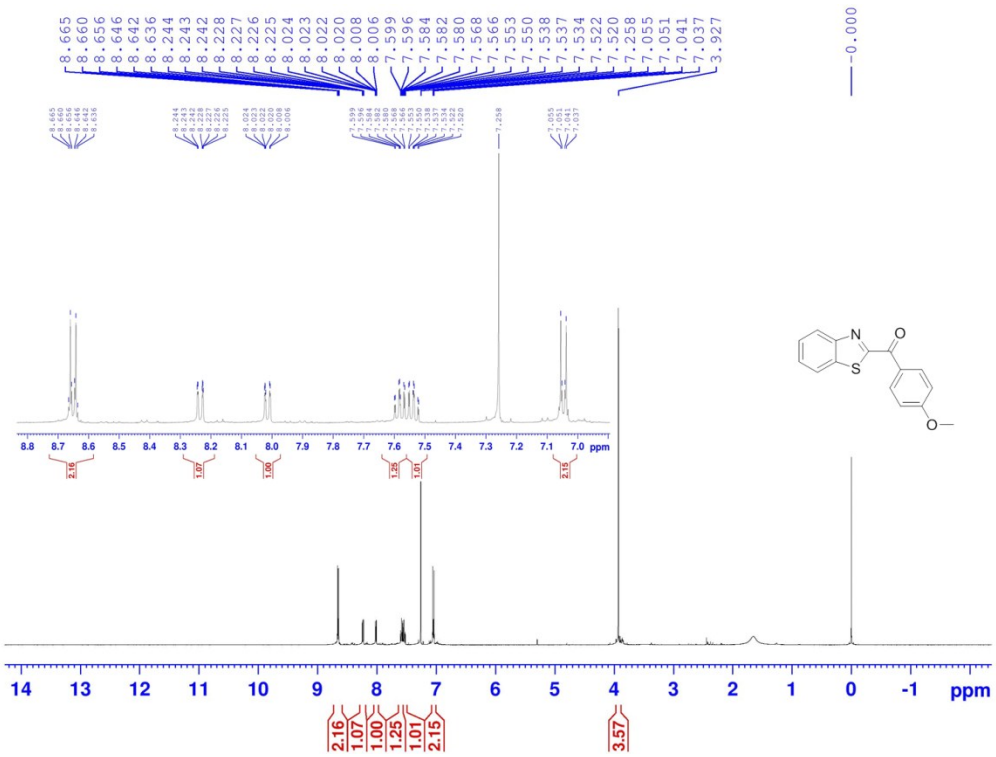

Fig.S3. ^{1}H-NMR spectra of benzo[*d*]thiazol-2-yl(4-methoxyphenyl)methanone.

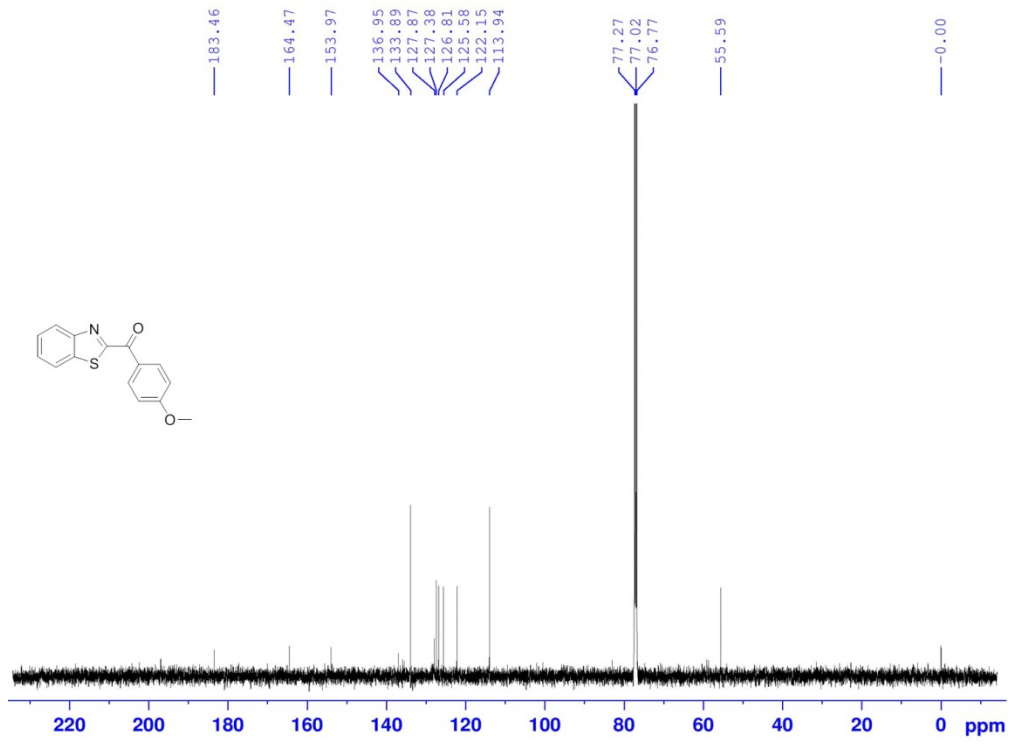

Fig.S4. ^{13}C-NMR spectra of benzo[*d*]thiazol-2-yl(4-methoxyphenyl)methanone.

Characterization data for benzo[*d*]thiazol-2-yl(4-methoxyphenyl)methanone (3ab)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 80 % yield (43 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 3.92 (s, 3H), 7.03 (dd, J_1 = 7.0 Hz, J_2 = 2.0 Hz, 2H), 7.52 – 7.59 (m, 2H), 8.00 (dd, J_1 = 7.0 Hz, J_2 = 1.0 Hz, 1H), 8.22 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 8.63 (dt, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 55.5, 113.9, 122.1, 125.5, 126.8, 127.3, 127.8, 133.8, 136.9, 153.9, 164.4, 183.4.

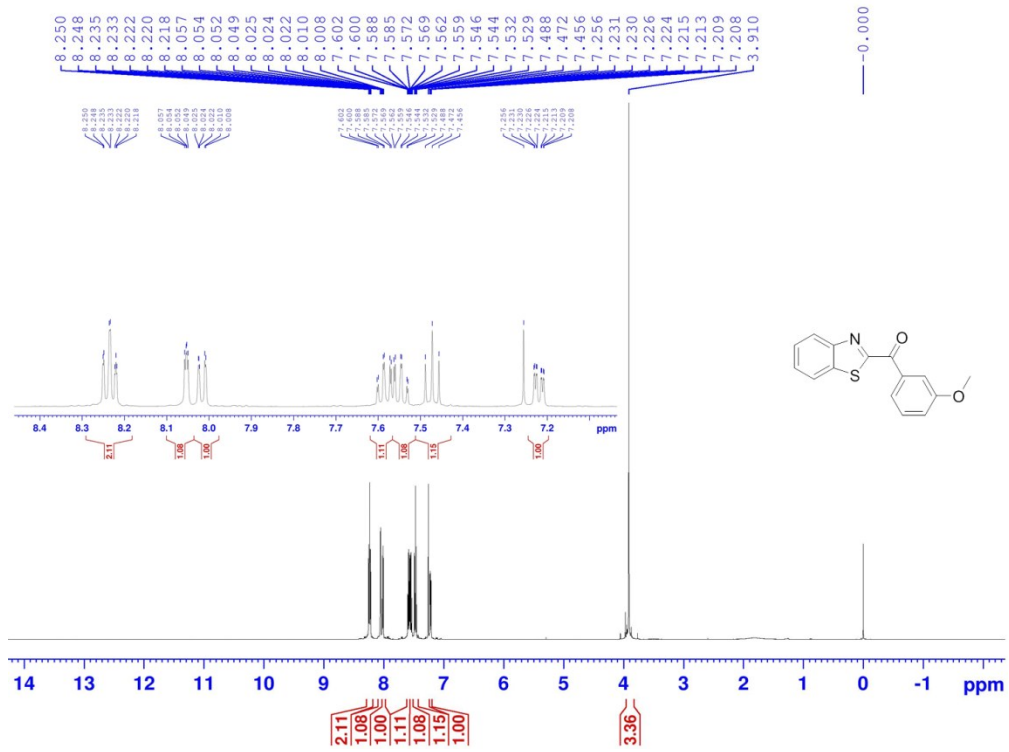

Fig.S5. ^{1}H-NMR spectra of benzo[*d*]thiazol-2-yl(3-methoxyphenyl)methanone.

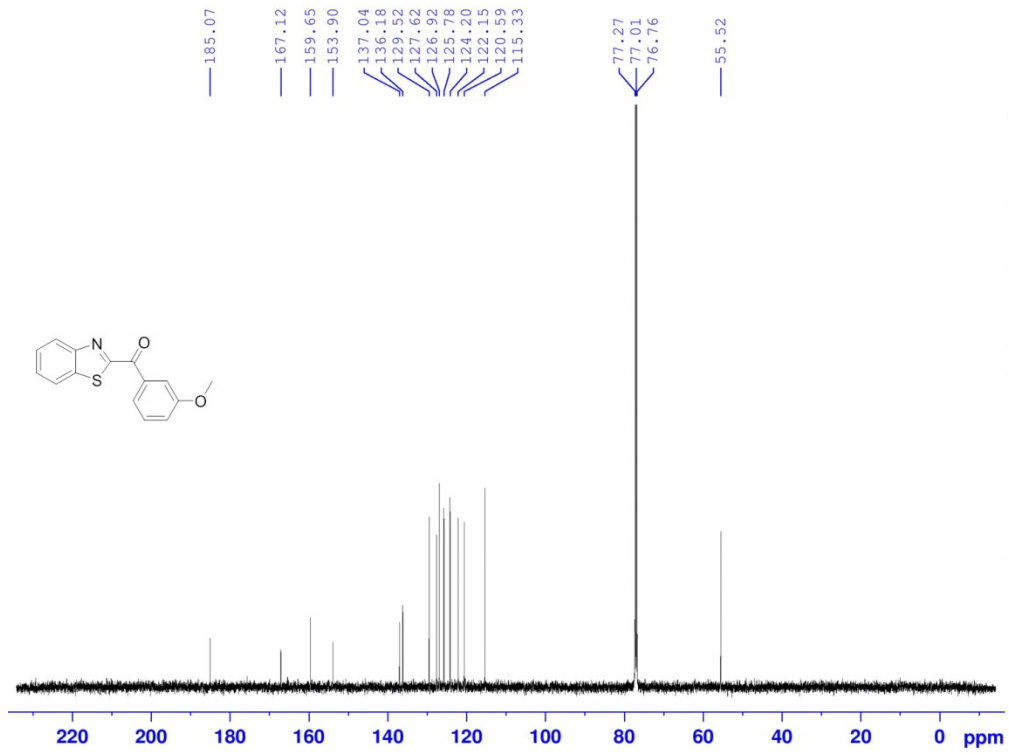

Fig.S6. ^{13}C-NMR spectra of benzo[*d*]thiazol-2-yl(3-methoxyphenyl)methanone.

Characterization data for benzo[*d*]thiazol-2-yl(3-methoxyphenyl)methanone (3ac)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 77 % yield (41.4 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 3.91 (s, 3H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 2.5 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.52 – 7.60 (m, 2H), 8.00 (dd, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 8.04 (q, J = 1.5 Hz, 1H), 8.21 (td, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 55.5, 115.3, 120.5,122.1, 124.2, 125.7, 126.9, 127.6, 129.5, 136.1, 137.0, 153.9, 159.6, 167.1, 185.0.

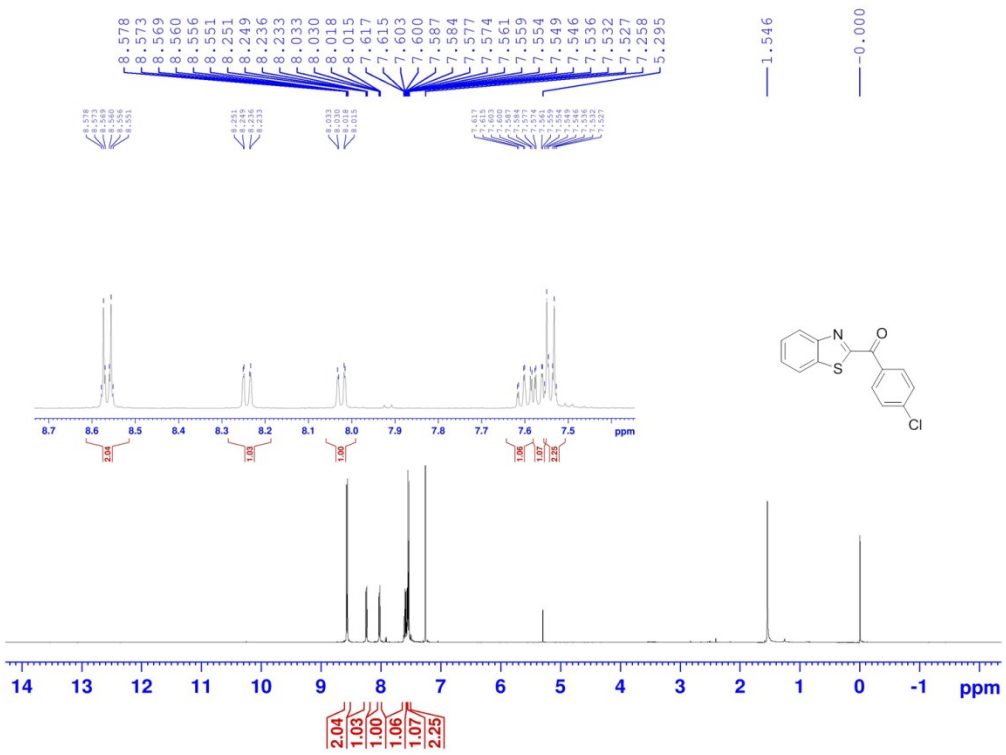

Fig.S7. ^{1}H-NMR spectra of benzo[*d*]thiazol-2-yl(4-chlorophenyl)methanone.

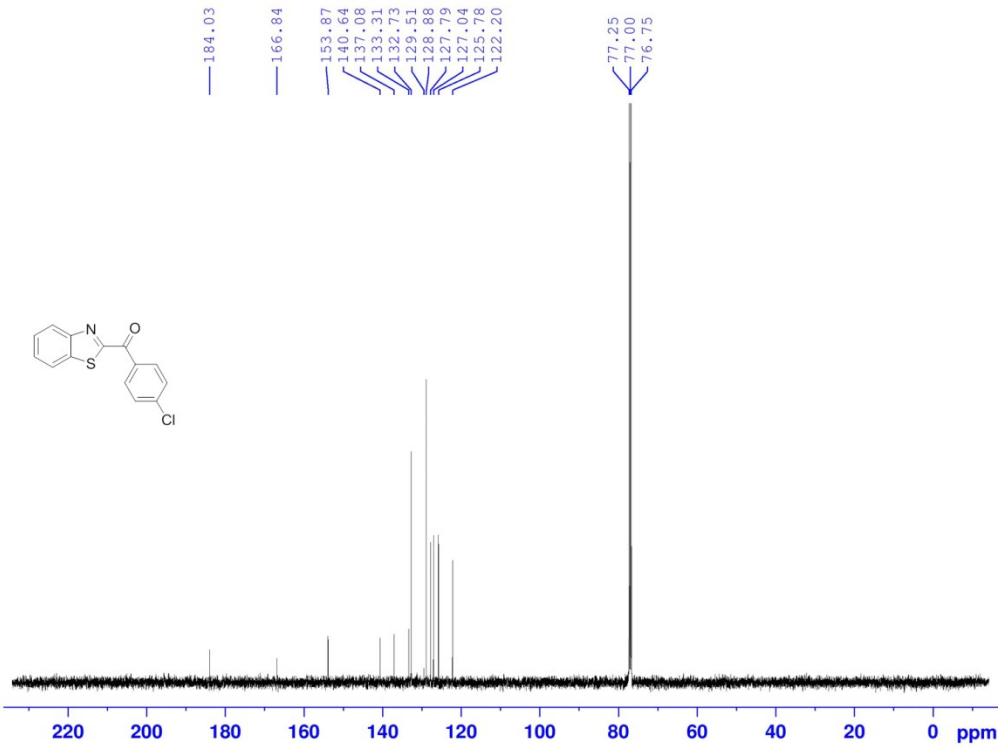

Fig.S8. ^{13}C-NMR spectra of benzo[*d*]thiazol-2-yl(4-chlorophenyl)methanone.

Characterization data for benzo[*d*]thiazol-2-yl(4-chlorophenyl)methanone (3ad)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 63 % yield (34.4 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.52 – 7.61 (m, 4H), 8.01 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 8.23 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 8.55 (dt, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.2, 125.7, 127.0, 127.7, 128.8, 129.5, 132.7, 133.3, 137.0, 140.6, 153.8, 166.8, 184.0.

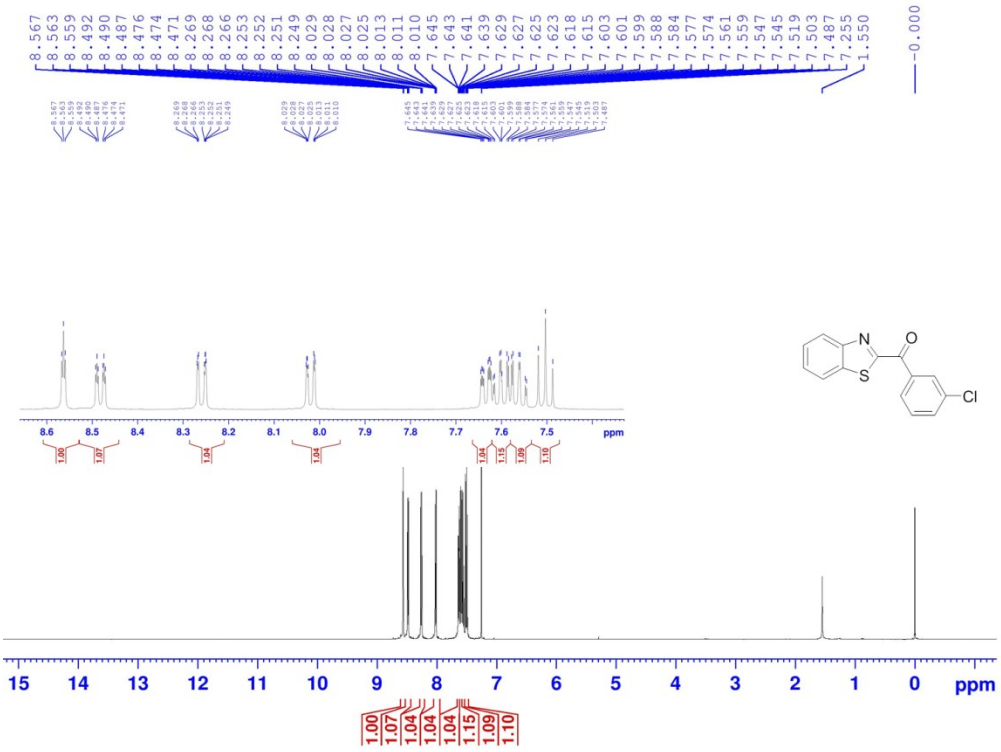

Fig.S9. ^{1}H-NMR spectra of benzo[*d*]thiazol-2-yl(3-chlorophenyl)methanone.

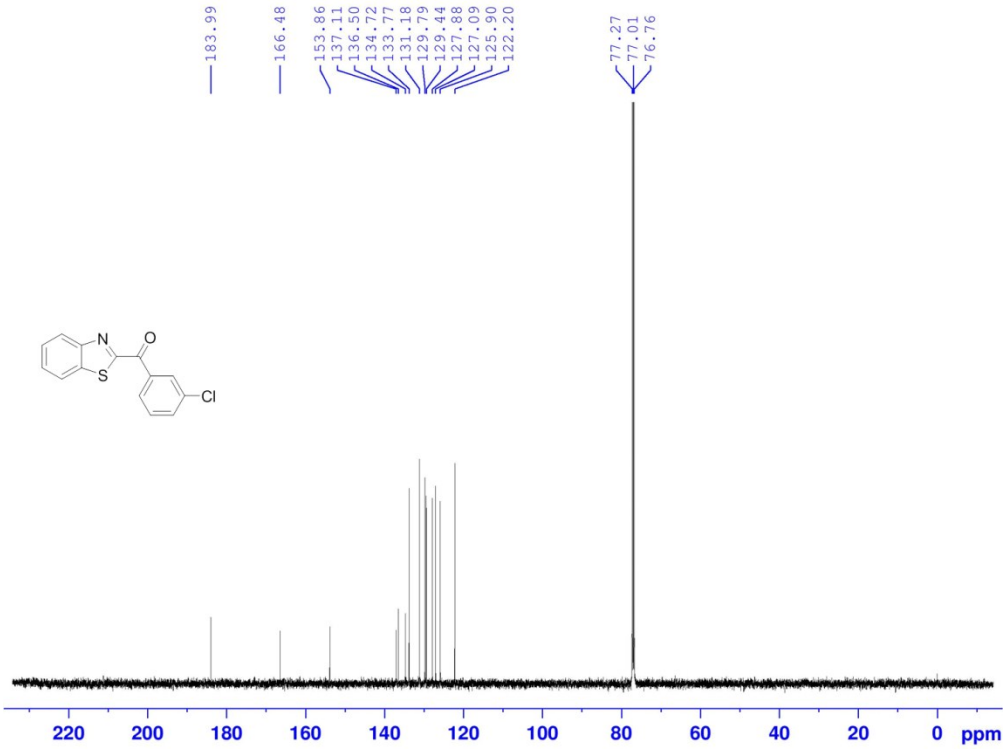

Fig.S10. ^{13}C-NMR spectra of benzo[*d*]thiazol-2-yl(3-chlorophenyl)methanone.

Characterization data for benzo[*d*]thiazol-2-yl(3-chlorophenyl)methanone (3ae)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 72 % yield (39.3 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.48 – 7.64 (m, 4H), 8.01 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1H), 8.24 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 8.47 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 8.55 (t, J = 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.2, 125.9, 127.0, 127.8, 129.4, 129.7, 131.1, 133.7, 134.7, 136.5, 137.1, 153.8, 166.4, 183.9.

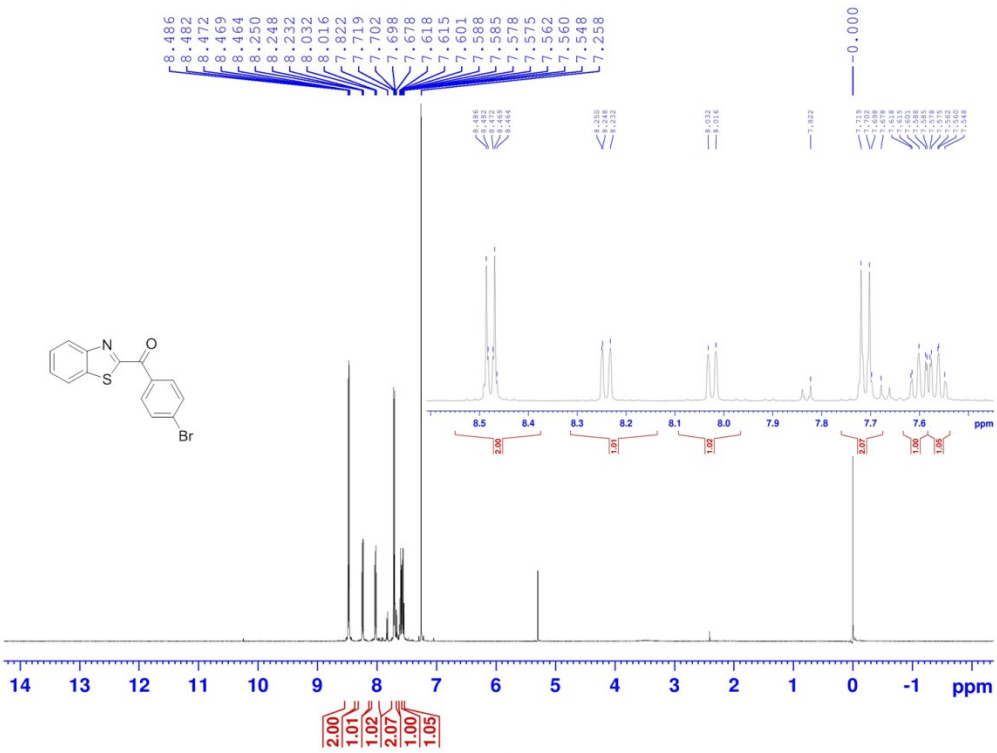

Fig.S11. ^{1}H-NMR spectra of benzo*[d]*thiazol-2-yl(4-bromophenyl)methanone.

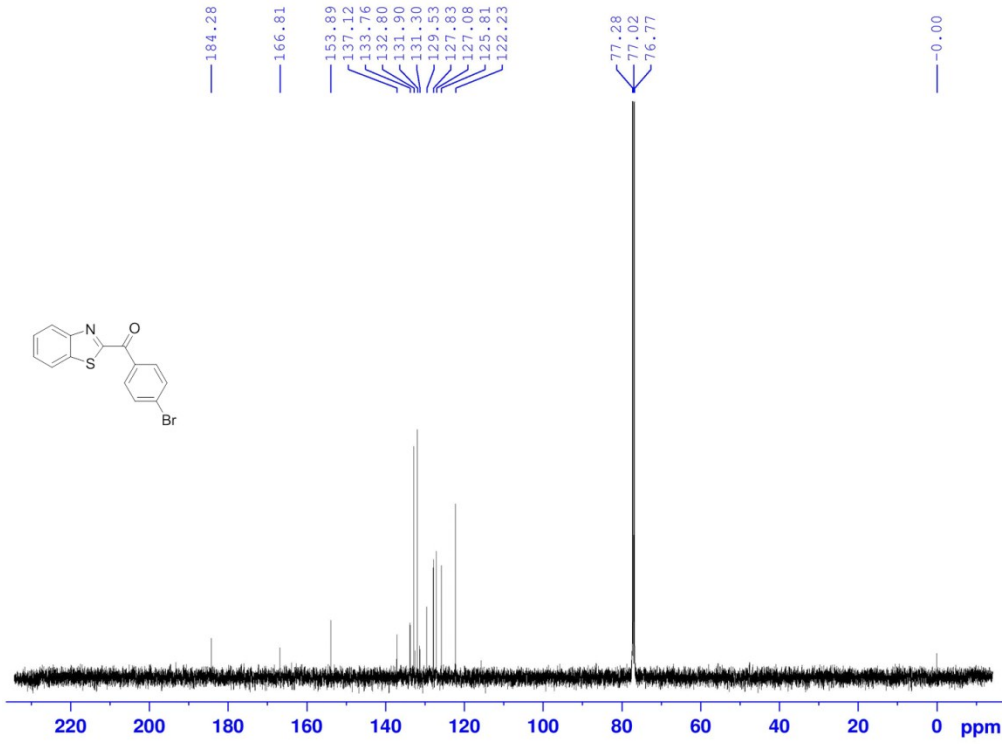

Fig.S12. ^{13}C-NMR spectra of benzo*[d]*thiazol-2-yl(4-bromophenyl)methanone.

Characterization data for benzo*[d]*thiazol-2-yl(4-bromophenyl)methanone (3af)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 54 % yield (34.2 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.54 – 7.61 (m, 2H), 7.69 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 9.0 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.2, 125.8,127.0, 127.8, 129.5, 131.3, 131.9, 132.8, 133.7, 137.1, 153.8, 166.8, 184.2.

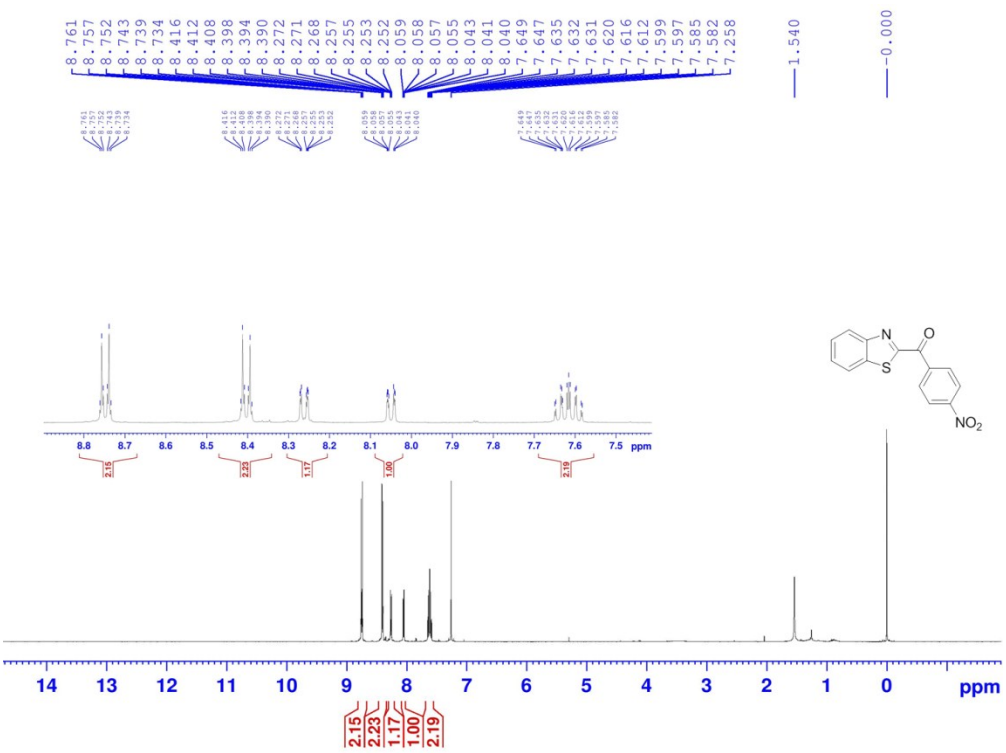

Fig.S13. ^{1}H-NMR spectra of benzo*[d]*thiazol-2-yl(4-nitrophenyl)methanone.

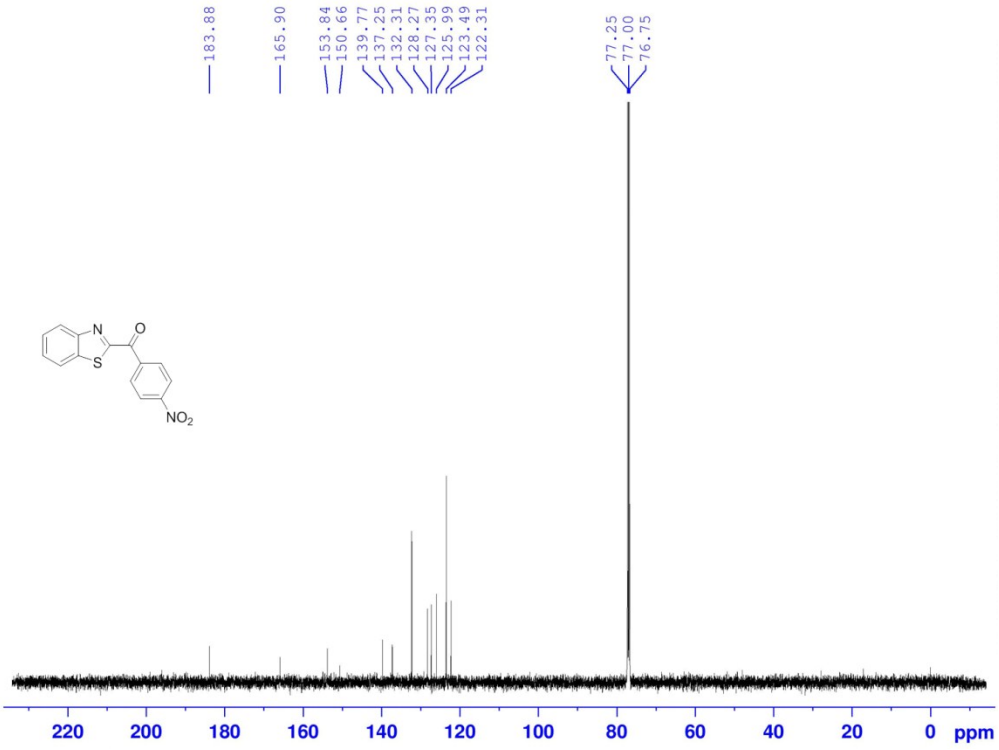

Fig.S14. ^{13}C-NMR spectra of benzo*[d]*thiazol-2-yl(4-nitrophenyl)methanone.

Characterization data for benzo*[d]*thiazol-2-yl(4-nitrophenyl)methanone (3ag)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 42 % yield (23.8 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.58 – 7.64 (m, 2H), 8.04 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 8.25 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 8.39 (dt, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 2H), 8.73 (dt, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.3, 123.4, 125.9, 127.3, 128.2, 132.3, 137.2, 139.7, 150.6, 153.8, 165.9, 183.8.

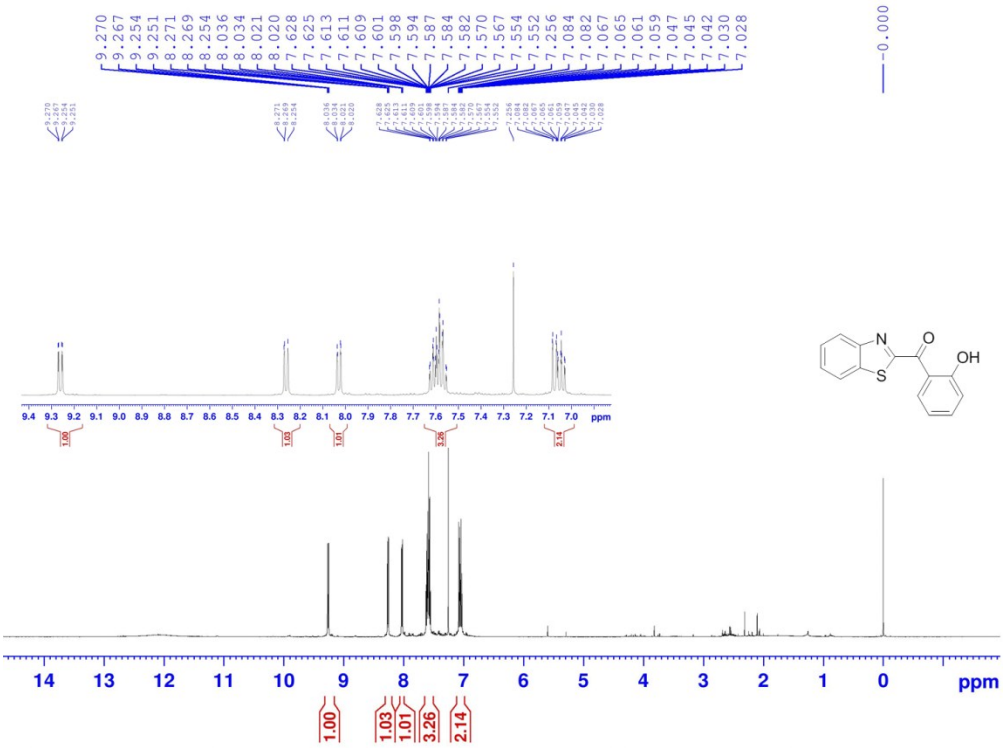

Fig.S15. ^{1}H-NMR spectra of benzo*[d]*thiazol-2-yl(2-hydroxyphenyl)methanone.

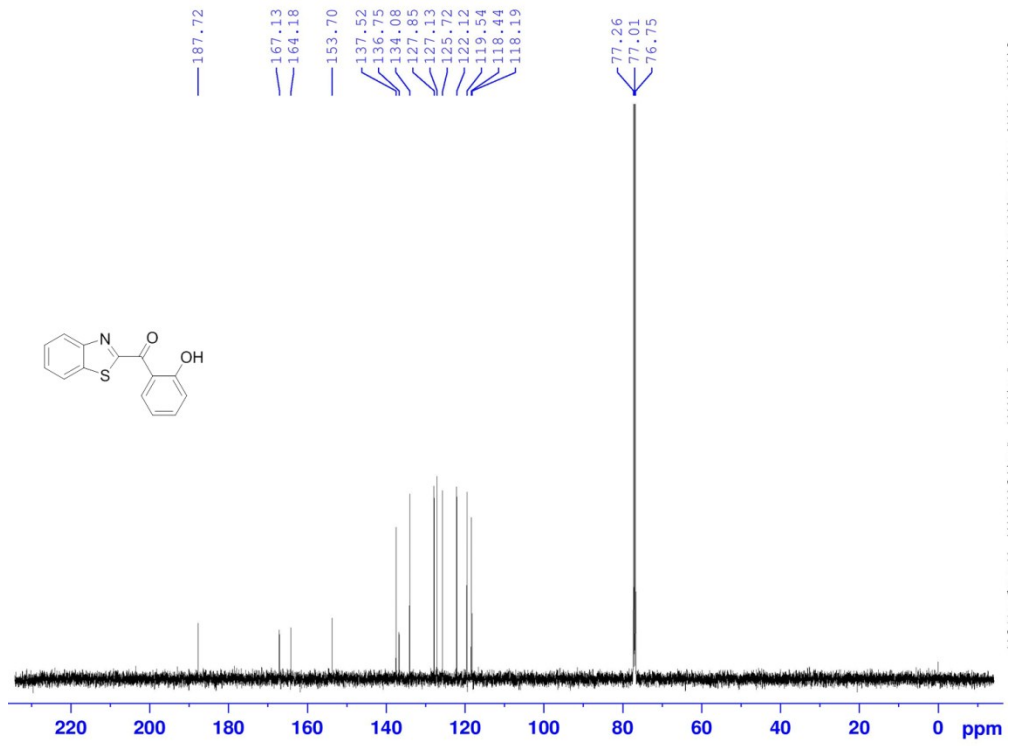

Fig.S16. ^{13}C-NMR spectra of benzo*[d]*thiazol-2-yl(2-hydroxyphenyl)methanone.

Characterization data for benzo*[d]*thiazol-2-yl(2-hydroxyphenyl)methanone (3ah)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 45 % yield (22.9 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.02 – 7.08 (m, 2H), 7.55 – 7.62 (m, 3H), 8.02 (d, *J* = 7.5 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 1H), 9.25 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 118.1, 118.4, 119.5, 122.1, 125.7, 127.1, 127.8, 134.0, 136.7, 137.5, 153.7, 164.1, 167.1, 187.7.

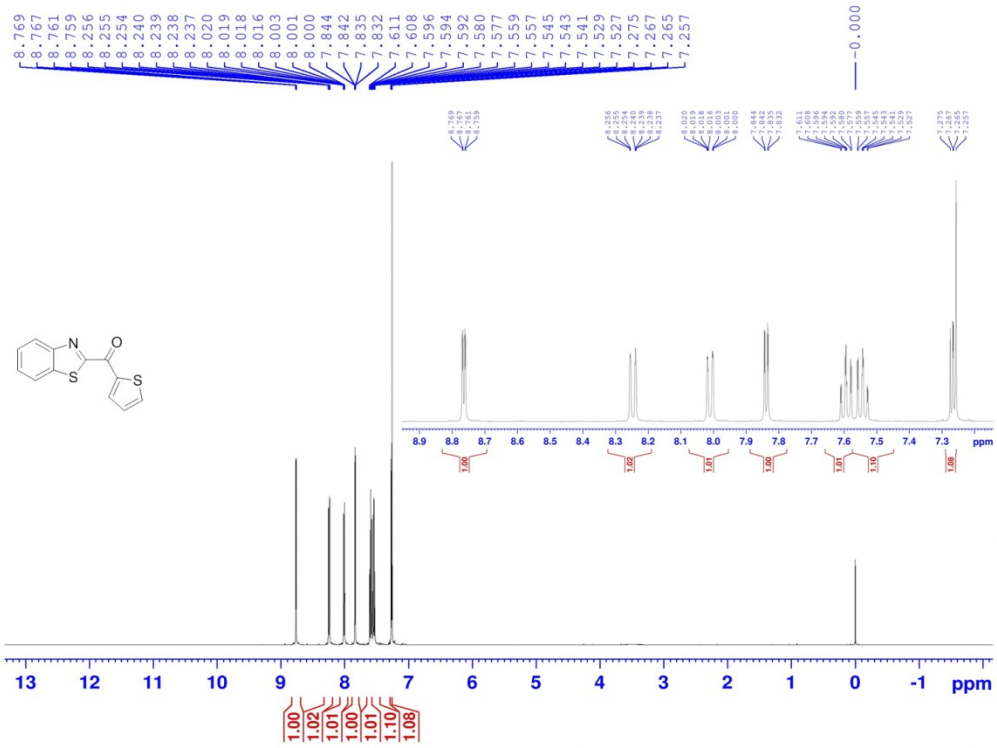

Fig.S17. ^{1}H-NMR spectra of benzo*[d]*thiazol-2-yl(thiophen-2-yl)methanone.

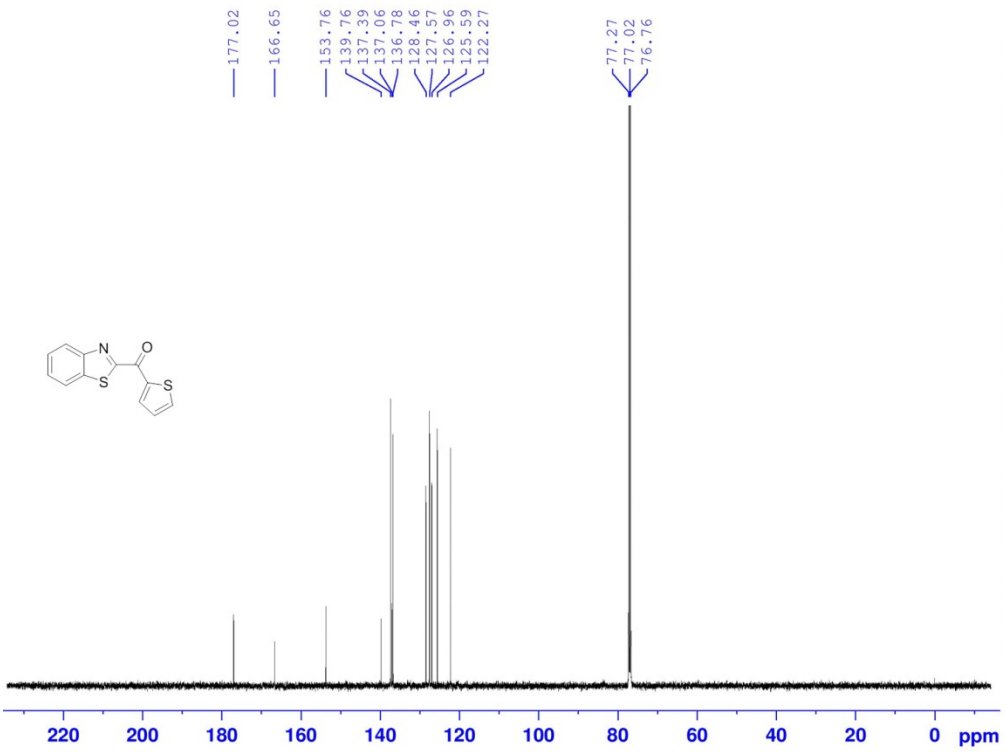

Fig.S18. ^{13}C-NMR spectra of benzo*[d]*thiazol-2-yl(thiophen-2-yl)methanone.

Characterization data for benzo*[d]*thiazol-2-yl(thiophen-2-yl)methanone (3ak)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 61 % yield (29.8 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.25 – 7.27 (m, 1H), 7.52 – 7.61 (m, 2H), 7.83 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 8.00 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 8.23 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 8.75 (dd, J_1 = 4.0 Hz, J_2 = 1.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.2, 125.5, 126.9, 127.5, 128.4, 136.7, 137.0, 137.3, 139.7, 153.7, 166.6, 177.0.

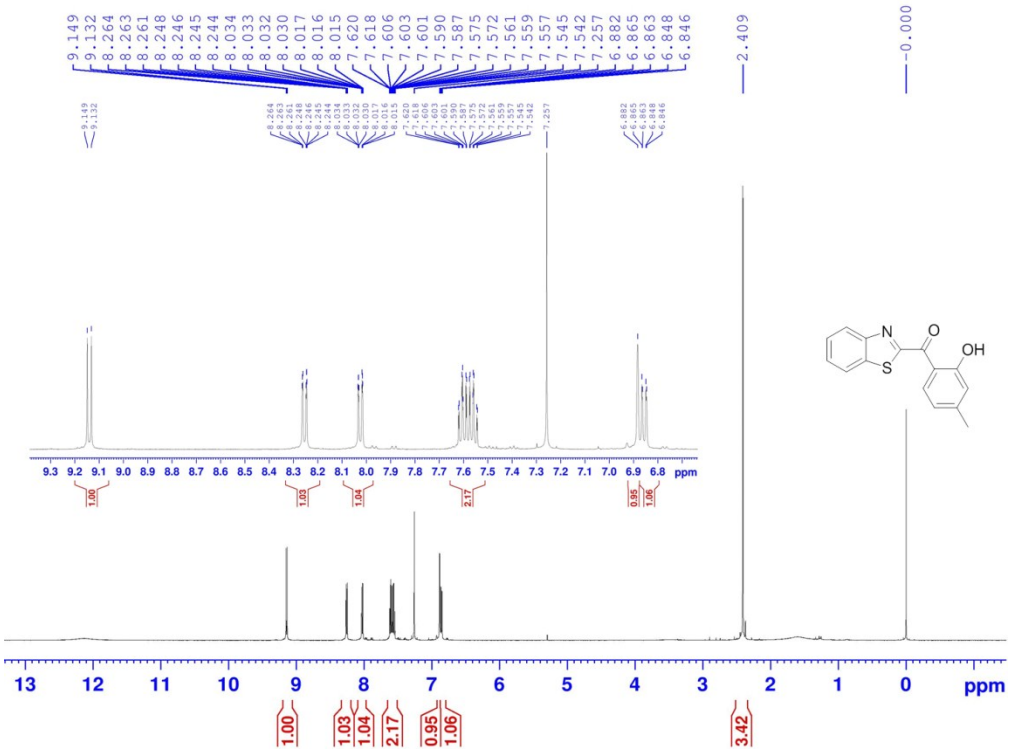

Fig.S19. ^{1}H-NMR spectra of benzo*[d]*thiazol-2-yl(2-hydroxy-4-methylphenyl)methanone.

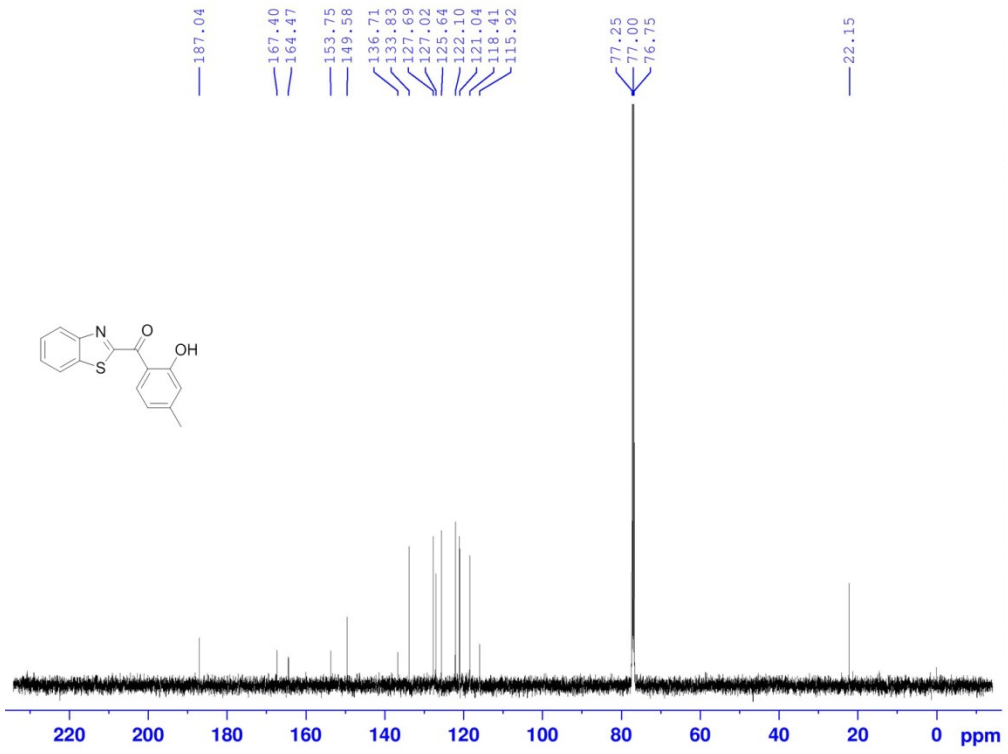

Fig.S20. ^{13}C-NMR spectra of benzo*[d]*thiazol-2-yl(2-hydroxy-4-methylphenyl)methanone.

Characterization data for benzo*[d]*thiazol-2-yl(2-hydroxy-4-methylphenyl)methanone (3al)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 53 % yield (28.5 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 2.40 (s, 3H), 6.84 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1H), 6.88 (s, 1H), 7.54 – 7.62 (m, 2H), 8.01 (dd, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 1H), 8.24 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 9.13 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 22.1, 115.9, 118.4, 121.0, 122.1, 125.6, 127.0, 127.6, 133.8, 136.7, 149.5, 153.7, 164.4, 167.4, 187.0.

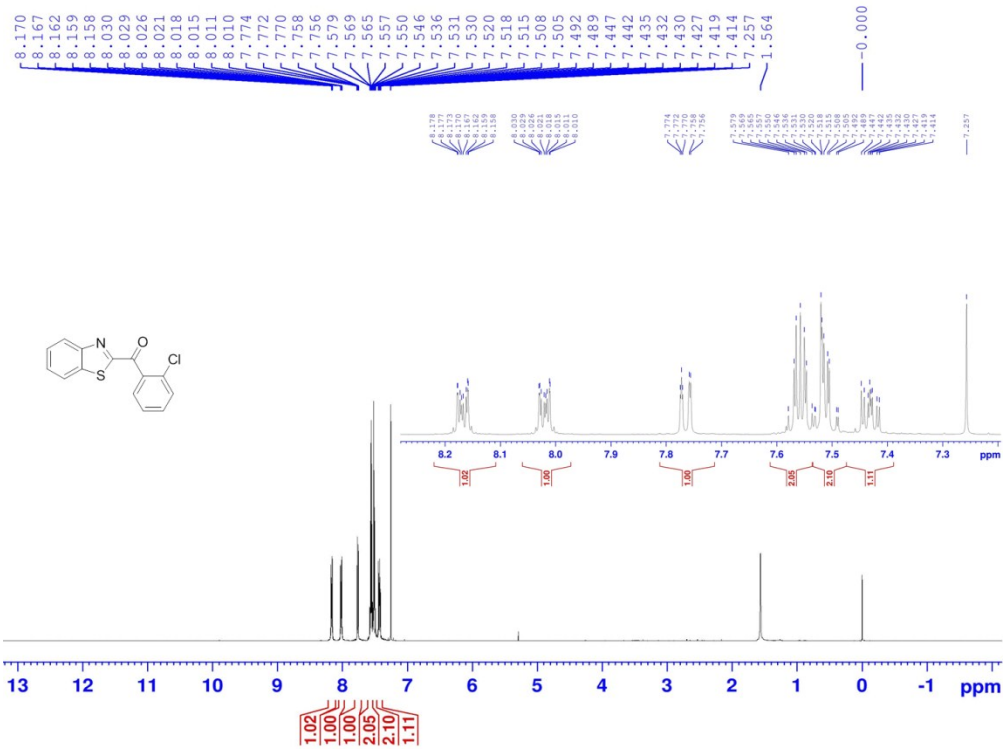

Fig.S21. ^{1}H-NMR spectra of benzo[d]thiazol-2-yl(2-chlorophenyl)methanone.

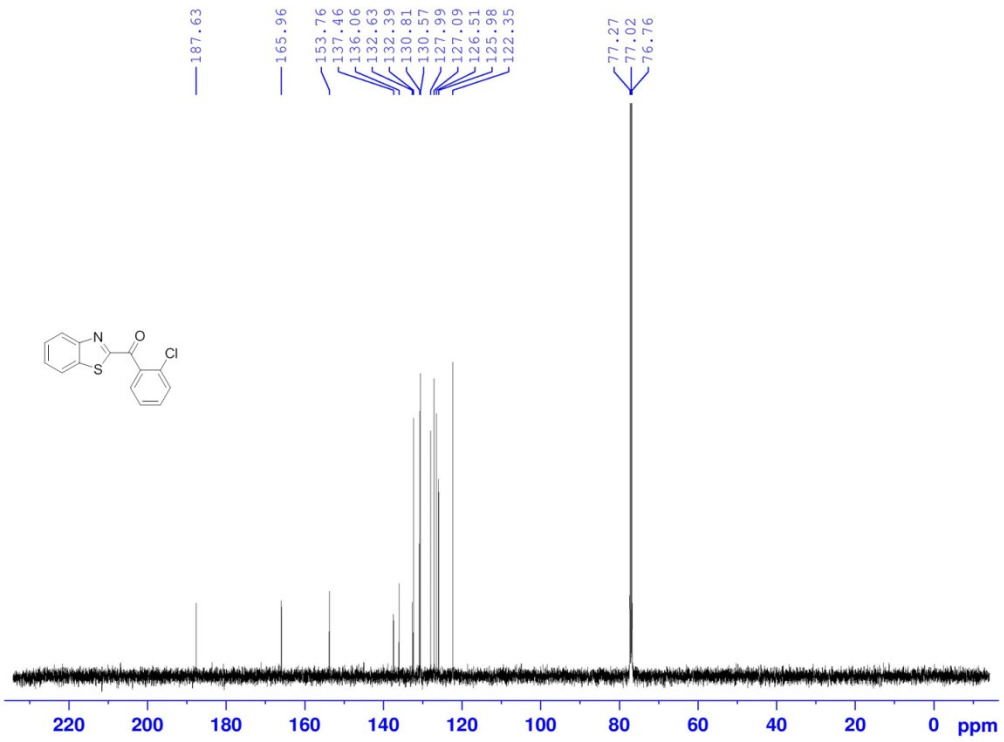

Fig.S22. ^{13}C-NMR spectra of benzo[d]thiazol-2-yl(2-chlorophenyl)methanone.

Characterization data for benzo[d]thiazol-2-yl(2-chlorophenyl)methanone (3an)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 61% yield (33.3 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.41 – 7.44 (m, 1H), 7.48 – 7.57 (m, 1H), 7.75 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 8.01 – 8.03 (m, 1H), 8.15 – 8.17 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.3, 125.9, 126.5, 127.0, 127.9, 130.5, 130.8, 132.3, 132.6, 136.0, 137.4, 153.7, 165.9, 187.6.

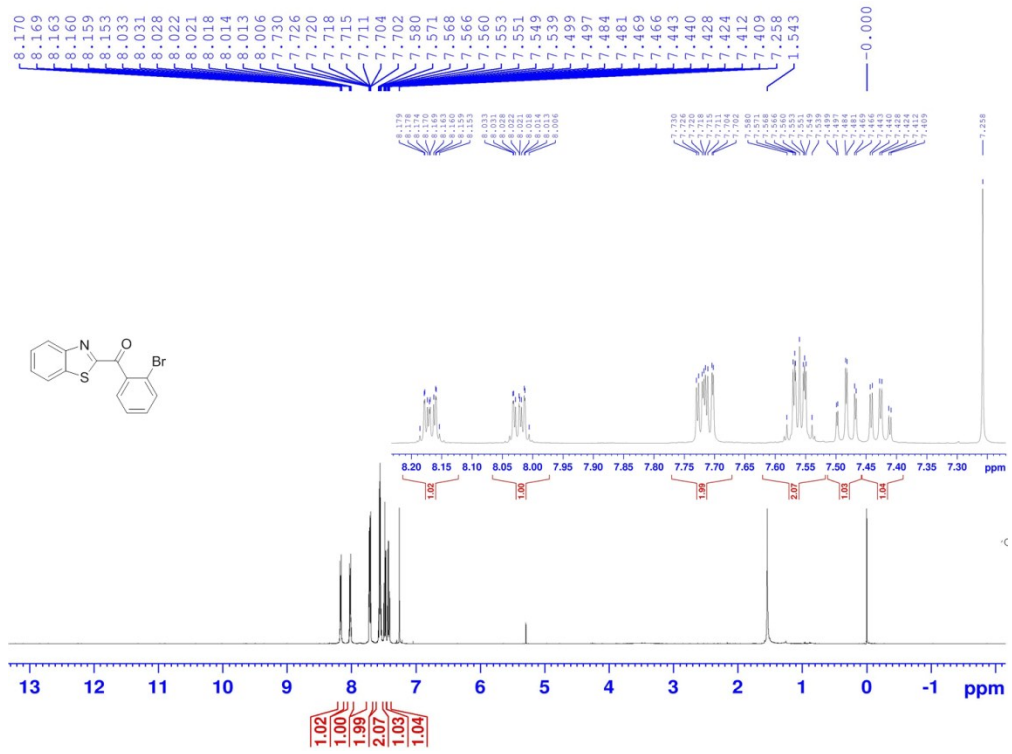

Fig.S23. ^{1}H-NMR spectra of benzo[d]thiazol-2-yl(2-bromophenyl)methanone.

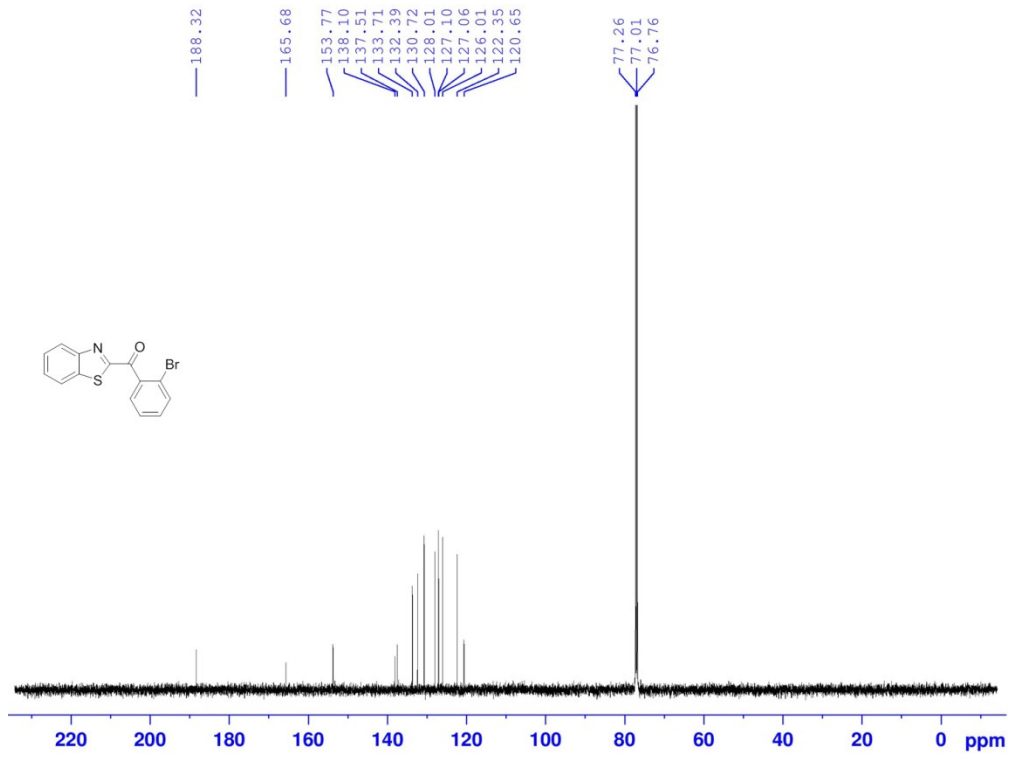

Fig.S24. ^{13}C-NMR spectra of benzo[d]thiazol-2-yl(2-bromophenyl)methanone

Characterization data for benzo[d]thiazol-2-yl(2-bromophenyl)methanone (3ap)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 51% yield (32.4 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.40 (td, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.46 (td, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.70 – 7.73 (m, 2H), 8.00 – 8.03 (m, 1H), 8.15 – 8.17 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 120.6, 122.3, 126.0, 127.0, 127.1, 128.0, 130.7, 132.3, 133.7, 137.5, 138.1, 153.7, 165.6, 188.3.

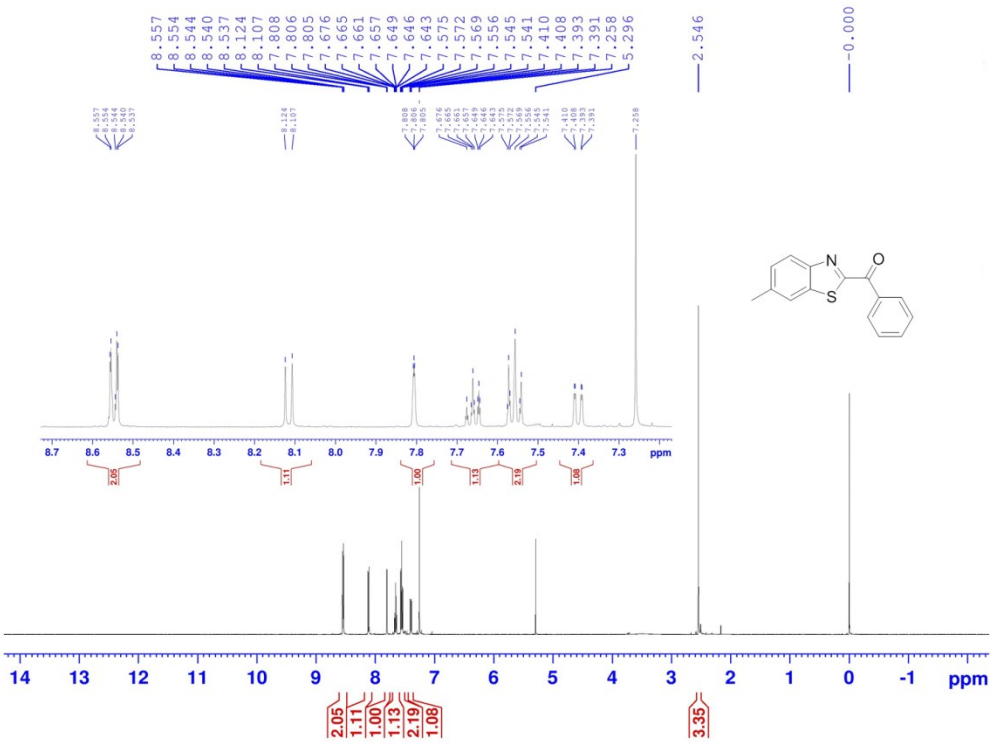

Fig.S25. ^{1}H-NMR spectra of (6-methylbenzo[d]thiazol-2-yl)(phenyl)methanone.

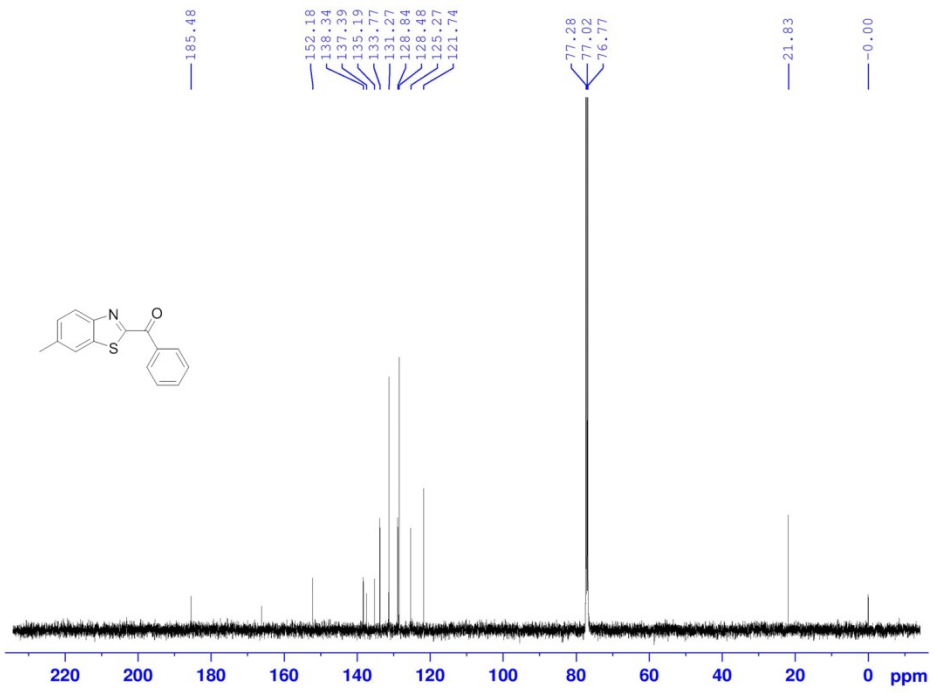

Fig.S26. ^{13}C-NMR spectra of (6-methylbenzo[d]thiazol-2-yl)(phenyl)methanone.

Characterization data for (6-methylbenzo[d]thiazol-2-yl)(phenyl)methanone (3ba)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 74 % yield (37.4 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 2.54 (s, 3H), 7.39 (dd, J_1 = 8.5 Hz, J_2 = 1.0 Hz, 1H), 7.54 – 7.57 (m, 2H), 7.64 – 7.67 (m, 1H), 7.80 (t, J = 1.0 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.53 (dd, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.8, 121.7, 125.2, 128.4, 128.8, 131.2, 133.7, 135.1, 137.3, 138.3, 152.1, 185.4.

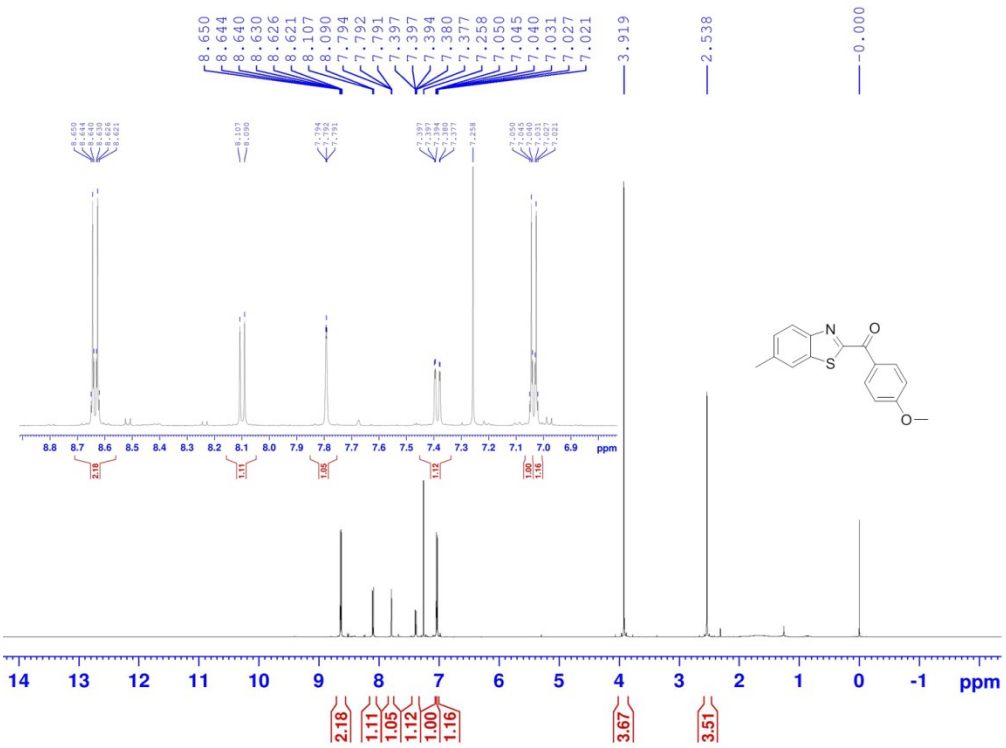

Fig.S27. [1]H-NMR spectra of (4-methoxyphenyl)(6-methylbenzo[d]thiazol-2-yl)methanone .

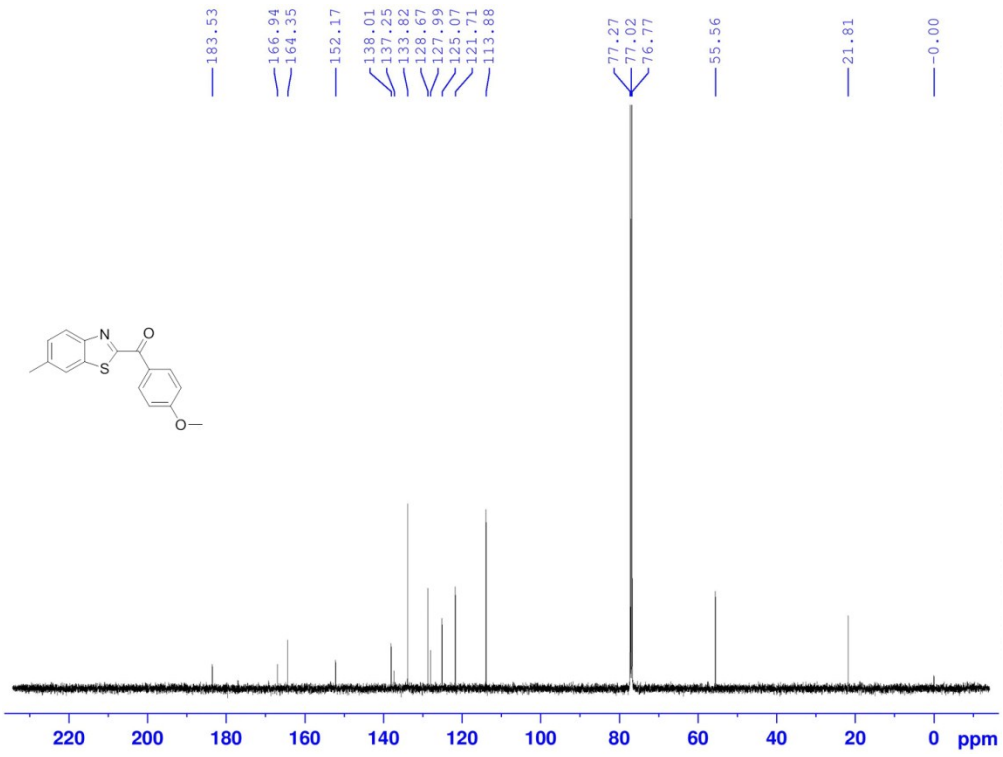

Fig.S28. ^{13}C-NMR spectra of (4-methoxyphenyl)(6-methylbenzo[d]thiazol-2-yl)methanone.

Characterization data for (4-methoxyphenyl)(6-methylbenzo[d]thiazol-2-yl)methanone (3bb)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 78 % yield (44.1 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 2.53 (s, 3H), 3.91 (s, 3H), 7.02 (dt, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 2H), 7.37 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.79 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 8.62 (dt, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.8, 55.5, 113.8, 121.7, 125.0, 127.9, 128.6, 133.8, 137.2, 138.0, 152.1, 164.3, 166.9, 183.5.

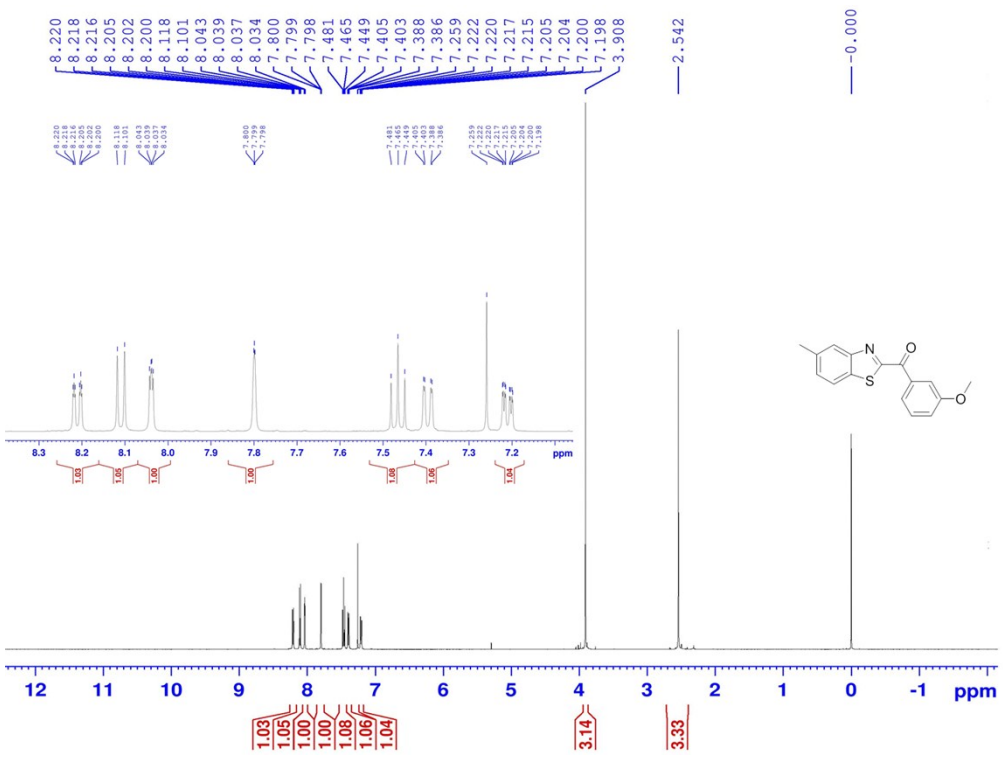

Fig.S29. [1]H-NMR spectra of (3-methoxyphenyl)(5-methylbenzo[d]thiazol-2-yl)methanone .

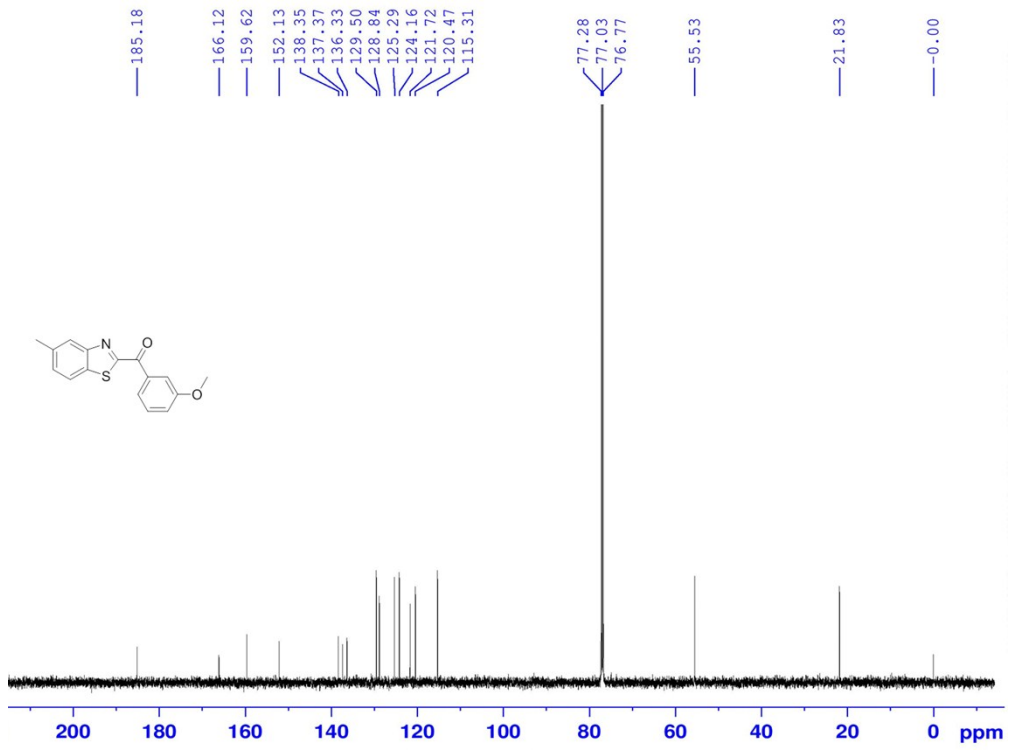

Fig.S30. ^{13}C-NMR spectra of (3-methoxyphenyl)(5-methylbenzo[d]thiazol-2-yl)methanone.

Characterization data for (3-methoxyphenyl)(5-methylbenzo[d]thiazol-2-yl)methanone (3bc)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 75% yield (42.5 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 2.54 (s, 3H), 3.90 (s, 3H), 7.19 – 7.22 (m, 1H), 7.38 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.80 (s, 1H) , 8.03 – 8.04 (m, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.20 (td, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H) . ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.8, 55.5, 115.3, 120.4, 121.7, 124.1, 125.2, 128.8, 129.5, 136.3, 137.3, 138.3, 152.1, 159.6, 166.1, 185.1.

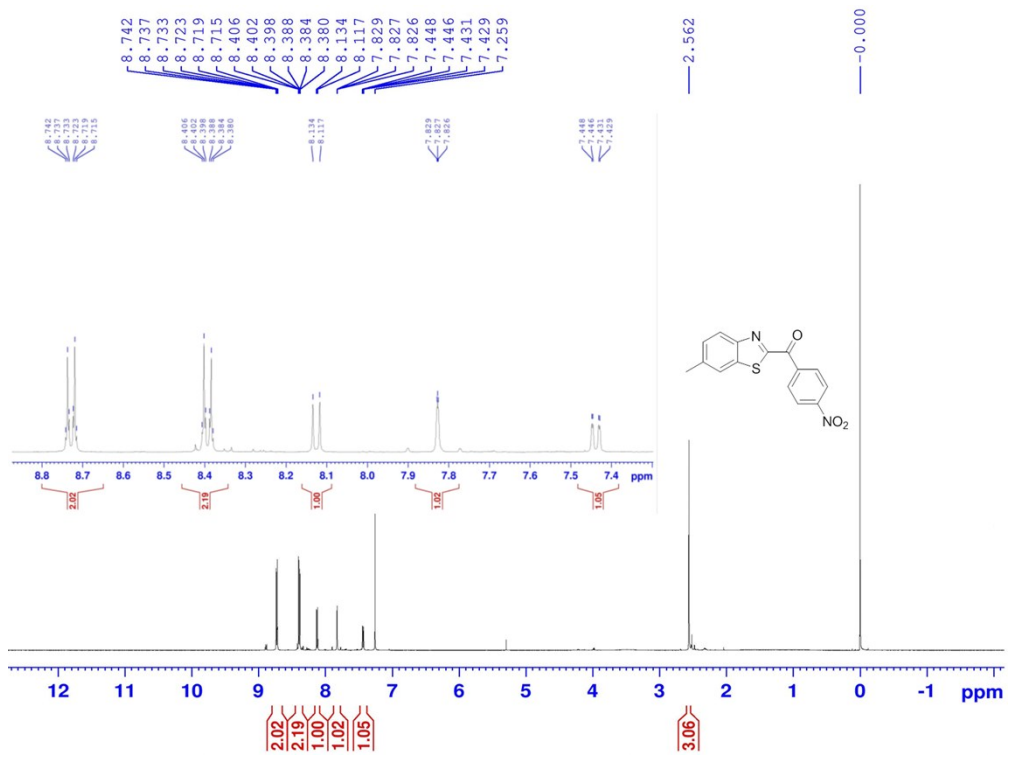

Fig.S31. ^{1}H-NMR spectra of (6-methylbenzo*[d]*thiazol-2-yl)(4-nitrophenyl)methanone.

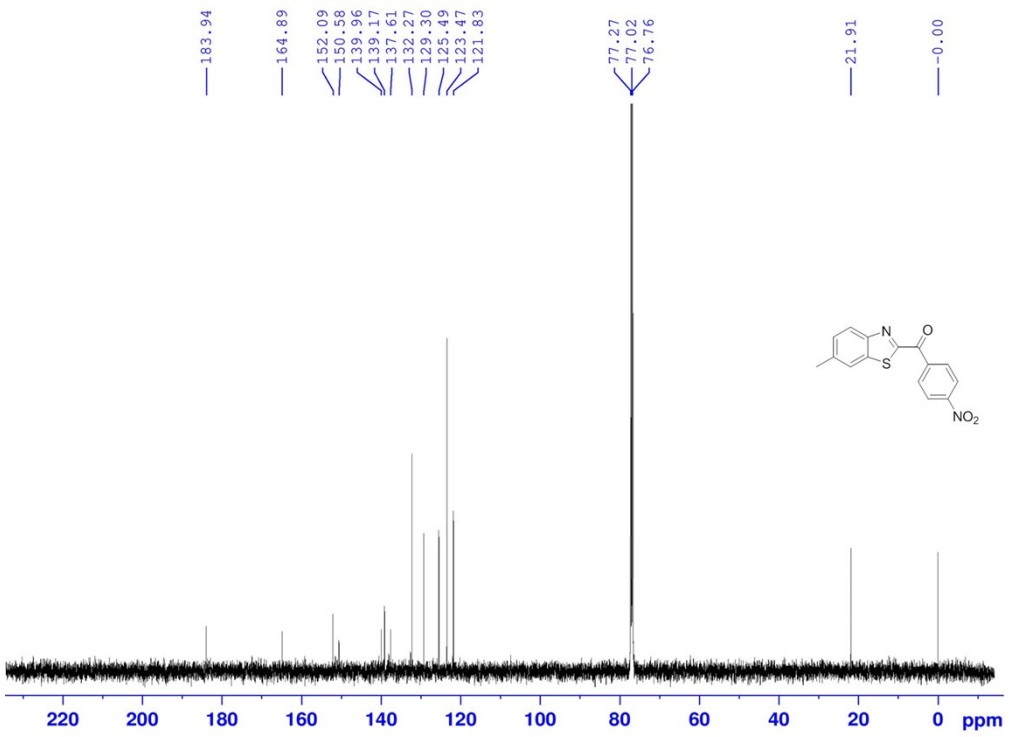

Fig.S32. ^{13}C-NMR spectra of (6-methylbenzo*[d]*thiazol-2-yl)(4-nitrophenyl)methanone.

Characterization data for (6-methylbenzo*[d]*thiazol-2-yl)(4-nitrophenyl)methanone (3bg)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 52 % yield (31 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 2.56 (s, 3H), 7.42 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.82 (s, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.38 (dt, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 2H), 8.71 (dt, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.9, 121.8, 123.4, 125.4, 129.3, 132.2, 137.6, 139.1, 139.9, 152.0, 164.8, 183.9.

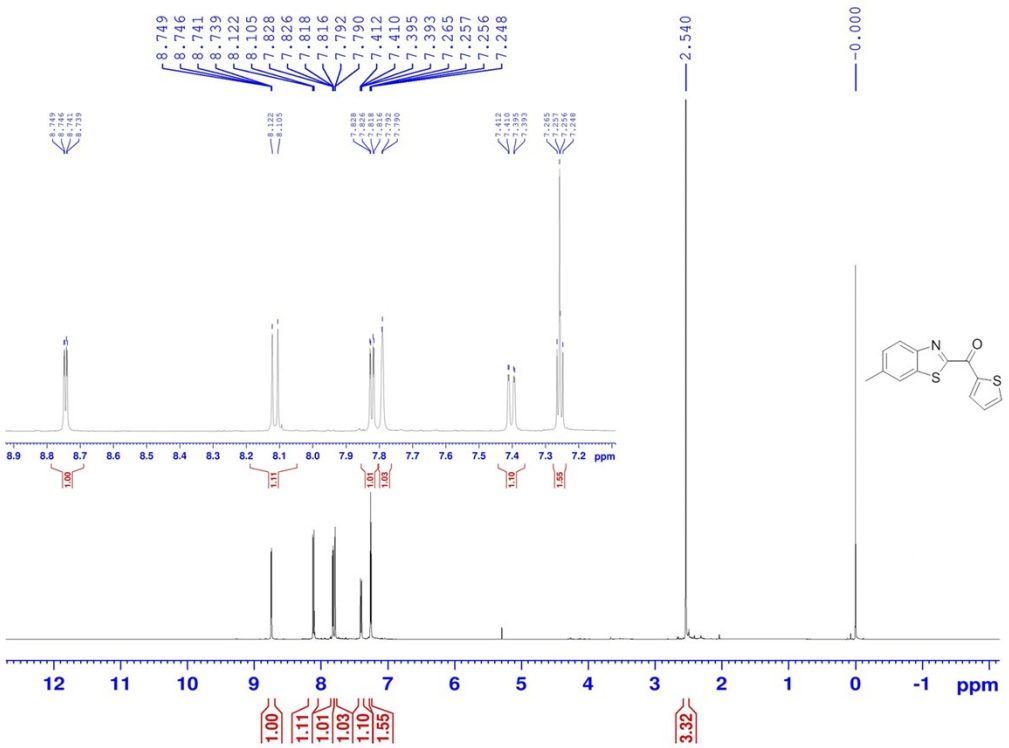

Fig.S33. ^{1}H-NMR spectra of (6-methylbenzo[d]thiazol-2-yl)(thiophen-2-yl)methanone.

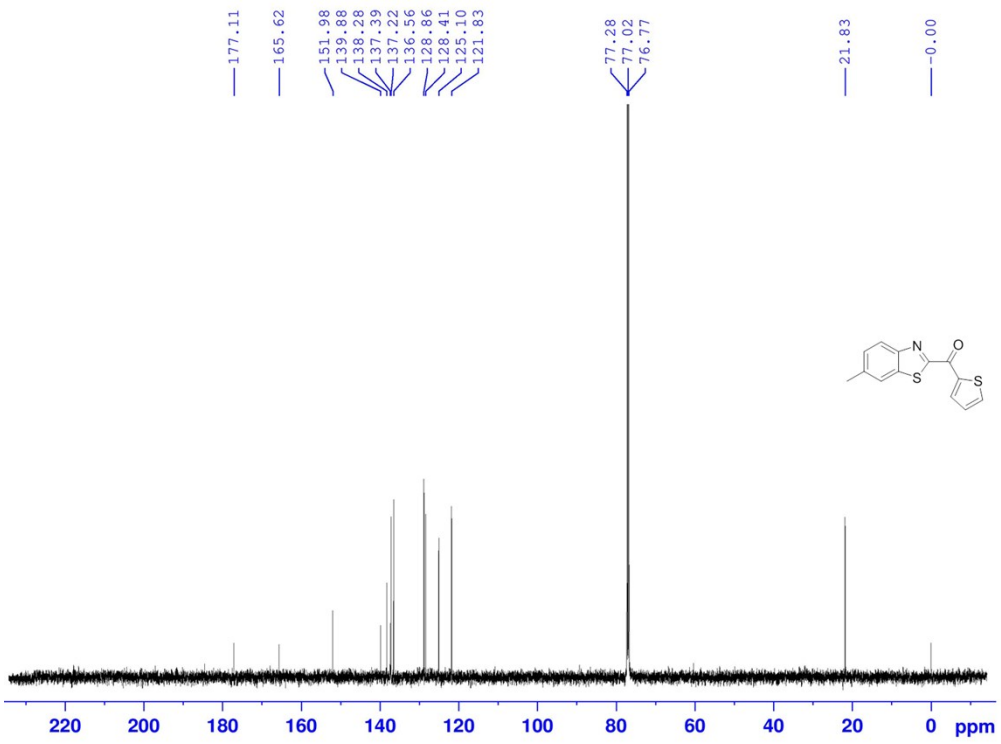

Fig.S34. ^{13}C-NMR spectra of (6-methylbenzo[d]thiazol-2-yl)(thiophen-2-yl)methanone.

Characterization data for (6-methylbenzo[d]thiazol-2-yl)(thiophen-2-yl)methanone (3bk)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 63 % yield (32.6 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 2.54 (s, 3H), 7.24 (d, *J*=5.0 Hz, 1H), 7.39 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.79 (s, 1H), 7.81 (dd, J_1 = 5.0 Hz, J_2 = 1.5 Hz, 1H), 8.10 (d, *J*=8.5 Hz, 1H), 8.73 (dd, J_1 = 4.0 Hz, J_2 = 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 21.8, 121.8, 125.1, 128.4, 128.8, 136.5, 137.2, 137.4, 138.2, 139.8, 151.9, 165.6, 177.1.

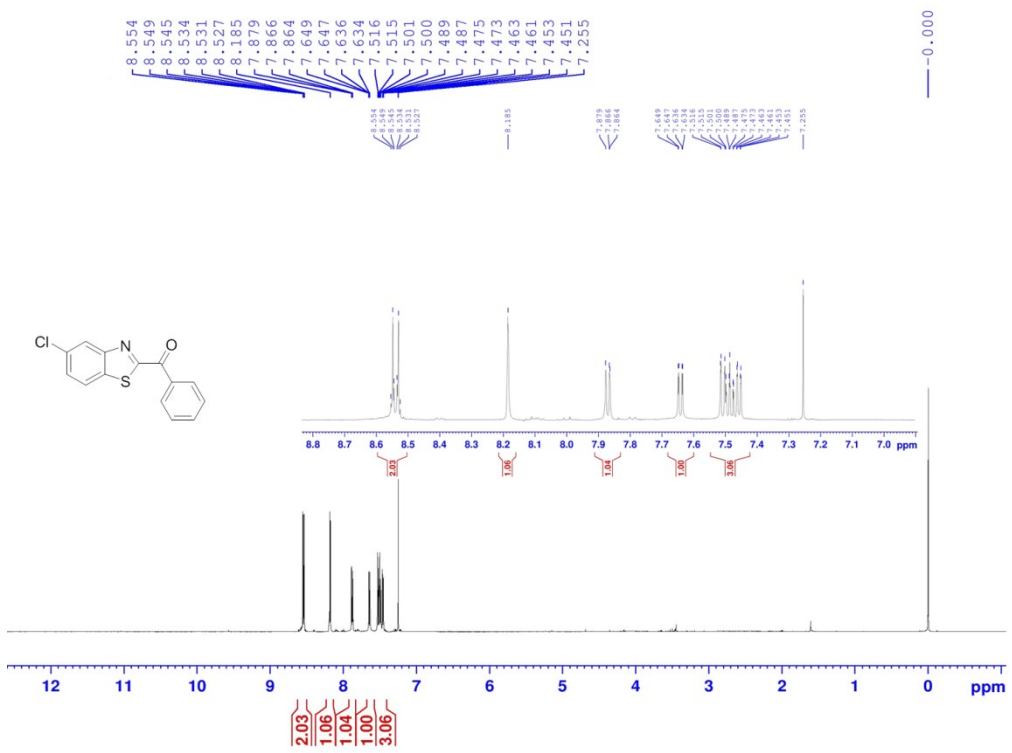

Fig.S35. ^{1}H-NMR spectra of (5-chlorobenzo*[d]*thiazol-2-yl)(phenyl)methanone.

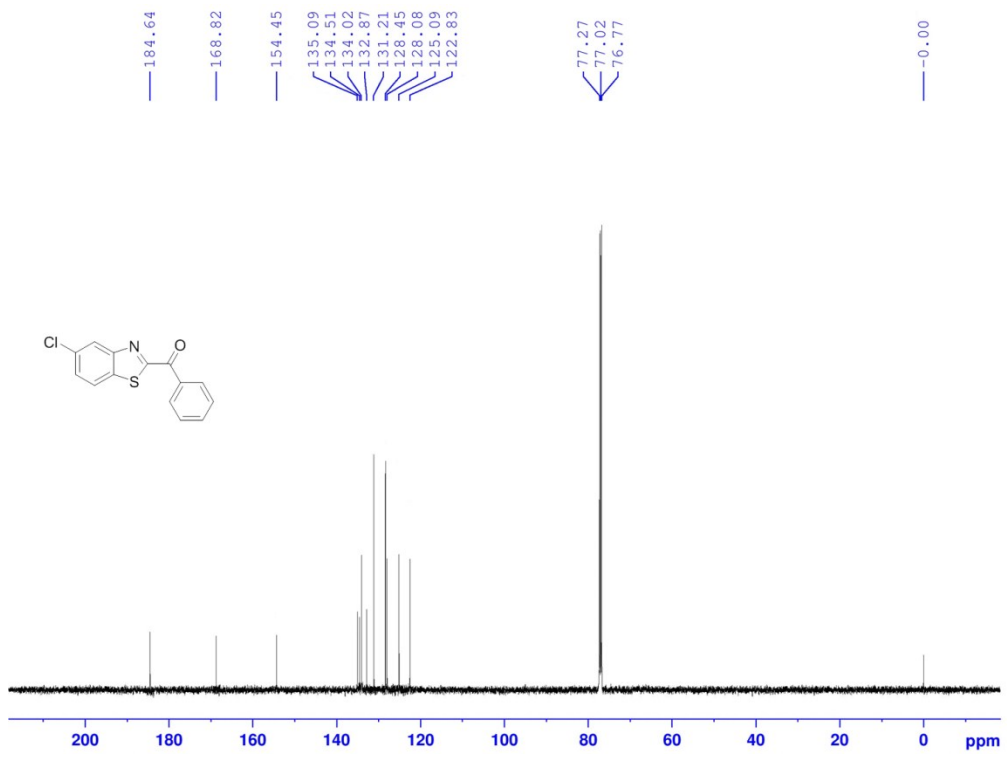

Fig.S36. ^{13}C-NMR spectra of (5-chlorobenzo*[d]*thiazol-2-yl)(phenyl)methanone .

Characterization data for (5-chlorobenzo*[d]*thiazol-2-yl)(phenyl)methanone (3ca)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 59 % yield (32.2 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.45 – 7.51 (m, 3H), 7.63 (dd, J_1 = 7.0 Hz, J_2 = 1.0 Hz, 1H), 7.86 (d, J=7.5 Hz, 1H), 8.18 (s, 1H), 8.52 (dt, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 2H),. ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.8, 125.0, 128.0, 128.4, 131.2, 132.8, 134.0, 134.5, 135.0, 154.4, 168.8, 184.6.

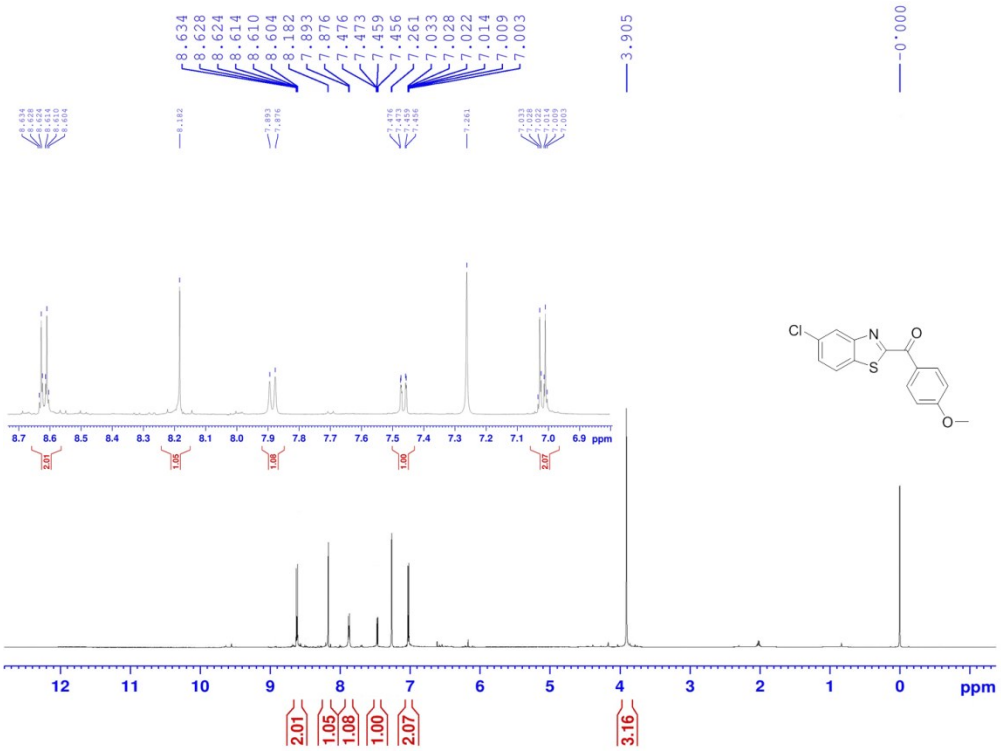

Fig.S37. [1]H-NMR spectra of (5-chlorobenzo*[d]*thiazol-2-yl)(4-methoxyphenyl)methanone.

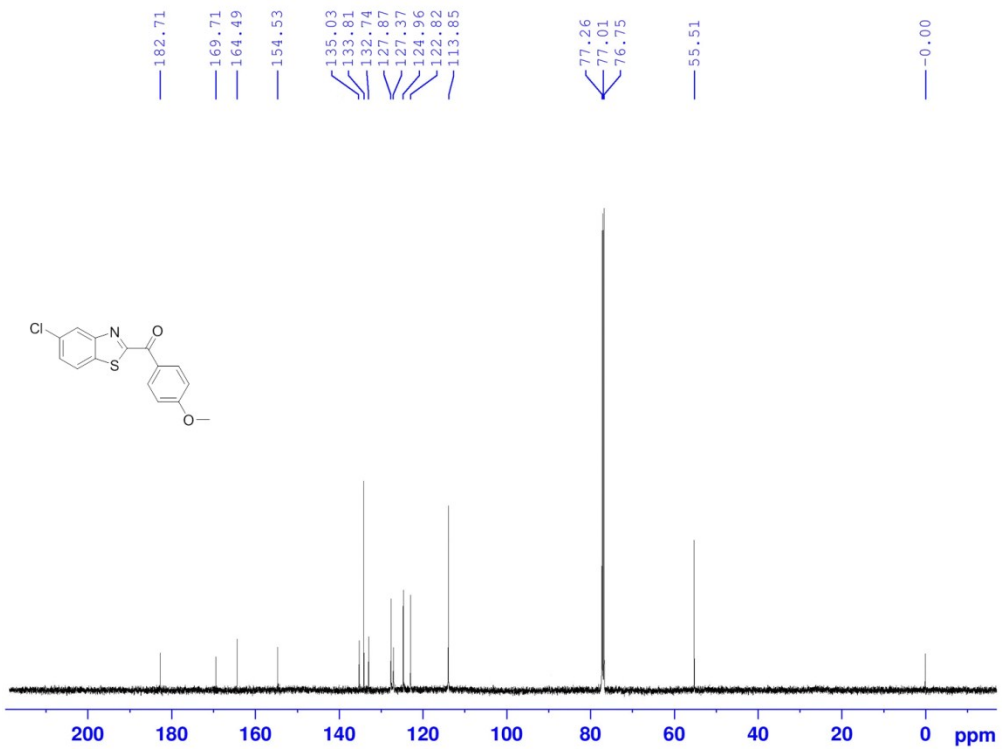

Fig.S38. ^{13}C-NMR spectra of (5-chlorobenzo*[d]*thiazol-2-yl)(4-methoxyphenyl)methanone.

Characterization data for (5-chlorobenzo*[d]*thiazol-2-yl)(4-methoxyphenyl)methanone (3cb)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 62% yield (37.5 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 3.9 (s, 3H), 7.00 (dt, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 2H), 7.45 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.87 (d, J = 8.5 Hz,1H), 8.18 (s, 1H), 8.60 (dt, J_1 = 9.0 Hz, J_2 = 2.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 55.5, 113.8, 122.8, 124.9, 127.3, 127.8, 132.7, 133.8, 135.0, 154.5, 164.4, 169.7, 182.7.

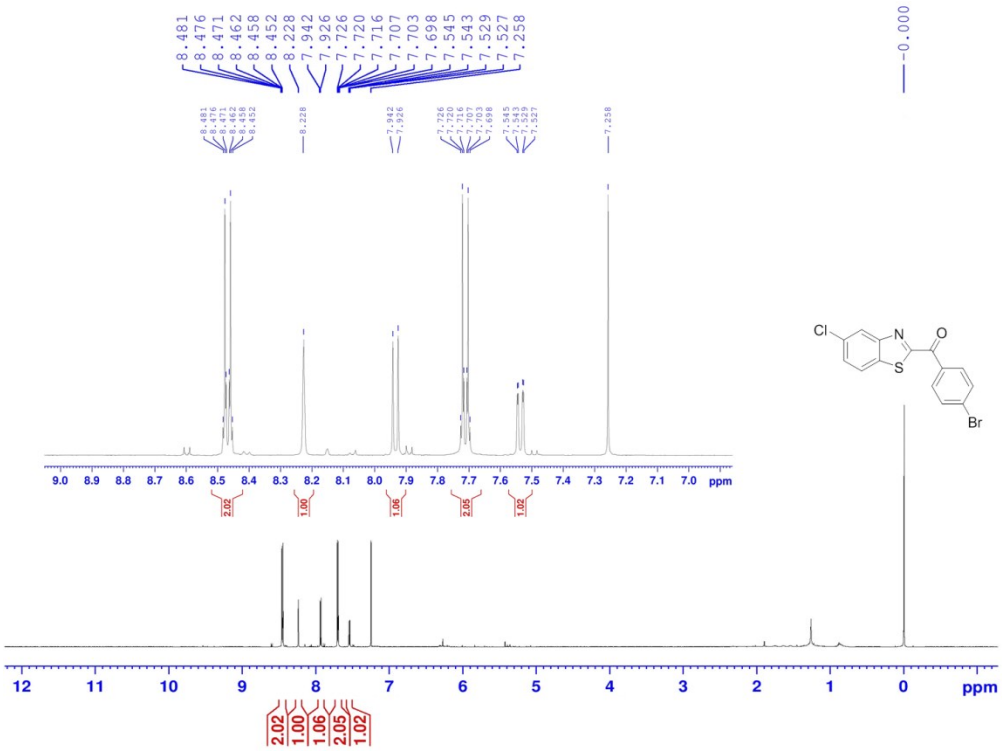

Fig.S39. ^{1}H-NMR spectra of (4-bromophenyl)(5-chlorobenzo*[d]*thiazol-2-yl)methanone.

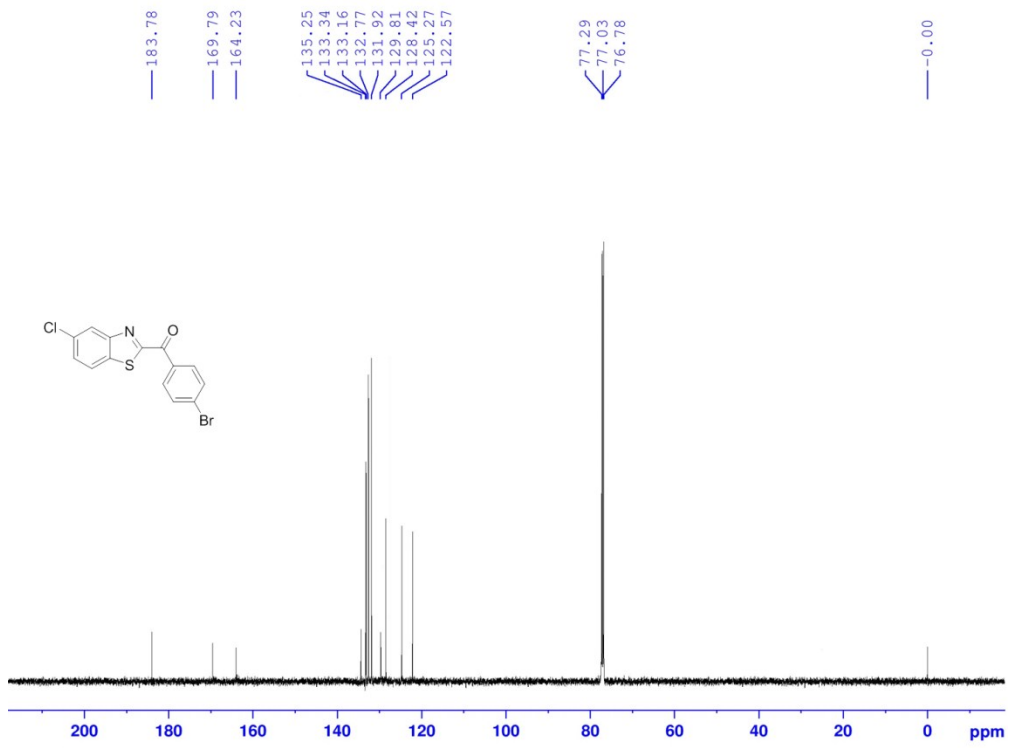

Fig.S40. ^{13}C-NMR spectra of (4-bromophenyl)(5-chlorobenzo*[d]*thiazol-2-yl)methanone.

Characterization data for (4-bromophenyl)(5-chlorobenzo*[d]*thiazol-2-yl)methanone (3cf)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 45 % yield (31.5 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.52 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 7.69 (dt, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 1H), 8.22 (s, 1H), 8.45 (dt, J_1 = 9.5 Hz, J_2 = 2.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 122.5, 125.2, 128.4, 129.8, 131.9, 132.7, 133.1, 133.3, 135.2, 164.2, 169.7, 183.7

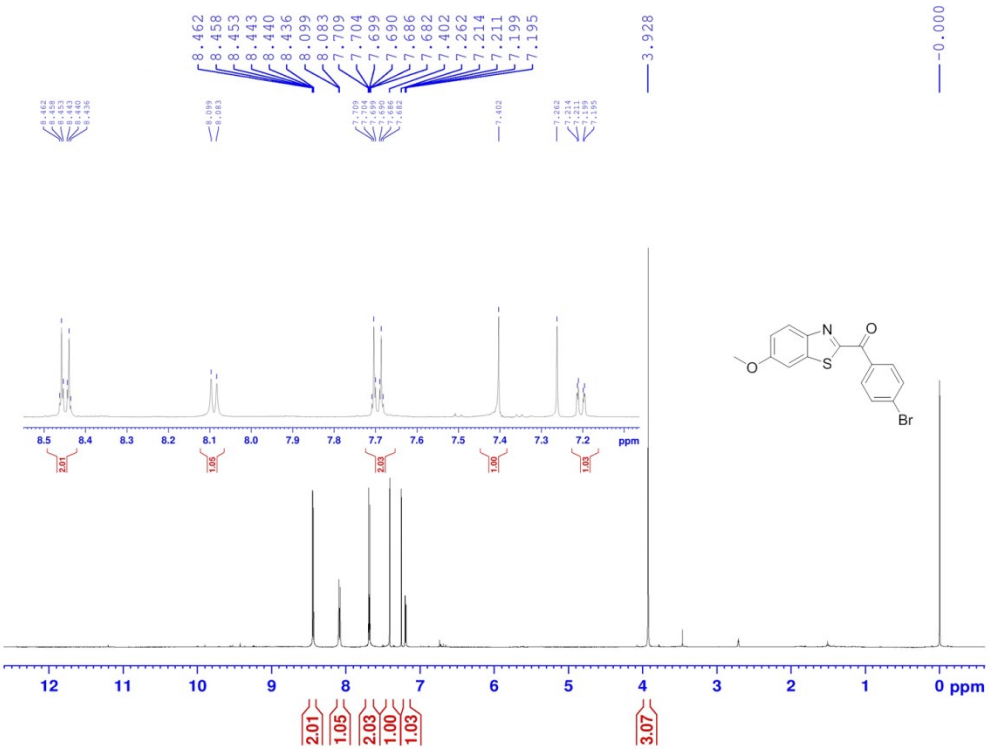

Fig.S41. [1]H-NMR spectra of (4-bromophenyl)(6-methoxybenzo*[d]*thiazol-2-yl)methanone.

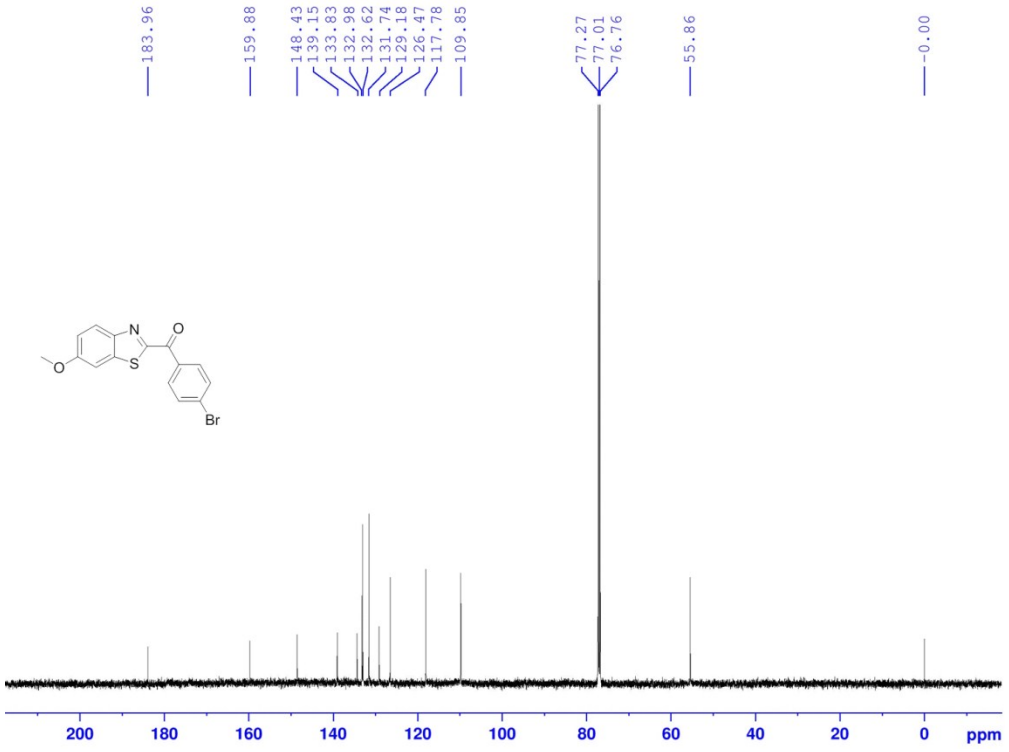

Fig.S42. ^{13}C-NMR spectra of (4-bromophenyl)(6-methoxybenzo*[d]*thiazol-2-yl)methanone.

Characterization data for (4-bromophenyl)(6-methoxybenzo*[d]*thiazol-2-yl)methanone (3df)

Prepared as shown in the general experimental procedure and purified on silica gel (230-400 mesh or 37-63 μm, ethyl acetate/hexane = 1:25 (v./v.), TLC silica gel 60 F_{254}): Yellow solid, 57 % yield (39.4 mg). ^{1}H-NMR (500 MHz, $CDCl_3$) δ(ppm) 7.19 (dd, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 1H), 7.40 (s, 1H), 7.68 (dt, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 2H), 8.08 (d, J = 8.0 Hz,1H), 8.43 (dt, J_1 = 9.5 Hz, J_2 = 2.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ(ppm) 55.8, 109.8, 117.7, 126.4, 129.1, 131.7, 132.6, 132.9, 133.8, 139.1, 148.4, 159.8, 183.9.

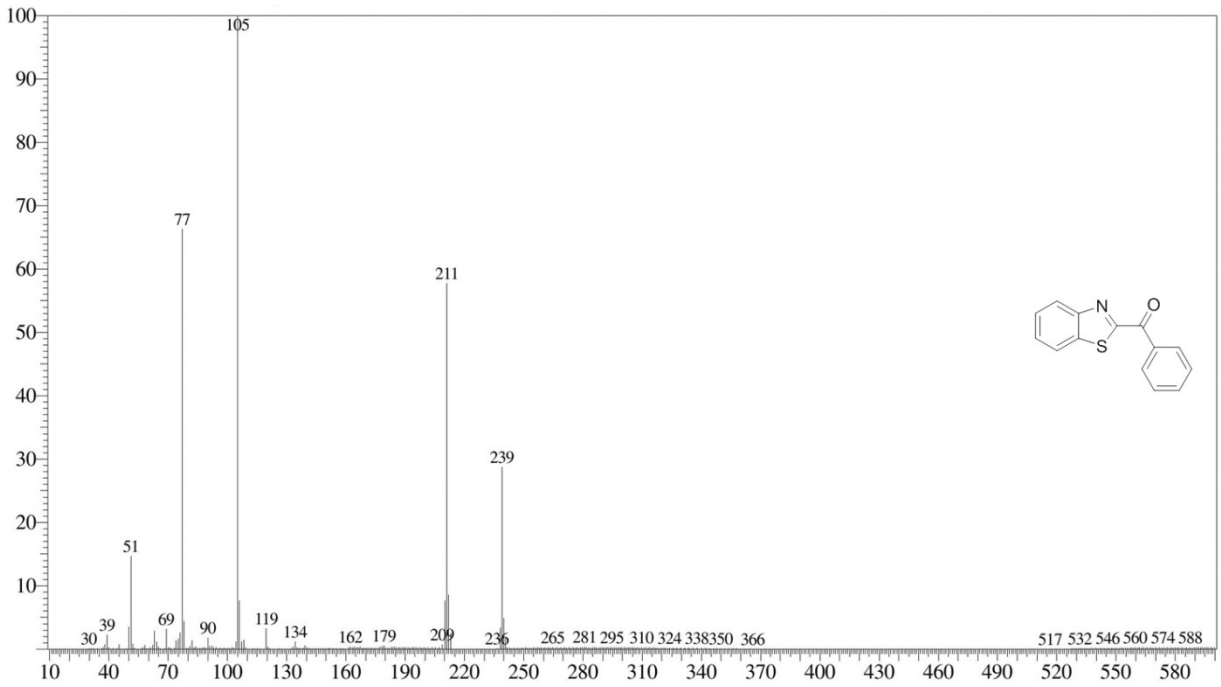

Fig.S43. MS analysis indicated the presence of benzo*[d]*thiazol-2-yl(phenyl)methanone **3aa** with m/z = 239.

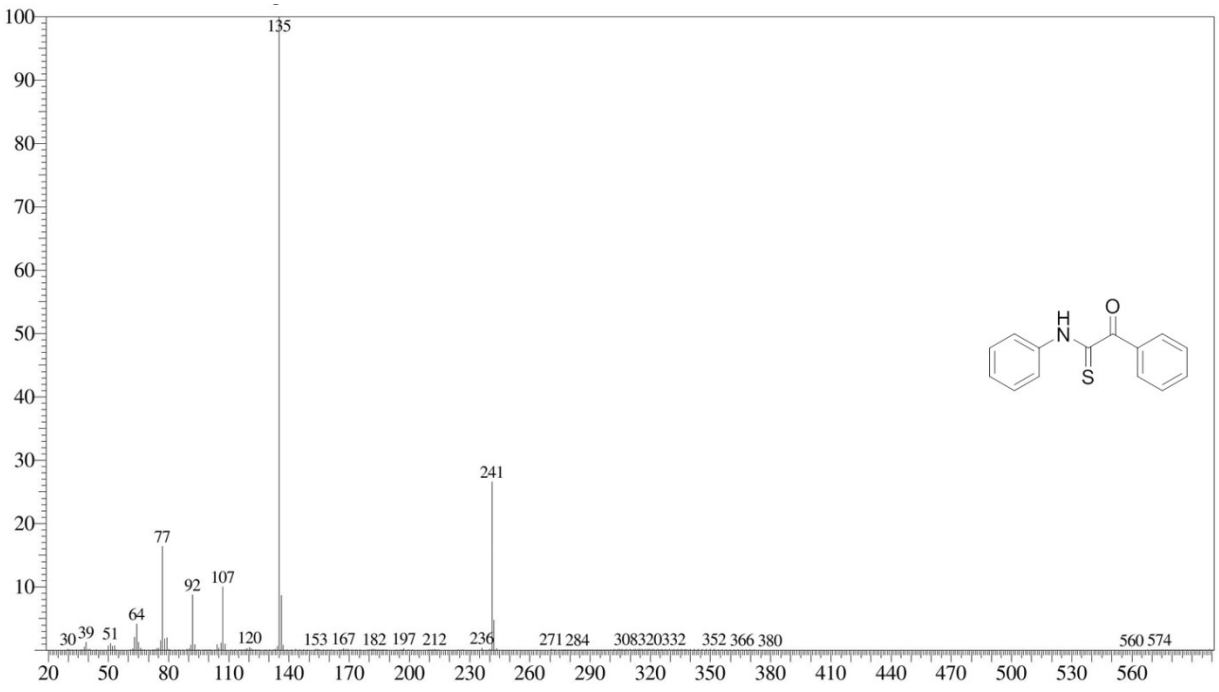

Fig.S44. MS analysis indicated the presence of 2-oxo-*N*,2-diphenylethanethioamide **6** with m/z = 241.

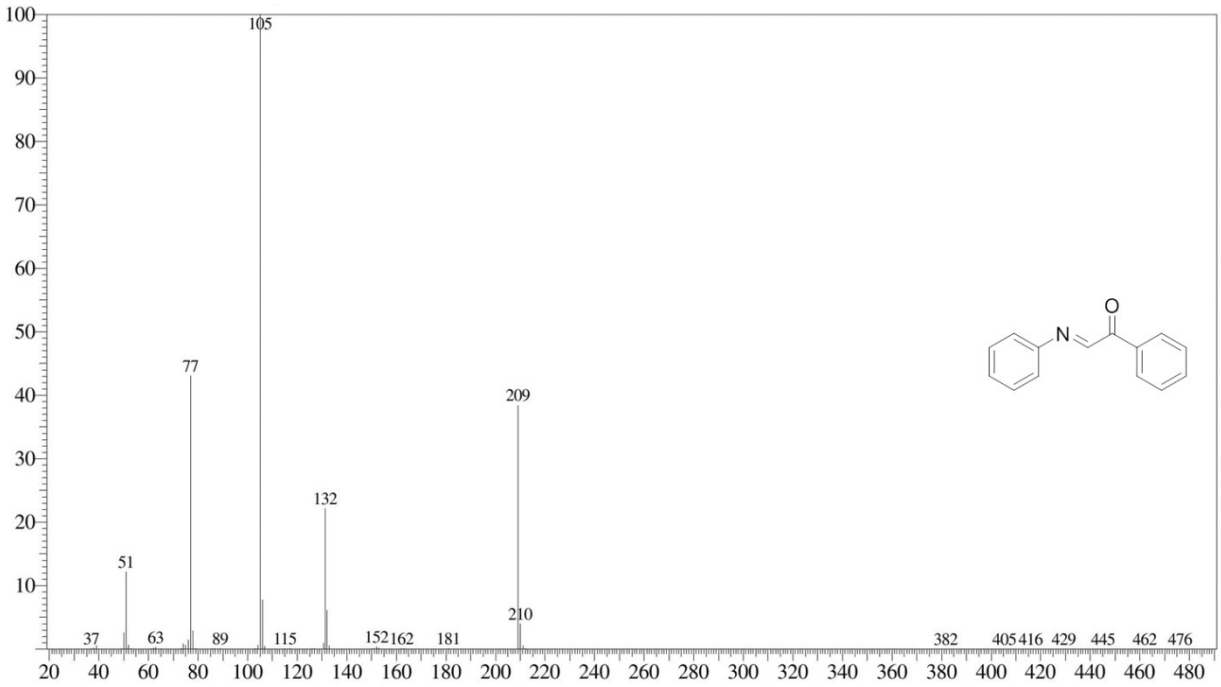

Fig.S45. MS analysis indicated the presence of *(E)*-1-phenyl-2-(phenylimino)ethanone **5** with m/z = 209.