Supporting Information

Ring-Contraction of Hantzsch Ester and Derivatives to Pyrrole via Electrochemical Extrusion of Ethyl Acetate out of Aromatic Rings

Xu Liu, †a Chang Liu †b and Xu Cheng *a,b,c

[a] *Institute of Chemistry and Biomedical Sciences, Jiangsu Key Laboratory of Advanced Organic Materials, National Demonstration Center for Experimental Chemistry Education, School of Chemistry and Chemical Engineering, Nan-jing University, Nanjing, 210023, China.*

[b] *State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin, 300071, China.*

[c] *State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou, 310032, China.*

Contents

1. General Information

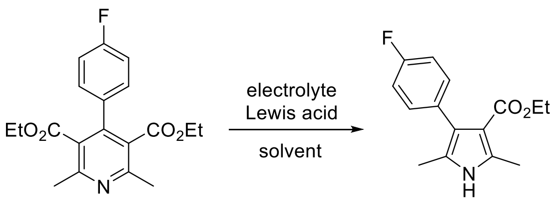
Unless otherwise noted, all reactions were carried out under nitrogen or argon atmosphere. All materials were obtained from commercial suppliers and used directly without further purification. The solvents were dried by distillation over the appropriate drying reagents before use. Other chemical reagents were purchased from commercial sources and used without further purification.

Flash chromatography utilized 300-400 mesh silica gel from Qingdao Haiyang Chemical Co., Ltd. Reactions were monitored by thin-layer chromatography (TLC) using 254 nm UV light to visualize the progress of the reactions.

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Ascend III 400 (400 MHz and 100 MHz). All ^{1}H NMR and ^{13}C NMR spectra are reported in parts per million (ppm) downfield of TMS. Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration.

Melting points were measured with digital melting point detector. High-resolution mass spectra (HRMS) were recorded on Agilent 6540 UHD Accurate-Mass Q-TOF.

2. Optimization of reaction conditions



1a → 2a

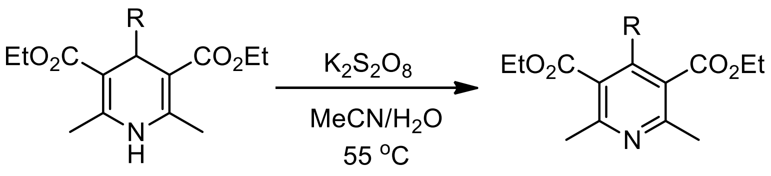
Entry	Electrolyte	Lewis acid (eq)	Solvent	Yield (%)[b]
1	$LiClO_4$	$BF_3 \cdot Et_2O$ (3)	THF	26
2	$LiClO_4$	-	THF	0
3[c]	$LiClO_4$	$BF_3 \cdot Et_2O$ (3)	THF	0
4	*n*Bu_4NPF_6	$BF_3 \cdot Et_2O$ (3)	THF	24
5	*n*Bu_4NCl	$BF_3 \cdot Et_2O$ (3)	THF	17
6	*n*Bu_4NBF_4	$BF_3 \cdot Et_2O$ (3)	THF	35
7	$LiBF_4$	$BF_3 \cdot Et_2O$ (3)	THF	34
8	*n*Bu_4NBF_4	$B(C_6F_5)_3$ (3)	THF	trace
9	*n*Bu_4NBF_4	$Sc(OTf)_3$ (3)	THF	41

10	*n*Bu_4NBF_4	$InCl_3$ (3)	THF	trace
11	*n*Bu_4NBF_4	$CeCl_3$ (3)	THF	6
12	*n*Bu_4NBF_4	$Cu(OTf)_2$ (3)	THF	0
13	*n*Bu_4NBF_4	$Zn(OTf)_2$ (3)	THF	0
14	*n*Bu_4NBF_4	$BF_3·Et_2O$ (3)	MeCN	trace
15	*n*Bu_4NBF_4	$BF_3·Et_2O$ (3)	MeOH	trace
16	*n*Bu_4NBF_4	$BF_3·Et_2O$ (3)	DMF	15
17	*n*Bu_4NBF_4	$BF_3·Et_2O$ (3)	DMSO	trace
18	*n*Bu_4NBF_4	$BF_3·Et_2O$ (3)	DCM	0
19	*n*Bu_4NBF_4	$BF_3·Et_2O$ (4)	THF	45
20	***n*Bu_4NBF_4**	**$BF_3·Et_2O$ (5)**	**THF**	**90 (75)[d]**
21[e]	*n*Bu_4NBF_4	$BF_3·Et_2O$ (5)	THF	83
22[f]	*n*Bu_4NBF_4	$BF_3·Et_2O$ (5)	THF	0

[a]Reaction conditions: **1a** (0.2 mmol), electrolyte (0.1 mmol), Lewis acid, H_2O (40 equiv), solvent (5 mL), Zn (+)/C(-), 20 mA, rt, 12 h. [b]GC yield. [c]No H_2O. [d]Isolated yield. [e]Mg(+)/C(-). [f]C(+)/C(-).

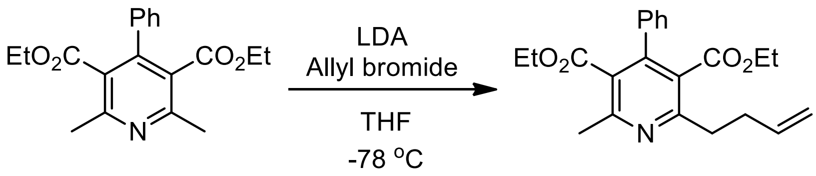
2.1 General Procedures

General Procedure A



A flask was charged with Hantzsch ester (5 mmol, 1.0 equiv), $K_2S_2O_8$ (1.5 eqiuv), MeCN/H_2O (v/v = 1:1, 30 mL). The mixture was stirred at 55 °C until the Hantzsch ester was consumed. Then the reaction was cooled to ambient temperature. The mixture was extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

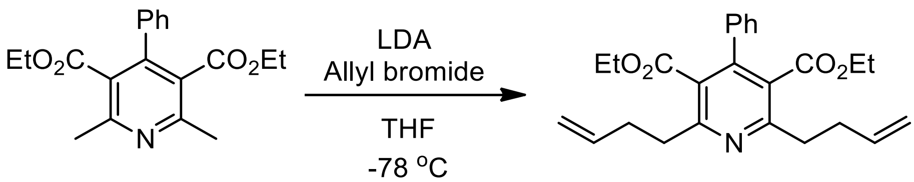
General Procedure B



A flask was charged with polysubstituted pyridine (10 mmol) and anhydrous THF (30 mL) under argon. Then LDA (1.1 equiv) was added at -78 °C and the mixture was stirred for 1 h. Allyl bromide (1.1 equiv) was added subsequently to the reaction mixture that was stirred at room temperature until the reaction was complete. The reaction was quenched with sat. NH_4Cl, and the mixture was extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 3H), 7.28 – 7.26 (m, 2H), 5.96 – 5.86 (m, 1H), 5.09 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.00 (d, *J* = 10.1 Hz, 1H), 4.04 – 3.98 (m, 4H), 2.95 – 2.91 (m, 2H), 2.63 (s, 3H), 2.56 – 2.51 (m, 2H), 0.92 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 167.9, 158.4, 155.6, 146.3, 137.8, 136.7, 128.5, 128.3, 128.2, 127.1, 127.0, 115.2, 61.5, 61.4, 35.9, 33.8, 23.1, 13.7. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{22}H_{26}NO_4$: 368.1862, found: 368.1858.

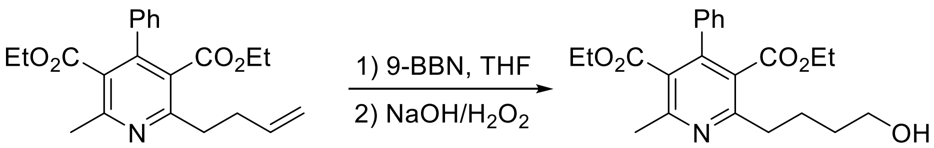
General Procedure C



A flask was charged with polysubstituted pyridine (1 mmol) and anhydrous THF (3 mL) under argon. LDA (1.1 equiv) was added at -78 °C and the mixture was stirred for 1 h. Allyl bromide (1.1 equiv) was added subsequently and the reaction mixture was stirred at room temperature for 2 h. Then LDA (1.1 equiv) was added at -78 °C and the mixture was stirred for 1 h. Allyl bromide (1.1 equiv) was added subsequently to the reaction mixture that was stirred at room temperature until the reaction was finished. The reaction was quenched with sat. NH_4Cl, and the mixture was extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.37 (m, 3H), 7.29 – 7.27 (m, 2H), 5.97 – 5.87 (m, 2H), 5.09 (d, *J* = 17.1 Hz, 2H), 5.00 (d, *J* = 10.2 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 4H), 2.97 – 2.93 (m, 2H), 2.56 (dd, *J* = 15.1, 7.1 Hz, 2H), 0.93 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 158.4, 146.2, 137.9, 136.8, 128.5, 128.4, 128.2, 127.1, 115.1, 61.5, 35.8, 33.5, 13.7. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{25}H_{38}NO_4$: 408.2175, found: 408.2179.

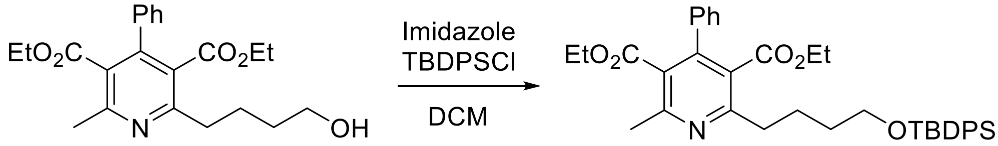
General Procedure D



A flask was charged with polysubstituted pyridine (5 mmol) and anhydrous THF (5 mL) under argon. Then 9-BBN (1.2 equiv.) was added dropwise at 0 ºC and the mixtre was then stirred at 65 ºC for 1.5 h. NaOH (3 M, 5 mL) and H_2O_2 (30%, 5 mL) was then added under 0 ºC. The mixture was stirred at room temperature until the reaction was finished. The mixture was extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 3H), 7.28 – 7.26 (m, 2H), 4.05 – 3.97 (m, 4H), 3.70 (t, *J* = 6.3 Hz, 2H), 2.91 – 2.87 (m, 2H), 2.63 (s, 3H), 1.89 (dt, *J* = 15.0, 7.3 Hz, 2H), 1.68 (dt, *J* = 13.5, 6.6 Hz, 2H), 0.94 – 0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 168.0, 159.0, 155.6, 146.5, 136.7, 128.6, 128.3, 128.2, 127.2, 127.1, 62.5, 61.5, 35.6, 32.2, 25.8, 23.0, 13.7, 13.7. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{22}H_{28}NO_5$: 386.1967, found: 386.1964.

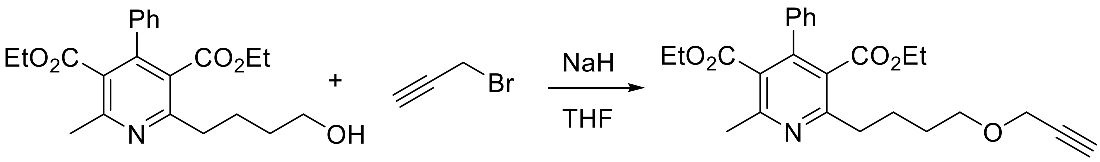
General Procedure E



A flask was charged with polysubstituted pyridine (1 mmol), imidazole (1.2 equiv), TBDPSCl (1.2 equiv) and DCM (4 mL) under argon. The mixture was stirred at room temperature until the reaction was finished. The mixture was extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 6.5 Hz, 4H), 7.43 – 7.37 (m, 9H), 7.31 – 7.27 (m, 2H), 4.03 (q, J = 7.1 Hz, 2H), 3.97 (q, J = 7.1 Hz, 2H), 3.72 (t, J = 6.4 Hz, 2H), 2.88 – 2.84 (m, 2H), 2.63 (s, 3H), 1.91 – 1.83 (m, 2H), 1.72 – 1.65 (m, 2H), 1.07 (s, 9H), 0.94 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 168.0, 159.2, 155.6, 146.2, 136.8, 135.7, 134.3, 129.6, 128.5, 128.3, 128.2, 127.7, 127.0, 127.0, 64.0, 61.4, 61.4, 36.3, 32.7, 27.1, 27.0, 26.3, 23.1, 19.4, 13.7. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{38}H_{46}NO_5Si$: 624.3145, found: 624.3140.

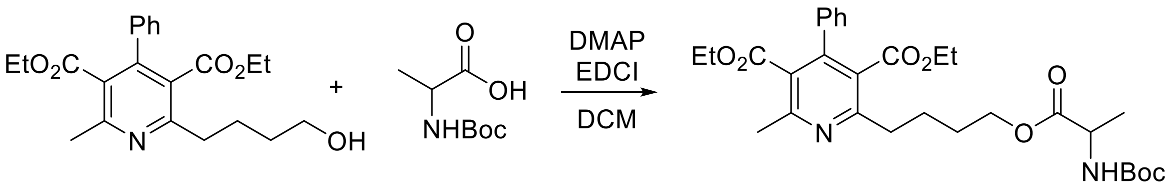
General Procedure F



A flask was charged with NaH (1.2 mmol) and anhydrous THF (5 mL) was added at 0 ^{o}C. Then polysubstituted pyridine (1 mmol) was added and the mixture was stirred for 10 min. Propargyl bromide (1.5 equiv) was added subsequently and the mixture was stirred until the reaction was finished. The mixture was extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 3H), 7.25 – 7.22 (m, 2H), 4.11 (d, J = 2.4 Hz, 2H), 4.01 – 3.94 (m, 4H), 3.52 (t, J = 6.5 Hz, 2H), 2.85 – 2.82 (m, 2H), 2.59 (s, 3H), 2.40 (t, J = 2.4 Hz, 1H), 1.88 – 1.78 (m, 2H), 1.71 – 1.63 (m, 2H), 0.90 – 0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 167.9, 158.9, 155.5, 146.1, 136.7, 128.4, 128.2, 128.1, 127.0, 126.9, 80.1, 74.2, 69.9, 61.3, 58.0, 36.0, 29.3, 26.3, 23.0, 13.6. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{25}H_{30}NO_5$: 424.2124, found: 424.2128.

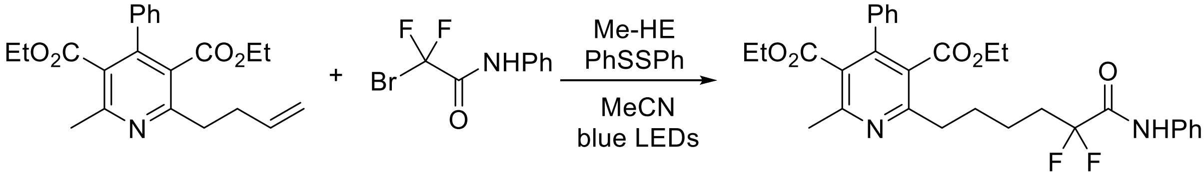
General Procedure G



A flask was charged with polysubstituted pyridine (1 mmol) and anhydrous DCM (20 mL). (*tert*-butoxycarbonyl)alanine (1.5 equiv) was added at 0 °C under argon. Then EDCI (1.5 equiv) and DMAP (0.2 mol%) was added and the mixture was stirred until the reaction was finished. The reaction was quenched with H_2O and the resulting mixture was extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.36 (m, 3H), 7.28 – 7.25 (m, 2H), 5.11 (s, 1H), 4.21 – 4.10 (m, 2H), 4.13 (q, J = 7.1 Hz, 1H), 4.04 – 3.96 (m, 4H), 2.86 (t, J = 7.6 Hz, 2H), 2.62 (s, 3H), 1.89 – 1.82 (m, 2H), 1.79 – 1.72 (m, 2H), 1.45 (s, 9H), 1.40 (d, J = 7.2 Hz, 3H), 0.92 – 0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 168.0, 167.9, 158.5, 155.7, 155.2, 146.4, 136.7, 128.6, 128.3, 128.2, 127.2, 127.0, 79.8, 65.2, 61.5, 60.5, 35.8, 28.5, 27.1, 26.1, 23.1, 18.9, 13.7. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{30}H_{41}N_2O_8$: 557.2863, found: 557.2868.

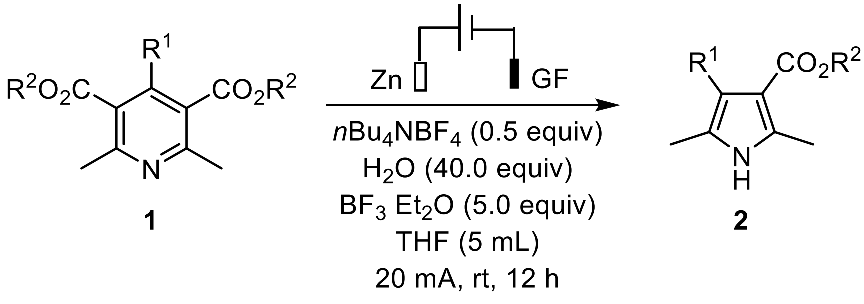
General Procedure H



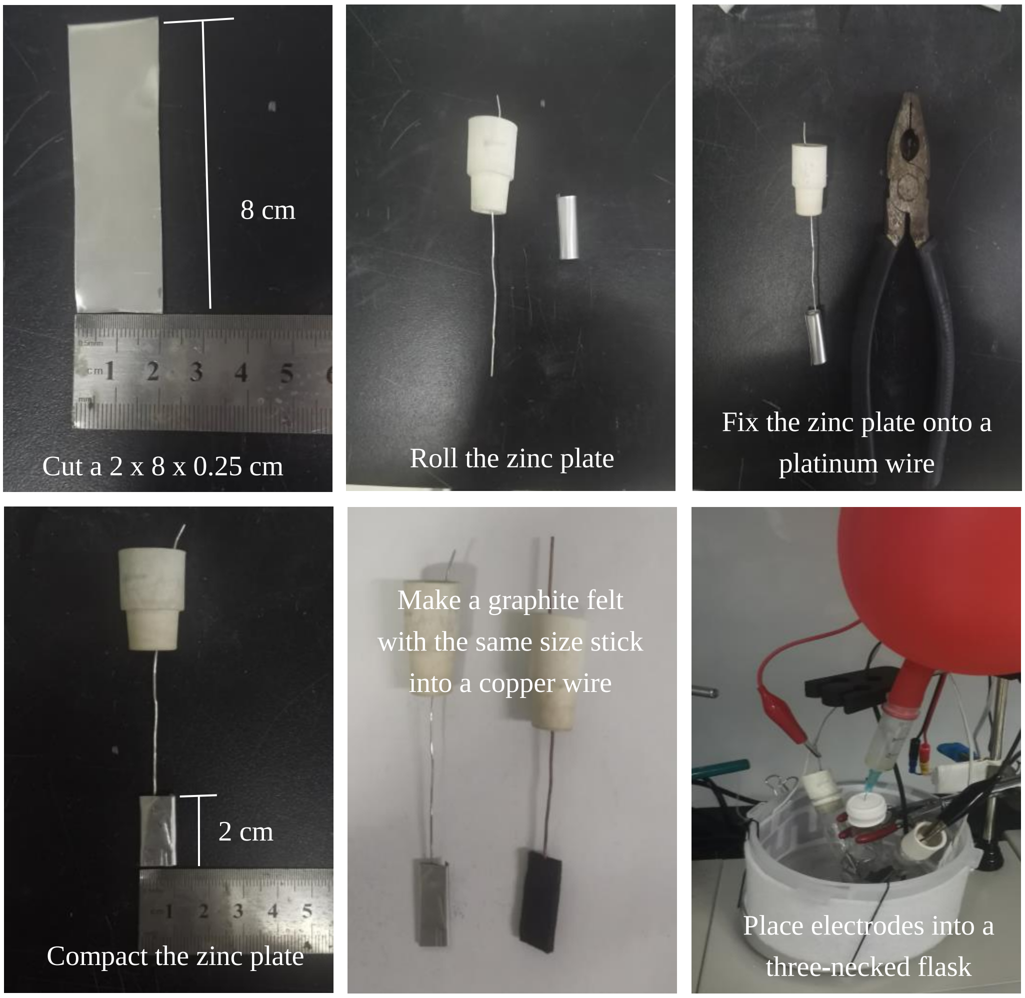
A flask was charged withpolysubstituted pyridine (2.8 mmol), 2-bromo-2,2-difluoro-N-phenylacetamide (1.4 mmol), Me-HE (1.5 equiv), PhSSPh (10 mol%) and MeCN (10 mL) under argon. The mixture was irradiation by blue LEDs for 24 h. Then the reaction was quenched with H_2O and the resulting mixture was extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.36 (m, 5H), 7.27 – 7.24 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 4.05 – 3.95 (m, 4H), 2.88 – 2.84 (m, 2H), 2.61 (s, 3H), 2.30 – 2.19 (m, 2H), 1.90 – 1.84 (m, 2H), 1.68 – 1.60 (m, 2H), 0.94 – 0.87 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 167.9, 162.3 (t, *J* = 28.7 Hz), 162.0, 158.5, 155.7, 146.4, 136.7, 136.2, 129.3, 128.6, 128.3, 128.2, 125.6, 120.4, 118.4 (t, *J* = 252.0 Hz), 61.5, 61.5, 36.0, 33.8 (t, *J* = 23.1 Hz), 29.3, 27.1, 23.0, 21.7 (t, *J* = 4.4 Hz), 13.7, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.51. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{30}H_{33}F_2N_2O_5$: 539.2358, found: 539.2347.

General Procedure I



A 10 mL three-necked flask was charged with the substrate **1** (0.2 mmol), *n*Bu_4NBF_4 (0.1 mmol) and a magnetic stir bar. The flask was equipped with rubber stoppers, graphite felt as cathode and zinc plate as anode. The zinc plate anode attached to a platinum wire and the graphite felt cathode attached to a copper wire. The flask was evacuated and backfilled with argon for 3 times. H_2O (40.0 equiv), BF_3 Et_2O (5 equiv) and anhydrous THF (5 mL) were added by syringe. The mixture was stirred at room temperature under constant current electrolysis. After the reaction reached completion with monitoring with TLC or GC-MS analysis, the mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product.



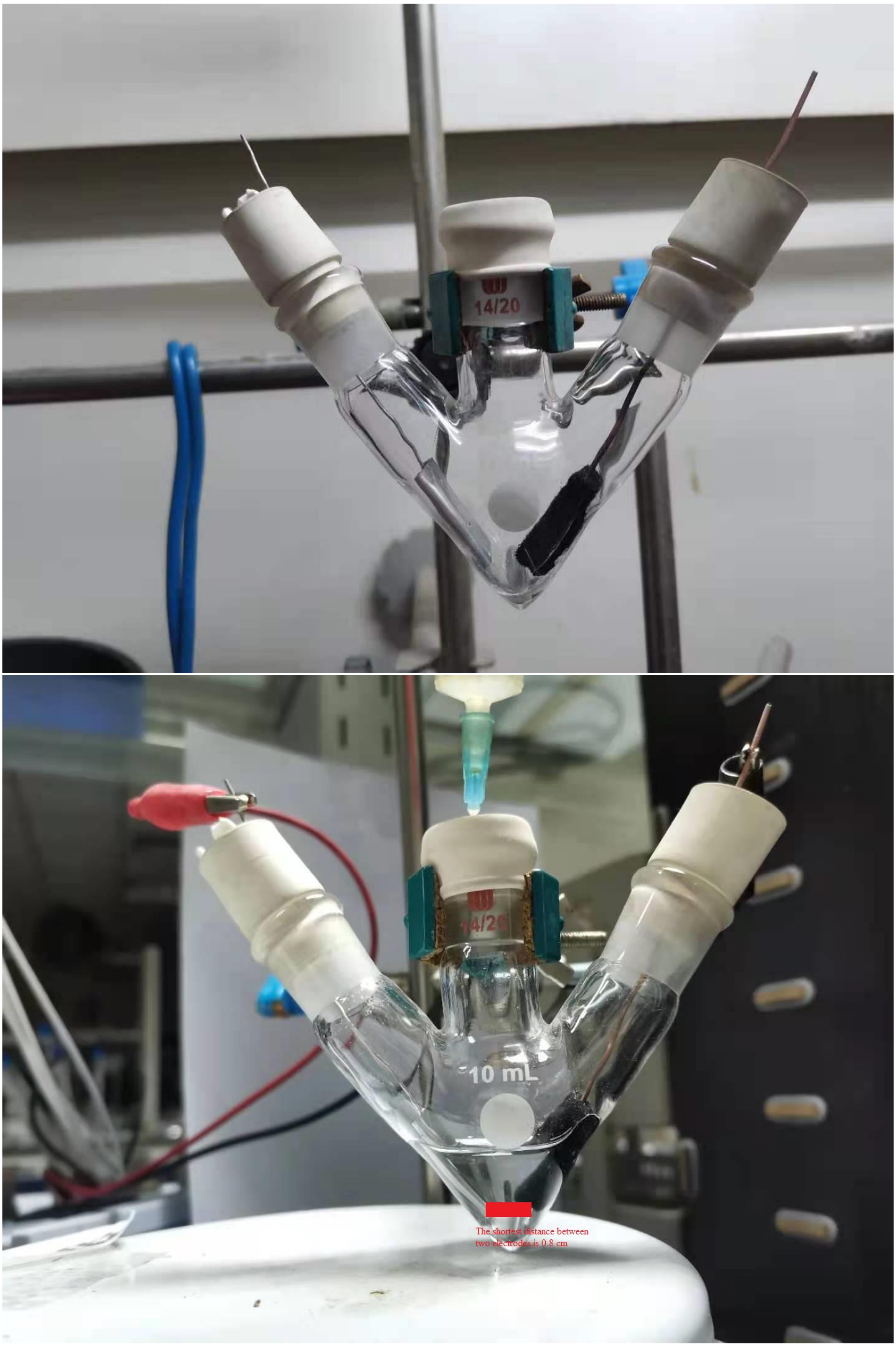
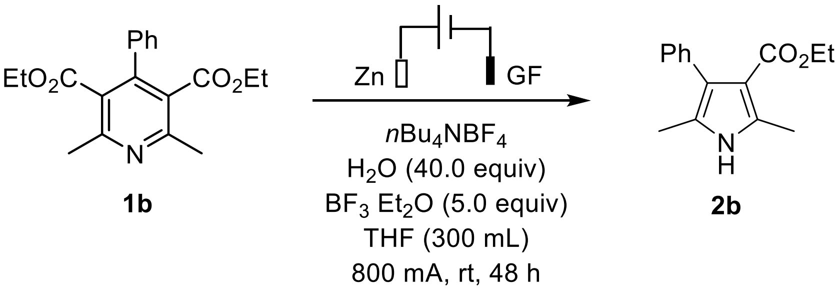


Figure S1. Procedures on making electrodes

Gram Scale Experiment



A 500 mL cup was charged with the substrate **1b** (15.0 g, 45.9 mmol), *n*Bu_4NBF_4 (2.0 g) and a magnetic stir bar. The cup was equipped with a plastic cover, graphite felt (8 cm x 5 cm x 1 cm) as cathode and zinc plate as anode. The zinc plate anode (8 cm X 12 cm X 4 pieces) attached to a platinum wire and the graphite felt cathode attached to a copper wire. The cup was flushed with argon for 1 minute. Anhydrous DMF (300 mL), H_2O (40 equiv) and BF_3 Et$_2$O (5 equiv) were added via syringe. The mixture was stirred at room temperature under constant current electrolysis. After the reaction reached completion by monitoring with TLC or GC-MS analysis, the mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product.

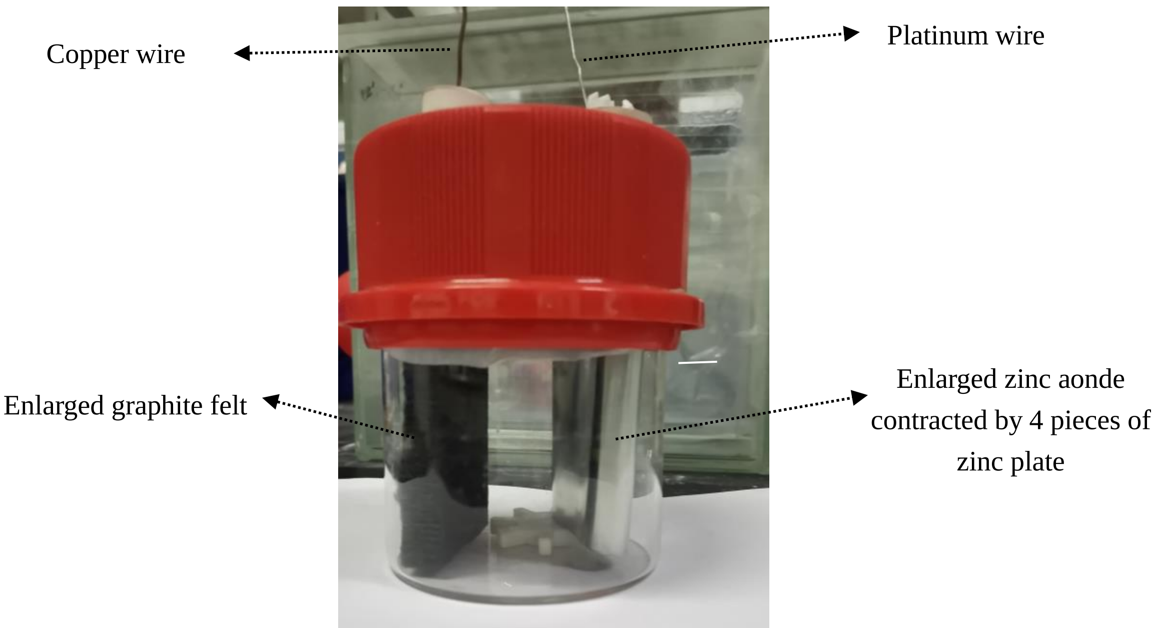
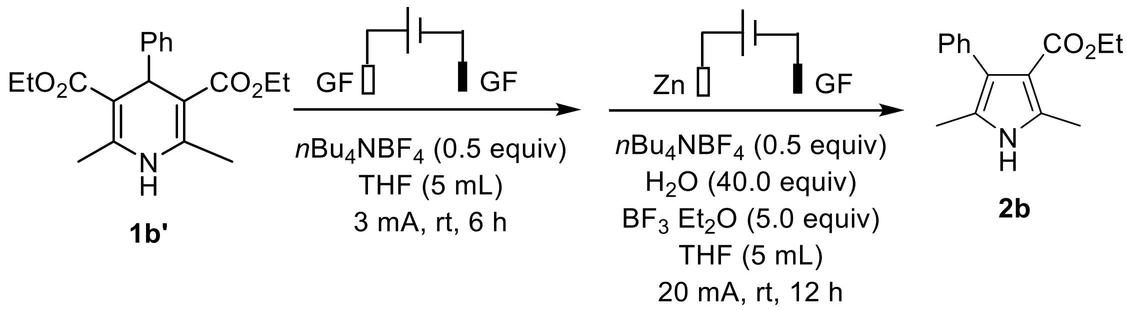
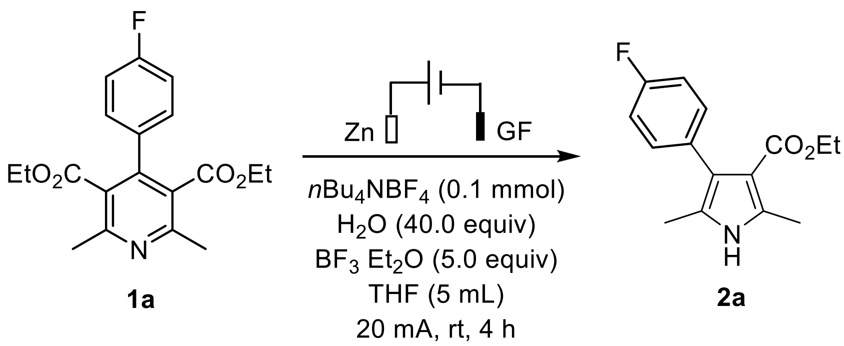


Figure S2. Reactor for gram scale experiment



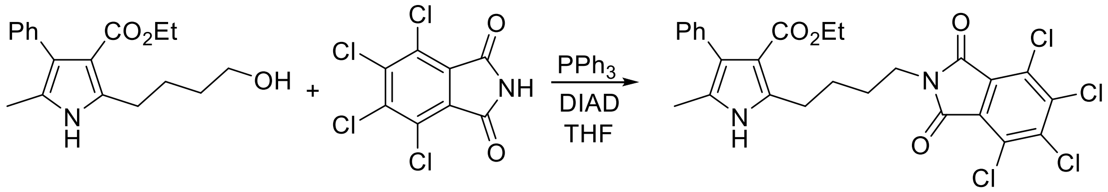
A 10 mL three-necked flask was charged with the substrate **1b'** (0.2 mmol), *n*Bu_4NBF_4 (32.9 mg, 0.1 mmol) and a magnetic stir bar. The flask was equipped with a rubber stopper, graphite felt (2 cm x 1 cm x 0.5 cm) as anode and cathode. The graphite felt anode attached to a platinum wire and cathode attached to a copper wire. The flask was evacuated and backfilled with argon for 3 times. Anhydrous THF (5 mL) was added and the mixture was stirred under 3 mA electrolysis until the was finished. Then the anode was changed to zinc plate and BF_3 Et_2O (5 equiv) and H_2O (40 equiv) was added. The mixture was stirred under 20 mA electrolysis for 12 h. When the reaction was finished, the mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product.

Faradaic efficiency



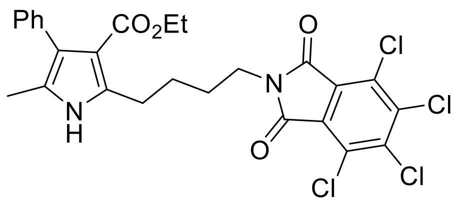
A 10 mL three-necked flask was charged with the substrate **1a** (0.8 mmol), *n*Bu_4NBF_4 (0.1 mmol) and a magnetic stir bar. The flask was equipped with rubber stoppers, graphite felt as cathode and zinc plate as anode. The zinc plate anode attached to a platinum wire and the graphite felt cathode attached to a copper wire. The flask was evacuated and backfilled with argon for 3 times. H_2O (40.0 equiv), BF_3 Et$_2$O (5 equiv) and anhydrous THF (5 mL) were added via syringes. The mixture was stirred at room temperature under constant current electrolysis. The reaction was stopped after 4h, the 55% yield of **2a** was analyzed by ^{1}H NMR spectrum, CH_2Br_2 was used as internal standard. Faradaic efficiency *FE* = 0.55*0.8*0.001*4*96485/(0.02*4*3600)= 59%

Preparation and X-ray analysis of compound 3



2ai **3**, 86%

A flask was charged with **2ai** (301 mg, 1 mmol), 4,5,6,7-tetrachloroisoindoline-1,3-dione (283 mg, 1 mmol), PPh_3 (393 mg, 1.5 mmol) and anhydrous THF (10 mL) under Ar atmosphere. The mixture was stirred for 30 min at room temperature. DIAD (303 mg, 1.5 mmol) was then added and the mixture was stirred until the reaction was finished. The reaction was diluted with H_2O and the resulting mixture was extracted with DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to afford the desired product **3** as yellow solid (489 mg, 86% yield). The product was crystallized by EtOH.



^{1}H NMR (400 MHz, DMSO) δ 11.93 (s, 1H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 2H), 3.92 (q, *J* = 5.9 Hz, 2H), 3.61 (s, 2H), 2.83 (s, 2H), 2.02 (s, 3H), 1.63 (s, 4H), 0.98 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 165.0, 163.9, 138.4, 130.6, 129.6, 128.9, 128.4, 128.4, 127.5, 58.6, 38.7, 27.8, 27.3, 26.8, 14.3, 11.5.

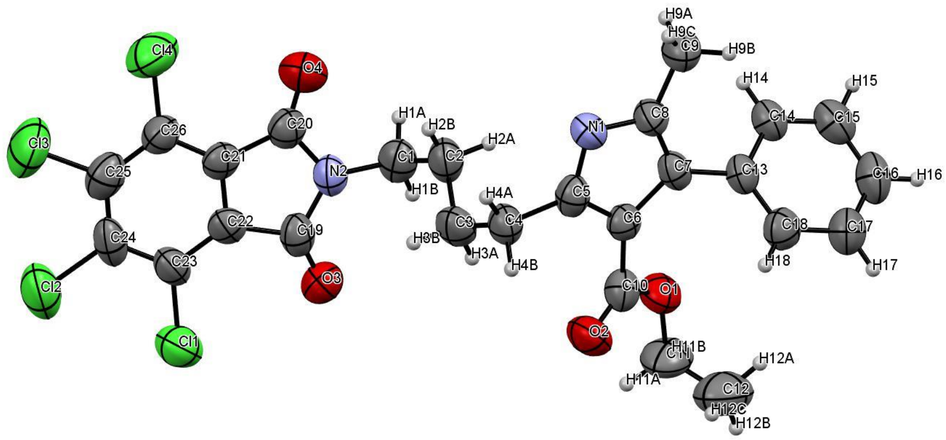
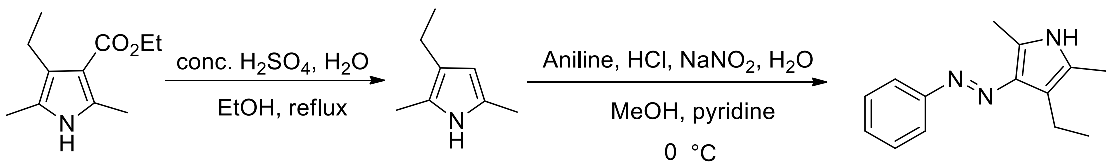


Figure S3. X-ray crystallographic analysis of compound 3

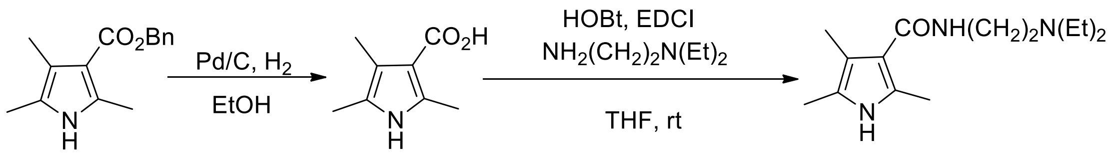
General procedure for application of pyrrole products



2q **5** **6**

According to the literature procedure[1], a solution of pyrrole **2q** (97.5 mg, 0.5 mmol) in conc. H_2SO_4 (0.28 mL), EtOH (1 mL) and water (25 μL) was refluxed for 1 h and poured into water (2 mL). This mixture was extracted with DCM (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford **5** as a yellow oil which was used in the next step without further purification. 12 M HCl (0.17 mL) was added to a suspension of aniline (0.5 mmol, 1.0 equiv.) on water (0.4 mL) at 0 ℃ and the mixture was stirred for 5 min. $NaNO_2$ (0.55 mmol, 1.1 equiv.) in water (0.4 mL) was added dropwise and the resulting solution was stirred at 0 ℃ for 1 h. A suspension of the appropriate pyrrole derivative (1.0 equiv.) in MeOH (2.4 mL) and pyridine (0.4 mL) was added, resulting in the formation of an orange red precipitate. The suspension was stirred for 1 h at 0 ℃, then concentrated under reduced pressure. The resulting residue was extracted with EtOAc (3 × 10 mL/mmol). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to afford the crude product. The residue was purified by chromatography on silica gel to afford the desire product **6** as an orange solid (40.0 mg, 18%).

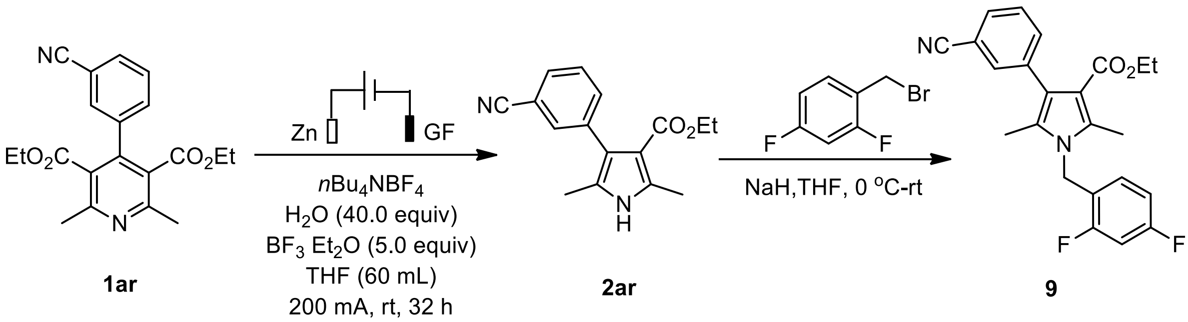
^{1}H NMR (400 MHz, CDCl3) δ 7.91 – 7.73 (m, 2H), 7.69 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 2.75 (d, *J* = 7.4 Hz, 2H), 2.56 (s, 3H), 2.17 (s, 3H), 1.16 (t, *J* = 7.3 Hz, 3H); 13C NMR (100 MHz, $CDCl_3$) δ 154.42, 138.03, 131.33, 128.88, 128.32, 123.30, 121.63, 115.19, 18.49, 15.39, 11.51, 10.63. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{14}H_{19}N_3$: 228.1501, found: 228.1497.



2ae **7** **8**

A suspension of **2ae** (12.1 mg, 0.5 mmol) and 10% Pd/C catalyst (110.0 mg, 50% wet, 0.05 mmol) on anhydrous EtOH (2 mL) was stirred vigorously under a hydrogen atmosphere (20 atm) at room temperature until the complete conversion of substrate **2ae** (12 hours) was achieved. Then the reaction mixture was filtered through celite. The filtration was concentrated, and the residue **7** was used in next step without further purification. **7** (49.0 mg, 0.32 mmol) in THF (2 mL) was added with 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (92.2 mg, 0.48 mmol), hydroxybenzotriazole (64.9 mg, 0.48 mmol), and amine (90 μL, 0.64 mmol). The resulting mixture was stirred at room temperature for 12 hours, then concentrated under reduced pressure. The resulting residue was extracted with EtOAc (3 × 10 mL/mmol). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to afford the crude product. The residue was purified by chromatography on silica gel to afford the desire product **8** as a colorless oil (39.0 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 6.41 (s, 1H), 3.44 (dt, *J* = 6.1, 4.9 Hz, 2H), 2.62 (t, *J* = 6.0 Hz, 2H), 2.55 (q, *J* = 7.1 Hz, 4H), 2.41 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.27, 129.80, 122.22, 114.82, 112.42, 51.88, 46.61, 36.78, 13.26, 11.86, 11.05, 10.61. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{14}H_{26}N_3O$: 252.2076, found: 252.2072.



A 100 mL cup was charged with the substrate **1ar** (4.6 g, 13 mmol), $n\mathrm{Bu_4NBF_4}$ (0.6 g) and a magnetic stir bar. The cup was equipped with a plastic cover, graphite felt (8 cm x 5 cm x 1 cm) as cathode and zinc plate as anode. The zinc plate anode (8 cm X 12 cm X 4 pieces) attached to a platinum wire and the graphite felt cathode attached to a copper wire. The cup was flushed with argon for 1 minute. Anhydrous THF (60 mL), H_2O (9.4 mL, 520 mmol) and $BF_3 \cdot Et_2O$ (7.8 mL, 65 mmol) were added via syringe. The mixture was stirred at room temperature under constant current electrolysis. After the reaction reached completion by monitoring with TLC or GC-MS analysis, the mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product **2ar** (2.5 g, 72%). **2ar** (2.5 g, 9.3 mmol) was added into the suspension of 60% NaH (740.0 mg, 18.6 mmol) on anhydrous THF (20 mL) at 0 ℃ and stirred for 1 h, then 2,4-Difluorobenzyl bromide (3.8 g, 18.6 mmol) was added, the mixture was stirred under room temperature until the reaction reached completion by monitoring with TLC. The reaction residue was purified by chromatography on silica gel to afford the desire product **9** as a yellow oil (3.0 g, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.35 (m, 4H), 6.92 – 6.70 (m, 2H), 6.48 (q, J = 8.4 Hz, 1H), 5.10 (s, 2H), 4.06 (q, J = 7.2 Hz, 2H), 2.49 (s, 3H), 2.00 (s, 3H), 1.02 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 163.7, 163.6, 161.2, 161.1, 160.9, 160.8, 158.4, 158.3, 138.0, 135.8, 135.3, 134.2, 129.6, 128.2, 127.9, 127.8, 127.8, 127.7, 126.6, 120.8, 119.9, 119.9, 119.8, 119.7, 119.2, 112.0, 112.0, 111.8, 111.8, 111.4, 110.9, 104.3, 104.0, 103.8, 59.3, 40.9, 40.9, 13.9, 11.4, 10.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.62 (d, J = 6.9 Hz), -114.11 (d, J = 7.4 Hz). HRMS (ESI) ($[M + H]^+$) Calcd For $C_{23}H_{21}F_2N_2O_2$: 395.1571, found: 395.1568.

3. Electrochemistry analysis

3.1 Cyclic Voltammetry Experiments

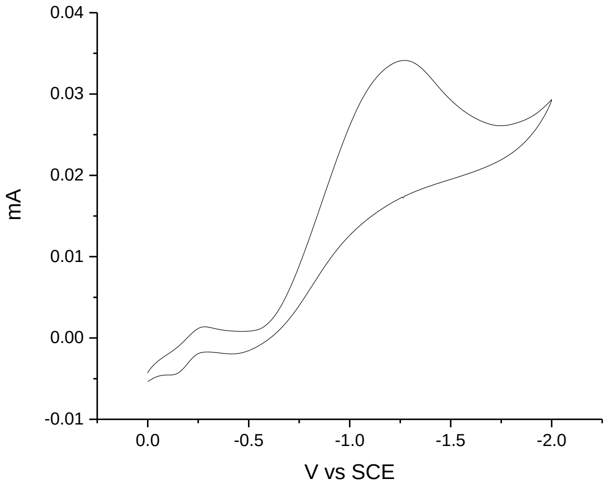


Figure S4. CV of **Blank** sample using **glassy carbon** working electrode at **50 mV/s**

A solution of Bu_4NBF_4 (0.1 mmol), H_2O (8 mmol) in 5 mL anhydrous THF was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.

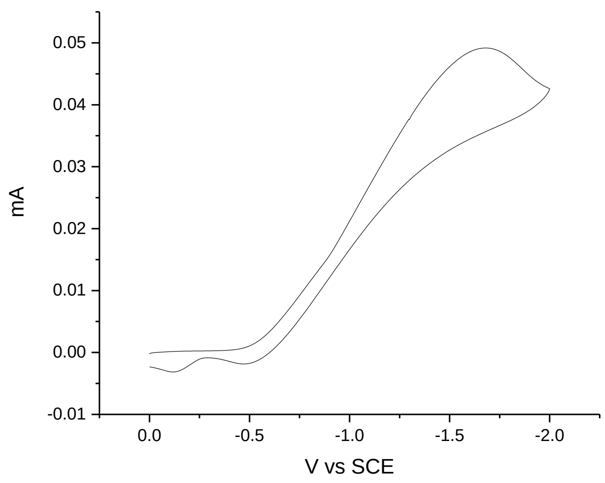


Figure S5. CV of **1b** using **glassy carbon** working electrode at **50** mV/s

A solution of **1b** (0.2 mmol), H_2O (8 mmol) and Bu_4NBF_4 (0.1 mmol) in 5 mL anhydrous THF was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.

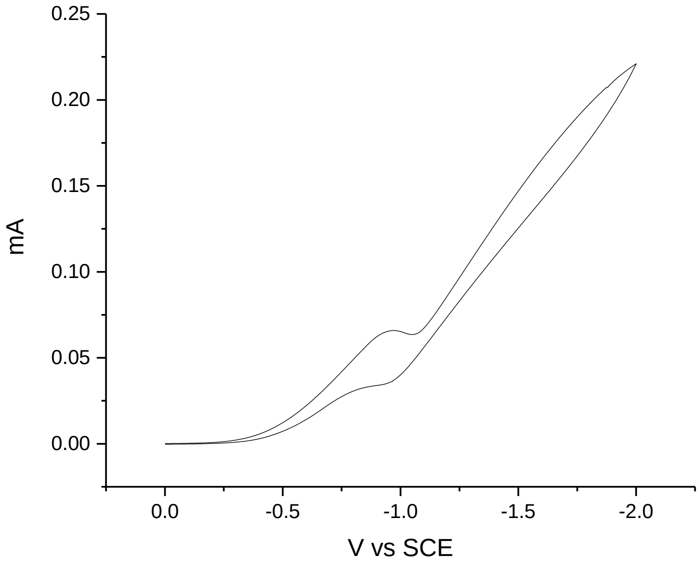


Figure S6. CV of **1b** and BF_3 Et$_2$O using **glassy carbon** working electrode at **50** mV/s

A solution of **1b** (0.2 mmol), BF_3 Et$_2$O (1 mmol), H_2O (8 mmol) and Bu_4NBF_4 (0.1 mmol) in 5 mL anhydrous THF was subject to cyclic voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Potential sweep rate was **50** mV/s.

3.2 Square wave Voltammetry Experiments

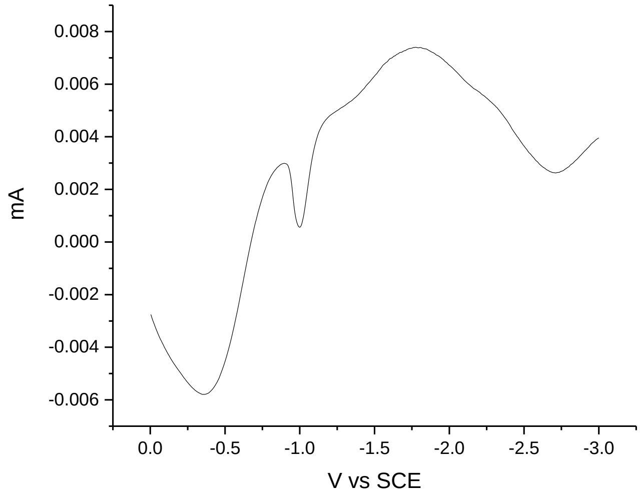


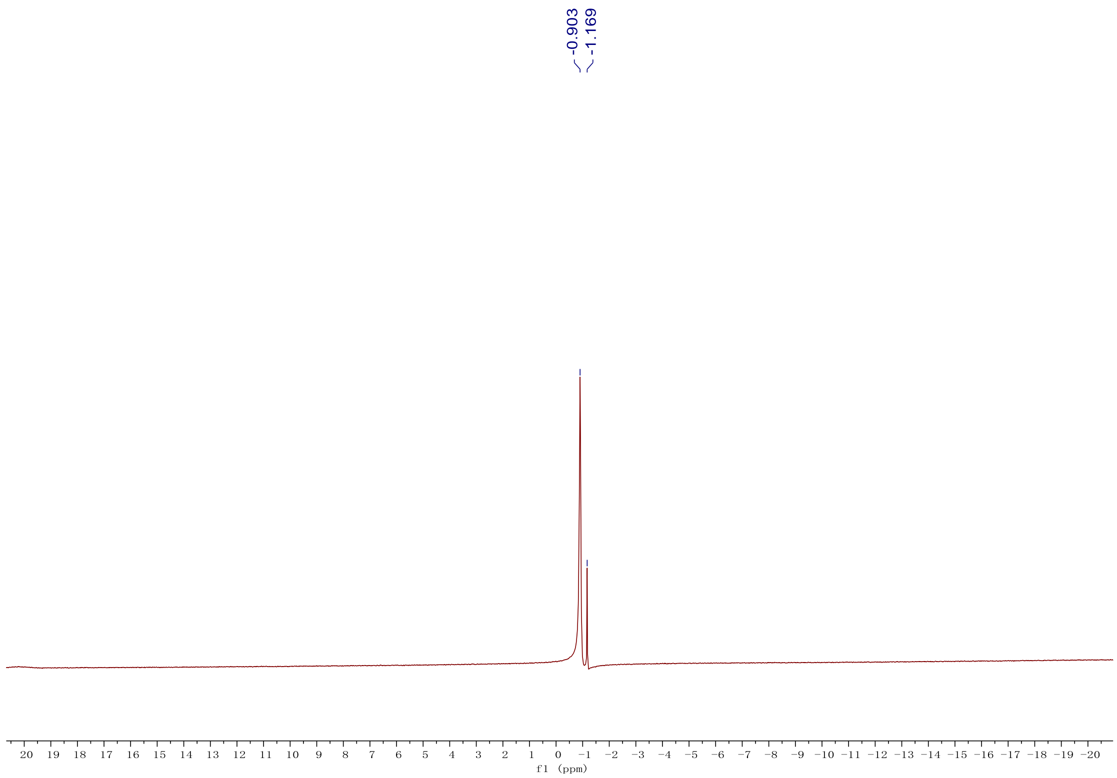
Figure S7. SWV of **1b** and BF_3 Et_2O using **glassy carbon** working electrode at **10** Hz

A solution of **1b** (0.2 mmol), BF_3 Et_2O (1 mmol), H_2O (8 mmol) and Bu_4NBF_4 (0.1 mmol) in 5 mL anhydrous THF was subject to square wave voltammetry experiment. Electrodes included a carbon working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE). Frequency was 10 Hz

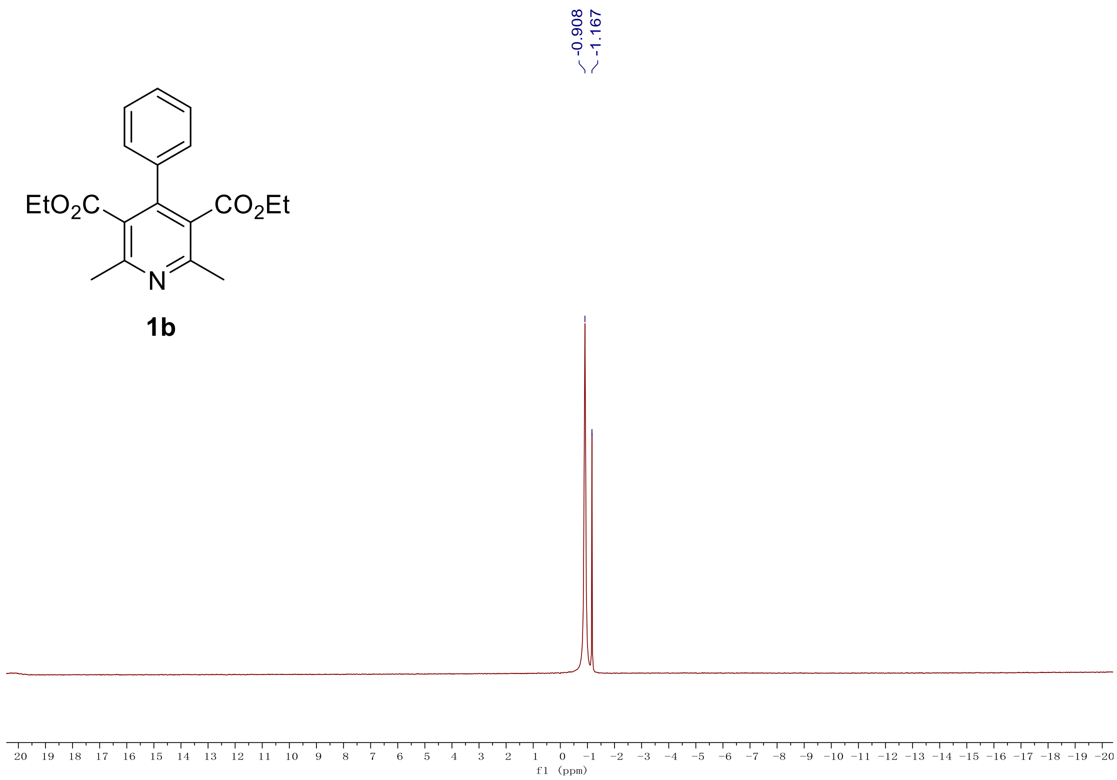
4. Mechanism experiments

4.1 ^{13}B NMR analysis

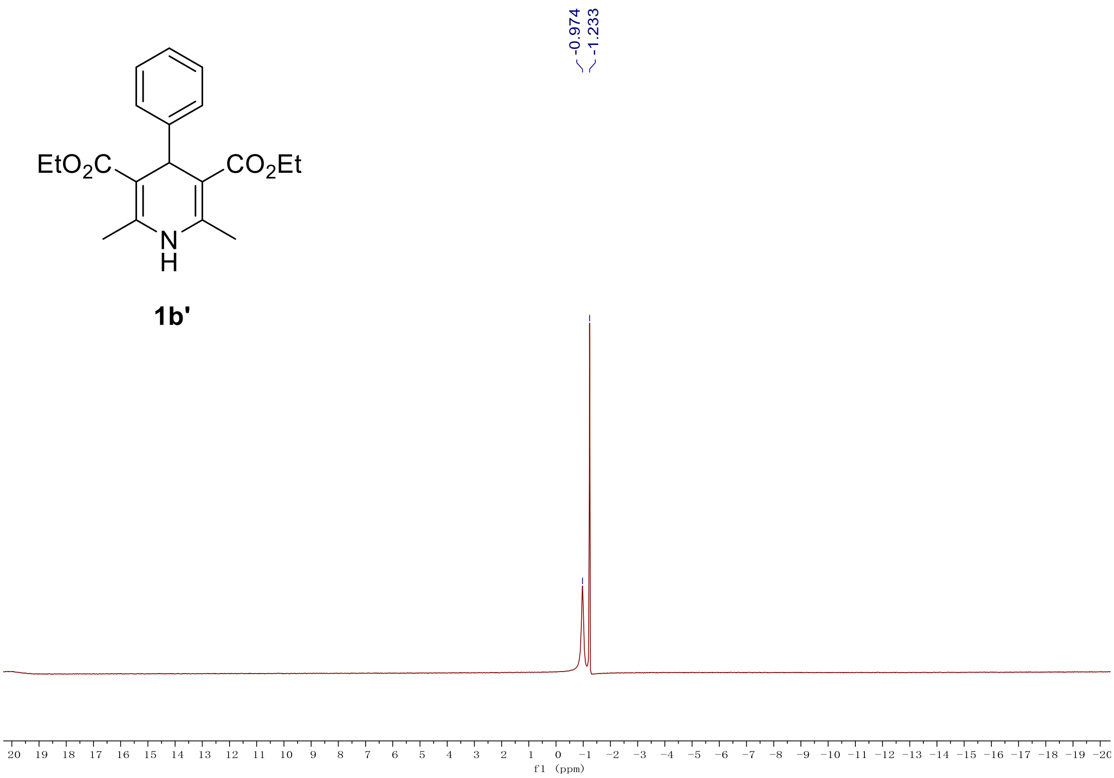
BF_3 Et_2O (1.0 equiv), H_2O (40.0 equiv) in 5 mL d_8-THF



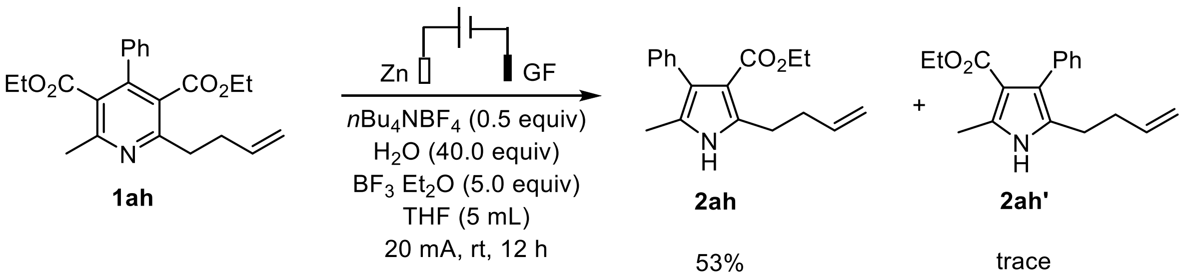
1b, BF_3 ·Et_2O (1.0 equiv), H_2O (40.0 equiv) in 5 mL *d*$_8$-THF



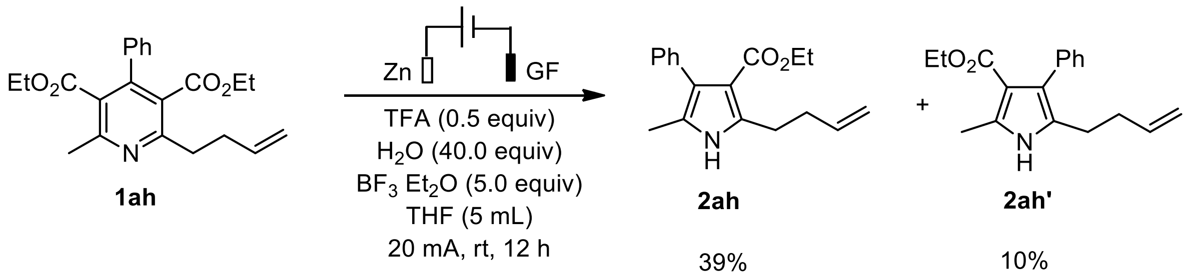
1b’, BF_3 ·Et_2O (1.0 equiv), H_2O (40.0 equiv) in 5 mL *d*$_8$-THF



4.2 Comparison of BF_3 and protonic acid



A 10 mL three-necked flask was charged with the substrate **1ah** (0.2 mmol), *n*Bu_4NBF_4 (0.1 mmol) and a magnetic stir bar. The flask was equipped with rubber stoppers, graphite felt as cathode and zinc plate as anode. The zinc plate anode attached to a platinum wire and the graphite felt cathode attached to a copper wire. The flask was evacuated and backfilled with argon for 3 times. H_2O (40.0 equiv), BF_3 Et_2O (5.0 equiv) and anhydrous THF (5 mL) were added via syringe. The mixture was stirred at room temperature under constant current electrolysis. After the reaction was completed by monitoring with TLC or GC-MS analysis, the mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product **2ah**.



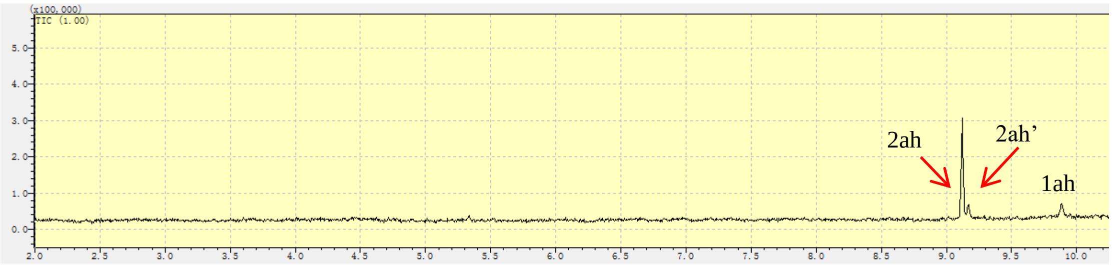
A 10 mL three-necked flask was charged with the substrate **1ah** (0.2 mmol), *n*Bu_4NBF_4 (0.1 mmol) and a magnetic stir bar. The flask was equipped with rubber stoppers, graphite felt as cathode and zinc plate as anode. The zinc plate anode attached to a platinum wire and the graphite felt cathode attached to a copper wire. The flask was evacuated and backfilled with argon for 3 times. H_2O (40.0 equiv), TFA (5.0 equiv) and anhydrous THF (5 mL) were added via syringe. The mixture was stirred at room temperature under constant current electrolysis. After the reaction was completed by monitoring with TLC or GC-MS analysis, the mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product **2ah** and **2ah'**.

2ah, 19.8 mg, 39%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 3H), 5.93 (ddt, *J* = 17.0, 10.5, 6.7 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.13 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 138.1, 137.7, 136.4, 130.5, 127.4, 126.0, 123.7, 122.7, 115.6, 110.5, 59.2, 33.8, 27.2, 14.1, 11.4. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{18}H_{22}NO_2$: 284.1651, found: 284.1656.

2ah', 5.1 mg, 10%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.37 – 7.28 (m, 2H), 7.29 – 7.20 (m, 3H), 5.80 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.08 – 4.93 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.52 (s, 2H), 2.26 (q, *J* = 6.9 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 138.0, 136.3, 134.0, 130.6, 127.7, 127.5, 126.1, 122.9, 115.9, 110.8, 59.2, 34.2, 24.8, 14.1, 13.9. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{18}H_{21}NNaO_2$: 306.1470, found: 306.1462.

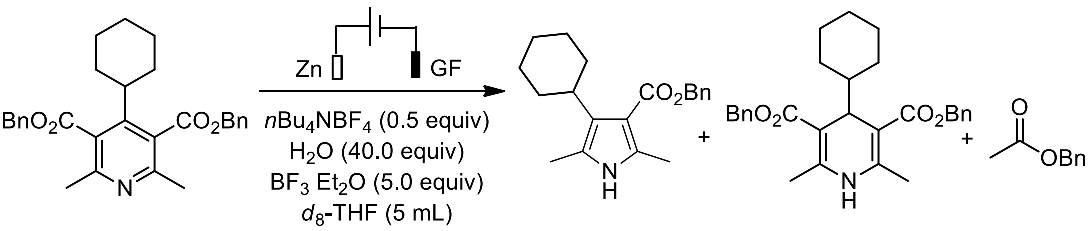
GC-MS analysis:

1ah reacted with BF_3 Ɛt$_2$O



1ah reacted with TFA

4.3 Isotope-labelling experiment



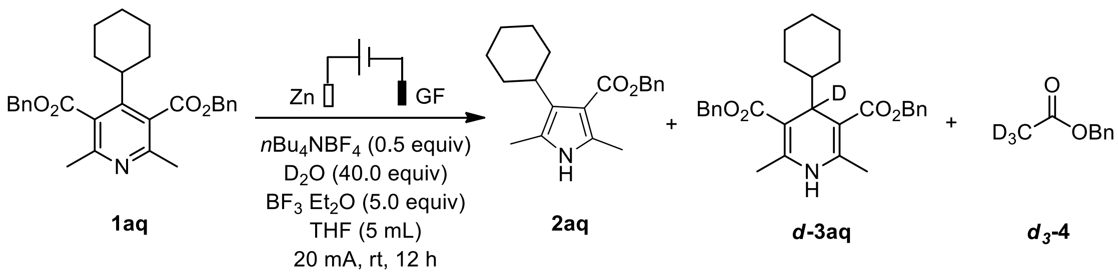
1aq **2aq** **3aq** **4**

A 10 mL three-necked flask was charged with the substrate **1aq** (0.2 mmol), *n*Bu$_4$NBF$_4$ (0.1 mmol) and a magnetic stir bar. The flask was equipped with rubber stoppers, graphite felt as cathode and zinc plate as anode. The zinc plate anode attached to a platinum wire and the graphite felt cathode attached to a copper wire. The flask was evacuated and backfilled with argon for 3 times. D_2O (40.0 equiv), BF_3 Ɛt$_2$O (5.0 equiv) and anhydrous *d*$_8$-THF (5 mL) were added via syringe. The mixture was stirred at room temperature under constant current electrolysis. After the reaction was completed by monitoring with TLC or GC-MS analysis, the mixture was extracted with EtOAc. The organic layers were washed with brine, dried over Mg_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product.

2aq, 22.4 mg, 36%. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.31 (m, 3H), 5.27 (s, 2H), 3.16 (t, *J* = 12.0 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H), 1.74 – 1.63 (m, 8H), 1.32 – 1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 136.9, 133.4, 128.4, 128.2, 127.8, 126.0, 121.44 110.0, 65.2, 35.9, 32.7, 27.4, 26.3, 14.5, 13.0. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{20}H_{26}NO_2$: 312.1964, found: 312.1969.

3aq, 36.8 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 10H), 5.76 (s, 1H), 5.17 (q, *J* = 12.7 Hz, 4H), 4.05 (d, *J* = 5.4 Hz, 1H), 2.30 (s, 6H), 1.60 – 1.49 (m, 5H), 1.29 – 1.21 (m, 1H), 1.05 – 1.00 (m, 3H), 0.91 – 0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 145.2, 136.9, 128.5, 128.0, 127.9, 101.8, 65.6, 46.1, 38.6, 28.9, 26.8, 26.7, 19.6. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{29}H_{32}NNaO_4$: 483.2307, found: 482.2299.

4, 9.5 mg, 32%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 5H), 5.11 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 136.0, 128.7, 128.4, 66.5, 21.2.



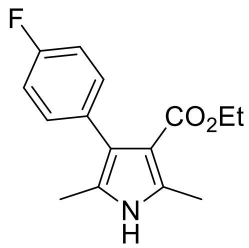
A 10 mL three-necked flask was charged with the substrate **1ad** (0.2 mmol), *n*Bu_4NBF_4 (0.1 mmol) and a magnetic stir bar. The flask was equipped with rubber stoppers, graphite felt as cathode and zinc plate as anode. The zinc plate anode attached to a platinum wire and the graphite felt cathode attached to a copper wire. The flask was evacuated and backfilled with argon for 3 times. D_2O (40.0 equiv), BF_3 Et_2O (5 equiv) and anhydrous THF (5 mL) were added via syringes. The mixture was stirred at room temperature under constant current electrolysis. After the reaction reached completion by monitoring with TLC or GC-MS analysis, the mixture was extracted with EtOAc for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by chromatography on silica gel to afford the desire product ***d*$_3$-4**.

2aq, 24.2 mg, 39%**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.43 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.27 (m, 3H), 5.27 (s, 2H), 3.16 (tt, *J* = 12.1, 3.5 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H), 1.78 – 1.61 (m, 8H), 1.34 – 1.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.11, 137.00, 133.47, 128.52, 128.30, 127.91, 126.07, 121.54, 110.04, 65.33, 35.91, 32.72, 27.46, 26.42, 14.61, 13.14. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{20}H_{26}NO_2$: 312.1964, found: 312.1969.

***d*-3aq**, 28.4 mg, 31%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 10H), 5.74 (s, 1H), 5.23 – 5.11 (m, 4H), 2.30 (s, 6H), 1.62 – 1.46 (m, 5H), 1.27 – 1.19 (m, 1H), 1.01 (d, *J* = 8.3 Hz, 3H), 0.93 – 0.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, CDCl3) δ 168.4, 145.1, 136.9, 128.5, 128.0, 127.9, 101.7, 65.6, 46.0, 38.4 – 38.0 (m), 28.9, 26.8, 19.6. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{29}H_{32}DNNaO_4$: 483.2370, found: 483.2363.

***d*$_3$-4,** 10.3 mg, 34%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 5H), 5.11 (s, 2H), 2.09 (dq, *J* = 4.3, 2.4 Hz, 0.65H, 78%D); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 136.1, 128.70 128.4, 66.4, 20.9 – 20.5 (m).

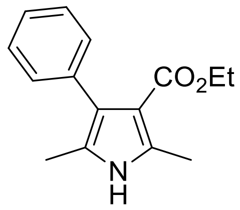
5. Synthesis and characterization of compounds



Ethyl 4-(4-fluorophenyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2a)

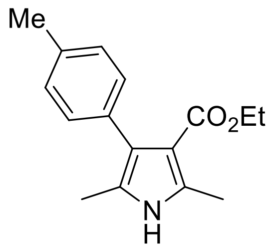
Following the general procedure I, the product **2a** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (39.2 mg, 75%). Mp. 127.0-127.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.20 (dd, *J* = 8.4, 5.7 Hz, 2H), 7.01 (t, *J* = 8.7 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.49 (s, 3H), 2.06 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 161.6 (d, *J* = 244.0 Hz), 134.2, 132.3 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 7.8 Hz), 123.7, 121.6, 114.2 (d, *J* = 21.2 Hz), 110.6, 59.2, 14.2, 13.8, 11.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.56. HRMS (ESI)

([M + H]$^+$) Calcd For $C_{15}H_{17}FNO_2$: 262.1243, found: 262.1231.



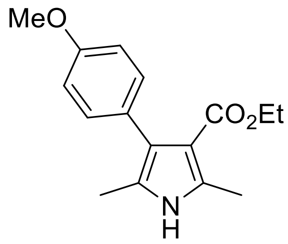
Ethyl 2,5-dimethyl-4-phenyl-1*H*-pyrrole-3-carboxylate (2b)

Following the general procedure I, the product **2b** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (28.7 mg, 59%). Mp. 121.0-122.1 ℃.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 3H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.49 (s, 3H), 2.09 (s, 3H), 1.06 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 136.3, 134.0, 130.5, 127.4, 125.9, 123.6, 122.5, 110.6, 59.2, 14.1, 13.7, 11.3. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{15}H_{18}NO_2$: 244.1338, found: 244.1336.



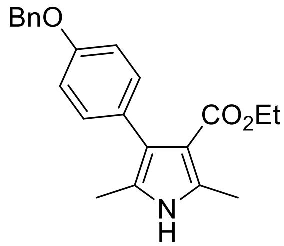
Ethyl 2,5-dimethyl-4-(p-tolyl)-1*H*-pyrrole-3-carboxylate (2c)

Following the general procedure I, the product **2c** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (39.2 mg, 76%). Mp. 120.7-122.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.17-7.13 (m, 4H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 2.36 (s, 3H), 2.09 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 135.4, 133.9, 133.2, 130.3, 128.2, 123.5, 122.4, 110.6, 59.2, 21.3, 14.2, 13.8, 11.3. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{16}H_{20}NO_2$: 258.1494, found: 258.1490.



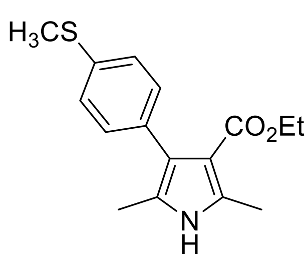
Ethyl 4-(4-methoxyphenyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2d)

Following the general procedure I, the product **2d** was isolated by chromatography on silica gel (PE/EA = 3/1, eluent) as a yellow oil (31.1 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 2.48 (s, 3H), 2.08 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 157.9, 133.9, 131.5, 128.7, 123.5, 122.1, 112.9, 110.6, 59.1, 55.3, 14.3, 13.9, 11.2. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{16}H_{19}NNaO_3$: 296.1263, found: 296.1272.



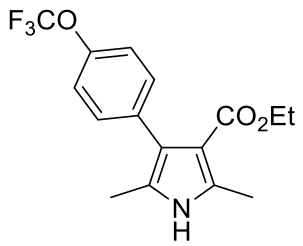
Ethyl 4-(4-(benzyloxy)phenyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2e)

Following the general procedure I, the product **2e** was isolated by chromatography on silica gel (PE/EA = 4/1, eluent) as a white solid (44.6 mg, 64%). Mp. 151.5-151.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.08 (s, 2H), 4.11 (q, *J* = 8.0, 7.1 Hz, 2H), 2.49 (s, 3H), 2.09 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 157.2, 137.4, 133.9, 131.6, 129.0, 128.7, 128.0, 127.7, 123.5, 122.1, 113.9, 110.6, 70.1, 59.2, 14.3, 13.8, 11.3. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{22}H_{23}NNaO_3$: 372.1576, found: 372.1571.



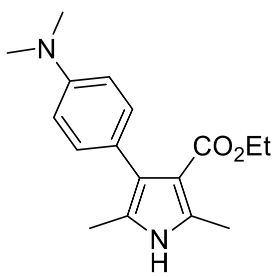
Ethyl 2,5-dimethyl-4-(4-(methylthio)phenyl)-1*H*-pyrrole-3-carboxylate (2f)

Following the general procedure I, the product **2f** was isolated by chromatography on silica gel (PE/EA = 4/1, eluent) as a white solid (34.6 mg, 60%). Mp. 143.5-144.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 2.48 (s, 3H), 2.08 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 135.4, 134.1, 133.4, 131.0, 126.1, 123.7, 122.0, 110.6, 59.2, 16.3, 14.2, 13.8, 11.3. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{16}H_{19}NNaO_2S$: 312.1034, found: 312.1029.



Ethyl 2,5-dimethyl-4-(4-(trifluoromethoxy)phenyl)-1*H*-pyrrole-3-carboxylate (2g)

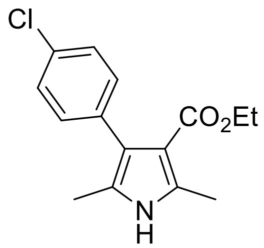
Following the general procedure I, the product **2g** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (35.3 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.52 (s, 3H), 2.10 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 147.6, 135.3, 134.4, 131.8, 123.9, 120.7 (q, *J* = 256.5 Hz), 120.0, 110.6, 59.3, 14.0, 13.7, 11.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.81. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{16}H_{17}F_3NO_3$: 328.1161, found: 328.1158.



Ethyl 4-(4-(dimethylamino)phenyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2h)

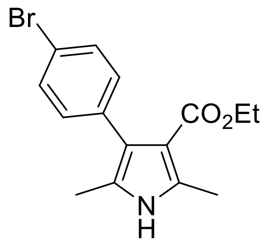
Following the general procedure I, the product **2h** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (33.0 mg, 58%). Mp. 150.9-151.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 8.3 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.95 (s, 6H), 2.47 (s, 3H), 2.09 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

166.1, 149.0, 133.7, 131.1, 124.6, 123.3, 122.5, 112.1, 110.6, 59.1, 40.9, 14.3, 13.9, 11.3. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{17}H_{23}N_2O_2$: 287.1760, found: 287.1759.



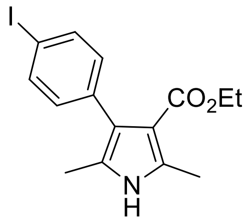
Ethyl 4-(4-chlorophenyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2i)

Following the general procedure I, the product **2i** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a pale yellow solid (40.1 mg, 72%). Mp. 102.1-102.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.48 (s, 3H), 2.06 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 134.8, 134.3, 131.8, 131.8, 127.6, 123.8, 121.4, 110.4, 59.3, 14.2, 13.8, 11.2. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{15}H_{17}ClNO_2$: 278.0948, found: 278.0943.



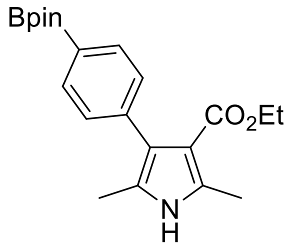
Ethyl 4-(4-bromophenyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2j)

Following the general procedure I, the product **2j** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (34.9 mg, 54%). Mp. 133.1-134.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 2.07 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 135.3, 134.3, 132.2, 130.5, 123.8, 121.4, 120.0, 110.4, 59.3, 14.2, 13.8, 11.2. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{15}H_{17}BrNO_2$: 322.0443, found: 322.0429.



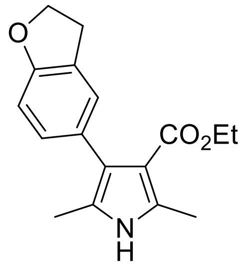
Ethyl 4-(4-iodophenyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2k)

Following the general procedure I, the product **2k** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (38.0 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.74 – 7.54 (m, 2H), 7.07 – 6.94 (m, 2H), 4.10 (q, J = 7.1 Hz, 2H), 2.49 (s, 3H), 2.08 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 136.6, 136.0, 134.2, 132.6, 123.7, 121.6, 110.6, 91.5, 59.3, 14.2, 13.8, 11.3. HRMS (ESI) ([M + H]$^{+}$) Calcd For $C_{15}H_{17}INO_2$: 370.0304, found: 370.0292.



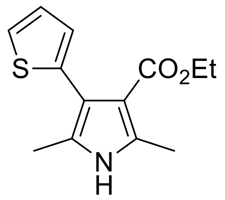
Ethyl 2,5-dimethyl-4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1*H*-pyrrole-3-carboxylate (2l)

Following the general procedure I, the product **2l** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (31.3 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.79 (d, J = 7.7 Hz, 2H), 7.28 (d, J = 9.4 Hz, 2H), 4.10 (q, J = 7.1 Hz, 2H), 2.51 (s, 3H), 2.11 (s, 3H), 1.38 (s, 12H), 1.09 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 139.5, 134.1, 134.0, 129.9, 123.8, 122.4, 110.6, 83.7, 59.2, 25.0, 25.0, 14.2, 13.7, 11.3; ^{11}B NMR (128 MHz, $CDCl_3$) δ 37.11. HRMS (ESI) ([M + Na]$^{+}$) Calcd For $C_{21}H_{28}BNNaO_4$: 392.2009, found: 392.2004.



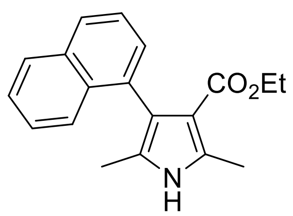
Ethyl 4-(2,3-dihydrobenzofuran-5-yl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2m)

Following the general procedure I, the product **2m** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (34.8 mg, 61%). Mp. 112.9-113.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.08 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 4.56 (t, *J* = 8.6 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.19 (t, *J* = 8.6 Hz, 2H), 2.47 (s, 3H), 2.07 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 158.4, 133.8, 130.0, 128.4, 127.1, 125.9, 123.4, 122.4, 110.5, 108.2, 71.2, 59.1, 29.9, 14.3, 13.8, 11.2. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{17}H_{20}NO_3$: 286.1443, found: 286.1441.



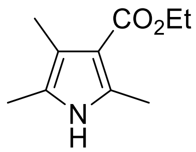
Ethyl 2,5-dimethyl-4-(thiophen-2-yl)-1*H*-pyrrole-3-carboxylate (2n)

Following the general procedure I, the product **2n** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (18.9 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.27 (d, *J* = 4.8 Hz, 1H), 7.03 – 7.00 (m, 1H), 6.89 (d, *J* = 3.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 2.16 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 137.3, 134.1, 127.1, 126.3, 125.7, 124.7, 114.5, 111.7, 59.3, 14.2, 13.8, 11.6. HRMS (ESI) ([M + Na]$^+$) Calcd For $C_{13}H_{15}NNaO_2S$: 250.0902, found: 250.0905.



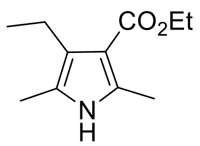
Ethyl 2,5-dimethyl-4-(naphthalen-1-yl)-1*H*-pyrrole-3-carboxylate (2o)

Following the general procedure I, the product **2o** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a pale yellow solid (40.6 mg, 69%). Mp. 160.4-161.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.47 (t, *J* = 7.1 Hz, 1H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.34 (dd, *J* = 17.8, 7.5 Hz, 2H), 3.84 – 3.71 (m, 2H), 2.56 (s, 3H), 1.95 (s, 3H), 0.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 135.0, 134.3, 133.9, 133.5, 128.0, 127.7, 126.7, 126.7, 125.3, 125.3, 125.2, 124.3, 120.0, 112.0, 58.8, 13.6, 13.3, 11.2. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{19}H_{19}NNaO_2$: 294.1494, found: 294.1483.



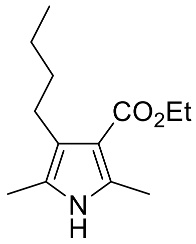
Ethyl 2,4,5-trimethyl-1*H*-pyrrole-3-carboxylate (2p)

Following the general procedure I, the product **2p** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (28.6 mg, 79%). Mp. 93.9-94.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 133.8, 122.1, 116.0, 110.7, 59.1, 14.6, 13.9, 11.1, 10.6. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{10}H_{16}NO_2$:182.1181, found:182.1175.



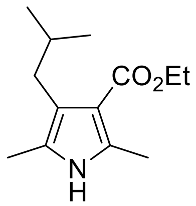
Ethyl 4-ethyl-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2q)

Following the general procedure I, the product **2q** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a yellow oil (24.2 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.62 (d, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 2.13 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 133.8, 123.0, 121.7, 110.0, 59.1, 18.7, 16.0, 14.6, 14.0, 10.5. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{11}H_{17}NNaO_2$: 218.1157, found: 218.1152.



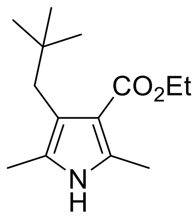
Ethyl 4-butyl-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (**2r**)

Following the general procedure I, the product **2r** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (24.6 mg, 55%). Mp. 91.7-92.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.59 (t, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 2.11 (s, 3H), 1.50 – 1.42 (m, 2H), 1.38 – 1.29 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 134.0, 122.1, 121.4, 110.2, 59.1, 33.9, 25.3, 22.9, 14.6, 14.2, 14.1, 10.7. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{13}H_{22}NO_2$: 224.1651, found: 224.1648.



Ethyl 4-isobutyl-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2s)

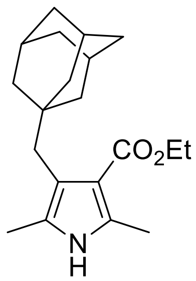
Following the general procedure I, the product **2s** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a yellow oil (25.5 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.48 (hept, *J* = 7.1 Hz, 1H), 2.41 (s, 3H), 2.20 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 133.2, 126.7, 121.3, 110.2, 59.2, 25.3, 22.6, 14.6, 14.4, 12.6. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{13}H_{22}NO_2$: 224.1651, found: 224.1647.



Ethyl 2,5-dimethyl-4-neopentyl-1*H*-pyrrole-3-carboxylate (2t)

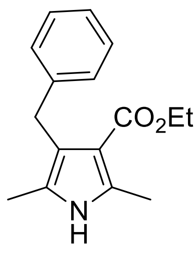
Following the general procedure I, the product **2t** was isolated by chromatography on silica gel

(PE/EA = 5/1, eluent) as a white solid (26.2 mg, 55%). Mp. 123.0-123.5 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 2H), 2.43 (s, 3H), 2.10 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 133.3, 123.7, 118.1, 111.9, 59.1, 37.4, 33.8, 29.6, 14.6, 14.1, 11.9. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{14}H_{24}NO_2$: 238.1807, found: 238.1801.



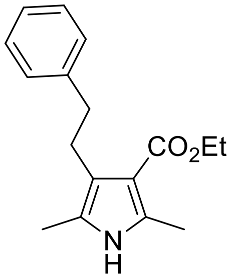
Ethyl 4-(((3*r*,5*r*,7*r*)-adamantan-1-yl)methyl)-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2u)

Following the general procedure I, the product **2u** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (36.4 mg, 58%). Mp. 179.7-180.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 2H), 2.44 (s, 3H), 2.10 (s, 3H), 1.88 (s, 3H), 1.59 (q, *J* = 11.8 Hz, 6H), 1.48 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 133.1, 123.8, 116.7, 112.2, 59.1, 42.5, 38.5, 37.3, 35.6, 29.0, 14.6, 14.1, 12.0. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{19}H_{28}NO_2$: 302.2020, found: 302.2121.



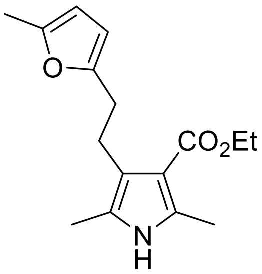
Ethyl 4-benzyl-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2v)

Following the general procedure I, the product **2v** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (30.6 mg, 59%). Mp. 108.8-109.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.28 – 7.23 (m, 2H), 7.19 – 7.12 (m, 3H), 4.18 (q, *J* = 7.0 Hz, 2H), 4.08 (s, 2H), 2.49 (s, 3H), 2.15 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 142.7, 134.3, 130.2, 128.2, 128.1, 125.3, 123.4, 118.8, 110.6, 59.1, 31.0, 14.4, 14.1, 10.9. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{16}H_{19}NNaO_2$: 280.1313, found: 280.1308.



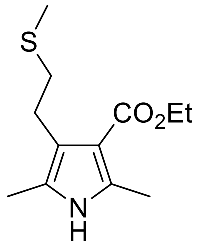
Ethyl 2,5-dimethyl-4-phenethyl-1*H*-pyrrole-3-carboxylate (2w)

Following the general procedure I, the product **2w** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a yellow oil (37.1 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.31 – 7.27 (m, 2H), 7.21 – 7.20 (m, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.93 (dd, *J* = 8.9, 6.0 Hz, 2H), 2.83 (dd, *J* = 9.0, 6.1 Hz, 2H), 2.51 (s, 3H), 1.91 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 143.0, 134.1, 128.8, 128.2, 125.6, 122.8, 120.1, 110.0, 59.2, 37.8, 28.0, 14.7, 14.1, 10.3. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{17}H_{21}NNaO_2$: 294.1470, found: 294.1462.



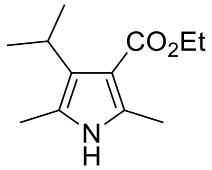
Ethyl 2,5-dimethyl-4-(2-(5-methylfuran-2-yl)ethyl)-1*H*-pyrrole-3-carboxylate (2x)

Following the general procedure I, the product **2x** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (32.3 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 5.83 – 5.79 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 2.46 (s, 3H), 2.26 (s, 3H), 2.01 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 154.9, 150.0, 134.2, 122.8, 119.7, 110.1, 105.9, 105.5, 59.2, 29.9, 24.7, 14.6, 14.0, 13.6, 10.4. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{16}H_{21}NNaO_3$: 298.1419, found: 298.1414.



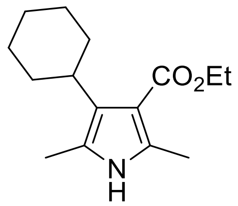
Ethyl 2,5-dimethyl-4-(2-(methylthio)ethyl)-1*H*-pyrrole-3-carboxylate (2y)

Following the general procedure I, the product **2y** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (29.4 mg, 61%). Mp. 83.6-84.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.1 Hz, 2H), 2.66 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 2.13 (s, 3H), 2.13 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 134.3, 123.0, 119.2, 109.9, 59.15, 35.7, 25.8, 15.6, 14.6, 14.0, 10.8. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{12}H_{20}NO_2S$: 242.1215, found: 242.1217.



Ethyl 4-isopropyl-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2z)

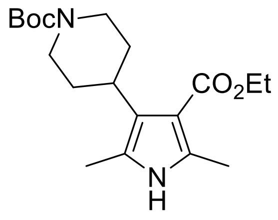
Following the general procedure I, the product **2z** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (25.5 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.48 (hept, *J* = 7.1 Hz, 1H), 2.41 (s, 3H), 2.20 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.26 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 133.2, 126.7, 121.3, 110.2, 59.2, 25.3, 22.6, 14.6, 14.4, 12.6. HRMS (ESI) ([M + Na]$^+$) Calcd For $C_{12}H_{19}NNaO_2$: 232.1313, found: 232.1300.



Ethyl 4-cyclohexyl-2,5-dimethyl-1*H*-pyrrole-3-carboxylate (2aa)

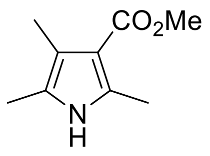
Following the general procedure I, the product **2aa** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (15.3 mg, 30%). Mp. 164.0-164.6 ℃. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.73 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.12 (tt, *J* = 11.7, 3.8 Hz, 1H), 2.41 (s, 3H), 2.22 (s, 3H), 1.80 – 1.62 (m, 8H), 1.40 – 1.28 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 133.1, 125.9, 121.4, 110.5, 59.2, 36.1, 32.8, 27.6, 26.5, 14.7, 14.4, 13.1. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{15}H_{24}NO_2$: 250.1807, found: 250.1797.



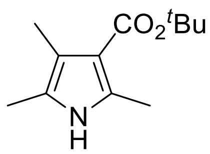
***tert*-Butyl 4-(4-(ethoxycarbonyl)-2,5-dimethyl-1*H*-pyrrol-3-yl)piperidine-1-carboxylate (2ab)**

Following the general procedure I, the product **2ab** was isolated by chromatography on silica gel (PE/EA = 3/1, eluent) as a colorless oil (40.1 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.21 – 4.12 (m, 2H), 3.31 (tt, *J* = 12.4, 3.6 Hz, 1H), 2.74 (s, 2H), 2.40 (s, 3H), 2.19 (s, 3H), 1.88 – 1.77 (m, 2H), 1.69 – 1.64 (m, 2H), 1.46 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 155.1, 133.5, 123.6, 121.9, 110.2, 79.3, 45.0, 59.2, 34.3, 31.7, 28.6, 14.6, 14.3, 13.0. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{19}H_{31}N_2O_4$: 351.2284, found: 351.2284.



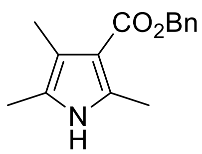
Methyl 2,4,5-trimethyl-1*H*-pyrrole-3-carboxylate (2ac)

Following the general procedure I, the product **2ac** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (24.4 mg, 73%). Mp. 104.4-104.9 ℃. ^1H NMR (400 MHz, $CDCl_3$ δ 8.08 (s, 1H), 3.79 (s, 3H), 2.44 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 133.9, 122.2, 116.1, 110.6, 50.4, 13.9, 11.0, 10.6. HRMS (ESI) ($[M + H]^+$) Calcd For $C_9H_{14}NO_2$: 168.1025, found: 168.1019.



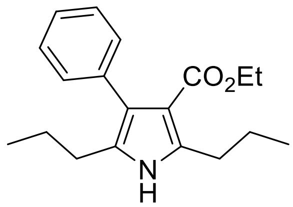
***tert*-Butyl 2,4,5-trimethyl-1*H*-pyrrole-3-carboxylate (2ad)**

Following the general procedure I, the product **2ad** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (24.2 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 2.43 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 1.55 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 133.1, 121.8, 116.0, 112.34, 79.2, 28.8, 14.1, 11.2, 10.7. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{12}H_{20}NO_2$: 210.1494, found: 210.1496.



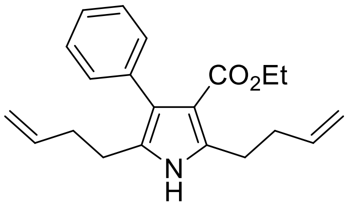
Benzyl 2,4,5-trimethyl-1*H*-pyrrole-3-carboxylate (2ae)

Following the general procedure I, the product **2ae** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a white solid (37.5 mg, 77%). Mp. 84.5-85.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.44-7.26 (m, 5H), 5.30 (s, 2H), 2.45 (s, 3H), 2.18 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 137.2, 134.2, 128.5, 127.9, 127.8, 122.2, 116.2, 110.4, 65.0, 14.1, 11.2, 10.5. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{15}H_{17}NNaO_2$: 266.1157, found: 266.1152.



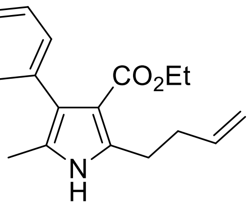
Ethyl 4-phenyl-2,5-dipropyl-1*H*-pyrrole-3-carboxylate (2af)

Following the general procedure I, the product **2af** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a pale yellow oil (33.9 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 2H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.69 (h, *J* = 7.4 Hz, 2H), 1.50 (h, *J* = 7.4 Hz, 2H), 1.03 – 0.96 (m, 6H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.5, 136.7, 130.6, 128.3, 127.4, 125.9, 122.6, 110.3, 59.1, 29.8, 27.5, 23.4, 23.1, 14.1, 14.0, 13.8. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{19}H_{26}NO_2$: 300.1964, found: 300.1966.



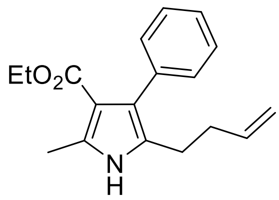
Ethyl 2,5-di(but-3-en-1-yl)-4-phenyl-1*H*-pyrrole-3-carboxylate (2ag)

Following the general procedure I, the product **2ag** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a pale yellow oil (34.5 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.34 – 7.30 (m, 2H), 7.26 – 7.23 (m, 3H), 5.95 – 5.85 (m, 1H), 5.84 – 5.74 (m, 1H), 5.13 – 4.99 (m, 4H), 4.06 (q, *J* = 7.1 Hz, 2H), 3.04 (t, *J* = 7.5 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.43 (q, *J* = 7.2 Hz, 2H), 2.25 (q, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 138.2, 138.0, 137.7, 136.4, 130.6, 127.8, 127.4, 126.1, 122.8, 115.9, 115.7, 110.5, 59.2, 34.1, 33.6, 27.1, 24.9, 14.0. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{21}H_{26}NO_2$: 324.1964, found: 324.1968.



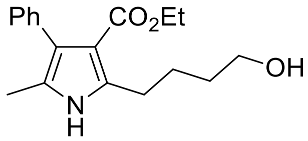
Ethyl 2-(but-3-en-1-yl)-5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (2ah)

Following the general procedure I, the product **2ah** was isolated by chromatography on silica gel (PE/EA = 4/1, eluent) as a pale yellow oil (30.0 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 3H), 5.93 (ddt, *J* = 17.0, 10.5, 6.7 Hz, 1H), 5.14 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 2.13 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 138.1, 137.7, 136.4, 130.5, 127.4, 126.0, 123.7, 122.7, 115.6, 110.5, 59.2, 33.8, 27.2, 14.1, 11.4. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{18}H_{22}NO_2$: 284.1651, found: 284.1656.



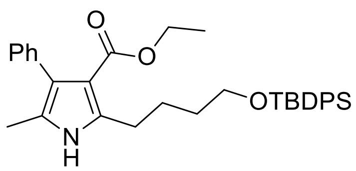
Ethyl 2-(but-3-en-1-yl)-5-methyl-3-phenyl-1*H*-pyrrole-4-carboxylate (2ah')

Following the general procedure I, the product **2ah'** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a pale yellow oil (5.1 mg, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.37 – 7.28 (m, 2H), 7.29 – 7.20 (m, 3H), 5.80 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.08 – 4.93 (m, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.52 (s, 2H), 2.26 (q, *J* = 6.9 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 138.0, 136.3, 134.0, 130.6, 127.7, 127.5, 126.1, 122.9, 115.9, 110.8, 59.2, 34.2, 24.8, 14.1, 13.9. HRMS (ESI) ([M + Na]$^+$) Calcd For $C_{18}H_{21}NNaO_2$: 306.1470, found: 306.1462.



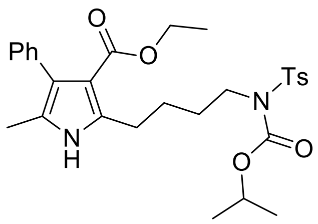
Ethyl 2-(4-hydroxybutyl)-5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (2ai)

Following the general procedure I, the product **2ai** was isolated by chromatography on silica gel (PE/EA = 3/1, eluent) as a colorless oil (24.6 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.74 (t, *J* = 6.1 Hz, 2H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.12 (s, 3H), 1.82 – 1.75 (m, 2H), 1.70 – 1.63 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.4, 136.5, 130.6, 127.4, 126.0, 123.6, 116.3, 110.4, 62.6, 59.2, 31.8, 27.0, 26.1, 14.0, 11.4. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{18}H_{24}NO_3$: 302.1756, found: 302.1759.



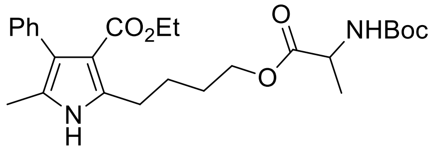
Ethyl 2-(4-((*tert*-butyldiphenylsilyl)oxy)butyl)-5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (2aj)

Following the general procedure I, the product **2aj** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (51.8 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.69 (d, *J* = 6.4 Hz, 4H), 7.46 – 7.38 (m, 7H), 7.36 – 7.32 (m, 2H), 7.26 (d, *J* = 7.3 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.07 (s, 3H), 1.81 – 1.73 (m, 2H), 1.70 – 1.63 (m, 2H), 1.09 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 138.3, 136.4, 135.7, 134.1, 130.5, 129.8, 127.8, 127.4, 125.9, 123.5, 110.3, 64.1, 59.1, 32.2, 27.4, 27.1, 26.1, 19.4, 14.1, 11.3. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{34}H_{42}NO_3Si$: 540.2934, found: 540.2930.



Ethyl 2-(4-((*N*-(isopropoxycarbonyl)-4-methylphenyl)sulfonamido)butyl)-5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (2ak)

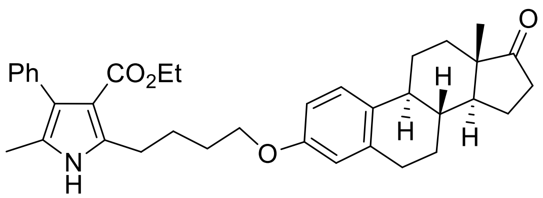
Following the general procedure I, the product **2ak** was isolated by chromatography on silica gel (PE/EA = 3/1, eluent) as a colorless oil (40.9 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.34 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.74 (t, *J* = 6.1 Hz, 2H), 2.97 (t, *J* = 6.1 Hz, 2H), 2.12 (s, 3H), 1.82 – 1.75 (m, 2H), 1.70 – 1.63 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.4, 136.5, 130.6, 127.4, 126.0, 123.6, 116.3, 110.4, 62.6, 59.2, 31.8, 27.0, 26.1, 14.0, 11.4. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{29}H_{37}N_2O_6S$: 541.2372, found: 541.2375.



Ethyl 2-(4-(((*tert*-butoxycarbonyl)alanyl)oxy)butyl)-5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate

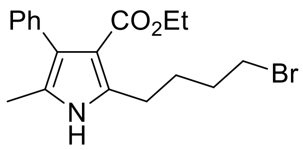
(2al)

Following the general procedure I, the product **2al** was isolated by chromatography on silica gel (PE/EA = 3/1, eluent) as a colorless oil (37.9 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.33 – 7.29 (m, 2H), 7.25 – 7.20 (m, 3H), 5.08 (d, *J* = 6.4 Hz, 1H), 4.32 – 4.26 (m, 2H), 4.18 – 4.13 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.00 – 2.87 (m, 2H), 2.11 (s, 3H), 1.75 – 1.72 (m, 4H), 1.44 (s, 9H), 1.39 (d, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 173.6, 165.7, 155.4, 137.8, 136.4, 130.4, 127.3, 125.7, 123.9, 122.3, 110.2, 80.0, 64.7, 59.0, 49.4, 28.3, 28.0, 26.7, 25.8, 18.2, 13.9, 11.2. HRMS (ESI) ([M + H]$^+$) Calcd For $C_{26}H_{37}N_2O_6$: 473.2652, found: 473.2655.



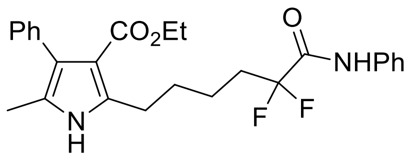
Ethyl 5-methyl-2-(4-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)butyl)-4-phenyl-1H-pyrrole-3-carboxylate (2am)

Following the general procedure I, the product **2am** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (48.7 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.36 – 7.30 (m, 2H), 7.27 – 7.15 (m, 4H), 6.72 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 4.00 (q, J = 4.1, 3.4 Hz, 2H), 3.07 – 2.96 (m, 2H), 2.95 – 2.85 (m, 2H), 2.50 (dd, J = 18.8, 8.6 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.29 – 2.22 (m, 1H), 2.21 – 1.92 (m, 7H), 1.87 (p, J = 3.4 Hz, 4H), 1.70 – 1.38 (m, 8H), 1.03 (t, J = 7.1 Hz, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.0, 165.8, 157.1, 138.0, 138.0, 136.4, 132.3, 130.6, 127.4, 126.5, 126.0, 123.7, 122.7, 114.7, 112.3, 110.6, 68.0, 59.1, 50.6, 48.2, 44.1, 38.5, 36.0, 31.8, 29.8, 28.9, 27.2, 26.7, 26.4, 26.1, 21.7, 14.1, 14.0, 11.43. HRMS (ESI) ([M + Na]$^+$) Calcd For $C_{36}H_{43}NNaO_4$: 576.3090, found: 576.3073.



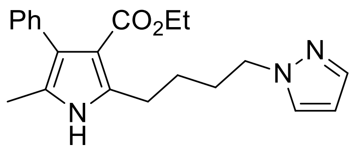
Ethyl 2-(4-bromobutyl)-5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (2an)

Following the general procedure I, the product **2an** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a colorless oil (30.5 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.34 – 7.31 (m, 2H), 7.25 – 7.22 (m, 3H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.97 – 2.93 (m, 2H), 2.11 (s, 3H), 1.98 – 1.91 (m, 2H), 1.86 – 1.78 (m, 2H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 137.5, 136.3, 130.5, 127.4, 126.0, 123.9, 122.7, 110.7, 59.2, 33.8, 32.5, 28.4, 26.8, 14.1, 11.4. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{18}H_{23}BrNO_2$: 364.0912, found: 364.0916.



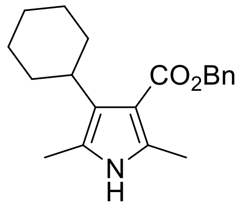
Ethyl 2-(5,5-difluoro-6-oxo-6-(phenylamino)hexyl)-5-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (2ao)

Following the general procedure I, the product **2ao** was isolated by chromatography on silica gel (PE/EA = 3/1, eluent) as a colorless oil (35.4 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.15 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.18 (m, 4H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.31 – 2.19 (m, 2H), 2.06 (s, 3H), 1.79 – 1.72 (m, 2H), 1.62 – 1.54 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 162.5 (t, *J* = 28.7 Hz), 137.6, 136.4, 136.1, 130.5, 129.3, 127.4, 125.9, 125.8, 124.0, 122.6, 120.6, 118.6 (t, *J* = 252.0 Hz), 110.5, 59.2, 33.2 (t, *J* = 23.1 Hz), 27.0, 26.8, 21.3 (t, *J* = 4.4 Hz), 14.0, 11.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.81. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{26}H_{29}F_2N_2O_3$: 455.2146, found: 455.2142.



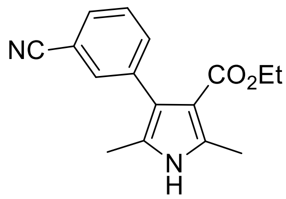
Ethyl 2-(4-(1H-pyrazol-1-yl)butyl)-5-methyl-4-phenyl-1H-pyrrole-3-carboxylate (2ap)

Following the general procedure I, the product **2ap** was isolated by chromatography on silica gel (PE/EA = 3/1, eluent) as a colorless oil (33.2 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.53 (d, *J* = 1.5 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H), 7.30 (d, *J* = 6.6 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 3H), 6.26 (t, *J* = 2.0 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 4.05 (q, *J* = 7.1 Hz, 4H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 2.01 – 1.93 (m, 2H), 1.72 – 1.65 (m, 2H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 139.2, 137.8, 136.5, 130.5, 129.6, 127.4, 125.9, 123.9, 122.5, 110.3, 105.6, 59.1, 51.6, 29.6, 26.4, 26.3, 14.1, 11.4. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{21}H_{26}N_3O_2$: 352.2025, found: 352.2016.



Benzyl 4-cyclohexyl-2,5-dimethyl-1H-pyrrole-3-carboxylate (2aq)

Following the general procedure I, the product **2aq** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a pale yellow solid (22.4 mg, 36%). Mp. 111.7-112.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.31 (m, 3H), 5.27 (s, 2H), 3.16 (t, *J* = 12.0 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H), 1.74 – 1.63 (m, 8H), 1.32 – 1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 136.9, 133.4, 128.4, 128.2, 127.8, 126.0, 121.44 110.0, 65.2, 35.9, 32.7, 27.4, 26.3, 14.5, 13.0. HRMS (ESI) ($[M + H]^+$) Calcd For $C_{20}H_{26}NO_2$: 312.1964, found: 312.1969.



Ethyl 4-(3-cyanophenyl)-2,5-dimethyl-1H-pyrrole-3-carboxylate (2ar)

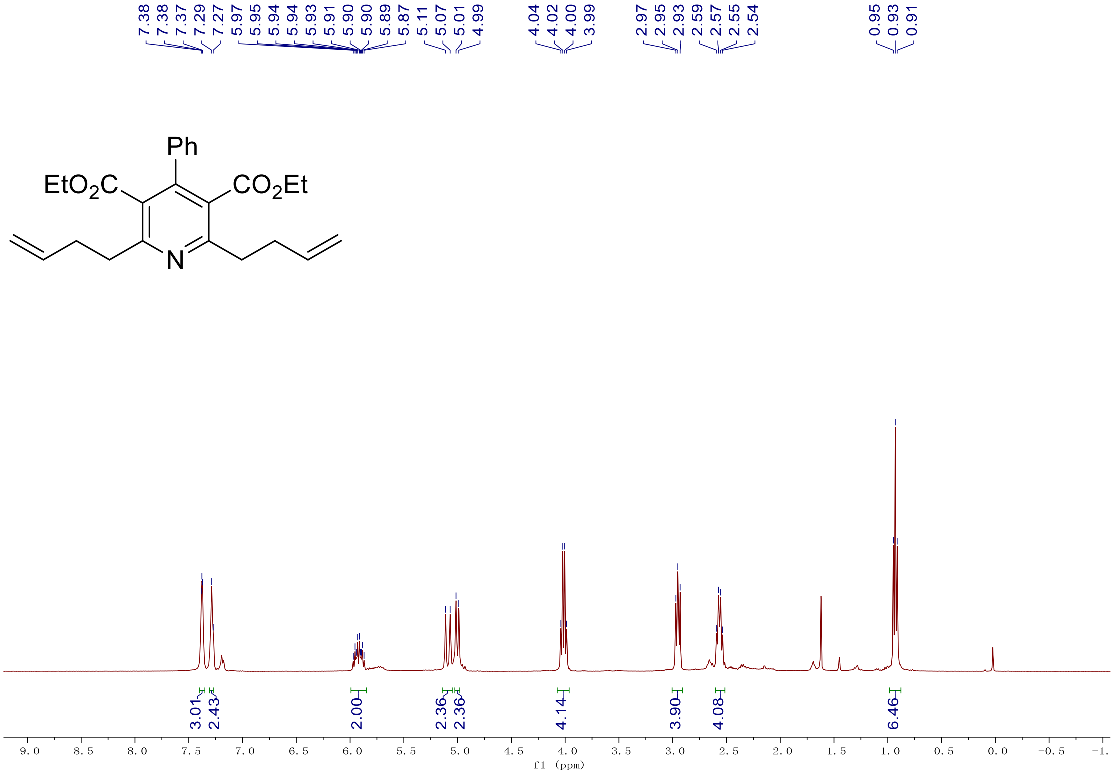
Following the general procedure of I, the product **2ar** was isolated by chromatography on silica gel (PE/EA = 5/1, eluent) as a yellow oil (2.5 g, 72%, starting from 13.0 mmol of **1ar**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.57 – 7.47 (m, 3H), 7.42 (t, *J* = 8.0 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.52 (s, 3H), 2.10 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.41, 137.80, 135.29, 134.72, 134.12, 129.67, 128.25, 124.16, 120.54, 119.46, 111.49, 110.48, 59.38, 14.18, 13.84, 11.28. HRMS (ESI) ($[M + Na]^+$) Calcd For $C_{16}H_{16}N_2NaO_2$: 291.1109, found: 291.1103.

6. Reference

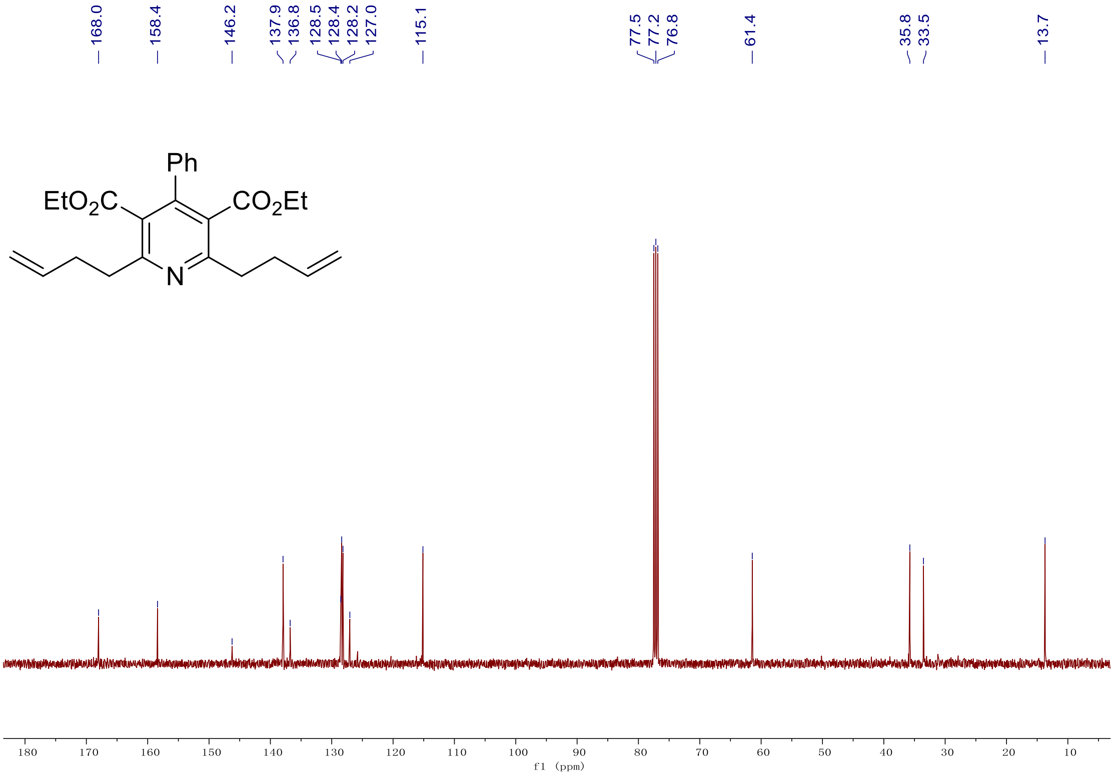
1. J. Calbo, C. E. Weston, A. J. P. White, H. S. Rzepa, J. Contreras-García and M. J. Fuchter, *J. Am. Chem. Soc*. 2017, **139**, 1261-1274.

7. NMR spectra

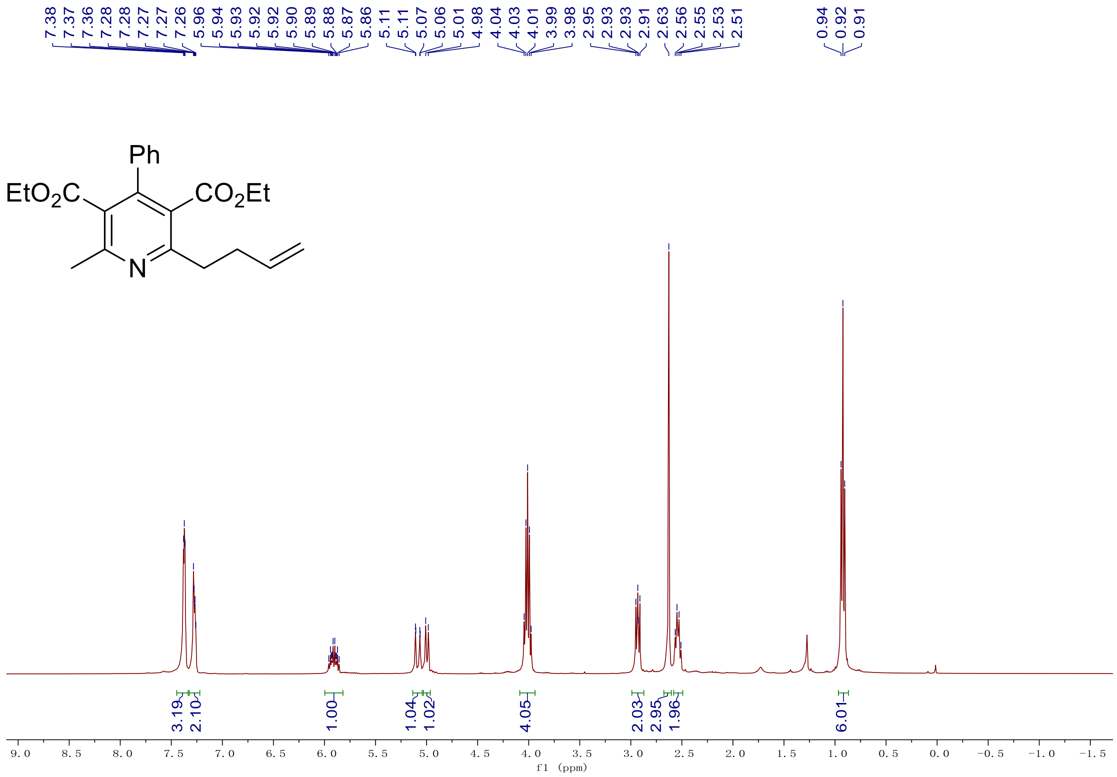
^{1}H NMR (400 MHz, $CDCl_3$) of **1ag**



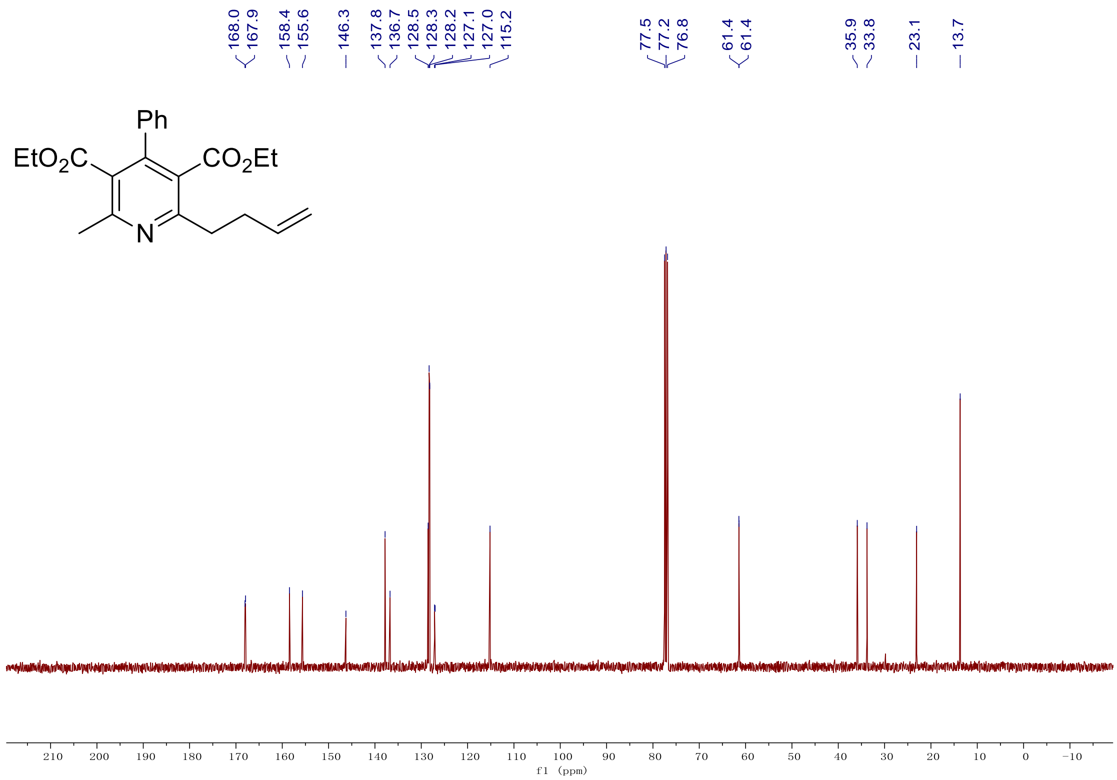
^{13}C NMR (100 MHz, $CDCl_3$) of **1ag**



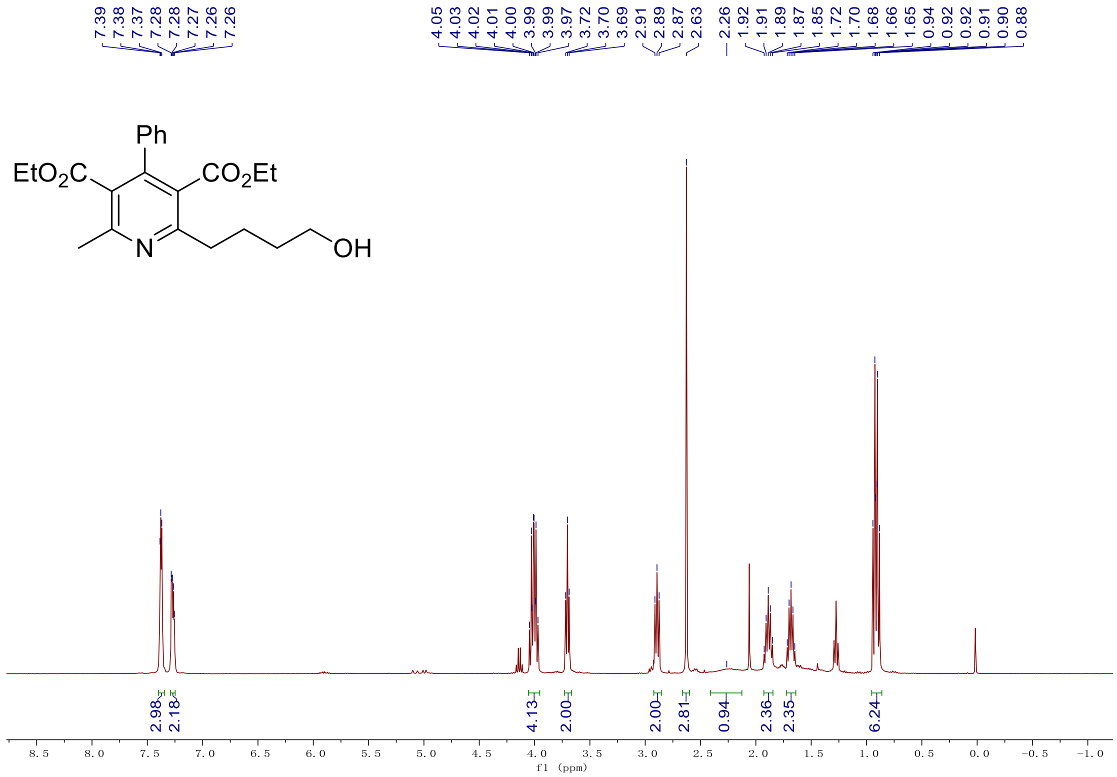
^{1}H NMR (400 MHz, $CDCl_3$) of **1ah**



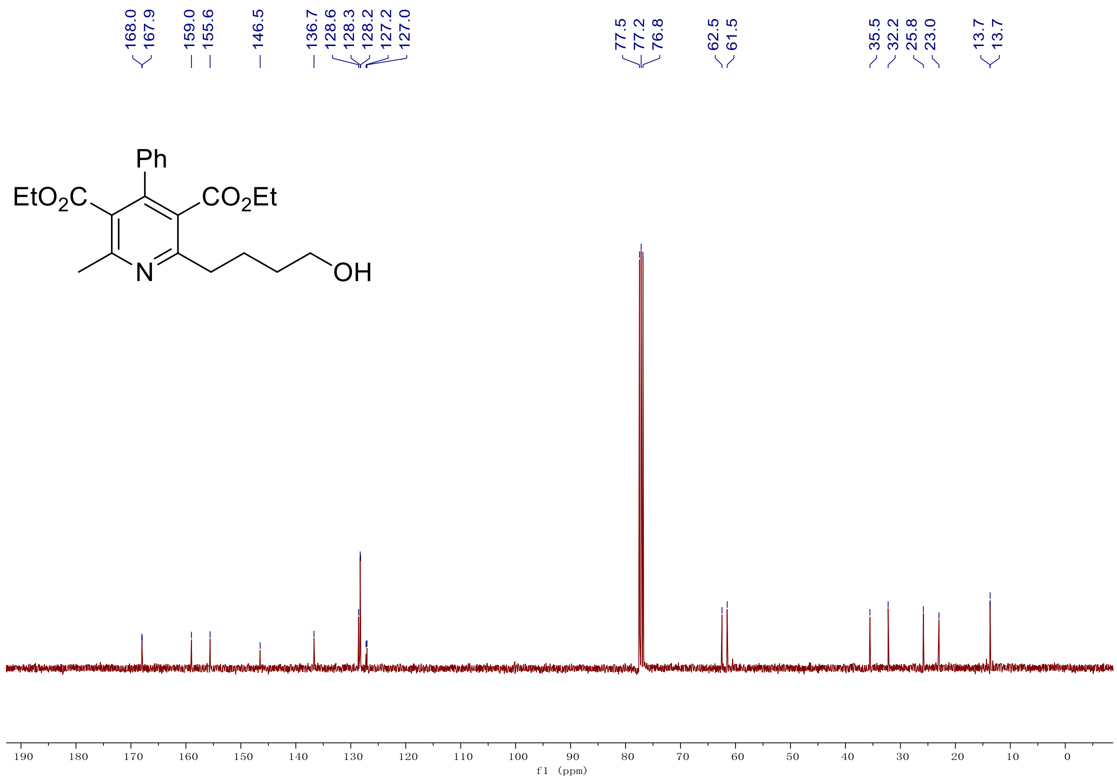
^{13}C NMR (100 MHz, $CDCl_3$) of **1ah**



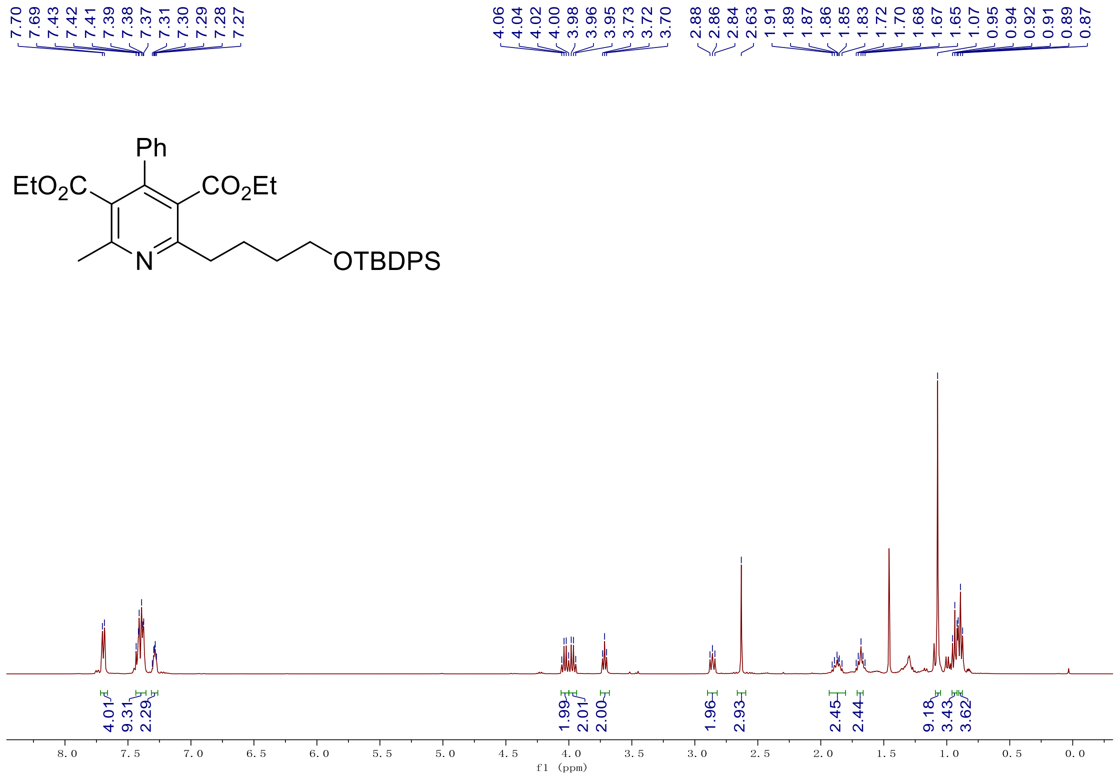
^{1}H NMR (400 MHz, $CDCl_3$) of **1ai**



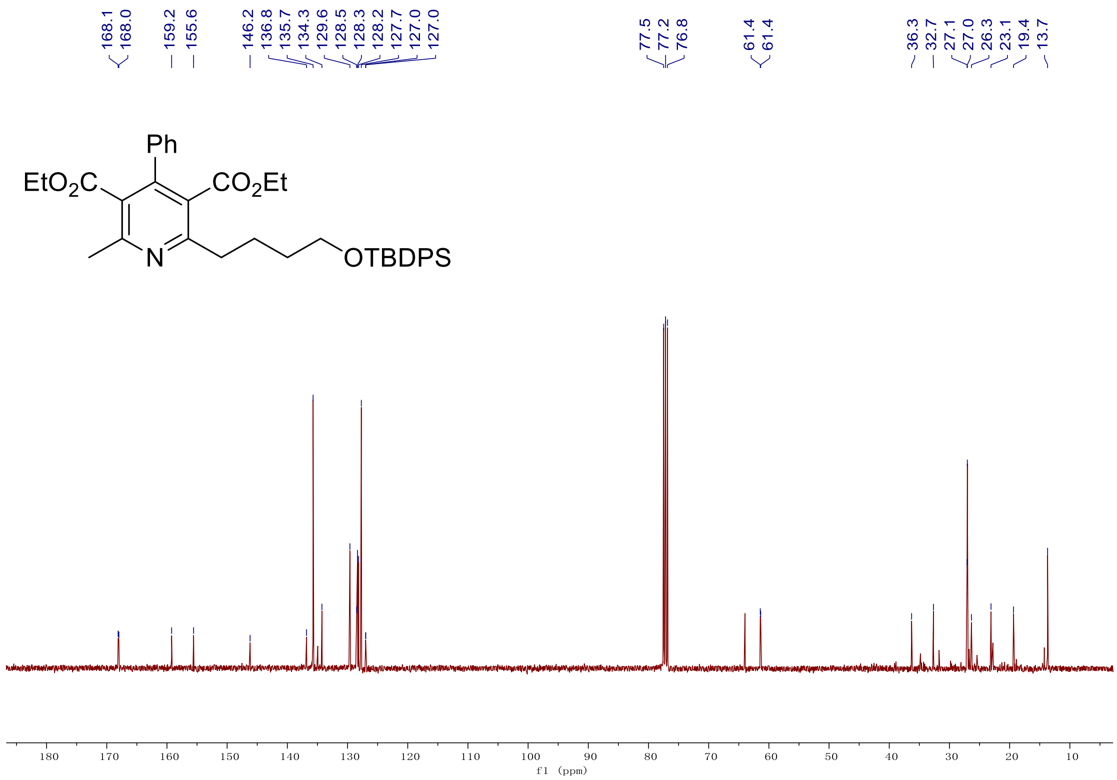
^{13}C NMR (100 MHz, $CDCl_3$) of **1ai**



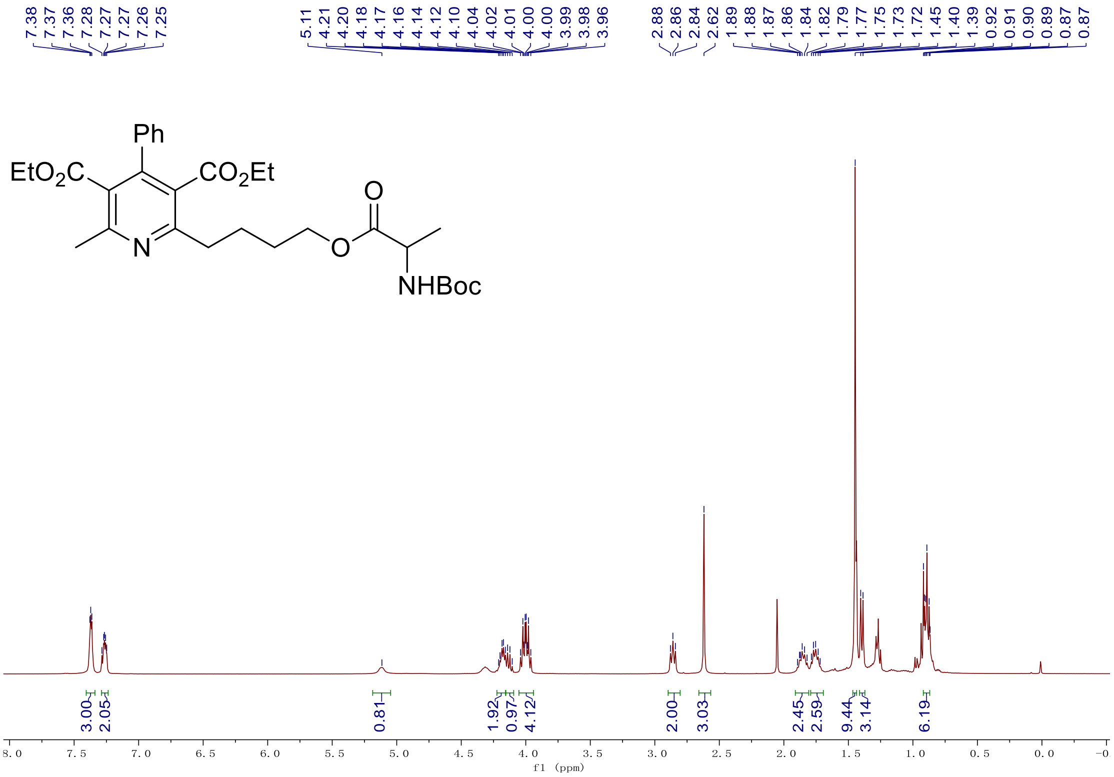
^{1}H NMR (400 MHz, $CDCl_3$) of **1aj**



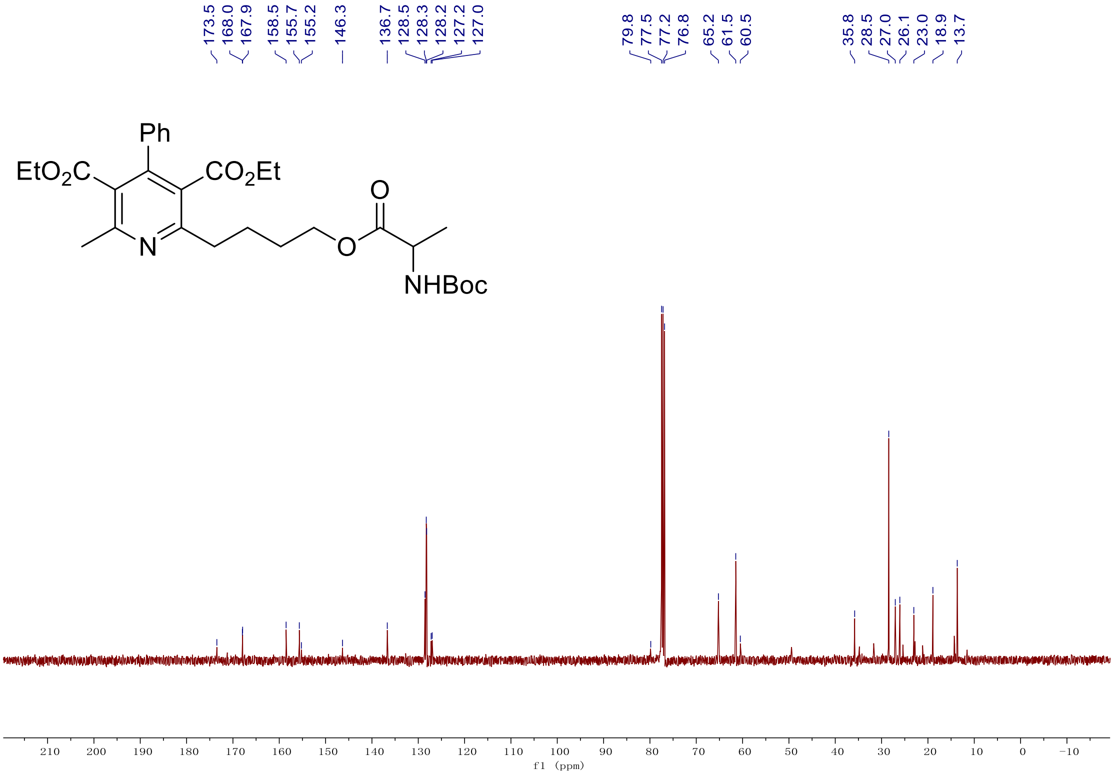
^{13}C NMR (100 MHz, $CDCl_3$) of **1aj**



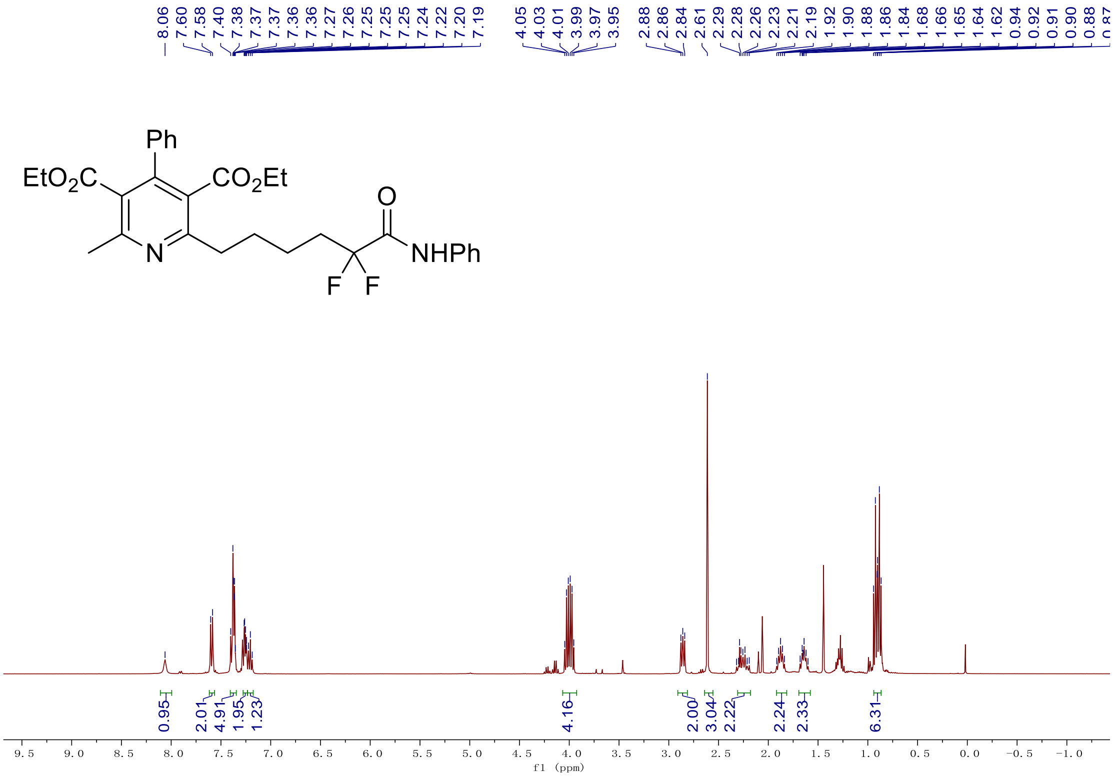
^{1}H NMR (400 MHz, $CDCl_3$) of **1al**



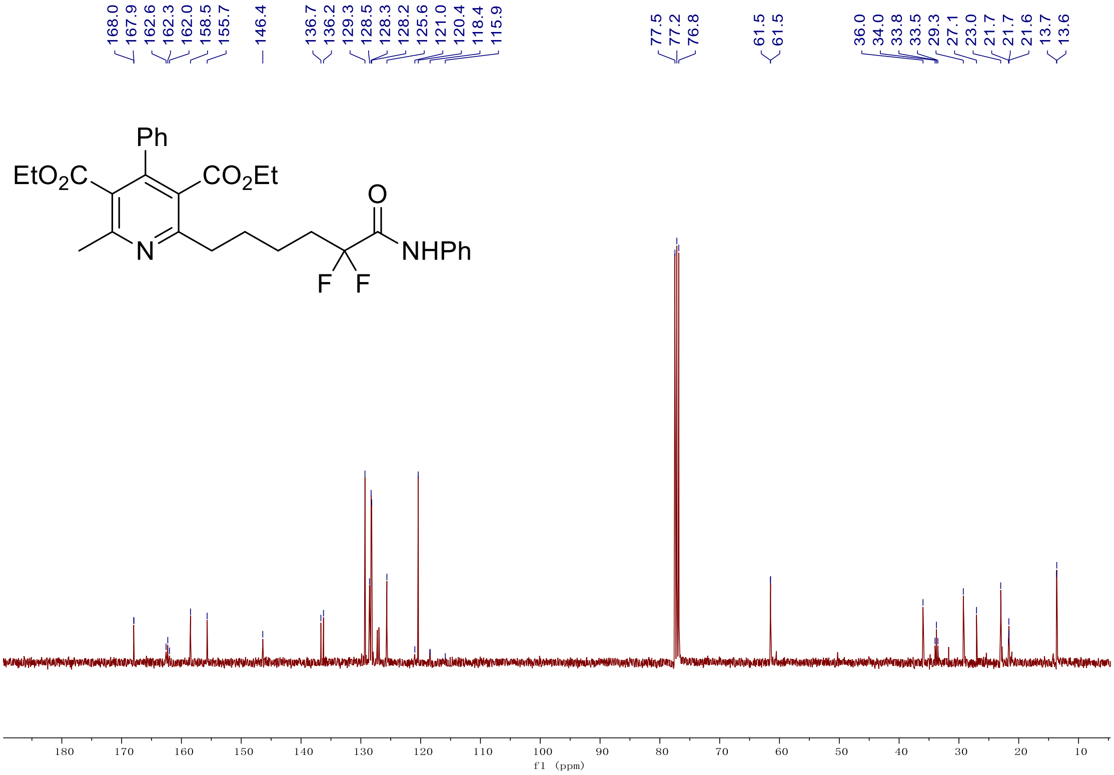
^{13}C NMR (100 MHz, $CDCl_3$) of **1al**



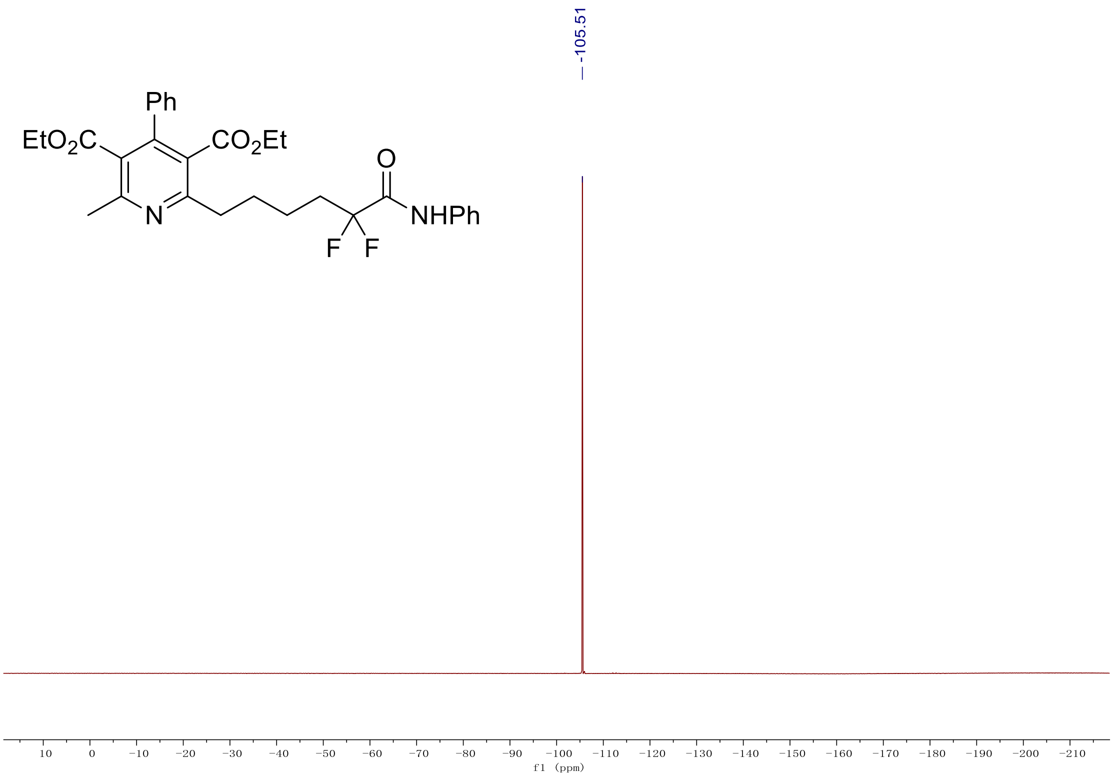
[1]H NMR (400 MHz, $CDCl_3$) of **1ao**



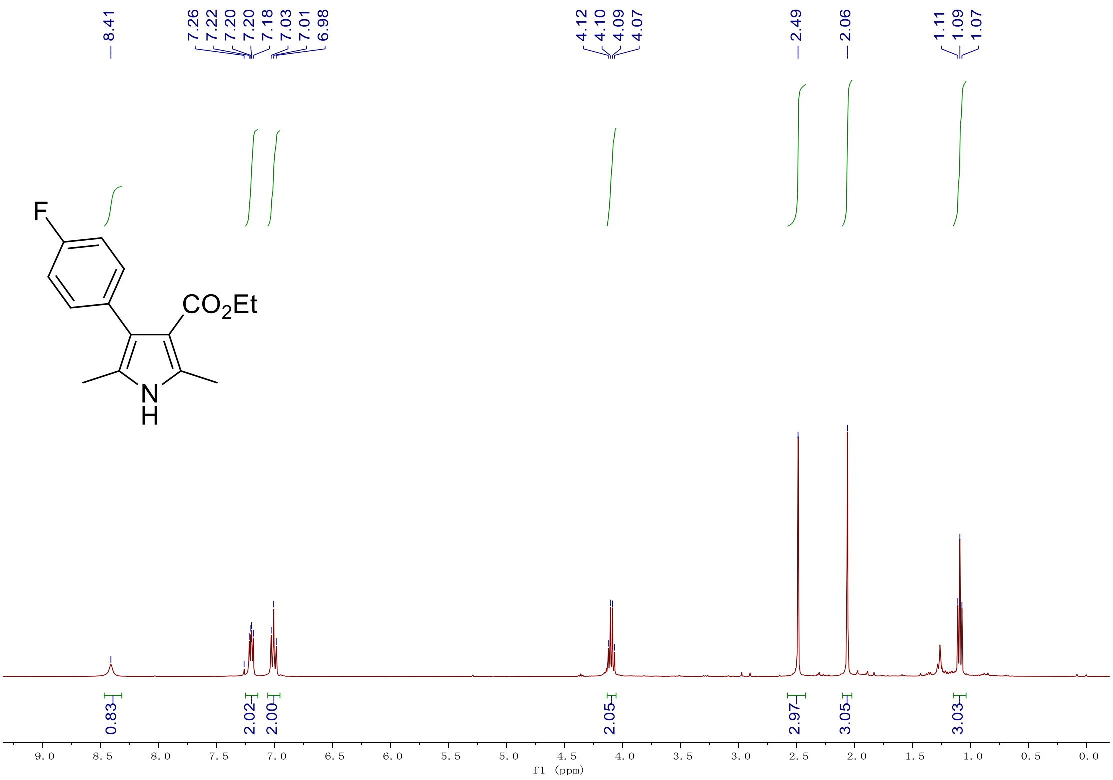
[13]C NMR (100 MHz, $CDCl_3$) of **1ao**



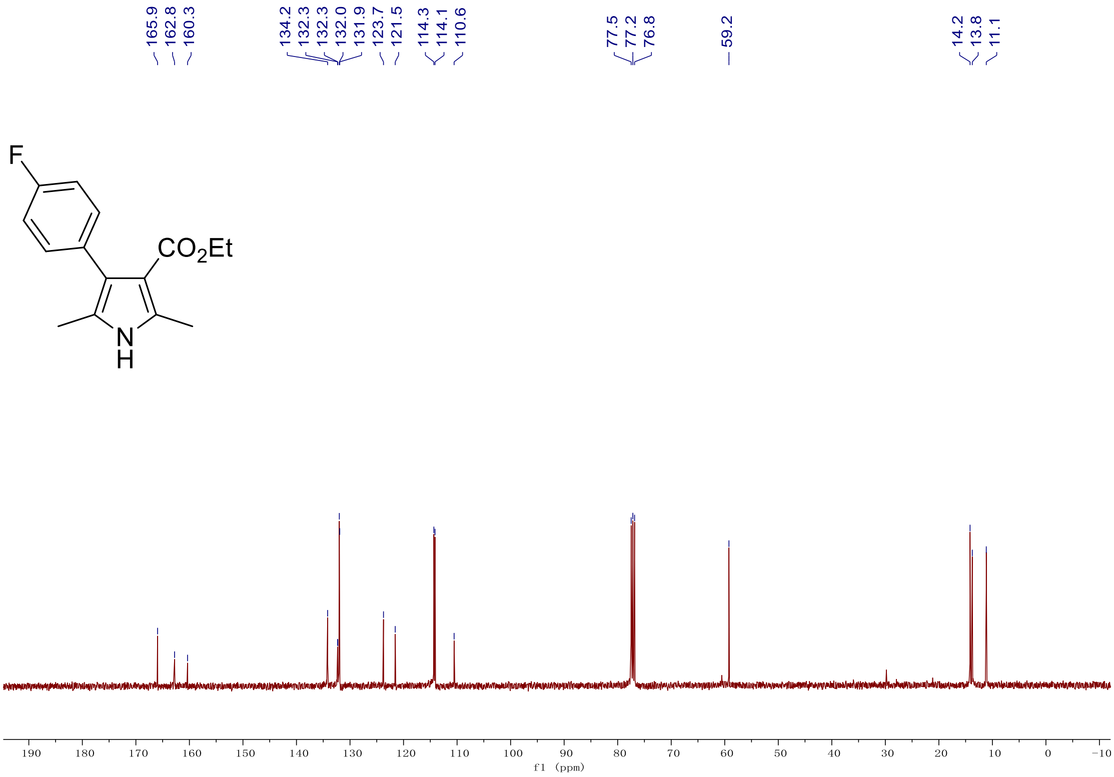
[19]F NMR (376 MHz, $CDCl_3$) of **1ao**



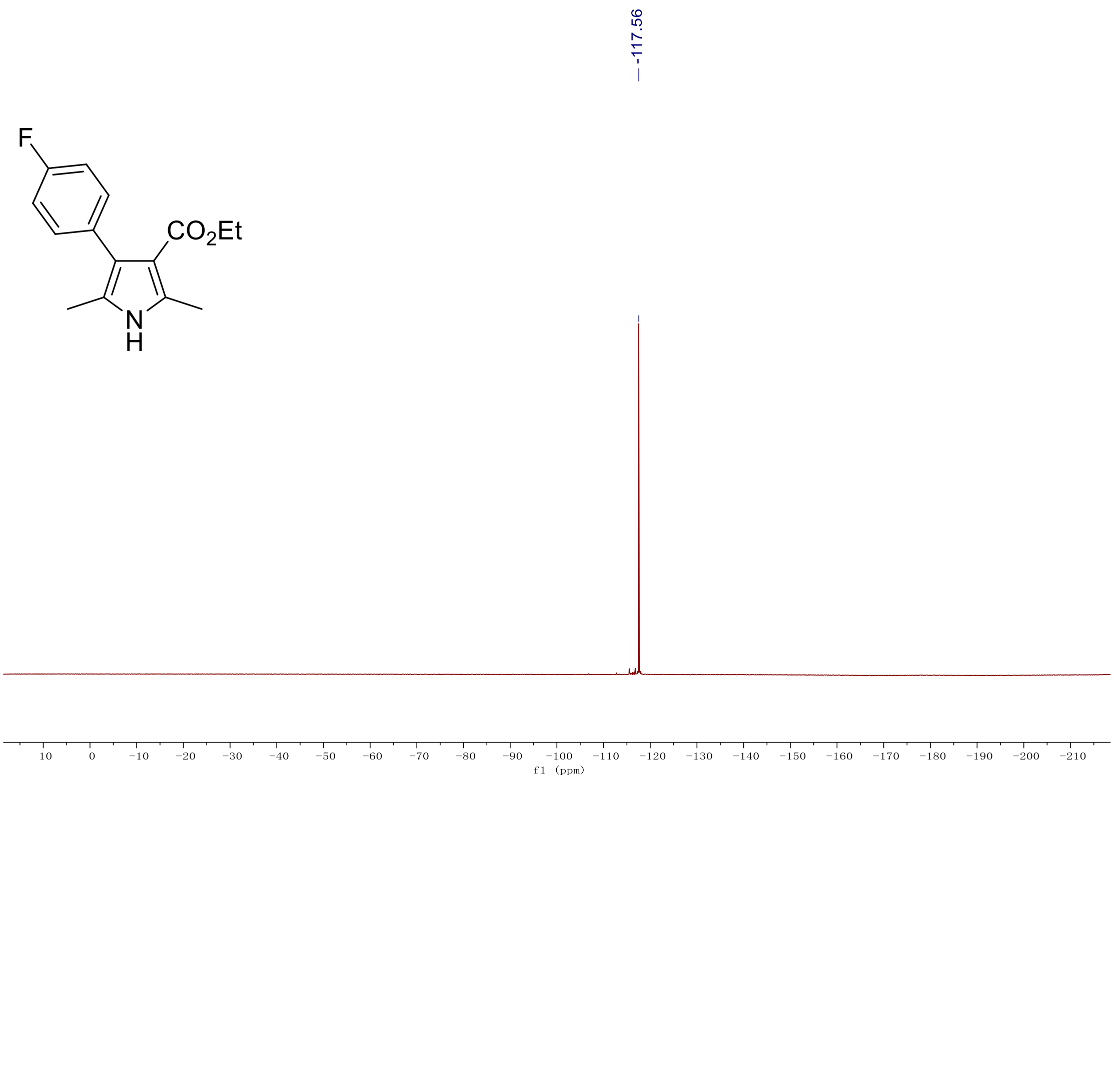
[1]H NMR (400 MHz, $CDCl_3$) of **2a**



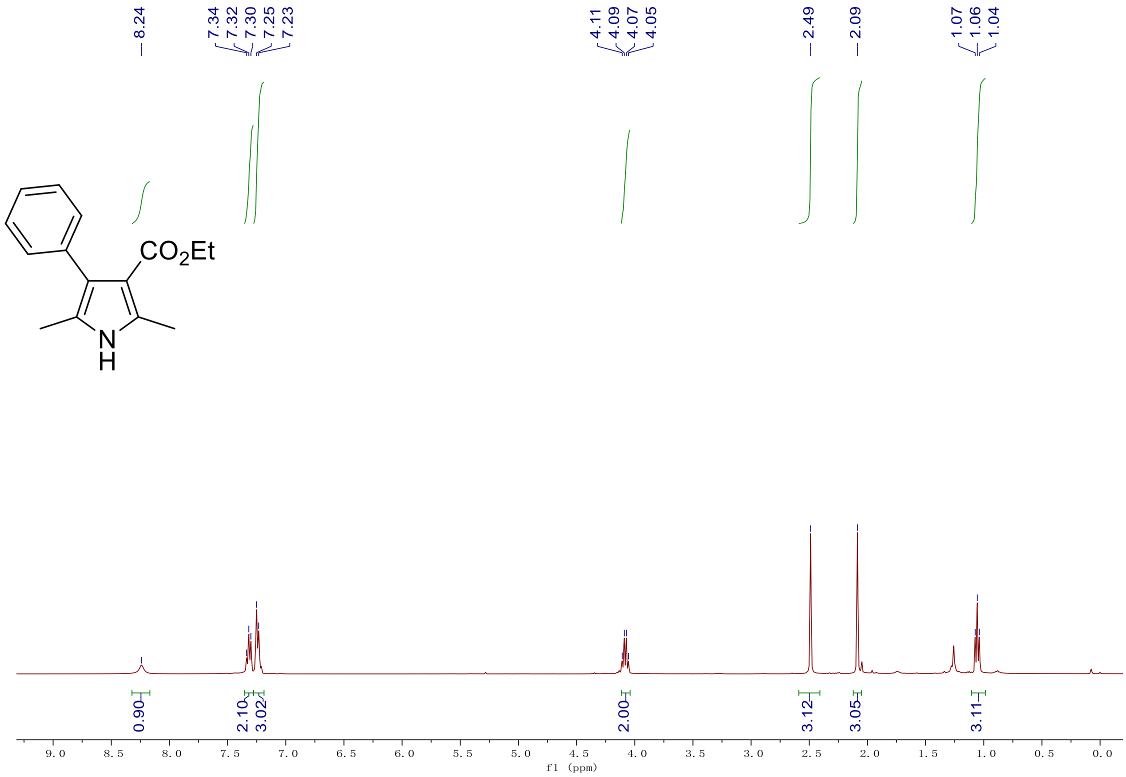
^{13}C NMR (100 MHz, $CDCl_3$) of **2a**



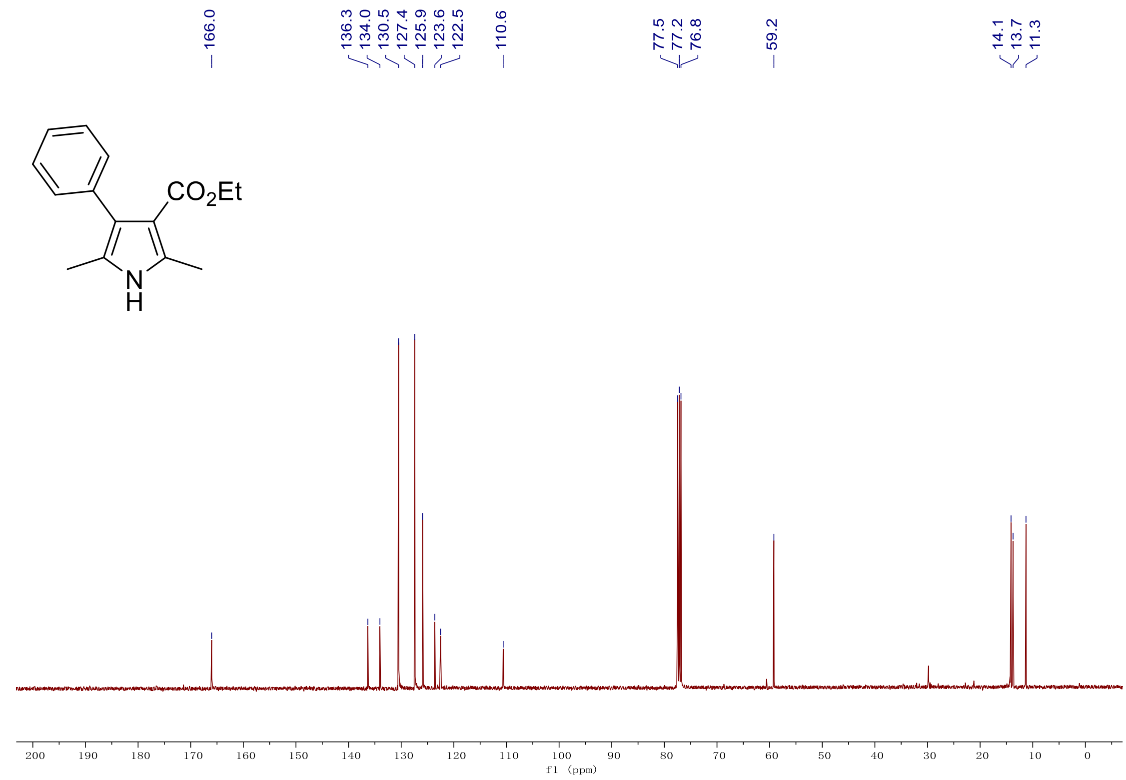
^{19}F NMR (376 MHz, $CDCl_3$) of **2a**



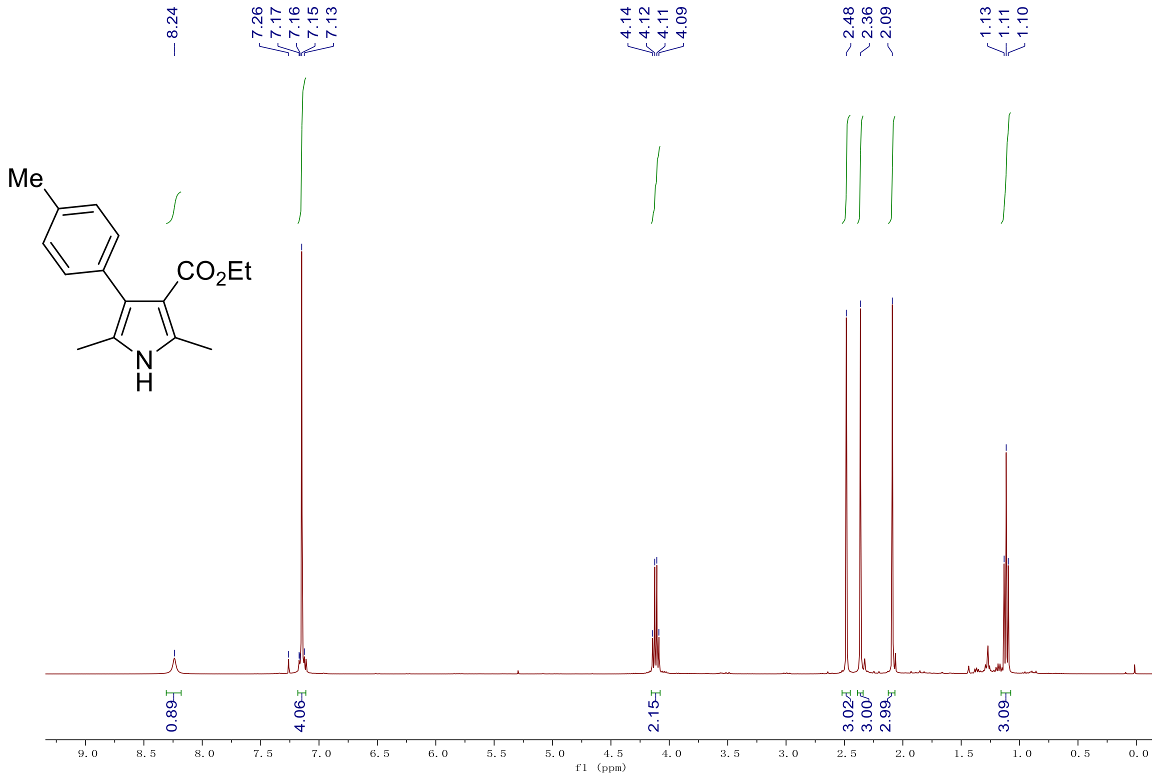
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



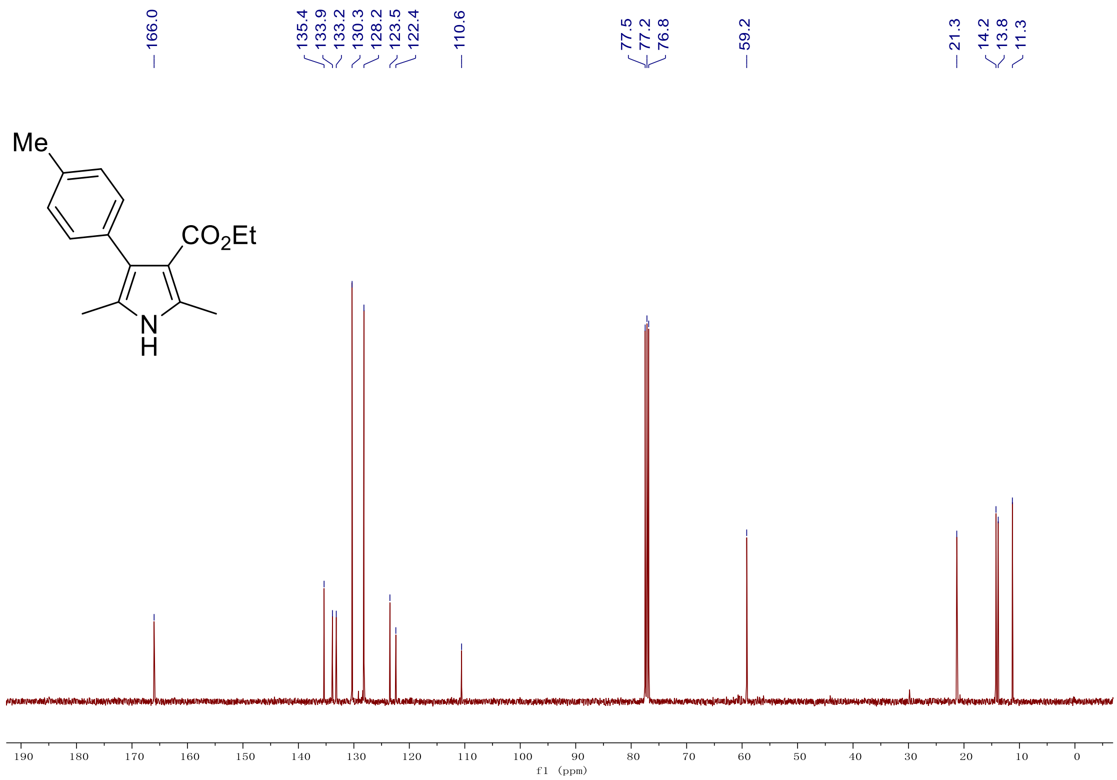
^{13}C NMR (100 MHz, $CDCl_3$) of **2b**



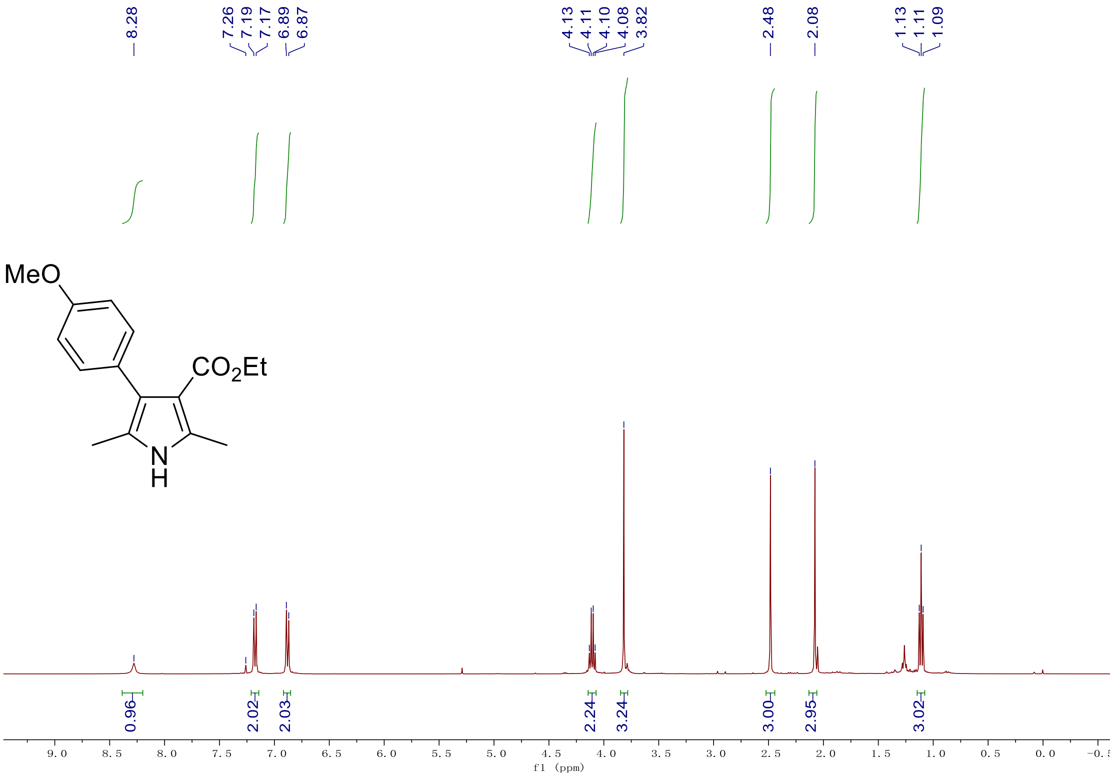
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



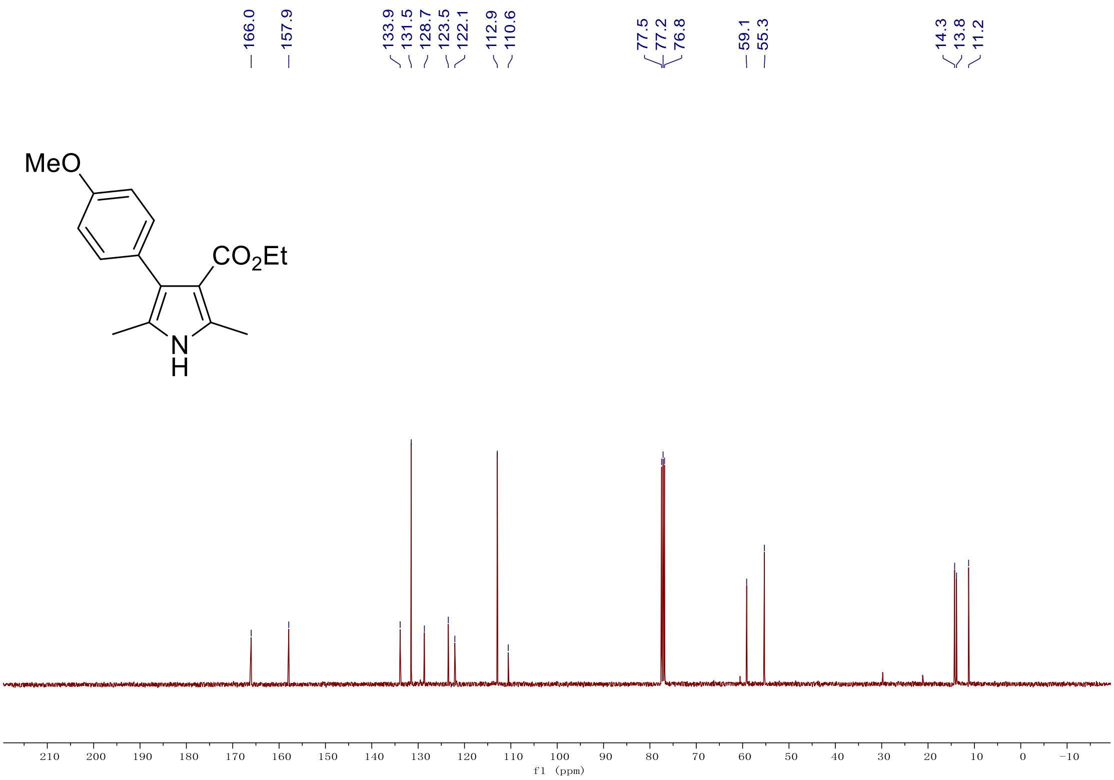
^{13}C NMR (100 MHz, $CDCl_3$) of **2c**



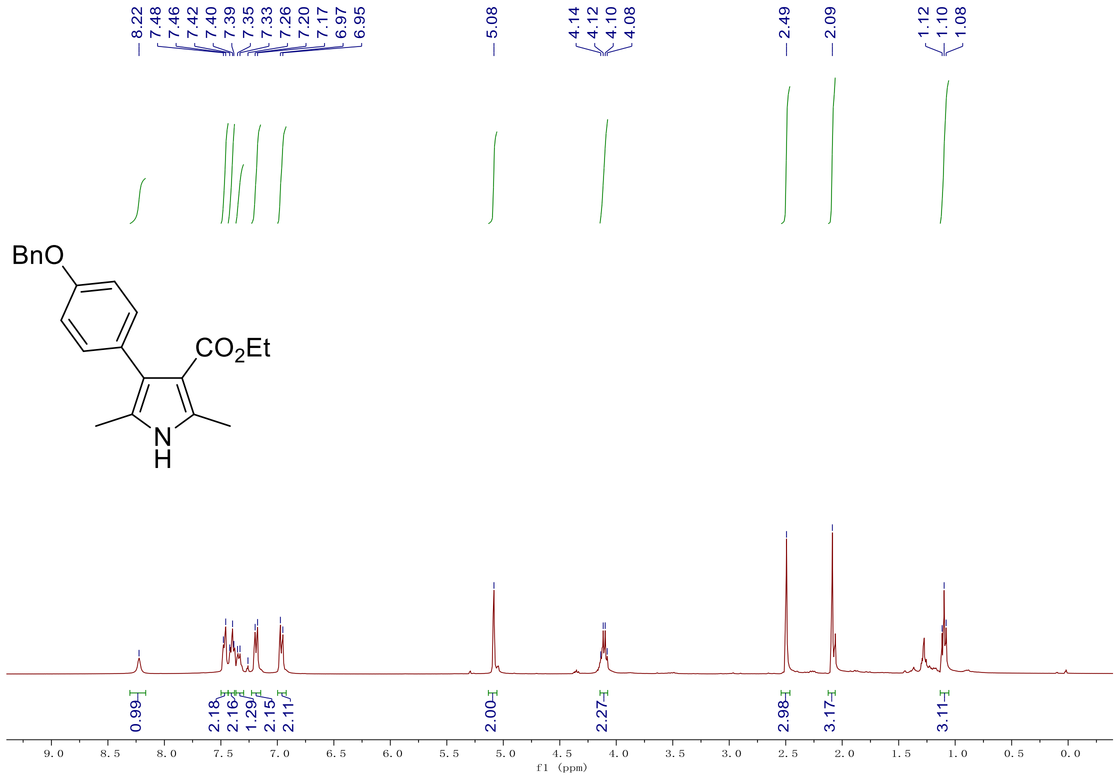
[1]H NMR (400 MHz, $CDCl_3$) of **2d**



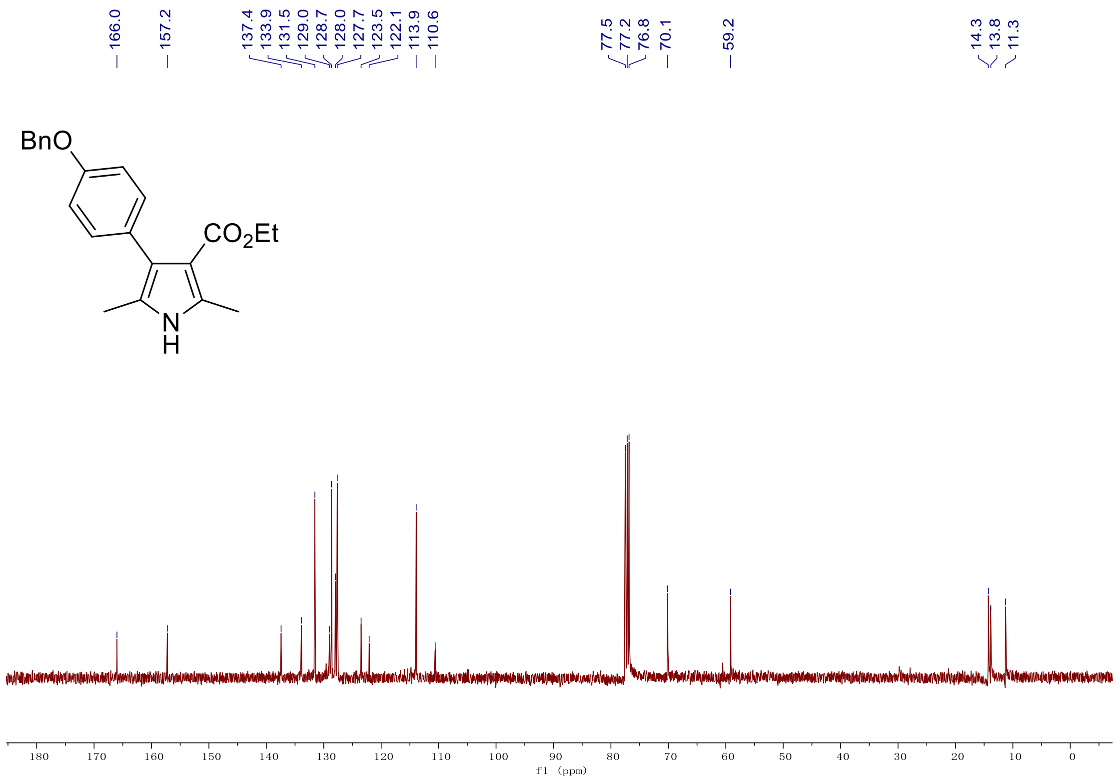
[13]C NMR (100 MHz, $CDCl_3$) of **2d**



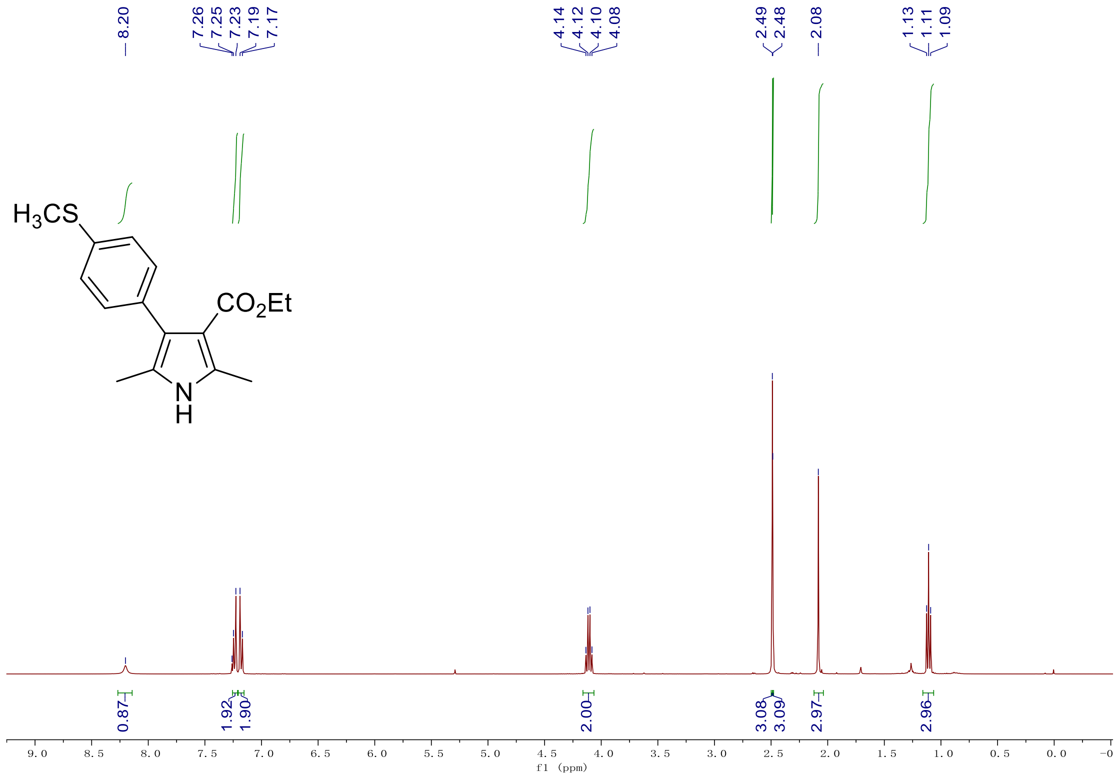
[1]H NMR (400 MHz, $CDCl_3$) of **2e**



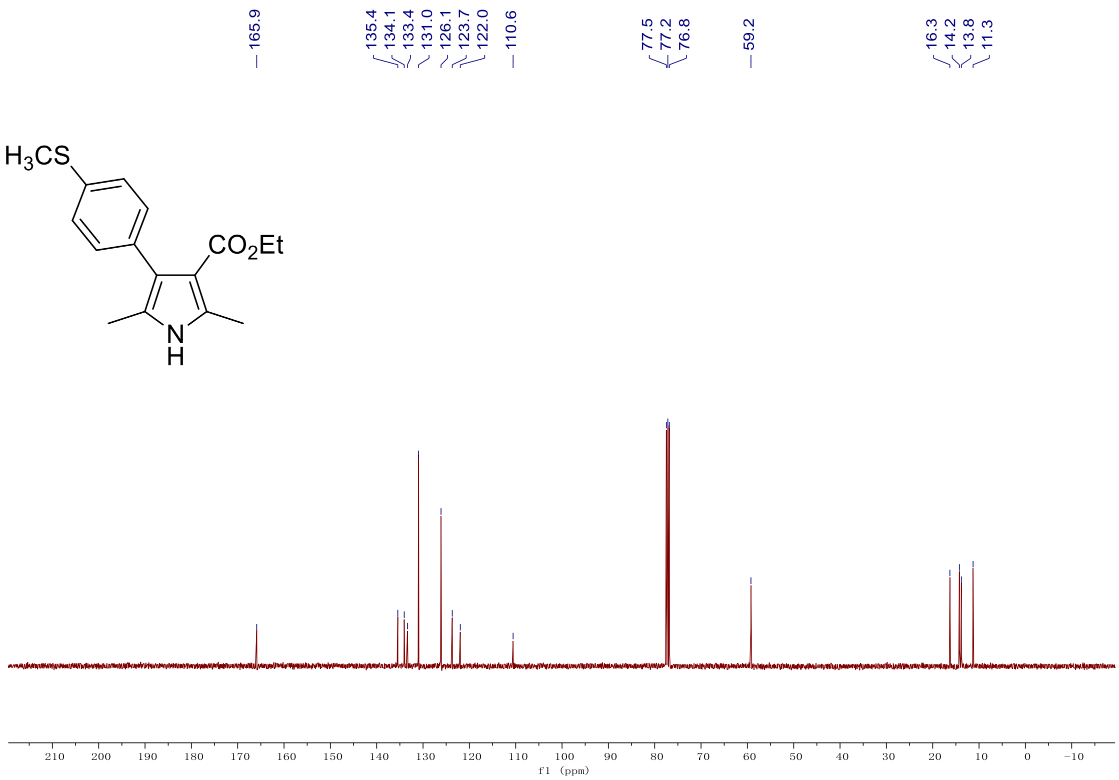
[13]C NMR (100 MHz, $CDCl_3$) of **2e**



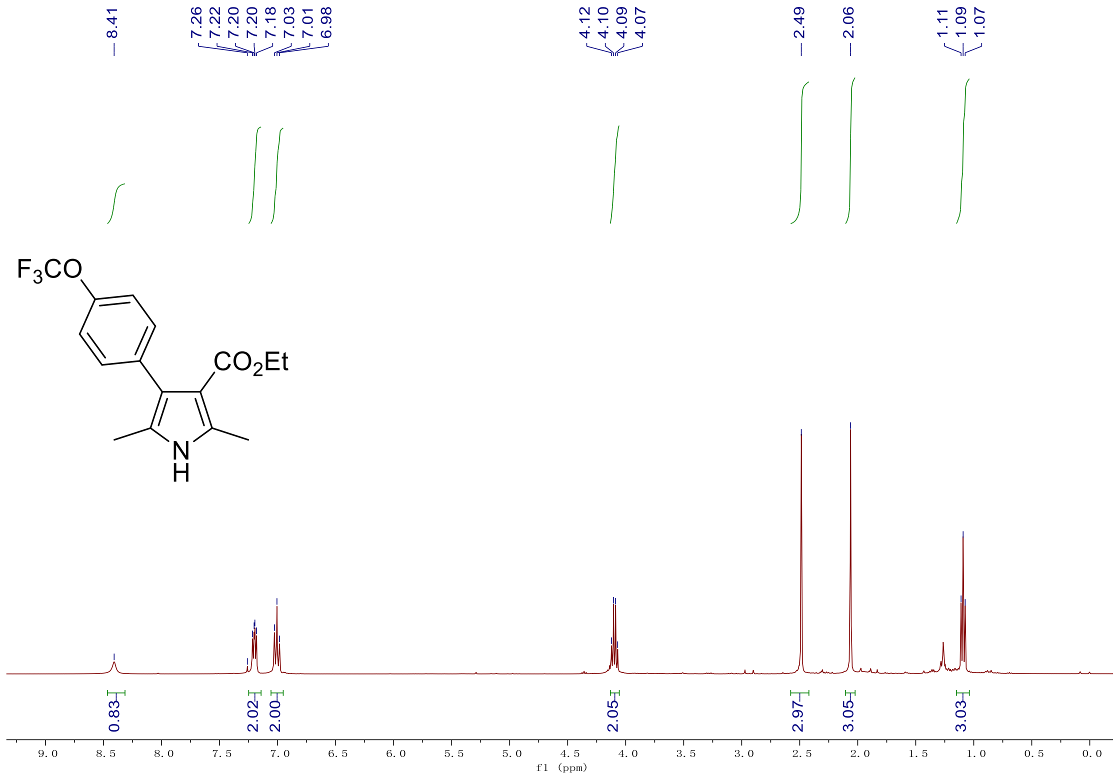
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



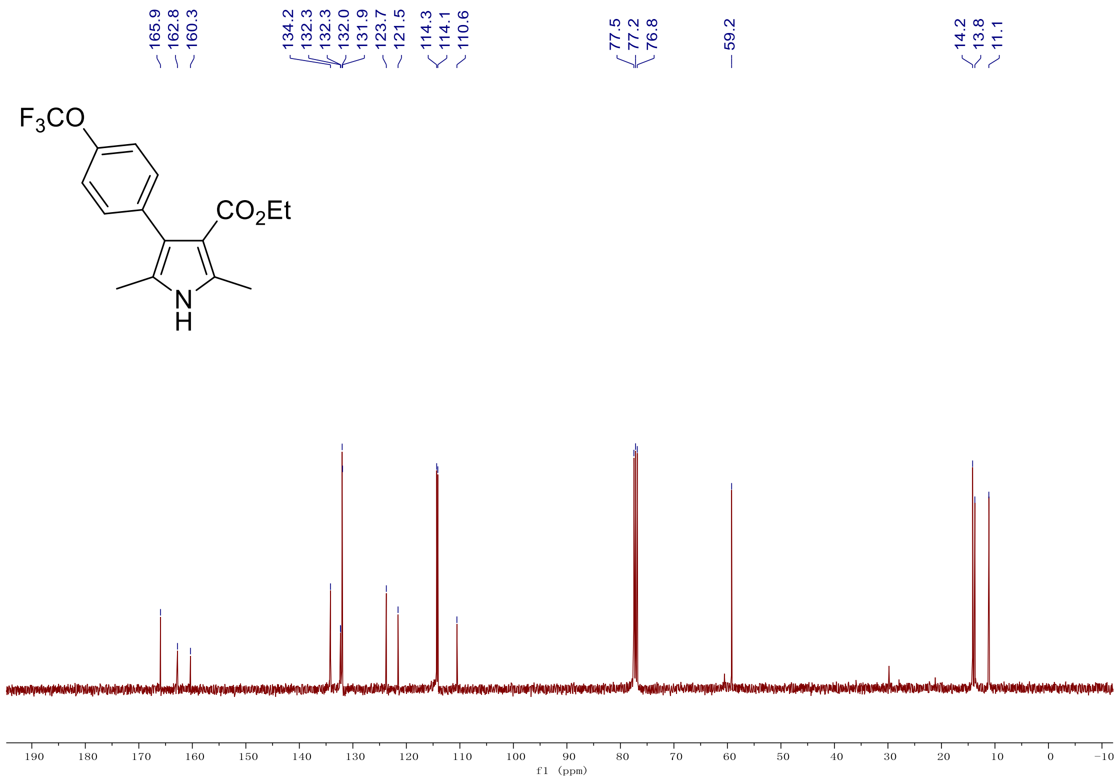
^{13}C NMR (100 MHz, $CDCl_3$) of **2f**



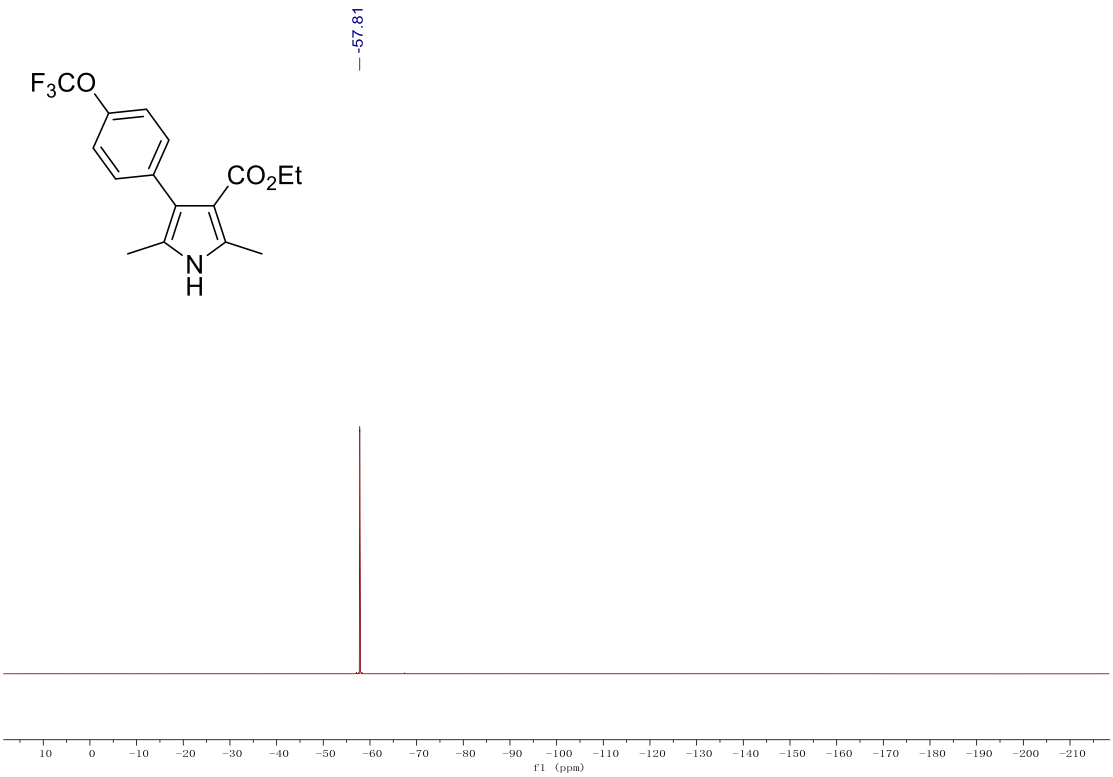
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



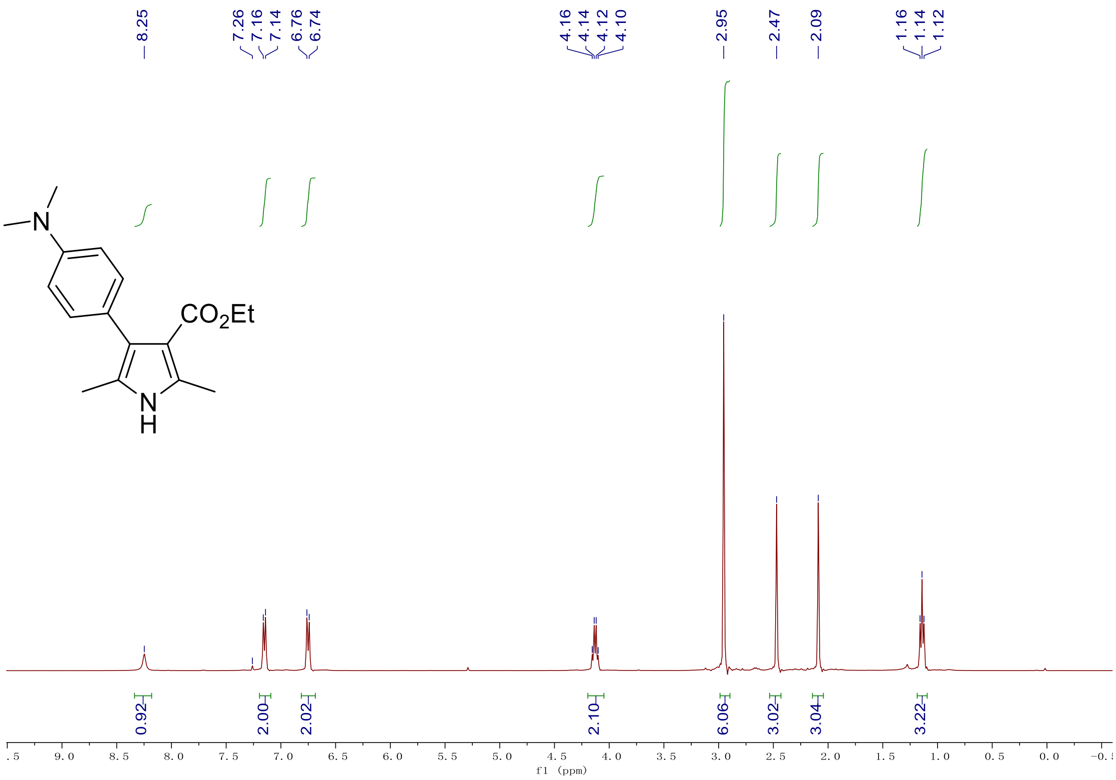
^{13}C NMR (100 MHz, $CDCl_3$) of **2g**



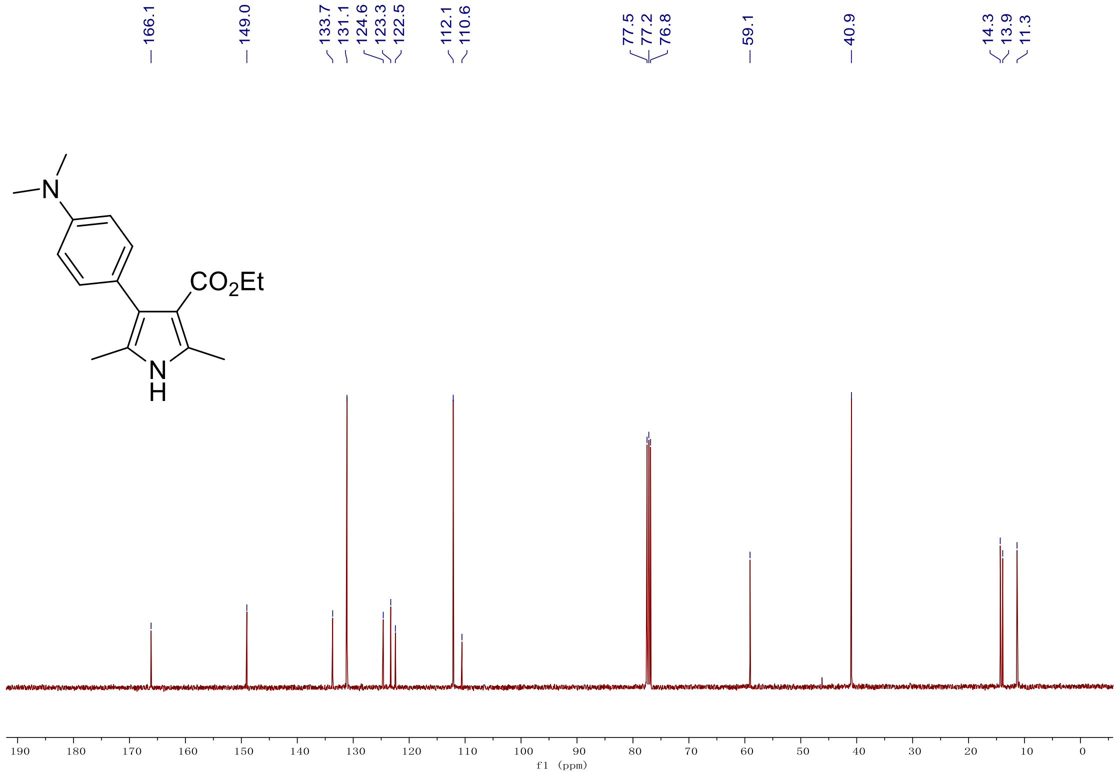
^{19}F NMR (376 MHz, $CDCl_3$) of **2g**



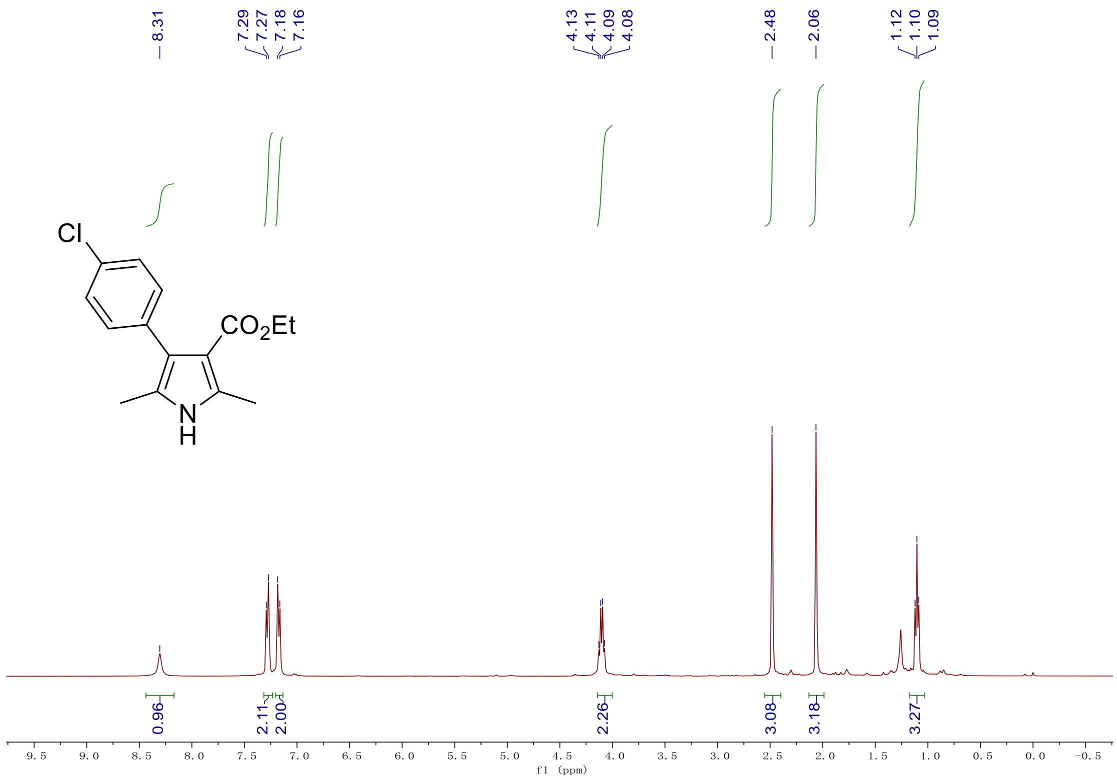
^{1}H NMR (400 MHz, $CDCl_3$) of **2h**



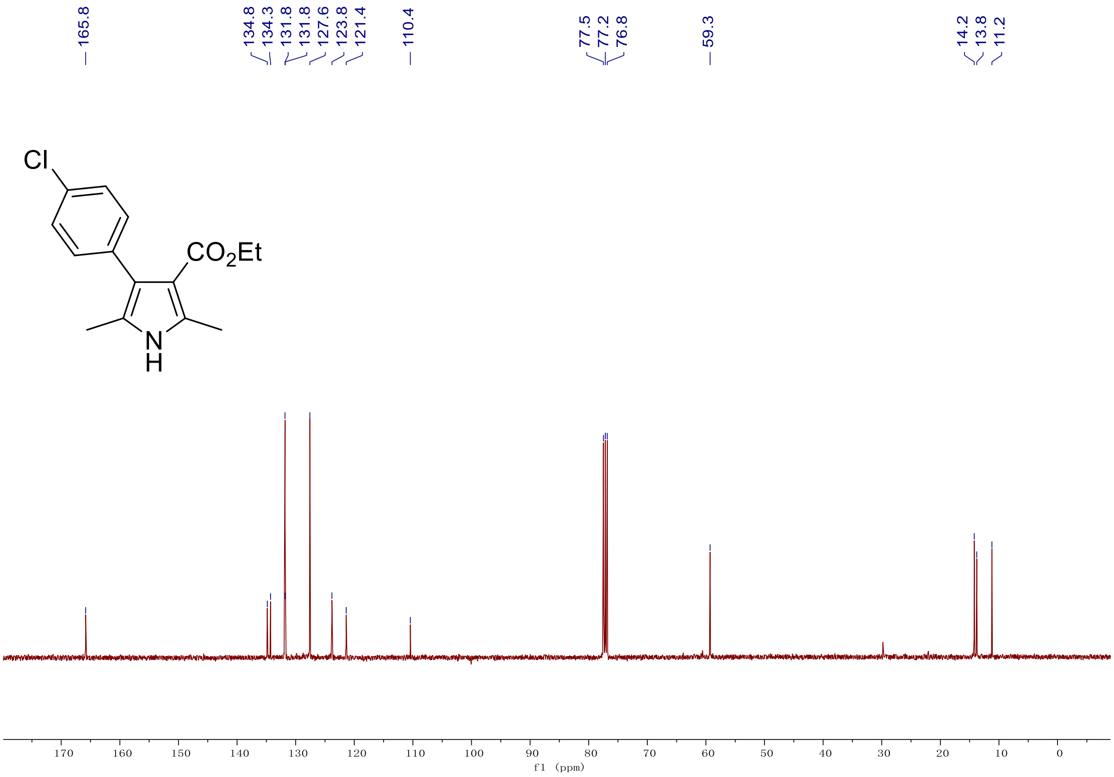
^{13}C NMR (100 MHz, $CDCl_3$) of **2h**



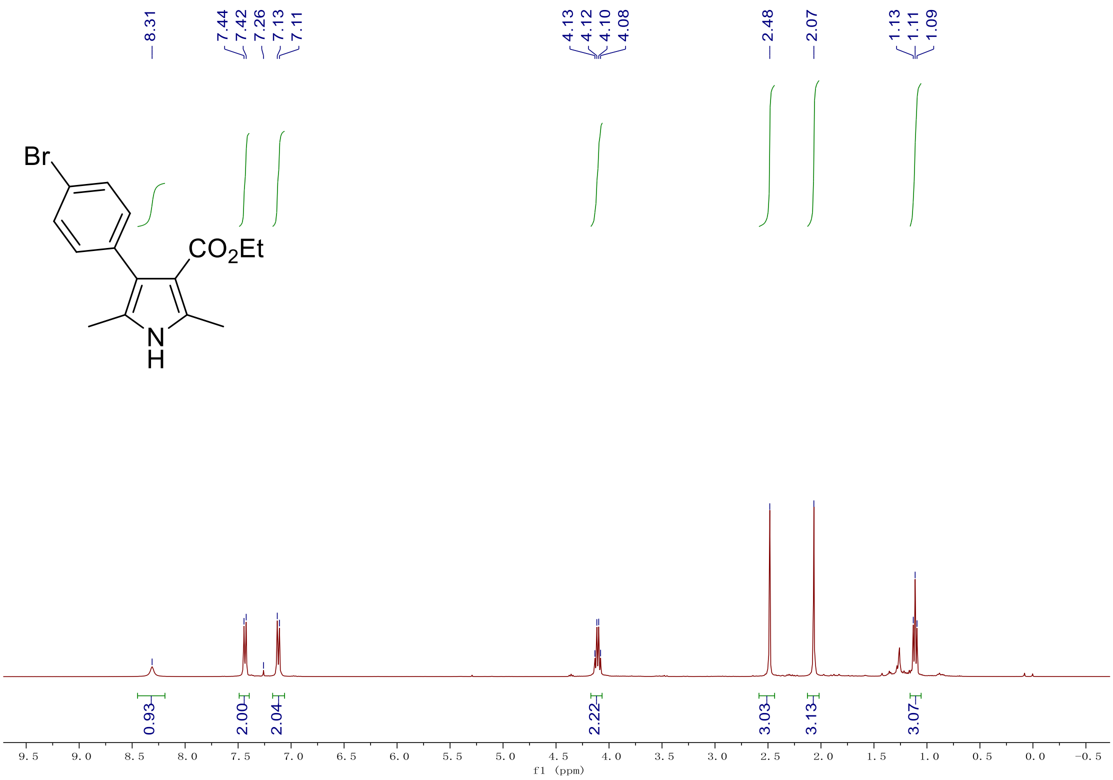
^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



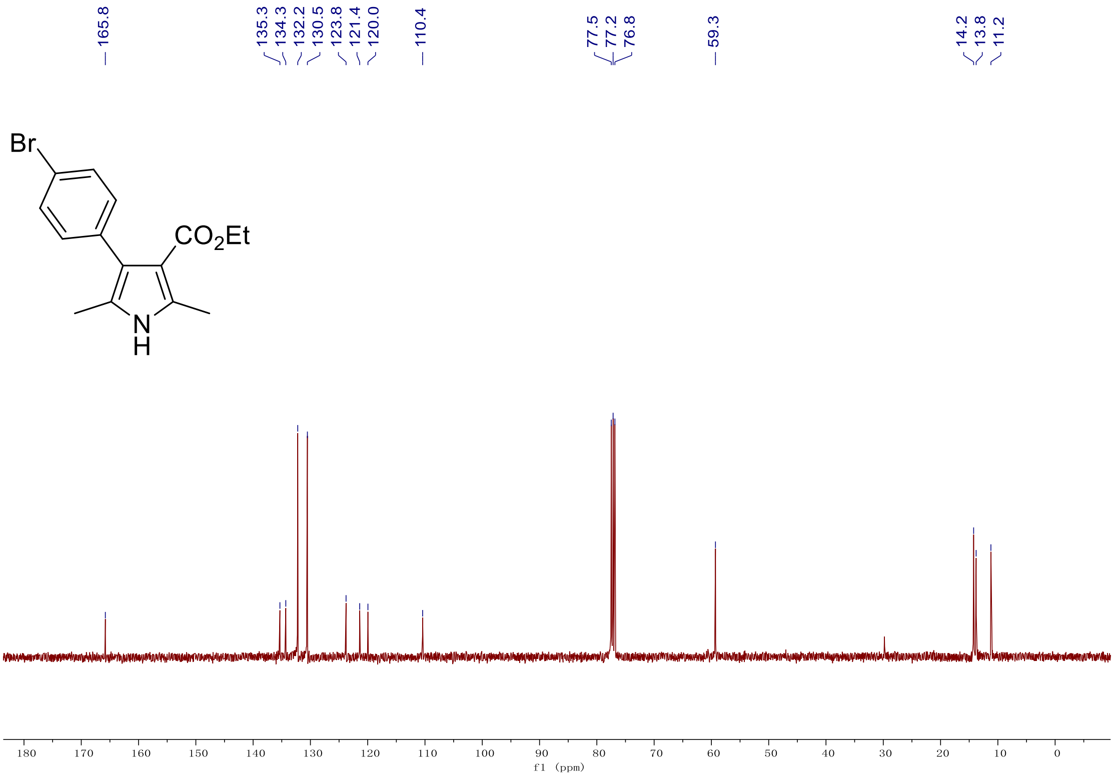
^{13}C NMR (100 MHz, $CDCl_3$) of **2i**



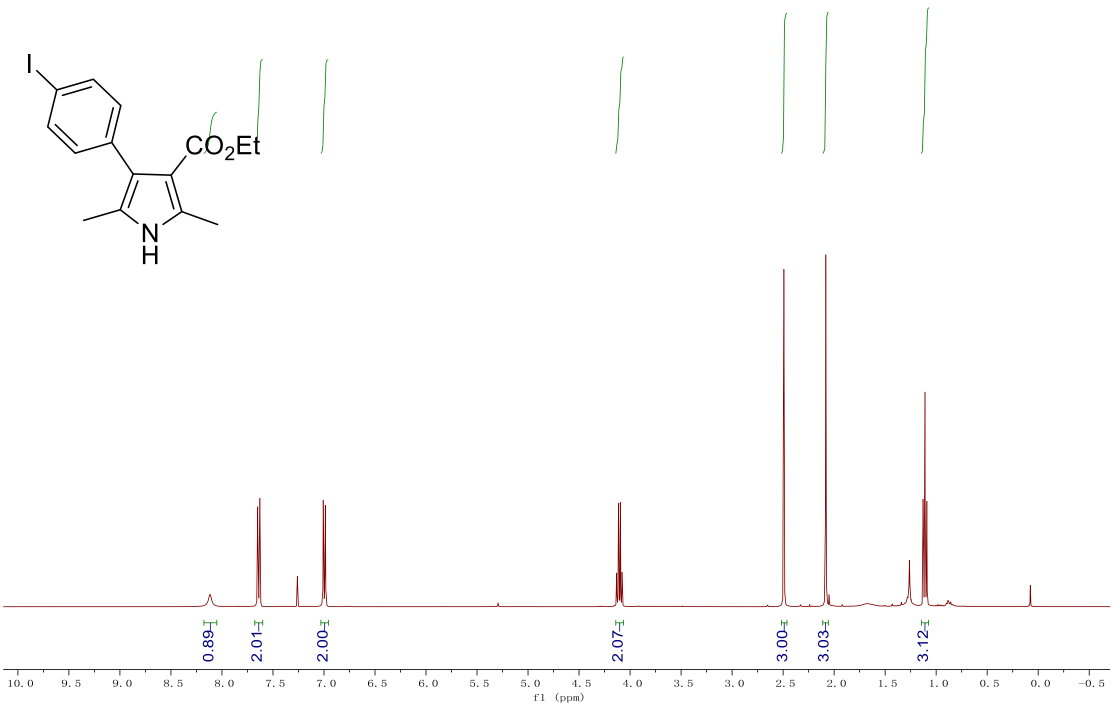
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



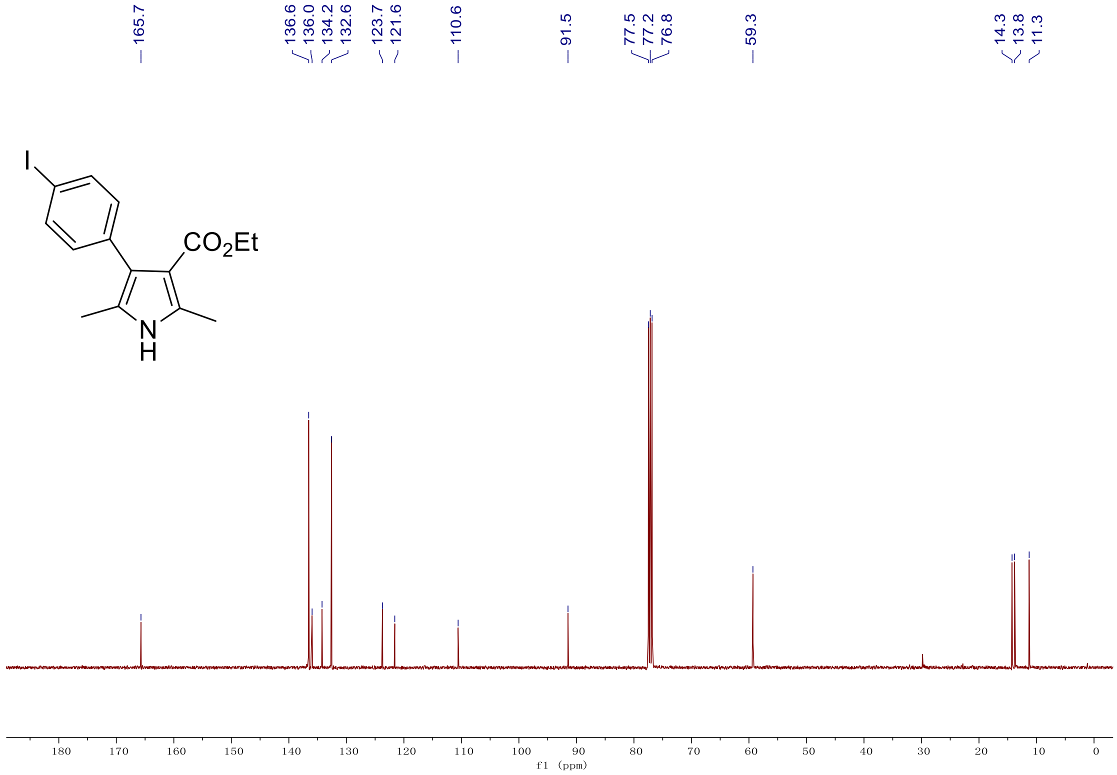
^{13}C NMR (100 MHz, $CDCl_3$) of **2j**



^{1}H NMR (400 MHz, $CDCl_3$) of **2k**

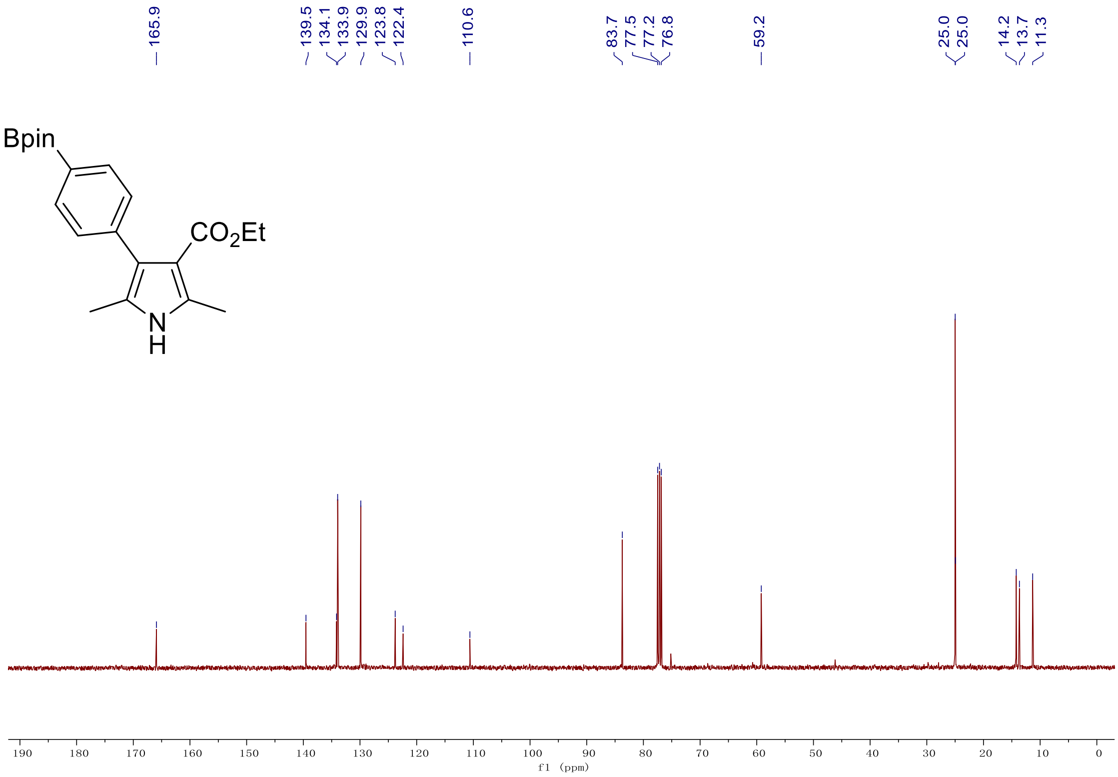


^{13}C NMR (100 MHz, $CDCl_3$) of **2k**

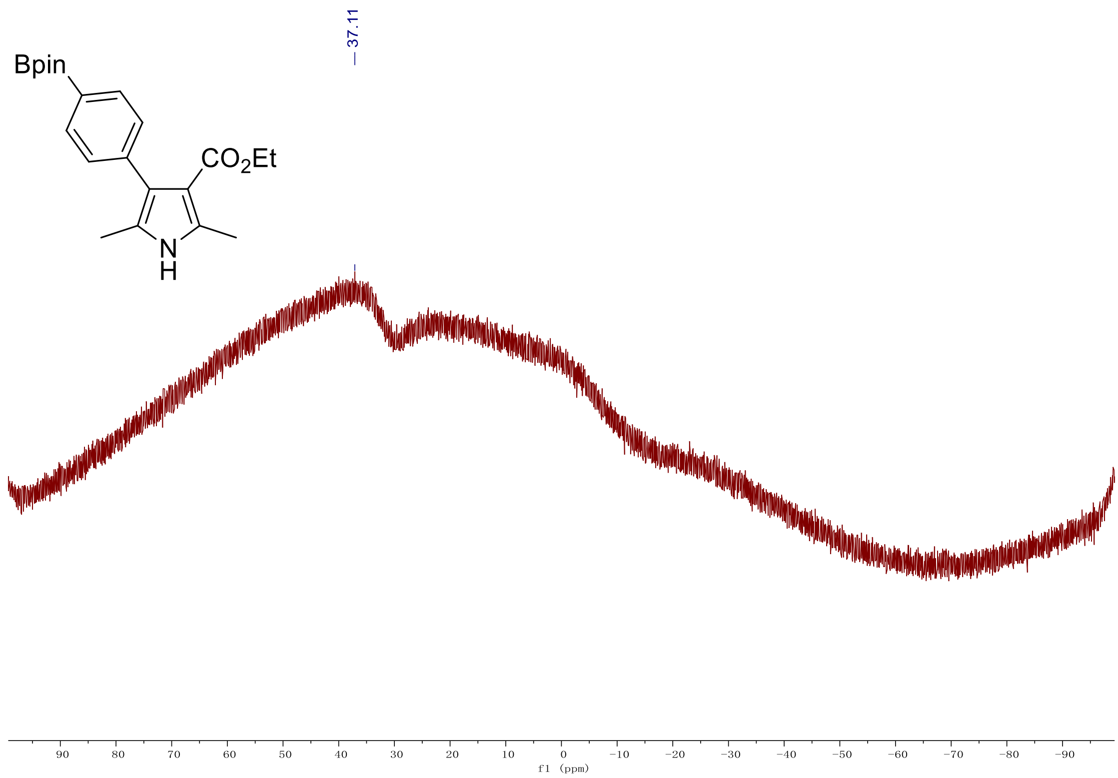


^{1}H NMR (400 MHz, $CDCl_3$) of **2l**

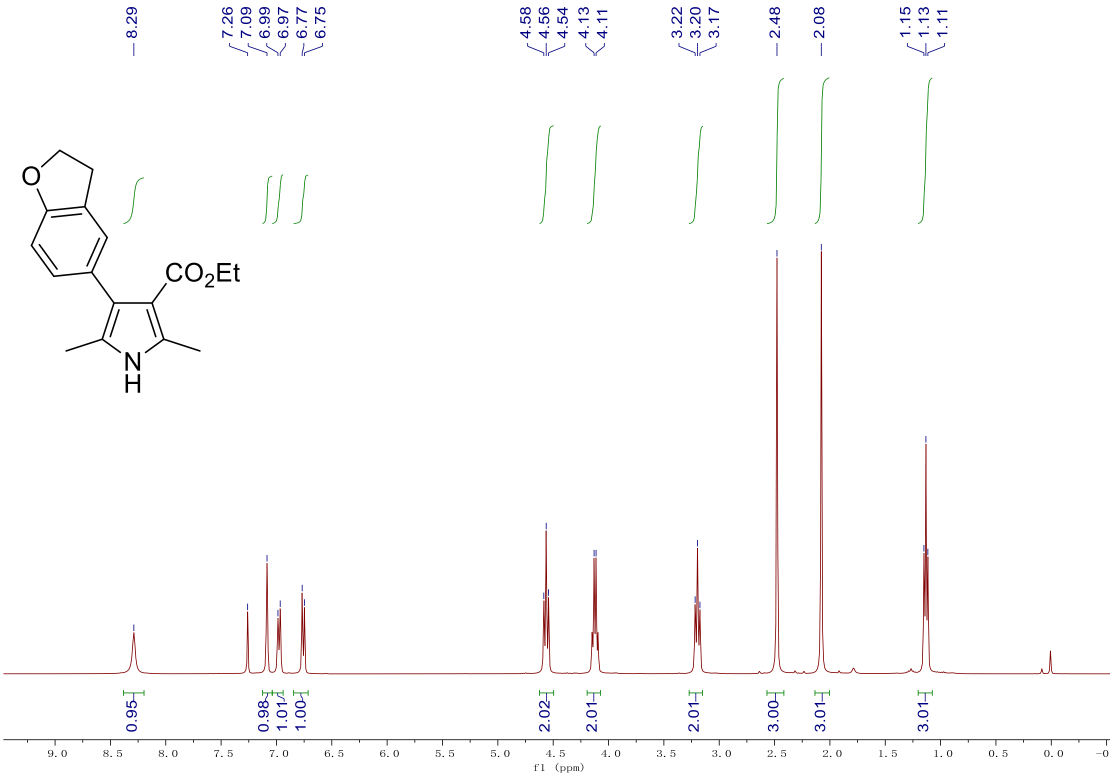
^{13}C NMR (100 MHz, $CDCl_3$) of **2l**



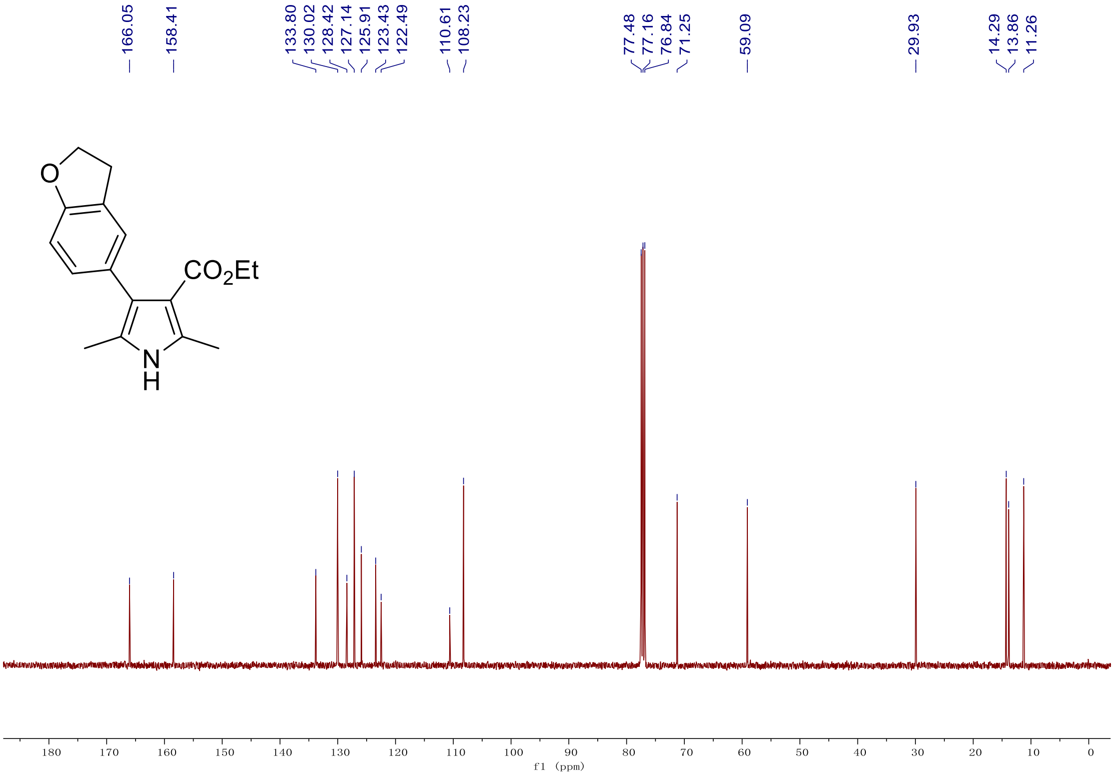
^{11}B NMR (128 MHz, $CDCl_3$) of **2l**



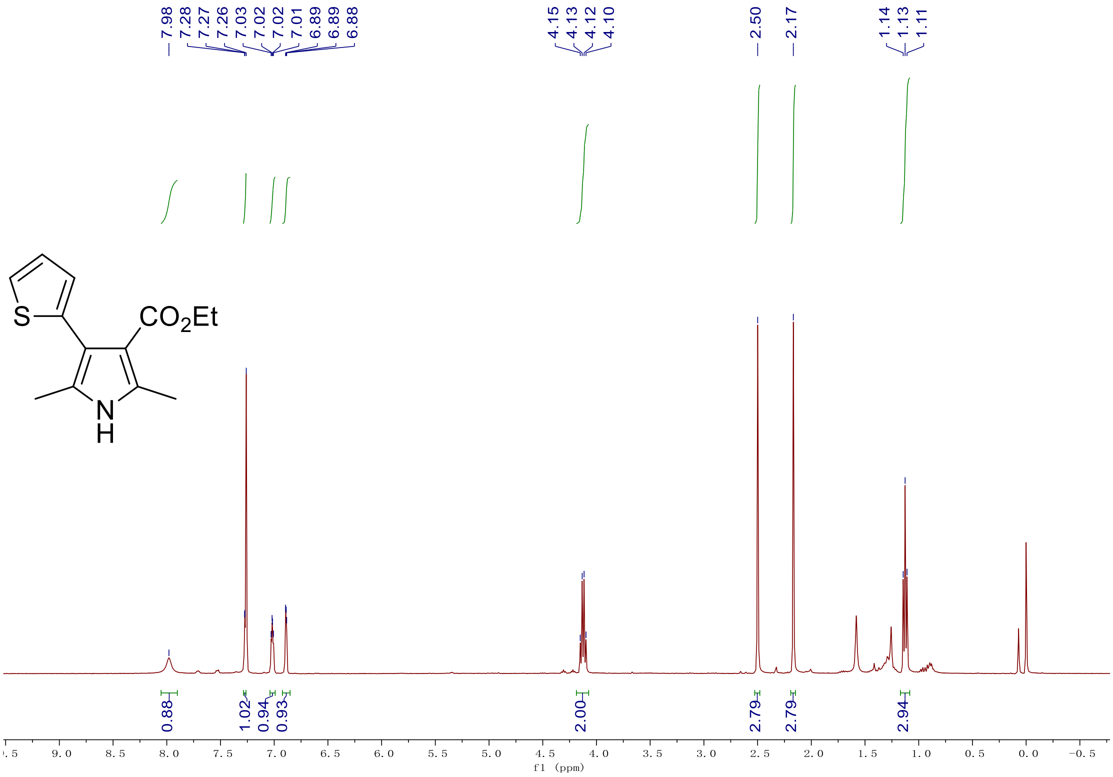
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



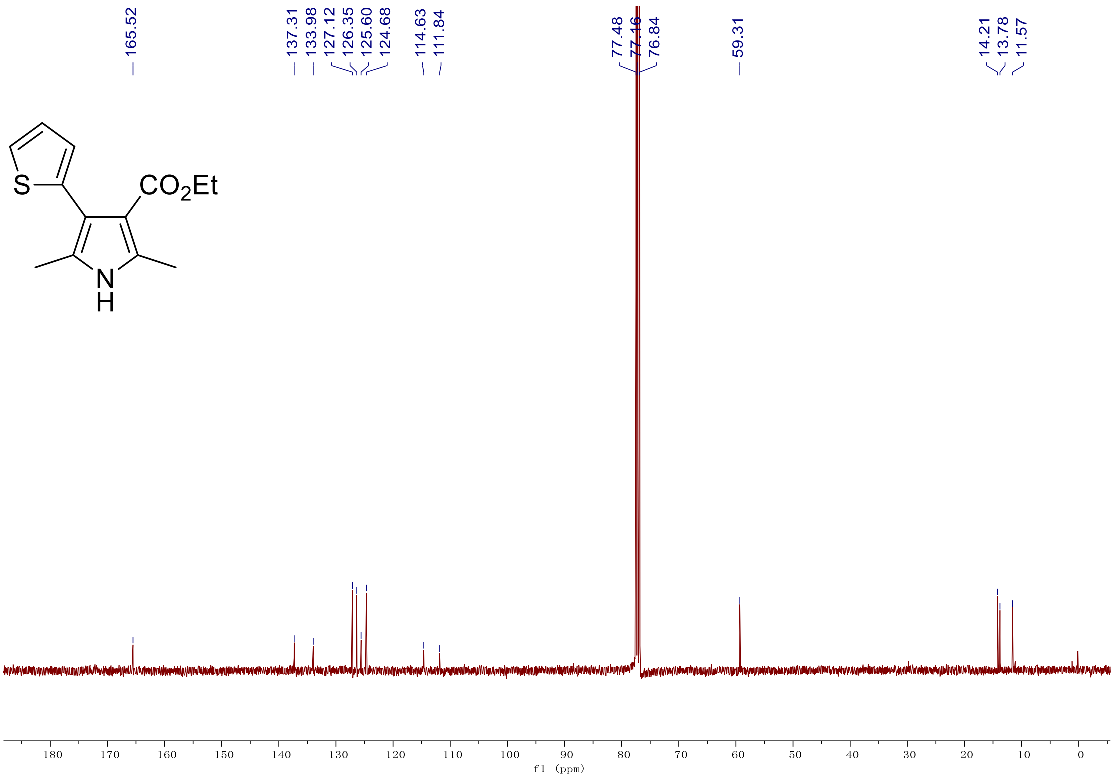
^{13}C NMR (100 MHz, $CDCl_3$) of **2m**



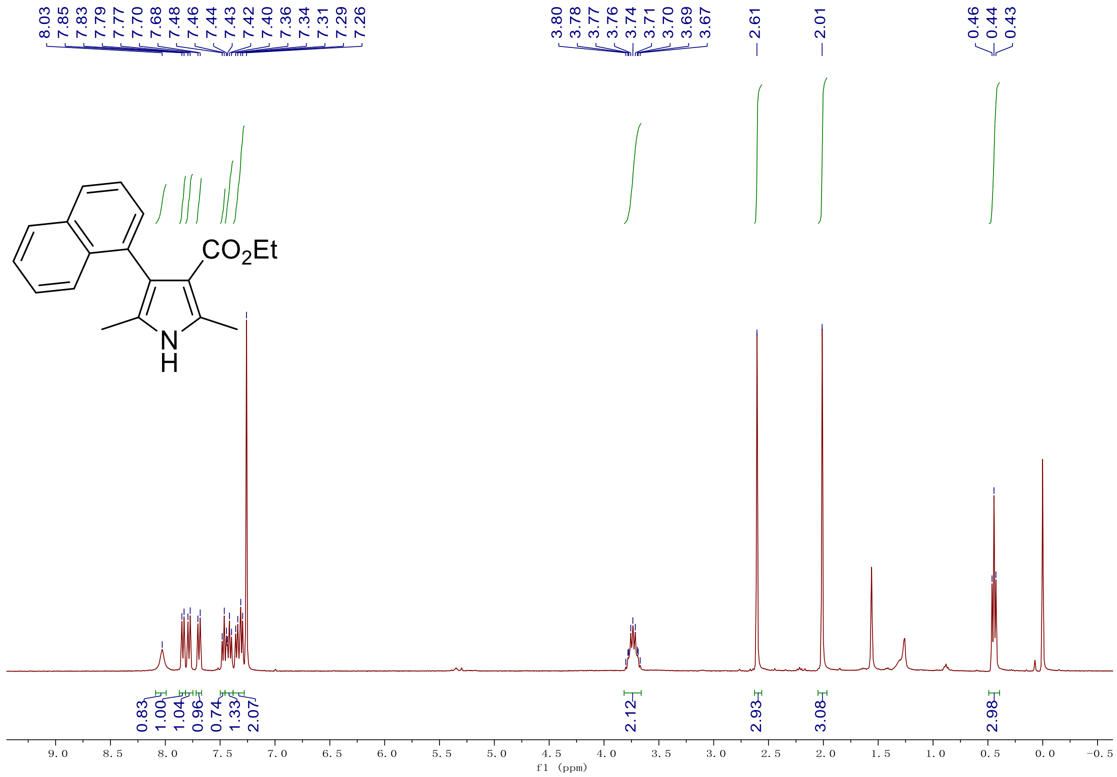
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



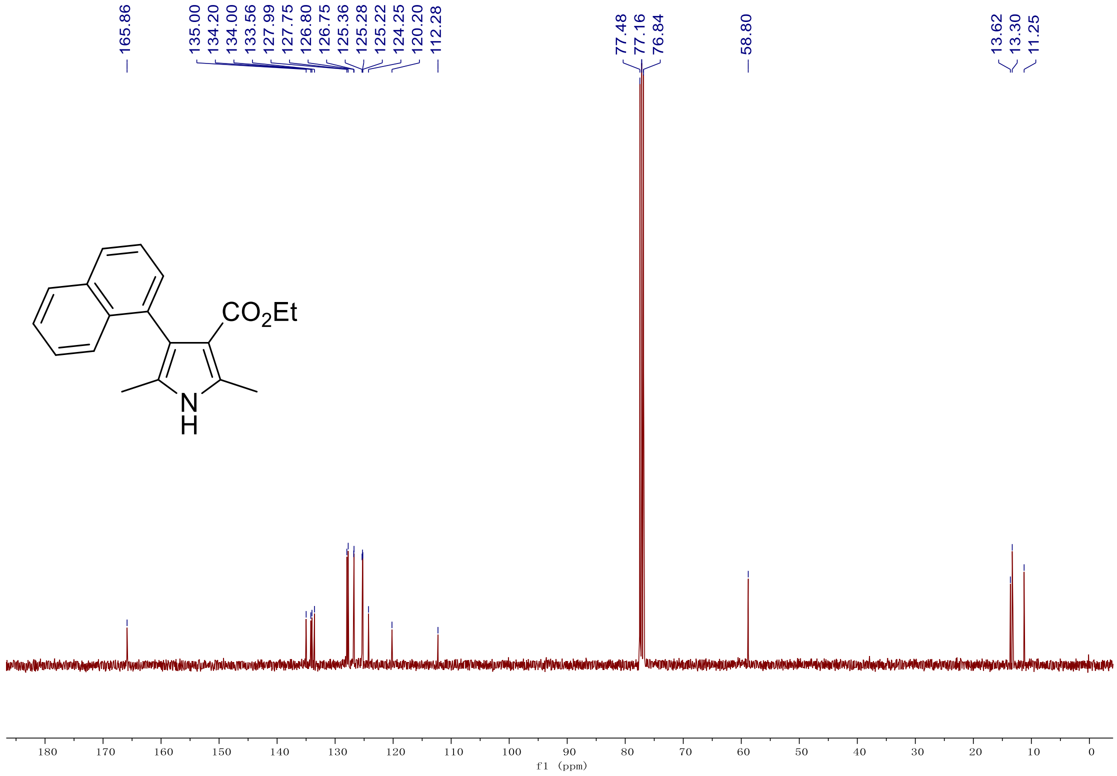
^{13}C NMR (100 MHz, $CDCl_3$) of **2n**



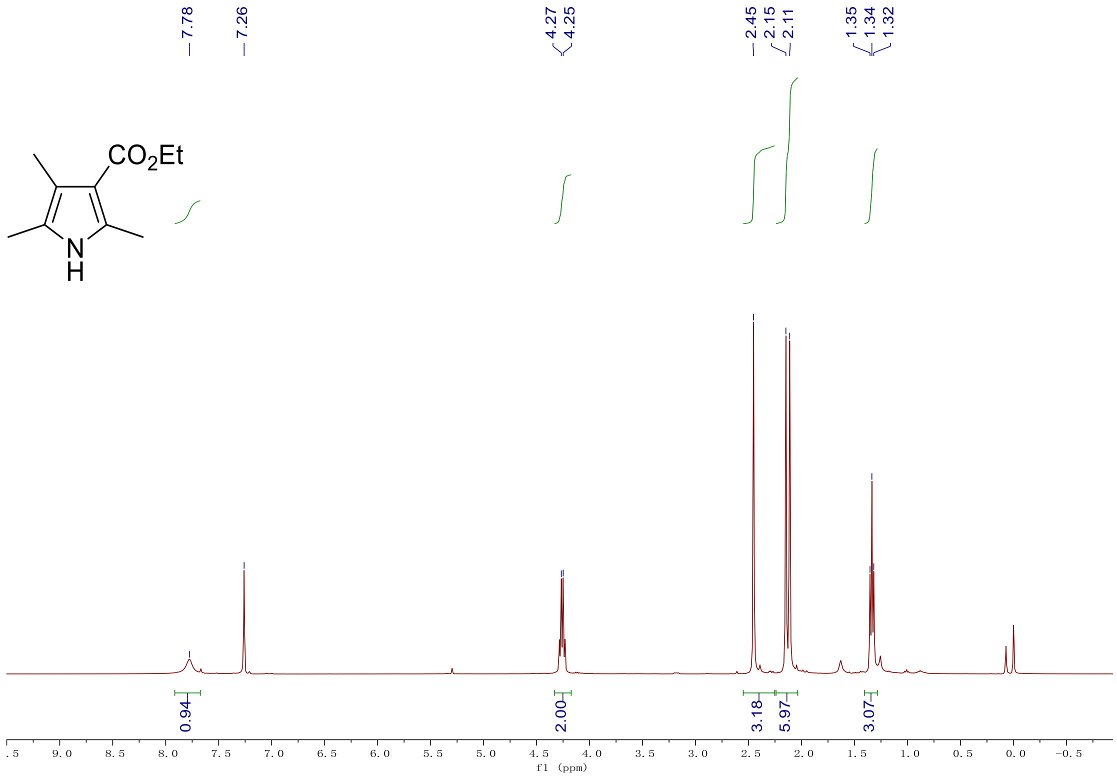
[1]H NMR (400 MHz, $CDCl_3$) of **2o**



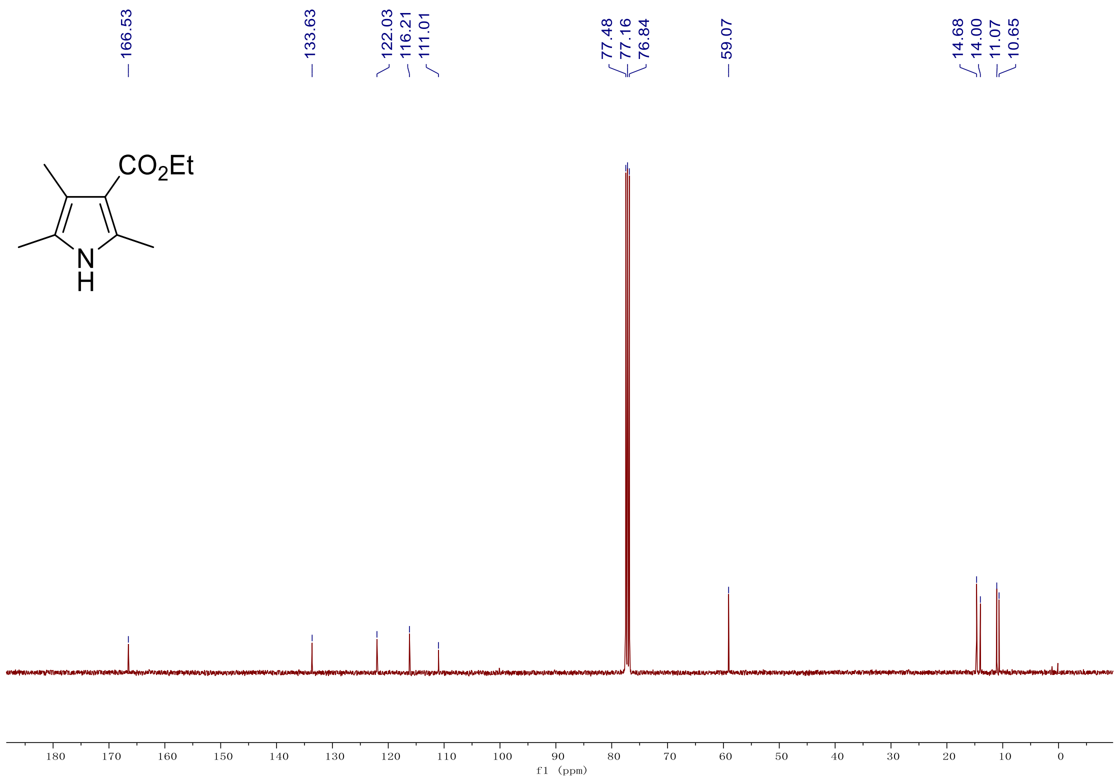
[13]C NMR (100 MHz, $CDCl_3$) of **2o**



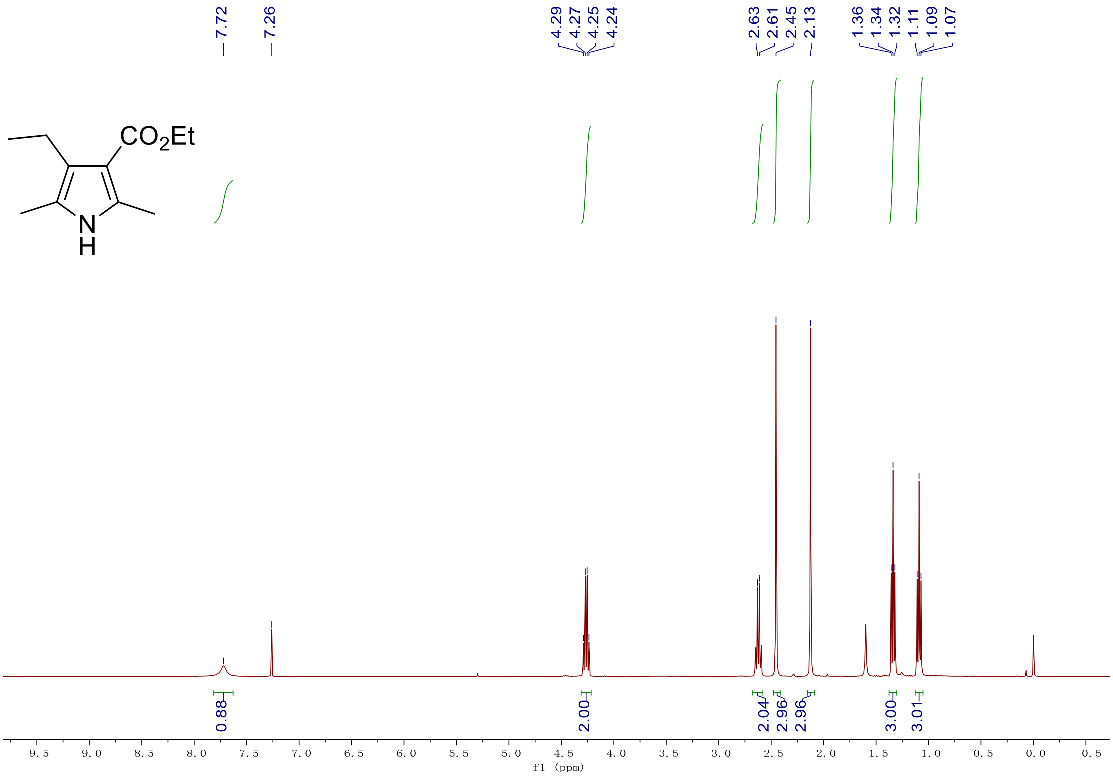
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



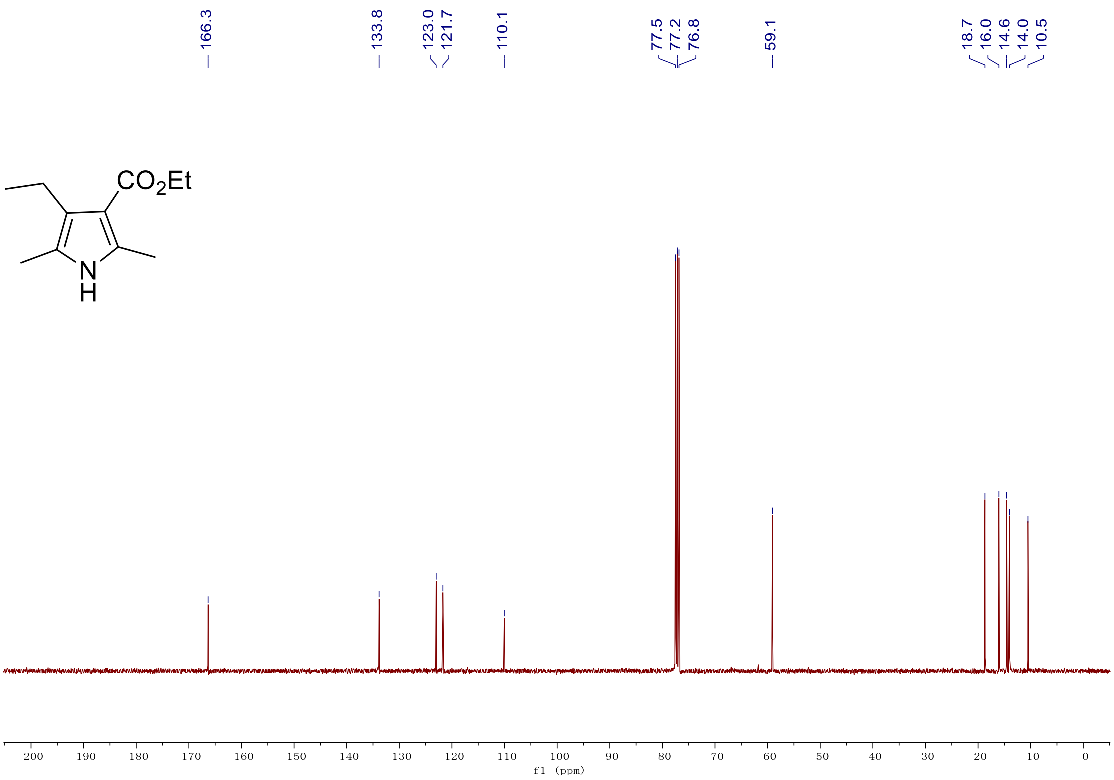
^{13}C NMR (100 MHz, $CDCl_3$) of **2p**



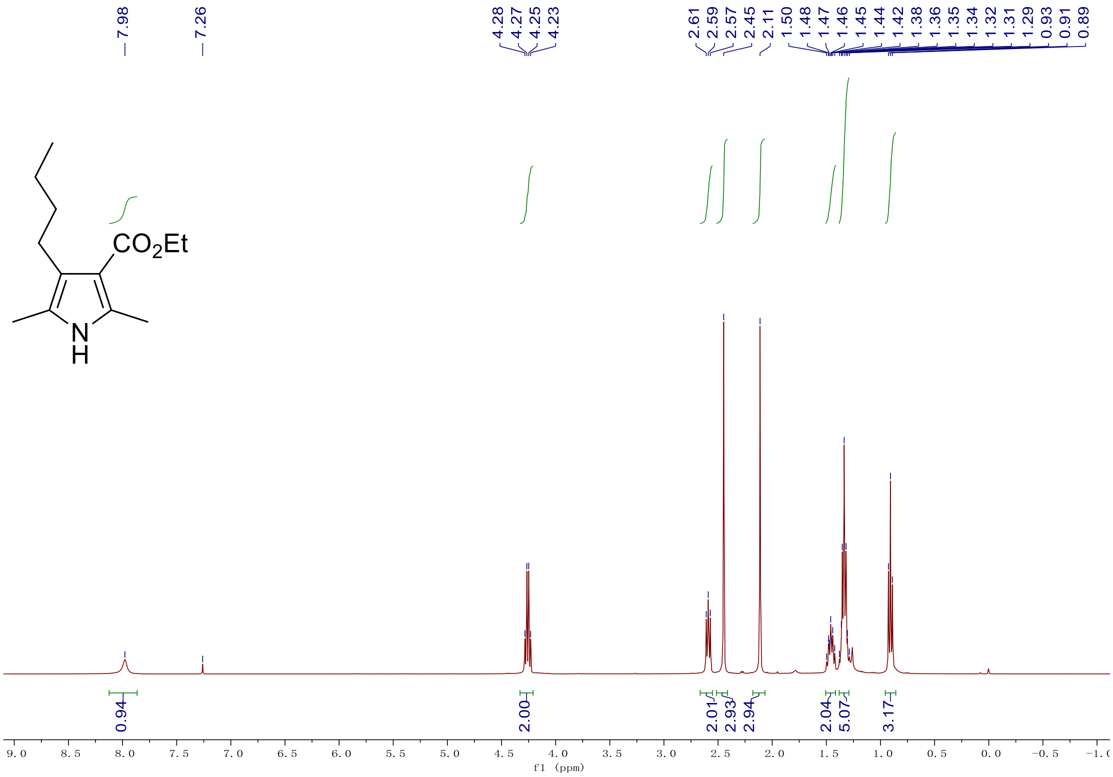
^{1}H NMR (400 MHz, $CDCl_3$) of **2q**



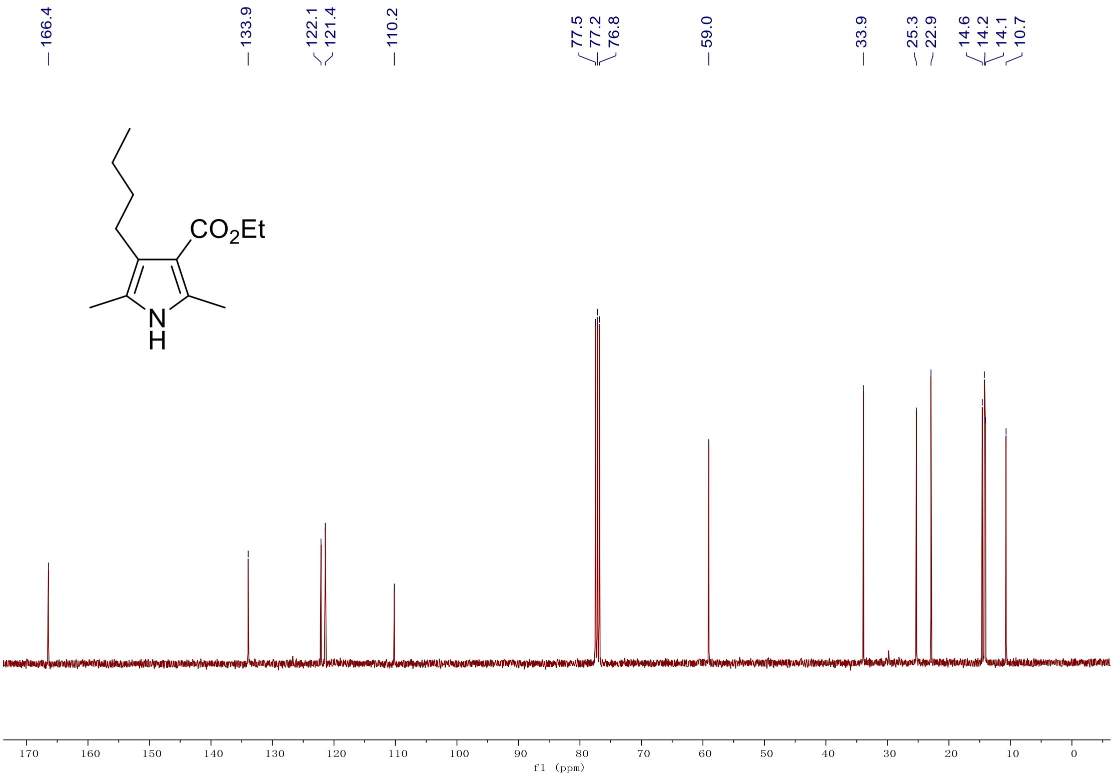
^{13}C NMR (100 MHz, $CDCl_3$) of **2q**



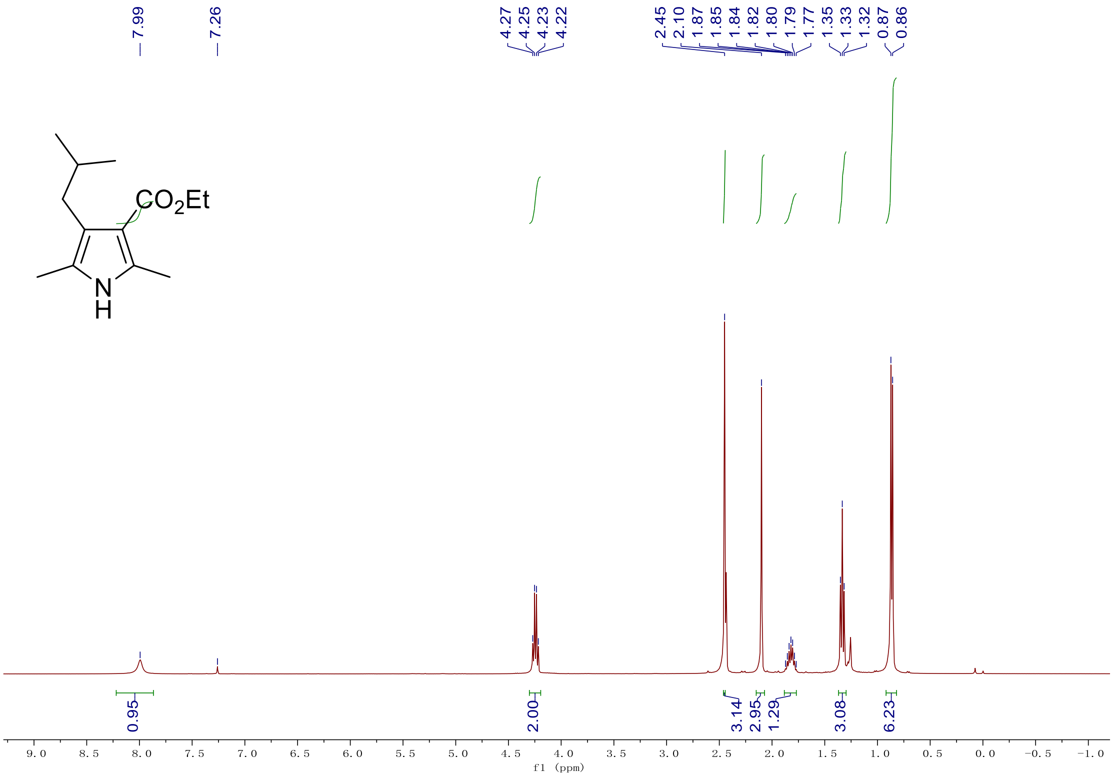
^{1}H NMR (400 MHz, $CDCl_3$) of **2r**



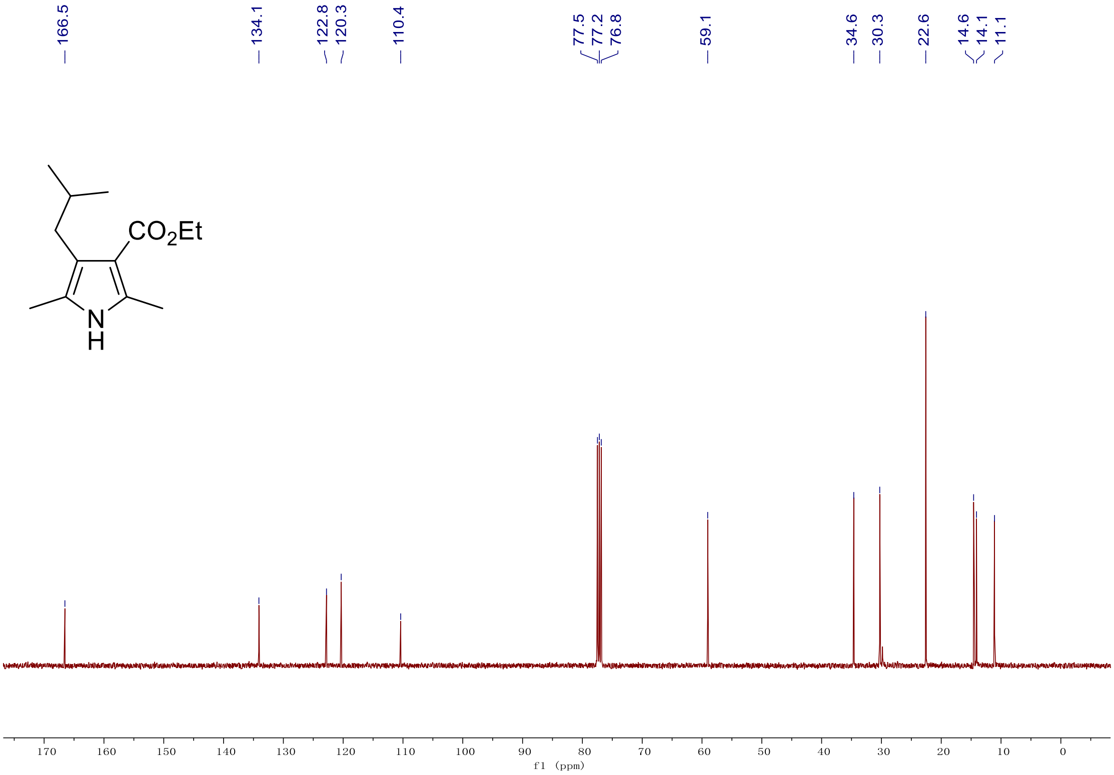
^{13}C NMR (100 MHz, $CDCl_3$) of **2r**



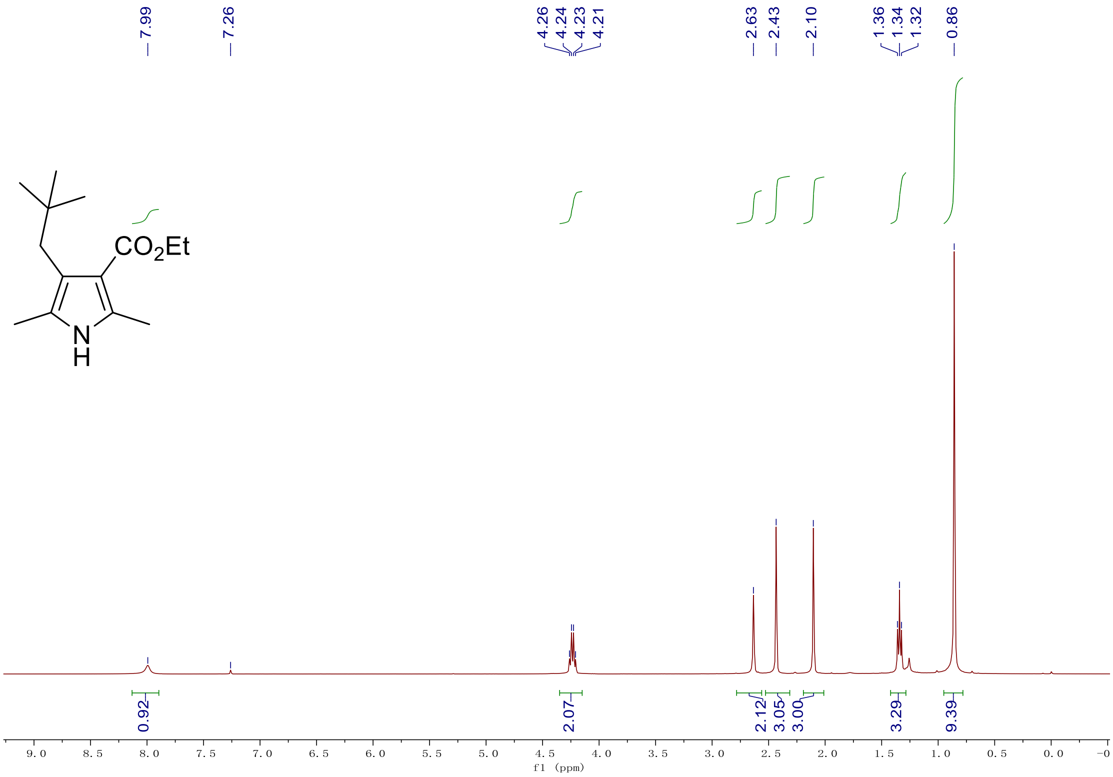
^{1}H NMR (400 MHz, $CDCl_3$) of **2s**



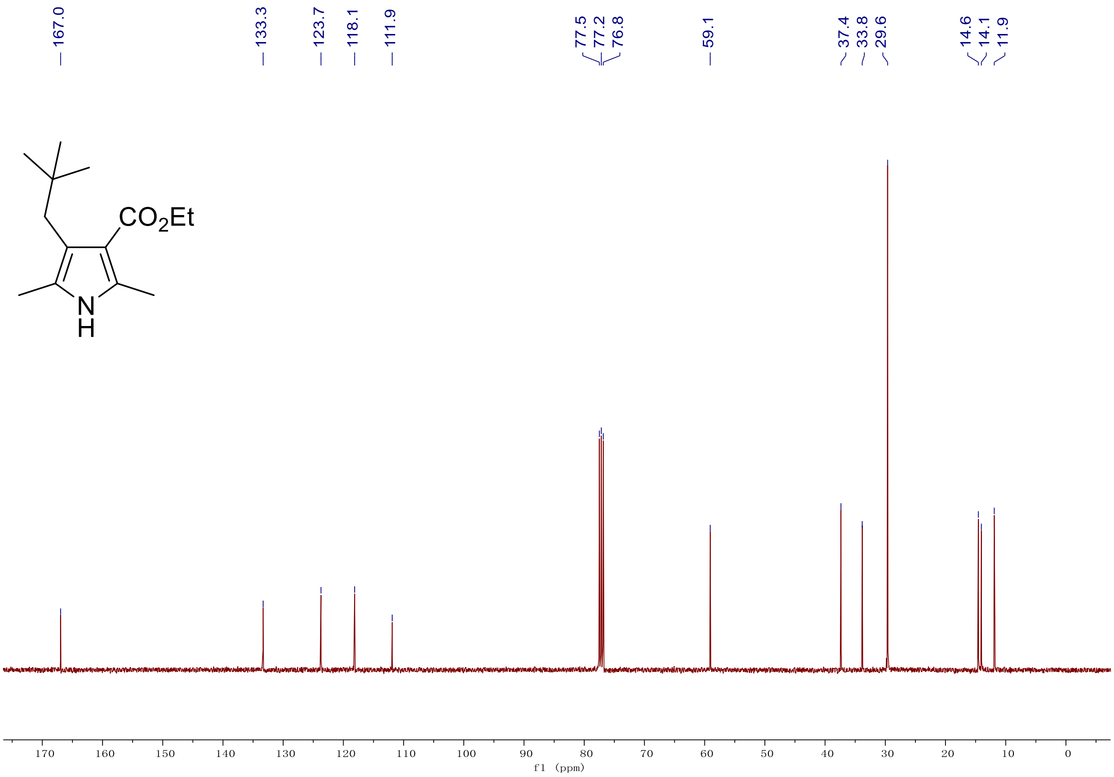
^{13}C NMR (100 MHz, $CDCl_3$) of **2s**



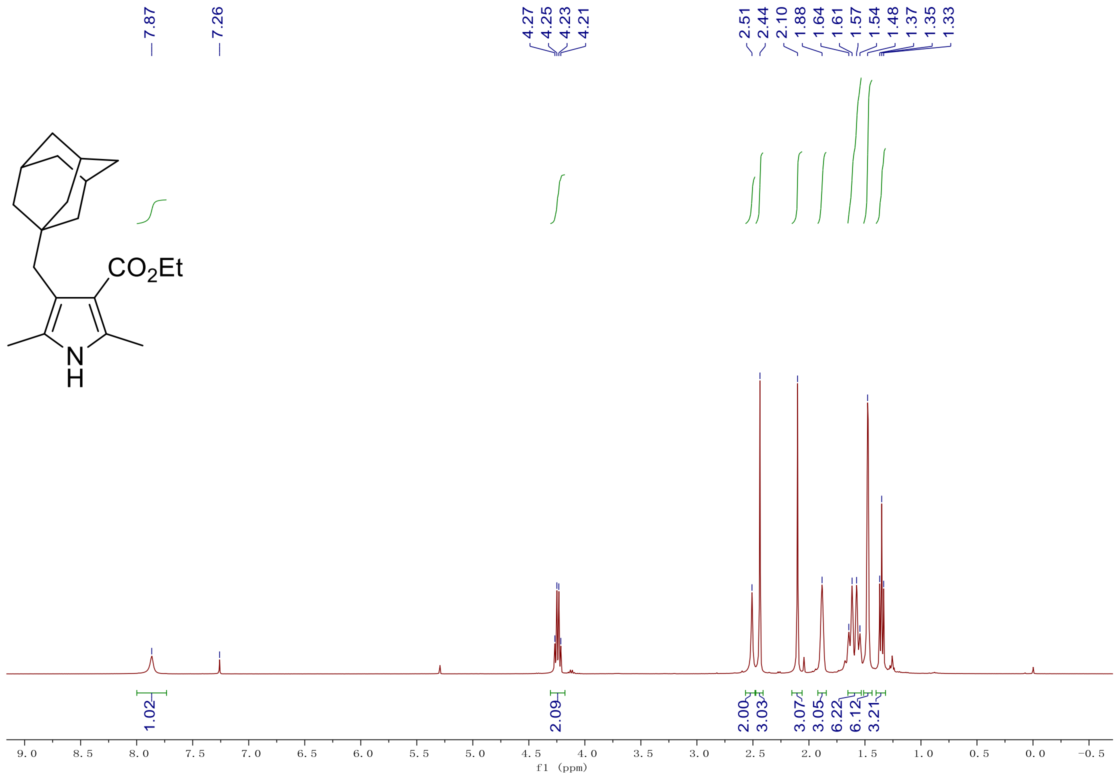
^{1}H NMR (400 MHz, $CDCl_3$) of **2t**



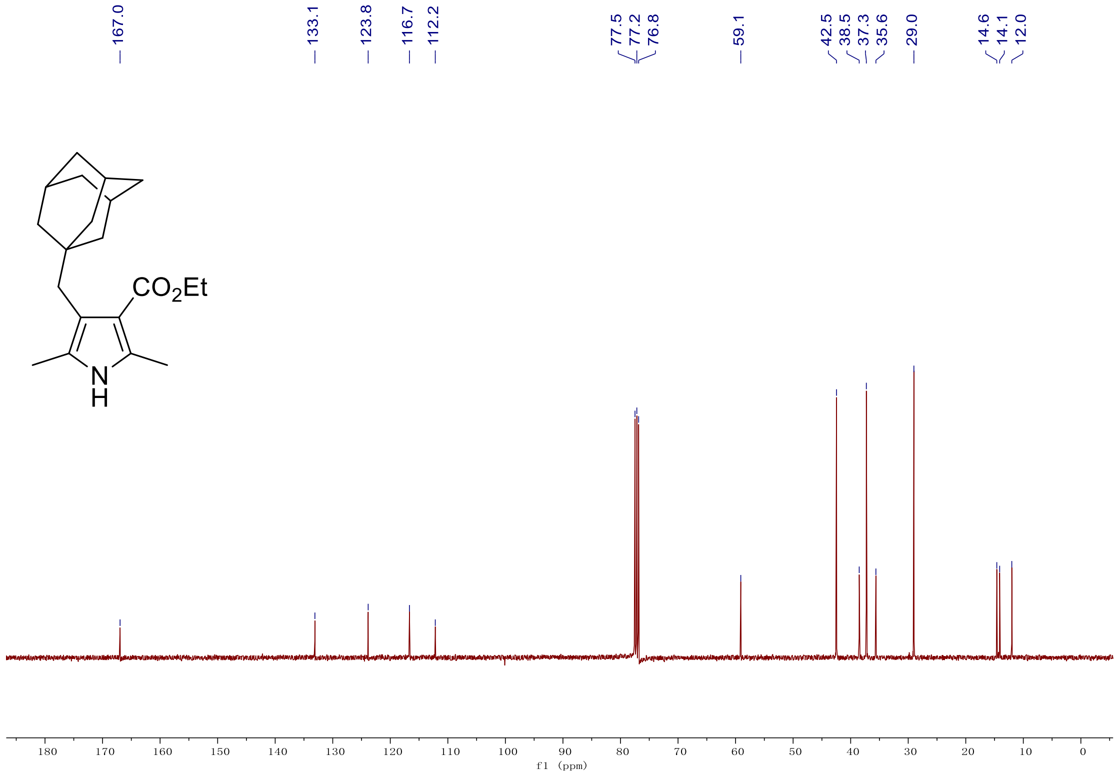
^{13}C NMR (100 MHz, $CDCl_3$) of **2t**



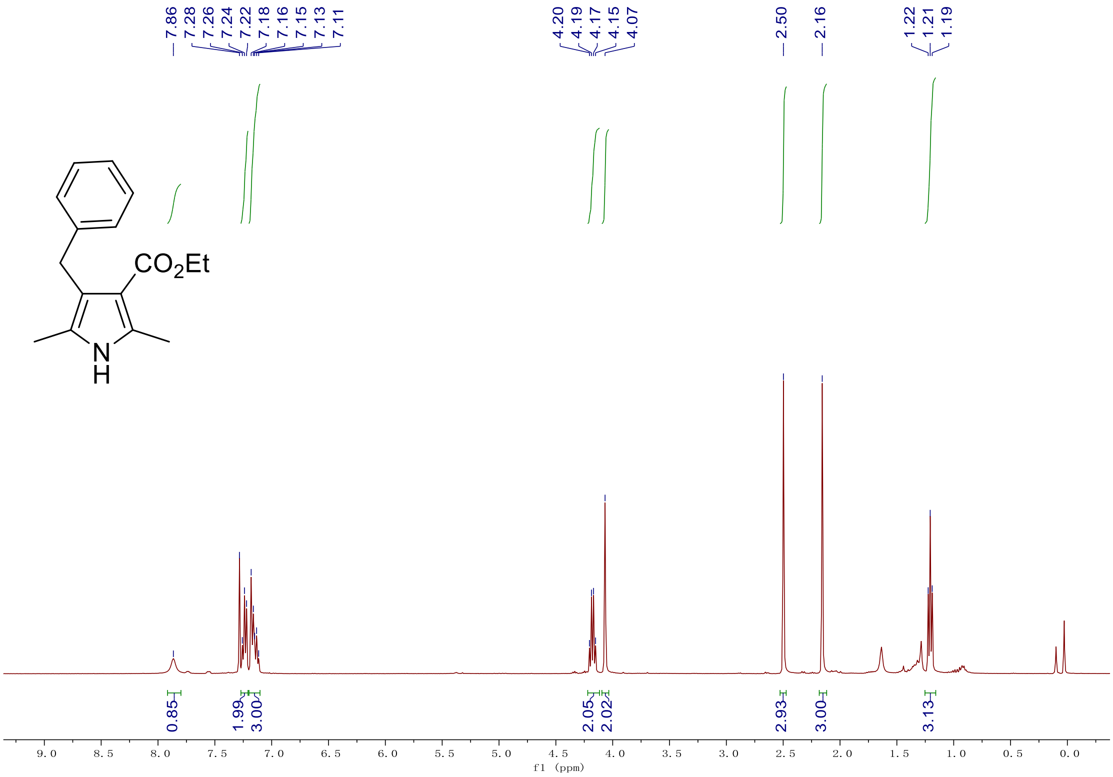
^{1}H NMR (400 MHz, $CDCl_3$) of **2u**



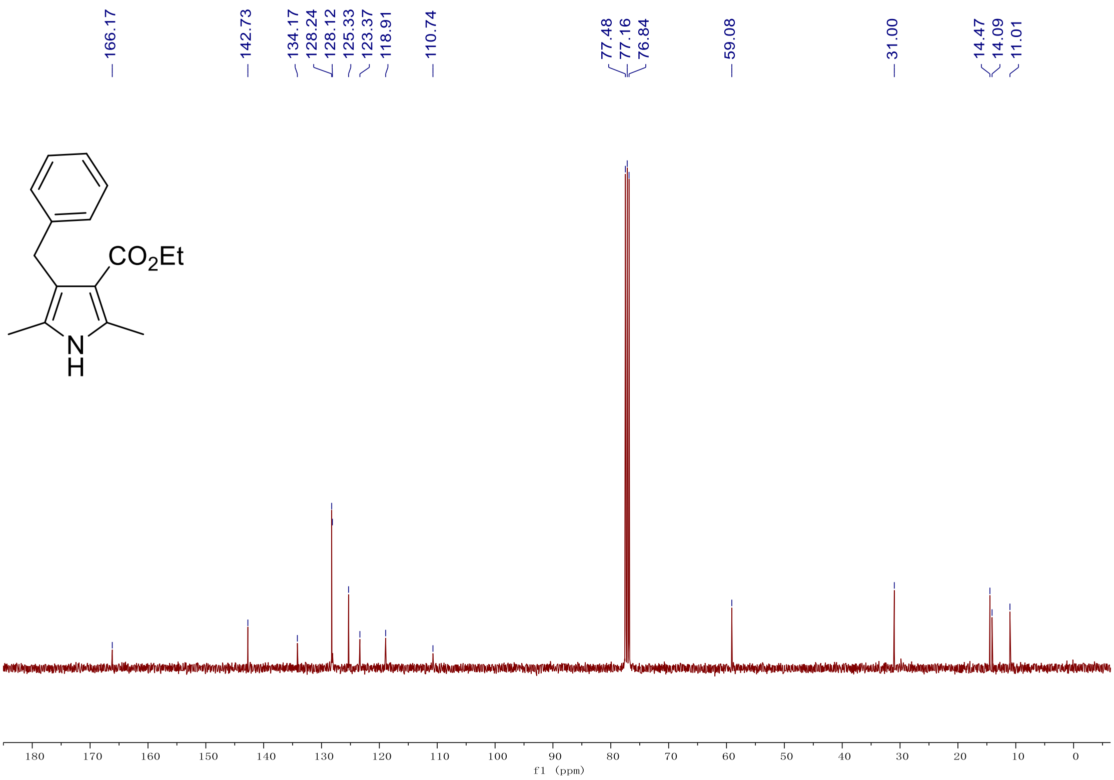
^{13}C NMR (100 MHz, $CDCl_3$) of **2u**



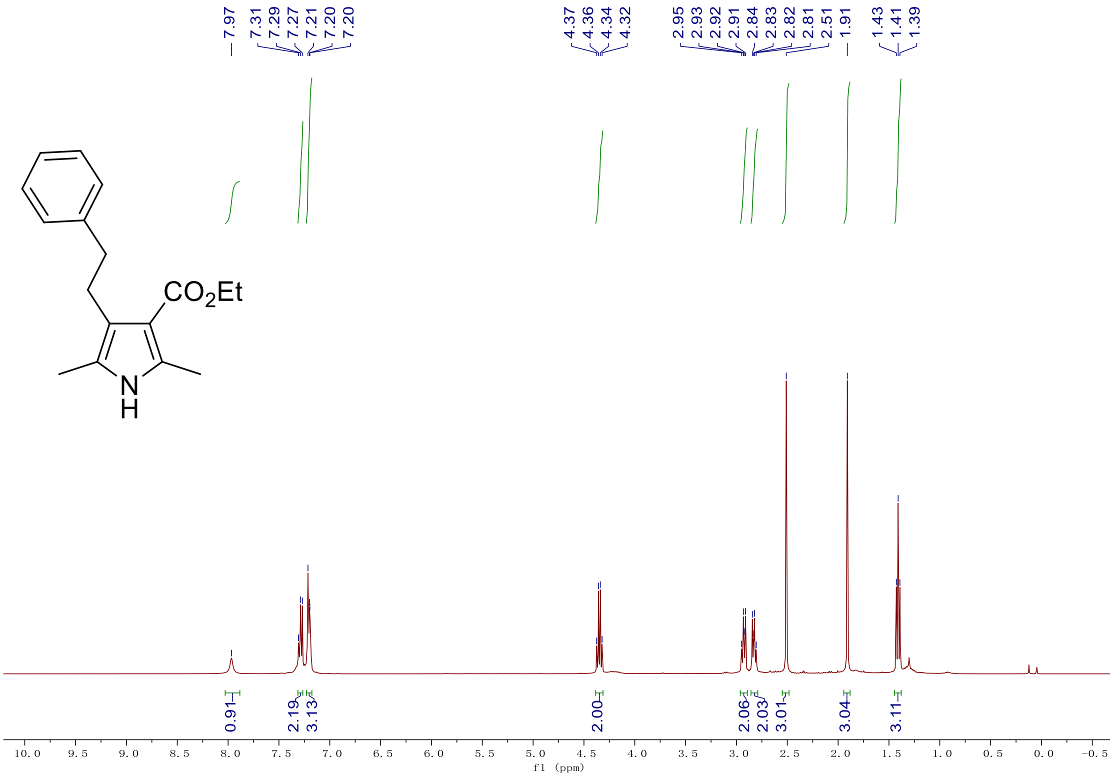
^{1}H NMR (400 MHz, $CDCl_3$) of **2v**



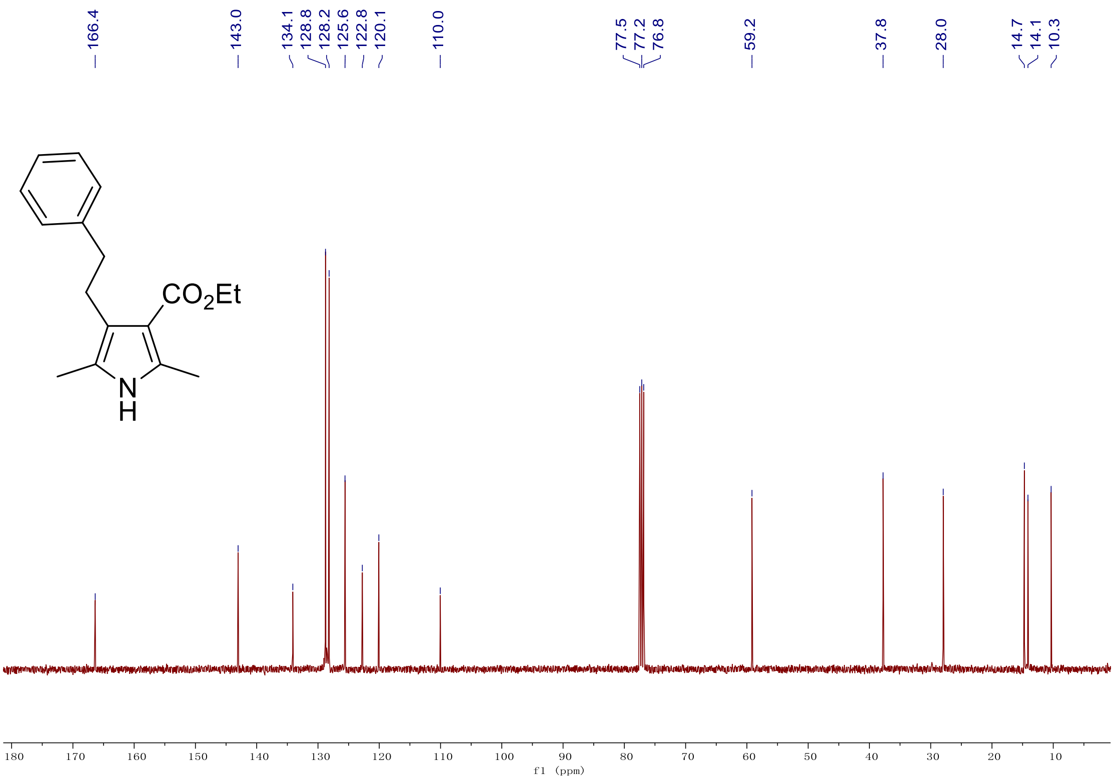
^{13}C NMR (100 MHz, $CDCl_3$) of **2v**



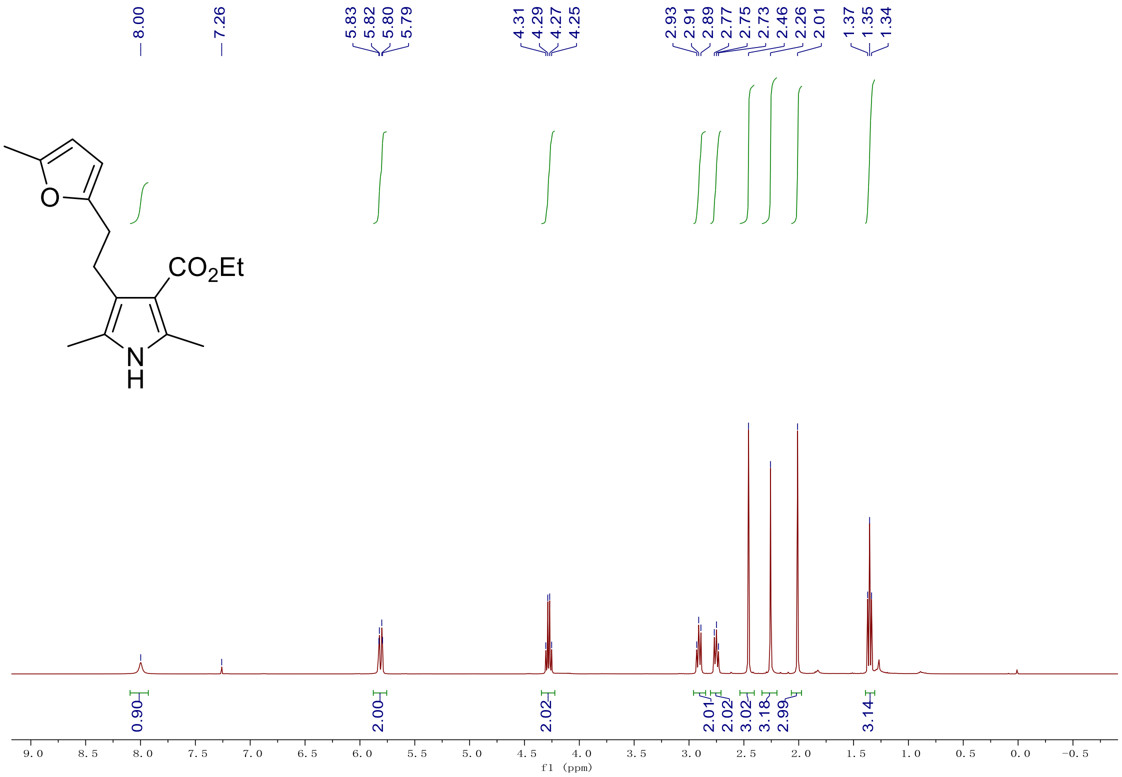
^{1}H NMR (400 MHz, $CDCl_3$) of **2w**



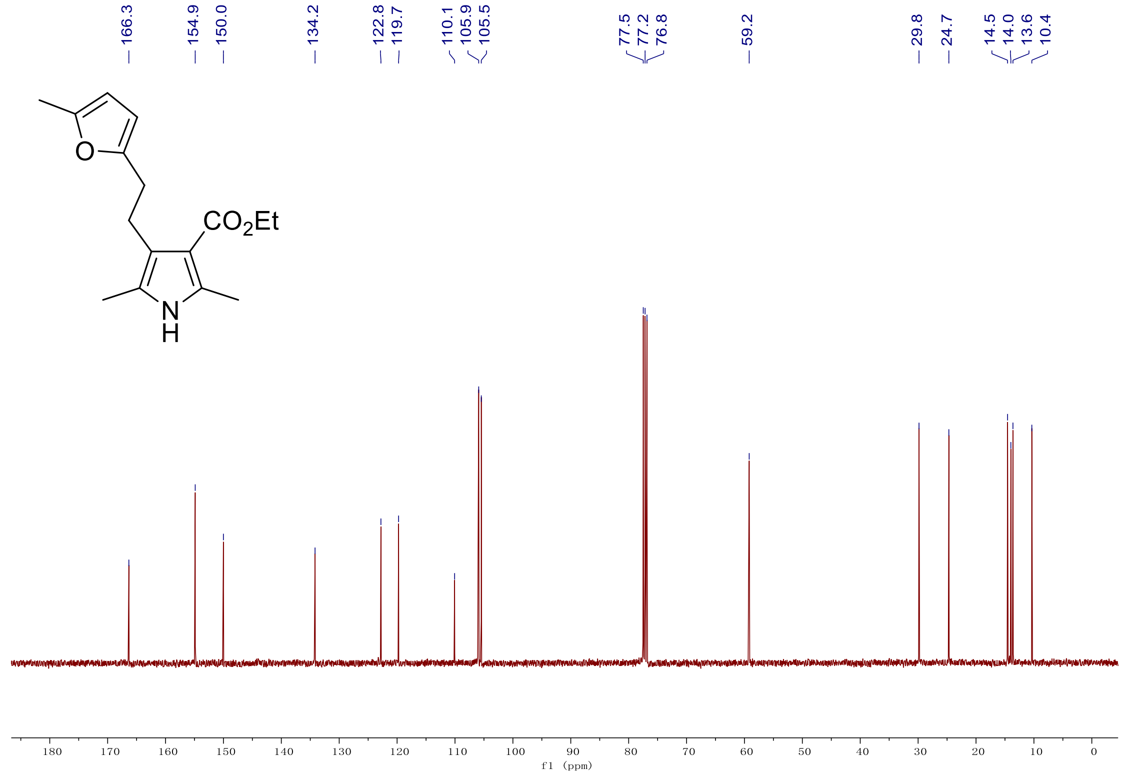
^{13}C NMR (100 MHz, $CDCl_3$) of **2w**



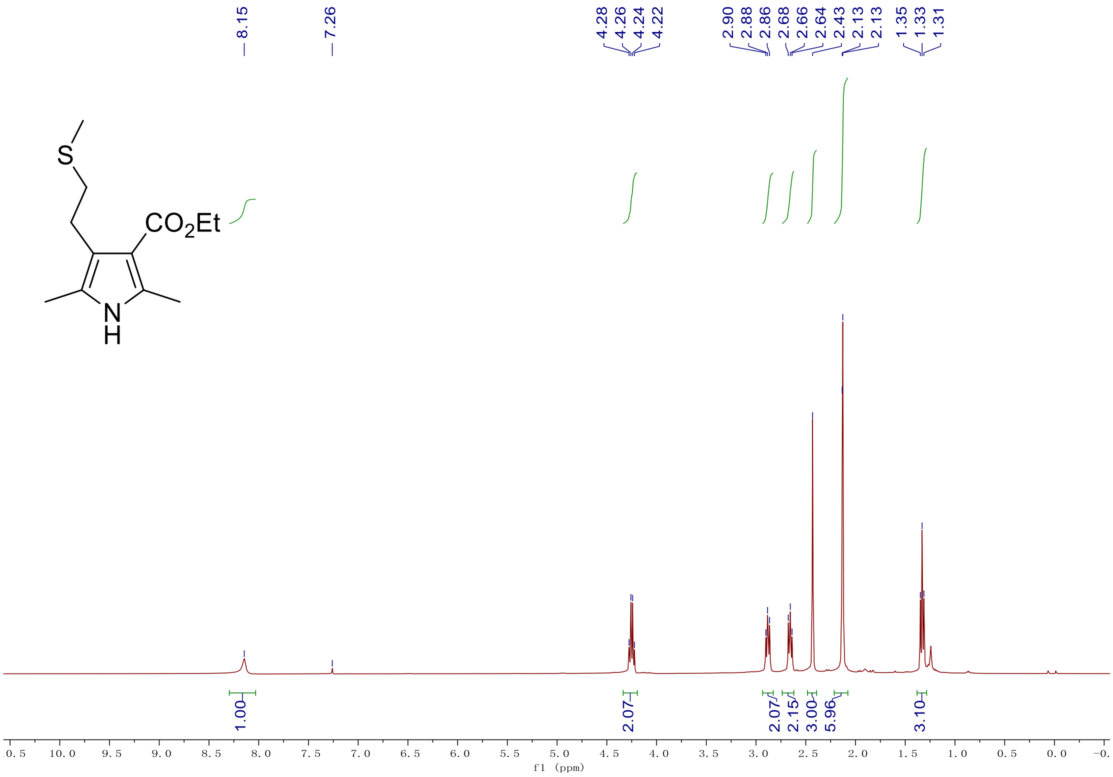
[1]H NMR (400 MHz, $CDCl_3$) of **2x**



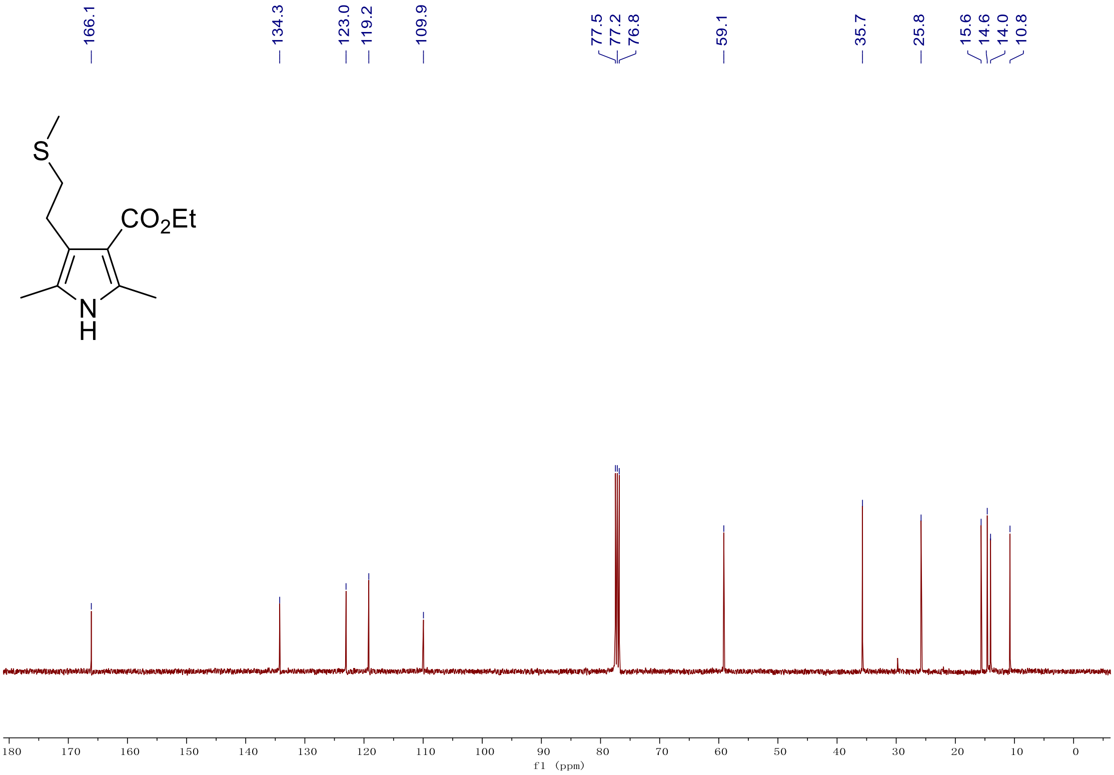
[13]C NMR (100 MHz, $CDCl_3$) of **2x**



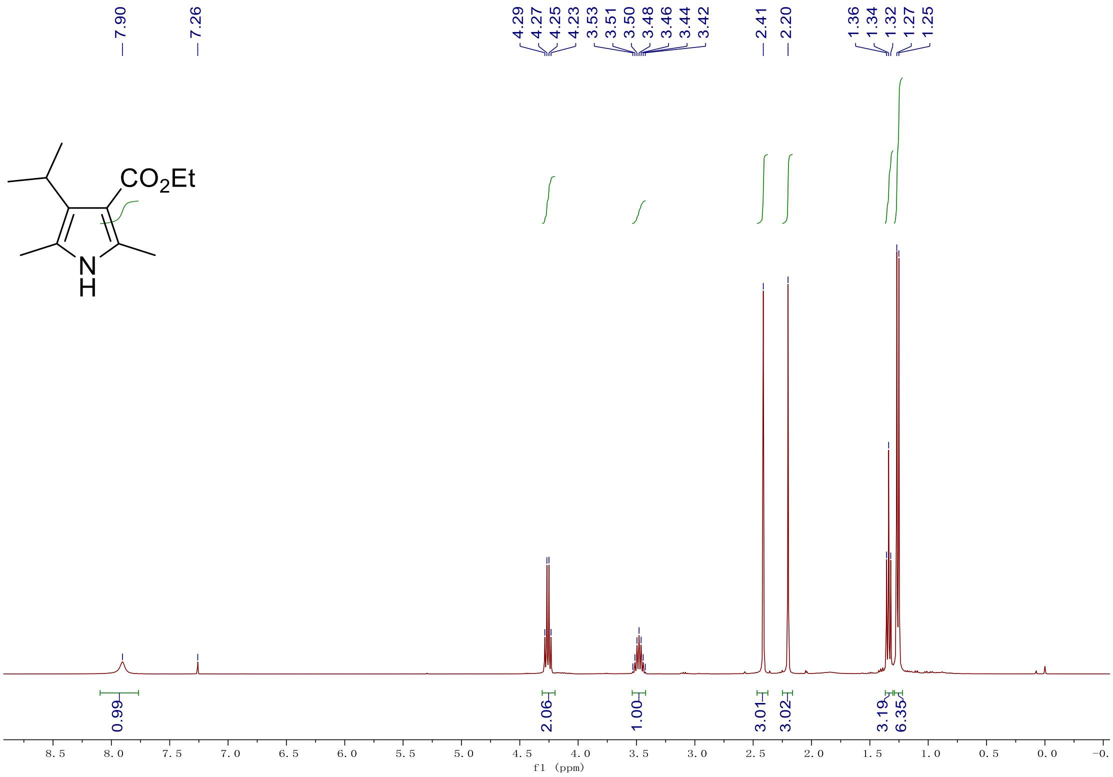
^{1}H NMR (400 MHz, $CDCl_3$) of **2y**



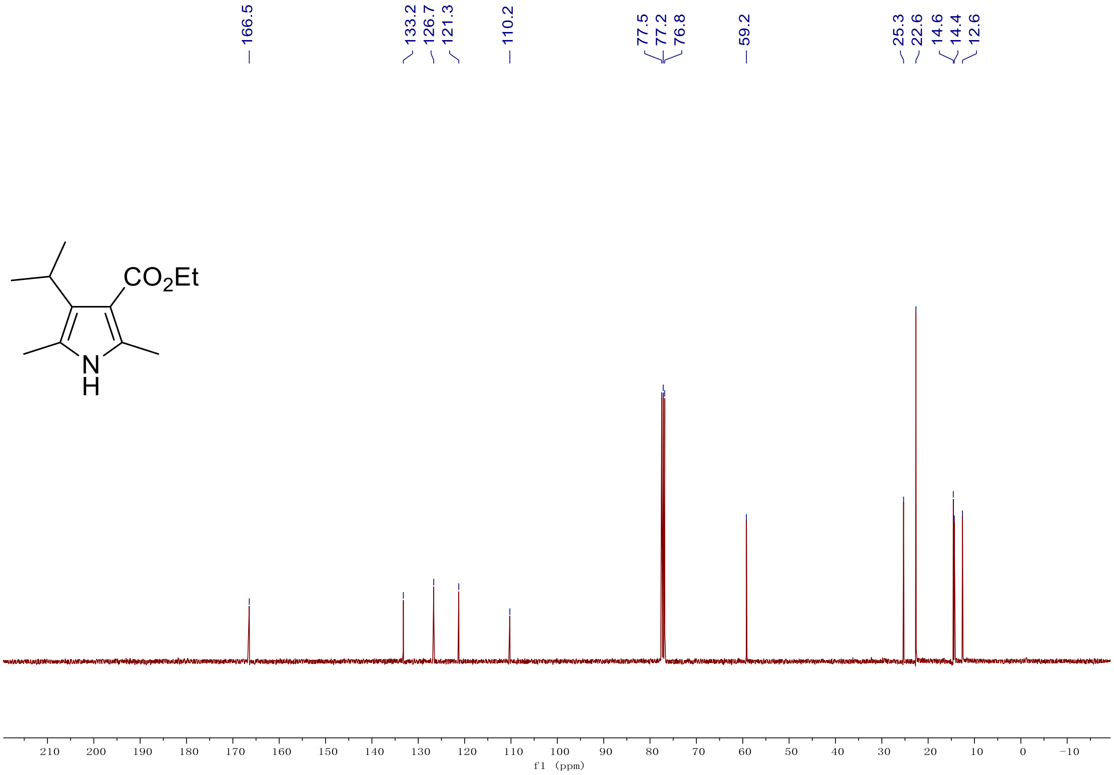
^{13}C NMR (100 MHz, $CDCl_3$) of **2y**



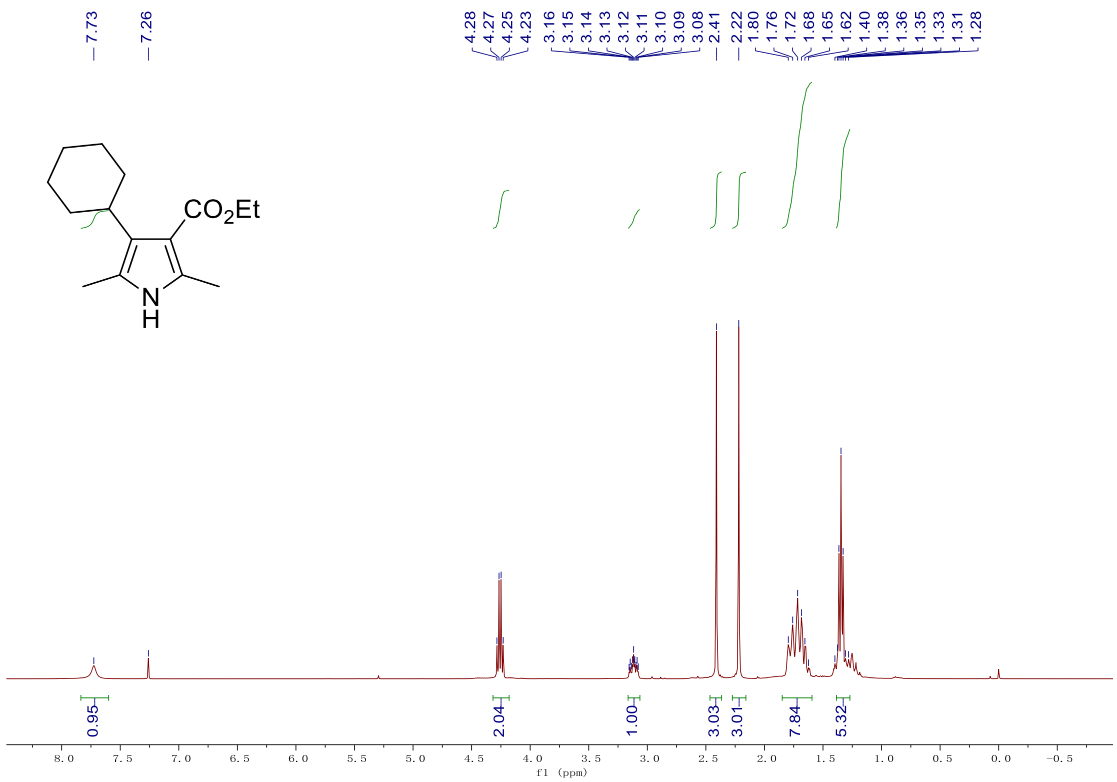
^{1}H NMR (400 MHz, $CDCl_3$) of **2z**



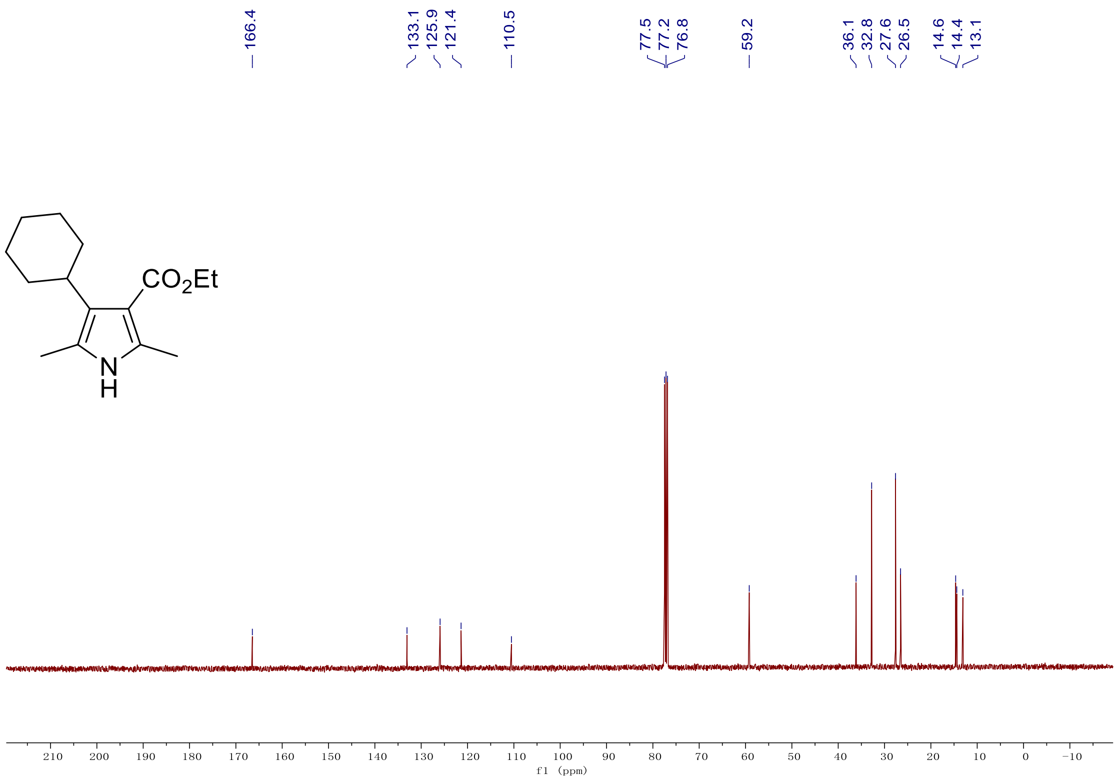
^{13}C NMR (100 MHz, $CDCl_3$) of **2z**



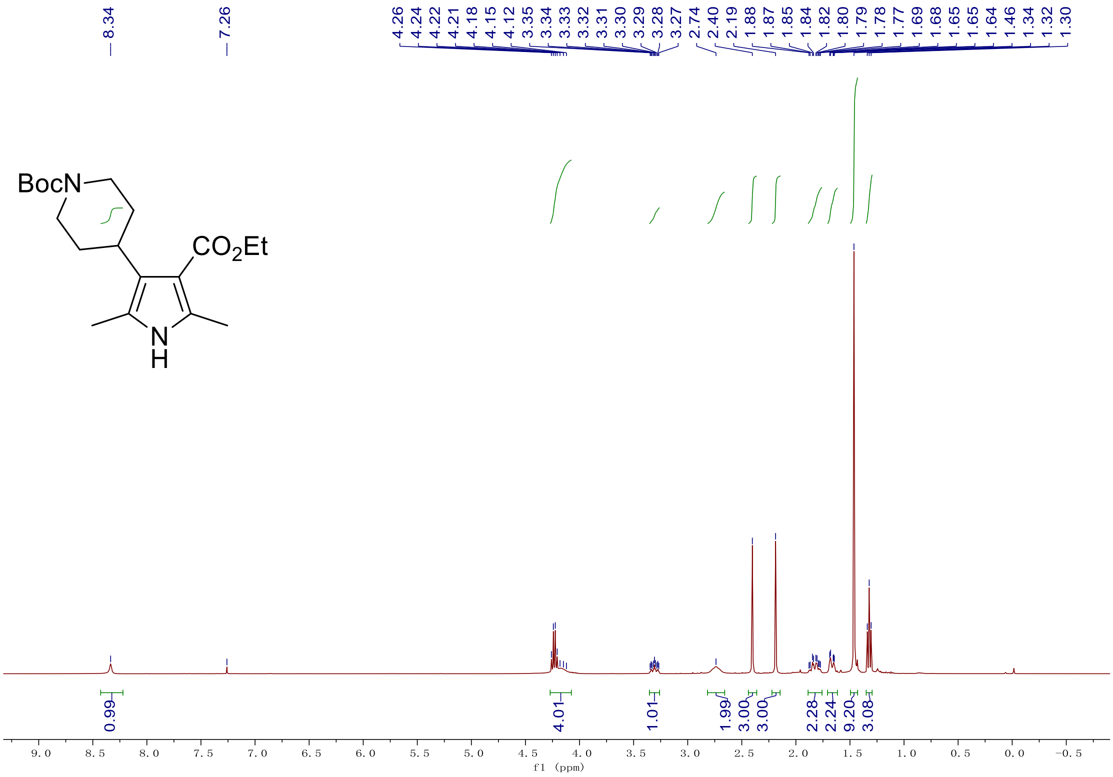
[1]H NMR (400 MHz, $CDCl_3$) of **2aa**



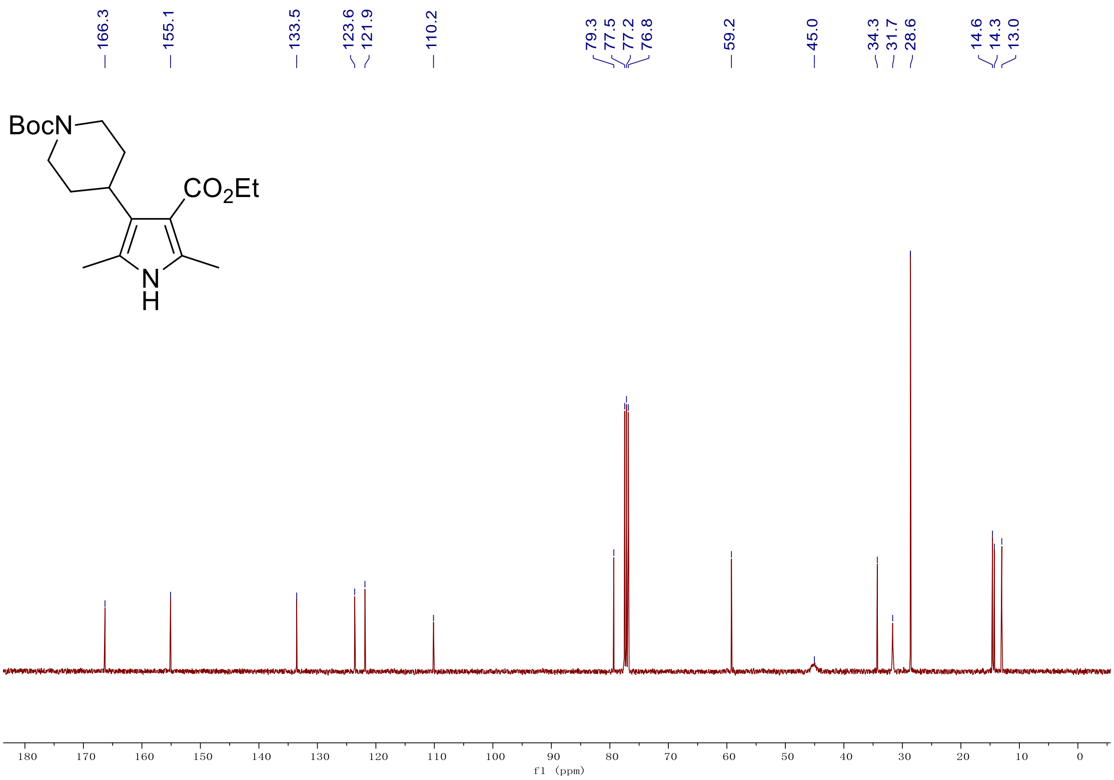
[13]C NMR (100 MHz, $CDCl_3$) of **2aa**



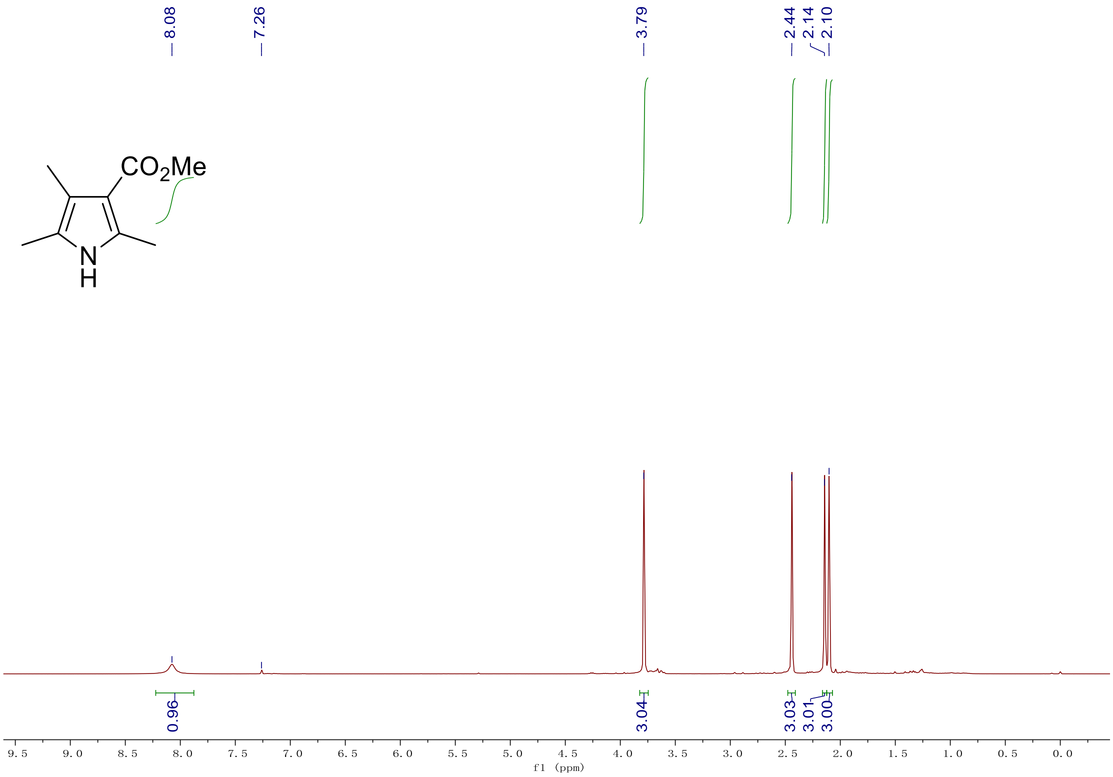
[1]H NMR (400 MHz, $CDCl_3$) of **2ab**



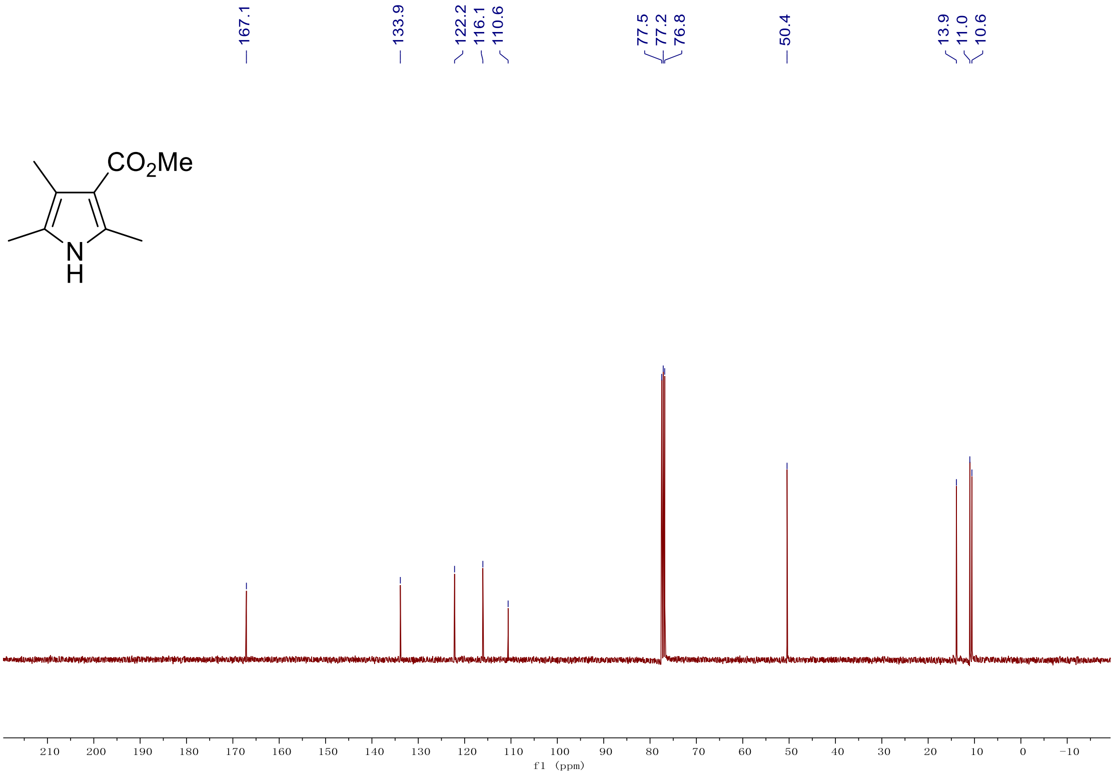
[13]C NMR (100 MHz, $CDCl_3$) of **2ab**



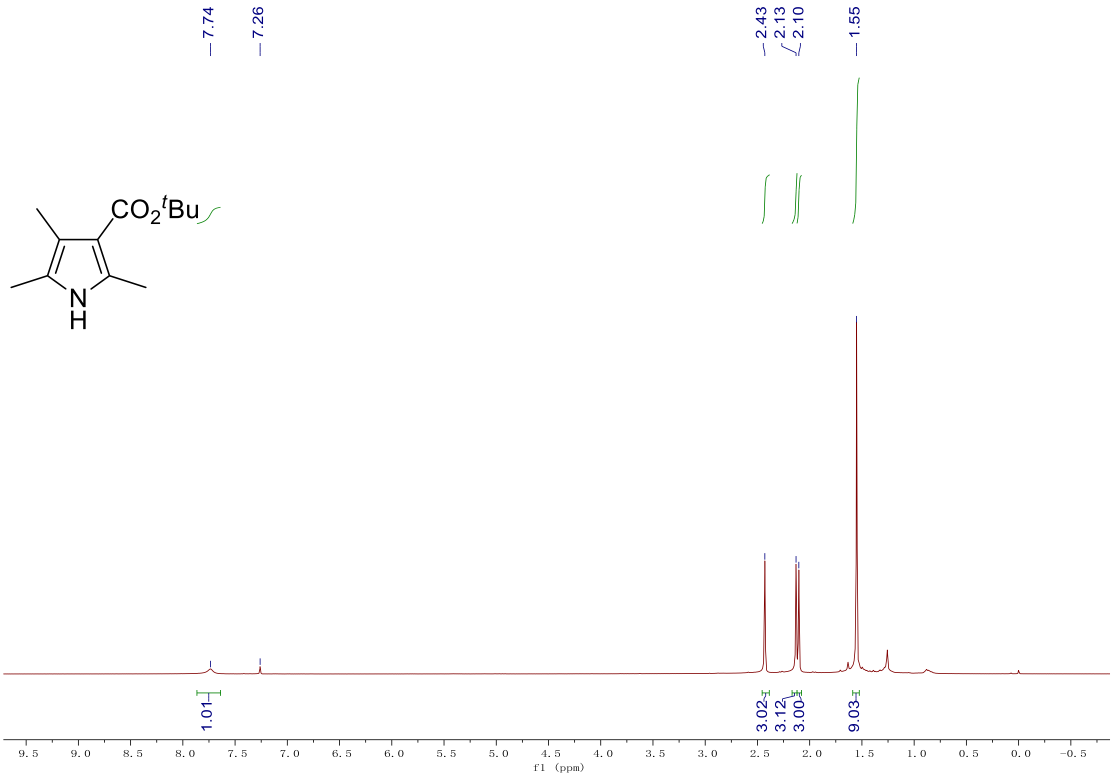
^{1}H NMR (400 MHz, $CDCl_3$) of **2ac**



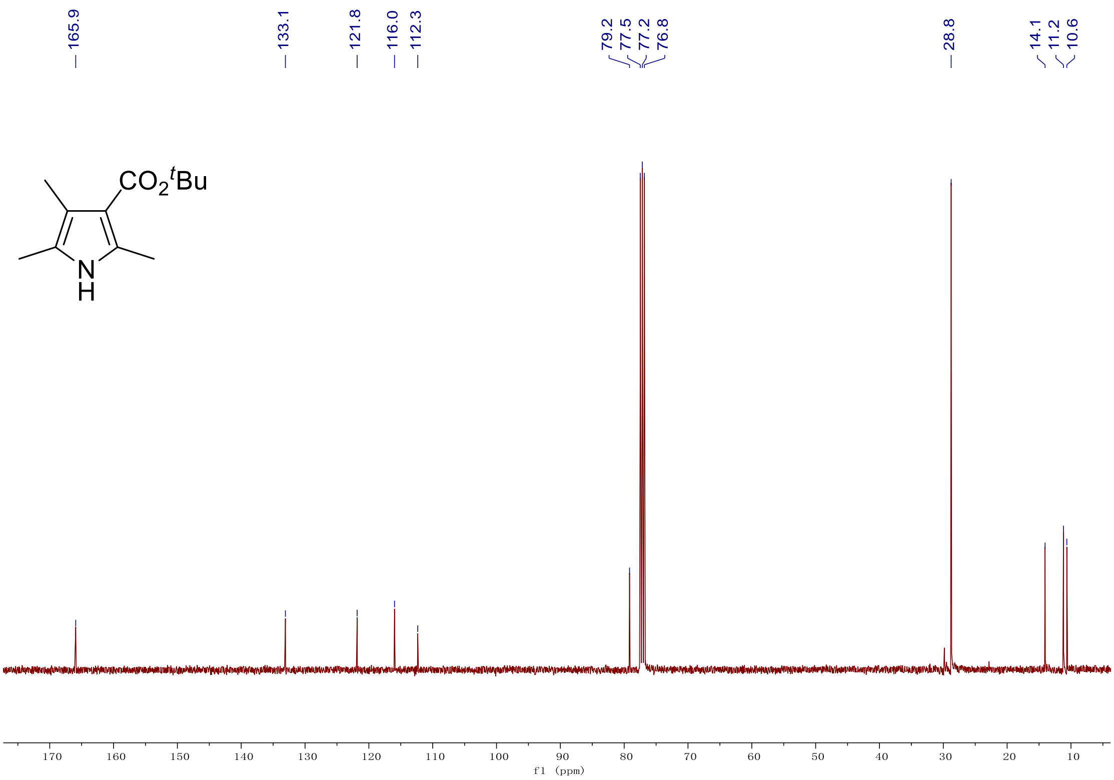
^{13}C NMR (100 MHz, $CDCl_3$) of **2ac**



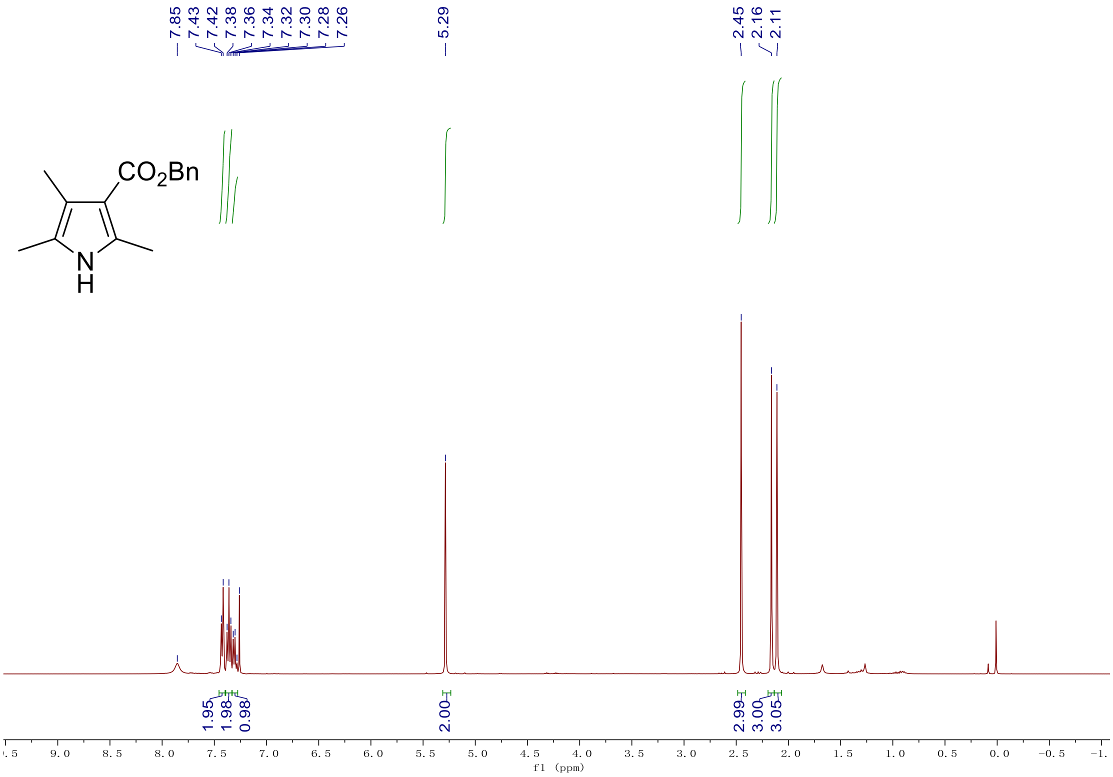
^{1}H NMR (400 MHz, $CDCl_3$) of **2ad**



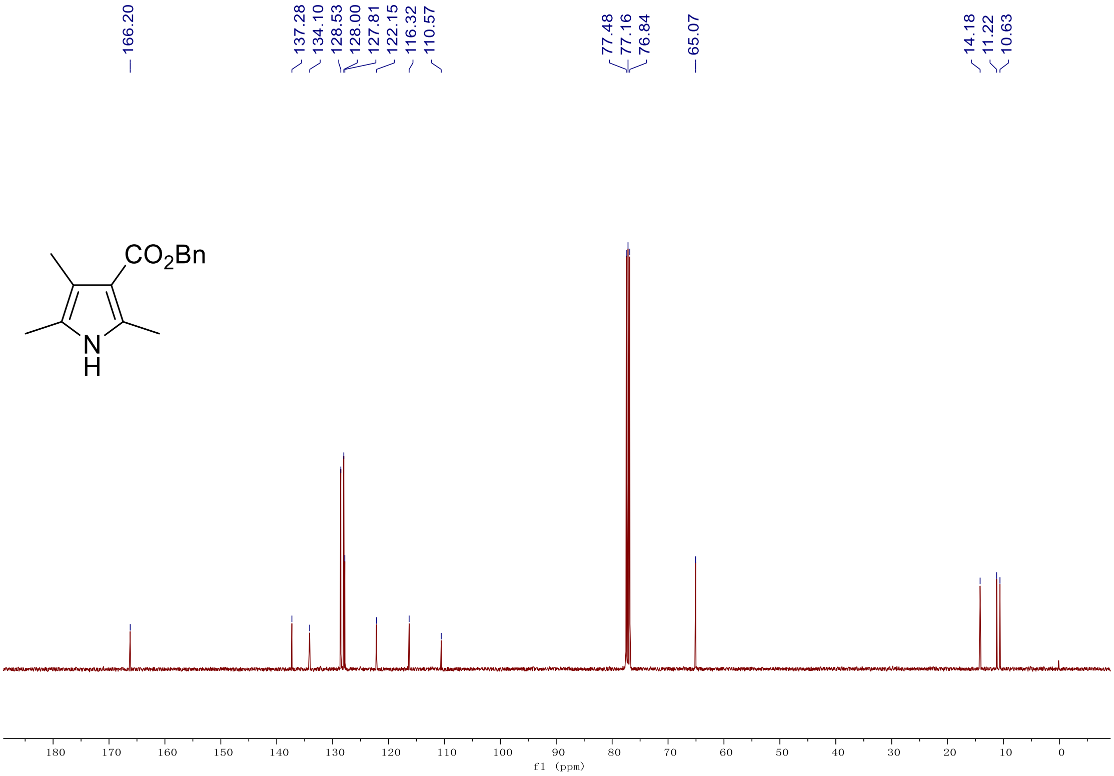
^{13}C NMR (100 MHz, $CDCl_3$) of **2ad**



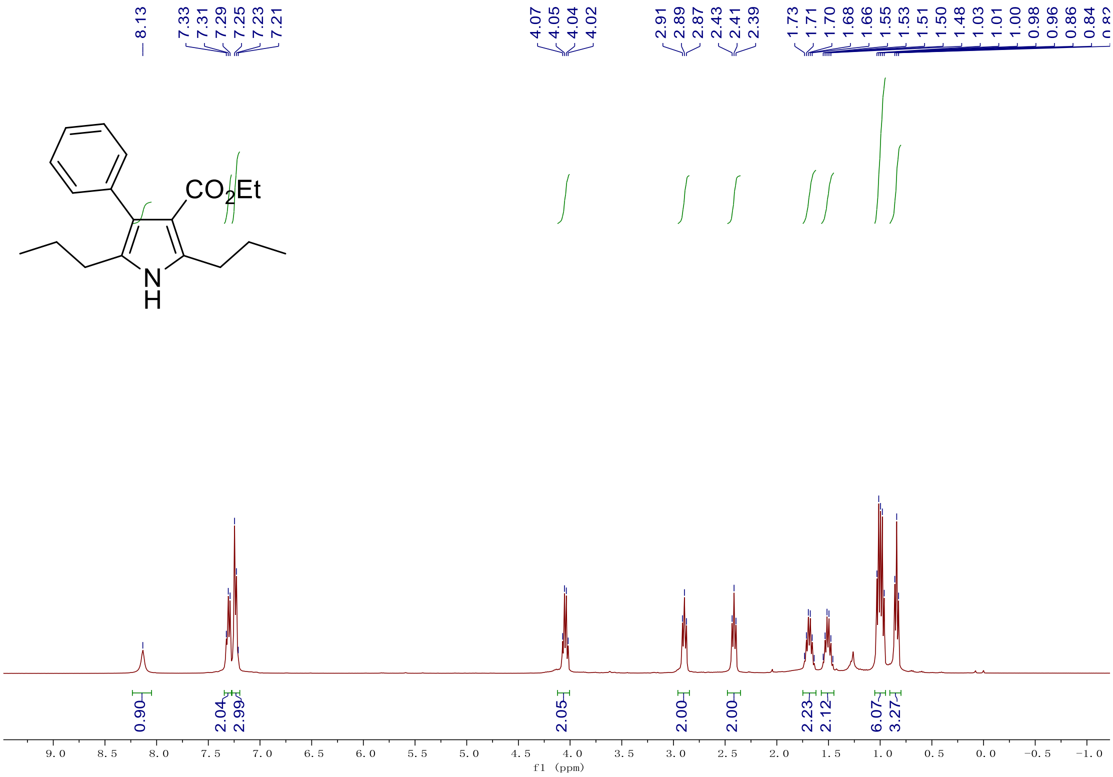
[1]H NMR (400 MHz, $CDCl_3$) of **2ae**



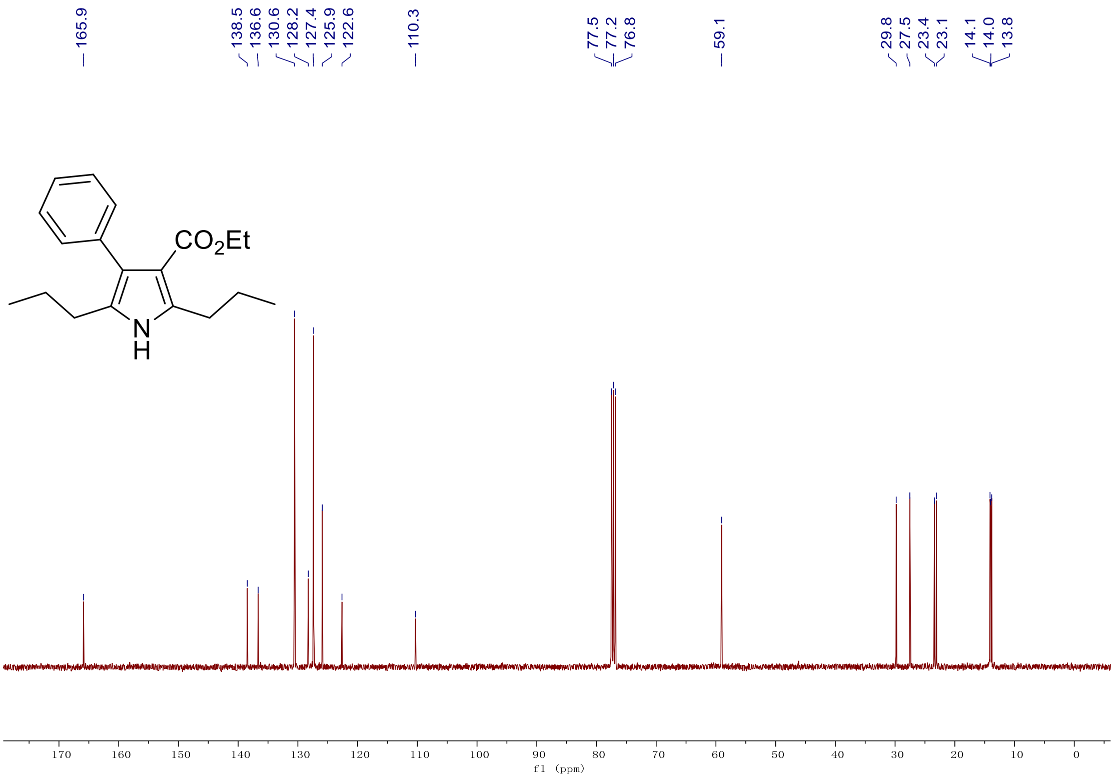
[13]C NMR (100 MHz, $CDCl_3$) of **2ae**



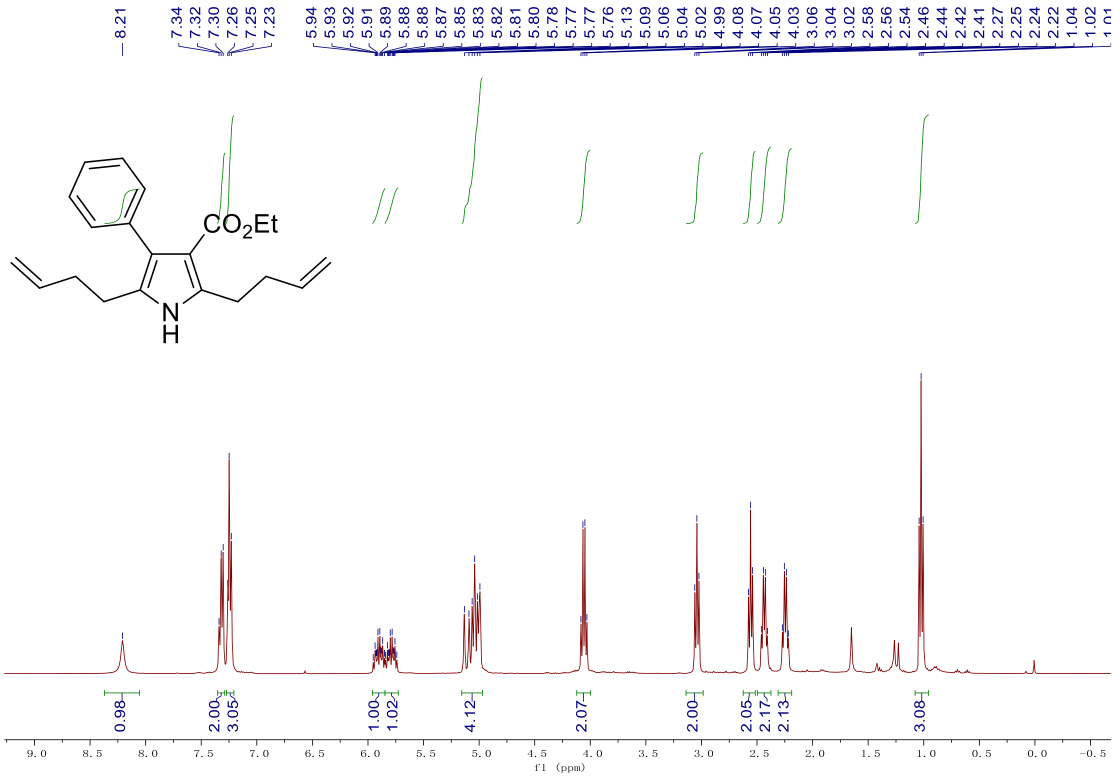
^{1}H NMR (400 MHz, $CDCl_3$) of **2af**



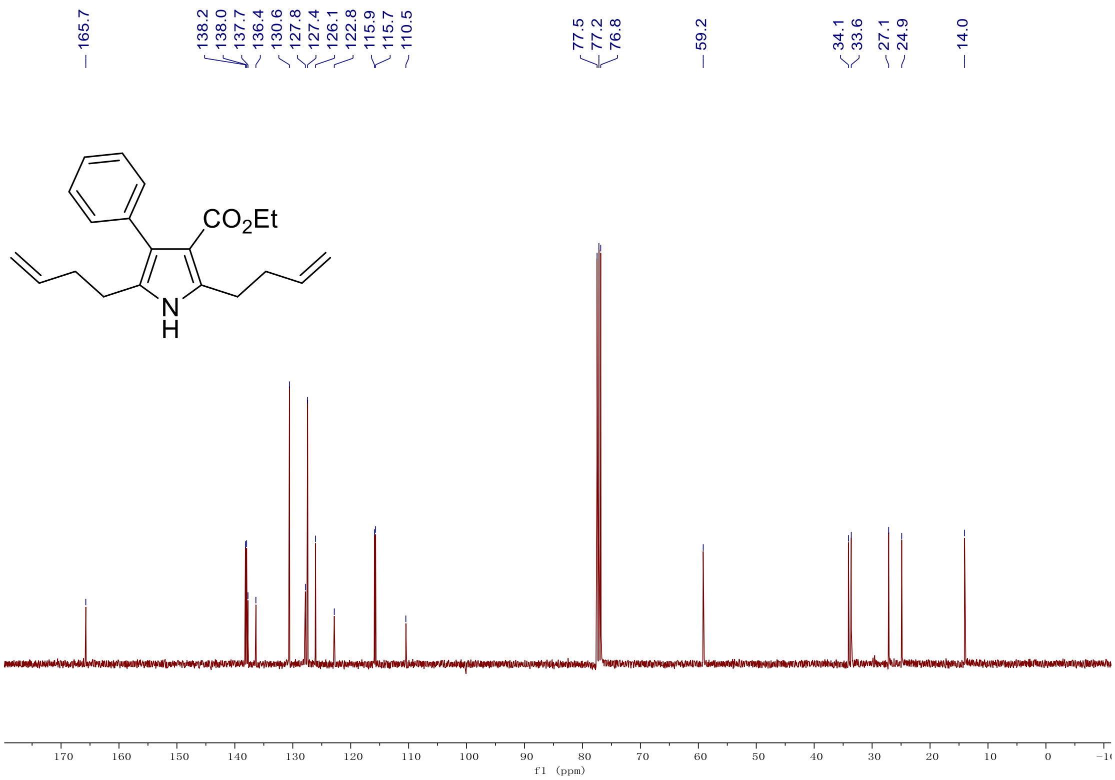
^{13}C NMR (100 MHz, $CDCl_3$) of **2af**



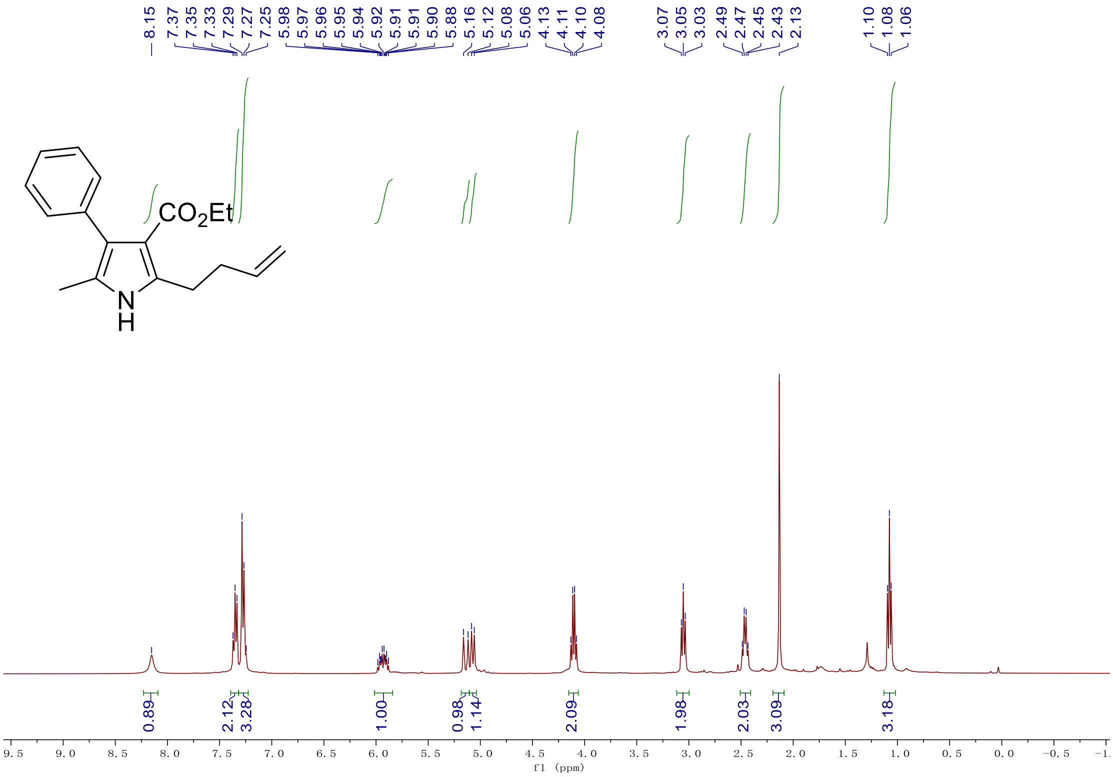
[1]H NMR (400 MHz, $CDCl_3$) of **2ag**



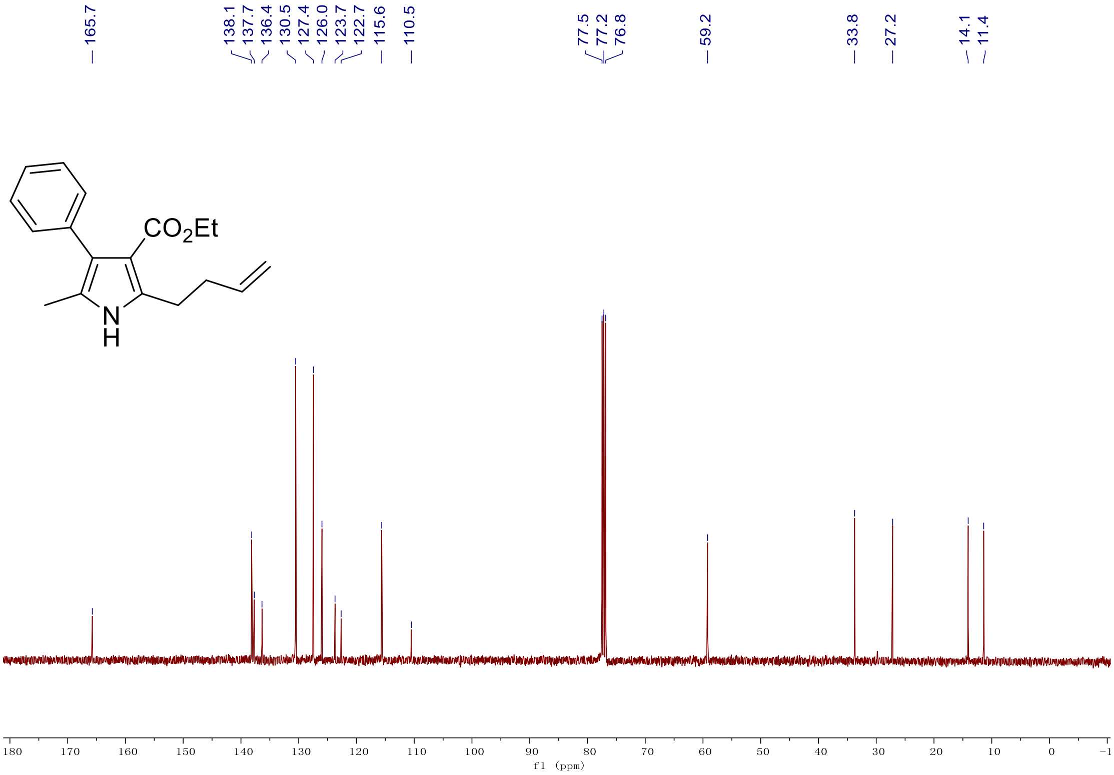
[13]C NMR (100 MHz, $CDCl_3$) of **2ag**



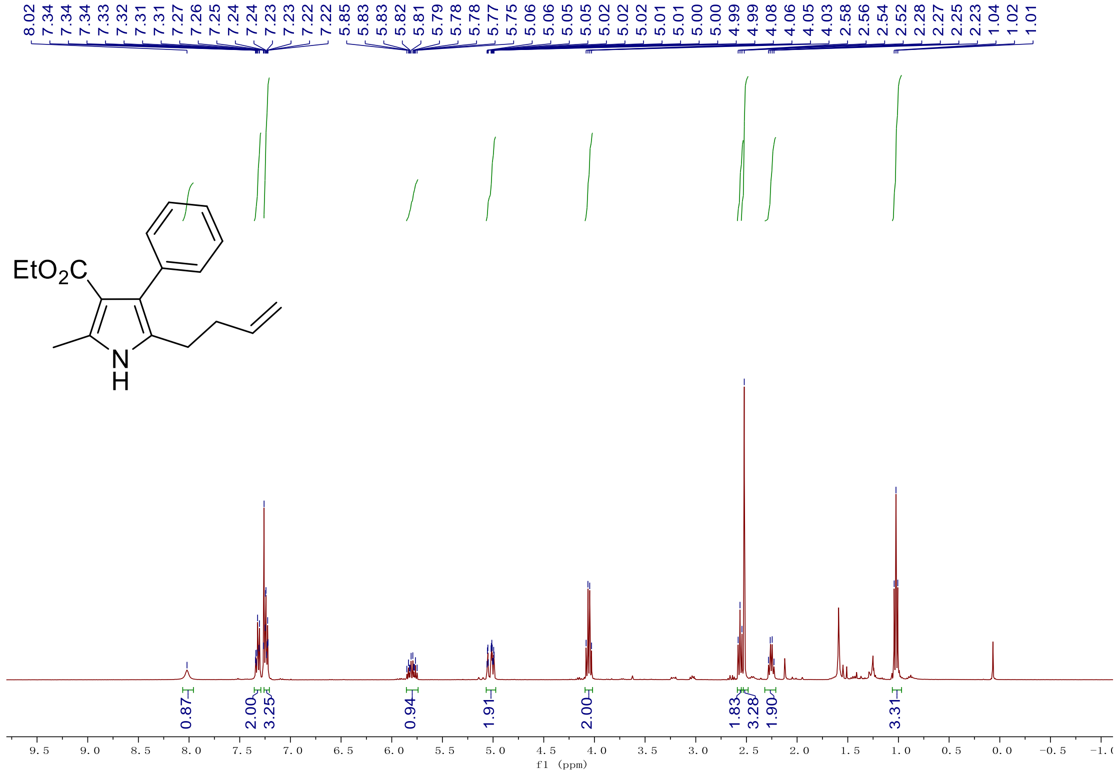
^{1}H NMR (400 MHz, $CDCl_3$) of **2ah**



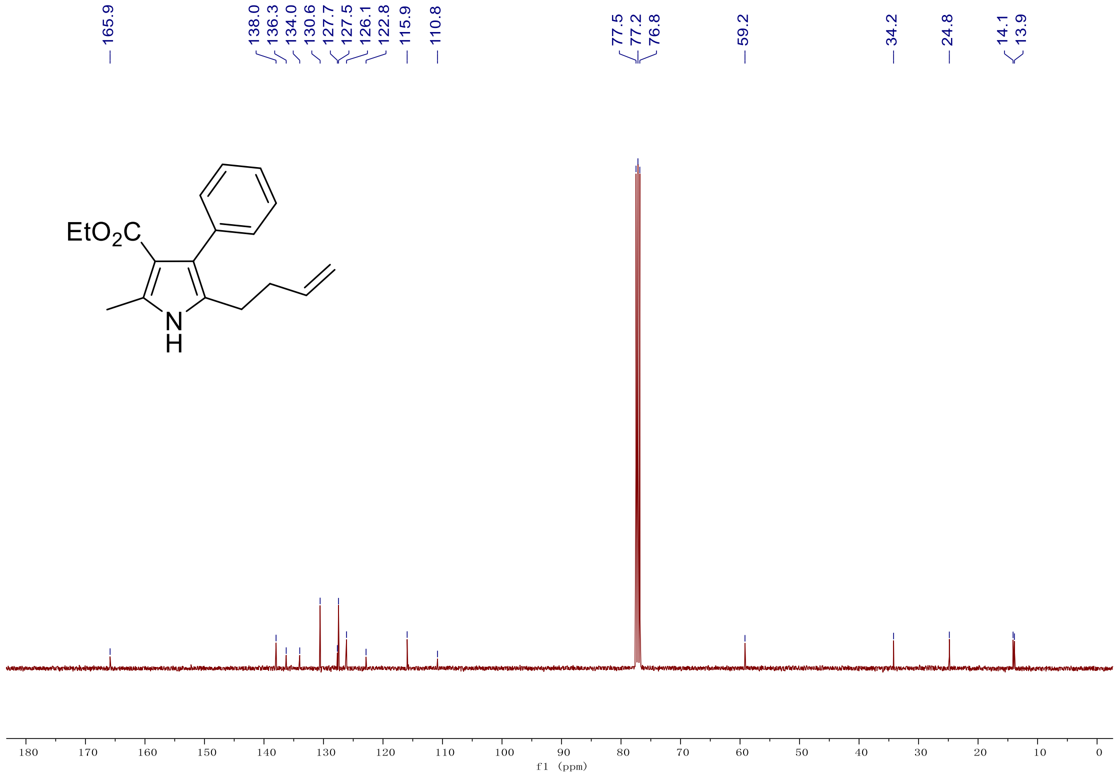
^{13}C NMR (100 MHz, $CDCl_3$) of **2ah**



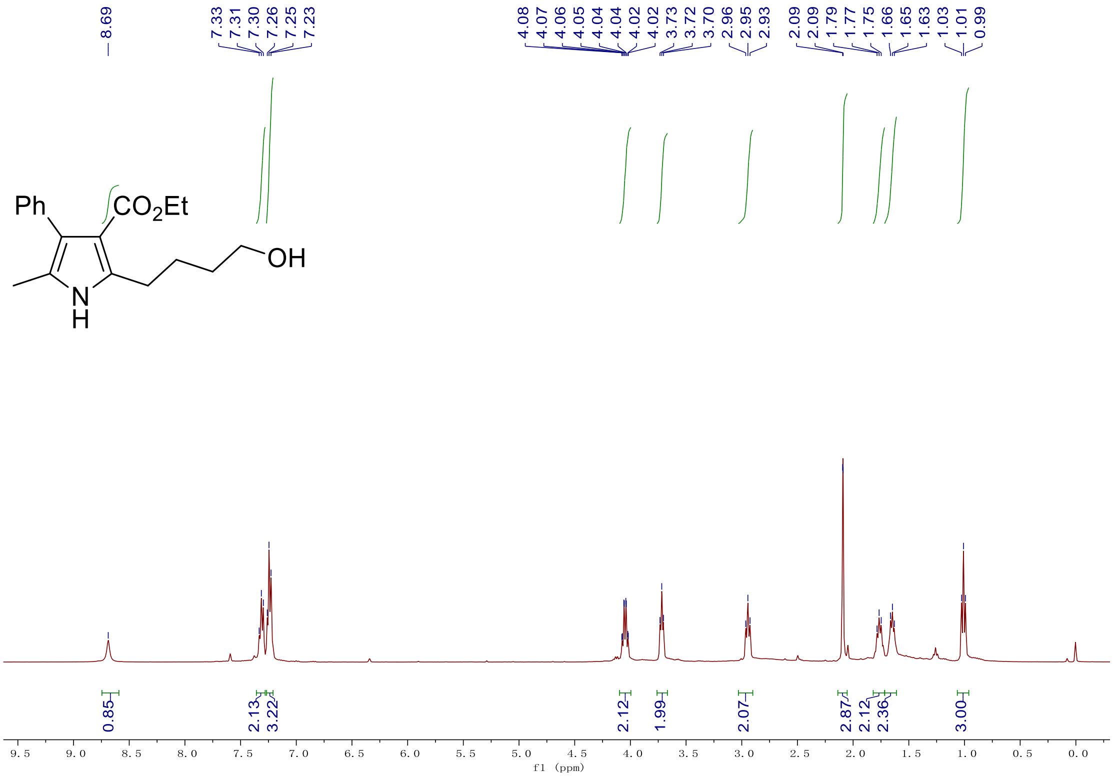
^{1}H NMR (400 MHz, $CDCl_3$) of **2ah'**



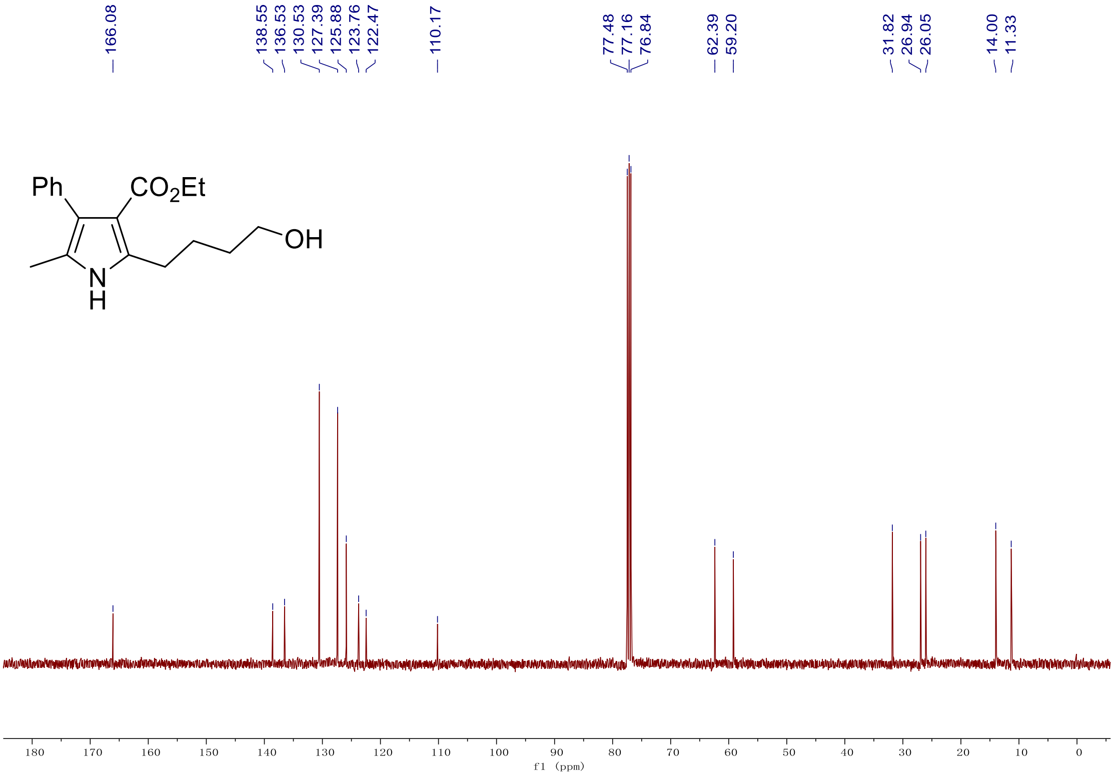
^{13}C NMR (100 MHz, $CDCl_3$) of **2ah'**



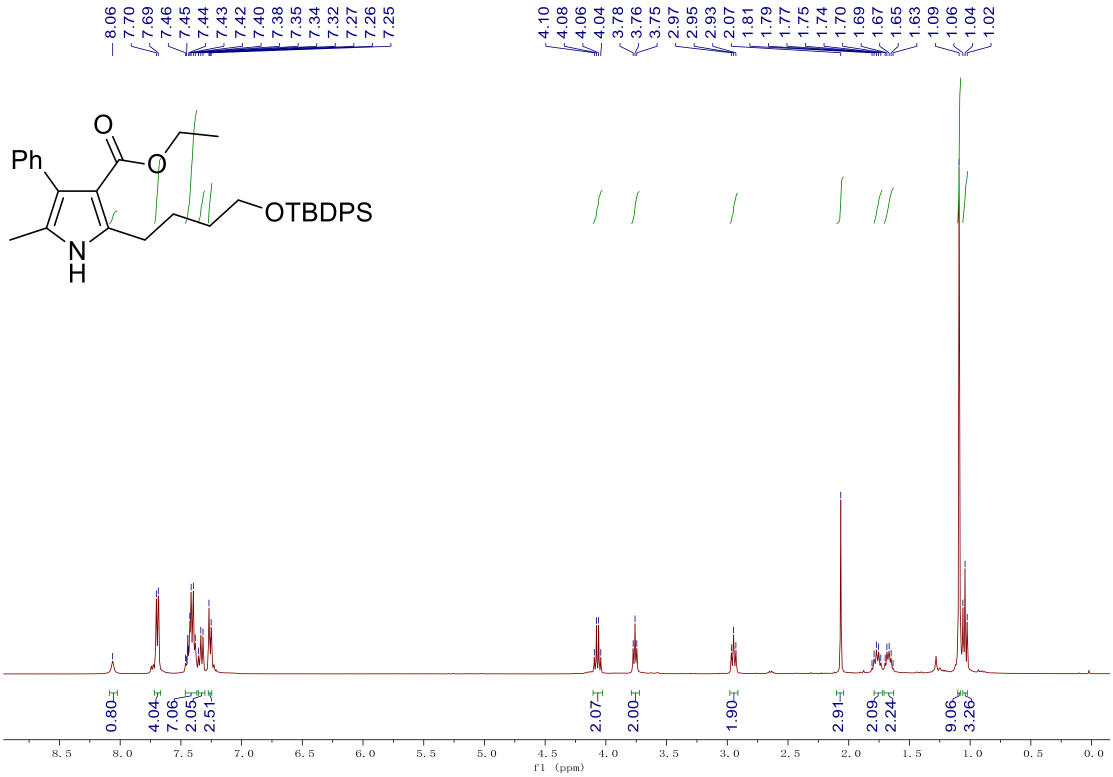
[1]H NMR (400 MHz, $CDCl_3$) of **2ai**



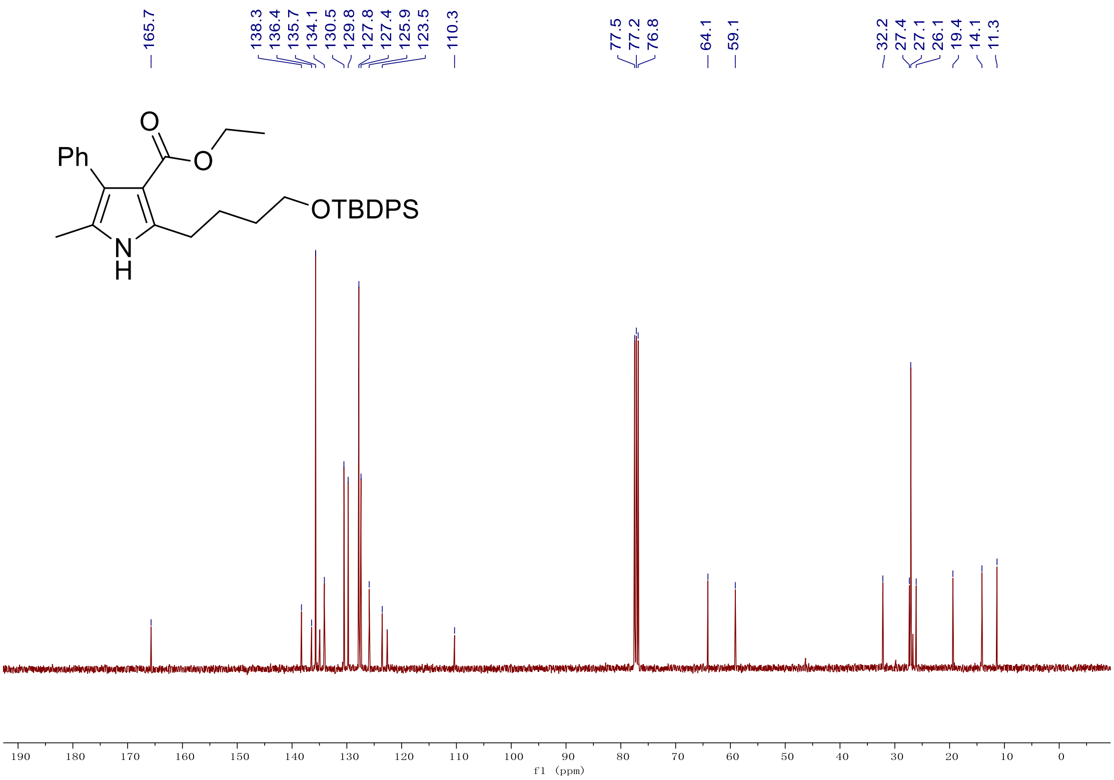
[13]C NMR (100 MHz, $CDCl_3$) of **2ai**



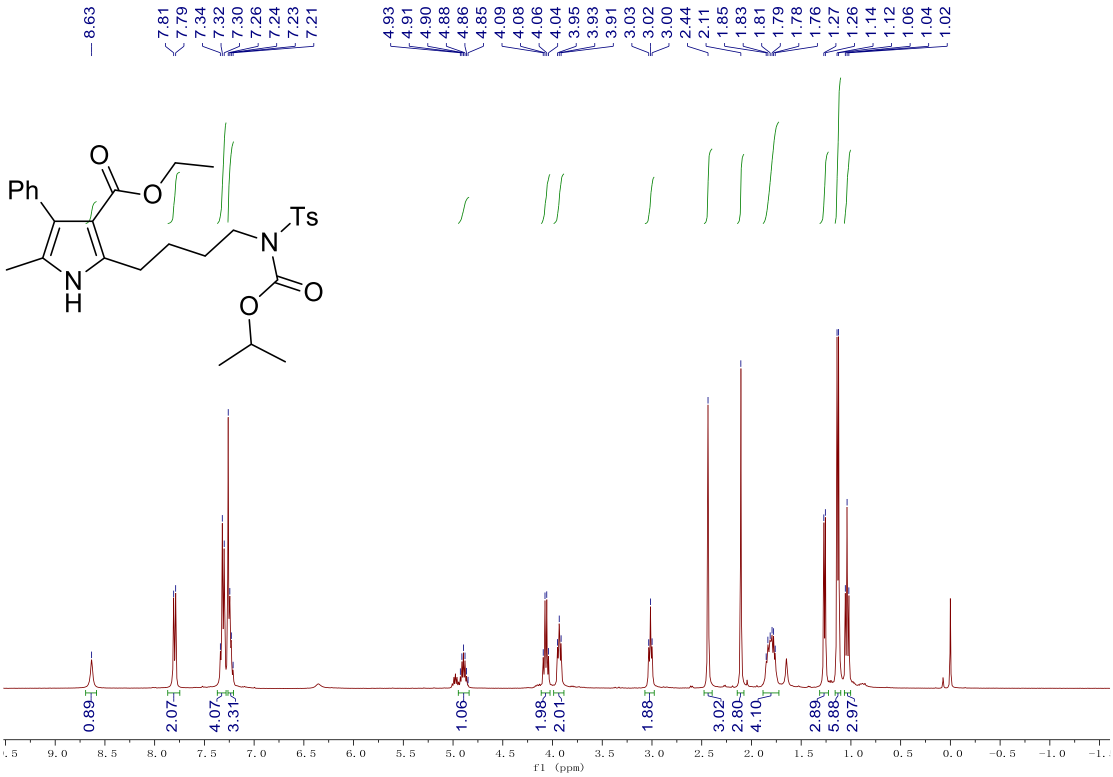
^{1}H NMR (400 MHz, $CDCl_3$) of **2aj**



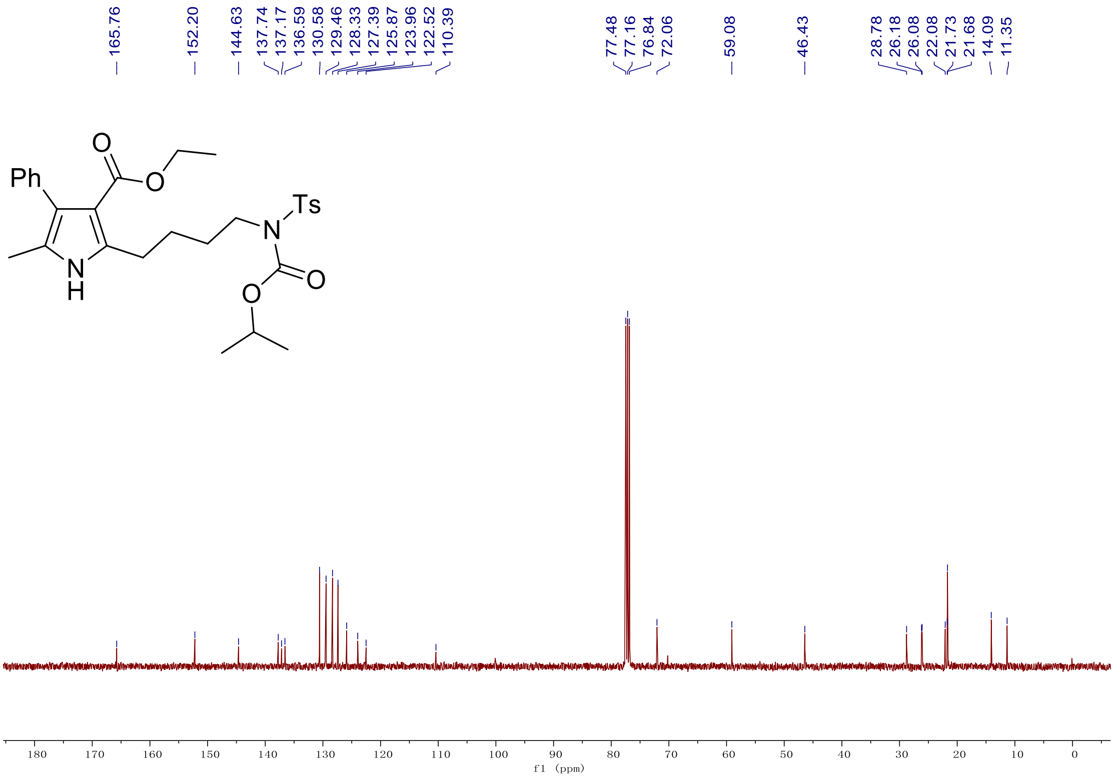
^{13}C NMR (100 MHz, $CDCl_3$) of **2aj**



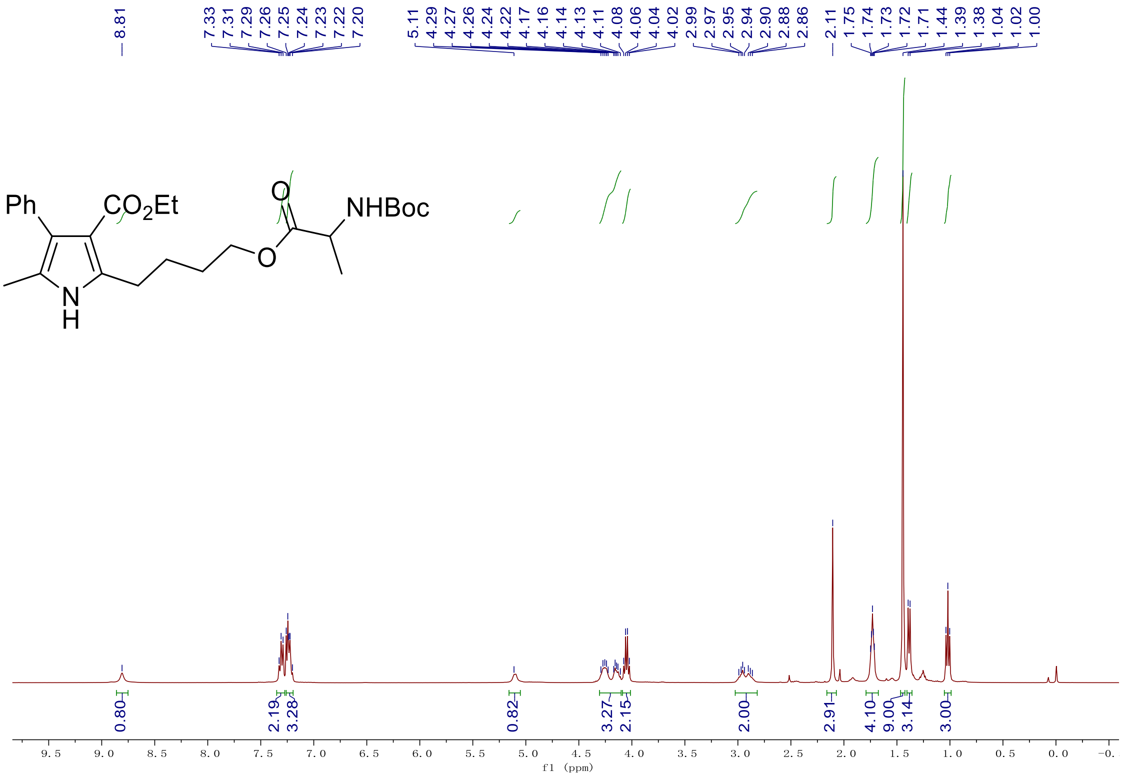
[1]H NMR (400 MHz, $CDCl_3$) of **2ak**



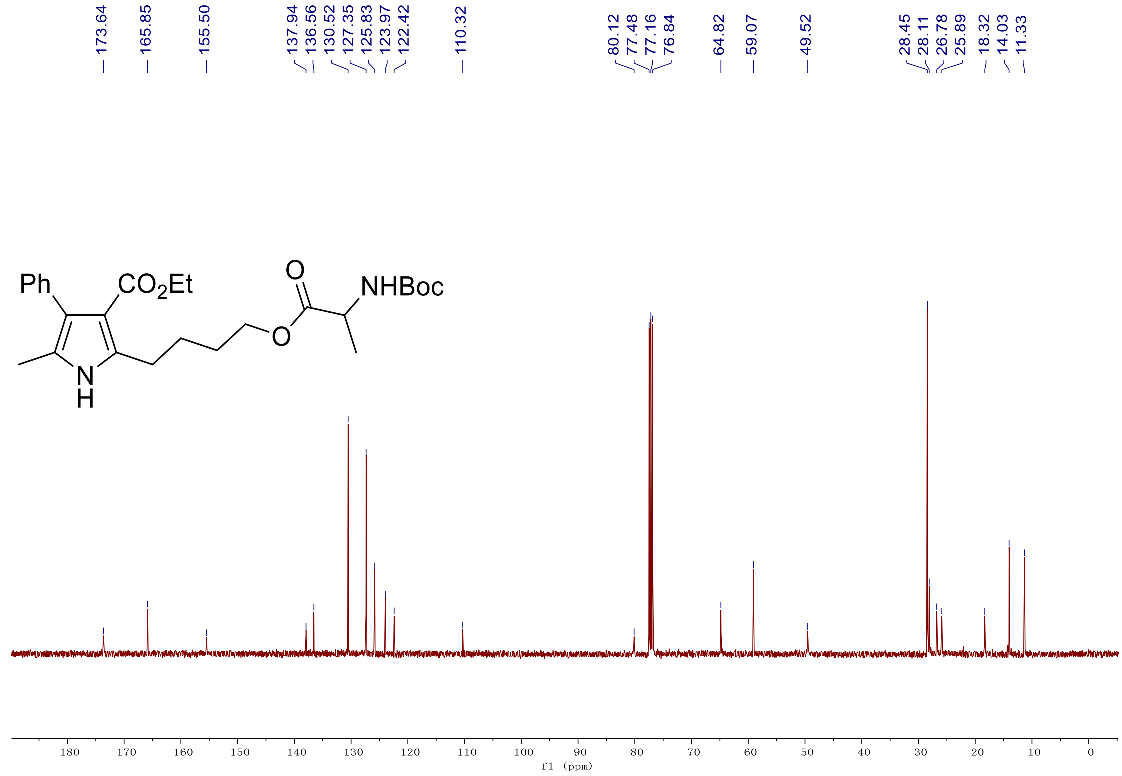
[13]C NMR (100 MHz, $CDCl_3$) of **2ak**



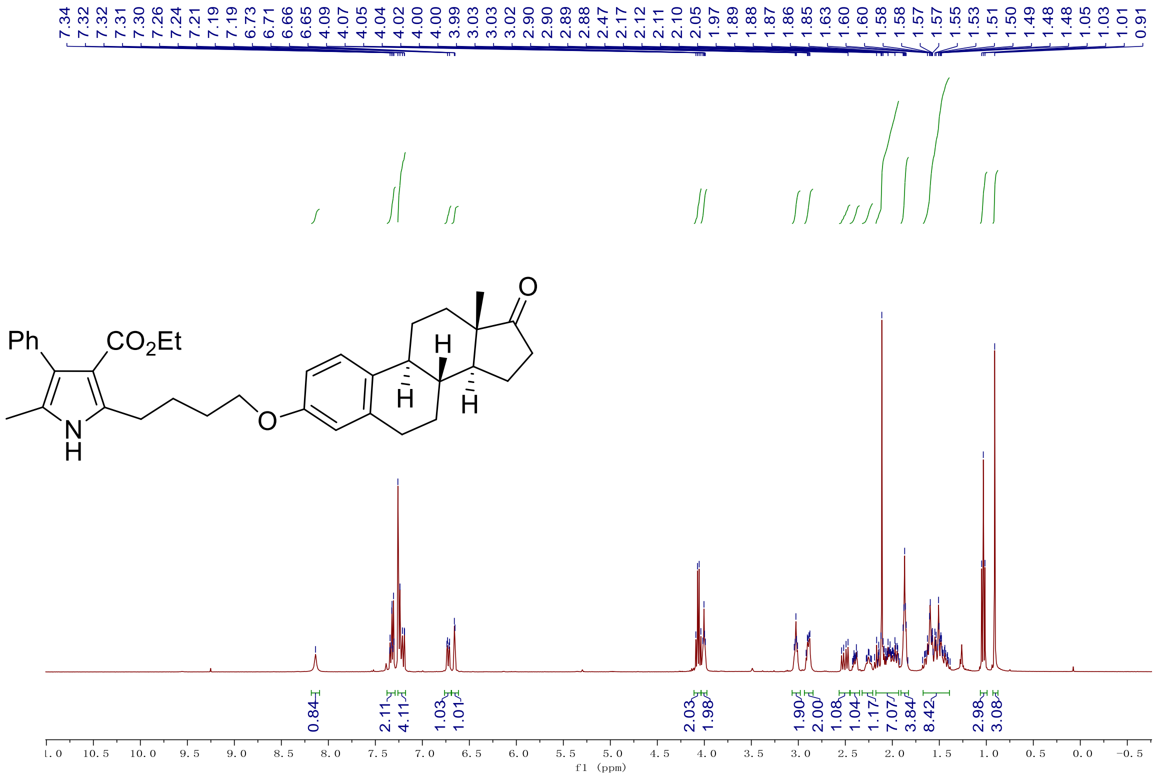
^{1}H NMR (400 MHz, $CDCl_3$) of **2al**



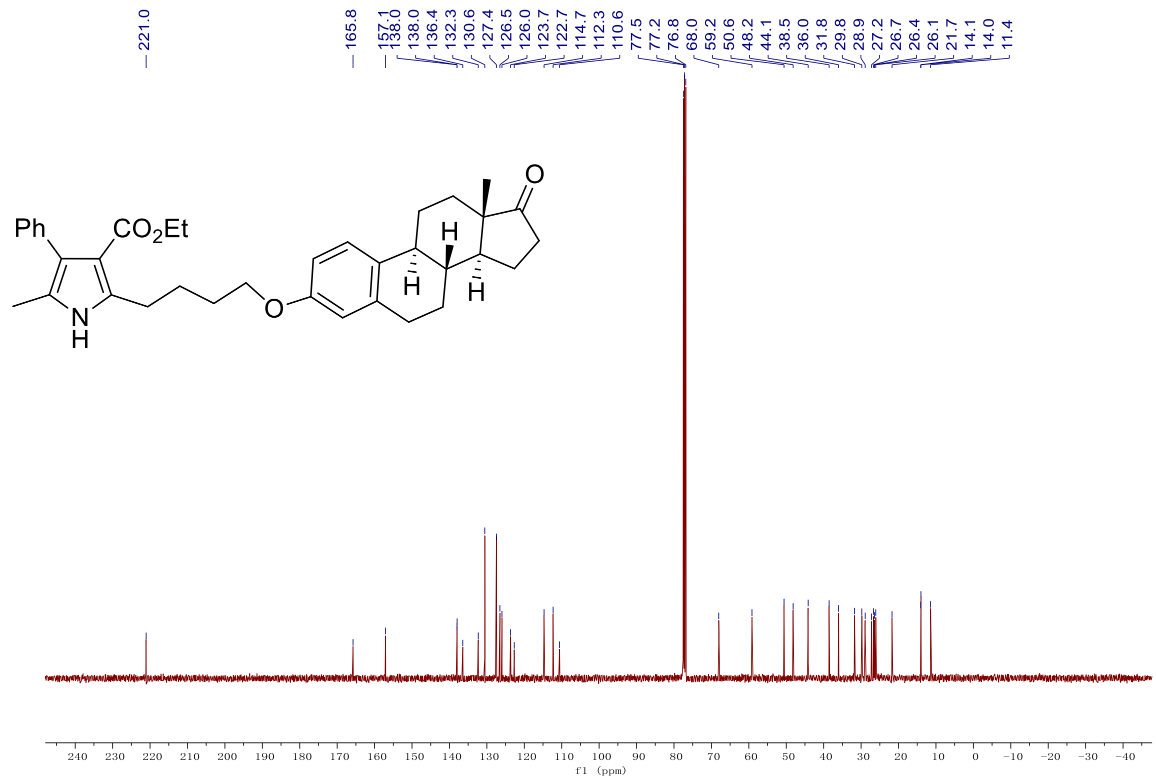
^{13}C NMR (100 MHz, $CDCl_3$) of **2al**



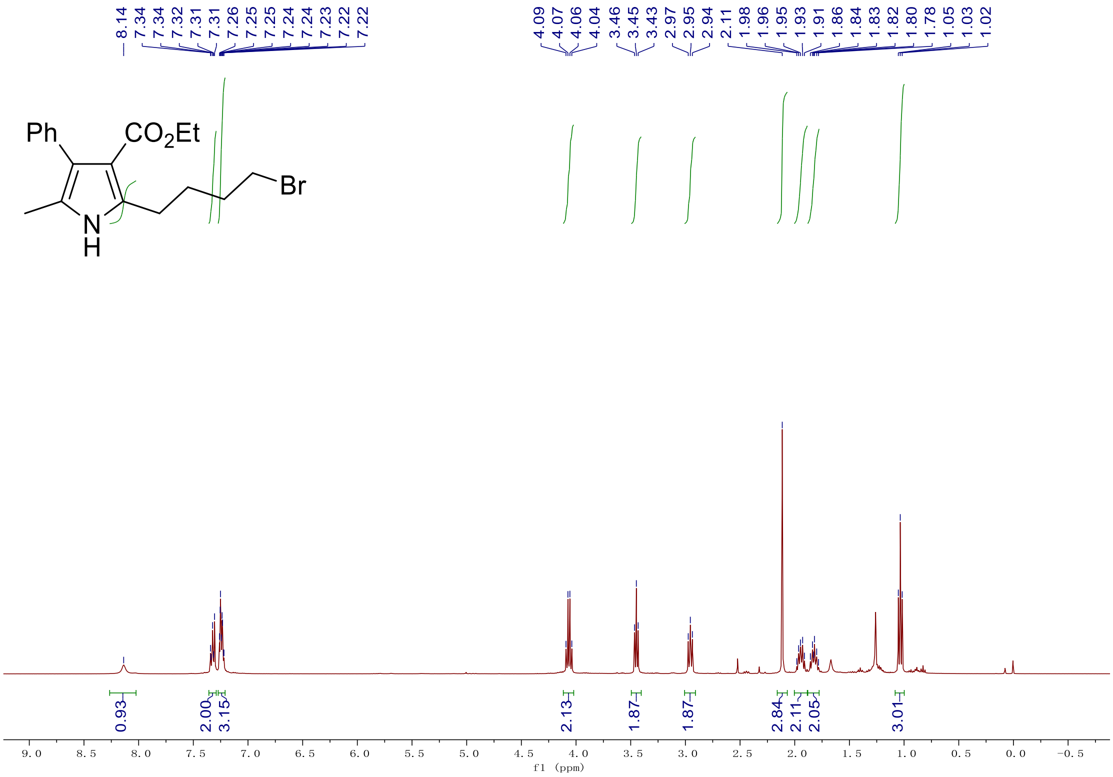
^{1}H NMR (400 MHz, $CDCl_3$) of **2am**



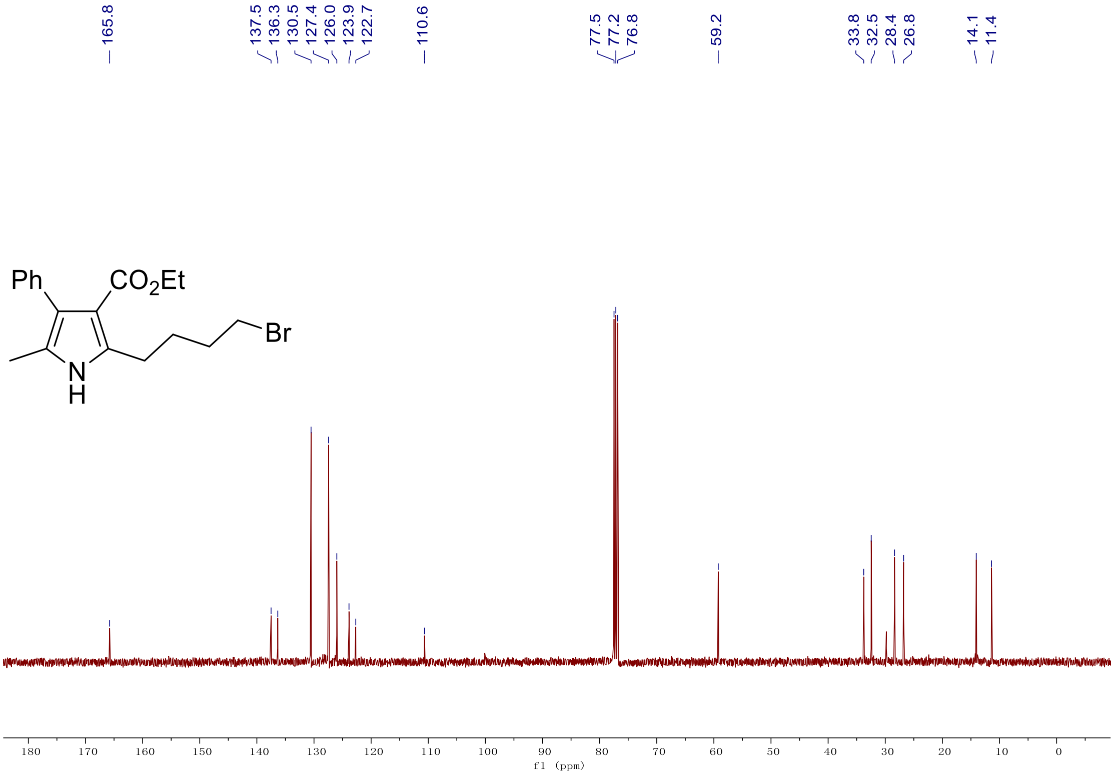
^{13}C NMR (100 MHz, $CDCl_3$) of **2am**



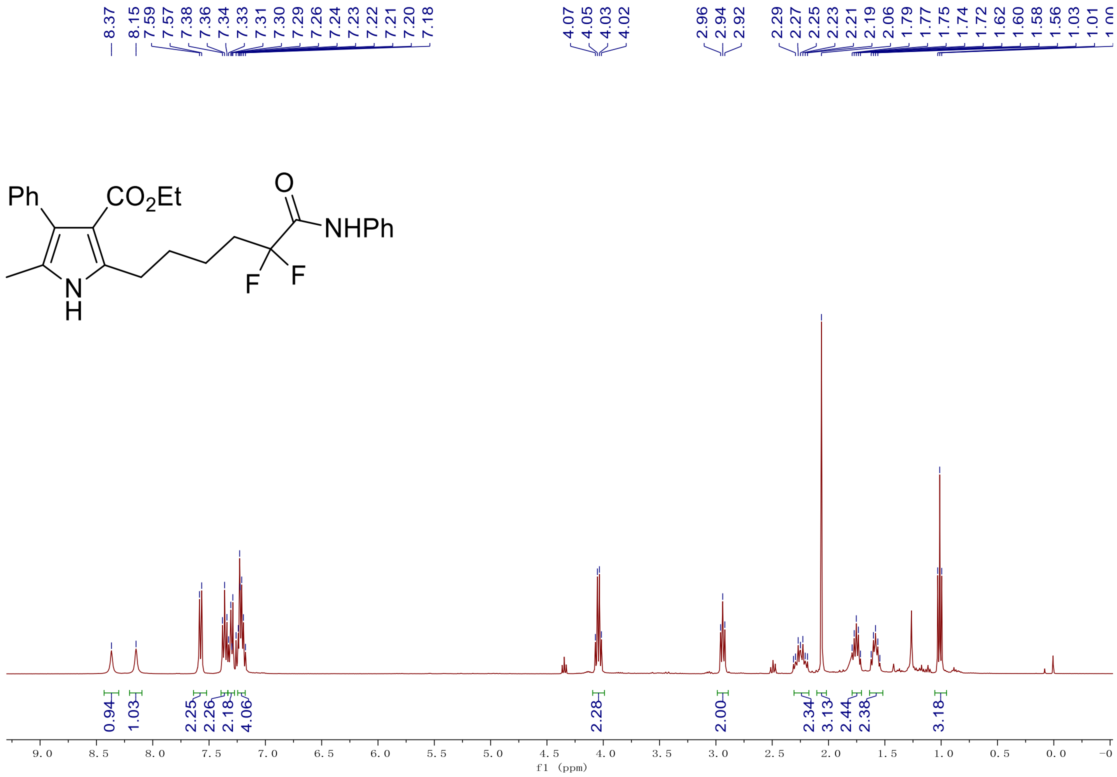
[1]H NMR (400 MHz, $CDCl_3$) of **2an**



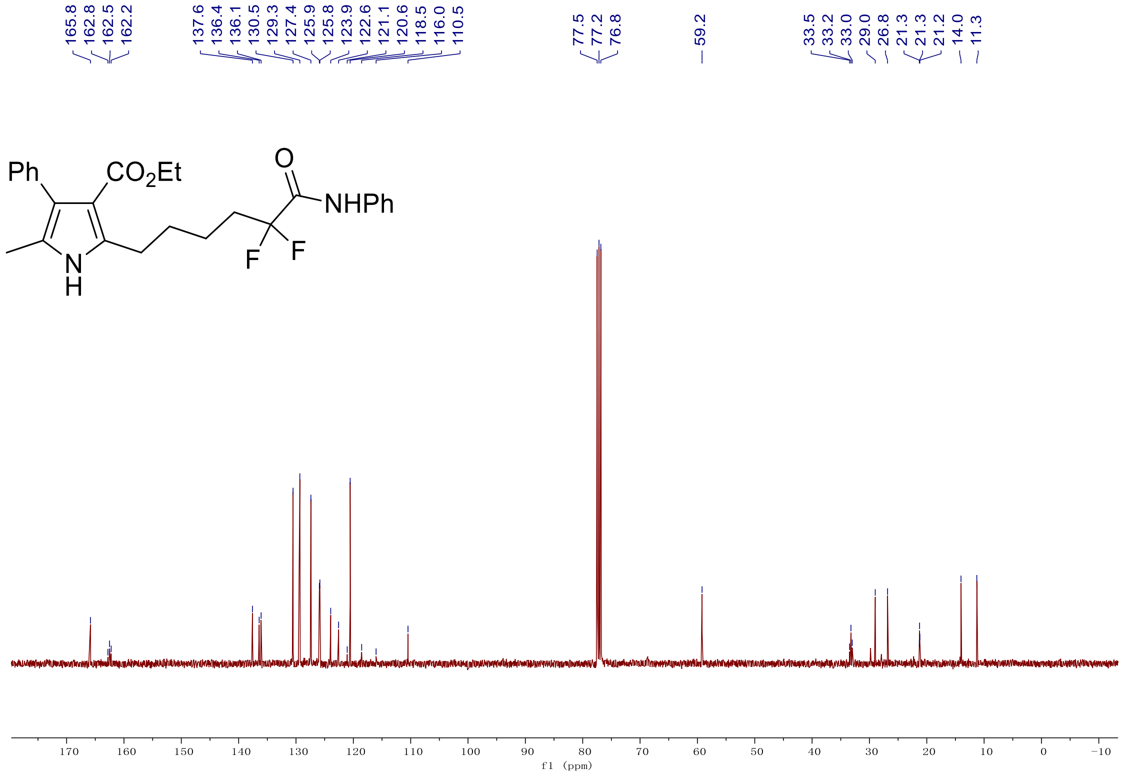
[13]C NMR (100 MHz, $CDCl_3$) of **2an**



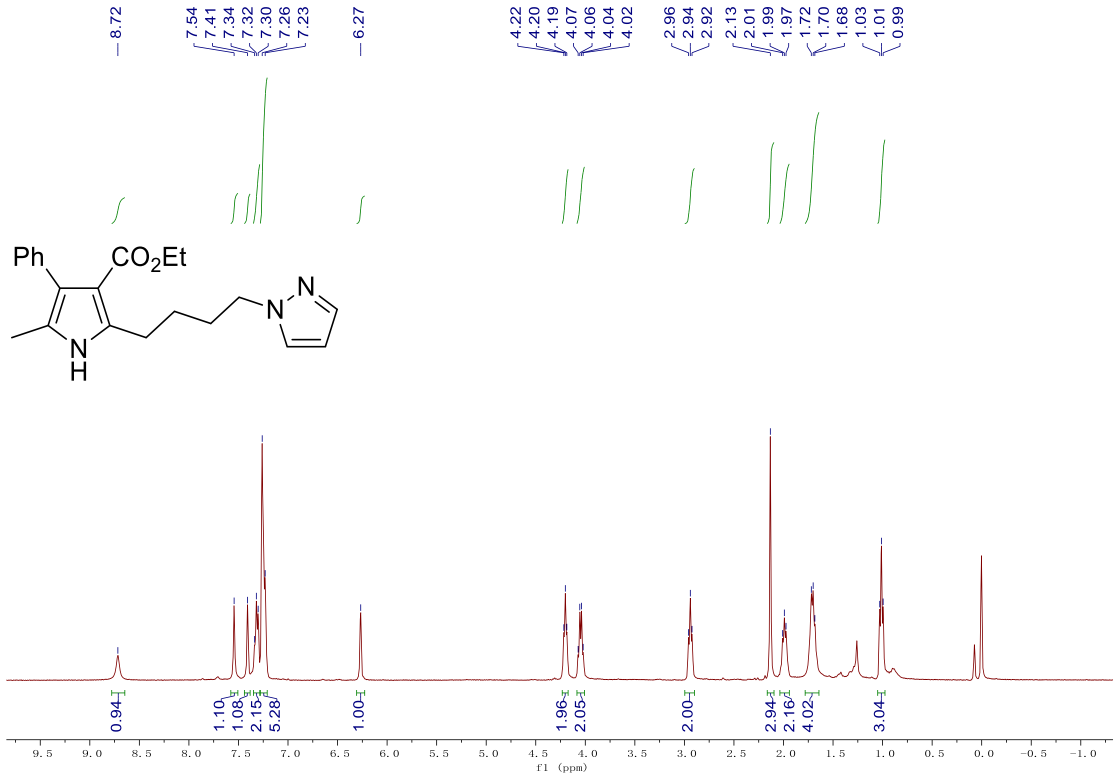
^{1}H NMR (400 MHz, $CDCl_3$) of **2ao**



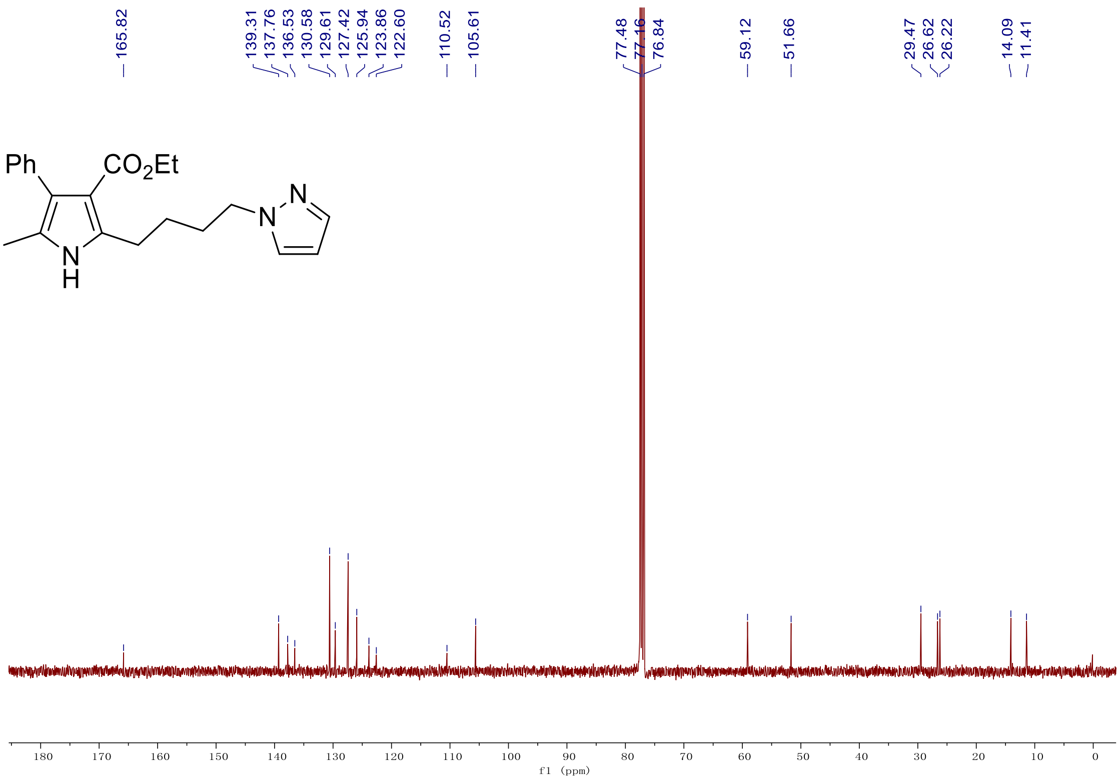
^{13}C NMR (100 MHz, $CDCl_3$) of **2ao**



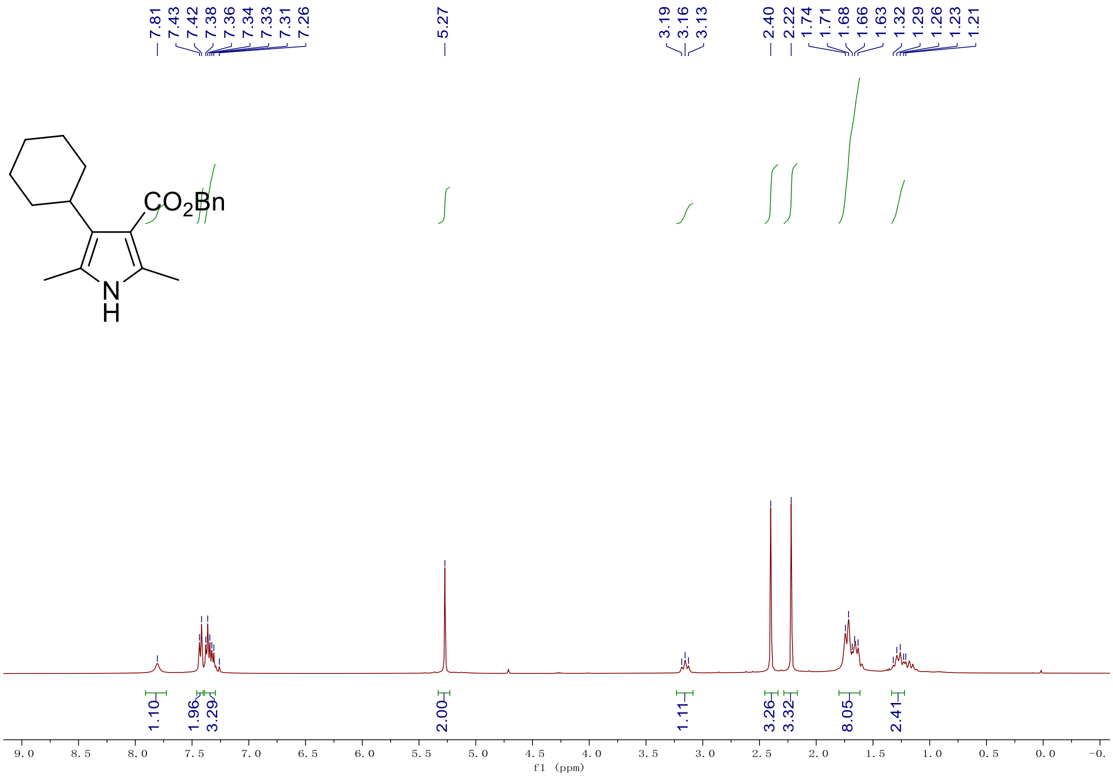
[1]H NMR (400 MHz, $CDCl_3$) of **2ap**



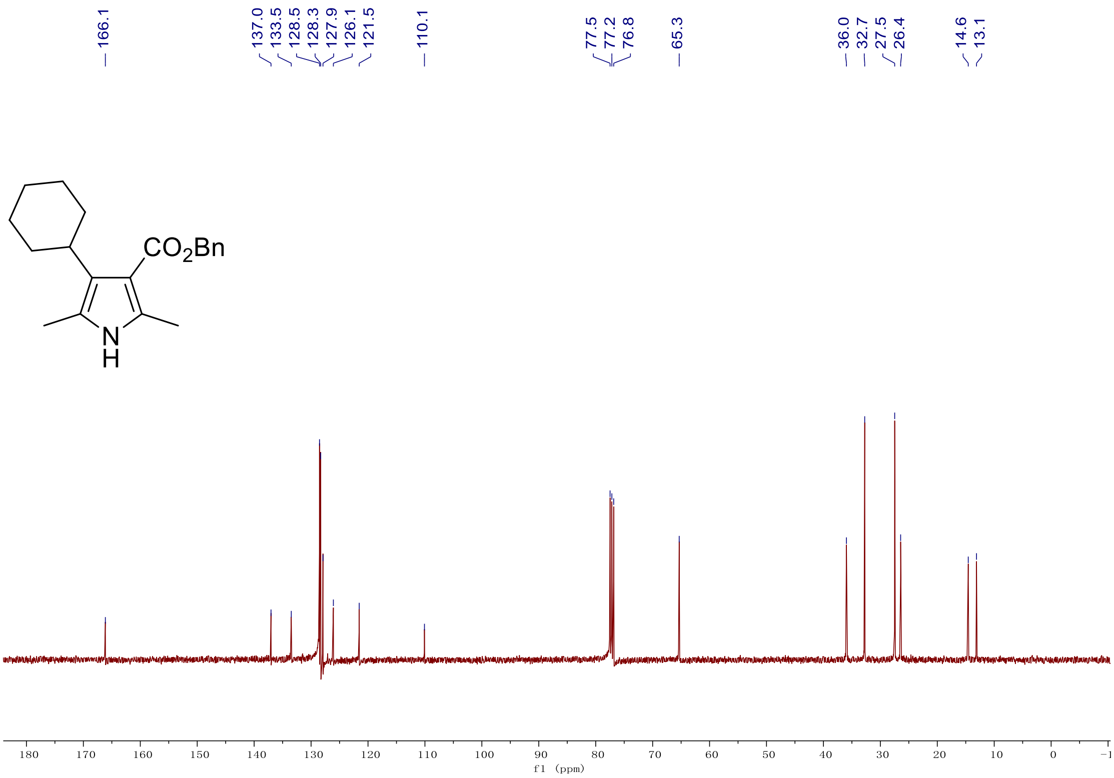
[13]C NMR (100 MHz, $CDCl_3$) of **2ap**



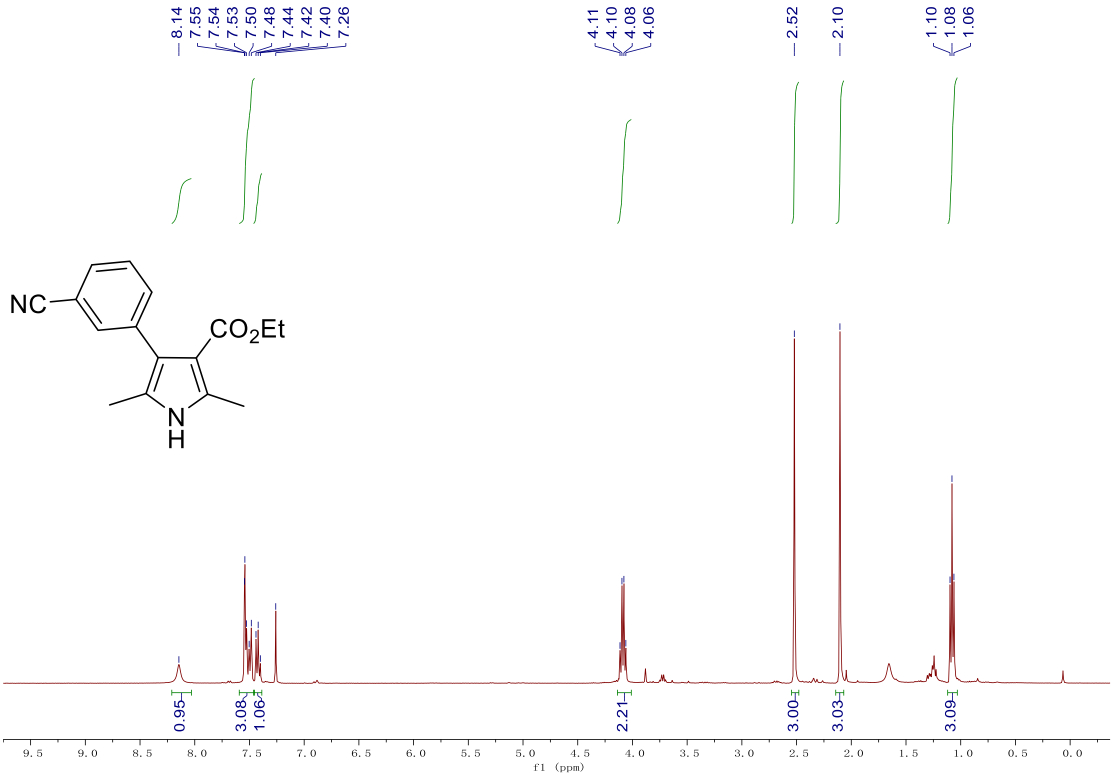
^{1}H NMR (400 MHz, $CDCl_3$) of **2aq**



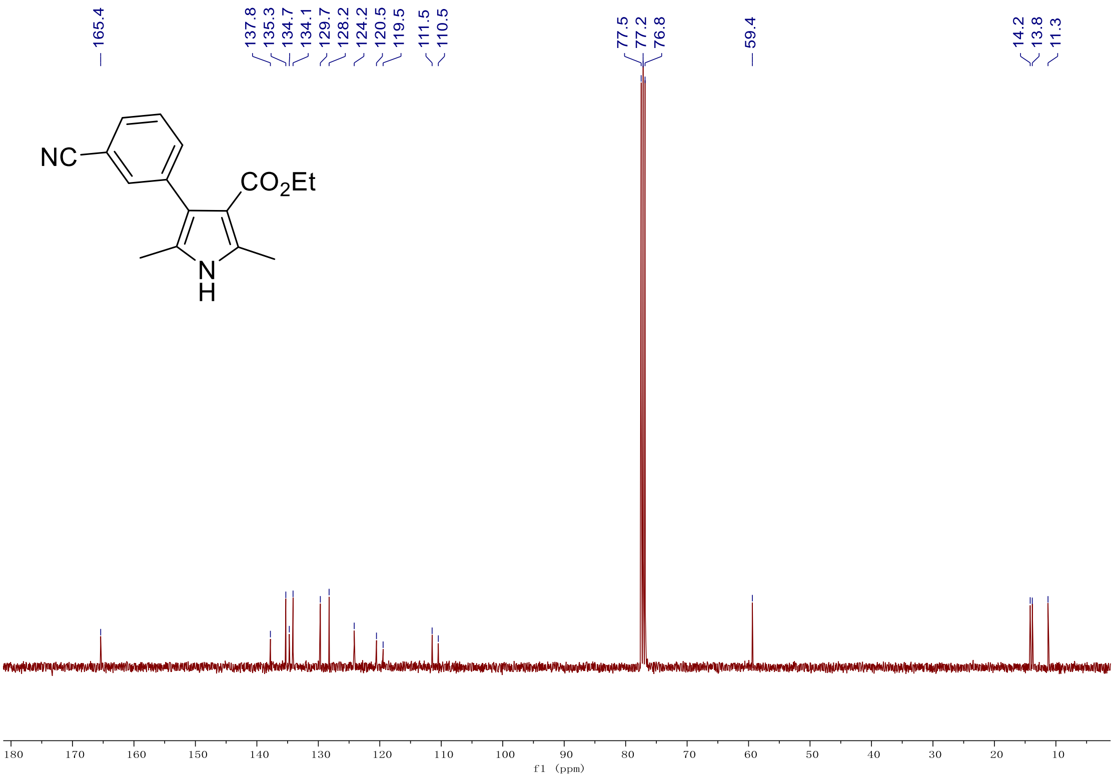
^{13}C NMR (100 MHz, $CDCl_3$) of **2aq**



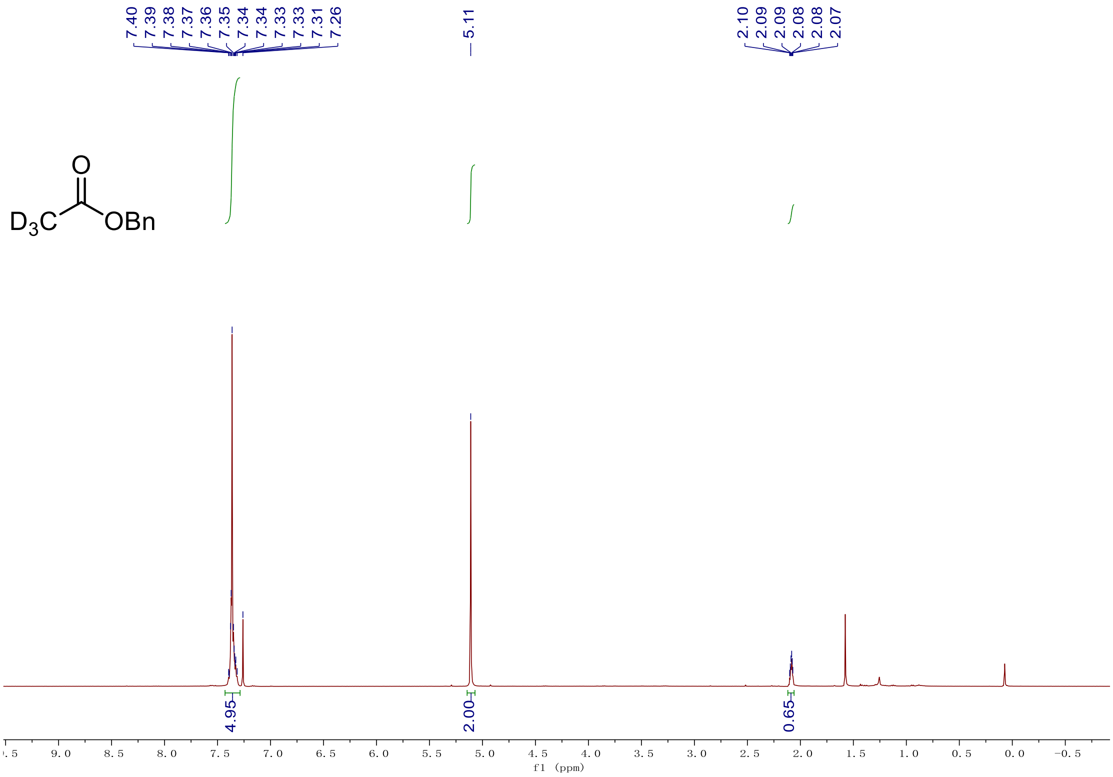
^{1}H NMR (400 MHz, $CDCl_3$) of **2ar**



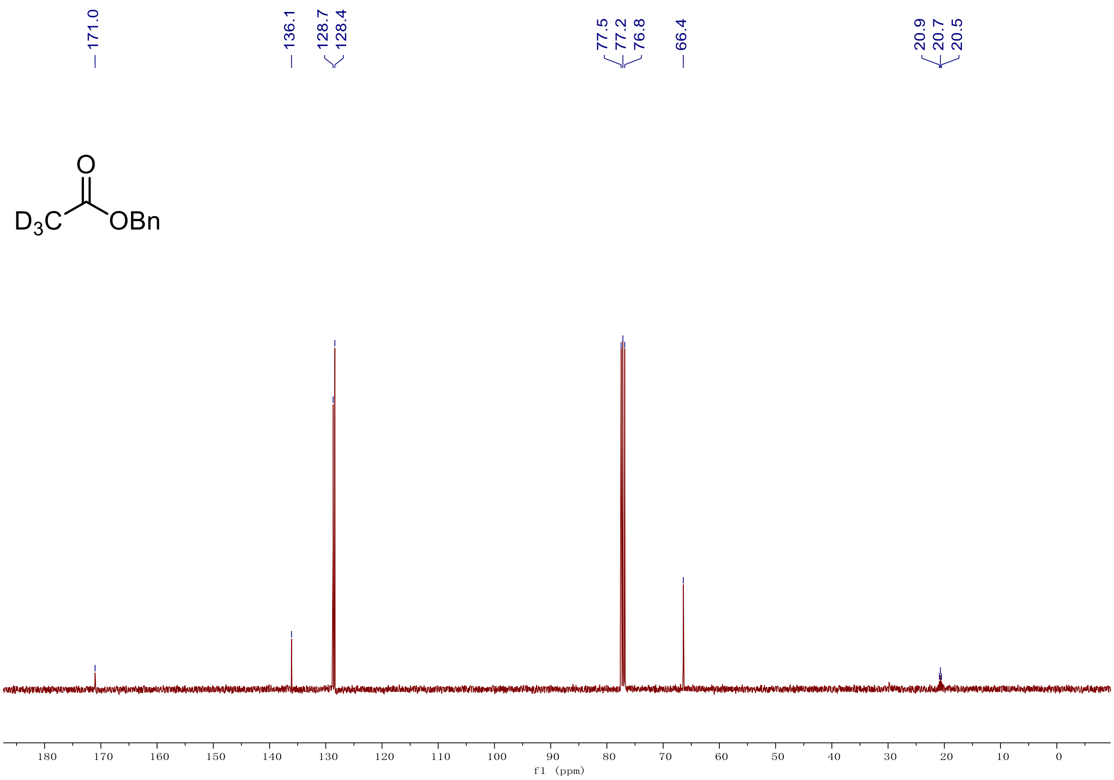
^{13}C NMR (100 MHz, $CDCl_3$) of **2ar**



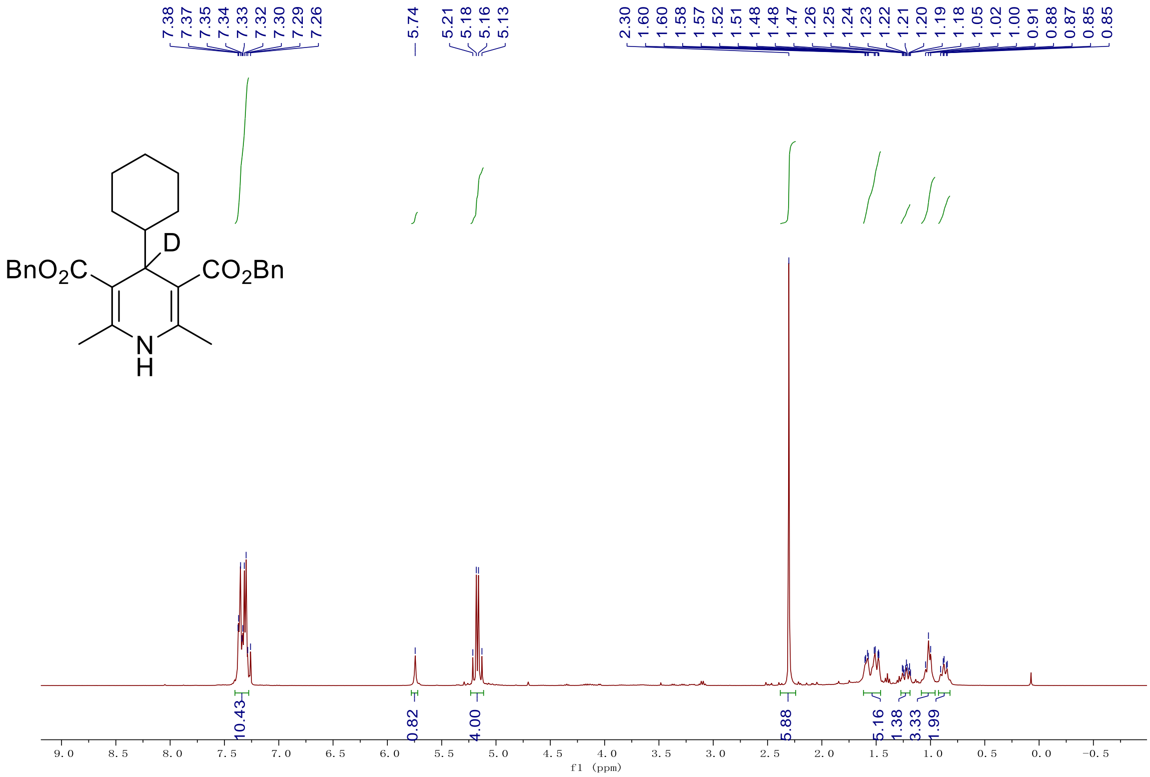
[1]H NMR (400 MHz, $CDCl_3$) of ***d*₃-4**



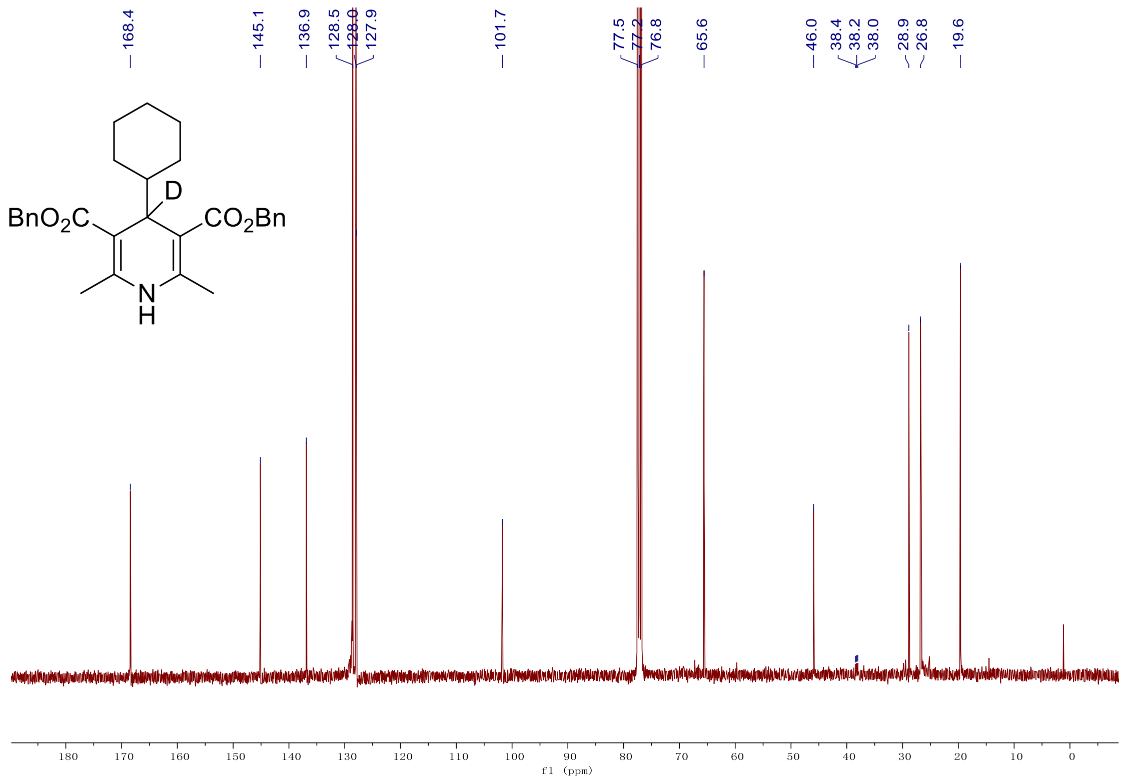
[13]C NMR (100 MHz, $CDCl_3$) of ***d*₃-4**



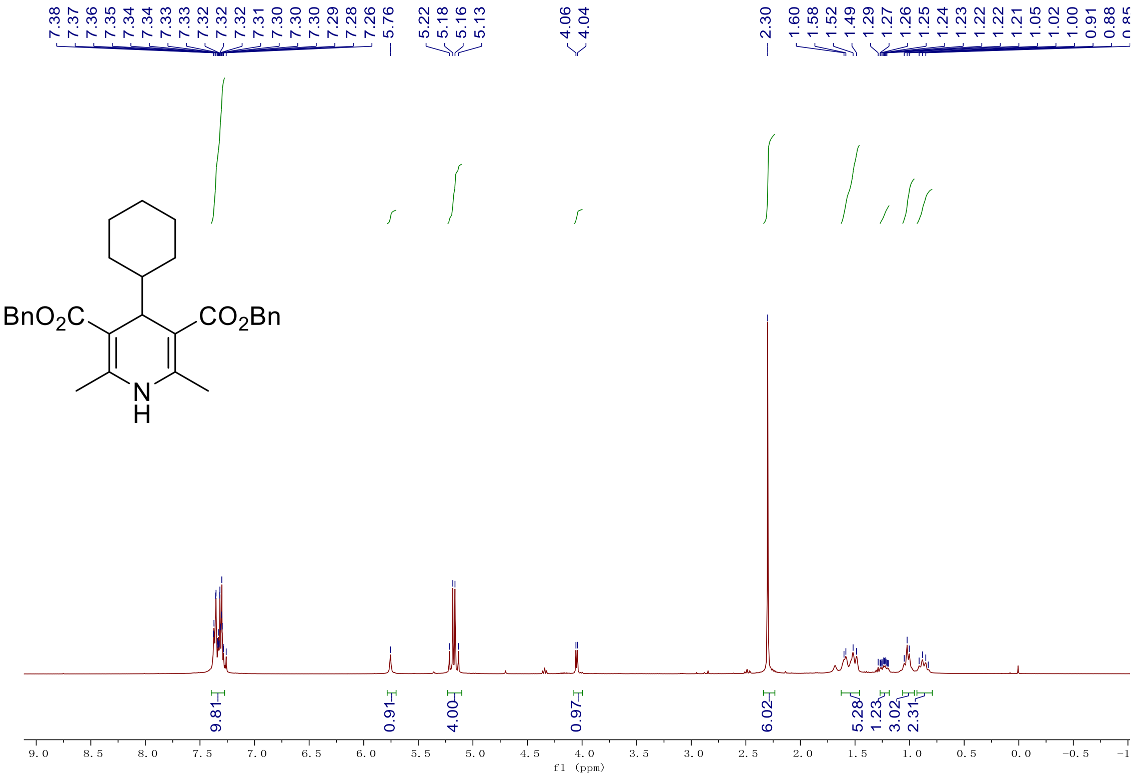
^{1}H NMR (400 MHz, $CDCl_3$) of ***d*-3aq**



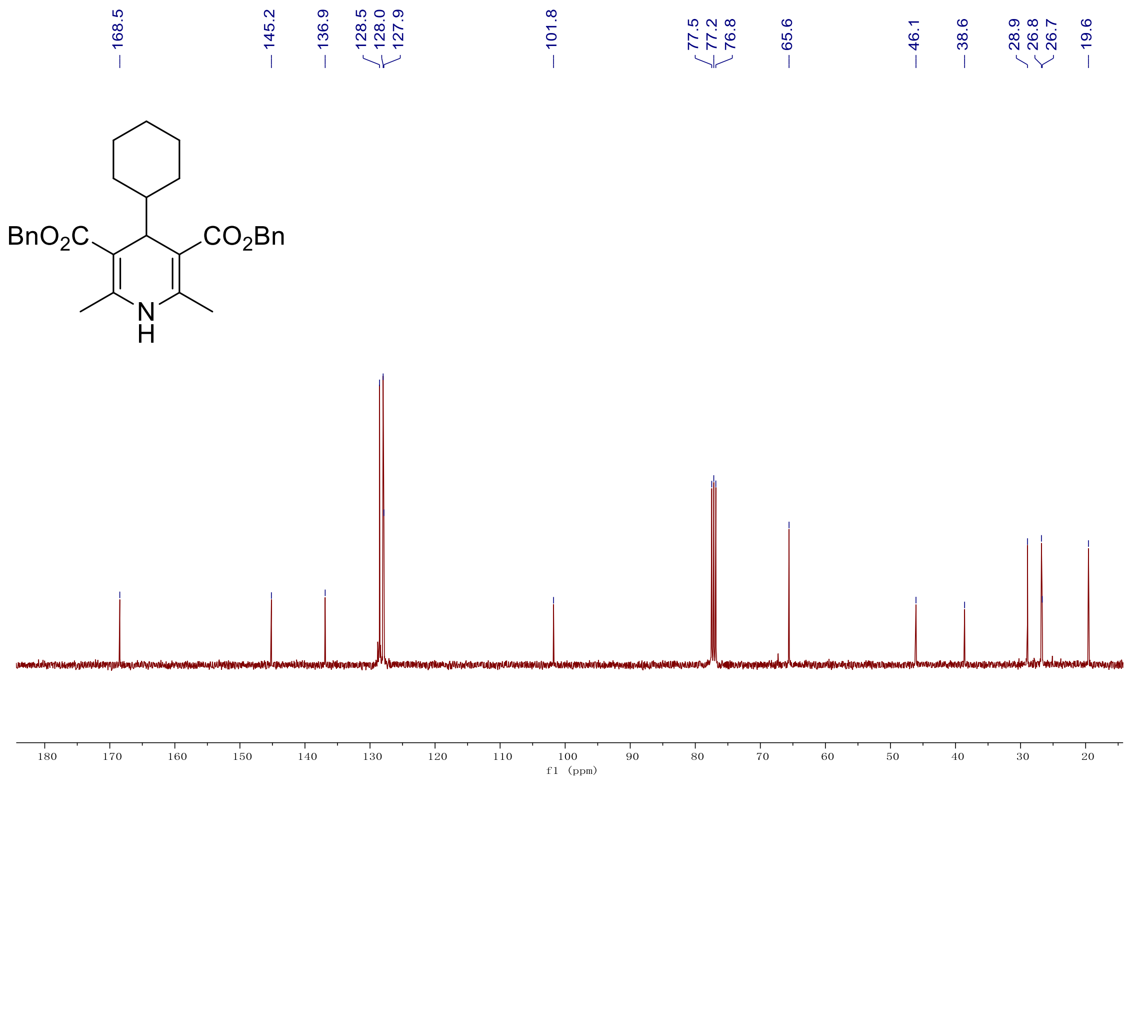
^{13}C NMR (100 MHz, $CDCl_3$) of ***d*-3aq**



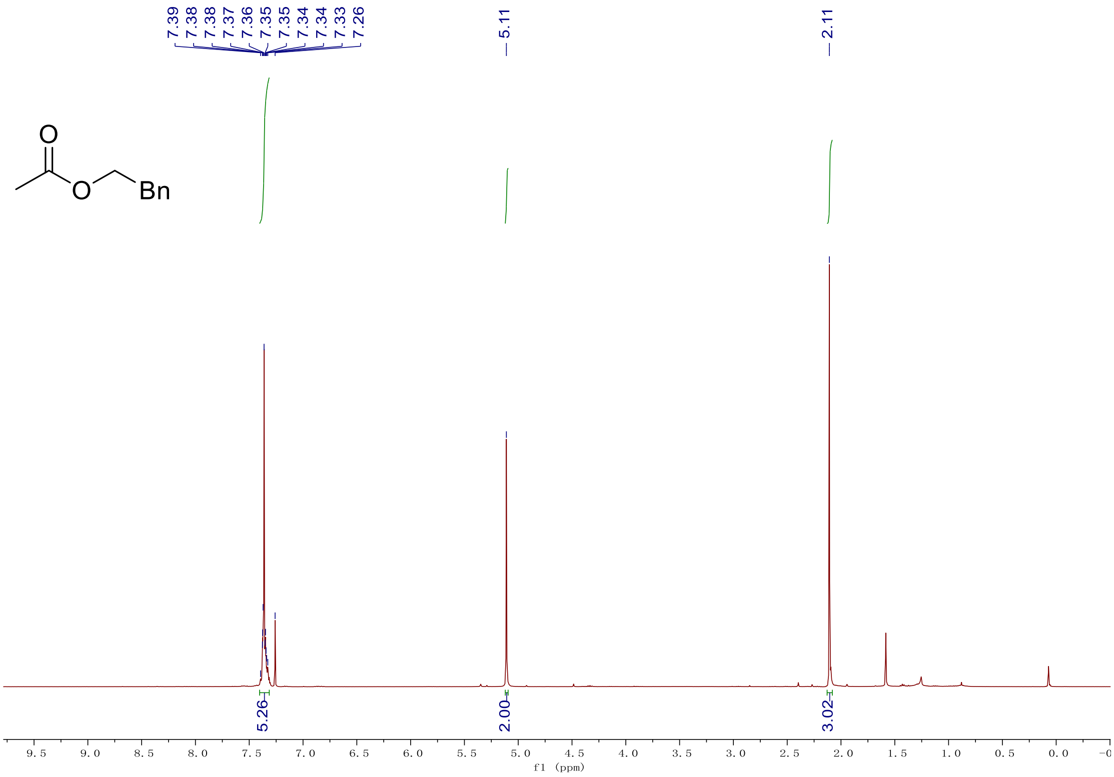
[1]H NMR (400 MHz, $CDCl_3$) of **3aq**



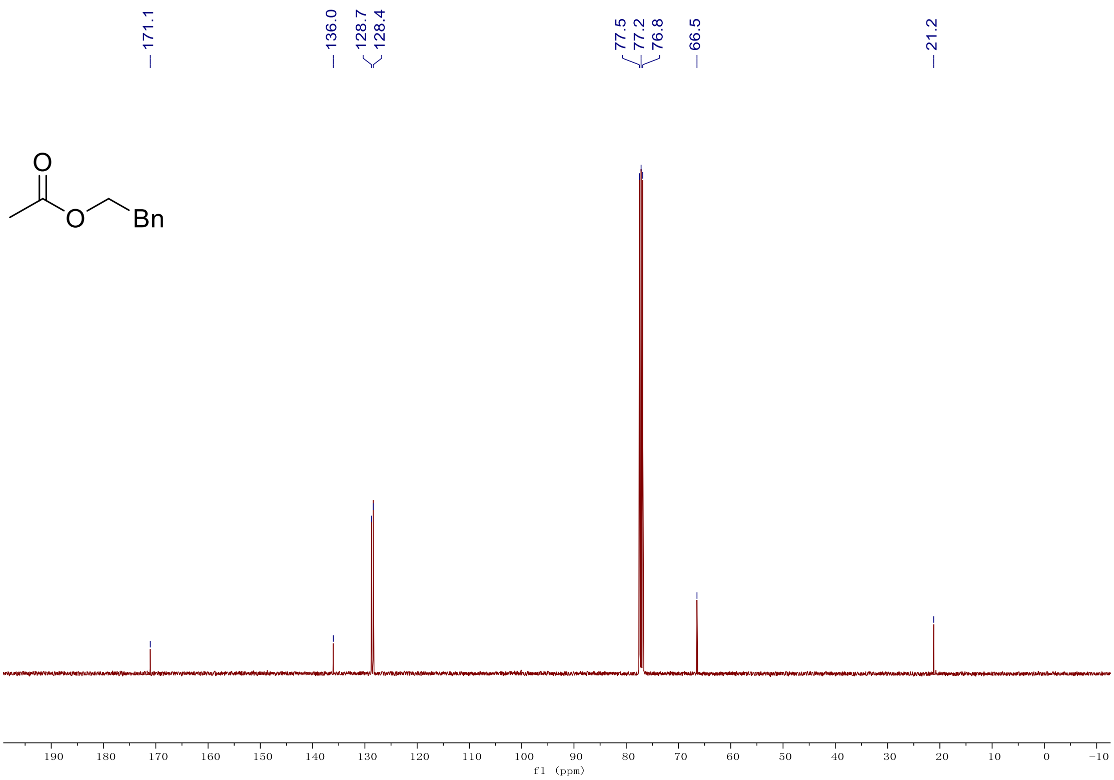
[13]C NMR (100 MHz, $CDCl_3$) of **3aq**



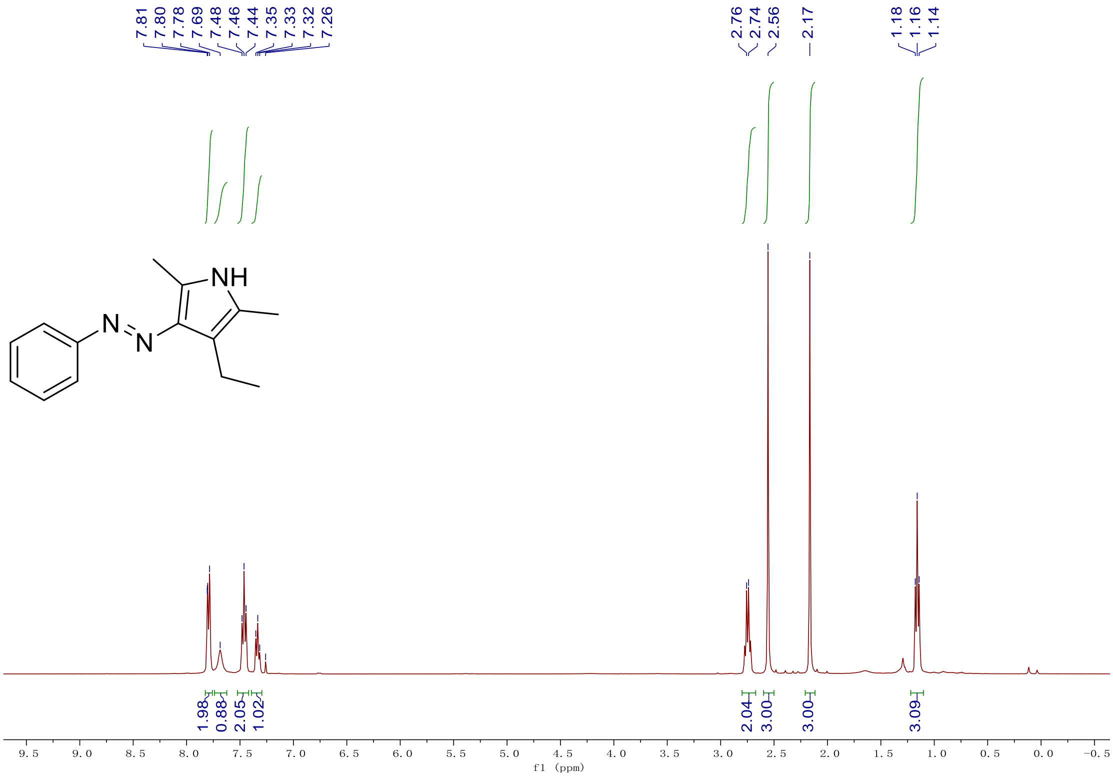
[1]H NMR (400 MHz, $CDCl_3$) of **4**



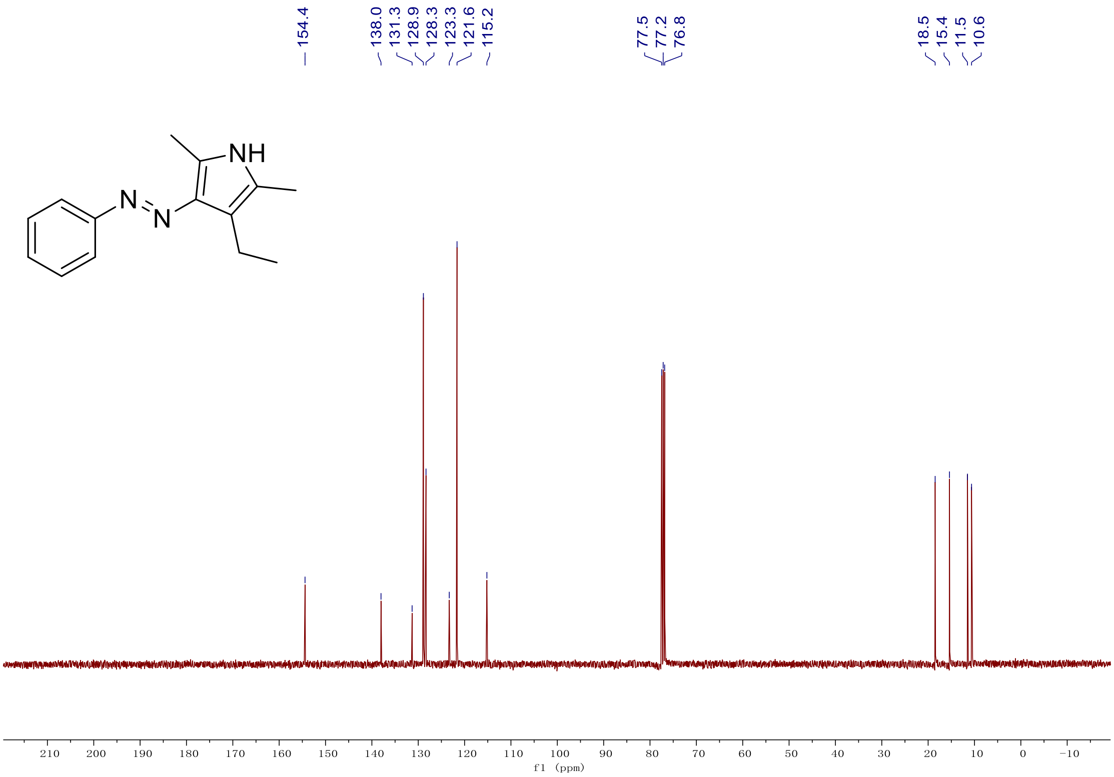
[13]C NMR (100 MHz, $CDCl_3$) of **4**



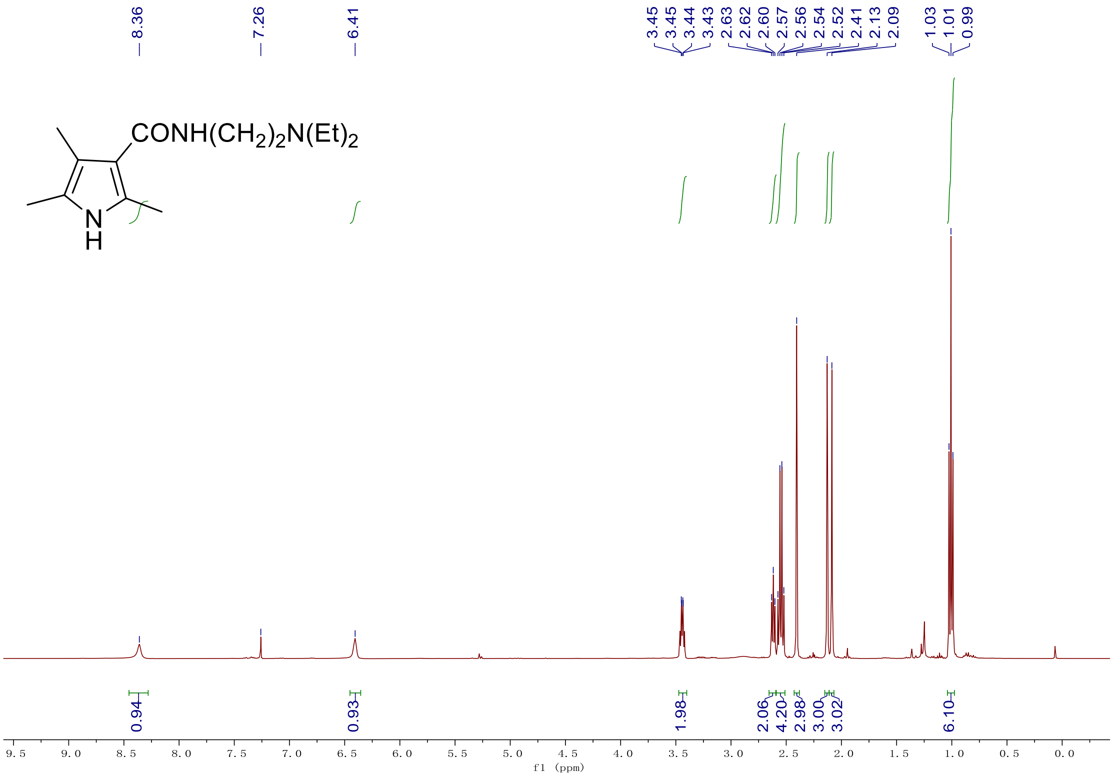
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



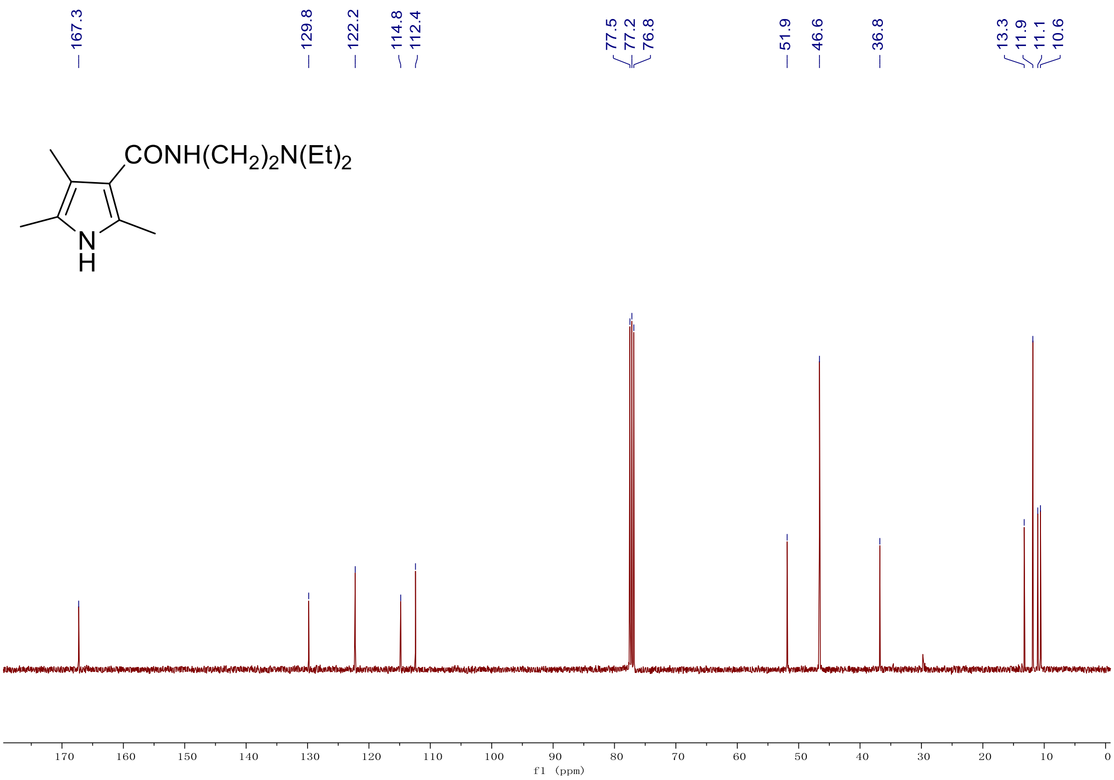
^{13}C NMR (100 MHz, $CDCl_3$) of **6**



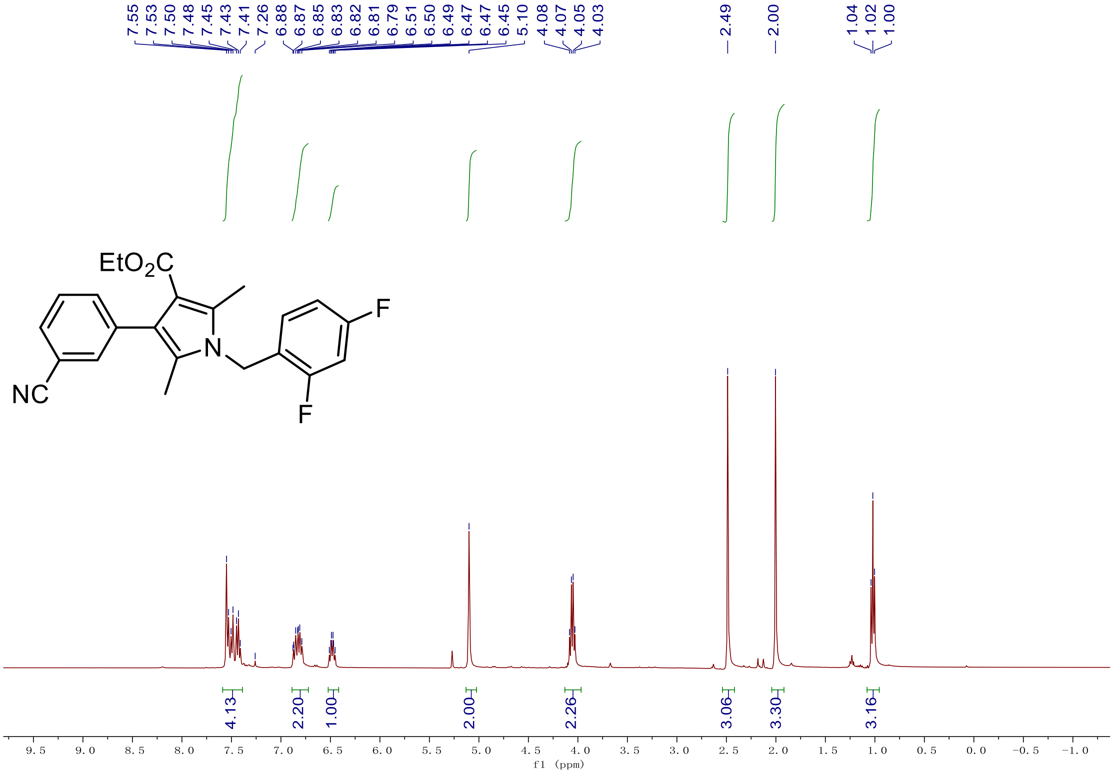
^1H NMR (400 MHz, $CDCl_3$) of **8**



^{13}C NMR (100 MHz, $CDCl_3$) of **8**



[1]H NMR (400 MHz, $CDCl_3$) of **9**



[13]C NMR (100 MHz, $CDCl_3$) of **9**