Supporting Information

Tandem Site-Selective Bromination and Highly Regioselective Heck Reaction of N-Allyl Enaminones: Chemodivergent Synthesis of Polysubstituted Pyrroles and Pyridines

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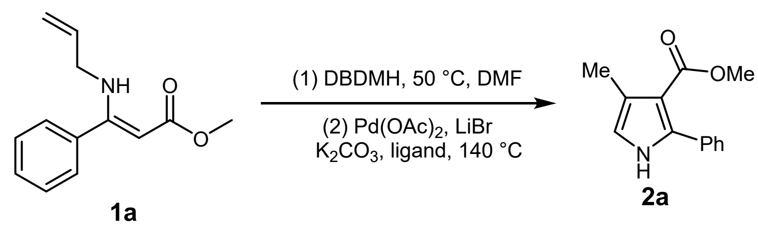
General Information

All reagents and solvent were commercial available with analytical grade and used as received. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. The used solvents were purified and dried according to common procedures. High-resolution mass spectra (HRMS) were obtained with a FTICR-MS (Ionspec 7.0T) spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on a Bruker AV 400 MHz spectrometer. Chemical shifts are reported in parts per million (δ) relative to $CDCl_3$ (7.26 ppm) for ^{1}H NMR data and $CDCl_3$ (77.0 ppm) for ^{13}C NMR data or the peak of DMSO-d_6, defined at δ = 2.50 (^{1}H NMR) or δ = 39.5 (^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). Flash column chromatography was performed over silica gel 200−300 mesh, and the eluent was a mixture of ethyl acetate (EA) and petroleum ether (PE).

Supplementary Data

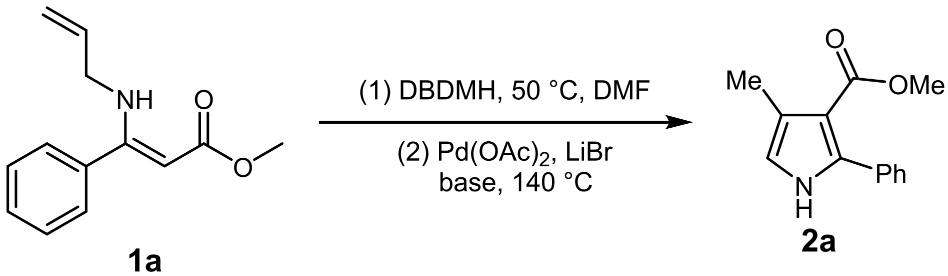
Table S1: Reaction optimization- ligands screening [a-b]



Entry	ligand	Yield of **2a** (%)[b]
1	PPh_3	15
2	JohnPhos	20
3	P(o-tol)$_3$	10
4	Dave-phos	12
5	Cy_3P	trace
6	s-phos	trace
7	none	79

[a]Reagents and conditions: (a) All reactions were performed with **1a** (0.2 mmol), DBDMH (0.1 mmol), DMF (1.5 mL), 50 °C, 40 min; and then $Pd(OAc)_2$ (20% mol), LiBr (1.2 equiv), K_2CO_3 (1.2 equiv), N_2, 140 °C, 5h. [b]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

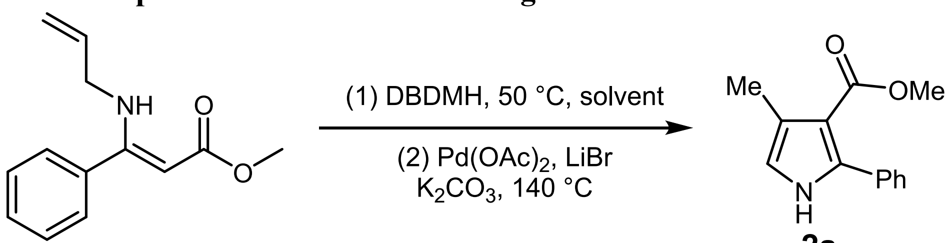
Table S2: Reaction optimization-base screening [a-b]



Entry	Base	Yield of **2a** (%)[b]
1	K_2CO_3	79
2	DBU	37
3	DIPEA	23
4	$NaHCO_3$	70
5	N,N-Dicyclohexylmethylamine	20
6	KOH	30

[a]Reagents and conditions: (a) All reactions were performed with **1a** (0.2 mmol), DBDMH (0.1 mmol), DMF (1.5 mL), 50 °C, 40 min; and then $Pd(OAc)_2$ (20% mol), LiBr (1.2 equiv), base (1.2 equiv), N_2, 140 °C, 12 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

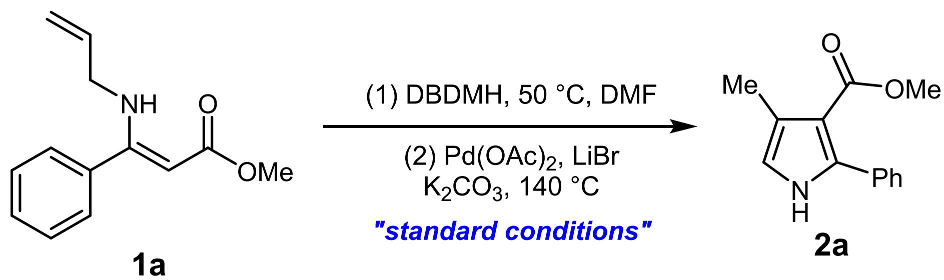
Table S3: Reaction optimization-solvent screening [a-b]



Entry	Solvent	Yield of **2a** (%)[b]
1	DMF	79
2	DMA	60
3	NMP	31
4	HMPA	trace

[a]Reagents and conditions: (a) All reactions were performed with **1a** (0.2 mmol), DBDMH (0.1 mmol), solvent (1.5 mL), 50 °C, 40 min; and then $Pd(OAc)_2$ (20% mol), LiBr (1.2 equiv), base (1.2 equiv), N_2, 140 °C, 12 h. [b]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

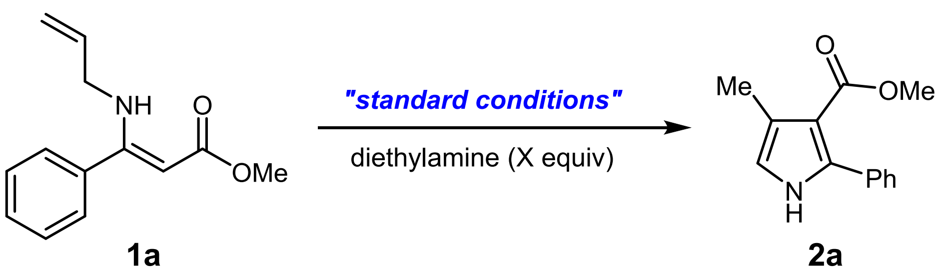
Table S4: Reaction optimization-temperature screening [a-b]



Entry	variation from the "standard condition"	Yield of **2a** (%)[b]
1	none	79
2	120 °C, instead of 140 °C	61
3	100 °C, instead of 140 °C	57
4	80 °C, instead of 140 °C	40
5	rt, instead of 140 °C	trace

[a]Reagents and conditions: (a) All reactions were performed with **1a** (0.2 mmol), DBDMH (0.1 mmol), DMF (1.5 mL), 50 °C, 40 min; and then $Pd(OAc)_2$ (20% mol), LiBr (1.2 equiv), K_2CO_3 (1.2 equiv), N_2, 140 °C, 12 h. [b]Determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Figure 1: The effect of amine group



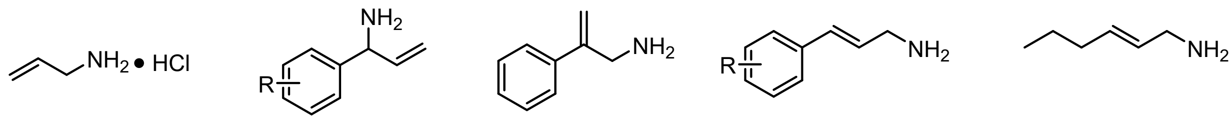
X = 0, Y = 79% X = 0.5, Y = 35% X = 1, Y = trace Y = yield of **2a**

Experimental Procedure

Procedure for the Synthesis of the Substituted N-allyl amine

There are five-types allyl amines in this paper. Allylamine hydrochloride **S1** was purchased in reagent grade from commercial suppliers and used directly. **S2-S13** were synthesized by the following methods.

allyl amines:



S1 **S2-S9** **S10** **S11-S12** **S13**

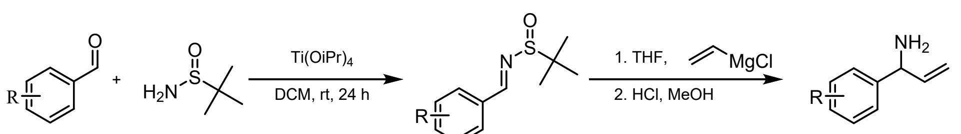
S2, R = H,
S3, R = *p*-Me,
S4, R = *p*-Br,
S5, R = *p*-Cl,
S6, R = *p*-CF_3,
S7, R = *m*-Me,
S8, R = *m*-F,
S9, R = *m*-Cl,

S11, R = H,
S12, R = *p*-OMe

Scheme S1

Method A:

Allyl amines **S2**-**S9** were prepared following Method A[1].



S2-S9

S2, R = H,
S3, R = *p*-Me,
S4, R = *p*-Br,
S5, R = *p*-Cl,
S6, R = *p*-CF_3,
S7, R = *m*-Me,
S8, R = *m*-F,
S9, R = *m*-Cl,

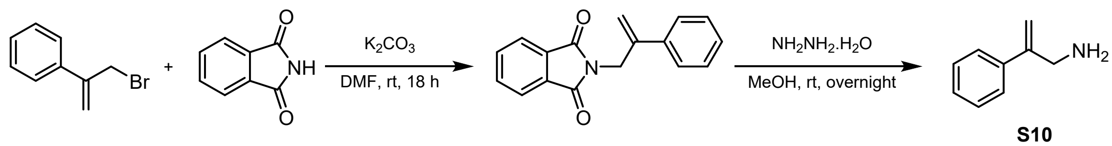
Scheme 2

To a solution of titanium tetraisopropanolate (1.0 equiv) in CH_2Cl_2 (1.0 M), 2-methylpropane-2-sulfinamide (1.0 equiv) was added. Subsequently, the corresponding aldehyde (1.2 equiv) was added, and the solution was stirred at room temperature for 24 hours. Upon completion, saturated sodium bicarbonate solution was added. The mixture was filtered through a short pad of celite. The aqueous layer was further extracted with CH_2Cl_2. The combined organic layer was dried with Na_2SO_4, filtered, and concentrated in vacuo to yield the corresponding imine.

The crude imine intermediate was dissolved in THF (1.0 M), and the reaction was cooled to 0 °C. Vinyl Grignard (1.2 equiv) was subsequently added, and the solution was warmed to room temperature and stirred overnight (approximately 12 hours). The reaction progress was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to 0 °C, and saturated ammonium chloride solution was added. The aqueous layer was further extracted with CH_2Cl_2. The combined organic layer was dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was dissolved in MeOH and cooled to 0 °C. Excess HCl (6.0 M) was subsequently added dropwise over 10 minutes, and the solution was warmed to room temperature and stirred overnight (approximately 12 hours). The solvent (MeOH) was removed under reduced pressure, and H_2O was added to the reaction mixture. The aqueous phase was then washed with ethyl acetate. Aqueous KOH solution was added to the aqueous phase until the pH reached 12. The aqueous solution was extracted with CH_2Cl_2. The combined organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure to yield the crude amine.

Method B:

Allyl amines **S10** were prepared following Method B[2].



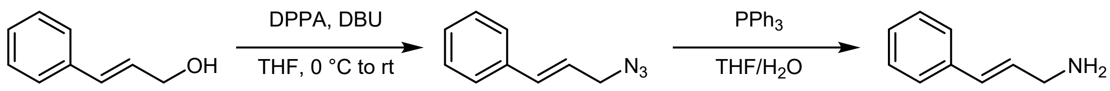
Scheme 3

To a solution of (3-bromoprop-1-en-2-yl)benzene (5 mmol) in DMF (20 mL), phthalimide (5.5 mmol) and K_2CO_3 (5.5 mmol) were added at room temperature. The resulting mixture was stirred for 18 hours. Then, water and CH_2Cl_2 (25 mL) were added. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield the product 2-(2-phenylallyl)isoindoline-1,3-dione.

The crude product 2-(2-phenylallyl)isoindoline-1,3-dione in methanol (40 mL) was treated with hydrazine hydrate (12 mmol). The reaction mixture was refluxed for 3 hours. The mixture was cooled to room temperature and concentrated HCl (6 mL) was added. The reaction mixture was refluxed for 1 h. The reaction mixture was cooled back to room temperature and filtered to remove solids. The solvent (MeOH) was concentrated under reduced pressure to obtain the residue, which was then dissolved in H_2O (5 mL). The aqueous layer was washed with ethyl acetate. After removed the organic layer, the pH of aqueous layer was adjusted to 10 using a NaOH aqueous solution. The aqueous solution was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield amine **S10**. Amine **S10** was directly utilized for the subsequent step.

The crude product 2-(2-phenylallyl)isoindoline-1,3-dione in methanol (40 mL) was treated with hydrazine hydrate (12 mmol). The reaction mixture was refluxed for 3 hours. After cooling to room temperature, concentrated HCl (6 mL) was added, and the reaction mixture was refluxed for 1 hour. It was then cooled again to room temperature and filtered to remove solids. The solvent (MeOH) was evaporated under reduced pressure to obtain the residue, which was dissolved in H_2O (5 mL). The aqueous layer was washed with ethyl acetate. After removing the organic layer, the pH of the aqueous layer was adjusted to 10 using a NaOH aqueous solution. The resulting solution was then extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield amine **S10**, which was directly utilized for the subsequent step.

Method C:



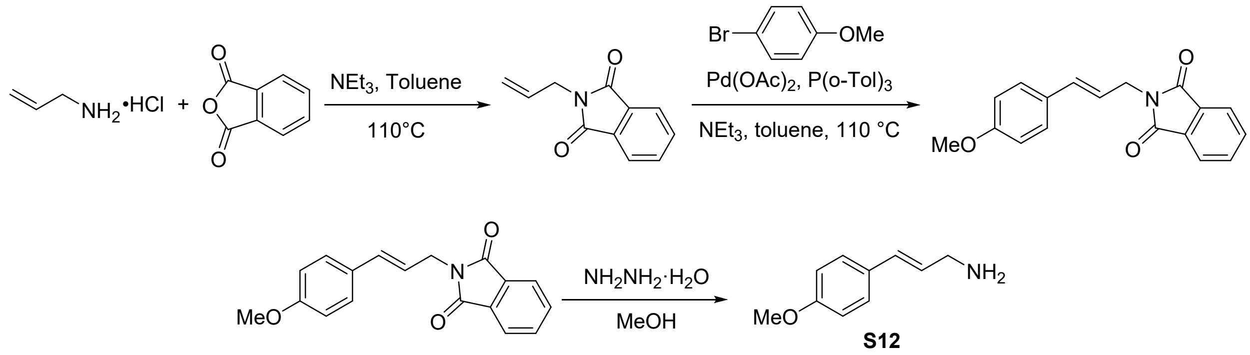
S11

Scheme 4

To a solution of (E)-3-phenylprop-2-en-1-ol (4.03 g, 30 mmol) in THF (120 mL) was added diphenylphosphoryl azide (9.7 mL, 45 mmol) and 1,8-Diazabicyclo[5.4.0]undec-7-ene (6.73 mL, 45 mmol) at 0 °C. The reaction mixture was stirred for 12 hours at room temperature and then filtered. The filtrate was evaporated under vacuum, and dichloromethane (60 mL) was added. The organic layer was washed with brine, and the aqueous phase was further extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield the crude product (E)-(3-azidoprop-1-en-1-yl)benzene.

The crude (E)-(3-azidoprop-1-en-1-yl)benzene was dissolved in THF (120 mL) and water (30 mL). PPh_3 (15.7 g, 60 mmol) was added, and the solution was stirred at room temperature overnight. The solvent was removed under reduced pressure to give a residue. The residue was dissolved in MeOH, and concentrated HCl (6 mL) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 1 hour. The solvent (MeOH) was then concentrated under reduced pressure to obtain the residue, which was dissolved in H_2O (5 mL). The aqueous layer was washed with ethyl acetate. After removing the organic layer, the pH of the aqueous layer was adjusted to 10 using a NaOH aqueous solution. The resulting reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layer was dried over anhydrous Na_2SO_4. The organic layer was filtered and concentrated under reduced pressure to afford amine **S11**.

Method D[3]:

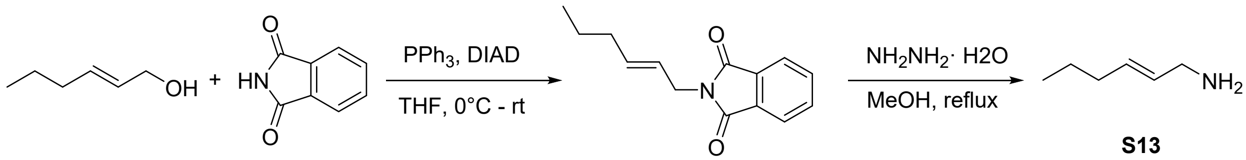


Scheme 5

Under a nitrogen atmosphere, aryl bromide (10 mmol), N-allylphthalimide (10.3 mmol), triethylamine (30 mmol), palladium acetate (0.1 mmol), tri-o-tolylphosphine (0.2 mmol), and toluene were combined in a flask. The reaction mixture was heated at 110 °C for 16 hours. After cooling the reaction mixture to ambient temperature, CH_2Cl_2 (50 mL) and H_2O (50 mL) were added. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain the crude product. This crude product was then purified by column chromatography to yield (E)-2-(3-(4-methoxyphenyl)allyl)isoindoline-1,3-dione.

To a solution of (E)-2-(3-(4-methoxyphenyl)allyl)isoindoline-1,3-dione (10 mmol) in methanol (40 mL), hydrazine hydrate (12 mmol) was added. The reaction mixture was heated under reflux for 3 hours. After cooling to room temperature, concentrated HCl (6 mL) was added, and the reaction mixture was refluxed for an additional 30 minutes. The reaction mixture was then cooled back to room temperature and filtered to remove solids. The filtrate was concentrated under reduced pressure to obtain the residue, which was dissolved in H_2O. The aqueous layer was washed with ethyl acetate. After removing the organic layer, the pH of the aqueous layer was adjusted to 10 using a NaOH aqueous solution. The resulting aqueous solution was then extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield amine **S12**, which was directly utilized for the subsequent step.

Method E[4]*:*



Scheme 6

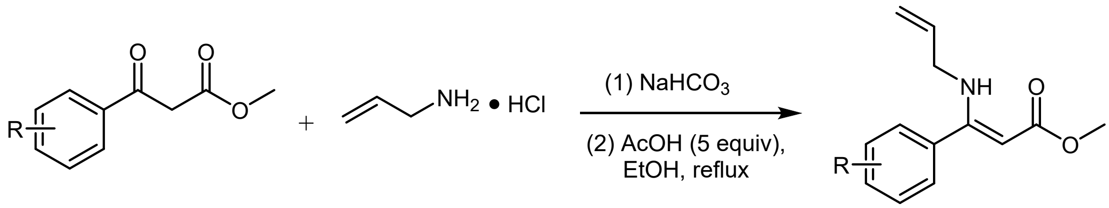
Under a nitrogen atmosphere, (E)-hex-2-en-1-ol (20 mmol), isoindoline-1,3-dione (22 mmol), PPh_3 (22 mmol), and THF (100 mL) were sequentially added to a flask. The reaction mixture was then cooled to 0 °C, and DIAD (1,2-diisopropoxydiazene, 22 mmol) was added. The reaction mixture was stirred at room temperature for 4 hours. THF was removed under reduced pressure to give a residue, which was then dissolved in CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to afford the crude (E)-2-(hex-2-en-1-yl)isoindoline-1,3-dione.

To a solution of (E)-2-(hex-2-en-1-yl)isoindoline-1,3-dione (10 mmol) in methanol (40 mL) was added hydrazine hydrate (12 mmol). The reaction mixture was heated under reflux for 3 h. After cooling to room temperature, concentrated HCl (6 mL) was added, and the reaction mixture was refluxed for 0.5 h. The reaction mixture was then cooled back to room temperature and filtered to remove solids. The filtrate was concentrated under reduced pressure to obtain the residue, which was then dissolved in H_2O. The aqueous layer was washed with ethyl acetate. After removed the organic layer, the pH of aqueous layer was adjusted to 10 using a NaOH aqueous solution. The resulting aqueous solution was then extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield amine **S13**, which was directly utilized for the subsequent step.

Procedure for the Synthesis of the N-allyl enamine 1 and 3

Four different procedures were employed for the synthesis of N-allyl enamines **1** and **3** from the respective allyl amines.

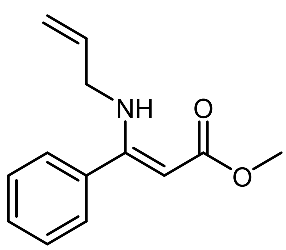
General procedure A[5]*:*



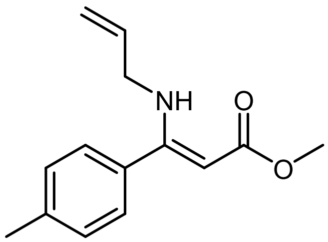
1a-1p

Scheme 7

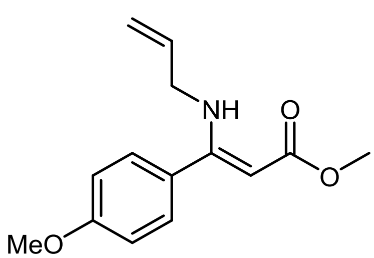
Allylamine hydrochloride (50.0 mmol) and $NaHCO_3$ (50.0 mmol) were added to a flask and stirred at room temperature for 30 minutes. Then, methyl 3-oxo-3-phenylpropanoate (10.0 mmol), acetic acid (50.0 mmol), 4Å molecular sieve (1 g), and ethanol (20 mL) were successively added. The reaction mixture was heated under reflux for 6 hours. Afterward, the mixture was filtered through a short pad of celite and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2. The organic layer was washed with 1M HCl solution and water, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography to yield N-allyl enamines **1a-1p**.



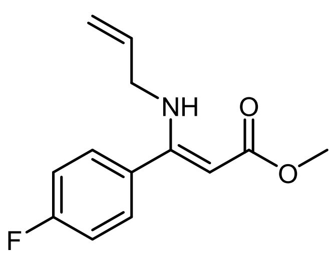
methyl (Z)-3-(allylamino)-3-phenylacrylate (**1a**)[6]. General procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1a** as a yellow oil. Yield: 1.84 g, 85%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.43–7.31 (m, 5H), 5.90–5.70 (m, 1H), 5.26–5.17 (m, 1H), 5.15–5.06 (m, 1H), 4.64 (s, 1H), 3.69 (s, 3H), 3.68–3.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 164.9, 135.8, 135.3, 129.3, 128.3, 127.7, 115.8, 85.4, 50.2, 46.7.



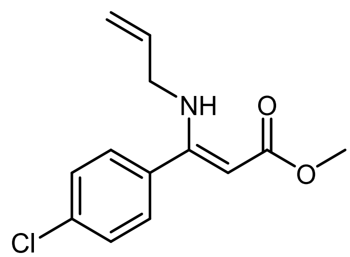
methyl (Z)-3-(allylamino)-3-(p-tolyl)acrylate (**1b**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1b** as a yellow oil. Yield: 1.38 g, 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 7.25–7.22 (m, 2H), 7.20–7.16 (m, 2H), 5.86–5.70 (m, 1H), 5.24–5.19 (m, 1H), 5.13–5.09 (m, 1H), 4.63 (s, 1H), 3.71–3.65 (m, 5H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 165.1, 139.3, 135.4, 132.9, 128.9, 127.7, 115.7, 85.1, 50.2, 46.8, 21.2. HRMS (ESI): m/z [M + H^+] calcd for $C_{14}H_{18}NO_2$:232.1332; found: 232.1331.



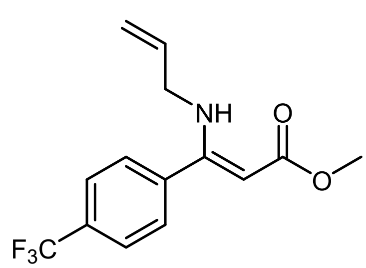
methyl (Z)-3-(allylamino)-3-(4-methoxyphenyl)acrylate (**1c**)[7]. The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1c** as a yellow oil. Yield: 1.11 g, 45%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.31–7.28 (m, 2H), 6.95–6.85 (m, 2H), 5.87–5.72 (m, 1H), 5.22 (ddd, J = 17.1, 3.1, 1.8 Hz, 1H), 5.11 (ddd, J = 10.3, 2.9, 1.5 Hz, 1H), 4.63 (s, 1H), 3.82 (s, 3H), 3.74–3.68 (m, 2H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 164.8, 160.4, 135.4, 129.2, 128.1, 115.7, 113.7, 85.1, 55.3, 50.2, 46.8.



methyl (Z)-3-(allylamino)-3-(4-fluorophenyl)acrylate (**1d**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1d** as a yellow oil. Yield: 1.64 g, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.43–7.29 (m, 2H), 7.15–6.96 (m, 2H), 5.89–5.63 (m, 1H), 5.20 (ddd, J = 17.1, 3.1, 1.8 Hz, 1H), 5.11 (ddd, J = 10.4, 2.9, 1.5 Hz, 1H), 4.61 (s, 1H), 3.68 (s, 3H), 3.67–3.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 163.8, 163.3 (d, J =248.0 Hz), 135.2, 131.8 (d, J = 3.0 Hz), 129.7 (d, J = 8.0 Hz), 115.9, 115.4 (d, J = 22.0 Hz), 85.8, 50.3, 46.7. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{13}H_{15}FNO_2$:236.1081; found: 236.1077.

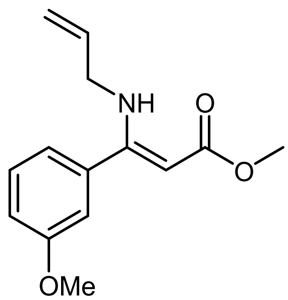


methyl (Z)-3-(allylamino)-3-(4-chlorophenyl)acrylate (**1e**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1e** as a yellow oil. Yield: 1.73 g, 69%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 7.43–7.35 (m, 2H), 7.34–7.29 (m, 2H), 5.90–5.70 (m, 1H), 5.22 (ddd, J = 17.1, 3.0, 1.7 Hz, 1H), 5.14 (ddd, J = 10.3, 2.9, 1.5 Hz, 1H), 4.64 (s, 1H), 3.71 (s, 3H), 3.69–3.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 163.6, 135.4, 135.2, 134.2, 129.2, 128.6, 115.9, 85.9, 50.3, 46.7. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{13}H_{15}ClNO_2$:252.0786; found: 252.0783.

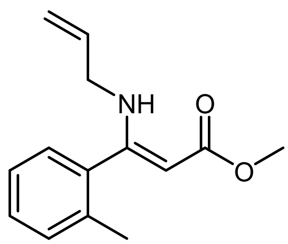


methyl (Z)-3-(allylamino)-3-(4-(trifluoromethyl)phenyl)acrylate (**1f**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1f** as a yellow solid. Yield: 2.34 g, 82%; mp 51-52 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1H), 7.65 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 5.83–5.70 (m, 4.9 Hz, 1H), 5.20 (ddd, J = 17.1, 3.0, 1.7 Hz, 1H), 5.13 (ddd, J = 10.4, 2.8, 1.5 Hz, 1H), 4.63 (s, 1H), 3.69 (s, 3H), 3.66–3.61 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 163.1, 139.4, 135.1, 131.4 (q, J = 33

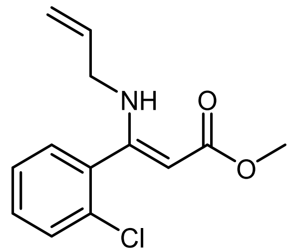
Hz), 128.2, 125.4 (q, J = 3.7 Hz), 123.8 (d, J = 271 Hz), 116.0, 86.3, 50.4, 46.7. HRMS (ESI): m/z [M + H^+] calcd for $C_{14}H_{15}F_3NO_2$:286.1049; found: 286.1050.



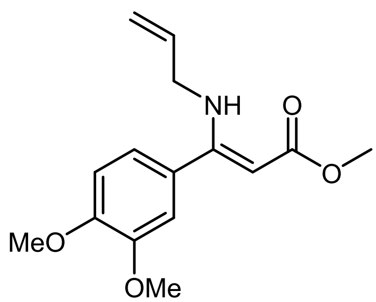
methyl (Z)-3-(allylamino)-3-(3-methoxyphenyl)acrylate (**1g**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1g** as a yellow oil. Yield: 1.36 g, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.33–7.27 (m, 1H), 6.99–6.90 (m, 2H), 6.89–6.86 (m, 1H), 5.86–5.70 (m, 1H), 5.22 (ddd, J = 17.1, 3.1, 1.8 Hz, 1H), 5.11 (ddd, J = 10.3, 3.0, 1.6 Hz, 1H), 4.65 (s, 1H), 3.80 (s, 3H), 3.71–3.66 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 164.7, 159.4, 137.1, 135.4, 129.4, 120.1, 115.7, 115.0, 113.1, 85.2, 55.3, 50.2, 46.8. HRMS (ESI): m/z [M + H^+] calcd for $C_{14}H_{18}NO_3$:248.1281; found: 248.1278.



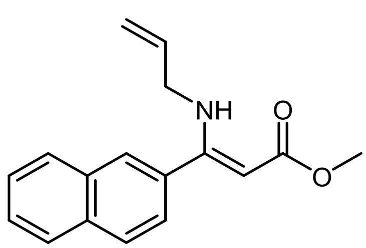
methyl (Z)-3-(allylamino)-3-(o-tolyl)acrylate (**1h**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1h** as a yellow oil. Yield: 1.16 g, 50%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.32–7.26 (m, 1H), 7.22–7.12 (m, 3H), 5.83–5.65 (m, 1H), 5.18–5.11 (m, 1H), 5.10–5.04 (m, 1H), 4.50 (s, 1H), 3.68 (s, 3H), 3.58–3.40 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9, 163.9, 135.3, 135.3, 134.8, 130.0, 128.8, 127.9, 125.6, 115.9, 83.9, 50.1, 46.1, 19.1. HRMS (ESI): m/z [M + H^+] calcd for $C_{14}H_{18}NO_2$:232.1332; found: 232.1332.



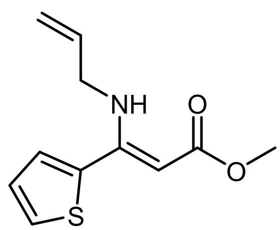
methyl (Z)-3-(allylamino)-3-(2-chlorophenyl)acrylate (**1i**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1i** as a yellow oil. Yield: 1.81 g, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (s, 1H), 7.44–7.38 (m, 1H), 7.35–7.26 (m, 2H), 7.26–7.22 (m, 1H), 5.83–5.67 (m, 1H), 5.17–5.11 (m, 1H), 5.09–5.04 (m, 1H), 4.51 (s, 1H), 3.67 (s, 3H), 3.66–3.57 (m, 1H), 3.51–3.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 160.9, 134.6, 134.5, 132.2, 130.1, 129.9, 129.4, 126.7, 116.0, 84.4, 50.1, 46.2. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{13}H_{15}ClNO_2$:252.0786; found: 252.0784.



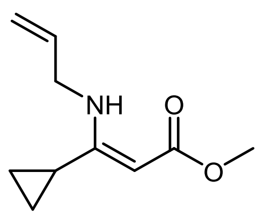
methyl (Z)-3-(allylamino)-3-(3,4-dimethoxyphenyl)acrylate (**1j**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1j** as a yellow oil. Yield: 1.27 g, 46%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.00–6.92 (m, 1H), 6.89–6.80 (m, 2H), 5.90–5.72 (m, 1H), 5.25 (ddd, J = 17.1, 3.1, 1.7 Hz, 1H), 5.13 (ddd, J = 10.4, 2.9, 1.5 Hz, 1H), 4.66 (s, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 3.75–3.70 (m, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.7, 164.9, 149.9, 148.6, 135.6, 128.4, 120.5, 115.7, 110.9, 110.8, 85.2, 55.9, 55.9, 50.2, 46.9. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{15}H_{20}NO_4$:278.1387; found:278.1385.



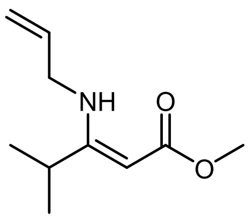
methyl (Z)-3-(allylamino)-3-(naphthalen-2-yl)acrylate (**1k**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1k** as a white solid. Yield: 2.11 g, 79%; mp 110-111 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.92–7.84 (m, 4H), 7.64–7.53 (m, 2H), 7.47 (dd, J = 8.4, 1.7 Hz, 1H), 5.91–5.73 (m, 1H), 5.27 (ddd, J = 17.1, 3.1, 1.7 Hz, 1H), 5.16 (ddd, J = 10.3, 2.8, 1.5 Hz, 1H), 4.80 (s, 1H), 3.78–3.72 (m, 5H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 164.9, 135.3, 133.5, 133.3, 132.8, 128.3, 127.9, 127.7, 127.3, 126.8, 126.6, 125.2, 115.8, 85.9, 50.3, 46.9. HRMS (ESI): m/z [M + H^+] calcd for $C_{17}H_{18}NO_2$:268.1332; found: 268.1331.



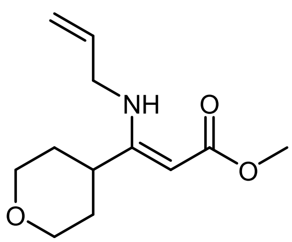
methyl (Z)-3-(allylamino)-3-(thiophen-2-yl)acrylate (**1l**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1l** as a yellow oil. Yield: 0.94 g, 42%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 7.43–7.32 (m, 1H), 7.23–7.15 (m, 1H), 7.09–6.99 (m, 1H), 5.93–5.77 (m, 1H), 5.26 (ddd, J = 17.1, 3.0, 1.7 Hz, 1H), 5.15 (ddd, J = 10.4, 2.8, 1.5 Hz, 1H), 4.86 (s, 1H), 3.93–3.82 (m, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 157.2, 136.6, 135.4, 128.0, 127.2, 127.1, 116.0, 86.5, 50.4, 47.0. HRMS (ESI): m/z [M + H^+] calcd for $C_{11}H_{14}NO_2S$:224.0740; found: 224.0738.



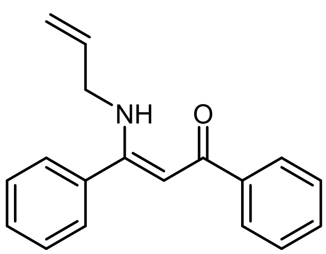
methyl (Z)-3-(allylamino)-3-cyclopropylacrylate (**1m**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1m** as a yellow oil. Yield: 1.43 g, 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1H), 6.02–5.82 (m, 1H), 5.24 (ddd, J = 17.2, 3.1, 1.8 Hz, 1H), 5.15 (ddd, J = 10.3, 3.0, 1.6 Hz, 1H), 4.32 (s, 1H), 4.06–4.00 (m, 2H), 3.61 (s, 3H), 1.57–1.38 (m, 1H), 0.91–0.73 (m, 2H), 0.72–0.56 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.4, 166.5, 135.0, 115.8, 78.1, 50.0, 45.00, 12.2, 6.5. HRMS (ESI): m/z [M + H^+] calcd for $C_{10}H_{16}NO_2$:182.1176; found: 182.1175.



methyl (Z)-3-(allylamino)-4-methylpent-2-enoate (**1n**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **1n** as a yellow oil. Yield: 1.37 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 1H), 6.02–5.78 (m, 1H), 5.23 (ddd, J = 17.1, 3.0, 1.8 Hz, 1H), 5.15 (ddd, J = 10.3, 2.9, 1.6 Hz, 1H), 4.53 (s, 1H), 3.90–3.82 (m, 2H), 3.61 (s, 3H), 2.66–2.56 (m, 1H), 1.10 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.9, 171.6, 134.9, 115.9, 77.7, 49.9, 44.3, 28.3, 21.5. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{10}H_{18}NO_2$:184.1332; found: 184.1329.



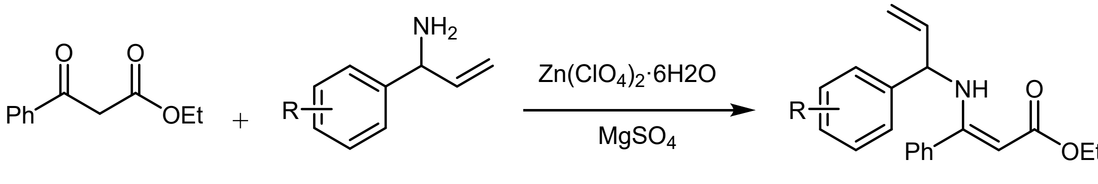
methyl (Z)-3-(allylamino)-3-(tetrahydro-2H-pyran-4-yl)acrylate (**1o**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 10:1) afforded **1o** as a yellow oil. Yield: 1.20 g, 53%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 1H), 5.96–5.77 (m, 1H), 5.27–5.20 (m, 1H), 5.17 (ddd, J = 10.3, 2.8, 1.6 Hz, 1H), 4.56 (s, 1H), 4.05–3.97 (m, 2H), 3.90–3.81 (m, 2H), 3.63 (s, 3H), 3.45–3.36 (m, 2H), 2.60–2.36 (m, 1H), 1.71–1.63 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.5, 168.4, 135.0, 116.1, 79.5, 67.8, 50.1, 44.4, 36.4, 31.6. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{12}H_{20}NO_3$:226.1438; found: 226.1438.



(Z)-3-(allylamino)-1,3-diphenylprop-2-en-1-one (**1p**)[8]. The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 50:1) afforded **1p** as

a yellow oil. Yield: 2.1 g, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.41 (s, 1H), 7.99–7.86 (m, 2H), 7.53–7.35 (m, 8H), 5.96–5.81 (m, 1H), 5.81 (s, 1H), 5.29 (ddd, J = 17.1, 2.9, 1.7 Hz, 1H), 5.18 (ddd, J = 10.4, 2.7, 1.5 Hz, 1H), 3.90–3.74 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.5, 166.8, 140.1, 135.4, 134.5, 130.7, 129.5, 128.4, 128.1, 127.6, 127.0, 116.3, 93.7, 46.9.

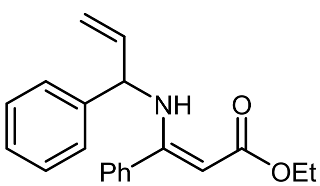
General procedure B[5]:



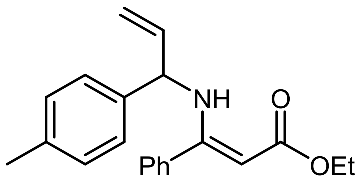
S2-S9

3a-3h

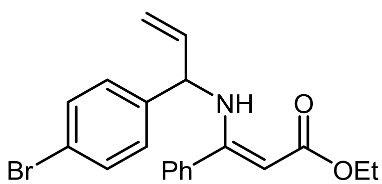
To a solution of $MgSO_4$ (1.50 mmol) and $Zn(ClO_4)_2{\bullet}6H_2O$ (93.10 mg, 0.25 mmol) in dichloromethane (5 mL), ethyl 3-oxo-3-phenylpropanoate (0.96 g, 5.00 mmol) was added. Subsequently, corresponding amine (7.50 mmol) was introduced at room temperature. The resulting mixture was heated to reflux for 42 hours. After cooling to room temperature, the reaction mixture was filtered. The solvent was then removed under reduced pressure to obtain crude products. These crude products were further purified by column chromatography to yield compounds **3a**-**3h** and **3l**.



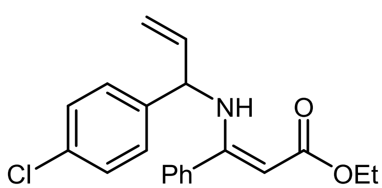
ethyl (Z)-3-phenyl-3-((1-phenylallyl)amino)acrylate (**3a**)[5]. The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3a** as a yellow oil. Yield: 997.75 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (d, J = 9.8 Hz, 1H), 7.42–7.27 (m, 7H), 7.23–7.20 (m, 1H), 7.20–7.14 (m, 2H), 6.01–5.92 (m, 1H), 5.24–5.14 (m, 2H), 4.90 (dd, J = 10.0, 5.1 Hz, 1H), 4.70 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 164.0, 141.4, 138.9, 136.1, 129.3, 128.6, 128.3, 127.8, 127.3, 126.7, 115.3, 87.3, 60.2, 58.8, 14.5.



ethyl (Z)-3-phenyl-3-((1-(p-tolyl)allyl)amino)acrylate (**3b**). The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3b** as a yellow oil. Yield: 1.07 g, 67%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (d, J = 9.9 Hz, 1H), 7.43–7.31 (m, 5H), 7.18–7.04 (m, 4H), 5.96 (ddd, J = 16.9, 10.3, 5.1 Hz, 1H), 5.30–5.11 (m, 2H), 4.89 (dd, J = 9.9, 5.0 Hz, 1H), 4.71 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 164.0, 139.2, 138.4, 136.9, 136.2, 129.3, 129.2, 128.2, 127.8, 126.6, 115.1, 87.1, 59.9, 58.8, 21.0, 14.5. HRMS (ESI): m/z [M + H^+] calcd for $C_{21}H_{24}NO_2$:322.1802; found: 322.1801.

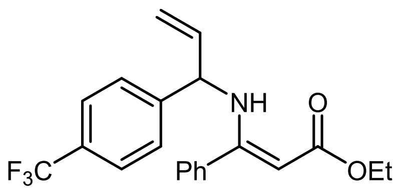


ethyl (Z)-3-((1-(4-bromophenyl)allyl)amino)-3-phenylacrylate (**3c**). The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3c** as a yellow oil. Yield: 1.16 g, 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (dd, J = 33.0, 10.6 Hz, 1H), 7.44–7.31 (m, 5H), 7.28–7.25 (m, 2H), 7.09–6.95 (m, 2H), 5.93 (ddd, J = 17.0, 10.4, 5.2 Hz, 1H), 5.26–5.11 (m, 2H), 4.85 (dd, J = 10.0, 5.1 Hz, 1H), 4.72 (s, 1H), 4.17 (q, J = 6.9 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 163.8, 140.5, 138.3, 135.9, 131.7, 129.4, 128.5, 128.3, 127.7, 121.2, 115.9, 87.9, 59.6, 58.9, 14.5. HRMS (ESI): m/z [M + H^+] calcd for $C_{20}H_{21}BrNO_2$:386.0750; found: 386.0752.

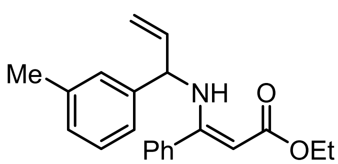


ethyl (Z)-3-((1-(4-chlorophenyl)allyl)amino)-3-phenylacrylate (**3d**). The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3d** as a yellow oil. Yield: 1.04 g, 61%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (d, J = 9.9 Hz, 1H), 7.42–7.32 (m, 3H), 7.29–7.27 (m, 2H), 7.26–7.24 (m, 2H), 7.12–7.04 (m, 2H), 5.94–5.89

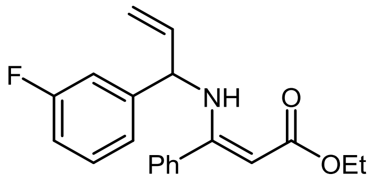
(m, 1H), 5.30–5.08 (m, 2H), 4.86 (dd, J = 9.9, 5.1 Hz, 1H), 4.72 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 163.8, 140.0, 138.4, 136.0, 133.1, 129.4, 128.8, 128.3, 128.1, 127.7, 115.8, 87.9, 59.6, 58.9, 14.5. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{20}H_{20}ClNNaO_2$: 364.1075; found: 364.1076.



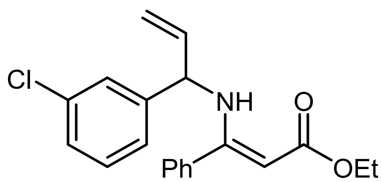
ethyl (Z)-3-phenyl-3-((1-(4-(trifluoromethyl)phenyl)allyl)amino)acrylate (**3e**). The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3e** as a yellow oil. Yield: 0.94 g, 50%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.98 (d, J = 9.9 Hz, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.42–7.32 (m, 3H), 7.29–7.23 (m, 4H), 5.95 (ddd, J = 17.1, 10.4, 5.2 Hz, 1H), 5.31–5.11 (m, 2H), 4.98–4.91 (m, 1H), 4.74 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 163.8, 145.5, 138.1, 135.9, 129.5, 128.4, 127.7, 127.1, 125.6 (q, J = 4 Hz), 116.3, 88.3, 59.9, 59.0, 14.5. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{21}H_{21}F_3NO_2$:376.1519; found: 376.1518.



ethyl (Z)-3-phenyl-3-((1-(m-tolyl)allyl)amino)acrylate (**3f**). The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3f** as a yellow oil. Yield: 0.83 g, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (d, J = 9.9 Hz, 1H), 7.45–7.30 (m, 5H), 7.24–7.18 (m, 1H), 7.09–7.05 (m, 1H), 7.04–6.93 (m, 2H), 6.04–5.89 (m, 1H), 5.30–5.12 (m, 2H), 4.88 (dd, J = 10.0, 5.1 Hz, 1H), 4.71 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 164.0, 141.2, 139.1, 138.2, 136.1, 129.2, 128.5, 128.2, 128.1, 127.7, 127.4, 123.8, 115.1, 87.1, 60.2, 58.8, 21.4, 14.5. HRMS (ESI): m/z [M + Na$^+$] calcd for $C_{21}H_{23}NNaO_2$: 344.1621; found: 344.1623.

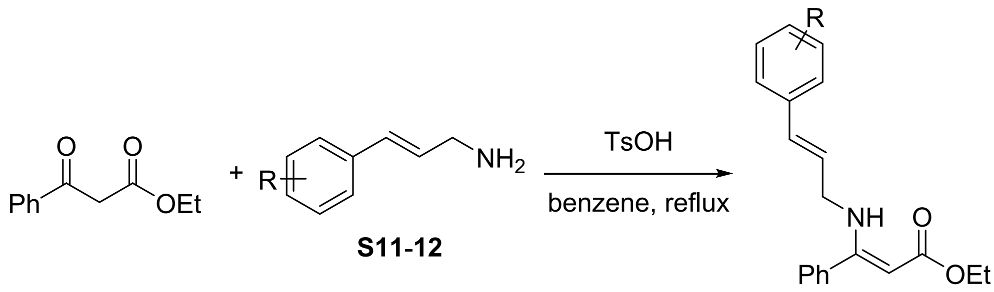


ethyl (Z)-3-((1-(3-fluorophenyl)allyl)amino)-3-phenylacrylate (**3g**). The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3g** as a yellow oil. Yield: 0.86 g, 53%; ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.95 (d, J = 9.9 Hz, 1H), 7.40–7.32 (m, 3H), 7.30–7.27 (m, 2H), 7.26–7.22 (m, 1H), 6.98–6.83 (m, 3H), 5.94 (ddd, J = 16.8, 10.5, 5.3 Hz, 1H), 5.25–5.16 (m, 2H), 4.88 (dd, J = 10.0, 5.2 Hz, 1H), 4.73 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 163.8, 162.9 (d，J = 246 Hz) 144.1, 138.2, 135.9, 130.1 (d，J = 8 Hz), 129.3, 128.3, 127.7, 122.3, 115.9, 113.9(q, J = 25 Hz), 87.9, 59.8, 58.89, 14.5. HRMS (ESI): m/z [M + Na^+] calcd for $C_{20}H_{20}FNNaO_2$: 348.1370; found: 348.1374.

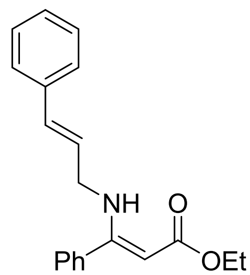


ethyl (Z)-3-((1-(3-chlorophenyl)allyl)amino)-3-phenylacrylate (**3h**). The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3h** as a yellow oil. Yield: 0.97 g, 57%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (d, J = 9.9 Hz, 1H), 7.42–7.33 (m, 3H), 7.31–7.26 (m, 2H), 7.25–7.18 (m, 2H), 7.15–7.10 (m, 1H), 7.09–7.03 (m, 1H), 5.92 (ddd, J = 17.0, 10.4, 5.2 Hz, 1H), 5.27–5.15 (m, 2H), 4.93–4.81 (m, 1H), 4.73 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 163.8, 143.5, 138.2, 135.9, 134.4, 129.9, 129.4, 128.4, 127.7, 127.5, 127.0, 124.9, 116.0, 88.0, 59.8, 58.9, 14.5. HRMS (ESI): m/z [M + Na^+] calcd for $C_{20}H_{20}ClNNaO_2$: 364.1075; found: 364.1079.

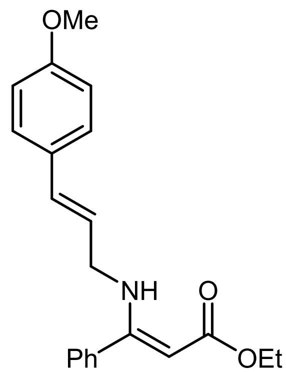
General procedure C[5]:



To a solution of ethyl 3-oxo-3-phenylpropanoate (5.0 mmol) in toluene (7 mL) was added amine (6.0 mmol) and p-toluenesulfonic acid (0.34 mmol). The reaction mixture was refluxed for 16 h and then quenched with water. The aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded corresponding product.

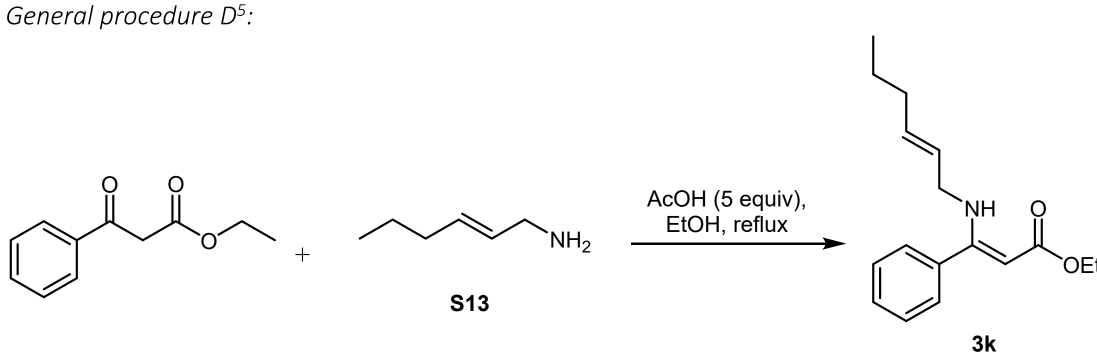


ethyl (Z)-3-(cinnamylamino)-3-phenylacrylate (**3i**)[5]. The general procedure C was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3i** as a yellow solid. Yield: 1.1 g, 70%. mp 44-45 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.72 (s, 1H), 7.45–7.37 (m, 5H), 7.36–7.29 (m, 4H), 7.25–7.21 (m, 1H), 6.47 (d, J = 15.9 Hz, 1H), 6.17–6.10 (m, 1H), 4.67 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.94–3.75 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 164.6, 136.6, 135.9, 131.2, 129.2, 128.5, 128.3, 127.8, 127.5, 126.8, 126.3, 86.1, 58.7, 46.4, 14.6.



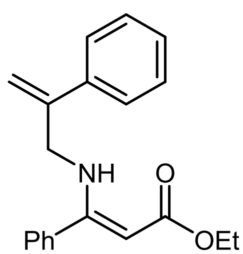
ethyl (Z)-3-(((E)-3-(4-methoxyphenyl)allyl)amino)-3-phenylacrylate (**3j**). The general procedure C was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3j** as a yellow oil. Yield: 1.26 g, 75%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (t, J = 5.7 Hz, 1H), 7.43–7.38 (m, 5H), 7.31–7.26 (m, 2H), 6.89–6.83 (m, 2H), 6.41 (d, J = 15.8 Hz, 1H), 6.04–5.98 (m, 1H), 4.68 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.88–3.83 (m, 2H), 3.82 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 164.7, 159.2, 135.9, 130.8, 129.4, 129.2, 128.3, 127.8, 127.5, 124.5, 113.9, 85.9, 58.7, 55.2, 46.5, 14.6. HRMS (ESI): m/z [M + Na^+] calcd for $C_{21}H_{23}NNaO_3$: 360.1570; found: 360.1573.

General procedure D[5]:



Allylamine **S13** (50.0 mmol) was dissolved in ethanol (20 mL), to which ethyl 3-oxo-3-phenylpropanoate (10.0 mmol), acetic acid (50.0 mmol), and 4Å molecular sieve (1 g) were added. The reaction mixture was heated under reflux for 6 hours. Subsequently, the resulting mixture was filtered through a short pad of celite and c oncentrated under reduced pressure. The residue was dissolved in dichloromethane (CH_2Cl_2), and the organic layer was washed with a 1M HCl solution and water, dried over Na_2SO_4, and concentrated. The crude product was then purified by flash column chromatography to yield the N-allyl enamine.

ethyl (Z)-3-(((E)-hex-2-en-1-yl)amino)-3-phenylacrylate (**3k**). The general procedure D was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 100:1) afforded **3k** as a colorless oil. Yield: 0.55 g, 40%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1H), 7.39–7.32 (m, 5H), 5.57–5.49 (m, 1H), 5.42–5.35 (m, 1H), 4.60 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.62–3.58 (m, 2H), 1.99–1.93 (m, 2H), 1.41–1.31 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 164.7, 136.1, 132.8, 129.1, 128.2, 127.8, 126.8, 85.3, 58.6, 46.4, 34.3, 22.2, 14.6, 13.6. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{17}H_{24}NO_2$:274.1802; found: 274.1801.



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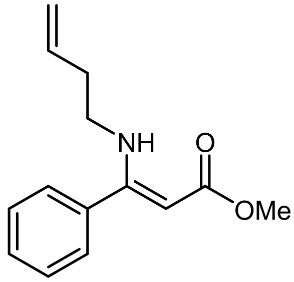
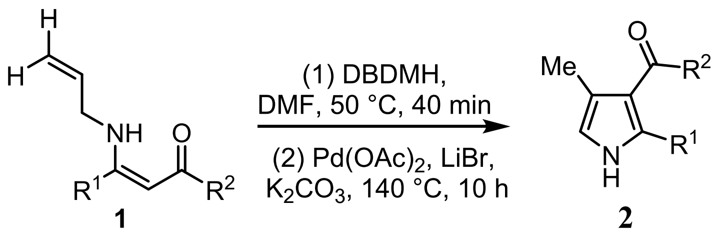
ethyl (Z)-3-phenyl-3-((2-phenylallyl)amino)acrylate (**3l**)[5]. The general procedure B was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **3l** as a yellow oil. Yield: 0.62 g, 40 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 7.42–7.35 (m, 5H), 7.33–7.26 (m, 3H), 7.22–7.19 (m, 2H), 5.43 (s, 1H), 5.35 (s, 1H), 4.69 (s, 1H), 4.17 (q, J = 6.8 Hz, 2H), 4.06 (d, J = 6.6 Hz, 2H), 1.30 (t, J = 5.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3, 164.7, 146.2, 139.2, 135.8, 129.3, 128.3, 128.3, 127.8, 127.7, 125.9, 112.9, 86.2, 58.7, 48.0, 14.5.



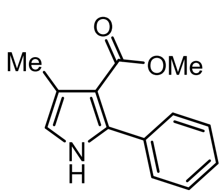
methyl (Z)-3-(but-3-en-1-ylamino)-3-phenylacrylate (**11a**). The general procedure A was followed, and purification by flash column chromatography (petroleum ether/EtOAc = 80:1) afforded **11a** as a yellow oil. Yield: 0.52 g, 45%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (s, 1H), 7.41–7.36 (m, 3H), 7.36–7.31 (m, 2H), 5.80–5.59 (m, 1H), 5.14–5.04 (m, 2H), 4.59 (s, 1H), 3.67 (s, 3H), 3.12 (q, J = 4.0, 2H), 2.21 (q, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.6, 164.7, 136.2, 134.6, 129.1, 128.3, 127.7, 117.4, 84.9, 50.1, 43.9, 35.1. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{14}H_{17}NNaO_2$: 254.1151; found: 254.1153.

Procedure for the Synthesis of the Pyrroles 2 from N-allyl enamine 1

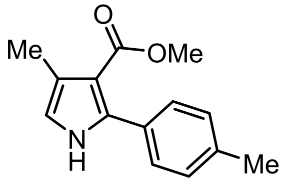
Procedure E:



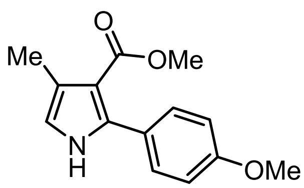
To a solution of N-allyl enamine **1** (1 mmol) in DMF (1 mL) was added DBDMH (0.5 mmol). The reaction mixture was stirred at 50 °C for 40 min. Then, $Pd(OAc)_2$ (0.2 mmol), LiBr (1.2 mmol), K_2CO_3 (1.2 mmol) and additional DMF (7 mL) were introduced to the flask under a nitrogen atmosphere. Then the reaction mixture was stirred at 140 °C for 10 hours. After monitoring the reaction to completion by TLC, the reaction mixture was cooled to room temperature, and EtOAc (50 mL) was added. The reaction mixture was washed with brine (15 mL×2). The organic layer was dried over with Na_2SO_4, filtered and concentrated under reduced pressure to obtain a residue. This residue was purified by flash column chromatography to yield pyrroles **2**.



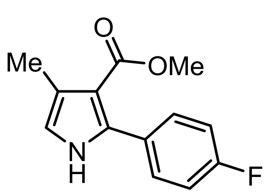
methyl 4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**2a**)[9]. The general procedure E was followed and purification by flash column chromatography afforded **2a** as a yellow oil (PE:EA = 12:1). Yield: 154.8 mg, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 7.52–7.45 (m, 2H), 7.43–7.30 (m, 3H), 6.56 (dd, J = 2.3, 1.0 Hz, 1H), 3.69 (s, 3H), 2.30 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 137.6, 133.0, 128.9, 128.0, 128.0, 122.6, 116.6, 111.1, 50.5, 12.5.



methyl 4-methyl-2-(p-tolyl)-1H-pyrrole-3-carboxylate (**2b**). The general procedure E was followed and purification by flash column chromatography afforded **2b** as a yellow solid (PE:EA = 12:1). Yield: 153.5 mg, 67%; mp 134-135 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.21–7.16 (m, 2H), 6.51 (s, 1H), 3.68 (s, 3H), 2.38 (s, 3H), 2.30 (d, J = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 137.8, 137.7, 130.0, 128.7, 128.7, 122.3, 116.5, 110.7, 50.5, 21.2, 12.5. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{14}H_{16}NO_2$:230.1176; found: 230.1174.

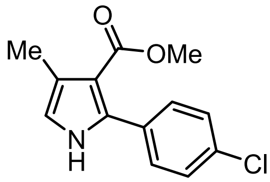


methyl 2-(4-methoxyphenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2c**). The general procedure E was followed and purification by flash column chromatography afforded **2c** as a yellow solid (PE:EA = 10:1). Yield: 215.6 mg, 88%; mp 105-106 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 7.47–7.36 (m, 2H), 6.97–6.85 (m, 2H), 6.51 (dd, J = 2.3, 1.0 Hz, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 2.29 (d, J = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 159.4, 137.7, 130.1, 125.4, 122.3, 116.2, 113.4, 110.5, 55.2, 50.5, 12.6. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{14}H_{16}NO_3$:246.1125; found: 246.1123.

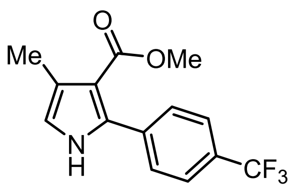


methyl 2-(4-fluorophenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2d**). The general procedure E was followed and purification by flash column chromatography afforded **2d** as a yellow oil (PE:EA = 12:1). Yield: 167.7 mg, 72%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1H), 7.50–7.37 (m, 2H), 7.11–7.01 (m, 2H), 6.55 (dd, J = 2.2, 1.0 Hz, 1H), 3.69 (s, 3H), 2.29 (d, J = 0.9 Hz, 3H). ^{13}C NMR

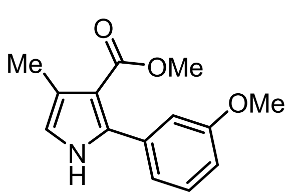
(100 MHz, $CDCl_3$): δ = 166.1, 162.5 (d, J = 247 Hz),136.7, 130.7 (d, J = 8 Hz), 129.0, 122.6, 116.7, 115.0 (d, J = 22 Hz), 111.2, 50.6, 12.5. HRMS (ESI): m/z [M + H^+] calcd for $C_{13}H_{13}FNO_2$:234.0925; found: 234.0923.



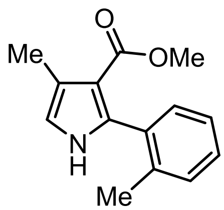
methyl 2-(4-chlorophenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2e**)[10]. The general procedure E was followed and purification by flash column chromatography afforded **2e** as a yellow solid (PE:EA = 12 :1). Yield: 157.5 mg, 63%; mp 123-124 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (s, 1H), 7.46–7.38 (m, 2H), 7.38–7.32 (m, 2H), 6.57 (s, 1H), 3.70 (s, 3H), 2.29 (d, J = 0.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 136.4, 134.0, 131.4, 130.2, 128.3, 122.8, 117.0, 111.5, 50.7, 12.6.



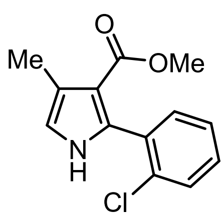
methyl 4-methyl-2-(4-(trifluoromethyl)phenyl)-1H-pyrrole-3-carboxylate (**2f**)[10]. The general procedure E was followed and purification by flash column chromatography afforded **2f** as a yellow solid (PE:EA = 11:1). Yield: 147.7 mg, 52%; mp 152-153 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 7.61–7.54 (m, 4H), 6.56 (dd, J = 2.3, 1.0 Hz, 1H), 3.69 (s, 3H), 2.28 (d, J = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 136.4, 135.8, 129.7 (d, J = 32 Hz), 129.1, 124.9 (q, J = 4.0 Hz), 124.1(d, J = 270 Hz), 123.0, 117.6, 111.9, 50.7, 12.5.



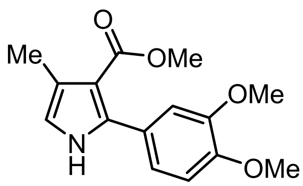
methyl 2-(3-methoxyphenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2g**). The general procedure E was followed and purification by flash column chromatography afforded **2g** as a yellow oil (PE:EA = 12:1). Yield: 196.9 mg, 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (s, 1H), 7.37–7.27 (m, 1H), 7.07–7.02 (m, 2H), 6.95–6.82 (m, 1H), 6.54 (dd, J = 2.3, 1.0 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 2.29 (d, J = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =166.2, 159.2, 137.2, 134.2, 129.0, 122.6, 121.2, 116.6, 114.5, 113.7, 111.1, 55.2, 50.6, 12.5. HRMS (ESI): m/z [M + H^+] calcd for $C_{14}H_{16}NO_3$:246.1125; found: 246.1124.



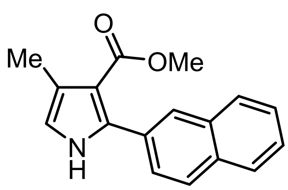
methyl 4-methyl-2-(o-tolyl)-1H-pyrrole-3-carboxylate (**2h**). The general procedure E was followed and purification by flash column chromatography afforded **2h** as a yellow oil (PE:EA = 20 :1). Yield: 73.6 mg, 32%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.31–7.27 (m, 1H), 7.25–7.19 (m, 3H), 6.55 (dd, J = 2.2, 1.1 Hz, 1H), 3.60 (s, 3H), 2.32 (d, J = 1.0 Hz, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 137.7, 137.2, 133.3, 130.0, 129.7, 128.4, 125.2, 121.7, 116.0, 112.3, 50.5, 19.8, 12.4. HRMS (ESI): m/z [M + Na^+] calcd for $C_{14}H_{15}NNaO_2$: 252.0995; found: 252.0996.



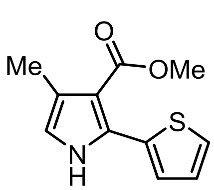
methyl 2-(2-chlorophenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2i**). The general procedure E was followed and purification by flash column chromatography afforded **2i** as a yellow oil (PE:EA = 20:1). Yield: 175.0 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 1H), 7.46–7.43 (m, 1H), 7.39–7.36 (m, 1H), 7.31–7.28 (m, 2H), 6.61 (dd, J = 2.2, 1.0 Hz, 1H), 3.63 (s, 3H), 2.32 (d, J = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 133.9, 132.3, 132.2, 129.5, 129.5, 126.2, 121.9, 116.7, 112.99, 50.6, 12.3. HRMS (ESI): m/z [M + H^+] calcd for $C_{13}H_{13}ClNO_2$:250.0629; found: 250.0628.



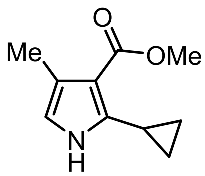
methyl 2-(3,4-dimethoxyphenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2j**). The general procedure E was followed and purification by flash column chromatography afforded **2j** as a yellow solid (PE:EA = 3:1). Yield: 151.3 mg, 55%; mp 114-115 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.05 (d, J = 1.9 Hz, 1H), 7.00 (dd, J = 8.3, 2.0 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.52 (d, J = 1.2 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 148.8, 148.2, 137.6, 125.7, 122.4, 121.2, 116.3, 112.7, 110.6, 55.8, 50.5, 12.6. HRMS (ESI): m/z [M + H^+] calcd for $C_{15}H_{18}NO_4$:276.1230; found: 276.1227.



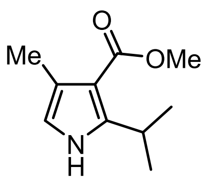
methyl 4-methyl-2-(naphthalen-2-yl)-1H-pyrrole-3-carboxylate (**2k**). The general procedure E was followed and purification by flash column chromatography afforded **2k** as a yellow oil (PE:EA = 8:1). Yield: 210.2 mg, 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.87–7.82 (m, 2H), 7.82–7.78 (m, 2H), 7.60–7.56 (m, 1H), 7.51–7.45 (m, 2H), 6.48 (dd, J = 2.3, 1.0 Hz, 1H), 3.65 (s, 3H), 2.31 (d, J = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 137.5, 133.0, 132.8, 130.5, 128.0, 127.6, 127.4, 127.3, 127.2, 126.2, 126.2, 122.6, 117.0, 111.2, 50.50, 12.5. HRMS (ESI): m/z [M + H^+] calcd for $C_{17}H_{16}NO_2$:266.1176; found: 266.1174.



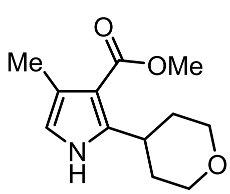
methyl 4-methyl-2-(thiophen-2-yl)-1H-pyrrole-3-carboxylate (**2l**). The general procedure E was followed and purification by flash column chromatography afforded **2l** as a yellow oil (PE:EA = 20:1). Yield: 168.0 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 7.36–7.28 (m, 2H), 7.04 (dd, J = 5.1, 3.6 Hz, 1H), 6.54 (dd, J = 2.3, 1.0 Hz, 1H), 3.77 (s, 3H), 2.28 (d, J = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 133.9, 130.4, 127.0, 126.9, 125.9, 122.8, 117.0, 111.7, 50.6, 12.6. HRMS (ESI): m/z [M + H^+] calcd for $C_{11}H_{12}NO_2S$:222.0583; found: 222.0583.



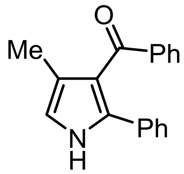
methyl 2-cyclopropyl-4-methyl-1H-pyrrole-3-carboxylate (**2m**). The general procedure E was followed and purification by flash column chromatography afforded **2m** as a yellow oil (PE:EA = 12:1). Yield: 62.6 mg, 35%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (s, 1H), 6.29 (dd, J = 2.3, 1.1 Hz, 1H), 3.82 (s, 3H), 2.61–2.49(m, 1H), 2.22 (d, J = 1.0 Hz, 3H), 1.01–0.94 (m, 2H), 0.68–0.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 140.9, 121.7, 113.9, 111.5, 50.4, 12.5, 9.0, 7.2. HRMS (ESI): m/z [M + H^+] calcd for $C_{10}H_{14}NO_2$:180.1019; found: 180.1017.



methyl 2-isopropyl-4-methyl-1H-pyrrole-3-carboxylate (**2n**)[10]. The general procedure E was followed and purification by flash column chromatography afforded **2n** as a yellow oil (PE:EA = 12:1). Yield: 165.6 mg, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 6.40 (dd, J = 2.3, 1.1 Hz, 1H), 3.82 (s, 3H), 2.25 (d, J = 1.0 Hz, 3H), 1.27 (d, J = 1.27 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 145.8, 121.4, 114.3, 109.1, 50.4, 26.2, 22.0, 12.6.



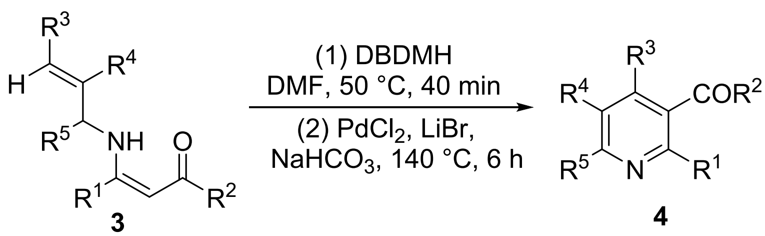
methyl 4-methyl-2-(tetrahydro-2H-pyran-4-yl)-1H-pyrrole-3-carboxylate (**2o**). The general procedure E was followed and purification by flash column chromatography afforded **2o** as a white solid (PE:EA = 5:1). Yield: 207.4 mg, 93%; mp 126-127 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 6.41 (dd, J = 2.2, 1.1 Hz, 1H), 4.07–4.02 (m, 2H), 3.80 (s, 3H), 3.77–3.72 (m, 1H), 3.60–3.52 (m, 2H), 2.22 (d, J = 1.0 Hz, 3H), 1.90–1.83 (m, 2H), 1.72–1.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 143.1, 121.3, 114.9, 109.6, 68.1, 50.5, 33.3, 32.1, 12.7. HRMS (ESI): m/z [M + H^+] calcd for $C_{12}H_{18}NO_3$:224.1281; found: 224.1280.



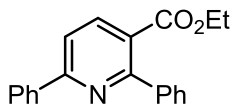
(4-methyl-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**2p**)[11]. The general procedure E was followed and purification by flash column chromatography afforded **2p** as a yellow oil (PE:EA = 15:1). Yield: 143.6 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 7.71–7.62 (m, 2H), 7.33–7.28 (m, 1H), 7.20–7.08 (m, 7H), 6.66 (dd, J = 2.3, 1.0 Hz, 1H), 2.18 (d, J = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.6, 139.4, 136.1, 132.3, 131.7, 129.8, 128.2, 128.0, 127.7, 127.3, 122.3, 120.5, 117.1, 11.6.

Procedure for the Synthesis of the Pyridine 4 from Substituted N-allyl enamine 3

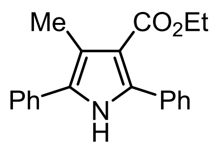
Procedure F:



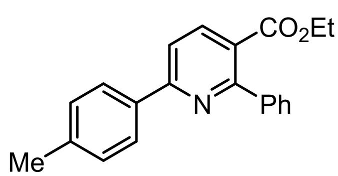
To a solution of substituted N-allyl enamine **3** (1 mmol) in DMF (1 mL) was added DBDMH (0.5 mmol). The reaction mixture was stirred at 50 °C for 40 min. Then, $PdCl_2$ (0.2 mmol), LiBr (1.2 mmol), $NaHCO_3$ (1.2 mmol) and DMF (5 mL) were introduced to the flask under a nitrogen atmosphere. The reaction mixture was then stirred at 140 °C for 6 h. After monitoring the reaction to completion by TLC, the reaction mixture was cooled to room temperature, and EtOAc (50 mL) was added. The reaction mixture was washed with brine (15 mL×2). The organic layer was dried over with Na_2SO_4, filtered and concentrated under reduced pressure to obtain a residue. This residue was purified by flash column chromatography to yield pyridines **4** or a mixture of pyridines **4** and pyrroles **5**.



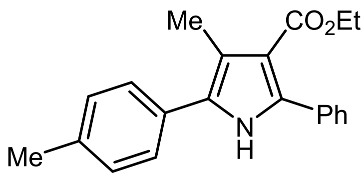
ethyl 2,6-diphenylnicotinate (**4a**)[12]. The general procedure E was followed and purification by flash column chromatography afforded **4a** as a yellow oil (PE: EA = 20:1). Yield: 106 mg, 35%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.2 Hz, 1H), 8.16–8.11 (m, 2H), 7.78 (d, J = 8.2 Hz, 1H), 7.70–7.61 (m, 2H), 7.54–7.39 (m, 6H), 4.19 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 158.7, 158.4, 140.5, 138.8, 138.3, 129.7, 128.8, 128.7, 128.5, 128.0, 127.3, 125.3, 117.8, 61.3, 13.6.



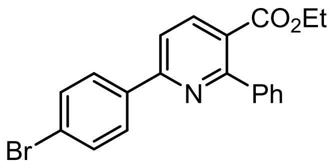
ethyl 4-methyl-2,5-diphenyl-1H-pyrrole-3-carboxylate (**5a**)[13]. The general procedure E was followed and purification by flash column chromatography afforded **5a** as a yellow oil (PE:EA = 15:1). Yield: 100 mg, 33%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.56–7.50 (m, 2H), 7.46–7.42 (m, 4H), 7.42–7.37 (m, 2H), 7.37–7.28 (m, 2H), 4.20 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 136.8, 132.8, 132.5, 129.5, 129.0, 128.8, 128.0, 127.4, 127.0, 118.9, 113.1, 59.5, 14.1, 11.7.



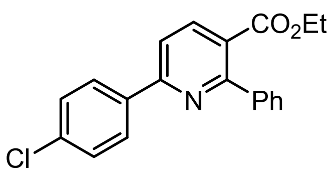
ethyl 2-phenyl-6-(p-tolyl) nicotinate (**4b**)[12]. The general procedure F was followed and purification by flash column chromatography afforded **4b** as a yellow oil (PE:EA = 20:1). Yield: 126 mg, 40%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 1H), 7.70–7.58 (m, 2H), 7.53–7.40 (m, 3H), 7.29 (d, J = 8.0 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 158.7, 158.4, 140.6, 139.9, 138.8, 135.5, 129.5, 128.8, 128.5, 127.9, 127.2, 124.9, 117.4, 61.3, 21.3, 13.6.



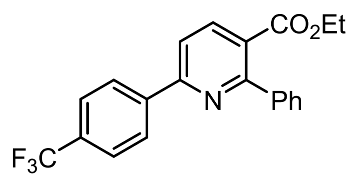
ethyl 4-methyl-2-phenyl-5-(p-tolyl)-1H-pyrrole-3-carboxylate (**5b**). The general procedure F was followed and purification by flash column chromatography afforded **5b** as a yellow oil (PE:EA = 15:1). Yield: 81 mg, 25%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 1H), 7.55–7.51 (m, 2H), 7.46–7.31 (m, 6H), 7.24 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 136.8, 136.5, 132.8, 129.6, 129.4, 128.9, 128.0, 127.9, 127.4, 118.5, 112.9, 59.5, 21.2, 14.1, 11.7. HRMS (ESI): m/z [M + Na^+] calcd for $C_{21}H_{21}NNaO_2$: 342.1465; found: 342.1467.



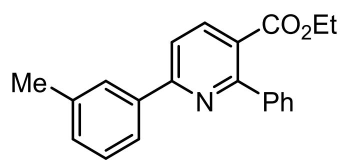
ethyl 6-(4-bromophenyl)-2-phenylnicotinate (**4c**)[12]. The general procedure F was followed and purification by flash column chromatography afforded **4c** as a yellow oil (PE:EA = 20:1). Yield: 224.8 mg, 59%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.2 Hz, 1H), 7.64–7.59 (m, 3H), 7.50–7.41 (m, 4H), 4.17 (q, J = 7.1 Hz, 2H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 158.8, 157.2, 140.3, 139.0, 137.1, 131.9, 128.8, 128.8, 128.7, 128.0, 127.3, 125.7, 124.4, 117.6, 61.4, 13.7.



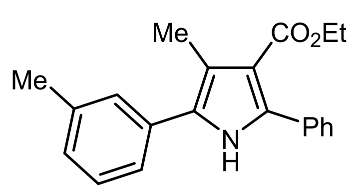
ethyl 6-(4-chlorophenyl)-2-phenylnicotinate (**4d**)[14]. The general procedure F was followed and purification by flash column chromatography afforded **4d** as a yellow oil (PE:EA = 20:1). Yield: 185 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.2 Hz, 1H), 7.65–7.60 (m, 2H), 7.47–7.43 (m, 5H), 4.18 (q, J = 7.1 Hz, 2H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 158.8, 157.1, 140.4, 139.0, 136.7, 135.9, 129.0, 128.8, 128.7, 128.6, 128.0, 125.6, 117.6, 61.4, 13.6.



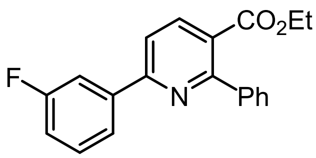
ethyl 2-phenyl-6-(4-(trifluoromethyl)phenyl)nicotinate (**4e**)[12]. The general procedure F was followed and purification by flash column chromatography afforded **4e** as a yellow oil (PE:EA = 20:1). Yield: 222 mg, 60%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27–8.18 (m, 3H), 7.80 (d, J = 8.1 Hz, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.68–7.60 (m, 2H), 7.50–7.43 (m, 3H), 4.19 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 158.9, 156.8, 141.5, 140.2, 139.1, 131.4 (d, J = 32.0 Hz), 128.8, 128.1, 127.6, 126.3, 125.7 (q, J = 4.0 Hz), 118.2, 61.5, 13.6.



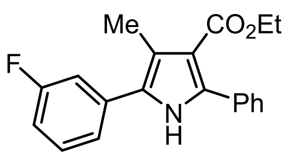
ethyl 2-phenyl-6-(m-tolyl)nicotinate (**4f**). The general procedure F was followed and purification by flash column chromatography afforded **4f** as a yellow oil (PE:EA = 20:1). Yield: 126.8 mg, 40%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.2 Hz, 1H), 7.96 (s, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.68–7.62 (m, 2H), 7.48–7.43 (m, 3H), 7.42–7.34 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 2.45 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 158.7, 158.7, 140.6, 138.8, 138.5, 138.3, 130.5, 128.8, 128.7, 128.5, 128.0, 128.0, 125.2, 124.5, 117.9, 61.3, 21.5, 13.7. HRMS (ESI): m/z [M + H^+] calcd for $C_{21}H_{20}NO_2$:318.1489; found: 318.1490.



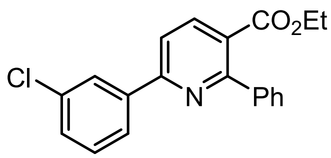
ethyl 4-methyl-2-phenyl-5-(m-tolyl)-1H-pyrrole-3-carboxylate (**5f**). The general procedure F was followed and purification by flash column chromatography afforded **5f** as a yellow oil (PE:EA = 15:1). Yield: 93 mg, 29%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.71–7.50 (m, 2H), 7.49–7.31 (m, 4H), 7.28 (s, 2H), 7.16 (d, J = 7.5 Hz, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 2.43 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 138.4, 136.7, 132.8, 132.4, 129.6, 129.0, 128.7, 128.0, 128.0, 128.0, 127.8, 124.6, 118.8, 113.0, 59.5, 21.5, 14.1, 11.8. HRMS (ESI): m/z [M + Na^+] calcd for $C_{21}H_{21}NNaO_2$: 342.1465; found: 342.1466.



ethyl 6-(3-fluorophenyl)-2-phenylnicotinate (**4g**)[12]. The general procedure F was followed and purification by flash column chromatography afforded **4g** as a yellow oil (PE:EA = 30:1). Yield: 112 mg, 35%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.1 Hz, 1H), 7.92–7.85 (m, 2H), 7.75 (d, J = 8.1 Hz, 1H), 7.68–7.60 (m, 2H), 7.52–7.40 (m, 4H), 7.19–7.10 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 163.3 (d, J = 245 Hz), 158.8, 156.9 (d, J = 2 Hz), 140.6 (d, J = 8 Hz), 140.3, 139.0, 130.3 (d, J = 8 Hz), 128.8, 128.7, 128.0, 125.9, 122.8 (d, J = 3 Hz), 117.9, 116.6 (d, J = 21 Hz), 114.3 (d, J = 22 Hz), 61.4, 13.6.

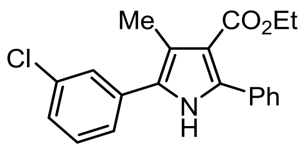


ethyl 5-(3-fluorophenyl)-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**5g**). The general procedure F was followed and purification by flash column chromatography afforded **5g** as a yellow oil (PE:EA = 30:1). Yield: 81 mg, 25%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.57–7.48 (m, 2H), 7.44–7.33 (m, 4H), 7.25–7.18 (m, 1H), 7.17–7.11 (m, 1H), 7.04–6.96 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 162.9 (d, J = 245 Hz), 137.3, 134.6, 134.5, 132.6, 130.3 (d, J = 8 Hz), 129.0, 128.2, 128.0, 122.9 (d, J = 2 Hz), 119.7, 113.9 (q, J = 21 Hz), 113.3, 59.6, 14.1, 11.7. HRMS (ESI): m/z [M + Na^+] calcd for $C_{20}H_{18}FNNaO_2$: 346.1214; found: 346.1215.

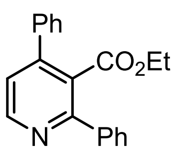


ethyl 6-(3-chlorophenyl)-2-phenylnicotinate (**4h**)[14]. The general procedure F was followed and purification by flash column chromatography afforded **4h** as a yellow oil (PE:EA = 40:1). Yield:

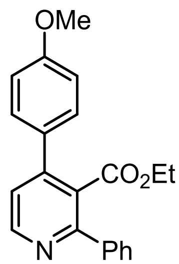
101 mg, 30%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (d, J = 8.1 Hz, 1H), 8.16–8.12 (m, 1H), 8.04–7.95 (m, 1H), 7.76–7.74 (m, 1H), 7.69–7.60 (m, 2H), 7.49–7.44 (m, 3H), 7.44–7.39 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 158.8, 156.8, 140.2, 140.0, 139.0, 134.9, 130.0, 129.7, 128.8, 128.7, 128.0, 127.4, 125.9, 125.3, 117.9, 61.5, 13.6.



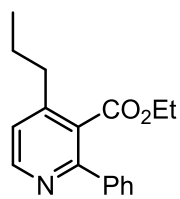
ethyl 5-(3-chlorophenyl)-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**5h**). The general procedure F was followed and purification by flash column chromatography afforded **5h** as a yellow oil (PE:EA = 20:1). Yield: 68 mg, 20%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.57–7.49 (m, 2H), 7.46–7.43 (m, 1H), 7.43–7.37 (m, 3H), 7.36–7.34 (m, 1H), 7.32–7.28 (m, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.6, 137.4, 134.6, 134.2, 132.5, 130.0, 129.0, 128.2, 128.0, 128.0, 127.2, 126.9, 125.5, 119.8, 113.2, 59.6, 14.0, 11.7. HRMS (ESI): m/z [M + Na^+] calcd for $C_{20}H_{18}ClNNaO_2$: 362.0918; found: 362.0920.



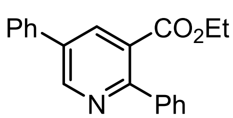
ethyl 2,4-diphenylnicotinate (**4i**)[15]. The general procedure F was followed and purification by flash column chromatography afforded **4i** as a yellow oil (PE:EA = 20:1). Yield: 176.3 mg, 58%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, J = 5.1 Hz, 1H), 7.68–7.60 (m, 2H), 7.48–7.38 (m, 8H), 7.30 (d, J = 5.1 Hz, 1H), 3.96 (q, J = 7.1 Hz, 2H), 0.87 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 156.8, 149.7, 148.6, 139.6, 138.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 122.7, 61.4, 13.4.



ethyl 4-(4-methoxyphenyl)-2-phenylnicotinate (**4j**). The general procedure F was followed and purification by flash column chromatography afforded **4j** as a yellow oil (PE:EA = 10:1). Yield: 169.8 mg, 51%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, J = 5.1 Hz, 1H), 7.66–7.59 (m, 2H), 7.45–7.40 (m, 3H), 7.37 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 5.1 Hz, 1H), 6.97 (d, J = 8.8 Hz, 2H), 3.98 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 160.1, 156.9, 149.7, 148.2, 139.8, 130.3, 129.4, 128.7, 128.4, 128.3, 122.7, 114.1, 61.4, 55.3, 13.5. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{21}H_{20}NO_3$:334.1438; found: 334.1439.



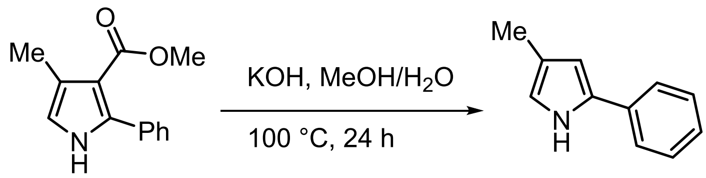
ethyl 2-phenyl-4-propylnicotinate (**4k**)[16]. The general procedure F was followed and purification by flash column chromatography afforded **4k** as a colourless oil (PE:EA = 20:1). Yield: 148.0 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 5.1 Hz, 1H), 7.66–7.51 (m, 2H), 7.45–7.34 (m, 3H), 7.15 (d, J = 5.1 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 2.77–2.58 (m, 2H), 1.74–1.63 (m, 2H), 1.05–0.92 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 156.8, 149.8, 149.6, 140.1, 129.0, 128.5, 128.3, 122.6, 61.4, 35.0, 23.6, 13.9, 13.6.



ethyl 2,5-diphenylnicotinate (**4l**)[8]. The general procedure F was followed and purification by flash column chromatography afforded **4l** as a yellow solid (PE:EA = 20:1). Yield: 90 mg, 30%; mp 124-125 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.00 (d, J = 2.3 Hz, 1H), 8.29 (d, J = 2.3 Hz, 1H), 7.69–7.64 (m, 2H), 7.62–7.57 (m, 2H), 7.55–7.50 (m, 2H), 7.49 – 7.42 (m, 4H), 4.19 (q, J = 7.1 Hz, 2H), 1.07 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.2, 157.4, 149.4, 139.9, 136.5, 136.0, 134.7, 129.2, 128.6, 128.6, 128.5, 128.1, 127.1, 61.6, 13.6.

Application

*Synthesis of **6a**:*

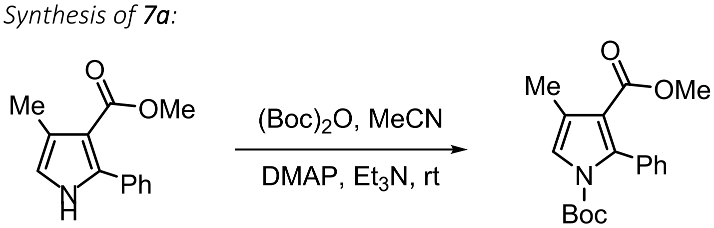


2a **6a,** 85%

4-methyl-2-phenyl-1H-pyrrole (**6a**)[17]

To a solution of methyl 4-methyl-2-phenyl-1H-pyrrole-3-carboxylate **2a** (215.1 mg, 1.0 mmol) in methanol (6 mL) and water (1 mL) was added potassium hydroxide (505.0 mg, 9.0 mmol). The mixture underwent reflux for 24 hours, was then cooled to room temperature, and quenched with water. The aqueous layer was extracted twice with ethyl acetate. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by flash column chromatography (petroleum ether/EtOAc = 20:1) afforded **6a** (133.5 mg) in 85% yield as a purple solid. mp 149-150 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1H), 7.42–7.37 (m, 2H), 7.33–7.27 (m, 2H), 7.20–7.12 (m, 1H), 6.54 (s, 1H), 6.36 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.8, 131.9, 128.8, 125.9, 123.6, 120.5, 116.8, 107.4, 11.9.

*Synthesis of **7a**:*



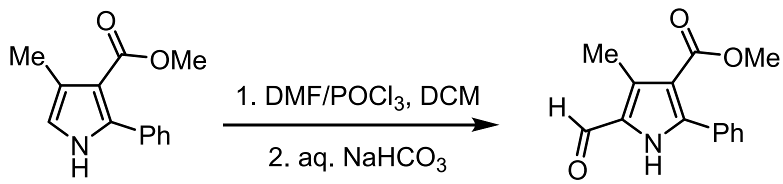
2a **7a,** 51%

1-(tert-butyl) 3-methyl 4-methyl-2-phenyl-1H-pyrrole-1,3-dicarboxylate (**7a**)

To a solution of compound **2a** (215.1 mg, 1.0 mmol) in acetonitrile (2 mL) were added di-tert-butyl dicarbonate (218.3 mg, 1.0 mmol), triethylamine (101.2 mg, 1 mmol) and a catalytic amount of dimethylaminopyridine (18.3 mg, 0.15 mmol) at room temperature. The mixture was stirred at room temperature for 1 h then diluted with ethyl acetate, washed with water, saturated sodium chloride solution, dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. Purification of the crude product by flash column chromatography (petroleum ether/EtOAc = 30:1) afforded

7a (160.7 mg, 0.51 mmol) in 51% yield as a white solid; mp 74-75 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.34 (m, 3H), 7.32–7.25 (m, 2H), 7.14 (d, J = 1.2 Hz, 1H), 3.59 (s, 3H), 2.28 (d, J = 1.2 Hz, 3H), 1.25 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.1, 148.6, 138.6, 133.7, 129.7, 127.7, 127.2, 121.6, 119.4, 117.7, 84.0, 50.7, 27.2, 12.2. HRMS (ESI): m/z [M + Na^+] calcd for $C_{18}H_{21}NNaO_4$: 338.1363; found: 338.1365.

*Synthesis of **8a**:*

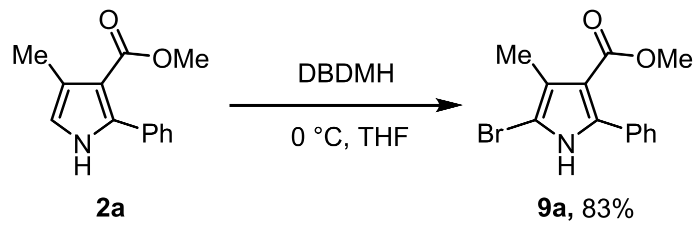


2a **8a,** 60%

methyl 5-formyl-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**8a**)

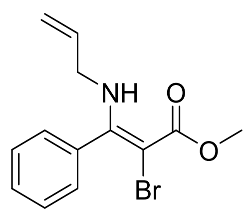
To a stirred solution of DMF (80.4 mg, 1.1 mmol) in dichloromethane (0.5 mL) at 0 °C was added dropwise $POCl_3$ (168.6 mg, 1.1 mmol) in dichloromethane (0.5 mL) under nitrogen. The solution was stirred at room temperature for 15 minutes. A solution of **2a** (215.1 mg, 1.0 mmol) in dichloromethane (1 mL) was added dropwise to the reaction mixture at 0 °C over a period of 15 minutes. Then the reaction mixture was refluxed for 2 hours. After cooling to room temperature, 1M aqueous $NaHCO_3$ (5 mL, 5.0 mmol) was added to the reaction mixture and then the mixture was refluxed for 1 hour. The aqueous layer was extracted with ethyl acetate (3 × 40 mL). The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification of the crude product by flash column chromatography (petroleum ether/EtOAc = 30:1) afforded **8a** (145.8 mg, 0.60 mmol) in 60% yield as a white solid. mp 114-115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.81 (s, 1H), 9.67 (s, 1H), 7.54–7.47 (m, 2H), 7.44–7.38 (m, 3H), 3.71 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.1, 164.9, 143.3, 135.4, 130.8, 129.4, 129.3, 129.0, 128.1, 113.9, 51.0, 10.5. HRMS (ESI): m/z [M + Na^+] calcd for $C_{14}H_{13}NNaO_3$: 266.0788; found: 266.0789.

*Synthesis of **9a**:*



Methyl 5-bromo-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**9a**).

To a solution of **2a** (215.1 mg, 1.0 mmol) in THF (2 mL) was added DBDMH (143.0 mg, 0.5 mmol) at 0 °C. After being stirred for 0.5 hour at the same temperature, the mixture was poured into ice-water (5 mL). The mixture was extracted with ethyl acetate (20 mL). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash column chromatography (petroleum ether/EtOAc = 15:1) afforded **9a** (243.19 mg, 0.83 mmol) in 83% yield as a purple solid; mp 116-117 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 7.47–7.39 (m, 2H), 7.39–7.29 (m, 3H), 3.67 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 138.0, 131.8, 128.8, 128.3, 128.0, 121.2, 111.8, 99.7, 50.8, 12.0. HRMS (ESI): m/z [M + Na$^+$] calcd for $C_{13}H_{12}BrNNaO_2$: 315.9944; found: 315.9945.



10a

methyl (E)-3-(allylamino)-2-bromo-3-phenylacrylate (**10a**)

To a solution of **1a** (217.1 mg, 1.0 mmol) in DMF (1 mL) was added DBDMH (143.0 mg, 0.5 mmol). The mixture was stirred at 50 °C for 40 min then diluted with ethyl acetate, washed with water, saturated sodium chloride solution, dried on anhydrous Na_2SO_4, filtered and evaporated to dryness. Purification of the crude product by flash column chromatography (petroleum ether/EtOAc = 70:1) afforded **10a** (265.5 mg, 0.9 mmol) in 90% yield as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.32 (s, 1H), 7.47–7.38 (m, 3H), 7.24–7.18 (m, 2H), 5.77–5.63 (m, 1H), 5.22–5.05 (m, 2H), 3.79 (s, 3H), 3.55–3.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 163.6, 135.6, 134.7, 129.0, 128.5, 128.3, 127.7, 116.1, 51.9, 47.7. HRMS (ESI): m/z [M + H$^+$] calcd for $C_{13}H_{15}BrNO_2$:296.0281; found: 296.0275.

X-Ray crystallographic studies

Method of crystallization: A solution of **2o** in CH_2Cl_2 was left in the hood, and slow evaporation of solvent occurred. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2353681 (**2o**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/

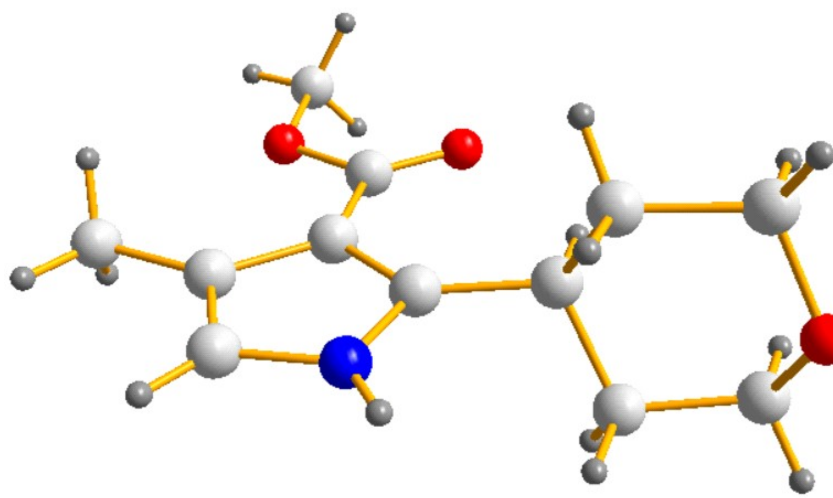


Figure S1. ORTEP X-ray structure of **2o**

Table S4. Crystal data and structure refinement for **2o**

Empirical formula	$C_{12}H_{17}NO_3$
Formula weight	223.26
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a= 6.995(3) Å alpha = 90° b= 11.544(5) Å beta = 99.400(9)° c= 14.861(7) Å gamma = 90°
Volume	1183.9(9) $Å^3$
Z, Calculated density	4, 1.253 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	480.0
Crystal size	0.22 x 0.20 x 0.18 mm^3
Theta range for data collection	4.49 to 49.984°
Index ranges	-7<=h<=8, -13<=k<=13, -17<=l<=17
Reflections collected	13003

Independent reflections	2064 [R(int) = 0.0807, R(sigma) = 0.0681]
Completeness to theta = 25.110°	0.992 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2064 / 0 / 147
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0611, wR2 = 0.1421
R indices (all data)	R1 = 0.1293, wR2 = 0.1940
Extinction coefficient	n/a
Largest diff. peak and hole	0.18 and -0.21 e. Å $^{-3}$

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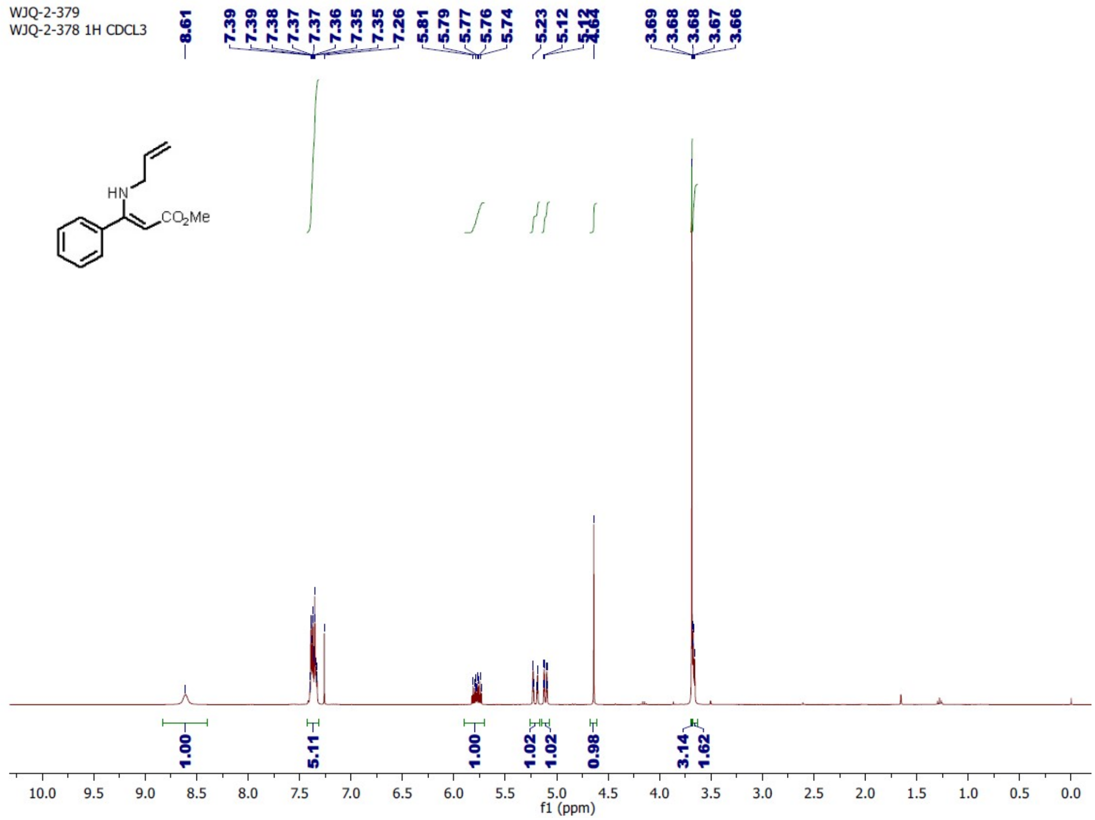
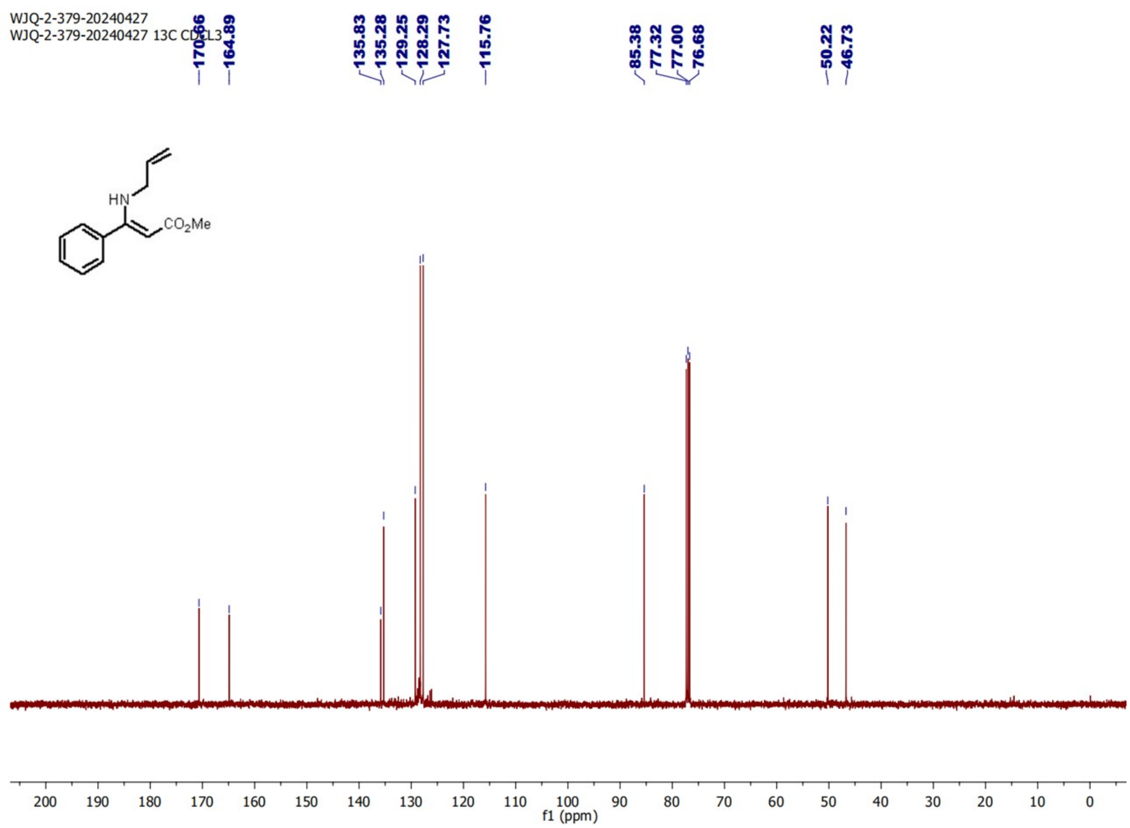
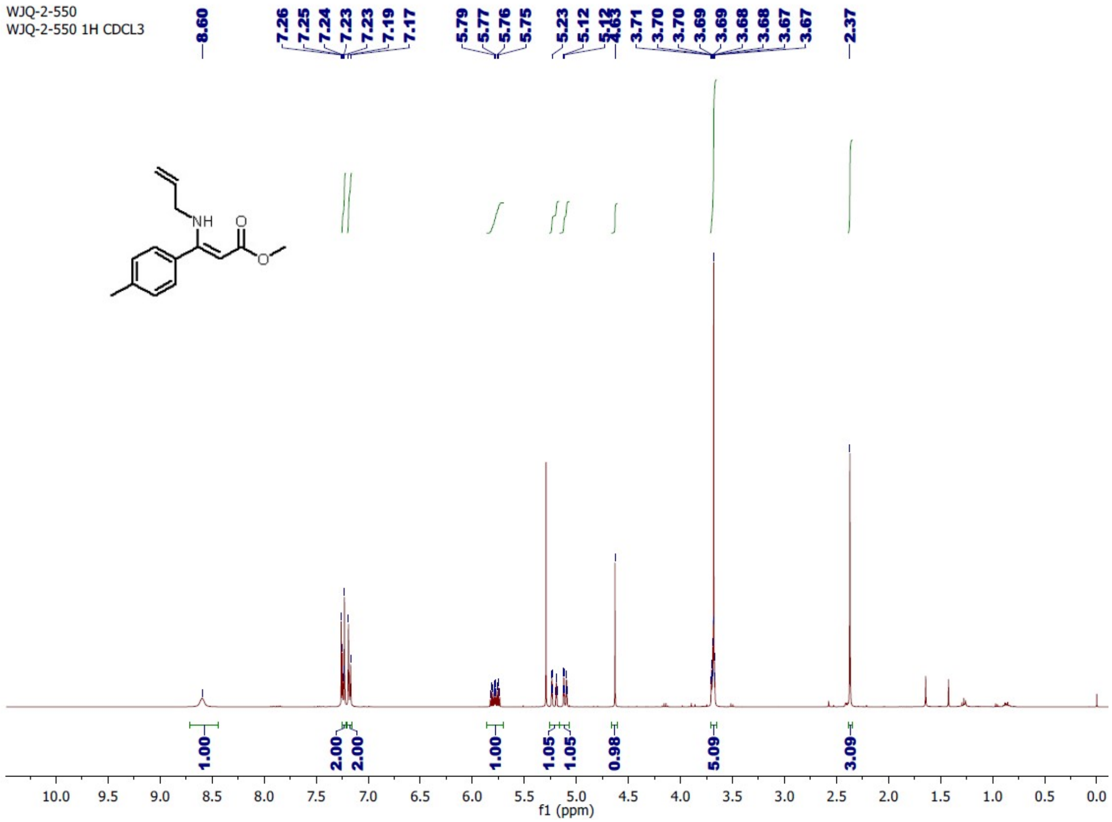
NMR Spectra

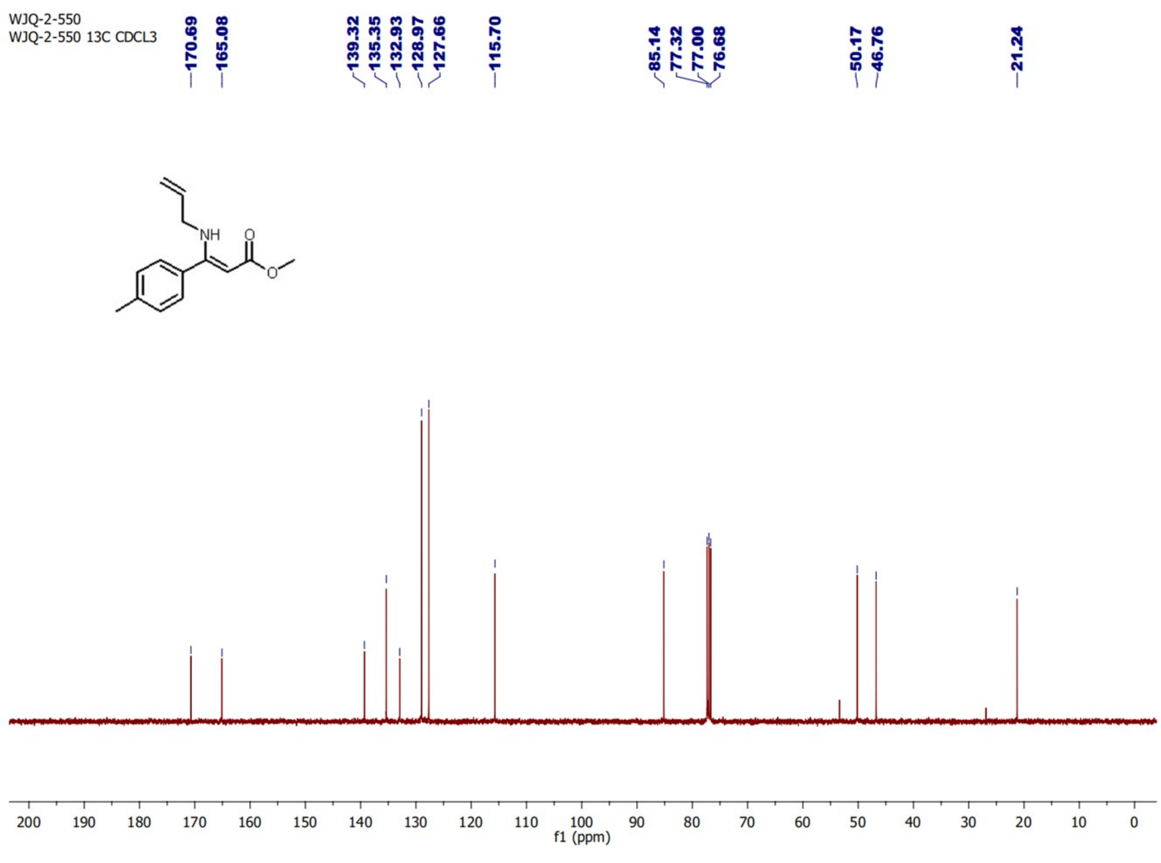
***methyl (Z)-3-(allylamino)-3-phenylacrylate* (1a)**



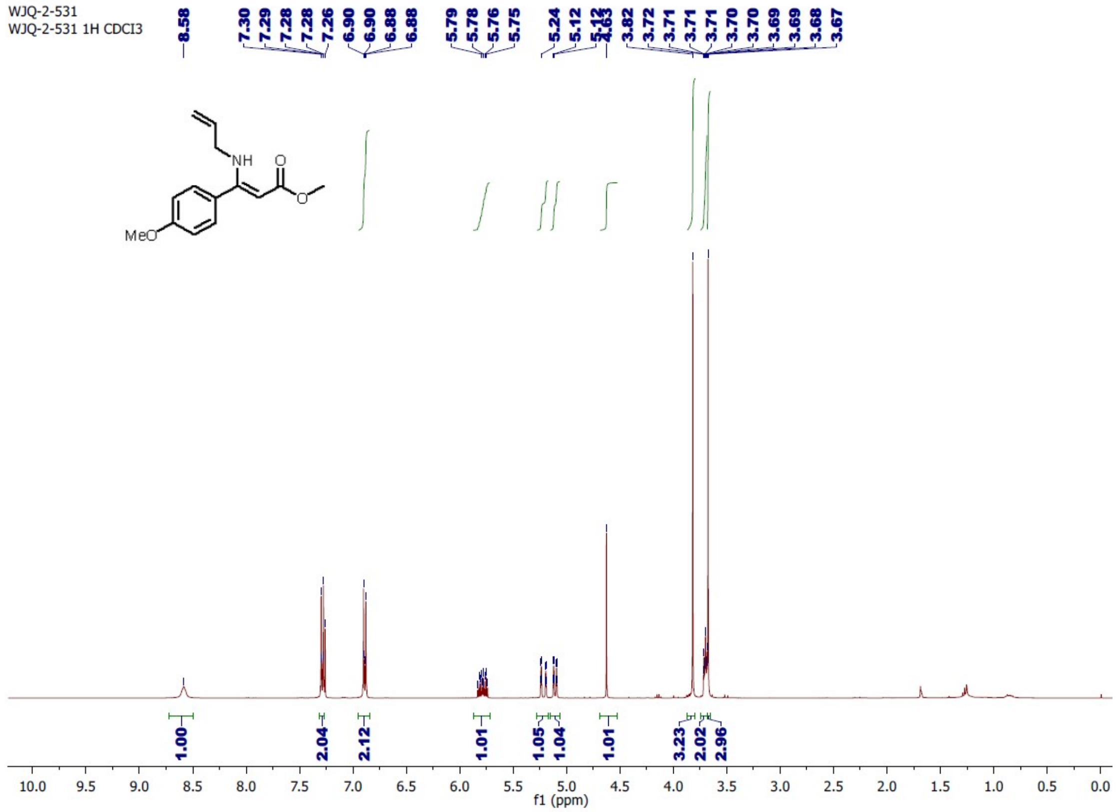


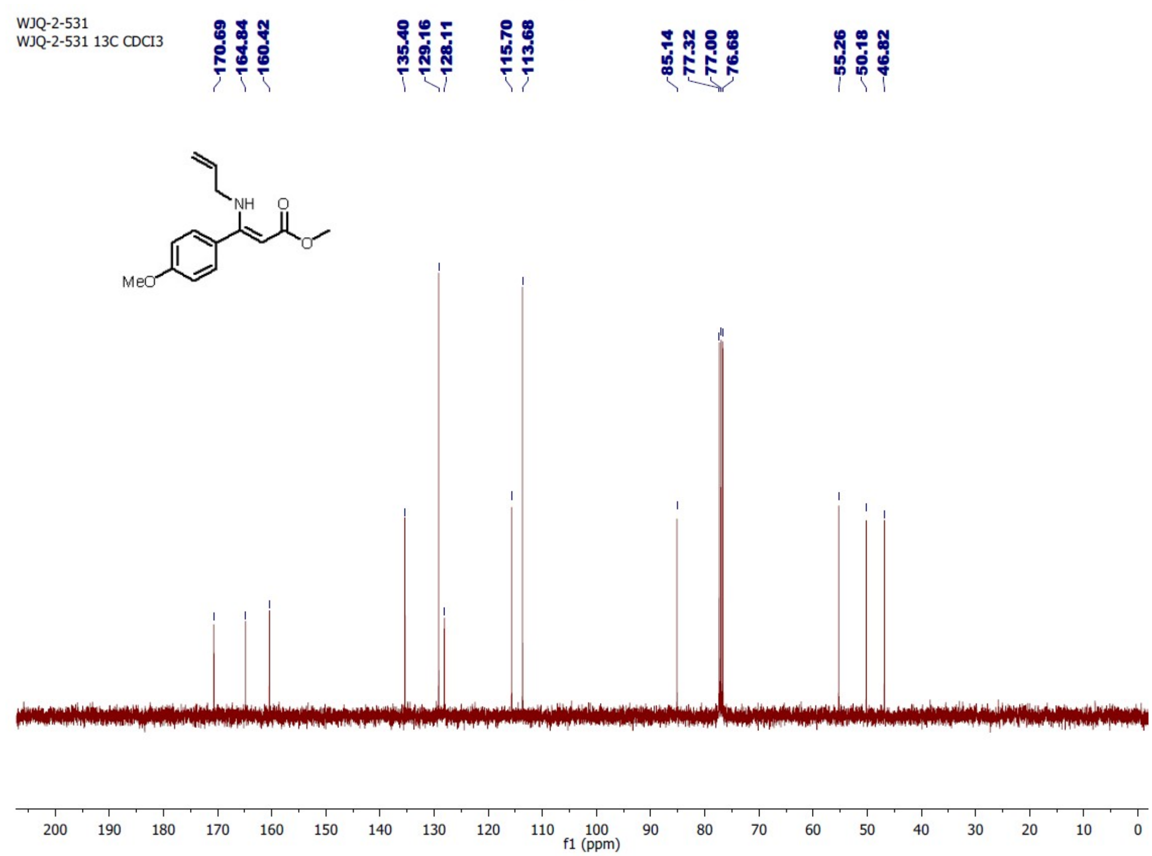
methyl (Z)-3-(allylamino)-3-(p-tolyl)acrylate (**1b**)



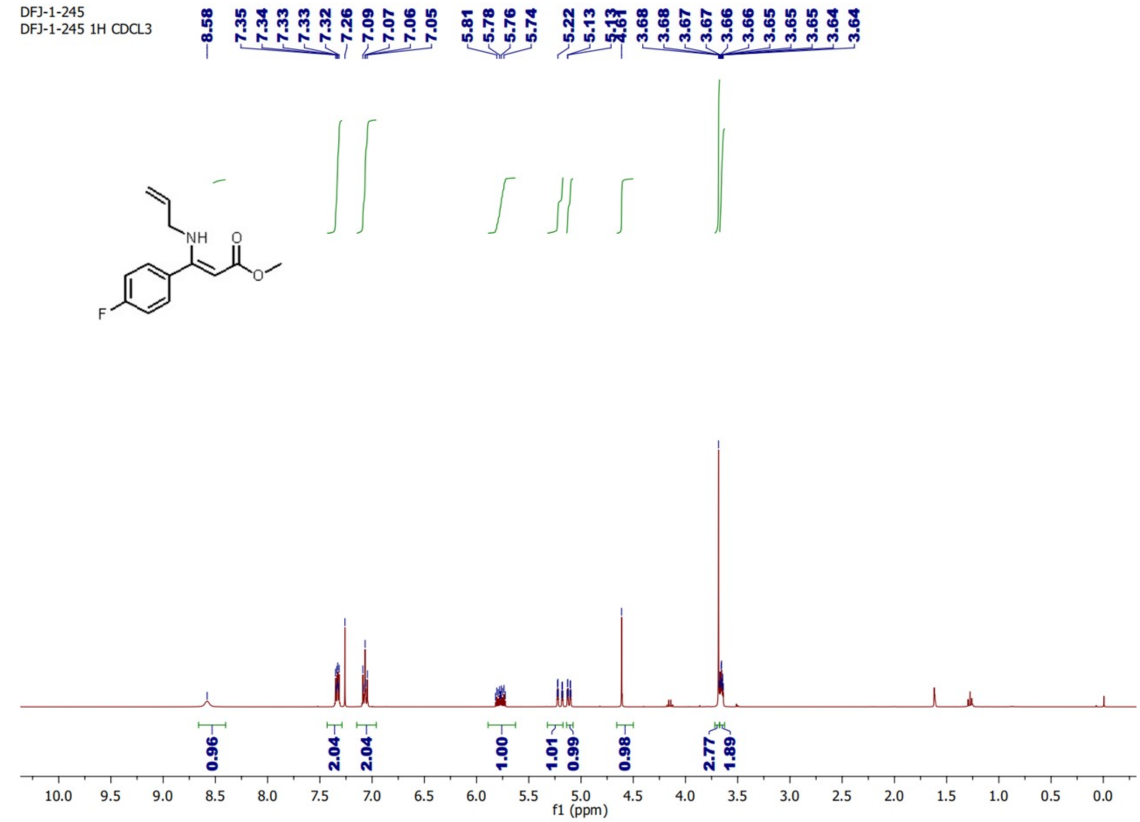


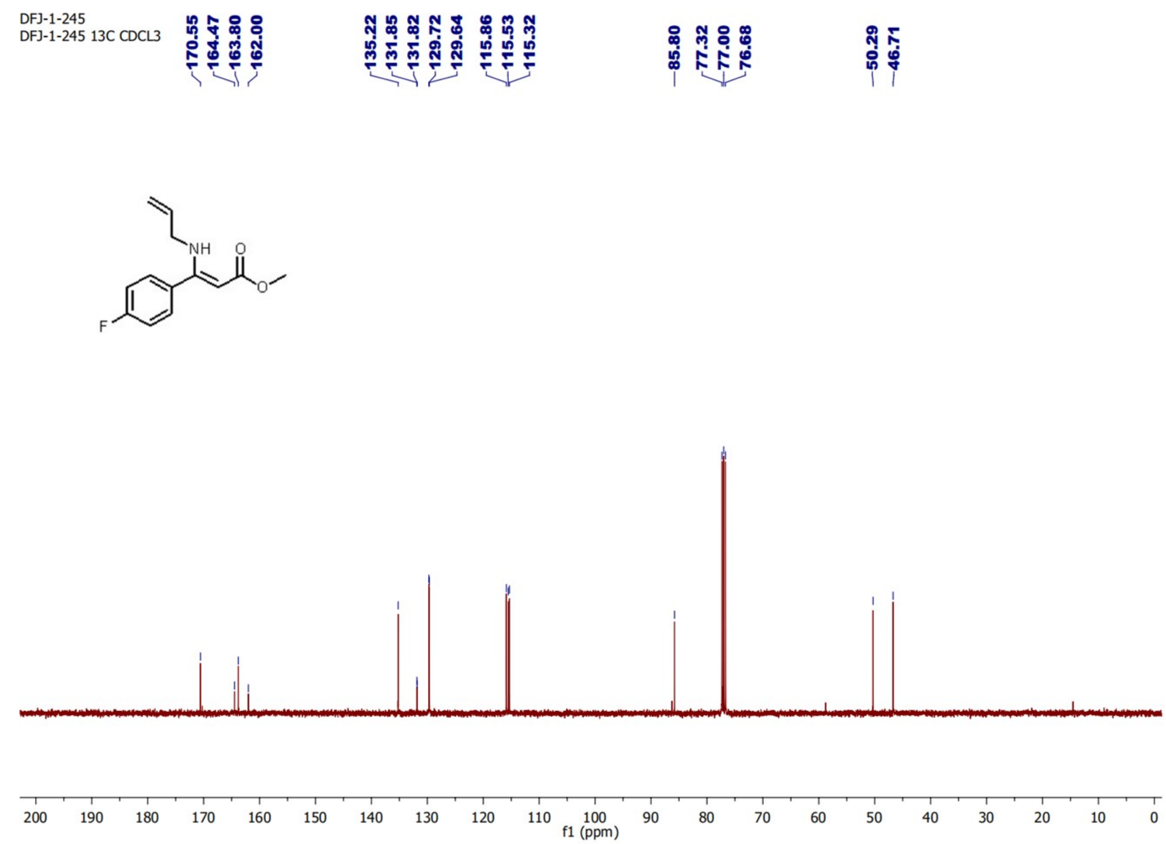
methyl (Z)-3-(allylamino)-3-(4-methoxyphenyl)acrylate (**1c**)



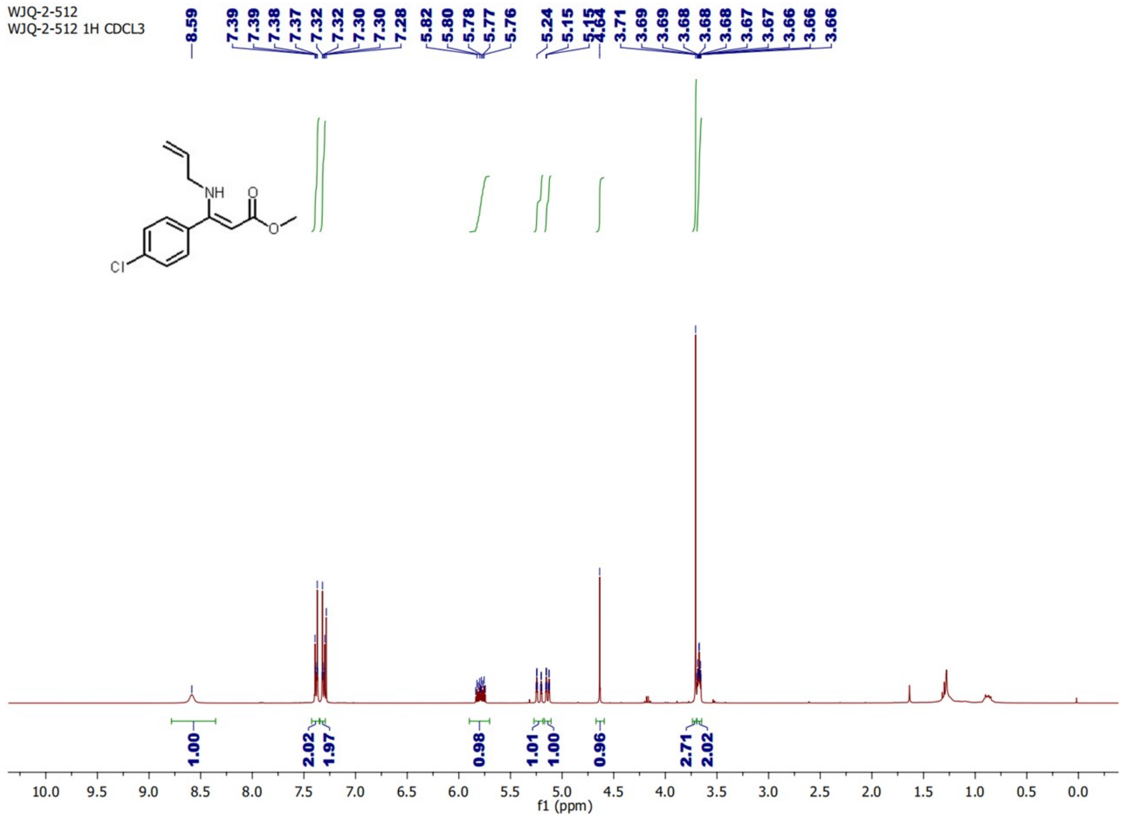


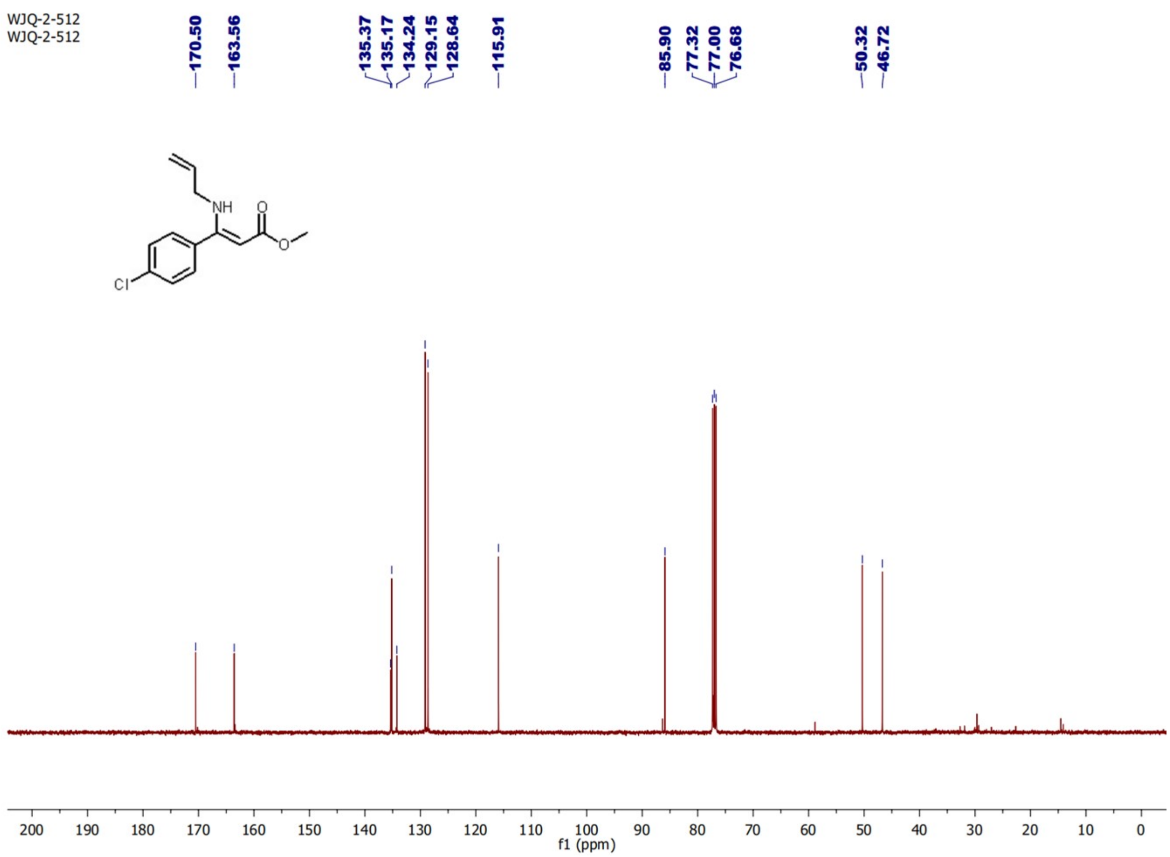
methyl (Z)-3-(allylamino)-3-(4-fluorophenyl)acrylate (**1d**)



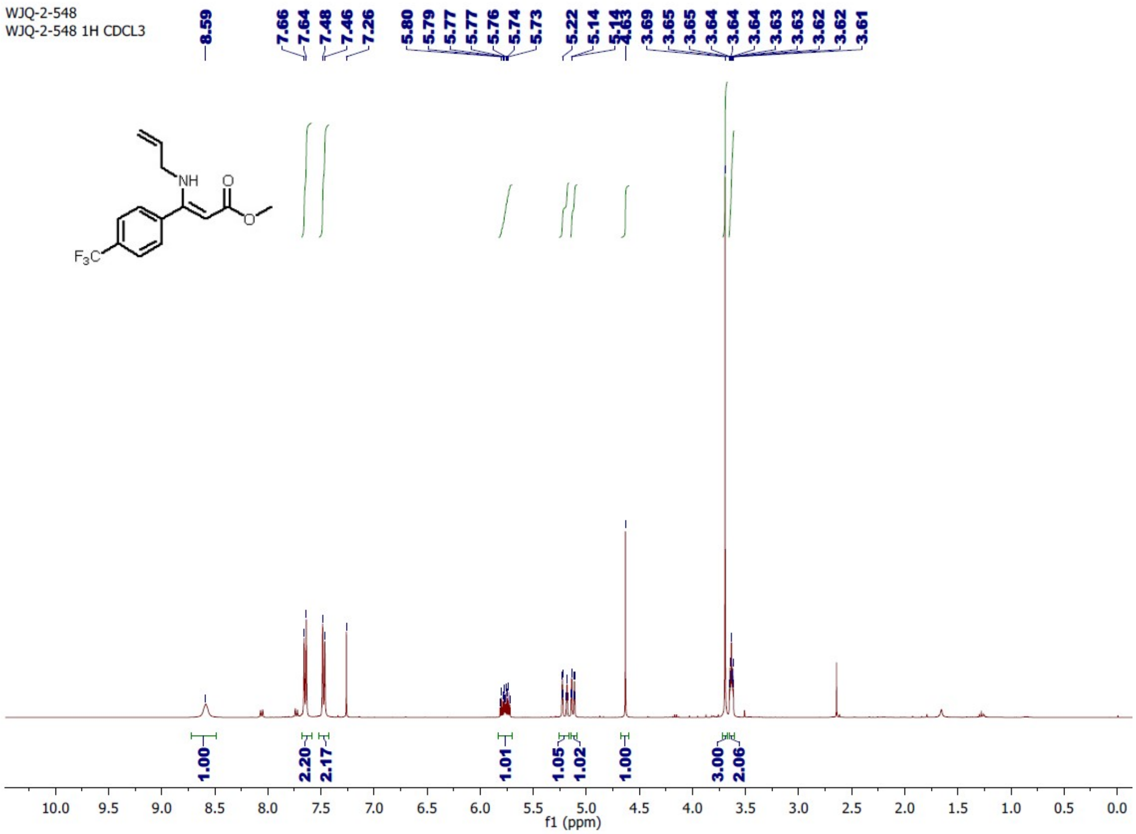


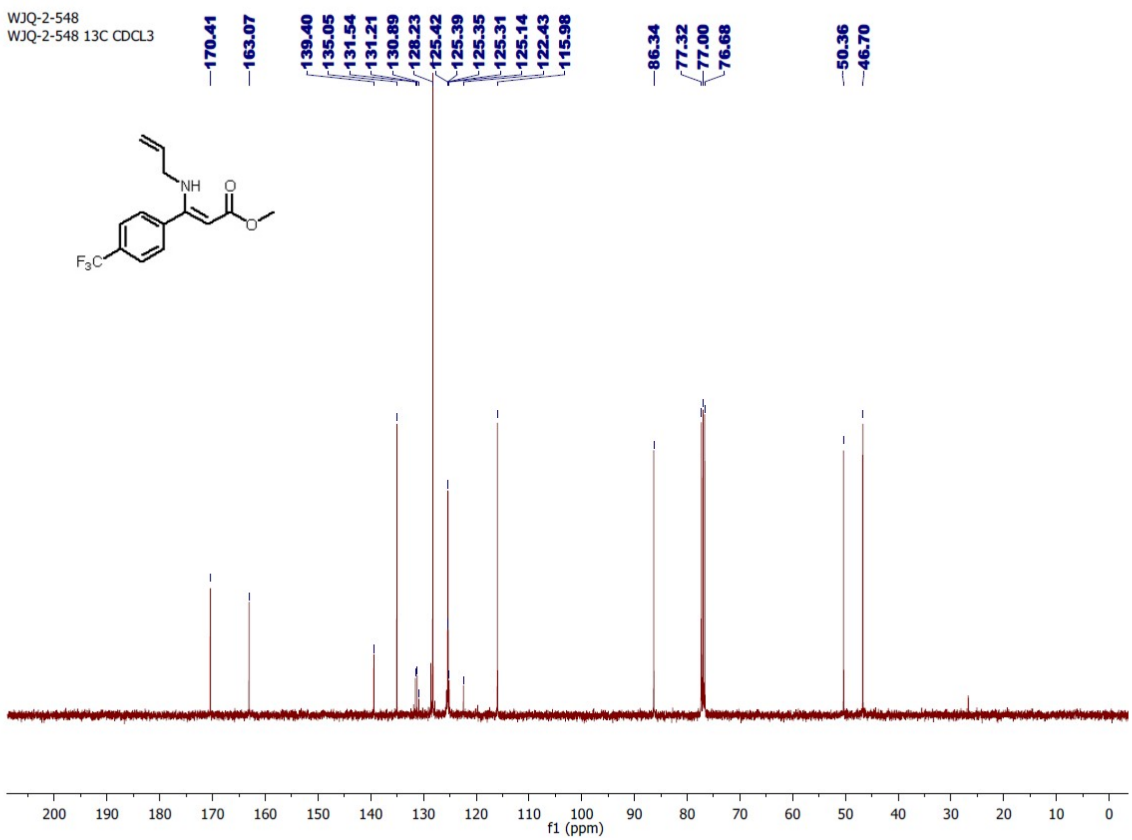
methyl (Z)-3-(allylamino)-3-(4-chlorophenyl)acrylate (**1e**)



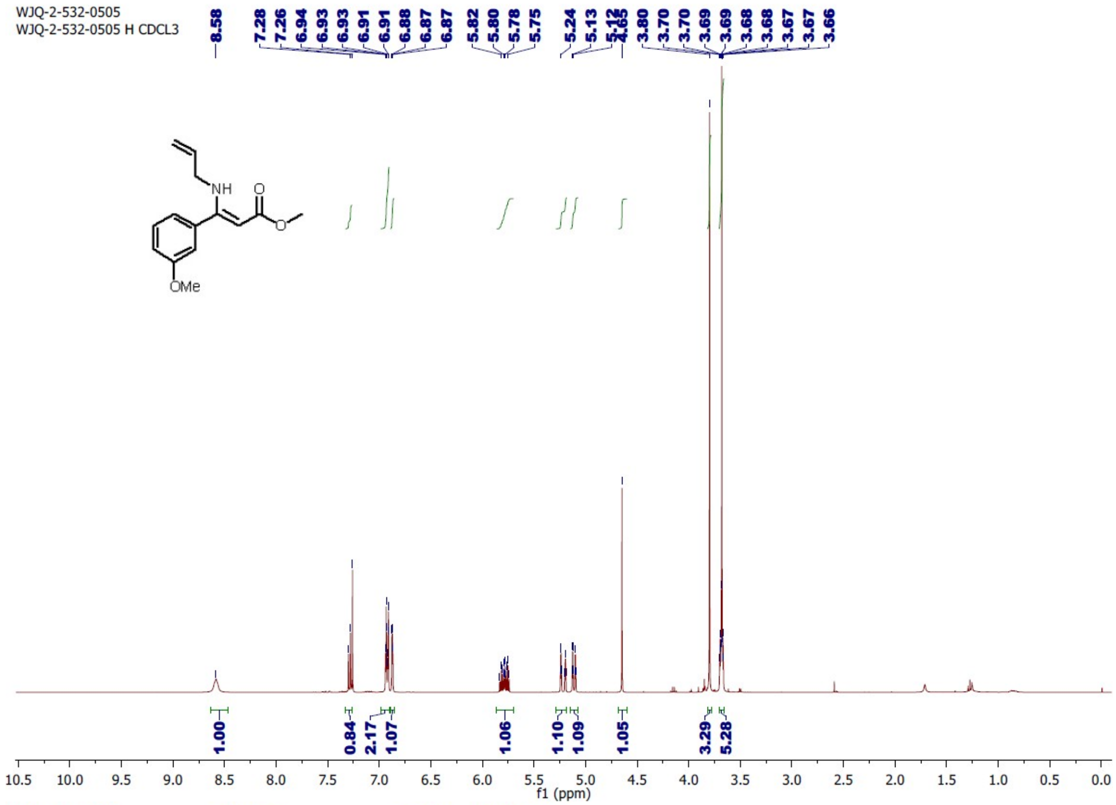


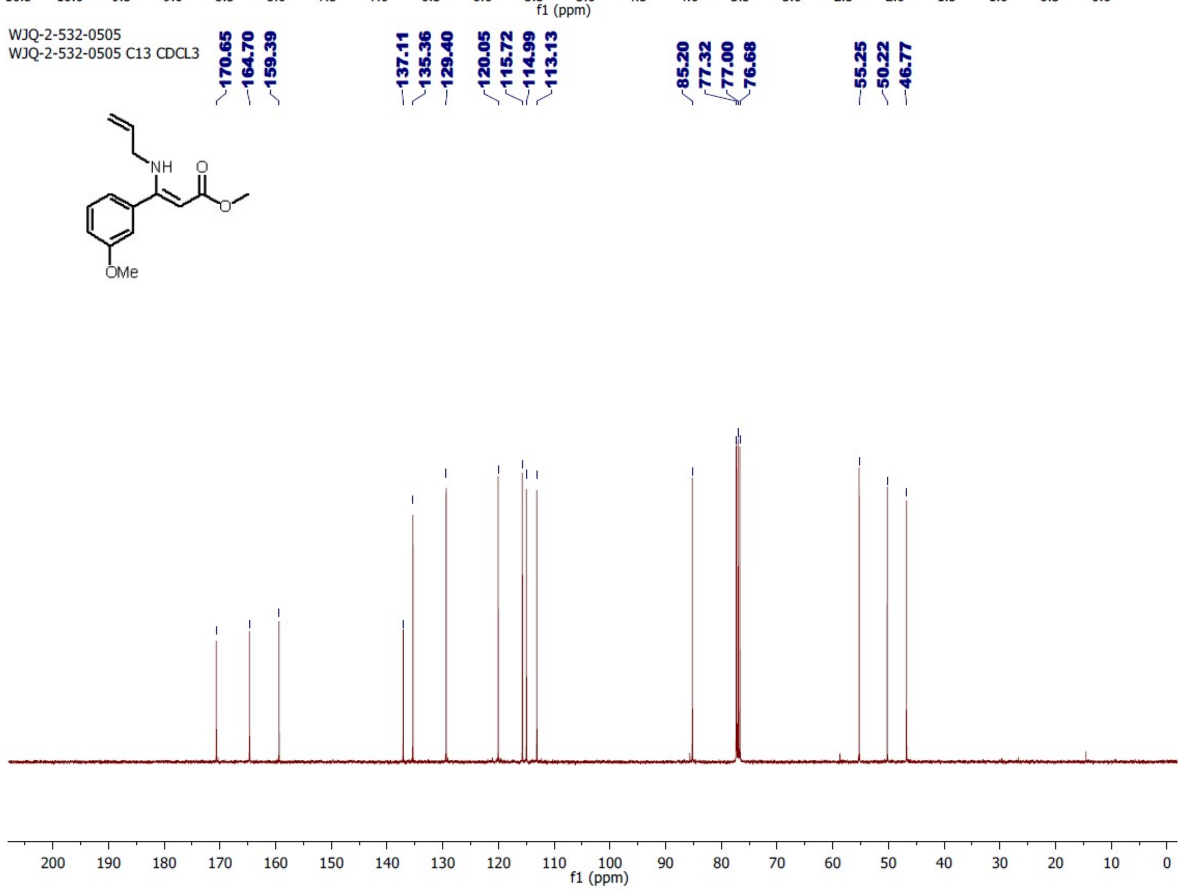
methyl (Z)-3-(allylamino)-3-(4-(trifluoromethyl)phenyl)acrylate (**1f**)



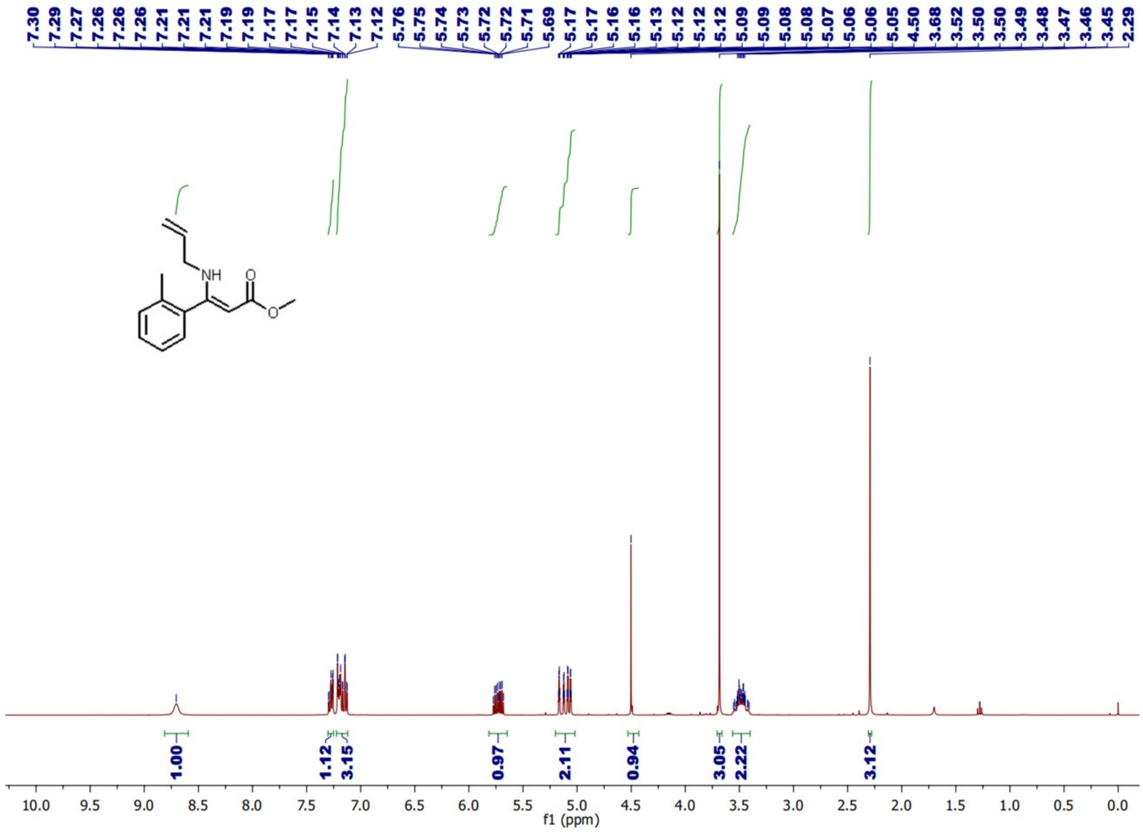


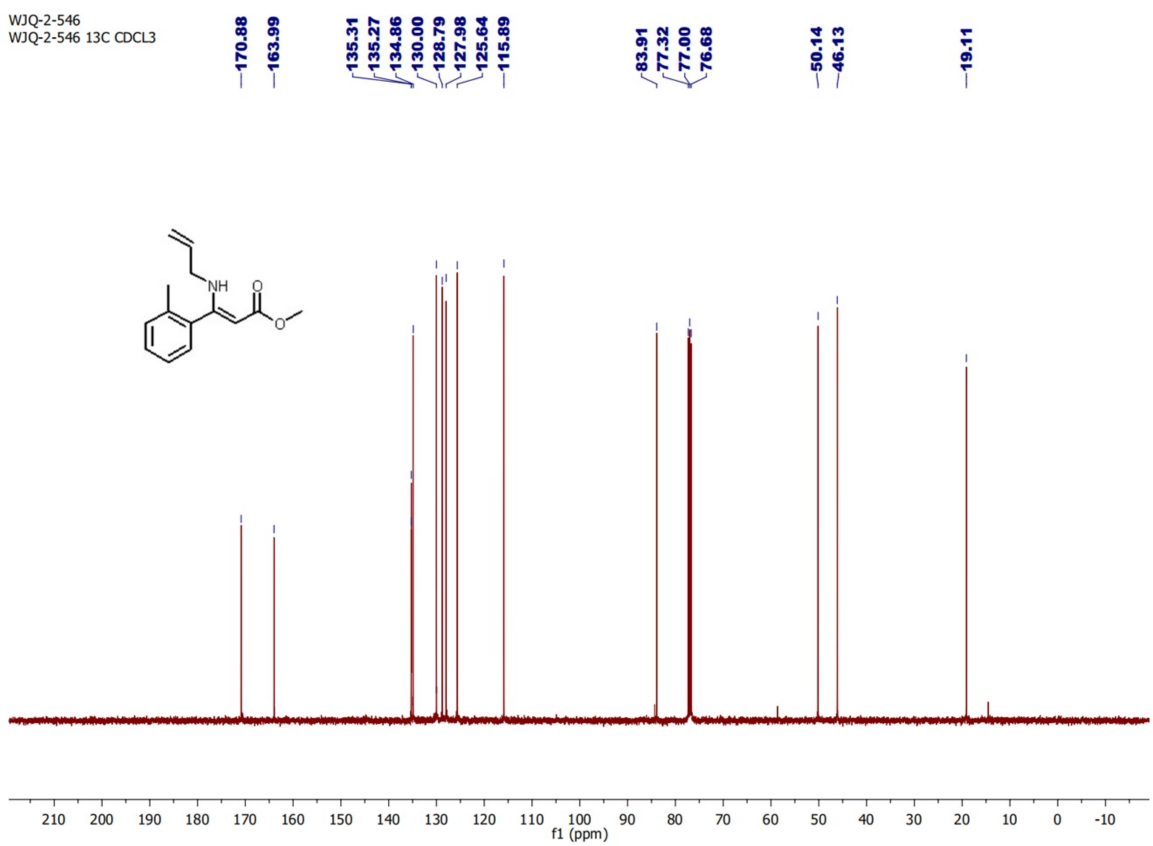
methyl (Z)-3-(allylamino)-3-(3-methoxyphenyl)acrylate (**1g**)



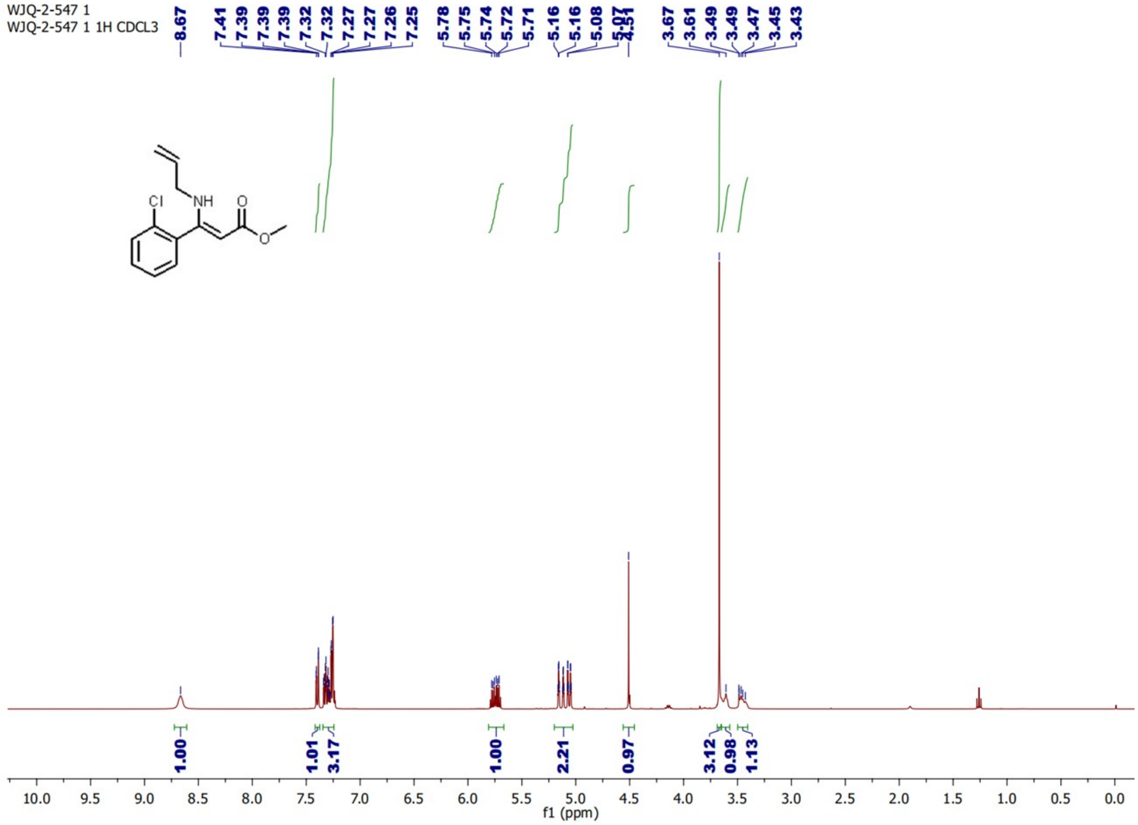


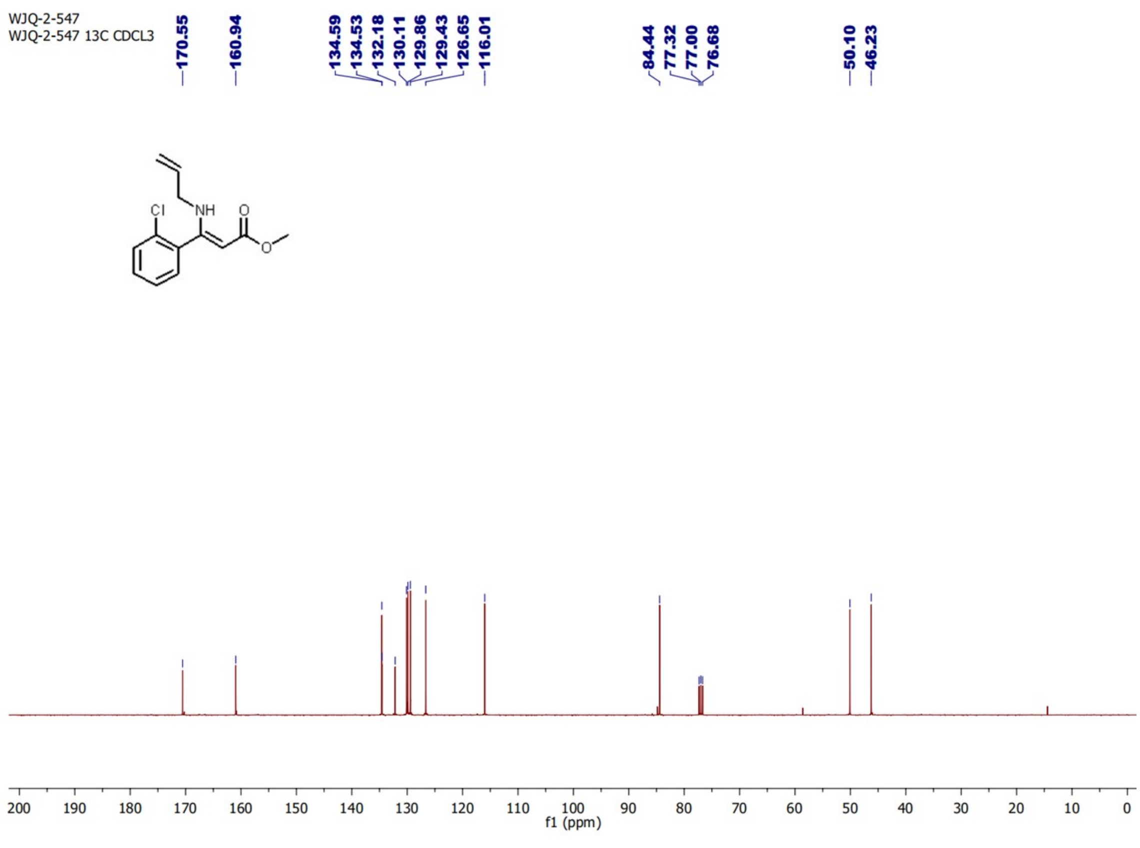
methyl (Z)-3-(allylamino)-3-(o-tolyl)acrylate (**1h**)



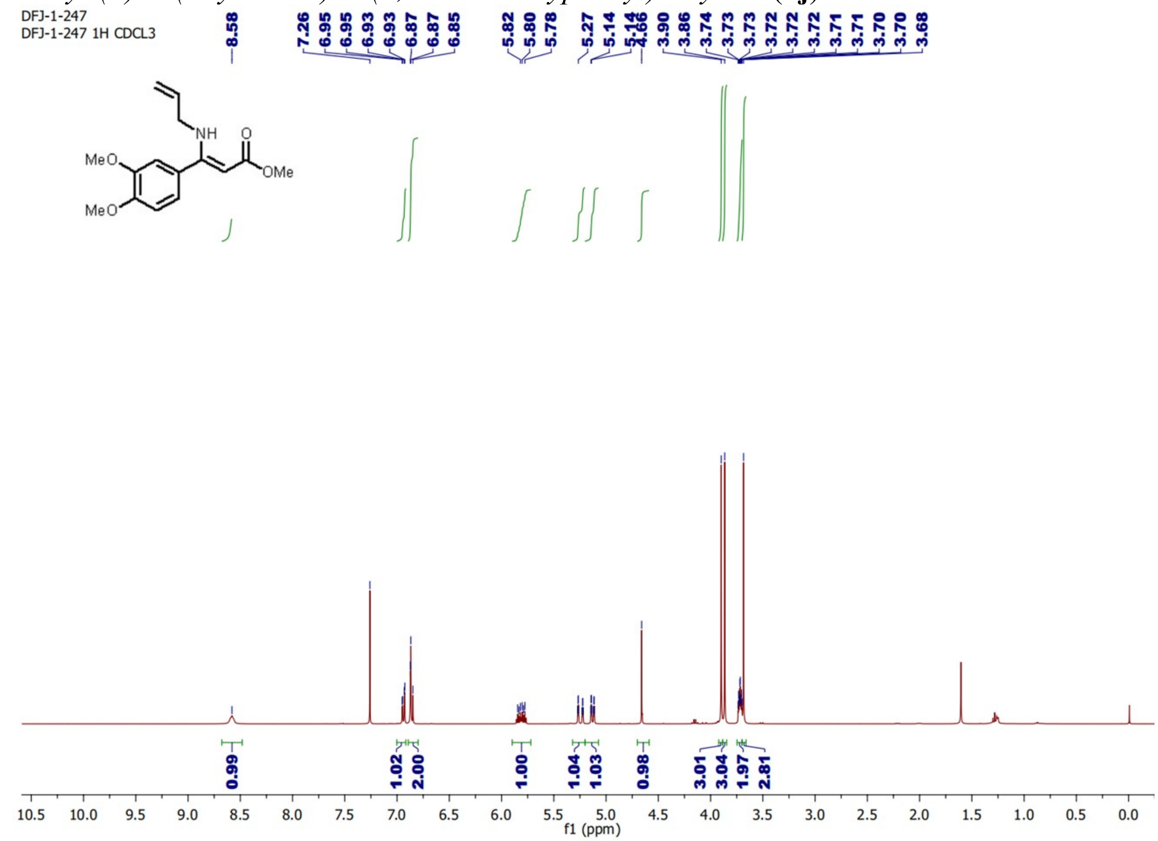


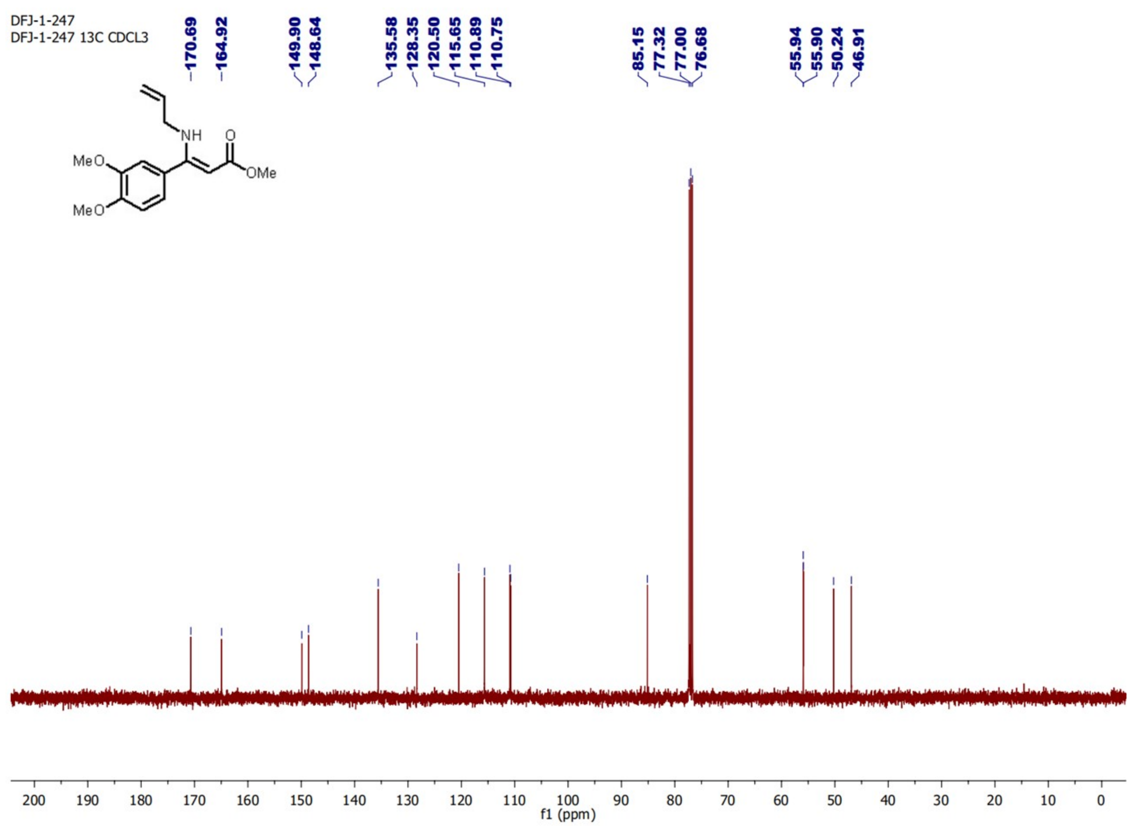
methyl (Z)-3-(allylamino)-3-(2-chlorophenyl)acrylate (**1i**)



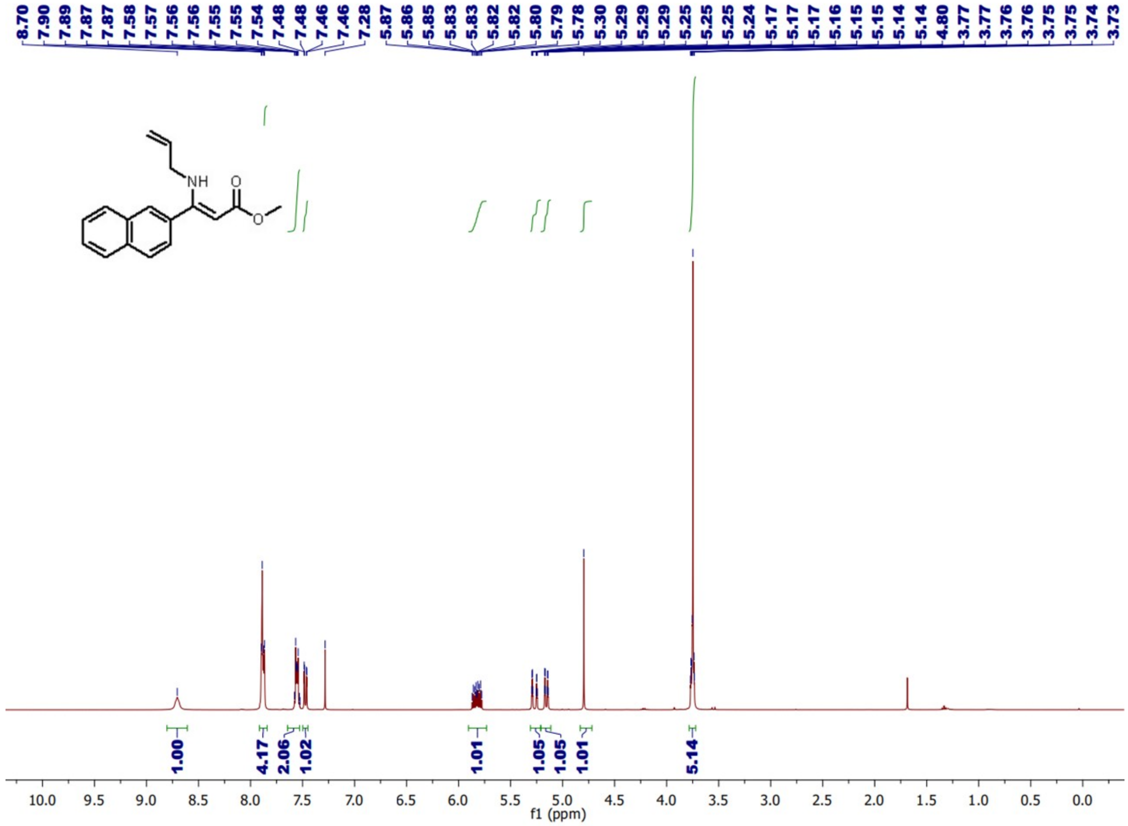


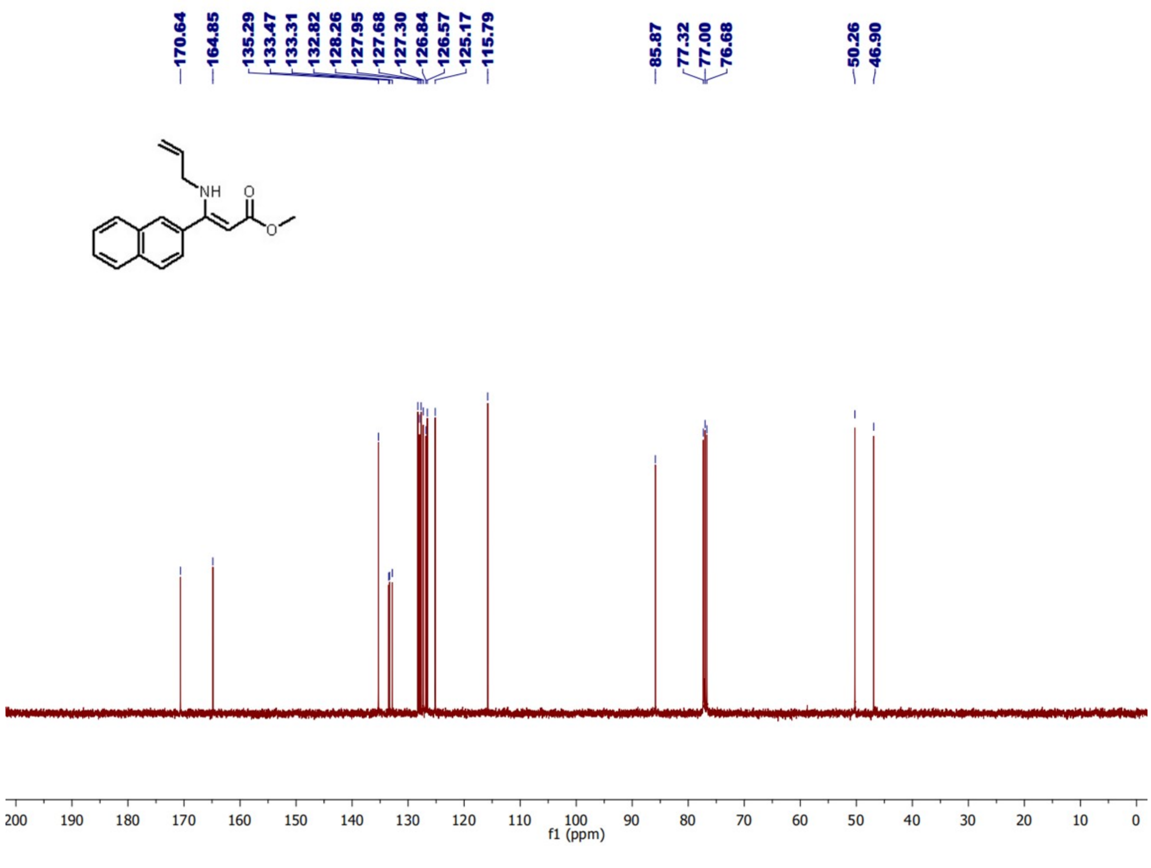
methyl (Z)-3-(allylamino)-3-(3,4-dimethoxyphenyl)acrylate (**1j**)



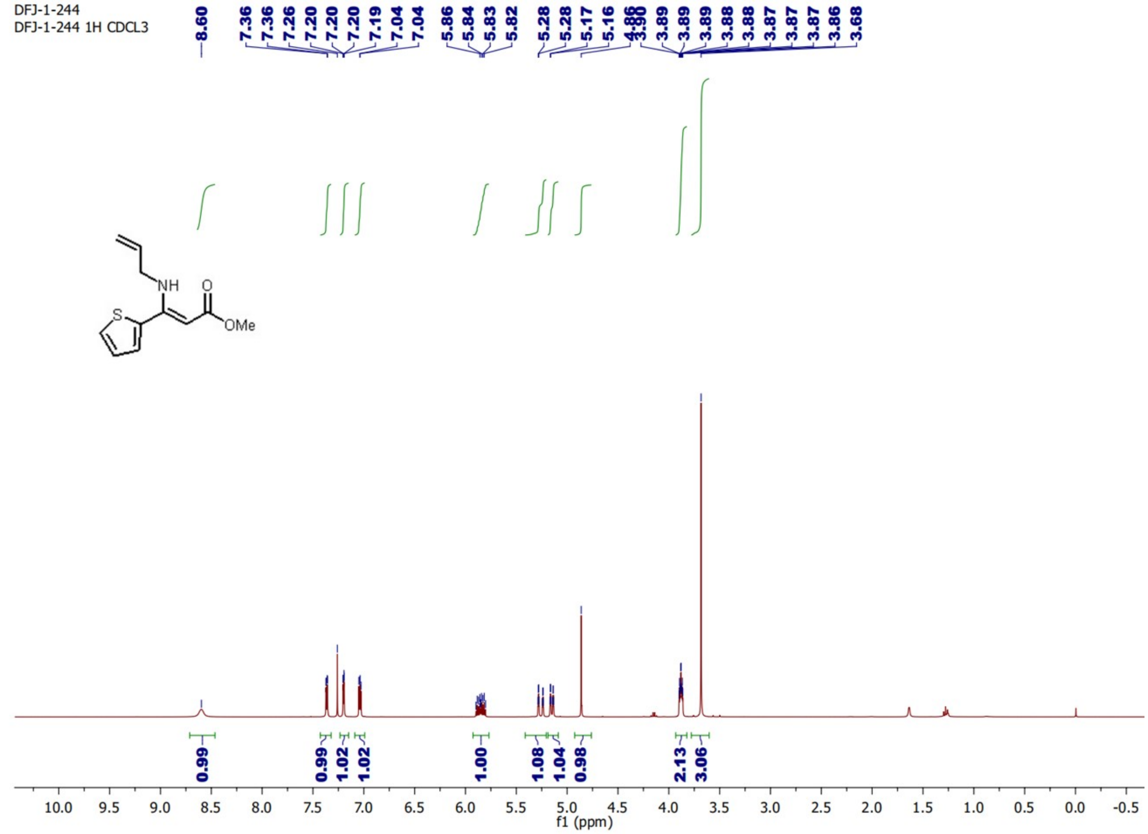


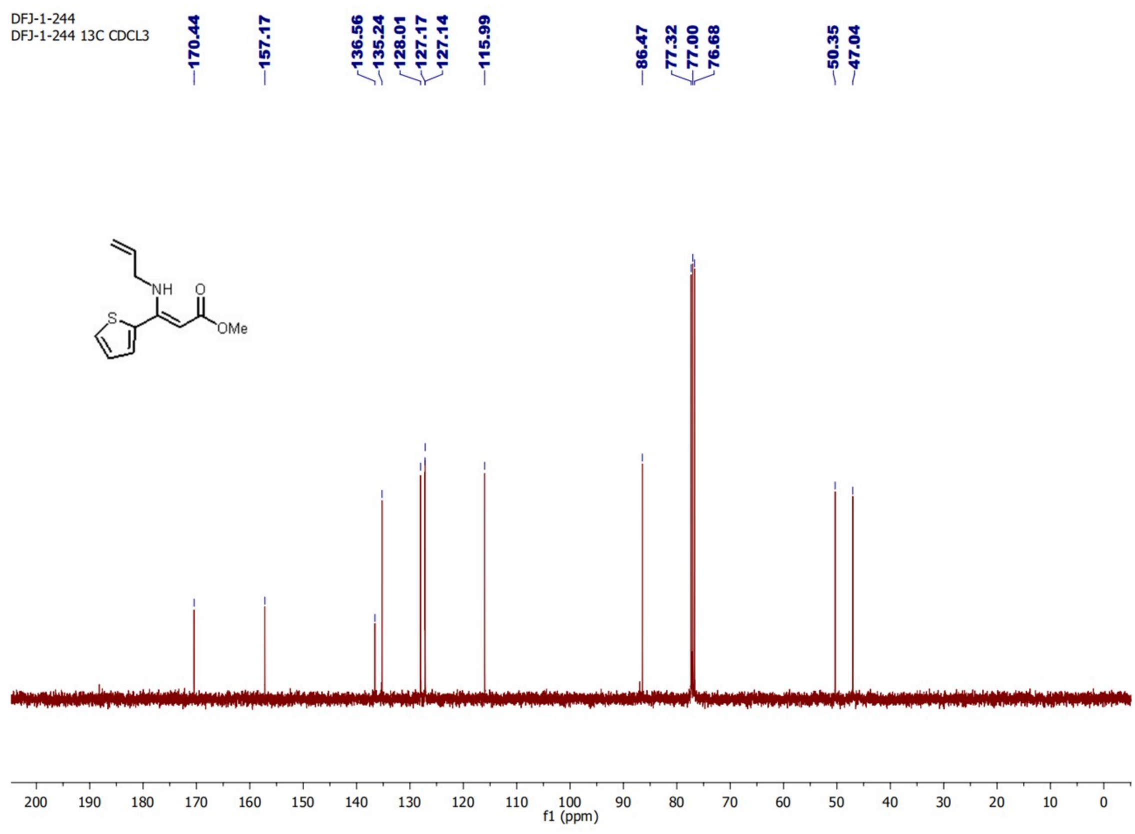
methyl (Z)-3-(allylamino)-3-(naphthalen-2-yl)acrylate (**1k**)



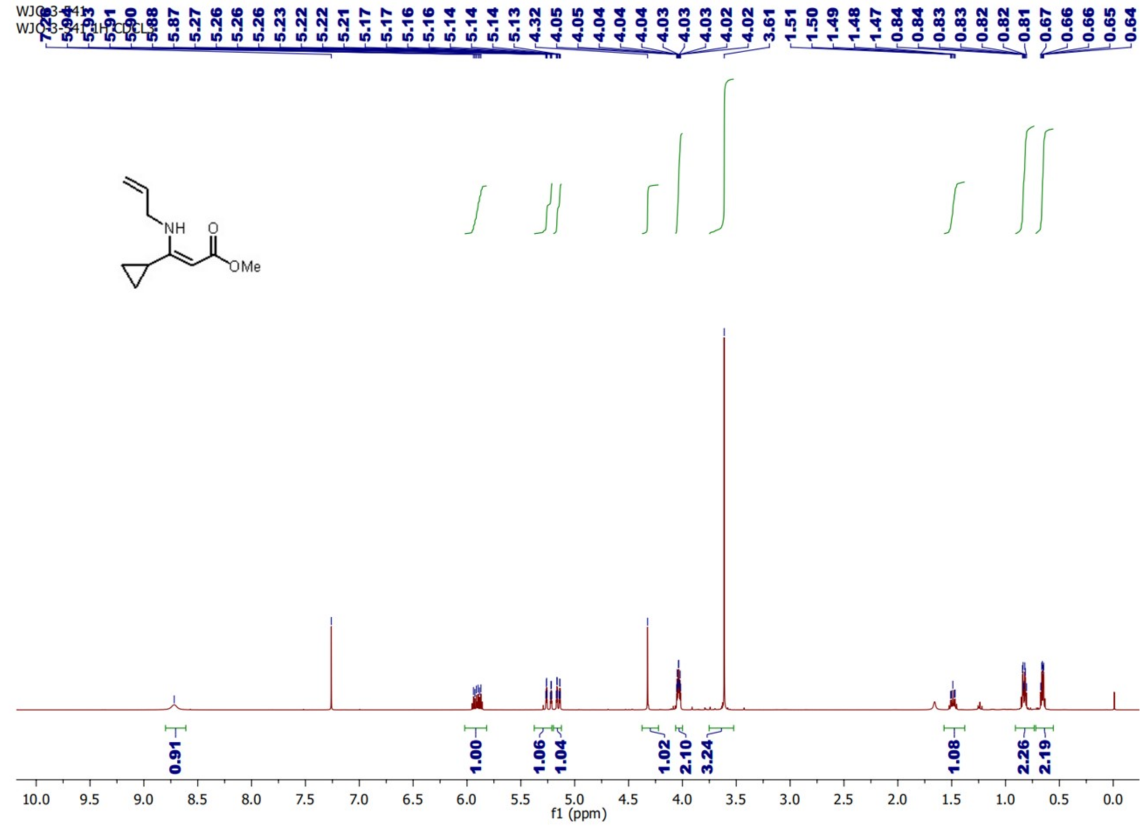


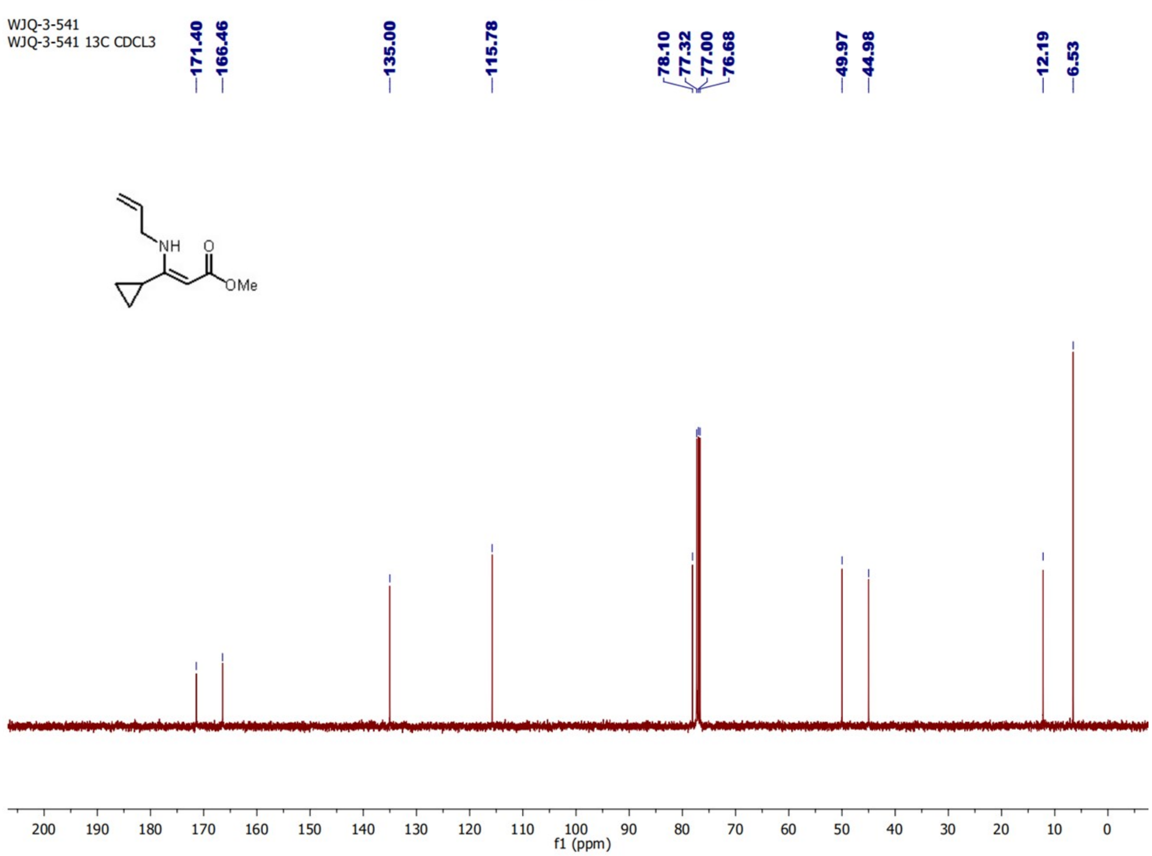
methyl (Z)-3-(allylamino)-3-(thiophen-2-yl)acrylate (**1l**)



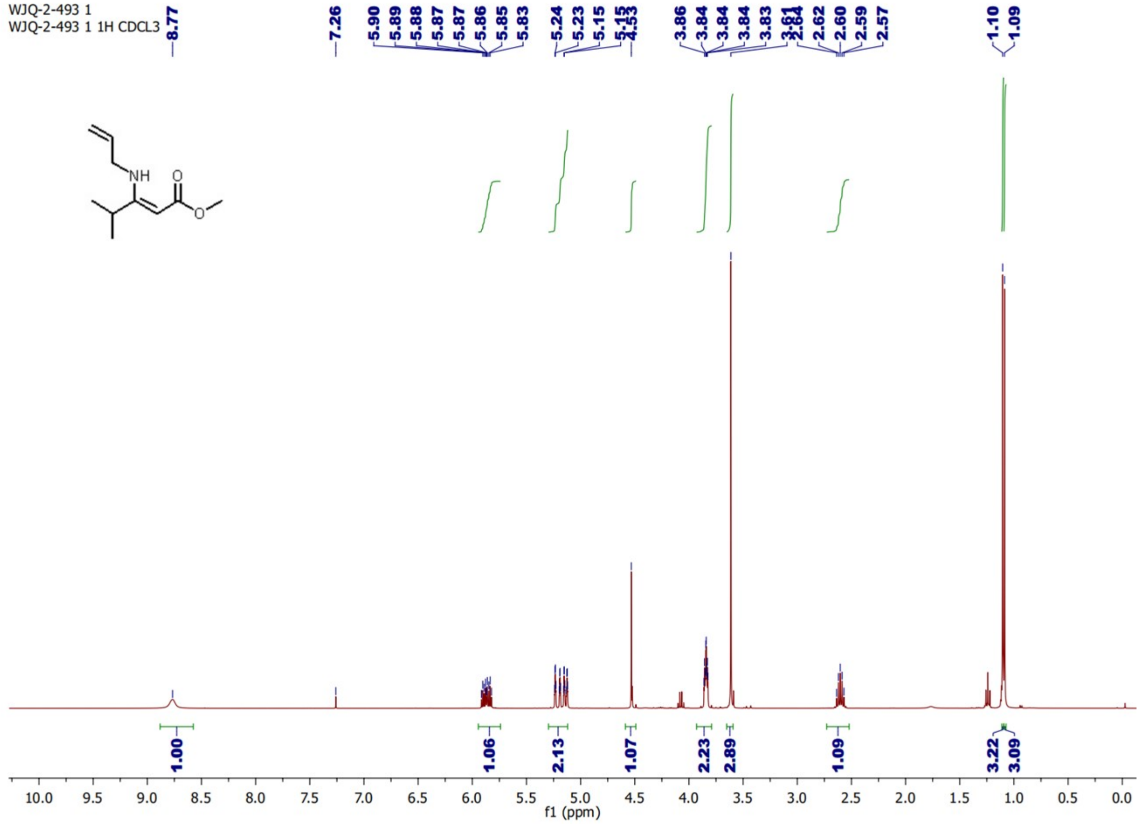


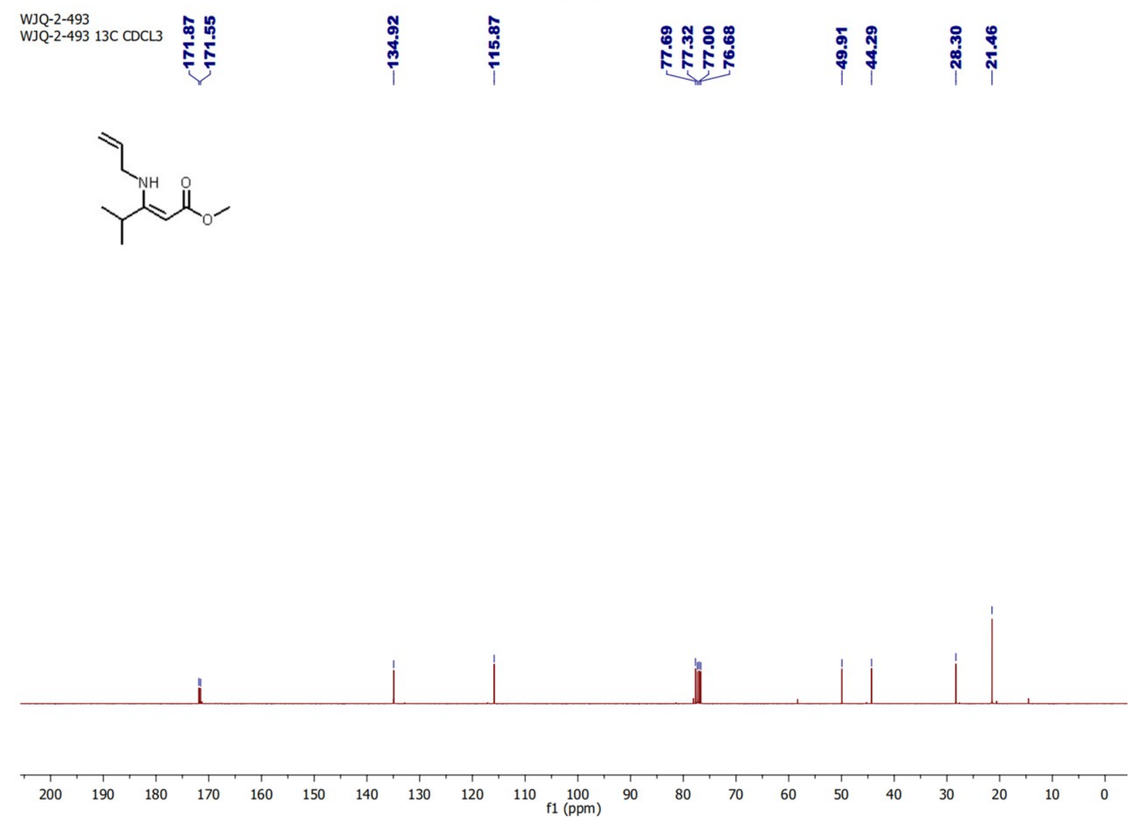
methyl (Z)-3-(allylamino)-3-cyclopropylacrylate (**1m**)



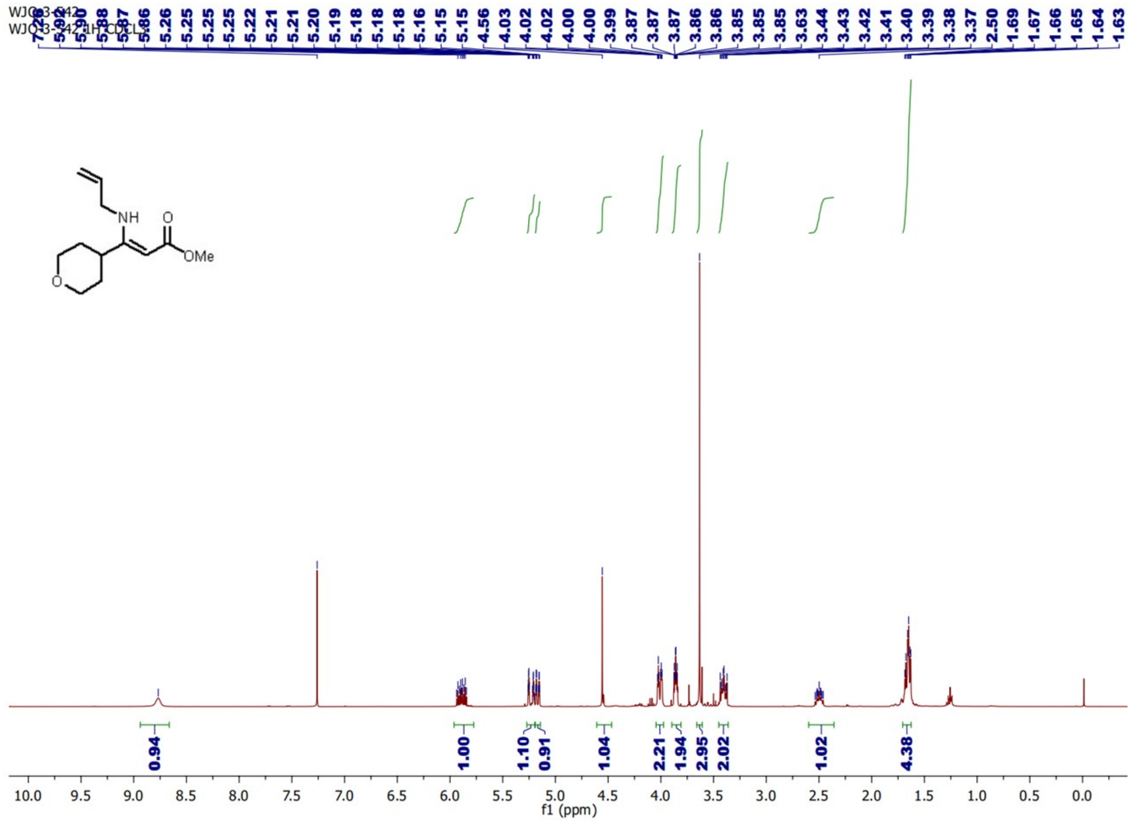


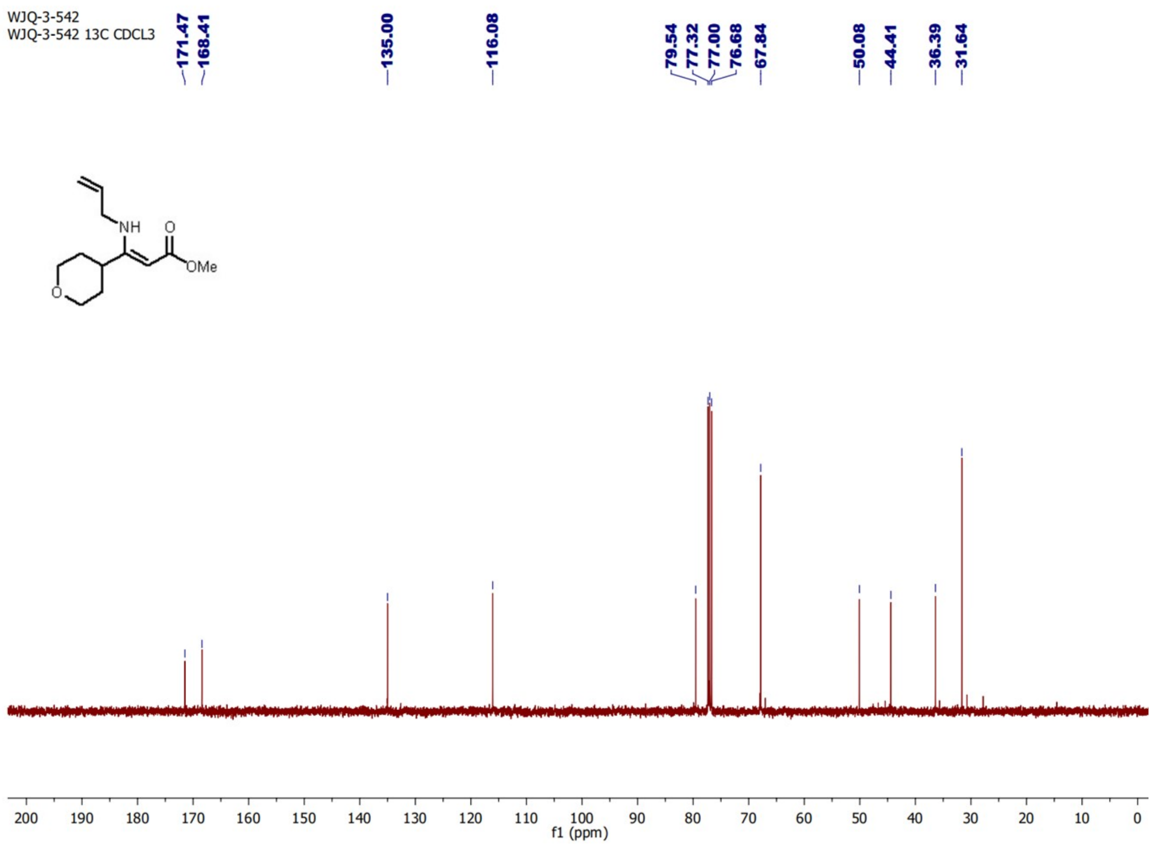
methyl (Z)-3-(allylamino)-4-methylpent-2-enoate (**1n**)



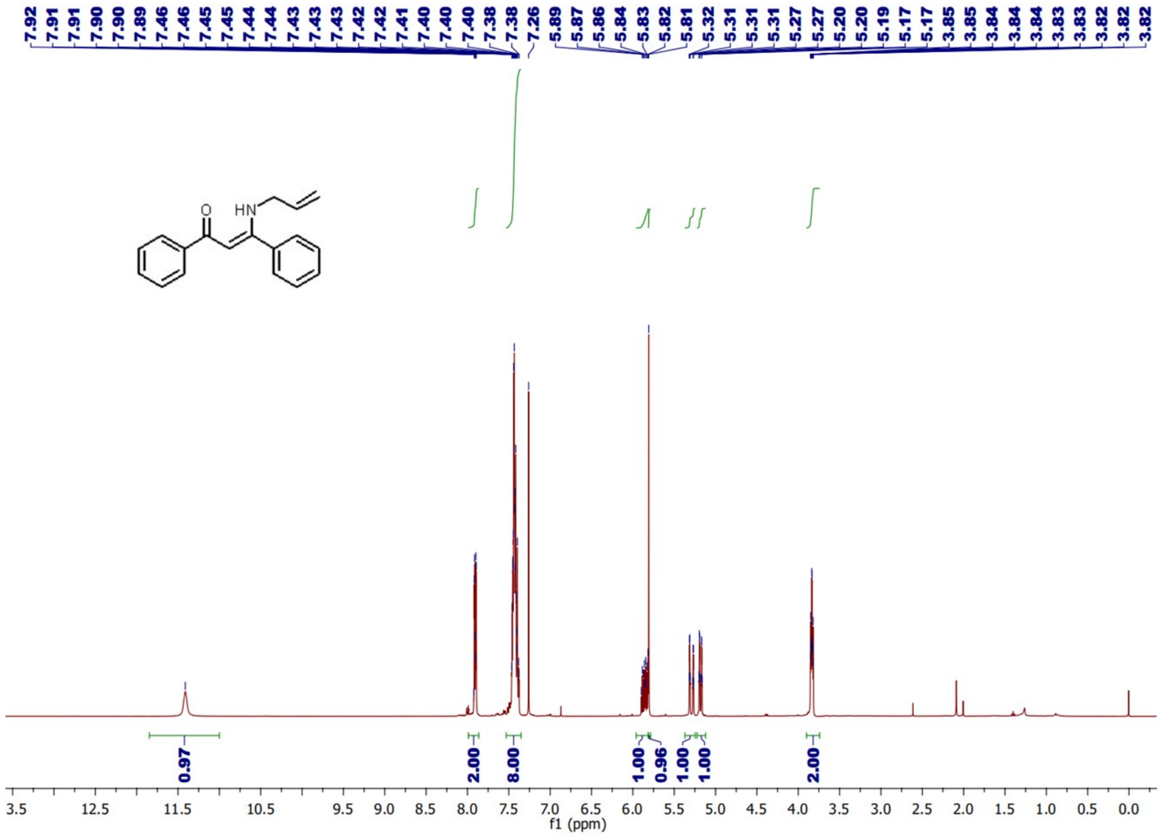


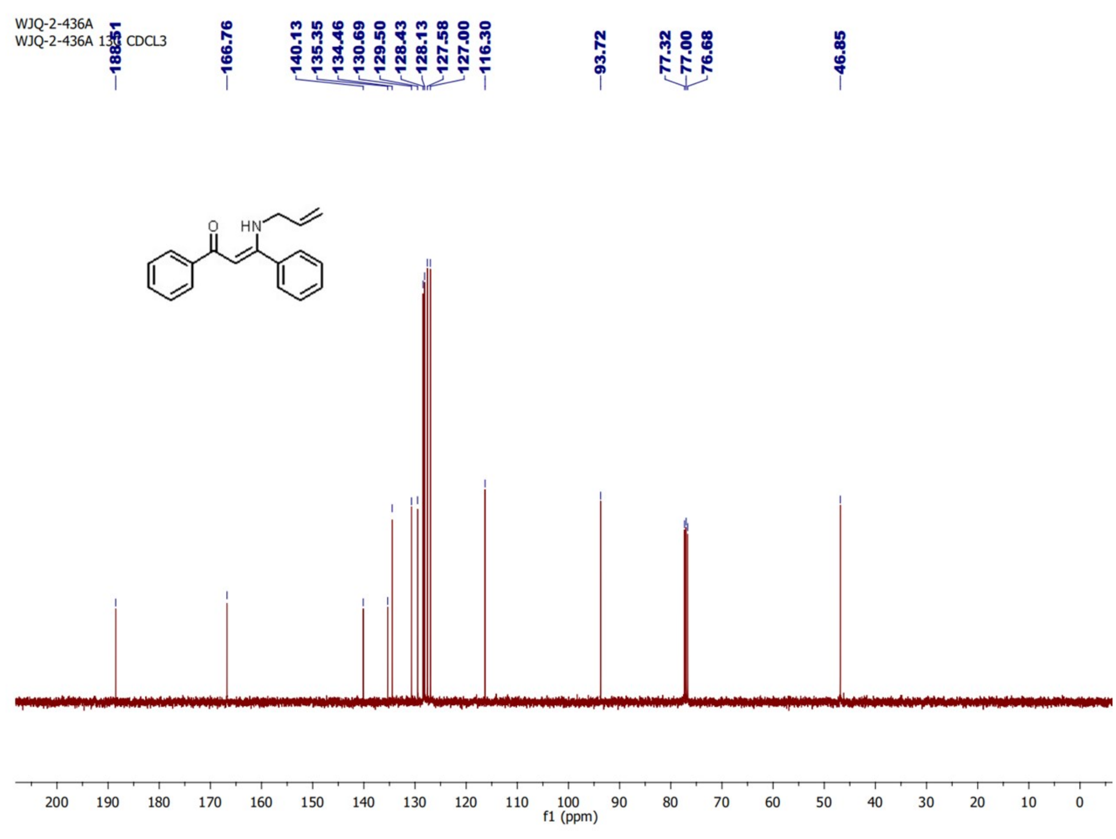
methyl (Z)-3-(allylamino)-3-(tetrahydro-2H-pyran-4-yl)acrylate (**1o**)



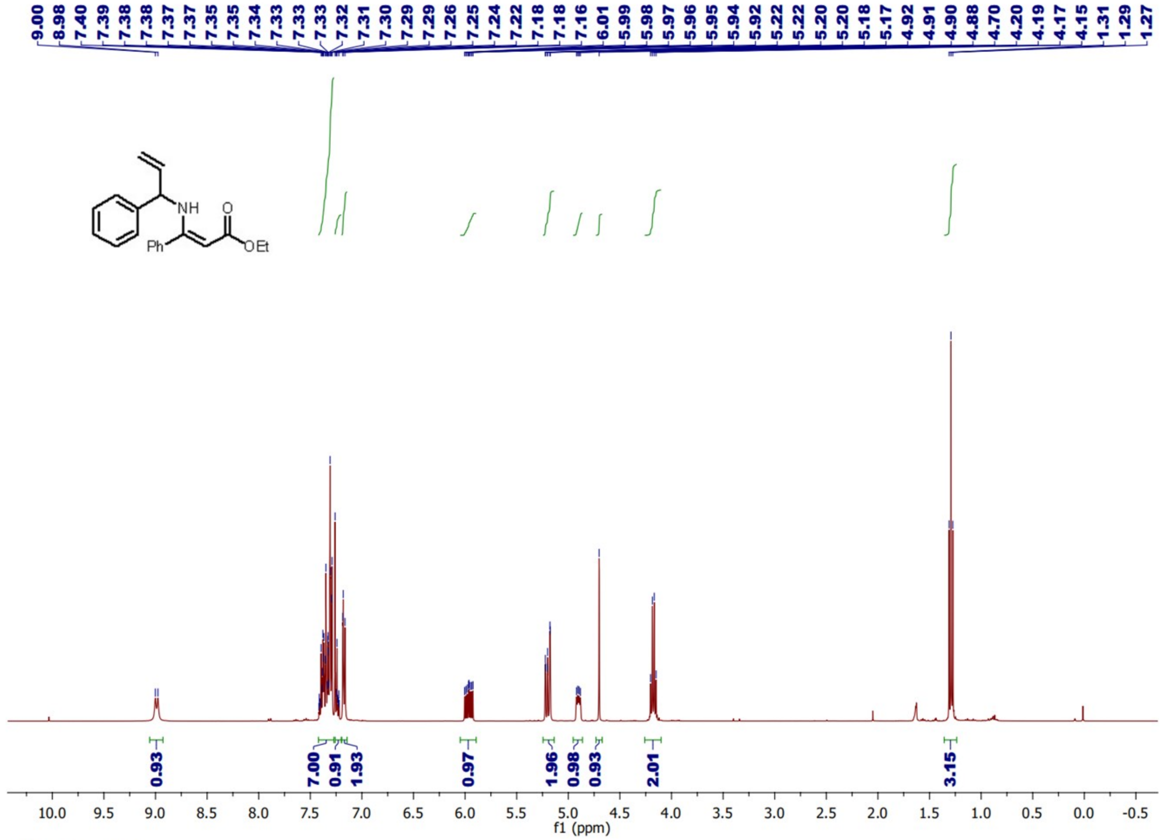


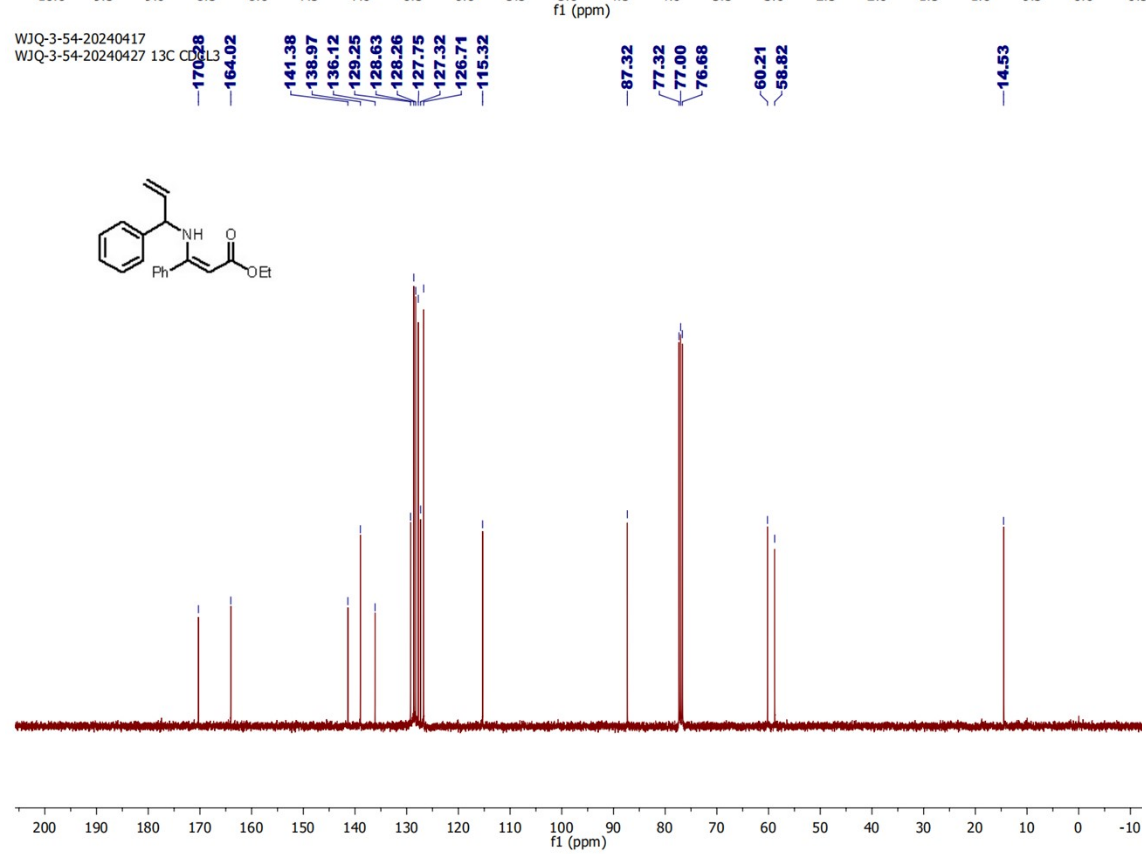
(Z)-3-(allylamino)-1,3-diphenylprop-2-en-1-one (**1p**)



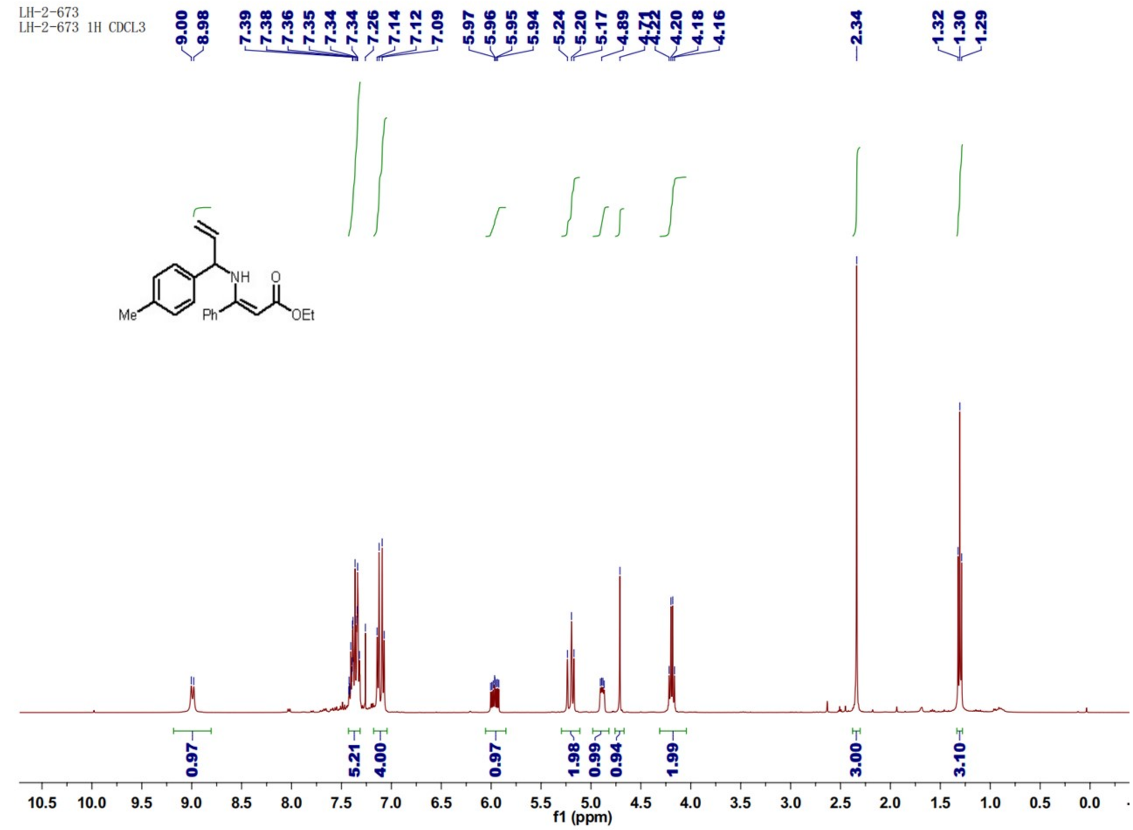


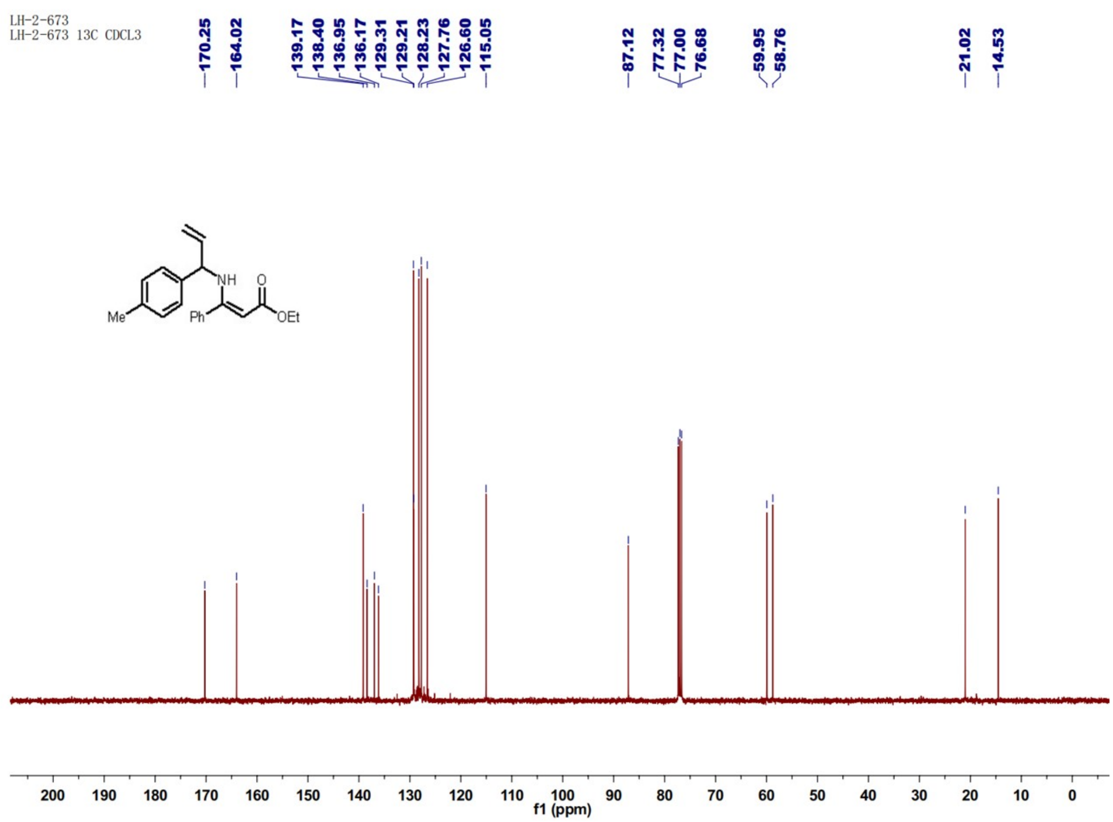
ethyl (Z)-3-phenyl-3-((1-phenylallyl)amino)acrylate (**3a**)



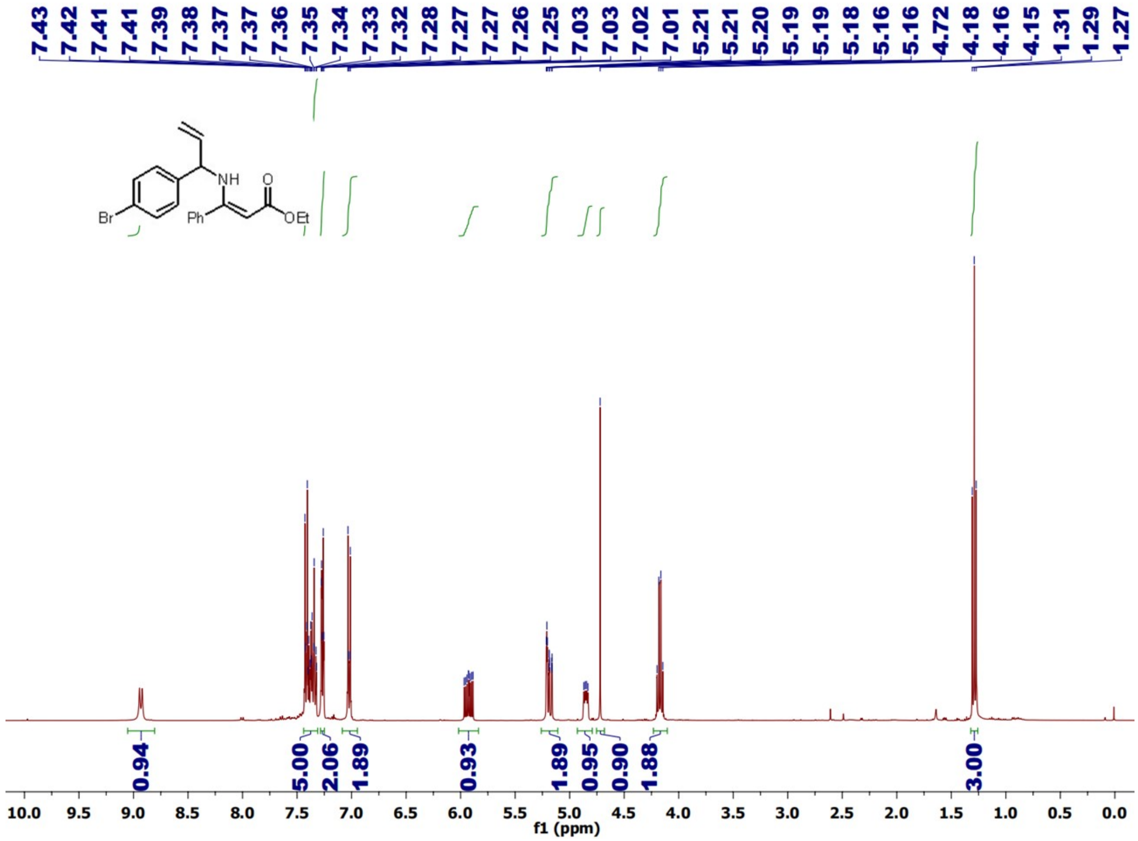


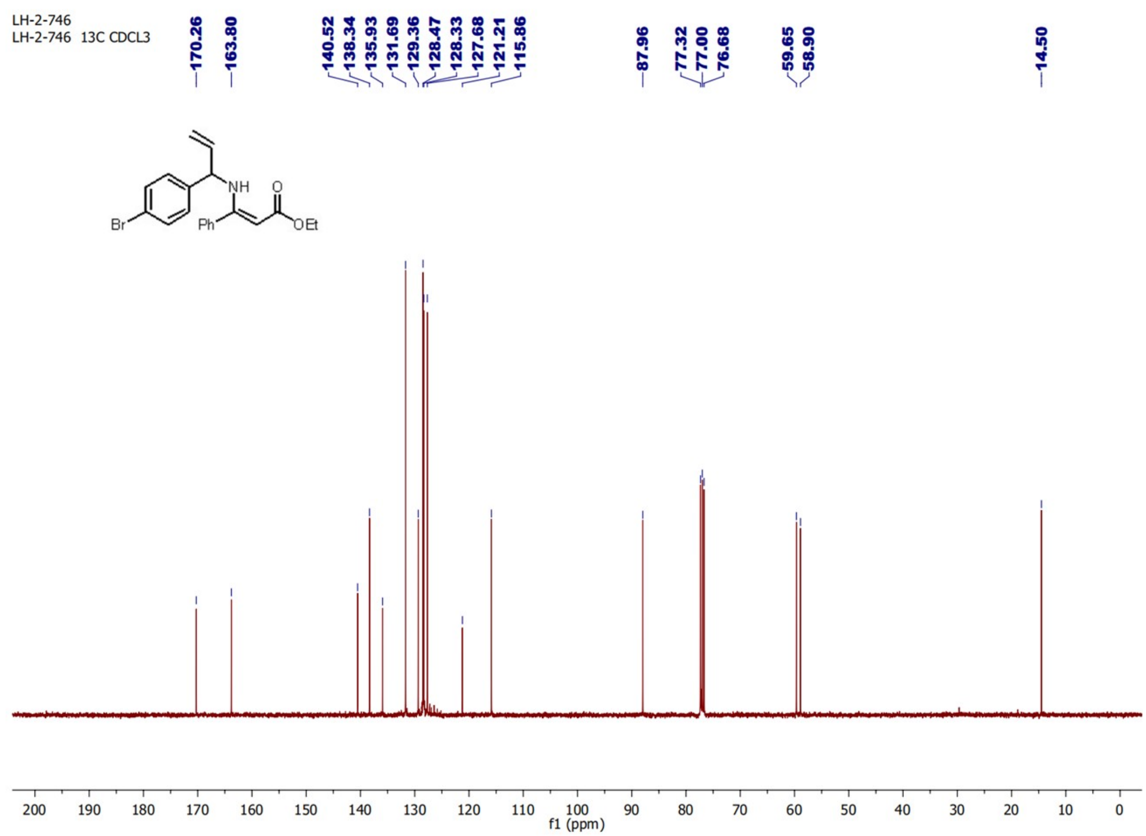
ethyl (Z)-3-phenyl-3-((1-(p-tolyl)allyl)amino)acrylate (**3b**)



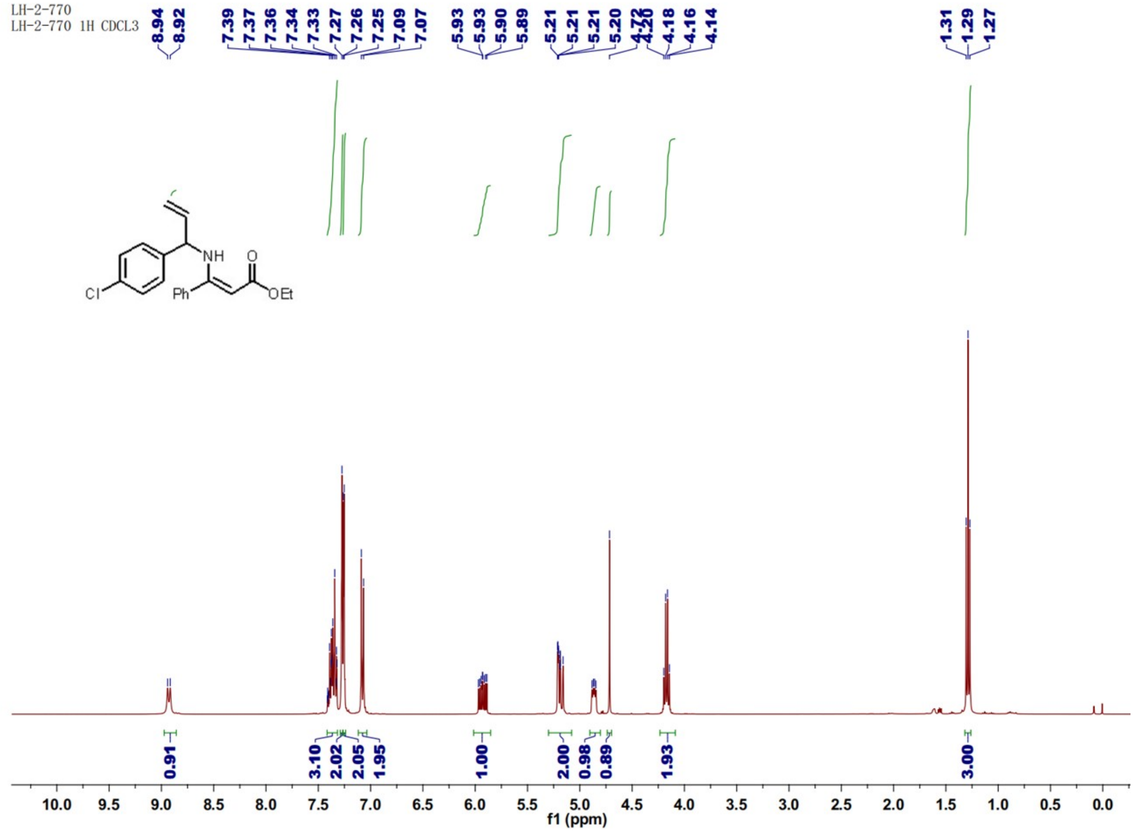


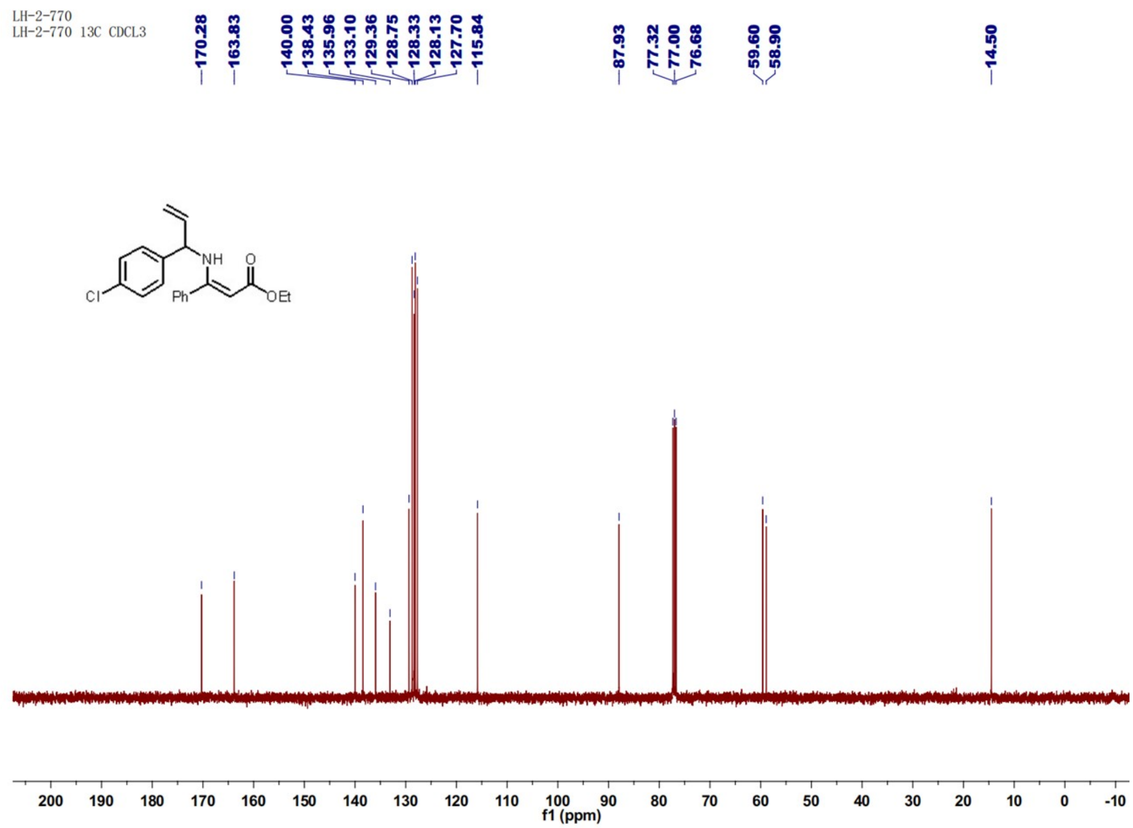
ethyl (Z)-3-((1-(4-bromophenyl)allyl)amino)-3-phenylacrylate (**3c**)



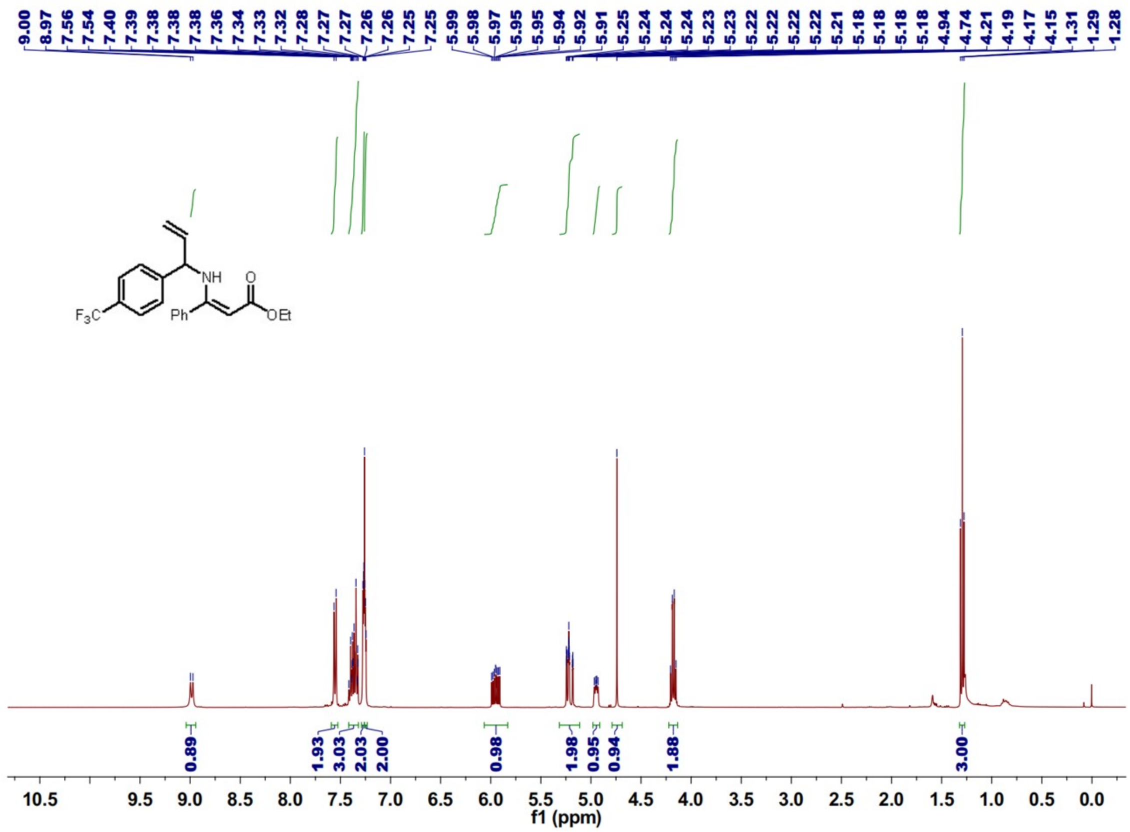


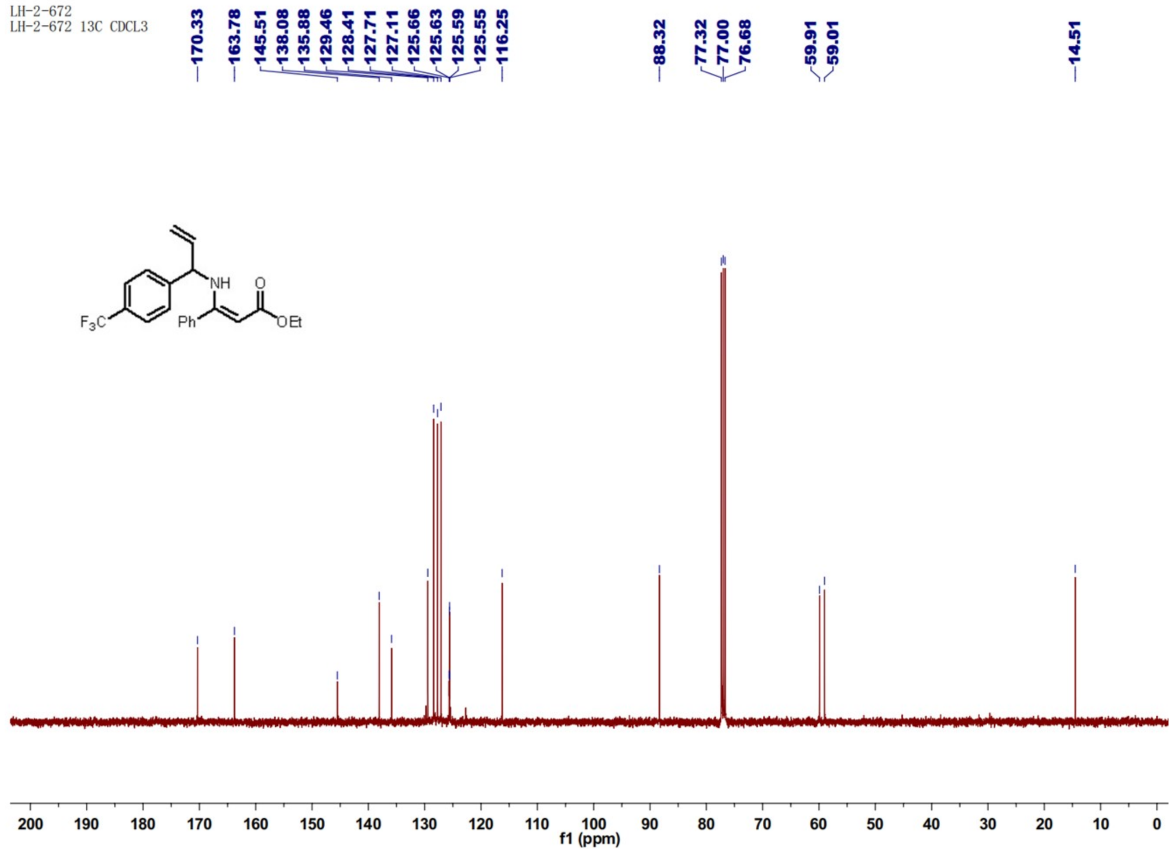
ethyl (Z)-3-((1-(4-chlorophenyl)allyl)amino)-3-phenylacrylate (**3d**)



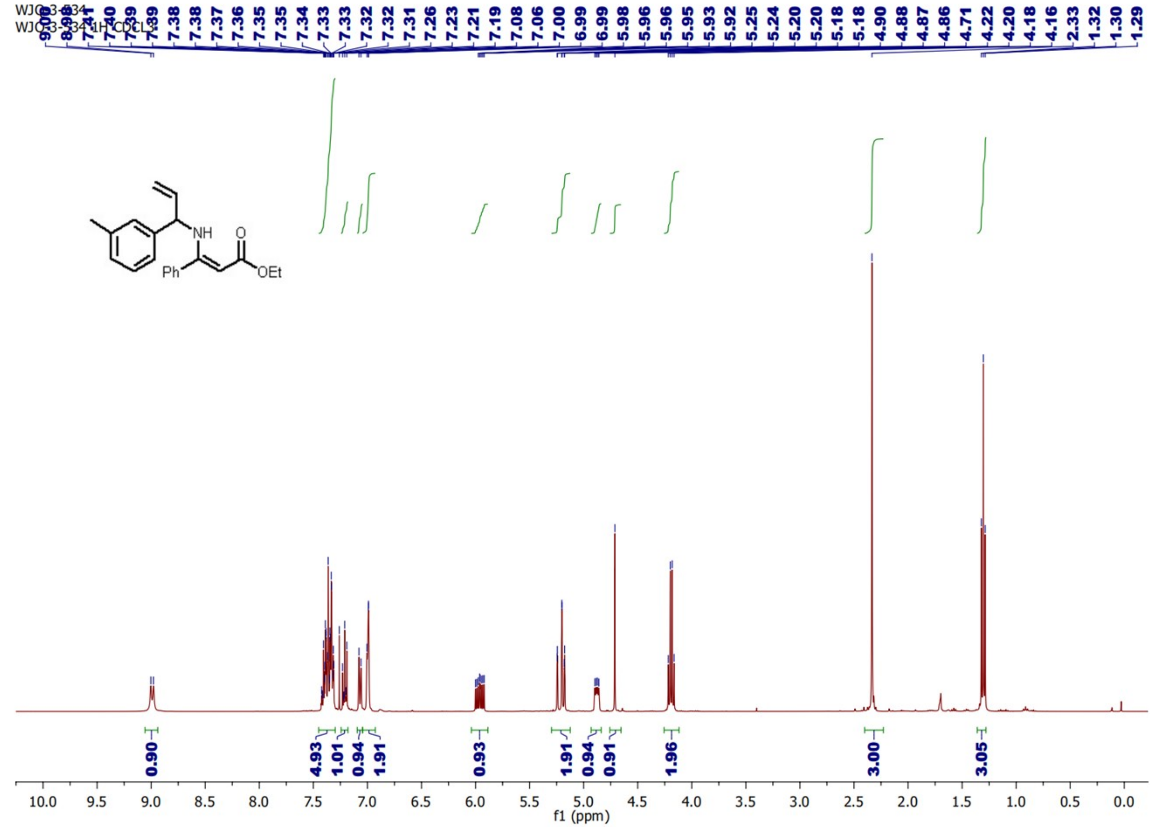


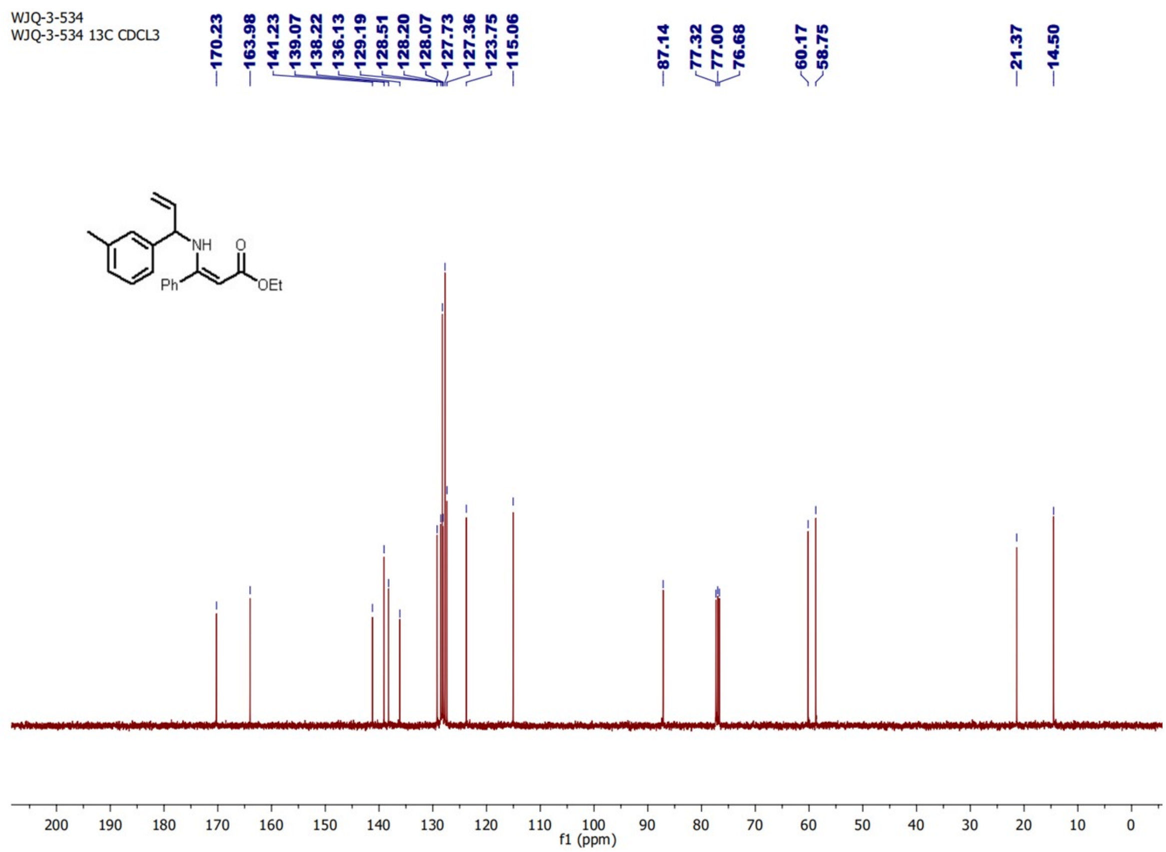
ethyl (Z)-3-phenyl-3-((1-(4-(trifluoromethyl)phenyl)allyl)amino)acrylate (**3e**)



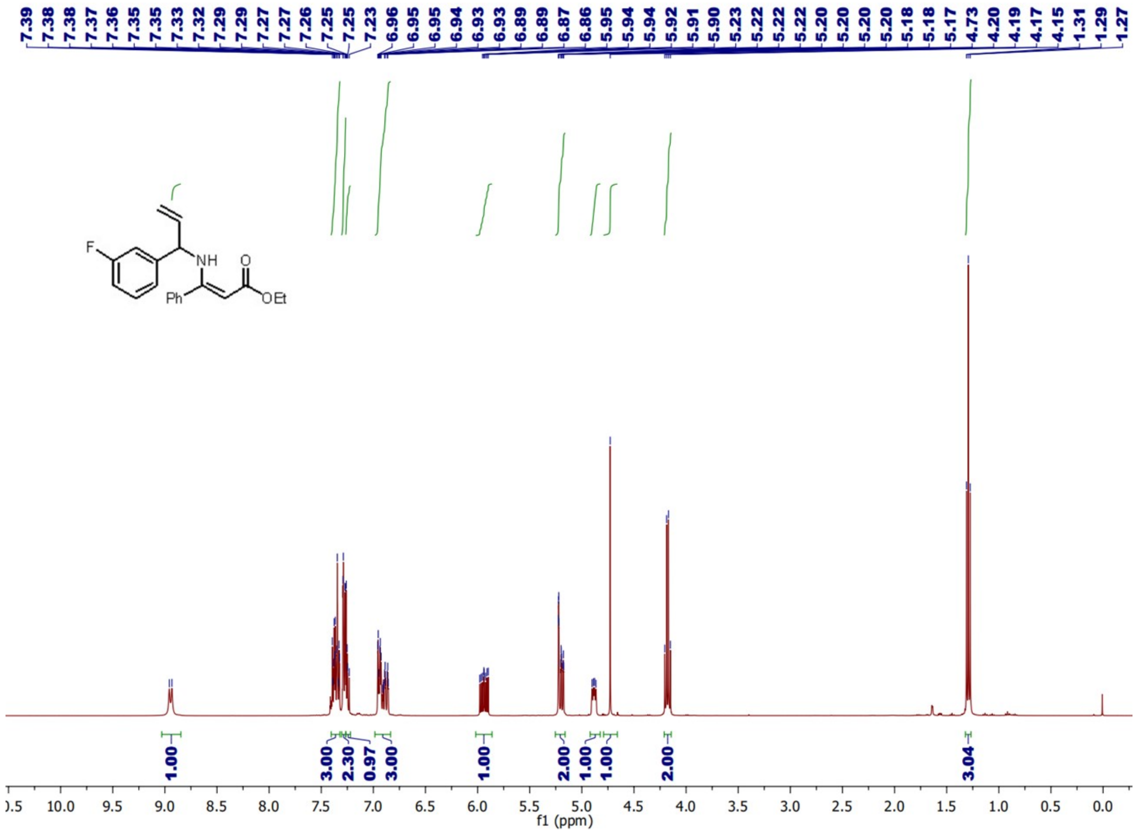


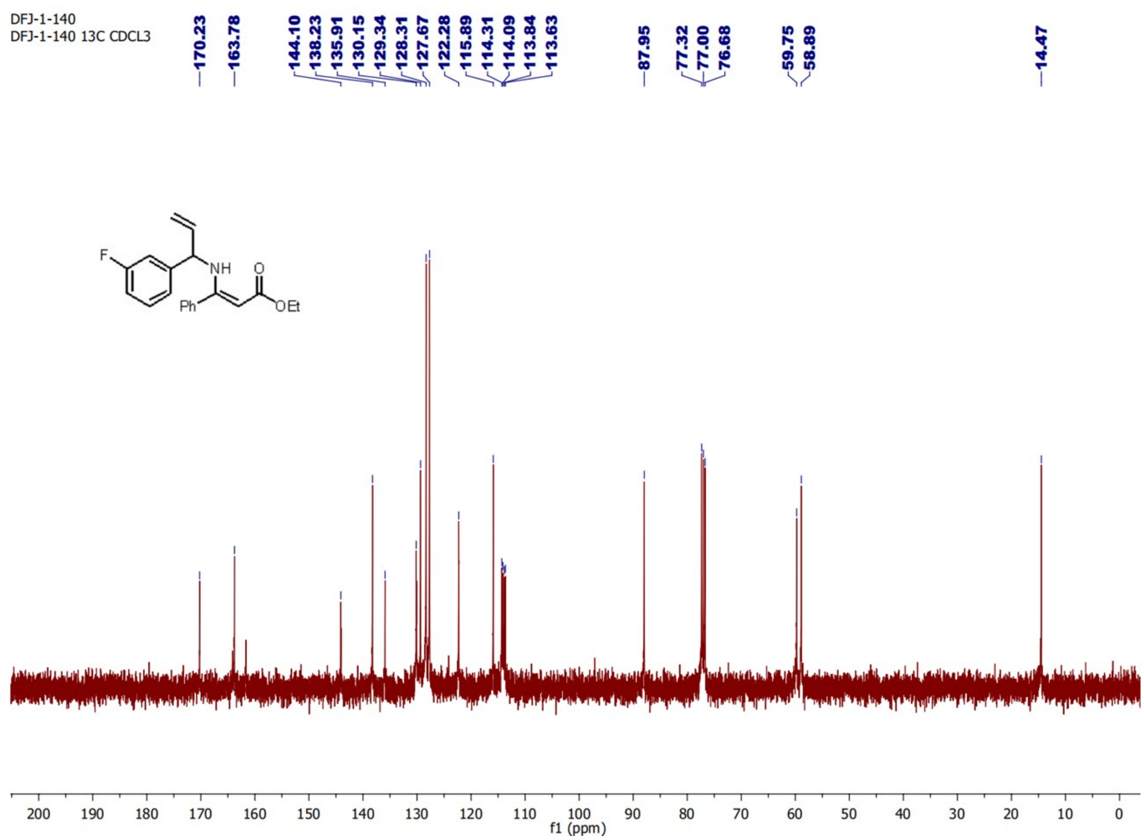
ethyl (Z)-3-phenyl-3-((1-(m-tolyl)allyl)amino)acrylate (**3f**)



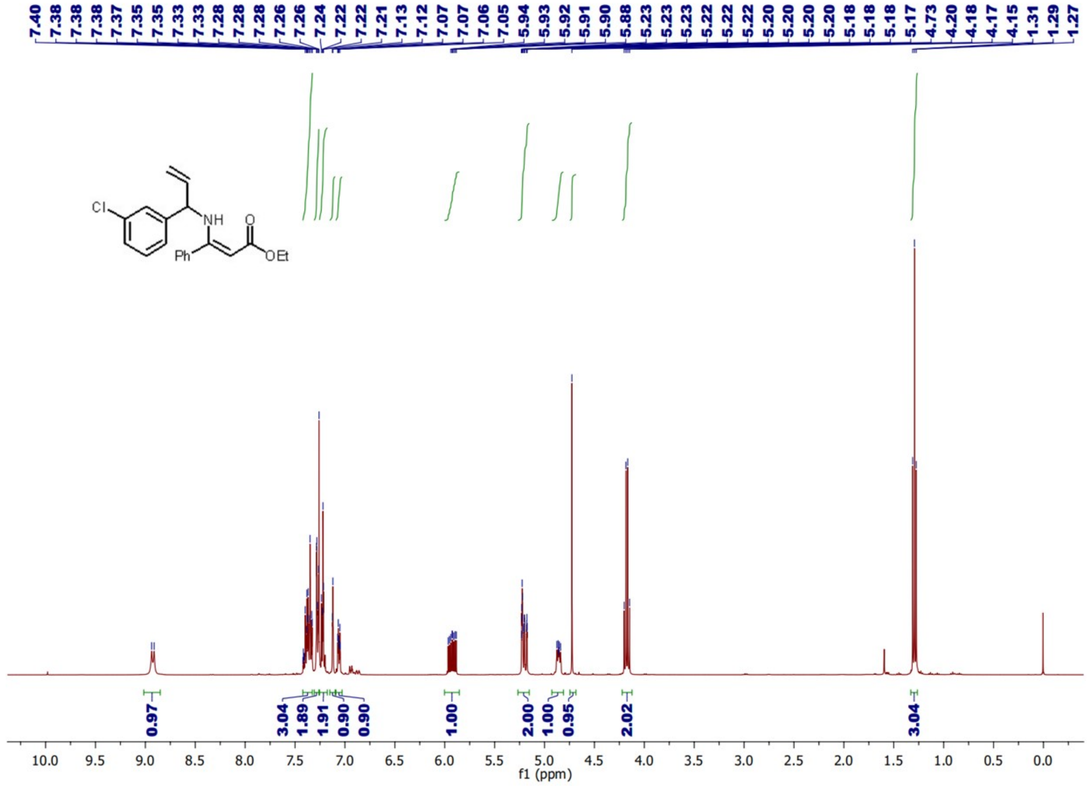


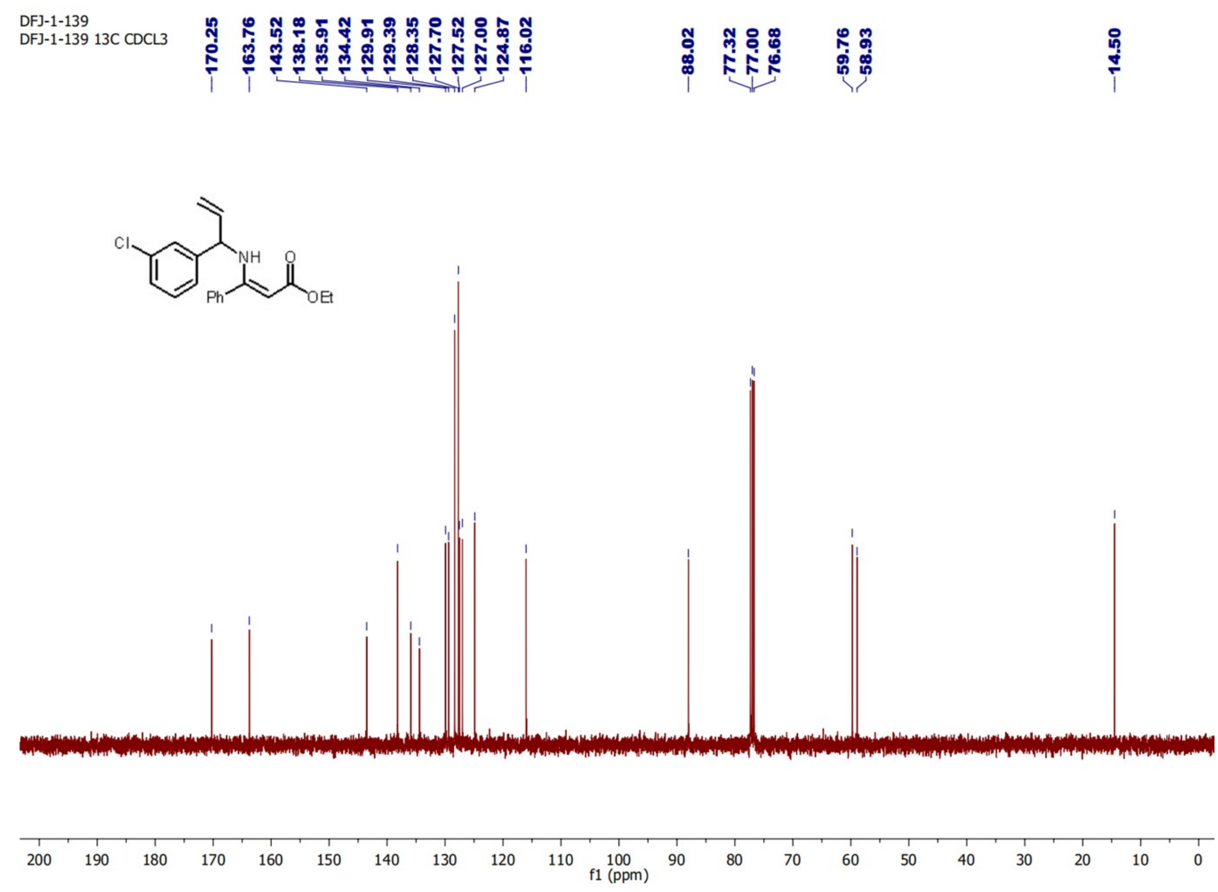
ethyl (Z)-3-((1-(3-fluorophenyl)allyl)amino)-3-phenylacrylate (**3g**)



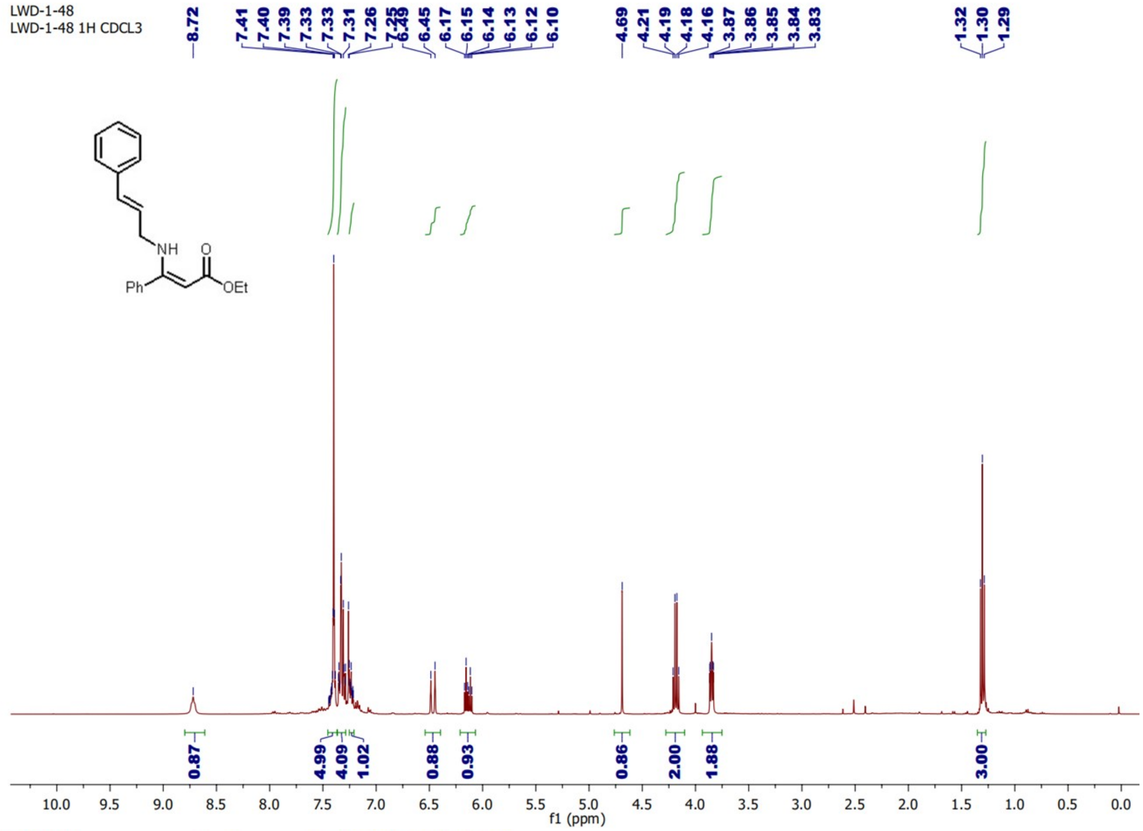


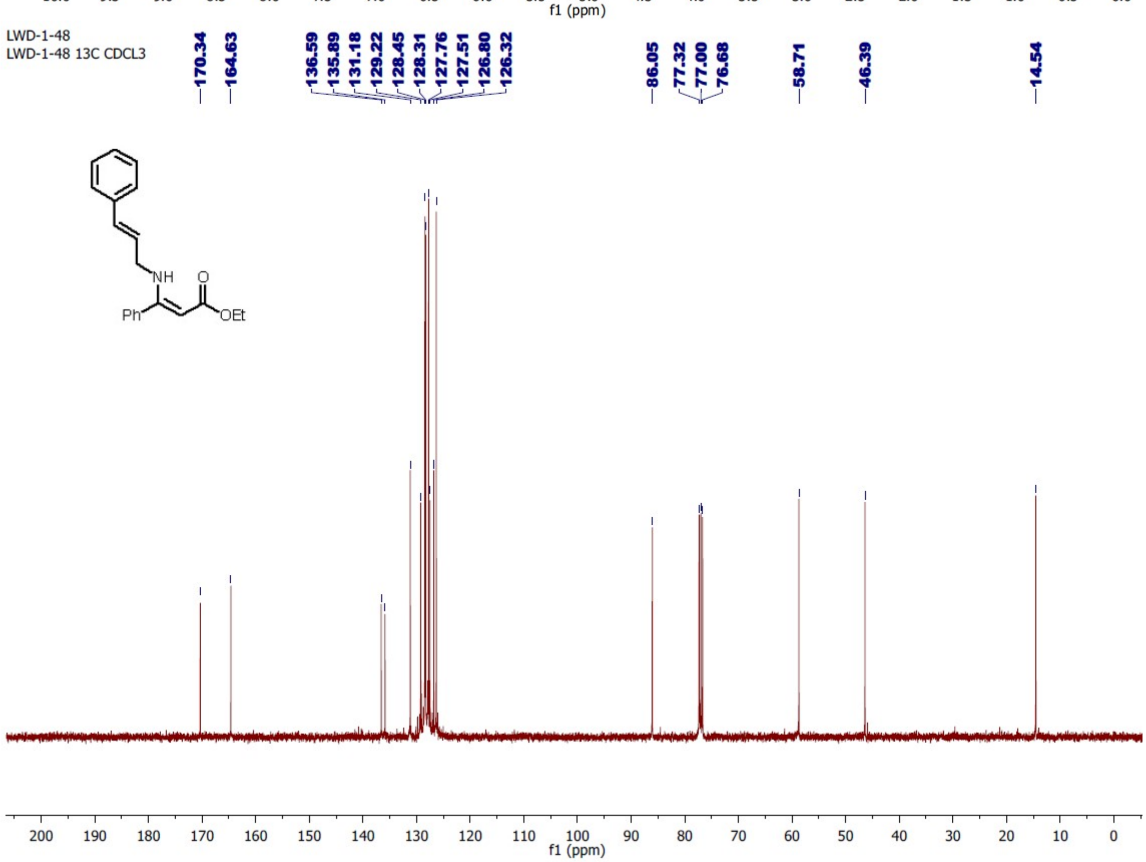
ethyl (Z)-3-((1-(3-chlorophenyl)allyl)amino)-3-phenylacrylate (**3h**)



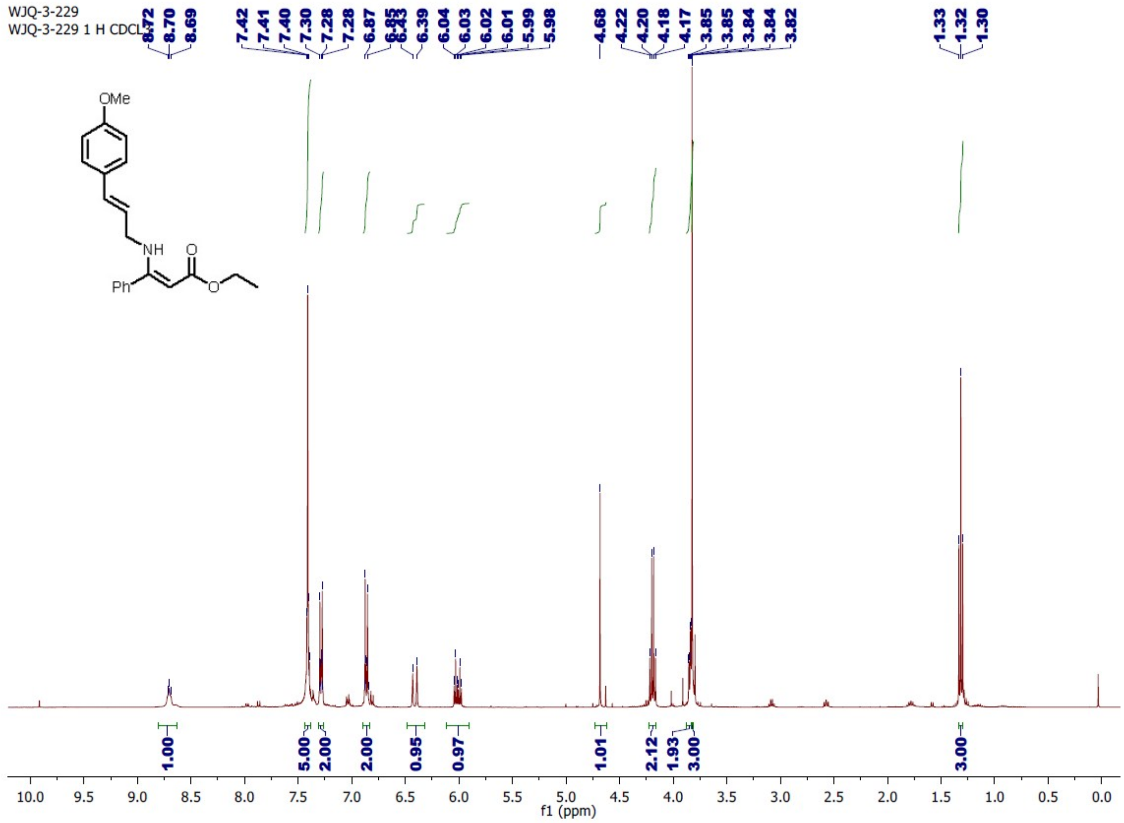


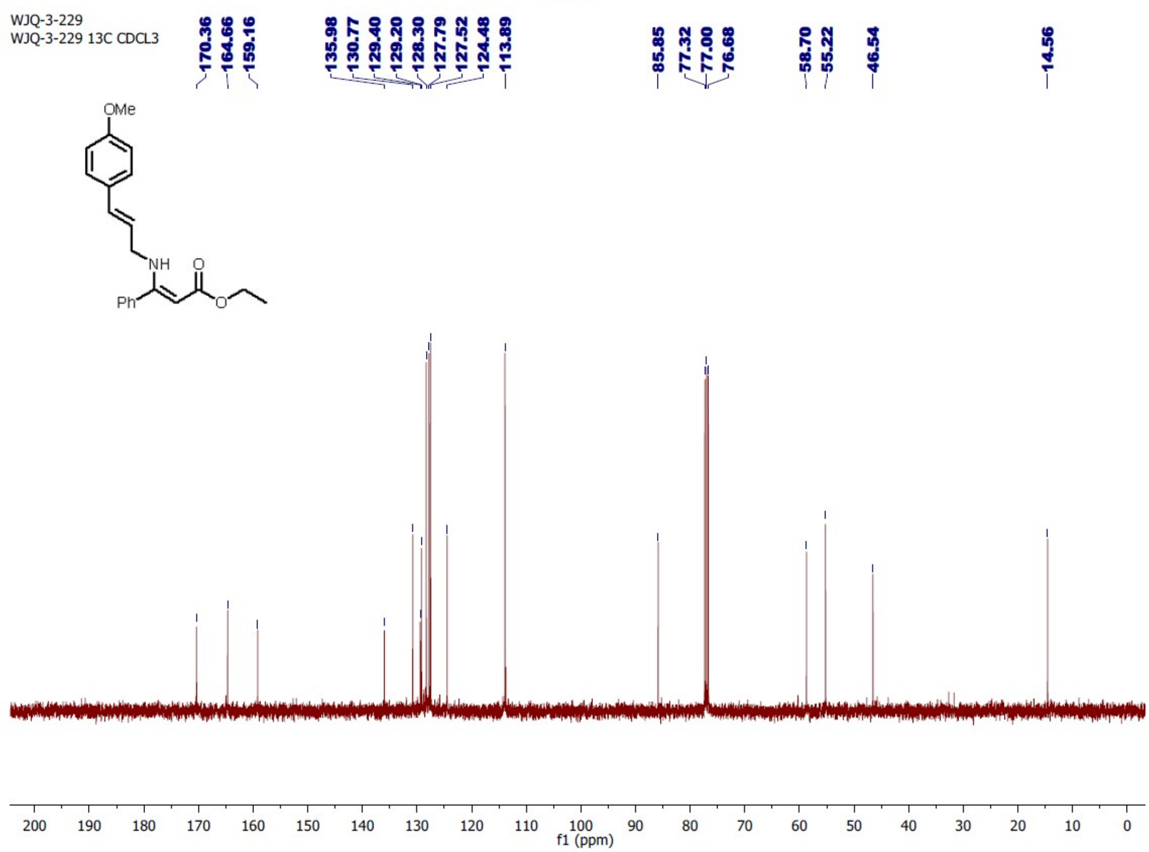
ethyl (Z)-3-(cinnamylamino)-3-phenylacrylate (**3i**)



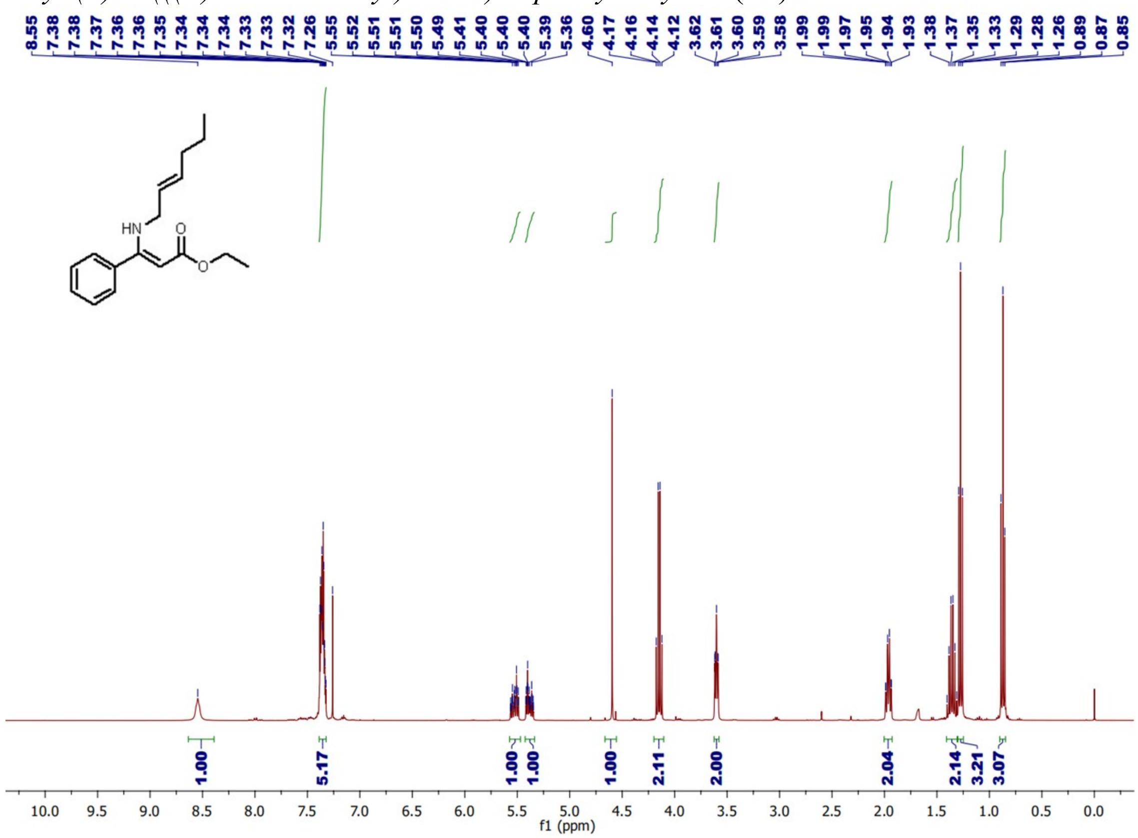


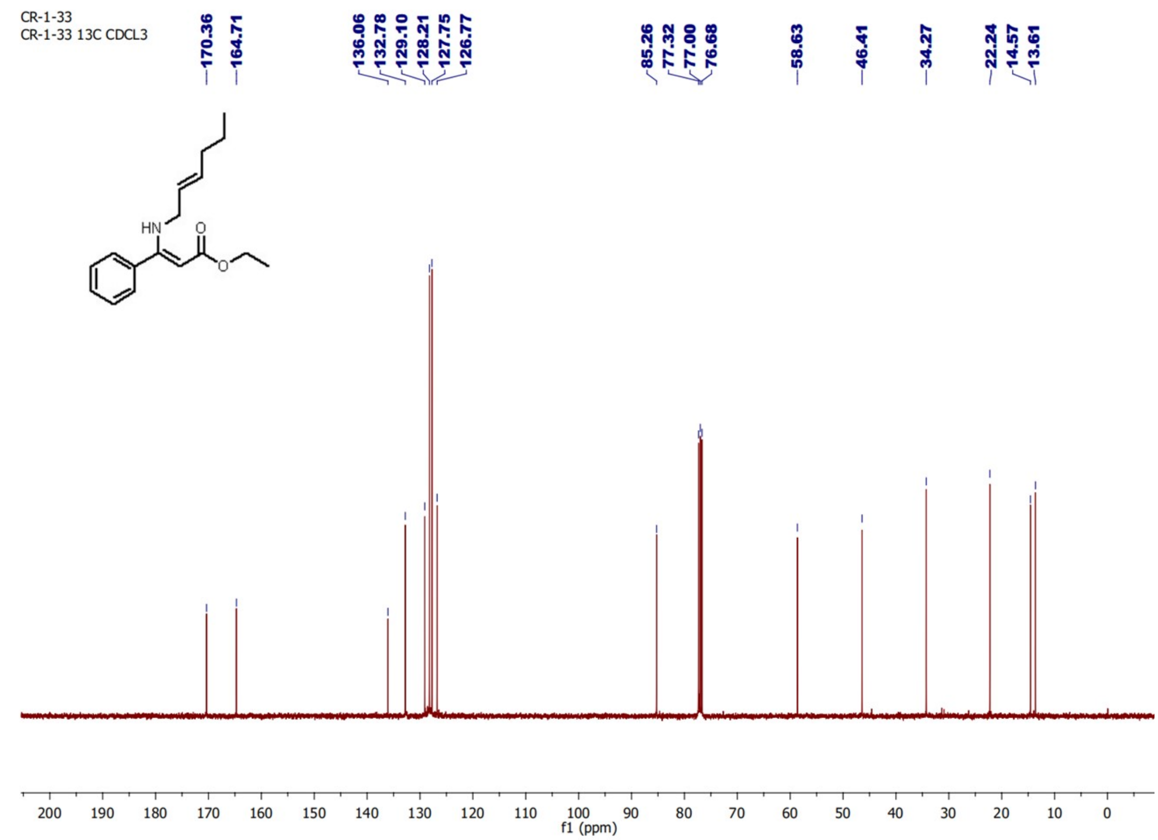
ethyl (Z)-3-(((E)-3-(4-methoxyphenyl)allyl)amino)-3-phenylacrylate (**3j**)



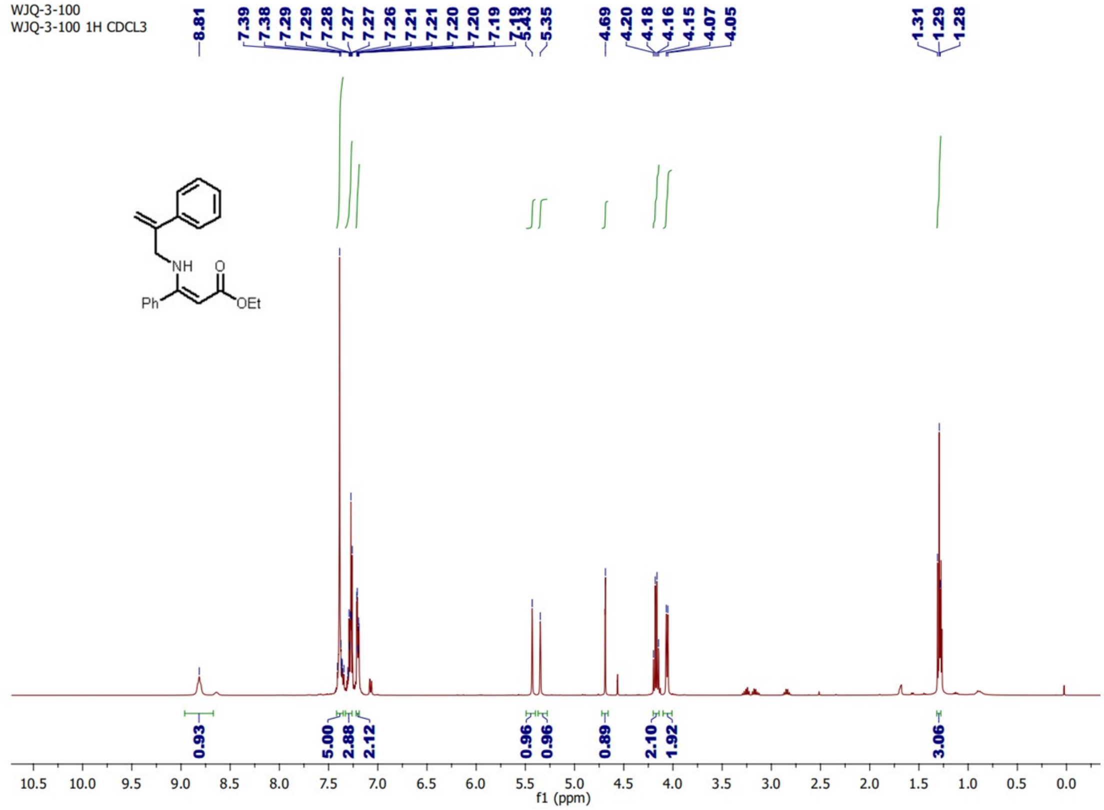


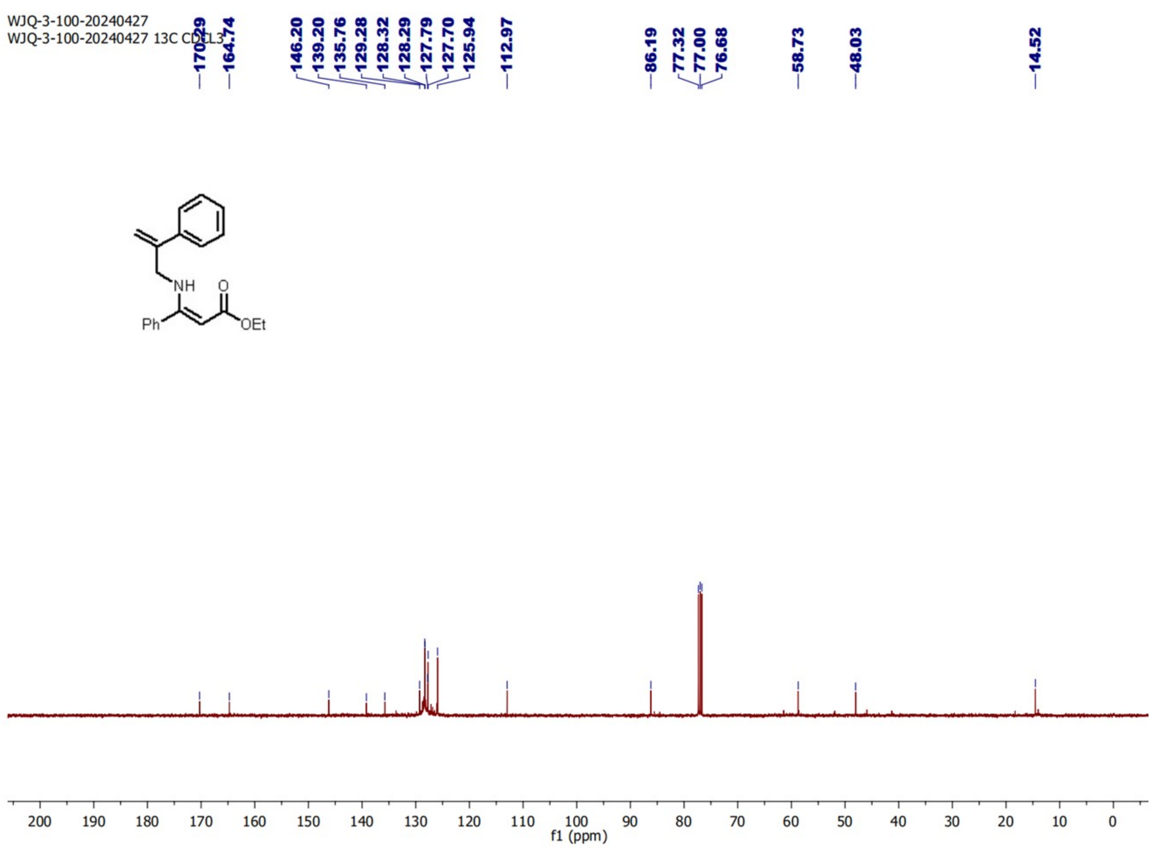
ethyl (Z)-3-(((E)-hex-2-en-1-yl)amino)-3-phenylacrylate (**3k**)



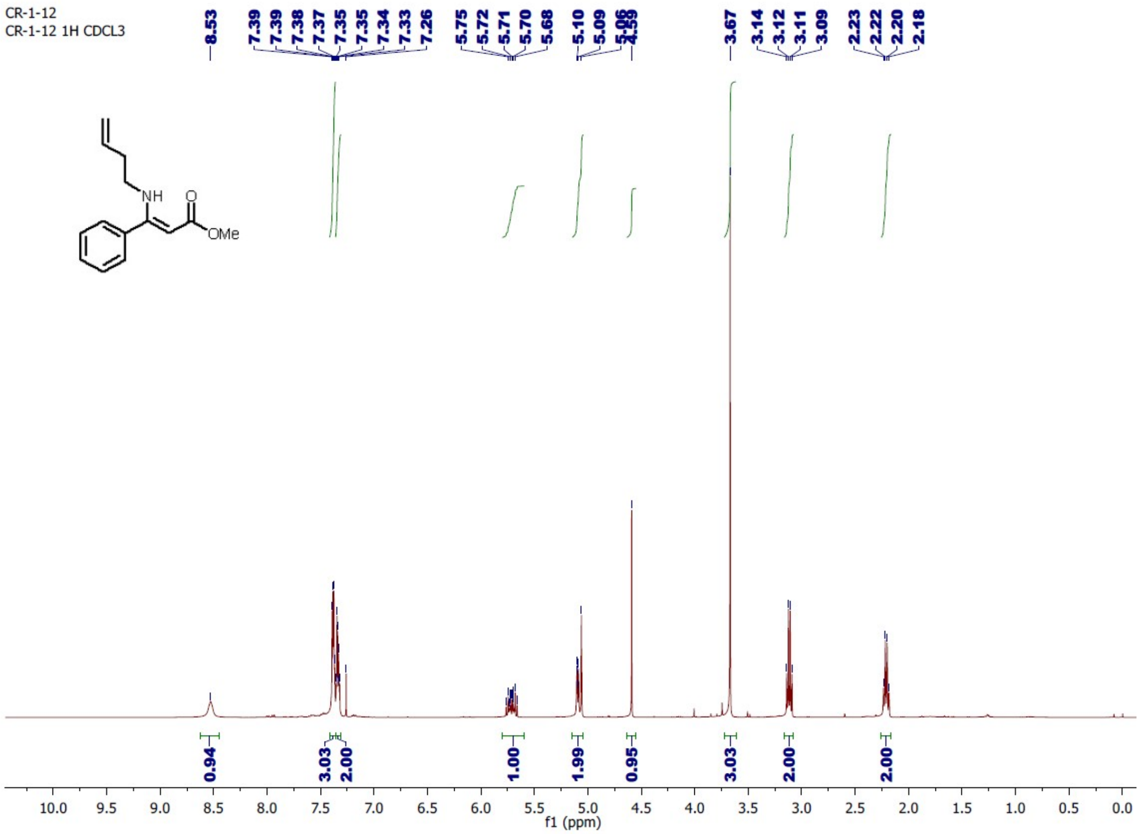


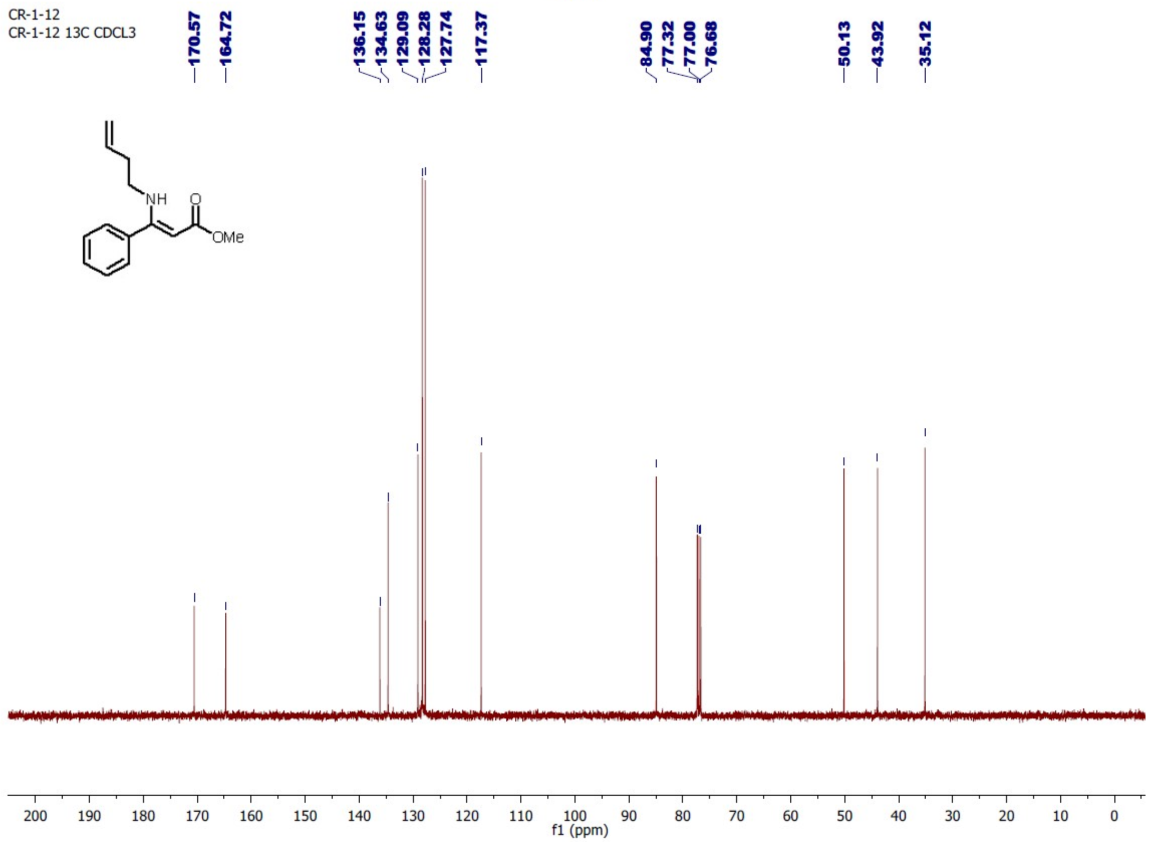
ethyl (Z)-3-phenyl-3-((2-phenylallyl)amino)acrylate (**3l**)



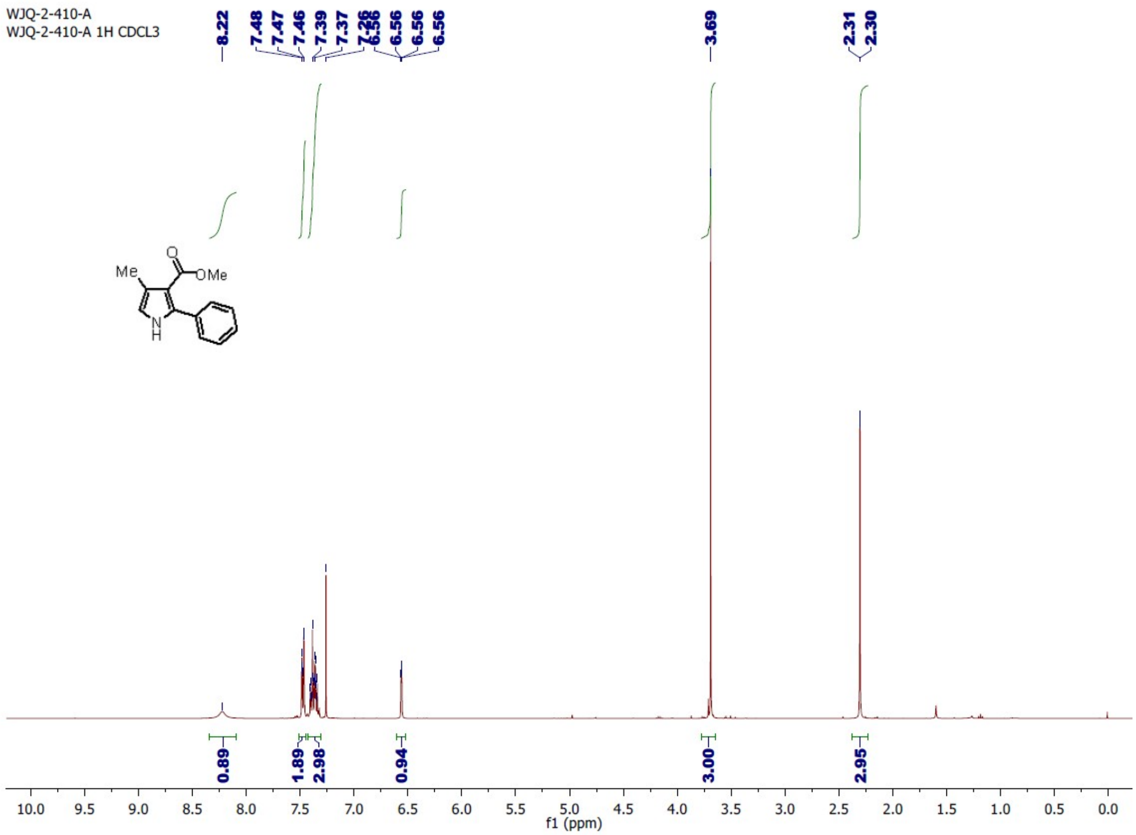


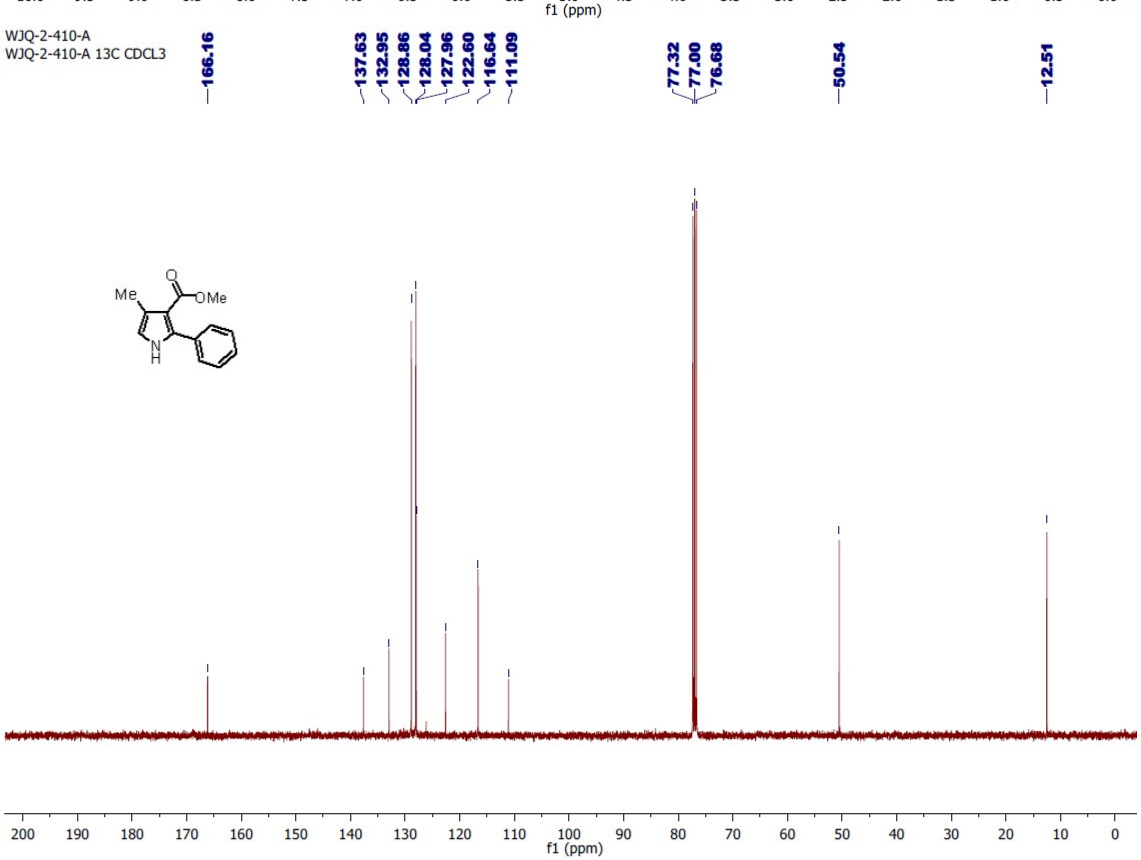
methyl (Z)-3-(but-3-en-1-ylamino)-3-phenylacrylate (**9a**)



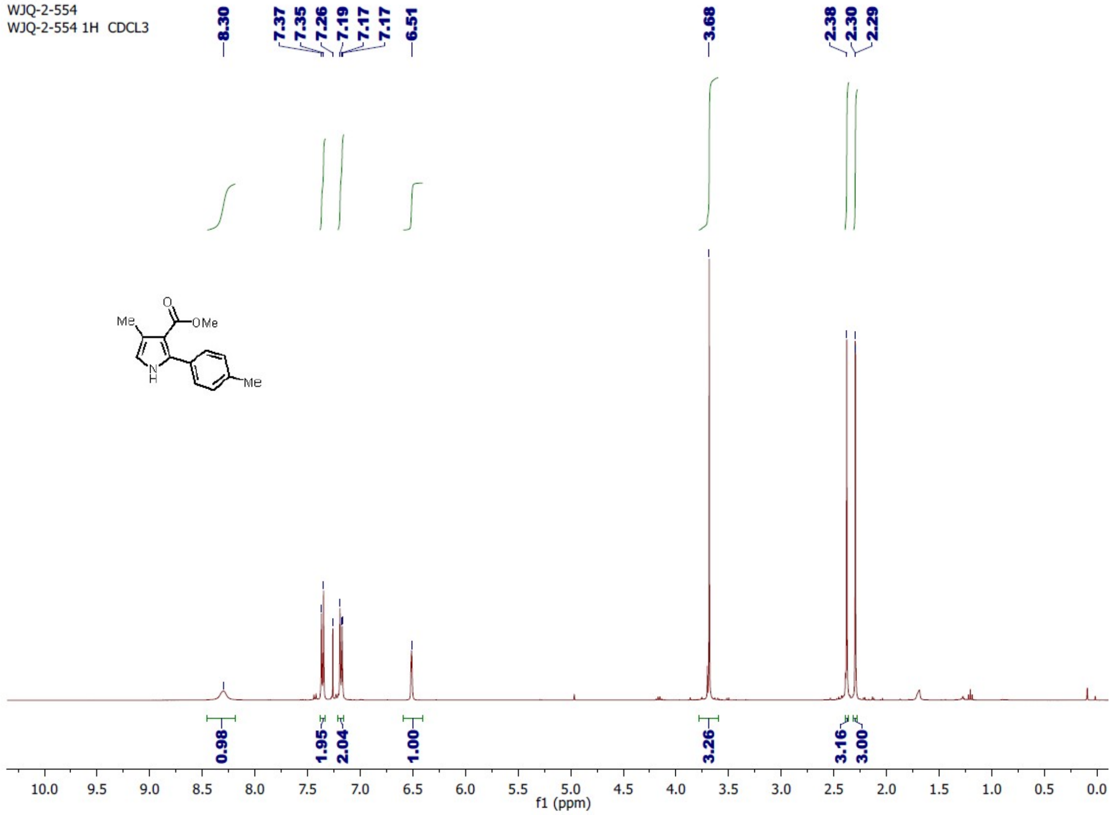


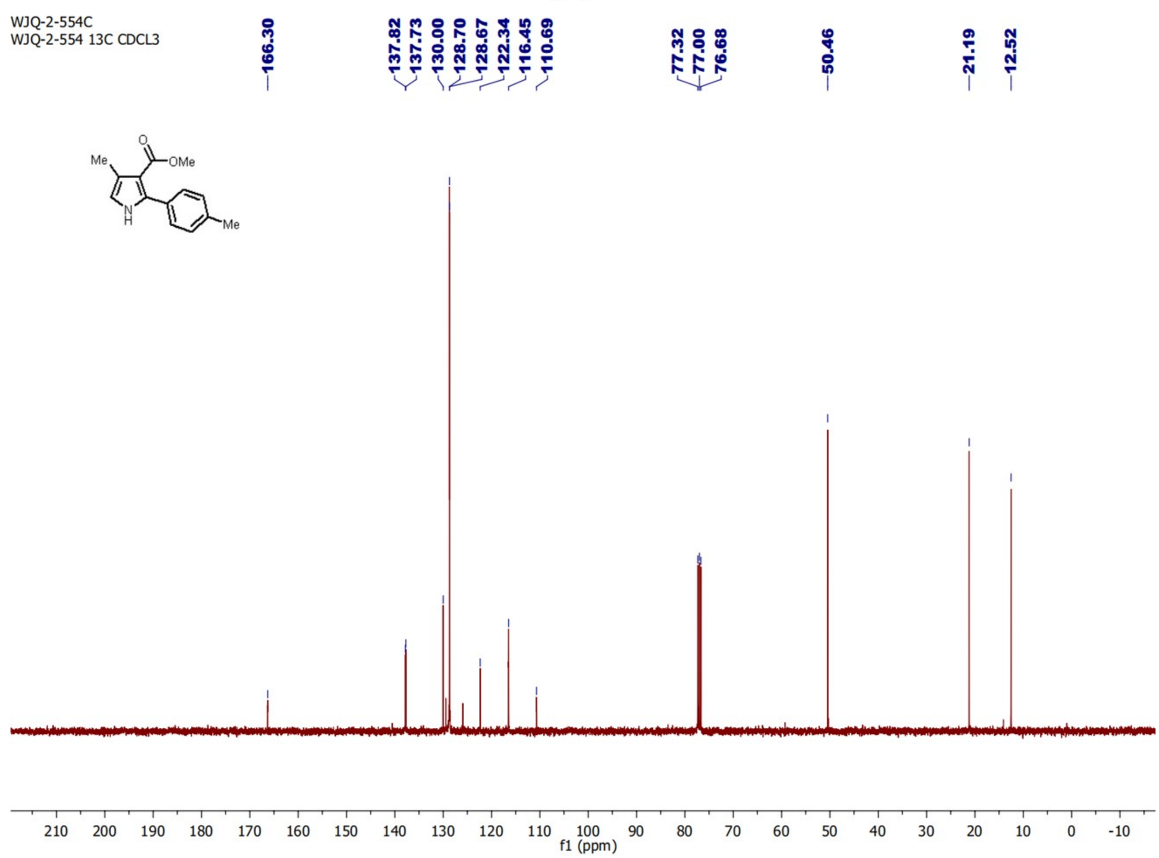
methyl 4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**2a**)



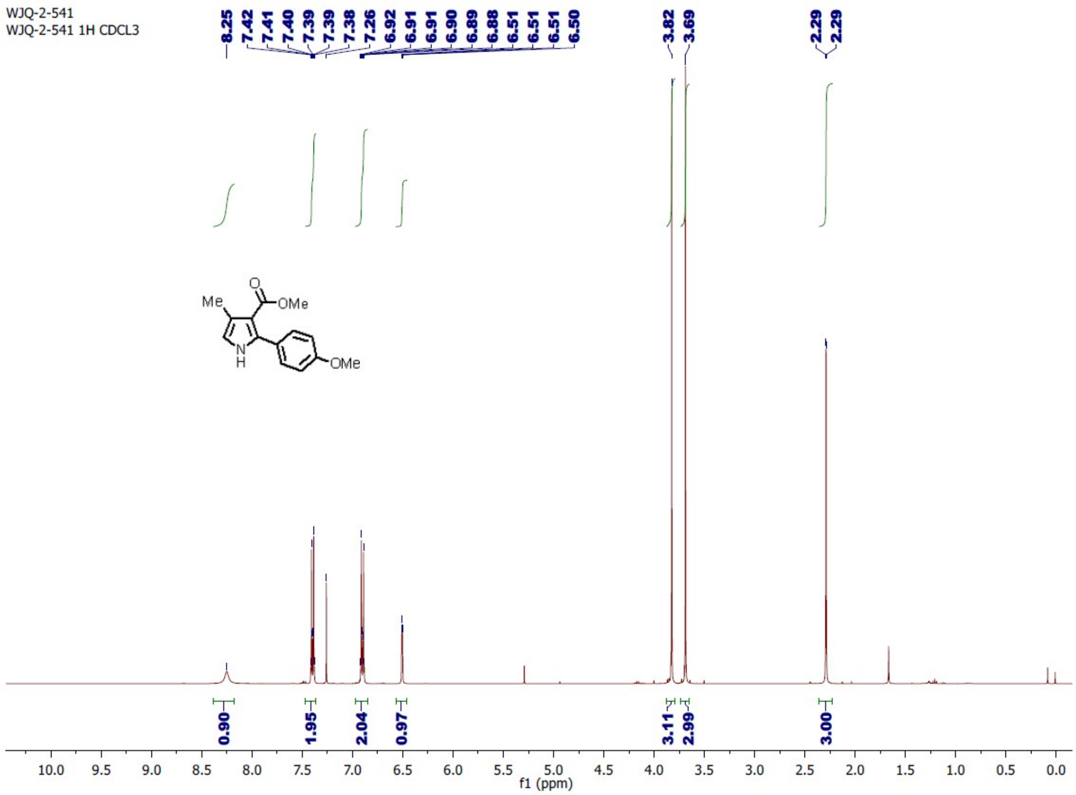


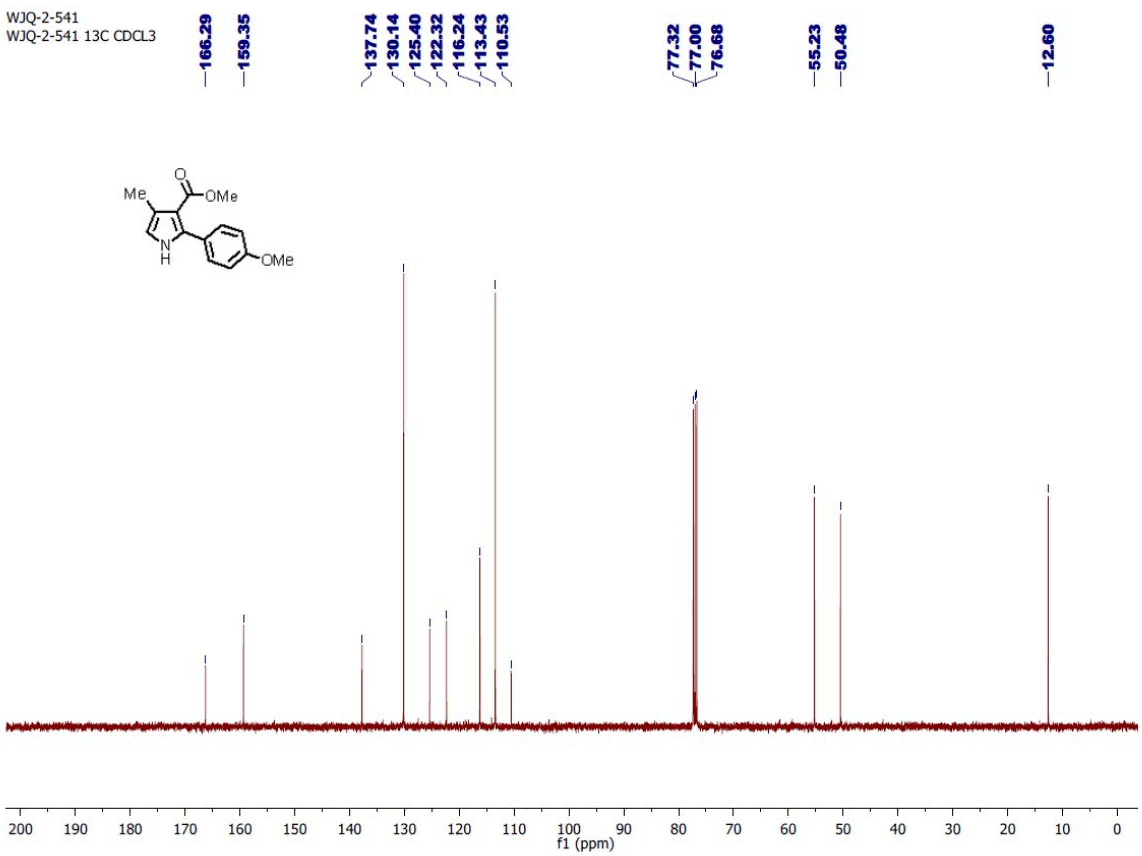
methyl 4-methyl-2-(p-tolyl)-1H-pyrrole-3-carboxylate (**2b**)



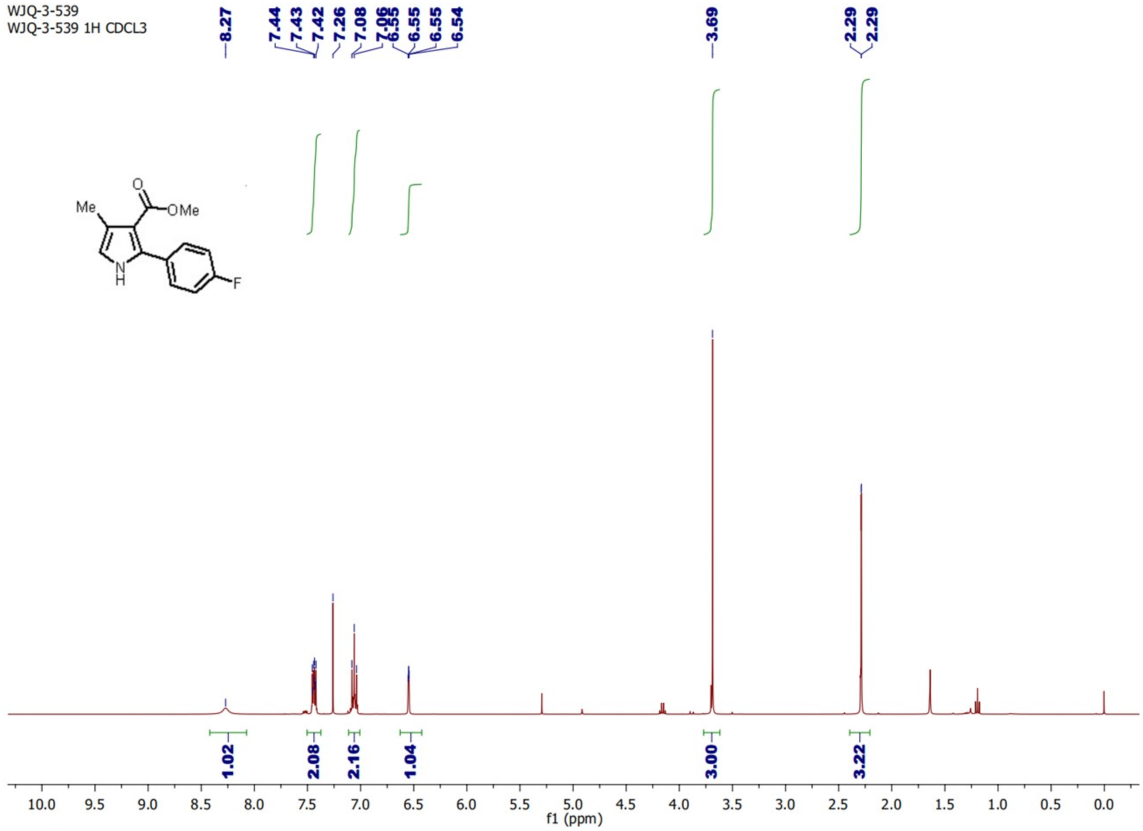


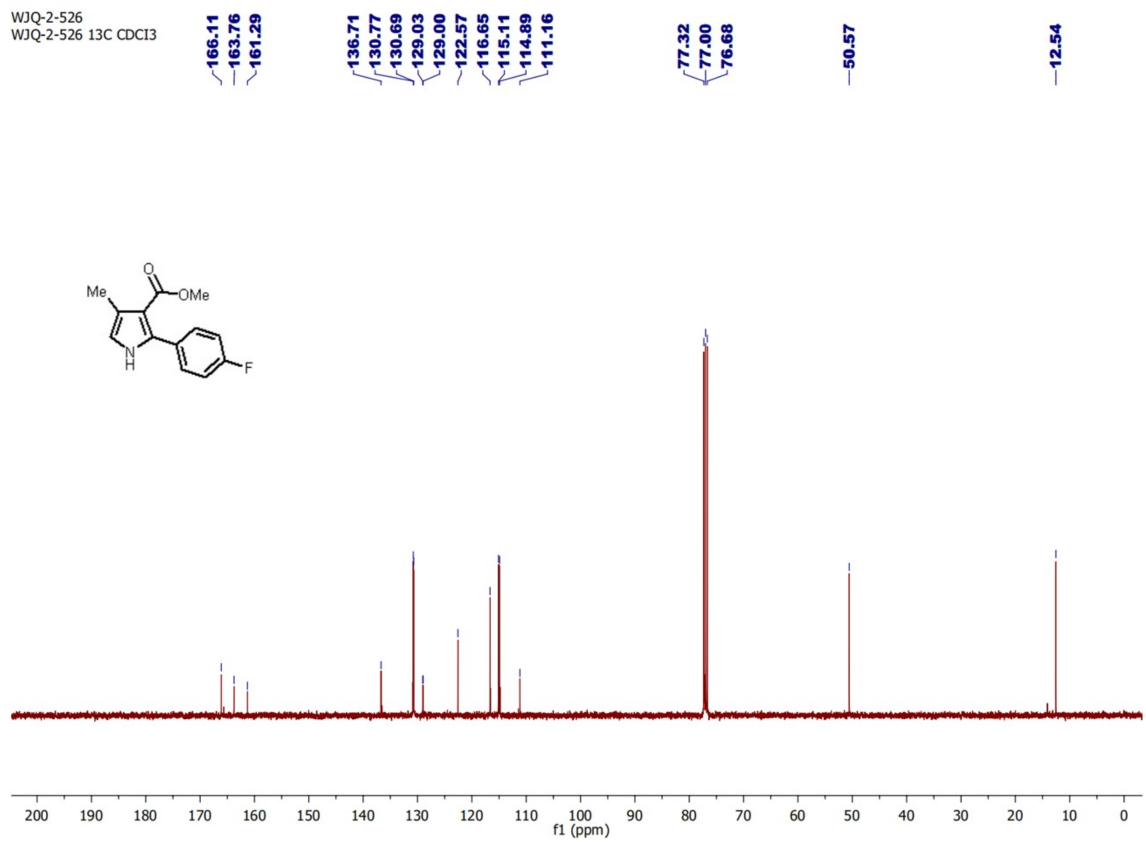
methyl 2-(4-methoxyphenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2c**)



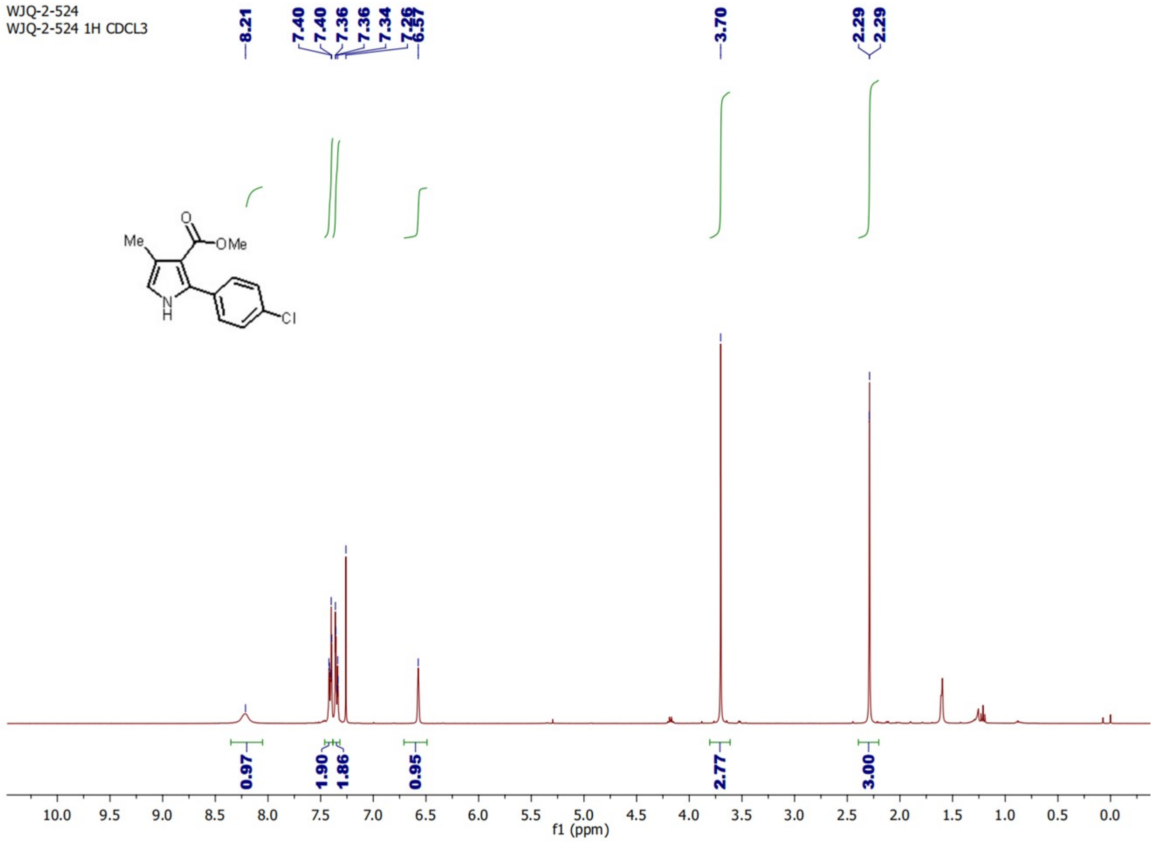


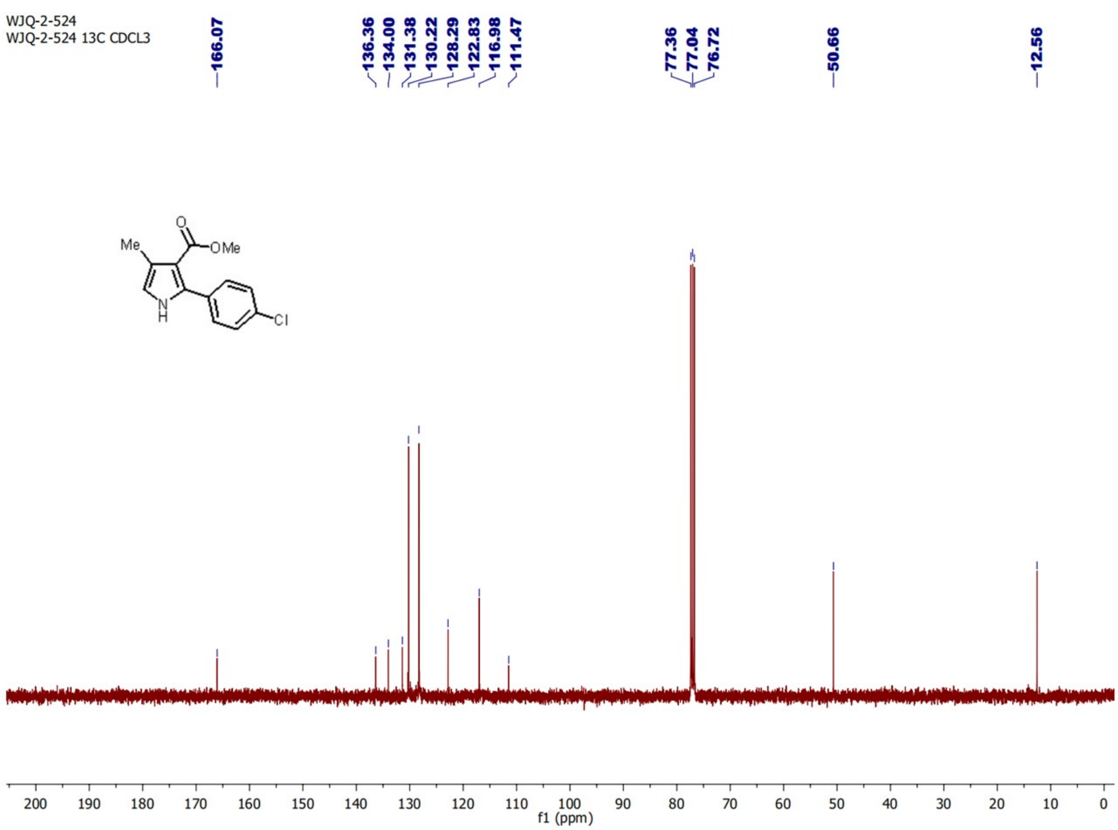
methyl 2-(4-fluorophenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2d**)



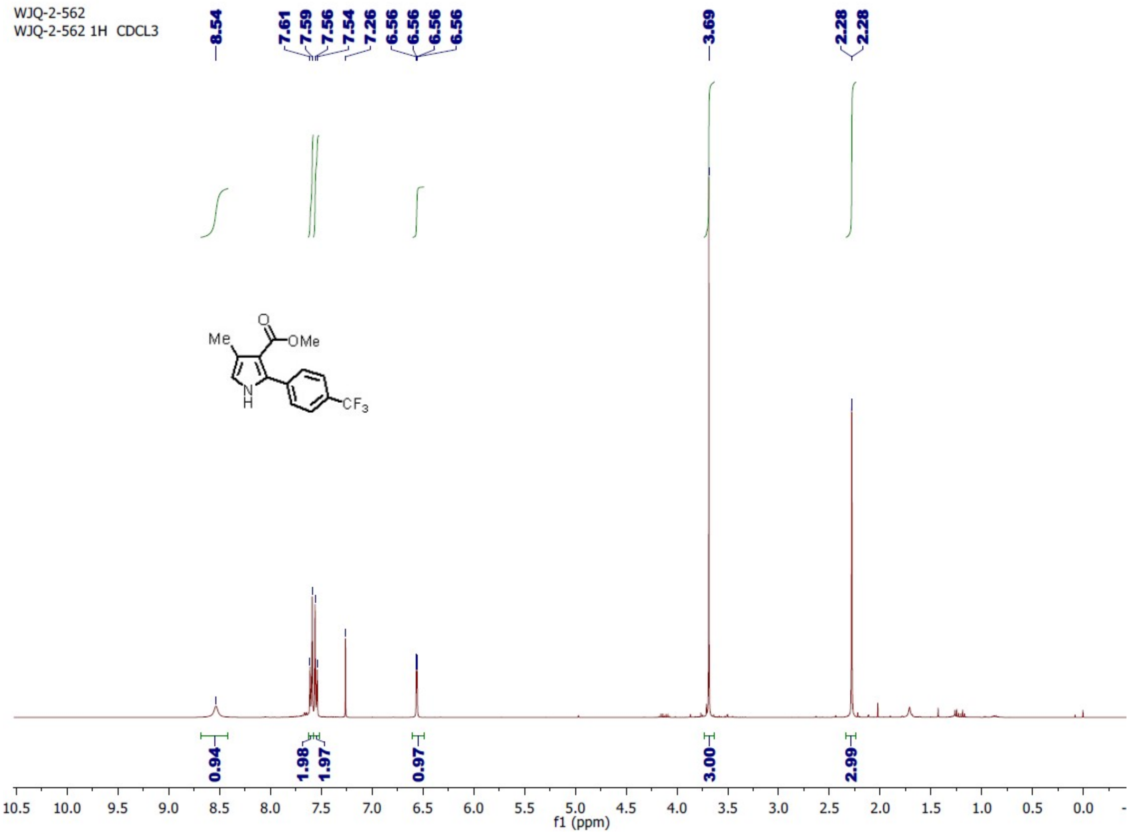


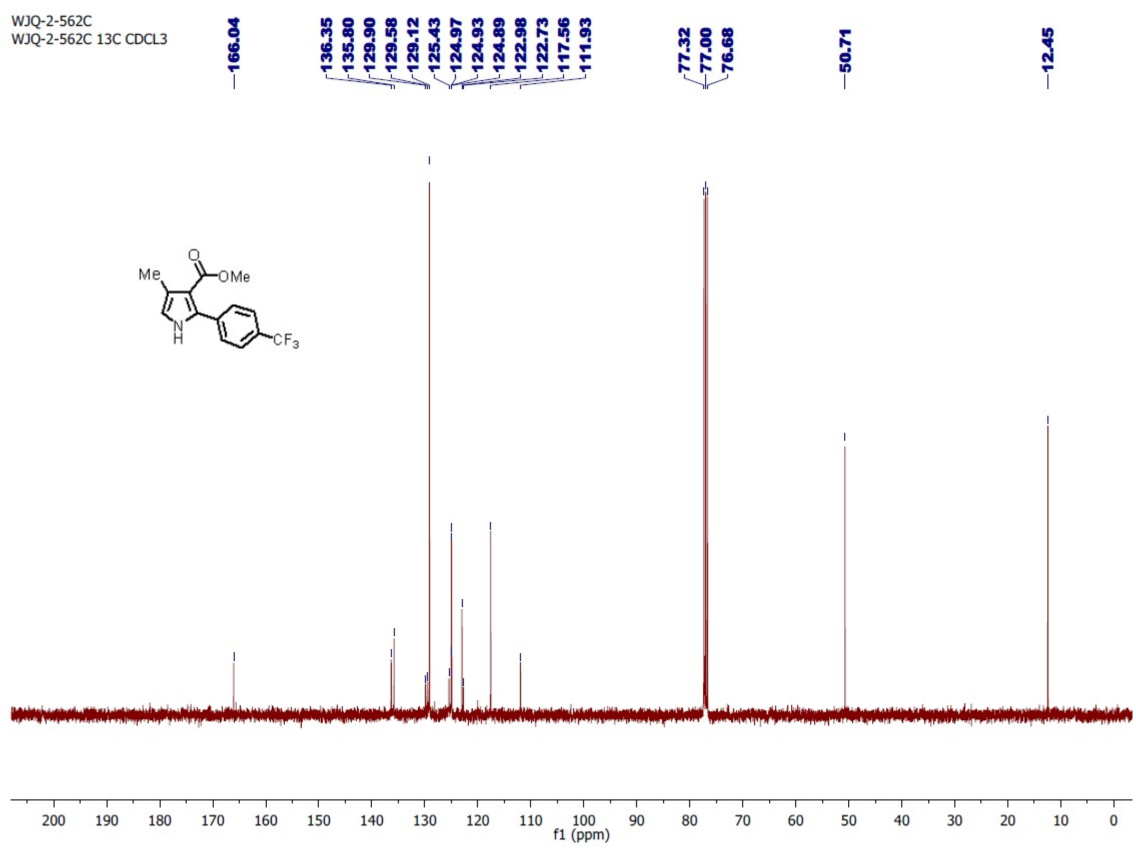
methyl 2-(4-chlorophenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2e**)



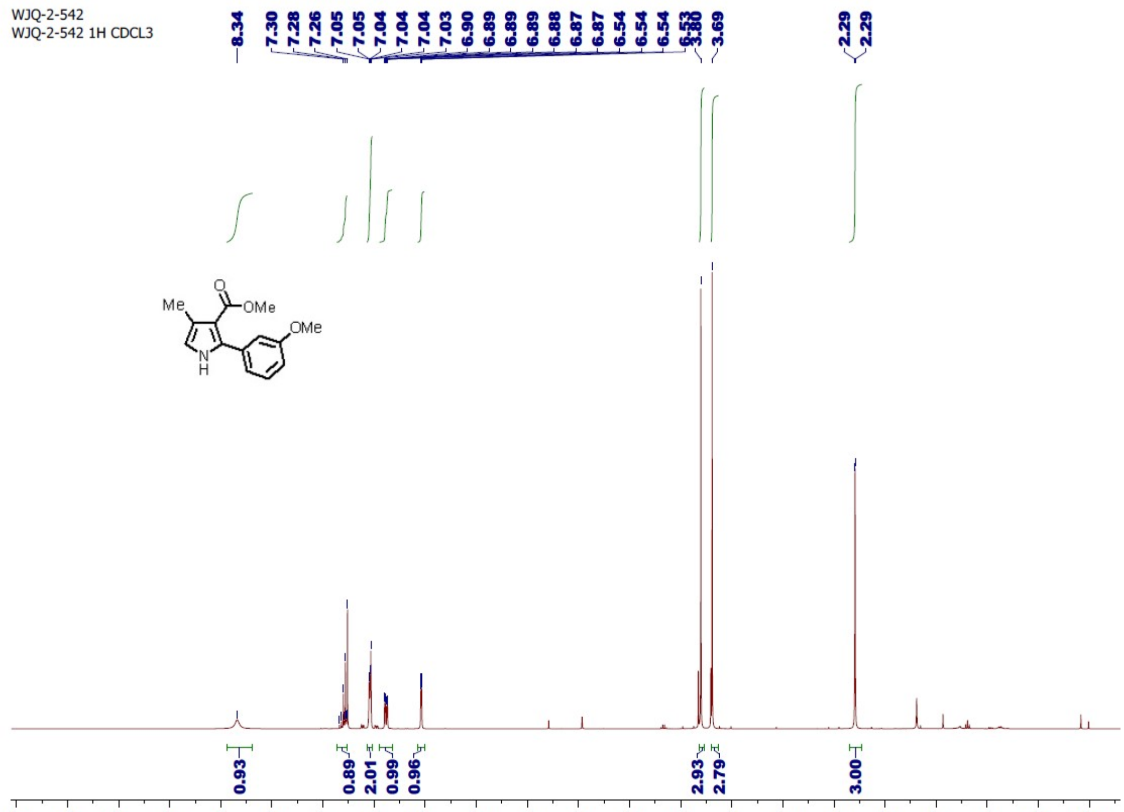


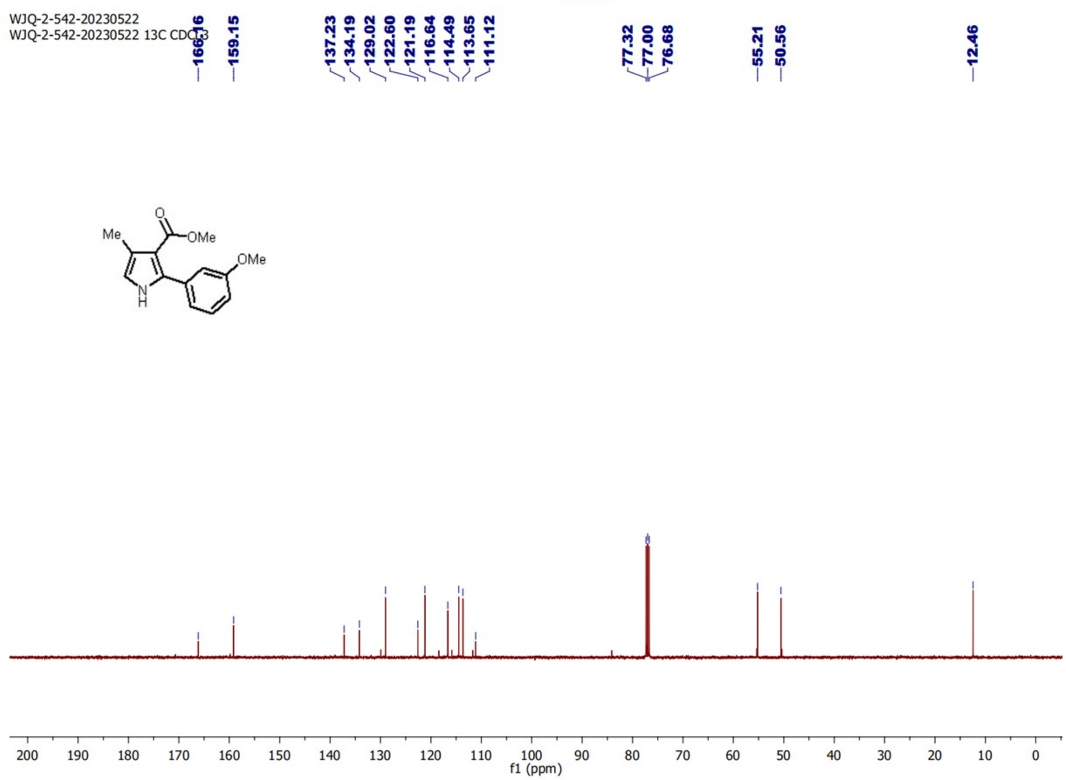
methyl 4-methyl-2-(4-(trifluoromethyl)phenyl)-1H-pyrrole-3-carboxylate (**2f**)



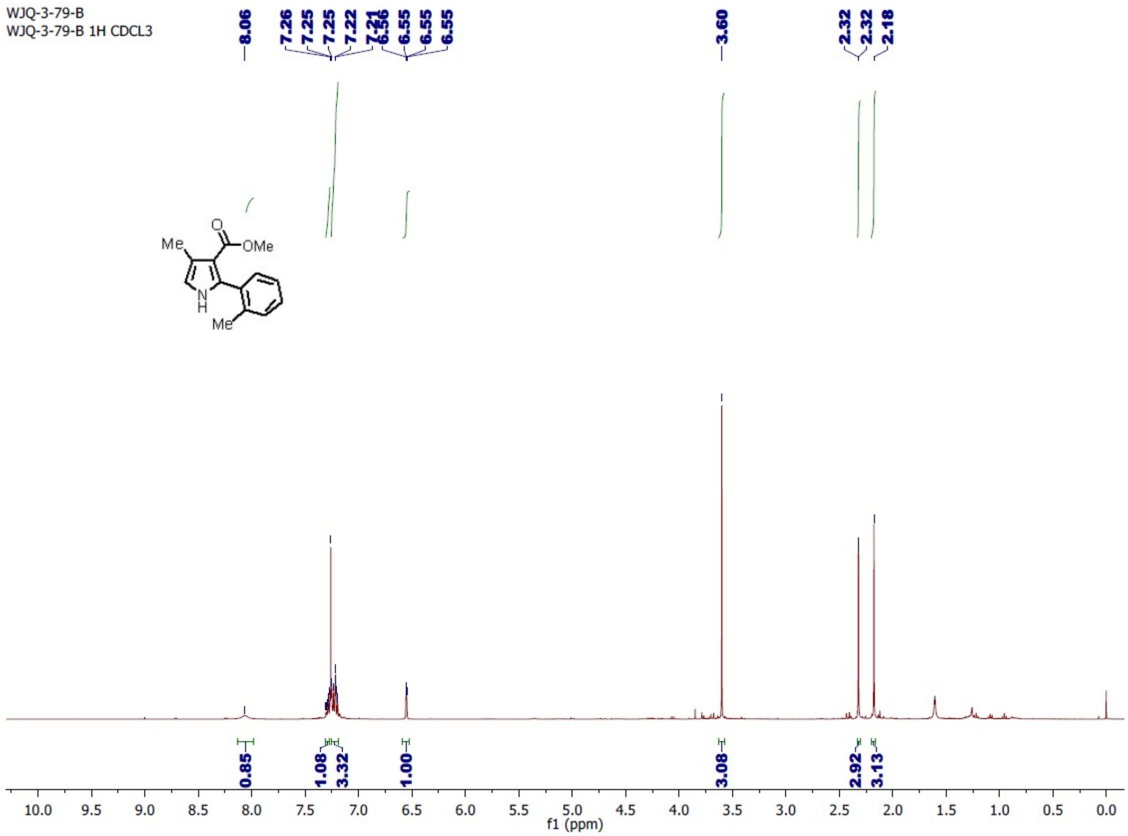


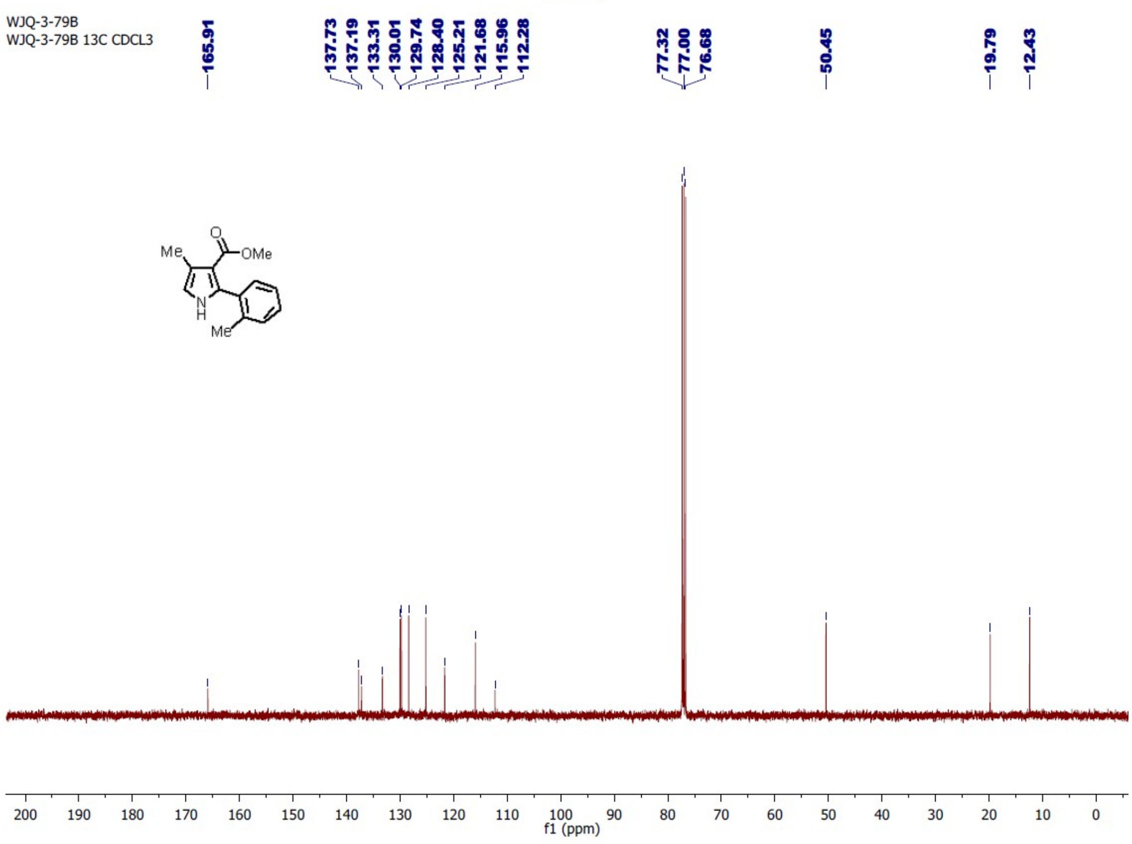
methyl 2-(3-methoxyphenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2g**)



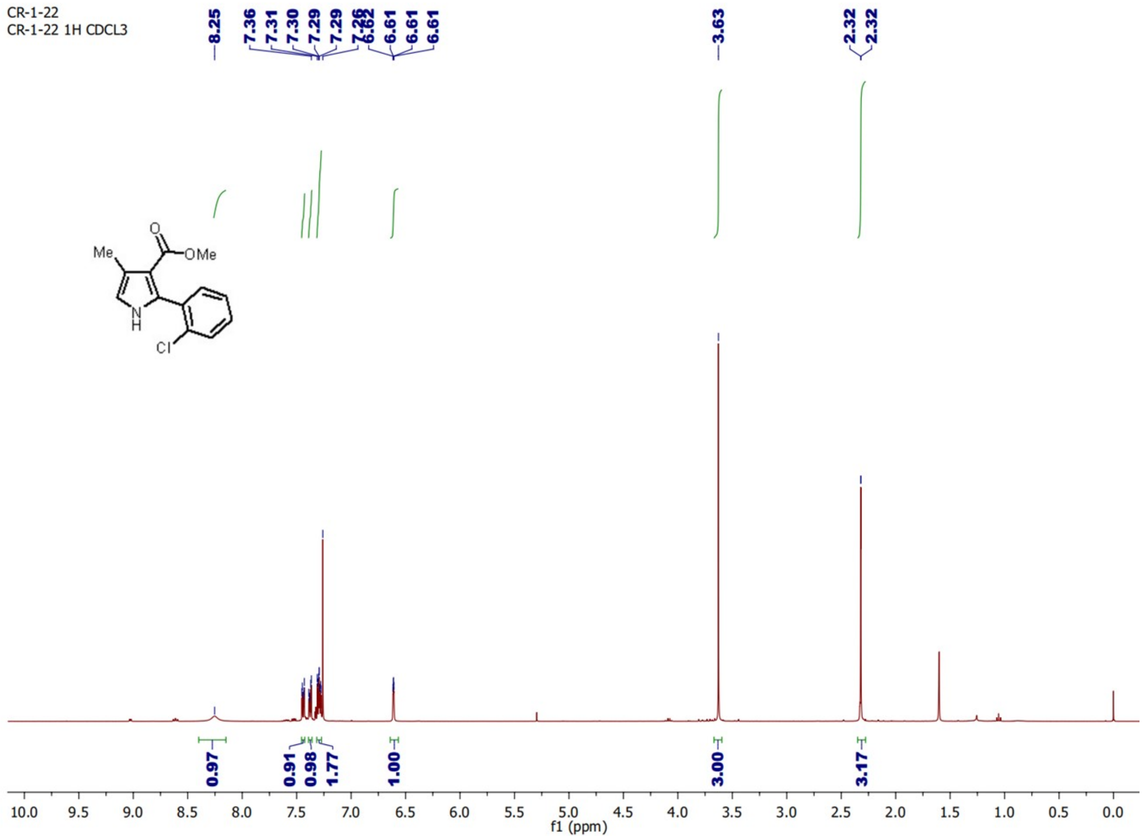


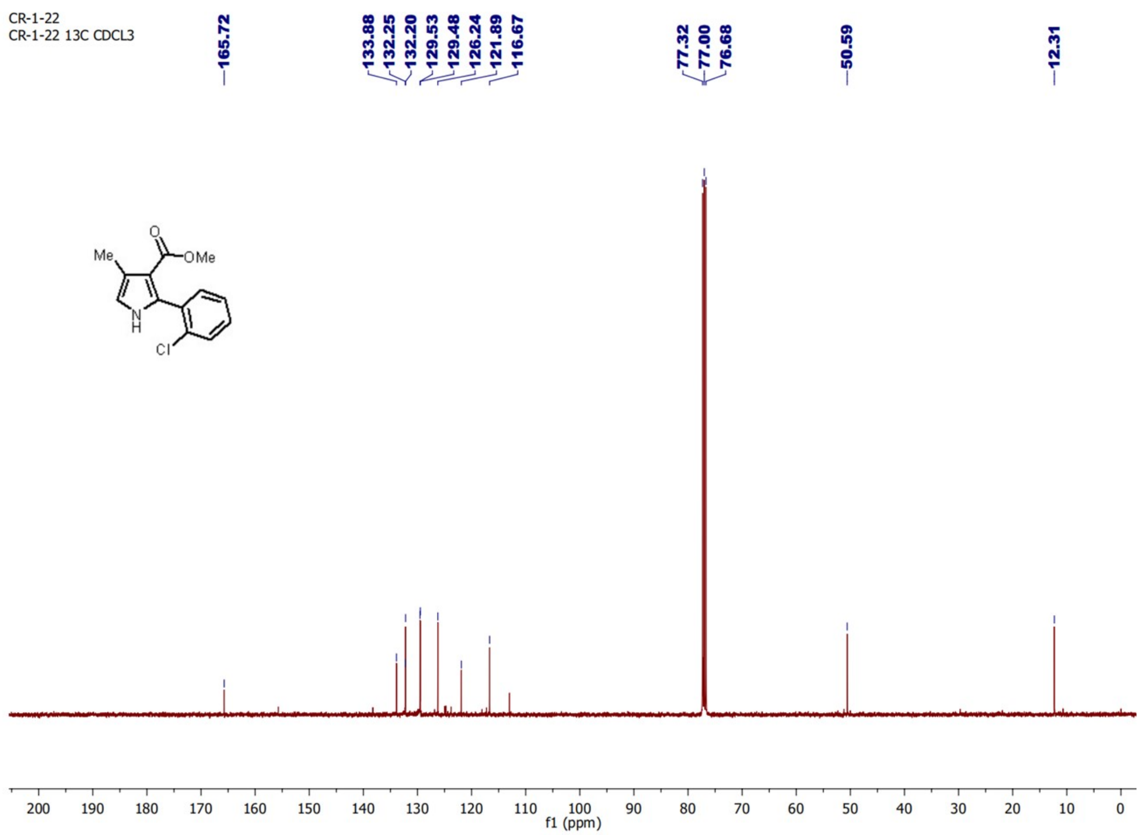
methyl 4-methyl-2-(o-tolyl)-1H-pyrrole-3-carboxylate (**2h**)



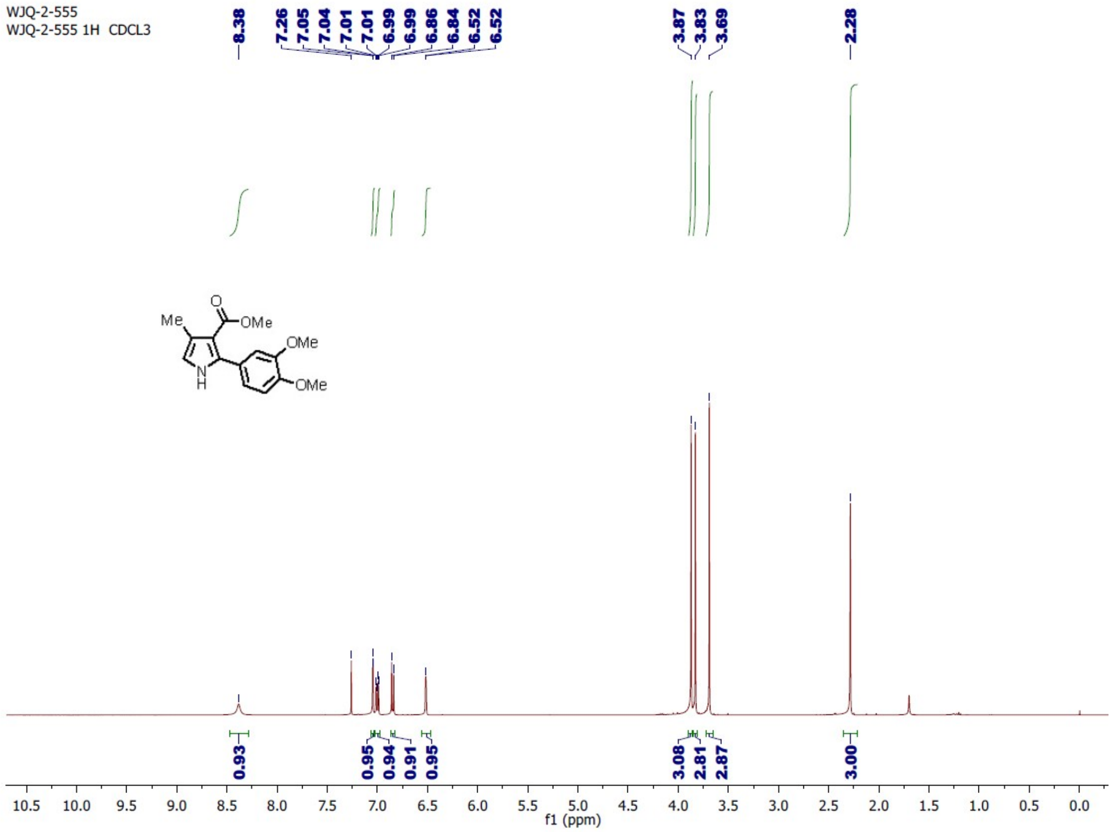


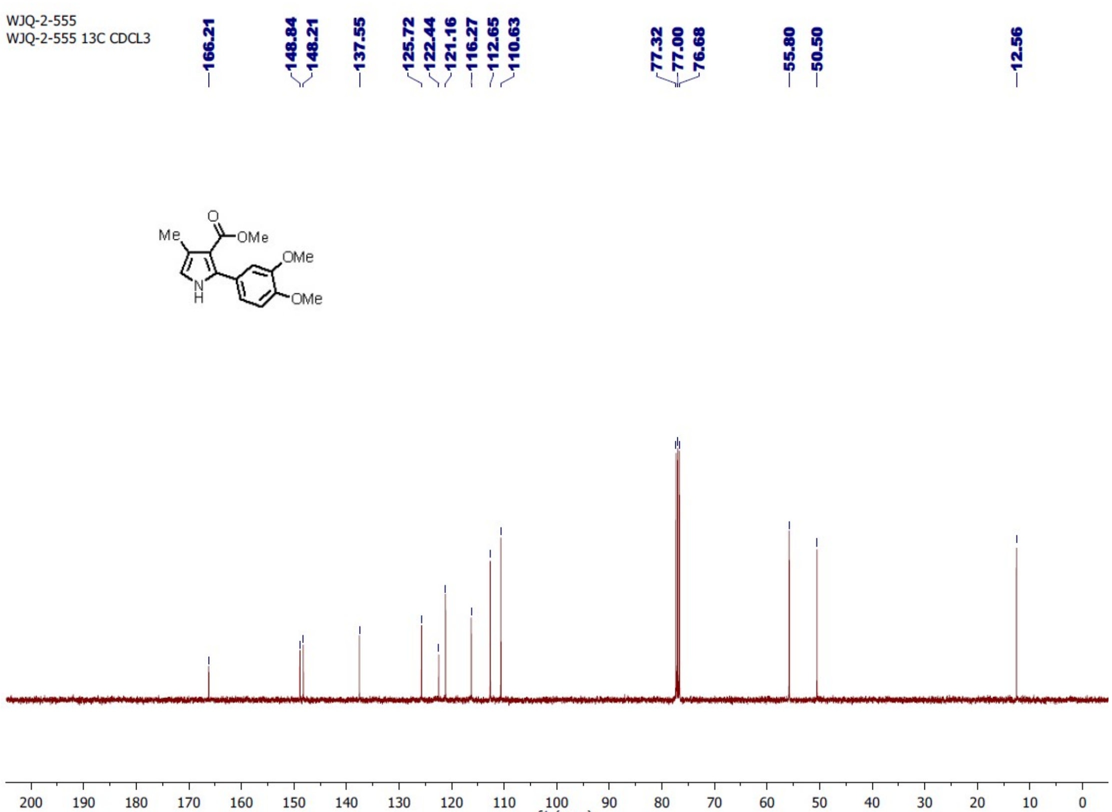
methyl 2-(2-chlorophenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2i**)



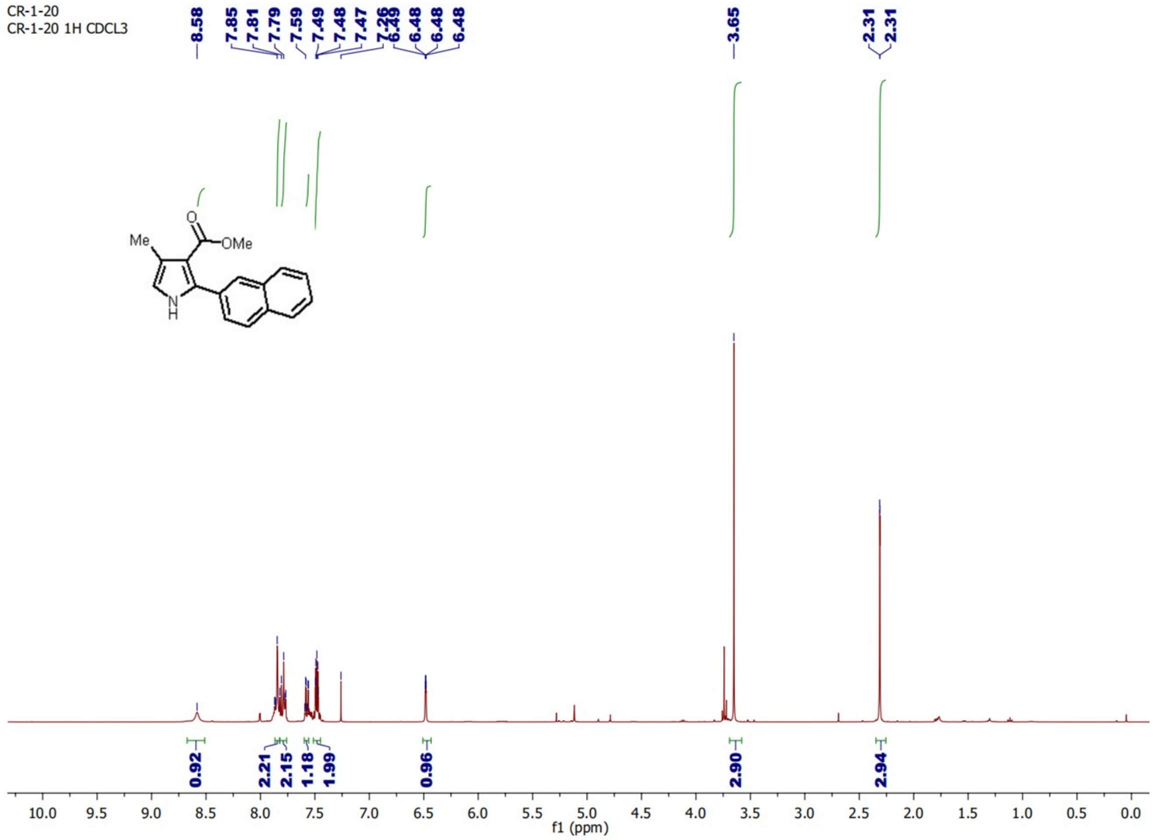


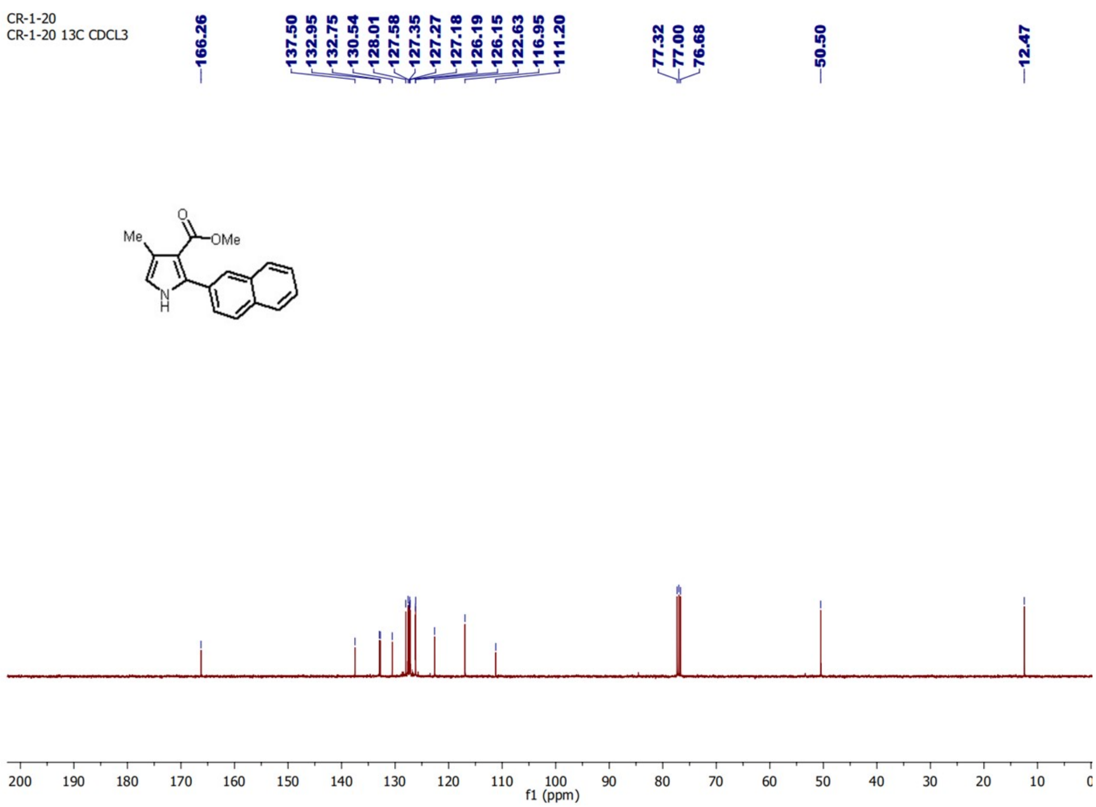
methyl 2-(3,4-dimethoxyphenyl)-4-methyl-1H-pyrrole-3-carboxylate (**2j**)



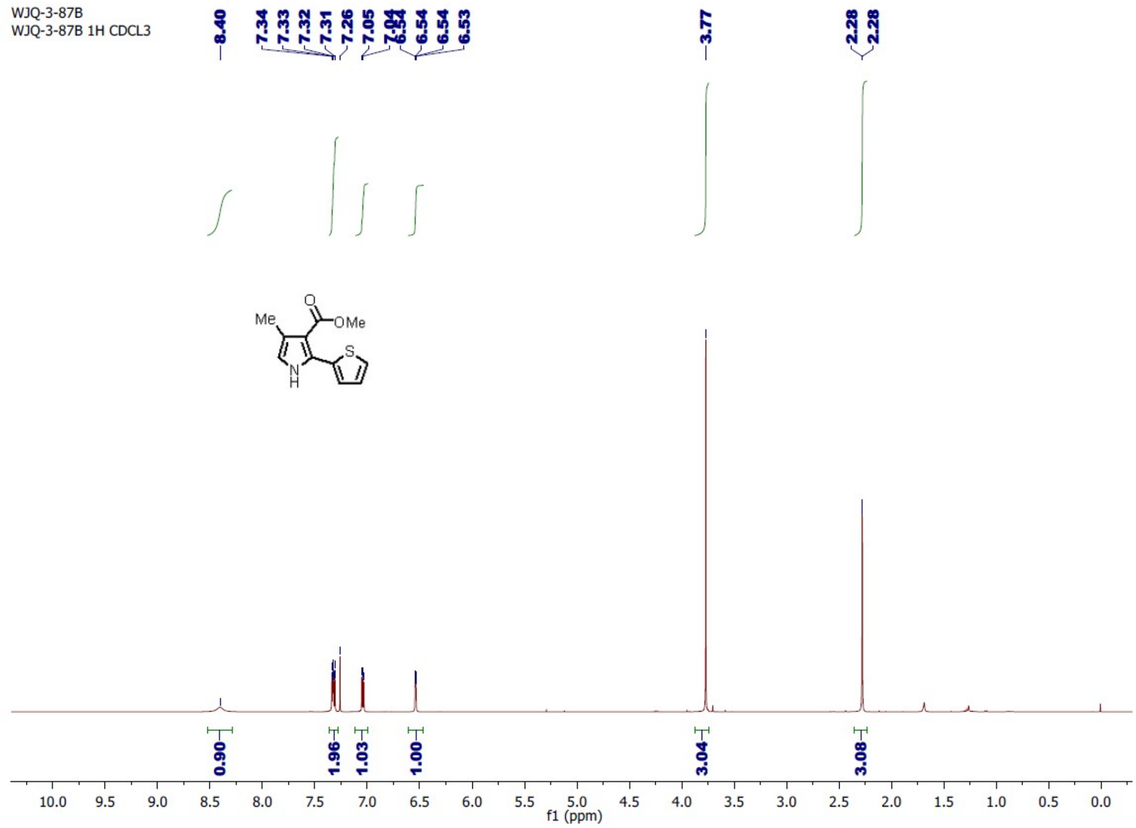


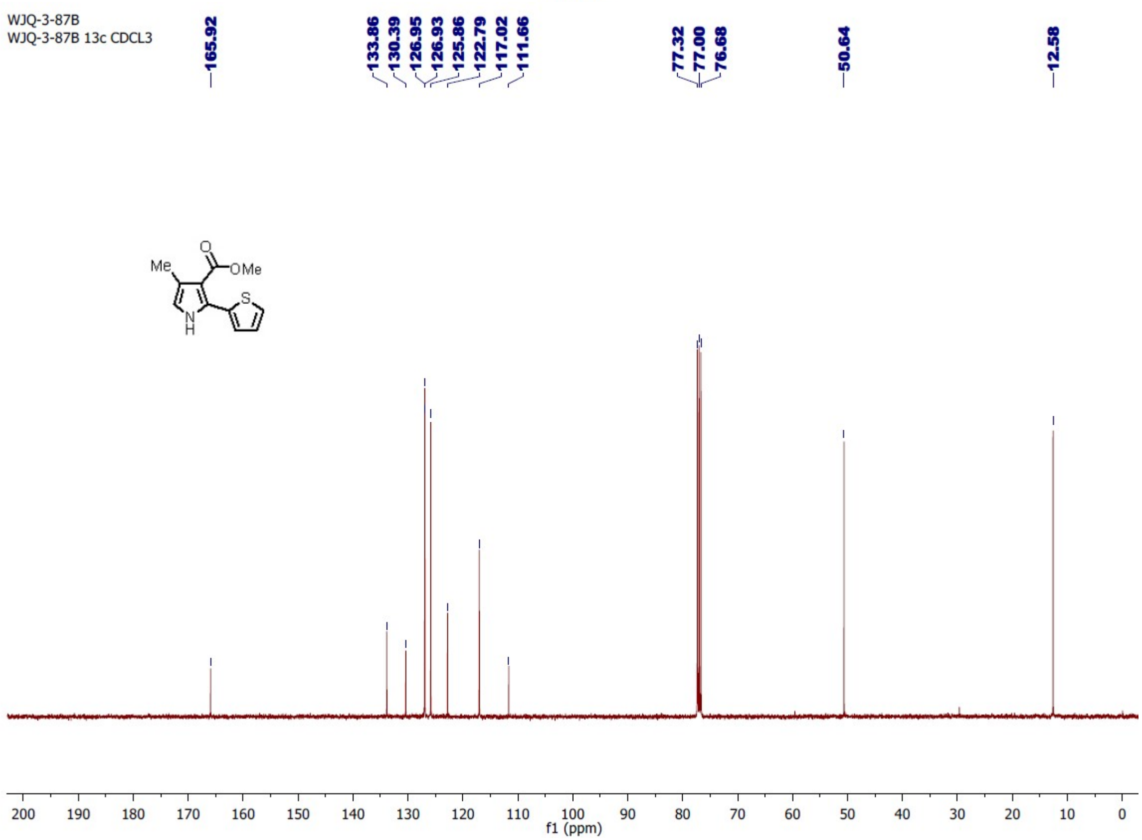
methyl 4-methyl-2-(naphthalen-2-yl)-1H-pyrrole-3-carboxylate (**2k**)



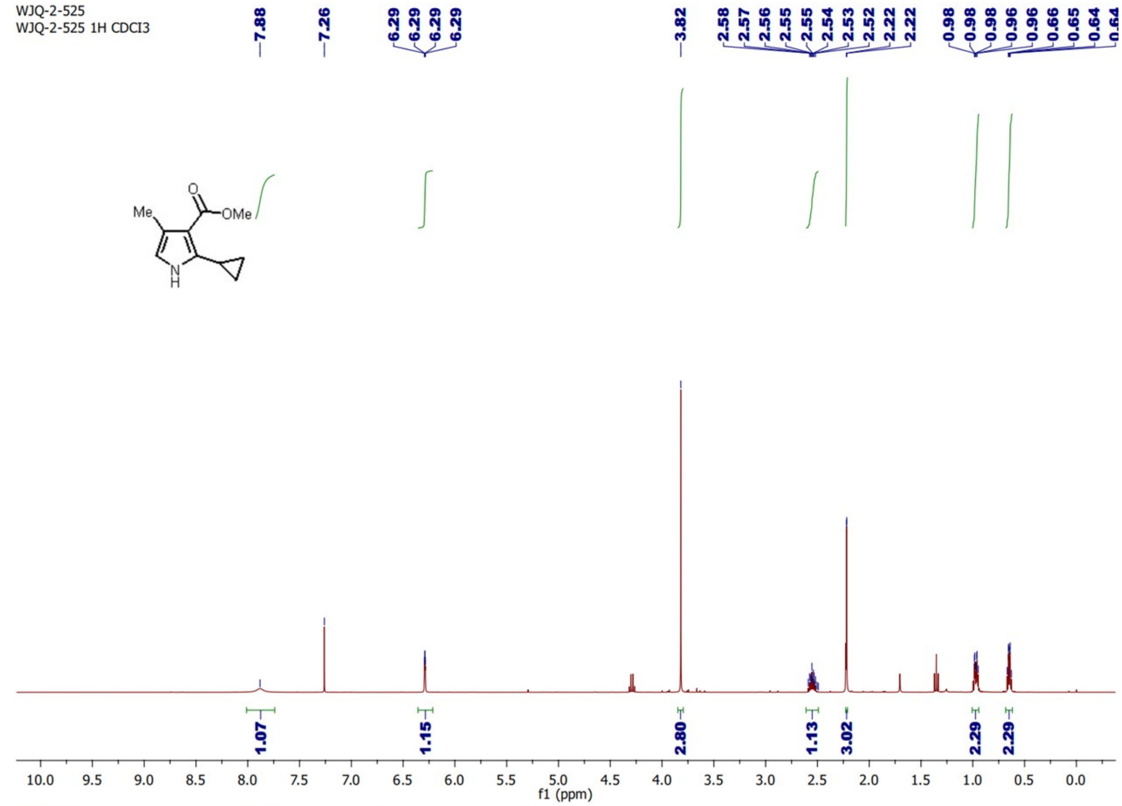


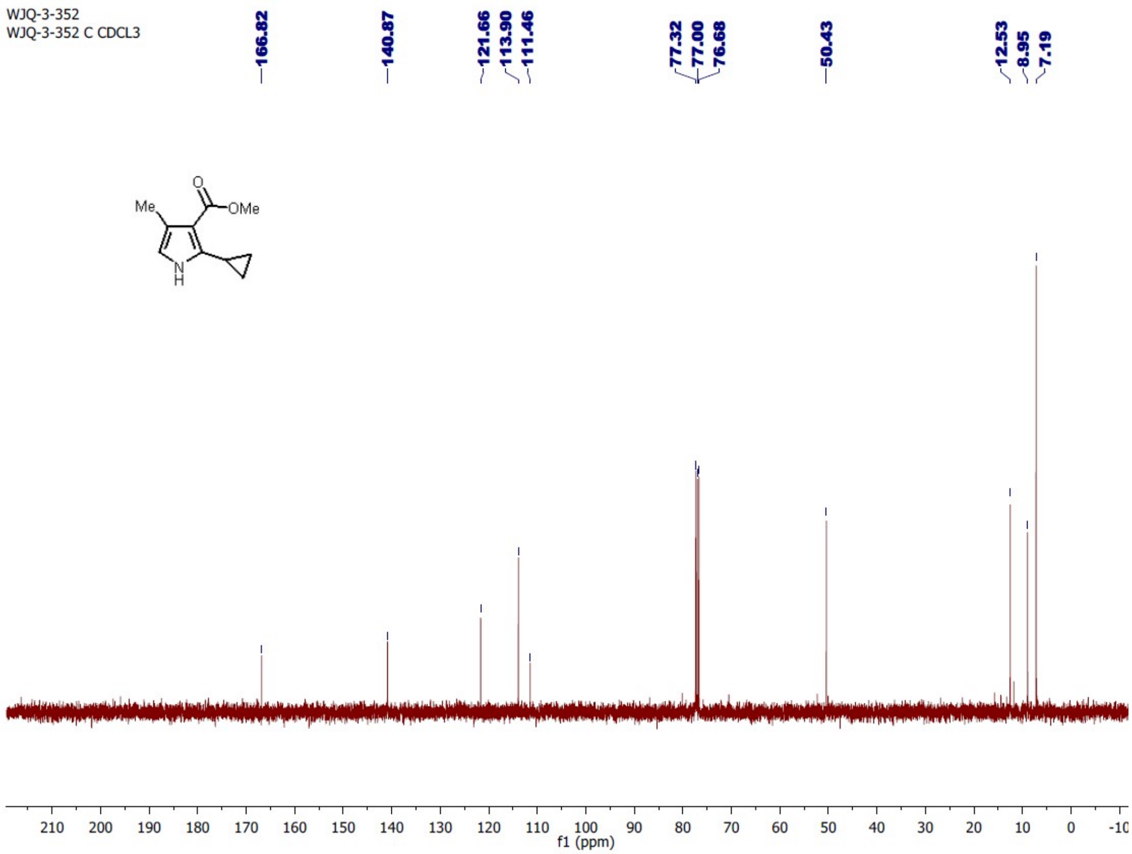
methyl 4-methyl-2-(thiophen-2-yl)-1H-pyrrole-3-carboxylate (**2l**)



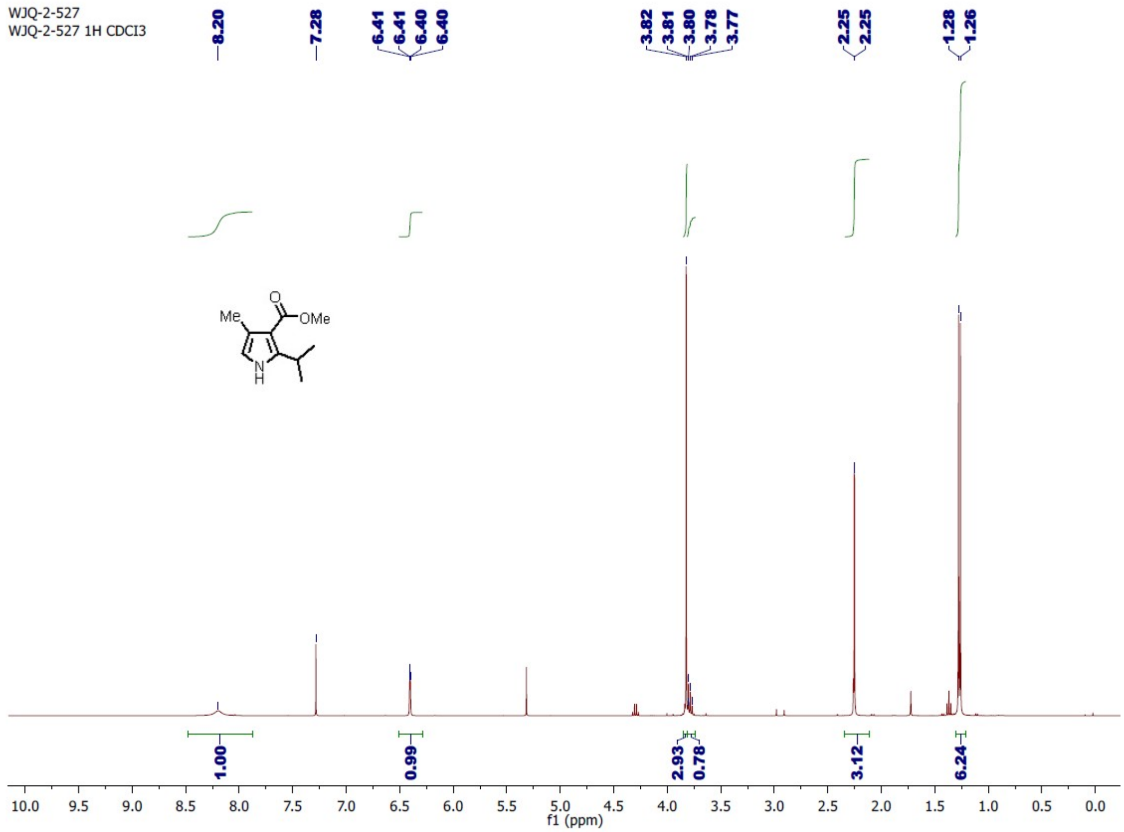


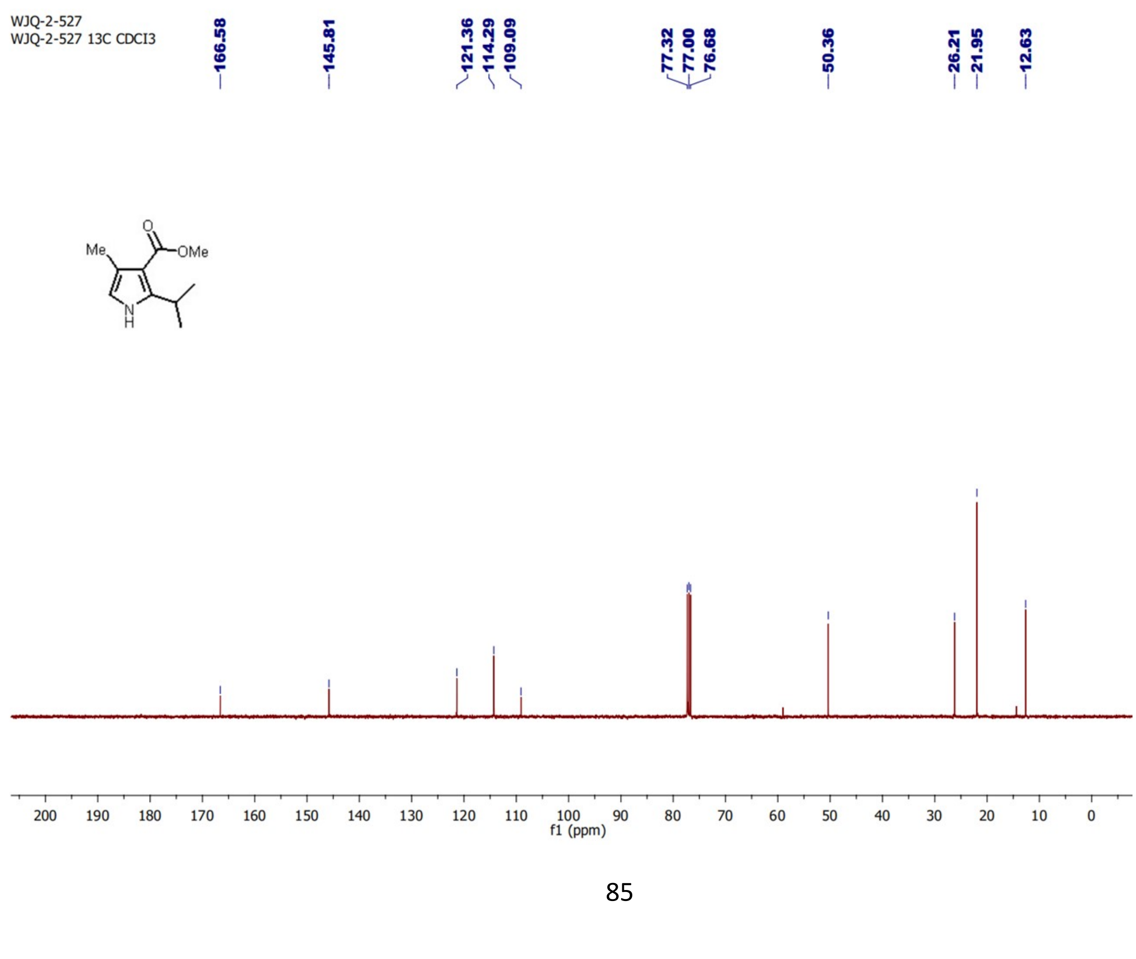
methyl 2-cyclopropyl-4-methyl-1H-pyrrole-3-carboxylate (**2m**)



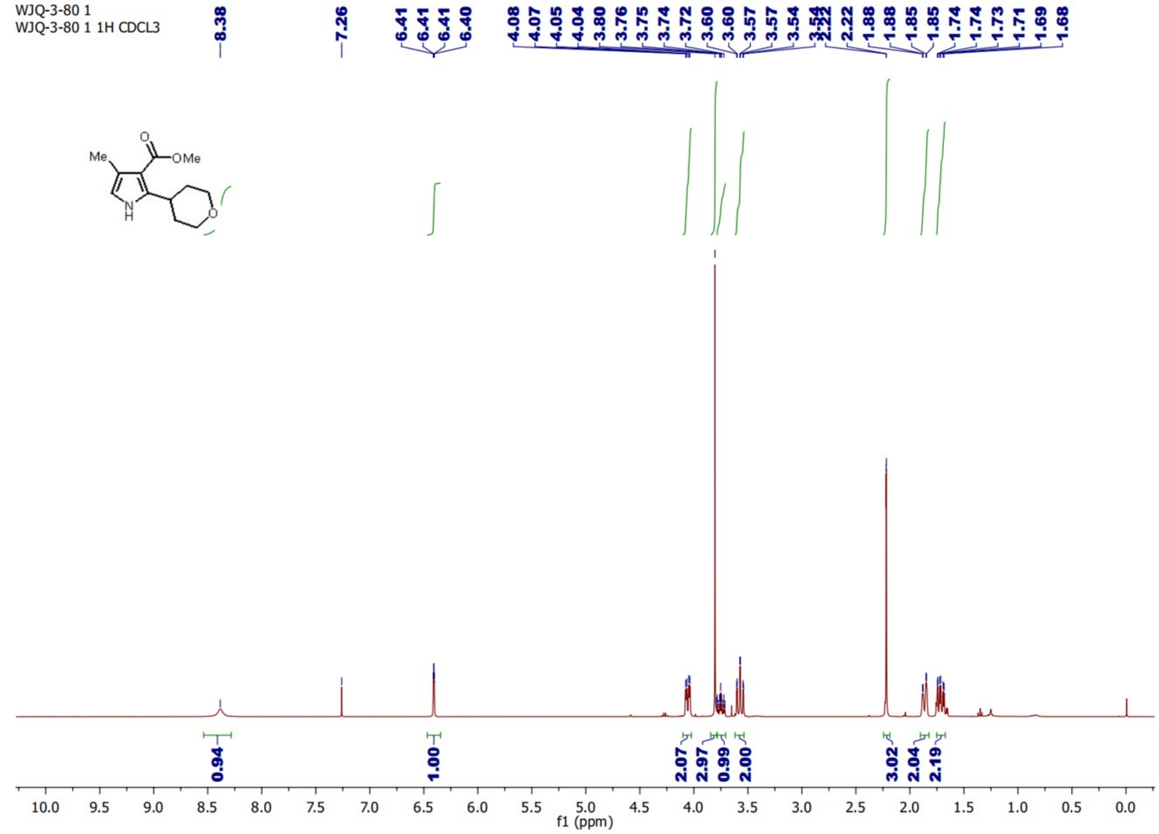


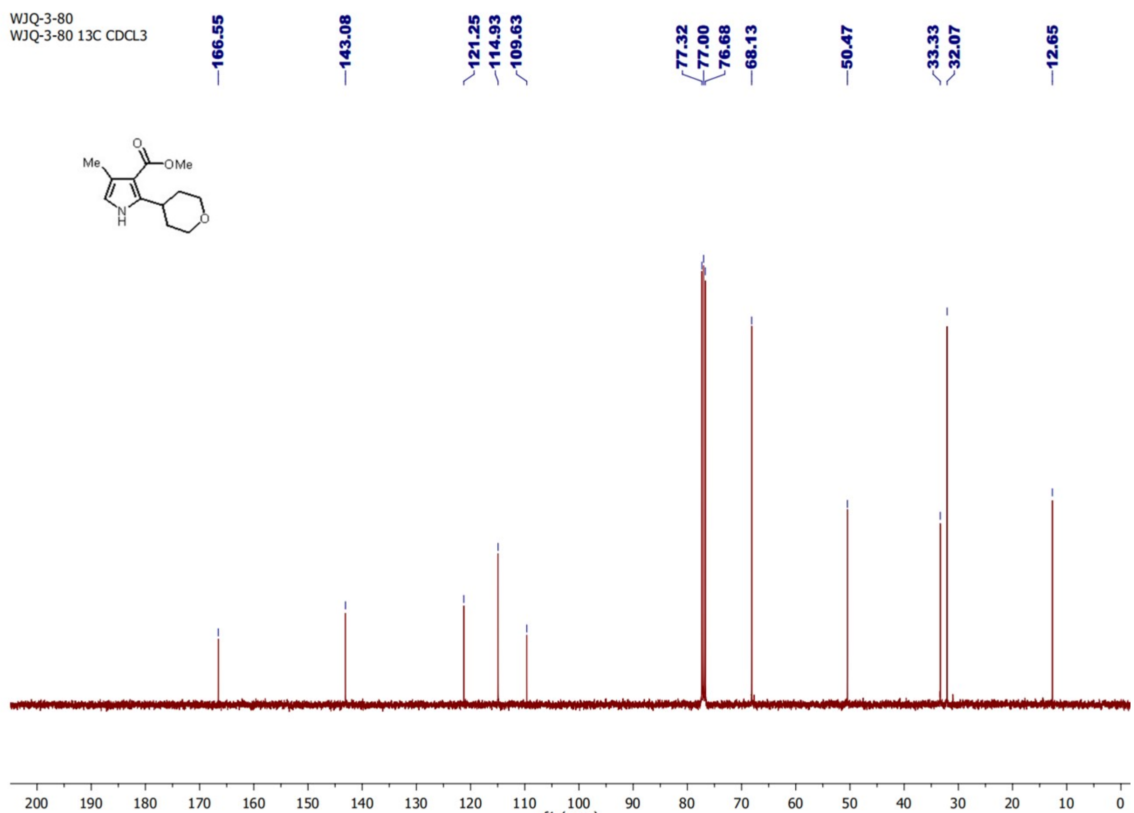
methyl 2-isopropyl-4-methyl-1H-pyrrole-3-carboxylate (**2n**)



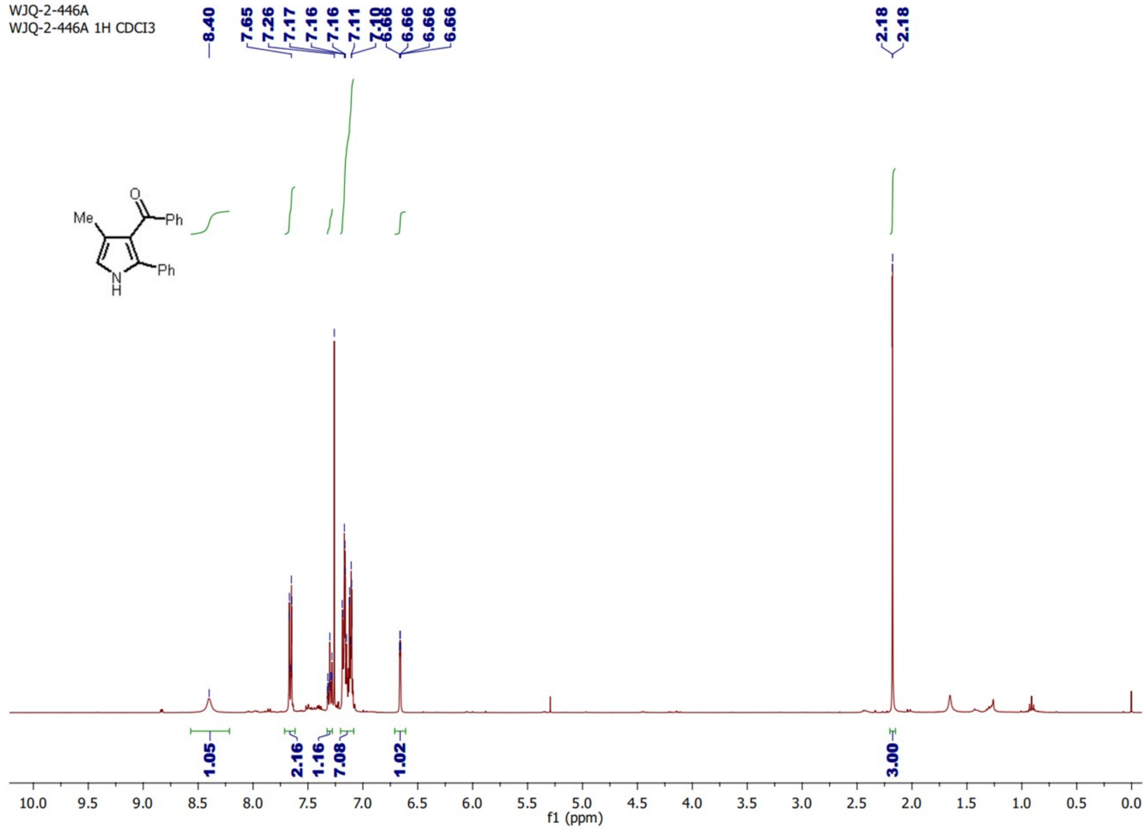


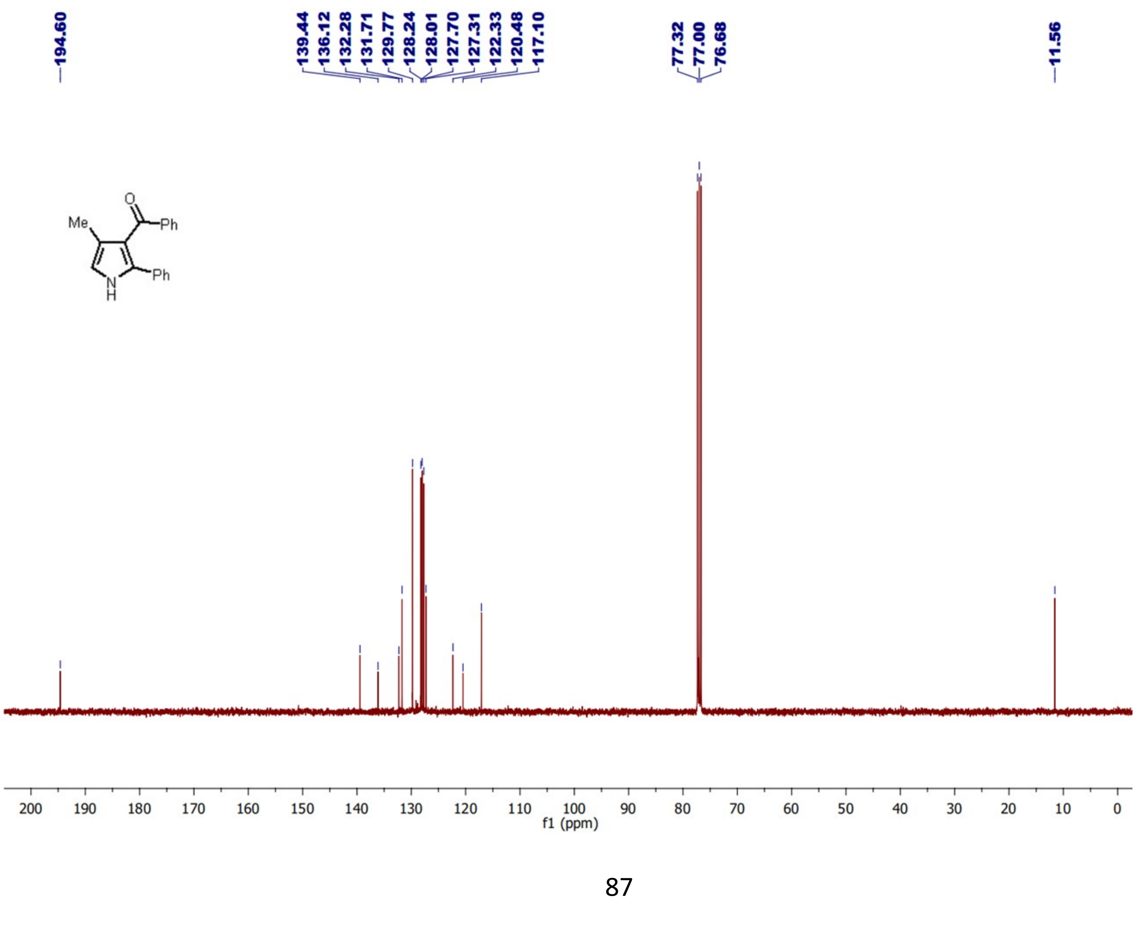
methyl 4-methyl-2-(tetrahydro-2H-pyran-4-yl)-1H-pyrrole-3-carboxylate (**2o**)



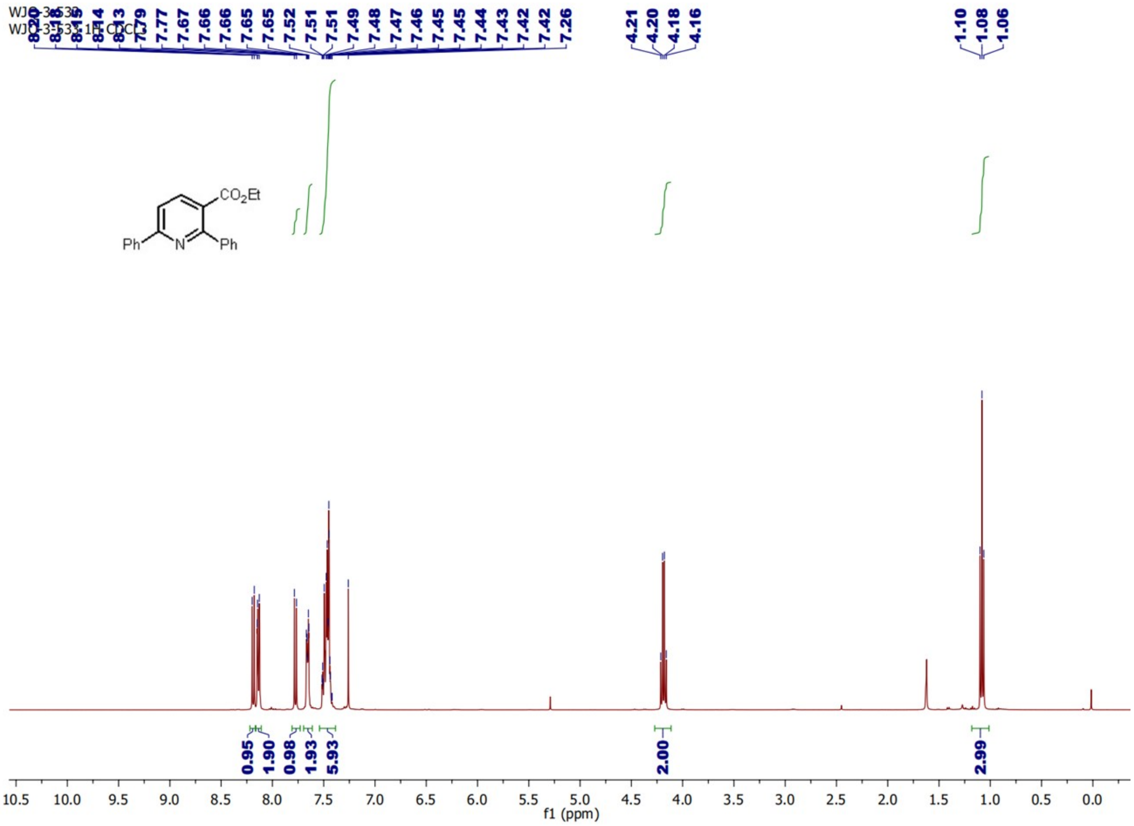


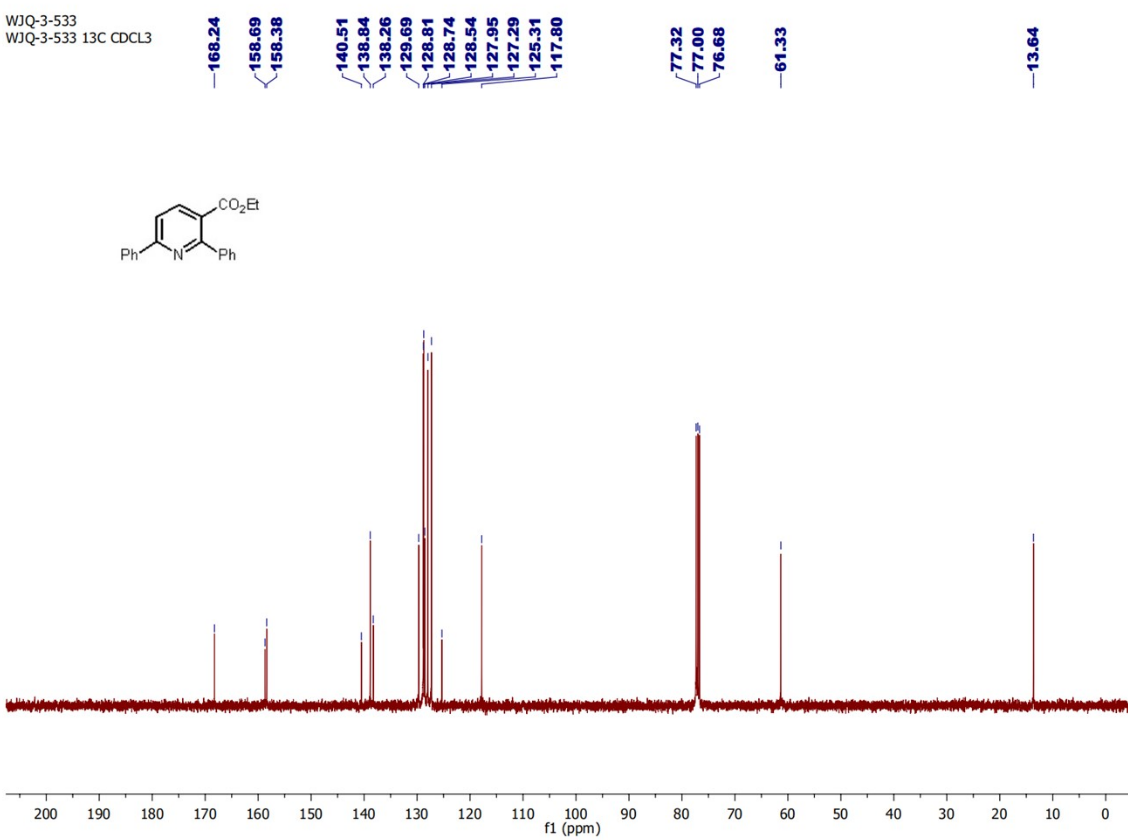
(4-methyl-2-phenyl-1H-pyrrol-3-yl)(phenyl)methanone (**2p**)



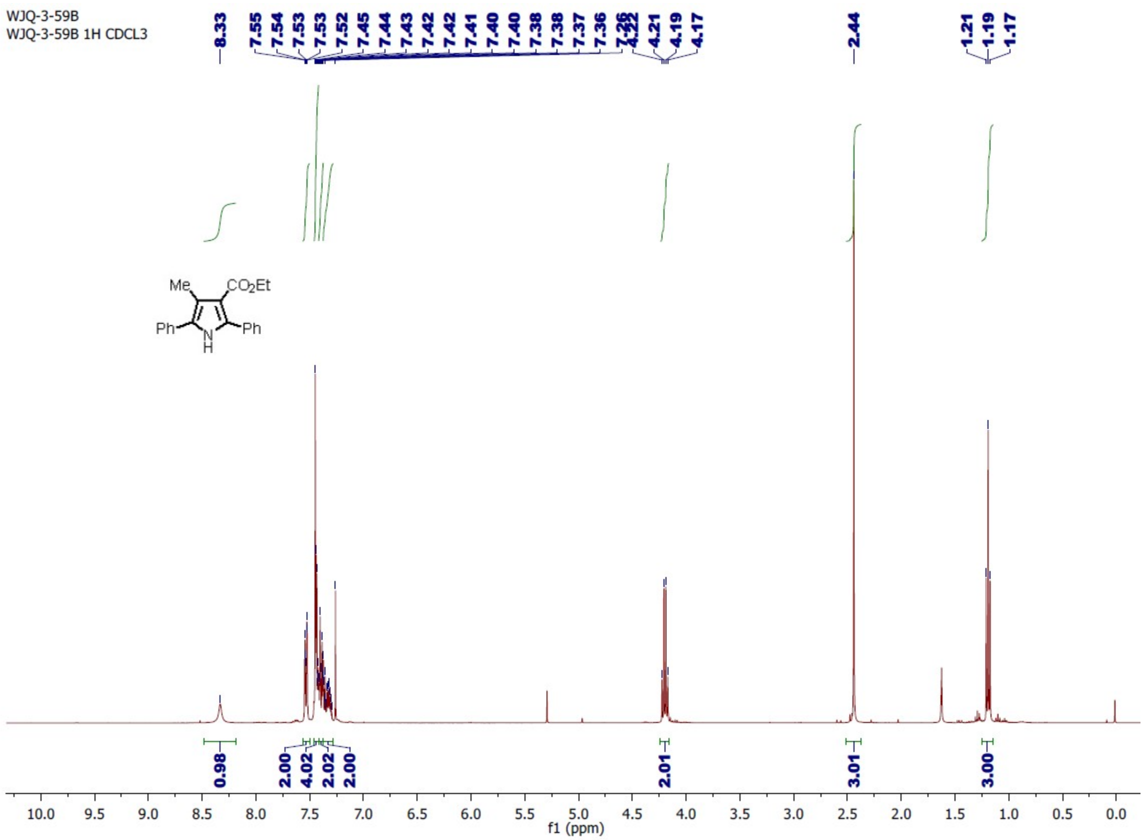


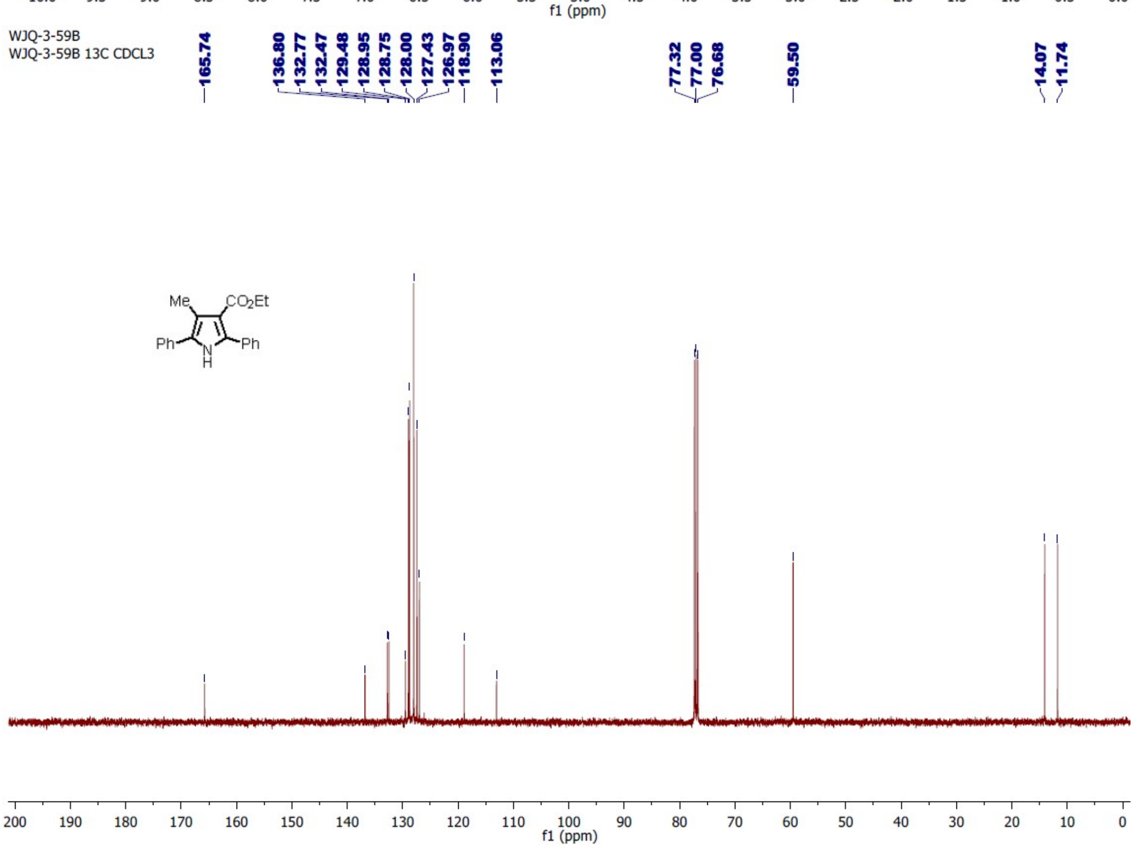
ethyl 2,6-diphenylnicotinate (**4a**)



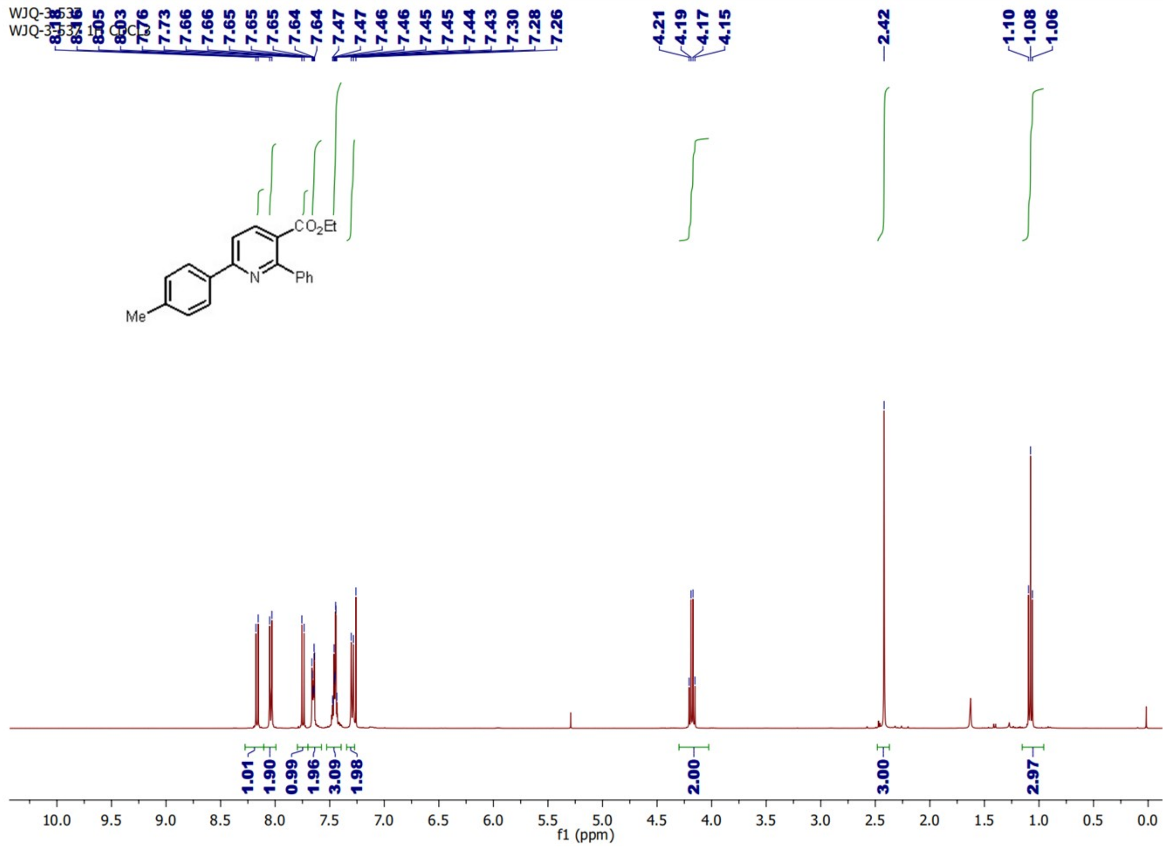


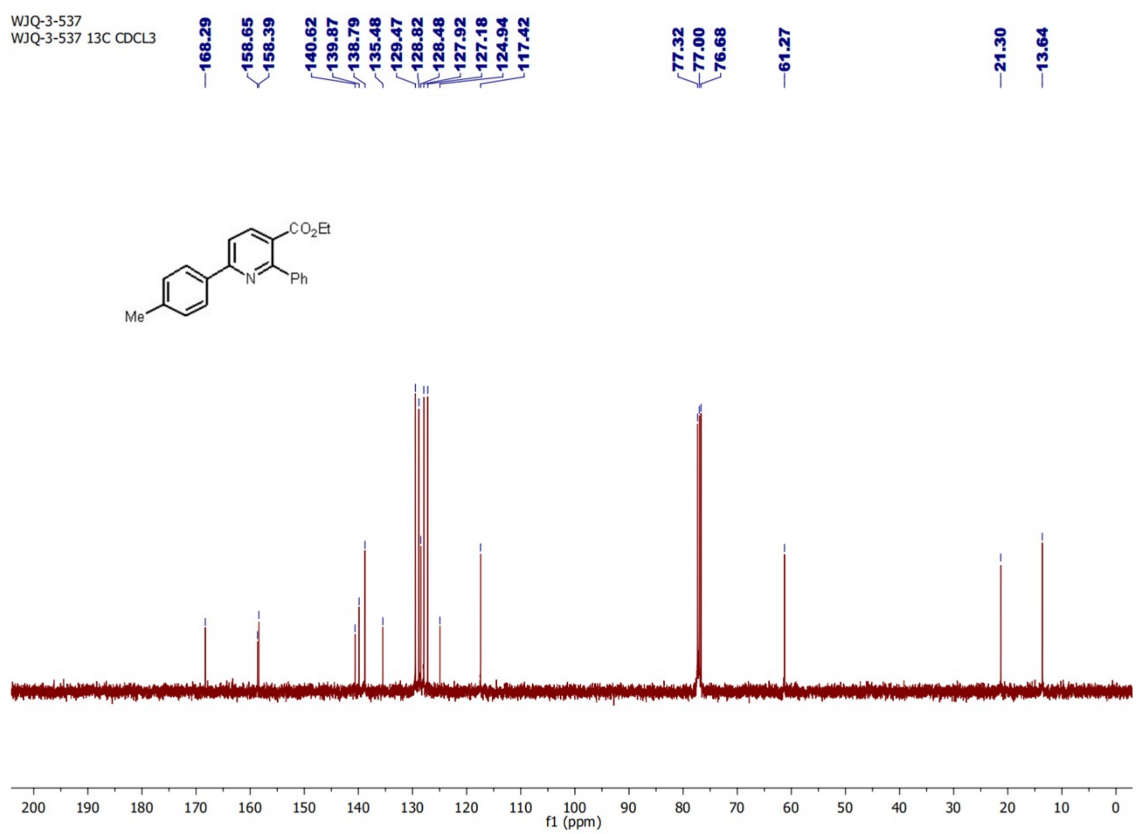
ethyl 4-methyl-2,5-diphenyl-1H-pyrrole-3-carboxylate (**5a**)



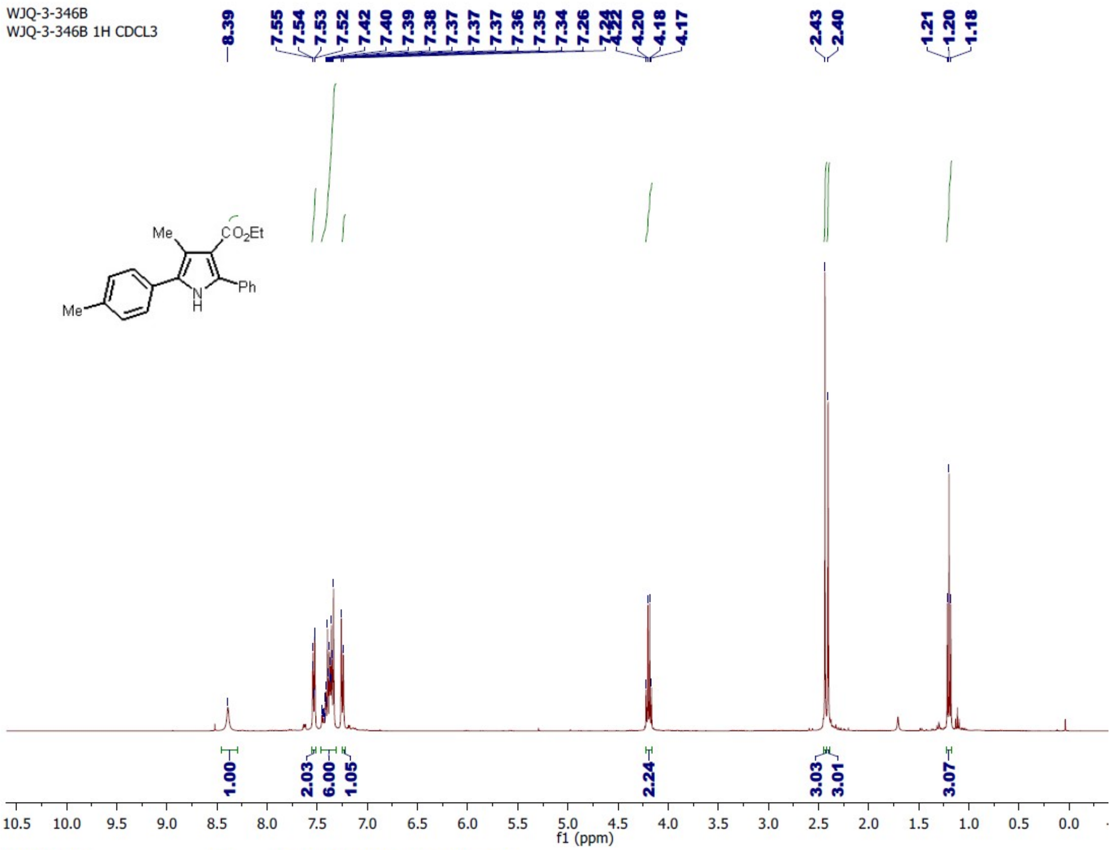


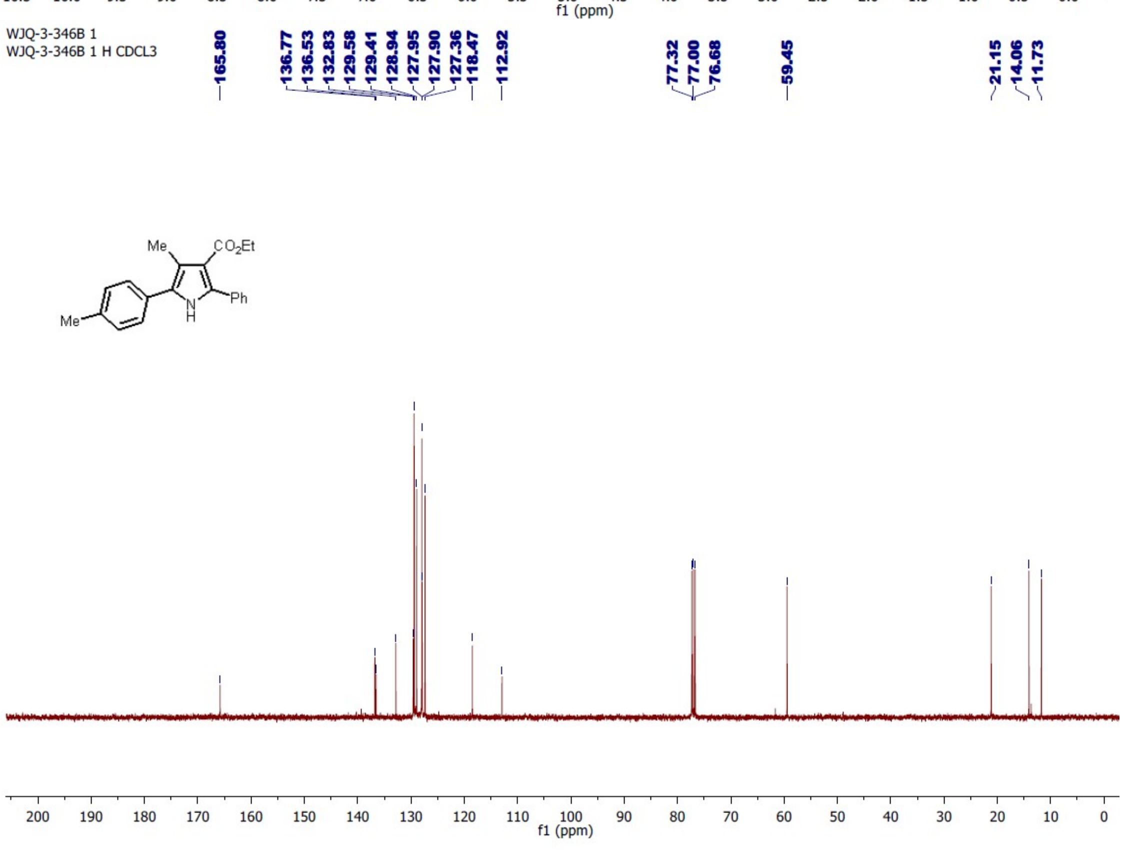
ethyl 2-phenyl-6-(p-tolyl) nicotinate (**4b**)



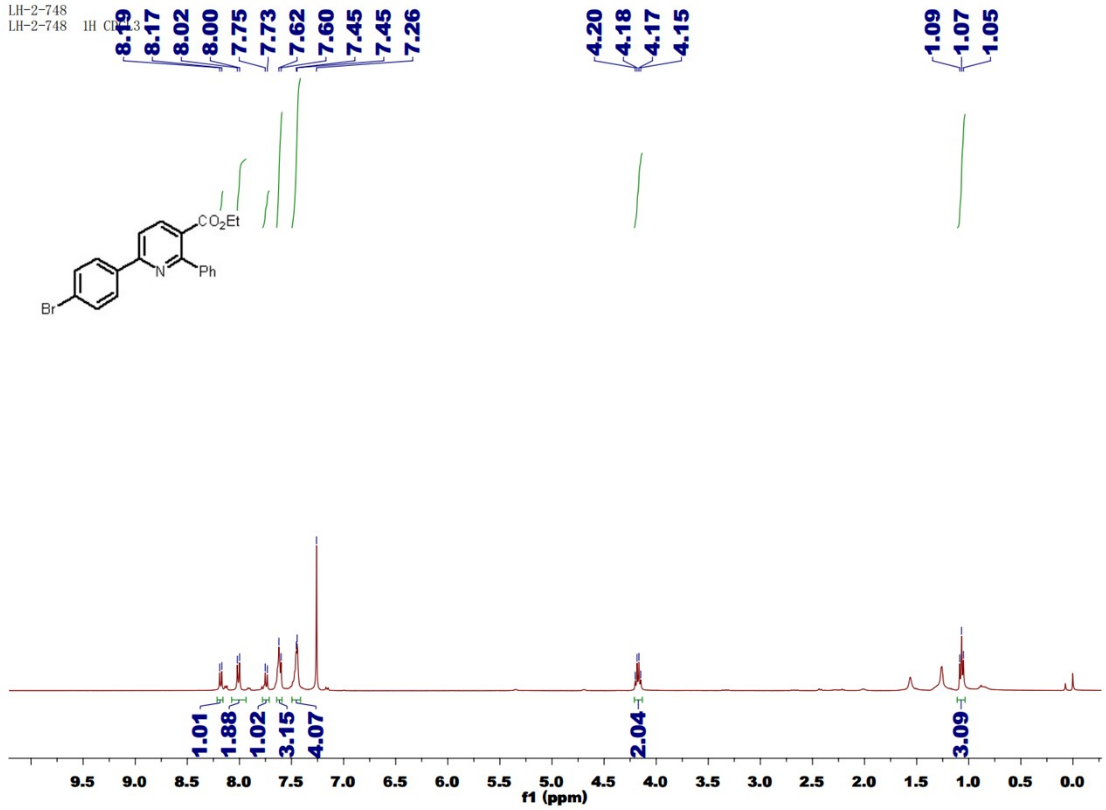


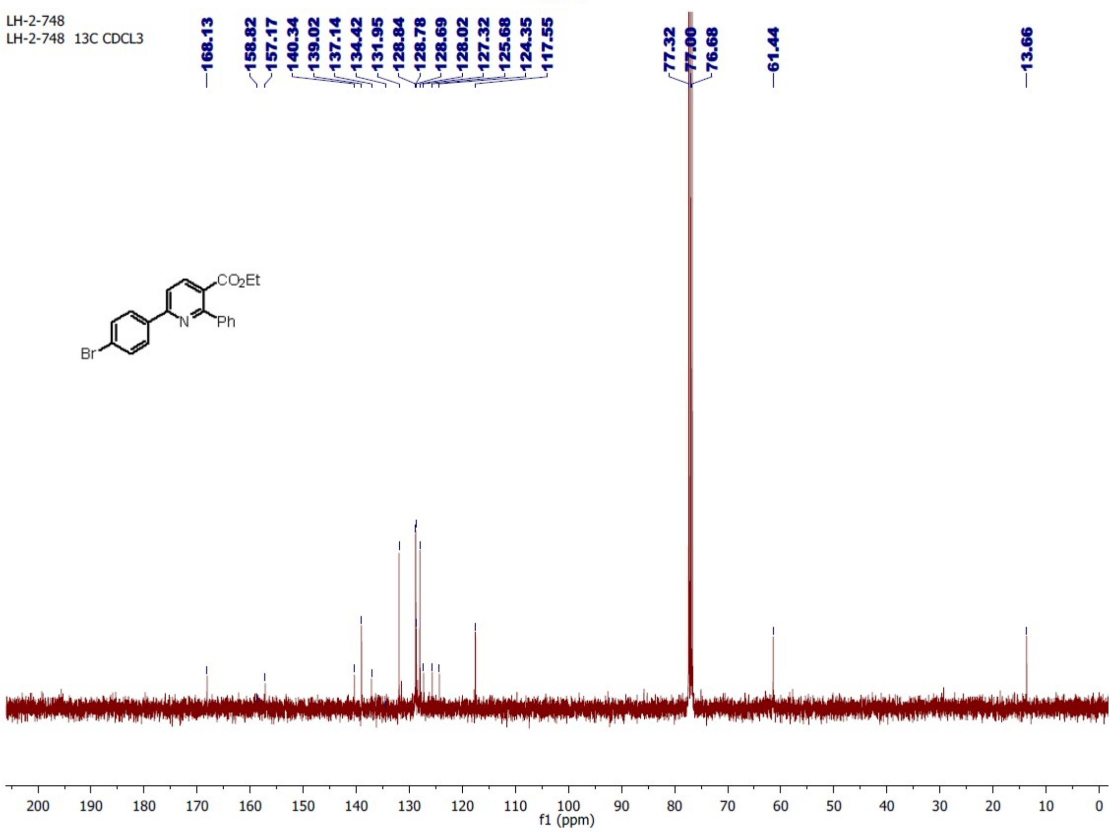
ethyl 4-methyl-2-phenyl-5-(p-tolyl)-1H-pyrrole-3-carboxylate (**5b**)



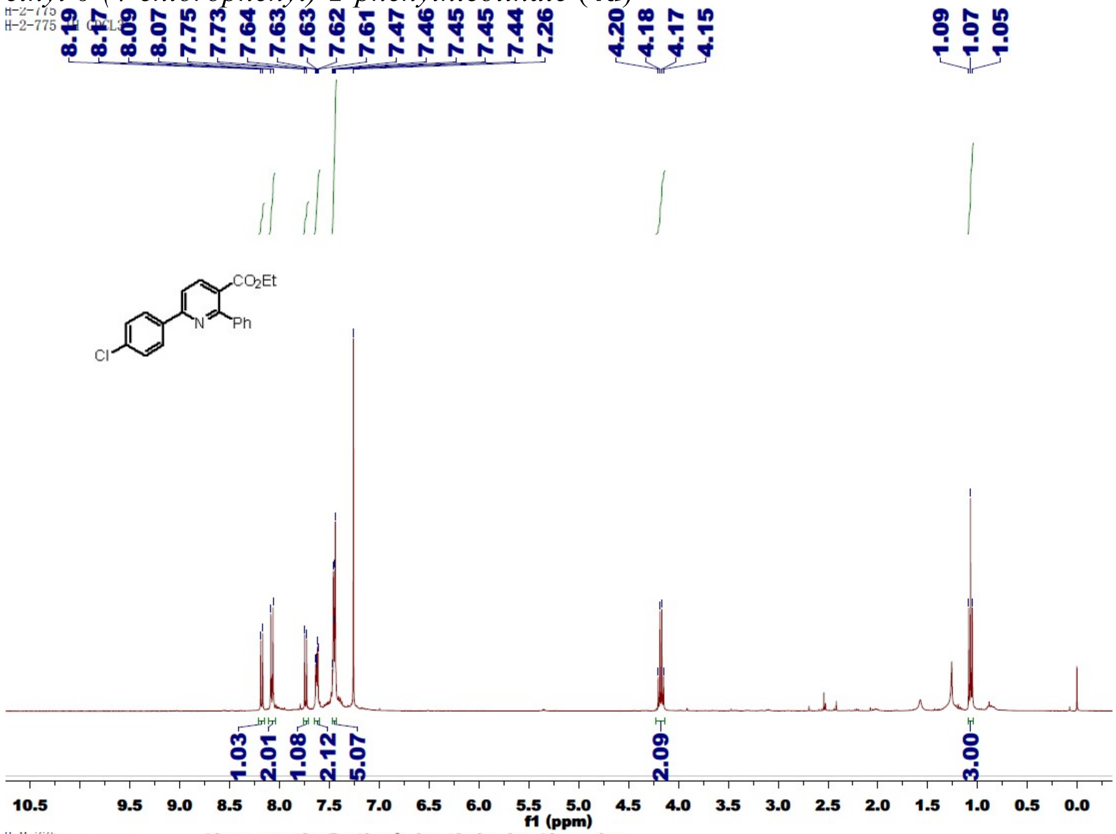


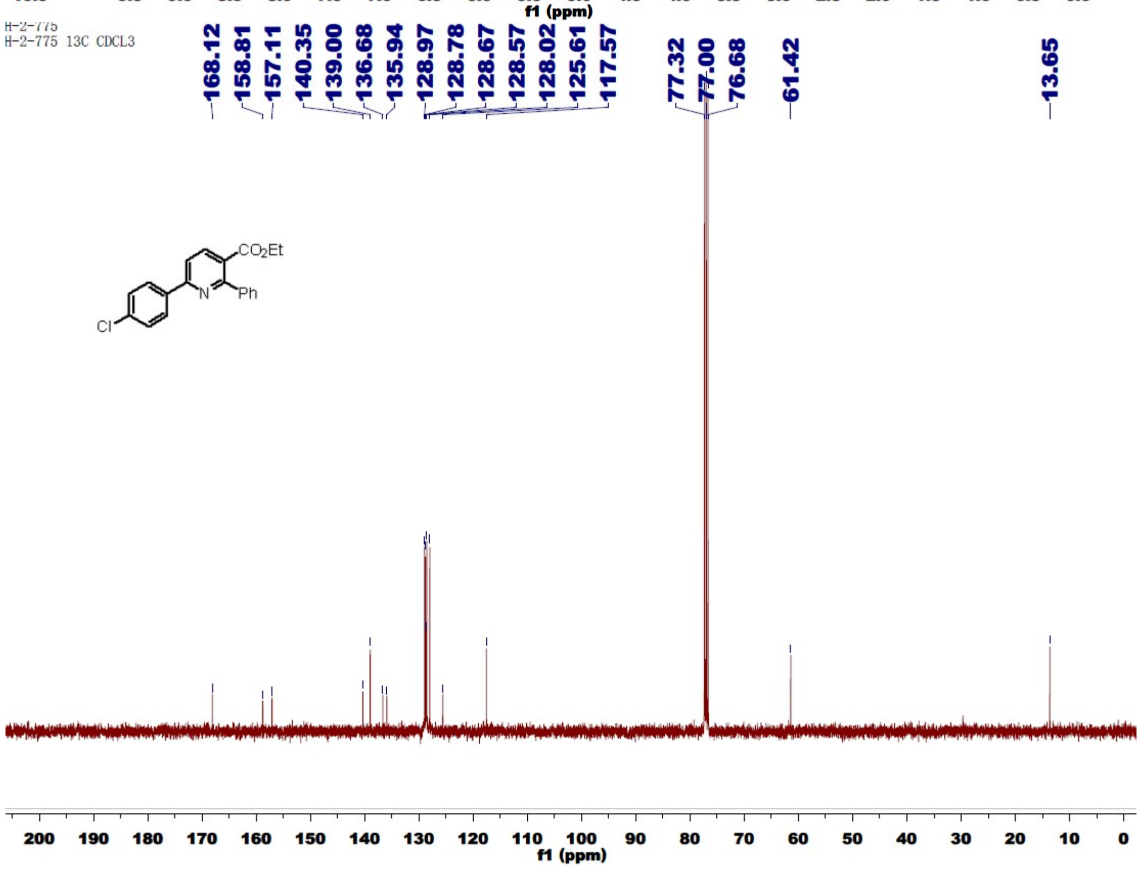
ethyl 6-(4-bromophenyl)-2-phenylnicotinate (**4c**)



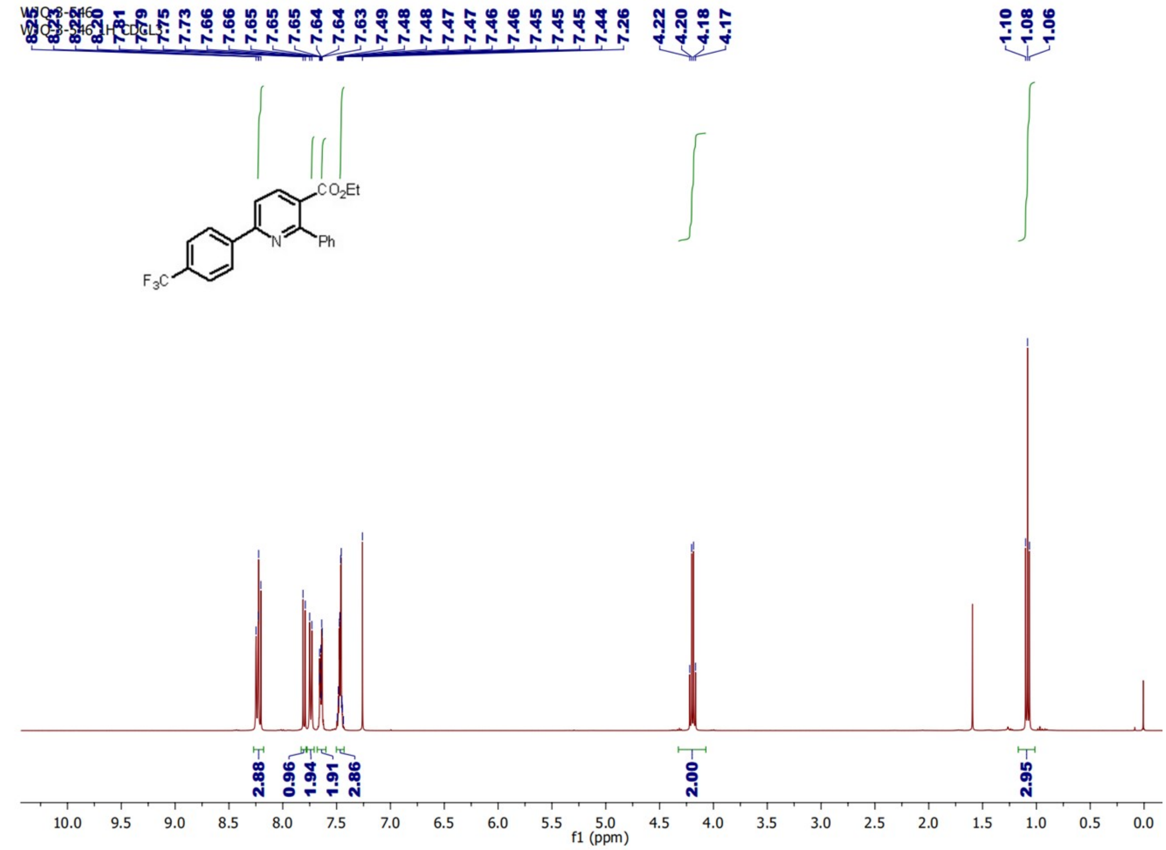


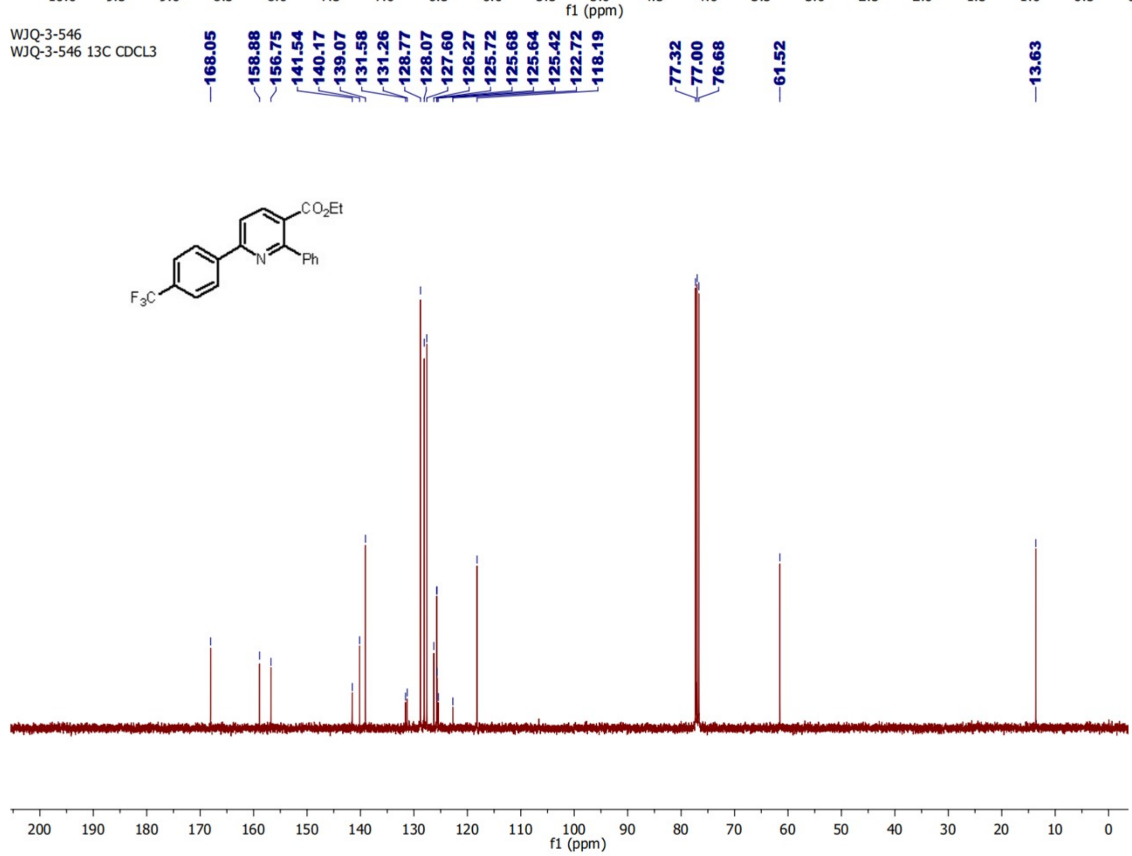
ethyl 6-(4-chlorophenyl)-2-phenylnicotinate (**4d**)



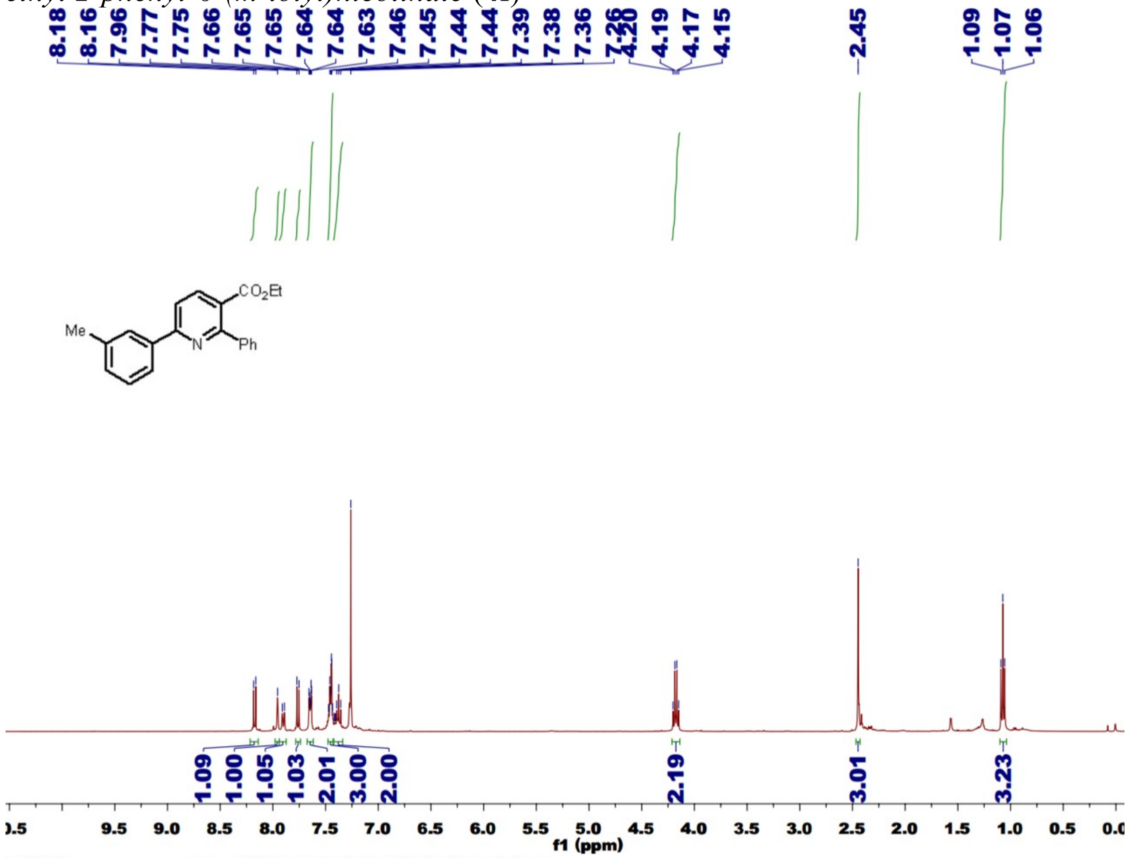


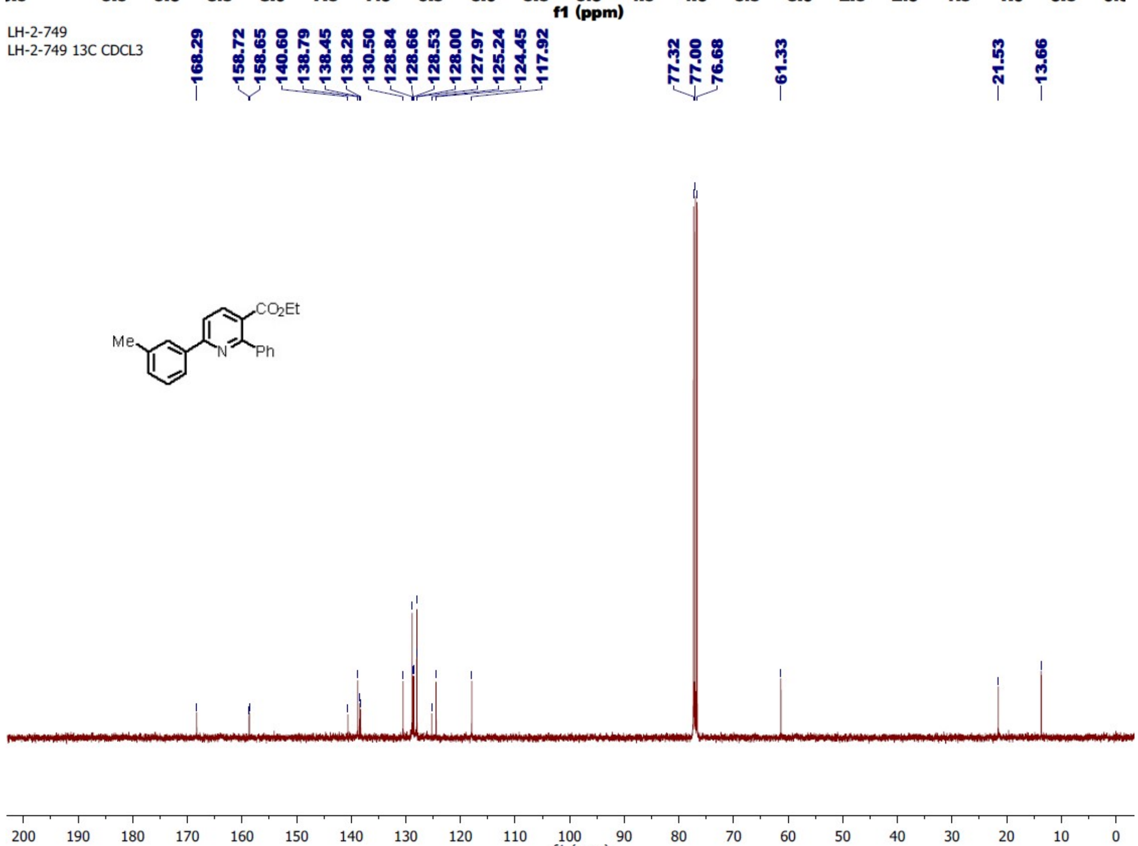
ethyl 2-phenyl-6-(4-(trifluoromethyl)phenyl)nicotinate (**4e**)



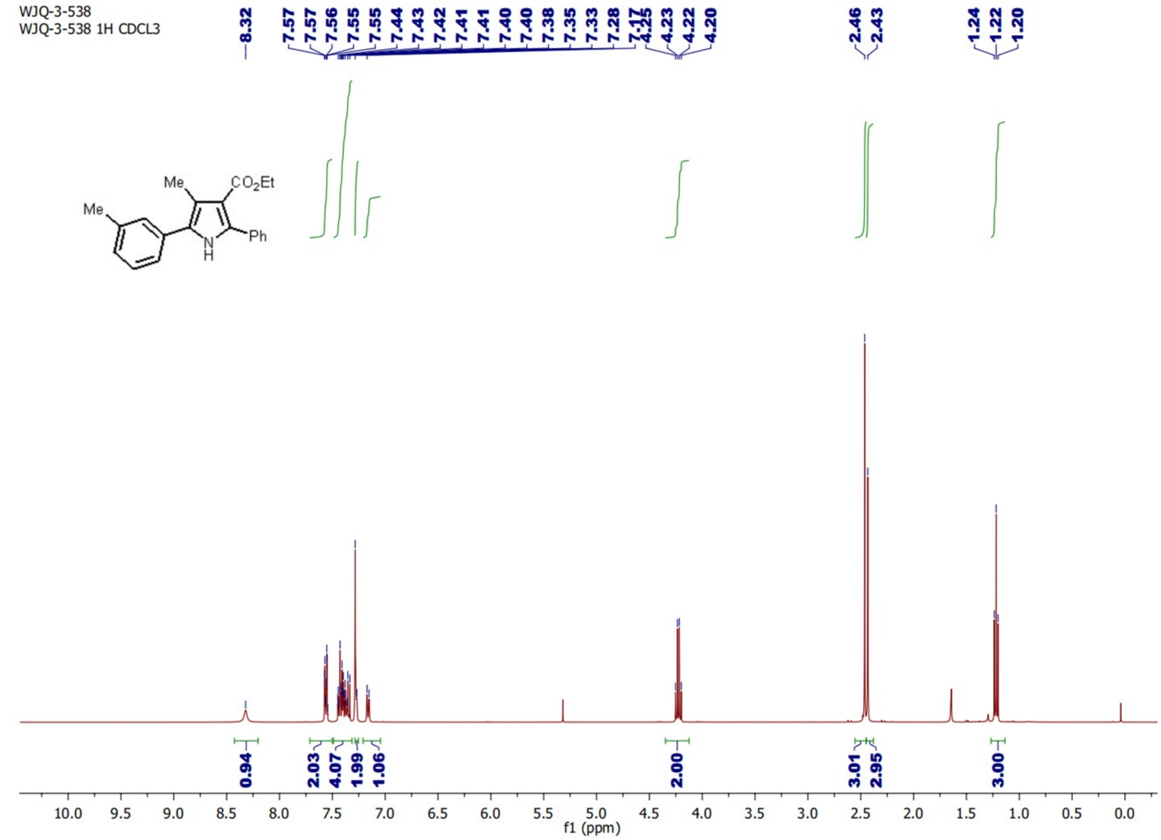


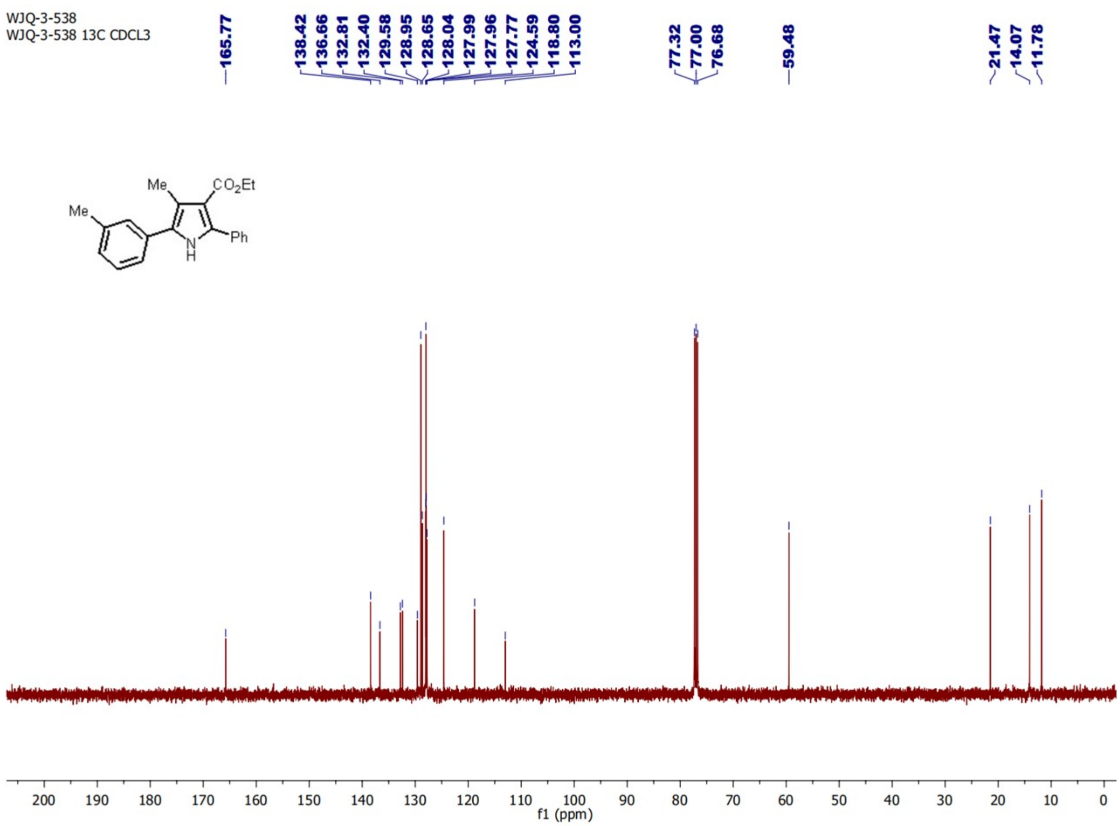
ethyl 2-phenyl-6-(m-tolyl)nicotinate (**4f**)



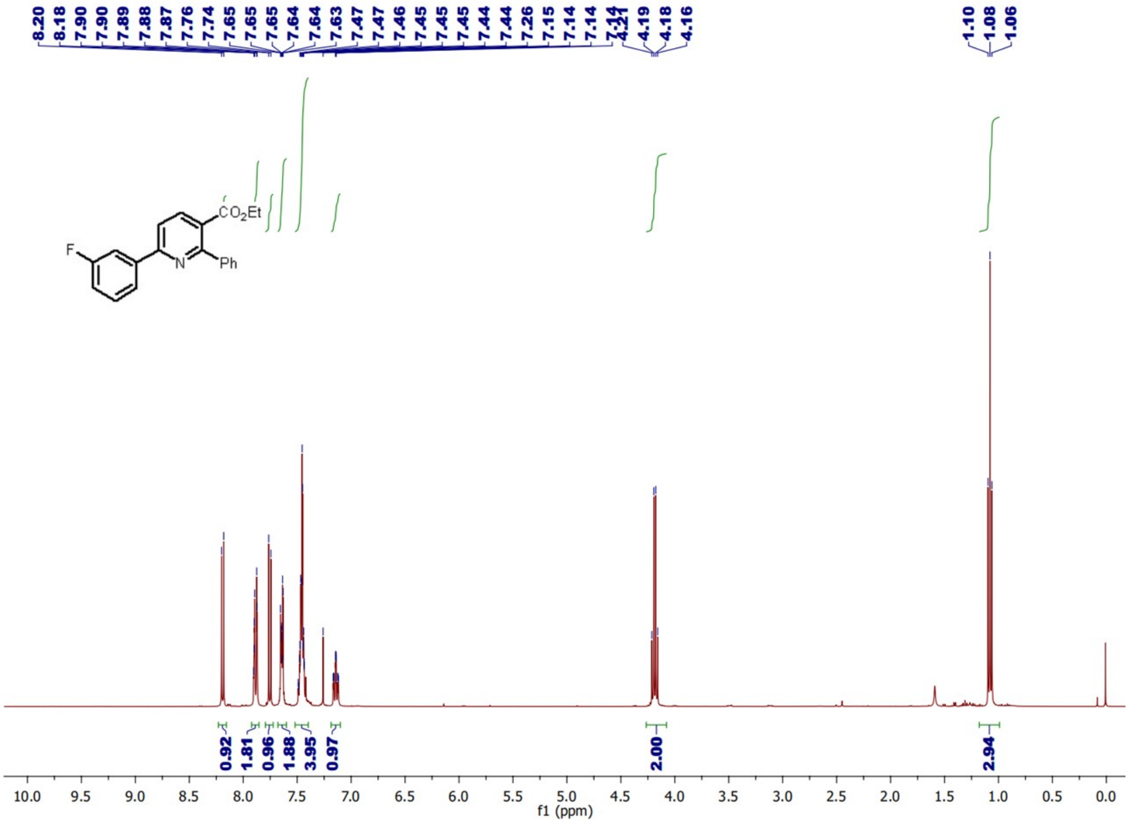


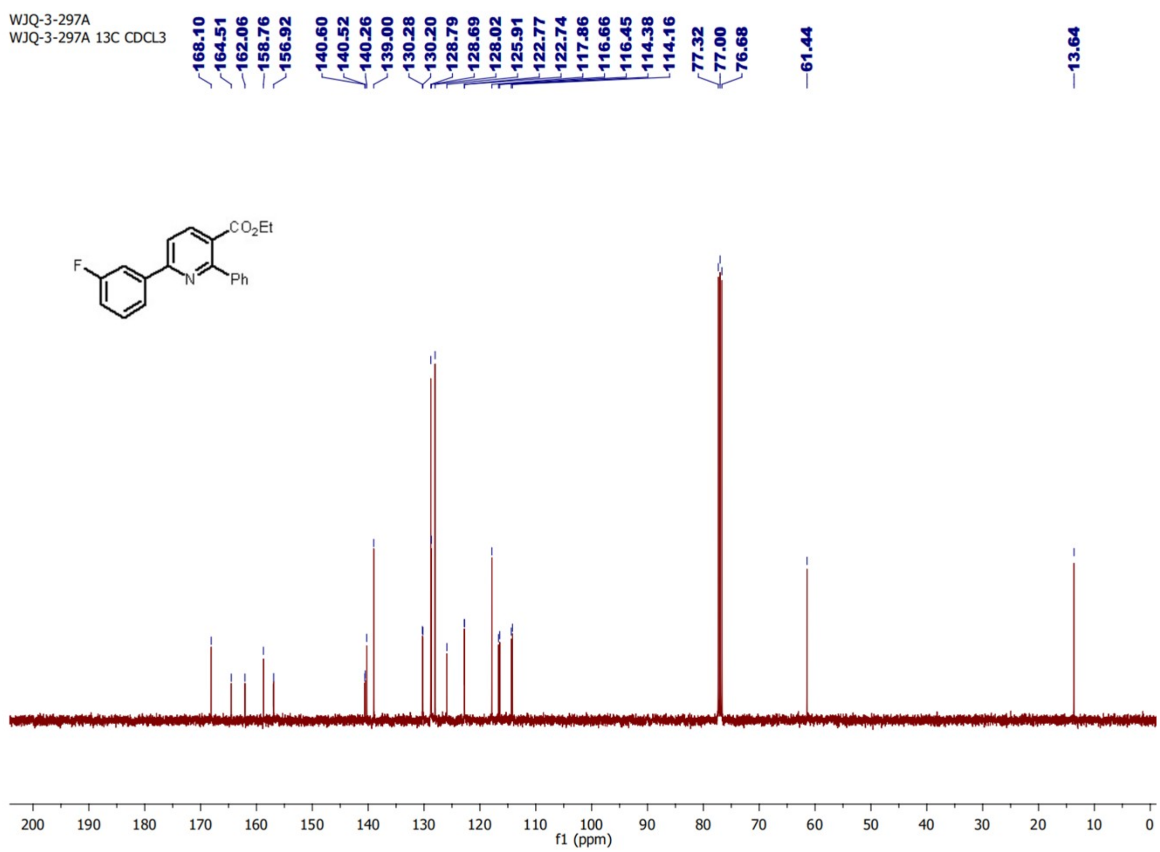
ethyl 4-methyl-2-phenyl-5-(m-tolyl)-1H-pyrrole-3-carboxylate (**5f**)



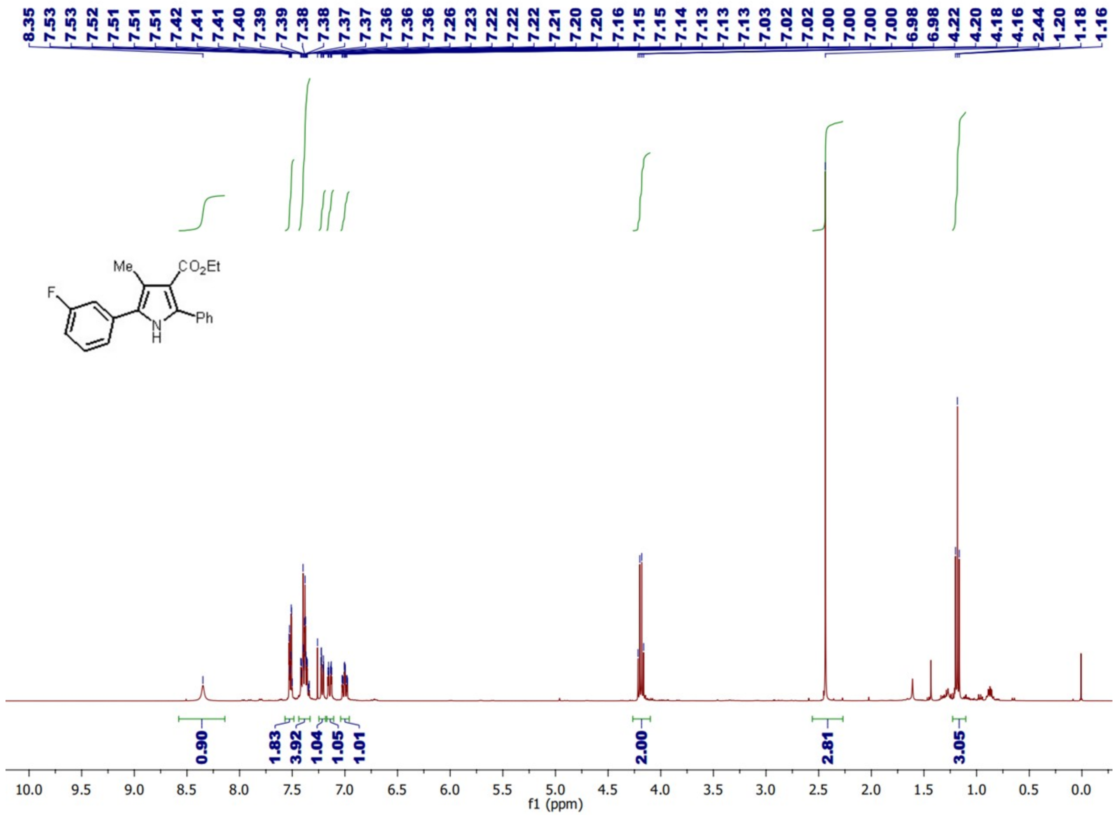


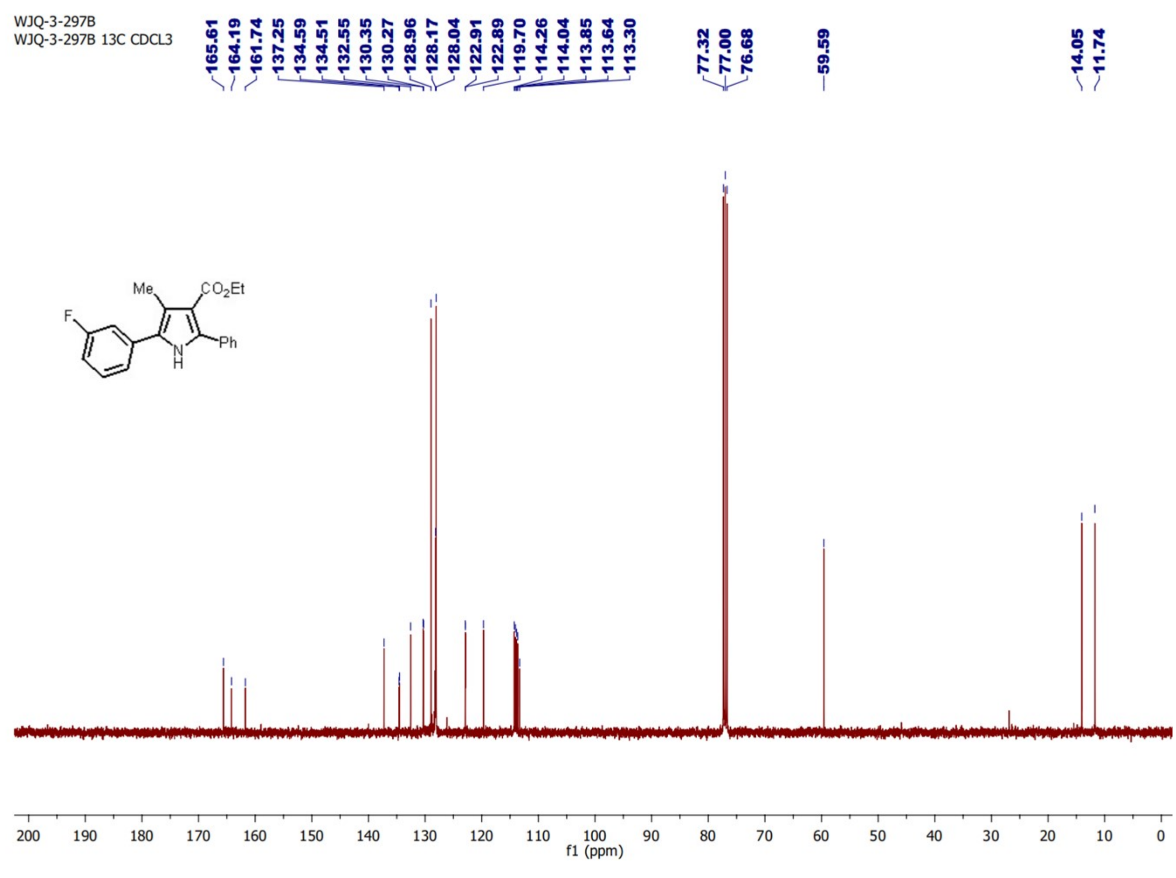
ethyl 6-(3-fluorophenyl)-2-phenylnicotinate (**4g**)



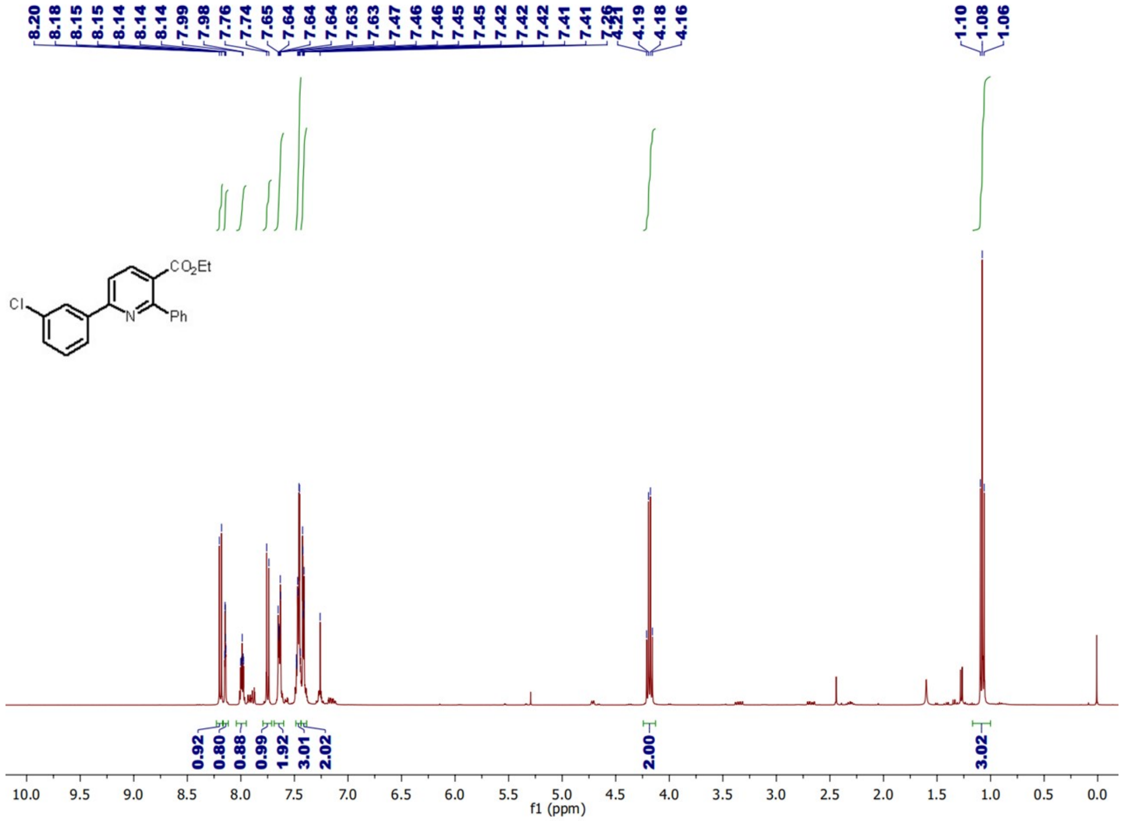


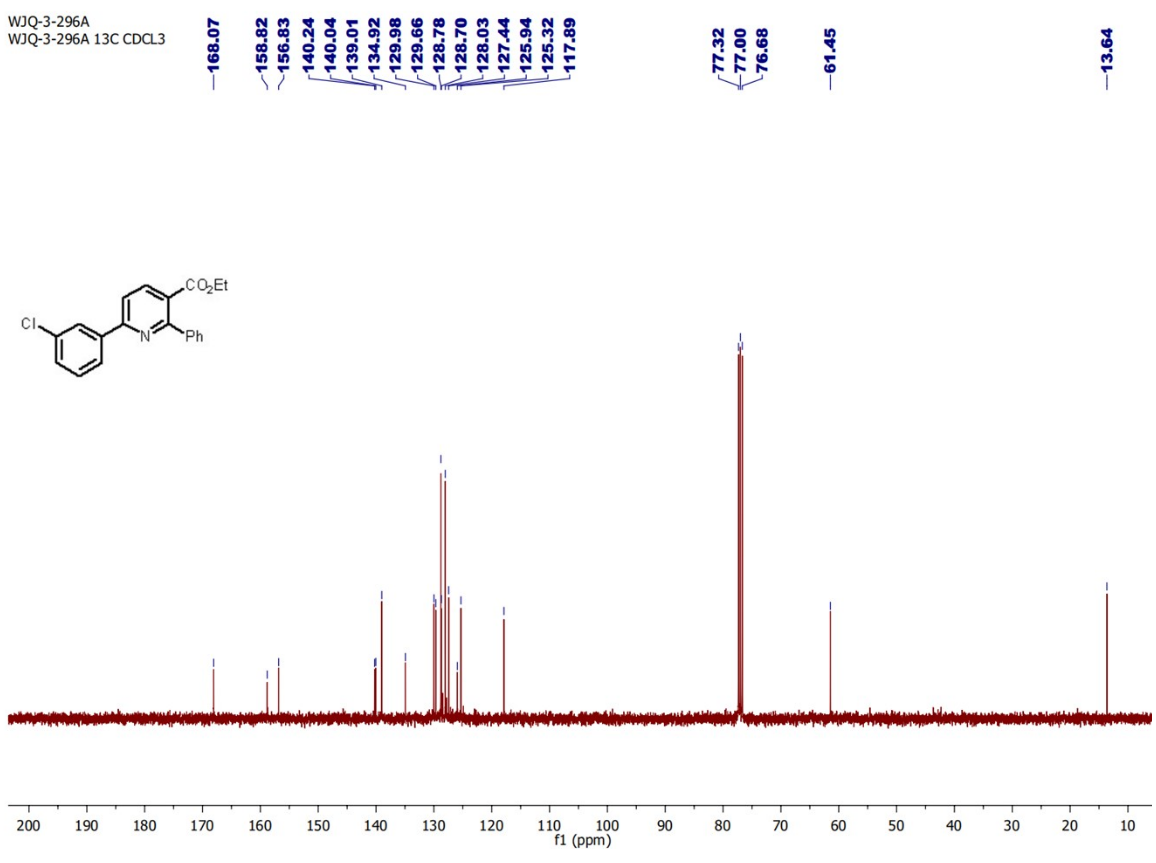
ethyl 5-(3-fluorophenyl)-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**5g**)



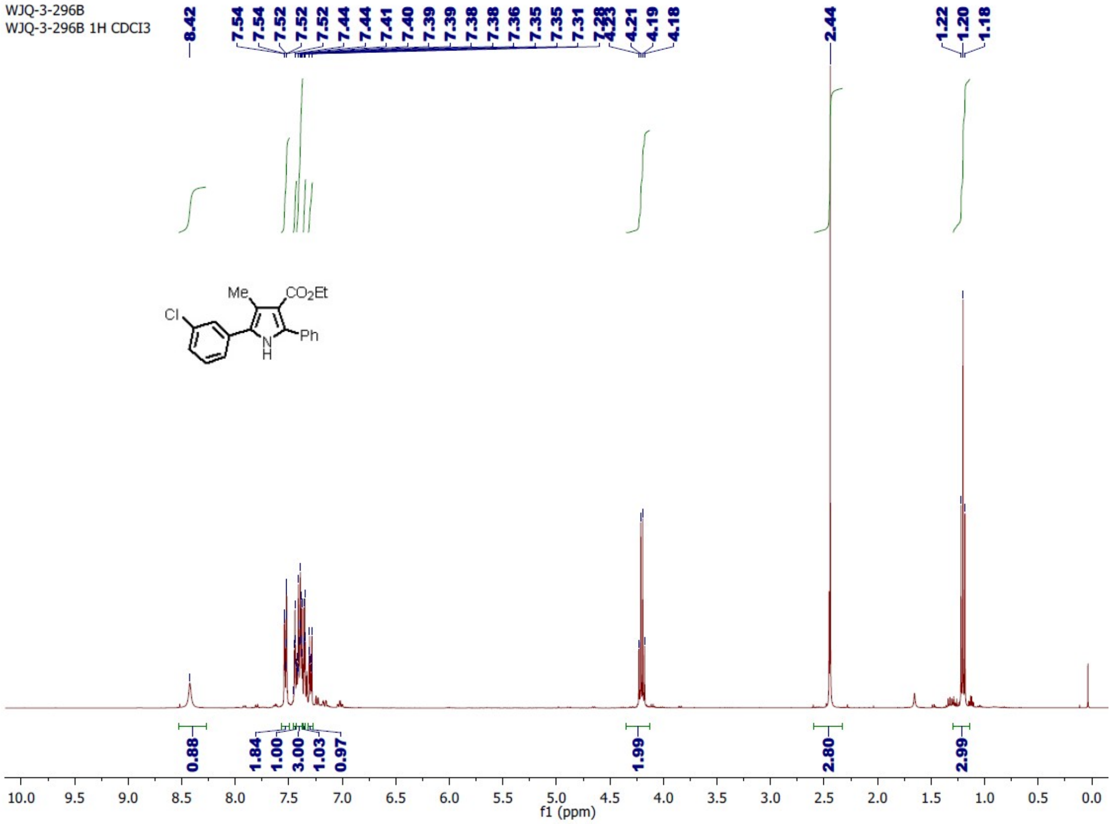


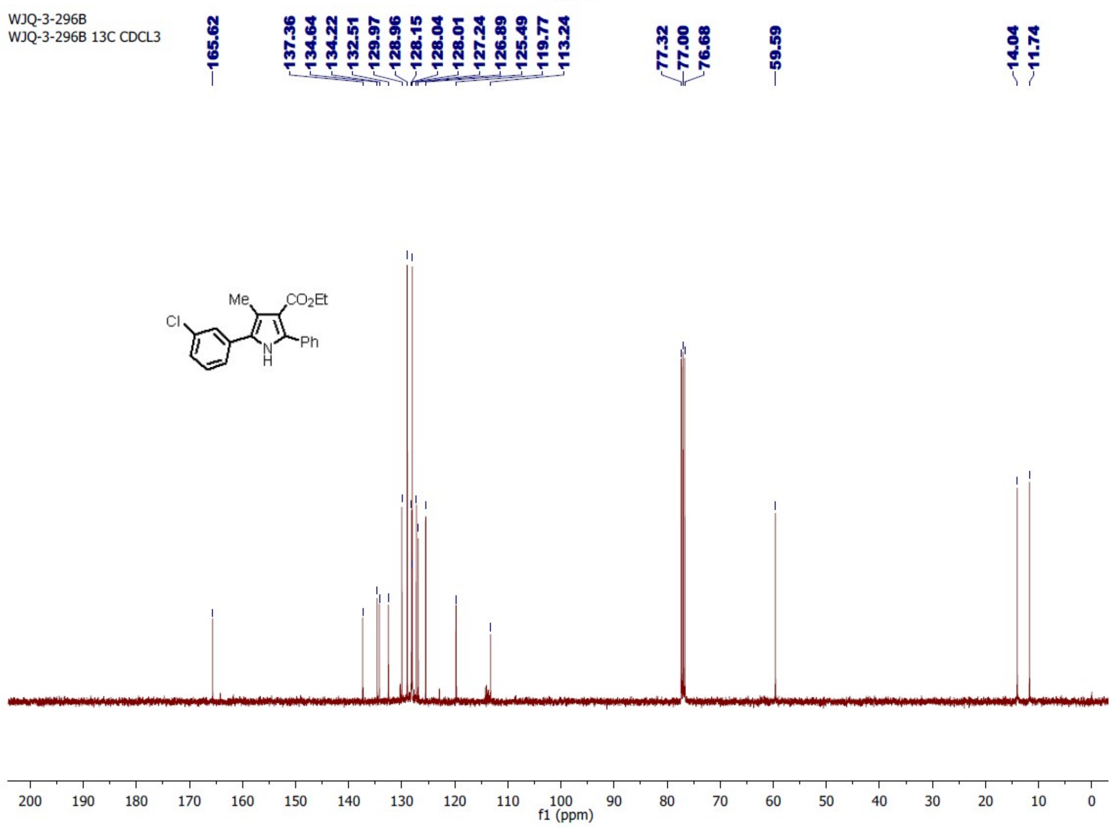
ethyl 6-(3-chlorophenyl)-2-phenylnicotinate (**4h**)



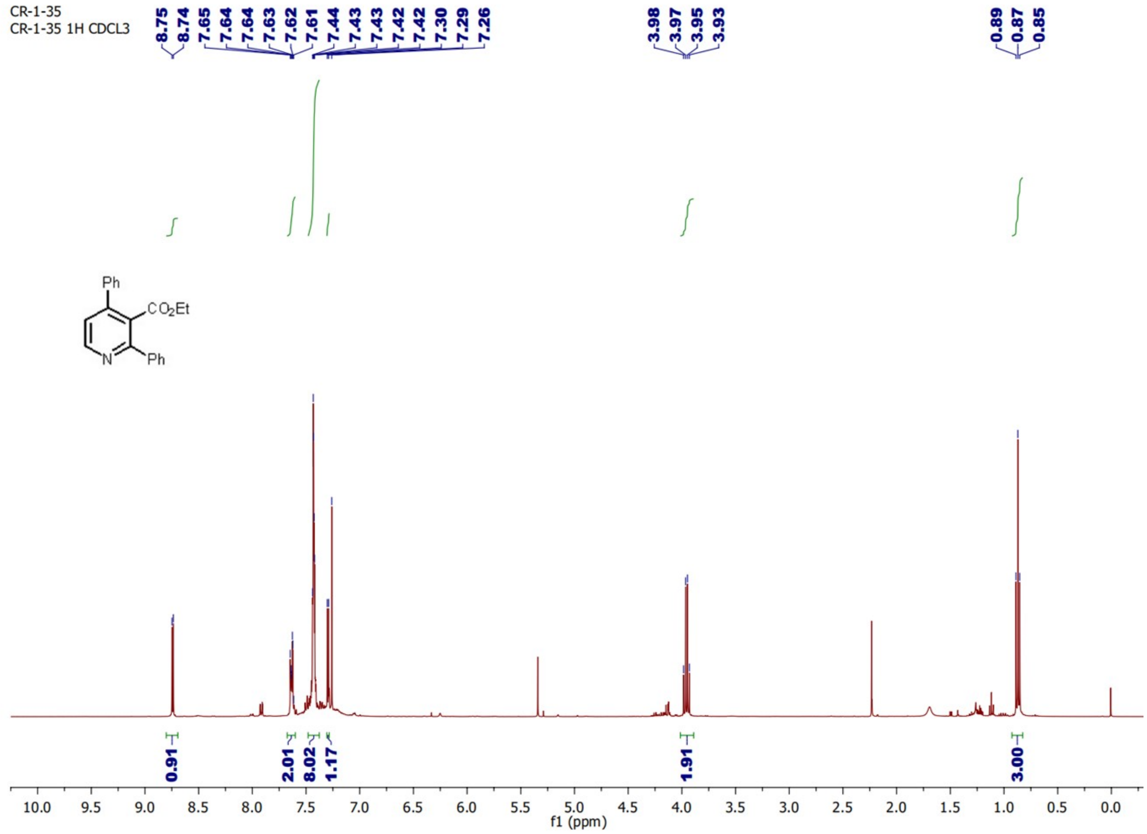


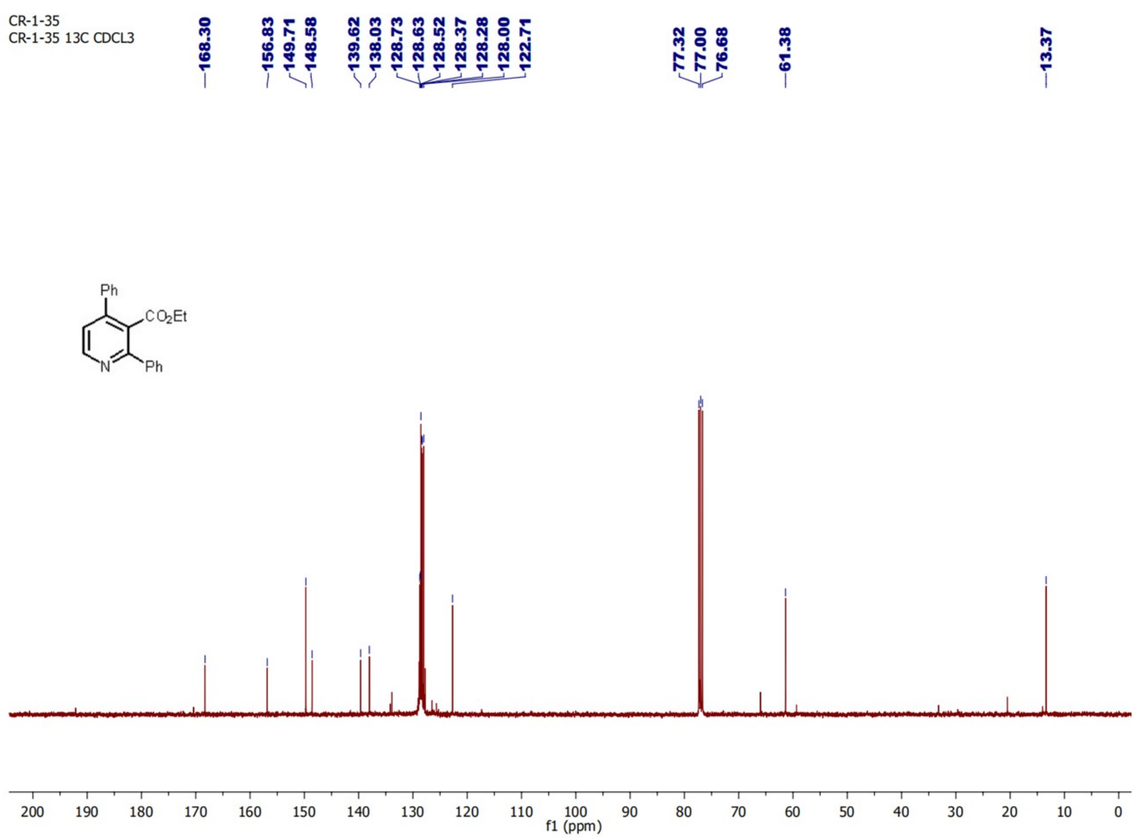
ethyl 5-(3-chlorophenyl)-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**5h**)



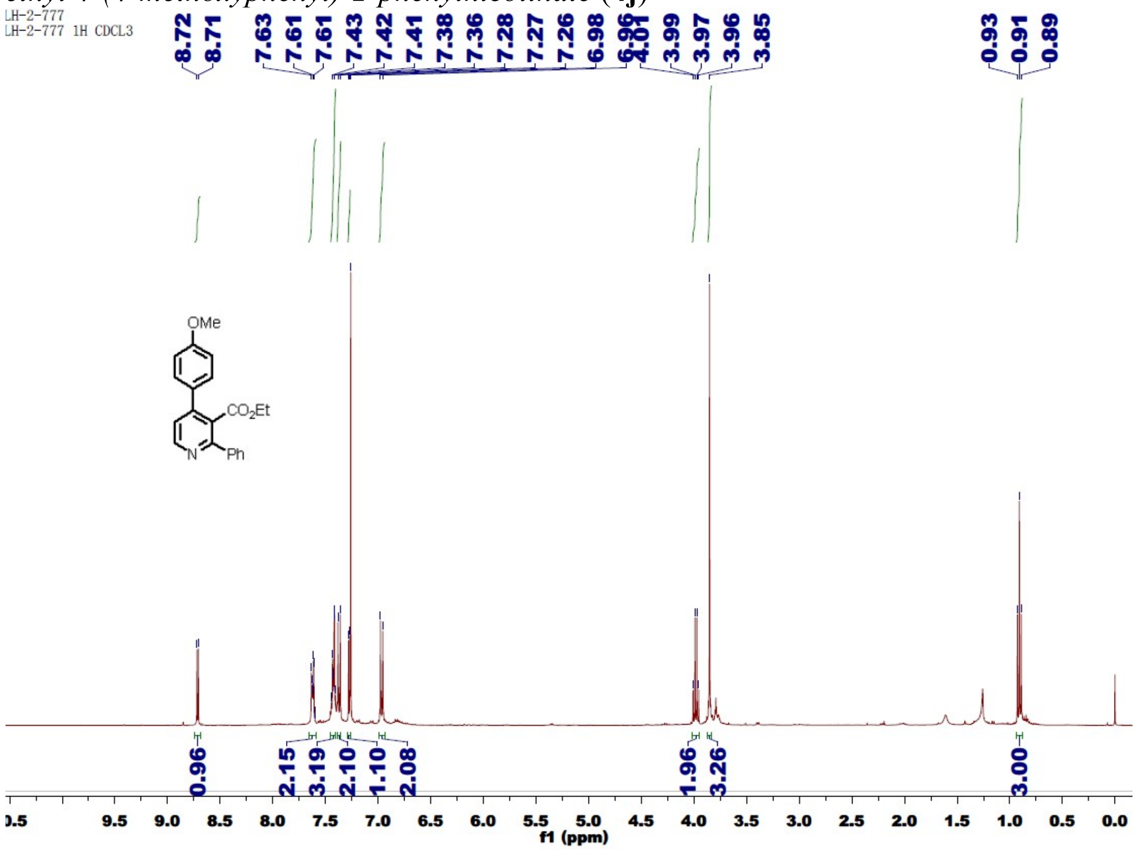


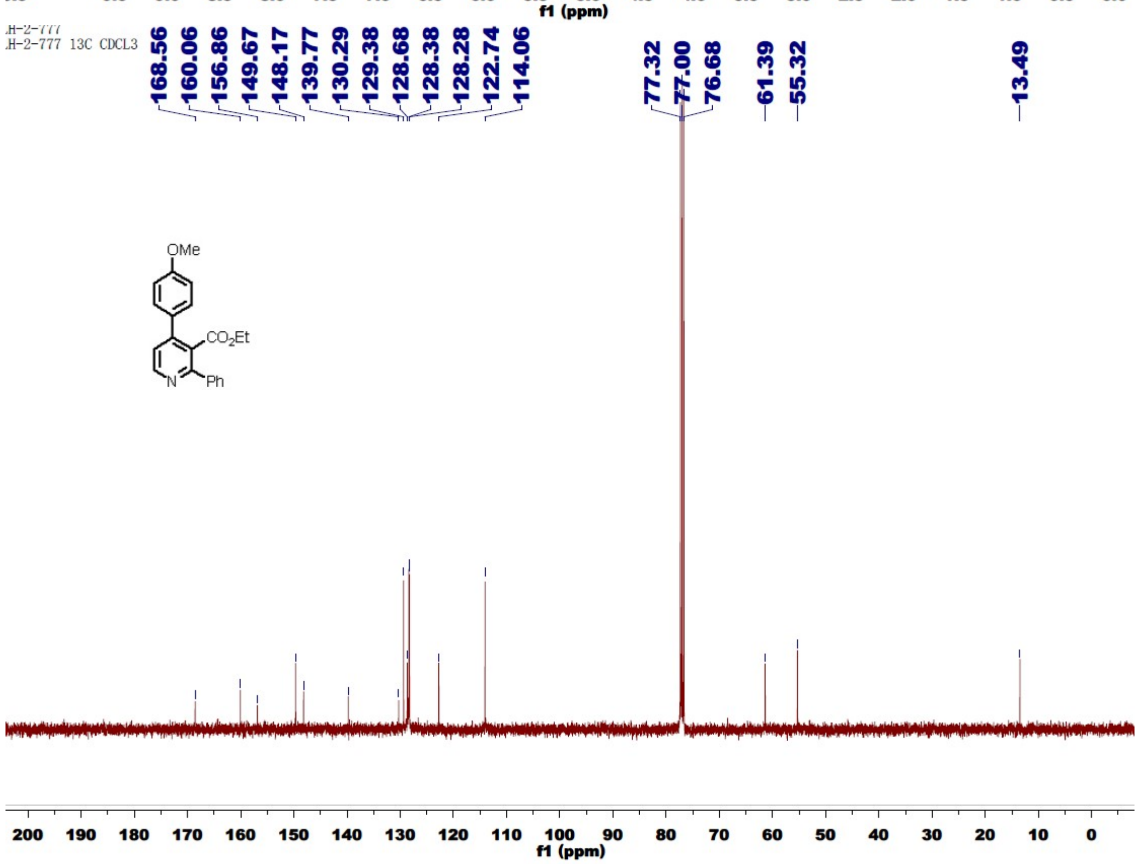
ethyl 2,4-diphenylnicotinate (**4i**)



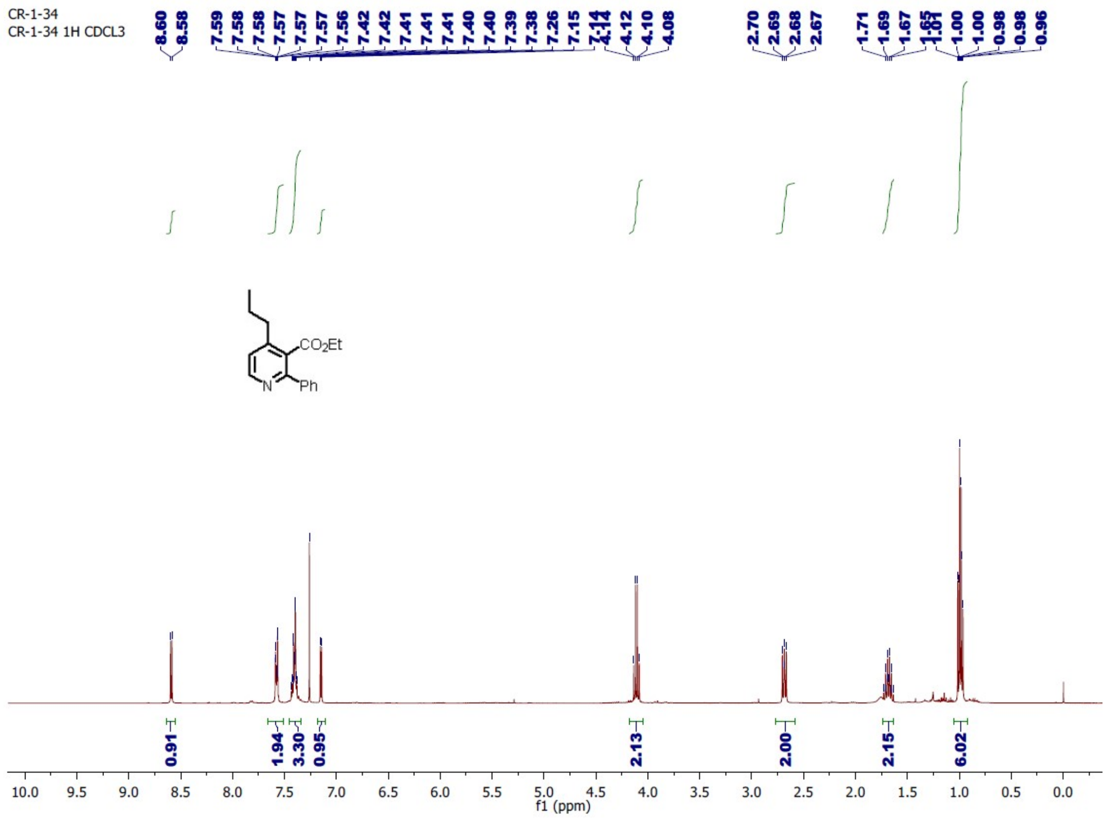


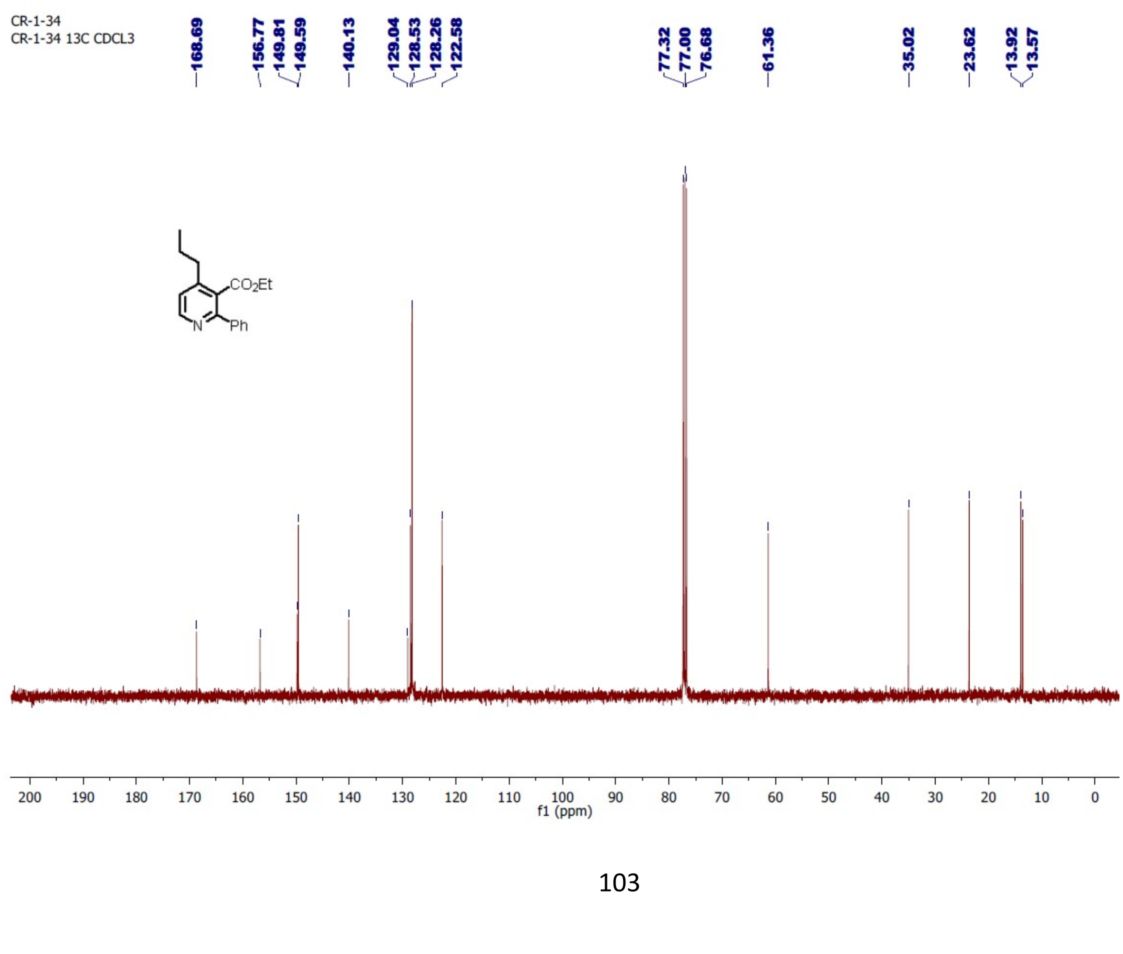
ethyl 4-(4-methoxyphenyl)-2-phenylnicotinate (**4j**)



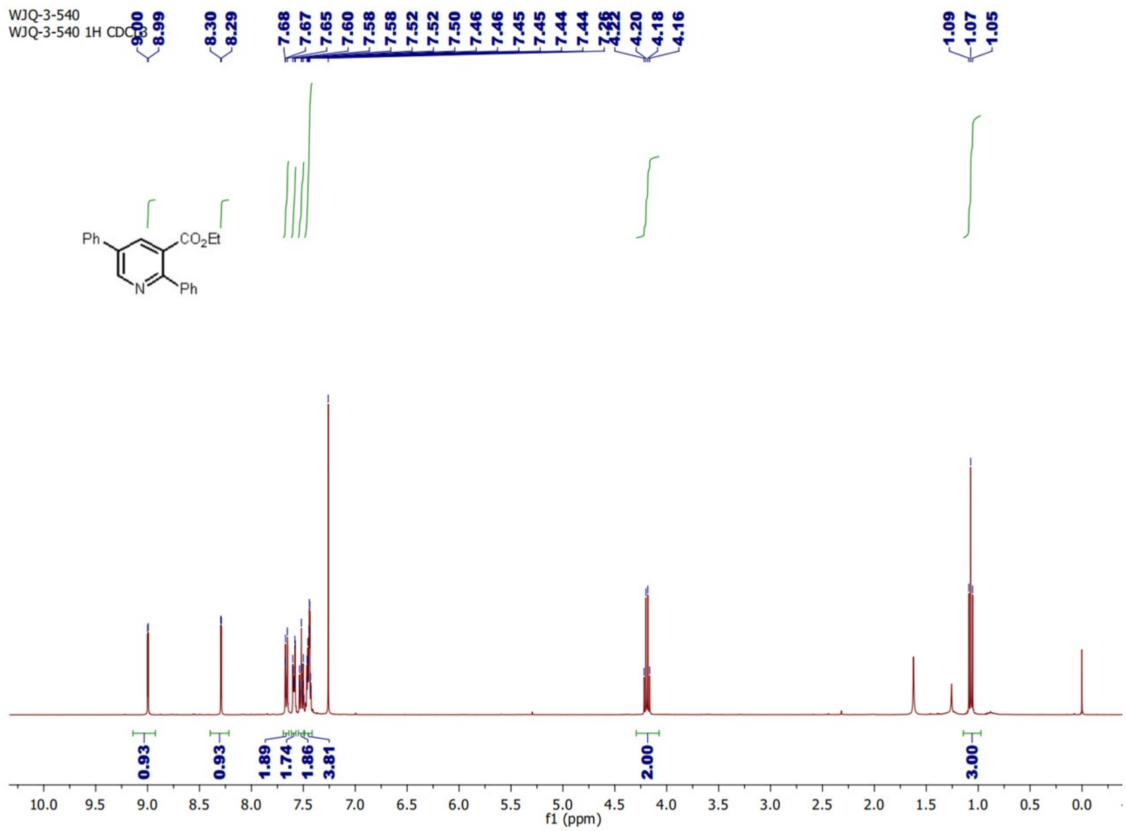


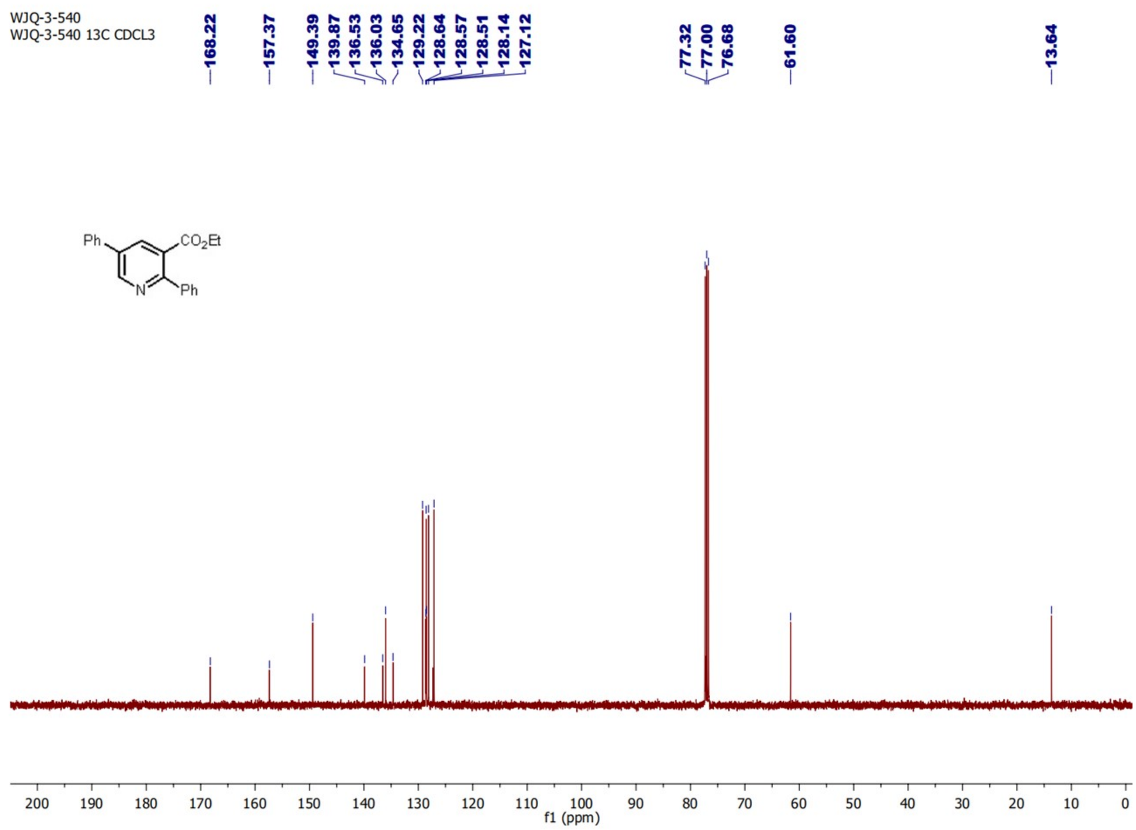
ethyl 2-phenyl-4-propylnicotinate (**4k**)



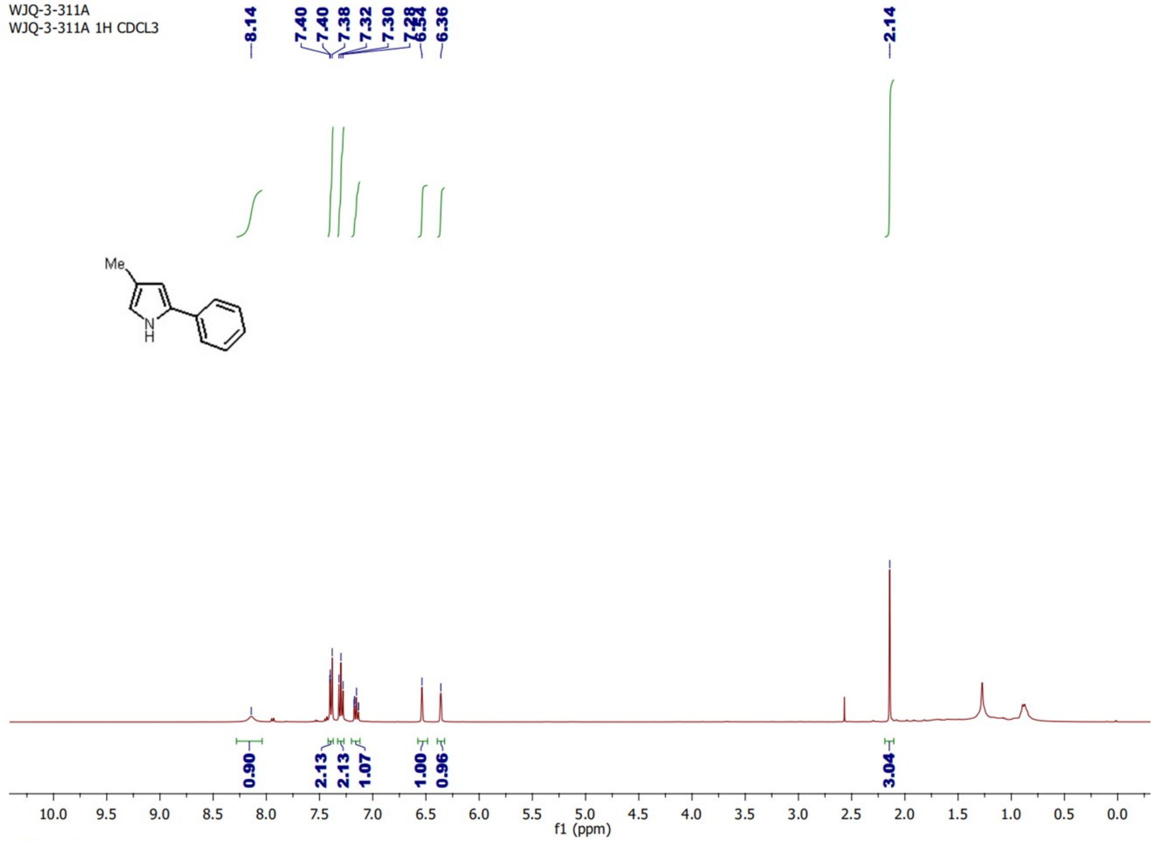


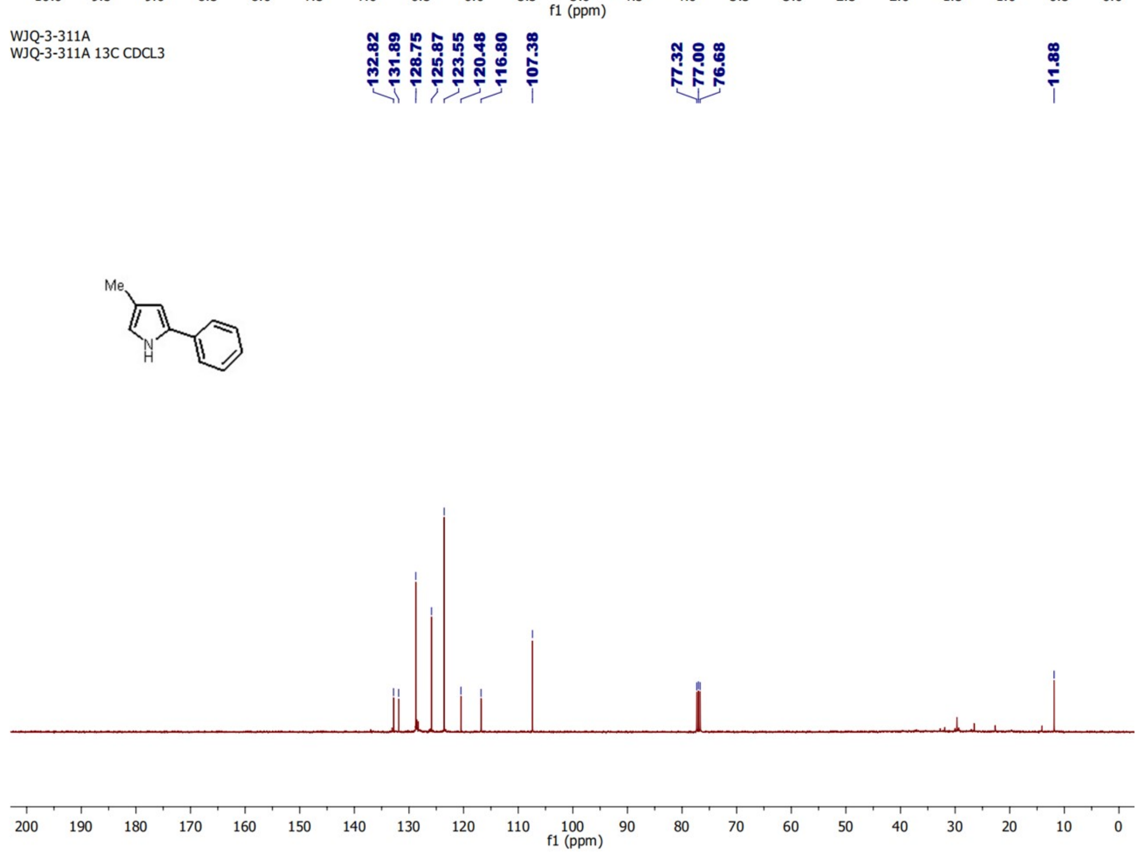
ethyl 2,5-diphenylnicotinate (**4l**)



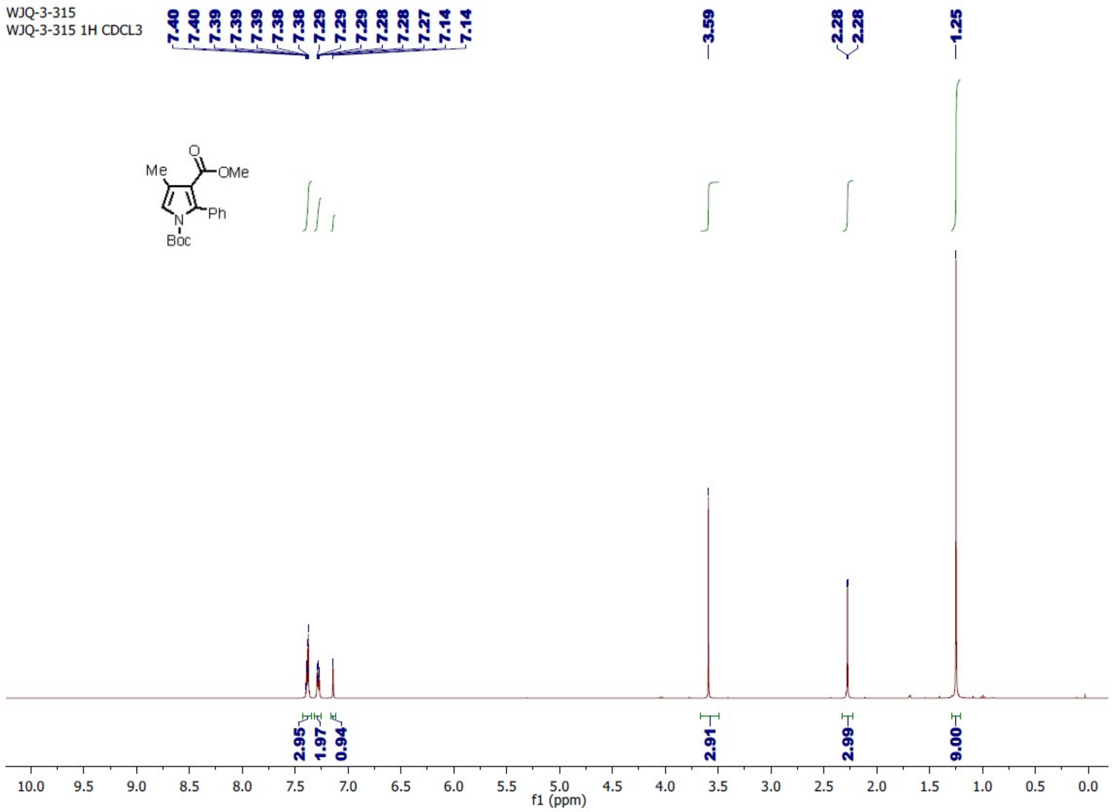


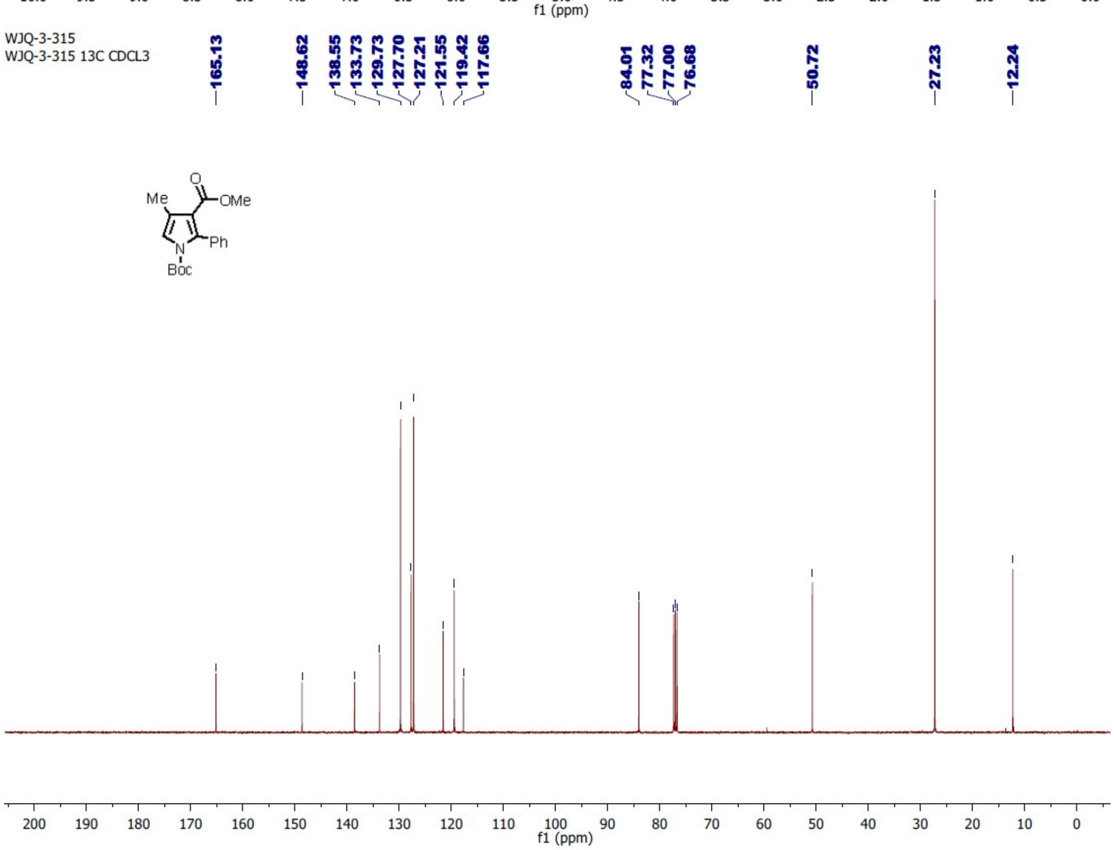
4-methyl-2-phenyl-1H-pyrrole (**6a**)



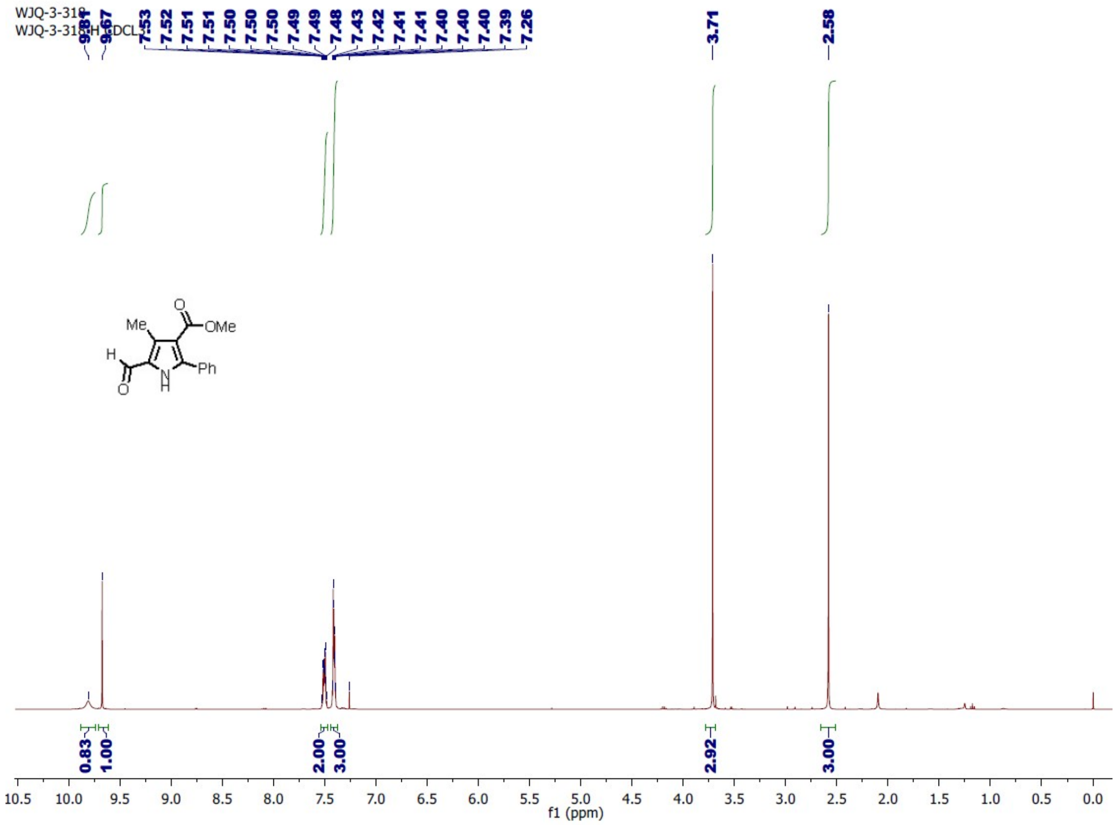


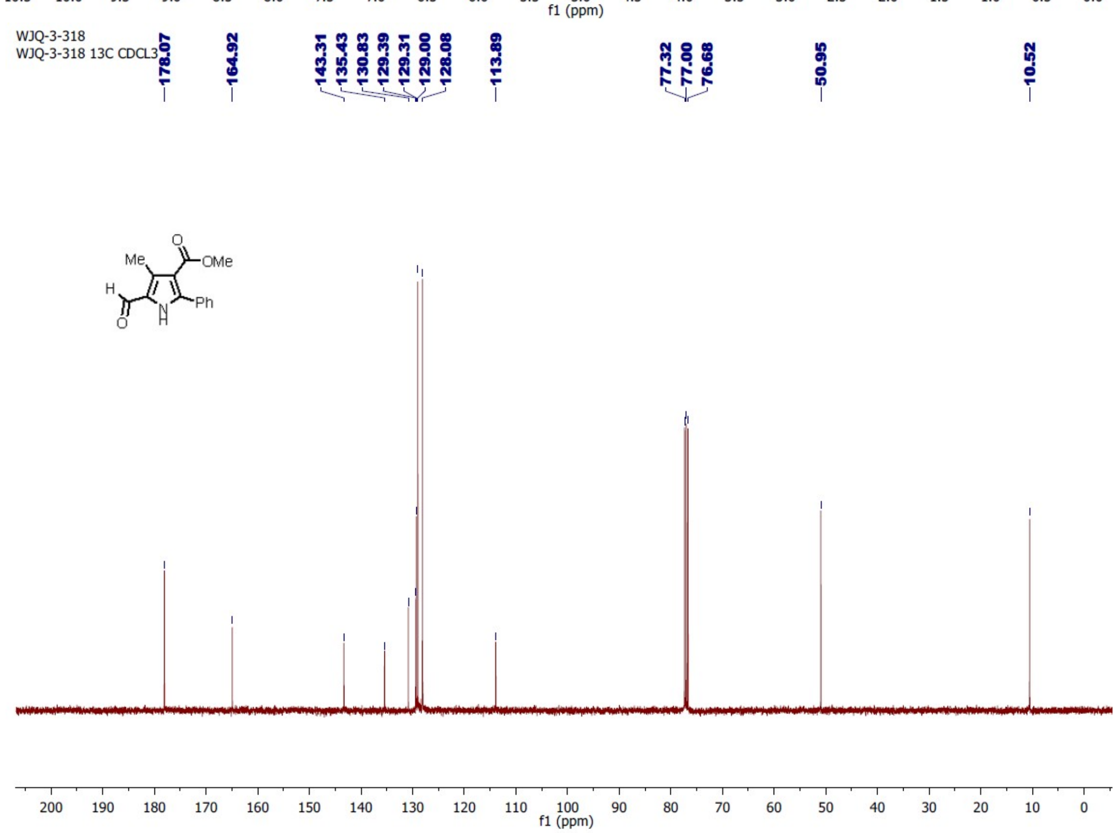
1-(tert-butyl) 3-methyl 4-methyl-2-phenyl-1H-pyrrole-1,3-dicarboxylate (**7a**)



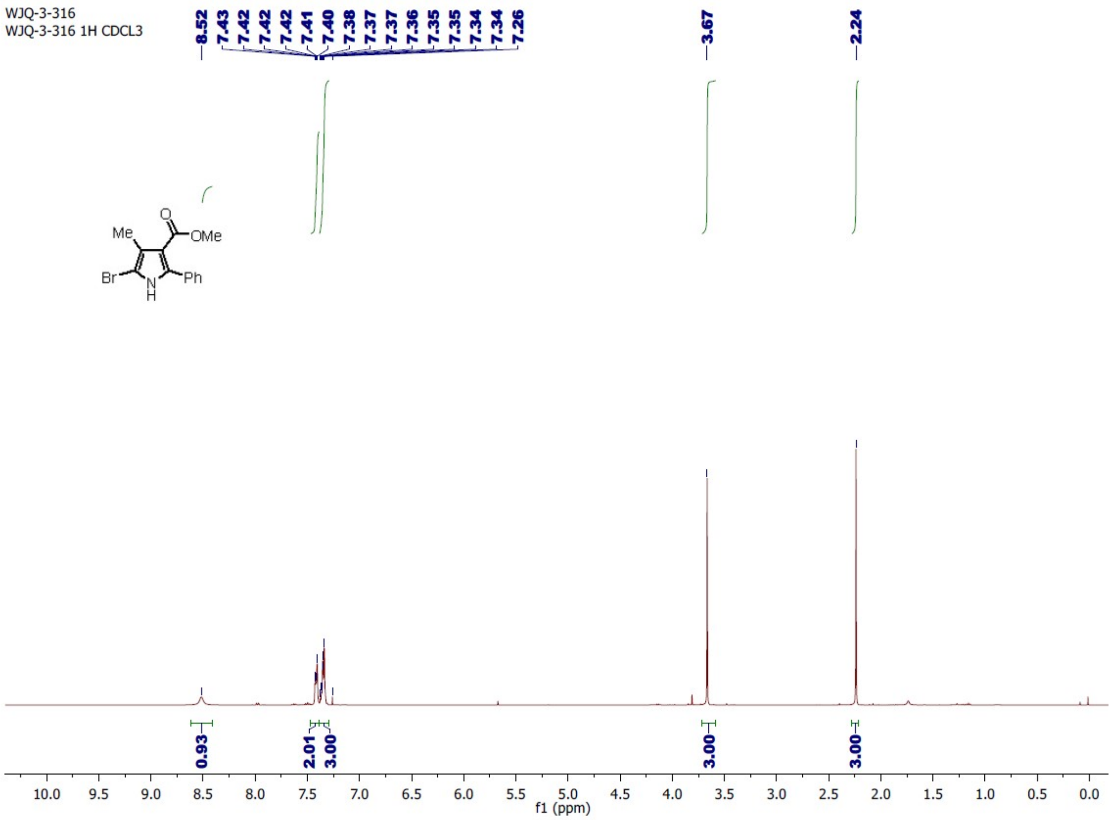


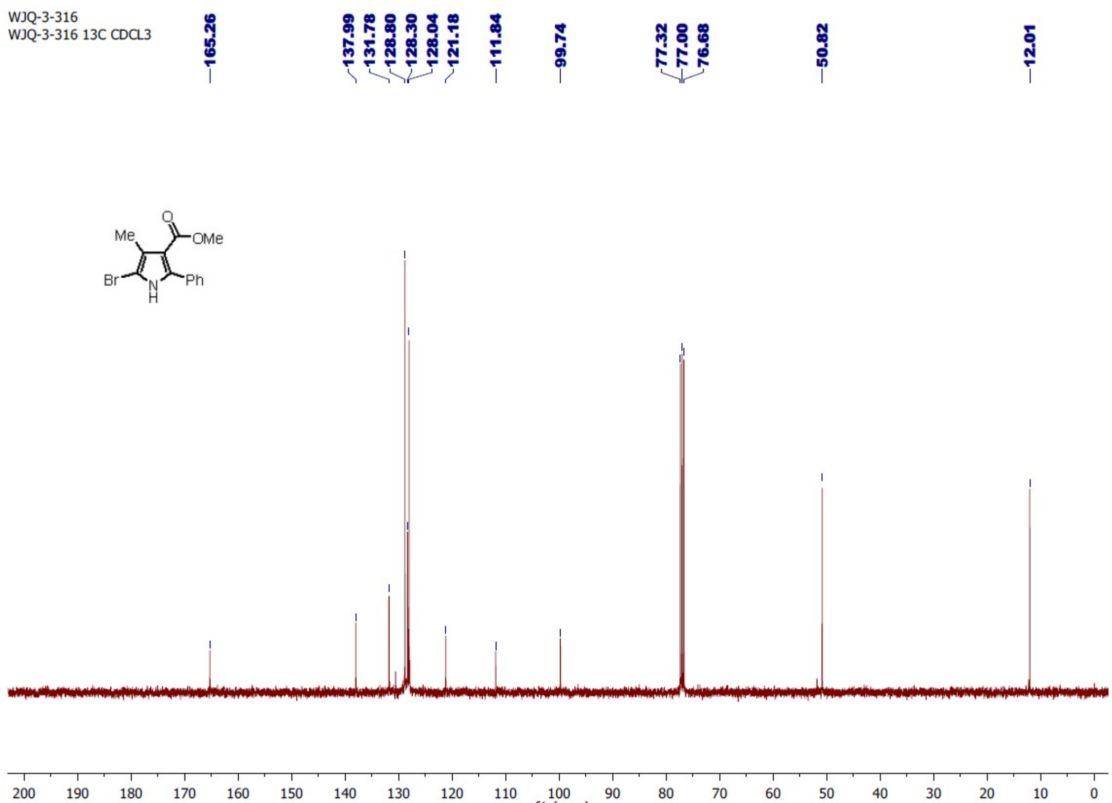
methyl 5-formyl-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**8a**)





Methyl 5-bromo-4-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**9a**)





methyl (E)-3-(allylamino)-2-bromo-3-phenylacrylate (**10a**)