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Supplementary Information

Microwave-Assisted Synthesis of Indole-2-Carboxylic Acid Esters in Ionic Liquid

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Ethyl 1H-indole-2-carboxylate

White solid; mp 120-122 °C (lit.[1] mp 121-123 °C); IR (KBr) ν_{max}/cm^{-1} 3463, 3431, 2929, 1711 and 1695; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41 (t, 3H, *J* 6.8 Hz), 4.39 (q, 2H, *J* 6.8 Hz), 7.23-7.16 (m, 1H), 7.29-7.33 (m, 2H), 7.49-7.56 (m, 1H), 7.69 (d, 1H, *J* 9.6 Hz), 9.41 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.7, 135.4, 128.2, 126.5, 122.6, 121.7, 121.1, 110.6, 109.2, 62.3, 14.7; MALDI-TOF MS *m/z* 189 (M^+); Anal. calcd. for $C_{11}H_{11}NO_2$: C 69.83, H 5.86, N 7.40; found: C 70.01, H 5.69, N 7.21.

Ethyl 3-methyl-1H-indole-2-carboxylate

White solid; mp 132-134 °C (lit.[2] mp 134-136 °C); IR (KBr) ν_{max}/cm^{-1} 3466, 3429, 2928, 1716 and 1691; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.43 (t, 3H, *J* 9.6 Hz), 2.61 (s, 3H), 4.33 (q, 2H, *J* 9.6 Hz), 7.21-7.25 (m, 1H), 7.31-7.39 (m, 2H), 7.61 (d, 1H, *J* 8.0 Hz), 9.01 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 136.1, 128.7, 125.6, 123.7, 121.3, 120.4, 119.2, 110.5, 61.2, 14.8, 10.3; MALDI-TOF MS *m/z* 203 (M^+); Anal. calcd. for $C_{12}H_{13}NO_2$: C 70.92, H 6.45, N 6.89; found: C 71.14, H 6.49, N 6.92.

Ethyl 5-nitrol-1H-indole-2-carboxylate

Yellow solid; mp 221-223 °C (lit.[3] mp 220-222 °C); IR (KBr) ν_{max}/cm^{-1} 3460, 3431, 2931, 1506 and 1341; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.39 (t, 3H, *J* 4.0 Hz), 4.38 (q, 2H, *J* 4.0 Hz), 7.41 (s, 1H), 7.59 (d, 1H, *J* 4.0 Hz), 8.11 (d, 1H, *J* 8.0 Hz), 8.63 (s, 1H), 10.11 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.4, 146.3, 138.9, 131.1, 125.8, 120.7, 119.5, 112.2, 110.6, 61.7, 14.3; MALDI-TOF MS *m/z* 234 (M^+); Anal. calcd. for $C_{11}H_{10}N_2O_4$: C 56.41, H 4.30, N 11.96; found: C 56.53, H 4.39, N 11.74.

Ethyl 6-methoxyl-3-methyl-1H-indole-2-carboxylate

Brown solid; mp 121-123 °C (lit.[4] mp 122-124 °C); IR (KBr) ν_{max}/cm^{-1} 3467, 3336, 2990, 1706 and 1681; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (t, 3H, *J* 7.2 Hz), 2.59 (s, 3H), 3.81 (s, 3H), 4.42 (q, 2H, *J* 7.2 Hz), 6.83 (d, 1H, *J* 2.4 Hz), 6.91-7.03 (m, 1H), 7.49 (d, 1H, *J* 8.0 Hz), 9.06 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.8, 144.1, 130.6, 128.4, 127.0, 121.3, 118.5 109.7, 105.2, 61.7, 56.2, 14.1, 11.6; MALDI-TOF MS *m/z* 233 (M^+); Anal. calcd. for $C_{13}H_{15}NO_3$: C 66.94, H 6.48, N 6.00; found: C 66.81, H 6.44, N 6.03.

Ethyl 5-chloro-1H-indole-2-carboxylate

White solid; mp 169-171 °C (lit.[1] mp 167-169 °C); IR (KBr) ν_{max}/cm^{-1} 3461, 3343, 2928, 1715 and 1693; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.39 (t, 3H, *J* 4.8 Hz), 4.41 (q, 2H, *J* 4.8 Hz), 7.31 (s, 1H), 7.41-7.44 (m, 1H), 7.53 (d, 1H, *J* 3.2 Hz), 7.67 (s, 1H), 9.89 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.9, 137.1, 129.4, 128.6, 127.2, 122.8, 120.7, 111.5, 109.3, 62.4, 14.5; MALDI-TOF MS *m/z* 223 (M^+); Anal. calcd. for $C_{11}H_{10}ClNO_2$: C 59.07, H 4.51, N 6.26; found: C 59.16, H 4.57, N 6.32.

Ethyl 3H-benz[e]indole-2-carboxylate

Brown solid; mp 164-166 °C (lit.[5] mp 164-165 °C); IR (KBr) ν_{max}/cm^{-1} 3464, 3340, 2929, 1710 and 1691; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (t, 3H, *J* 6.0 Hz), 4.43 (q, 2H, *J* 6.0 Hz), 7.33-7.51 (m, 4H), 7.66-7.79 (m, 2H), 8.03 (d, 1H, *J* 8.0 Hz), 9.92 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.4, 135.2, 130.1, 129.0, 128.6, 127.7, 126.5, 124.8,124.1, 122.9, 121.6, 112.3, 109.1, 61.8, 14.2; MALDI-TOF MS *m/z* 239 (M^+); Anal. calcd. for $C_{15}H_{13}NO_2$: C 75.30, H 5.48, N 5.85; found: C 75.42, H 5.51, N 5.83.

Ethyl 6-chloro-3-methyl-1H-indole-2-carboxylate

White solid; mp 159-161 °C (lit.[6] mp 159-160 °C); IR (KBr) ν_{max}/cm^{-1} 3460, 3339, 2929, 1710 and 1691; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41 (t, 3H, *J* 8.0 Hz), 2.59 (s, 3H), 4.31 (q, 2H, *J* 8.0 Hz), 7.11-713 (m, 1H), 7.31-7.35 (d, 1H, *J* 1.8 Hz), 7.59 (d, 1H, *J* 9.6 Hz), 9.09

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(br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.7, 137.2, 130.1, 128.4, 125.6, 122.5, 121.3, 120.5, 110.2, 61.3, 14.9, 9.7; MALDI-TOF MS *m/z* 237 (M^+); Anal. calcd. for $C_{12}H_{12}ClNO_2$: C 60.64, H 5.09, N 5.89; found: C 60.33, H 5.02, N 5.97.

Ethyl 7-methoxyl-1H-indole-2-carboxylate

White solid; mp 159-161 °C (lit.[1] mp 160-162 °C); IR (KBr) ν_{max}/cm^{-1} 3465, 3335, 2930, 1711 and 1695; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.39 (t, *J* 6.0 Hz, 3H), 3.83 (s, 3H), 4.41 (q, 2H, *J* 6.0 Hz), 6.87 (s, 1H), 7.01-7.09 (m, 1H), 7.25 (d, 1H, *J* 2.0 Hz), 7.29 (d, 1H, *J* 7.2 Hz), 9.11 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.9, 145.2, 130.2, 129.1, 128.8, 122.3, 118.6, 111.0, 105.4, 61.7, 56.2, 14.4; MALDI-TOF MS *m/z* 219 (M^+); Anal. calcd. for $C_{12}H_{13}NO_3$: C 65.74, H 5.98, N 6.39; found: C 65.69, H 5.91, N 6.44.

Ethyl 1H-pyrrolo[3,2-b]pyridine-2-carboxylate

Brown solid; mp 179-181 °C (lit.[7] mp 179 °C); IR (KBr) ν_{max}/cm^{-1} 3405, 3300, 2887 and 1685; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (t, 3H, *J* 7.2 Hz), 4.35 (q, 2H, *J* 7.2 Hz), 7.19 (d, 1H, *J* 7.2 Hz), 7.27 (dd, 1H, *J* 4.8, 8.1 Hz), 7.79 (d, 1H, *J* 7.2 Hz), 8.37-8.41 (m, 1H), 9.23 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.3, 142.5, 141.7, 131.2, 130.1, 121.4, 120.6, 108.5, 61.1, 14.8; MALDI-TOF MS *m/z* 190 (M^+); Anal. calcd. for $C_{10}H_{10}N_2O_2$: C 63.15, H 5.30, N 14.73; found: C 63.01, H 5.37, N 14.81.

Ethyl thieno[3,2-b]pyrrole-5-carboxylate

White solid; mp 132-134 °C (lit.[8] mp 132.5-133 °C); IR (KBr) ν_{max}/cm^{-1} 3400, 3315, 2893 and 1693; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.33 (t, 3H, *J* 7.1 Hz), 4.30 (q, 2H, *J* 7.1 Hz), 7.0 (d, 1H, *J* 2.4 Hz), 7.18 (d, 1H, *J* 2.4 Hz), 7.26 (d, 1H, *J* 3.2 Hz), 9.31 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.1, 131.7, 130.0, 125.1, 122.4, 118.3, 109.2, 61.7, 14.1; MALDI-TOF MS *m/z* 195 (M^+); Anal. calcd. for $C_9H_9NO_2S$: C 55.37, H 4.65, N 7.17, S 16.42; found: C 55.41, H 4.57, N 7.21, S 16.33.

Ethyl 6-methyl-thieno[3,2-b]pyrrole-5-carboxylate

White solid; mp 144-146 °C (lit.[8] mp 144-145 °C); IR (KBr) ν_{max}/cm^{-1} 3430, 3300, 2993 and 1687; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (t, 3H, *J* 7.2 Hz), 2.43 (s, 3H), 4.31 (q, 2H, *J* 7.2 Hz), 6.69 (d, 1H, *J* 5.4 Hz), 7.31 (d, 1H, *J* 5.4 Hz), 9.42 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.8, 140.4, 130.6, 127.2, 122.9, 121.3, 109.6, 61.5, 14.8, 11.7; MALDI-TOF MS *m/z* 209 (M^+); Anal. calcd. for $C_{10}H_{11}NO_2S$: C 57.39, H 5.30, N 6.69, S 15.32; found: C 57.27, H 5.38, N 6.57, S 15.26.

Ethyl 2-nitrothieno[3,2-b]pyrrole-5-carboxylate

Yellow solid; mp 187-189 °C (lit.[9] mp 188-189 °C); IR (KBr) ν_{max}/cm^{-1} 3410, 3303, 1689, 1490 and 1370; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (t, 3H, *J* 7.0 Hz), 4.33 (q, 2H, *J* 7.0 Hz), 7.11 (m, 1H), 7.76 (d, 1H, *J* 4.8 Hz), 9.39 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.7, 151.3, 137.4, 131.6, 128.1, 122.2, 108.5, 60.6, 14.1; MALDI-TOF MS *m/z* 240 (M^+); Anal. calcd. for $C_9H_8N_2O_4S$: C 45.00, H 3.36, N 11.66, S 13.35; found: C 45.06, H 3.38, N 11.59, S 13.29.

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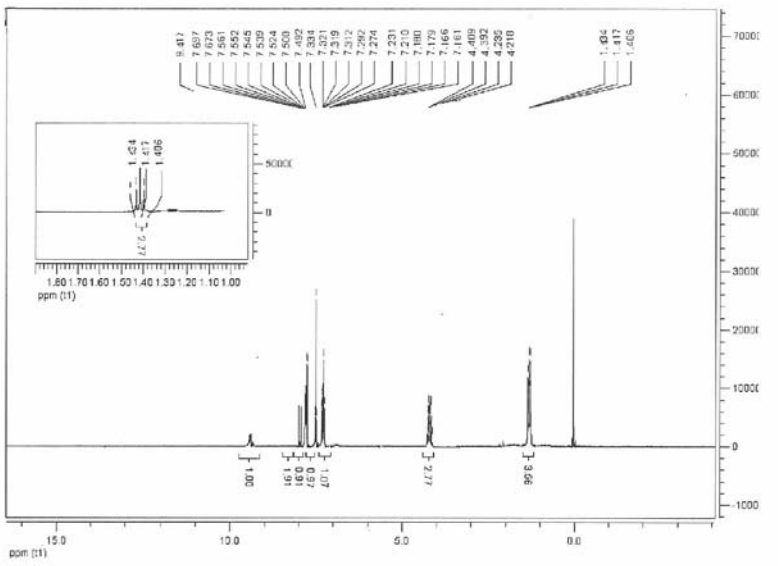

Figure S1. [1]H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 1*H*-indole-2-carboxylate.

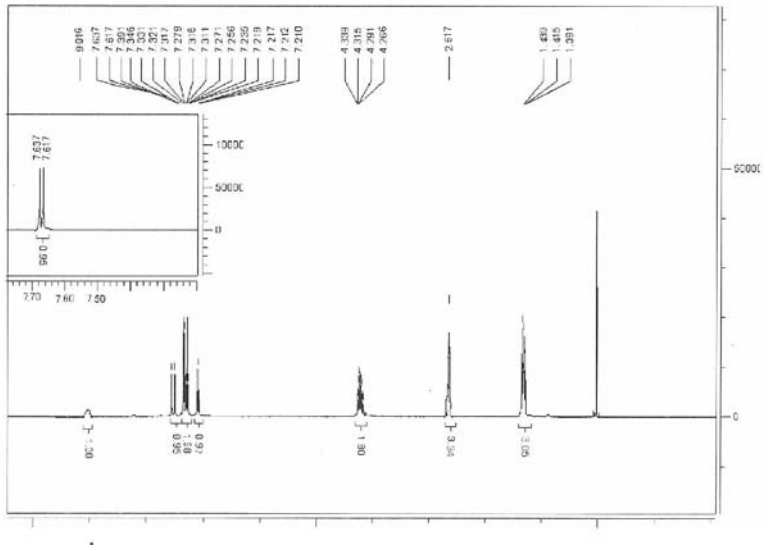

Figure S2. [1]H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 3-methyl-1*H*-indole-2-carboxylate.

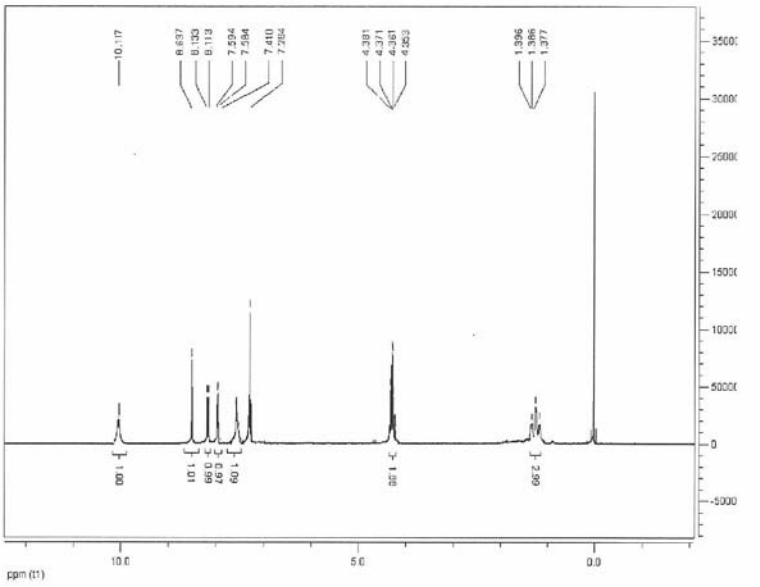

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 5-nitrol-1*H*-indole-2-carboxylate.

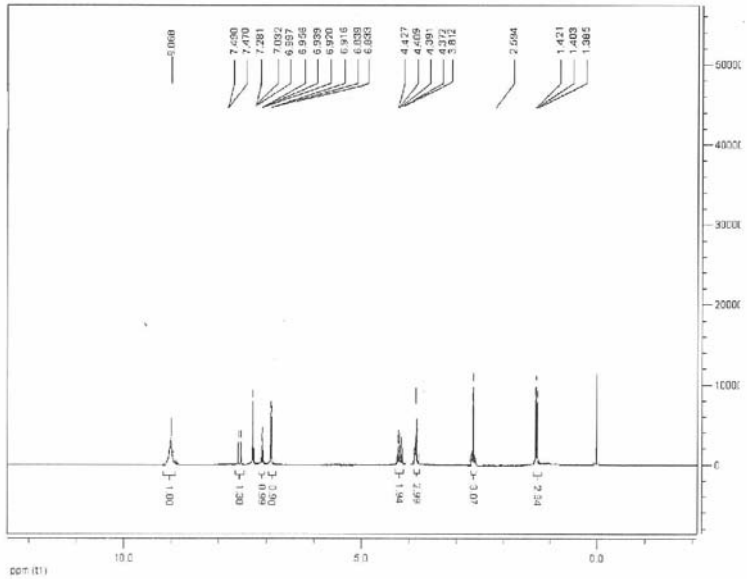

Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 6-methoxyl-3-methyl-1*H*-indole-2-carboxylate.

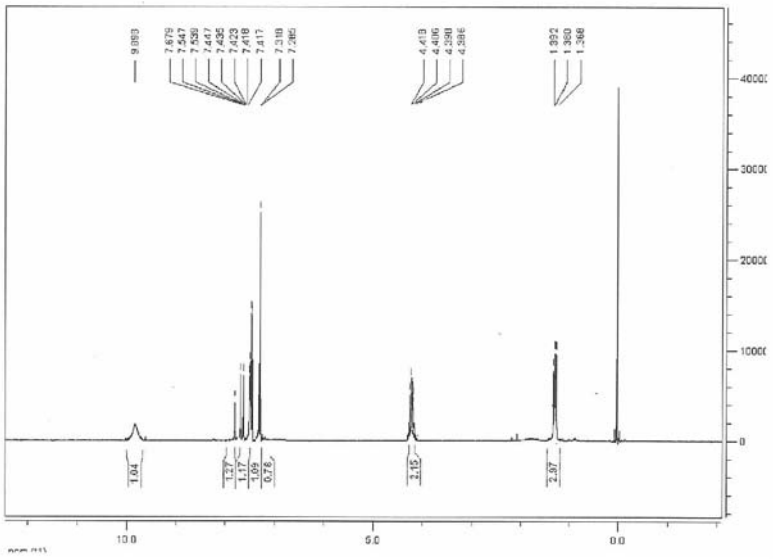

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 5-chloro-1*H*-indole-2-carboxylate.

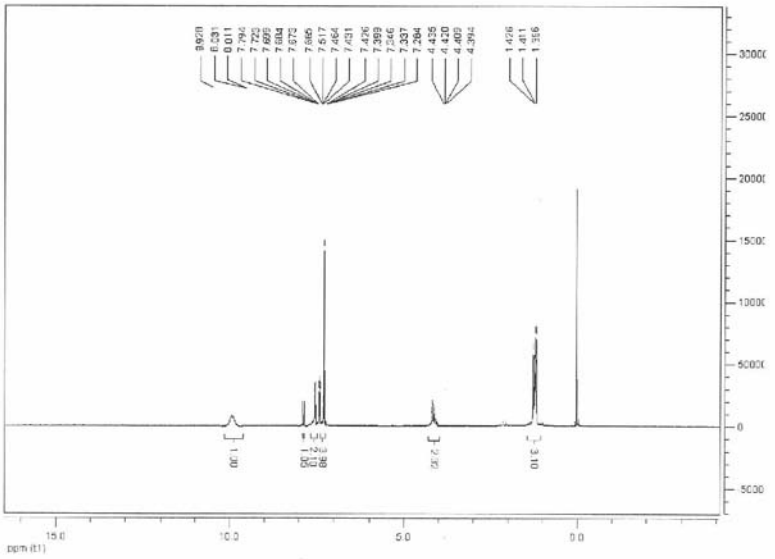

Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 3*H*-benz[e]indole-2-carboxylate.

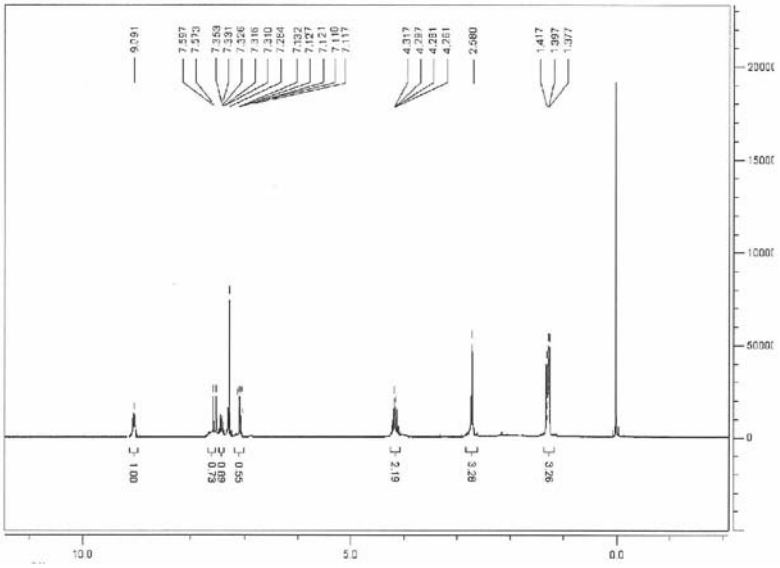

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 6-chloro-3-methyl-1*H*-indole-2-carboxylate.

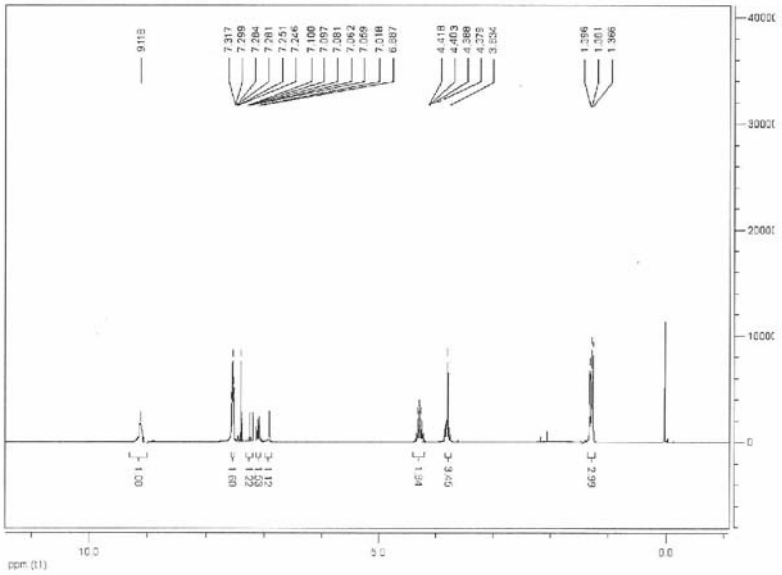

Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 7-methoxyl-1*H*-indole-2-carboxylate.

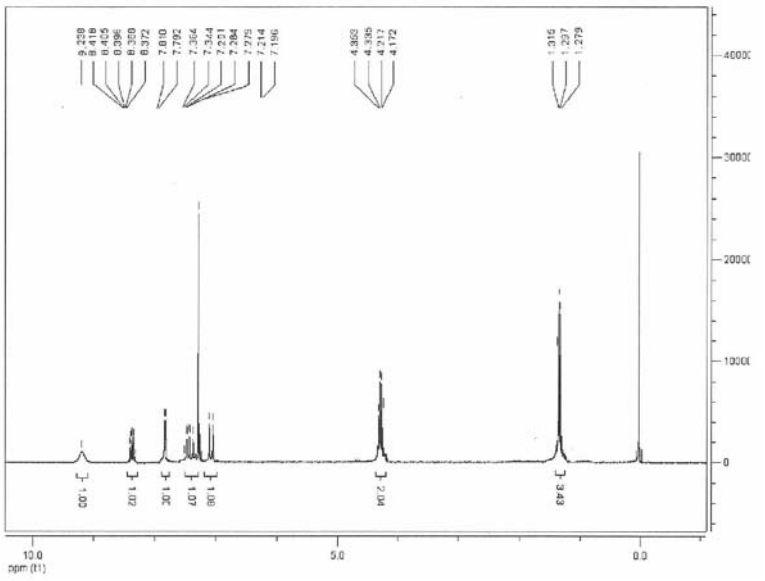

Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 1*H*-pyrrolo[3,2-b]pyridine-2-carboxylate.

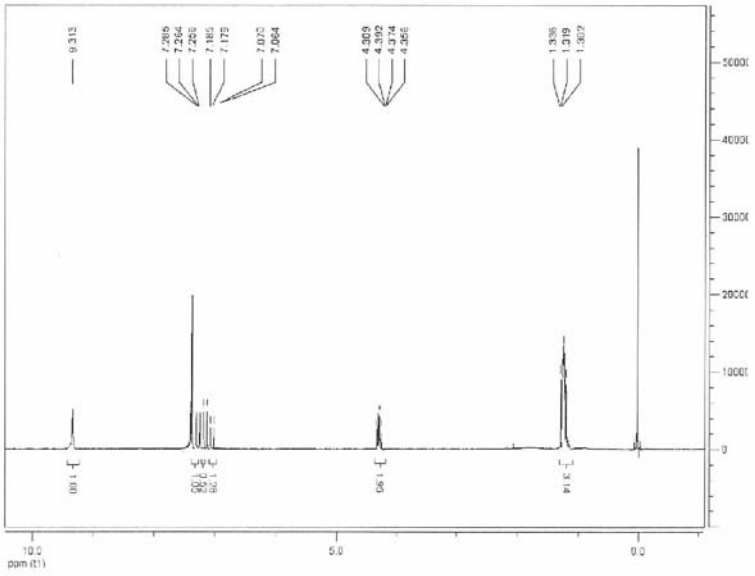

Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl thieno[3,2-b]pyridine-5-carboxylate.

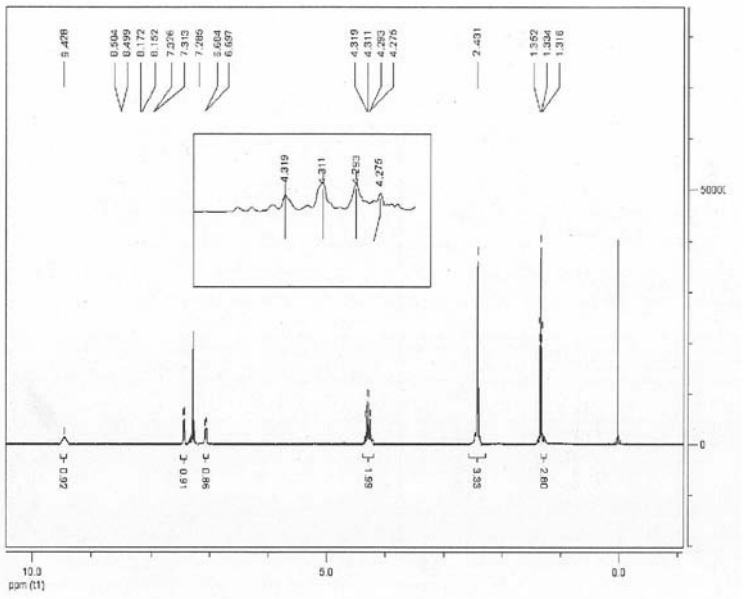

Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 6-methyl-thieno[3,2-b]pyrrole-5-carboxylate.

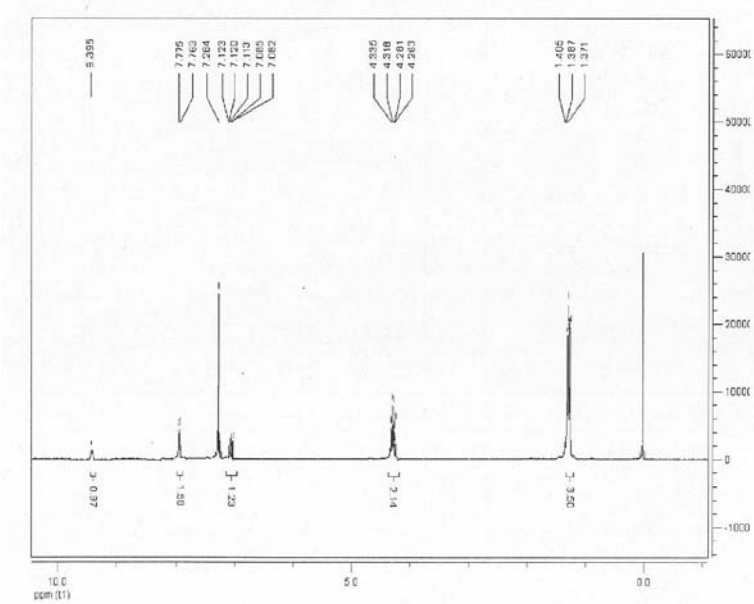

Figure S12. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ethyl 2-nitrothieno[3,2-b]pyrrole-5-carboxylate.

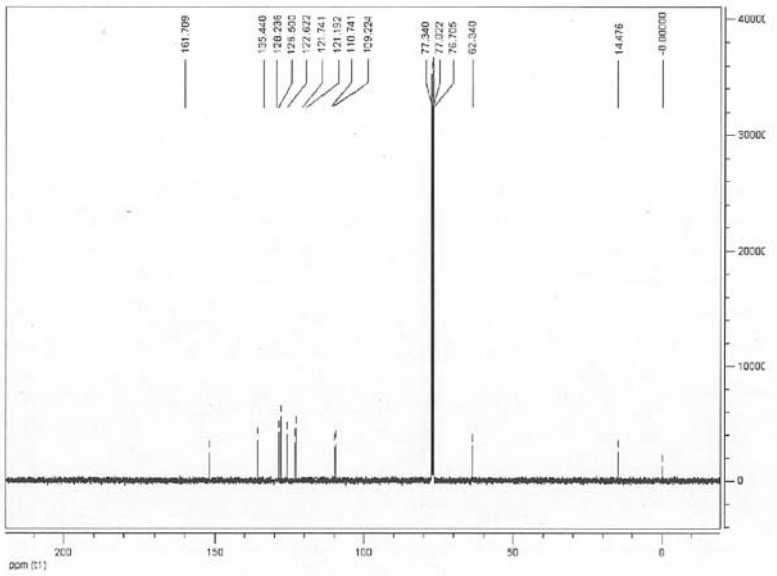

Figure S13. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 1*H*-indole-2-carboxylate.

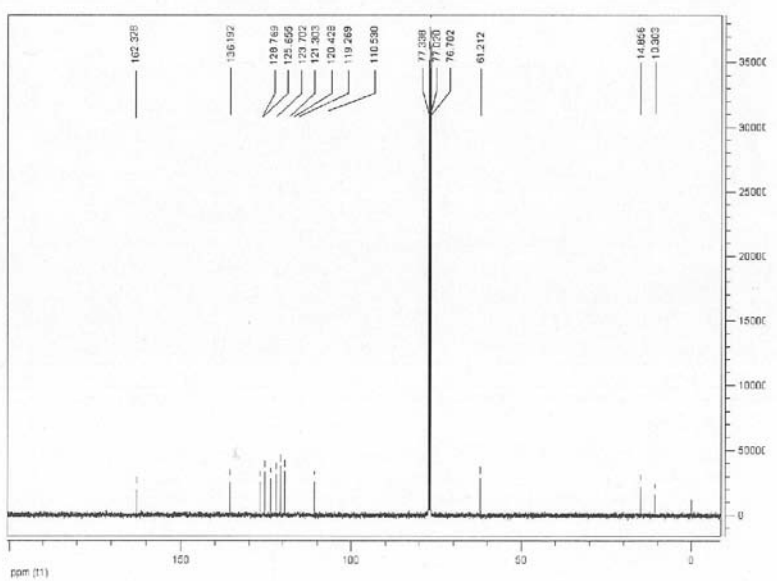

Figure S14. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 3-methyl-1*H*-indole-2-carboxylate.

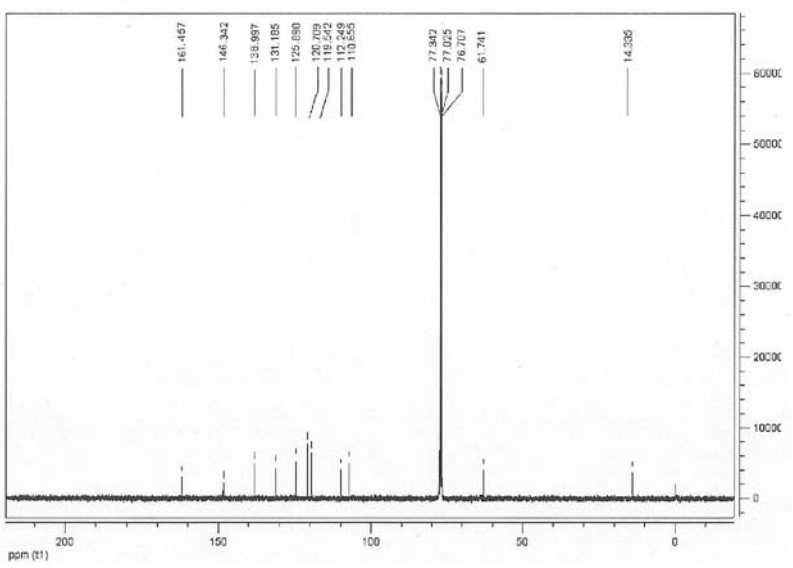

Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 5-nitrol-1*H*-indole-2-carboxylate.

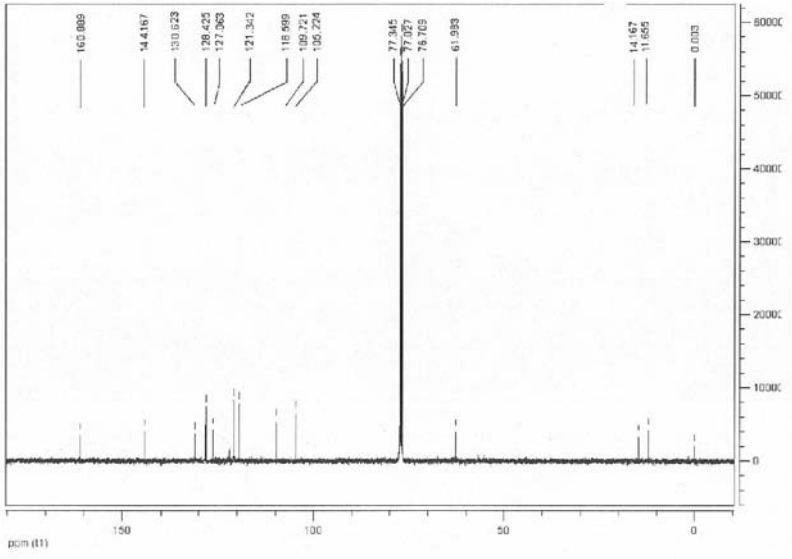

Figure S16. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 6-methoxyl-3-methyl-1*H*-indole-2-carboxylate.

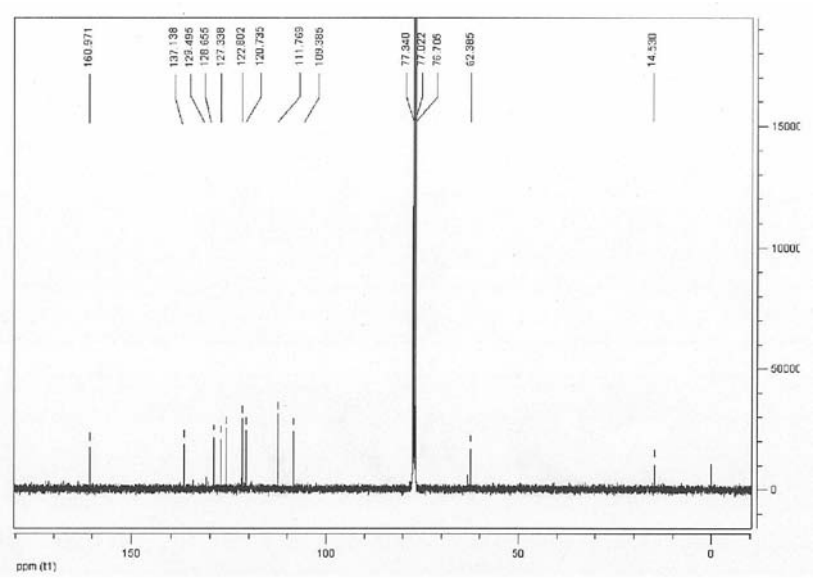

Figure S17. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 5-chloro-1*H*-indole-2-carboxylate.

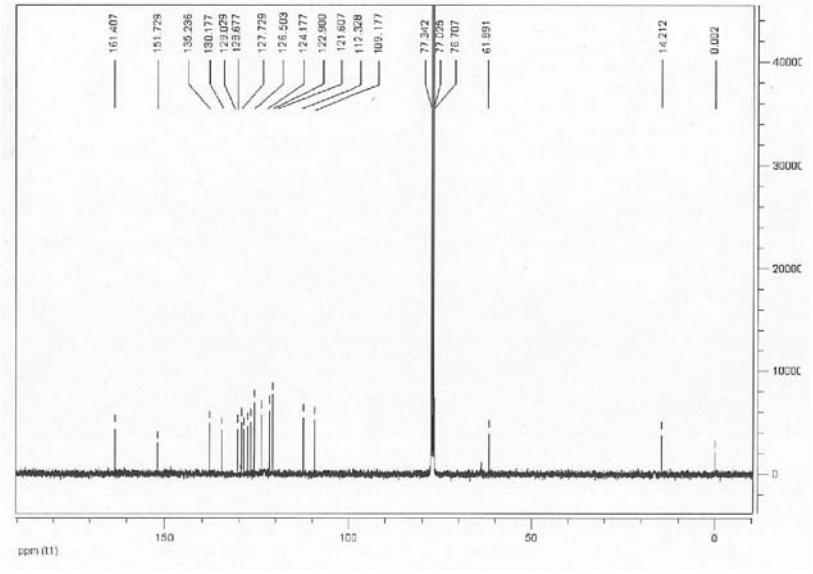

Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 1*H*-benz[e]indole-2-carboxylate.

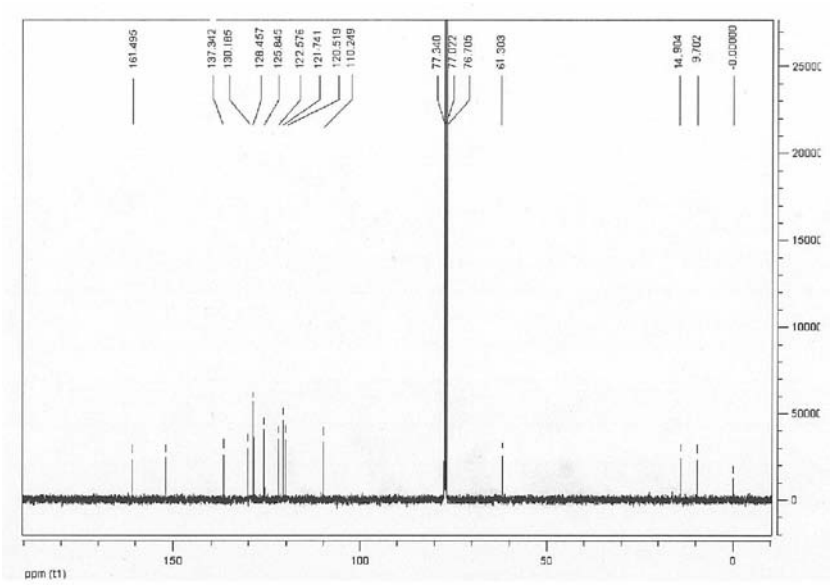

Figure S19. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 6 chloro-3-methyl-1*H*-indole-2-carboxylate.

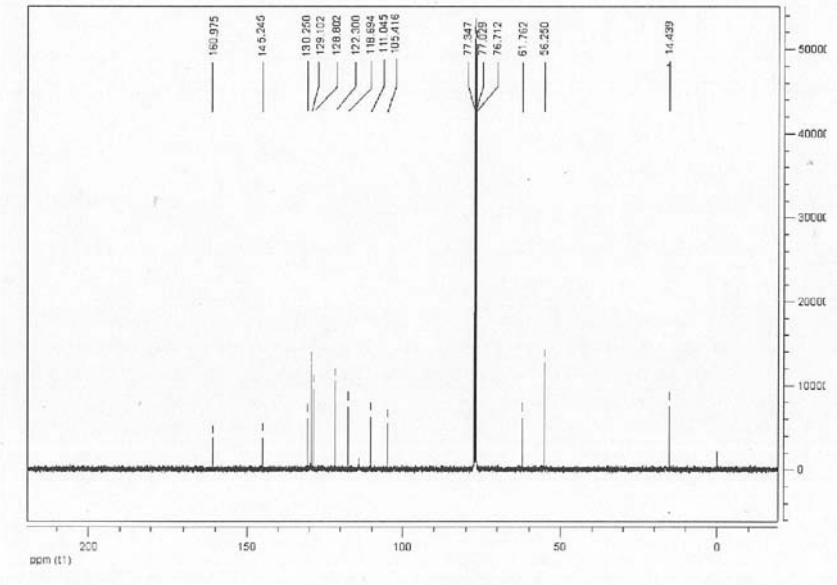

Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 7-methoxyl-1*H*-indole-2-carboxylate.

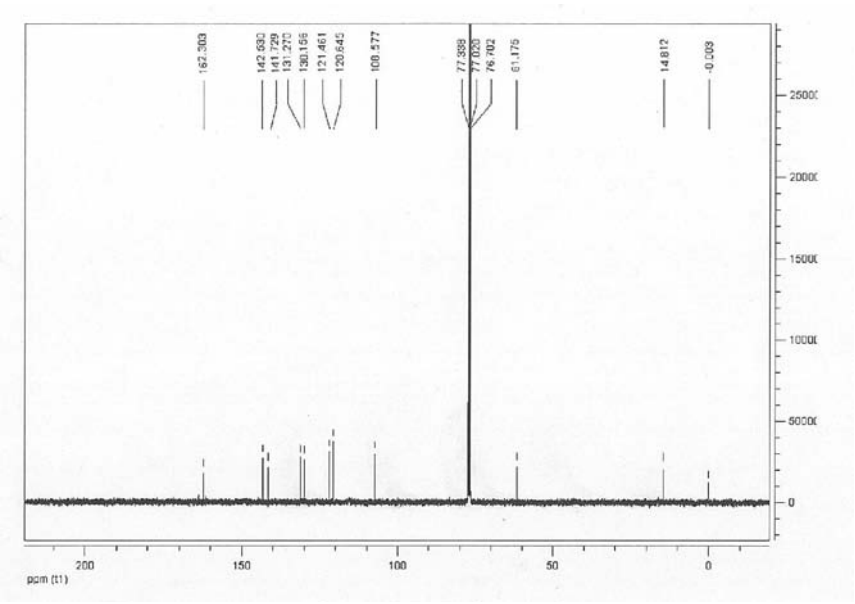

Figure S21. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 1*H*-pyrrolo[3,2-b]pyridine-2-carboxylate.

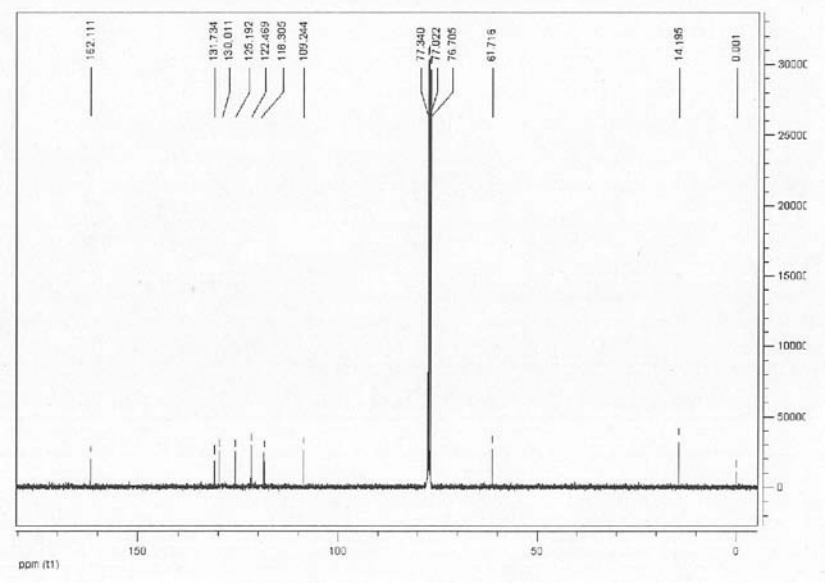

Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl thieno[3,2-b]pyrrole-5-carboxylate.

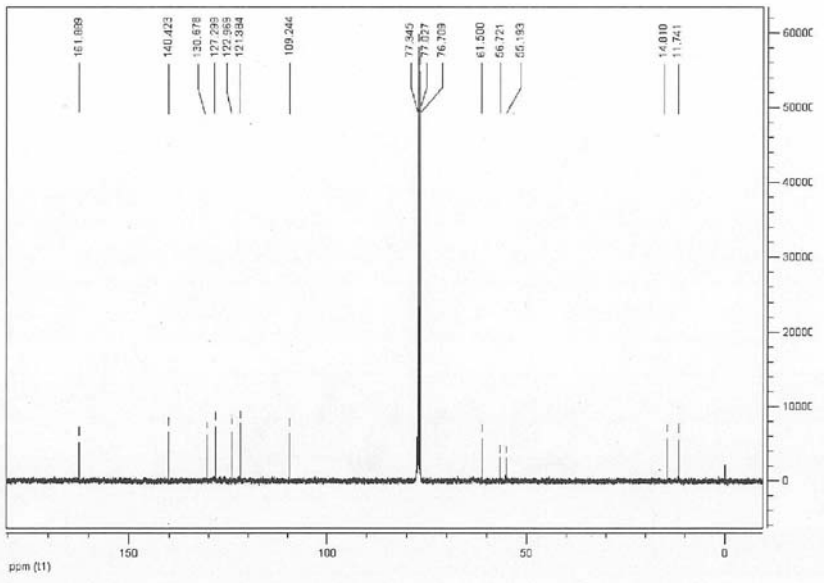

Figure S23. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 6-methyl-thieno[3,2-b]pyrrole-5-carboxylate.

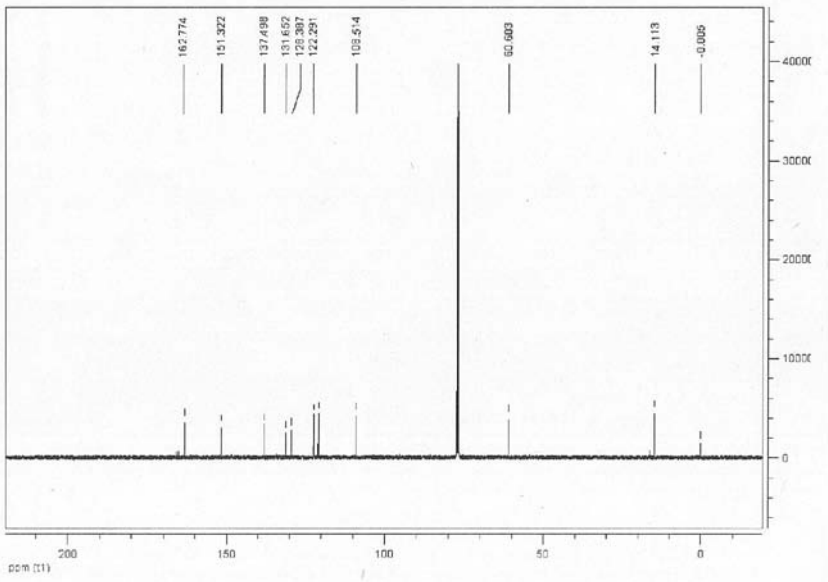

Figure S24. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of ethyl 2-nitrothieno[3,2-b]pyrrole-5-carboxylate.