Direct Methyl C(sp^3)−H Azolation of Thioanisoles via Oxidative Radical Coupling

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Supporting Information

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I. General remarks.

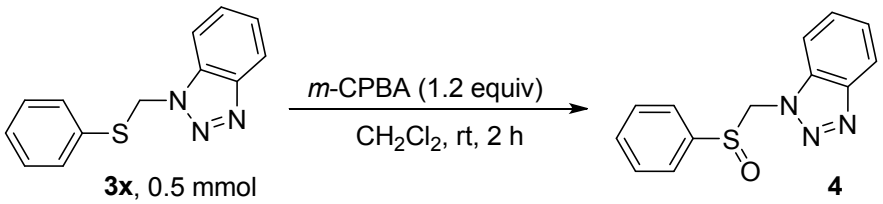
All reagents were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer in deuterated solvents containing TMS as an internal reference standard. High-resolution mass spectrometry (HRMS) analyses were conducted on a Waters LCT Premier/XE. Melting points were measured on a melting point apparatus equipped with a thermometer and were uncorrected. All the reactions were monitored by thin-layer chromatography (TLC) using GF254 silica gel-coated TLC plates. Purification by flash column chromatography was performed over SiO_2 (silica gel 200−300 mesh).

II. General procedure:

Synthesis procedure for compounds 3:

To a reaction tube equipped with a stir bar was sequentially added thioanisoles **1** (1.8 mmol), azoles **2** (0.3 mmol) and DBDMH (0.3 mmol, 1.0 equiv.). Then the reaction mixture was stirred in CH_3CN (1.0 mL) at 90 °C. Upon completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **3**.

Synthesis procedure for compounds 4:



3x, 0.5 mmol **4**

To a reaction tube equipped with a stir bar was sequentially added **3w** (0.5 mmol), and 3-chloroperbenzoic acid (*m*-CPBA, 1.2 equiv). Then the reaction mixture was stirred in CH_2Cl_2 (2.0 mL) at room temperature for 2 hours. Upon completion of the reaction, the mixture was cooled to room temperature and quenched with water before being extracted with dichloromethane (5 × 3 mL). The combined organic layers were

dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a residue, which was purified by flash column chromatography to give the desired product **4** (81%, 104.1 mg).

III. Analytical data of products obtained in this study

2-chloro-1-((phenylthio)methyl)-1*H*-benzo[*d*]imidazole (3a). White solid (76%, 62.2 mg), melting point: 96-97 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.42 (s, 2H), 4.47 (d, J = 7.2, 1H), 7.22-7.28 (m, 6H), 7.34 (d, J = 2.4, 1H), 7.68 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 49.7, 110.3, 119.5, 123.0, 123.3, 129.3, 129.5, 131.0, 134.1, 135.1, 140.4, 141.6. HRMS (ESI-TOF) Calcd for $C_{14}H_{12}ClSN_2$, $[M+H]^+$ 275.0411; Found 275.0417.

2-chloro-1-(((2-methoxyphenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3b). Colourless liquid (78%, 71.1 mg). ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.69 (s, 3H), 5.44 (s, 2H), 6.79 (t, J = 8.4, 2H), 7.18-7.32 (m, 5H), 7.63 (d, J = 7.6, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 47.6, 55.5, 110.1, 110.9, 118.1, 119.3, 121.0, 122.8, 123.1, 131.6, 134.4, 137.3, 140.4, 141.5, 160.1. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}ClSON_2$, $[M+H]^+$ 305.0515; Found 305.0519.

2-chloro-1-(((2-chlorophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3c). White solid (64%, 59.3 mg), melting point: 92-93 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.46 (s, 2H), 7.02 (t, J = 7.6, 1H), 7.10-7.29 (m, 5H), 7.43 (d, J = 8.0, 1H), 7.63 (d, J = 7.6, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 47.7, 109.9, 119.5, 123.1, 123.3, 127.4, 129.4, 130.2, 131.2, 134.2, 137.6, 139.5, 140.3, 141.5. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}Cl_2SN_2$, $[M+H]^+$ 309.0021; Found 309.0028.

2-chloro-1-(((3-chlorophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3d). White solid (60%, 55.6 mg), melting point: 99-100 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.43 (s, 2H), 7.03 (d, J = 7.6, 1H), 7.12-7.26 (m, 2H), 7.27-7.30 (m, 3H), 7.32 (d, J = 8.0, 1H), 7.68 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 49.4, 110.1, 119.6, 123.2, 123.4, 129.6, 130.3, 132.8, 132.9, 134.5, 134.8, 140.2, 141.6. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}Cl_2SN_2$, $[M+H]^+$ 309.0021; Found 309.0027.

2-chloro-1-(((4-methoxyphenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3e). White solid (74%, 67.7 mg), melting point: 96-97 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.77 (s, 3H), 5.33 (s, 2H), 6.73 (d, J = 8.4, 2H), 7.10 (d, J = 8.8, 2H), 7.18 (d, J = 8.2, 1H), 7.28 (t, J = 5.6, 2H), 7.69 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 50.1, 55.3, 110.4, 114.8, 119.4, 121.4, 123.0, 123.2, 134.1, 137.1, 140.4, 141.6, 161.0. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}ClSON_2$, $[M+H]^+$ 305.0515; Found 305.0520.

2-chloro-1-(((4-ethoxyphenyl)thio)methyl)-1*H*-benzo[d]imidazole (3f). White solid (73%, 69.8 mg), melting point: 61-62 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 1.40 (t, J = 7.2, 3H), 3.98 (d, J = 7.8, 2H), 5.33 (s, 2H), 6.71 (d, J = 8.8, 2H), 7.09 (d, J = 8.8, 2H), 7.18 (d, J = 7.2, 1H), 7.25-7.28 (m, 2H), 7.67 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 14.6, 50.1, 63.5, 110.4, 115.3, 119.4, 121.1, 123.0,123.2, 134.1, 137.1, 140.5, 141.6, 160.3. HRMS (ESI-TOF) Calcd for $C_{16}H_{16}ClSON_2$, $[M+H]^+$ 319.0672; Found 319.0677.

2-chloro-1-(((4-fluorophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3g). White solid (43%, 37.8 mg), melting point: 52-53 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.37 (s, 2H), 6.92 (t, J = 8.8, 2H), 7.16-7.30 (m, 5H), 7.67 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 49.8, 110.2, 116.4, 116.6, 119.6, 123.1, 123.3, 126.1, 134.0, 137.5, 137.6, 140.3, 141.6, 162.5, 165.0. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}ClFSN_2$, $[M+H]^+$ 293.0315; Found 293.0310.

2-chloro-1-(((4-chlorophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3h). White solid (70%, 64.9 mg), melting point: 110-111 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.39 (s, 2H), 7.14-7.22 (m, 5H), 7.30 (dd, J_1 = 1.2, J_2 = 7.6, 2H), 7.68 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 49.6, 110.2, 119.6, 123.2, 123.4, 129.3, 129.5, 133.9, 136.1, 136.5, 140.3, 141.6 . HRMS (ESI-TOF) Calcd for $C_{14}H_{11}Cl_2SN_2$, $[M+H]^+$ 309.0021; Found 309.0024.

1-(((4-bromophenyl)thio)methyl)-2-chloro-1*H*-benzo[*d*]imidazole (3i). White solid (64%, 67.9 mg), melting point: 102-103 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.40 (s, 2H), 7.08 (d, J = 8.0, 2H), 7.18 (t, J = 7.2, 1H), 7.29 (dd, J_1 = 2.0, J_2 = 7.2, 2H), 7.38 (d, J = 8.4, 2H), 7.69 (d, J = 1.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 49.5,

110.2, 119.6, 123.2, 123.4, 124.3, 130.0, 132.5, 133.9, 136.6, 140.3, 141.6. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}ClBrSN_2$, $[M+H]^+$ 352.9517; Found 352.9512.

2-chloro-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3j). White solid (52%, 45.1 mg), melting point: 95-96 ^oC; ^1H NMR (400 MHz; $CDCl_3$): δ = 2.31 (s, 3H), 5.35 (s, 2H), 7.01 (d, J = 7.6, 2H), 7.11 (d, J = 8.0, 2H), 7.18-7.27 (m, 3H), 7.66 (d, J = 7.6, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 21.1, 49.9, 110.4, 119.4, 123.0, 123.2, 127.4, 130.0, 134.1, 135.1, 139.7, 140.4, 141.6. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}ClSN_2$, $[M+H]^+$ 289.0566; Found 289.0571.

1-((phenylthio)methyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3k). White solid (68%, 62.8 mg), melting point: 2-43 ^oC; ^1H NMR (400 MHz; $CDCl_3$): δ = 5.54 (s, 2H), 7.17 (d, J = 7.6, 1H), 7.23-7.26 (m, 4H), 7.30-7.38 (m, 3H), 7.85 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 50.4, 111.5, 120.1, 121.6, 123.9, 125.3, 129.3, 129.5, 131.2, 134.7, 135.0, 141.0. HRMS (ESI-TOF) Calcd for $C_{15}H_{12}F_3SN_2$, $[M+H]^+$ 309.0673; Found 309.0667.

1-(((4-methoxyphenyl)thio)methyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3l). White solid (73%, 74.0 mg), melting point: 67-68 ^oC; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.76 (s, 3H), 5.45 (s, 2H), 6.71 (d, J = 8.4, 2H), 7.09 (d, J = 8.8, 2H), 7.21 (d, J = 7.2, 1H), 7.35 (t, J = 6.4, 2H), 7.85 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 50.8, 55.3, 111.7, 114.8, 120.1, 121.5, 123.8, 125.2, 134.7, 137.0, 141.0. HRMS (ESI-TOF) Calcd for $C_{16}H_{14}F_3SON_2$, $[M+H]^+$ 339.0781; Found 339.0776.

1-(((4-fluorophenyl)thio)methyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3m). White solid (41%, 40.1 mg), melting point: 77-78 ^oC; ^1H NMR (400 MHz; $CDCl_3$): δ = 5.50 (s, 2H), 6.93 (t, J = 8.4, 2H), 7.17-7.27 (m, 3H), 7.36-7.39 (m, 2H), 7.87 (d, J = 6.8, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 50.5, 111.5, 116.4, 116.6, 121.7, 124.0, 124.3, 125.4, 126.2, 134.6, 137.4, 137.5, 141.0, 162.5, 165.0. HRMS (ESI-TOF) Calcd for $C_{15}H_{11}F_4SN_2$, $[M+H]^+$ 327.0579; Found 327.0573.

1-(((4-bromophenyl)thio)methyl)-2-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (3n). White solid (59%, 68.5 mg), melting point: 115-116 ^oC; ^1H NMR (400 MHz; $CDCl_3$): δ = 5.55 (s, 2H), 7.09 (d, J = 8.4, 2H), 7.21 (d, J = 7.2, 1H), 7.34-7.86 (m,

4H), 7.87 (d, J = 8.8, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 50.1, 111.4, 121.7, 124.0, 124.4, 125.5, 126.5, 130.1, 132.1, 132.5, 136.5, 141.0. HRMS (ESI-TOF) Calcd for $C_{15}H_{11}F_3SBrN_2$, $[M+H]^+$ 386.9779; Found 386.9785.

2-bromo-1-((phenylthio)methyl)-1*H*-benzo[*d*]imidazole (3o). White solid (69%, 66.0 mg), melting point: 98-99 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.39(s, 2H), 7.14-7.25 (m, 7H), 7.31 (t, J = 2.8, 1H), 7.67 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 50.7, 110.4, 119.4, 122.9, 123.2, 129.3, 129.5, 129.8, 130.9, 134.5, 135.3, 143.1. HRMS (ESI-TOF) Calcd for $C_{14}H_{12}BrSN_2$, $[M+H]^+$ 318.9905; Found 318.9911.

2-bromo-1-(((4-methoxyphenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3p). White solid (70%, 73.3 mg), melting point: 52-53 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.76 (s, 3H), 5.33(s, 2H), 6.72 (d, J = 8.8, 2H), 7.09 (d, J = 8.4, 2H), 7.19-7.25 (m, 3H), 7.68 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 51.1, 55.3, 110.4, 114.8, 119.4, 121.3, 122.9, 123.2, 129.9, 132.9, 134.5, 137.3, 143.1, 161.0. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}BrSON_2$, $[M+H]^+$ 349.0010; Found 349.0015.

2-bromo-1-(((4-bromophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3q). White solid (65%, 77.6 mg), melting point: 98-99 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.39 (s, 2H), 7.13 (d, J = 8.4, 2H), 7.19-7.26 (m, 5H), 7.28 (d, J = 5.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 50.6, 110.3, 119.6, 123.1, 123.4, 129.2, 129.5, 129.8, 134.4, 136.1, 136.7, 143.1. HRMS (ESI-TOF) Calcd for $C_{14}H_{11}Br_2SN_2$, $[M+H]^+$ 396.9010; Found 396.9017.

5-phenyl-1-((phenylthio)methyl)-1*H*-tetrazole (3r). White solid (82%, 65.9 mg), melting point: 68-69 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.89 (s, 2H), 7.34 (dd, J_1 = 1.2, J_2 = 5.6, 3H), 7.45-7.50 (m, 5H), 8.14 (d, J = 7.6, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 56.9, 126.9, 127.1, 128.8, 129.4, 130.4, 131.8, 132.8, 165.6. HRMS (ESI-TOF) Calcd for $C_{14}H_{13}SN_4$, $[M+H]^+$ 269.0861; Found 269.0865.

5-(4-chlorophenyl)-1-((phenylthio)methyl)-1*H*-tetrazole (3s). White solid (75%, 68.1 mg), melting point: 66-67 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.89 (s, 2H), 7.36 (d, J = 5.2, 3H), 7.44-7.48 (m, 4H), 8.07 (d, J = 8.4, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 57.0, 124.3, 125.6, 128.2, 128.9, 129.2, 129.4, 131.7, 132.8, 136.5, 164.7. HRMS (ESI-TOF) Calcd for $C_{14}H_{12}SClN_4$, $[M+H]^+$ 303.0471; Found 303.0478.

5-(4-bromophenyl)-1-((phenylthio)methyl)-1*H*-tetrazole (3t). White solid (73%, 76.0 mg), melting point: 93-94 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.89 (s, 2H), 7.35 (d, J = 4.8, 3H), 7.43 (d, J = 3.6, 2H), 7.63 (d, J = 8.4, 2H), 8.00 (d, J = 8.4, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 57.0, 124.9, 126.0, 128.4, 128.9, 129.4, 131.7, 132.1, 132.8, 164.8. HRMS (ESI-TOF) Calcd for $C_{14}H_{12}SBrN_4$, $[M+H]^+$ 346.9966; Found 346.9961.

1-(((4-chlorophenyl)thio)methyl)-5-phenyl-1*H*-tetrazole (3u). White solid (75%, 68.1 mg), melting point: 80-81 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.86 (s, 2H), 7.30 (d, J = 8.8, 2H), 7.37 (d, J = 8.8, 2H), 7.49-7.52 (m, 3H), 8.14 (t, J = 4.4, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 56.8, 126.7, 126.9, 128.9, 129.6, 130.2, 130.3, 130.6, 134.3, 135.4, 165.7. HRMS (ESI-TOF) Calcd for $C_{14}H_{12}SClN_4$, $[M+H]^+$ 303.0471; Found 303.0477.

1-(((4-methoxyphenyl)thio)methyl)-5-phenyl-1*H*-tetrazole (3v). Colourless liquid (74%, 66.2 mg). ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.81 (s, 3H), 5.77 (s, 2H), 6.85 (d, J = 8.8, 2H), 7.32-7.37 (m, 2H), 7.49 (dd, J_1 = 1.6, J_2 = 5.2, 3H), 8.15 (dd, J_1 = 2.0, J_2 = 7.6, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 55.3, 58.1, 114.9, 121.9, 123.4, 124.3, 126.9, 128.8, 130.4, 136.0, 165.5. HRMS (ESI-TOF) Calcd for $C_{15}H_{14}SON_4$, $[M+H]^+$ 299.0967; Found 299.0962.

1-((phenylthio)methyl)-1*H*-benzo[*d*][1,2,3]triazole (3w). White solid (79%, 57.1 mg), melting point: 84-85 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.95 (s, 2H), 7.21-7.27 (m, 5H), 7.35-7.45 (m, 3H), 8.03 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 52.7, 110.1, 120.1, 124.1, 127.4, 128.7, 129.3, 131.9, 132.1, 133.0, 146.3. HRMS (ESI-TOF) Calcd for $C_{13}H_{12}SN_3$, $[M+H]^+$ 242.0752; Found 242.0758.

1-(((4-chlorophenyl)thio)methyl)-1*H*-benzo[*d*][1,2,3]triazole (3x). White solid (78%, 64.5 mg), melting point: 96-97 ^{o}C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.93 (s, 2H), 7.16-7.22 (m, 4H), 7.41 (q, J = 4.0, 1H), 7.49 (d, J = 3.6, 2H), 8.06 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 52.5, 109.9, 120.3, 124.2, 127.6, 129.5, 130.1, 134.4, 135.2, 146.4. HRMS (ESI-TOF) Calcd for $C_{13}H_{11}SClN_3$, $[M+H]^+$ 276.0362; Found 276.0371.

1-(((4-bromophenyl)thio)methyl)-1*H*-benzo[*d*][1,2,3]triazole (3y). White solid (77%, 73.9 mg), melting point: 114-115 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.92 (s, 2H), 7.09 (d, J = 8.8, 2H), 7.34-7.42 (m, 3H), 7.48 (d, J = 4.0, 2H), 8.05 (d, J = 8.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 52.4, 109.9, 120.2, 123.3, 124.3, 127.6, 130.8, 132.0, 132.4, 134.4, 146.4. HRMS (ESI-TOF) Calcd for $C_{13}H_{11}SBrN_3$, $[M+H]^+$ 319.9857; Found 319.9851.

1-(((4-methoxyphenyl)thio)methyl)-1*H*-benzo[*d*][1,2,3]triazole (3z). White solid (82%, 66.7 mg), melting point: 107-108 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.76 (s, 3H), 5.83 (s, 2H), 6.72 (d, J = 8.8, 2H), 7.09 (d, J = 8.4, 2H), 7.38-7.46 (m, 3H), 8.05 (d, J = 8.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 53.7, 55.3, 110.1, 114.8, 120.1, 122.0, 124.1, 127.3, 136.0, 146.3, 160.6. HRMS (ESI-TOF) Calcd for $C_{14}H_{14}SON_3$, $[M+H]^+$ 272.0858; Found 272.0884.

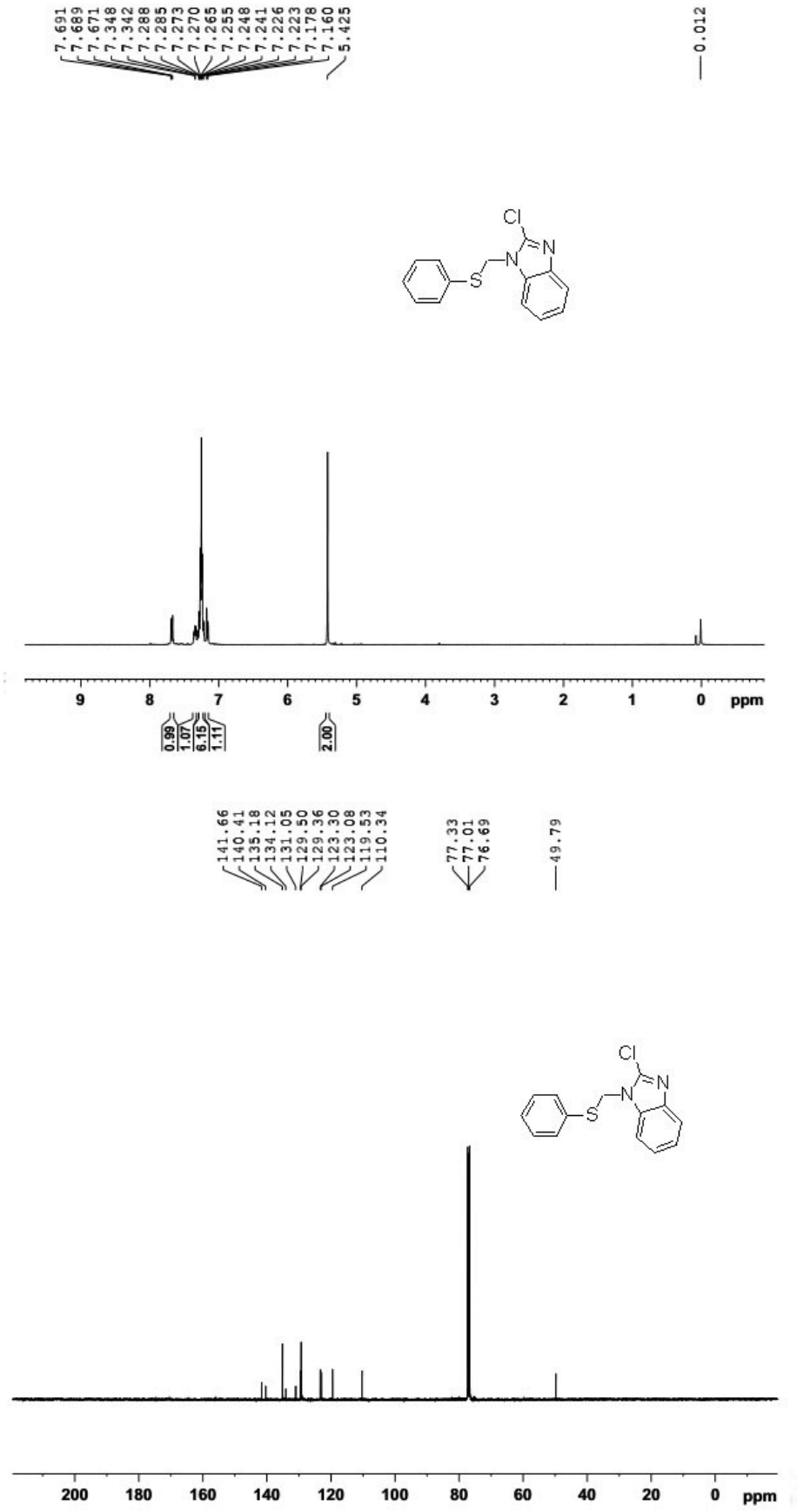
1-((phenylsulfinyl)methyl)-1*H*-benzo[*d*][1,2,3]triazole (4). White solid (81%, 104.1 mg), melting point: 143-144 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.68 (d, J = 13.2, 2H), 7.38 (d, J = 7.6, 1H), 7.45-7.56 (m, 7H), 8.02 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 69.7, 110.0, 120.0, 124.2, 124.5, 128.4, 128.7, 129.5, 132.3, 133.6, 140.1, 145.8. HRMS (ESI-TOF) Calcd for $C_{14}H_{14}SON_3$, $[M+H]^+$ 258.0695; Found 258.0694.

2,6-di-*tert*-butyl-4-((2-chloro-1*H*-benzo[*d*]imidazol-1-yl)methyl)phenol (5). ^{1}H NMR (400 MHz; $CDCl_3$): δ = 1.40 (s, 18H), 5.28 (s, 2H), 6.64 (s, 1H), 7.12 (s, 1H), 7.27 (t, J = 4.0, 2H), 7.35 (s, 1H), 7.70 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 69.7, 110.0, 120.0, 124.2, 124.5, 128.4, 128.7, 129.5, 132.3, 133.6, 140.1, 145.8.

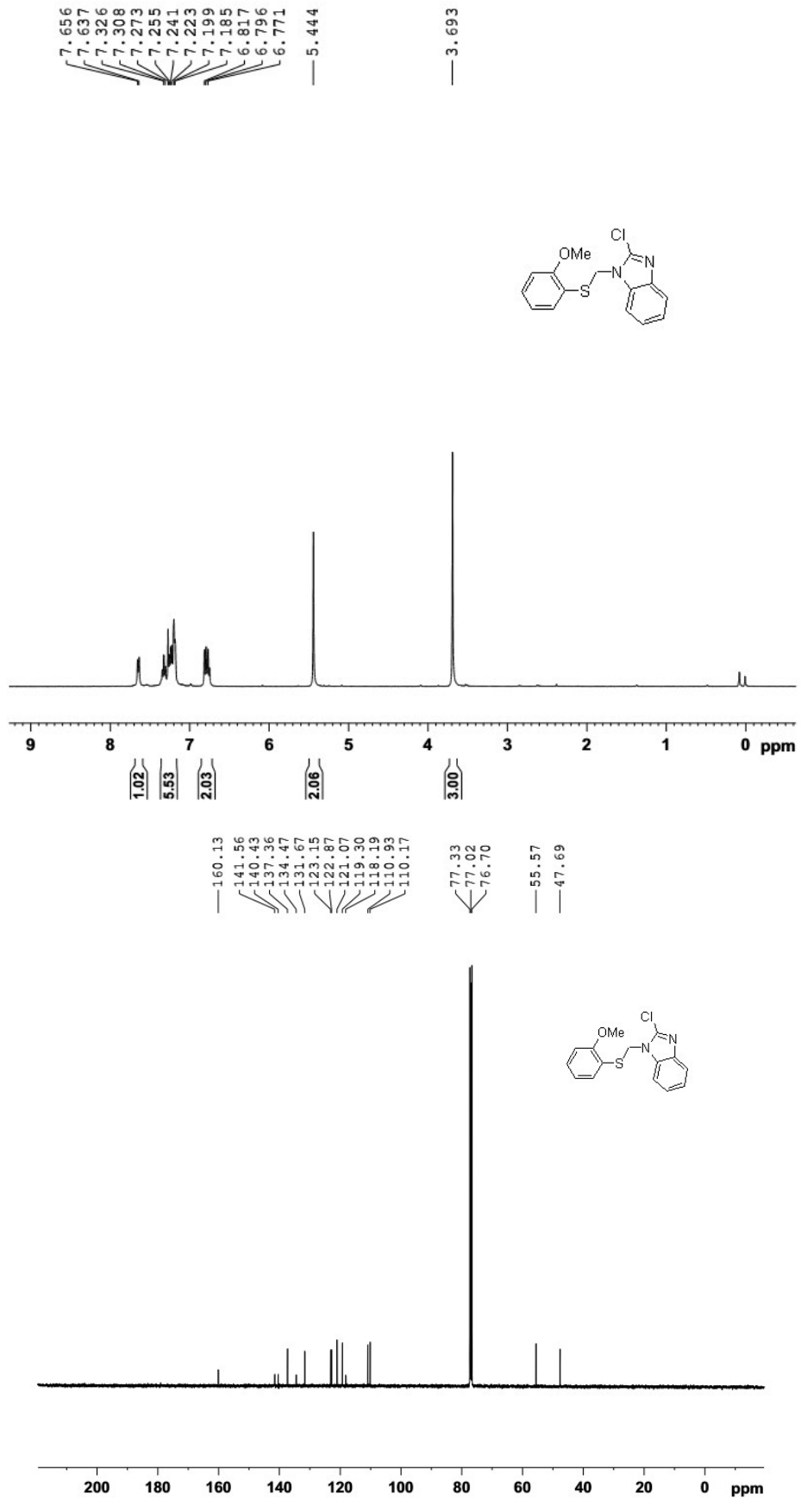
1-(2-bromo-1,1-diphenylethyl)-2-chloro-1*H*-benzo[*d*]imidazole (6). ^{1}H NMR (400 MHz; $CDCl_3$): δ = 5.02 (s, 2H), 5.43 (d, J = 4.4, 1H), 6.82 (t, J = 7.6, 1H), 7.17 (t, J = 8.0, 1H), 7.39-7.41 (m, 10H), 7.68 (d, J = 8.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.7, 70.3, 114.3, 119.4, 122.4, 122.7, 128.5, 128.7, 137.1, 141.4, 141.6, 141.7.

IV. ^{1}H and ^{13}C-NMR spectra for compounds 3, 4, 5 and 6

Compound 3a

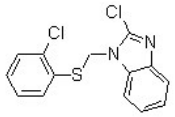

7.691
7.689
7.671
7.348
7.342
7.288
7.285
7.273
7.270
7.265
7.255
7.248
7.241
7.226
7.223
7.178
7.160
5.425
0.012
Cl
N
S
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.07
6.15
1.11
2.00
141.66
140.41
135.18
134.12
131.05
129.50
129.36
123.30
123.08
119.53
110.34
77.33
77.01
76.69
49.79
200
180
160
140
120
100
80
60
40
20
0
ppm

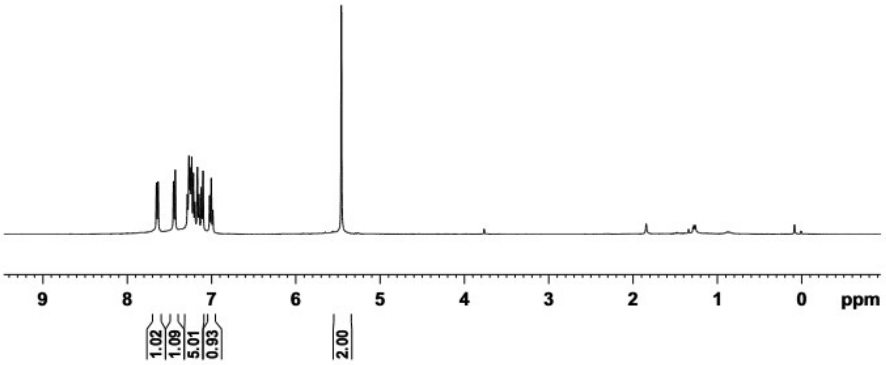
Compound 3b

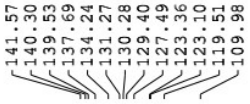

7.656
7.637
7.326
7.308
7.273
7.255
7.241
7.223
7.199
7.185
6.817
6.796
6.771
5.444
3.693
Cl
OMe
N
S
9
8
7
6
5
4
3
2
1
0 ppm
1.02
5.53
2.03
2.06
3.00
160.13
141.56
140.43
137.36
134.47
131.67
123.15
122.87
121.07
119.30
118.19
110.93
110.17
77.33
77.02
76.70
55.57
47.69
200
180
160
140
120
100
80
60
40
20
0 ppm

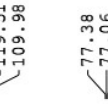
Compound 3c


7.657
7.638
7.454
7.434
7.290
7.271
7.258
7.239
7.219
7.201
7.172
7.152
7.124
7.105
7.026
7.007
6.988
5.465

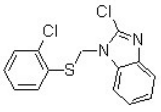

Cl
Cl
S
N
N

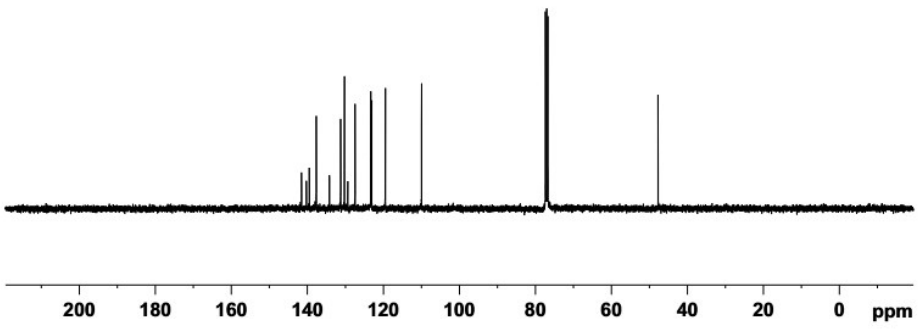

9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.09
5.01
0.93
2.00


141.57
140.30
139.53
137.69
134.24
131.27
130.28
129.40
127.49
123.36
123.10
119.51
109.98

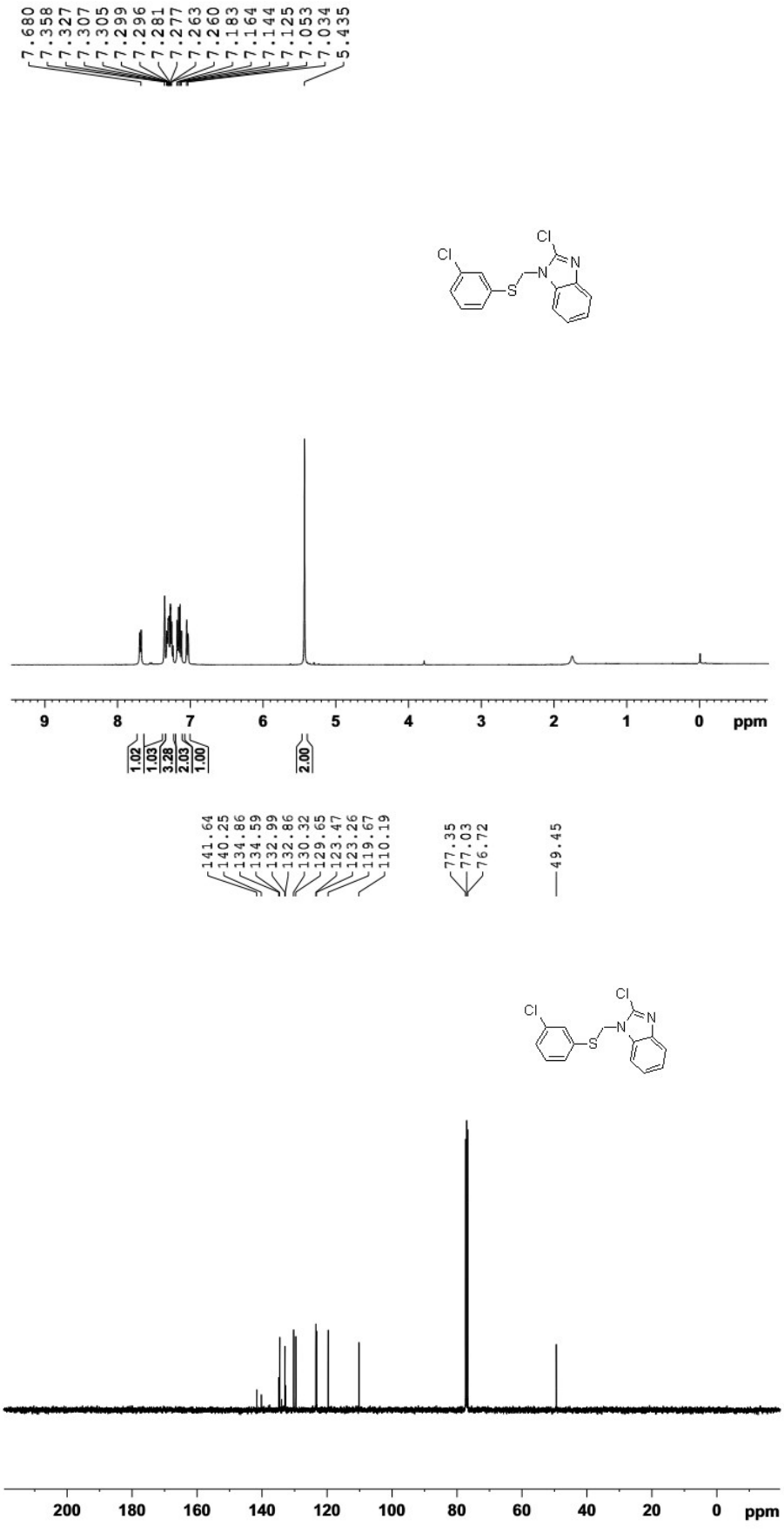

77.38
77.06
76.75


47.76

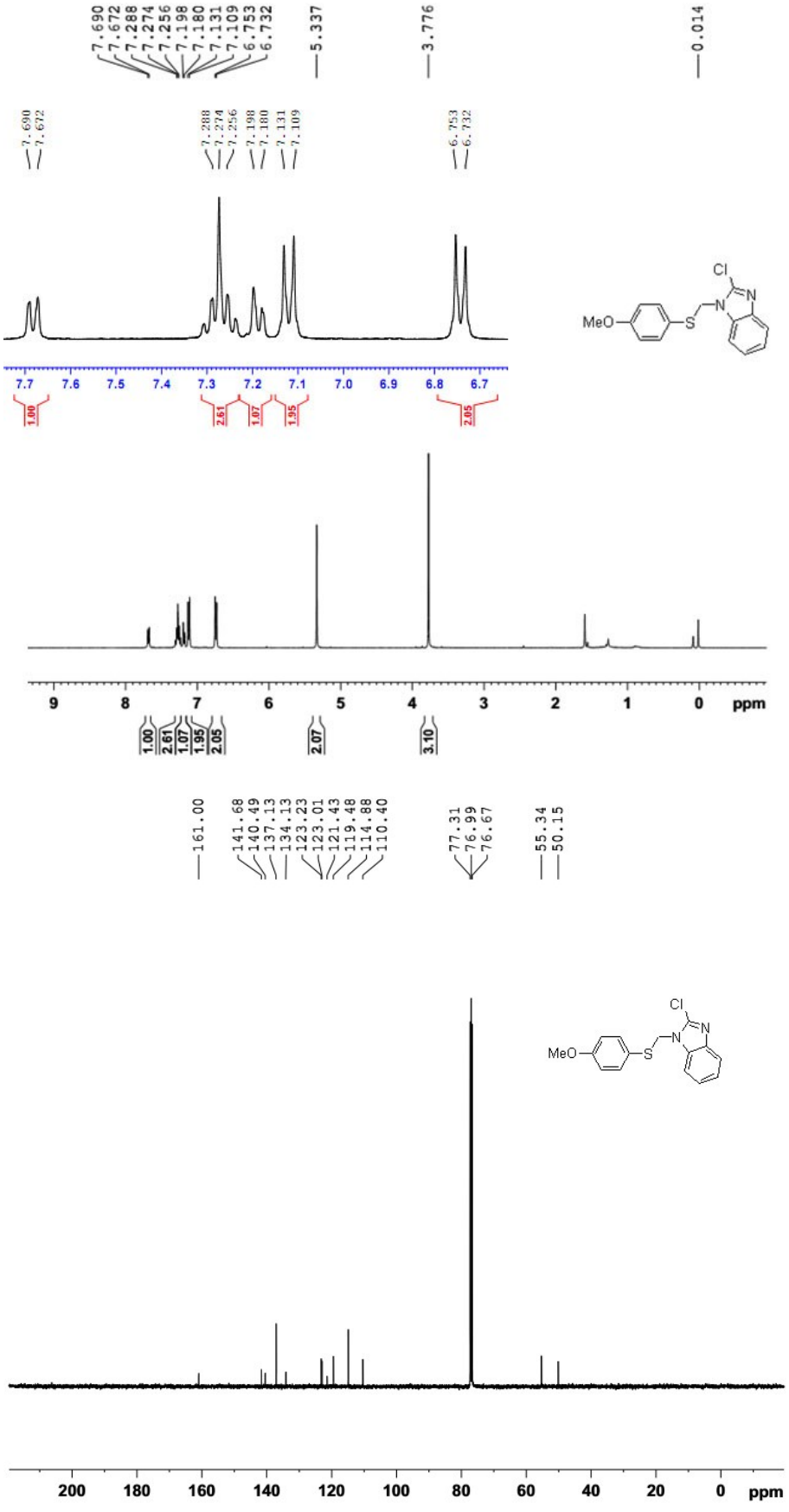

Cl
Cl
S
N
N


200
180
160
140
120
100
80
60
40
20
0
ppm

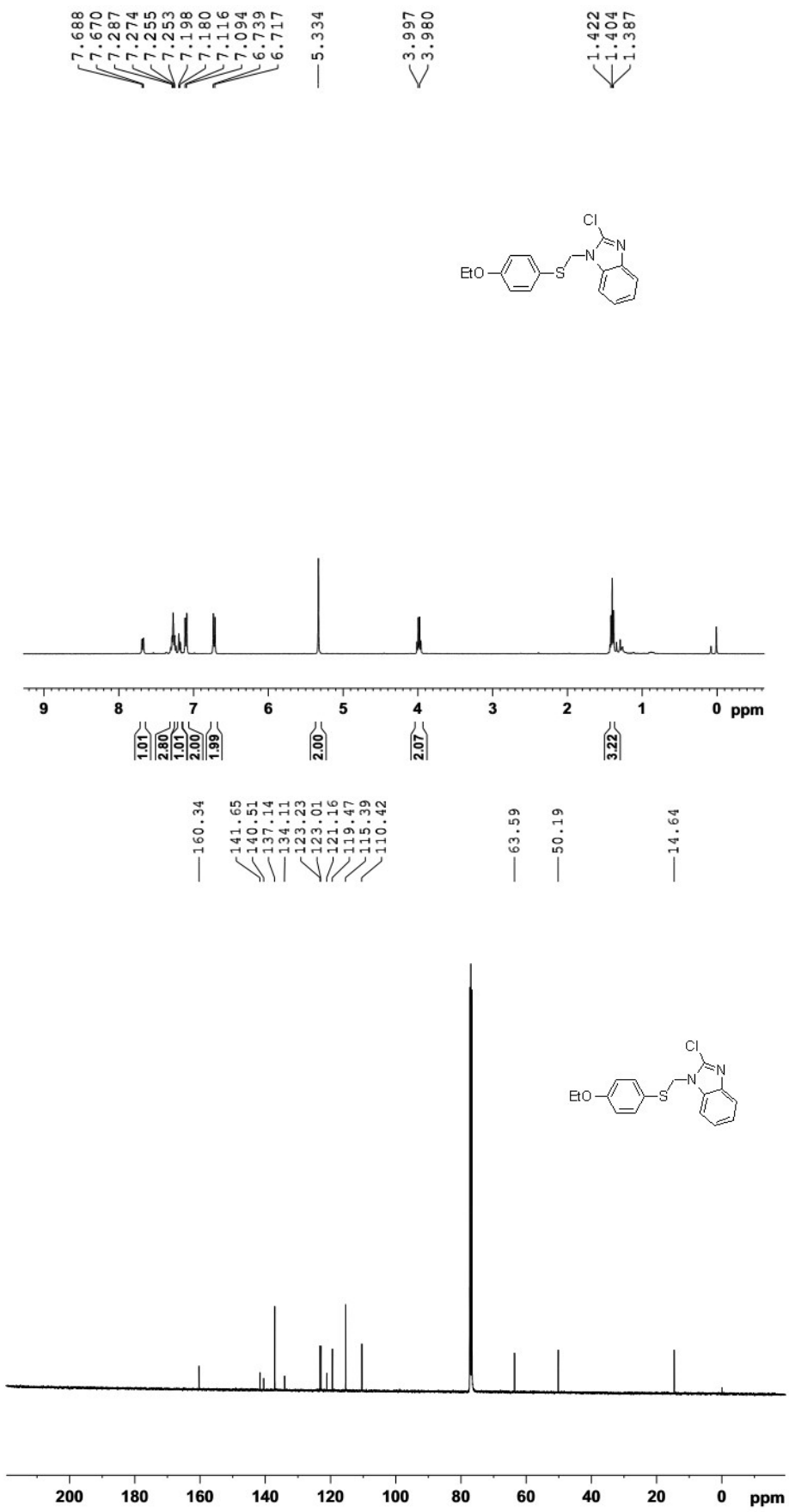
Compound 3d


7.680
7.358
7.327
7.307
7.305
7.299
7.296
7.281
7.277
7.263
7.260
7.183
7.164
7.144
7.125
7.053
7.034
5.435
Cl
Cl
N
S
9
8
7
6
5
4
3
2
1
0
ppm
1.02
1.03
3.28
2.03
1.00
2.00
141.64
140.25
134.86
134.59
132.99
132.86
130.32
129.65
123.47
123.26
119.67
110.19
77.35
77.03
76.72
49.45
200
180
160
140
120
100
80
60
40
20
0
ppm

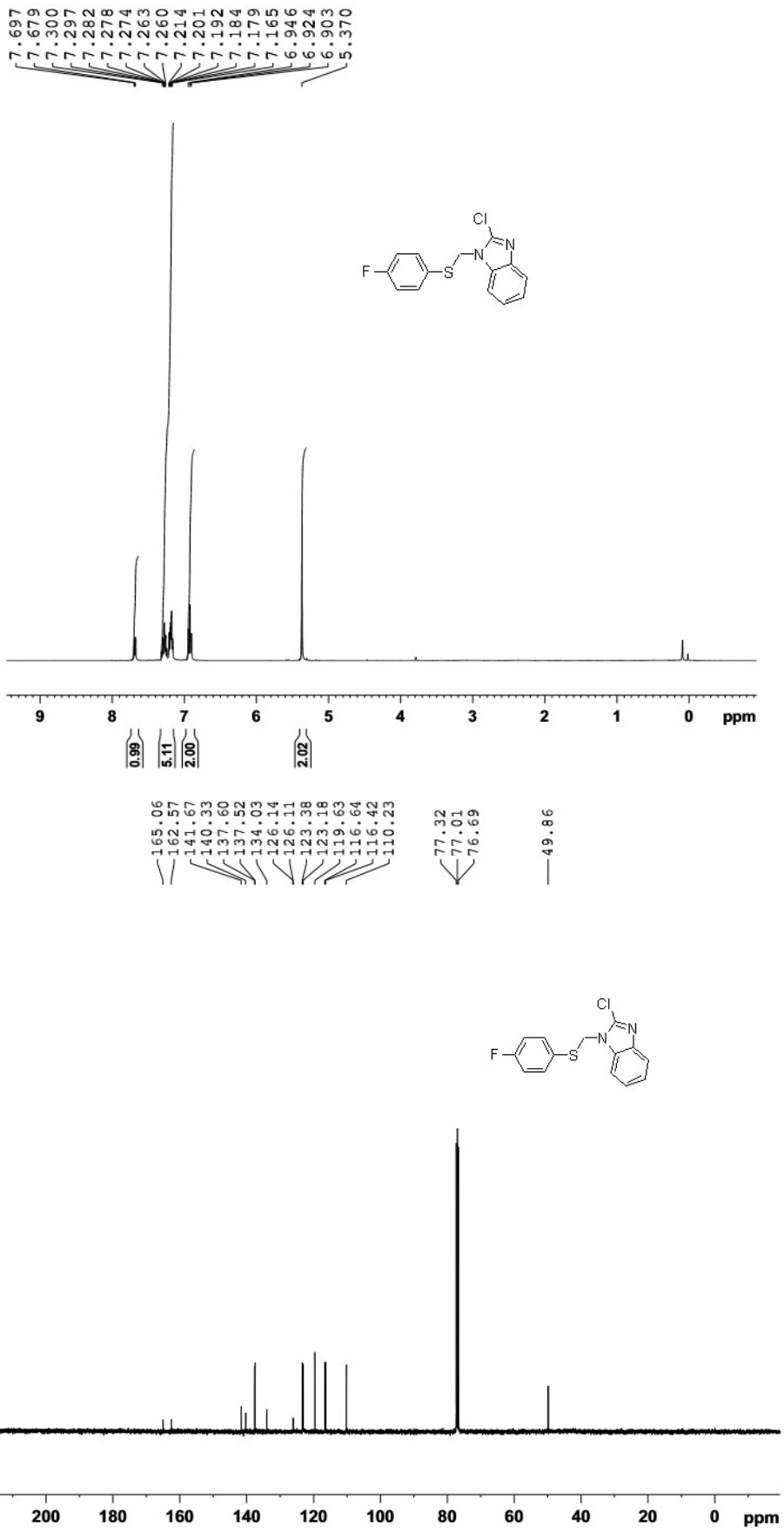
Compound 3e


7.690
7.672
7.288
7.274
7.256
7.198
7.180
7.131
7.109
6.753
6.732
5.337
3.776
0.014
Cl
N
MeO
S
ppm
161.00
141.68
140.49
137.13
134.13
123.23
123.01
121.43
119.48
114.88
110.40
77.31
76.99
76.67
55.34
50.15

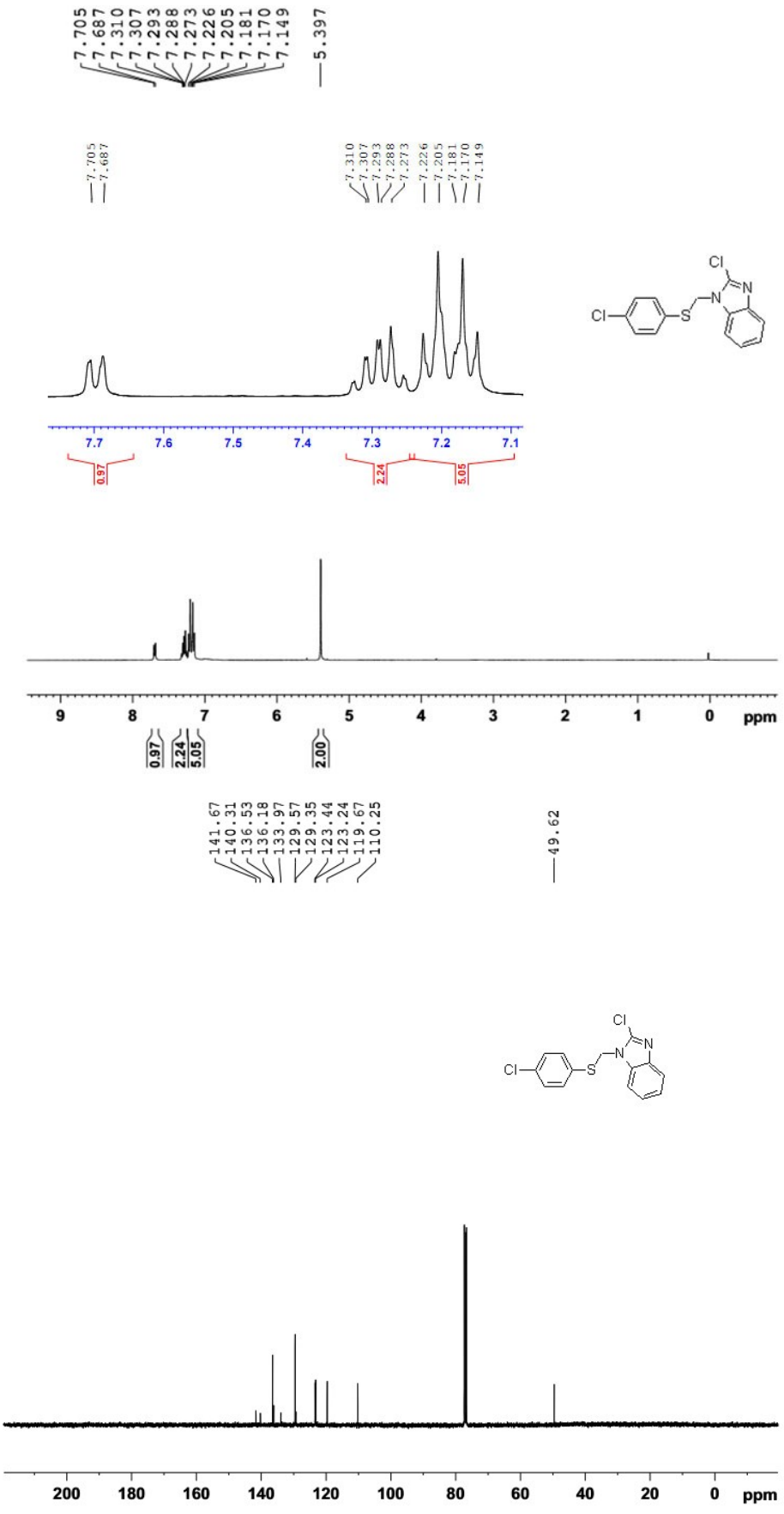
Compound 3f


7.688
7.670
7.287
7.274
7.255
7.253
7.198
7.180
7.116
7.094
6.739
6.717
5.334
3.997
3.980
1.422
1.404
1.387
Cl
N
N
S
EtO
9
8
7
6
5
4
3
2
1
0 ppm
1.01
2.80
1.01
2.00
1.99
2.00
2.07
3.22
160.34
141.65
140.51
137.14
134.11
123.23
123.01
121.16
119.47
115.39
110.42
63.59
50.19
14.64
200
180
160
140
120
100
80
60
40
20
0 ppm

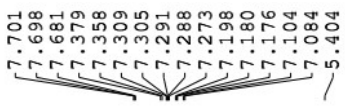
Compound 3g

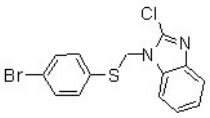

7.697
7.679
7.300
7.297
7.282
7.278
7.274
7.263
7.260
7.214
7.201
7.192
7.184
7.179
7.165
6.946
6.924
6.903
5.370
Cl
N
N
F
S
9
8
7
6
5
4
3
2
1
0
ppm
0.99
5.11
2.00
2.02
165.06
162.57
141.67
140.33
137.60
137.52
134.03
126.14
126.11
123.38
123.18
119.63
116.64
116.42
110.23
77.32
77.01
76.69
49.86
Cl
N
N
F
S
200
180
160
140
120
100
80
60
40
20
0
ppm

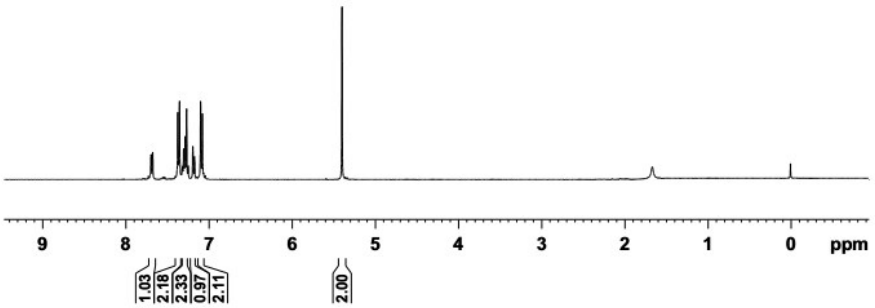
Compound 3h

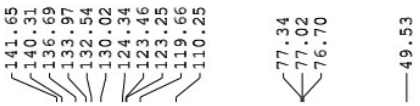

7.705
7.687
7.310
7.307
7.293
7.288
7.273
7.226
7.205
7.181
7.170
7.149
5.397
Cl
N
S
Cl
7.7
7.6
7.5
7.4
7.3
7.2
7.1
0.97
2.24
5.05
9
8
7
6
5
4
3
2
1
0
ppm
0.97
2.24
5.05
2.00
141.67
140.31
136.53
136.18
133.97
129.57
129.35
123.44
123.24
119.67
110.25
49.62
200
180
160
140
120
100
80
60
40
20
0
ppm

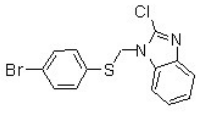
Compound 3i


7.701
7.698
7.681
7.379
7.358
7.309
7.305
7.291
7.288
7.273
7.198
7.180
7.176
7.104
7.084
5.404


Cl
N
Br
S
N

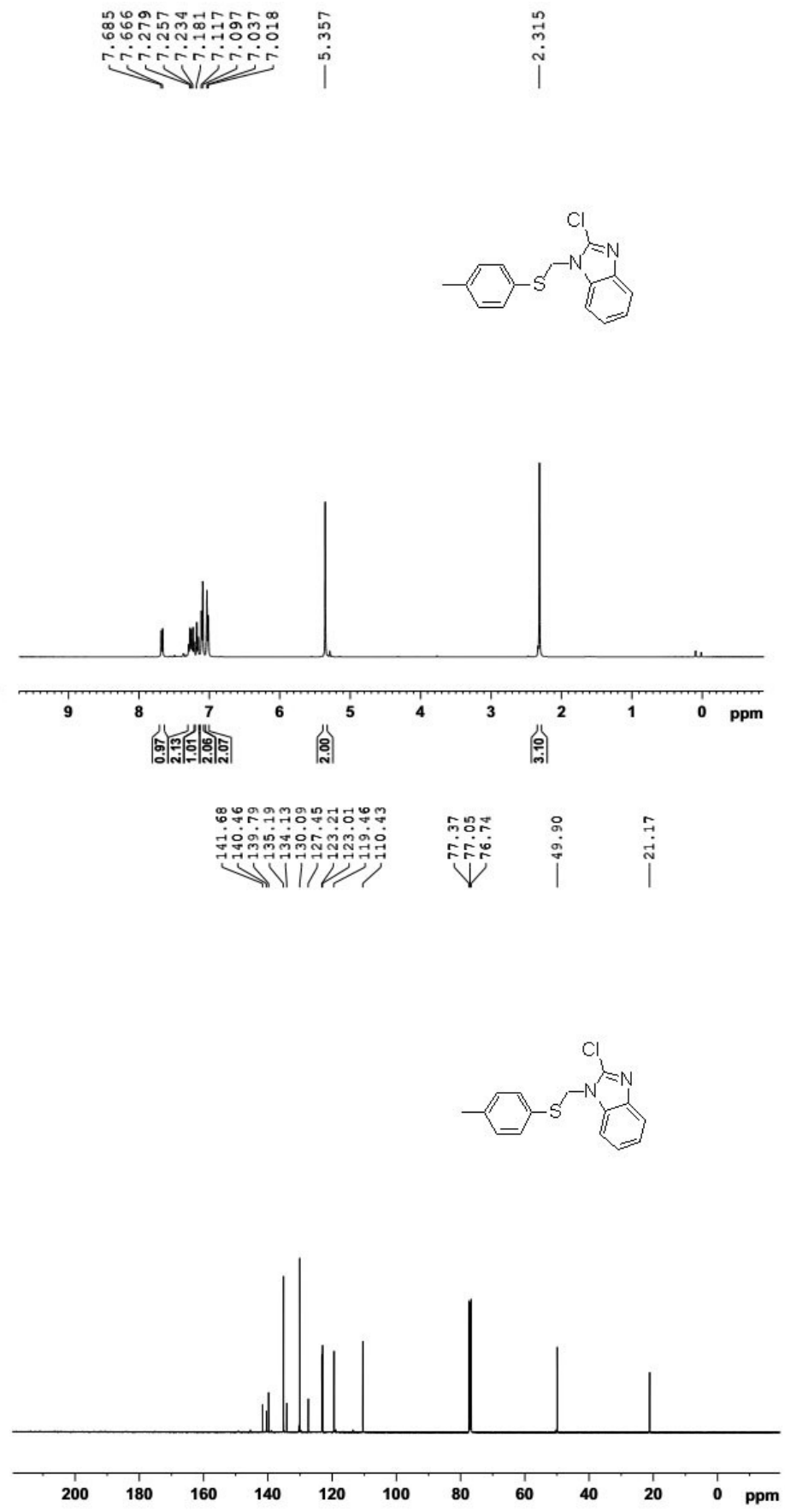

9
8
7
6
5
4
3
2
1
0
ppm
1.03
2.18
2.33
0.97
2.11
2.00


141.65
140.31
136.69
133.97
132.54
130.02
124.34
123.46
123.25
119.66
110.25
77.34
77.02
76.70
49.53


Cl
N
Br
S
N

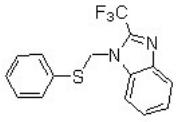
200
180
160
140
120
100
80
60
40
20
0
ppm

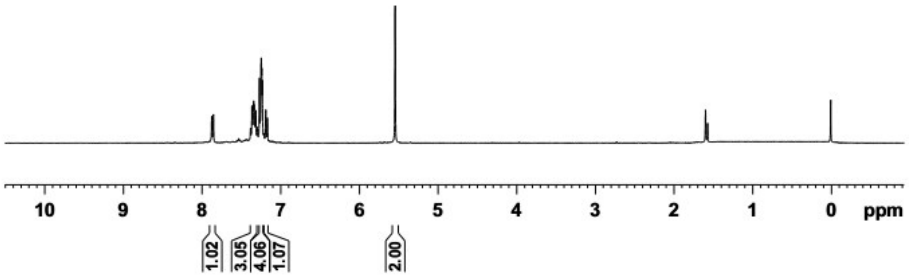
Compound 3j

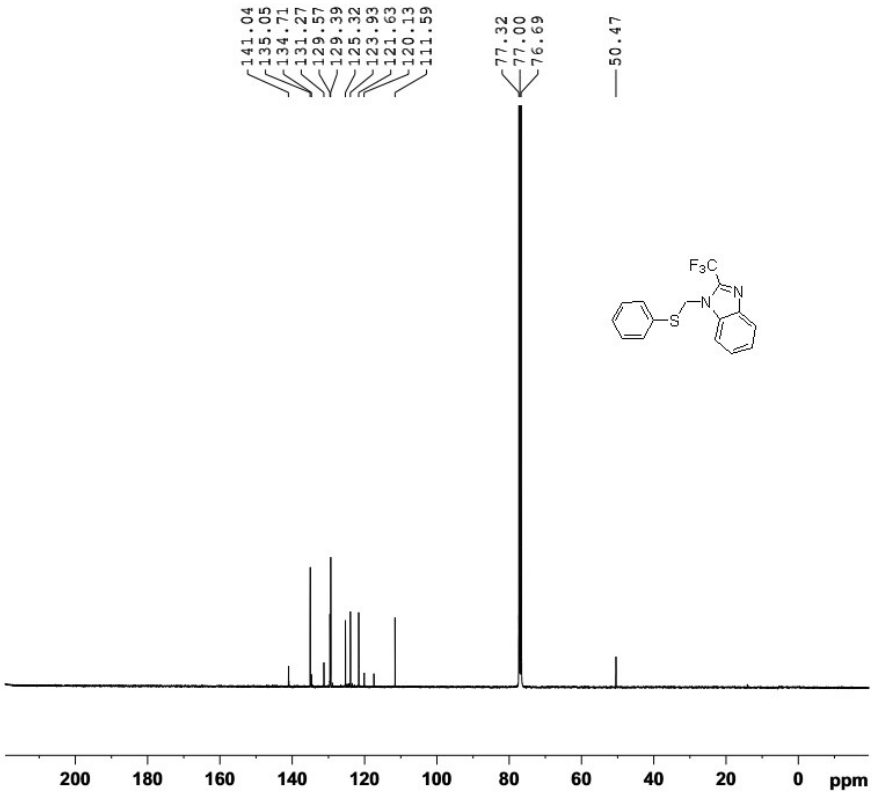

7.685
7.666
7.279
7.257
7.234
7.181
7.117
7.097
7.037
7.018
5.357
2.315
Cl
N
N
S
9
8
7
6
5
4
3
2
1
0
ppm
0.97
2.13
1.01
2.06
2.07
2.00
3.10
141.68
140.46
139.79
135.19
134.13
130.09
127.45
123.21
123.01
119.46
110.43
77.37
77.05
76.74
49.90
21.17
Cl
N
N
S
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 3k

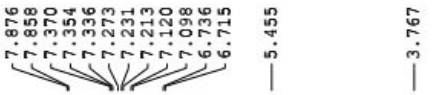

7.880
7.859
7.385
7.370
7.350
7.347
7.341
7.334
7.321
7.303
7.273
7.265
7.251
7.243
7.237
7.193
7.174
5.549

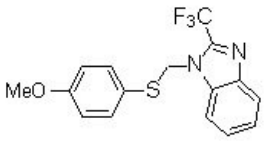

F3C
N
N
S

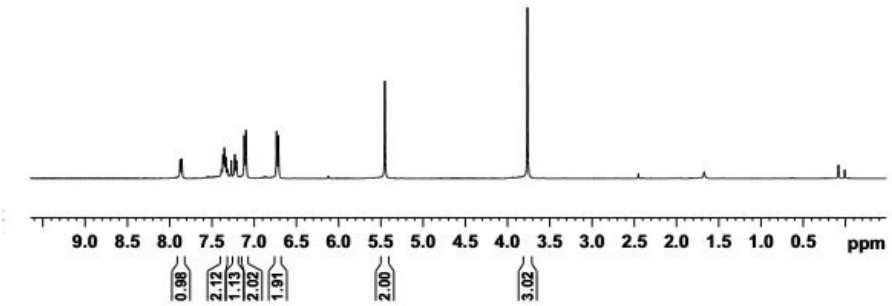

10
9
8
7
6
5
4
3
2
1
0
ppm
1.02
3.05
4.06
1.07
2.00

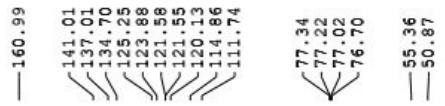

141.04
135.05
134.71
131.27
129.57
129.39
125.32
123.93
121.63
120.13
111.59
77.32
77.00
76.69
50.47
F3C
N
N
S
200
180
160
140
120
100
80
60
40
20
0
ppm

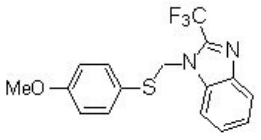
Compound 3l

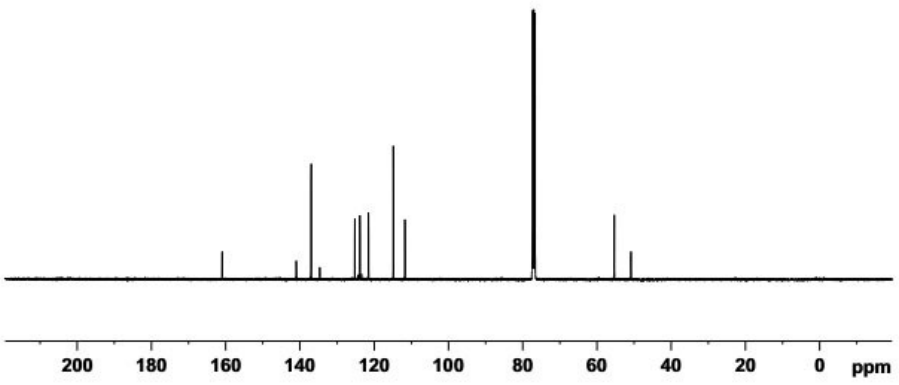

7.876
7.858
7.370
7.354
7.336
7.273
7.231
7.213
7.120
7.098
6.736
6.715
5.455
3.767


F3C
N
N
S
MeO

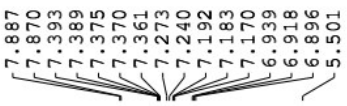

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
2.12
1.13
2.02
1.91
2.00
3.02

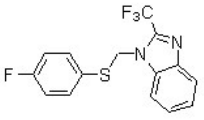

160.99
141.01
137.01
134.70
125.25
123.88
121.58
121.55
120.13
114.86
111.74
77.34
77.22
77.02
76.70
55.36
50.87

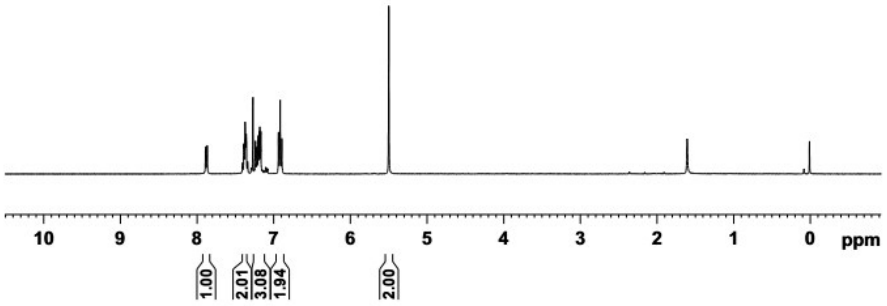

F3C
N
N
S
MeO

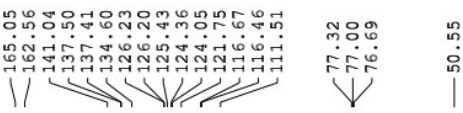

200 180 160 140 120 100 80 60 40 20 0 ppm

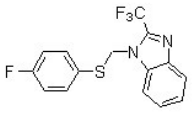
Compound 3m

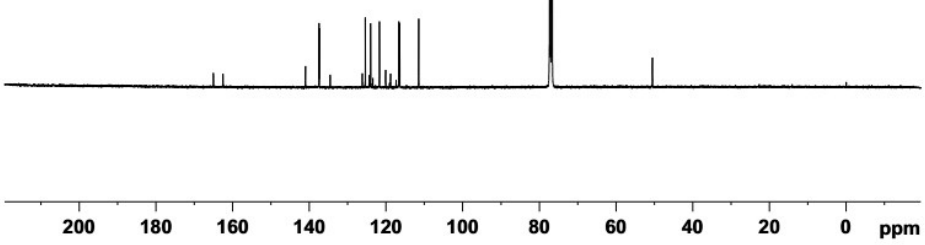

7.887
7.870
7.393
7.389
7.375
7.370
7.361
7.273
7.240
7.192
7.183
7.170
6.939
6.918
6.896
5.501


F3C
N
N
S
F


10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.01
3.08
1.94
2.00

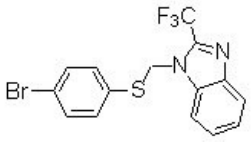

165.05
162.56
141.04
137.50
137.41
134.60
126.23
126.20
125.43
124.36
124.05
121.75
116.67
116.46
111.51
77.32
77.00
76.69
50.55

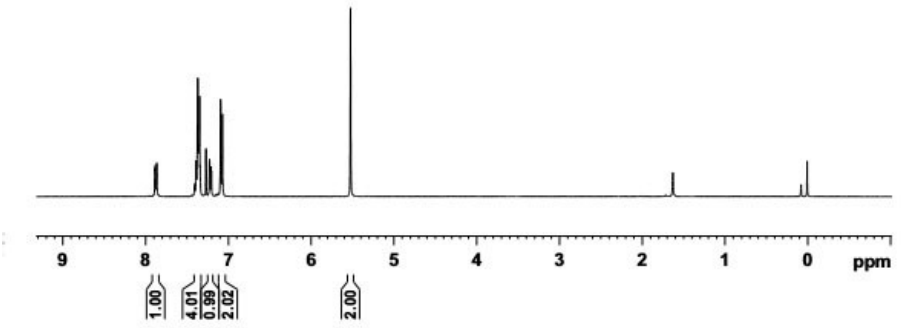

F3C
N
N
S
F

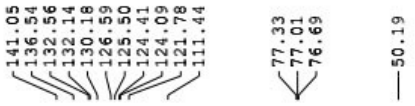

200
180
160
140
120
100
80
60
40
20
0
ppm

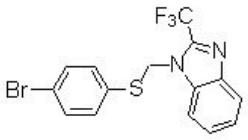
Compound 3n

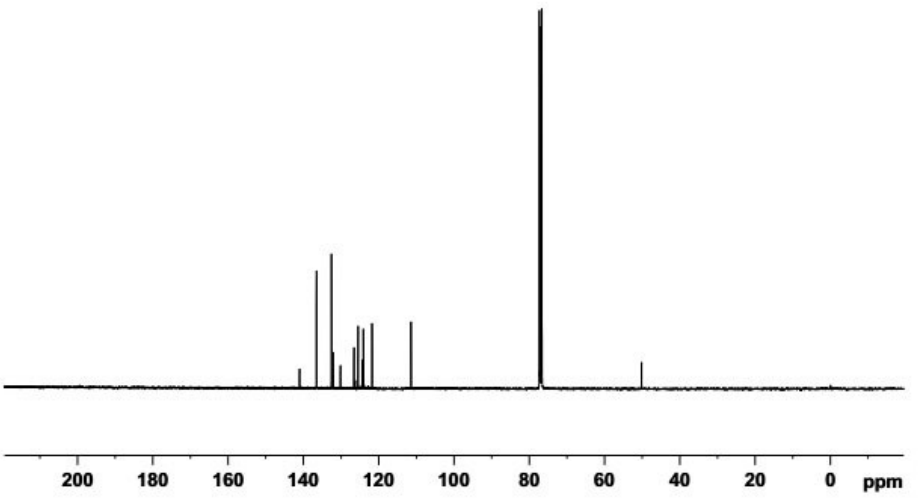

7.885
7.873
7.868
7.394
7.391
7.376
7.372
7.362
7.358
7.351
7.345
7.272
7.229
7.211
7.096
7.075
5.526


F3C
N
N
S
Br

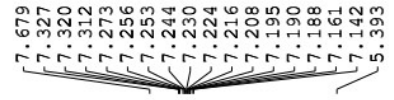

9
8
7
6
5
4
3
2
1
0
ppm
1.00
4.01
0.99
2.02
2.00

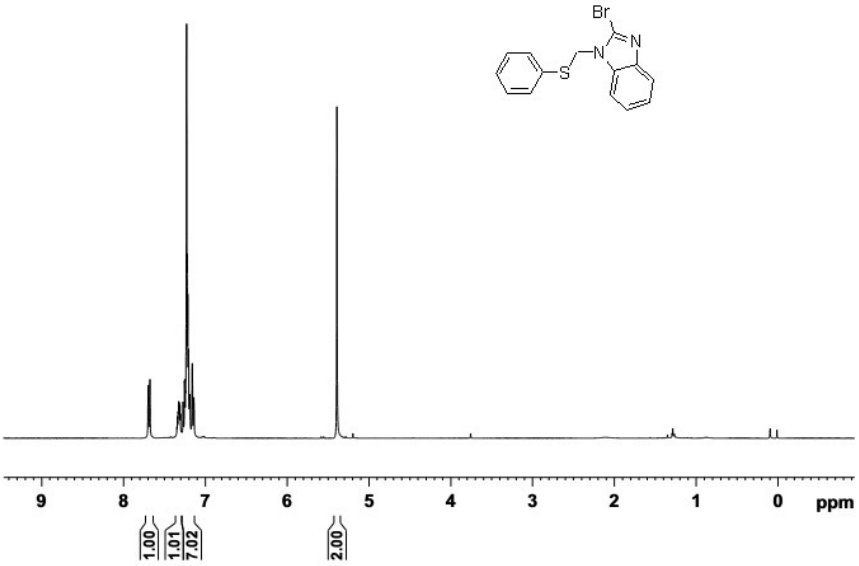

141.05
136.54
132.56
132.14
130.18
126.59
125.50
124.41
124.09
121.78
111.44
77.33
77.01
76.69
50.19

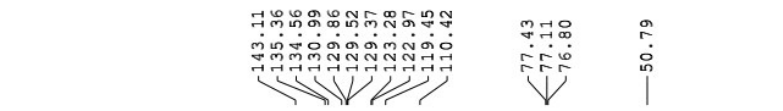

F3C
N
N
S
Br

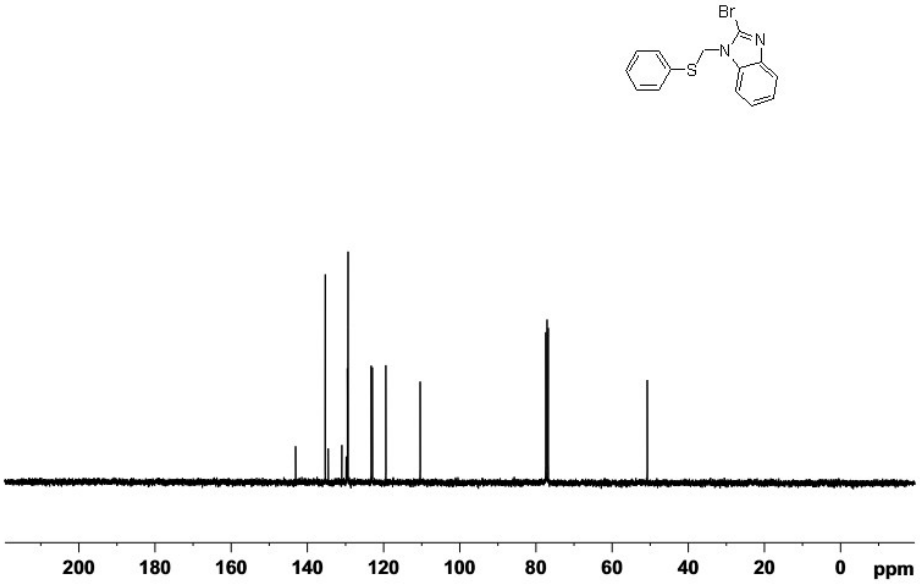

200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 3o

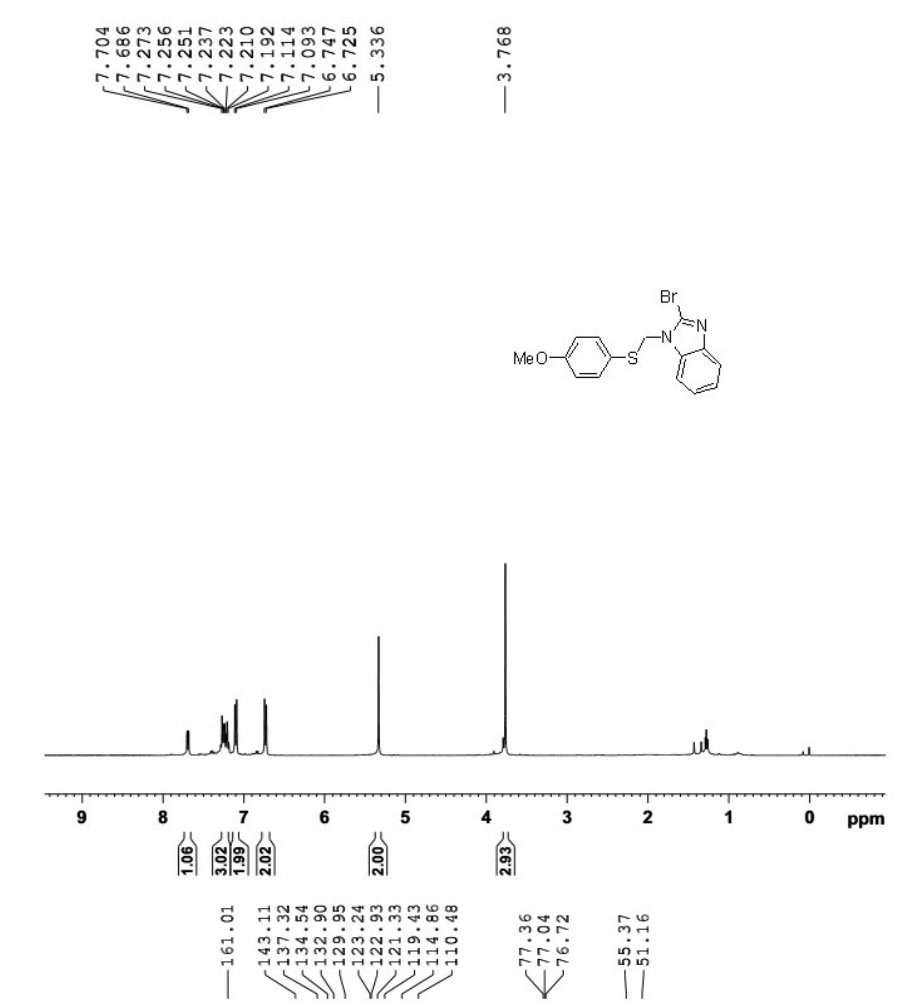

7.679
7.327
7.320
7.312
7.273
7.256
7.253
7.244
7.230
7.224
7.216
7.208
7.195
7.190
7.188
7.161
7.142
5.393


Br
N
S
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
7.02
2.00

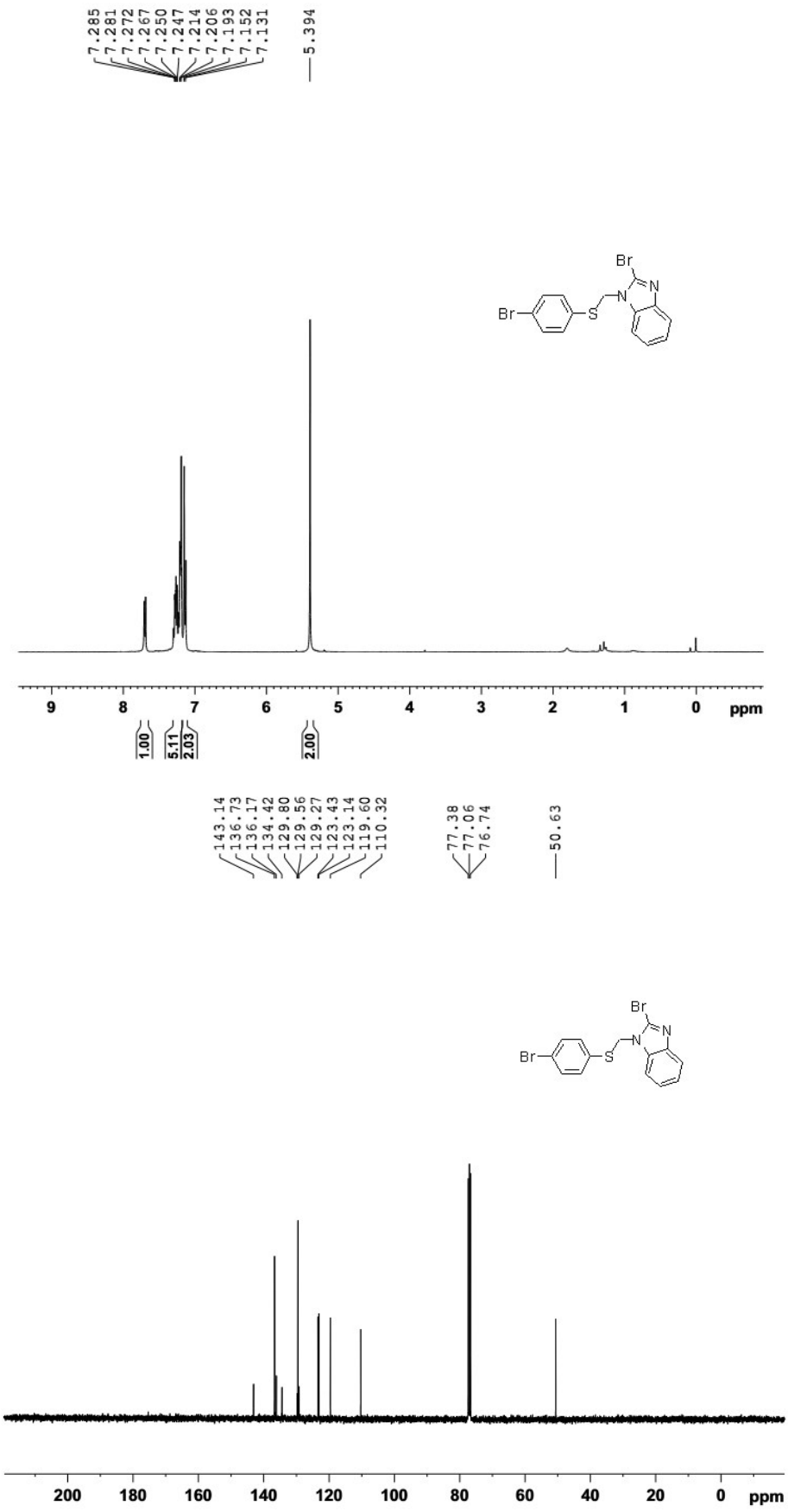

143.11
135.36
134.56
130.99
129.86
129.52
129.37
123.28
122.97
119.45
110.42
77.43
77.11
76.80
50.79


Br
N
S
200
180
160
140
120
100
80
60
40
20
0
ppm

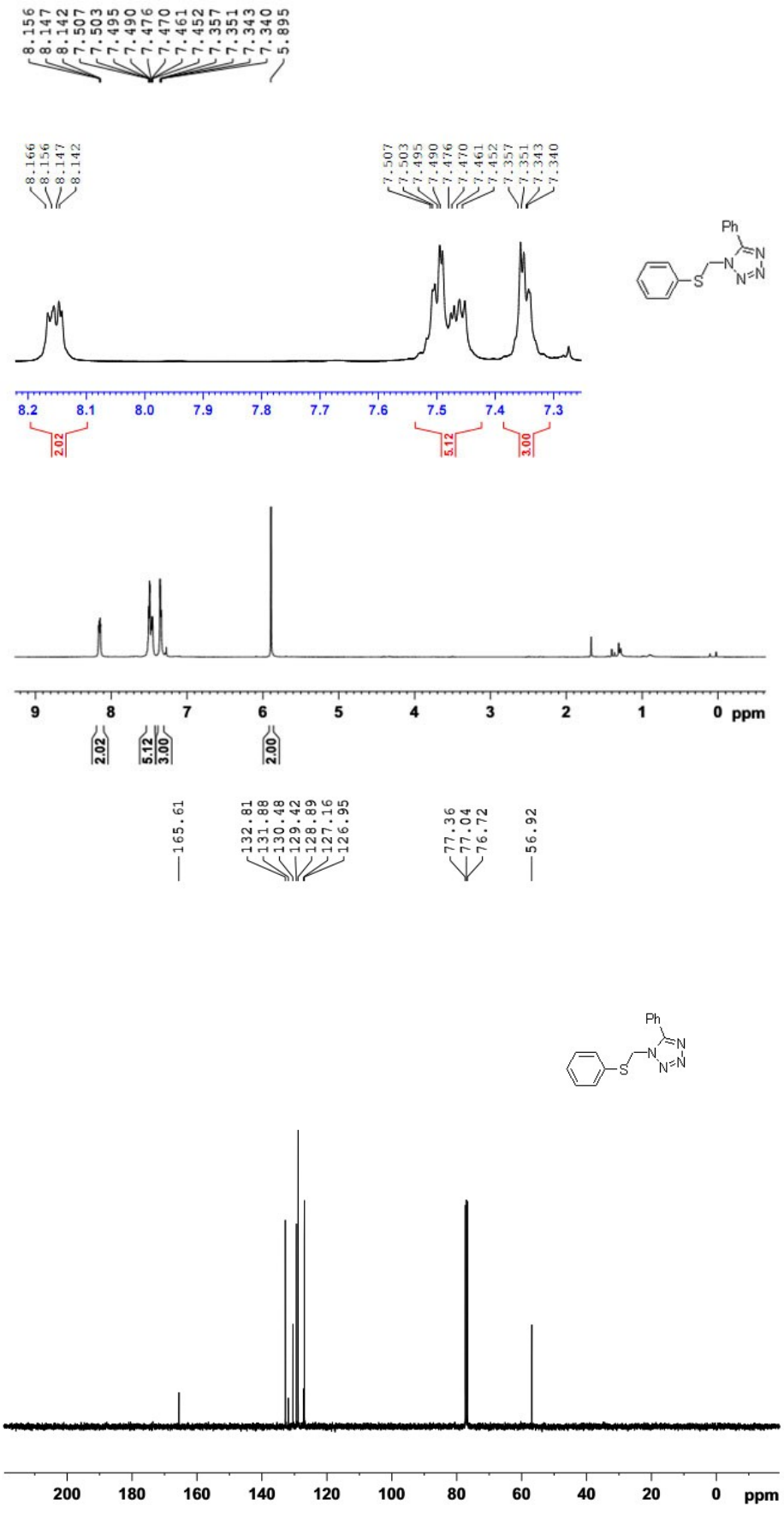
Compound 3p


7.704
7.686
7.273
7.256
7.251
7.237
7.223
7.210
7.192
7.114
7.093
6.747
6.725
5.336
3.768
Br
N
N
MeO
S
9
8
7
6
5
4
3
2
1
0
ppm
1.06
3.02
1.99
2.02
2.00
2.93
161.01
143.11
137.32
134.54
132.90
129.95
123.24
122.93
121.33
119.43
114.86
110.48
77.36
77.04
76.72
55.37
51.16
Br
N
N
MeO
S
200
180
160
140
120
100
80
60
40
20
0
ppm

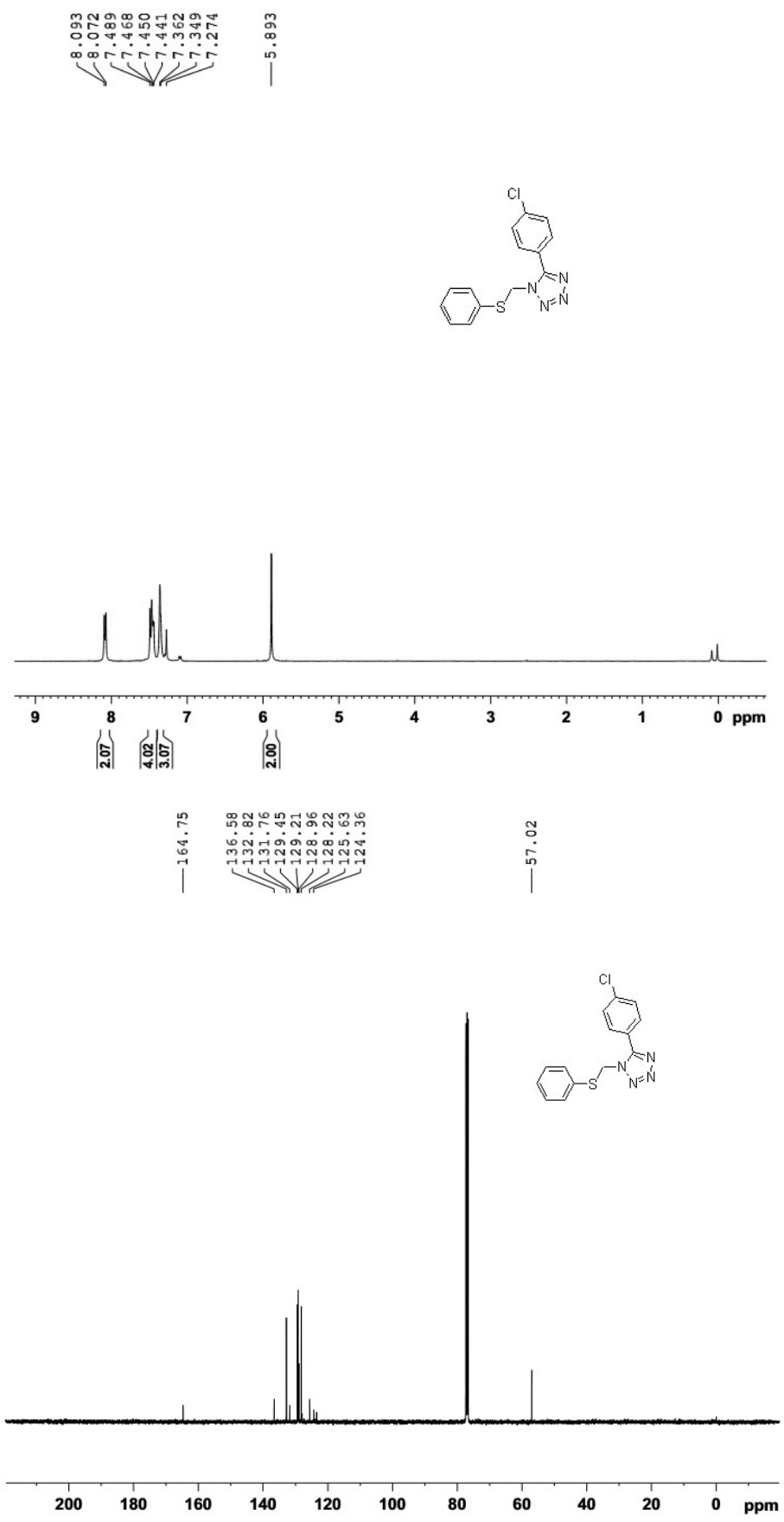
Compound 3q


7.285
7.281
7.272
7.267
7.250
7.247
7.214
7.206
7.193
7.152
7.131
5.394
Br
Br
N
N
S
9
8
7
6
5
4
3
2
1
0
ppm
1.00
5.11
2.03
2.00
143.14
136.73
136.17
134.42
129.80
129.56
129.27
123.43
123.14
119.60
110.32
77.38
77.06
76.74
50.63
Br
Br
N
N
S
200
180
160
140
120
100
80
60
40
20
0
ppm

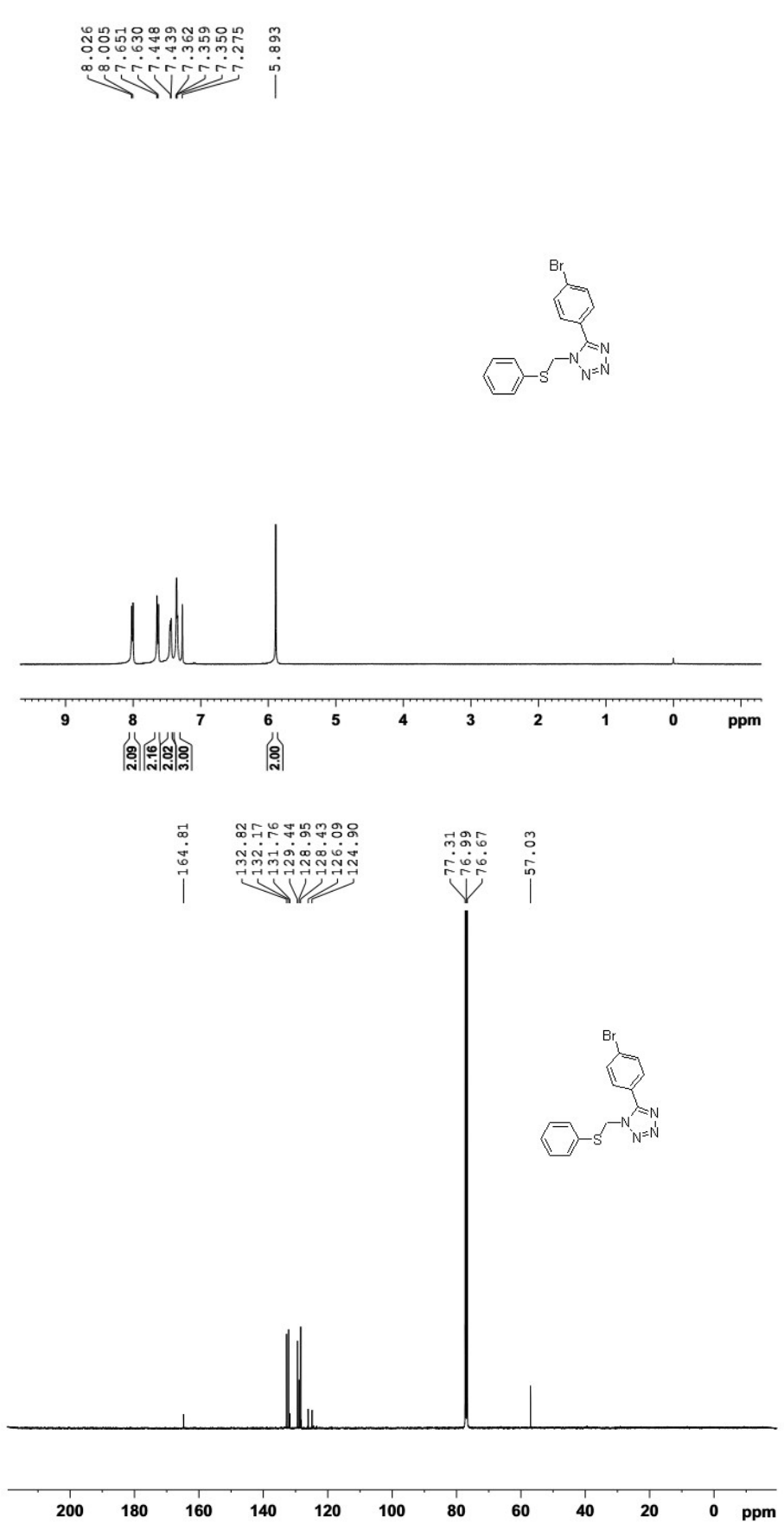
Compound 3r


8.156
8.147
8.142
7.507
7.503
7.495
7.490
7.476
7.470
7.461
7.452
7.357
7.351
7.343
7.340
5.895
8.166
8.156
8.147
8.142
7.507
7.503
7.495
7.490
7.476
7.470
7.461
7.452
7.357
7.351
7.343
7.340
Ph
N
N
N
S
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
2.02
5.12
3.00
9
8
7
6
5
4
3
2
1
0 ppm
2.02
5.12
3.00
2.00
165.61
132.81
131.88
130.48
129.42
128.89
127.16
126.95
77.36
77.04
76.72
56.92
Ph
N
N
N
S
200
180
160
140
120
100
80
60
40
20
0 ppm

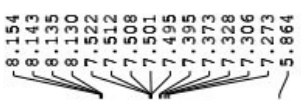
Compound 3s

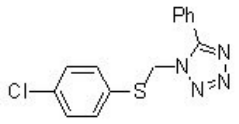

8.093
8.072
7.489
7.468
7.450
7.441
7.362
7.349
7.274
5.893
Cl
N
N
N
S
9
8
7
6
5
4
3
2
1
0 ppm
2.07
4.02
3.07
2.00
164.75
136.58
132.82
131.76
129.45
129.21
128.96
128.22
125.63
124.36
57.02
Cl
N
N
N
S
200
180
160
140
120
100
80
60
40
20
0 ppm

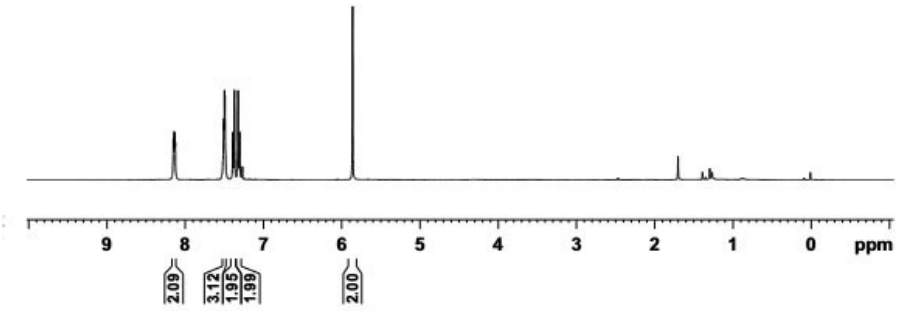
Compound 3t


8.026
8.005
7.651
7.630
7.448
7.439
7.362
7.359
7.350
7.275
5.893
Br
N
N
N
N
S
9
8
7
6
5
4
3
2
1
0
ppm
2.09
2.16
2.02
3.00
2.00
164.81
132.82
132.17
131.76
129.44
128.95
128.43
126.09
124.90
77.31
76.99
76.67
57.03
Br
N
N
N
N
S
200
180
160
140
120
100
80
60
40
20
0
ppm

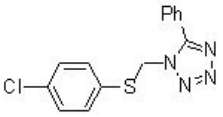
Compound 3u

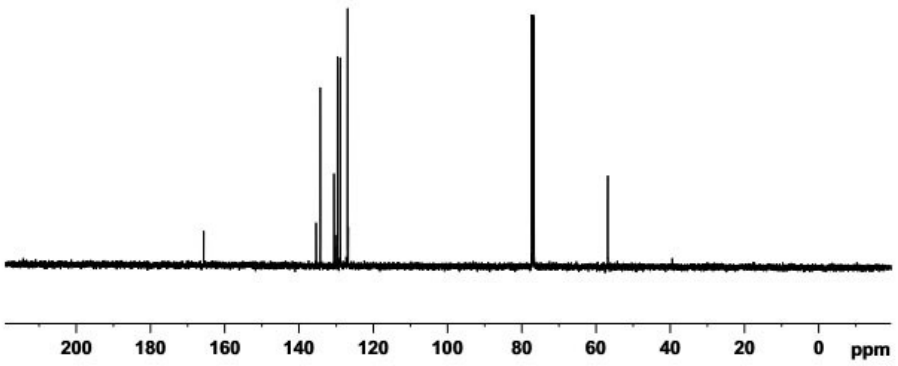

8.154
8.143
8.135
8.130
7.522
7.512
7.508
7.501
7.495
7.395
7.373
7.328
7.306
7.273
5.864


Ph
N
N
N
Cl
S

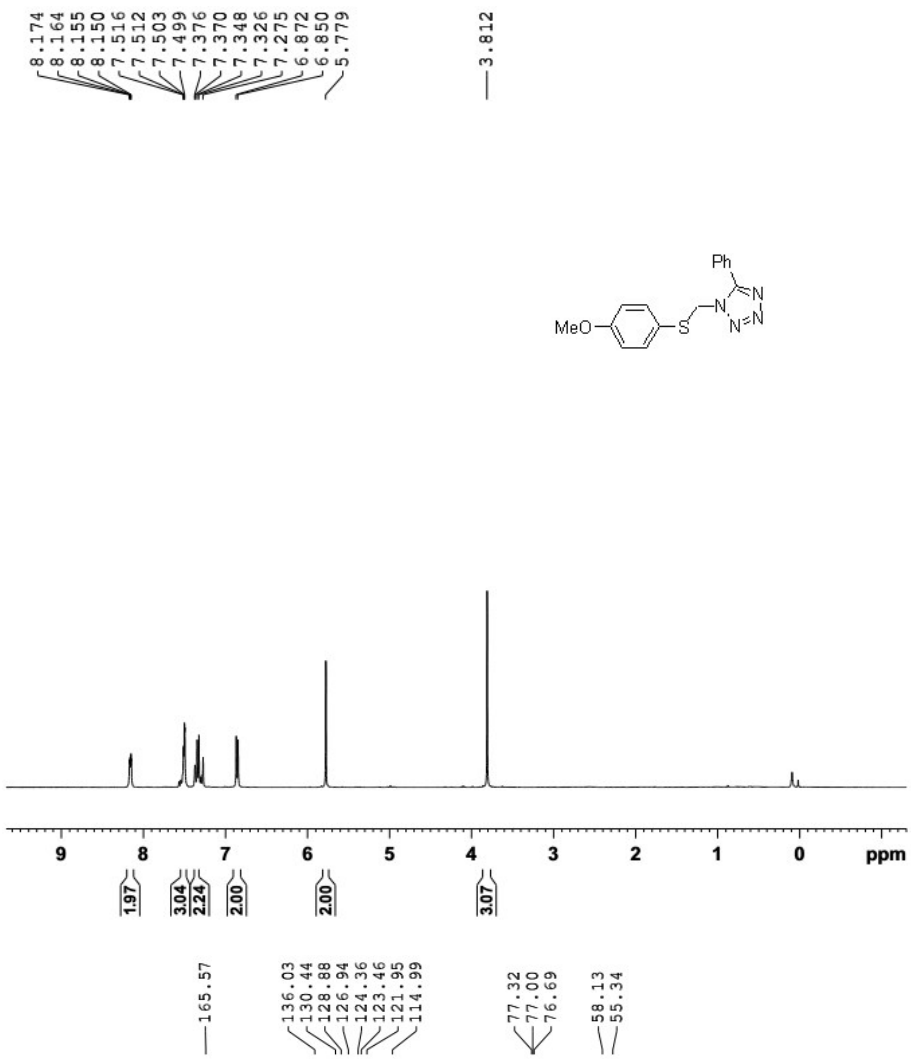

9
8
7
6
5
4
3
2
1
0
ppm
2.09
3.12
1.95
1.99
2.00


165.70
135.43
134.31
130.61
130.32
130.20
129.65
128.96
128.92
126.98
126.94
126.79
77.38
77.06
76.74
56.87

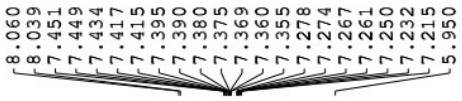

Ph
N
N
N
Cl
S

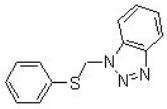

200
180
160
140
120
100
80
60
40
20
0
ppm

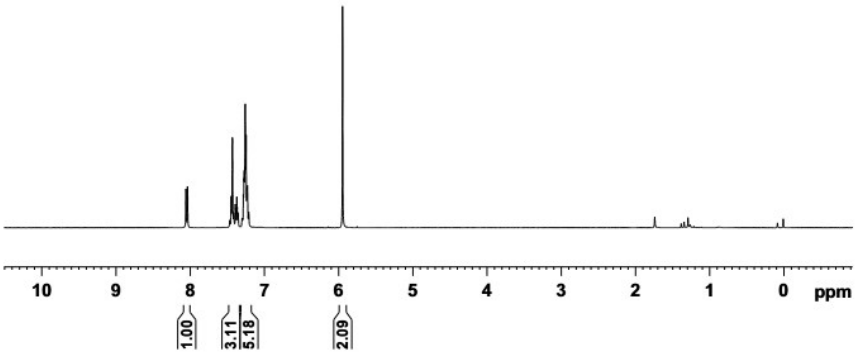
Compound 3v

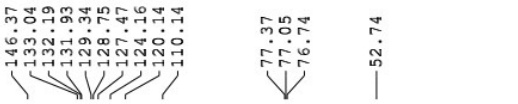

8.174
8.164
8.155
8.150
7.516
7.512
7.503
7.499
7.376
7.370
7.348
7.326
7.275
6.872
6.850
5.779
3.812
Ph
MeO
S
N
N
N
9
8
7
6
5
4
3
2
1
0
ppm
1.97
3.04
2.24
2.00
2.00
3.07
165.57
136.03
130.44
128.88
126.94
124.36
123.46
121.95
114.99
77.32
77.00
76.69
58.13
55.34
200
180
160
140
120
100
80
60
40
20
0
ppm

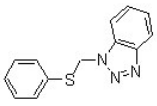
Compound 3w

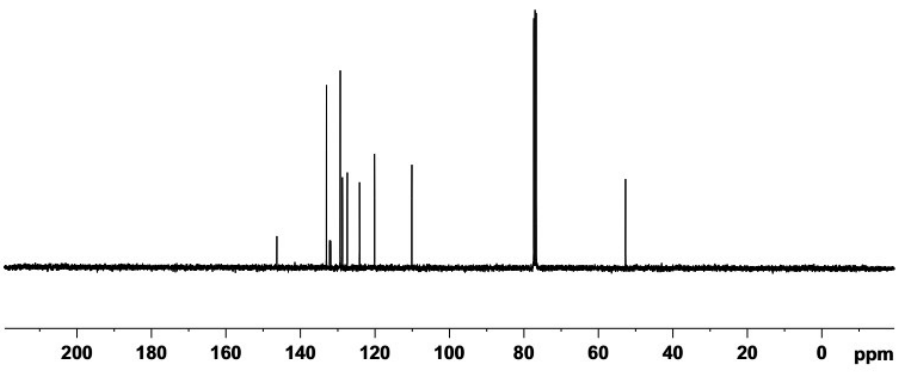

8.060
8.039
7.451
7.449
7.434
7.417
7.415
7.395
7.390
7.380
7.375
7.369
7.360
7.355
7.278
7.274
7.267
7.261
7.250
7.232
7.215
5.950




10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
3.11
5.18
2.09

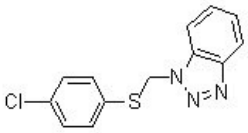

146.37
133.04
132.19
131.93
129.34
128.75
127.47
124.16
120.14
110.14
77.37
77.05
76.74
52.74

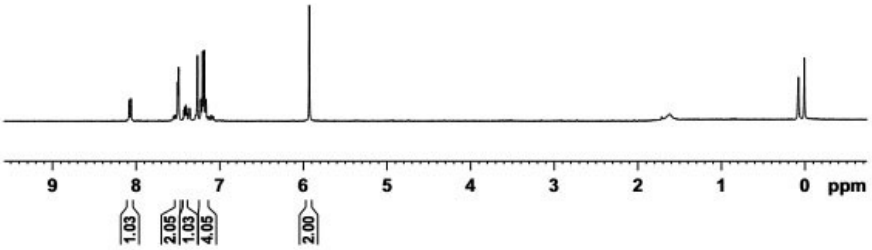



200
180
160
140
120
100
80
60
40
20
0
ppm

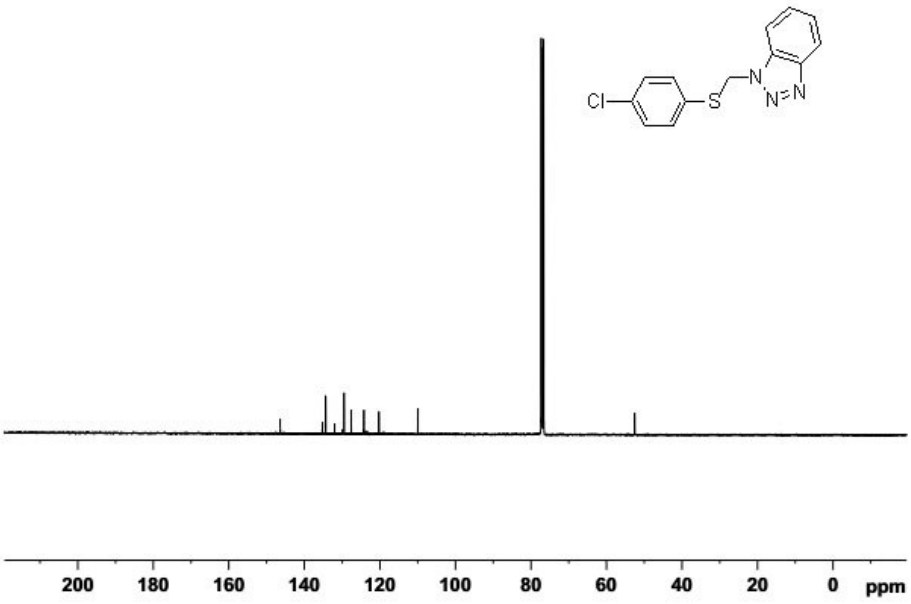
Compound 3x


8.084
8.063
7.506
7.497
7.431
7.421
7.410
7.400
7.390
7.272
7.229
7.208
7.189
7.168
5.932

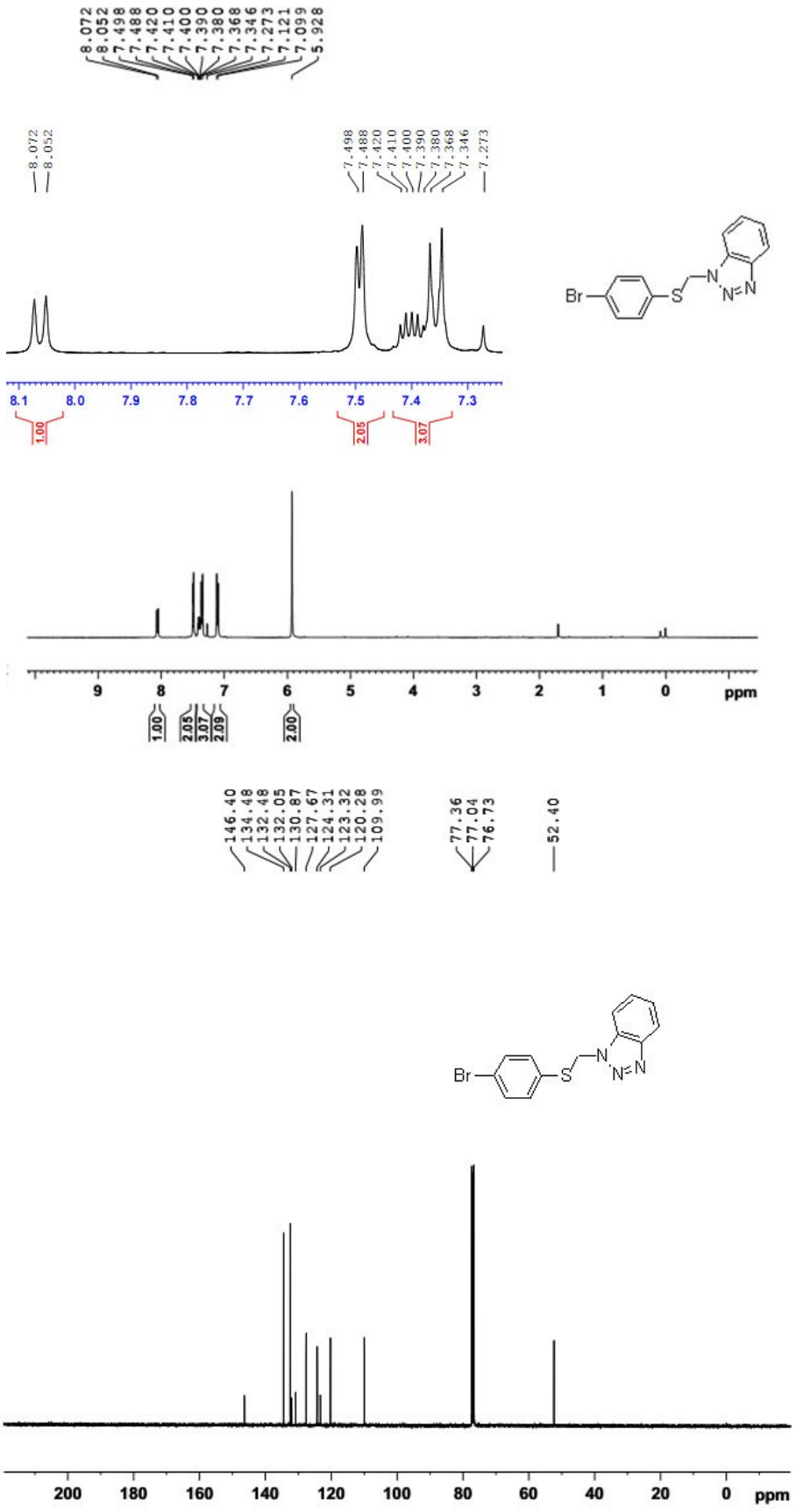

Cl
S
N
N=N


9
8
7
6
5
4
3
2
1
0
ppm
1.03
2.05
1.03
4.05
2.00


146.43
135.27
134.40
130.18
129.54
127.64
124.28
120.30
109.96
77.31
76.99
76.68
52.57


Cl
S
N
N=N
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 3y

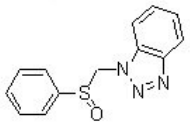

8.072
8.052
7.498
7.488
7.420
7.410
7.400
7.390
7.380
7.368
7.346
7.273
7.121
7.099
5.928
Br
S
N
N=N
ppm
146.40
134.48
132.48
132.05
130.87
127.67
124.31
123.32
120.28
109.99
77.36
77.04
76.73
52.40

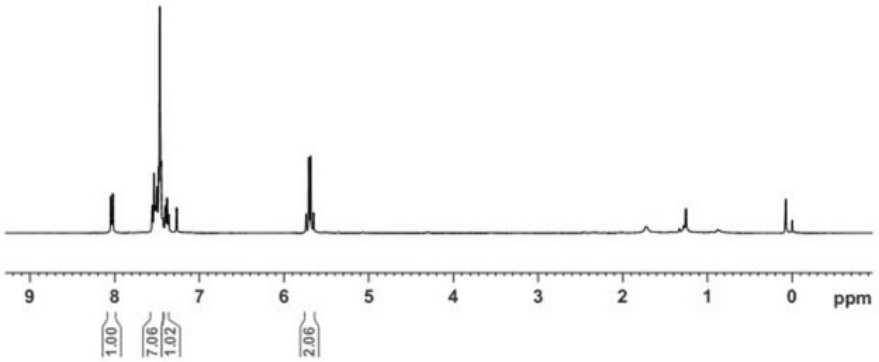
Compound 3z

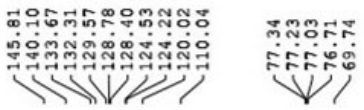

8.072
8.052
7.468
7.452
7.441
7.423
7.409
7.389
7.273
7.116
7.095
6.751
6.729
5.837
3.768
0.009
MeO
S
N
N=N
9
8
7
6
5
4
3
2
1
0
ppm
1.04
3.14
2.06
2.06
2.03
3.00
160.61
146.35
136.04
127.38
124.10
122.00
120.12
114.88
110.19
77.33
77.01
76.70
55.32
53.79
MeO
S
N
N=N
200
180
160
140
120
100
80
60
40
20
0
ppm

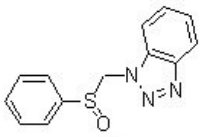
Compound 4

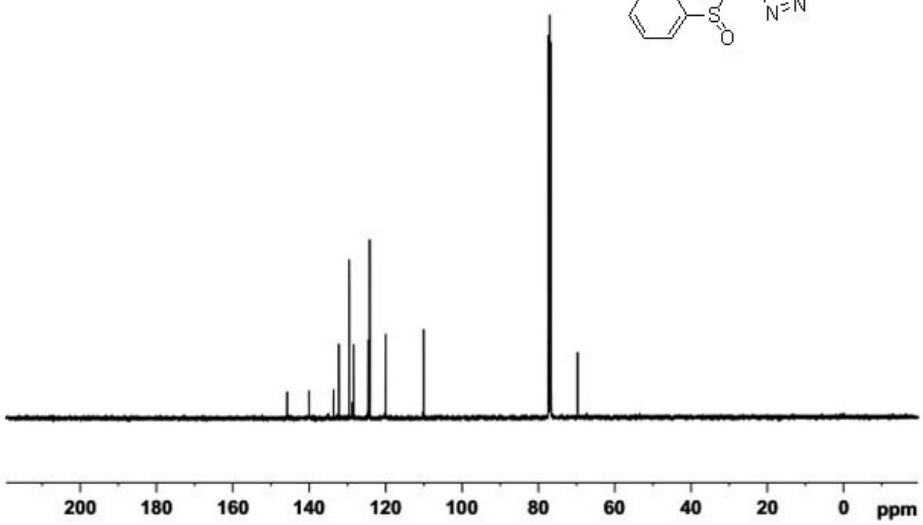

8.047
8.026
7.560
7.539
7.524
7.518
7.503
7.486
7.470
7.456
7.404
7.385
7.271
5.743
5.710
5.689
5.655



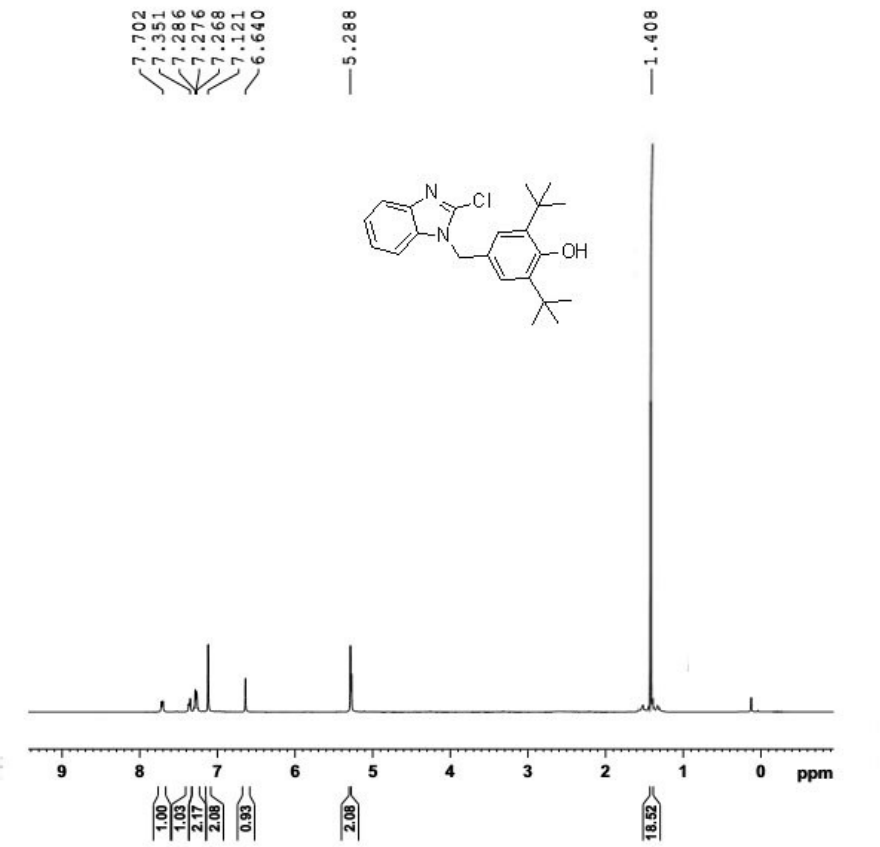

9
8
7
6
5
4
3
2
1
0
ppm
1.00
7.06
1.02
2.06


145.81
140.10
133.67
132.31
129.57
128.78
128.40
124.53
124.22
120.02
110.04
77.34
77.23
77.03
76.71
69.74

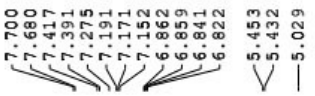


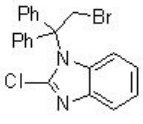

200
180
160
140
120
100
80
60
40
20
0
ppm

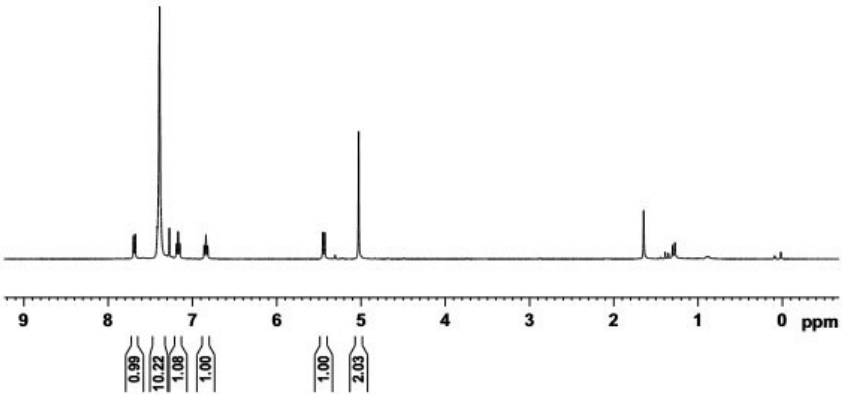
Compound 5


7.702
7.351
7.286
7.276
7.268
7.121
6.640
5.288
1.408
N
Cl
N
OH
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.03
2.17
2.08
0.93
2.08
18.52

Compound 6


7.700
7.680
7.417
7.391
7.275
7.191
7.171
7.152
6.862
6.859
6.841
6.822
5.453
5.432
5.029


Ph
Br
Ph
N
Cl
N


9
8
7
6
5
4
3
2
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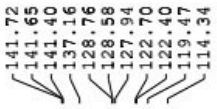
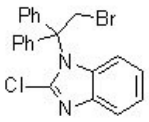
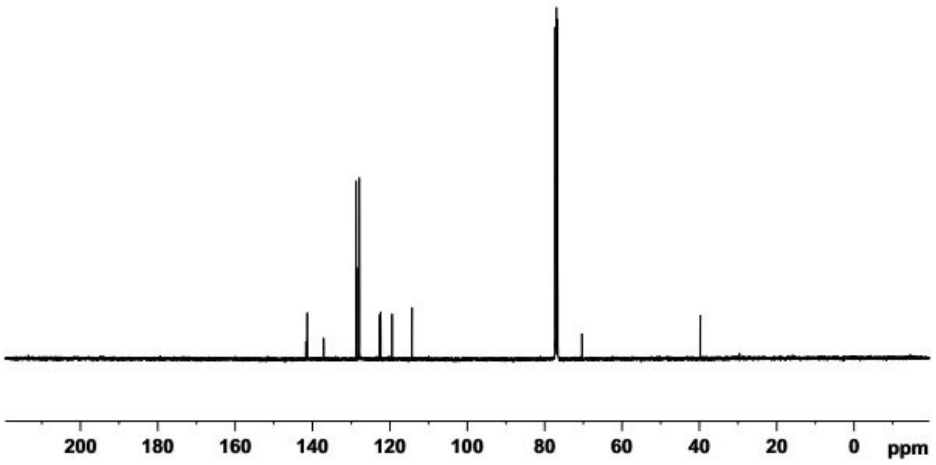
0
ppm
0.99
10.22
1.08
1.00
1.00
2.03


141.72
141.65
141.40
137.16
128.76
128.58
127.94
122.70
122.40
119.47
114.34


77.32
77.01
76.69
70.37

39.78


Ph
Br
Ph
N
Cl
N


200
180
160
140
120
100
80
60
40
20
0
ppm