Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Visible light photoredox catalysis: Conversion of mixture of thiophenols and nitriles into 2-substituted benzothiazoles via consecutive C-S and C-N bonds formation reactions

Palani Natarajan*, Manjeet, Muskan, Navpreet Kaur Brar and Jaskamal Jot Kaur

Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh - 160014, India

pnataraj@pu.ac.in

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Experimental Section

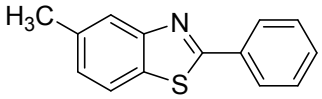
General Aspects: All commercial chemicals, reagents and precursors were used as received. All reactions were carried out under open air atmosphere. All solvents were double-distilled prior to use. Reactions were monitored by analytical thin layer chromatography on silica gel with visualization under UV light. Column chromatography was carried out on silica gel using 60-120 mesh powder. All NMR spectra were recorded on a Bruker Avance (300 MHz) spectrometer in CD_3CN: chemical shifts are expressed in parts per million (ppm) and were calibrated using the residual protonated solvent peak. IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrometer. High resolution mass spectra were collected on Waters-Q-TOF-Premier and LCMS-IT-TOF (ESI). Melting points were measured with PERFIT and are uncorrected.

Cyclic voltammograms were obtained in a Pyrex cell containing a standard three electrode setup (1 mm platinum disk working electrode, a platinum wire counter electrode and a silver wire as a pseudoreference electrode) connected to a potentiostat. The working electrode in each case was polished on a felt pad with an alumina slurry and then rinsed with water followed by acetone and subsequently dried with air. Tetra-n-butylammonium hexafluorophosphate was used as the supporting electrolyte. Potentials were measured at a scan rate of 50/100 mV/s in a dry solvent. Solutions for each electrochemical experiment contained the compound of interest at 5×10^{-4} M and the supporting electrolyte (0.1 M). Prior to each experiment, solutions were deaerated by bubbling N_2 gas.

General procedure for the synthesis of 2-substituted benzothiazoles

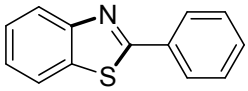
To an oven-dried round bottom flask equipped with a magnetic stir bar was charged with eosin Y (2.0 mol% in respect to amount of nitriles), nitrile (**BN**, 1.0 equiv.), aryl thiol (**TP**, 2.0 equiv.) and DMSO solvent. The mixture was stirred few minutes to mix well and then the flask was irradiated under a 5W green LED bulb at a distance of 5 cm. After stirring at 30 °C for 12-15 h, the solvent was removed under reduced pressure and the residue was then diluted with water. The aqueous solution was extracted (3 times) with ethyl acetate. The combined organic phases were dried over $MgSO_4$ and filtered. The filtrate was evaporated under reduced pressure to get the crude product, which was purified by column chromatography using hexane-ethyl acetate mixtures. The purity of the compound was confirmed by melting point analysis, IR, ^1H, and ^{13}C NMR and HRMS measurements, vide infra.

Experimental characterization data for products



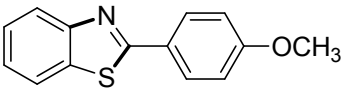
BT1

5-Methyl-2-phenylbenzo[d]thiazole (**BT1**): Pale yellow solid (413 mg, 91% yield); M.p.: 117-119 °C; R_f 0.31 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3052, 2924, 2851, 1483, 1448, 1075, 840, 756; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.11-8.09 (m, 2H), 7.91 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 4.0 Hz, 3H), 7.21 (d, *J* = 8.0 Hz, 1H), 2.56 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 167.9, 154.6, 136.4, 134.1, 132.1, 130.5, 128.8, 127.4, 126.5, 123.2, 121.1, 21.5. HRMS (ESI^+): calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690 found 226.0694.



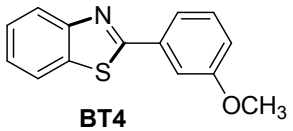
BT2

2-phenylbenzo[d]thiazole (BT2): Pale yellow solid (380 mg, 89% yield); M.p.: 113-115 °C; R_f 0.33 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3076, 3065, 1511, 1480, 1464, 1446, 1434, 1316, 1226, 966, 787, 733, 687; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.12-8.03 (m, 3H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.59-7.52 (m, 4H), 7.48-7.35 (m, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 168.3, 154.1, 135.2, 133.8, 131.1, 129.0, 127.7, 126.2, 125.3, 123.3, 121.8. HRMS (ESI^+): calcd for C13H10NS $[M+H]^+$ 212.0534 found 212.0533.



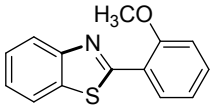
BT3

2-(4-methoxyphenyl)benzo[d]thiazole (BT3): Pale yellow solid (418 mg, 86% yield); M.p.: 127-130 °C; R_f 0.28 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 2925, 2854, 1457, 1435, 1377, 833; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.08-8.01 (m, 3H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 168.0, 161.9, 154.4, 134.8, 129.2, 126.5, 126.2, 124.9, 122.8, 121.7, 114.6, 55.6. HRMS (ESI^+): calcd for $C_{14}H_{12}NOS$ $[M+H]^+$ 242.0640 found 242.0643.



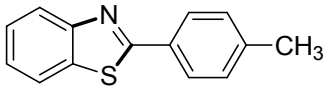
BT4

2-(3-methoxyphenyl)benzo[d]thiazole (BT4): Pale yellow solid (420 mg, 87% yield); M.p.: 82-84 °C; R_f 0.29 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 2924, 2851, 2381, 1453, 1431, 1369, 961, 836; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.08 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.49 (t, J = 8.0 Hz, 1H), 7.42-7.37 (m, 2H), 7.07-7.03 (m, 1H), 3.93 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 167.7, 159.9, 154.2, 135.3, 134.8, 130.1, 126.3, 125.4, 123.2, 121.4, 120.3, 117.3, 112.2, 55.5. HRMS (ESI^+): calcd for $C_{14}H_{12}NOS$ $[M+H]^+$ 242.0640 found 242.0647.



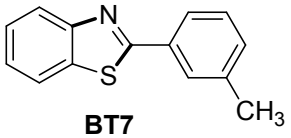
BT5

2-(2-methoxyphenyl)benzo[d]thiazole (BT5): Pale yellow solid (374 mg, 77% yield); M.p.: 104-105 °C; R_f 0.28 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3043, 2931, 2854, 1457, 1079, 832, 753; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.61-8.56 (m, 1H), 8.16-8.11 (m, 1H), 7.98-7.91 (m, 1H), 7.53-7.46 (m, 2H), 7.42-7.37 (m, 1H), 7.18-7.15 (m, 1H), 7.08-7.06 (m, 1H), 4.06 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 163.2, 157.4, 152.2, 136.0, 131.8, 129.5, 125.7, 124.5, 122.8, 122.4, 121.3, 121.2, 111.8, 55.6. HRMS (ESI^+): calcd for $C_{14}H_{12}NOS$ $[M+H]^+$ 242.0640 found 242.0641.



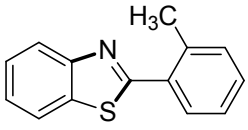
BT6

2-(*p*-tolyl)benzo[d]thiazole (BT6): Pale yellow solid (408 mg, 90% yield); M.p.: 85-87 °C; R_f 0.31 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3044, 2926, 2854, 1456, 1075, 833, 758; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.10 (d, J = 8.4 Hz, 1H), 8.03 (d, J = 8.4 Hz, 2H), 7.92-7.87 (m, 1H), 7.54-7.48 (m, 1H), 7.41-7.38 (m, 1H), 7.32 (d, J = 8.2 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 168.4, 154.3, 141.4, 135.1, 131.0, 129.8, 127.5, 126.3, 124.9, 123.1, 121.6, 21.5. HRMS (ESI^+): calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690 found 226.0695.



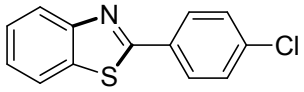
BT7

2-(*m*-tolyl)benzo[d]thiazole (**BT7**): Pale yellow solid (385 mg, 85% yield); M.p.: 68-70 °C; R_f 0.32 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3052, 2926, 2853, 1457, 1081, 835, 759; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.14 (d, J = 8.2 Hz, 1H), 7.96 (s, 1H), 7.92-7.87 (m, 2H), 7.54-7.51 (m, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.30 (d, J = 7.6 Hz, 1H), 2.47 (s, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 168.3, 154.2, 138.8, 135.1, 133.6, 131.9, 128.7, 128.1, 126.4, 125.2, 124.7, 123.2, 121.5, 21.3. HRMS (ESI^+): calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690 found 226.0692.



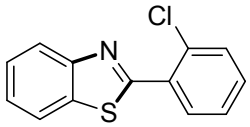
BT8

2-(*o*-tolyl)benzo[d]thiazole (BT8): Pale yellow solid (360 mg, 79% yield); M.p.: 55-58 °C; R_f 0.32 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 2924, 2855, 1454, 1428, 1072, 1026, 967; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.07 (d, J = 8.0 Hz, 1H), 8.02-7.96 (m, 2H), 7.92 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.35-7.27 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 167.8, 153.7, 137.2, 135.4, 133.2, 131.6, 130.4, 129.9, 126.2, 125.1, 124.9, 123.5, 121.4, 21.4. HRMS (ESI^+): calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690 found 226.0692.



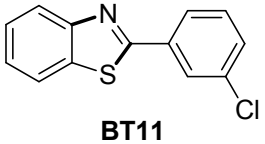
BT9

2-(4-chlorophenyl)benzo[d]thiazole (BT9): Pale yellow solid (454 mg, 92% yield); M.p.: 119-121 °C; R_f 0.34 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 2925, 2854, 1474, 1457, 1074, 829, 757; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.06 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 1H), 7.55-7.42 (m, 3H), 7.38 (t, J = 8.4 Hz, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 166.7, 154.2, 136.9, 135.2, 132.1, 129.4, 128.8, 126.6, 125.4, 123.4, 121.8. HRMS (ESI^+): calcd for $C_{13}H_9ClNS$ $[M+H]^+$ 246.0144 found 246.0148.



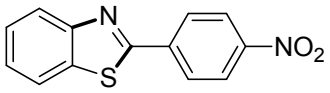
BT10

2-(2-chlorophenyl)benzo[d]thiazole (BT10): Pale yellow solid (375 mg, 76% yield); M.p.: 79-81 °C; R_f 0.33 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 2931, 2853, 1479, 1457, 1079, 831, 758, 709; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.31-8.19 (m, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.60-7.47 (m, 2H), 7.45-7.38 (m, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 164.2, 152.6, 136.2, 132.8, 132.3, 131.7, 131.3, 130.8, 127.2, 126.3, 125.5, 123.4, 121.5. HRMS (ESI^+): calcd for $C_{13}H_9ClNS$ $[M+H]^+$ 246.0144 found 246.0149.



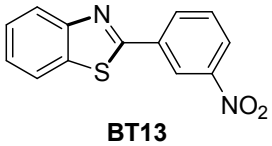
BT11

2-(3-chlorophenyl)benzo[d]thiazole (BT11): Pale yellow solid (408 mg, 83% yield); M.p.: 92-95 °C; R_f 0.33 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3054, 2933, 2852, 1454, 1075, 837, 753; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.13-8.11 (m, 1H); 8.09 (d, J = 8.0 Hz, 1H); 7.96-7.92 (m, 1H), 7.91-7.87 (m, 1H); 7.55-7.51 (m, 1H), 7.48-7.45 (m, 1H), 7.43-7.40 (m, 2H); ^{13}C NMR (CD_3CN, 75 MHz) δ 166.4, 154.0, 135.2, 135.1, 130.7, 130.1, 127.4, 126.4, 125.6, 125.7, 123.3, 121.5. HRMS (ESI^+): calcd for $C_{13}H_9ClNS$ $[M+H]^+$ 246.0144 found 246.0147.



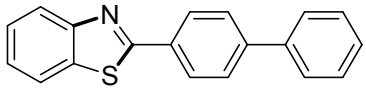
BT12

2-(4-nitrophenyl)benzo[d]thiazole (BT12): Yellow solid (400 mg, 78% yield); M.p.: 225-228 °C; R_f 0.19 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3070, 2966, 2854, 1603, 1572, 1617, 1506, 1440, 1376, 1334, 1271, 1130, 824, 721; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.41-8.37 (m, 2H), 8.30-8.27 (m, 2H), 8.17-8.14 (m, 1H), 7.99-7.96 (m, 1H), 7.59-7.56 (m, 1H), 7.51-7.48 (m, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 164.6, 154.2, 149.1, 139.3, 135.3, 128.4, 126.8, 126.2, 124.3, 124.0, 121.9. HRMS (ESI^+): calcd for $C_{13}H_9N_2O_2S$ $[M+H]^+$ 257.0385 found 257.0381.



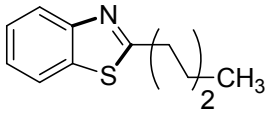
BT13

2-(3-nitrophenyl)benzo[d]thiazole (BT13): Pale yellow solid (390 mg, 76% yield); M.p.: 184-186 °C; R_f 0.19 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3064, 2938, 1529, 1463, 1349, 1107, 757, 729; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.89 (s, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.33-8.28 (m, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 7.8 Hz, 1H), 7.66-7.62 (m, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 165.0, 154.0, 148.9, 135.4, 135.2, 133.1, 130.3, 126.9, 126.2, 125.2, 123.9, 122.5, 121.9. HRMS (ESI^+): calcd for $C_{13}H_9N_2O_2S$ $[M+H]^+$ 257.0385 found 257.0384.



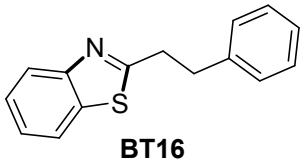
BT14

2-([1,1'-biphenyl]-4-yl)benzo[d]thiazole (BT14): Pale yellow solid (393 mg, 68% yield); M.p.: 242-245 °C; R_f 0.28 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3066, 3034, 2996, 2965, 2923, 1697, 1666, 1531, 1457, 1374, 1312, 1278, 1242, 1180, 1168, 759, 733, 711; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.19-8.10 (m, 3H), 7.93 (d, J = 4.0 Hz, 1H), 7.76-7.68 (m, 4H), 7.51-7.40 (m, 5H); ^{13}C NMR (CD_3CN, 75 MHz) δ 167.5, 154.2, 143.6, 140.0, 135.2, 132.6, 128.9, 128.1, 127.6, 127.0, 126.4, 125.1, 123.3, 121.7. HRMS (ESI^+): calcd for $C_{19}H_{14}NS$ $[M+H]^+$ 288.0847 found 288.0848.



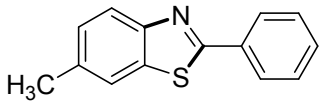
BT15

2-pentylbenzo[d]thiazole (BT15): White solid (294 mg, 71% yield); M.p.: 98-100 °C; R_f 0.36 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 2955, 2924, 2855, 1527, 1468, 1578, 1174, 797, 611; ^{1}H NMR (CD_3CN, 300 MHz) δ 7.99-7.96 (m, 1H), 7.85-7.81 (m, 1H), 7.47-7.43 (m, 1H), 7.35-7.32 (m, 1H), 3.14 (t, J = 8.0 Hz, 2H), 1.91 (q, J = 8.0 Hz, 2H), 1.42-1.37 (m, 4H), 0.98(t, J = 7.6 Hz, 2H); ^{13}C NMR (CD_3CN, 75 MHz) δ 172.3, 153.4, 135.1, 125.9, 124.7, 122.5, 121.4, 34.2, 31.3, 29.3, 22.1, 13.9. HRMS (ESI^+): calcd for $C_{12}H_{16}NS$ $[M+H]^+$ 206.1003 found 206.1006.



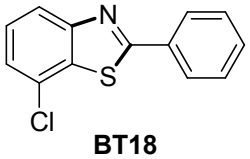
BT16

2-phenethylbenzo[d]thiazole (**BT16**): White solid (332 mg, 69% yield); M.p.: 94-96 °C; R_f 0.34 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): ν 3038, 2991, 2966, 1698, 1667, 1531, 1456, 1432, 1376, 1310, 1276, 1240, 1166, 730, 647; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.04-8.01 (m, 1H), 7.87-7.83 (m, 1H), 7.51-7.46 (m, 1H), 7.40-7.36 (m, 1H), 7.33-7.28 (m, 3H), 7.26-7.23 (m, 1H), 3.51 (t, J = 8.4 Hz, 2H), 3.46 (t, J = 8.4 Hz, 2H); ^{13}C NMR (CD_3CN, 75 MHz) δ 170.9, 153.2, 140.1, 135.3, 128.7, 128.5, 126.4, 126.0, 124.8, 122.6, 121.4, 36.1, 35.6. HRMS (ESI^+): calcd for $C_{15}H_{14}NS$ $[M+H]^+$ 240.0847 found 240.0849.



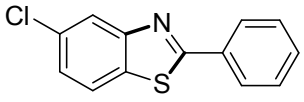
BT17

6-methyl-2-phenylbenzo[d]thiazole (BT17): Pale yellow solid (350 mg, 77% yield); M.p.: 129-131 °C; R_f 0.31 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): ν 3079, 3066, 1512, 1480, 1463, 1447, 1433, 1321, 1227, 968, 785, 734, 687; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.13-8.06 (m, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.55-7.45 (m, 3H), 7.31 (d, J = 8.0, 1H), 2.51 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 167.1, 152.4, 135.5, 133.8, 130.9, 129.1, 128.0, 127.7, 122.9, 121.5, 21.5. HRMS (ESI^+): calcd for $C_{14}H_{12}NS$ $[M+H]^+$ 226.0690 found 226.0694.



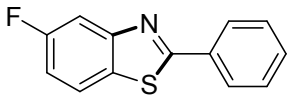
BT18

7-chloro-2-phenylbenzo[d]thiazole (BT18): Pale yellow solid (340 mg, 69% yield); M.p.: 84-86 °C; R_f 0.32 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): ν 3083, 3067, 1514, 1478, 1464, 1451, 1434, 1323, 1233, 969, 787, 735, 687; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.11 (d, J = 4.0 Hz, 2H), 7.97 (d, J = 8.6 Hz, 1H), 7.55-7.46 (m, 2H), 7.44-7.35 (m, 3H); ^{13}C NMR (CD_3CN, 75 MHz): δ 168.8, 154.7, 135.4, 133.2, 131.4, 129.1, 127.6, 127.3, 126.9, 124.7, 121.6. HRMS (ESI^+): calcd for $C_{13}H_9ClNS$ $[M+H]^+$ 246.0144 found 246.0148.



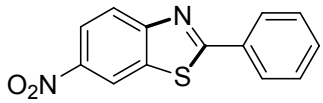
BT19

5-chloro-2-phenylbenzo[d]thiazole (BT19): Pale yellow solid (365 mg, 74% yield); M.p.: 138-140 °C; R_f 0.32 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3046, 2931, 2852, 1453, 1072, 826, 749; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.09-8.05 (m, 3H), 7.82 (d, J = 8.4 Hz, 1H), 7.54-7.49 (m, 3H), 7.35 (d, J = 8.4 Hz, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 169.8, 155.1, 133.5, 133.3, 132.3, 131.4, 129.1, 127.5, 125.6, 123.1, 122.2. HRMS (ESI^+): calcd for $C_{13}H_9ClNS$ $[M+H]^+$ 246.0144 found 246.0147.



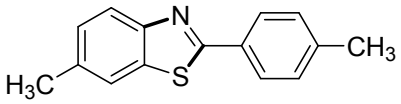
BT20

5-fluoro-2-phenylbenzo[d]thiazole (BT20): Pale yellow solid (341 mg, 74% yield); M.p.: 122-125 °C; R_f 0.33 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3051, 2932, 2855, 1453, 1079, 836, 753; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.09-8.04 (m, 2H), 7.81-7.72 (m, 2H), 7.46-7.39 (m, 3H), 7.19-7.11 (m, 1H); ^{13}C NMR (CD_3CN, 75 MHz) δ 170.6, 163.3, 160.4, 155.0 (d, J = 14.0 Hz), 133.6, 131.3, 130.4, 129.1, 127.6, 122.1 (d, J = 10.0 Hz), 113.9 (d, J = 25.4 Hz), 109.2 (d, J = 23.8 Hz). HRMS (ESI^+): calcd for $C_{13}H_9FNS$ $[M+H]^+$ 230.0440 found 230.0445.



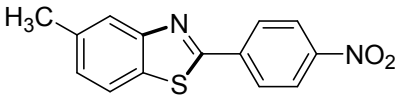
BT21

6-nitro-2-phenylbenzo[d]thiazole (BT21): Yellow solid (398 mg, 77% yield); M.p.: 189-190 °C; R_f 0.20 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3073, 2969, 2861, 1603, 1582, 1617, 1509, 1441, 1336, 1132, 826, 723; ^{1}H NMR (CD_3CN, 300 MHz) δ 8.86 (d, J = 2.4 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 8.18-8.11 (m, 3H), 7.61-7.54 (m, 3H); ^{13}C NMR (CD_3CN, 75 MHz) δ 173.8, 157.9, 144.8, 135.4, 132.7, 132.3, 129.4, 128.0, 123.5, 122.0, 118.3. HRMS (ESI^+): calcd for $C_{13}H_9N_2O_2S$ $[M+H]^+$ 257.0385 found 257.0388.



BT22

6-methyl-2-(*p*-tolyl)benzo[d]thiazole (**BT22**): Pale yellow solid (342 mg, 71% yield); M.p.: 94-96 °C; R_f 0.29 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3052, 2929, 2853, 1457, 1078, 832, 752; ^{1}H NMR (CD_3CN, 300 MHz) *δ* 8.01-7.95 (m, 3H), 7.66-7.64 (m, 1H), 7.32-7.26 (m, 3H), 2.49 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) *δ* 167.2, 152.1, 141.3, 135.2, 131.1, 129.6, 127.9, 127.4, 122.7, 121.4, 21.6, 21.5. HRMS (ESI^+): calcd for $C_{15}H_{14}NS$ $[M+H]^+$ 240.0847 found 240.0848.



BT23

5-methyl-2-(4-nitrophenyl)benzo[d]thiazole (BT23): Pale yellow solid (414 mg, 76% yield); M.p.: 201-202 °C; R_f 0.23 in ethyl acetate-hexane (25:75); IR (nujol, cm^{-1}): *v* 3074, 2962, 2859, 1619, 1584, 1507, 1338, 826; ^{1}H NMR (CD_3CN, 300 MHz) *δ* 8.02-7.97 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.56-7.51 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21-7.17 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (CD_3CN, 75 MHz) *δ* 164.7, 154.3, 149.0, 139.4, 135.5, 128.4, 126.9, 126.4, 124.5, 124.1, 121.9, 21.7. HRMS (ESI^+): calcd for $C_{14}H_{11}N_2O_2S$ $[M+H]^+$ 271.0541 found 271.0544.

References

1) Deng, H.; Li, Z. K.; Ke, F.; Zhou, X. G. *Chem. Eur. J.* **2012**, *18*, 4840.
2) Yang, Z. Y.; Chen, X.; Wang, S. Z.; Liu, J. D.; Xie, K.; Wang, A. W.; Tan, Z. *J. Org. Chem.* **2012**, *77*, 7086.
3) Ma, D. W.; Xie, S. W.; Xue, P.; Zhang, X. J.; Dong, J. H.; Jiang, Y. W. *Angew. Chem. Int. Ed.* **2009**, *48*, 4222.
4) Yamamoto, T.; Muto, K.; Komiyama, M.; Canivet, J.; Yamaguchi, J.; Itami, K. *Chem. Eur. J.* **2011**, *17*, 10113.
5) Ding, Q. P.; Huang, X. G.; Wu, J. *J. Comb. Chem.* **2009**, *11*, 1047.
6) Inamoto, K.; Hasegawa, C.; Hiroya, K.; Doi, T. *Org. Lett.* **2008**, *10*, 5147.
7) Praveen, C.; Hemanth Kumar, K.; Muralidharan, D.; Perumal, P.T. *Tetrahedron* **2008**, *64*, 2369.
8) Zhang, M.: Lu, W.-T.; Ruan, W.; Zhang, H.-J.; Wen, T.-B. *Tetrahedron Lett*. **2014**, *55*, 1806.

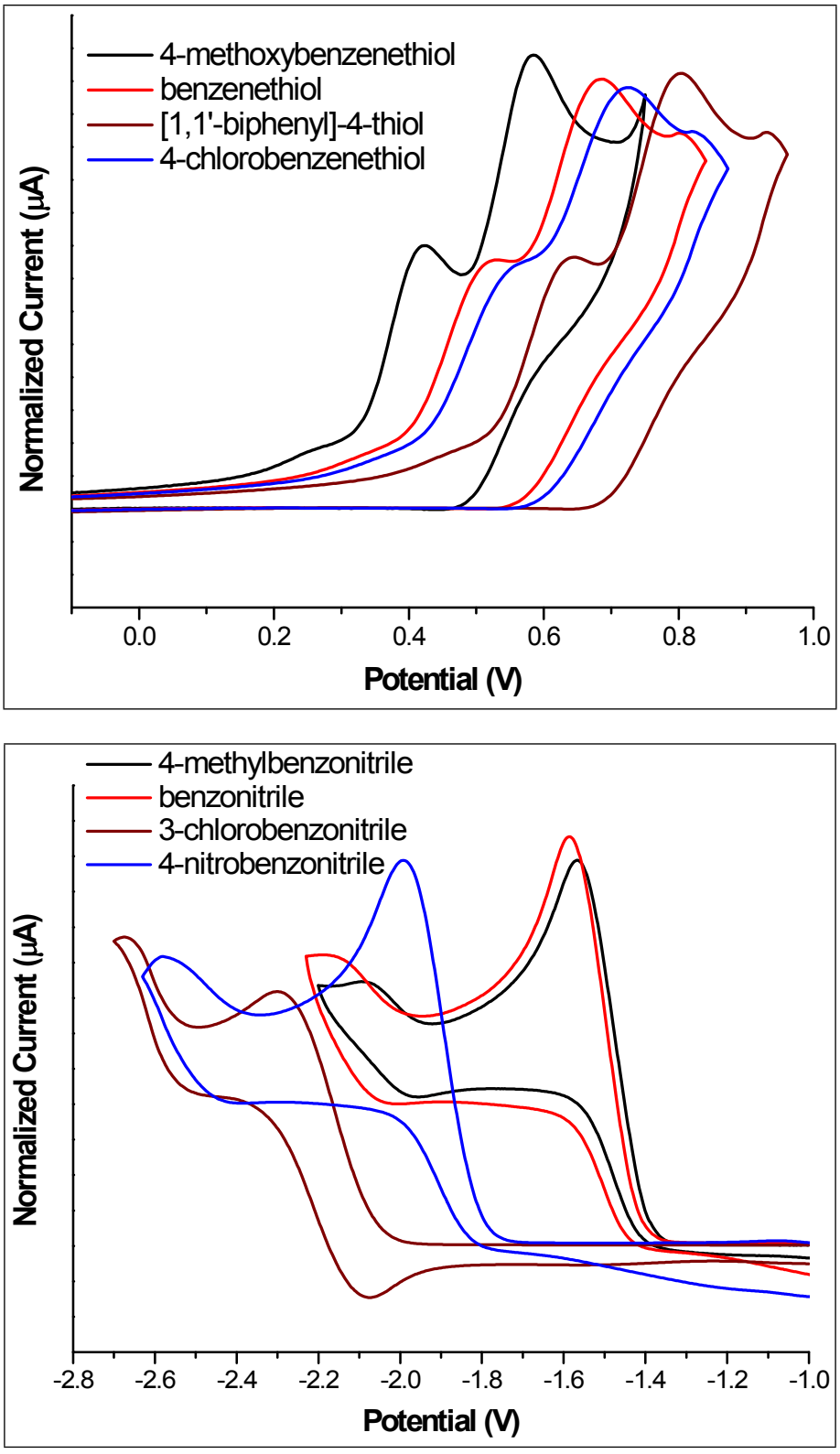


Figure S1. The cyclic voltammogram of aryl thiols (top) and aryl nitriles (bottom) at a scan rate of 50 mV/s.

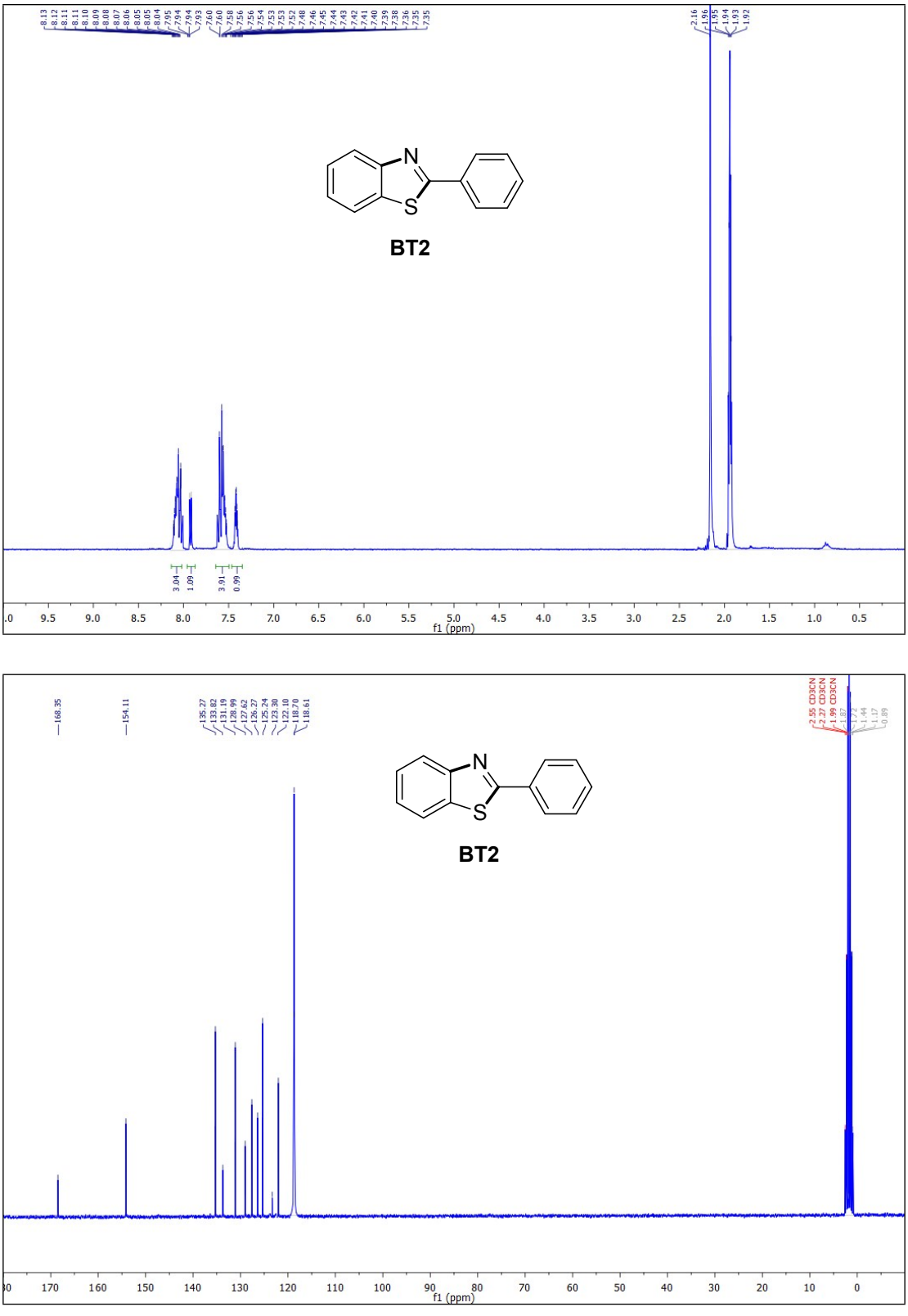


Figure S2. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT2** in CD_3CN.

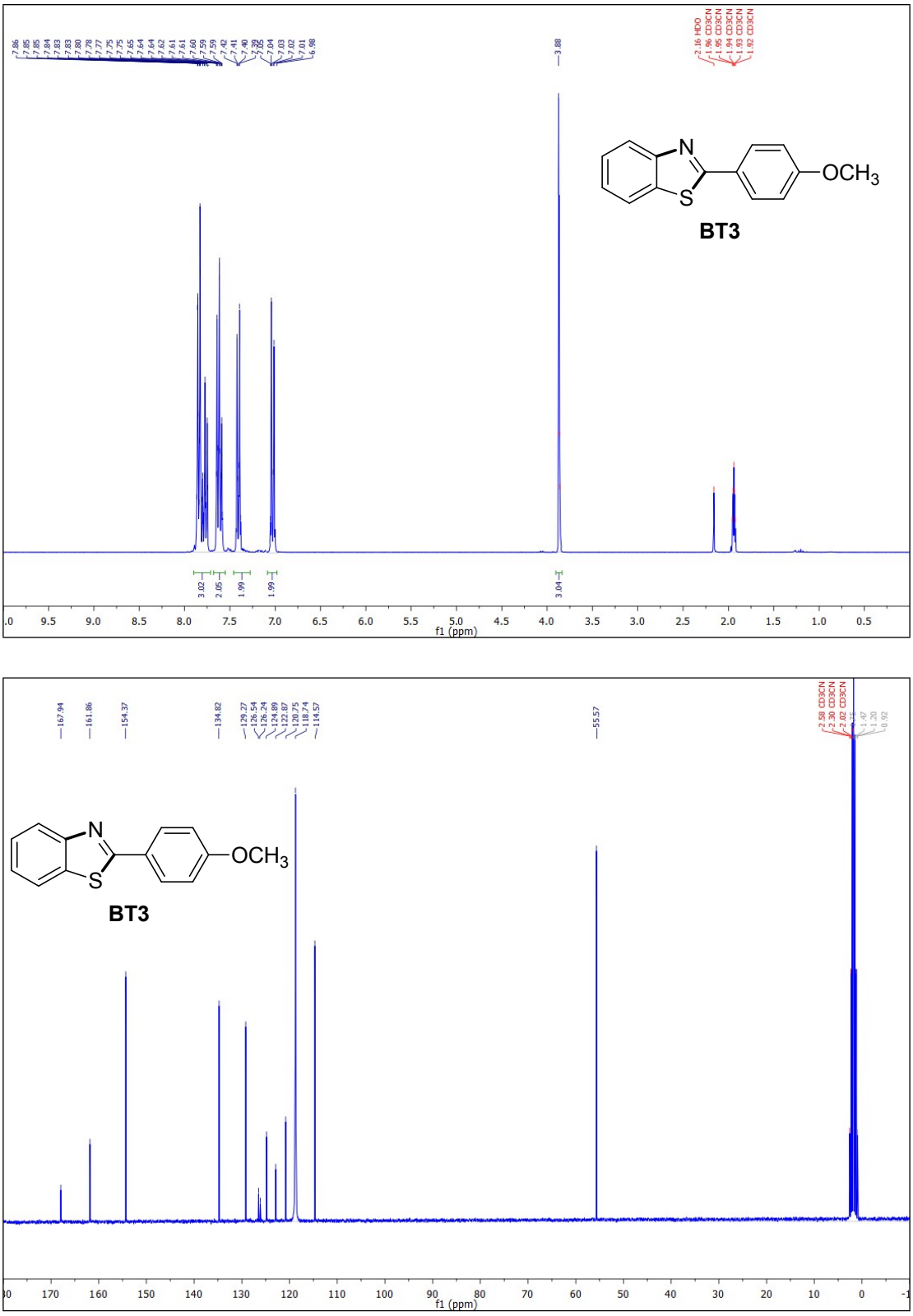


Figure S3. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT3** in CD_3CN.

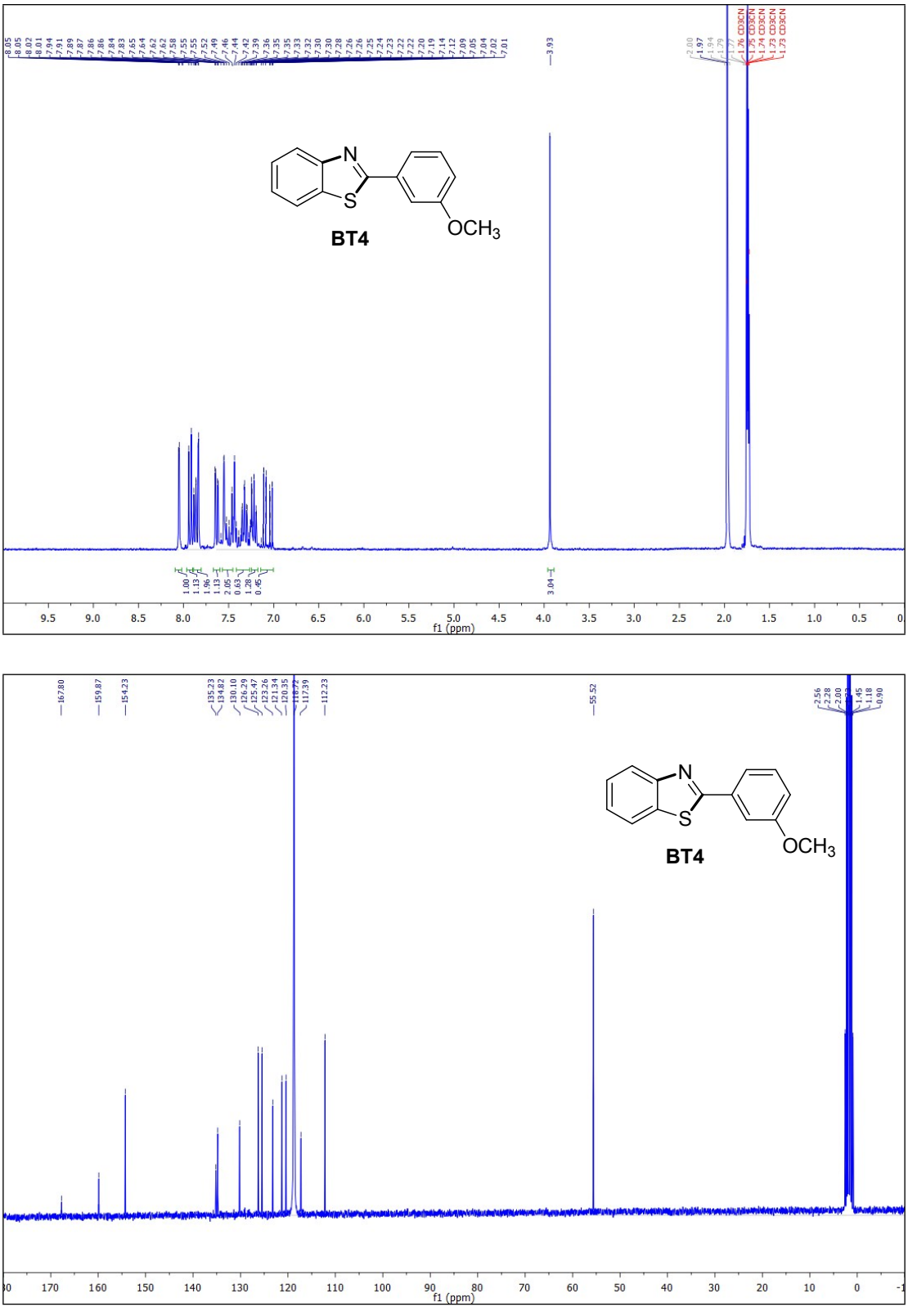


Figure S4. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT4** in CD_3CN.

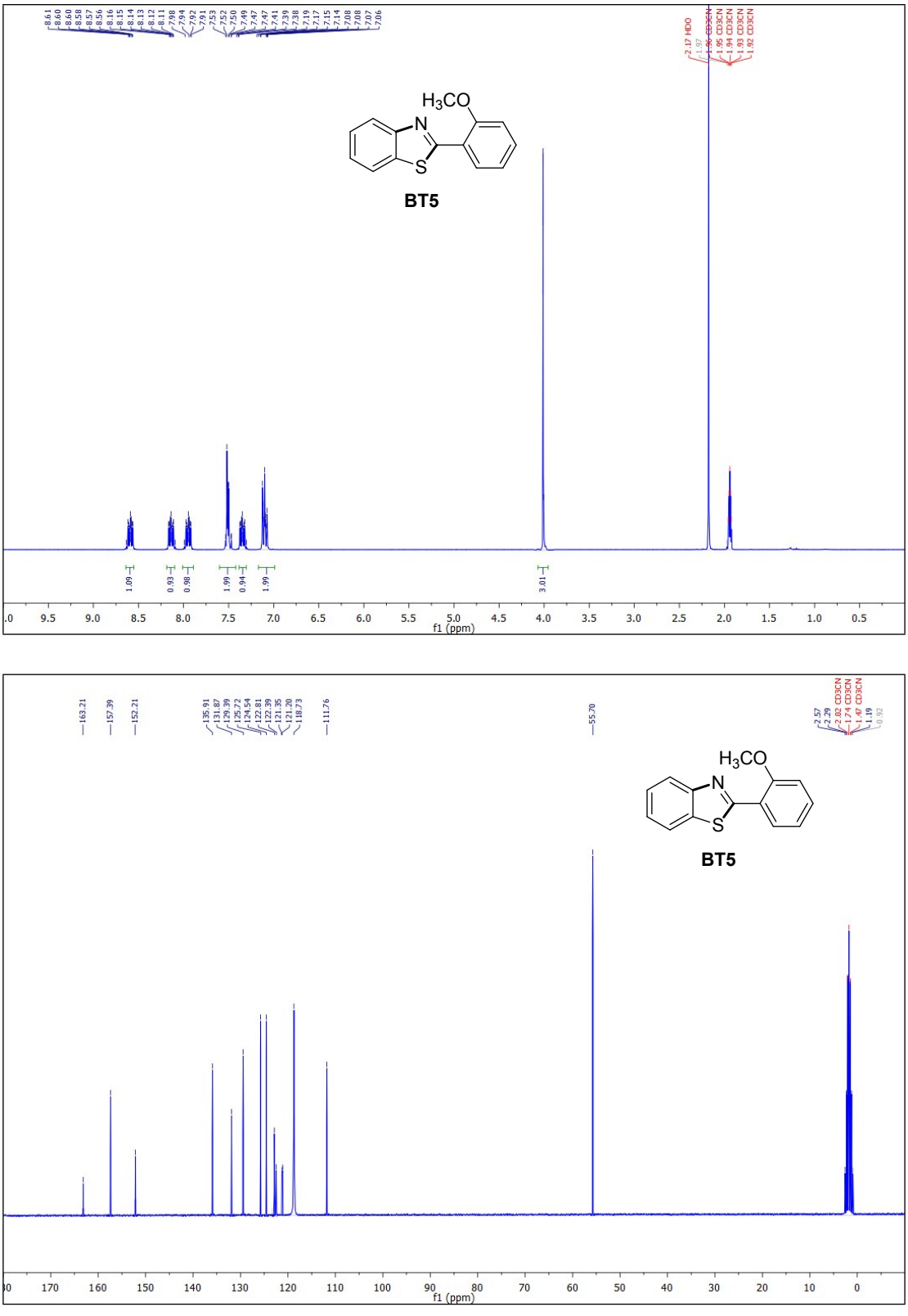


Figure S5. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT5** in CD_3CN.

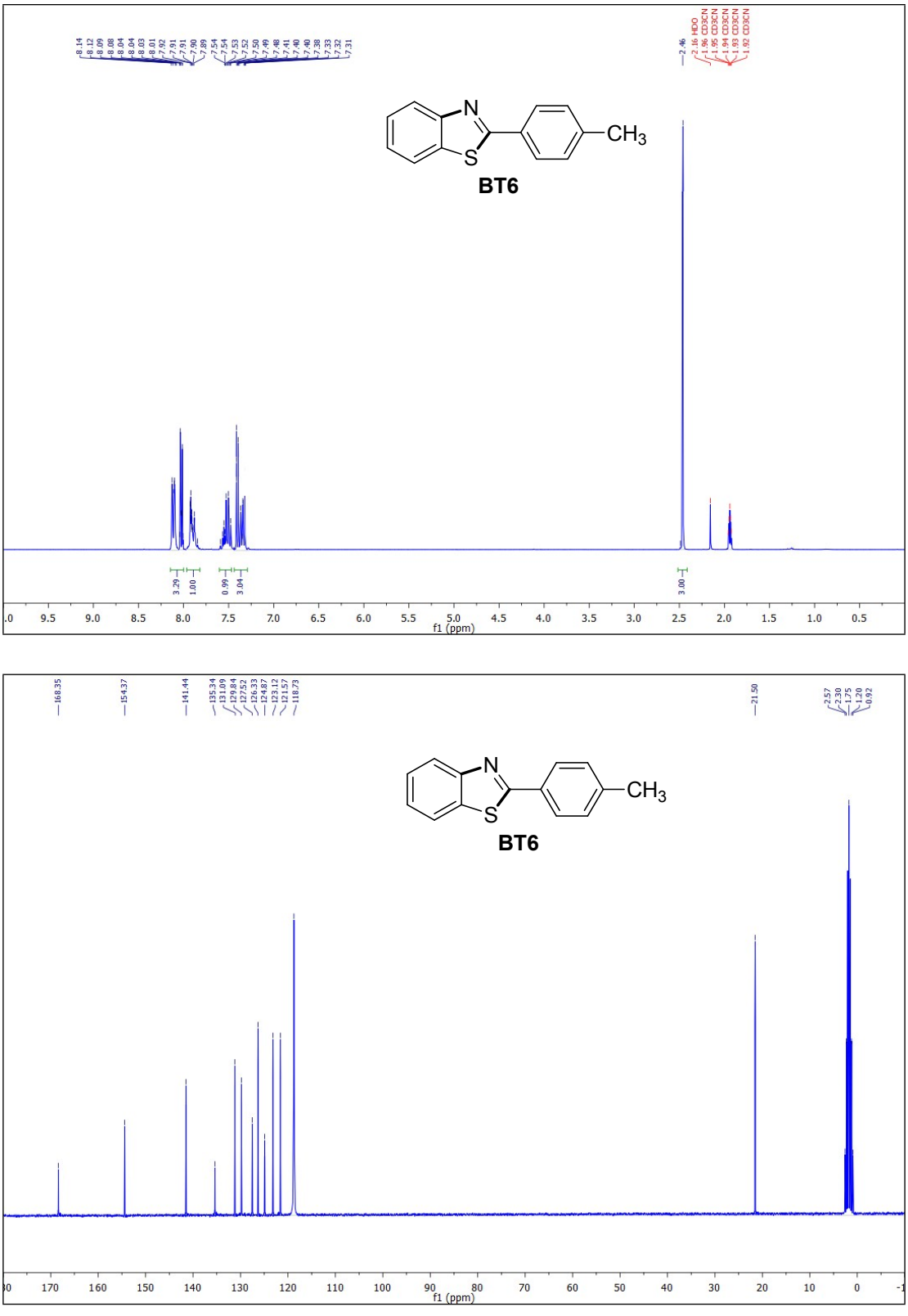


Figure S6. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT6** in CD_3CN.

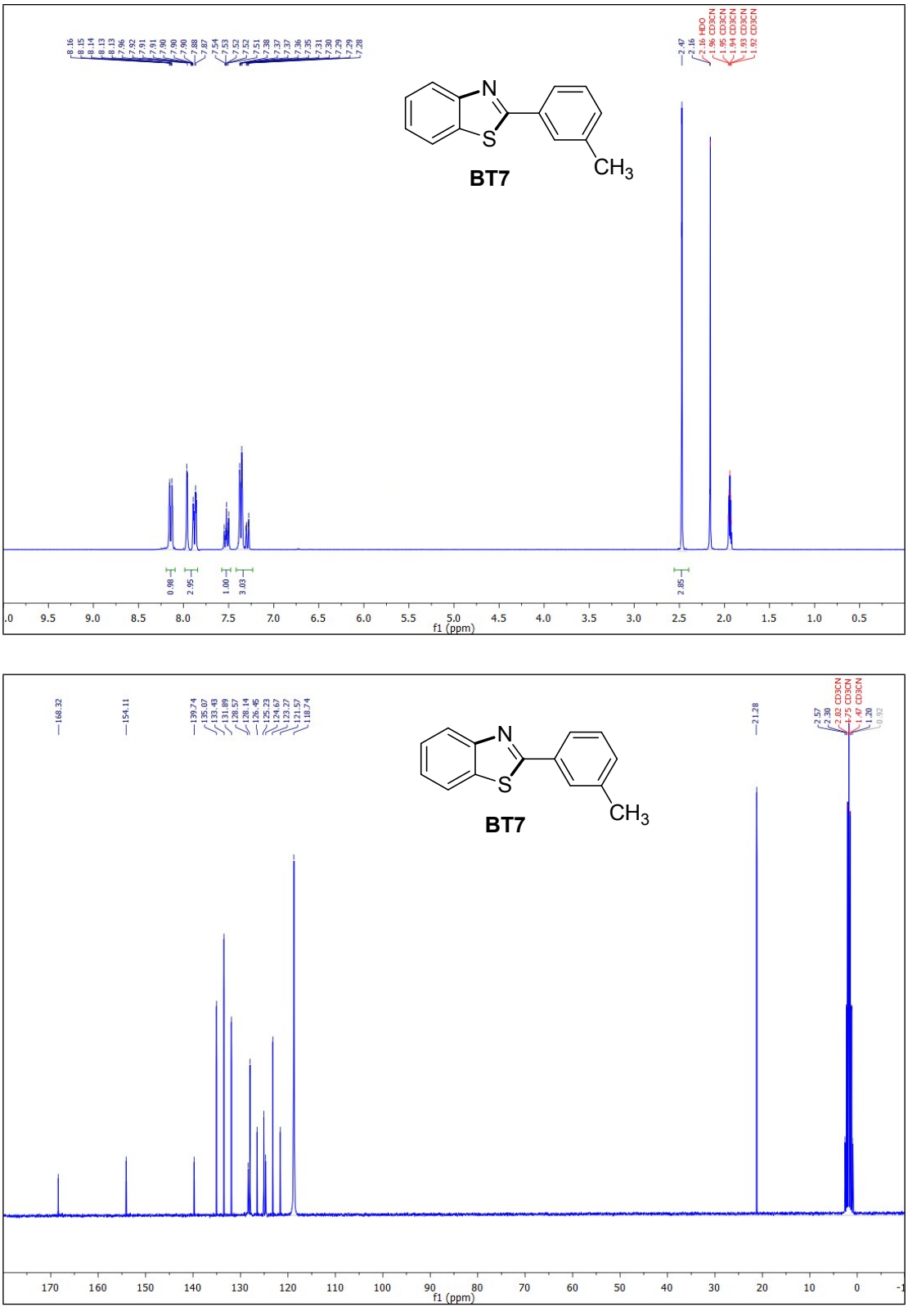


Figure S7. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT7** in CD_3CN.

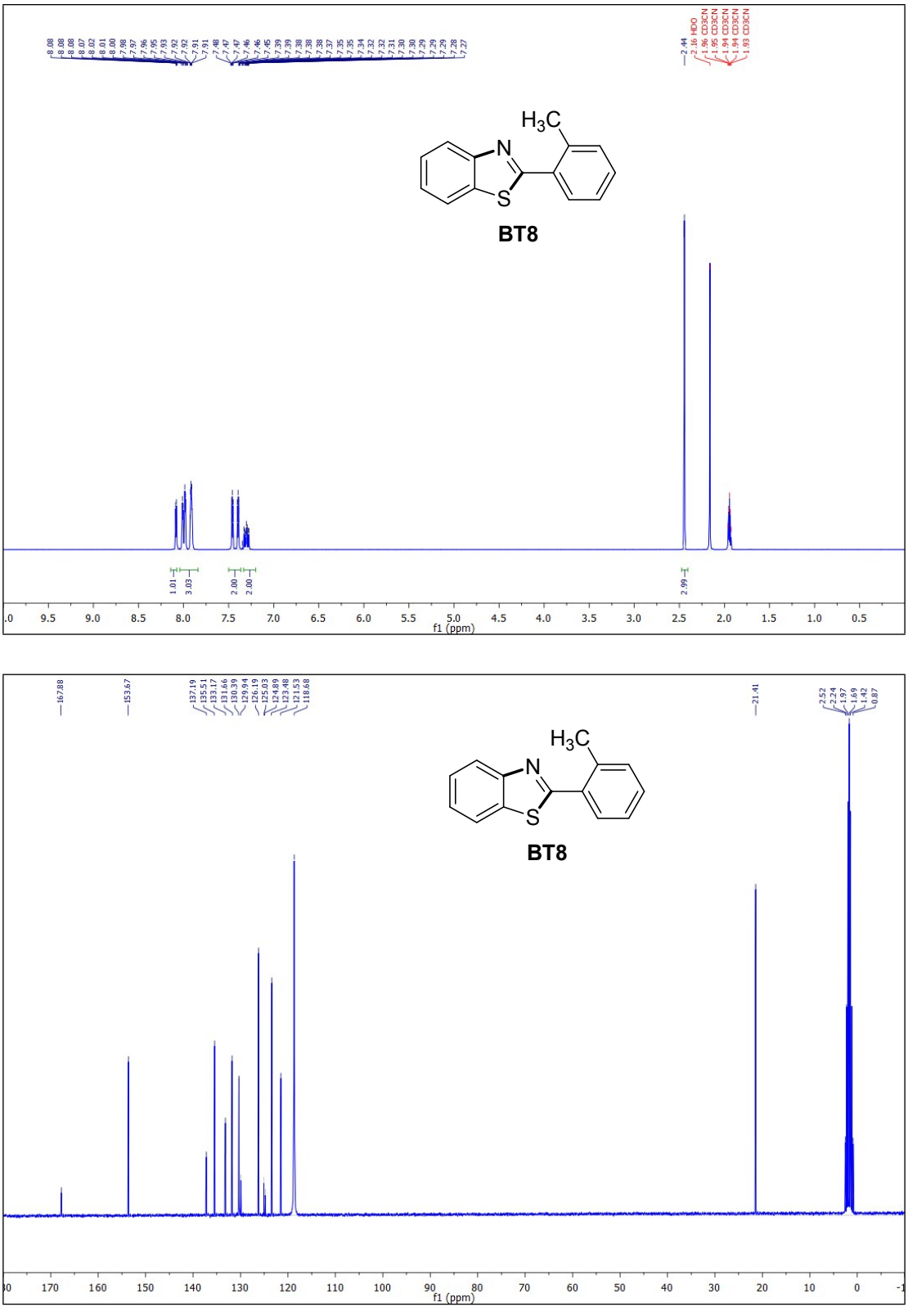


Figure S8. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT8** in CD_3CN.

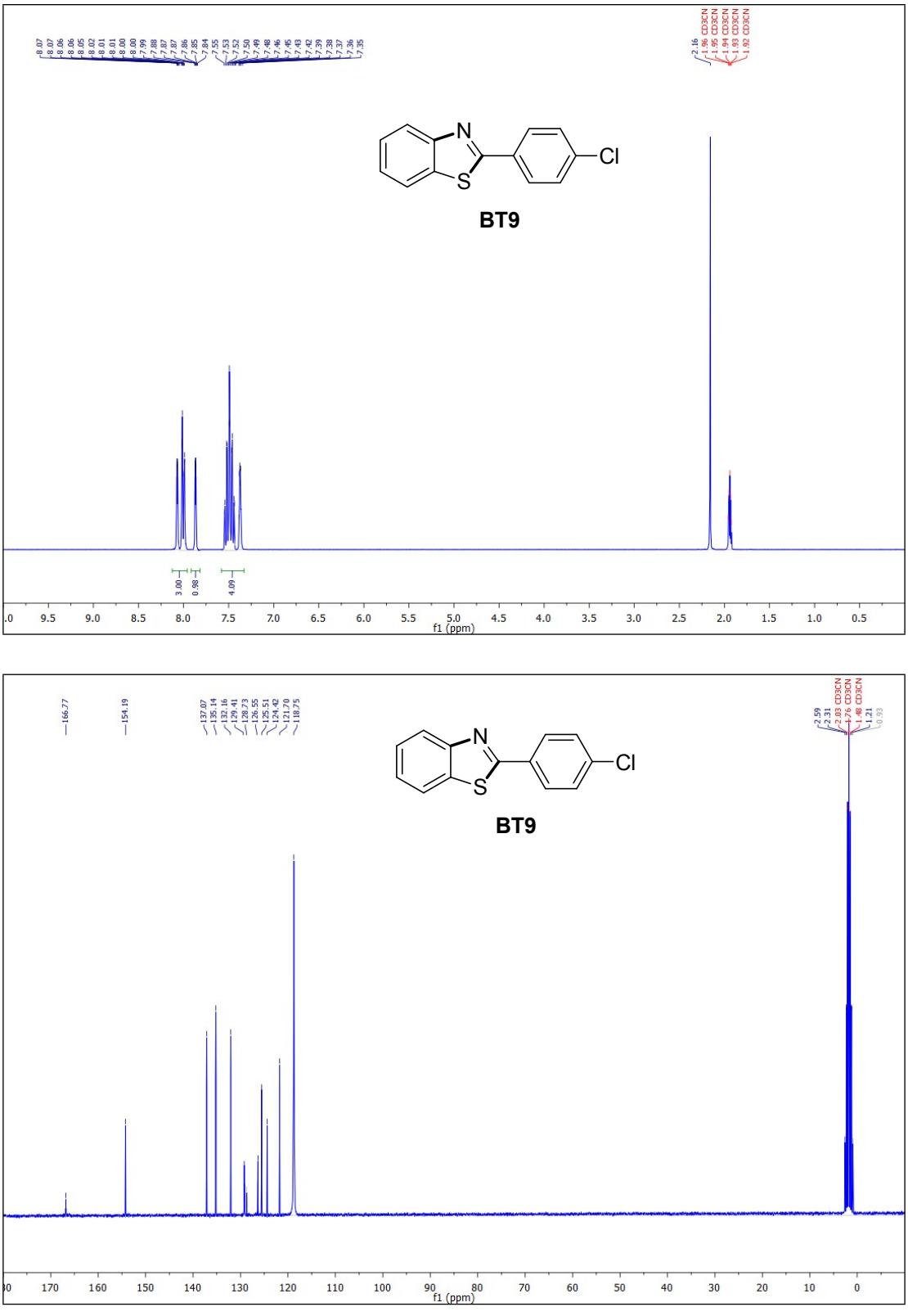


Figure S9. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT9** in CD_3CN.

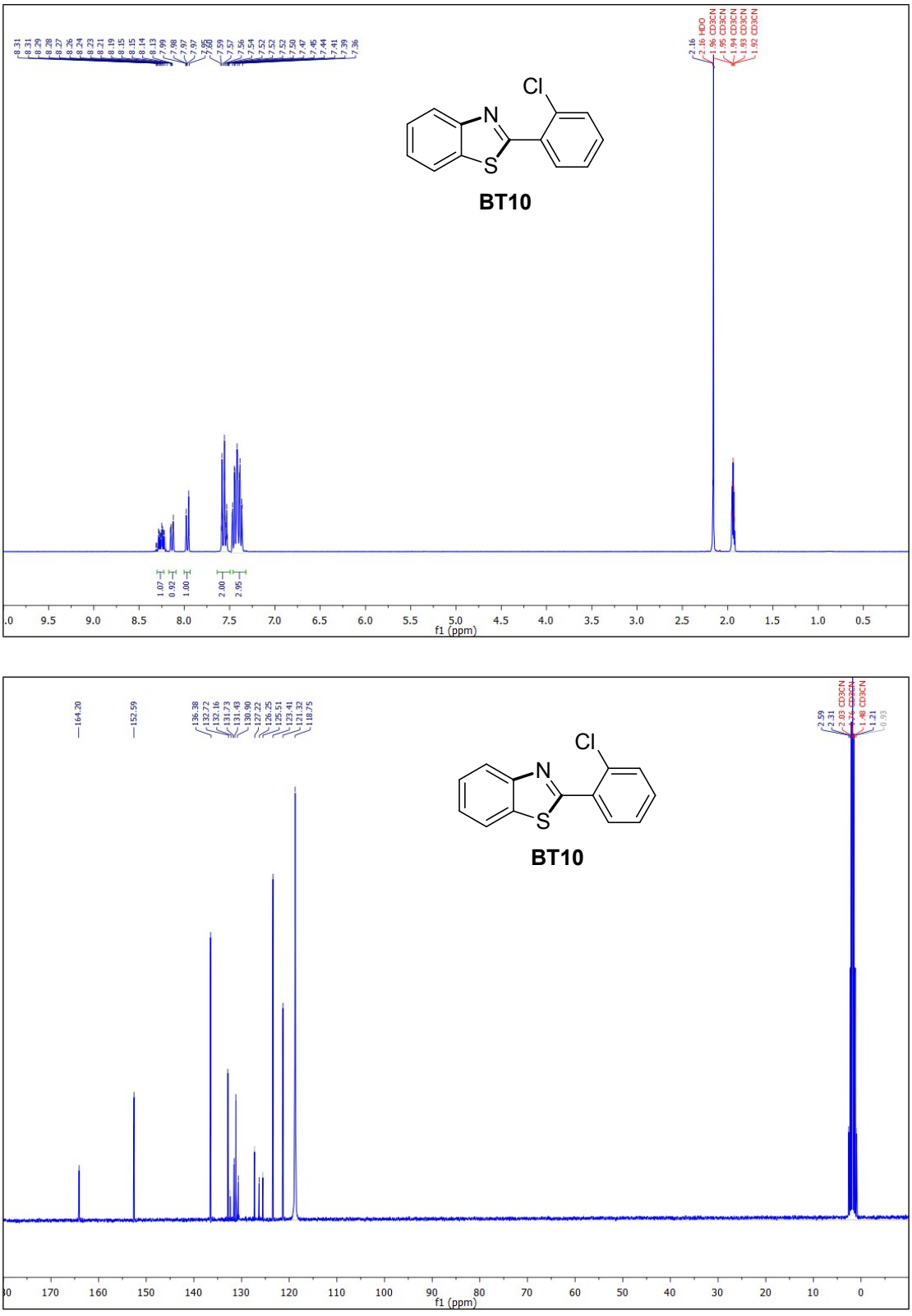


Figure S10. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT10** in CD_3CN.

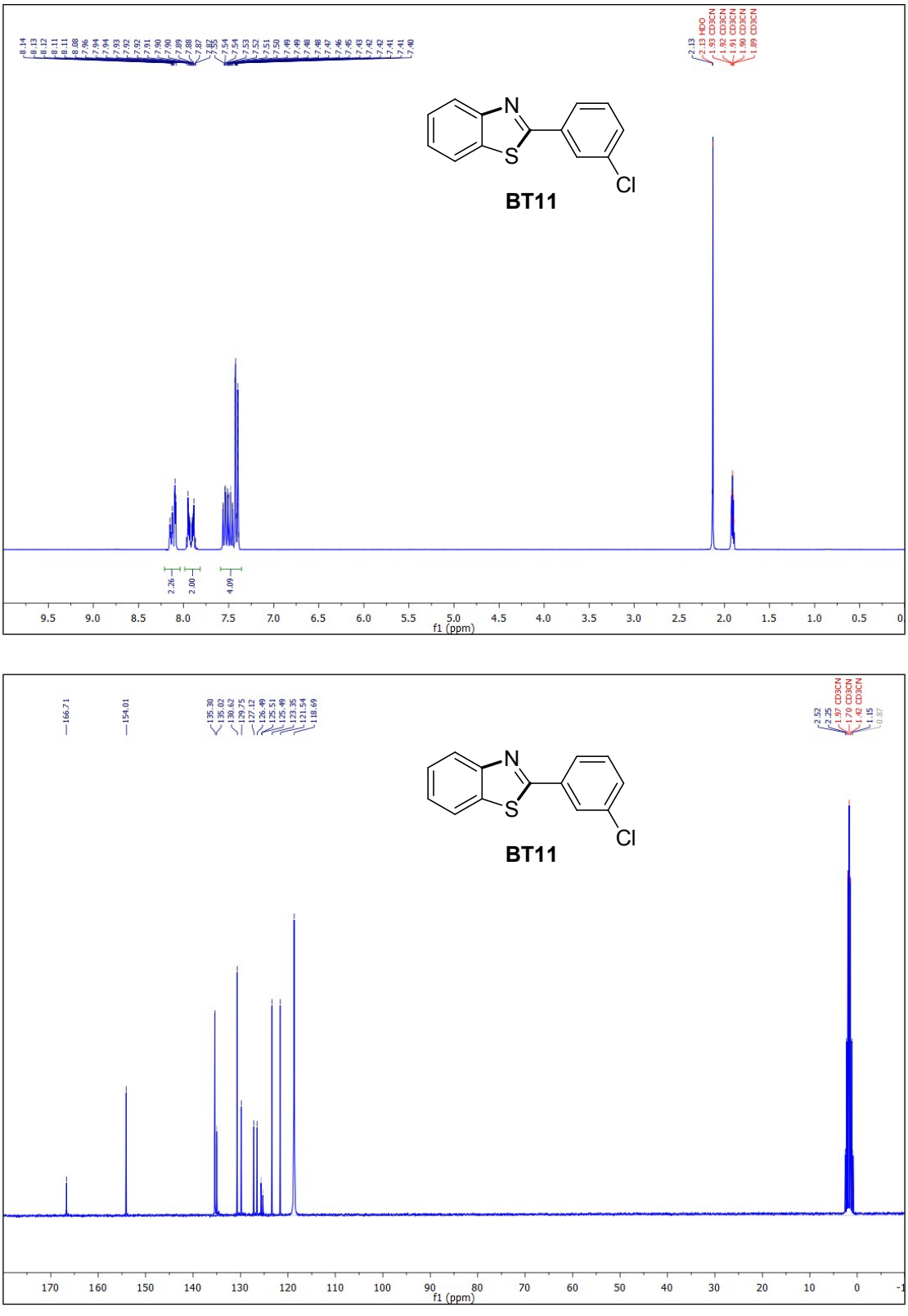


Figure S11. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT11** in CD_3CN.

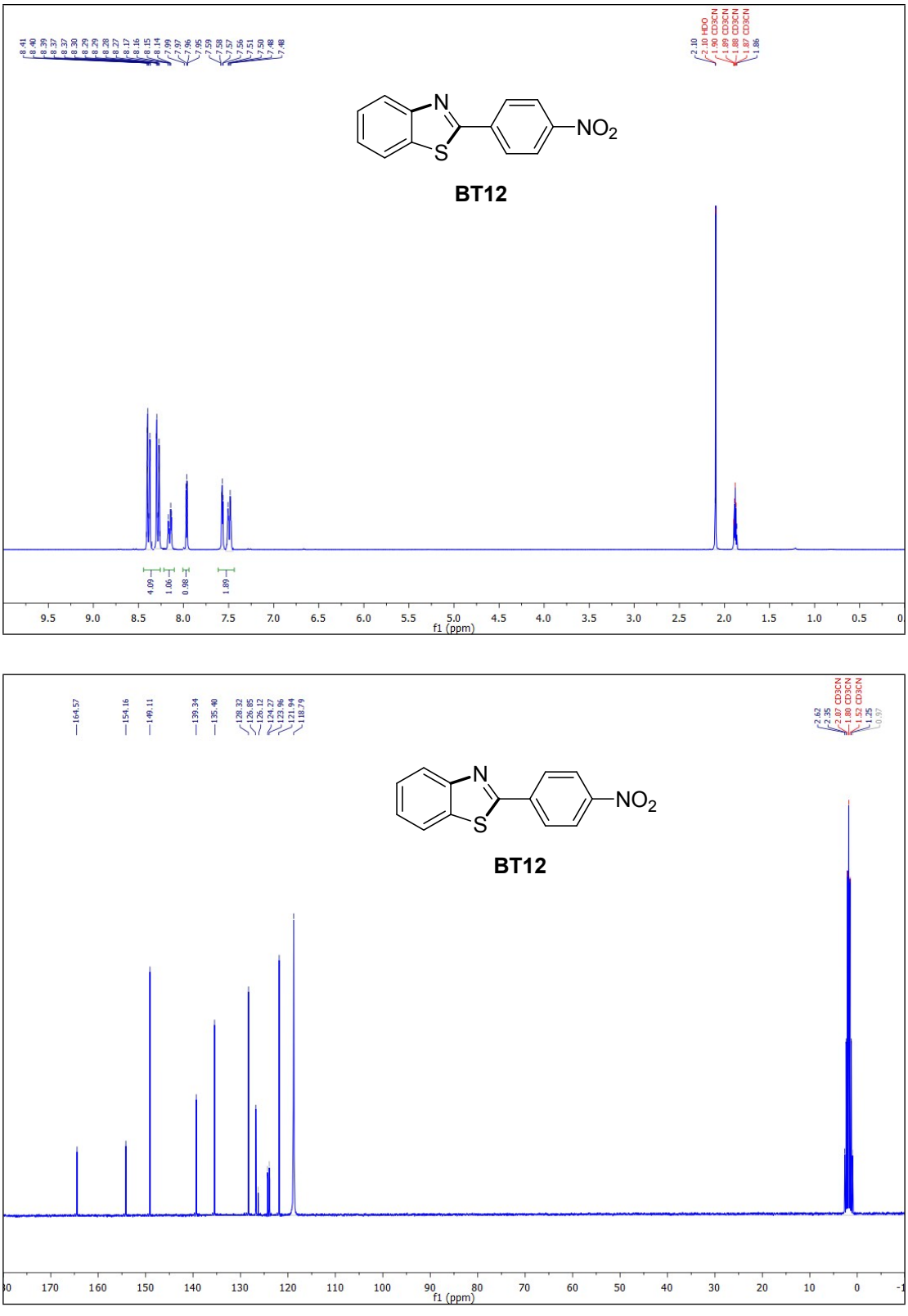


Figure S12. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT12** in CD_3CN.

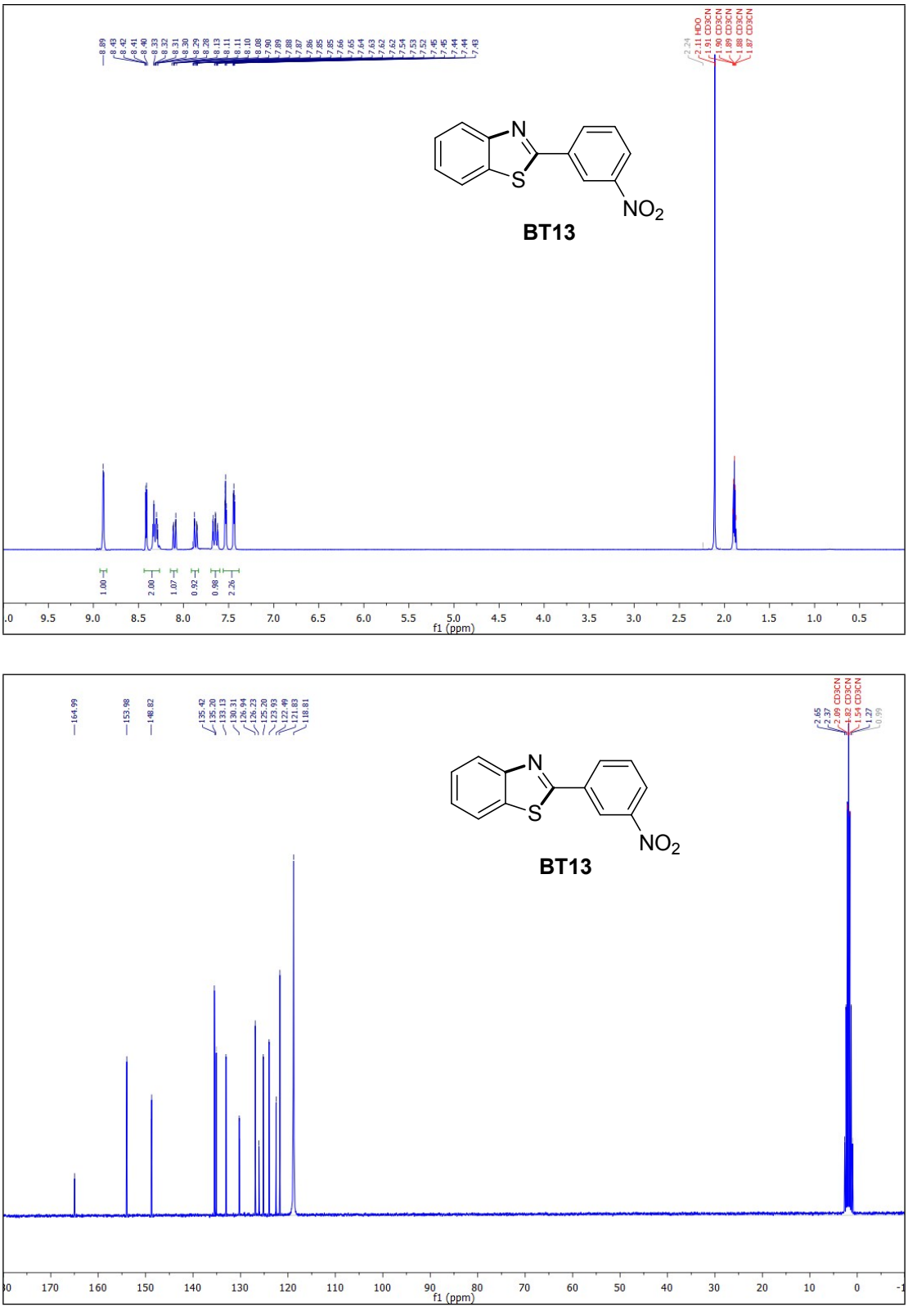


Figure S13. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT13** in CD_3CN.

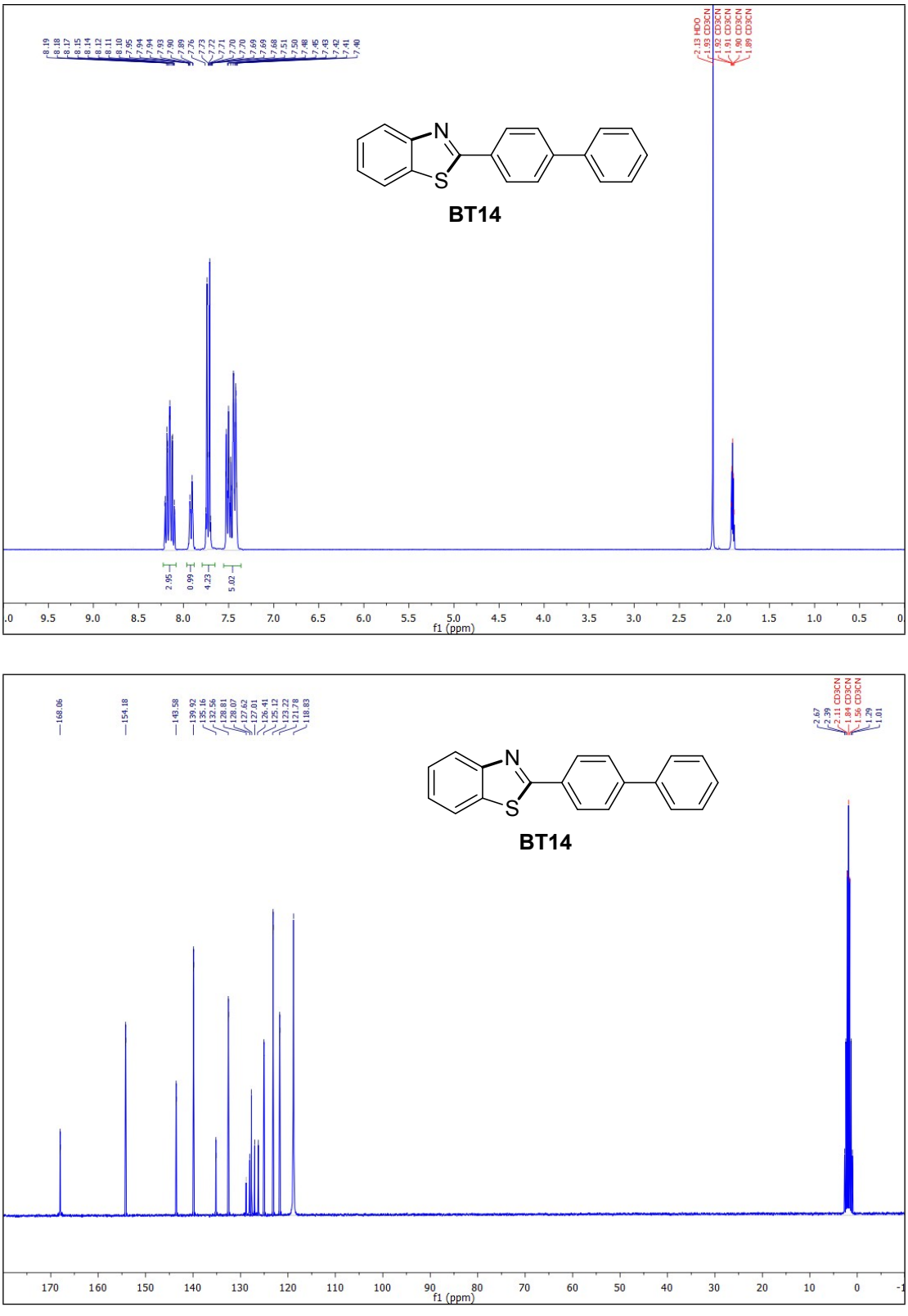


Figure S14. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT14** in CD_3CN.

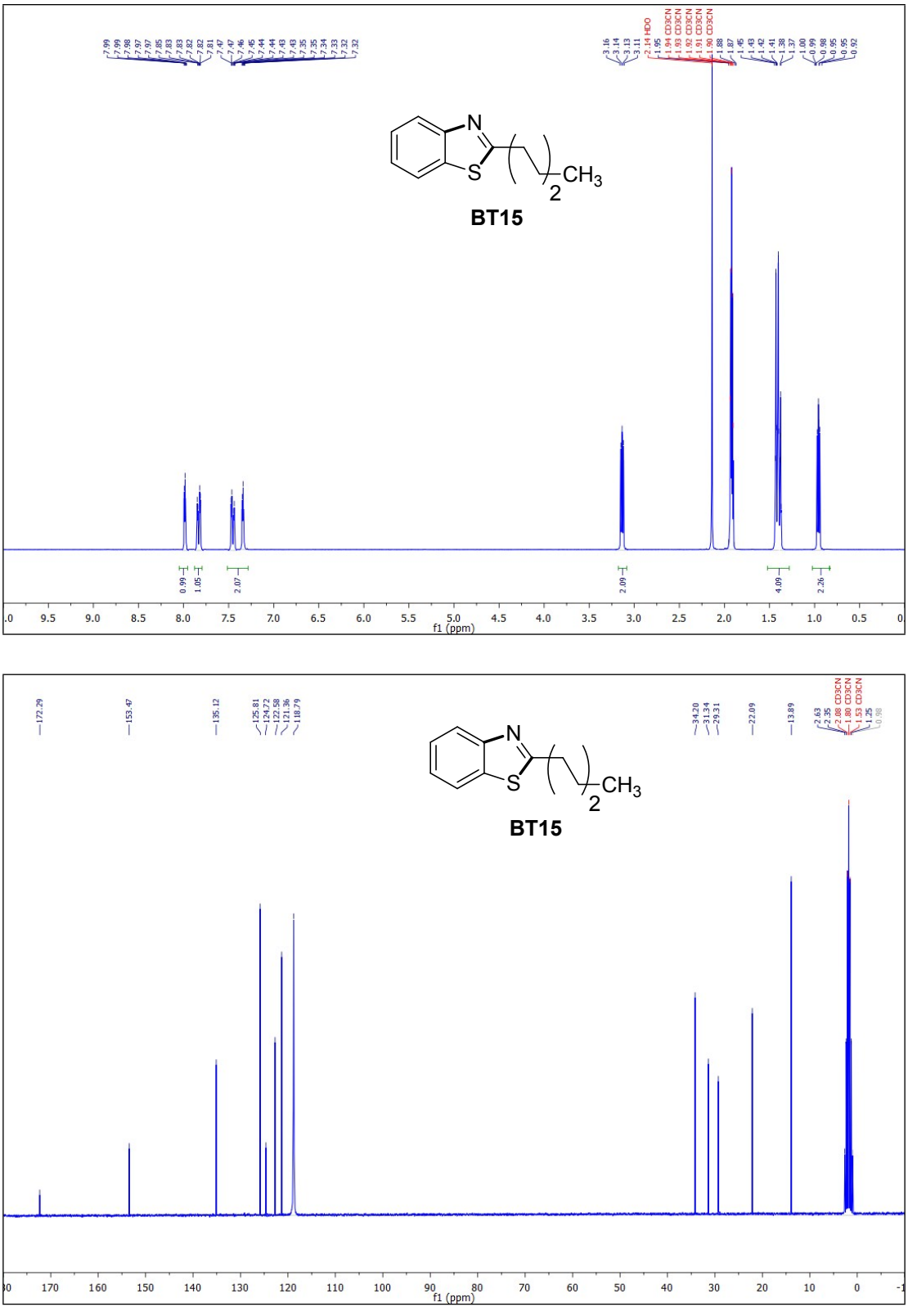


Figure S15. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT15** in CD_3CN.

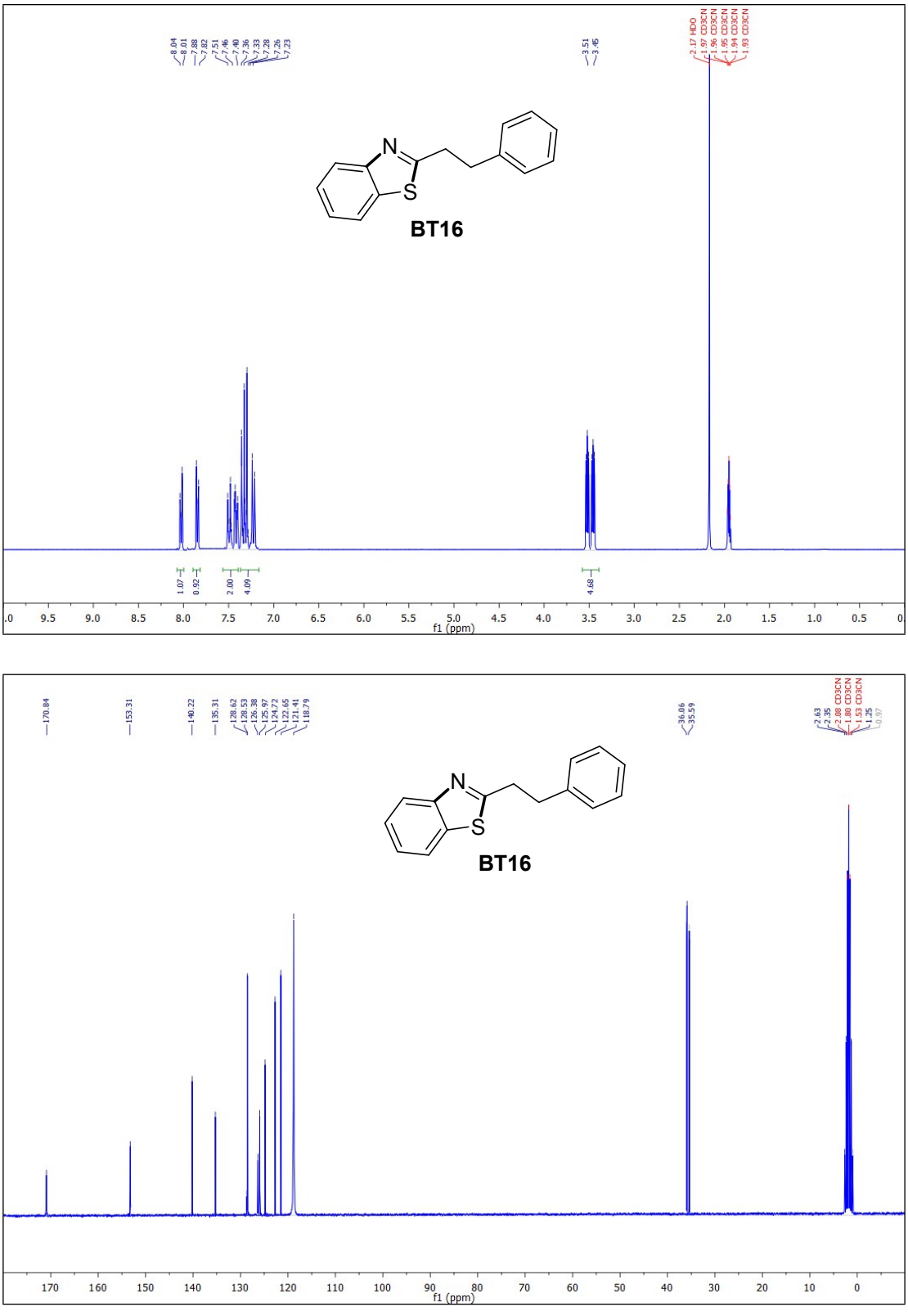


Figure S16. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT16** in CD_3CN.

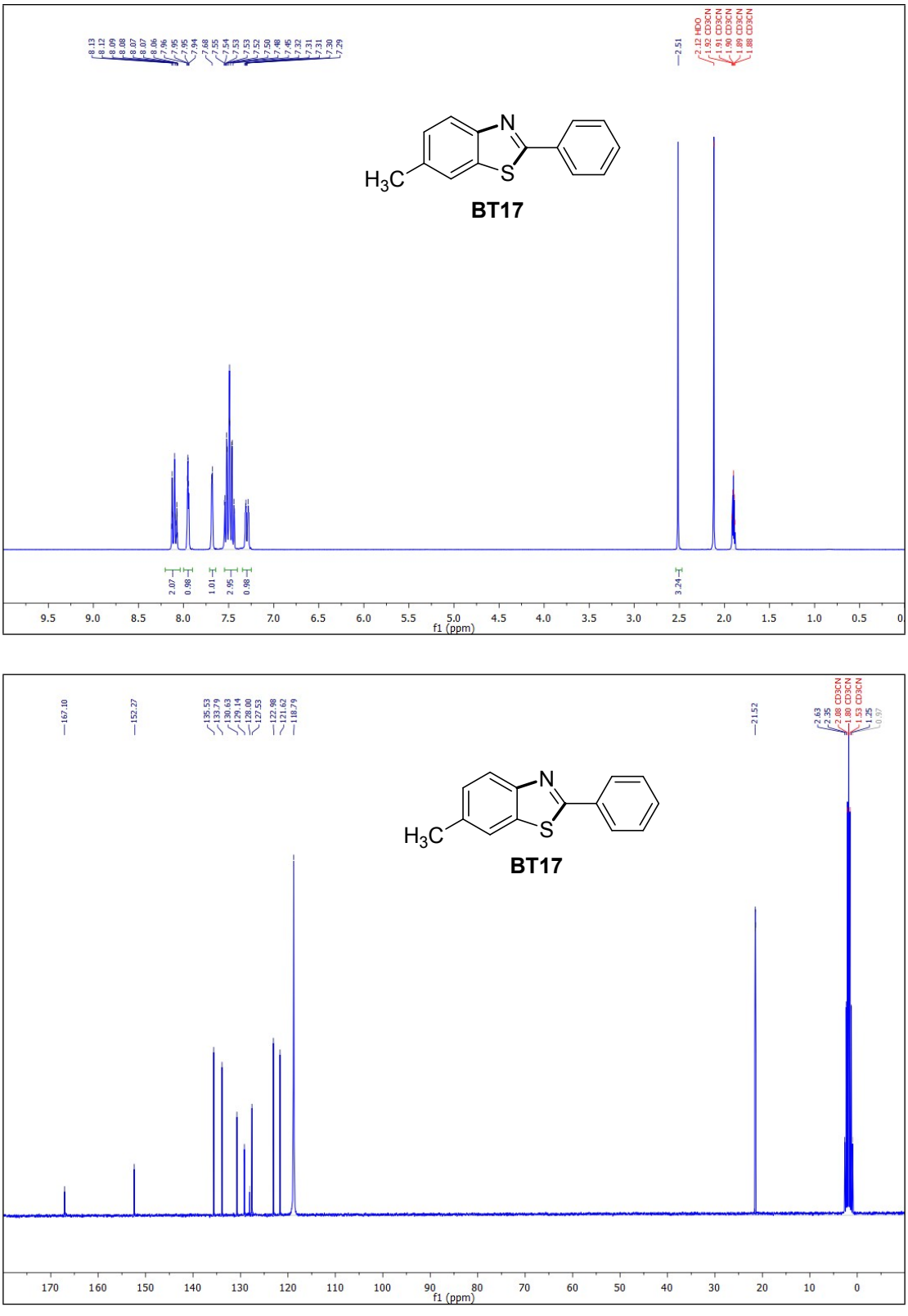


Figure S17. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT17** in CD_3CN.

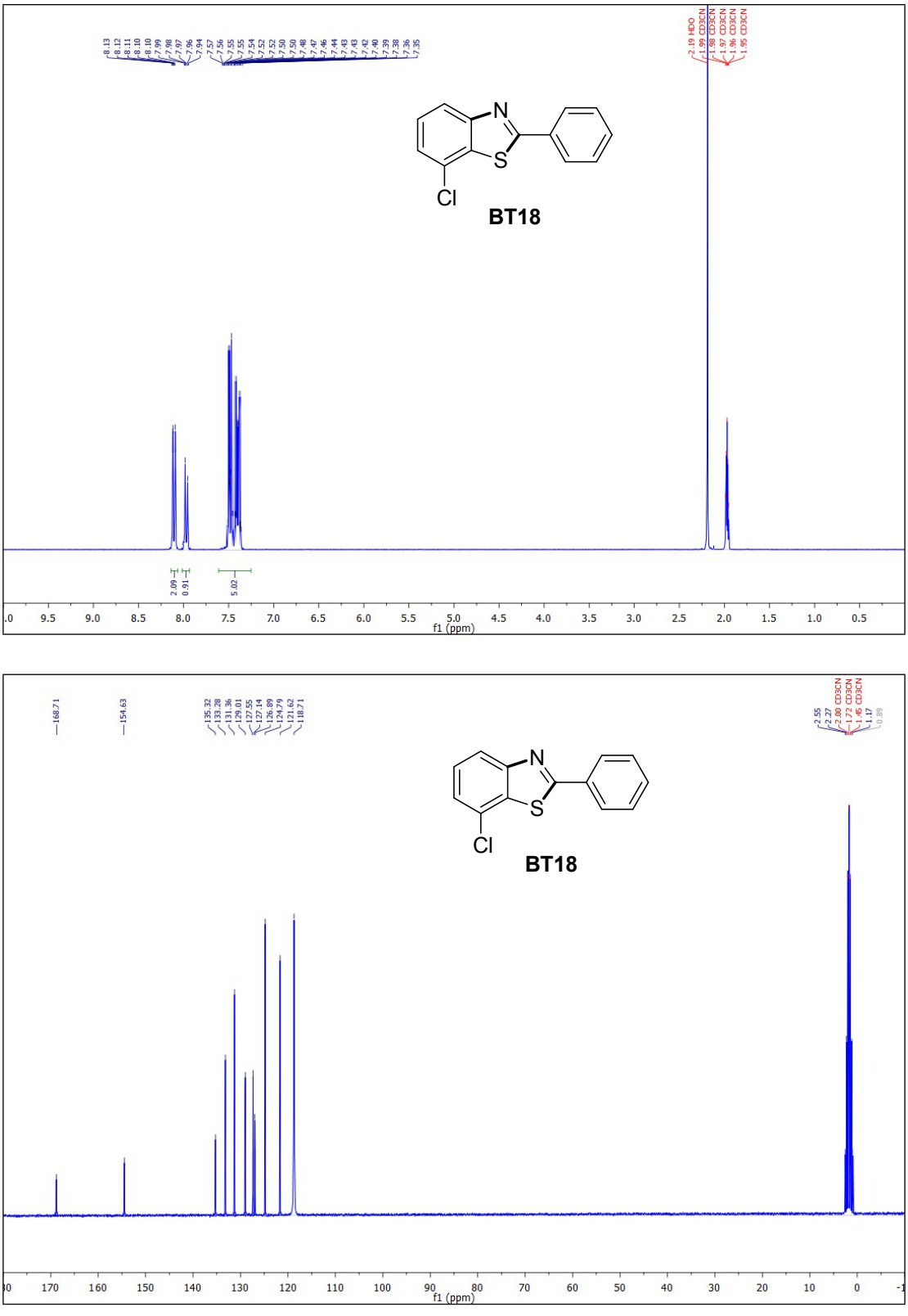


Figure S18. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT18** in CD_3CN.

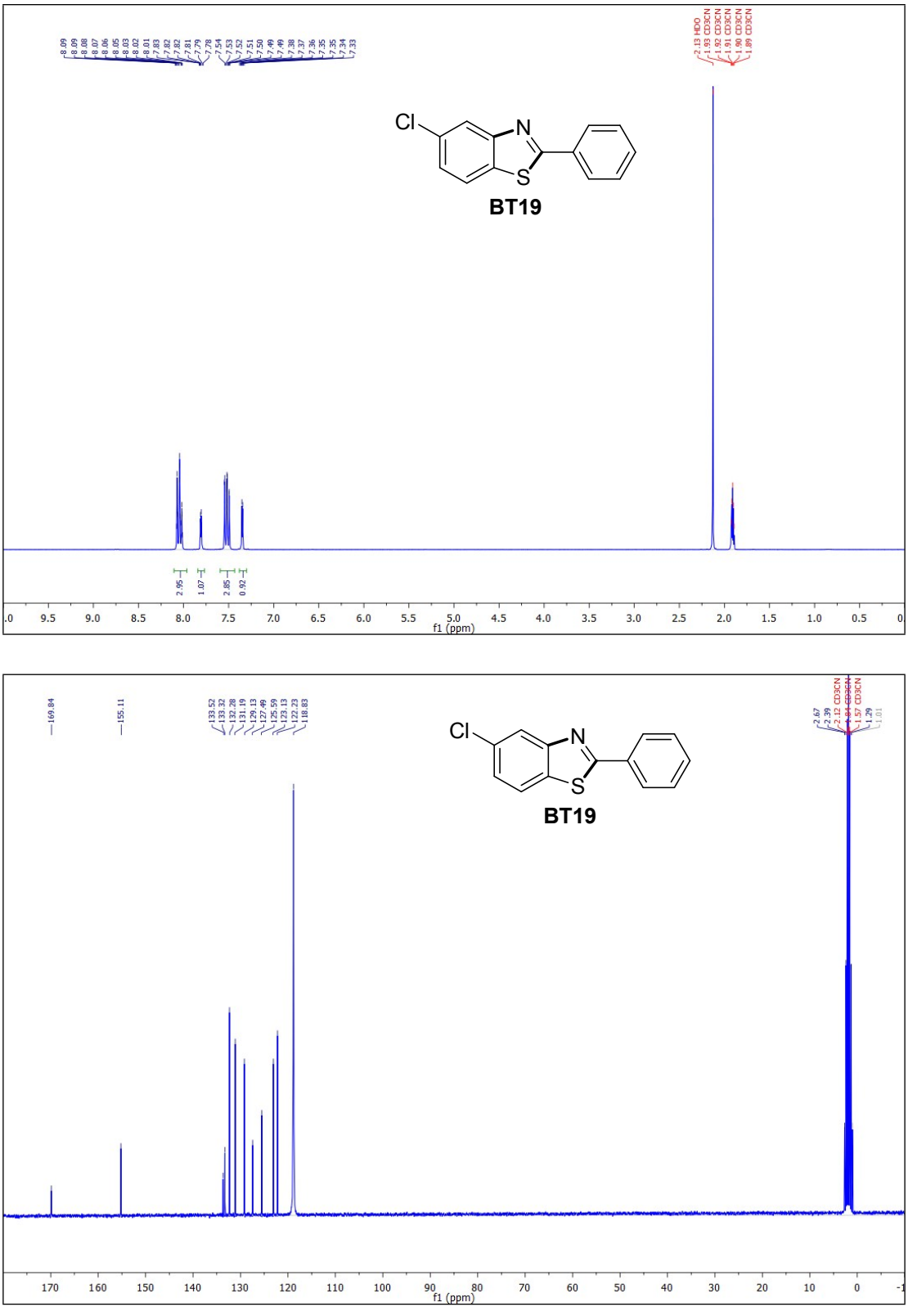


Figure S19. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT19** in CD_3CN.

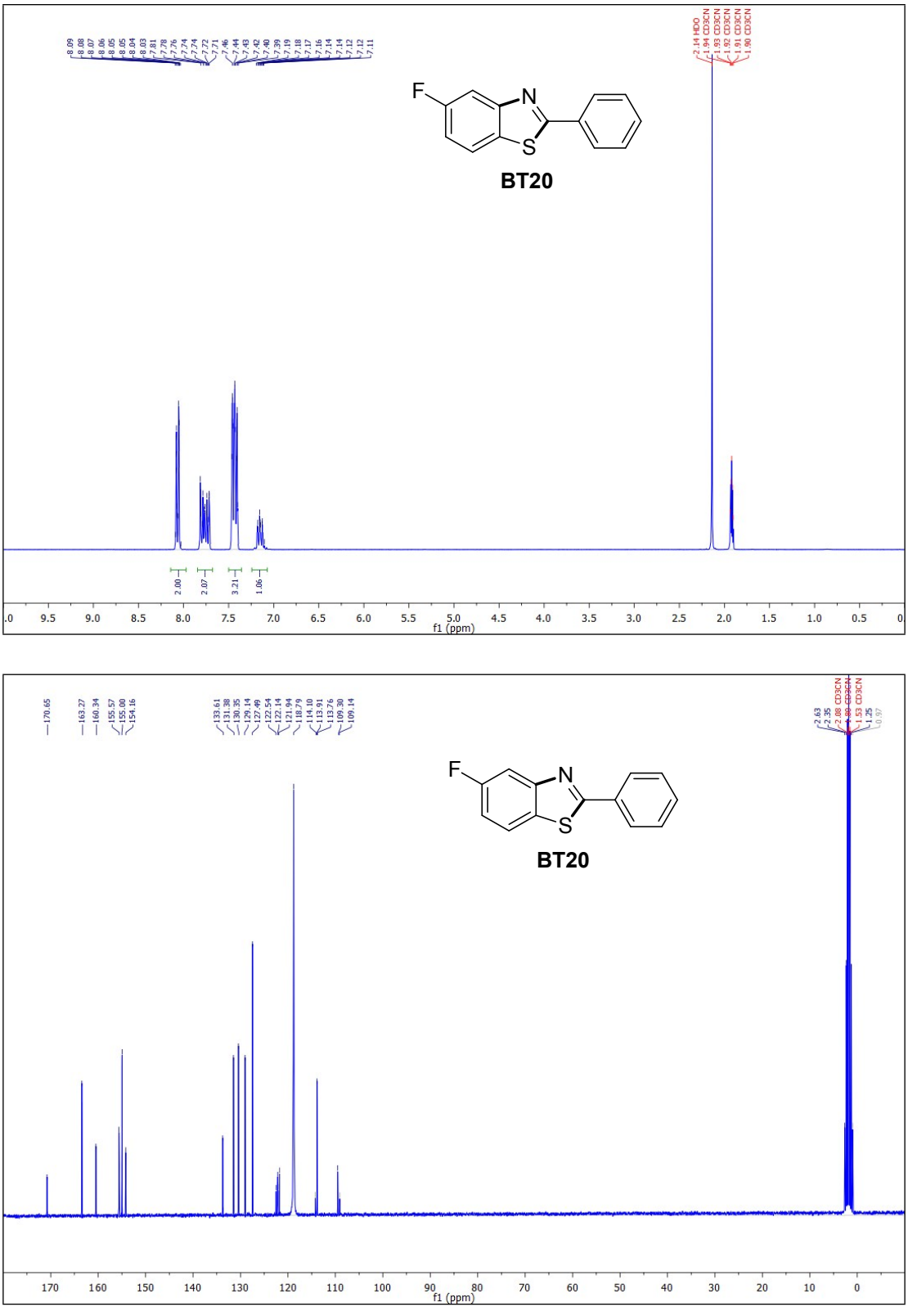


Figure S20. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT20** in CD_3CN.

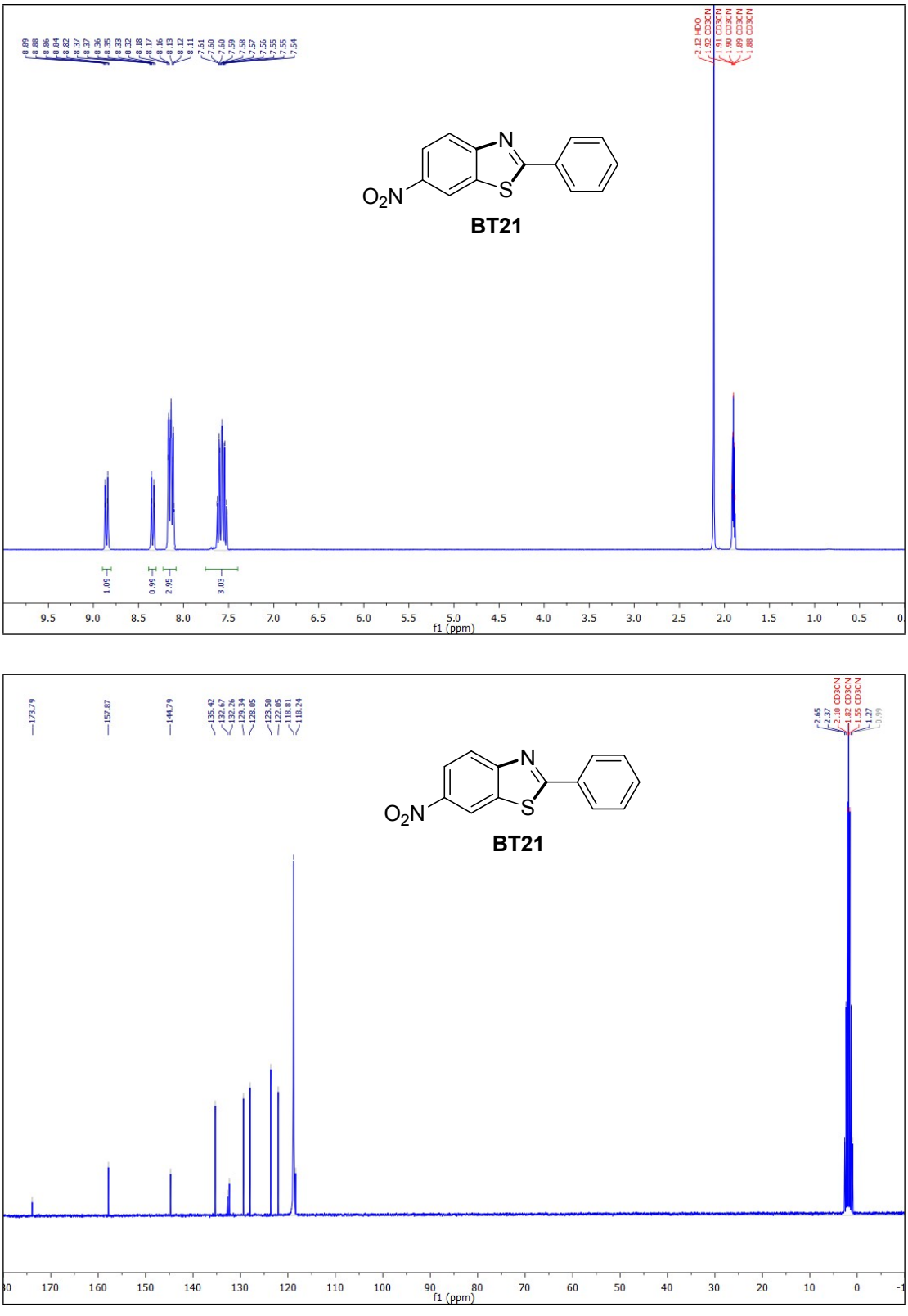


Figure S21. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT21** in CD_3CN.

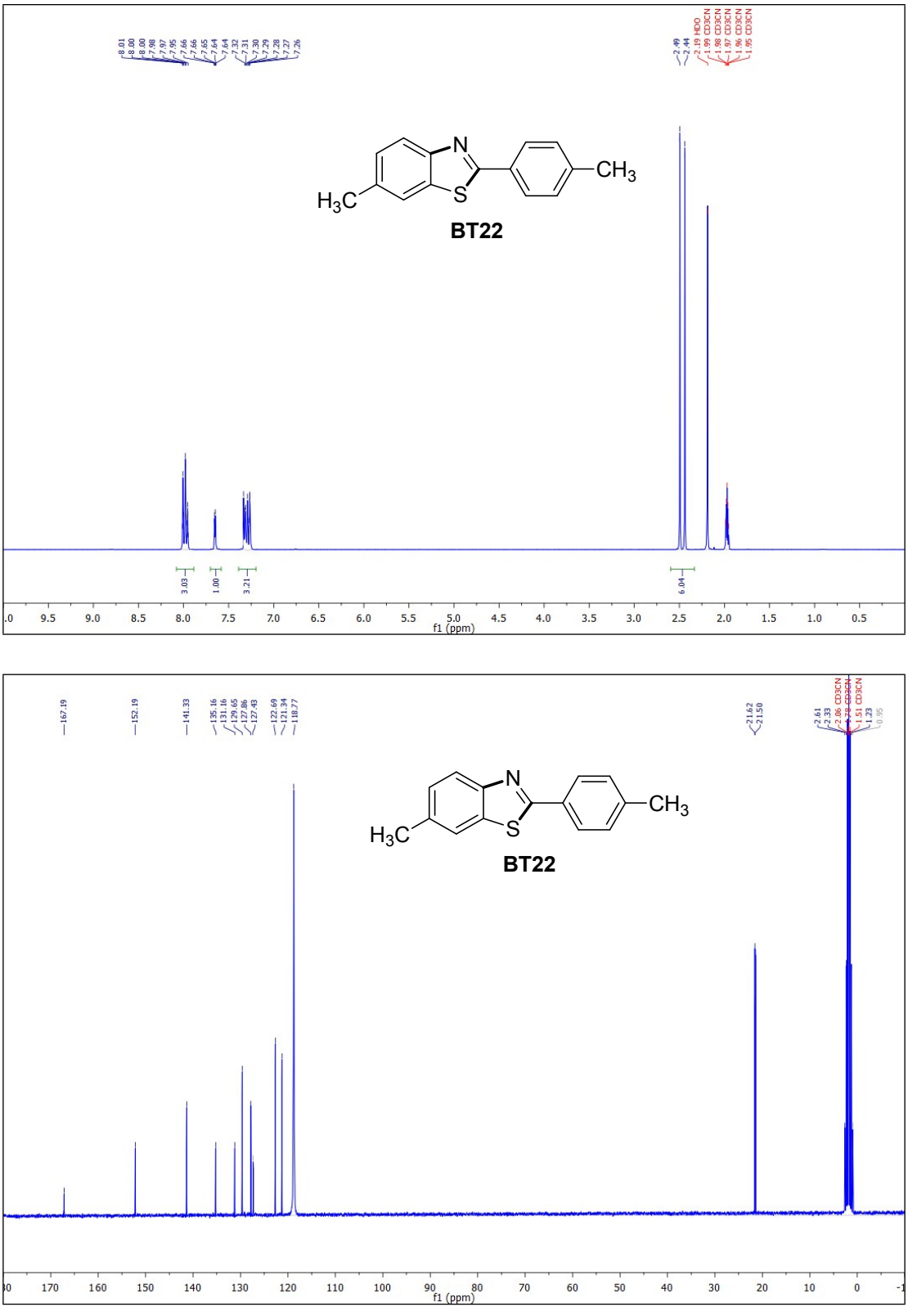
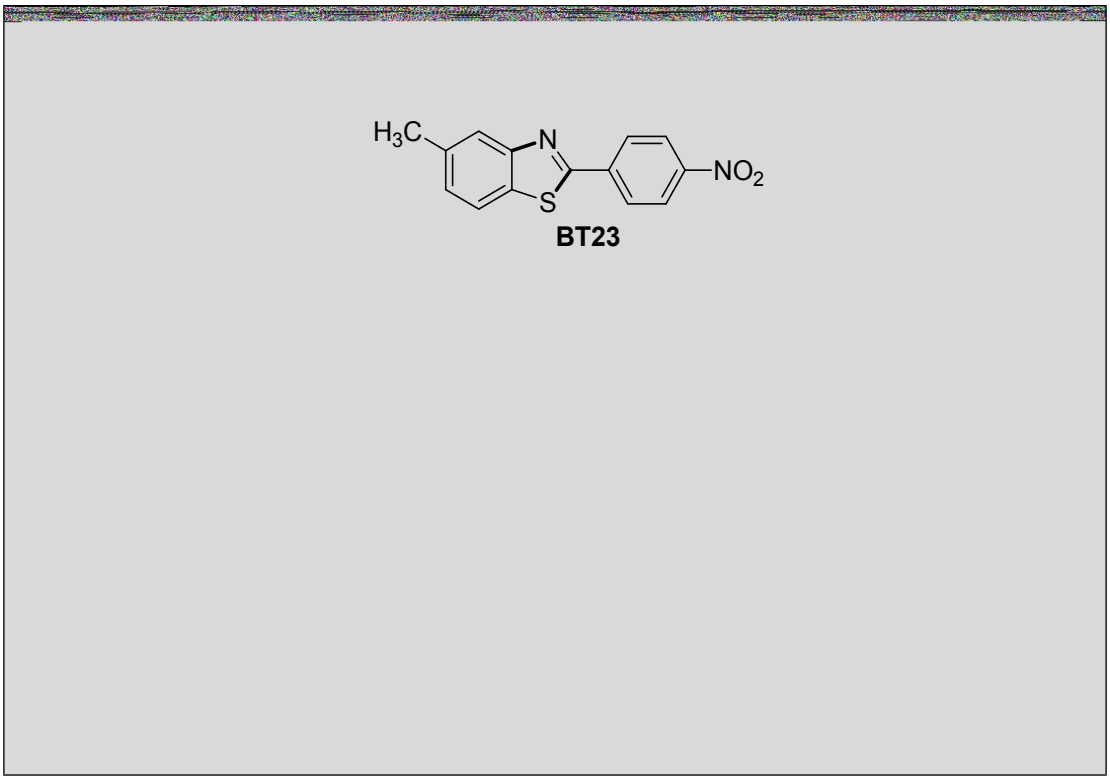


Figure S22. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT22** in CD_3CN.



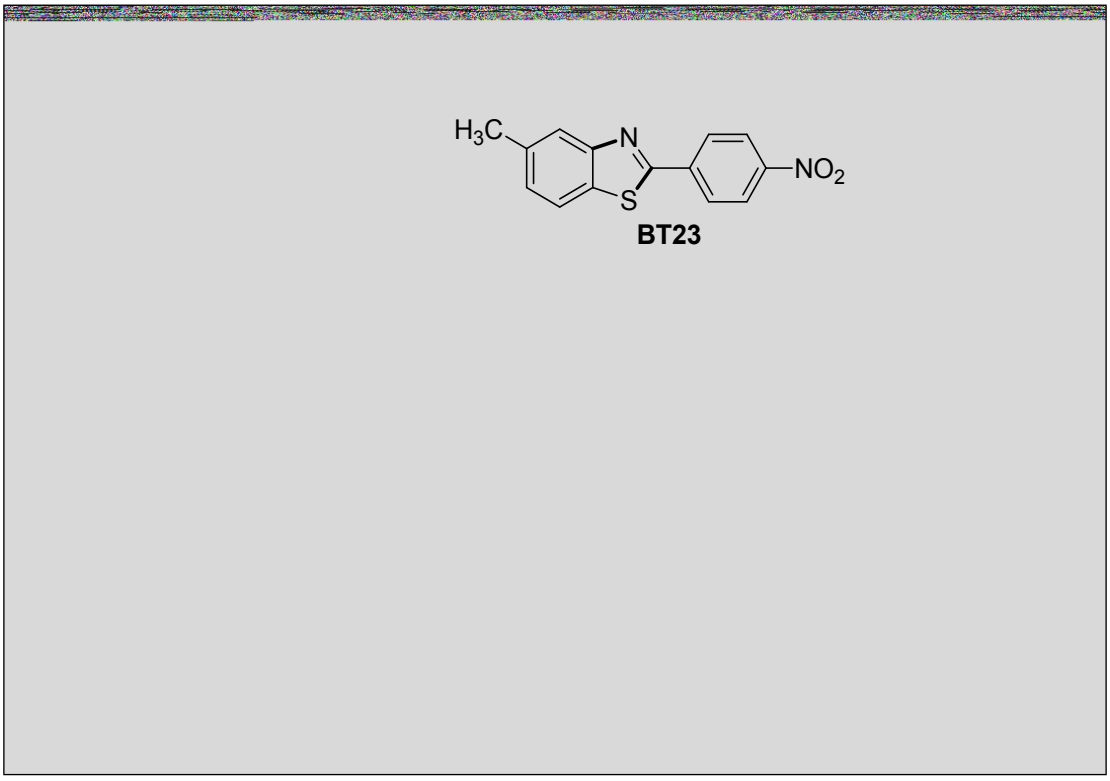


Figure S23. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT23** in CD_3CN.

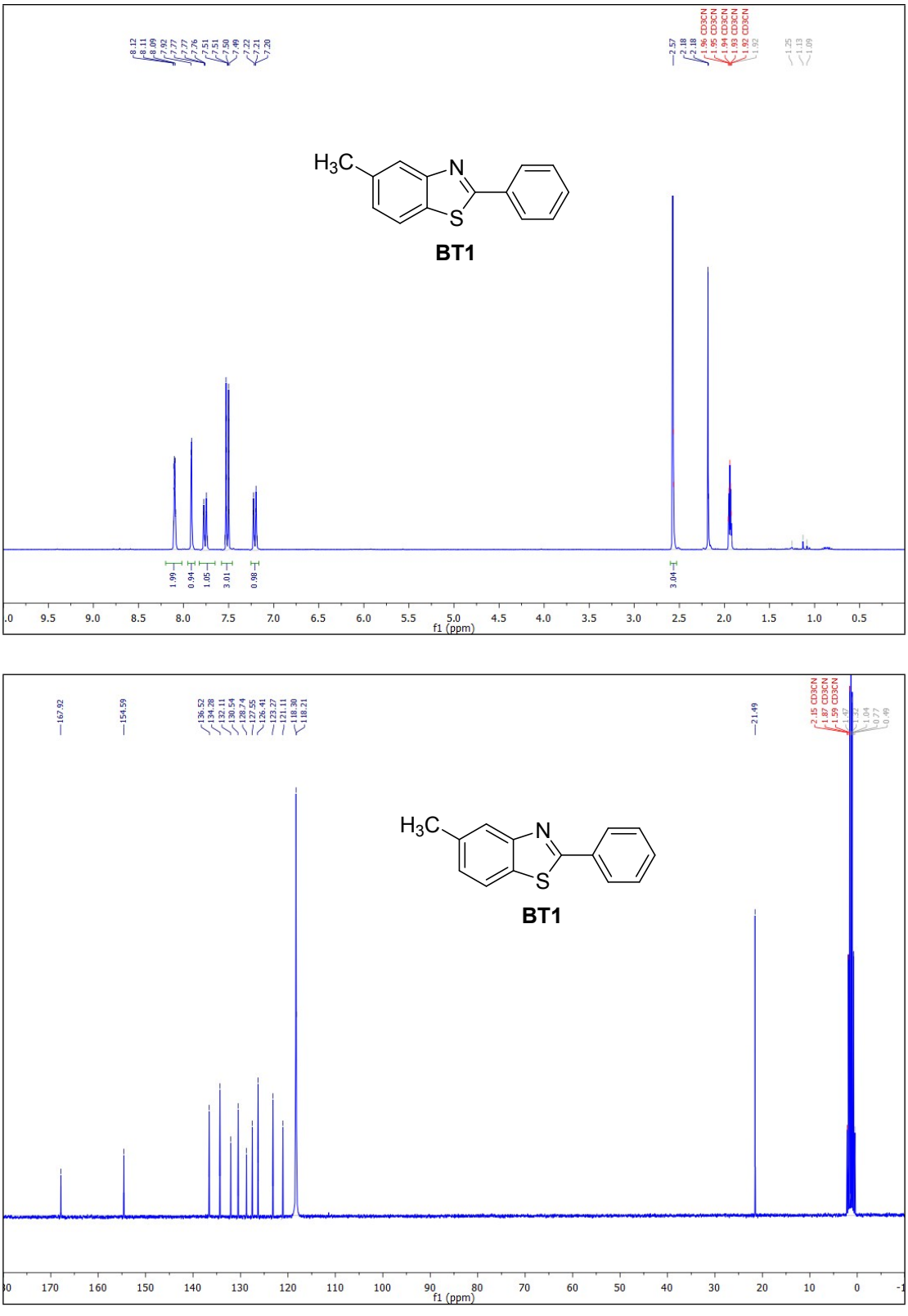


Figure S24. ^{1}H (top, 300 MHz) and ^{13}C (bottom, 75 MHz) NMR spectra of **BT1** in CD_3CN.