Facile synthesis of *N*-acyl 2-aminobenzothiazoles by NHC-catalyzed direct oxidative amidation of aldehydes

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Supporting Information

1. General Information

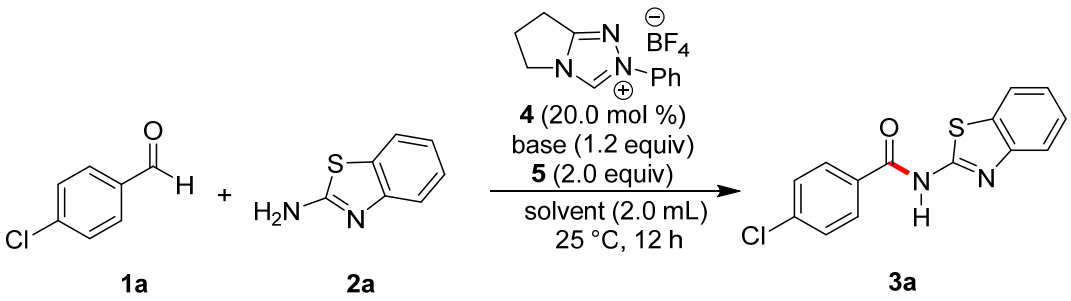
Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Dry CH_2Cl_2 was purchased from commercial sources and stored under argon over 4 Å molecular sieves. All aldehydes were purchased from commercial sources and used without further purification. Benzothiazole-2-amine derivatives **2** were synthesized by following the literature procedure.[1] Cs_2CO_3 was purchased from commercial sources and was used without further purification. The triazolium salt **4** was synthesized by following the literature procedure.[2]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. ether-EtOAc solvent system.

All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400, in either $CDCl_3$ or DMSO-d_6 as solvent as specified. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm; (DMSO-d_6: δH = 2.52 ppm, δC = 39.5 ppm). Infrared spectra were recorded on a Perkin-Elmer 1615 FT Infrared Spectrophotometer Model 60B. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump.

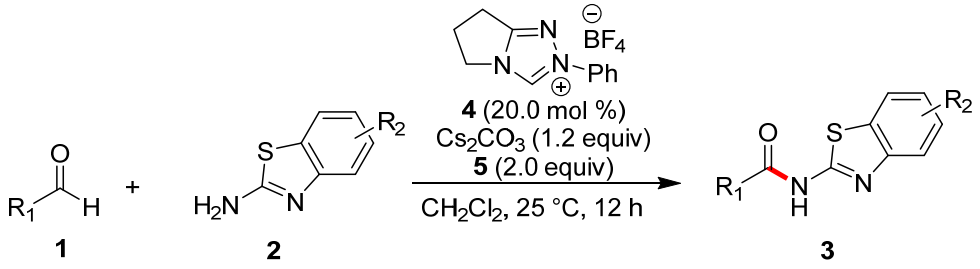
[1] D. Munirajasekhar, M. Himaja and V. M. Sunil, *IRJP.*, 2011, **2**, 114.
[2] F. Romanov-Michailidis, C. Besnard and A. Alexakis, *Org. Lett*., 2012, **14**, 4906.

2. General Procedure for the Optimization of Reaction Conditions



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was taken the triazolium salt **4** (0.05 mmol, 20 mol %), 4-chlorobenzaldehyde **1a** (0.5 mmol, 2.0 equiv), 2-aminobenzothiazole **2a** (0.25 mmol, 1.0 equiv), oxidant **5** (204.0 mg, 0.5 mmol, 2.0 equiv) and base (0.3 mmol, 1.2 equiv) were added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added solvent (2.0 mL) under argon atmosphere and the mixture was kept stirring at 25 °C for 12 hours. When the reaction is complete, the crude residue was purified by flash column chromatography on silica gel to afford the corresponding *N*-(benzothiazol-2-yl)amide derivative **3a.**

3. General Procedure for the Synthesis of *N*-(Benzothiazol-2-yl)amide Derivatives

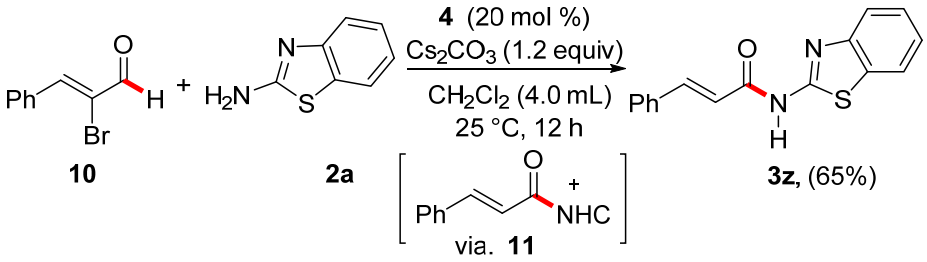


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was taken the triazolium salt **4** (28.0 mg, 0.1 mmol, 20 mol %), aldehyde **1** (1.0 mmol, 2.0 equiv), 2-aminobenzothiazole **2** (0.50 mmol, 1.0 equiv), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol, 1.2 equiv) were added. Then the screw-capped tube was

evacuated and backfilled with argon. To this mixture was added CH_2Cl_2 (4.0 mL) under argon atmosphere and the mixture was kept stirring at 25 °C for 12 hours. When the reaction is complete, the crude residue was purified by flash column chromatography on silica gel to afford the corresponding *N*-(benzothiazol-2-yl)amide derivatives **3**.

4. General Procedure for the Mechanistic Studies

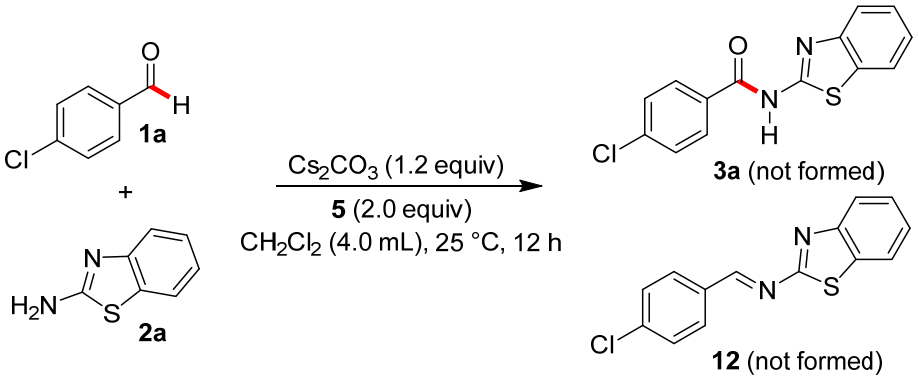
NHC-Catalyzed Reaction of 2-Bromoenal with 2-aminobenzothiazole [Scheme 4 (eq 1)]



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was taken the triazolium salt **4** (28.0 mg, 0.1 mmol, 20 mol %), 2-bromoenal **10** (211.0 mg, 1.0 mmol, 2.0 equiv), 2-aminobenzothiazole **2** (76.0 mg, 0.50 mmol, 1.0 equiv), and Cs_2CO_3 (196.0 mg, 0.6 mmol, 1.2 equiv) were added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added CH_2Cl_2 (4.0 mL) under argon atmosphere and the mixture was kept stirring at 25 °C for 12 hours. When the reaction is complete, the crude residue was purified by flash column chromatography on Silica get to afford the corresponding *N*-(benzothiazol-2-yl)amide **3z** as white solid (91 mg, 65% yield).

*This Experiment indicates the intermediacy of NHC-bound acyl azolium **11** in the present direct amidation reaction*

*Reaction Performed in the absence of **4** [Scheme 4 (eq 2)[*

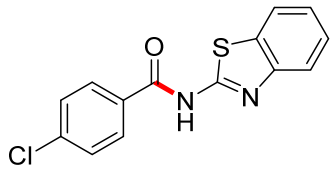


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was taken the aldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv), 2-aminobenzothiazole **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol, 1.2 equiv) were added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added CH_2Cl_2 (4.0 mL) under argon atmosphere and the mixture was kept stirring at 25 °C for 12 hours. The crude residue was purified by flash column chromatography and the unreacted **1a** and **2a** were recovered quantitatively. The formation of amide **3a** as well as imine **12** were not observed.

The formation of no imine rules out the amide formation from imines under oxidative conditions under the present reaction conditions

5. Synthesis and Characterization of *N*-(Benzothiazol-2-yl)amide Derivatives

***N*-(Benzo[*d*]thiazol-2-yl)-4-chlorobenzamide (3a)**[3]

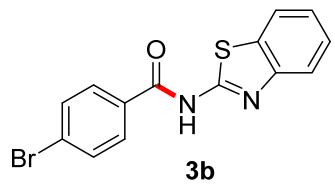


3a

Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-4-chlorobenzamide **3a** as white solid (134.0 mg, 93% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.63; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.46 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.87-7.85 (m, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.34-7.31 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.0, 159.7, 147.8, 139.8, 132.1, 130.6, 129.5, 129.41, 126.4, 124.4, 121.7, 120.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{10}ClN_2OS$: 289.0197, found: 289.0195. **FTIR (cm^{-1})** 3019, 2976, 2400, 2361, 1679, 1598, 1538, 1277, 1215, 928, 774, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-4-bromobenzamide (3b)**[4]



3b

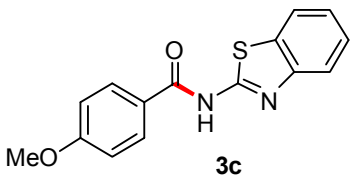
Following the general procedure, treatment of 4-bromobenzaldehyde **1b** (185.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-4-bromobenzamide **3b** as white solid (140.0 mg, 84% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.60; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 13.02 (s, 1H), 8.06 (dd, J_1= 22.8 Hz, J_2= 8.0 Hz, 3H), 7.80 (d, *J* = 8.1 Hz, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 131.9, 130.5, 127.0, 126.5, 124.0, 122.0.

[3] S.-G. Kim, S.-L. Jung, G.-H. Lee and Y.-D. Gong, *ACS Comb. Sci*., 2013, **15**, 29.
[4] (*a*) P. Subramanian, S. Indu and K. P. Kaliappan, *Org. Lett.,* 2014, **16**, 6212; (*b*) T. Castanheiro, J. Suffert, M. Gulea and M. Donnard, *Org. Lett*., 2016, **18**, 2588.

HRMS (ESI) calculated $[M+H]^+$ for $C_{14}H_{10}BrN_2OS$: 332.9692, found: 332.9693. **FTIR (cm^{-1})** 3019, 2400, 2361, 1677, 1597, 1535, 1215, 1045, 929, 773, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-4-methoxybenzamide (3c)**[5b]

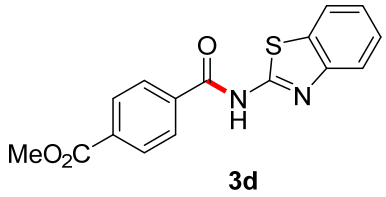


3c

Following the general procedure, treatment of 4-methoxybenzaldehyde **1c** (136.0 mg, 122 µL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with traizolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-4-chlorobenzamide **3c** as white solid (126.0 mg, 88% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.37; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.53 (s, 1H), 7.98 (d, *J*=8.7 Hz, 2H), 7.88-7.85 (m, 1H), 7.38-7.28 (m, 3H), 6.89 (d, *J*= 8.7Hz, 2H), 3.84 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.4, 163.6, 160.0, 148.0, 132.1, 130.1, 126.2, 124.2, 124.0, 121.5, 120.8, 114.4, 55.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{12}N_2O_2S$: 285.0692, found: 285.0691. **FTIR (cm^{-1})** 3019, 2976, 2400, 1674, 1605, 1535, 1215, 1045, 928, 773, 669.

Methyl 4-(benzo[*d*]thiazol-2-ylcarbamoyl)benzoate (3d)

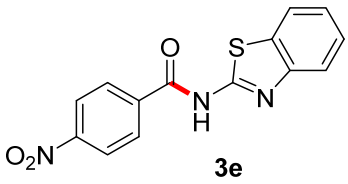


3d

Following the general procedure, treatment of methyl 4-formylbenzoate **1d** (165.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford methyl 4-(benzo[*d*]thiazol-2-ylcarbamoyl)benzoate **3d** as white solid (145.0 mg, 93% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.33; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 13.13 (s, 1H), 8.27 (d, *J* = 8.1 Hz, 2H), 8.12 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 165.7, 133.1, 129.4, 128.9, 126.5, 124.0, 122.0, 52.6. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{13}N_2O_3S$: 313.0641, found: 313.0641. **FTIR (cm^{-1})** 3019, 2974, 2400, 2361, 1723, 1599, 1538, 1216, 928, 773, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-4-nitrobenzamide (3e)**[5]

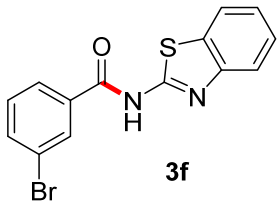


3e

Following the general procedure, treatment of 4-nitrobenzaldehyde **1e** (152.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-4-nitrobenzamide **3e** as yellow solid (121.0 mg, 80% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.43; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 13.29 (s, 1H), 8.37 (s, 4H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 6.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 158.2, 149.9, 130.1, 126.6, 124.1, 123.8, 122.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{10}N_3O_3S$: 300.0437, found: 300.0437. **FTIR (cm^{-1})** 3681, 3019, 2400, 2361, 1675, 1599, 1517, 1442, 1216, 1045, 928, 774, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-3-bromobenzamide (3f)**[6]



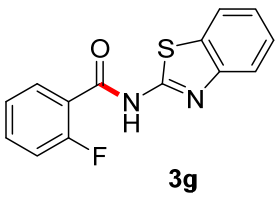
3f

Following the general procedure, treatment of 3-bromobenzaldehyde **1f** (185.0 mg, 117 µL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-3-bromobenzamide **3f** as white solid (107.0 mg, 65% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.52; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 12.34 (s, 1H), 8.10 (s, 1H), 7.88 (dd, J_1 = 16.0 Hz, J_2 = 7.7 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.34-7.20 (m, 4H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.1, 160.2, 147.4, 136.0, 134.2, 131.9, 131.4, 130.6, 126.6, 126.4, 124.4, 123.4, 121.7, 120.5. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{10}BrN_2OS$: 332.9692, found: 332.9693. **FTIR (cm^{-1})** 3019, 2973, 2928, 2400, 2226, 1678, 1601, 1538, 1513, 1213, 1044, 877, 781, 669.

[5] J. Wang , F. Peng , J. Jiang, Z. Lu, L. Wang, Y. Bai and J. Pan, *Tetrahedron Lett.*, 2008, **49**, 467.
[6] K. Waisser, J. Kuneš and Ž**.** Odlerová, *Collect. Czech. Chem. Commun.,* 1991, **56**, 2978.

***N*-(Benzo[*d*]thiazol-2-yl)-2-fluorobenzamide (3g)**[7]

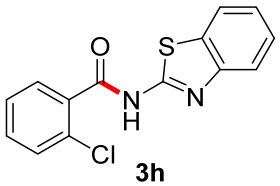


3g

Following the general procedure, treatment of 2-fluorobenzaldehyde **1g** (124.0 mg, 106 µL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-2-fluorobenzamide **3g** as white solid (100.0 mg, 74% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.44; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.14 (s, 1H), 8.24 (t, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.64-7.61 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.39-7.32 (m, 2H), 7.26-7.21 (m, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.2 (d, *J* = 250 Hz), 161.3, 157.7, 148.7, 135.5 (d, *J* = 9.5 Hz), 132.6, 126.5, 125.6 (d, *J* = 2.5 Hz), 124.3, 121.6, 121.3, 116.8 (d, *J* = 23.2 Hz). **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{10}FN_2OS$: 273.0492, found: 273.0491. **FTIR (cm^{-1})** 3019, 2976, 2400, 2249, 1678, 1599, 1541, 1270, 1216, 922, 776, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-2-chlorobenzamide (3h)**[8]



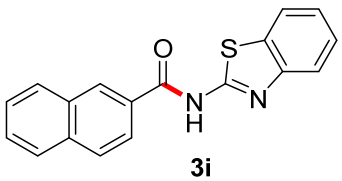
3h

Following the general procedure, treatment of 2-chlorobenzaldehyde **1h** (141.0 mg, 112 µL 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-2-chlorobenzamide **3h** as white solid (131.0 mg, 91% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.40; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.15 (s, 1H), 7.85-7.78 (m, 2H), 7.38-7.26 (m, 4H), 7.20 (t, J= 7.6 Hz, 1H), 7.02 (d, J= 8.0 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.1, 159.3, 147.8, 133.0, 132.8, 131.8, 131.7, 130.8, 130.7, 127.4, 126.3, 124.1, 121.4, 120.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{10}ClN_2OS$: 289.0197, found: 289.0195. **FTIR (cm^{-1})** 3019, 2975, 2400, 2361, 1679, 1598, 1538, 1215, 1046, 928, 876, 776, 669.

[7] D. H. Kim, *J. Het. Chem.,* 1981, **18**, 801.
[8] I. Caleta, D. Cincic, G. Karminski-Zamola and B. Kaitner, *J. Chem. Crystallogr*., 2008, **38**, 775.

***N*-(Benzo[*d*]thiazol-2-yl)-2-naphthamide (3i)**

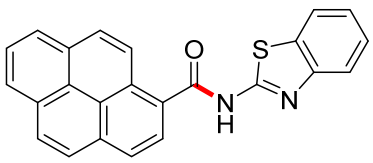


3i

Following the general procedure, treatment of 2-naphthaldehyde **1i** (157.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-2-naphthamide **3i** as white solid (121.0 mg, 79% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.46 (s, 1H), 8.43 (s, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.84- 7.80 (m, 3H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.42-7.38 (m, 1H), 7.21-7.16 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.5, 160.5, 147.7, 135.4, 132.5, 131.96, 129.3, 129.2, 129.0, 128.5, 127.8, 127.0, 126.1, 124.1, 123.9, 121.4, 120.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{13}N_2OS$: 305.0743, found: 305.0746. **FTIR (cm^{-1})** 3019, 2976, 2400, 2247, 1675, 1629, 1537, 1299, 1283, 1216, 926, 776, 669.

***N*-(Benzo[*d*]thiazol-2-yl)pyrene-1-carboxamide (3j)**

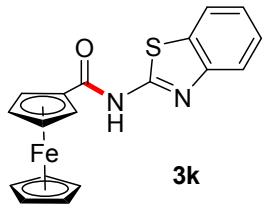


3j

Following the general procedure, treatment of pyrene-1-carbaldehyde **1j** (230.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)pyrene-1-carboxamide **3j** as yellow solid (169.0 mg, 89% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.36; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 12.95 (s, 1H), 8.68 (d, *J* = 9.3 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 7.5 Hz, 3H), 8.21 (dd, J_1 = 9.1 Hz, J_2 = 4.0 Hz, 2H), 8.14 (d, *J* = 8.9 Hz, 1H), 8.07 (t, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 168.4, 158.6, 157.7, 132.9, 131.6, 130.8, 130.2, 129.4, 129.2, 128.7, 128.1, 127.3, 127.0, 126.5, 126.4, 126.3, 124.5, 124.2, 124.0, 123.6, 121.9, 120.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{15}N_2OS$: 379.0900, found: 379.0898. **FTIR (cm^{-1})** 3019, 2976, 2400, 2361, 1678, 1599, 1531, 1479, 1216, 1045, 928, 776, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-ferrocenylamide (3k)**

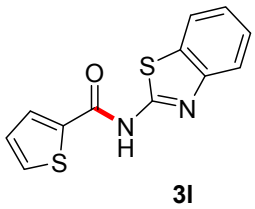


3k

Following the general procedure, treatment of ferrocenecarboxaldehyde **1k** (214.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-ferrocenylamide **3k** as orange solid (132.0 mg, 73% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.48; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.49 (s, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 4.88 (s, 2H), 4.52 (s, 2H), 4.26 (s, 5H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 169.2, 158.4, 148.4, 132.4, 126.4, 124.0, 121.6, 120.9, 72.8, 72.3, 70.4, 68.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{18}H_{15}FeN_2OS$: 363.0249, found: 363.0248. **FTIR (cm^{-1})** 3019, 2974, 2400, 2250, 1740, 1674, 1601, 1216, 1045, 928, 776, 669.

***N*-(Benzo[*d*]thiazol-2-yl)thiophene-2carboxamide (3l)**[4,5]

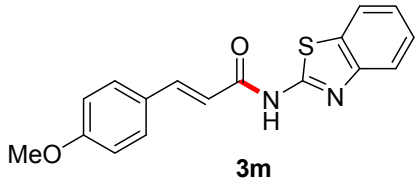


3l

Following the general procedure, treatment of thiophene-3-carboxaldehyde **1l** (112.2 mg, 94 μL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)thiophene-2carboxamide **3l** as white solid (88.0 mg, 68% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.40; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 2.7 Hz, 1H), 7.64 (d, *J* = 4.5 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.38-7.26(m, 2H), 7.07 (d, *J* = 3.7 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 160.4, 159.5, 147.8, 136.6, 133.2, 132.2, 130.8, 128.4, 126.4, 124.2, 121.7, 120.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{12}H_8N_2OS_2$: 261.0151, found: 261.0150. **FTIR (cm^{-1})** 3019, 2400, 2361, 1538, 1422, 1216, 1045, 928, 773, 669.

(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-3-(4-methoxyphenyl)acrylamide (3m)[9]

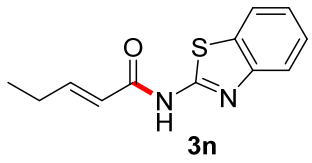


3m

Following the general procedure, treatment of (*E*)-3-(4-methoxyphenyl)acrylaldehyde **1m** (162.2 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by filtration and washing with *n*-hexane to afford (*E*)-*N*-(benzo[*d*]thiazol-2-yl)-3-(4-methoxyphenyl)acrylamide **3m** as white solid (125.0 mg, 80% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.24; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.78-7.75 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 15.7 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 164.4, 161.2, 158.3, 148.7, 142.9, 131.7, 129.9, 126.8, 126.1, 123.4, 121.7, 120.4, 116.8, 114.6, 55.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{15}N_2O_2S$: 311.0849, found: 311.0847. **FTIR (cm^{-1})** 3019, 2976, 2400, 2248, 1676, 1601, 1530, 1216, 1045, 928, 776, 669.

***(E)*-*N*-(Benzo[*d*]thiazol-2-yl)pent-2-enamide (3n)**



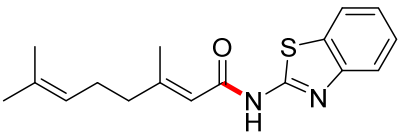
3n

Following the general procedure, treatment of (*E*)-pent-2-enal **1n** (84.0 mg, 98μL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *(E)*-*N*-(benzo[*d*]thiazol-2-yl)pent-2-enamide **3n** as white solid (87.0 mg, 75% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.47; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 12.46 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J*= 8.0 Hz, 1H), 7.47 (t, *J*= 7.6 Hz, 1H), 7.36 (t, *J*= 7.36 Hz, 1H), 7.29-7.22 (m, 1H), 6.09 (d, *J*= 15.4 Hz, 1H), 2.23-2.17 (m, 2H), 0.98 (t, *J*= 7.4 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 164.6, 160.9, 151.7, 147.8, 132.2, 126.4, 124.1, 121.8, 121.2, 120.4, 25.6, 12.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{12}H_{13}N_2OS$: 233.0743, found: 233.0743. **FTIR (cm^{-1})** 3019, 2976, 2400, 2361, 1686, 1643, 1601, 1215, 1045, 928, 774, 669.

[9] N. D. Amnerkar and K. P. Bhusari, *Eur. J. Med. Chem.*, 2010, **45**, 149.

(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-3,7-dimethylocta-2,6-dienamide (3o)

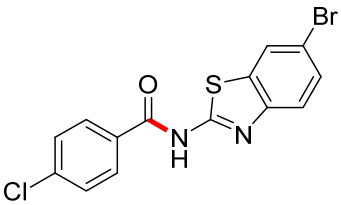


3o

Following the general procedure, treatment of (*E*)-3,7-dimethylocta-2,6-dienal **1o** (153.0 mg, 171 μL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford (*E*)-*N*-(benzo[*d*]thiazol-2-yl)-3,7-dimethylocta-2,6-dienamide **3o** as white solid (120.0 mg, 80% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.60; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.95 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 5.82 (s, 1H), 4.96 (s, 1H), 2.31 (s, 3H), 2.07 (s, 4H), 1.64 (s, 3H), 1.50 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.9, 162.5, 160.7, 148.0, 132.8, 132.0, 126.3, 123.9, 122.8, 121.7, 120.4, 116.5, 41.4, 26.1, 25.8, 19.3, 17.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{17}H_{21}N_2OS$: 301.1369, found: 301.1372. **FTIR (cm^{-1})** 3019, 2975, 2400, 1677, 1599, 1533, 1479, 1270, 1216, 928, 776, 669.

***N*-(6-Bromobenzo[d]thiazol-2-yl)-4-chlorobenzamide (3p)**

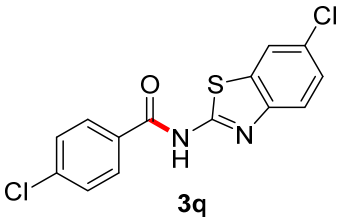


3p

Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and 6-bromobenzo[d]thiazol-2-amine **2b** (115.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196 mg, 0.60 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(6-bromobenzo[d]thiazol-2-yl)-4-chlorobenzamide **3p** as white solid (168.0 mg, 91% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.7; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 13.09 (s, 1H), 8.31 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69 – 7.60 (m, 3H). **13C NMR (100 MHz, DMSO-*d*$_6$)** δ 165.1, 159.5, 147.7, 137.9, 133.7, 130.3, 129.3, 128.8, 124.3, 122.1, 115.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_9ClBrN_2OS$: 366.9302, found: 366.9302. **FTIR (cm^{-1})** 3422, 1671, 1593, 1551, 1296, 1215, 842, 820, 754.

4-Chloro-*N*-(6-chlorobenzo[d]thiazol-2-yl)benzamide (3q)

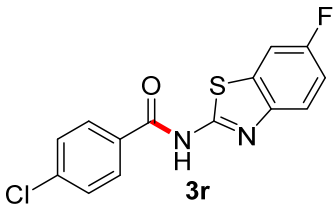


3q

Following the general procedure, treatment of 4-Chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0equiv) and 6-chlorobenzo[d]thiazol-2-amine **2c** (92.3 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford 4-chloro-N-(6-chlorobenzo[d]thiazol-2-yl)benzamide **3q** as white solid (145.0 mg, 90% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.7; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 13.08 (s, 1H), 8.16 (d, *J* = 8.5 Hz, 3H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 1H). **13C NMR (100 MHz, DMSO-*d*$_6$)** δ 165.2, 159.6, 147.4, 137.9, 133.2, 130.3, 128.8, 127.8, 126.6, 121.5. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_9Cl_2N_2OS$: 322.9807, found: 322.9805. **FTIR (cm^{-1})** 3618, 3019, 2975, 2400, 1524, 1423, 1215, 1045, 928, 773, 669.

4-Chloro-*N*-(6-fluorobenzo[d]thiazol-2-yl)benzamide (3r)

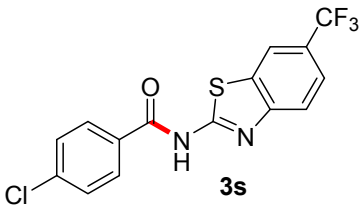


3r

Following the general procedure, treatment of 4-Chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and 6-fluorobenzo[d]thiazol-2-amine **2d** (84.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford 4-chloro-*N*-(6-fluorobenzo[d]thiazol-2-yl)benzamide **3r** as white solid (122.0 mg, 89% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.6; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 13.00 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.80 (dd, J_1 = 8.4 Hz, J_2= 4.6 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 8.9 Hz, 1H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 160.0 (d, *J* = 246 Hz), 137.8, 132.9, 130.3, 128.7, 121.5 (m), 114.45 (d, *J* = 27 Hz), 108.3, 108.1. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_9ClFN_2OS$: 307.0103, found: 307.0101. **FTIR (cm^{-1})** 3618, 3019, 2975, 2400, 2360, 1523, 1413, 1215, 1045, 928, 775, 669.

4-Chloro-*N*-(6-(trifluoromethyl)benzo[*d*]thiazol-2-yl)benzamide (3s)

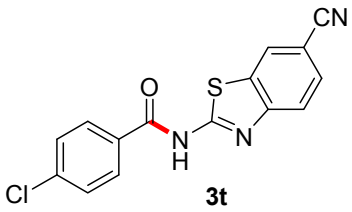


3s

Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and 6-(trifluoromethyl)benzo[*d*]thiazol-2-amine **2e** (109.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford 4-chloro-*N*-(6-(trifluoromethyl)benzo[*d*]thiazol-2-yl)benzamide **3s** as white solid (133.0 mg, 75% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.56; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 13.23 (s, 1H), 8.55 (s, 1H), 8.18 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 165.7, 162.2, 138.1, 132.1, 130.6, 130.5, 128.9, 123.2 (q, *J* = 228.9 Hz,), 120.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_9ClF_3N_2OS$: 357.0071, found: 357.0070. **FTIR (cm^{-1})** 3019, 2975, 2400, 2360, 1534, 1321, 1277, 1216, 928, 774, 669.

4-Chloro-*N*-(6-cyanobenzo[d]thiazol-2-yl)benzamide (3t)

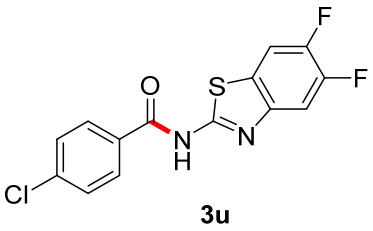


3t

Following the general procedure, treatment of 4-Chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and 2-aminobenzo[d]thiazole-6-carbonitrile **2f** (87.6 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by filtration and washing with *n*-hexane to afford 4-chloro-*N*-(6-cyanobenzo[d]thiazol-2-yl)benzamide **3t** as white solid (130.0 mg, 82% yield).

***R*$_f$** (Pet. ether /EtOAc = 70/30): 0.51; **^{1}H NMR (500 MHz, DMSO-*d*$_6$)** δ 8.19 (d, *J* = 8.3 Hz, 2H), 8.14 (s, 1H), 7.57-7.47 (m, 4H). **^{13}C NMR (125 MHz, DMSO-*d*$_6$)** δ 172.9, 171.0, 154.8, 138.4, 134.7, 133.7, 130.2, 127.9, 127.7, 125.0, 120.5, 118.3, 100.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_9ClN_3OS$: 314.0149, found: 314.0148. **FTIR (cm^{-1})** 3618, 3019, 2976, 2400, 1523, 1423, 1215, 1045 928, 774, 669.

4-Chloro-*N*-(5,6-difluorobenzo[*d*]thiazol-2-yl)benzamide (3u)

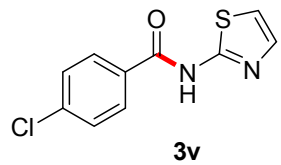


3u

Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and 5,6-difluorobenzo[*d*]thiazol-2-amine **2g** (94.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford 4-chloro-*N*-(5,6-difluorobenzo[*d*]thiazol-2-yl)benzamide **3u** as white solid (122.0 mg, 75 % yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.60; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** 13.11 (s, 1H), 8.18 (dd, J_1 = 19.7 Hz, J_2 = 8.9 Hz, 3H), 7.88 (dd, J_1 = 10.6 Hz, J_2 = 7.5 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H).**^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 138.1, 130.4, 128.9, 127.4, 116.2, 110.2, 109.9, 108.7, 108.5. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_8ClF_2N_2OS$: 325.0008, found: 325.0006. **FTIR (cm^{-1})** 3019, 2976, 2400, 2361, 1672, 1540, 1477, 1425, 1216, 928, 775, 669.

4-Chloro-*N*-(thiazol-2-yl)benzamide (3v)

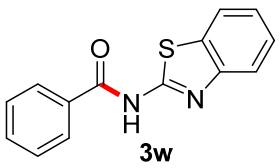


3v

Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and thiazol-2-amine **2h** (51.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford 4-chloro-*N*-(thiazol-2-yl)benzamide **3v** as white solid (50.0 mg, 42% yield).

***R*$_f$**(Pet. ether /EtOAc = 80/20): 0.36; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 12.79 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.02 (dd, J_1 = 23.9 Hz, J_2 = 3.5 Hz, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.0, 160.5, 139.4, 137.1, 131.2, 129.7, 129.3, 114.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{10}H_8ClN_2OS$: 239.0040, found: 239.0042. **FTIR (cm^{-1})** 3019, 2976, 2400, 2239, 1674, 1596, 1534, 1215, 928, 775, 669.

***N*-(Benzo[*d*]thiazol-2-yl)benzamide (3w)**[4,5]



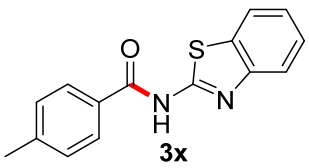
3w

Following the general procedure, treatment of benzaldehyde **1p** (106.0 mg, 102 µL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)benzamide **3w** as white solid (93.0 mg, 74% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.48; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.02 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30-7.17 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.2, 160.0, 147.8, 133.2, 132.2, 132.0, 129.1, 128.1, 126.2, 124.1, 121.5, 120.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_{11}N_2OS$: 255.0587, found: 255.0586. **FTIR (cm^{-1})** 3019, 2976, 2400, 2248, 1677, 1538, 1279, 1215, 928, 775, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-4-methylbenzamide (3x)**[5,6]

Following the general procedure, treatment of 4-methylbenzaldehyde **1q** (121.0 mg, 120 µL 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and

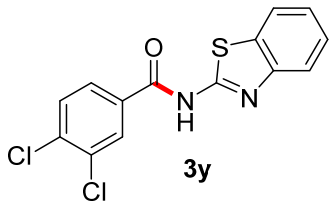


3x

Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-4-methylbenzamide **3x** as white solid 90.0 mg, 67% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.57; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.54 (s, 1H), 7.89 (d, *J*=8.0 Hz, 2H), 7.86-7.84 (m, 1H), 7.29-7.27 (m, 3H), 7.21 (d, *J*= 8.0Hz, 2H), 2.38 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 166.0, 159.8, 148.0, 144.1, 132.1, 129.8, 129.3, 128.1, 126.1, 124.0, 121.5, 120.9, 21.7. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{13}N_2OS$: 269.0743, found: 269.0744. **FTIR (cm^{-1})** 3019, 2976, 2400, 2361, 1676, 1600, 1536, 1215, 1045, 928, 774, 669.

***N*-(Benzo[*d*]thiazol-2-yl)-3,4-dichlorobenzamide (3y)**[10]

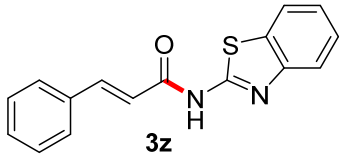


3y

Following the general procedure, treatment of 3,4-dichlorobenzaldehyde **1r** (175.0 mg, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)-3,4-dichlorobenzamide **3y** as white solid (151.0 mg, 93% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.63; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 11.99 (s, 1H), 8.02 (s, 1H), 7.88-7.86 (m, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.35-7.33 (m, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.5, 160.2, 147.1, 137.8, 133.9, 132.1, 131.8, 131.1, 130.3, 127.0, 126.6, 124.6, 121.8, 120.4. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_9Cl_2N_2OS$: 322.9807, found: 322.9807. **FTIR (cm^{-1})** 3019, 2400, 2361, 1676, 1599, 1536, 1215, 928, 876, 775, 669.

***N*-(Benzo[*d*]thiazol-2-yl)cinnamamide (3z)**[11]



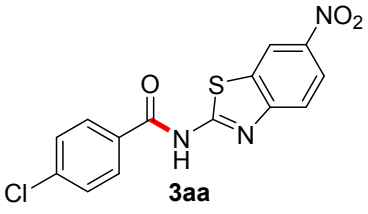
3z

Following the general procedure, treatment of cinnamaldehyde **1s** (133.0 mg, 126 µL, 1.0 mmol, 2.0 equiv) and benzo[*d*]thiazol-2-amine **2a** (76.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford *N*-(benzo[*d*]thiazol-2-yl)cinnamamide **3z** as white solid (98 mg, 70% yield).

***R*$_f$** (Pet. ether /EtOAc = 80/20): 0.40; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 12.40 (s. 1H), 7.94-7.85 (m, 3H), 7.47-7.28 (m, 7H), 6.67 (d, *J*= 15.6 Hz, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.5, 160.8, 147.9, 145.5, 134.0, 132.4, 130.9, 129.0, 128.6, 126.8, 124.3, 122.0, 120.5, 118.3. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{16}H_{13}N_2OS$: 281.0743, found: 281.0741. **FTIR (cm^{-1})** 3618, 3019, 2975, 2400, 1535, 1423, 1217, 1045, 928, 771, 669.

[10] S. Kerwin, L. H. Hurley, M. R. DeLuca and B. M. Moore, III. PCT Int. Appl., 9748694, Dec 24, 1997.
[11] S. Durgamma, P. R. Reddy Padmavathi and A. Padmaja, *J. Het. Chem*,. 2016, **53**, 738.

4-Chloro-*N*-(6-nitrobenzo[*d*]thiazol-2-yl)benzamide (3aa)[12]

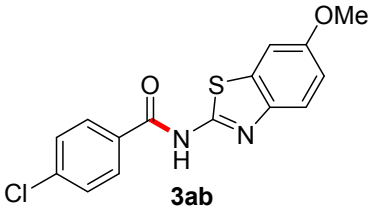


3aa

Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and 6-nitrobenzo[*d*]thiazol-2-amine **2i** (98.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by filtration and washing with *n*-hexane to afford 4-chloro-*N*-(6-nitrobenzo[*d*]thiazol-2-yl)benzamide **3aa** as yellow solid (130.0 mg, 78% yield).

R_f (Pet. ether /EtOAc = 80/20): 0.44; **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.78 (s, 1H), 8.19 (t, *J* = 8.2 Hz, 3H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR (100 MHz, DMSO-*d*$_6$)** δ 172.1, 170.2, 156.1, 141.0, 136.0, 135.9, 133.1, 130.5, 128.3, 121.2, 118.4, 117.8. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{14}H_9ClN_3O_3S$: 334.0048, found: 334.0045. **FTIR (cm^{-1})** 3019, 2976, 2400, 1724, 1601, 1529, 1479, 1216, 928, 877, 775, 669.

4-Chloro-*N*-(6-methoxybenzo[*d*]thiazol-2-yl)benzamide (3ab)[13]



3ab

Following the general procedure, treatment of 4-chlorobenzaldehyde **1a** (141.0 mg, 1.0 mmol, 2.0 equiv) and 6-methoxybenzo[d]thiazol-2-amine **2j** (91.0 mg, 0.50 mmol, 1.0 equiv), with triazolium salt **4** (28.0 mg, 0.10 mmol), oxidant **5** (408.0 mg, 1.0 mmol, 2.0 equiv) and Cs_2CO_3 (196.0 mg, 0.6 mmol) in CH_2Cl_2 (4.0 mL) and stirring the reaction mixture for 12 h followed by flash chromatography to afford 4-chloro-*N*-(6-methoxybenzo[*d*]thiazol-2-yl)benzamide **3ab** as white solid (96.0 mg, 61% yield).

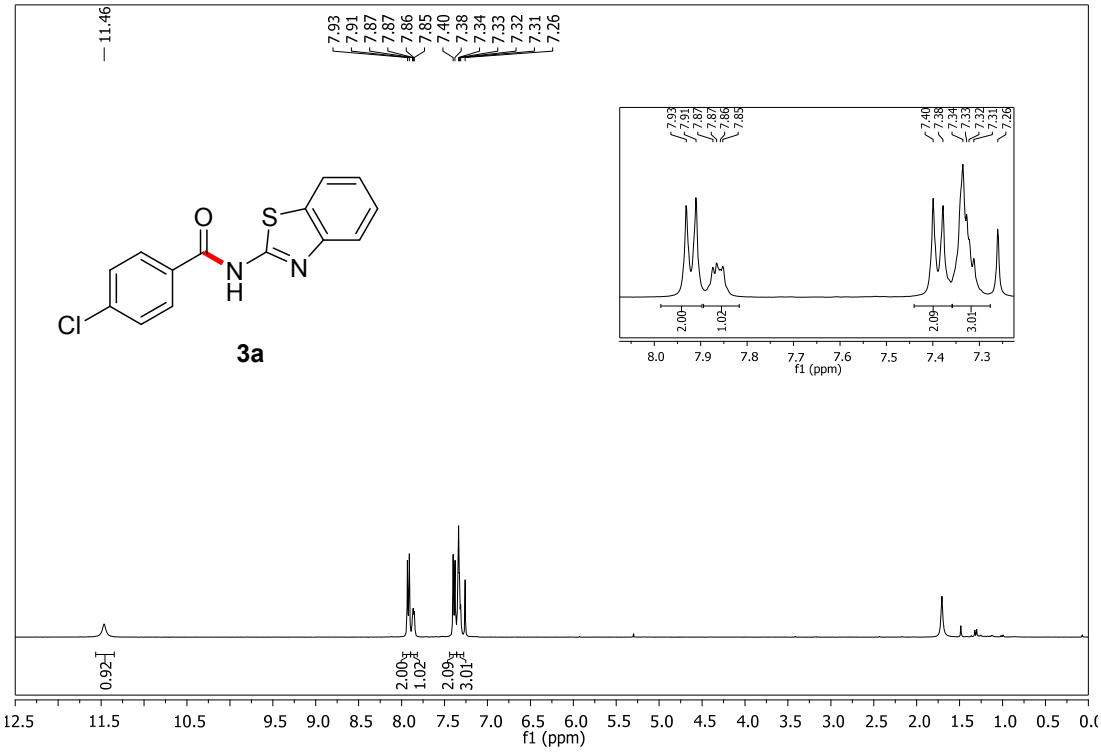
R_f (Pet. ether /EtOAc = 80/20): 0.40; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 11.96 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.36-7.26 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 165.1, 158.0, 157.1, 141.8, 139.6, 133.2, 130.7, 129.5, 129.4, 121.3, 115.3, 104.4, 56.0. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{15}H_{12}ClN_2O_2S$: 319.0303, found: 319.0305. **FTIR (cm^{-1})** 3019, 2975, 2400, 1675, 1605, 1547, 1472, 1215, 927, 775, 669.

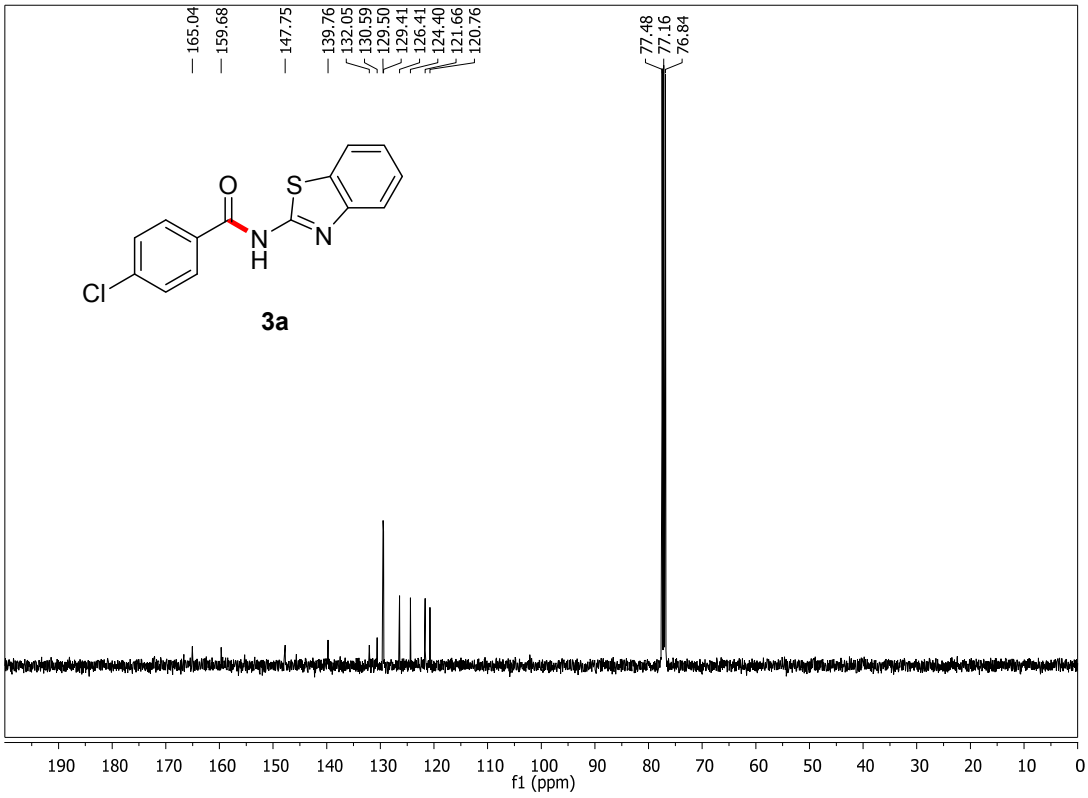
[12] A. Kamal, R. V. C. R. N. C. Shetti, P. Swapna, S. Azeeza, A. M. Reddy, I. A. Khan, S. T. Abdullah, S. Sharma and N. P. Kalia, Indian Pat. Appl., 2010DE02179, Mar 16, 2012.

[13] J. M. Ready, D. Nijhawan, S. S. Gonzales and P. Theodoropoulos, PCT Int. Appl., 2015035051, Mar 12, 2015.

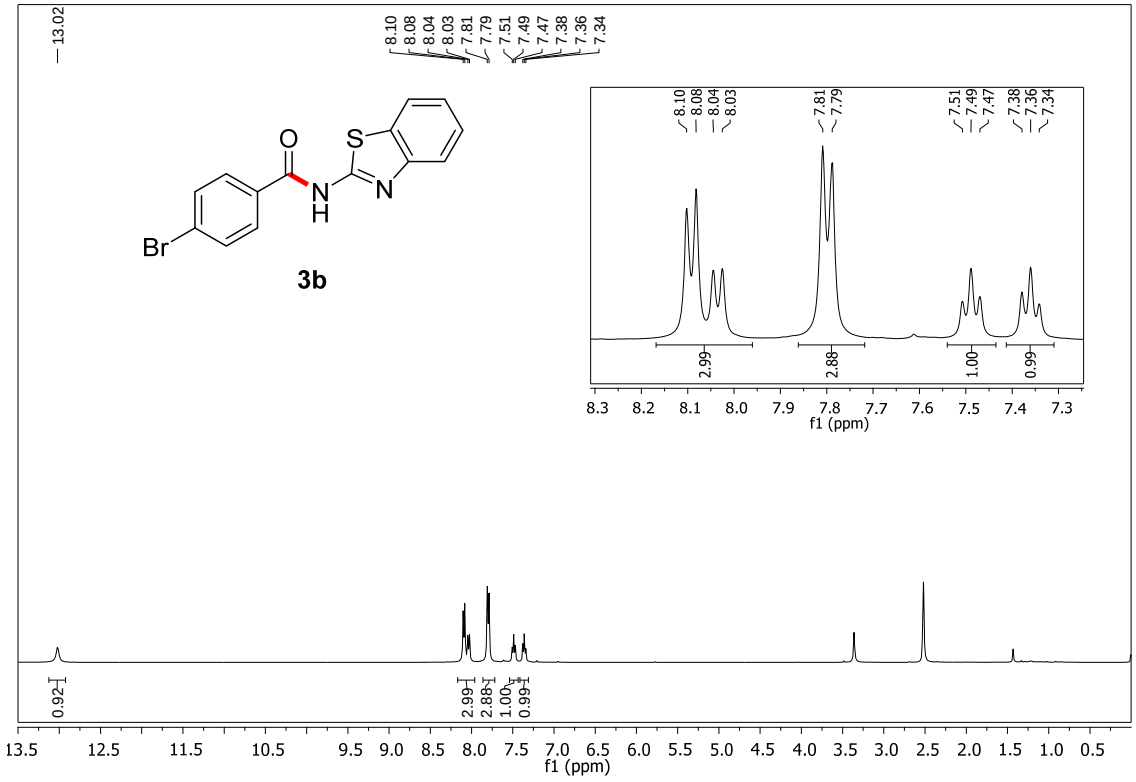
6. ^{1}H and ^{13}C Spectra of *N*-(Benzothiazol-2-yl)amide Derivatives

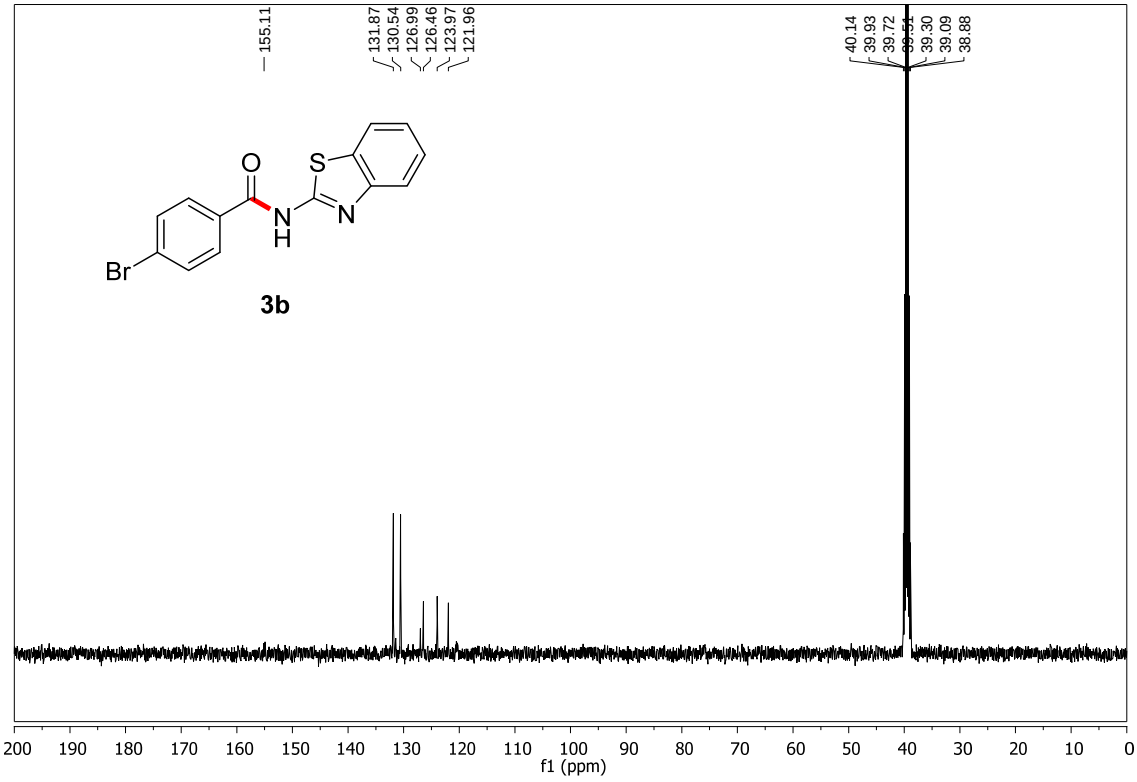
N-(Benzo[*d*]thiazol-2-yl)-4-chlorobenzamide (3a)



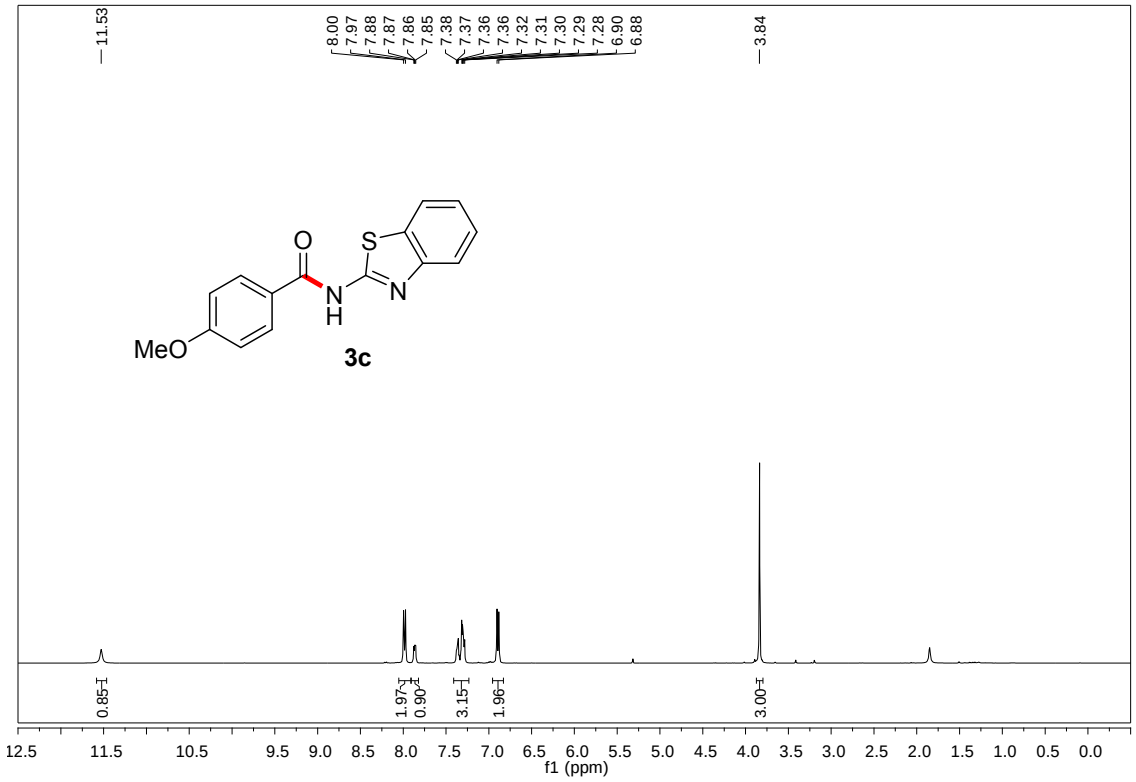


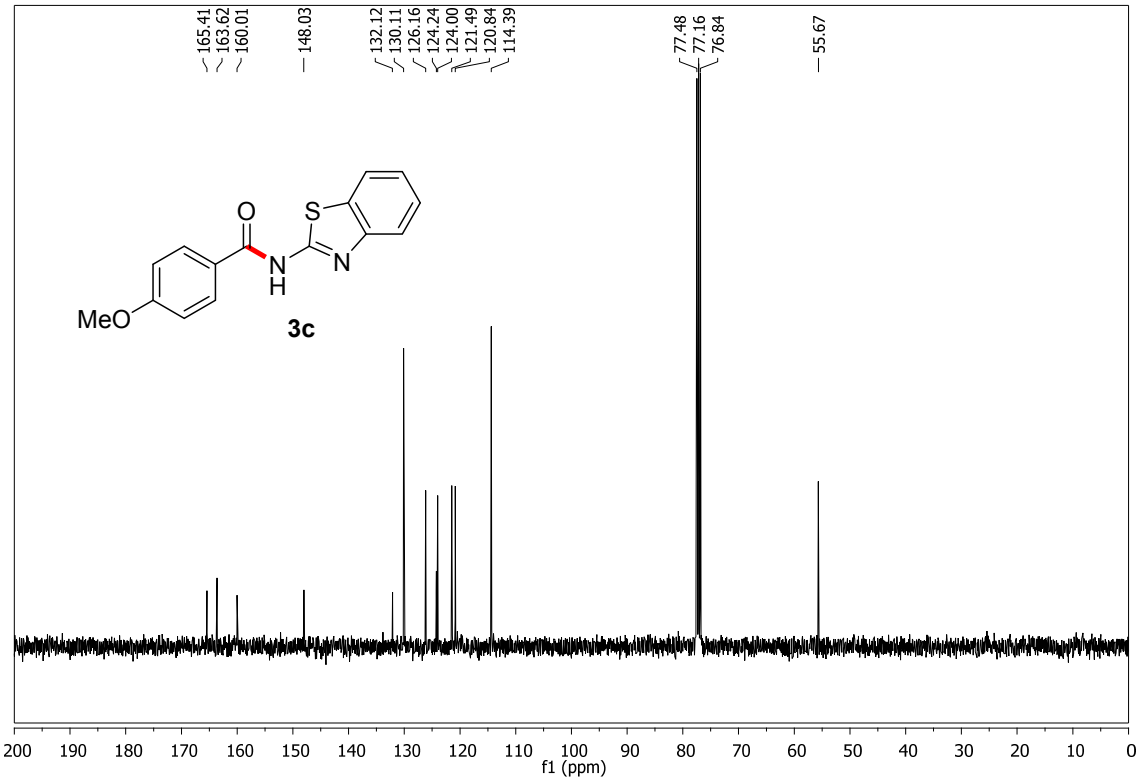
***N*-(Benzo[*d*]thiazol-2-yl)-4-bromobenzamide (3b)**



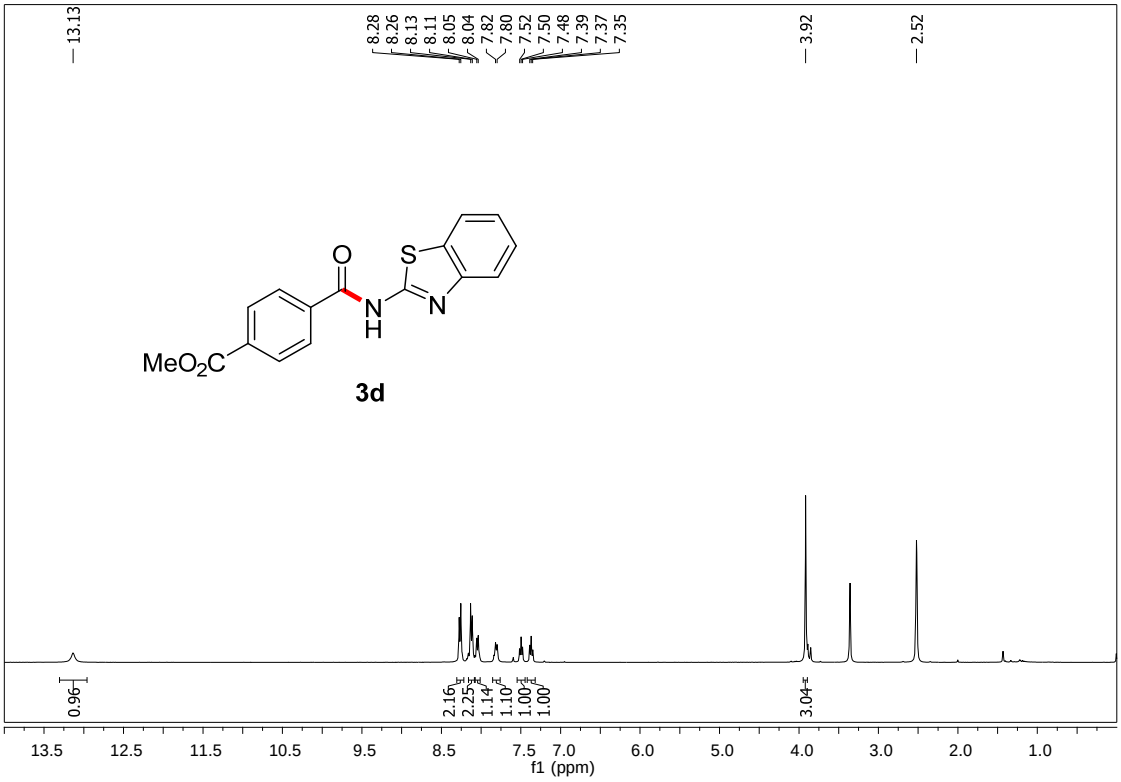


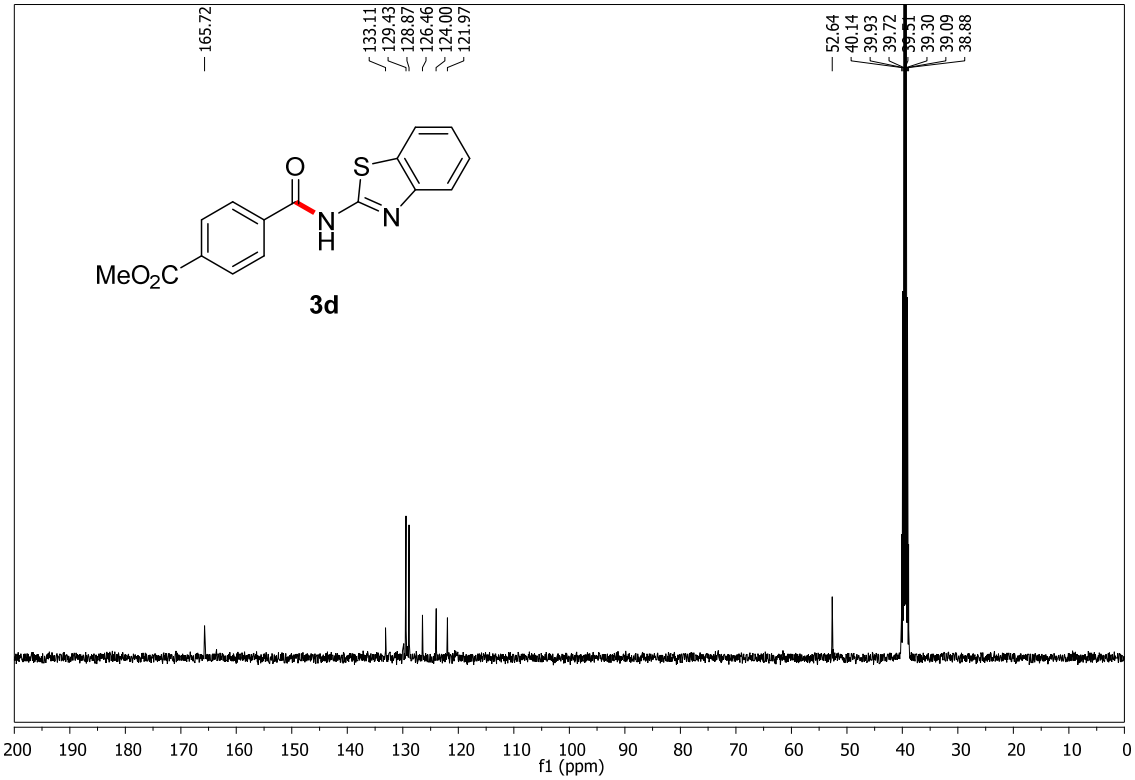
_N_-(Benzo[_d_]thiazol-2-yl)-4-methoxybenzamide (3c)



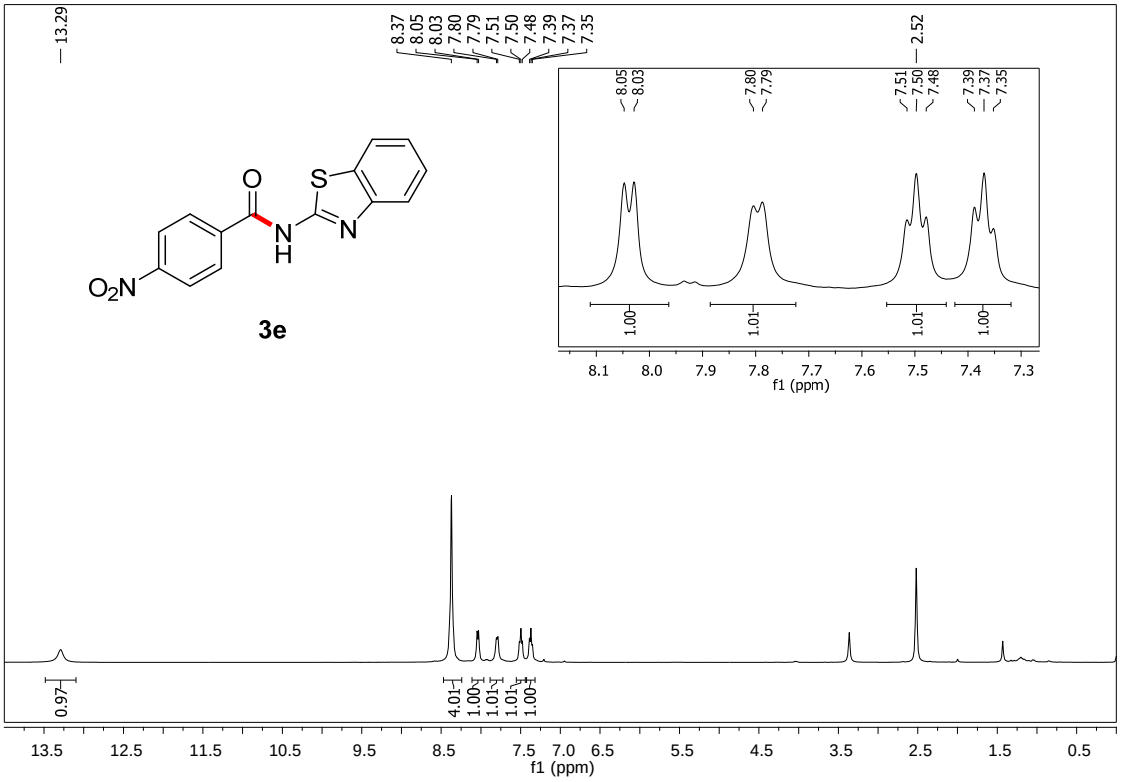


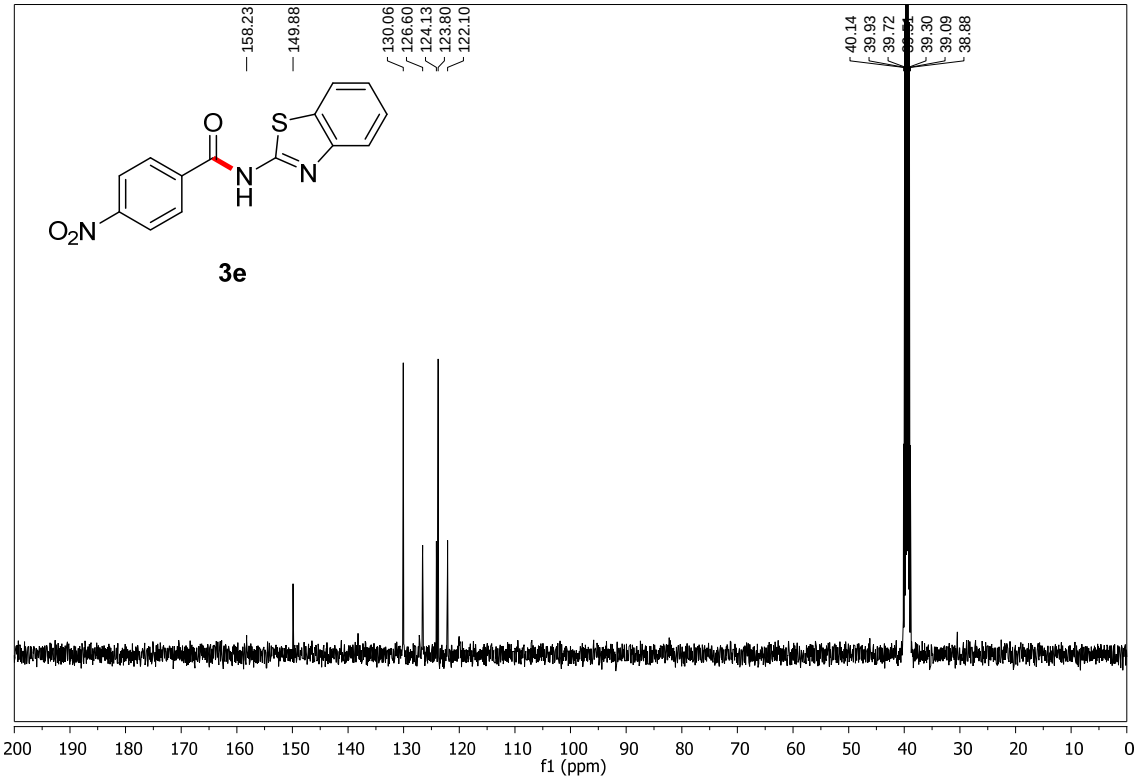
Methyl 4-(benzo[*d*]thiazol-2-ylcarbamoyl)benzoate (3d)



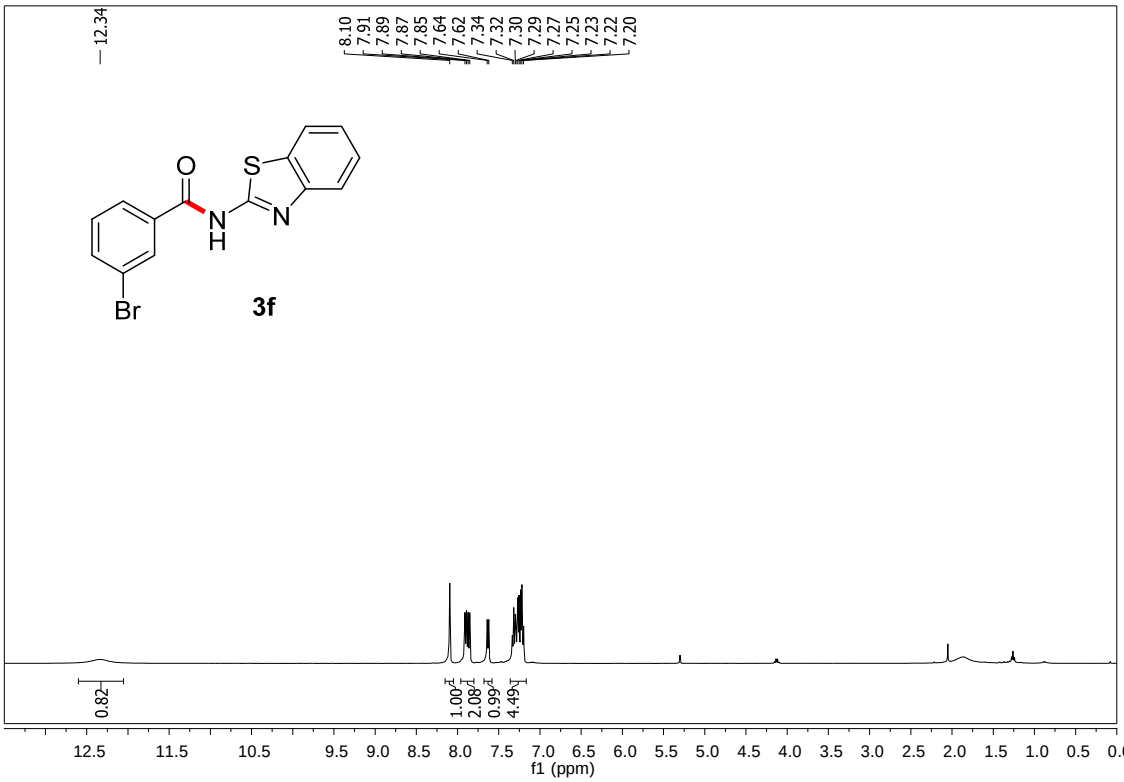


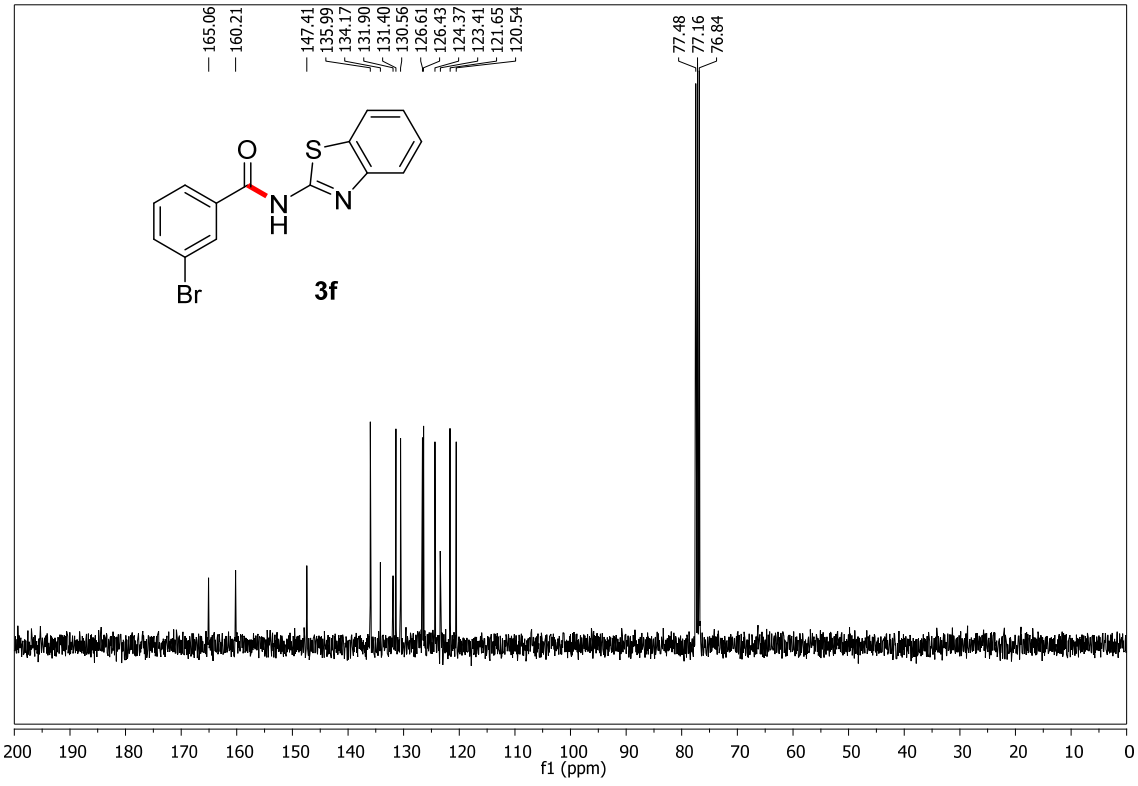
***N*-(Benzo[*d*]thiazol-2-yl)-4-nitrobenzamide (3e)**



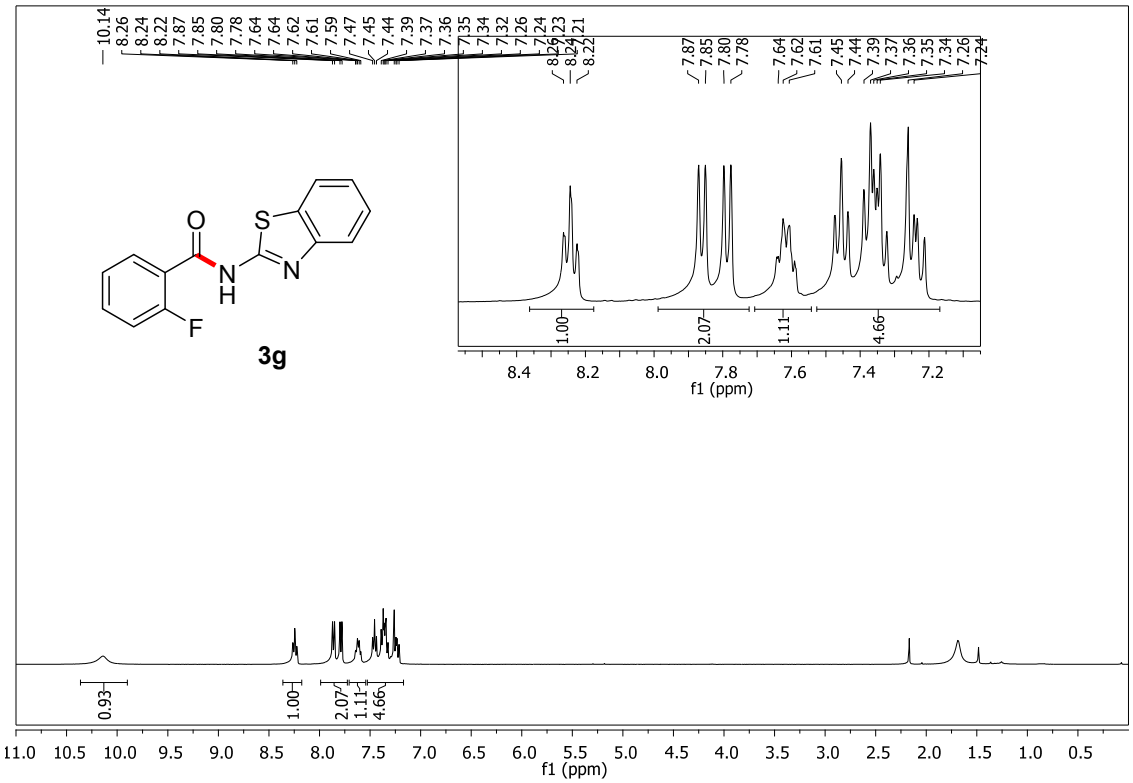


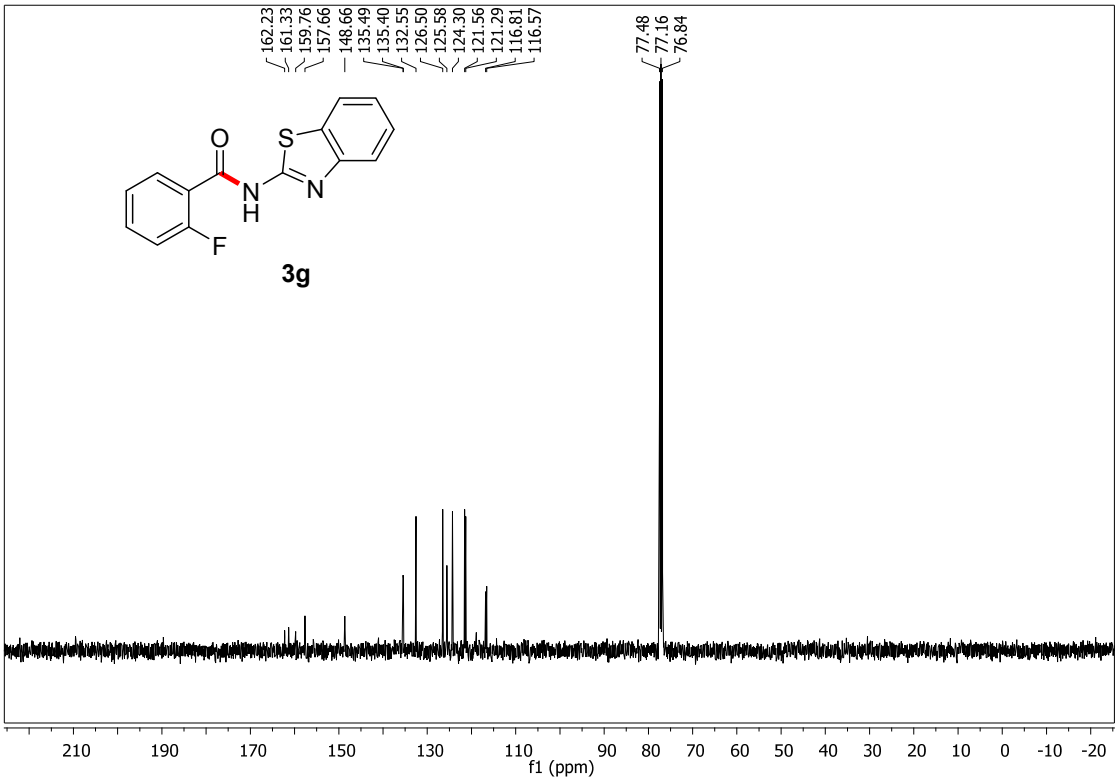
***N*-(Benzo[*d*]thiazol-2-yl)-3-bromobenzamide (3f)**



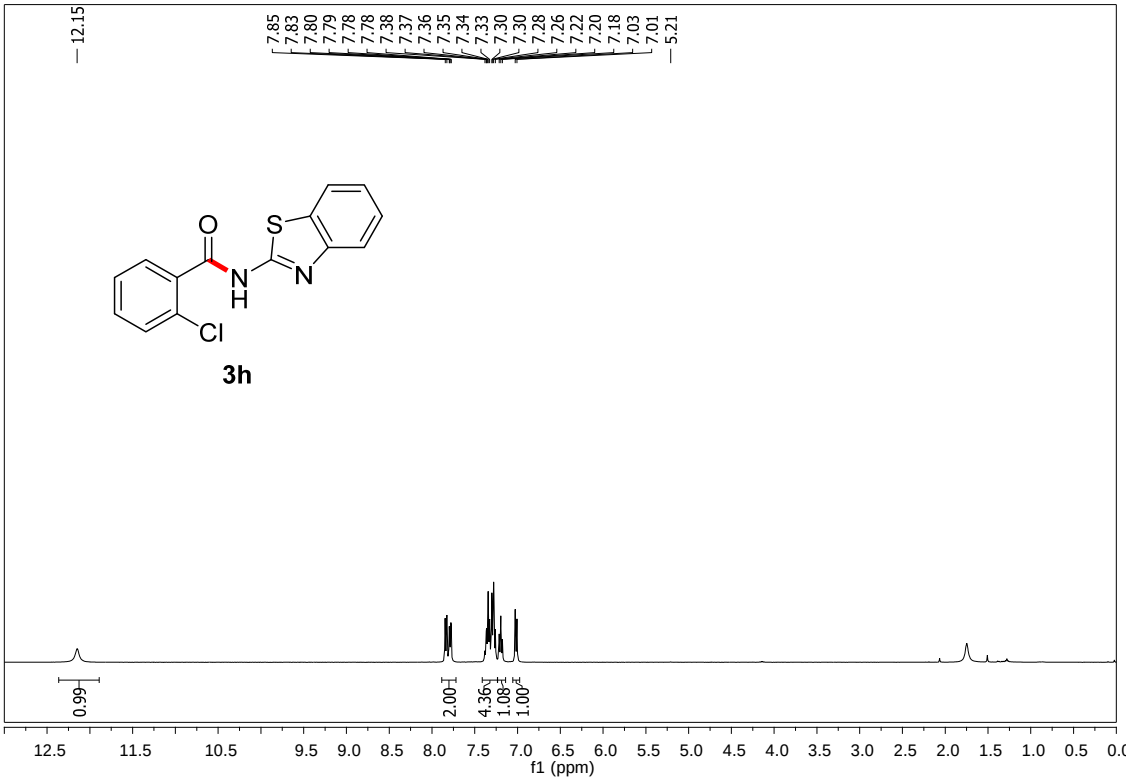


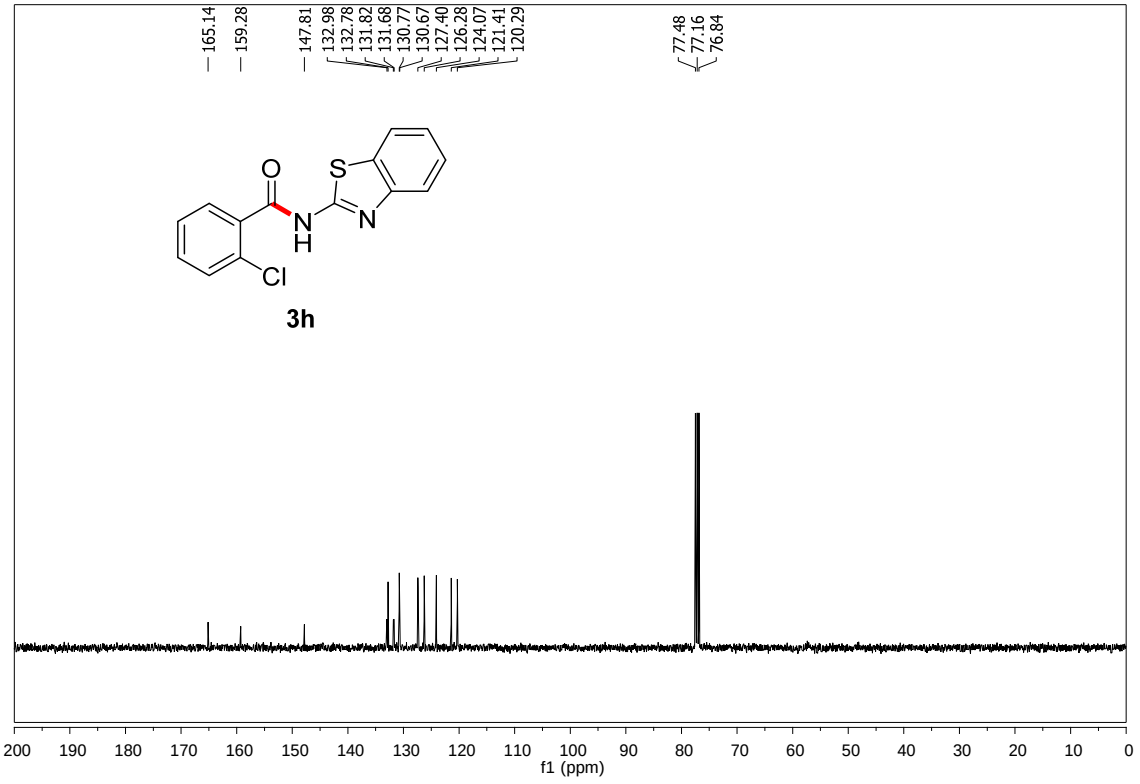
_N_-(Benzo[_d_]thiazol-2-yl)-2-fluorobenzamide (3g)



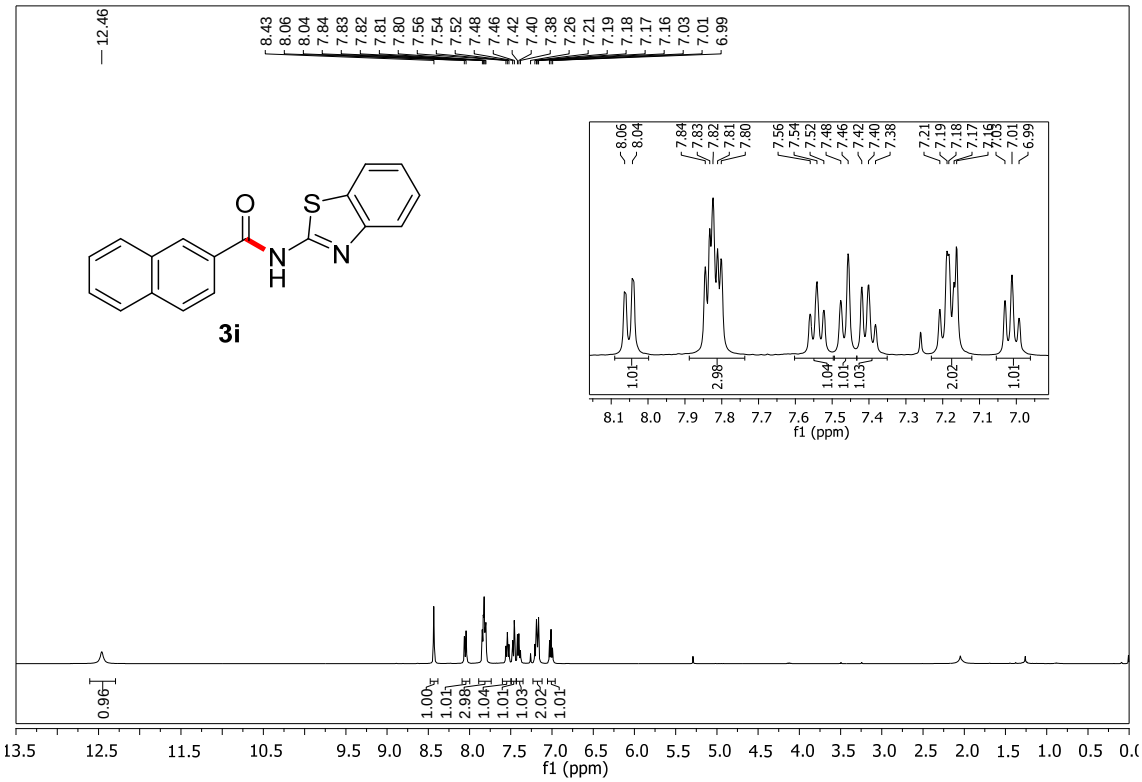


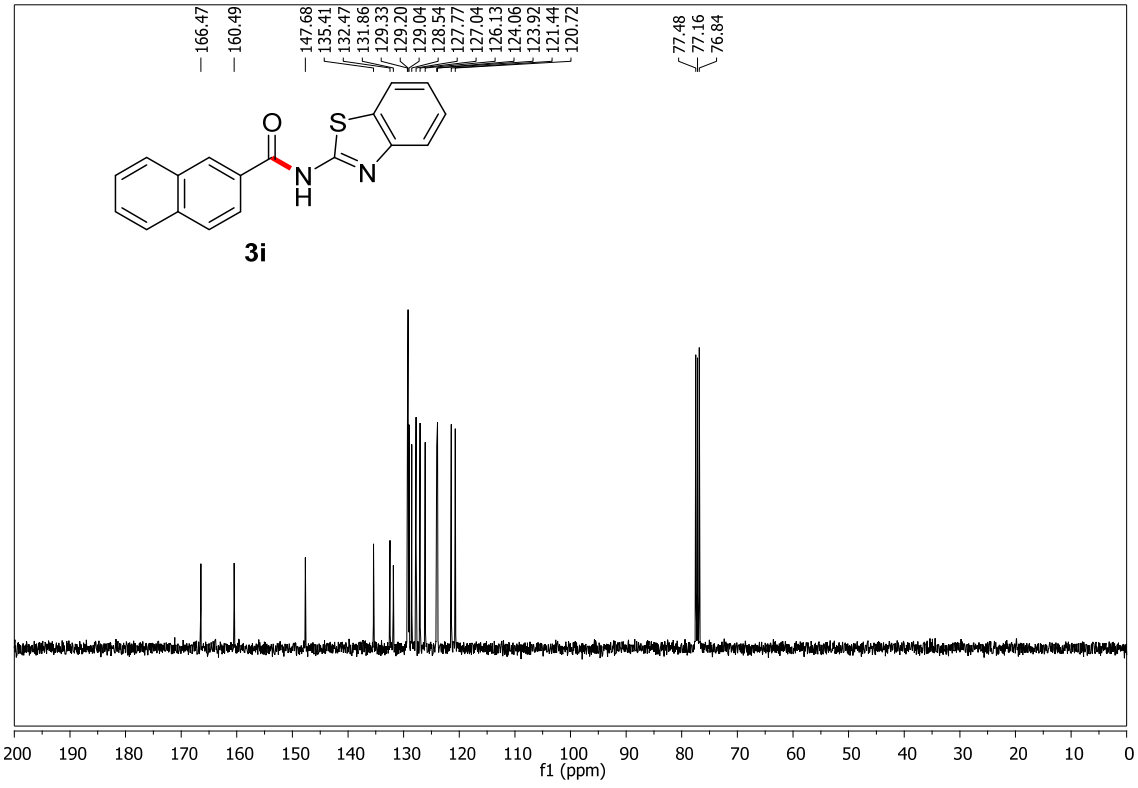
***N*-(Benzo[*d*]thiazol-2-yl)-2-chlorobenzamide (3h)**



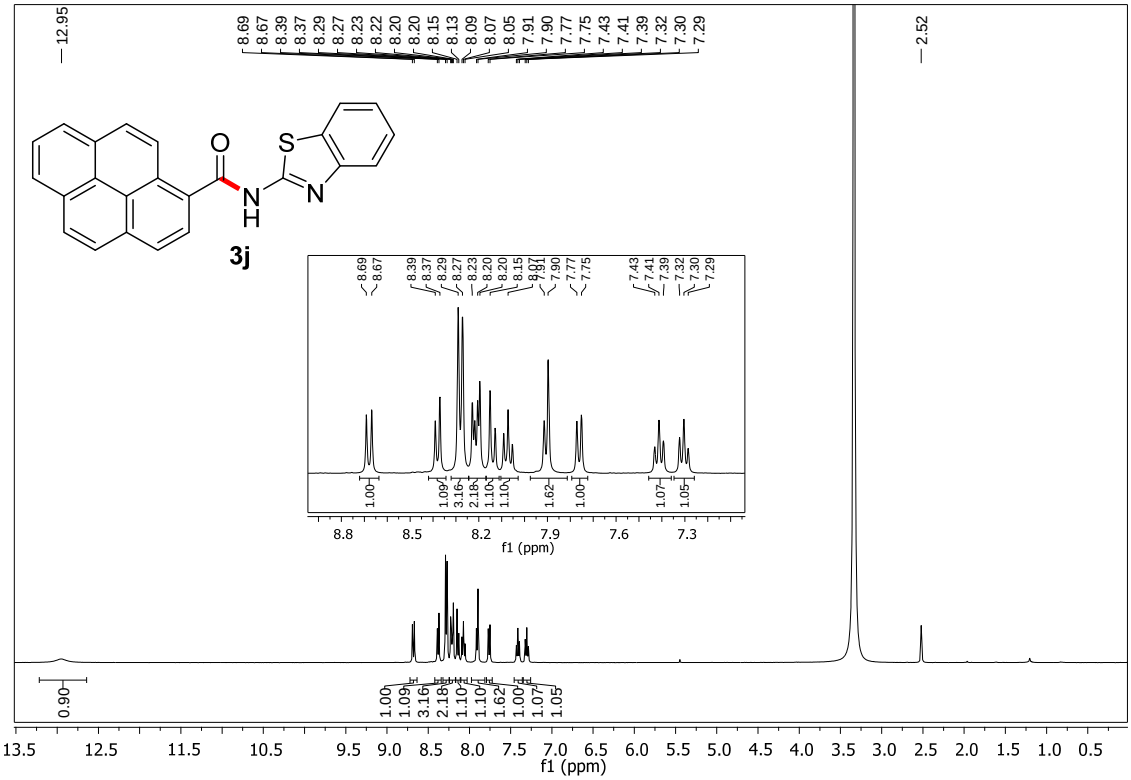


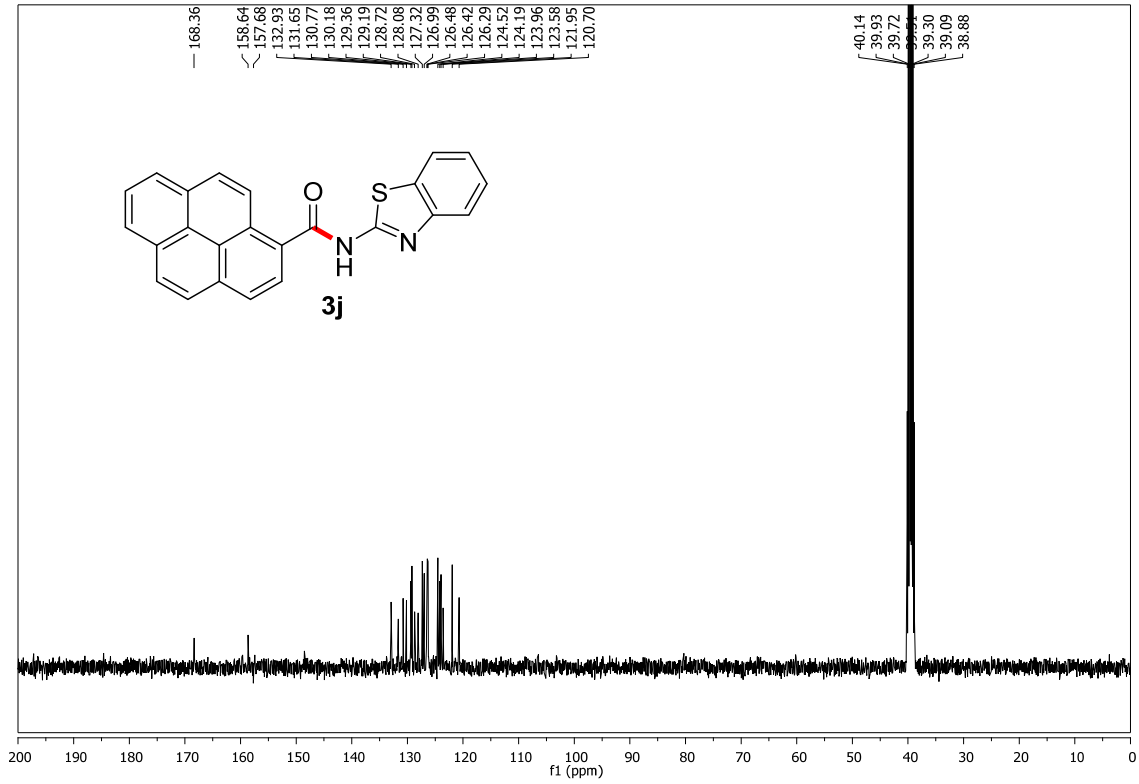
***N*-(Benzo[*d*]thiazol-2-yl)-2-naphthamide (3i)**



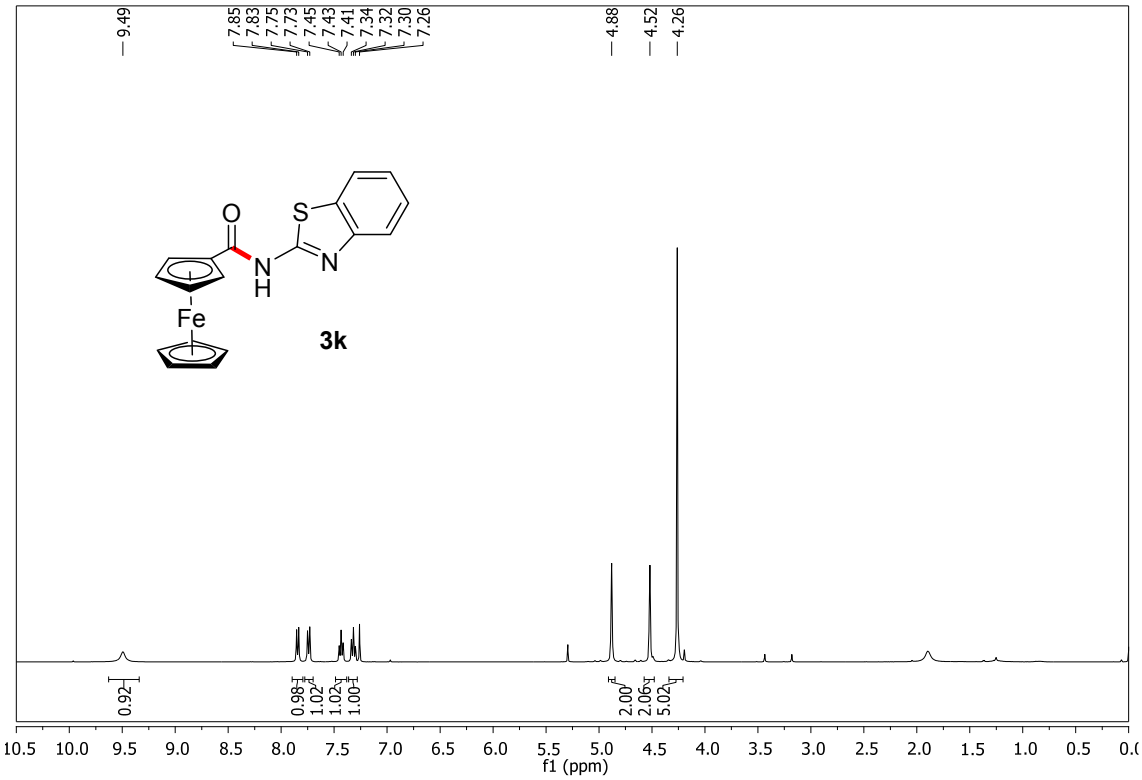


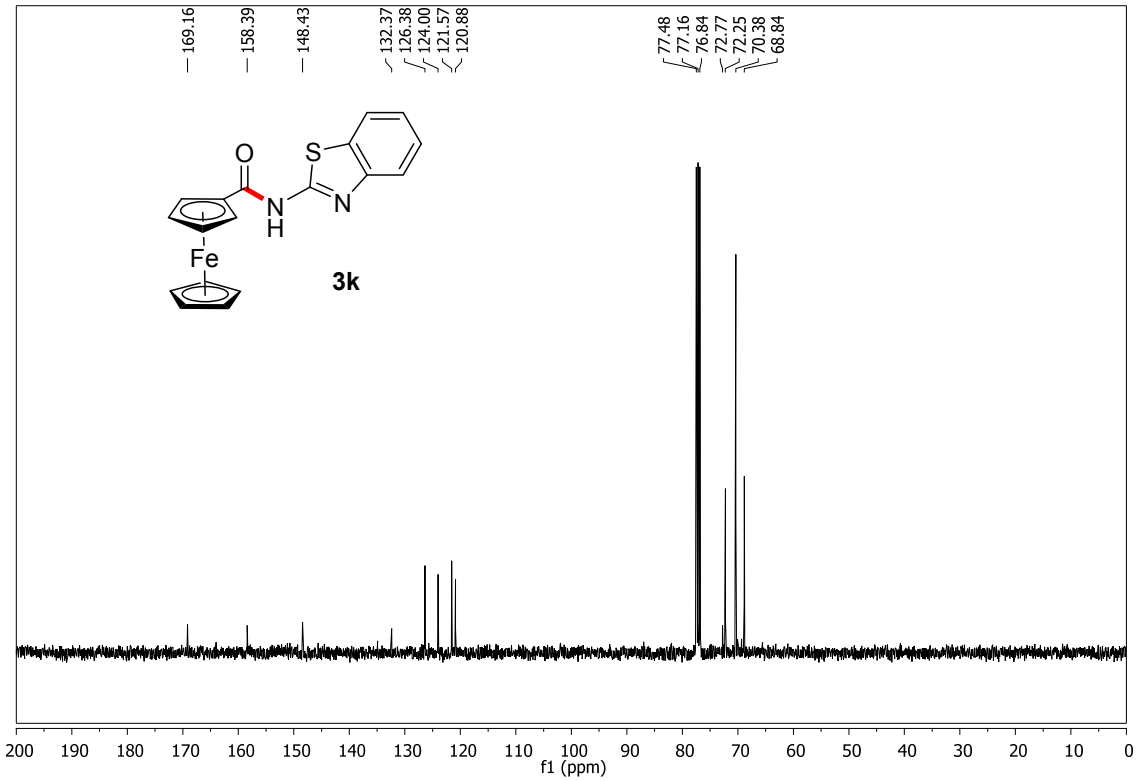
***N*-(Benzo[*d*]thiazol-2-yl)pyrene-1-carboxamide (3j)**



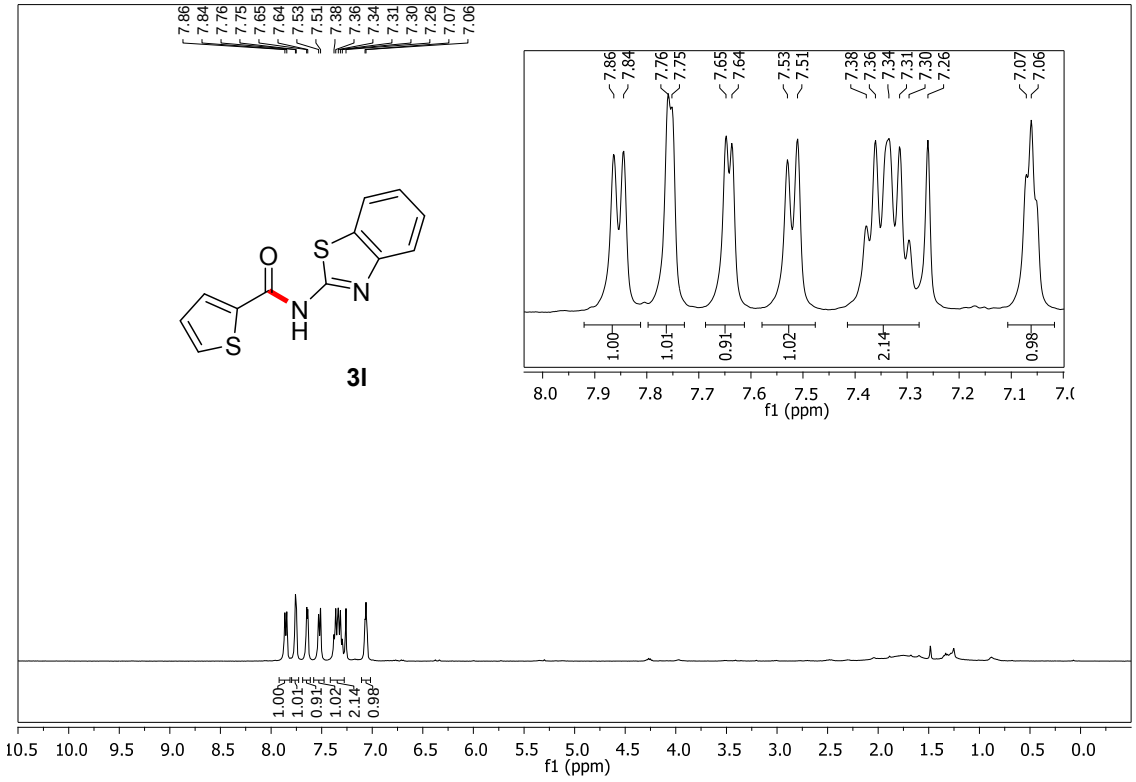


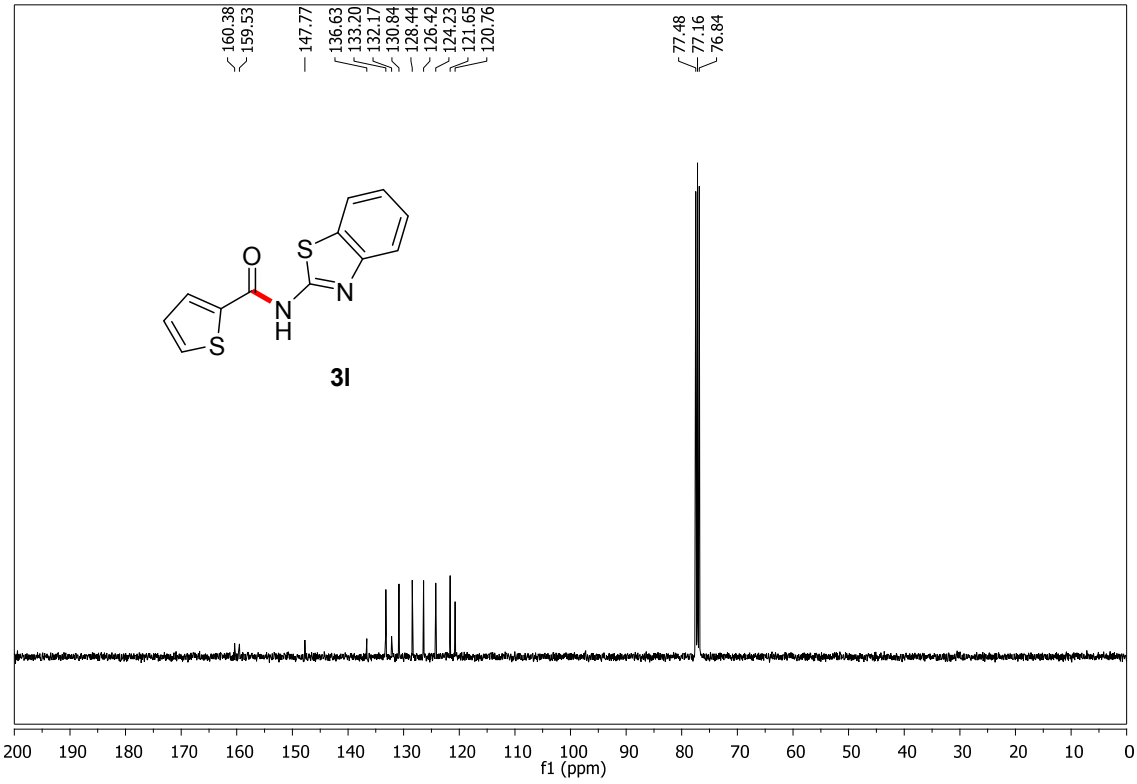
***N*-(Benzo[*d*]thiazol-2-yl)-ferrocenylamide (3k)**



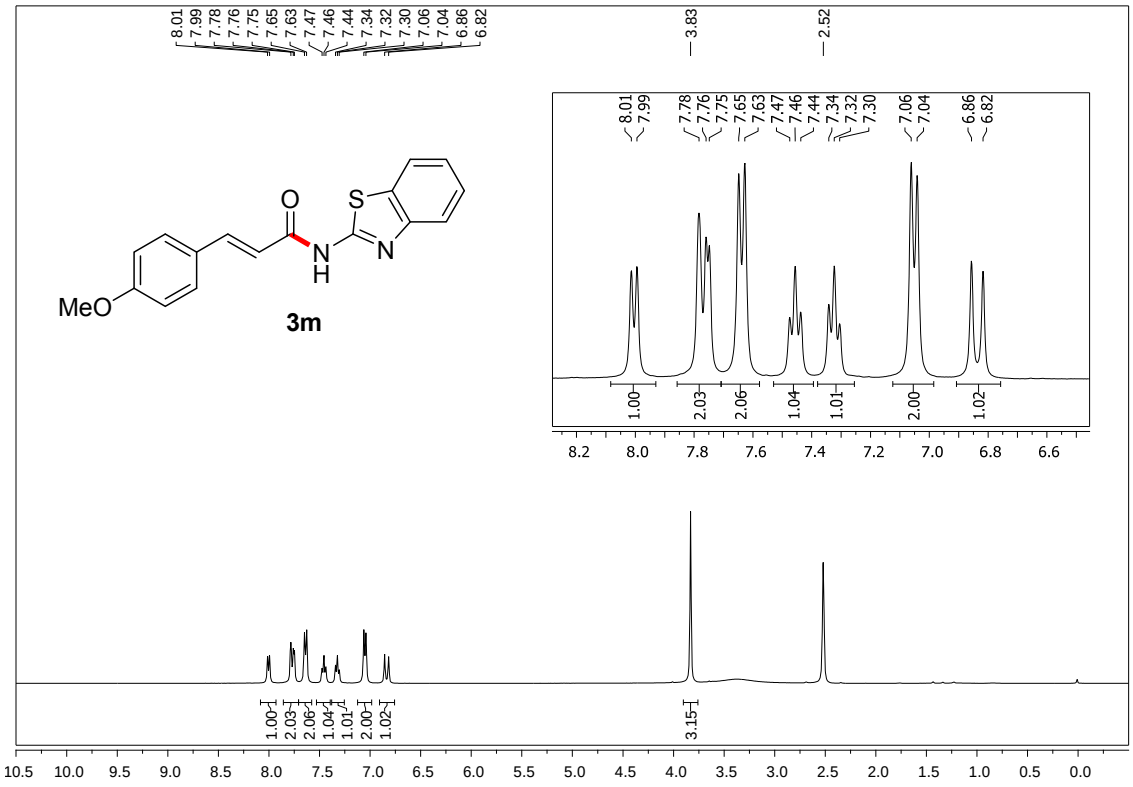


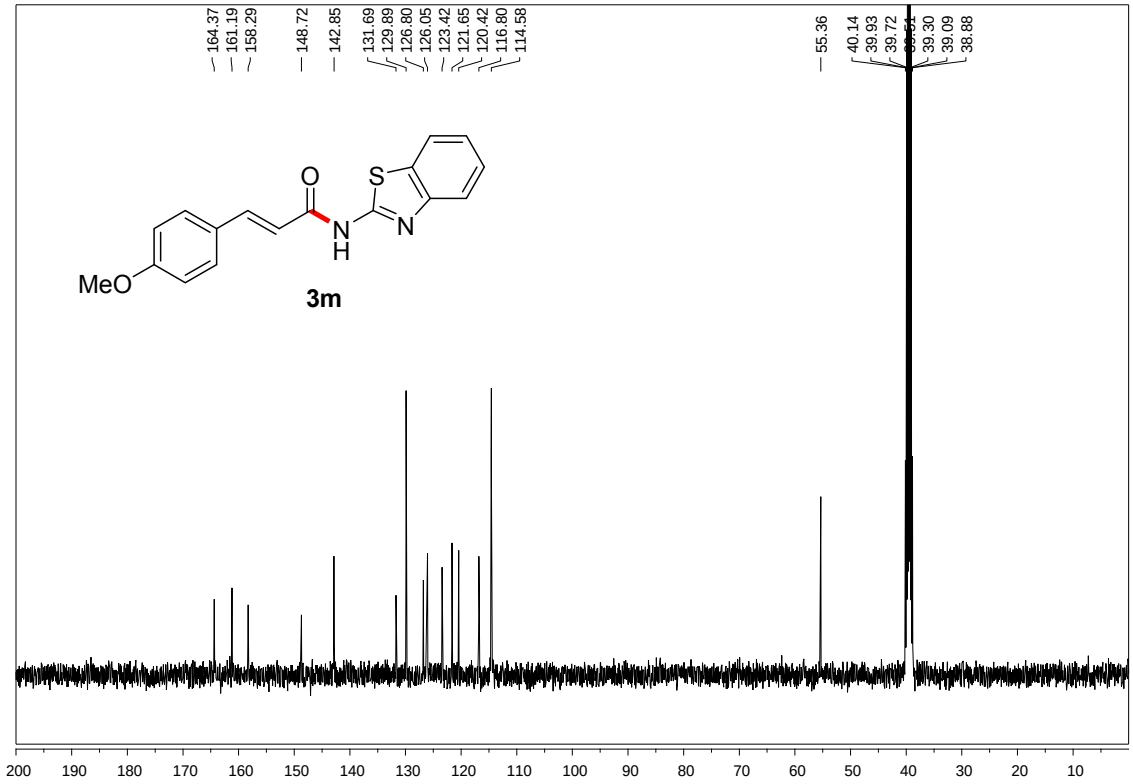
***N*-(Benzo[*d*]thiazol-2-yl)thiophene-2carboxamide (3l)**



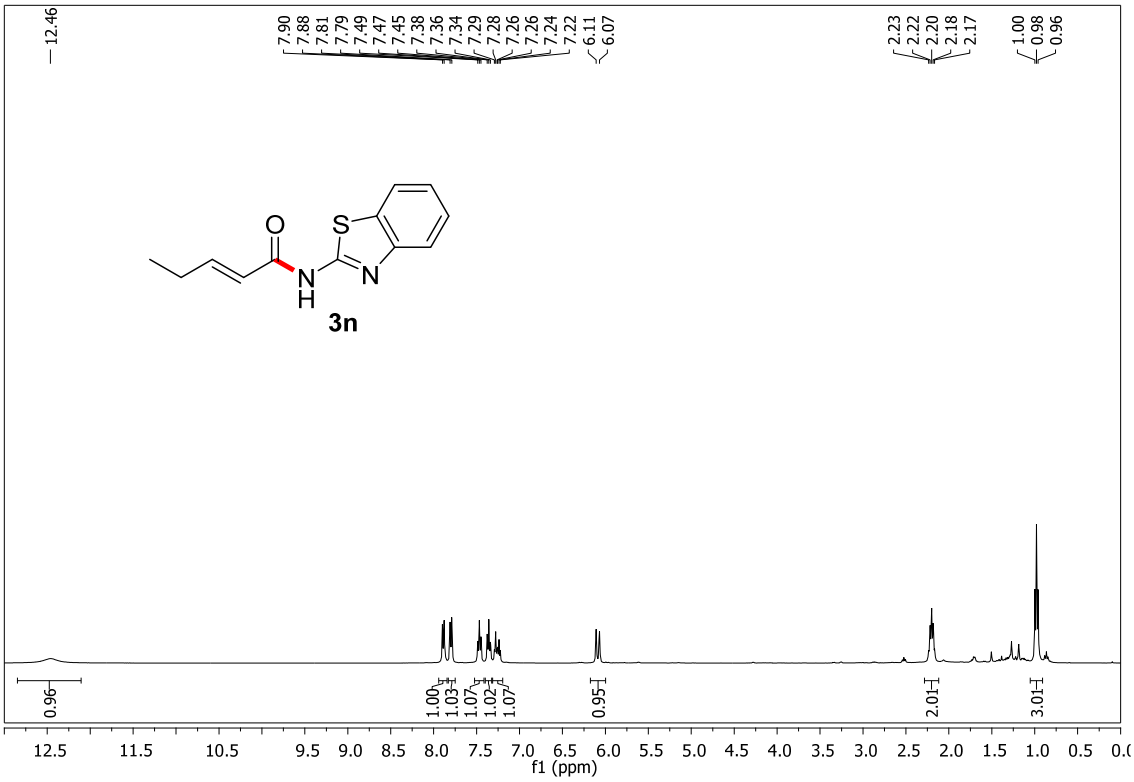


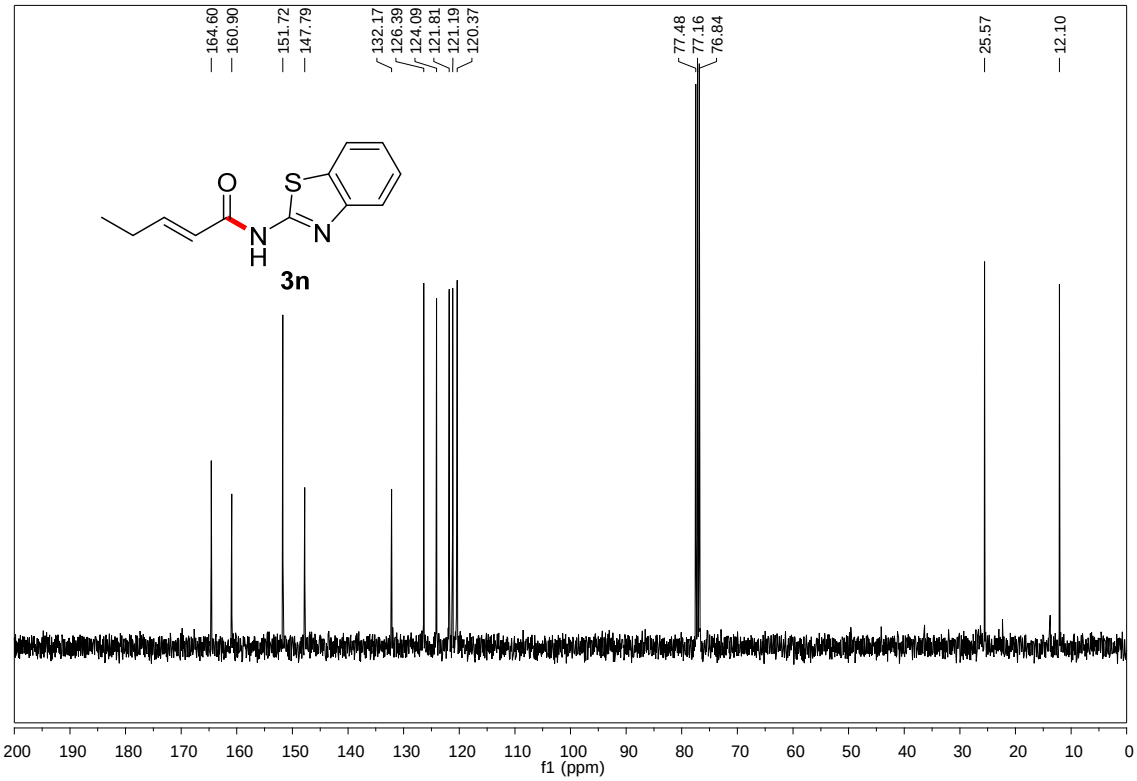
(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-3-(4-methoxyphenyl)acrylamide (3m)



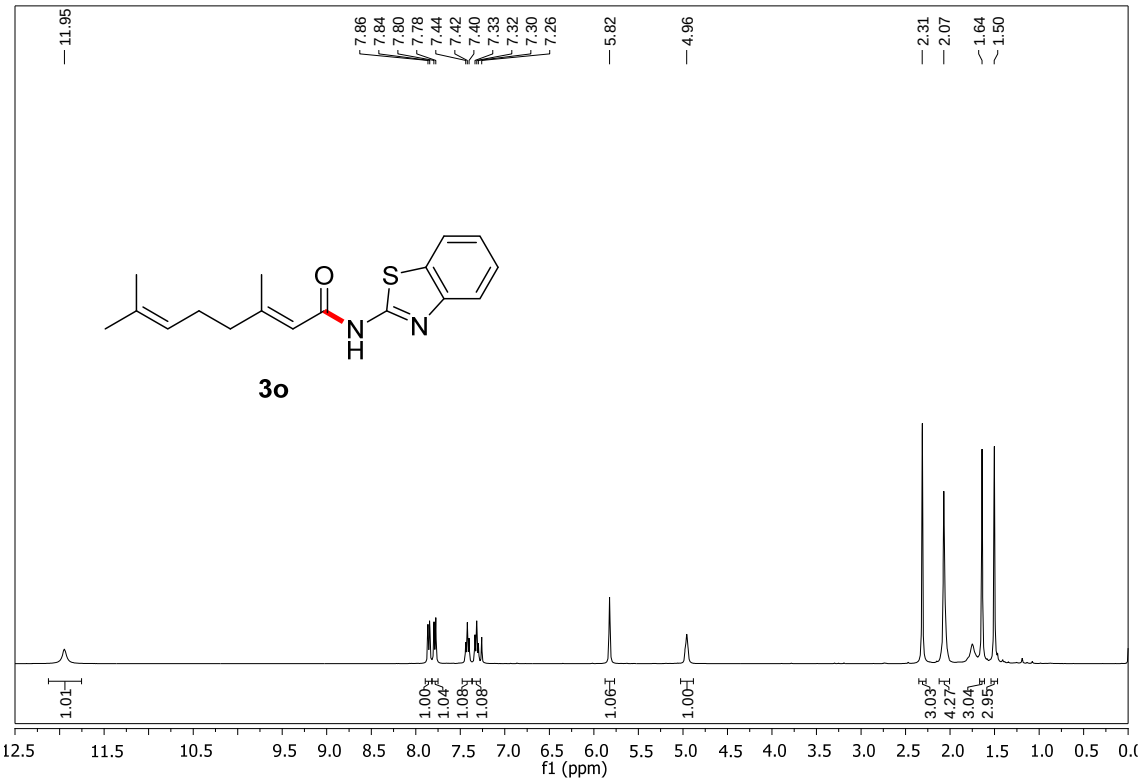


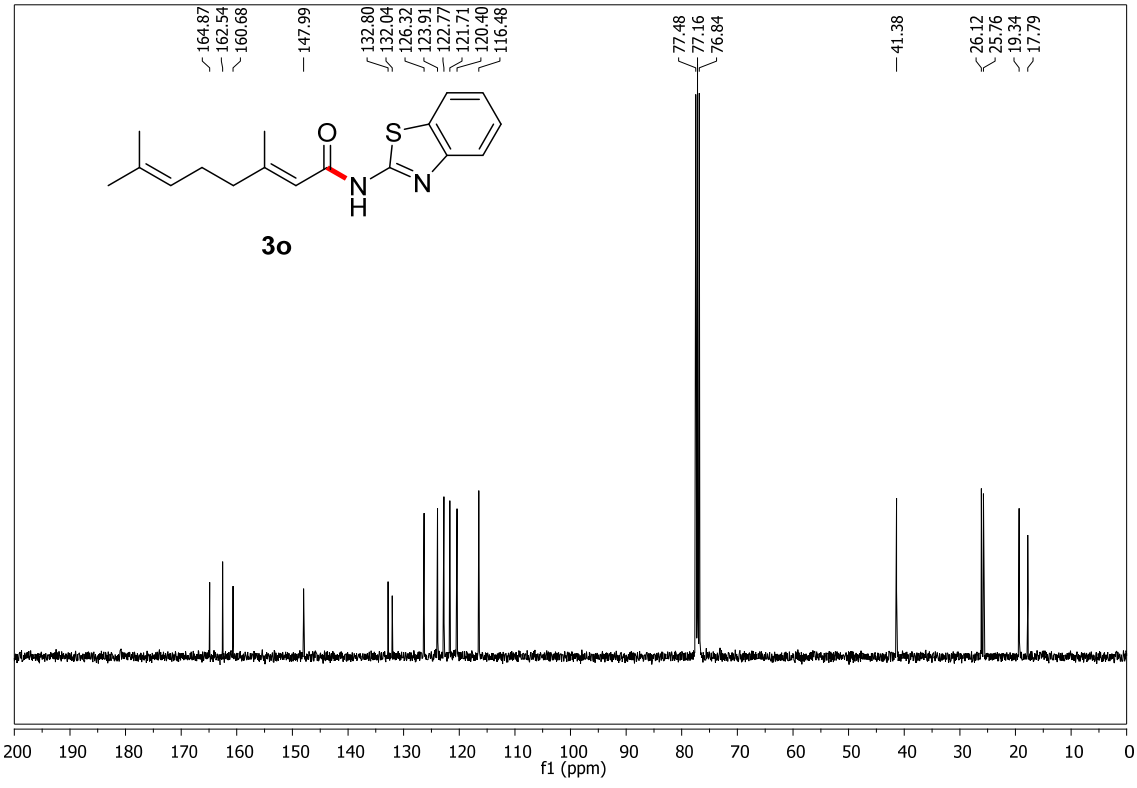
***(E)*-*N*-(Benzo[*d*]thiazol-2-yl)pent-2-enamide (3n)**



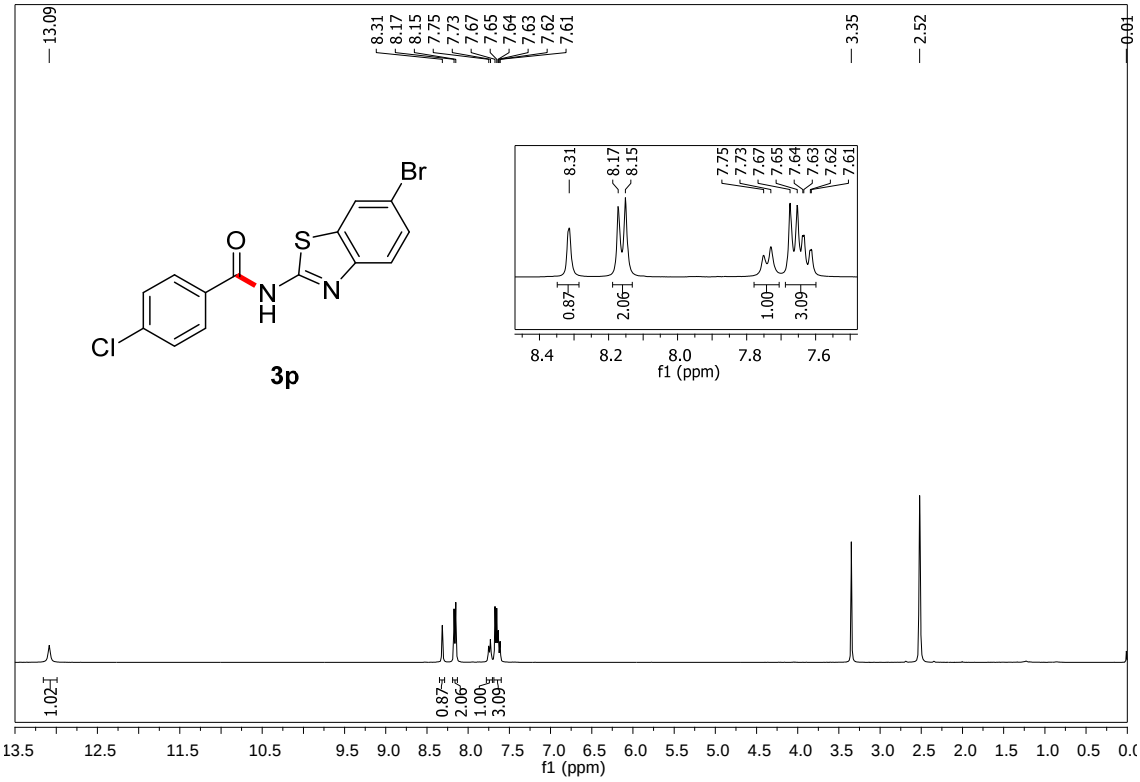


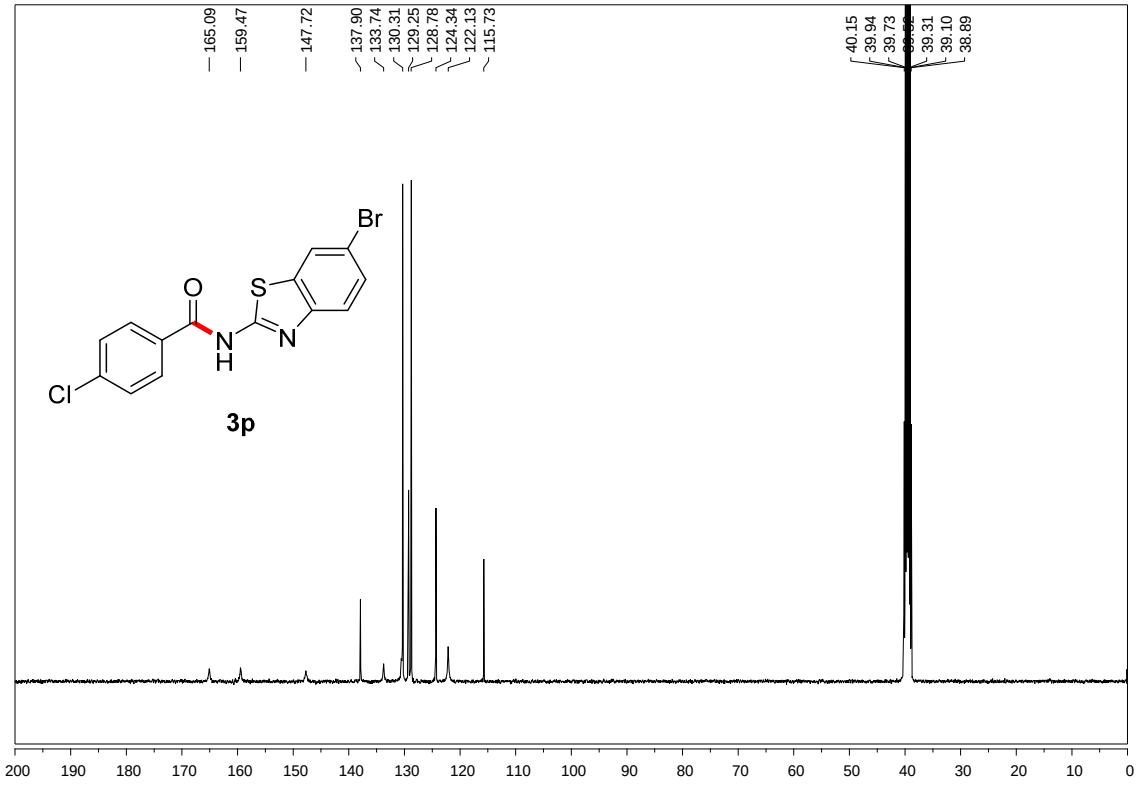
(*E*)-*N*-(Benzo[*d*]thiazol-2-yl)-3,7-dimethylocta-2,6-dienamide (3o)



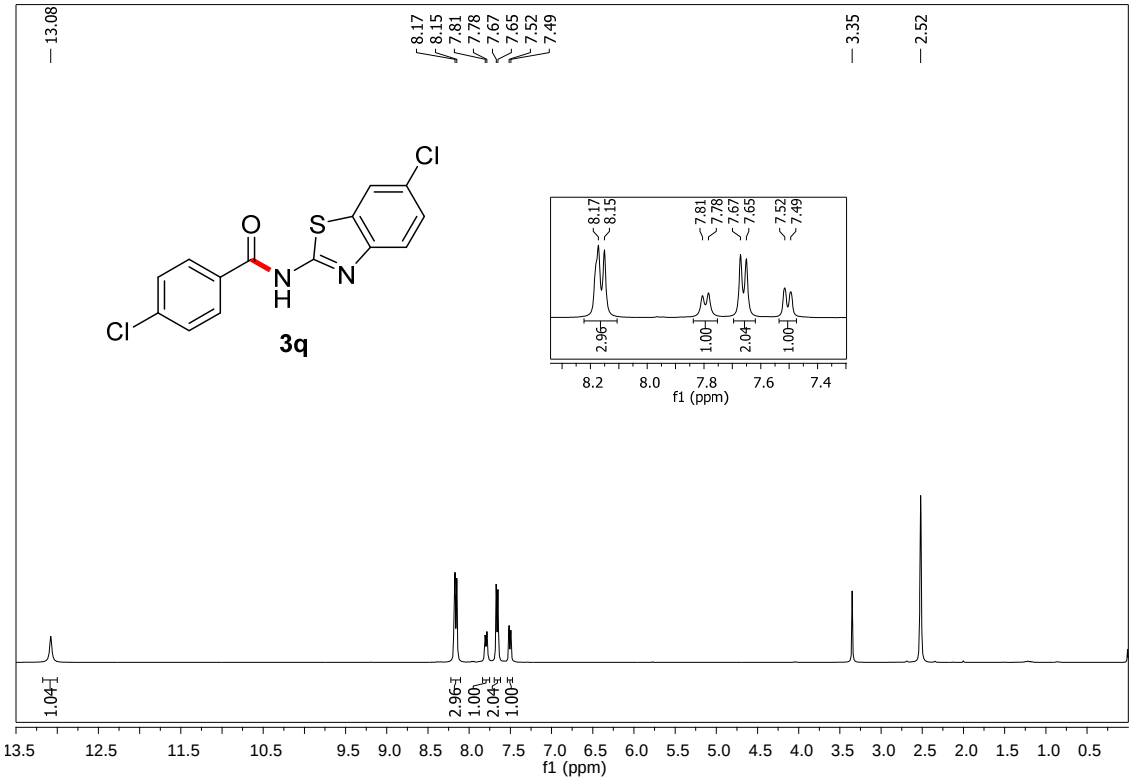


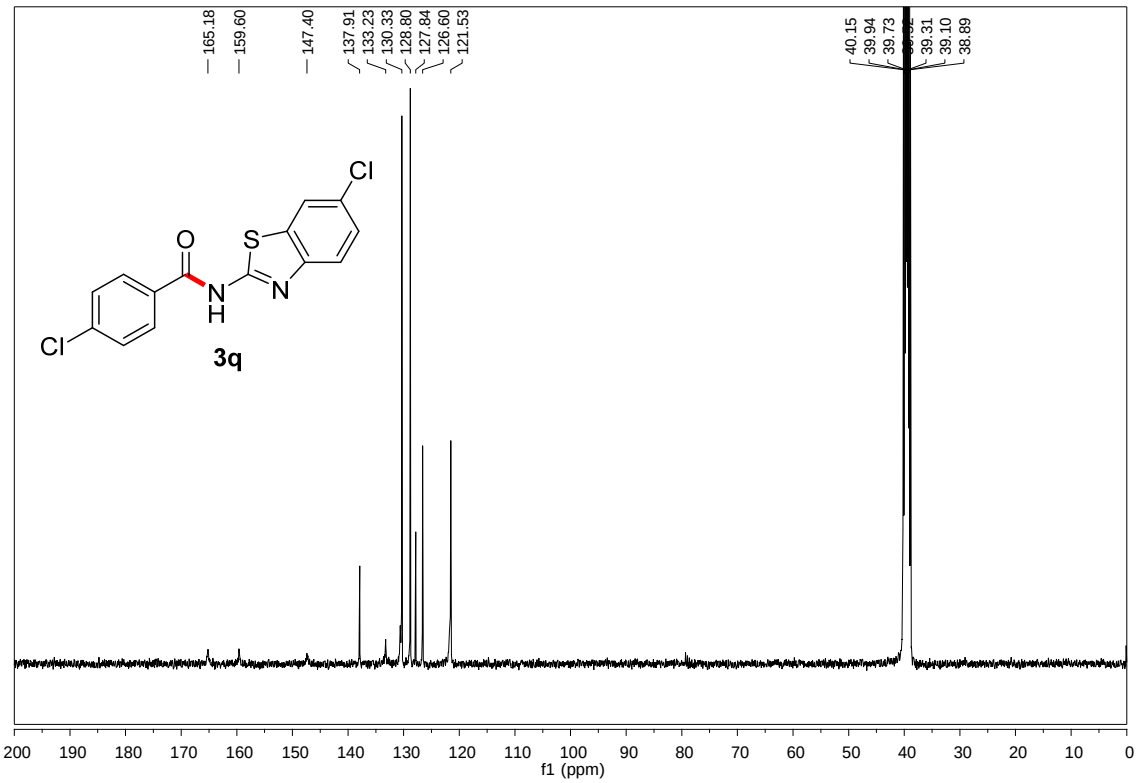
***N*-(6-Bromobenzo[d]thiazol-2-yl)-4-chlorobenzamide (3p)**



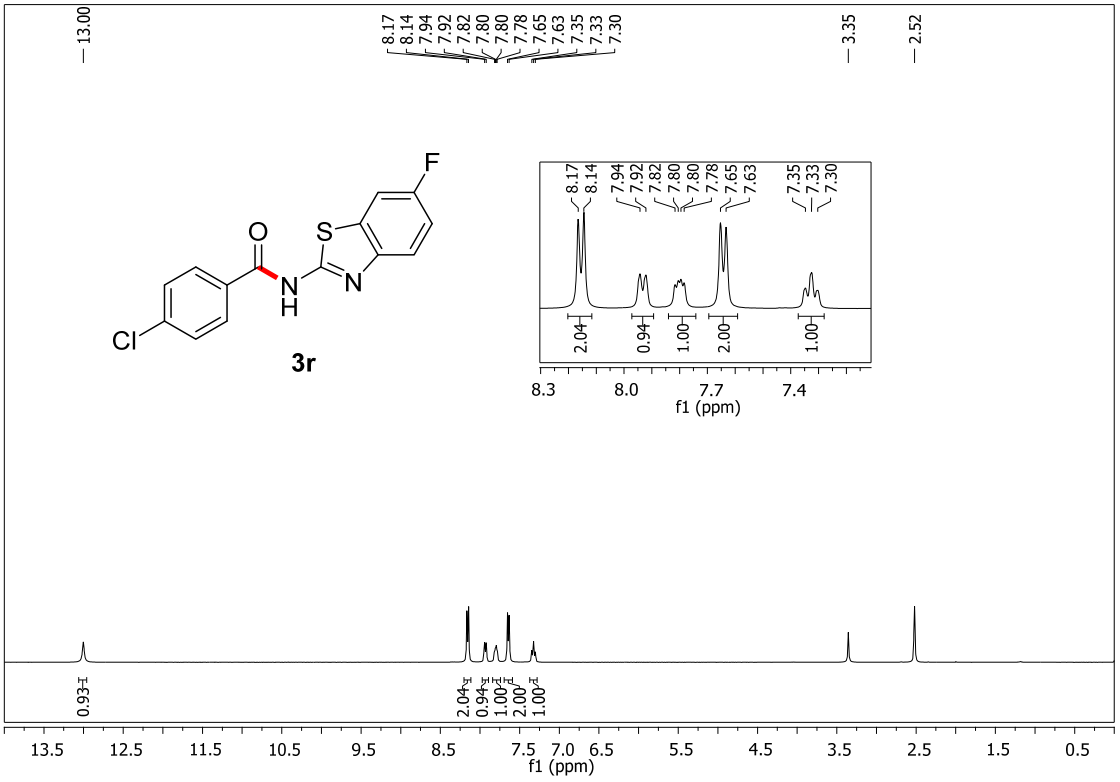


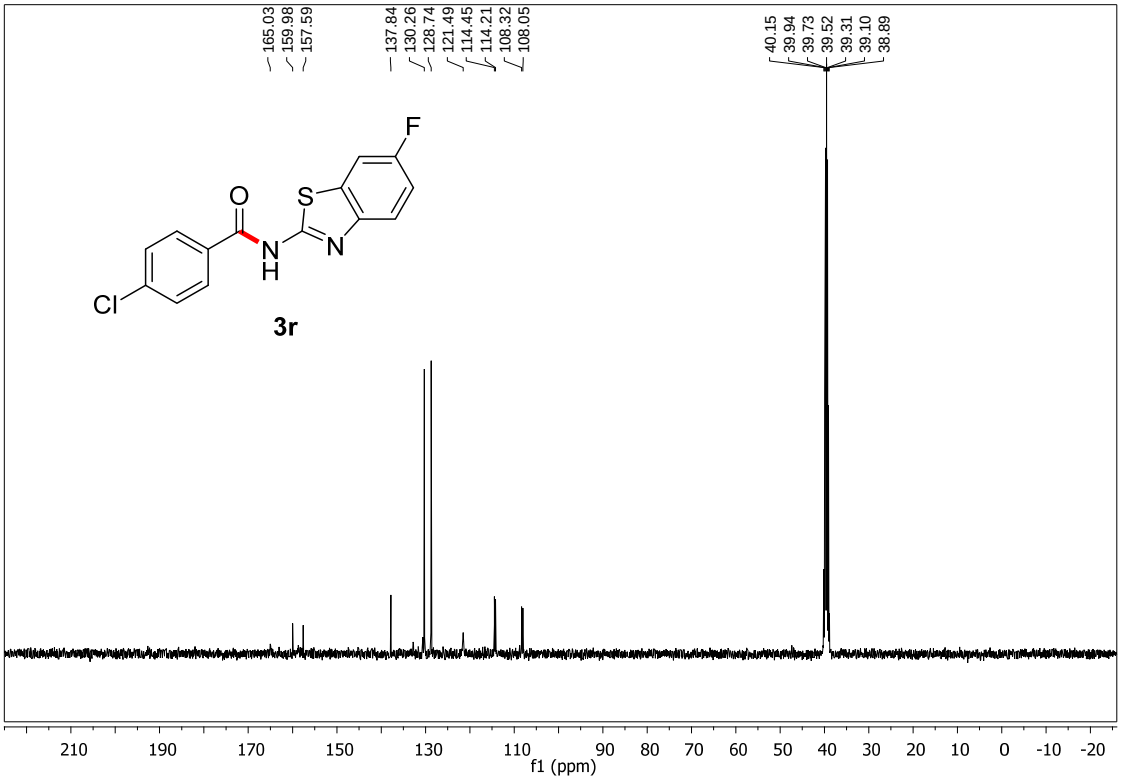
4-Chloro-*N*-(6-chlorobenzo[d]thiazol-2-yl)benzamide (3q)



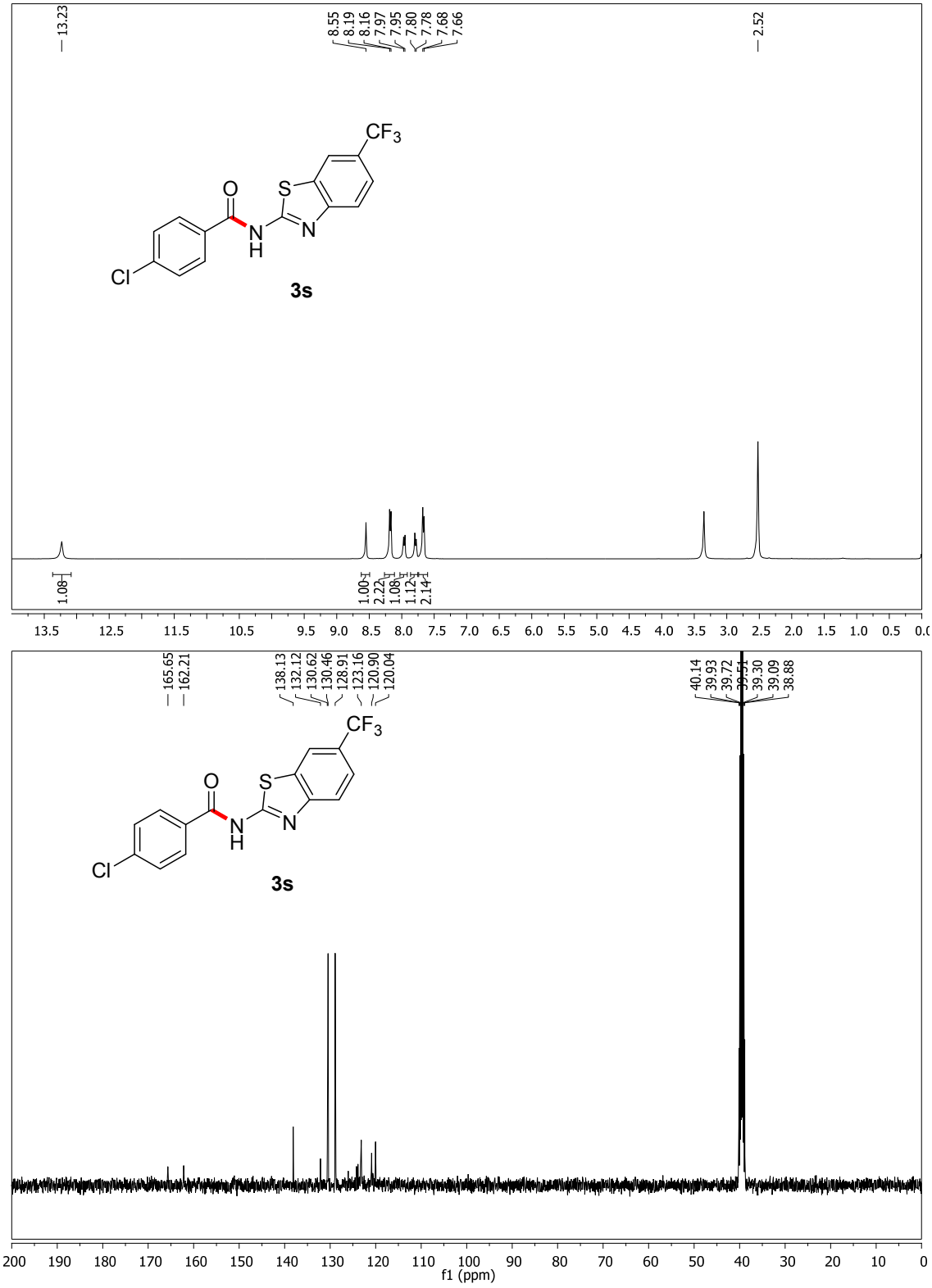


4-Chloro-*N*-(6-fluorobenzo[d]thiazol-2-yl)benzamide (3r)

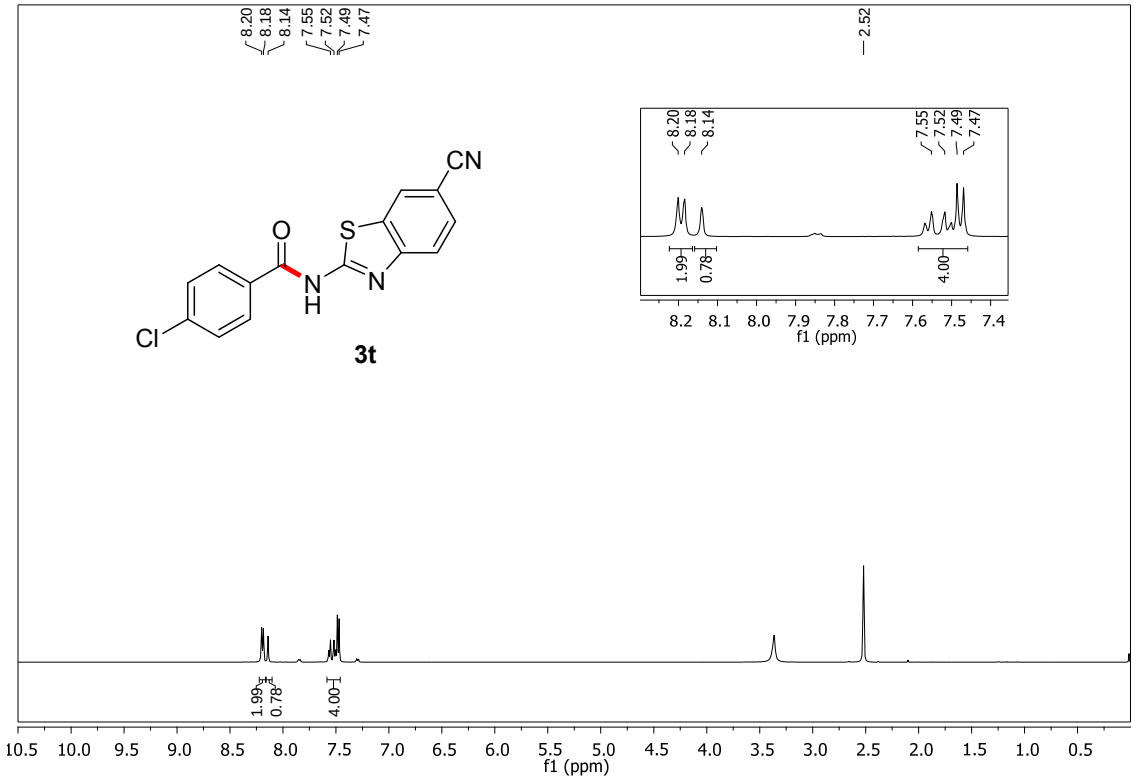


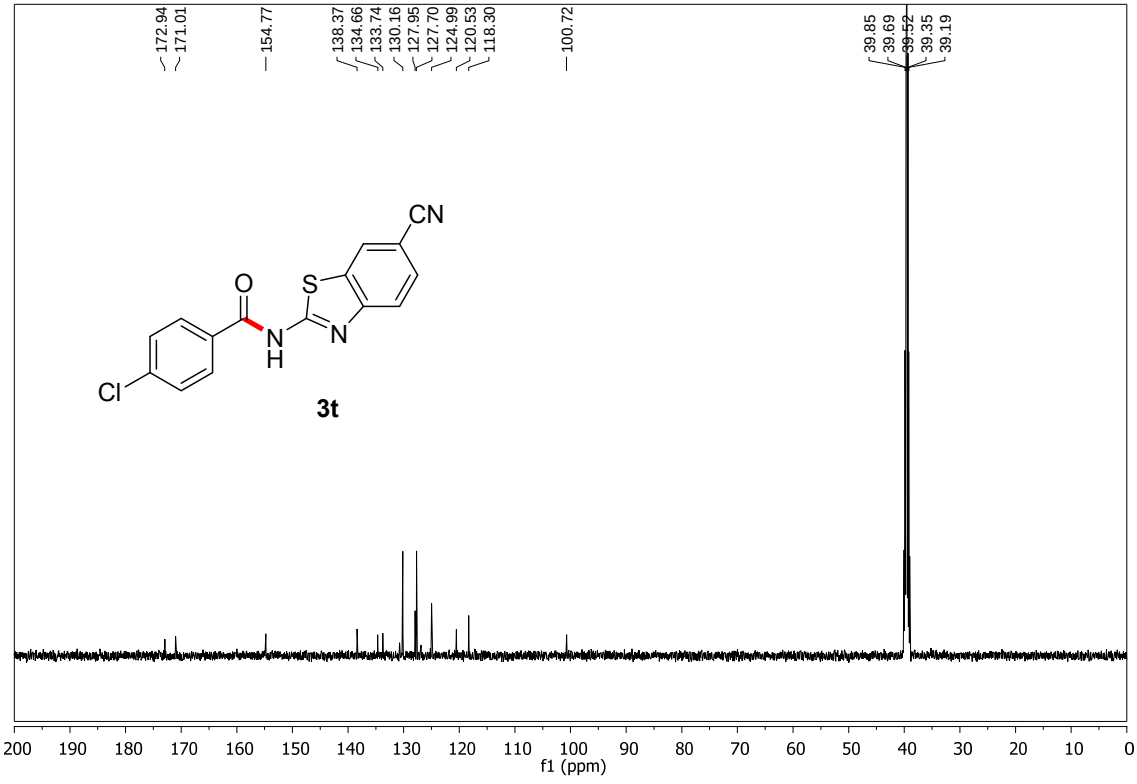


4-Chloro-*N*-(6-(trifluoromethyl)benzo[*d*]thiazol-2-yl)benzamide (3s)

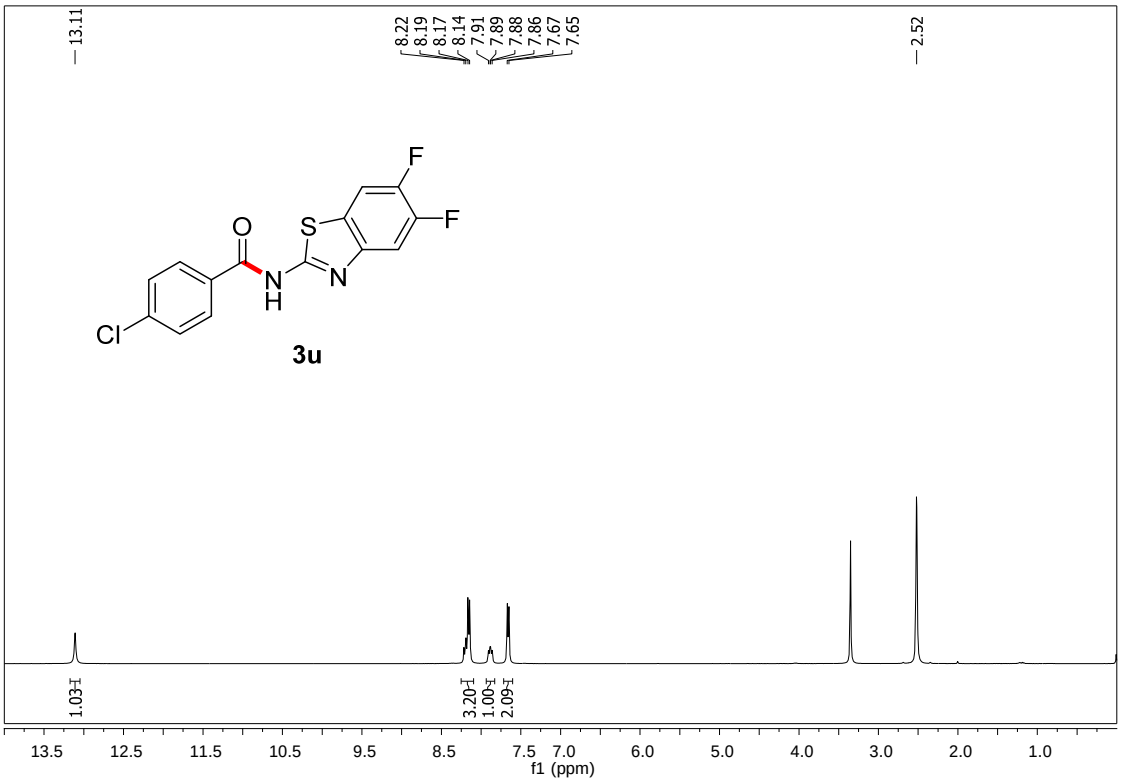


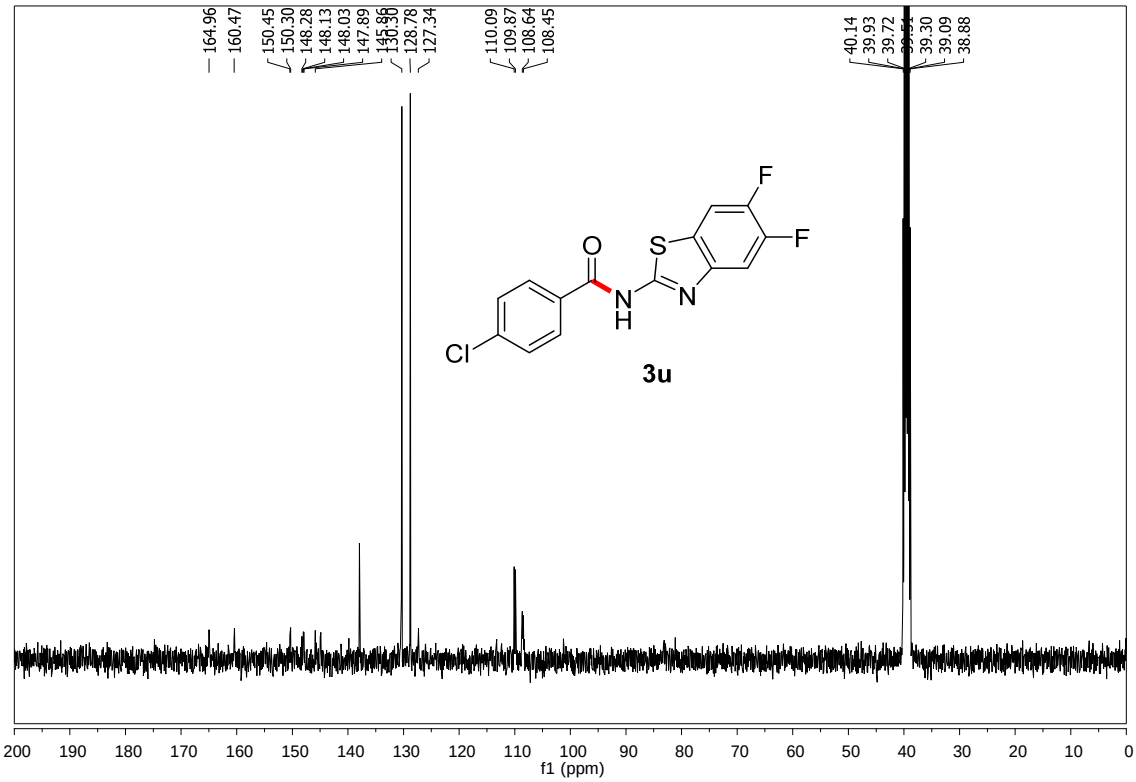
4-Chloro-*N*-(6-cyanobenzo[d]thiazol-2-yl)benzamide (3t)



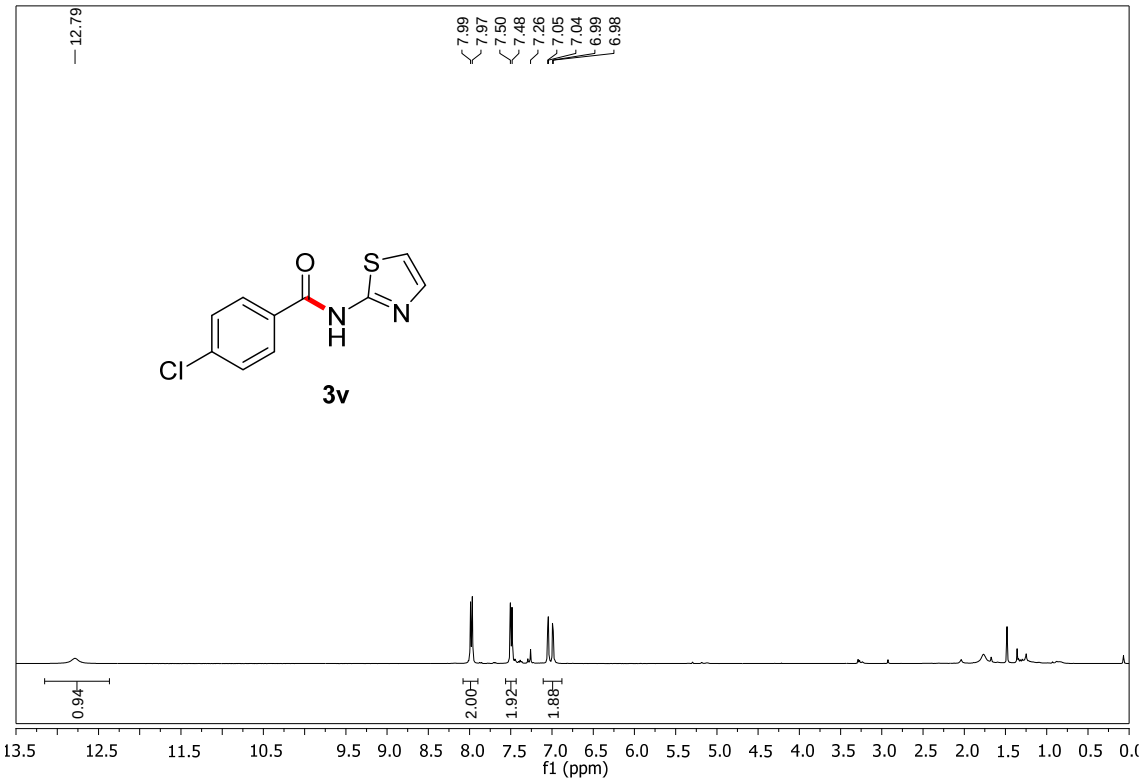


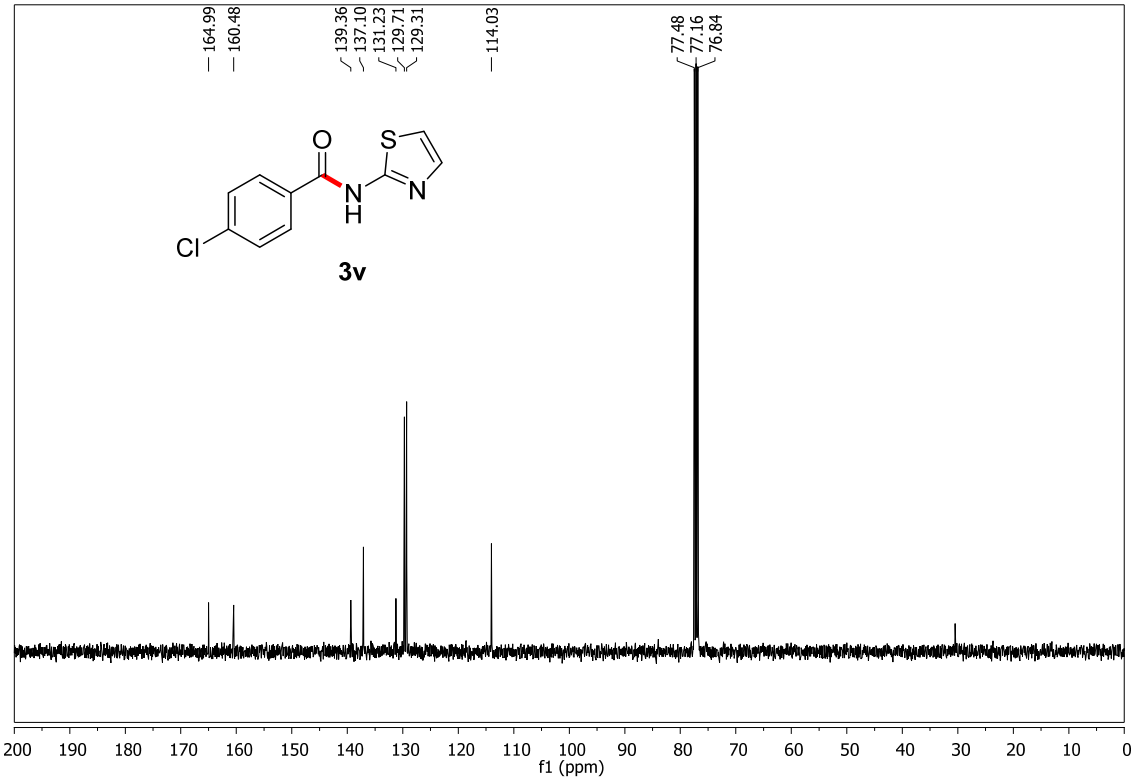
4-Chloro-*N*-(5,6-difluorobenzo[*d*]thiazol-2-yl)benzamide (3u)



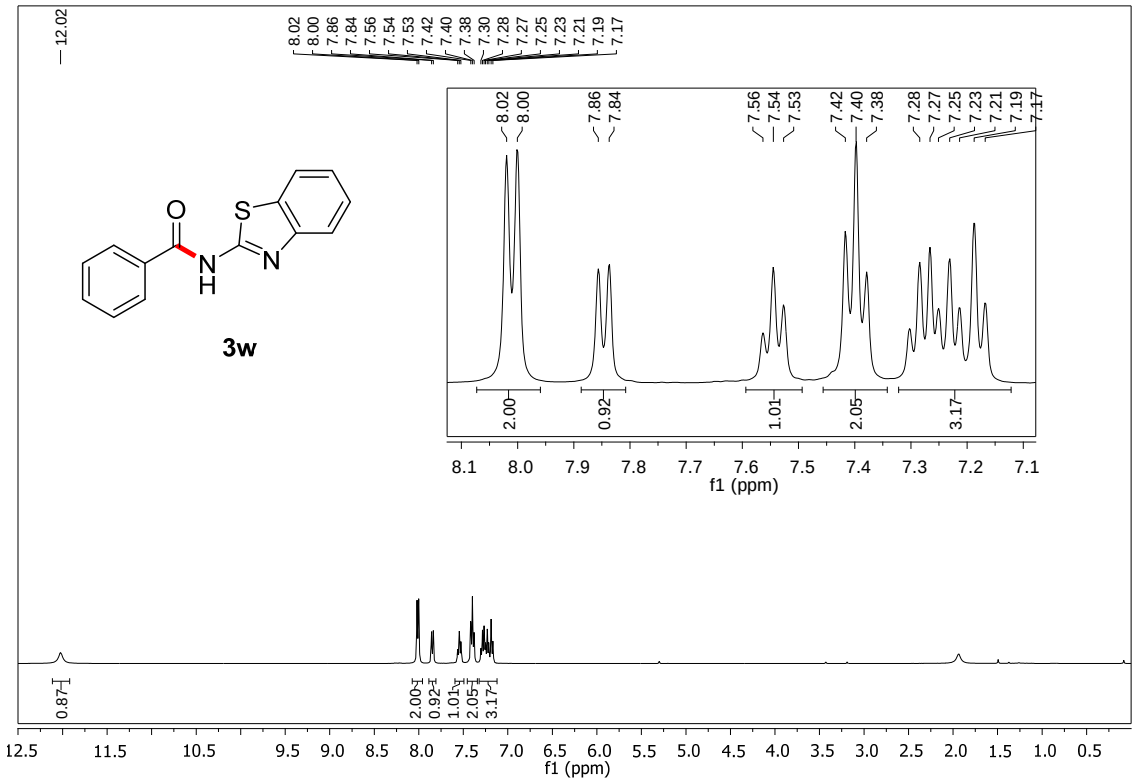


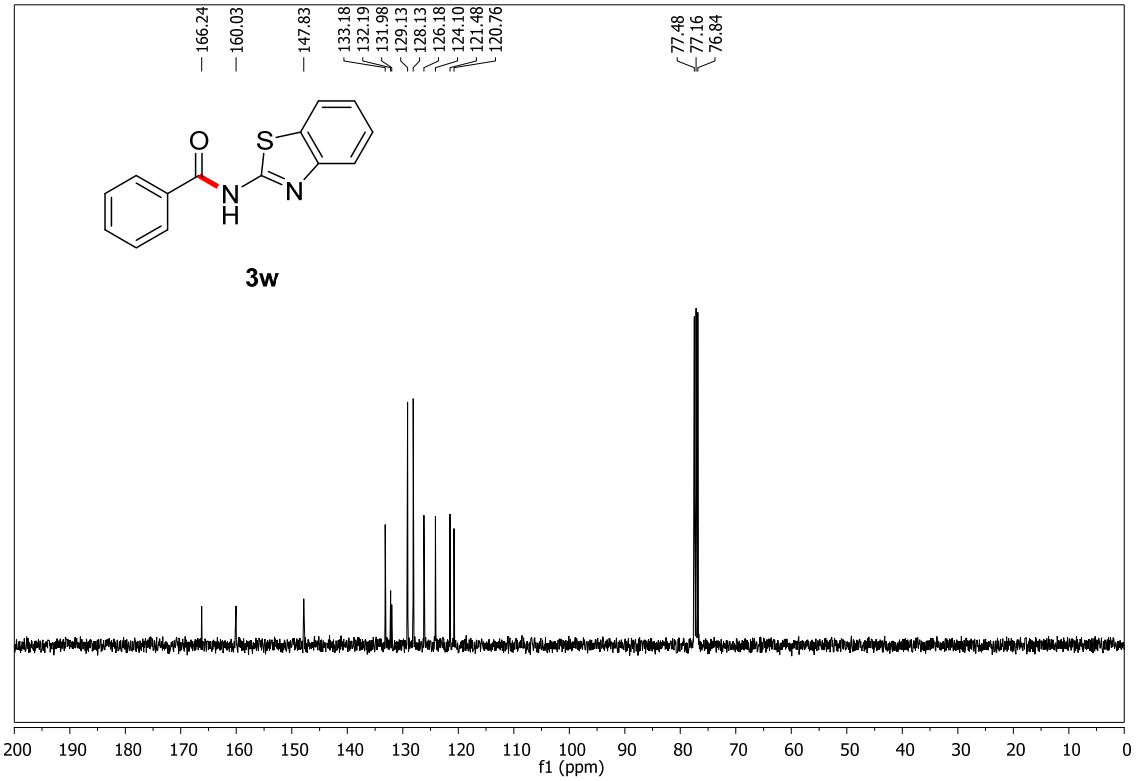
4-Chloro-*N*-(thiazol-2-yl)benzamide (3v)



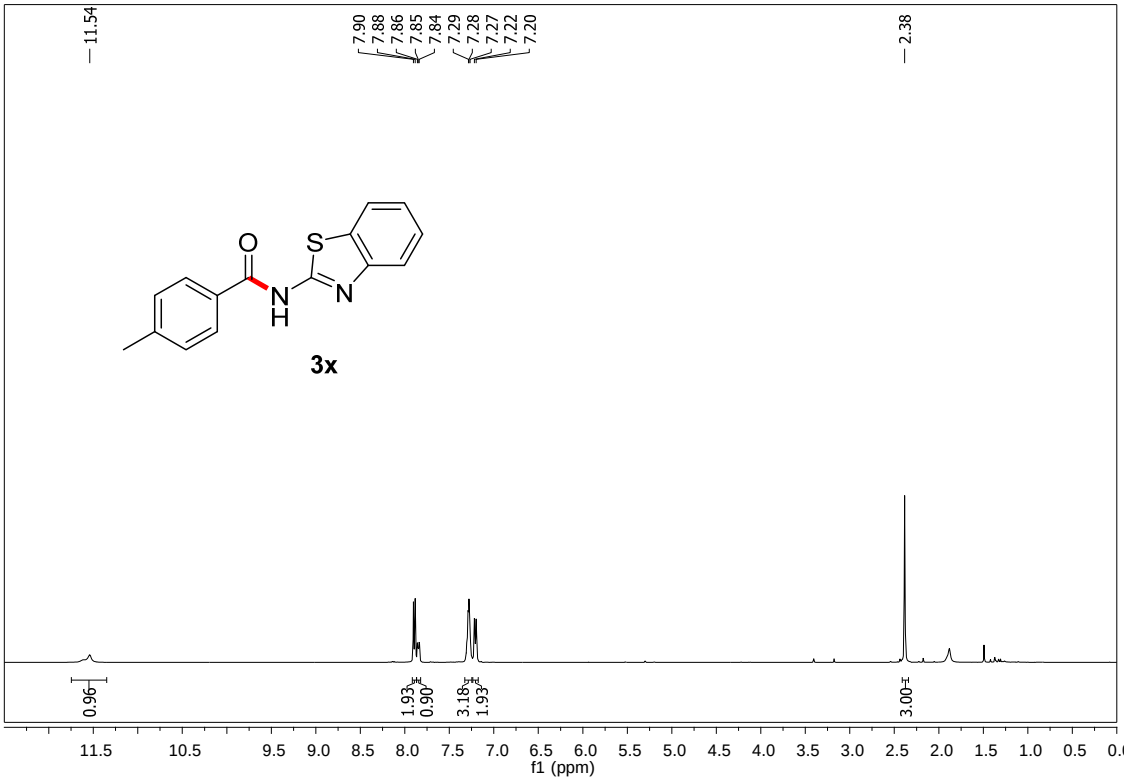


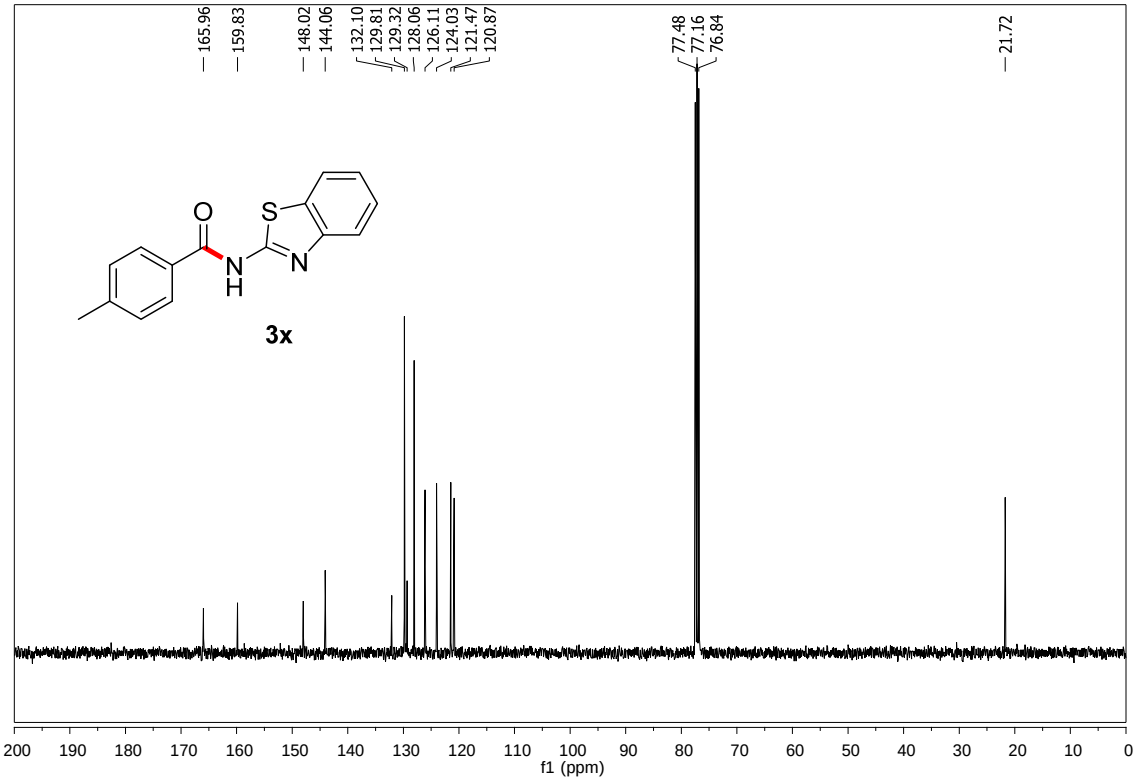
***N*-(Benzo[*d*]thiazol-2-yl)benzamide (3w)**



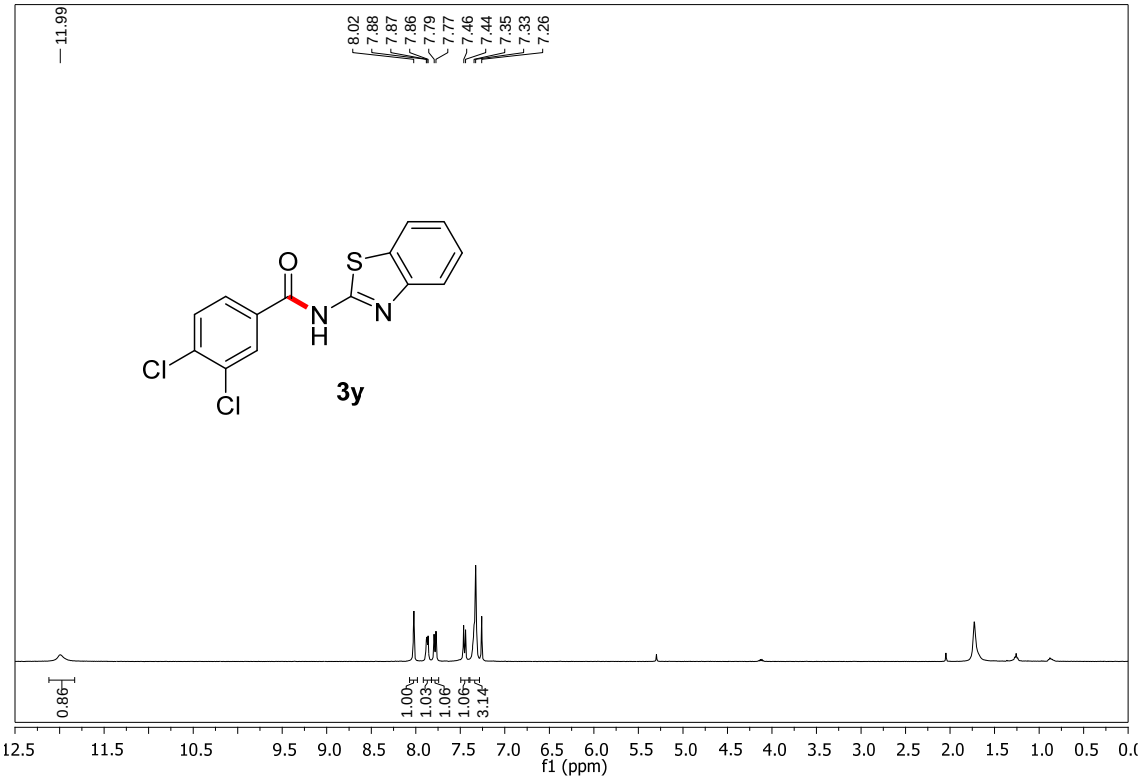


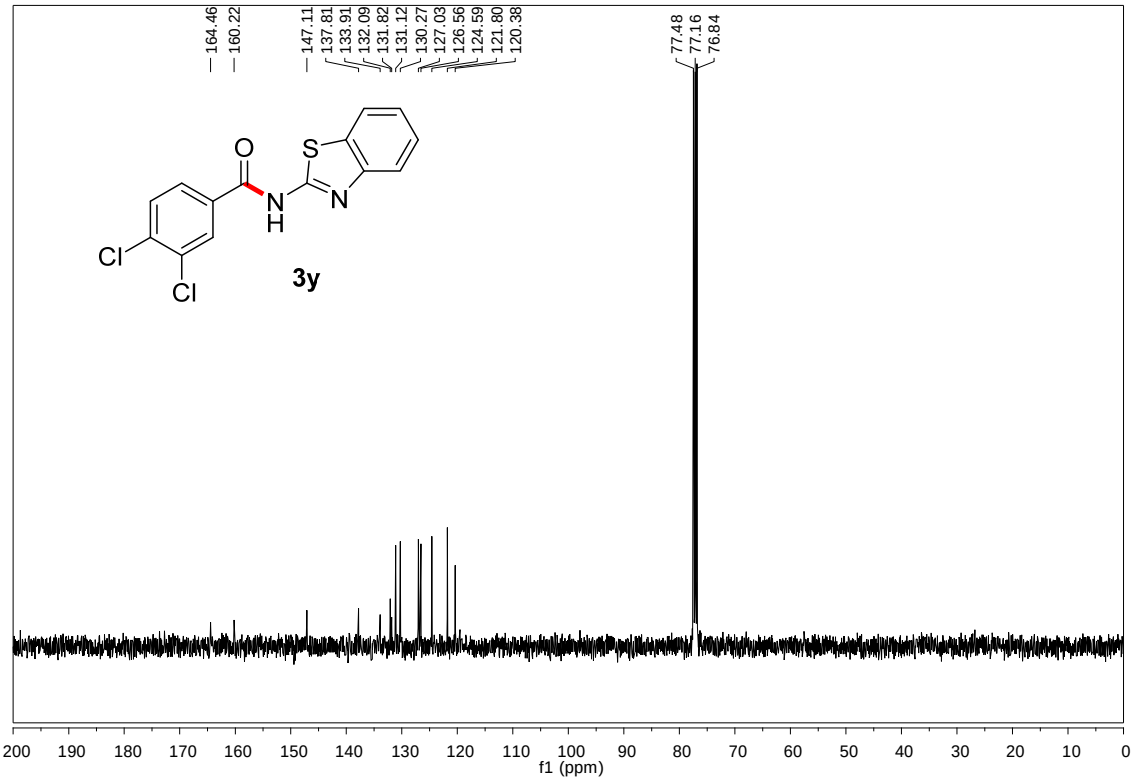
***N*-(Benzo[*d*]thiazol-2-yl)-4-methylbenzamide (3x)**



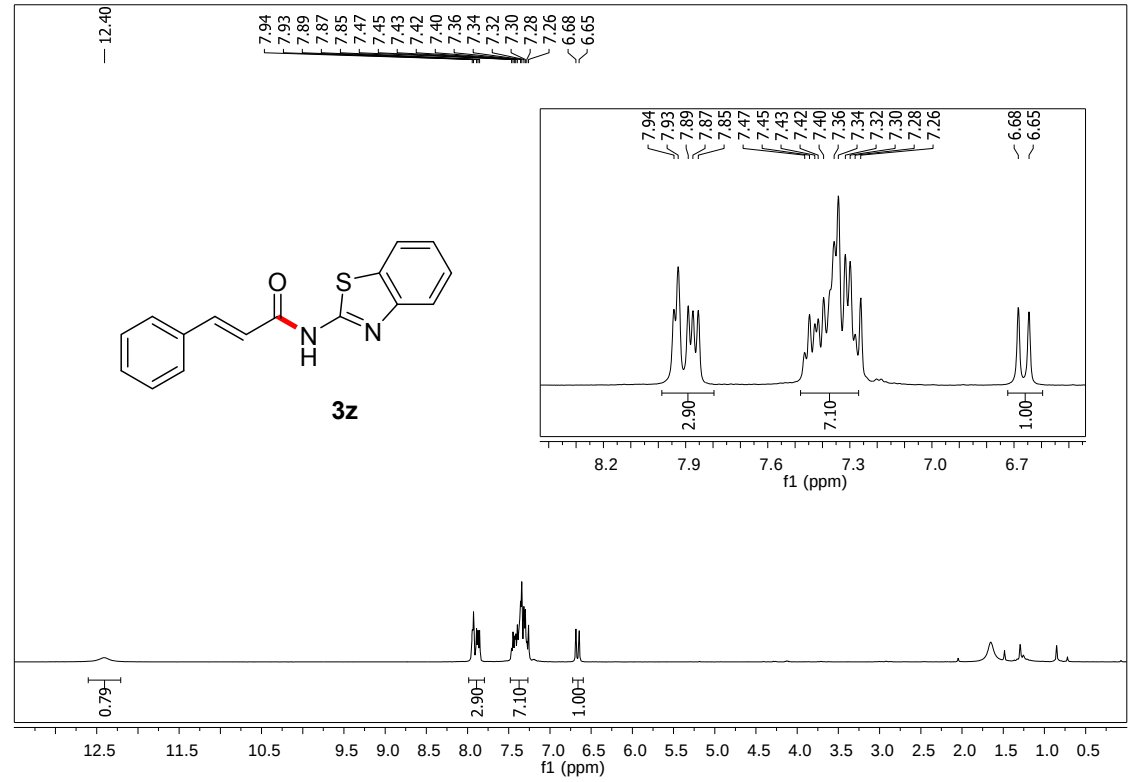


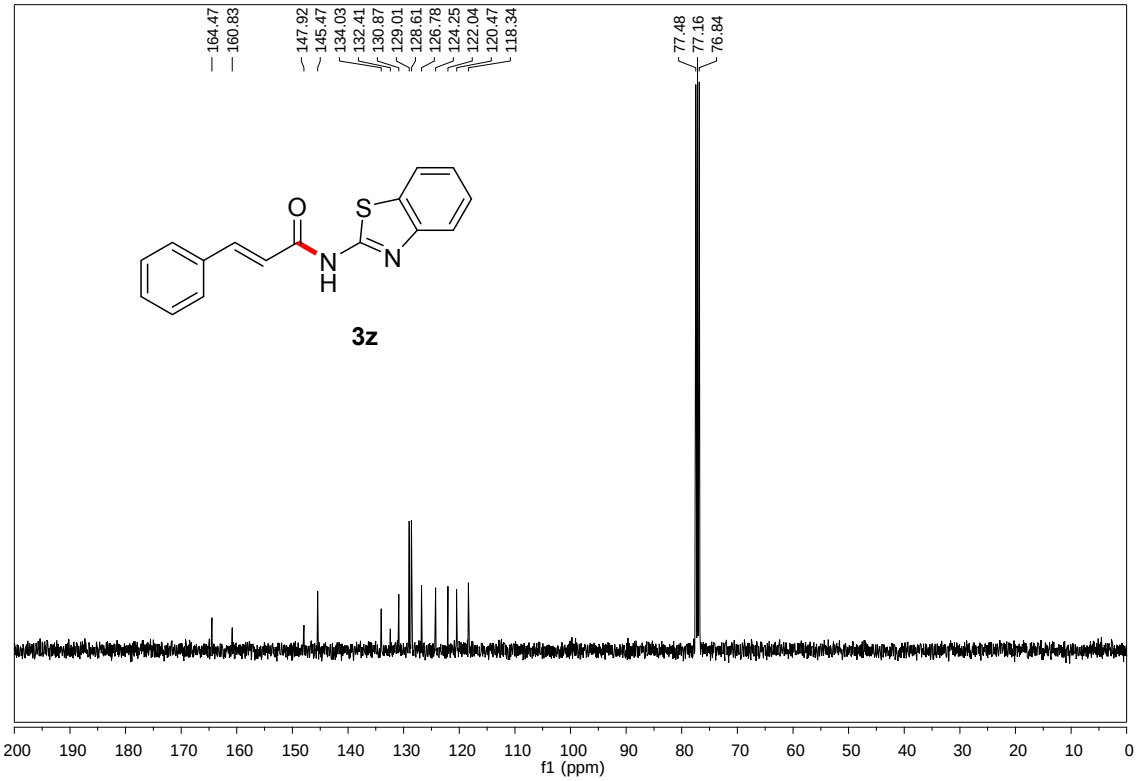
***N*-(Benzo[*d*]thiazol-2-yl)-3,4-dichlorobenzamide (3y)**



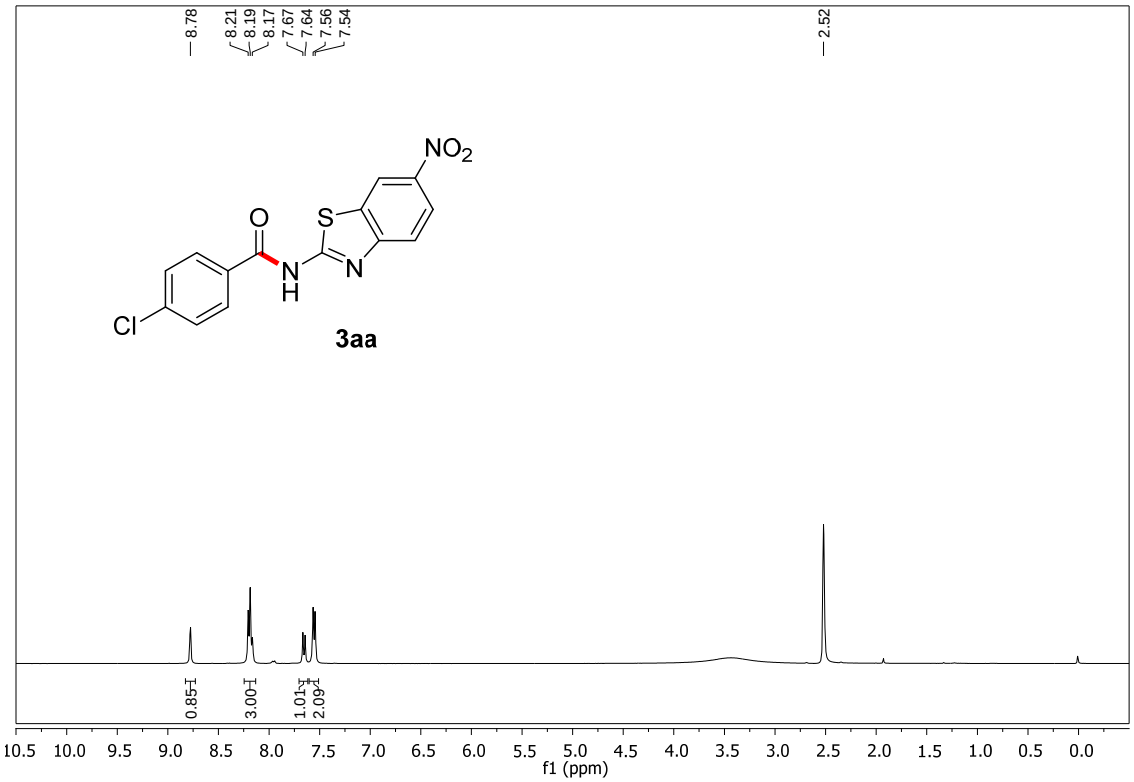


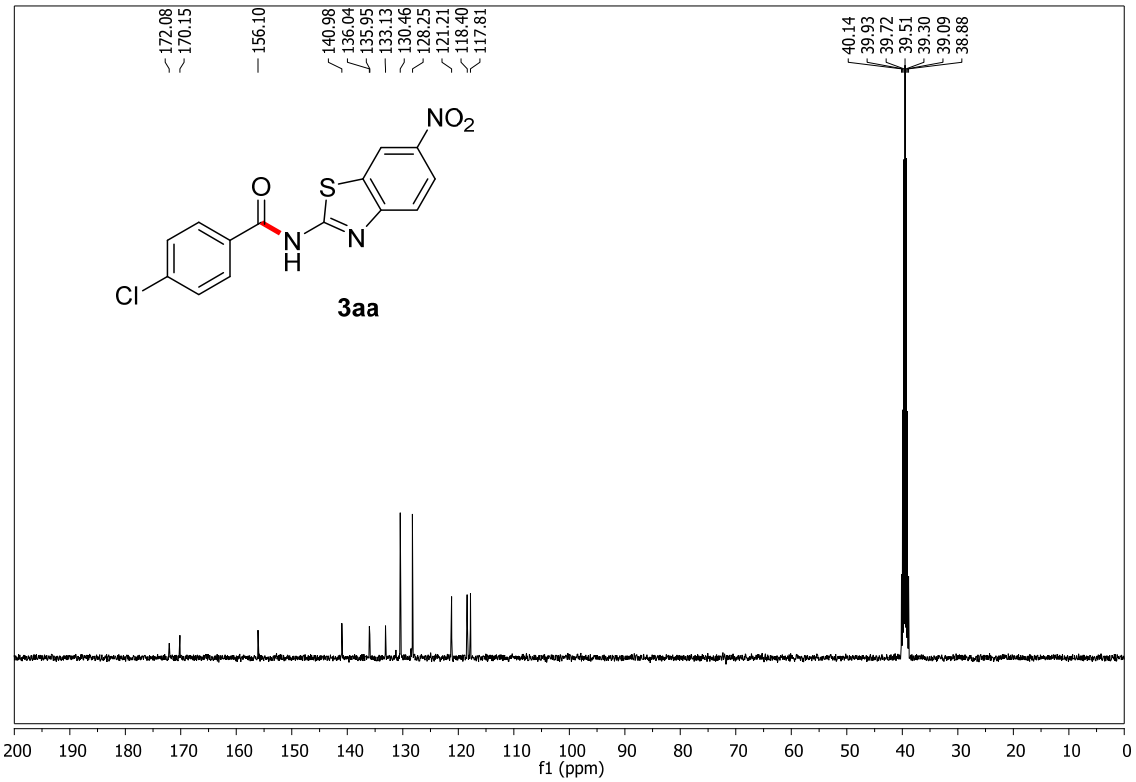
_N_-(Benzo[_d_]thiazol-2-yl)cinnamamide (3z)





4-Chloro-*N*-(6-nitrobenzo[*d*]thiazol-2-yl)benzamide (3aa)





4-Chloro-*N*-(6-methoxybenzo[*d*]thiazol-2-yl)benzamide (3ab)