

Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supplementary data

Cu-catalyzed *in situ* generation of thiol using xanthate as thiol surrogate for the one-pot synthesis of benzothiazoles and benzothiophenes

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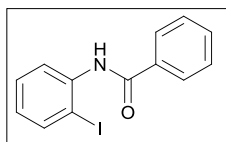
General considerations

Cu(OAc)₂.H₂O was purchased from Merck, India and oven dried to obtain anhydrous Cu(OAc)₂. Aryl halides, acid chlorides, alkynes and potassium ethyl xanthogenate were purchased from sigma Aldrich Chemical Company. All the solvents used for the reactions were obtained from Rankem, India and dried by Vogel's procedure. Reaction temperatures were controlled by Varivolt temperature modulator, Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm) and visualized by UV fluorescence quenching. Silica gel (particle size 100-200 mesh) purchased from SRL India was used for chromatography. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz instrument. ¹H NMR spectra were reported relative to Me₄Si (δ 0.0 ppm) or residual CHCl₃ (δ 7.26 ppm). ¹³C NMR were reported relative to CDCl₃ (δ 77.16 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and are reported in frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were recorded on Q-ToF Micro mass spectrometer.

Typical experimental procedure for synthesis of 2-iodoanilides

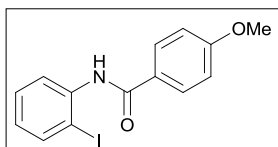
To a solution of *o*-iodoaniline (2 mmol) in dry THF (10 mL), acid chloride (2.4 mmol) was added and the resulting mixture was stirred at room temperature for 12 hours.¹ Then, ethyl acetate was added and the organic layer was washed twice with saturated NaHCO₃, once with brine, twice with HCl (2N aqueous solution), then dried over anhydrous Na₂SO₄ and concentrated. The crude residue was purified by column chromatography.

N-(2-Iodophenyl)benzamide (2)¹



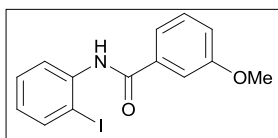
White solid; mp 132-133 °C (lit. 133–134 °C); *R_f* 0.44 (1:9 ethyl acetate : hexanes); ¹H NMR (400 MHz, CDCl₃): δ 6.86-6.93 (m, 1H), 7.38-7.45 (m, 1H), 7.50-7.63 (m, 3H), 7.82 (dd, *J* = 0.4 & 7.8 Hz, 1H), 7.95-8.00 (m, 2H), 8.30 (bs, 1H), 8.46 (dd, *J* = 0.8 & 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 90.5, 116.1, 116.3, 122.0, 126.3, 129.6, 129.7, 129.8, 138.2, 139.0, 164.4; FTIR (neat): 3400, 1668, 1035 cm⁻¹; HRMS: *m/z* [M+H]⁺ calcd for C₁₃H₁₁NOI: 323.9885; found: 323.9884.

***N*-(2-Iodophenyl)-4-methoxybenzamide (4)²**



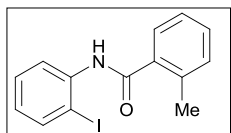
White solid; mp 150–153 °C (lit. 151–152 °C); R_f 0.32 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 3.88 (s, 3H), 6.81–6.89 (m, 1H), 6.97–7.05 (m, 2H), 7.35–7.41 (m, 1H), 7.80 (dd, $J = 1.6$ & 7.8 Hz, 1H), 7.91–7.96 (m, 2H), 8.20 (bs, 1H), 8.44 (dd, $J = 1.6$ & 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 55.7, 90.3, 114.4, 121.9, 125.9, 127.1, 129.3, 129.6, 138.8, 138.9, 163.0, 165.0; FTIR (neat): 3281, 1649, 1026, 843, 759 cm^{-1} ; HRMS: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{NO}_2\text{NaI}$: 375.9811, found: 375.9813.

***N*-(2-Iodophenyl)-3-methoxybenzamide (6)³**



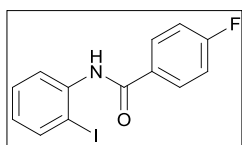
White solid; mp 95 °C (lit. 94–95.5 °C); R_f 0.33 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 3.9 (s, 3H), 6.86–6.93 (m, 1H), 7.10–7.15 (m, 1H), 7.38–7.47 (m, 2H), 7.49–7.55 (m, 2H), 7.83 (dd, $J = 1.6$ & 8.0 Hz, 1H), 8.29 (bs, 1H), 8.46 (dd, $J = 1.2$ & 8.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 55.7, 90.3, 112.7, 118.6, 119.0, 121.9, 126.2, 129.5, 130.1, 136.2, 138.4, 139.0, 160.2, 165.3; FTIR (neat): 3400, 1668, 1035, 750 cm^{-1} ; HRMS: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{NO}_2\text{NaI}$: 375.9810; found: 359.9806.

***N*-(2-Iodophenyl)-2-methylbenzamide (8)⁴**



White solid; mp 100–101 °C (Lit. 101–102 °C); R_f 0.48 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 2.6 (s, 3H), 6.89 (td, $J = 1.2$ & 7.6, 1H), 7.25–7.36 (m, 2H), 7.38–7.45 (m, 2H), 7.58–7.65 (m, 1H), 7.82 (dd, $J = 1.2$ & 8.0 Hz, 2H), 8.38–8.46 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.3, 90.4, 122.2, 126.2, 126.3, 126.9, 129.5, 130.8, 131.7, 136.0, 137.1, 138.6, 139.0, 168.0; FTIR (neat): 3260, 1654, 1047, 752, 672 cm^{-1} ; HRMS: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{NONaI}$: 359.9861; found: 359.9863.

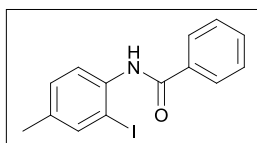
4-Fluoro-*N*-(2-iodophenyl)benzamide (10)⁵



White solid; mp 113–115 °C (lit. 114–118 °C); R_f 0.44 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 6.89 (td, $J = 1.2$ & 7.6 Hz, 1H), 7.10–7.27 (m, 2H), 7.37–7.44 (m, 1H), 7.82 (dd, $J = 1.2$ & 7.6 Hz, 1H), 7.91–7.96 (m, 2H), 8.20 (bs, 1H), 8.44 (dd, $J = 1.6$ & 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 55.7, 90.3, 114.4, 121.9, 125.9, 127.1, 129.3, 129.6, 138.8, 138.9, 163.0, 165.0; FTIR (neat): 3281, 1649, 1026, 843, 759 cm^{-1} ; HRMS: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{FNO}_2\text{NaI}$: 375.9711, found: 375.9713.

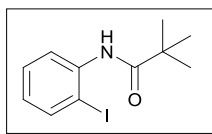
=1.2 & 8.0 Hz, 1H), 7.94-8.03 (m, 2H), 8.22 (bs, 1H), 8.41 (dd, $J = 1.2$ & 8.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 90.5, 116.2 (d, $J = 22.0$ Hz), 121.9, 126.3, 129.6 (d, $J = 8.6$ Hz), 129.8, 130.9, 138.2, 139.0, 164.4, 165.3 (d, $J = 249.6$ Hz); FTIR (neat): 3275, 1648, 1020, 758 cm^{-1} ; HRMS: m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{13}\text{H}_9\text{NONaFI}$: 363.9611, found: 363.9616.

***N*-(2-Iodo-4-methylphenyl)benzamide (12)**



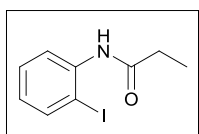
White solid; mp 160-162 °C; R_f 0.31 (1:19 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 2.31 (s, 3H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.49-7.61 (m, 3H), 7.65 (d, $J = 0.8$ Hz, 1H), 7.94-7.99 (m, 2H), 8.21 (bs, 1H), 8.29 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 20.5, 90.5, 121.7, 127.3, 129.1, 130.2, 132.2, 134.8, 135.9, 136.2, 139.1, 165.4; IR (neat): 3252, 3055, 3000, 1648, 818, 711 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{14}\text{H}_{12}\text{NONaI}$: 359.9861; found: 359.9875.

***N*-(2-Iodophenyl)pivalamide (14)⁶**



White solid; mp 68-69 °C (lit. 67-69 °C); R_f 0.70 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 1.29 (s, 9H), 6.70-6.82 (m, 1H), 7.22-7.31 (m, 1H), 7.64-7.83 (m, 1H), 8.21 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 29.0, 41.0, 92.0, 123.0, 127.0, 130.0, 139.0, 139.5, 174.0; FTIR (neat): 2932, 1556, 1170, 735 cm^{-1} .

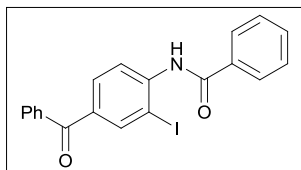
***N*-(2-Iodophenyl)propionamide (16)**



White solid; mp 94-95 °C; R_f 0.37 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 1.29 (t, $J = 7.6$ Hz, 3H), 2.47 (q, $J = 7.6$ Hz, 2H), 6.80-6.87 (m, 1H), 7.31-7.37 (m, 1H), 7.46 (bs, 1H), 7.77 (dd, $J = 8.0$ & 1.2 Hz, 1H), 8.24 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 9.8, 31.2, 90.1, 122.1, 125.9, 129.4, 138.3, 138.9, 172.1; IR (neat): 3276, 3025, 2969, 2934,

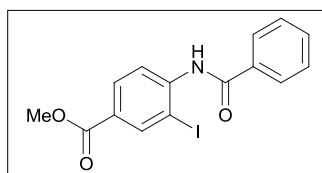
2873, 1656, 760, 671 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_9\text{H}_{11}\text{NOI}$: 275.9885; found: 275.9893.

***N*-(4-benzoyl-2-iodophenyl)benzamide (18)**



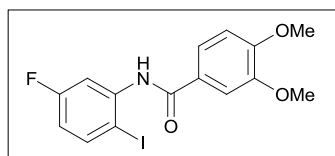
White solid; mp 162-163 °C; R_f 0.36 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.48-7.66 (m, 6H), 7.76-7.81 (m, 2H), 7.83 (d, $J = 8.4$ Hz, 1H), 7.97-8.03 (m, 2H), 8.36 (d, $J = 1.6$ Hz, 1H), 8.56 (bs, 1H), 8.65 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 89.5, 120.0, 127.4, 128.6, 129.2, 130.0, 130.3, 132.0, 132.8, 134.2, 134.6, 137.4, 140.7, 141.9, 165.5, 194.2; IR (neat): 3286, 3059, 1659, 1650, 799, 724, 701 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{I}$: 428.0148; found: 428.0136.

Methyl 4-benzamido-3-iodobenzoate (20)⁷



White solid; mp 146-147 °C (lit. 144-146 °C); R_f 0.40 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 3.92 (s, 3H), 7.50-7.65 (m, 3H), 7.95-8.01 (m, 2H), 8.07 (dd, $J = 8.8$ & 1.6 Hz, 1H), 8.50 (d, $J = 2.0$ Hz, 1H), 8.52 (bs, 1H), 8.63 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 52.5, 88.9, 120.2, 127.2, 127.4, 129.2, 131.2, 132.7, 134.3, 140.4, 142.3, 165.4, 165.5; IR (neat): 3378, 2957, 2923, 2853, 1710, 1683, 763, 699 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{I}$: 381.9940; found: 381.9945.

***N*-(5-Fluoro-2-iodophenyl)-3,4-dimethoxybenzamide (24)**



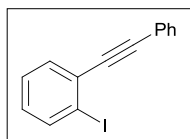
White solid; mp 166-168 °C; R_f 0.27 (1:4 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 3.96 (s, 3H), 3.97 (s, 3H), 6.62-6.69 (m, 1H), 6.96 (d, $J = 8.0$ Hz, 1H), 7.51 (dd, $J = 8.4$ & 2.4 Hz, 1H), 7.54 (d, $J = 2.0$ Hz, 1H), 7.73 (dd, $J = 8.4$ & 6.0 Hz, 1H), 8.30 (bs, 1H), 8.37 (dd, $J = 11.2$ & 2.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 56.19, 56.24, 82.4, 108.9 (d, $J = 28.6$ Hz), 110.7, 110.8, 113.0 (d, $J = 22.5$ Hz), 119.9, 126.8, 139.2 (d, $J = 8.9$ Hz), 139.8 (d, $J = 11.8$ Hz), 149.5, 152.7, 163.5 (d, $J = 224.8$ Hz), 164.9; IR

(neat): 3385, 3061, 3011, 2931, 2837, 1665, 745 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{14}\text{NO}_3\text{FI}$: 402.0002; found: 402.0004.

Typical experimental procedure for synthesis of *o*-haloalkynylbenzenes

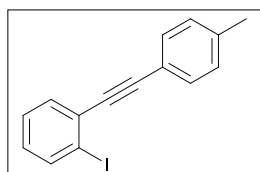
A solution of Et_3N (12.5 mL), $\text{PdCl}_2(\text{PPh}_3)_2$ (2 mol%), CuI (1 mol%), 1,2-dihalobenzene (5 mmol) and terminal alkyne (6 mmol) was stirred for 5 minutes before flushing with N_2 and then the round bottom flask was closed.⁸ The reaction mixture was allowed to stir at room temperature for 8-12 hours and the resulting solution was filtered and washed with saturated aq. NaCl solution and extracted with ethyl acetate (2 x 15 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 and then the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexanes as eluents.

1-Iodo-2-(phenylethynyl)benzene (31)⁸



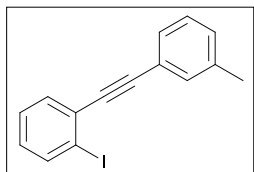
Pale yellow oil; R_f 0.64 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 6.99-7.05 (m, 1H), 7.31-7.40 (m, 4H), 7.52-7.56 (m, 1H), 7.59-7.64 (m, 2H), 7.89 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 91.8, 93.2, 101.3, 123.0, 127.9, 128.5, 128.8, 129.5, 129.9, 131.8, 132.6, 138.9; IR (neat): 3057, 2955, 2924, 2218, 753, 689 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{14}\text{H}_{10}\text{I}$: 304.9827; found: 304.9820.

1-Iodo-2-(*p*-tolylethynyl)benzene (33)⁹



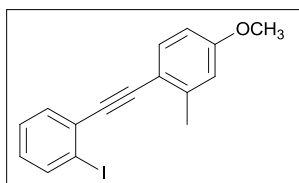
White solid; mp 89-90 $^\circ\text{C}$ (lit. 88-90 $^\circ\text{C}$); R_f 0.60 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 2.38 (s, 3H), 6.96-7.04 (m, 1H), 7.18 (d, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.47-7.57 (m, 3H), 7.88 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.7, 91.2, 93.5, 101.3, 119.9, 127.9, 129.3, 130.1, 131.7, 132.4, 132.5, 138.8, 139.0; IR (neat): 3050, 2916, 2854, 2213, 814, 755 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{12}\text{I}$: 318.9984; found: 318.9972.

1-Iodo-2-(*m*-tolylethynyl)benzene (35)



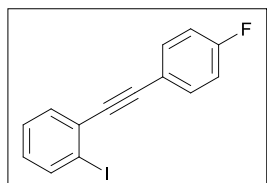
Colorless liquid; R_f 0.70 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 2.29 (s, 3H), 6.89-6.96 (m, 1H), 7.10 (d, $J = 7.6$ Hz, 1H), 7.14-7.29 (m, 2H), 7.30-7.36 (m, 2H), 7.42-7.47 (m, 1H), 7.80 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.4, 91.4, 93.4, 101.3, 122.9, 127.9, 128.4, 128.9, 129.4, 129.7, 130.0, 132.3, 132.5, 138.2, 138.9; IR (neat): 3052, 2921, 2857, 2208, 784, 751, 689 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{K}]^+$ calcd. for $\text{C}_{15}\text{H}_{11}\text{KI}$: 356.9543; found: 356.9543.

1-((2-Iodophenyl)ethynyl)-4-methoxy-2-methylbenzene (37)



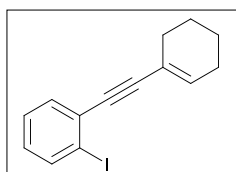
White solid; mp 50-52 °C; R_f 0.38 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 2.58 (s, 3H), 3.82 (s, 3H), 6.74 (dd, $J = 8.4$ & 2.8 Hz, 1H), 6.79 (d, $J = 2.4$ Hz, 1H), 6.99 (td, $J = 7.6$ & 1.6 Hz, 1H), 7.32 (td, $J = 7.6$ & 0.8 Hz, 1H), 7.48-7.56 (m, 2H), 7.85-7.90 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.7, 55.4, 92.5, 94.0, 100.6, 111.5, 115.1, 115.3, 127.9, 129.0, 130.6, 132.6, 133.7, 138.8, 142.6, 160.0; IR (neat): 3053, 3006, 2962, 2921, 2840, 2203, 811, 749 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{14}\text{OI}$: 349.0089; found: 349.0091.

1-((4-Fluorophenyl)ethynyl)-2-iodobenzene (39)



White solid; mp 55-56 °C; R_f 0.70 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 6.97-7.15 (m, 3H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.52 (d, $J = 7.2$ Hz, 1H), 7.55-7.66 (m, 2H), 7.88 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 91.5, 92.1, 101.2, 115.9 (d, $J = 22.0$ Hz), 119.2, 127.9, 129.6, 129.8, 132.5, 133.7 (d, $J = 8.3$ Hz), 138.9, 162.9 (d, $J = 248.6$ Hz); IR (neat): 3054, 2985, 2221, 838, 798, 740, 706 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{14}\text{H}_9\text{IF}$: 322.9733; found: 322.9747.

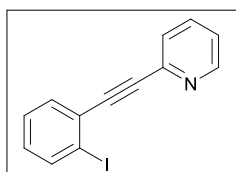
1-(Cyclohexenylethynyl)-2-iodobenzene (41)



Colorless liquid; R_f 0.72 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 1.59-1.74 (m, 4H), 2.12-2.20 (m, 2H), 2.25-2.32 (m, 2H), 6.28-

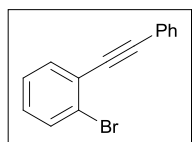
6.33 (m, 1H), 6.95 (td, $J = 8.0$ & 1.6 Hz, 1H), 7.27 (td, $J = 8.0$ & 0.8 Hz, 1H), 7.42 (dd, $J = 7.6$ & 1.6 Hz, 1H), 7.81-7.85 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.6, 22.4, 26.0, 29.0, 89.4, 95.2, 101.3, 120.8, 127.9, 128.9, 130.4, 132.3, 136.2, 138.7; IR (neat): 2985, 2940, 2204, 2086, 848, 787, 758 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{K}]^+$ calcd. for $\text{C}_{14}\text{H}_{13}\text{KI}$: 346.9699; found: 346.9695.

2-((2-Iodophenyl)ethynyl)pyridine (43)¹⁰



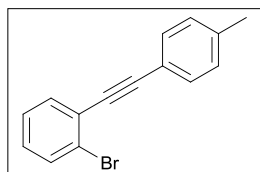
Yellow color liquid; R_f 0.31 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 6.99 (td, $J = 8.0$ & 1.6 Hz, 1H), 7.17-7.23 (m, 1H), 7.28 (t, $J = 7.6$ Hz, 1H), 7.52-7.58 (m, 2H), 7.64 (td, $J = 8.0$ & 1.6 Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 8.58 (d, $J = 4.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 91.2, 92.0, 101.3, 123.2, 127.7, 128.0, 129.0, 130.2, 133.3, 136.3, 138.9, 143.3, 150.3; IR (neat): 2925, 2941, 2225, 2087, 848, 783, 761 cm^{-1} .

1-Bromo-2-(phenylethynyl)benzene (45)¹¹



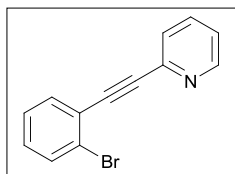
Pale yellow oil; R_f 0.62 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.18 (td, $J = 7.6$ & 2.0 Hz, 1H), 7.30 (td, $J = 7.6$ & 1.2 Hz, 1H), 7.34-7.39 (m, 3H), 7.54-7.64 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 88.1, 94.1, 123.0, 125.5, 125.8, 127.2, 128.5, 128.8, 129.5, 131.8, 132.6, 133.4; IR (neat): 3063, 2984, 2223, 760, 692 cm^{-1} .

1-Bromo-2-(*p*-tolylethynyl)benzene (46)¹¹



Pale yellow solid; mp 85-86 °C (lit. 86-87 °C); R_f 0.66 (in hexanes); ^1H NMR (400 MHz, CDCl_3): δ 2.42 (s, 3H), 7.16-7.42 (m, 4H), 7.49-7.72 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 21.7, 87.6, 94.3, 119.9, 125.7, 127.1, 129.3, 129.7, 131.7, 132.5, 133.3, 139.0, 139.6; IR (neat): 3056, 3025, 2918, 2853, 2214, 812, 750 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{12}\text{Br}$: 271.0122; found: 271.0121.

2-((2-Bromophenyl)ethynyl)pyridine (47)



Yellow color liquid; R_f 0.30 (1:9 ethyl acetate : hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.12-7.21 (m, 2H), 7.24 (td, $J = 7.6$ & 1.2 Hz, 1H), 7.50-7.58 (m, 3H), 7.62 (td, $J = 8.0$ & 2.0 Hz, 1H), 8.55-8.59 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 87.7, 92.9, 123.2, 124.6, 126.0, 127.2, 127.7, 130.2, 132.6, 133.9, 136.3, 143.3, 150.3; IR (neat): 3053, 2983, 2253, 743, 651 cm^{-1} ; HRMS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{13}\text{H}_9\text{NBr}$: 257.9918; found: 257.9912.

References

- 1 G. Evindar and R. A. Batey, *J. Org. Chem.*, 2006, **71**, 1802.
- 2 K. C. Christiane, B. Benoit, P. Sandro, G. Nadine and P. Knochel, *Chem. Commun.*, 2007, 1954.
- 3 H. Nishioka, N. Chie, A. Hitoshi, T. Yasuo and H. Takashi, *Heterocycles*, 2006, **70**, 549.
- 4 I. Hiroki, E. Toru, T. Nozomi, O. Hiroaki and T. Tetsuaki, *J. Org. Chem.*, 2008, **73**, 7145.
- 5 N. Barbero, M. Carril, R. SanMartin and E. Domínguez, *Tetrahedron*, 2007, **63**, 10425.
- 6 C. Gimbert and V. Adelina, *Org. Lett.*, 2009, **11**, 269.
- 7 A. C. Spivey, J. McKendrick and R. Srikanan, *J. Org. Chem.*, 2003, **68**, 1843.
- 8 A. K. Verma, T. Kesharwani, J. Singh, V. Tandon and R. C. Larock, *Angew. Chem., Int. Ed.*, 2009, **48**, 1138.
- 9 M. J. Wu, L. J. Chang, L. M. Wei and C. F. Lin, *Tetrahedron*, 1999, **55**, 13193.
- 10 K. F. Tseng, C. F. Lin, Y. H. Lo, Y. L. Hu, L. Y. Chen, S. H. Yang, S. R. Lin, L. S. Chang and M. J. Wu, *Eur. J. Med. Chem.*, 2009, **44**, 35.
- 11 L. L. Sun, C. L. Deng, R. Y. Tang and X. G. Zhang, *J. Org. Chem.*, 2011, **76**, 7546.

^1H and ^{13}C spectra for all products

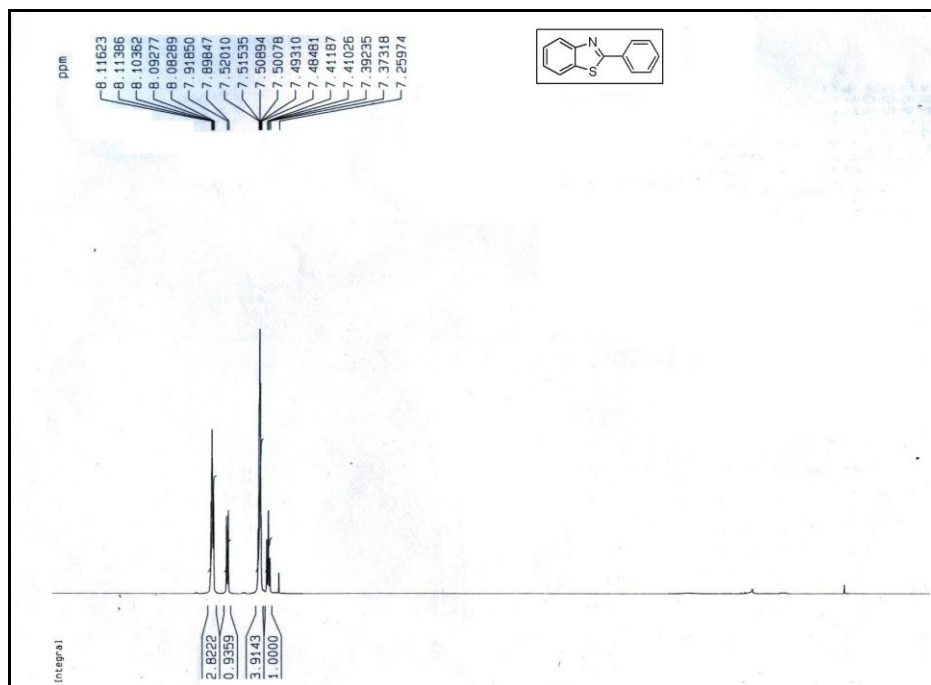


Figure 1 400 MHz ^1H NMR spectrum of compound **3** in CDCl_3

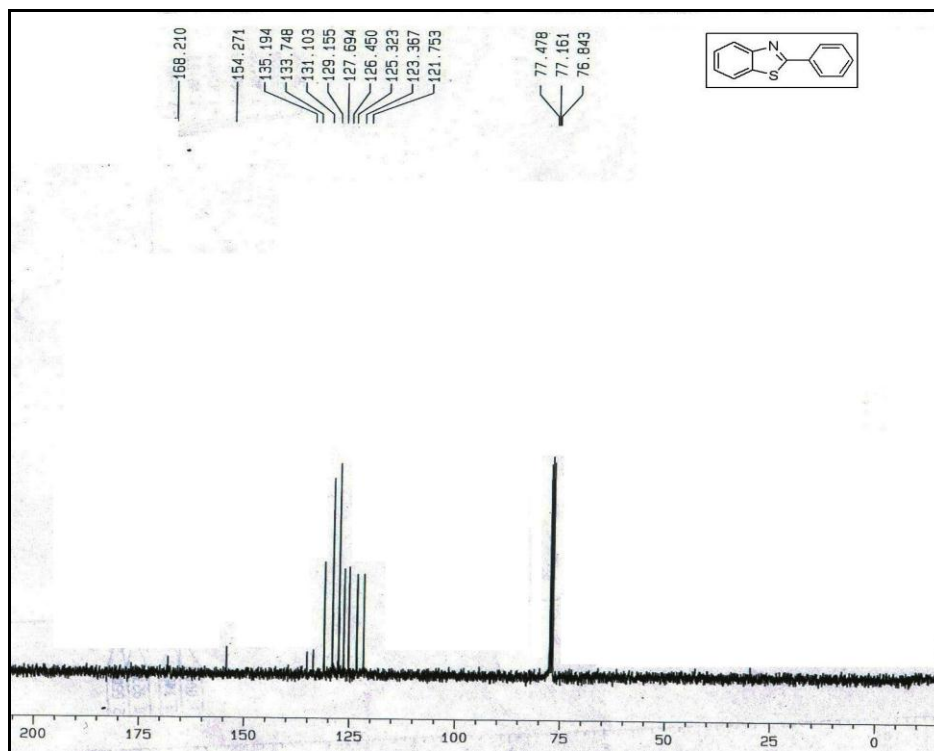


Figure 2 100 MHz ^{13}C NMR spectrum of compound **3** in CDCl_3

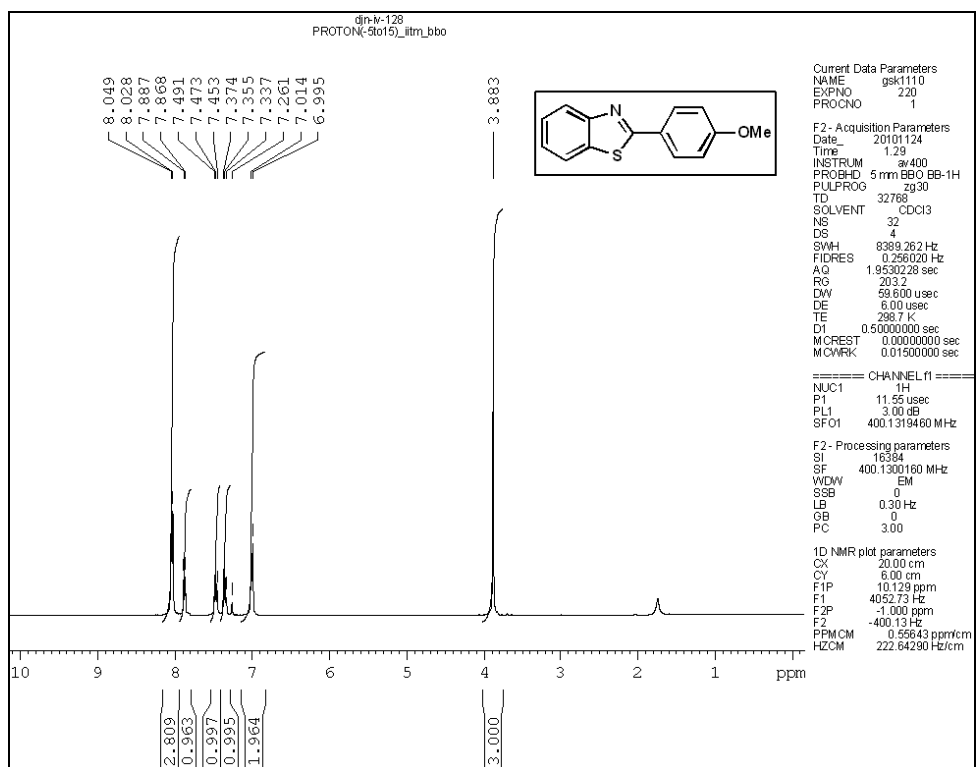


Figure 3 400 MHz ^1H NMR spectrum of compound **5** in CDCl_3

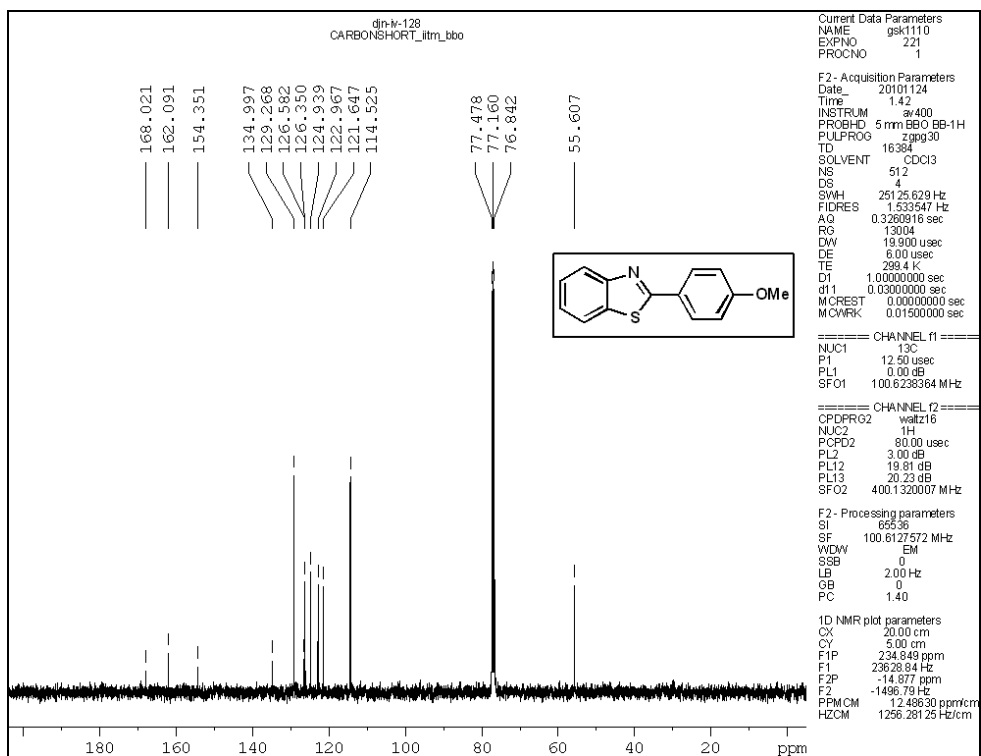


Figure 4 100 MHz ^{13}C NMR spectrum of compound **5** in CDCl_3

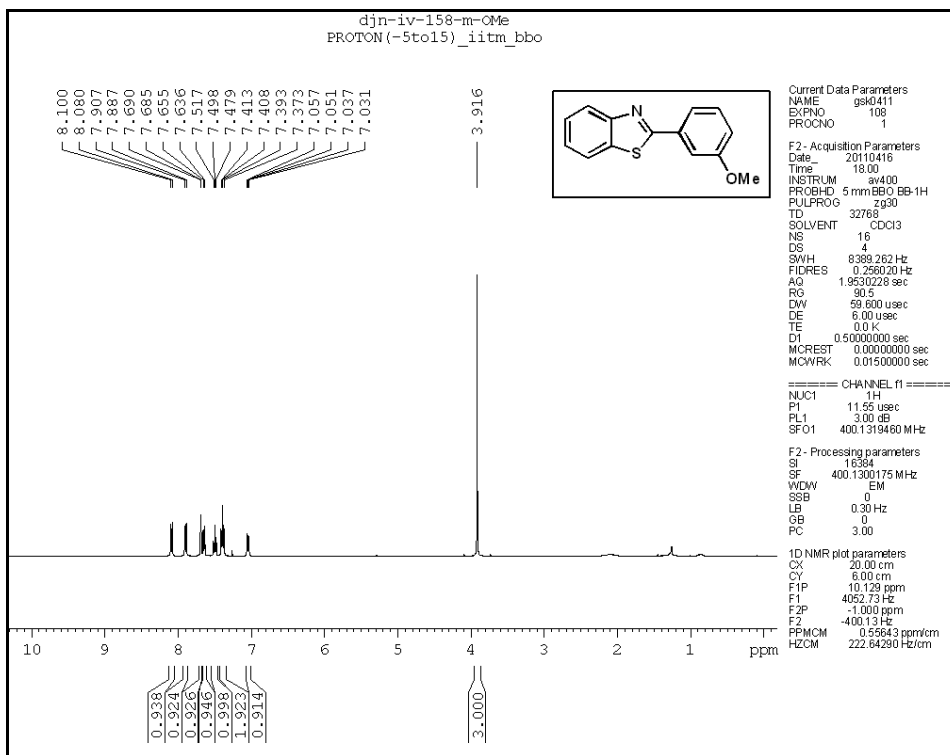


Figure 5 400 MHz ^1H NMR spectrum of compound **7** in CDCl_3

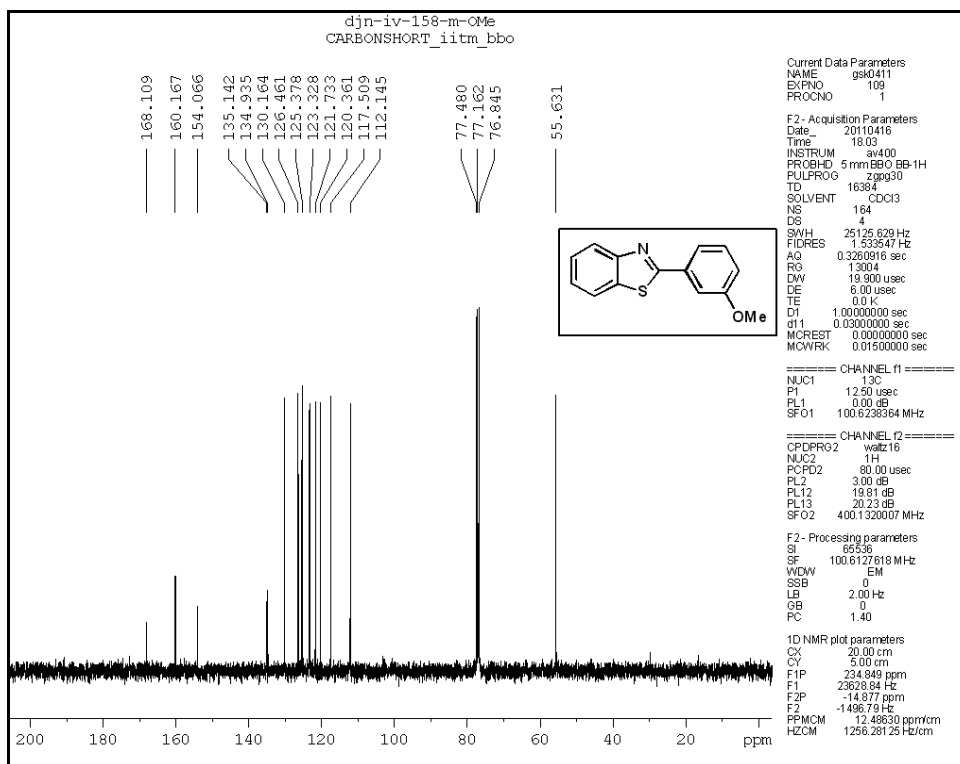


Figure 6 400 MHz ^{13}C NMR spectrum of compound **7** in CDCl_3

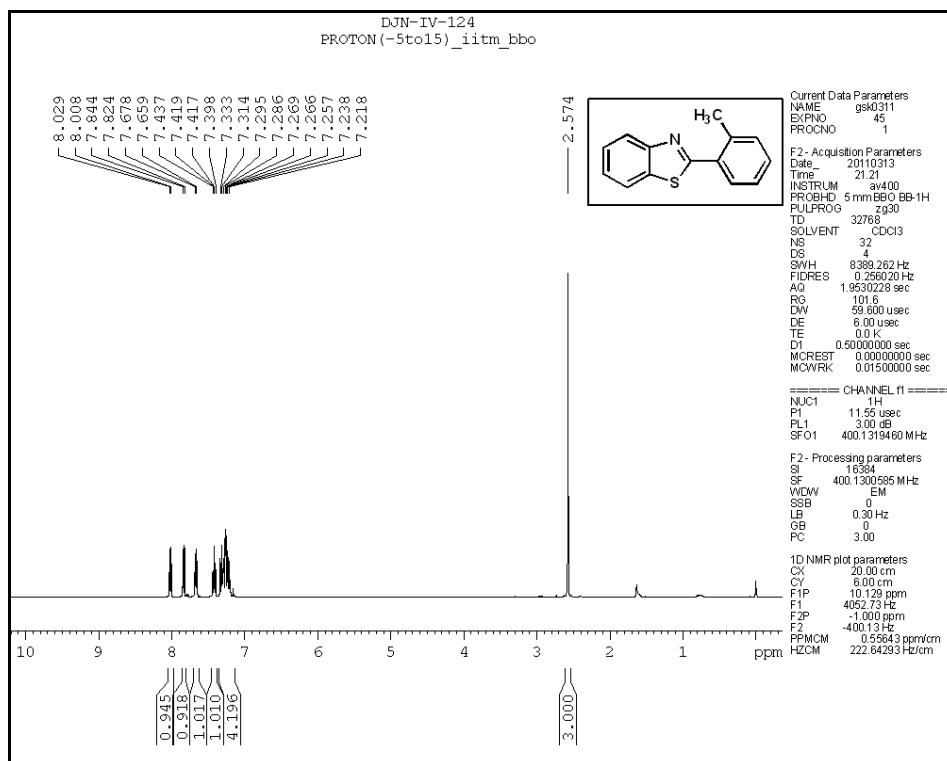


Figure 7 400 MHz ^1H NMR spectrum of compound **9** in CDCl_3

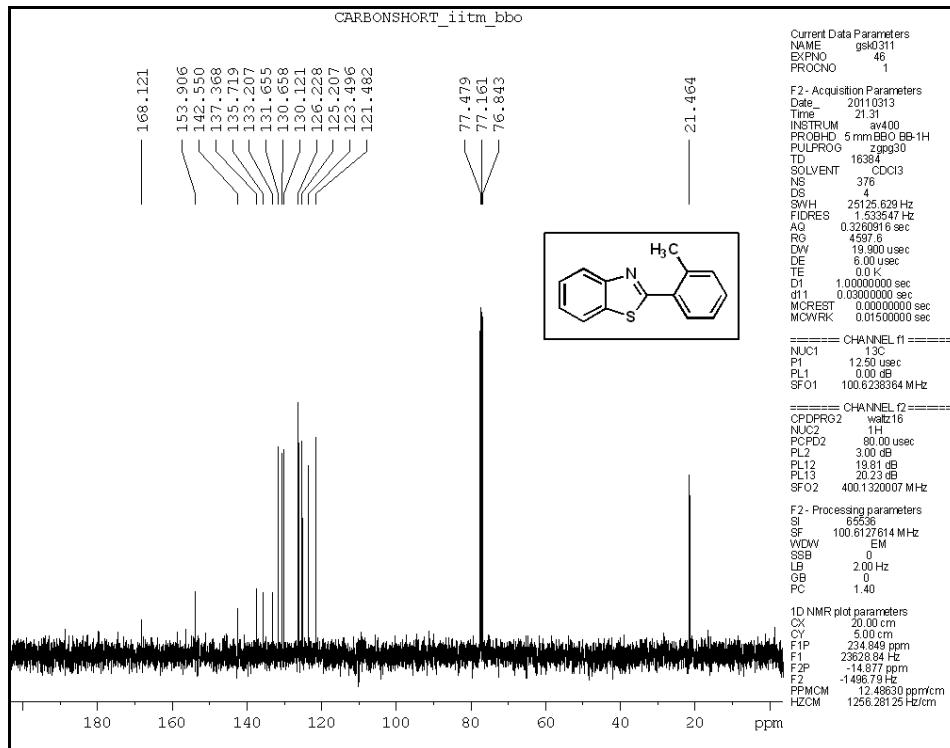


Figure 8 400 MHz ^1H NMR spectrum of compound **9** in CDCl_3

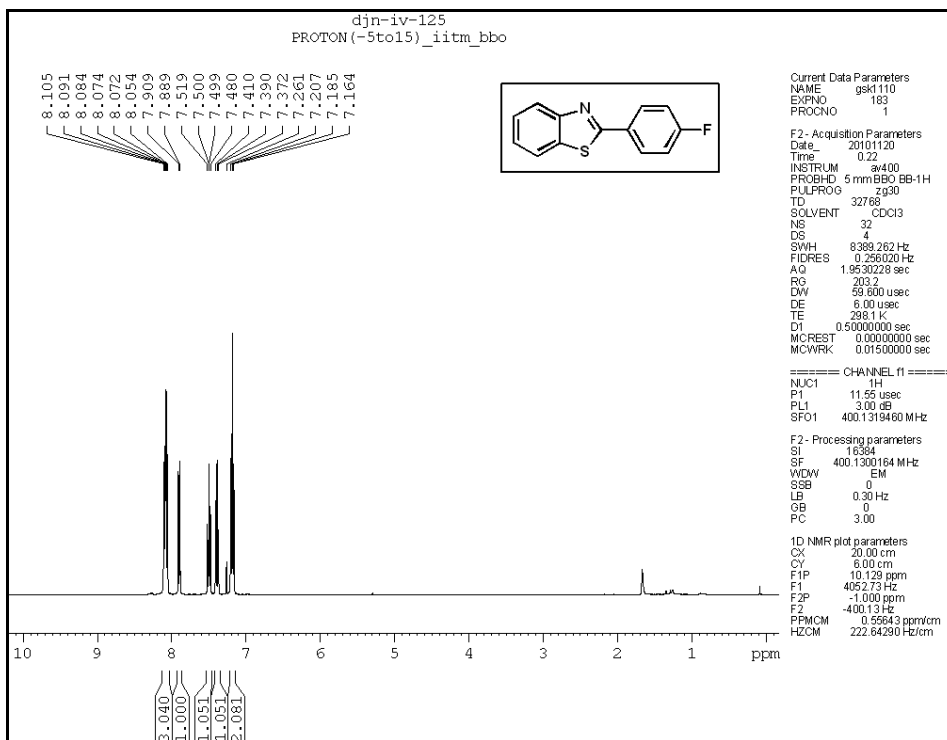


Figure 9 400 MHz ^1H NMR spectrum of compound **11** in CDCl_3

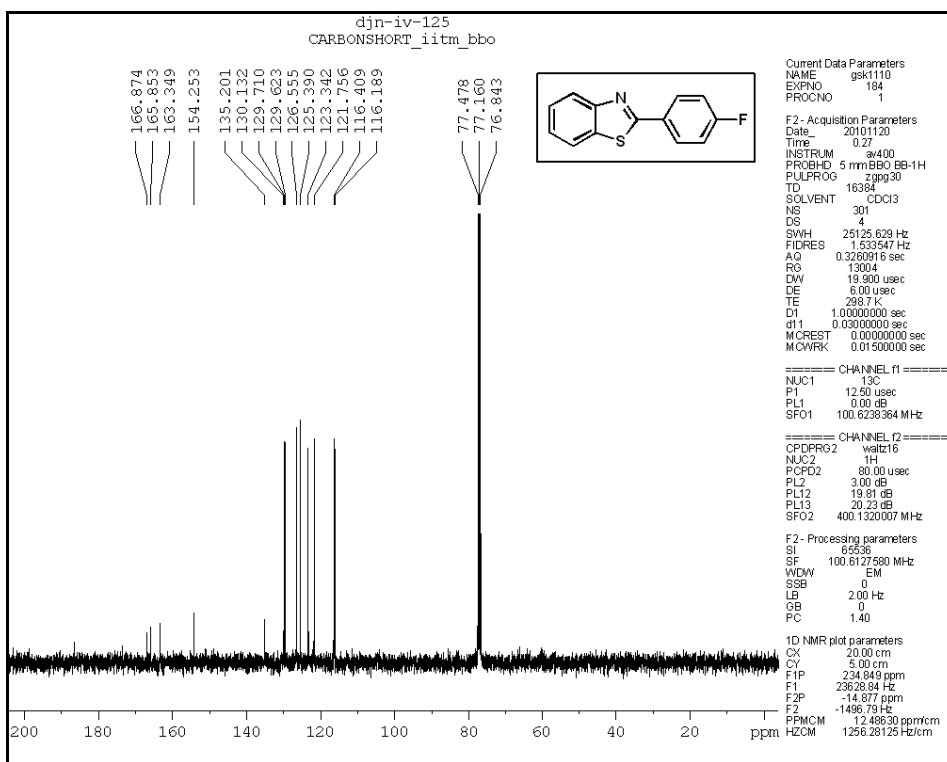


Figure 10 400 MHz ^1H NMR spectrum of compound **11** in CDCl_3

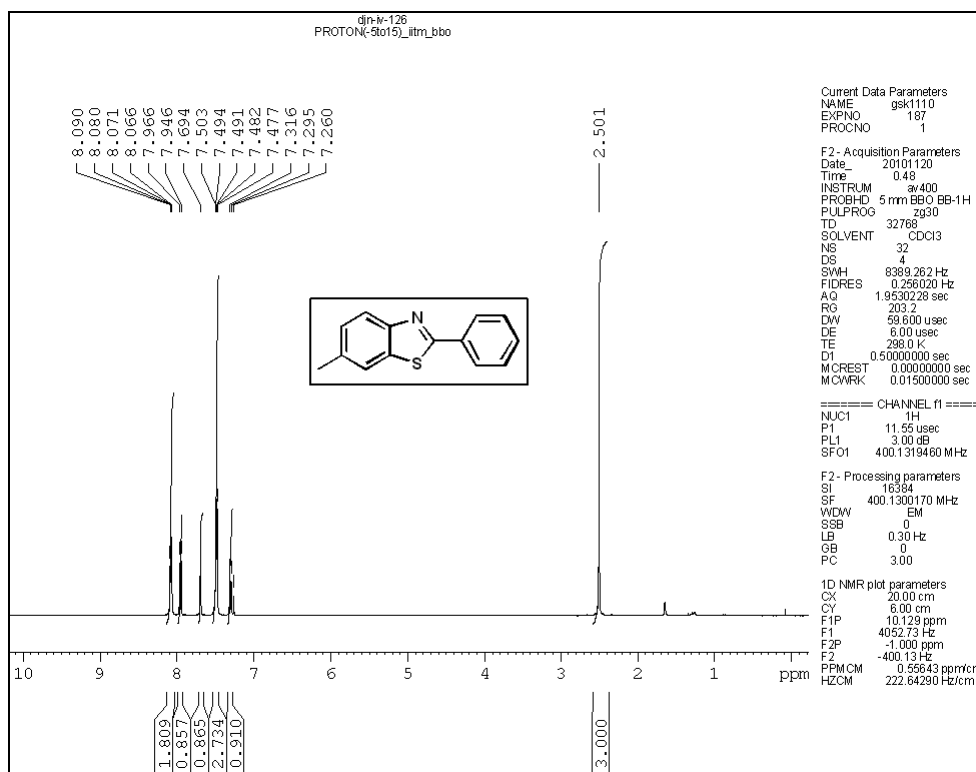


Figure 11 400 MHz ^1H NMR spectrum of compound **13** in CDCl_3

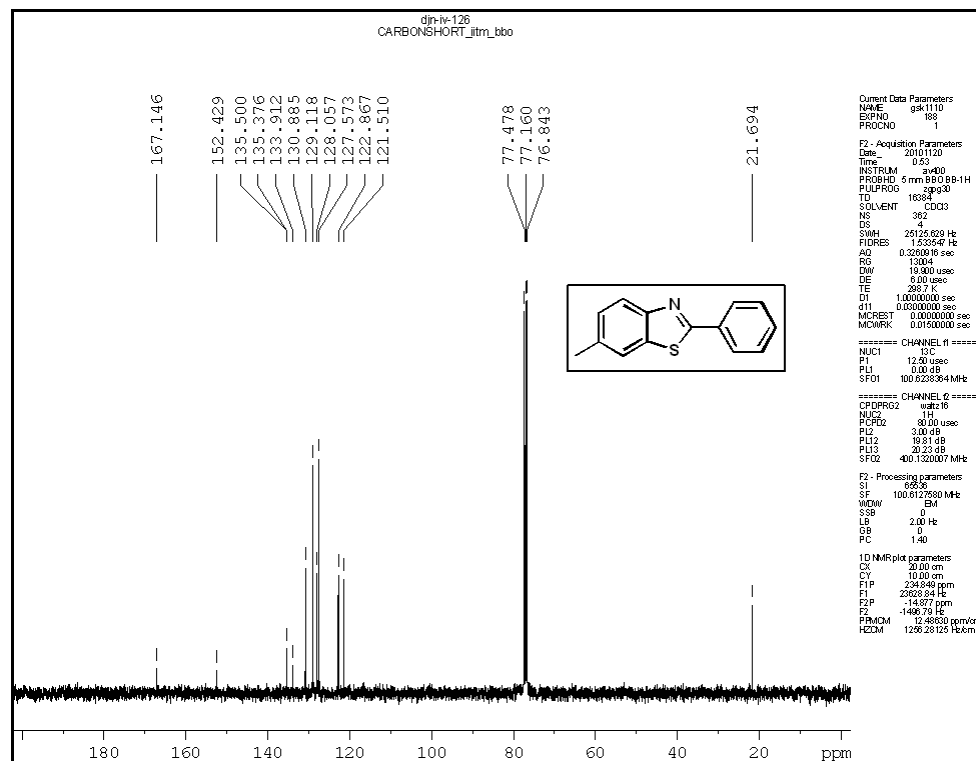


Figure 12 100 MHz ^{13}C NMR spectrum of compound **13** in CDCl_3

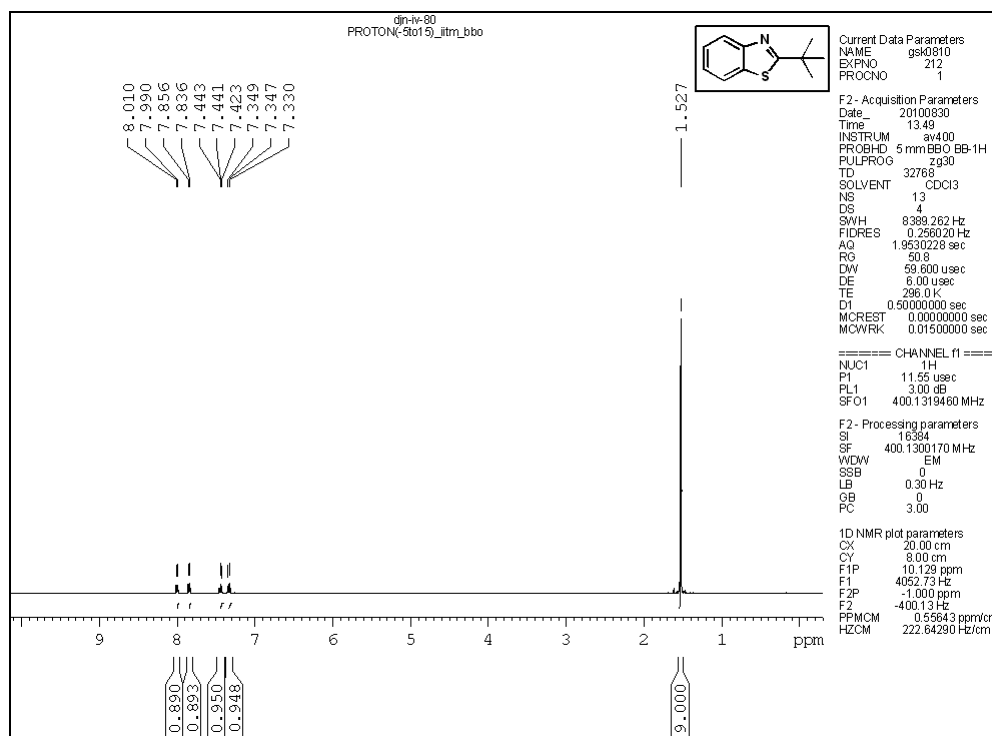


Figure 13 400 MHz ^1H NMR spectrum of compound **15** in CDCl_3

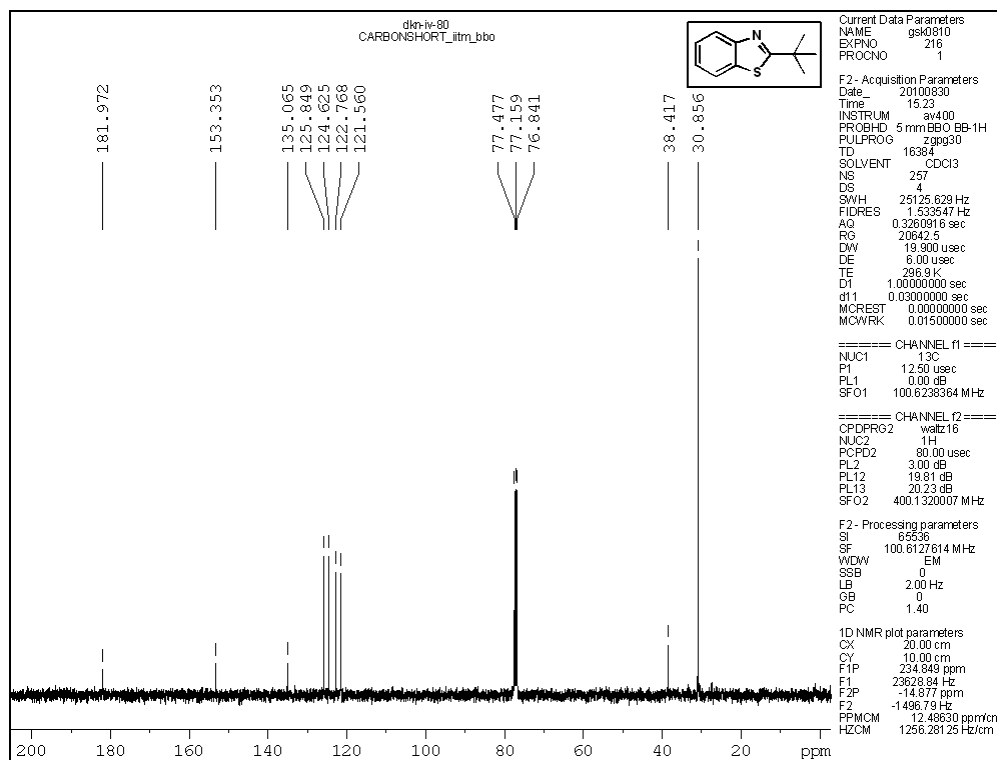


Figure 14 100 MHz ^{13}C NMR spectrum of compound **15** in CDCl_3

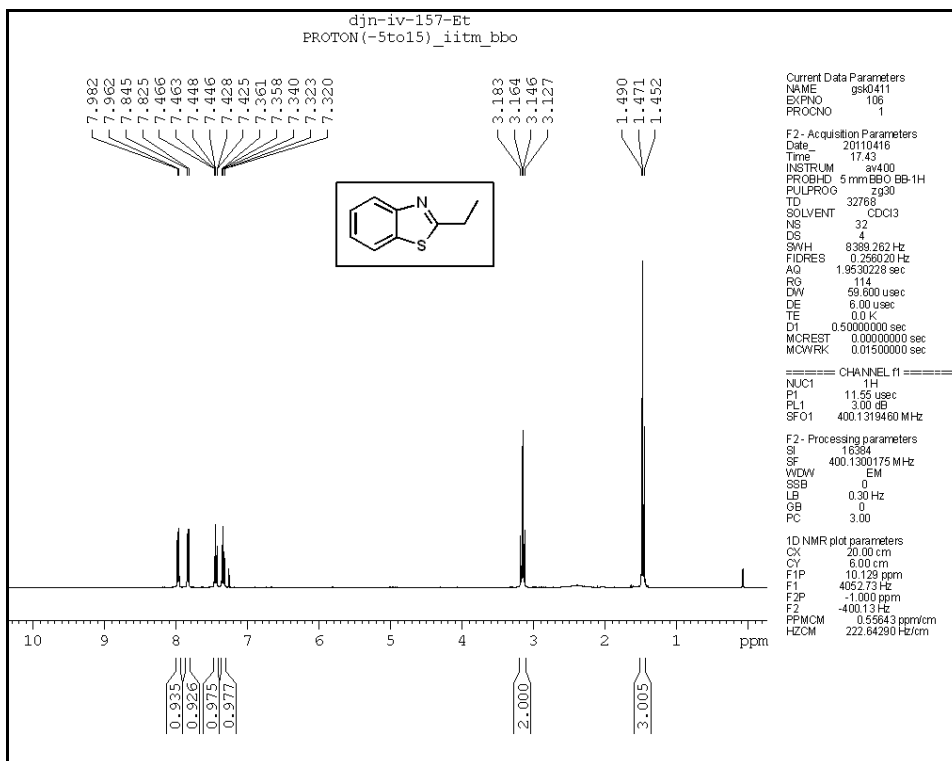


Figure 15 400 MHz ^1H NMR spectrum of compound **17** in CDCl_3

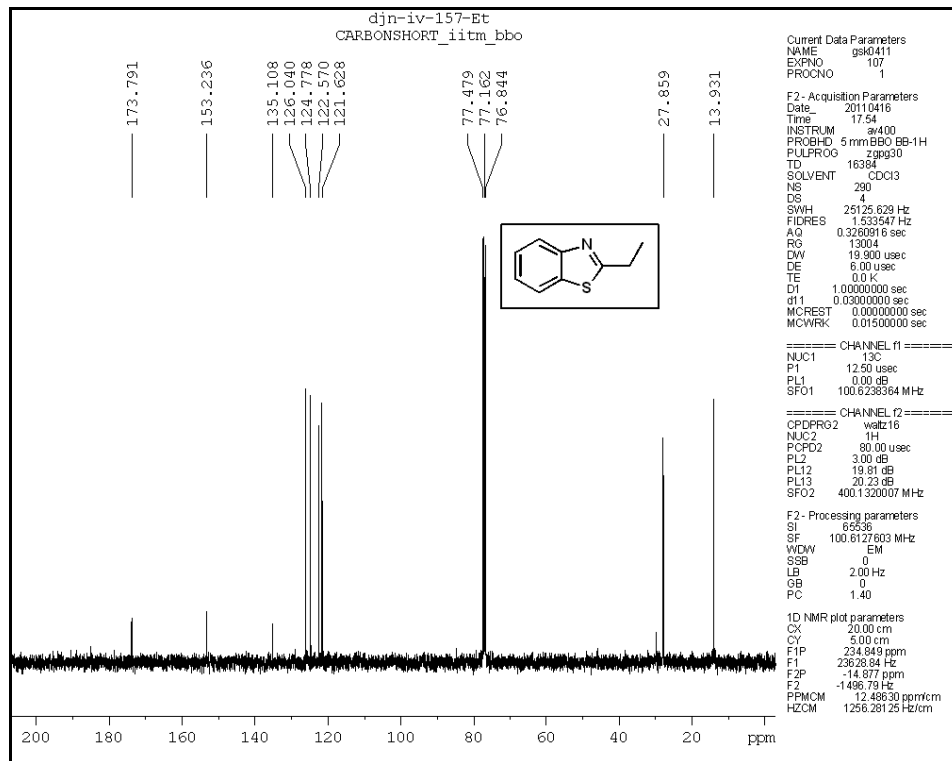


Figure 16 100 MHz ^{13}C NMR spectrum of compound **17** in CDCl_3

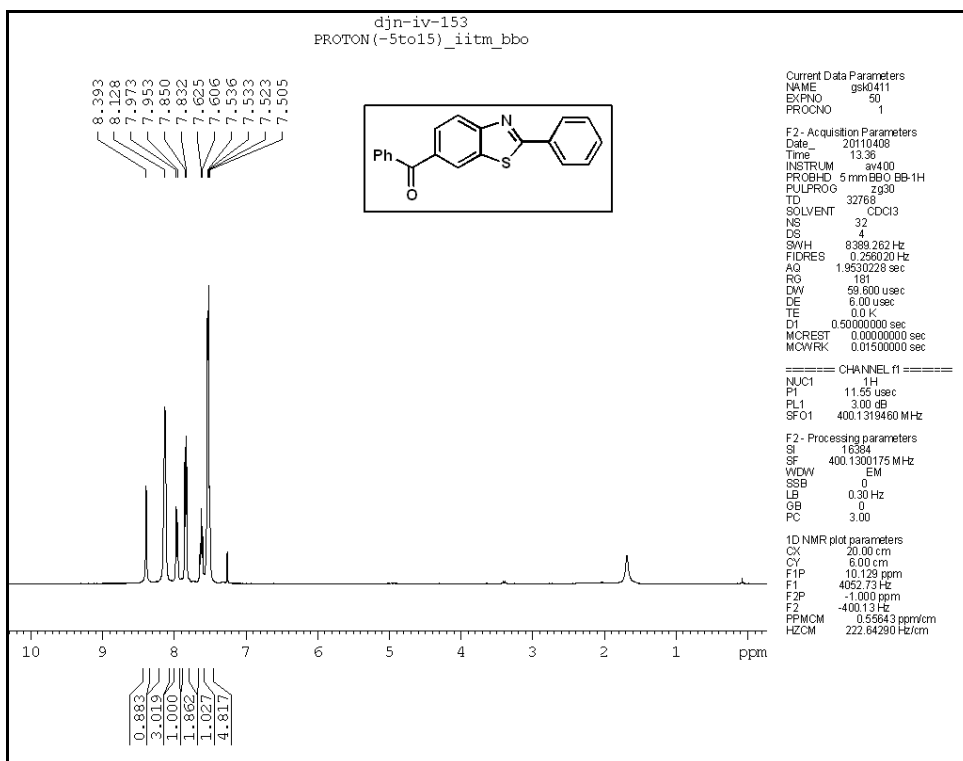


Figure 17 400 MHz ^1H NMR spectrum of compound **19** in CDCl_3

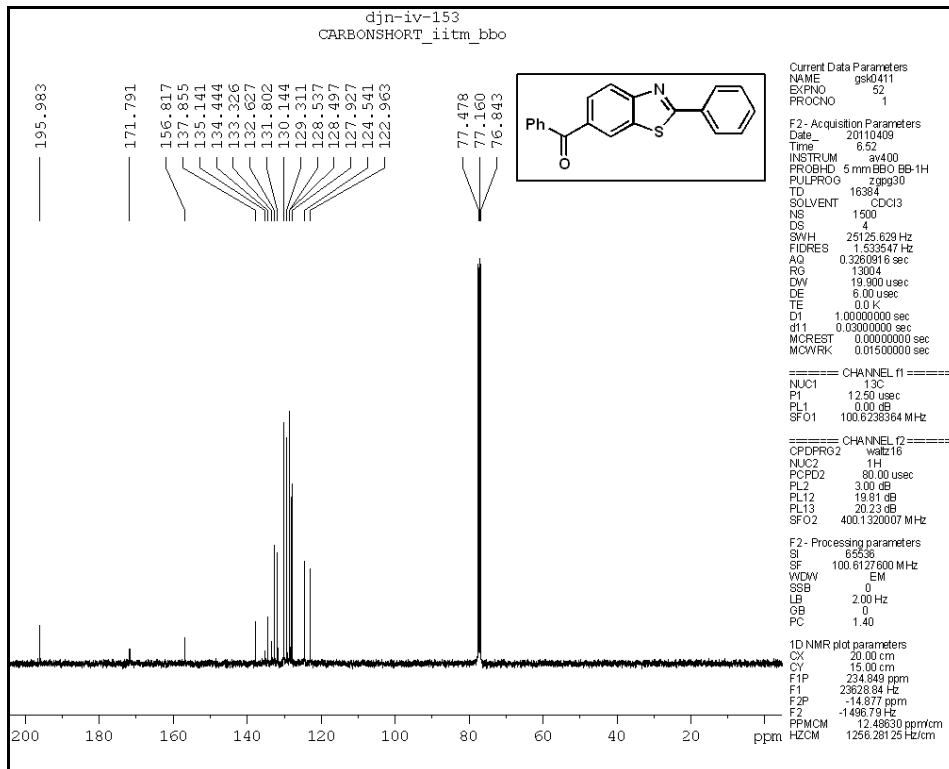


Figure 18 100 MHz ^{13}C NMR spectrum of compound **19** in CDCl_3

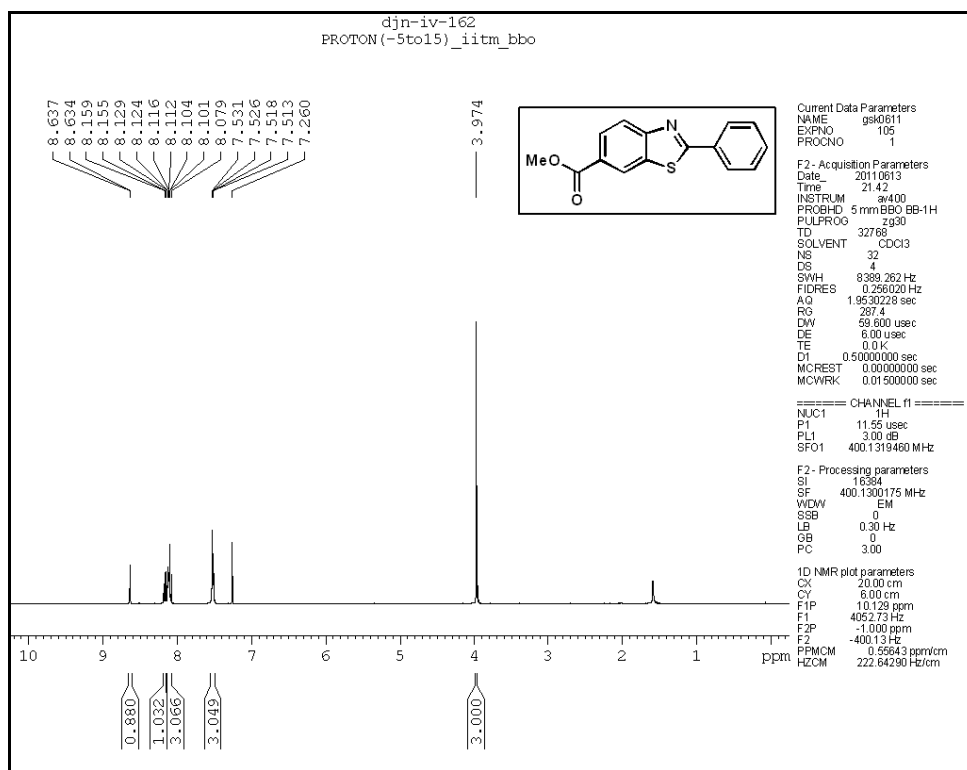


Figure 19 400 MHz ^1H NMR spectrum of compound **21** in CDCl_3

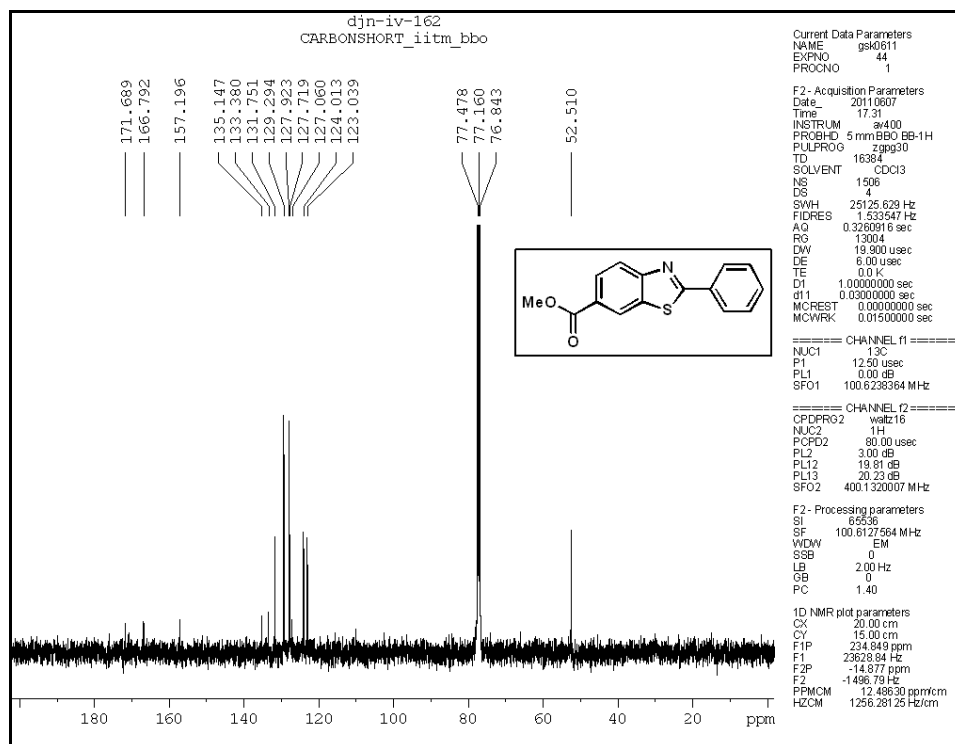


Figure 20 100 MHz ^{13}C NMR spectrum of compound **21** in CDCl_3

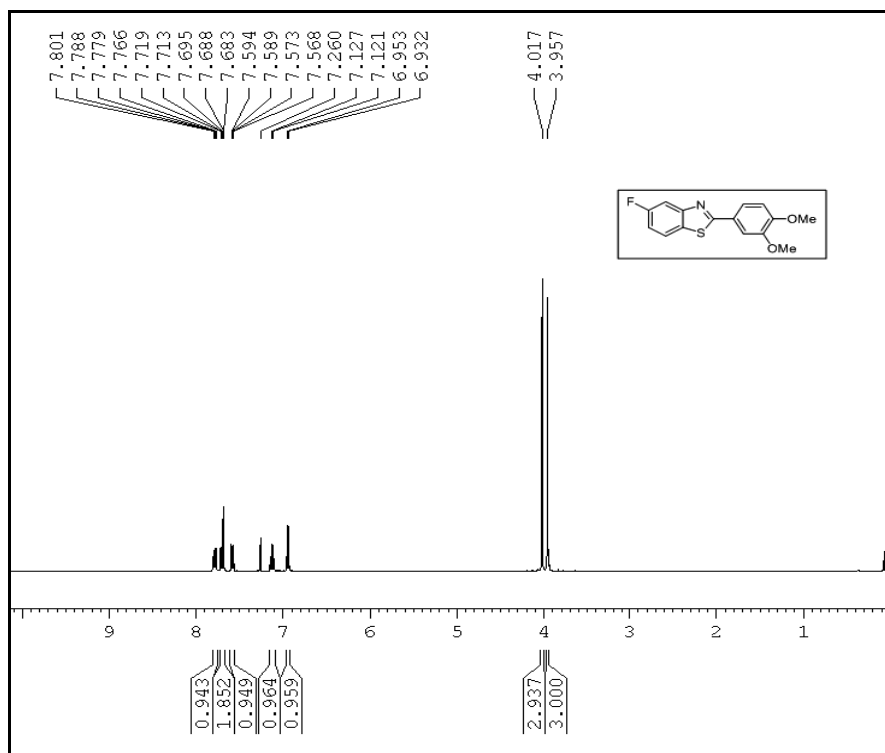


Figure 21 400 MHz ^1H NMR spectrum of compound **25** in CDCl_3

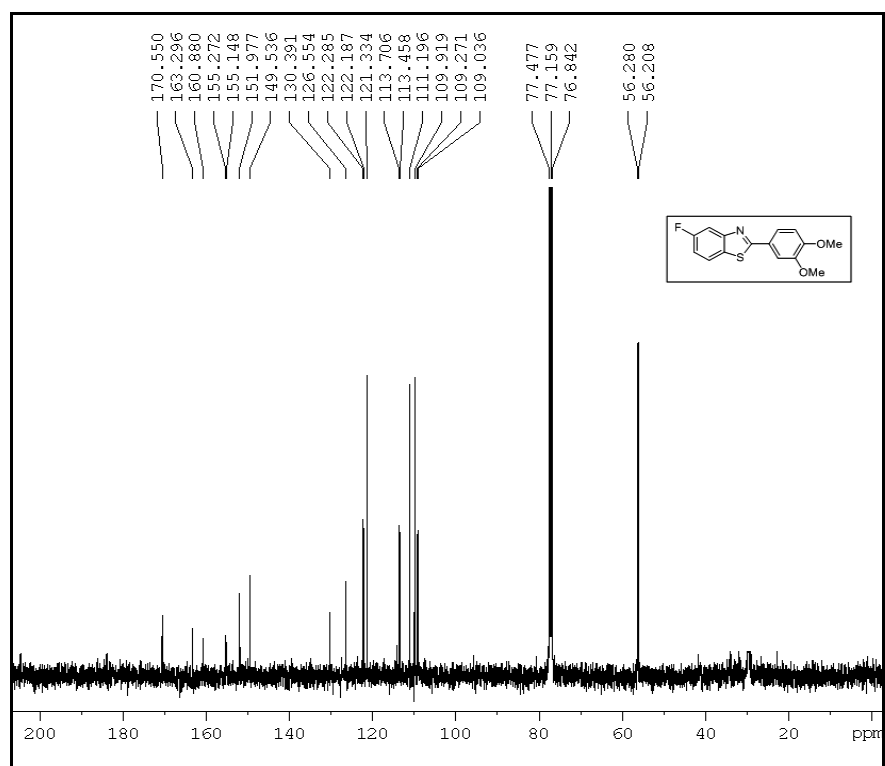


Figure 22 100 MHz ^{13}C NMR spectrum of compound **25** in CDCl_3

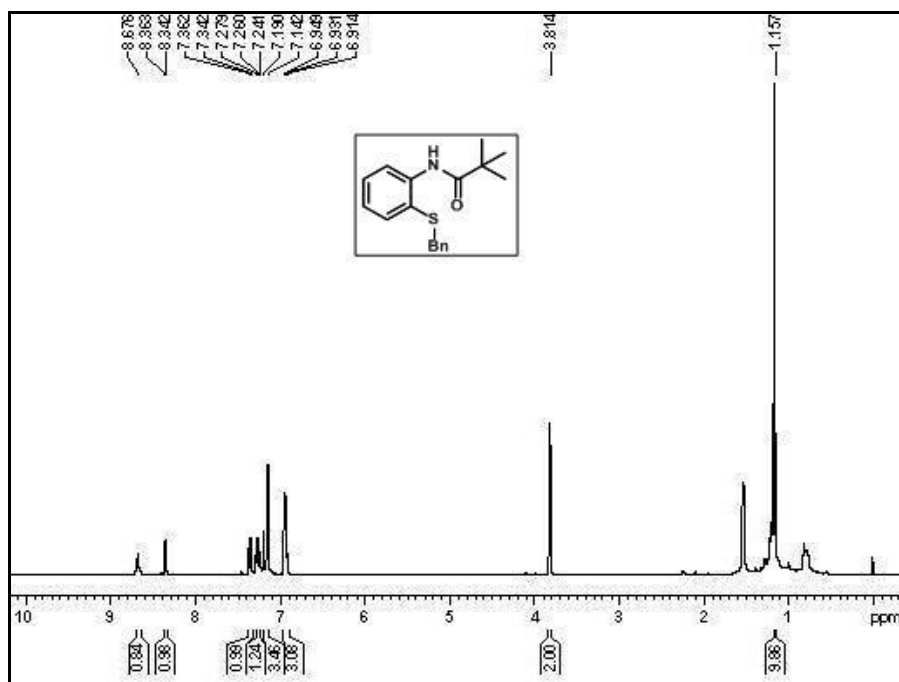


Figure 23 400 MHz ^1H NMR spectrum of compound **28a** in CDCl_3

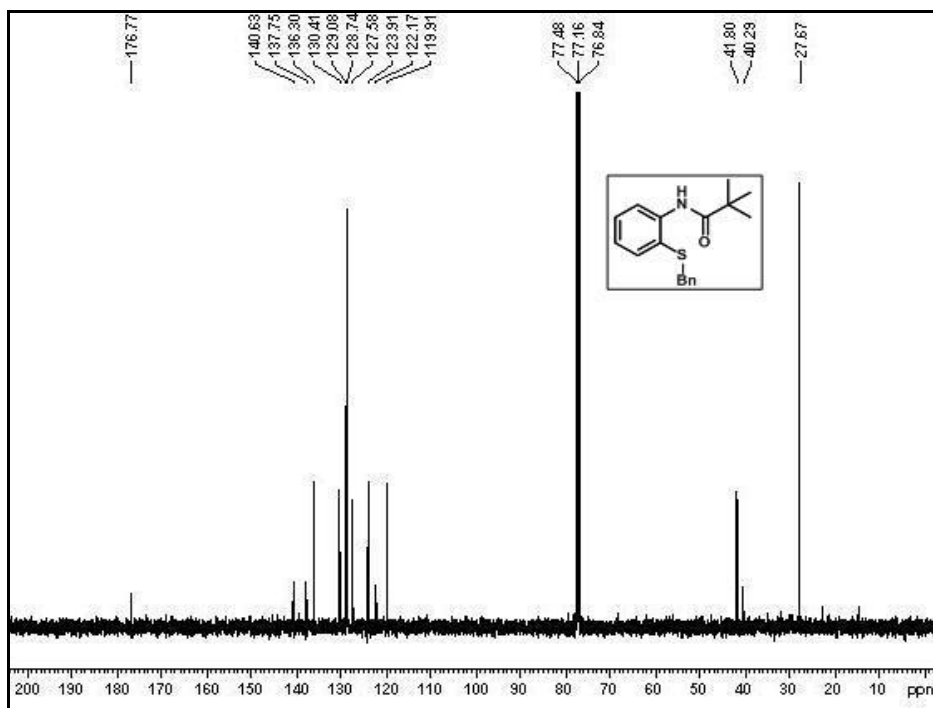


Figure 24 100 MHz ^{13}C NMR spectrum of compound **28a** in CDCl_3

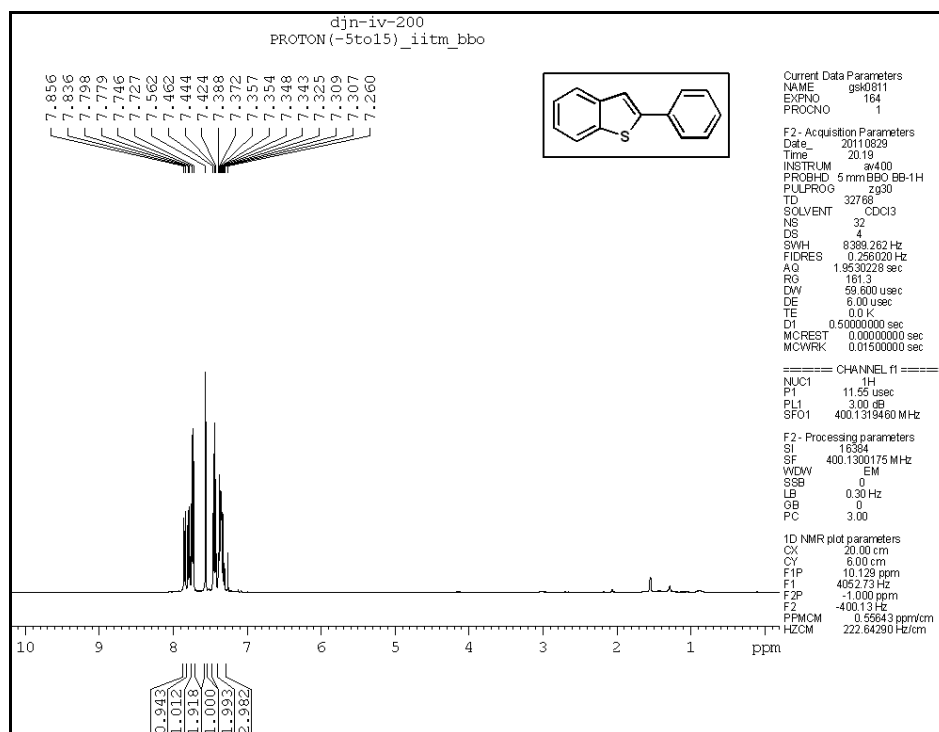


Figure 25 400 MHz ^1H NMR spectrum of compound **32** in CDCl_3

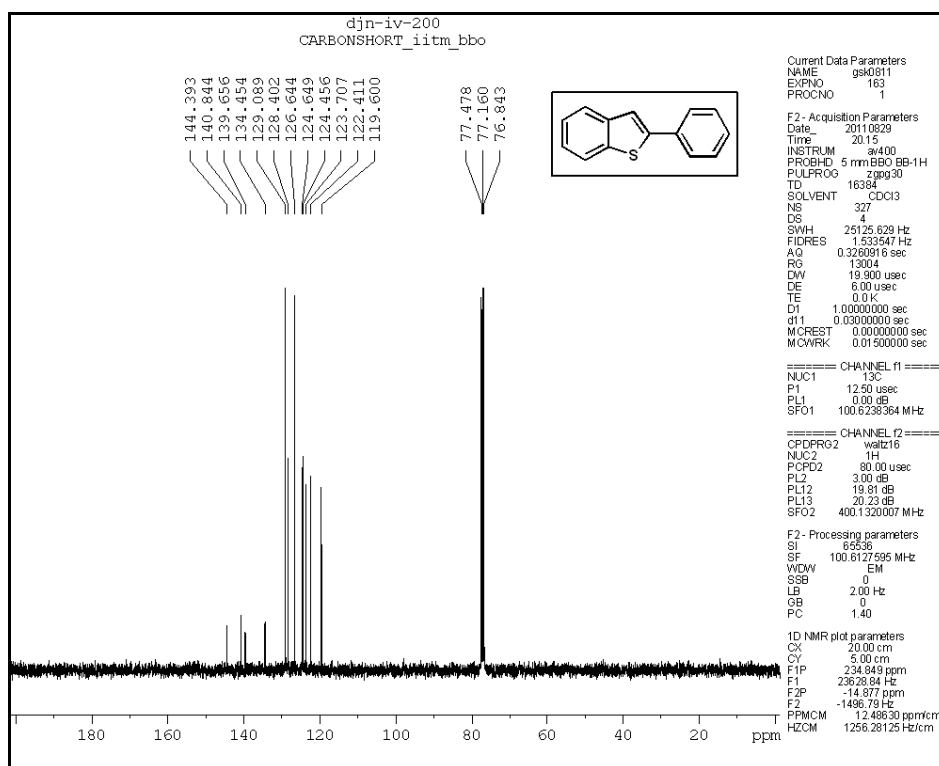


Figure 26 100 MHz ^{13}C NMR spectrum of compound **32** in CDCl_3

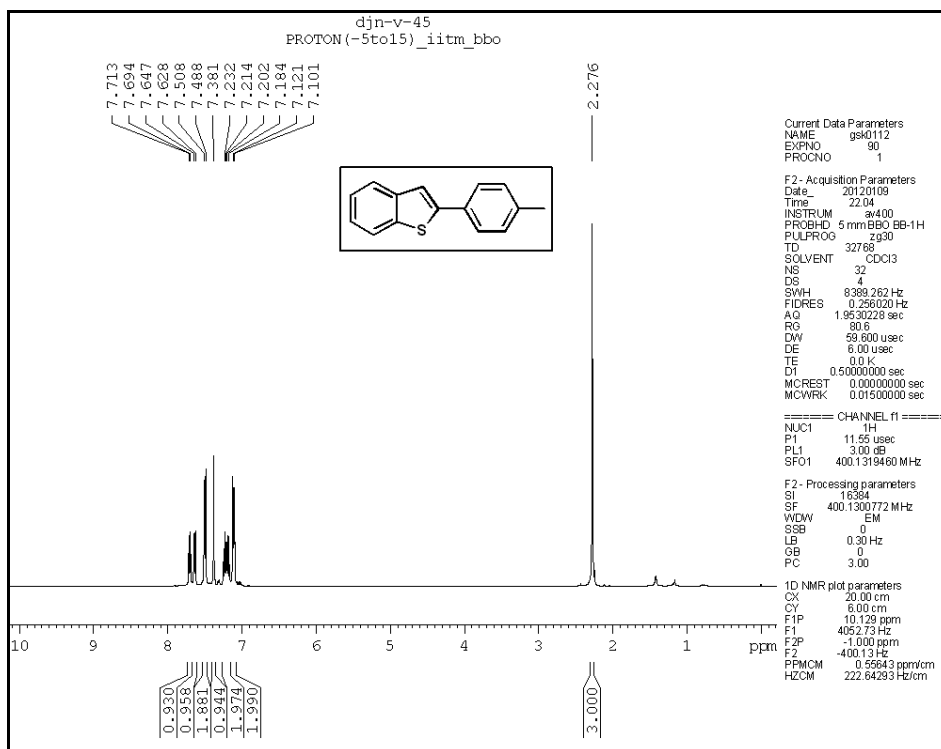


Figure 27 400 MHz ^1H NMR spectrum of compound **34** in CDCl_3

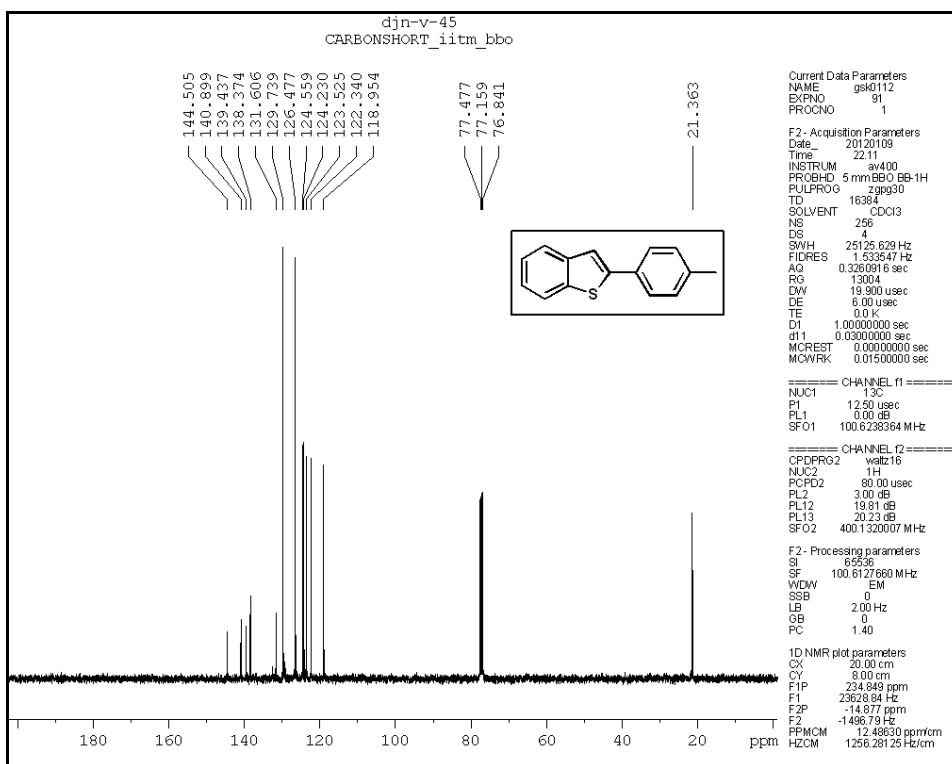


Figure 28 100 MHz ^{13}C NMR spectrum of compound **34** in CDCl_3

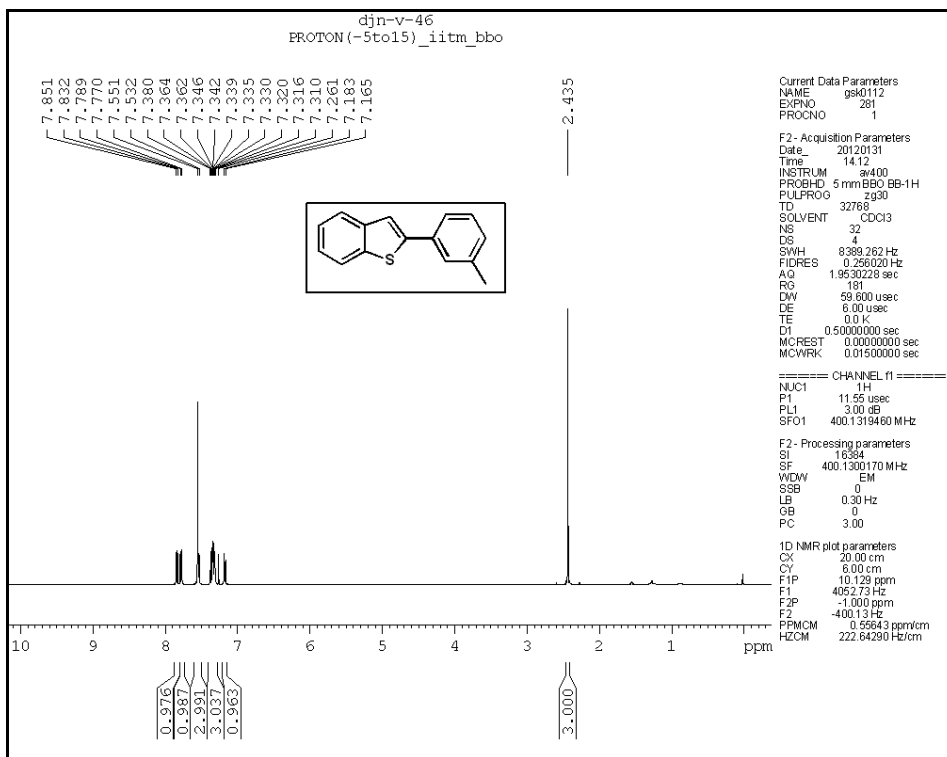


Figure 29 400 MHz ^1H NMR spectrum of compound **36** in CDCl_3

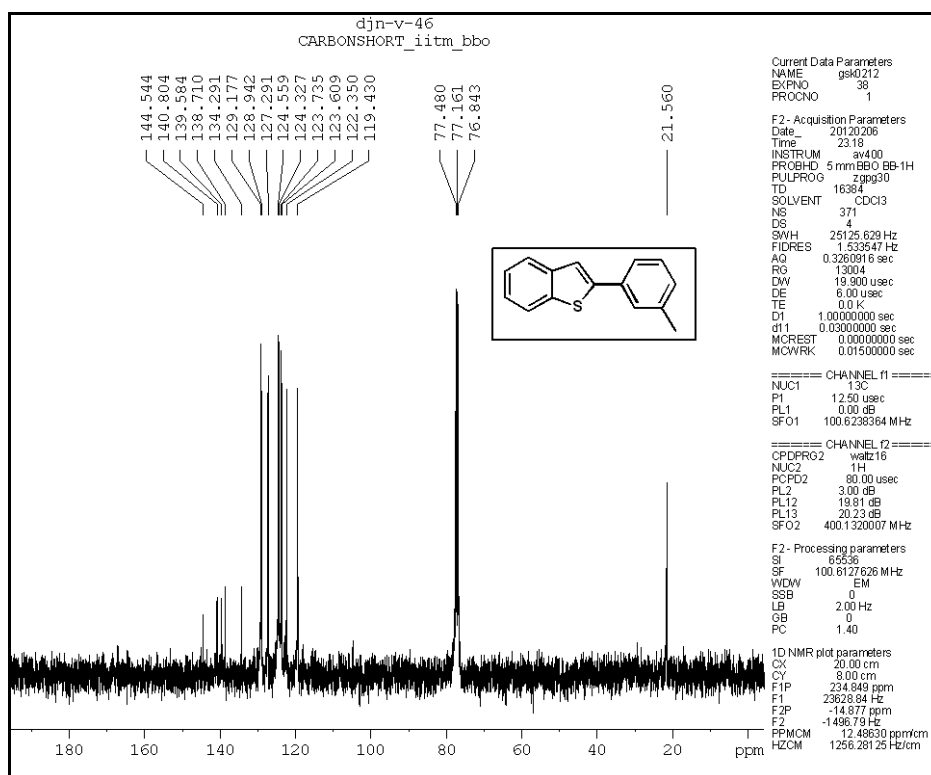


Figure 30 100 MHz ^{13}C NMR spectrum of compound **36** in CDCl_3

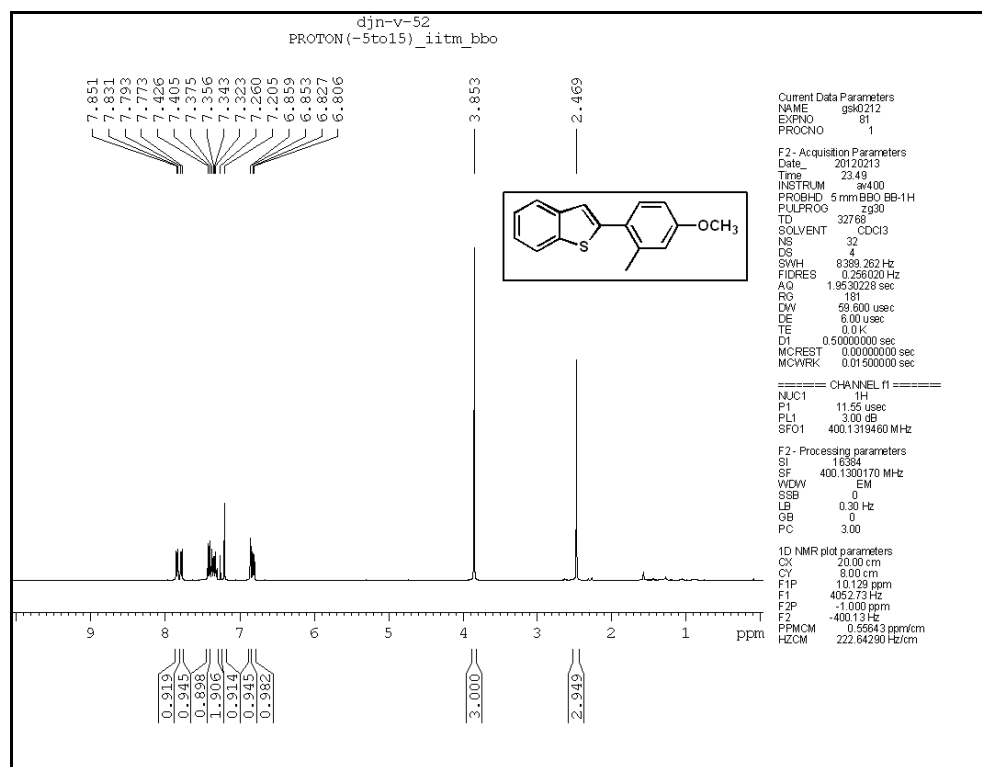


Figure 31 400 MHz ^1H NMR spectrum of compound **38** in CDCl_3

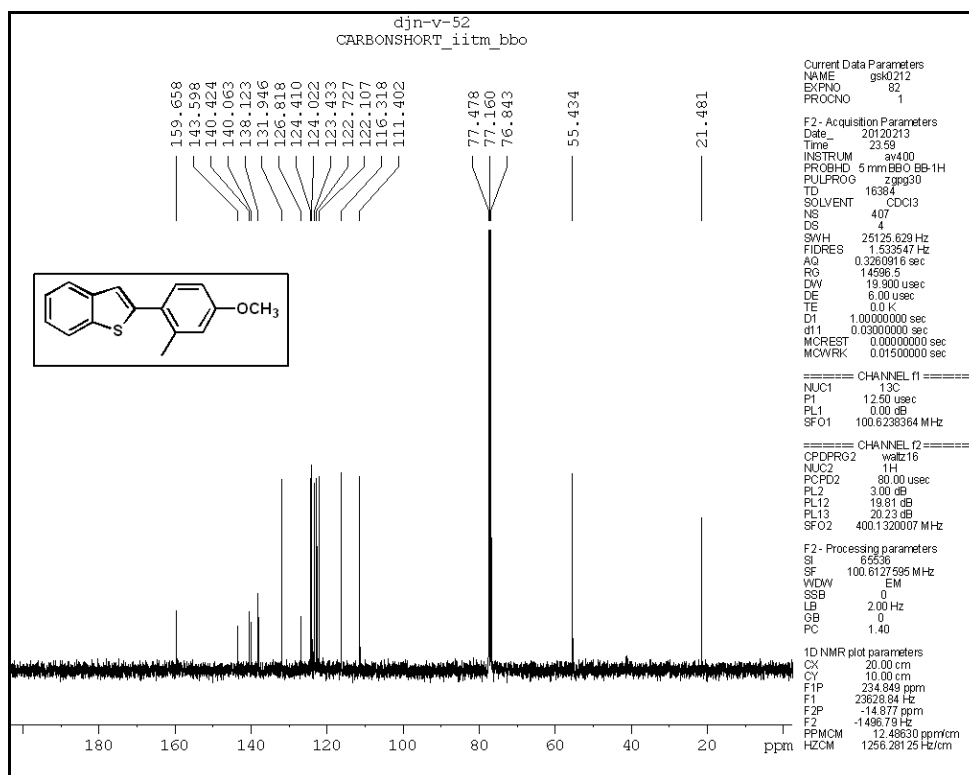


Figure 32 100 MHz ^{13}C NMR spectrum of compound **38** in CDCl_3

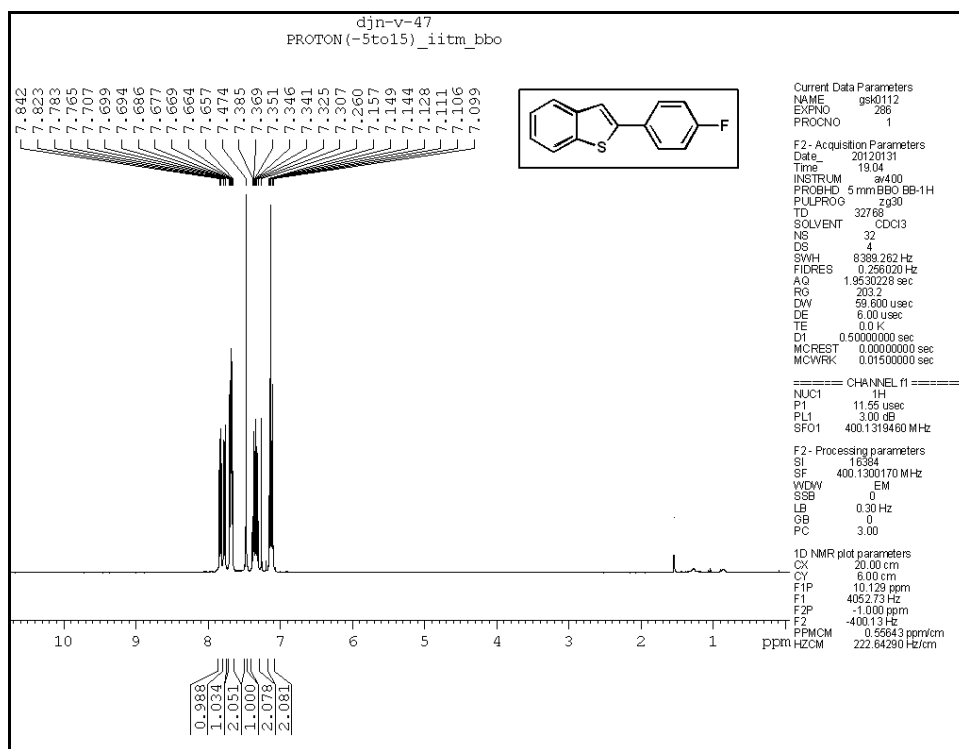


Figure 33 400 MHz ^1H NMR spectrum of compound **40** in CDCl_3

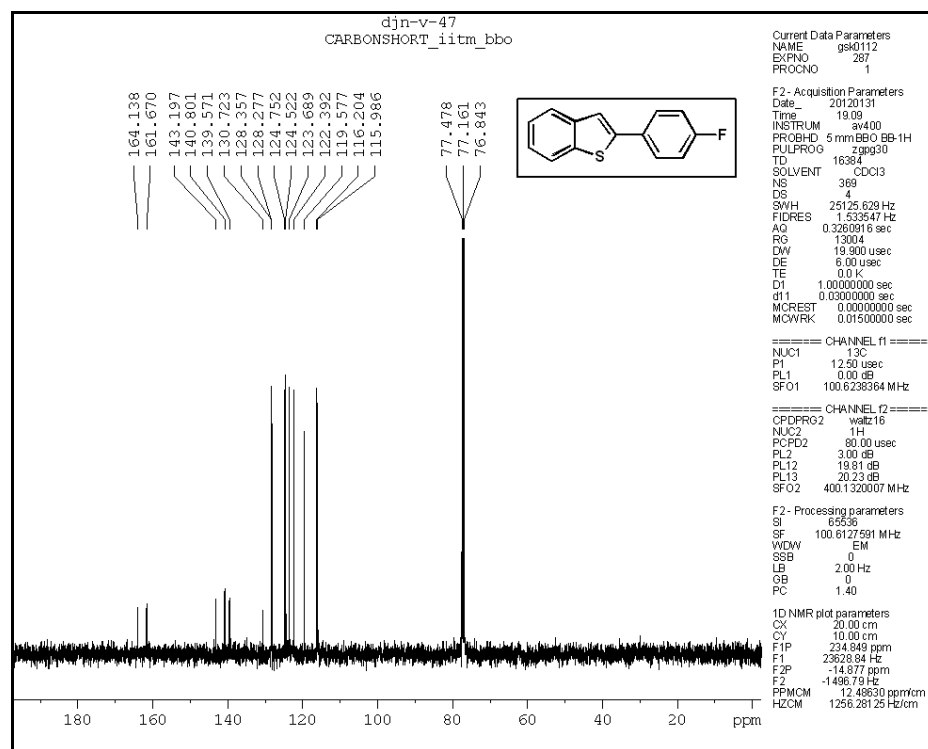


Figure 34 100 MHz ^{13}C NMR spectrum of compound **40** in CDCl_3

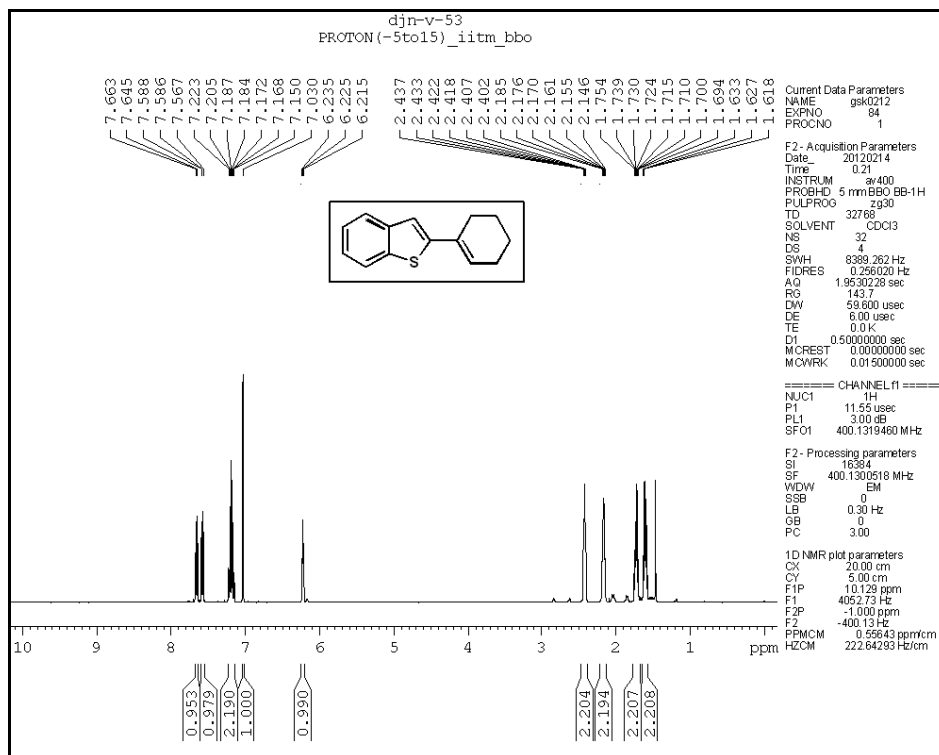


Figure 35 400 MHz ^1H NMR spectrum of compound **42** in CDCl_3

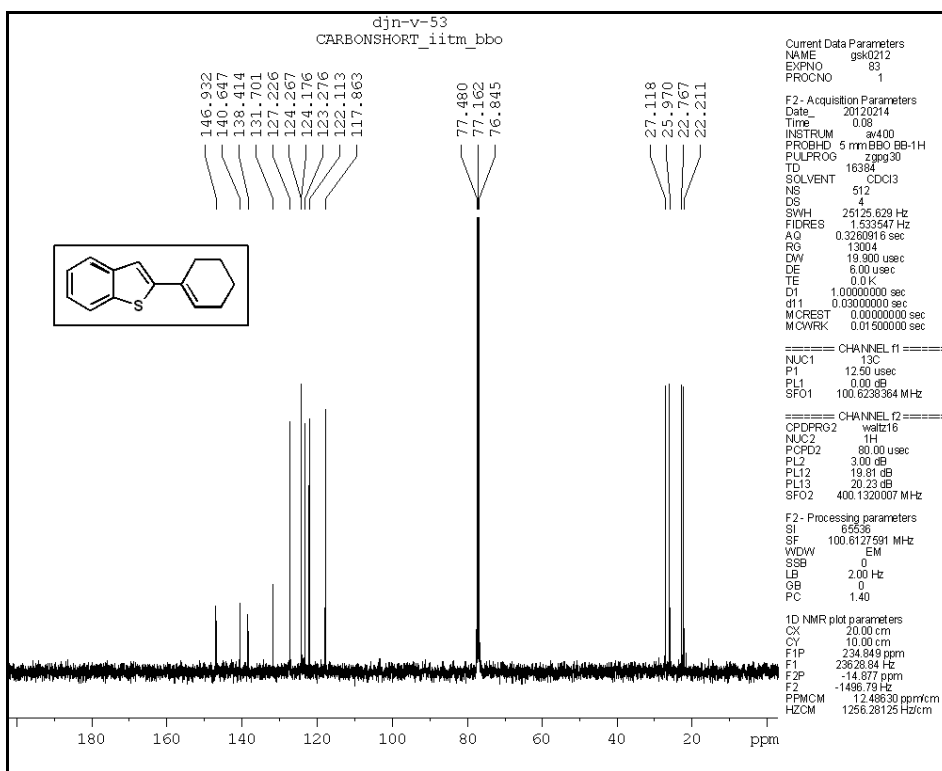


Figure 36 100 MHz ^{13}C NMR spectrum of compound **42** in CDCl_3

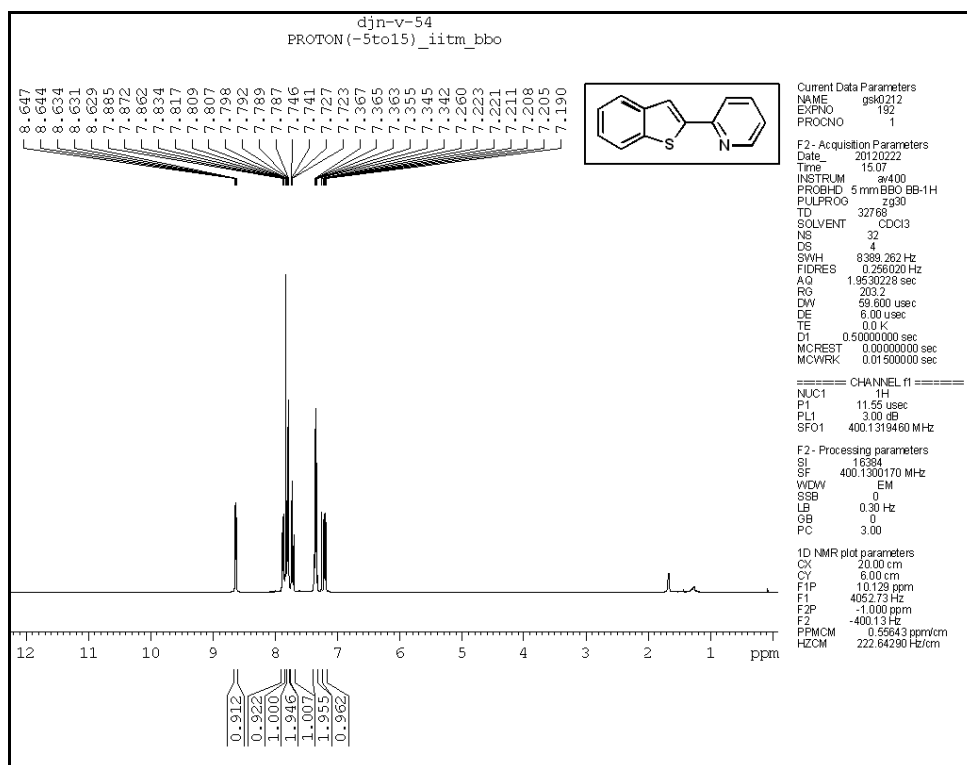


Figure 37 400 MHz ^1H NMR spectrum of compound **44** in CDCl_3

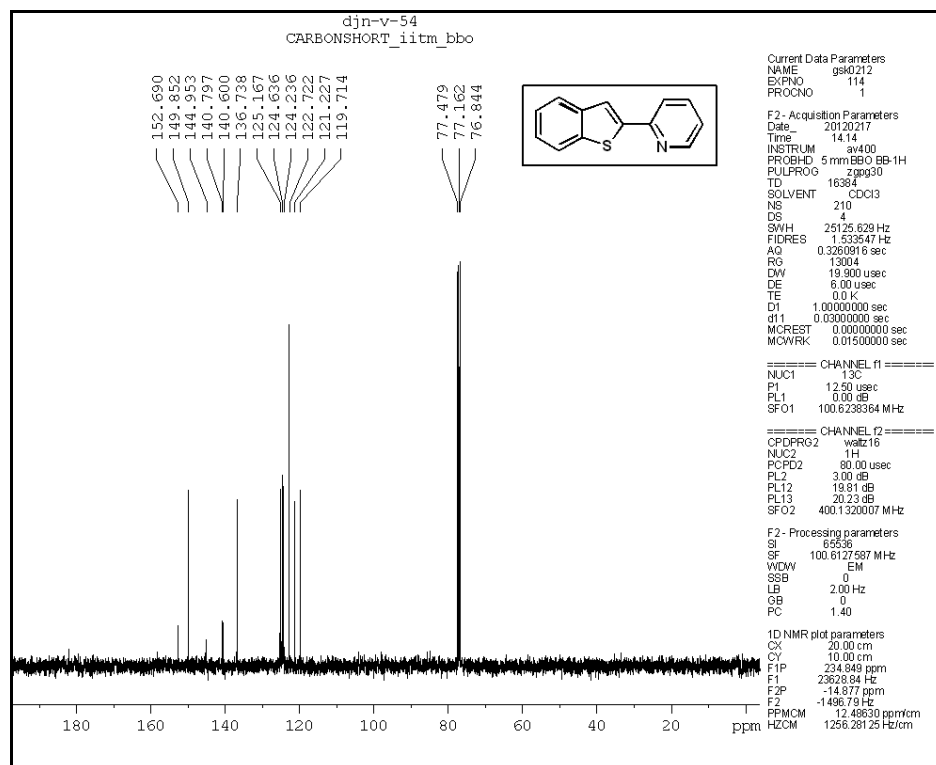


Figure 38 100 MHz ^{13}C NMR spectrum of compound **44** in CDCl_3