Electronic supplementary information (ESI)

N-Unsubstituted 2- and 3-Thiophenimines

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I. General Information

NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Spectra were recorded in deuterochloroform referenced to $CHCl_3$ (δ_H: 7.26 ppm) (δ_C: 77.16 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are reported in Hertz. The following abbreviations are used to describe multiplicity: s-singlet, d-doublet, q-quadruplet, m-multiplet, and br-broad. The IR spectra were recorded on the Nicolet Infra-Red spectrometer, model 320 AVATAR. The sample is deposited on a KBr window. The following abbreviations are used: m-medium, s-strong, vs-very strong. High resolution mass spectra were performed using a time of flight Maxis 4G (Bruker Daltonik Gmbh, Bremen, Germany) in Electrospray positive ionization mode. Ionization mode: ASAP.

2-Thiophenecarboxaldehyde, 3-thiophenecarboxaldehyde, 2-acetylthiophene, 3-acetylthiophene, 2-thiophenecarbonitrile, 3-thiophenecarbonitrile, superhydride, allylamine, aniline, hydroxylamine, cyanamide and propylamine were purchased from the Aldrich company and used without further purification.

Caution! *Potassium cyanide and probably α-aminonitriles are highly toxic compounds. All reactions and handling should be carried out in a well-ventilated hood. After the Strecker reaction, the aqueous phase should be kept alkaline and was treated with hydrogen peroxide or bleach.*

II. Synthesis of α-aminonitriles (2a),(2b). (For similar experiments, see refs. 1,2). In a 250 mL three necked flask under nitrogen atmosphere and at room temperature were added NH_4Cl (6.7 g, 0.125 mol), methanol (25 mL), 32% NH_4OH (25 mL) and KCN (7.5 g, 0.115 mol). The aldehyde (0.10 mol) was added dropwise over 5 min with vigorous stirring. The mixture was stirred at room temperature for 3 hours and the organic products were then extracted with dichloromethane (3 x 40mL) and dried over $MgSO_4$. After removal of $MgSO_4$ by filtration, the solvent was evaporated under reduced pressure to give α-aminonitrile **2a,2b** in good yield.

Procedure for the synthesis of α-aminonitriles (2c),(2d). NH_4Cl (8.5 g, 0.16 mol), methanol (30 ml), 32% NH_4OH (30 ml) and KCN (9.8 g, 0.15 mol) were added to a 250-ml three-necked flask under a nitrogen atmosphere at room temperature. Ketone (0.10 mol) was added dropwise over 5 minutes with vigorous stirring. The mixture was stirred at room temperature for 24 hours and the organic products were extracted with dichloromethane (3 x 40mL) and dried over $MgSO_4$. After removal of $MgSO_4$ by filtration, the solvent was evaporated under reduced pressure to give the crude product **2c**,**2d** in good yield and sufficient purity for the next step.

α-Amino-2-thiophenacetonitrile (2a). [3] Yield from 2-thiophenecarboxaldehyde: 92% (12.7 g, 92.0 mmol), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, ^3J = 5.0 Hz, 1H); 7.25 (d, ^3J = 3.7 Hz,

1H); 7.03 (dd, ^3J = 5.0, 3.7 Hz, 1H); 5.13 (s, 1H, CH); 2.15 (s, br, 2H, NH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.8, 127.0, 126.7, 125.9, 120.1, 43.4 ppm. **IR** (KBr): 3381 (vs, ν_{NH}), 2232 (m, ν_{CN}), 1423 (s), 1240 (m). **HRMS** *m/z* calculated for $C_6H_7N_2S^+$ $[M+H]^{+\cdot}$ 139.0325; found: 139.0325.

α-Amino-3-thiophenacetonitrile (2b). [4] Yield from 3-thiophenecarboxaldehyde: 91% (12.5 g, 91.0 mmol), colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45 (d, ^3J = 3.1 Hz, 1H); 7.38 (dd, ^3J = 5.1, 3.1 Hz, 1H); 7.20 (d, ^3J = 5.1 Hz, 1H); 4.94 (s, 1H, CH); 2.01 (s, 2H, NH_2) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.3, 127.5, 125.9, 123.1, 120.9, 43.3 ppm. **IR** (KBr): 3265 (m, ν_{NH}), 2226 (m, ν_{CN}), 1421(s), 1240 (m). **HRMS** *m/z* calculated for $C_6H_7N_2S^+$ $[M+H]^+$: 139.0325; found: 139.0325.

α-Amino-α-methyl-2-thiophenacetonitrile (2c). Yield from 2-acetylthiophene: 86% (13.1 g, 86.0 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.27 (d, ^3J = 5.1 Hz, 1H); 7.22 (d, ^3J = 3.6 Hz, 1H); 6.96 (dd, ^3J = 5.1, 3.6 Hz, 1H); 2.33 (s, 2H, NH_2); 1.84 (s, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.0, 126.9, 125.7, 124.7, 123.2, 50.3, 32.4 ppm. **IR** (KBr): 3367 (m, ν_{NH}), 2209 (m, ν_{CN}), 1413(s), 1280 (m). **HRMS** m/z calculated for $C_7H_9N_2S^+$ $[M+H]^+$: 153.0481; found: 153.0478.

α-Amino-α-methyl-3-thiophenacetonitrile (2d). Yield from 3-acetylthiophene: 90% (13.7 g, 90.0 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 (d, ^3J = 2.9 Hz, 1H); 7.36 (dd, ^3J = 5.0, 2.9 Hz, 1H); 7.22 (d, ^3J = 5.0 Hz, 1H); 2.15 (s, br, 2H, NH_2); 1.79 (s, 3H, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.7, 127.3, 124.9, 123.9, 121.5, 50.6, 30.9 ppm. **IR** (KBr): 3362 (m, ν_{NH}), 2204 (m, ν_{CN}), 1409 (s), 1228 (m). **HRMS** m/z calculated for $C_7H_9N_2S^+$ $[M+H]^+$:153.0481; found: 153.0480.

III. Synthesis of N-Allylamines (4a),(4b). [5,6] Allylamine (1.71 g, 30 mmol), dry CH_2Cl_2 (150 mL) and $MgSO_4$ (4.00 g) were stirred, under nitrogen, in a two-necked round bottom flask (500 mL) fitted with a dropping funnel. The aldehyde (25 mmol) diluted in dry CH_2Cl_2 (3 mL) was added dropwise. After 3 h, the mixture was filtered to remove hydrated $MgSO_4$, and concentrated under reduced pressure. The crude products were then dissolved in CH_3OH (50 mL), the mixture was cooled in a water bath and $NaBH_4$ (0.46 g, 12.5 mmol) was gradually added under vigorous stirring. After 5 h, the mixture was diluted with water (100 mL) and extracted with ether (3 X 30 mL). The organic phases were collected, dried with $MgSO_4$ and concentrated under reduced pressure to give N-allylamines **4a**,**4b** in good yields. The crude N-allylamines **4a**,**4b** were sufficiently pure to be used for the thermolysis.

***N*-2-Propen-1-yl-2-thiophenemethanamine (4a).** [8] Yield from 2-thiophenecarboxaldehyde: 92% (3.52 g, 23 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24 (d, ^3J = 5.0 Hz, 1H); 6.97 (dd, ^3J = 5.0, 3.4 Hz, 1H); 6.95 (d, ^3J = 3.4 Hz, 1H), 5.94 (ddt, ^3J = 17.1, 10.2, 6.1 Hz, 1H, CH=C), 5.23 (d, ^3J = 17.1 Hz, 1H, C=C(H)H), 5.14 (d, ^3J = 10.2 Hz, 1H, C=C(H)H), 4.01 (s, 2H, CH_2), 3.33 (d, J = 6.1 Hz, 2H, CH_2),

1.48 (s, 1H, NH) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.4, 136.5, 126.6, 124.9, 124.4, 116.3, 51.4, 47.6 ppm.

***N*-2-Propen-1-yl-3-thiophenemethanamine (4b).** [7] Yield from 3-thiophenecarboxaldehyde: 88% (3.36 g, 22 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (dd, ^{3}J = 5.0, 3.0 Hz, 1H); 7.15 (d, ^{3}J = 3.0 Hz, 1H); 7.07 (d, ^{3}J = 5.0 Hz, 1H), 5.90 (ddt, ^{3}J = 17.1, 10.2, 6.0 Hz, 1H, CH=C), 5.18 (d, ^{3}J = 17.1 Hz, 1H, C=C(H)H), 5.10 (d, ^{3}J = 10.2 Hz, 1H, C=C(H)H), 3.84 (s, 2H, CH_2), 3.31 (dt, J = 6.0, 1.4 Hz, 2H, CH_2), 1.44 (s, 1H, NH) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.4, 136.7, 127.6, 125.7, 121.6, 116.1, 51.8, 48.2 ppm. **IR** (KBr): 3309 (s), 3077 (m), 2917 (s) 1448 (s), 1343(s).

Synthesis of N-Allylamines (4c),(4d). [6,9] In a 250 mL round bottomed flask under nitrogen, to ketone (1.9 g, 15 mmol) and allylamine (3.42 g, 60 mmol) in diethyl ether (75 mL) was added a 1M solution of $TiCl_4$ in dichloromethane (7.5 mmol, 0.5 equiv.) at 0 ˚C in drop-wise manner over a period of 15 minutes. The reaction mixture was warmed to room temperature and stirred for 2h. The precipitate was filtered through celite and washed with diethyl ether (60 mL). The filtrate was washed with brine (30 mL), dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude products were then dissolved in CH_3OH (50 mL), the mixture was cooled in a water bath and $NaBH_4$ (0.28 g, 7.5 mmol) was gradually added under vigorous stirring. After 5 h, the mixture was diluted with water (60 mL) and extracted with ether (3 x 20 mL). The organic phases were collected, dried with $MgSO_4$ and concentrated under reduced pressure to give N-Allylamines **4c,4d** in good yield. The crude N-allylamines was pure enough to be used for the thermolysis.

α-Methyl-*N*-2-propen-1-yl-2-thiophenemethanamine (4c). Yield from 2-acetylthiophene: 80% (2.00 g, 12 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21 (d, ^{3}J = 5.0 Hz, 1H); 6.95 (dd, ^{3}J = 5.0, 3.4 Hz, 1H); 6.92 (d, ^{3}J = 3.4 Hz, 1H), 5.92 (ddt, ^{3}J = 17.1, 10.2, 6.0 Hz, 1H, CH=C), 5.16 (d, ^{3}J = 17.1 Hz, 1H, C=C(H)H), 5.10 (d, ^{3}J = 10.2 Hz, 1H, C=C(H)H), 4.14 (q, J = 6.6 Hz, 1H, CH-N), 3.28-3.15 (m, 2H, CH_2-N), 1.48 (d, J = 6.6 Hz, 3H, CH_3), 1.37 (s, 1H, NH) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.6, 136.8, 126.4, 123.6, 123.4, 115.9, 52.9, 50.0, 24.8 ppm. **IR** (KBr): 3318 (m), 3074 (m), 2925 (s) 1440 (s), 1369(s). **HRMS** *m/z* calculated for $C_9H_{14}NS^+[M+H]^+$: 168.08415; found: 168.0841.

α-Methyl-*N*-2-propen-1-yl-3-thiophenemethanamine (4d). Yield from 3-acetylthiophene: 77% (1.93 g, 11.6 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 (dd, ^{3}J = 5.0, 3.0 Hz, 1H); 7.11 (d, ^{3}J = 3.0 Hz, 1H); 7.09 (d, ^{3}J = 5.0 Hz, 1H), 5.91 (ddt, ^{3}J = 17.1, 10.2, 6.0 Hz, 1H, CH=C), 5.18 (d, ^{3}J = 17.1 Hz, 1H, C=C(H)H), 5.10 (d, ^{3}J = 10.2 Hz, 1H, C=C(H)H), 3.95 (q, J = 6.6 Hz, 1H, CH-N), 3.17 (dd, J = 6.0, 1.2 Hz, 2H, CH_2-N), 1.40 (d, J = 6.6 Hz, 3H, CH_3), 1.30 (s, 1H, NH) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.9, 137.0, 126.0, 125.7, 120.3, 115.8, 52.9, 50.2, 23.3 ppm. **IR** (KBr): 3337 (m), 3077

(s), 2973 (s), 1457 (s), 1313 (s). **HRMS** m/z calculated for $C_9H_{14}NS^+$ $[M+H]^+$: 168.08415; found: 168.0841.

IV. Synthesis of imines

The synthesis of imines has been described in the main text. The pictures of the apparatus are below.

Picture 1 Apparatus for the gas solid reaction of α-aminonitriles **2a**-**2d** on KOH heated to 90°C

Picture 2 Apparatus for the flash Vacuum Thermolysis of allylamines **4a**-**4d** at 800°C

V. Determination of the major isomer for ketimines (1c,1d). In the lack of $^{3}J_{HH}$ coupling constant, we identified for each C-methylated 2-thiophenimine **1c** and 3-thiophenimine **1d**, the major stereoisomer (*E*) by 2D NOESY analysis. Figure 1 shows the corresponding NOESY spectrum for α-methyl-3-thiophenemethanimine **1c**. Correlation spots between the methyl group (δ_H: 2.36 ppm) and the nitrogen proton (δ_H: 9.14 ppm) are observed as well as between the methyl group (δ_H: 2.36 ppm) and a ring proton (δ_H: 7.31 ppm). These two red spots, symbolized by E and F respectively, reflect interactions between protons H_1 and H_2, H_2 and H_3.

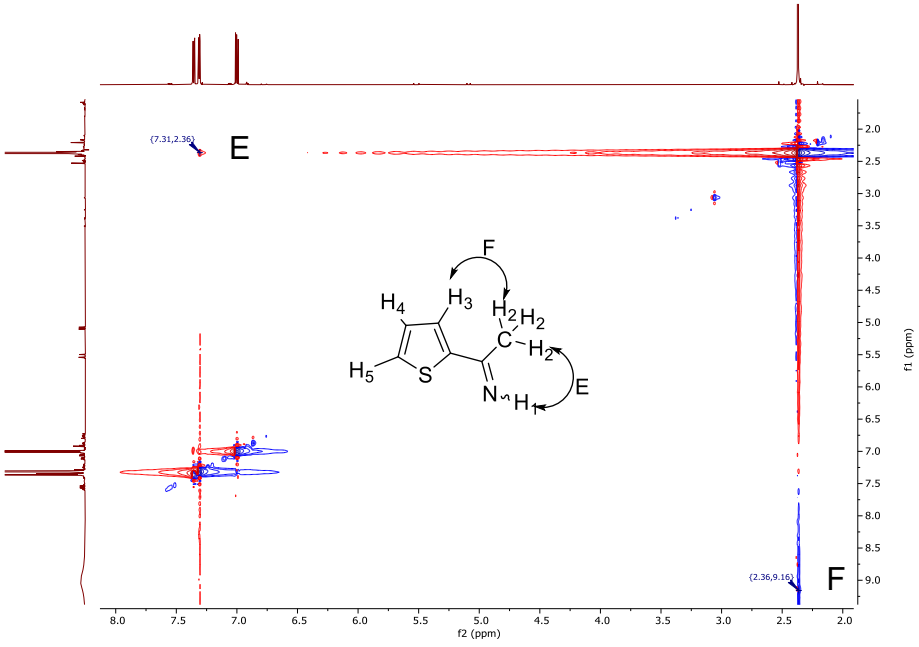

Figure S1 2D NOESY analysis of α-methyl-2-thiophenemethanimine **1c**

For **1d**, we observed correlation spots between the methyl group (δ_H: 2.42 ppm) and the nitrogen proton (δ_H: 9.17 ppm) and between the methyl group (δ_H: 2.42 ppm) and a ring proton (δ_H: 7.63 ppm). These two blue spots, symbolized by A and B respectively, reflect interactions between protons H_5 and H_4, H_5 and H_3. Two additional correlation spots are observed between the methyl group (δ_H: 2.42 ppm) and the other two protons of the ring (δ_H: 7.73 and 7.36 ppm) symbolized by C and D. They are due to the spatial orientation of the methyl group (Figure S1).

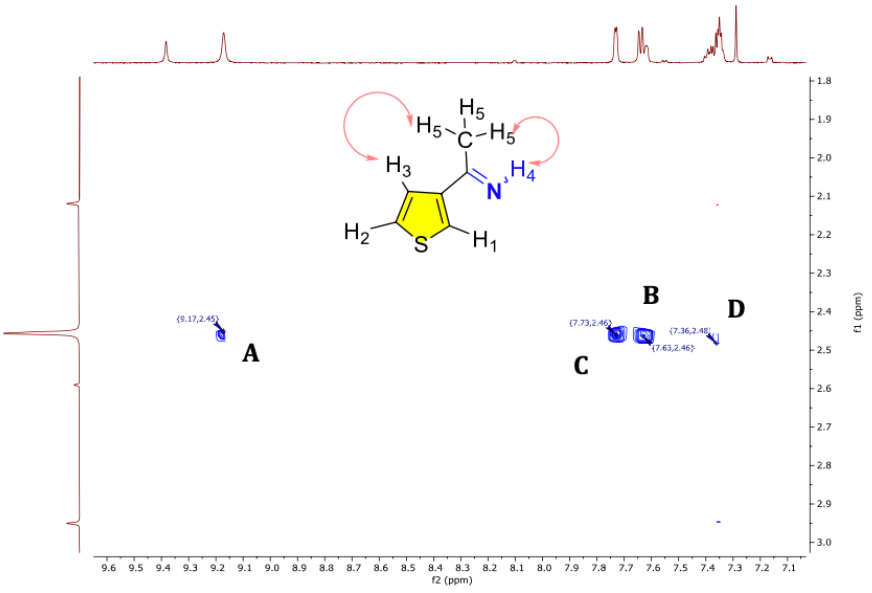

Figure S2 2D NOESY analysis of α-methyl-3-thiophenemethanimine **1d**

VI. Synthesis of thiophenemethanimine-triethylborane complexes (5a),(5b). [10,11] To a solution of thiophenecarbonitrile (0.451 g, 4.85 mmol) in diethyl ether (10 ml), lithium triethylborohydride (1M in THF; 4.85 mL, 4.85 mmol) was added at 0 °C and the solution was stirred for 2 hours at 0 °C. Methanol (155 mg, 4.85 mmol) was added to the reaction mixture and stirred for 30 minutes. Next, the solvent was evaporated under reduced pressure and the residue was dissolved in dry pentane (5 mL) and filtered through a Kramer filter. Thiophenemethanimine-triethylborane complexe **5a**, **5b** was then precipitated out by slowly cooling the solution to -80 °C, removing the liquid using a pipette, and drying in vacuo. Only (E) isomers of thiophenemethanimine-triethylborane complexes **5a**, **5b** were obtained with a good yield. They are stable at room temperature. Attempts to record HRMS spectra (ASAP) were unsuccessful as for the corresponding furanimine complexes. [2]

***(E)*-(*T*-4)-Triethyl[(α*E*)-2-thiophenemethanimine-κ*N*^{2}]boron (5a).** [10] Yield: 82% (0.93 g, 4.45 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.81 (d, ^3J = 22.3 Hz, 1H, NH); 8.14 (d, ^3J = 21.0 Hz, 1H, CH=N); 7.75, 7.62, 7.26 (m, 3H, H-cycl); 0.76 (t, ^3J = 7.7 Hz, 9H, 3 CH_3); 0.32 (q, ^3J = 7.7 Hz, 6H, 3 CH_2) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.5, 135.8, 134.6, 133.4, 129.2, 14.2, 9.7 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ -2.12 ppm. **IR** (KBr): 3393 (s), 2862 (s), 1631 (vs, $\nu_{C=N}$), 1415 (s), 1258 (m).

***(E)*- (*T*-4)-Triethyl[(α*E*)-3-thiophenemethanimine-κ*N*^{2}]boron (5b).** Yield: 84% (0.86 g, 4.12 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.94 (d, *J* = 20.8 Hz, 1H, NH); 8.06 (d, *J* = 21.2 Hz, 1H, CH=N); 7.95, 7.54, 7.43 (m, 3H, H-cycl); 0.78 (t, ^3J = 7.8 Hz, 9H, 3 CH_3), 0.33 (q, ^3J = 7.8 Hz, 6H, 3 CH_2) ppm. **^{13}C**

NMR (100 MHz, $CDCl_3$): δ 157.6, 134.6, 134.0, 129.0, 123.1, 14.1, 9.6 ppm. ^{11}B NMR (128 MHz, $CDCl_3$) δ -2.17 ppm. **IR** (KBr): 3293 (s), 2860 (vs), 1638 (vs, $\nu_{C=N}$), 1413 (m), 1250 (m).

VII. General procedure for the transimination with N-H thiophenimines. The imine **1a**-**1d** was synthesized as reported above starting from α-aminonitrile **2a**,**2b** (2.0 mmol) or allylamine **4c**,**4d** (2.0 mmol), and dry dichloromethane (2 mL) was added as solvent. A 50 mL two necked flask was fitted at the bottom of the cold finger and was immersed in a cold bath (-50°C). The imine **1a**-**1d** and the solvent flowed rapidly as soon as they melted into the flask. The amine (1.1 equiv) was added to the reaction mixture and stirred for 1 hour at the same temperature and allowed to warm to room temperature for 1 hour. The solvent and amine in excess were evaporated under reduced pressure. Overall yields (starting from **2a**,**2b**,**4c**,**4d**) are given below but, on the basis of the yields found for imines **1a**-**1d** the yield of the transimination reaction ranges between 75 and 92%. For compounds **6b**,**6e**-**6j,** the ^1H and ^{13}C NMR spectra were identical to those described in the literature. As spectroscopic data of compounds **6a**, **6d** and **6i** are partially reported in the literature, ^1H and ^{13}C NMR and IR data are reported below as their NMR spectra. [9]

***N*-(2-Thienylmethylene)-1-propaneamine (6a).** Yield: 25% from **2a** (route A) (77.5 mg, 0.50 mmol). **^1H NMR** (400 MHz, $CDCl_3$): δ 8.38 (t, ^3J = 1.3 Hz, 1H); 7.39 (d, ^3J = 5.0 Hz, 1H), 7.30 (d, ^3J = 3.6 Hz, 1H), 7.08 (dd, ^3J = 5.0, 3.6 Hz, 1H); 3.56 (td, ^3J = 7.0, ^4J = 1.3 Hz, 2H); 1.73 (tq, ^3J = 7.3, 7.0 Hz, 2H); 0.96 (t, ^3J = 7.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.0, 142.7, 130.1, 128.5, 127.3, 63.2, 24.0, 11.8 ppm. **IR** (KBr): 2933 (m, ν_{C-H}), 1638 (s, $\nu_{C=N}$), 1434 (m), 1219 (m). **HRMS** *m/z* calculated for $C_8H_{12}NS^+$ $[M+H]^+$: 154.0685; found: 154.0685.

***(E)*-*N*-(2-Thienylmethylene)benzenamine (6b).** [12,13] Yield: 26 % from **2a** (route A) (98 mg, 0.52 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ 8.60 (d, J = 1.0 Hz, 1H), 7.56 (d, ^3J = 5.0 Hz, 1H), 7.52 (d, ^3J = 3.6 Hz, 1H), 7.47-7.41 (m, 2H), 7.31-7.26 (m, 3H), 7.17 (dd, J = 5.0, 3.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 151.5, 142.9, 132.4, 130.4, 129.2, 127.8, 126.1, 121.1.

***N*-(2-Thienylmethylene)cyanamide (6c).** [14] Yield: 24 % from **2a** (route A) (65 mg, 0.48 mmol). **^1H NMR** (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 7.85 (d, ^3J = 6.0 Hz, 1H), 7.82 (d, ^3J = 3.9 Hz, 1H), 7.27 (dd, ^3J = 3.9, 6.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.5, 139.9, 139.1, 137.6, 129.3, 115.7.

***N*-(2-Thienylethylidene)-1-propanamine (6d).** Yield: 62% from **4c** (route B) (0.17 g, 1.24 mmol)**. ^1H NMR** (400 MHz, $CDCl_3$): δ 7.33 (d, ^3J = 5.1 Hz, 1H), 7.31 (d, ^3J = 3.7 Hz, 1H), 7.04 (dd, ^3J = 5.0, 3.7 Hz, 1H), 3.45 (t, ^3J = 7.3 Hz, 2H, CH_2-N), 2.24 (s, 3H), 1.73 (qt, $^3J_{H,H}$ = 7.4, 7.3 Hz, 2H), 1.01 (t, $^3J_{H,H}$ = 7.4 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ_C 159.5, 148.1, 128.2, 127.2, 126.3, 53.5, 24.0, 15.2, 12.1 ppm. **IR** (KBr): 2930 (s, ν_{C-H}), 1623 (s, $\nu_{C=N}$), 1433 (m), 1234 (s). **HRMS** m/z calculated for $C_9H_{14}NS^+$ $[M+H]^+$: 168.08415; found: 168.0841.

***(E)-N*-[1-(2-Thienyl)ethylidene]benzenamine (6e).** [15] Yield: 60% from **4c** (route B) (0.224 g, 1.20 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.34 (t, *J* = 8.4 Hz, 2H), 7.11 (dd, ^3J = 5.1, 3.7 Hz, 1H), 7.09 (t, ^3J = 8.4 Hz 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 2.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.4, 151.2, 147.0, 130.6, 129.4, 129.2, 127.9, 123.6, 120.1, 17.5.

***(E)-N*-(3-Thienylmethylene)-1-propanamine (6f).** [16] Yield: 32% from **2b** (route A) (98 mg, 0.64 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.60 (d, ^3J = 2.9 Hz, 1H), 7.54 (d, ^3J = 5.1 Hz, 1H), 7.32 (dd, ^3J = 5.1, 2.9 Hz, 1H), 3.55 (t, ^3J = 7.4 Hz, 2H), 1.73 (qt, ^3J = 7.4, 7.4 Hz, 2H), 0.96 (t, ^3J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 140.7, 128.0, 126.3, 125.8, 63.6, 24.1, 11.8.

***(E)-N*-(3-Thienylmethylene)benzenamine (6g).** [17,18] Yield: 35% from **2b** (route A) (0.13 g, 0.70 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.86 (dd, ^3J = 1.2 Hz, 1H), 7.69 (dd, ^3J = 5.1, 1.2 Hz, 1H), 7.43 – 7.35 (m, 3H), 7.25 – 7.16 (m, 3H), 6.77 (d, ^3J = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.2, 151.7, 140.4, 130.2, 129.0, 128.9, 126.5, 125.6, 120.6

3-Thiophenecarboxaldehyde Oxime (6h). [19] Yield: 31% from **2b** (route A) (79 mg, 0.62 mmol). *E*/*Z*=64/36. **(*E*) ^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.23 (s,1H) 7.53 (d, ^3J = 2.9 Hz, 1H), 7.43 (d, ^3J = 5.2 Hz, 1H), 7.36 (dd, ^3J = 5.2, 2.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7, 134.2, 131.5, 126.9, 124.8. **(*Z*) ^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.22 (s, 1H), 7.54 (d, ^3J = 2.9 Hz, 1H), 7.44 (d, ^3J = 5.2 Hz, 1H), 7.36 (dd, ^3J = 5.2, 2.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.2, 131.5, 131.3, 126.8, 125.3.

***N*-(3-Thienylethylene)-1-propanamine (6i).** Yield: 60% from **4d** (route B) (0.19 g, 1.20 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, ^3J = 5.0 Hz, 1H), 7.58 (d, ^3J = 3.0 Hz, 1H), 7.27 (dd, ^3J = 5.0, 3.0 Hz, 1H), 3.44 (t, ^3J = 7.2 Hz, 2H, CH_2-N), 2.22 (s, 3H, CH_3), 1.76 (tq, ^3J = 7.3, 7.3 Hz, 2H, CH_2), 1.02 (t, ^3J = 7.3 Hz, 3H, CH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.4, 145.0, 126.6, 125.4, 124.5, 53.6, 24.2, 15.9, 12.2 ppm. **IR** (KBr): 2930 (s, ν_{C-H}), 1628 (s, $\nu_{C=N}$), 1463 (m), 1265 (s). **HRMS** m/z calculated for $C_8H_{12}NS^+$ $[M+H]^+$: 154.0685; found: 154.0685.

***N*-[1-(3-Thienyl)ethylidene]benzenamine (6j).** [20] Yield: 67% from **4d** (route B) (0.14 g, 1.24 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.42 (m, 2H), 7.28 (t, ^3J = 7.6 Hz, 2H), 6.93 (d, ^3J = 6.6 Hz, 1H), 6.88 (d, ^3J = 7.6 Hz, 1H), 6.76 (d, ^3J = 7.6 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.8, 150.9, 146.2, 128.7, 126.7, 126.5, 125.6, 123.0, 119.3, 17.7.

VIII. References

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IX. ^{1}H and ^{13}C NMR spectra of compounds 2a-2d, 1a-1d, 5a,5c,5d, 6a,6b.

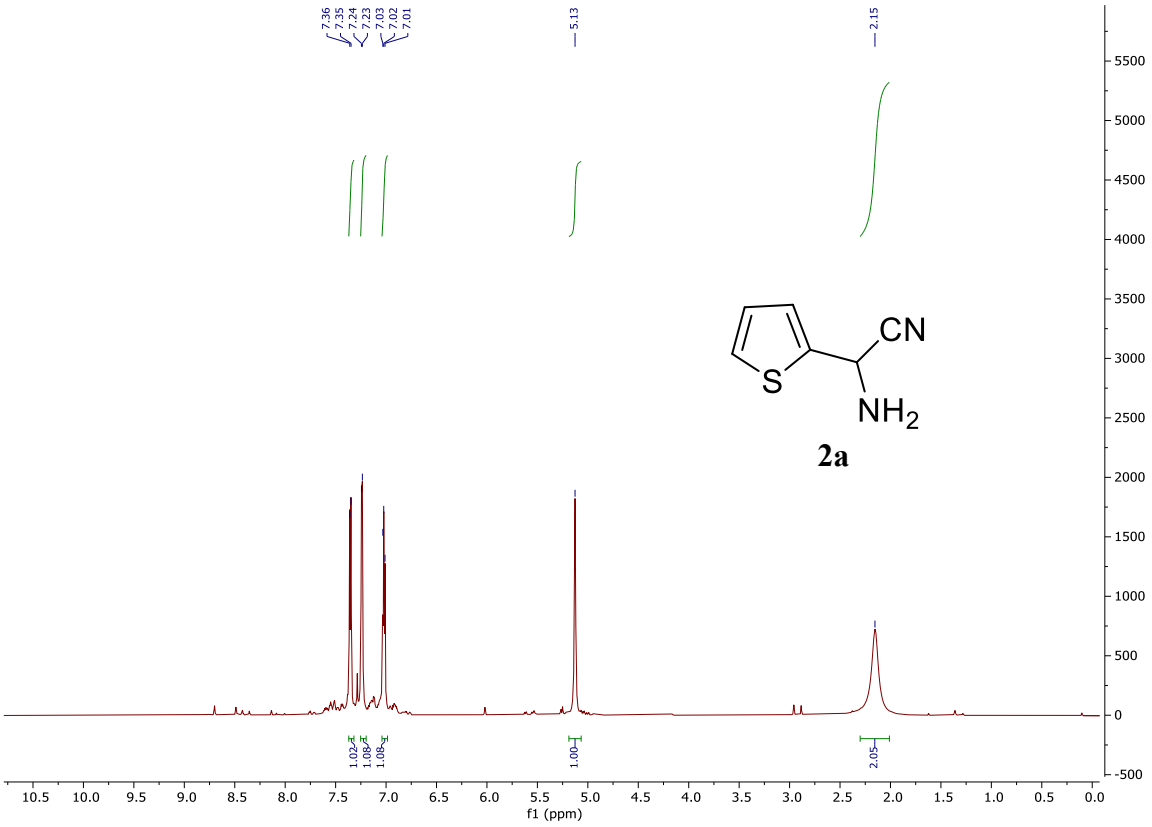

Figure S1 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of α-Amino-2-thiopheneacetonitrile **2a**.

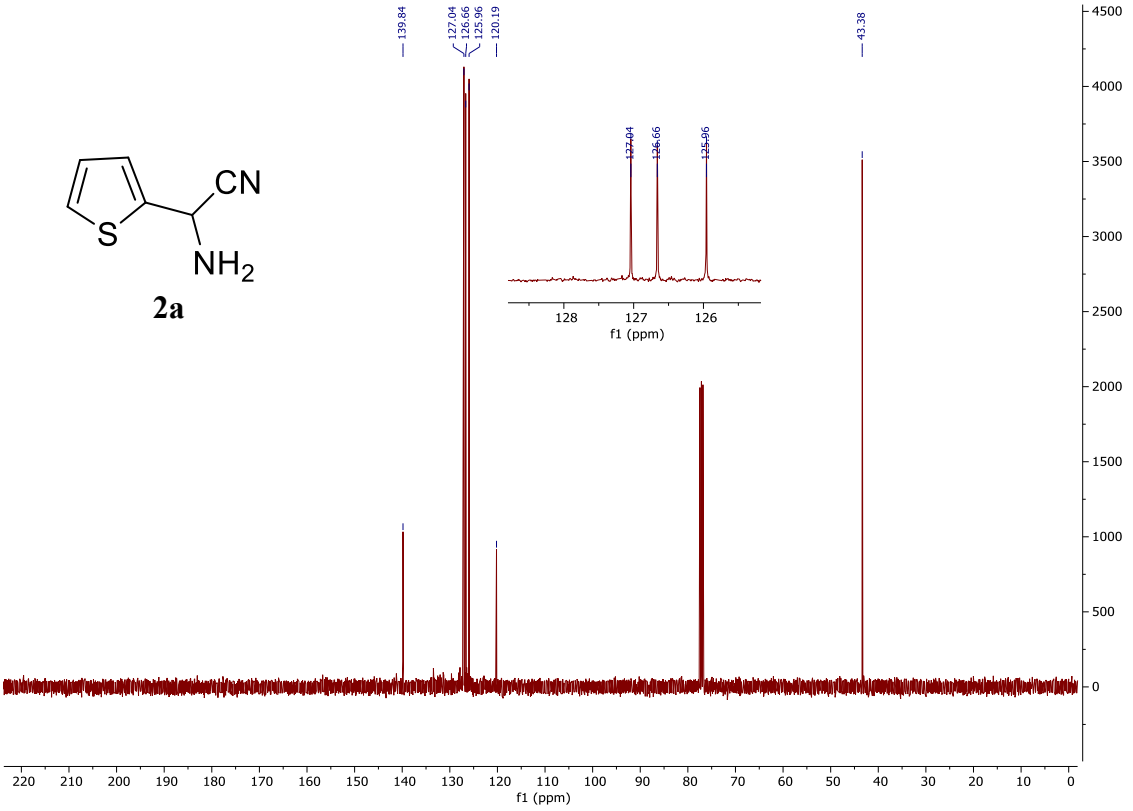

Figure S2 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 296K) of α-Amino-2-thiopheneacetonitrile **2a**.

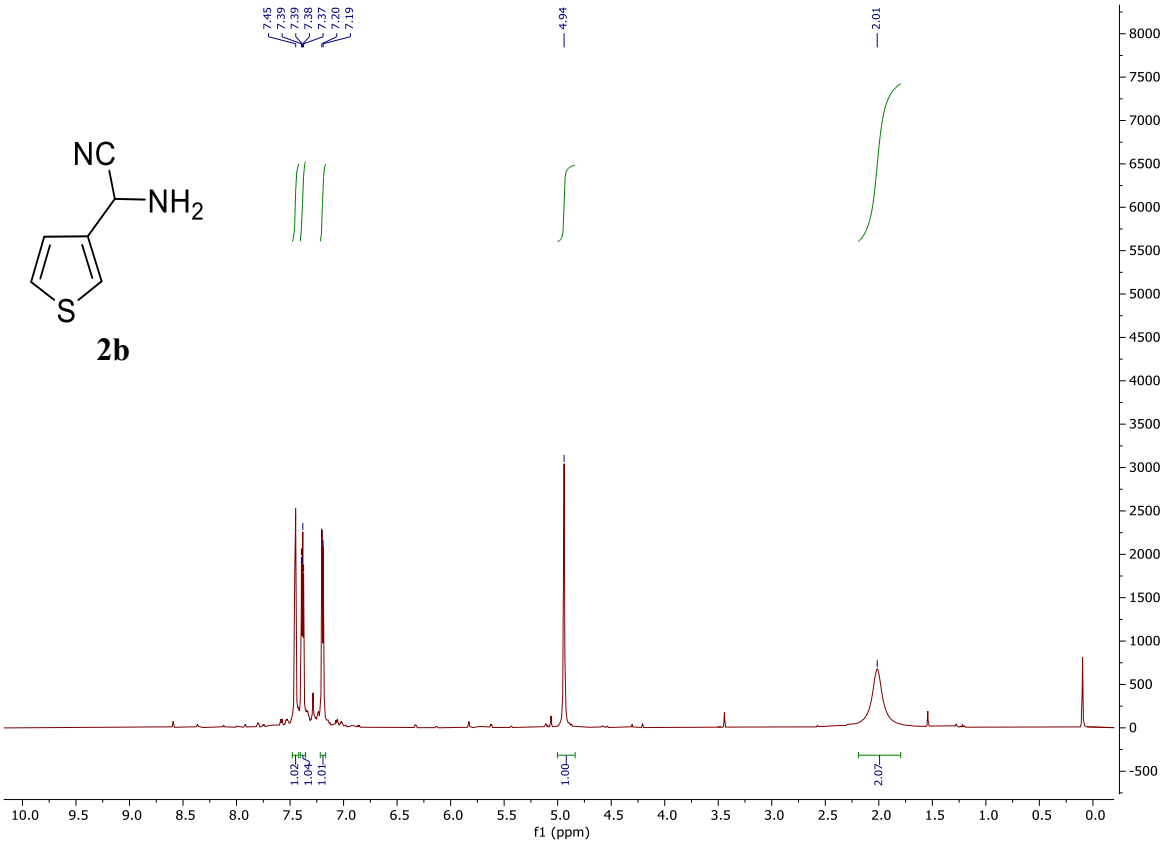

Figure S3 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of α-Amino-3-thiopheneacetonitrile **2b.**

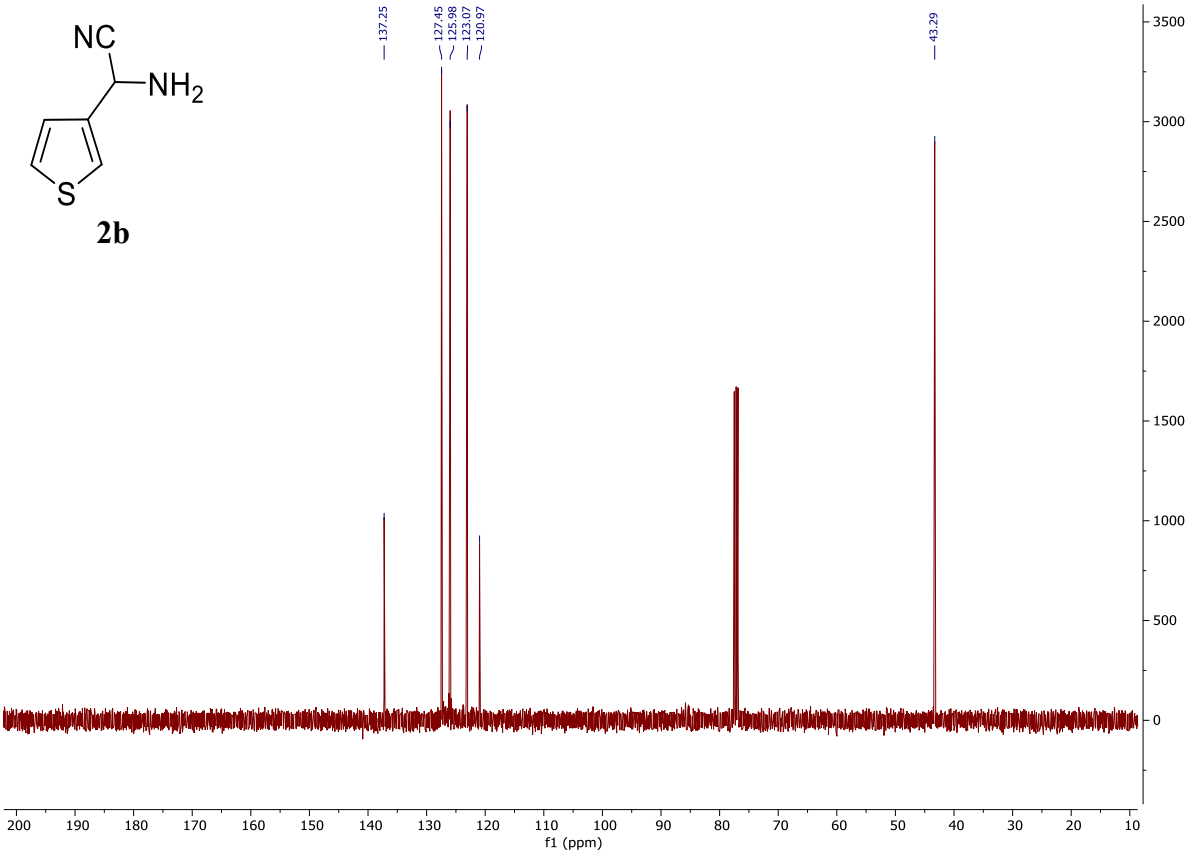

Figure S4 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 296K) of α-Amino-2-thiopheneacetonitrile **2b**.

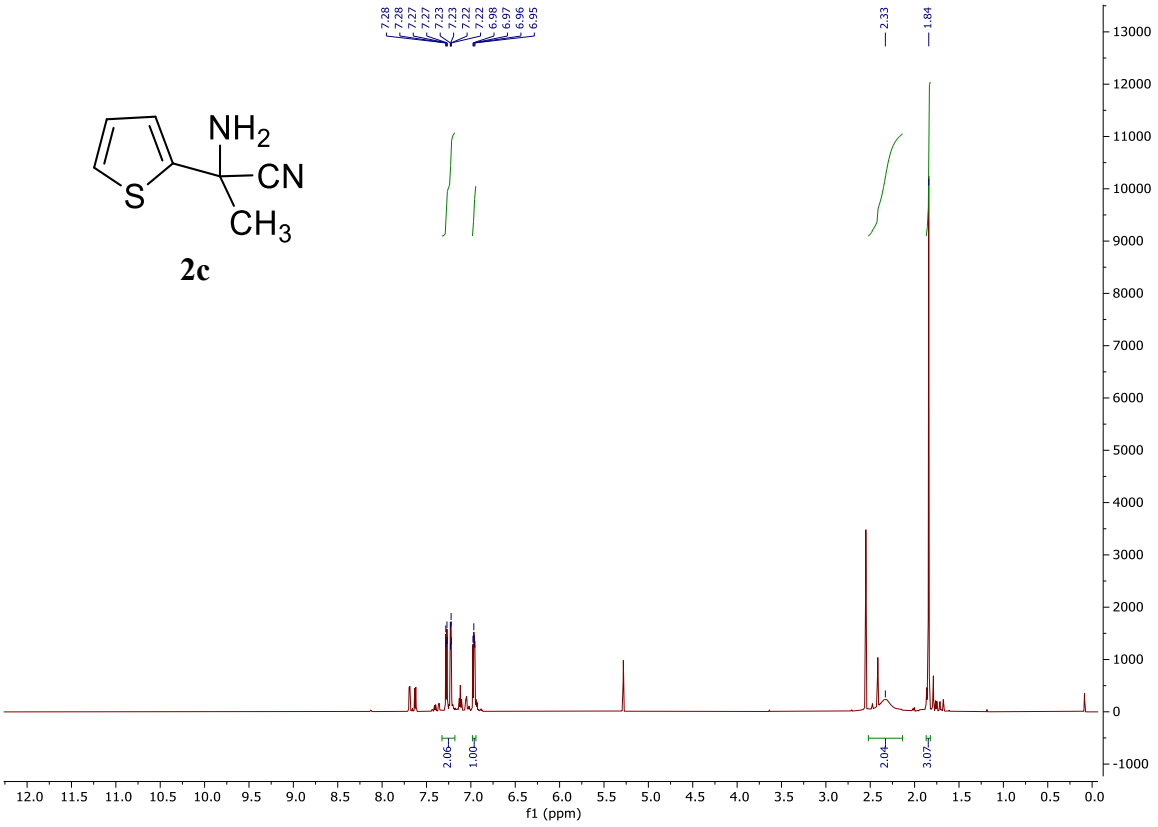

Figure S5 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of α-Amino-α-methyl-2-thiopheneacetonitrile **2c**.

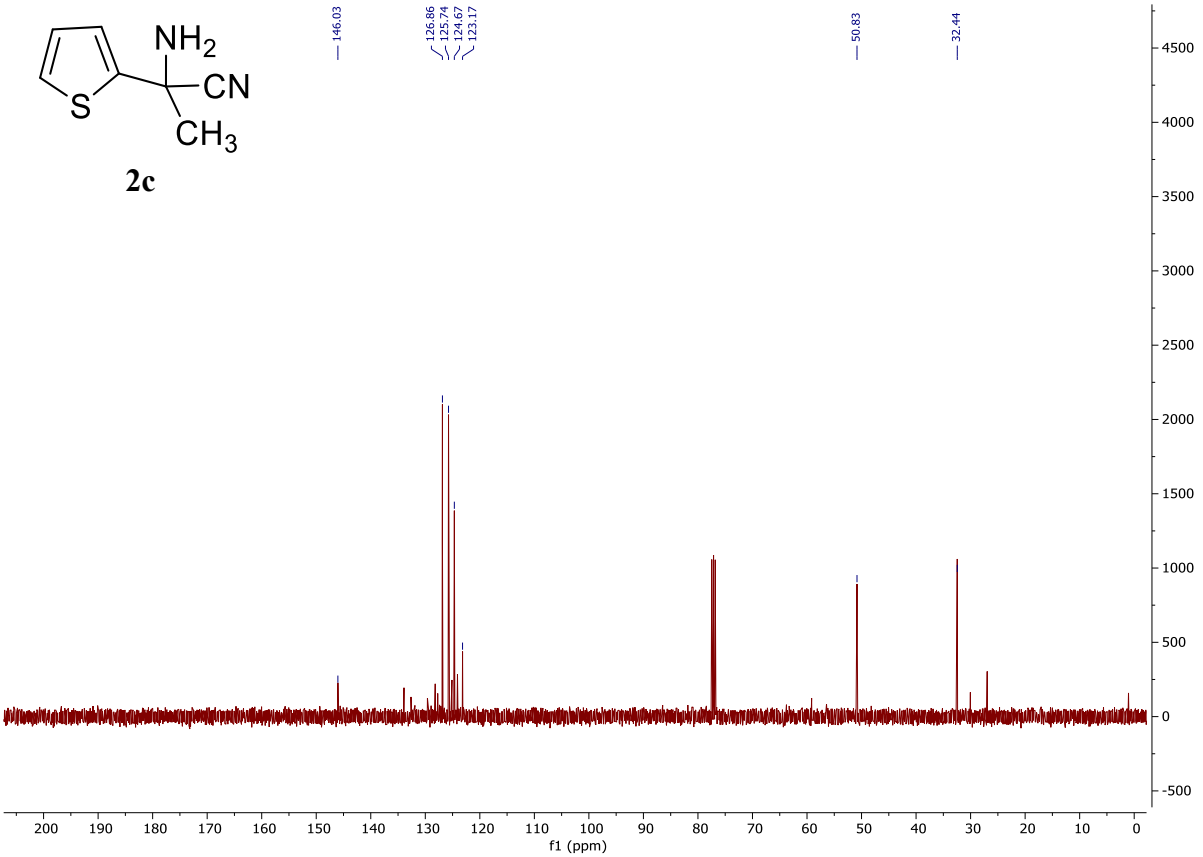

Figure S6 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 296K) of α-Amino-α-methyl-2-thiopheneacetonitrile **2c.**

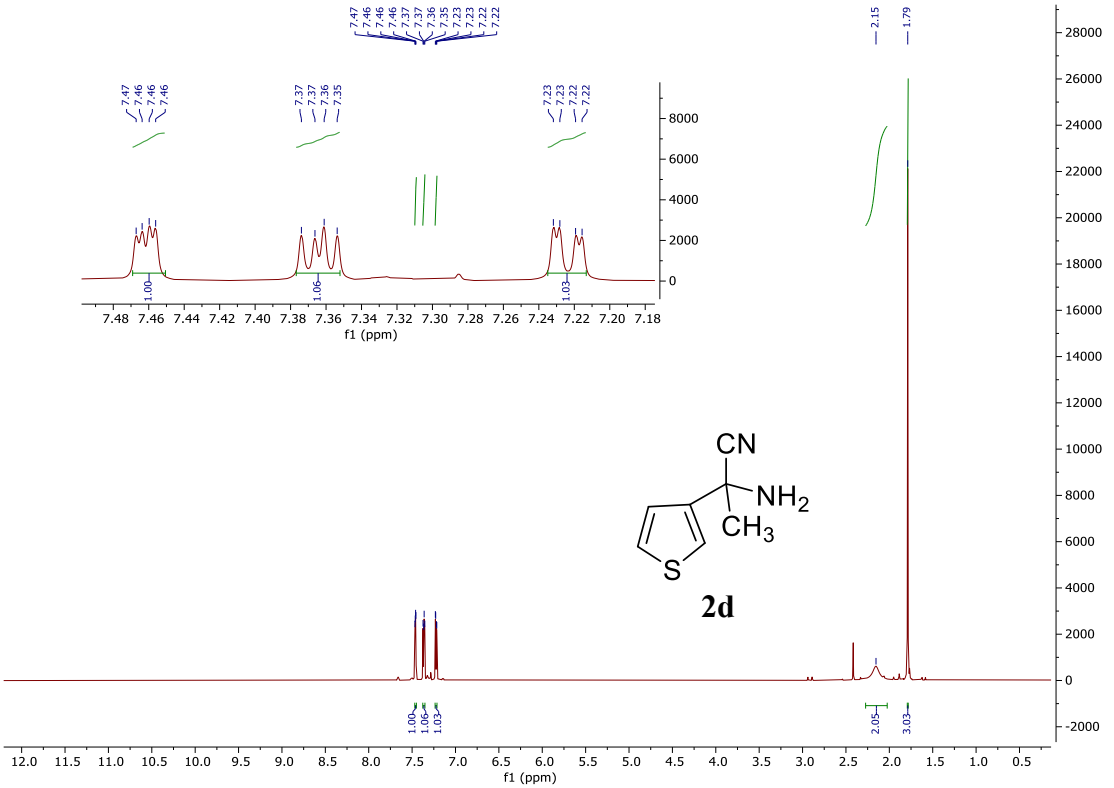

Figure S7 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of α-Amino-α-methyl-3-thiopheneacetonitrile **2d**.

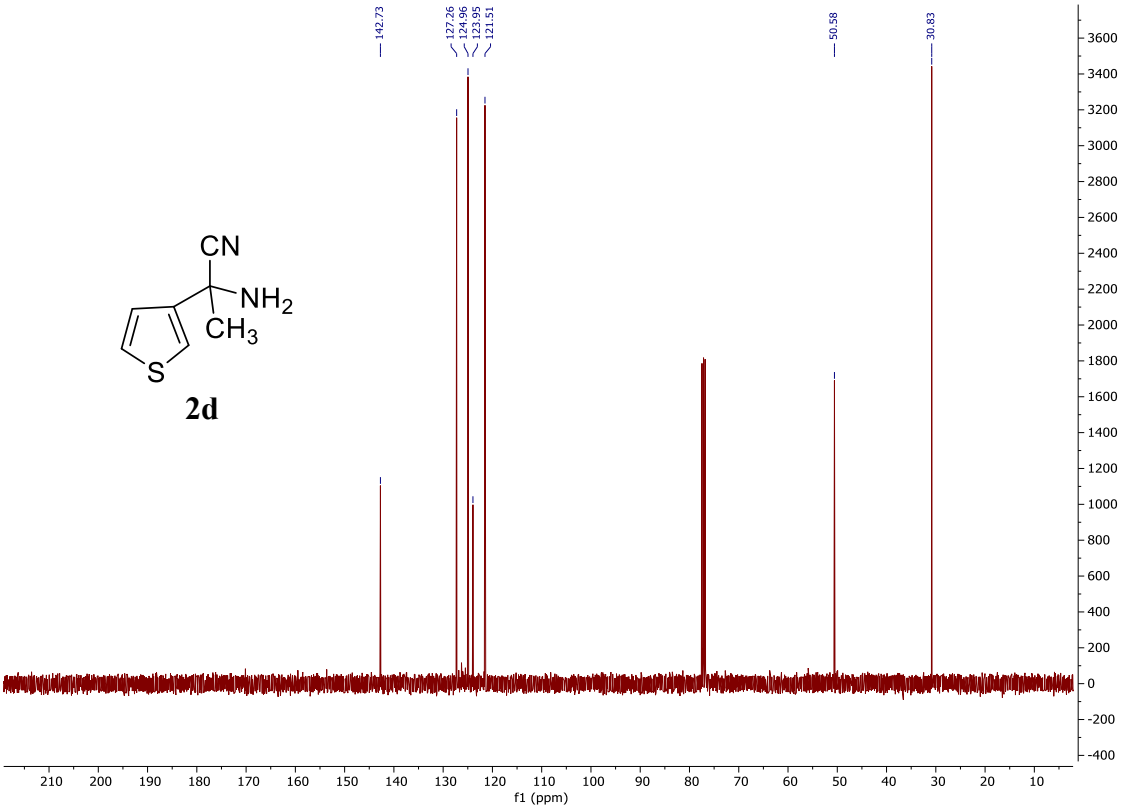

Figure S8 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 296K) of α-Amino-α-methyl-3-thiopheneacetonitrile **2d**.

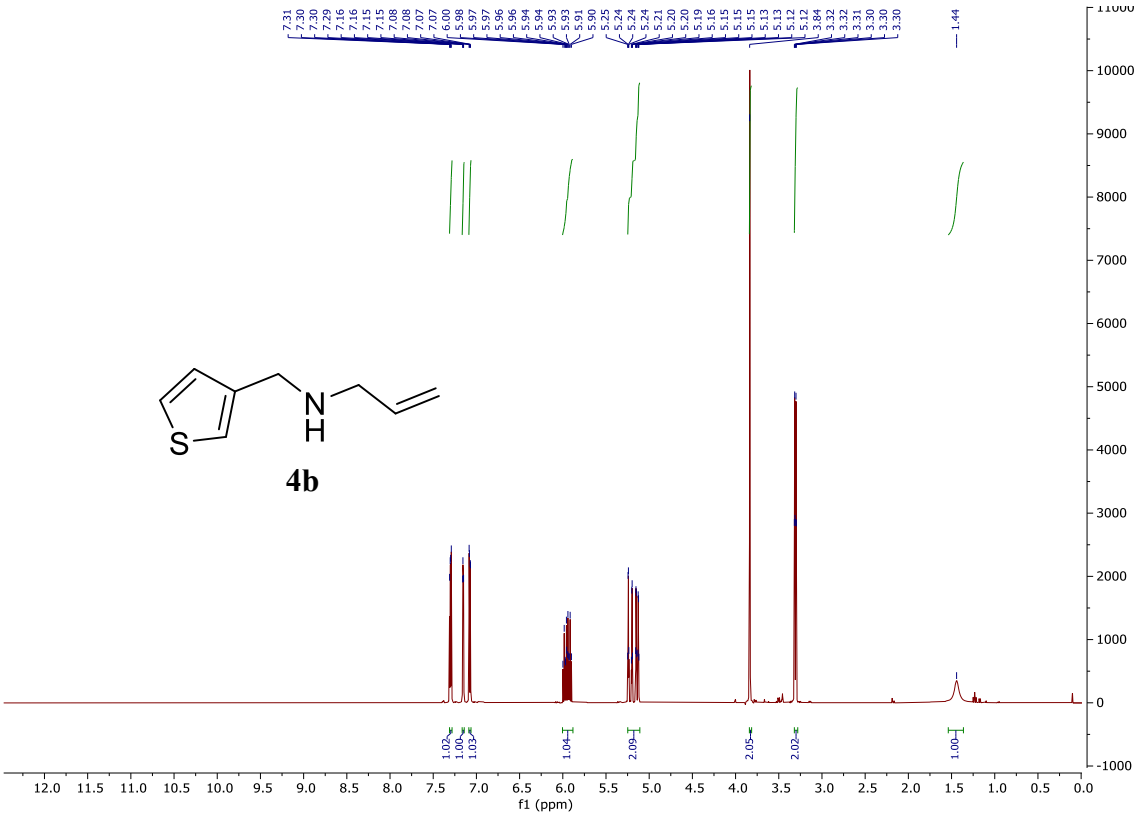

Figure S9 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *N*-2-Propen-1-yl-3-thiophenemethanamine **4b**.

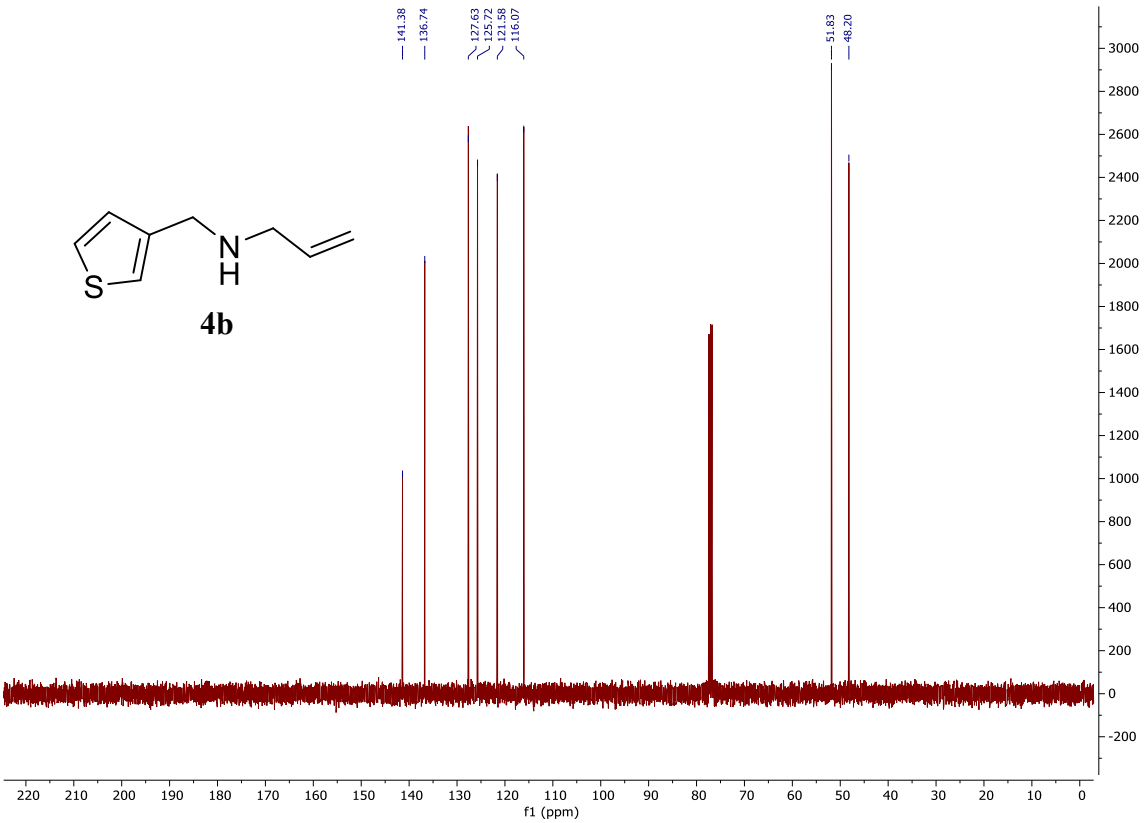

Figure S10 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 296K) of *N*-2-Propen-1-yl-3-thiophenemethanamine **4b.**

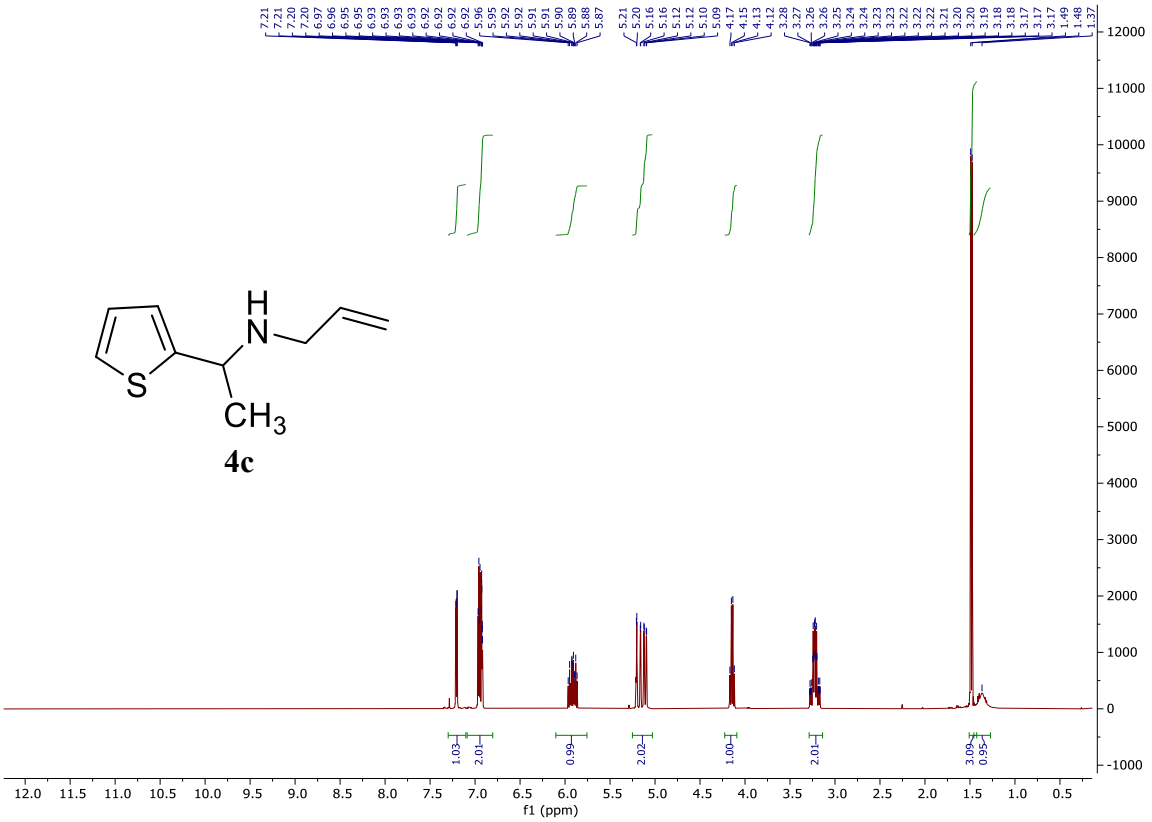

Figure S11 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of α-Methyl-*N*-2-propen-1-yl-2-thiophenemethanamine **4c**.

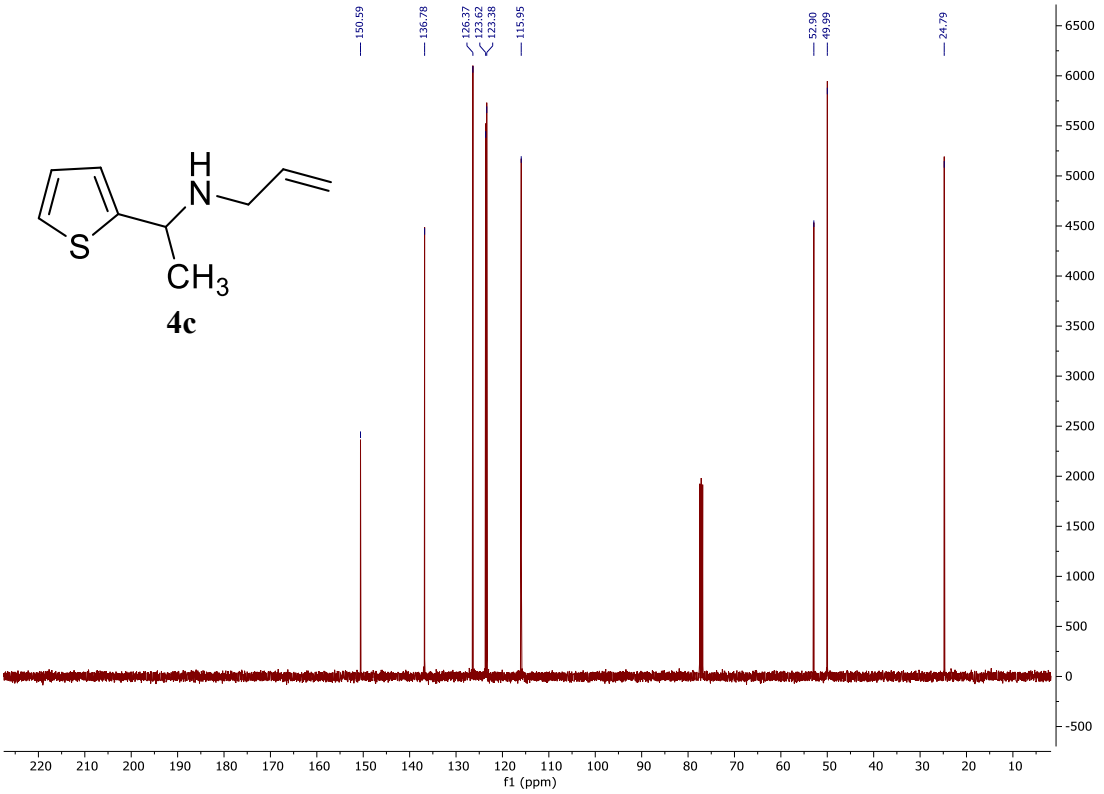

Figure S12 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 296K) of α-Methyl-*N*-2-propen-1-yl-2-thiophenemethanamine **4c**.

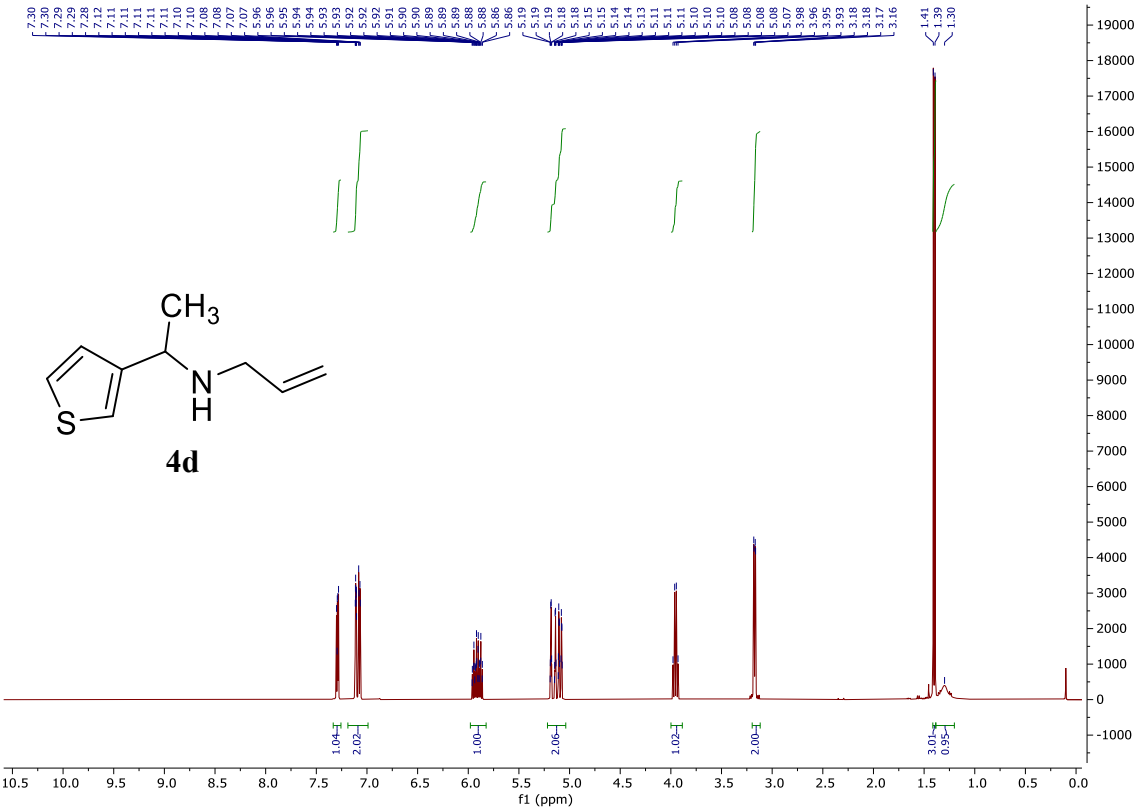

Figure S13 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of α-Methyl-*N*-2-propen-1-yl-3-thiophenemethanamine **4d.**

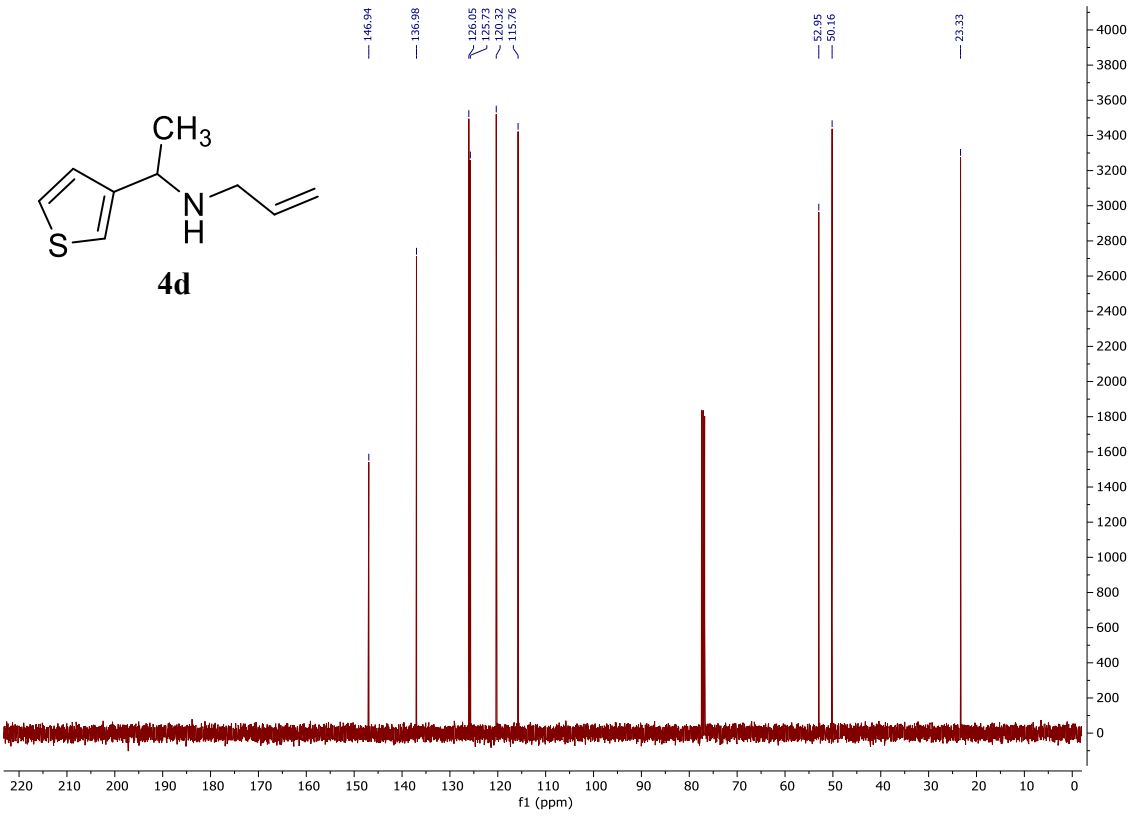

Figure S14 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 296K) of α-Methyl-*N*-2-propen-1-yl-3-thiophenemethanamine **4d.**

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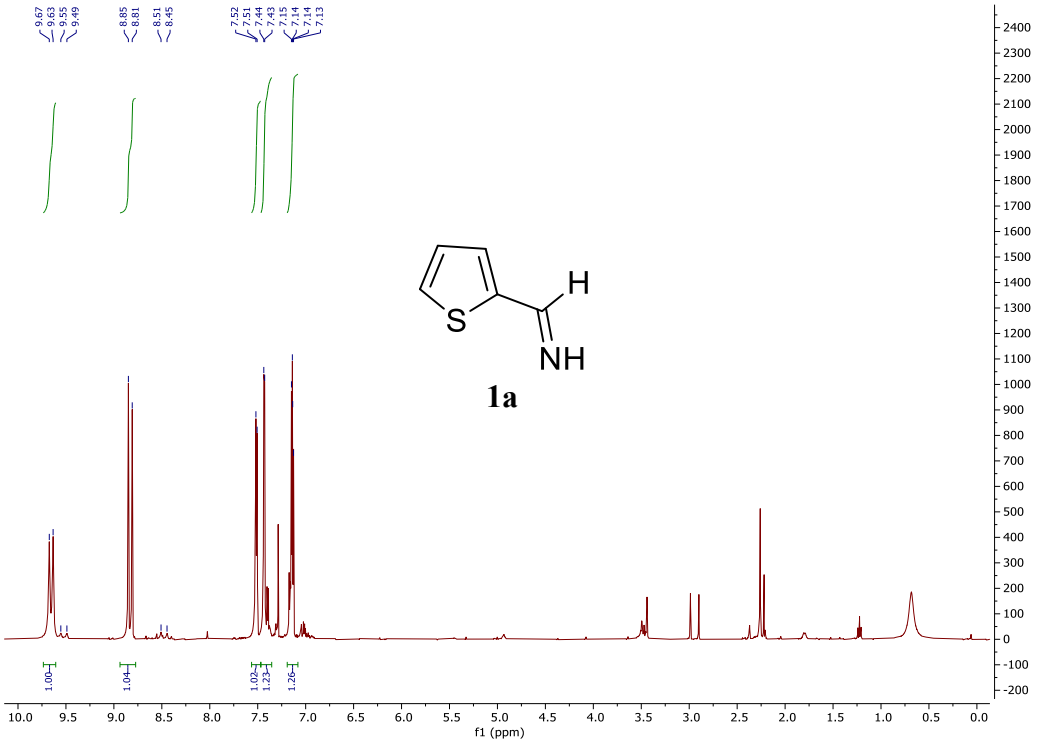

Figure S15 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-2-thiophenemethanimine **1a** (Route A).

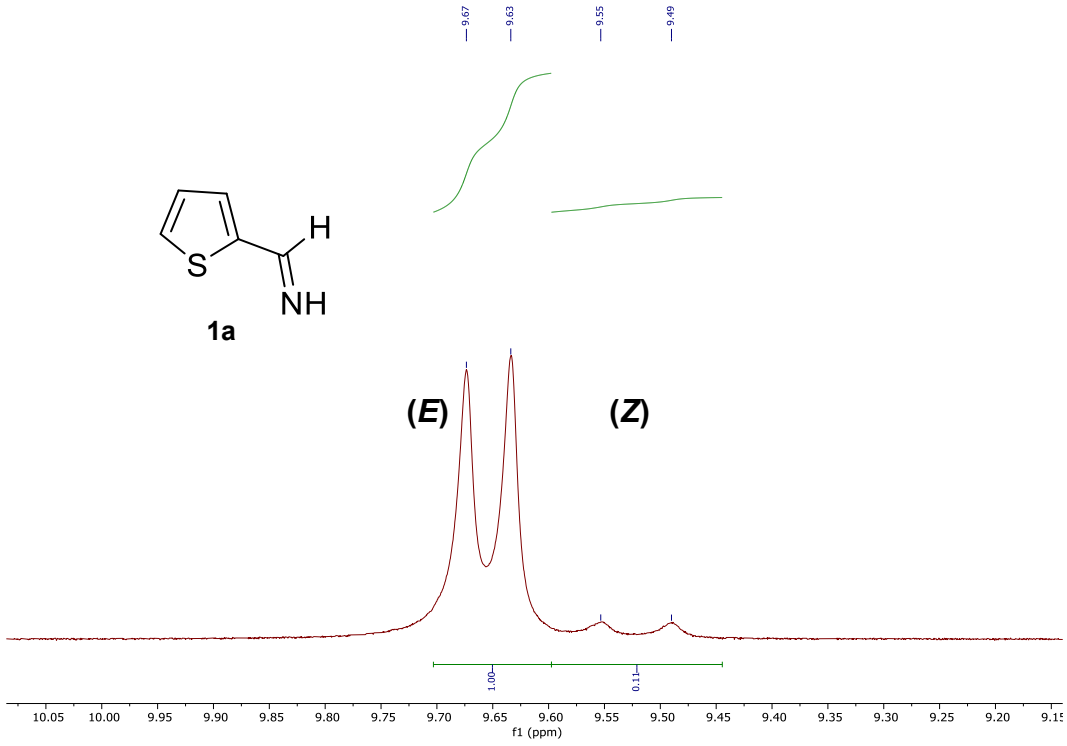

Figure S16 N-H signal on the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-2-thiophenemethanimine **1a** (Route A).

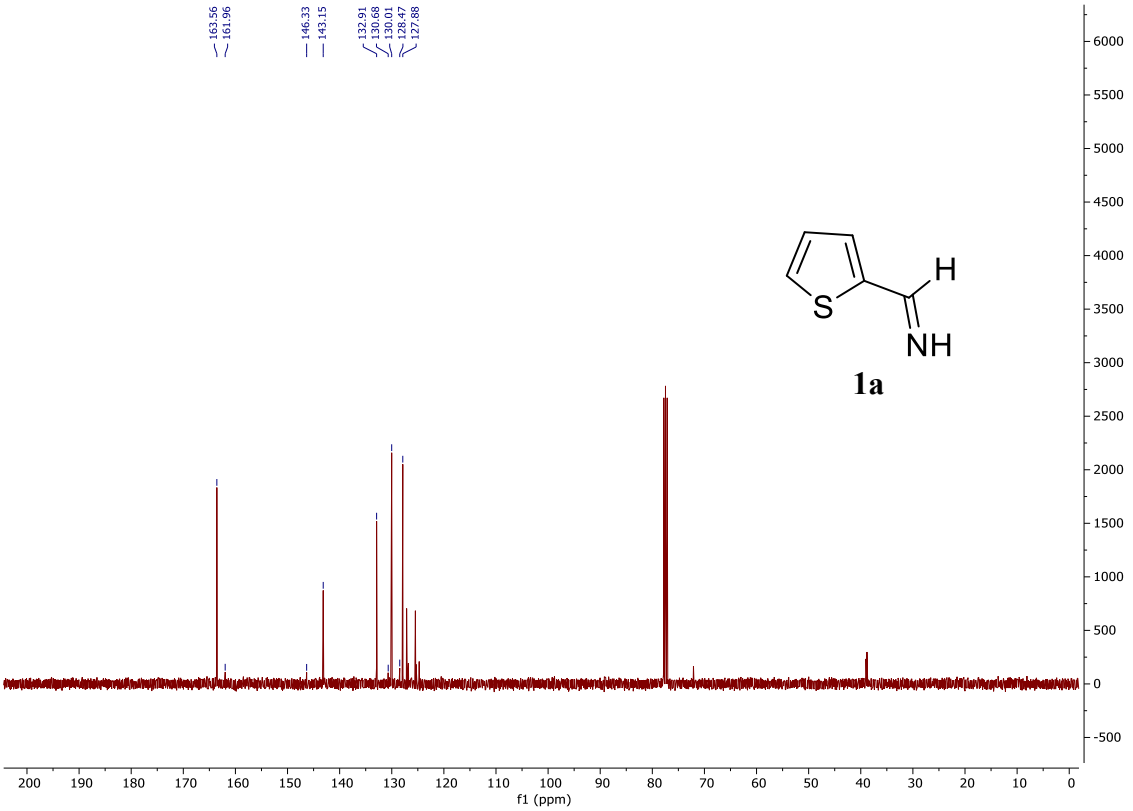

Figure S17 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 223K) of (*Z*)- and (*E*)-2-thiophenemethanimine **1a** (Route A).

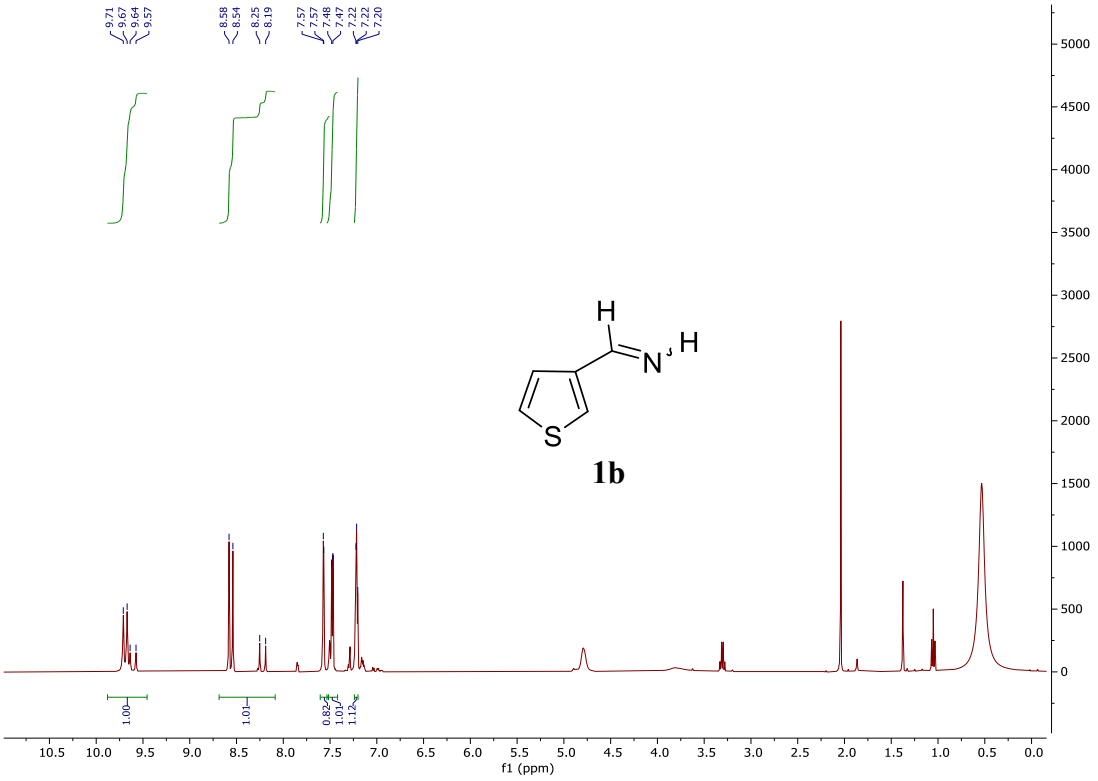

Figure S18 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-3-thiophenemethanimine **1b** (Route A).

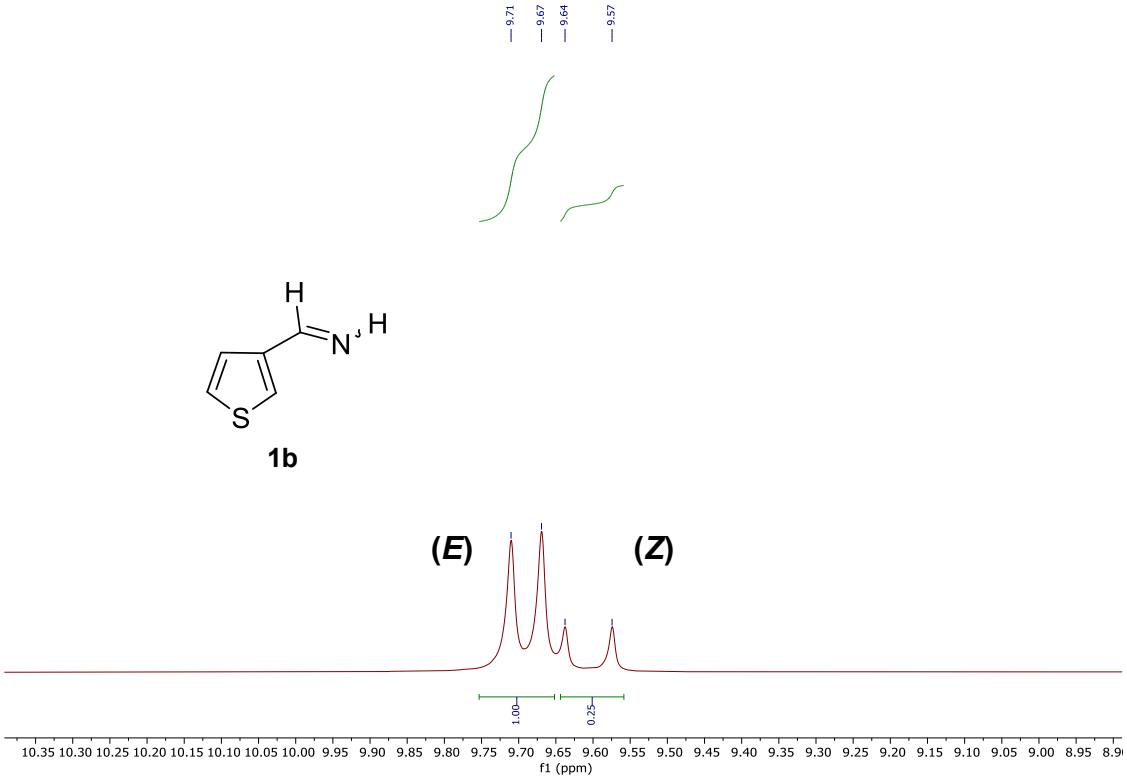

Figure S19 N-H signals on the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-3-thiophenemethanimine **1b** (Route A).

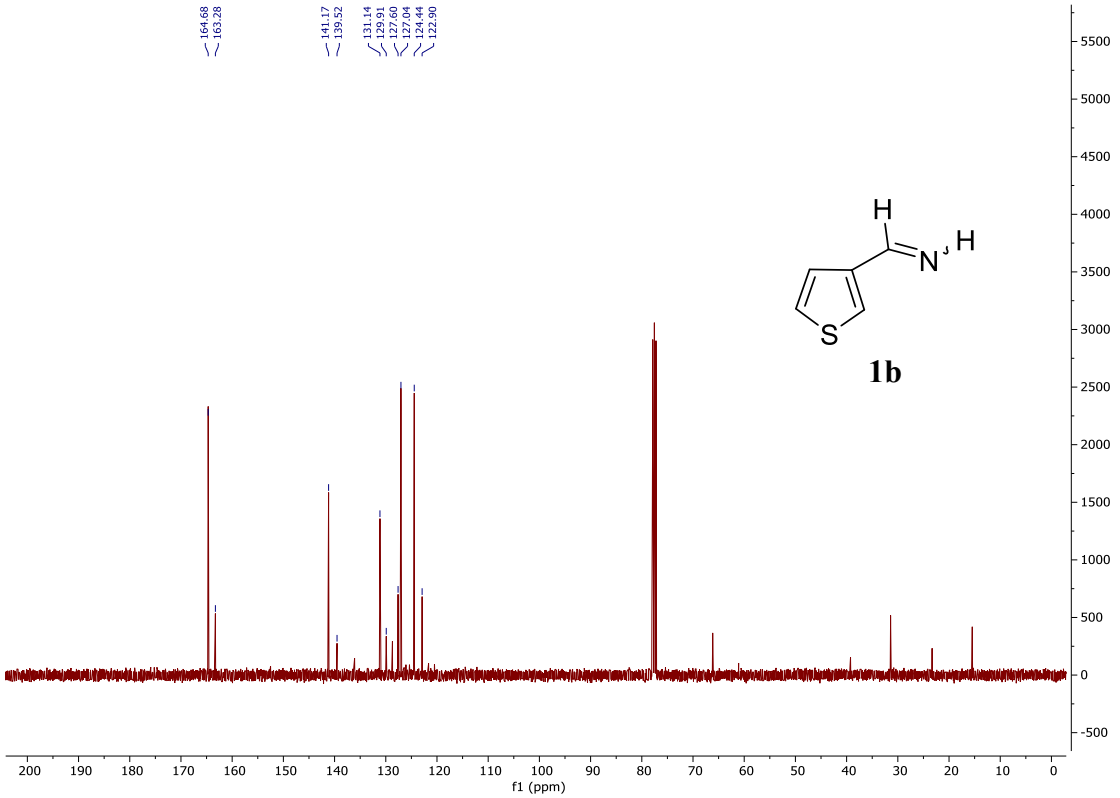

Figure S20 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 223K) of (*Z*)- and (*E*)-3-thiophenemethanimine **1b** (Route A).

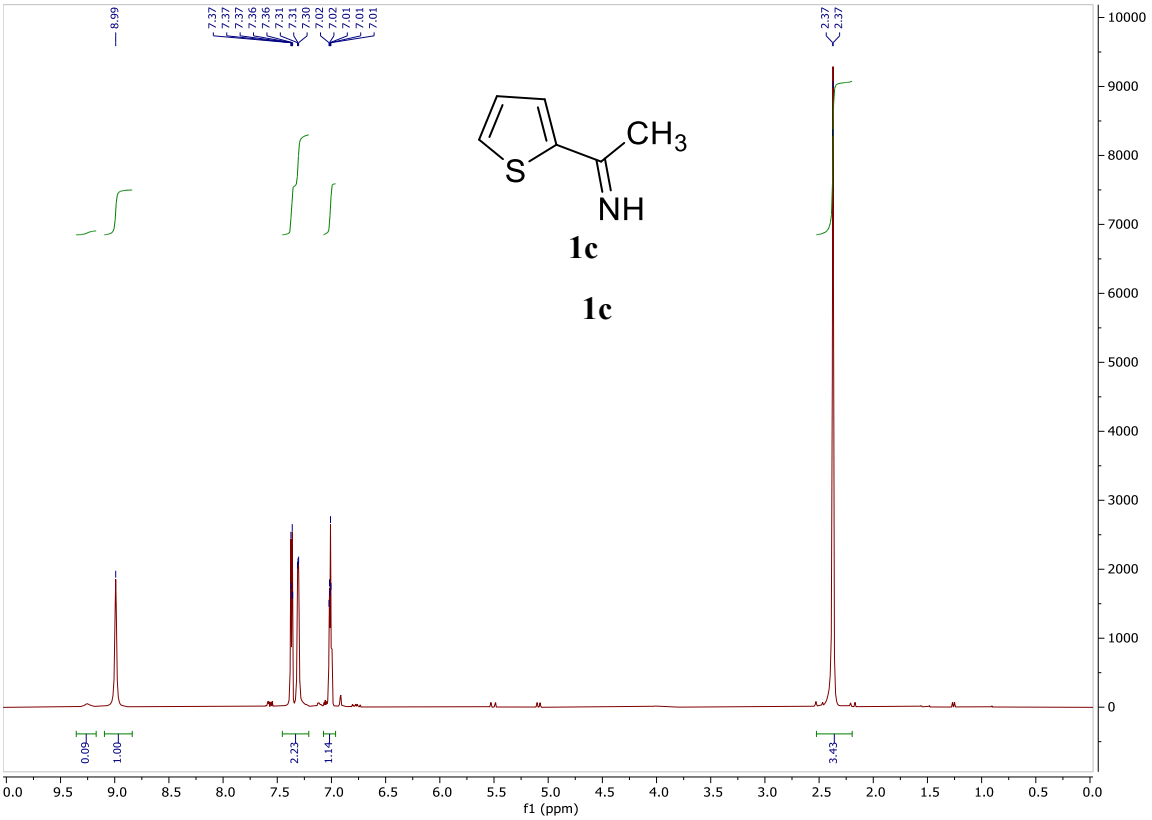

Figure S21 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-α-Methyl-2-thiophenemethanimine **1c** (Route B).

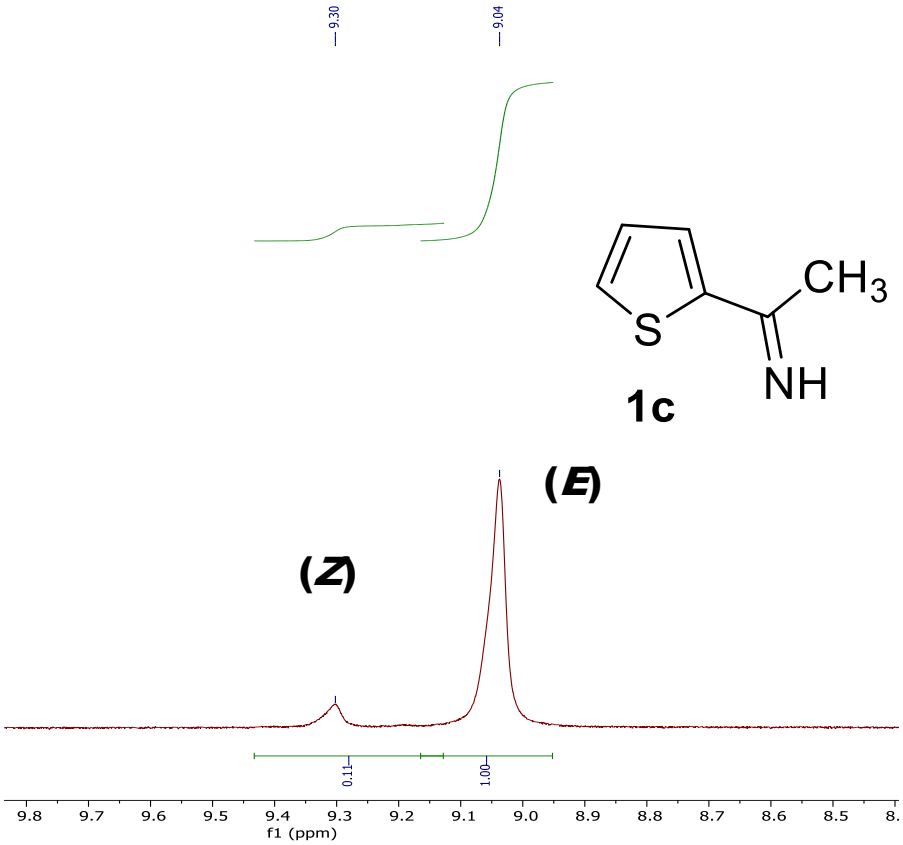

Figure S22 N-H signals on the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-α-Methyl-2-thiophenemethanimine **1c** (Route A).

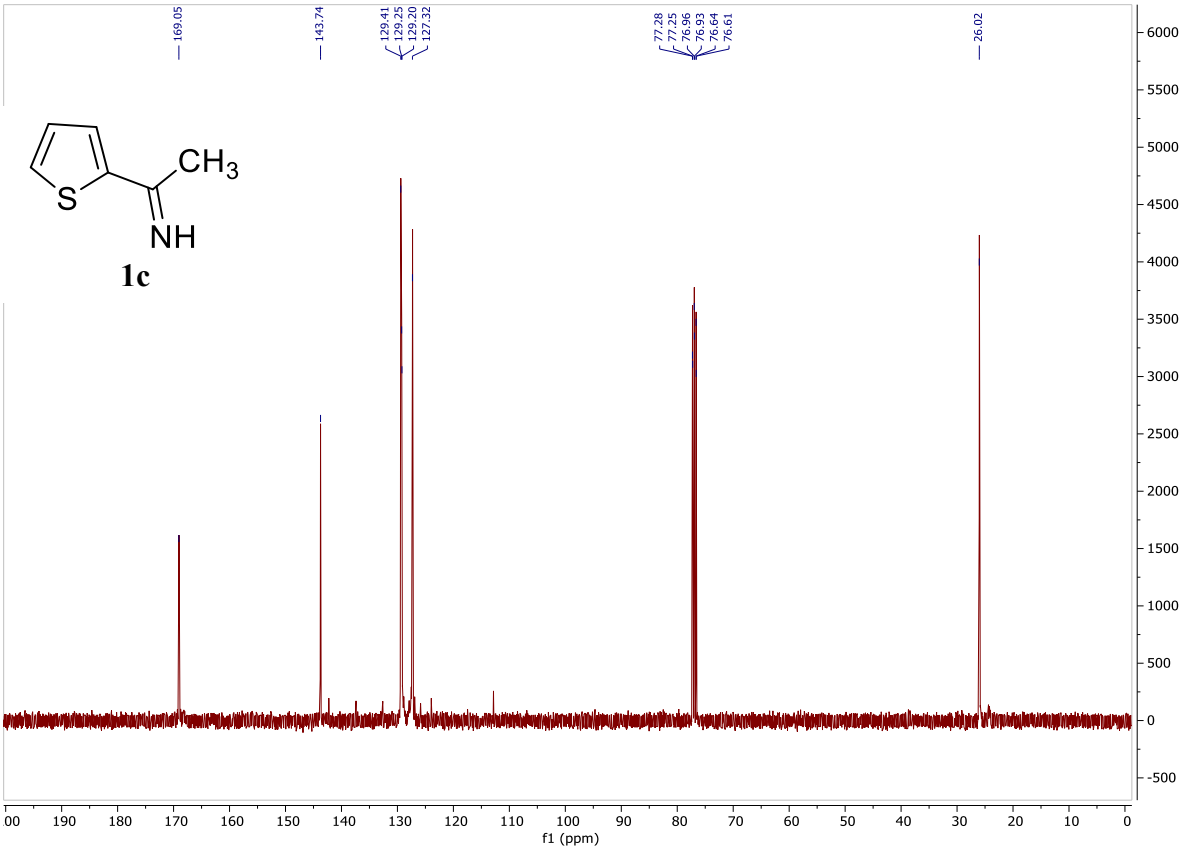

Figure S23 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 223K) of (*Z*)- and (*E*)-α-Methyl-2-thiophenemethanimine **1c** (Route B).

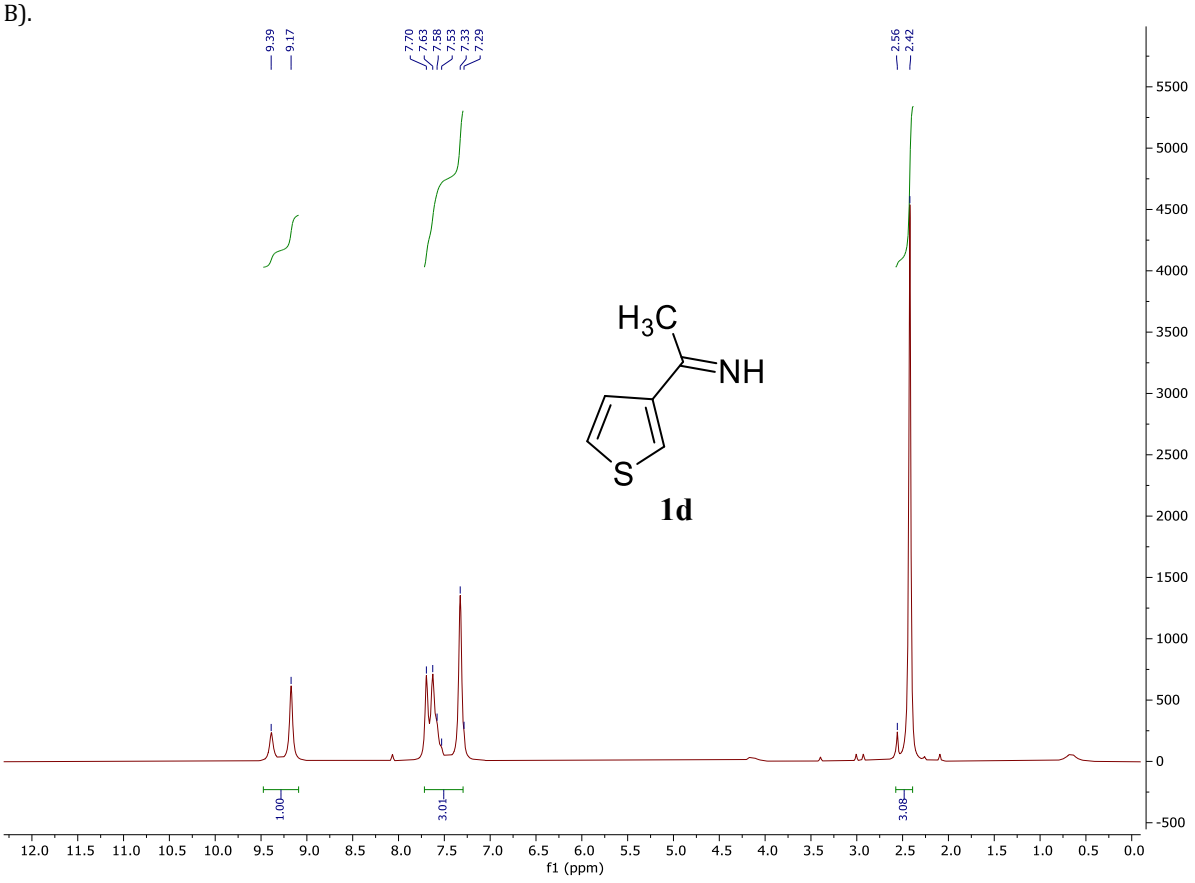

Figure S24 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-α-methyl-3-thiophenemethanimine **1d** (Route A).

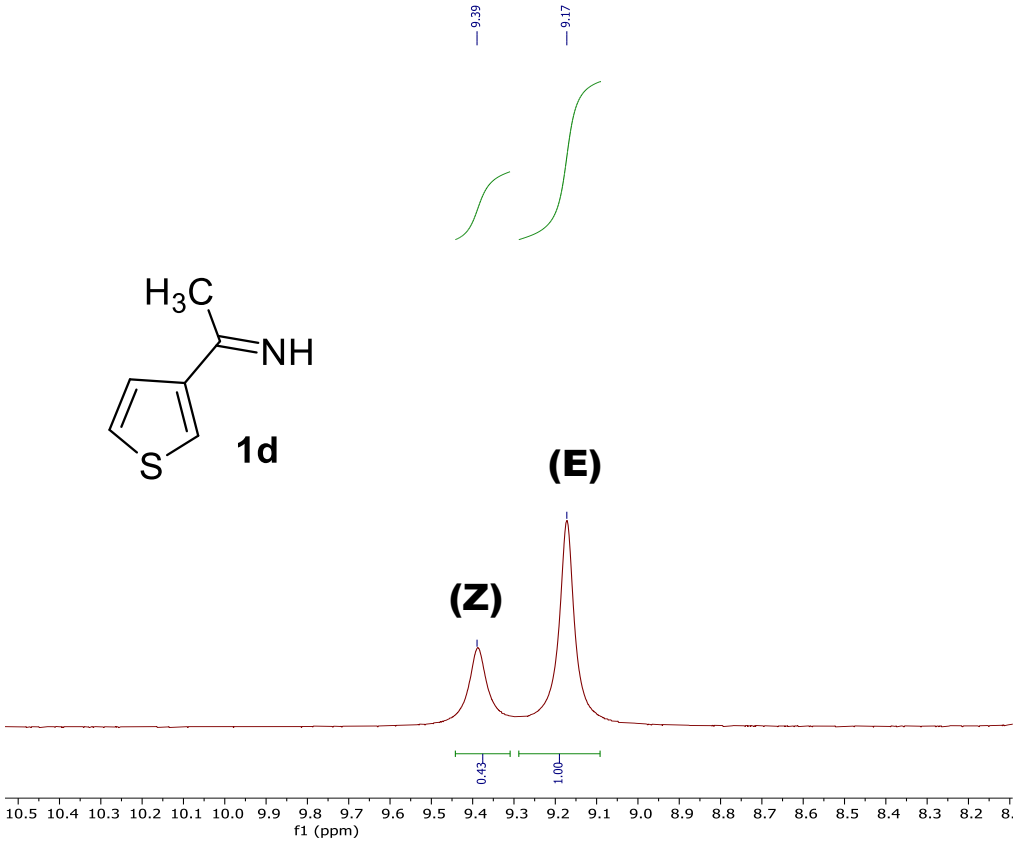

Figure S25 N-H signals on the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 223K) of (*Z*)- and (*E*)-α-methyl-3-thiophenemethanimine **1d** (Route A).

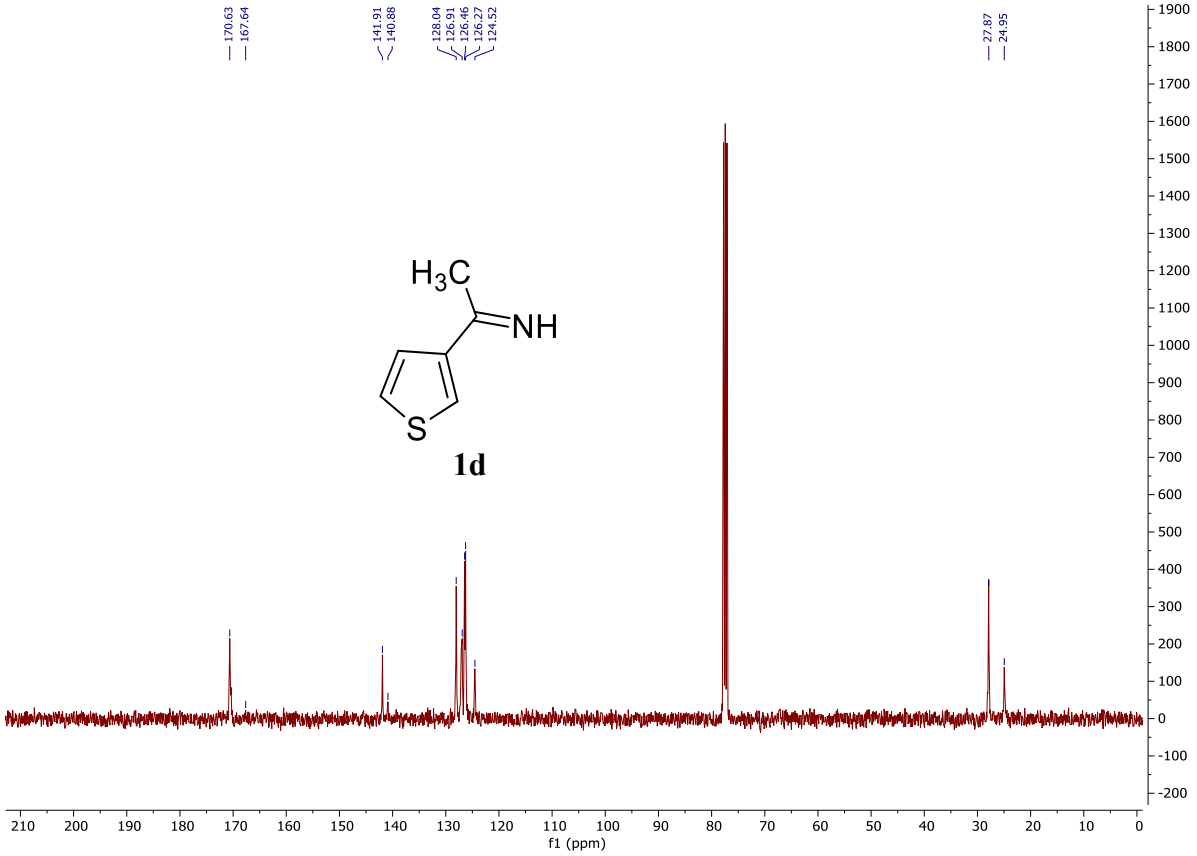

Figure S24 ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 223K) of (*Z*)- and (*E*)-α-Methyl-3-thiophenemethanimine **1d** (Route A).

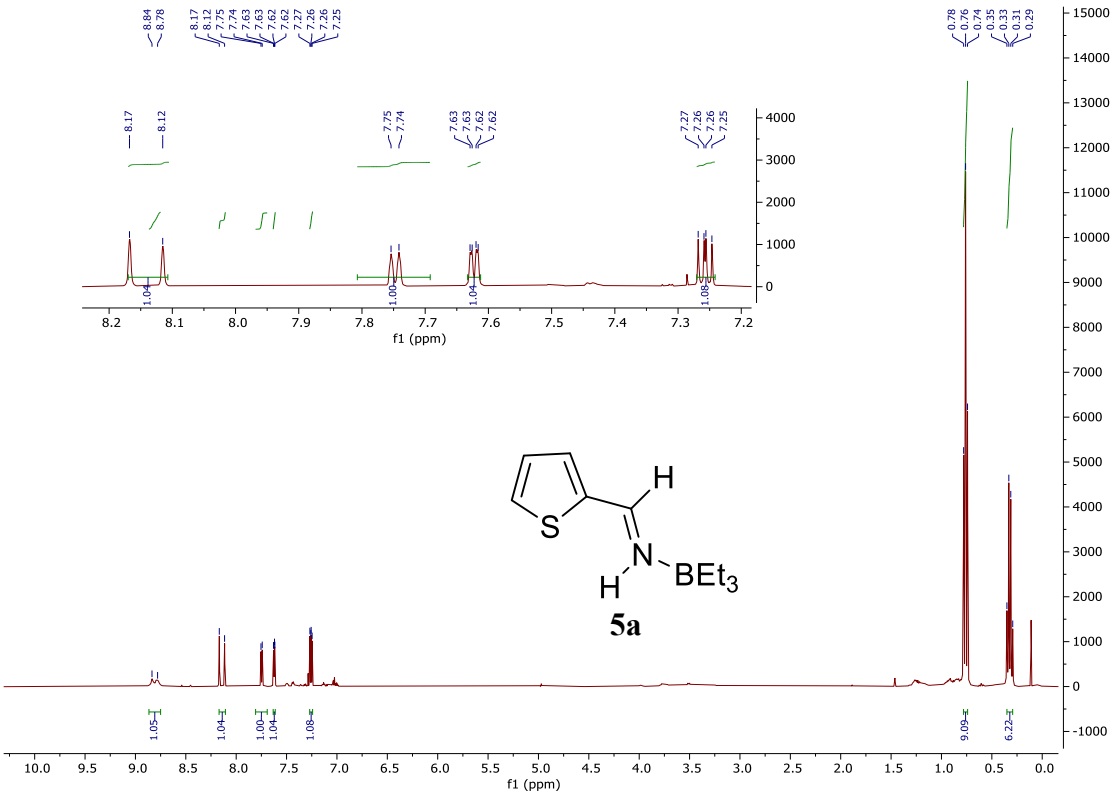

Figure S25 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)*-(*T*-4)-Triethyl[(α*E*)-2-thiophenemethanimine-κN^2]boron **5a**

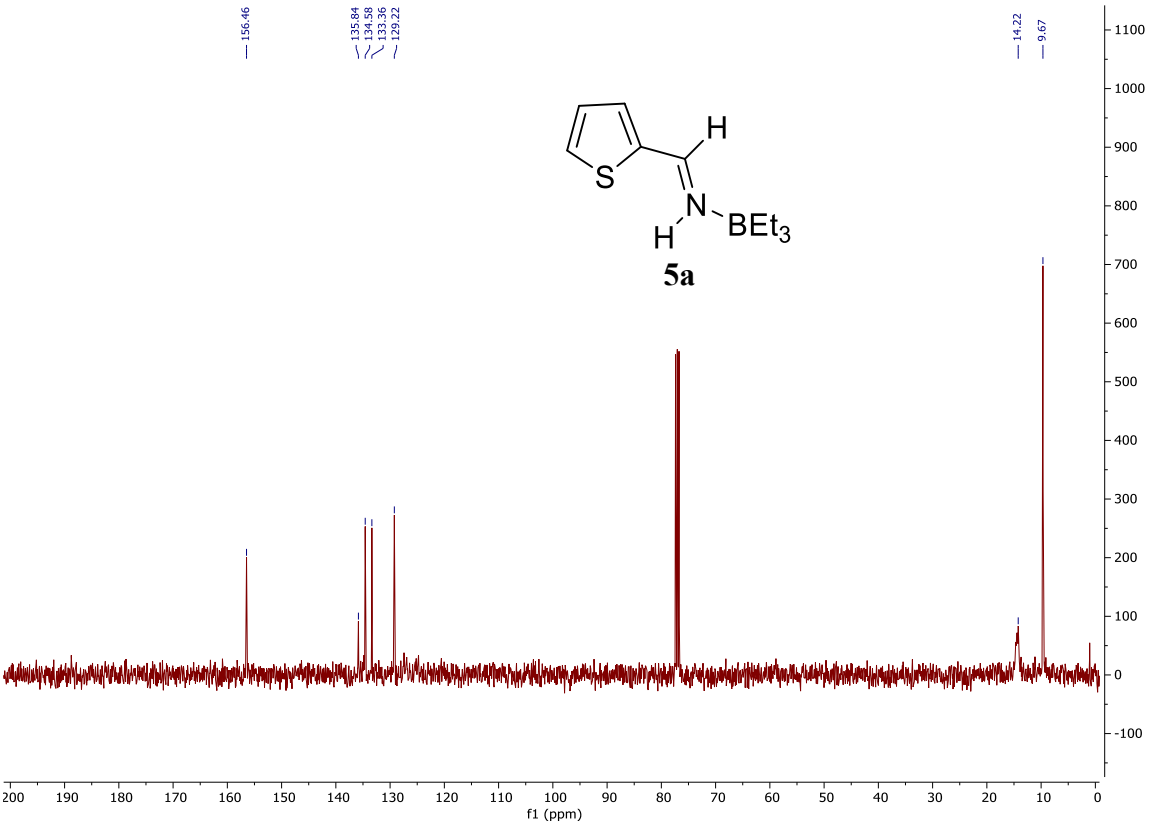

Figure S26 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)*-(*T*-4)-Triethyl[(α*E*)-2-thiophenemethanimine-κN^2]boron **5a**

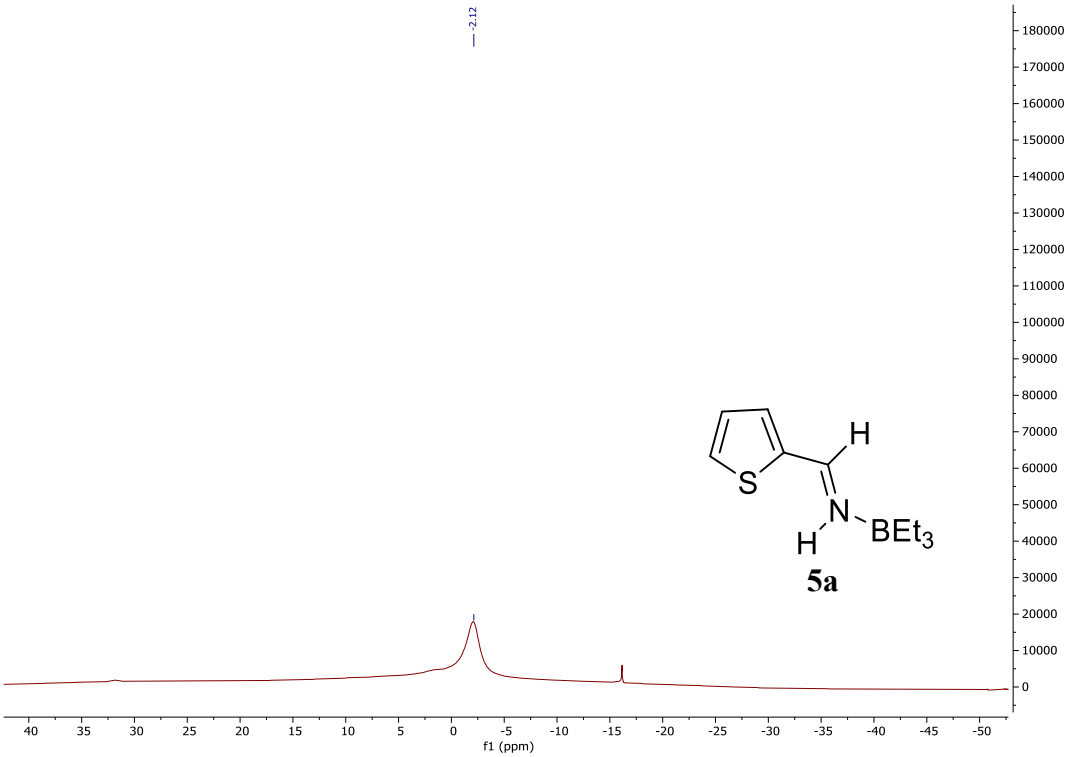

Figure S27 ^{11}B NMR spectrum ($CDCl_3$, 400 MHz, 296K) of (*(E)*-(*T*-4)-Triethyl[(α*E*)-2-thiophenemethanimine-κN^2]boron **5a**

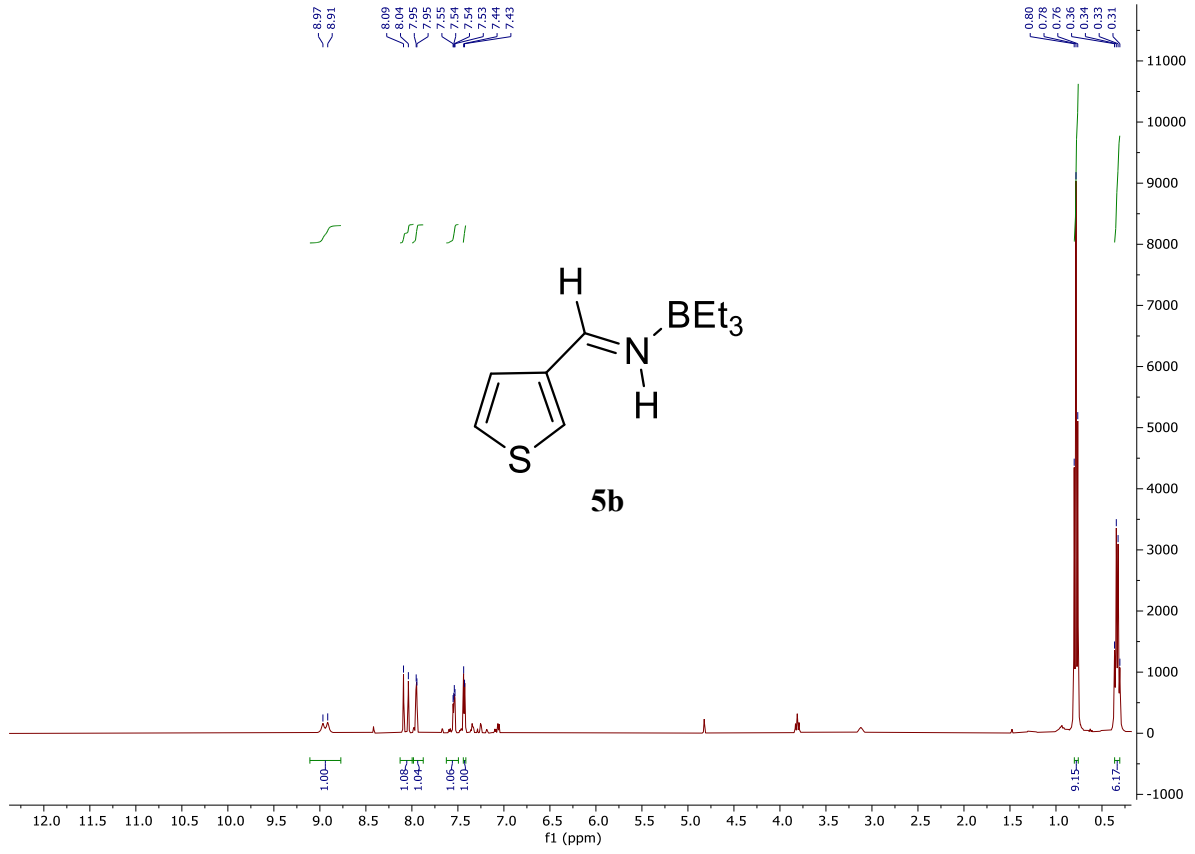

Figure S28 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)*-(*T*-4)-Triethyl[(α*E*)-3-thiophenemethanimine-κN^2]boron **5b**

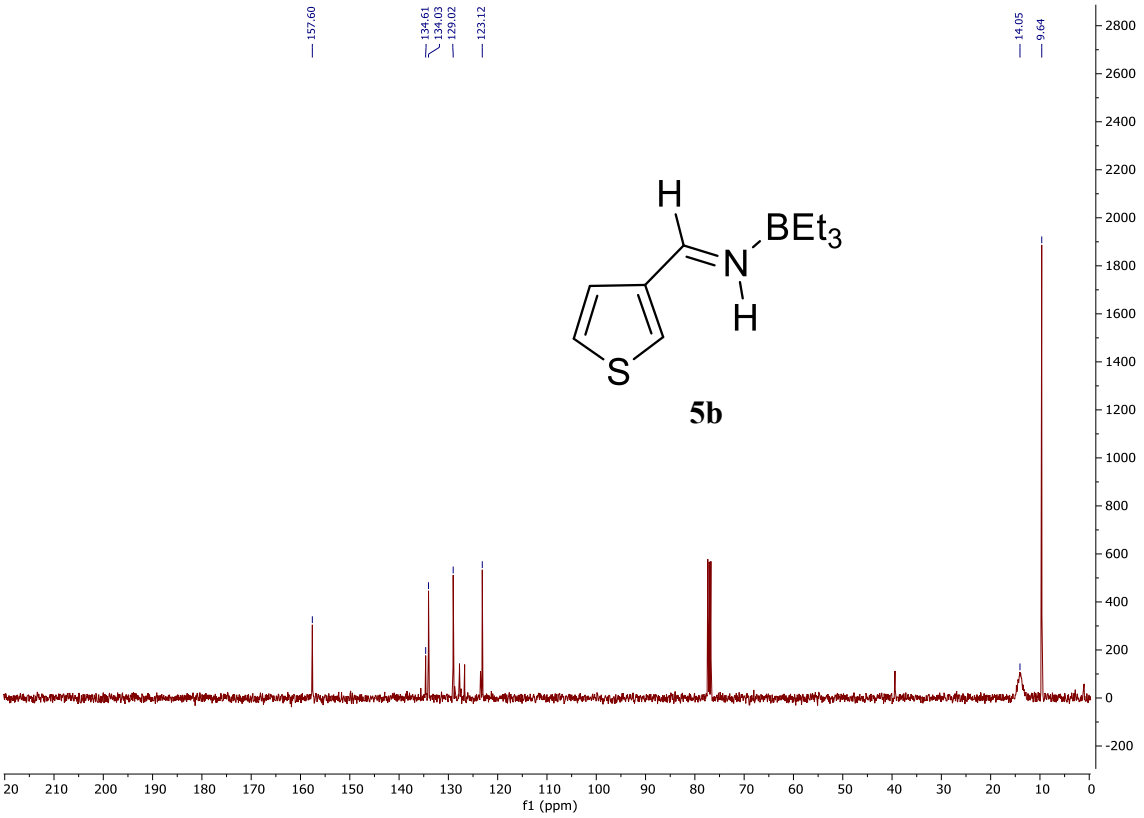

Figure S29 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)*-(*T*-4)-Triethyl[(α*E*)-3-thiophenemethanimine-κN^2]boron **5b**

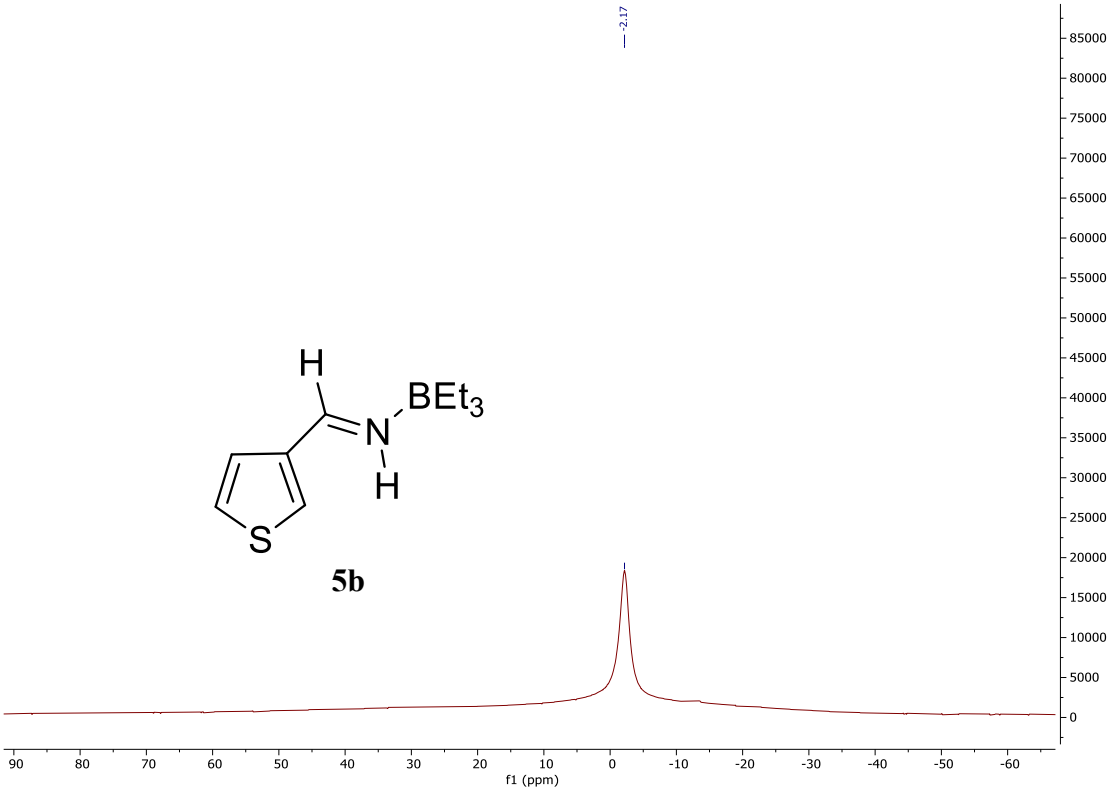

Figure S30 ^{11}B NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)*-(*T*-4)-Triethyl[(α*E*)-3-thiophenemethanimine-κN^2]boron **5b**.

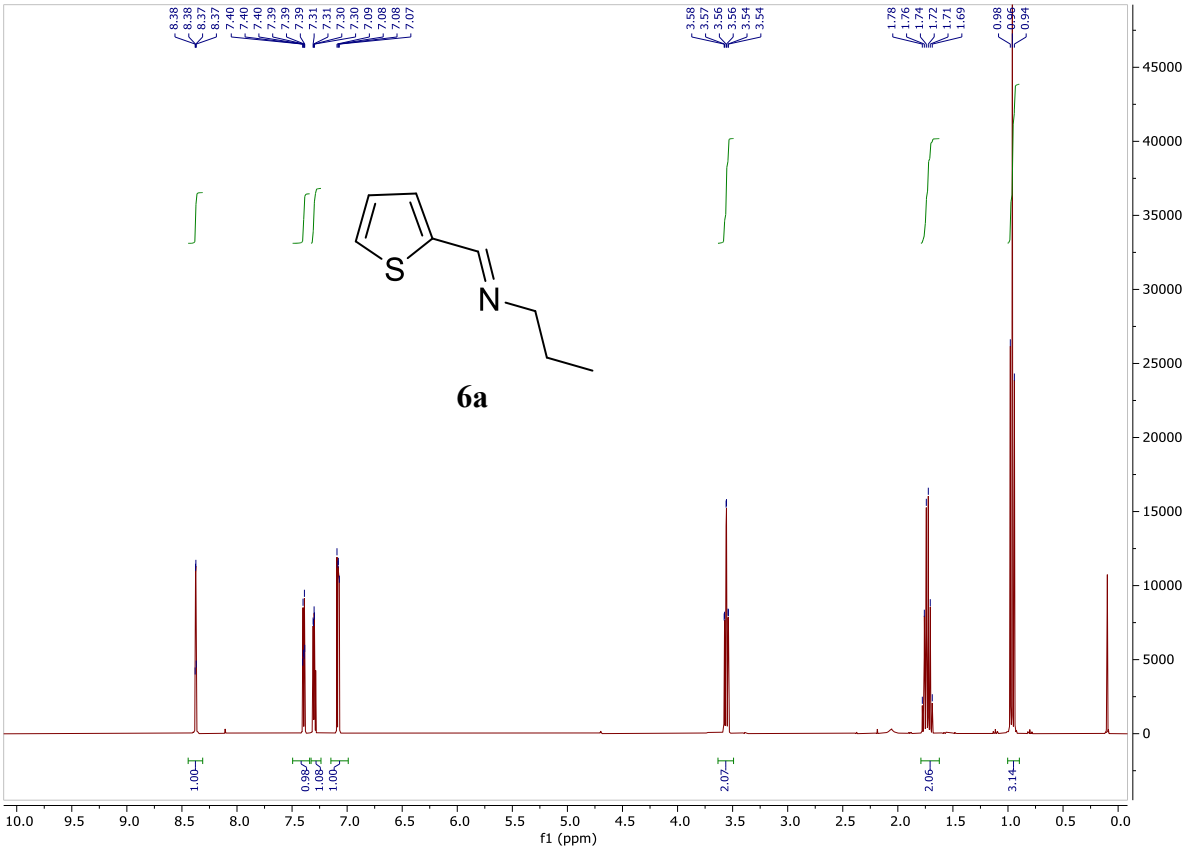

Figure S31 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)*-N-(2-Thienylmethylene)-1-propanamine **6a**.

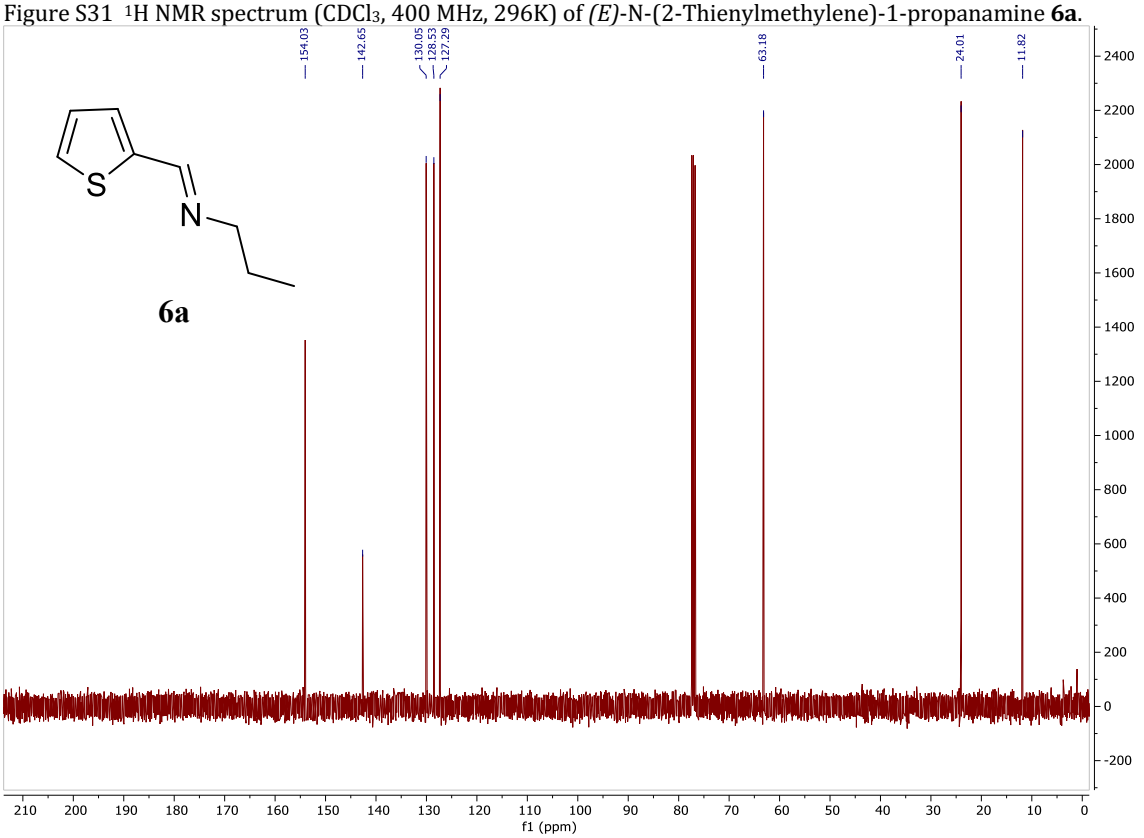

Figure S32 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)*-N-(2-Thienylmethylene)-1-propanamine **5a**.

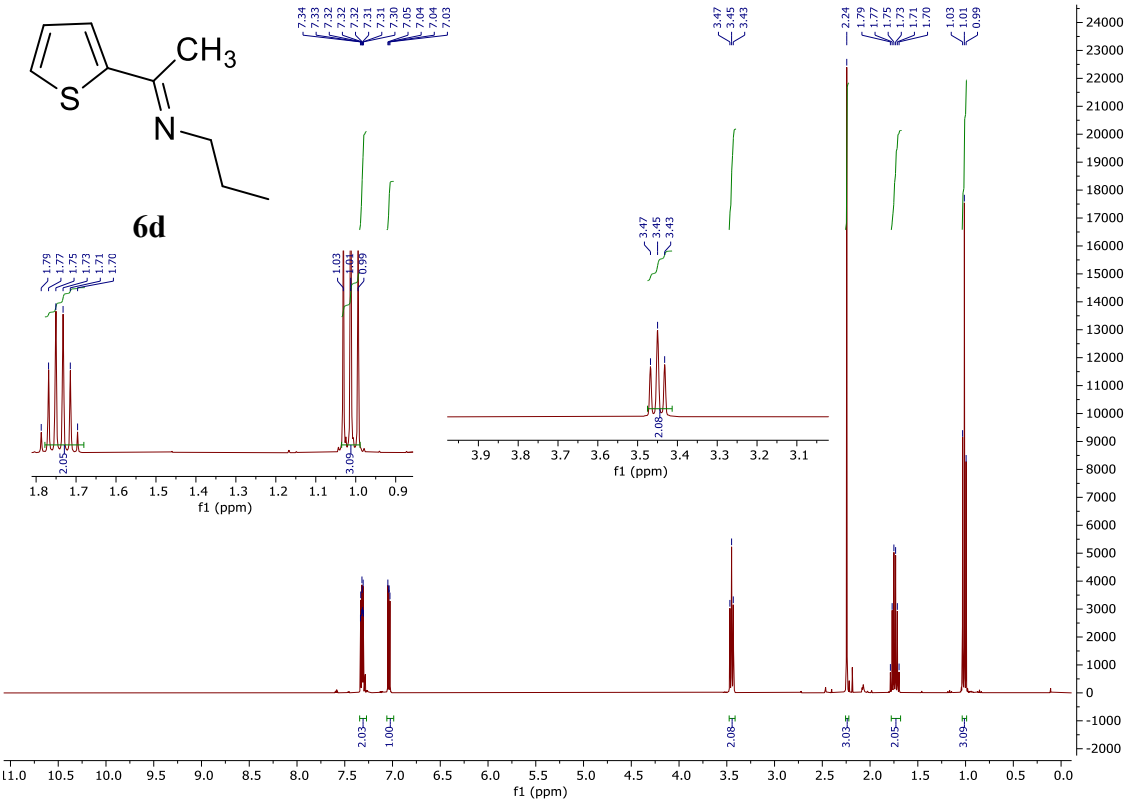

Figure S33 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)-N*-[1-(2-Thienyl)ethylene]-1-propanamine **6d**.

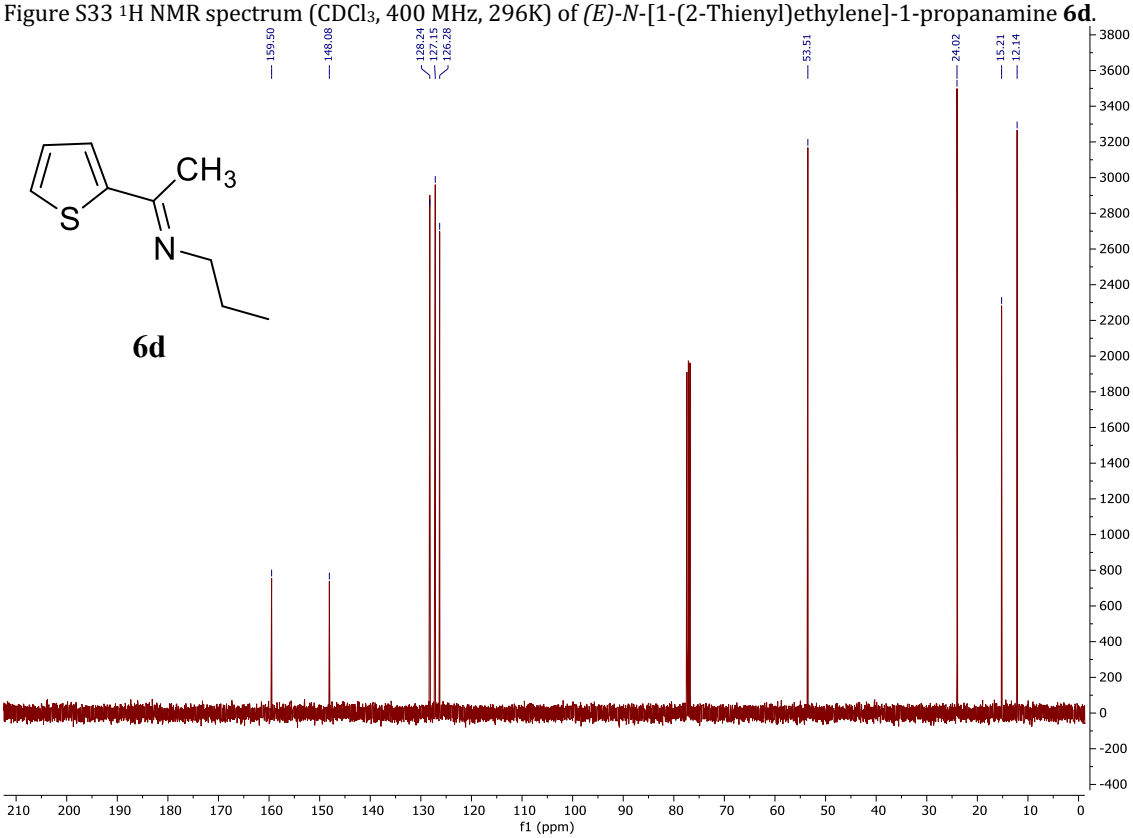

Figure S34 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)-N*-[1-(2-Thienyl)ethylene]-1-propanamine **6d**.

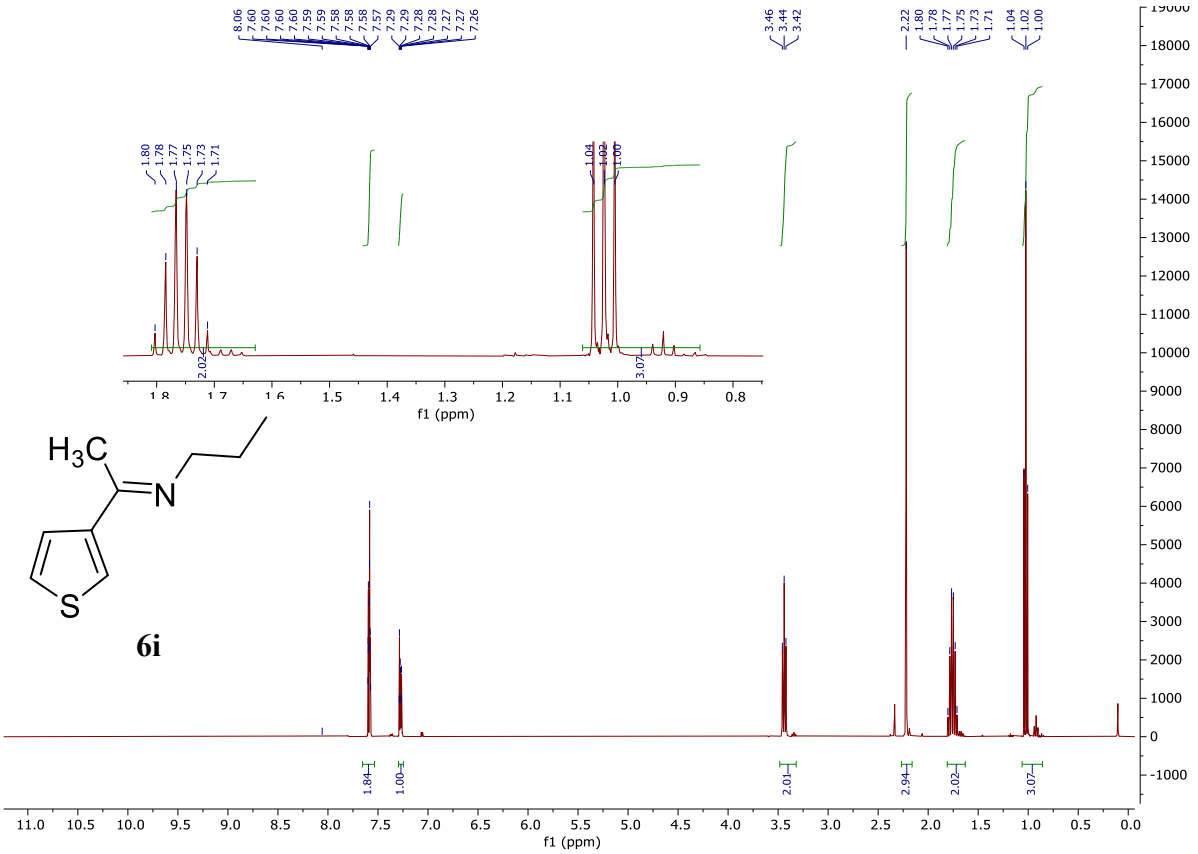

Figure S35 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)-N*-[1-(3-Thienyl)ethylene]-1-propanamine **6i**.

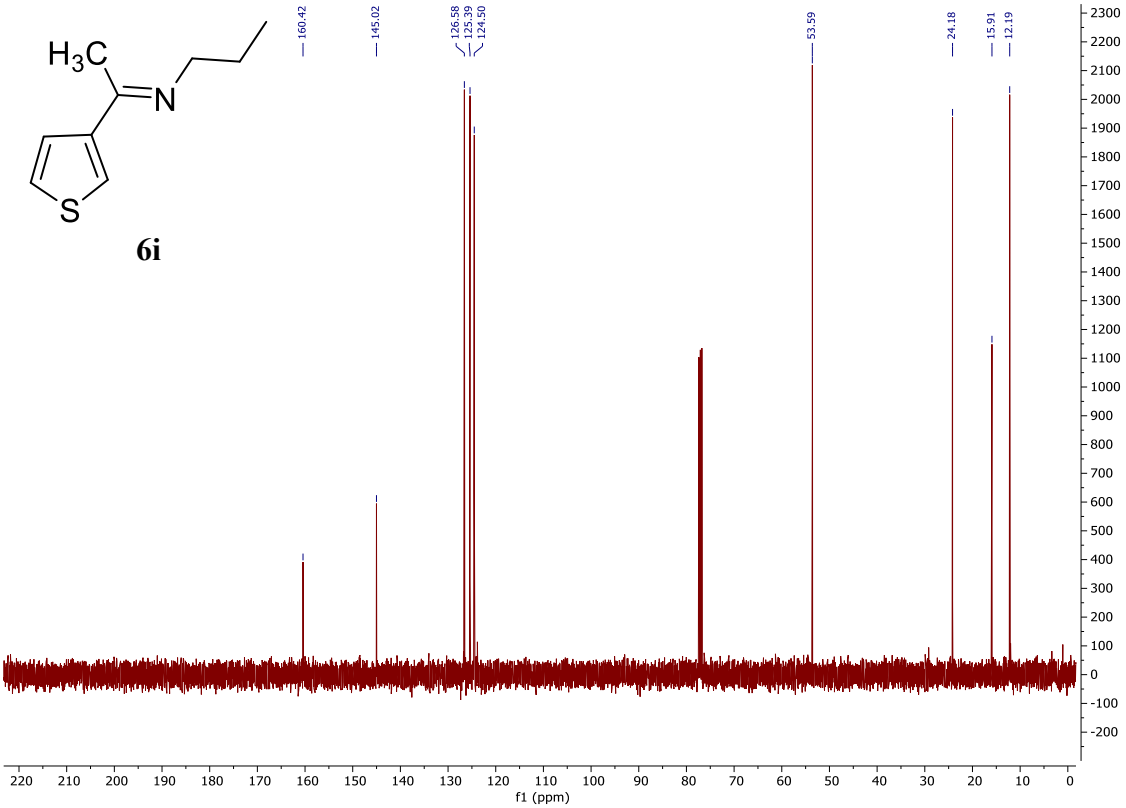

Figure S36 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz, 296K) of *(E)-N*-[1-(2-Thienyl)ethylene]-1-propanamine **6i.**