Electronic Supplementary Information

Regiodivergent Heterocyclization: A Strategy for the Synthesis of Substituted Pyrroles and Furans Using α-Formyl Ketene Dithioacetals as Common Precursors

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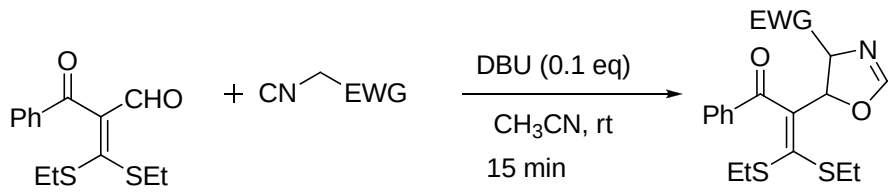
I. General Information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300−400 mesh). Melting points were uncorrected. NMR spectra were obtained on a Varian Inova 500 spectrometer (500 MHz for ^{1}H NMR; 125 MHz for ^{13}C NMR), with TMS as the internal standard. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). α-Formyl ketene dithioacetals **1** were synthesized according to the literature.[1]

II. Typical Procedures and Analytical Data of Compounds 3, 4, 5, 6, 7

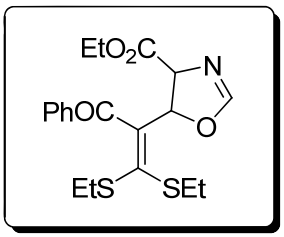


1a **2** **3**

2a EWG= CO_2Et; **2b** EWG= Tos

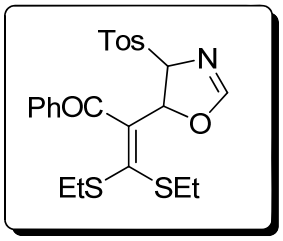
General procedure for the synthesis of 3 (**3a** as an example):

To the mixture of **1a** (140.1 mg, 0.50 mmol) and ethyl isocyanoacetate **2a** (65 μL, 0.55 mmol) in CH_3CN (2 mL) was added 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU, 7.5 μL, 0.05 mmol) in one portion at room temperature and stirred for about 15 min. After **1a** was consumed as indicated by TLC, the resulting mixture was poured into water (15 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give crude **3a** (190.7 mg, 97%).

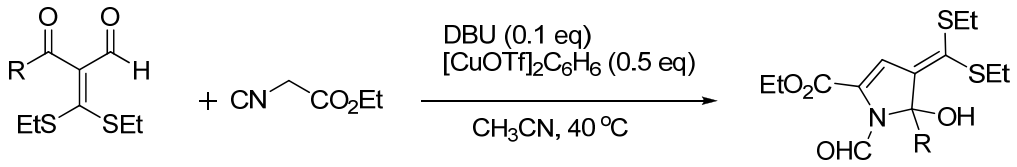


3a, Ethyl 5-(1,1-bis(ethylthio)-3-oxo-3-phenylprop-1-en-2-yl)-4,5-dihydrooxazole-4-carboxylate. Colorless viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.04 (t, *J* = 7.5 Hz, 3H), 1.31–1.35 (m, 6H), 2.59–2.66 (m, 1H), 2.68–2.73 (m, 1H), 2.77–2.84 (m, 1H), 2.88–2.95 (m, 1H), 4.29 (q, *J* = 7.5 Hz, 2H), 5.00 (d, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 7.5 Hz, 1H), 6.71 (s, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.0, 14.3, 15.2, 27.6, 28.2, 61.8, 73.1, 80.3, 128.5, 129.2, 133.4, 137.3, 137.4, 144.3, 155.5, 170.3, 194.5. **HRMS** (ESI-TOF) Calcd for $C_{19}H_{24}NO_4S_2^+$ ($[M + H]^+$) 394.1141. Found 394.1151.

(1) (a) R. K. Verma, G. K. Verma, G. Shukla and M. S. Singh, *RSC Adv.,* 2012, **2**, 2413; (b) E. R. Anabha and C. V. Asokan, *Synthesis,* 2006, 151.



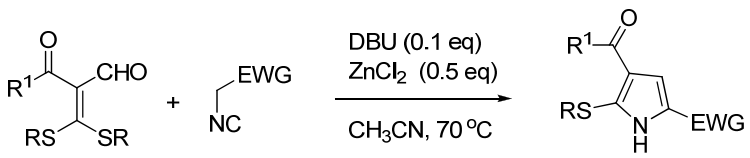
3a', 3,3-Bis(ethylthio)-1-phenyl-2-(4-tosyl-4,5-dihydrooxazol-5-yl)prop-2-en-1-one. Colorless crystals. m.p. 116–117 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.01 (t, *J* = 7.5 Hz, 3H), 1.41 (t, *J* = 7.5 Hz, 3H), 2.45 (s, 3H), 2.67–2.74 (m, 2H), 2.94 (q, *J* = 7.5 Hz, 2H), 5.59 (dd, J_1 = 6.0 Hz, J_2 = 1.5 Hz, 1H), 6.73 (d, *J* = 6.0 Hz, 1H), 6.78 (d, *J* = 1.5 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.84–7.86 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.4, 15.1, 21.7, 28.3 (2C), 77.7, 89.1, 128.5, 129.2, 129.6, 129.7, 133.3, 133.5, 137.3, 140.2, 142.6, 145.4, 158.6, 194.9. **HRMS** (ESI-TOF) Calcd for $C_{23}H_{26}NO_4S_3^+$ ($[M + H]^+$) 476.1018. Found 476.1020.



1 **2** **4**

General procedure for the synthesis of 4 (**4a** as an example):

To the mixture of **1a** (140.1 mg, 0.50 mmol) and ethyl isocyanoacetate **2a** (65 μL, 0.55 mmol) in CH_3CN (2 mL) was added 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU, 7.5 μL, 0.05 mmol) in one portion at room temperature. The mixture was stirred for about 15 min for the formation of **3a** as indicated by TLC. Then, $[CuOTf]_2C_6H_6$ (126 mg, 0.25 mmol) was added at 40 °C and the reaction mixture was stirred at 40 °C for about 1.0 h. After **3a** was consumed as indicated by TLC, the resulting mixture was poured into water (15 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 5 : 1, V/V) to give **4a** (190.6 mg, 97%). **4a** was obtained as a yellow crystal (m.p. 78–79°C) and identified by the X-ray diffraction analysis (see the crystal data of **4a** in part III) since it has equilibrium isomers in solution. [2]



1 **2** **5**

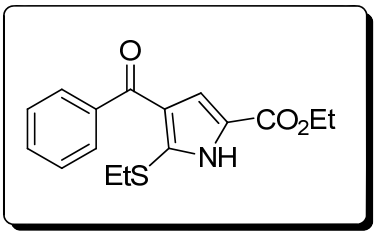
2a EWG= CO_2Et; **2b** EWG= Tos

General procedure for the synthesis of 5 (**5a** as an example):

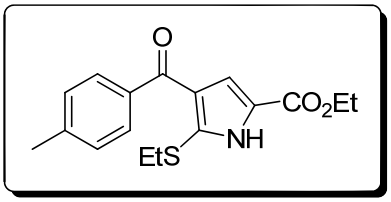
To the mixture of **1a** (140.1 mg, 0.50 mmol) and ethyl isocyanoacetate **2a** (65 μL, 0.55 mmol) in CH_3CN (2 mL) was added 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU, 7.5 μL, 0.05 mmol) in one portion at room temperature. The

(2) I. S. Kondratov, V. G. Dolovanyuk, N. A. Tolmachova, I. I. Gerus, K. Bergander, R. Fröhlich and G. Haufe, *Org. Biomol. Chem.*, 2012, **10**, 8778.

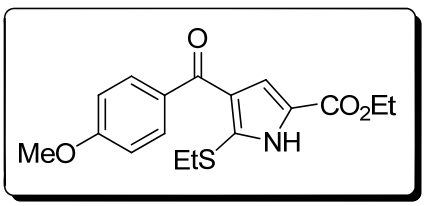
mixture was stirred for about 15 min for the formation of **3a** as indicated by TLC. Then, $ZnCl_2$ (34 mg, 0.25 mmol) was added at 70 °C and the reaction mixture was stirred at 70 °C for about 2.0 h. After **3a** was consumed as indicated by TLC, the resulting mixture was poured into water (15 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 10 : 1, V/V) to give **5a** (140.9 mg, 93%).



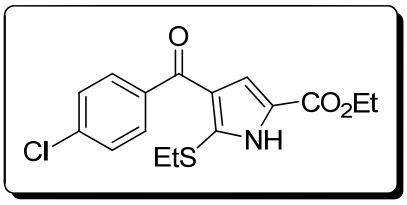
5a, Ethyl 4-benzoyl-5-(ethylthio)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 82–83 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.35–1.38 (m, 6H), 3.07 (q, *J* = 7.5 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 9.42 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1, 14.3, 27.3, 61.0, 118.8, 122.8, , 124.2, 128.2, 129.1, 131.8, 136.7, 139.0, 160.5, 190.2. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{18}NO_3S^+$ ($[M + H]^+$) 304.1002. Found 304.1008.



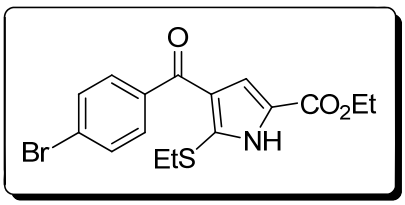
5b, Ethyl 5-(ethylthio)-4-(4-methylbenzoyl)-1*H*-pyrrole-2-carboxylate. Colorless viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.33–1.37 (m, 6H), 2.43 (s, 3H), 3.06 (q, *J* = 7.5 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.73(t, *J* = 8.0 Hz, 2H), 9.45 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.2, 14.4, 21.6, 27.5, 60.9, 118.7, 122.7, 124.5, 128.9, 129.3, 136.1, 136.2, 142.5, 160.5, 190.0. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{20}NO_3S^+$ ($[M + H]^+$) 318.1158. Found 318.1166.



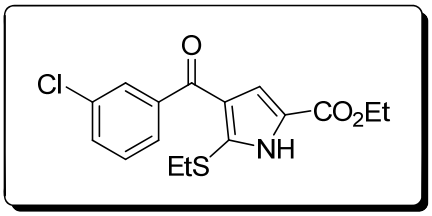
5c, Ethyl 5-(ethylthio)-4-(4-methoxybenzoyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 87–88 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.5 Hz, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 3.04 (q, *J* = 7.5 Hz, 2H), 3.88 (s, 3H), 4.35 (q, *J* = 7.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.84(d, *J* = 9.0 Hz, 2H), 9.65 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.2, 14.3, 27.9, 55.4, 60.9, 113.5, 118.5, 122.7, 125.0, 131.5, 131.6, 135.4, 160.5, 162.7, 189.0. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{20}NO_4S^+$ ($[M + H]^+$) 334.1113. Found 334.1120.



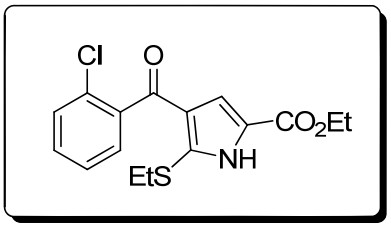
5d, Ethyl 4-(4-chlorobenzoyl)-5-(ethylthio)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 93–94 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.31–1.38 (m, 6H), 3.08 (q, *J* = 7.5 Hz, 2H), 4.35 (q, *J* = 7.0 Hz, 2H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.77 (t, *J* = 8.5 Hz, 2H), 9.93 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.0, 14.3, 27.4, 61.0, 118.5, 123.0, 124.0, 128.5, 130.4, 136.8, 137.3, 138.0, 160.5, 188.8. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}ClNO_3S^+$ ($[M + H]^+$) 338.0612. Found 338.0612.



5e, Ethyl 4-(4-bromobenzoyl)-5-(ethylthio)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 123–124 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.35–1.38 (m, 6H), 3.06 (q, *J* = 7.5 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 2.5 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.69(d, *J* = 8.5 Hz, 2H), 9.37 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.1, 14.4, 27.3, 61.0, 118.4 , 123.0, 123.7, 126.7, 130.6, 131.6, 137.0, 137.7, 160.3, 189.0. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}BrNO_3S^+$ ($[M + H]^+$) 382.0107. Found 382.0102.

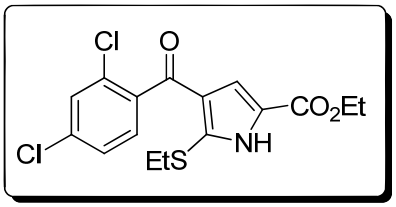


5f, Ethyl 4-(3-chlorobenzoyl)-5-(ethylthio)-1*H*-pyrrole-2-carboxylate. Colorless viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.34–1.39 (m, 6H), 3.08 (q, *J* = 7.5 Hz, 2H), 4.36 (q, *J* = 7.0 Hz, 2H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.52(d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 9.70 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.0, 14.3, 27.2, 61.1, 118.5, 123.1, 123.6, 127.1, 129.0, 129.6, 131.7, 134.4, 137.3, 140.6, 160.4, 188.6. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}ClNO_3S^+$ ($[M + H]^+$) 338.0618. Found 338.0614.

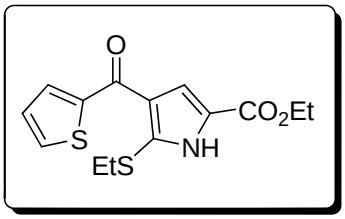


5g, Ethyl 4-(2-chlorobenzoyl)-5-(ethylthio)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 108–109 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.32–1.38 (m, 6H), 3.06 (q, *J* = 7.5 Hz, 2H), 4.31 (q, *J* = 7.0 Hz, 2H), 6.91 (d, *J* = 2.5

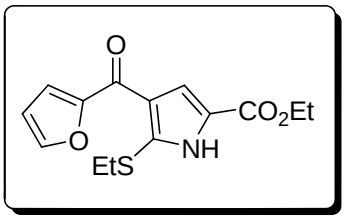
Hz, 1H), 7.32–7.41 (m, 3H), 7.44 (d, J = 7.5 Hz, 1H), 9.37 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.0, 14.3, 26.9, 61.0, 118.9, 123.2, 124.1, 126.6, 128.6, 130.0, 130.7, 130.9, 137.2, 139.4, 160.3, 189.0. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{16}ClNNaO_3S^+$ ($[M + Na]^+$) 360.0437. Found 360.0439.



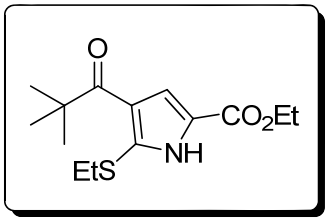
5h, Ethyl 4-(2,4-dichlorobenzoyl)-5-(ethylthio)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 89–90 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.33–1.38 (m, 6H), 3.06 (q, J = 7.5 Hz, 2H), 4.32 (q, J = 7.0 Hz, 2H), 6.89 (d, J = 2.5 Hz, 1H), 7.31–7.35 (m, 2H), 7.47(s, 1H), 9.47 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.0, 14.3, 26.8, 61.1, 118.7, 123.4, 123.8, 127.0, 129.7, 130.0, 132.0, 136.1, 137.7, 137.8, 160.3, 187.9. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{16}Cl_2NO_3S^+$ ($[M + H]^+$) 372.0222. Found 372.0217.



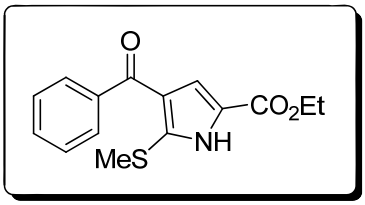
5i, Ethyl 5-(ethylthio)-4-(thiophene-2-carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 90–91 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.34 (t, J = 7.5 Hz, 3H), 1.39 (t, J = 7.0 Hz, 3H), 3.07 (q, J = 7.5 Hz, 2H), 4.37 (q, J = 7.0 Hz, 2H), 7.16 (d, J = 4.5 Hz, 1H), 7.42 (d, J = 2.5 Hz, 1H), 7.65 (d, J = 4.5 Hz, 1H), 7.77 (d, J = 3.5 Hz, 1H), 9.45 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.2, 14.4, 27.9, 61.0, 117.4, 123.1, 124.5, 127.8, 132.6, 132.9, 136.0, 144.5, 160.3, 181.0. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{16}NO_3S_2^+$ ($[M + H]^+$) 310.0566. Found 310.0564.



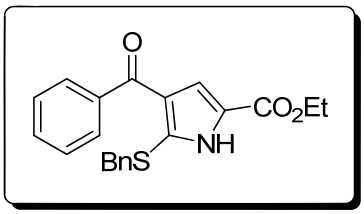
5j, Ethyl 5-(ethylthio)-4-(furan-2-carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 150–151 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.33–1.39 (m, 6H), 3.06 (q, J = 7.5 Hz, 2H), 4.35 (q, J = 7.0 Hz, 2H), 6.55 (d, J = 2.0 Hz, 1H) 7.29 (d, J = 3.0 Hz, 1H), 7.64 (s, 1H), 7.70 (d, J = 2.0 Hz, 1H), 9.43 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 13.9, 14.4, 26.8, 60.9, 112.1, 117.8, 117.9, 122.5, 123.1, 138.2, 145.7, 153.5, 160.5, 175.6. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{15}NNaO_4S^+$ ($[M + Na]^+$) 316.0619. Found 316.0611.



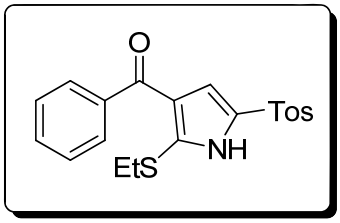
5k, Ethyl 5-(ethylthio)-4-pivaloyl-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 103–104 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.34 (s, 9H), 1.36–1.40 (m, 6H), 3.01 (q, *J* = 7.5 Hz, 2H), 4.35 (q, *J* = 7.0 Hz, 2H), 7.35 (d, *J* = 2.5 Hz, 1H), 9.26 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 13.5, 14.4, 25.9, 27.7, 43.6, 60.8, 116.7, 121.3, 122.2, 139.0, 160.5, 201.5. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{22}NO_3S^+$ ($[M + H]^+$) 284.1315. Found 284.1314.



5l, Ethyl 4-benzoyl-5-(methylthio)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 164–165°C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.34 (t, *J* = 7.0 Hz, 3H), 2.59 (s, 3H), 4.32 (q, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 9.51 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 15.0, 60.9, 118.9, 122.5, 122.8, 128.2, 128.8, 131.6, 139.0, 139.8, 160.5, 190.0. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{16}NO_3S^+$ ($[M + H]^+$) 290.0845. Found 290.0845.

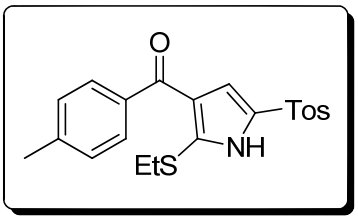


5m, Ethyl 4-benzoyl-5-(benzylthio)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 143–144 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.24 (t, *J* = 7.0 Hz, 3H), 4.17 (s, 2H), 4.20 (q, *J* = 7.0 Hz, 2H), 7.04 (d, *J* = 2.5 Hz, 1H), 7.16–7.18 (m, 1H), 7.18–7.24 (m, 4H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 9.24 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 38.7, 60.9, 118.4, 123.0, 125.2, 127.8, 128.2, 128.7, 128.9, 129.2, 131.9, 135.1, 136.7, 138.9, 160.1, 190.3. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{19}NNaO_3S^+$ ($[M + Na]^+$) 388.0983. Found 388.0982.

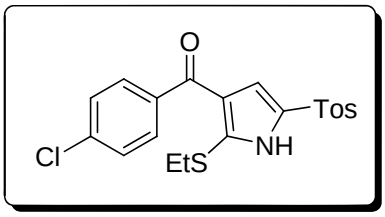


5n, (2-(Ethylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methanone. Colorless crystals. m.p. 180–181 °C. **^{1}H NMR** (500

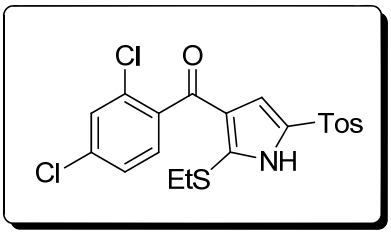
MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.5 Hz, 3H), 2.41 (s, 3H), 3.01 (q, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 3.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 9.85 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.0, 21.6, 27.4, 118.9, 124.3, 127.0, 128.4, 128.9, 129.0, 130.1, 132.1, 138.2, 138.4, 138.5, 144.6, 189.7. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{20}NO_3S_2^+$ ($[M + H]^+$) 386.0879. Found 386.0869.



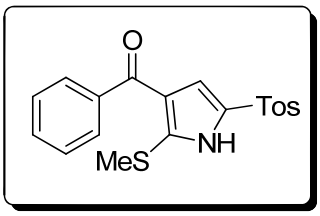
5o, (2-(Ethylthio)-5-tosyl-1*H*-pyrrol-3-yl)(*p*-tolyl)methanone. Colorless crystals. m.p. 151–152 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.30 (t, *J* = 7.5 Hz, 3H), 2.42 (s, 3H), 2.43 (s, 3H), 3.00 (q, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 9.35 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.0, 21.6, 27.5, 29.7, 118.7, 124.7, 126.9, 128.7, 129.0, 129.3, 130.1, 135.8, 137.5, 138.5, 142.9, 144.6, 189.4. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{22}NO_3S_2^+$ ($[M + H]^+$) 400.1036. Found 400.1044.



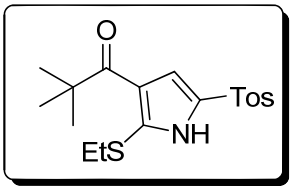
5p, (4-Chlorophenyl)(2-(ethylthio)-5-tosyl-1*H*-pyrrol-3-yl)methanone. Colorless crystals. m.p. 170–171 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.26 (t, *J* = 7.5 Hz, 3H), 2.41 (s, 3H), 3.00 (q, *J* = 7.5 Hz, 2H), 7.08 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 9.88 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 13.9, 21.6, 27.4, 118.5, 124.0, 126.9, 128.7, 129.2, 130.1, 130.4, 136.8, 137.5, 138.4, 138.5, 144.7, 188.4. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{19}ClNO_3S_2^+$ ($[M + H]^+$) 420.0489. Found 420.0495.



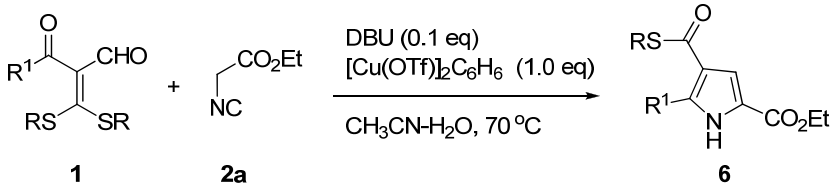
5q, (2,4-Dichlorophenyl)(2-(ethylthio)-5-tosyl-1*H*-pyrrol-3-yl)methanone. Colorless crystals. m.p. 210–211 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.28 (t, *J* = 7.5 Hz, 3H), 2.43 (s, 3H), 3.00 (q, *J* = 7.5 Hz, 2H), 6.88 (d, *J* = 2.5 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.31–7.34 (m, 3H), 7.46 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 9.84 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 13.8, 21.6, 26.8, 119.0, 123.5, 127.0, 127.1, 129.4, 129.8, 130.1, 130.2, 132.0, 136.5, 137.2, 138.1, 139.7, 144.9, 187.4. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{18}Cl_2NO_3S^+$ ($[M + H]^+$) 454.0100. Found 454.0106.



5r, (2-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methanone. Colorless crystals. m.p. 76–77 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.41 (s, 3H), 2.53 (s, 3H), 7.17 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 9.91 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.2, 21.6, 119.3, 122.6, 126.9, 128.4, 128.6, 128.9, 130.1, 132.0, 138.5, 138.6, 141.5, 144.6, 189.5. **HRMS** (ESI-TOF) Calcd for $C_{19}H_{18}NO_3S_2^+$ ($[M + H]^+$) 372.0723. Found 372.0731.



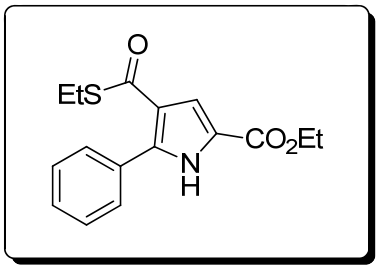
5s, 1-(2-(ethylthio)-5-tosyl-1*H*-pyrrol-3-yl)-2,2-dimethylpropan-1-one. Colorless crystals. m.p. 146–147 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.29 (m, 12H), 2.42 (s, 3H), 2.94 (q, *J* = 7.5 Hz, 2H) 7.29 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 9.40 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 13.4, 21.6, 26.1, 27.4, 43.7, 117.0, 121.4, 126.8, 128.0, 130.1, 138.7, 140.7, 144.5, 201.2. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{24}NO_3S_2^+$ ($[M + H]^+$) 366.1192. Found 366.1190.



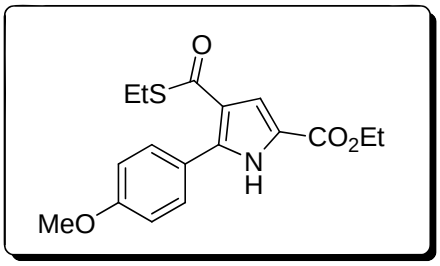
1 **2a** **6**

General procedure for the synthesis of 6 (**6a** as an example):

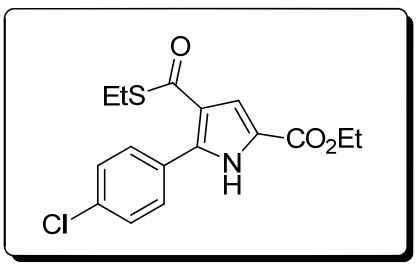
To the mixture of **1a** (140.1 mg, 0.50 mmol) and ethyl isocyanoacetate **2a** (65 μL, 0.55 mmol) in CH_3CN (2 mL) was added 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU, 7.5 μL, 0.05 mmol) in one portion at room temperature. The mixture was stirred for about 15 min for the formation of **3a** as indicated by TLC. Then, H_2O (100 μL, 5.6 mmol) and $[Cu(OTf)]_2C_6H_6$ (252 mg, 0.50 mmol) were added at 70 °C and the reaction mixture was stirred at 70 °C for about 12.0 h. After **3a** was consumed as indicated by TLC, the resulting mixture was poured into water (15 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 15 : 1, V/V) to give **6a** (136.4 mg, 90%).



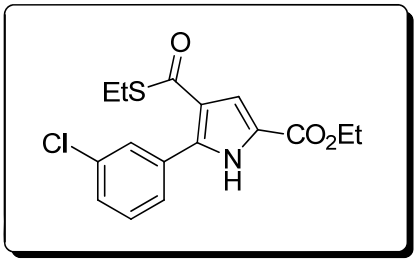
6a, Ethyl 4-((ethylthio)carbonyl)-5-phenyl-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 164–165 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.27–1.33 (m, 6H), 2.96 (q, *J* = 7.5 Hz, 2H), 4.22 (q, *J* = 7.0 Hz, 2H), 7.42–7.44 (m, 4H), 7.61–7.63 (m, 2H), 9.84 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 15.0, 23.1, 61.0, 116.8, 121.6, 122.4, 128.3, 129.1, 129.3, 130.6, 138.3, 160.9, 186.4. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{18}NO_3S^+$ ($[M + H]^+$) 304.1002. Found 304.1012.



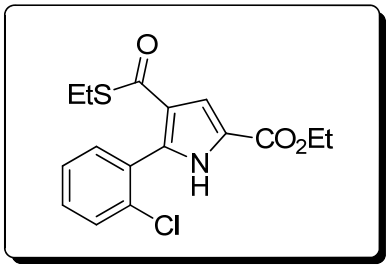
6b, Ethyl 4-((ethylthio)carbonyl)-5-(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 159–160 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.29 (t, *J* = 7.5 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H), 2.96 (q, *J* = 7.5 Hz, 2H), 3.85 (s, 3H), 4.27 (q, *J* = 7.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 2H), 9.63 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 15.0, 23.1, 55.3, 60.9, 113.7, 116.9, 121.1, 122.0, 122.8, 130.5, 138.4, 160.4, 160.9, 186.4. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{19}NNaO_4S^+$ ($[M + H]^+$) 356.0932. Found 356.0949.



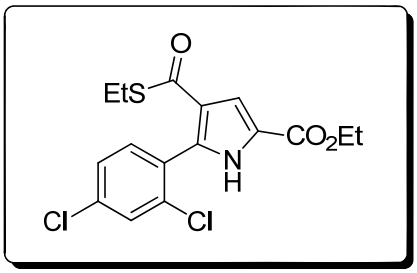
6c, Ethyl 5-(4-chlorophenyl)-4-((ethylthio)carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 163–164 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.29 (t, *J* = 7.5 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H), 2.97 (q, *J* = 7.5 Hz, 2H), 4.25 (q, *J* = 7.0 Hz, 2H), 7.41 (q, *J* = 5.0 Hz, 3H), 7.56 (q, *J* = 5.0 Hz, 2H), 9.73 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 14.9, 23.2, 61.1, 116.8, 121.8, 122.6, 128.5, 129.0, 130.5, 135.4, 137.0, 160.9, 186.5. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}ClNO_3S^+$ ($[M + H]^+$) 338.0612. Found 338.0620.



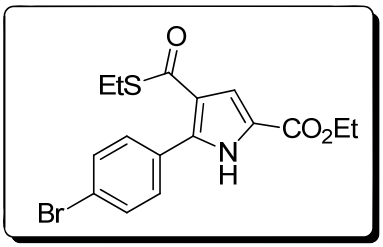
6d, Ethyl 5-(3-chlorophenyl)-4-((ethylthio)carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 154–155 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.28–1.34 (m, 6H), 2.97 (q, *J* = 7.5 Hz, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 7.34–7.42 (m, 3H), 7.52–7.54 (m, 1H), 7.59 (d, *J* = 1.5 Hz, 1H), 10.01 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 14.9, 23.2, 61.2, 116.8, 122.0, 122.8, 127.6, 129.0, 129.3, 129.5, 132.3, 134.2, 136.5, 160.9, 186.4. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}ClNO_3S^+$ ($[M + H]^+$) 338.0612. Found 338.0617.



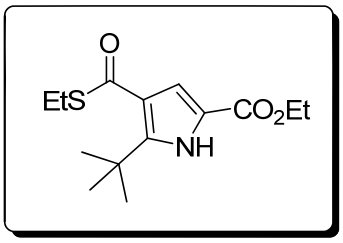
6e, Ethyl 5-(2-chlorophenyl)-4-((ethylthio)carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p.155–156 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.5 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H), 2.93 (q, *J* = 7.5 Hz, 2H), 4.19 (q, *J* = 7.0 Hz, 2H), 7.32–7.35 (m, 1H), 7.37–7.41 (m, 2H), 7.44–7.49 (m, 2H), 9.92 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 15.0, 23.0, 61.0, 115.4, 122.7, 123.4, 126.5, 129.7, 130.2, 130.6, 132.1, 134.0, 134.6, 160.9, 185.9. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}ClNO_3S^+$ ($[M + H]^+$) 338.0612. Found 338.0603.



6f, Ethyl 5-(2,4-dichlorophenyl)-4-((ethylthio)carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 145–146 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.26 (t, *J* = 7.5 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H), 2.94 (q, *J* = 7.5 Hz, 2H), 4.24 (q, *J* = 7.0 Hz, 2H), 7.32–7.34 (m, 1H), 7.38–7.40 (m, 2H), 7.50 (d, *J* = 1.5 Hz, 1H), 9.77 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 14.9, 23.0, 61.1, 115.4, 123.0, 123.6, 127.0, 128.7, 129.6, 133.0, 133.2, 134.8, 136.1, 160.8, 186.0. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{16}Cl_2NO_3S^+$ ($[M + H]^+$) 372.0222. Found 372.0214.

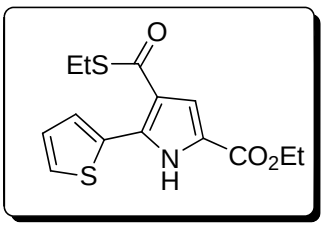


6g, Ethyl 5-(4-bromophenyl)-4-((ethylthio)carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 168–169 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.27–1.33 (m, 6H), 2.96 (q, *J* = 7.5 Hz, 2H), 4.18 (q, *J* = 7.0 Hz, 2H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 10.09 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 14.9, 23.2, 61.2, 116.9, 121.8, 122.6, 123.6, 129.5, 130.8, 131.4, 137.1, 161.0, 186.5. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{17}BrNO_3S^+$ ($[M + H]^+$) 382.0107. Found 382.0101.

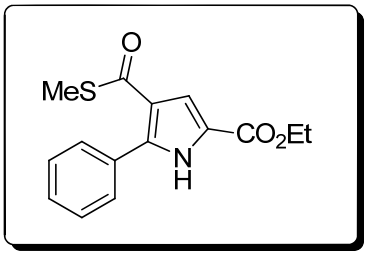


6h, Ethyl 5-(tert-butyl)-4-((ethylthio)carbonyl)-1*H*-pyrrole-2-carboxylate. Colorless viscous oil. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.5 Hz, 3H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.45 (s, 9H), 2.98 (q, *J* = 7.5 Hz, 2H), 4.33 (q, *J* = 7.0 Hz, 2H), 7.42 (d, *J* = 2.5 Hz, 1H), 9.07 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.4, 15.0, 23.3, 28.3, 33.4, 60.7, 116.3, 119.2, 120.9, 147.8, 160.7, 186.9. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{22}NO_3S^+$ ($[M + H]^+$) 284.1315. Found 284.1312.

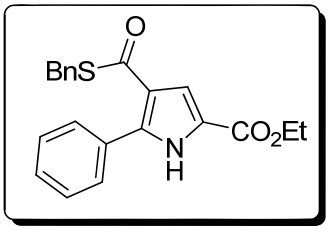
* The crude product was re-purified by flash column chromatography (silica gel, n-Hexane: EtOAc = 14 : 1, V/V)



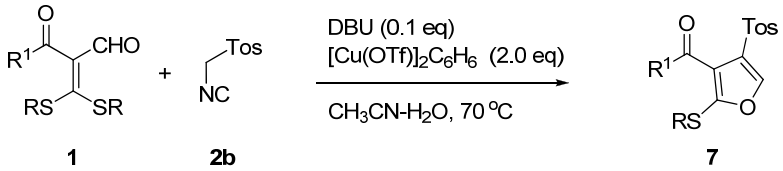
6i, Ethyl 4-((ethylthio)carbonyl)-5-(thiophen-2-yl)-1H-pyrrole-2-carboxylate. Colorless crystals. m.p. 140–141 ^{o}C.**^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.5 Hz, 3H), 1.37 (t, *J* = 7.0 Hz, 3H), 3.01 (q, *J* = 7.5 Hz, 2H), 4.32 (q, *J* = 7.0 Hz, 2H), 7.10–7.11 (m, 1H), 7.41–7.42 (m, 2H) 7.67 (dd, J_1 = 2.5 Hz, J_2 = 1.5 Hz, 1H), 9.63 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.4, 14.9, 23.3, 61.1, 116.9, 121.5, 122.4, 127.4, 127.6, 128.9, 131.2, 131.3, 160.6, 186.3. **HRMS** (ESI-TOF) Calcd for $C_{14}H_{16}NO_3S_2^+$ ($[M + H]^+$) 310.0566. Found 310.0558.



6j, Ethyl 4-((methylthio)carbonyl)-5-phenyl-1*H*-pyrrole-2-carboxylate. Colorless crystals. m.p. 164–165 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.30 (t, *J* = 7.0 Hz, 3H), 2.36 (s, 3H), 4.19 (q, *J* = 7.0 Hz, 2H), 7.41–7.42 (m, 4H), 7.61–7.62 (m, 2H), 10.04 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 11.5, 14.3, 61.0, 116.7, 121.5, 122.4, 128.2, 129.1, 129.2, 130.5, 138.4, 161.0, 186.7. **HRMS** (ESI-TOF) Calcd for $C_{15}H_{16}NO_3S^+$ ($[M + H]^+$) 290.0845. Found 290.0854.



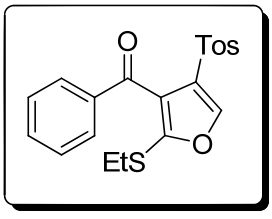
6k, S-benzyl 2-phenyl-5-tosyl-1*H*-pyrrole-3-carbothioate. Colorless crystals. m.p. 130–131 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.0 Hz, 3H), 4.23 (s, 2H), 4.32 (q, *J* = 7.0 Hz, 2H), 7.22–7.24 (m, 1H), 7.27–7.33 (m, 4H), 7.42–7.43 (m, 1H), 7.45–7.46 (m, 3H), 7.61–7.63 (m, 2H), 9.34 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 14.3, 33.0, 61.0, 116.9, 121.1, 122.5, 127.1, 128.3, 128.5, 128.9, 129.1, 129.3, 130.5, 137.8, 138.7, 161.0, 185.5. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{20}NO_3S^+$ ($[M + H]^+$) 366.1158. Found 366.1159.



1 **2b** **7**

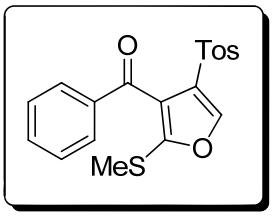
General procedure for the synthesis of 7 (**7a** as an example):

To the mixture of **1a** (140.1 mg, 0.50 mmol) and TosMIC **2b** (105.8 mg, 0.55 mmol) in CH_3CN (2 mL) was added 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU, 7.5 μL, 0.05 mmol) in one portion at room temperature. The mixture was stirred for about 15 min for the formation of **3n** as indicated by TLC. Then, H_2O (200 μL, 5.6 mmol) and $[Cu(OTf)]_2C_6H_6$ (504 mg, 1.00 mmol) were added at 70 °C and the reaction mixture was stirred at 70 °C for about 24.0 h. Then the resulting mixture was poured into water (15 mL) and extracted with dichloromethane (15 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography (silica gel, petroleum ether: EtOAc = 15 : 1, V/V) to give **5a** (96.5 mg, 50%).

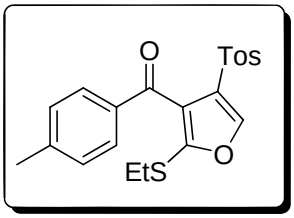


7a, (2-(ethylthio)-4-tosylfuran-3-yl)(phenyl)methanone. Colorless crystals. m.p. 155–156 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.5 Hz, 3H), 2.40 (s, 3H), 2.79 (q, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 7.5 Hz, 2H), 8.17 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.2, 21.6, 29.4, 125.4, 128.2, 128.5, 129.6, 129.8, 131.0, 133.7, 137.3, 137.9, 144.6, 147.8, 151.0,

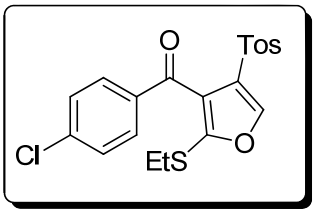
189.0. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{19}O_4S_2^+$ ([M + H]$^+$) 387.0719. Found 387.0722.



7b, (2-(methylthio)-4-tosylfuran-3-yl)(phenyl)methanone. Colorless crystals. m.p. 164–165 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.41 (s, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H), 8.18 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 17.0, 21.7, 123.6, 128.3, 128.5, 129.5, 129.6, 131.1, 133.7, 137.3, 137.8, 144.6, 148.6, 152.4, 188.8. **HRMS** (ESI-TOF) Calcd for $C_{19}H_{17}O_4S_2^+$ ([M + H]$^+$) 373.0563. Found 373.0567.



7c, (2-(ethylthio)-4-tosylfuran-3-yl)(p-tolyl)methanone. Colorless crystals. m.p. 86–87 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.5 Hz, 3H), 2.39 (s, 3H), 2.42 (s, 3H), 2.78 (q, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.25–7.27 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.5 Hz, 2H), 8.16 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.2, 21.6, 21.8, 29.4, 125.6, 128.1, 129.2, 129.5, 129.9, 130.9, 134.7, 137.9, 144.5, 144.9, 148.6, 150.6, 188.5. **HRMS** (ESI-TOF) Calcd for $C_{21}H_{21}O_4S_2^+$ ([M + H]$^+$) 401.0876. Found 401.0879.



7d, (4-chlorophenyl)(2-(ethylthio)-4-tosylfuran-3-yl)methanone. Colorless crystals. m.p. 136–137 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 1.19 (t, *J* = 7.5 Hz, 3H), 2.41 (s, 3H), 2.81 (q, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 8.17 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 15.2, 21.6, 29.4 , 124.9, 128.1, 128.8, 129.6, 130.9, 131.1, 135.5, 137.7, 140.4, 144.7, 148.7, 151.3, 187.7. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{18}ClO_4S_2^+$ ([M + H]$^+$) 421.0330. Found 421.0337.

III . Crystal data and OPTEP drawings of compound 4a, 5a, 6a and 7b.

Single-crystal X-ray diffraction data was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-Kα (λ = 0.71073 Å) radiation with a ω scan technique. The crystal structures were solved by direct method of SHELXS-97[3] and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined anisotropic.

(1) Crystal data and OPTEP drawing of compound **4a** (CCDC 949219)

ORTEP drawing:

Crystal data:

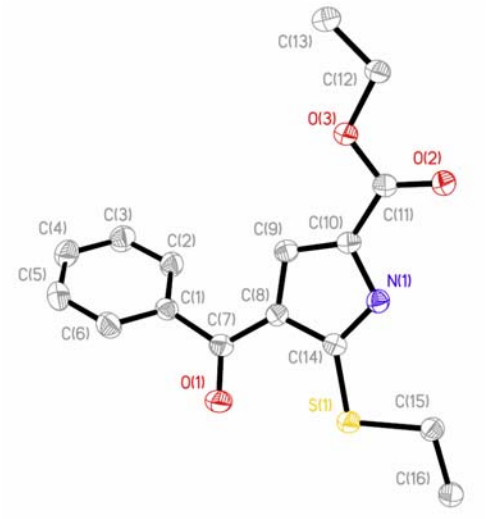
Empirical formula	$C_{19}H_{23}NO_4S_2$
Formula weight	393.50
Crystal system	Triclinic
Space group	P -1
a (Å)	8.6230(6)
b (Å)	10.8704(7)
c (Å)	10.8806(7)
α (deg)	81.701(1)
β (deg)	86.189(1)
γ (deg)	78.490(1)
Volume ($Å^3$)	988.18(11)
Z	2
Calculated density (mg/m^3)	1.32
Absorption coefficient (mm^{-1})	0.293
F(000)	416.0
Theta range for data collection (deg)	1.9 to 26.0
Reflections collected/unique	5443/3829
Goodness-of-fit on F^2	1.024
Final R indices [$I > 2\sigma(I)$]	R1=0.044, WR2 = 0.111

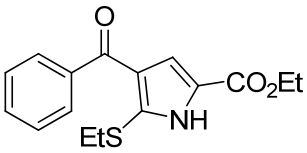
(3) G. M. Sheldrick, *SHELXS-97*, *Programs for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997.

R indices (all data)	R1=0.052, WR2 =0.117

(2) Crystal data and OPTEP drawing of compound **5a** (CCDC 949218)

ORTEP drawing:



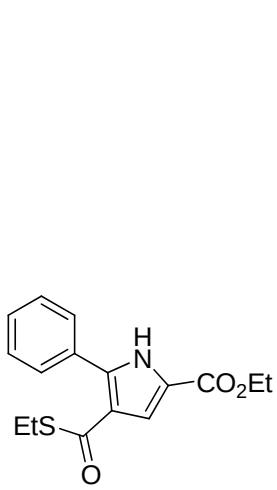


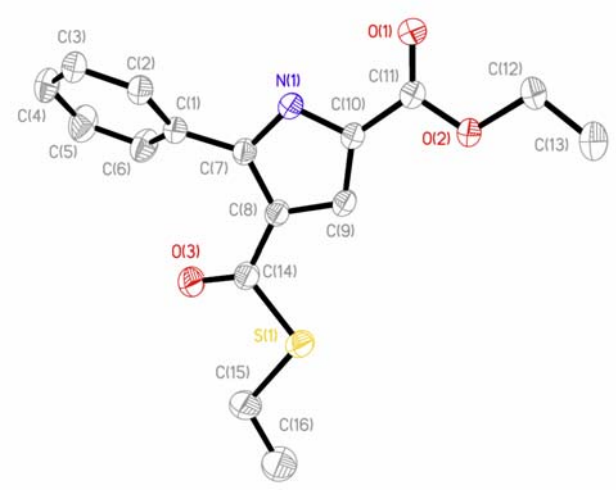
Crystal data:

Empirical formula	$C_{16}H_{17}NO_3S$
Formula weight	303.4
Crystal system	Monoclinic
Space group	P 21/c
a (Å)	15.908(4)
b (Å)	5.9035(14)
c (Å)	16.411(4)
α (deg)	90.00
β (deg)	102.783(4)
γ (deg)	90.00
Volume ($Å^3$)	1503.0(6)
Z	4
Calculated density (mg/m^3)	1.34
Absorption coefficient (mm^{-1})	0.225
F(000)	639.9
Theta range for data collection (deg)	2.5 to 26.0
Reflections collected/unique	9166/2954
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$]	R1=0.042, WR2 = 0.098
R indices (all data)	R1=0.062, WR2 =0.108

(3) Crystal data and OPTEP drawing of compound **6a** (CCDC 949220)

ORTEP drawing:



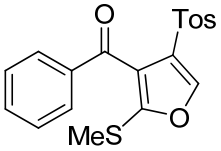


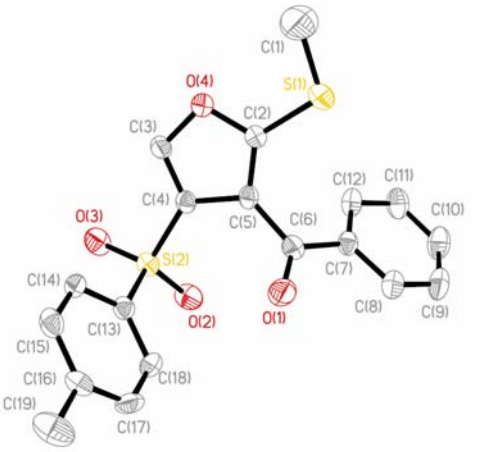
Crystal data:

Empirical formula	$C_{16}H_{17}NO_3S$
Formula weight	303.4
Crystal system	Triclinic
Space group	P -1
a (Å)	8.094(2)
b (Å)	9.747(3)
c (Å)	10.514(3)
α (deg)	76.657(5)
β (deg)	81.203(6)
γ (deg)	78.138(5)
Volume ($Å^3$)	785.0(4)
Z	2
Calculated density (mg/m^3)	1.28
Absorption coefficient (mm^{-1})	0.215
F(000)	320.0
Theta range for data collection (deg)	2.0 to 26.0
Reflections collected/unique	4281/3015
Goodness-of-fit on F^2	1.028
Final R indices [$I > 2\sigma(I)$]	R1=0.063, WR2 = 0.148
R indices (all data)	R1=0.090, WR2 =0.168

(4) Crystal data and OPTEP drawing of compound **7b** (CCDC 965705)

ORTEP drawing:

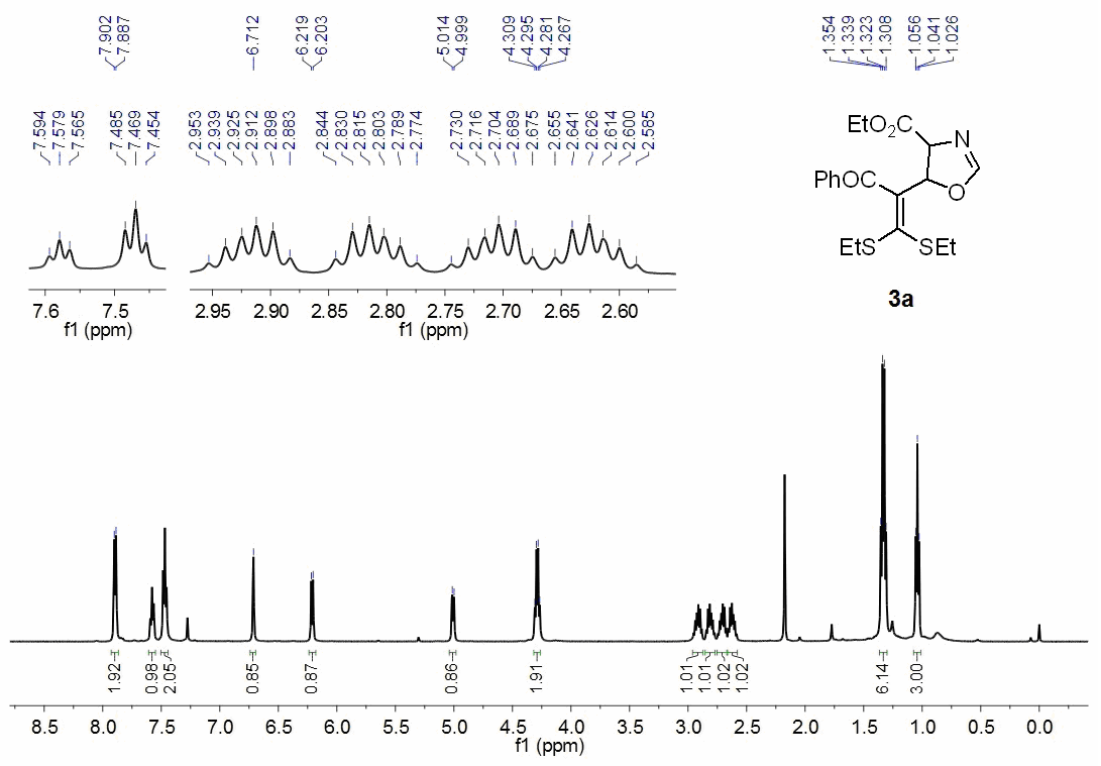


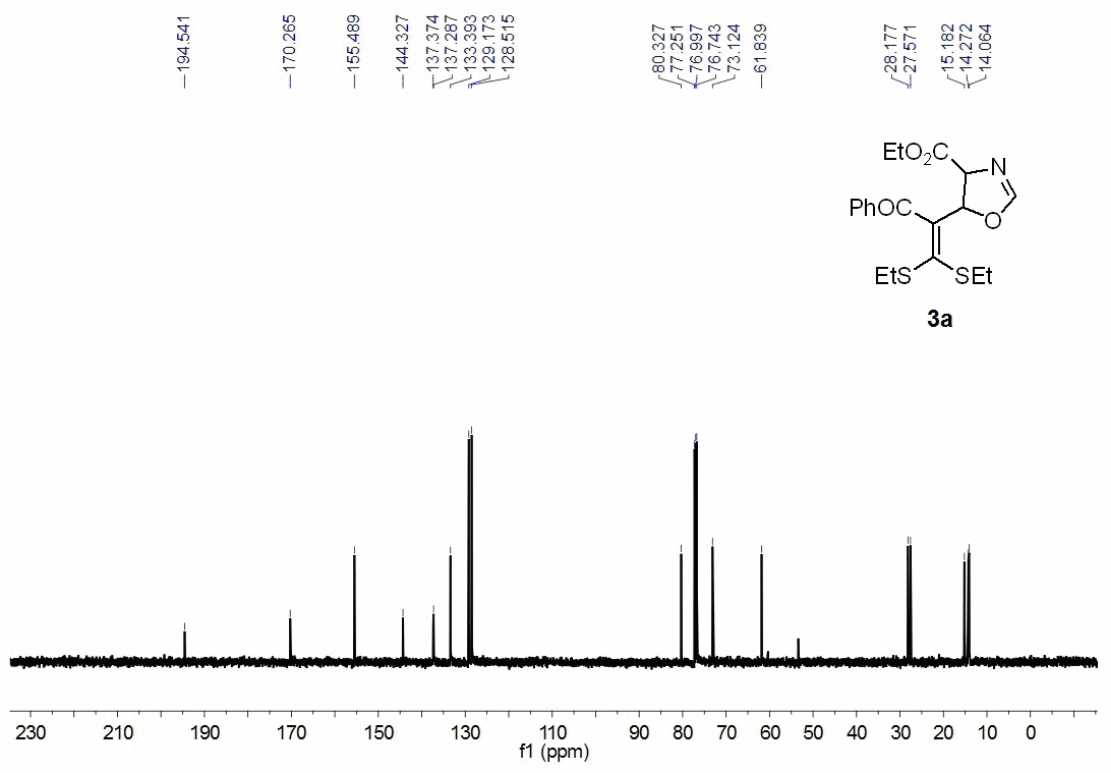


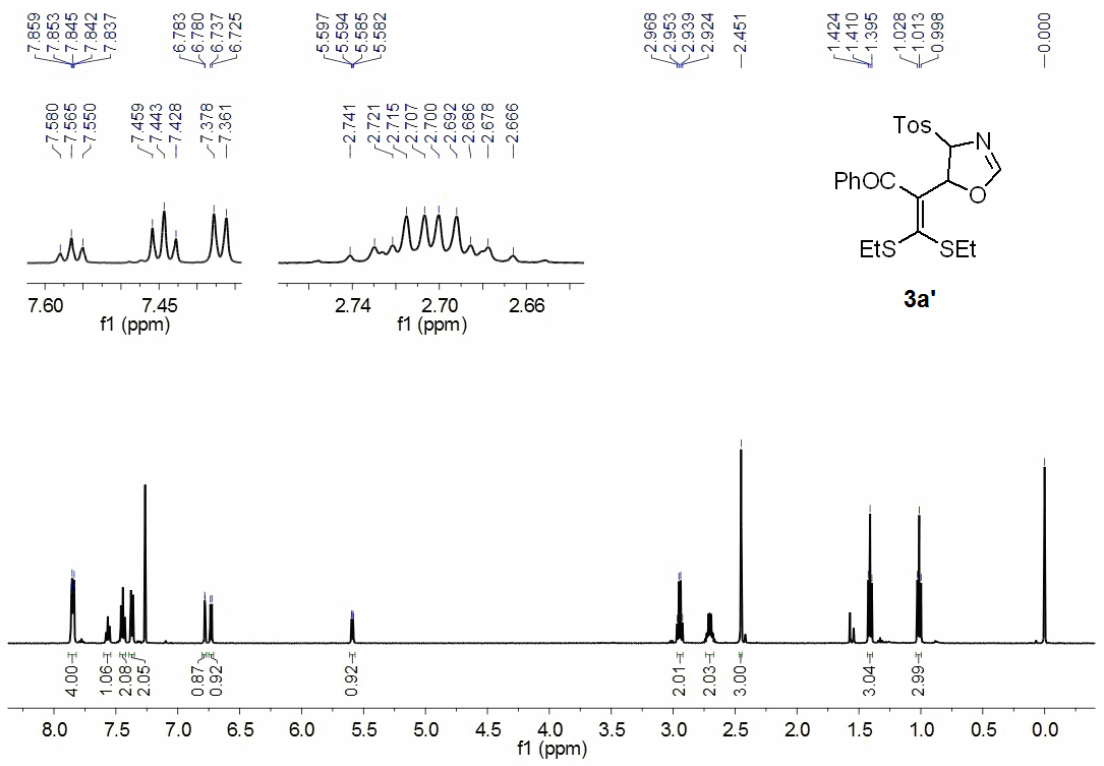
Crystal data:

Empirical formula	$C_{19}H_{16}O_4S_2$
Formula weight	372.44
Crystal system	Monoclinic
Space group	P 21/c
a (Å)	13.510 (4)
b (Å)	8.068(3)
c (Å)	17.081(5)
α (deg)	90
β (deg)	107.751(6)
γ (deg)	90
Volume ($Å^3$)	1773.2(10)
Z	4
Calculated density (mg/m^3)	1.395
Absorption coefficient (mm^{-1})	0.321
F(000)	776.0
Theta range for data collection (deg)	2.8 to 25.0
Reflections collected/unique	7945/3032
Goodness-of-fit on F^2	0.863
Final R indices [$I > 2\sigma(I)$]	R1=0.068, WR2 = 0.179
R indices (all data)	R1=0.131, WR2 =0.234

IV. Copies of ^{1}H NMR and ^{13}C NMR spectra



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7.845
7.842
7.837
6.783
6.780
6.737
6.725
5.597
5.594
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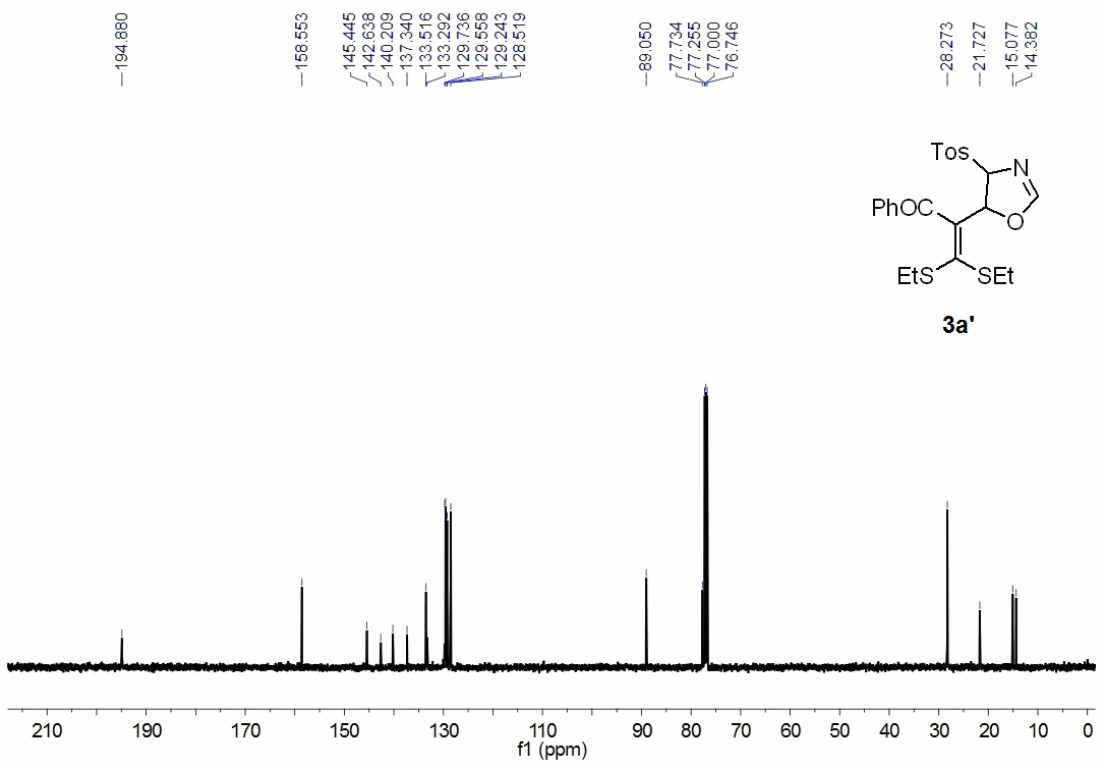
5.582
2.968
2.953
2.939
2.924
2.451
1.424
1.410
1.395
1.028
1.013
0.998
0.000
7.580
7.565
7.550
7.459
7.443
7.428
7.378
7.361
2.741
2.721
2.715
2.707
2.700
2.692
2.686
2.678
2.666
7.60
7.45
f1 (ppm)
2.74
2.70
2.66
f1 (ppm)
Tos
N
PhOC
O
EtS
SEt
3a'
4.00
1.06
2.08
2.05
0.87
0.92
0.92
2.01
2.03
3.00
3.04
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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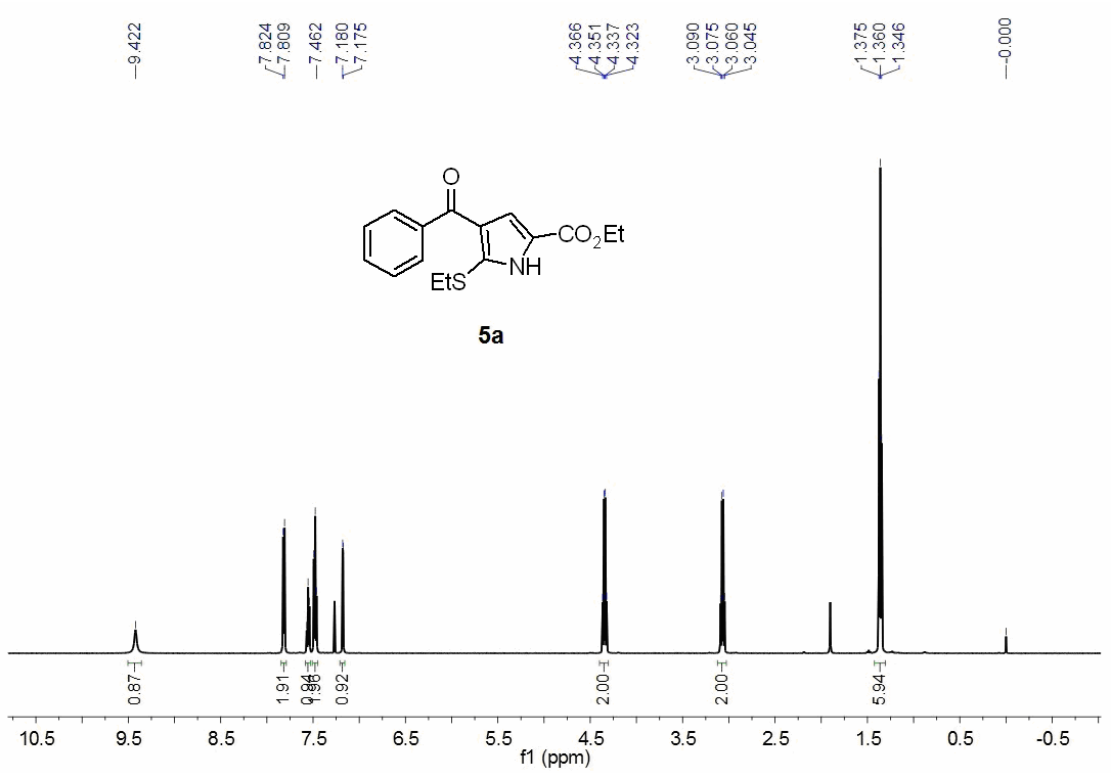
158.553
145.445
142.638
140.209
137.340
133.516
133.292
129.736
129.558
129.243
128.519
89.050
77.734
77.255
77.000
76.746
28.273
21.727
15.077
14.382
Tos
N
PhOC
O
EtS
SEt
3a'
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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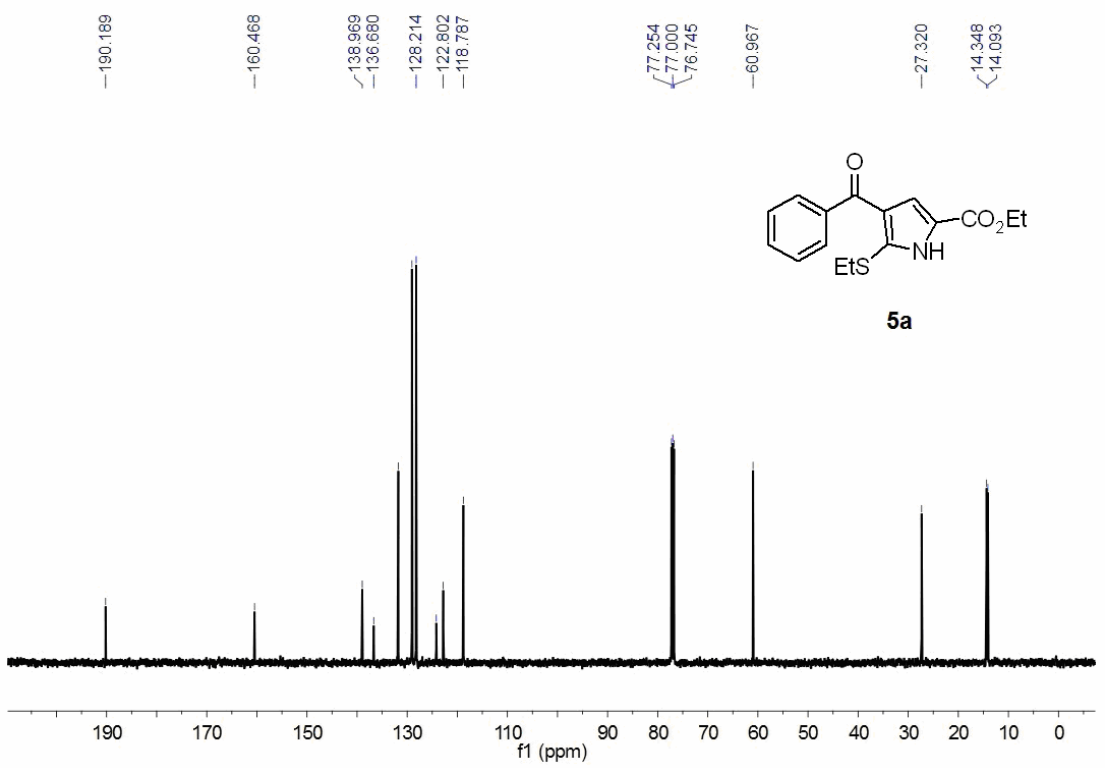
7.824
7.809
7.462
7.180
7.175
4.366
4.351
4.337
4.323
3.090
3.075
3.060
3.045
1.375
1.360
1.346
0.000
O
CO2Et
NH
EtS
5a
0.87
1.91
0.92
2.00
2.00
5.94
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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77.254
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76.745
60.967
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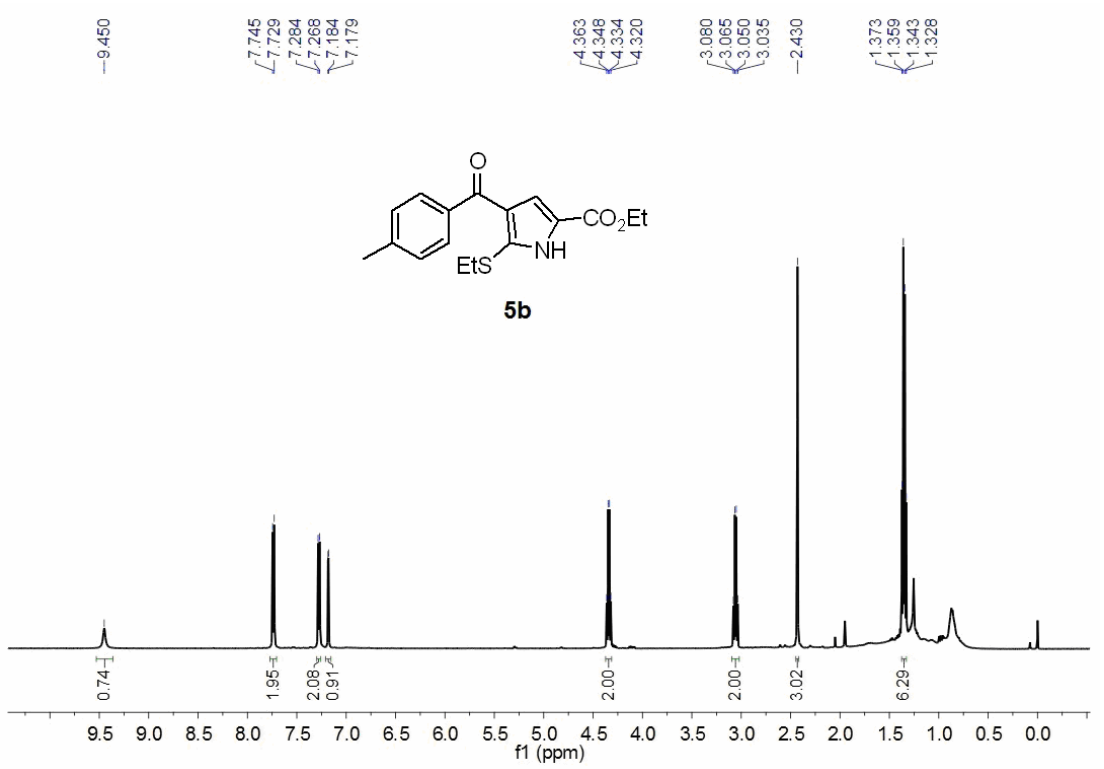
14.093
O
CO2Et
NH
EtS
5a
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.184
7.179
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4.334
4.320
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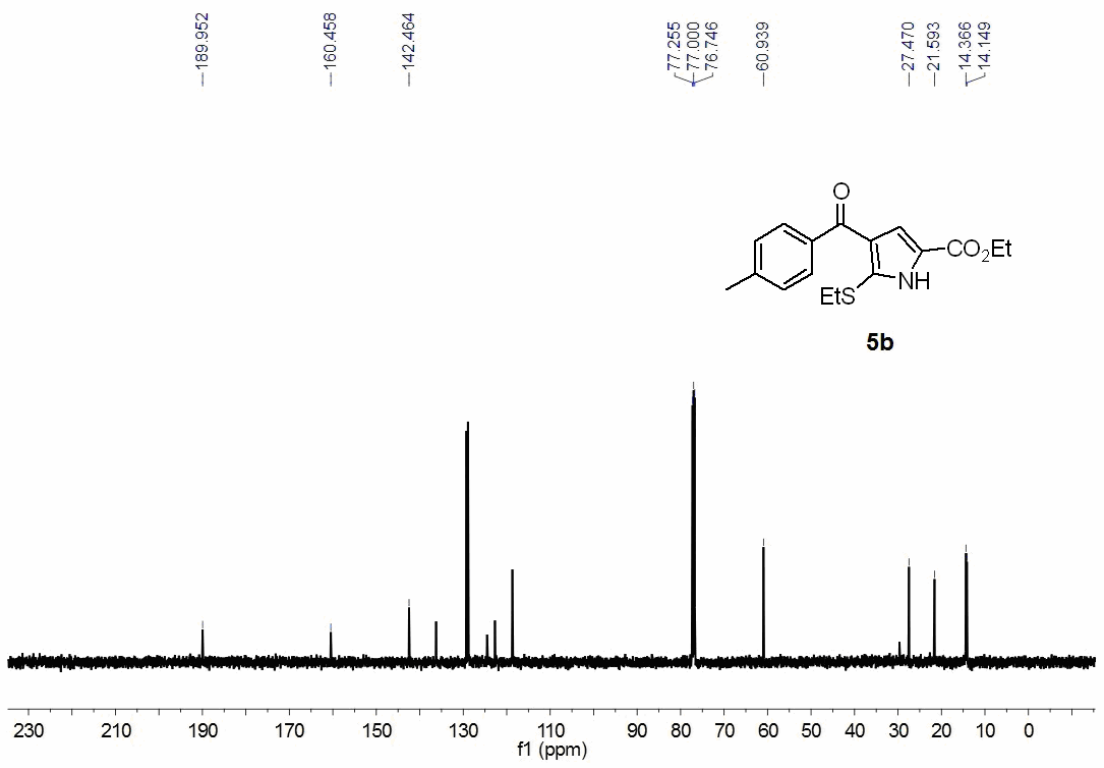
3.065
3.050
3.035
2.430
1.373
1.359
1.343
1.328
O
CO2Et
EtS
NH
5b
0.74
1.95
2.08
0.91
2.00
2.00
3.02
6.29
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.000
76.746
60.939
27.470
21.593
14.366
14.149
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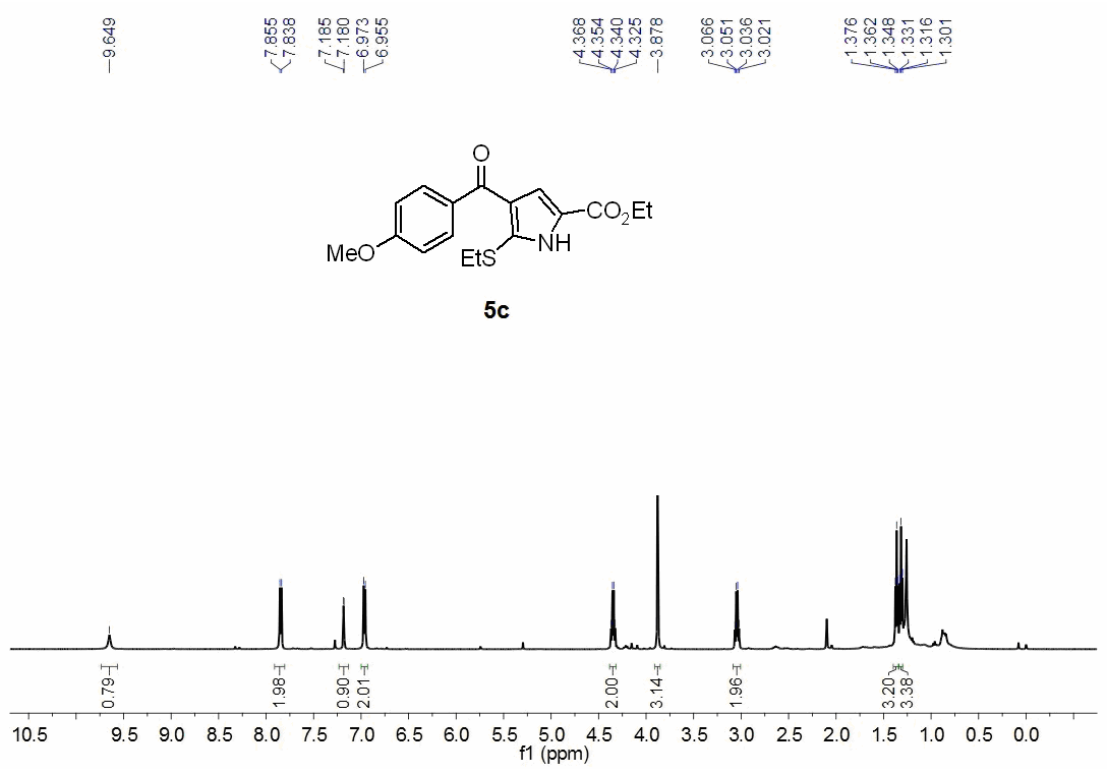
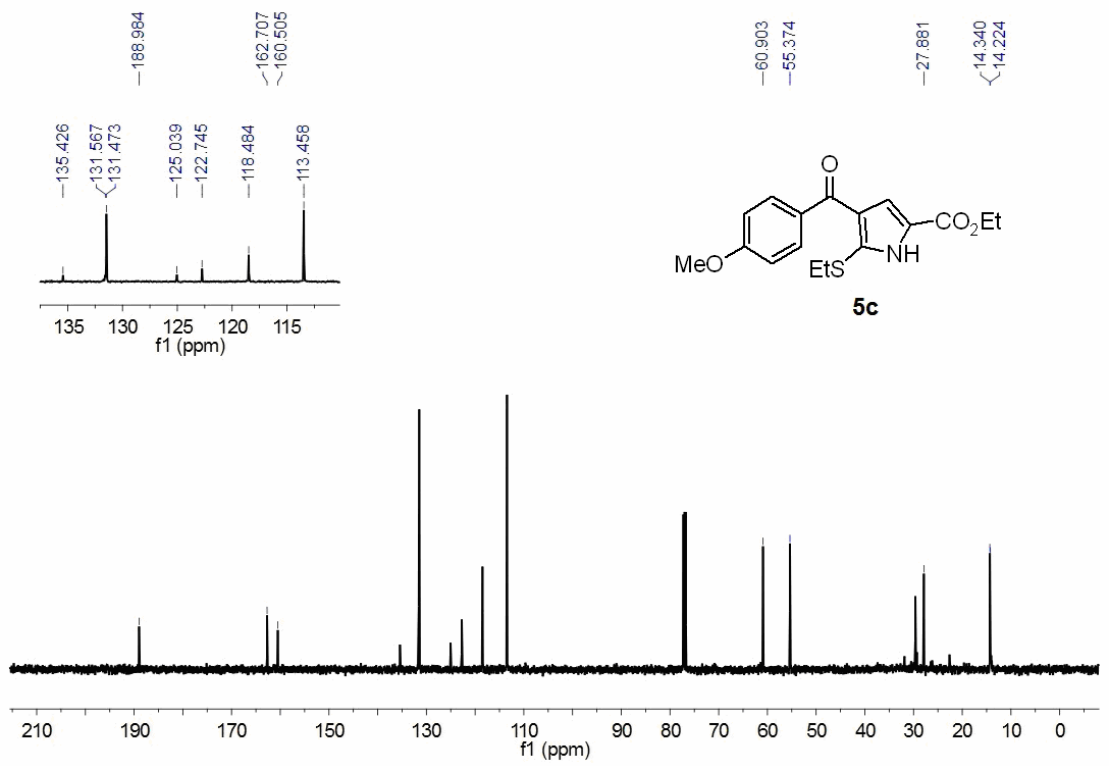
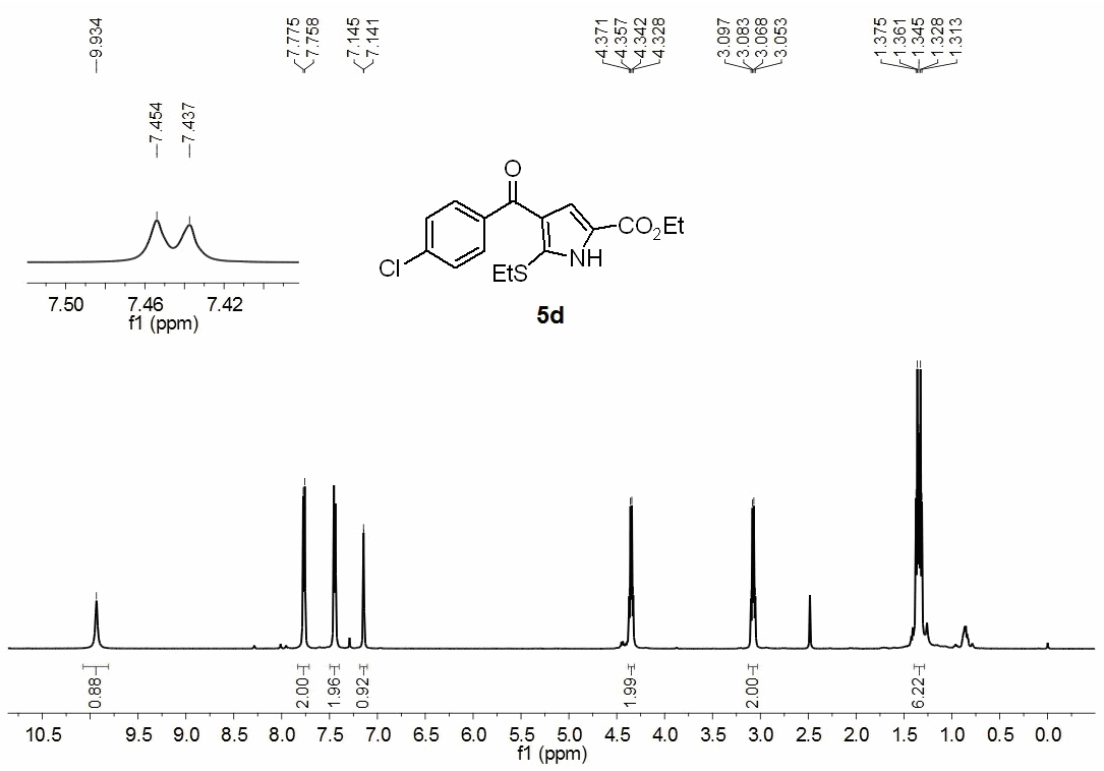
CO2Et
EtS
NH
5b
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

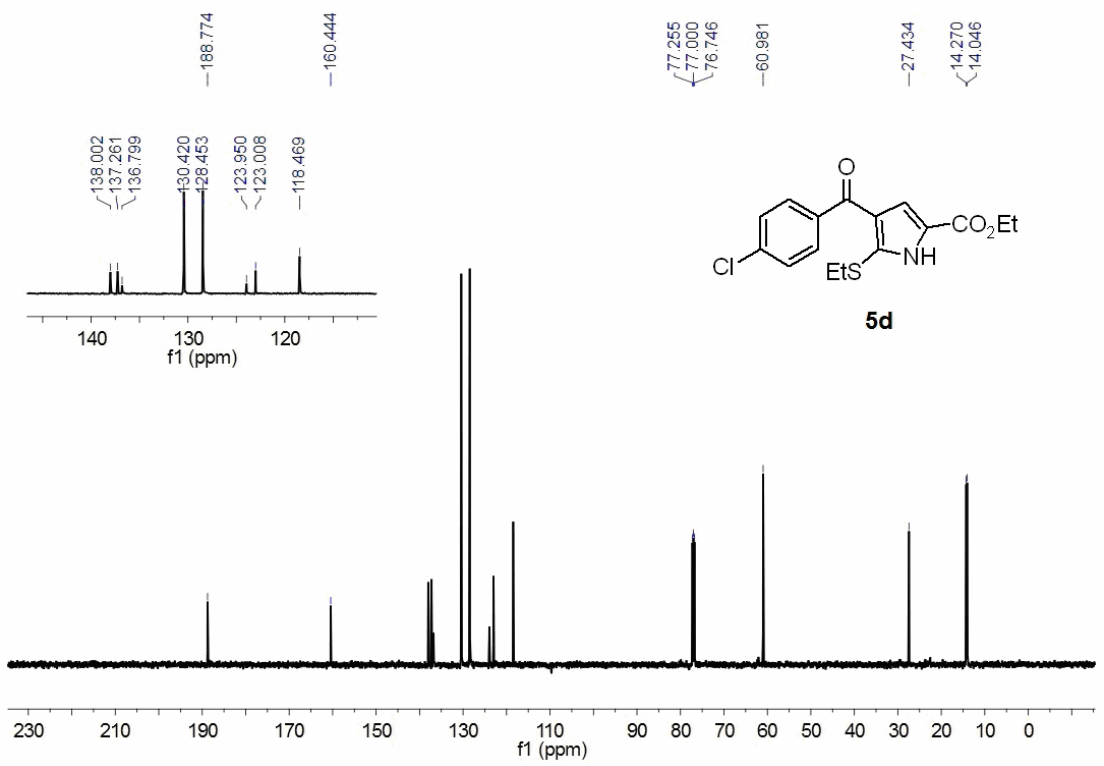

9.649
7.855
7.838
7.185
7.180
6.973
6.955
4.368
4.354
4.340
4.325
3.878
3.066
3.051
3.036
3.021
1.376
1.362
1.348
1.331
1.316
1.301
O
CO2Et
MeO
EtS
NH
0.79
1.98
0.90
2.01
2.00
3.14
1.96
3.20
3.38
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

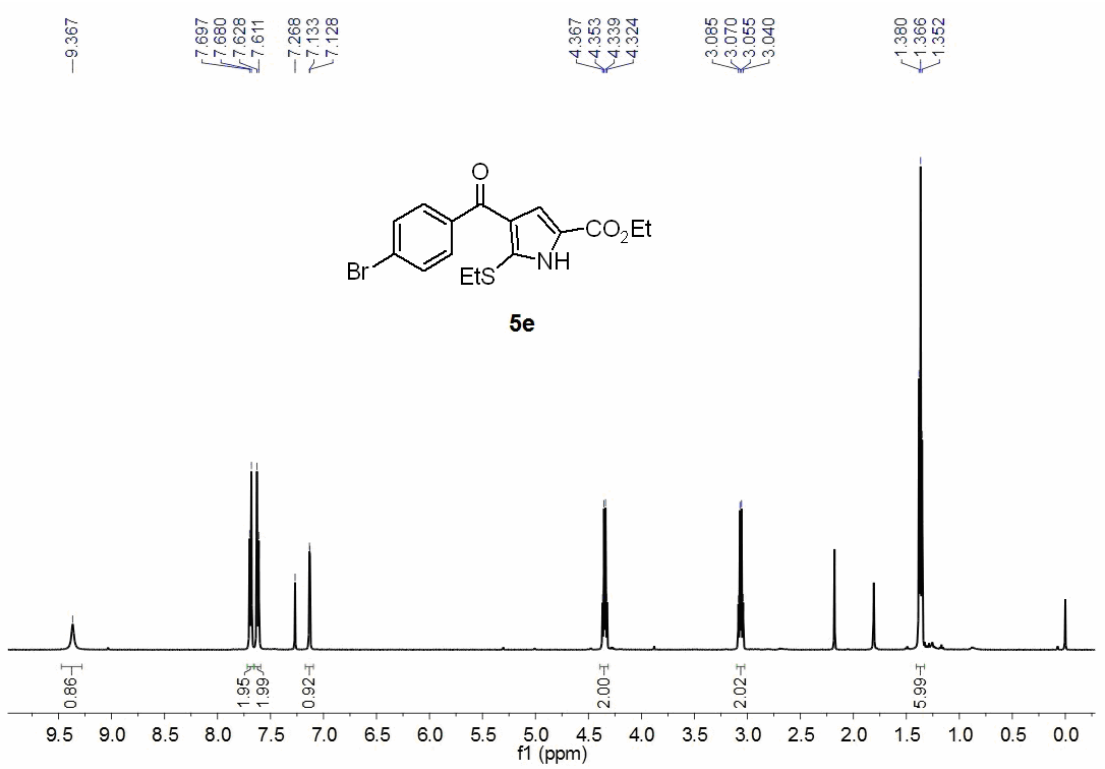
5c

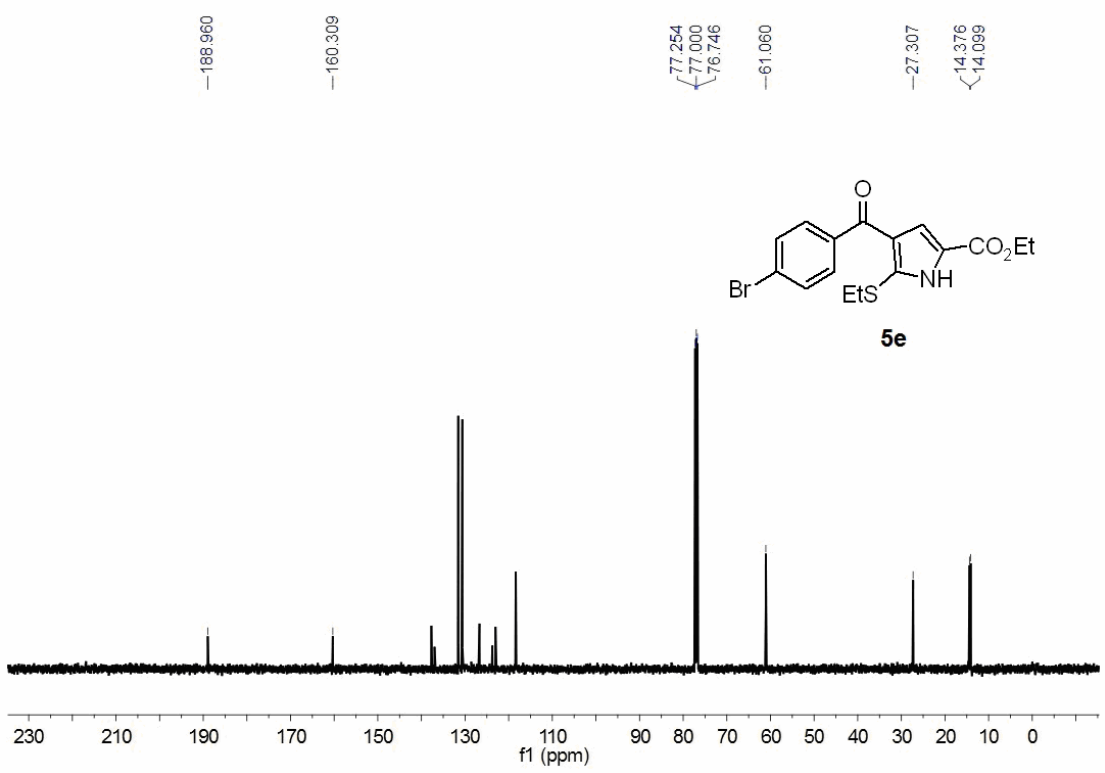

188.984
162.707
160.505
135.426
131.567
131.473
125.039
122.745
118.484
113.458
135 130 125 120 115
f1 (ppm)
60.903
55.374
27.881
14.340
14.224
O
CO2Et
MeO
EtS
NH
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

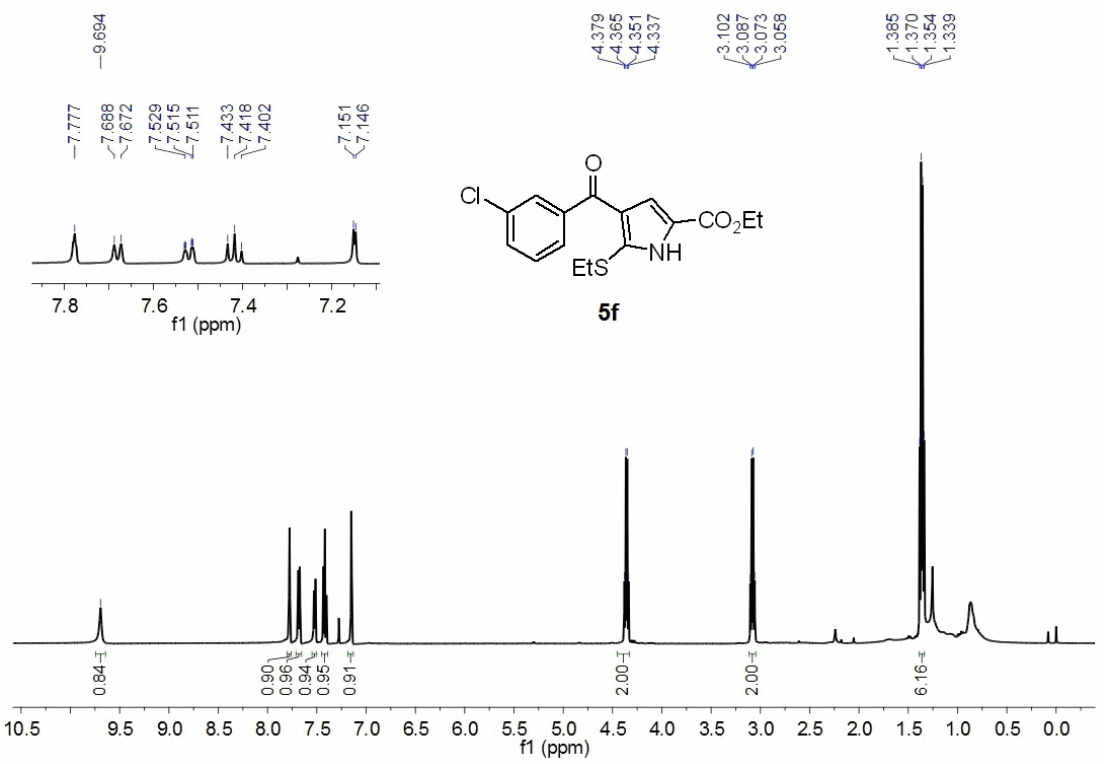
5c

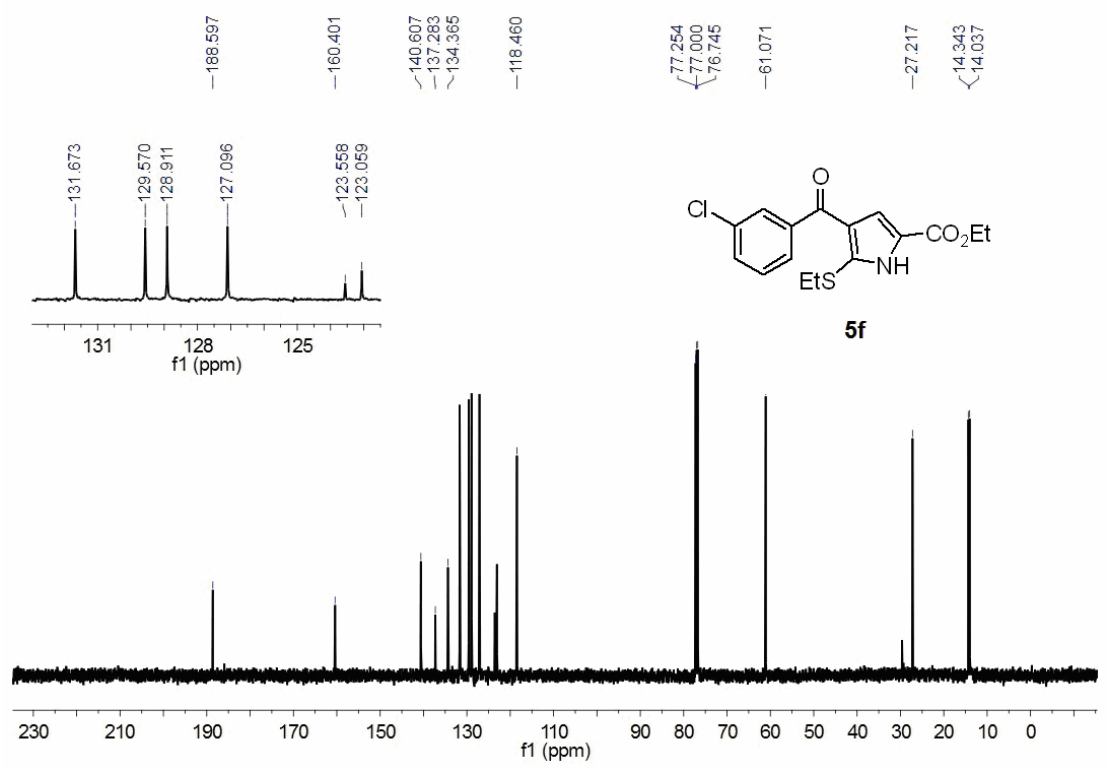

9.934
7.775
7.758
7.454
7.437
7.145
7.141
4.371
4.357
4.342
4.328
3.097
3.083
3.068
3.053
1.375
1.361
1.345
1.328
1.313
7.50
7.46
7.42
f1 (ppm)
O
CO2Et
Cl
EtS
NH
5d
0.88
2.00
1.96
0.92
1.99
2.00
6.22
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

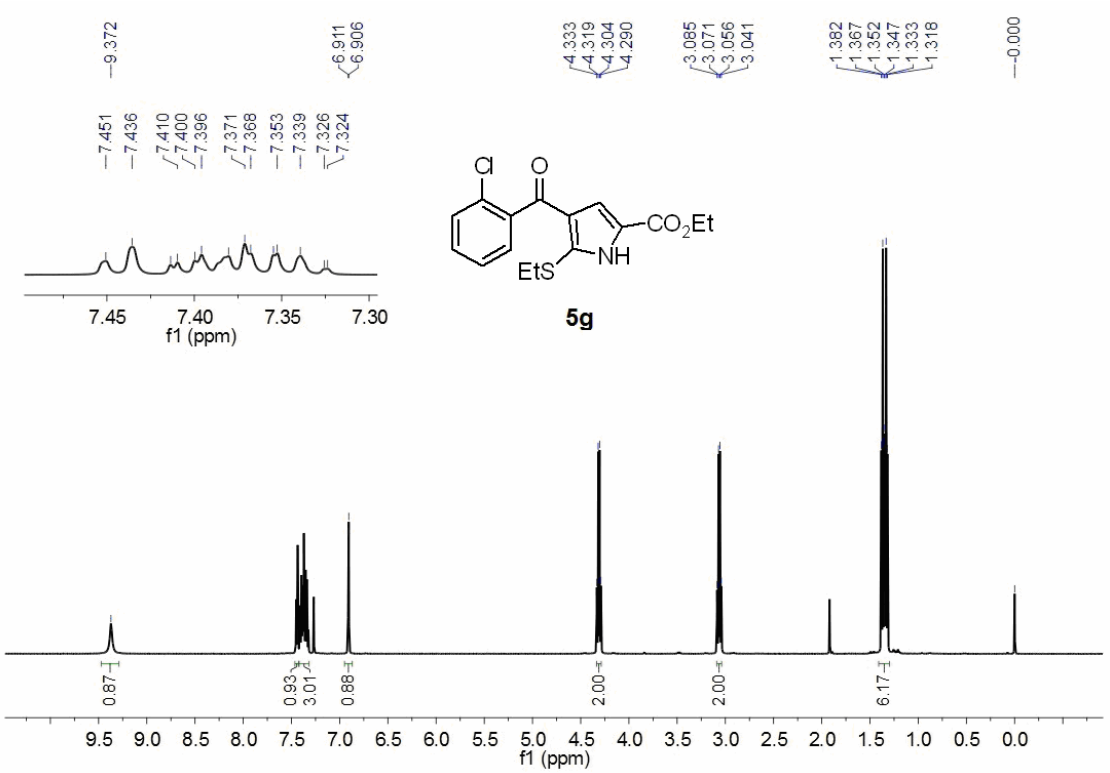

188.774
160.444
77.255
77.000
76.746
60.981
27.434
14.270
14.046
138.002
137.261
136.799
130.420
128.453
123.950
123.008
118.469
140
130
120
f1 (ppm)
O
CO2Et
Cl
EtS
NH
5d
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

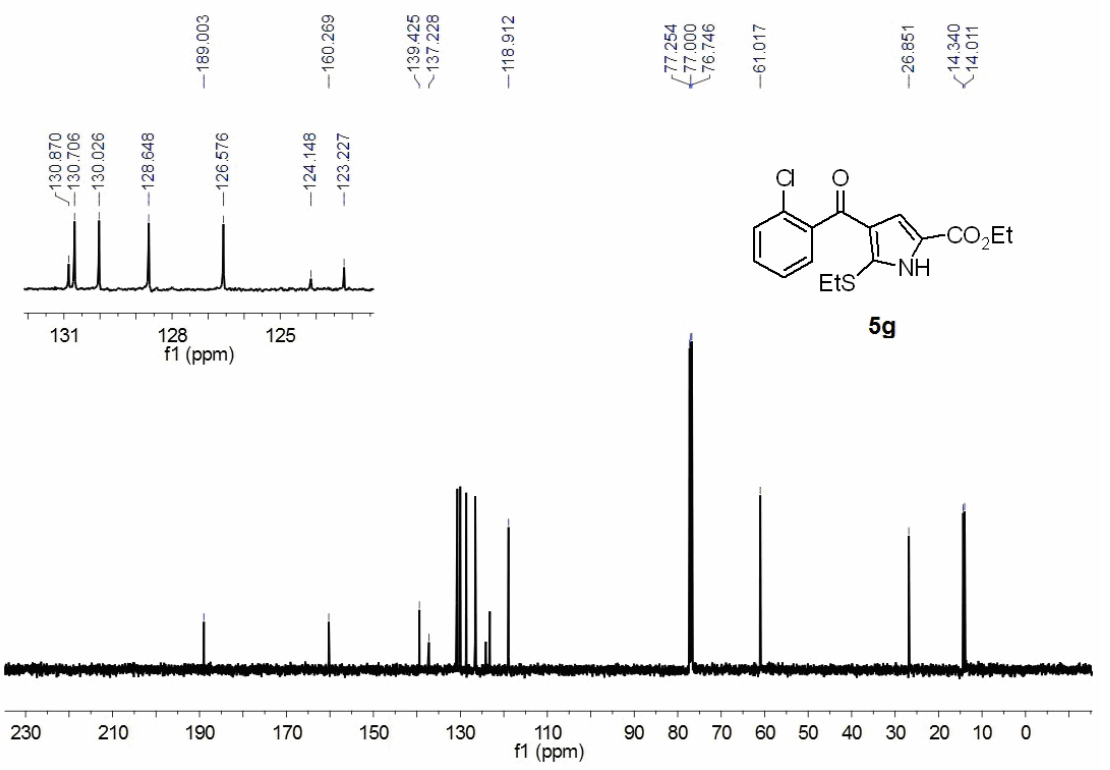

9.367
7.697
7.680
7.628
7.611
7.268
7.133
7.128
4.367
4.353
4.339
4.324
3.085
3.070
3.055
3.040
1.380
1.366
1.352
O
CO2Et
Br
EtS
NH
5e
0.86
1.95
1.99
0.92
2.00
2.02
5.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

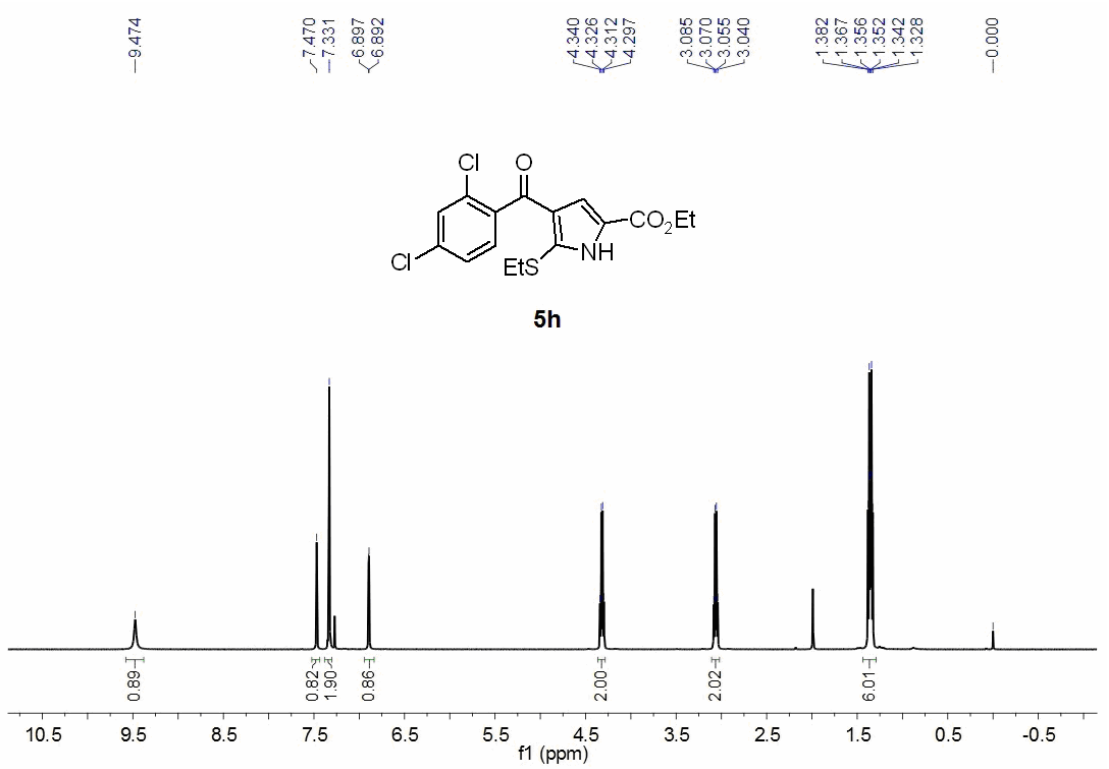

188.960
160.309
77.254
77.000
76.746
61.060
27.307
14.376
14.099
O
CO2Et
Br
EtS
NH
5e
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

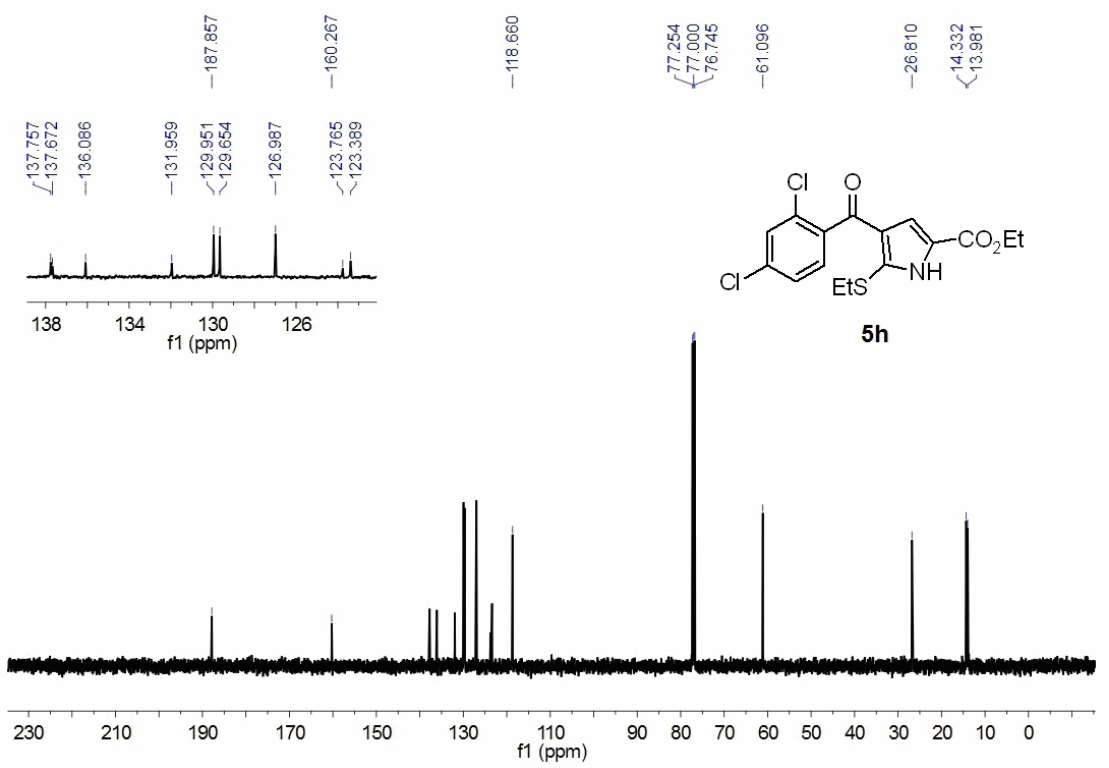

9.694
7.777
7.688
7.672
7.529
7.515
7.511
7.433
7.418
7.402
7.151
7.146
4.379
4.365
4.351
4.337
3.102
3.087
3.073
3.058
1.385
1.370
1.354
1.339
Cl
O
CO2Et
EtS
NH
5f
0.84
0.90
0.96
0.94
0.95
0.91
2.00
2.00
6.16
f1 (ppm)

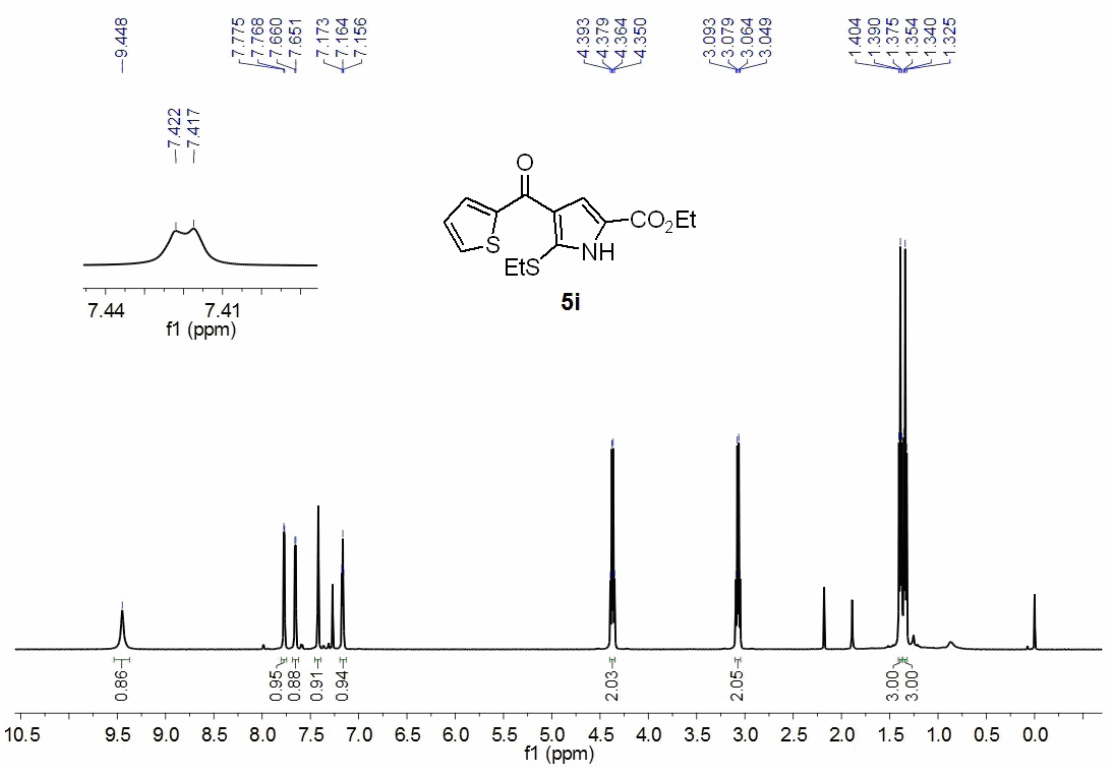

188.597
160.401
140.607
137.283
134.365
118.460
77.254
77.000
76.745
61.071
27.217
14.343
14.037
131.673
129.570
128.911
127.096
123.558
123.059
Cl
O
CO2Et
EtS
NH
5f
f1 (ppm)

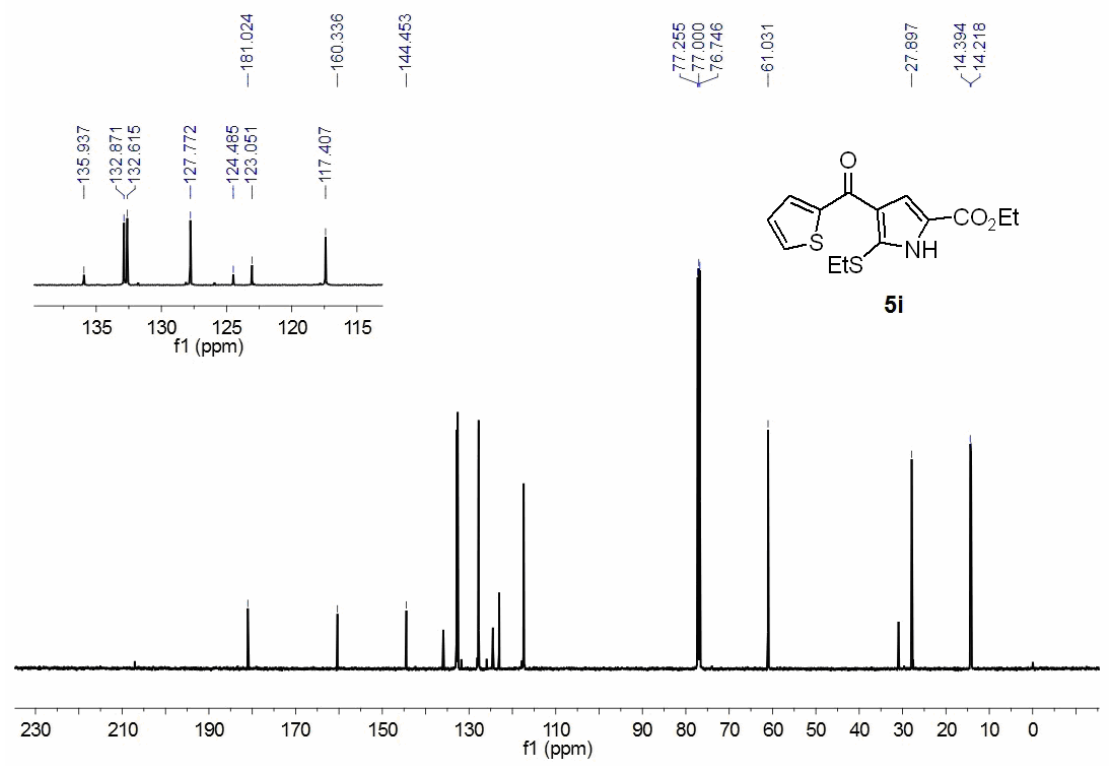

9.372
7.451
7.436
7.410
7.400
7.396
7.371
7.368
7.353
7.339
7.326
7.324
6.911
6.906
4.333
4.319
4.304
4.290
3.085
3.071
3.056
3.041
1.382
1.367
1.352
1.347
1.333
1.318
0.000
Cl
O
CO2Et
EtS
NH
5g
7.45
7.40
7.35
7.30
f1 (ppm)
0.87
0.93
3.01
0.88
2.00
2.00
6.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

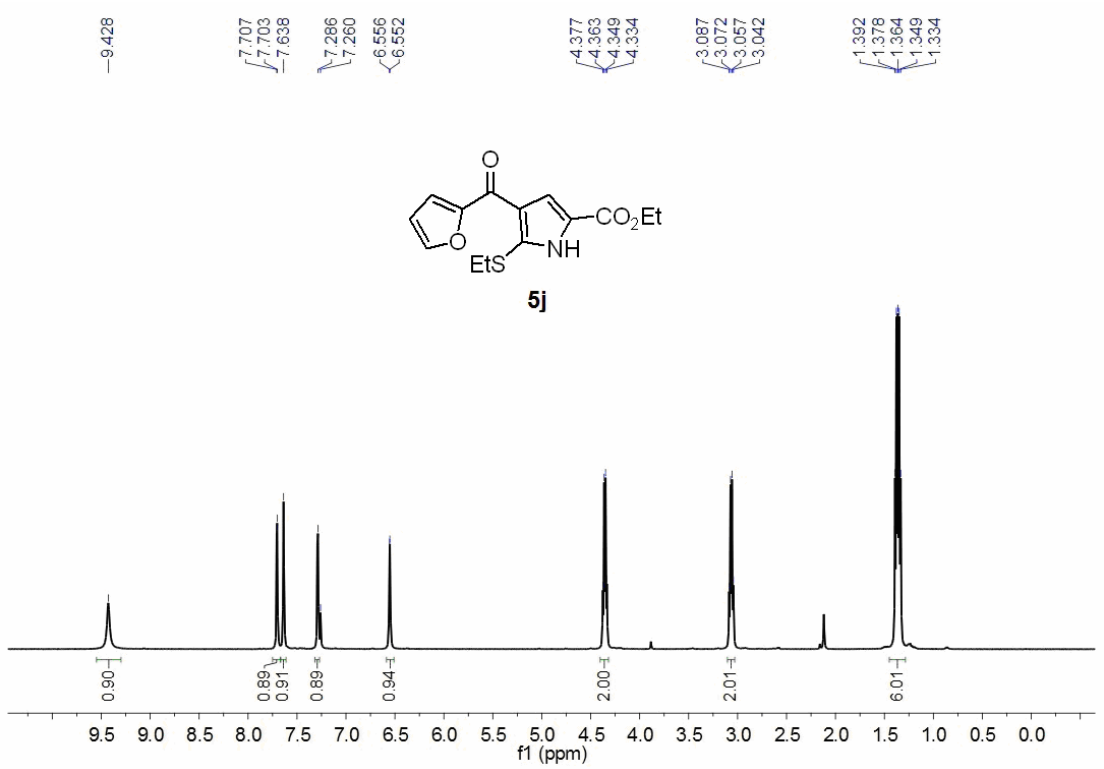

189.003
160.269
139.425
137.228
118.912
77.254
77.000
76.746
61.017
26.851
14.340
14.011
130.870
130.706
130.026
128.648
126.576
124.148
123.227
Cl
O
CO2Et
EtS
NH
5g
131
128
125
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

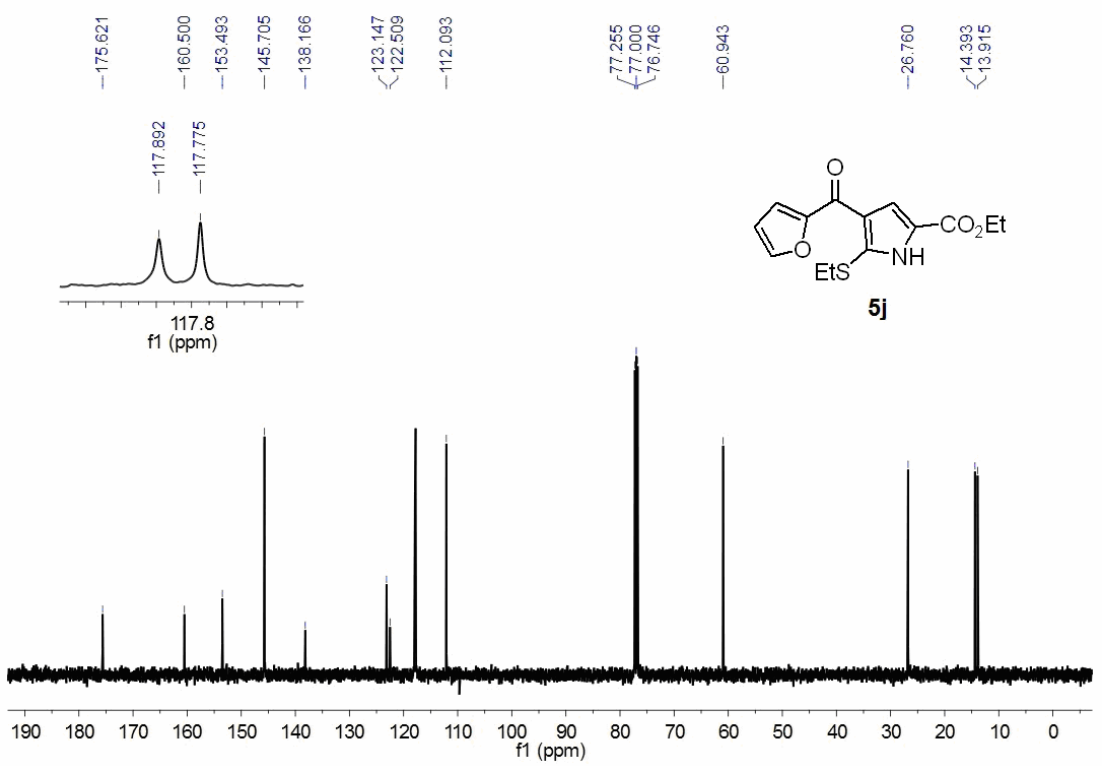

9.474
7.470
7.331
6.897
6.892
4.340
4.326
4.312
4.297
3.085
3.070
3.055
3.040
1.382
1.367
1.356
1.352
1.342
1.328
0.000
Cl
O
CO2Et
Cl
EtS
NH
5h
0.89
0.82
1.90
0.86
2.00
2.02
6.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

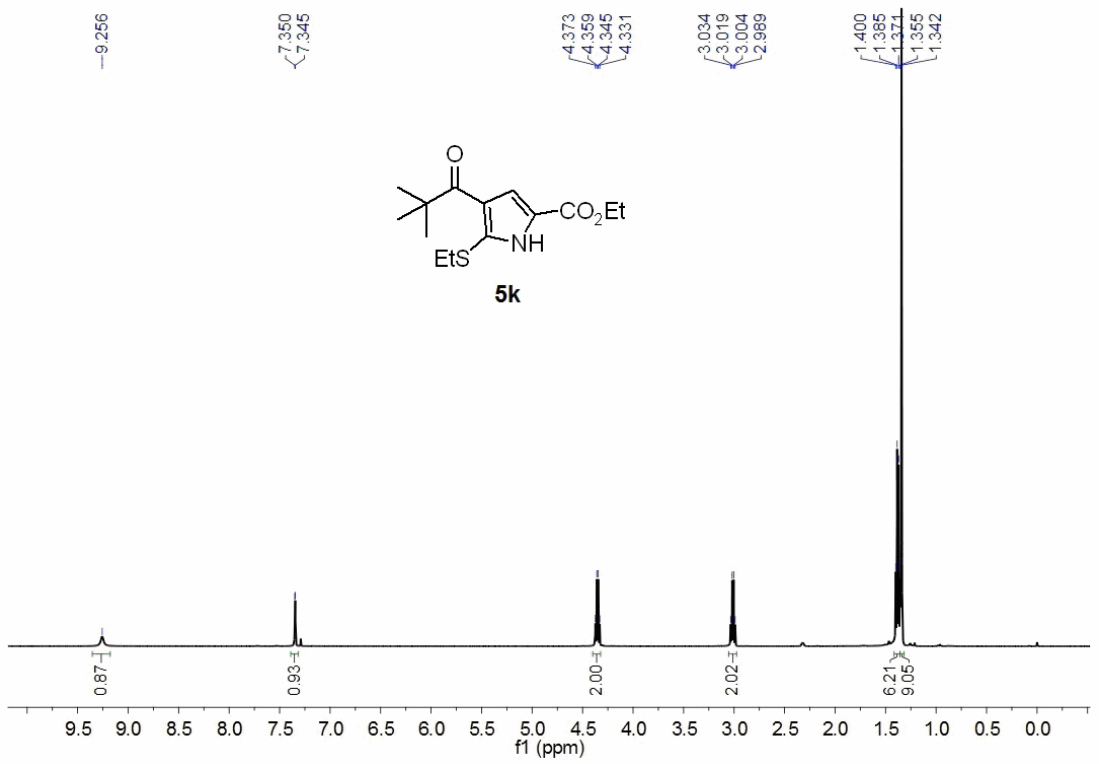

187.857
160.267
118.660
77.254
77.000
76.745
61.096
26.810
14.332
13.981
137.757
137.672
136.086
131.959
129.951
129.654
126.987
123.765
123.389
Cl
O
CO2Et
Cl
EtS
NH
5h
138
134
130
126
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

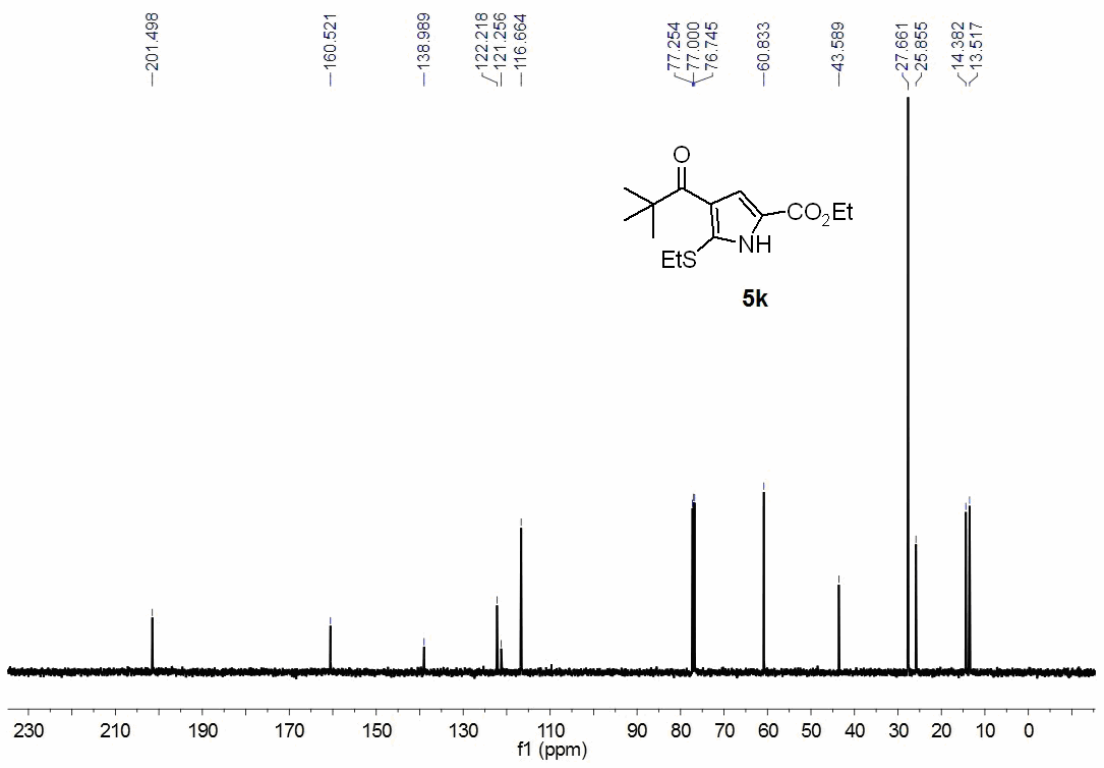

9.448
7.775
7.768
7.660
7.651
7.173
7.164
7.156
4.393
4.379
4.364
4.350
3.093
3.079
3.064
3.049
1.404
1.390
1.375
1.354
1.340
1.325
7.422
7.417
7.44
7.41
f1 (ppm)
O
CO2Et
S
NH
EtS
5i
0.86
0.95
0.88
0.91
0.94
2.03
2.05
3.00
3.00
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

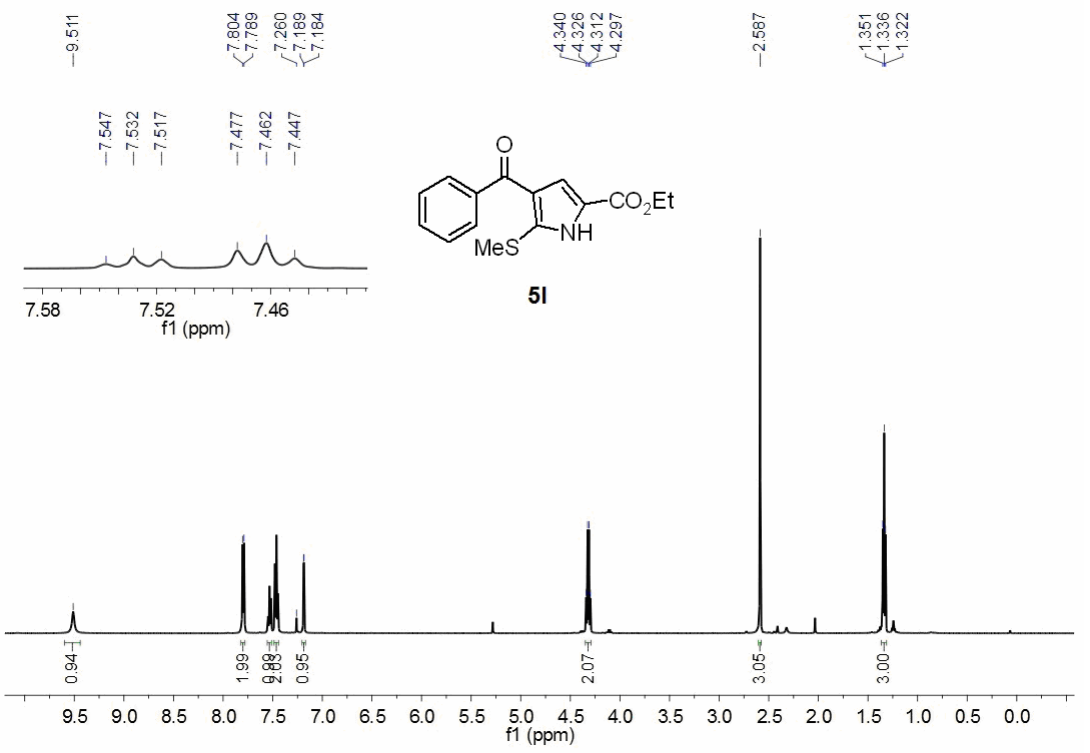

181.024
160.336
144.453
77.255
77.000
76.746
61.031
27.897
14.394
14.218
135.937
132.871
132.615
127.772
124.485
123.051
117.407
135 130 125 120 115
f1 (ppm)
O
CO2Et
S
NH
EtS
5i
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

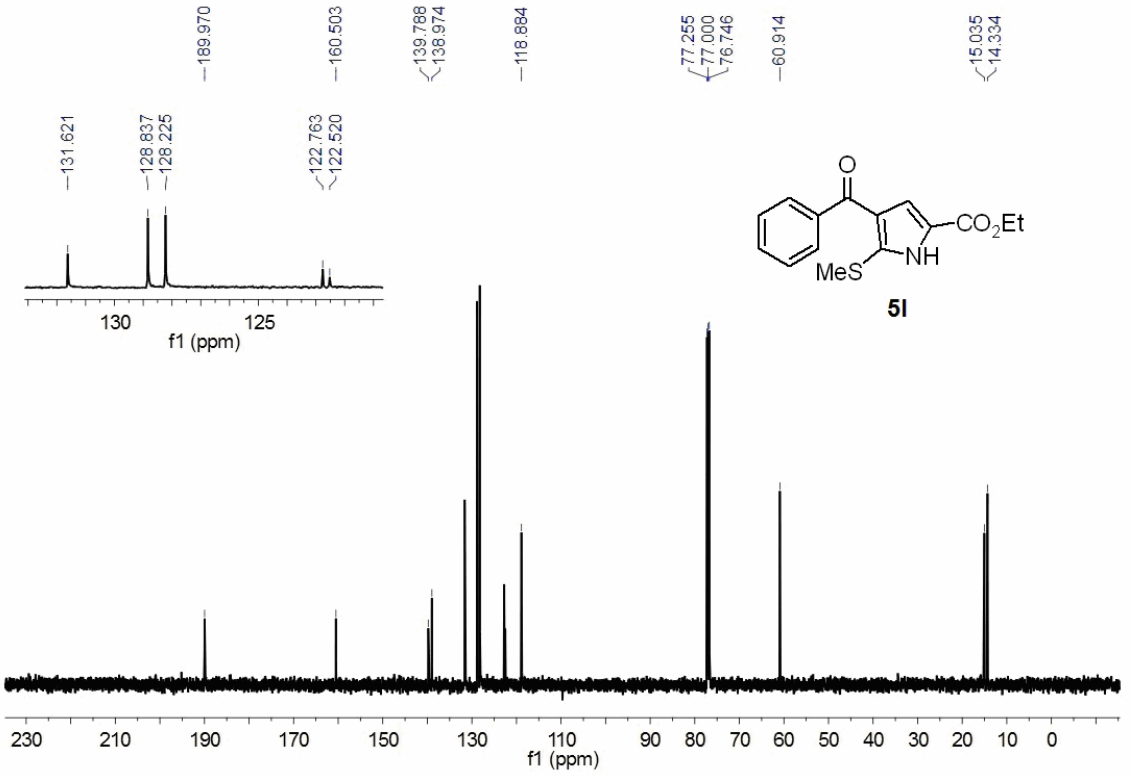

9.428
7.707
7.703
7.638
7.286
7.260
6.556
6.552
4.377
4.363
4.349
4.334
3.087
3.072
3.057
3.042
1.392
1.378
1.364
1.349
1.334
O
CO2Et
O
NH
EtS
5j
0.90
0.89
0.91
0.89
0.94
2.00
2.01
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

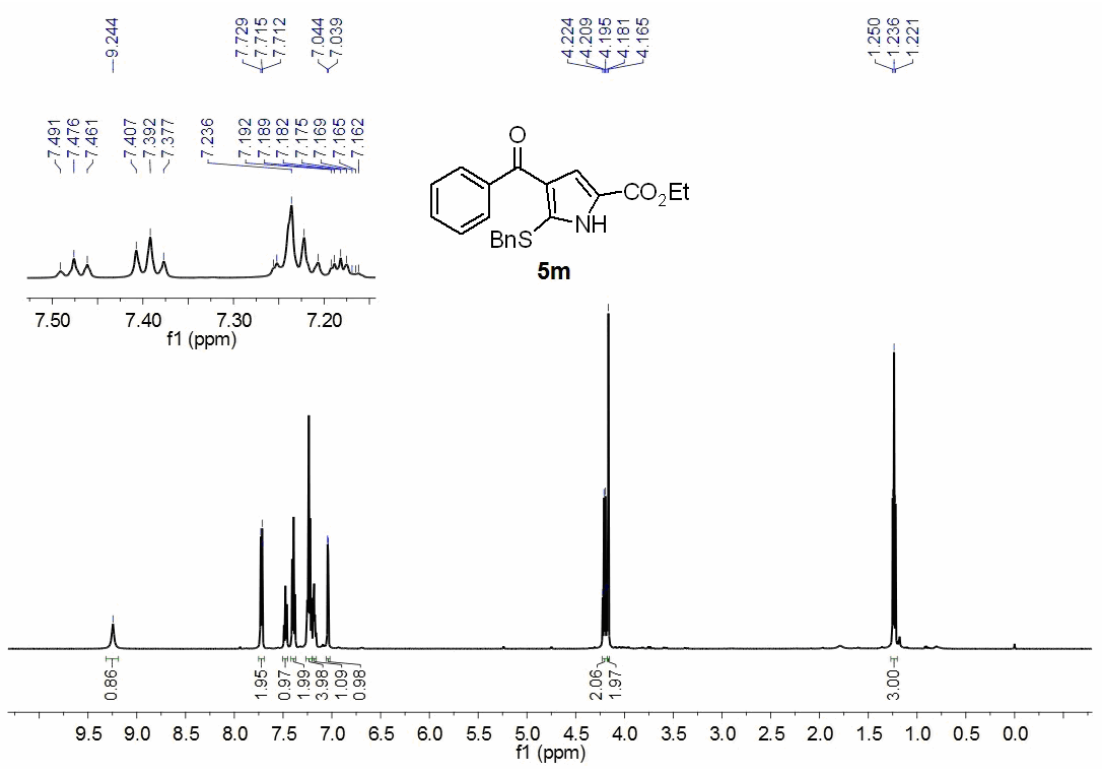

175.621
160.500
153.493
145.705
138.166
123.147
122.509
112.093
77.255
77.000
76.746
60.943
26.760
14.393
13.915
117.892
117.775
117.8
f1 (ppm)
O
CO2Et
O
NH
EtS
5j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

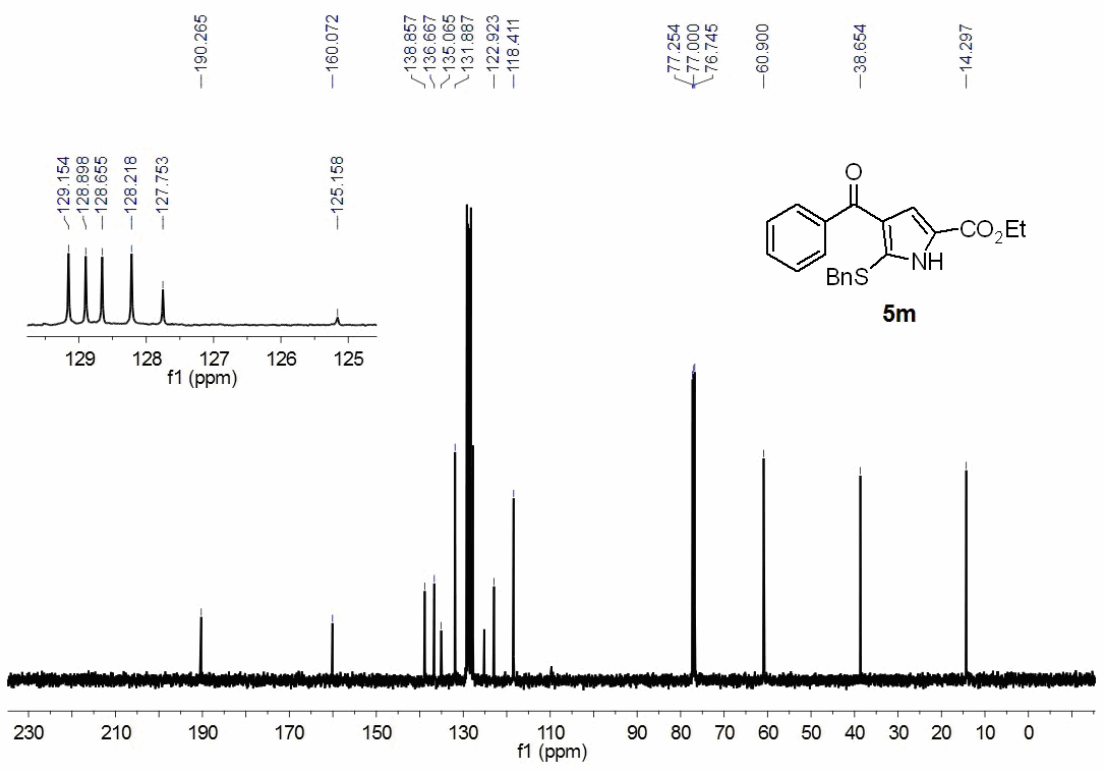

9.256
7.350
7.345
4.373
4.359
4.345
4.331
3.034
3.019
3.004
2.989
1.400
1.385
1.371
1.355
1.342
O
CO2Et
NH
EtS
5k
0.87
0.93
2.00
2.02
6.21
9.05
f1 (ppm)

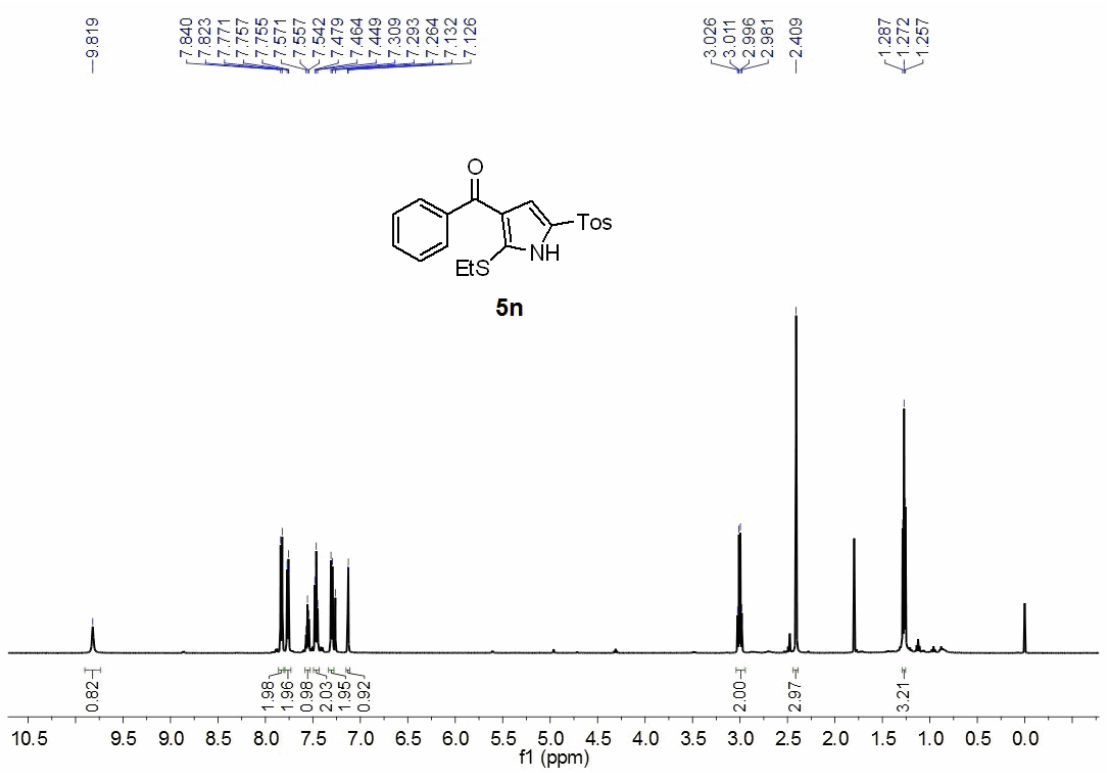

201.498
160.521
138.989
122.218
121.256
116.664
77.254
77.000
76.745
60.833
43.589
27.661
25.855
14.382
13.517
O
CO2Et
NH
EtS
5k
f1 (ppm)

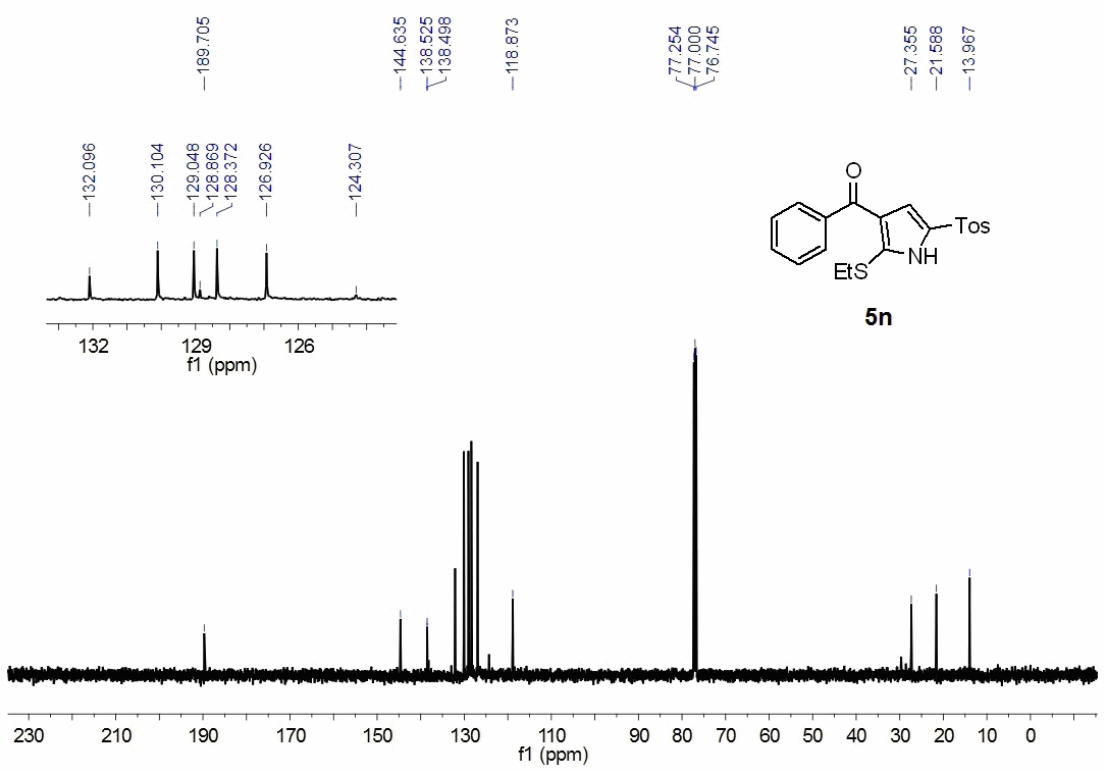

9.511
7.804
7.789
7.260
7.189
7.184
4.340
4.326
4.312
4.297
2.587
1.351
1.336
1.322
7.547
7.532
7.517
7.477
7.462
7.447
O
CO2Et
NH
MeS
5l
7.58
7.52
7.46
f1 (ppm)
0.94
1.99
0.95
2.07
3.05
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

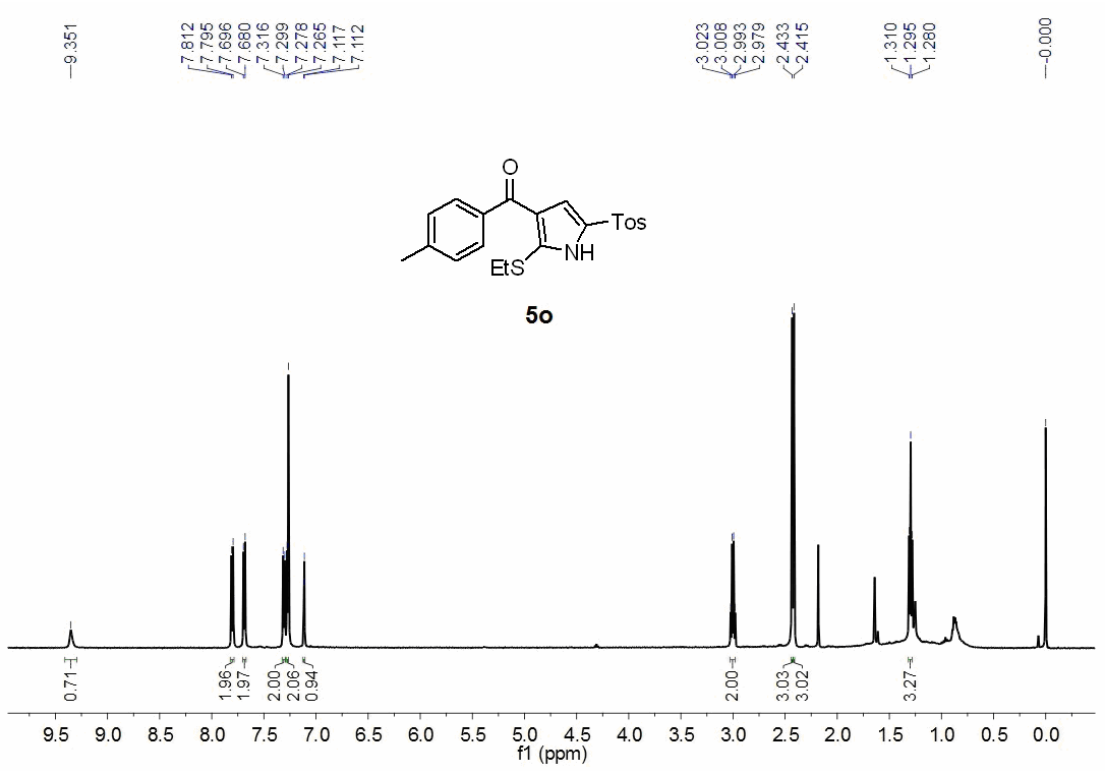

189.970
160.503
139.788
138.974
118.884
77.255
77.000
76.746
60.914
15.035
14.334
131.621
128.837
128.225
122.763
122.520
O
CO2Et
NH
MeS
5l
130
125
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

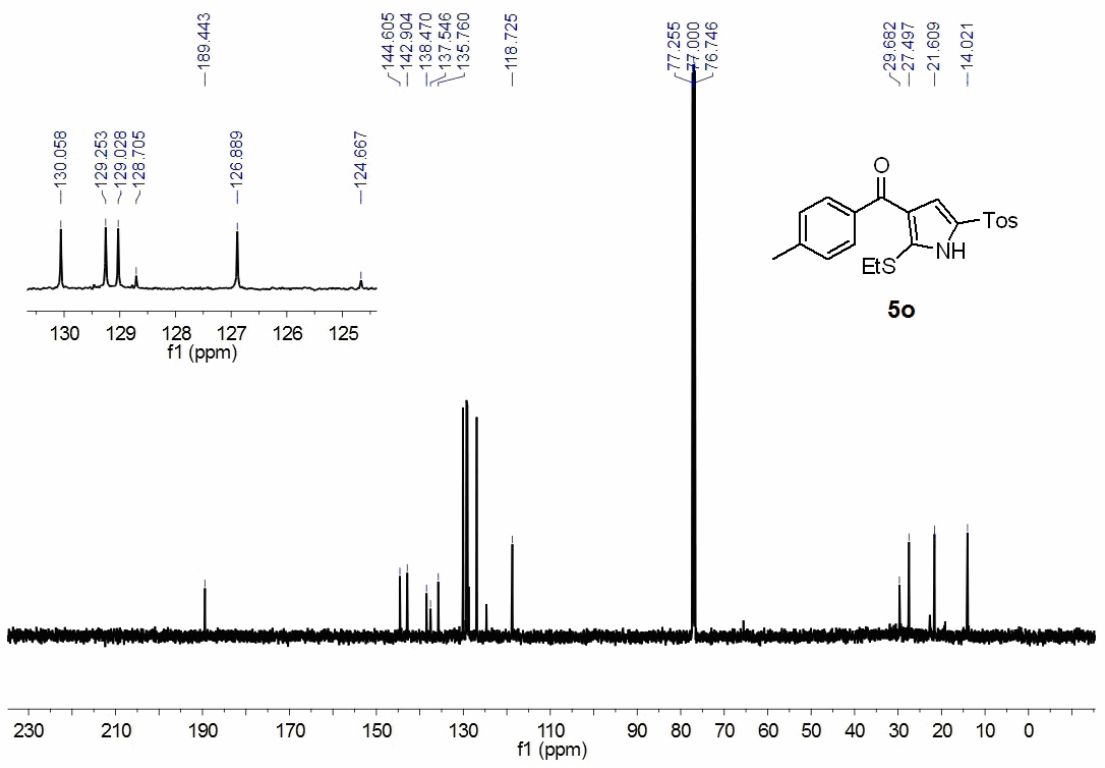

9.244
7.729
7.715
7.712
7.044
7.039
4.224
4.209
4.195
4.181
4.165
1.250
1.236
1.221
7.491
7.476
7.461
7.407
7.392
7.377
7.236
7.192
7.189
7.182
7.175
7.169
7.165
7.162
O
CO2Et
NH
BnS
5m
7.50
7.40
7.30
7.20
f1 (ppm)
0.86
1.95
0.97
1.99
3.98
1.09
0.98
2.06
1.97
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

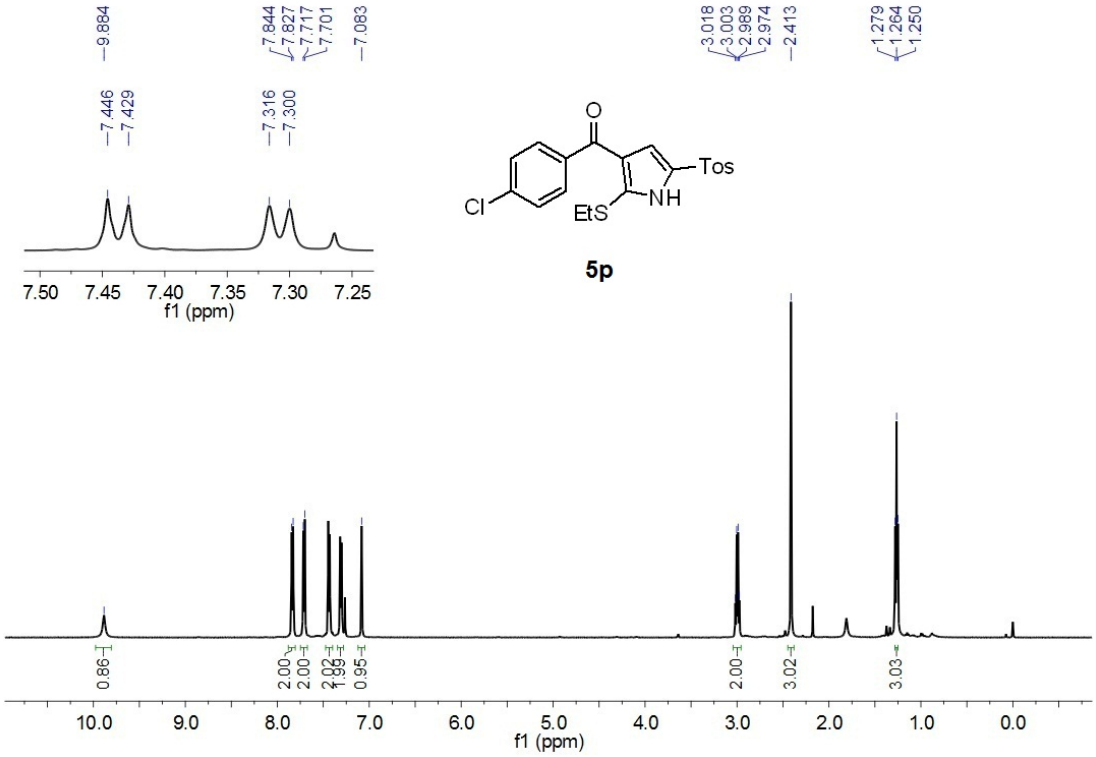

190.265
160.072
138.857
136.667
135.065
131.887
122.923
118.411
77.254
77.000
76.745
60.900
38.654
14.297
129.154
128.898
128.655
128.218
127.753
125.158
O
CO2Et
NH
BnS
5m
129
128
127
126
125
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

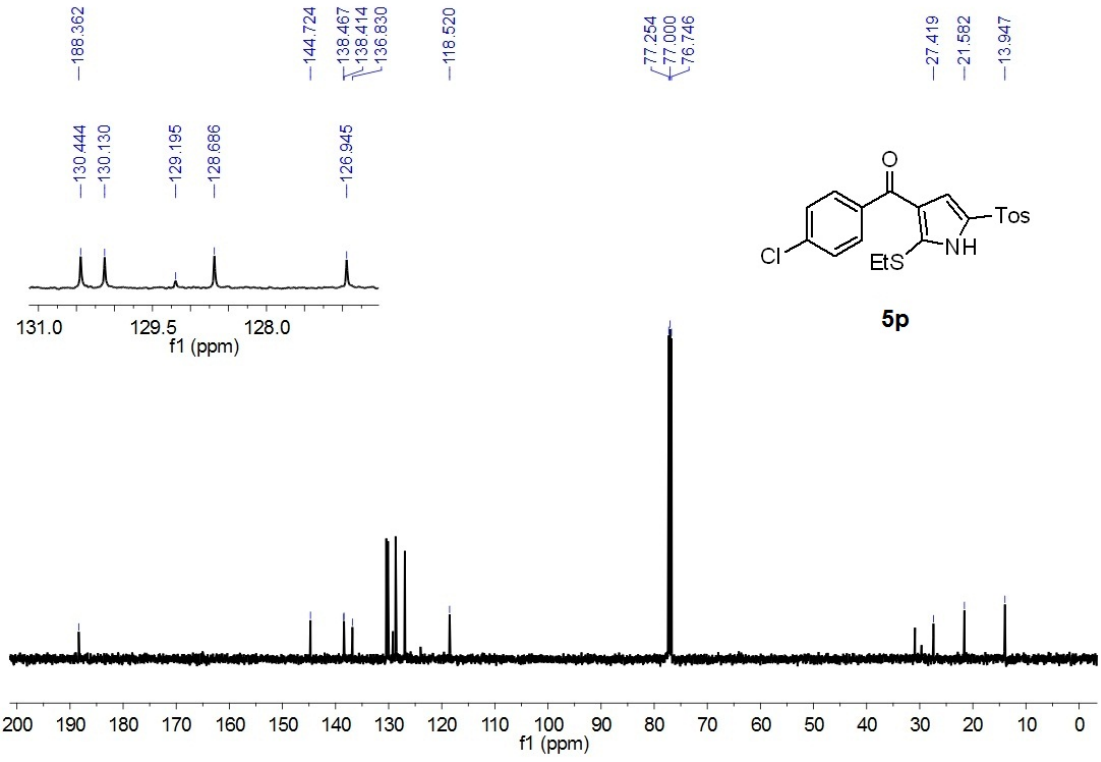

9.819
7.840
7.823
7.771
7.757
7.755
7.571
7.557
7.542
7.479
7.464
7.449
7.309
7.293
7.264
7.132
7.126
3.026
3.011
2.996
2.981
2.409
1.287
1.272
1.257
O
Tos
NH
EtS
5n
0.82
1.98
1.96
0.98
2.03
1.95
0.92
2.00
2.97
3.21
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

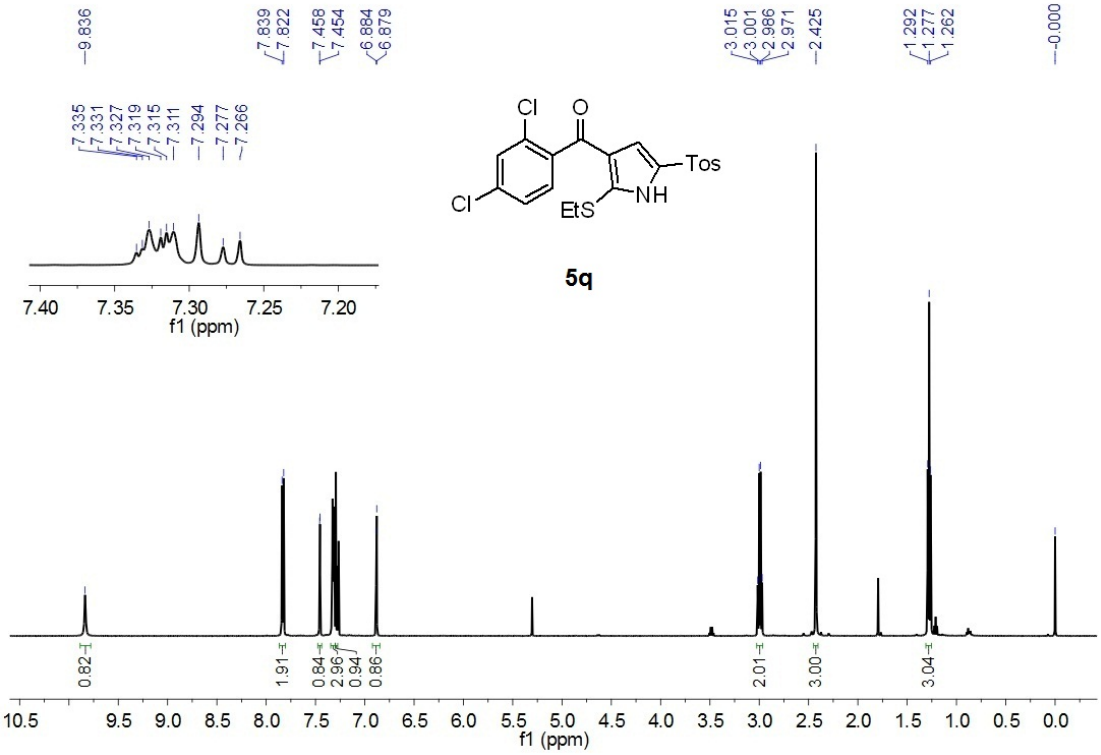

189.705
144.635
138.525
138.498
118.873
77.254
77.000
76.745
27.355
21.588
13.967
132.096
130.104
129.048
128.869
128.372
126.926
124.307
O
Tos
NH
EtS
5n
132
129
126
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

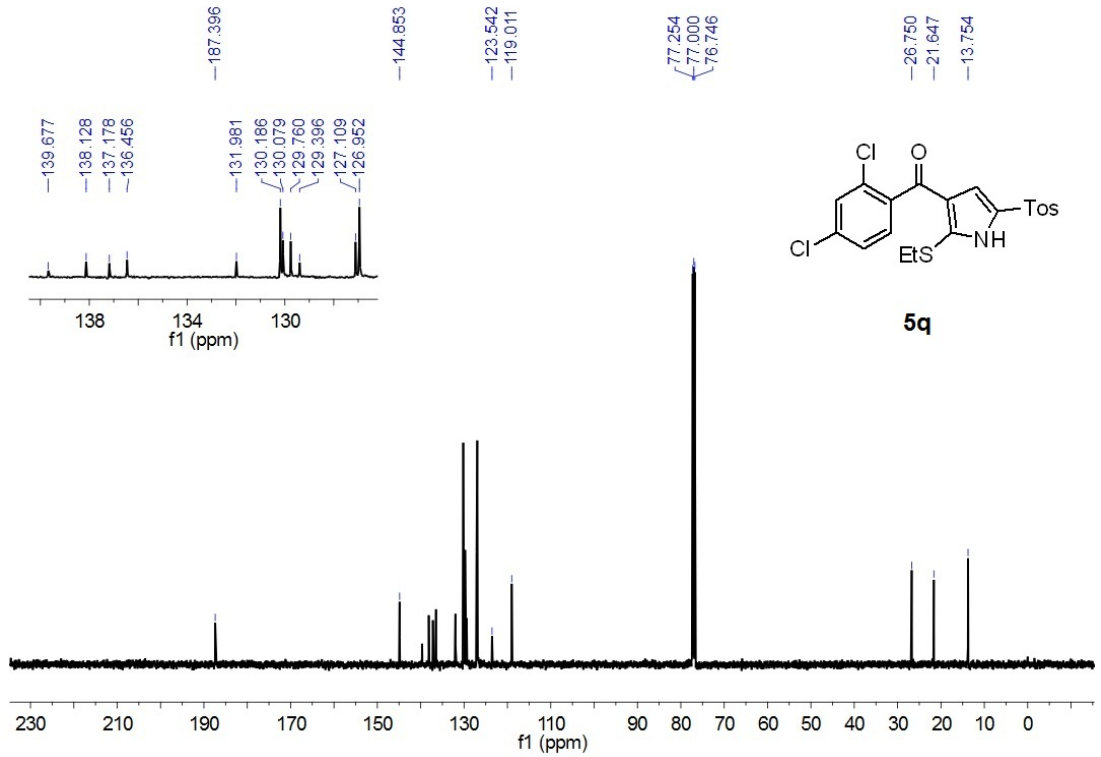

9.351
7.812
7.795
7.696
7.680
7.316
7.299
7.278
7.265
7.117
7.112
3.023
3.008
2.993
2.979
2.433
2.415
1.310
1.295
1.280
0.000
O
Tos
NH
EtS
5o
0.71
1.96
1.97
2.00
2.06
0.94
2.00
3.03
3.02
3.27
f1 (ppm)

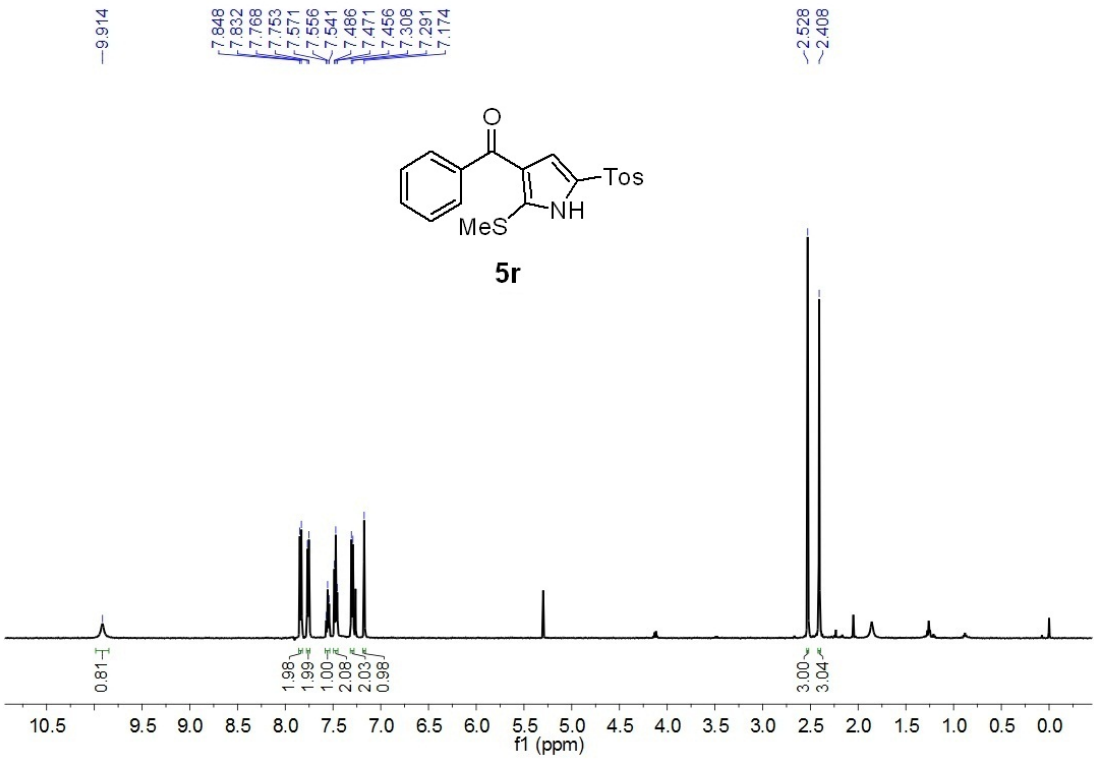

189.443
144.605
142.904
138.470
137.546
135.760
118.725
77.255
77.000
76.746
29.682
27.497
21.609
14.021
130.058
129.253
129.028
128.705
126.889
124.667
O
Tos
NH
EtS
5o
f1 (ppm)

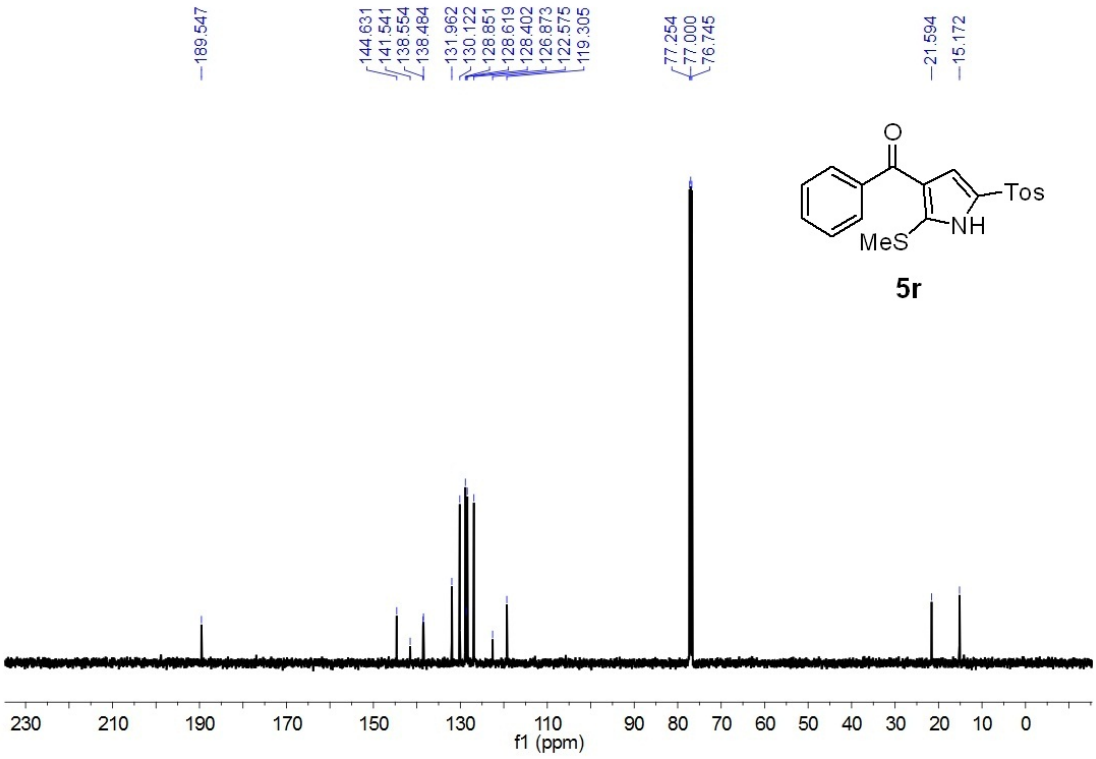

9.884
7.844
7.827
7.717
7.701
7.083
3.018
3.003
2.989
2.974
2.413
1.279
1.264
1.250
7.446
7.429
7.316
7.300
O
Tos
Cl
NH
EtS
5p
0.86
2.00
2.00
2.02
1.99
0.95
2.00
3.02
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
7.50
7.45
7.40
7.35
7.30
7.25
f1 (ppm)

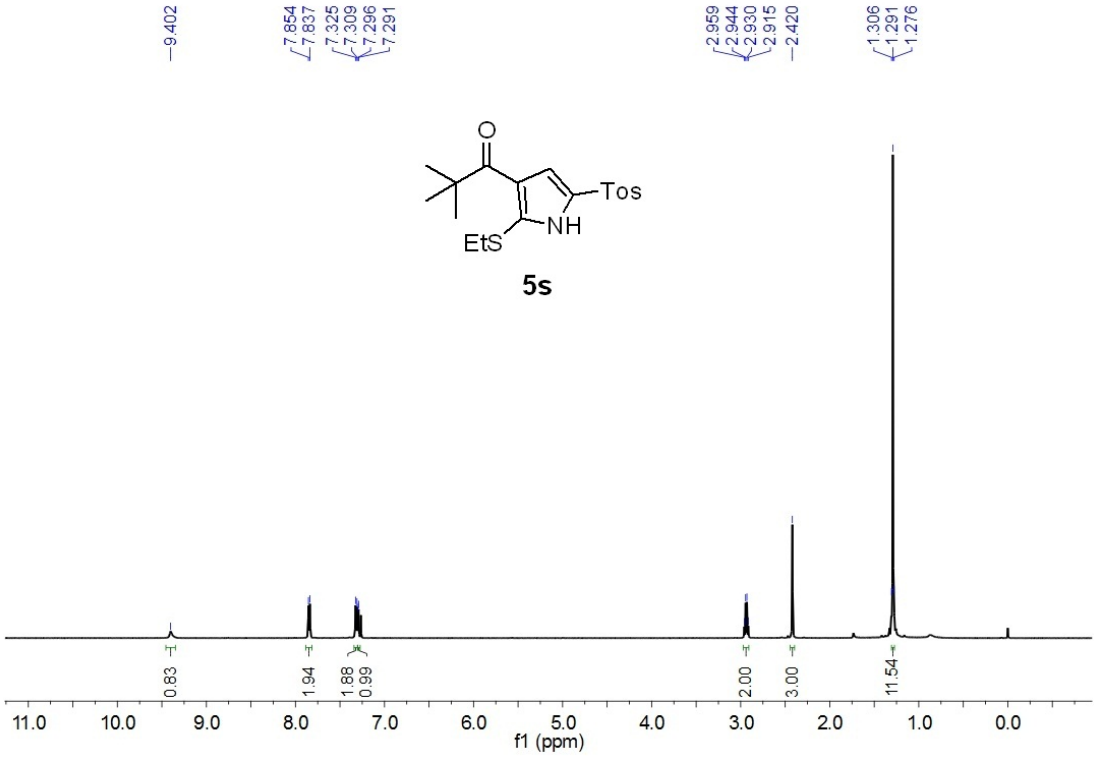

188.362
144.724
138.467
138.414
136.830
118.520
77.254
77.000
76.746
27.419
21.582
13.947
130.444
130.130
129.195
128.686
126.945
O
Tos
Cl
NH
EtS
5p
131.0
129.5
128.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

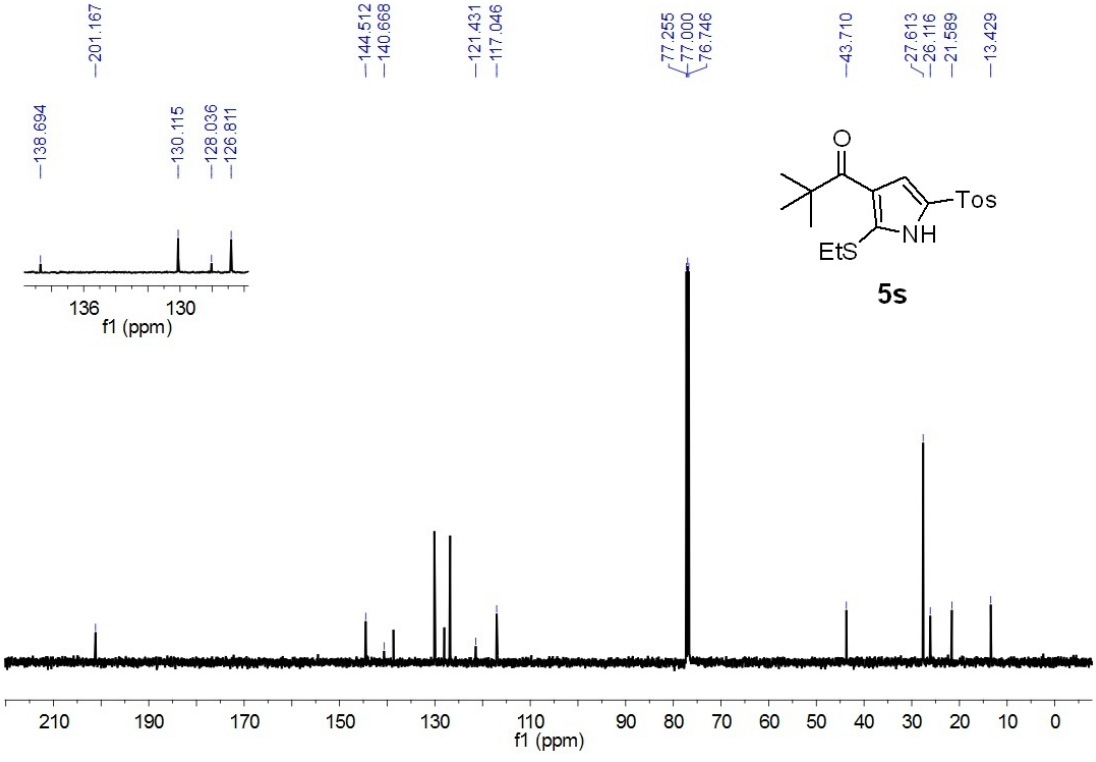

9.836
7.839
7.822
7.458
7.454
6.884
6.879
3.015
3.001
2.986
2.971
2.425
1.292
1.277
1.262
0.000
7.335
7.331
7.327
7.319
7.315
7.311
7.294
7.277
7.266
Cl
O
Tos
Cl
NH
EtS
5q
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
0.82
1.91
0.84
2.96
0.94
0.86
2.01
3.00
3.04
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

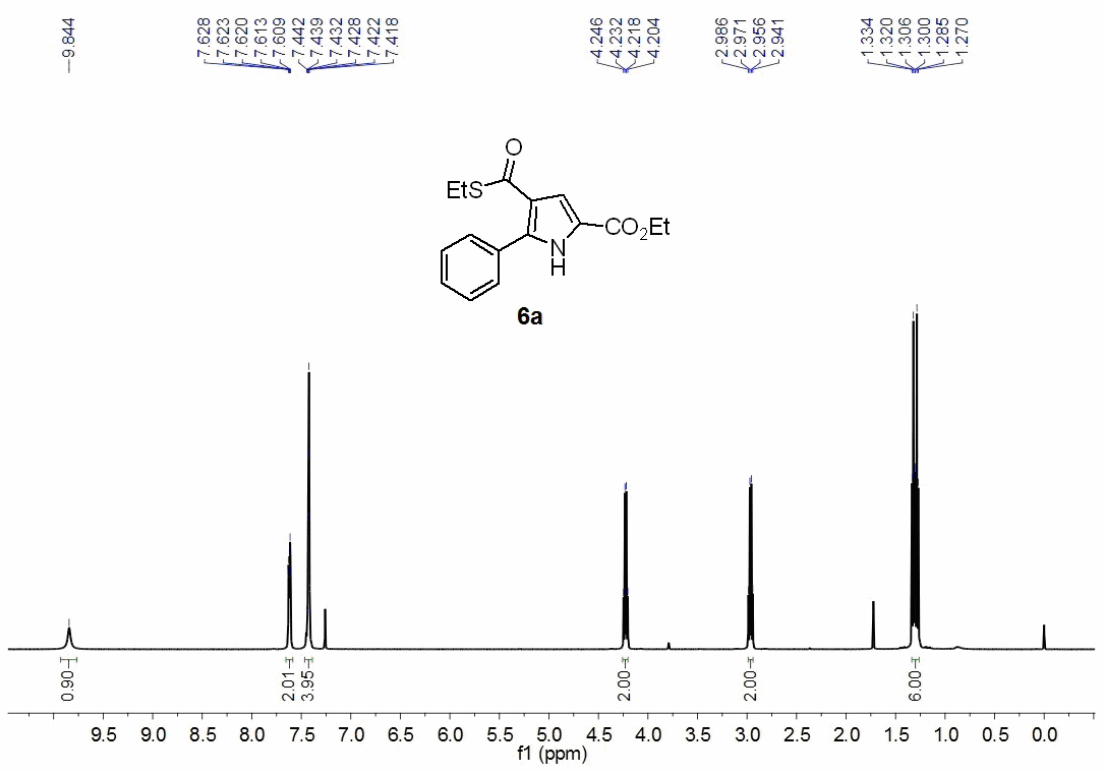

187.396
144.853
123.542
119.011
77.254
77.000
76.746
26.750
21.647
13.754
139.677
138.128
137.178
136.456
131.981
130.186
130.079
129.760
129.396
127.109
126.952
Cl
O
Tos
Cl
NH
EtS
5q
138
134
130
f1 (ppm)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

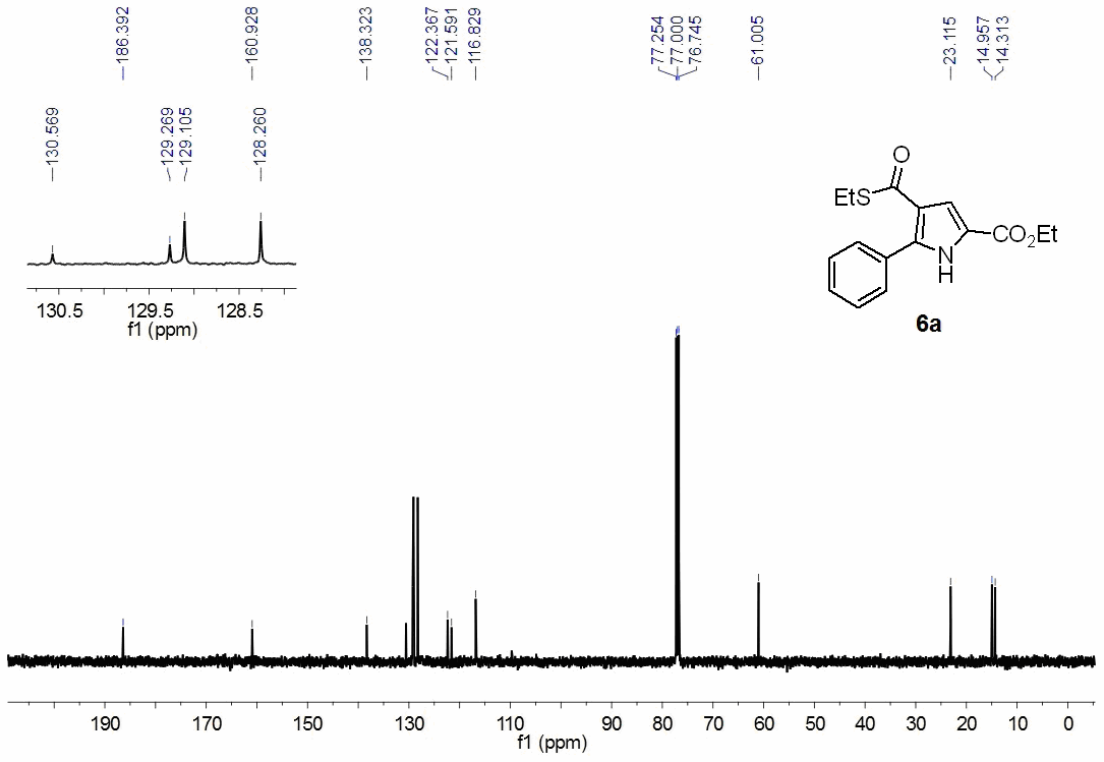

9.914
7.848
7.832
7.768
7.753
7.571
7.556
7.541
7.486
7.471
7.456
7.308
7.291
7.174
2.528
2.408
O
Tos
NH
MeS
5r
0.81
1.98
1.99
1.00
2.08
2.03
0.98
3.00
3.04
f1 (ppm)

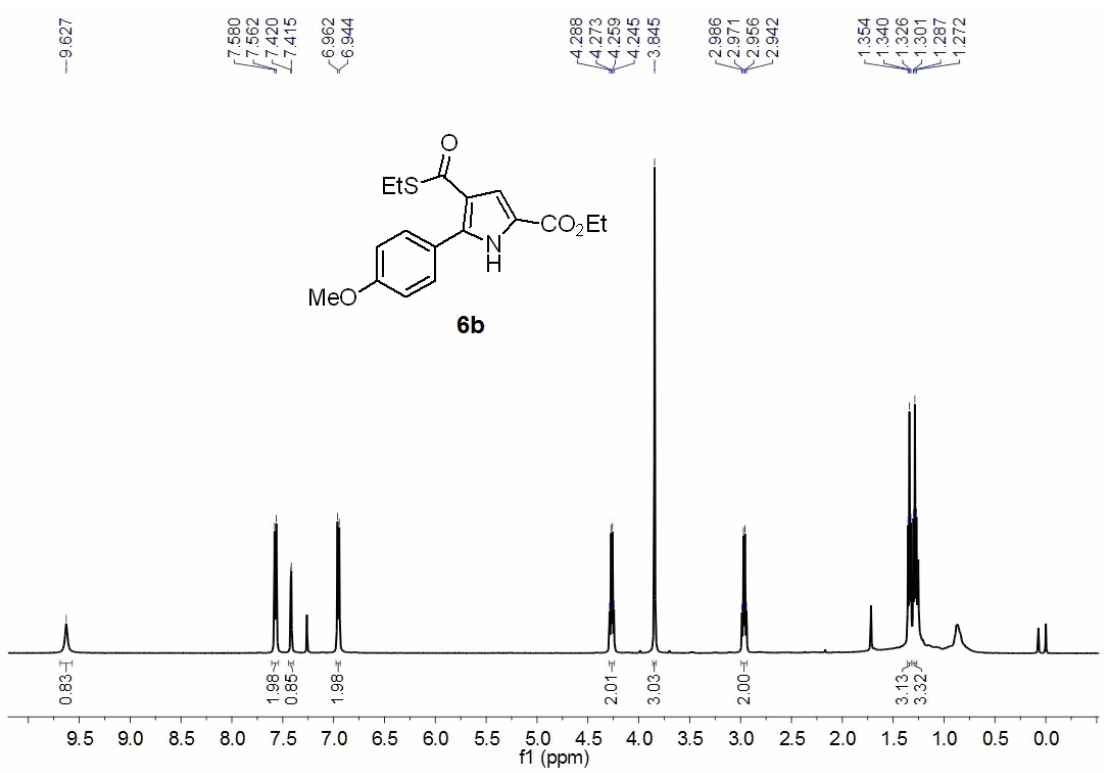

189.547
144.631
141.541
138.554
138.484
131.962
130.122
128.851
128.619
128.402
126.873
122.575
119.305
77.254
77.000
76.745
21.594
15.172
O
Tos
NH
MeS
5r
f1 (ppm)

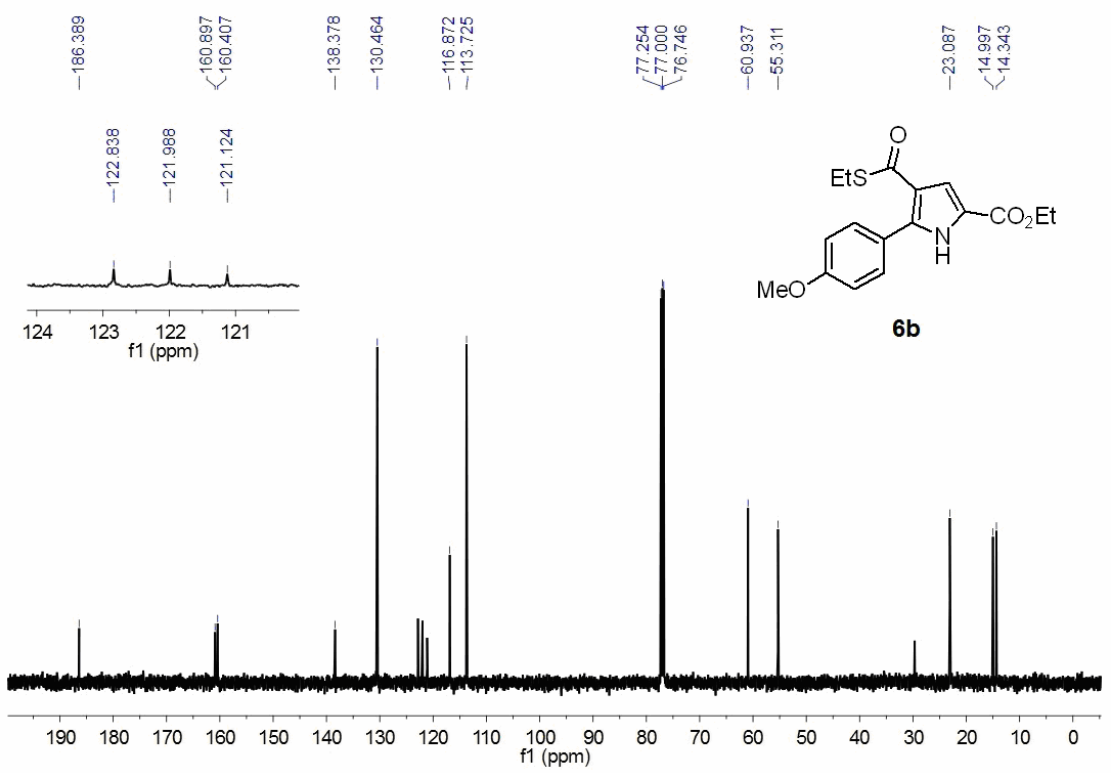

9.402
7.854
7.837
7.325
7.309
7.296
7.291
2.959
2.944
2.930
2.915
2.420
1.306
1.291
1.276
O
Tos
NH
EtS
5s
0.83
1.94
1.88
0.99
2.00
3.00
11.54
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

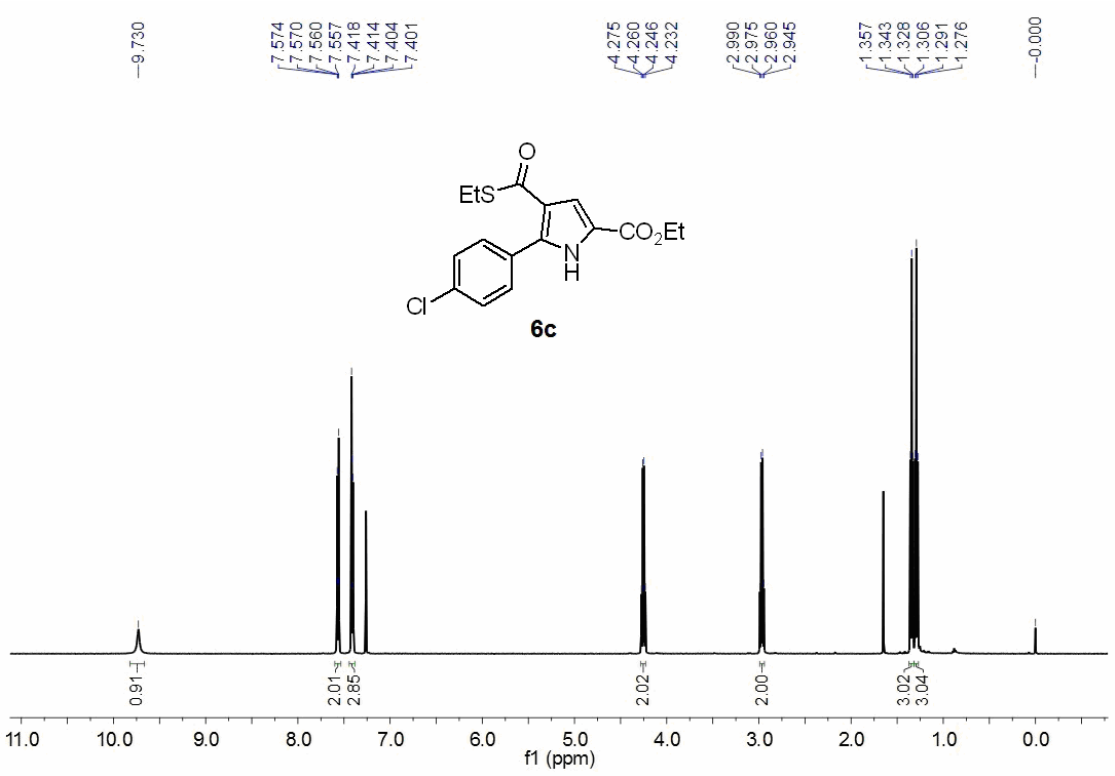

201.167
144.512
140.668
121.431
117.046
77.255
77.000
76.746
43.710
27.613
26.116
21.589
13.429
138.694
130.115
128.036
126.811
136
130
f1 (ppm)
O
Tos
NH
EtS
5s
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

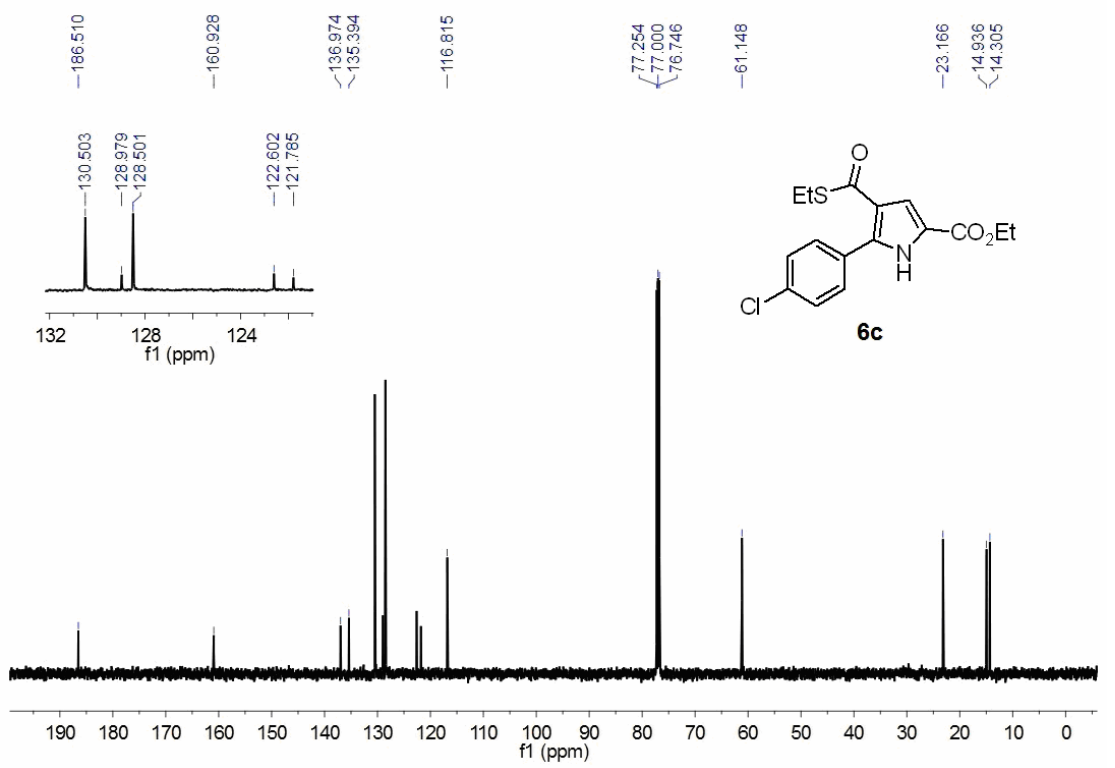

9.844
7.628
7.623
7.620
7.613
7.609
7.442
7.439
7.432
7.428
7.422
7.418
4.246
4.232
4.218
4.204
2.986
2.971
2.956
2.941
1.334
1.320
1.306
1.300
1.285
1.270
EtS
O
CO2Et
N
H
6a
0.90
2.01
3.95
2.00
2.00
6.00
f1 (ppm)

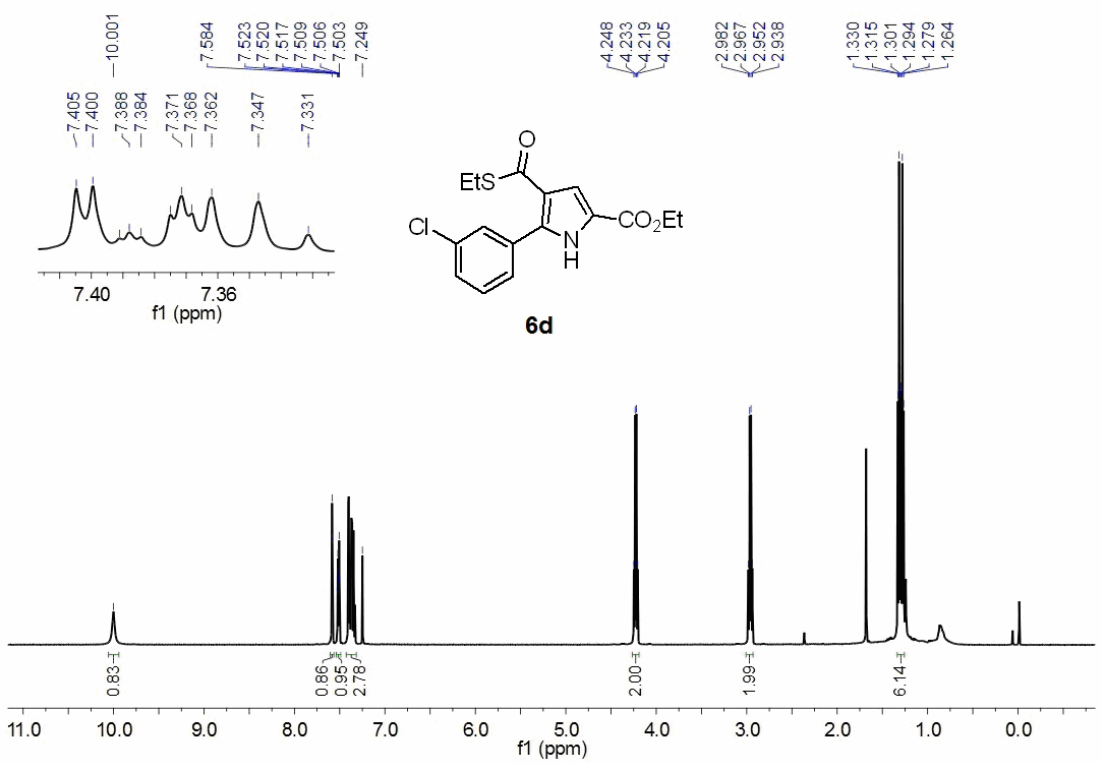

186.392
160.928
138.323
122.367
121.591
116.829
77.254
77.000
76.745
61.005
23.115
14.957
14.313
130.569
129.269
129.105
128.260
130.5
129.5
128.5
f1 (ppm)
EtS
O
CO2Et
N
H
6a
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

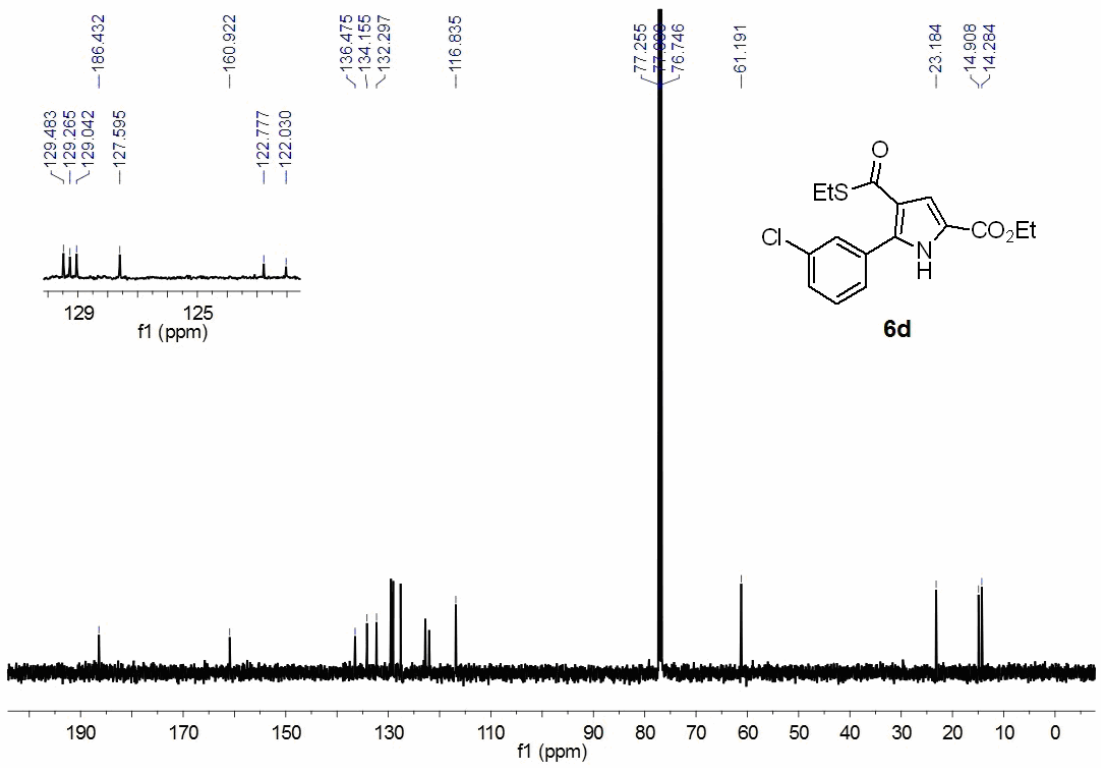

9.627
7.580
7.562
7.420
7.415
6.962
6.944
4.288
4.273
4.259
4.245
3.845
2.986
2.971
2.956
2.942
1.354
1.340
1.326
1.301
1.287
1.272
EtS
O
CO2Et
N
H
MeO
6b
0.83
1.98
0.85
1.98
2.01
3.03
2.00
3.13
3.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

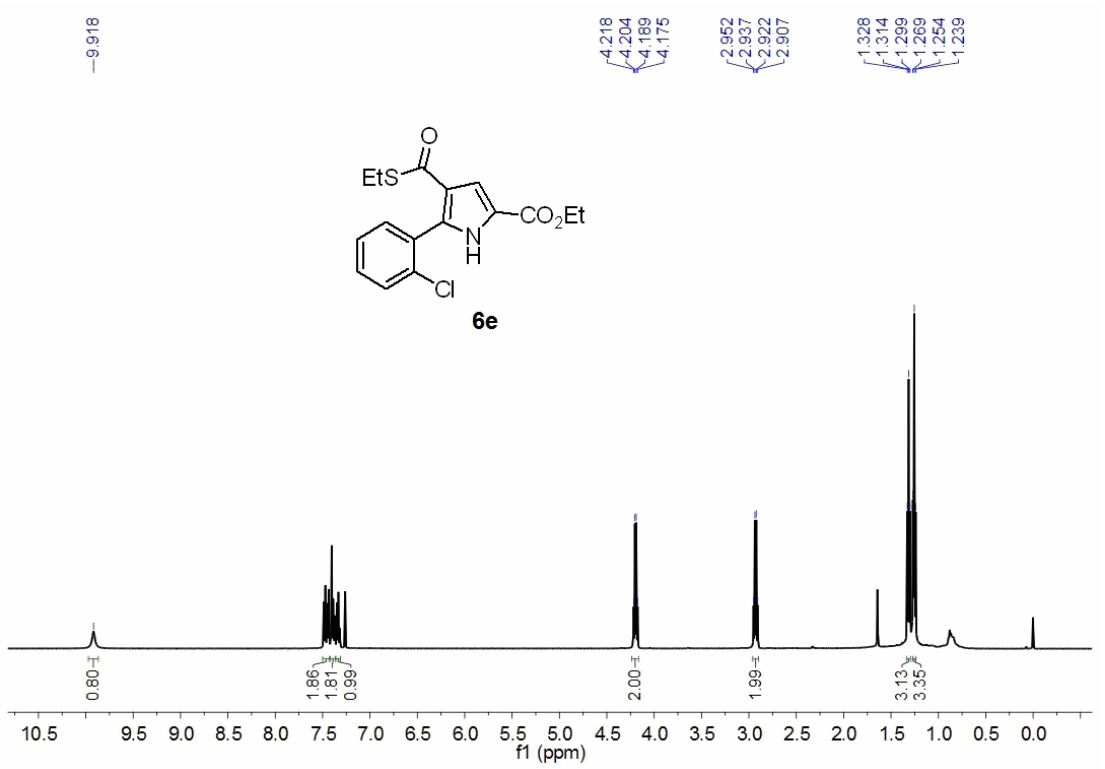

186.389
160.897
160.407
138.378
130.464
116.872
113.725
77.254
77.000
76.746
60.937
55.311
23.087
14.997
14.343
122.838
121.988
121.124
124 123 122 121
f1 (ppm)
EtS
O
CO2Et
N
H
MeO
6b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

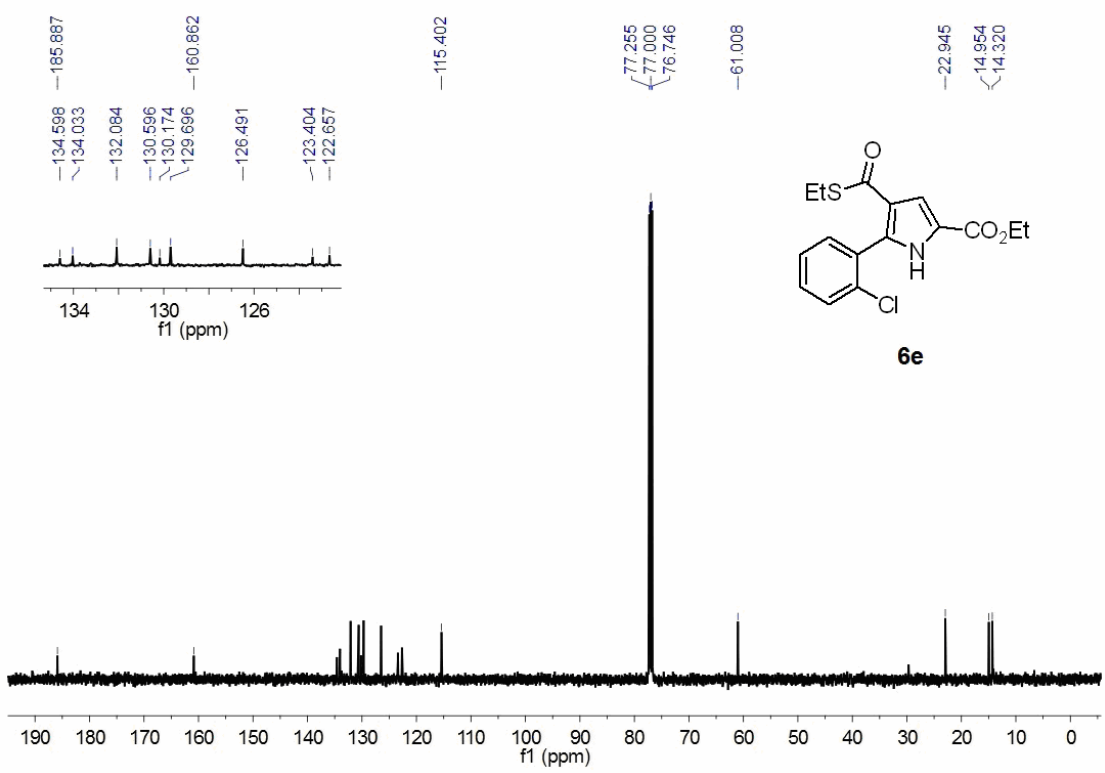

9.730
7.574
7.570
7.560
7.557
7.418
7.414
7.404
7.401
4.275
4.260
4.246
4.232
2.990
2.975
2.960
2.945
1.357
1.343
1.328
1.306
1.291
1.276
0.000
EtS
O
CO2Et
N
H
Cl
6c
0.91
2.01
2.85
2.02
2.00
3.02
3.04
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

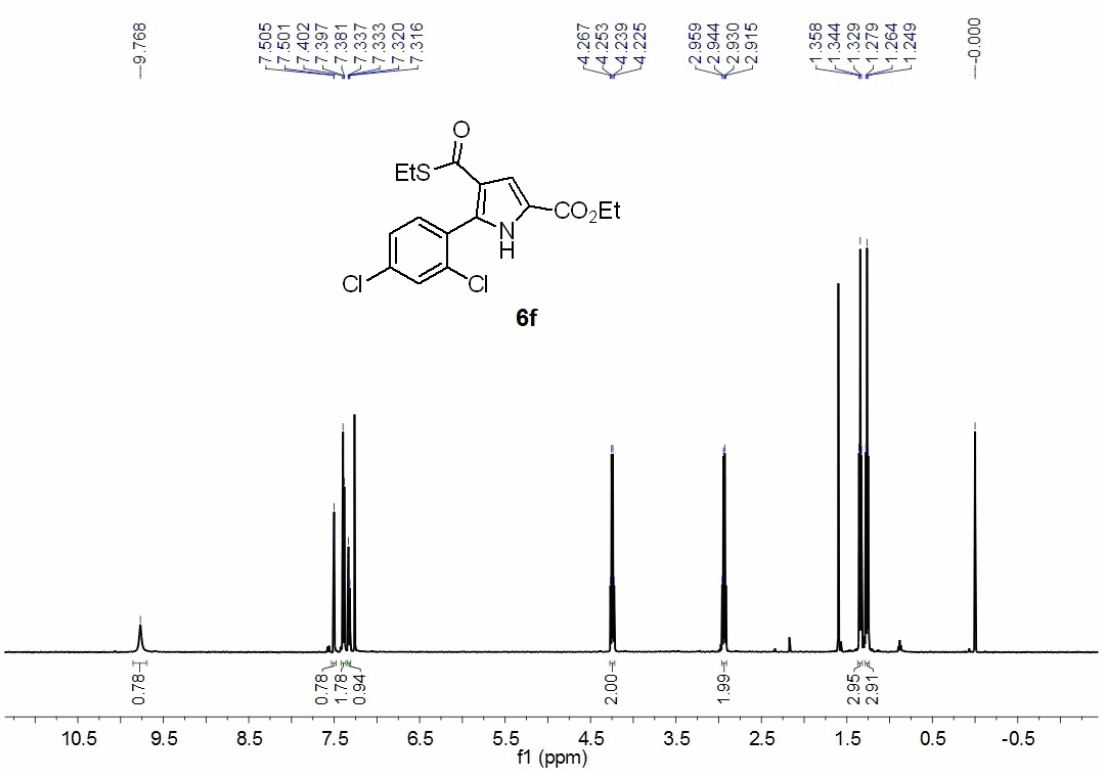

186.510
160.928
136.974
135.394
116.815
77.254
77.000
76.746
61.148
23.166
14.936
14.305
130.503
128.979
128.501
122.602
121.785
132
128
124
f1 (ppm)
EtS
O
CO2Et
N
H
Cl
6c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

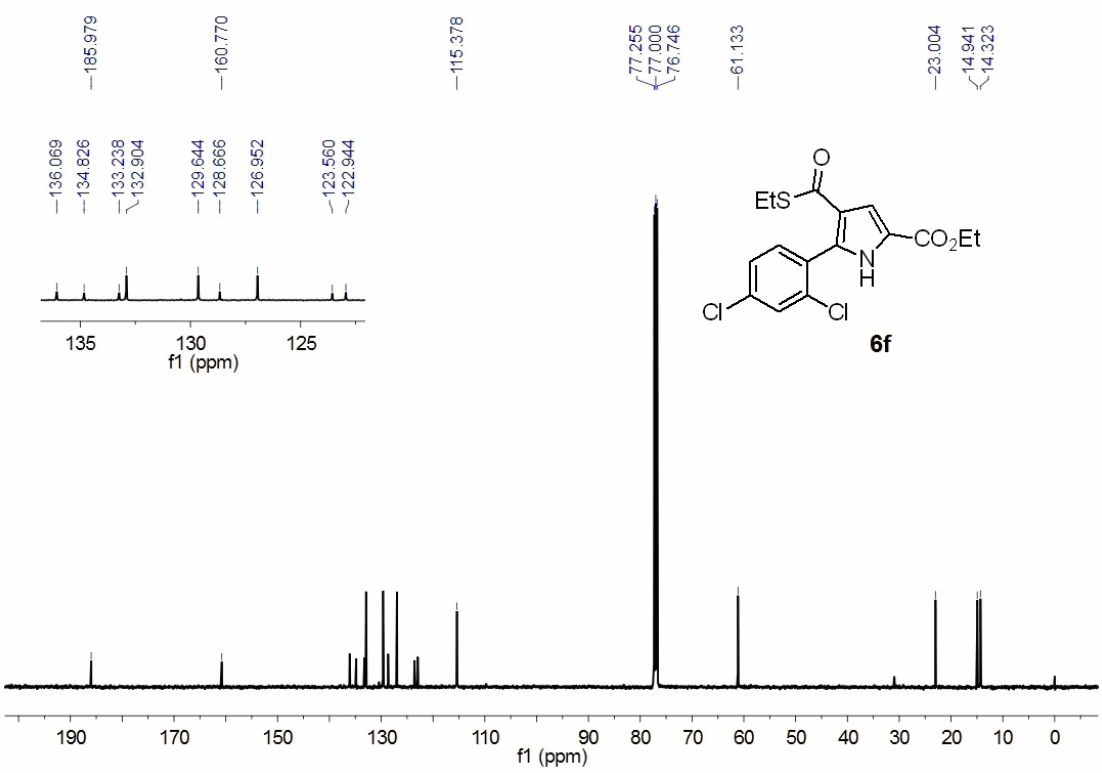

10.001
7.584
7.523
7.520
7.517
7.509
7.506
7.503
7.249
4.248
4.233
4.219
4.205
2.982
2.967
2.952
2.938
1.330
1.315
1.301
1.294
1.279
1.264
7.405
7.400
7.388
7.384
7.371
7.368
7.362
7.347
7.331
7.40
7.36
f1 (ppm)
EtS
O
Cl
N
H
CO2Et
6d
0.83
0.86
0.95
2.78
2.00
1.99
6.14
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

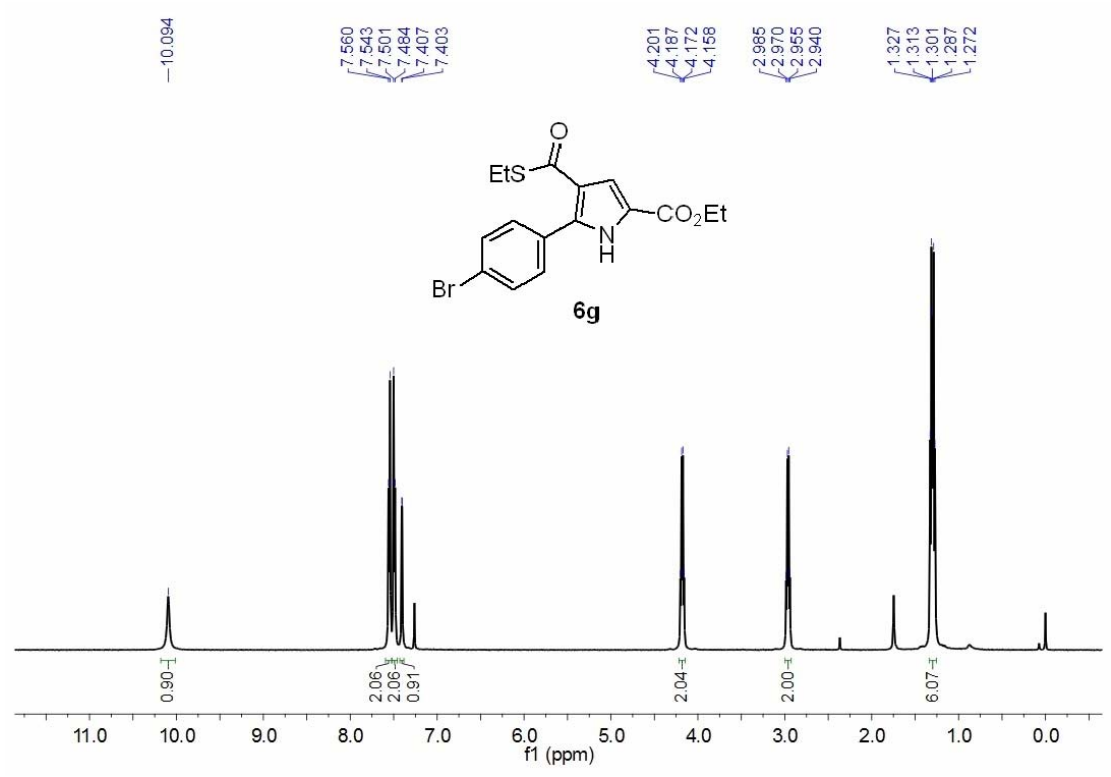

186.432
160.922
136.475
134.155
132.297
116.835
77.255
77.000
76.746
61.191
23.184
14.908
14.284
129.483
129.265
129.042
127.595
122.777
122.030
129
125
f1 (ppm)
EtS
O
Cl
N
H
CO2Et
6d
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

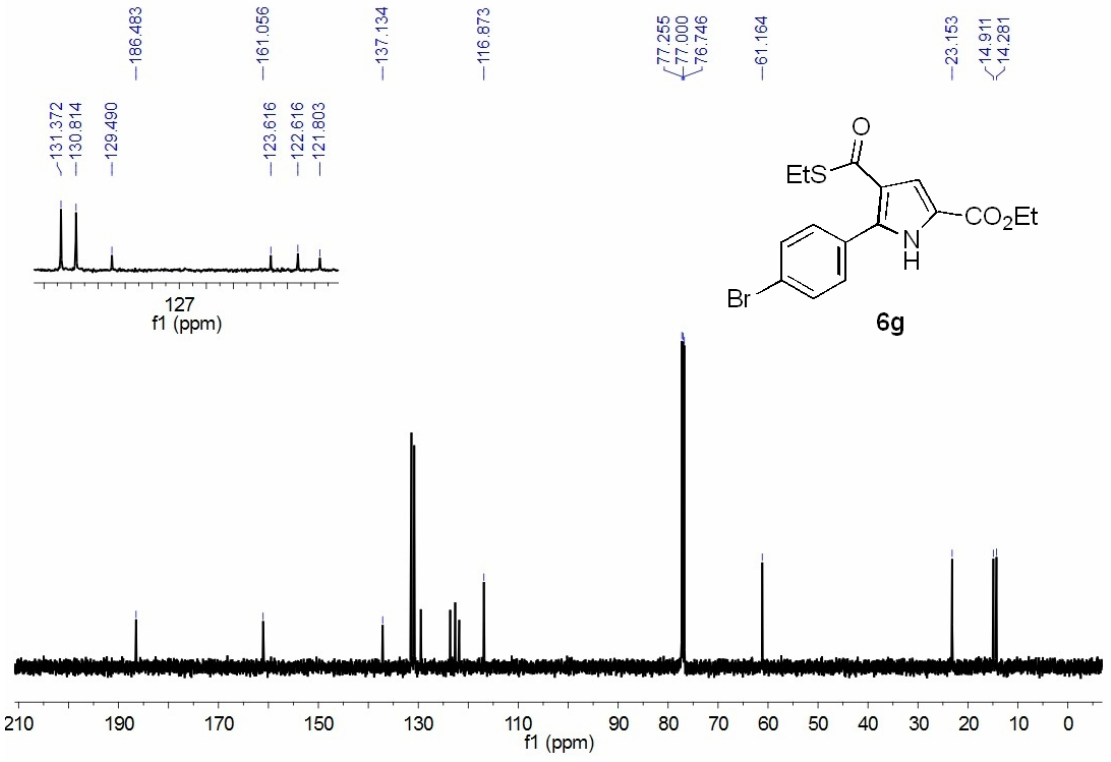

9.918
4.218
4.204
4.189
4.175
2.952
2.937
2.922
2.907
1.328
1.314
1.299
1.269
1.254
1.239
EtS
O
CO2Et
N
H
Cl
6e
0.80
1.86
1.81
0.99
2.00
1.99
3.13
3.35
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

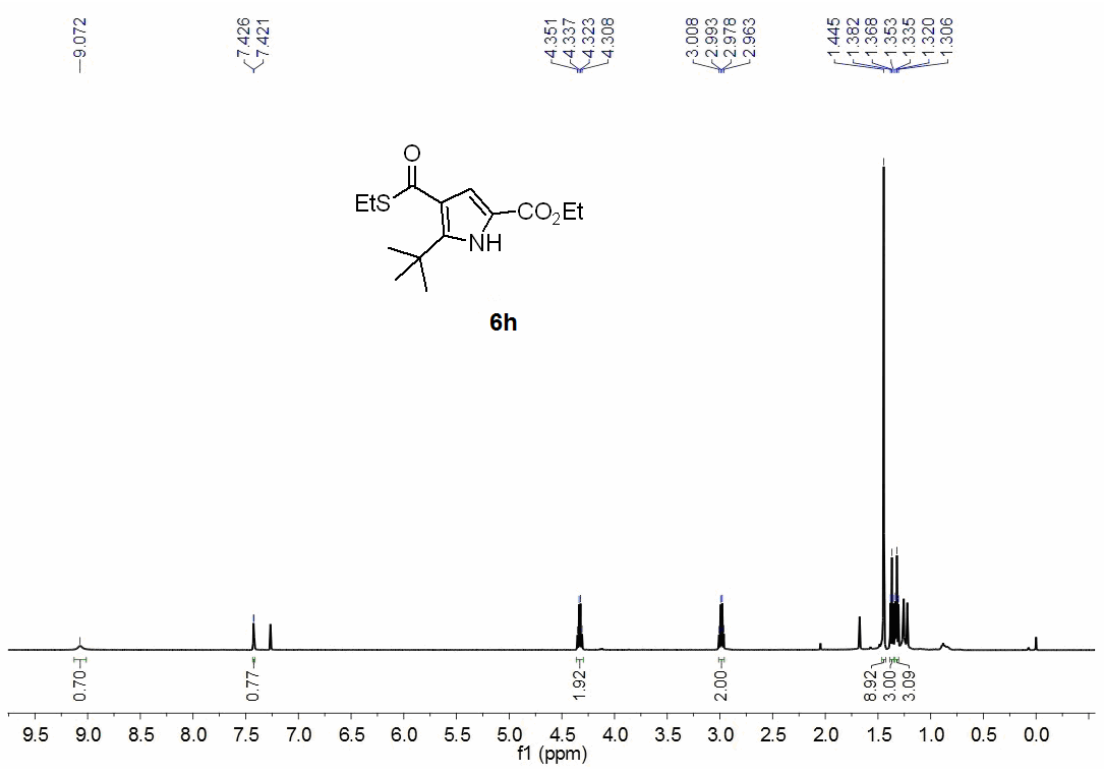

185.887
160.862
115.402
77.255
77.000
76.746
61.008
22.945
14.954
14.320
134.598
134.033
132.084
130.596
130.174
129.696
126.491
123.404
122.657
134
130
126
f1 (ppm)
EtS
O
CO2Et
N
H
Cl
6e
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

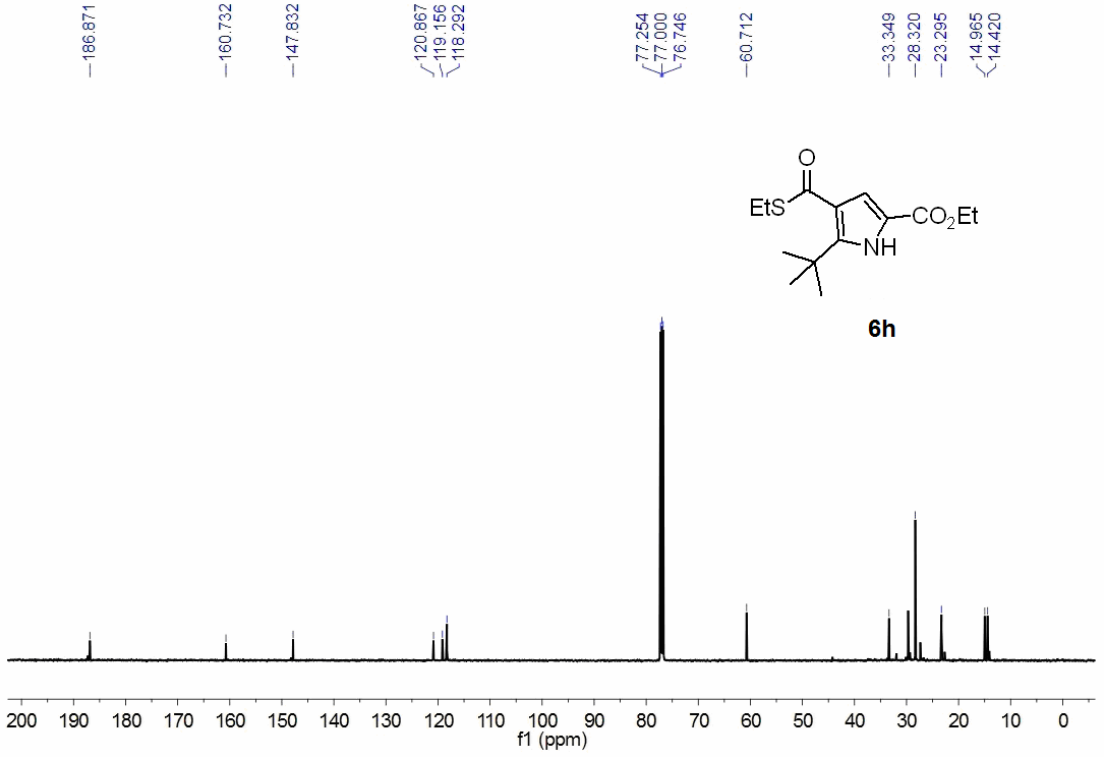

9.768
7.505
7.501
7.402
7.397
7.381
7.337
7.333
7.320
7.316
4.267
4.253
4.239
4.225
2.959
2.944
2.930
2.915
1.358
1.344
1.329
1.279
1.264
1.249
0.000
EtS
O
CO2Et
N
H
Cl
Cl
6f
0.78
0.78
1.78
0.94
2.00
1.99
2.95
2.91
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

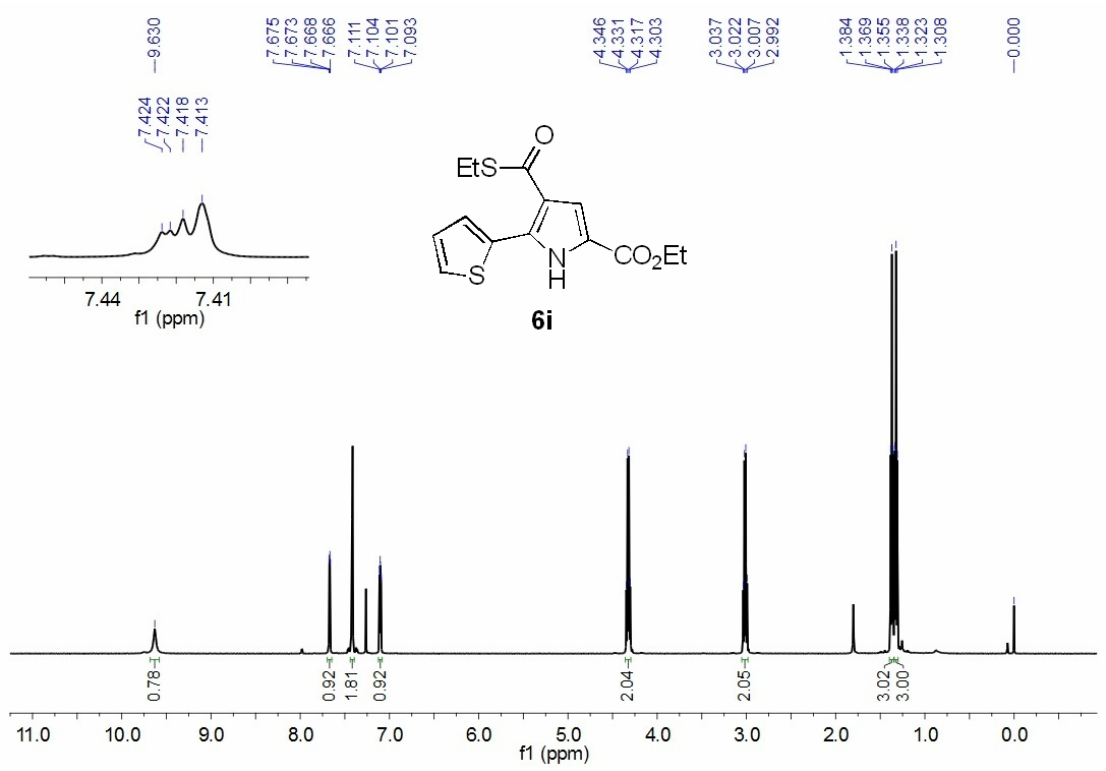

185.979
160.770
115.378
77.255
77.000
76.746
61.133
23.004
14.941
14.323
136.069
134.826
133.238
132.904
129.644
128.666
126.952
123.560
122.944
135
130
125
f1 (ppm)
EtS
O
CO2Et
N
H
Cl
Cl
6f
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

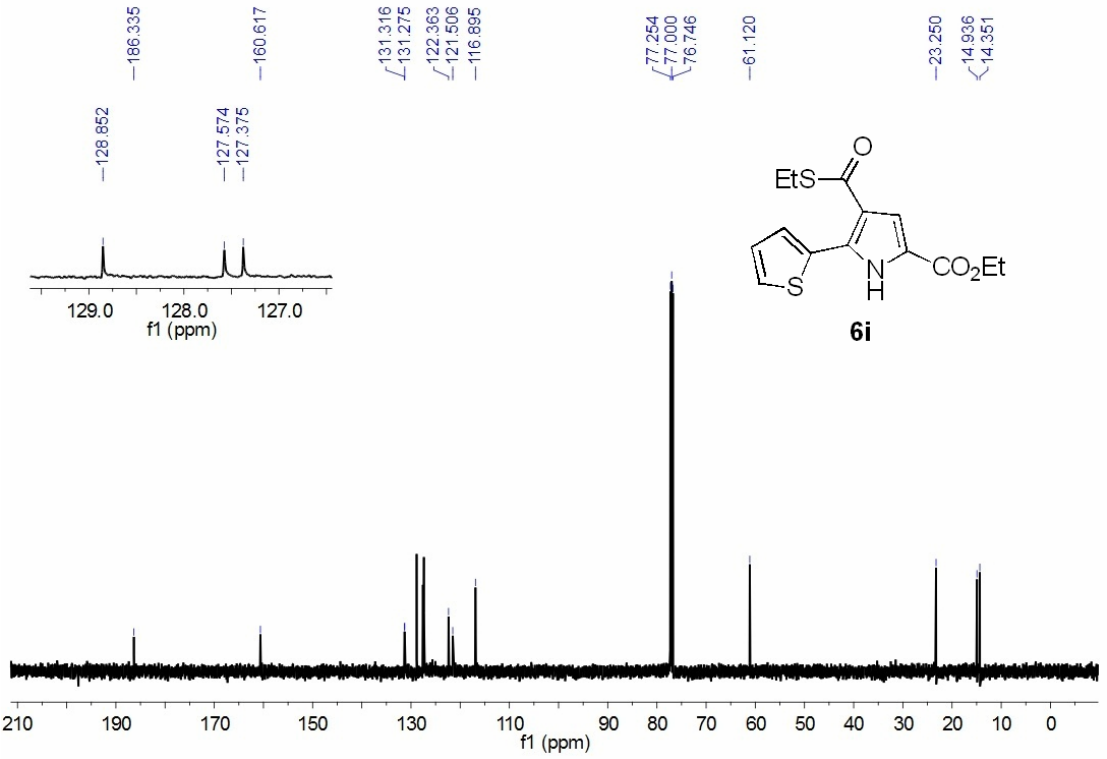

10.094
7.560
7.543
7.501
7.484
7.407
7.403
4.201
4.187
4.172
4.158
2.985
2.970
2.955
2.940
1.327
1.313
1.301
1.287
1.272
EtS
O
CO2Et
N
H
Br
6g
0.90
2.06
2.06
0.91
2.04
2.00
6.07
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

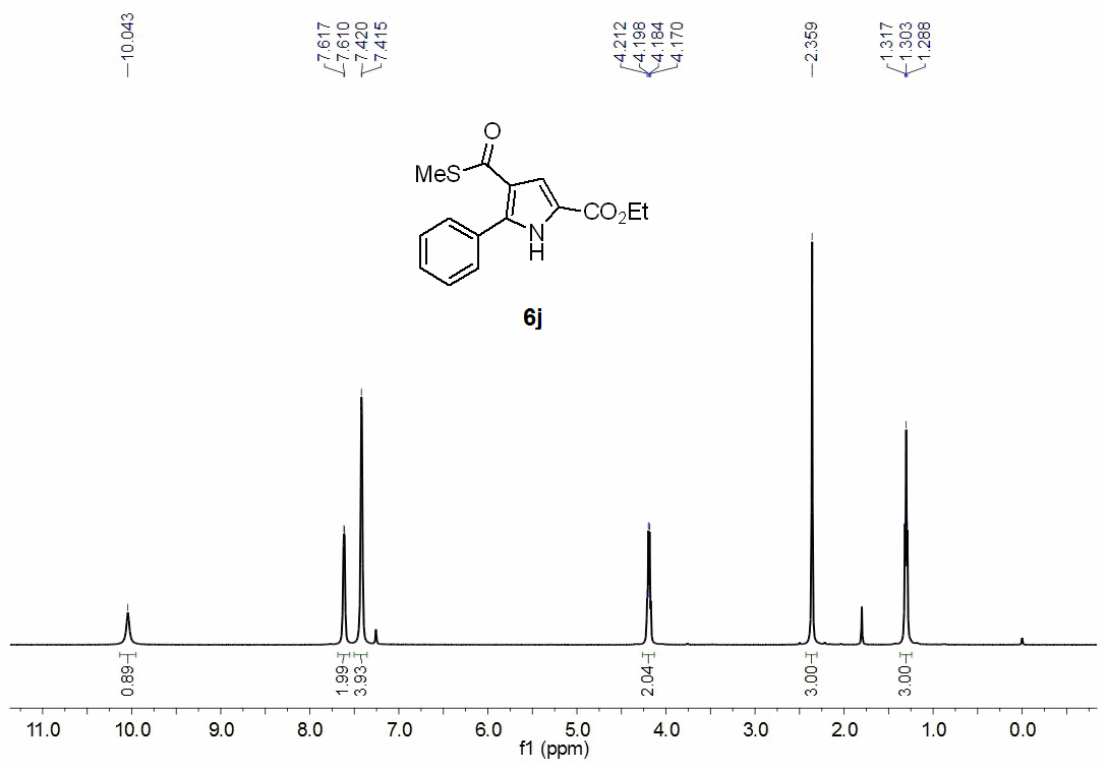

186.483
161.056
137.134
116.873
77.255
77.000
76.746
61.164
23.153
14.911
14.281
131.372
130.814
129.490
123.616
122.616
121.803
127
f1 (ppm)
EtS
O
CO2Et
N
H
Br
6g
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

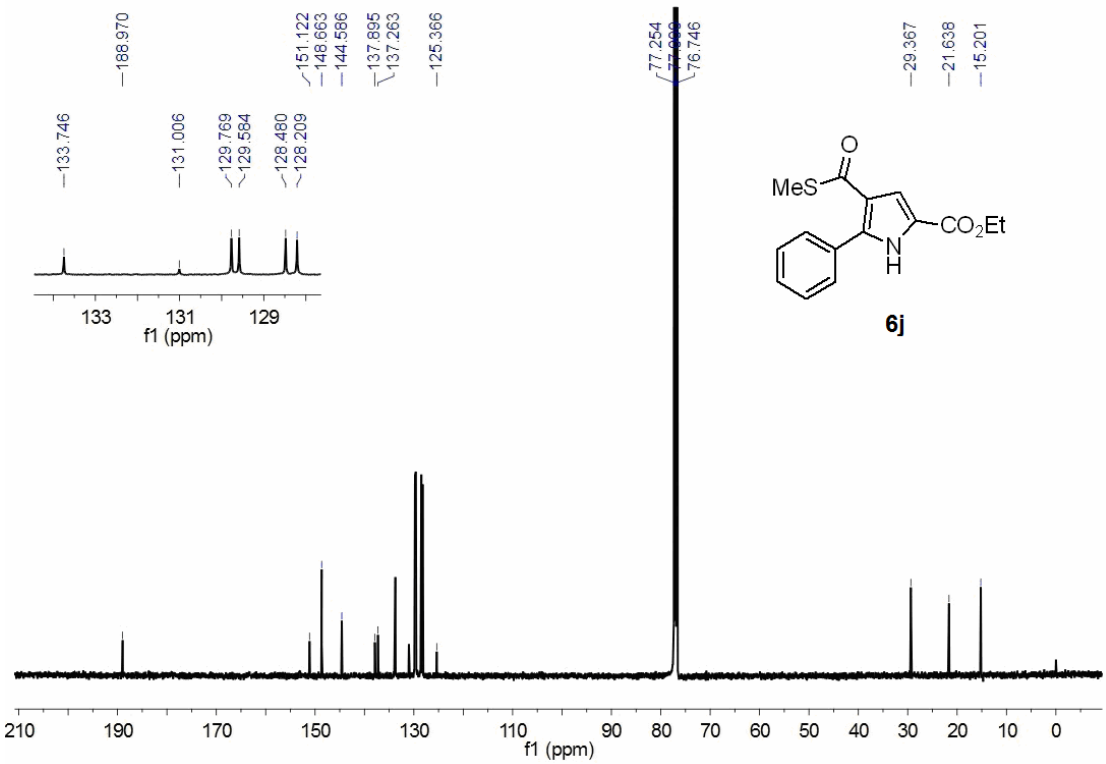

9.072
7.426
7.421
4.351
4.337
4.323
4.308
3.008
2.993
2.978
2.963
1.445
1.382
1.368
1.353
1.335
1.320
1.306
EtS
O
CO2Et
NH
6h
0.70
0.77
1.92
2.00
8.92
3.00
3.09
f1 (ppm)

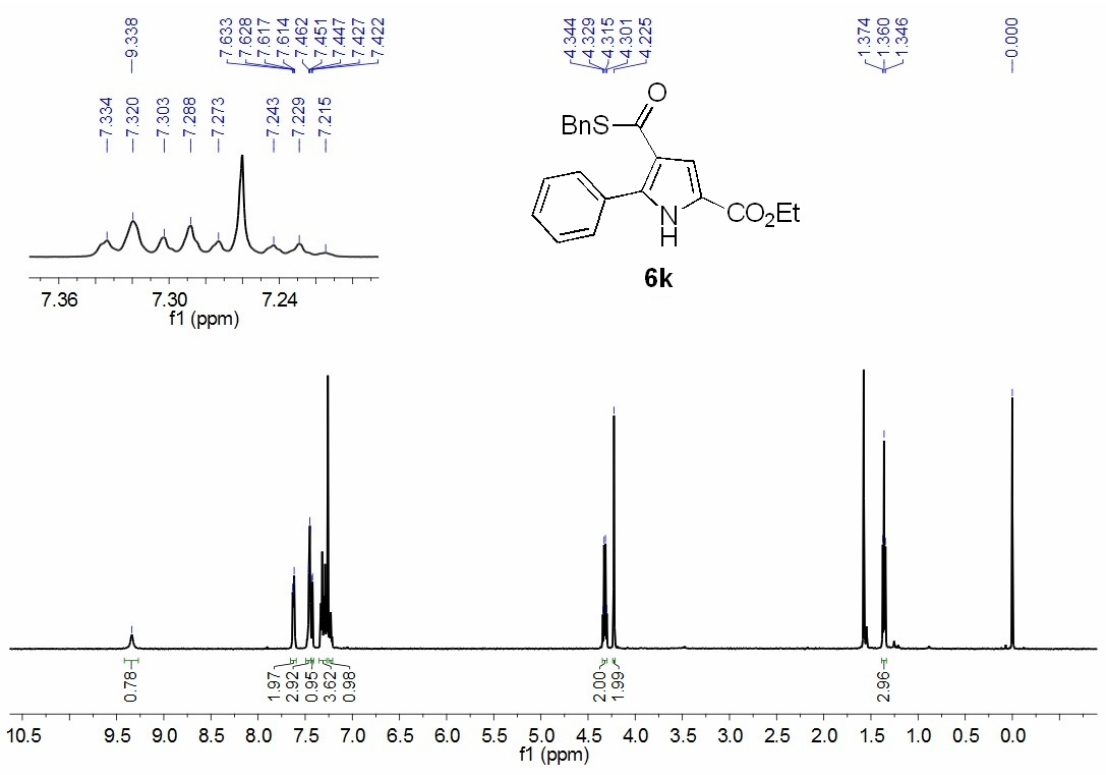

186.871
160.732
147.832
120.867
119.156
118.292
77.254
77.000
76.746
60.712
33.349
28.320
23.295
14.965
14.420
EtS
O
CO2Et
NH
6h
f1 (ppm)

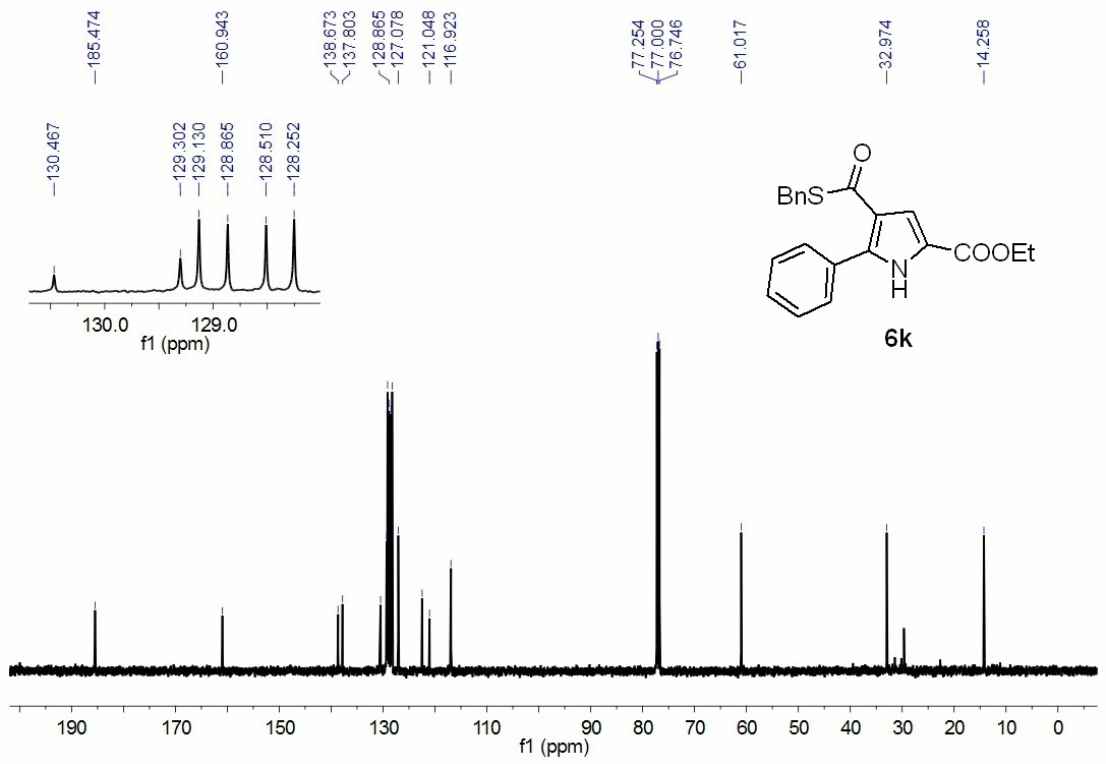

9.630
7.675
7.673
7.668
7.666
7.424
7.422
7.418
7.413
7.111
7.104
7.101
7.093
4.346
4.331
4.317
4.303
3.037
3.022
3.007
2.992
1.384
1.369
1.355
1.338
1.323
1.308
0.000
EtS
O
N
H
S
CO2Et
6i
7.44
7.41
f1 (ppm)
0.78
0.92
1.81
0.92
2.04
2.05
3.02
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

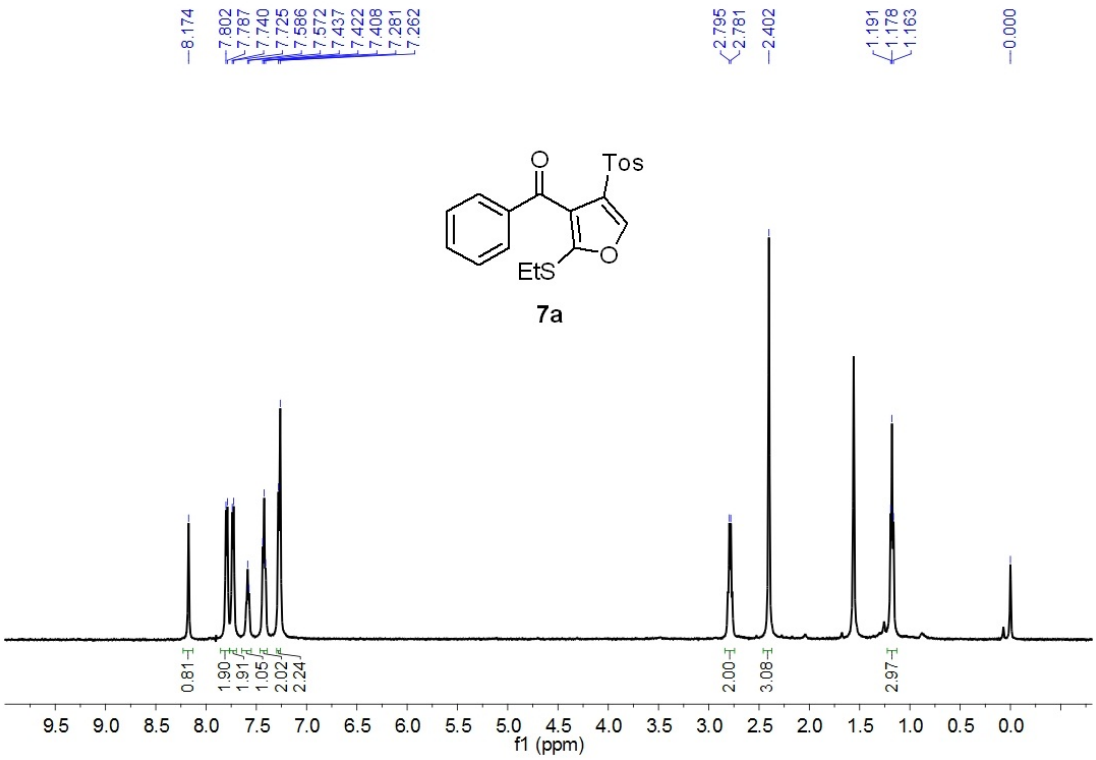

186.335
160.617
131.316
131.275
122.363
121.506
116.895
77.254
77.000
76.746
61.120
23.250
14.936
14.351
128.852
127.574
127.375
EtS
O
N
H
S
CO2Et
6i
129.0
128.0
127.0
f1 (ppm)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

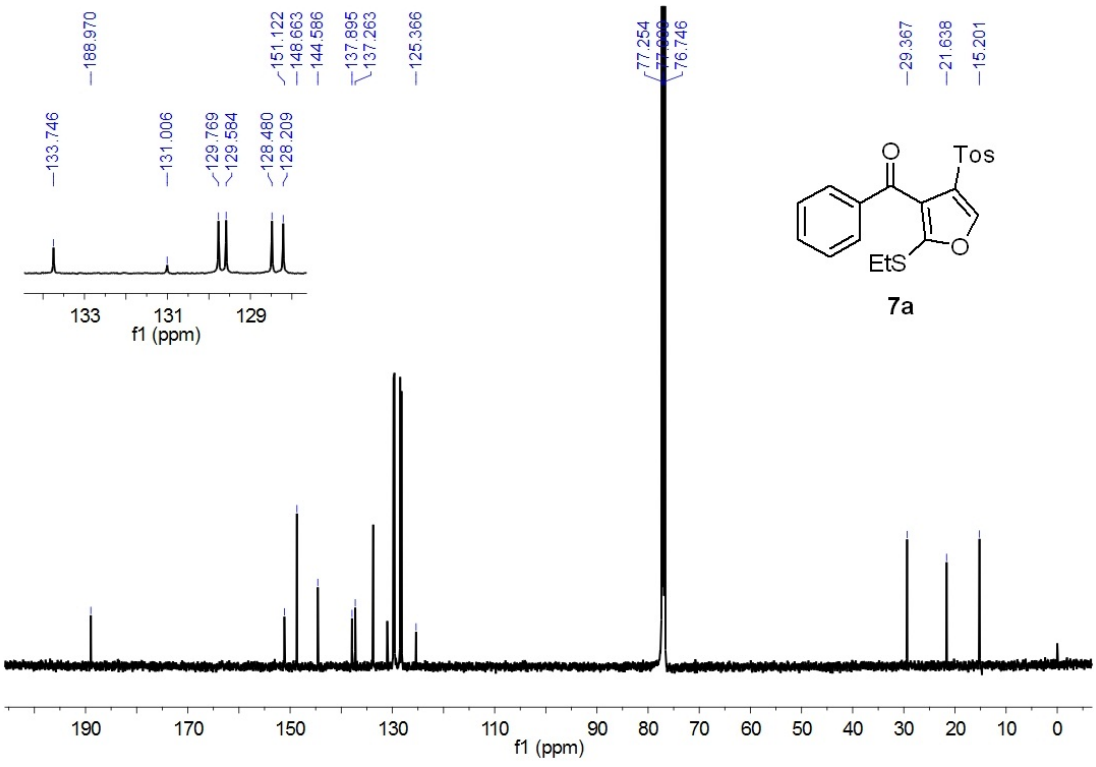

10.043
7.617
7.610
7.420
7.415
4.212
4.198
4.184
4.170
2.359
1.317
1.303
1.288
MeS
O
CO2Et
N
H
6j
0.89
1.99
3.93
2.04
3.00
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

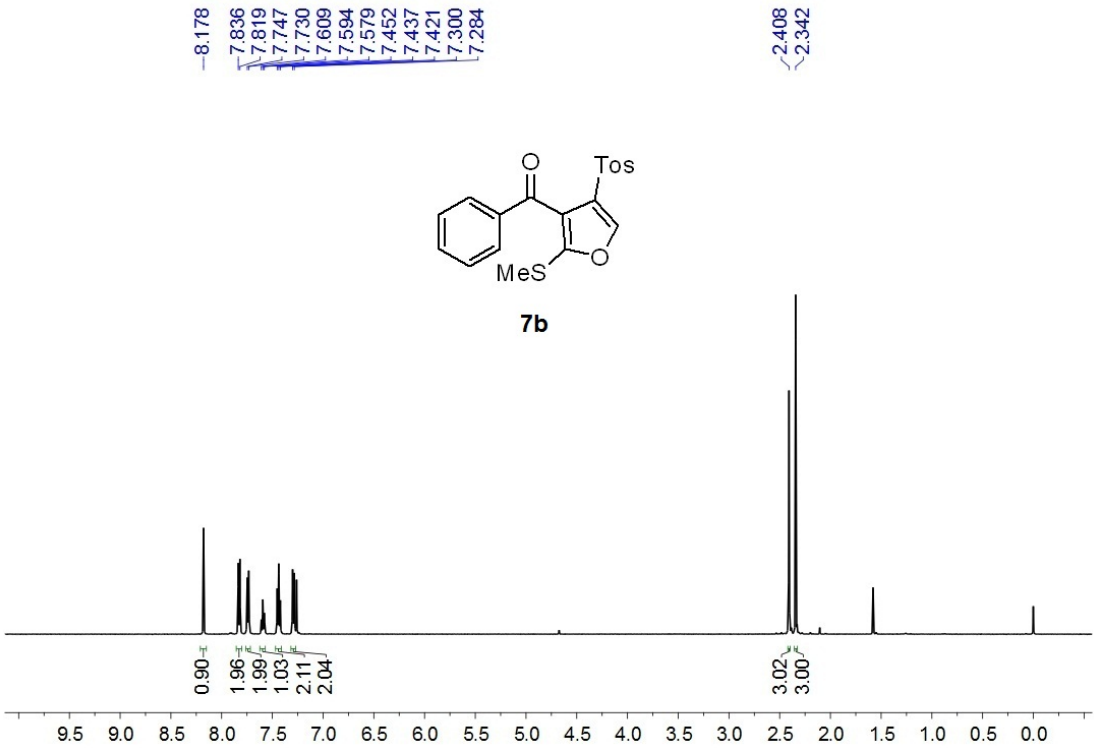

188.970
151.122
148.663
144.586
137.895
137.263
125.366
77.254
76.746
29.367
21.638
15.201
133.746
131.006
129.769
129.584
128.480
128.209
133
131
129
f1 (ppm)
MeS
O
CO2Et
N
H
6j
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.338
7.633
7.628
7.617
7.614
7.462
7.451
7.447
7.427
7.422
4.344
4.329
4.315
4.301
4.225
1.374
1.360
1.346
0.000
7.334
7.320
7.303
7.288
7.273
7.243
7.229
7.215
BnS
O
N
H
CO2Et
6k
7.36
7.30
7.24
f1 (ppm)
0.78
1.97
2.92
0.95
3.62
0.98
2.00
1.99
2.96
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

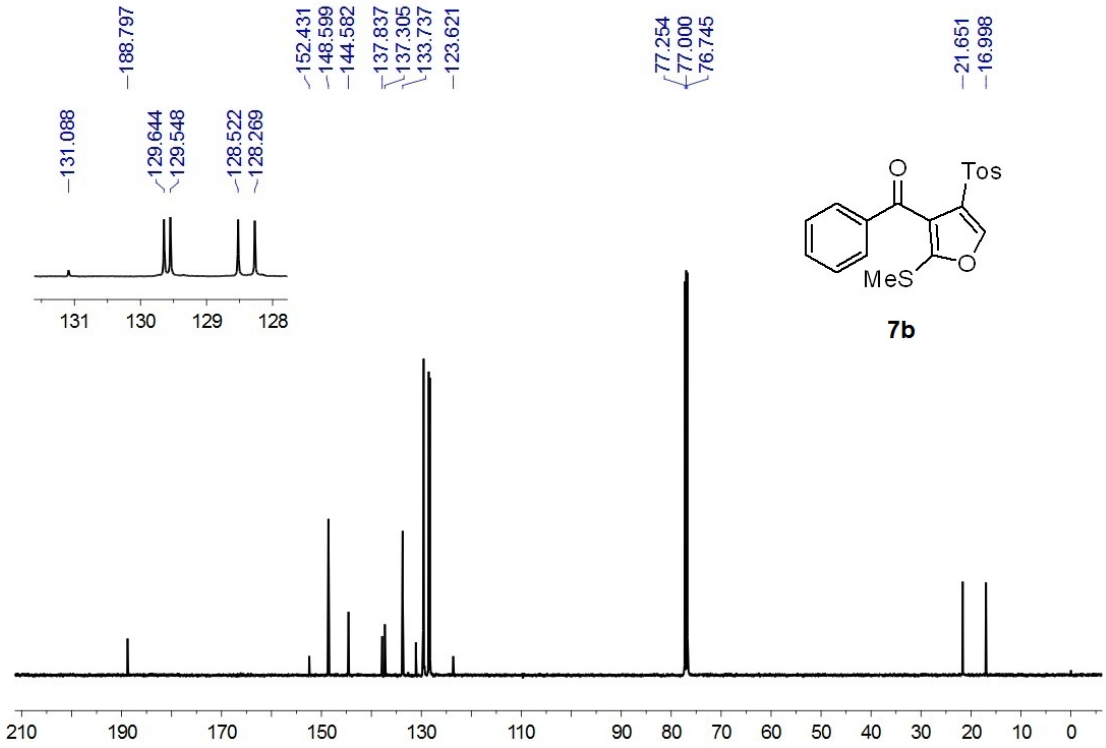

185.474
160.943
138.673
137.803
128.865
127.078
121.048
116.923
77.254
77.000
76.746
61.017
32.974
14.258
130.467
129.302
129.130
128.865
128.510
128.252
BnS
O
N
H
COOEt
6k
130.0
129.0
f1 (ppm)
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.174
7.802
7.787
7.740
7.725
7.586
7.572
7.437
7.422
7.408
7.281
7.262
2.795
2.781
2.402
1.191
1.178
1.163
0.000
Tos
EtS
O
O
7a
0.81
1.90
1.91
1.05
2.02
2.24
2.00
3.08
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

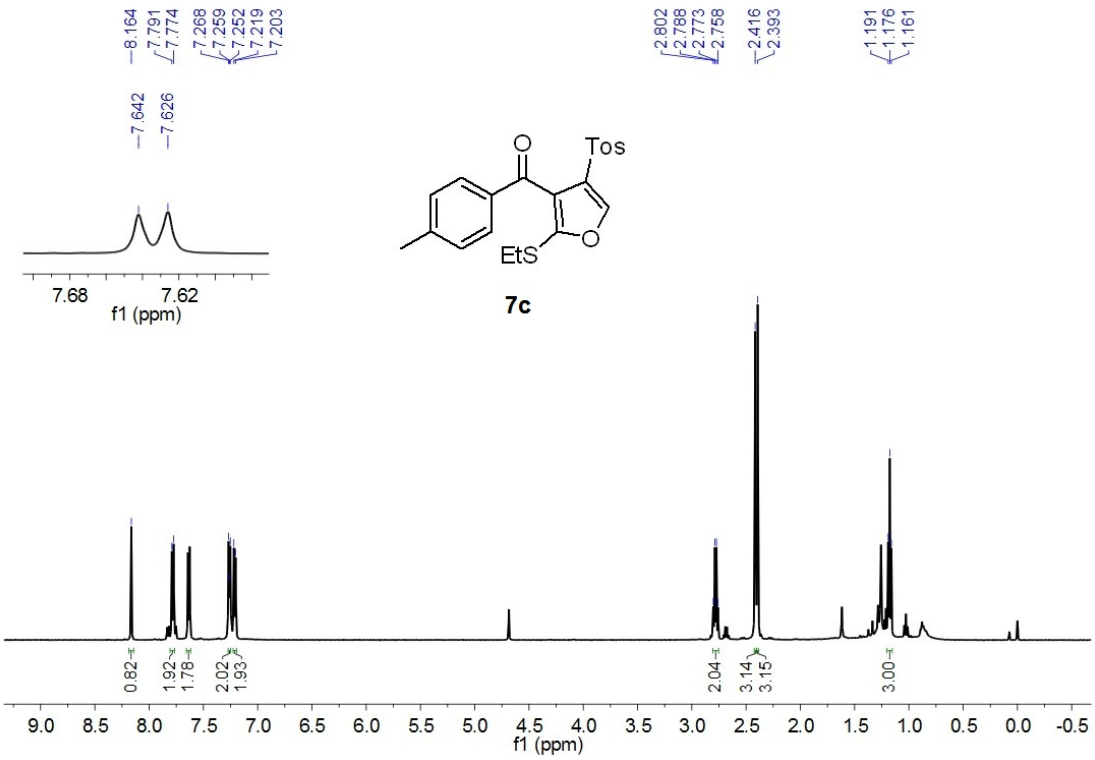

188.970
151.122
148.663
144.586
137.895
137.263
125.366
77.254
76.746
29.367
21.638
15.201
133.746
131.006
129.769
129.584
128.480
128.209
Tos
EtS
O
O
7a
133
131
129
f1 (ppm)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

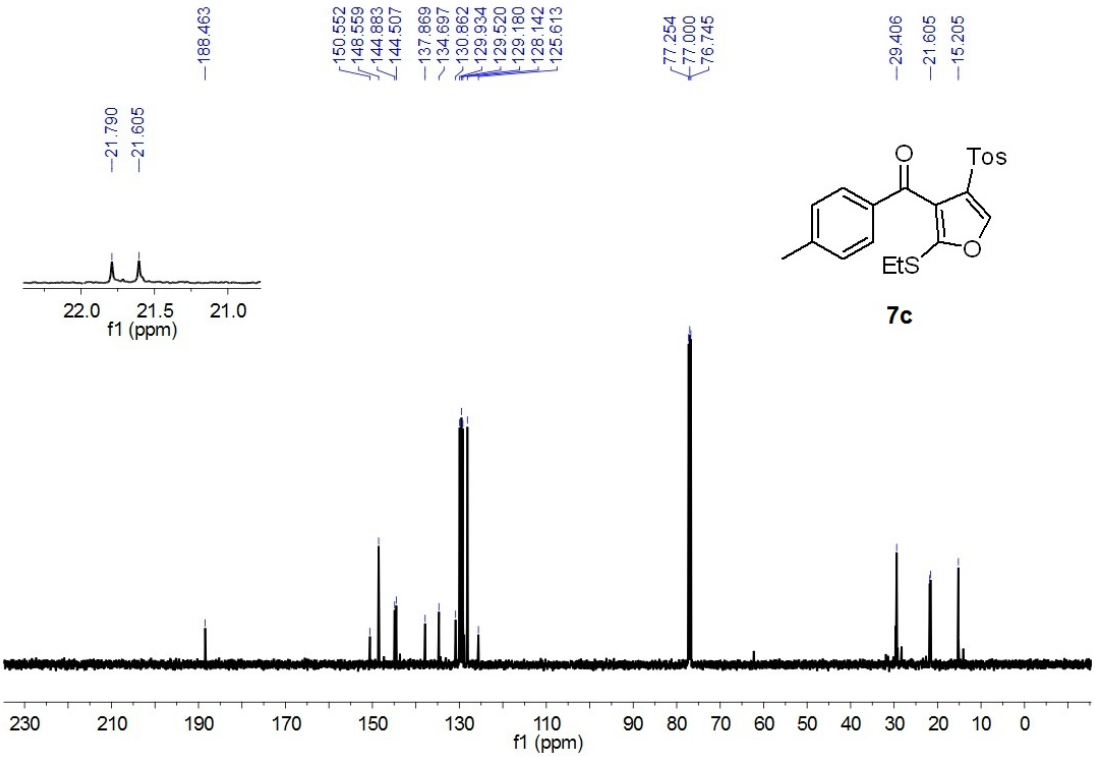

8.178
7.836
7.819
7.747
7.730
7.609
7.594
7.579
7.452
7.437
7.421
7.300
7.284
2.408
2.342
O
Tos
MeS
O
0.90
1.96
1.99
1.03
2.11
2.04
3.02
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

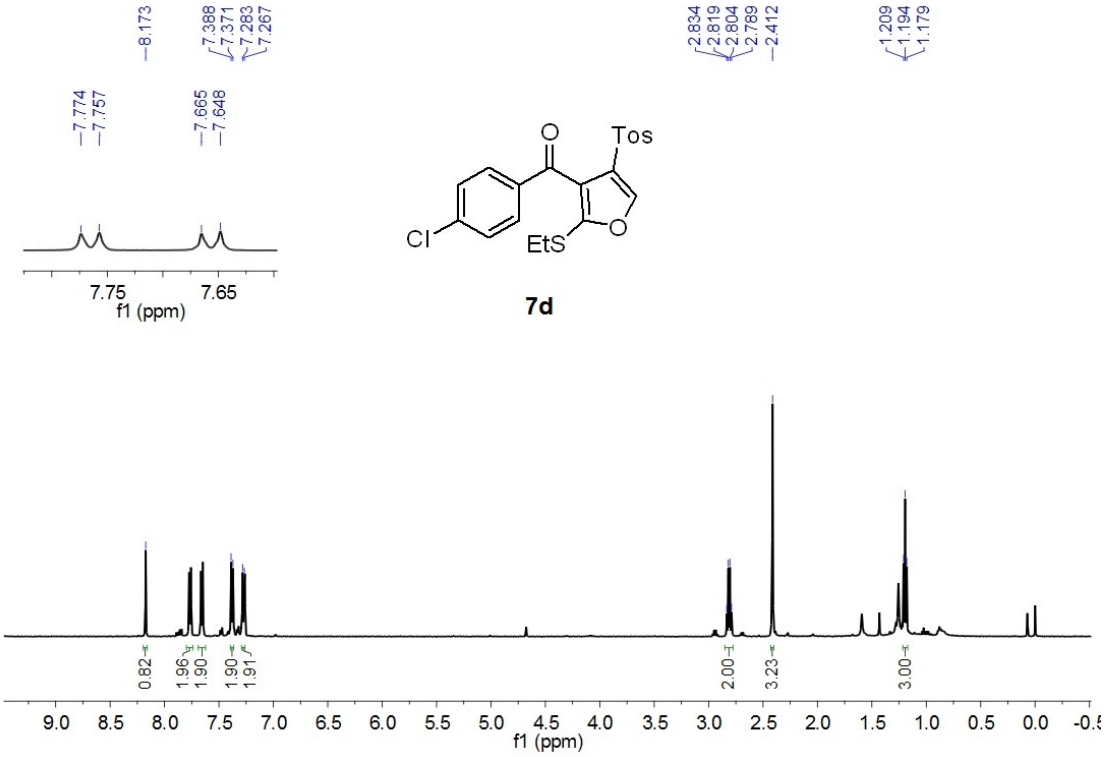
7b

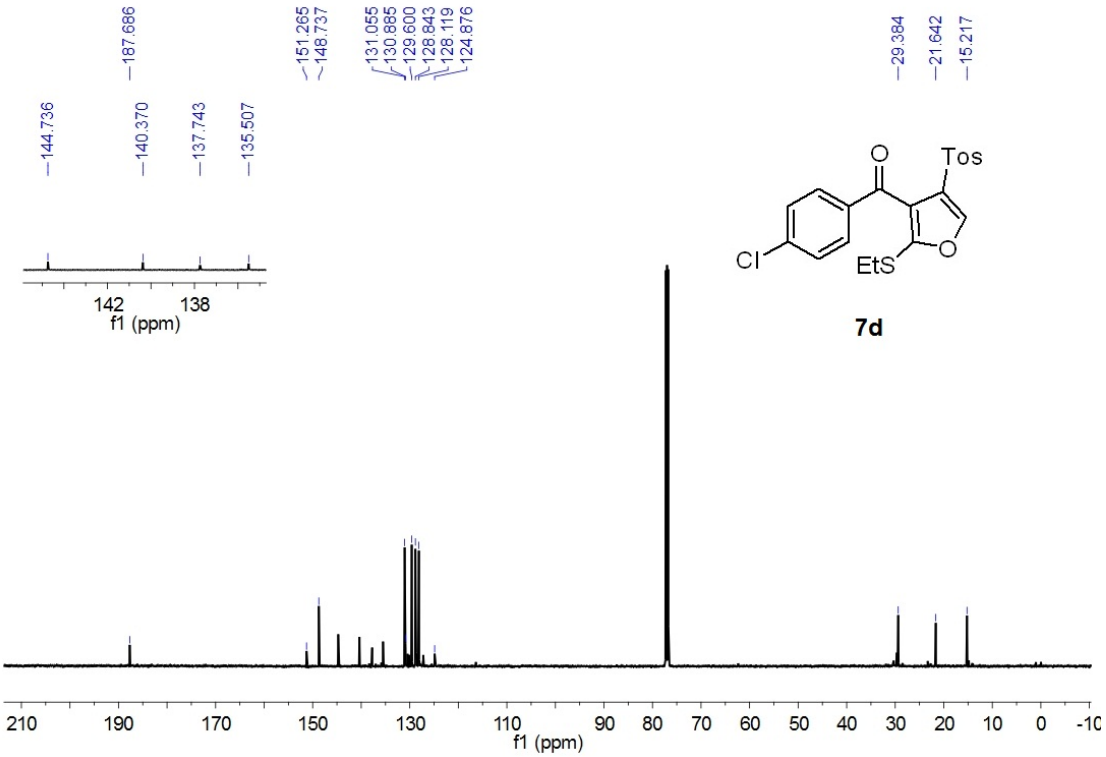

188.797
152.431
148.599
144.582
137.837
137.305
133.737
123.621
77.254
77.000
76.745
21.651
16.998
131.088
129.644
129.548
128.522
128.269
131 130 129 128
O
Tos
MeS
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0

7b


8.164
7.791
7.774
7.642
7.626
7.268
7.259
7.252
7.219
7.203
2.802
2.788
2.773
2.758
2.416
2.393
1.191
1.176
1.161
Tos
EtS
O
O
7c
7.68
7.62
f1 (ppm)
0.82
1.92
1.78
2.02
1.93
2.04
3.14
3.15
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


188.463
150.552
148.559
144.883
144.507
137.869
134.697
130.862
129.934
129.520
129.180
128.142
125.613
77.254
77.000
76.745
29.406
21.605
15.205
21.790
21.605
Tos
EtS
O
O
7c
22.0
21.5
21.0
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.173
7.774
7.757
7.665
7.648
7.388
7.371
7.283
7.267
2.834
2.819
2.804
2.789
2.412
1.209
1.194
1.179
Tos
O
Cl
EtS
O
7.75
7.65
f1 (ppm)
7d
0.82
1.96
1.90
1.90
1.91
2.00
3.23
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


187.686
151.265
148.737
131.055
130.885
129.600
128.843
128.119
124.876
29.384
21.642
15.217
144.736
140.370
137.743
135.507
Tos
O
Cl
EtS
O
142
138
f1 (ppm)
7d
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)