Enantioselective Synthesis of N-Arylpyrrole Aldehydes *via* NHC-Organocatalytic Atroposelective Desymmetrization Followed by Kinetic Resolution

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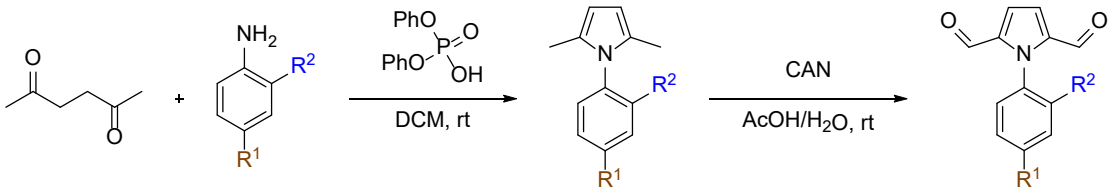
1. General methods

All reactions were carried out in dry glassware and were monitored by analytical thin-layer chromatography (TLC), which was visualized by ultraviolet light (254 nm). All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of the products was accomplished by flash chromatography using silica gel (200-300 mesh). Substrates **1** were prepared according to the known procedures. [1]Alcohols were used as received from commercially available sources. All NMR spectra were recorded on Bruker spectrometers, running at 300 MHz or 400 MHz for ^{1}H and 75 MHz or 101 MHz for ^{13}C respectively. Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hz respectively. The solvent signals were used as references (residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm, δ_c = 77.0 ppm). The following abbreviations are used to indicate the multiplicity in NMR spectra: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). High resolution mass spectrometry (HRMS) was recorded on TOF perimer for ESI^+. The ee. values were determined via chiral HPLC analysis.

2. Substrate synthesis

Synthesis of 1a-1e

The dicarbaldehydes were synthesized according to a literature procedure.[1]



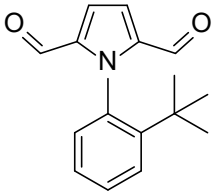
1a-1e

Diphenyl phosphonate (20 mol%) was added to a solution of 1,4-diketones (12.0 mmol) and aromatic amines (10.0 mmol) in methylene chloride. The mixture was stirred until aromatic amines completely consumed (monitored by TLC). The mixture was concentrated in vacuo and purified by flash chromatography on silica gel eluted with PE/EA to afford the corresponding N-arylpyrrole derivatives.

N-arylpyrrole derivatives (1.0 equiv., 500 mg) was dissolved in THF (50 mL), HOAc (10

mL), and H_2O (10 mL). Then ceric ammonium nitrate (8.7 equiv.) was added to the mixture all in once. The reaction mixture was stirred at room temperature for 6h until the reaction was complete (monitored by TLC). Then, the mixture was poured into water and extracted with EA. The organic layer was washed with water three times followed by saturated aqueous NaCl. Then the organic extracts were combined and dried over anhydrous Na_2SO_4. the solution was concentrated under vacuum to remove the solvents. The residue was purified by column chromatography on silica gel to afford **1a-1e**.

Characterization of 1a-1e

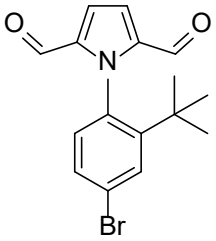


1-(2-(*tert*-butyl)phenyl)-1*H*-pyrrole-2,5-dicarbaldehyde (1a). **1a** was isolated as a white solid (84mg, 15% yield for the last step). Column chromatography eluent: petroleum ether: EtOAc = 80 : 1. MP: 83 –85 ºC.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.50 (s, 2H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.12 (s, 2H), 7.04 (d, *J* = 7.7 Hz, 1H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 147.1, 138.0, 133.4, 130.6, 130.3, 129.4, 127.1, 117.7, 77.5, 76.8, 36.3, 31.6.

HRMS (ESI) calcd for $C_{16}H_{18}NO_2^+$ $[M+H]^+$: 256.1332, found: 256.1334.

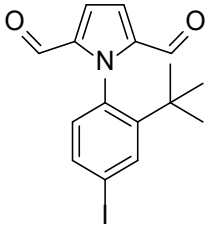


1-(4-bromo-2-(*tert*-butyl)phenyl)-1*H*-pyrrole-2,5-dicarbaldehyde (1b). **1b** was isolated as a yellow oil (60mg, 11% yield for the last step). Column chromatography eluent: petroleum ether: EtOAc = 80 : 1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.54 (s, 2H), 7.76 (d, *J* = 2.2 Hz, 1H), 7.40 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.12 (s, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.12, 181.0, 149.0, 137.8, 132., 131.7, 130.2, 124.2, 118.8, 36.4, 31.2.

HRMS (ESI) calcd for $C_{16}H_{17}BrNO_2^+$ $[M+H]^+$: 334.0437, found: 334.0436.

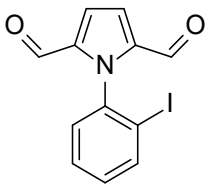


1-(2-(*tert*-butyl)-4-iodophenyl)-1*H*-pyrrole-2,5-dicarbaldehyde (1c). **1c** was isolated as a yellow oil (81mg, 15% yield for the last step). Column chromatography eluent: petroleum ether: EtOAc = 80 : 1.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.52 (s, 2H), 7.93 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.09 (s, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.8, 148.9, 138.5, 137.6, 136.0, 133.8, 131.8, 96.4, 36.2, 31.2.

HRMS (ESI) calcd for $C_{16}H_{17}INO_2^+$ $[M+H]^+$: 382.0299, found: 382.0302.

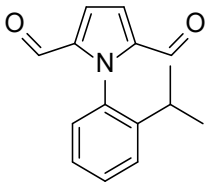


1-(2-iodophenyl)-1*H*-pyrrole-2,5-dicarbaldehyde (1d). 1d was isolated as a yellow oil (109mg, 20% yield for the last step). Column chromatography eluent: petroleum ether: EtOAc = 80 : 1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.53 (s, 2H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.53 – 7.46 (m, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.15 (s, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 180.5, 139.8, 139.4, 135.9, 131.2, 129.3, 129.0, 119.0, 97.9, 76.7.

HRMS (ESI) calcd for $C_{12}H_9INO_2^+$ $[M+H]^+$: 325.9672, found: 325.9670.



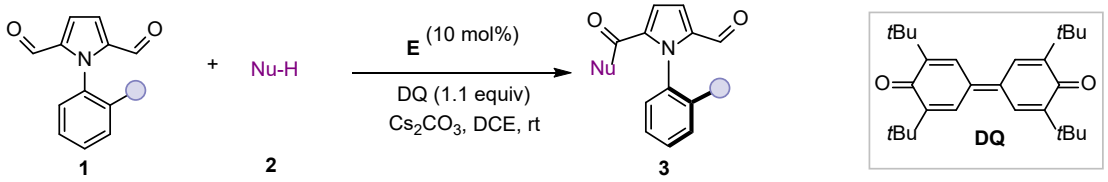
1-(2-isopropylphenyl)-1*H*-pyrrole-2,5-dicarbaldehyde (1e). 1e was isolated as a yellow oil (90mg, 14% yield for the last step). Column chromatography eluent: petroleum ether: EtOAc = 80 : 1.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.48 (s, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 2H), 2.37 (h, *J* = 6.9 Hz, 1H), 1.10 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.7, 146.6, 137.0, 133.2, 130.6, 128.1, 126.9, 126.7, 117.6, 77.5, 76.8, 28.0, 23.8.

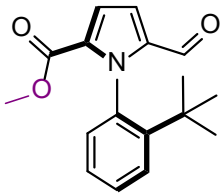
HRMS (ESI) calcd for $C_{15}H_{16}NO_2^+$ $[M+H]^+$: 242.1176, found: 242.1174.

3. Synthesis of C-N axially chiral N-arylpyrroles 3



General procedure: To a 10 mL oven-dried Schlenk tube equipped with a PTFE-coated stirring bar were charged with substrate **1** (0.20 mmol, 1.0 equiv.), substrate **2** (0.24 mmol, 1.2 equiv.), DQ (90 mg, 0.22 mmol, 1.1 equiv.), Cs_2CO_3 (26 mg, 0.08 mmol, 0.4 equiv), cat. **E** (10 mg, 0.02 mmol, 10 mol %) and 4 ÅMS (25 mg) under air. The vessel was evacuated and back-filled with N_2 three times. Then, anhydrous DCE (4 mL) was added to the tube. The resulting mixture was stirred at room temperature under N_2 for 12 h. After that, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the product **3a-3ad**.

Characterization of product 3



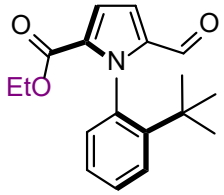
methyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3a). 3a was isolated as a yellow oil (40 mg, 70% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -2.873 (c = 0.116 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.582 min (minor), 6.039 min (major), 97% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.46 (t, 1H), 7.29 – 7.22 (m, 1H), 7.07 (s, 2H), 6.98 (d, *J* = 7.7 Hz, 1H), 3.70 (s, 3H), 1.12 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.7, 160.2, 148.7, 138.4, 137.8, 135.7, 135.2, 131.6, 130.5, 117.8, 117.5, 95.8, 51.9, 31.2.

HRMS (ESI) calcd for $C_{17}H_{20}NO_3^+$ $[M+H]^+$: 286.1438, found: 286.1440.



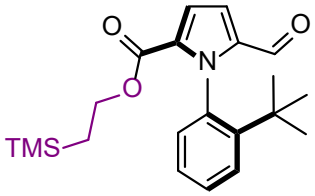
ethyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3b). 3b was isolated as a yellow oil (42 mg, 70% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -8.871 (c = 0.124 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.548 min (minor), 10.129 min (major), 86% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 6.8 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.99 (d, *J* = 9.4 Hz, 1H), 4.20 – 4.06 (m, 2H), 1.13 (d, *J* = 7.2 Hz, 3H), 1.12 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.3, 160.0, 146.5, 138.0, 135.2, 131.0, 130.3, 129.6, 129.1, 126.5, 117.4, 116.6, 77.5, 76.8, 60.8, 36.2, 31.5, 14.1.

HRMS (ESI) calcd for $C_{18}H_{22}NO_3^+$ $[M+H]^+$: 300.1594, found: 300.2897.



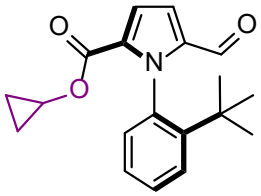
2-(trimethylsilyl)ethyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3c). 3c was isolated as a yellow oil (60 mg, 80% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -6.812 (c = 0.230 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 97/3, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 8.203 min (minor), 9.544 min (major), 94% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 1H), 7.23 (s, 1H), 7.11 – 7.03 (m, 2H), 7.00 (s, 1H), 4.27 – 4.11 (m, 2H), 1.12 (s, 9H), 0.95 – 0.88 (m, 2H), 0.01 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.3, 160.1, 146.5, 138.0, 135.1, 131.1, 130.3, 129.6, 129.1, 126.5, 117.2, 116.6, 76.8, 63.2, 36.2, 31.5, 17.3, -1.4.

HRMS (ESI) calcd for $C_{21}H_{30}NO_3Si^+$ $[M+H]^+$: 286.1438, found: 286.1440.



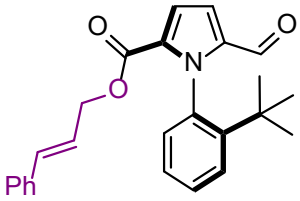
cyclopropyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3d). 3d was isolated as a yellow oil (32 mg, 51% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -43.182 (c = 0.044 in $CHCl_3$). HPLC DAICEL CHIRALCEL IF, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.740 min (minor), 13.574 min (major), 88% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.45 (t, 1H), 7.24 (t, 1H), 7.08 – 7.03 (m, 2H), 6.97 (d, *J* = 7.7 Hz, 1H), 4.18 – 4.09 (m, 1H), 1.11 (s, 9H), 0.67 – 0.60 (m, 2H), 0.53 – 0.45 (m, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 181.3, 160.8, 146.5, 138.1, 135.1, 130.6, 130.3, 129.6, 129.1, 126.5, 117.6, 116.6, 76.7, 49.2, 36.2, 31.5, 5.3, 5.1.

HRMS (ESI) calcd for $C_{19}H_{22}NO_3^+$ $[M+H]^+$: 312.1594, found: 312.1591.



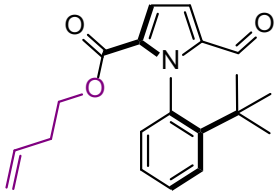
cinnamyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3e). 3e was isolated as a yellow oil (56 mg, 73% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -9.151 (c = 0.204 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 25.689 min (minor), 35.793 min (major), 86% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 6.9 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.29 – 7.23 (m, 2H), 7.16 – 7.07 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.83 – 4.66 (m, 2H), 1.12 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 181.2, 159.6, 146.5, 138.1, 136.1, 135.0, 134.4, 130.5, 130.2, 129.5, 129.1, 128.6, 128.2, 126.6, 126.5, 122.6, 117.6, 116.5, 65.2, 36.2, 31.4.

HRMS (ESI) calcd for $C_{25}H_{26}NO_3^+$ $[M+H]^+$: 388.1907, found: 388.1903.



but-3-en-1-yl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3f). 3f was isolated as a yellow oil (48 mg, 75% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

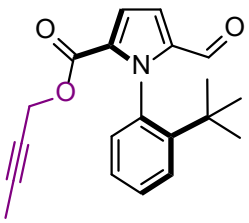
$[\alpha]_D^{25}$ = -166.667 (c = 0.006 in $CHCl_3$). HPLC DAICEL CHIRALCEL IF, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.808 min (minor), 11.275 min (major), 90% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 8.2

Hz, 1H), 7.23 (s, 1H), 7.08 (s, 2H), 6.99 (d, *J* = 8.7 Hz, 1H), 5.73 – 5.57 (m, 1H), 5.10 – 4.99 (m, 2H), 4.24 – 4.05 (m, 2H), 2.27 (q, *J* = 6.7 Hz, 2H), 1.12 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 181.2, 159.8, 146.4, 138.0, 135.0, 133.7, 130.7, 130.2, 129.5, 129.0, 126.5, 117.4, 117.4, 116.5, 63.8, 36.1, 32.9, 31.4.

HRMS (ESI) calcd for $C_{20}H_{24}NO_3^+$ $[M+H]^+$: 326.1451, found: 326.1447.



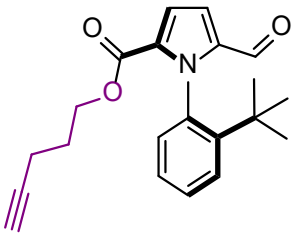
but-2-yn-1-yl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3g). 3g was isolated as a yellow oil (54 mg, 85% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -11.278 (c = 0.266 in $CHCl_3$). HPLC DAICEL CHIRALCEL IF, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.628 min (minor), 13.158 min (major), 92% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.17 – 7.05 (m, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 4.66 (s, 2H), 1.82 (s, 3H), 1.12 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 181.2, 159.2, 146.4, 138.2, 134.8, 130.2, 129.9, 129.5, 129.1, 126.5, 117.8, 116.4, 83.5, 72.8, 53.0, 36.1, 31.4, 3.6.

HRMS (ESI) calcd for $C_{20}H_{22}NO_3^+$ $[M+H]^+$: 324.1594, found: 324.1592.



pent-4-yn-1-yl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3h). 3h was isolated as a yellow oil (48 mg, 72% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

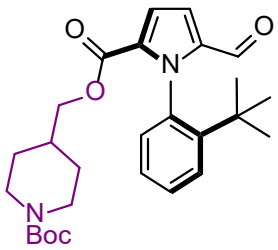
$[\alpha]_D^{25}$ = -32.353 (c = 0.034 in $CHCl_3$). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol

= 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.663 min (major), 16.986 min (minor), 92% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.13 – 7.06 (m, 2H), 7.00 (d, *J* = 8.3 Hz, 1H), 4.28 – 4.09 (m, 2H), 2.10 – 2.03 (m, 2H), 1.93 (t, *J* = 2.7 Hz, 1H), 1.75 – 1.66 (m, 2H), 1.11 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 181.2, 159.9, 146.4, 138.0, 135.1, 130.7, 130.3, 129.6, 129.1, 126.5, 117.7, 116.6, 82.8, 69.1, 63.3, 36.1, 31.4, 27.3, 15.1.

HRMS (ESI) calcd for $C_{21}H_{24}NO_3^+$ $[M+H]^+$: 338.1751, found: 338.1754.



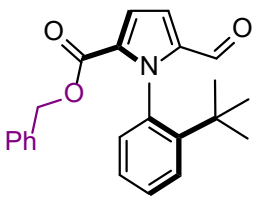
***tert*-butyl *(R)-4-(((1-(2-(tert-butyl)phenyl)-5-formyl-1H-pyrrole-2-carbonyl)oxy)methyl) piperidine-1-carboxylate* (3i). 3i** was isolated as a yellow oil (32 mg, 34% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -0.915 (c = 1.530 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 14.834 min (minor), 18.719 min (major), 92% ee.

^{1}H NMR (400 MHz, Chloroform-d) δ 9.30 (s, 1H), 7.61 (d, J = 8.2 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.28 – 7.21 (m, 1H), 7.12 – 7.05 (m, 2H), 7.00 (d, J = 7.8 Hz, 1H), 4.12 – 3.76 (m, 4H), 2.59 (s, 2H), 1.65 – 1.55 (m, 1H), 1.44 (s, 11H), 1.10 (s, 9H), 1.05 – 0.91 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 160.0, 154.8, 146.5, 138.0, 135.2, 130.7, 130.3, 129.5, 129.1, 126.5, 117.7, 116.6, 79.5, 68.8, 36.1, 35.5, 31.4, 28.5.

HRMS (ESI) calcd for $C_{27}H_{37}N_2O_5^+$ $[M+H]^+$: 469.2697, found: 469.2694.



benzyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3j). 3j was

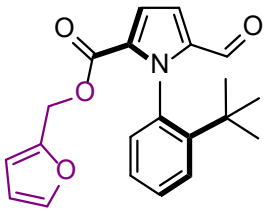
isolated as a yellow oil (44 mg, 61% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -29.167 (c = 0.096 in $CHCl_3$). HPLC DAICEL CHIRALCEL IF, *n*-hexane/2-propanol = 99.2/0.8, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.544 min (minor), 21.664 min (major), 92% ee.

1H NMR (400 MHz, Chloroform-d) δ 9.37 (s, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.33 (dd, J = 5.7, 2.3 Hz, 3H), 7.27 (t, J = 7.5 Hz, 1H), 7.21 (dt, J = 5.8, 2.4 Hz, 2H), 7.18 (d, J = 4.2 Hz, 1H), 7.11 (d, J = 4.2 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 5.27 – 5.06 (m, 2H), 1.11 (s, 9H).

13C NMR (75 MHz, Chloroform-d) δ 181.2, 159.7, 146.4, 138.1, 135.3, 135.0, 130.5, 130.2, 129.5, 129.1, 128.5, 128.3, 128.2, 126.5, 117.8, 116.5, 76.7, 66.5, 36.1, 31.4.

HRMS (ESI) calcd for $C_{23}H_{24}NO_3^+$ $[M+H]^+$: 362.1751, found: 362.1755.



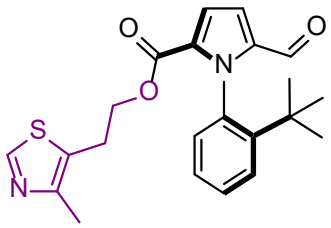
furan-2-ylmethyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3k). 3k was isolated as a yellow oil (38 mg, 54% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -30.006 (c = 0.054 in $CHCl_3$). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 25.579 min (major), 30.354 min (minor), 90% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.38 (t, *J* = 1.4 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.04 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.36 – 6.28 (m, 2H), 5.07 (s, 2H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 159.4, 148.9, 146.4, 143.3, 138.1, 134.8, 130.2, 129.5, 129.0, 126.4, 117.8, 116.4, 110.9, 110.5, 58.1, 36.1, 31.4.

HRMS (ESI) calcd for $C_{21}H_{22}NO_4^+$ $[M+H]^+$: 352.1543, found: 352.1550.



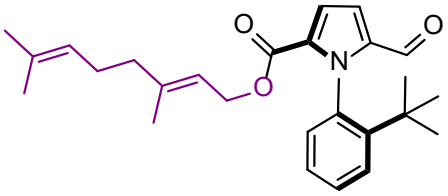
2-(4-methylthiazol-5-yl)ethyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3l). 3l was isolated as a yellow oil (56 mg, 70% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -16.337 (c = 0.023 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.164 min (minor), 10.551 min (major), >99% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 8.61 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.21 (m, 1H), 7.08 (s, 2H), 6.96 (d, *J* = 7.8 Hz, 1H), 4.38 – 4.17 (m, 2H), 3.04 (t, *J* = 6.7 Hz, 2H), 2.38 (s, 3H), 1.10 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.3, 146.6, 130.3, 129.7, 129.2, 126.6, 117.7, 116.6, 77.5, 76.8, 64.2, 31.5, 29.8.

HRMS (ESI) calcd for $C_{22}H_{25}N_2O_3S^+$ $[M+H]^+$: 397.1580, found: 397.1579.



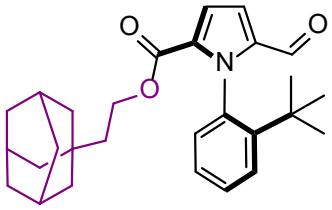
(*E*)-3,7-dimethylocta-2,6-dien-1-yl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1H-pyrrole-2-carboxylate (3m). 3m was isolated as a yellow oil (72 mg, 88% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -20.349 (c = 0.172 in $CHCl_3$). HPLC DAICEL CHIRALCEL IC, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.121 min (major), 10.797 min (minor), 91% ee.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.99 (d, *J* = 7.8 Hz, 1H), 5.23 – 5.00 (m, 2H), 4.59 (m, 2H), 2.10 – 1.95 (m, 4H), 1.68 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H), 1.11 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 160.0, 146.4, 142.5, 137.9, 135.1, 131.9, 131.0, 130.2, 129.4, 129.0, 126.4, 123.7, 117.8, 117.4, 116.5, 61.6, 39.5, 36.1, 26.2, 25.7, 17.7, 16.5.

HRMS (ESI) calcd for $C_{26}H_{34}NO_3^+$ $[M+H]^+$: 408.2533, found: 408.2531.



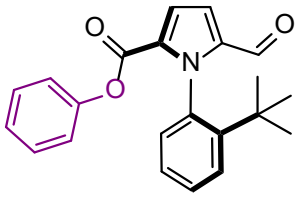
2-(adamantan-1-yl)ethyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3n). 3n was isolated as a yellow oil (36 mg, 40% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -20.732 (c = 0.164 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.461 min (minor), 8.312 min (major), 99% ee.

^{1}H NMR (400 MHz, Chloroform-d) δ 9.34 (s, 1H), 7.63 (d, J = 8.2 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.09 – 7.04 (m, 2H), 6.99 (d, J = 7.8 Hz, 1H), 4.25 – 4.06 (m, 2H), 1.93 (s, 3H), 1.72 – 1.57 (m, 6H), 1.47 (s, 6H), 1.31 (t, J = 7.3 Hz, 2H), 1.12 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 160.0, 146.4, 137.9, 135.0, 131.0, 130.3, 129.5, 129.0, 126.4, 117.2, 116.5, 61.2, 42.5, 42.2, 37.0, 36.1, 31.7, 31.4, 28.5.

HRMS (ESI) calcd for $C_{28}H_{36}NO_3^+$ $[M+H]^+$: 434.2690, found: 434.2690.



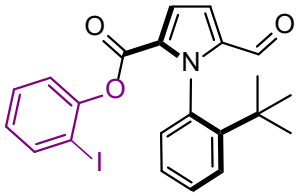
phenyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3o). 3o was isolated as a yellow oil (48 mg, 70% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -3.827 (c = 0.046 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.95 min (minor), 17.29 min (major), 84% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 6.5 Hz, 2H), 7.31 (s, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.06 (d, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 2H), 1.17 (s, 9H).

13C NMR (101 MHz, Chloroform-d) δ 181.4, 158.2, 150.2, 146.5, 138.7, 134.8, 130.3, 129.8, 129.8, 129.5, 129.2, 126.7, 126.0, 121.5, 118.6, 116.5, 77.5, 76.8, 36.3, 31.6.

HRMS (ESI) calcd for $C_{22}H_{22}NO_3^+$ $[M+H]^+$: 348.1594, found: 348.1596.



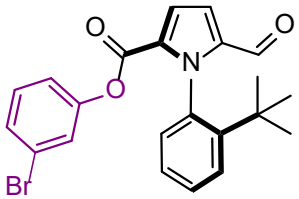
2-iodophenyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3p). 3p was isolated as a yellow oil (62 mg, 65% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -3.827 (c = 0.784 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 98/2, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 10.015 min (major), 11.611 min (minor), 78% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.42 (s, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.31 (m, 1H), 7.28 – 7.23 (m, 1H), 7.18 (d, *J* = 4.3 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.95 (t, *J* = 7.7 Hz, 1H), 1.18 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 181.3, 157.2, 150.6, 146.5, 139.4, 138.9, 134.4, 130.2, 129.7, 129.4, 129.2, 129.1, 127.8, 126.6, 123.2, 119.1, 116.4, 90.3, 36.2, 31.6.

HRMS (ESI) calcd for $C_{22}H_{21}INO_3^+$ $[M+H]^+$: 474.0561, found: 474.0559.



3-bromophenyl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3q). 3q was isolated as a yellow oil (42mg, 50% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

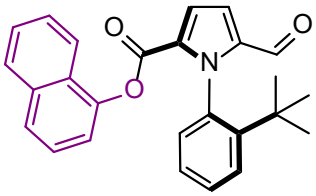
$[\alpha]_D^{25}$ = -62.222 (c = 0.090 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol

= 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.111 min (minor), 15.902 min (major), 99% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 4.4 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.24 (t, *J* = 1.9 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 4.3 Hz, 1H), 7.05 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.99 (dd, *J* = 8.1, 1.5 Hz, 1H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 157.6, 150.6, 146.4, 138.8, 134.6, 130.5, 130.2, 129.8, 129.2, 129.2, 129.1, 126.7, 124.9, 122.4, 120.3, 118.8, 116.4, 36.2, 31.5.

HRMS (ESI) calcd for $C_{22}H_{21}BrNO_3^+$ $[M+H]^+$: 426.0700, found: 426.0697.



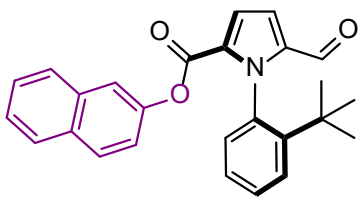
naphthalen-1-yl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3r). 3r was isolated as a yellow oil (48 mg, 60% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -25.472 (c = 0.318 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 18.905 min (major), 23.117 min (minor), 99% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.44 (s, 1H), 7.85 (m, 1H), 7.81 – 7.78 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.59 (m, 1H), 7.51 – 7.46 (m, 3H), 7.44 – 7.37 (m, 2H), 7.27 – 7.21 (m, 3H), 7.11 (d, *J* = 7.8 Hz, 1H), 1.18 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.3, 158.3, 146.4, 145.9, 138.8, 134.6, 134.6, 130.2, 129.7, 129.5, 129.2, 128.0, 126.8, 126.7, 126.5, 126.5, 126.2, 125.3, 121.1, 118.6, 118.2, 116.5, 36.2, 31.5.

HRMS (ESI) calcd for $C_{26}H_{24}NO_3^+$ $[M+H]^+$: 398.1751, found: 398.1749.



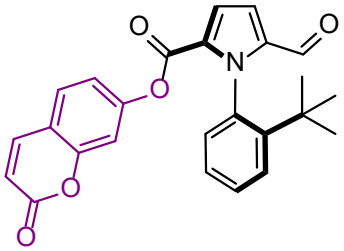
naphthalen-2-yl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3s). 3s was isolated as a yellow oil (64 mg, 80% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -26.156 (c = 0.427 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 16.504 min (minor), 17.222 min (major), 91% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.45 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 2.1 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 3H), 7.39 (d, *J* = 4.3 Hz, 1H), 7.29 (s, 1H), 7.21 (d, *J* = 4.3 Hz, 1H), 7.16 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.11 (d, *J* = 9.1 Hz, 1H), 1.21 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.3, 158.3, 147.8, 146.5, 138.7, 134.8, 133.7, 131.5, 130.3, 129.7, 129.5, 129.2, 127.8, 127.7, 126.7, 126.7, 125.9, 120.9, 118.7, 118.5, 116.6, 77.5, 76.8, 36.3, 31.6, 31.6.

HRMS (ESI) calcd for $C_{26}H_{24}NO_3^+$ $[M+H]^+$: 398.1751, found: 398.1751.



2-oxo-2*H*-chromen-7-yl (*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3t). 3t was isolated as a yellow oil (70 mg, 85% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

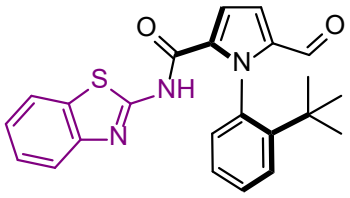
$[\alpha]_D^{25}$ = -20.862 (c = 0.890 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.547 min (minor), 16.610 min (major), 80% ee.

^{1}H NMR (400 MHz, Chloroform-d) δ 9.42 (s, 1H), 7.64 (t, J = 9.2 Hz, 2H), 7.49 – 7.41 (m, 2H), 7.34 (d, J = 4.3 Hz, 1H), 7.30 – 7.24 (m, 1H), 7.16 (d, J = 4.4 Hz, 1H), 7.08 – 6.97 (m, 3H), 6.37 (d, J = 9.6 Hz, 1H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-d) δ 181.2, 160.2, 157.4, 154.6, 152.5, 146.5, 142.8, 139.0,

134.6, 130.1, 129.9, 129.2, 128.8, 128.5, 126.7, 119.1, 118.2, 116.7, 116.5, 116.2, 110.2, 36.2, 31.5.

HRMS (ESI) calcd for $C_{25}H_{22}NO_5^+$ $[M+H]^+$: 416.1492, found: 416.1495.



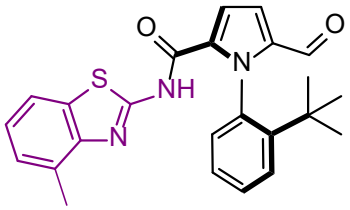
(*R*)-*N*-(benzo[*d*]thiazol-2-yl)-1-(2-(tert-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxamide (3u). 3u was isolated as a yellow oil (40 mg, 50% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -15.299 (c = 0.268 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.484 min (minor), 22.487 min (major), 92% ee.

1H NMR (400 MHz, Chloroform-d) δ 9.38 (s, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.0 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.10 (dd, J = 7.8, 1.5 Hz, 1H), 7.06 (d, J = 4.4 Hz, 1H), 7.01 (d, J = 4.4 Hz, 1H), 1.19 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.2, 156.0, 157.9, 147.6, 146.6, 138.4, 134.5, 131.8, 131.3, 130.3, 130.0, 129.5, 126.9, 126.2, 124.1, 121.4, 120.7, 116.9, 115.6, 36.3, 31.5.

HRMS (ESI) calcd for $C_{23}H_{22}N_3O_5S^+$ $[M+H]^+$: 404.1427, found: 404.1426.



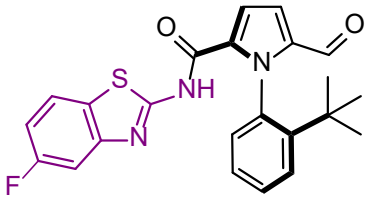
(*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-*N*-(4-methylbenzo[*d*]thiazol-2-yl)-1*H*-pyrrole-2-carboxamide (3v). 3v was isolated as a yellow solid (50 mg, 60% yield). Column chromatography eluent: petroleum ether : EtOAc = 10 : 1.

MP: 202 – 204 ºC. $[\alpha]_D^{25}$ = -107.692 (c = 0..026 in $CHCl_3$). HPLC DAICEL CHIRALCEL IF, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.528 min (minor), 7.256 min (major), 88% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.39 (s, 1H), 7.69 (d, *J* = 6.8 Hz, 1H), 7.60 – 7.49 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.13 – 7.05 (m, 3H), 2.58 (s, 3H), 1.15 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.1, 157.3, 156.8, 147.2, 146.6, 138.4, 134.3, 131.8, 131.5, 130.5, 130.2, 130.0, 129.6, 127.0, 126.9, 124.0, 118.8, 117.0, 114.9, 36.3, 31.4, 18.1.

HRMS (ESI) calcd for $C_{24}H_{24}N_3O_2S^+$ $[M+H]^+$: 418.1584, found: 417.1581.



(*R*)-1-(2-(*tert*-butyl)phenyl)-*N*-(5-fluorobenzo[*d*]thiazol-2-yl)-5-formyl-1*H*-pyrrole-2-carboxamide (3w) 3w was isolated as a yellow solid (54 mg, 63% yield). Column chromatography eluent: petroleum ether : EtOAc = 10 : 1.

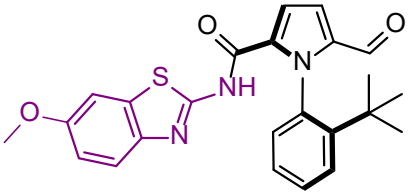
MP: 154 –156 °C. $[\alpha]_D^{25}$ = -136.364 (c = 0.022 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.139 min (minor), 13.365 min (major), 98% ee.

^{1}H NMR (400 MHz, Chloroform-d) δ 9.40 (s, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.66 (dd, J = 8.7, 5.1 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.37 – 7.25 (m, 3H), 7.14 (d, J = 4.3 Hz, 1H), 7.10 (d, J = 7.1 Hz, 2H), 7.07 – 7.00 (m, 1H), 1.17 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-d) δ 181.1,162.1 (d, $^1J_{C\text{-}F}$ = 242.9 Hz), 157.4, 146.9, 138.6, 130.3, 129.8, 127.5, 127.2, 122.2 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 117.2, 115.7, 112.8, 107.6, 107.3,77.5, 76.8, 36.4, 31.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.61.

HRMS (ESI) calcd for $C_{23}H_{21}FN_3O_2S^+$ $[M+H]^+$: 422.1333, found: 422.1332.



(*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-*N*-(6-methoxybenzo[*d*]thiazol-2-yl)-1*H*-pyrrole-2-carboxamide (3x). 3x was isolated as a yellow soild (52 mg, 60% yield). Column

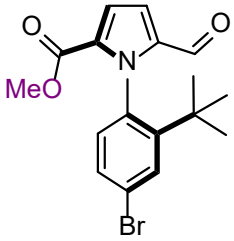
chromatography eluent: petroleum ether : EtOAc = 10 : 1.

MP: 215 – 217 °C. $[\alpha]_D^{25}$= -85.556 (c = 0.030 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 11.039 min (minor), 19.792 min (major), 98% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 2.6 Hz, 1H), 7.13 – 7.05 (m, 3H), 6.97 (d, *J* = 8.9 Hz, 1H), 3.84 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.1, 146.9, 133.4, 130.4, 130.2, 129.8, 127.1, 121.5, 117.2, 115.5, 115.3, 104.4, 77.5, 76.8, 56.0, 36.4, 31.6.

HRMS (ESI) calcd for $C_{24}H_{24}N_3O_3S^+$ $[M+H]^+$: 434.1534, found: 434.1529.



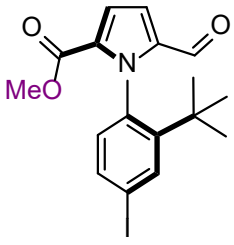
methyl (*R*)-1-(4-bromo-2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3aa). **3aa** was isolated as a yellow oil (60 mg, 82% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -0.515 (c = 0.388 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.365 min (minor), 17.016 min (major), >99% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.41 (s, 1H), 7.73 (d, *J* = 2.3 Hz, 1H), 7.37 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.07 (s, 2H), 6.83 (d, *J* = 8.3 Hz, 1H), 3.72 (s, 3H), 1.10 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.6, 160.2, 148.6, 137.8, 134.4, 132.4, 131.5, 130.6, 129.7, 123.6, 117.9, 117.5, 51.9, 36.4, 31.2.

HRMS (ESI) calcd for $C_{17}H_{19}BrNO_3^+$ $[M+H]^+$: 364.0543, found: 364.0548.



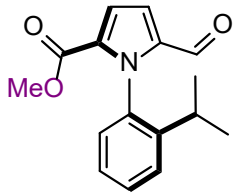
methyl (*R*)-1-(2-(*tert*-butyl)-4-iodophenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3ab). 3ab was isolated as a yellow oil (70 mg, 86% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = -0.962 (c = 0.520 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 12.644 min (major), 13.267 min (minor), >99% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.40 (s, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.56 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.07 (s, 2H), 6.68 (d, *J* = 8.3 Hz, 1H), 3.72 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.8, 160.4, 148.8, 138.6, 137.9, 135.8, 135.3, 131.7, 130.62, 117.9, 117.6, 95.8, 77.5, 76.8, 52.0, 36.3, 31.3.

HRMS (ESI) calcd for $C_{17}H_{19}INO_3^+$ $[M+H]^+$: 412.0404, found: 412.0410.



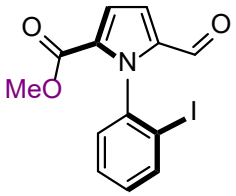
methyl (*R*)-5-formyl-1-(2-isopropylphenyl)-1*H*-pyrrole-2-carboxylate (3ac). 3ac was isolated as a yellow oil (34 mg, 62% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = 1.154 (c = 0.340 in $CHCl_3$).HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 13.055 min (major), 17.016 min (minor), 66% ee.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 – 7.07 (m, 2H), 3.70 (s, 3H), 2.42 – 2.27 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 180.7, 160.0, 146.2, 137.2, 134.9, 129.9, 129.4, 127.78, 126.5, 126.2, 117.3, 116.4, 51.8, 28.0, 23.9, 23.5.

HRMS (ESI) calcd for $C_{16}H_{18}NO_3^+$ $[M+H]^+$: 272.1281, found: 272.1285.



methyl (*R*)-5-formyl-1-(2-iodophenyl)-1*H*-pyrrole-2-carboxylate (3ad). 3ad was isolated as a yellow oil (26 mg, 51% yield). Column chromatography eluent: petroleum ether : EtOAc = 50 : 1.

$[\alpha]_D^{25}$ = 0.897(c = 0.260 in $CHCl_3$).HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 19.555 min (minor), 21.443 min (major), 36% ee.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.42 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.22 (td, *J* = 7.7, 1.7 Hz, 1H), 7.11 (s, 2H), 3.74 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.1, 159.9, 140.8, 139.3, 135.8, 130.6, 128.9, 128.8, 128.7, 118.3, 117.6, 98.0, 52.0.

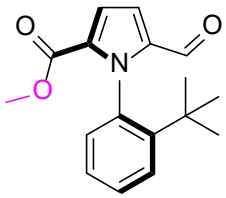
HRMS (ESI) calcd for $C_{13}H_{11}INO_3^+$ $[M+H]^+$: 355.9778, found: 355.9773.

4. Thermal racemization study of C-N axially chiral N-aryl pyrroles 3a

The enantiomerization barrier, corresponding to the barrier to rotation for the following atropisomers, was obtained by kinetic of racemization of an enantiomer. The slope of the first order kinetic line gives the racemization constant ($k_{racemization}$ =2 × $k_{enantiomerization}$). Eyring equation gives the enantiomerization barrier ($\Delta G^{\ddagger}_{enantiomerization}$) from enantiomerization constant ($k_{enantiomerization}$), R = Gas constant = 8.31451 $J{\cdot}K^{-1}.mol^{-1}$, h = Planck constant = 6.62608 × 10^{-34} J.s and k_B = Boltzmann constant = 1.38066 × 10^{-23} $J{\cdot}K^{-1}$.

$\Delta G^{\ddagger}_{enantiomerization} = RT_1\ln(k_BT_1/h\ k_{enantiomerization})$

The half-life time ($t_{1/2}$) given below, is at the temperature used for the kinetic. Racemization of 3a in toluene at 100 °C (oil bath temperature).



3a

Table S1. The detailed racemization results of **3a** at different times.

Time(sec)	M	m	M-m	M+m	(M+m)/ (M-m)	ln((M+m)/ (M-m))
0	97.229	2.771	94.458	100	1.0587	0.0570
10800	93.869	6.131	87.738	100	1.1398	0.1308
14400	90.552	9.448	81.104	100	1.2330	0.2094
18000	86.596	13.404	73.192	100	1.366	0.3121
21600	84.997	15.003	69.994	100	1.4287	0.3568

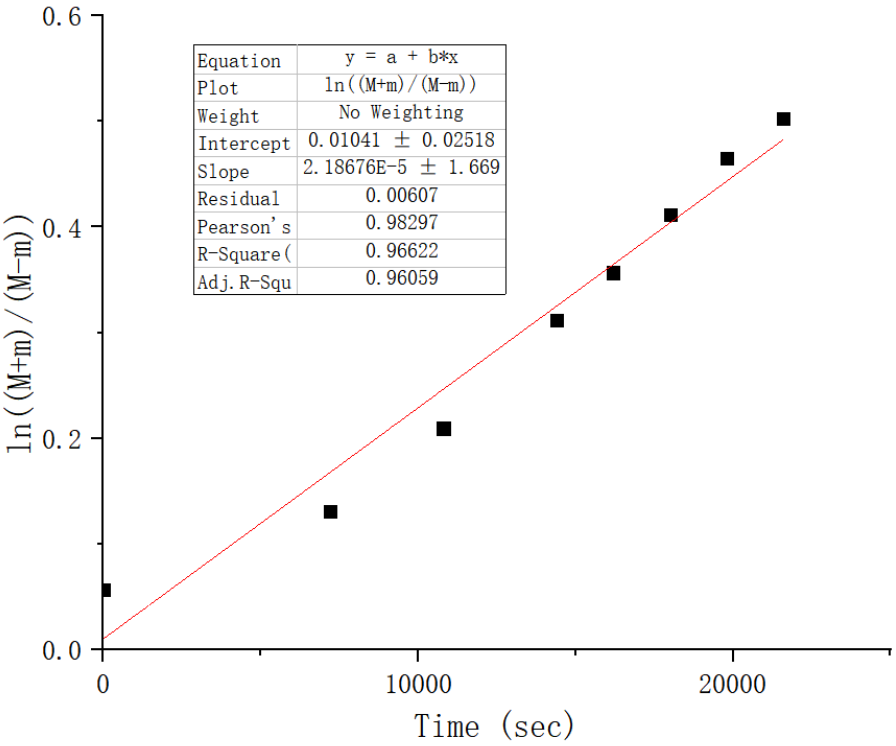


Figure S1. Thermal racemization of 3a.

$$ln\left(\frac{ee_0}{ee_t}\right) = 2k_{ent}t + C$$

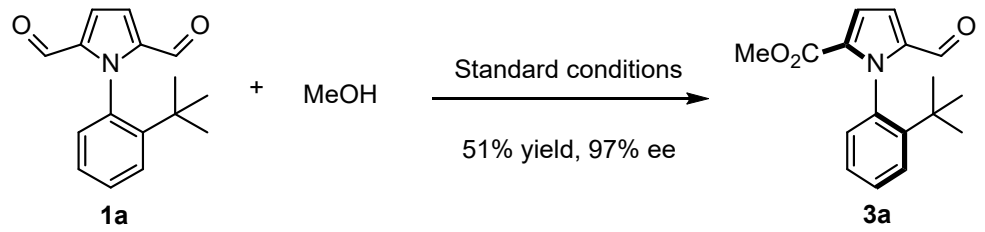
$$k_{ent} = {}^{1}/_{2}\,\text{slope} = 1.09338 \times 10^{-5}$$

$$k_{rac} = 2k_{ent} = 2.18676 \times 10^{-5} s^{-1}$$

$$t_{\frac{1}{2}}^{373.15K}{}_{rac} = \frac{ln2}{k_{rac}} = 3.170 \times 10^{4} s = 8.8\,h$$

$$\Delta G = -RTln\left({}^{k_{ent}h}/_{k_B T}\right) = 127.52\,\text{kJ}/mol = 30.48\,kcal/mol$$

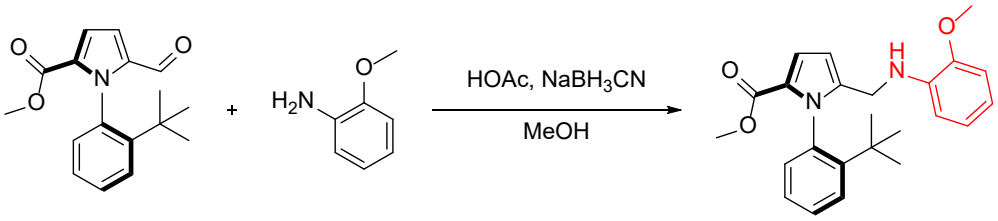
5. A scale-up synthesis of product 3a



1a **3a**

To an oven-dried 50 mL flask was charged with substrate **1a** (255 mg, 1.0 mmol, 1.0 equiv.), substrate **2a** (38.4 mg, 1.2 mmol, 1.2 equiv.), Cs_2CO_3 (130 mg, 0.4 mmol, 0.4 equiv.), cat. **E** (48.0 mg, 0.1 mmol, 0.1 equiv.), **DQ** (449 mg, 1.1 mmol, 1.1 equiv.) and 4 ÅMS (250 mg). Then anhydrous DCE (20 mL) was added to the flask. The resulting mixture was stirred at 0 ℃ under N_2 for 12 h. After that, the mixture was filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 20/1 as eluent to afford product **3a** (145 mg, 51% yield, 97% ee).

6. Further chemical transformation



3a, □99% ee **4a**, 78%, 96% ee

To an oven-dried 25 mL round-bottomed flask equipped with a magnetic stir bar, **3a** (40 mg, 0.14 mmol, 1.0 equiv.) and 2-methoxyaniline (17 mg, 0.14 mmol, 1.0 equiv.) were added. To this mixture was added MeOH (10 mL) and HOAc (8 mg, 0.14 mmol, 1.0 equiv.). After

stirring at r.t. under N_2 for 2 h. To this mixture was added $NaBH_3CN$ (13 mg, 0.21 mmol, 1.5 equiv.). After stirring at r.t. under N_2 for 12 h. (monitored by TLC), the reaction was concentrated under reduced pressure, then purifiedby flash column chromatography on silica gel using petroleum ether/ethyl acetate = 10/1 as eluent to afford the **4a** as a yellow oil (43 mg, 78% yield, 96% ee).

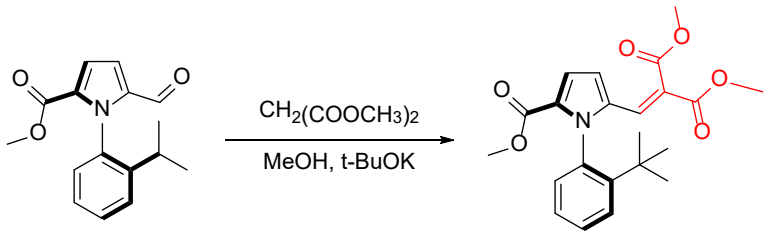
methyl (R)-1-(2-(*tert*-butyl)phenyl)-5-(((2-methoxyphenyl)amino)methyl)-1*H*-pyrrole-2-carboxylate (4a)

$[\alpha]_D^{25}$ = 2.263 (c = 0.0.38 in $CHCl_3$).HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.437 min (minor), 7.584 min (major), 96% ee.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 (d, J = 8.2 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.26 – 7.20 (m, 1H), 7.04 (d, J = 3.9 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.85 – 6.74 (m, 2H), 6.68 (t, J = 7.7 Hz, 1H), 6.50 (d, J = 7.9 Hz, 1H), 6.29 (d, J = 4.0 Hz, 1H), 4.07 (d, J = 15.4 Hz, 1H), 3.92 (d, J = 15.3 Hz, 1H), 3.84 (s, 3H), 3.64 (s, 3H), 1.16 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.91, 146.96, 146.47, 139.66, 137.42, 135.81, 130.31, 129.45, 128.97, 126.48, 125.28, 121.15, 117.54, 117.15, 110.40, 109.56, 108.20, 55.46, 50.98, 40.94, 36.19, 31.52.

HRMS (ESI) calcd for $C_{24}H_{29}N_2O_3^+$ $[M+H]^+$: 393.2173, found: 393.2178.



3a, □99% **4b**, 55%, >99% ee

To an oven-dried 25 mL round-bottomed flask equipped with a magnetic stir bar, **3a** (75 mg, 0.2 mmol, 1.0 equiv.) and dimethyl malonate (40 mg, 0.3 mmol, 1.5 equiv.) were added. To this mixture was added MeOH (10 mL) and *t*-BuOK (34 mg, 0.3 mmol, 1.5 equiv.). After stirring at r.t. under N_2 for 12 h (monitored by TLC), the reaction was concentrated under reduced pressure, then purified by flash column chromatography on silica gel using petroleum

ether/ethyl acetate = 20/1 as eluent to afford the **4b** as a yellow oil (44 mg, 55% yield, >99% ee).

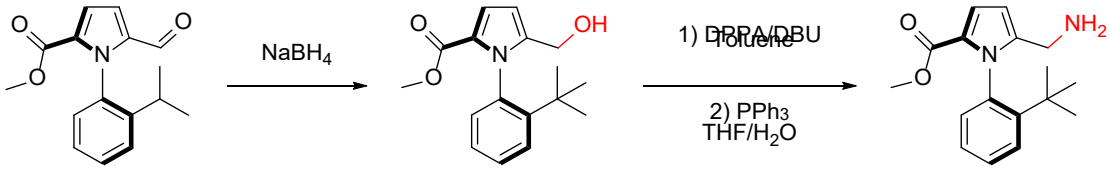
dimethyl (*R*)-2-((1-(2-(*tert*-butyl)phenyl)-5-(methoxycarbonyl)-1*H*-pyrrol-2-yl)methylene)malonate (4b)

$[\alpha]_D^{25}$ = -775.000 (c = 0.004 in $CHCl_3$).HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.485 min (major), 9.850 min (minor), >99% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 4.3 Hz, 1H), 7.02 (s, 1H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 4.4 Hz, 1H), 3.91 (s, 3H), 3.70 (s, 3H), 3.66 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 164.3, 160.4, 147.1, 134.6, 134.2, 130.6, 130.4, 129.7, 129.4, 128.8, 126.7, 122.9, 118.4, 113.1, 77.5, 76.8, 52.9, 52.6, 51.6, 36.2, 31.4.

HRMS (ESI) calcd for $C_{22}H_{26}NO_6^+$ $[M+H]^+$: 400.1755, found: 400.1750.



3a, □99% ee **4c**, 70%, 98% ee

To an oven-dried 25 mL round-bottomed flask equipped with a magnetic stir bar, **3a** (60 mg, 0.2 mmol, 1.0 equiv.) THF (12 ml) and MeOH (4 ml) were added at 0 ℃. To this mixture was added $NaBH_4$ (3.8 mg, 0.1 mmol, 0.5 equiv.) After stirring at r.t. for 2 h (monitored by TLC), the reaction was concentrated under reduced pressure, then purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate = 20/1 as eluent to afford the methyl 1-(2-(*tert*-butyl)phenyl)-5-(hydroxymethyl)-1*H*-pyrrole-2-carboxylate as a yellow oil.

To a solution of methyl 1-(2-(tert-butyl)phenyl)-5-(hydroxymethyl)-1H-pyrrole-2-carboxylate (40 mg, 0.14 mmol, 1.0 equiv.) and DPPA (45 μL, 0.21 mmol, 1.5 equiv.) in toluene (10 mL) at 0º C, was added DBU (38 mg, 0.25 mmol, 1.75 equiv.) via syringe. The mixture was stirred at rt for 2 h. Ethyl acetate (0.2 mL) was added, and the mixture was washed with water, brine, dried over anhydrous Na_2SO_4, filtrated and concentrated in vacuo. The reaction crude

was directly used for the next step without further purification. The reaction crude was dissolved in THF (400 μL), and PPh_3 (66 mg, 0.25 mmol, 1.75 equiv.) was added portionwise. After 5 min, H_2O was added and the mixture was stirred at rt for 12 h. Then, the reaction mixture was concentrated in vacuo. Purification by flash chromatography (1:3 EtOAc/PE) afforded **4c** as a light-yellow oil (28 mg, 70% yield, 98% ee).

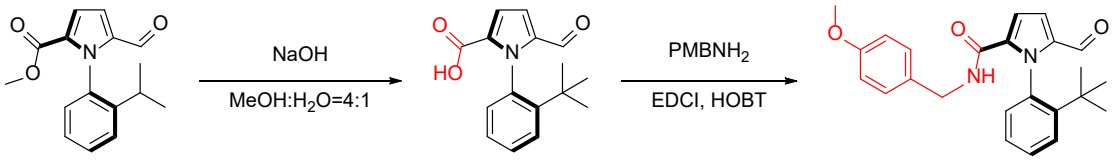
methyl (*R*)-5-(aminomethyl)-1-(2-(*tert*-butyl)phenyl)-1*H*-pyrrole-2-carboxylate (4c)

$[\alpha]_D^{25}$ = -89.394(c = 0.022 in $CHCl_3$).HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.294 min (major), 6.142 min (minor), 98% ee.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.20 – 7.14 (m, 1H), 6.99 (d, *J* = 3.9 Hz, 1H), 6.87 – 6.83 (m, 1H), 6.15 (d, *J* = 4.0 Hz, 1H), 4.49 (d, *J* = 5.7 Hz, 1H), 4.13 (m, 1H), 3.84 (m, 1H), 3.62 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 160.8, 157.0, 146.5, 139.1, 139.0, 135.7, 130.1, 129.5, 129.1, 126.4, 125.4, 117.6, 107.9, 51.0, 37.4, 36.1, 31.4.

HRMS (ESI) calcd for $C_{17}H_{23}N_2O_2^+$ $[M+H]^+$: 287.1754, found: 287.1758.



3a, □99% ee

4d, 76%, 99% ee

To an oven-dried 25 mL round-bottomed flask equipped with a magnetic stir bar, **3a** (60 mg, 0.2 mmol, 1.0 equiv.) MeOH (12 ml) and H_2O (3ml) were added. To this mixture was added NaOH (40 mg, 2.0 mmol, 10 equiv.) After stirring at 60℃ for 2 h (monitored by TLC), To this mixture was added HCl to pH<7 this mixture was diluted with ethyl acetate, washed with brine for 3 times. The organic layer was dried over Na_2SO_4 and concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 5/1 as eluent to afford 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylic acid as a white solid.

To an oven-dried 25 mL round-bottomed flask equipped with a magnetic stir bar, 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylic acid (27 mg, 0.1 mmol, 1.0 equiv.) EDCI (58

mg, 0.3 mmol, 3.0 equiv.) and HOBT (41 mg, 0.3 mmol, 3.0 equiv.) were added. To this mixture was added anhydrous DCM (10 mL). After stirring at r.t. under N_2 for 2 h. To this mixture was added (4-methoxyphenyl)methanamine (21 mg, 0.15 mmol, 1.5 equiv.) and Et_3N (30 mg, 0.3 mmol, 3.0 equiv.) After stirring at r.t. under N_2 for 2 h. (monitored by TLC), the reaction was concentrated under reduced pressure, then purified by flash column chromatography on silica gel using ether/ethyl acetate = 5/1 as eluent to afford the **4d** as a white solid (30 mg, 76% yield, 99% ee).

(*R*)-1-(2-(*tert*-butyl)phenyl)-5-formyl-*N*-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxamide (4d)

MP: 121 – 123 °C. $[\alpha]_D^{25}$ = -129.630(c = 0.018 in $CHCl_3$). HPLC DAICEL CHIRALCEL IG, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 17.891 min (minor), 18.780 min (major). 99% ee.

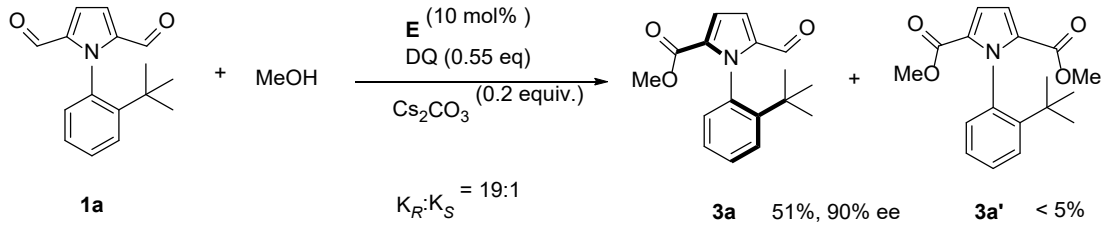
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.24 (t, *J* = 6.8 Hz, 1H), 7.06 – 7.02 (m, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 4.3 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.81 (s, 1H), 4.27 (d, *J* = 5.4 Hz, 2H), 3.78 (s, 3H), 1.08 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.8, 159.5, 159.1, 146.9, 136.8, 134.8, 134.7, 130.3, 130.0, 129.7, 129.5, 129.2, 126.9, 118.0, 114.3, 114.0, 55.3, 43.2, 36.2, 31.3.

HRMS (ESI) calcd for $C_{24}H_{27}N_2O_3^+$ $[M+H]^+$: 391.2016, found: 391.2021.

7. Control experiments

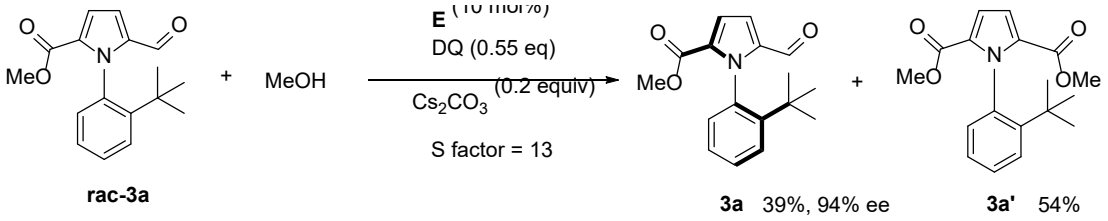
7.1 Desymmetrization



To an oven-dried 25 ml Schlenk tube equipped with a stir bar was charged with catalysts **E** (5 mg, 10 mmol%), oxidant DQ (22 mg, 0.55 equiv),**1a** (30 mg, 0.1 mmol), Cs_2CO_3 (13mg, 0.02 mmol) and MeOH (4 mg, 0.12 mmol). The tube was closed with a septum, evacuated, back-filled with nitrogen three times. To this mixture was added freshly distilled DCE (4 mL).

The reaction mixture was stirred vigorously for 12 h until the reaction was completed as monitored by TLC. The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 20:1-10:1) to furnish the corresponding product **3a** (15 mg, 51%, 90% ee) and **3a'** (<5%).

7.2 Kinetic resolution (KR)



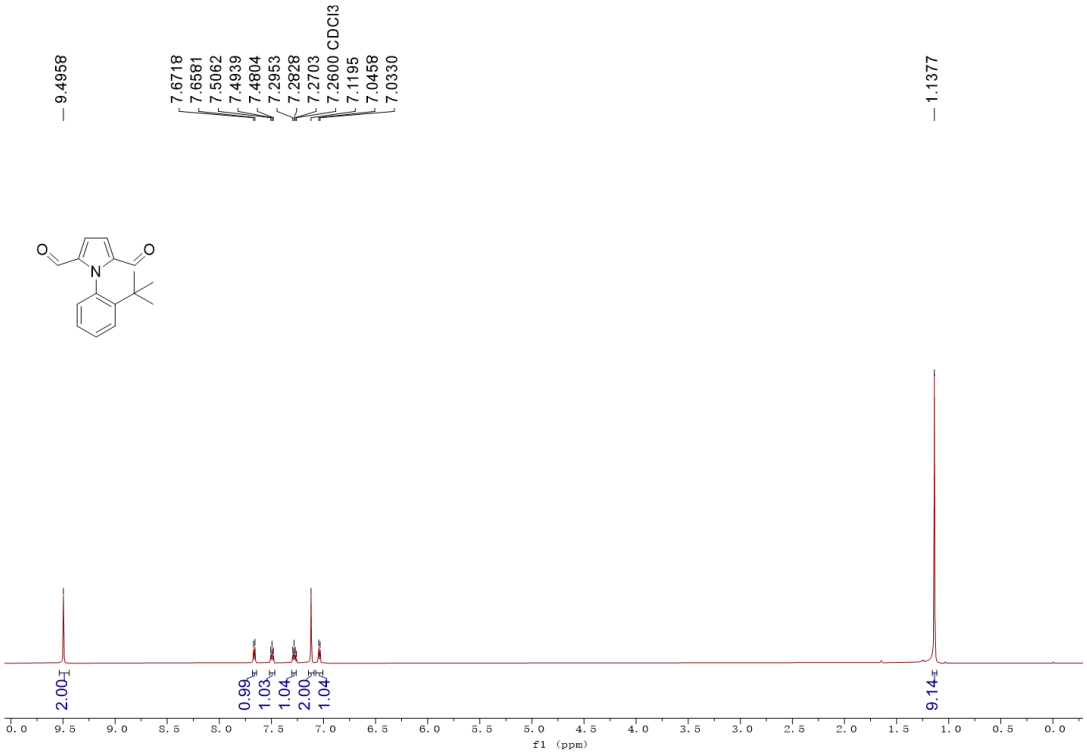
To an oven-dried 25 ml Schlenk tube equipped with a stir bar was charged with catalysts **E** (5 mg, 10 mmol%), oxidant DQ (22 mg, 0.55 equiv),**rac 3a** (30 mg, 0.1 mmol), Cs_2CO_3 (13mg, 0.02 mmol) and MeOH (4 mg, 0.12 mmol). The tube was closed with a septum, evacuated, back-filled with nitrogen three times. To this mixture was added freshly distilled DCE (4 mL). The reaction mixture was stirred vigorously for 12 h until the reaction was completed as monitored by TLC. The reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (PE/EA = 20:1-10:1) to recover the starting material **3a** (11 mg, 39% yield, 94% ee), along with diesterification product **3a'** (17 mg, 54% yield).

8 References

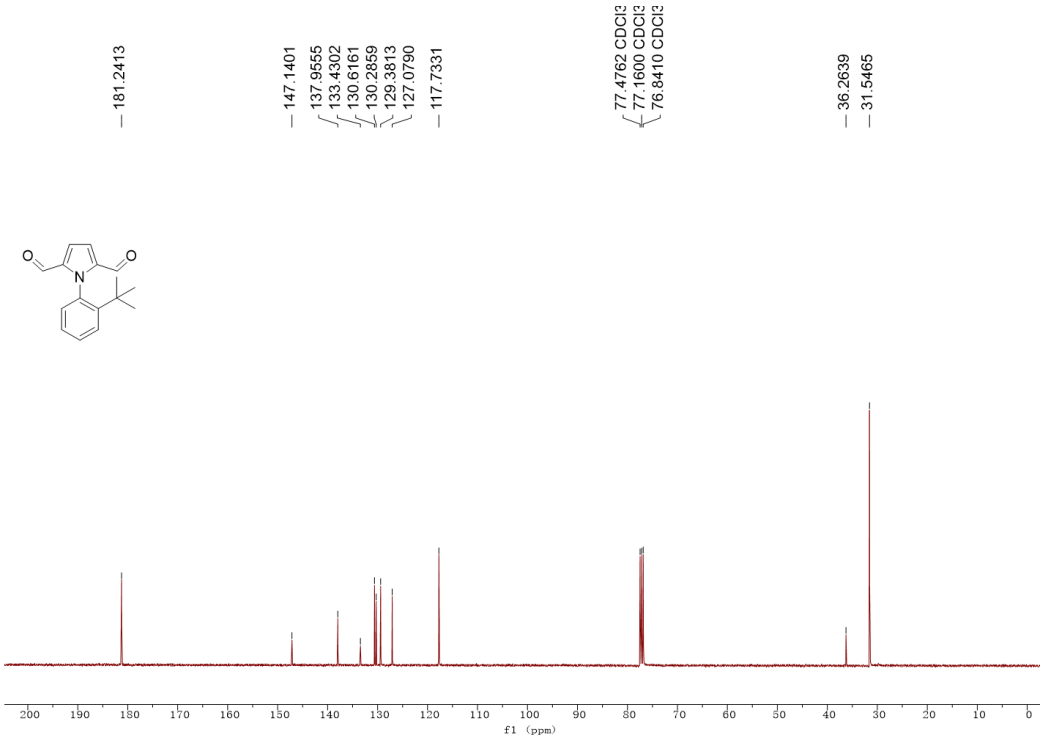
[1] Zhang, L., Xiang, SH., Wang, J. et al. *Nat Commun.***2019***,* 10, 566.

9. Copies of the NMR spectra

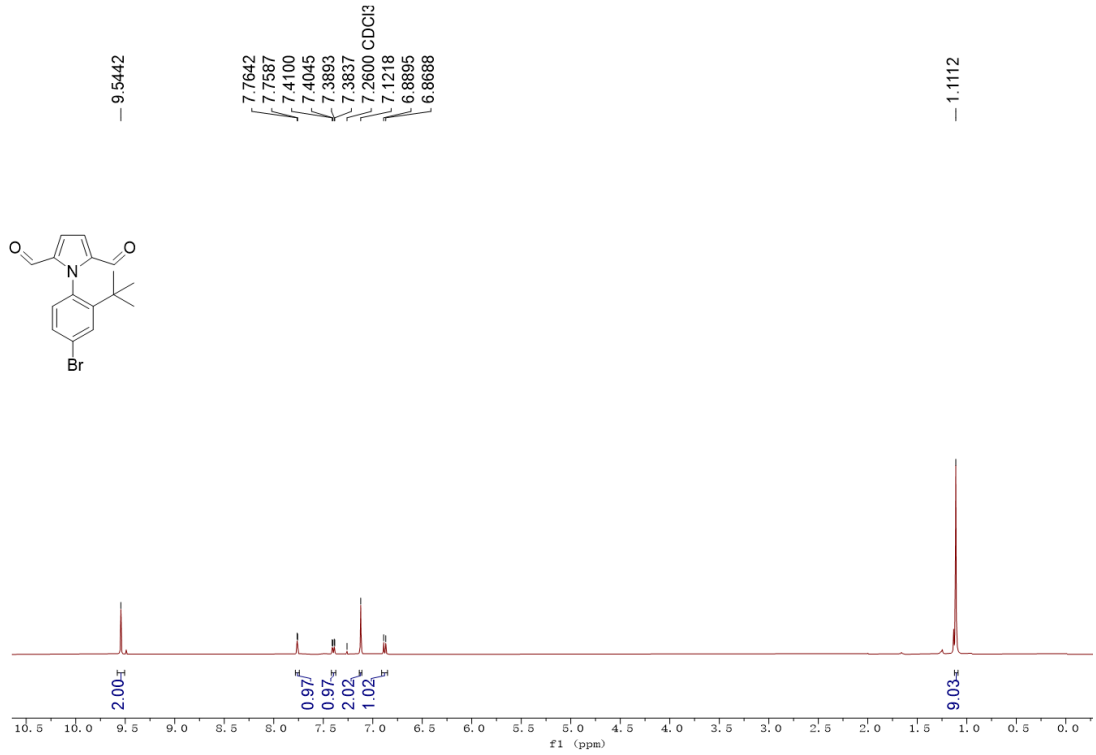
^{1}H NMR (400 MHz, Chloroform-*d*) of **1a**



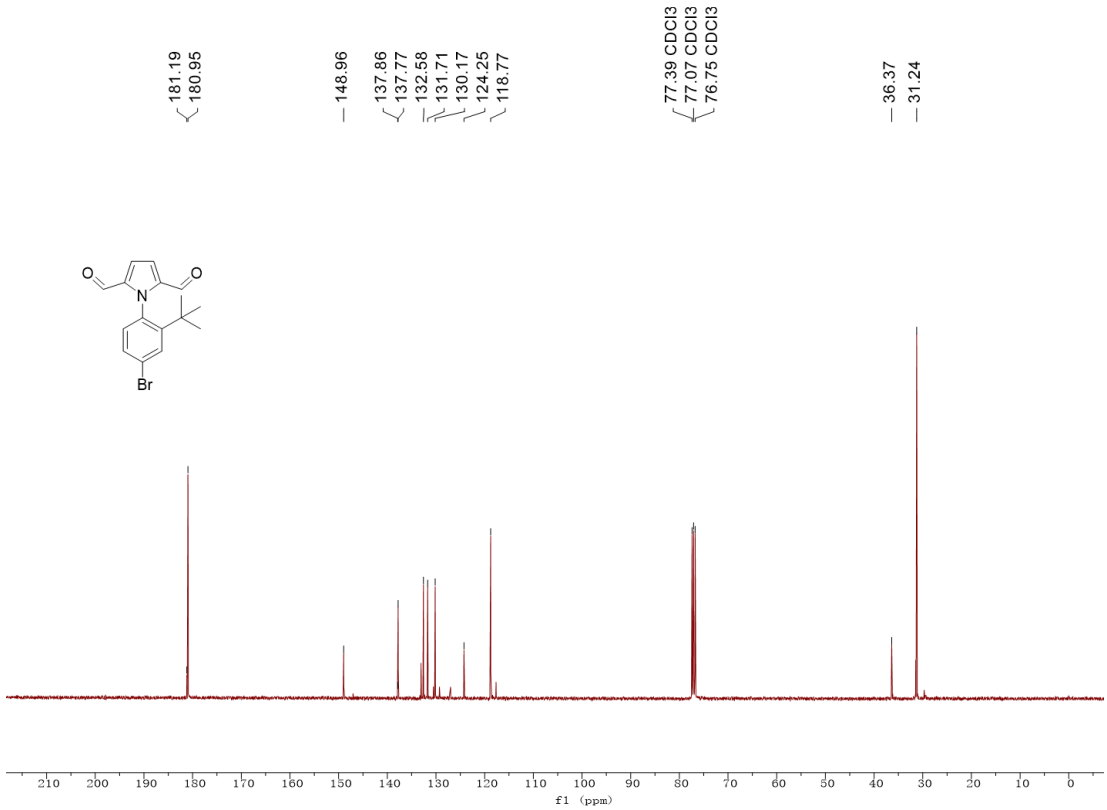
^{13}C NMR (75 MHz, Chloroform-*d*) of **1a**



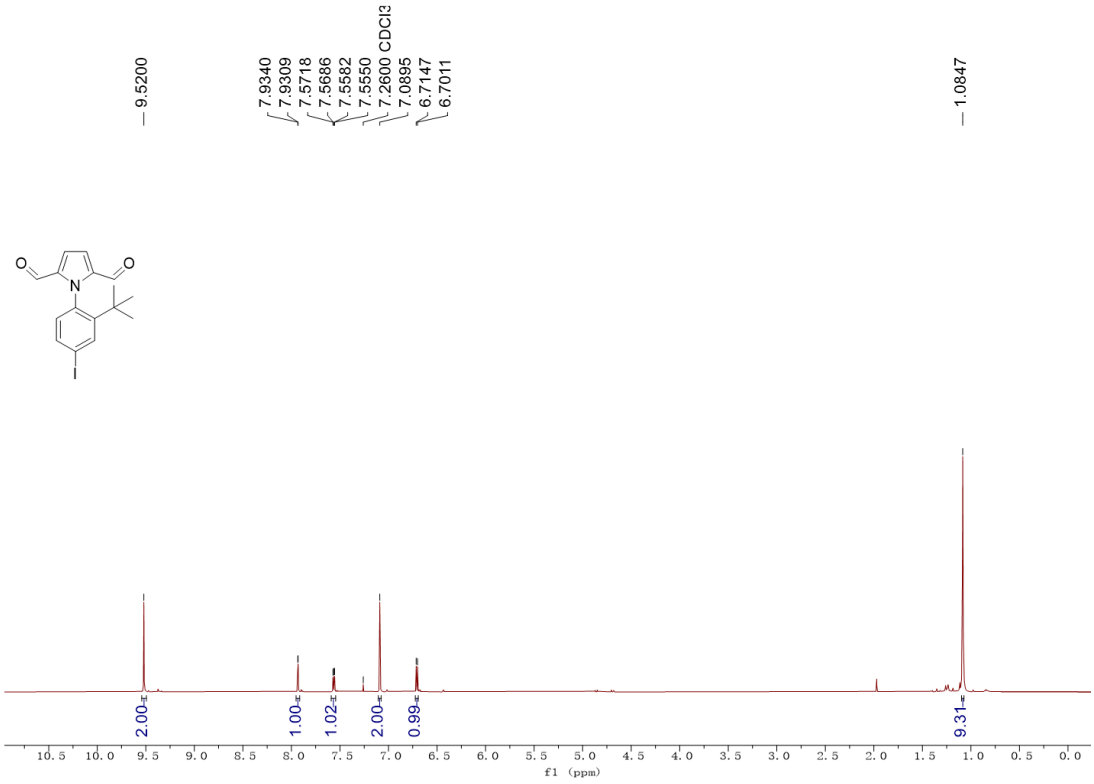
^{1}H NMR (400 MHz, Chloroform-*d*) of **1b**



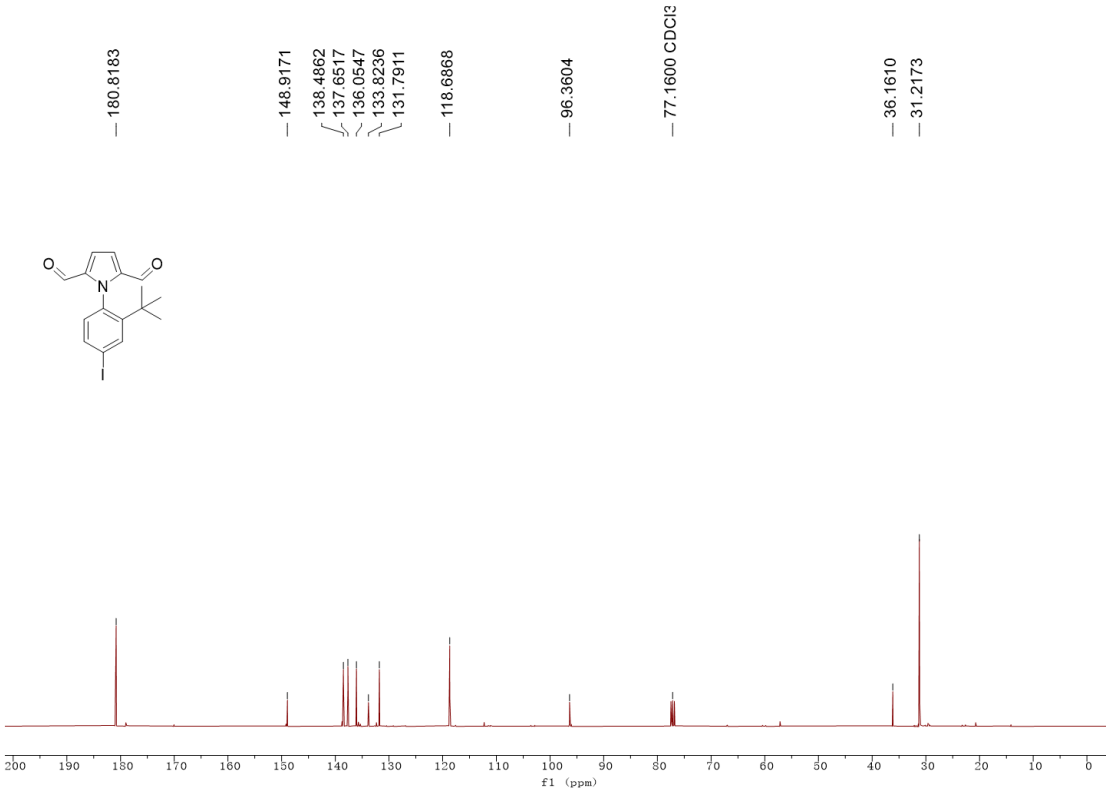
^{13}C NMR (75 MHz, Chloroform-*d*) of **1b**



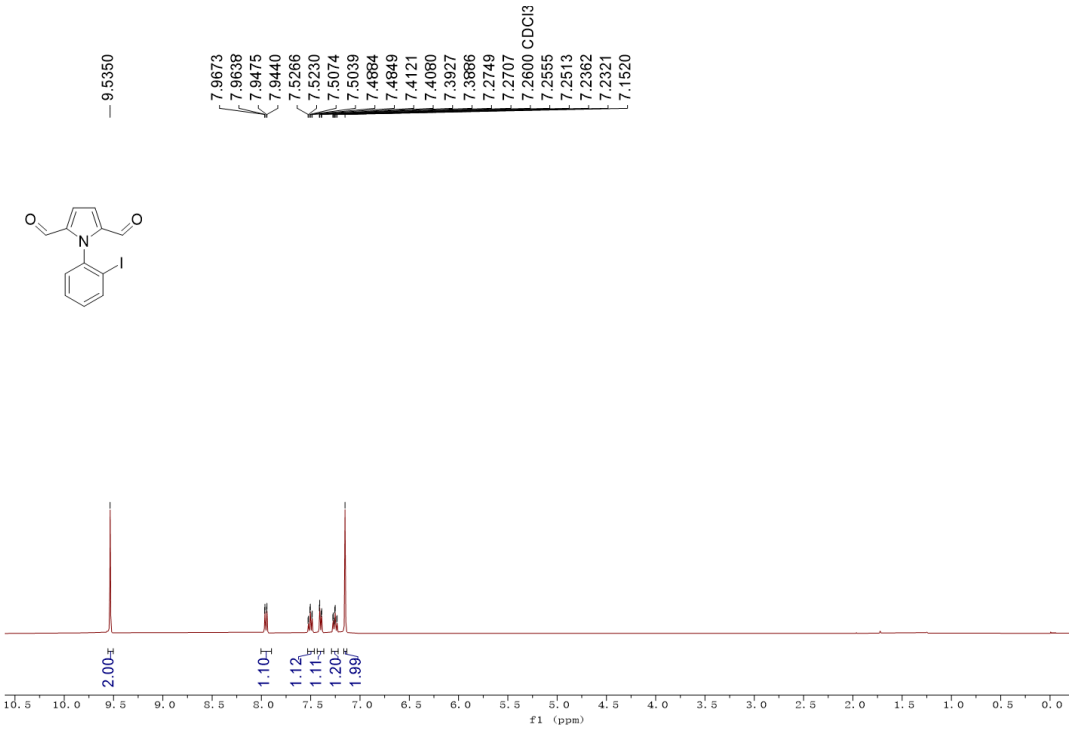
^{1}H NMR (600 MHz, Chloroform-*d*) of **1c**



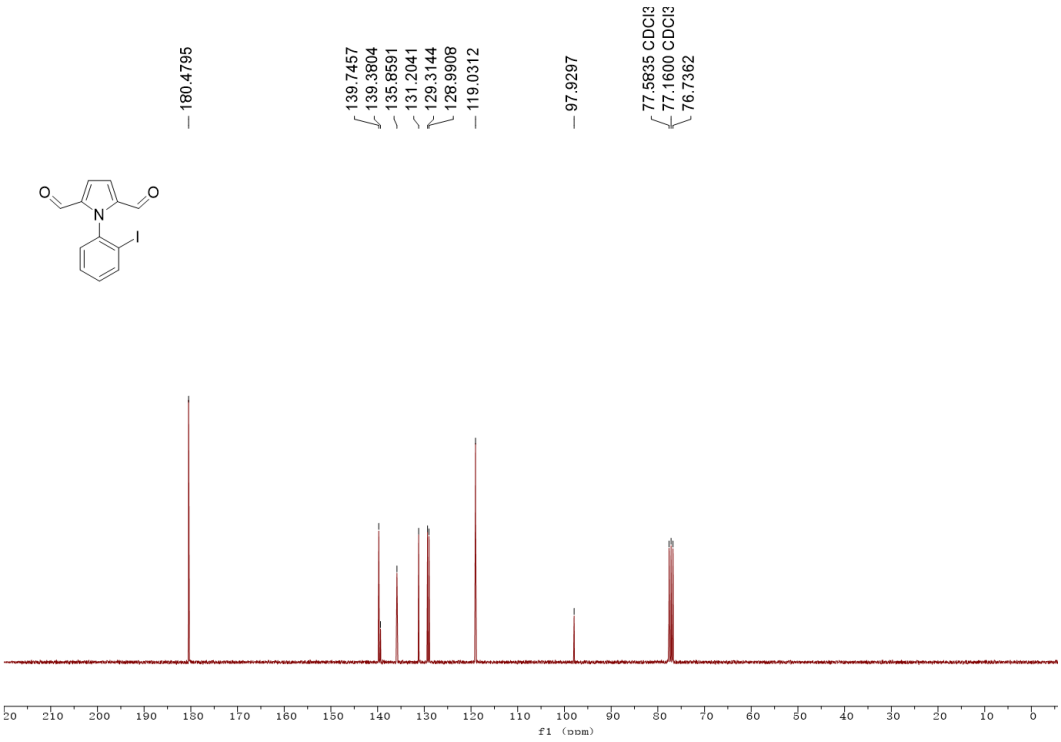
^{13}C NMR (101 MHz, Chloroform-*d*) of **1c**



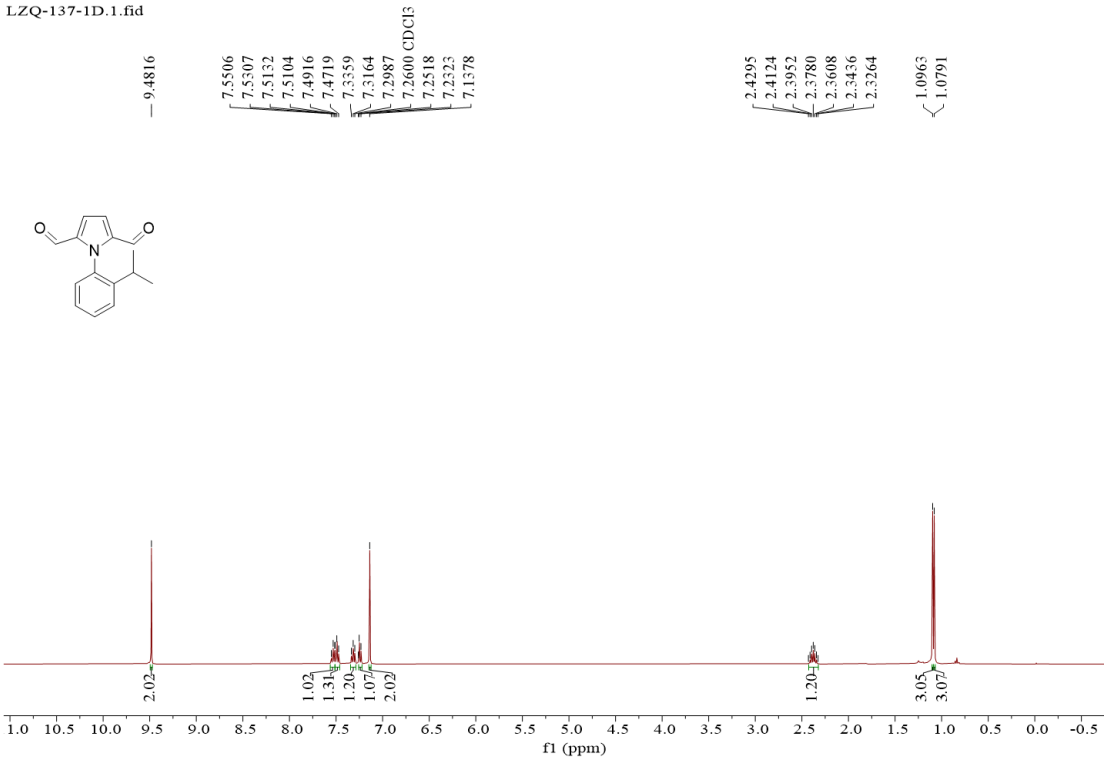
^{1}H NMR (400 MHz, Chloroform-*d*) of **1d**



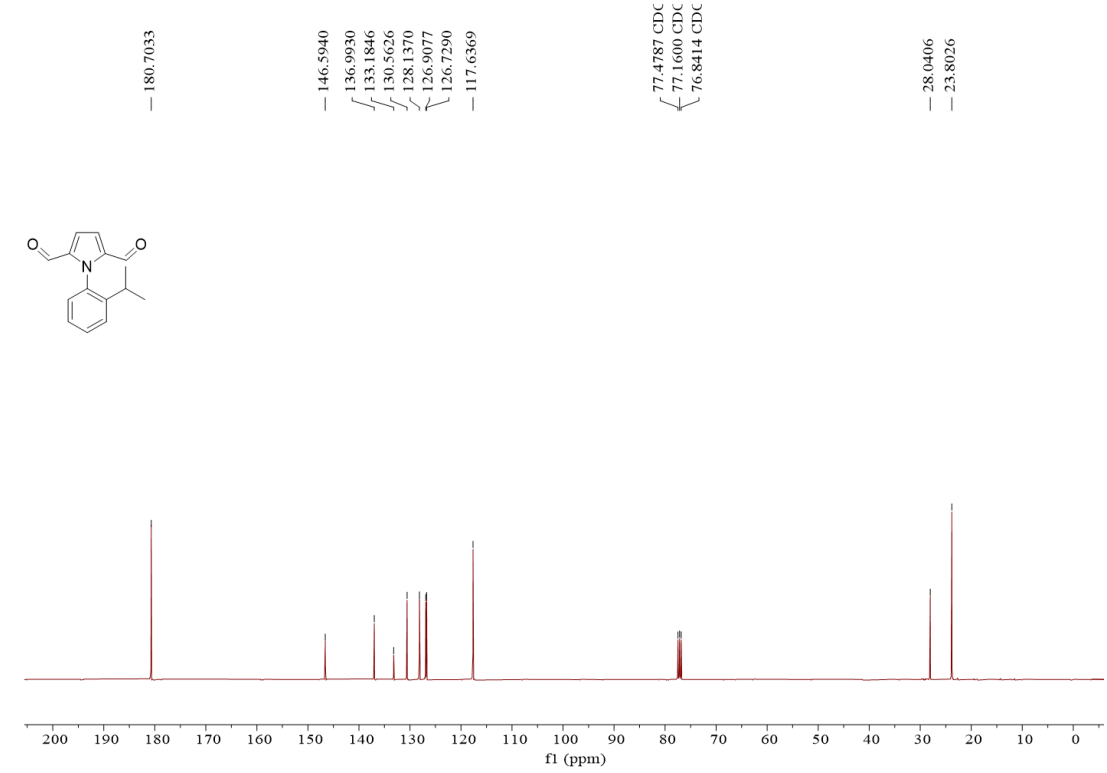
^{13}C NMR (75 MHz, Chloroform-*d*) of **1d**



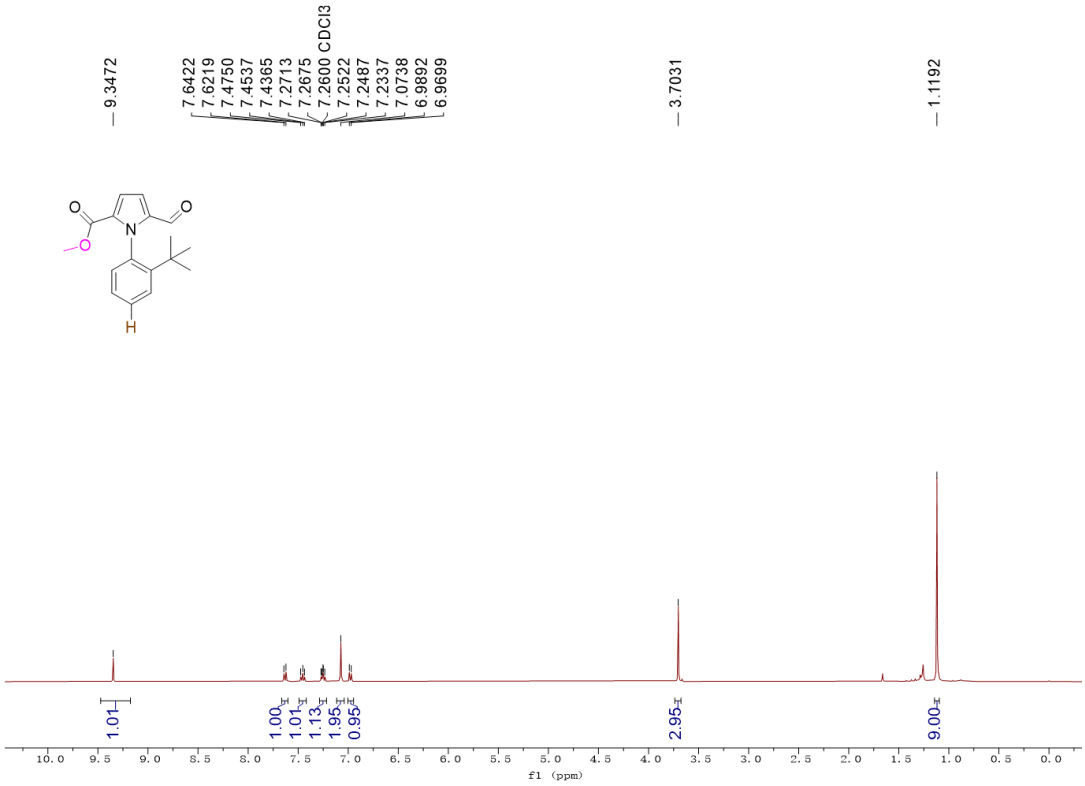
^{1}H NMR (400 MHz, Chloroform-*d*) of **1e**



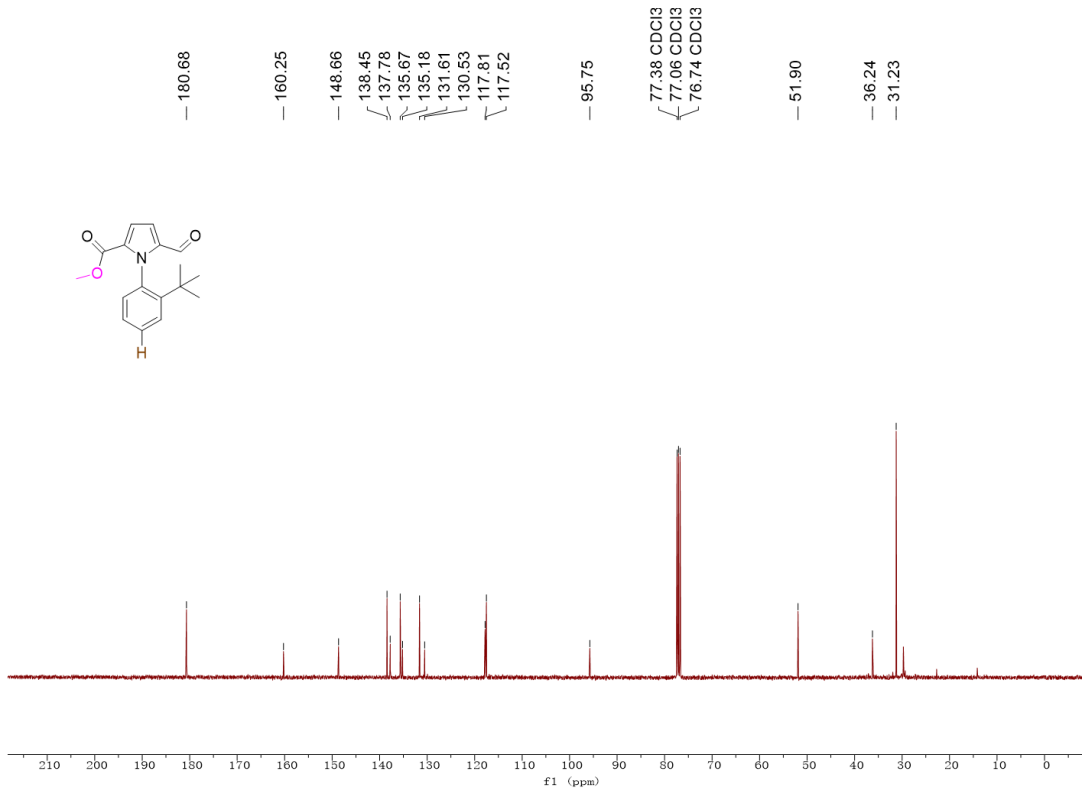
^{13}C NMR (101 MHz, Chloroform-*d*) of **1e**



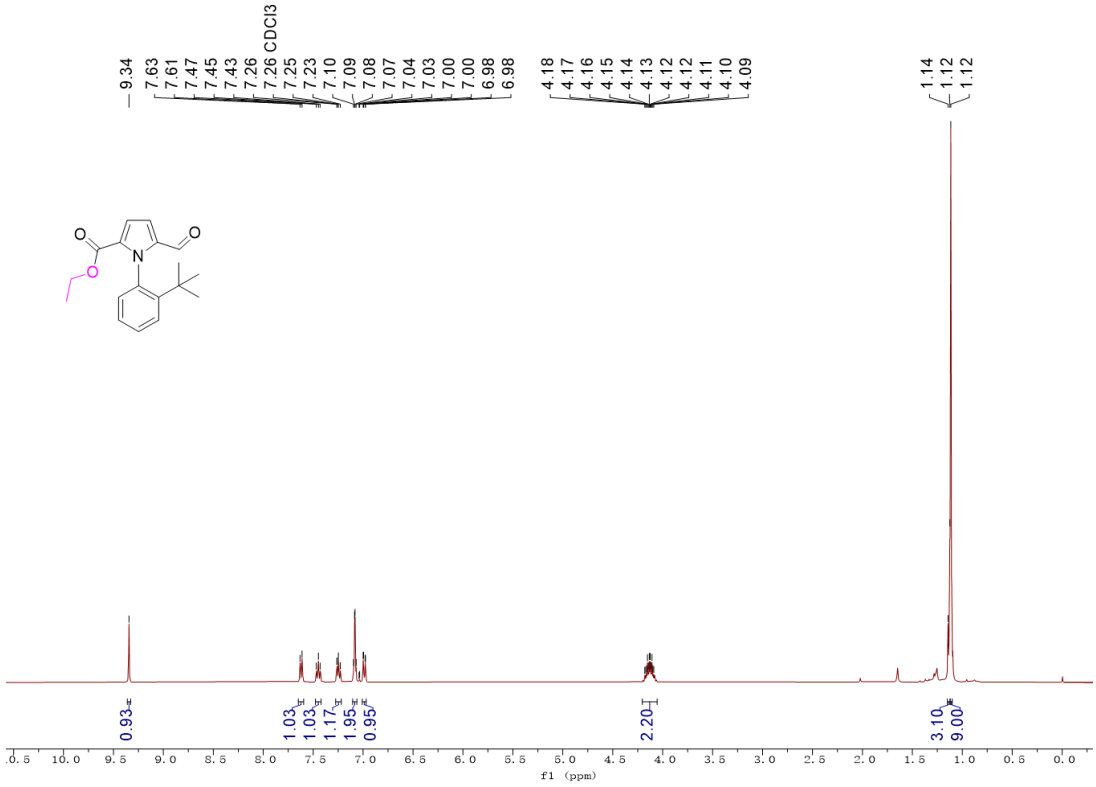
^{1}H NMR (400 MHz, Chloroform-*d*) of **3a**



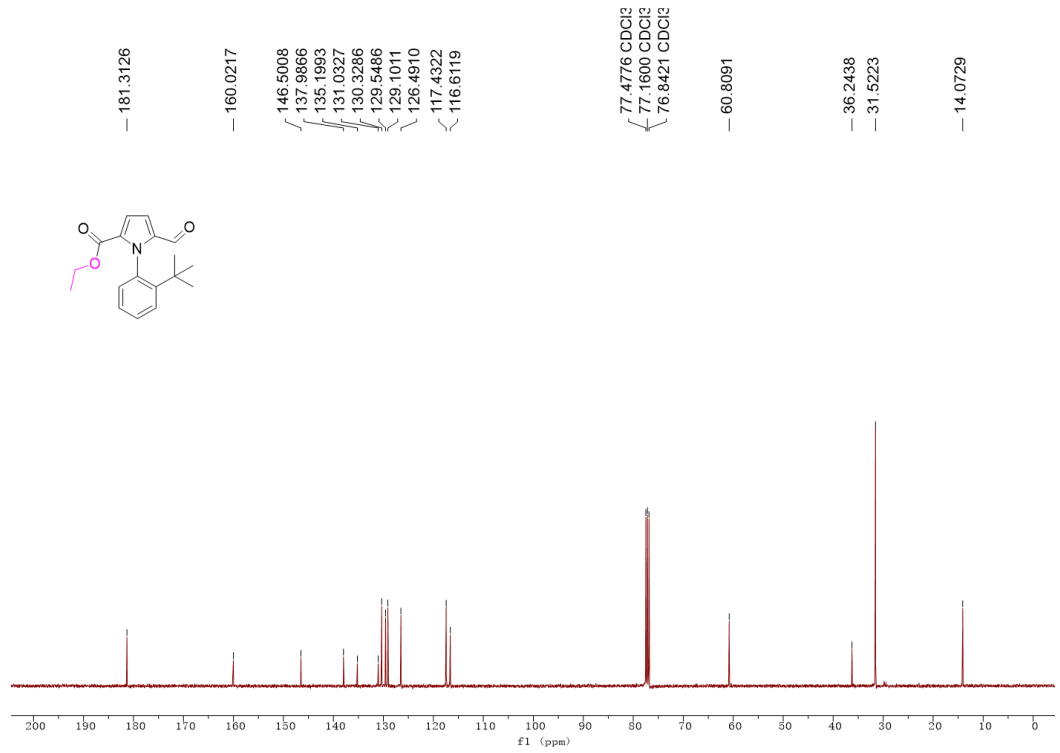
^{13}C NMR (101 MHz, Chloroform-*d*) of **3a**



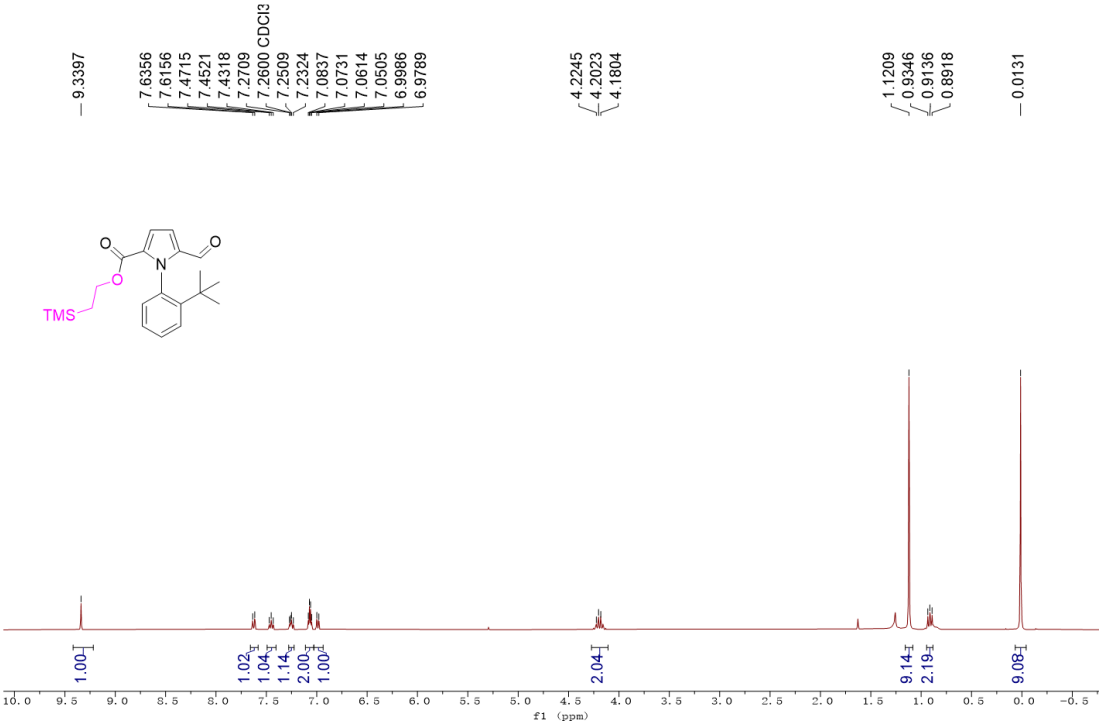
^{1}H NMR (400 MHz, Chloroform-*d*) of **3b**



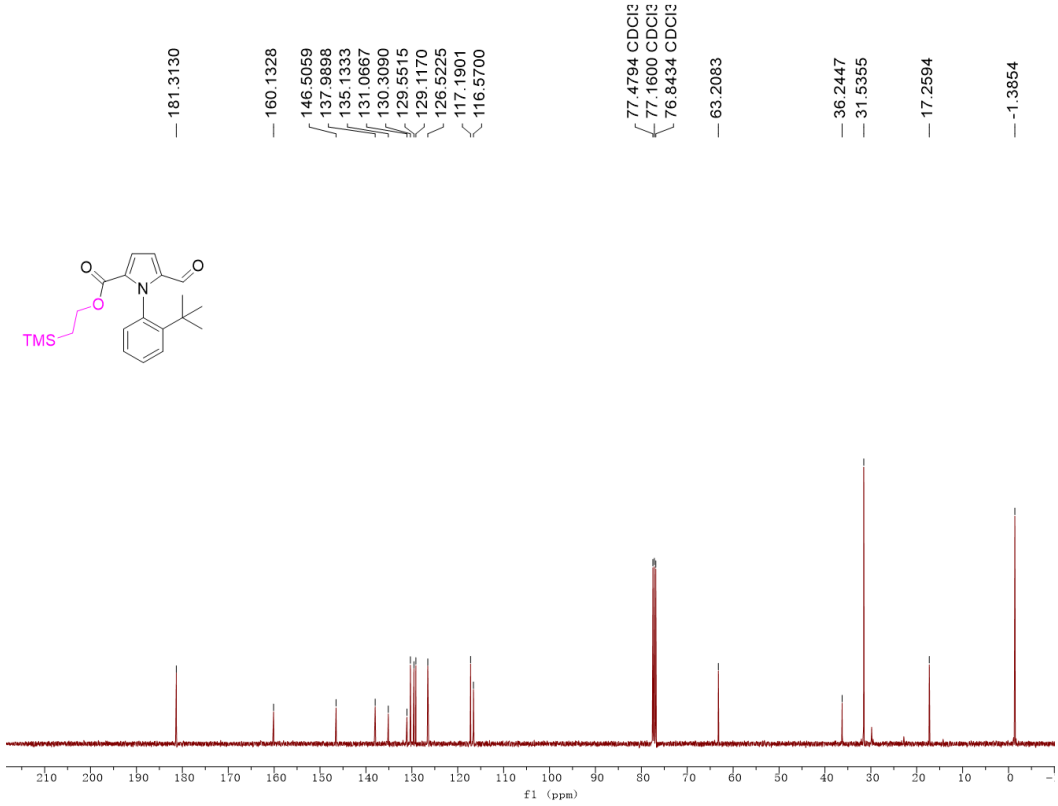
^{13}C NMR (101 MHz, Chloroform-*d*) of **3b**



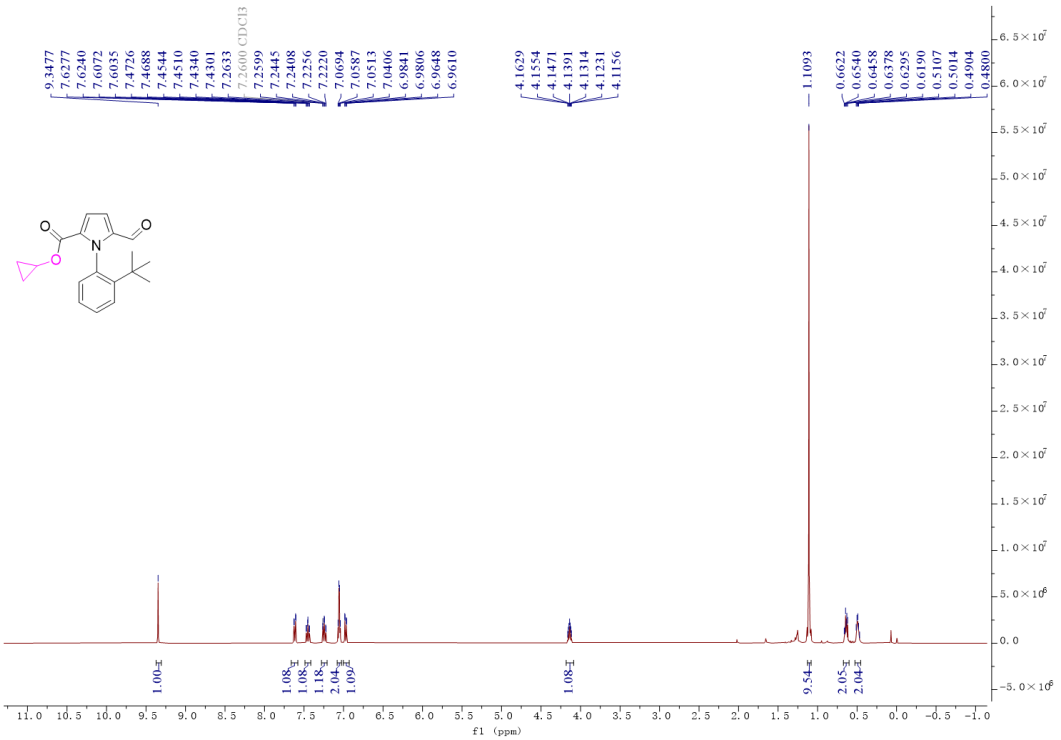
^{1}H NMR (400 MHz, Chloroform-*d*) of **3c**



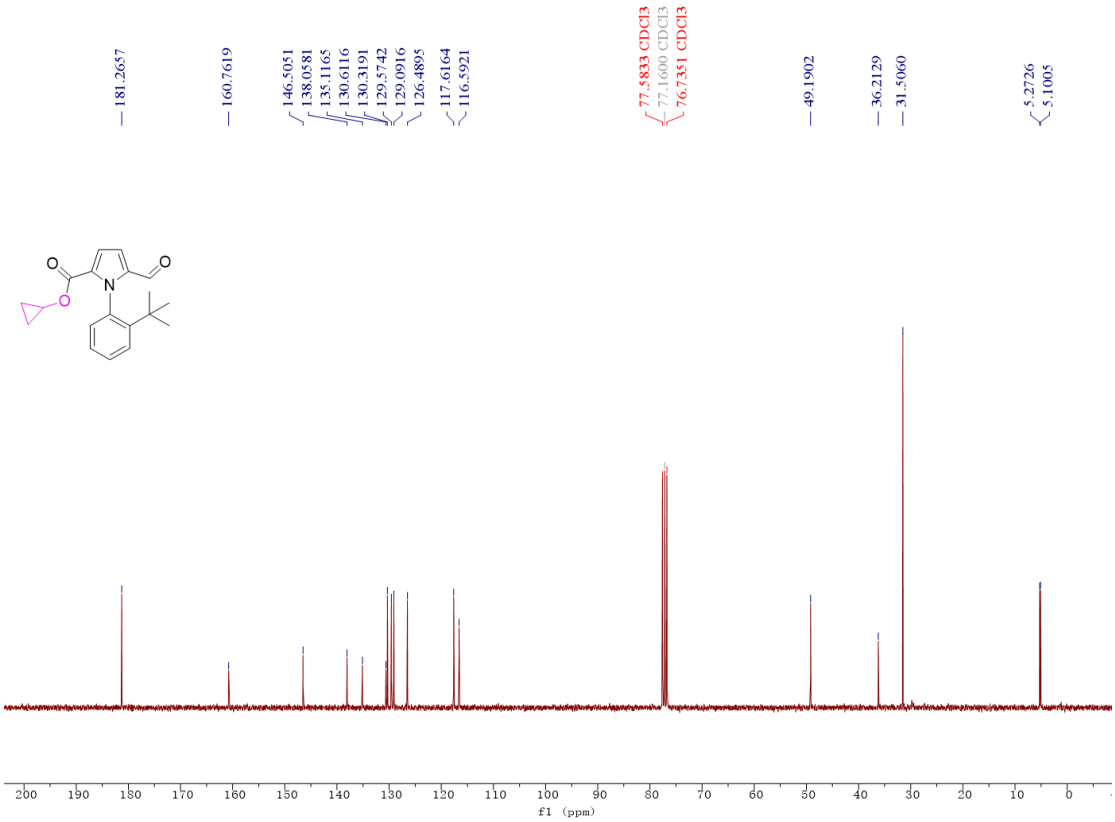
^{13}C NMR (101 MHz, Chloroform-*d*) of **3c**



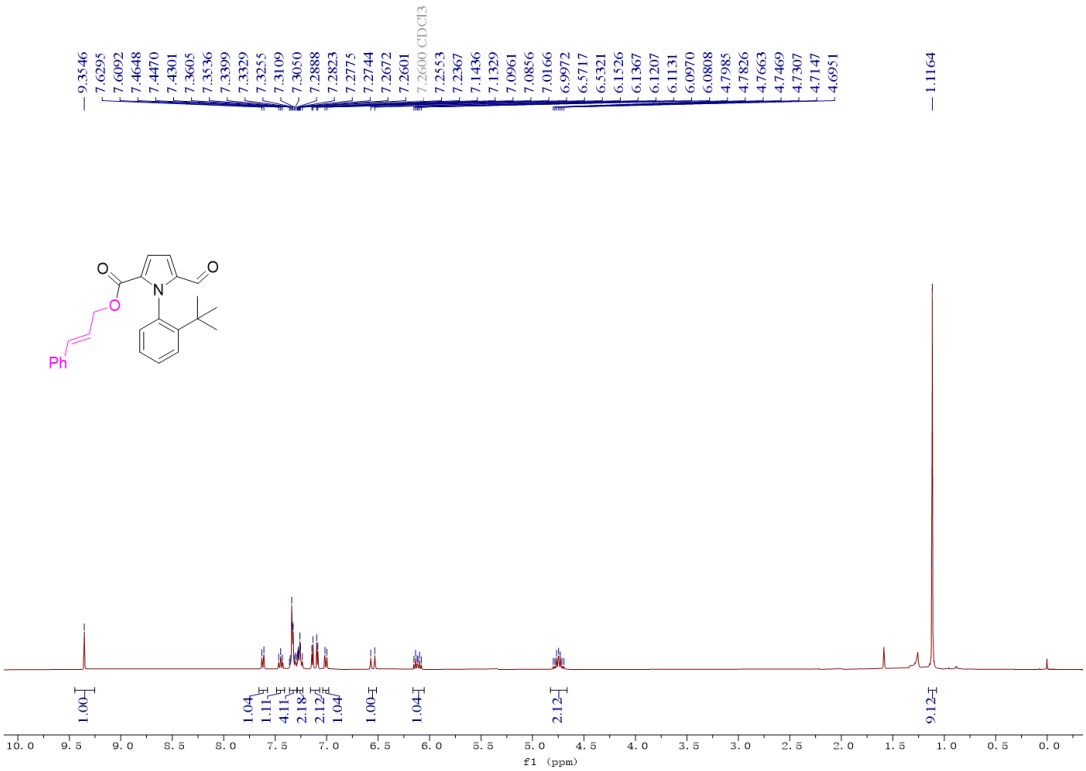
^{1}H NMR (400 MHz, Chloroform-*d*) of **3d**



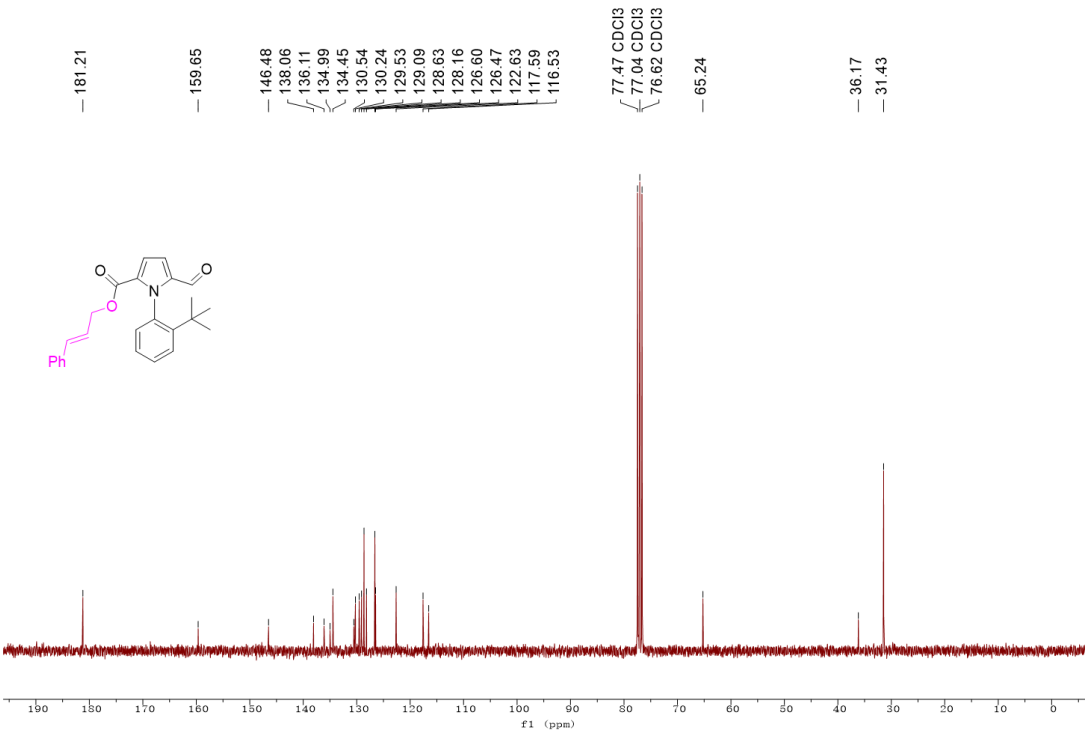
^{13}C NMR (75 MHz, Chloroform-*d*) of **3d**



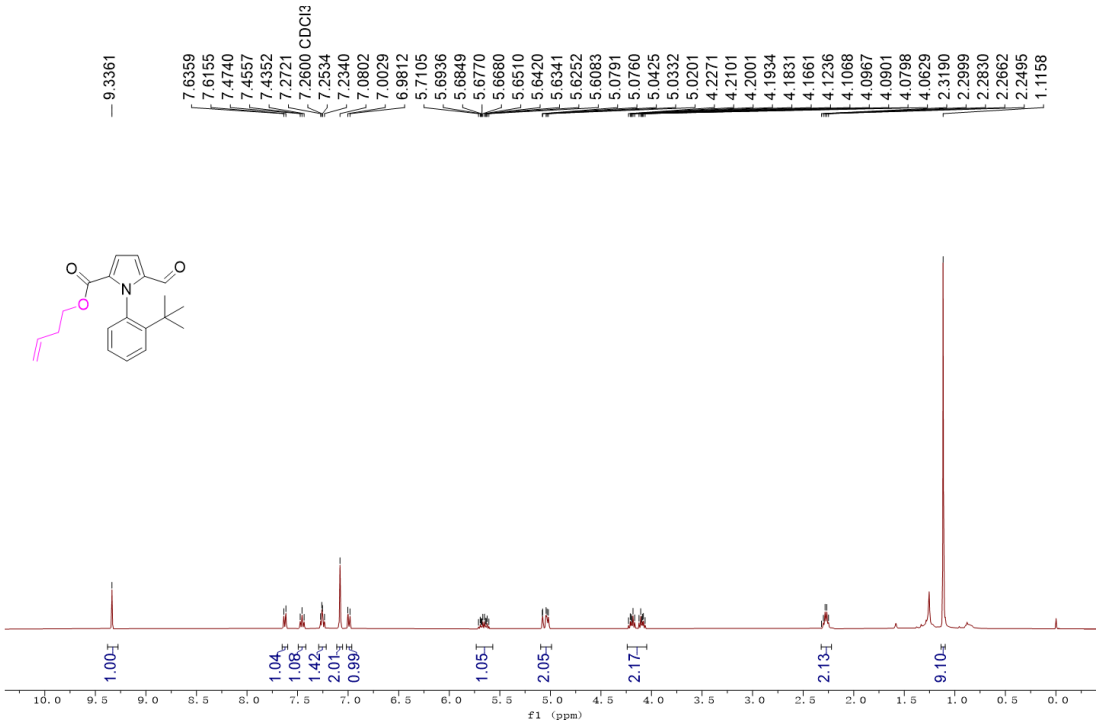
^{1}H NMR (400 MHz, Chloroform-*d*) of **3e**



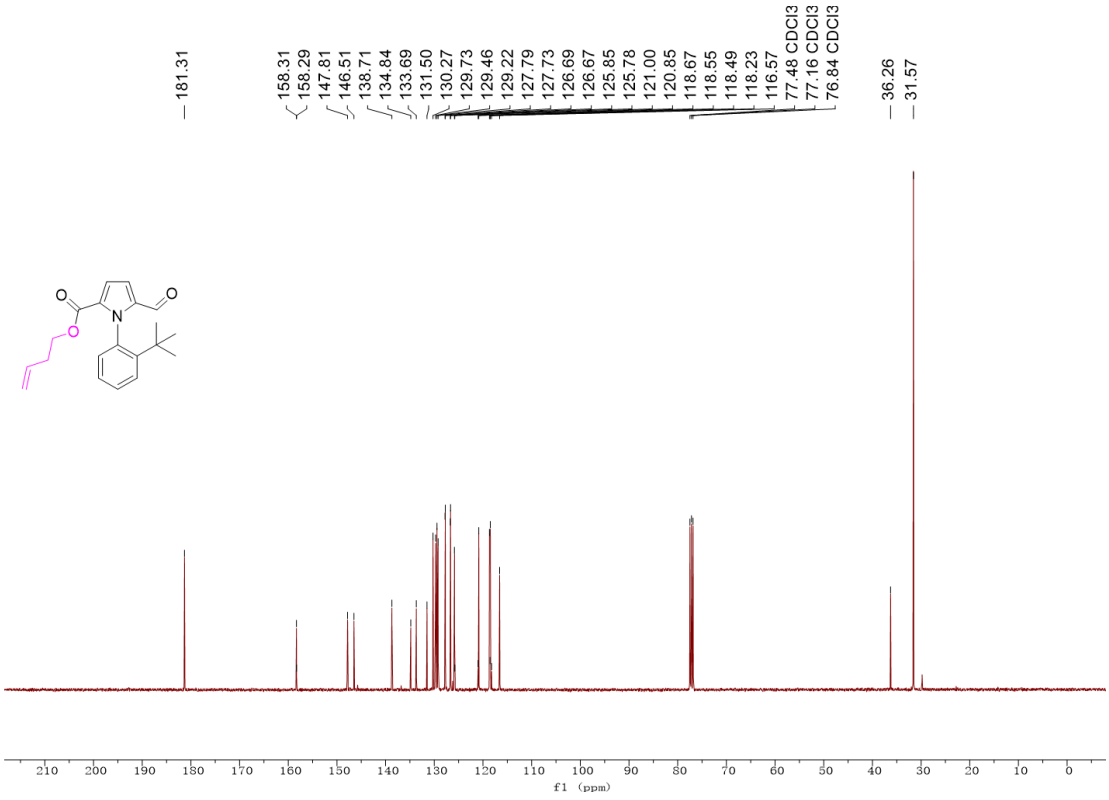
^{13}C NMR (75 MHz, Chloroform-*d*) of **3e**



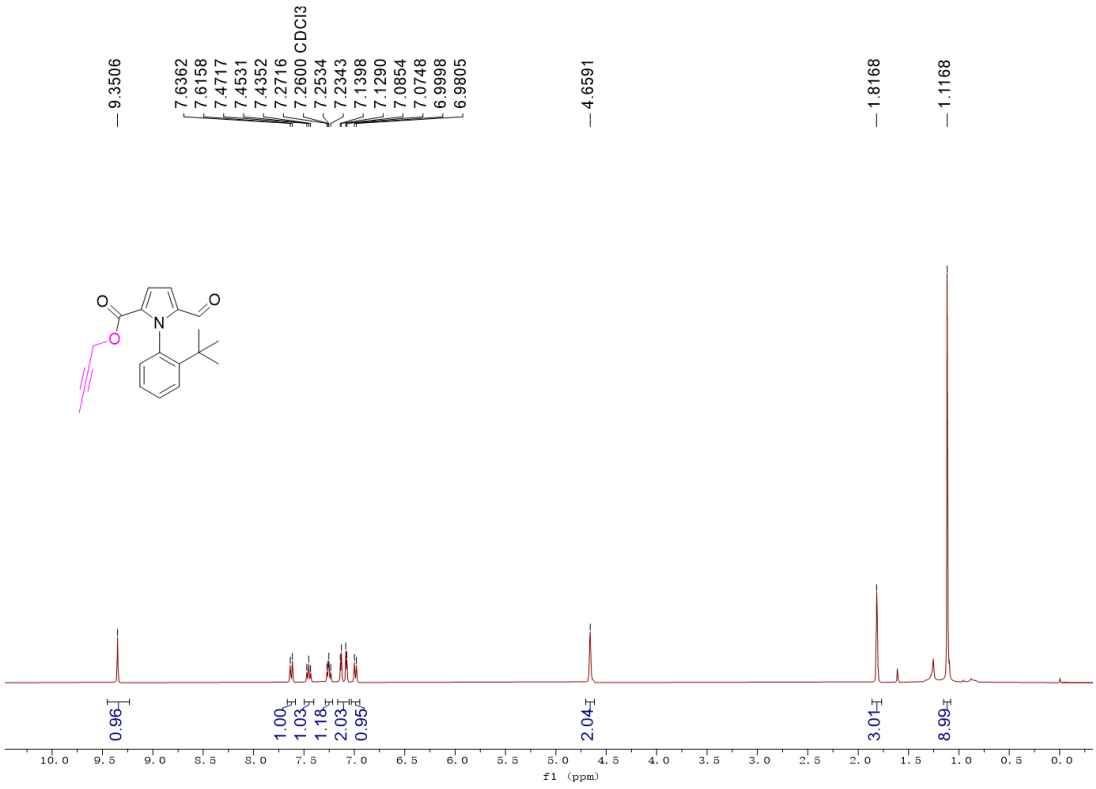
^{1}H NMR (400 MHz, Chloroform-*d*) of **3f**



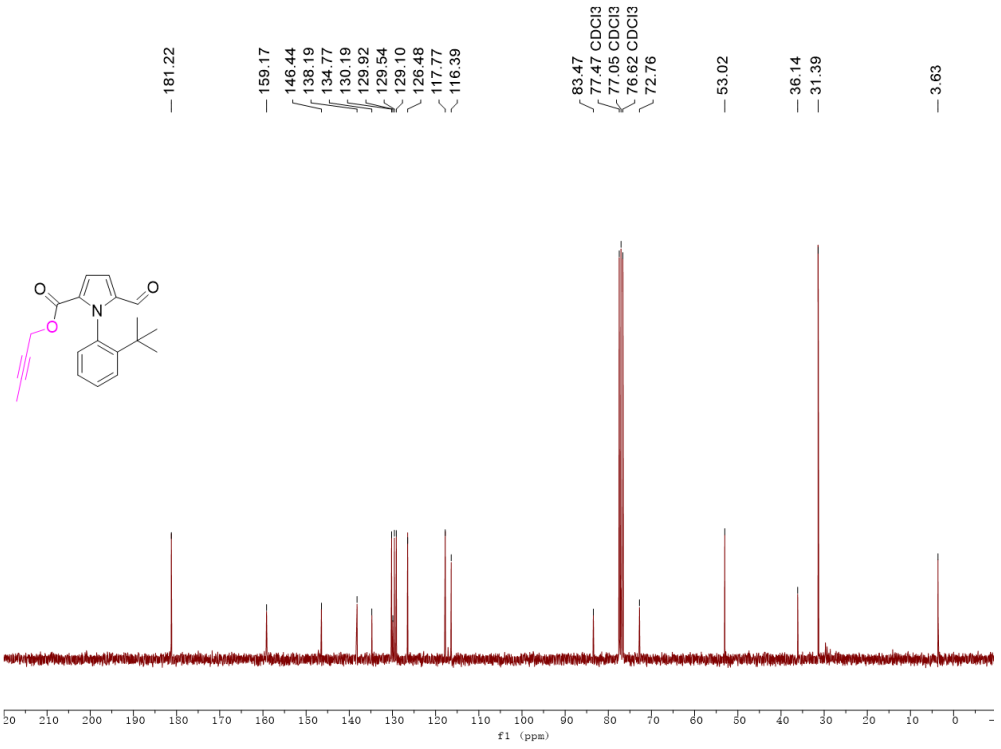
^{13}C NMR (101 MHz, Chloroform-*d*) of **3f**



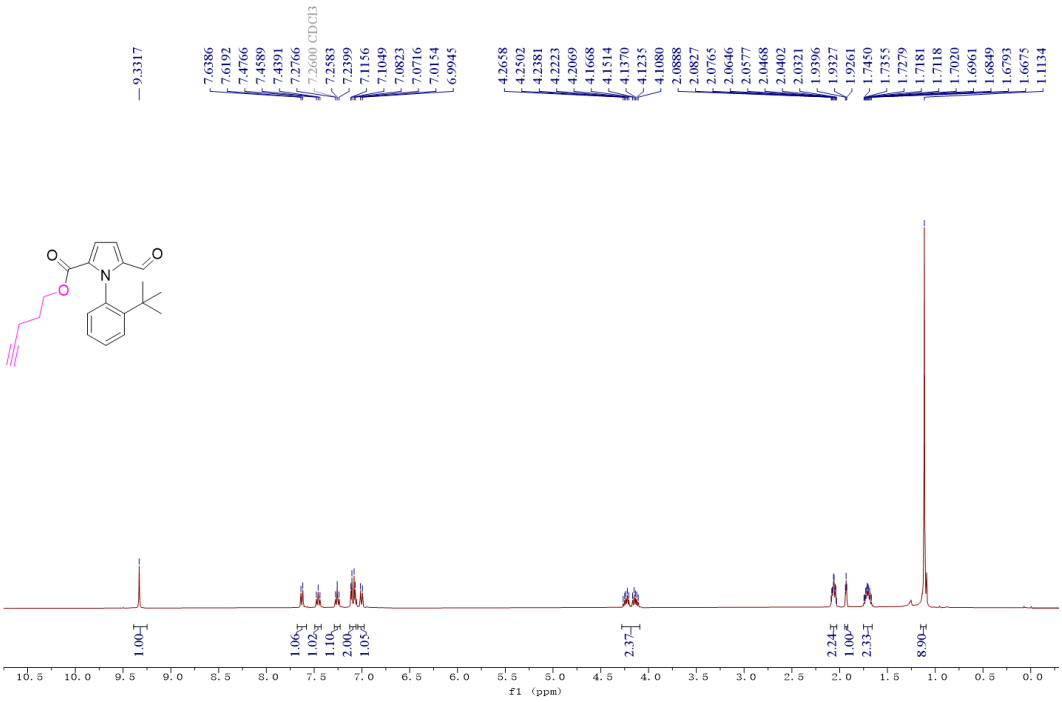
^{1}H NMR (400 MHz, Chloroform-*d*) of **3g**



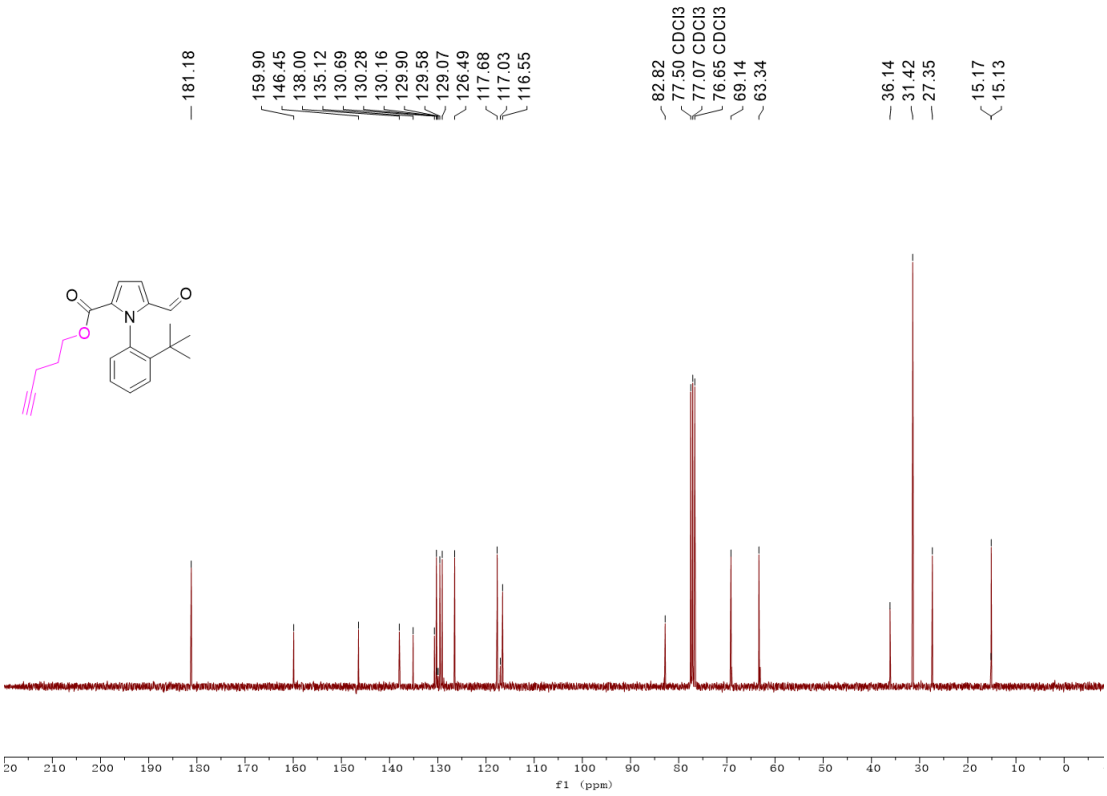
^{13}C NMR (75 MHz, Chloroform-*d*) of **3g**



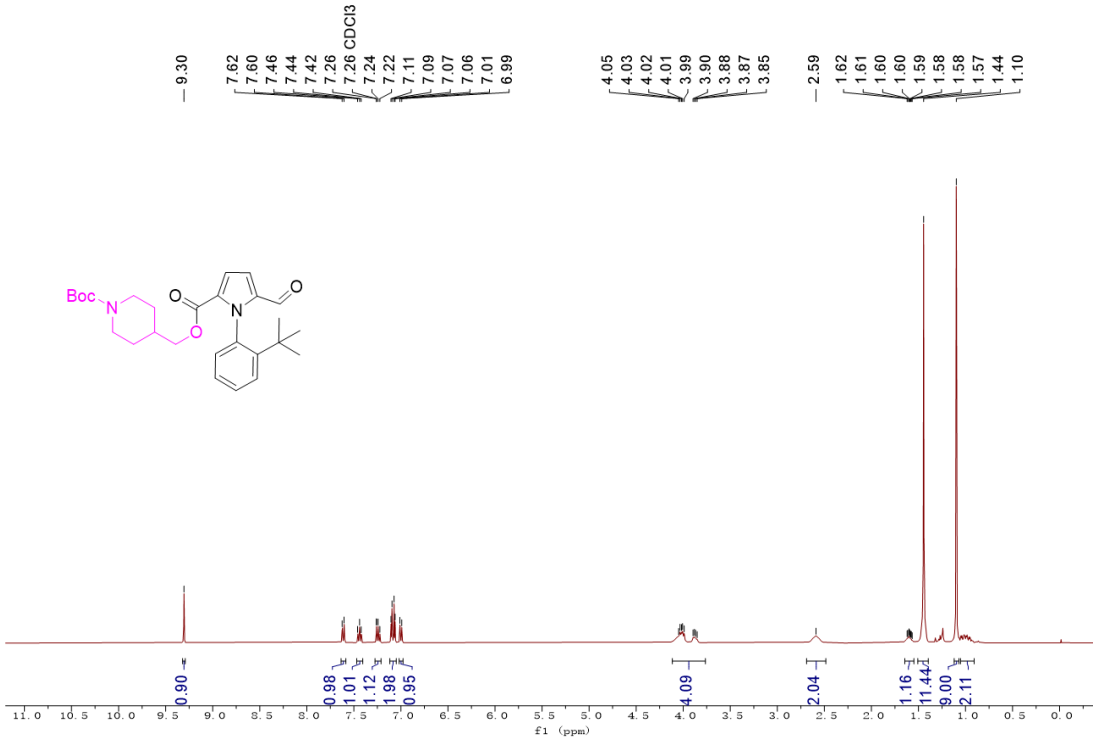
^{1}H NMR (400 MHz, Chloroform-*d*) of **3h**



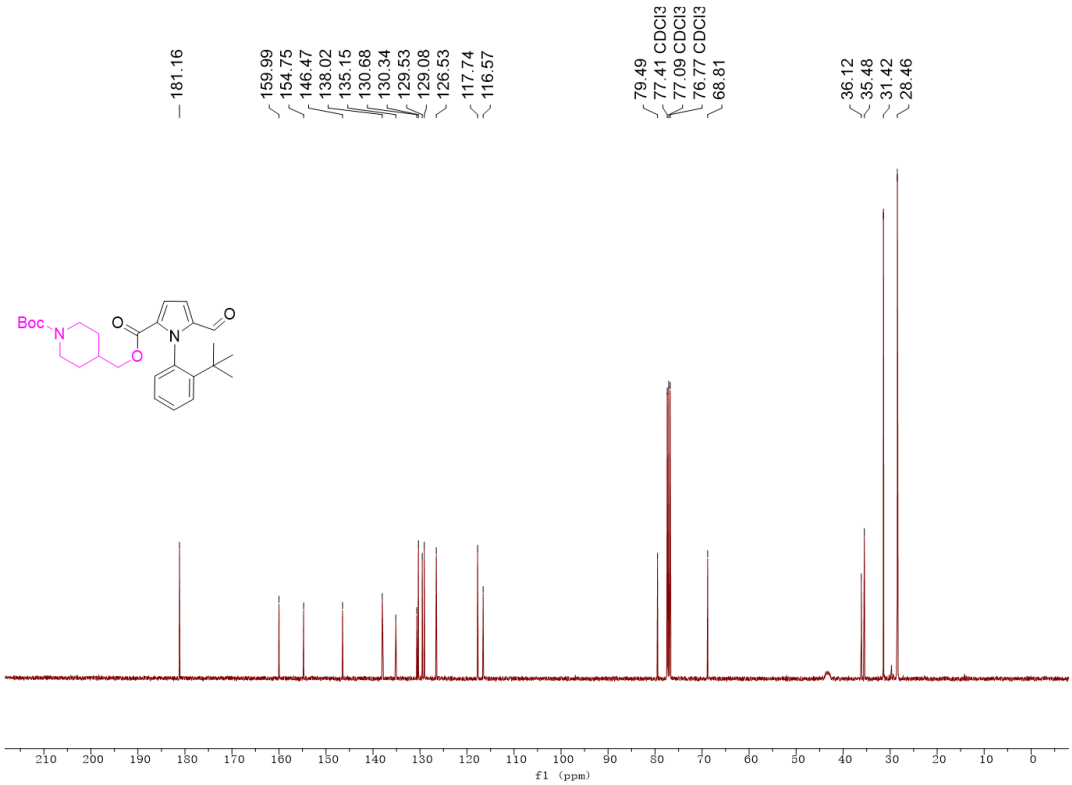
^{13}C NMR (75 MHz, Chloroform-*d*) of **3h**



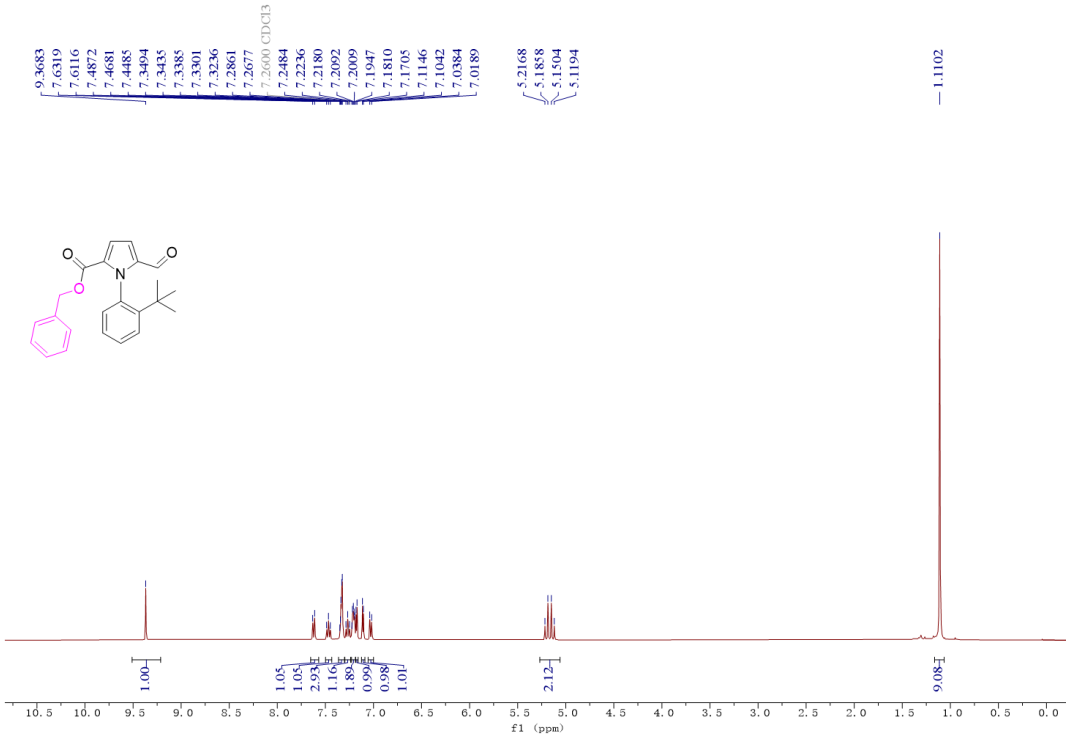
^{1}H NMR (400 MHz, Chloroform-*d*) of **3i**



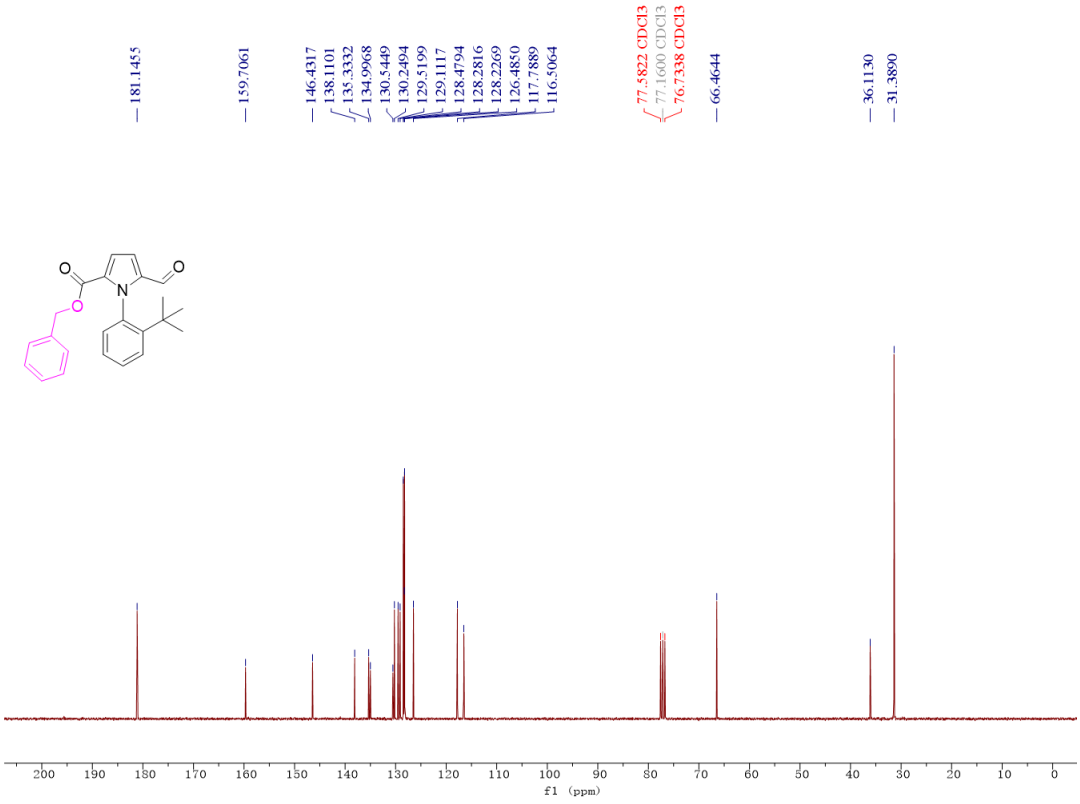
^{13}C NMR (101 MHz, Chloroform-*d*) of **3i**



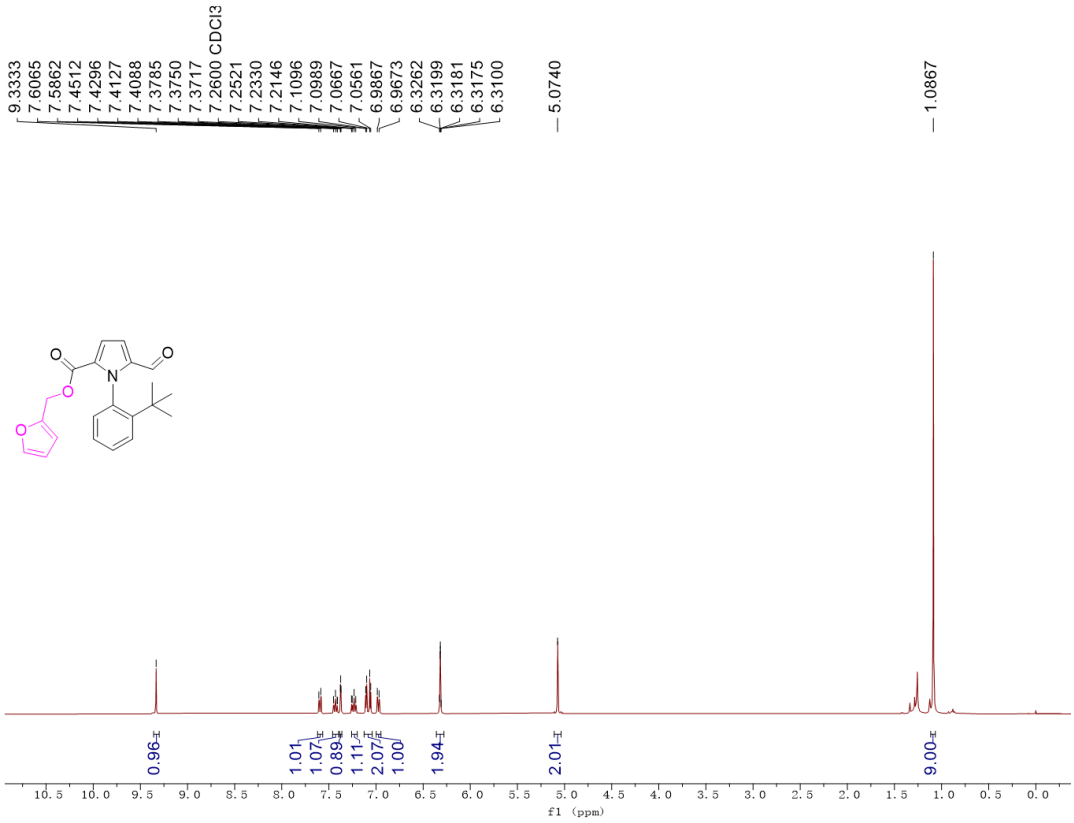
^{1}H NMR (400 MHz, Chloroform-*d*) of **3j**



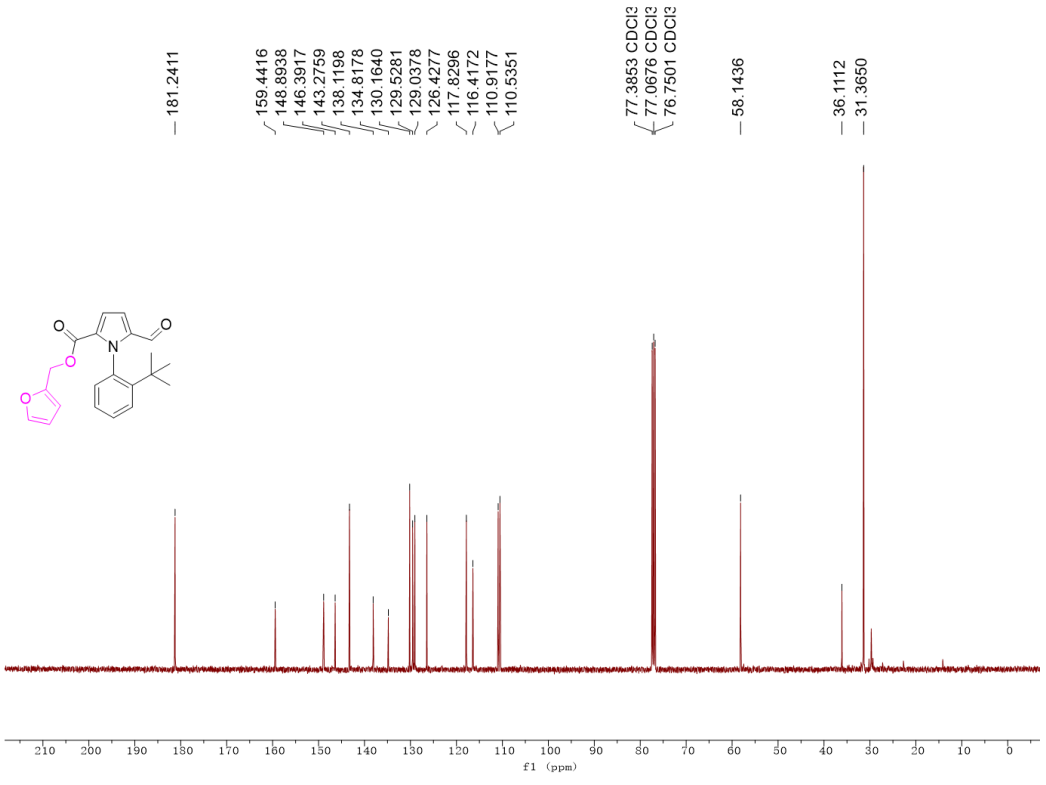
^{13}C NMR (75 MHz, Chloroform-*d*) of **3j**



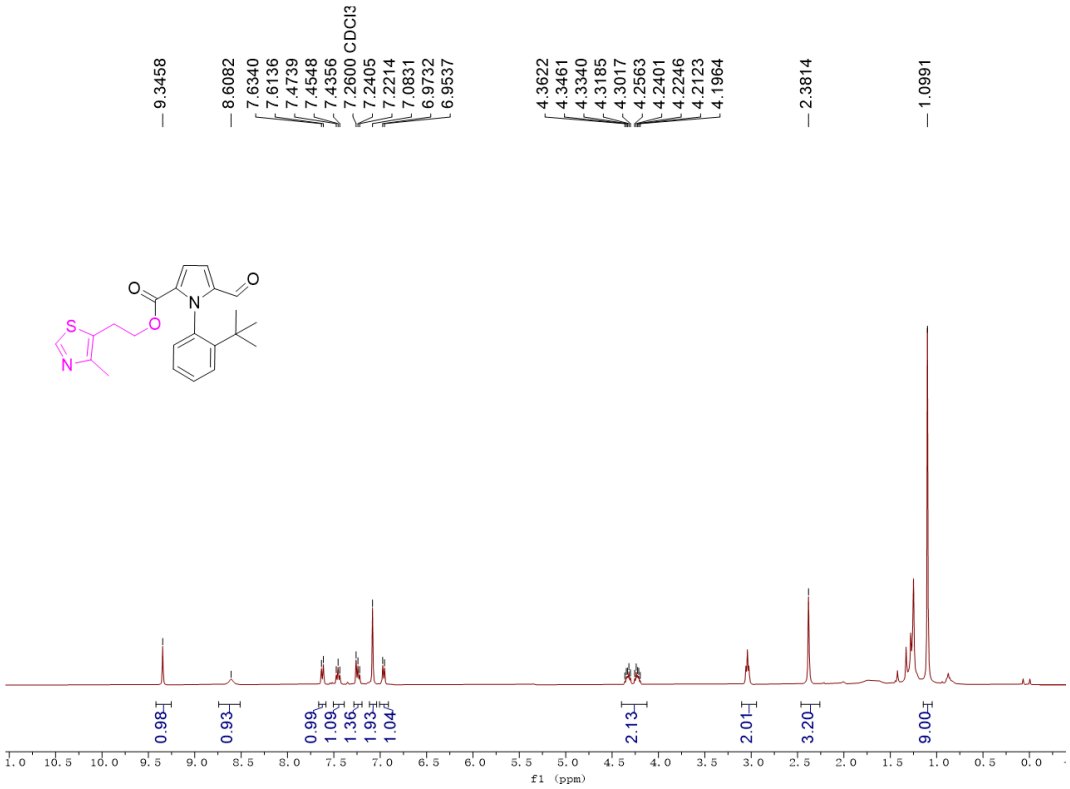
^{1}H NMR (400 MHz, Chloroform-*d*) of **3k**



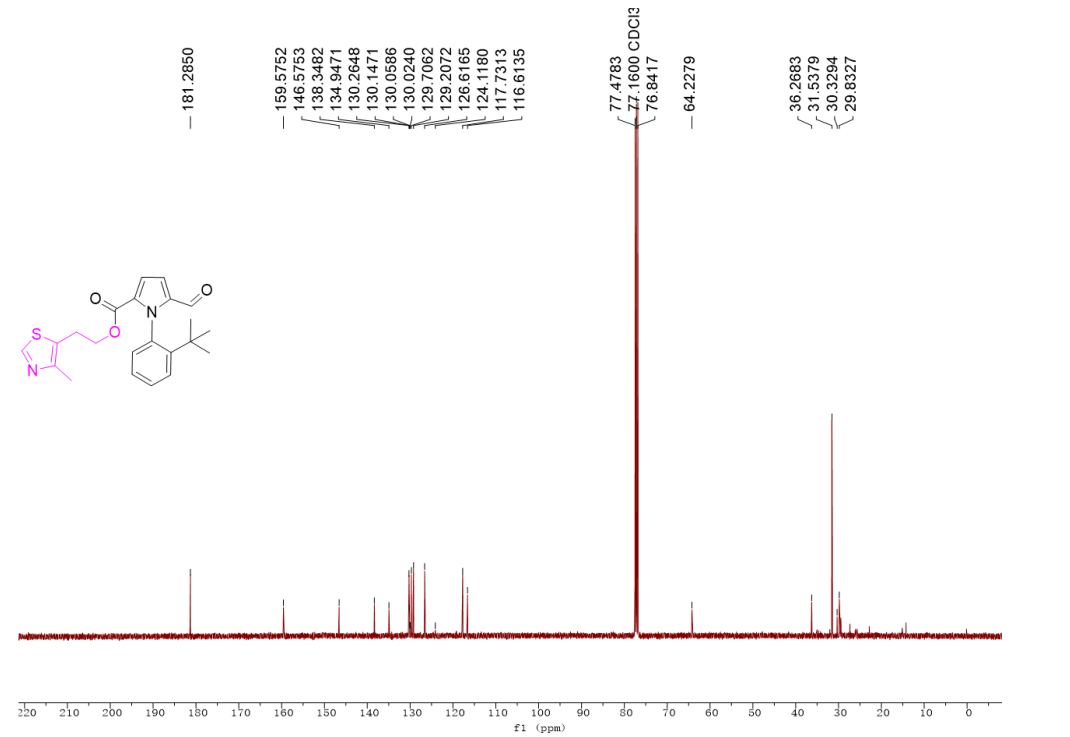
^{13}C NMR (101 MHz, Chloroform-*d*) of **3k**



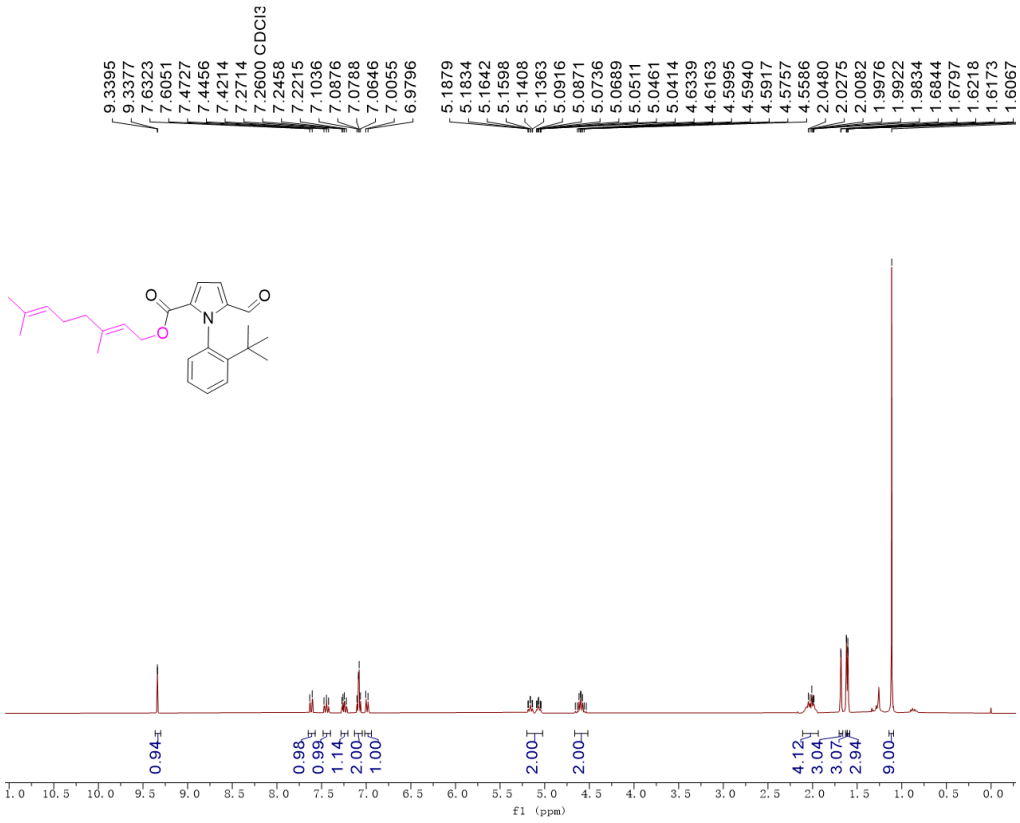
^{1}H NMR (400 MHz, Chloroform-*d*) of **3l**



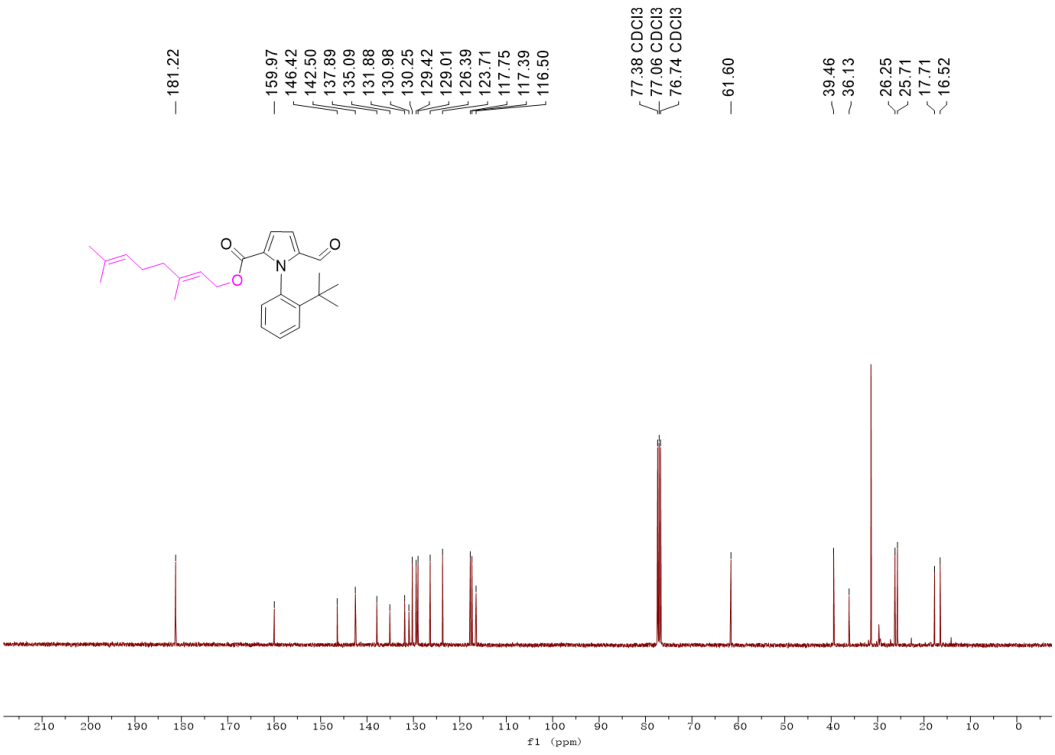
^{13}C NMR (101 MHz, Chloroform-*d*) of **3l**



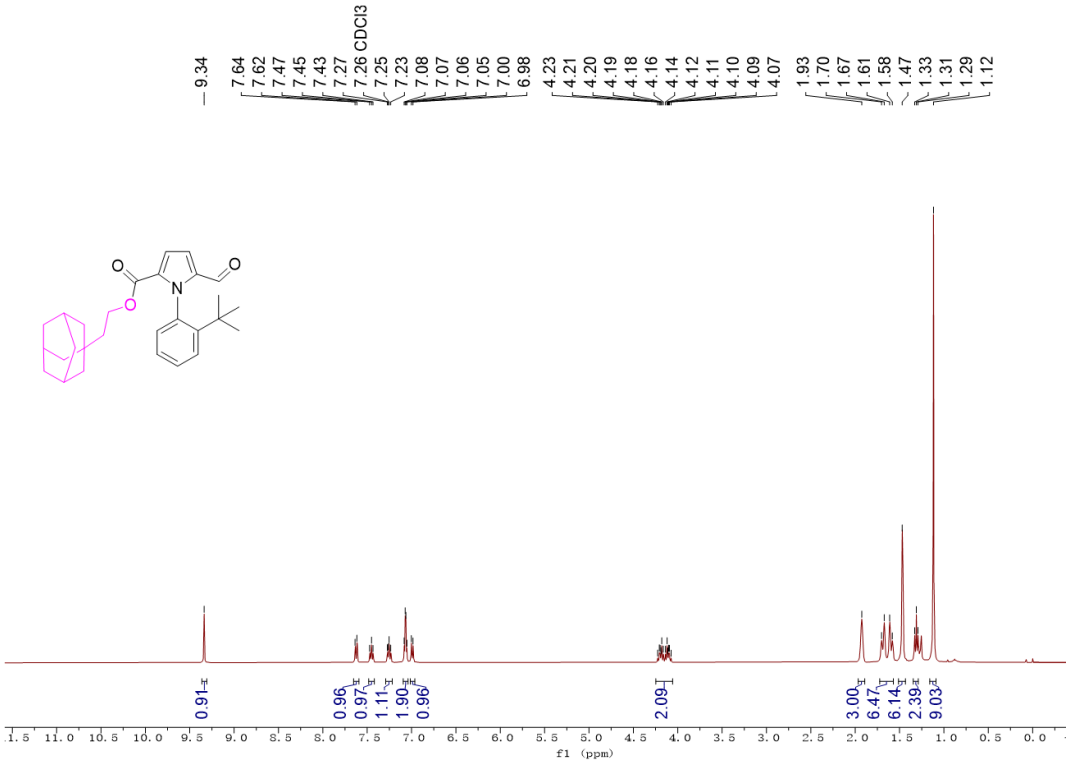
^{1}H NMR (300 MHz, Chloroform-*d*) of **3m**



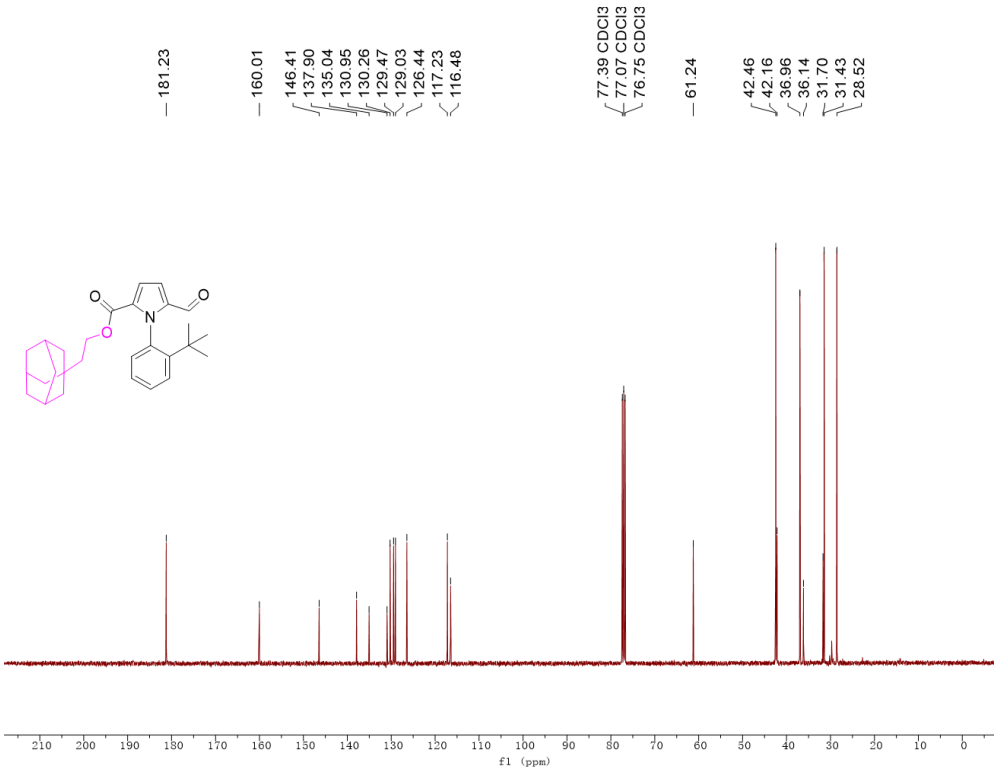
^{13}C NMR (101 MHz, Chloroform-*d*) of **3m**



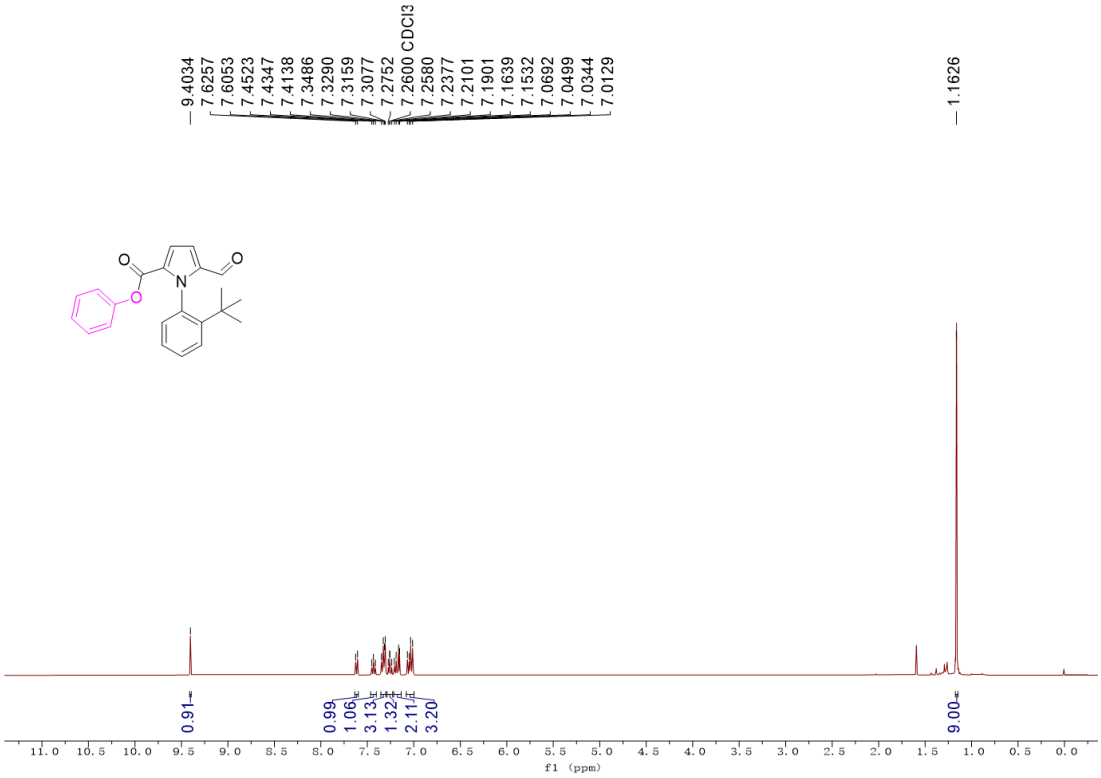
^{1}H NMR (400 MHz, Chloroform-*d*) of **3n**



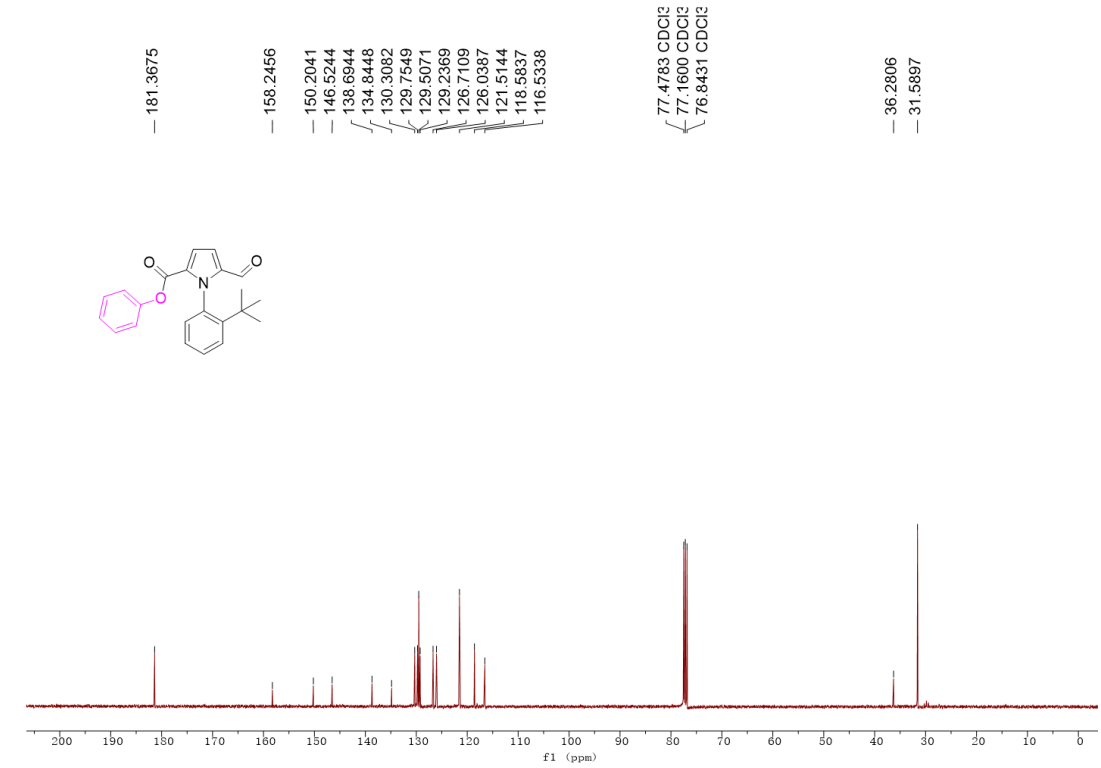
^{13}C NMR (101 MHz, Chloroform-*d*) of **3n**



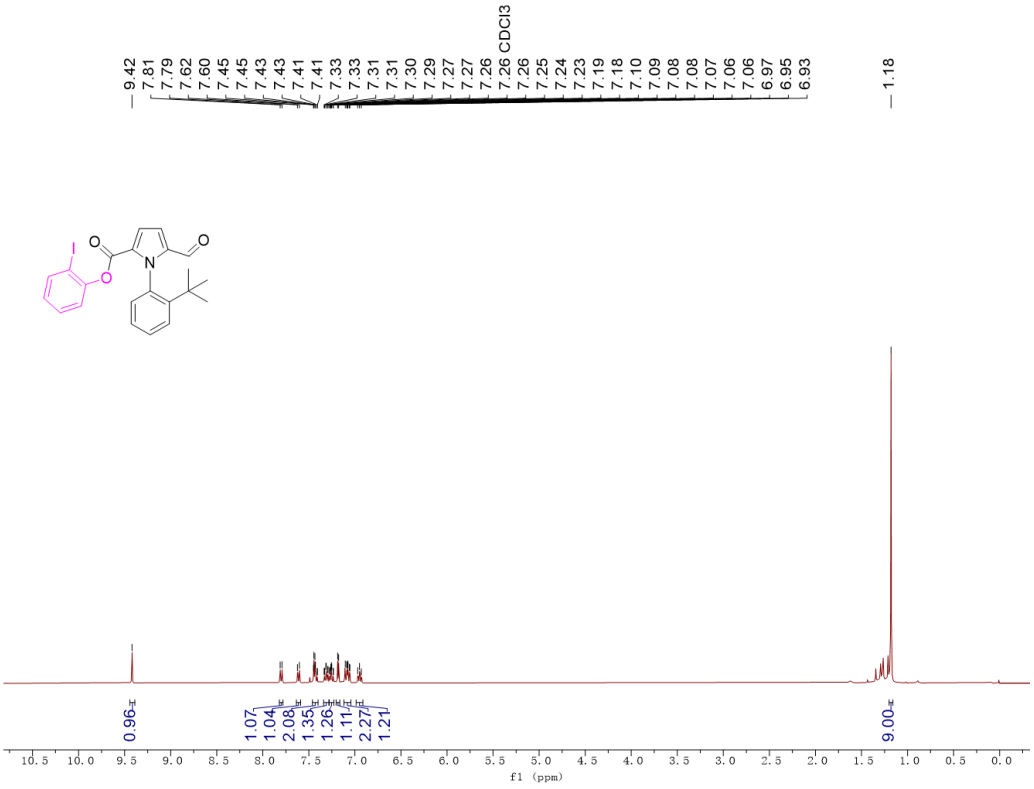
^{1}H NMR (400 MHz, Chloroform-*d*) of **3o**



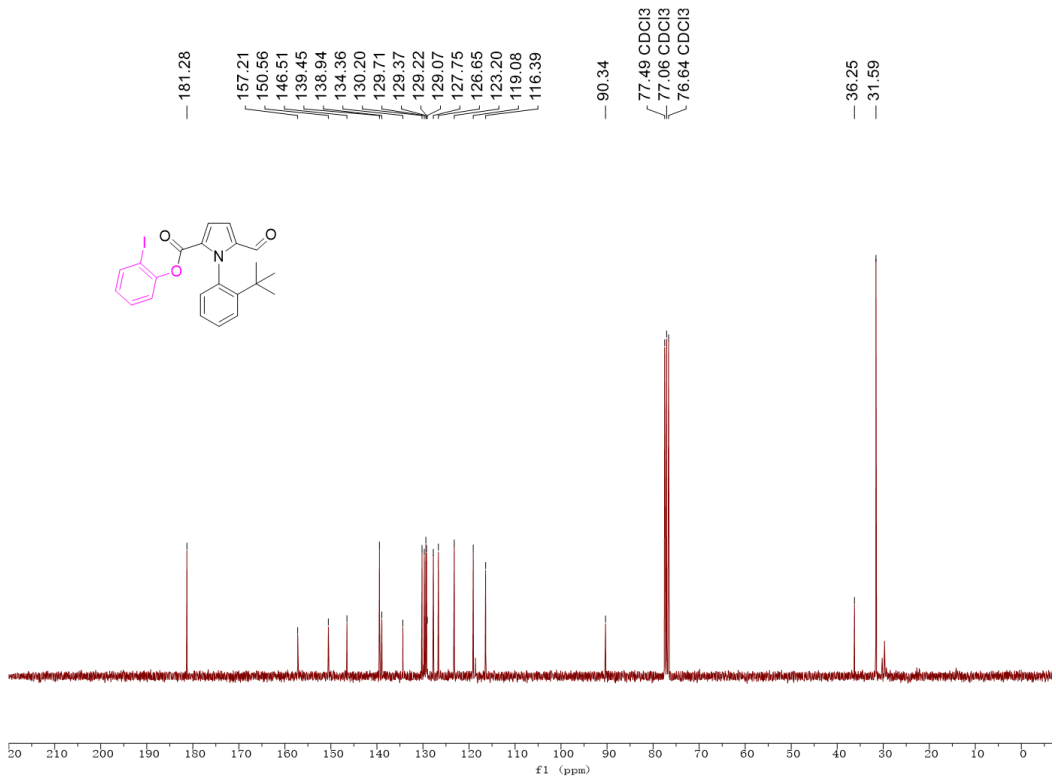
^{13}C NMR (101 MHz, Chloroform-*d*) of **3o**



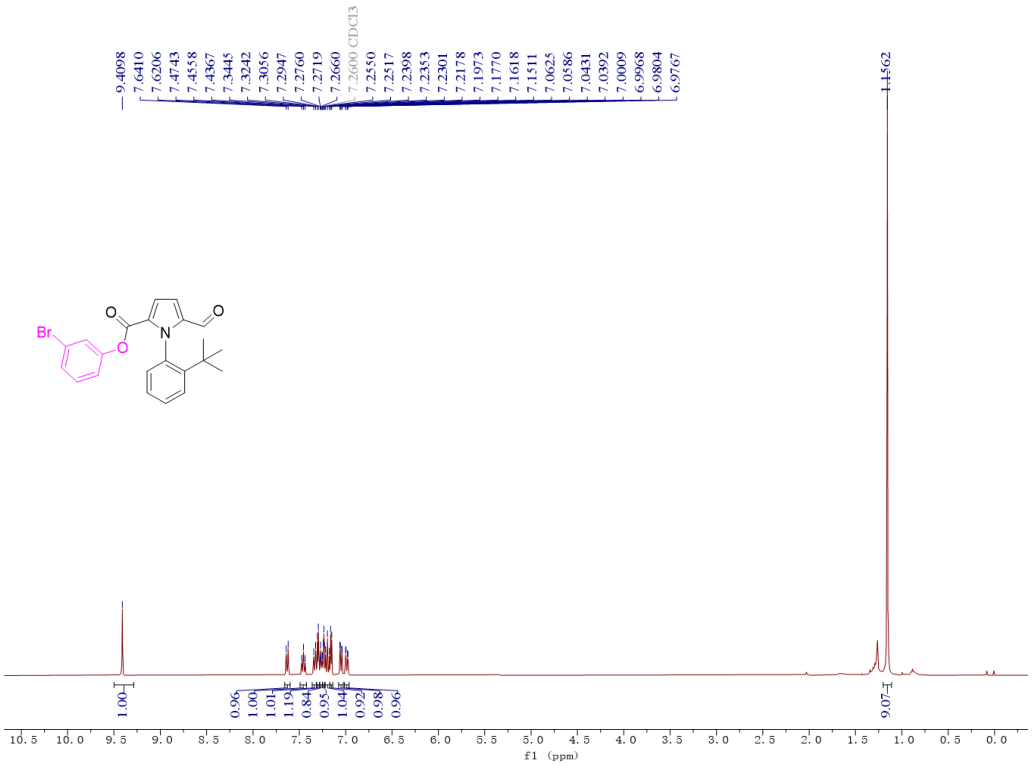
^{1}H NMR (400 MHz, Chloroform-*d*) of **3p**



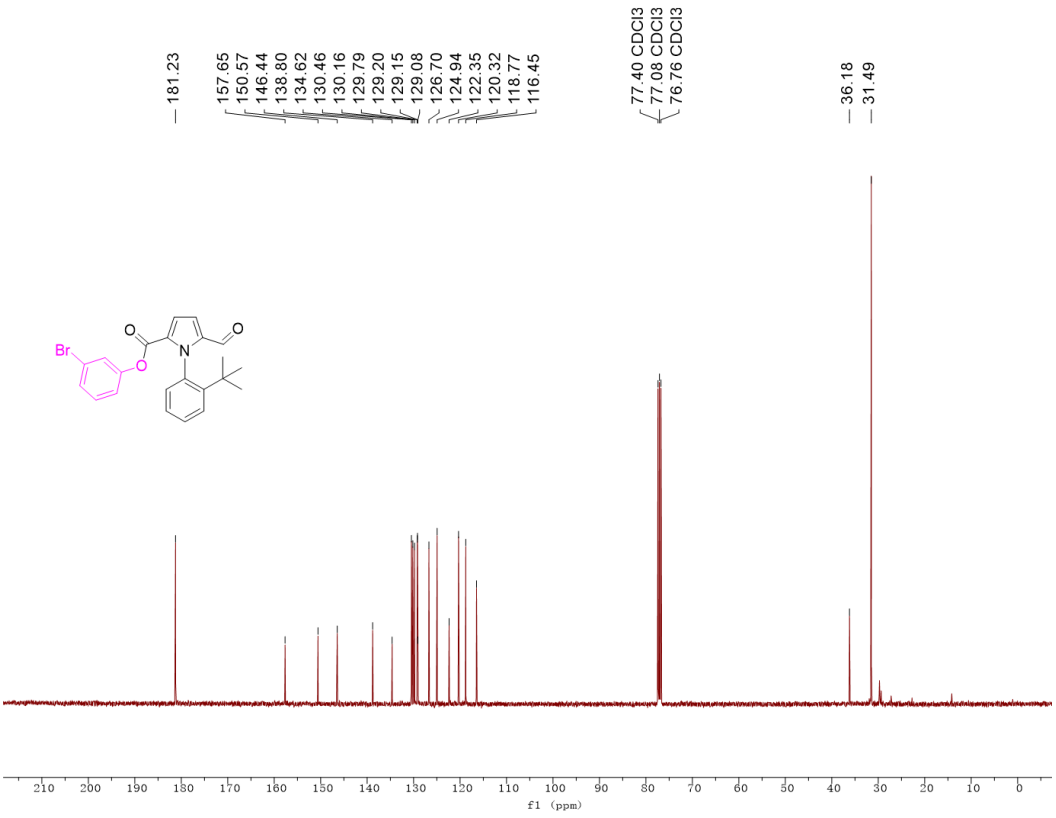
^{13}C NMR (75 MHz, Chloroform-*d*) of **3p**



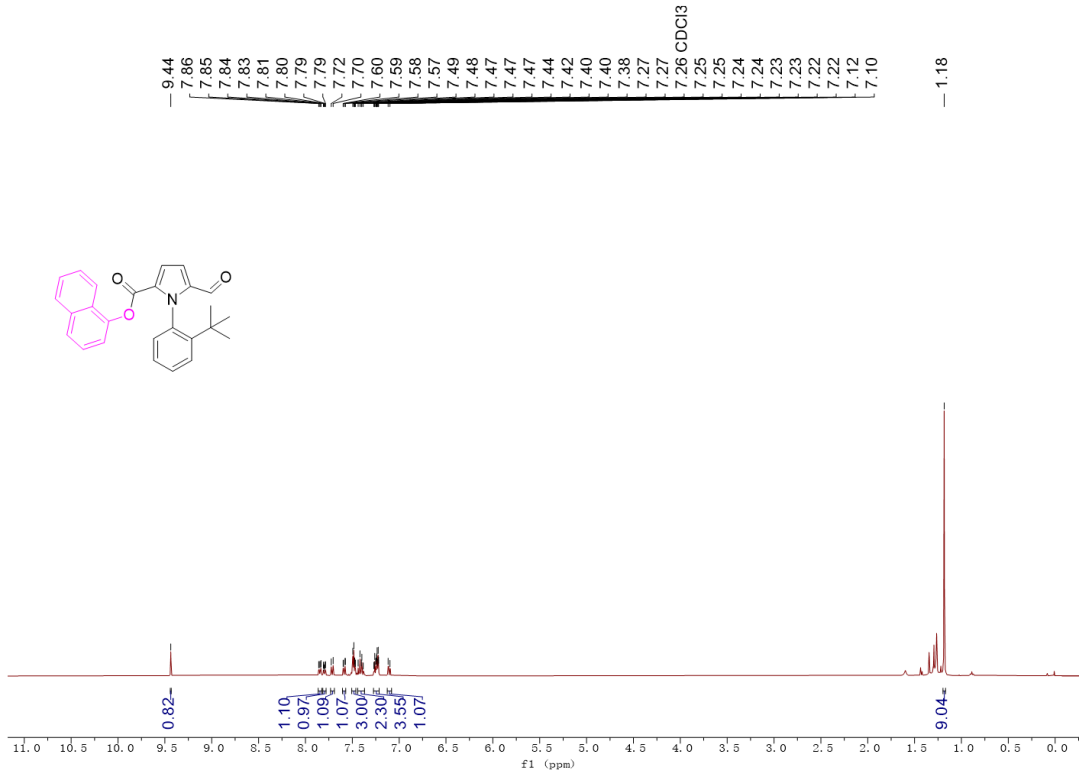
^{1}H NMR (400 MHz, Chloroform-*d*) of **3q**



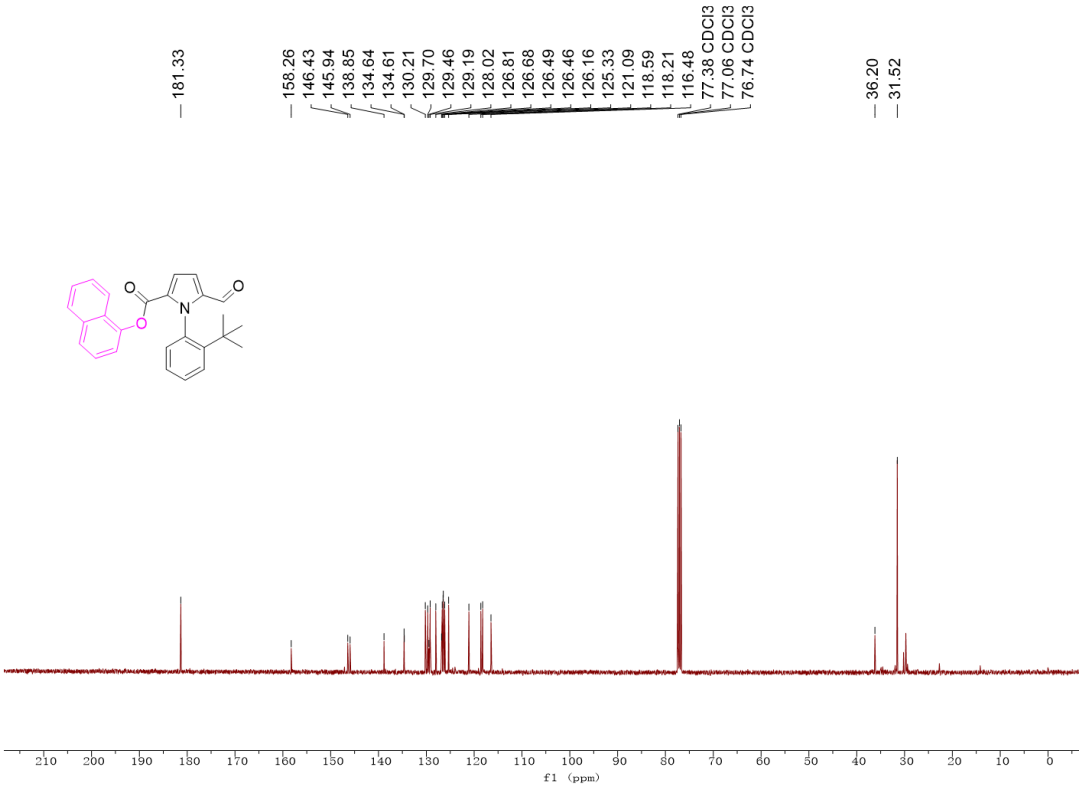
^{13}C NMR (101 MHz, Chloroform-*d*) of **3q**



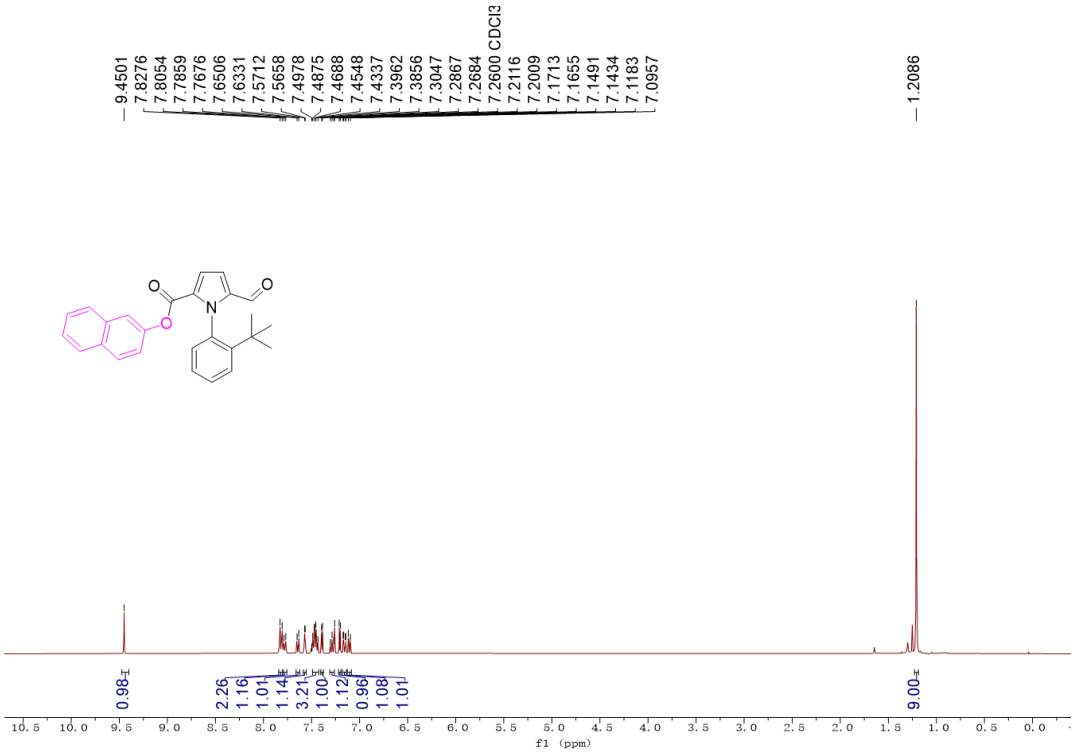
^{1}H NMR (400 MHz, Chloroform-*d*) of **3r**



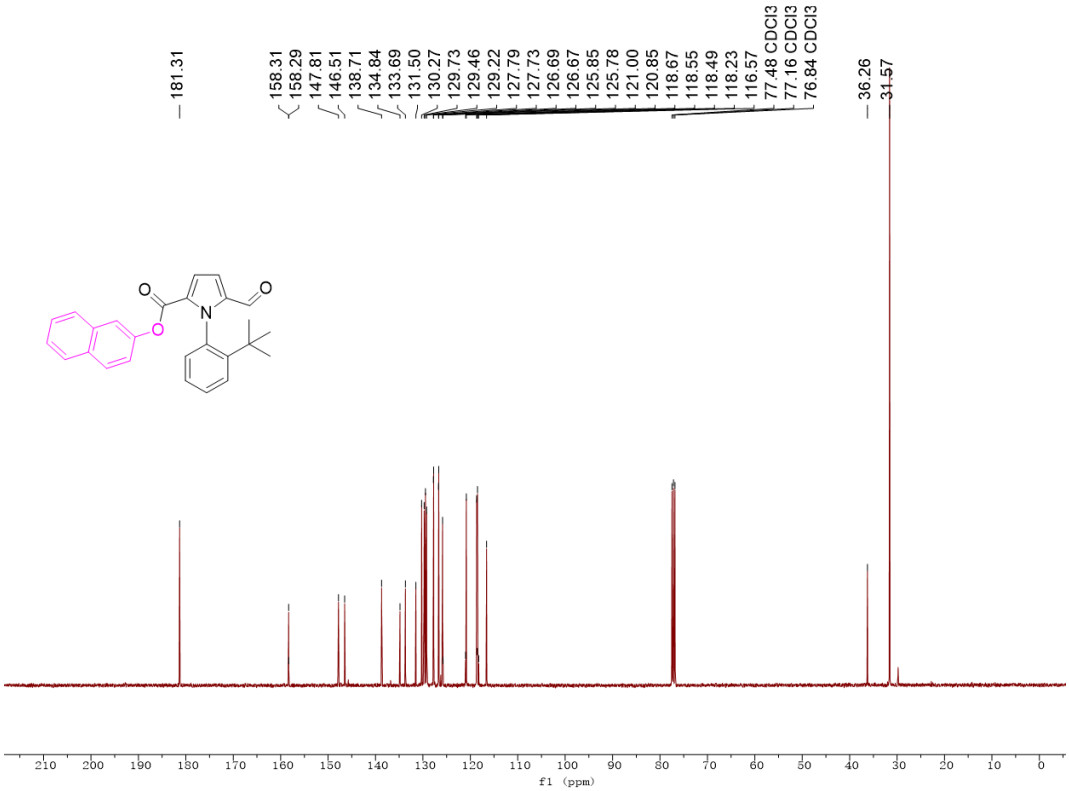
^{13}C NMR (101 MHz, Chloroform-*d*) of **3r**



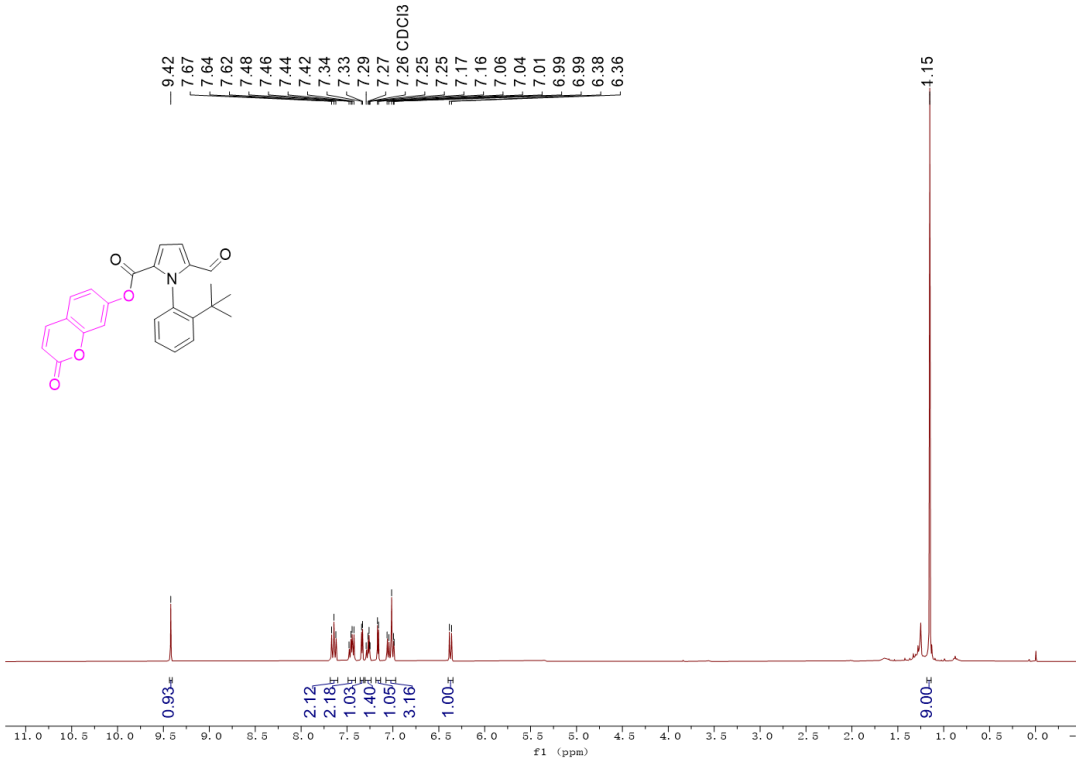
^{1}H NMR (400 MHz, Chloroform-*d*) of **3s**



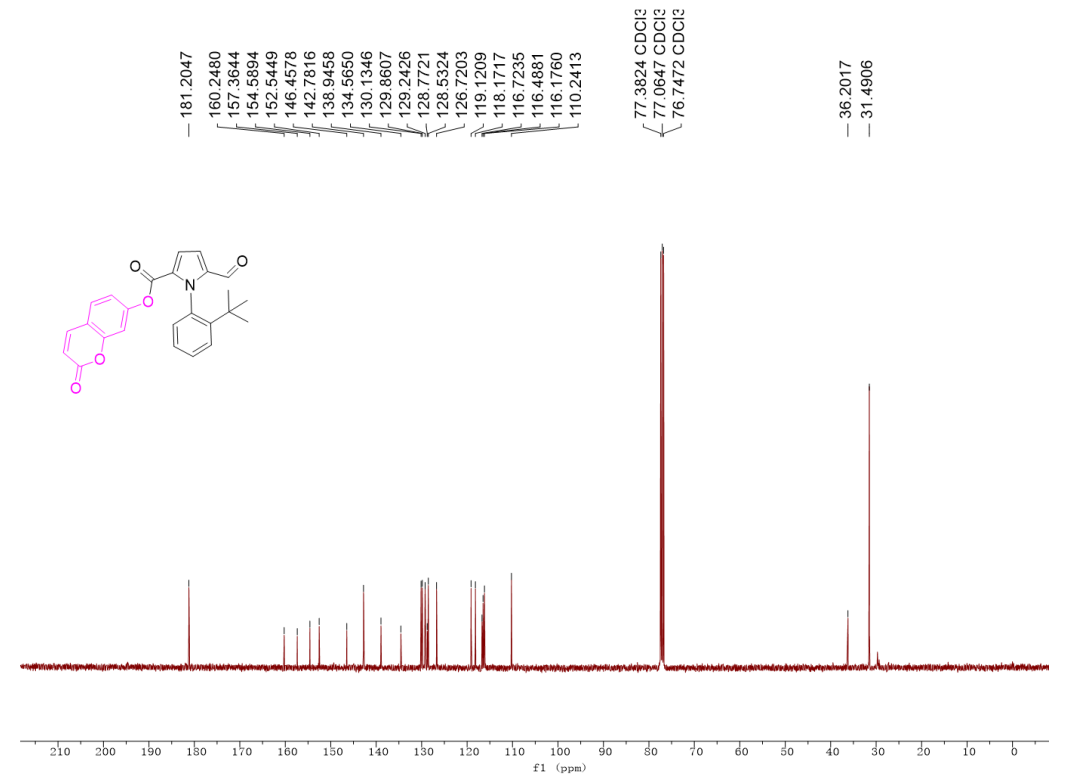
^{13}C NMR (101 MHz, Chloroform-*d*) of **3s**



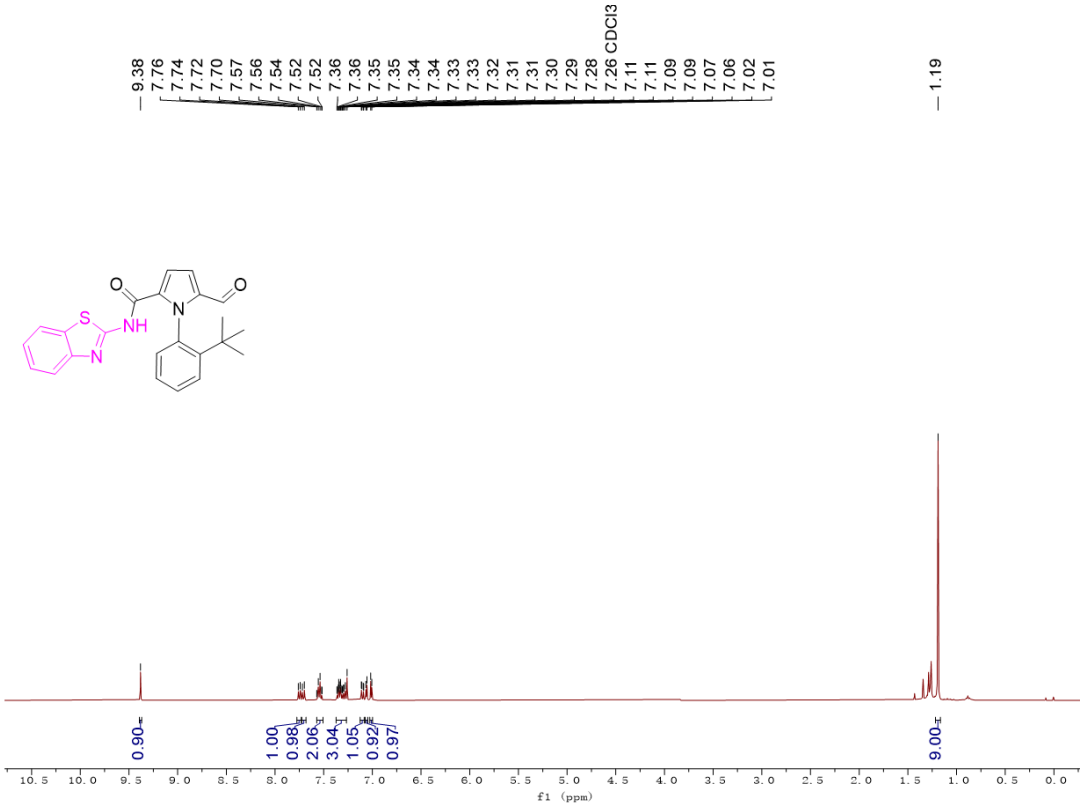
^{1}H NMR (400 MHz, Chloroform-*d*) of **3t**



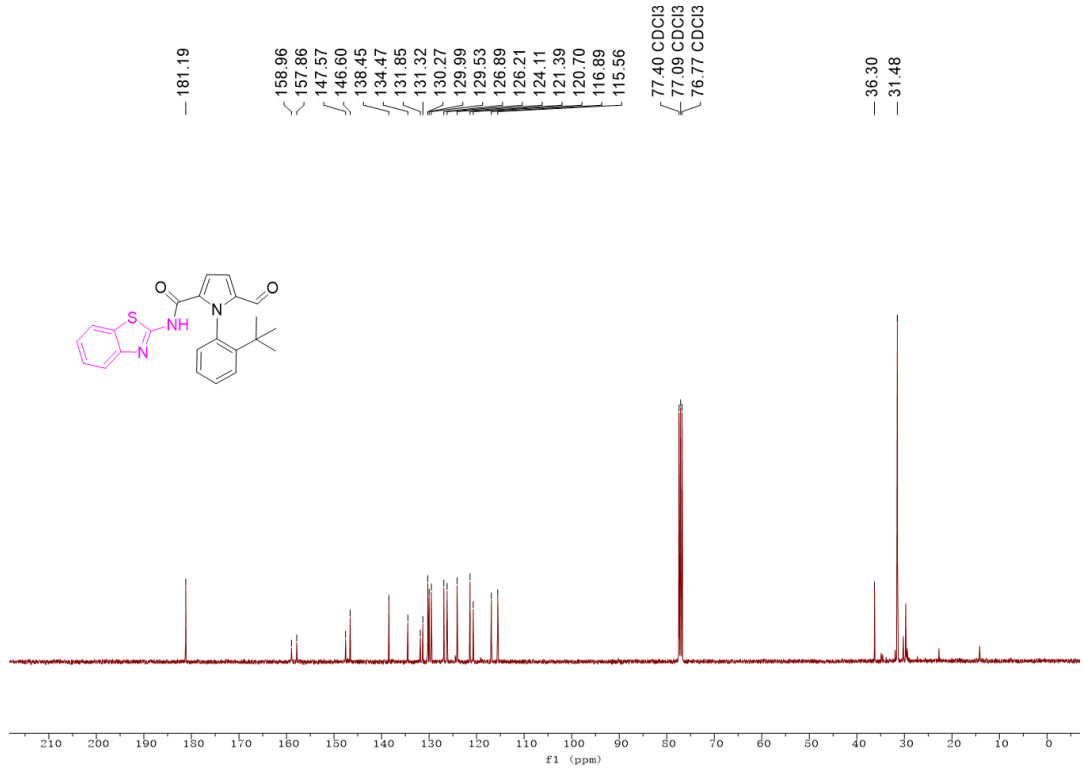
^{13}C NMR (101 MHz, Chloroform-*d*) of **3t**



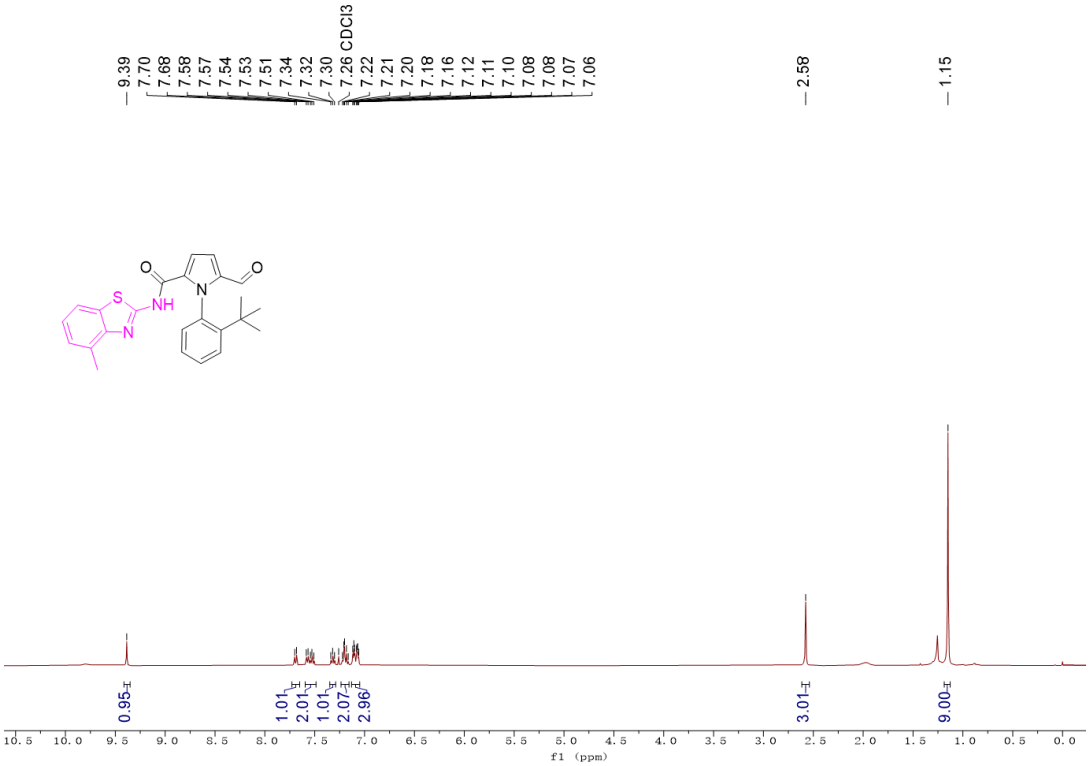
^{1}H NMR (400 MHz, Chloroform-*d*) of **3u**



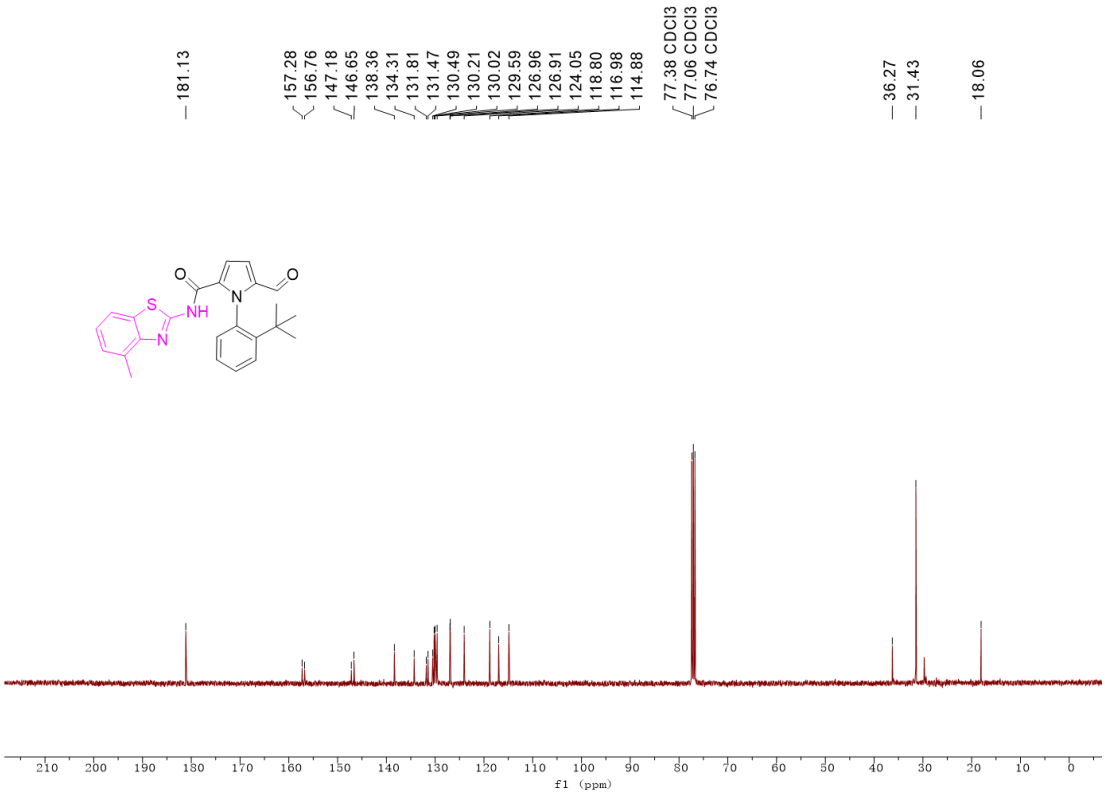
^{13}C NMR (101 MHz, Chloroform-*d*) of **3u**



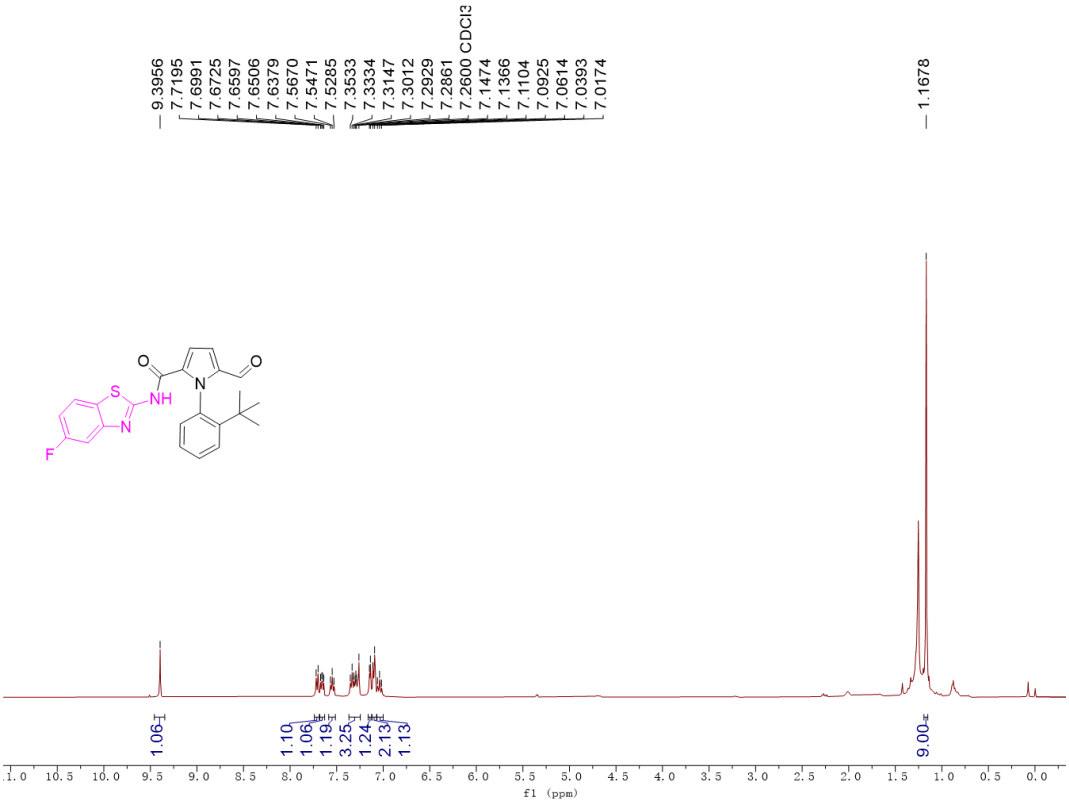
^{1}H NMR (400 MHz, Chloroform-*d*) of **3v**



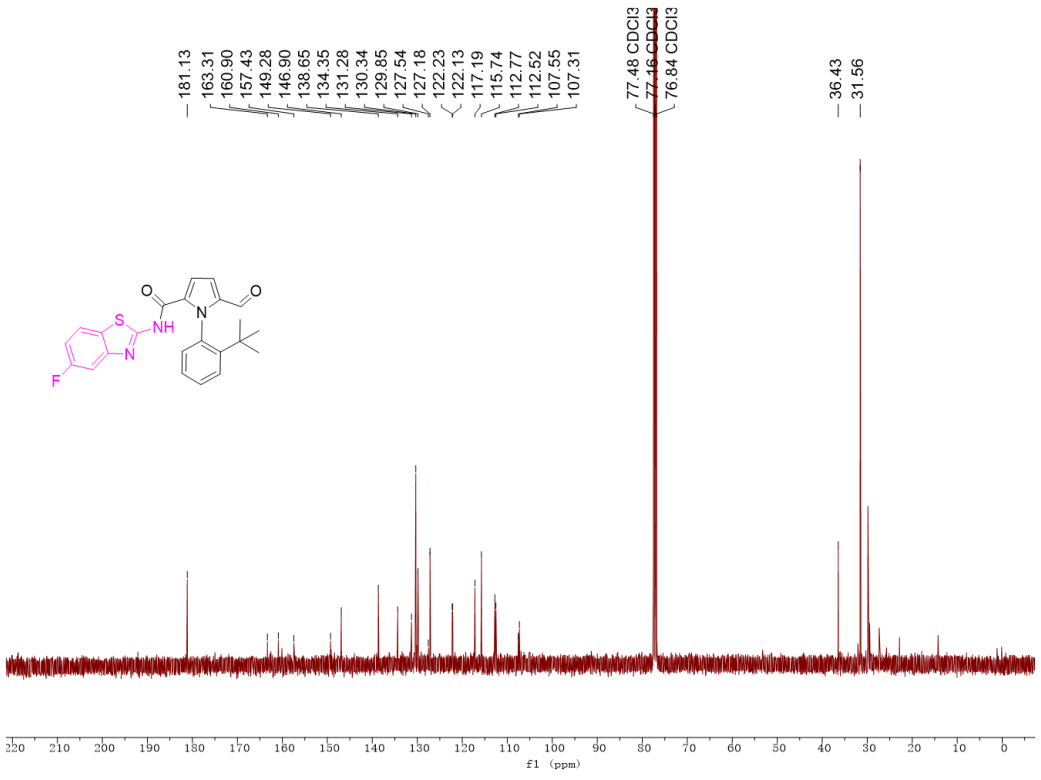
^{13}C NMR (101 MHz, Chloroform-*d*) of **3v**



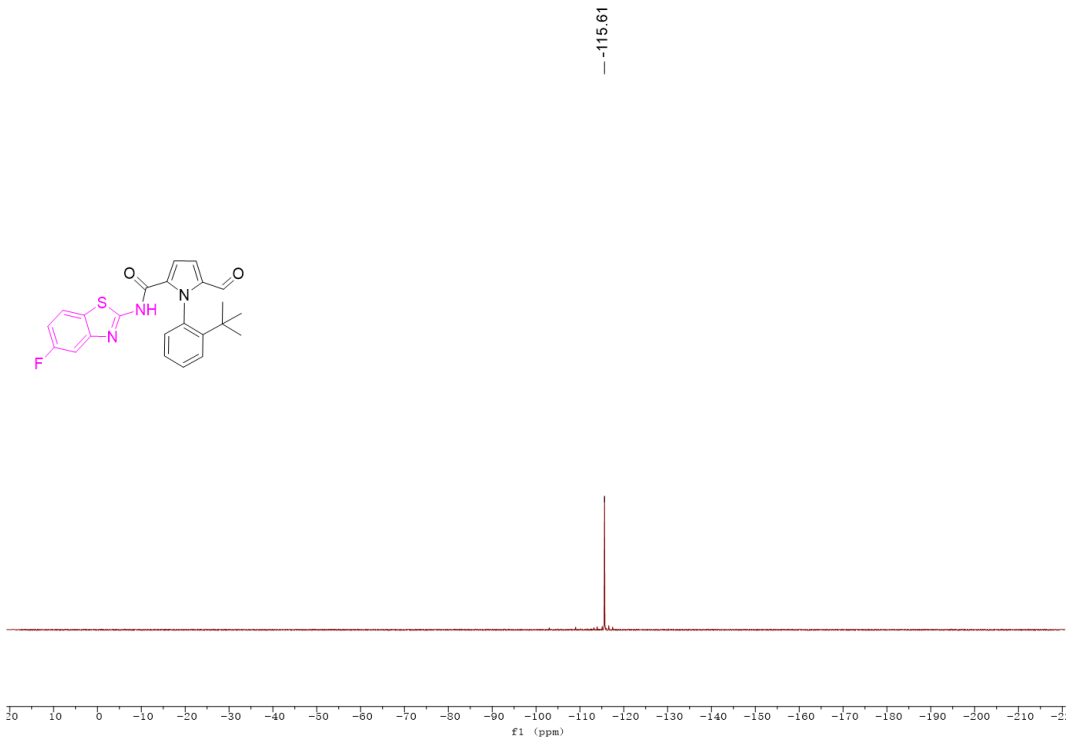
^{1}H NMR (400 MHz, Chloroform-*d*) of **3w**



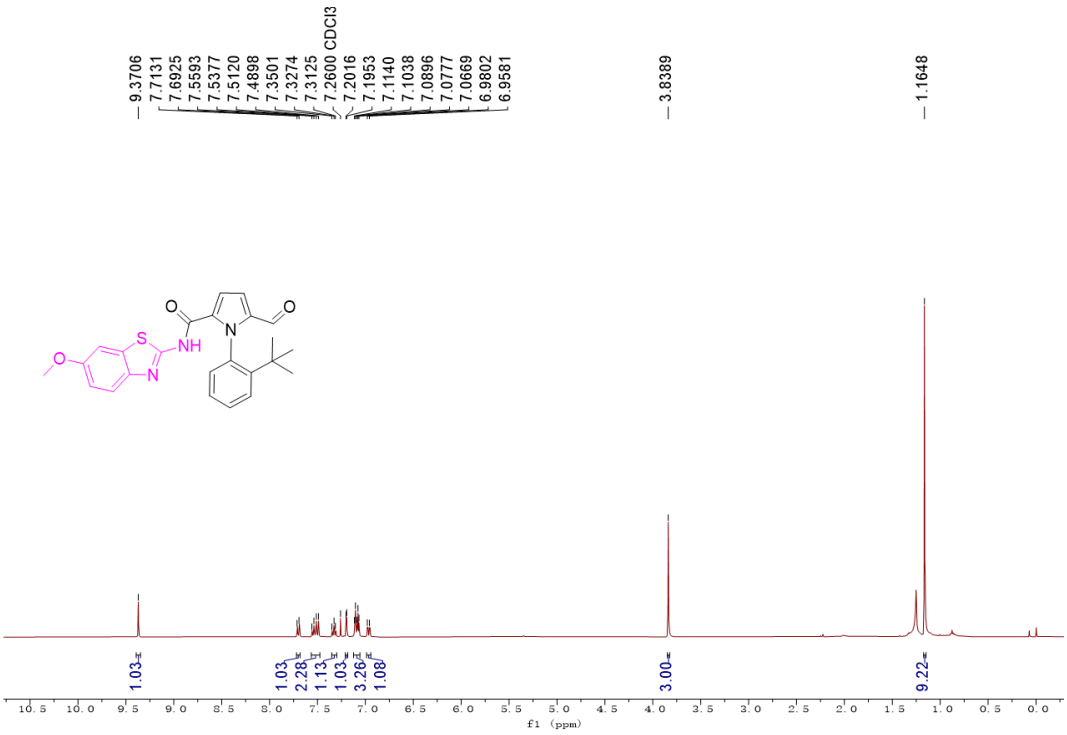
^{13}C NMR (101 MHz, Chloroform-*d*) of **3w**



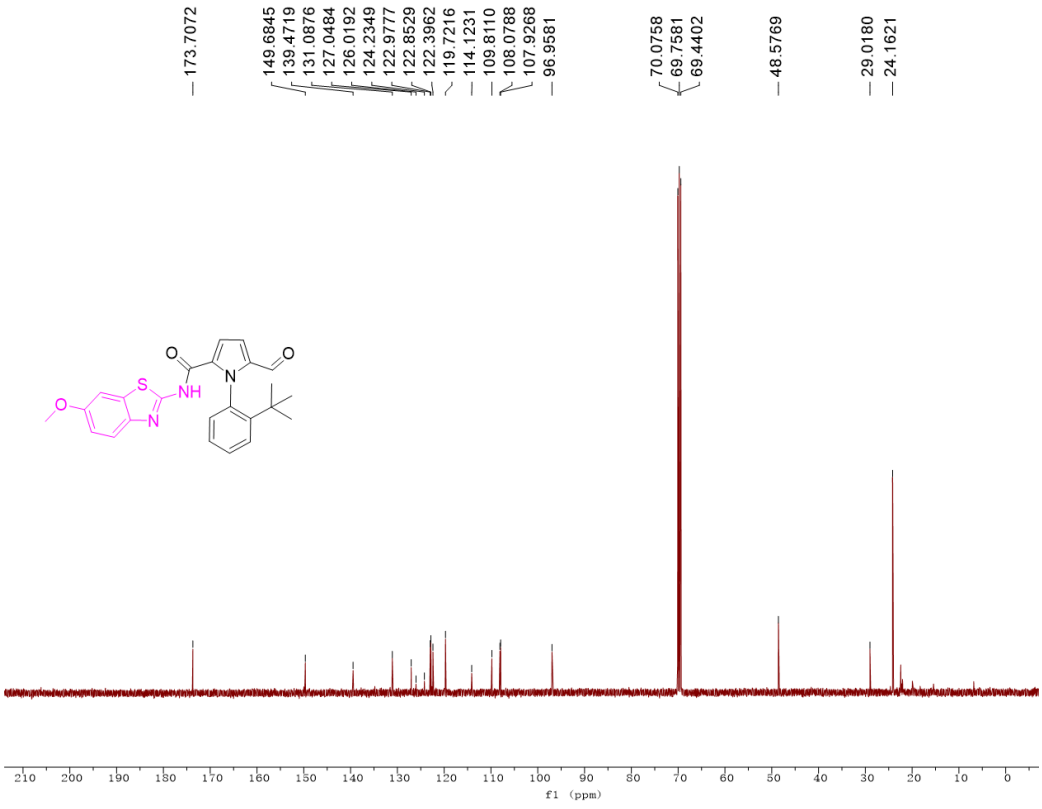
^{19}F NMR (376 MHz, Chloroform-d) of **3w**



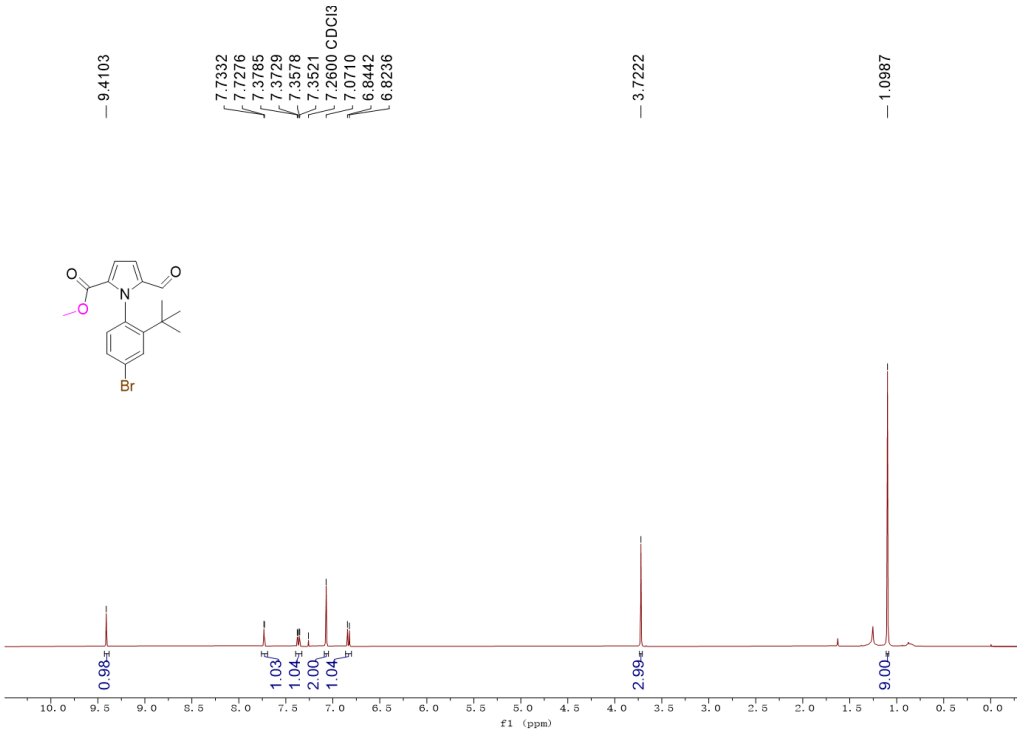
^{1}H NMR (400 MHz, Chloroform-*d*) of **3x**



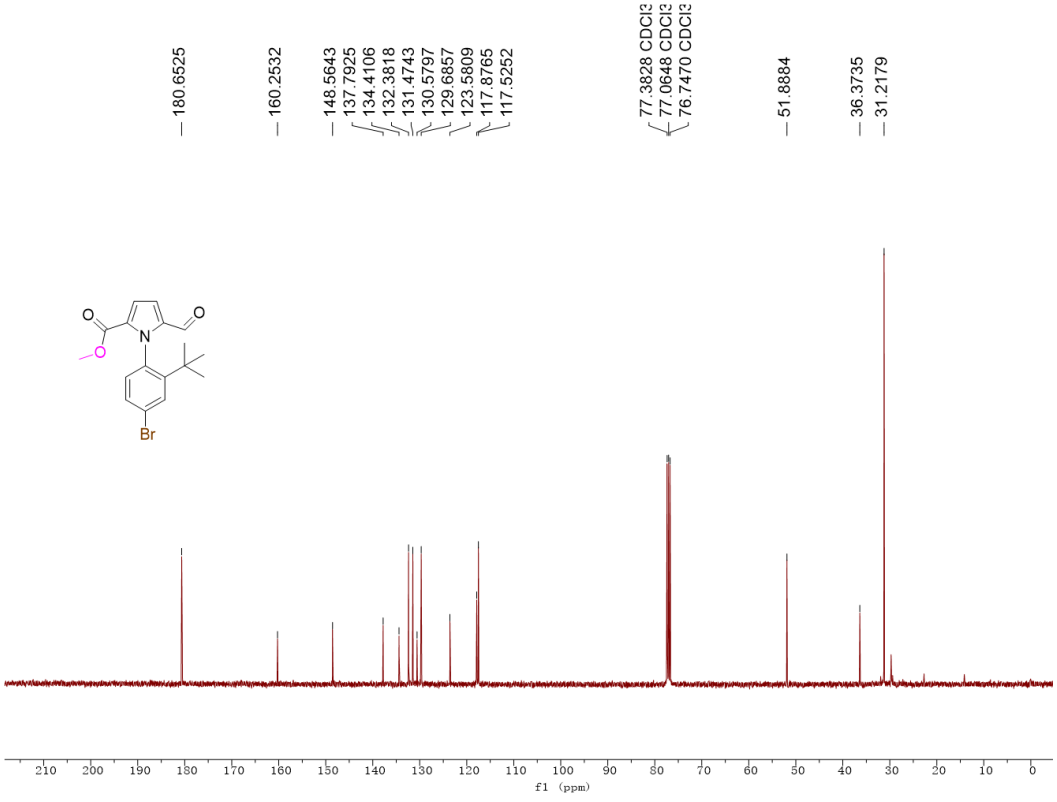
^{13}C NMR (101 MHz, Chloroform-*d*) of **3x**



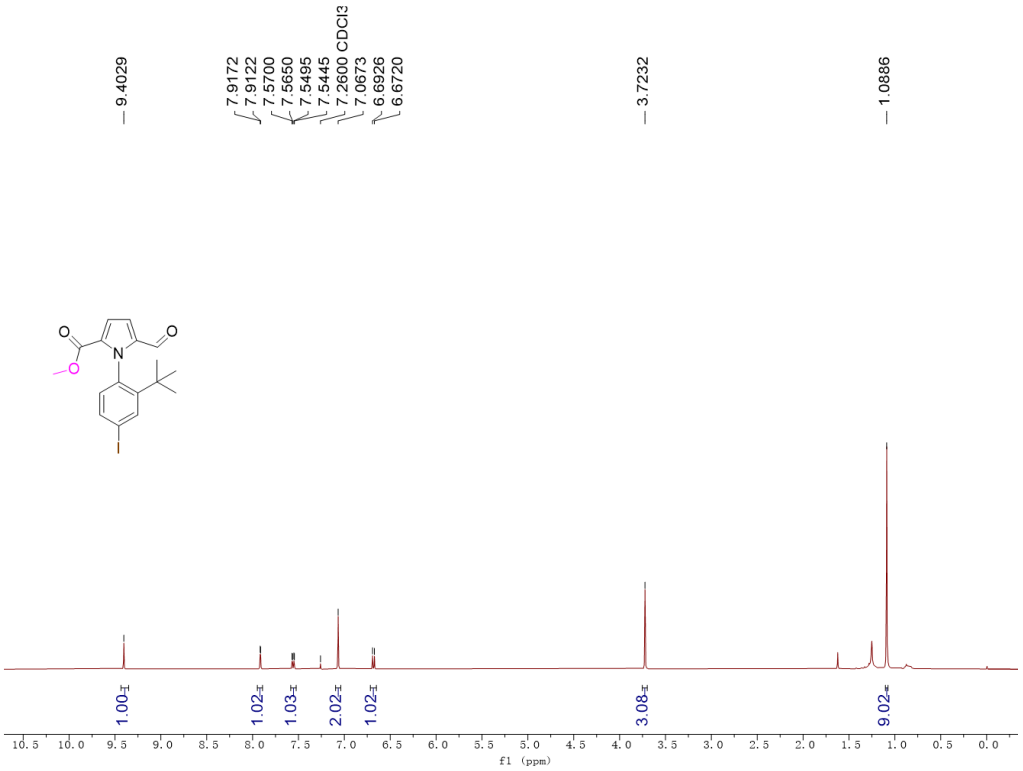
^{1}H NMR (400 MHz, Chloroform-*d*) of **3aa**



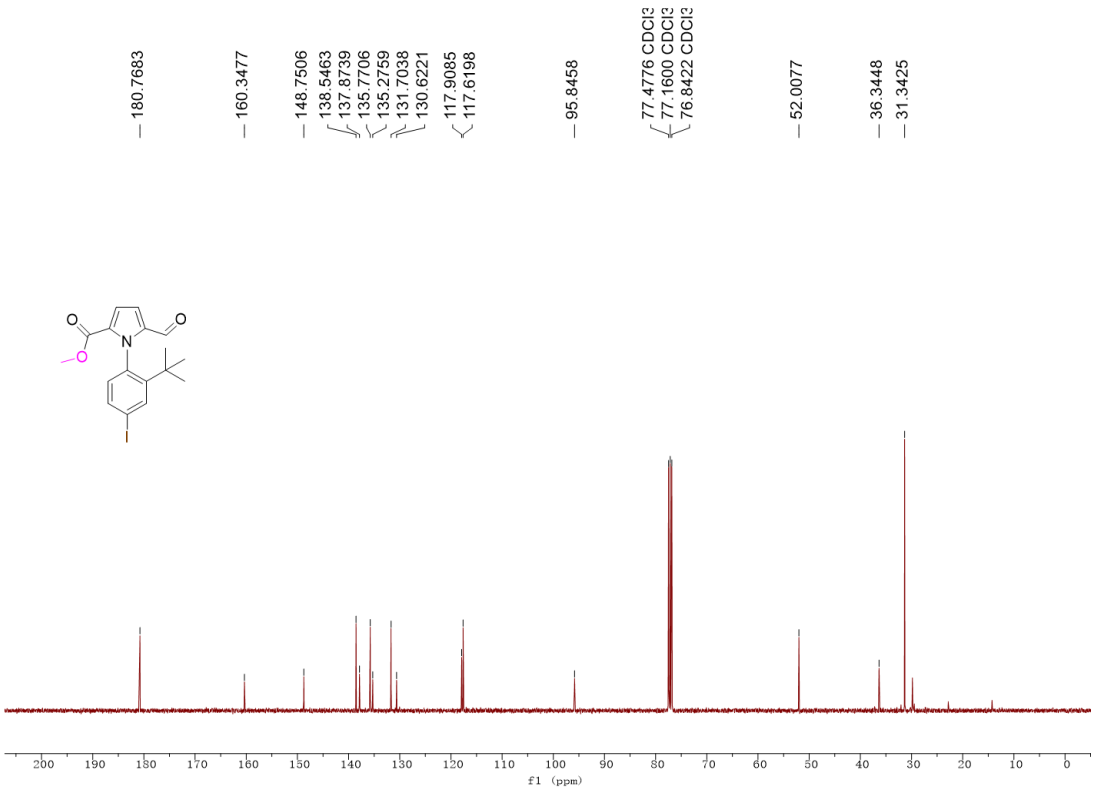
^{13}C NMR (101 MHz, Chloroform-*d*) of **3aa**



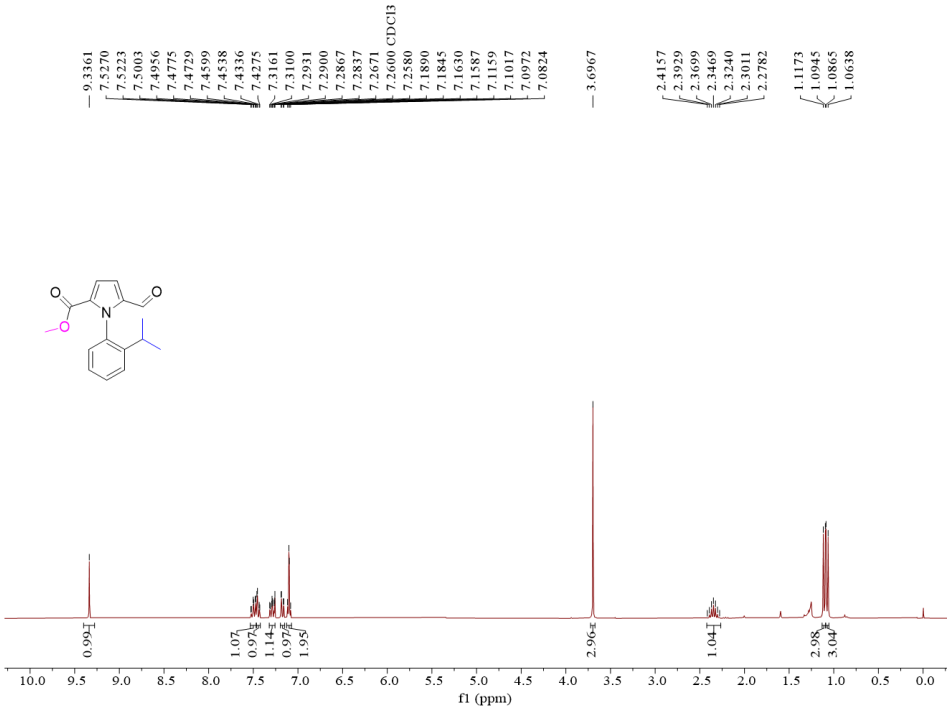
^{1}H NMR (400 MHz, Chloroform-*d*) of **3ab**



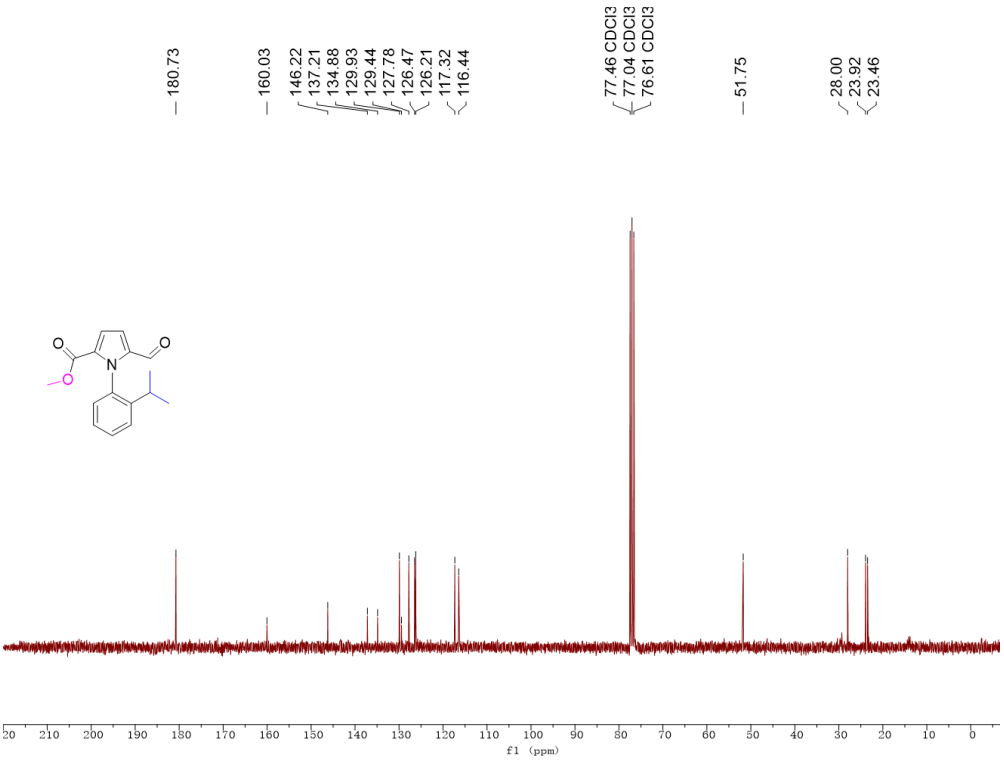
^{13}C NMR (101 MHz, Chloroform-*d*) of **3ab**



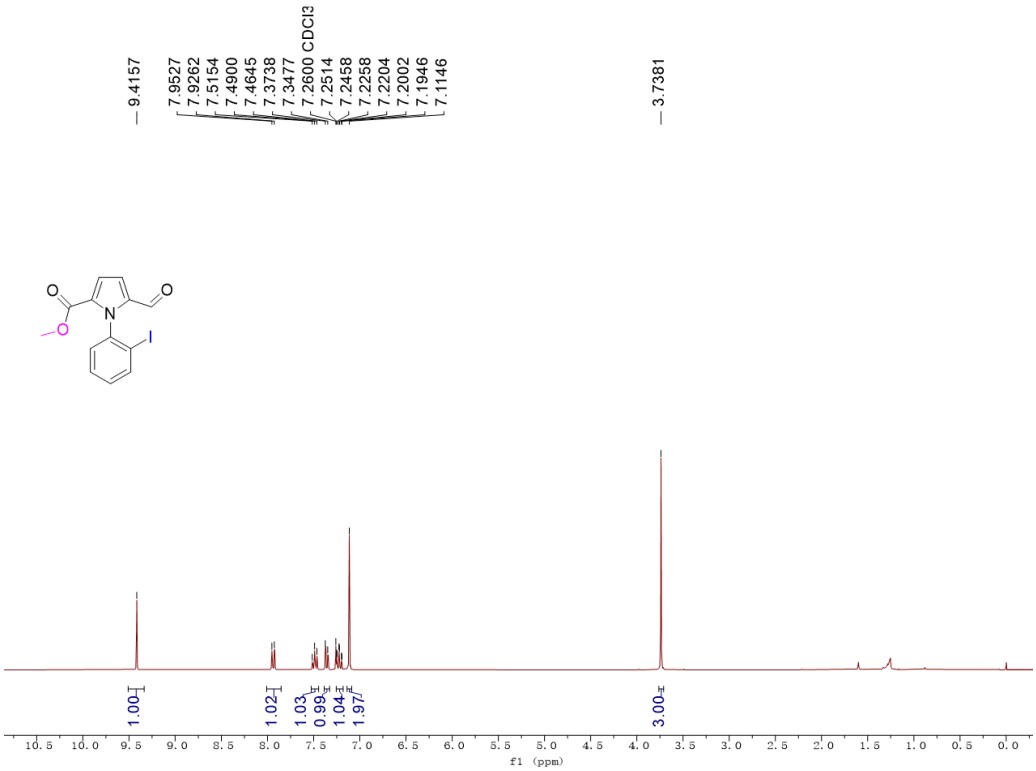
^{1}H NMR (400 MHz, Chloroform-*d*) of **3ac**



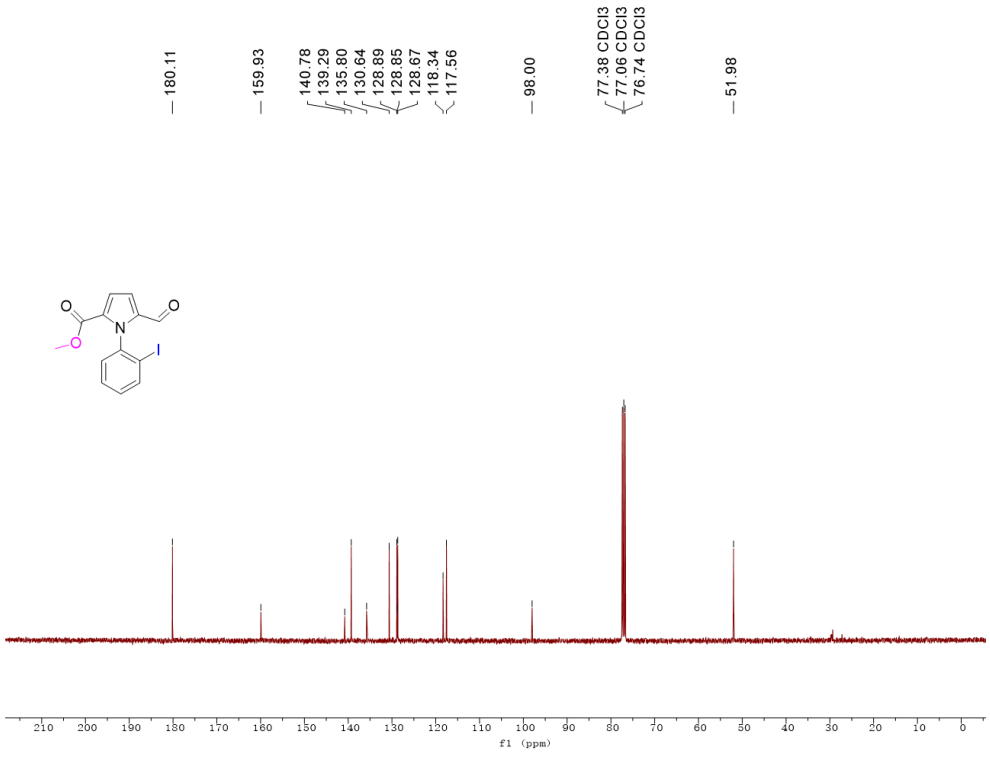
^{13}C NMR (101 MHz, Chloroform-*d*) of **3ac**



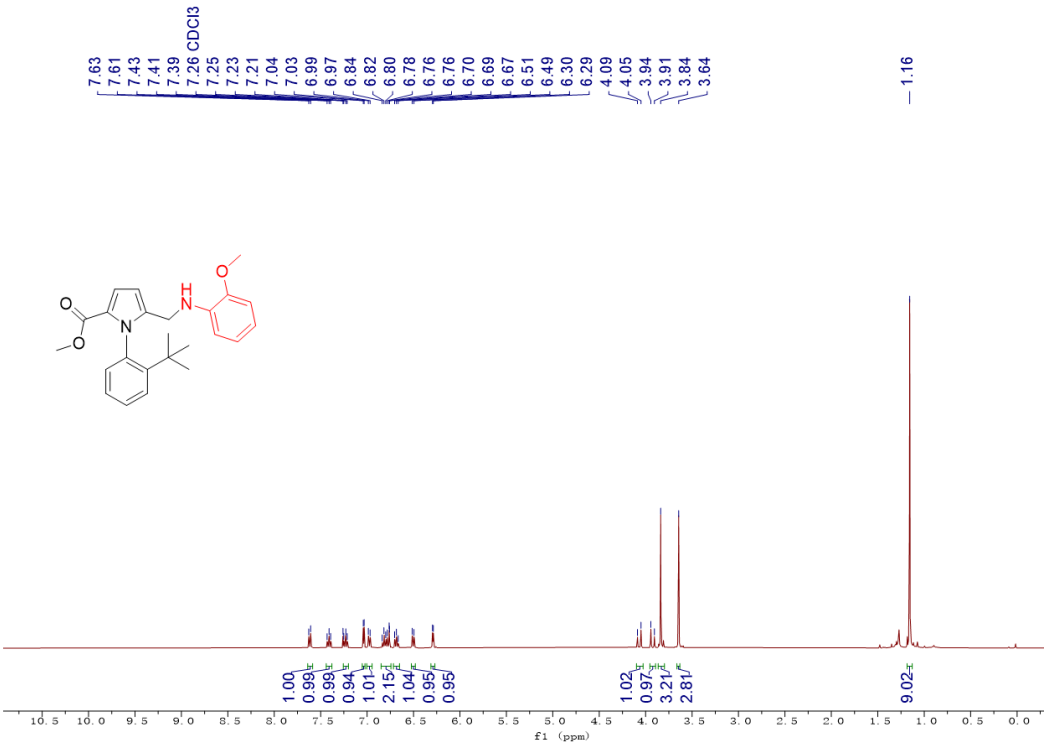
^{1}H NMR (400 MHz, Chloroform-*d*) of **3ad**



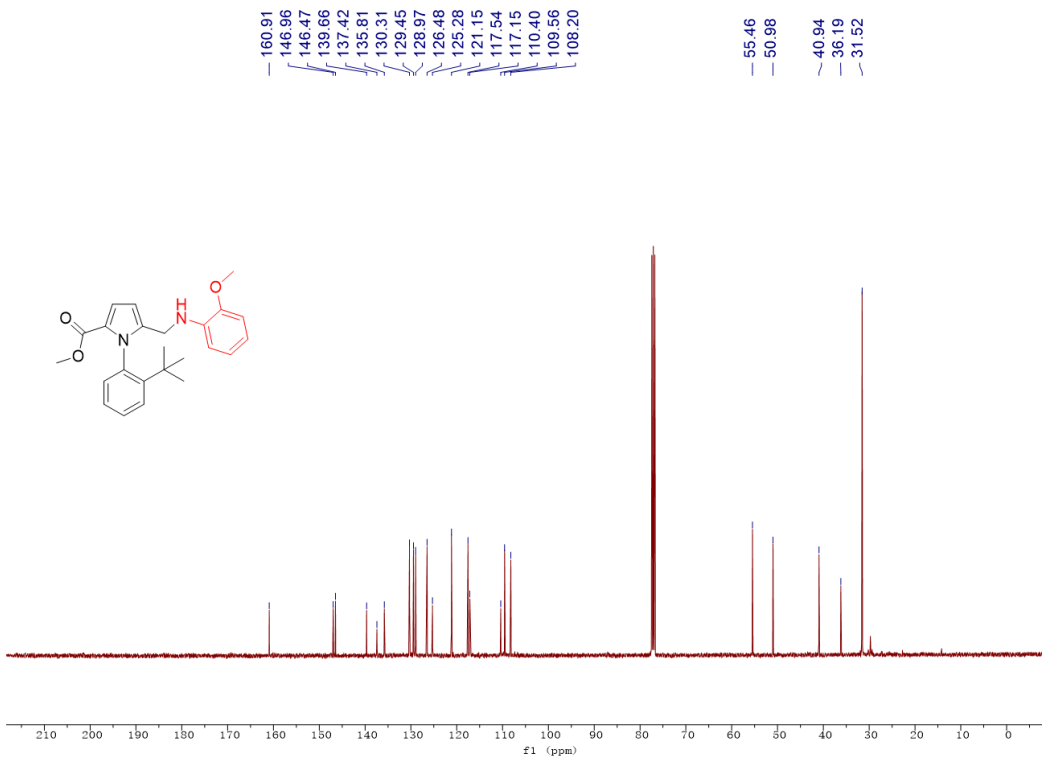
^{13}C NMR (101 MHz, Chloroform-*d*) of **3ad**



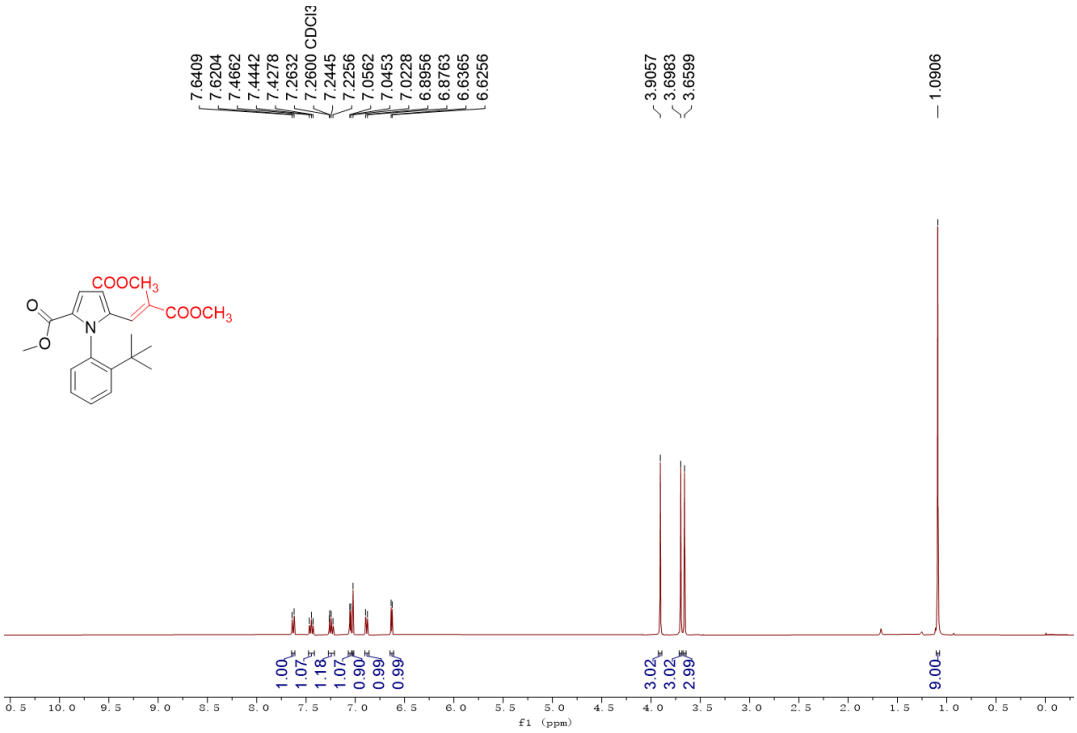
^{1}H NMR (400 MHz, Chloroform-*d*) of **4a**



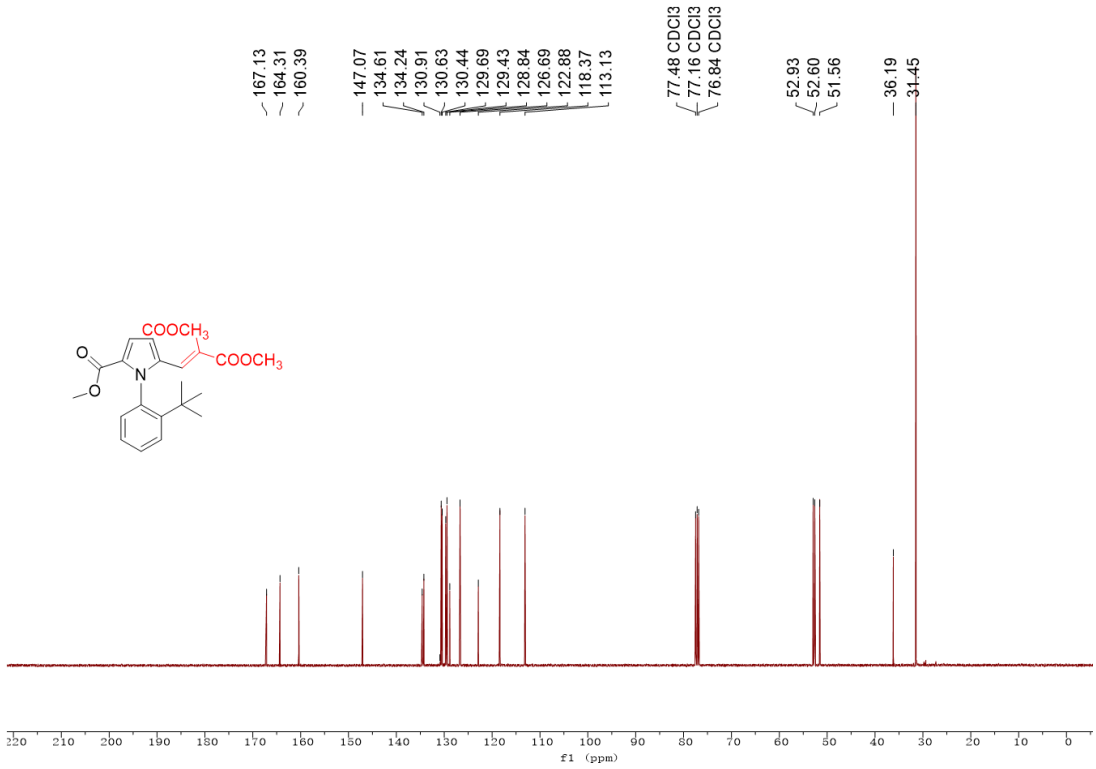
^{13}C NMR (101 MHz, Chloroform-*d*) of **4a**



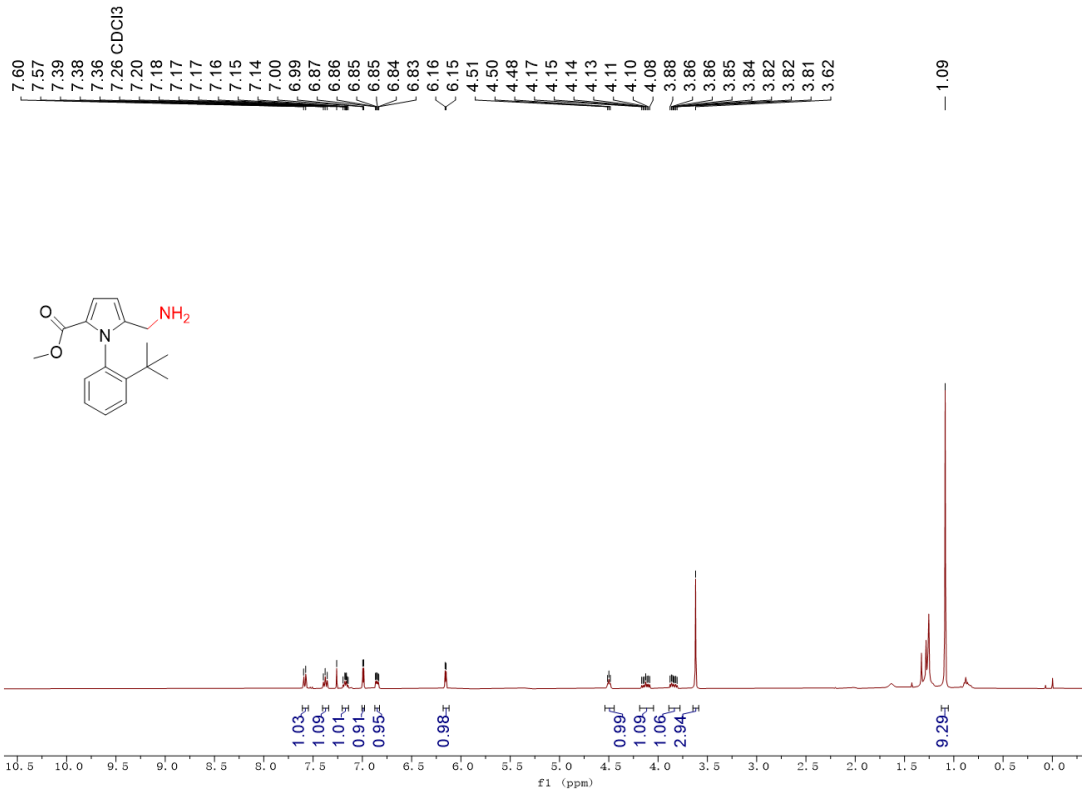
^{1}H NMR (400 MHz, Chloroform-*d*) of **4b**



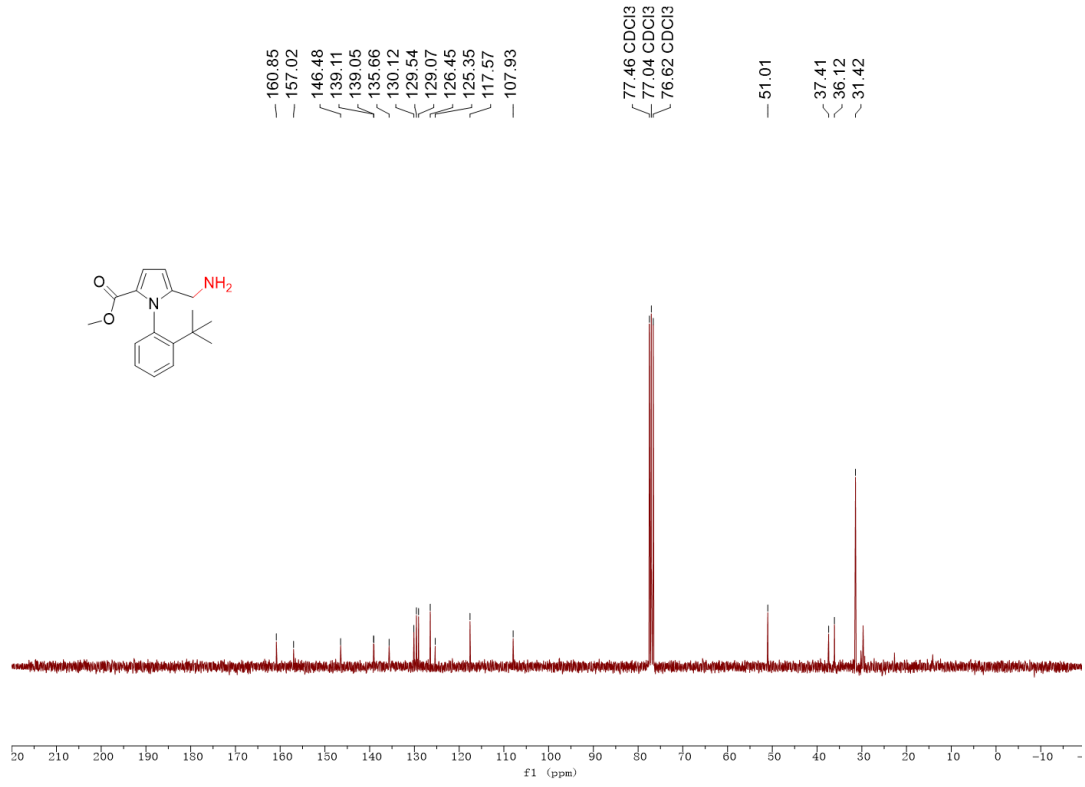
^{13}C NMR (101 MHz, Chloroform-*d*) of **4b**



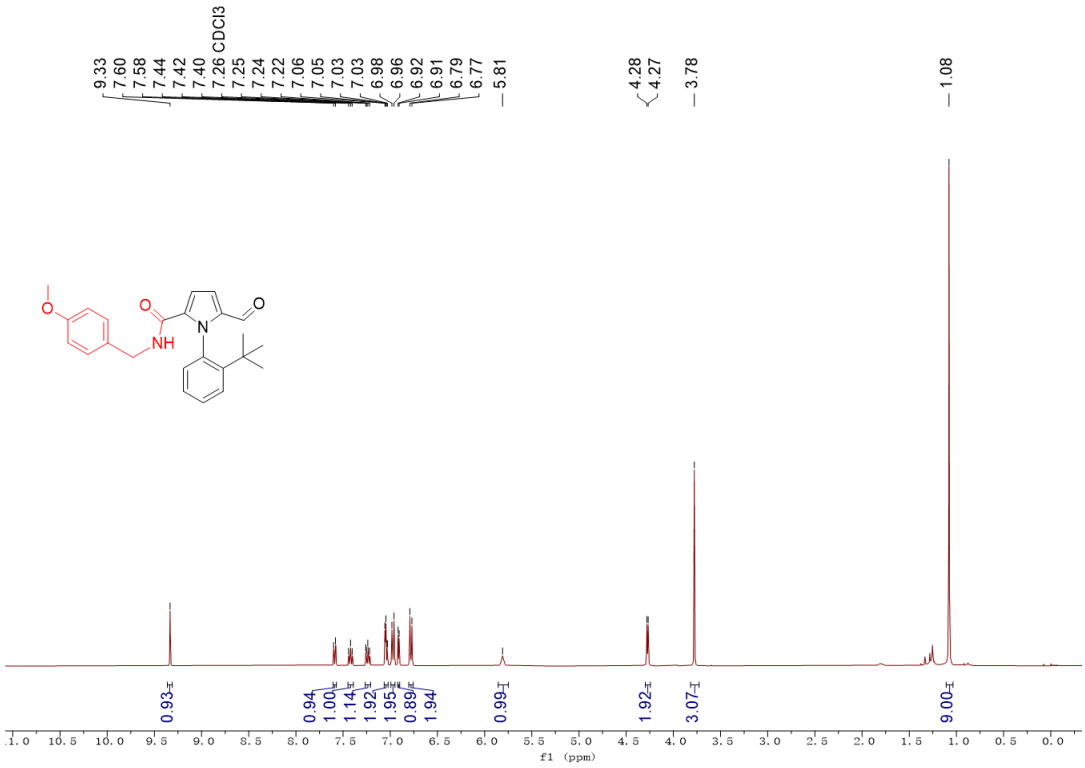
^{1}H NMR (400 MHz, Chloroform-*d*) of **4c**



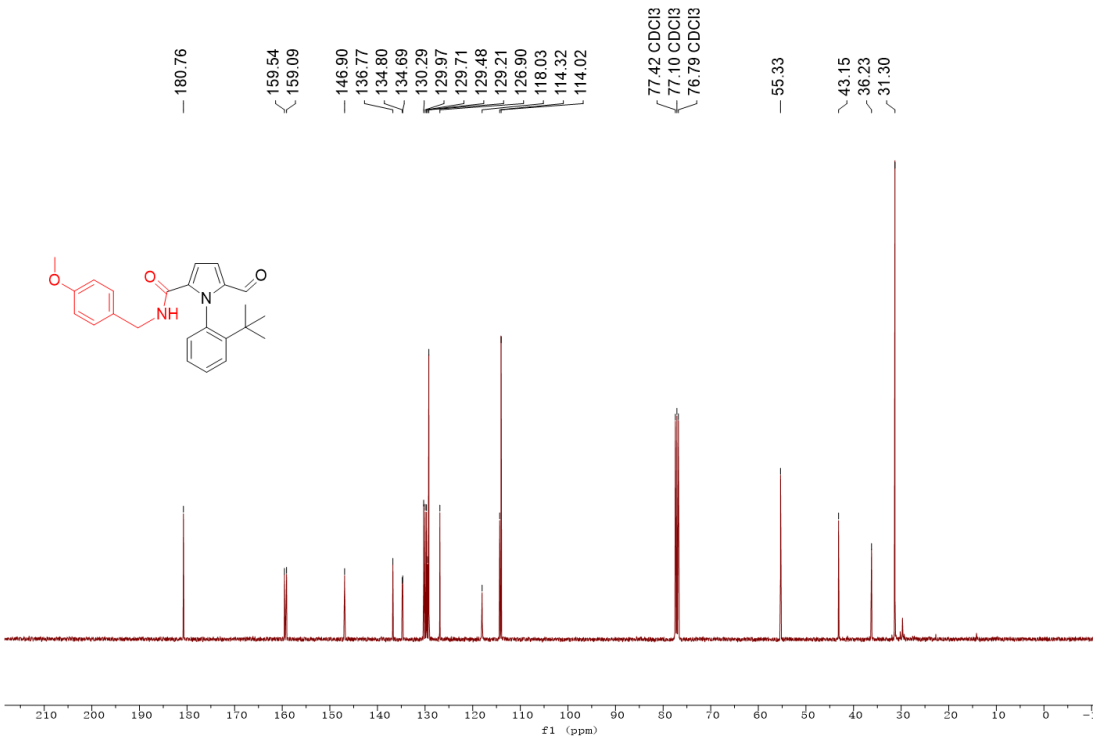
^{13}C NMR (75 MHz, Chloroform-*d*) of **4c**



^{1}H NMR (400 MHz, Chloroform-*d*) of **4d**

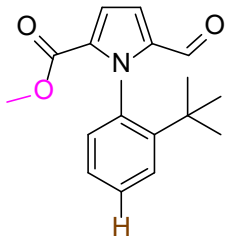


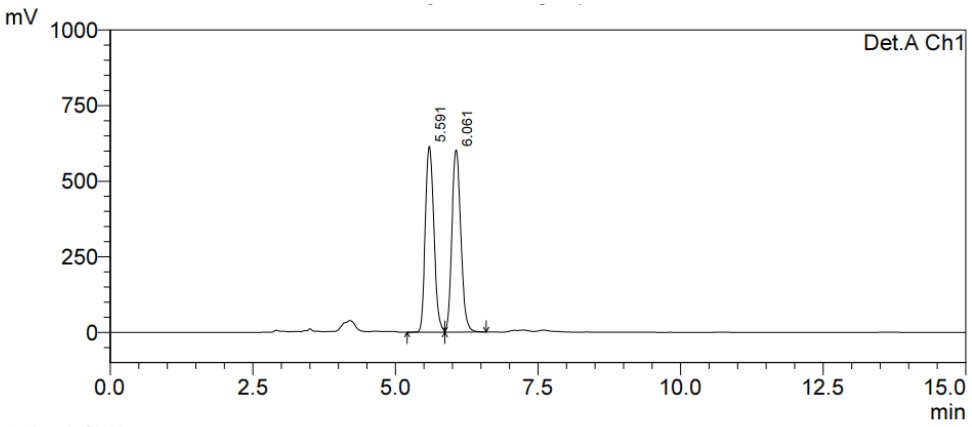
^{13}C NMR (101 MHz, Chloroform-*d*) of **4d**



10 Copies of the HPLC spectra

methyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3a)



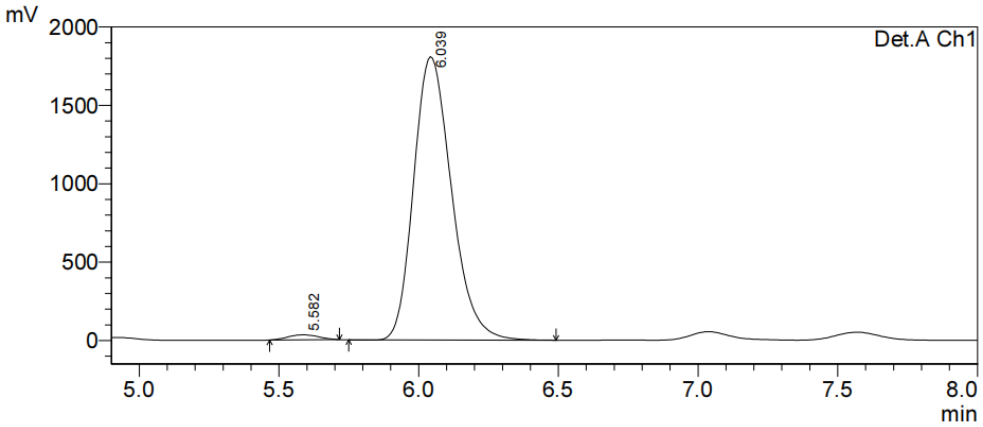


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.591	6480027	614313	49.646
2	6.061	6572401	602982	50.354
Total		13052428	1217295	100.000



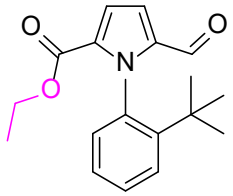
1 Det.A Ch1/254nm

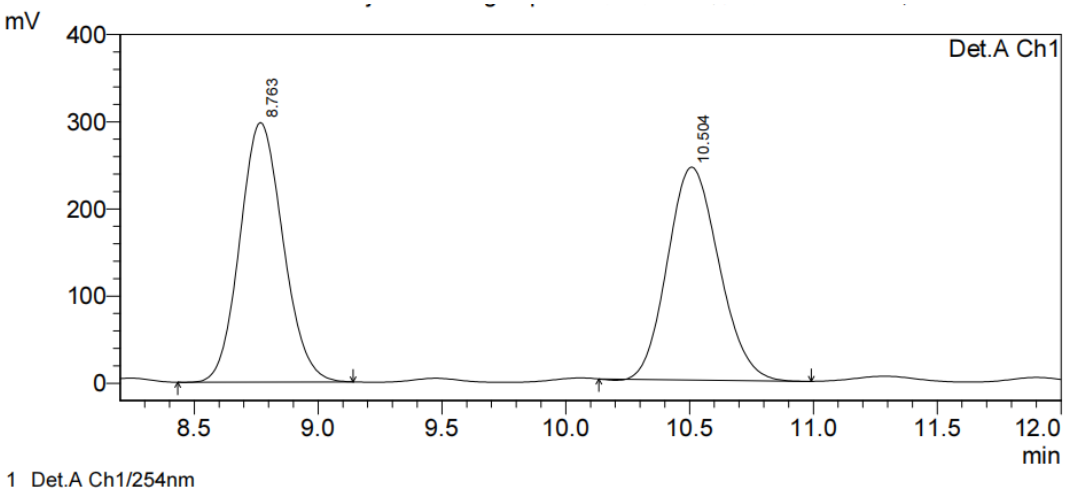
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.582	242818	31933	1.406
2	6.039	17025289	1808669	98.594
Total		17268108	1840602	100.000

ethyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3b)



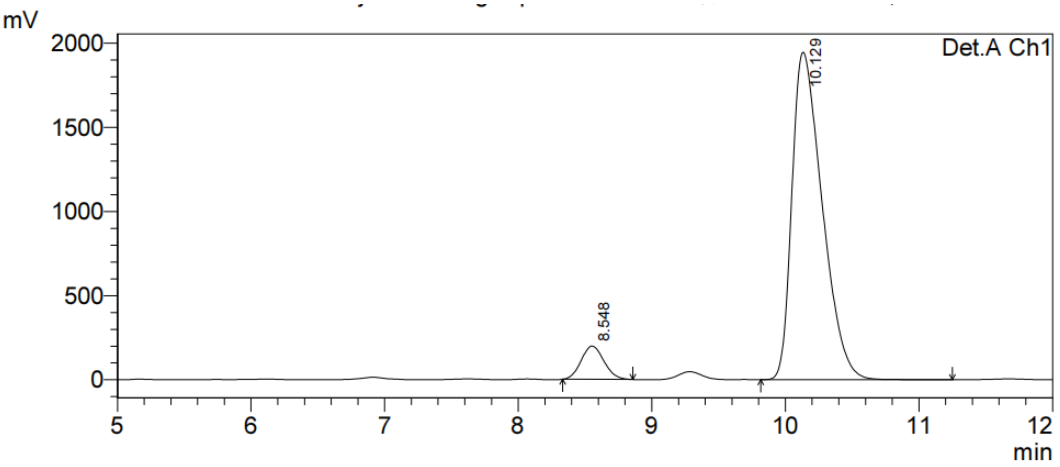


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.763	3614883	297862	50.633
2	10.504	3524496	244387	49.367
Total		7139379	542249	100.000



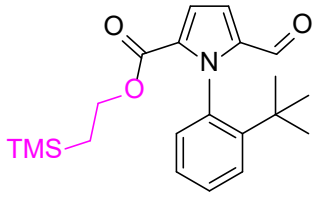
1 Det.A Ch1/254nm

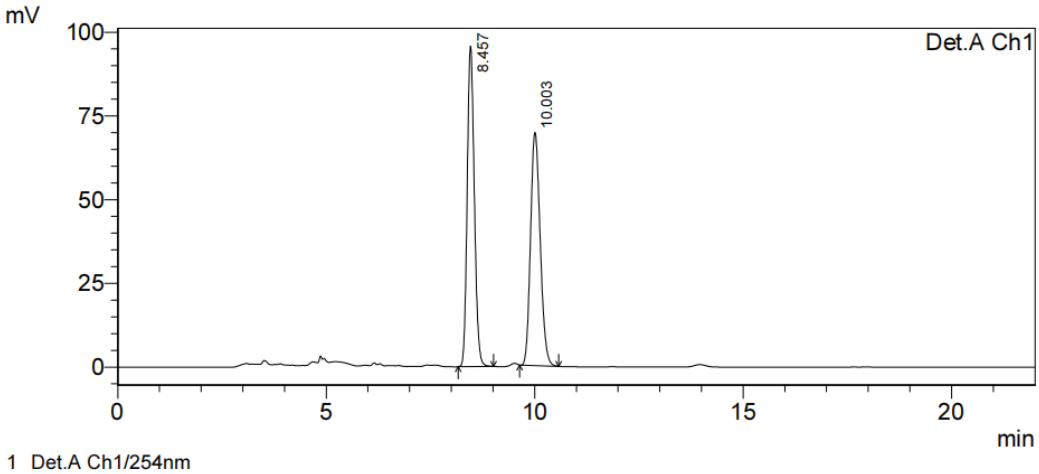
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.548	2354432	197675	7.144
2	10.129	30604574	1945063	92.856
Total		32959006	2142738	100.000

2-(trimethylsilyl)ethyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3c)



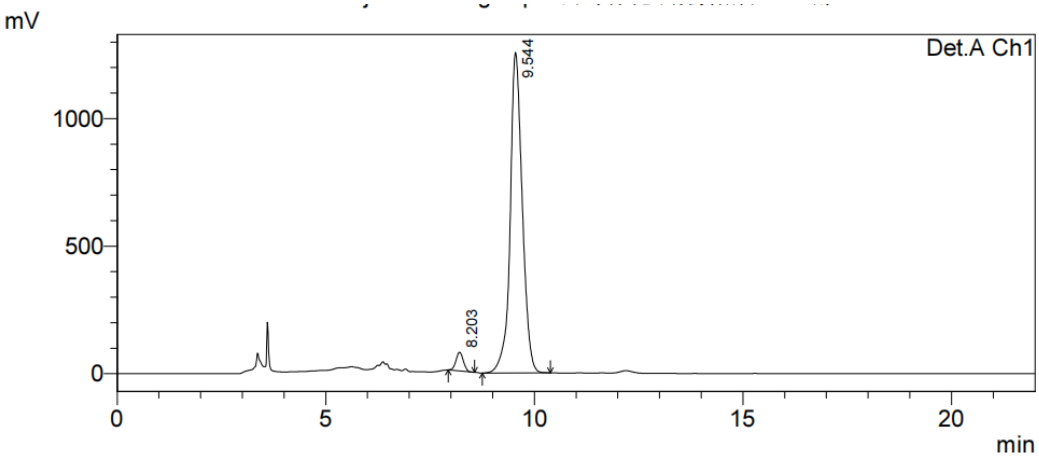


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.457	1135515	95633	50.372
2	10.003	1118722	69642	49.628
Total		2254237	165276	100.000



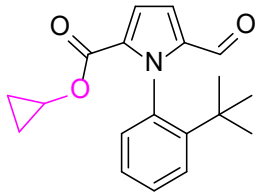
1 Det.A Ch1/254nm

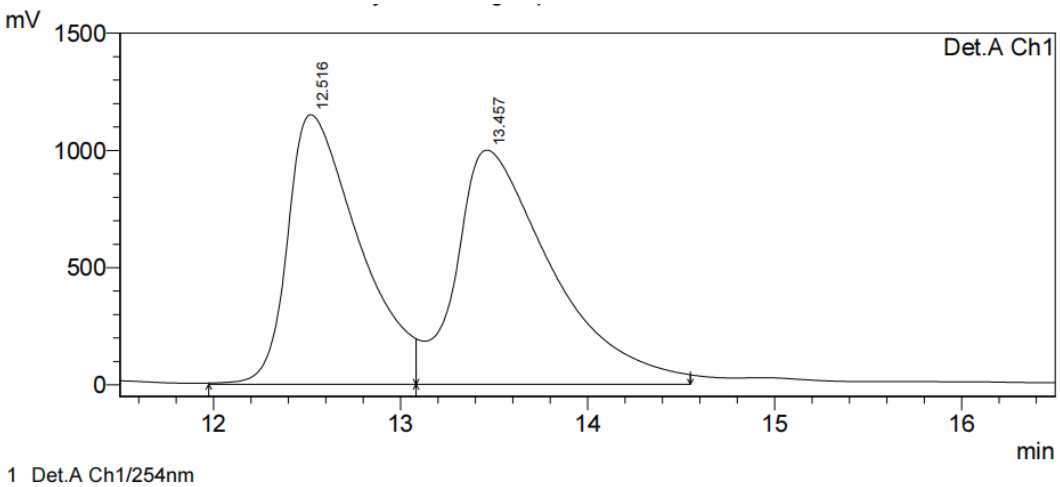
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	8.203	895406	72998	3.405
2	9.544	25399778	1256279	96.595
Total		26295184	1329277	100.000

cyclopropyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3d)



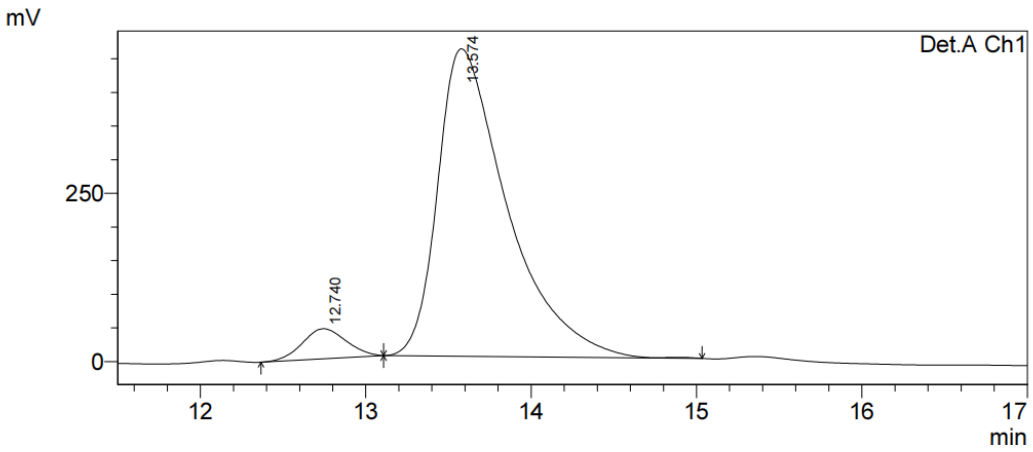


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.516	30590578	1149771	46.207	53.519
2	13.457	35612391	998558	53.793	46.481
Total		66202969	2148329	100.000	100.000



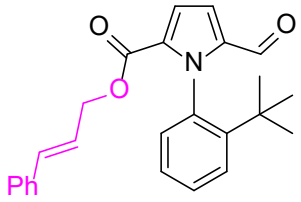
1 Det.A Ch1/254nm

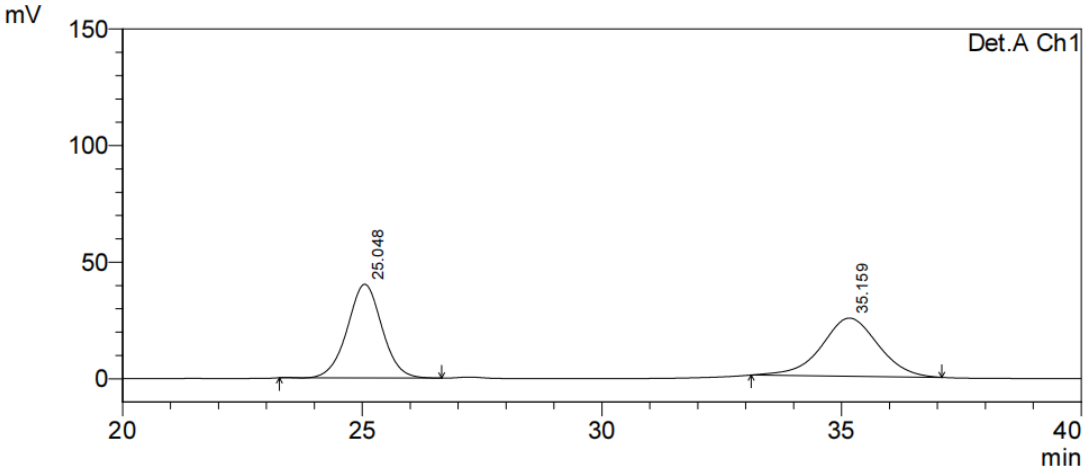
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.740	824670	44797	5.813
2	13.574	13362766	456753	94.187
Total		14187437	501550	100.000

cinnamyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3e)



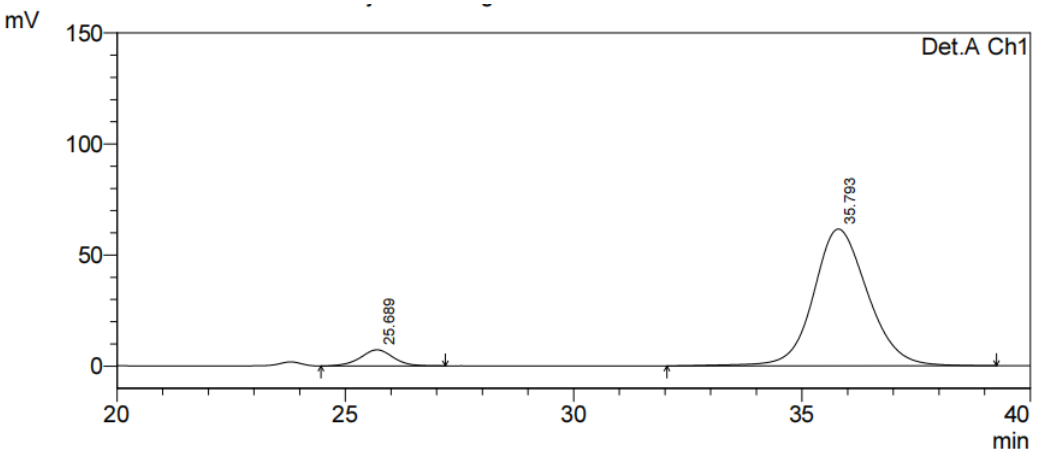


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.048	2024854	40206	49.646
2	35.159	2053771	24939	50.354
Total		4078625	65145	100.000



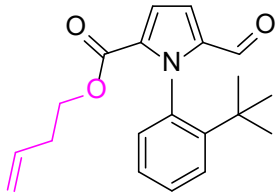
1 Det.A Ch1/254nm

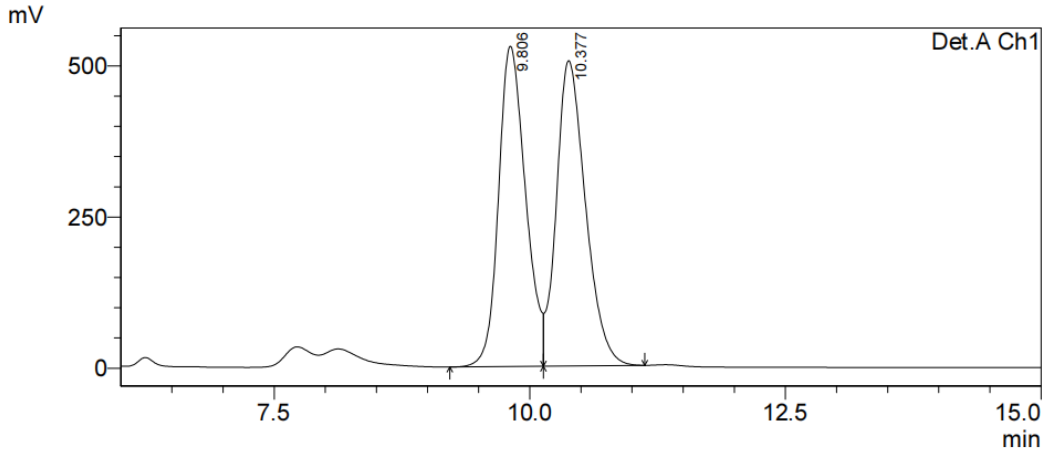
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.689	363182	7258	6.644
2	35.793	5102913	61596	93.356
Total		5466095	68854	100.000

but-3-en-1-yl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3f)



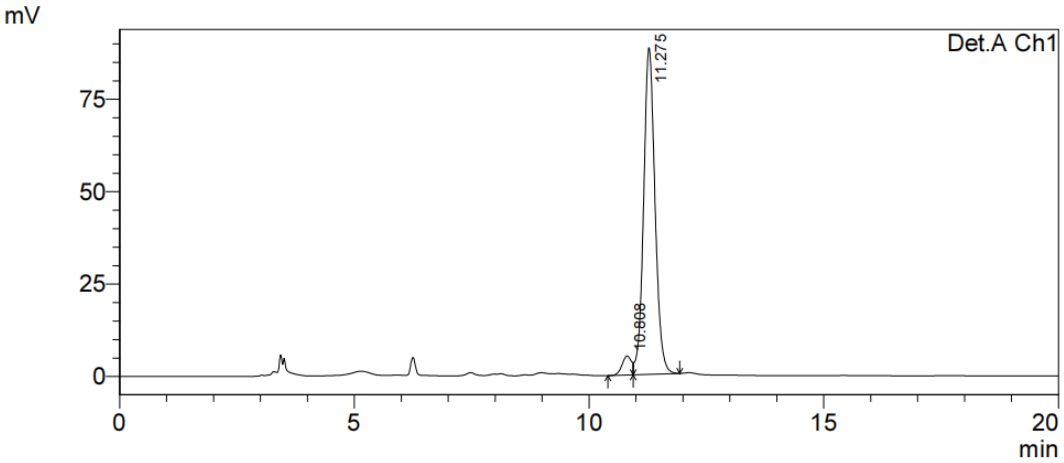


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	9.806	9750551	530196	49.374
2	10.377	9997870	505288	50.626
Total		19748421	1035485	100.000



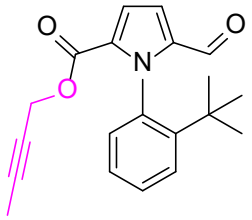
1 Det.A Ch1/254nm

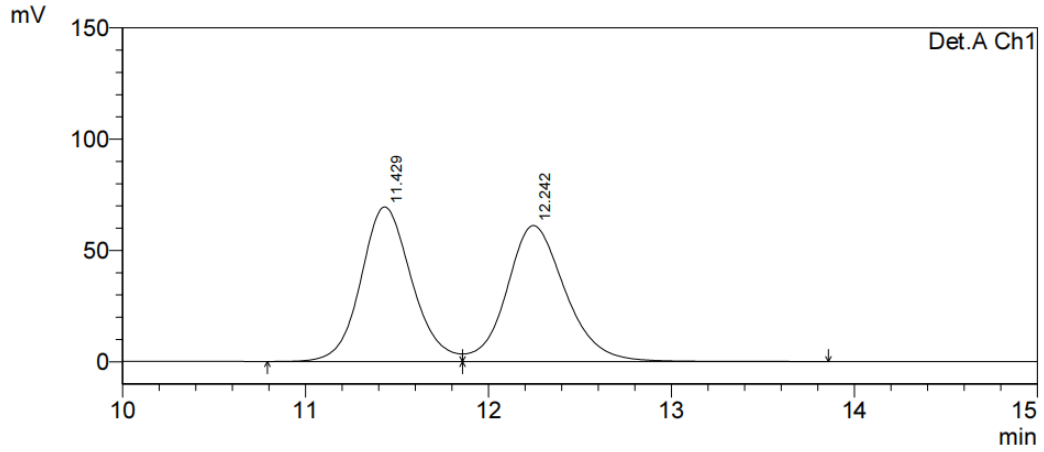
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.808	72893	5178	4.652
2	11.275	1494082	88337	95.348
Total		1566975	93516	100.000

but-2-yn-1-yl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3g)



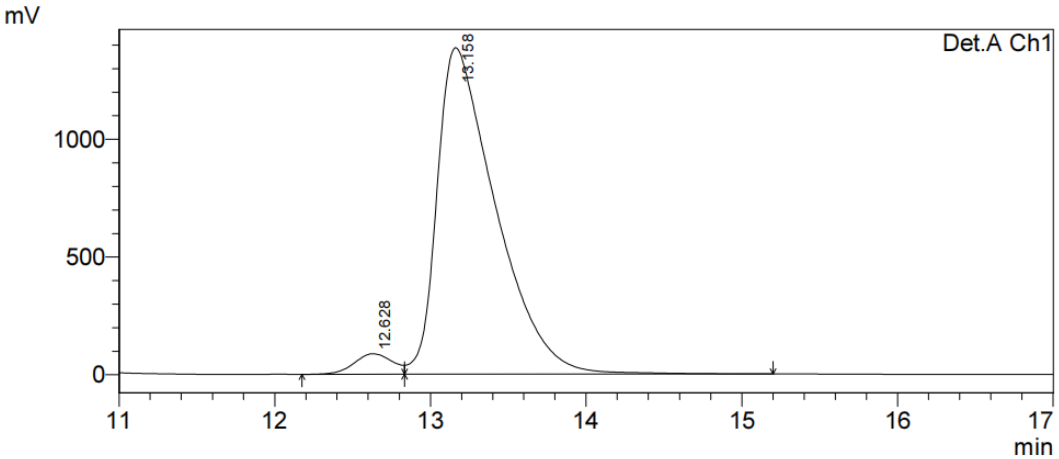


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.429	1338973	69454	49.636
2	12.242	1358587	61053	50.364
Total		2697560	130507	100.000



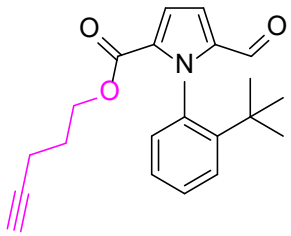
1 Det.A Ch1/254nm

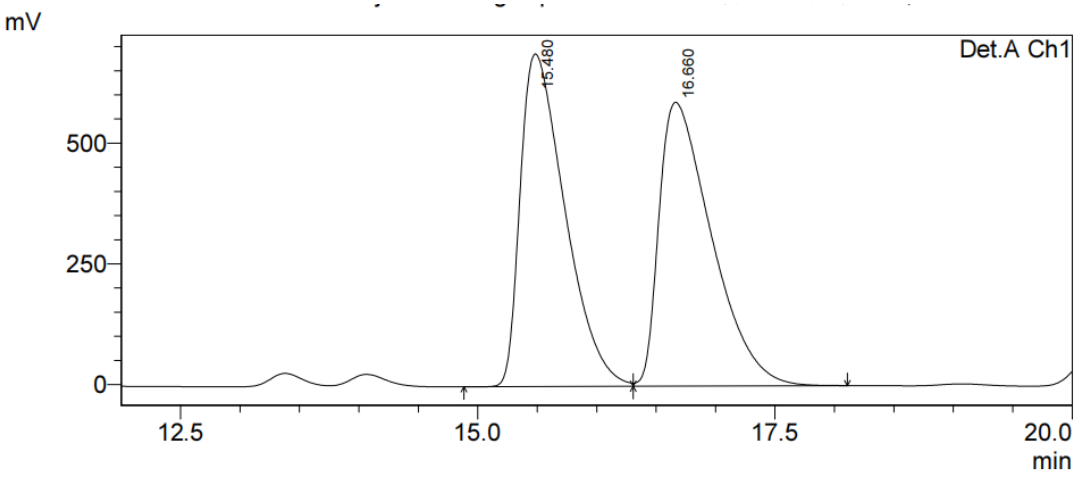
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.628	1502405	87287	3.974
2	13.158	36306745	1386377	96.026
Total		37809150	1473664	100.000

pent-4-yn-1-yl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3h)



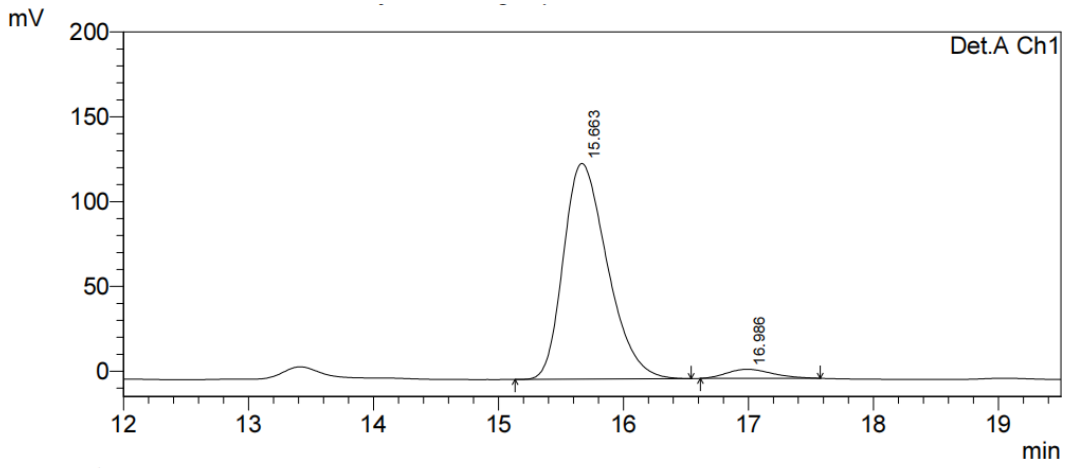


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.480	18028971	689266	49.900
2	16.660	18100984	587883	50.100
Total		36129955	1277149	100.000



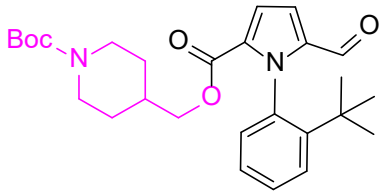
1 Det.A Ch1/254nm

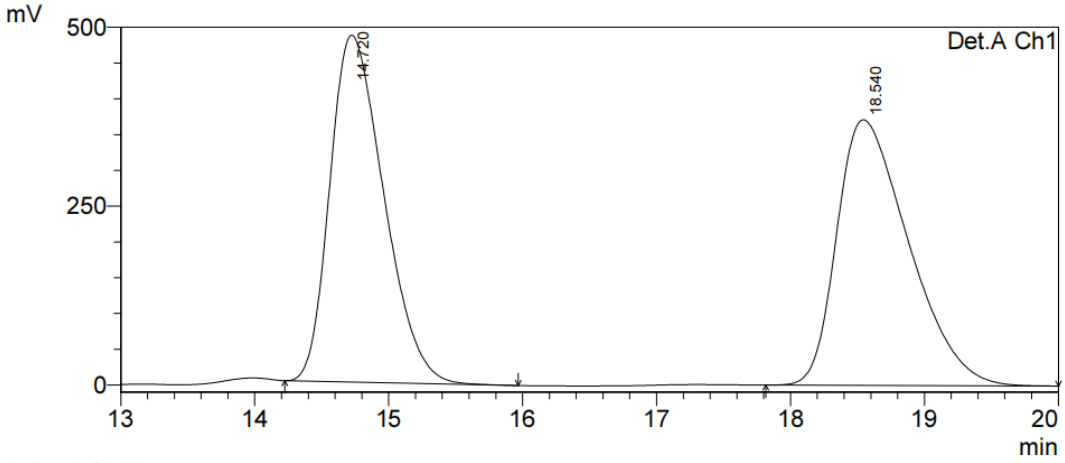
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.663	3110780	127198	95.805
2	16.986	136223	5380	4.195
Total		3247003	132579	100.000

***tert*-butyl 4-(((1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carbonyl)oxy)methyl) piperidine-1-carboxylate (3i)**



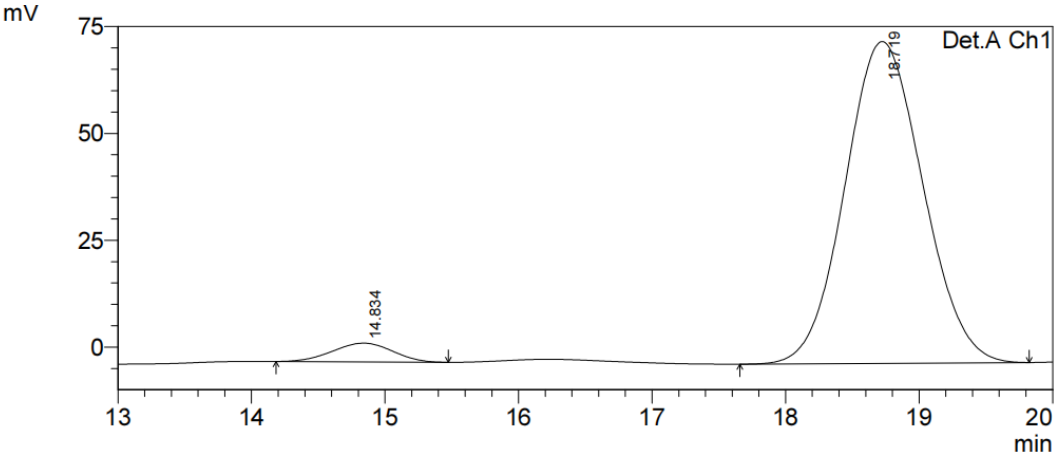


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.720	13583425	484955	49.546
2	18.540	13832511	371144	50.454
Total		27415936	856099	100.000



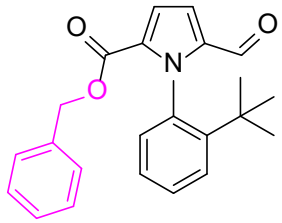
1 Det.A Ch1/254nm

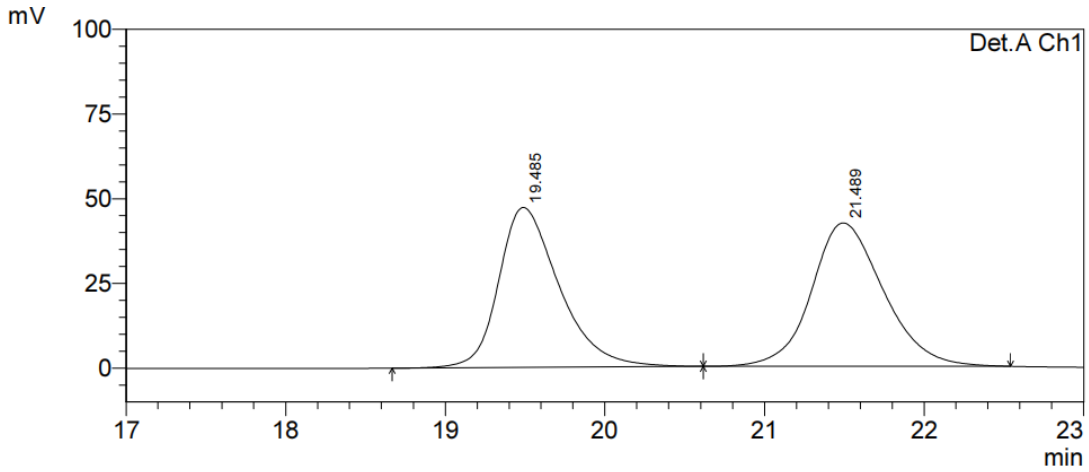
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.834	137792	4390	4.322
2	18.719	3050213	75304	95.678
Total		3188005	79694	100.000

benzyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3j)



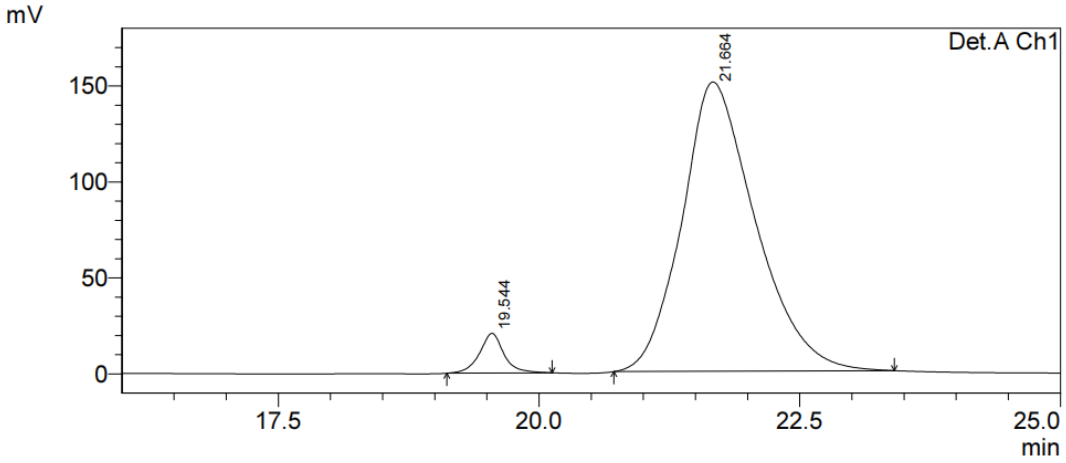


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.485	1248599	47241	48.427
2	21.489	1329739	42334	51.573
Total		2578338	89575	100.000



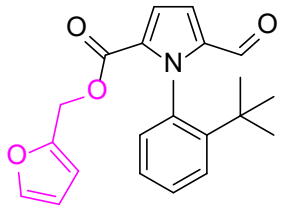
1 Det.A Ch1/254nm

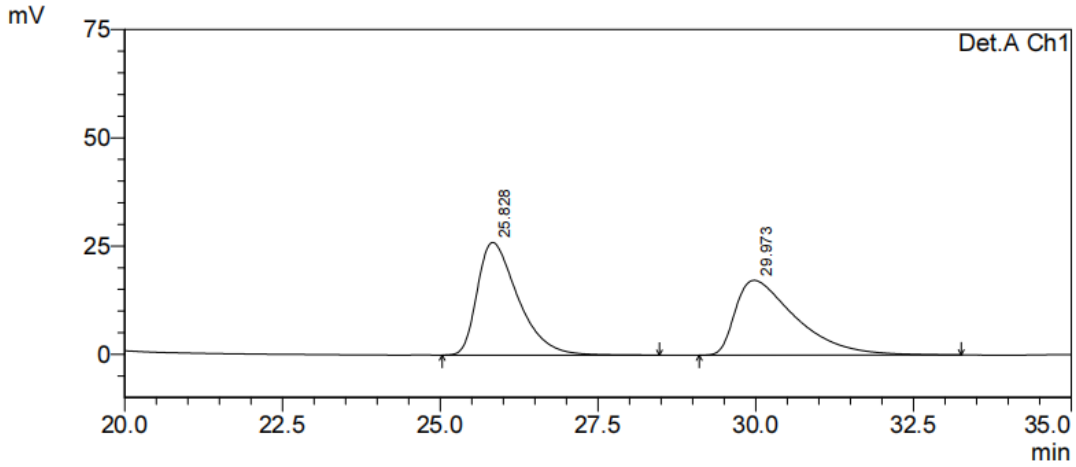
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.544	337556	20695	4.365
2	21.664	7396400	150680	95.635
Total		7733956	171376	100.000

furan-2-ylmethyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3k)



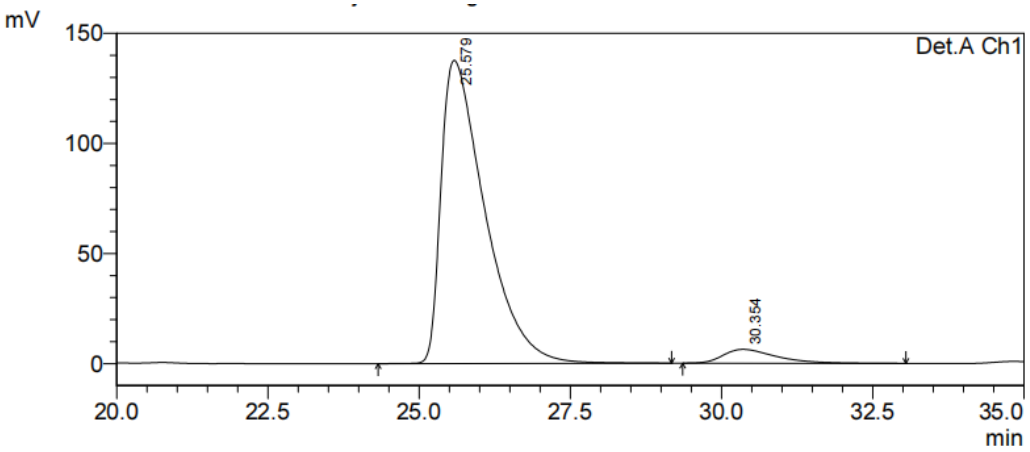


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.828	1171710	26017	50.333
2	29.973	1156229	17293	49.667
Total		2327940	43310	100.000



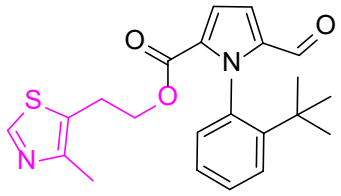
1 Det.A Ch1/254nm

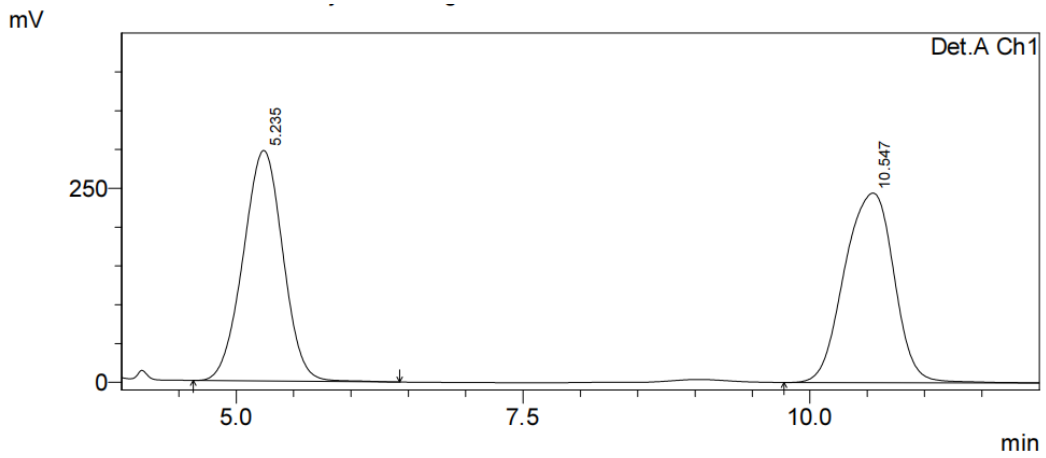
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	25.579	6939305	137707	94.793
2	30.354	381210	6280	5.207
Total		7320515	143986	100.000

2-(4-methylthiazol-5-yl)ethyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3l)



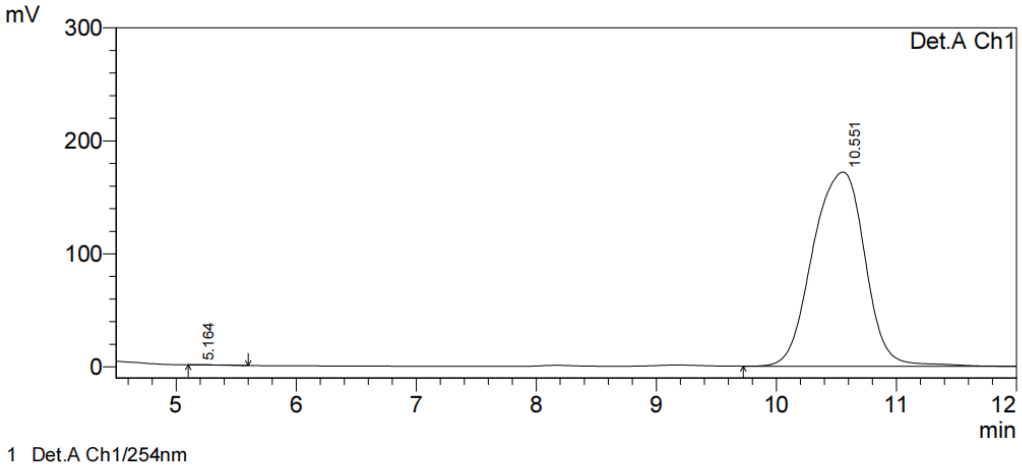


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.235	7168228	297172	49.406
2	10.547	7340458	244273	50.594
Total		14508686	541445	100.000



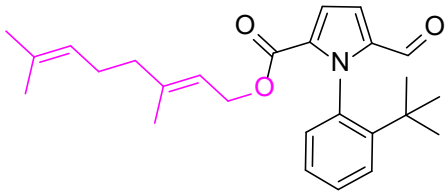
1 Det.A Ch1/254nm

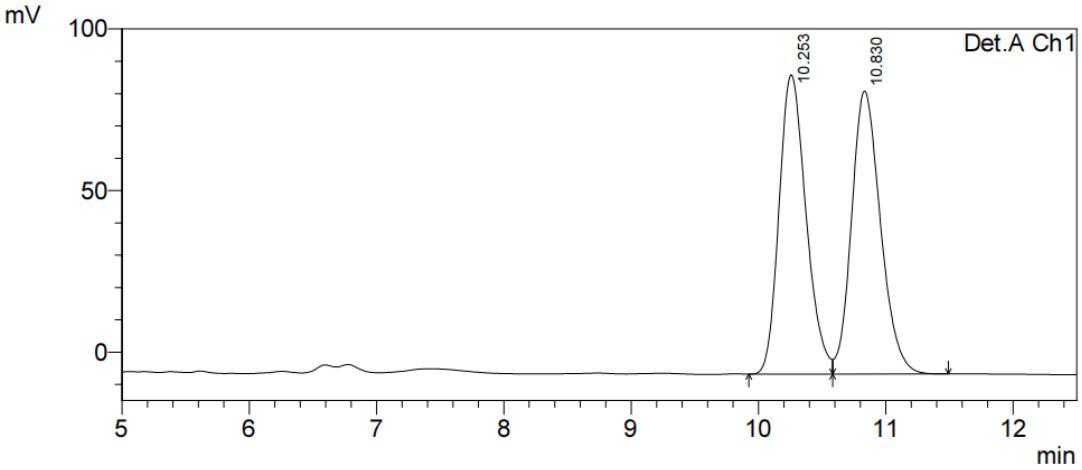
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.164	2781	118	0.053
2	10.551	5207890	171827	99.947
Total		5210670	171945	100.000

(*E*)-3,7-dimethylocta-2,6-dien-1-yl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3m)



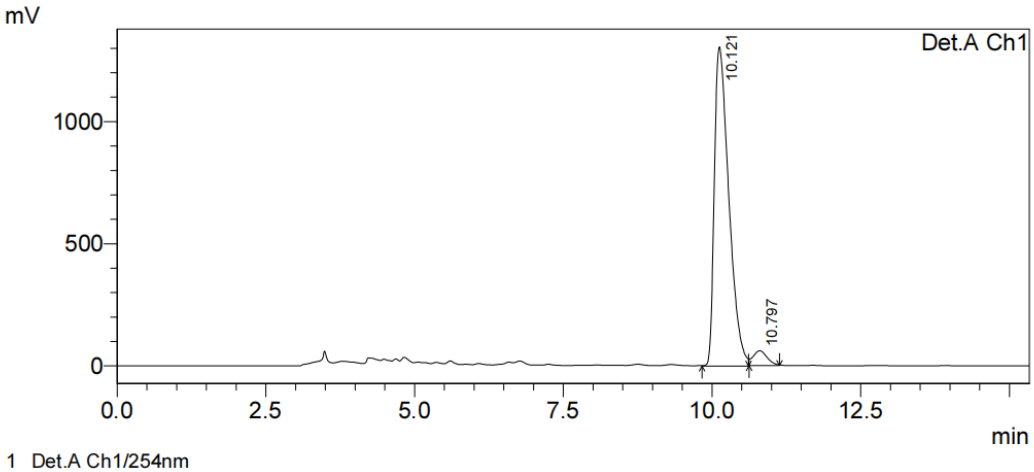


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.253	1367433	92715	49.673
2	10.830	1385438	87582	50.327
Total		2752872	180297	100.000



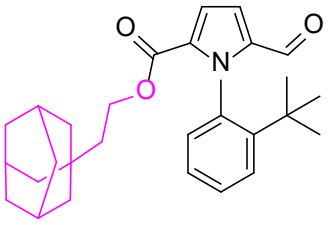
1 Det.A Ch1/254nm

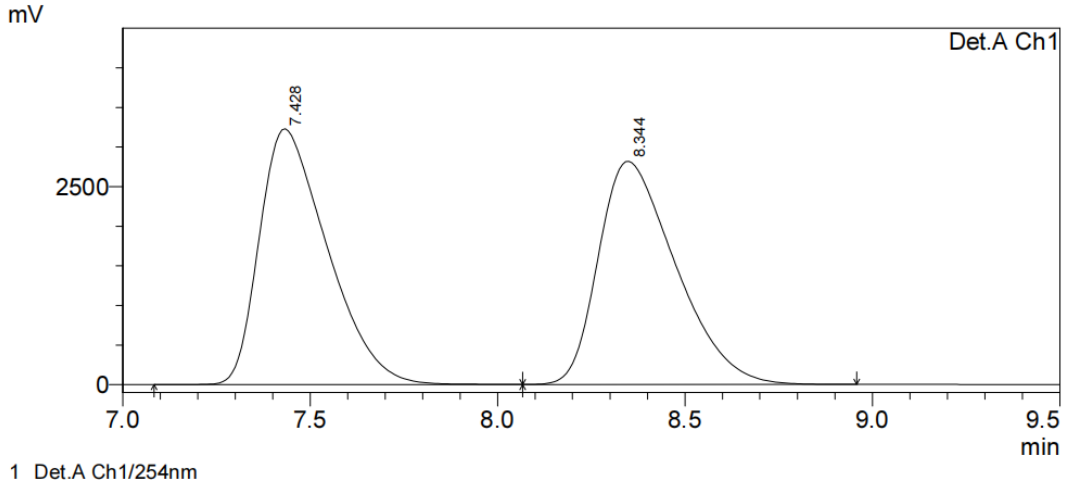
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.121	22113984	1306164	95.658
2	10.797	1003716	61029	4.342
Total		23117700	1367193	100.000

2-(adamantan-1-yl)ethyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3n)



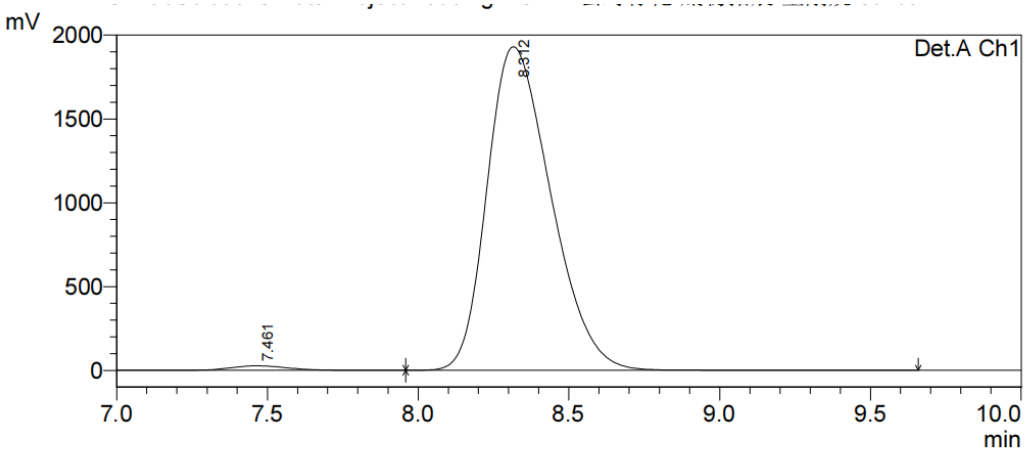


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.428	40735171	3228406	50.194
2	8.344	40419835	2818287	49.806
Total		81155006	6046694	100.000



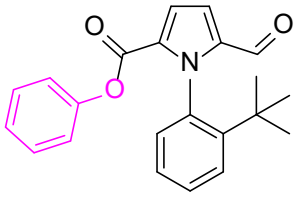
1 Det.A Ch1/254nm

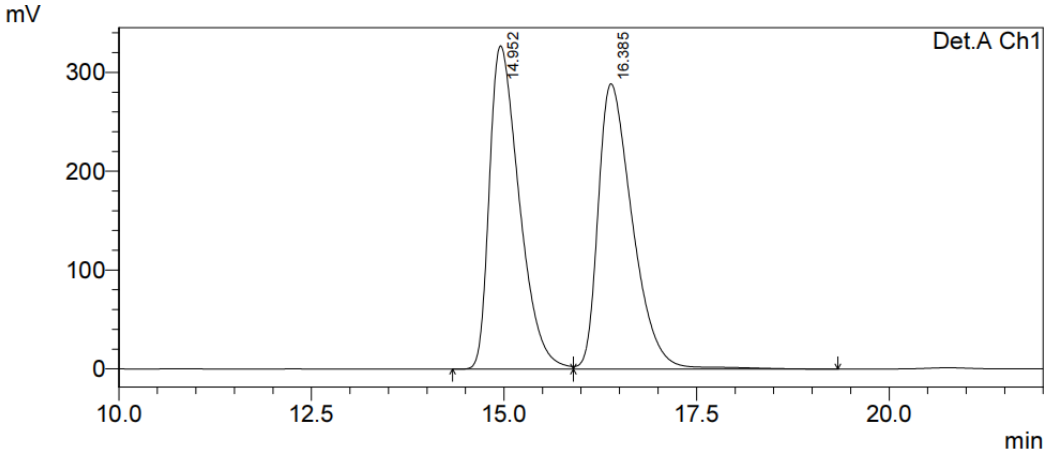
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.461	354874	26624	1.235
2	8.312	28386849	1931231	98.765
Total		28741723	1957855	100.000

phenyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3o)



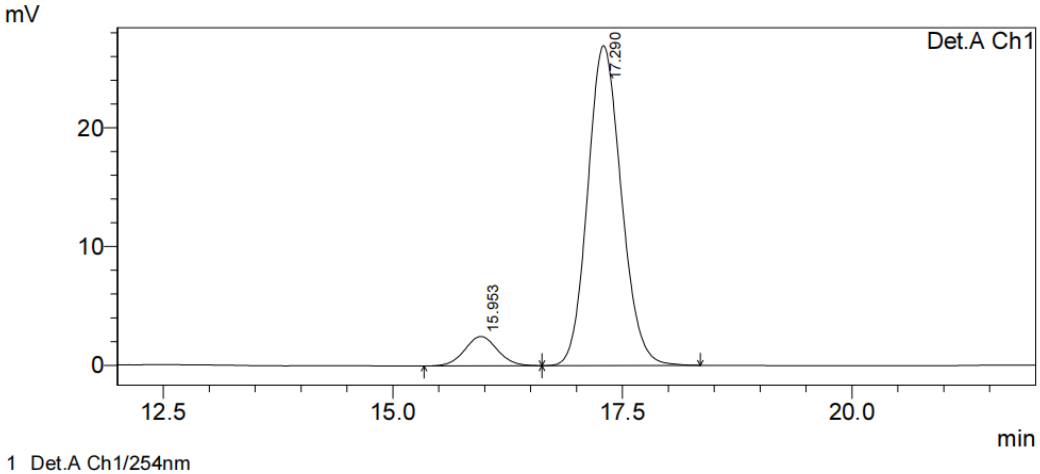


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.952	8828668	327243	49.654
2	16.385	8951586	288817	50.346
Total		17780254	616060	100.000



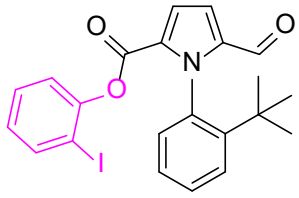
1 Det.A Ch1/254nm

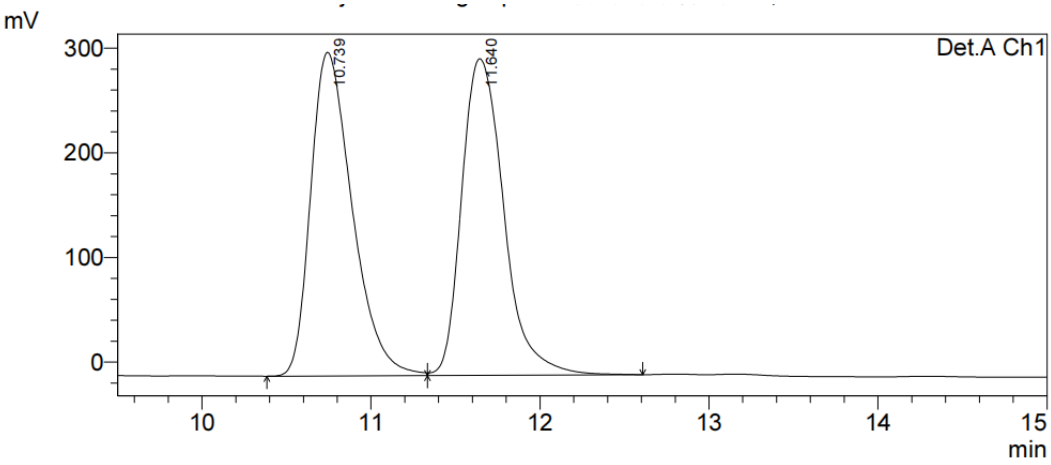
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.953	61583	2470	8.244
2	17.290	685443	26918	91.756
Total		747026	29388	100.000

2-iodophenyl 1-(2-(tert-butyl)phenyl)-5-formyl-1H-pyrrole-2-carboxylate (3p)



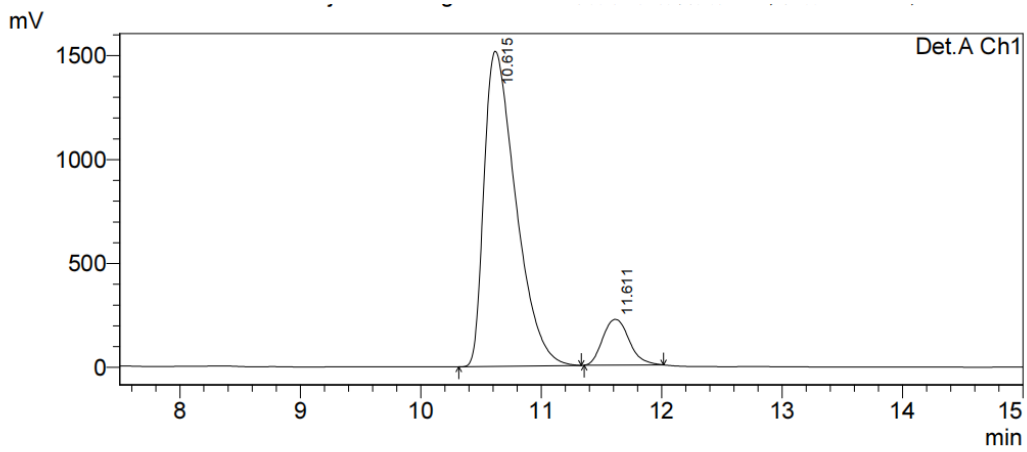


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.739	5288145	309372	50.204
2	11.640	5245140	302764	49.796
Total		10533285	612137	100.000



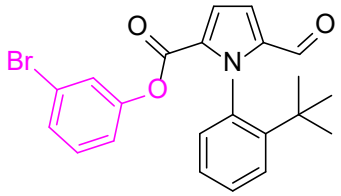
1 Det.A Ch1/254nm

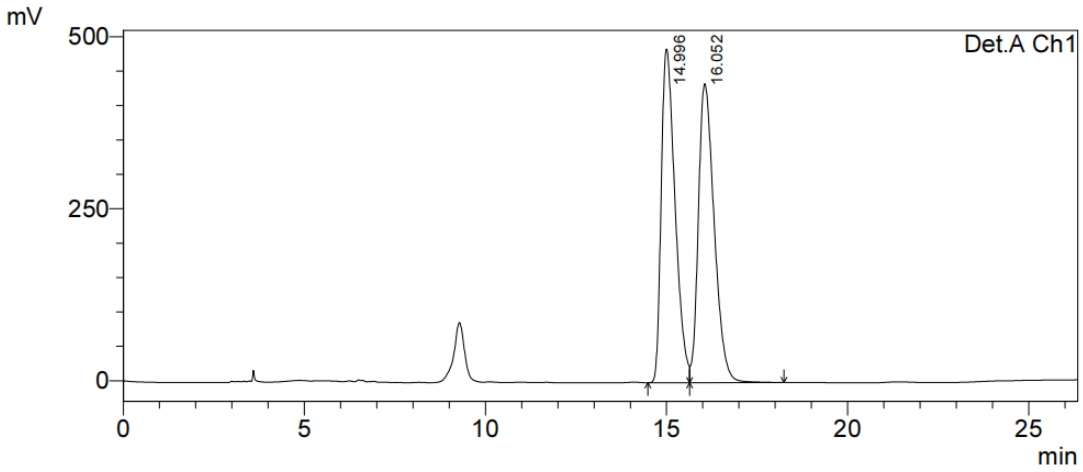
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.615	27846220	1516981	89.186
2	11.611	3376526	220300	10.814
Total		31222747	1737282	100.000

3-bromophenyl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3q)



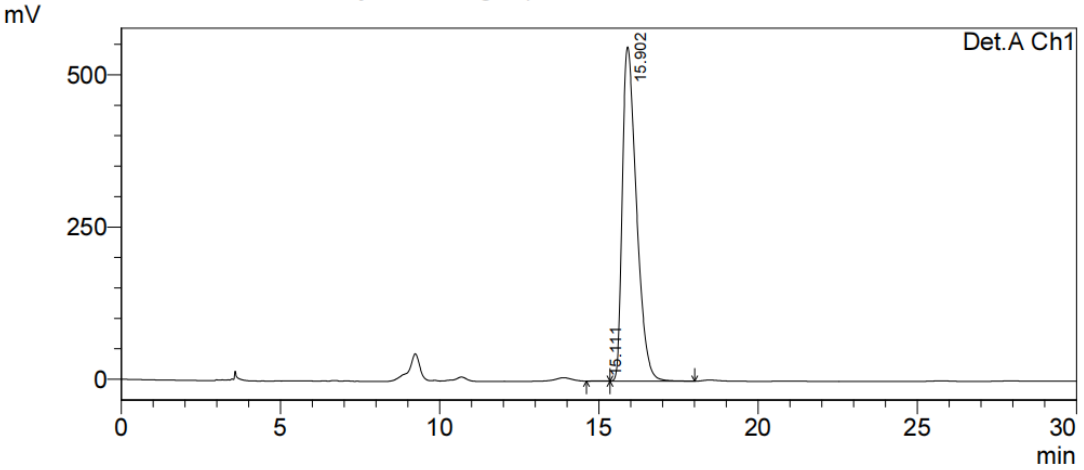


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	14.996	12898497	484863	49.408
2	16.052	13207674	434599	50.592
Total		26106171	919462	100.000



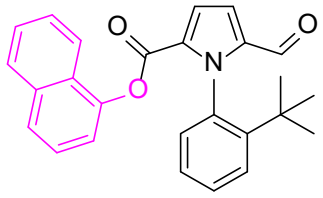
1 Det.A Ch1/254nm

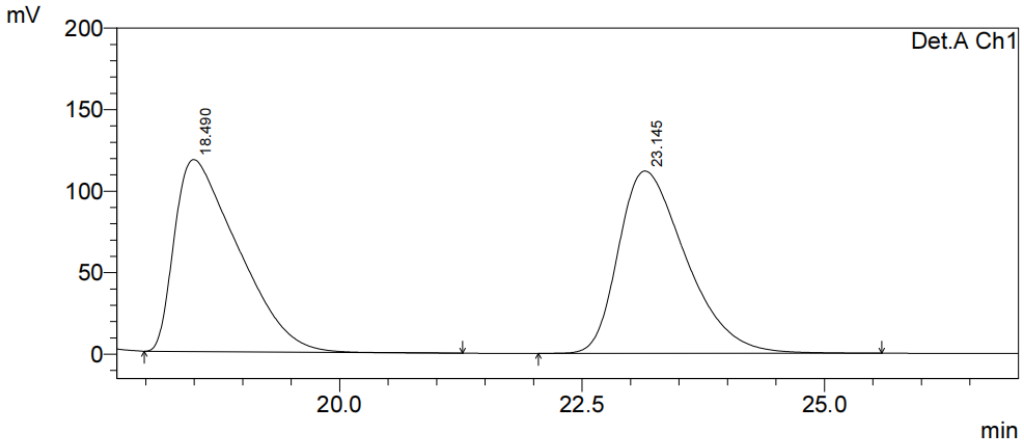
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.111	15574	583	0.092
2	15.902	16964100	549041	99.908
Total		16979673	549624	100.000

naphthalen-1-yl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3r)



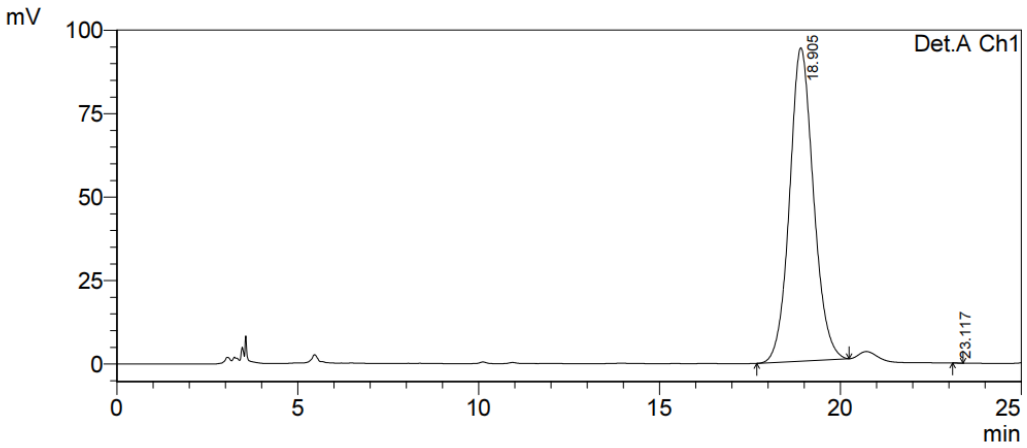


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.490	5380441	117797	49.800
2	23.145	5423707	111874	50.200
Total		10804148	229672	100.000



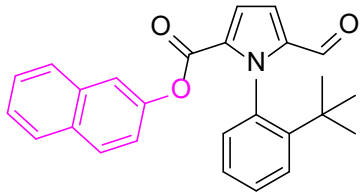
1 Det.A Ch1/254nm

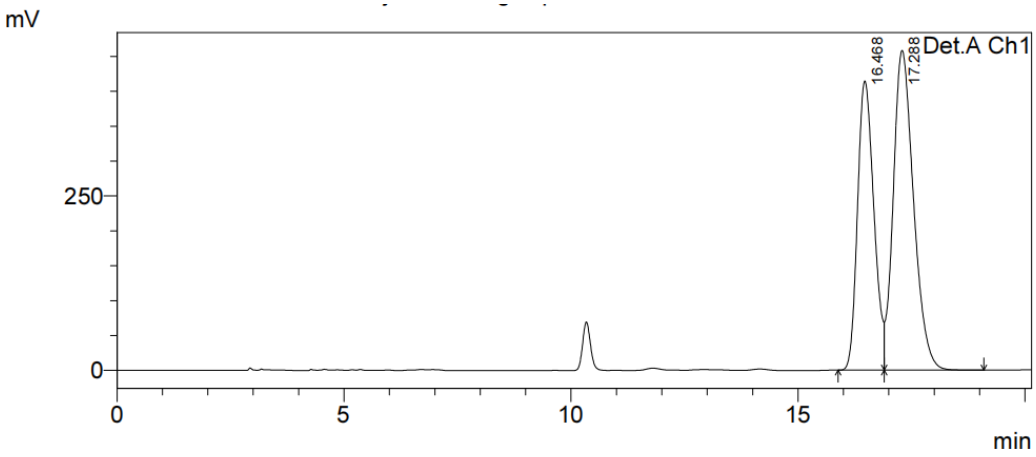
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	18.905	4317009	93910	99.999
2	23.117	41	1	0.001
Total		4317050	93911	100.000

naphthalen-2-yl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3s)



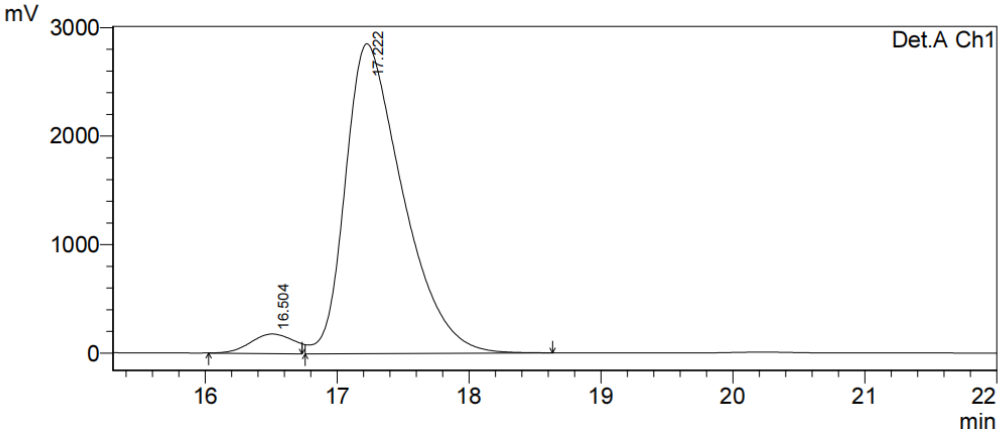


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.468	10384432	414511	42.188
2	17.288	14229961	458110	57.812
Total		24614392	872620	100.000



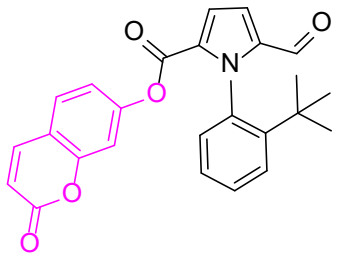
1 Det.A Ch1/254nm

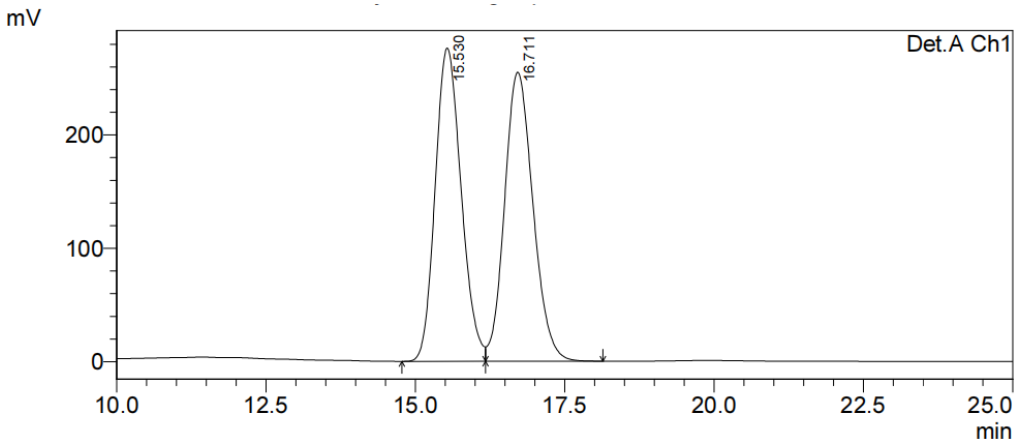
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	16.504	4088405	181801	4.509
2	17.222	86590632	2857015	95.491
Total		90679038	3038816	100.000

2-oxo-2*H*-chromen-7-yl 1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3t)



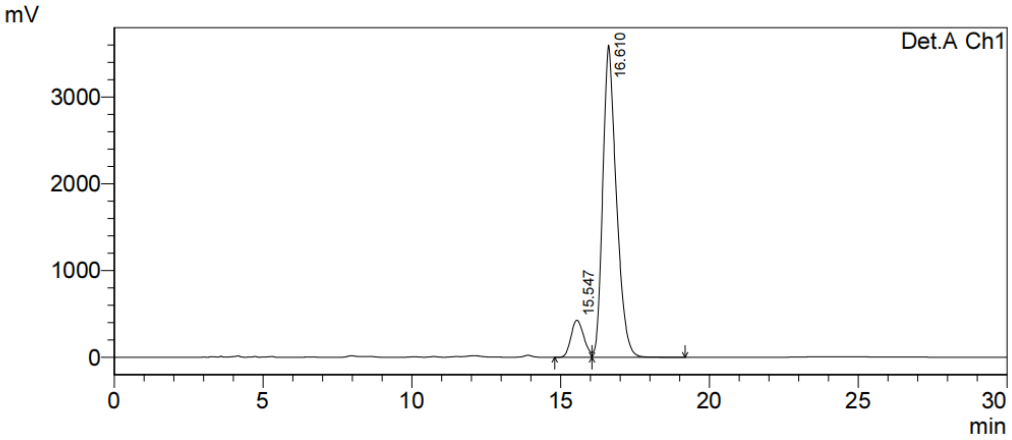


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.530	8358818	276272	49.755
2	16.711	8441153	255049	50.245
Total		16799971	531321	100.000



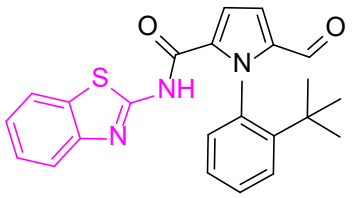
1 Det.A Ch1/254nm

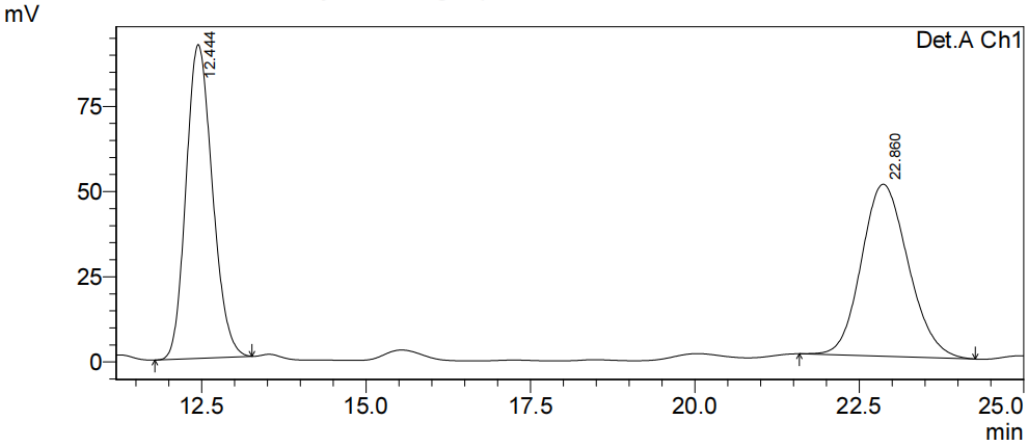
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	15.547	12761657	427638	10.044
2	16.610	114295935	3598326	89.956
Total		127057592	4025964	100.000

***N*-(benzo[*d*]thiazol-2-yl)-1-(2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxamide (3u)**



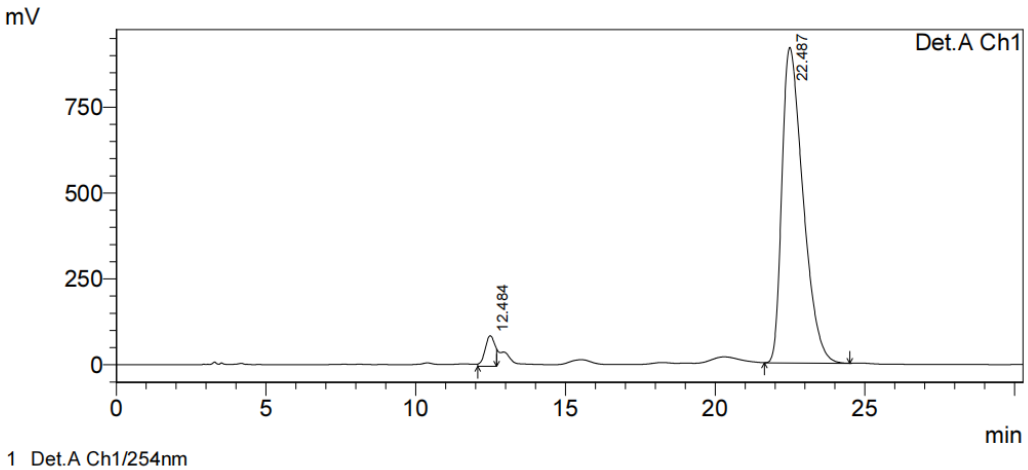


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.444	2573312	92094	50.704
2	22.860	2501850	50496	49.296
Total		5075162	142590	100.000



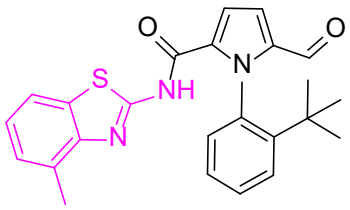
1 Det.A Ch1/254nm

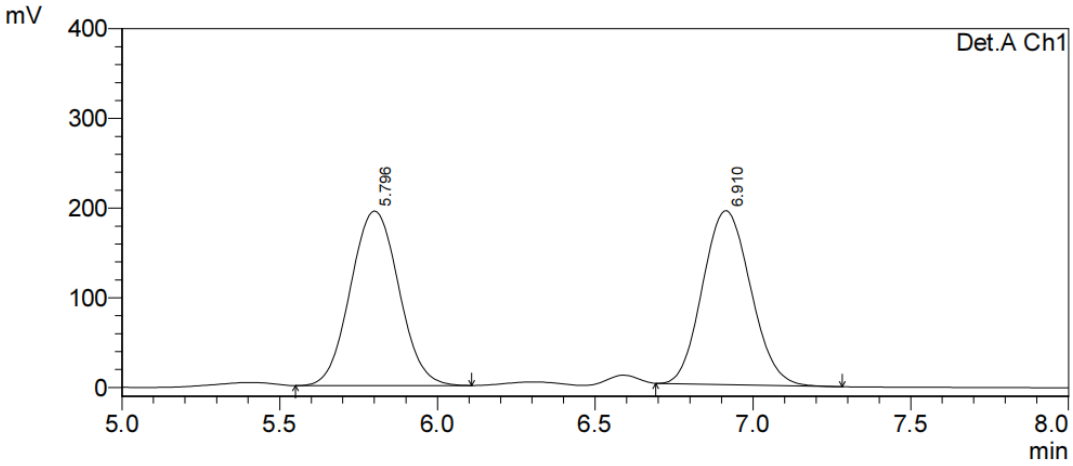
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.484	2014415	89117	4.281
2	22.487	45043015	918402	95.719
Total		47057431	1007519	100.000

1-(2-(*tert*-butyl)phenyl)-5-formyl-*N*-(4-methylbenzo[*d*]thiazol-2-yl)-1*H*-pyrrole-2-carboxamide (3v)



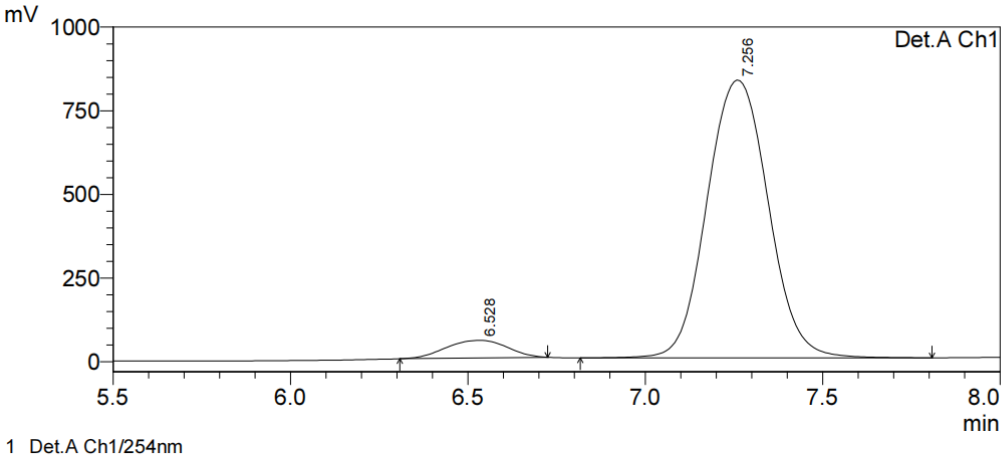


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.796	2074933	194841	50.229
2	6.910	2055984	193994	49.771
Total		4130917	388835	100.000



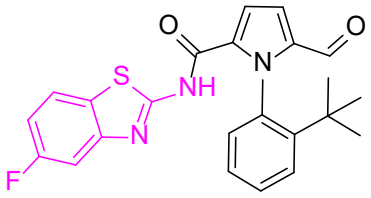
1 Det.A Ch1/254nm

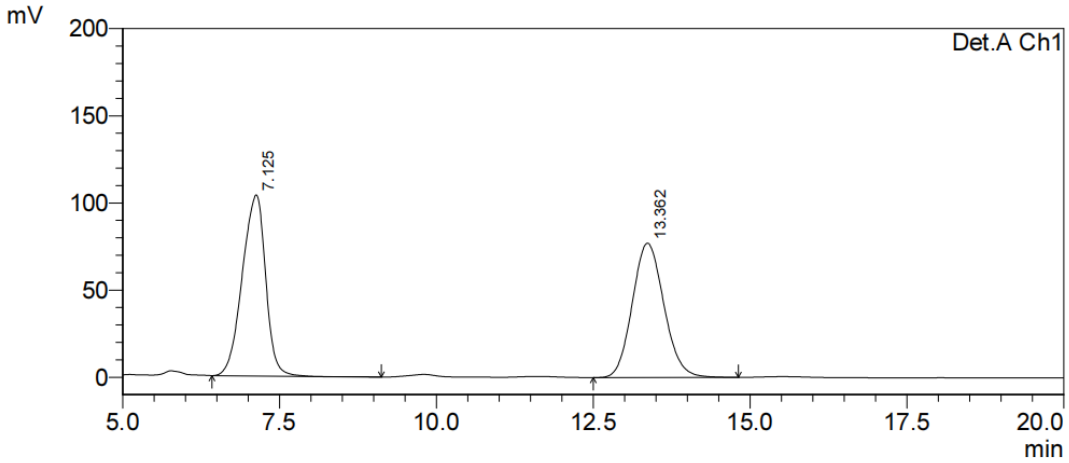
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.528	630135	52686	5.949
2	7.256	9961661	830247	94.051
Total		10591796	882933	100.000

1-(2-(*tert*-butyl)phenyl)-*N*-(5-fluorobenzo[*d*]thiazol-2-yl)-5-formyl-1*H*-pyrrole-2-carboxamide (3w)



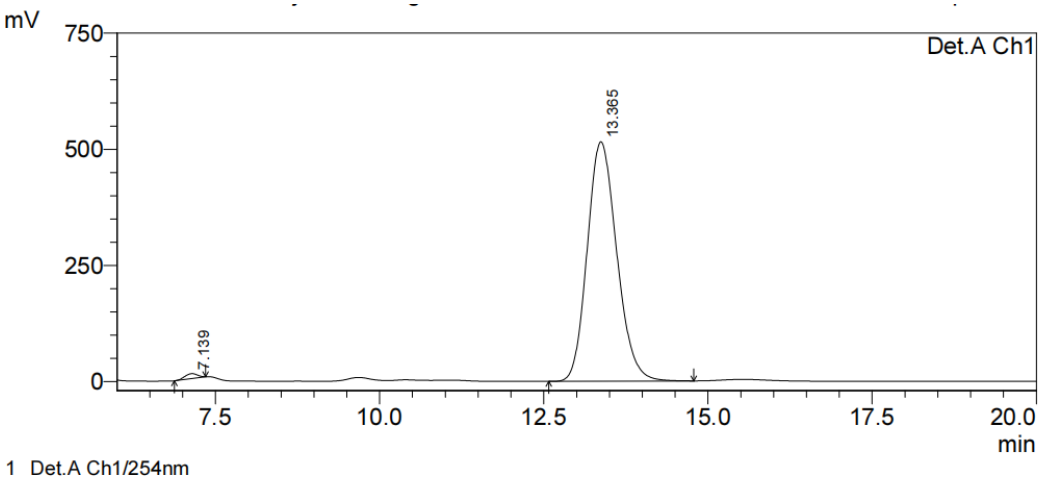


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.125	2691793	103859	49.887
2	13.362	2703983	77073	50.113
Total		5395775	180932	100.000



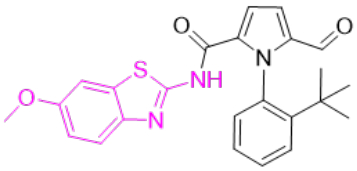
1 Det.A Ch1/254nm

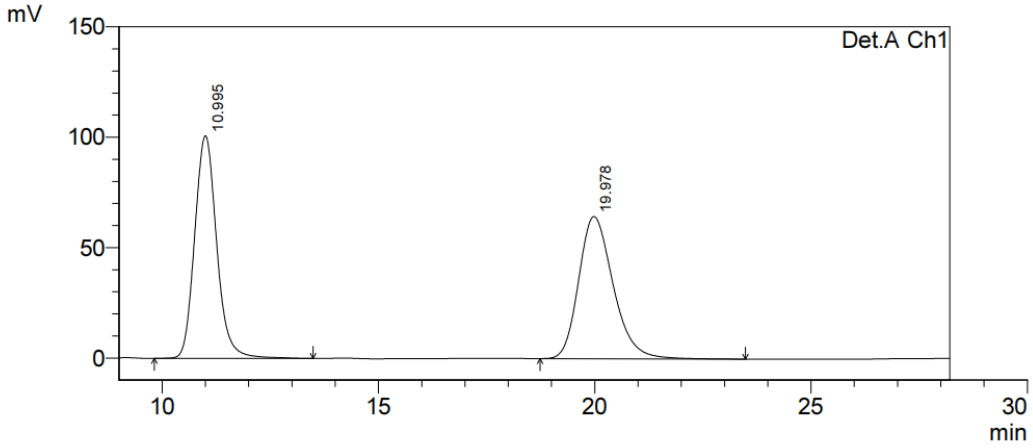
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.139	146294	10712	0.898
2	13.365	16148938	515719	99.102
Total		16295232	526431	100.000

1-(2-(*tert*-butyl)phenyl)-5-formyl-*N*-(6-methoxybenzo[*d*]thiazol-2-yl)-1*H*-pyrrole-2-carboxamide (3x)



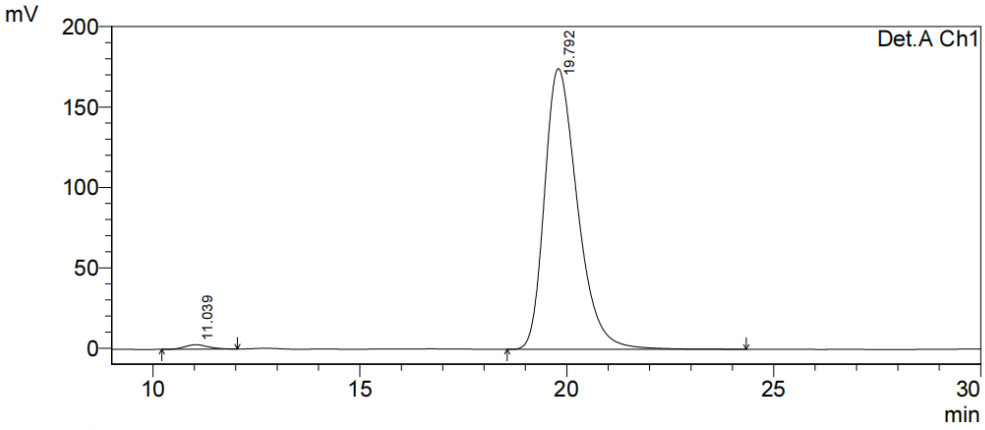


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	10.995	3578650	100915	50.028
2	19.978	3574654	64403	49.972
Total		7153304	165319	100.000



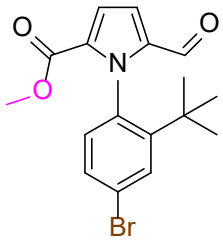
1 Det.A Ch1/254nm

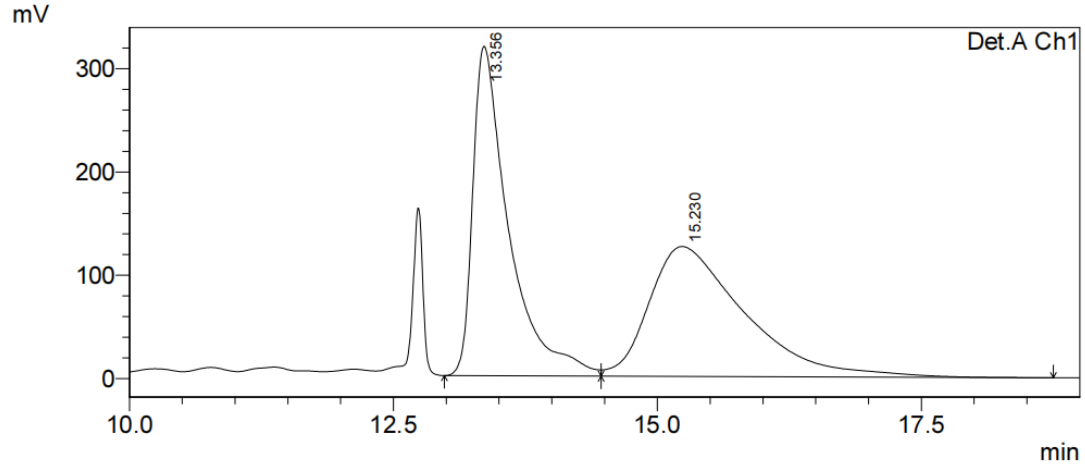
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	11.039	111457	2831	1.139
2	19.792	9677337	174628	98.861
Total		9788793	177459	100.000

methyl 1-(4-bromo-2-(*tert*-butyl)phenyl)-5-formyl-1*H*-pyrrole-2-carboxylate (3aa)



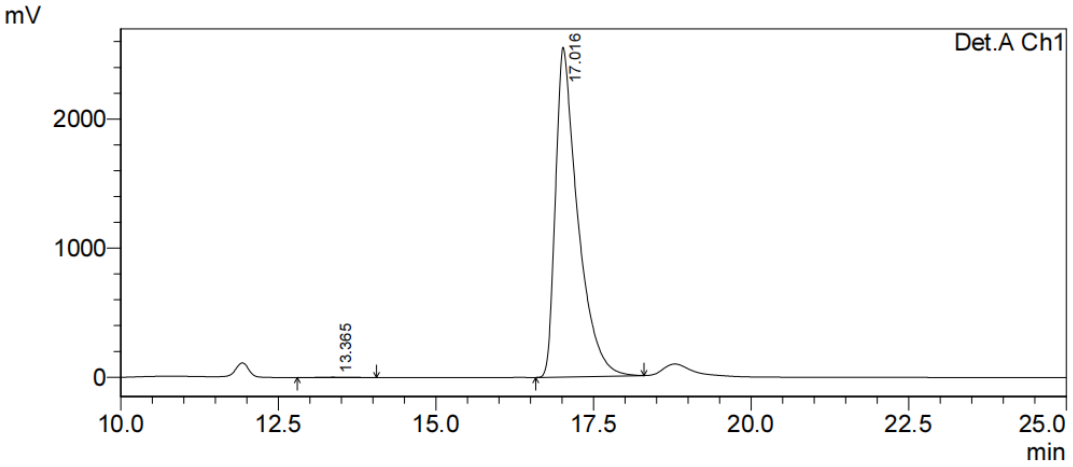


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.356	7578259	319000	48.885
2	15.230	7924007	125834	51.115
Total		15502266	444834	100.000



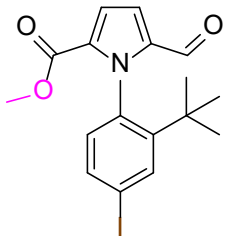
1 Det.A Ch1/254nm

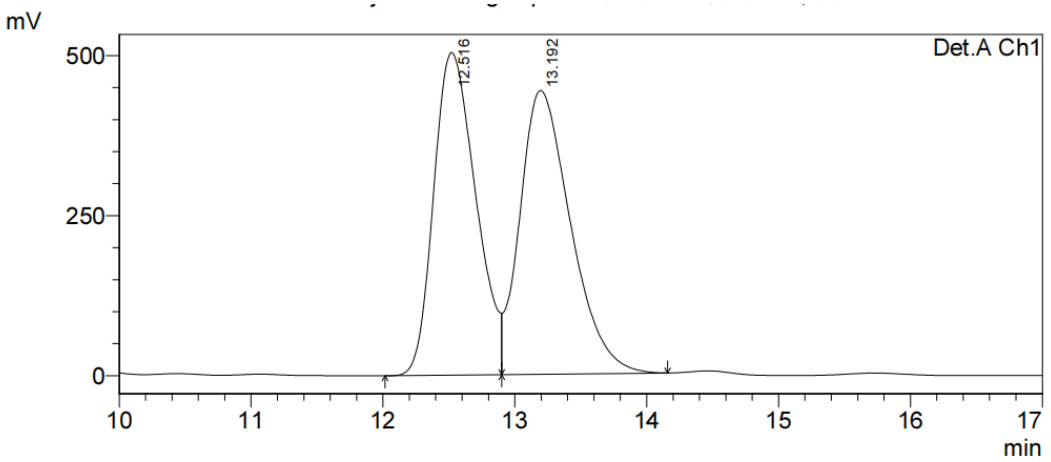
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.365	102091	3102	0.163
2	17.016	62645457	2553552	99.837
Total		62747548	2556654	100.000

methyl 1-(2-(*tert*-butyl)-4-iodophenyl)-5-formyl-1*H*-pyrrole-2-carboxylat (3ab)





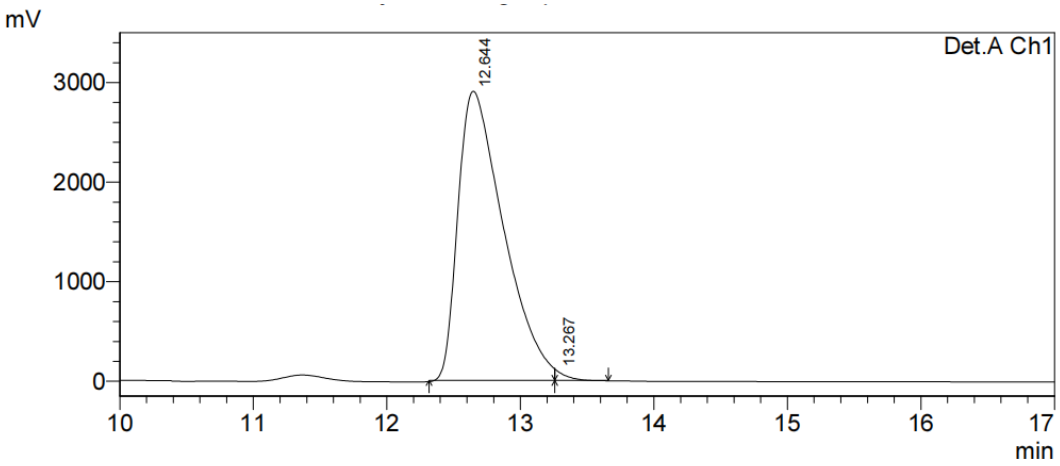
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.516	11203255	504025	48.601
2	13.192	11848459	443303	51.399
Total		23051714	947327	100.000

56



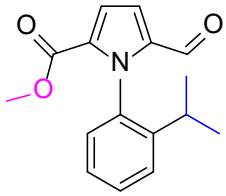
1 Det.A Ch1/254nm

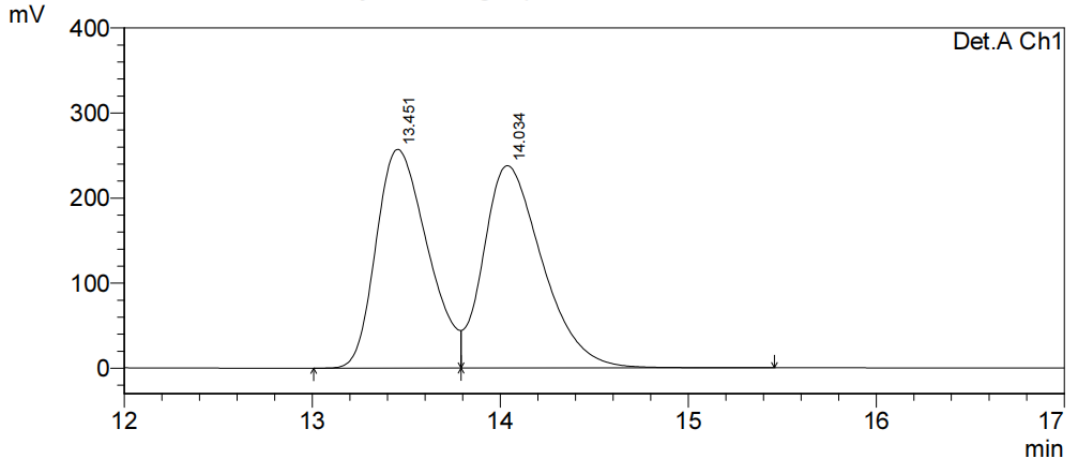
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	12.644	68659259	2902988	99.302
2	13.267	482941	103910	0.698
Total		69142200	3006898	100.000

methyl 5-formyl-1-(2-isopropylphenyl)-1*H*-pyrrole-2-carboxylate (3ac)



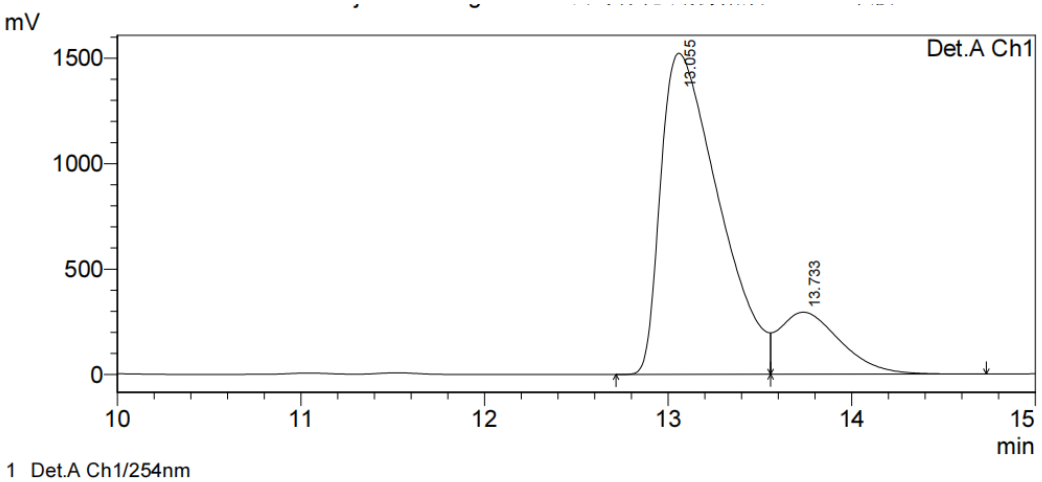


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.451	4905745	257115	48.596
2	14.034	5189184	237968	51.404
Total		10094929	495083	100.000



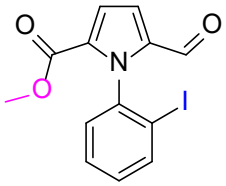
1 Det.A Ch1/254nm

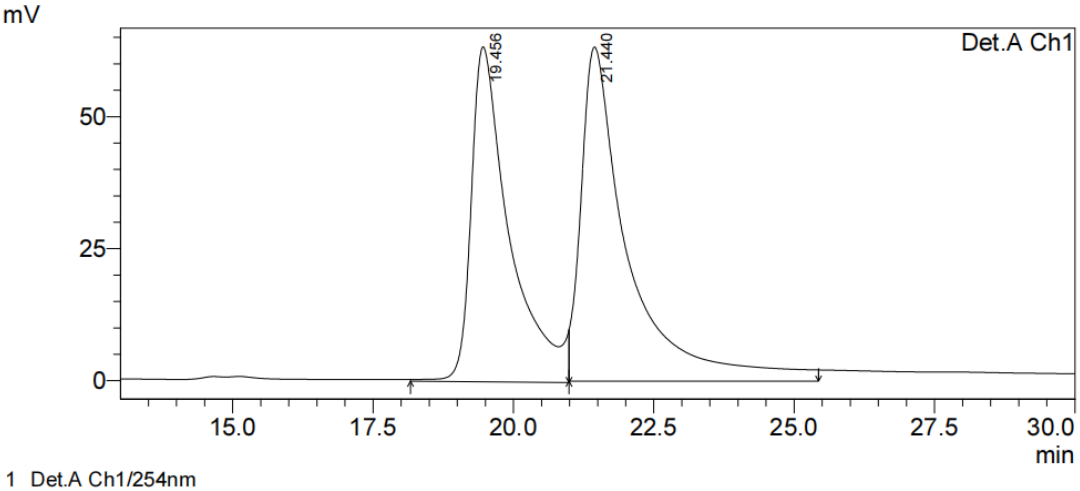
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	13.055	33570305	1522562	83.142
2	13.733	6806720	294688	16.858
Total		40377026	1817249	100.000

methyl 5-formyl-1-(2-iodophenyl)-1H-pyrrole-2-carboxylate (3ad)



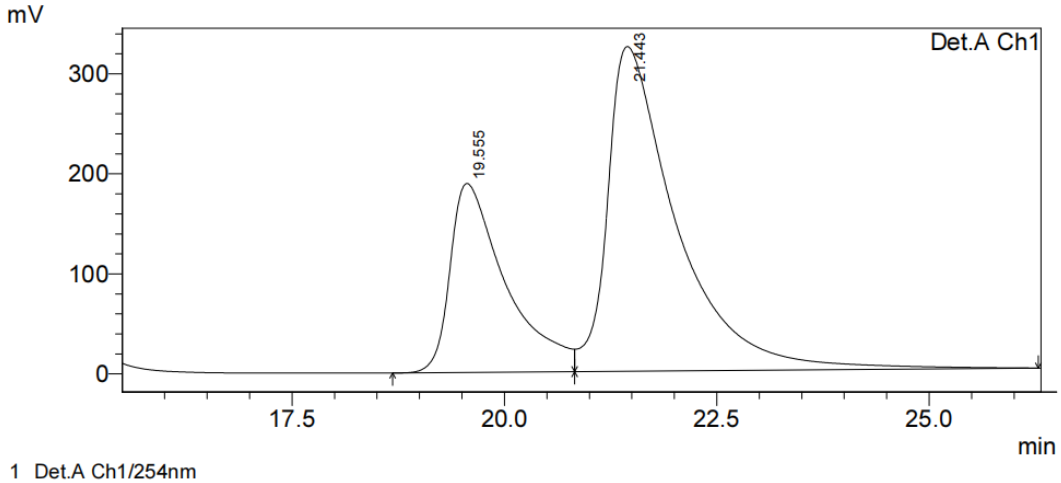


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.456	3023449	63404	44.973
2	21.440	3699414	63284	55.027
Total		6722863	126688	100.000



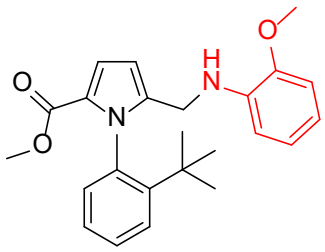
1 Det.A Ch1/254nm

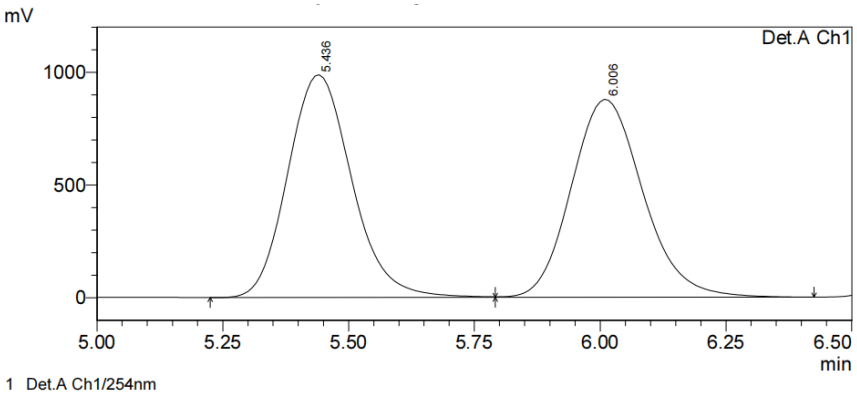
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	19.555	8625377	188923	31.848
2	21.443	18457895	324610	68.152
Total		27083272	513533	100.000

methyl 1-(2-(*tert*-butyl)phenyl)-5-(((2-methoxyphenyl)amino)methyl)-1*H*-pyrrole-2-carboxylate（4a）



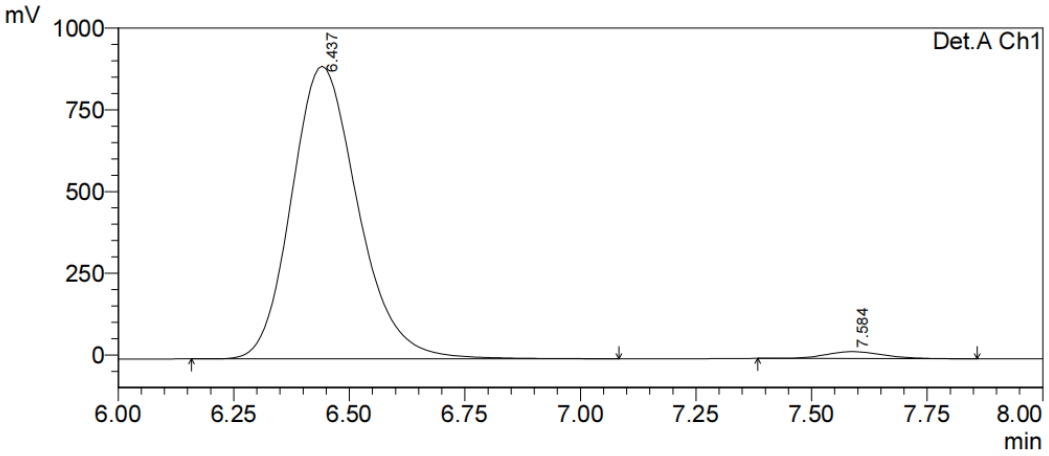


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.436	8739134	987295	50.126
2	6.006	8695052	877494	49.874
Total		17434186	1864789	100.000



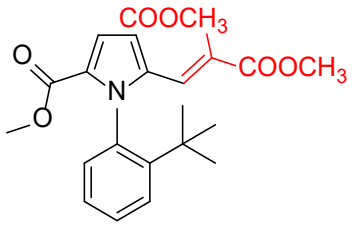
1 Det.A Ch1/254nm

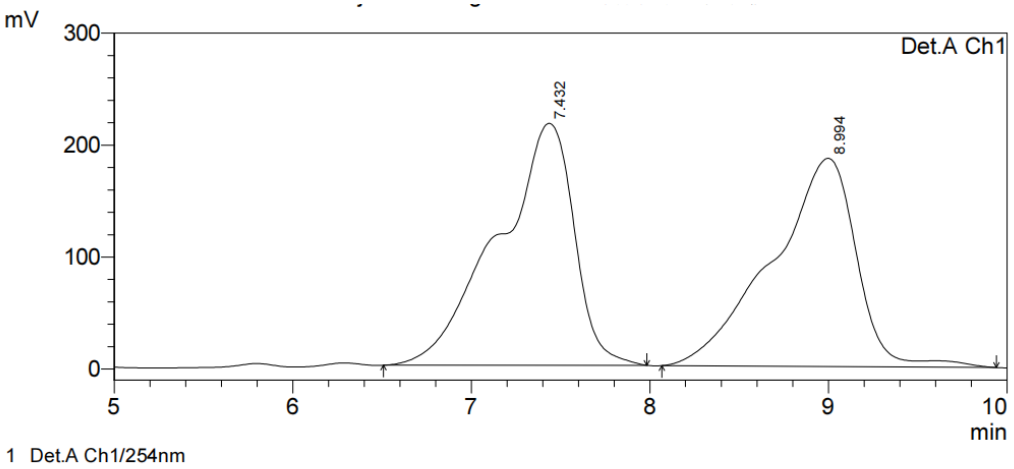
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	6.437	8955216	895699	98.001
2	7.584	182712	21089	1.999
Total		9137928	916788	100.000

dimethyl 2-((1-(2-(*tert*-butyl)phenyl)-5-(methoxycarbonyl)-1*H*-pyrrol-2-yl)methylene)malonate (4b)



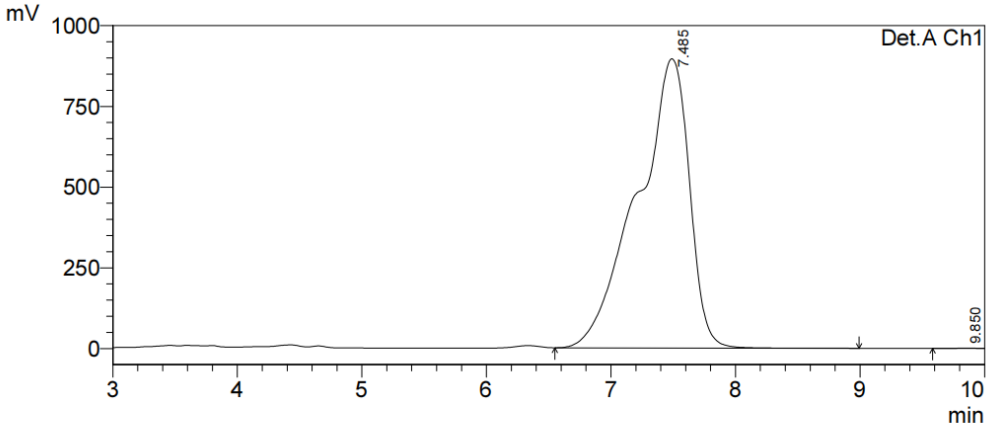


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.432	6434609	216096	51.251
2	8.994	6120460	186032	48.749
Total		12555069	402128	100.000



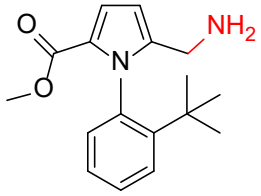
1 Det.A Ch1/254nm

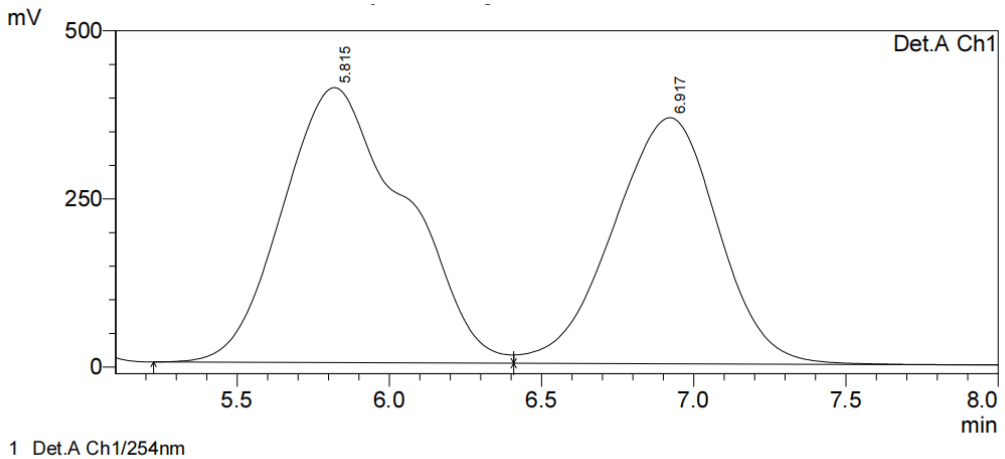
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	7.485	25991770	895896	99.947
2	9.850	13665	987	0.053
Total		26005435	896883	100.000

1-(2-(*tert*-butyl)phenyl)-5-formyl-*N*-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxamide (4c)



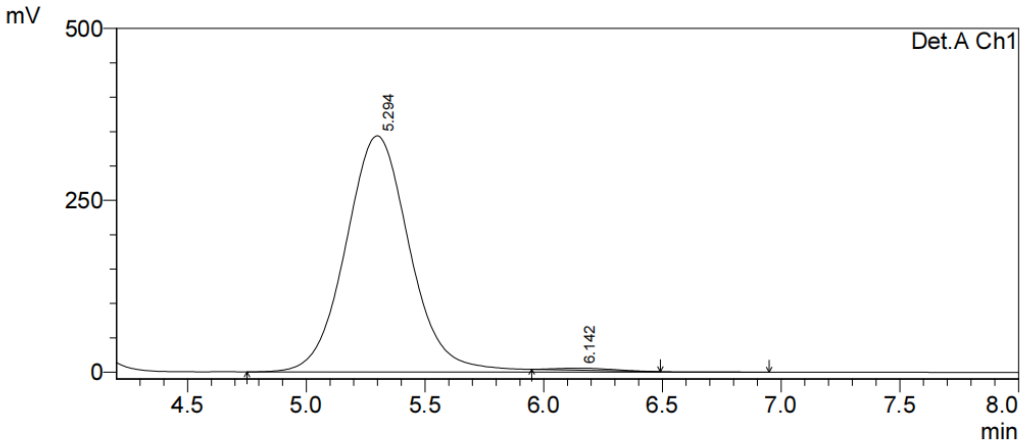


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.815	11485846	409046	56.504
2	6.917	8841566	366007	43.496
Total		20327411	775053	100.000



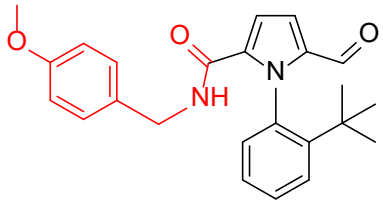
1 Det.A Ch1/254nm

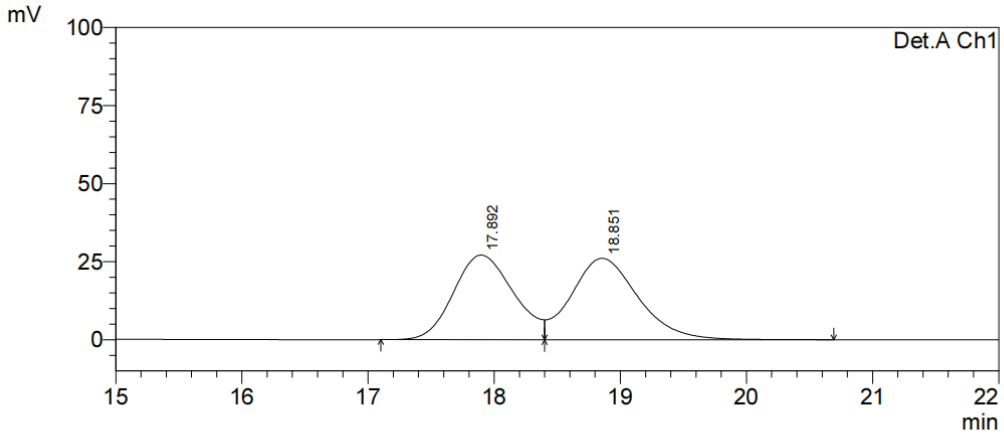
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	5.294	6521354	343582	99.295
2	6.142	46334	2853	0.705
Total		6567688	346435	100.000

1-(2-(*tert*-butyl)phenyl)-5-formyl-*N*-(4-methoxybenzyl)-1*H*-pyrrole-2-carboxamide （4d）



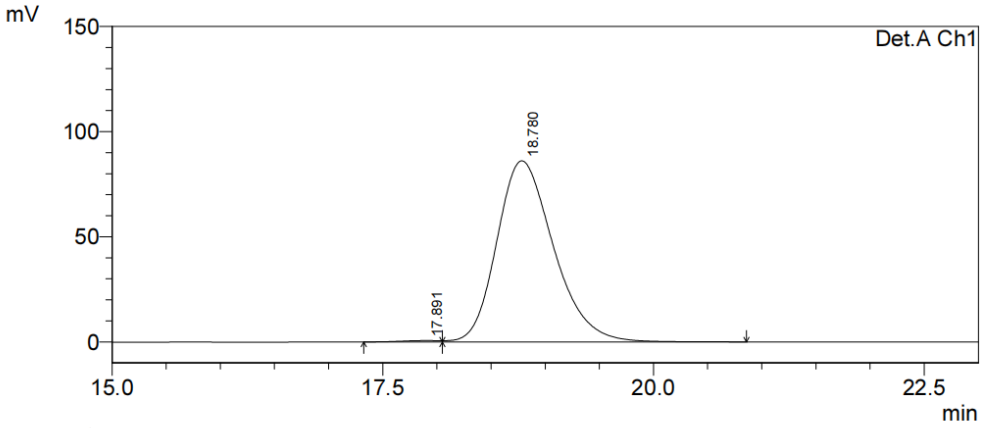


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.892	894727	27106	48.302
2	18.851	957651	26086	51.698
Total		1852377	53191	100.000



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %
1	17.891	15861	653	0.503
2	18.780	3140263	86136	99.497
Total		3156124	86789	100.000