Supporting Information

Synthetic Utility of Ammonium Salts in the Cu-Catalyzed Three-Component Reaction as a Facile Coupling Partner

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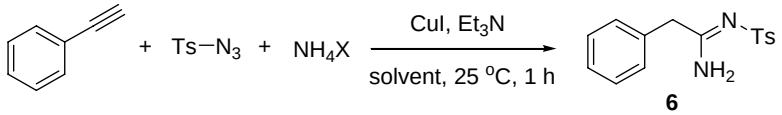
General Information: Unless otherwise stated, all commercial reagents and solvents were used as purchased without additional purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid or anisaldehyde stain followed by heating. Flash column chromatography was undertaken on silica gel (60 F_{254} 400-630 mesh). ^{1}H NMR was recorded on 400 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell and frequencies are given in reciprocal centimeters (cm^{-1}) and only selected absorbance is reported. High resolution mass spectra were recorded using FAB method.

General procedure of Table 1: To a stirred mixture of NH_4Cl or NH_3 (aq, 28%) (0.5 mmol), CuI (9.5 mg, 0.05 mmol), phenylacetylene (0.066 mL, 0.6 mmol) in the indicated solvent (1 mL) was slowly added triethylamine under N_2 at room temperature. After color changed to yellow, *p*-toluenesulfonyl azide (98.6 mg, 0.5 mmol) was added dropwise. After the reaction was completed, which was monitored with TLC, the reaction mixture was diluted by adding CH_2Cl_2 (2 mL) and aqueous NH_4Cl solution (3 mL). The mixture was stirred for an additional 30 min and two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatograph with an appropriate eluting solvent system.

Table S1. Screen of the Cu-Cataltzed Three-Component Reactions Using Ammonium Salts[a].



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entry	NH_4X	Et_3N (equiv)	solvent	yield (%)[b]
1	NH_4Cl	2	$CHCl_3$	68
2	NH_4Cl	2	CH_2Cl_2	85
3	NH_4Cl	2	$ClCH_2CH_2Cl$	72

4	NH_4Cl	2	THF	58
5	NH_4Cl	2	DMF	45
6	NH_4Cl	2	DMSO	25
7	NH_4Cl	2	1,4-dioxane	52
8	NH_4Cl	1.5	CH_2Cl_2	84
9	NH_4Cl	0.5	CH_2Cl_2	62
10[c]	NH_4Cl	1.5	CH_2Cl_2	87
11[c]	NH_3 (aq)	2	$CHCl_3$	87
12[c]	NH_3 (aq)	2	CH_2Cl_2	88
13[c]	NH_3 (aq)	2	THF	63
14[c]	NH_3 (aq)	1.5	CH_2Cl_2	89

[a] Phenylacetylene (0.5 mmol), *p*-toluenesulfonyl azide (0.5 mmol), Et_3N, NH_4X (0.5 mmol), and CuI (0.05 mmol) in the indicated solvent (1.0 mL) at 25 ^oC for 1 h under N_2. [b] ^1H NMR yield (internal standard: 1,1,2,2-tetrachloroethane). [c] Run open to the air.

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Reaction profile of the Cu-catalyzed three-component coupling reactions with benzylamine, benzyl alcohol, water, NH_4Cl, and NH_3 (aq). To a stirred mixture of each coupling partner (0.5 mmol), CuI (9.5 mg, 0.05 mmol), phenylacetylene (0.056 mL, 0.5 mmol) in CH_2Cl_2 (1 mL) was slowly added triethylamine under N_2 at room temperature. After color changed to yellow, *p*-toluenesulfonyl azide (98.6 mg, 0.5 mmol) was added dropwise, and the reaction mixture was stirred at room temperature. An aliquot was taken over time from the reaction mixture and product yield from the corresponding reaction was monitored by ^1H NMR using an internal standard (1,1,2,2-tetrachloroethane) in the indicated interval, and the results are presented in Figure S1.

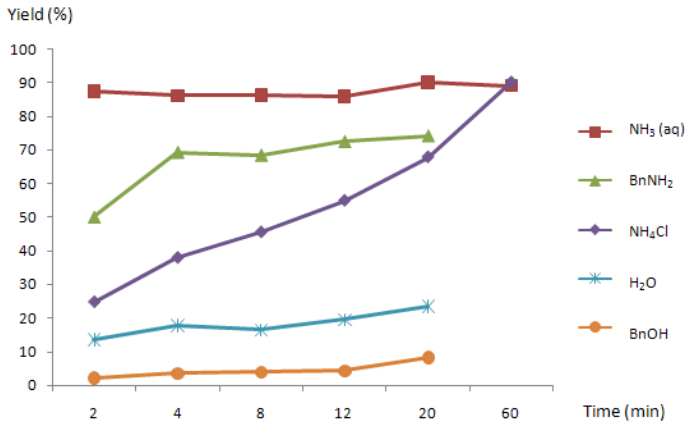
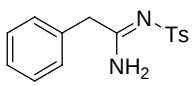
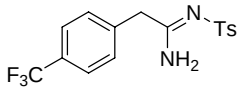


Figure S1. Product yield in the Cu-catalyzed three-component coupling reactions with NH_3 (aq), benzylamine, NH_4Cl, water, and benzylalcohol.

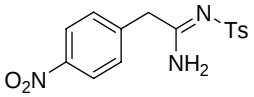
General procedure for the Cu-catalyzed three-component coupling reaction with NH_4Cl (Table 2 and 3). To a stirred mixture of NH_4Cl (26.7 mg, 0.5 mmol), CuI (9.5 mg, 0.05 mmol), alkyne (0.5 mmol) in CH_2Cl_2 (1 mL) was slowly added triethylamine (0.14 mL, 0.75 mmol) at room temperature. After color changed to yellow, indicated azide (0.5 mmol) was added dropwise. After the reaction was completed, which was monitored with TLC, the reaction mixture was diluted by adding CH_2Cl_2 (2 mL) and aqueous NH_4Cl solution (3 mL). The mixture was stirred for an additional 30 min and two layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatograph with an appropriate eluting solvent system. Sometimes, polar products were purified by recrystallization using dichloromethane and hexane.



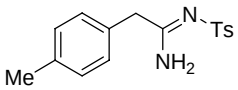
2-Phenyl-*N*-(*p*-toluenesulfonyl)acetamidine (entry 1, Table 2): white solid; m.p. 115–116 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (br, 1H), 7.75 (d, J = 8.2 Hz, 2H), 7.30-7.16 (m, 7H), 5.97 (br, 1H), 3.58 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 143.0, 139.0, 133.4, 129.5, 129.3, 129.1, 127.9, 126.3, 43.6, 21.4; IR (NaCl) ν 3327, 3328, 3238, 1654, 1545, 1449, 1414, 1277, 1103, 801 cm^{-1}; HRMS(FAB) m/z calcd. for $C_{15}H_{17}O_2N_2S$ $[M+H]^+$: 289.1011, found: 289.1001.



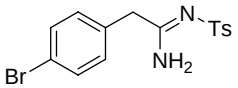
2-[4-(Trifluoromethyl)phenyl]-*N*-(*p*-toluenesulfonyl)acetamidine (entry 2, Table 2): white solid; m.p. 194–195 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 1H), 8.06 (s, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.63 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.7, 142.0, 140.5, 139.6, 129.6, 129.0, 127.5 (q, J_2 = 31.3 Hz), 125.8, 125.1 (q, J_3 = 3.8 Hz), 124.4 (q, J_1 = 291.9 Hz), 41.7, 20.8; IR (KBr) ν 3380, 3340, 3252, 1672, 1567, 1412, 1331, 1254, 1140, 818, 698 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{15}O_2N_2F_3S$ $[M]^+$: 356.0806, found: 356.0805.



2-(4-Nitrophenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 3, Table 2): yellowish solid; m.p. 173–174 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.87 (s, 1H), 8.13 (d, J = 8.8 Hz, 2H), 8.09 (s, 1H), 7.60 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 3.69 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.3, 146.5, 143.7, 142.2, 139.5, 130.1, 129.1, 125.9, 123.4, 41.6, 20.9; IR (NaCl) ν 3429, 3324, 3245, 1636, 1548, 1520, 1273, 1141, 1083, 617, 778 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{15}O_4N_3S$ $[M]^+$: 333.0783, found: 333.0780.

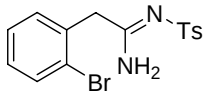


2-(4-Methylphenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 4, Table 2): white solid; m.p. 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 5.99 (br, 1H), 3.54 (s, 2H), 2.38(s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 142.9, 139.0, 137.6, 130.2, 129.7, 129.3, 129.2, 126.3, 43.1, 21.4, 21.0; IR (NaCl) ν 3397, 3320, 1638, 1544, 1264, 1141, 1084, 809 cm^{-1}; HRMS (EI) m/z calcd. for $C_{16}H_{18}O_2N_2S$ $[M]^+$: 302.1089, found: 302.1087.

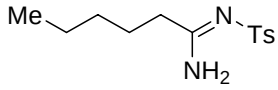


2-(4-Bromophenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 5, Table 2): white solid; m.p. 177–178 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.77 (s, 1H), 8.00 (s, 1H), 7.60 (d, J = 8.2 Hz, 2H), 7.45

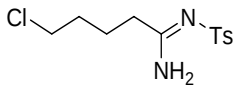
(d, J = 8.4 Hz , 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 3.49(s, 2H), 2.34(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 142.1, 139.6, 135.1, 131.1, 131.0, 129.1, 125.9, 120.0, 41.3, 20.9; IR (NaCl) ν 3375, 3211, 1664, 1581, 1565, 1404, 1250, 1139, 1085, 767, 530, 514 cm^{-1}; HRMS (EI) m/z calcd. for $C_{15}H_{15}O_2N_2BrS$ $[M]^+$: 366.0038, found: 366.0038.



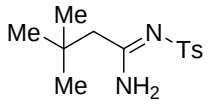
2-(2-Bromophenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 6, Table 2): white solid; m.p. 95–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 7.9 Hz, 1H), 7.24-7.20 (m, 4H), 7.15-7.11 (m, 1H), 6.00 (br, 1H), 3.73 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 142.9, 138.8, 133.5, 133.1, 131.8, 129.6, 129.2, 128.0, 126.3, 125.0, 43.8, 21.4; IR (NaCl) ν 3420, 3320, 3239, 1633, 1497, 1271, 1141, 1083, 814, 764 cm^{-1}; HRMS(FAB) m/z calcd. for $C_{15}H_{15}O_2N_2BrS$ $[M+H]^+$: 367.0116, found: 367.0111.



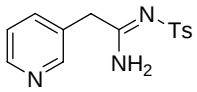
***N*-(*p*-Toluenesulfonyl)hexanamidine (entry 7, Table 2):** white solid; m.p. 71–72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (br, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 6.26 (br, 1H), 2.38 (s, 3H), 2.20 (t, J = 7.5 Hz, 2H), 1.58-1.50 (m, 2H), 1.22-1.13 (m, 4H), 0.78 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 142.8, 139.3, 129.3, 126.3, 37.7, 30.9, 26.2, 22.2, 21.4, 13.8; IR (NaCl) ν 3416, 3328, 3242, 1637, 1552, 1270, 1141, 1084, 814 cm^{-1}; HRMS (EI) m/z calcd. for $C_{13}H_{20}O_2N_2S$ $[M]^+$: 268.1245, found: 268.1248.



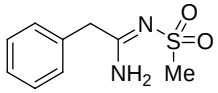
5-Chloro-*N*-(*p*-toluenesulfonyl)pentanamidine (entry 8, Table 2): white solid; m.p. 100–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (br, 1H), 7.76 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.27 (br, 1H), 3.43 (t, J = 6.3 Hz, 2H), 2.39 (s, 3H), 2.27 (t, J = 6.9 Hz, 2H), 1.75-1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 143.1, 139.0, 129.4, 126.2, 44.2, 36.7, 31.3, 23.7, 21.5; IR (NaCl) ν 3390, 3323, 3246, 1647, 1547, 1275, 1146, 1085, 609 cm^{-1}; HRMS (EI) m/z calcd. for $C_{12}H_{17}O_2N_2ClS$ $[M]^+$: 288.0699, found: 288.0704.



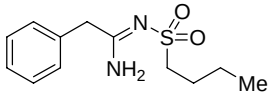
3,3-Dimethyl-*N*-(*p*-toluenesulfonyl)butanamidine (entry 9, Table 2): yellowish solid; m.p. 87–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (br, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.17 (br, 1H), 2.38 (s, 3H), 2.08 (s, 2H), 0.89 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 142.9, 139.3, 129.2, 126.3, 51.2, 31.9, 29.6, 21.5; IR (NaCl) ν 3414, 3328, 3241, 1636, 1550, 1267, 1140, 1083 cm^{-1}; HRMS (EI) m/z calcd. for $C_{13}H_{20}O_2N_2S$ $[M]^+$: 268.1245, found: 268.1241.



2-(Pyridin-3-yl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 10, Table 2): yellow solid; m.p. 143–144 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 1H), 8.43 (s, 1H), 8.41 (s, 1H), 8.03 (s, 1H), 7.61-7.58 (m, 3H), 7.30-7.27 (m, 3H), 3.56 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.9, 149.8, 148.0, 142.1, 139.6, 136.2, 131.5, 129.1, 125.9, 123.4, 39.2, 20.9; IR (NaCl) ν 3415, 3328, 3242, 1638, 1559, 1273, 1141, 1084, 815 cm^{-1}; HRMS (EI) m/z calcd. for $C_{14}H_{15}O_2N_3S$ $[M]^+$: 289.0885, found: 289.0886.

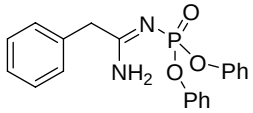


***N*-(Methanesulfonyl)-2-phenylacetamidine (entry 1, Table 3):** yellow solid; m.p. 94–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (br, 1H), 7.37-7.24 (m, 5H), 5.79 (br, 1H), 3.61 (s, 2H), 2.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 133.3, 129.5, 129.2, 128.0, 43.6, 42.0; IR (NaCl) ν 3411, 3328, 3246, 1639, 1561, 1266, 1117, 971, 798 cm^{-1}; HRMS (EI) m/z calcd. for $C_9H_{12}O_2N_2S$ $[M]^+$: 212.0619, found: 212.0616.

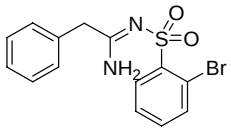


***N*-(Butanesulfonyl)-2-phenylacetamidine (entry 2, Table 3):** white solid; m.p. 50–51 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (br, 1H), 7.33-7.23 (m, 5H), 6.11 (br, 1H), 3.57 (s, 2H), 2.95 (t, *J* = 7.9 Hz, 2H), 1.71-1.64 (m, 2H), 1.40-1.31 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 133.8, 129.3, 129.0, 127.7, 53.9, 43.6, 25.2, 21.4, 13.5; IR (NaCl) ν 3407, 3325,

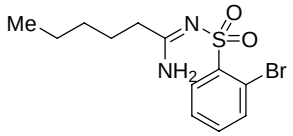
3244, 1638, 1561, 1260, 1114, 813 cm^{-1}; HRMS (EI) m/z calcd. for $C_{12}H_{18}O_2N_2S$ $[M]^+$: 254.1089, found: 254.1092.



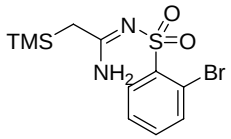
***N*-(Diphenylphosphoryl)-2-phenylacetamidine (entry 3, Table 3):** white solid; m.p. 72–73 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.35-7.30 (m, 6H), 7.23-7.16 (m, 9H) 6.04 (s, 1H), 3.66 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.8, 151.1, 151.0, 134.3, 129.7, 129.4, 129.3, 128.9, 127.6, 125.0, 124.6, 120.5, 120.4, 120.3, 120.2, 44.5, 44.3; IR (NaCl) ν 3449, 3317, 1649, 1577, 1489, 1194, 933 cm^{-1}; HRMS(FAB) m/z calcd. for $C_{20}H_{20}O_3N_2P$ $[M+H]^+$: 367.1212, found: 367.1214.



***N*-(2-Bromobenzenesulfonyl)-2-phenylacetamidine (entry 4, Table 3):** white solid; m.p. 138–139 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (br, 1H), 8.21 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.70 (dd, *J* = 7.8 Hz, 1H), 7.43-7.24 (m, 7H), 5.78 (br, 1H), 3.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 140.8, 134.9, 133.2, 132.8, 130.0, 129.9, 129.4, 128.2, 127.5, 120.8, 43.8; IR (NaCl) ν 3416, 3327, 3242, 1634, 1551, 1272, 1145, 777 cm^{-1}; HRMS (EI) m/z calcd. for $C_{14}H_{13}O_2N_2BrS$ $[M]^+$: 351.9881, found: 351.9878.

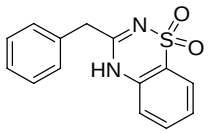


***N*-(2-Bromobenzenesulfonyl)hexanamidine (entry 5, Table 3):** yellow solid; m.p. 60–61 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.08 (s, 1H), 7.68 (dd *J* = 7.8, 1.0 Hz, 1H), 7.42 (td, *J* = 7.6, 1.0 Hz, 1H), 7.34 (td, *J* = 7.8, 1.7 Hz, 1H, 6.23 (s, 1H), 2.26 (t, *J* = 8.0 Hz, 2H), 1.63-1.60 (m, 2H), 1.27-1.22 (m, 4H), 0.81 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 140.9, 134.9, 133.0, 129.9, 127.4, 120.7, 38.0, 31.1, 26.1, 22.2, 13.8; IR (NaCl) ν 3419, 3329, 3243, 1636, 1548, 1271, 1145, 1026, 953, 758 cm^{-1}; HRMS (EI) m/z calcd. for $C_{12}H_{17}O_2N_2BrS$ $[M]^+$: 332.0194, found: 332.0197.

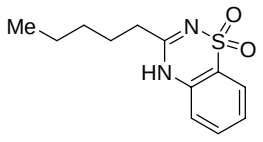


***N*-(2-Bromobenzenesulfonyl)-2-(trimethylsilyl)acetamidine (entry 6, Table 3):** white solid; m.p. 94–95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.02 (br, 1H), 7.67 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.41 (td, *J* = 7.6, 1.1 Hz, 1H), 7.33 (td, *J* = 7.7, 1.8 Hz, 1H), 5.99 (br, 1H), 1.87 (s, 2H), 0.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 141.3, 134.9, 132.9, 129.9, 127.3, 120.5, 30.5, -1.43; IR (NaCl) ν 3422, 3329, 3235, 1633, 1533, 1447, 1252, 1144, 854, 760 cm^{-1}; HRMS (EI) m/z calcd. for $C_{11}H_{17}O_2N_2BrSiS$ $[M]^+$: 347.9963, found: 347.9963.

General procedure for the Cu-catalyzed C-N cross coupling reaction (Table 4). To a mixture of 2-bromobenzenesulfonyl amidine derivatives (0.3 mmol), CuI (0.03 mmol, 0.1 equiv), 1,10-phenanathroline (0.06 mmol, 0.2 equiv), and Cs_2CO_3 (0.6 mmol, 2.0 equiv) was added DMF (4 mL). The reaction mixture was heated at 80 °C for 16 h under N_2. The reaction was diluted with EtOAc and washed with H_2O and saturated NaCl solution. The organic layer was dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by a recrystallization (ethyl acetate and hexane).

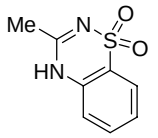


3-Benzyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (entry 1, Table 4): yellowish solid; m.p. 213–214 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.2 (s, 1H), 7.78(d, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.45-7.28 (m, 7H), 3.87(s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.5, 135.1, 135.0, 133.1, 129.0, 128.6, 127.1, 126.4, 123.4, 121.1, 117.5, 41.5; IR (KBr) ν 3436, 3255, 1613, 1578, 1531, 1492, 1274, 1162, 767 cm^{-1}; HRMS(FAB) m/z calcd. for $C_{14}H_{13}O_2N_2S$ $[M+H]^+$: 273.0698, found: 273.0695.



3-Pentyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (entry 2, Table 4): white solid; m.p. 158–159 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.9 (s, 1H), 7.77 (d, *J* = 7.3 Hz, 1H), 7.65 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.70-1.63 (m, 2H), 1.32-1.30 (m, 4H), 0.87 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.3, 135.1, 133.0,

126.1, 123.4, 121.2, 117.3, 35.2, 30.4, 25.7, 21.7, 13.8; IR (NaCl) ν 3274, 3184, 3126, 1611, 1582, 1534, 1288, 1154, 1134, 759 cm^{-1}; HRMS (EI) m/z calcd. for $C_{12}H_{16}O_2N_2S$ $[M]^+$: 252.0932, found: 252.0936.



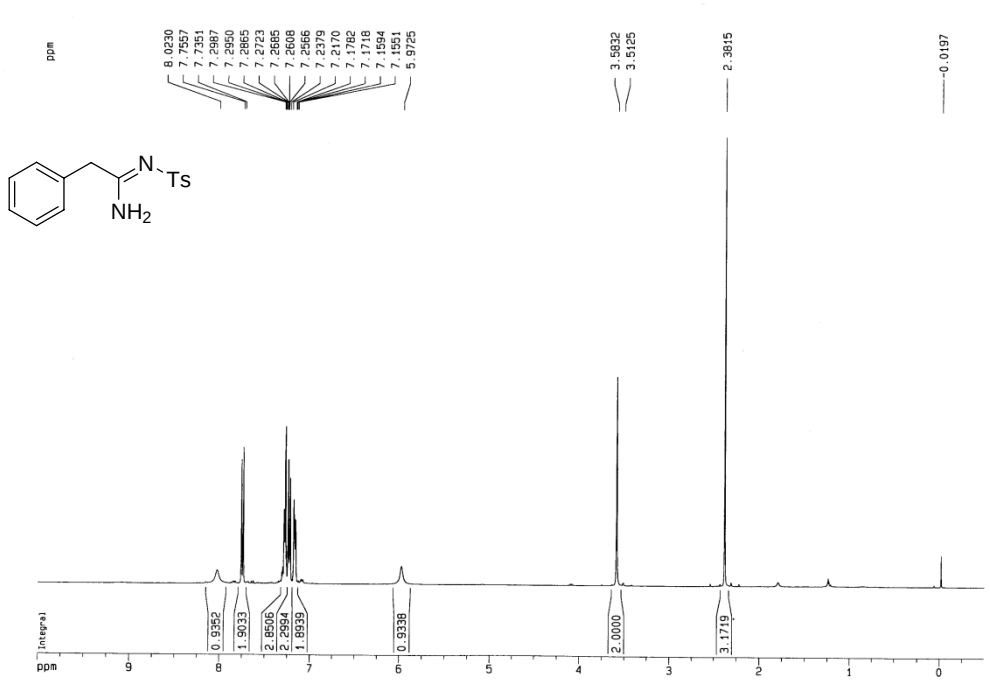
3-Methyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (entry 3, Table 4): yellowish solid; m.p. 254–255 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.0 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.1, 135.1, 133.0, 126.1, 123.4, 121.0, 117.2, 22.6; IR (KBr) ν 3446, 3265, 3184, 3124, 1614, 1585, 1534, 1479, 1277, 1159, 813, 763 cm^{-1}; HRMS (EI) m/z calcd. for $C_8H_8O_2N_2S$ $[M]^+$: 196.0306, found: 196.0304.

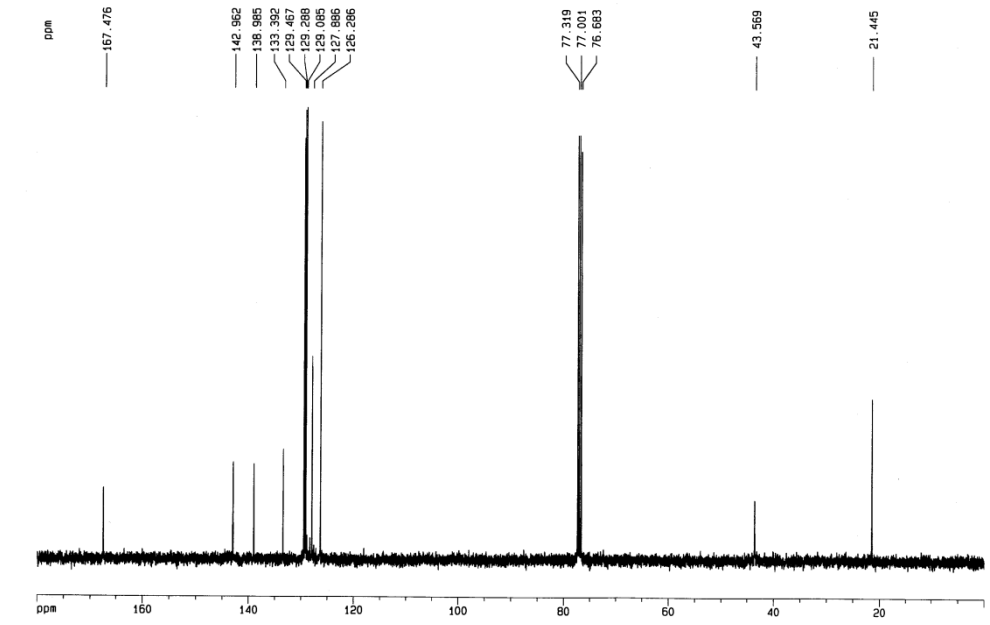
General procedure for the one-pot synthesis of 2*H*-1,2,4-benzothiadiazine 1,1-dioxide (Scheme 3). To a stirred mixture of NH_4Cl (26.7 mg, 0.5 mmol), CuI (9.5 mg, 0.05 mmol), phenylacetylene (0.5 mmol) in CH_2Cl_2 (1 mL) was slowly added triethylamine (0.14 mL, 0.75 mmol) at room temperature. After color changed to yellow, indicated azide (2-bromobenzenesulfonyl azide) (0.5 mmol) was added dropwise. After the reaction was completed, which was monitored with TLC, the reaction mixture was concentrated in vacuo. To the above crude residue, 1,10-phenanathroline (0.06 mmol, 0.2 equiv), Cs_2CO_3 (0.6 mmol, 2.0 equiv), and DMF (4 mL) were added. The reaction mixture was heated at 80 °C for 16 h under N_2. The reaction was diluted with EtOAc and washed with H_2O and saturated NaCl. The organic layer was dried over $MgSO_4$, and then concentrated in vacuo. The crude product was purified by recrystallization (ethyl acetate and hexane) to afford 3-benzyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide in 77 % yield.

Appendix Ⅰ

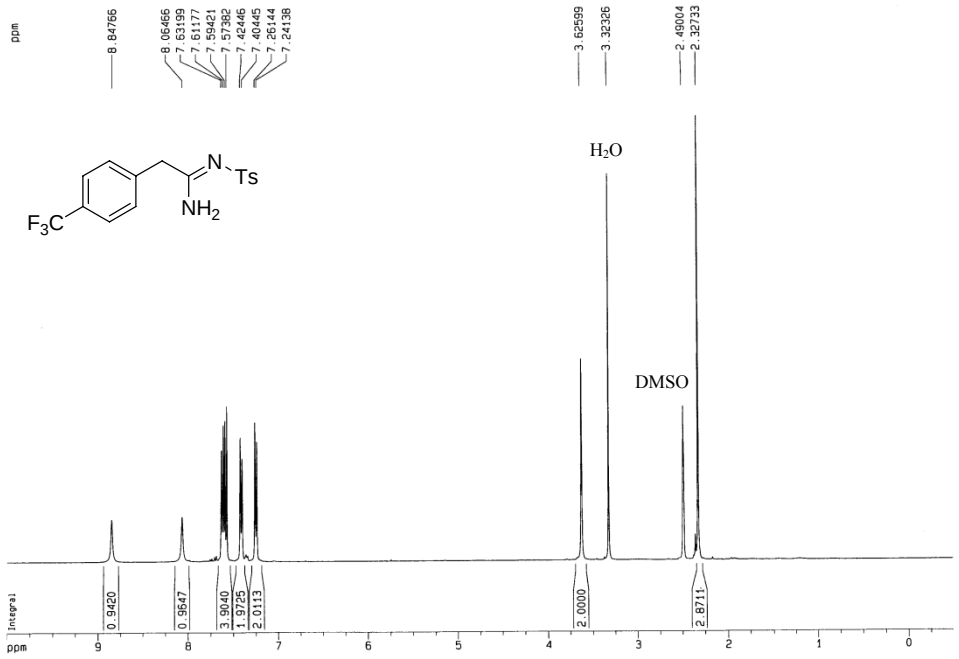
Spectral Copies of ^{1}H and ^{13}C NMR of Products Obtained in this Study

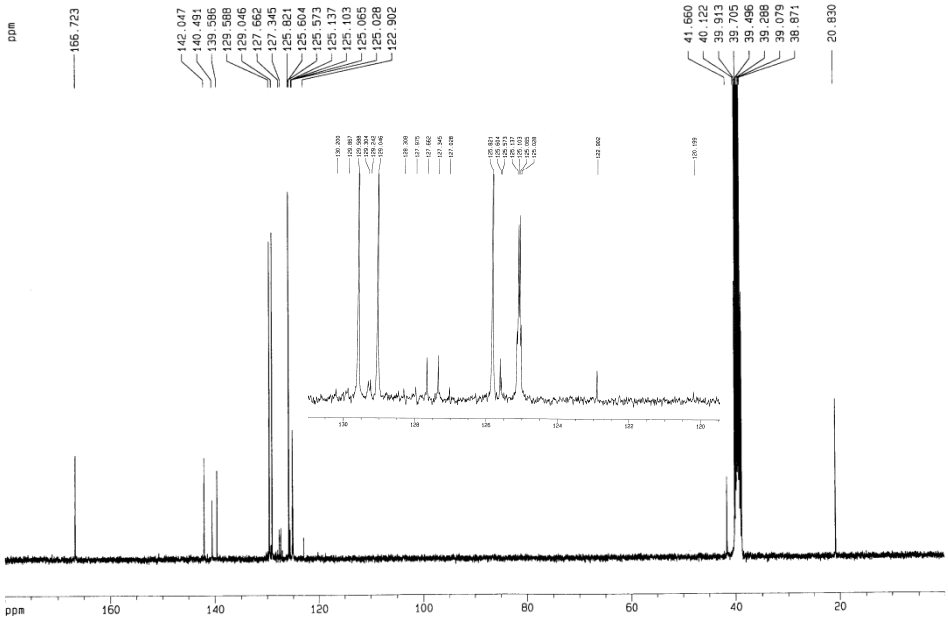
2-Phenyl-*N*- (*p*-toluenesulfonyl)acetamidine (entry 1, Table 2)



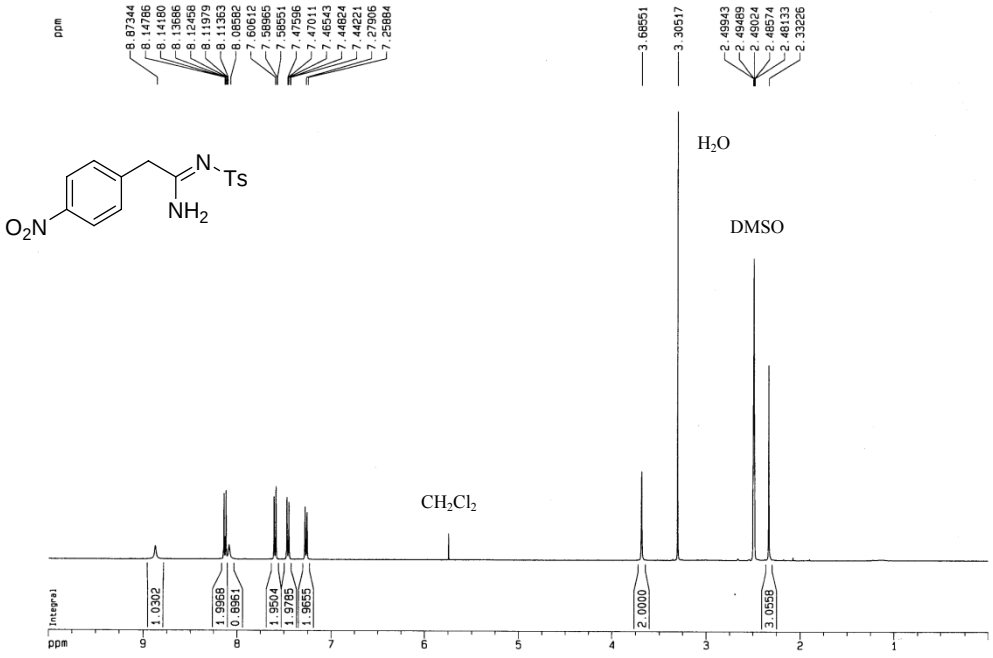


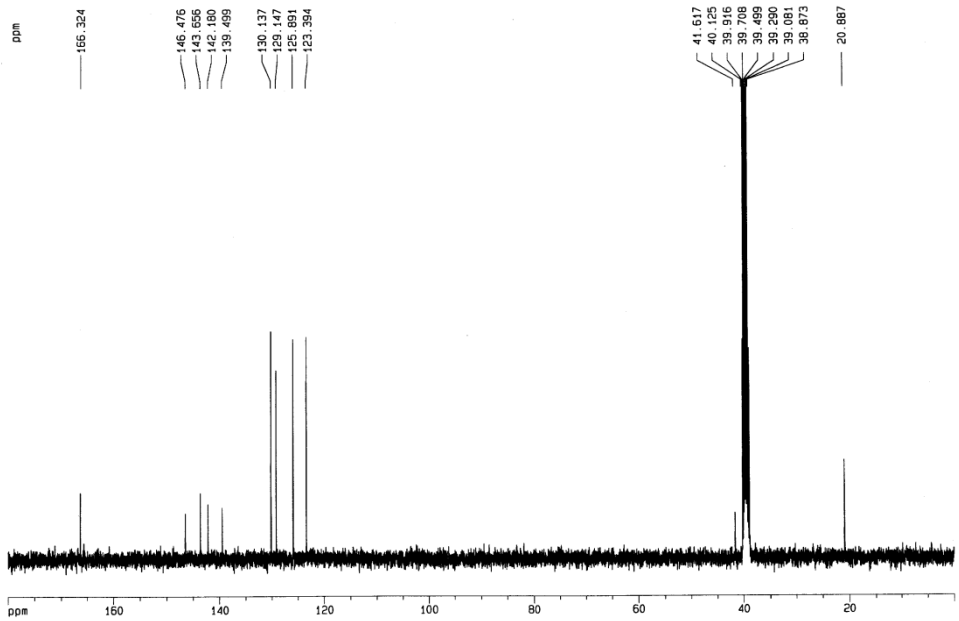
2-[4-(Trifluoromethyl)phenyl]-*N*-(*p*-toluenesulfonyl)acetamidine (entry 2, Table 2)



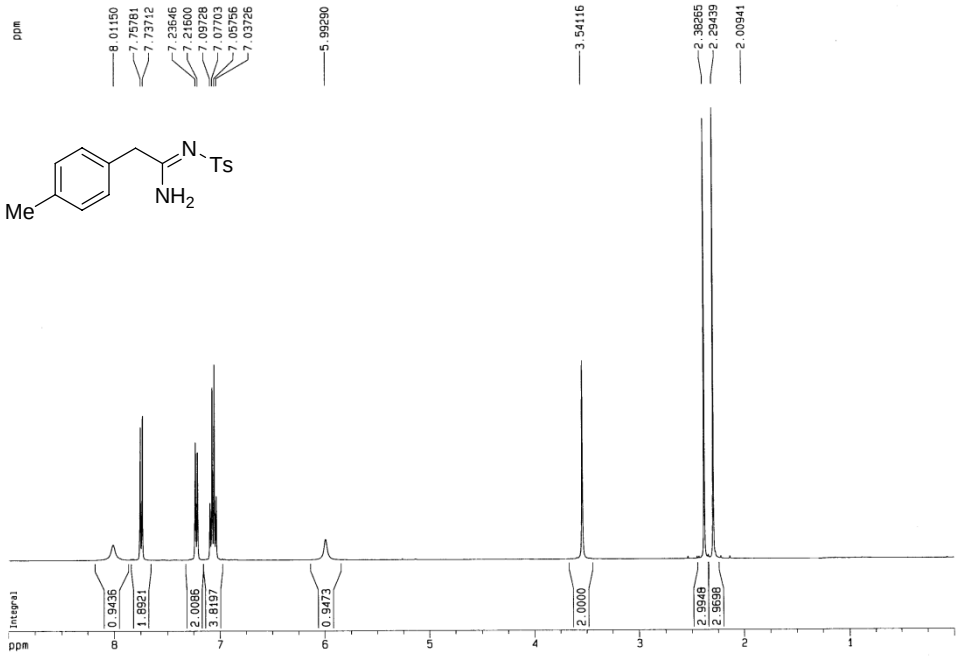


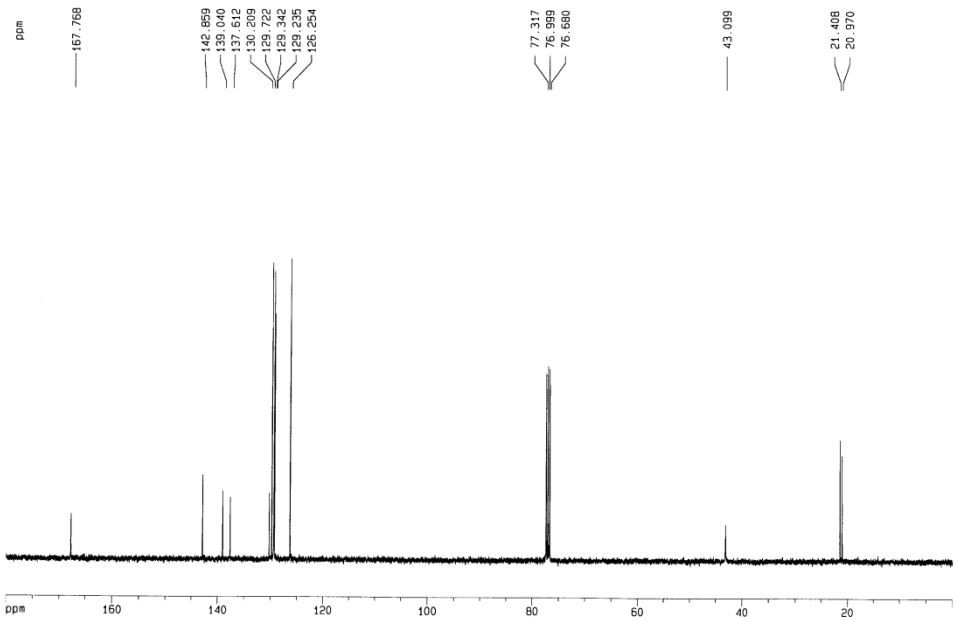
2-(4-Nitrophenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 3, Table 2)



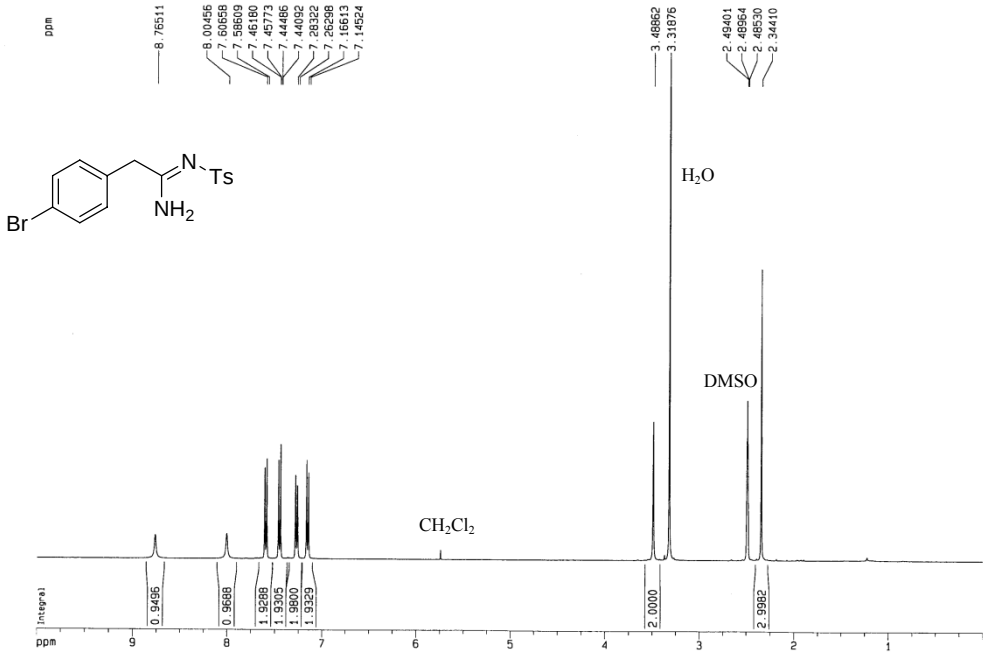


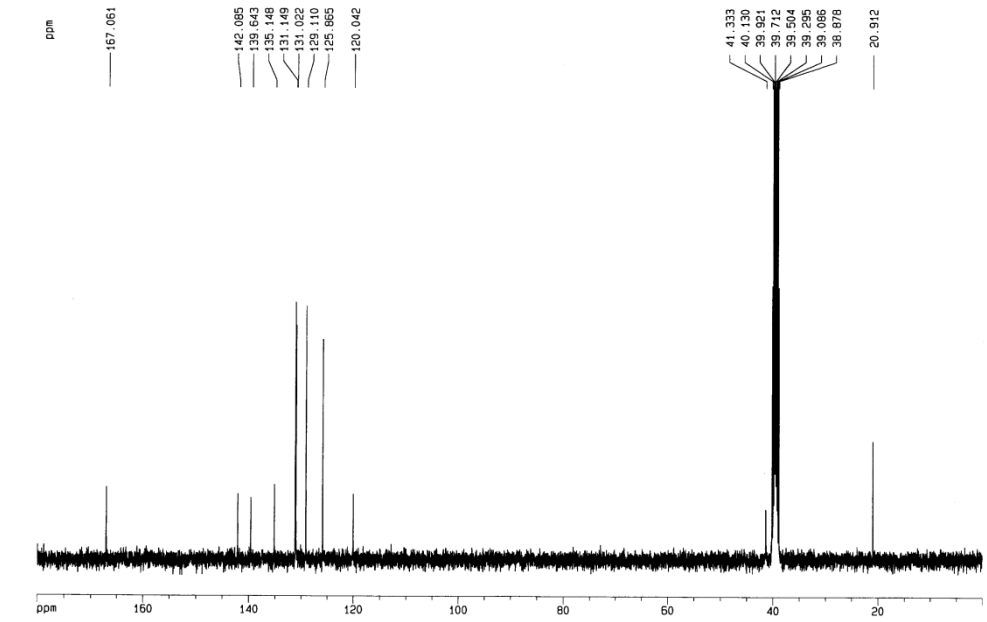
2-(4-Methylphenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 4, Table 2)



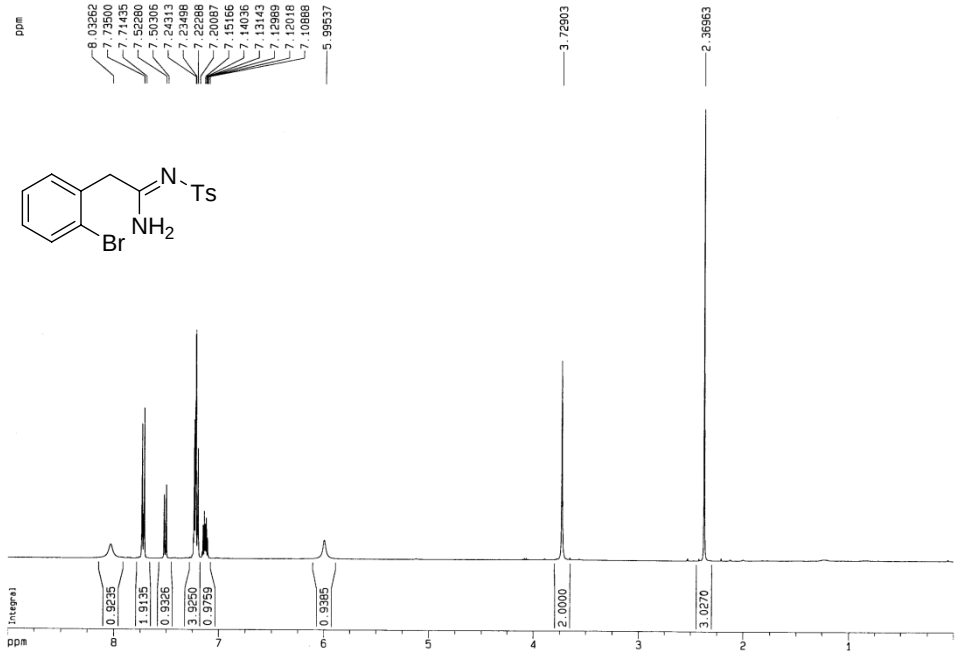


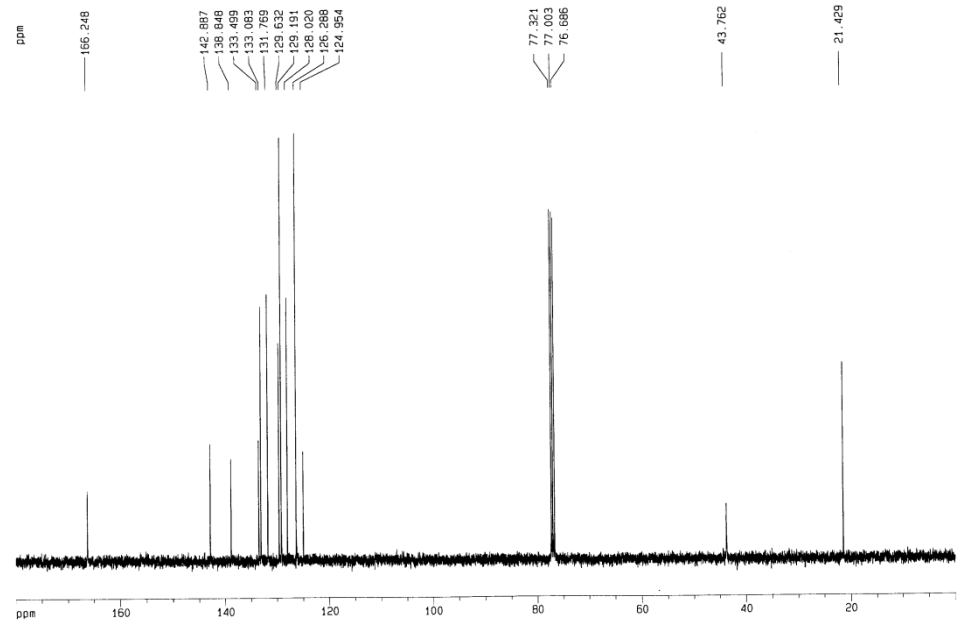
2-(4-Bromophenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 5, Table 2)



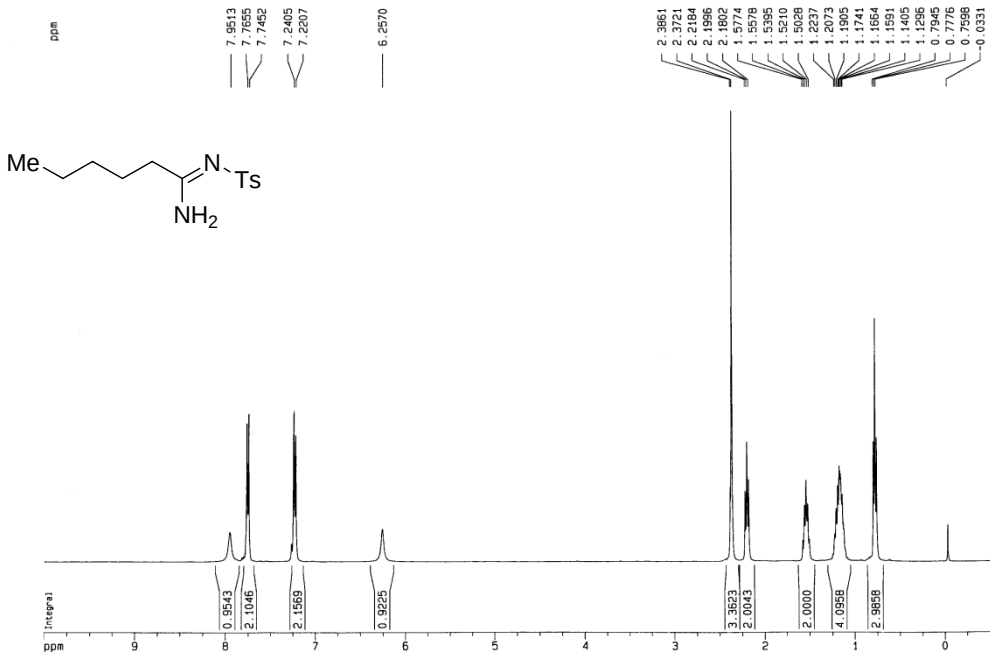


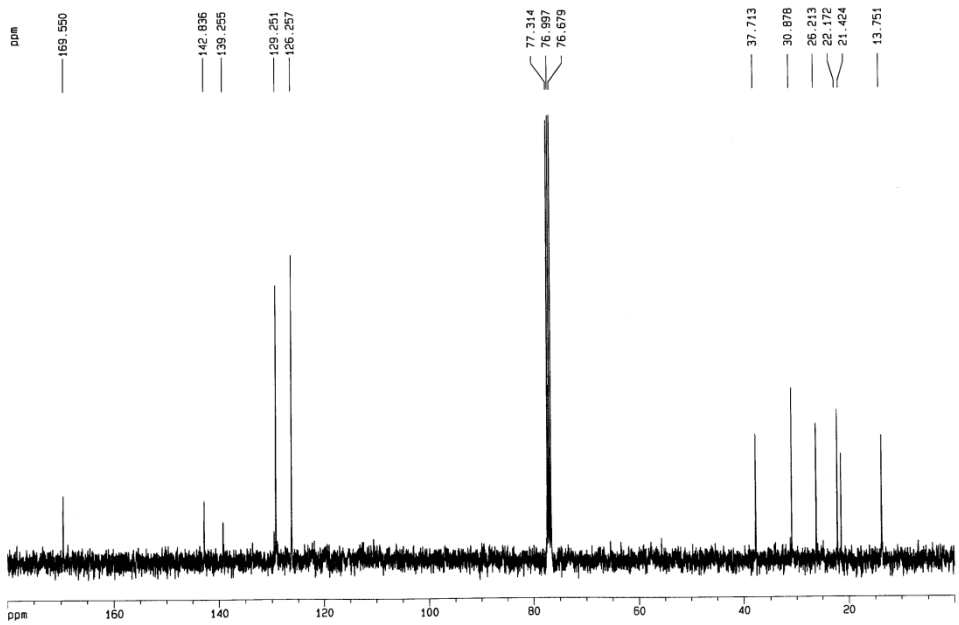
2-(2-Bromophenyl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 6, Table 2)



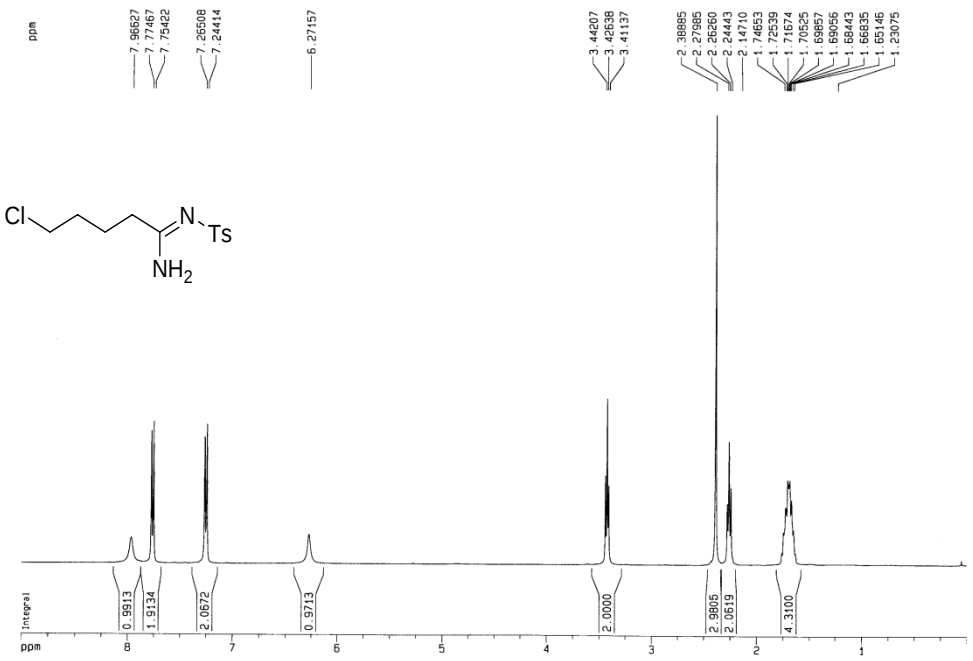


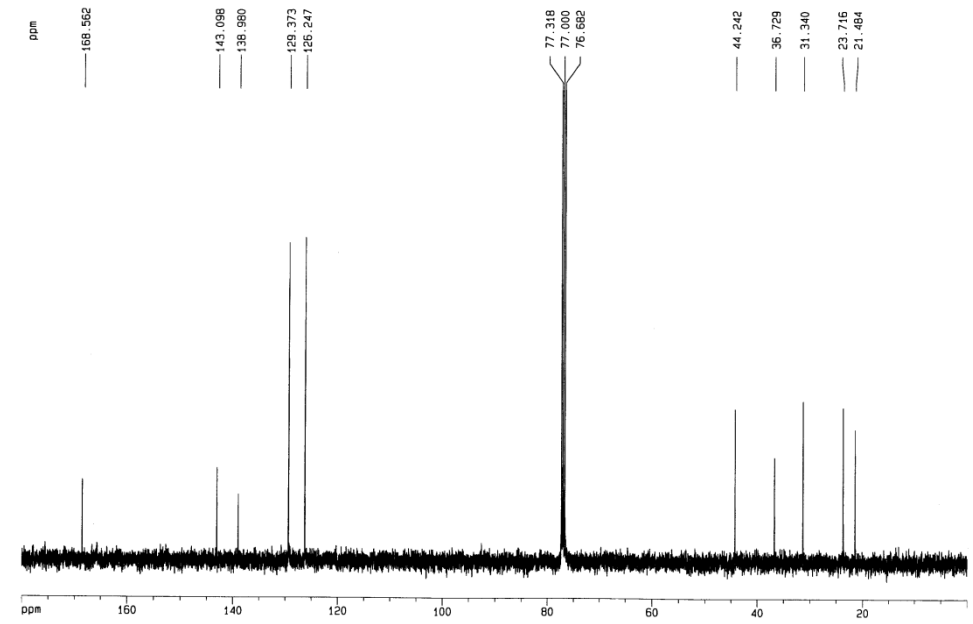
***N*-(*p*-Toluenesulfonyl)hexanamidine (entry 7, Table 2)**



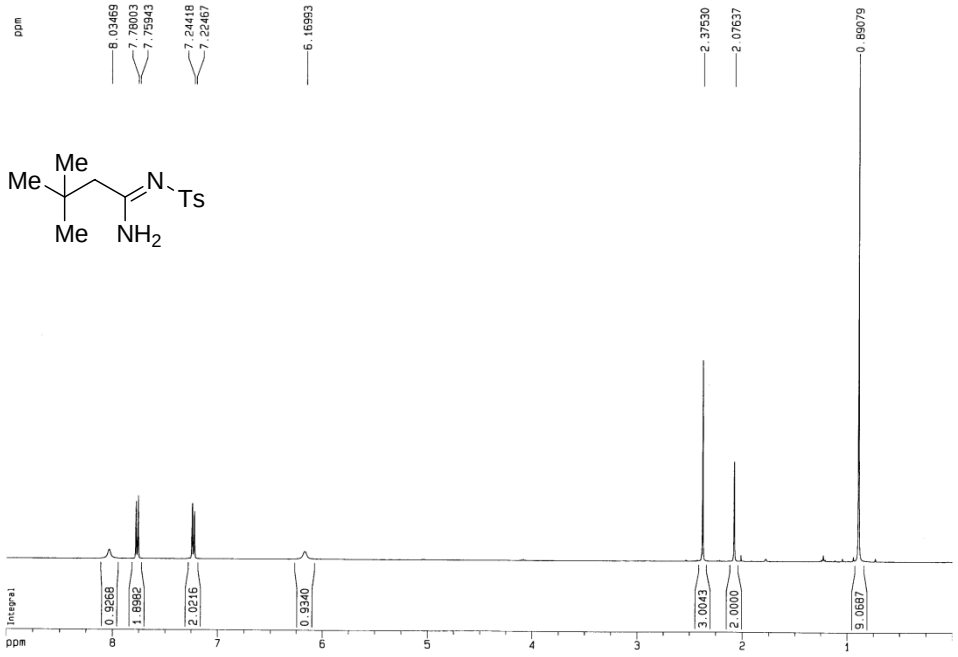


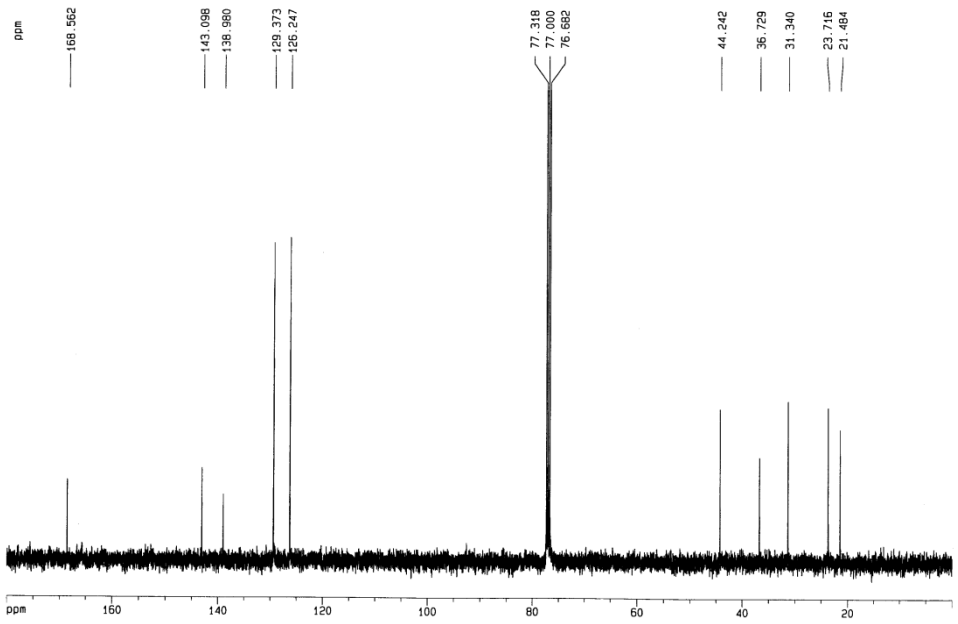
5-Chloro-*N*-(*p*-toluenesulfonyl)pentanamidine (entry 8, Table 2)



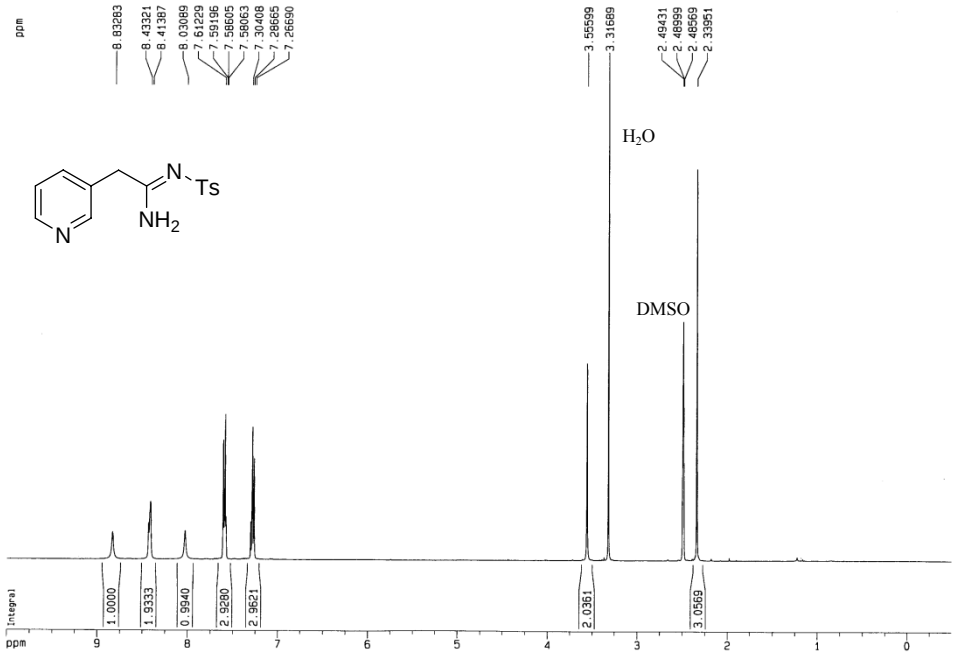


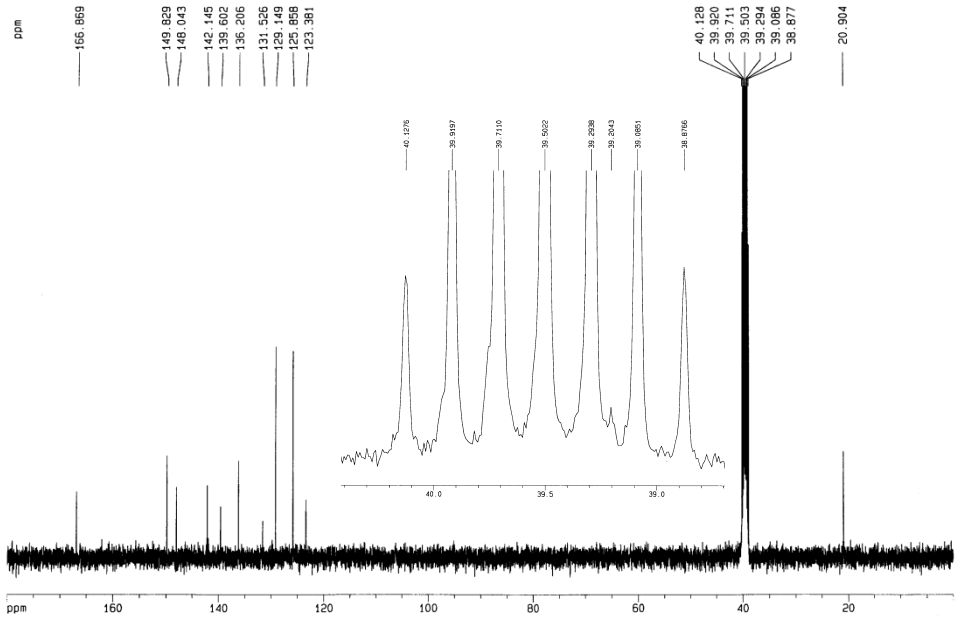
3,3-Dimethyl-*N*-(*p*-toluenesulfonyl)butanamidine (entry 9, Table 2)



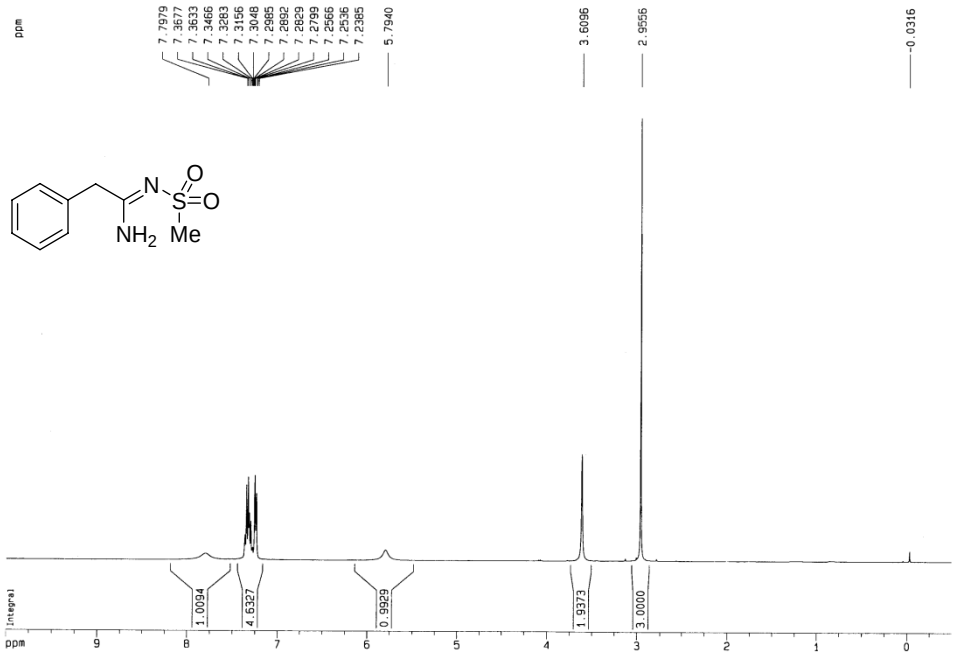


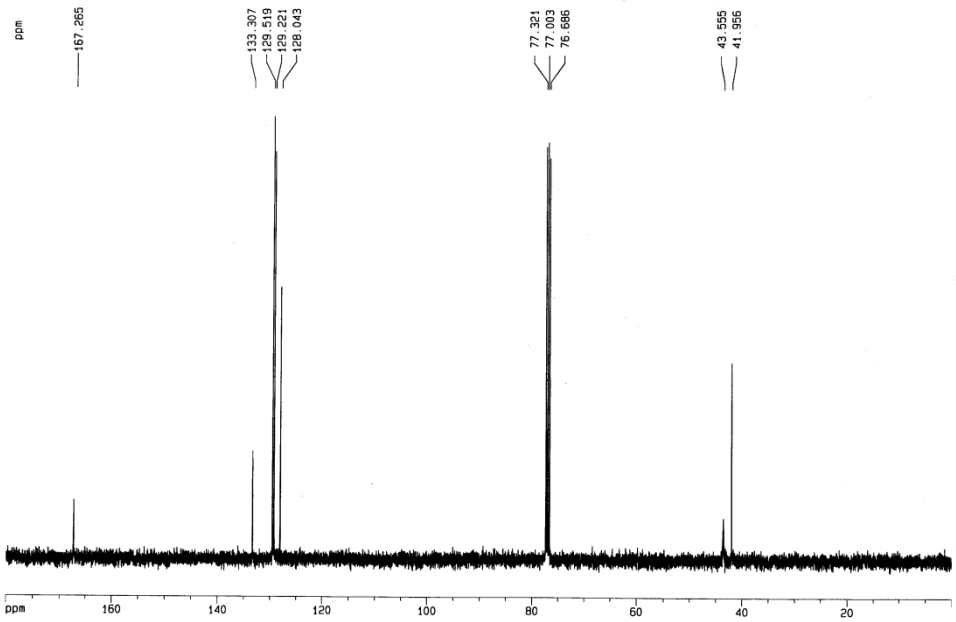
2-(Pyridin-3-yl)-*N*-(*p*-toluenesulfonyl)acetamidine (entry 10, Table 2)



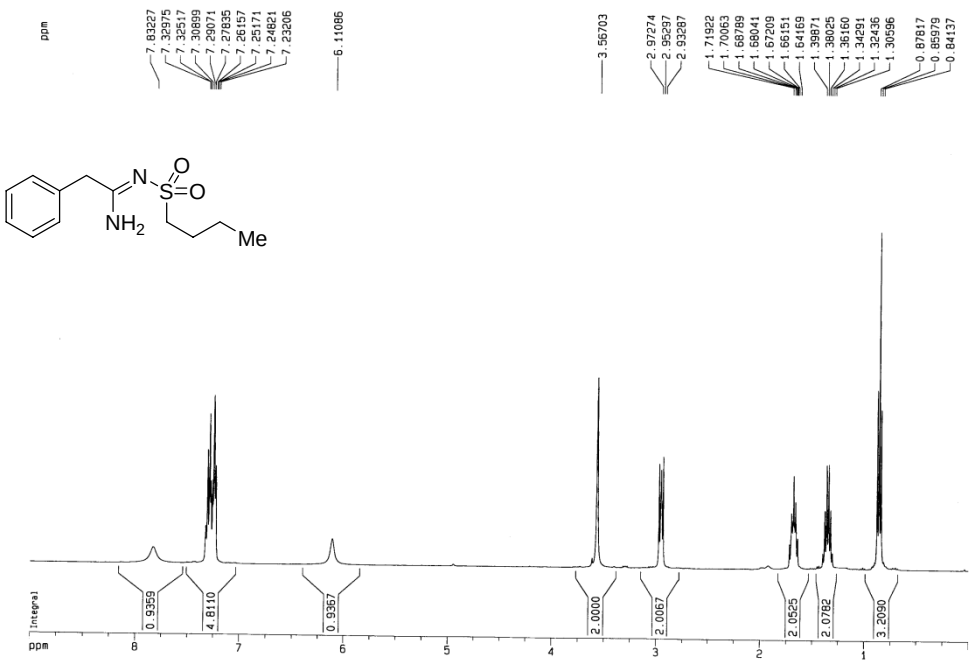


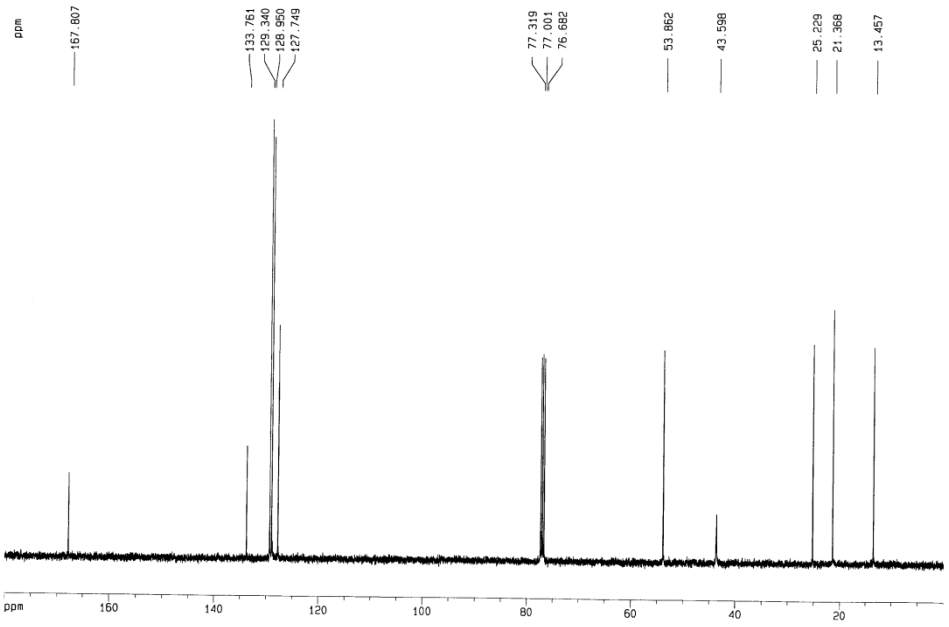
***N*-(Methanesulfonyl)-2-phenylacetamidine (entry 1, Table 3)**



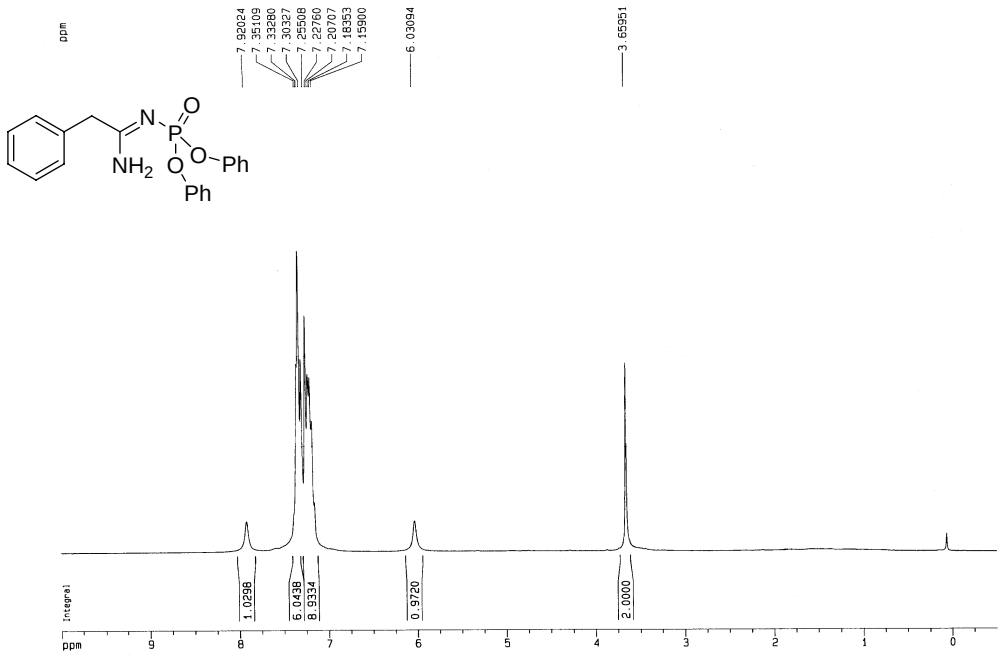


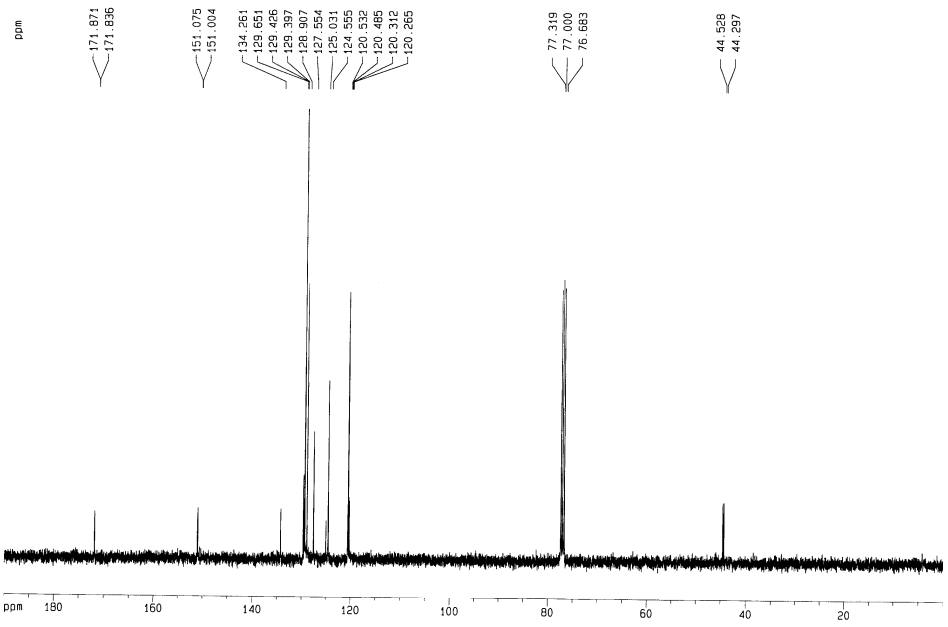
***N*-(Butanesulfonyl)-2-phenylacetamidine (entry 2, Table 3)**



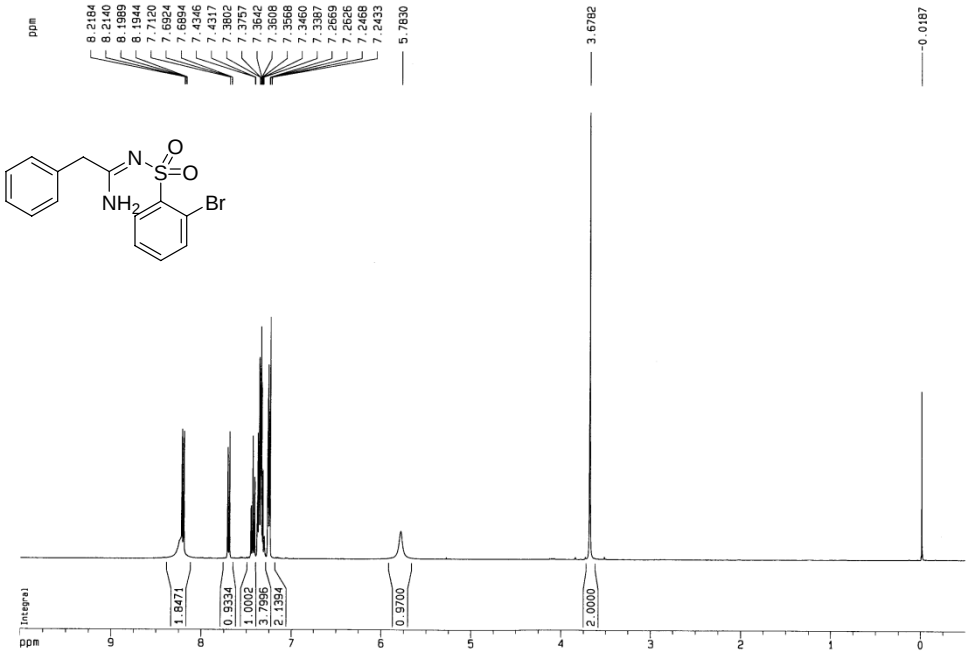


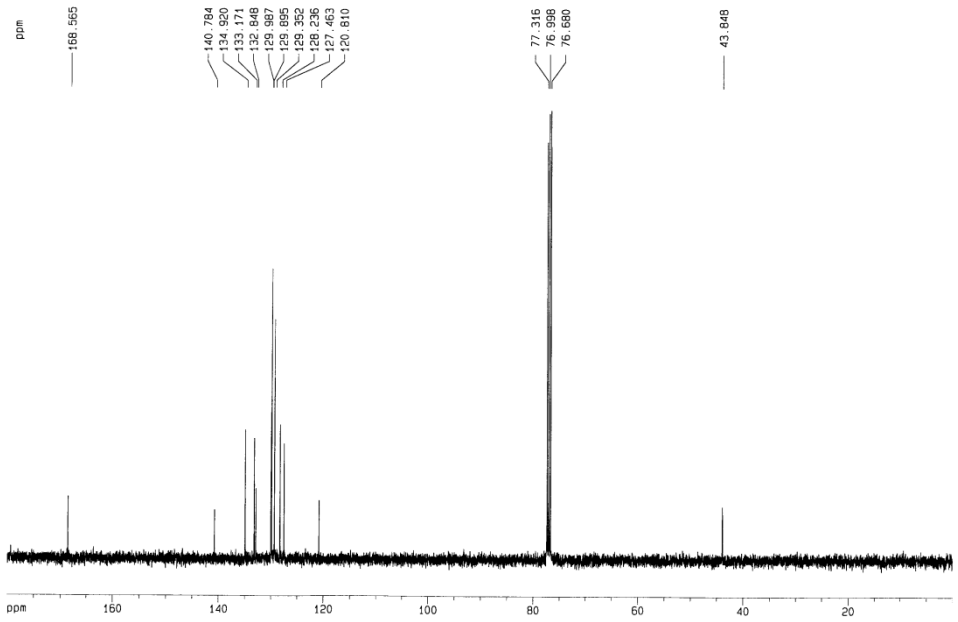
***N*-(Diphenylphosphoryl)-2-phenylacetamidine (entry 3, Table 3)**



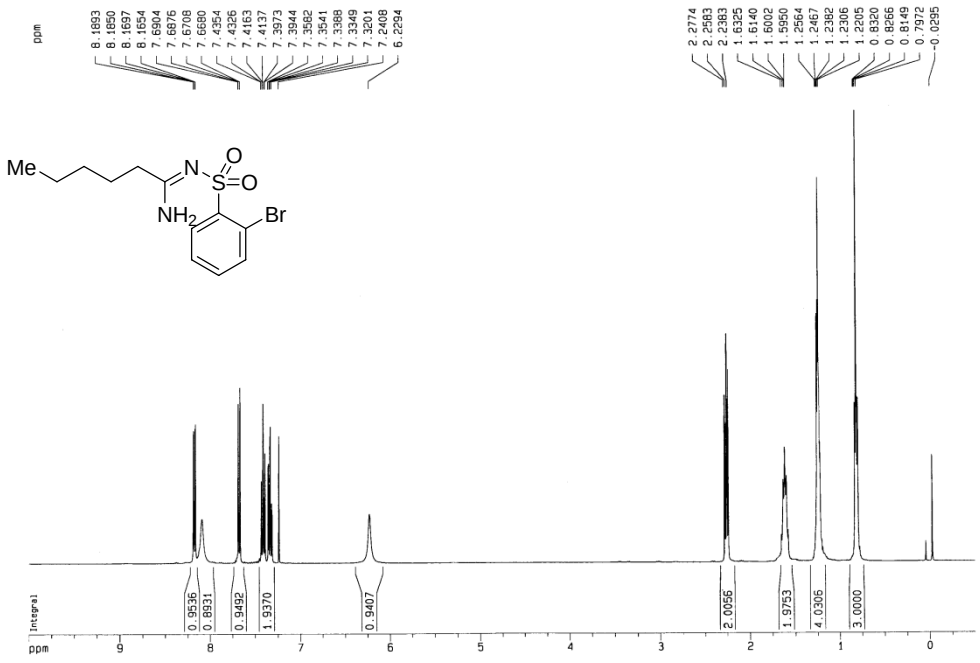


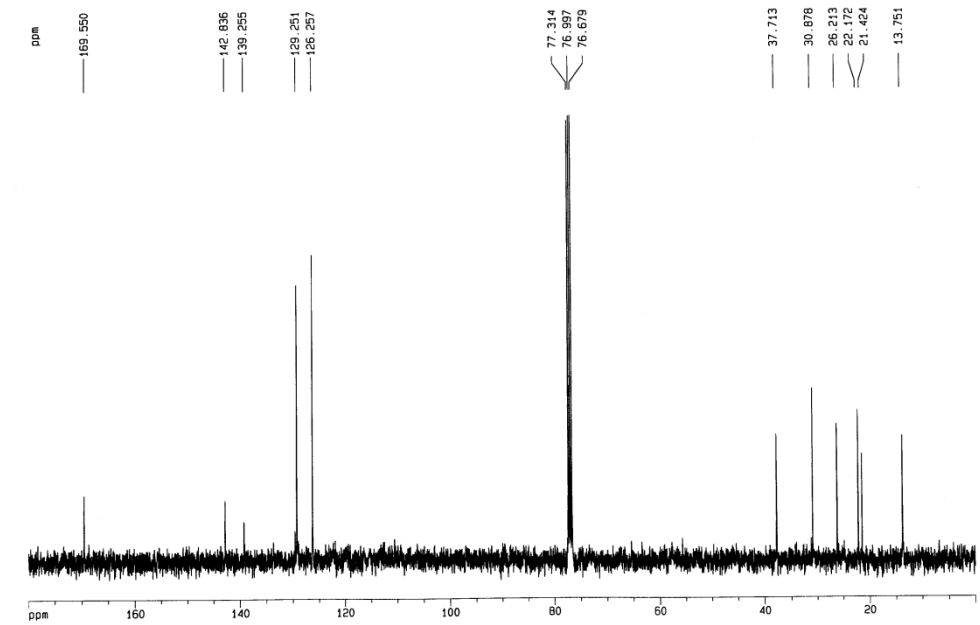
***N*-(2-Bromophenylsulfonyl)-2-phenylacetamidine (entry 4, Table 3)**



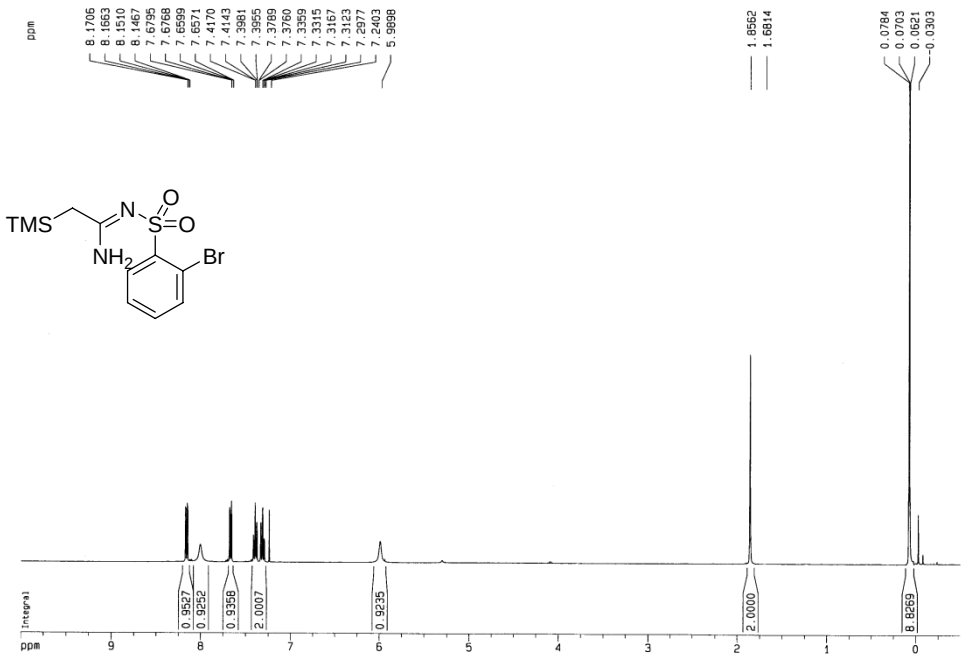


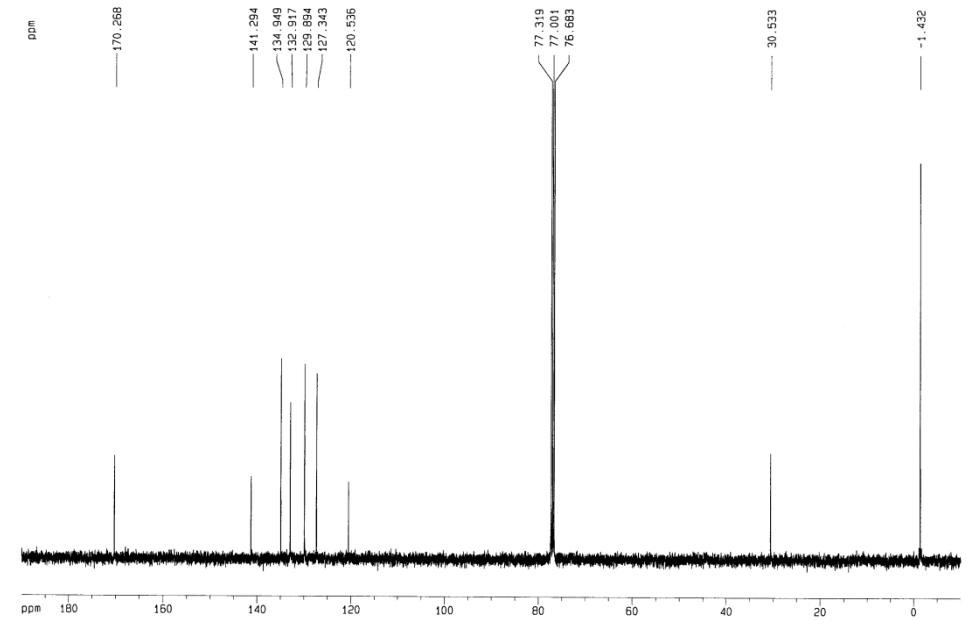
***N*-(2-Bromophenylsulfonyl)hexanamidine (entry 5, Table 3)**



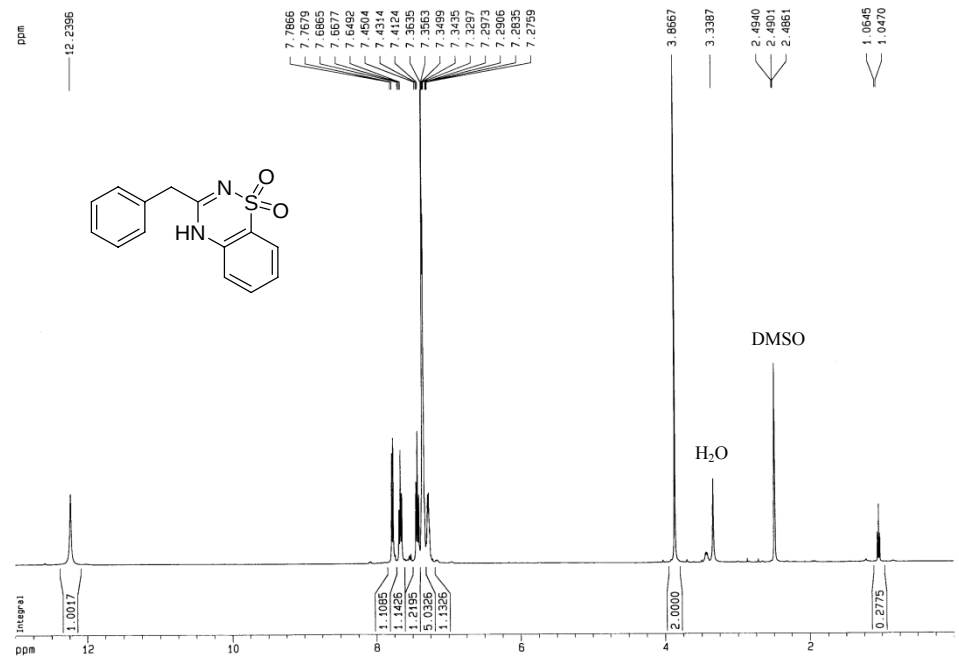


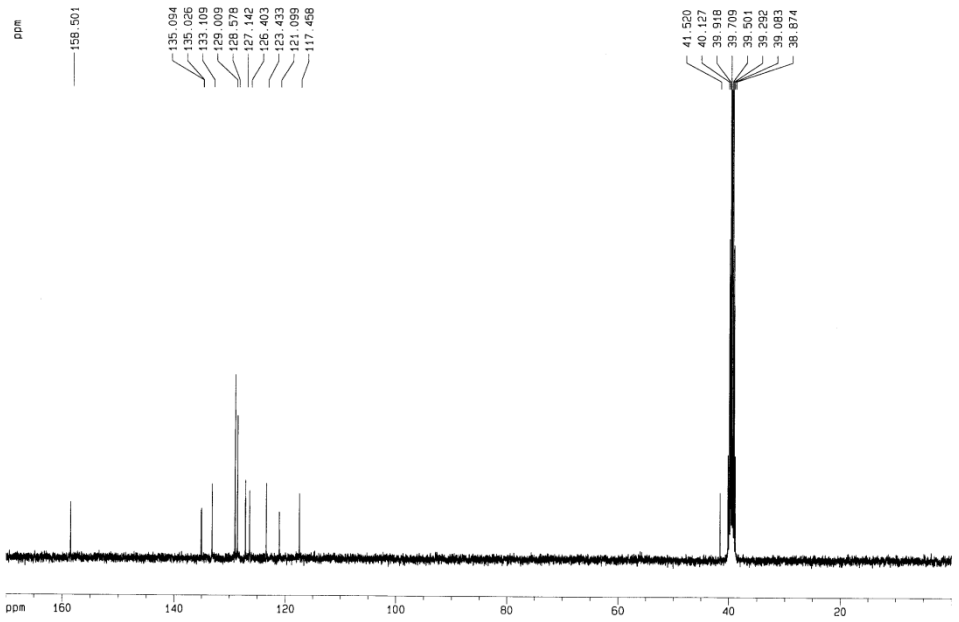
***N*-(2-Bromophenylsulfonyl)-2-(trimethylsilyl)acetamidine (entry 6, Table 3)**



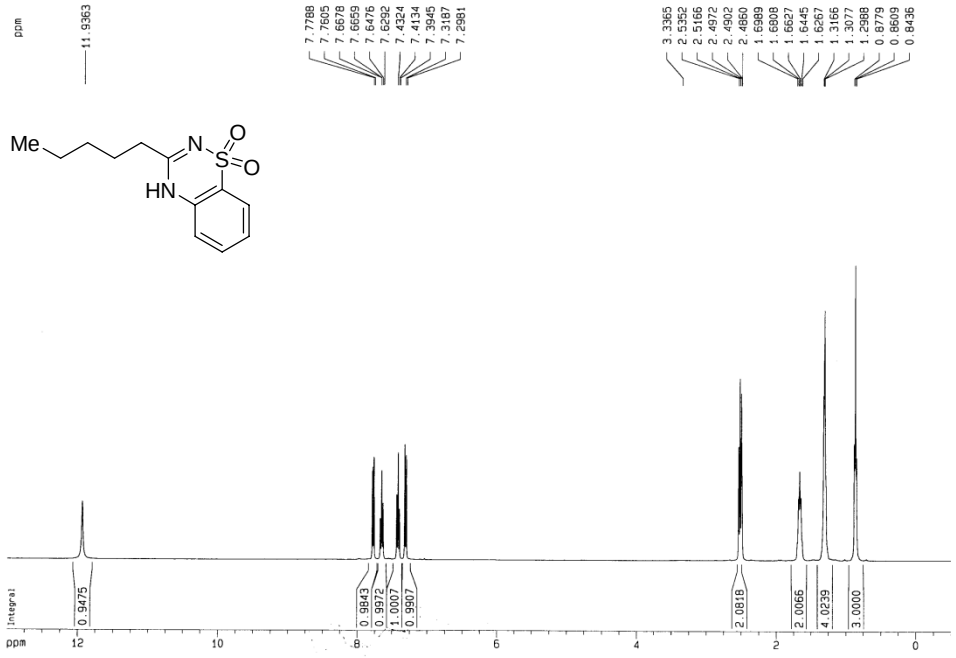


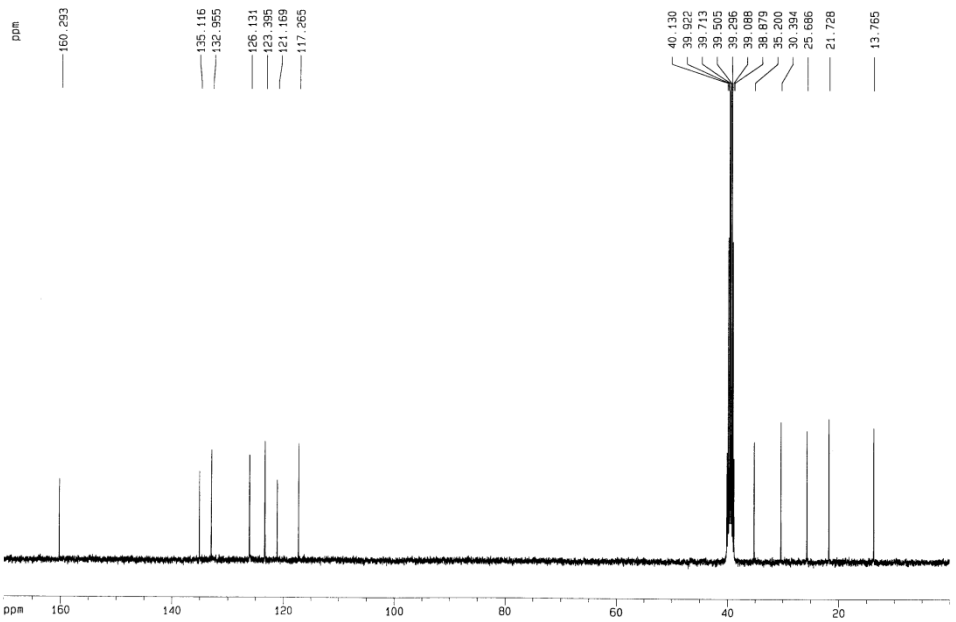
3-Benzyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (entry 1, Table 4)



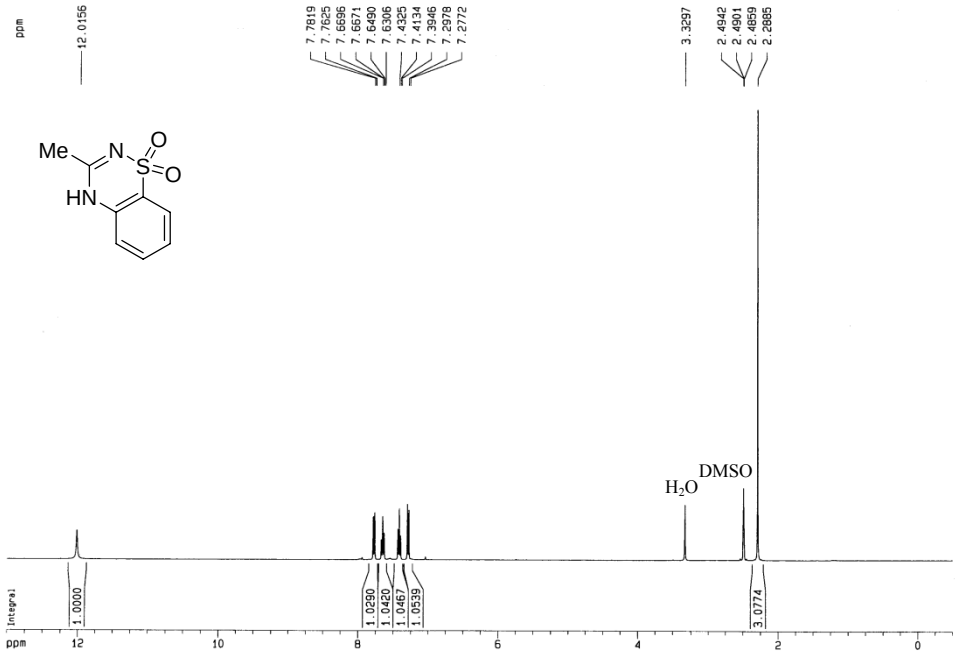


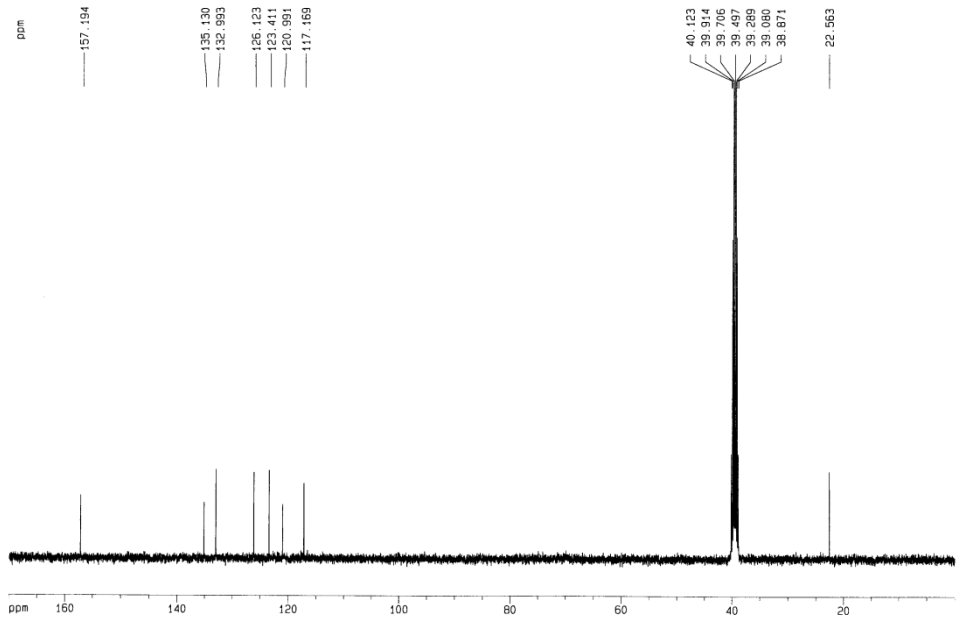
3-Pentyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (entry 2, Table 4):





3-Methyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (entry 3, Table 4)





Appendix Ⅱ

X-Ray Crystallographic Data for

2-(4-Bromophenyl)-*N*-(*p*-toluenesulfonyl)acetamidine

(sbc08-2)

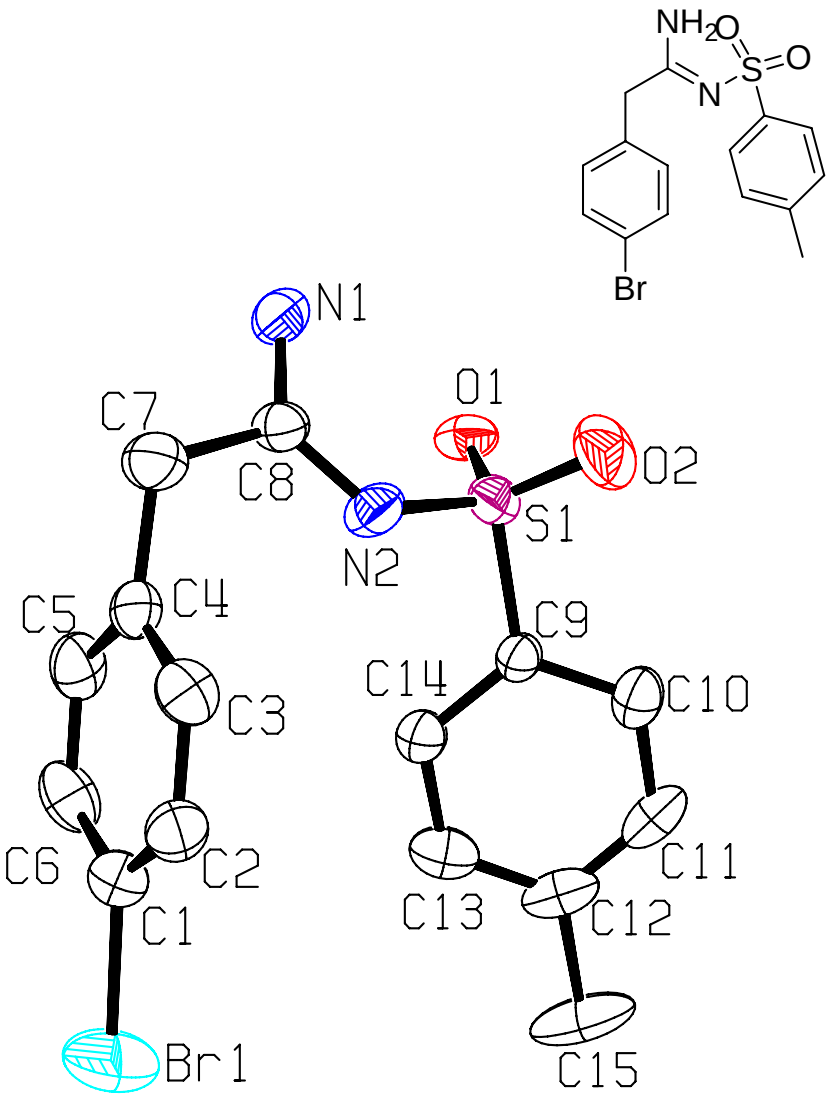


Table S1. Crystal data and structure refinement for **2-(4-Bromophenyl)-N-(p-toluene-sulfonyl)acetamidine (sbc08-2)**.

Identification code	sbc08-2	
Empirical formula	C15 H15 Br N2 O2 S	
Formula weight	367.26	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.515(2) Å	alpha = 90 °
	b = 11.0857(12) Å	beta = 95.619(6) °
	c = 7.8824(9) Å	gamma = 90 °
Volume	1610.1(3) $Å^3$	
Z	4	
Calculated density	1.515 Mg/m^3	
Absorption coefficient	2.687 mm^{-1}	
F(000)	744	
Crystal size	0.2 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.14 to 26.94°	
Limiting indices	-15<=h<=23, -13<=k<=14, -10<=l<=9	
Reflections collected / unique	11662 / 3232 [R(int) = 0.0689]	
Completeness to theta = 25.00	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.76 and 0.68	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3232 / 0 / 191	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0672, wR2 = 0.1646	
R indices (all data)	R1 = 0.1899, wR2 = 0.2145	
Largest diff. peak and hole	1.024 and -0.687 $e.A^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **sbc08-2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	829(1)	11004(1)	10324(2)	150(1)
C(1)	1840(4)	11171(7)	10248(9)	70(2)
C(2)	2283(4)	10302(6)	10998(8)	72(2)
C(3)	3024(4)	10388(6)	10920(8)	67(2)
C(4)	3320(4)	11344(6)	10112(8)	60(2)
C(5)	2864(4)	12215(6)	9390(8)	72(2)
C(6)	2121(5)	12130(6)	9450(9)	79(2)
C(7)	4126(4)	11402(7)	9907(9)	84(2)
C(8)	4298(3)	10763(6)	8296(8)	57(2)
N(1)	4863(3)	11156(5)	7623(7)	73(2)
N(2)	3872(3)	9879(5)	7736(6)	66(2)
S(1)	3886(1)	9254(2)	5925(2)	57(1)
O(1)	4118(2)	10056(4)	4637(5)	65(1)
O(2)	4267(3)	8128(4)	6064(7)	99(2)
C(9)	2960(3)	8935(5)	5435(7)	49(1)
C(10)	2435(3)	9738(6)	5854(8)	62(2)
C(11)	1711(4)	9497(7)	5369(9)	82(2)
C(12)	1498(4)	8463(9)	4487(10)	84(2)
C(13)	2022(5)	7679(7)	4080(9)	85(2)
C(14)	2757(4)	7898(5)	4534(8)	68(2)
C(15)	701(4)	8187(10)	3973(12)	144(4)

Table S3. Bond lengths [Å] and angles [°] for **sbc08-2**.

Br(1)-C(1)	1.886(7)
C(1)-C(2)	1.362(9)
C(1)-C(6)	1.365(9)
C(2)-C(3)	1.382(9)
C(2)-H(2)	0.9300
C(3)-C(4)	1.378(8)
C(3)-H(3)	0.9300
C(4)-C(5)	1.370(9)
C(4)-C(7)	1.517(8)
C(5)-C(6)	1.385(9)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.515(8)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-N(1)	1.295(7)
C(8)-N(2)	1.306(7)
N(1)-H(1A)	0.8600
N(1)-H(1B)	0.8600
N(2)-S(1)	1.590(5)
S(1)-O(2)	1.432(4)
S(1)-O(1)	1.446(4)
S(1)-C(9)	1.756(6)
C(9)-C(10)	1.381(8)
C(9)-C(14)	1.384(8)
C(10)-C(11)	1.385(9)
C(10)-H(10)	0.9300
C(11)-C(12)	1.378(10)
C(11)-H(11)	0.9300
C(12)-C(13)	1.363(10)
C(12)-C(15)	1.523(10)
C(13)-C(14)	1.394(9)
C(13)-H(13)	0.9300
C(14)-H(14)	0.9300

C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600

C(2)-C(1)-C(6)	120.7(6)
C(2)-C(1)-Br(1)	118.3(6)
C(6)-C(1)-Br(1)	121.0(6)
C(1)-C(2)-C(3)	119.3(6)
C(1)-C(2)-H(2)	120.3
C(3)-C(2)-H(2)	120.3
C(4)-C(3)-C(2)	121.1(6)
C(4)-C(3)-H(3)	119.5
C(2)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	118.5(6)
C(3)-C(4)-C(7)	121.6(7)
C(5)-C(4)-C(7)	119.9(7)
C(4)-C(5)-C(6)	120.8(6)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(1)-C(6)-C(5)	119.6(6)
C(1)-C(6)-H(6)	120.2
C(5)-C(6)-H(6)	120.2
C(8)-C(7)-C(4)	111.0(5)
C(8)-C(7)-H(7A)	109.4
C(4)-C(7)-H(7A)	109.4
C(8)-C(7)-H(7B)	109.4
C(4)-C(7)-H(7B)	109.4
H(7A)-C(7)-H(7B)	108.0
N(1)-C(8)-N(2)	126.8(6)
N(1)-C(8)-C(7)	115.5(6)
N(2)-C(8)-C(7)	117.7(6)
C(8)-N(1)-H(1A)	120.0
C(8)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0
C(8)-N(2)-S(1)	124.6(4)
O(2)-S(1)-O(1)	114.3(3)

O(2)-S(1)-N(2)	111.3(3)
O(1)-S(1)-N(2)	113.2(3)
O(2)-S(1)-C(9)	107.8(3)
O(1)-S(1)-C(9)	108.6(2)
N(2)-S(1)-C(9)	100.6(3)
C(10)-C(9)-C(14)	119.7(6)
C(10)-C(9)-S(1)	120.8(4)
C(14)-C(9)-S(1)	119.4(5)
C(9)-C(10)-C(11)	119.7(6)
C(9)-C(10)-H(10)	120.2
C(11)-C(10)-H(10)	120.2
C(10)-C(11)-C(12)	121.4(7)
C(10)-C(11)-H(11)	119.3
C(12)-C(11)-H(11)	119.3
C(13)-C(12)-C(11)	118.3(7)
C(13)-C(12)-C(15)	120.2(9)
C(11)-C(12)-C(15)	121.5(9)
C(12)-C(13)-C(14)	121.9(7)
C(12)-C(13)-H(13)	119.1
C(14)-C(13)-H(13)	119.1
C(13)-C(14)-C(9)	119.1(7)
C(13)-C(14)-H(14)	120.5
C(9)-C(14)-H(14)	120.5
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **sbc08-2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Br(1)	61(1)	194(1)	198(1)	-23(1)	23(1)	4(1)
C(1)	58(4)	71(5)	80(5)	-5(4)	7(4)	6(4)
C(2)	79(5)	61(4)	78(5)	3(4)	27(4)	-15(4)
C(3)	72(5)	66(5)	63(4)	7(4)	5(4)	11(4)
C(4)	63(4)	66(4)	51(4)	-16(4)	6(3)	-5(4)
C(5)	89(6)	51(4)	78(5)	5(4)	26(4)	-2(4)
C(6)	92(6)	66(5)	78(5)	8(4)	10(4)	37(4)
C(7)	64(5)	111(6)	77(5)	-27(5)	14(4)	-13(4)
C(8)	49(4)	67(4)	54(4)	-5(4)	2(3)	-2(4)
N(1)	65(4)	79(4)	76(4)	-19(3)	16(3)	-22(3)
N(2)	65(3)	85(4)	50(3)	-18(3)	14(3)	-24(3)
S(1)	48(1)	61(1)	63(1)	-9(1)	4(1)	7(1)
O(1)	47(2)	93(3)	57(3)	1(2)	13(2)	-13(2)
O(2)	90(4)	82(3)	119(4)	-9(3)	-11(3)	39(3)
C(9)	51(4)	39(3)	56(4)	-2(3)	3(3)	-2(3)
C(10)	59(4)	51(4)	77(5)	-3(3)	4(4)	-4(3)
C(11)	57(5)	99(6)	90(5)	8(5)	10(4)	5(4)
C(12)	63(5)	110(7)	76(5)	18(5)	-3(4)	-33(5)
C(13)	94(6)	74(5)	84(5)	2(4)	-9(5)	-44(5)
C(14)	84(5)	51(4)	70(5)	-2(3)	11(4)	-5(4)
C(15)	74(6)	219(11)	133(8)	33(7)	-20(5)	-80(7)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **sbc08-2**.

	x	y	z	U(eq)
H(2)	2089	9657	11558	86
H(3)	3327	9791	11421	81
H(5)	3056	12872	8854	86
H(6)	1815	12723	8949	95
H(7A)	4276	12239	9861	100
H(7B)	4396	11029	10885	100
H(1A)	4991	10828	6711	87
H(1B)	5110	11747	8088	87
H(10)	2568	10437	6458	75
H(11)	1360	10044	5644	98
H(13)	1885	6979	3484	102
H(14)	3106	7355	4236	82
H(15A)	567	8485	2843	216
H(15B)	409	8571	4757	216
H(15C)	625	7330	3997	216

Table S6. Torsion angles [°] for **sbc08-2**.

C(6)-C(1)-C(2)-C(3)	-1.1(10)
Br(1)-C(1)-C(2)-C(3)	178.3(5)
C(1)-C(2)-C(3)-C(4)	0.7(10)
C(2)-C(3)-C(4)-C(5)	0.3(9)
C(2)-C(3)-C(4)-C(7)	-175.5(6)
C(3)-C(4)-C(5)-C(6)	-0.9(9)
C(7)-C(4)-C(5)-C(6)	175.0(6)
C(2)-C(1)-C(6)-C(5)	0.6(10)
Br(1)-C(1)-C(6)-C(5)	-178.8(5)
C(4)-C(5)-C(6)-C(1)	0.5(10)
C(3)-C(4)-C(7)-C(8)	87.5(7)
C(5)-C(4)-C(7)-C(8)	-88.2(8)
C(4)-C(7)-C(8)-N(1)	152.3(6)
C(4)-C(7)-C(8)-N(2)	-28.0(9)
N(1)-C(8)-N(2)-S(1)	-11.1(10)
C(7)-C(8)-N(2)-S(1)	169.3(5)
C(8)-N(2)-S(1)-O(2)	100.9(6)
C(8)-N(2)-S(1)-O(1)	-29.5(6)
C(8)-N(2)-S(1)-C(9)	-145.2(5)
O(2)-S(1)-C(9)-C(10)	154.7(5)
O(1)-S(1)-C(9)-C(10)	-80.9(5)
N(2)-S(1)-C(9)-C(10)	38.2(5)
O(2)-S(1)-C(9)-C(14)	-28.9(6)
O(1)-S(1)-C(9)-C(14)	95.5(5)
N(2)-S(1)-C(9)-C(14)	-145.4(5)
C(14)-C(9)-C(10)-C(11)	0.0(9)
S(1)-C(9)-C(10)-C(11)	176.4(5)
C(9)-C(10)-C(11)-C(12)	0.6(10)
C(10)-C(11)-C(12)-C(13)	-0.7(11)
C(10)-C(11)-C(12)-C(15)	179.1(7)
C(11)-C(12)-C(13)-C(14)	0.1(11)
C(15)-C(12)-C(13)-C(14)	-179.7(6)
C(12)-C(13)-C(14)-C(9)	0.5(10)
C(10)-C(9)-C(14)-C(13)	-0.6(9)

S(1)-C(9)-C(14)-C(13)	-177.0(5)

Symmetry transformations used to generate equivalent atoms: