Enal-Azomethine Ylides: Application to the Synthesis of Functionalized Pyrroles

Pratap Kumar Mandal, Sandeep Patel and Sreenivas Katukojvala*

Department of Chemistry, Indian Institute of Science Education & Research Bhopal
Madhya Pradesh-462066 India

sk@iiserb.ac.in

Supporting Information

Contents :

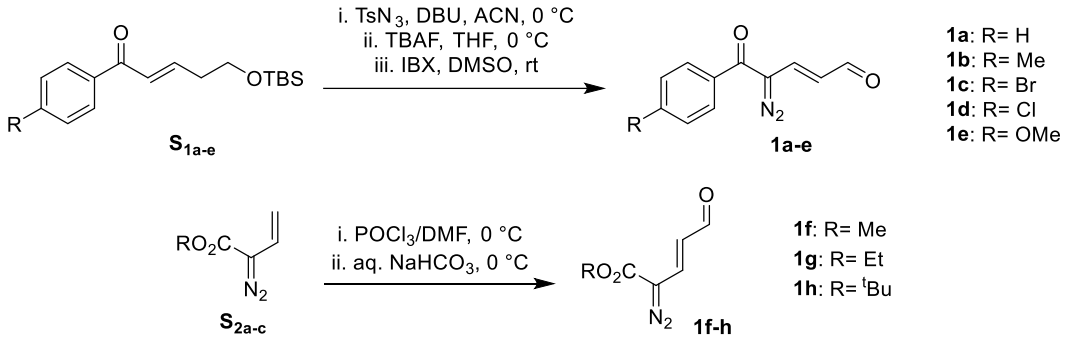
1. General Methods:

All the reactions were performed in oven-dried glassware. Solvents were dried using standard methods. Unless otherwise stated, all the commercial reagents were used as received. Reactions that require heating were carried out using an oil bath. Progress of the reaction was monitored by thin layer chromatography (Merck Silica gel 60 F-254, 0.25 nm, precoated plates on alumina). Column chromatographic purifications were performed on Merck silica gel (100-200 mesh). Melting points were recorded on a digital melting point apparatus and were uncorrected. Spectroscopic characterizations were conducted at the Central Instrumentation Facility (CIF), Indian Institute of Science Education and Research (IISER) Bhopal. ^{1}H-NMR spectra were recorded on Bruker Avance III FT-NMR spectrometers at 400 MHz, 500 MHz, or 700 MHz, and ^{13}C-NMR spectra were recorded at 101 MHz, 126 MHz, or 176 MHz. ^{1}H-NMR chemical shifts are reported in ppm relative to the TMS (δ=0) or $CDCl_3$ signal (δ= 7.26) and are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). ^{13}C-NMR chemical shifts are reported in ppm relative to the residual $CDCl_3$ signal (δ= 77.16). Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at low temperatures. IR spectra were recorded on a Perkin Elmer FT-IR spectrometer. HRMS data were obtained on a Bruker micro TOF-QII or Agilent 5975C high-resolution mass spectrometers.

2. Preparation of starting materials:

(a) Preparation of diazoenals:

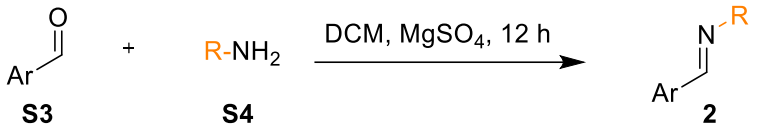
Keto diazoenals **8a-j** and ester diazoenals **8k-q** were prepared according to our reported procedures (Scheme S1).[1]



Scheme S1: Preparation of diazoenals **1a-1h**

(b) Preparation of aldimines:

Aldimines **2a-2y** were prepared according to the literature procedure (Scheme S2).[2]



Scheme S2: Preparation of N-alkyl aldimines **2**

Method: An oven-dried 25 mL R. B. flask with a magnetic stir bar was charged with aryl aldehyde S_3 (1.75 mmol), alkyl amine 3 (1.75 mmol), 500 mg $MgSO_4$ and 15 mL dry DCM under N_2 atmosphere. The reaction mixture was stirred overnight at room temperature, filtered through a celite pad, and washed with DCM (50 mL). The filtrate was concentrated under reduced pressure to afford the aldimine **2**.

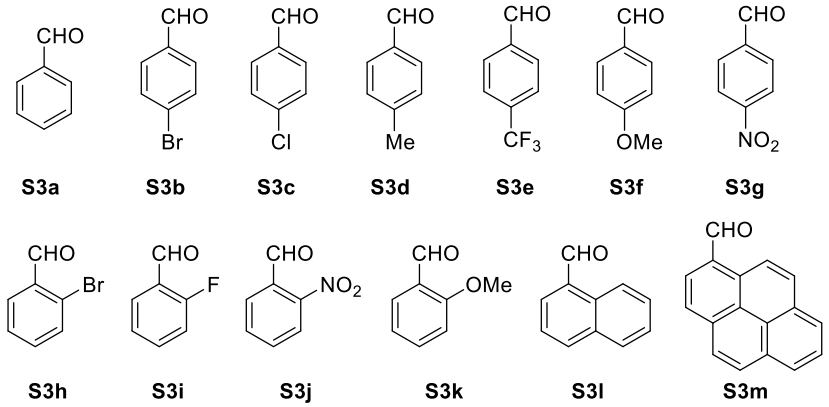


Fig. S2: List of aryl aldehydes **S3**

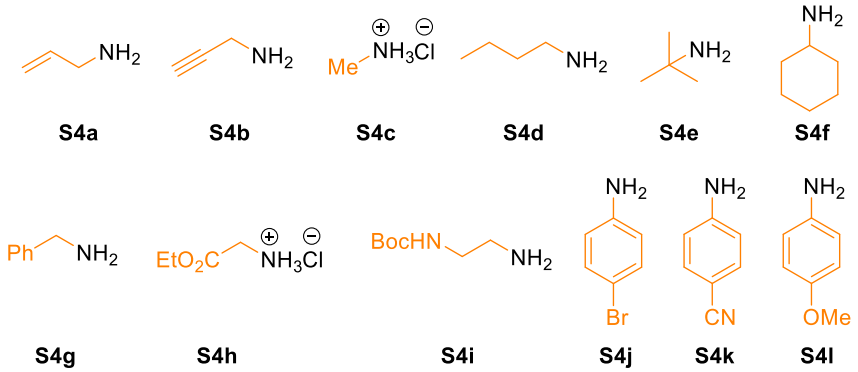


Fig. S3: List of aliphatic and aryl amines **S4**

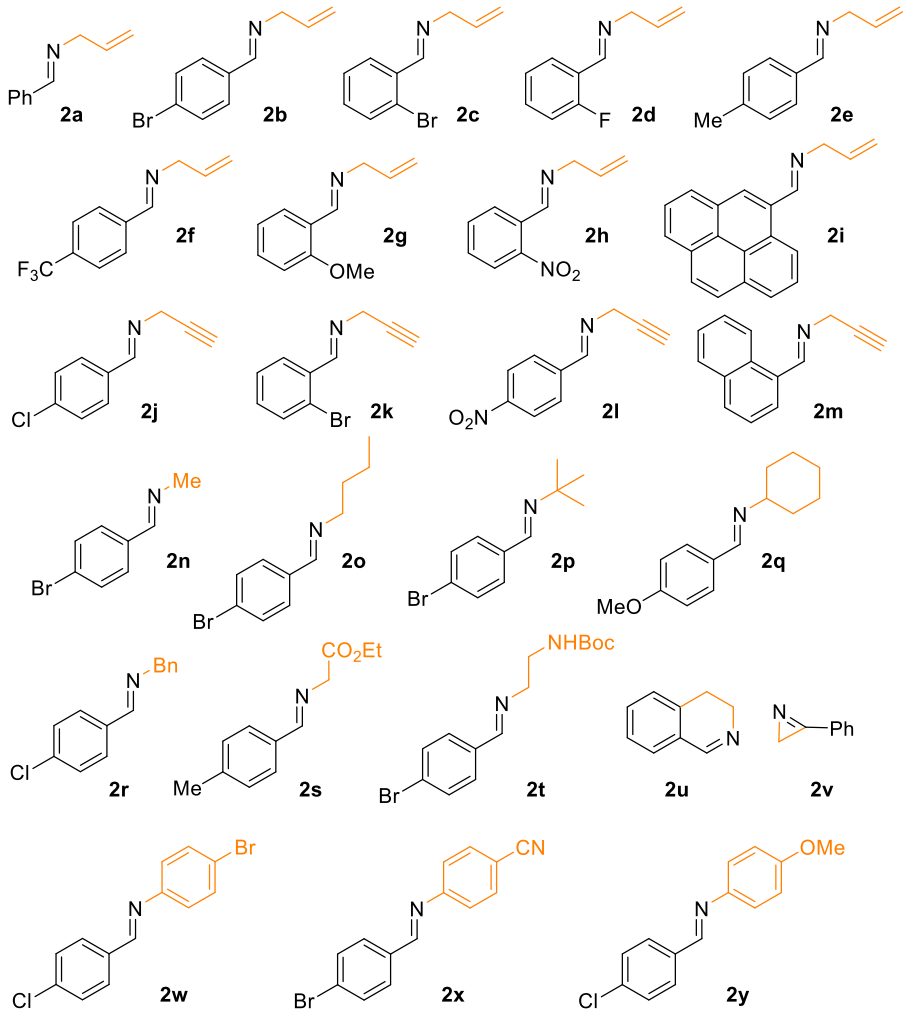


Fig. S3: List of aldimines **2**

2*H*-Azirine **2v** was synthesized according to the literature procedure.[2c]

3. Optimization of the [3+2] annulation reaction:

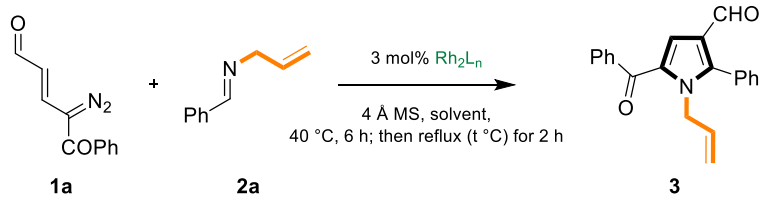


Table 1:

Entry	Rh_2L_n	Solvent	t (°C)	Yield (%)[a]
1	$Rh_2(OAc)_4$	DCM	40	0
2	$Rh_2(OAc)_4$	DCE	80	<5

3	$Rh_2(OAc)_4$	toluene	110	57
4	**$Rh_2(oct)_4$**	**toluene**	**110**	72
5	$Rh_2(esp)_2$	toluene	100	54
7	Rh_2(*S*-DOSP)$_4$	toluene	110	<10
8	$Rh_2(TFA)_4$	toluene	110	12
9	$Rh_2(oct)_4$	trifluorotoluene	102	59
10	$Rh_2(oct)_4$	benzene	80	34
10	$Rh_2(oct)_4$	Xylene	reflux	53
11[b]	$Rh_2(oct)_4$	Toluene	100	0
12	$Rh_2(oct)_4$	1,4-dioxane	100	0

[b]Yield was calculated after excluding the recovered aldehyde. [a]10 mol% Brønsted acid (diphenyl phosphate, DPP) was used.

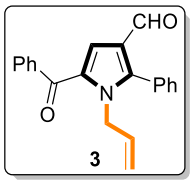
Procedure for optimization reactions:

An oven-dried 10 mL round bottom flask containing a stir bar under nitrogen atmosphere was charged with aldimine **2** (19 mg, 0.13 mmol), Rh(II)-catalyst (0.004 mmol), 4Å MS (50 mg), 2 ml dry solvent and stirred at 40 ˚C temperature. Then a solution of diazoenal **1a** (40 mg, 0.2 mmol) in 2 ml dry solvent was added dropwise over 1.5 h to the reaction mixture via a syringe pump. After completion of the addition, the reaction was continued until the diazoenal was completely consumed (judged by TLC). Then the temperature of the reaction vessel was brought to 110 ˚C and continued for another 3 h. The crude reaction mixture was filtered through celite and washed with DCM (5 mL). The filtrate was concentrated under reduced pressure. The crude material was purified by a silica gel flash column chromatography using ethyl acetate/hexane (5:95) as the eluent to furnish the pyrrole.

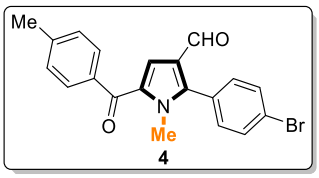
4. Substrate scope of [3+2] annulation:

General procedure B: To an oven-dried 10 mL round bottom flask containing a stir bar under nitrogen atmosphere was charged with appropriate aldimine **2** (0.13 mmol), $Rh_2(oct)_4$ (3 mg, 0.004 mmol), 4Å MS (50 mg), 2 ml dry toluene and stirred at 40 ˚C temperature. Then a solution of appropriate diazoenal **1** (0.2 mmol) in 2 ml dry toluene was added dropwise over 1.5 h to the reaction mixture via a syringe pump. After completion of the addition, the reaction

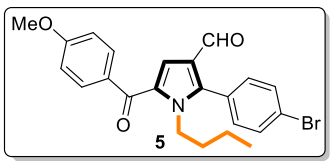
was continued until the diazoenal was completely consumed (3-6 h judged by TLC). Then the temperature of the reaction vessel was brought to 110 ˚C and continued for another 3 h. The crude reaction mixture was filtered through a celite pad and washed with DCM (5 mL). The filtrate was concentrated under reduced pressure. The crude material was purified by a silica gel flash column chromatography using ethyl acetate/hexane (5:95) as the eluent to furnish the pyrrole compounds.



1-Allyl-5-benzoyl-2-phenyl-1*H*-pyrrole-3-carbaldehyde (3): Prepared by following general procedure B using aldimine **2a** (19 mg, 0.13 mmol) as a limiting reagent and obtained as a yellow viscous liquid; yield = 72% (22 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 26% (3.5 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.86 – 7.83 (m, 2H), 7.61 – 7.57 (m, 1H), 7.57 – 7.51 (m, 3H), 7.51 – 7.45 (m, 4H), 7.29 (s, 1H), 5.92 (ddt, *J* = 17.1, 10.0, 4.9 Hz, 1H), 5.10 (dd, *J* = 10.4, 0.9 Hz, 1H), 4.99 (dt, *J* = 4.6, 1.5 Hz, 2H), 4.82 (dd, *J* = 17.1, 0.9 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 187.0, 186.4, 148.9, 139.0, 134.5, 132.5, 131.2, 130.8, 130.2, 129.5, 128.9, 128.5, 128.2, 123.6, 120.7, 116.6, 48.3; **HRMS** (ESI) *m/z* calc. for $C_{21}H_{18}NO_2$ $(M+H)^+$ 316.1338 found 316.1332.

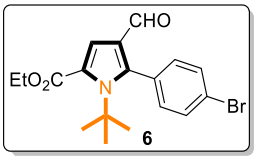


2-(4-Bromophenyl)-5-(4-methylbenzoyl)-1-methyl-1*H*-pyrrole-3-carbaldehyde (4): Prepared by following general procedure B using aldimine **2n** (26 mg, 0.13 mmol) as a limiting reagent and obtained as a white semi-solid; yield = 55% (20.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.28 (s, 1H), 3.87 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.6, 185.8, 146.7, 143.3, 135.9, 132.4, 132.2, 132.2, 129.6, 129.1, 127.1, 124.7, 123.2, 120.0, 34.8, 21.7; **HRMS** (ESI) *m/z* calc. for $C_{20}H_{17}BrNO_2$ $(M+H)^+$ 382.0443 found 382.0437.

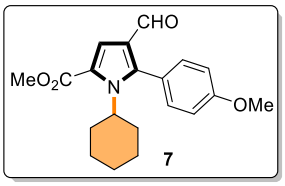


2-(4-Bromophenyl)-1-butyl-5-(4-methoxybenzoyl)-1*H*-pyrrole-3-carbaldehyde (5): Prepared by following general procedure B using aldimine **2o** (31 mg, 0.13 mmol) as a limiting reagent and obtained as a yellow solid; m.p. = 89-91 ˚C; yield = 68% (29 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H**

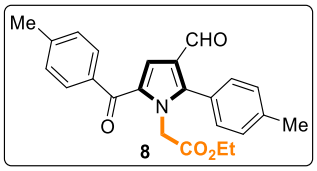
NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.22 (s, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.30 (dd, *J* = 8.6, 6.5 Hz, 2H), 3.90 (s, 3H), 1.55 – 1.51 (m, 2H), 1.13 (q, *J* = 7.5 Hz, 2H), 0.76 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.9, 185.8, 163.3, 146.5, 132.2, 132.1, 131.8, 131.5, 131.4, 127.6, 124.5, 123.3, 119.9, 113.7, 55.6, 45.8, 33.6, 19.7, 13.5; **HRMS** (ESI) *m/z* calc. for $C_{23}H_{23}BrNO_3$ $(M+H)^+$ 440.0861 found 440.0856.



Ethyl 5-(4-bromophenyl)-1-(tert-butyl)-4-formyl-1*H*-pyrrole-2-carboxylate (6): Prepared by following general procedure B using aldimine **2p** (31 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 65% (25.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 7.79 – 7.76 (m, 2H), 7.69 – 7.67 (m, 2H), 7.59 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.55 (s, 9H), 1.40 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.6, 161.4, 158.2, 144.6, 132.6, 129.9, 127.0, 126.2, 124.1, 117.4, 61.8, 29.8, 22.8, 14.4; **HRMS** (ESI) *m/z* calc. for $C_{18}H_{20}BrNO_3Na$ $(M+Na)^+$ 400.0524 found 400.0519.

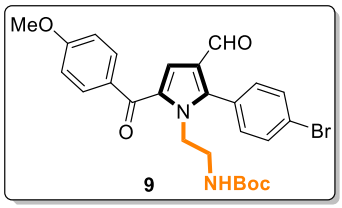


Methyl 1-cyclohexyl-4-formyl-5-(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (7): Prepared by following general procedure B using aldimine **2q** (28 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 66% (22 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 7.53 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 4.49 – 4.33 (m, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 2.27 – 2.09 (m, 2H), 1.80 – 1.70 (m, 4H), 1.15-1.20 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.6, 161.6, 160.7, 147.9, 132.2, 124.3, 123.7, 121.9, 118.3, 114.1, 59.3, 55.5, 51.8, 29.9, 26.3, 24.9; **HRMS** (ESI) *m/z* calc. for $C_{20}H_{24}NO_4$ $(M+H)^+$ 342.1705 found 342.1700.

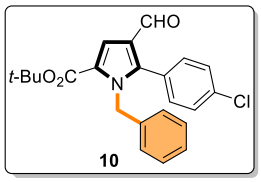


Ethyl-2-(3-formyl-5-(4-methylbenzoyl)-2-(p-tolyl)-1*H*-pyrrol-1-yl)acetate (8): Prepared by following general procedure B using aldimine **2s** (27 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 67% (25.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.33 (m, 4H), 7.33 (s, 1H), 7.28 (d, *J* = 7.9 Hz, 2H), 4.93 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 2.44 (s, 3H), 1.26 – 1.28 (m, 3H); **^{13}C**

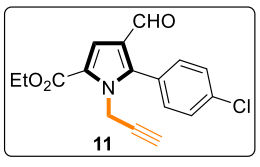
NMR (126 MHz, $CDCl_3$) δ 186.8, 186.4, 168.5, 149.2, 143.1, 140.6, 135.9, 131.4, 130.6, 129.7, 129.5, 129.1, 124.5, 123.5, 119.9, 61.7, 48.3, 21.6, 21.5, 14.1; **HRMS** (ESI) *m/z* calc. for $C_{24}H_{24}NO_4$ $(M+H)^+$ 390.1705 found 390.1700.



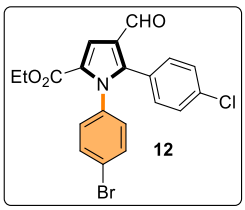
Tert-butyl-(2-(2-(4-bromophenyl)-3-formyl-5-(4-methoxybenzoyl)-1*H*-pyrrol-1-yl)ethyl)carbamate (9): Prepared by following general procedure B using aldimine **2t** (42.5 mg, 0.13 mmol) as a limiting reagent and obtained as a white semi-solid; yield = 49% (26 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 23% (6 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.25 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 4.70 (s, 1H), 4.44 (t, *J* = 6.0 Hz, 2H), 3.91 (s, 3H), 3.34 (q, *J* = 6.0 Hz, 2H), 1.32 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.2, 185.8, 163.3, 155.5, 147.2, 132.3, 132.3, 131.9, 131.4, 127.2, 124.7, 123.7, 120.3, 113.7, 79.6, 55.6, 45.6, 41.2, 29.7, 28.3; **HRMS** (ESI) *m/z* calc. for $C_{26}H_{27}BrN_2O_5Na$ $(M+Na)^+$ 549.1001 found 549.0996.



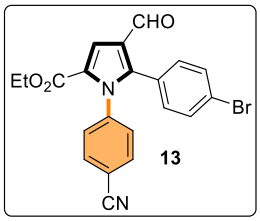
Tert-butyl 1-benzyl-5-(4-chlorophenyl)-4-formyl-1*H*-pyrrole-2-carboxylate (10): Prepared by following general procedure B using aldimine **2r** (30 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 65% (25 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.50 (s, 1H), 7.41 – 7.37 (m, 2H), 7.25 – 7.20 (m, 3H), 7.20 – 7.18 (m, 2H), 6.82 – 6.79 (m, 2H), 5.49 (s, 2H), 1.46 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.0, 160.1, 145.8, 137.9, 136.3, 132.2, 129.1, 128.8, 127.5, 127.0, 126.3, 125.9, 123.7, 116.6, 81.9, 49.2, 28.3; **HRMS** (ESI) *m/z* calc. for $C_{23}H_{23}ClNO_3$ $(M+H)^+$ 396.1366 found 396.1361.



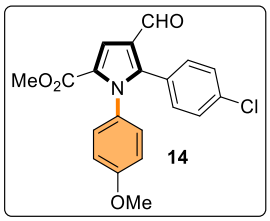
Ethyl 1-allyl-5-(4-chlorophenyl)-4-formyl-1*H*-pyrrole-2-carboxylate (11): Prepared by following general procedure B using aldimine **2j** (23 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 68% (21 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.55 – 7.52 (m, 2H), 7.52 (s, 1H), 7.50 – 7.47 (m, 2H), 4.97 (d, *J* = 2.4 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.37 (t, *J* = 2.4 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.6, 160.6, 145.2, 136.6, 132.1, 129.3, 126.2, 124.1, 123.6, 116.8, 78.7, 73.2, 60.9, 36.1, 14.3; **HRMS** (ESI) *m/z* calc. for $C_{17}H_{15}ClNO_3$ $(M+H)^+$ 316.0740 found 316.0735.



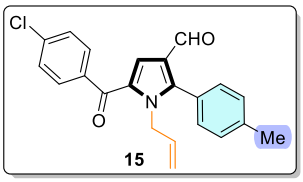
Ethyl 1-(4-bromophenyl)-5-(4-chlorophenyl)-4-formyl-1*H*-pyrrole-2-carboxylate (12): Prepared by following general procedure B using aldimine **2w** (38 mg, 0.13 mmol) as a limiting reagent and obtained as a yellow solid; m.p. = 108-110 ˚C; yield = 36% (15 mg); R_f = 0.6 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.032 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.64 (s, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.31 (d, *J* = 6.8 Hz, 2H), 7.12 (d, *J* = 7.0 Hz, 2H), 7.03 (d, *J* = 6.8 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.9, 159.9, 145.4, 136.3, 135.8, 132.1, 132.0, 129.9, 128.8, 126.4, 126.1, 123.9, 123.0, 116.7, 60.8, 14.1; **HRMS** (Agilent QTOF-ESI) m/z calc. for $C_{20}H_{16}BrClNO_3$, $(M+H)^+$ 431.9997 found 432.0008.



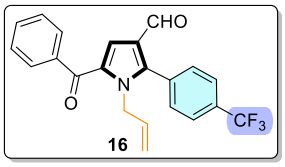
Ethyl 5-(4-bromophenyl)-1-(4-cyanophenyl)-4-formyl-1*H*-pyrrole-2-carboxylate (13): Prepared by following general procedure B using aldimine **2x** (37 mg, 0.13 mmol) as a limiting reagent and obtained as a brown solid; m.p. = 138-140 ˚C; yield = 28% (12 mg); R_f = 0.7 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 24% (5.5 mg, 0.03 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.65 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.4, 159.7, 143.5, 135.9, 132.8, 132.2, 132.1, 131.6, 129.8, 126.6, 124.1, 123.3, 117.9, 117.2, 113.3, 61.0, 14.1; **HRMS** (Agilent QTOF-ESI) m/z calc. for $C_{21}H_{16}BrN_2O_3$, $(M+H)^+$ 423.0339 found 423.0350.



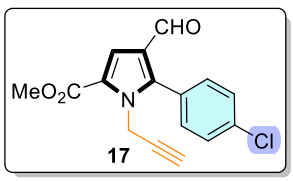
Methyl 5-(4-chlorophenyl)-4-formyl-1-(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (14): Prepared by following general procedure B using aldimine **2y** (32 mg, 0.13 mmol) as a limiting reagent and obtained as a yellow gummy liquid; yield = 11% (4 mg); R_f = 0.65 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.61 (s, 1H), 7.30 – 7.28 (m, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.77 (s, 3H); **HRMS** (Agilent QTOF-ESI) m/z calc. for $C_{21}H_{19}ClNO_4$, $(M+H)^+$ 384.0997 found 384.0999.



1-Allyl-5-(4-chlorobenzoyl)-2-(*p*-tolyl)-1*H*-pyrrole-3-carbaldehyde (15): Prepared by following general procedure B using aldimine **2e** (21 mg, 0.13 mmol) as a limiting reagent and obtained as a yellow solid; m.p. = 85-87 ˚C; yield = 62% (21.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4 mg, 0.033 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.26 (s, 1H), 5.91 (ddd, *J* = 15.1, 10.1, 4.7 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 4.97 (dd, *J* = 4.6, 2.0 Hz, 2H), 4.82 (d, *J* = 17.1 Hz, 1H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.3, 185.4, 149.3, 140.4, 138.7, 137.2, 134.4, 130.8, 130.6, 130.5, 129.5, 128.7, 124.8, 123.5, 120.5, 116.4, 48.1, 21.5; **HRMS** (ESI) *m/z* calc. for $C_{22}H_{19}ClNO_2$ $(M+H)^+$ 364.1104 found 364.1099.

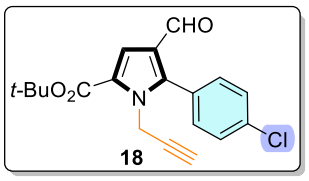


5-Benzoyl-1-(prop-2-yn-1-yl)-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-3-carbaldehyde (16): Prepared by following general procedure B using aldimine **2f** (28 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 69% (26 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (5.5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.91 – 7.89 (m, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.53 – 7.50 (m, 2H), 7.32 (s, 1H), 5.09 (d, *J* = 2.5 Hz, 2H), 2.37 (s, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.9, 185.5, 146.0, 138.5, 132.8, 132.7, 132.4, 131.5, 131.4, 131.3, 129.6, 128.6, 126.1 (q, *J* = 3.6 Hz), 124.0, 121.0, 78.7, 73.6, 36.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.9; **HRMS** (ESI) *m/z* calc. for $C_{22}H_{15}F_3NO_2$ $(M+H)^+$ 382.1055 found 382.1049.

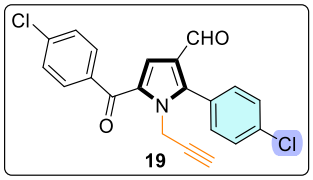


Methyl 5-(4-chlorophenyl)-4-formyl-1-(prop-2-yn-1-yl)-1*H*-pyrrole-2-carboxylate (17): Prepared by following general procedure B using aldimine **2j** (23 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 63% (18.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.55 – 7.52 (m, 2H), 7.51 (s, 1H), 7.50 – 7.48 (m, 2H), 4.98 (d, *J* = 2.4 Hz, 2H), 3.91 (s, 3H), 2.37 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.8, 161.2, 145.5, 136.8, 132.2, 129.4, 126.3, 123.8, 123.8, 117.1, 78.8, 73.4, 52.0, 36.2; **HRMS** (ESI) *m/z* calc. for $C_{16}H_{13}ClNO_3$ $(M+H)^+$ 302.0584 found 302.0578.

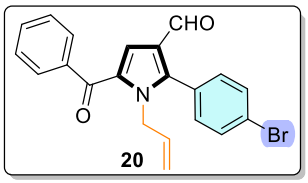
Tert-butyl 5-(4-chlorophenyl)-4-formyl-1-(prop-2-yn-1-yl)-1*H*-pyrrole-2-carboxylate (18): Prepared by following general procedure B using aldimine **2j** (23 mg, 0.13 mmol) as a



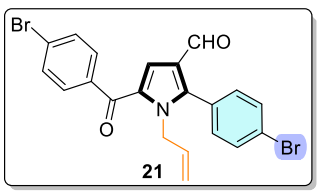
limiting reagent and obtained as a viscous liquid; yield = 59% (20 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.44 (s, 1H), 4.95 (d, *J* = 2.4 Hz, 2H), 2.36 (t, *J* = 2.4 Hz, 1H), 1.59 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.8, 159.9, 145.0, 136.5, 132.1, 129.2, 126.4, 125.4, 123.4, 116.4, 82.0, 78.8, 73.1, 36.0, 28.3; **HRMS** (ESI) *m/z* calc. for $C_{19}H_{19}ClNO_3$ $(M+H)^+$ 344.1053 found 344.1048.



5-(4-Chlorobenzoyl)-2-(4-chlorophenyl)-1-(prop-2-yn-1-yl)-1*H*-pyrrole-3-carbaldehyde (19): Prepared by following general procedure B using aldimine **2j** (23 mg, 0.13 mmol) as a limiting reagent and obtained as a white solid; m.p. = 142-144 ˚C; yield = 65% (24 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.28 (s, 1H), 5.06 (d, *J* = 2.5 Hz, 2H), 2.35 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.6, 185.4, 146.9, 139.1, 137.0, 136.7, 132.0, 130.9, 130.6, 129.4, 128.8, 125.8, 123.7, 120.6, 78.6, 73.4, 36.3; **HRMS** (ESI) *m/z* calc. for $C_{21}H_{14}Cl_2NO_2$ $(M+H)^+$ 382.0402 found 382.0396.

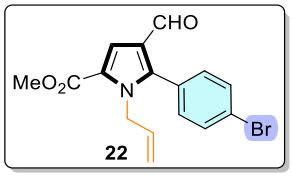


1-Allyl-5-benzoyl-2-(4-bromophenyl)-1*H*-pyrrole-3-carbaldehyde (20): Prepared by following general procedure B using aldimine **2b** (29 mg, 0.13 mmol) as a limiting reagent and obtained as a yellow viscous liquid; yield = 67% (26 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.83 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.70 – 7.66 (m, 2H), 7.62 – 7.57 (m, 1H), 7.49 (dd, *J* = 10.6, 4.7 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.28 (s, 1H), 5.97 – 5.88 (m, 1H), 5.12 (dd, *J* = 10.4, 0.9 Hz, 1H), 4.97 (dt, *J* = 4.6, 1.6 Hz, 2H), 4.81 (dd, *J* = 17.1, 0.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.9, 185.9, 147.1, 138.8, 134.4, 132.6, 132.3, 132.2, 131.4, 129.5, 128.5, 127.1, 125.0, 123.7, 120.8, 116.7, 48.4; **HRMS** (ESI) *m/z* calc. for $C_{21}H_{17}BrNO_2$ $(M+H)^+$ 394.0443 found 394.0437.

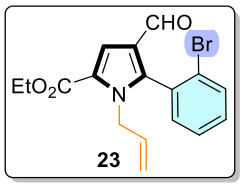


1-Allyl-5-(4-bromobenzoyl)-2-(4-bromophenyl)-1*H*-pyrrole-3-carbaldehyde (21): Prepared by following general procedure B using aldimine **2b** (29 mg, 0.13 mmol) as a limiting reagent and obtained as an off yellow solid; yield = 66% (30.5 mg); R_f = 0.5

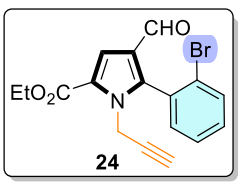
(EtOAc/Hexane: 20:80); m.p. = 110-112 ˚C; yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.25 (s, 1H), 5.91 (ddd, *J* = 19.9, 10.2, 5.0 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.95 (d, *J* = 4.8 Hz, 2H), 4.80 (d, *J* = 17.2 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.8, 185.7, 147.3, 137.6, 134.3, 132.3, 132.2, 132.2, 131.9, 131.0, 127.6, 127.0, 125.1, 123.8, 120.8, 116.8, 48.4; **HRMS** (ESI) *m/z* calc. for $C_{21}H_{16}Br_2NO_2$ $(M+H)^+$ 471.9548 found 471.9542.



Methyl 1-allyl-4-formyl-5-(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (22): Prepared by following general procedure B using aldimine **2b** (29 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 64% (21.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.52 (s, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.91 (ddt, *J* = 15.2, 9.7, 4.6 Hz, 1H), 5.13 (d, *J* = 10.5 Hz, 1H), 4.88 – 4.83 (m, 2H), 4.74 (d, *J* = 17.2 Hz, 1H), 3.86 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.7, 161.0, 145.6, 134.2, 132.2, 132.0, 127.2, 124.6, 123.9, 123.5, 116.8, 116.3, 51.7, 48.1; **HRMS** (ESI) *m/z* calc. for $C_{16}H_{15}BrNO_3$ $(M+H)^+$ 348.0235 found 348.0230.

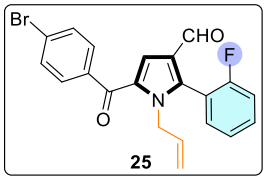


Ethyl 1-allyl-5-(2-bromophenyl)-4-formyl-1*H*-pyrrole-2-carboxylate (23): Prepared by following general procedure B using aldimine **2c** (29 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 53% (19 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.46 – 7.38 (m, 2H), 7.35 (dd, *J* = 7.2, 2.1 Hz, 1H), 5.82 (ddt, *J* = 16.9, 10.2, 5.1 Hz, 1H), 5.11 (ddt, *J* = 16.0, 4.6, 2.2 Hz, 1H), 5.04 (d, *J* = 10.6 Hz, 1H), 4.72 (d, *J* = 17.3 Hz, 1H), 4.49 – 4.43 (m, 1H), 4.31 (qt, *J* = 7.1, 3.6 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.5, 160.7, 144.8, 133.4, 133.2, 132.9, 131.6, 130.0, 127.3, 125.2, 124.1, 123.4, 116.8, 116.3, 60.6, 48.3, 14.3; **HRMS** (ESI) *m/z* calc. for $C_{17}H_{17}BrNO_3$ $(M+H)^+$ 362.0392 found 362.0386.

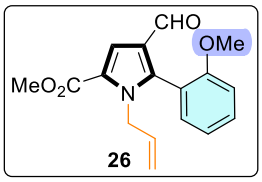


Ethyl 5-(2-bromophenyl)-4-formyl-1-(prop-2-yn-1-yl)-1*H*-pyrrole-2-carboxylate (24): Prepared by following general procedure B using aldimine **2c** (29 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 57% (20 mg); R_f = 0.5 (EtOAc/Hexane: 20:80);

yield of recovered aldehyde = 25% (6 mg, 0.032 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.53 (s, 1H), 7.49 (d, *J* = 4.5 Hz, 2H), 7.43 (dt, *J* = 10.7, 4.3 Hz, 1H), 5.32 (dt, *J* = 17.2, 2.1 Hz, 1H), 4.58 (d, *J* = 17.2 Hz, 1H), 4.37 (q, *J* = 6.2 Hz, 2H), 2.23 (t, *J* = 2.3 Hz, 1H), 1.39 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.4, 160.6, 144.6, 133.3, 133.1, 131.9, 129.5, 127.6, 125.2, 123.9, 123.7, 116.4, 77.9, 72.8, 60.9, 35.8, 14.3; **HRMS** (ESI) *m/z* calc. for $C_{17}H_{15}BrNO_3$ $(M+H)^+$ 360.0235 found 360.0230.

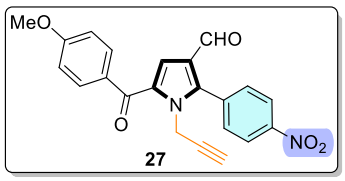


1-Allyl-5-(4-bromobenzoyl)-2-(2-fluorophenyl)-1*H*-pyrrole-3-carbaldehyde (25): Prepared by following general procedure B using aldimine **2d** (22 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 61% (24.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4 mg, 0.032 mmol); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.57 (q, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 4.2 Hz, 2H), 5.85 (ddt, *J* = 16.3, 10.2, 5.2 Hz, 1H), 5.15 – 5.01 (m, 2H), 4.78 (d, *J* = 16.0 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.6, 185.6, 160.5 (d, *J* = 249.5 Hz), 142.0, 137.6, 133.6, 132.8 (d, *J* = 1.6 Hz), 132.7, 131.8, 131.5, 131.1, 127.6, 124.7 (d, *J* = 3.7 Hz), 124.2, 120.8, 117.1, 116.6 (d, *J* = 21.4 Hz), 116.2 (d, *J* = 15.6 Hz), 48.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.3; **HRMS** (ESI) *m/z* calc. for $C_{21}H_{16}BrFNO_2$ $(M+H)^+$ 412.0348 found 412.0343.

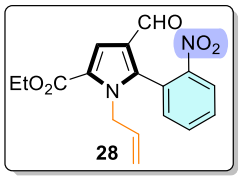


Methyl 1-allyl-4-formyl-5-(2-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (26): Prepared by following general procedure B using aldimine **2g** (23 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 65% (19 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (4.5 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.52 (s, 1H), 7.49 (ddd, *J* = 8.4, 7.5, 1.8 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.80 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.07 – 4.99 (m, 2H), 4.76 – 4.68 (m, 1H), 4.55 (ddt, *J* = 15.9, 5.3, 1.7 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.4, 161.4, 157.9, 144.4, 134.0, 132.9, 131.9, 123.9, 123.6, 120.7, 117.2, 116.5, 116.3, 111.3, 55.7, 51.7, 48.3; **HRMS** (ESI) *m/z* calc. for $C_{17}H_{18}NO_4$ $(M+H)^+$ 300.1236 found 300.1230.

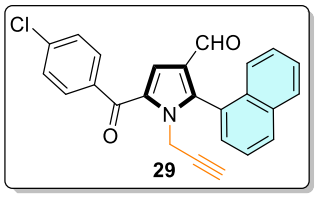
5-(4-Methoxybenzoyl)-2-(4-nitrophenyl)-1-(prop-2-yn-1-yl)-1*H*-pyrrole-3-carbaldehyde (27): Prepared by following general procedure B using aldimine **2l** (25 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 71% (26.5 mg); R_f = 0.5



(EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (5 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.44 (d, *J* = 8.7 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 2H), 7.30 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.08 (d, *J* = 2.4 Hz, 2H), 3.91 (s, 3H), 2.36 (t, *J* = 2.4 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.5, 185.3, 163.8, 149.0, 134.5, 132.1, 132.1, 131.9, 130.9, 130.0, 124.2, 124.0, 120.1, 114.0, 78.5, 73.9, 55.7, 36.4; **HRMS** (ESI) *m/z* calc. for $C_{22}H_{17}N_2O_5$ $(M+H)^+$ 389.1137 found 389.1132.

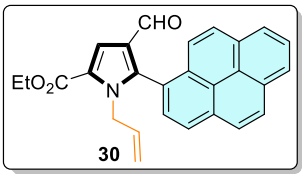


Ethyl 1-allyl-4-formyl-5-(2-nitrophenyl)-1*H*-pyrrole-2-carboxylate (28): Prepared by following general procedure B using aldimine **2h** (25 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 61% (21 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (5 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.27 – 8.20 (m, 1H), 7.78 – 7.69 (m, 2H), 7.52 (s, 1H), 7.47 – 7.42 (m, 1H), 5.85 (ddt, *J* = 17.2, 10.3, 5.2 Hz, 1H), 5.06 (dd, *J* = 10.4, 1.3 Hz, 1H), 4.99 (ddt, *J* = 16.0, 5.1, 1.7 Hz, 1H), 4.74 (dt, *J* = 18.1, 1.7 Hz, 1H), 4.53 (ddt, *J* = 16.1, 5.3, 1.8 Hz, 1H), 4.33 (qd, *J* = 7.1, 5.4 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 184.9, 160.4, 149.2, 139.9, 133.4, 133.4, 133.2, 131.3, 125.1, 124.4, 124.4, 123.0, 118.1, 116.8, 116.1, 60.7, 48.8, 14.3; **HRMS** (ESI) *m/z* calc. for $C_{17}H_{16}N_2O_5Na$ $(M+Na)^+$ 351.0957 found 351.0951.



5-(4-Chlorobenzoyl)-2-(naphthalen-1-yl)-1-(prop-2-yn-1-yl)-1*H*-pyrrole-3-carbaldehyde (29): Prepared by following general procedure B using aldimine **2m** (25 mg, 0.13 mmol) as a limiting reagent and obtained as a off yellow solid; m.p. = 48-50 ˚C; yield = 50% (19.5 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (5 mg, 0.032 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.09 (dd, *J* = 7.4, 2.1 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.66 (q, *J* = 6.8 Hz, 2H), 7.59 (dt, *J* = 8.2, 3.9 Hz, 1H), 7.55 – 7.49 (m, 4H), 7.39 (s, 1H), 5.19 (dd, *J* = 17.2, 2.4 Hz, 1H), 4.69 (dd, *J* = 17.2, 2.5 Hz, 1H), 2.16 (t, *J* = 2.5 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 185.9, 185.4, 147.1, 139.1, 136.7, 133.5, 132.8, 131.1, 130.9, 130.9, 130.1, 128.8, 128.7, 127.8, 126.9, 125.1, 125.0, 124.74, 124.66, 120.2, 78.2, 72.9, 36.3; **HRMS** (ESI) *m/z* calc. for $C_{25}H_{17}ClNO_2$ $(M+H)^+$ 398.0948 found 398.0942.

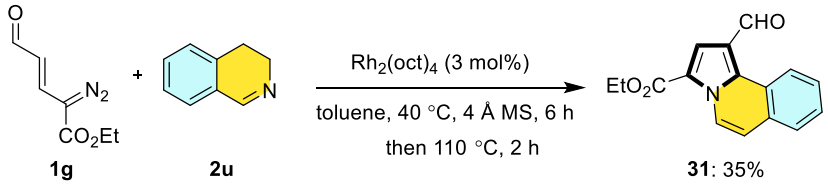
Ethyl 1-allyl-4-formyl-5-(pyren-1-yl)-1*H*-pyrrole-2-carboxylate (30): Prepared by following general procedure B using aldimine **2i** (35 mg, 0.13 mmol) as a limiting reagent and



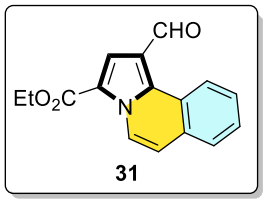
obtained as a yellow solid; m.p. = 71-73 ˚C; yield = 51% (20 mg); R_f = 0.5 (EtOAc/Hexane: 20:80); yield of recovered aldehyde = 25% (7.5 mg, 0.033 mmol); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.29 (d, *J* = 7.6 Hz, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 8.25 (d, *J* = 7.4 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 8.16 (d, *J* = 8.9 Hz, 1H), 8.09 (dd, *J* = 12.6, 5.1 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.71 (s, 1H), 7.70 (d, *J* = 9.1 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.3, 5.1 Hz, 1H), 5.06 (ddt, *J* = 15.9, 4.9, 1.6 Hz, 1H), 4.97 (dd, *J* = 10.3, 1.1 Hz, 1H), 4.64 (dd, *J* = 17.1, 1.1 Hz, 1H), 4.49 (ddt, *J* = 15.9, 5.2, 1.6 Hz, 1H), 4.43 – 4.33 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 186.2, 160.9, 145.9, 133.7, 132.6, 131.3, 131.2, 130.7, 129.2, 129.0, 128.9, 127.2, 126.6, 126.2, 126.0, 124.8, 124.6, 124.6, 124.3, 124.3, 124.0, 122.4, 116.8, 116.4, 60.7, 48.3, 14.4; **HRMS** (ESI) *m/z* calc. for $C_{27}H_{22}NO_3$ $(M+H)^+$ 408.1600 found 408.1594.

5. Reaction with cyclic imines

(a) Synthesis of pyrrolo[2,1-*a*]isoquinoline 31:

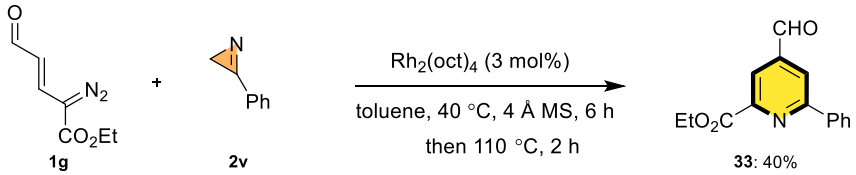


Scheme S3: Synthesis of pyrrolo[2,1-*a*]isoquinoline from 3,4-dihydroisoquinoline

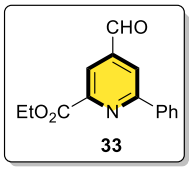


Ethyl 1-formylpyrrolo[2,1-*a*]isoquinoline-3-carboxylate (31): Prepared by following general procedure B using 3,4-dihydroisoquinoline **2u** (17 mg, 0.13 mmol) as a limiting reagent and obtained as a white semi-solid; yield = 35% (12 mg); R_f = 0.45 (EtOAc/Hexane: 20:80); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 9.72 (dd, *J* = 7.8, 1.1 Hz, 1H), 9.44 (d, *J* = 7.4 Hz, 1H), 8.03 (s, 1H), 7.79 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.71 (pd, *J* = 7.1, 1.6 Hz, 2H), 7.31 (d, *J* = 7.4 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 184.6, 160.9, 135.8, 130.0, 129.7, 128.3, 127.7, 127.6, 126.8, 125.2, 124.4, 118.7, 117.5, 115.9, 60.7, 14.5; **HRMS** (ESI) *m/z* calc. for $C_{16}H_{14}NO_3$ $(M+H)^+$ 268.0974 found 268.0968.

(b) Synthesis of pyridine 33:



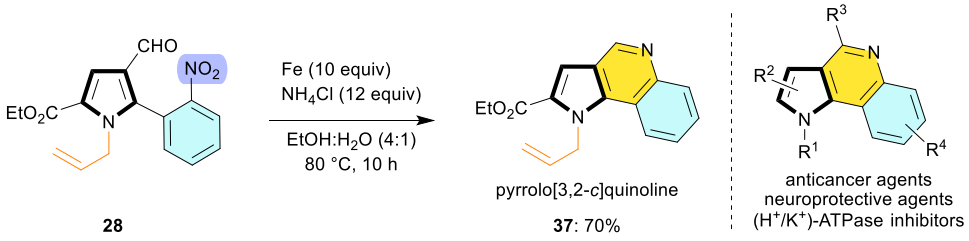
Scheme S4: Synthesis of pyridine from 2*H*-azirine **33**



Ethyl 4-formyl-6-phenylpicolinate (33): Prepared by following general procedure B using 2H-azirine **2v** (15 mg, 0.13 mmol) as a limiting reagent and obtained as a viscous liquid; yield = 40% (13 mg); R_f = 0.45 (EtOAc/Hexane: 20:80); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.41 (d, *J* = 1.3 Hz, 1H), 8.31 (d, *J* = 1.3 Hz, 1H), 8.17 – 8.11 (m, 2H), 7.55 – 7.47 (m, 3H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.8, 164.6, 159.4, 150.1, 143.6, 137.4, 130.2, 129.1, 127.3, 122.1, 121.4, 62.4, 14.3; **HRMS** (ESI) *m/z* calc. for $C_{15}H_{14}NO_3$ $(M+H)^+$ 256.0974 found 256.0968.

6. Synthetic applications:

(a) Synthesis of pyrrolo[3,2-c]quinoline 37:

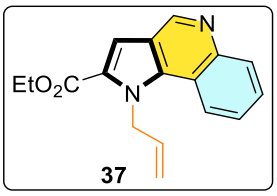


Scheme S5: Synthesis of pyrrolo[3,2-*c*]quinoline **37**

General procedure C:[3]

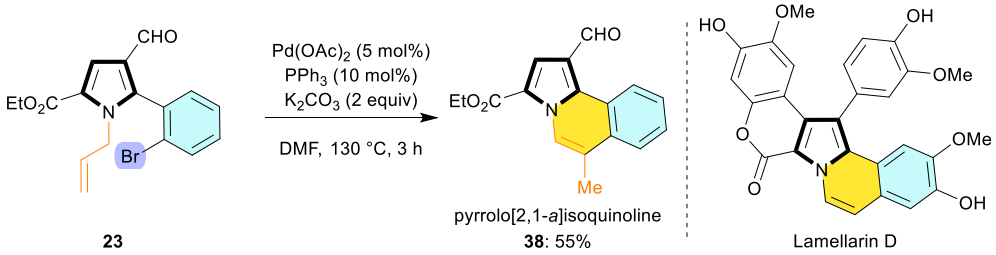
In an oven-dried round bottom flask, a mixture of pyrrole derivative **28** (20 mg, 0.06 mmol), Fe powder (34 mg, 0.6 mmol), and NH_4Cl (39 mg, 0.72 mmol) in 5 mL EtOH: H_2O (4:1) was stirred for 10 h at 80 ˚C. After completion of the reaction (checked by TLC), the solvent was evaporated using a rotary evaporator. To the residue, 15 mL of saturated $NaHCO_3$ solution was added and the contents were extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator.

Purification by silica gel column chromatography using hexane/ethyl acetate (85:15) as eluent gave the pure product **37**.



Ethyl 1-allyl-1*H*-pyrrolo[3,2-*c*]quinoline-2-carboxylate (37): Prepared by following general procedure C and obtained as a yellow gummy liquid; yield = 70% (11 mg); R_f = 0.2 (EtOAc/Hexane: 20:80); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.06 (dd, *J* = 8.6, 1.4 Hz, 1H), 8.94 (s, 1H), 8.33 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.80 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.74 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.49 (s, 1H), 6.24 (ddt, *J* = 17.2, 10.6, 4.0 Hz, 1H), 5.72 (s, 2H), 5.29 (dt, *J* = 10.6, 2.0 Hz, 1H), 4.91 (dt, *J* = 17.4, 2.1 Hz, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 160.7, 139.3, 132.5, 131.6, 131.0, 129.4, 128.7, 128.7, 122.1, 121.9, 119.2, 118.1, 117.0, 111.2, 61.2, 49.3, 14.3; **HRMS** (ESI) *m/z* calc. for $C_{17}H_{17}N_2O_2$ $(M+H)^+$ 281.1290 found 281.1285.

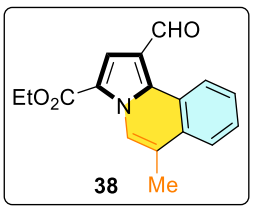
(b) Synthesis of pyrrolo[2,1-a]isoquinoline 38:



Scheme S6: Synthesis of pyrrolo[2,1-*a*]isoquinoline **38**

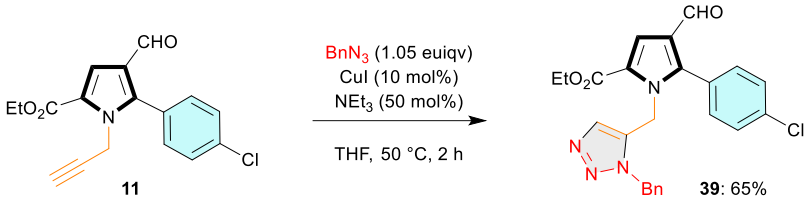
General procedure D:

In an oven-dried round bottom flask, a mixture of pyrrole derivative **23** (10 mg, 0.027 mmol), $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), and K_2CO_3 (7.5 mg, 0.054 mmol) in 2 mL DMF stirred for 3 h at 130 ˚C. After completion of the reaction, in this residue 10 mL water was added and the contents were extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. Purification by silica gel column chromatography using hexane/ethyl acetate (95:5) as eluent gave the pure product **38**.



Ethyl 1-formyl-6-methylpyrrolo[2,1-*a*]isoquinoline-3-carboxylate (38): Prepared by following general procedure D and obtained as a white semi-solid; yield = 53% (4 mg); R_f = 0.55 (EtOAc/Hexane: 20:80); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.84 – 9.79 (m, 1H), 9.34 (s, 1H), 7.99 (s, 1H), 7.91 (dd, *J* = 7.0, 2.6 Hz, 1H), 7.75 (dd, *J* = 6.6, 3.0 Hz, 2H), 4.43 (q, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 184.6, 161.0, 135.4, 130.5, 129.7, 128.1, 128.0, 127.8, 125.0, 123.4, 122.7, 122.3, 118.5, 117.1, 60.7, 16.8, 14.5; **HRMS** (ESI) *m/z* calc. for $C_{17}H_{15}NO_3Na$ $(M+Na)^+$ 304.0950 found 304.0944.

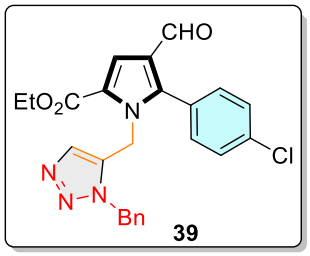
(c) Application toward click reaction:



Scheme S7: Synthesis of triazole tethered pyrrole **39**

General procedure E:

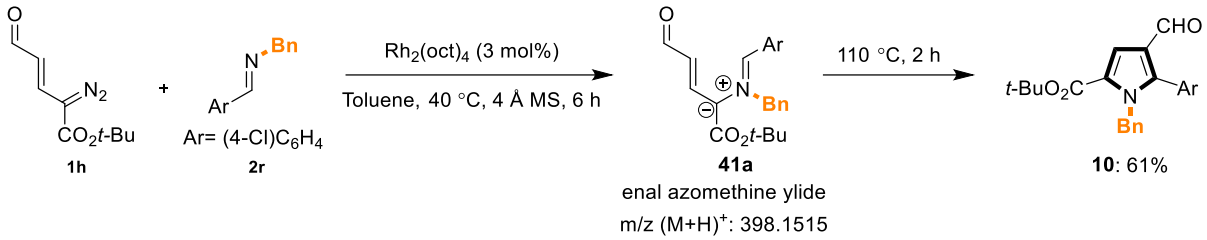
In an oven-dried round bottom flask, a mixture of pyrrole derivative **11** (20 mg, 0.063 mmol), benzyl azide (9 mg, 0.066 mmol), CuI (10 mol%), and NEt_3 (50 mol%) in 2 mL THF was stirred for 2 h at 50 ˚C. After completion of the reaction, the solvent was evaporated using a rotary evaporator. To this residue 10 mL water was added and the contents were extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator. Purification by silica gel column chromatography using hexane/ethyl acetate (9:1) as eluent gave the pure product **39**.



Ethyl 1-((1-benzyl-1H-1,2,3-triazol-5-yl)methyl)-5-(4-chlorophenyl)-4-formyl-1*H*-pyrrole-2-carboxylate (39): Prepared by following general procedure E and obtained as a viscous liquid; yield = 65% (18 mg); R_f = 0.35 (EtOAc/Hexane: 20:80); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.47 (s, 1H), 7.41 (s, 1H), 7.36 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.25 – 7.19 (m, 2H), 5.47 (s, 2H), 5.46 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 185.9, 160.9, 146.3, 144.1, 136.4, 134.5, 132.8, 129.1, 129.0, 128.8, 128.0, 126.4, 123.7, 123.6, 123.0, 117.0, 60.6, 54.2, 41.1, 14.2; **HRMS** (ESI) *m/z* calc. for $C_{24}H_{21}ClN_4O_3Na$ $(M+Na)^+$ 471.1200 found 471.1194.

7. Control Experiments

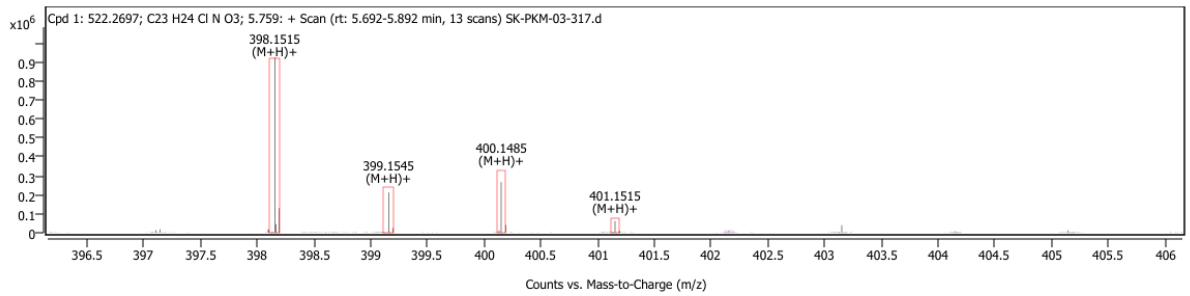
(a) Detection of EAY 41a by HRMS:



Scheme S8: Detection of enal-azomethine ylide **41a**

Procedure F: An oven-dried 10 mL round bottom flask containing a stir bar under nitrogen atmosphere was charged with aldimine **2r** (30 mg, 0.13 mmol), $Rh_2(oct)_4$ (3 mg, 0.004 mmol), 4Å MS (50 mg), 2 ml dry toluene and stirred at 40 ˚C. Then a solution of diazoenal **1h** (39 mg, 0.2 mmol) in 2 ml dry toluene was added dropwise over 1.5 h to the reaction mixture via a syringe pump. The reaction was continued until the diazoenal was completely consumed (6 h judged by TLC). The crude reaction mixture was submitted for mass spectroscopic characterization. HRMS data of EAY **41A**: (Agilent QTOF-ESI) m/z calc. for $C_{23}H_{25}ClNO_3$, $(M+H)^+$ 398.1517, found 398.1515.

The temperature of the reaction mixture was brought to 110 ˚C and continued for another 3 h. The crude reaction mixture was filtered through celite and washed with DCM (5 mL). The filtrate was concentrated under reduced pressure. The crude material was purified by a silica gel flash column chromatography using ethyl acetate/hexane (5:95) as the eluent. The 3-formyl pyrrole **10** was obtained as a viscous liquid. Yield = 61% (24 mg). Recovered 4-chloro benzaldehyde = 22% (5 mg, 0.035 mmol).

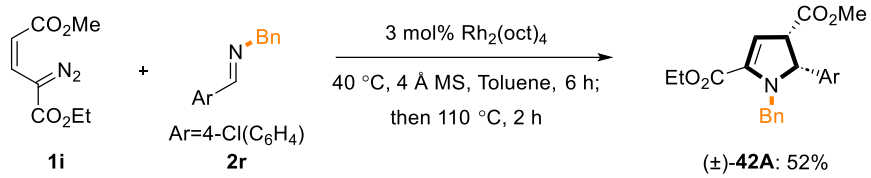


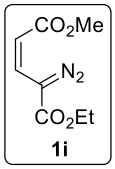
Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
398.1515	398.1517	-0.64	924830	100.00	100.00	(M+H)+	1
399.1545	399.1550	-1.27	211026	22.82	25.64	(M+H)+	1
400.1485	400.1498	-3.17	265537	28.71	35.76	(M+H)+	1
401.1515	401.1525	-2.49	60650	6.56	8.61	(M+H)+	1

Fig. S4: Mass report for enal azomethine ylide **41a**

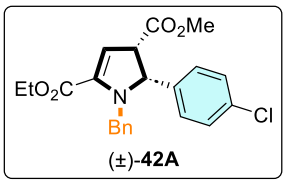
(b) Probing the role of formyl group: Formation of (±)-dihydropyrrole 42A:





The known (*Z*)-vinyl diazo ester **1i** was synthesized following the reported procedure.[4] Obtained as a viscous yellow liquid; R_f = 0.7 (EtOAc/Hexane: 20:80); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (d, *J* = 12.0 Hz, 1H), 5.66 (d, *J* = 12.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.72 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H).

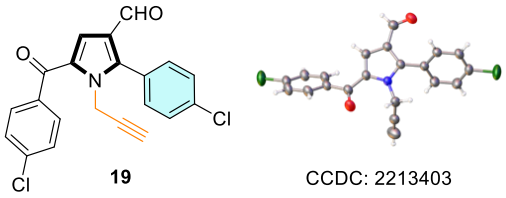
Procedure for formation of (±)-**42A**: An oven-dried 10 mL round bottom flask containing a stir bar under nitrogen atmosphere was charged with aldimine **2r** (30 mg, 0.13 mmol), $Rh_2(oct)_4$ (3 mg, 0.004 mmol), 4Å MS (50 mg), 2 ml dry toluene and stirred at 40 ˚C. Then a solution of vinyl diazo compound **1i** (40 mg, 0.2 mmol) in 2 ml dry toluene was added dropwise over 1.5 h to the reaction mixture via a syringe pump. After completion of the addition, the reaction was continued until the diazo compound was completely consumed (6 h judged by TLC). Then the temperature of the reaction vessel was brought to 110 ˚C and continued for another 3 h. The crude reaction mixture was filtered through a celite pad and washed with DCM (5 mL). The filtrate was concentrated under reduced pressure. The crude material was purified by a silica gel flash column chromatography using ethyl acetate/hexane (15:85) as the eluent to furnish the dihydropyrrole (±)-**42A**.



2-Ethyl 4-methyl (*4R*,5S)-1-benzyl-5-(4-chlorophenyl)-4,5-dihydro-1*H*-pyrrole-2,4-dicarboxylate (±)-42A:** Obtained as a colorless viscous liquid; yield = 52% (27 mg); R_f = 0.35 (EtOAc/Hexane: 20:80); **^{1}H NMR** (700 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 7.7 Hz, 2H), 6.27 (d, *J* = 8.9 Hz, 1H), 4.83 (d, *J* = 14.9 Hz, 1H), 4.29 (d, *J* = 2.3 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.00 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.83 (d, *J* = 14.9 Hz, 1H), 3.61 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$) δ 166.9, 162.8, 149.3, 135.5, 135.0, 134.6, 129.3, 128.9, 128.6, 128.0 (2C), 118.4, 61.4, 60.4, 60.2, 57.5, 44.9, 14.2; **HRMS** (Agilent QTOF-ESI) *m/z* calc. for $C_{22}H_{23}ClNO_4$ $(M+H)^+$ 400.1310 found 400.1313.

6. Crystallographic data:

Table 2: Crystal data and structure refinement parameters for **19**



ORTEP diagram for **19** (ellipsoid contour 50% probability)

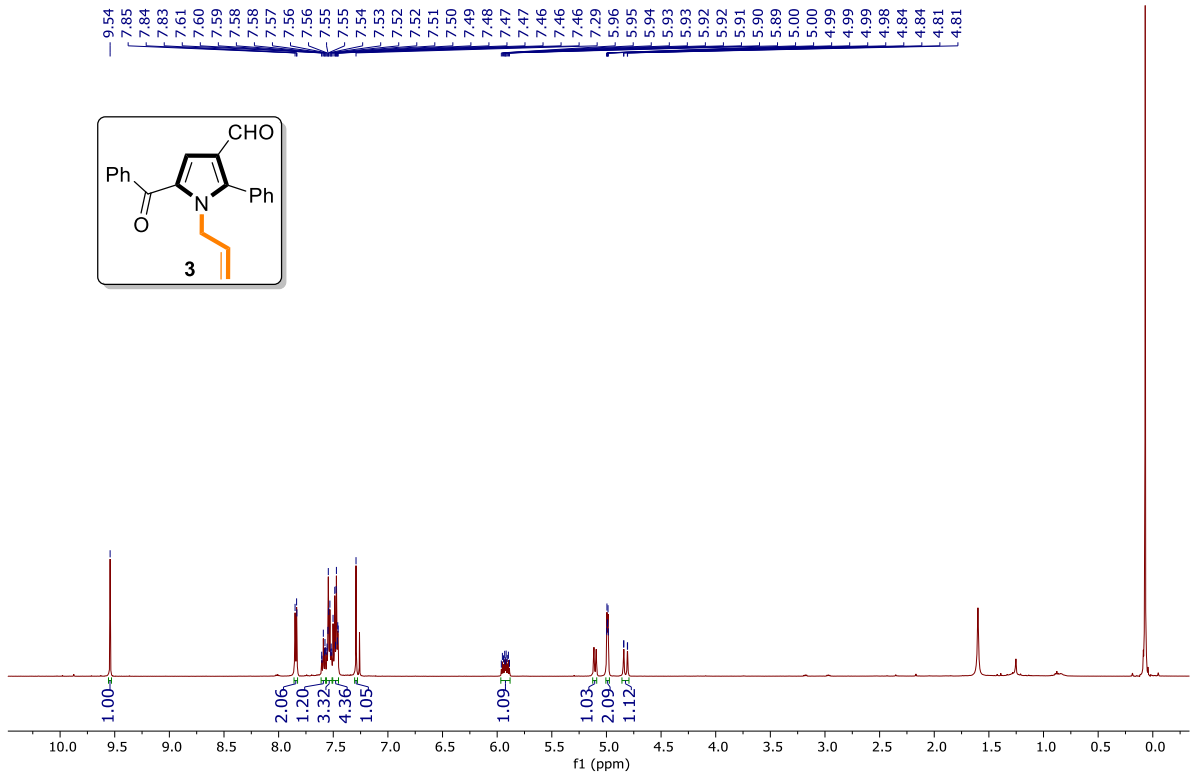
CCDC	2213403
Empirical formula	$C_{21}H_{13}Cl_2NO_2$
Formula weight	382.22
Temperature/K	300.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.445(3)
b/Å	19.168(6)
c/Å	9.550(3)
α/°	90
β/°	111.776(9)
γ/°	90
Volume/Å^3	1775.7(9)
Z	4
ρ_{calc}g/cm^3	1.430
μ/mm^{-1}	0.381
F(000)	784.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.2 to 56.688
Index ranges	$-13 \leq h \leq 13$, $-25 \leq k \leq 25$, $-12 \leq l \leq 12$

Reflections collected	33909
Independent reflections	4385 [R_{int} = 0.0606, R_{sigma} = 0.0464]
Data/restraints/parameters	4385/0/235
Goodness-of-fit on F^2	1.210
Final R indexes [I>=2σ (I)]	R_1 = 0.0484, wR_2 = 0.1475
Final R indexes [all data]	R_1 = 0.0885, wR_2 = 0.1934
Largest diff. peak/hole / e $Å^{-3}$	0.83/-0.98

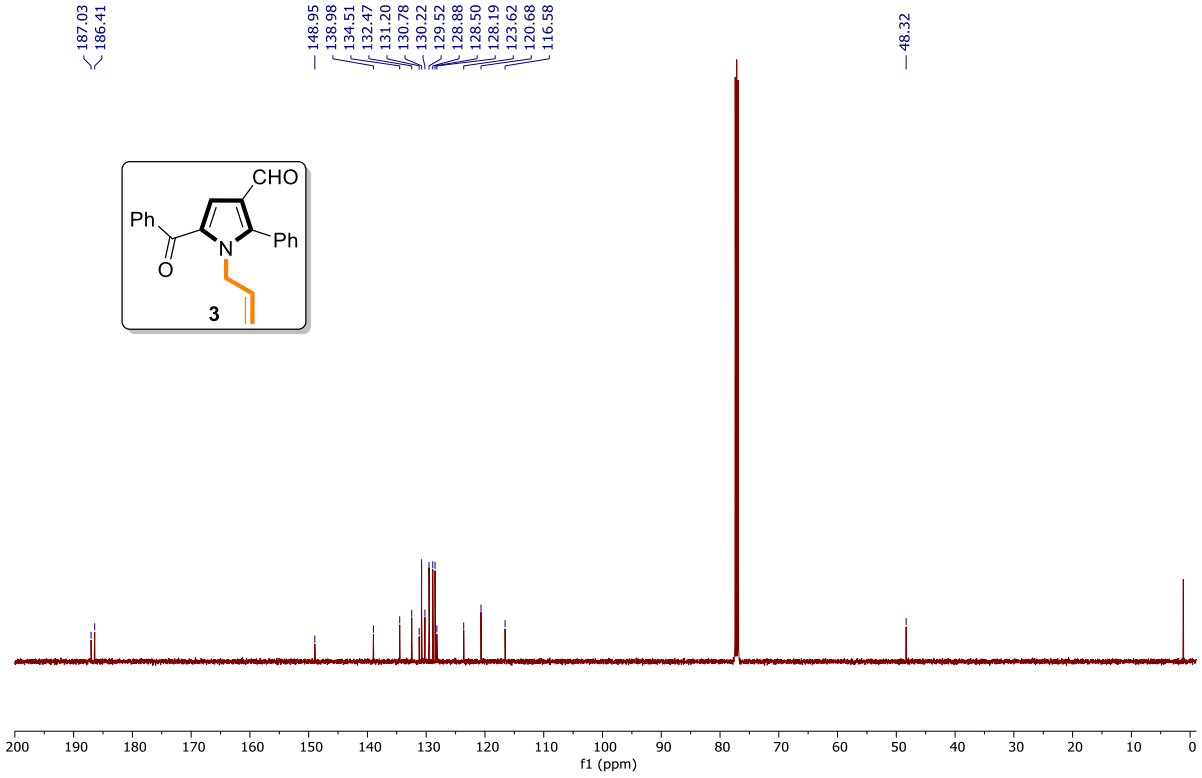
7. References:

1. S. G. Dawande, V. Kanchupalli, J. Kalepu, H. Chennamsetti, B. S. Lad and S. Katukojvala, *Angew. Chem., Int. Ed.*, 2014, **53**, 4076–4080.
2. (a) M. Vayer, S. P. Morcillo, J. Dupont, V. Gandon and C. Bour *Angew. Chem., Int. Ed.*, 2018, **57**, 3228–3232. (b) P. G. Cozzi, *Chem. Soc. Rev.,* 2004, **33**, 410–421. (c) K. Isomura, M. Okada and H. Taniguchi, *Tetrahedron Lett.,* 1969, **10**, 4073–4076.
3. S. Choudhary, J. Yadav, Mamta, A. P. Pawar, S. Vanaparthi, N. A. Mir, E. Iype, R. Sharma, R. Kant and I. Kumar, *Org. Biomol. Chem.*, 2020, **18**, 1155−1164.
4. F. Ye, S. Qu, L. Zhou, C. Peng, C. Wang, J. Cheng, M. L. Hossain, Y. Liu, Y. Zhang, Z.-X. Wang and J. Wang, *J. Am. Chem Soc.*, 2015, **137**, 4435−4444.

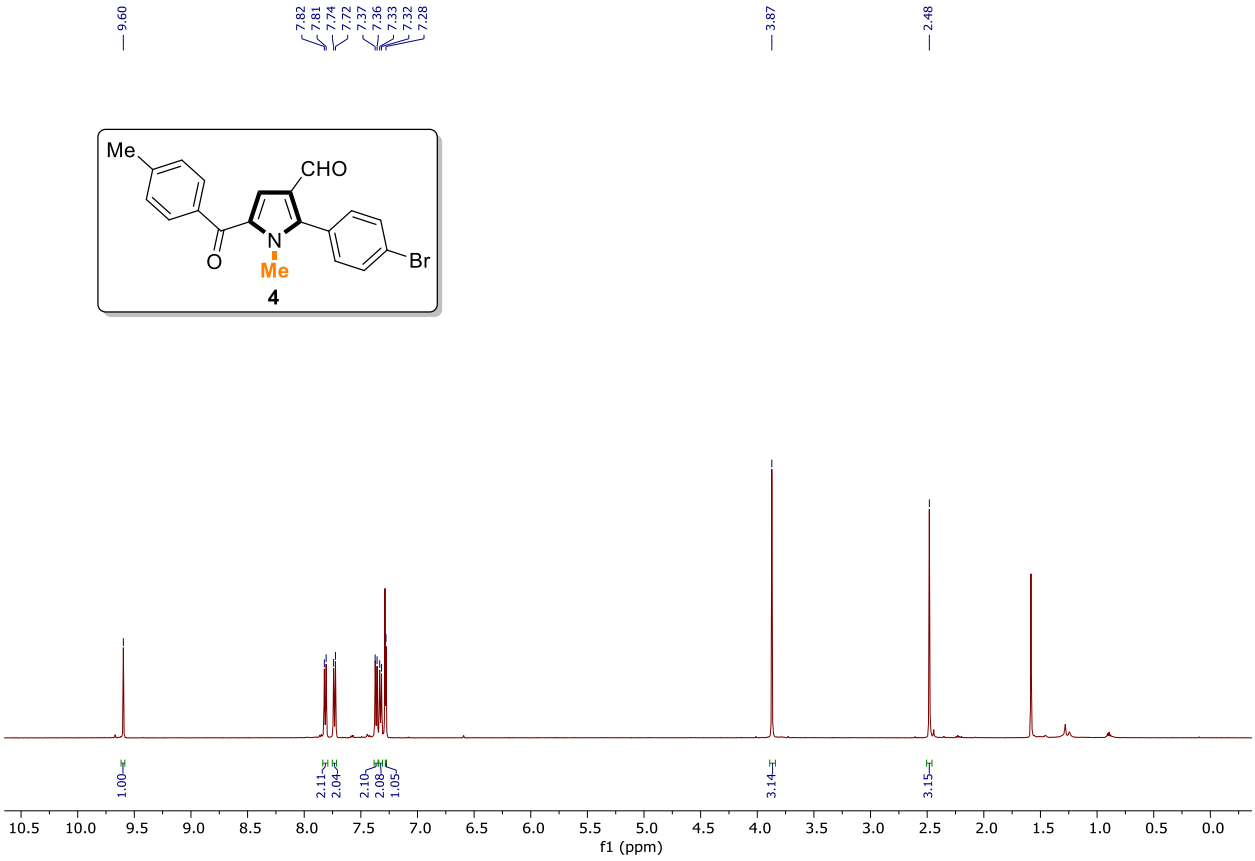
NMR Spectra:



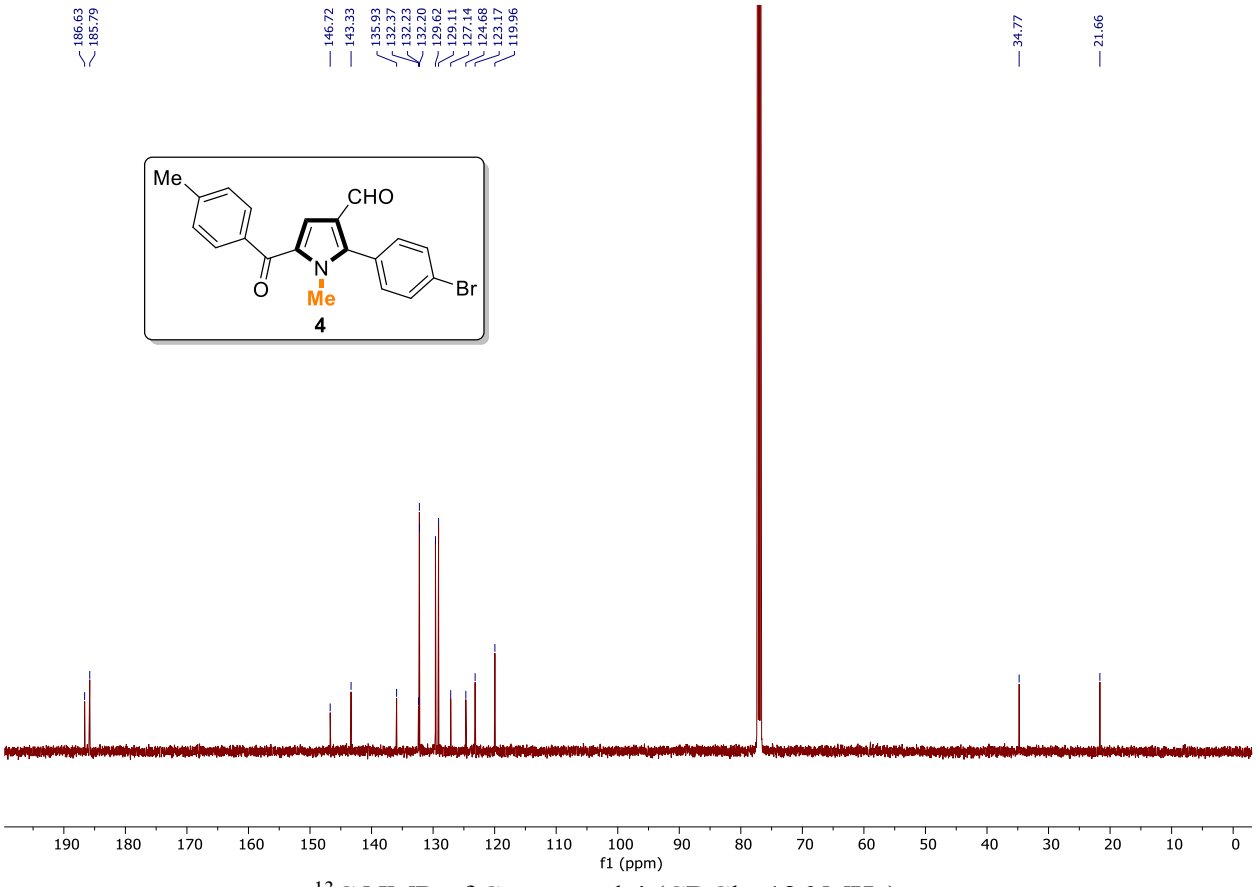
^{1}H NMR of Compound **3** ($CDCl_3$, 500 MHz)



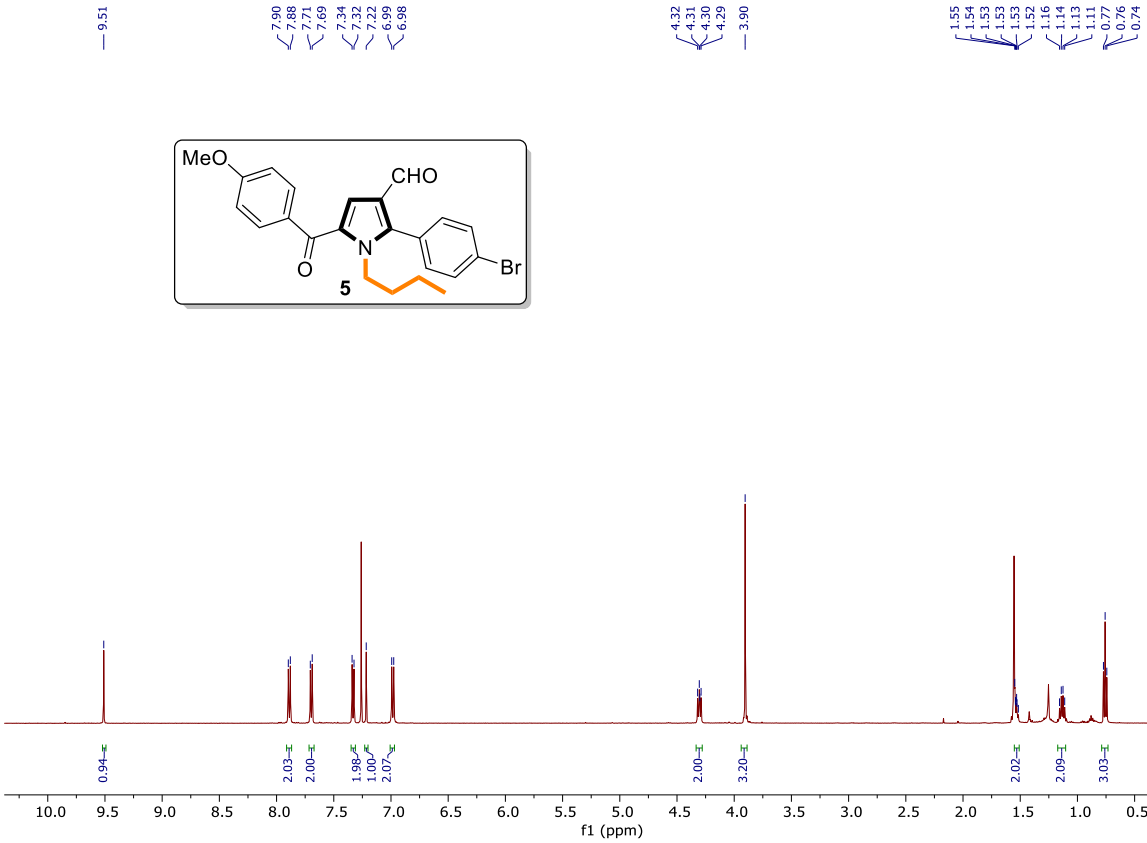
^{13}C NMR of Compound **3** ($CDCl_3$, 126 MHz)



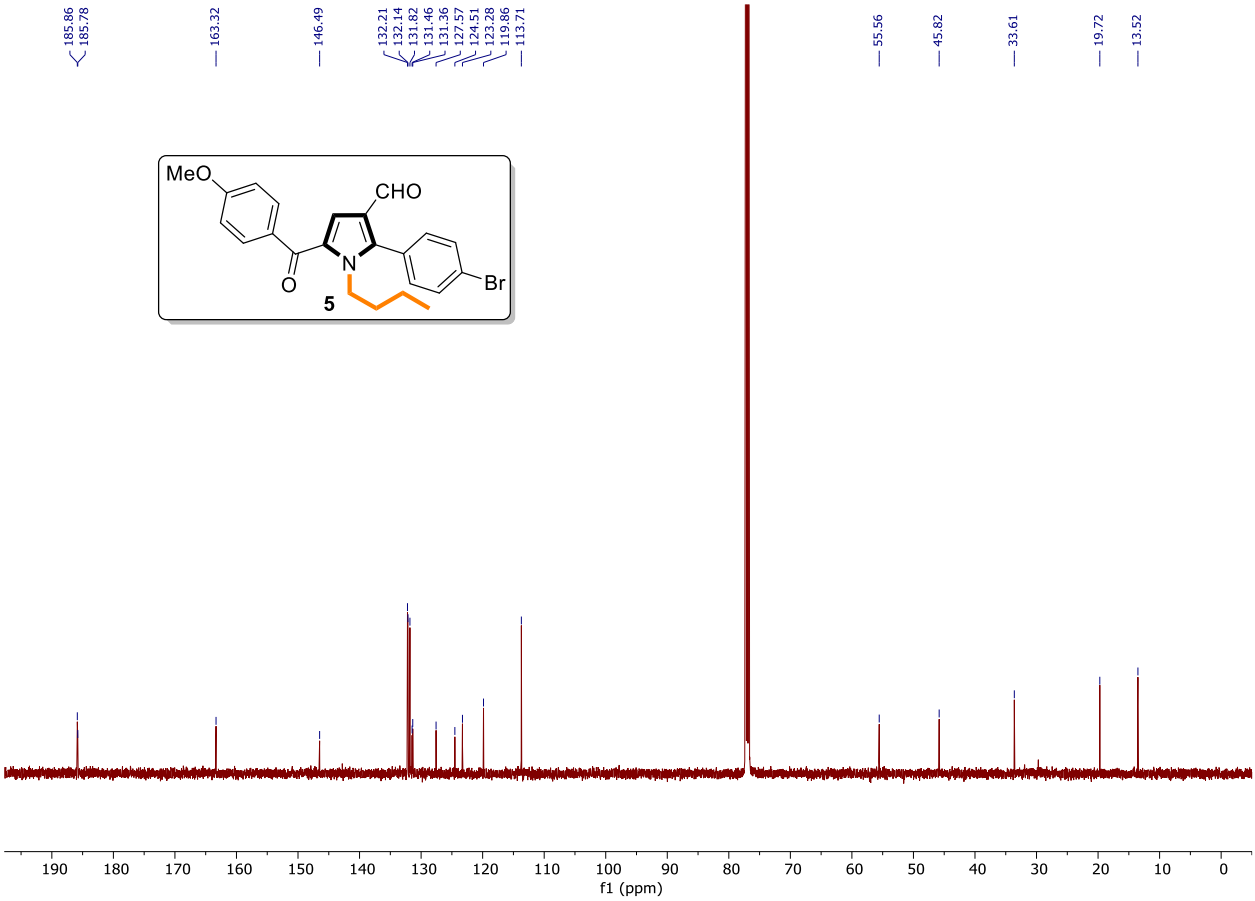
^{1}H NMR of Compound **4** ($CDCl_3$, 500 MHz)



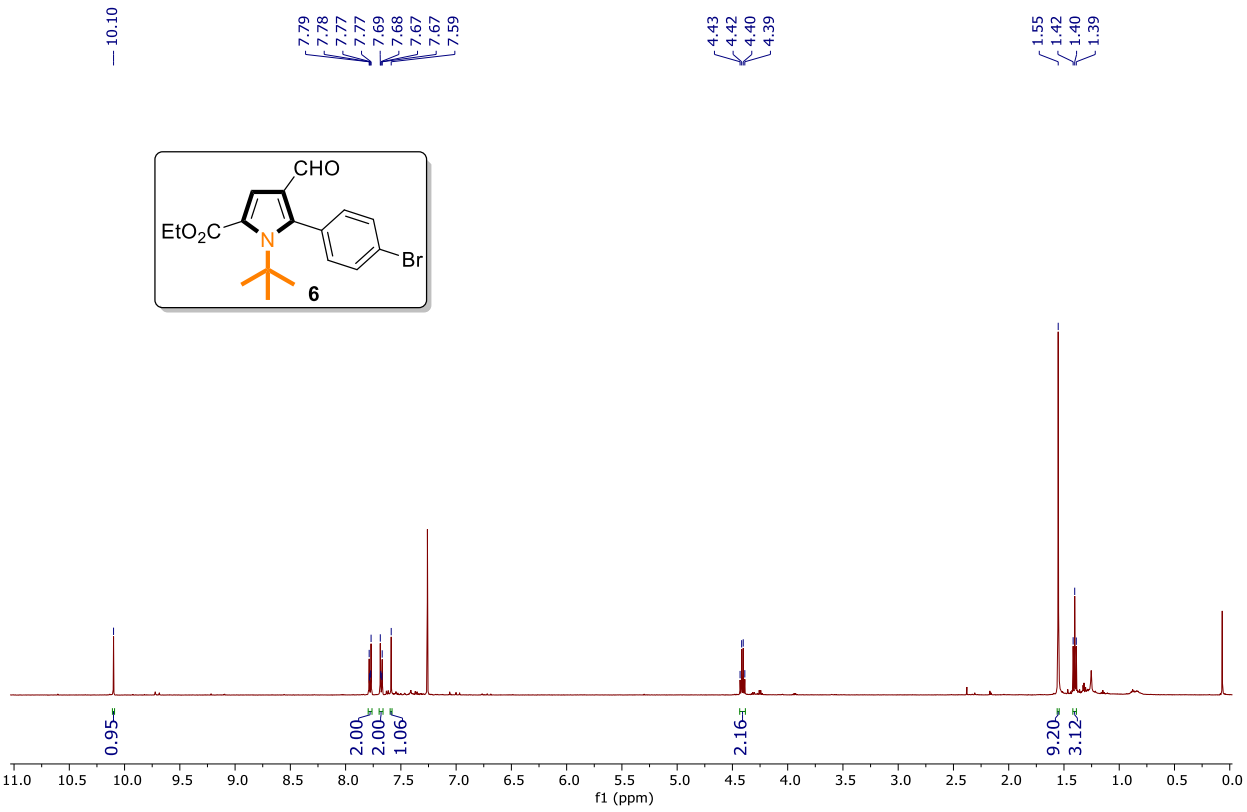
^{13}C NMR of Compound **4** ($CDCl_3$, 126 MHz)



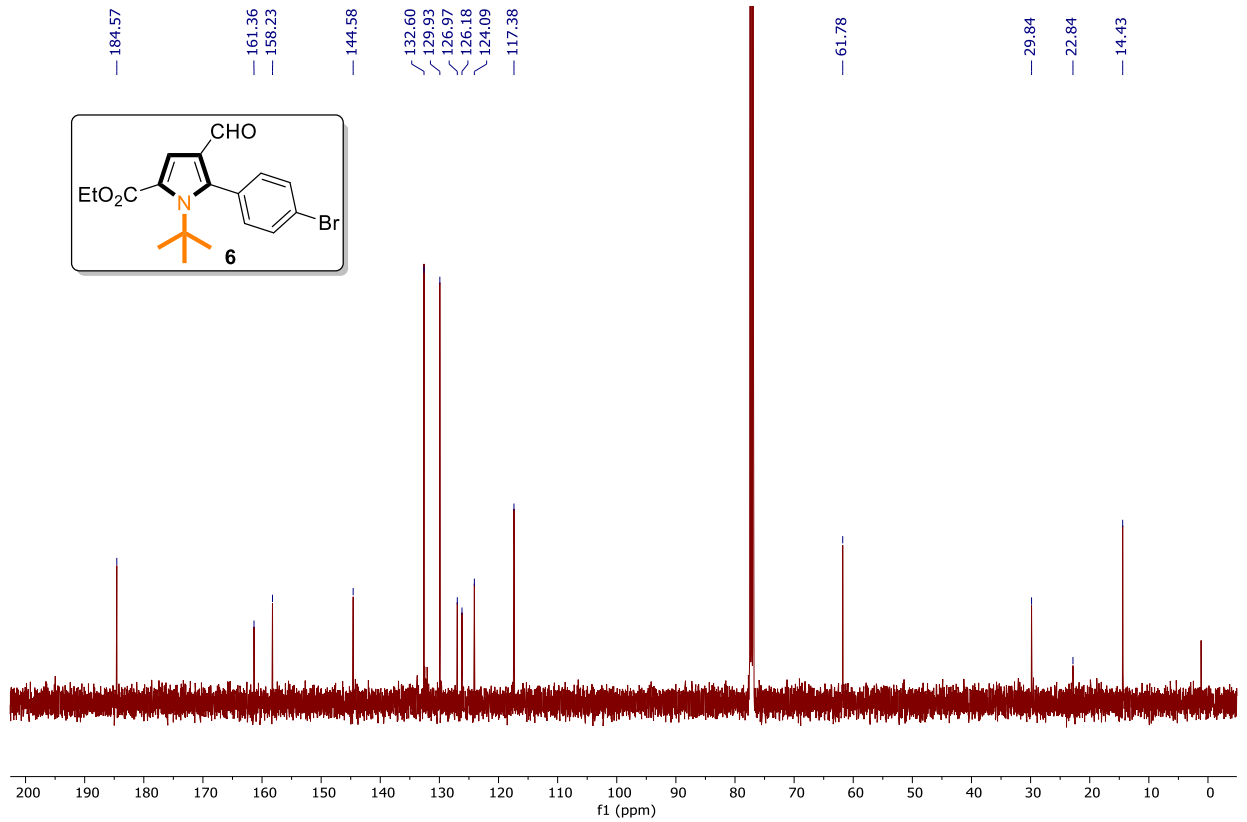
^{1}H NMR of Compound **5** ($CDCl_3$, 500 MHz)



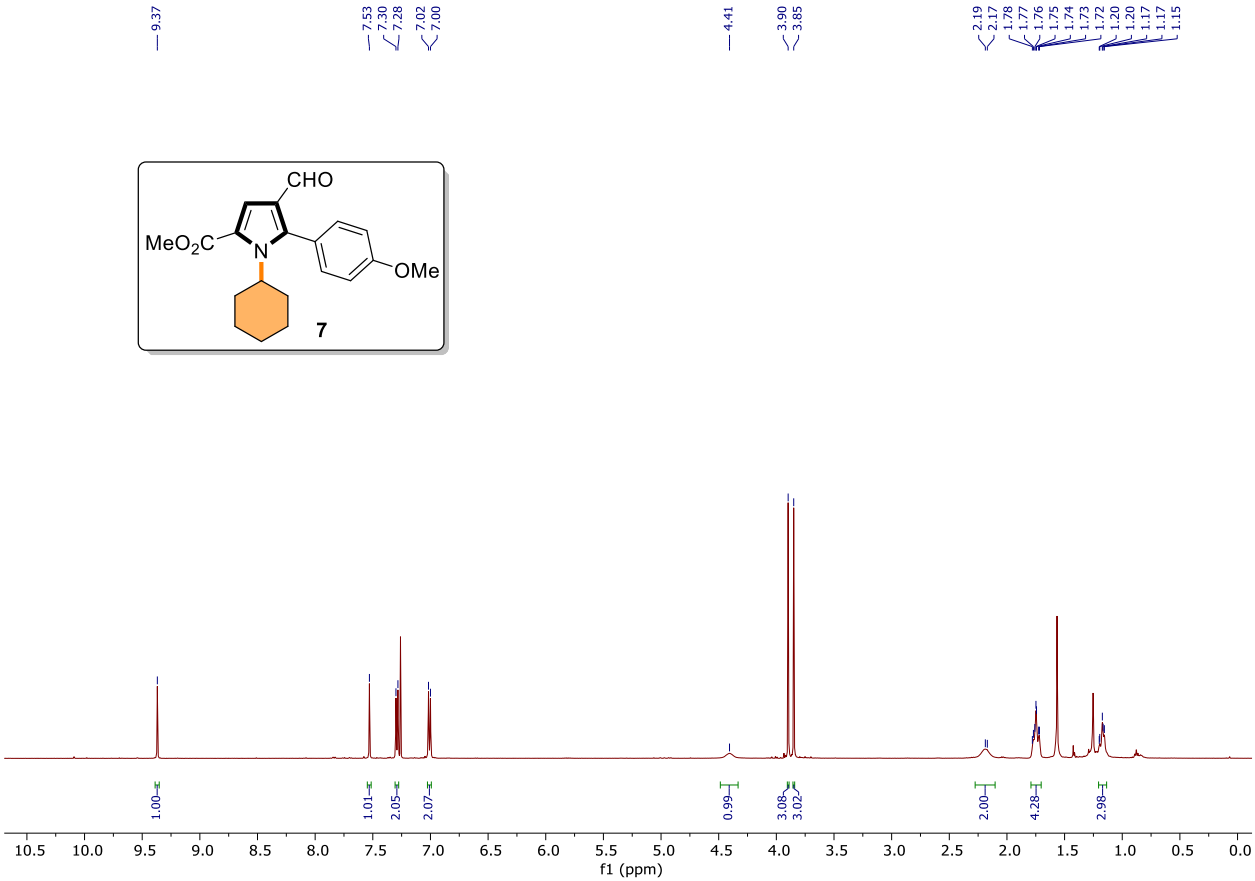
^{13}C NMR of Compound **5** ($CDCl_3$, 126 MHz)



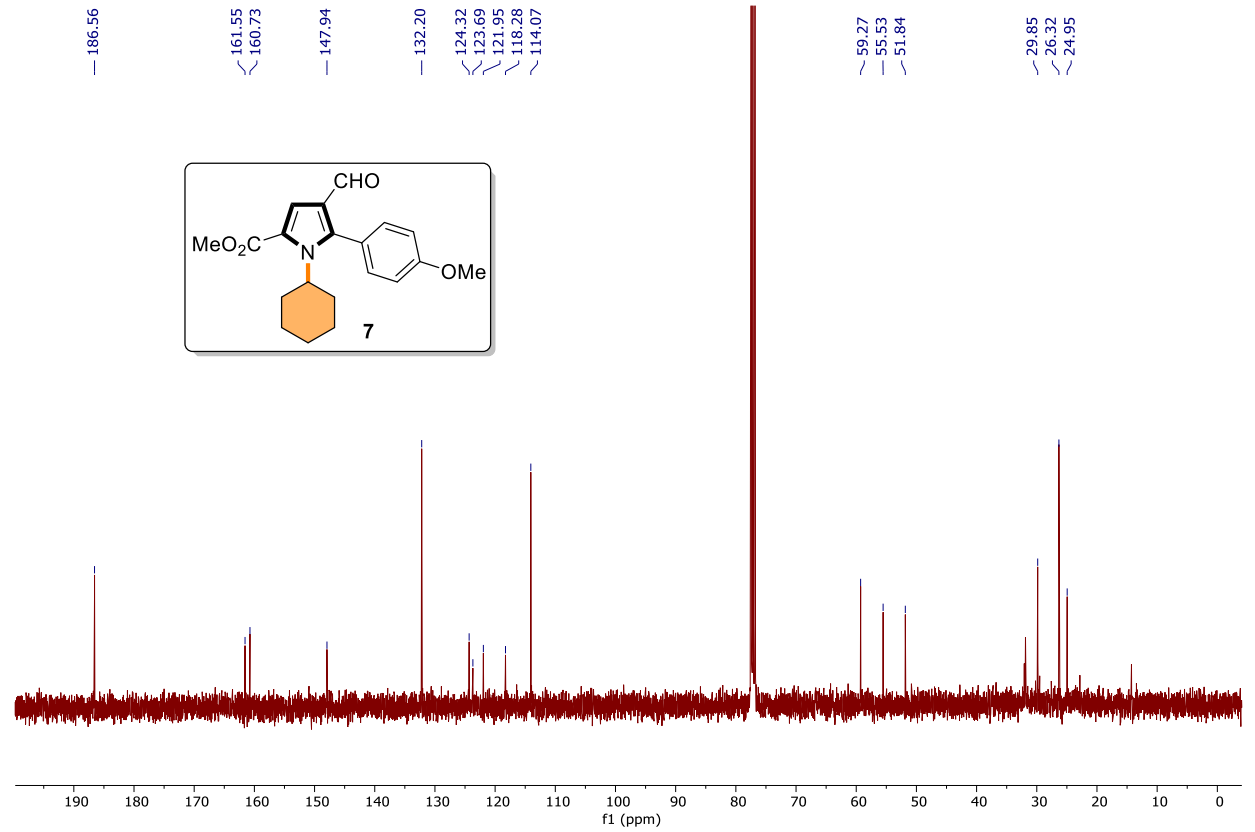
^{1}H NMR of Compound **6** ($CDCl_3$, 500 MHz)



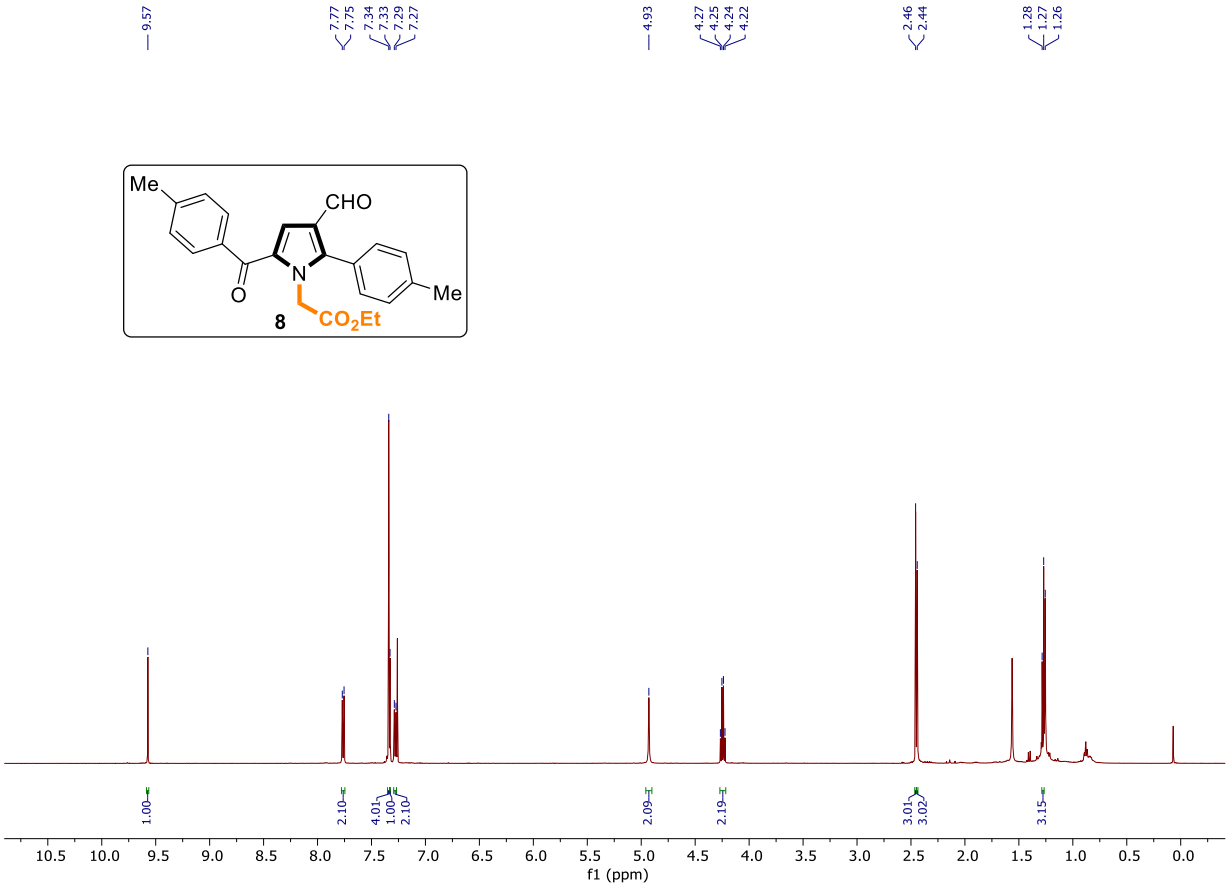
^{13}C NMR of Compound **6** ($CDCl_3$, 126 MHz)



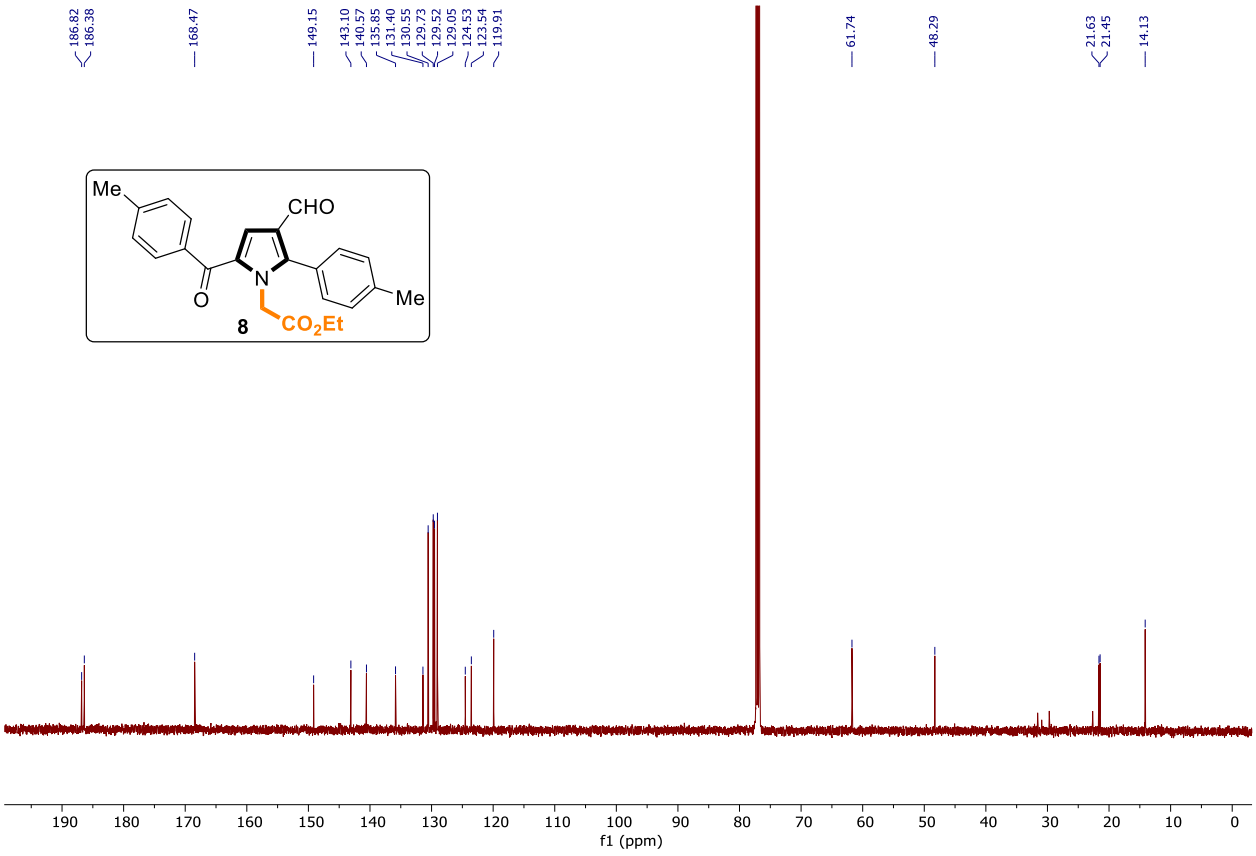
^{1}H NMR of Compound **7** ($CDCl_3$, 500 MHz)



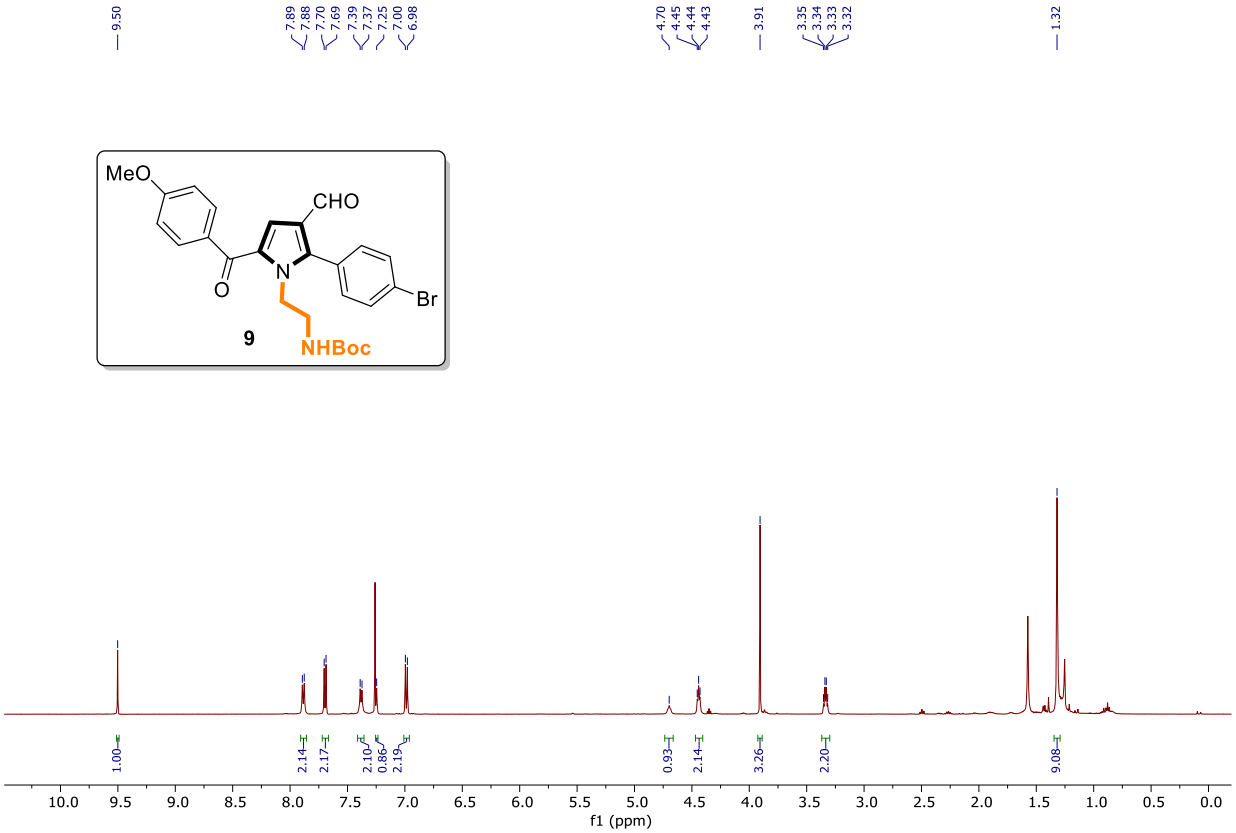
^{13}C NMR of Compound **7** ($CDCl_3$, 126 MHz)



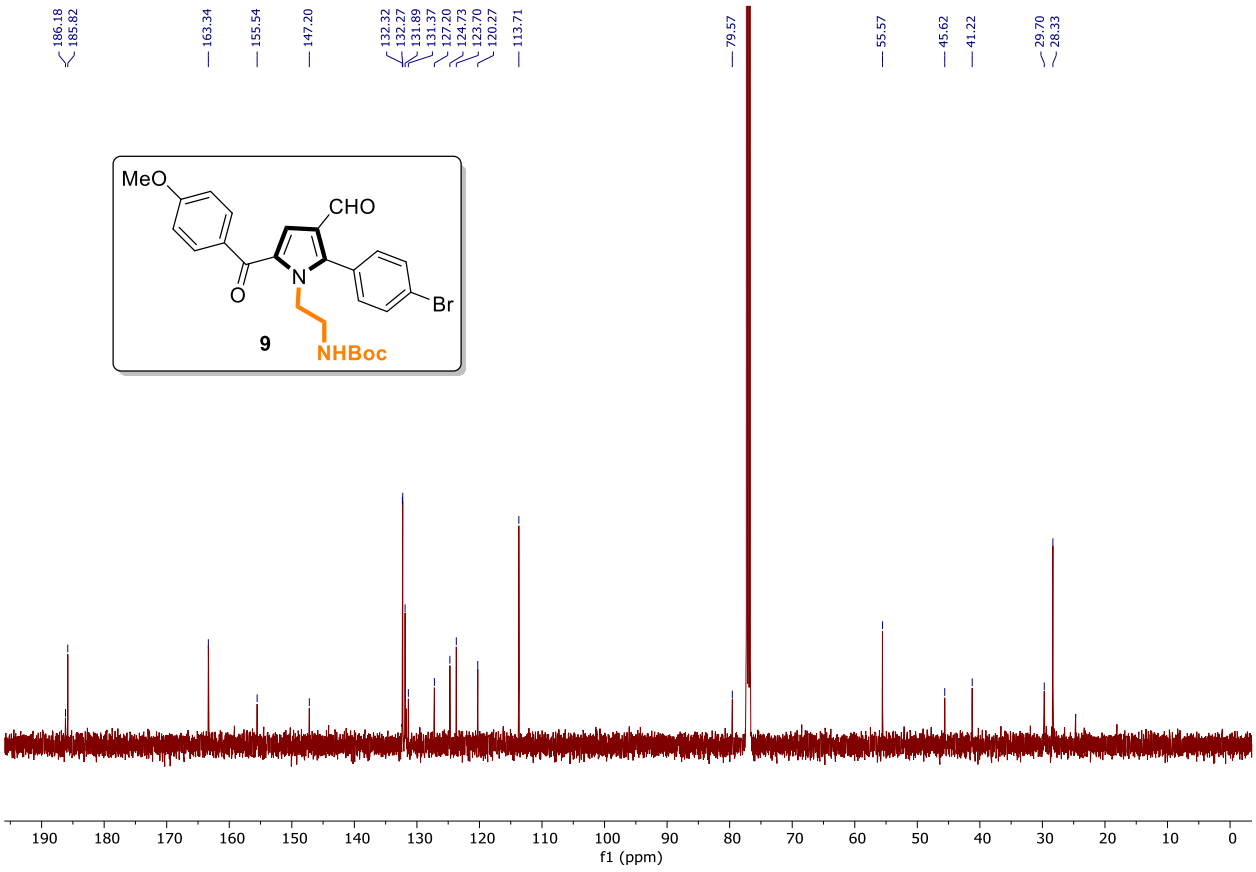
^{1}H NMR of Compound **8** ($CDCl_3$, 500 MHz)



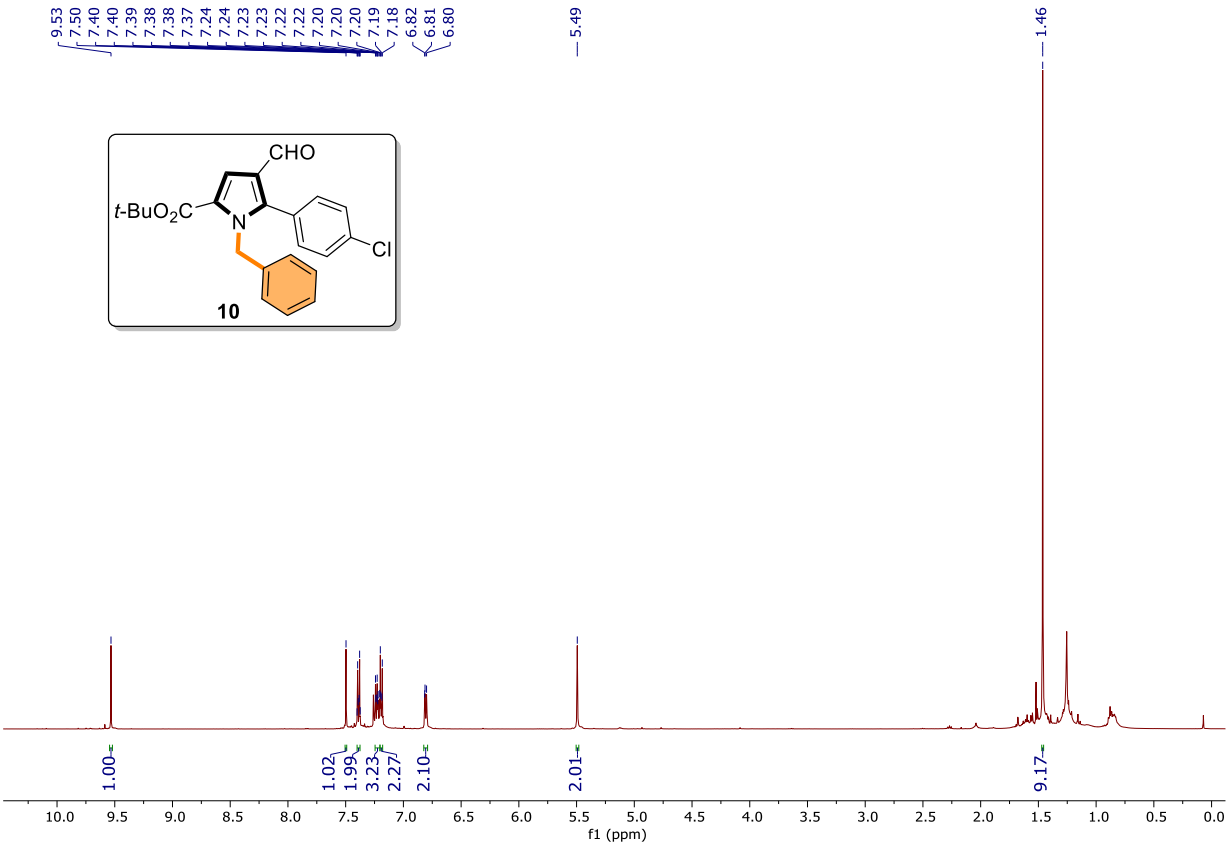
^{13}C NMR of Compound **8** ($CDCl_3$, 126 MHz)



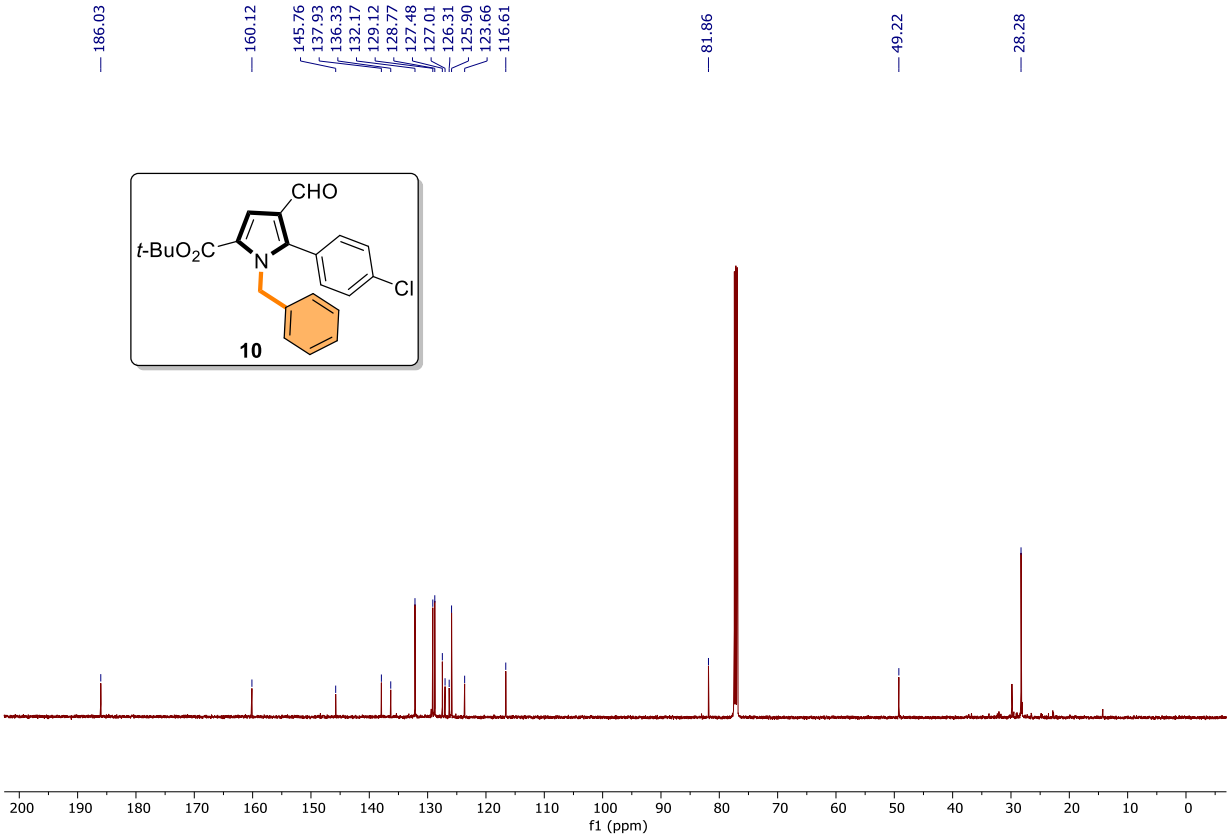
^{1}H NMR of Compound **9** ($CDCl_3$, 500 MHz)



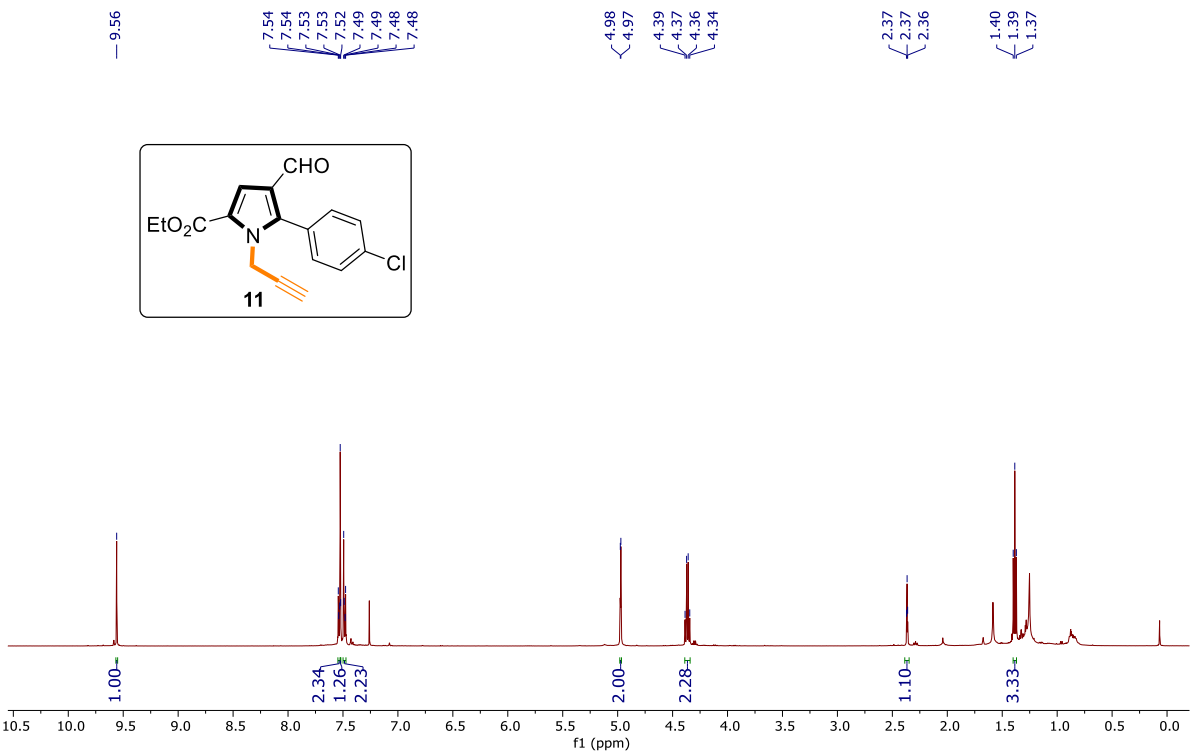
^{13}C NMR of Compound **9** ($CDCl_3$, 126 MHz)



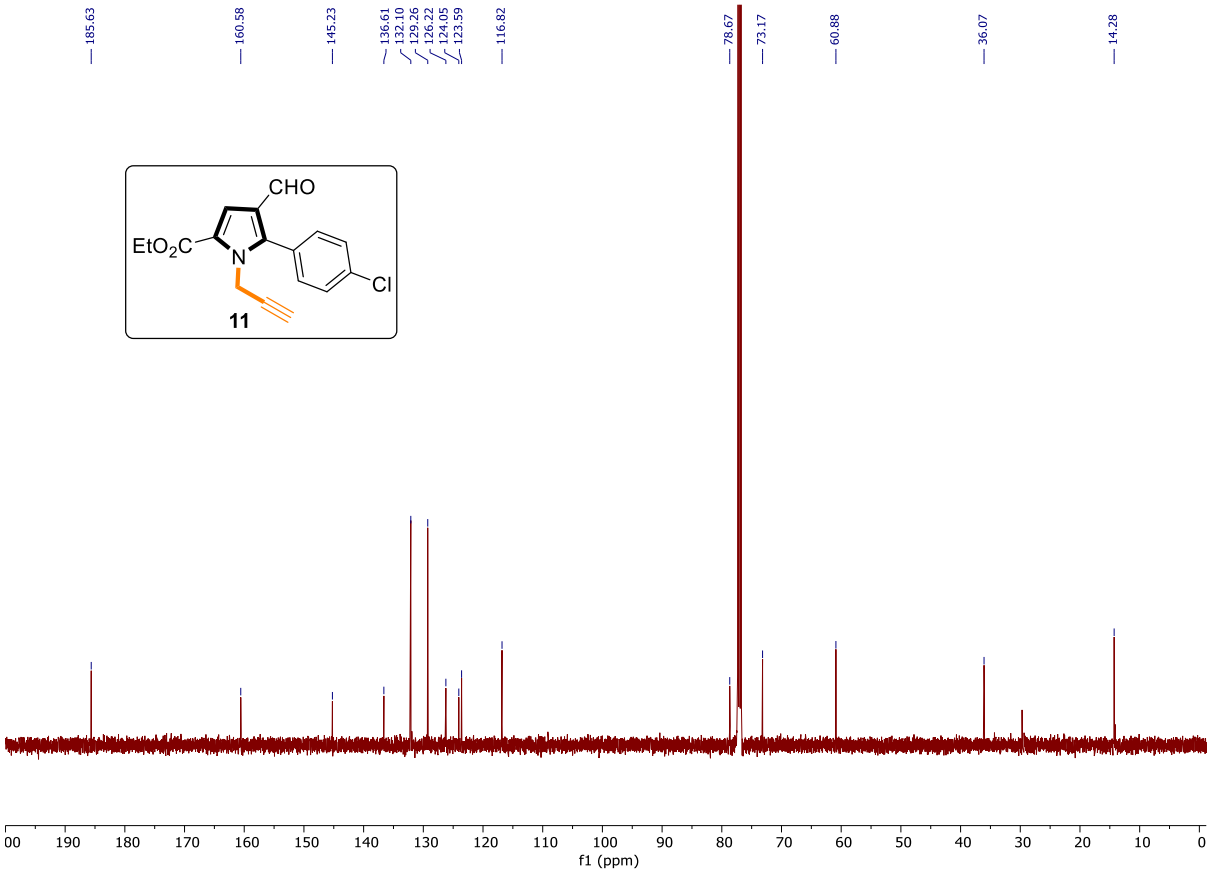
^{1}H NMR of Compound **10** ($CDCl_3$, 500 MHz)



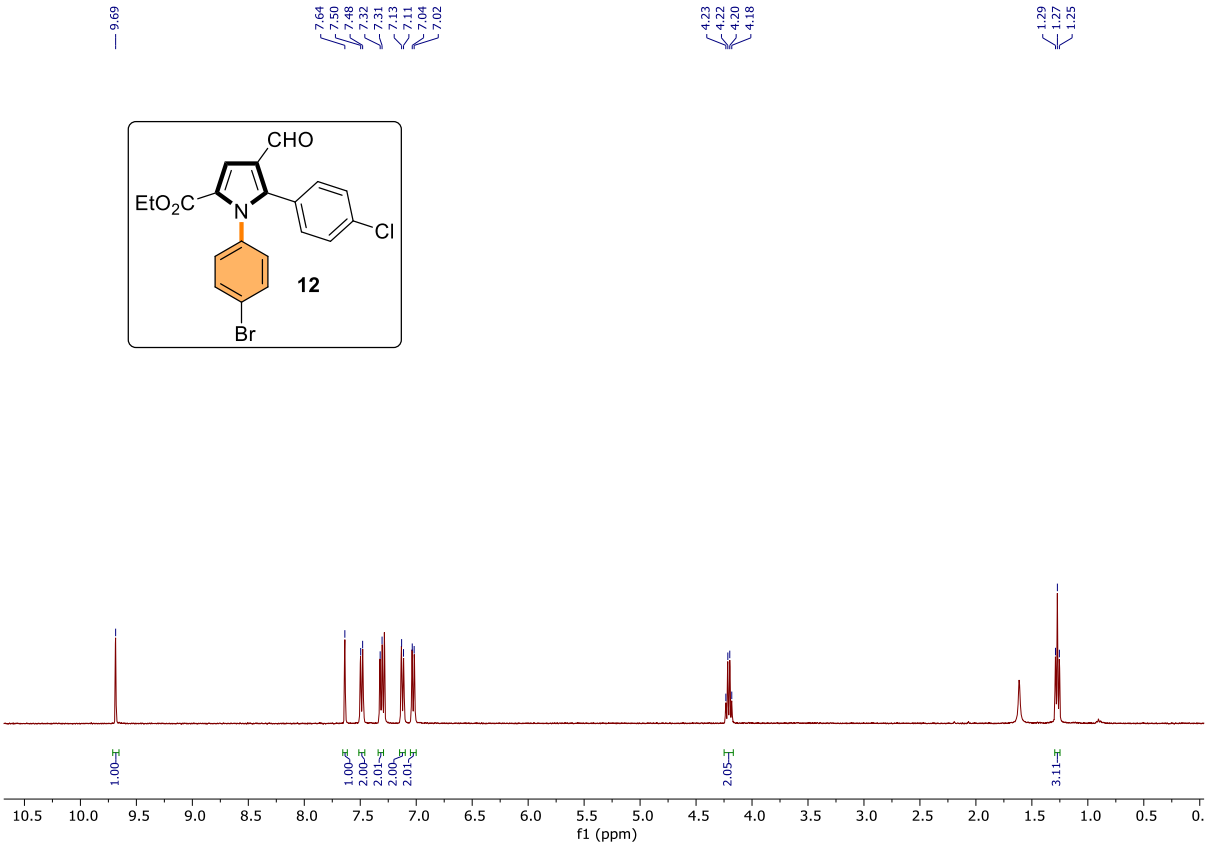
^{13}C NMR of Compound **10** ($CDCl_3$, 126 MHz)



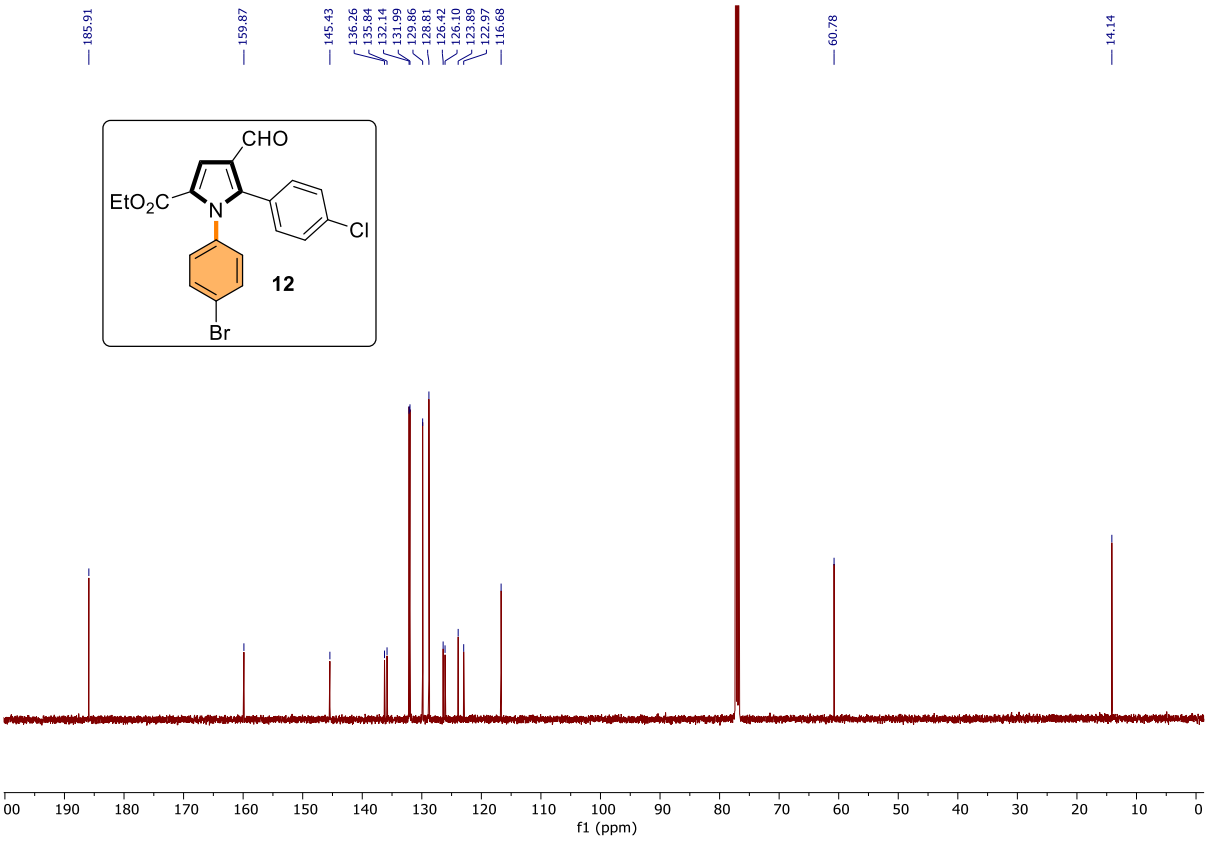
^{1}H NMR of Compound **11** ($CDCl_3$, 500 MHz)



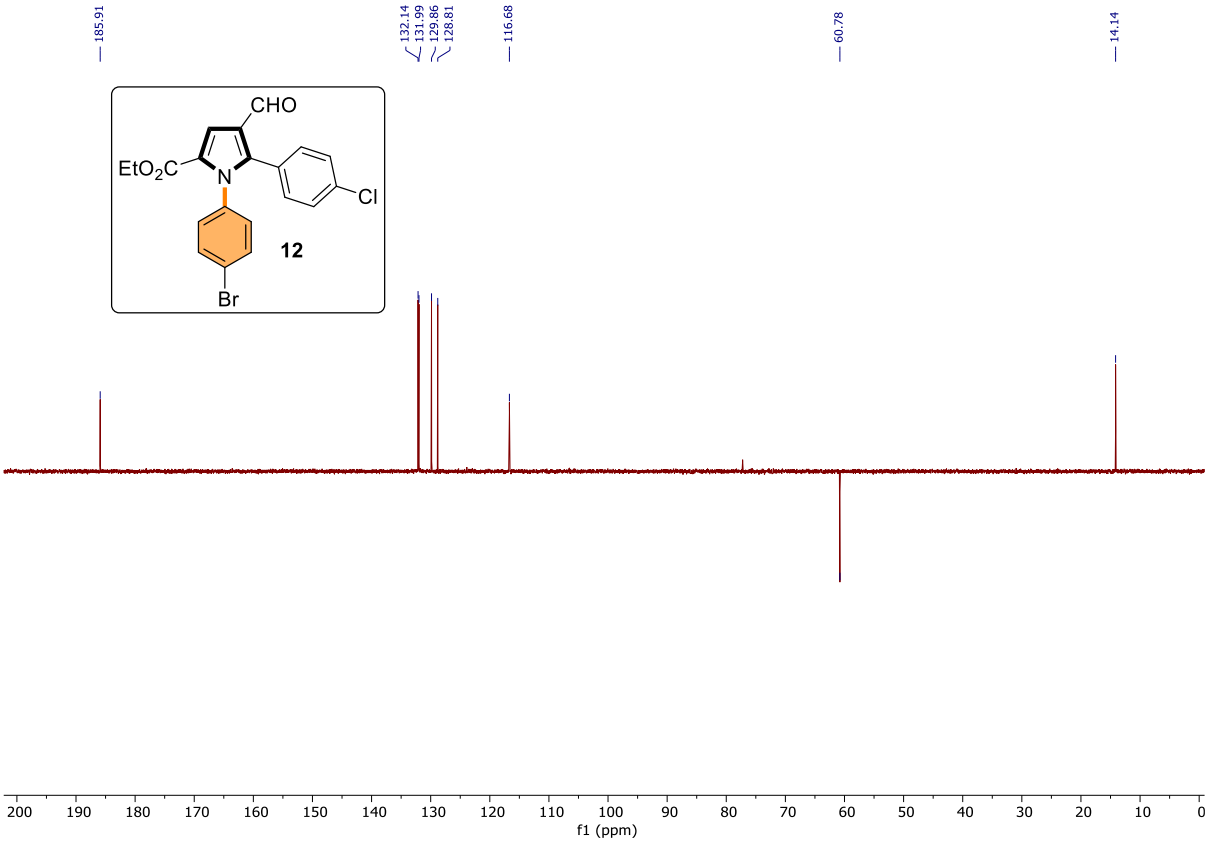
^{13}C-DEPT NMR of Compound **11** ($CDCl_3$, 126 MHz)



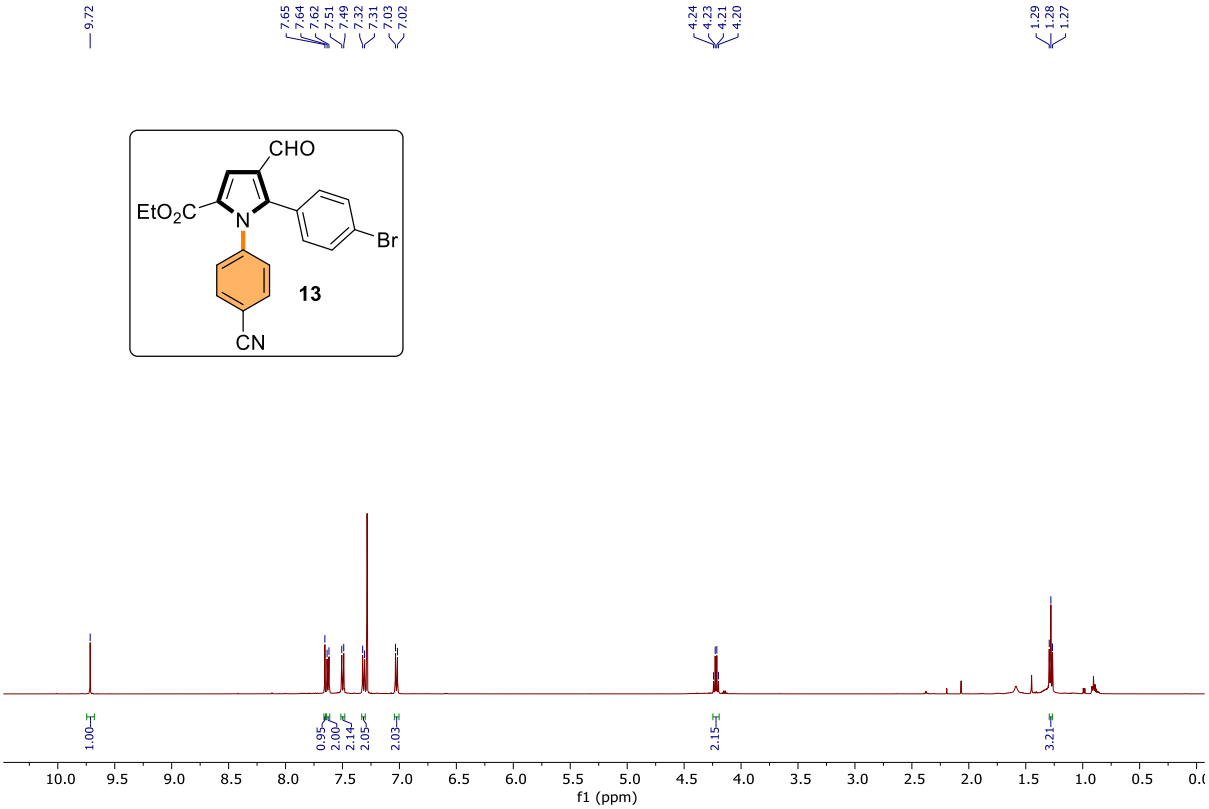
^{1}H NMR of Compound **12** ($CDCl_3$, 400 MHz)



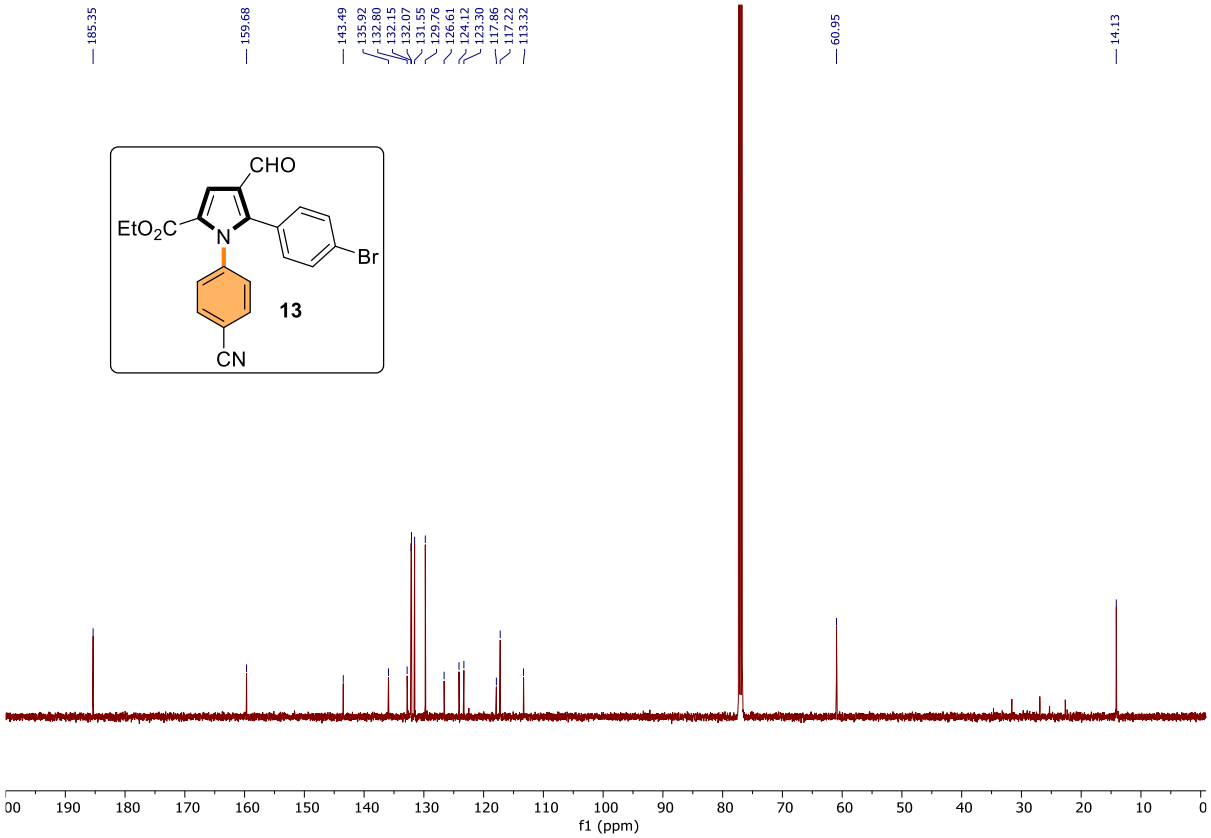
^{13}C NMR of Compound **12** ($CDCl_3$, 126 MHz)



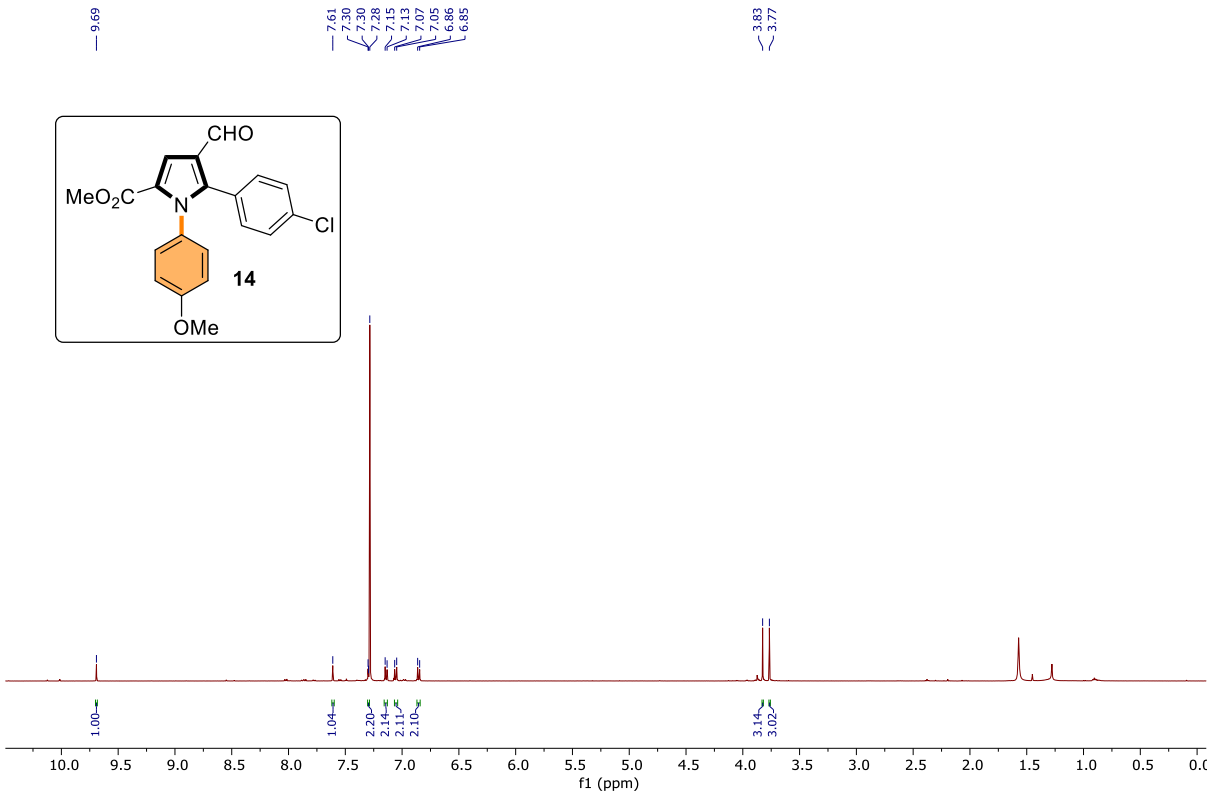
^{13}C-DEPT NMR of Compound **12** ($CDCl_3$, 126 MHz)



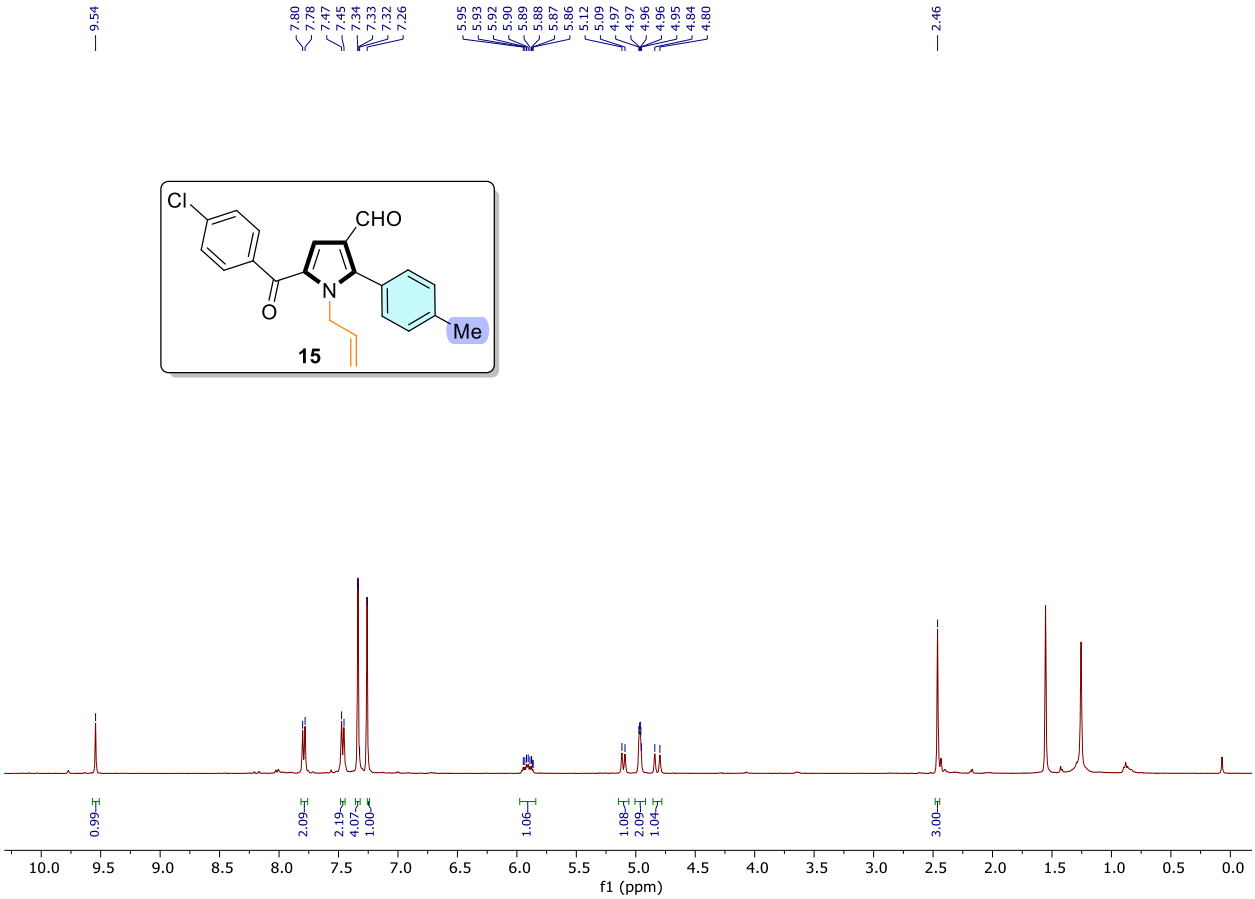
^{1}H NMR of Compound **13** ($CDCl_3$, 500 MHz)



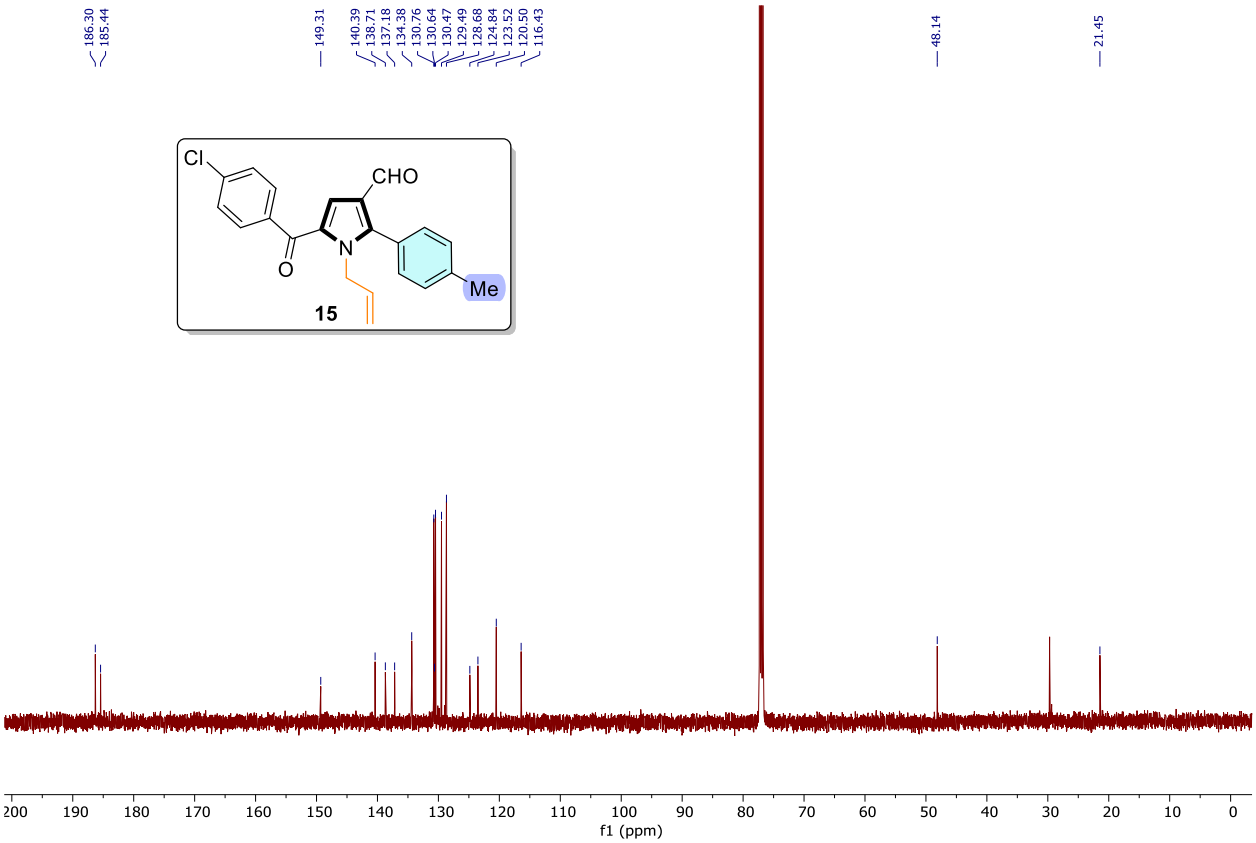
^{13}C NMR of Compound **13** ($CDCl_3$, 126 MHz)



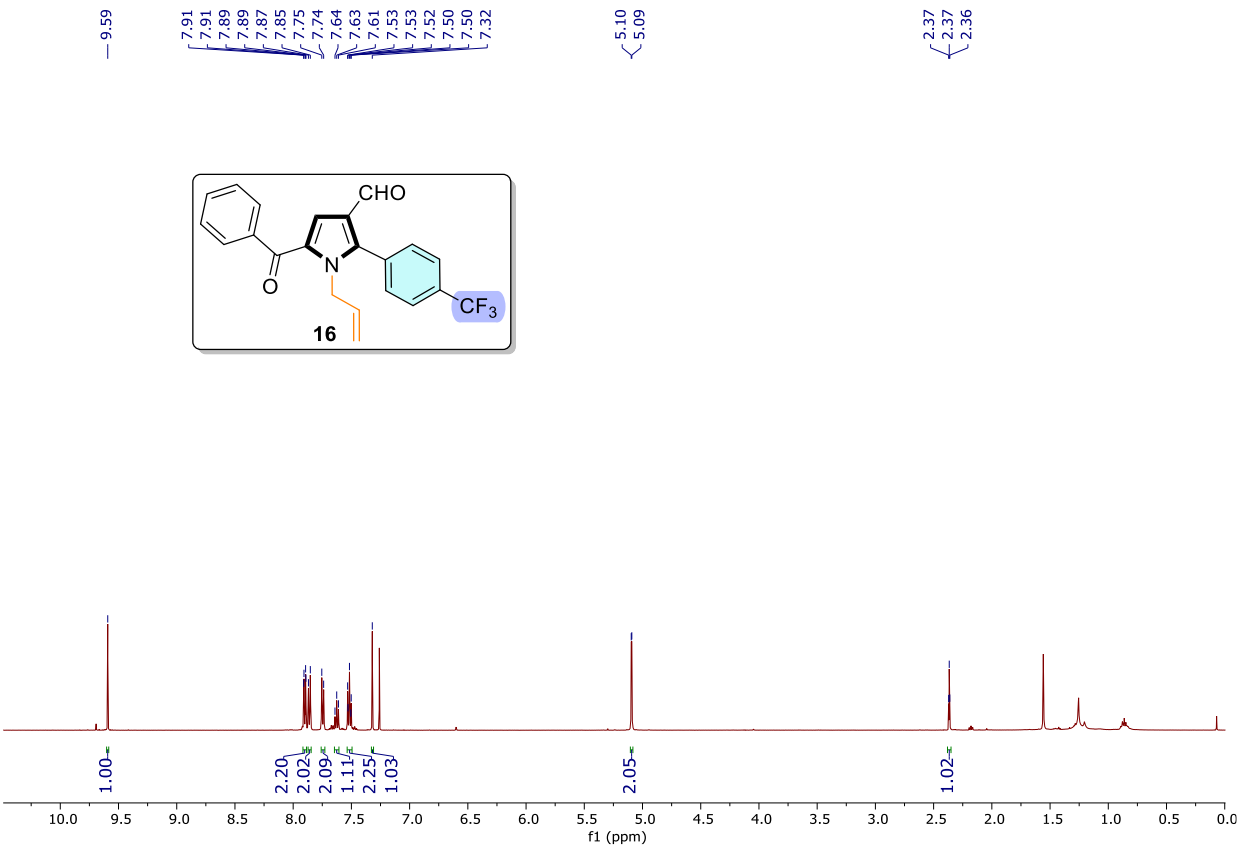
^{1}H NMR of Compound **14** ($CDCl_3$, 500 MHz)



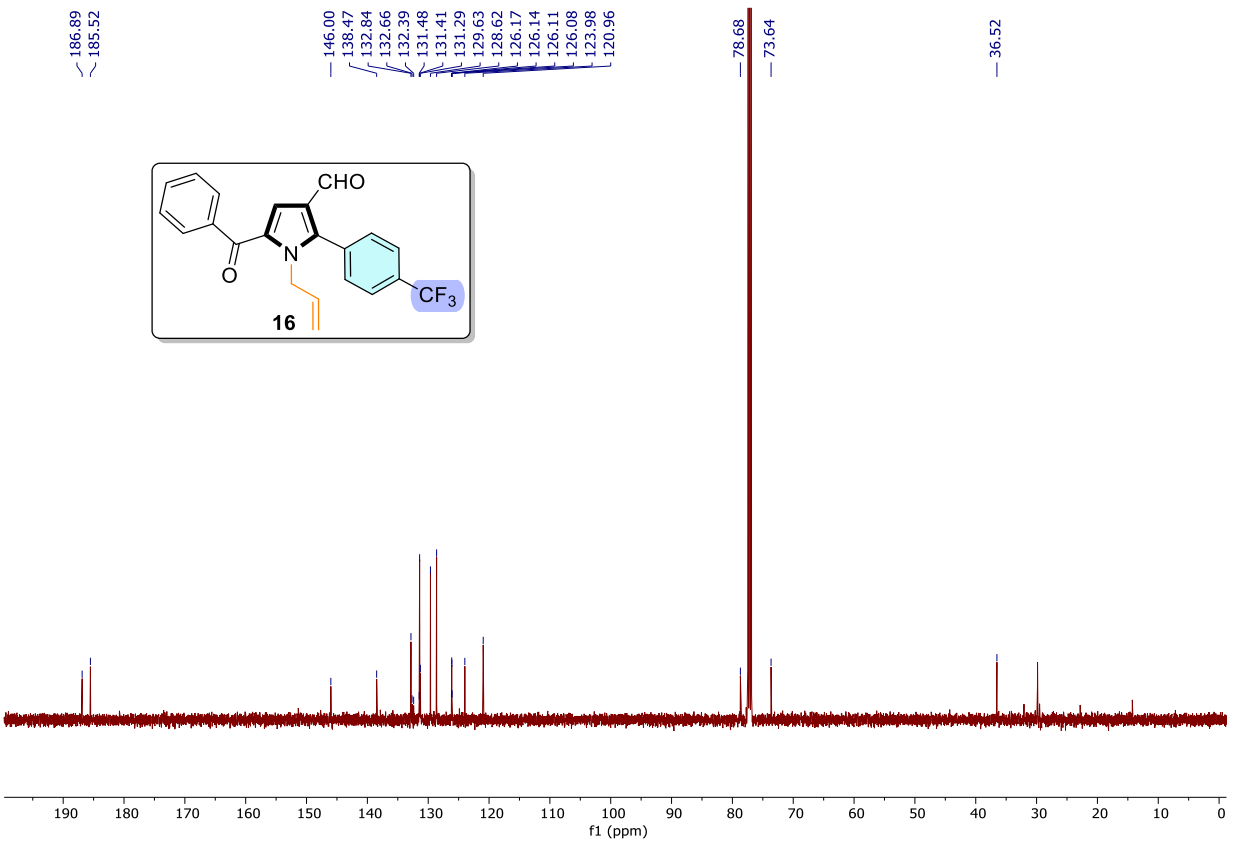
^{1}H NMR of Compound **15** ($CDCl_3$, 400 MHz)



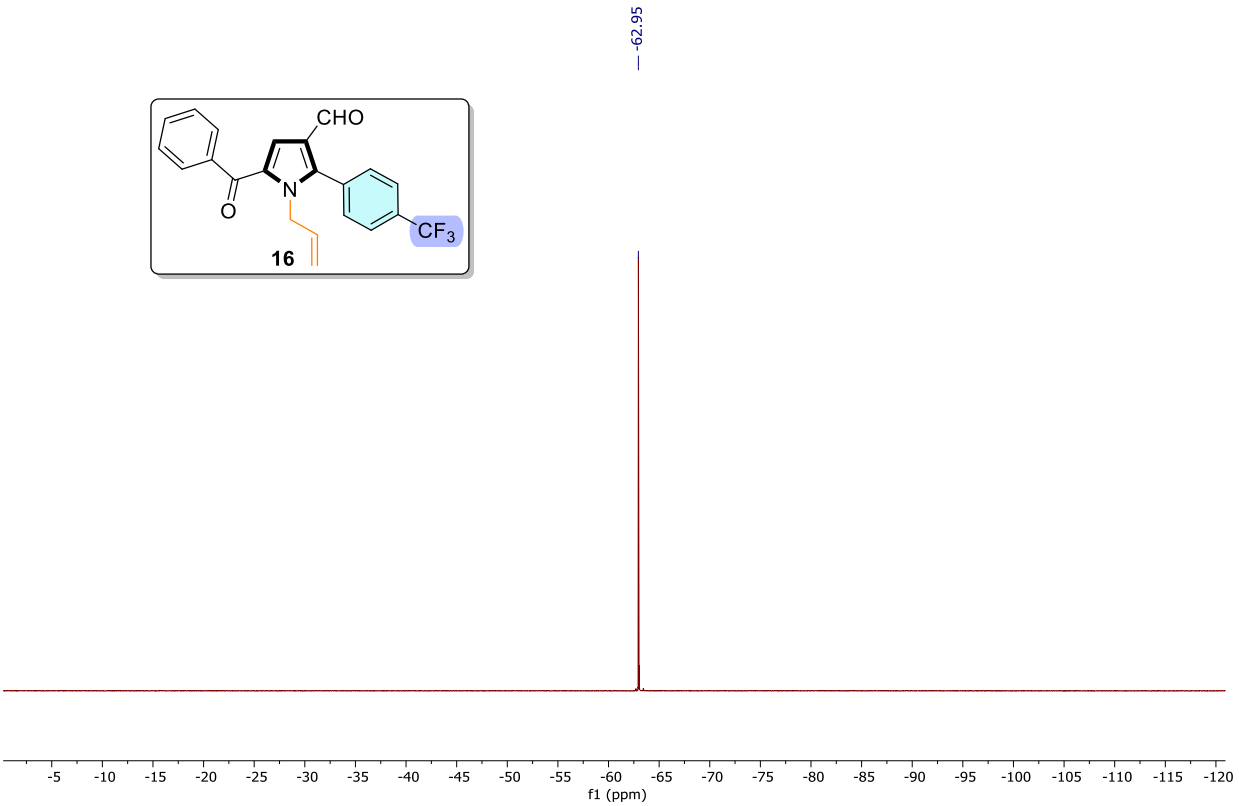
^{13}C NMR of Compound **15** ($CDCl_3$, 126 MHz)



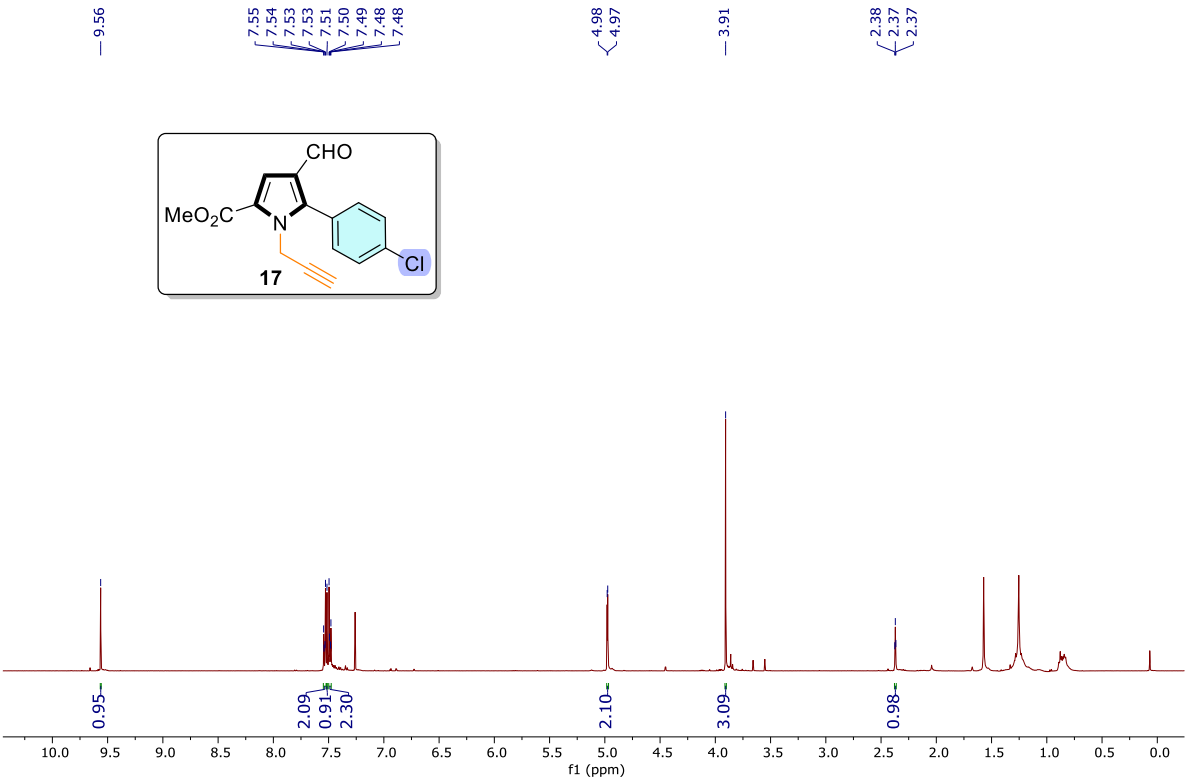
^{1}H NMR of Compound **16** ($CDCl_3$, 500 MHz)



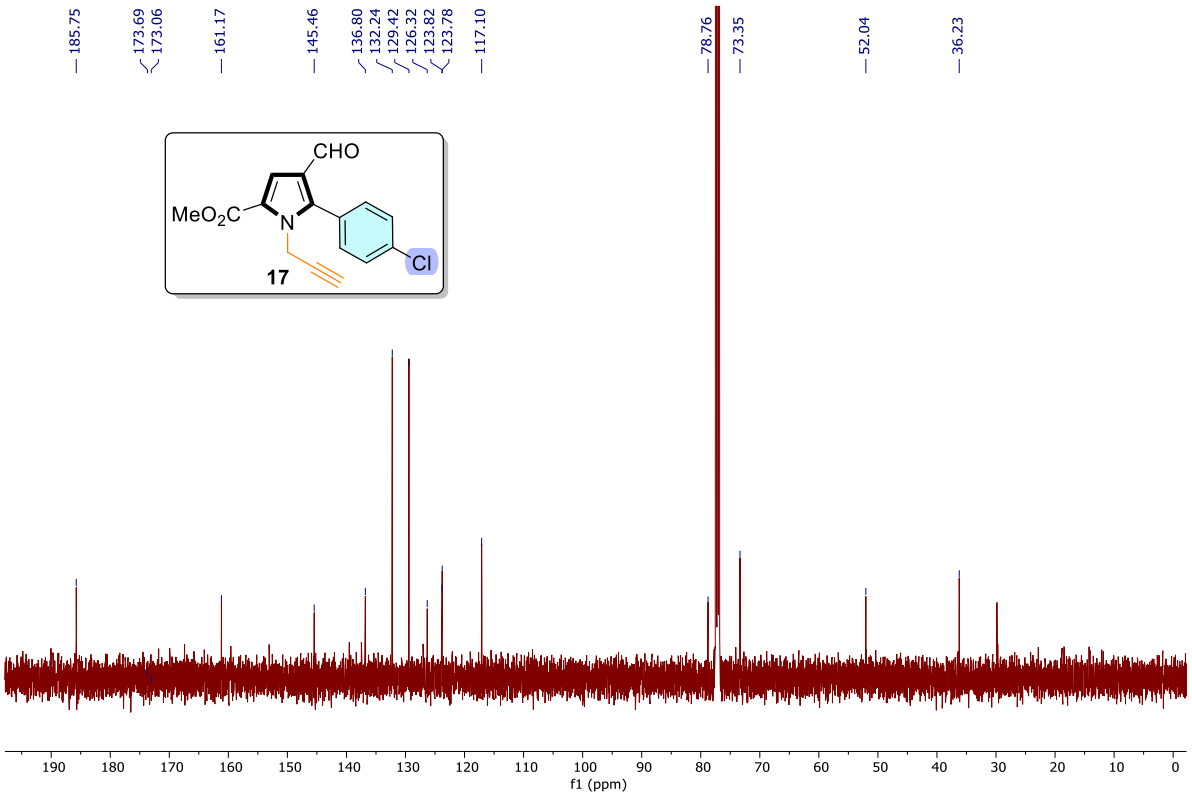
^{13}C NMR of Compound **16** ($CDCl_3$, 101 MHz)



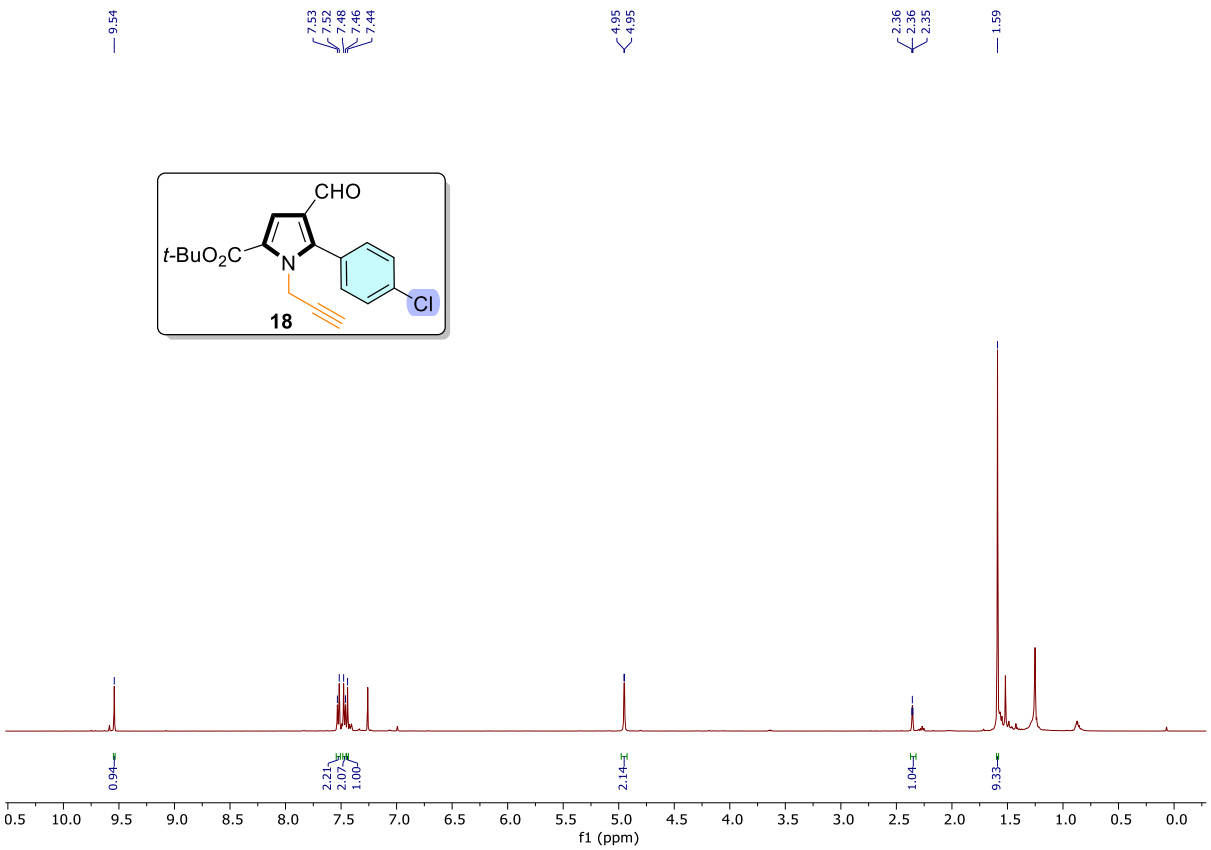
^{19}F NMR of Compound **16** ($CDCl_3$, 376 MHz)



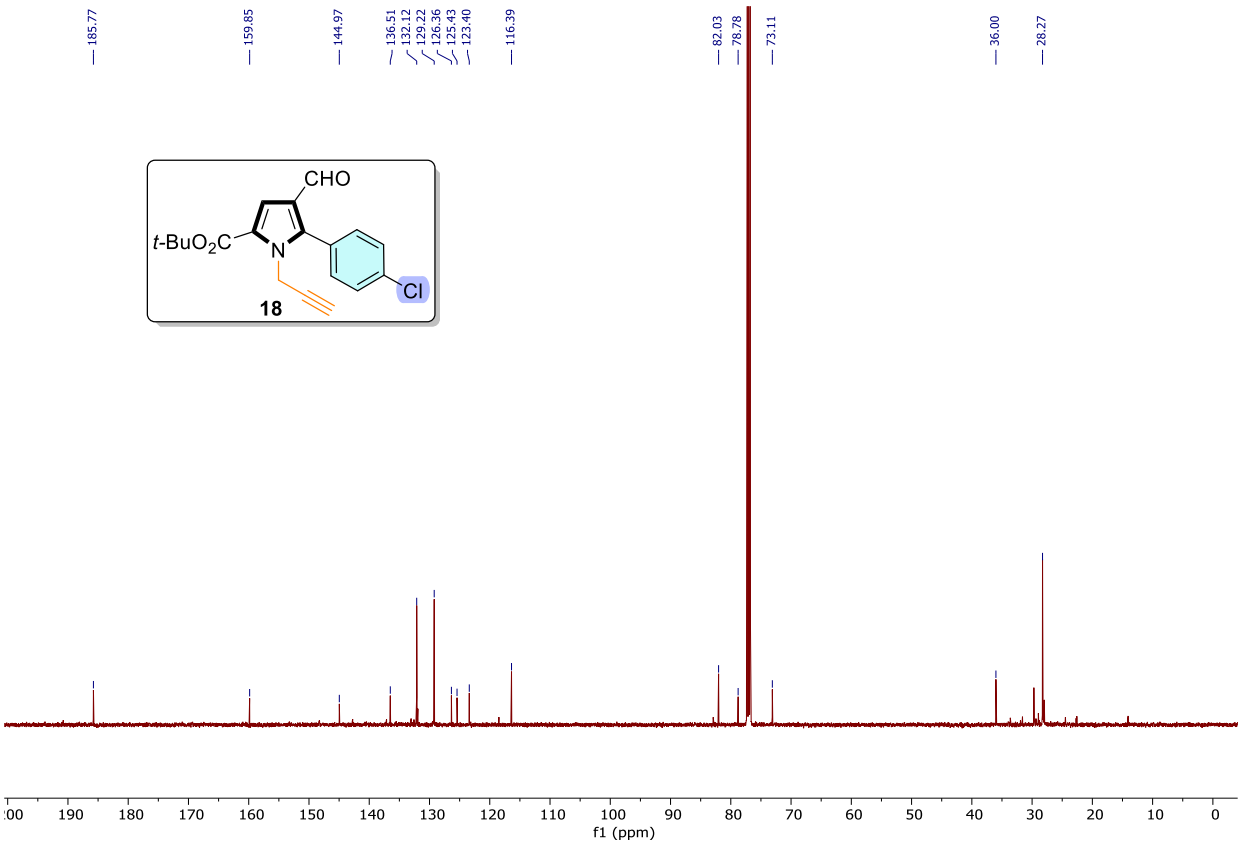
^{1}H NMR of Compound **17** ($CDCl_3$, 500 MHz)



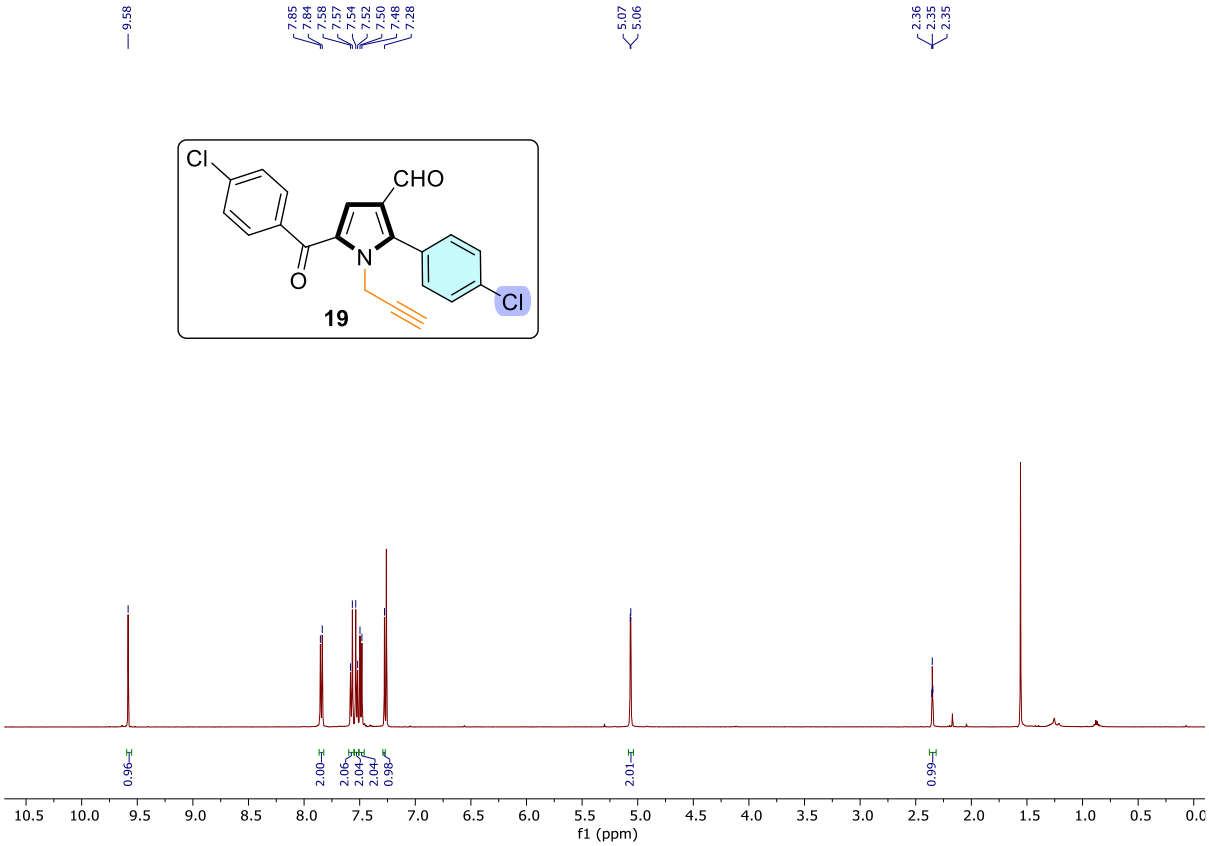
^{13}C NMR of Compound **17** ($CDCl_3$, 126 MHz)



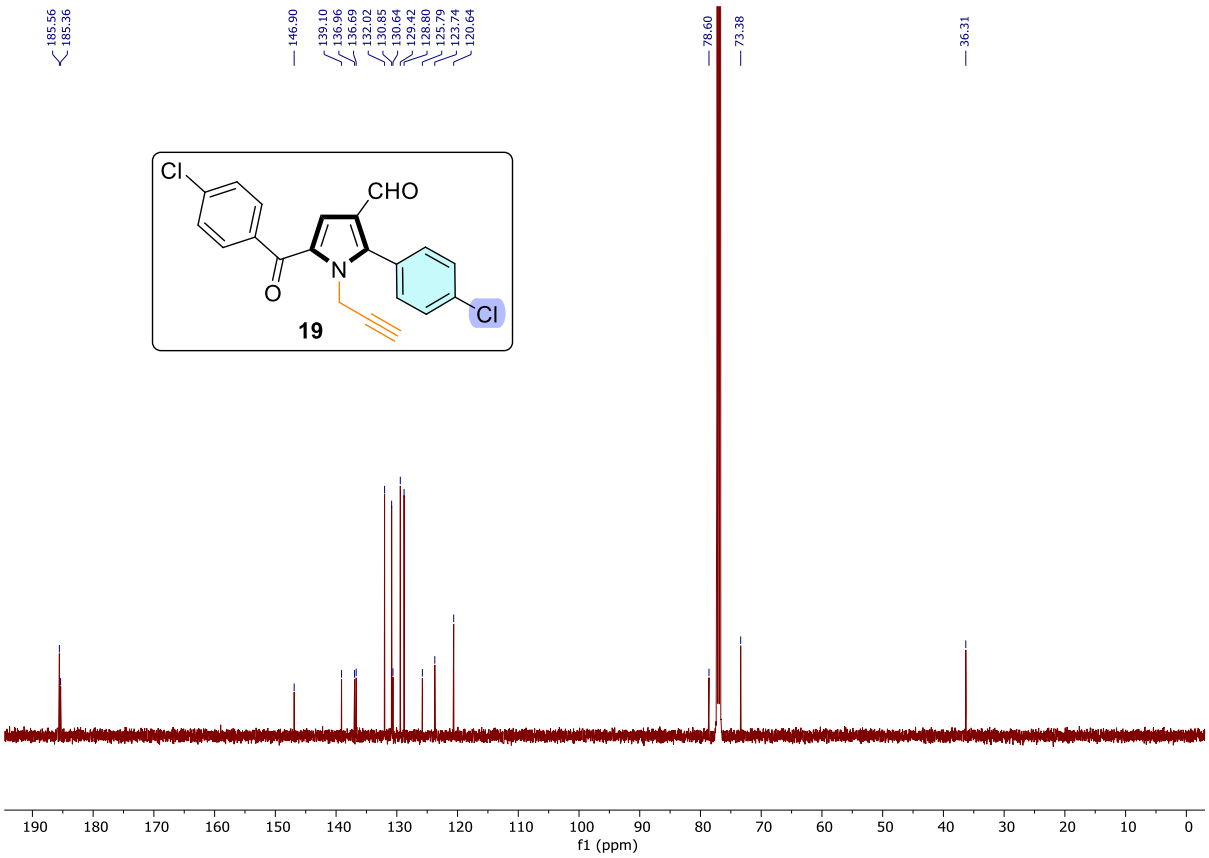
^{1}H NMR of Compound **18** ($CDCl_3$, 500 MHz)



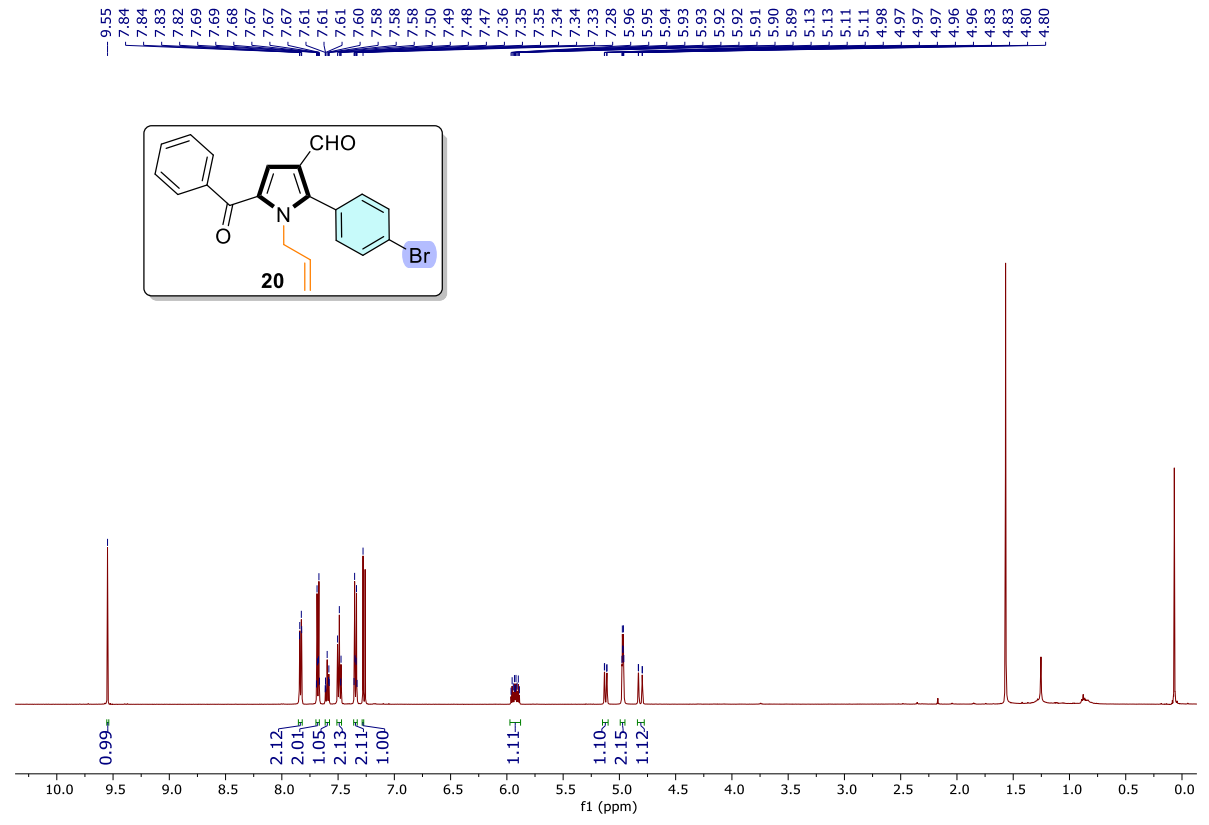
^{13}C NMR of Compound **18** ($CDCl_3$, 126 MHz)



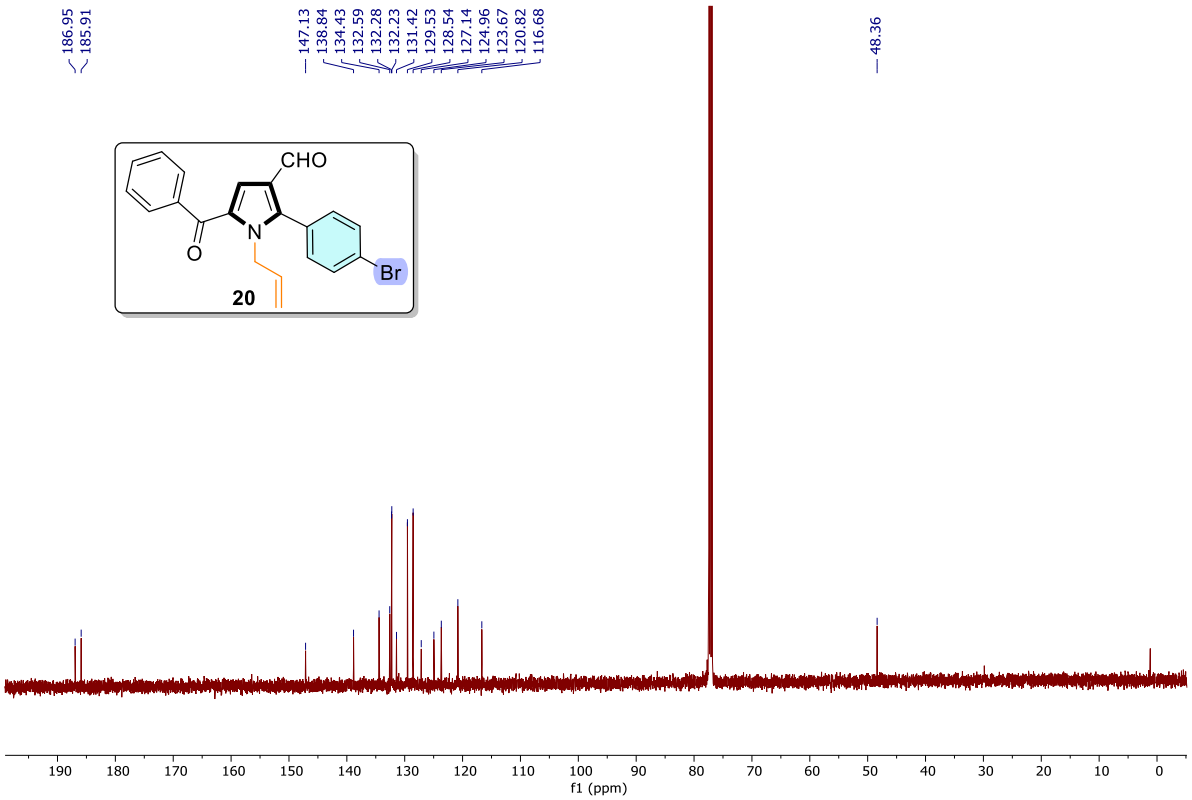
^{1}H NMR of Compound **19** ($CDCl_3$, 500 MHz)



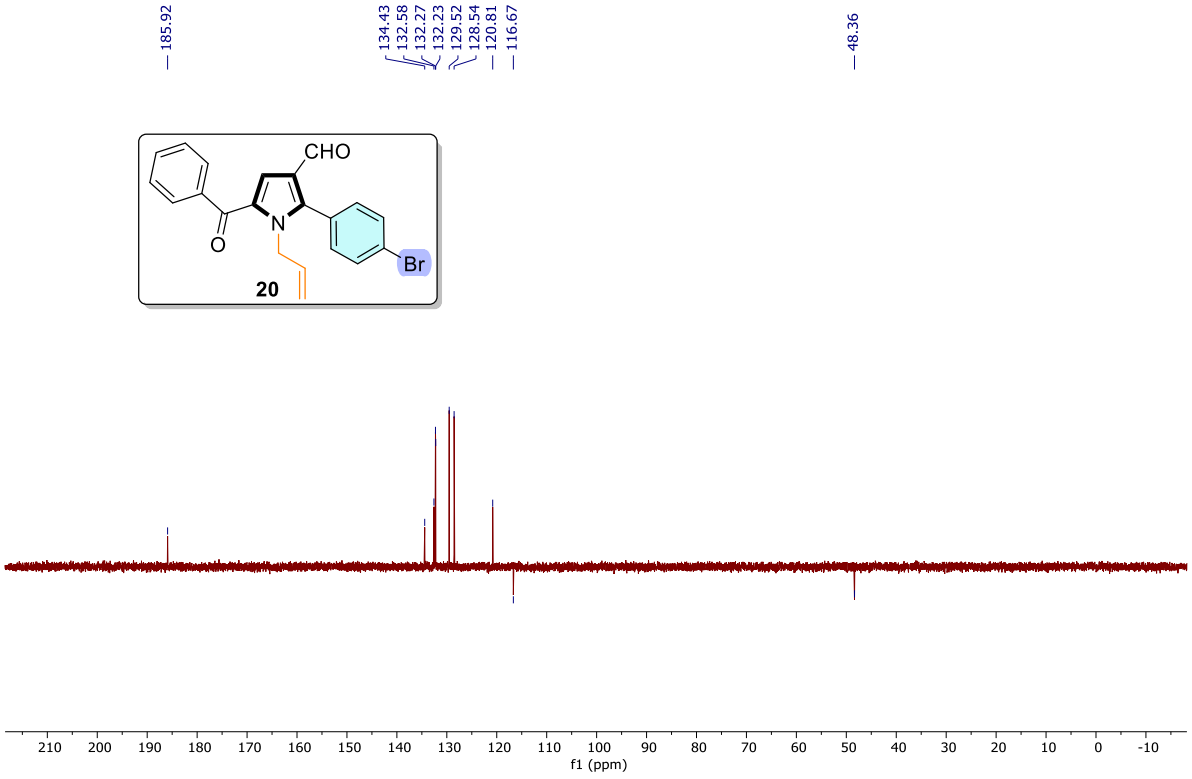
^{13}C NMR of Compound **19** ($CDCl_3$, 126 MHz)



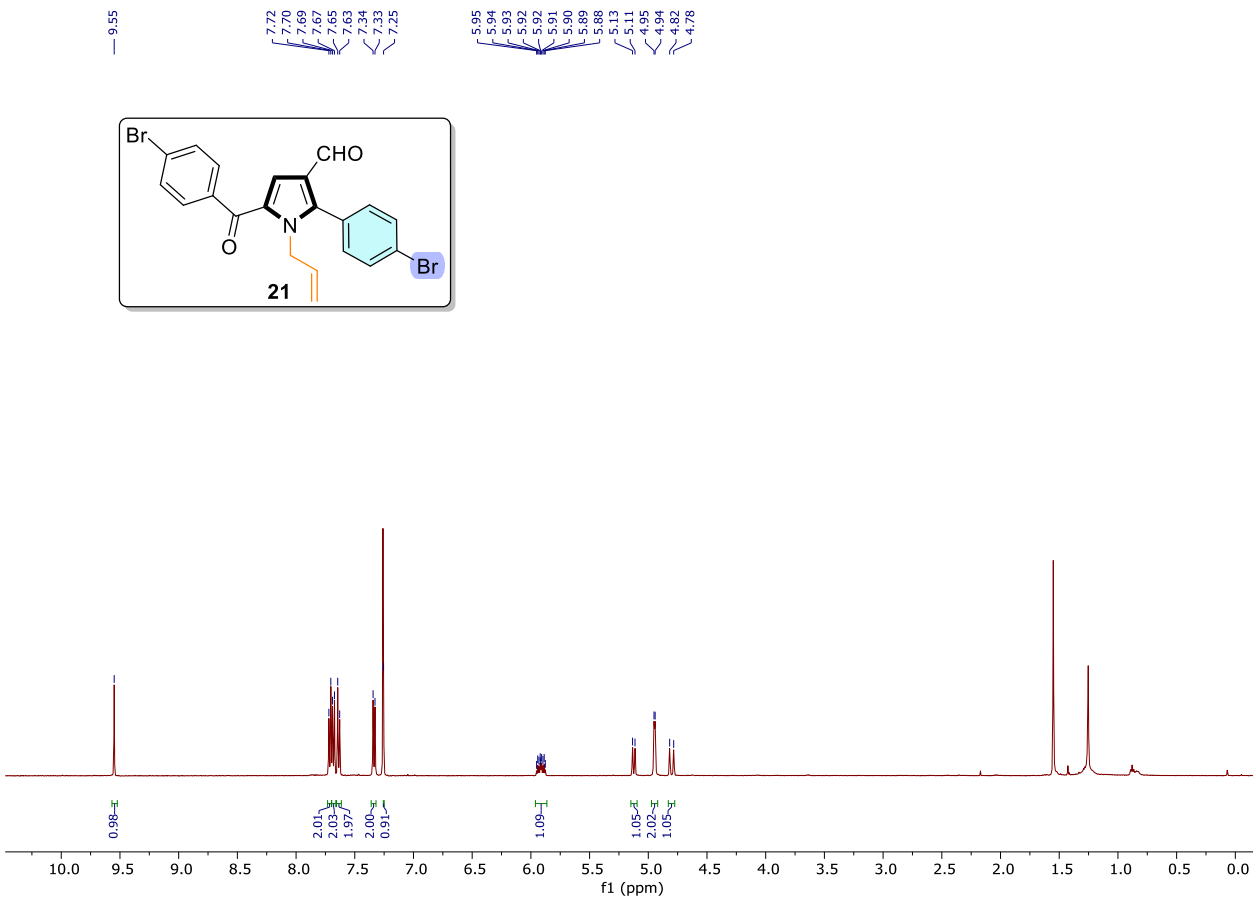
^{1}H NMR of Compound **20** ($CDCl_3$, 500 MHz)



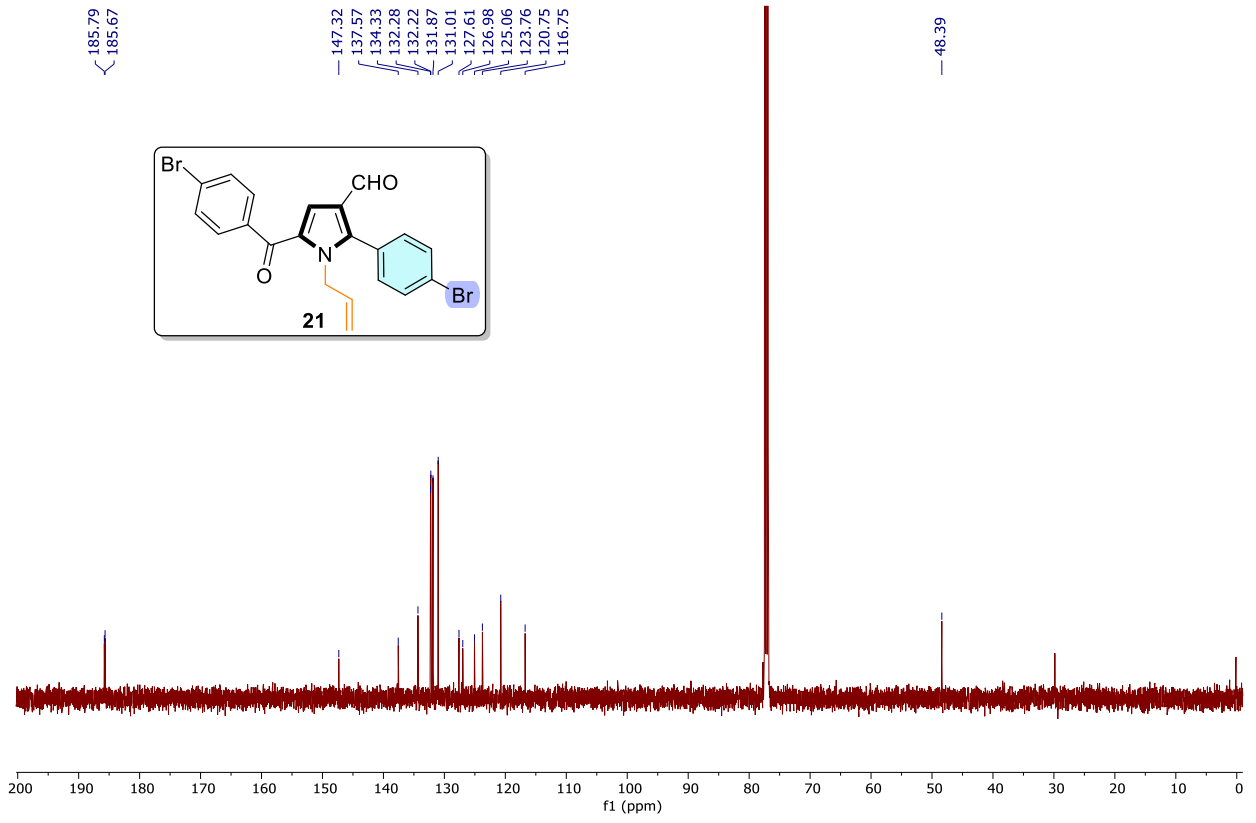
^{13}C NMR of Compound **20** ($CDCl_3$, 126 MHz)



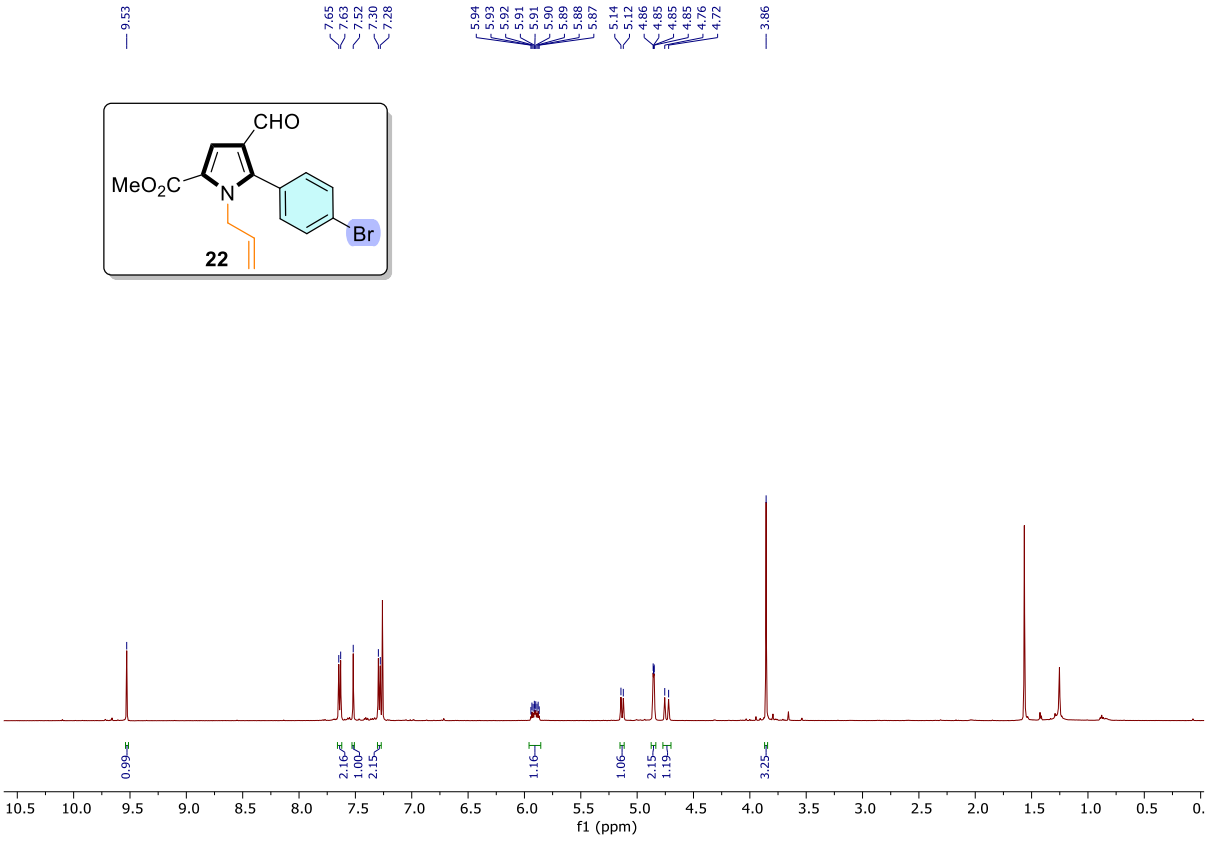
^{13}C-DEPT NMR of Compound **20** ($CDCl_3$, 126 MHz)



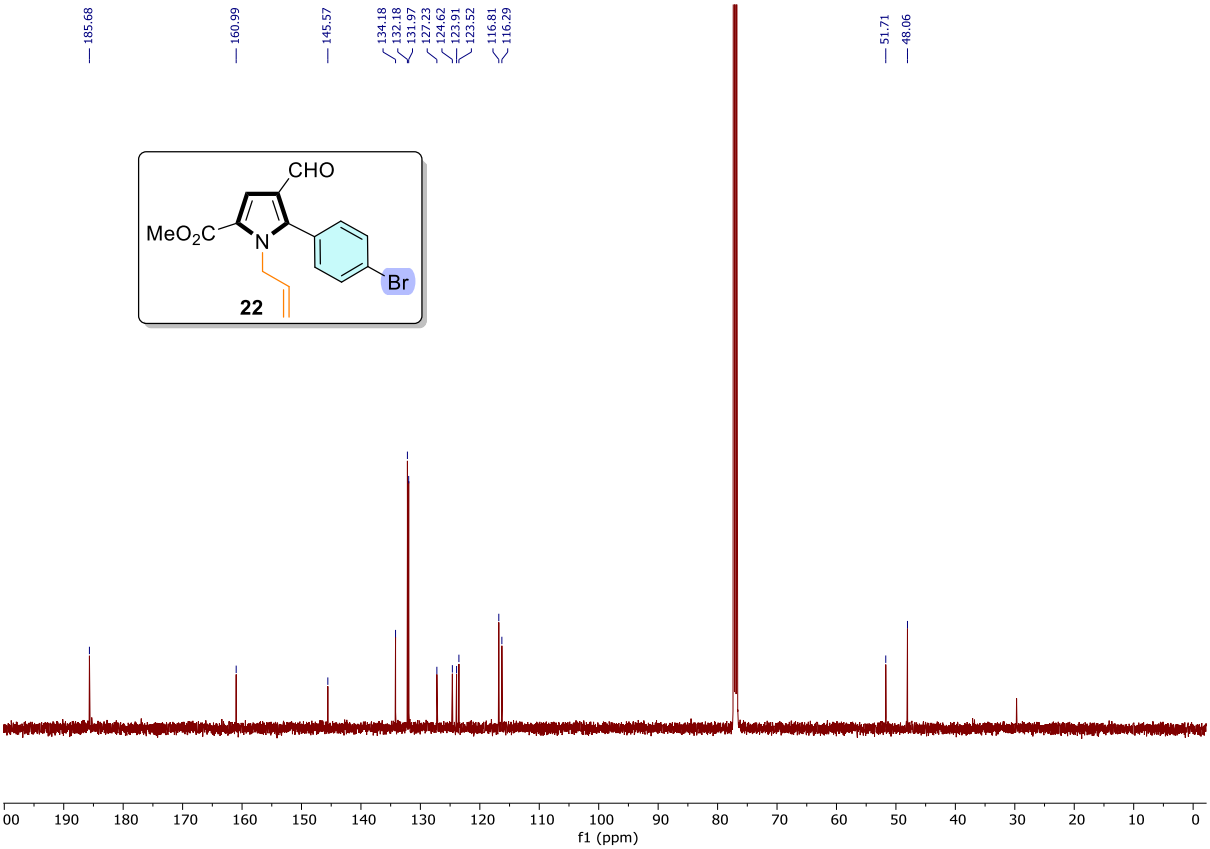
^{1}H NMR of Compound **21** ($CDCl_3$, 500 MHz)



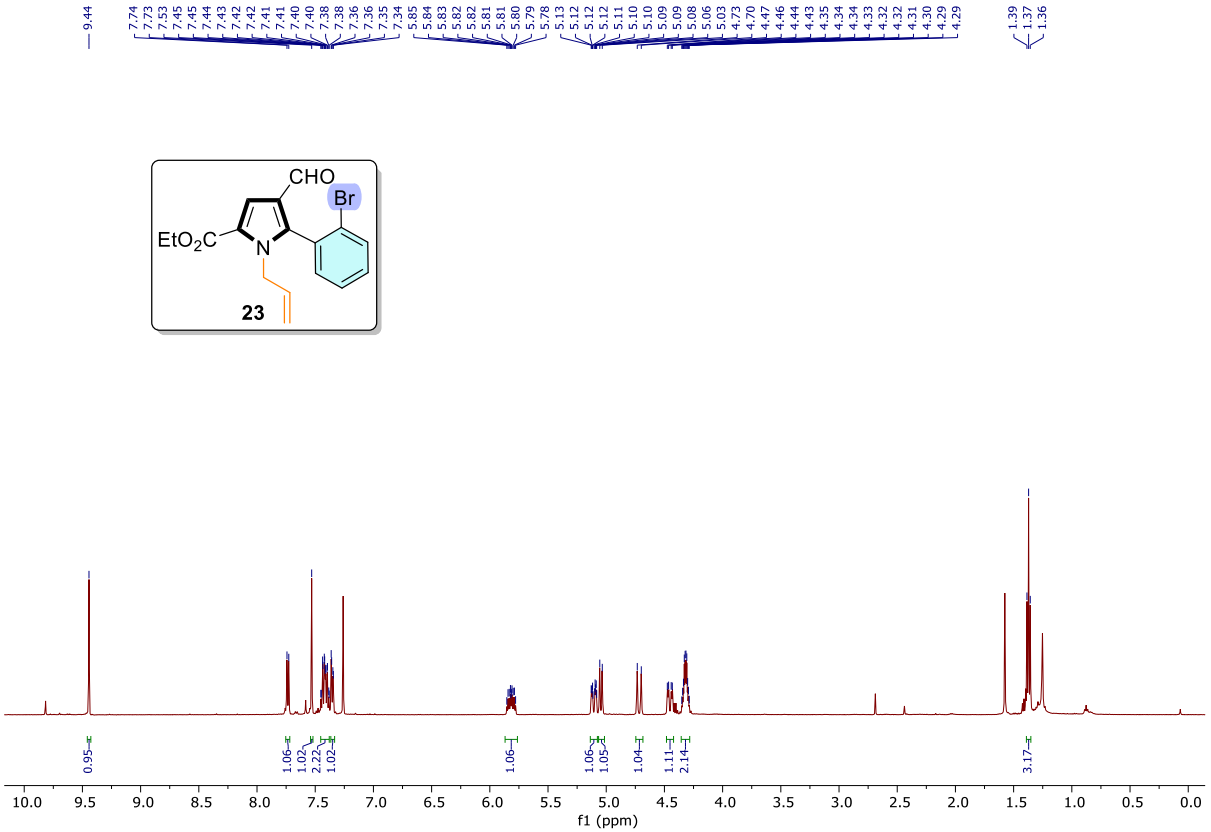
^{13}C NMR of Compound **21** ($CDCl_3$, 126 MHz)



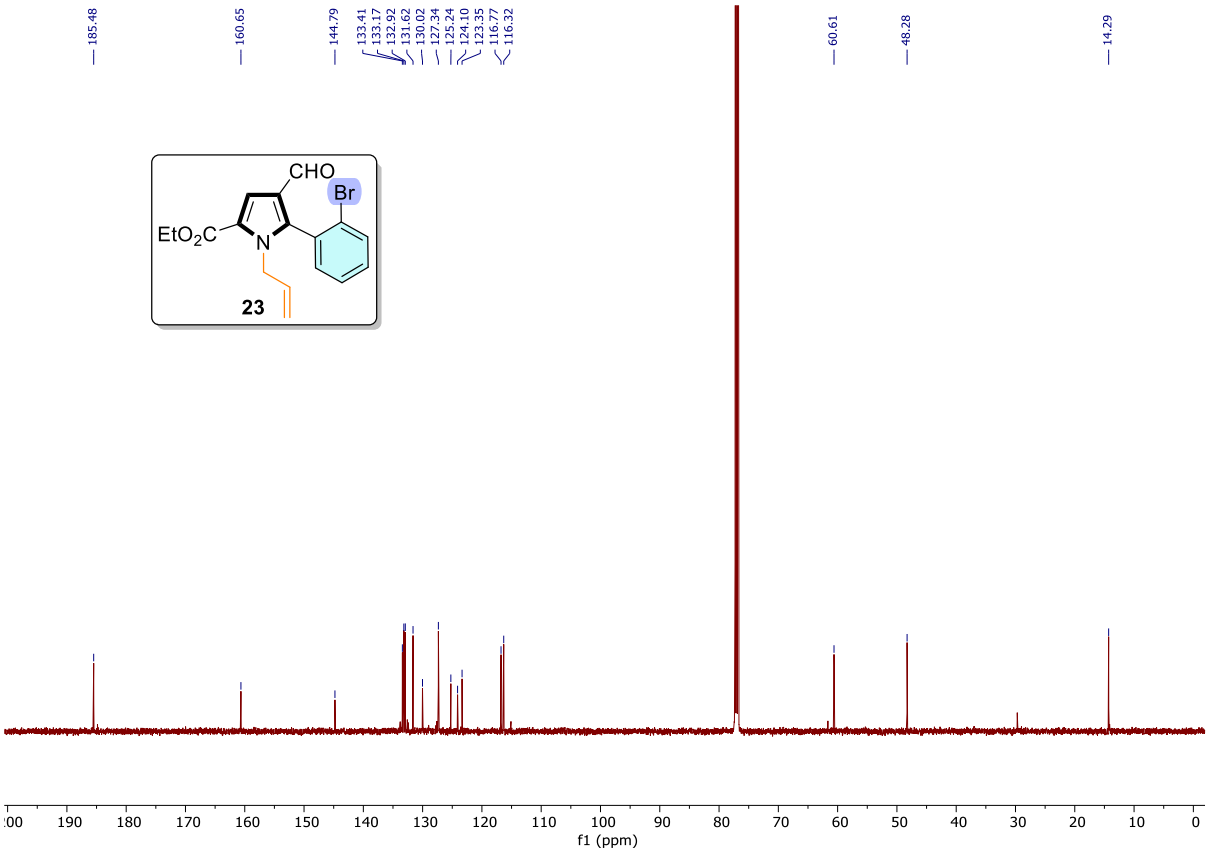
^{1}H NMR of Compound **22** ($CDCl_3$, 500 MHz)



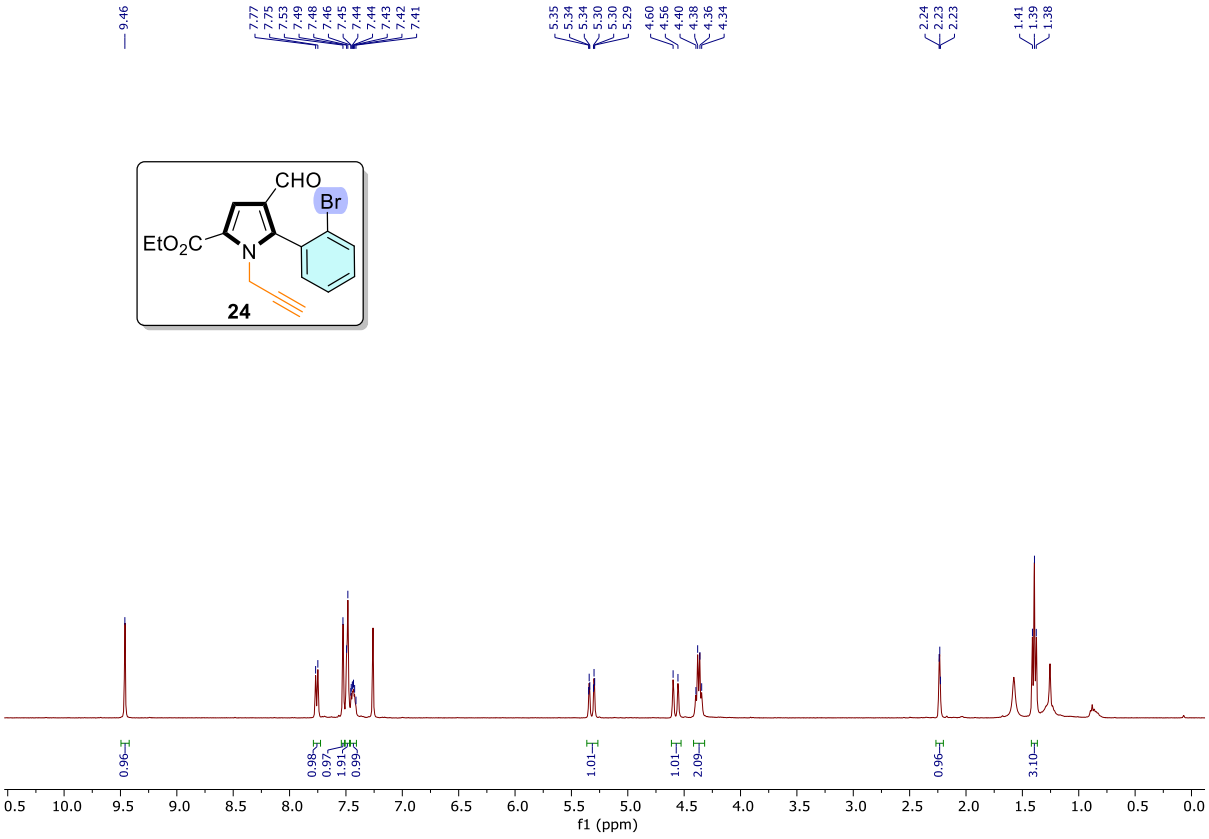
^{13}C NMR of Compound **22** ($CDCl_3$, 126 MHz)



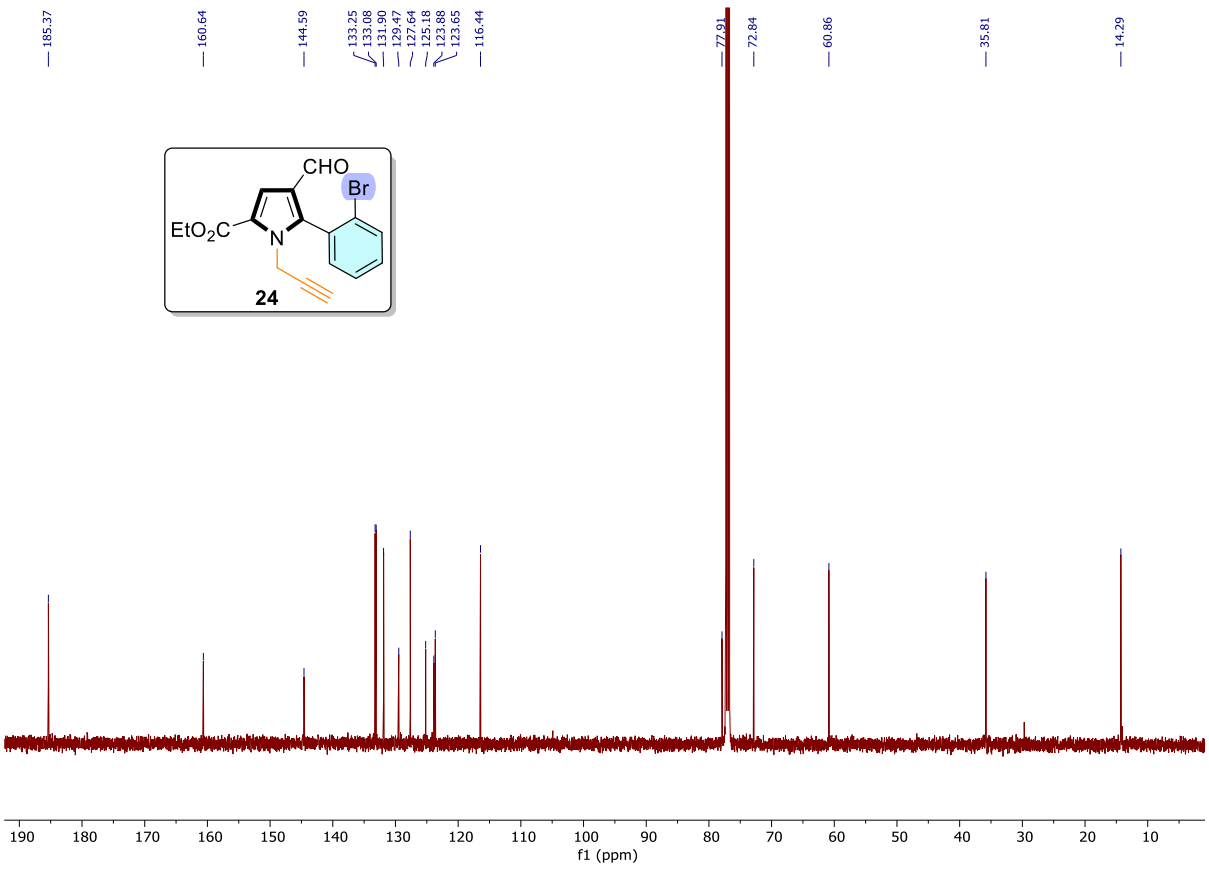
^{1}H NMR of Compound **23** ($CDCl_3$, 500 MHz)



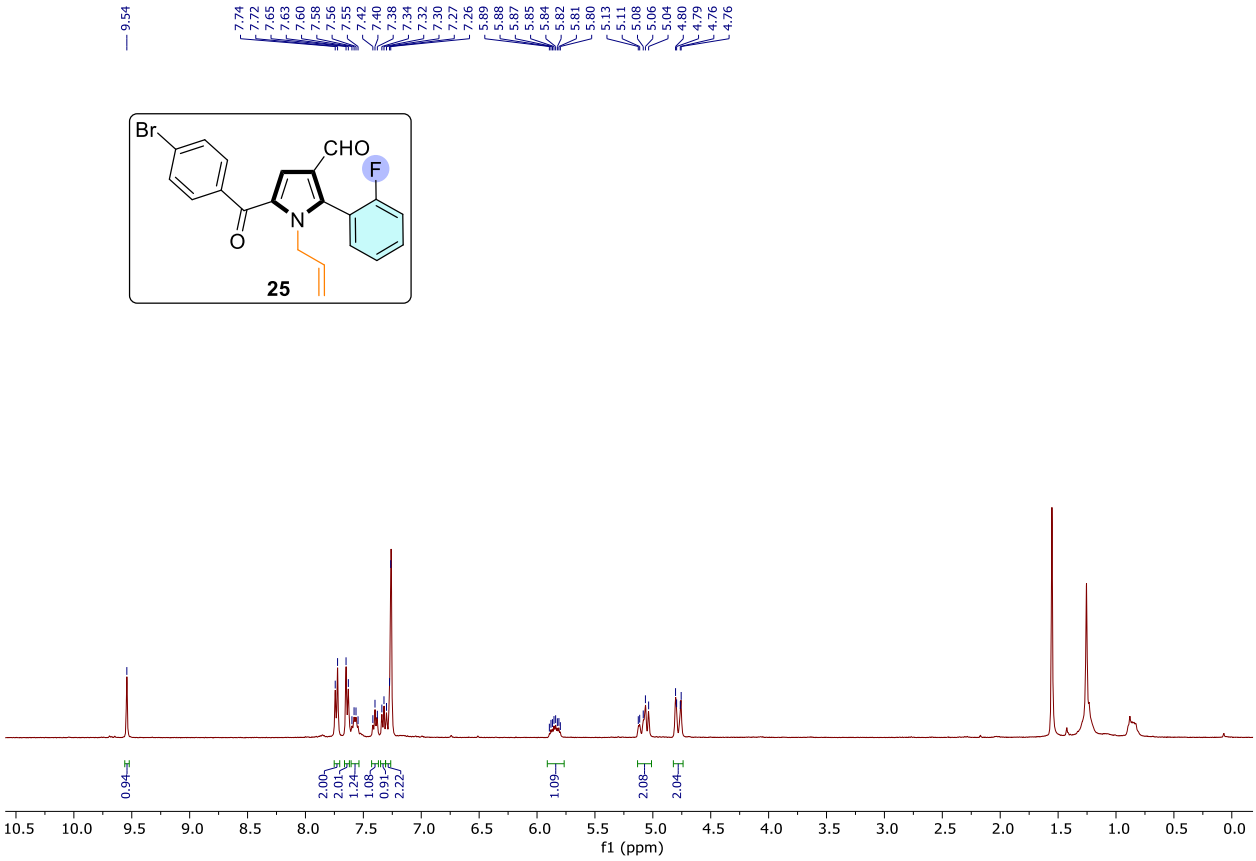
^{13}C NMR of Compound **23** ($CDCl_3$, 126 MHz)



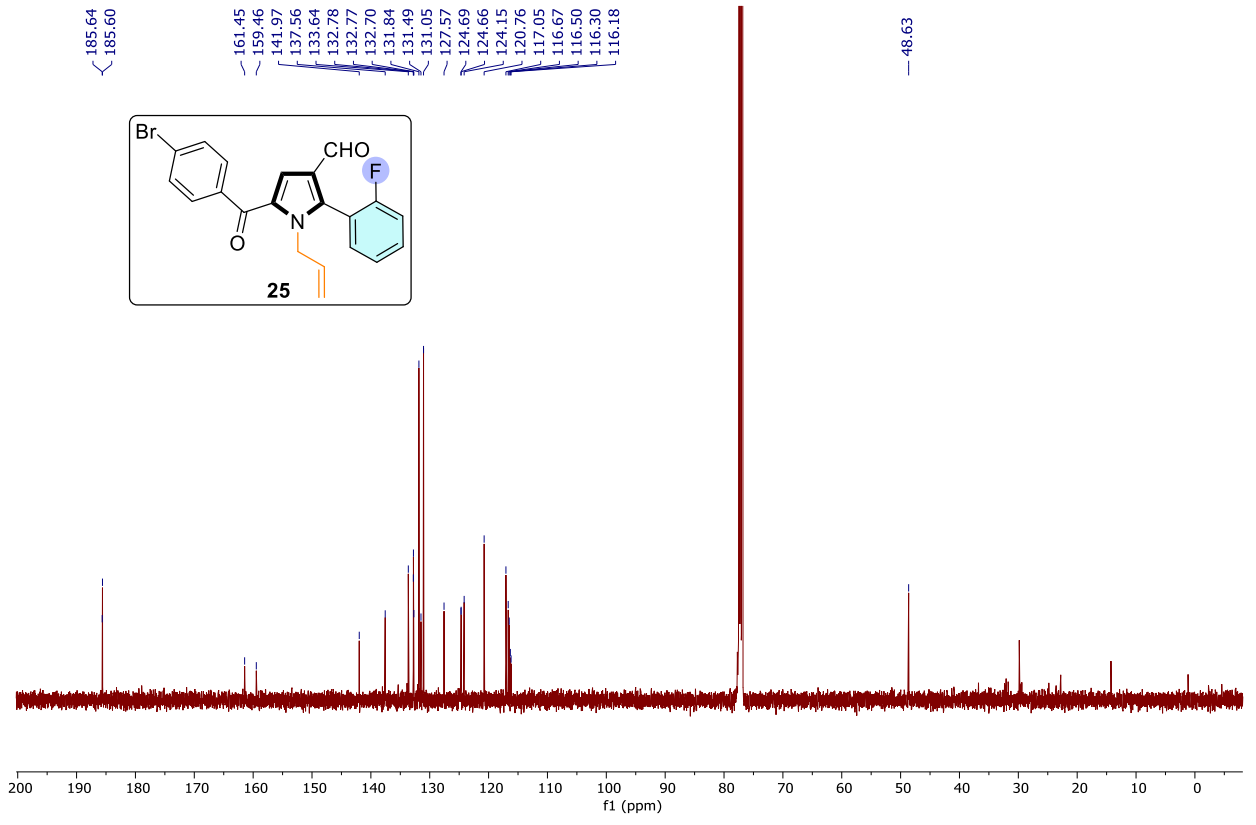
^{1}H NMR of Compound **24** ($CDCl_3$, 500 MHz)



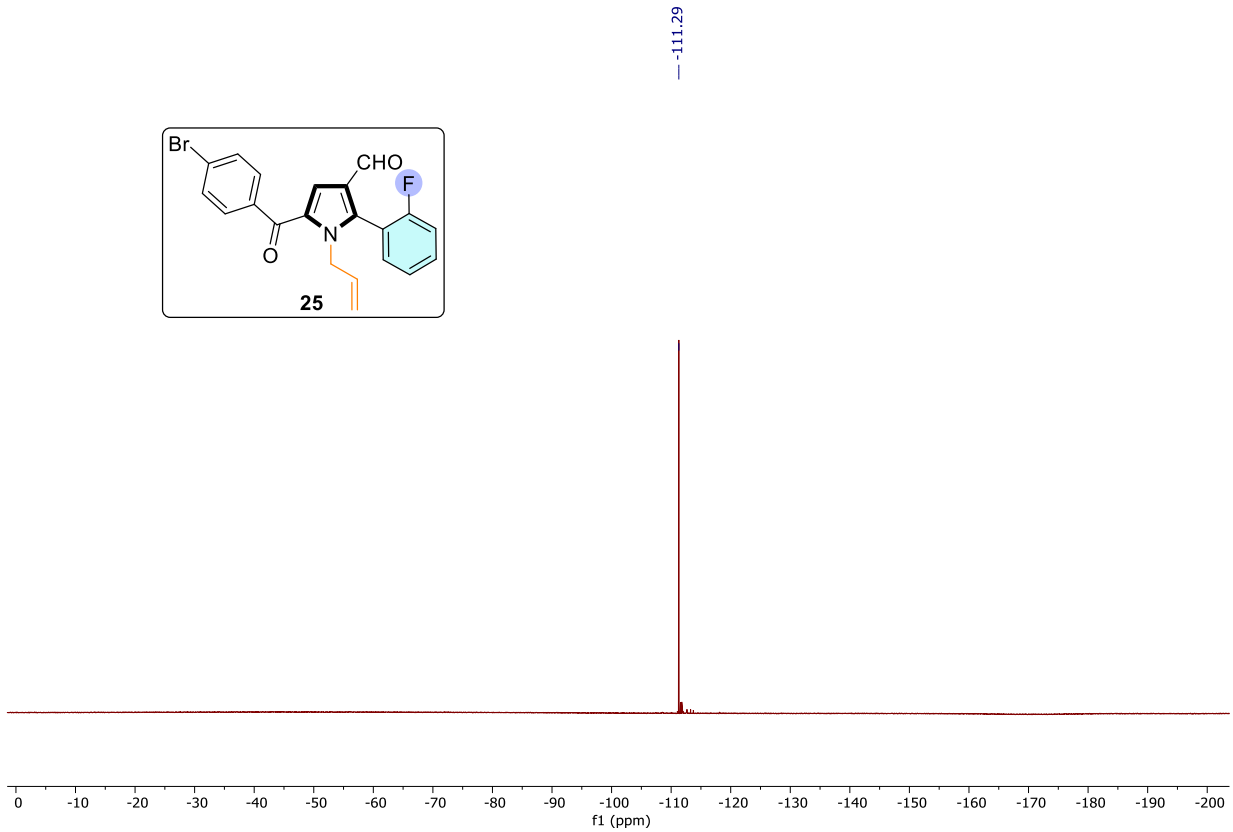
^{13}C NMR of Compound **24** ($CDCl_3$, 126 MHz)



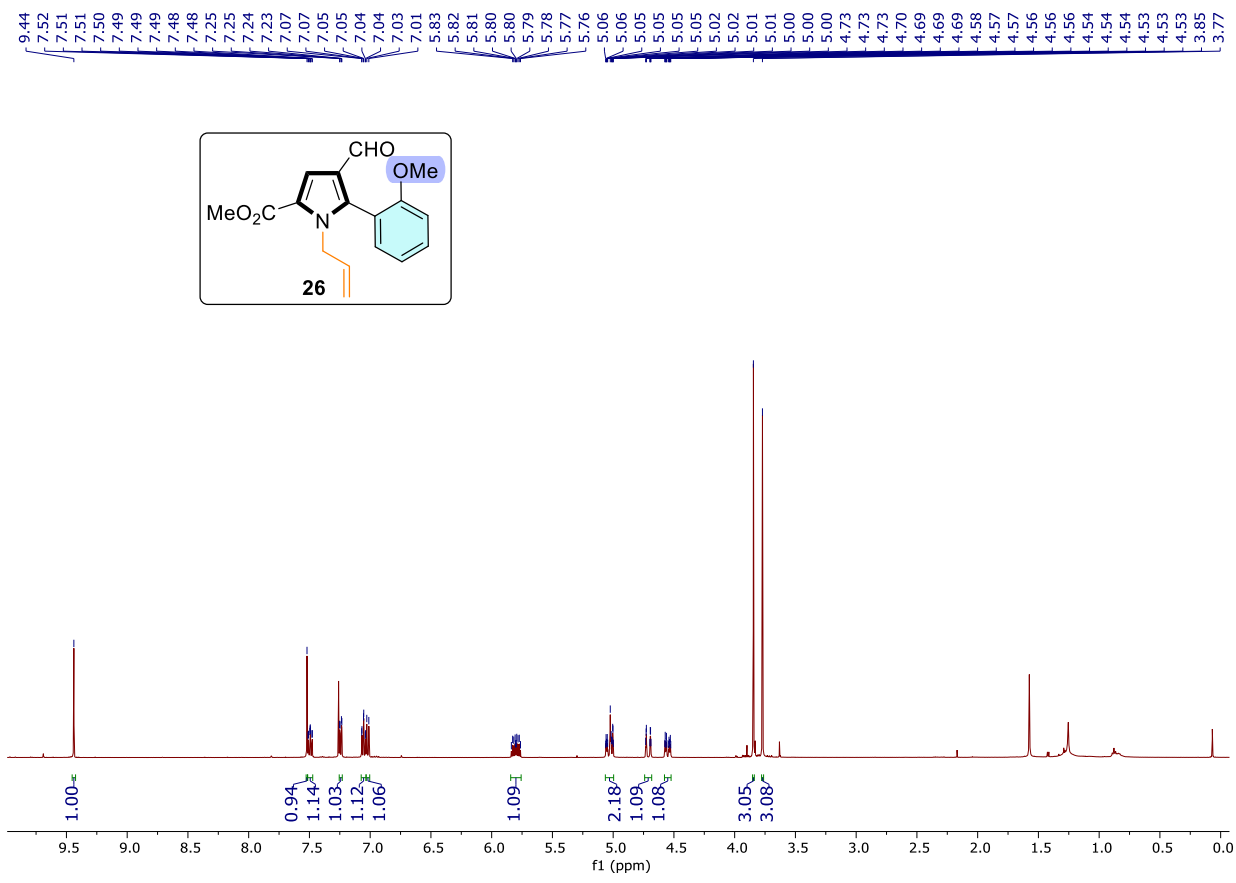
^{1}H NMR of Compound **25** ($CDCl_3$, 400 MHz)



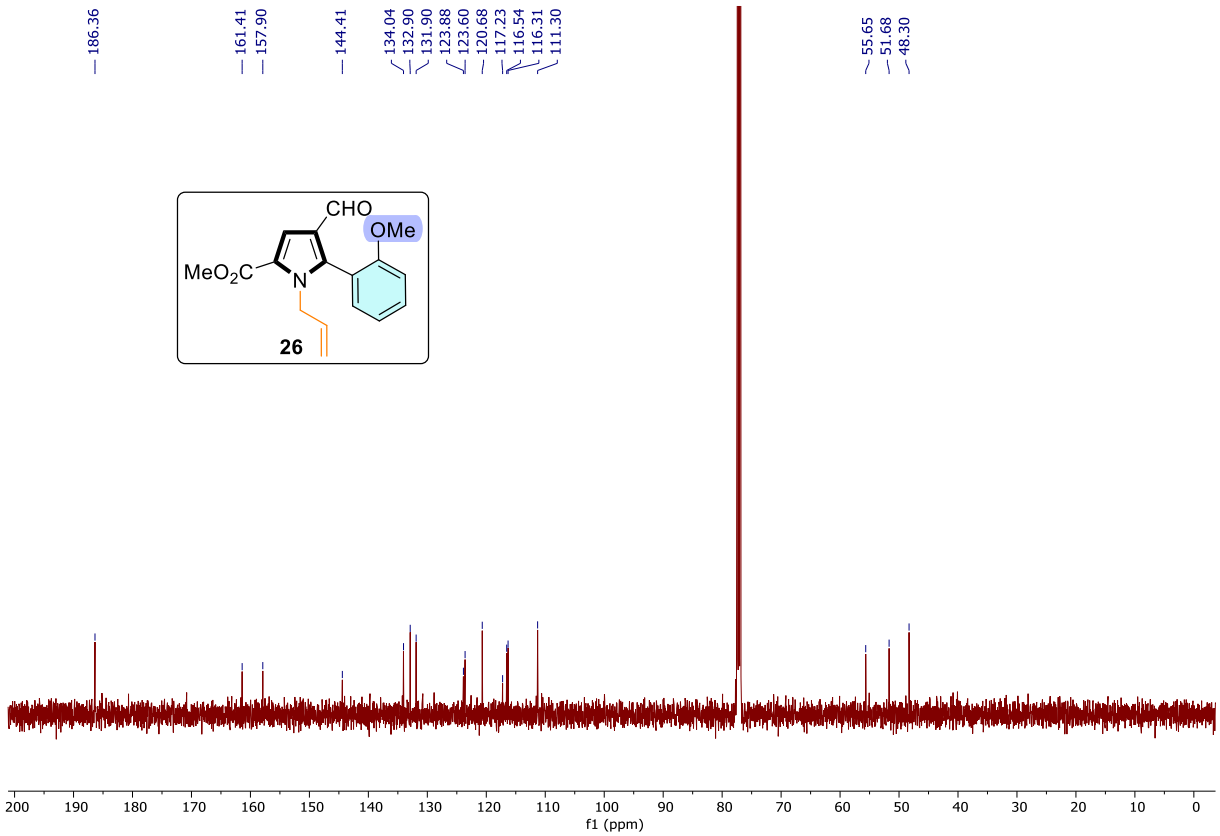
^{13}C NMR of Compound **25** ($CDCl_3$, 101 MHz)



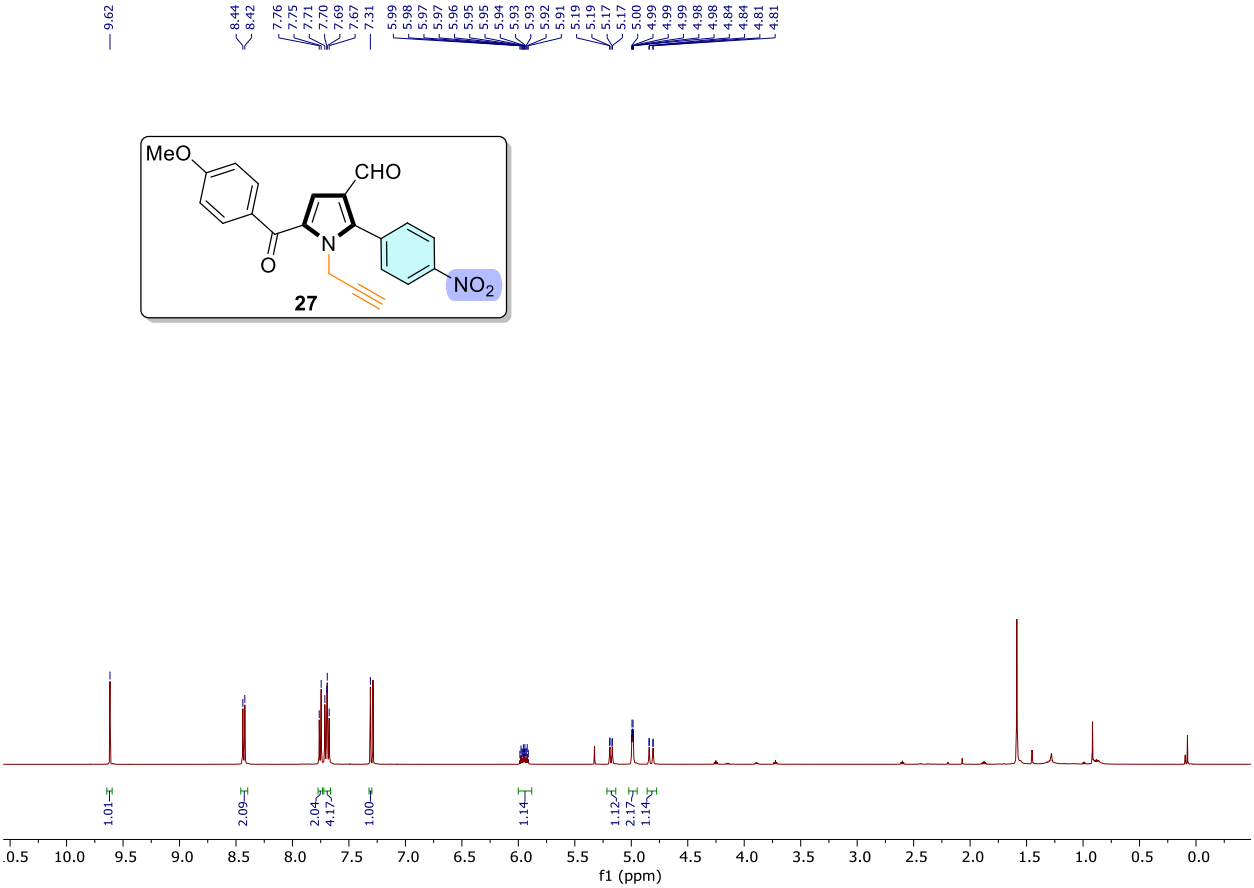
^{19}F NMR of Compound **25** ($CDCl_3$, 376 MHz)



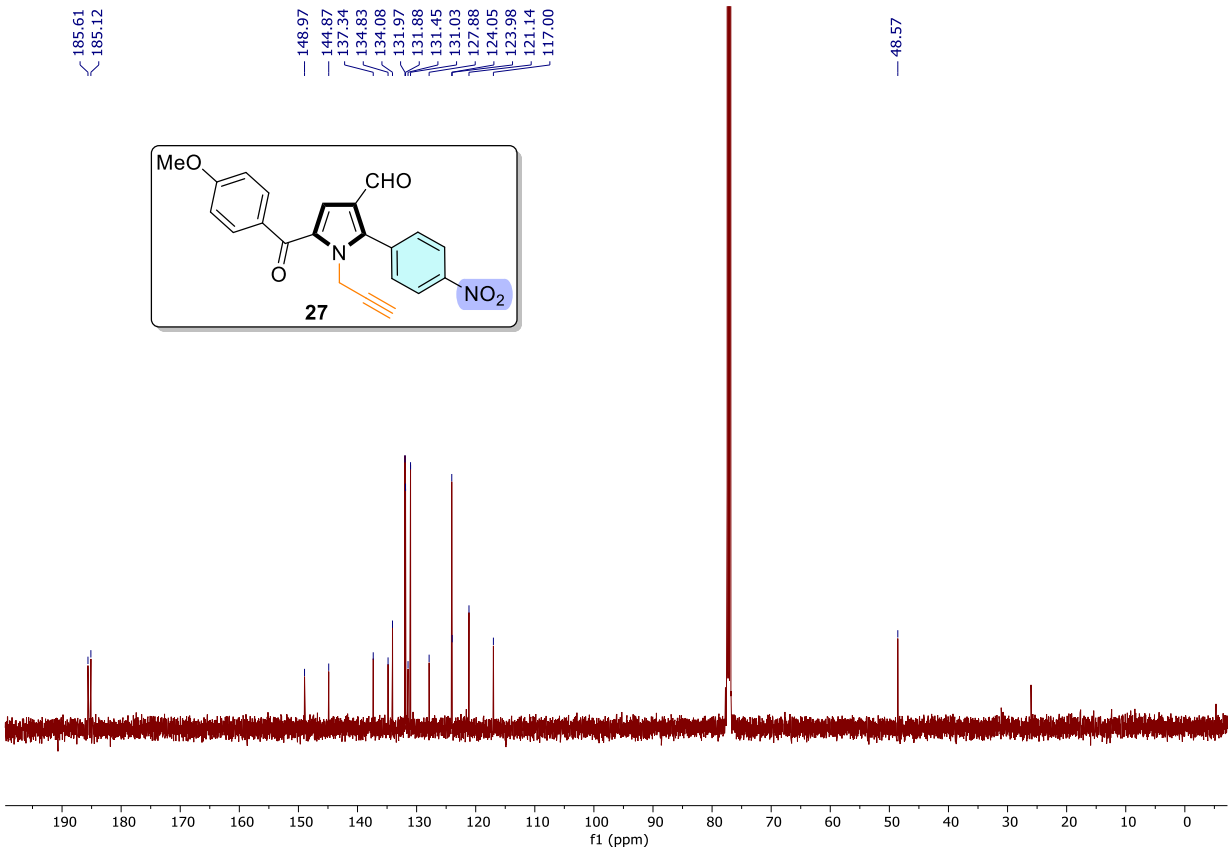
^{1}H NMR of Compound **26** ($CDCl_3$, 500 MHz)



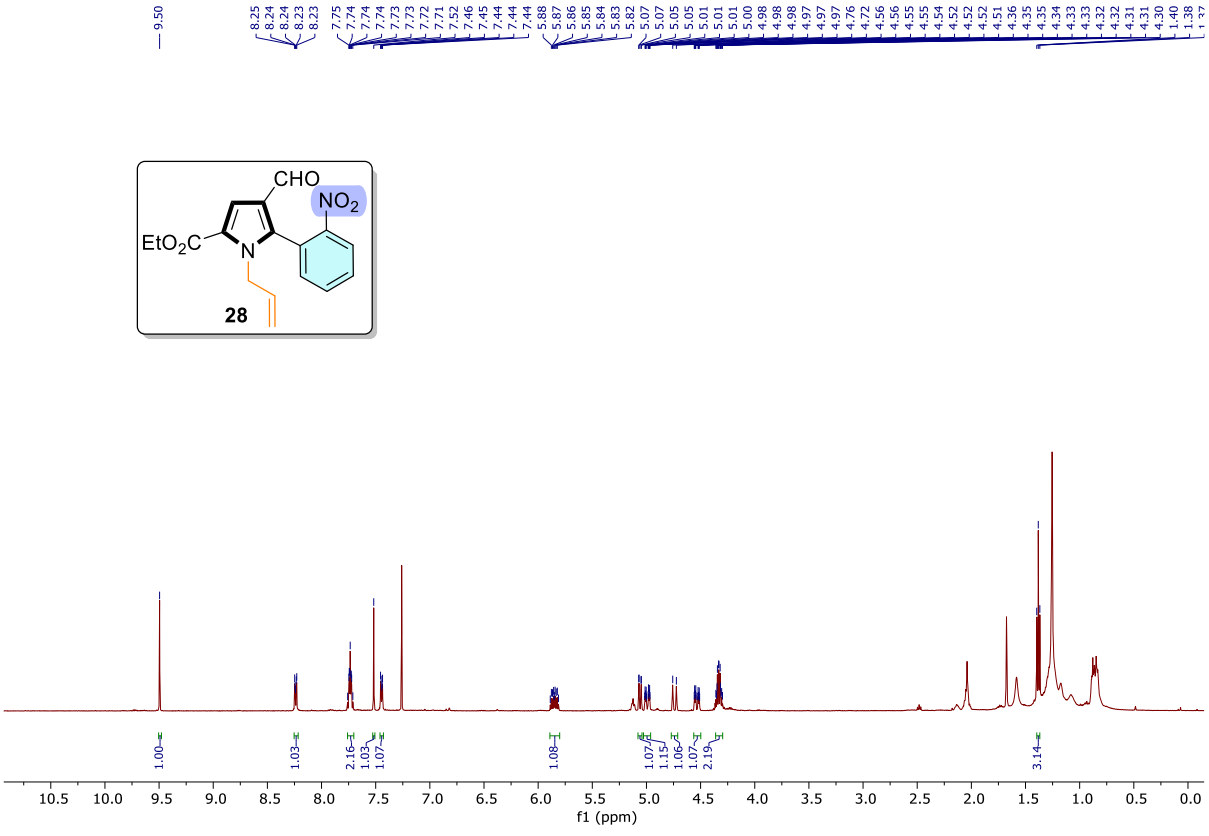
^{13}C NMR of Compound **26** ($CDCl_3$, 126 MHz)



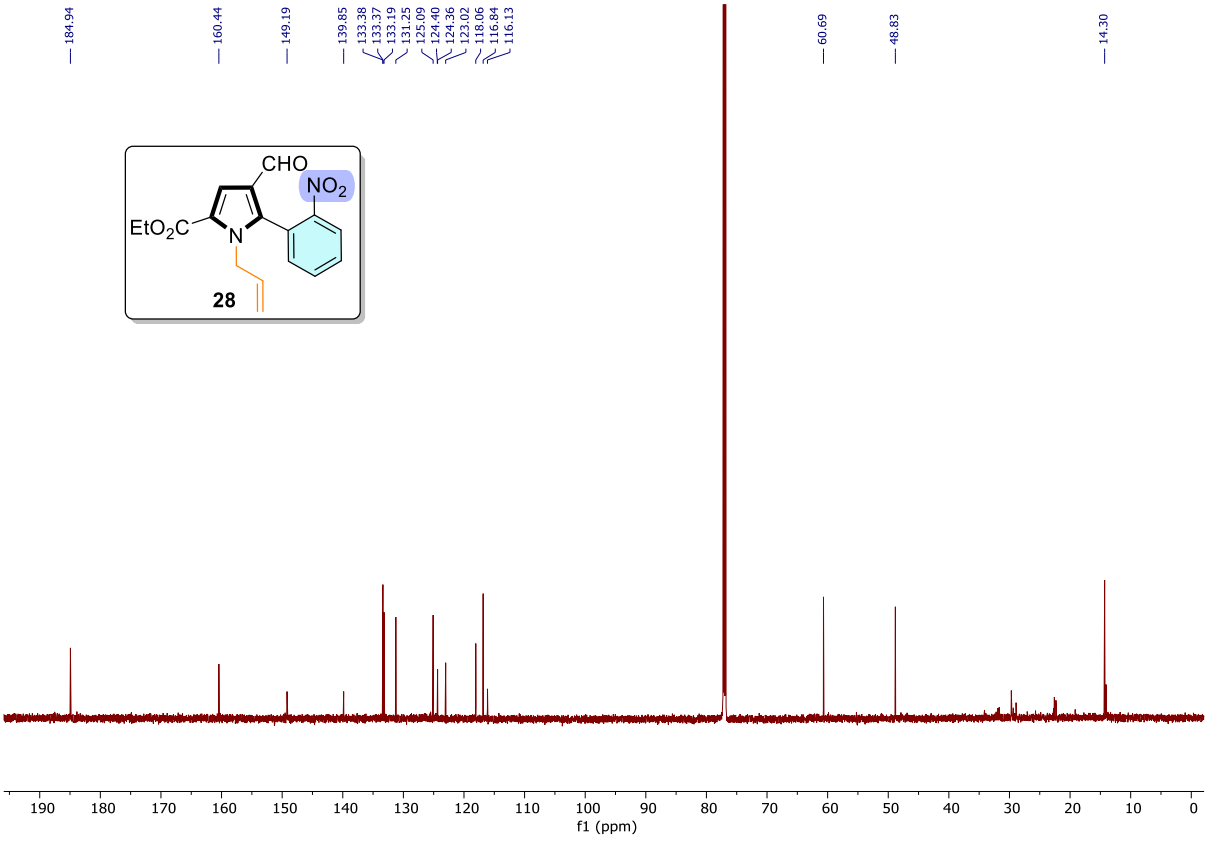
^{1}H NMR of Compound **27** ($CDCl_3$, 126 MHz)



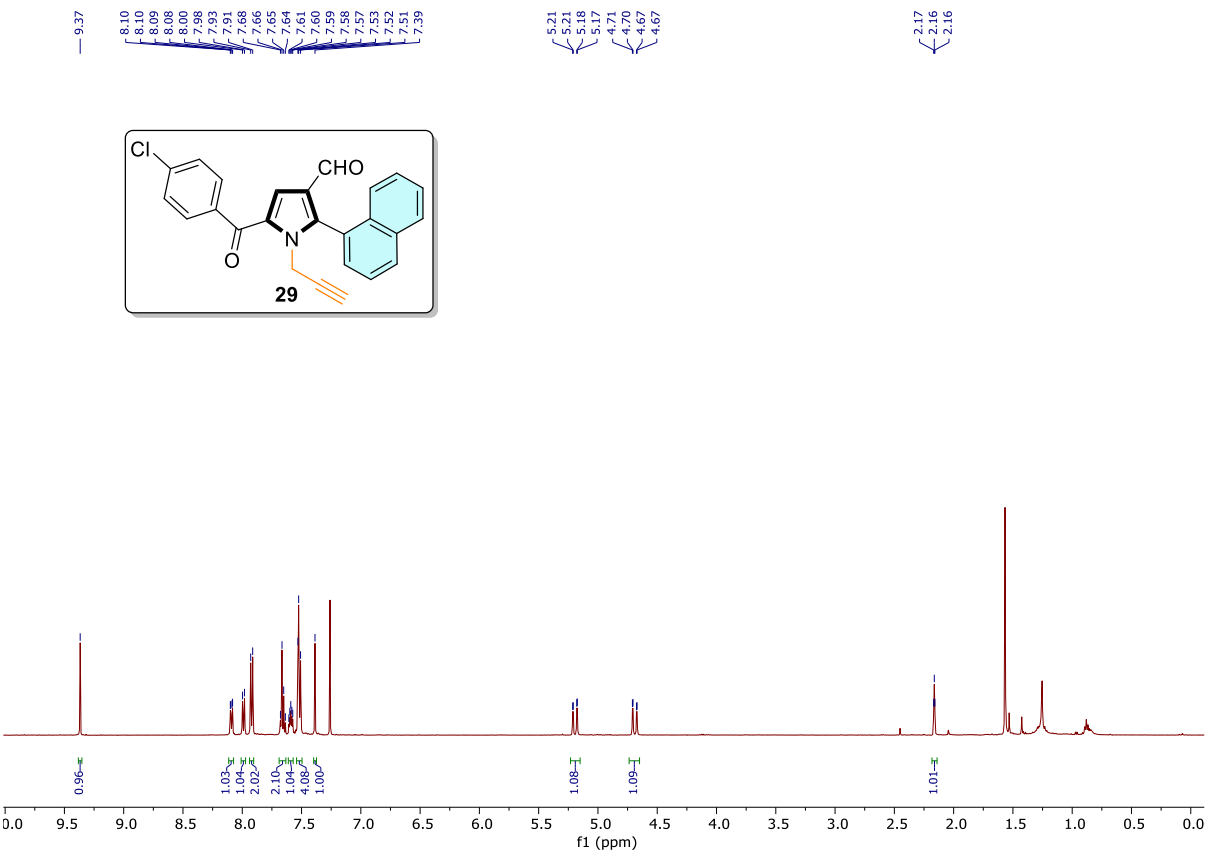
^{13}C NMR of Compound **27** ($CDCl_3$, 126 MHz)



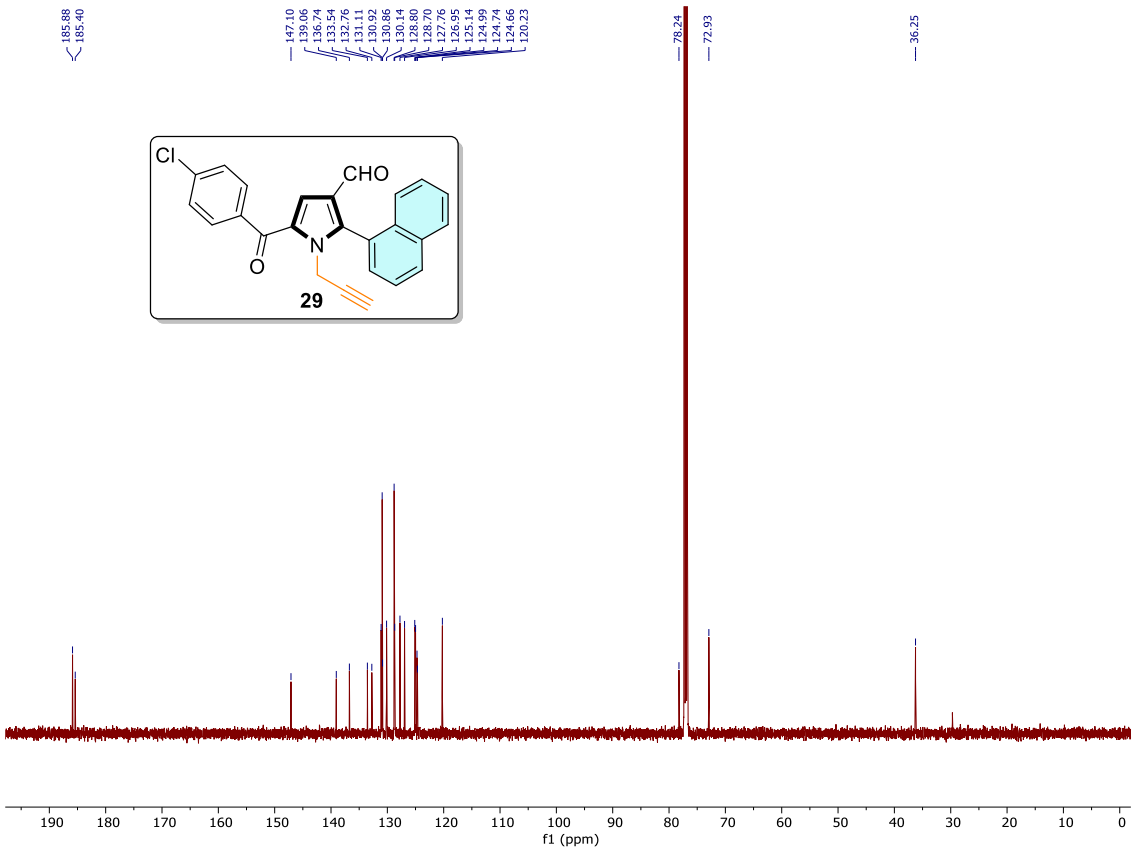
^{1}H NMR of Compound **28** ($CDCl_3$, 500 MHz)



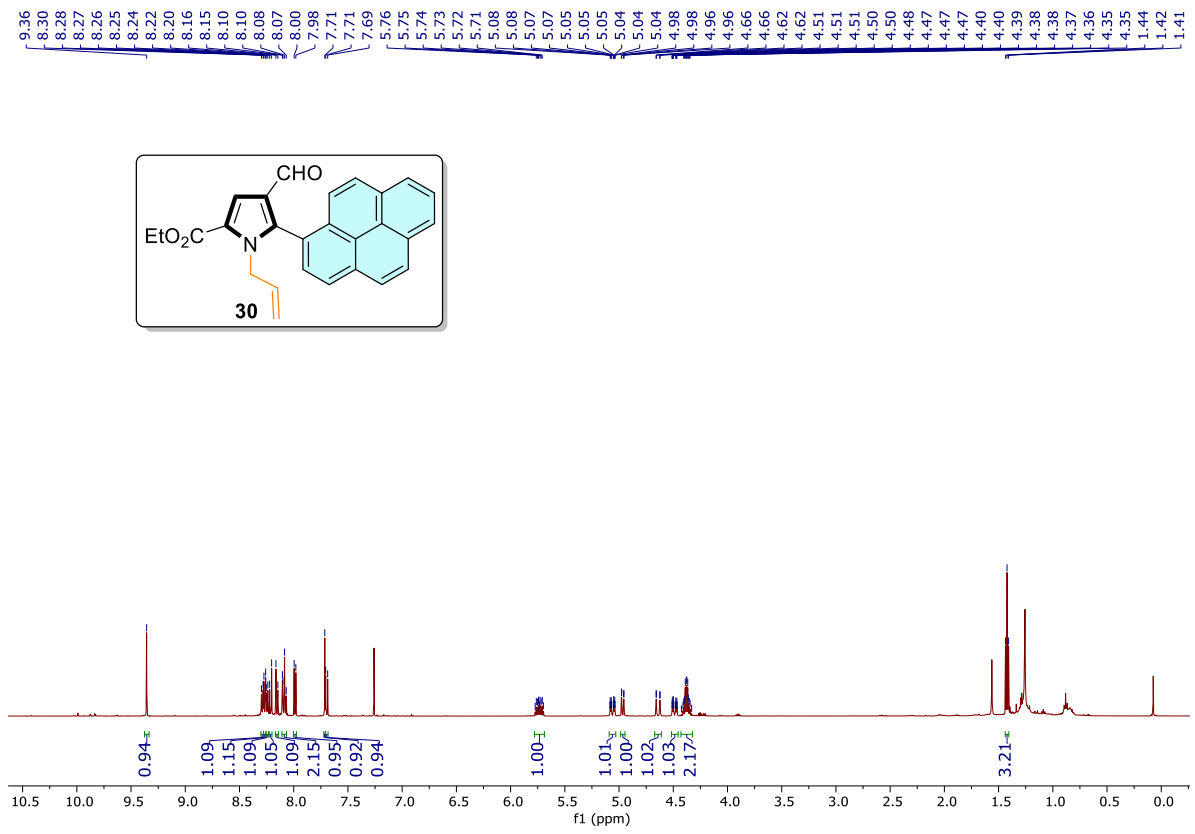
^{13}C NMR of Compound **28** ($CDCl_3$, 176 MHz)



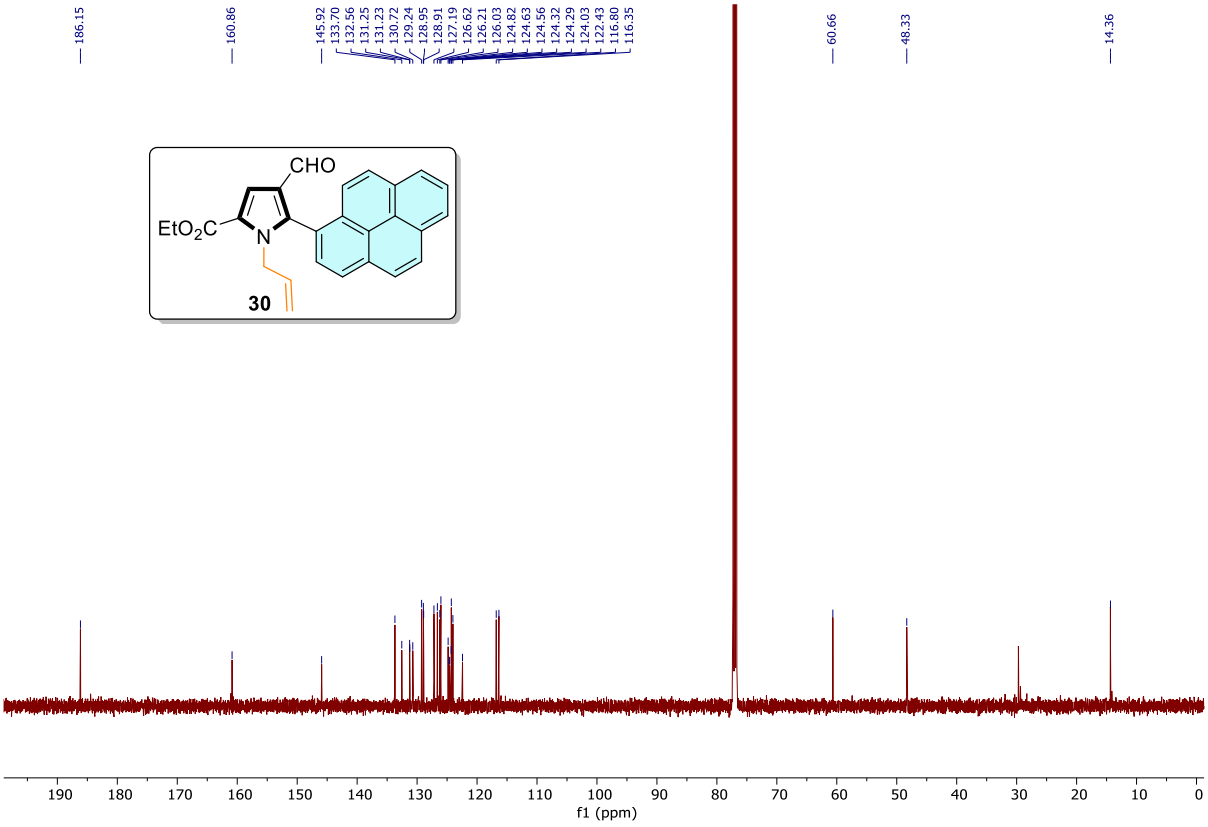
^{1}H NMR of Compound **29** ($CDCl_3$, 500 MHz)



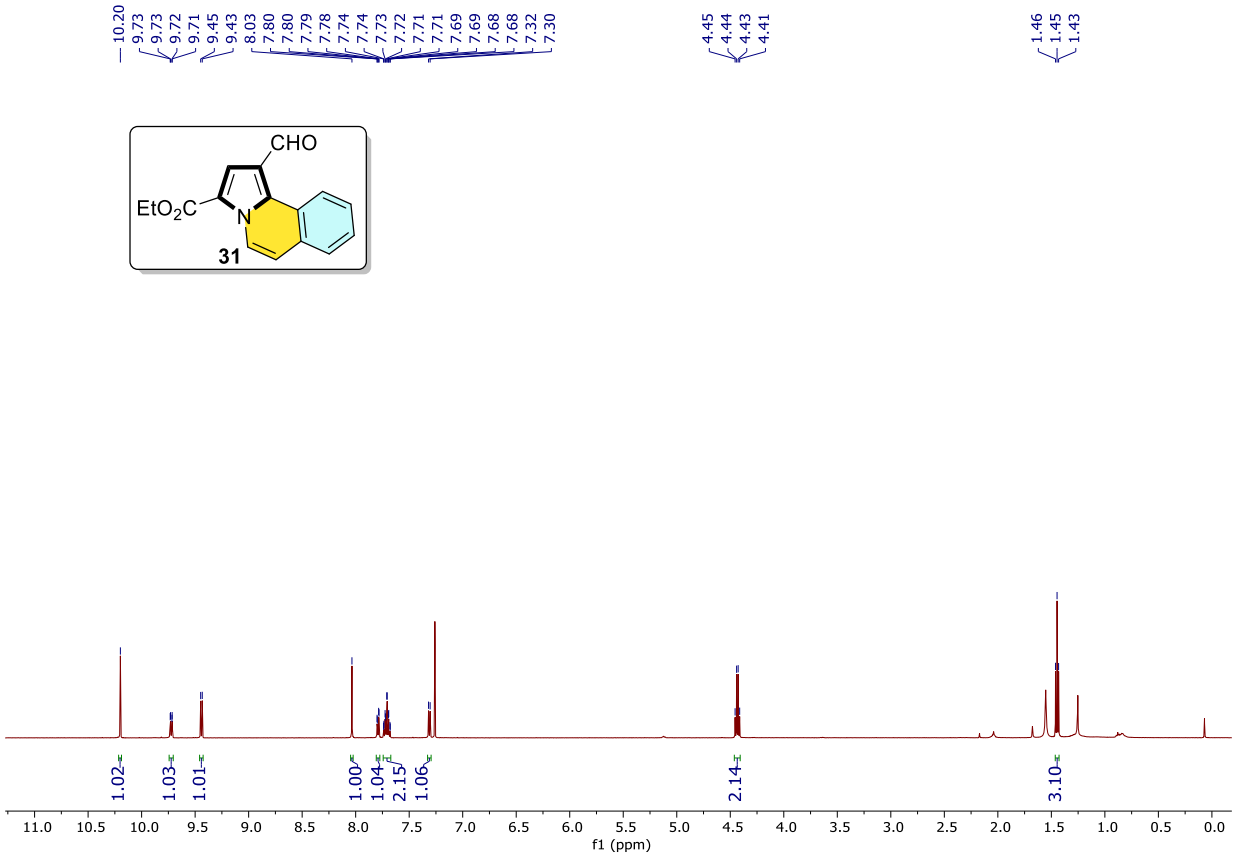
^{13}C NMR of Compound **29** ($CDCl_3$, 126 MHz)



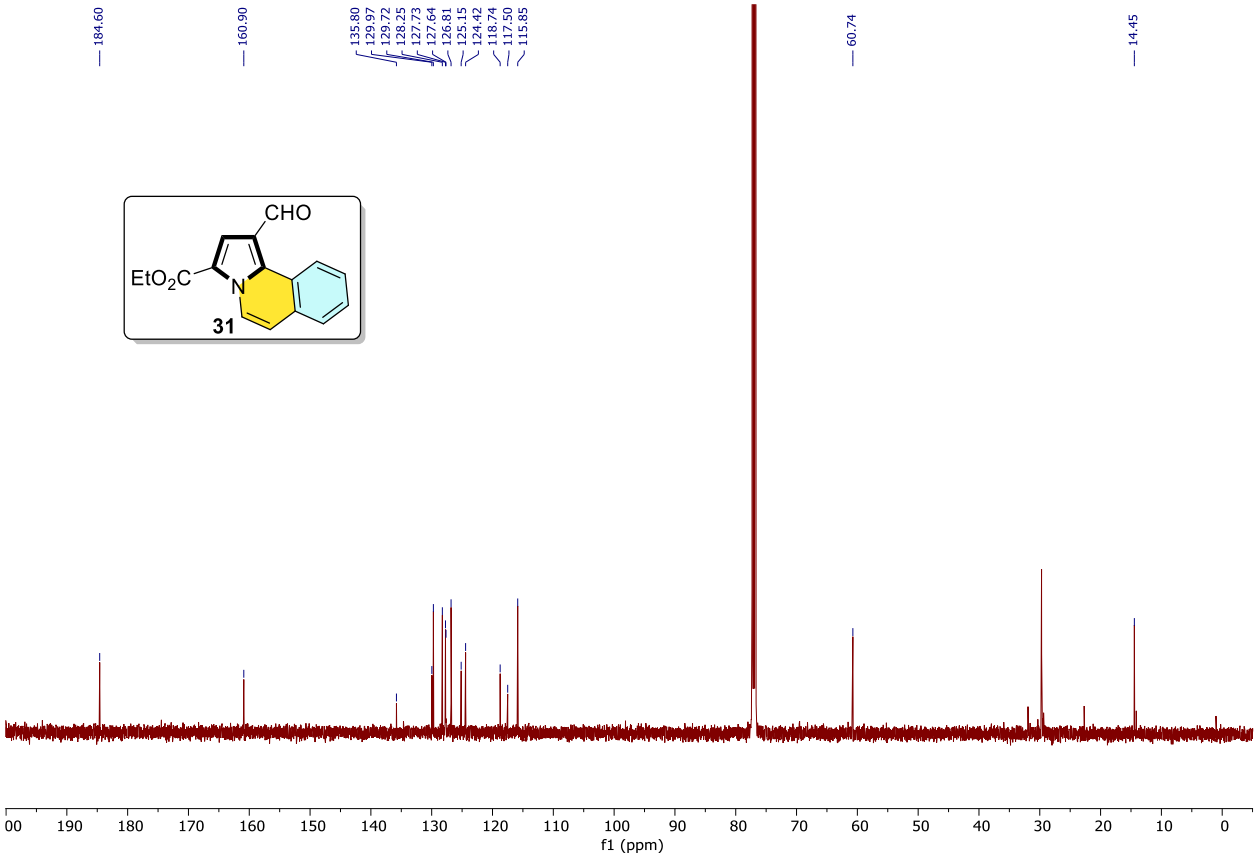
^{1}H NMR of Compound **30** ($CDCl_3$, 500 MHz)



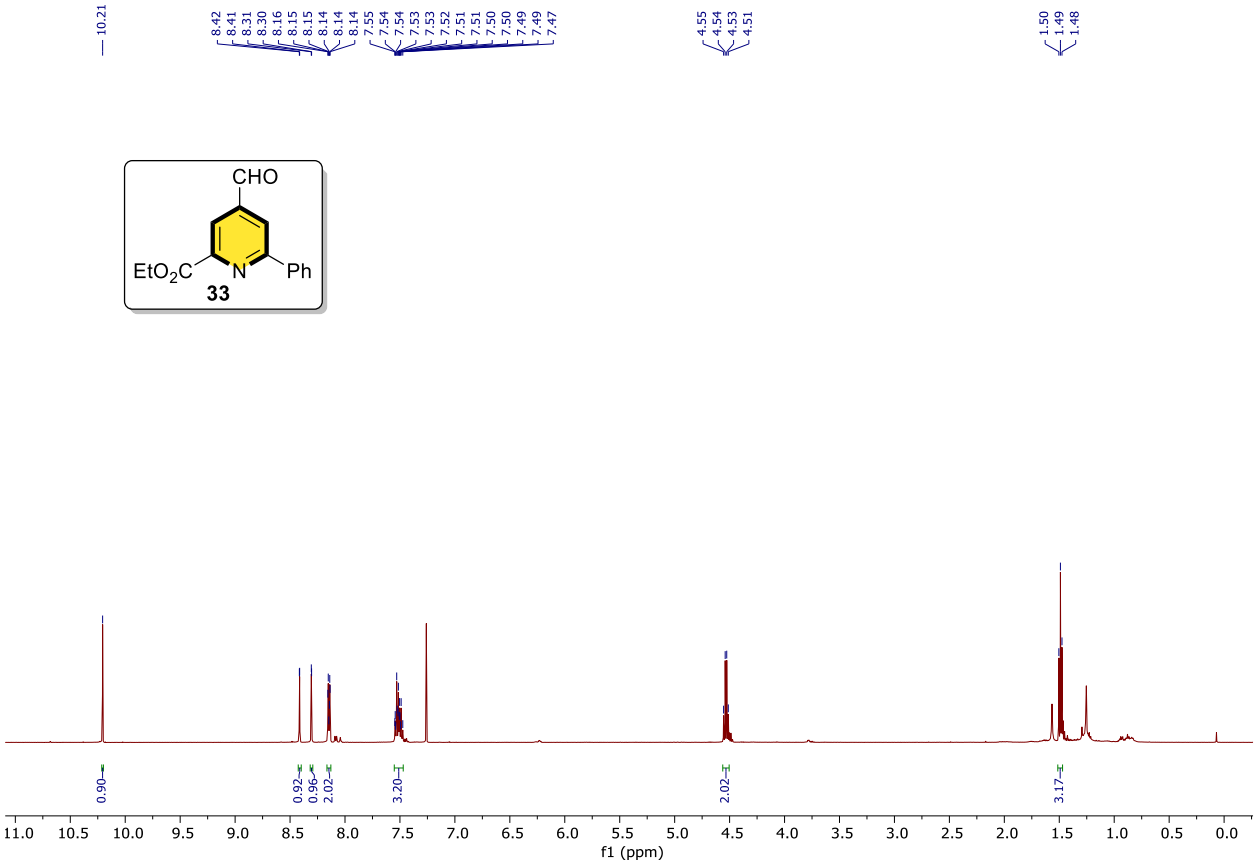
^{13}C NMR of Compound **30** ($CDCl_3$, 126 MHz)



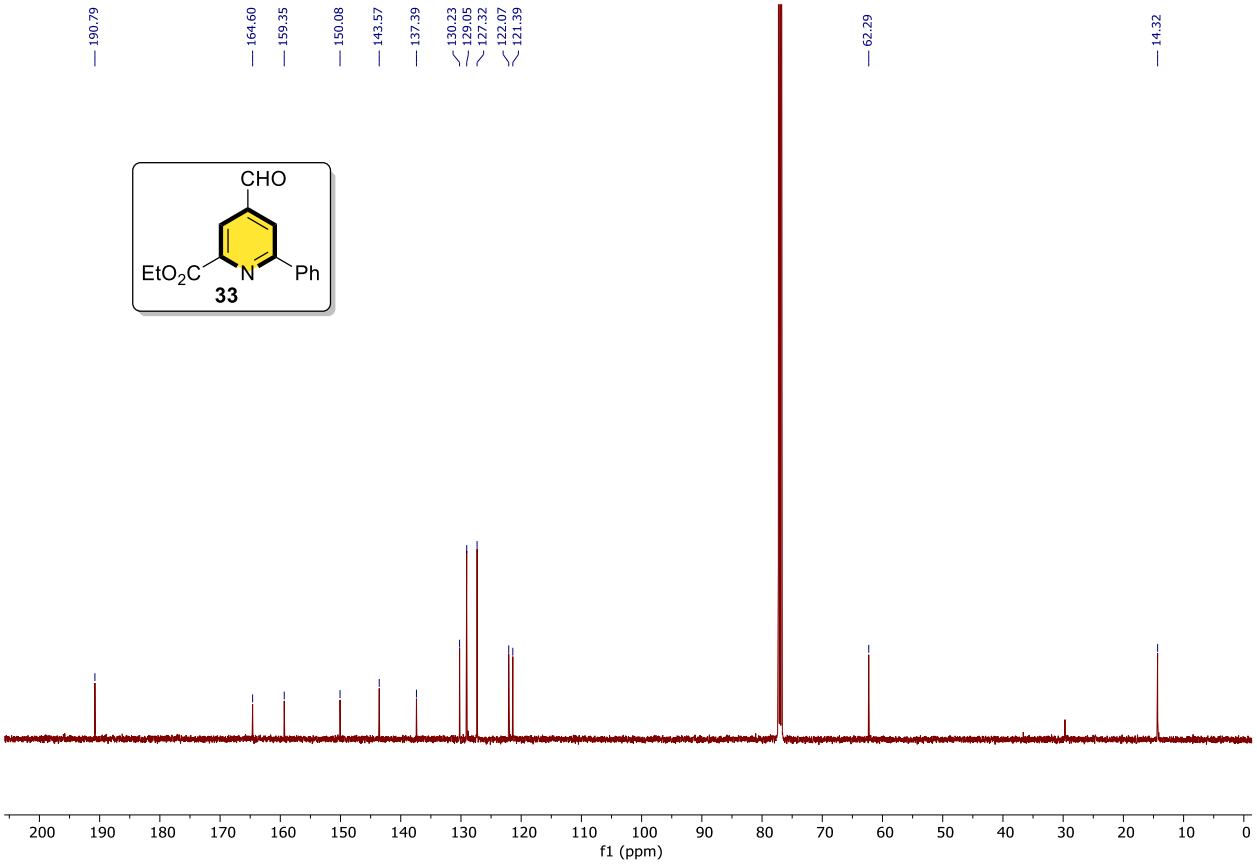
^{1}H NMR of Compound **31** ($CDCl_3$, 500 MHz)



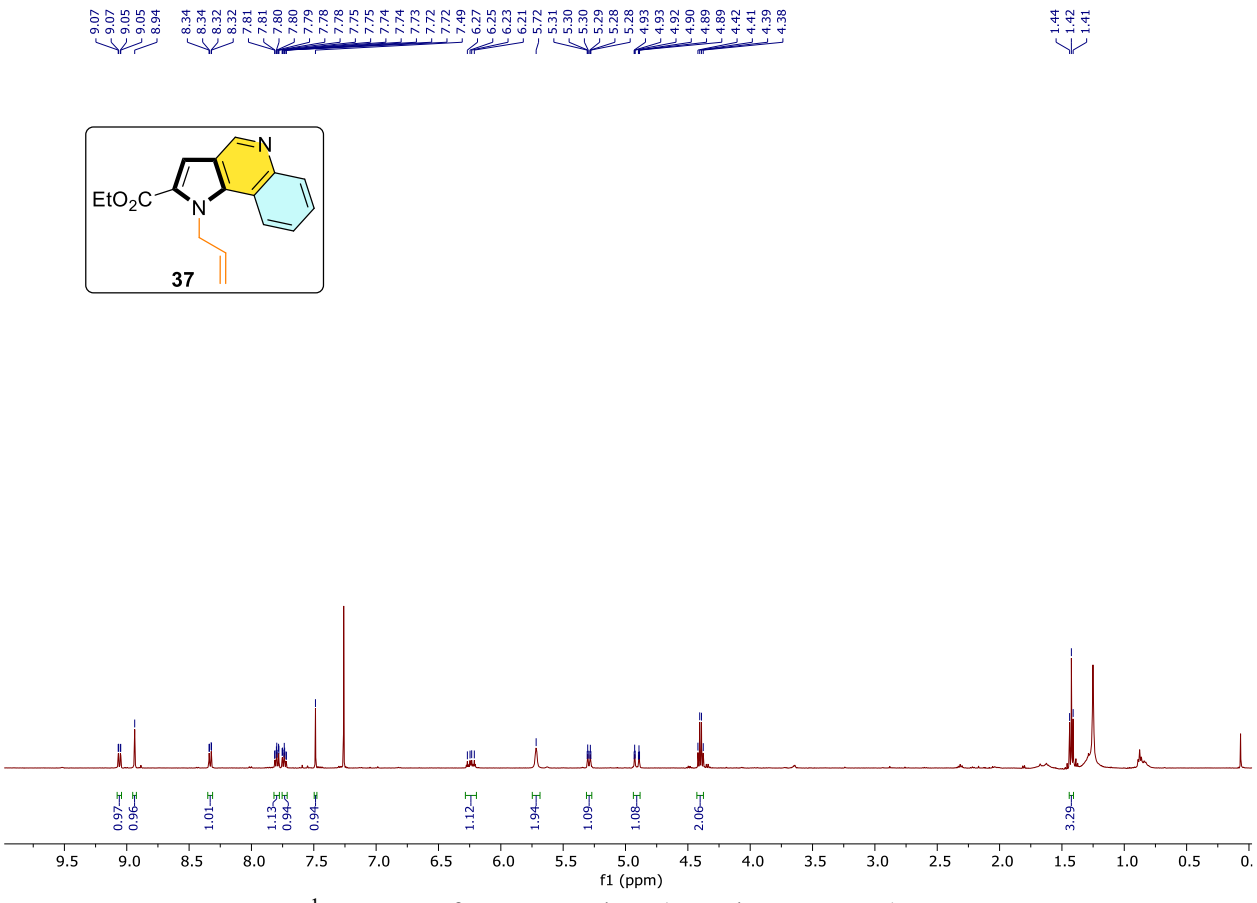
^{13}C NMR of Compound **31** ($CDCl_3$, 126 MHz)



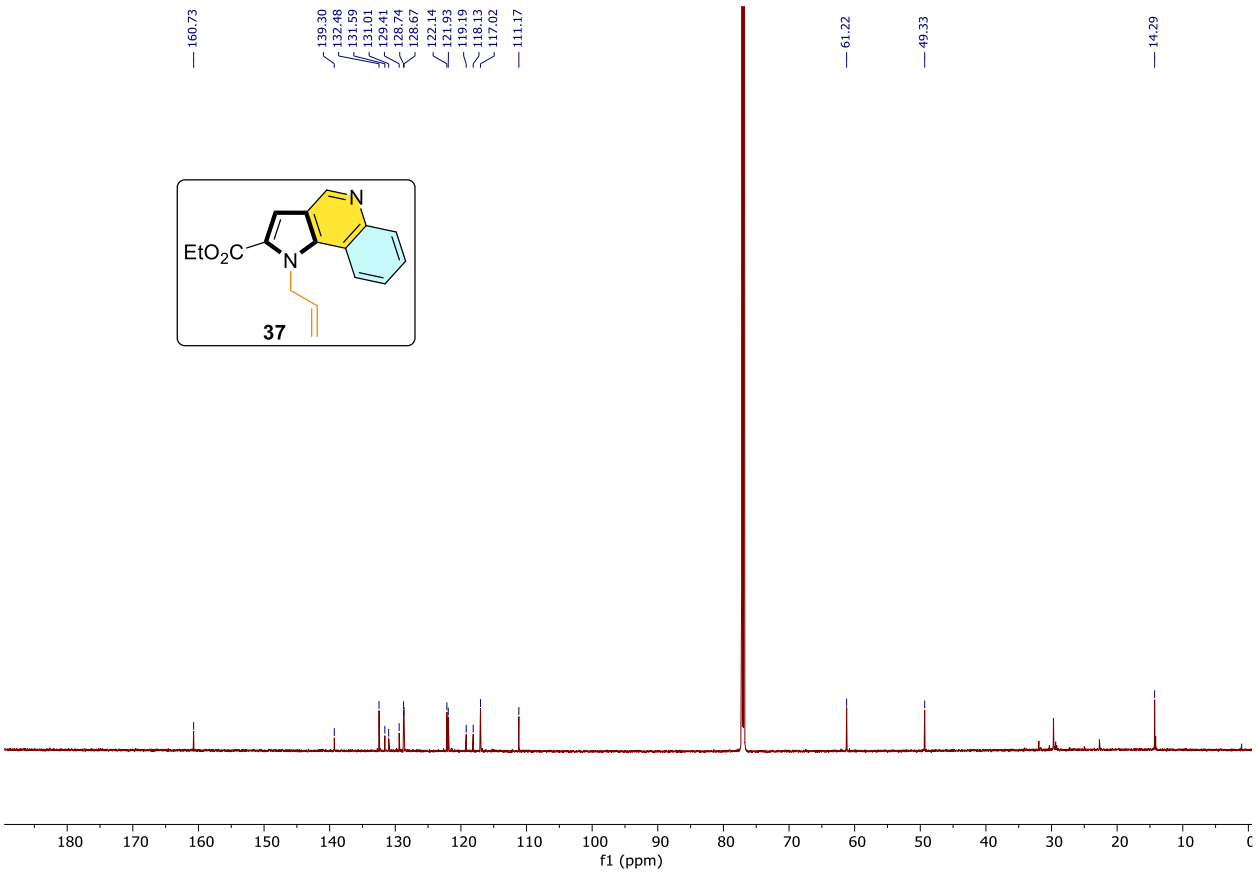
^{1}H NMR of Compound **33** ($CDCl_3$, 500 MHz)



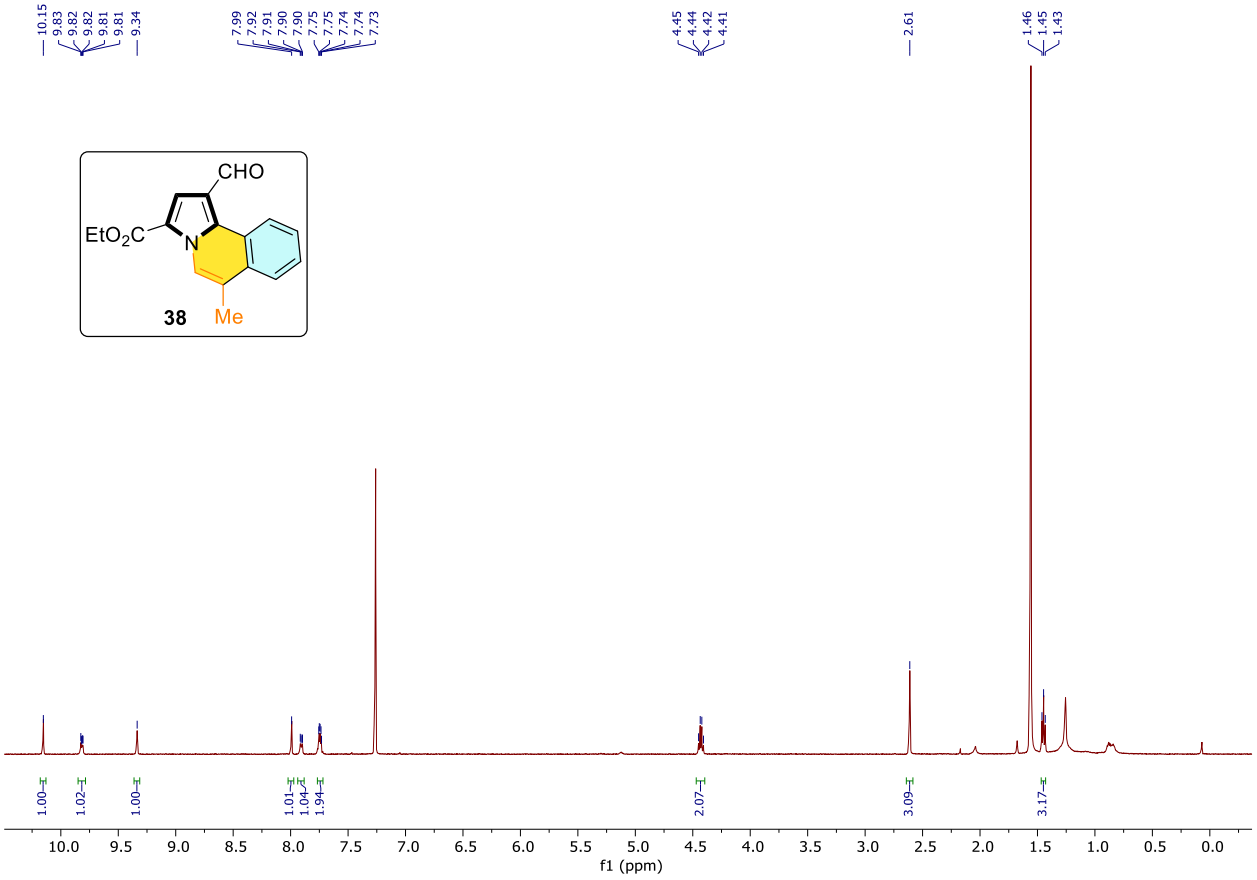
^{13}C NMR of Compound **33** ($CDCl_3$, 126 MHz)



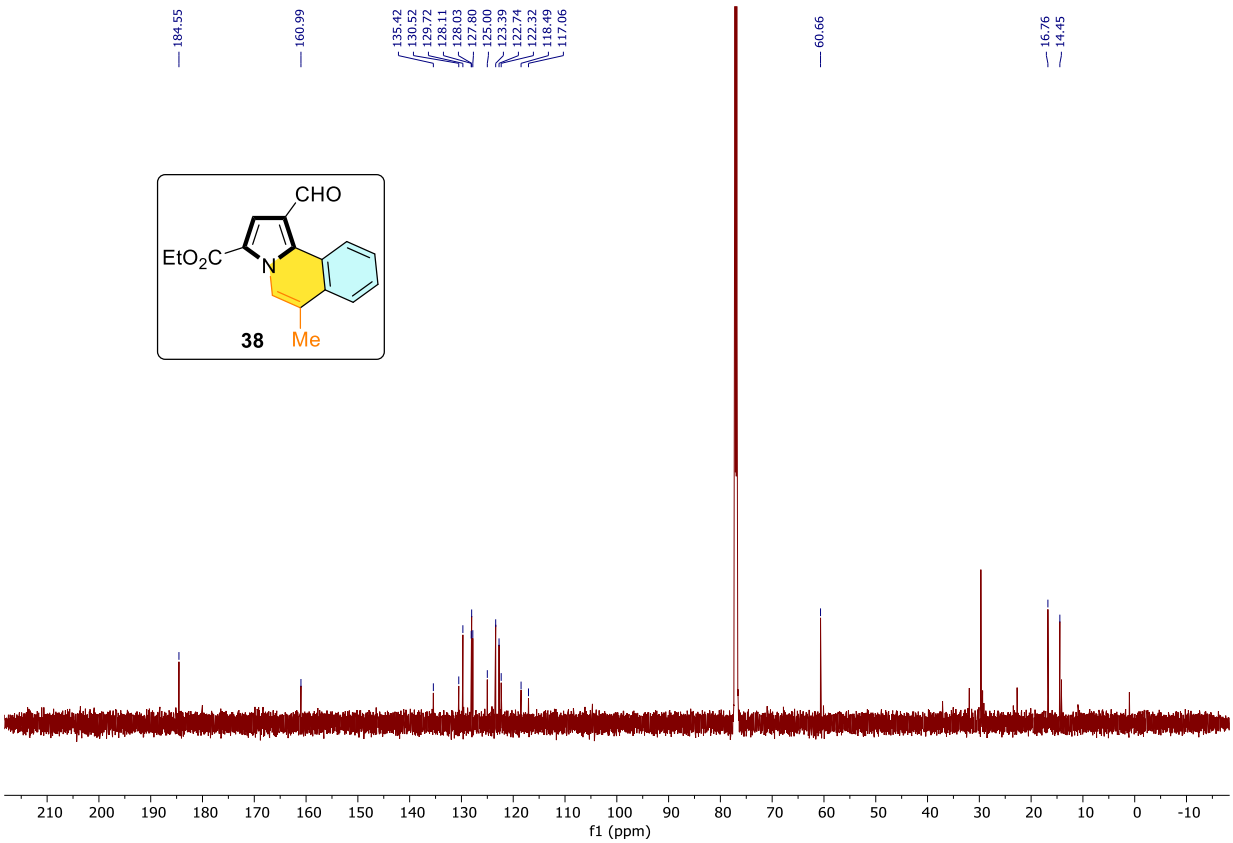
^{1}H NMR of Compound **37** ($CDCl_3$, 500 MHz)



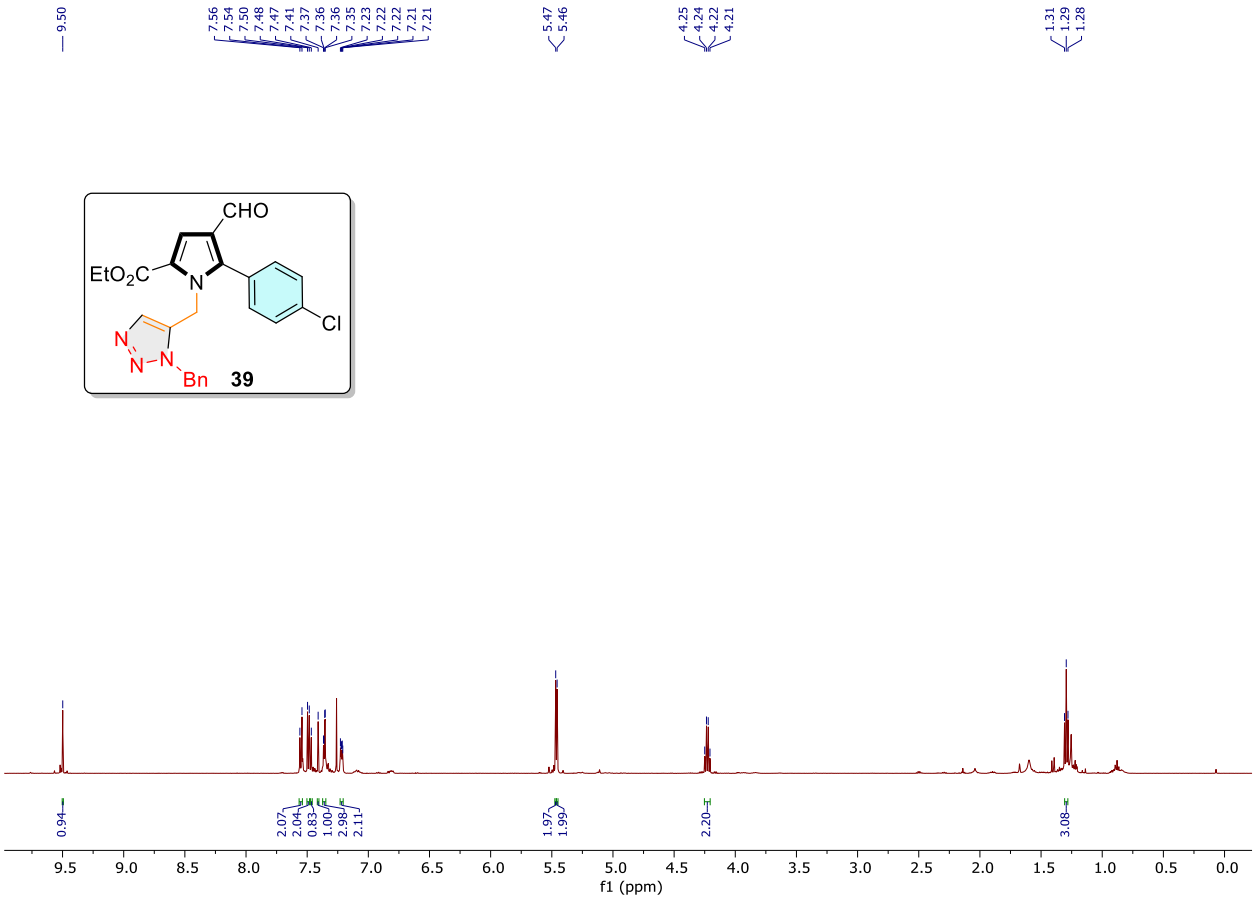
^{13}C NMR of Compound **37** ($CDCl_3$, 126 MHz)



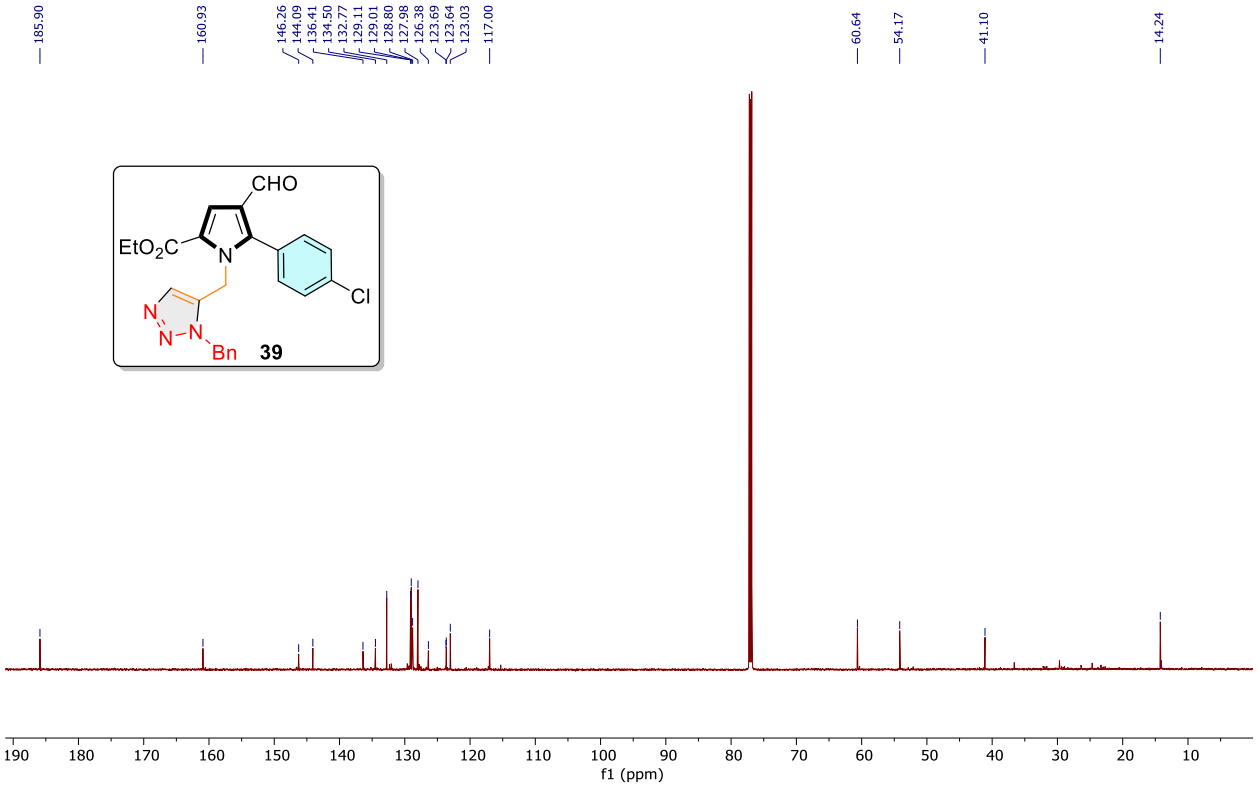
^{1}H NMR of Compound **38** ($CDCl_3$, 500 MHz)



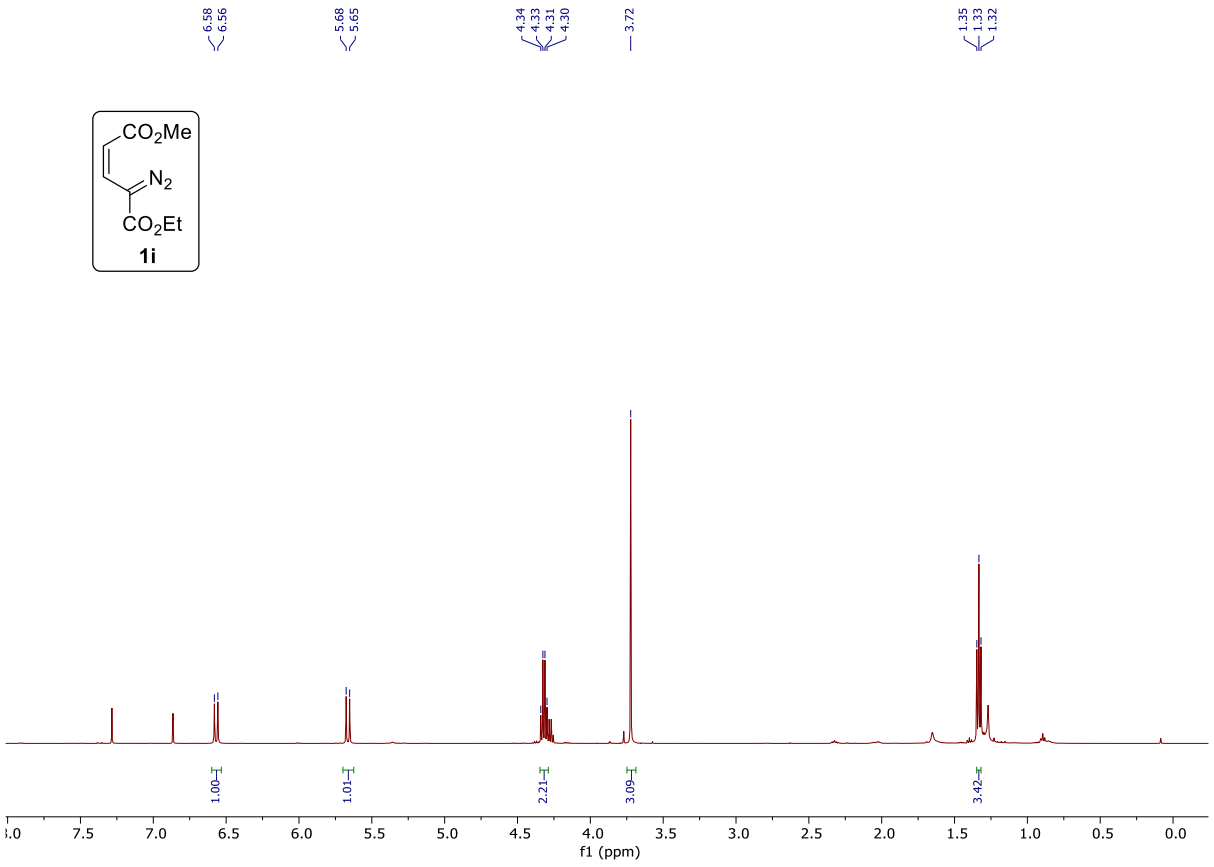
^{13}C NMR of Compound **38** ($CDCl_3$, 126 MHz)



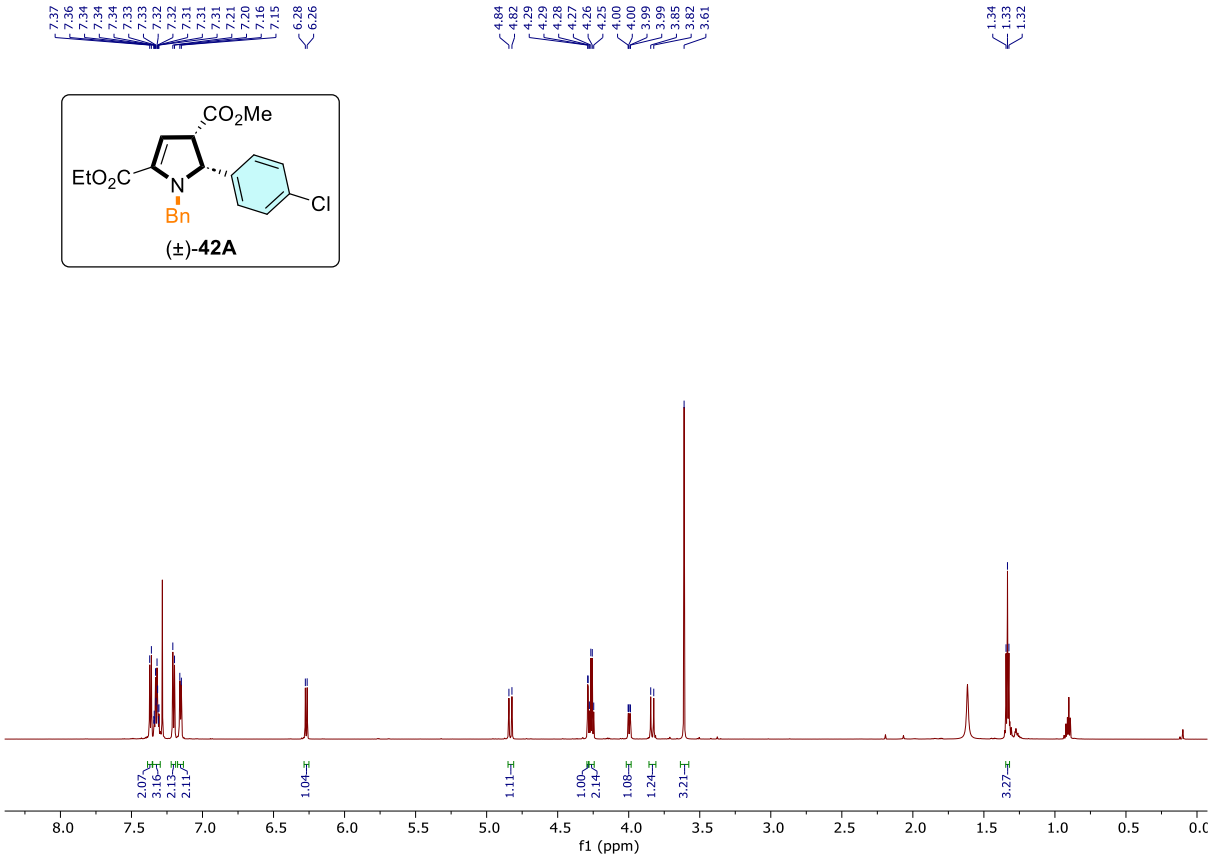
^{1}H NMR of Compound **39** ($CDCl_3$, 500 MHz)



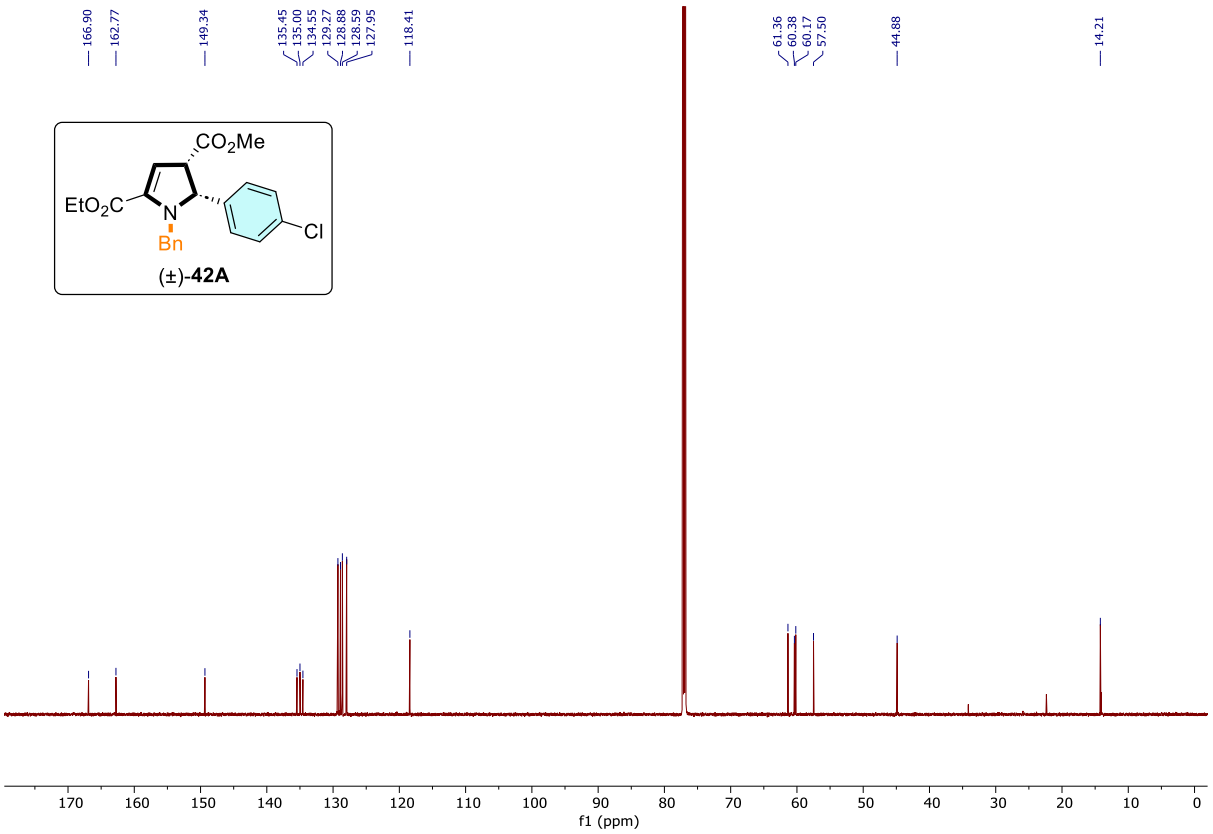
^{13}C NMR of Compound **39** ($CDCl_3$, 126 MHz)



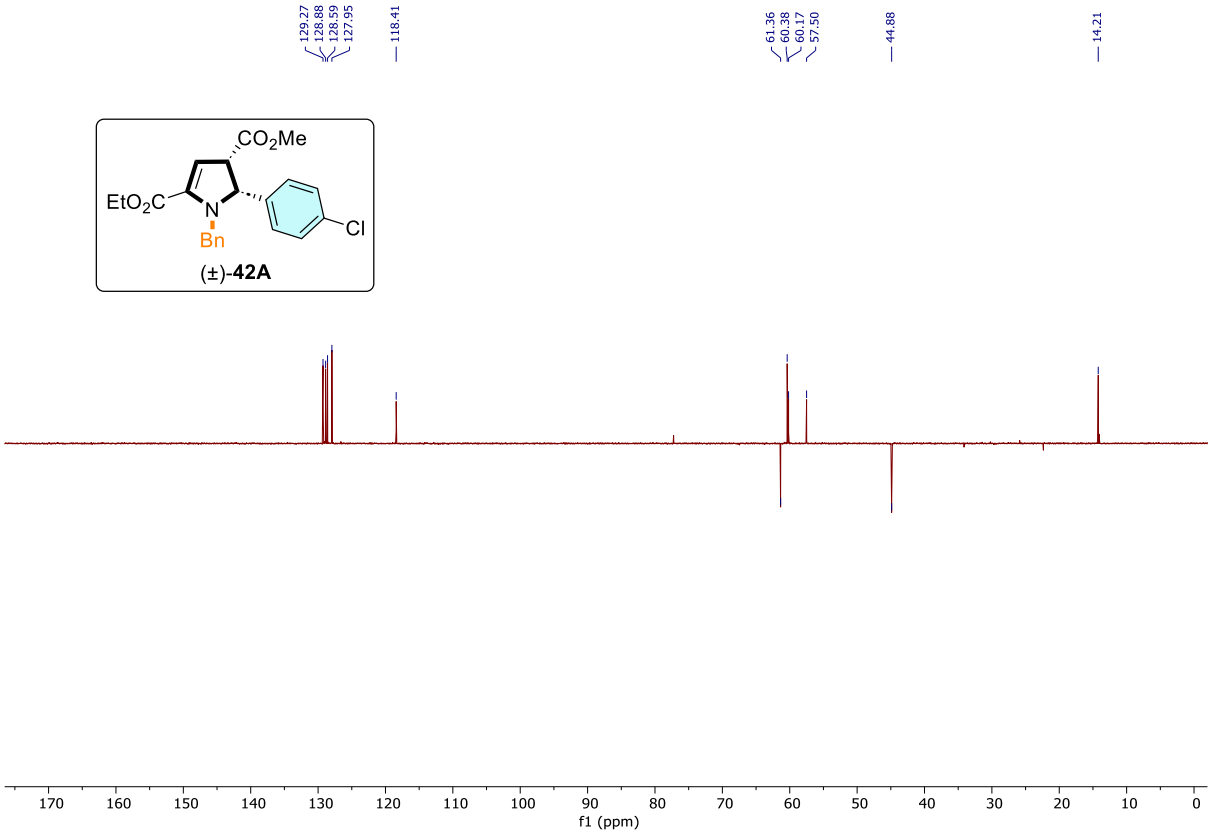
^{1}H NMR of Compound **1i** ($CDCl_3$, 500 MHz)



^{1}H NMR of Compound **(±)-42A** ($CDCl_3$, 700 MHz)



^{13}C NMR of Compound **(±)-42A** ($CDCl_3$, 176 MHz)



^{13}C-DEPT NMR of Compound **(±)-42A** ($CDCl_3$, 176 MHz)