Access to 2-Aminobenzothiazoles via Redox Condensation of *o*-Halonitrobenzenes, Sulfur and Isothiocyanates

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General information

Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 µm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^1H, 77.0 ppm for ^{13}C. DMSO-d6, δ 2.50 ppm for 1 H and δ 39.5 ppm for 13C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. The reaction tube was heated in a copper or aluminium block.

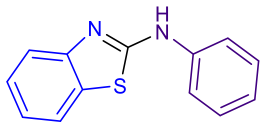
General procedure for the synthesis of 2-aminobenzothiazoles 3

Procedure 1 from isothiocyanates 2: A mixture of *o*-halonitrobenzene **1** (1 mmol), isothiocyanate **2** (1.5 mmol), S (2 mmol, 64 mg) and *N*-methylpiperidine (3 mmol, 297 mg) in *N*-methylpyrrolidin-2-one (0.2 mL) was stirred and heated under an argon atmosphere in a 7-mL test tube closed with a rubber septum at 80 ºC for 16 h (100 ºC when *o*-bromonitrobenzene or *o*-iodonitrobenzene was used); 120 ºC, 1 h with DABCO (1.5 mmol) as a base when 2-chloro-3-nitro-5-bromopyridine was used as the *o*-halonitrobenzene substrate. The crude mixture cooled to rt was purified by column chromatography on silica gel (hexanes:EtOAc 97:3 to 9:1 for all compounds except **3u** with CH_2Cl_2:MeOH 98:2 as an eluent) to afford the expected 2-aminobenzothiazole **3** as pale yellow solid.

Procedure 2 from anilines 5 and CS_2: aniline **5** (1.5 mmol) was added dropwise to a vigorously stirred cooled solution (0 ºC) of CS_2 (2 mmol, 152 mg) and *N*-methylpiperidine (3 mmol, 297 mg) in *N*-methylpyrrolidin-2-one (0.2 mL) in a 7-mL test tube. The resulting solution or slurry was warmed up to rt. Stirring was continued for additional 30 min followed by addition of *o*-chloronitrobenzene 1 (1 mmol). The resulting mixture was heated at 100 ºC for 16 h. The crude mixture cooled to rt was purified by column chromatography on silica gel (hexanes:EtOAc 97:3 to 9:1) to afford the expected 2-aminobenzothiazole **3** as pale yellow solid.

Characterization of products

N-Phenylbenzothiazol-2-amine (3a)[1]

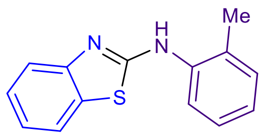


Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (129 mg, 57% from procedure 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.85 (broad s, 1H), 7.63 (dd, J = 7.9, J = 0.6 Hz, 1H), 7.59-7.57 (m, 1H), 7.51 (dd, J = 8.5 Hz, J = 1.0 Hz, 2H), 7.43-7.39 (m, 2H), 7.35-7.31 (m, 1H), 7.65-7.61 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 151.6, 140.1, 130.1, 129.7, 126.3, 124.6, 122.5, 121.0, 120.5, 119.5.

N-(o-Tolyl)benzothiazol-2-amine (3b)[1]

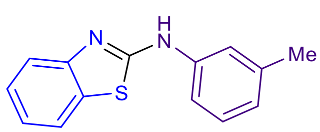


Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (87 mg, 36% from procedure 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 7.9 Hz, 1H), 7.52 (dd, J = 7.8 Hz, J = 0.7 Hz, 1H), 7.34 (dd, J = 8.1 Hz, J = 0.5 Hz, 1H), 7.30-7.27 (m, 2H), 7.24-7.18 (m, 2H), 7.07-7.04 (m, 1H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.7, 151.8, 138.5, 133.0, 131.4, 130.2, 127.4, 126.7, 126.6, 124.8, 122.0, 121.0, 118.8, 18.0.

N-(m-Tolyl)benzothiazol-2-amine (3c)[1]



Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (77 mg, 32% from procedure 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.8 Hz, J = 0.6 Hz, 1H), 7.55-7.50 (m, 1H), 7.31-7.24 (m, 4H), 7.14-7.09 (m, 1H), 6.96 (d, J = 6.6 Hz, 1H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 151.4, 140.1, 139.7, 130.0, 129.5, 126.2, 125.5, 122.4, 121.4, 121.0, 119.3, 117.7, 21.6.

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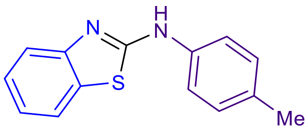
[1] B. Karimi, A. Mobaraki, H. M. Mirzaei, and Vali, H. *Org. Biomol. Chem.*, 2023, **21**, 1692.

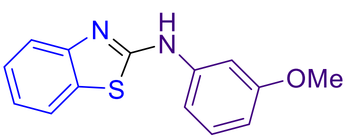
N-(p-Tolyl)benzothiazol-2-amine (3d)[1]



Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (84 mg, 35% from procedure 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.63-7.59 (m, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.39-7.36 (m, 2H), 7.33-7.29 (m, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.16-7.11 (m, 1H), 2.37 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 151.7, 137.5, 134.7, 130.3, 130.1, 126.2, 122.3, 121.2, 121.0, 119.3, 21.1.

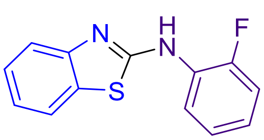
N-(3-Methoxyphenyl)benzothiazol-2-amine (3e)[1]



Purification of the crude mixture by column chromatography (hexanes:EtOAc 9:1) afforded the product (97 mg, 38% from procedure 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 7.19 – 7.14 (m, 2H), 6.69 (dd, J = 8.1, J = 2.3 Hz, 1H), 3.88 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 158.5, 148.0, 142.2, 139.2, 130.2, 124.5, 122.0, 117.2, 111.1, 109.3, 108.8, 104.8, 55.5.

N-(2-Fluorophenyl)benzothiazol-2-amine (3f)[2]



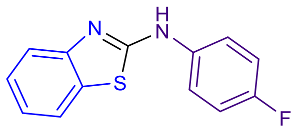
Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (81 mg, 33% from procedure 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48-8.39 (m, 1H), 7.67 (broad s, 1H), 7.56 (dd, J = 7.8, J = 0.5 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.30-7.24 (m, 2H), 7.21-7.15 (m, 2H), 7.11-7.03 (m, 1H).

[2] S. Radhika, A. Chandravarkar and G. Anilkumar, *RSC Adv.*, 2023, **13**, 17188.

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.4, 152.1 (d, J = 243.2 Hz), 147.8, 142.3, 126.3 (d, J = 10.5 Hz), 124.9 (d, J = 3.8 Hz), 124.3, 123.3 (d, J = 7.2 Hz), 122.3, 119.6, 117.6, 115.0 (d, J = 18.7 Hz), 109.2.

***N*-(4-Fluorophenyl)benzothiazol-2-amine (3g)**[2]

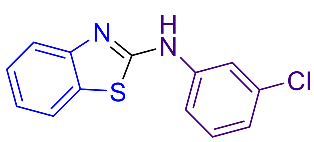


Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (81 mg, 33% from procedure 1).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (dd, J = 7.9 Hz, J = 0.6 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.52-7.46 (m, 2H), 7.36-7.31 (m, 1H), 7.18-7.14 (m, 1H), 7.13-7.08 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.7, 159.8 (d, J = 244.6 Hz), 151.5, 135.9, 130.0, 126.2, 122.7, 122.6 (d, J = 5.2 Hz), 120.9, 119.5, 116.3 (d, J = 22.8 Hz).

***N*-(3-Chlorophenyl)benzothiazol-2-amine (3h)**[3]

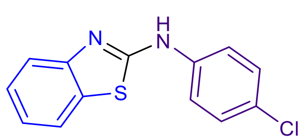


Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (109 mg, 42% from procedure 1 and 117 mg, 45 % from procedure 2).

^{1}H NMR (500 MHz, DMSO) δ 10.70 (s, 1H), 8.08, 8.08, 8.07 (m, 1H), 7.85-7.84 (m, 1H), 7.69, 7.68, 7.66 (m, 1H), 7.63-7.61 (m, 1H), 7.40-7.34 (m, 2H), 7.21-7.18 (m, 1H), 7.08-7.06 (m, 1H).

^{13}C NMR (126 MHz, DMSO) δ 161.2, 151.8, 141.9, 133.4, 130.6, 130.0, 126.0, 122.6, 121.5, 121.1, 119.5, 117.0, 116.1.

***N*-(4-Chlorophenyl)benzothiazol-2-amine (3i)**[2]



Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (96 mg, 37% from procedure 1 and 83 mg, 32% from procedure 2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, J = 7.4 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 7.4 Hz, 3H), 7.19 (d, J = 6.7 Hz, 1H).

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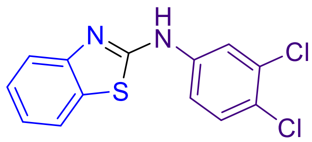
[3] Y. Xu, F. Li, N. Zhao, J. Su, C. Wang, C. Wang, Z. and Li, L. Wang, *Green Chem.*, 2021, **23**, 8047.

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 152.0, 138.8, 130.6, 129.7, 129.4, 126.5, 123.1, 121.2, 121.0, 120.2.

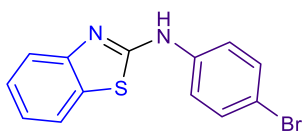
***N*-(3,4-Dichlorophenyl)benzothiazol-2-amine (3j)**



Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (126 mg, 43% from procedure 1).

^{1}H NMR (300 MHz, DMSO) δ 10.77 (s, 1H), 8.24-8.23 (m, 1H), 7.87-7.83 (m, 1H), 7.68-7.57 (m, 3H), 7.39-7.33 (m, 1H), 7.23-7.17 (m, 1H).
^{13}C NMR (75 MHz, DMSO) δ 161.0, 151.6, 140.5, 131.2, 130.7, 130.0, 126.0, 123.1, 122.8, 121.2, 119.6, 118.7, 117.8.
HRMS (ESI+) calcd for $C_{13}H_9Cl_2NS$ $[M + H]^+$ 294.9863. Found 294.9866.

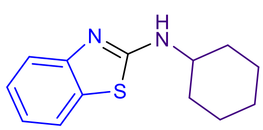
***N*-(4-Bromophenyl)benzothiazol-2-amine (3k)[3]**



Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (106 mg, 35% from procedure 1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (t, *J* = 6.9 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 1.49 (broad s, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 152.0, 139.3, 132.7, 130.6, 126.5, 123.1, 121.4, 121.0, 120.3, 116.7.

***N*-Cyclohexylbenzothiazol-2-amine (3l)[4]**



Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (106 mg, 35% from procedure 1).

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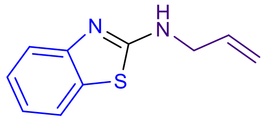
[4] N. Zhao, L. Liu, F. Wang, J. Li and W. Zhang, *Adv. Synth. Catal.*, 2014, **356**, 2575.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (dd, J = 7.8 Hz, J = 0.8 Hz, 1H), 7.50 (d, J = 7.8 Hz, 1H), 7.29-7.23 (m, 1H), 7.07-7.01 (m, 1H), 3.63-3.41 (m, 1H), 2.13-2.07 (m, 2H), 1.79-1.71 (m, 2H), 1.65-1.57 (m, 1H), 1.43-1.34 (m, 2H), 1.33-1.16 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 152.6, 130.3, 126.0, 121.4, 120.9, 118.7, 54.9, 33.3, 25.6, 24.9.

_N_-Allylbenzothiazol-2-amine (3m)[1]

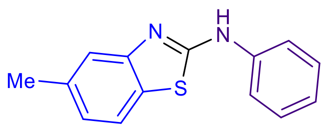


Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (80 mg, 42% from procedure 1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.54 (m, 2H), 7.39-7.28 (m, 2H), 7.14-7.08 (m, 1H), 6.06-5.93 (m, 1H), 5.41-5.34 (m, 1H), 5.28-5.23 (m, 1H), 4.09-4.07 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 151.9, 133.4, 128.5, 126.0, 121.7, 120.8, 118.8, 117.4, 47.8.

5-Methyl-_N_-phenylbenzothiazol-2-amine (3n)[2]

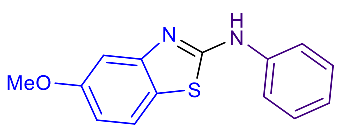


Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (89 mg, 37% from procedure 1 and 125 mg, 52% from procedure 2).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.52-7.47 (m, 3H), 7.52-7.47 (m, 3H), 7.18-7.12 (m, 1H), 6.99 (dd, J = 8.9 Hz, J = 0.9 Hz, 1H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.75, 151.83, 140.10, 136.29, 129.64, 126.95, 124.31, 123.90, 120.50, 120.20, 120.04, 21.63.

5-Methoxy-_N_-phenylbenzothiazol-2-amine (3o)[5]



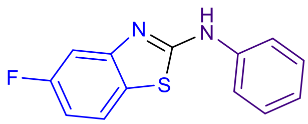
Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (97 mg, 38% from procedure 1).

[5] S. Sharma, R. S. Pathare, A. K. Maurya, K. Gopal, T. K. Roy, D. M. Sawant and R. T. Pardasani, *Org. Lett.*, 2016, **18**, 356.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.5 Hz, *J* = 0.9 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.42-7.38 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.6 Hz, *J* = 2.5 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 159.3, 152.7, 140.0, 129.7, 124.5, 121.5, 121.2, 120.4, 111.4, 103.7, 55.7.

5-Fluoro-*N*-phenylbenzothiazol-2-amine (3p)[6]

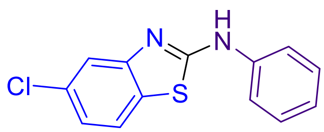


Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (81 mg, 33% from procedure 1 and 105 mg, 43% from procedure 2).

^{1}H NMR (500 MHz, DMSO) δ 10.60 (s, 1H), 7.83-7.78 (m, 3H), 7.45-7.36 (m, 3H), 7.06-7.00 (m, 2H).

^{13}C NMR (126 MHz, DMSO) δ 163.8, 161.3 (d, *J* = 238.8 Hz), 153.3 (d, *J* = 12.4 Hz), 140.3, 129.0 (2C), 125.5, 122.3, 122.0 (d, *J* = 10.1 Hz), 118.0 (2C), 109.6 (d, *J* = 24.1 Hz), 105.8 (d, *J* = 24.3 Hz).

5-Chloro-N-phenylbenzothiazol-2-amine (3q)[6]

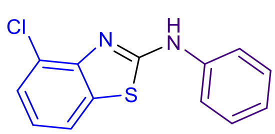


Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (117 mg, 45% from procedure 1 and 128 mg, 49% from procedure 2).

^{1}H NMR (500 MHz, DMSO) δ 10.63 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.79-7.77 (m, 2H), 7.65 (d, *J* = 2.1 Hz, 1H), 7.40-7.37 (m, 2H), 7.19 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.05 (tt, *J* = 7.3, 1.2 Hz, 1H).

^{13}C NMR (126 MHz, DMSO) δ 163.3, 153.3, 140.3, 130.5, 129.0, 128.8, 122.4, 122.4, 122.3, 122.0, 118.6, 118.0 (1 signals missing due to overlap).

4-Chloro-*N*-phenylbenzothiazol-2-amine (3r)[6]



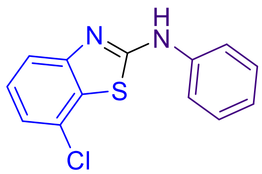
Purification of the crude mixture by column chromatography (hexanes:EtOAc 97:3) afforded the product (96 mg, 37% from procedure 1 and 81 mg, 31% from procedure 2).

[6] S. N. M. Boddapati, C. M. Kurmarayuni, B. R. Mutchu, R. Tamminana and H. B. Bollikolla, *Org. Biomol. Chem.*, 2018, **16**, 8267.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 7.9 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.9 Hz, 2H), 7.36 (d, J = 7.9 Hz, 1H), 7.19 (t, J = 7.3 Hz, 1H), 7.07 (t, J = 7.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 148.7, 139.5, 131.3, 129.8, 126.6, 125.1, 124.1, 123.0, 120.6, 119.5.

7-Chloro-*N*-phenylbenzothiazol-2-amine (3s)[6]

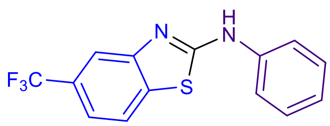


Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (115 mg, 44% from procedure 1).

^{1}H NMR (500 MHz, DMSO) δ 10.71 (s, 1H), 7.80-7.78 (m, 2H), 7.58-7.57 (m, 1H), 7.41-7.34 (m, 3H), 7.25-7.24 (m, 1H), 7.08-7.05 (m, 1H).

^{13}C NMR (126 MHz, DMSO) δ 161.3, 153.0, 140.1, 129.7, 129.1, 128.4, 127.3, 124.8, 123.6, 122.6, 121.9, 118.0, 117.8.

***N*-Phenyl-5-(trifluoromethyl)benzothiazol-2-amine (3t)[7]**

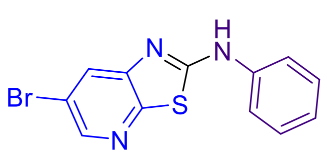


Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (97 mg, 33% from procedure 1 and 121 mg, 41% from procedure 2).

^{1}H NMR (500 MHz, DMSO) δ 10.72 (s, 1H), 8.06-8.05 (m, 1H), 7.89-7.88 (m, 1H), 7.82-7.80 (m, 2H), 7.48-7.46 (m, 1H), 7.41-7.38 (m, 2H), 7.09-7.06 (m, 1H).

^{13}C NMR (126 MHz, DMSO) δ 163.4, 152.2, 140.2, 134.6, 129.0, 128.3 (q, J = 130.1 Hz), 126.8 (q, J = 31.7 Hz), 125.6, 123.4, 122.6, 122.1, 118.3 (q, J = 3.7 Hz), 118.1, 115.3 (q, J = 4.2 Hz).

6-Bromo-*N*-phenylthiazolo[5,4-*b*]pyridin-2-amine (3u)



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[7] J. Yang, P. Li and L. Wang, *Tetrahedron*., 2011, **67**, 5543.

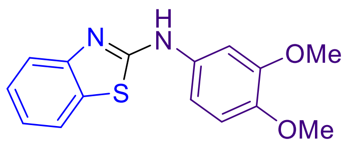
Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (156 mg, 51% from modified procedure 1 using DABCO (1.5 mmol) as a base at 120 ºC for 1 h).

^{1}H NMR (300 MHz, DMSO) δ 10.84 (s, 1H), 8.34-8.33 (m, 1H), 8.15-8.14 (m, 1H), 7.78-7.74 (m, 2H), 7.43-7.36 (m, 2H), 7.15-7.07 (m, 1H).

^{13}C NMR (75 MHz, DMSO) δ 162.3, 153.2, 147.3, 143.2, 139.7, 129.0, 128.4, 127.3, 123.6, 123.1, 118.7, 117.4.

HRMS (ESI+) calcd for $C_{12}H_9BrN_3S$ $[M + H]^+$ 305.9701. Found 305.9706.

***N*-(3,4-Dimethoxyphenyl)benzothiazol-2-amine (3v)**



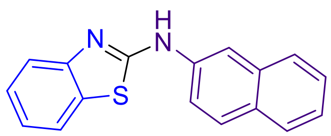
Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (137 mg, 48% from procedure 2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.45 (broad s, 1H), 7.63-7.50 (m, 2H), 7.40-7.28 (m, 2H), 7.19-7.04 (m, 2H), 6.97-6.91 (m, 1H), 3.93 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 151.6, 149.8, 146.9, 133.5, 129.9, 126.0, 122.1, 120.9, 118.9, 114.2, 112.0, 106.8, 56.2, 56.0.

HRMS (ESI+) calcd for $C_{15}H_{15}N_2O_2S$ $[M + H]^+$ 287.0854. Found 287.0850.

***N*-(Naphthalen-2-yl)benzothiazol-2-amine (3w)**



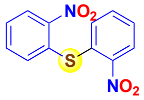
Purification of the crude mixture by column chromatography (DCM: 100%) afforded the product (80 mg, 29% from procedure 2).

^{1}H NMR (500 MHz, DMSO) δ 10.74 (s, 1H), 8.58-8.57 (m, 1H), 7.92-7.91 (m, 1H), 7.88-7.85 (m, 3H), 7.71-7.69 (m, 2H), 7.51-7.48 (m, 1H), 7.41-7.36 (m, 2H), 7.22-7.19 (m, 1H).

^{13}C NMR (126 MHz, DMSO) δ 161.4, 152.0, 138.2, 133.8, 130.0, 129.1, 128.7, 127.5, 127.1, 126.6, 125.9, 124.1, 122.4, 121.1, 119.4, 119.3, 112.9.

HRMS (ESI+) calcd for $C_{17}H_{13}N_2S$ $[M + H]^+$ 277.0799. Found 277.0795.

***Bis*(2-nitrophenyl)sulfane (6)**



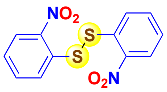
The product was obtained as one of the first fractions of each purification by column chromatography (heptane:DCM 1:1) in various amounts.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16-8.14 (m, 2H), 7.57-7.49 (m, 4H), 7.33-7.32 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 133.8, 133.5, 131.7, 128.6, 125.6.

HRMS (ESI+) calcd for $C_{12}H_9N_2O_4S$ $[M + H]^+$ 277.0283. Found 277.0289.

1,2-Bis(2-nitrophenyl)disulfane (7)



The product was obtained as one of the first fractions of each purification by column chromatography (heptane:DCM 1:1) in various amounts.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37-8.34 (m, 2H), 7.89-7.86 (m, 2H), 7.63-7.57 (m, 2H), 7.45-7.39 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.2, 134.9, 134.5, 127.2, 127.0, 126.3.

HRMS (ESI+) calcd for $C_{12}H_9N_2O_4S_2$ $[M + H]^+$ 309.0004. Found 309.0015.

Crystallographic data collection, structure determination and refinement

Pale yellow crystalline solids appeared to be smeared on the wells of a hemolysis tube following the rapid solvent evaporation at room temperature. Given the small size and low-diffraction quality of a representative crystal mounted on a RIGAKU XtaLabPro diffractometer equipped with a Mo Kα (λ = 0.71073 Å) microfocus sealed tube MM003 generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD PILATUS3R 200K detector, a data collection strategy was employed whereby atomic resolution data could be recorded at room temperature within a reasonable experimental time frame. CrysAlisPro [1] was employed for the data processing, with a combination of numerical and empirical absorption correction, implemented in SCALE3 ABSPACK scaling algorithm. The reduced data set was truncated at $sin\theta/\lambda$ = 0.538 (0.93Å). The structure was nevertheless solved by intrinsic phasing methods (*SHELXT* program),[2] then refined using full-matrix least-squares methods on F^2 with *SHELX-L*,[3] until convergence with R1 of 5.3%. Displacement parameters for all non-hydrogen (19) atoms, present inside the asymmetric unit (asu) of the orthorhombic cell were refined anisotropically. Aromatic H atoms were positioned geometrically and refined with U_{iso} set to $1.2U_{eq}$(C) of the parent carbon atom. Crystal data, data collection and structure refinement details are summarized below. The structure is shown in Ortep representation in Figure S1. Polymorphs for the 2,2'-Dinitrodiphenyl sulfide was known to exist in different space groups: CSD[4] refcode DEKDIG[5] structure was determined in the triclinic P-1, CSDrefcode DEKDIG01[6] was described in the monoclinic space group, Cc and CSD refcode DEKDIG02[7] measured at low temperature, 100K was found in a different unit cell, C2/c. Here a fourth polymorph is presented in the polar space group, $Pna2_1$. An overlay of the four polymorphic structures in Figure S2 is provided in order to facilitate a rapid identification of the principal geometric distinctions between them. However, a comprehensive study of the polymorphism propensity for this compound is beyond the scope of this paper.

CCDC 2377588 contains the supplementary crystallographic data for compound **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data of **7**:

$C_{12}H_8N_2O_4S$ (M = 276.26 g/mol): orthorhombic, space group $Pna2_1$, a = 7.850(3) Å, b= 7.904(16) Å, c = 19.553(5) Å, α = 90°, β = 90°, γ = 90°, V = 1213.2(6) Å^3, Z = 4, T = 293(2) K, μ(Mo Kα) = 0.278 mm^{-1}, F(000) = 568, crystal size = 0.16 × 0.08 × 0.04 mm^3, ρ_{calc} = 1.513 g/cm^3; out of the 9141 reflections measured (5.56° ≤ 2θ ≤ 44.93°), 1572 were unique (Rint = 0.0742, Rsigma = 0.0556) and 1569 were used in all calculations, with one floating origin restraint and 172 refined parameters. Max. and Min. of transmission: 1.000 and 0.704. The final R1 was 0.0528 ($I > 2\sigma(I)$), and wR2 was 0.1460 (all data). The goodness-of-fit on F^2 = 1.032, The largest difference peak and hole: 0.29/0.19 e.Å^3. Flack parameter (using 560 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$) = -0.01(9)).

References

1 Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.

2 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.

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4 C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Cryst.* 2016, **B72**, 171. V5.44 (update June 2024).

5 A., Kucsman, I. Kapovits, L. Parkanyi, G. Argay and A. Kalman, *J. Mol. Struct.*, 1984, **125**, 331.

6 P. J. Cox, and J. L. Wardell, *Int. J. Pharm.,* 2000, **194**, 147.

7 Y. Li, C. T. Hu and M. D. Ward, *CSD Communication*, 2019, (Private Communication).

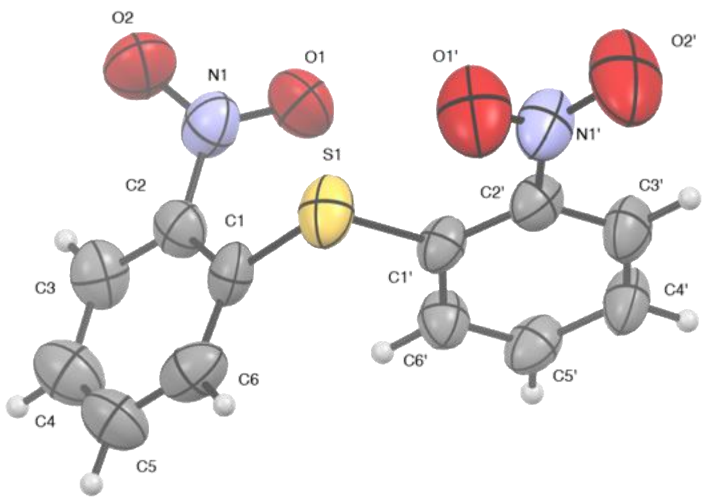


Figure S1 Ortep view of the structure of the 2,2'-dinitrodiphenyl sulfide **7** with the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

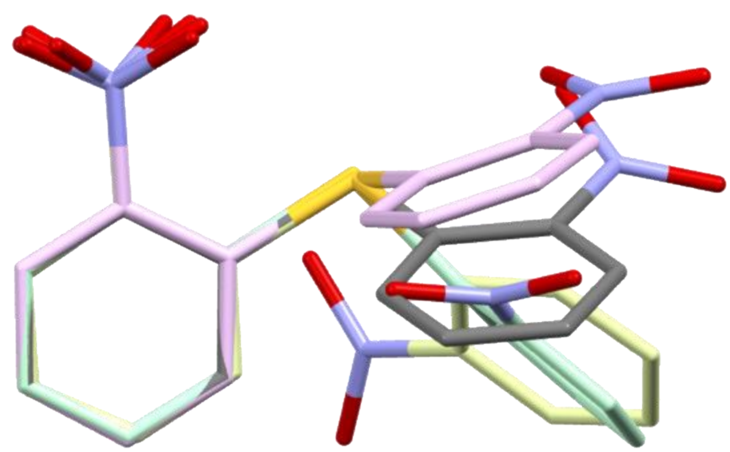
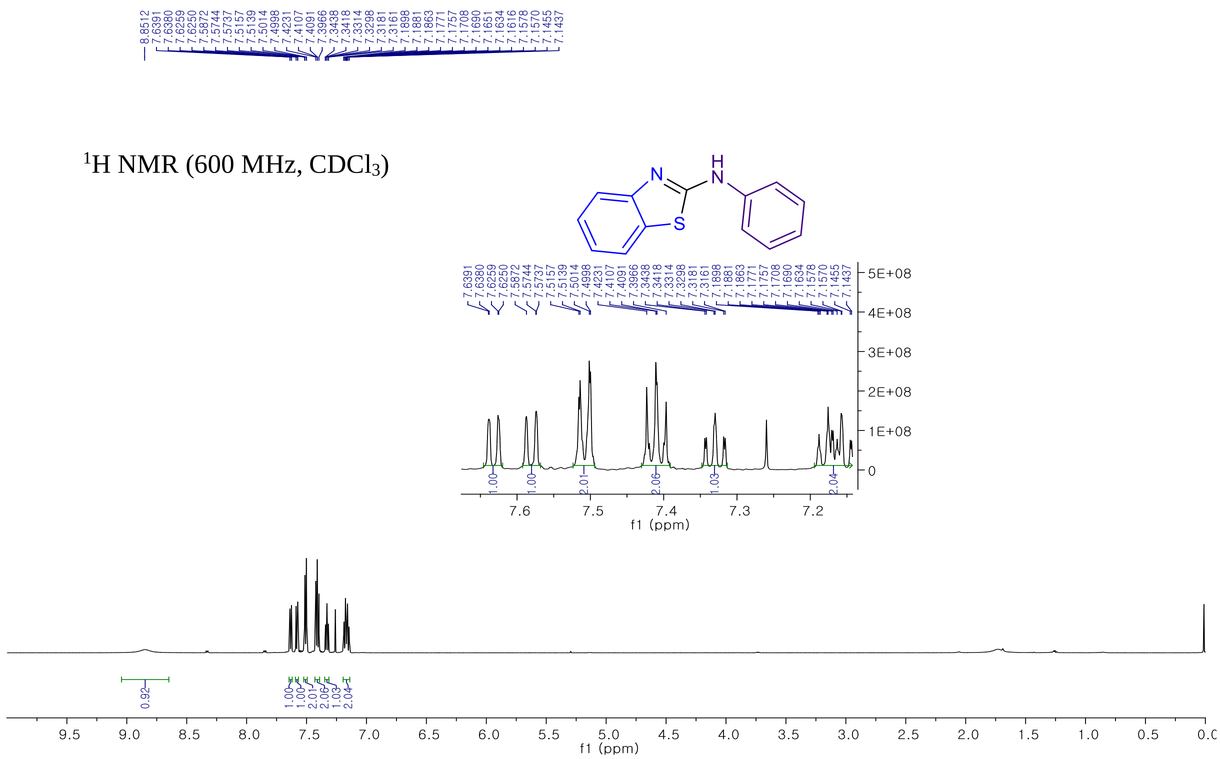


Figure S2 Overlay between 1 (carbon atoms in pale green) and DEKDIG (in grey), DEKDIG01 (in yellow), and DEKDIG02 (in pink).

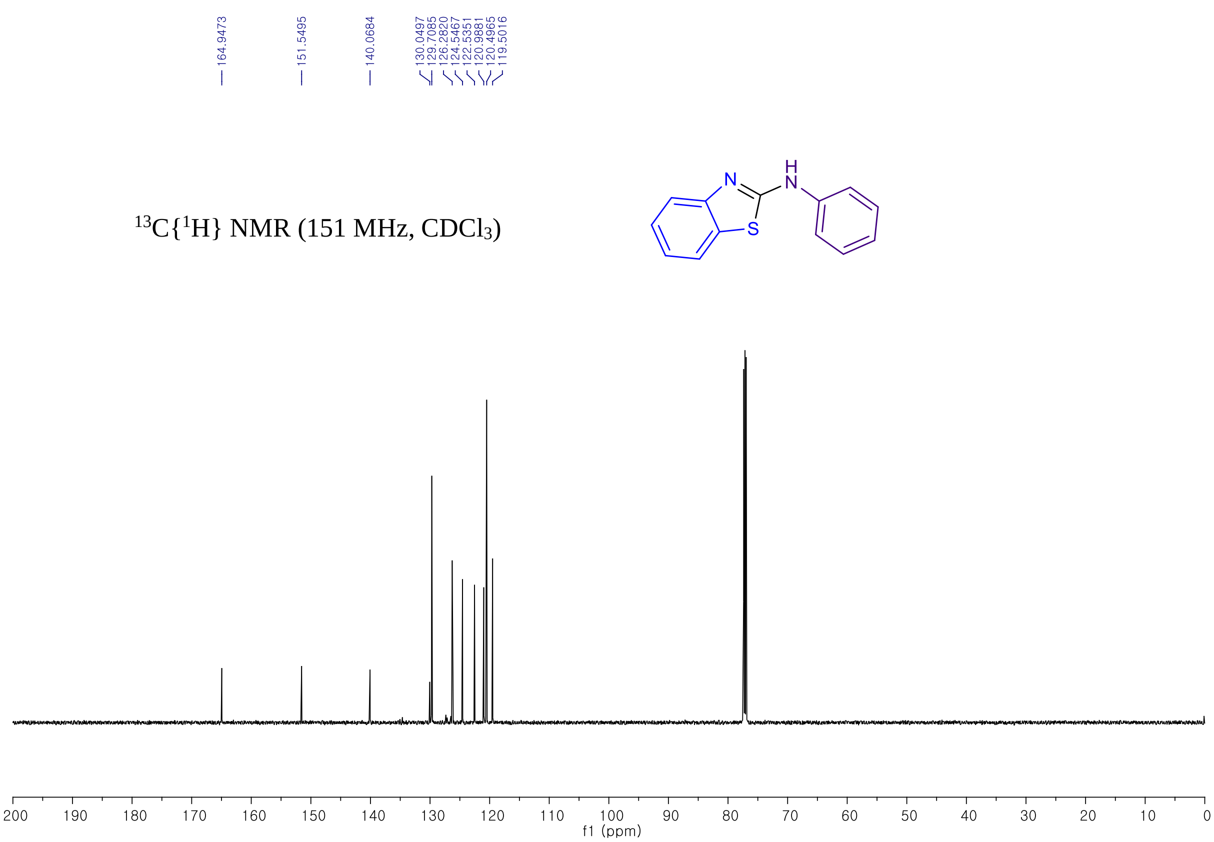
Copies of NMR spectra

N-Phenylbenzothiazol-2-amine (3a)

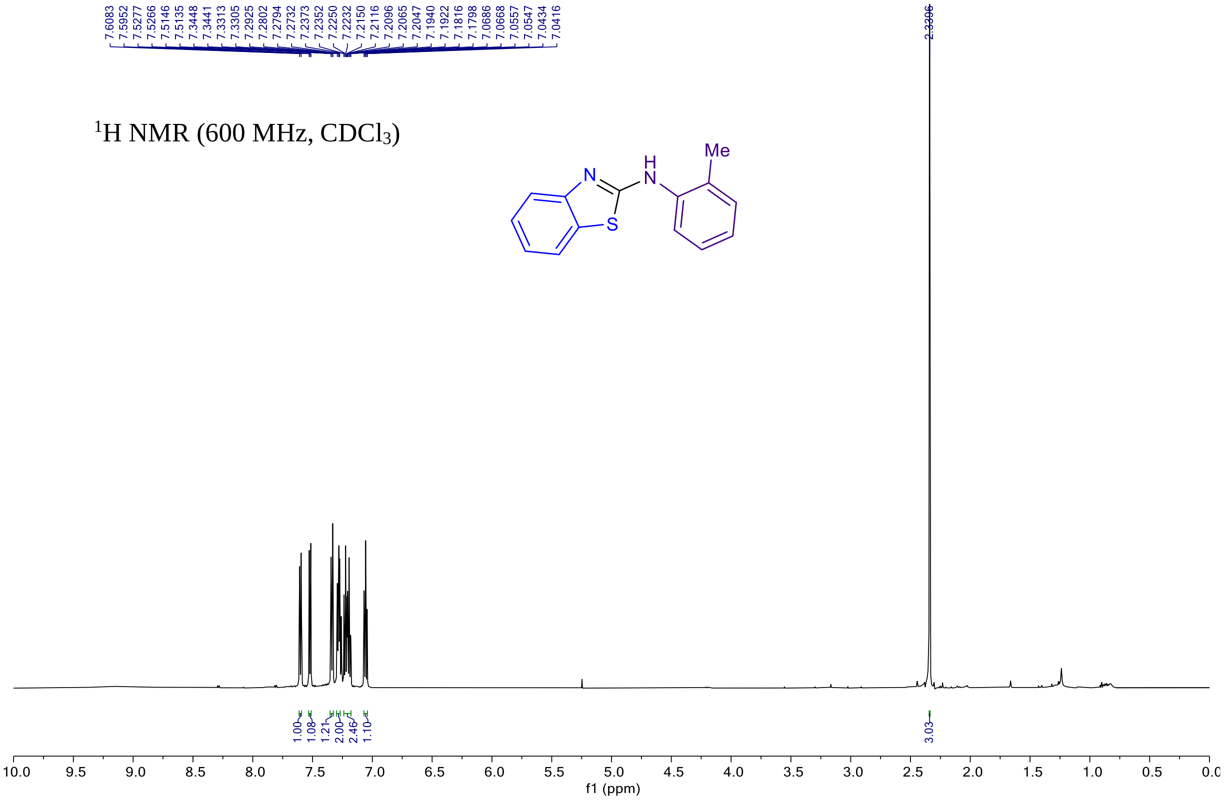
^{1}H NMR (600 MHz, $CDCl_3$)

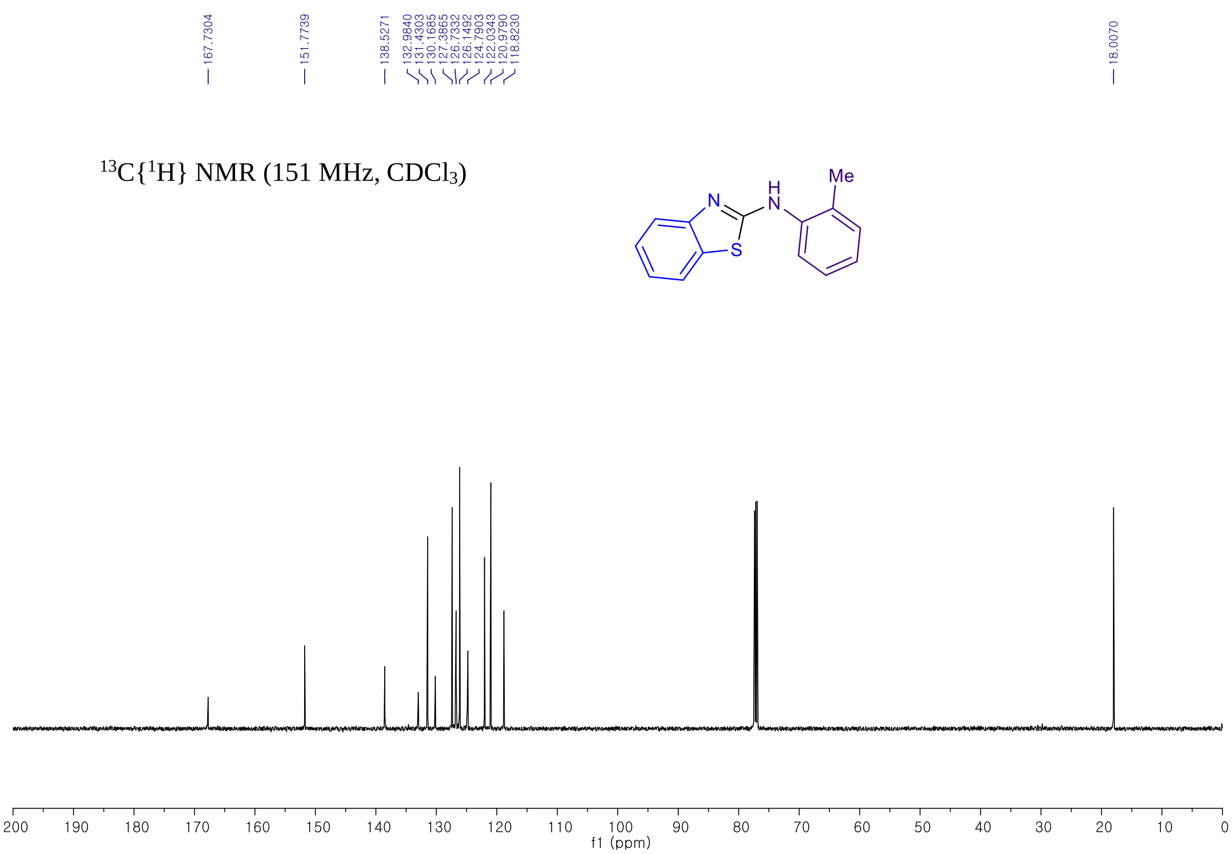


$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

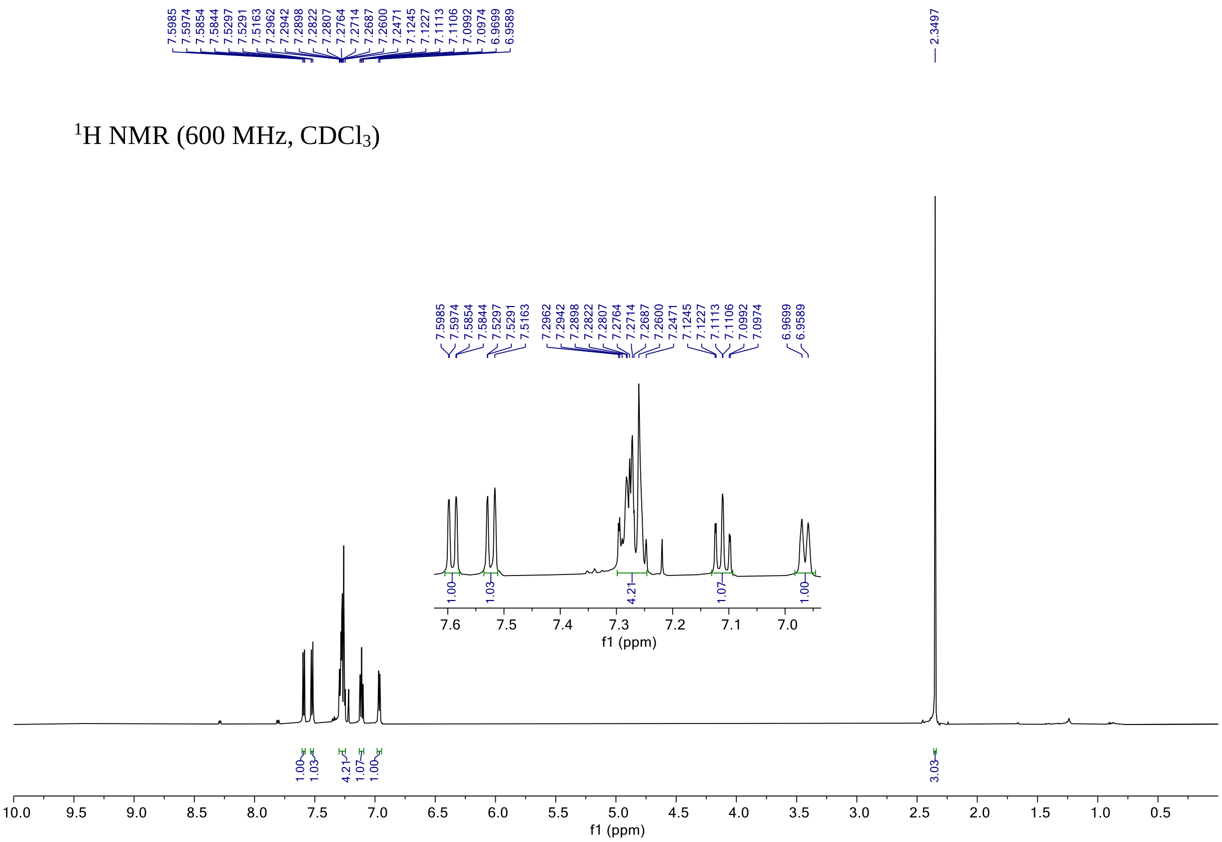


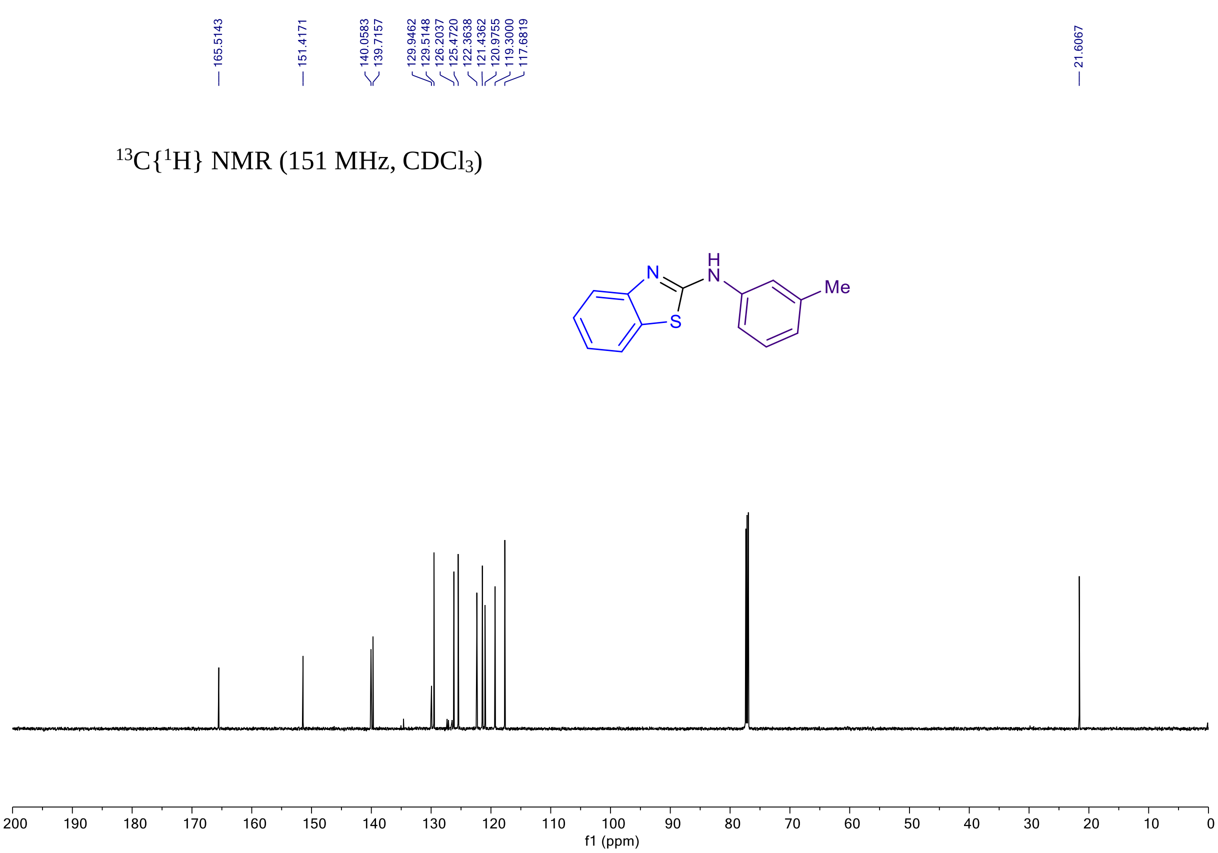
***N*-(*o*-Tolyl)benzothiazol-2-amine (3b)**





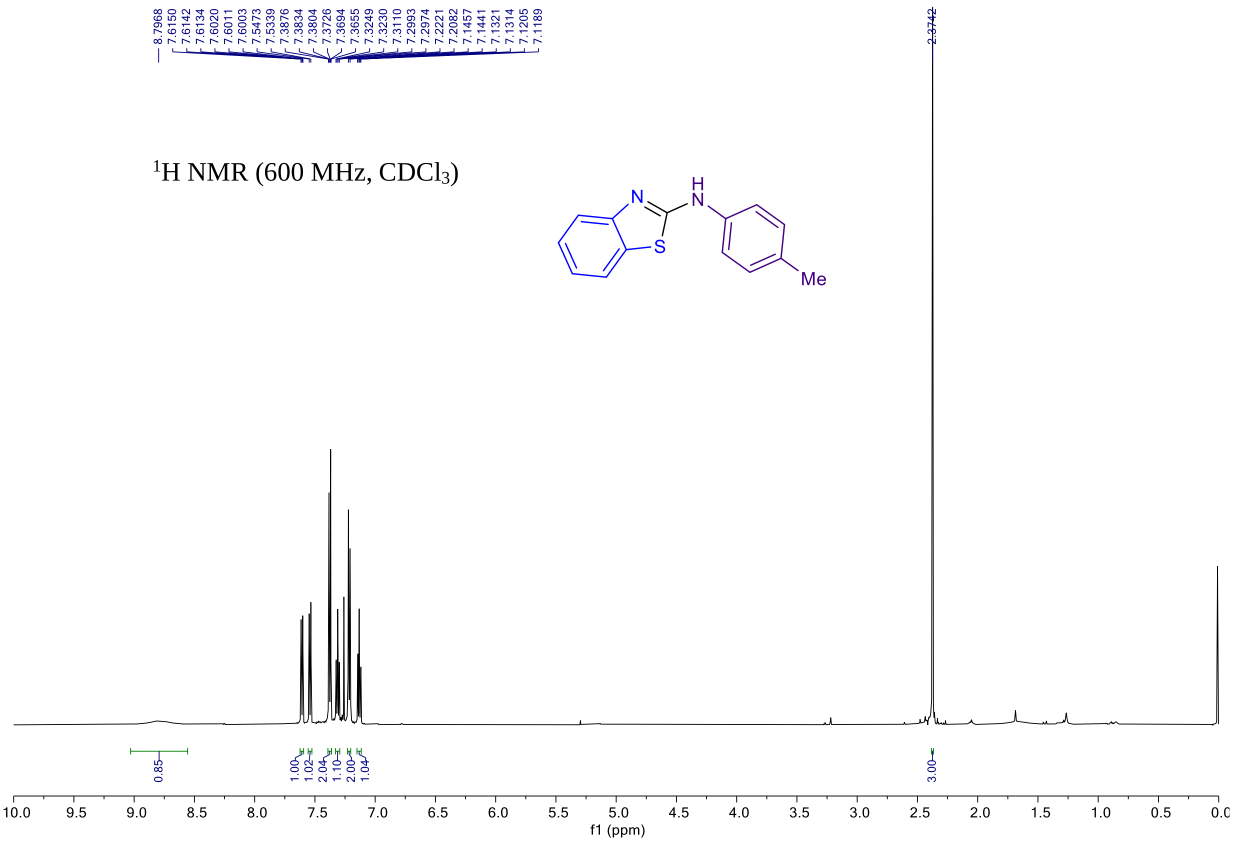
N-(*m*-Tolyl)benzothiazol-2-amine (3c)



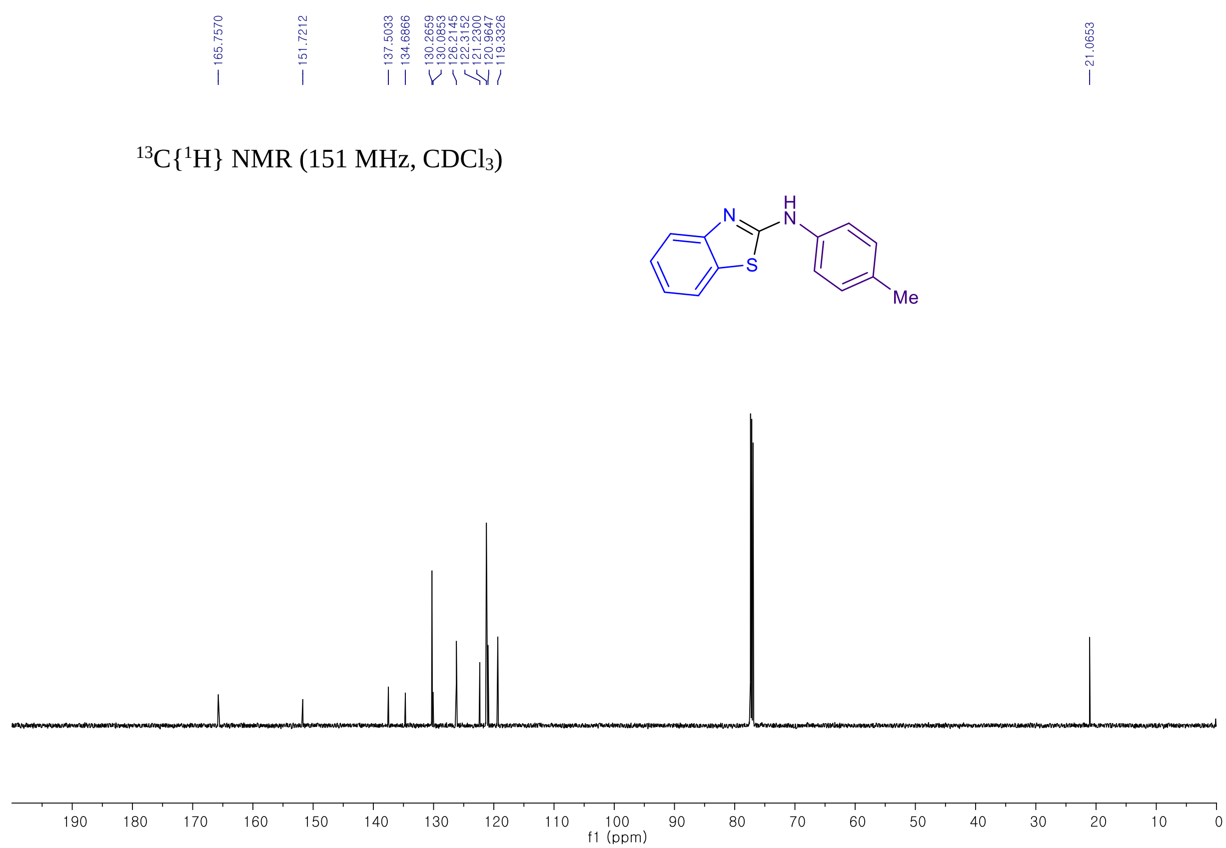


_N_-(_p_-Tolyl)benzothiazol-2-amine (3d)

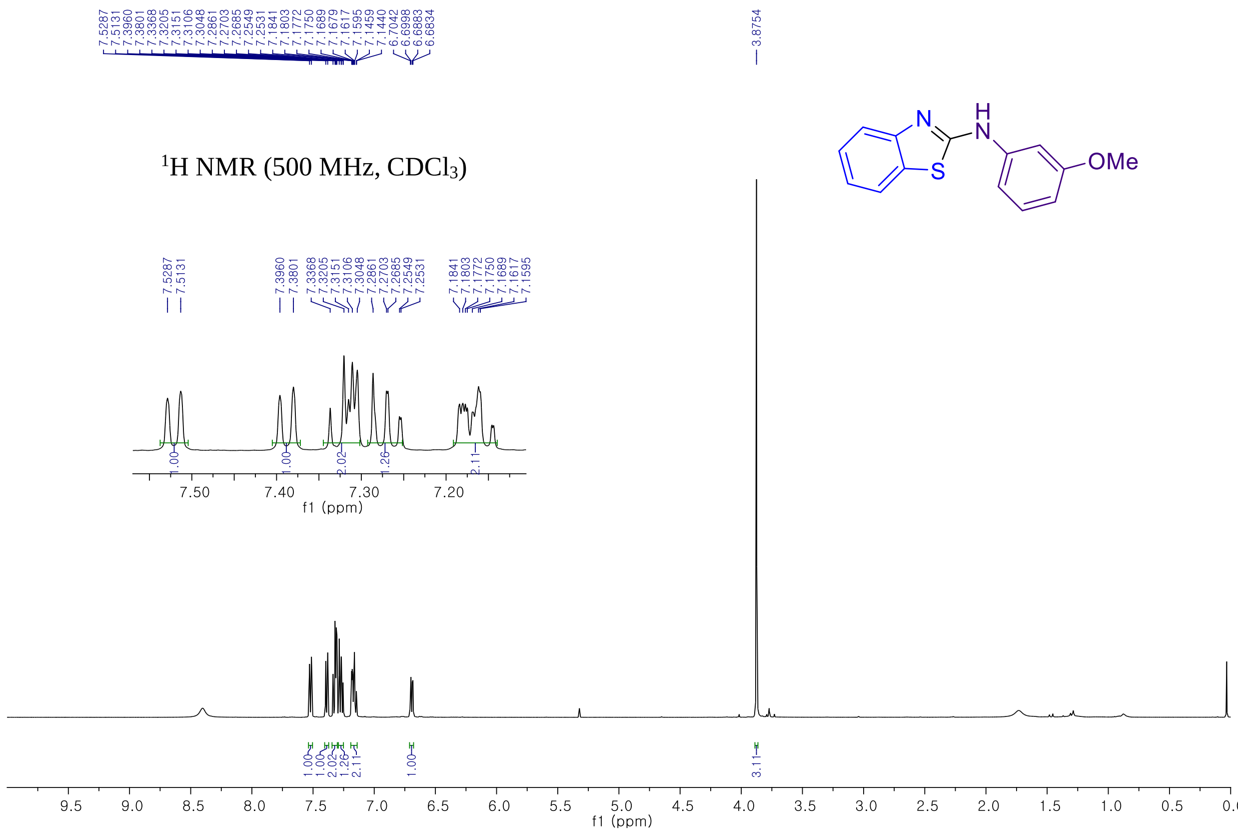
^{1}H NMR (600 MHz, $CDCl_3$)

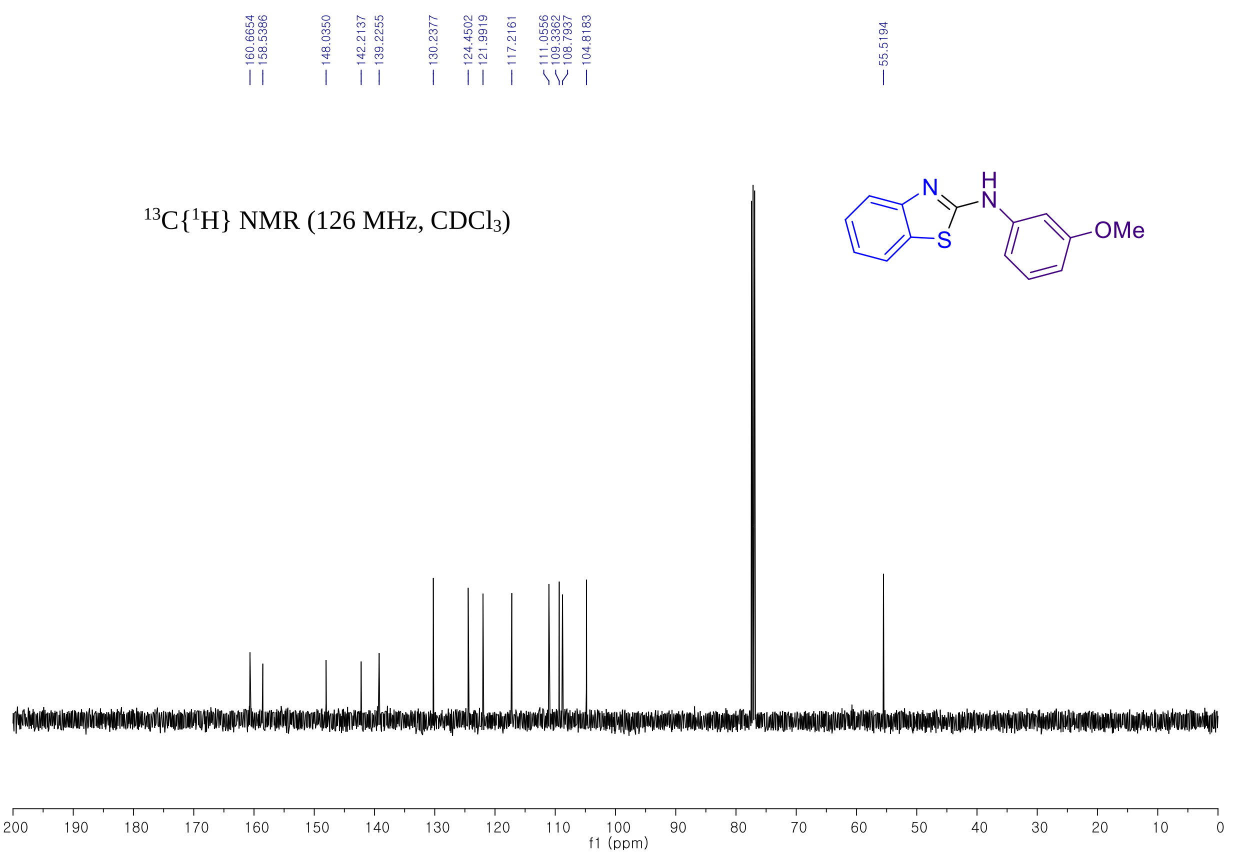


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

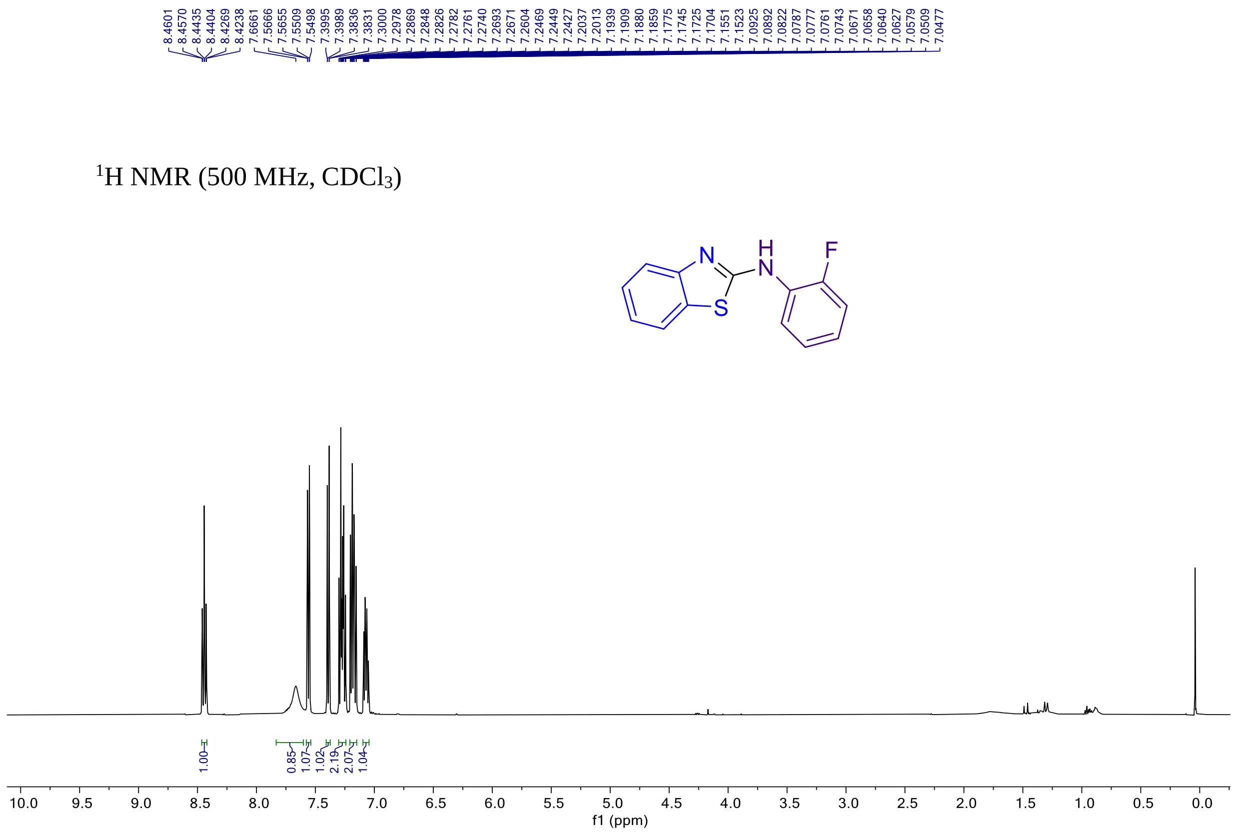


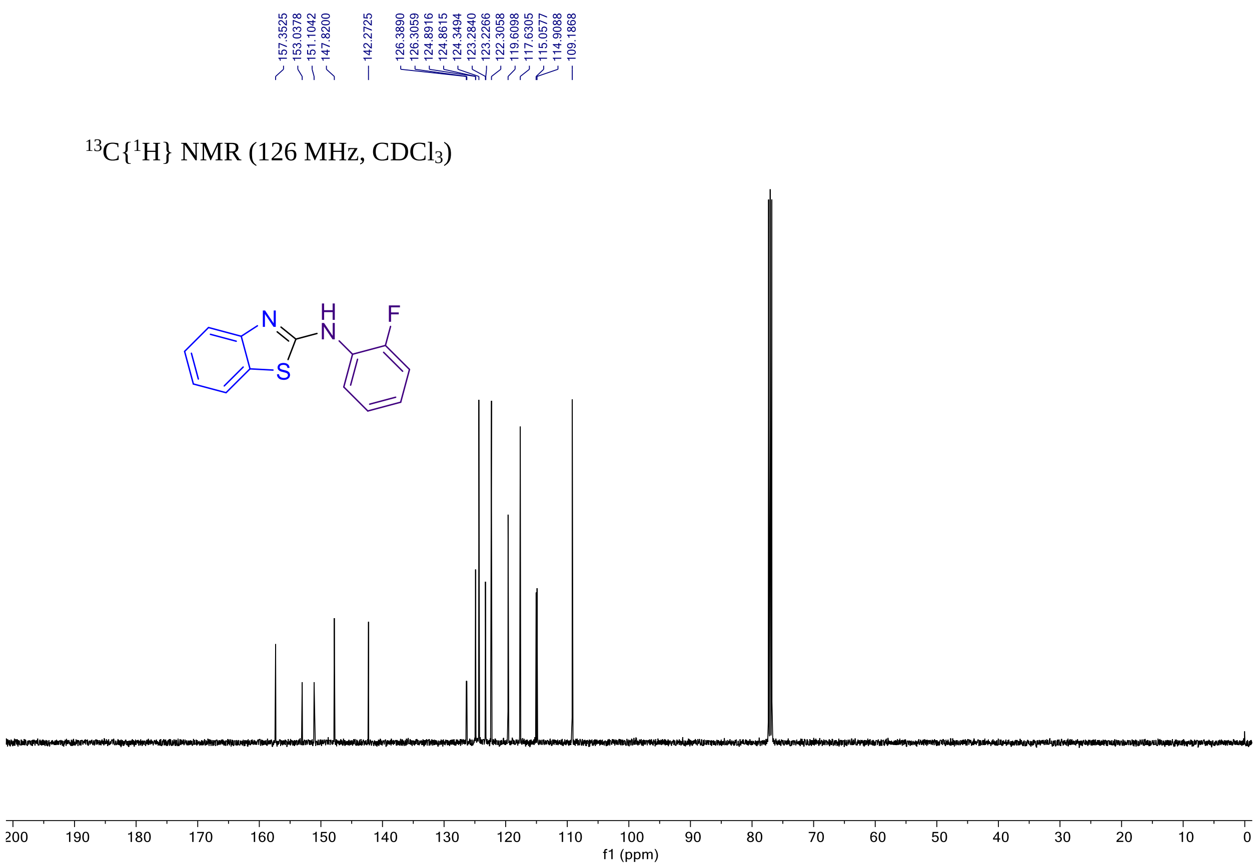
_N_-(3-Methoxyphenyl)benzothiazol-2-amine (3e)





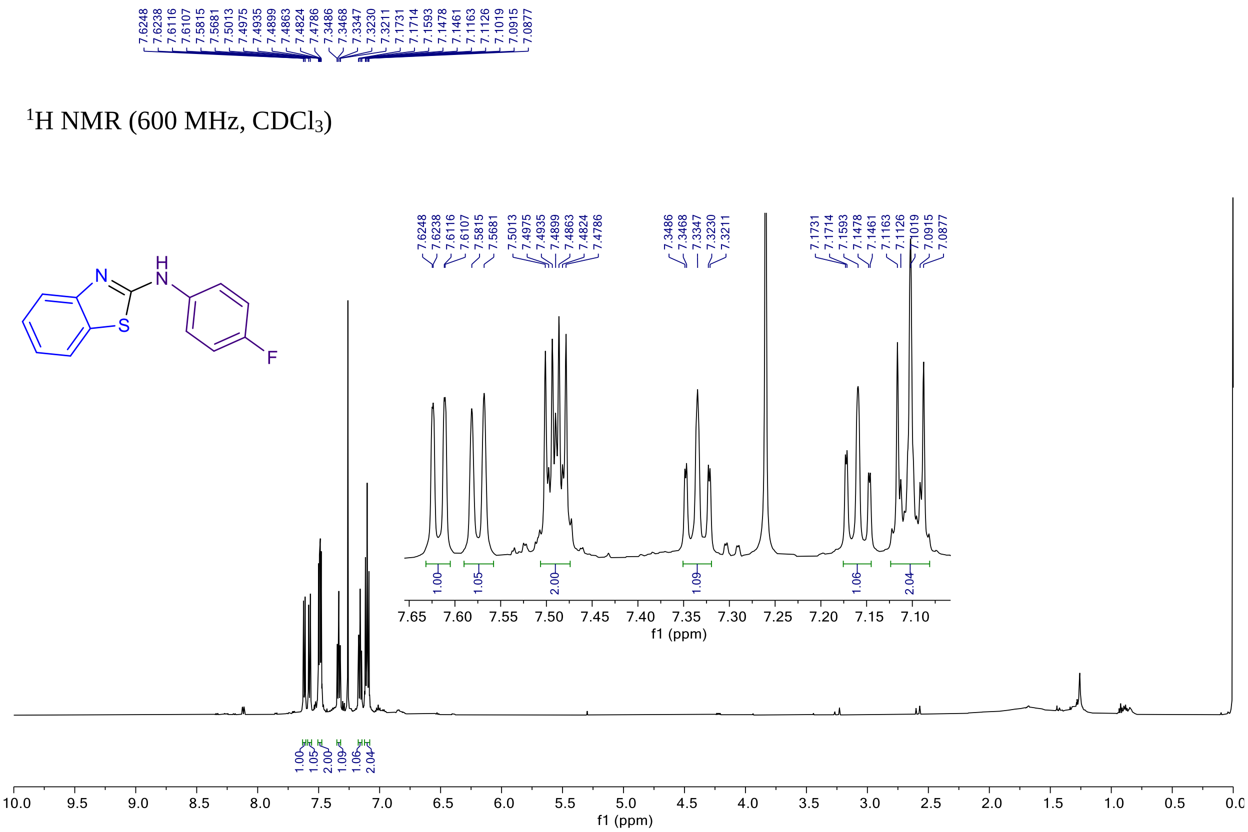
_N_-(2-Fluorophenyl)benzothiazol-2-amine (3f)



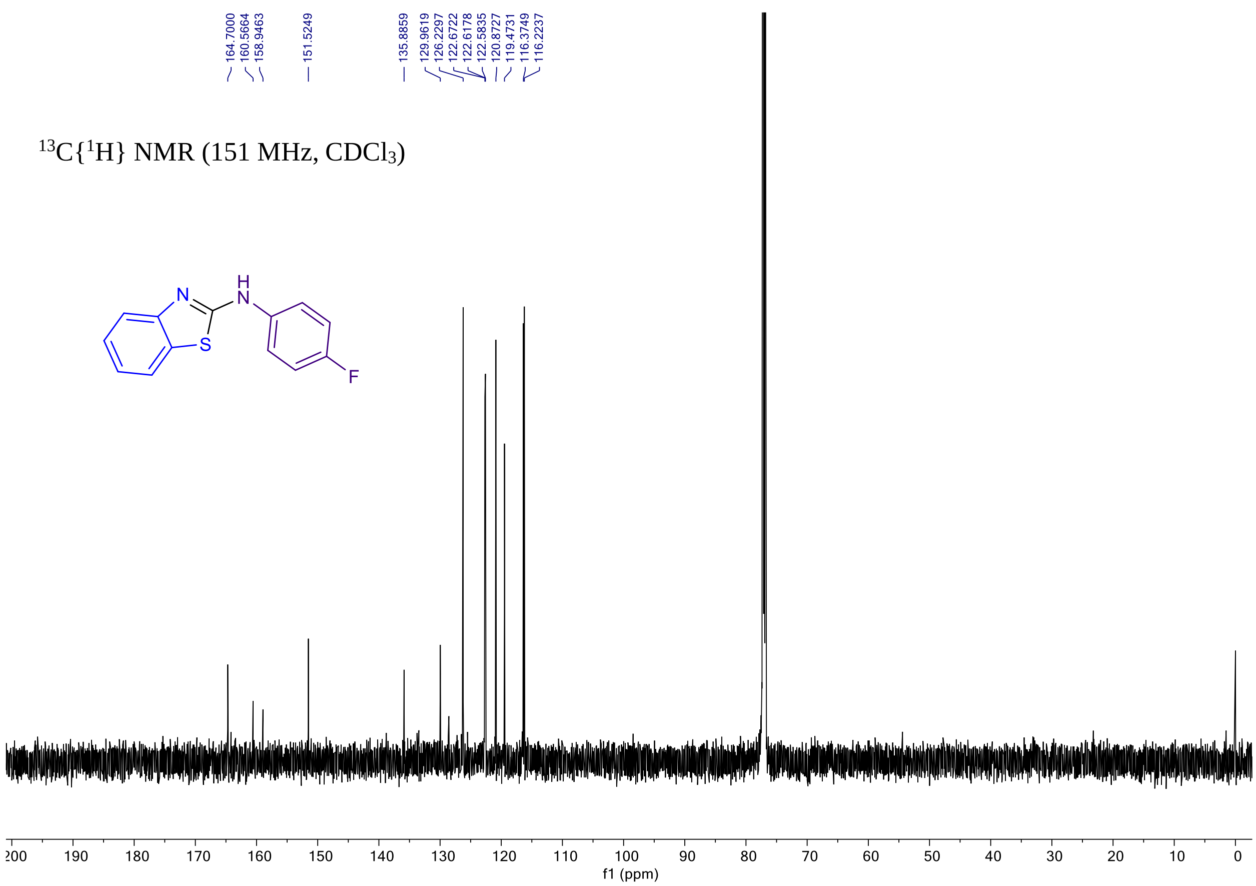


_N_-(4-Fluorophenyl)benzothiazol-2-amine (3g)

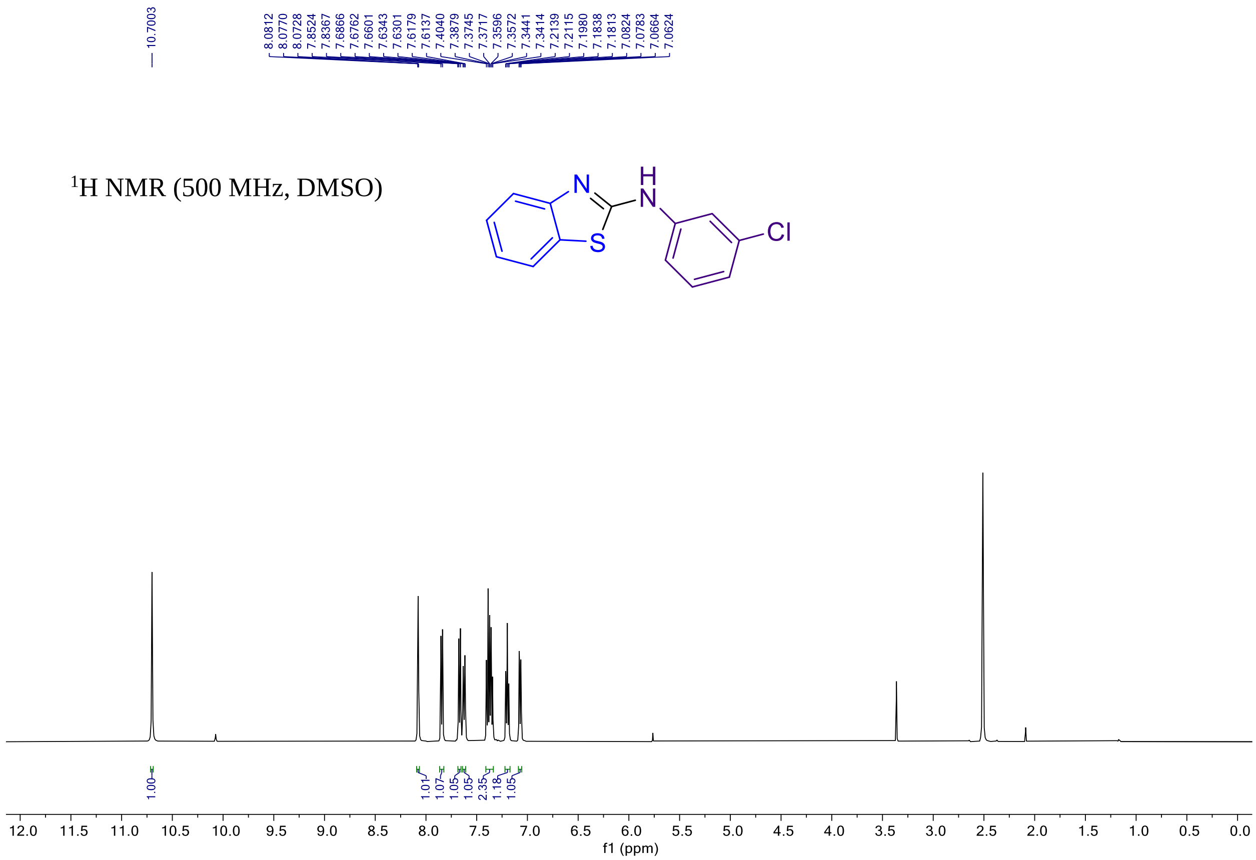
^{1}H NMR (600 MHz, $CDCl_3$)

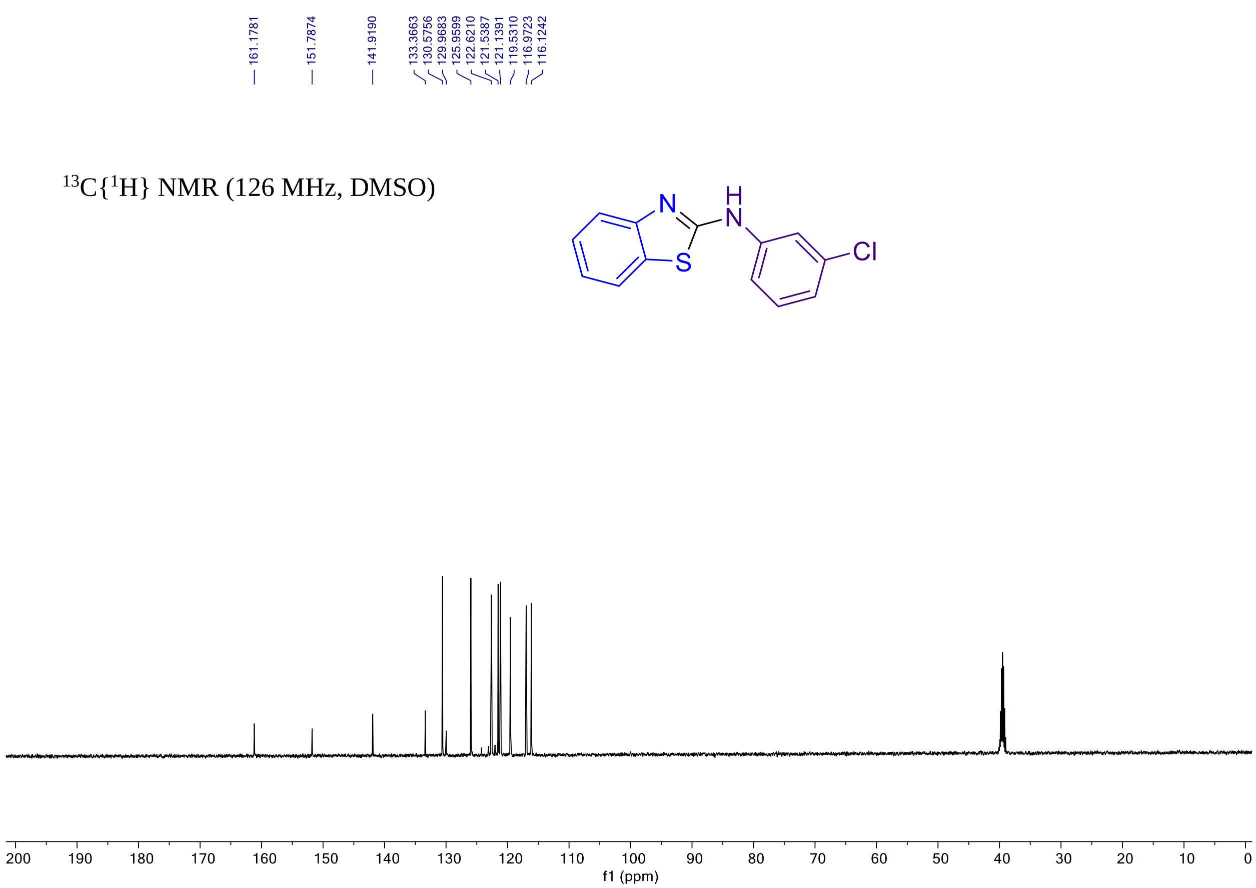


$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$)

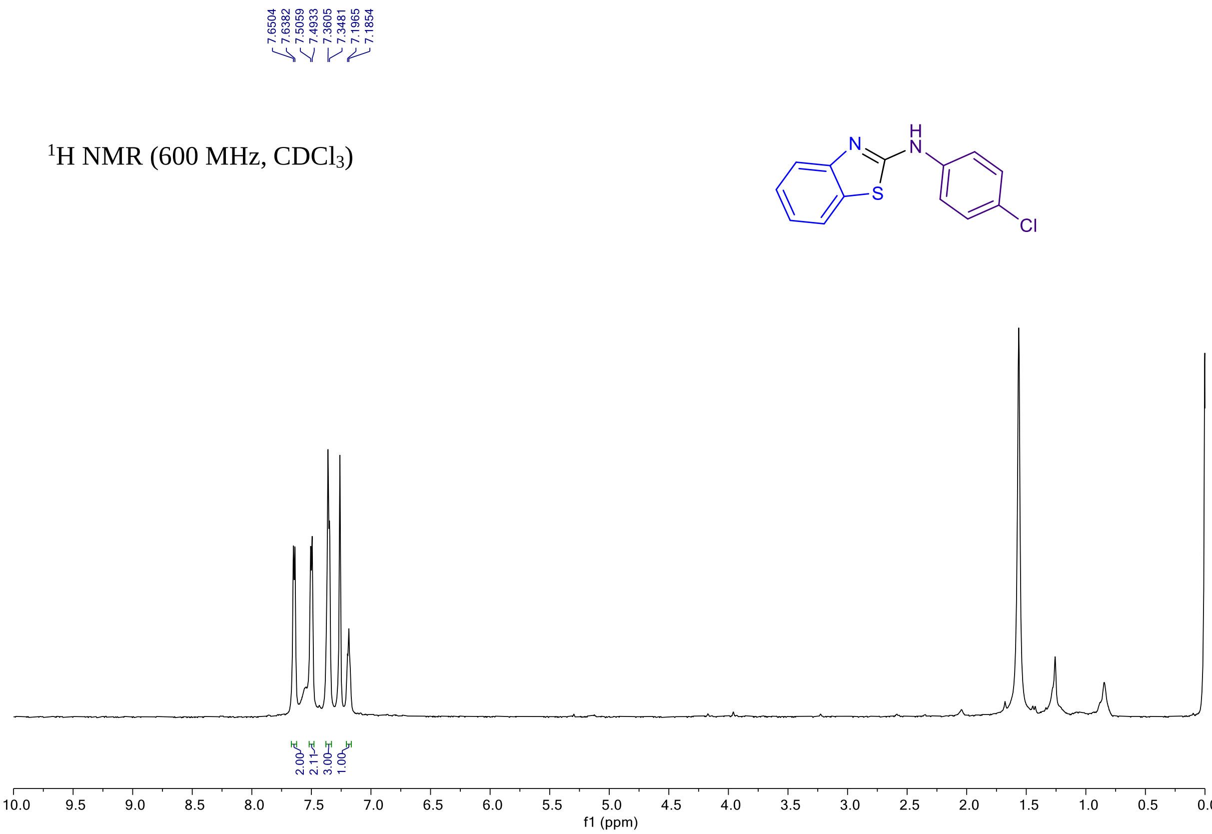


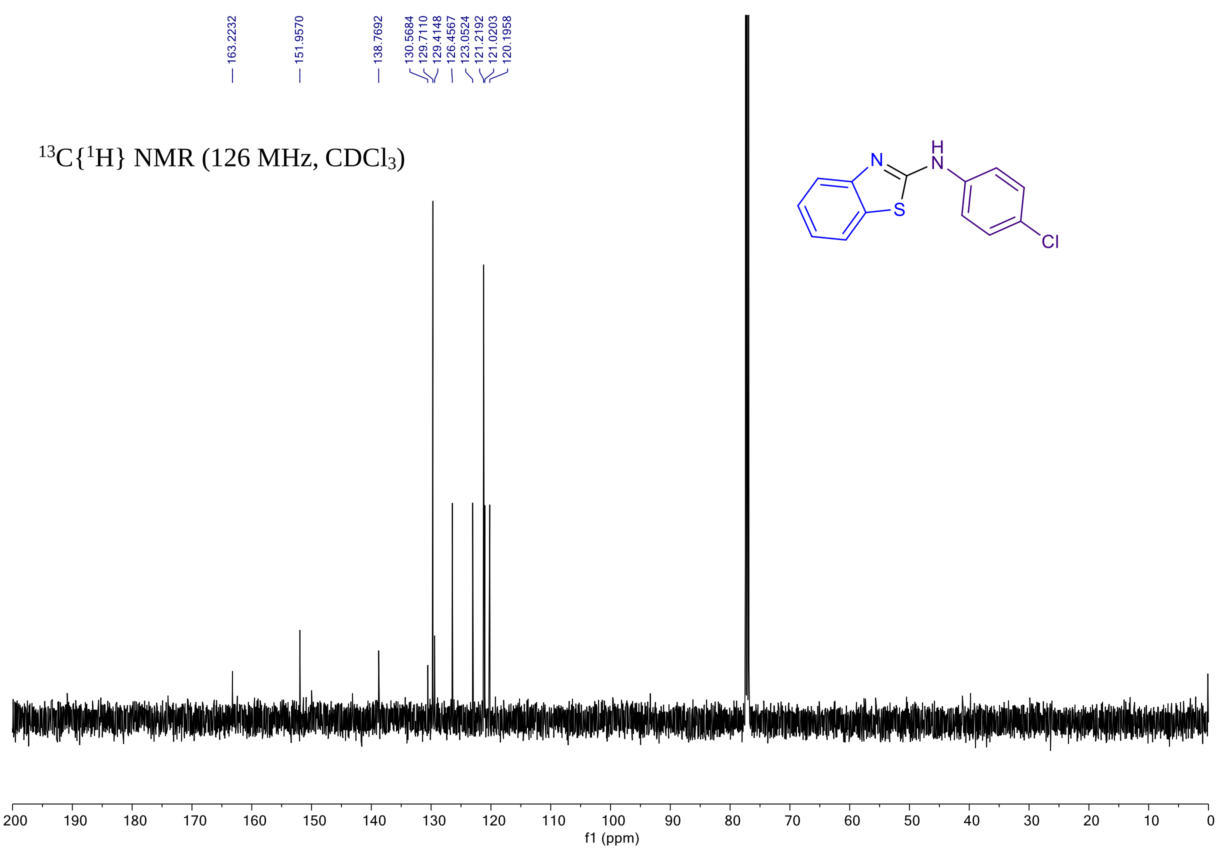
_N_-(3-Chlorophenyl)benzothiazol-2-amine (3h)





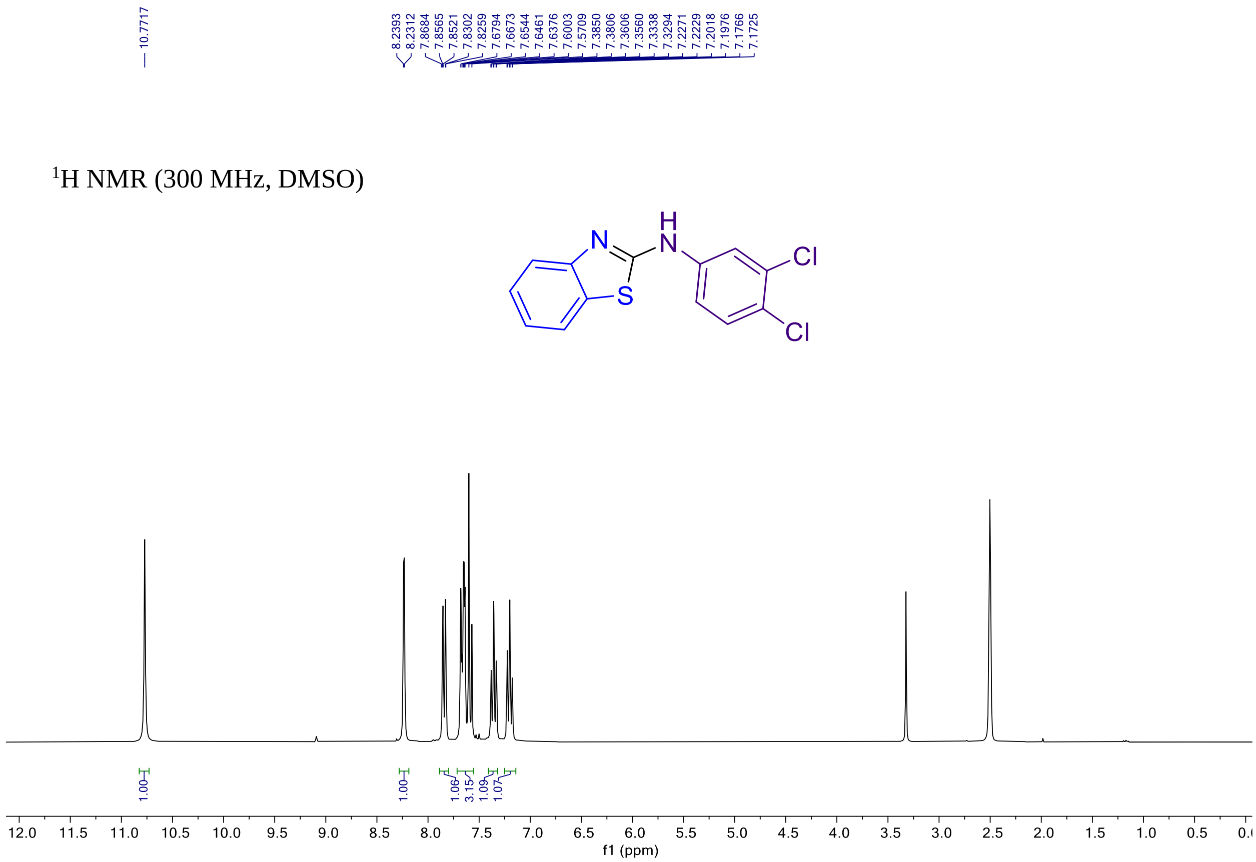
***N*-(4-Chlorophenyl)benzothiazol-2-amine (3i)**



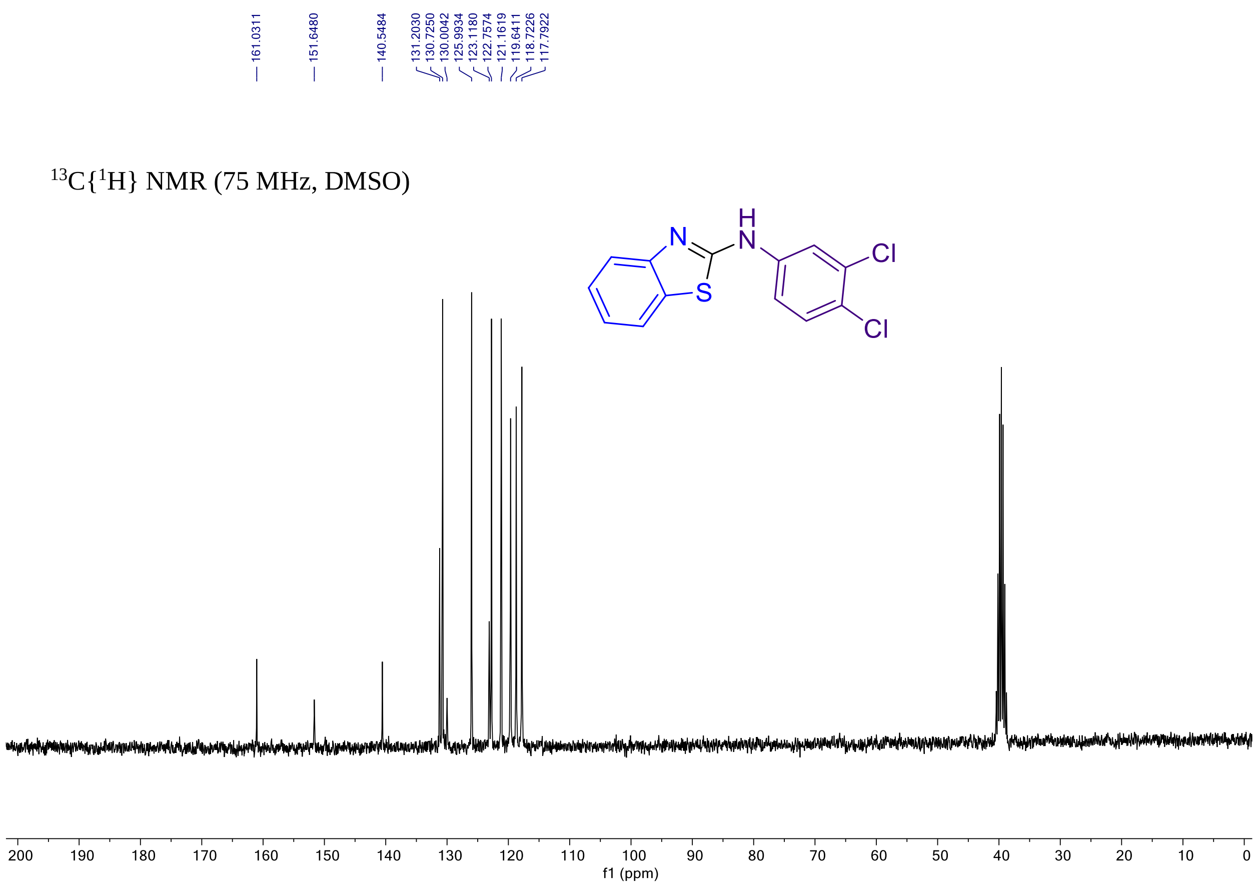


N-(3,4-Dichlorophenyl)benzothiazol-2-amine (3j)

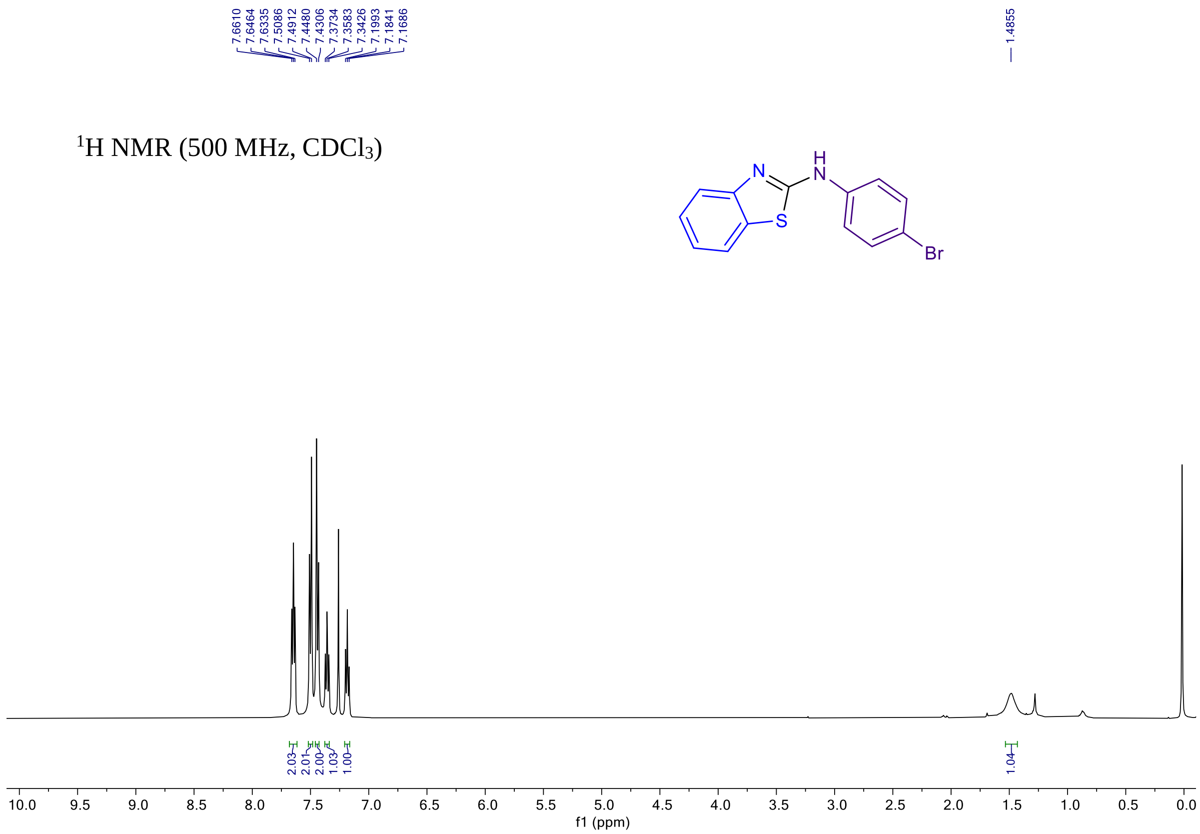
^{1}H NMR (300 MHz, DMSO)

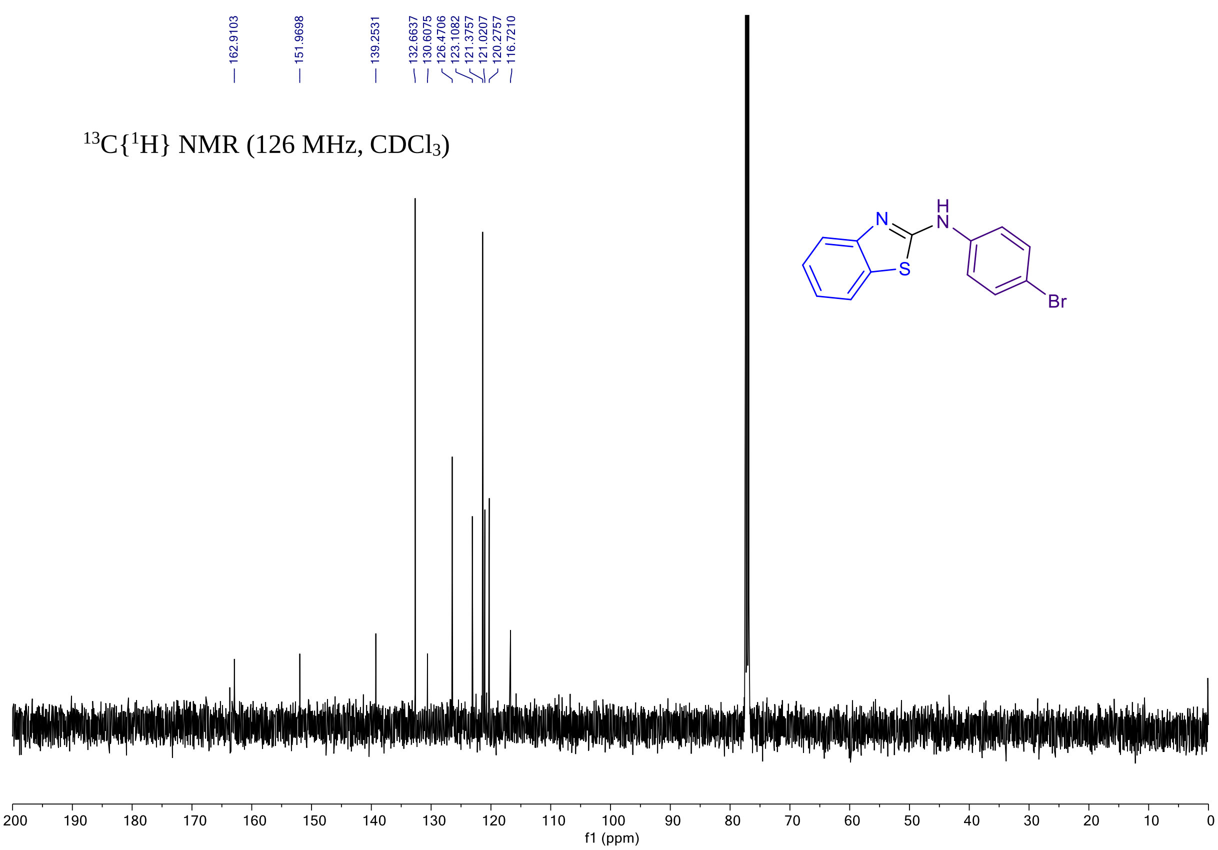


^{13}C{^{1}H} NMR (75 MHz, DMSO)



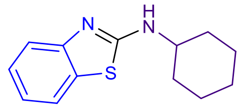
N-(4-Bromophenyl)benzothiazol-2-amine (3k)

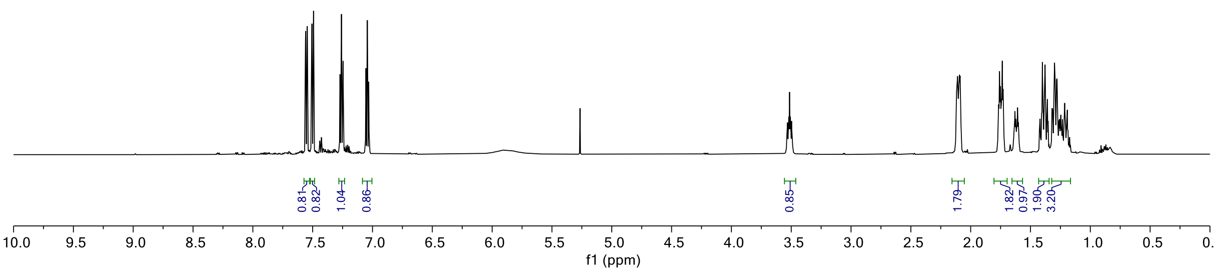




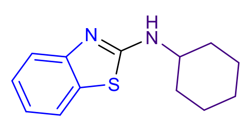
N-Cyclohexylbenzothiazol-2-amine (3l)

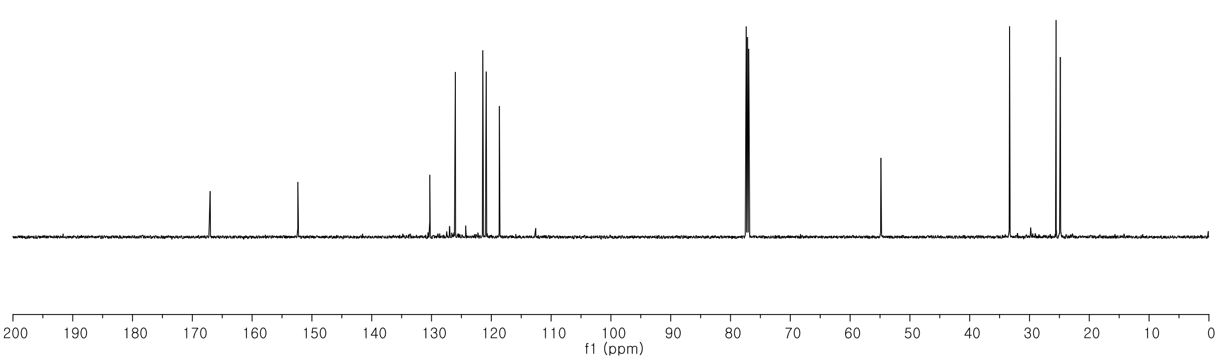
^{1}H NMR (600 MHz, $CDCl_3$)



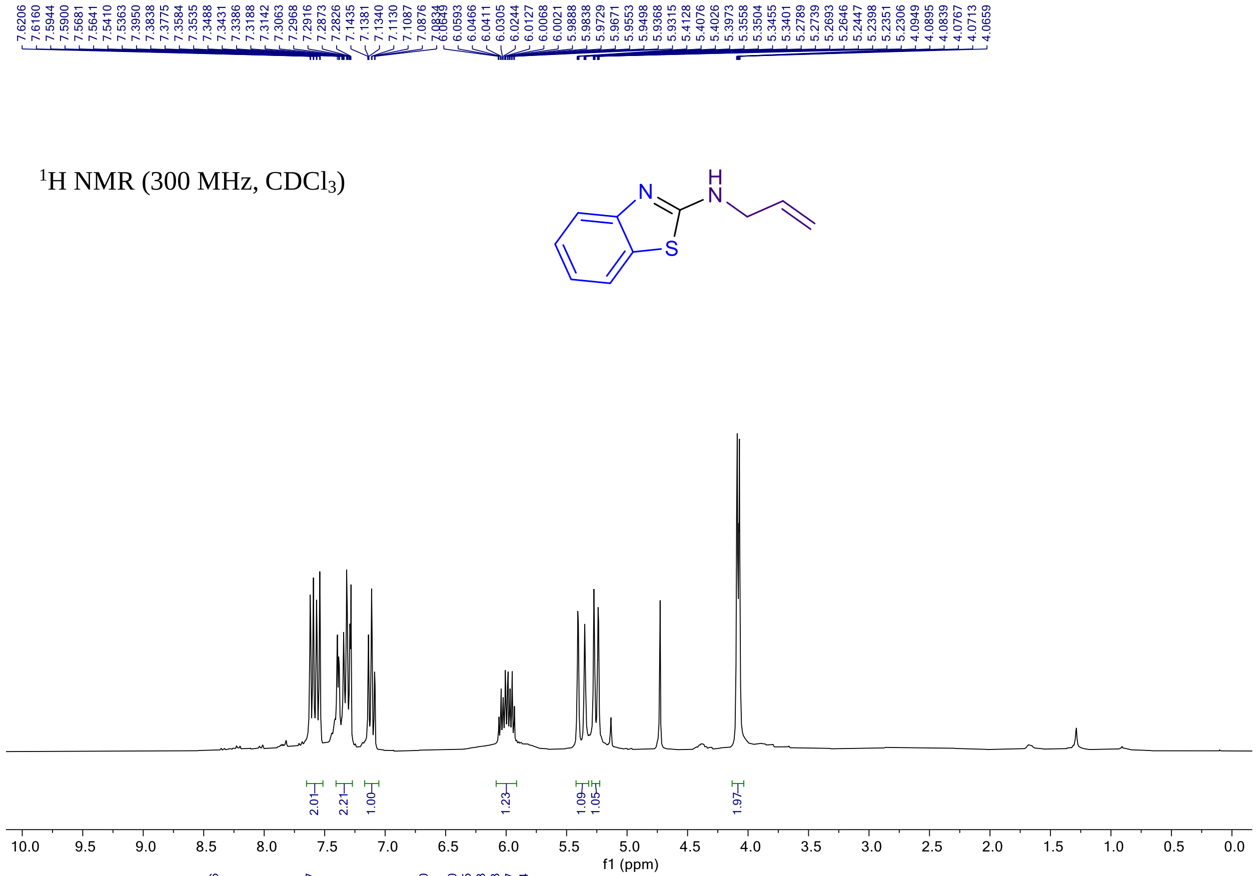


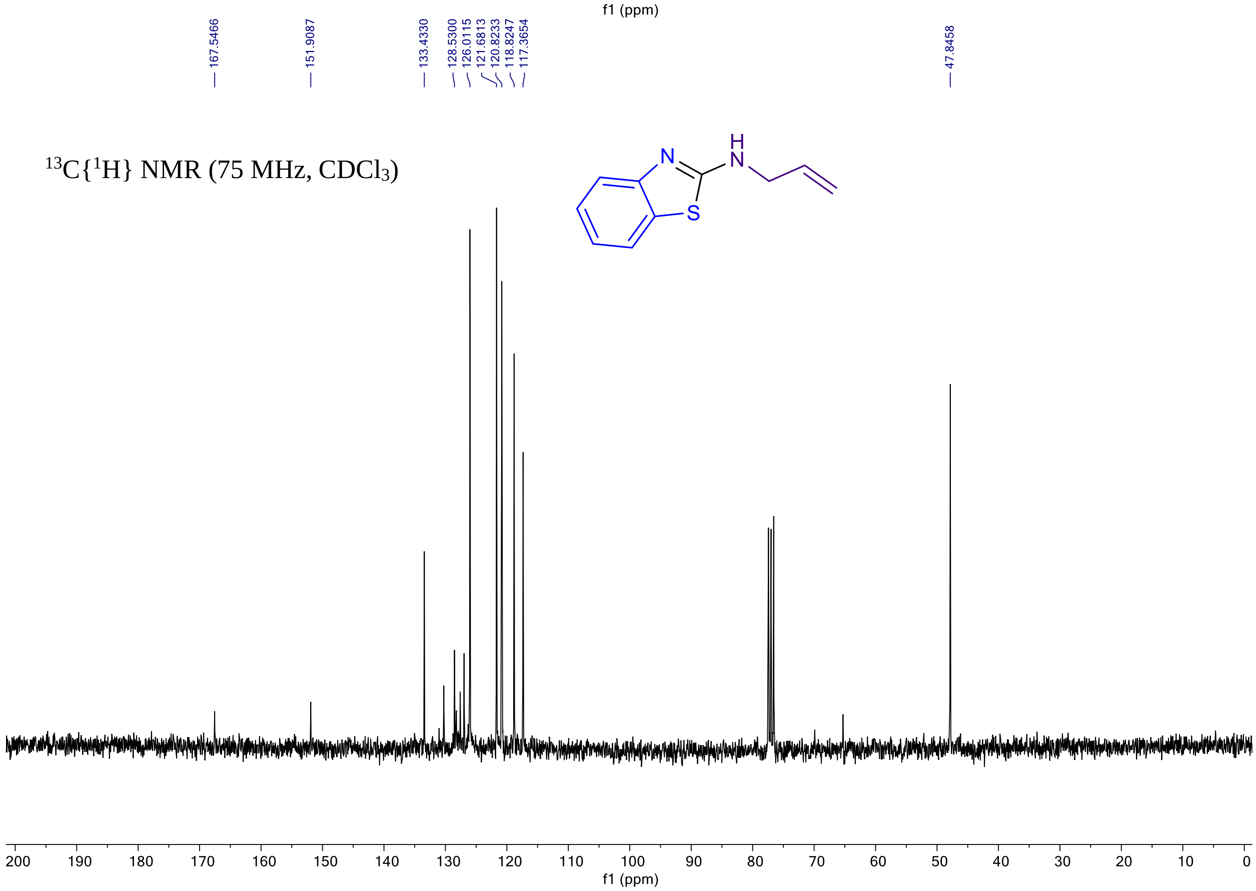
$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$)





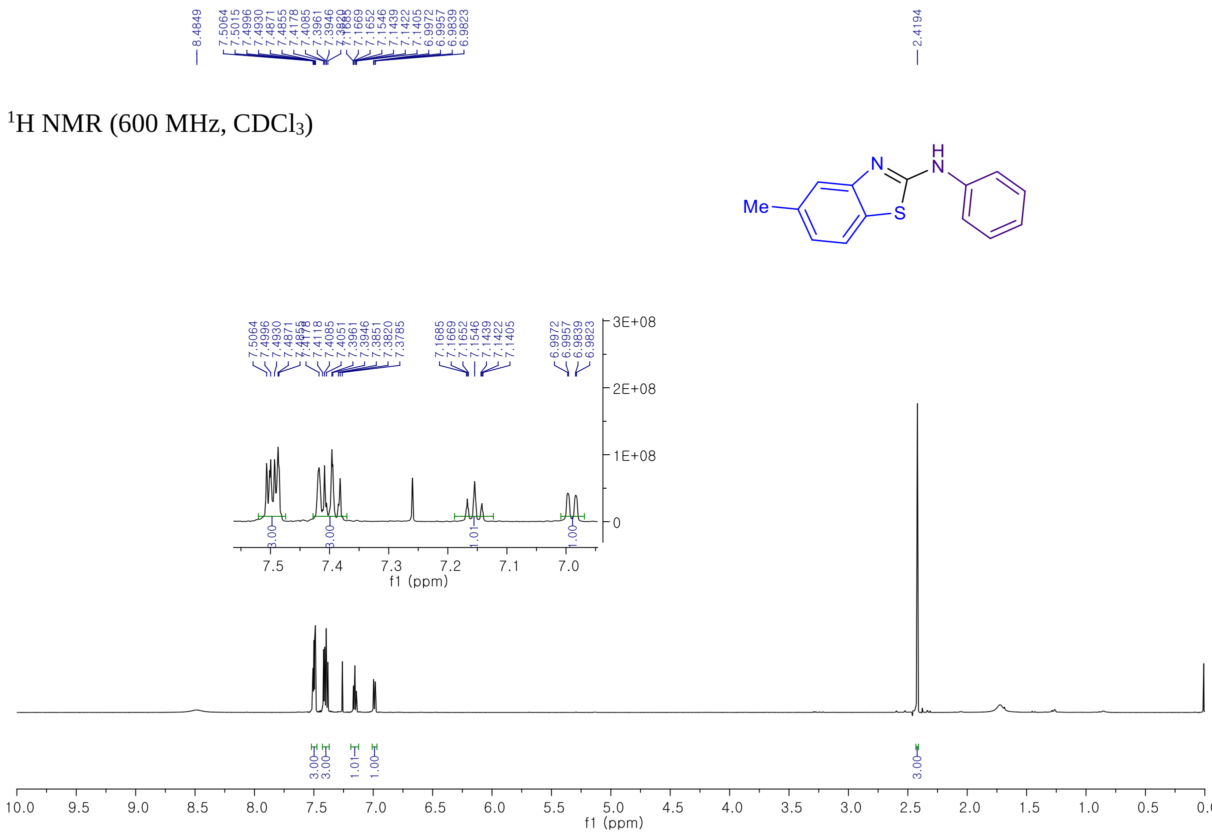
N-Allylbenzothiazol-2-amine (3m)



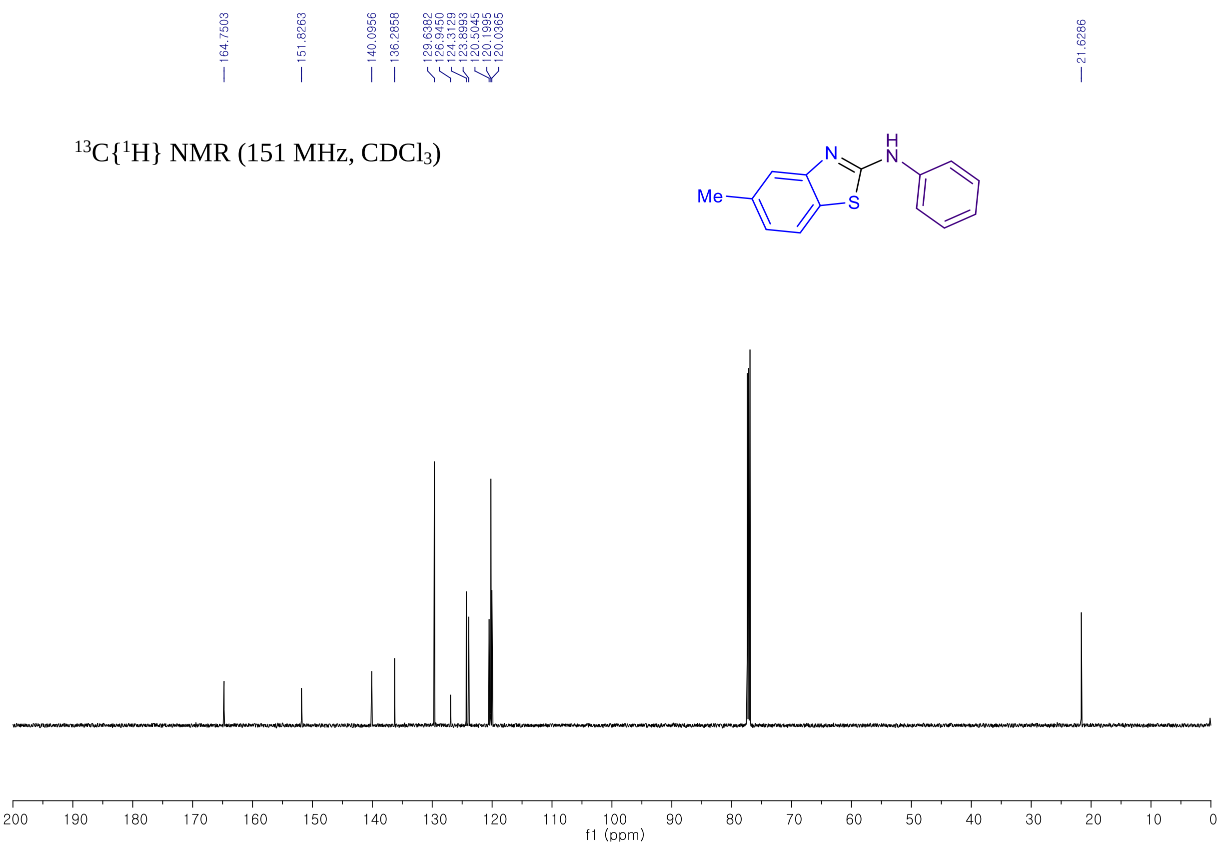


5-Methyl-*N*-phenylbenzothiazol-2-amine (3n)

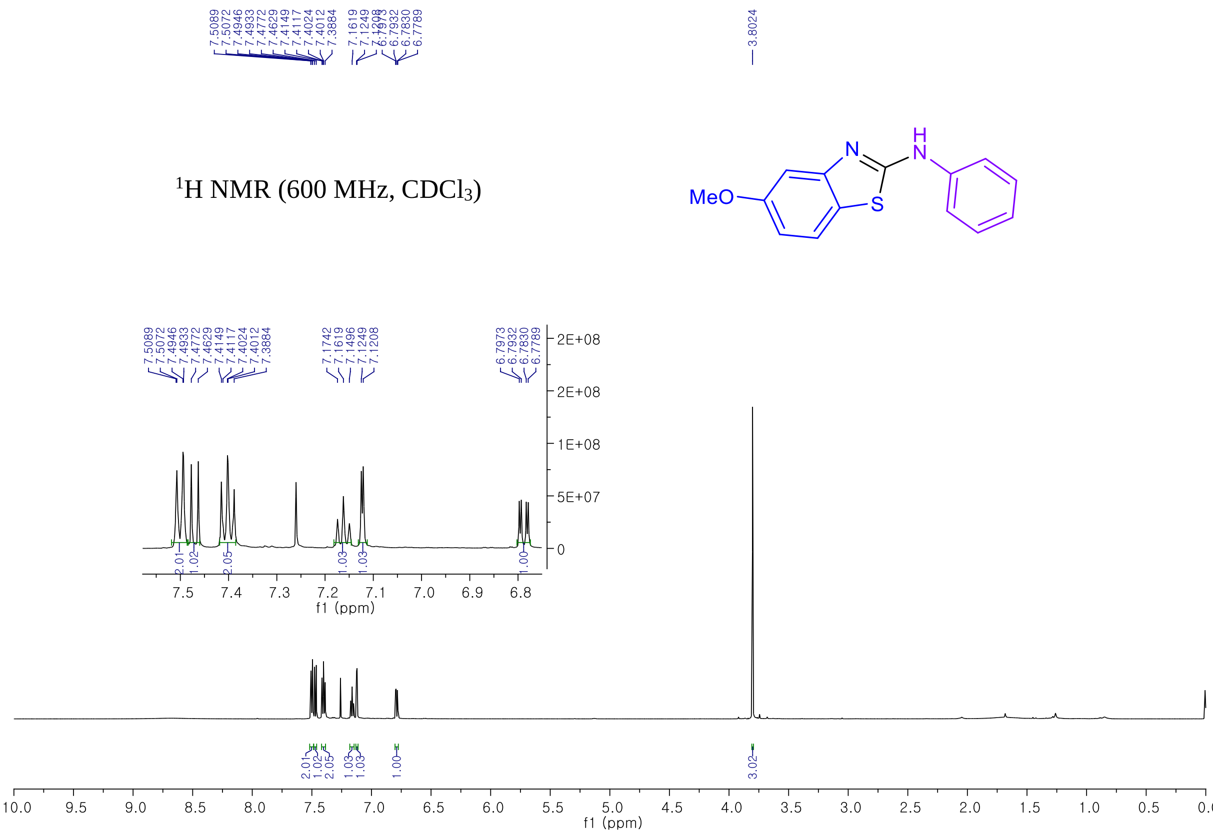
^{1}H NMR (600 MHz, $CDCl_3$)

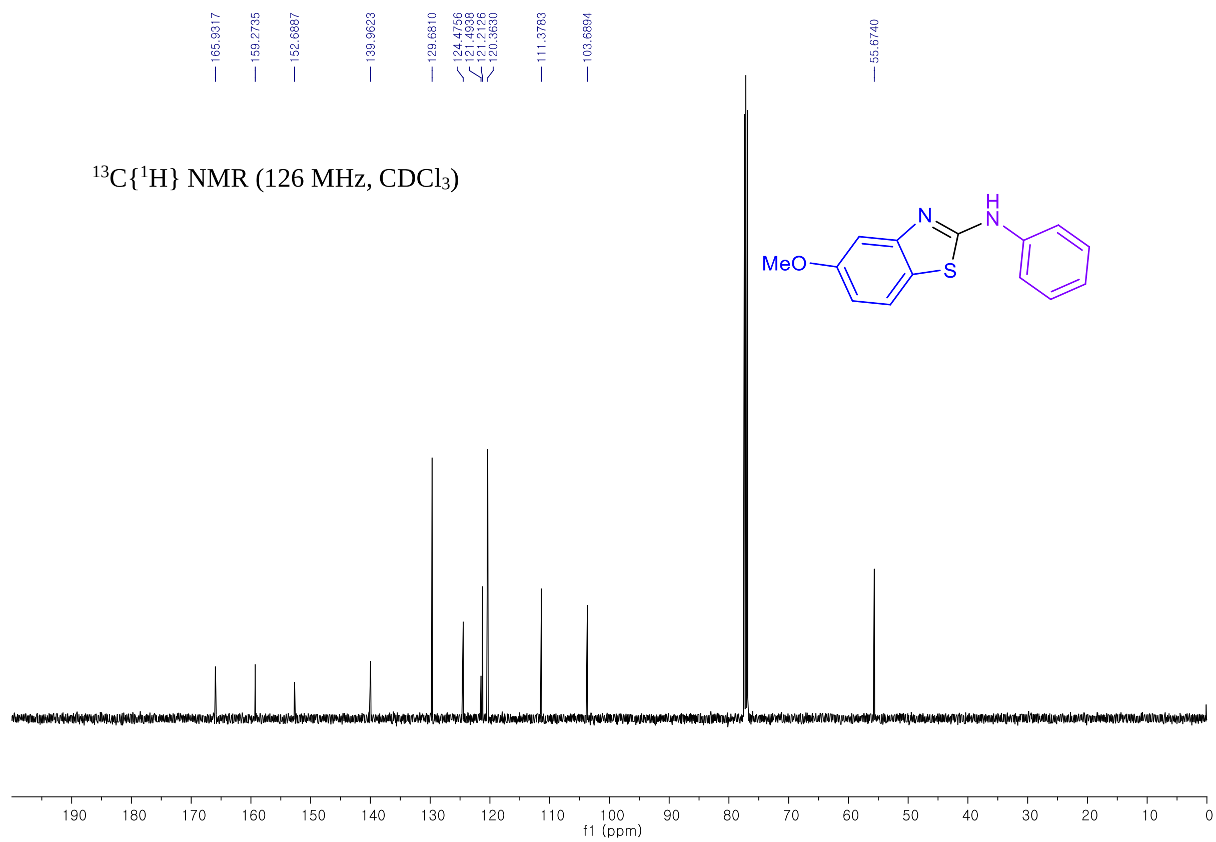


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

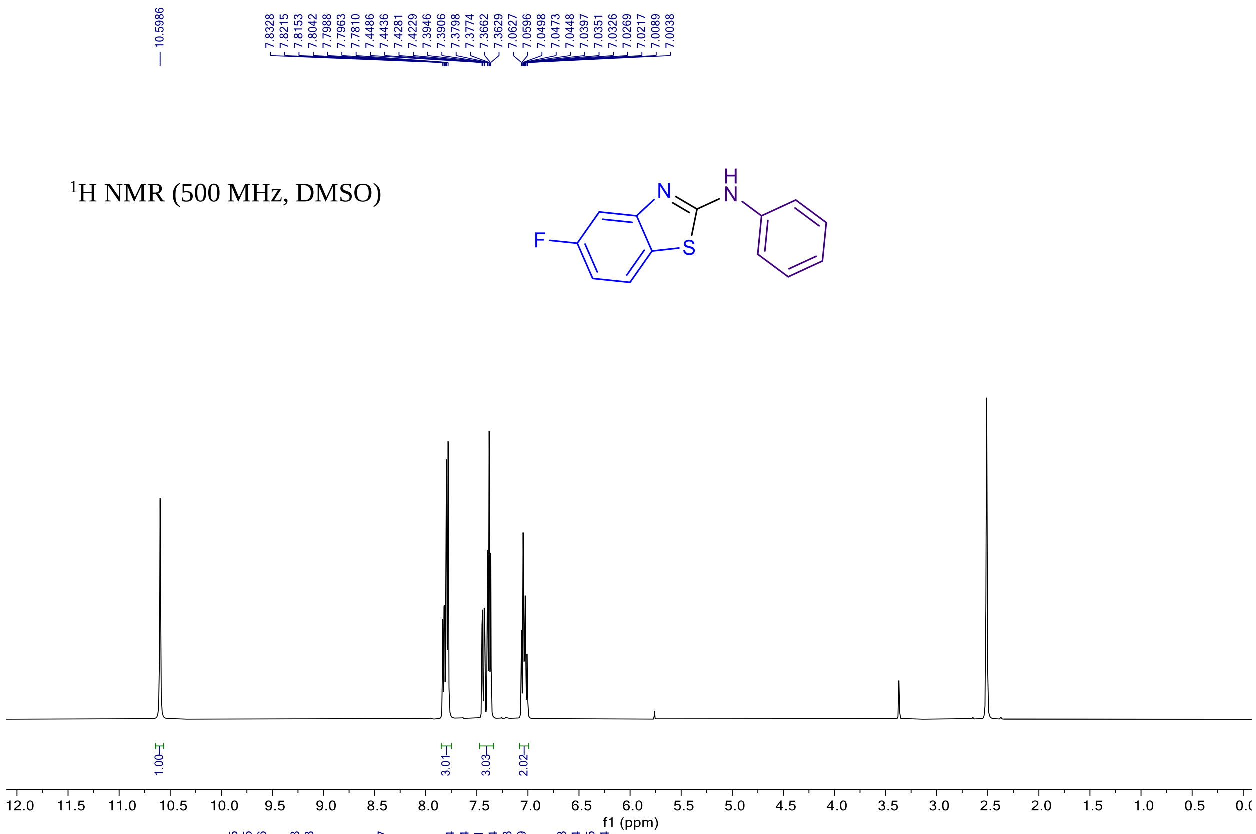


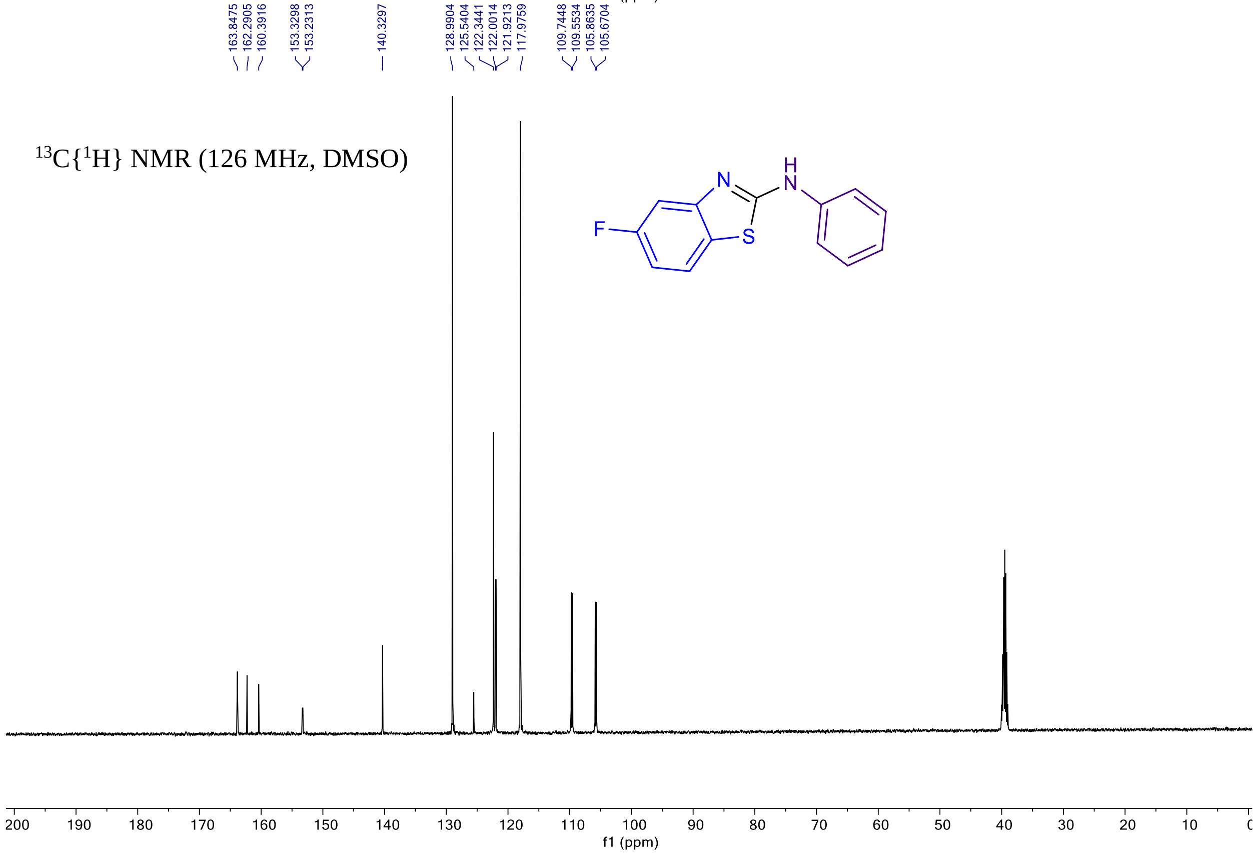
5-Methoxy-*N*-phenylbenzothiazol-2-amine (3o)





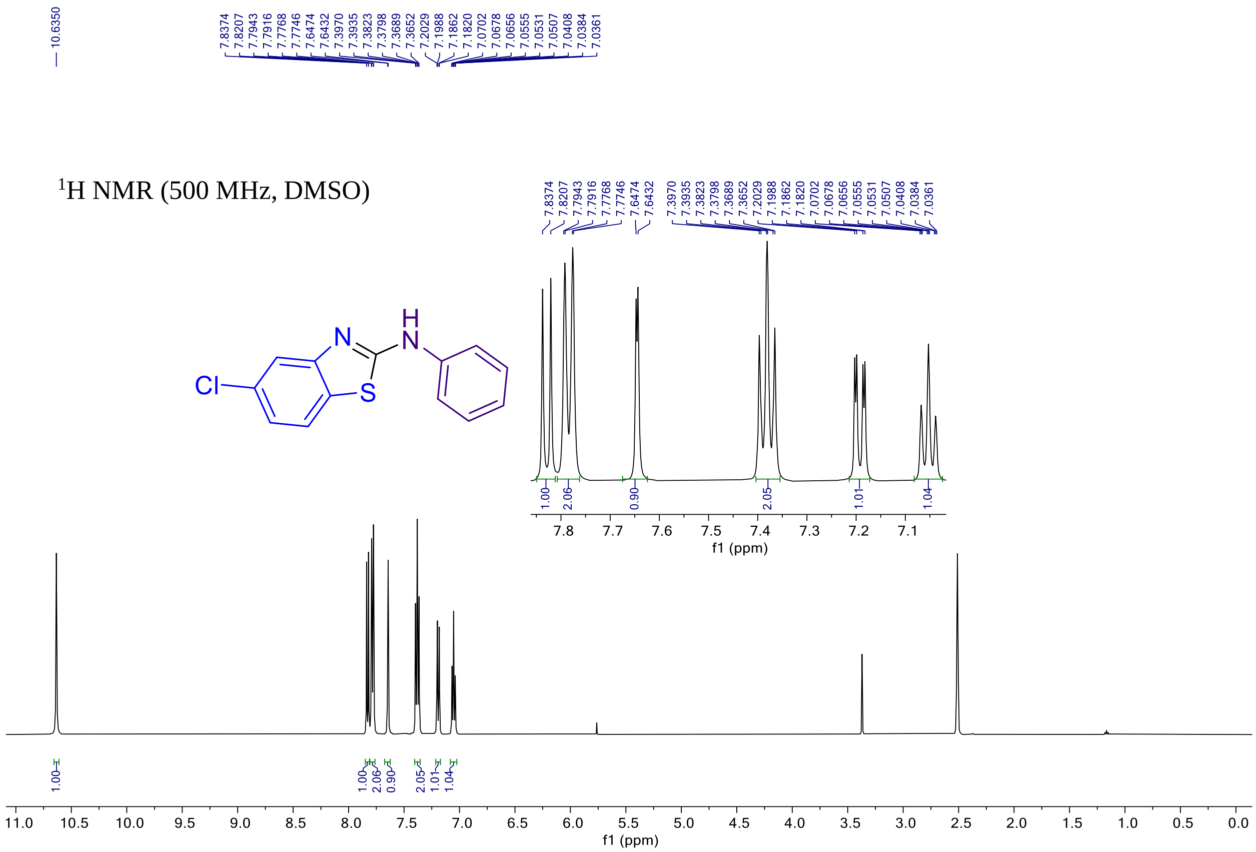
5-Fluoro-*N*-phenylbenzothiazol-2-amine (3p)



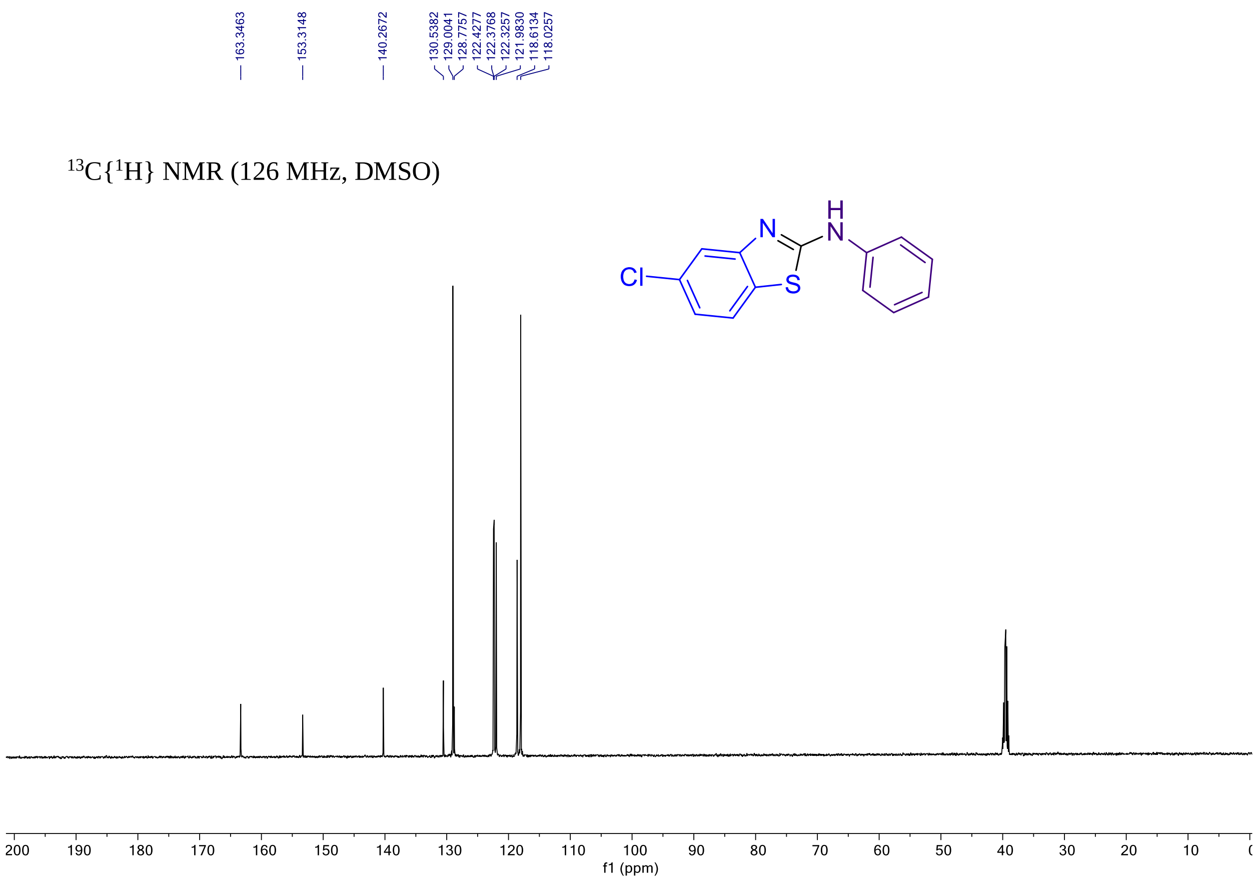


5-Chloro-*N*-phenylbenzothiazol-2-amine (3q)

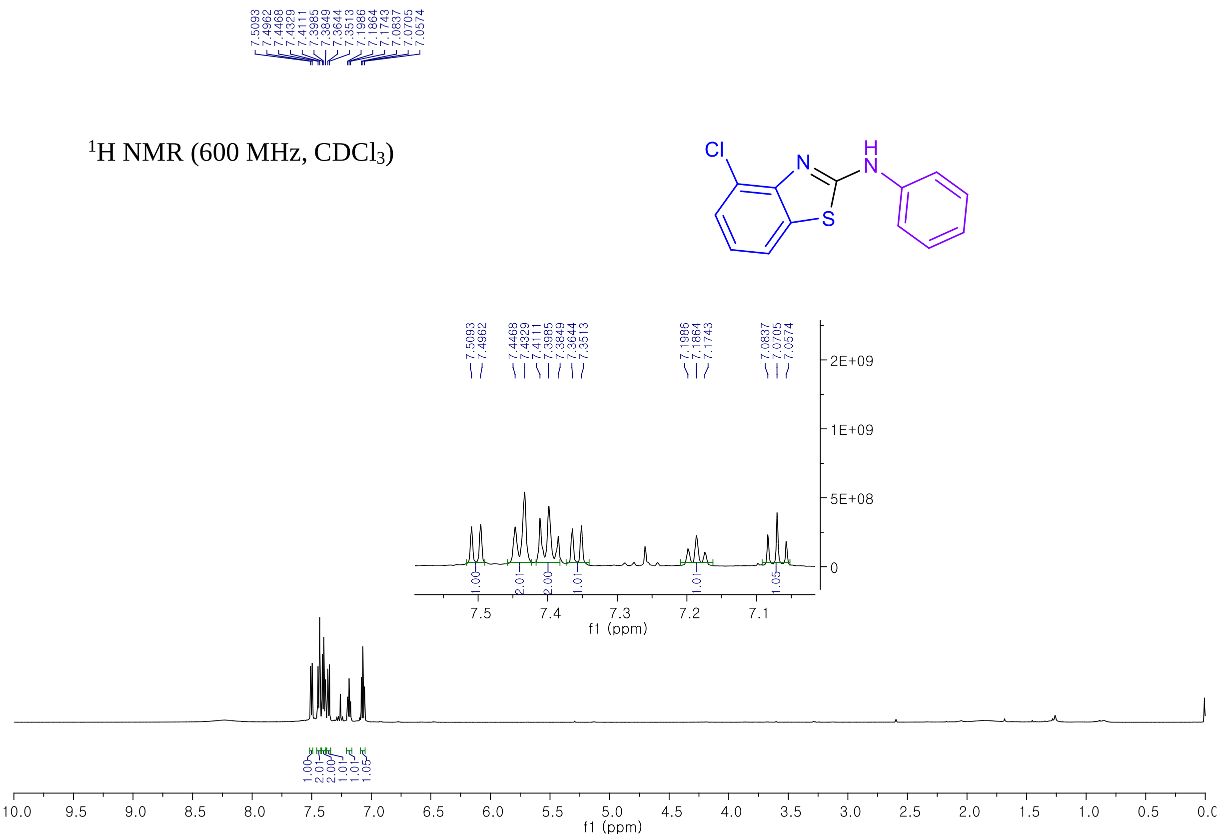
^{1}H NMR (500 MHz, DMSO)

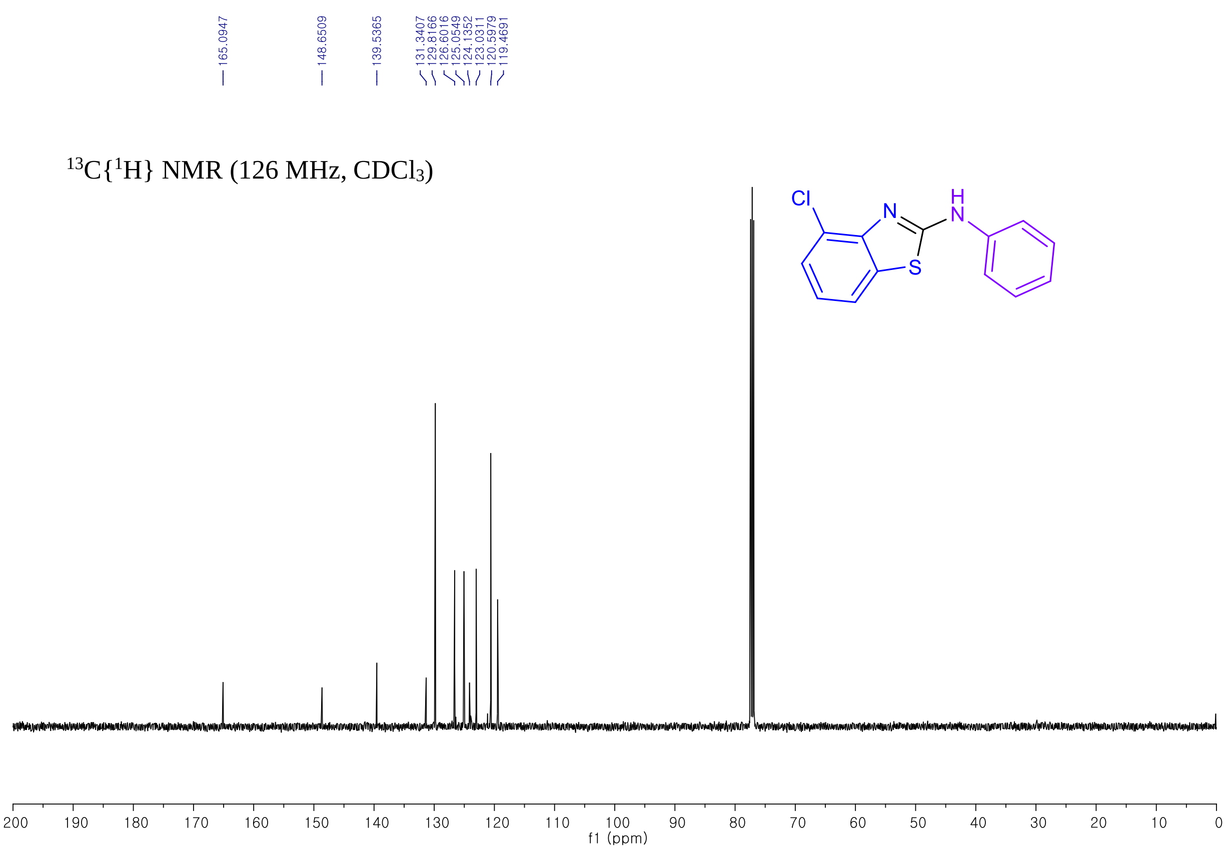


^{13}C{^{1}H} NMR (126 MHz, DMSO)

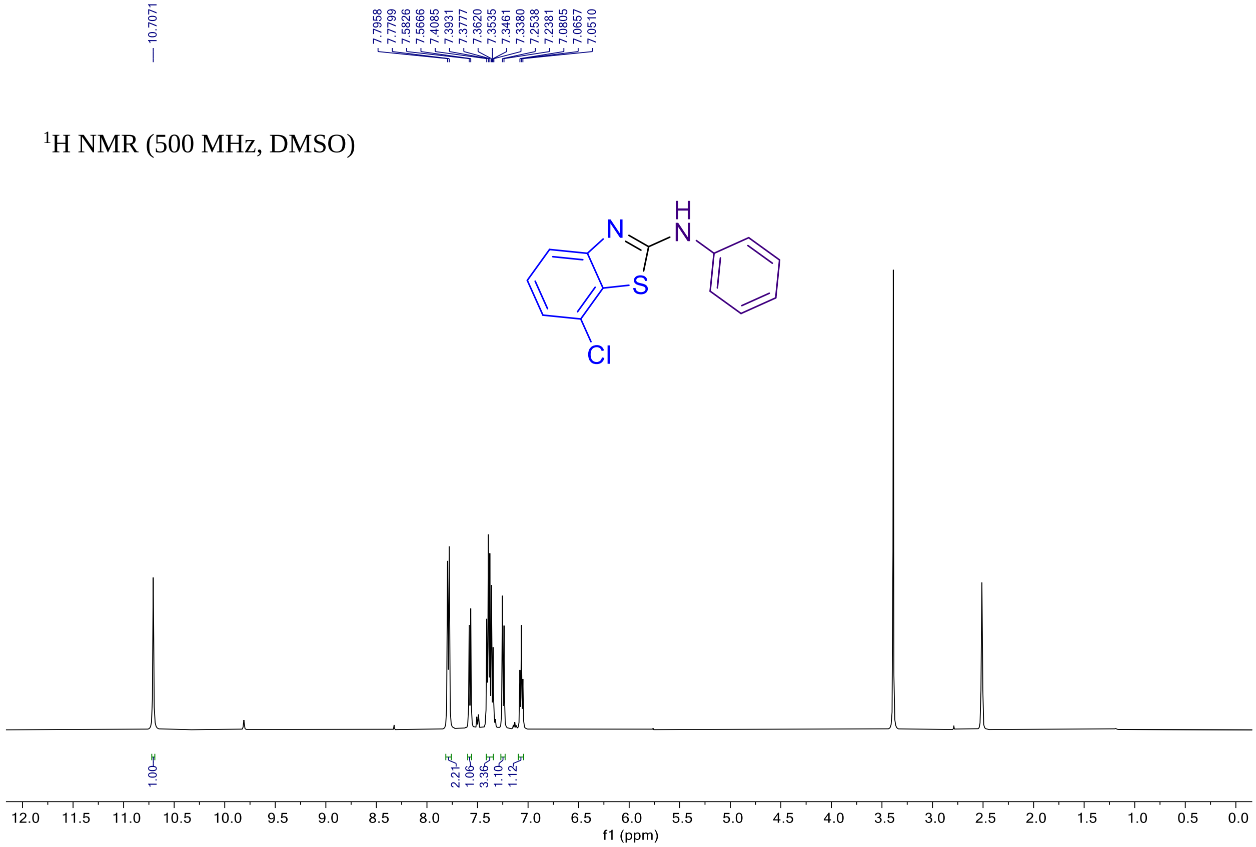


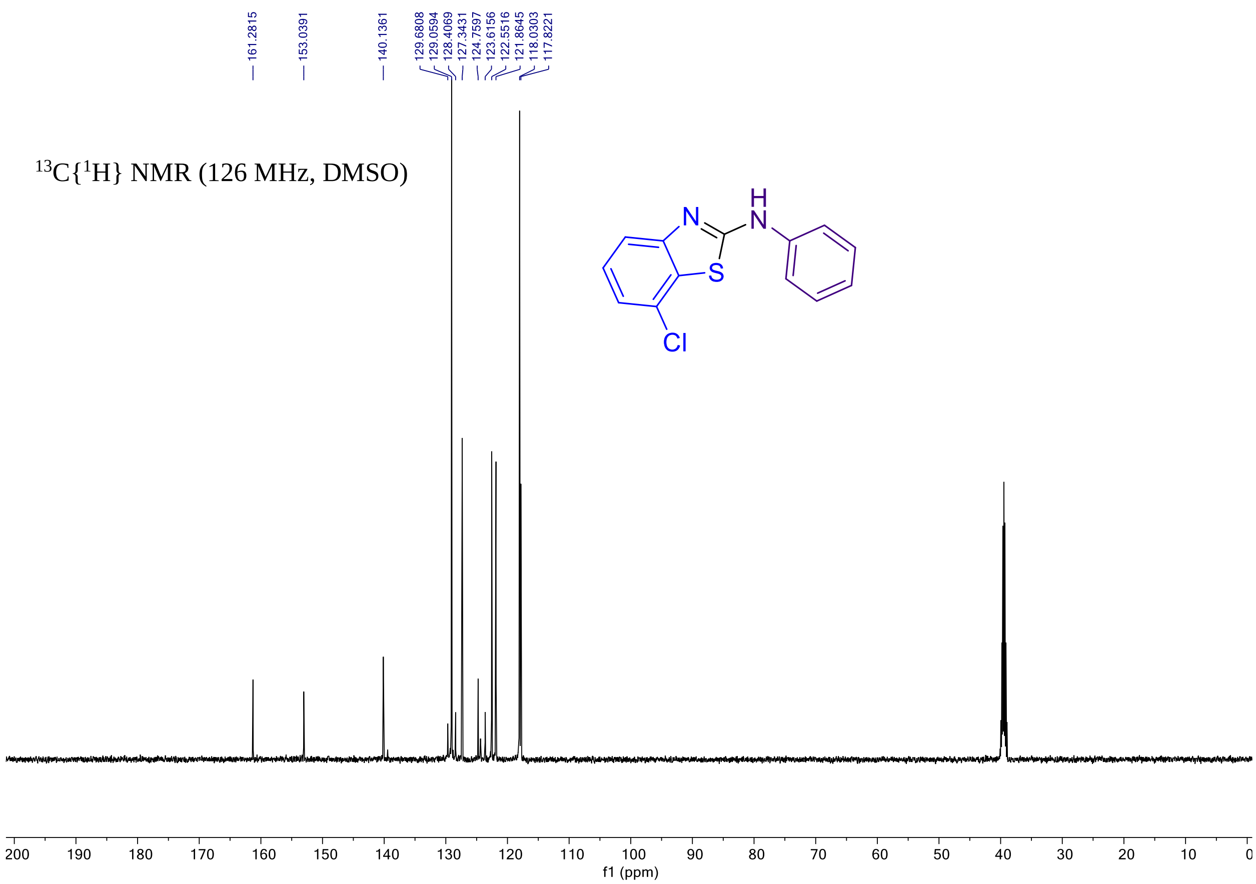
4-Chloro-*N*-phenylbenzothiazol-2-amine (3r)



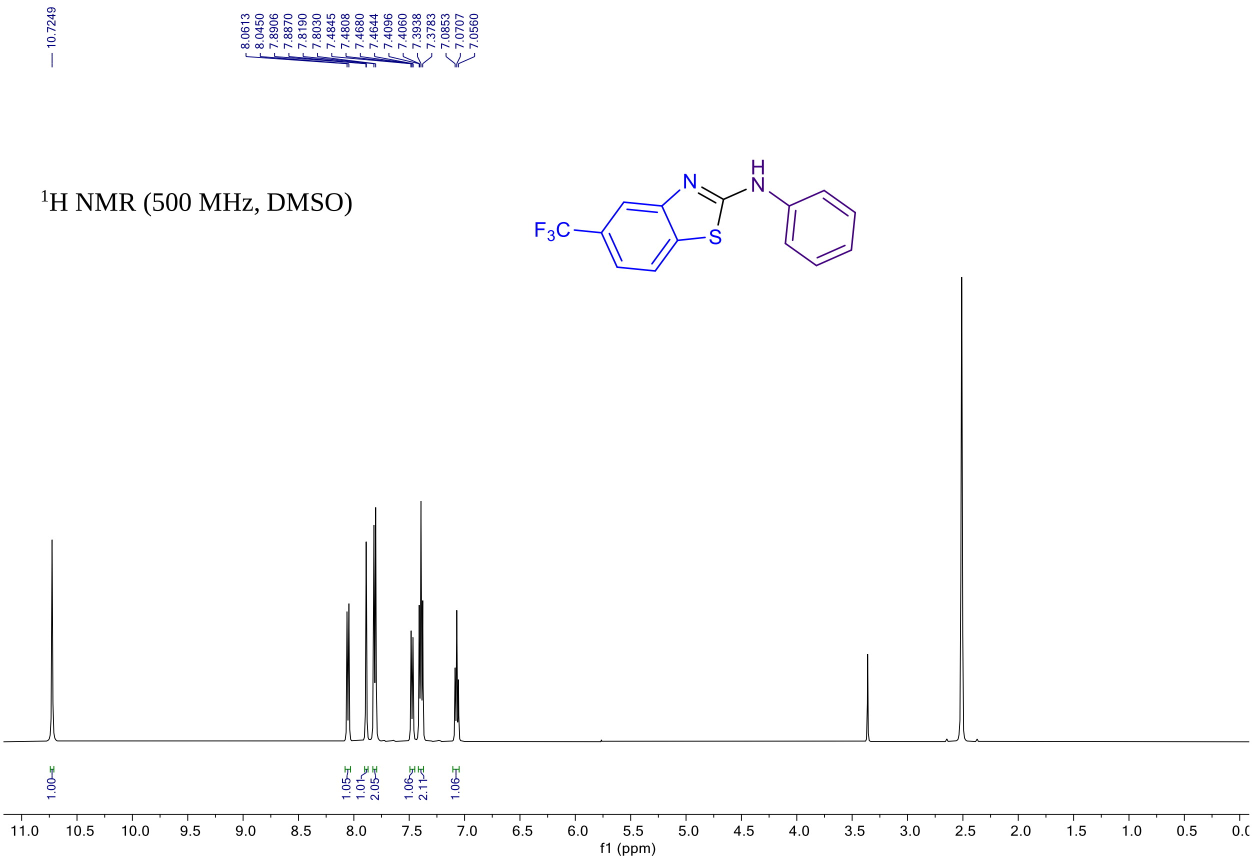


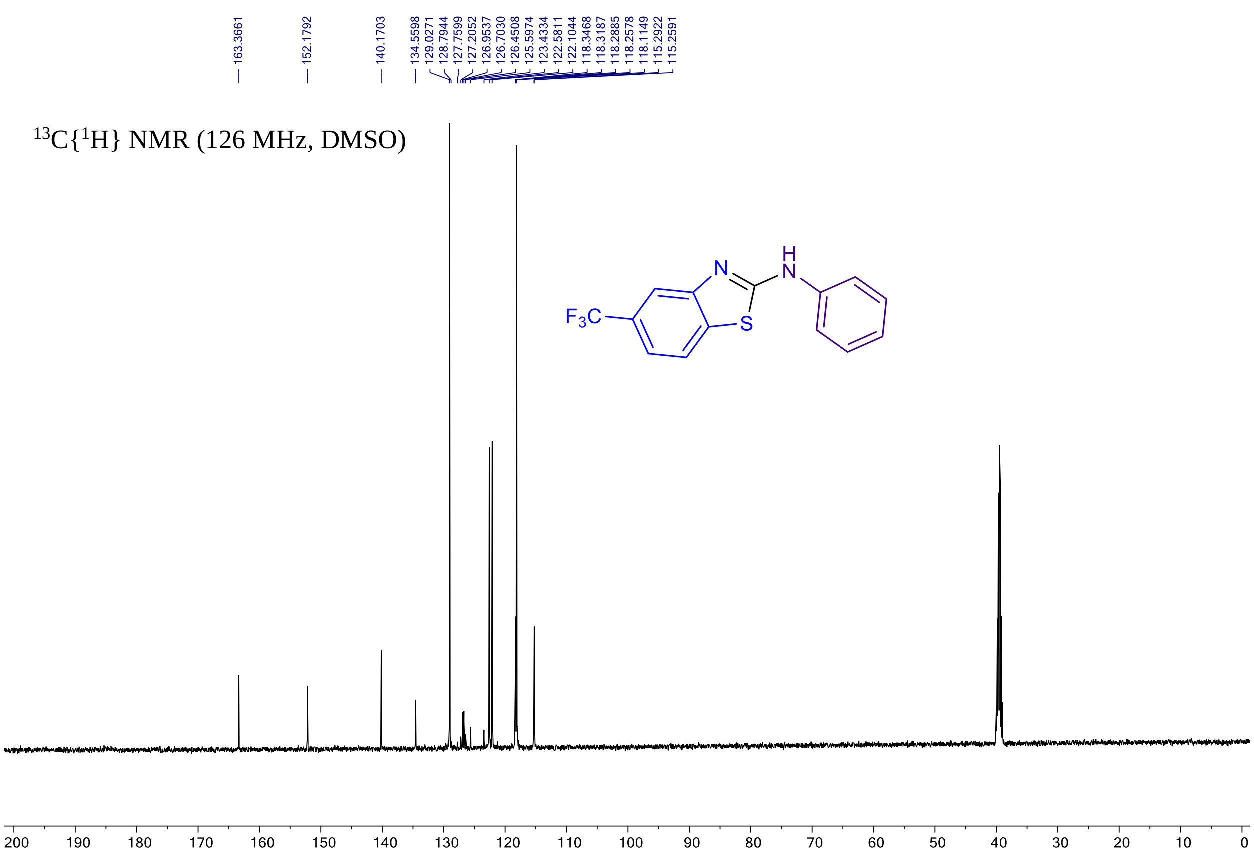
7-Chloro-*N*-phenylbenzothiazol-2-amine (3s)



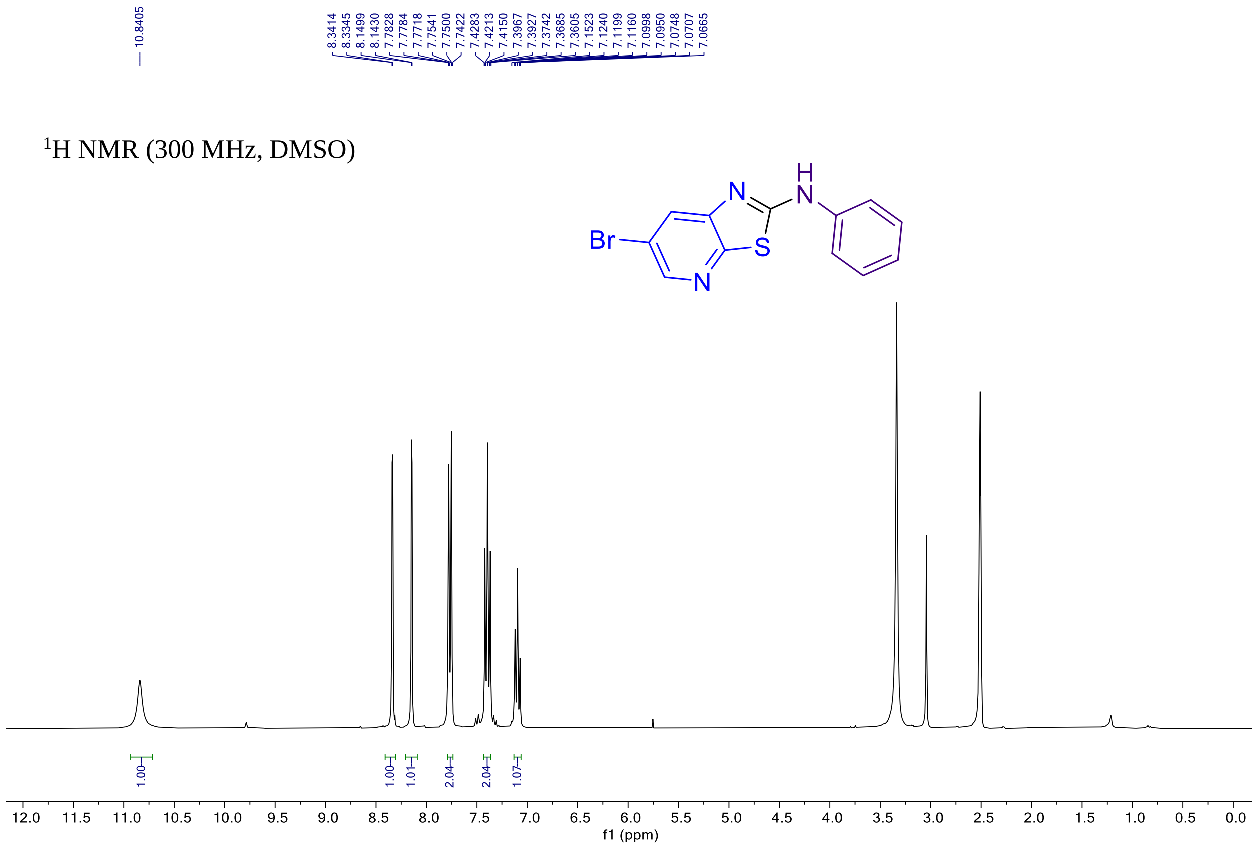


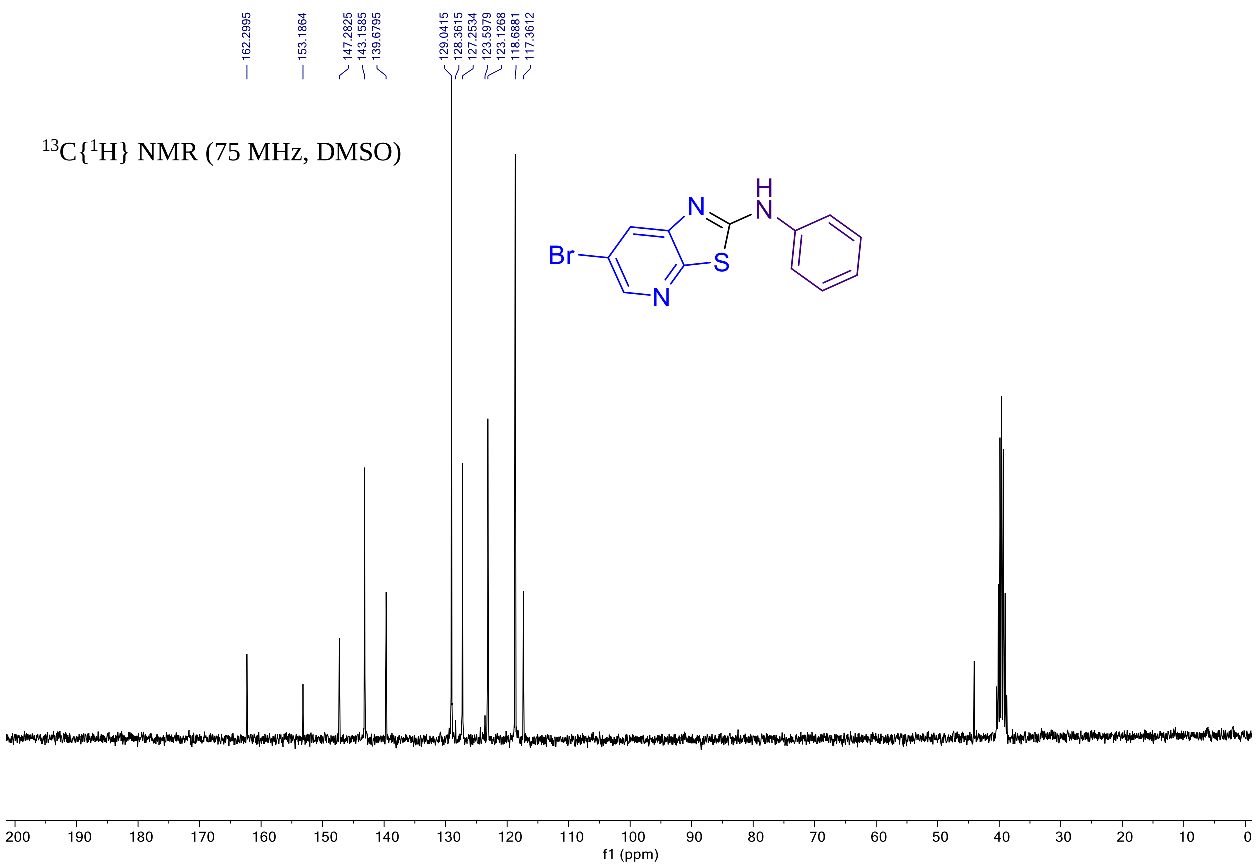
N-Phenyl-5-(trifluoromethyl)benzothiazol-2-amine (3t)



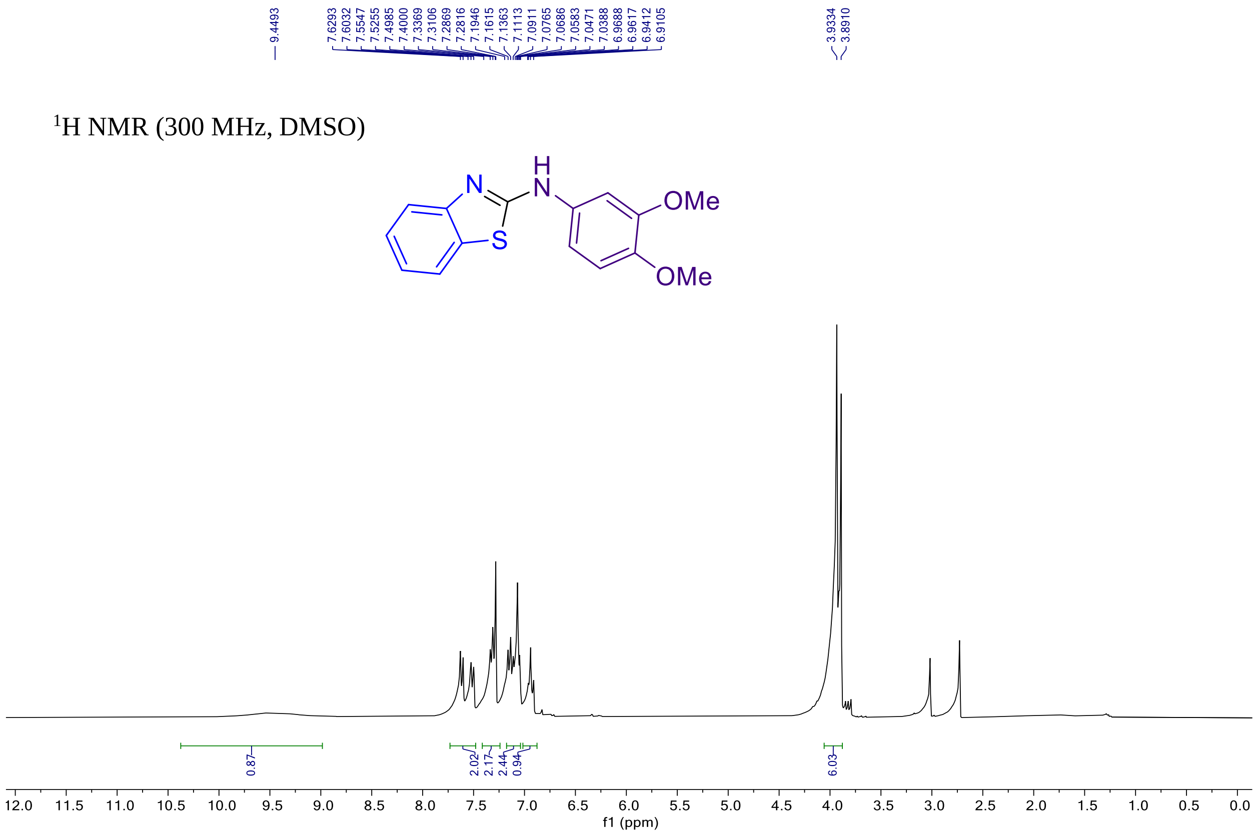


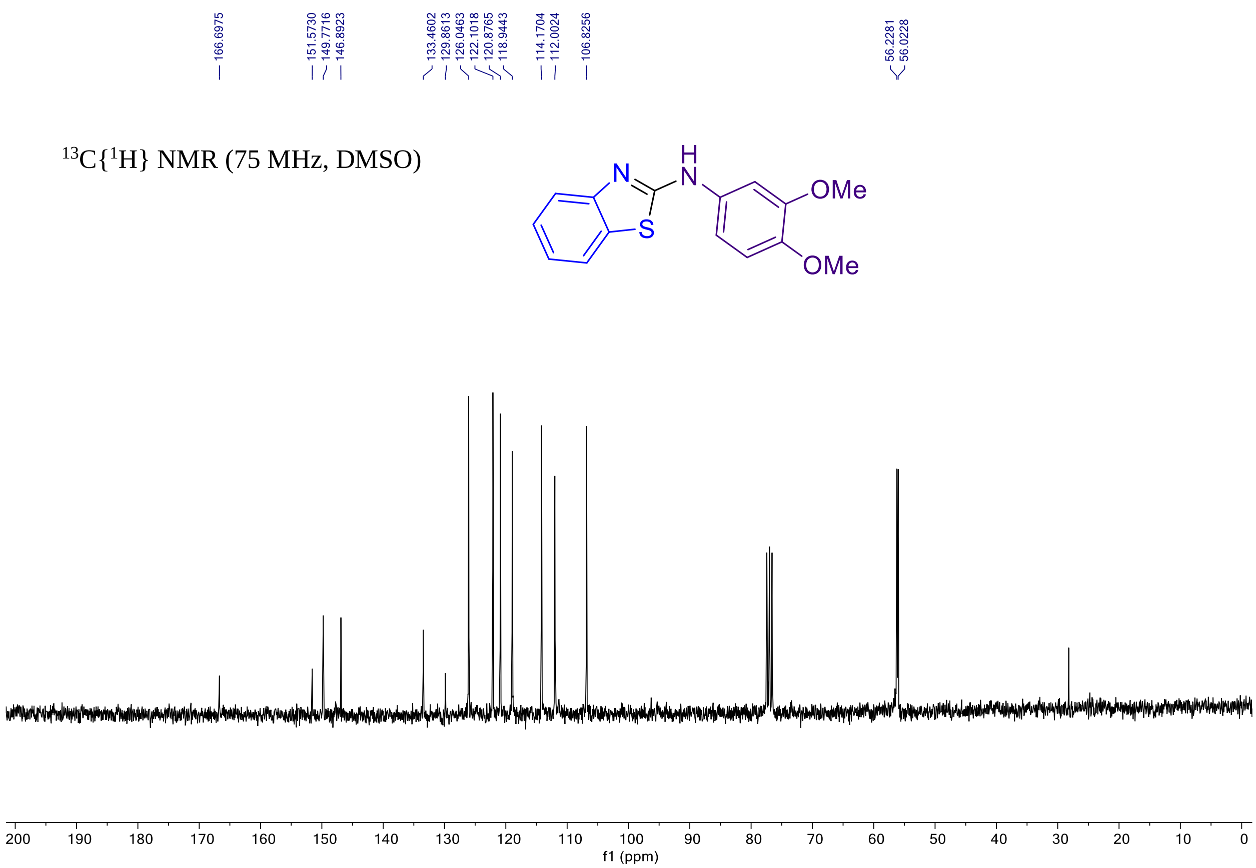
6-Bromo-*N*-phenylthiazolo[5,4-b]pyridin-2-amine (3u)





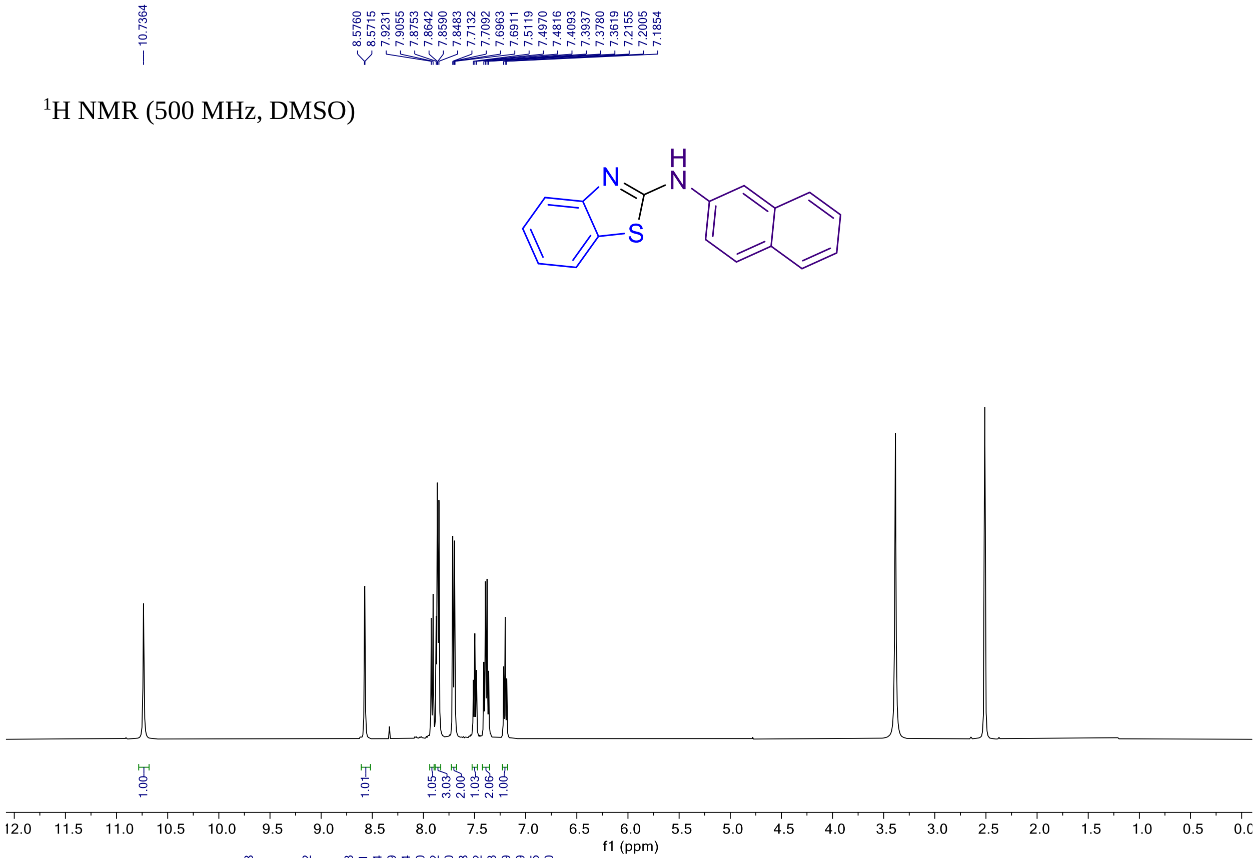
_N_-(3,4-Dimethoxyphenyl)benzothiazol-2-amine (3v)



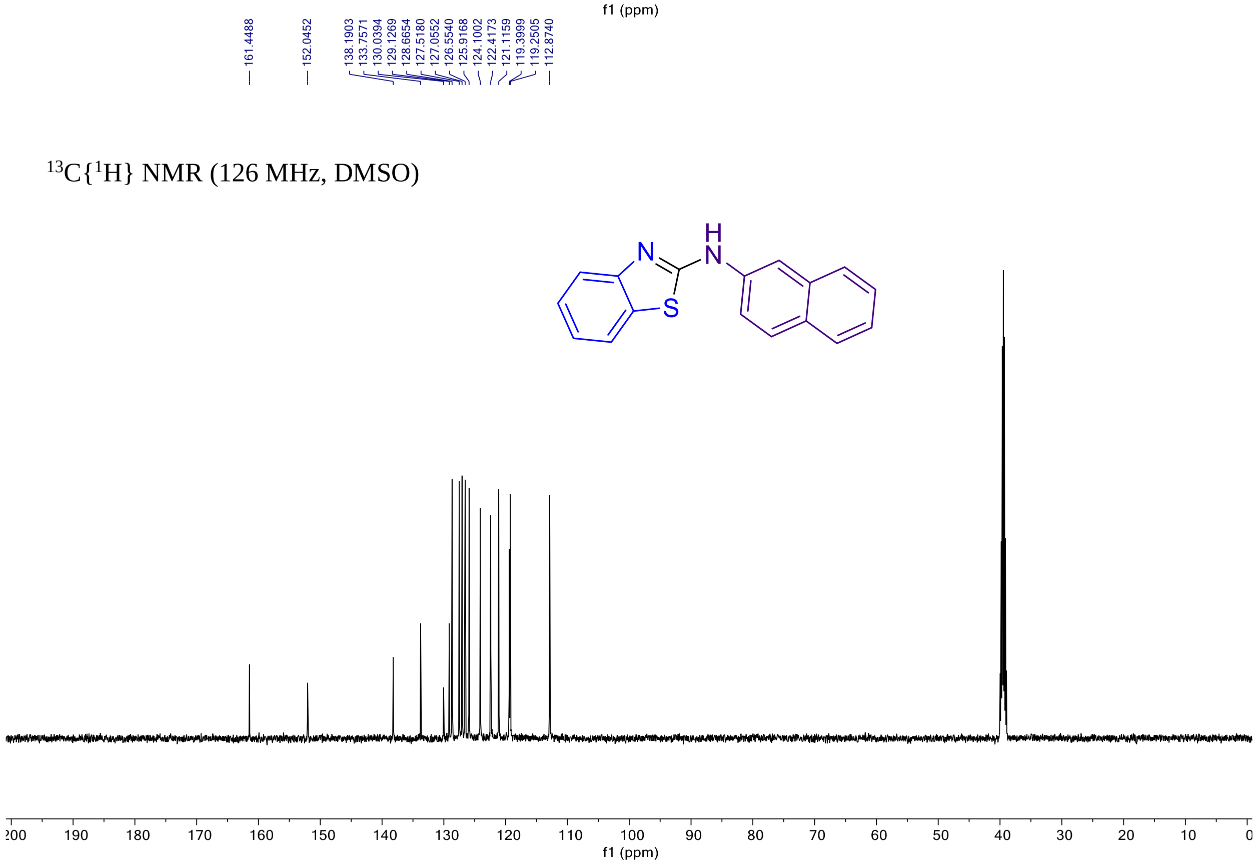


N-(Naphthalen-2-yl)benzothiazol-2-amine (3w)

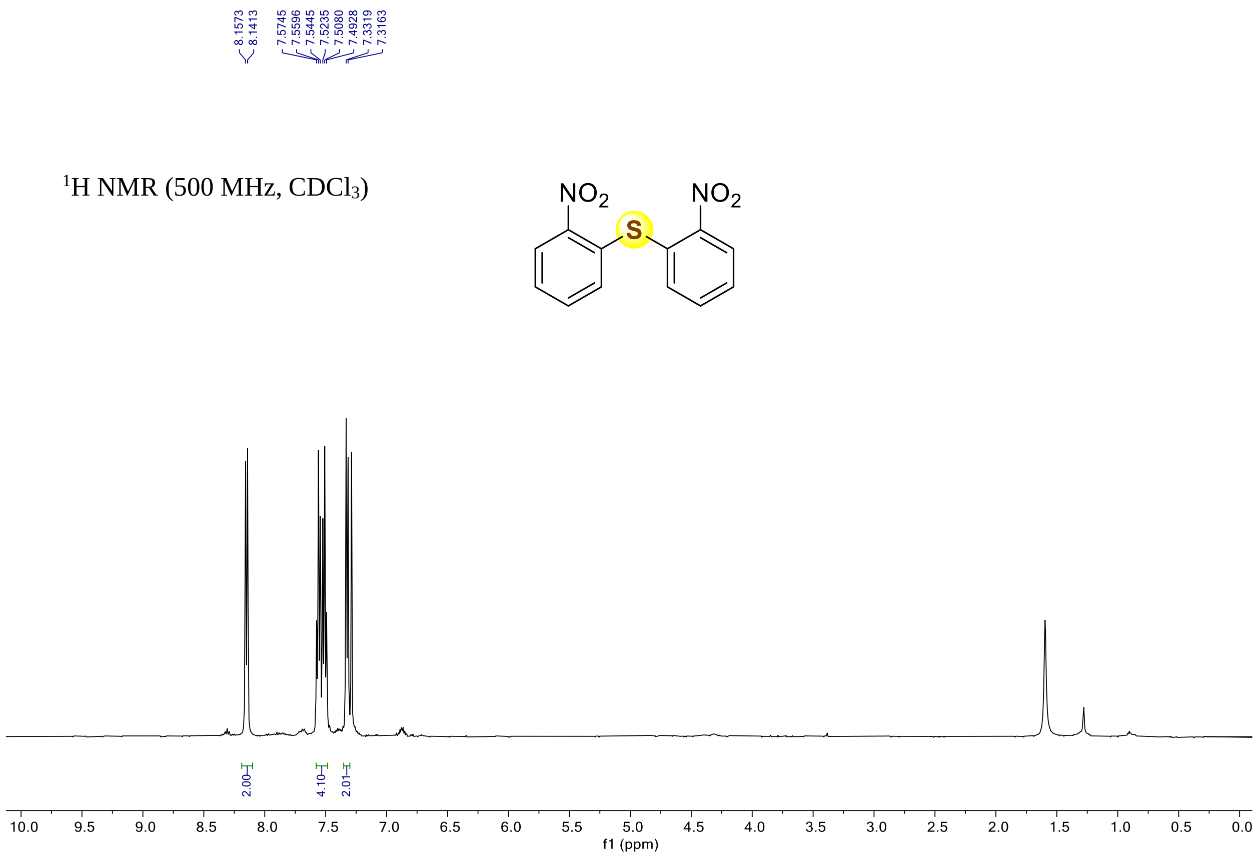
^{1}H NMR (500 MHz, DMSO)

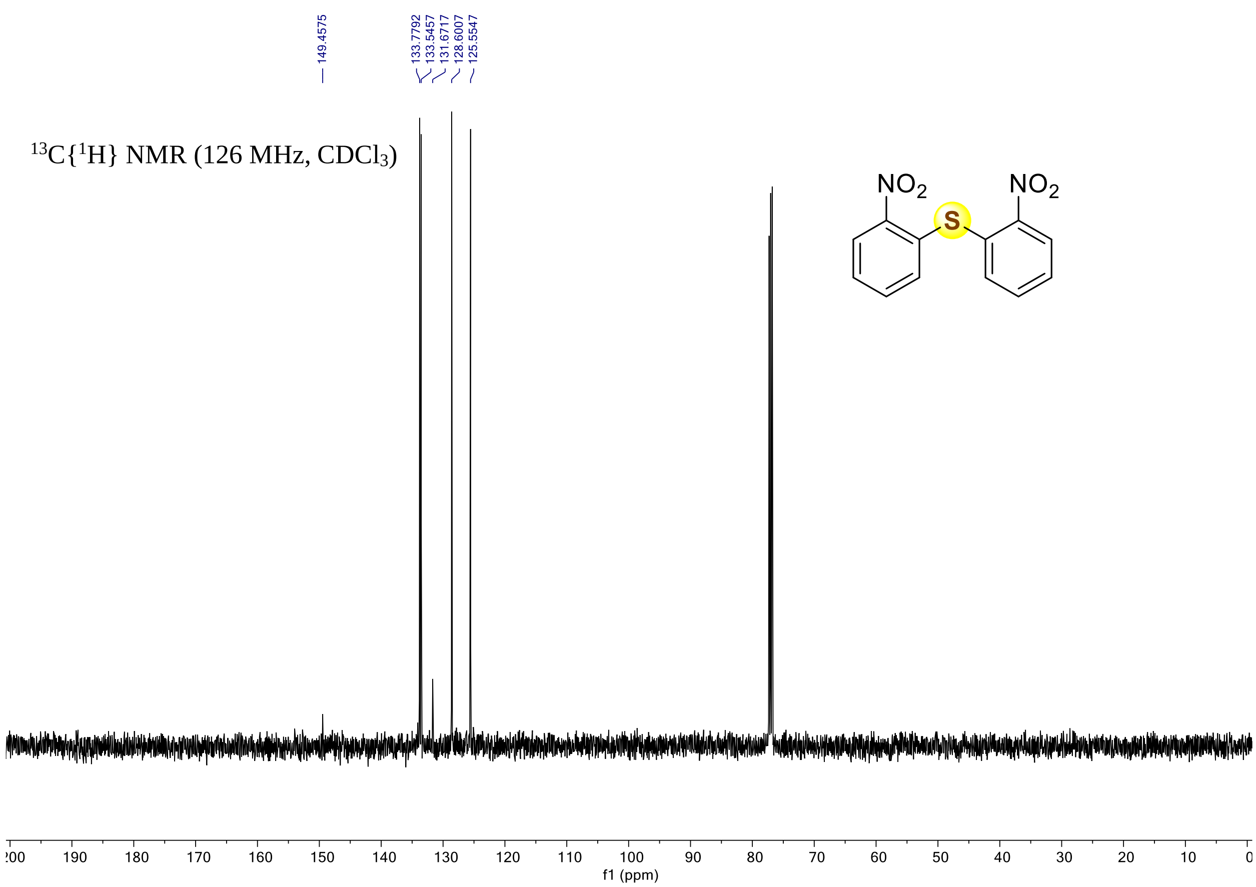


^{13}C{^{1}H} NMR (126 MHz, DMSO)



Bis(2-nitrophenyl)sulfane (6)





1,2-Bis(2-nitrophenyl)disulfane (7)