Supporting Information

A Novel Metal-Free Amidosulfenylation of Alkenes Leading to β-Amino Sulfides

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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 for the preparation of 4 (4a as an example):

Styrene **1a** (0.55 mmol, 57.2 mg), 1*H*-benzo[*d*][1,2,3]triazole **2a** (0.5 mmol, 59.5 mg), diphenyl sulfide **3a** (0.55 mmol, 119.9 mg) and I_2 (0.25 mmol, 64.5 mg) were added in ionic liquid **II** (2.0 mL). The mixture was stirred at room temperature for 5.0 h, upon completion of the reaction (as monitored by TLC), the mixture was quenched with water before extraction 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 over silica gel (EtOAc/petroleum ether = 1:6, v/v) to give compound **4a** (153.9 mg) in 93% yield.

General procedure for the preparation of 4w:

Styrene **1a** (7.15 mmol, 0.7 g), 6-chloropurine (6.5 mmol, 1.0 g), diphenyl sulfide **3a** (7.15 mmol, 1.6 g) and I_2 (3.25 mmol, 0.8 g) were added in ionic liquid **II** (30.0 mL). The mixture was stirred at room temperature for 5.0 h, upon completion of the reaction (as monitored by TLC), the mixture was quenched with water before extraction with dichloromethane (20 × 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 over silica gel (EtOAc/petroleum ether = 1:5, v/v) to give compound **4w** (1.9 g) in 81% yield.

III. Analytical data of products obtained in this study

1-(1-phenyl-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4a). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.92 (q, J = 5.6, 1H), 4.33 (q, J = 8.8, 1H), 5.82 (q, J = 5.6, 1H), 7.24-7.36 (m, 13H), 8.05 (d, J = 8.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.6, 62.3, 109.4, 120.0, 123.9, 127.0, 127.1, 127.2, 128.7, 129.0, 129.1, 130.9, 133.1, 134.4, 137.8, 146.0. HRMS (ESI-TOF) Calcd for $C_{20}H_{18}N_3S$, $[M+H]^+$ 332.1220, Found 332.1206.

1-(2-(phenylthio)-1-(*m*-tolyl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4b). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 2.30 (s, 3H), 3.89 (q, J = 5.6, 1H), 4.31 (q, J = 9.2, 1H), 5.78 (q, J = 5.6, 1H), 7.12-7.39 (m, 12H), 8.05 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 21.4, 39.6, 62.6, 109.5, 120.0, 122.9, 124.1, 127.1, 127.2, 127.5, 128.8, 129.0, 129.1, 129.5, 130.9, 133.2, 134.5, 137.7, 138.8, 146.0. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_3S$, $[M+H]^+$ 346.1376; Found 346.1379.

1-(2-(phenylthio)-1-(*p*-tolyl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4c). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 2.31 (s, 3H), 3.91 (q, J = 5.6, 1H), 4.31 (q, J = 9.2, 1H), 5.82 (q, J = 5.6, 1H), 7.14-7.33 (m, 12H), 7.34 (d, J = 6.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 21.1, 39.5, 62.4, 109.5, 120.0, 123.9, 126.6, 127.1, 127.2, 129.1, 129.6, 129.9, 133.1, 134.5, 138.7, 146.0. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_3S$, $[M+H]^+$ 346.1376; Found 346.1381.

1-(1-(4-(*tert*-butyl)phenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4d). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 1.28 (s, 9H), 3.92 (q, J = 5.6, 1H), 4.32 (q, J = 9.2, 1H), 5.82 (d, J = 5.2, 1H), 7.25-7.35 (m, 12H), 8.05 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 31.2, 39.6, 62.4, 109.5, 110.2, 120.0, 123.9, 125.8, 125.9, 126.0, 126.7, 127.1, 127.2, 130.8, 133.2, 134.5, 134.8, 137.1, 146.0, 151.7. HRMS (ESI-TOF) Calcd for $C_{24}H_{26}N_3S$, $[M+H]^+$ 388.1846; Found 388.1842.

1-(1-(4-(chloromethyl)phenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole

(4e). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.89 (q, J = 6.0, 1H), 4.28 (q, J = 8.8, 1H), 4.53 (s, 2H), 5.82 (d, J = 5.2, 1H), 7.24-7.37 (m, 12H), 7.39 (d, J = 6.8, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.6, 45.4, 62.2, 109.3, 120.1, 124.0, 126.7, 127.2, 127.4, 129.1, 129.2, 130.9, 131.0, 133.1, 134.2, 137.9, 138.0, 146.0. HRMS (ESI-TOF) Calcd for $C_{21}H_{19}N_3ClS$, $[M+H]^+$ 380.0988; Found 380.0993.

1-(1-(2-fluorophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4f). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.93 (q, J = 5.6, 1H), 4.29 (q, J = 9.2, 1H), 6.23 (d, J = 6.0, 1H), 7.07-7.45 (m, 12H), 7.49 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.0, 54.6, 109.2, 115.4, 115.7, 120.0, 124.9, 127.2, 127.4, 128.3, 129.1, 130.4, 130.5, 131.0, 133.3, 134.0, 145.8, 158.6, 161.0. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3$ FS, $[M+H]^+$ 350.1125; Found 350.1129.

1-(1-(4-fluorophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4g). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.90 (q, J = 6.4, 1H), 4.27 (q, J = 8.8, 1H), 5.80 (d, J = 6.4, 1H), 7.01 (t, d, J = 8.4, 2H), 7.24-7.40 (m, 10H), 8.05 (d, J = 12.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.8, 61.9, 109.3, 115.8, 116.0, 120.1, 124.0, 127.2, 127.4, 128.9, 129.2, 130.9, 133.0, 133.6, 134.2, 146.0, 161.5, 161.9. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3$ FS, $[M+H]^+$ 350.1125; Found 350.1131.

1-(1-(2-chlorophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4h). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.84 (q, J = 5.2, 1H), 4.27 (q, J = 9.2, 1H), 6.38 (d, J = 4.8, 1H), 7.22-7.41 (m, 12H), 7.51 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.4, 58.1, 109.4, 120.0, 124.1, 127.3, 127.4, 127.7, 128.5, 129.0, 129.7, 129.9, 131.5, 132.7, 133.5, 134.1, 135.5, 145.8. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3ClS$, $[M+H]^+$ 366.0832; Found 366.0839.

1-(1-(3-chlorophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4i). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.88 (q, J = 6.0, 1H), 4.26 (q, J = 9.2, 1H), 5.75 (d, J = 6.0, 1H), 7.25-7.44 (m, 12H), 8.07 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.7, 62.0, 109.2, 120.2, 124.1, 125.2, 127.2, 127.4, 127.5, 129.0, 129.2,

130.3, 131.1, 133.0, 134.0, 134.9, 139.7, 146.0. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3ClS$, $[M+H]^+$ 366.0832; Found 366.0837.

1-(1-(4-chlorophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4j). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.90 (q, J = 6.4, 1H), 4.26 (q, J = 8.4, 1H), 5.78 (d, J = 6.4, 1H), 7.23-7.42 (m, 12H), 8.08 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.6, 61.9, 109.2, 120.2, 124.1, 127.3, 127.4, 128.4, 129.1, 129.2, 131.0, 133.0, 134.1, 134.7, 136.2, 146.0. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3ClS$, $[M+H]^+$ 366.0832; Found 366.0838.

1-(1-(3-bromophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4k). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.88 (q, J = 6.0, 1H), 4.27 (q, J = 8.8, 1H), 5.75 (d, J = 6.0, 1H), 7.17-7.53 (m, 12H), 8.09 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.7, 61.9, 109.2, 120.2, 123.0, 124.1, 125.7, 127.4, 127.5, 129.2, 130.1, 130.5, 131.1, 131.9, 133.0, 134.0, 139.9, 145.9. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3BrS$, $[M+H]^+$ 410.0327; Found 410.0330.

1-(1-(4-bromophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4l). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.87 (q, J = 6.0, 1H), 4.27 (q, J = 8.8, 1H), 5.77 (d, J = 6.4, 1H), 7.23-7.40 (m, 12H), 7.45 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.6, 61.9, 109.2, 120.1, 122.9, 124.1, 127.3, 127.5, 128.7, 129.2, 131.0, 132.1, 133.0, 134.1, 136.7, 146.0. HRMS (ESI-TOF) Calcd for Calcd for $C_{20}H_{17}N_3BrS$, $[M+H]^+$ 410.0327; Found 410.0334.

1-(1-(2,6-dichlorophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4m). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 4.35 (q, J = 8.4, 1H), 4.83 (q, J = 6.4, 1H), 6.70 (d, J = 6.8, 1H), 7.00 (d, J = 7.2, 1H), 7.18-7.41 (m, 10H), 8.08 (d, J = 6.8, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 35.0, 59.8, 109.5, 120.0, 123.9, 126.9, 127.3, 129.0, 129.7, 130.5, 131.5, 132.8, 135.0, 136.0, 146.2. HRMS (ESI-TOF) Calcd for $C_{20}H_{16}N_3Cl_2S$, $[M+H]^+$ 400.0445; Found 400.0439.

1-(1,2-diphenylpropan-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (4n). Colourless liquid;

^{1}H NMR (400 MHz; $CDCl_3$): δ = 2.26 (s, 3H), 4.14 (d, J = 13.6, 1H), 4.35 (d, J = 13.6, 1H), 6.35 (d, J = 8.8, 1H), 7.09-7.32 (m, 12H), 8.02 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 26.5, 46.9, 67.8, 111.9, 120.0, 123.5, 126.1, 126.5, 126.6, 128.3, 128.7, 128.8, 130.5, 132.2, 135.8, 141.6, 146.8. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_3S$, $[M+H]^+$ 346.1377; Found 346.1382.

1-(1-phenyl-3-(phenylthio)propan-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (4o). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.27 (m, 1H), 4.00 (t, J = 7.2, 1H), 4.68-4.85 (m, 2H), 5.02 (t, J = 7.2, 1H), 7.21-7.31 (m, 13H), 7.35 (d, J = 7.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 38.8, 44.1, 55.2, 109.3, 120.0, 120.2, 123.9, 124.1, 126.9, 127.2, 127.3, 127.6, 127.7, 128.5, 128.6, 128.9, 129.1, 129.3, 132.5, 133.2, 137.5, 138.1. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_3S$, $[M+H]^+$ 346.1378; Found 346.1372.

1-(1-(phenylthio)pentan-2-yl)-1*H*-benzo[*d*][1,2,3]triazole (4p). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 0.82-0.90 (m, 3H), 1.55-1.63 (m, 2H), 2.30-2.34 (m, 2H), 3.51-3.67 (m, 2H), 4.77 (d, J = 4.4, 1H), 7.21-7.44 (m, 8H), 8.03 (q, J = 6.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 13.7, 19.3, 36.3, 39.5, 59.3, 109.2, 109.3, 120.0, 123.7, 126.9, 127.0, 127.3, 127.6, 129.0, 129.1, 130.4, 132.4, 145.7. HRMS (ESI-TOF) Calcd for $C_{17}H_{20}N_3S$, $[M+H]^+$ 298.1378; Found 298.1375.

5-chloro-1-(1-phenyl-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4q). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.87 (q, J = 5.2, 1H), 4.25-4.32 (m, 1H), 5.73-5.79 (m, 1H), 7.22-7.35 (m, 12H), 7.40 (t, J = 9.2, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.6, 62.9, 109.3, 110.4, 119.4, 121.0, 125.2, 126.6, 126.9, 128.9, 129.1, 129.2, 130.9, 131.0, 133.7, 137.4, 144.5, 146.6. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3ClS$, $[M+H]^+$ 366.0832; Found 366.0836.

5-chloro-1-(1-phenyl-2-(phenylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4r). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 3.62 (q, J = 5.6, 1H), 3.94 (q, J = 9.2, 1H), 5.37 (q, J = 5.6, 1H), 7.27-7.40 (m, 10H), 7.98 (s, 1H), 8.05 (s, 1H). ^{13}C

NMR (100 MHz; $CDCl_3$): δ = 39.3, 63.4, 127.1, 127.2, 128.9, 129.0, 129.2, 130.7, 134.2, 137.5, 143.3, 152.1. HRMS (ESI-TOF) Calcd for $C_{16}H_{16}N_3S$, $[M+H]^+$ 282.1063; Found 282.1069.

1-(1-phenyl-2-(phenylthio)ethyl)-1*H*-imidazole (4s). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.65 (q, J = 5.6, 1H), 4.04 (q, J = 8.8, 1H), 5.39 (q, J = 6.0, 1H), 6.28 (s, 1H), 7.24-7.40 (m, 11H), 7.62 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.5, 65.0, 105.5, 126.7, 126.9, 128.3, 128.8, 129.1, 129.4, 130.3, 135.2, 139.3, 139.7. HRMS (ESI-TOF) Calcd for $C_{17}H_{17}N_2S$, $[M+H]^+$ 281.1112; Found 281.1109.

4-chloro-1-(1-phenyl-2-(phenylthio)ethyl)-1*H*-pyrazole (4t). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.61 (q, J = 5.6, 1H), 3.97 (q, J = 9.2, 1H), 5.28 (q, J = 5.6, 1H), 7.25-7.38 (m, 11H), 7.49 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.1, 65.8, 110.1, 126.9, 127.4, 128.6, 128.9, 129.1, 130.5, 134.8, 138.0, 138.5. HRMS (ESI-TOF) Calcd for $C_{17}H_{16}N_2ClS$, $[M+H]^+$ 315.0723; Found 315.0726.

1-(1-phenyl-2-(phenylthio)ethyl)-1*H*-benzo[*d*]imidazole (4u). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.82 (dd, J_1 = 1.6, J_2 = 6.8, 1H), 5.56 (t, J = 7.6, 1H), 7.09-7.36 (m, 11H), 7.83 (d, J = 8.0 Hz, 1H), 8.05 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.1, 65.8, 110.1, 126.9, 127.4, 128.6, 128.9, 129.1, 130.5, 134.8, 138.0, 138.5. HRMS (ESI-TOF) Calcd for $C_{21}H_{19}N_2S$, $[M+H]^+$ 331.1267; Found 339.1264.

5-phenyl-1-(1-phenyl-2-(phenylthio)ethyl)-1*H*-tetrazole (4v). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.76 (q, J = 5.2, 1H), 4.11 (q, J = 10.0, 1H), 6.03 (q, J = 5.2, 1H), 7.25-7.50 (m, 13H), 8.14 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 40.0, 67.4, 126.9, 127.2, 127.4, 127.6, 128.8, 129.0, 129.2, 130.3, 131.7, 133.6, 136.4, 165.1. HRMS (ESI-TOF) Calcd for $C_{21}H_{19}N_4S$, $[M+H]^+$ 359.1330; Found 359.1335.

6-chloro-7-(1-phenyl-2-(phenylthio)ethyl)-7*H*-purine (4w). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.79 (q, J = 5.2, 1H), 4.29 (q, J = 10.0, 1H), 5.74 (q, J = 4.8, 1H), 7.19-7.41 (m, 10H), 7.43 (s, 1H), 8.07 (s, 1H). ^{13}C NMR (100 MHz; $CDCl_3$):

δ = 38.1, 60.9, 127.1, 127.5, 129.0, 129.1, 129.2, 131.2, 131.9, 133.1, 137.1, 144.5, 151.0, 151.6, 151.7. HRMS (ESI-TOF) Calcd for $C_{19}H_{16}N_4SCl$ $[M+H]^+$ 367.0785; Found 367.0790.

4-methyl-*N*-(1-phenyl-2-(phenylthio)ethyl)benzenesulfonamide (4x). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 2.39 (s, 3H), 3.22 (q, J = 7.6, 2H), 4.34 (d, J = 7.0, 1H), 7.08-7.24 (m, 12H), 7.27 (d, J = 6.8, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 21.4, 41.1, 56.6, 126.1, 126.8, 127.1, 127.2, 127.9, 128.5, 129.0, 129.4, 130.2, 134.3, 136.0, 139.2, 143.2. HRMS (ESI-TOF) Calcd for $C_{21}H_{22}NS_2O_2$ $[M+H]^+$ 384.1089; Found 384.1093.

4-chloro-*N*-(1-phenyl-2-(phenylthio)ethyl)benzenesulfonamide (4y). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.14-3.25 (m, 2H), 4.31-4.35 (m, 1H), 5.48 (d, J = 4.8, 1H), 7.06-7.26 (m, 11H), 7.28 (d, J = 8.8, 2H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 41.2, 56.6, 126.8, 127.0, 128.1, 128.6, 128.9, 129.2, 130.3, 133.8, 138.4, 138.8, 138.9. HRMS (ESI-TOF) Calcd for $C_{20}H_{19}NClS_2O_2$ $[M+H]^+$ 404.0545; Found 404.0549.

1-(1-phenyl-2-(*p*-tolylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4z). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 2.32 (s, 3H), 3.87 (q, J = 5.6, 1H), 4.29 (q, J = 9.2, 1H), 5.84 (q, J = 6.4, 1H), 7.07 (d, J = 8.0, 2H), 7.22-7.37 (m, 10H), 8.04 (d, J = 8.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 21.1, 40.2, 62.6, 109.5, 120.0, 123.9, 126.7, 128.7, 128.9, 129.9, 130.6, 131.6, 133.2, 137.4, 137.9, 146.0. HRMS (ESI-TOF) Calcd for $C_{21}H_{20}N_3S$ $[M+H]^+$ 346.1377; Found 346.1373.

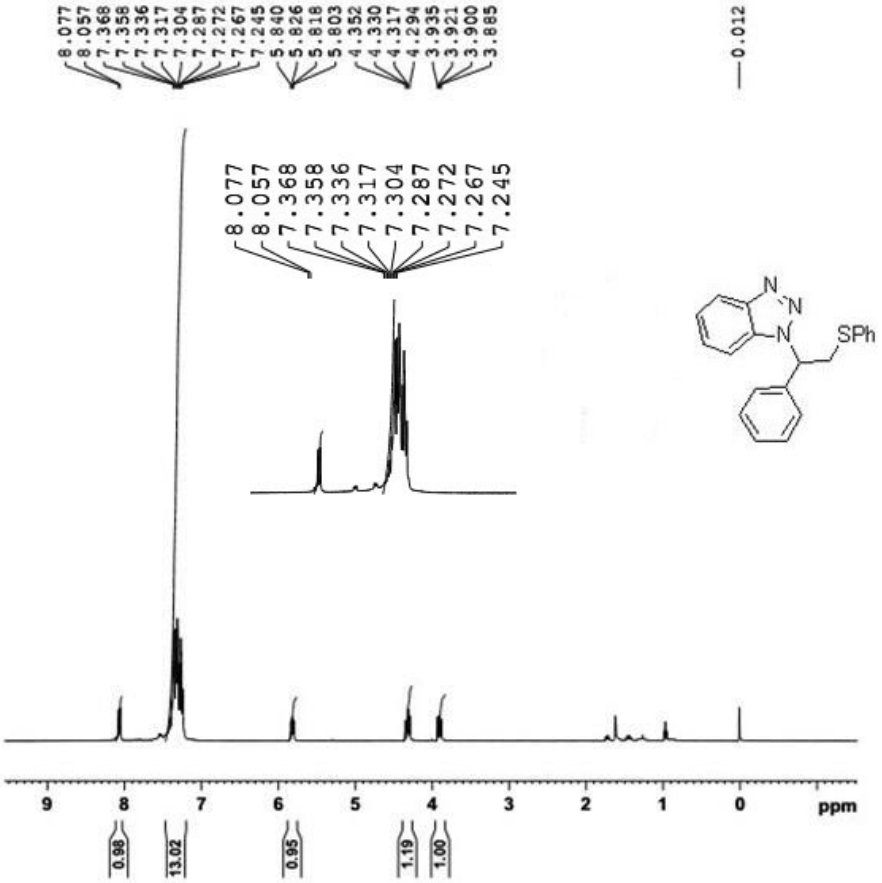
1-(2-((4-chlorophenyl)thio)-1-phenylethyl)-1*H*-benzo[*d*][1,2,3]triazole (4aa). Colourless liquid; ^1H NMR (400 MHz; $CDCl_3$): δ = 3.88 (q, J = 5.6, 1H), 4.30 (q, J = 9.2, 1H), 5.85 (q, J = 5.6, 1H), 7.19-7.35 (m, 11H), 7.36 (d, J = 3.6, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 39.8, 62.8, 109.5, 120.0, 124.0, 126.7, 127.4, 128.8, 129.0, 132.2, 132.9, 133.1, 133.2, 137.6, 146.0. HRMS (ESI-TOF) Calcd for $C_{20}H_{17}N_3ClS$ $[M+H]^+$ 366.0832; Found 366.0828.

1-(2-(methylthio)-1-phenylethyl)-1*H*-benzo[*d*][1,2,3]triazole (4ab). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 2.00 (s, 3H), 3.56 (q, J = 6.4, 1H), 3.91 (q, J = 8.8, 1H), 5.91 (q, J = 6.4, 1H), 7.27-7.43 (m, 8H), 8.07 (d, J = 8.4, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 16.3, 39.2, 63.7, 109.5, 120.1, 124.0, 127.0, 127.3, 128.7, 128.9, 133.0, 138.0, 146.1. HRMS (ESI-TOF) Calcd for $C_{15}H_{16}N_3S$, $[M+H]^+$ 270.1064; Found 270.1069.

1-(1-(4-chlorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4ac). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 2.01 (s, 3H), 3.54 (q, J = 6.8, 1H), 3.86 (q, J = 8.4, 1H), 5.88 (q, J = 6.8, 1H), 7.27-7.44 (m, 7H), 8.09 (d, J = 8.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 16.4, 39.2, 63.0, 109.3, 120.2, 124.1, 127.5, 128.4, 129.2, 132.9, 134.7, 136.5, 146.1. HRMS (ESI-TOF) Calcd for $C_{15}H_{15}ClN_3S$, $[M+H]^+$ 304.0677; Found 304.0673.

1-(2-(methylthio)-1-(p-tolyl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (4ad). Colourless liquid; ^{1}H NMR (400 MHz; $CDCl_3$): δ = 2.01 (s, 3H), 2.32 (s, 3H), 3.53 (q, J = 6.0, 1H), 3.88 (q, J = 8.8, 1H), 5.89 (t, J = 7.2, 1H), 7.16. (d, J = 7.6, 2H), 7.30-7.40 (m, 5H), 8.08 (d, J = 8.0, 1H). ^{13}C NMR (100 MHz; $CDCl_3$): δ = 16.3, 21.1, 39.2, 63.5, 109.6, 120.0, 123.9, 126.9, 127.2, 129.6, 133.0, 135.0, 138.6, 146.1. HRMS (ESI-TOF) Calcd for $C_{16}H_{18}N_3S$, $[M+H]^+$ 284.1221; Found 284.1226.

Compound 4a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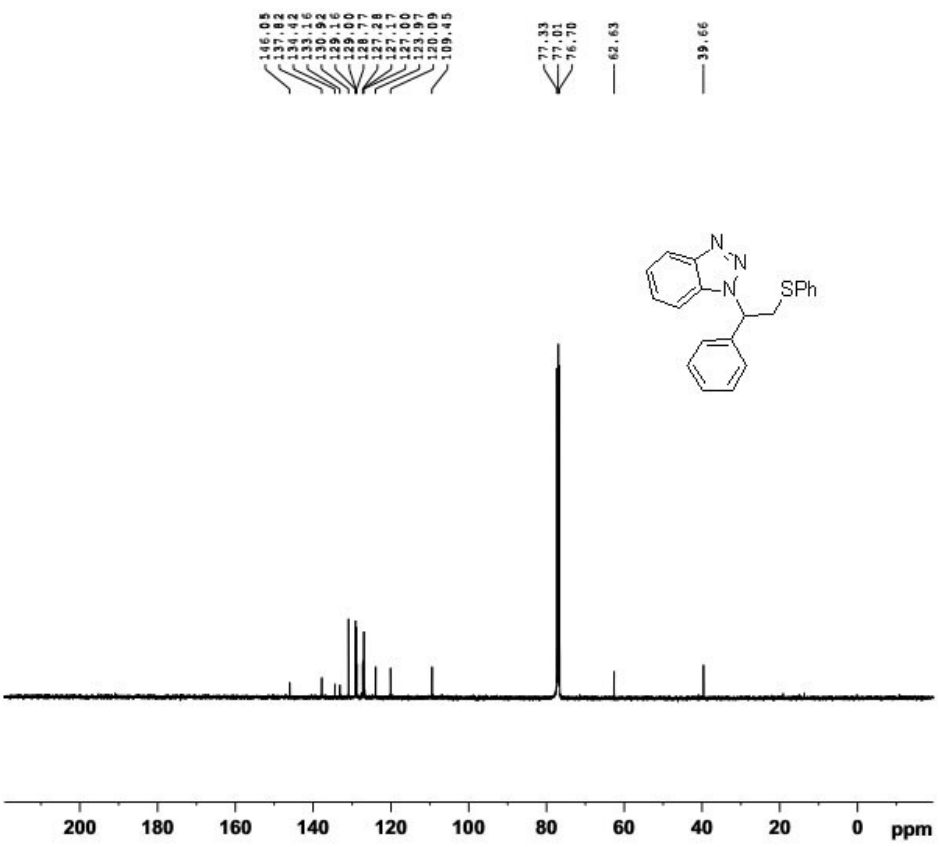
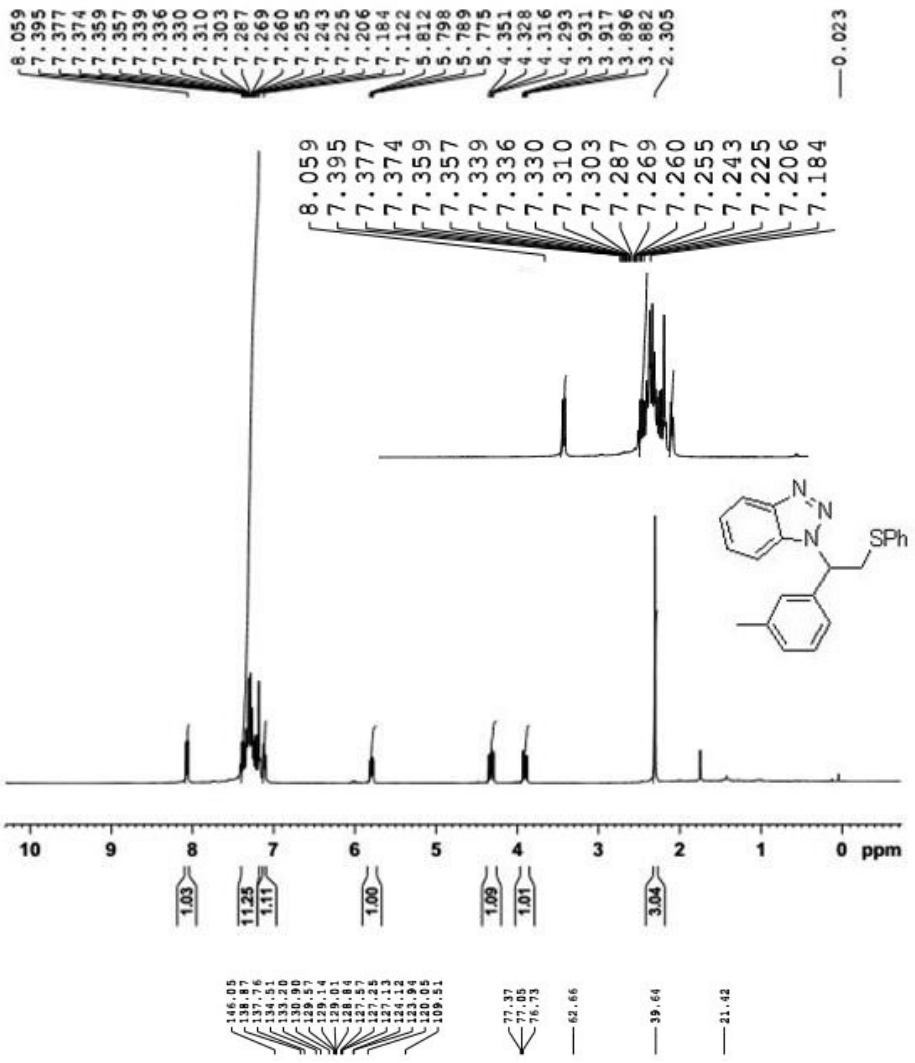
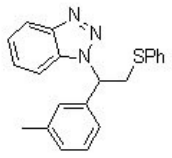
8.057
7.368
7.358
7.336
7.317
7.304
7.287
7.272
7.267
7.245
5.840
5.826
5.818
5.803
4.352
4.330
4.317
4.294
3.935
3.921
3.900
3.885
0.012
N
N
N
SPh
9
8
7
6
5
4
3
2
1
0
ppm
0.98
13.02
0.95
1.19
1.00

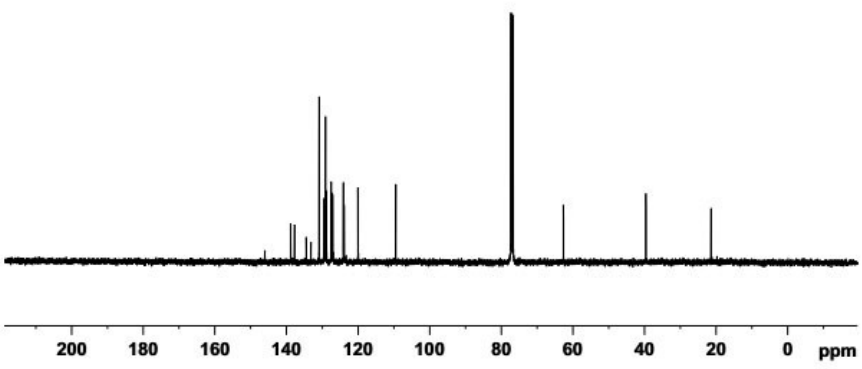

146.05
137.82
134.42
133.16
130.92
129.16
129.00
128.77
127.28
127.17
127.00
125.97
120.09
109.45
77.33
77.01
76.70
62.63
39.66
N
N
N
SPh
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 4b

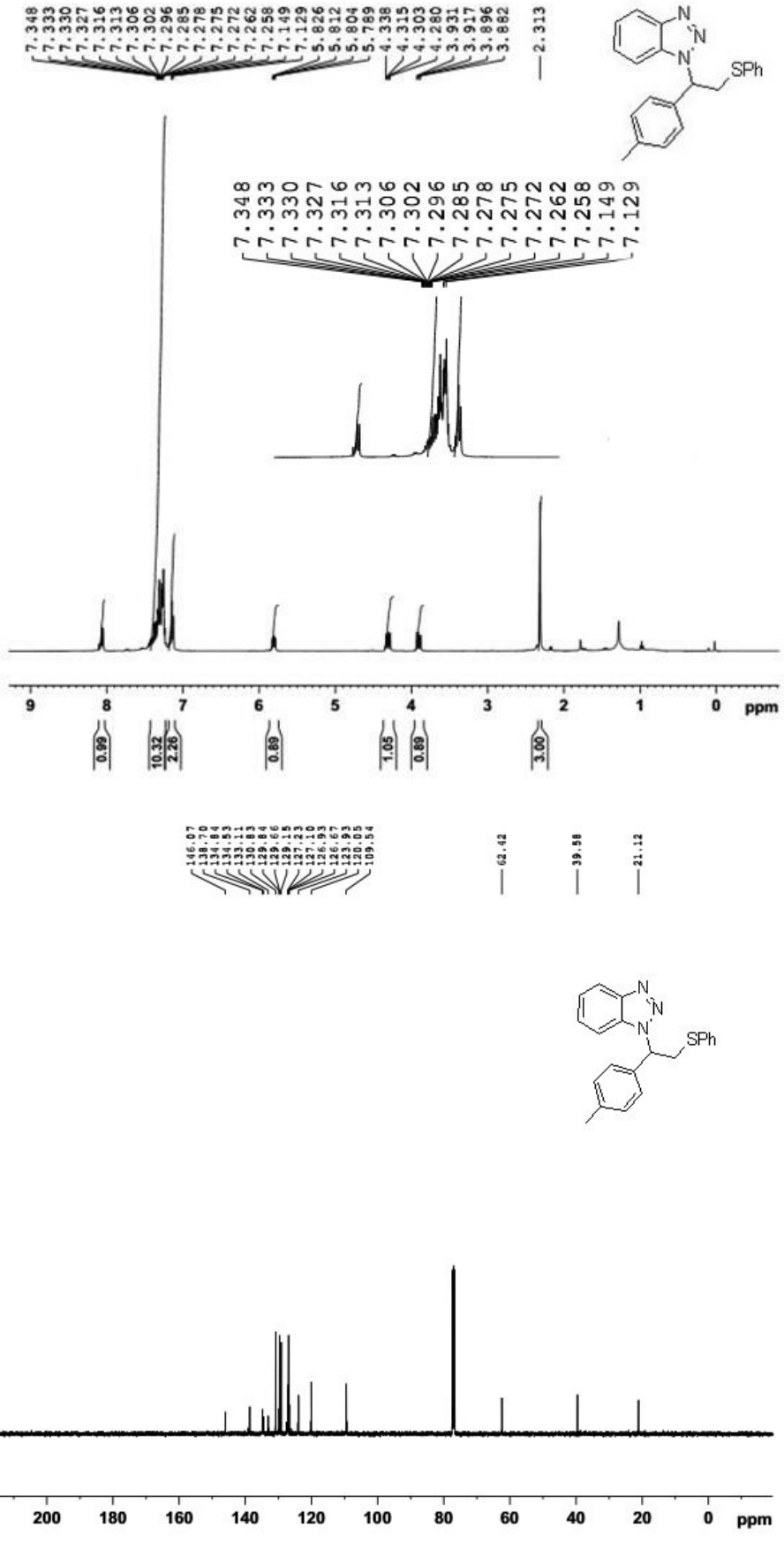

8.059
7.395
7.377
7.374
7.359
7.357
7.339
7.336
7.330
7.310
7.303
7.287
7.269
7.260
7.255
7.243
7.225
7.206
7.184
7.122
5.812
5.798
5.789
5.775
4.351
4.328
4.316
4.293
3.931
3.917
3.896
3.882
2.305
0.023
SPh
10 9 8 7 6 5 4 3 2 1 0 ppm
1.03
11.25
1.11
1.00
1.09
1.01
3.04

146.05
138.87
138.76
134.51
133.20
130.90
129.57
129.14
129.01
128.84
127.57
127.25
127.13
124.12
121.84
120.05
109.51
77.37
77.05
76.73
62.66
39.64
21.42

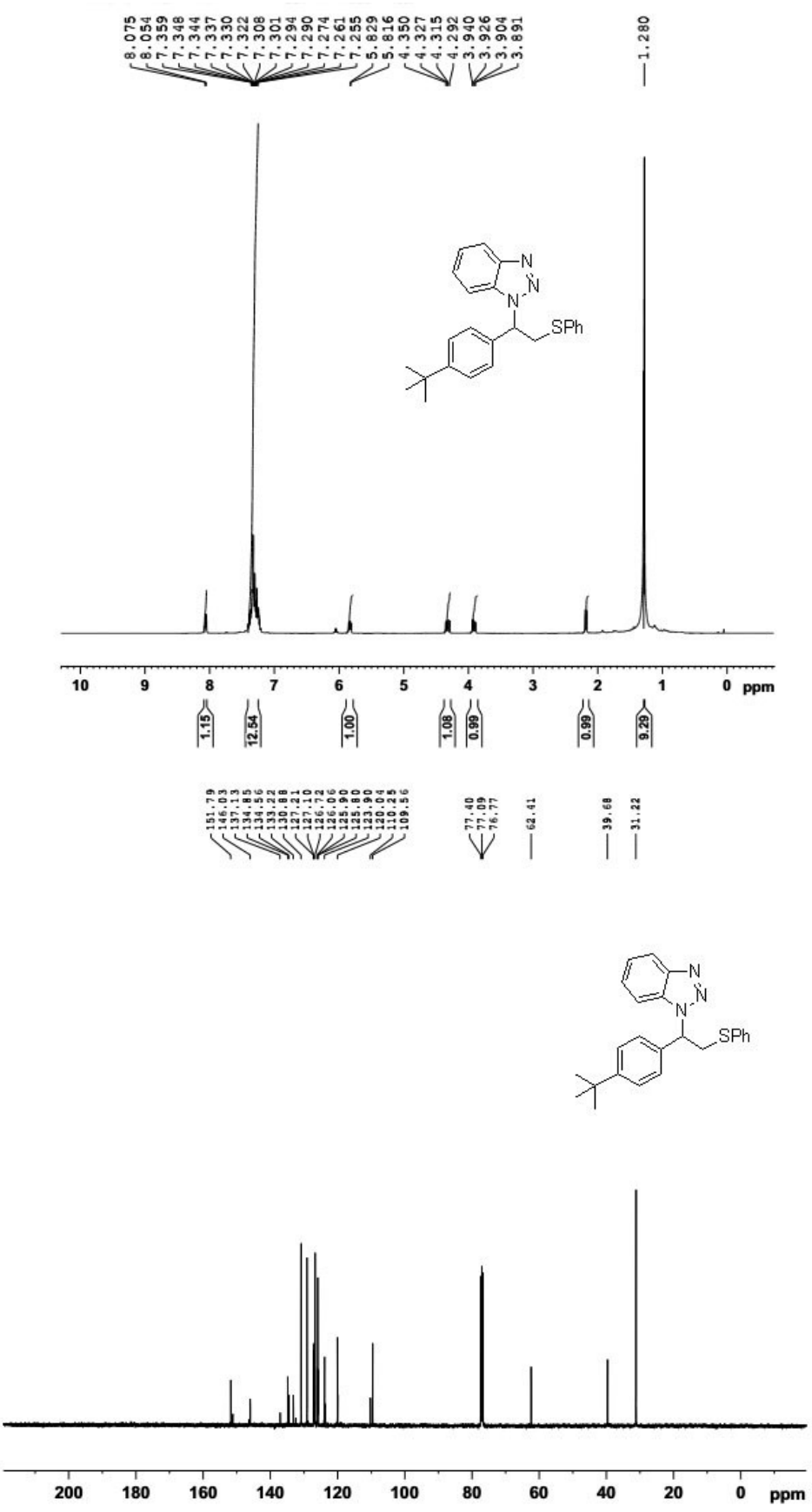

SPh


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

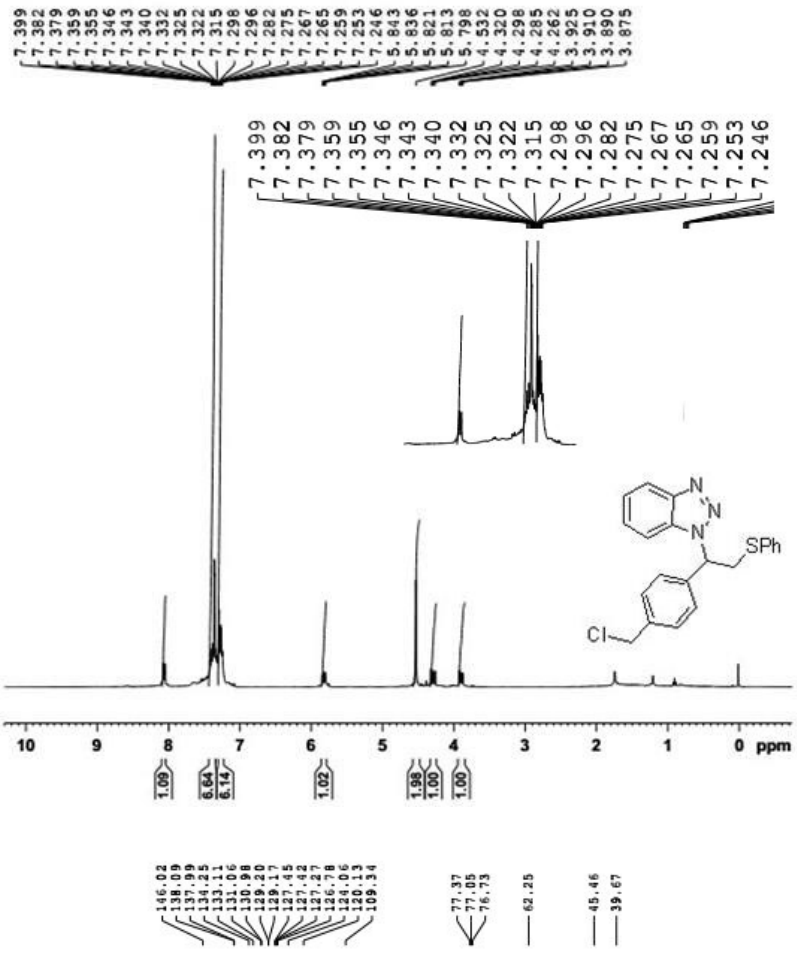
Compound 4c


7.348
7.333
7.330
7.327
7.316
7.313
7.306
7.302
7.296
7.285
7.278
7.275
7.272
7.262
7.258
7.149
7.129
5.826
5.812
5.804
5.789
4.338
4.315
4.303
4.280
3.931
3.917
3.896
3.882
2.313
SPh
9
8
7
6
5
4
3
2
1
0
ppm
0.99
10.32
2.26
0.89
1.05
0.89
3.00
146.07
138.70
134.44
134.53
133.11
130.83
129.84
129.66
129.15
127.23
127.10
126.93
126.67
123.93
120.05
109.54
62.42
39.58
21.12
200
180
160
140
120
100
80
60
40
20
0
ppm

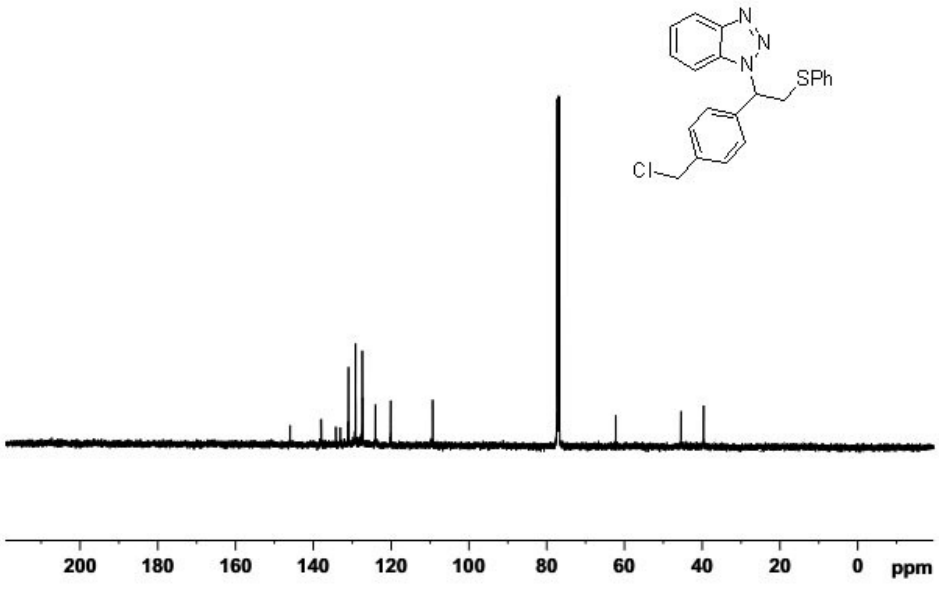
Compound 4d


8.075
8.054
7.359
7.348
7.344
7.337
7.330
7.322
7.308
7.301
7.294
7.290
7.274
7.261
7.255
5.829
5.816
4.350
4.327
4.315
4.292
3.940
3.926
3.904
3.891
1.280
N
N
N
SPh
10 9 8 7 6 5 4 3 2 1 0 ppm
1.15
12.54
1.00
1.08
0.99
0.99
9.29
151.79
146.03
137.13
134.85
134.56
133.22
130.88
127.21
127.10
126.72
126.06
125.90
125.80
123.90
120.04
110.25
109.56
77.40
77.09
76.77
62.41
39.68
31.22
N
N
N
SPh
200 180 160 140 120 100 80 60 40 20 0 ppm

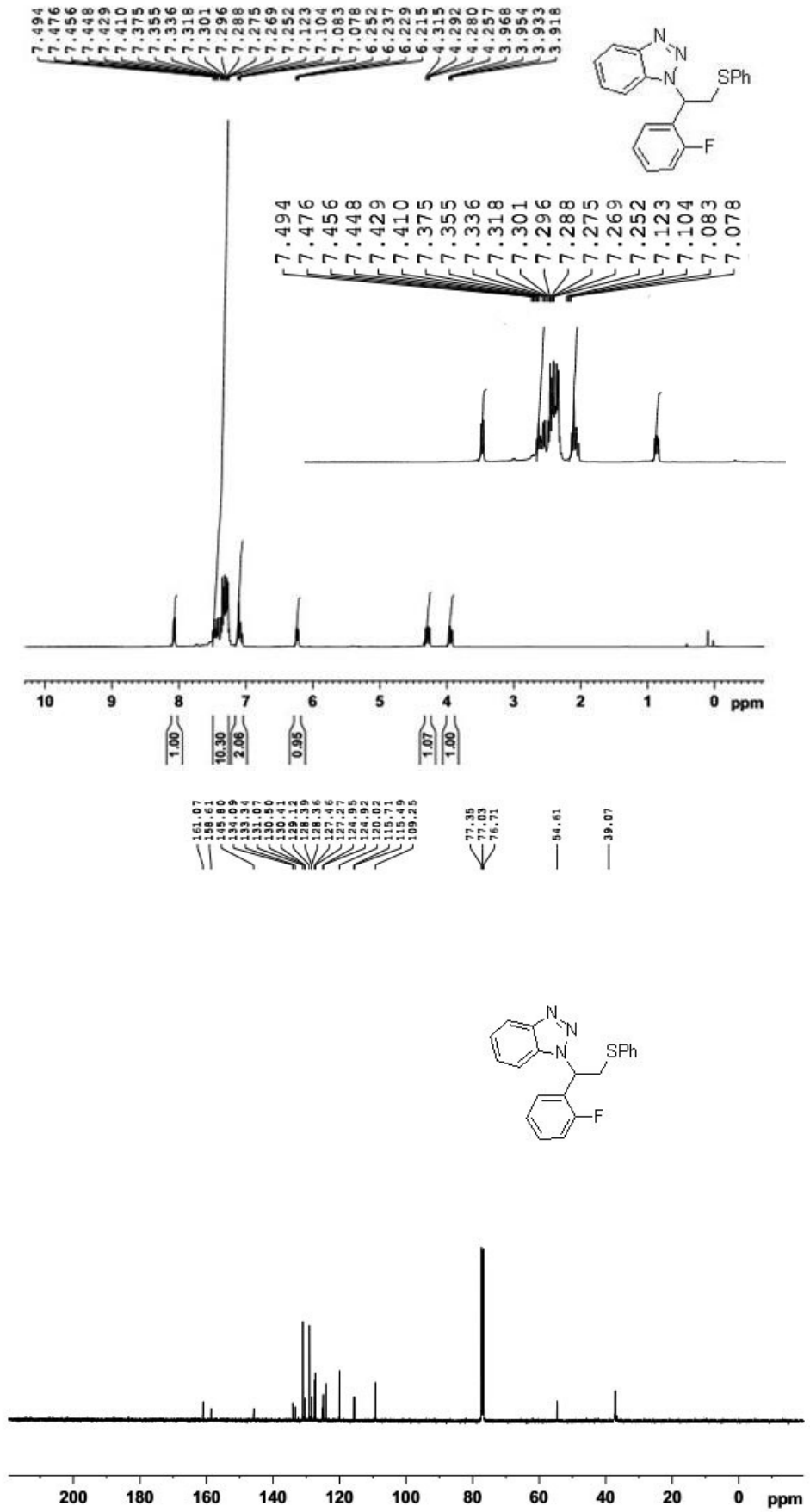
Compound 4e


7.399
7.382
7.379
7.359
7.355
7.346
7.343
7.340
7.332
7.325
7.322
7.315
7.298
7.296
7.282
7.275
7.267
7.265
7.259
7.253
7.246
5.843
5.836
5.821
5.813
5.798
4.532
4.320
4.298
4.285
4.262
3.925
3.910
3.890
3.875
N
N
N
SPh
Cl
10
9
8
7
6
5
4
3
2
1
0 ppm
1.09
6.64
6.14
1.02
1.98
1.00
1.00

146.02
138.09
137.99
134.25
133.11
131.06
130.98
129.20
129.17
127.45
127.42
127.27
126.78
124.06
120.13
109.34
77.37
77.05
76.73
62.25
45.46
39.67

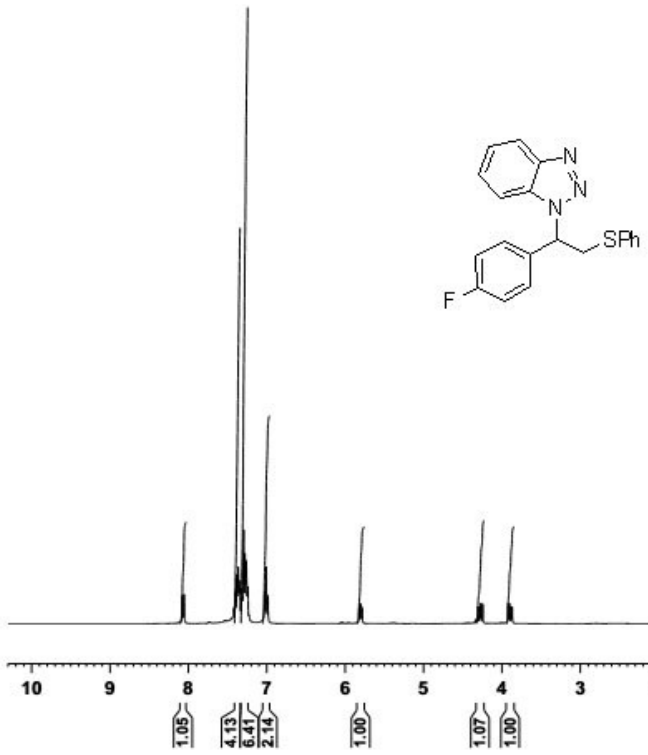

N
N
N
SPh
Cl
200
180
160
140
120
100
80
60
40
20
0 ppm

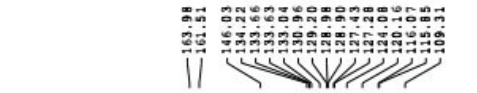
Compound 4f

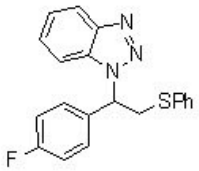

7.494
7.476
7.456
7.448
7.429
7.410
7.375
7.355
7.336
7.318
7.301
7.296
7.288
7.275
7.269
7.252
7.123
7.104
7.083
7.078
6.252
6.237
6.229
6.215
4.315
4.292
4.280
4.257
3.968
3.954
3.933
3.918
SPh
F
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
10.30
2.06
0.95
1.07
1.00
161.07
158.61
145.80
134.09
133.34
131.07
130.50
130.41
129.12
128.39
128.36
127.46
127.27
124.95
124.92
120.02
115.71
115.49
109.25
77.35
77.03
76.71
54.61
39.07
200 180 160 140 120 100 80 60 40 20 0 ppm

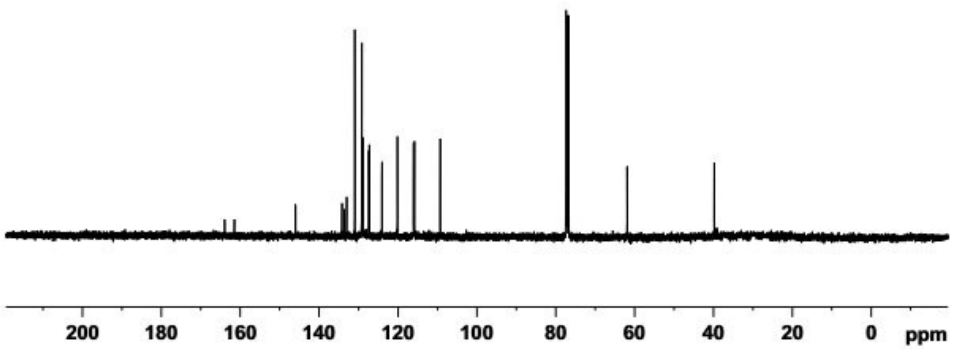
Compound 4g


8.080
8.059
7.405
7.388
7.376
7.367
7.354
7.346
7.299
7.282
7.276
7.265
7.247
7.032
7.011
6.989
5.825
5.809
5.803
5.788
4.306
4.284
4.271
4.249
3.924
3.908
3.889
3.873

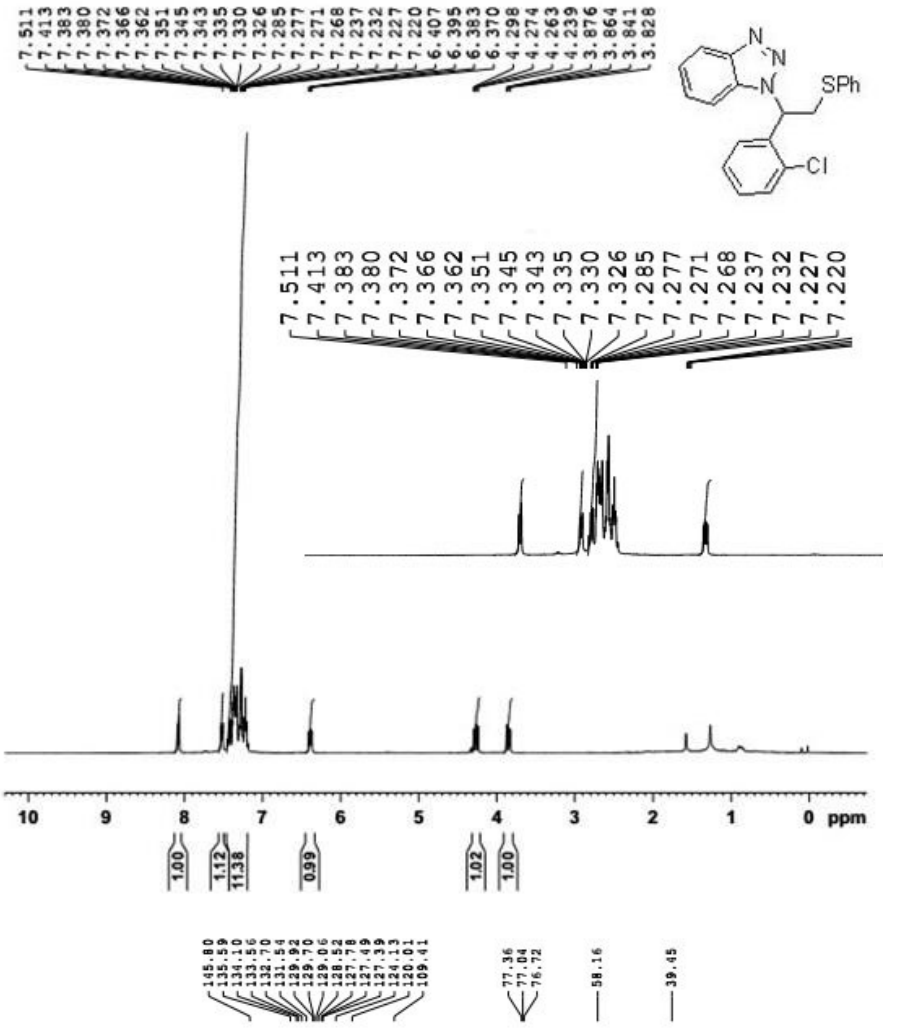

N
N
N
SPh
F
10
9
8
7
6
5
4
3
2
1
0 ppm
1.05
4.13
6.41
2.14
1.00
1.07
1.00

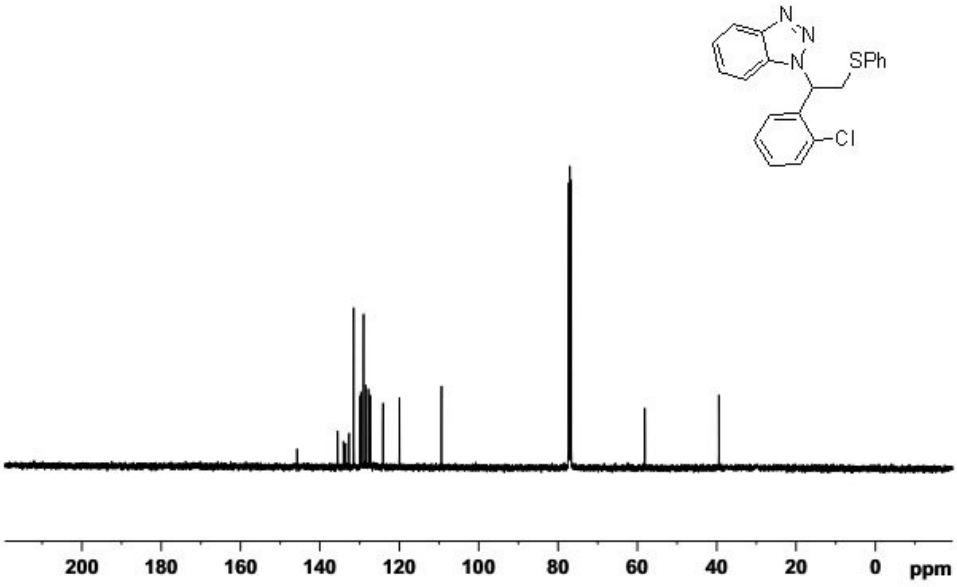

163.98
161.51
146.03
134.22
133.66
133.63
133.04
130.96
129.20
128.98
128.90
127.43
127.28
124.08
120.16
116.07
115.85
109.31
77.39
77.07
76.75
61.91
39.82


N
N
N
SPh
F

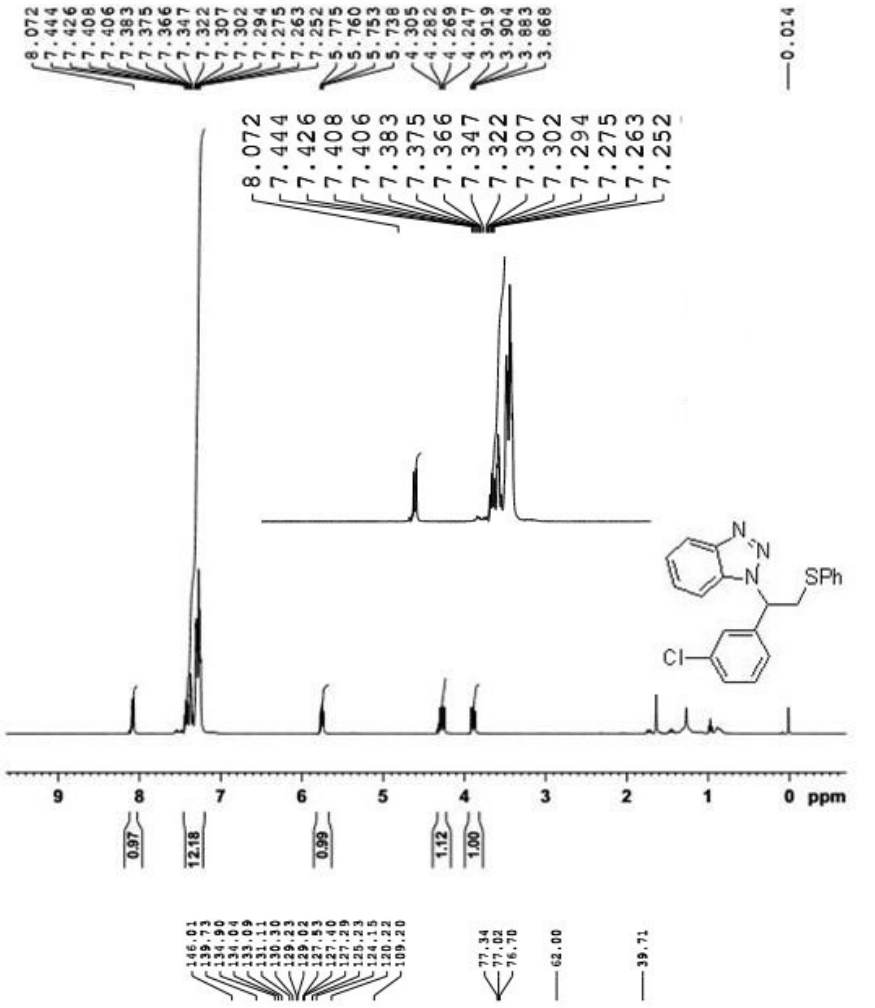

200
180
160
140
120
100
80
60
40
20
0 ppm

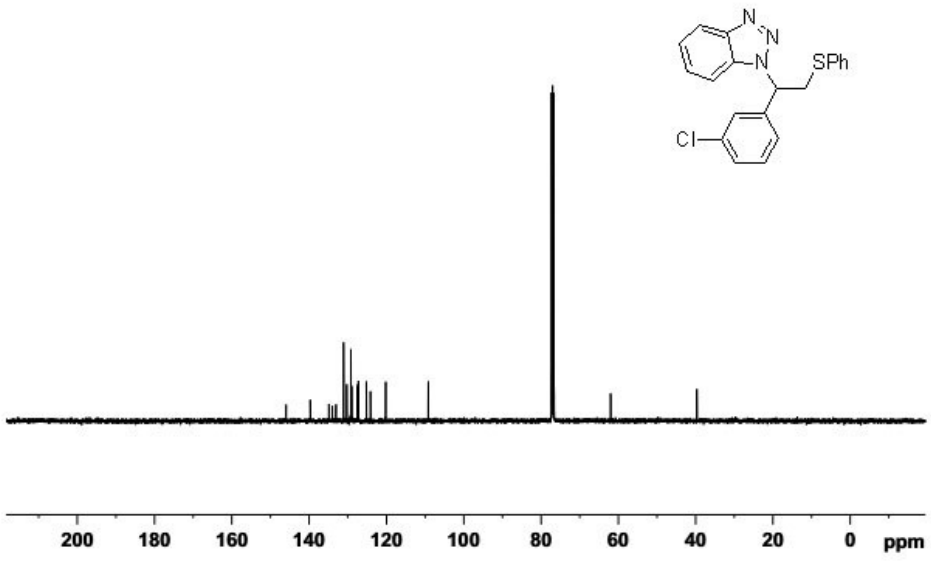
Compound 4h


7.511
7.413
7.383
7.380
7.372
7.366
7.362
7.351
7.345
7.343
7.335
7.330
7.326
7.285
7.277
7.271
7.268
7.237
7.232
7.227
7.220
6.407
6.395
6.383
6.370
4.298
4.274
4.263
4.239
3.876
3.864
3.841
3.828
N
N
N
SPh
Cl
10 9 8 7 6 5 4 3 2 1 0 ppm
1.00
1.12
11.38
0.99
1.02
1.00
145.80
135.59
134.10
133.56
132.70
131.54
129.92
129.70
129.06
128.52
127.78
127.49
127.39
124.13
120.01
109.41
77.36
77.04
76.72
58.16
39.45

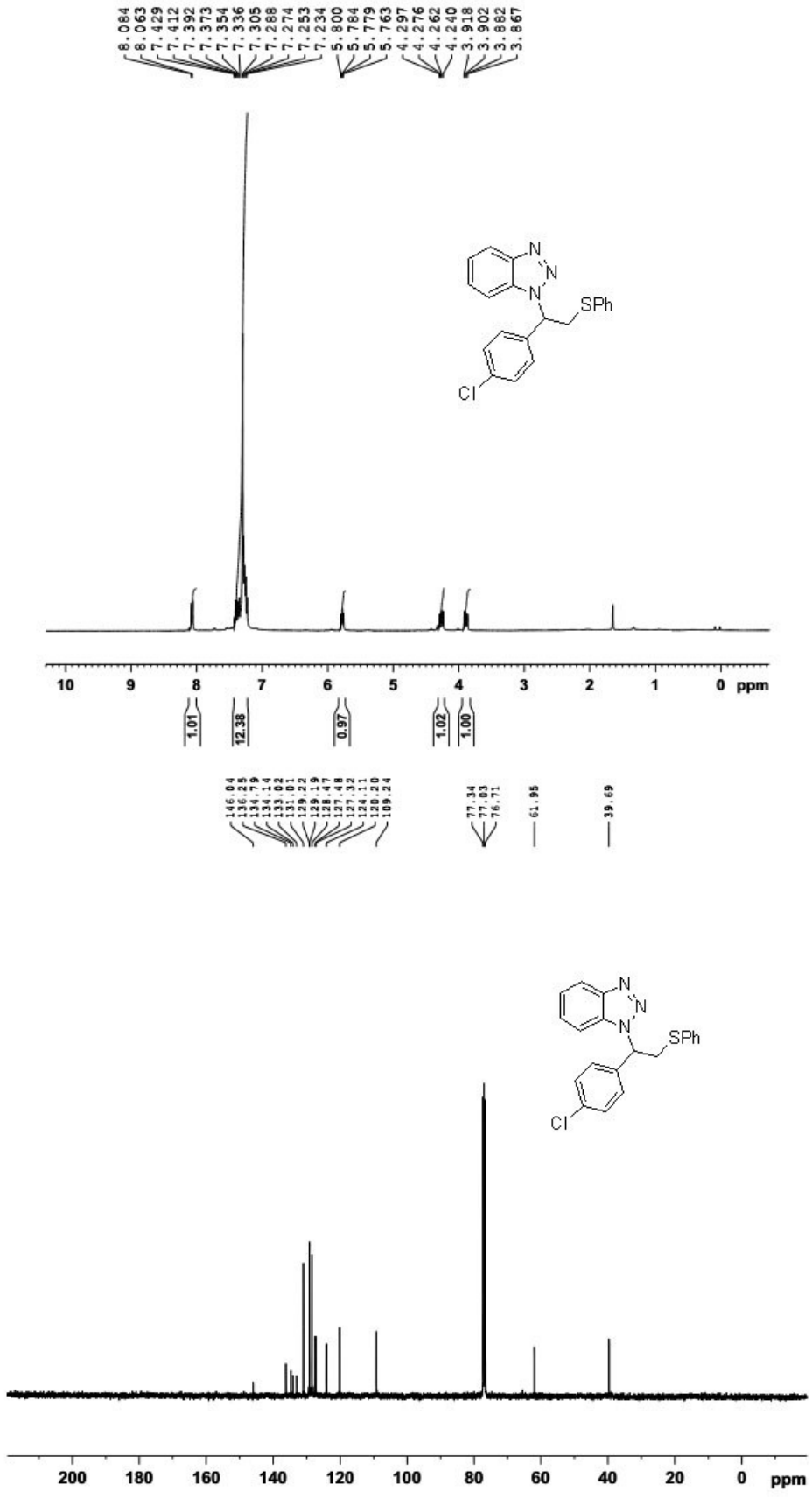

N
N
N
SPh
Cl
200 180 160 140 120 100 80 60 40 20 0 ppm

Compound 4i

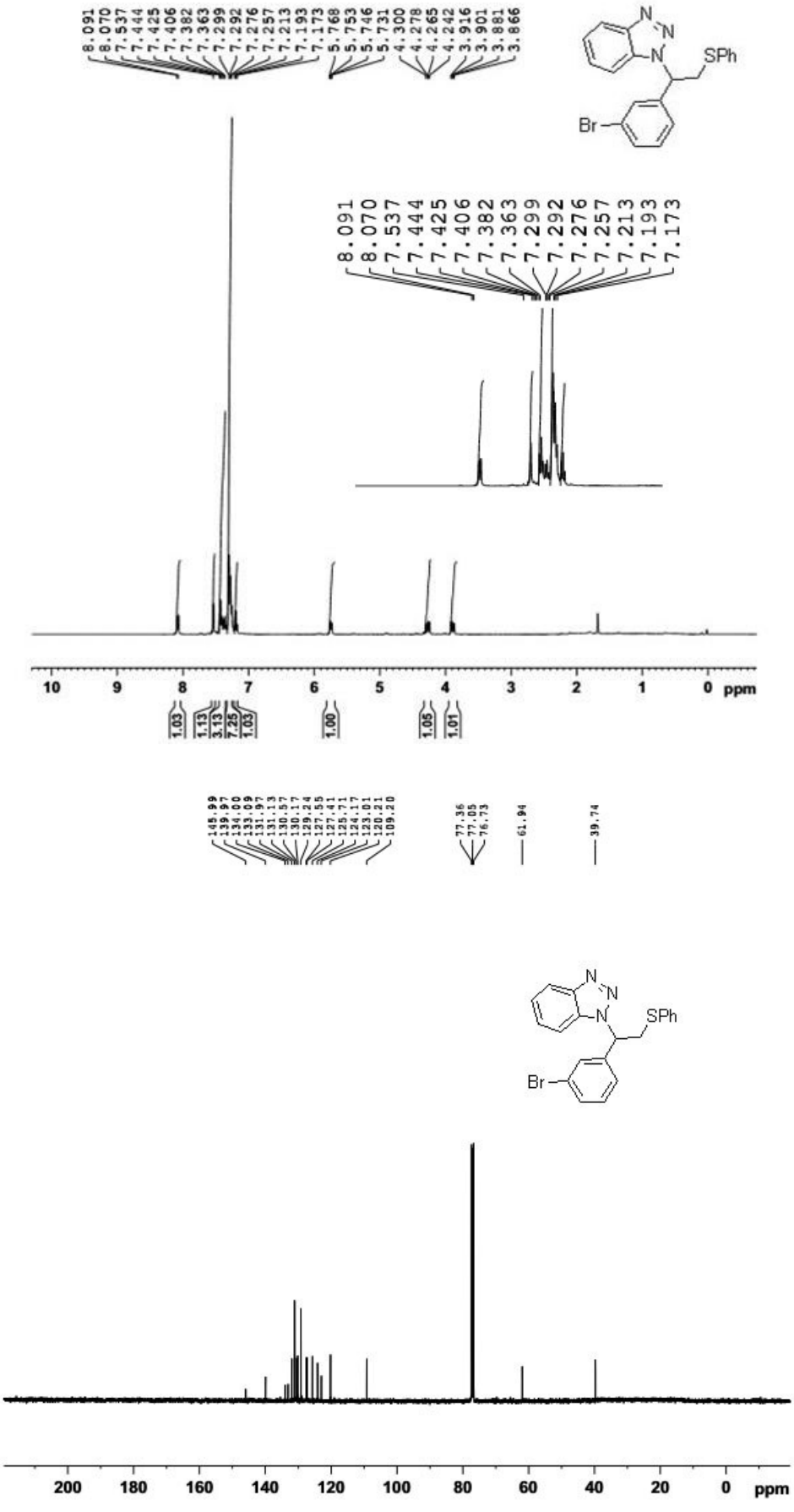

8.072
7.444
7.426
7.408
7.406
7.383
7.375
7.366
7.347
7.322
7.307
7.302
7.294
7.275
7.263
7.252
5.775
5.760
5.753
5.738
4.305
4.282
4.269
4.247
3.919
3.904
3.883
3.868
0.014
SPh
Cl
9
8
7
6
5
4
3
2
1
0 ppm
0.97
12.18
0.99
1.12
1.00


146.01
139.73
134.90
134.04
133.09
131.11
130.30
129.23
129.02
127.55
127.40
127.29
126.23
124.15
120.22
109.20
77.34
77.02
76.70
62.00
39.71
SPh
Cl
200
180
160
140
120
100
80
60
40
20
0 ppm

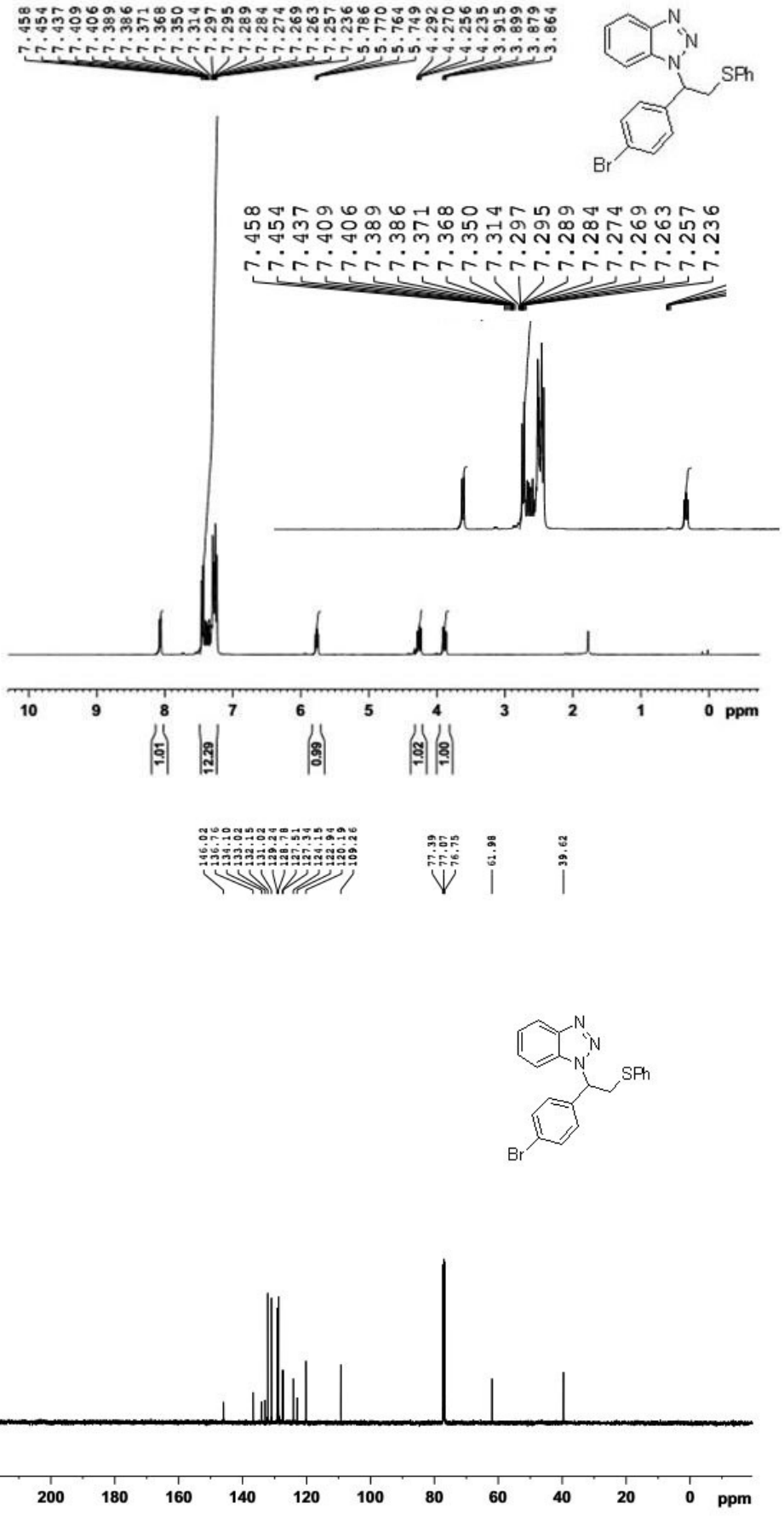
Compound 4j


8.084
8.063
7.429
7.412
7.392
7.373
7.354
7.336
7.305
7.288
7.274
7.253
7.234
5.800
5.784
5.779
5.763
4.297
4.276
4.262
4.240
3.918
3.902
3.882
3.867
N
N
N
SPh
Cl
10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
12.38
0.97
1.02
1.00
146.04
136.25
134.79
134.14
133.02
131.01
129.22
129.19
128.47
127.48
127.32
124.11
120.20
109.24
77.34
77.03
76.71
61.95
39.69
200 180 160 140 120 100 80 60 40 20 0 ppm

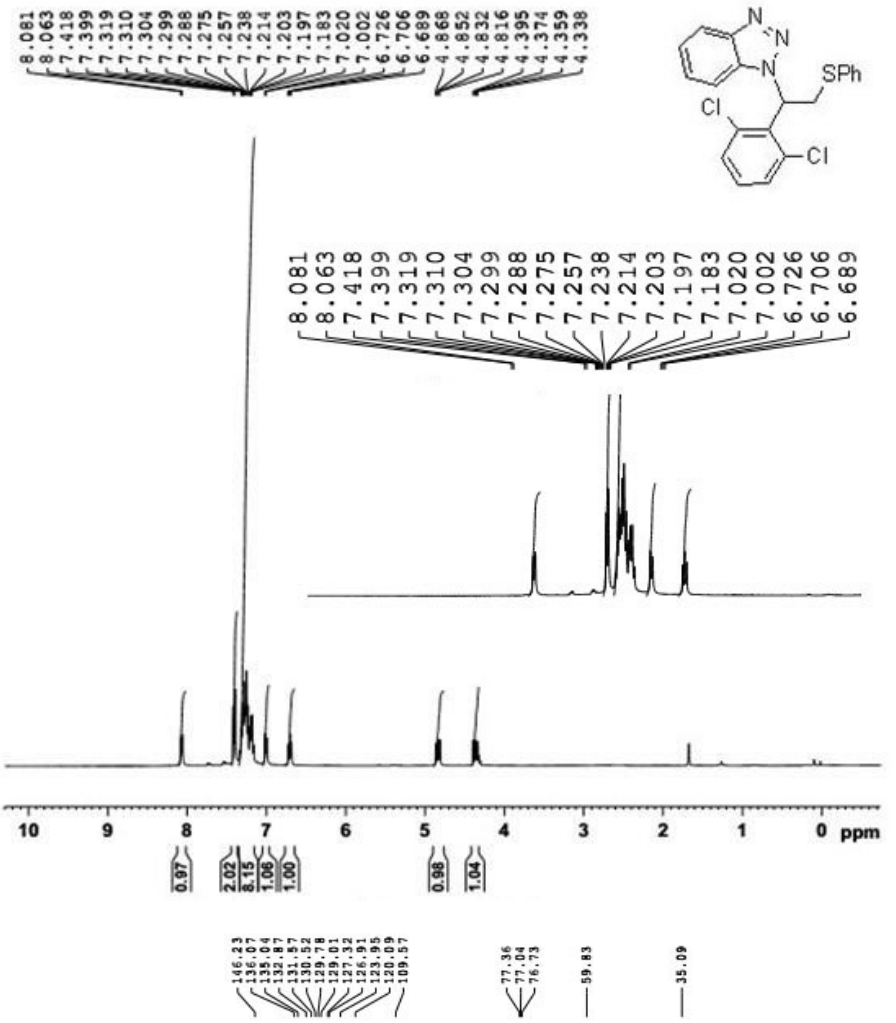
Compound 4k

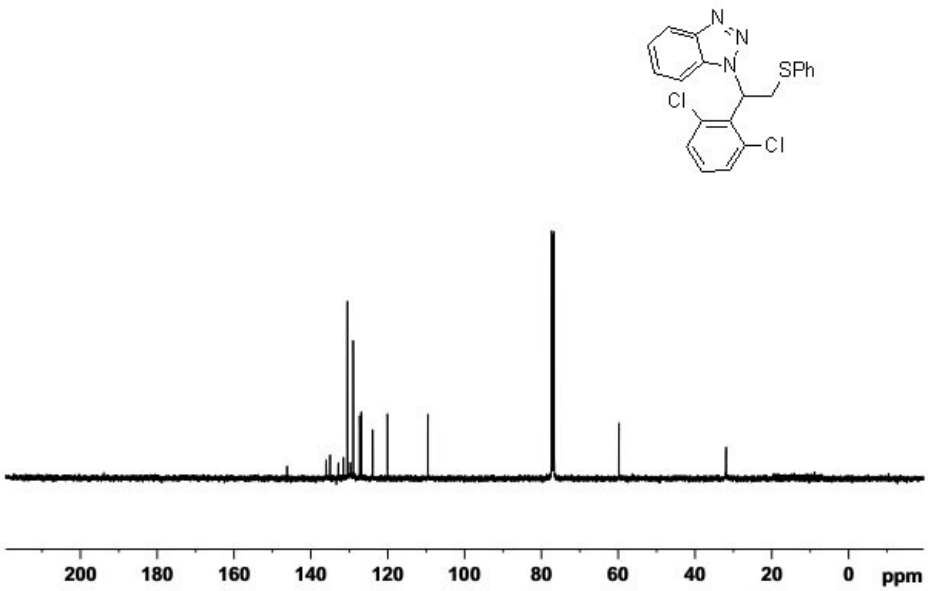

8.091
8.070
7.537
7.444
7.425
7.406
7.382
7.363
7.299
7.292
7.276
7.257
7.213
7.193
7.173
5.768
5.753
5.746
5.731
4.300
4.278
4.265
4.242
3.916
3.901
3.881
3.866
SPh
Br
10 9 8 7 6 5 4 3 2 1 0 ppm
1.03 1.13 3.13 7.25 1.03 1.00 1.05 1.01
145.99
139.97
134.00
133.09
131.97
131.13
130.57
130.17
129.24
127.55
127.41
125.71
124.17
123.01
120.21
109.20
77.36
77.05
76.73
61.94
39.74
200 180 160 140 120 100 80 60 40 20 0 ppm

Compound 4l

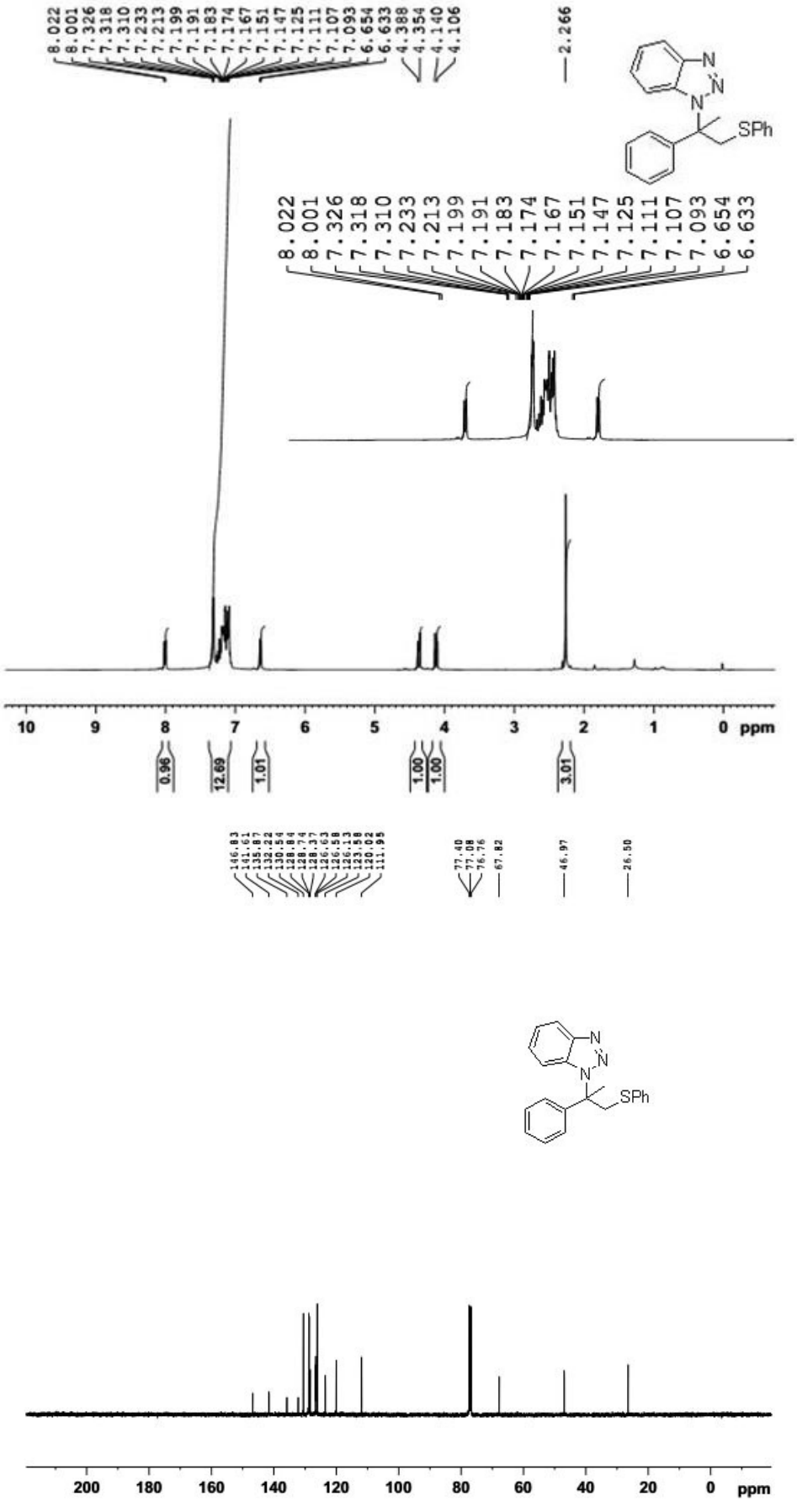

7.458
7.454
7.437
7.409
7.406
7.389
7.386
7.371
7.368
7.350
7.314
7.297
7.295
7.289
7.284
7.274
7.269
7.263
7.257
7.236
5.786
5.770
5.764
5.749
4.292
4.270
4.256
4.235
3.915
3.899
3.879
3.864
N
N
N
SPh
Br
10 9 8 7 6 5 4 3 2 1 0 ppm
1.01
12.29
0.99
1.02
1.00
146.02
136.76
134.10
133.02
132.15
131.02
129.24
128.78
127.51
127.34
124.15
122.94
122.19
109.26
77.39
77.07
76.75
61.98
39.62
200 180 160 140 120 100 80 60 40 20 0 ppm

Compound 4m

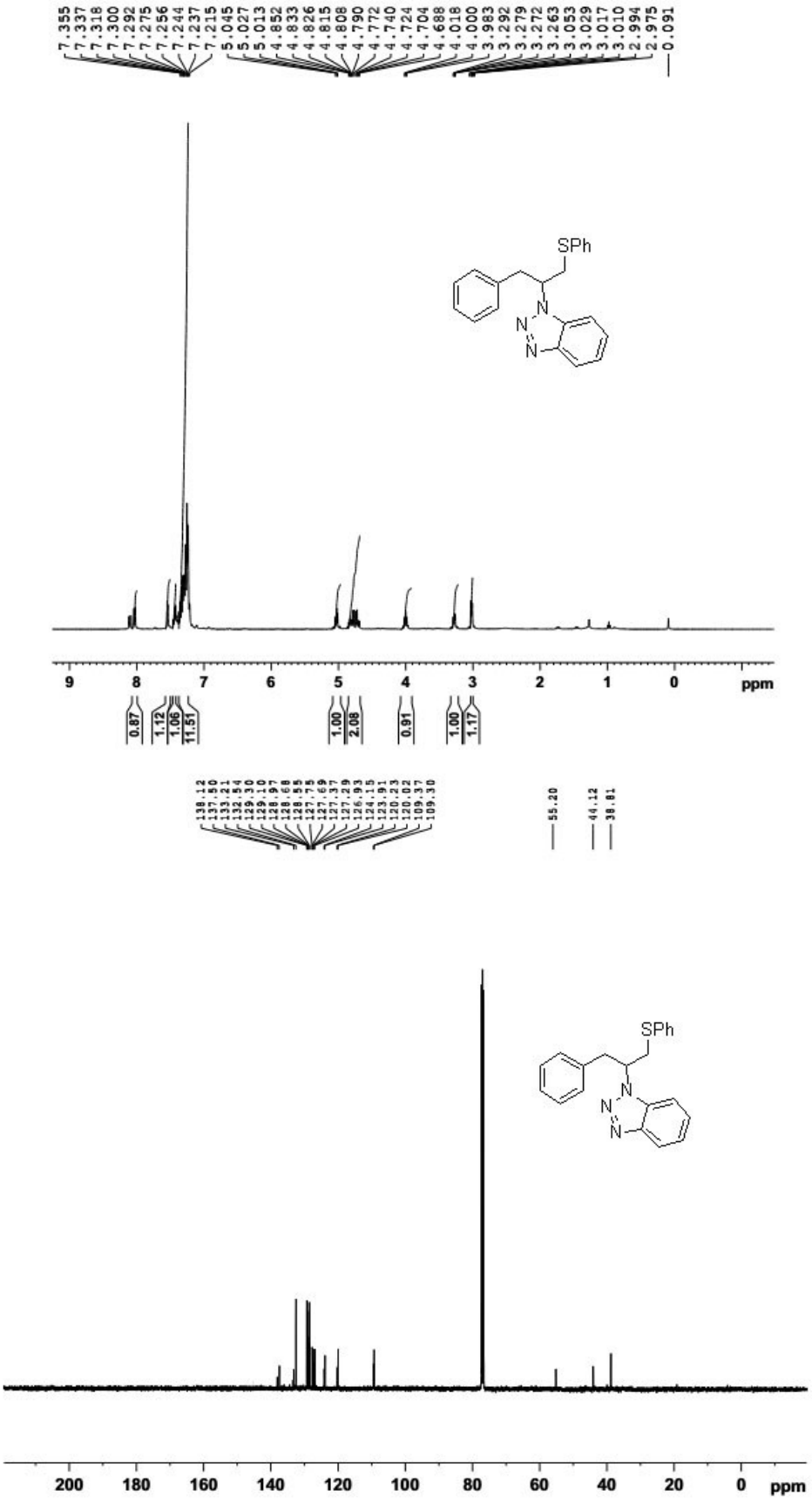

8.081
8.063
7.418
7.399
7.319
7.310
7.304
7.299
7.288
7.275
7.257
7.238
7.214
7.203
7.197
7.183
7.020
7.002
6.726
6.706
6.689
4.868
4.852
4.832
4.816
4.395
4.374
4.359
4.338
N
N
N
SPh
Cl
Cl
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
2.02
6.15
1.06
1.00
0.98
1.04
146.23
136.07
135.04
132.87
131.57
130.52
129.78
129.01
127.32
126.91
123.95
120.09
109.57
77.36
77.04
76.73
59.83
35.09


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

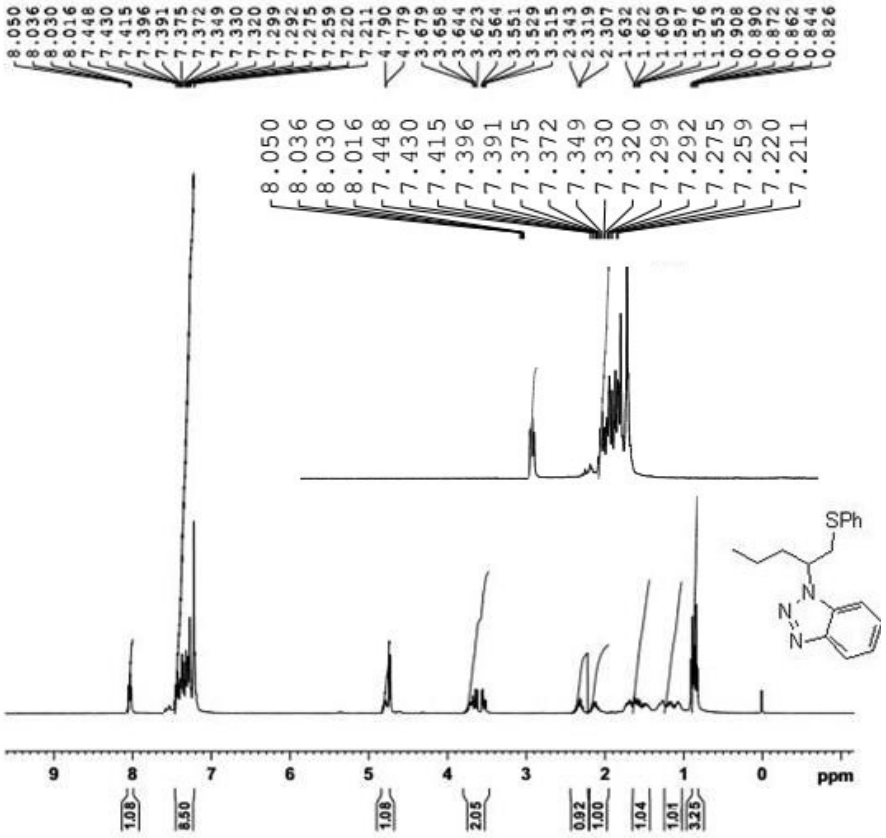
Compound 4n


8.022
8.001
7.326
7.318
7.310
7.233
7.213
7.199
7.191
7.183
7.174
7.167
7.151
7.147
7.125
7.111
7.107
7.093
6.654
6.633
4.388
4.354
4.140
4.106
2.266
N
N
N
SPh
10
9
8
7
6
5
4
3
2
1
0 ppm
0.96
12.69
1.01
1.00
1.00
3.01
146.83
141.61
135.87
132.22
130.54
128.84
128.74
128.37
126.63
126.58
126.13
123.58
120.02
111.95
77.40
77.08
76.76
67.82
46.97
26.50
200
180
160
140
120
100
80
60
40
20
0 ppm

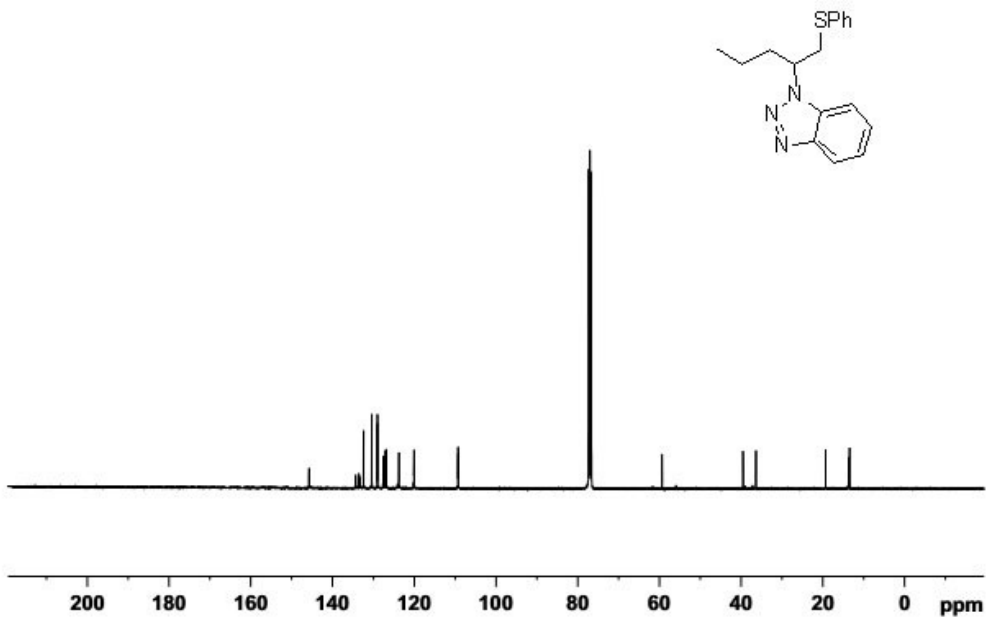
Compound 4o


7.355
7.337
7.318
7.300
7.292
7.275
7.256
7.244
7.237
7.215
5.045
5.027
5.013
4.852
4.833
4.826
4.815
4.808
4.790
4.772
4.740
4.724
4.704
4.688
4.018
4.000
3.983
3.292
3.279
3.272
3.263
3.053
3.029
3.017
3.010
2.994
2.975
0.091
SPh
N
N
N
9
8
7
6
5
4
3
2
1
0
ppm
0.87
1.12
1.06
11.51
1.00
2.08
0.91
1.00
1.17
138.12
137.50
133.21
132.54
129.30
129.10
128.97
128.68
128.55
127.75
127.69
127.37
127.29
126.93
124.15
123.91
120.23
120.02
109.37
109.30
55.20
44.12
38.81
SPh
N
N
N
200
180
160
140
120
100
80
60
40
20
0
ppm

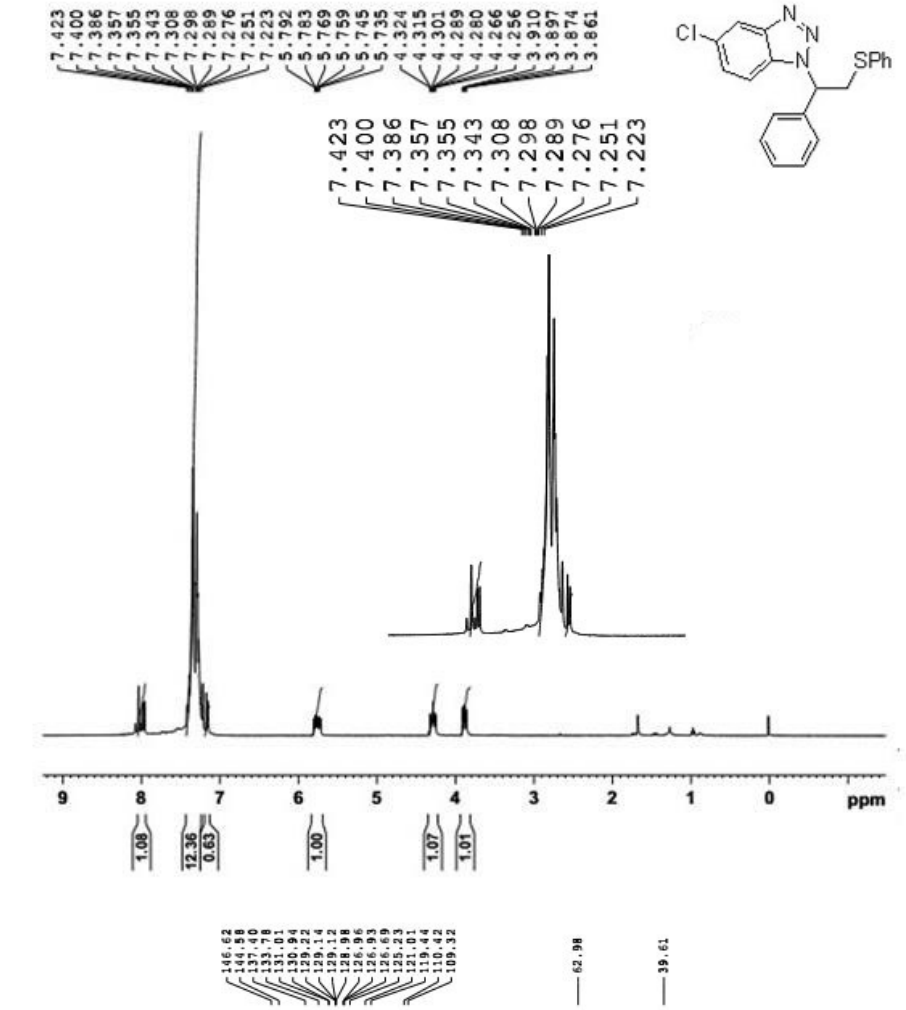
Compound 4p


8.050
8.036
8.030
8.016
7.448
7.430
7.415
7.396
7.391
7.375
7.372
7.349
7.330
7.320
7.299
7.292
7.275
7.259
7.220
7.211
4.790
4.779
3.679
3.658
3.644
3.623
3.564
3.551
3.529
3.515
2.343
2.319
2.307
1.632
1.622
1.609
1.587
1.576
1.553
0.908
0.890
0.872
0.862
0.844
0.826
SPh
ppm
1.08
8.50
1.08
2.05
0.92
1.00
1.04
1.01
3.25

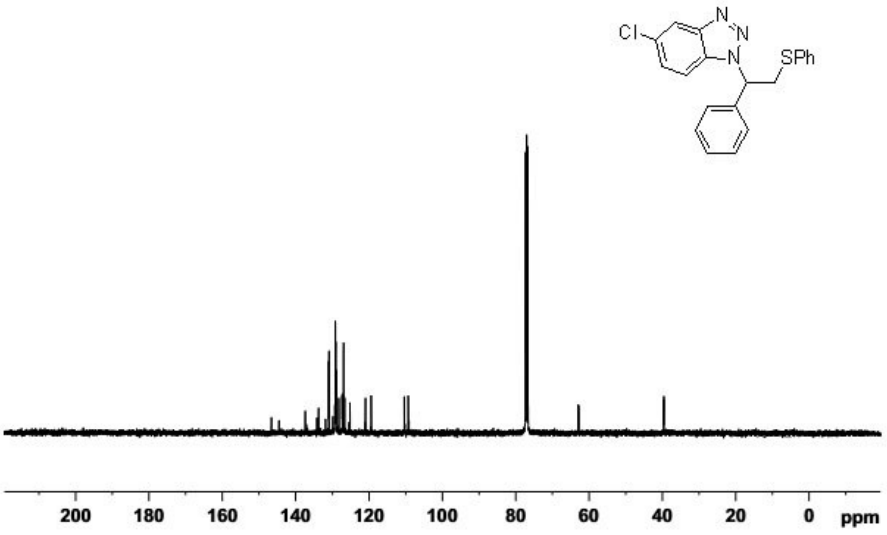

145.76
132.44
130.42
129.12
129.02
127.62
127.33
127.07
126.93
123.77
120.08
120.04
109.30
109.25
77.35
77.03
76.71
59.39
39.54
36.39
19.37
13.73


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

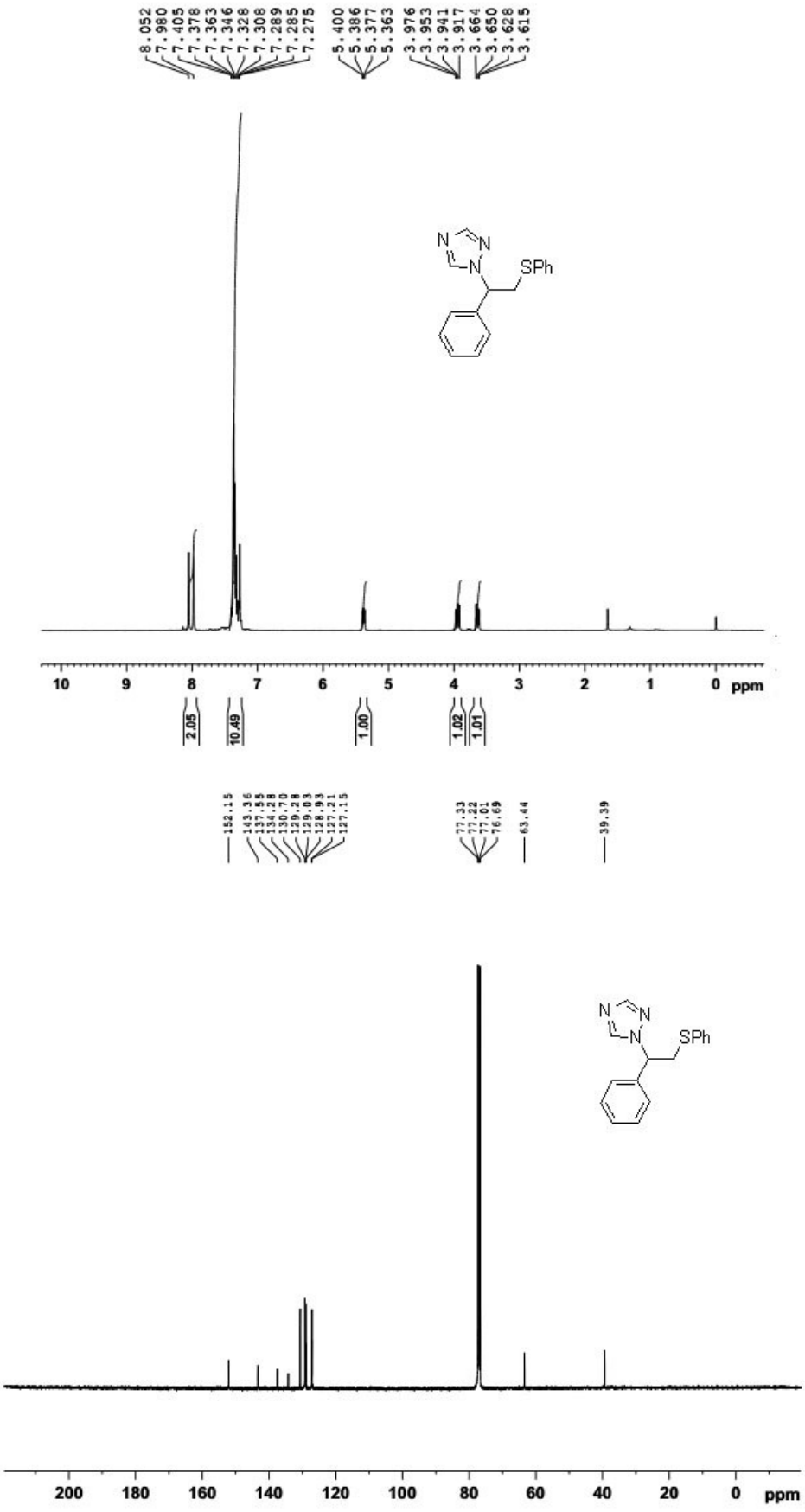
Compound 4q


7.423
7.400
7.386
7.357
7.355
7.343
7.308
7.298
7.289
7.276
7.251
7.223
5.792
5.783
5.769
5.759
5.745
5.735
4.324
4.315
4.301
4.289
4.280
4.266
4.256
3.910
3.897
3.874
3.861
Cl
N
N
N
SPh
9
8
7
6
5
4
3
2
1
0
ppm
1.08
12.36
0.63
1.00
1.07
1.01

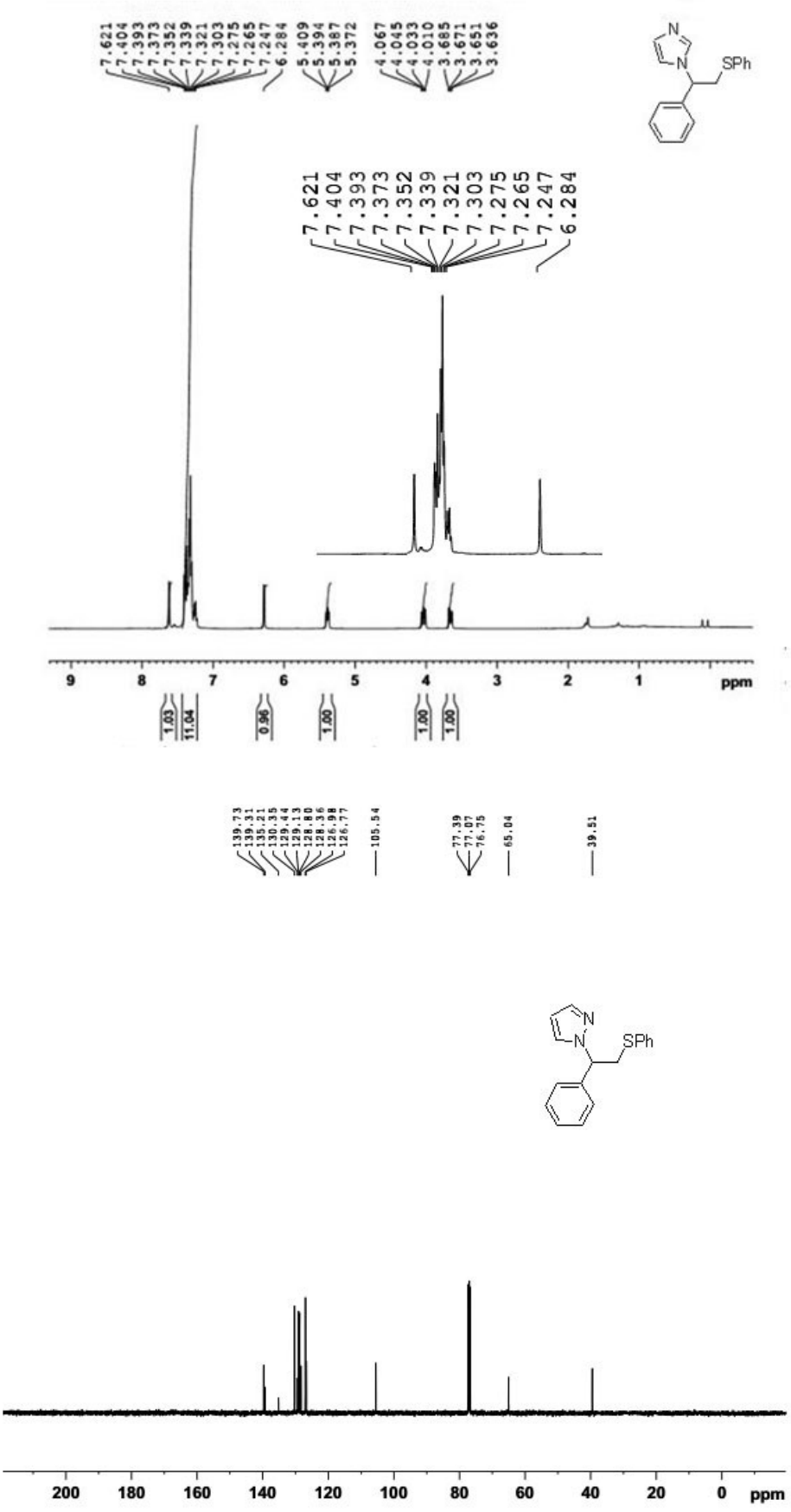
146.62
144.58
137.40
133.78
131.01
130.94
129.22
129.14
129.12
128.98
126.96
126.93
126.69
125.23
121.01
119.44
110.42
109.32
62.98
39.61


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

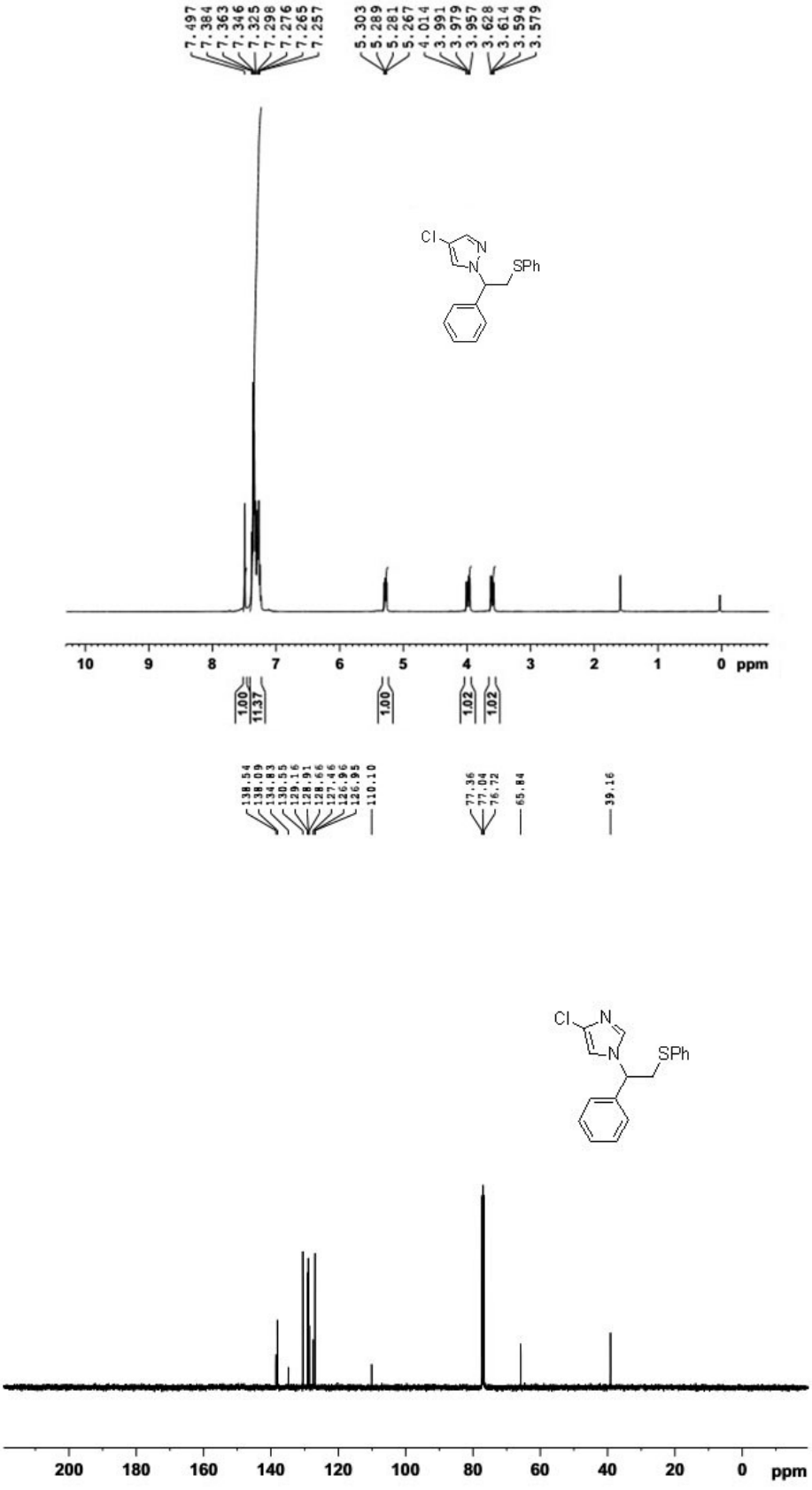
Compound 4r


8.052
7.980
7.405
7.378
7.363
7.346
7.328
7.308
7.289
7.285
7.275
5.400
5.386
5.377
5.363
3.976
3.953
3.941
3.917
3.664
3.650
3.628
3.615
N
N
N
SPh
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
10.49
1.00
1.02
1.01
152.15
143.36
137.55
134.28
130.70
129.28
129.03
128.93
127.21
127.15
77.33
77.22
77.01
76.69
63.44
39.39
N
N
N
SPh
200
180
160
140
120
100
80
60
40
20
0
ppm

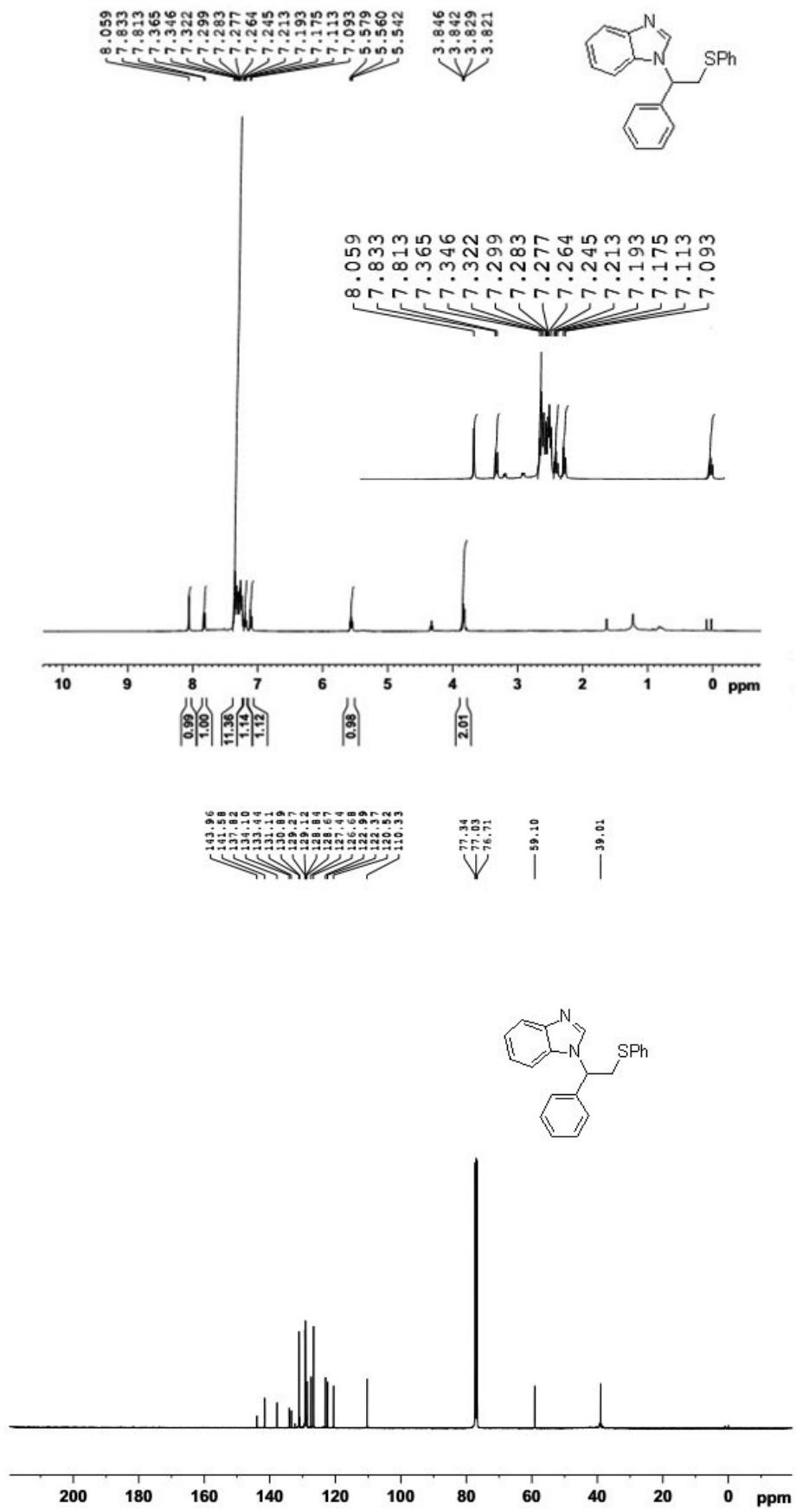
Compound 4s


7.621
7.404
7.393
7.373
7.352
7.339
7.321
7.303
7.275
7.265
7.247
6.284
5.409
5.394
5.387
5.372
4.067
4.045
4.033
4.010
3.685
3.671
3.651
3.636
N
N
SPh
ppm
1.03
11.04
0.96
1.00
1.00
1.00
139.73
139.31
135.21
130.35
129.44
129.13
128.80
128.36
126.98
126.77
105.54
77.39
77.07
76.75
65.04
39.51
200
180
160
140
120
100
80
60
40
20
0
ppm

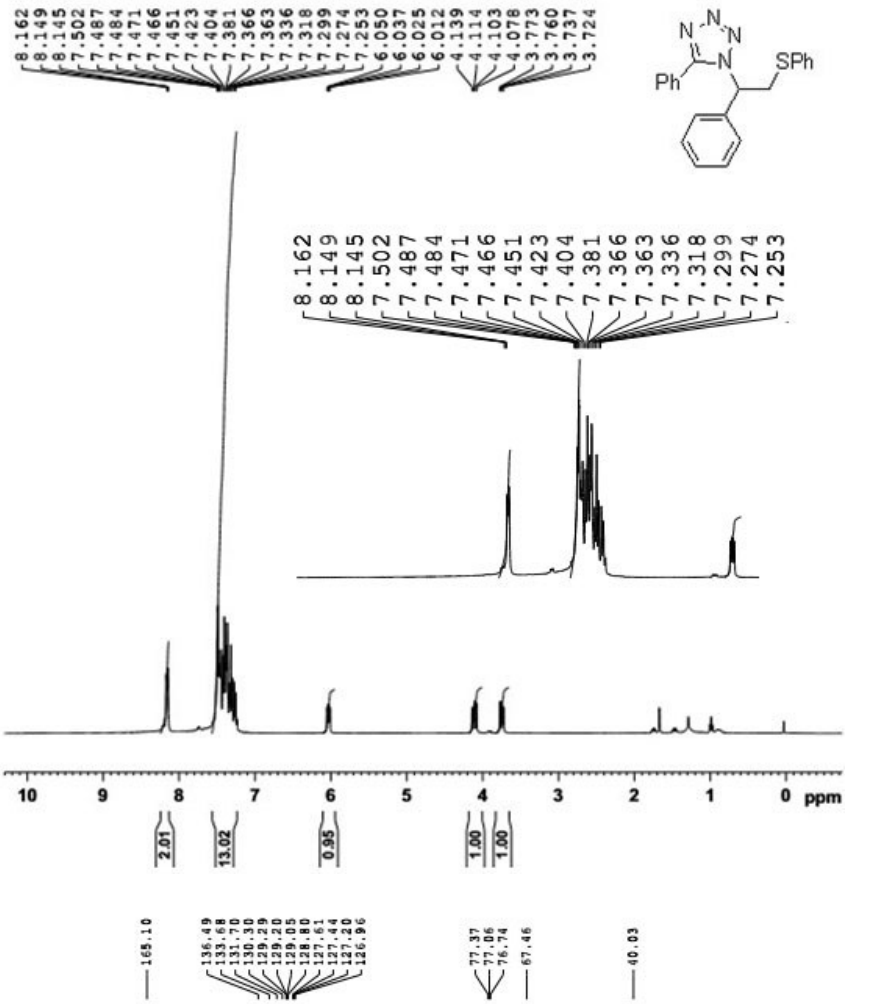
Compound 4t

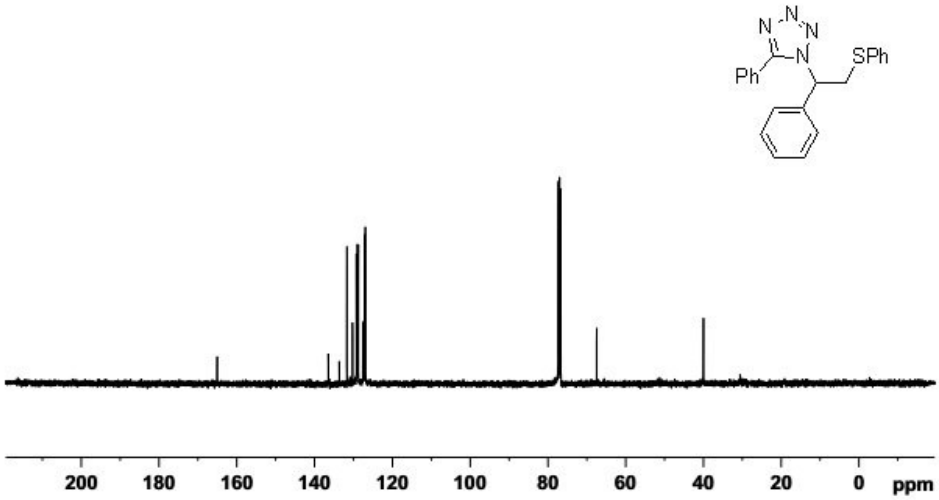

7.497
7.384
7.363
7.346
7.325
7.298
7.276
7.265
7.257
5.303
5.289
5.281
5.267
4.014
3.991
3.979
3.957
3.628
3.614
3.594
3.579
Cl
N
N
SPh
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
11.37
1.00
1.02
1.02
138.54
138.09
134.83
130.55
129.16
128.91
128.66
127.46
126.96
126.95
110.10
77.36
77.04
76.72
65.84
39.16
Cl
N
N
SPh
200
180
160
140
120
100
80
60
40
20
0 ppm

Compound 4u

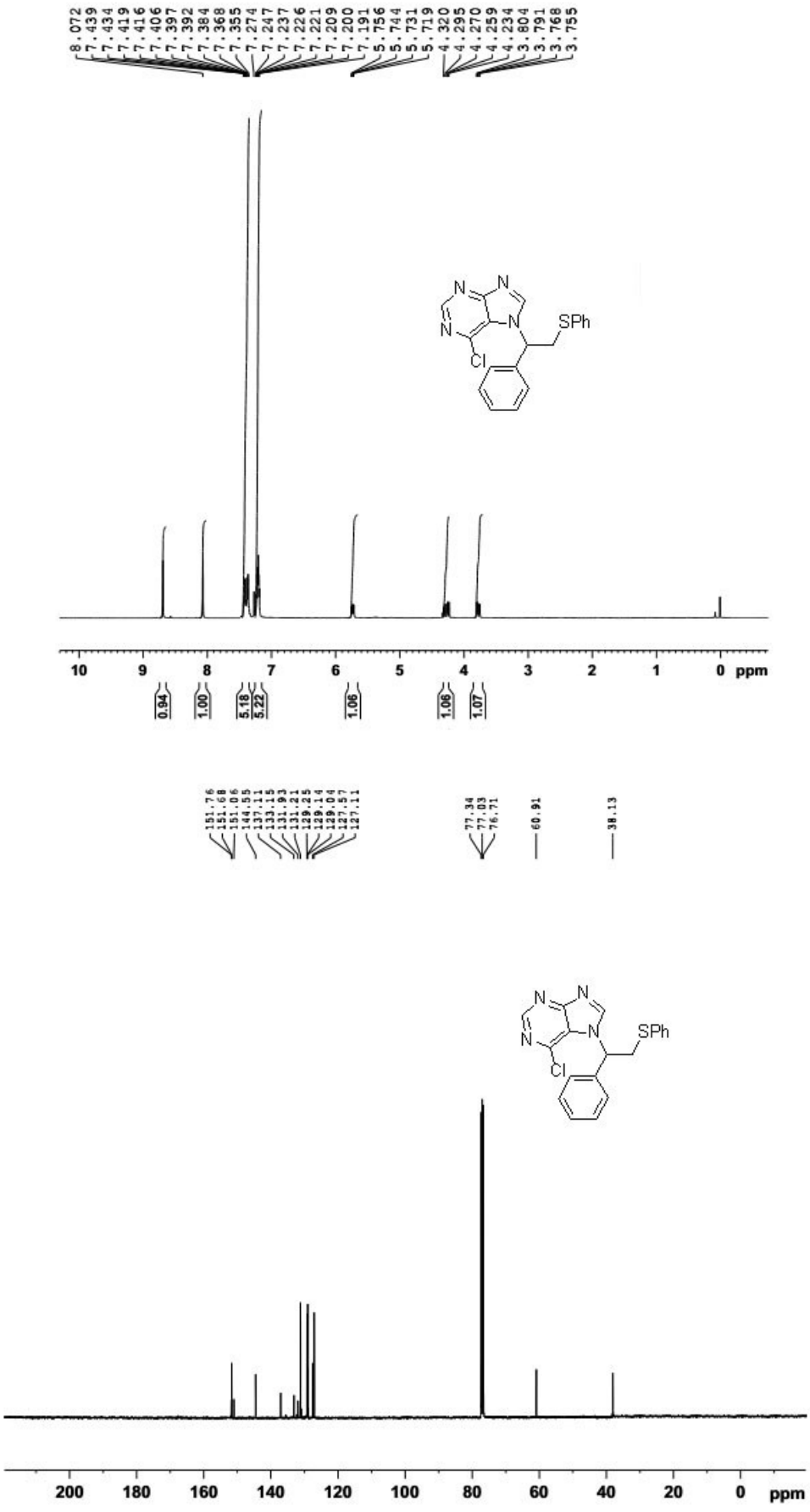

8.059
7.833
7.813
7.365
7.346
7.322
7.299
7.283
7.277
7.264
7.245
7.213
7.193
7.175
7.113
7.093
5.579
5.560
5.542
3.846
3.842
3.829
3.821
SPh
10 9 8 7 6 5 4 3 2 1 0 ppm
0.99
1.00
11.36
1.14
1.12
0.98
2.01
143.96
141.58
137.82
134.10
133.44
131.11
130.89
129.27
129.12
128.84
128.67
127.44
126.68
122.37
120.32
110.33
77.34
77.03
76.71
59.10
39.01
SPh
200 180 160 140 120 100 80 60 40 20 0 ppm

Compound 4v

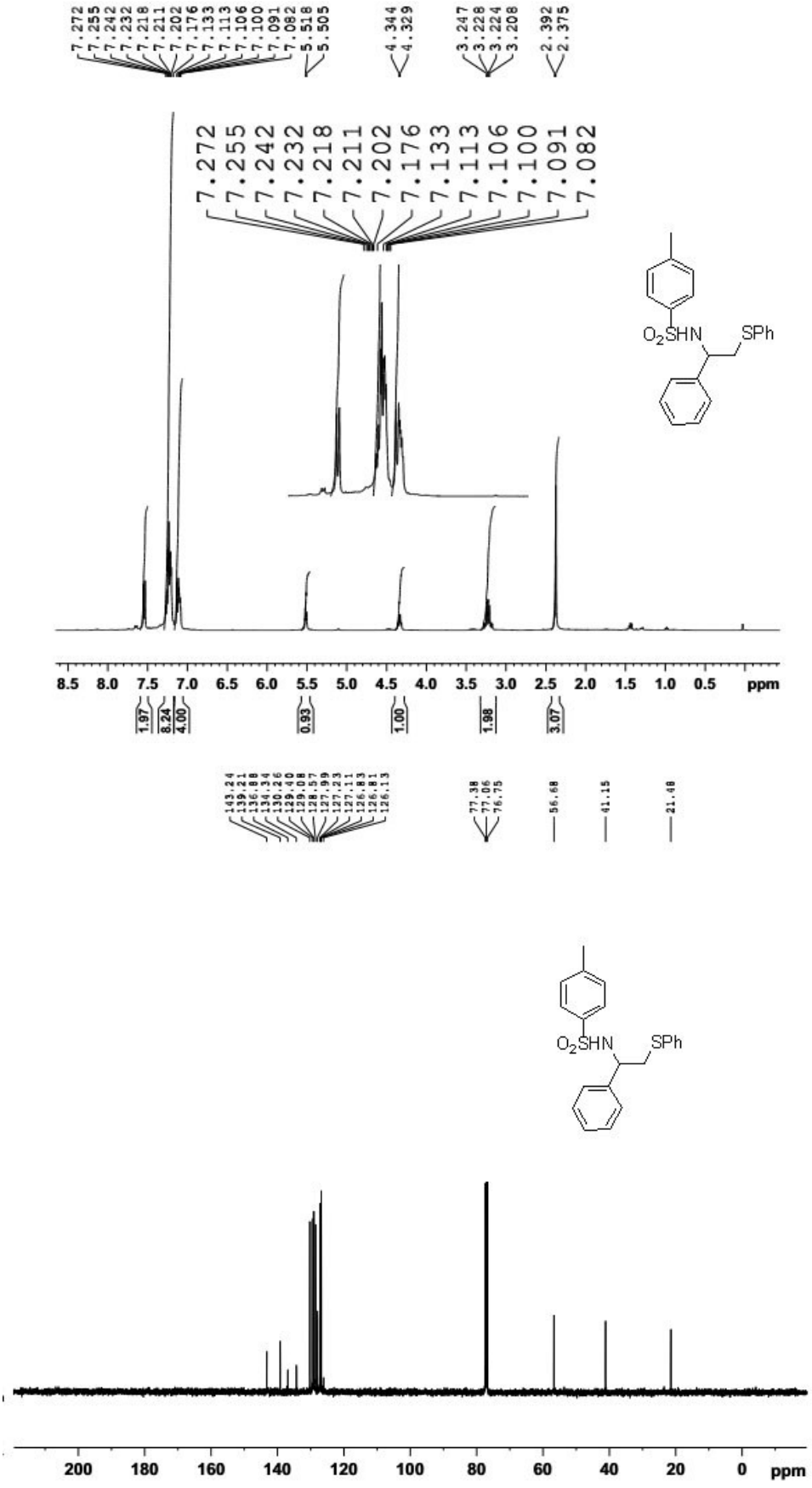

8.162
8.149
8.145
7.502
7.487
7.484
7.471
7.466
7.451
7.423
7.404
7.381
7.366
7.363
7.336
7.318
7.299
7.274
7.253
6.050
6.037
6.025
6.012
4.139
4.114
4.103
4.078
3.773
3.760
3.737
3.724
N
N
N
Ph
SPh
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
13.02
0.95
1.00
1.00
165.10
136.49
133.68
131.70
130.30
129.29
129.20
129.05
128.80
127.61
127.44
127.20
126.96
77.37
77.06
76.74
67.46
40.03


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

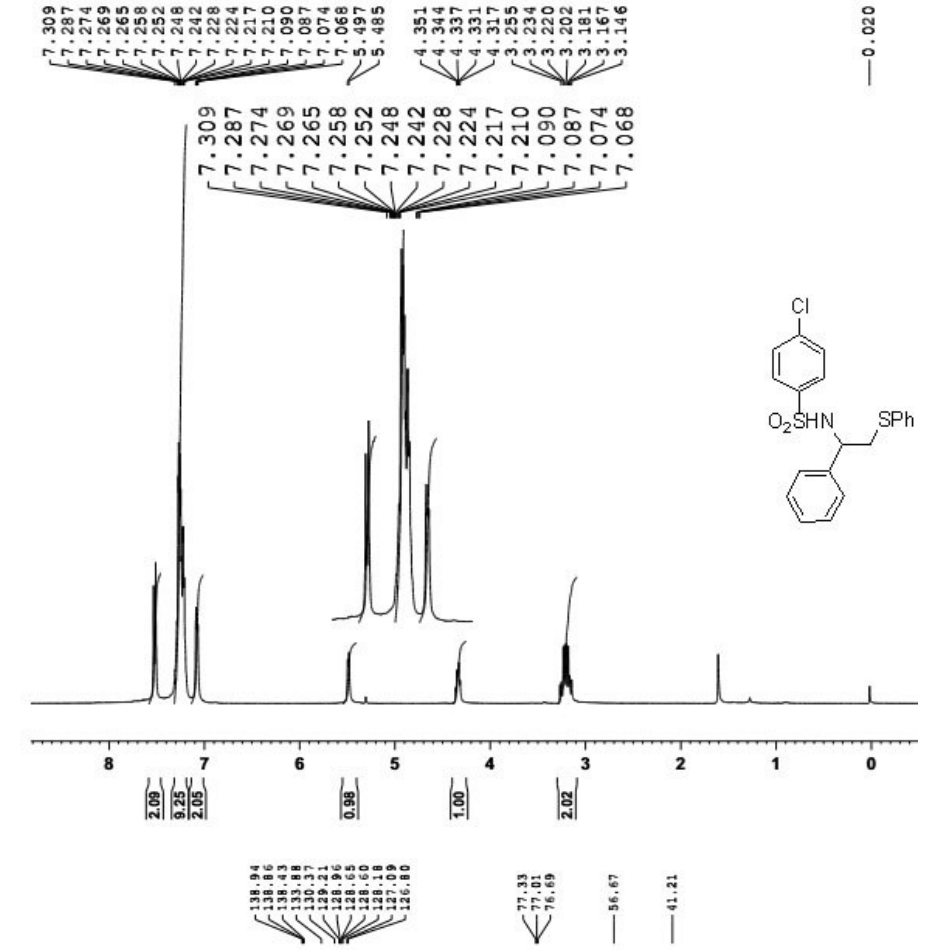
Compound 4w

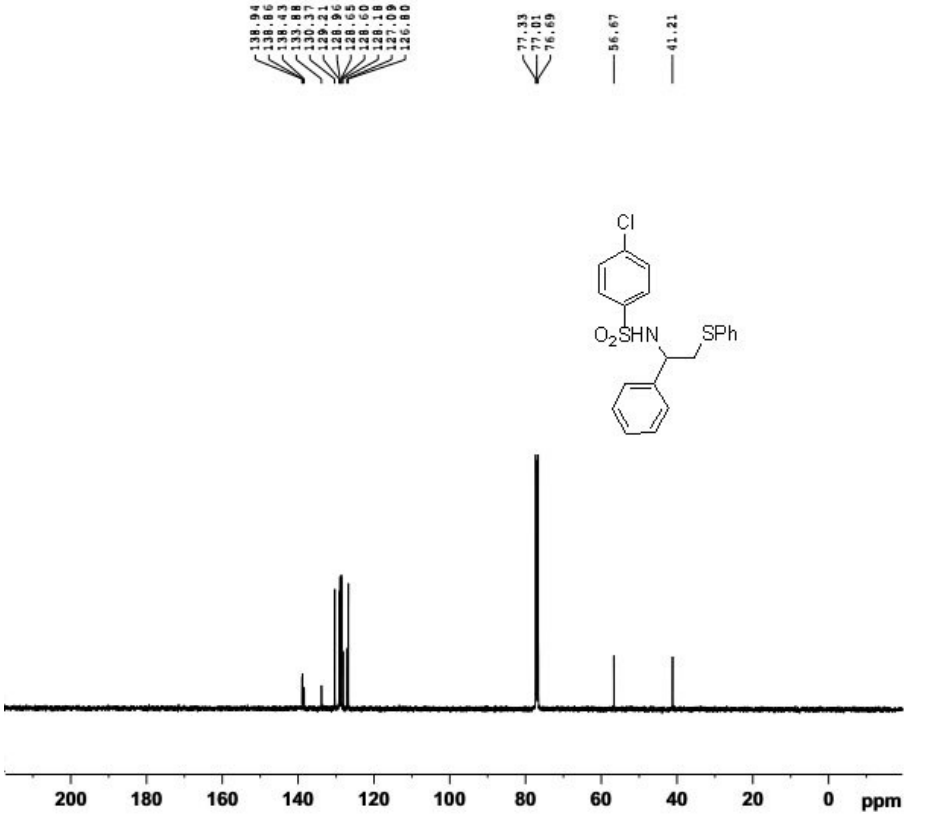

8.072
7.439
7.434
7.419
7.416
7.406
7.397
7.392
7.384
7.368
7.355
7.274
7.247
7.237
7.226
7.221
7.209
7.200
7.191
5.756
5.744
5.731
5.719
4.320
4.295
4.270
4.259
4.234
3.804
3.791
3.768
3.755
N
N
N
N
SPh
Cl
10
9
8
7
6
5
4
3
2
1
0 ppm
0.94
1.00
5.18
5.22
1.06
1.06
1.07
151.76
151.68
151.06
144.55
137.11
133.15
131.93
131.21
129.25
129.14
129.04
127.57
127.11
77.34
77.03
76.71
60.91
38.13
200
180
160
140
120
100
80
60
40
20
0 ppm

Compound 4x

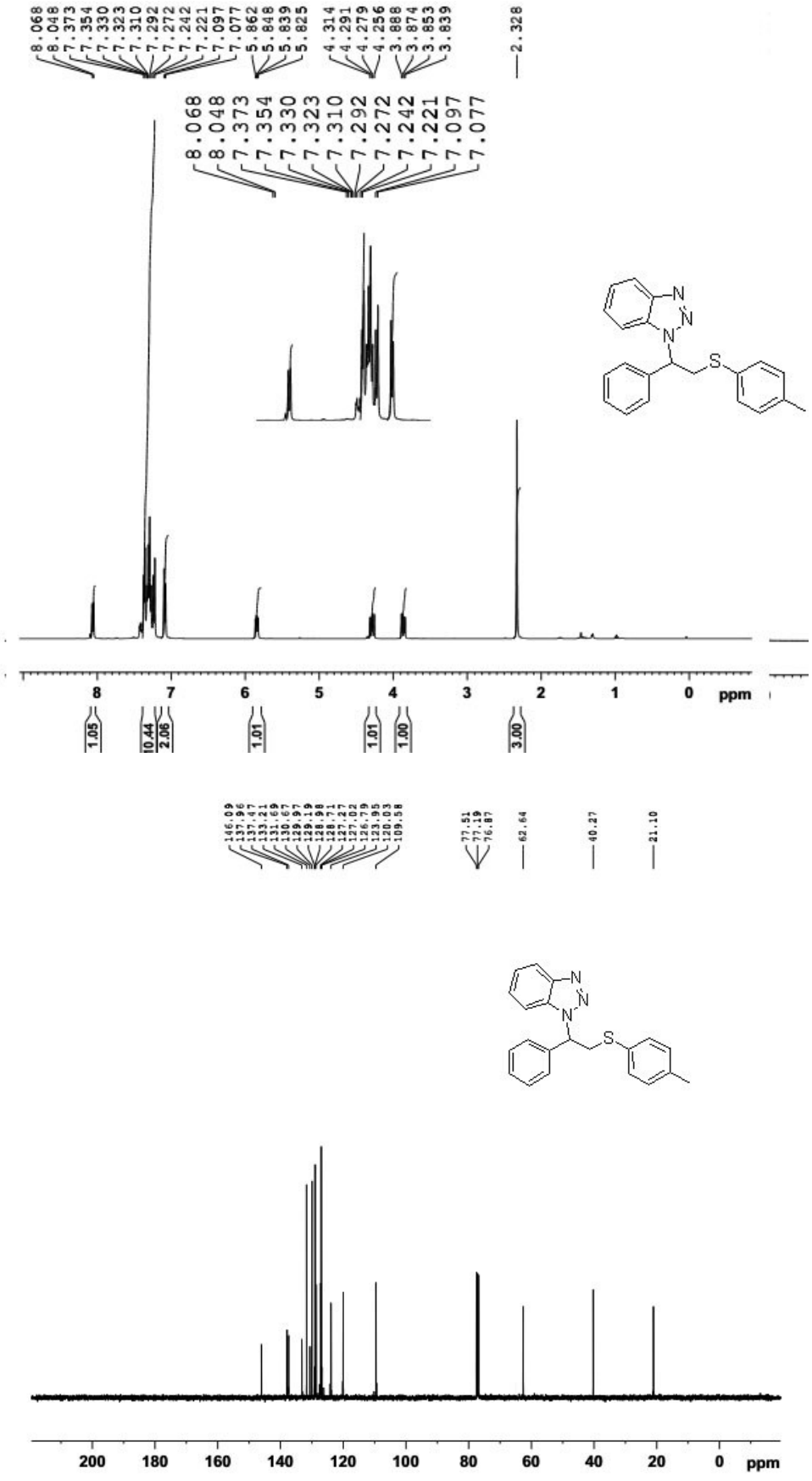

7.272
7.255
7.242
7.232
7.218
7.211
7.202
7.176
7.133
7.113
7.106
7.100
7.091
7.082
5.518
5.505
4.344
4.329
3.247
3.228
3.224
3.208
2.392
2.375
O2SHN
SPh
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.97
8.24
4.00
0.93
1.00
1.98
3.07
143.24
139.21
136.88
134.34
130.26
129.40
129.08
128.57
127.99
127.23
127.11
126.83
126.81
126.13
77.38
77.06
76.75
56.68
41.15
21.48
O2SHN
SPh
200 180 160 140 120 100 80 60 40 20 0 ppm

Compound 4y

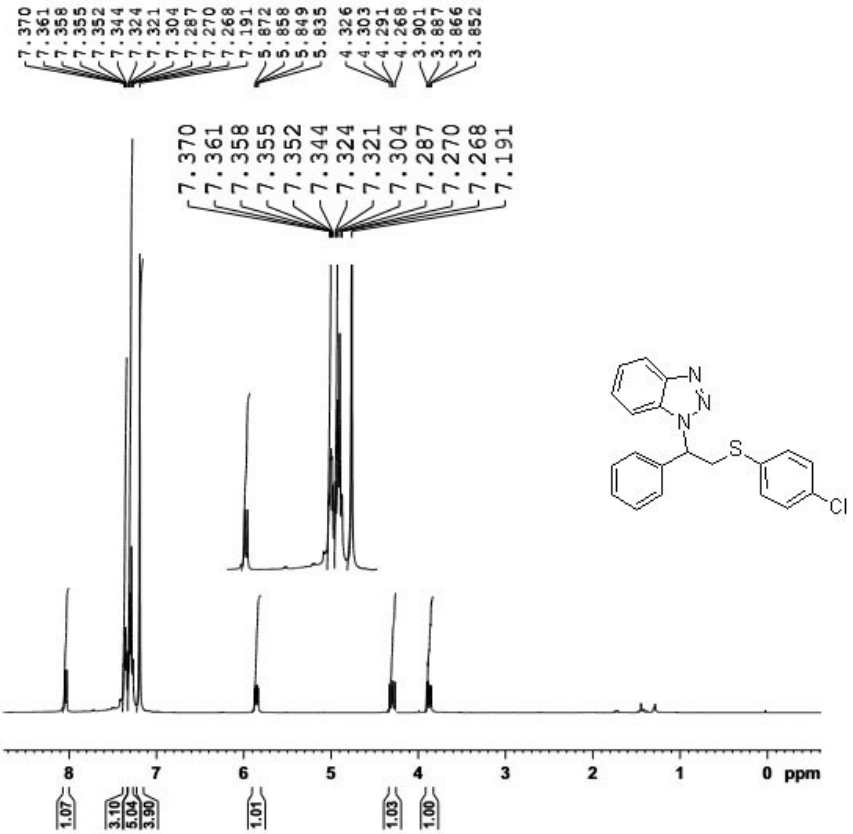

7.309
7.287
7.274
7.269
7.265
7.258
7.252
7.248
7.242
7.228
7.224
7.217
7.210
7.090
7.087
7.074
7.068
5.497
5.485
4.351
4.344
4.337
4.331
4.317
3.255
3.234
3.220
3.202
3.181
3.167
3.146
0.020
Cl
O2SHN
SPh
8
7
6
5
4
3
2
1
0
2.09
9.25
2.05
0.98
1.00
2.02

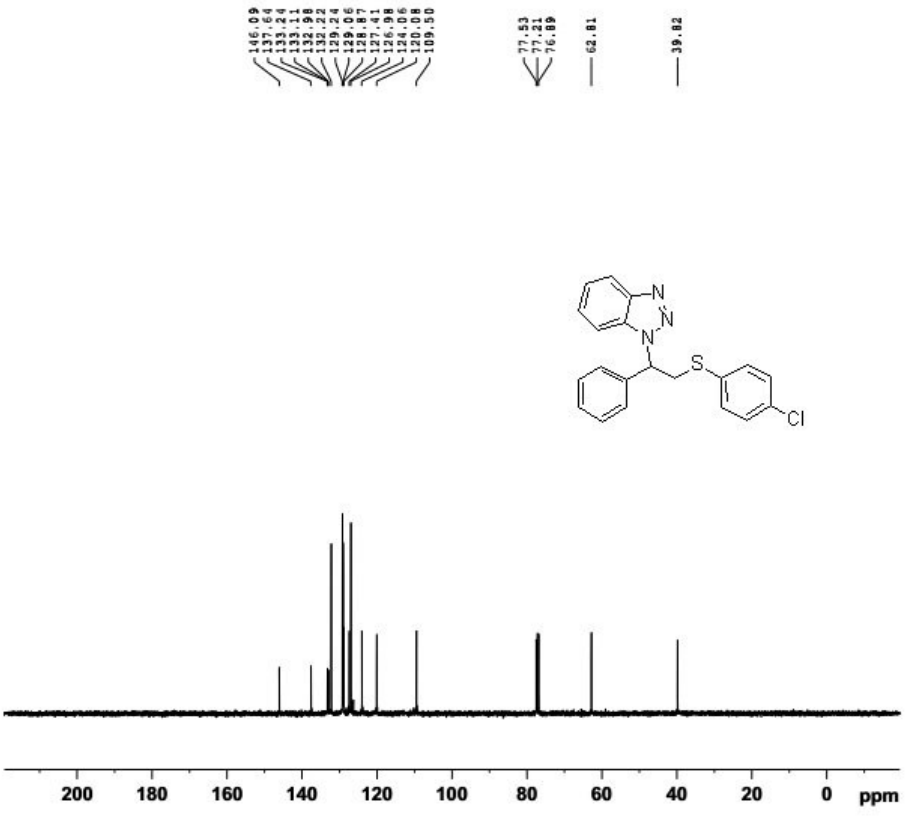

138.94
138.86
138.43
133.88
130.37
129.21
128.96
128.65
128.60
128.18
127.09
126.80
77.33
77.01
76.69
56.67
41.21
Cl
O2SHN
SPh
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 4z

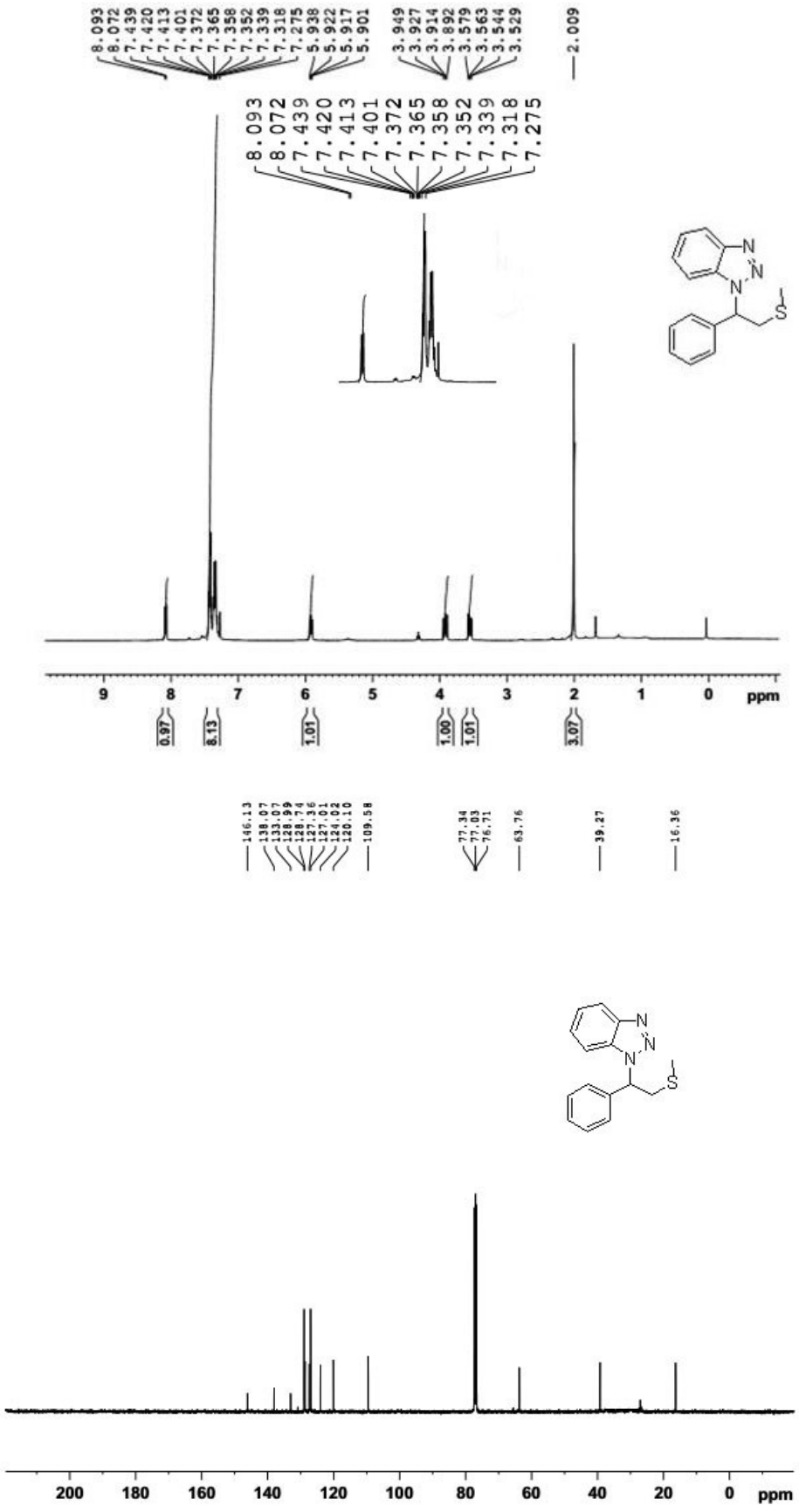

8.068
8.048
7.373
7.354
7.330
7.323
7.310
7.292
7.272
7.242
7.221
7.097
7.077
5.862
5.848
5.839
5.825
4.314
4.291
4.279
4.256
3.888
3.874
3.853
3.839
2.328
ppm
1.05
10.44
2.06
1.01
1.01
1.00
3.00
146.09
137.96
137.47
133.21
130.69
130.67
129.97
129.19
128.98
128.71
127.27
127.02
126.79
123.95
120.03
109.58
77.51
77.19
76.87
62.64
40.27
21.10
ppm

Compound 4aa

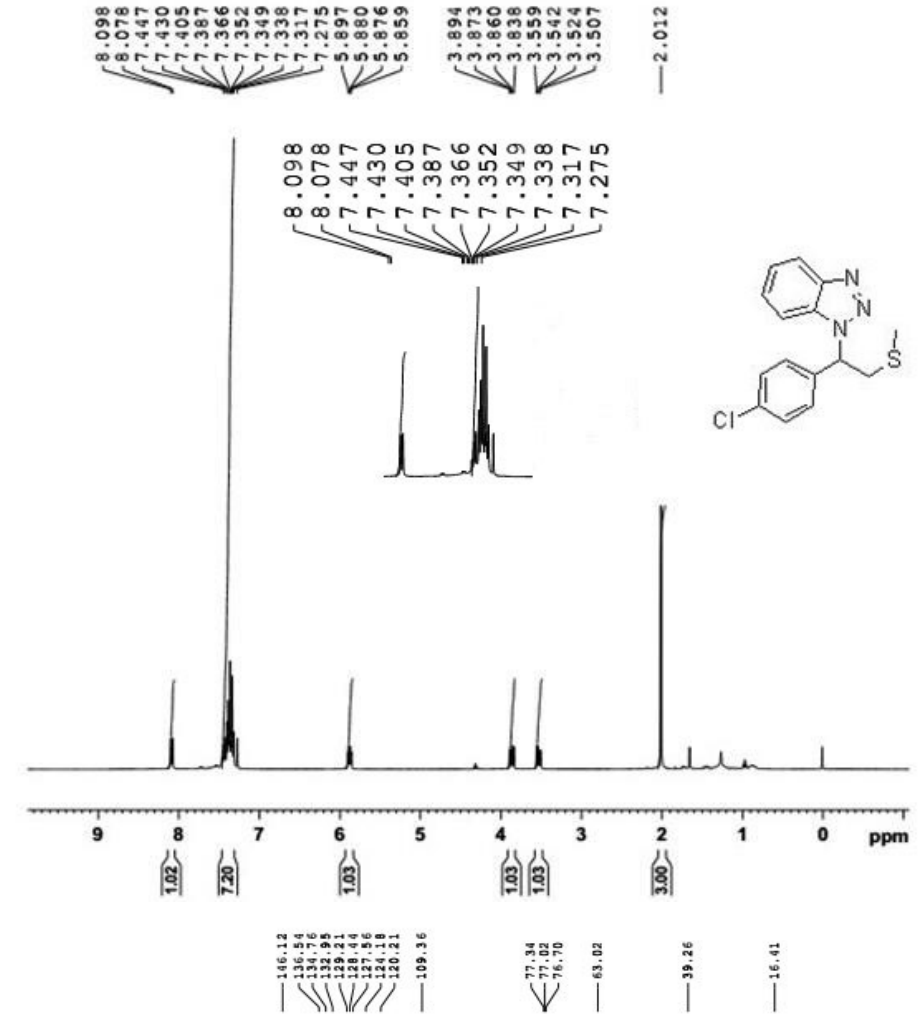


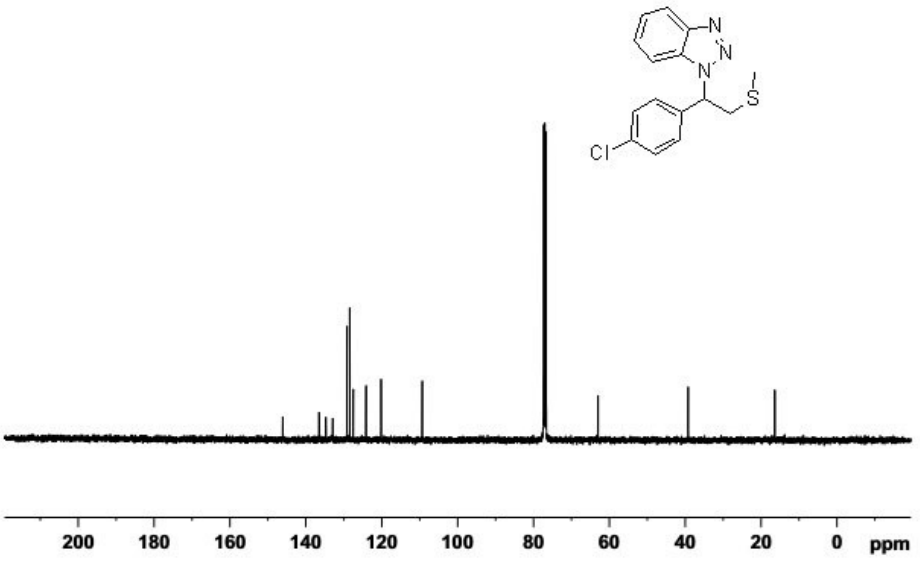


Compound 4ab



Compound 4ac





Compound 4ad