Supporting Information

for

Solvent-free and room temperature microwave-assisted direct C7 allylation of indolines via sequential C–H and C–C activation

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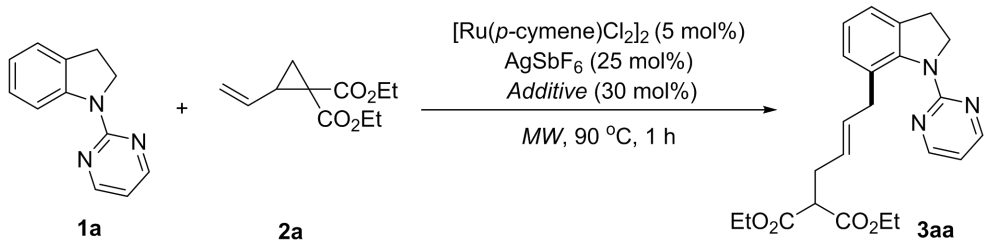
General Information

Unless otherwise mentioned, all materials were commercially obtained and used without further purification, and all procedures were performed under the nitrogen atmosphere. Indolines **1**,[1] vinylcyclopropanes **2**,[2-3] were synthesized according to previously described methods. The microwave irradiation experiments were carried out in a dedicated CEM Discover monomode microwave apparatus, operating at a frequency of 2.45 GHz with continuous irradiation power from 0 to 300 W and performed in glass vessels (capacity 10 mL) sealed with a septum. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 400 MHz or 600MHz, 151 MHz or 101MHz, and 376 MHz respectively on a Bruker DPX instrument using Me_4Si as an internal standard. New compounds for HRMS were tested on a Waters Q-Tof Micro MS/MS System ESI spectrometer. Chemical shift multiplicities are represented as follows: (s = singlet, d = doublet, m = multiplet, t = triple, dd = double doublet).

Experimental Section

1. Optimization of reaction conditions[a]

Table S1. Optimization of additive.[a]

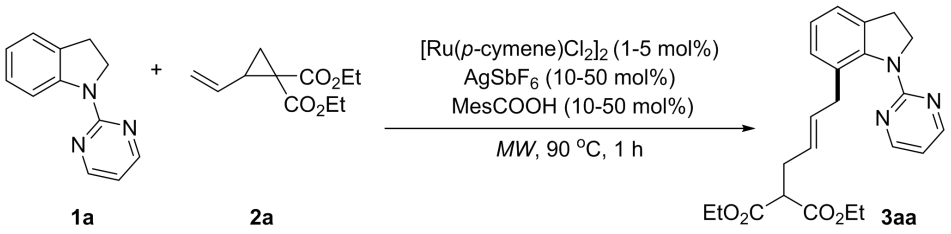


1a **2a** **3aa**

Entry	Additive	Yield [%]
1	NaOAc	20
2	$PivONa{\cdot}H_2O$	21
3	DABCO	trace
4	DBU	N.R.
5	Phen	trace
6	Pyridine	6
7	PivOH	29
8	AcOH	40
9	**MesCOOH**	**47**
10	1-AdCOOH	40

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), $AgSbF_6$ (25 mol%), additive (30 mol%), *MW*, 90 °C, 1 h. *MW* = microwave. Phen= 1,10-Phenanthroline hydrate; Isolated yield.

Table S2. Optimization of dosages[a]

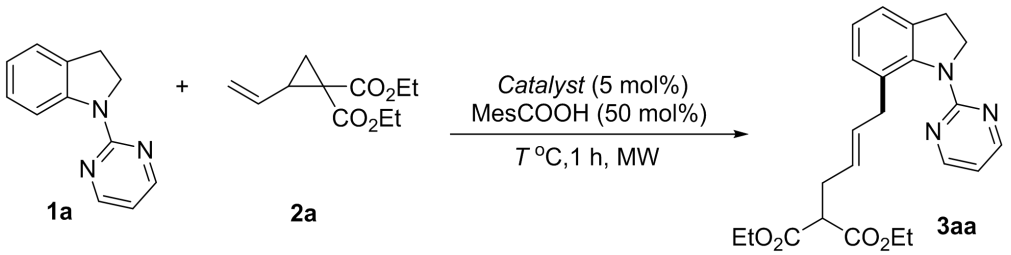


1a **2a** **3aa**

Entry	**2a** (mmol)	[Ru(*p*-cymene)Cl_2]$_2$ (mol%)	MesCOOH (mol%)	$AgSbF_6$ (mol%)	Yield [%]
1	0.2	5	30	25	23
2	0.4	5	30	25	47
4	0.4	1	30	25	21
5	0.4	2.5	30	25	37
6	0.4	5	10	25	33
7	**0.4**	**5**	**50**	**25**	**57**
8	0.4	5	50	10	14
9	0.4	5	50	50	20

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 - 0.4 mmol), Catalyst (1 - 5 mol%), $AgSbF_6$ (10 - 50 mol%), MesCOOH (10 - 50 mol%), *MW*, 90 °C, 1 h. *MW* = microwave. Isolated yield.

Table S3. Optimization of catalyst and temperature[a]

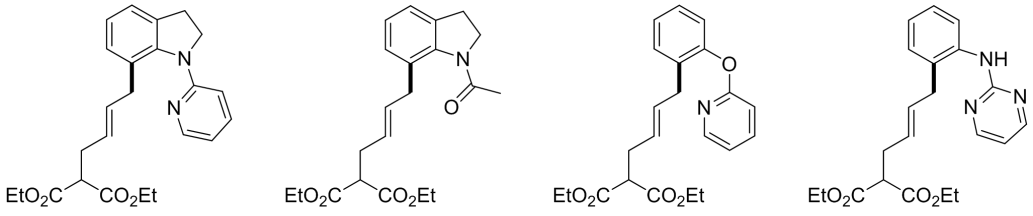


1a **2a** **3aa**

Entry	Catalyst (5 mol %)	T [°C]	Yield [%]
1	[Cp*$RuCl_2$]$_2$	90	N.R.
2	$RuCl_3 \cdot 3H_2O$	90	N.R.
3	[Ru(*p*-cymene)Cl_2]$_2$	90	57
4	[Ru(*p*-cymene)Cl_2]$_2$	110	10
5	[Ru(*p*-cymene)Cl_2]$_2$	70	68
6	[Ru(*p*-cymene)Cl_2]$_2$	50	83
7	[Ru(*p*-cymene)Cl_2]$_2$	25	65
8[b]	**[Ru(*p*-cymene)Cl_2]$_2$**	**25**	**87 (>20:1)[d]**
9[c]	**[Ru(*p*-cymene)Cl_2]$_2$**	**25**	**51 (>20:1)[d]**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Catalyst (5 mol%), $AgSbF_6$ (25 mol%), MesCOOH (50 mol%), *MW*, 1 h. *MW* = microwave. Isolated yield. [b]t = 2 h. [c]Oil bath. [d]The E:Z ratio was determined by ^{1}H NMR analysis.

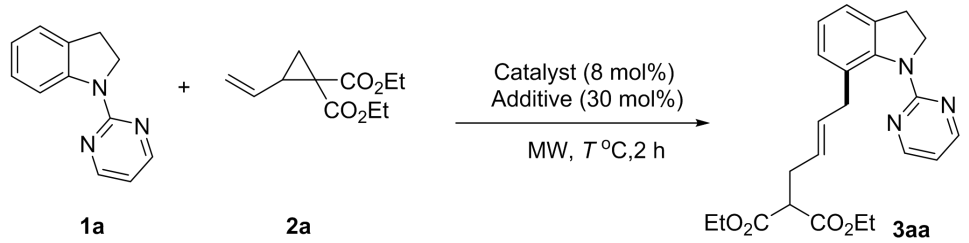
Table S4. Effect of the directing groups.



3b'a: 84% **3c'a**: ND **3d'a**: ND **3e'a**: ND

ND = not detect

Table S5. Optimization of the Reaction Conditions under Rh catalytic system[a]

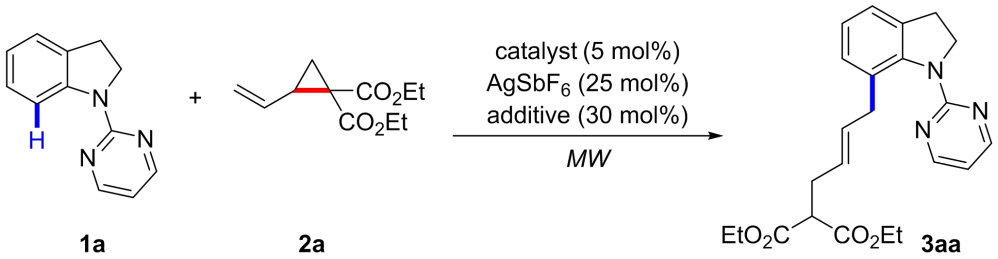


1a **2a** **3aa**

Entry	Catalyst (mol %)	Additive (mol%)	T [°C]	Yield [%]
1	$RhCl_3 \cdot 3H_2O$	AdCOOH	80	N.R.
2	$[Cp^*RhCl_2]_2$	AdCOOH	80	44
3	**$[RhCp^*(CH_3CN)_3](SbF_6)_2$**	**AdCOOH**	**80**	**78(10:1)[d]**
4	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	MesCOOH	80	43
5	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	PivOH	80	40
6	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	NaOAc	80	51
7	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	$PivONa \cdot H_2O$	80	47
8	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	DABCO	80	trace
9	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	AdCOOH	100	50
10	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	AdCOOH	90	55
11	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	AdCOOH	70	68
12	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	AdCOOH	25	trace
13[b]	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	AdCOOH	80	65
14[c]	$[RhCp^*(CH_3CN)_3](SbF_6)_2$	AdCOOH	80	21(>20:1)[d]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Catalyst (8 mol%), $AgSbF_6$ (20 mol%), Additive (30 mol%), *MW*, 80 °C, 2 h. *MW* = microwave. Isolated yield. [b]AdCOOH (50 mol%). [c]Oil bath. [d]The E:Z ratio was determined by ^1H NMR analysis.

Table S6. Summary of the Reaction Conditions[a]



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

entry	catalyst (mol%)	additive (mol%)	T (°C)	yield (%)
1	$[Ru(p\text{-cymene})Cl_2]_2$	AdCOOH	90	40
2	$RuCl_3{\cdot}3H_2O$	AdCOOH	90	N.R.
3	$[Cp^*RuCl_2]_2$	AdCOOH	90	N.R
4	$[Ru(p\text{-cymene})Cl_2]_2$	MesCOOH	90	47
5	$[Ru(p\text{-cymene})Cl_2]_2$	AcOH	90	40
6	$[Ru(p\text{-cymene})Cl_2]_2$	NaOAc	90	20
7	$[Ru(p\text{-cymene})Cl_2]_2$	$PivONa{\cdot}H_2O$	90	21
8	$[Ru(p\text{-cymene})Cl_2]_2$	DABCO	90	trace
9[b]	$[Ru(p\text{-cymene})Cl_2]_2$	MesCOOH	90	57
10[b]	$[Ru(p\text{-cymene})Cl_2]_2$	MesCOOH	70	68
11[b]	$[Ru(p\text{-cymene})Cl_2]_2$	MesCOOH	50	83
12[b]	$[Ru(p\text{-cymene})Cl_2]_2$	MesCOOH	25	65
13[b,c]	**$[Ru(p\text{-cymene})Cl_2]_2$**	**MesCOOH**	**25**	**87(>20:1)[e]**
14[c,d]	$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	AdCOOH	80	78(10:1)[e]

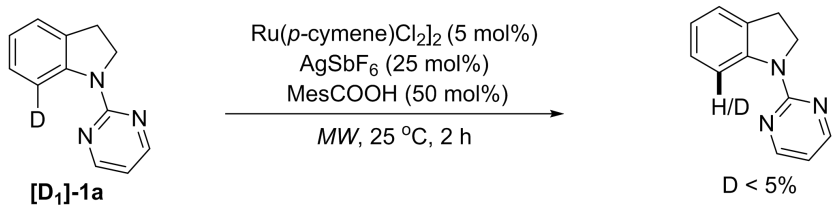
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), additive (30 mol%), *MW*, 1 h, 90 °C. [b]MesCOOH (50 mol%). [c]t = 2 h. [d]$[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (8 mol%). [e]The E:Z ratio was determined by ^1H NMR analysis. *MW* = microwave irradiation.

2. General procedure for the synthesis of 3

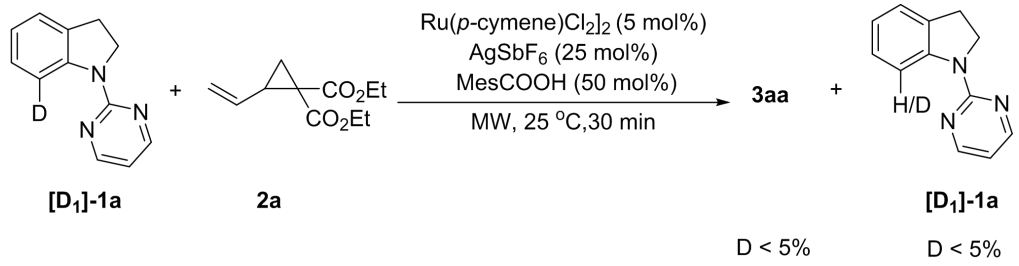
In a 10 mL glass vessel equipped with a magnetic stir bar was added indolines **1** (0.2 mmol), vinylcyclopropanes **2** (0.4 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and $AgSbF_6$ (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25°C for 2 h. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the desired products **3** were purified by preparative TLC on silica gel plates.

3. Control experiments and mechanistic studies

a) H/D exchange experiments

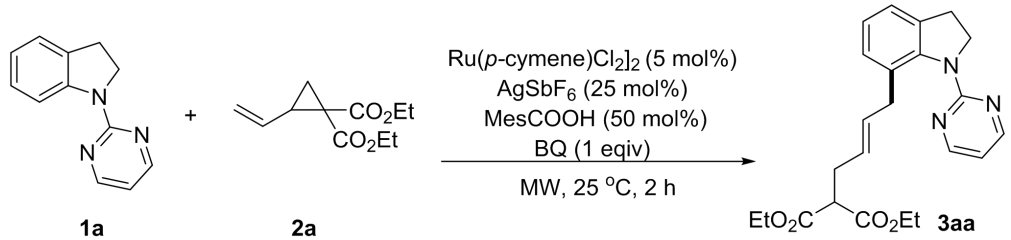


In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline **[D$_1$]-1a** (39.6 mg, 0.2 mmol), [Ru(*p*-cymene)Cl$_2$]$_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and $AgSbF_6$ (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25^{o}C for 2 h. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to recover **1a** in 86% yield (D < 5%). The H/D-ratio was determined by ^{1}H NMR.



In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline **[D$_1$]-1a** (39.6 mg, 0.2 mmol), vinylcyclopropane **2a** (84.8 mg, 0.4 mmol), [Ru(*p*-cymene)Cl$_2$]$_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and $AgSbF_6$ (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25^{o}C for 30 min. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue were purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give **3aa** in 32% yield (D < 5%). The H/D-ratio was determined by ^{1}H NMR.

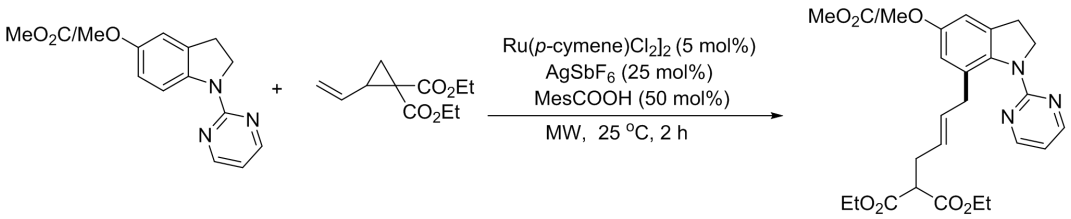
b) Radical scavenger reactions



General procedure for radical scavenger reactions

In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline **1a** (39.4 mg, 0.2 mmol), vinylcyclopropane **2a** (84.8 mg, 0.4 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%), $AgSbF_6$ (17.2 mg, 25 mol%), and a radical scavenger BQ (21.6 mg, 0.2 mmol). The vessel was sealed with a septum under microwave irradiated at 25^{o}C for 2 h. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue were purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give **3aa** in 68% yield.

c) Intermolecular Competition Experiment



1t/1o **2a** **3ta/3oa=1:2**

In a 10 mL glass vessel equipped with a magnetic stir bar was added indolines **1t** (51.1 mg, 0.2 mmol), **1o** (45.5 mg, 0.2 mmol), vinylcyclopropane **2a** (84.8 mg, 0.4 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%) and $AgSbF_6$ (17.2 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25^{o}C for 2 h. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue were purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give **3ta/3oa** = 1/2, which was determined by ^{1}H NMR analysis.

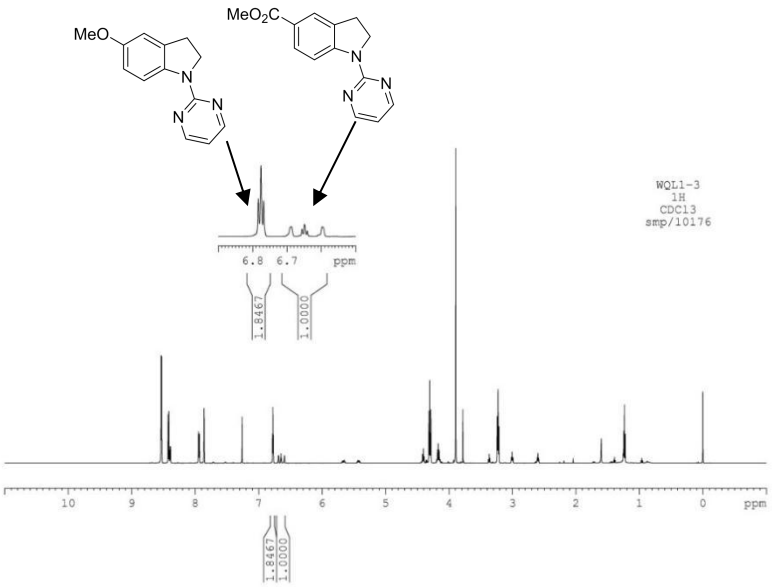
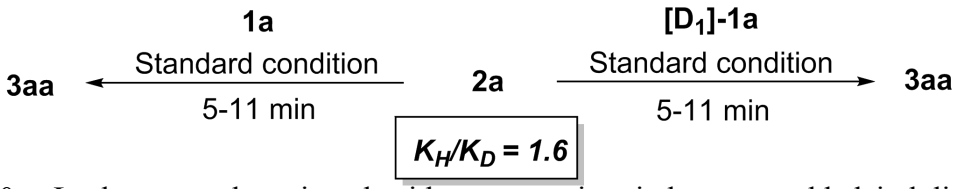


Figure S1. Intermolecular Competition Experiment

d) Kinetic isotope experiment



In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline **1a** (39.4 mg, 0.2 mmol) or **[D$_1$]-1a** (39.6 mg, 0.2 mmol),, vinylcyclopropane **2a** (84.8 mg, 0.4 mmol), [Ru(*p*-cymene)Cl$_2$]$_2$ (6.1 mg, 5 mol%), MesCOOH (16.4 mg, 50 mol%), AgSbF$_6$ (17.2 mg, 25 mol%). The tubes were heated at 25 ^{o}C for 11, 13, 15, 17 minutes and quenched separately with 1mL EA. Next, the reaction mixture was diluted with 25 mL EA and filtered through a celite pad. The solvent was removed in vacuum and ^{1}H NMR was taken separately using 0.2 mmol anisole (21.6 mg) as the internal standard. The KIE was determined as k_H/k_D = 2.7/1.7 $\approx$ 1.6

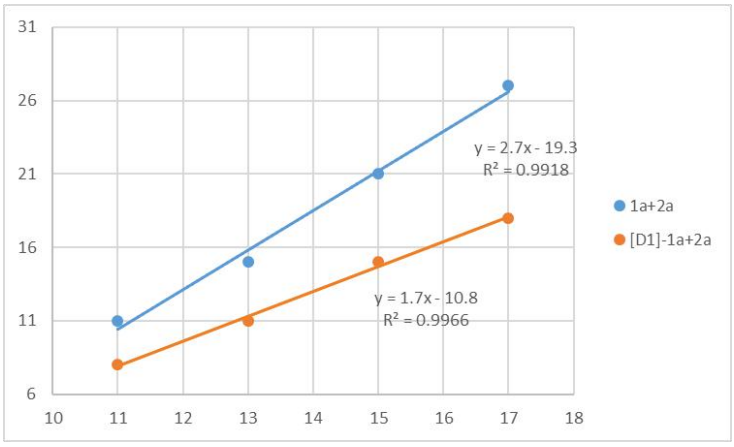
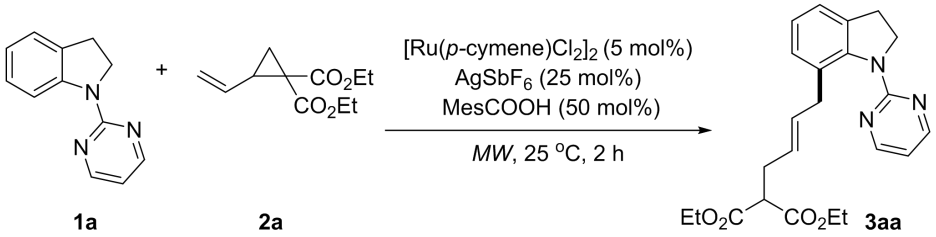


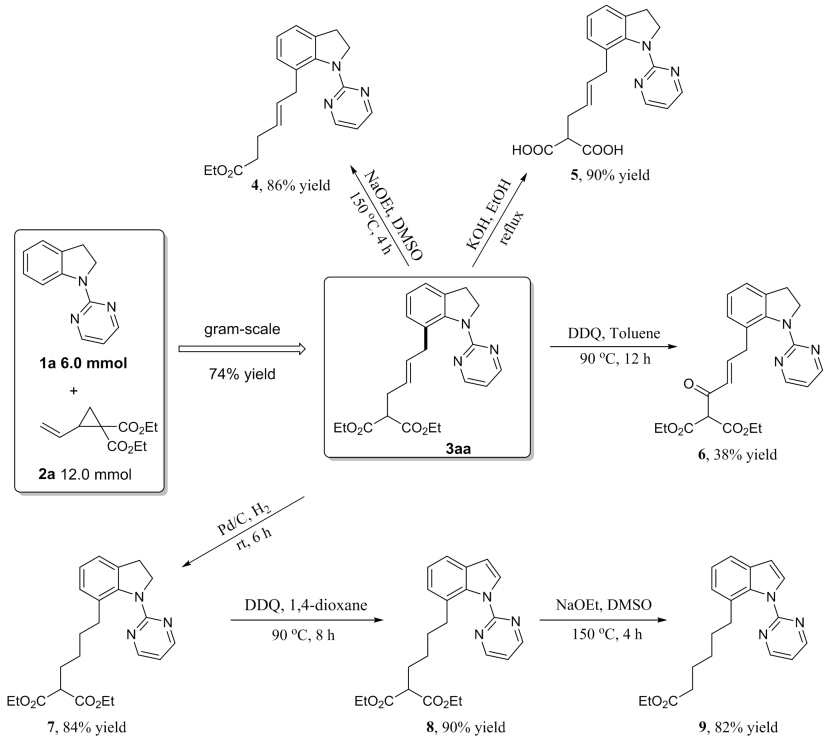
Figure S2. Kinetic isotope experiment

e) Scale-up experiment



In a 10 mL glass vessel equipped with a magnetic stir bar was added indoline **1a** (1.2 g, 6.0 mmol), vinylcyclopropane **2a** (2.5 g, 12.0 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (183.6 mg, 5 mol%), MesCOOH (492.6 mg, 50 mol%) and $AgSbF_6$ (515.4 mg, 25 mol%). The vessel was sealed with a septum under microwave irradiated at 25°C for 2 h. The reaction mixture was then diluted with CH_2Cl_2 (100 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 3/1) to give **3aa** in 74% yield.

4. Derivatization of 3aa



Scheme S1. Gram-scale reaction and further derivatization of product **3aa**

(E)-Ethyl 6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enoate 4

In a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added **3aa** (81.8 mg, 0.2 mmol) and NaOEt (68.1 mg, 1.0 mmol) in DMSO (0.5 mL). The reaction

mixture was stirred at 150 °C for 4 h, and then cooled down to room temperature. The solution was extracted with ethyl acetate and the combined organic layer was dried over magnesium sulfate. After removal of organic solvent, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to give product **4** in 86% yield.

(E)-2-(4-(1-(Pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonic acid 5

To a 50 mL schlenk flask was added **3aa** (794.4 mg, 19.4 mmol) in a solution of KOH (3.26 g, 58.1 mmol) in ethanol (9.8 mL) and H_2O (9.8 mL). After refluxed for 6 h, the organic phase was evaporated under vacuum. Aqueous phase was then neutralized with 1M HCl and extracted with ether. The combined organic phase was washed with water, brine, and dried over $MgSO_4$. After removal of organic solvent, product **5** was obtained in 90 % yield, which is pure enough for NMR characterizations .

(E)-Diethyl-2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-enoyl)malonate 6

To a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added **3aa** (81.8 mg, 0.2 mmol), DDQ (45.4 mg, 0.2 mmol) in toluene (1mL). The vessel was sealed and heated at 90 °C for 12 h. After cooled down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 6/1) to give product **6** in 38% yield.

Diethyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)butyl)malonate 7

To a solution of **3aa** (81.8 mg, 0.2 mmol) in MeOH (1.0 mL) was added Pd/C (9.5 mg, 10 wt.%) under hydrogen atmosphere. The mixture was stirred at 25 °C for 12 h and then filtered through a short celite pad. The residue was washed with EtOAc (10 mL), filtered, and the combined filtrate was concentrated in vacuo. The crude mixture was purified by preparative TLC on silica gel plates (PE/EA: 5/1) to give product **7** in 84% yield.

Diethyl 2-(4-(1-(pyrimidin-2-yl)-1H-indol-7-yl)butyl)malonate 8

To a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added **7** (82.2 mg, 0.2 mmol), DDQ (45.4 mg, 0.2 mmol) in 1,4-dioxane (1mL). The vessel was sealed and heated at 90 °C for 8 h. After cooled down to room temperature, the reaction mixture was diluted with CH_2Cl_2 (25 mL) and filtered through a celite pad. After removal of organic solvent under vacuum, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to give product **8** in 90% yield.

Ethyl 6-(1-(pyrimidin-2-yl)-1H-indol-7-yl)hexanoate 9

To a 35 mL dry screw-cap tube equipped with a magnetic stir bar was added **8** (81.8 mg, 0.2 mmol), NaOEt (68.1 mg, 1 mmol) in DMSO (0.5 mL). The vessel was sealed and heated at 150 ^{o}C for 4 h. After cooled down to room temperature, the solution was extracted with ethyl acetate and the combined organic layer was dried over magnesium sulfate. After removal of organic solvent, the residue was purified by preparative TLC on silica gel plates (PE/EA = 5/1) to give product **9** in 82% yield.

Reference

(1). Li, H.; Jie, J.; Wu, S.; Yang, X.; Xu, H., Rh(III)-Catalyzed direct C-7 amination of indolines with anthranils. *Org. Chem. Front.* **2017**, *4*, 250-254, DOI 10.1039/C6QO00709K.

(2) Dey, R.; Banerjee, P., Lewis Acid Catalyzed Diastereoselective Cycloaddition Reactions of Donor–Acceptor Cyclopropanes and Vinyl Azides: Synthesis of Functionalized Azidocyclopentane and Tetrahydropyridine Derivatives. *Org Lett.* **2017**, *19*, 304−307, DOI 10.1021/acs.orglett.6b03276.

(3) Dieskau, A. P.; Holzwarth, M. S.; Plietker, B., Fe-Catalyzed Allylic C–C-Bond Activation: Vinylcyclopropanes As Versatile a1, a3, d5-Synthons in Traceless Allylic Substitutions and [3 + 2]-Cycloadditions. *J. Am. Chem. Soc.* **2012**, *134*, 5048−5051, DOI 10.1021/ja300294a.

Characterization of Products

(E)-Diethyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3aa):** purified using PE/EA (3:1) as an eluent, R_f = 0.31; yellow oil (71.2 mg, 87%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 3.6 Hz, 2H), 7.14 – 6.94 (m, 3H), 6.68 (s, 1H), 5.69 – 5.58 (m, 1H), 5.45 – 5.34 (m, 1H), 4.41 (q, J = 7.3 Hz, 2H), 4.12 – 4.22 (m, 4H), 3.40 – 3.18 (m, 3H), 3.05 (t, J = 7.3 Hz, 2H), 2.60 (m, 2H), 1.24 (m, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.4, 157.6, 142.4, 134.8, 134.7, 131.8, 131.1, 130.5, 128.2, 128.1, 127.1, 125.8, 124.3, 124.2, 122.3, 112.2, 61.3, 53.3, 53.2, 52.2, 52.0, 36.9, 31.8, 29.9, 26.7, 14.1. HRMS (positive ESI): Calcd for $C_{23}H_{28}N_3O_4$ ($M + H^+$) 410.2075, found 410.2079.

(E)-Diethyl 2-(4-(2-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ba):** purified using PE/EA (3:1) as an eluent, R_f = 0.27; yellow oil (81.3mg, 96%, E/Z = 8:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (t, J = 5.8 Hz, 2H), 7.13 – 6.93 (m, 3H), 6.70 – 6.58 (m, 1H), 5.65 – 5.53 (m, 1H), 5.34 (m, 1H), 5.03 – 4.90 (m, 1H), 4.21 – 4.11 (m, 4H), 3.50 – 3.18 (m, 4H), 2.64 – 2.39 (m, 3H), 1.36 (t, J = 9.7 Hz, 3H), 1.27 – 1.18 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 160.8, 157.6, 140.8, 140.7, 133.5, 131.8, 131.2, 131.1, 130.8, 128.4, 128.2, 126.9, 125.6, 124.2, 124.1, 122.9, 112.3, 112.2, 61.3, 60.4, 52.2, 37.1, 36.9, 32.0, 31.8, 26.7, 21.1, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{30}N_3O_4$ ($M + H^+$) 424.2231, found 424.2234.

(E)-Diethyl 2-(4-(2-(tert-butyl)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ca):** purified using PE/EA (3:1) as an eluent, R_f = 0.39; yellow oil (75.3mg, 81%, E/Z = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 4.8 Hz, 2H), 7.34 – 7.22 (m, 4H), 7.09 – 6.95 (m, 3H), 6.70 (t, J = 4.8 Hz, 1H), 5.95 (d, J = 8.7 Hz, 1H), 5.70 (dt, J = 15.1, 7.0 Hz, 1H), 5.51 – 5.32 (m, 1H), 4.21 – 4.09 (m, 4H), 3.88 – 3.74 (m, 1H), 3.51 – 3.23 (m, 3H), 2.97 (d, J = 15.4 Hz, 1H), 2.69 – 2.54 (m, 2H), 1.28 – 1.18 (m, 15H).13C NMR (151 MHz, $CDCl_3$) δ 169.1, 161.3, 157.8, 149.8, 141.9, 140.3, 133.1, 131.9, 131.2, 130.6, 128.5, 127.3, 125.4, 125.3, 124.5, 122.7, 112.8, 112.7, 66.7, 61.3, 52.2, 52.1, 38.5, 37.2, 34.4, 31.9, 31.4, 26.8, 14.1. HRMS (positive ESI): Calcd for $C_{33}H_{39}N_3O_4$ ($M + H^+$) 542.3014, found 542.3015.

(E)-Diethyl 2-(4-(2-phenyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3da):** purified using PE/EA (3:1) as an eluent, R_f = 0.38; yellow oil (87.3mg, 90%, E/Z = 7:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45-8.39 (m, $2H_{[E]} + 2H_{[Z]}$), 7.38-7.32 (m,

$2H_{[E]}$ + $2H_{[Z]}$), 7.30-7.26 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.22-7.19 (m, $1H_{[E]}$ + $1H_{[Z]}$), 7.10 – 6.98 (m, $3H_{[E]}$ + $3H_{[Z]}$), 6.74-6.70 (m, $1H_{[E]}$ + $1H_{[Z]}$), 6.01-5.96 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.72-5.65 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.48 – 5.44 (m, $1H_{[Z]}$), 5.41-5.34 (m, $1H_{[E]}$), 4.21 – 4.10 (m, $4H_{[E]}$ + $4H_{[Z]}$), 3.84 (dd, *J* = 15.5, 9.1 Hz, $1H_{[E]}$ + $1H_{[Z]}$), 3.59 (dd, *J* = 16.5, 7.5 Hz, $1H_{[Z]}$), 3.44 (dd, *J* = 15.9, 6.9 Hz, $1H_{[E]}$), 3.37-3.31 (m, $2H_{[E]}$ + $2H_{[Z]}$), 2.97 (d, *J* = 15.5 Hz, $1H_{[E]}$ + $1H_{[Z]}$), 2.70 – 2.54 (m, $2H_{[E]}$ + $2H_{[Z]}$), 1.25 – 1.21 (m, $6H_{[E]}$ + $6H_{[Z]}$). ^{13}C NMR (151 MHz, $CDCl_3$) *δ* 169.0, 161.3, 158.1, 157.8, 143.5, 142.0, 141.9, 132.9, 131.9, 131.2, 130.8, 130.5, 128.6, 128.5, 128.4, 127.3, 127.1, 125.9, 125.7, 124.7, 122.7, 112.8, 67.0, 66.9, 61.4, 61.3, 52.2, 52.0, 38.5, 37.3, 32.0, 31.9, 26.8, 14.1. HRMS (positive ESI): Calcd for $C_{29}H_{32}N_3O_4$ (M + H+) 486.2388, found 486.2390.

*(E)-Diethyl2-(4-(2-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate***(3ea):** purified using PE/EA (3:1) as an eluent, R_f = 0.33; yellow oil (57.6mg, 65%, E/Z = 5:1). ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.45 – 8.39 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.32 – 7.23 (m, $4H_{[E]}$ + $4H_{[Z]}$), 7.22 – 7.19 (m, $1H_{[E]}$ + $1H_{[Z]}$), 7.10 – 6.98 (m, $3H_{[E]}$ + $3H_{[Z]}$), 6.76 – 6.72 (m, $1H_{[E]}$ + $1H_{[Z]}$), 6.00 – 5.90 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.70 – 5.61 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.48 – 5.44 (m, $1H_{[Z]}$), 5.41 – 5.34 (m, $1H_{[E]}$), 4.21 – 4.10 (m, $4H_{[E]}$ + $4H_{[Z]}$), 3.84 (dd, *J* = 15.5, 9.1 Hz, $1H_{[E]}$ + $1H_{[Z]}$), 3.59 (dd, *J* = 16.5, 7.5 Hz, $1H_{[Z]}$), 3.44 (dd, *J* = 15.9, 6.9 Hz, $1H_{[E]}$), 3.37-3.31 (m, $2H_{[E]}$ + $2H_{[Z]}$), 2.97 (d, *J* = 15.5 Hz, $1H_{[E]}$ + $1H_{[Z]}$), 2.70 – 2.54 (m, $2H_{[E]}$ + $2H_{[Z]}$), 1.25 – 1.21 (m, $6H_{[E]}$ + $6H_{[Z]}$).^{13}C NMR (151 MHz, $CDCl_3$) *δ* 169.0, 161.2, 157.8, 142.1, 141.6, 132.8, 132.6, 131.7, 131.0, 130.5, 128.8, 128.6, 127.4, 127.2, 126.0, 124.8, 124.7, 122.7, 113.0, 66.5, 66.4, 61.4, 61.3, 52.1, 52.0, 38.3, 37.3, 32.0, 31.8, 26.7, 14.1. HRMS (positive ESI): Calcd for $C_{29}H_{30}ClN_3O_4$ (M + H^+) 520.1998, found 520.2000.

*(E)-Diethyl2-(4-(2-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate***(3fa):** purified using PE/EA (3:1) as an eluent, R_f = 0.36; yellow oil (73.3mg, 75%, E/Z = 3:1). ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.45-8.39 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.43-7.38 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.27 – 7.21 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.10 – 6.98 (m, $3H_{[E]}$ + $3H_{[Z]}$), 6.76 – 6.72 (m, $1H_{[E]}$ + $1H_{[Z]}$), 6.00 – 5.90 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.70 – 5.61 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.48 – 5.44 (m, $1H_{[Z]}$), 5.41 – 5.34 (m, $1H_{[E]}$), 4.21 – 4.10 (m, $4H_{[E]}$ + $4H_{[Z]}$), 3.84 (dd, *J* = 15.5, 9.1 Hz, $1H_{[E]}$ + $1H_{[Z]}$), 3.59 (dd, *J* = 16.5, 7.5 Hz, $1H_{[Z]}$), 3.44 (dd, *J* = 15.9, 6.9 Hz, $1H_{[E]}$), 3.37-3.31 (m, $2H_{[E]}$ + $2H_{[Z]}$), 2.97 (d, *J* = 15.5 Hz, $1H_{[E]}$ + $1H_{[Z]}$), 2.70 – 2.54 (m, $2H_{[E]}$ + $2H_{[Z]}$), 1.25 – 1.21 (m, $6H_{[E]}$ + $6H_{[Z]}$).^{13}C NMR (151 MHz, $CDCl_3$) *δ* 169.0, 161.2, 157.8, 142.6, 141.7, 141.6, 132.5, 131.7, 131.6, 131.4, 131.0, 130.9,

130.5, 128.8, 128.6, 127.5, 127.4, 126.1, 124.9, 124.7, 122.7, 120.9, 113.0, 66.5, 61.4, 61.3, 52.1, 52.0, 38.3, 37.3, 32.0, 31.8, 26.7, 14.1. HRMS (positive ESI): Calcd for $C_{29}H_{30}BrN_3O_4$ (M + H^+) 564.1493, found 564.1495.

(E)-Diethyl 2-(4-(2-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ga):** purified using PE/EA (3:1) as an eluent, R_f = 0.27; yellow oil (77.0 mg, 91%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (t, J = 5.8 Hz, 2H), 7.13 – 6.93 (m, 3H), 6.70 – 6.58 (m, 1H), 5.65 – 5.53 (m, 1H), 5.34 (m, 1H), 5.03 – 4.90 (m, 1H), 4.21 – 4.11 (m, 4H), 3.50 – 3.18 (m, 4H), 2.64 – 2.39 (m, 3H), 1.36 (t, J = 9.7 Hz, 3H), 1.27 – 1.18 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 160.8, 157.6, 140.8, 140.7, 133.5, 131.8, 131.2, 131.1, 130.8, 128.4, 128.2, 126.9, 125.6, 124.2, 124.1, 122.9, 112.3, 112.2, 61.3, 60.4, 52.2, 37.1, 36.9, 32.0, 31.8, 26.7, 21.1, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{30}N_3O_4$ (M + H^+) 424.2231, found 424.2234.

(E)-Diethyl 2-(4-(4-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ha):** purified using PE/EA (3:1) as an eluent, R_f = 0.25; yellow oil (76.2mg, 90%, E/Z >20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 – 8.34 (m, 2H), 6.96 (d, J = 7.6 Hz, 1H), 6.89 – 6.78 (m, 1H), 6.68-6.64 (m, 1H), 5.69 – 5.57 (m, 1H), 5.43 – 5.29 (m, 1H), 4.41 (q, J = 7.6 Hz, 2H), 4.20 – 4.10 (m, 4H), 3.40 – 3.13 (m, 3H), 2.95 (t, J = 7.5 Hz, 2H), 2.65 – 2.55 (m, 2H), 2.24 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.5, 157.6, 142.0, 141.9, 133.4, 132.0, 131.6, 128.2, 127.7, 125.5, 112.7, 61.33, 61.30, 53.0, 52.2, 52.0, 36.7, 31.9, 31.5, 28.6, 26.7, 18.5, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{30}N_3O_4$ (M + H^+) 424.2231, found 424.2235.

(E)-Diethyl 2-(4-(4-methoxy-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ia):** purified using PE/EA (3:1) as an eluent, R_f = 0.33; yellow oil (80.8mg, 92%, E/Z > 20:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.39 (m, 2H), 7.01 (t, J = 6.9 Hz, 1H), 6.68 (dd, J = 15.3, 10.9 Hz, 1H), 6.60 (d, J = 8.4 Hz, 1H), 5.66 – 5.57 (m, 1H), 5.41 – 5.32 (m, 1H), 4.44- 4.38 (m, 2H), 4.23 – 4.07 (m, 4H), 3.82 (s, 3H), 3.42 – 3.11 (m, 3H), 2.98 (t, J = 7.4 Hz, 2H), 2.63 – 2.55 (m, 2H), 1.27 – 1.21 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.5, 157.6, 154.3, 143.7, 132.2, 131.5, 129.2, 126.7, 125.4, 123.3, 121.8, 121.7, 112.3, 106.9, 61.3, 55.5, 53.7, 52.3, 36.4, 31.8, 31.2, 26.7, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{30}N_3O_5$ (M + H^+) 440.2180, found 440.2184.

(E)-Diethyl 2-(4-(5-(benzyloxy)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ja):** purified using PE/EA (3:1) as an eluent, R_f = 0.27; yellow oil (95.5mg, 93%,

E/Z > 20:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46 – 8.38 (m, 2H), 7.44 – 7.29 (m, 5H), 7.00 – 6.94 (m, 1H), 6.72 – 6.61 (m, 2H), 5.66 – 5.57 (m, 1H), 5.41 – 5.33 (m, 1H), 5.10 (s, 2H), 4.45 – 4.38 (m, 2H), 4.21 – 4.11 (m, 4H), 3.38 – 2.97 (m, 5H), 2.64 – 2.53 (m, 2H), 1.28 – 1.16 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.4, 157.7, 153.5, 143.8, 137.5, 132.2, 131.5, 129.2, 128.5, 127.8, 126.8, 125.5, 123.6, 122.4, 112.4, 108.5, 70.1, 61.4, 53.7, 52.3, 36.4, 31.9, 26.8, 14.10, 14.0. HRMS (positive ESI): Calcd for $C_{30}H_{34}N_3O_5$ ($M + H^+$) 516.2493, found 516.2495.

*(E)-Diethyl -2-(4-(4-fluoro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate***(3ka):** purified using PE/EA (3:1) as an eluent, R_f = 0.32; yellow oil (80.3mg, 94%, E/Z > 20:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 4.8 Hz, 2H), 7.03 – 6.95 (m, 1H), 6.77 – 6.65 (m, 2H), 5.66 – 5.52 (m, 1H), 5.44 – 5.29 (m, 1H), 4.48 – 4.40 (m, 2H), 4.24 – 4.07 (m, 4H), 3.39 – 3.14 (m, 2H), 3.07 (t, J = 7.7 Hz, 2H), 2.58 (t, J = 7.3 Hz, 2H), 1.27 – 1.19 (q, J = 7.6 Hz, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.2, 157.7, 157.6 ($J_{C\text{-}F}$ = 245.3 Hz), 157.6, 144.4 ($J_{C\text{-}F}$ = 7.5 Hz), 131.6, 130.9, 129.8 ($J_{C\text{-}F}$ = 8.0 Hz), 127.3, 126.0 ($J_{C\text{-}F}$ = 3.2 Hz), 125.9, 120.4 ($J_{C\text{-}F}$ = 21.2 Hz), 112.7, 111.0, 110.8, 61.4, 61.3, 53.6, 52.2, 36.5, 31.8, 25.9, 14.1.^{19}F NMR (565 MHz, $CDCl_3$) δ -122.6. HRMS (positive ESI): Calcd for $C_{23}H_{26}FN_3O_4$($M + H^+$) 428.1980, found 428.1981.

*(E)-Diethyl 2-(4-(4-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate***(3la):** purified using PE/EA (3:1) as an eluent, R_f = 0.29; yellow oil (85.1mg, 96%, E/Z > 20:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 4.8 Hz, 2H), 6.99 (s, 2H), 6.76 – 6.71 (m, 1H), 5.67 – 5.53 (m, H), 5.45 – 5.31 (m, H), 4.47 – 4.39 (m, 2H), 4.23 – 4.10 (m, 4H), 3.41 – 3.16 (m, 3H), 3.09 (t, J = 7.8 Hz, 2H), 2.59 (t, J = 7.0 Hz, 2H), 1.28 – 1.19 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.2, 157.6, 143.6, 132.9, 131.3, 130.6, 128.8, 128.0, 127.5, 123.9, 112.8, 61.4, 6.32, 52.1, 36.6, 31.8, 29.2, 26.7, 14.2, 14.1. HRMS (positive ESI): Calcd for $C_{23}H_{26}ClN_3O_4$ ($M + H^+$) 444.1685, found 444.1684.

(E)-Diethyl 2-(4-(4-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ma):** purified using PE/EA (3:1) as an eluent, R_f = 0.33; yellow oil (53.1mg, 54%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 – 8.32 (m, 2H), 7.18 – 7.08 (m, 1H), 6.91 (t, J = 18.4 Hz, 1H), 6.73 (d, J = 4.3 Hz, 1H), 5.63 – 5.51 (m, 1H), 5.45 – 5.32 (m, 1H), 4.42 (q, J = 7.8 Hz, 2H), 4.22 – 4.09 (m, 4H), 3.41 – 2.98 (m, 5H), 2.62 – 2.52 (m, 2H), 1.29 – 1.18 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.2, 157.7,

143.4, 135.2, 131.2, 130.5, 129.9, 127.6, 126.9, 116.6, 112.8, 61.4, 52.5, 52.1, 51.9, 36.6, 31.8, 31.5, 26.7, 14.1. HRMS (positive ESI): Calcd for $C_{23}H_{27}BrN_3O_4$ (M + H^+) 488.1180, found 488.1182.

(E)-Diethyl 2-(4-(5-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3na):** purified using PE/EA (3:1) as an eluent, R_f = 0.37; yellow oil (73.6mg, 86%, E/Z = 11:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 – 8.31 (m, 2H), 6.92 (s, 1H), 6.85 (s, 1H), 6.66 (d, *J* = 4.3 Hz, 1H), 5.71 – 5.59 (m, 1H), 5.45 – 5.31 (m, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 4.22 – 4.09 (m, 4H), 3.40 – 3.16 (m, 3H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.63 – 2.58 (m, 2H), 2.31 (s, 3H), 1.30 – 1.16 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.5, 157.7, 140.0, 134.9, 133.9, 131.9, 130.2, 128.7, 127.0, 123.2, 112.0, 61.3, 53.3, 52.3, 36.8, 31.9, 31.6, 29.9, 26.7, 21.0, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{30}N_3O_4$ (M + H^+) 424.2231, found 424.2233.

(E)-Diethyl 2-(4-(5-methoxy-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3oa):** purified using PE/EA (3:1) as an eluent, R_f = 0.26; yellow oil (79.1mg, 90%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (t, *J* = 6.7 Hz, 2H), 6.73 – 6.56 (m, 3H), 5.72 – 5.61 (m, 1H), 5.49 – 5.36 (m, 1H), 4.41 (t, *J* = 7.4 Hz, 2H), 4.23 – 4.10 (m, 4H), 3.78 (s, 3H), 3.40 – 2.93 (m, 5H), 2.63 – 2.55 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.6, 157.7, 157.1, 136.2, 134.0, 131.7, 127.3, 126.0, 113.1, 111.9, 108.6, 61.3, 55.6, 53.4, 52.22, 52.0, 36.9, 31.8, 30.4, 26.7, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{30}N_3O_5$ (M + H^+) 440.2180, found 440.2181.

(E)-Diethyl 2-(4-(5-(benzyloxy)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3pa):** purified using PE/EA (3:1) as an eluent, R_f = 0.27; yellow oil (82.4mg, 80%, E/Z >20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (t, *J* = 7.1 Hz, 2H), 7.43 – 7.37 (m, 5H), 6.78 – 6.61 (m, 3H), 5.66 – 5.58 (m, 1H), 5.48 – 5.34 (m, 1H), 5.03 (s, 2H), 4.45 – 4.38 (m, 2H), 4.22 – 4.06 (m, 4H), 3.41 – 3.18 (m, 3H), 3.07 – 3.01 (m, 2H), 2.64 – 2.55 (m, 2H), 1.26 – 1.16 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.4, 157.7, 153.5, 143.8, 137.5, 132.2, 129.2, 128.5, 127.8, 126.8, 125.5, 123.6, 122.4, 112.4, 108.5, 70.1, 61.4, 53.7, 52.3, 36.4, 31.9, 31.2, 26.8, 26.8, 14.1. HRMS (positive ESI): Calcd for $C_{30}H_{34}N_3O_5$ (M + H^+) 516.2493, found 516.2495.

(E)-Diethyl 2-(4-(5-fluoro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3qa):** purified using PE/EA (3:1) as an eluent, R_f = 0.28; yellow oil (77.1mg, 91%, E/Z = 10:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.3 Hz, 2H), 7.05 – 7.00 (m, 1H), 6.79 – 6.62 (m, 2H), 5.65 – 5.47 (m, 1H), 5.27 – 5.09 (m, 1H), 4.42 (t, *J* = 7.5 Hz,

2H), 4.22 – 4.06 (m, 4H), 3.45 – 3.13 (m, 3H), 2.99 (t, J = 7.3 Hz, 2H), 2.49 (t, J = 7.0 Hz, 2H), 1.27 – 1.20 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 162.1, 161.1, 160.5, 157.7, 144.0, 143.9, 130.4, 130.2, 126.3, 125.1, 122.6, 122.5, 118.7, 118.6, 112.7, 110.6, 110.4, 61.3, 54.0, 52.1, 51.9, 31.8, 30.6, 30.5, 29.2, 26.6, 14.1, 14.0. 143.9($J_{C\text{-}F}$ = 8.1), 130.4, 130.2($J_{C\text{-}F}$ = 2.2), 126.3, 122.5 ($J_{C\text{-}F}$ = 10.4), 118.6 ($J_{C\text{-}F}$ = 19.1), 112.7, 110.5 ($J_{C\text{-}F}$ = 24.3), 61.3, 54.0, 52.1, 31.8, 30.5, 30.5, 29.2, 14.0. ^{19}F NMR(376 MHz, $CDCl_3$) δ -119.2. HRMS (positive ESI): Calcd for $C_{23}H_{27}FN_3O_4$ (M + H^+) 428.1980, found 428.1982.

(E)-Diethyl 2-(4-(5-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ra):** purified using PE/EA (3:1) as an eluent, R_f = 0.23; yellow oil (79.8mg, 90%, E/Z > 20:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 4.3, 2H), 7.07 (d, J = 1.9 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.75 – 6.66 (m, 1H), 5.67 – 5.57 (m, 1H), 5.48 – 5.38 (m, 1H), 4.46 – 4.37 (m, 2H), 4.25 – 4.11 (m, 4H), 3.42 – 3.15 (m, 3H), 3.03 (t, J = 7.7 Hz, 2H), 2.61 (t, J = 6.8 Hz, 2H), 1.27-1.22 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 161.3, 157.7, 141.2, 136.6, 132.0, 130.9, 129.2, 128.0, 122.5, 112.6, 61.4, 53.3, 52.1, 36.7, 31.8, 29.8, 14.1. HRMS (positive ESI): Calcd for $C_{23}H_{27}ClN_3O_4$ (M + H^+) 444.1685, found 444.1689.

(E)-Diethyl 2-(4-(5-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3sa):** purified using PE/EA (3:1) as an eluent, R_f = 0.21; yellow oil (71.2mg, 73%, E/Z > 20:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (t, J = 7.4 Hz, 2H), 7.21 (s, 1H), 7.15 (s, 1H), 6.72 (t, J = 4.5 Hz, 1H), 5.66 – 5.55 (m, 1H), 5.47 – 5.33 (m, 1H), 4.41 (q, J = 7.8 Hz, 2H), 4.24 – 4.12 (m, 4H), 3.41 – 3.15 (m, 3H), 3.03 (t, J = 7.5 Hz, 2H), 2.60 (t, J = 7.0 Hz, 2H), 1.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 161.2, 157.7, 141.7, 137.0, 132.4, 130.8, 128.0, 126.6, 125.4, 116.9, 112.6, 61.4, 53.3, 52.1, 51.9, 36.7, 31.8, 31.5, 3.67, 26.7, 14.1 HRMS (positive ESI): Calcd for $C_{23}H_{27}BrN_3O_4$ (M + H^+) 488.1880, found 488.1184.

(E)-Diethyl-2-(4-(5-(methoxycarbonyl)-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ta):** purified using PE/EA (3:1) as an eluent, R_f = 0.23; yellow oil (56.1mg, 72%, E/Z = 4:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 – 8.41 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.77 (s, $2H_{[E]}$ + $2H_{[Z]}$), 6.81 – 6.70 (m, $H_{[E]}$ + $H_{[Z]}$), 5.64 – 5.56 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.45 – 5.40 (m, $1H_{[Z]}$), 5.39 – 5.32 (m, $1H_{[E]}$), δ 4.47 – 4.40 (m, $2H_{[E]}$ + $2H_{[Z]}$) 4.21 – 4.12 (m, $4H_{[E]}$ + $4H_{[Z]}$), 3.91 – 3.87 (m, $3H_{[E]}$ + $3H_{[Z]}$), 3.40 – 3.27 (m, $3H_{[E]}$ + $3H_{[Z]}$), 3.13 – 3.08 (m, $2H_{[E]}$ + $2H_{[Z]}$), 2.61 – 2.54 (m, $2H_{[E]}$ + $2H_{[Z]}$), 1.25 – 1.21 (m, $6H_{[E]}$ + $6H_{[Z]}$).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 167.1, 160.8, 157.7, 146.6, 134.9, 130.9, 130.7, 130.4, 129.5, 127.6, 126.4, 125.6, 123.8, 113.0, 61.4, 61.3, 53.5, 53.4, 52.1, 51.9, 37.1, 31.9, 31.8, 29.2, 26.7, 14.1. HRMS (positive ESI): Calcd for $C_{25}H_{30}N_3O_6$ ($M + H^+$) 468.2129, found 468.2133.

(E)-Diethyl 2-(4-(5-methyl-2-phenyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ua):** purified using PE/EA (3:1) as an eluent, R_f = 0.35; yellow oil (81.9mg, 82%, E/Z = 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 – 8.39 (m, $2H_{[E]} + 2H_{[Z]}$), 7.38 – 7.32 (m, $2H_{[E]} + 2H_{[Z]}$), 7.30 – 7.26 (m, $2H_{[E]} + 2H_{[Z]}$), 7.22 – 7.19 (m, $1H_{[E]} + 1H_{[Z]}$),δ 6.86 (d, J = 6.8 Hz, $2H_{[E]} + 2H_{[Z]}$), 6.72 – 6.68 (m, $1H_{[E]} + 1H_{[Z]}$), 6.01 – 5.96 (m, $1H_{[E]} + 1H_{[Z]}$), 5.72 – 5.65 (m, $1H_{[E]} + 1H_{[Z]}$), 5.48 – 5.43 (m, $1H_{[Z]}$), 5.42 – 5.34 (m, $1H_{[E]}$), 4.21 – 4.10 (m, $4H_{[E]} + 4H_{[Z]}$), 3.80 (dd, J = 15.5, 9.1 Hz, $1H_{[E]} + 1H_{[Z]}$), 3.55 (dd, J = 16.5, 7.5 Hz, $1H_{[Z]}$), 3.42 (dd, J = 15.9, 6.9 Hz, $1H_{[E]}$), 3.40 – 3.33 (m, $2H_{[E]} + 2H_{[Z]}$), 2.92 (d, J = 15.5 Hz, $1H_{[E]} + 1H_{[Z]}$), 2.70 – 2.54 (m, $2H_{[E]} + 2H_{[Z]}$),2.27 (s, $3H_{[E]} + 3H_{[Z]}$). 1.25 – 1.21 (m, $6H_{[E]} + 6H_{[Z]}$).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.5, 157.8, 143.5, 139.5, 134.3, 133.0, 131.9, 131.3, 130.2, 129.1, 128.9, 128.5, 127.1, 127.0, 125.7, 123.5, 112.6, 112.5, 67.0, 61.3, 52.2, 52.0, 38.4, 37.1, 31.9, 31.8, 26.7, 21.0, 14.1. HRMS (positive ESI): Calcd for $C_{30}H_{30}N_3O_4$ ($M + H^+$) 500.2544, found 500.2547.

(E)-Diethyl-2-(4-(5-chloro-2-phenyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3va):** purified using PE/EA (3:1) as an eluent, R_f = 0.32; yellow oil (92.6mg, 89%, E/Z > 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 4.8 Hz, 2H), 7.36 – 7.18 (m, 5H), 7.03 (d, J = 9.2 Hz, 2H), 5.98 (d, J = 8.7 Hz, 1H), 5.70 – 5.59 (m, 1H), 5.47-5.37 (m, 1H), 4.26 – 4.11 (m, 4H), 3.85 – 3.76 (m, 1H), 3.46 – 3.20 (m, 3H), 2.94 (t, J = 12.7 Hz, 1H), 2.65 – 2.53 (m, 2H), 1.27 – 1.16 (m, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.2, 157.8, 143.0, 140.7, 134.9, 132.1, 130.9, 129.6, 128.6, 128.3, 128.1, 127.3, 125.5, 122.9, 113.1, 67.1, 61.4, 52.0, 38.3, 37.0, 31.8, 28.7, 14.1. HRMS (positive ESI): Calcd for $C_{29}H_{30}ClN_3O_4$ ($M + H^+$) 520.1998, found 520.1997.

(E)-Diethyl 2-(4-(6-fluoro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3wa):** purified using PE/EA (3:1) as an eluent, R_f = 0.29; yellow oil (81.2mg, 95%, E/Z = 5:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43 (d, J = 4.0 Hz, $2H_{[E]} + 2H_{[Z]}$), 7.05 – 6.97 (m, $1H_{[E]} + 1H_{[Z]}$), 6.77 – 6.66 (m, $2H_{[E]} + 2H_{[Z]}$), 5.63 – 5.49 (m, $1H_{[E]} + 1H_{[Z]}$), 5.30 – 5.25 (m, $1H_{[Z]}$), 5.25-5.17 (m, $1H_{[E]}$), 4.46 – 4.38 (m, $2H_{[E]} + 2H_{[Z]}$), 4.20 –

4.09 (m, $4H_{[E]}$ + $4H_{[Z]}$), 3.45 – 3.19 (m, $3H_{[E]}$ + $3H_{[Z]}$), 2.99 (t, J = 7.2 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 2.49 (t, J = 7.0 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 1.25 – 1.21 (m, $6H_{[E]}$ + $6H_{[Z]}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0,161.3 ($J_{C\text{-}F}$ = 241.3) 161.1, 157.7, 143.9 ($J_{C\text{-}F}$ = 8.1), 130.4, 130.2($J_{C\text{-}F}$ = 2.2), 126.3, 122.5($J_{C\text{-}F}$ = 10.3), 118.6($J_{C\text{-}F}$ = 19.1), 112.7, 110.5($J_{C\text{-}F}$ = 24.2), 61.3, 54.0, 52.1, 31.8, 30.5, 29.2, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.2. HRMS (positive ESI): Calcd for $C_{23}H_{27}FN_3O_4$ (M + H^+) 428.1980, found 428.1984.

(E)-Diethyl 2-(4-(6-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3xa):** purified using PE/EA (3:1) as an eluent, R_f = 0.23; yellow oil (80.7mg, 91%, E/Z = 14:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 4.7 Hz, 2H), 7.11 – 7.06 (m, 1H), 7.03 (t, J = 6.7 Hz, 1H), 6.73 (t, J = 4.8 Hz, 1H), 5.60 – 5.47 (m, 1H), 5.21 – 5.14 (m, 1H), 4.43 (t, J = 7.6 Hz, 2H), 4.20 – 4.07 (m, 4H), 3.45 (d, J = 6.3 Hz, 2H), 3.28 (t, J = 7.6 Hz, 1H), 2.99 (q, J = 7.4 Hz, 2H), 2.49 (t, J = 7.1 Hz, 2H), 1.24 – 1.16 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.3, 157.7, 144.4, 134.0, 133.7, 130.3, 130.1, 128.9, 126.6, 125.5, 125.0, 123.0, 112.8, 61.3, 54.0, 53.8, 52.2, 51.8, 34.4, 31.8, 30.0, 29.6, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{30}N_3O_4$ (M + H^+) 424.2231, found 424.2233.

(E)-Diethyl 2-(4-(6-bromo-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ya):** purified using PE/EA (3:1) as an eluent, R_f = 0.26; yellow oil (76.0mg, 78%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 – 8.39 (m, 2H), 7.27 (d, J = 7.7 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.73 (s, 1H), 5.58 – 5.45 (m, 1H), 5.21 – 5.05 (m, 1H), 4.42 (t, J = 7.3 Hz, 2H), 4.19 – 4.05 (m, 4H), 3.49 (d, J = 5.9 Hz, 2H), 3.28 (t, J = 7.5 Hz, 1H), 2.96 (t, J = 7.4 Hz, 2H), 2.48 (t, J = 7.1 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.3, 157.6, 144.4, 134.9, 130.5, 130.3, 128.9, 126.7, 125.0, 123.4, 112.8, 61.3, 61.2, 53.9, 52.1, 36.9, 31.80, 29.7, 26.8, 14.1, 14.0. HRMS (positive ESI): Calcd for $C_{23}H_{26}BrN_3O_4$ (M + H^+) 488.1180, found 488.1181.

(E)-Diethyl 2-(4-(1-(pyrimidin-2-yl)-1,2,3,4-tetrahydroquinolin-8-yl)but-2-en-1-yl)malonate **(3za):** purified using PE/EA (3:1) as an eluent, R_f = 0.36; yellow oil (60.1mg, 71%, E/Z = 3:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, $2H_{[E]}$ + $2H_{[Z]}$), 7.10 – 7.04 (m, $3H_{[E]}$ + $3H_{[Z]}$), 6.62 – 6.58 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.65 – 5.58 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.41 – 5.31 (m, $1H_{[E]}$ + $1H_{[Z]}$), 4.82 (s, $1H_{[E]}$ + $1H_{[Z]}$), 4.20 – 4.12 (m, $4H_{[E]}$ + $4H_{[Z]}$), 3.37 (t, J = 7.6 Hz, $1H_{[E]}$), 3.28 (t, J = 7.6 Hz, $4H_{[Z]}$), 3.20 (d, J = 7.3 Hz, $1H_{[E]}$), 3.09 (d, J = 6.7 Hz, $2H_{[E]}$), 2.69 (s, $2H_{[E]}$ + $2H_{[Z]}$), 2.60-2.53 (m, $2H_{[E]}$ + $2H_{[Z]}$), 2.19-1.90 (m, $2H_{[E]}$ +

2H$_{[Z]}$), 1.25-1.21 (m, 6H$_{[E]}$ + 6H$_{[Z]}$).^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 161.6, 157.9, 139.6, 137.1, 136.8, 134.9, 134.8, 131.9, 131.1, 127.1, 127.0, 126.7, 126.3, 125.7, 125.6, 125.4, 111.4, 111.3, 61.3, 52.2, 52.0, 44.8, 44.7, 34.9, 31.8, 29.8, 26.6, 26.5, 24.3, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{29}N_3O_4$ (M + H^+) 424.2231, found 424.2233.

(E)-Diethyl 2-(4-(9-(pyrimidin-2-yl)-9H-carbazol-1-yl)but-2-en-1-yl)malonate **(3a'a):** purified using PE/EA (3:1) as an eluent, R_f = 0.30; yellow oil (71.3mg, 78%, E/Z = 10:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (d, J = 4.4 Hz, 2H), 8.15 – 7.90 (m, 3H), 7.46 – 7.13 (m, 5H), 5.53 – 5.39 (m, 1H), 5.21 – 5.05 (m, 1H), 4.20 – 4.04 (m, 4H), 3.43 – 3.24 (m, 3H), 2.53 – 2.40 (m, 2H), 1.26 – 1.17 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 158.9, 158.3, 141.3, 138.3, 130.9, 128.5, 127.3, 126.7, 126.6, 126.3, 125.6, 122.4, 122.0, 119.8, 118.2, 117.9, 112.6, 61.4, 61.3, 51.9, 51.8, 37.4, 32.2, 31.7, 26.8, 14.1. HRMS (positive ESI): Calcd for $C_{27}H_{27}N_3O_4$ (M + H^+) 458.2075, found 458.2076.

(E)-Diethyl 2-(4-(1-(pyridin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3b'a):** purified using PE/EA (3:1) as an eluent, R_f = 0.25; yellow oil (76.2mg, 90%, E/Z > 20:1). purified using PE/EA (3:1) as an eluent, R_f = 0.45; yellow oil (66.0 mg, 84%, E/Z =10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.26 (m, H$_{[E]}$ + 1H$_{[Z]}$), 7.52 – 7.47 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 7.11 (d, J = 6.2 Hz, 1H$_{[E]}$ + 1H$_{[Z]}$), 7.00 – 6.93 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 6.78 – 6.75 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 6.64 (dd, J = 12.5, 8.3 Hz, 1H$_{[E]}$ + 1H$_{[Z]}$), 5.64 – 5.49 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 5.42 – 5.27 (m, 1H$_{[E]}$ + 1H$_{[Z]}$), 4.28-4.24 (m, 2H$_{[E]}$ + 2H$_{[Z]}$), 4.19 – 4.13 (m, 4H$_{[E]}$ + 4H$_{[Z]}$), 3.35 (t, J = 7.6 Hz, 1H$_{[E]}$), 3.28 (t, J = 7.7 Hz, 1H$_{[Z]}$), 3.18 (d, J = 7.1 Hz, 2H$_{[Z]}$), 3.09-3.03 (m, 4H$_{[E]}$ + 2H$_{[Z]}$), 2.56 (q, J = 7.0 Hz, 2H$_{[E]}$ + 2H$_{[Z]}$), 1.23 (t, J = 7.0 Hz, 6H$_{[E]}$ + 6H$_{[Z]}$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.0, 158.5, 158.4, 148.1, 148.0, 143.8, 143.6, 137.0, 134.7, 134.6, 131.2, 130.5, 128.6, 128.4, 128.2, 128.1, 127.3, 126.0, 123.4, 123.19, 122.7, 115.6, 111.4, 111.3, 61.3, 55.0, 54.9, 52.2, 52.0, 36.4, 36.0, 31.8, 30.8, 29.9, 26.6, 14.1. HRMS (positive ESI): Calcd for $C_{24}H_{28}N_2O_4$ (M + H^+) 409.2122, found 409.2126.

(E)-Dimethyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ab):** purified using PE/EA (3:1) as an eluent, R_f = 0.26; yellow oil (65.6mg, 86%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 – 8.35 (m, 2H), 7.10 (d, J = 6.3 Hz, 1H), 7.02 (q, J = 7.0 Hz, 2H), 6.69 (d, J = 4.6 Hz, 1H), 5.70 – 5.60 (m, 1H), 5.44 – 5.33 (m, 1H), 4.41 (q, J = 7.8 Hz, 2H), 3.70 (d, J = 7.9 Hz, 6H), 3.44 – 3.22 (m, 3H), 3.05 (t, J

= 7.4 Hz, 2H), 2.67 – 2.55 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.4, 161.4, 157.7, 142.4, 134.8, 132.0, 131.3, 128.2, 125.5, 122.4, 112.2, 53.2, 52.5, 51.9, 36.9, 31.9, 29.9, 26.8. HRMS (positive ESI): Calcd for $C_{21}H_{24}N_3O_4$ (M + H^+) 382.1762, found 382.1766.

(E)-Dibutyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ac):** purified using PE/EA (3:1) as an eluent, R_f = 0.26; yellow oil (81.0mg, 87%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 – 8.40 (m, 2H), 7.13 – 6.99 (m, 3H), 6.69 – 6.66 (m, 1H), 5.70 – 5.56 (m, 1H), 5.45 – 5.32 (m, 1H), 4.44 – 4.38 (m, 2H), 4.15 – 4.11 (m, 4H), 3.40 – 3.20 (m, 3H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.64 – 2.56 (m, 2H), 1.63 – 1.55 (m, 4H), 1.40 – 1.29 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 161.4, 157.6, 142.4, 134.7, 131.8, 128.2, 127.2, 125.8, 124.3, 122.3, 112.2, 65.2, 53.3, 53.2, 52.3, 36.9, 31.9, 31.8, 30.5, 29.9, 19.0, 13.6. HRMS (positive ESI): Calcd for $C_{27}H_{36}N_3O_4$ (M + H^+) 466.2701, found 466.2705.

(E)-Dipropyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ad):** purified using PE/EA (3:1) as an eluent, R_f = 0.28; yellow oil (64.7mg, 74%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 – 8.34 (m, 2H), 7.13 – 6.95 (m, 3H), 6.68 (s, 1H), 5.71 – 5.58 (m, 1H), 5.46 – 5.34 (m, 1H), 4.41 (t, *J* = 7.4 Hz, 2H), 4.12 – 4.01 (m, 4H), 3.42 – 3.20 (m, 3H), 3.05 (t, *J* = 7.3 Hz, 2H), 2.65-2.57 (m, 2H), 1.67 – 1.59 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 161.4, 157.6, 142.4, 134.7, 131.1, 130.5, 128.2, 127.2, 124.2, 122.3, 112.2, 66.9, 53.3, 53.2, 52.3, 36.9, 31.9, 29.9, 26.7, 21.9, 10.3. HRMS (positive ESI): Calcd for $C_{25}H_{31}N_3O_4$ (M + H^+) 438.2388, found 438.2391.

(E)-Dibenzyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3ae):** purified using PE/EA (3:1) as an eluent, R_f = 0.28; yellow oil (96.0mg, 90%, E/Z = 7:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (t, *J* = 4.7 Hz, 2H), 7.34 – 7.21 (m, 10H), 7.13 – 6.94 (m, 3H), 6.66 – 6.60 (m, 1H), 5.65 – 5.56 (m, 1H), 5.43 – 5.26 (m, 1H), 5.17 – 5.01 (m, 4H), 4.40 (t, *J* = 7.7 Hz, 2H), 3.49 (t, *J* = 7.6 Hz, 1H), 3.20 (d, *J* = 6.8 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 161.4, 161.3, 157.6, 142.4, 135.4, 134.8, 132.1, 131.4, 130.7, 130.4, 128.5, 128.3, 128.2, 126.8, 125.5, 124.3, 124.2, 122.4, 112.3, 67.1, 53.2, 52.2, 52.0, 36.9, 31.9, 31.8, 29.9, 26.8. HRMS (positive ESI): Calcd for $C_{33}H_{32}N_3O_4$ (M + H^+) 534.2388, found 534.2393.

(E)- Bis(2,2,2-trifluoroethyl)

2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3af):** purified using PE/EA (3:1) as an eluent, R_f = 0.32; yellow oil (78.6mg, 76%, E/Z = 8:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (t, J = 5.9 Hz, $2H_{[E]} + 2H_{[Z]}$), 7.11 (t, J = 4.3 Hz, $H_{[E]} + H_{[Z]}$), 7.05 – 6.94 (m, $2H_{[E]} + 2H_{[Z]}$), 6.70 – 6.67 (m, $H_{[E]} + H_{[Z]}$), 5.73 – 5.65 (m, $H_{[E]} + H_{[Z]}$), 5.41 – 5.37 (m, $H_{[Z]}$), 5.36 – 5.28 (m, $H_{[E]}$), 4.54 – 4.35 (m, $6H_{[E]} + 6H_{[Z]}$), 3.58 (t, J = 7.5 Hz, $H_{[E]} + H_{[Z]}$), 3.39 (d, J = 7.2 Hz, $H_{[Z]}$), 3.29 (d, J = 6.9 Hz, $2H_{[E]}$), 3.04 (t, J = 7.6 Hz, $2H_{[E]} + 2H_{[Z]}$), 2.70 – 2.61 (m, $2H_{[E]} + 2H_{[Z]}$). ^{13}C NMR (151 MHz,) δ 166.6, 161.3, 157.6, 142.5, 142.4, 135.0, 134.9, 133.2, 132.3, 130.4, 130.1, 128.3, 127.9, 125.3, 124.4, 124.3, 124.2, 122.5 ($J_{C\text{-}F}$ = 277.5 Hz), 112.3, 61.0 ($J_{C\text{-}F}$ = 36.7 Hz), 53.3, 53.2, 51.2, 50.9, 37.0, 31.7, 31.6, 29.9, 26.5.^{19}F NMR (565 MHz, $CDCl_3$) δ -73.8. HRMS (positive ESI): Calcd for $C_{23}H_{21}FN_3O_4$ ($M + H^+$) 518.1509, found 518.1512.

(E)-2,2-dimethyl-5-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)-1,3-dioxane-4,6-dione **(3ag):** purified using PE/EA (3:1) as an eluent, R_f = 0.36; yellow oil (51.3mg, 65%, E/Z > 20:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 4.8 Hz, 2H), 7.14 – 6.99 (m, 3H), 6.71 (t, J = 4.8 Hz, 1H), 5.69 (dt, J = 15.1, 6.9 Hz, 1H), 5.40 – 5.26 (m, 1H), 4.39 – 4.33 (m, 2H), 3.53 (t, J = 5.1 Hz, 1H), 3.30 (d, J = 6.9 Hz, 2H), 3.05 (t, J = 7.7 Hz, 2H), 2.80 – 2.73 (m, 2H), 1.81 (s, 3H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 161.3, 157.7, 142.5, 134.9, 132.1, 130.7, 128.6, 125.0, 124.4, 112.3, 104.9, 53.3, 46.5, 31.9, 29.9, 28.5, 26.8, 24.3. HRMS (positive ESI): Calcd for $C_{22}H_{23}N_3O_4$ ($M + H^+$) 394.1762, found 394.1761.

(E)-2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malononitrile **(3ah):** purified using PE/EA (3:1) as an eluent, R_f = 0.24; yellow oil (44.7mg, 71%, E/Z = 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.46-8.44 (m, $2H_{[E]} + 2H_{[Z]}$), 7.18 – 7.12 (m, $1H_{[E]} + 1H_{[Z]}$), 7.08 –7.03 (m, $2H_{[E]} + 2H_{[Z]}$), 6.75-6.70 (m, $1H_{[E]} + 1H_{[Z]}$), 5.93 – 5.85 (m, $1H_{[E]} + 1H_{[Z]}$), 5.54 – 5.48 (m, $1H_{[Z]}$), 5.40 – 5.34 (m, $1H_{[E]}$), 4.42 (q, J = 7.8 Hz, $2H_{[E]} + 2H_{[Z]}$), 3.66 (t, J = 6.7 Hz, $1H_{[E]}$), 3.53 (t, J = 7.1 Hz, $1H_{[Z]}$), 3.43 (t, J = 6.8 Hz, $2H_{[E]} + 2H_{[Z]}$), 3.06 (t, J = 7.7 Hz, $2H_{[E]} + 2H_{[Z]}$), 2.68 – 2.65 (m, $2H_{[E]} + 2H_{[Z]}$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 161.2, 157.8, 157.7, 142.5, 142.4, 136.9, 135.7, 135.3, 135.1, 129.6, 129.1, 128.5, 128.1, 124.6, 124.3, 122.9, 122.0, 121.2, 112.6, 112.5, 112.4, 60.4, 53.4, 53.3, 37.2, 33.9, 32.1, 29.9, 29.8, 28.8, 23.3, 22.7, 21.0, 14.2. HRMS (positive ESI): Calcd for $C_{19}H_{18}N_5$ ($M + H^+$) 316.1557, found 316.1561.

(E)-7-(5,5-bis(phenylsulfonyl)pent-2-en-1-yl)-1-(pyrimidin-2-yl)indoline **(3ai):** purified using PE/EA (3:1) as an eluent, R_f = 0.28; yellow oil (63.2mg, 58%, E/Z

=8:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 4.7 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 7.94 (t, J = 8.4 Hz, $4H_{[E]}$), 7.90 (t, J = 7.5 Hz, $4H_{[z]}$), 7.68 – 7.60 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.53 (t, J = 7.8 Hz, $4H_{[E]}$ + $4H_{[Z]}$), 7.12 (d, J = 6.7 Hz, $H_{[E]}$ + $H_{[Z]}$), 7.04 – 6.93 (m, $2H_{[E]}$ + $2H_{[Z]}$), 6.72- 6.68 (m, $H_{[E]}$ + $H_{[Z]}$), 5.67 -5.51 (m, $1H_{[Z]}$), 5.55 – 5.45 (m, $1H_{[E]}$), 5.40 – 5.33 (m, $H_{[E]}$ + $H_{[Z]}$), 4.41 (dd, J = 14.9, 6.8 Hz, $3H_{[E]}$ + $3H_{[Z]}$), 3.27 – 3.21 (m, $2H_{[E]}$ + $2H_{[Z]}$), 3.05 (t, J = 7.6 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 2.90 (t, J = 6.4 Hz, $2H_{[z]}$), 2.85 (t, J = 6.2 Hz, $2H_{[E]}$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.3, 157.7, 142.4, 138.0, 134.9, 134.5, 133.3, 132.0, 129.8, 129.7, 129.6, 129.0, 128.4, 127.9, 125.2, 124.4, 124.2, 122.6, 122.5, 112.4, 84.0, 83.8, 53.3, 37.0, 31.8, 29.9, 28.9, 23.8. HRMS (positive ESI): Calcd for $C_{29}H_{27}N_3O_4S_2$ ($M + H^+$) 546.1516, found 546.1517.

(E)-Methyl 2-cyano-6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enoate **(3aj):** purified using PE/EA (3:1) as an eluent, R_f = 0.26; yellow oil (54.3mg, 78%, E/Z = 3:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45-8.41 (m, $2H_{[E]}$ + $2H_{[Z]}$), 7.12 (d, J = 5.5 Hz, $1H_{[E]}$ + $1H_{[Z]}$), 7.08 – 7.01 (m, $2H_{[E]}$ + $2H_{[Z]}$), 6.73-6.69 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.85-5.73 (m, $1H_{[E]}$ + $1H_{[Z]}$), 5.53 – 5.47 (m, 1 $H_{[Z]}$), 5.44 – 5.35 (m, $1H_{[E]}$), 4.46 – 4.37 (m, $2H_{[E]}$ + $2H_{[Z]}$), 3.77 (d, J = 6.8 Hz, $3H_{[E]}$ + $3H_{[Z]}$), 3.50 (dd, J = 7.3, 6.2 Hz, $1H_{[E]}$), 3.47 – 3.42 (m, $1H_{[z]}$), 3.40 (d, J = 7.3 Hz, $2H_{[z]}$), 3.34 (d, J = 6.8 Hz, $2H_{[E]}$), 3.06 (t, J = 7.6 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 2.67-2.60 (m, $2H_{[E]}$ + $2H_{[Z]}$).^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 166.1, 161.3, 157.7, 142.5, 142.4, 135.0, 134.9, 134.5, 130.1, 129.8, 128.4, 128.0, 124.4, 124.2, 123.2, 122.6, 116.2, 112.4, 112.3, 53.4, 53.3, 53.2, 37.8, 37.3, 37.1, 33.0, 31.9, 29.9, 27.8. HRMS (positive ESI): Calcd for $C_{20}H_{21}N_4O_2$ ($M + H^+$) 349.1659, found 349.1663.

(E)-2-(phenylsulfonyl)-6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enenitrile **(3ak):** purified using PE/EA (3:1) as an eluent, R_f = 0.26; yellow oil (48.3mg, 56%, E/Z = 4:1).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 4.8 Hz, 2 $H_{[Z]}$), 8.42 (d, J = 4.7 Hz, $2H_{[E]}$), 8.00 (t, J = 7.3 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 7.76 (t, J = 7.5 Hz, $H_{[E]}$ + $H_{[Z]}$), 7.64 (t, J = 7.8 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 7.16 – 7.08 (m, $H_{[E]}$ + $H_{[Z]}$), 7.05 – 6.96 (m, $2H_{[E]}$ + $2H_{[Z]}$), 6.73 – 6.68 (m, $H_{[E]}$ + $H_{[Z]}$), 5.89 – 5.71 (m, $H_{[E]}$ + $H_{[Z]}$), 5.48 – 5.42 (m, $H_{[Z]}$), 5.34 – 5.21 (m, $H_{[E]}$), 4.45 – 4.33 (m, $2H_{[E]}$ + $2H_{[Z]}$), 3.88 (dd, J = 10.9, 4.2 Hz, $H_{[E]}$), 3.75 (dd, J = 10.7, 4.7 Hz, $H_{[Z]}$), 3.46 – 3.29 (m, $2H_{[E]}$ + $2H_{[Z]}$), 3.09 – 2.99 (m, $2H_{[E]}$ + $2H_{[Z]}$), 2.93 – 2.81 (m, $H_{[E]}$ + $H_{[Z]}$), 2.64 – 2.47 (m, $H_{[E]}$ + $H_{[Z]}$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.2, 157.7, 157.5, 142.5, 142.4, 135.6, 135.3, 135.1, 135.0, 134.6, 129.8, 129.7, 129.6, 129.3, 128.5, 128.0, 127.5, 124.4, 124.3, 122.7, 122.4, 121.6, 113.8,

112.4, 57.6, 57.1, 53.2, 37.2, 32.0, 30.1, 29.9, 29.8, 24.8. HRMS (positive ESI): Calcd for $C_{24}H_{22}N_4O_2S$ ($M + H^+$) 431.1536, found 431.1537.

*(E)-2,2-dimethyl-5-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)-1,3-dioxane-4,6-dione***(3fe):** purified using PE/EA (3:1) as an eluent, R_f = 0.29; yellow oil (101.4mg, 90%, E/Z = 4:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (d, J = 3.8 Hz, $2H_{[E]}$), 8.36 (d, J = 3.9 Hz, $2H_{[Z]}$), 7.32 – 7.23 (m, $10H_{[E]}$ + $10H_{[Z]}$), 6.97 (d, J = 8.3 Hz, $H_{[E]}$ + $H_{[Z]}$), 6.67 – 6.53 (m, $2H_{[E]}$ + $2H_{[Z]}$), 5.67 – 5.53 (m, $H_{[E]}$ + $H_{[Z]}$), 5.38 – 5.25 (m, $H_{[E]}$ + $H_{[Z]}$), 5.14 – 5.04 (m, $5H_{[E]}$ + $5H_{[Z]}$), 4.39 (t, J = 7.5 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 3.79 (s, $3H_{[E]}$ + $3H_{[Z]}$), 3.51 – 3.40 (m, $H_{[E]}$ + $H_{[Z]}$), 3.29 (d, J = 7.0 Hz, $H_{[Z]}$), 3.16 (d, J = 6.6 Hz, $H_{[E]}$), 2.97 (t, J = 7.5 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 2.67 – 2.59 (m, $2H_{[E]}$ + $2H_{[Z]}$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 161.5, 161.4, 157.6, 154.3, 143.7, 143.6, 135.5, 132.6, 131.8, 129.3, 129.1, 128.5, 128.3, 128.2, 128.1, 126.4, 125.2, 123.3, 123.1, 121.9, 121.7, 112.4, 112.3, 107.0, 106.9, 67.1, 55.5, 53.7, 53.6, 52.3, 52.0, 36.4, 31.9, 31.2, 3.72, 26.7. HRMS (positive ESI): Calcd for $C_{34}H_{33}N_3O_5$ ($M + H^+$) 564.2493, found 564.2496.

(E)-Dibutyl 2-(4-(5-methyl-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate **(3kc):** purified using PE/EA (3:1) as an eluent, R_f = 0.28; yellow oil (81.4mg, 85%, E/Z > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42- 8.38 (m, 2H), 6.92 (s, 1H), 6.85 (s, 1H), 6.65 (s, 1H), 5.70 – 5.58 (m, 1H), 5.45 – 5.33 (m, 1H), 4.40 (t, J = 4.4 Hz, 2H), 4.15 – 4.06 (m, 4H), 3.41 – 3.18 (m, 3H), 2.99 (t, J = 7.1 Hz, 2H), 2.65 – 2.55 (m, 2H), 2.30 (s, 3H), 1.62 – 1.55 (m, 4H), 1.40 – 1.30 (m, 4H), 0.90 (t, J = 7.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 157.6, 140.0, 134.9, 133.9, 131.2, 130.2, 128.7, 127.0, 125.6, 123.1, 112.0, 65.2, 65.1, 53.3, 52.0, 36.8, 31.9, 31.6, 30.5, 29.9, 21.0, 19.0, 13.6. HRMS (positive ESI): Calcd for $C_{28}H_{37}N_3O_4$ ($M + H^+$) 450.2857, found 450.2858.

*(E)-Dibutyl 2-(4-(6-chloro-1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonate***(3sc):** purified using PE/EA (3:1) as an eluent, R_f = 0.29; yellow oil (73.9mg, 74%, E/Z = 11:1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (d, J = 4.1 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 7.11 – 7.05 (m, $H_{[E]}$ + $H_{[Z]}$), 7.02 (d, J = 7.8 Hz, $H_{[E]}$ + $H_{[Z]}$), 6.76 – 6.60 (m, $H_{[E]}$ + $H_{[Z]}$), 5.60 – 5.48 (m, $H_{[E]}$ + $H_{[Z]}$), 5.31 – 5,23 (m, $H_{[Z]}$), 5.21 – 5.12 (m, $H_{[E]}$), 4.43 (t, J = 7.3 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 4.14 – 3.99 (m, $4H_{[E]}$ + $4H_{[Z]}$), 3.50 (d, J = 6.2 Hz, $2H_{[Z]}$), 3.45 (d, J = 6.0 Hz, $2H_{[E]}$), 3.29 (t, J = 7.5 Hz, $H_{[E]}$ + $H_{[Z]}$), 2.98 (t, J= 7.4 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 2.49 (t, J = 7.0 Hz, $2H_{[E]}$ + $2H_{[Z]}$), 1.62 – 1.52 (m, $4H_{[E]}$ + $4H_{[Z]}$), 1.40 – 1.28 (m, $4H_{[E]}$ + $4H_{[Z]}$), 0.90 (t, J = 7.4 Hz, $6H_{[E]}$ + $6H_{[Z]}$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 161.4,

157.6, 144.4, 134.0, 133.7, 130.2, 130.1, 128.9, 126.6, 125.5, 125.0, 123.0, 112.7, 65.1, 54.0, 53.8, 52.2, 51.8, 34.4, 31.8, 30.5, 30.0, 29.6, 26.8, 19.0, 13.6. HRMS (positive ESI): Calcd for $C_{27}H_{34}ClN_3O_4$ (M + H^+) 500.2311, found 500.2313.

(E)-Ethyl 6-(1-(pyrimidin-2-yl)indolin-7-yl)hex-4-enoate **4:**

purified using PE/EA (3:1) as an eluent, R_f = 0.40; yellow oil (58.1 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (t, *J* = 4.1 Hz, 2H), 7.13 – 6.98 (m, 3H), 6.70 – 6.66 (m, 1H), 5.60 – 5.52 (m, 1H), 5.45 – 5.34 (m, 1H), 4.48 – 4.34 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.27 (d, *J* = 6.8 Hz, 2H), 3.05 (t, *J* = 7.7 Hz, 2H), 2.37 – 2.26 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.2, 161.3, 157.6, 142.3, 134.73, 130.7, 129.8, 129.5, 128.3, 124.1, 122.3, 112.2, 60.3, 53.3, 37.0, 34.3, 29.9, 27.9, 14.2. HRMS (positive ESI): Calcd for $C_{20}H_{24}N_3O_2$ (M + H^+) 338.1863, found 338.1868.

(E)-2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-en-1-yl)malonic acid **5:**

purified using DCM/MeOH (4:1) (1% HAc) as an eluent, R_f = 0.42; gray solid (63.9 mg, 90%); Mp: 162.1−164.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 4.8, 1.8 Hz, 2H), 7.10 (d, *J* = 6.8 Hz, 1H), 7.07 – 6.85 (m, 2H), 6.81 (m, 1H), 5.61 – 5.49 (m, 1H), 5.34 (m, 1H), 4.93 (s, 4H), 4.34 (m, 2H), 3.32 – 3.18 (m, 3H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.47 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 162.4, 159.0, 143.5, 136.3, 132.3, 131.7, 129.5, 128.6, 127.4, 125.4, 123.4, 113.8, 54.8, 38.2, 33.0, 32.9, 30.7, 27.9. HRMS (positive ESI): Calcd for $C_{19}H_{19}N_3O_4$(M + H^+) 354.1449, found 354.1452.

(E)- Diethyl -2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)but-2-enoyl)malonate **6:**

purified using PE/EA (6:1) as an eluent, R_f = 0.28; yellow oil (32.0 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.7 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.56 (t, *J* = 4.5 Hz, 1H), 6.32 (dd, *J* = 20.9, 3.1 Hz, 2H), 4.44 (m, 3H), 4.20 (m, 4H), 3.14 (t, *J* = 7.9 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 160.1, 156.6, 153.6, 144.1, 140.3, 135.2, 126.7, 124.1, 123.3, 120.0, 112.3, 110.7, 107.3, 62.0, 52.3, 52.0, 29.2, 14.0. HRMS (positive ESI): Calcd for $C_{23}H_{25}N_3O_5$ (M + H^+) 424.1867, found 424.1873.

Diethyl 2-(4-(1-(pyrimidin-2-yl)indolin-7-yl)butyl)malonate **7:**

purified using PE/EA (5:1) as an eluent, R_f = 0.35; yellow oil (69.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (t, *J* = 4.5 Hz, 2H), 7.12 – 6.96 (m, 3H), 6.68 (t, *J* =

4.8 Hz, H), 4.40 (dd, *J* = 9.9, 5.4 Hz,2H), 4.20 – 4.10 (m, 4H), 3.28 – 3.17 (m, H), 3.03 (t, *J* = 7.6 Hz, 2H), 2.62 – 2.52 (m, 2H), 1.82 (m, 2H), 1.61 (m, 2H), 1.23 (mt, 8H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 161.4, 157.6, 142.4, 134.8, 132.5, 128.0, 124.3, 122.1, 112.2, 61.2, 53.4, 52.0, 33.5, 29.9, 28.6, 27.4, 14.1. HRMS (positive ESI): Calcd for $C_{23}H_{29}N_3O_4$ (M + H^+) 412.2231, found 412.2235.

Diethyl 2-(4-(1-(pyrimidin-2-yl)-1H-indol-7-yl)butyl)malonate **8:**

purified using PE/EA (5:1) as an eluent, R_f = 0.33; yellow oil (73.7 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.8 Hz, 2H), 7.70 (d, *J* = 3.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.11 – 7.03 (m, 3H), 6.62 (t, *J* = 6.8 Hz, 1H), 4.14 – 3.95 (m, 4H), 3.11 (t, *J* = 7.5 Hz, 1H), 2.86 – 2.79 (m, 2H), 1.64 (m, 2H), 1.35 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 6H), 1.08 – 1.00 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 158.3, 133.8, 132.2, 130.0, 128.6, 125.6, 122.3, 119.1, 117.5, 107.0, 61.2, 51.9, 34.8, 29.3, 28.6, 27.3, 14.1. HRMS (positive ESI): Calcd for $C_{23}H_{27}N_3O_4$ (M + H^+) 410.2075, found 410.2073.

Ethyl 6-(1-(pyrimidin-2-yl)-1H-indol-7-yl)hexanoate **9:**

purified using PE/EA (5:1) as an eluent, R_f = 0.28; yellow oil (55.3 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 4.8 Hz, 2H), 7.77 (d, *J* = 3.6 Hz, 1H), 7.49 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.16 (m, 3H), 6.70 (t, *J* = 4.8 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.85 (m, 2H), 2.15 (t, *J* = 7.6 Hz, 2H), 1.41 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.15 – 1.05 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 158.3, 133.8, 132.2, 130.0, 128.8, 125.6, 122.3, 119.0, 117.4, 107.1, 60.2, 34.9, 34.2, 29.3, 29.1, 24.8, 14.3. HRMS (positive ESI): Calcd for $C_{20}H_{23}N_3O_2$ (M + H^+) 338.1863, found 338.1865.

NMR Spectra

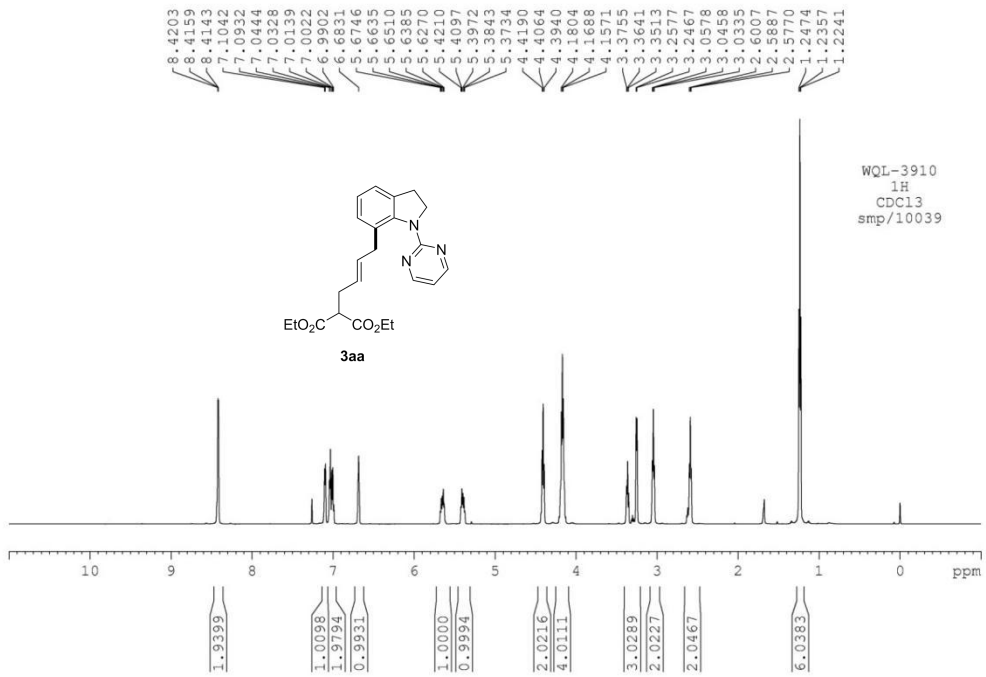


Figure S3. ^{1}H NMR spectrum of compound **3aa**

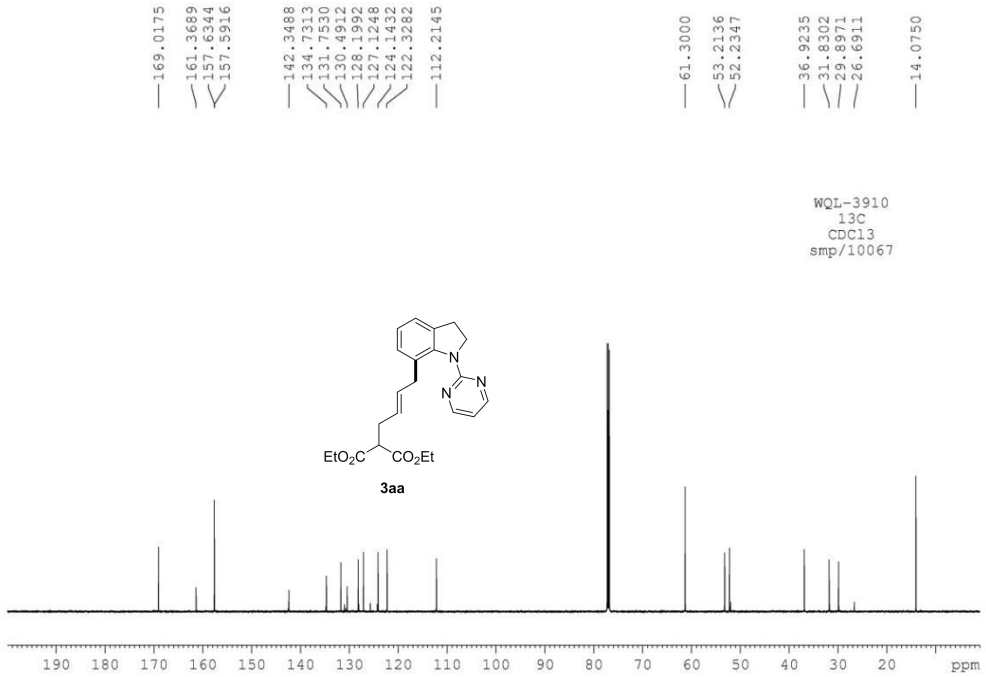


Figure S4. ^{13}C NMR spectrum of compound **3aa**

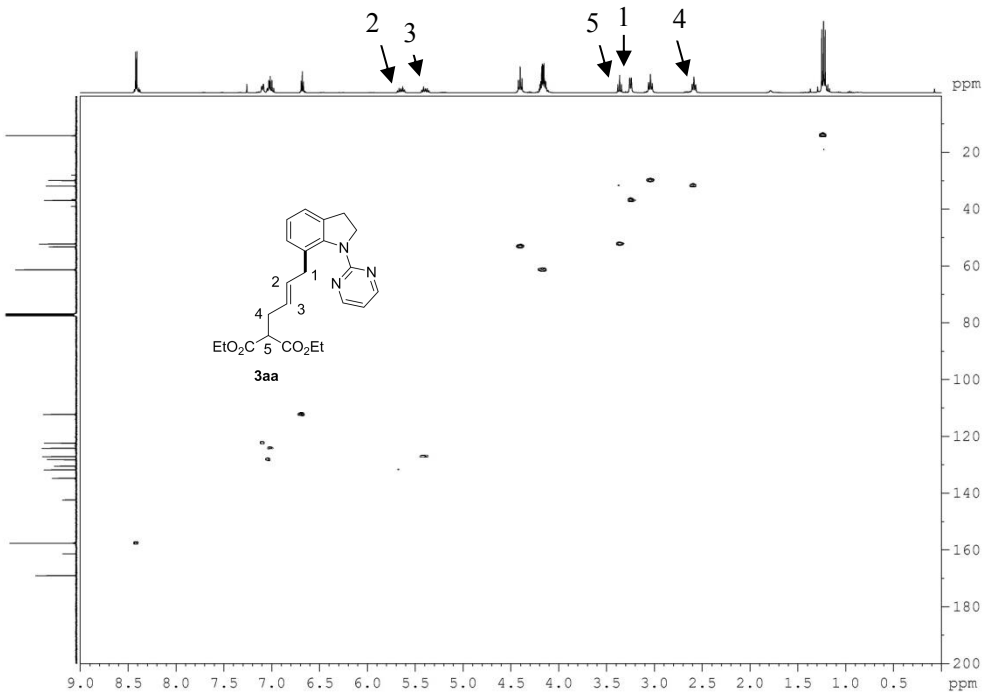


Figure S5. ^{1}H-^{1}H-COSY spectrum of compound **3aa**

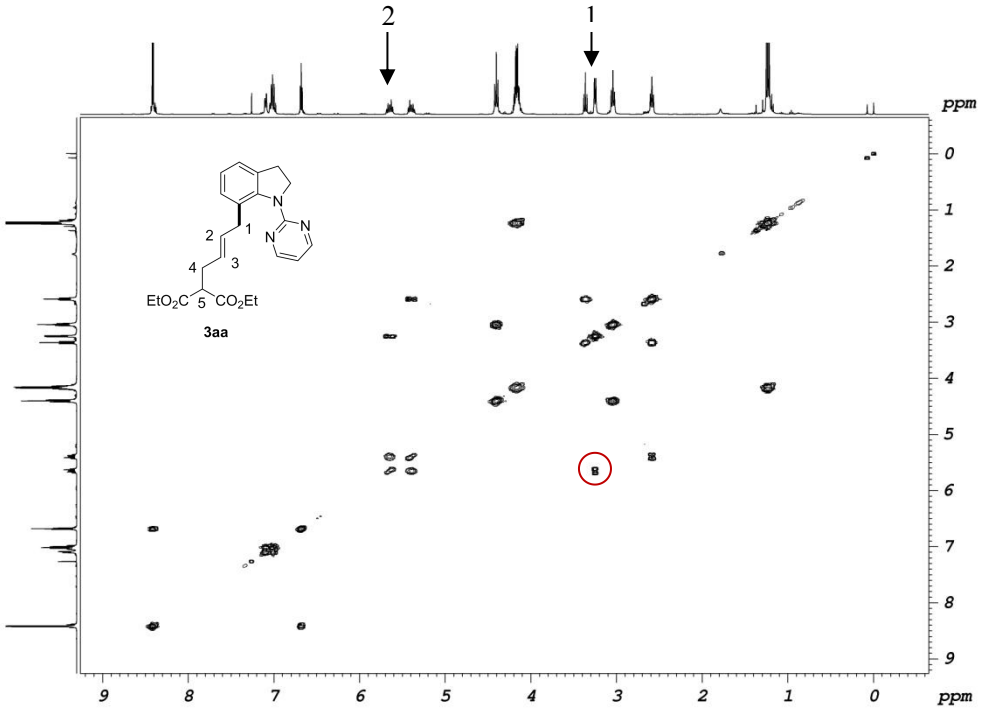


Figure S6. HMQC spectrum of compound **3aa**

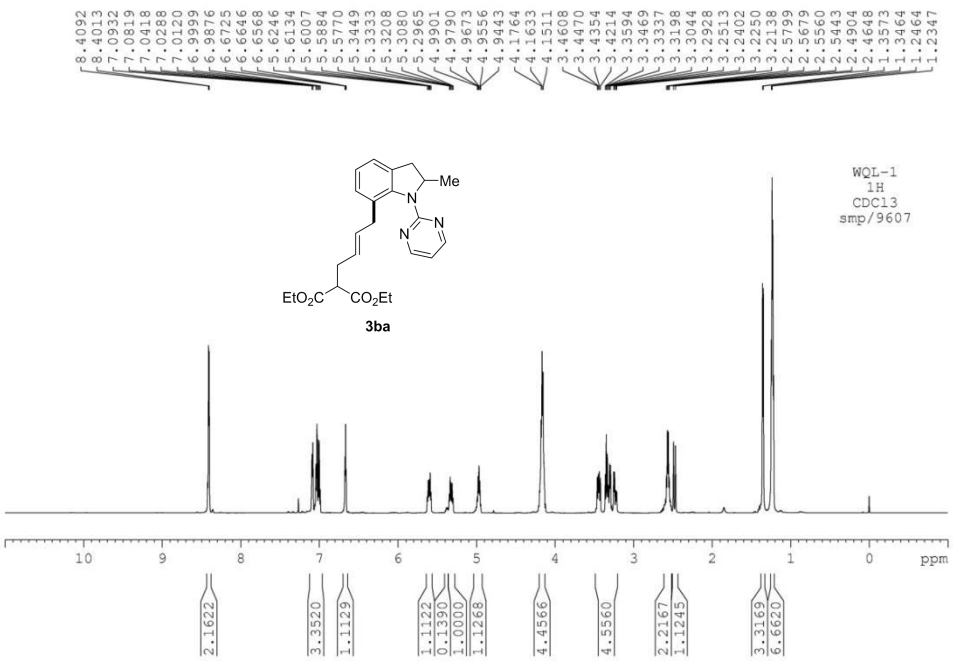


Figure S7. [1]H NMR spectrum of compound **3ba**

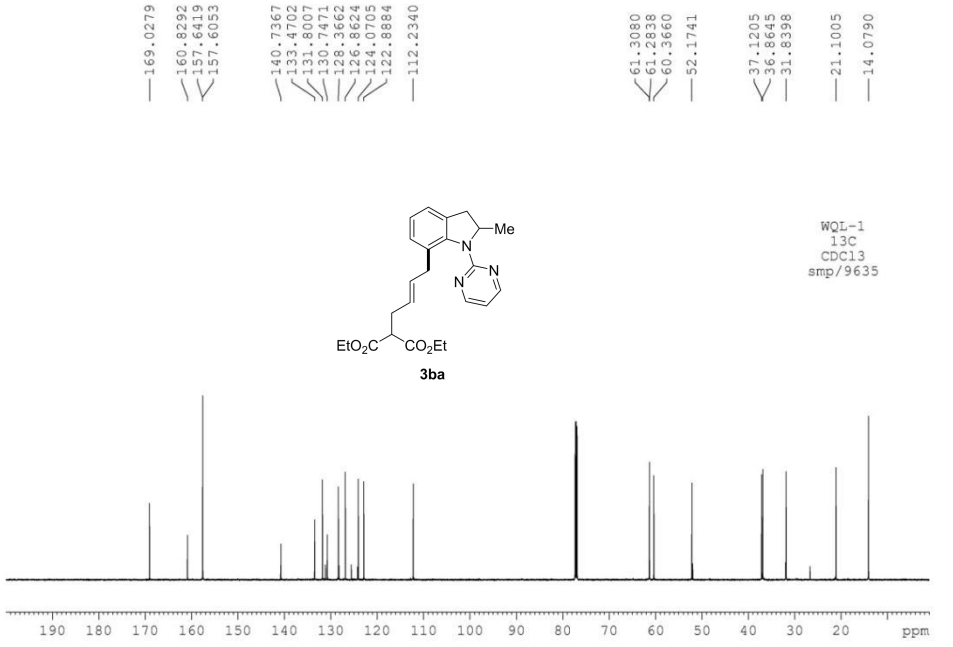


Figure S8. [13]C NMR spectrum of compound **3ba**

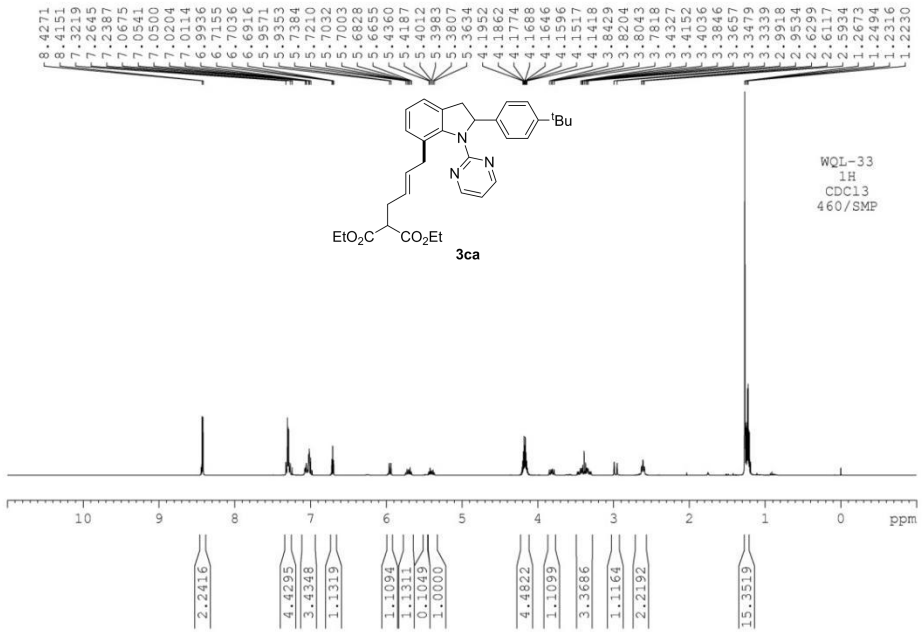


Figure S9. ^{1}H NMR spectrum of compound **3ca**

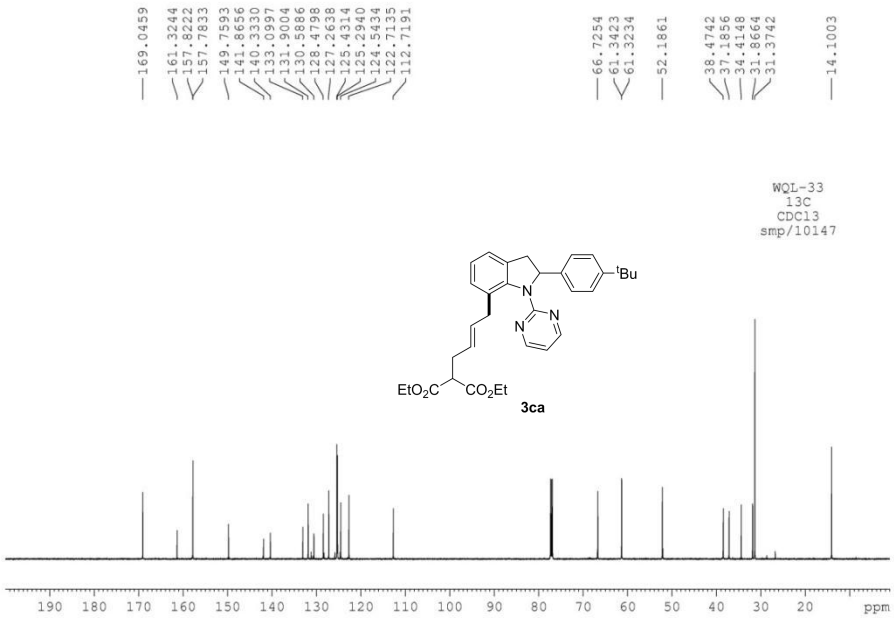


Figure S10. ^{13}C NMR spectrum of compound **3ca**

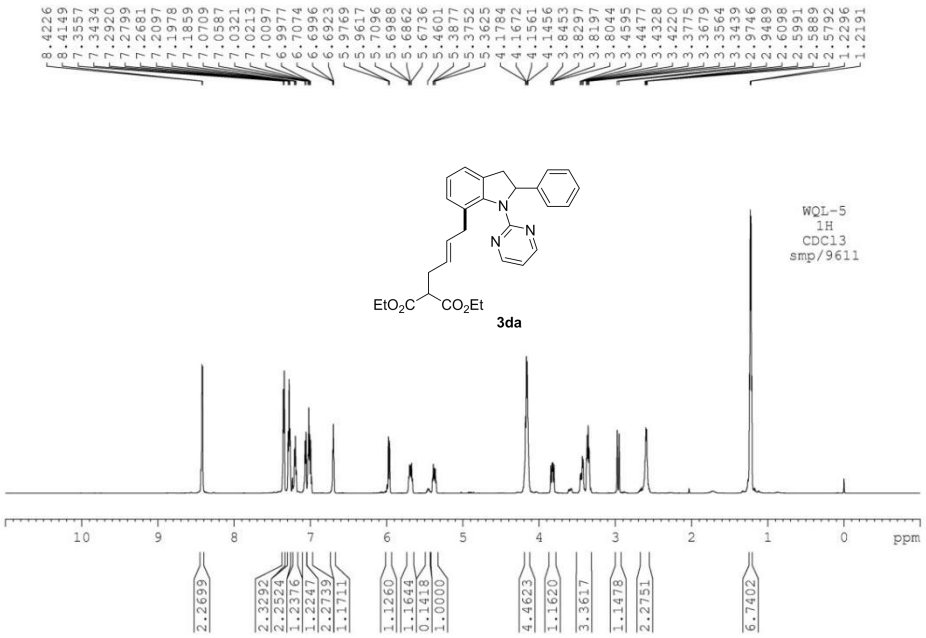


Figure S11. ^{1}H NMR spectrum of compound **3da**

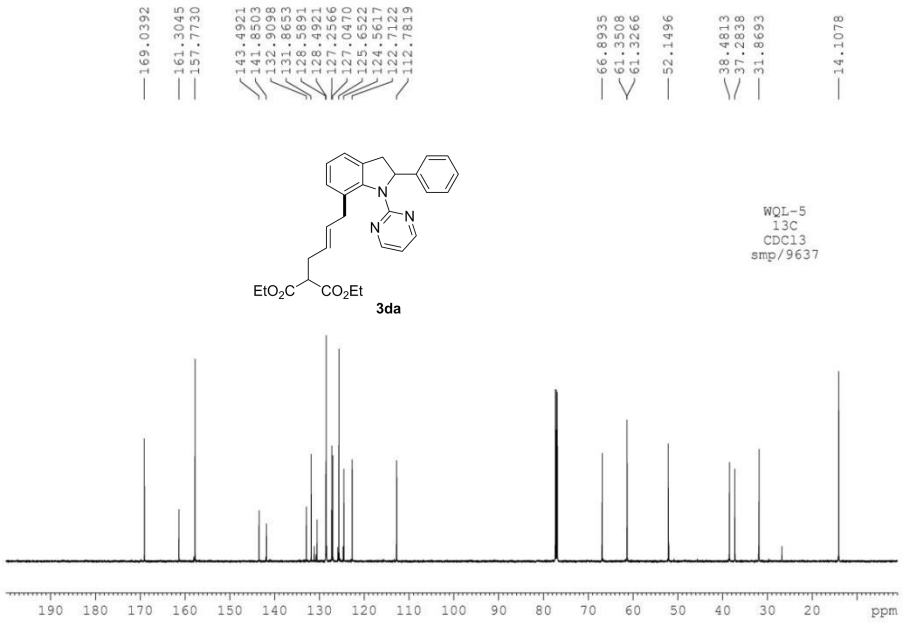


Figure S12. ^{13}C NMR spectrum of compound **3da**

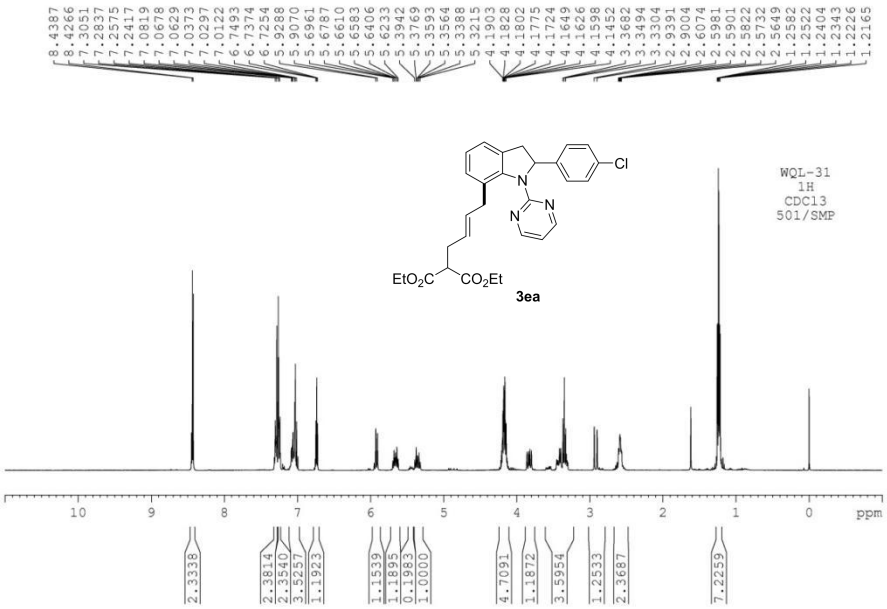


Figure S13. ^{1}H NMR spectrum of compound **3ea**

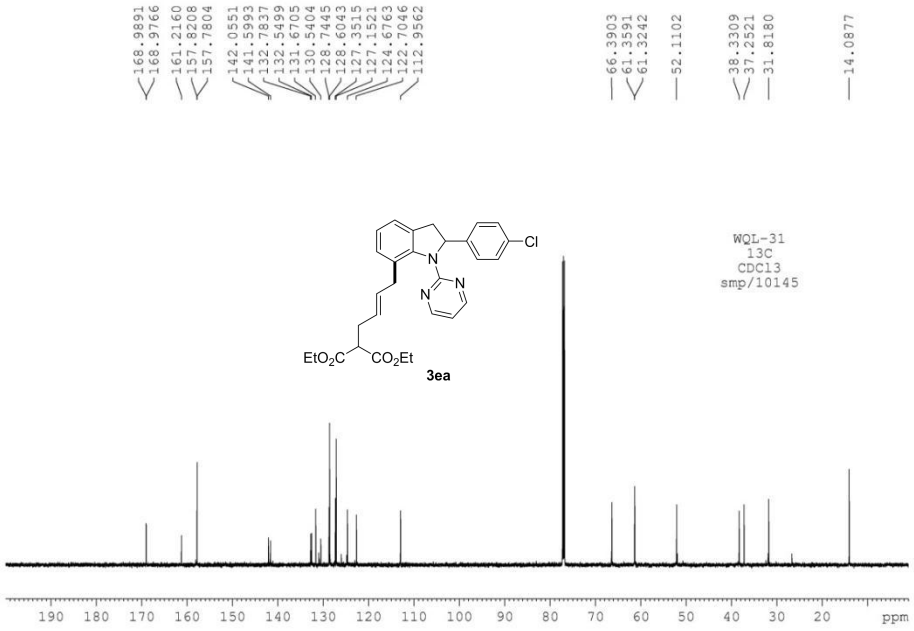


Figure S14. ^{13}C NMR spectrum of compound **3ea**

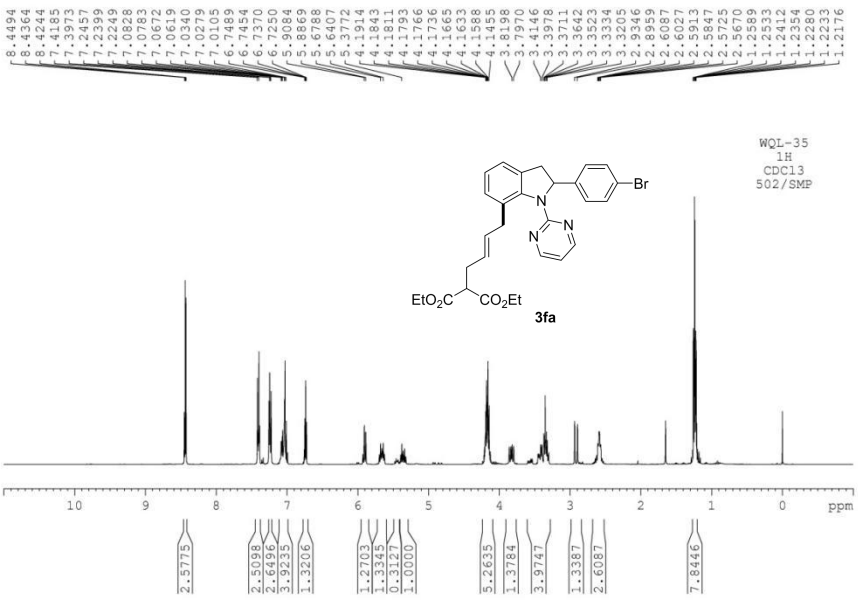


Figure S15. ^{1}H NMR spectrum of compound **3fa**

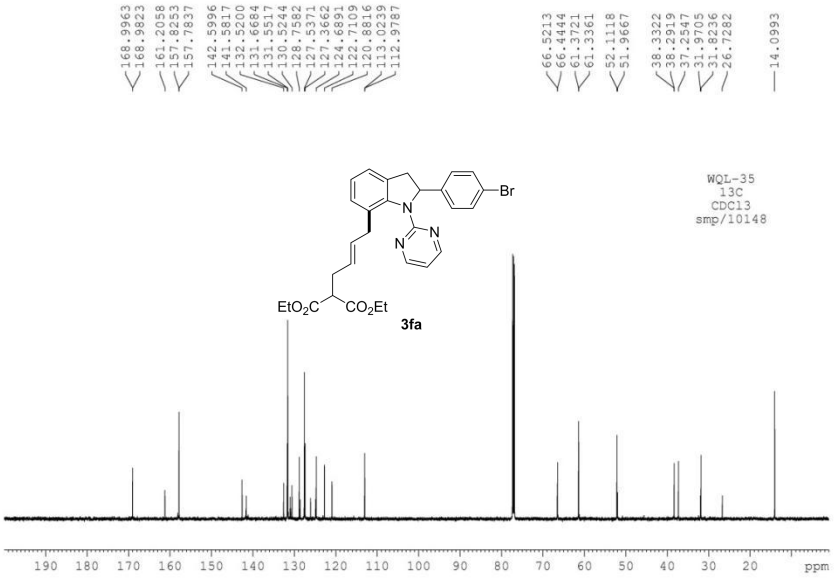


Figure S16. ^{13}C NMR spectrum of compound **3fa**

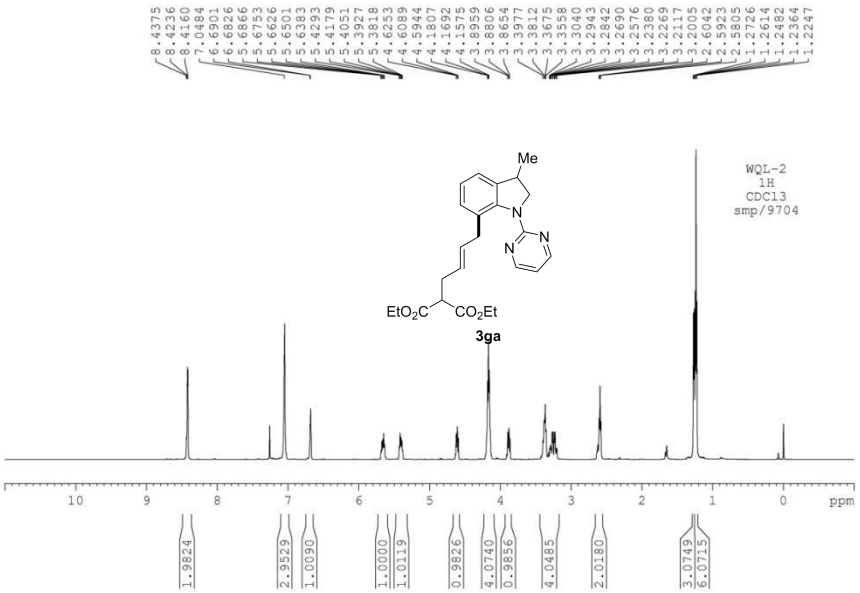


Figure S17. ^{1}H NMR spectrum of compound **3ga**

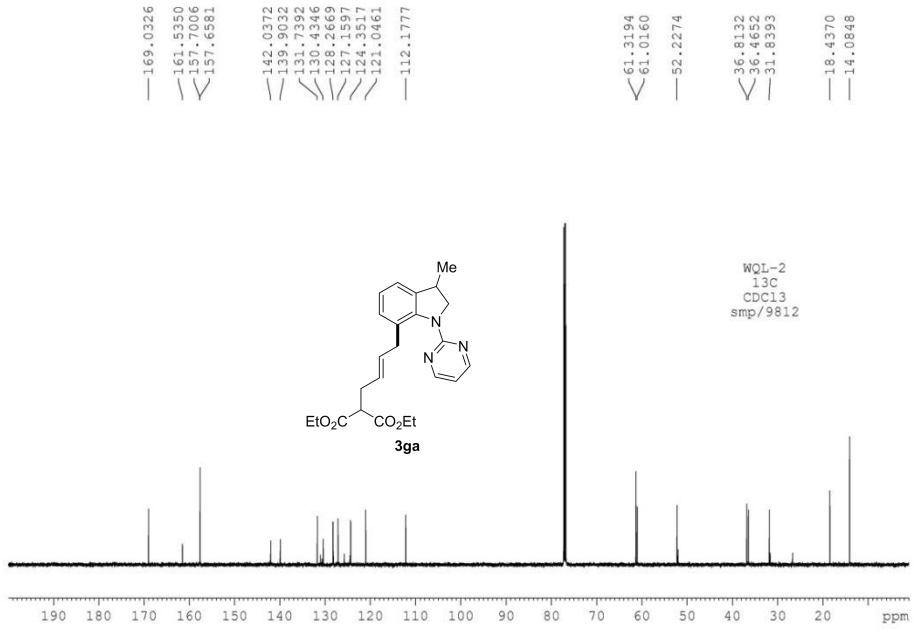


Figure S18. ^{13}C NMR spectrum of compound **3ga**

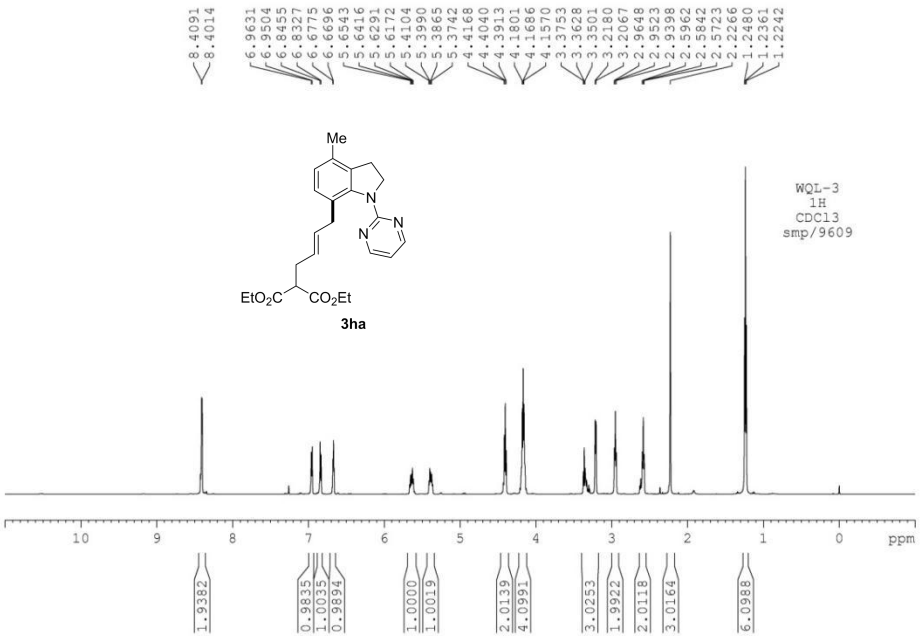


Figure S19. ^{1}H NMR spectrum of compound **3ha**

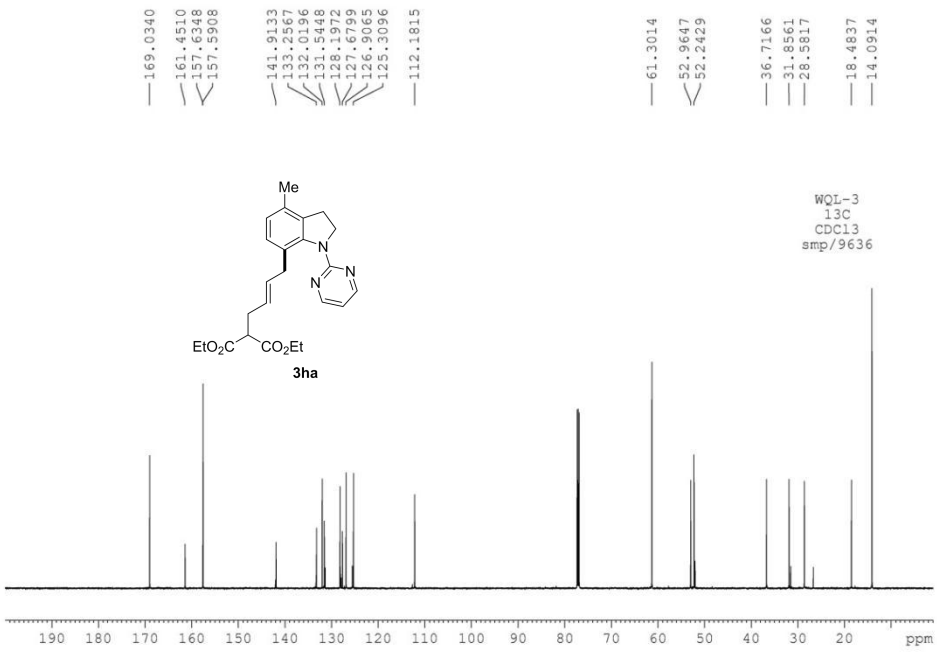


Figure S20. ^{13}C NMR spectrum of compound **3ha**

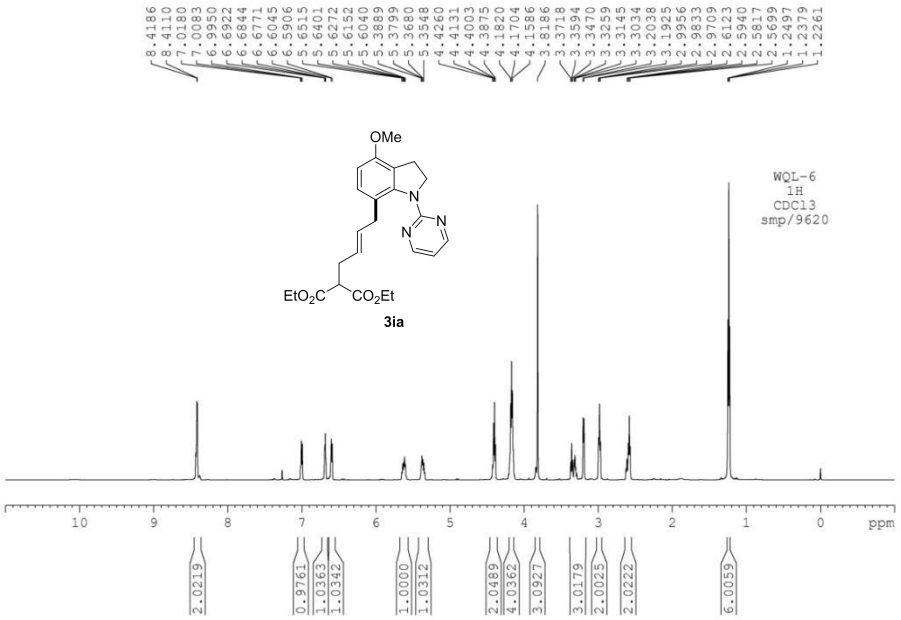


Figure S21. ^{1}H NMR spectrum of compound **3ia**

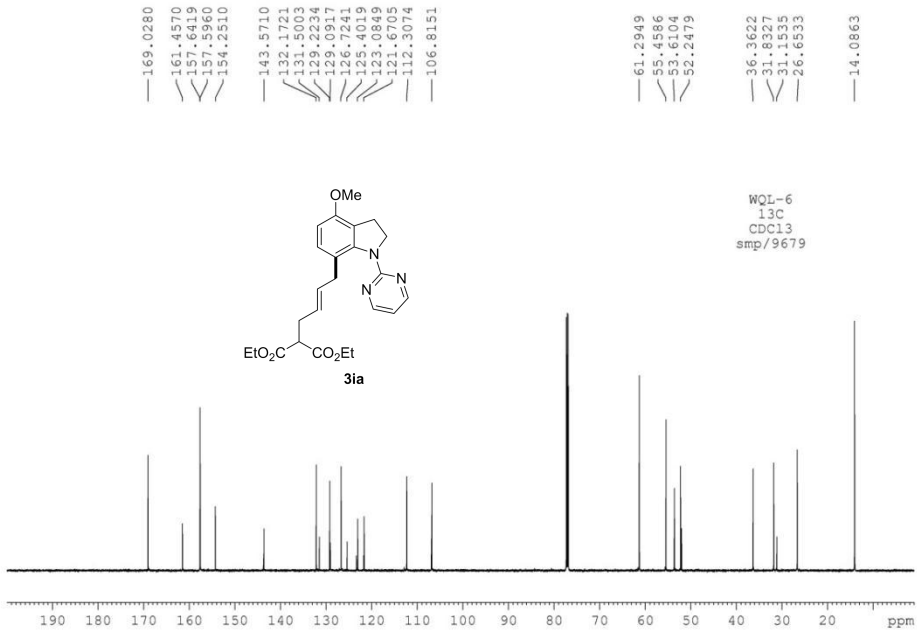


Figure S22. ^{13}C NMR spectrum of compound **3ia**

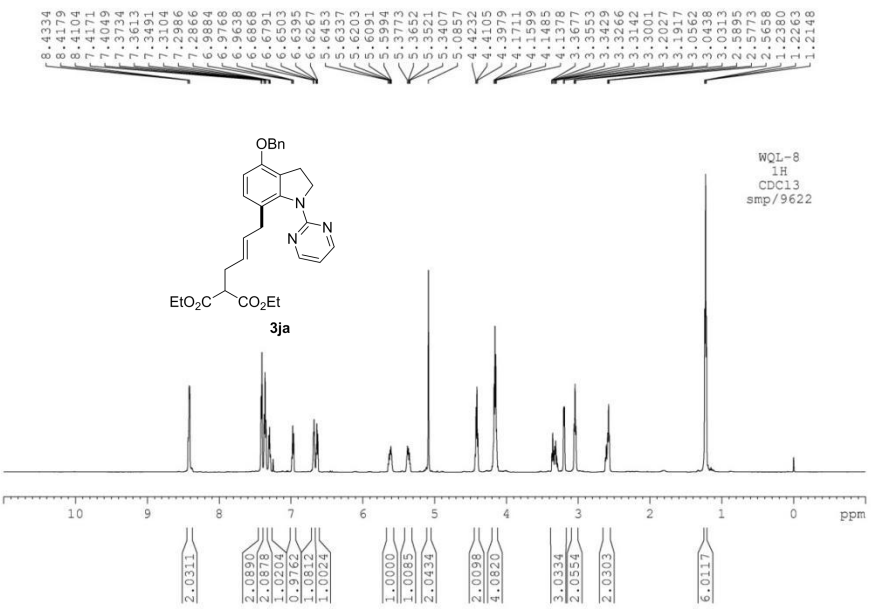


Figure S23. ^{1}H NMR spectrum of compound **3ja**

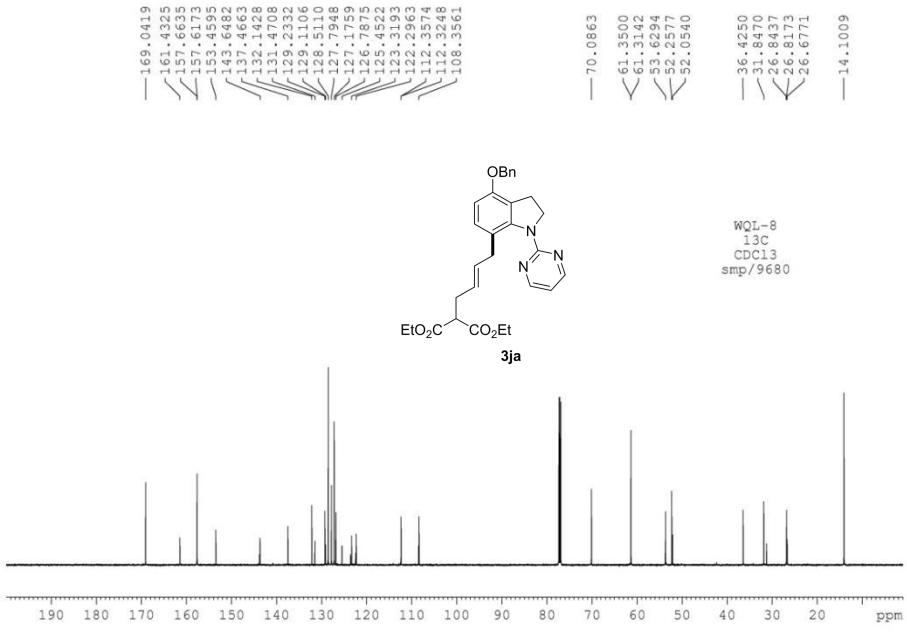


Figure S24. ^{13}C NMR spectrum of compound **3ja**

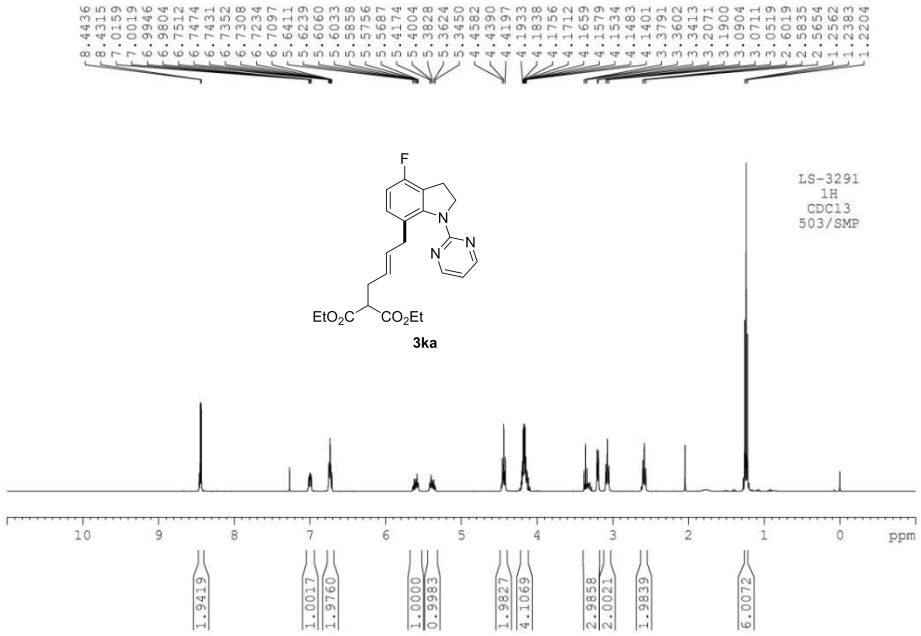


Figure S25. ^{1}H NMR spectrum of compound **3ka**

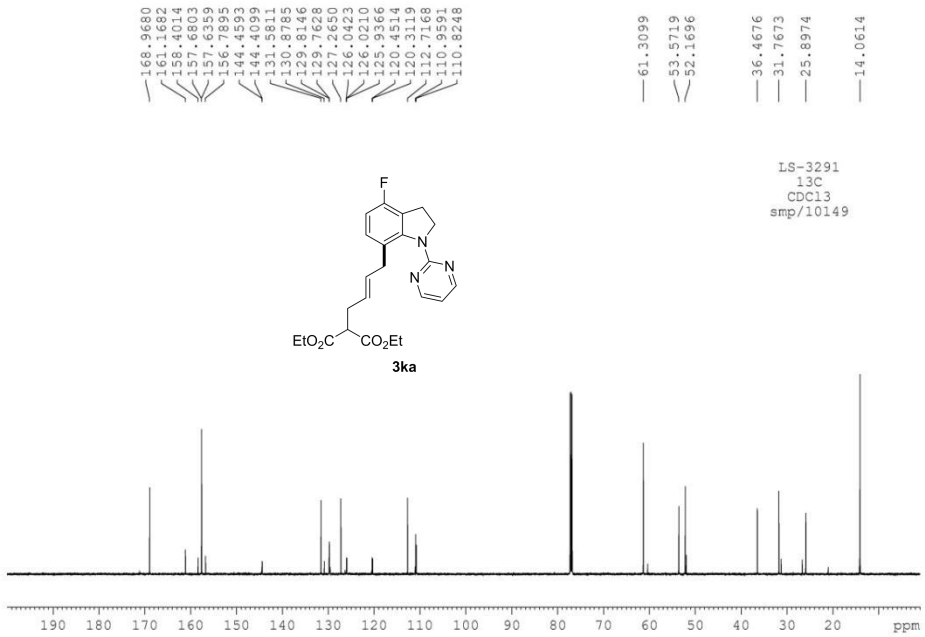


Figure S26. ^{13}C NMR spectrum of compound **3ka**

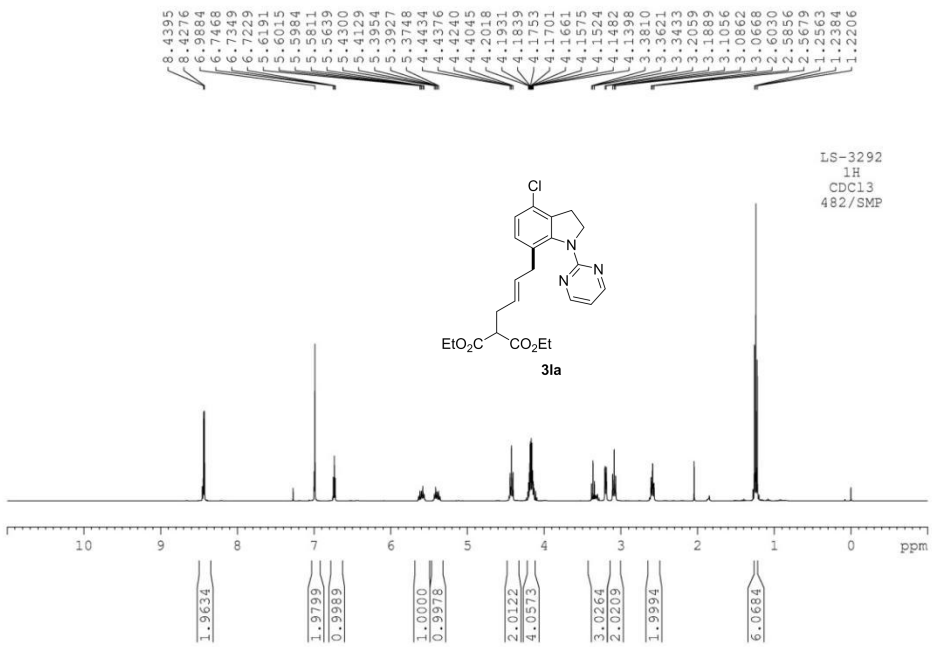


Figure S27. [1]H NMR spectrum of compound **3la**

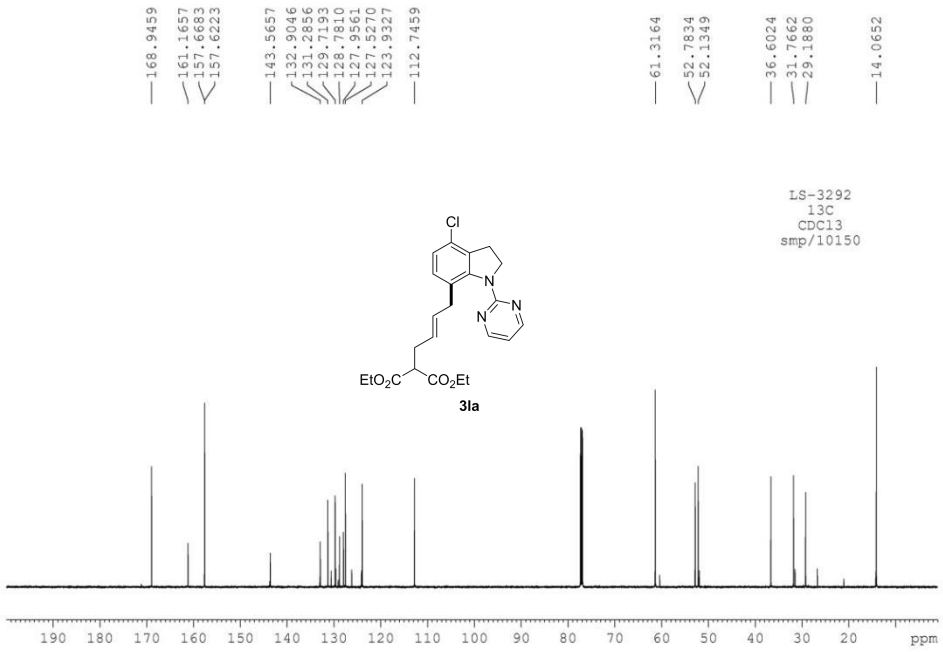


Figure S28. [13]C NMR spectrum of compound **3la**

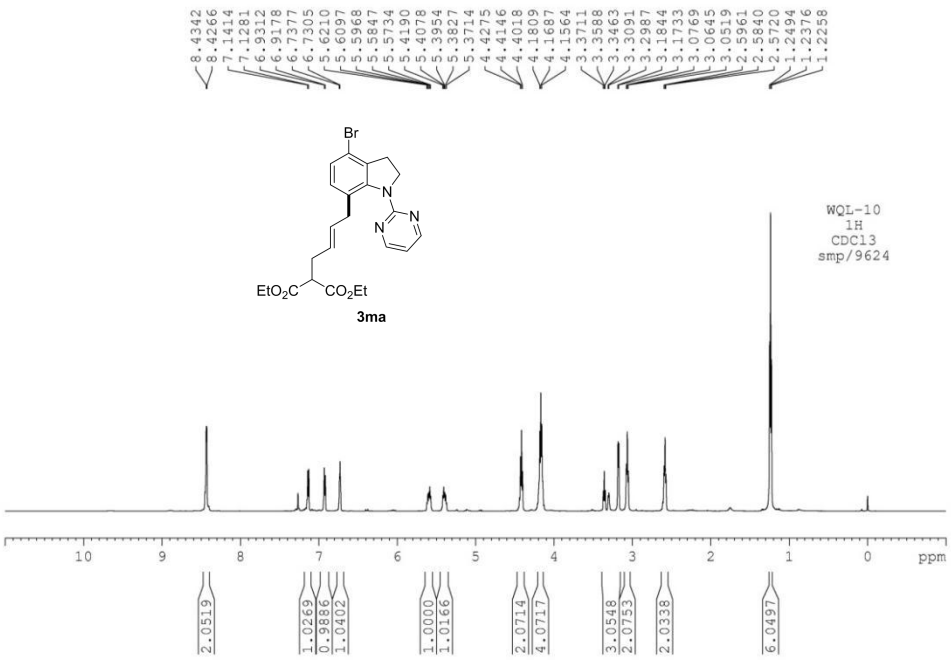


Figure S29. ^{1}H NMR spectrum of compound **3ma**

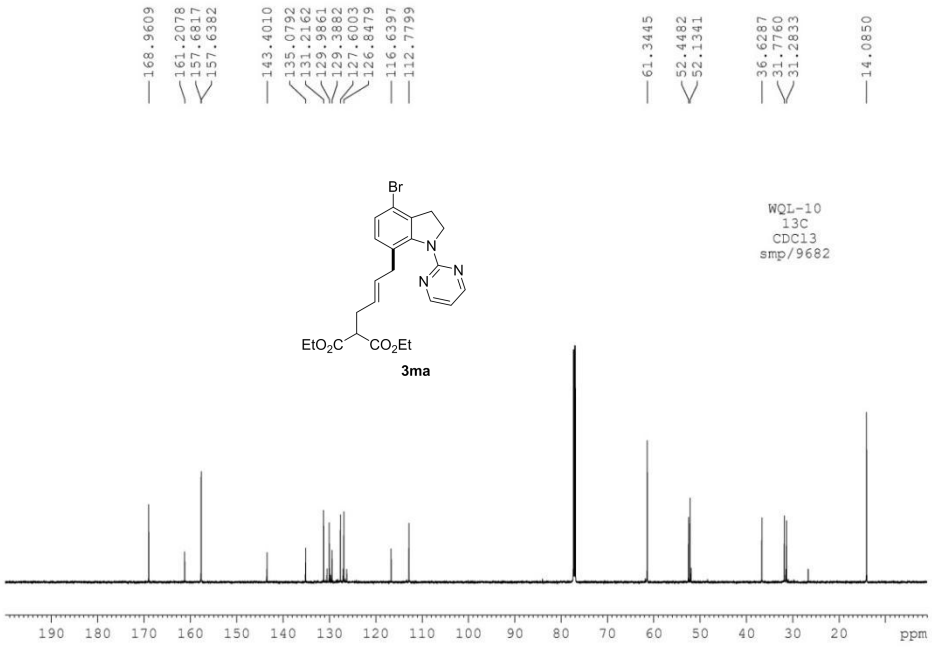


Figure S30. ^{13}C NMR spectrum of compound **3ma**

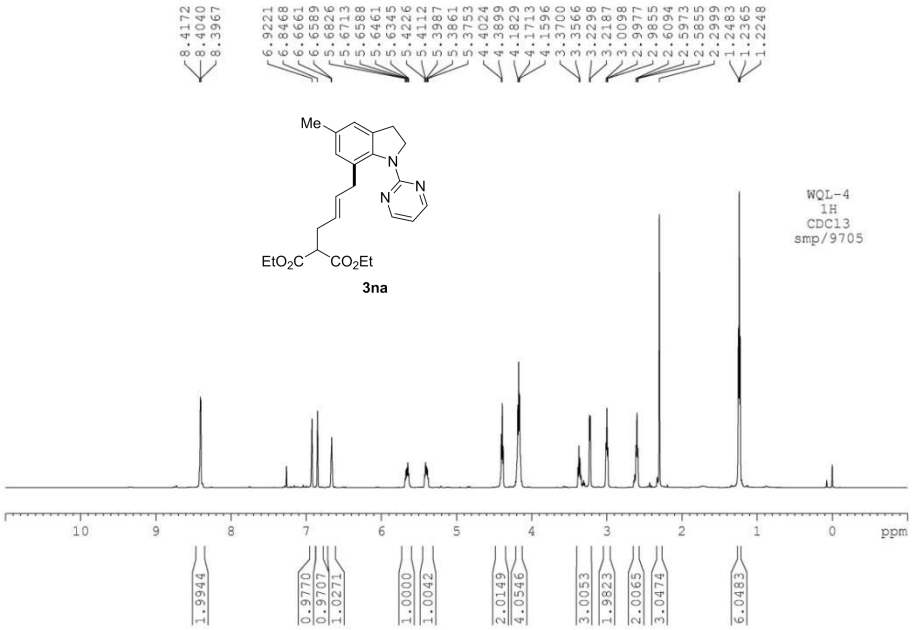


Figure S31. [1]H NMR spectrum of compound **3na**

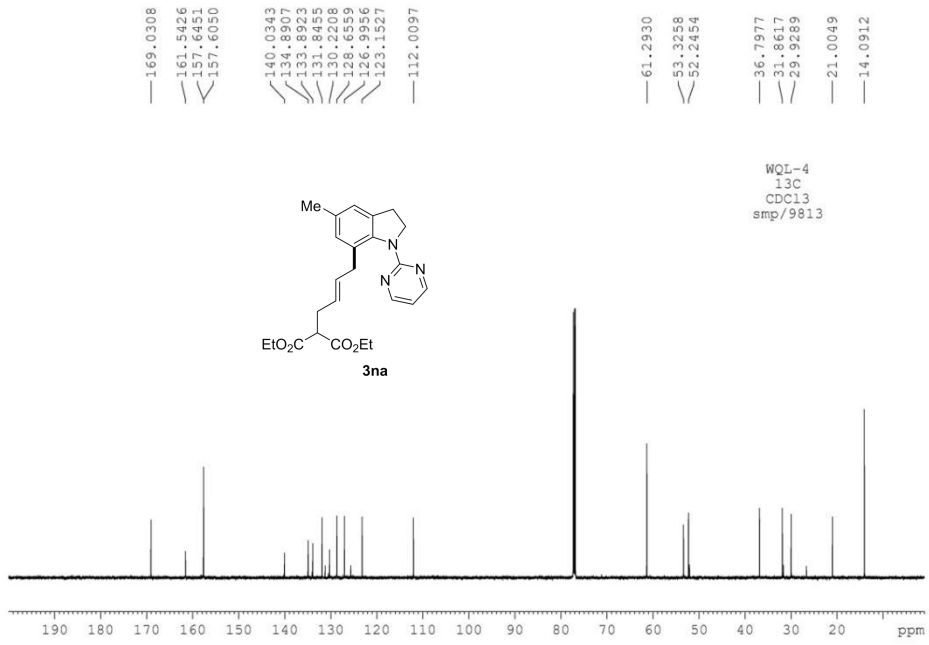


Figure S32. [13]C NMR spectrum of compound **3na**

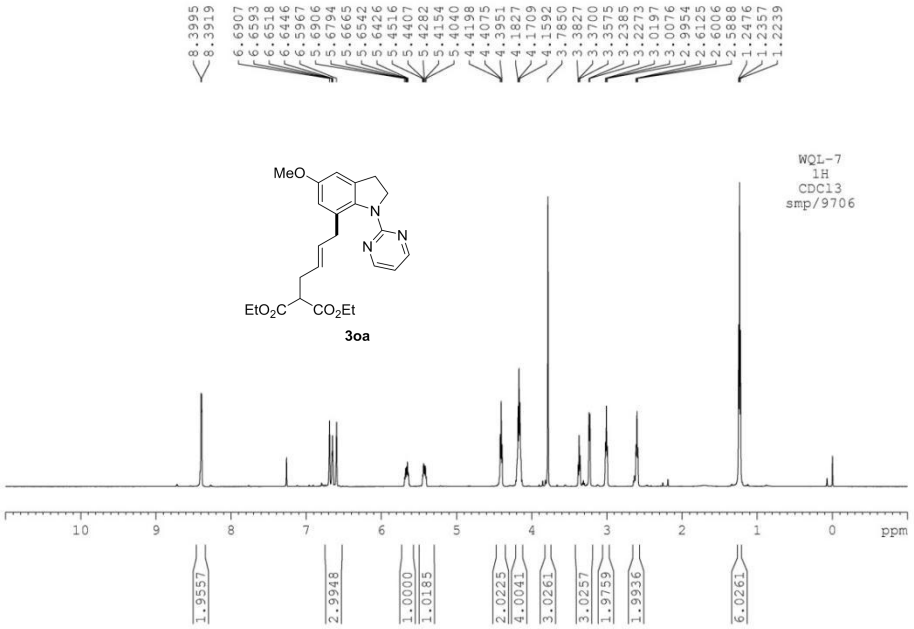


Figure S33. ^{1}H NMR spectrum of compound **3oa**

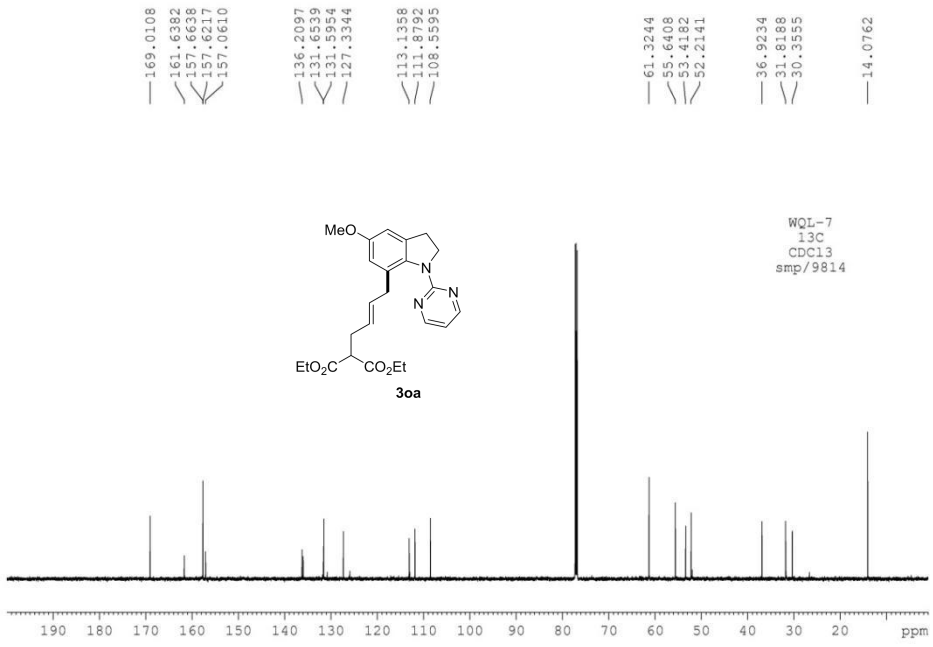


Figure S34. ^{13}C NMR spectrum of compound **3oa**

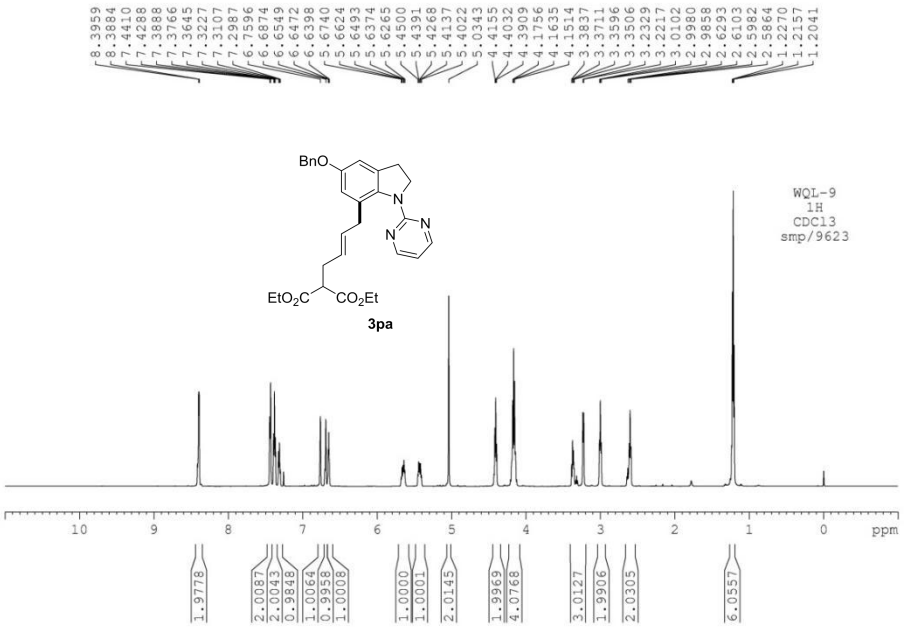


Figure S35. ^{1}H NMR spectrum of compound **3pa**

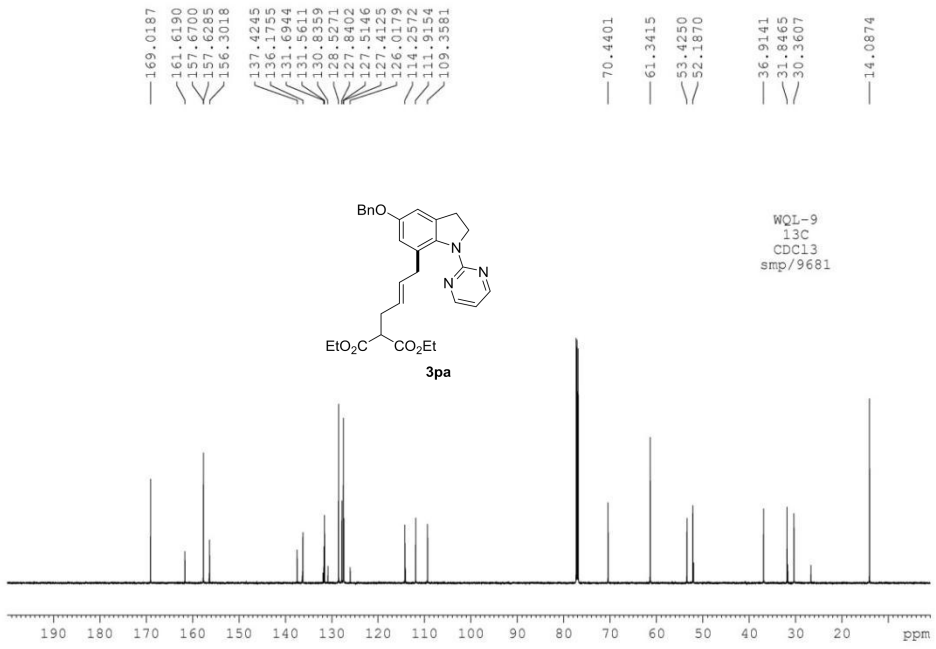


Figure S36. ^{13}C NMR spectrum of compound **3pa**

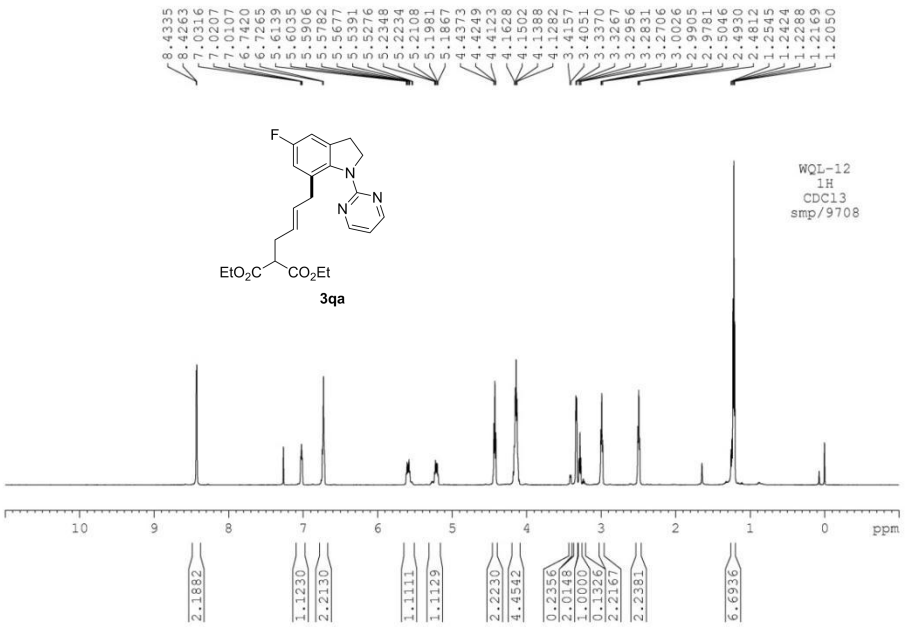


Figure S37. ^{1}H NMR spectrum of compound **3qa**

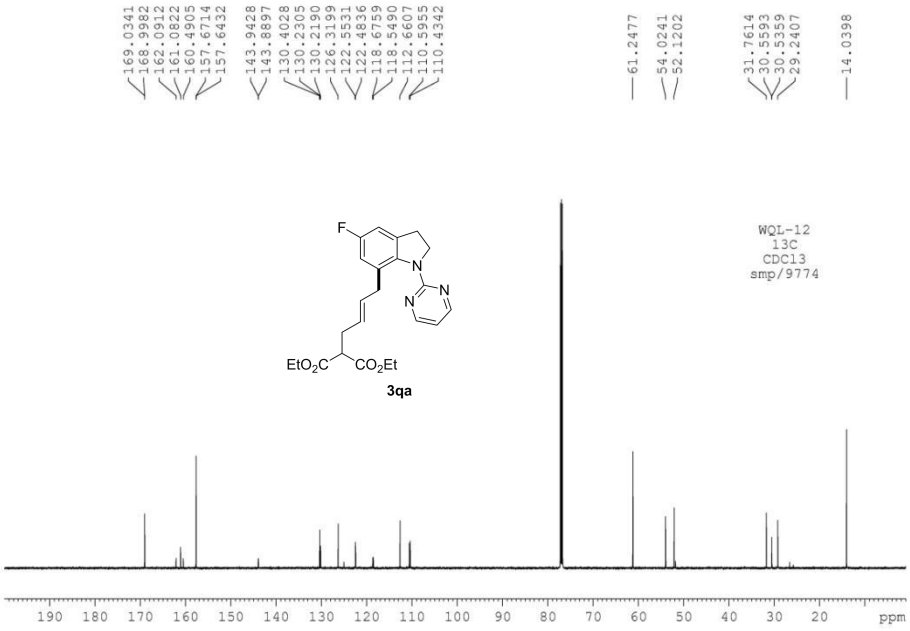


Figure S38. ^{13}C NMR spectrum of compound **3qa**

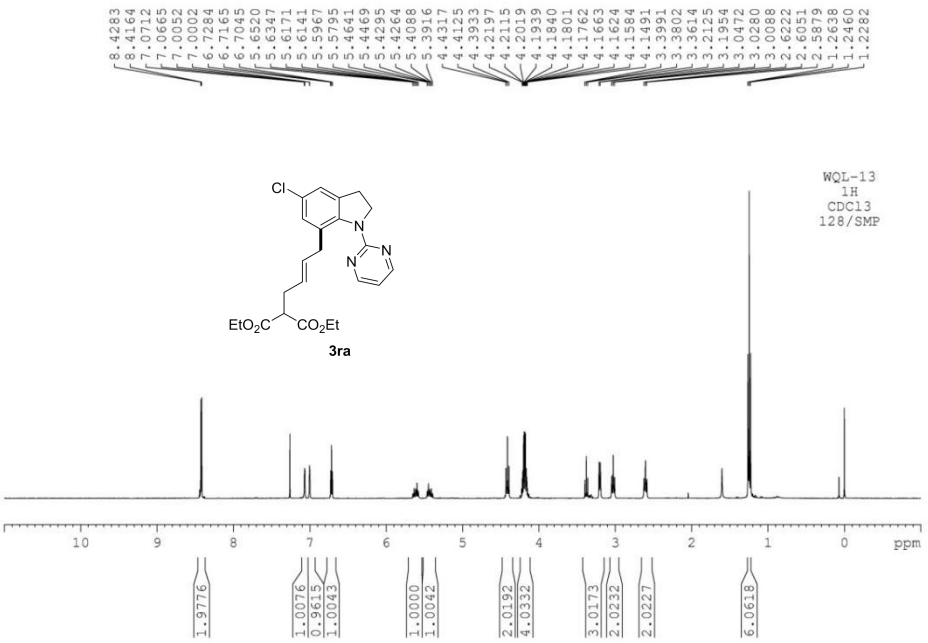


Figure S39. ^{1}H NMR spectrum of compound **3ra**

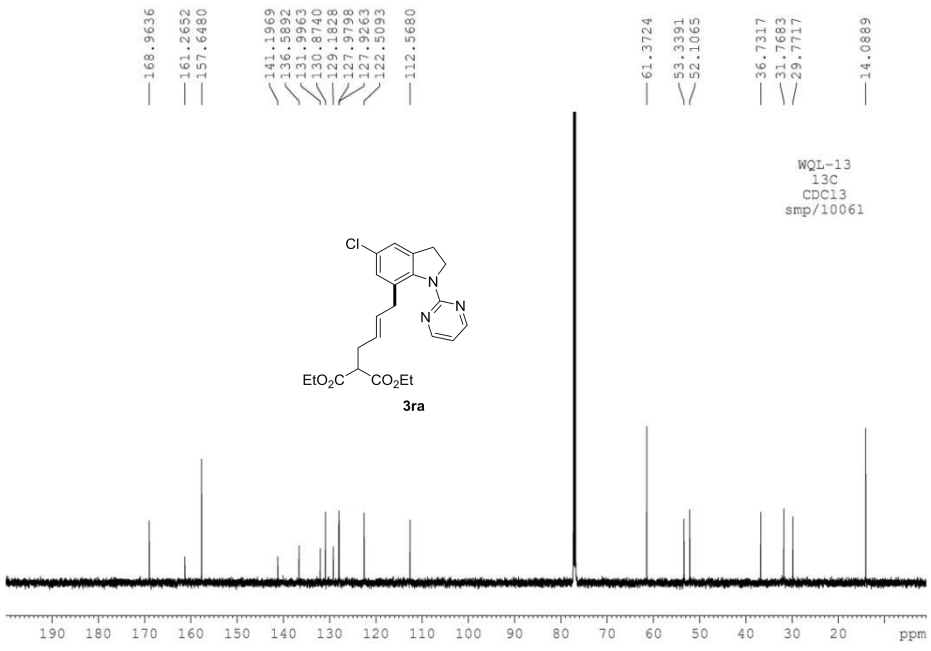


Figure S40. ^{13}C NMR spectrum of compound **3ra**

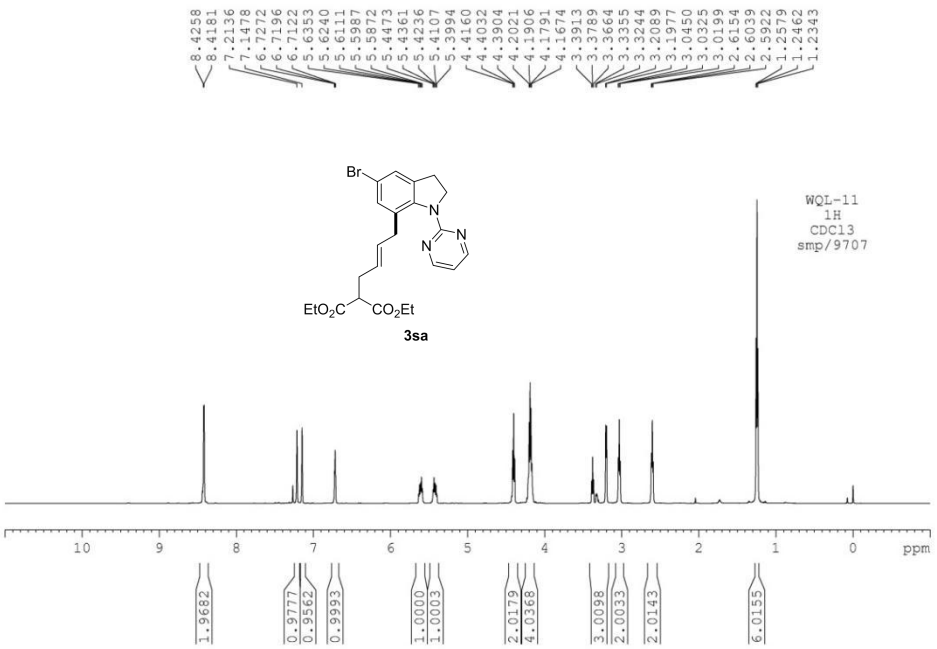


Figure S41. ^{1}H NMR spectrum of compound **3sa**

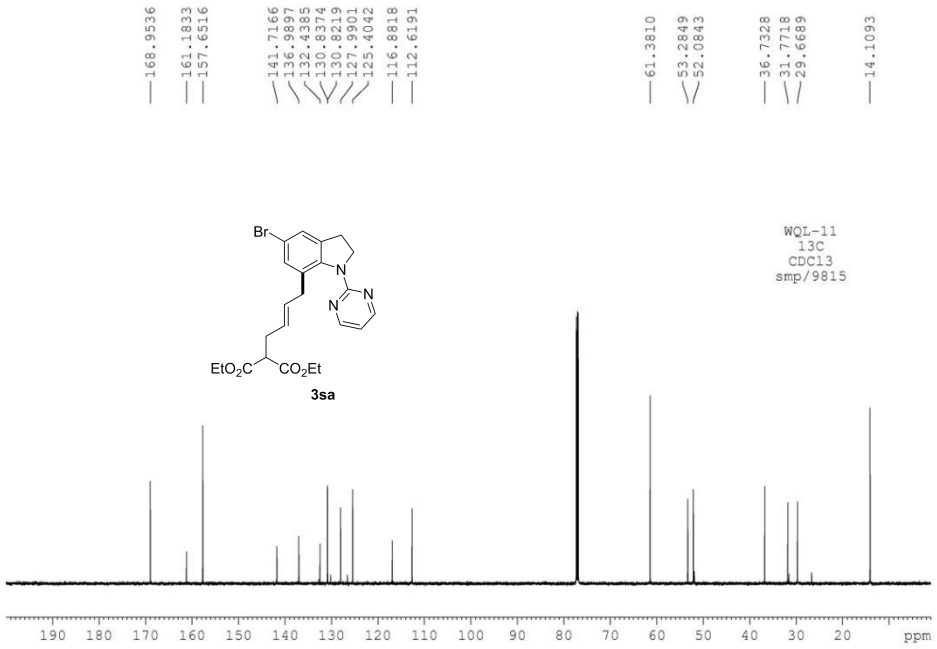


Figure S42. ^{13}C NMR spectrum of compound **3sa**

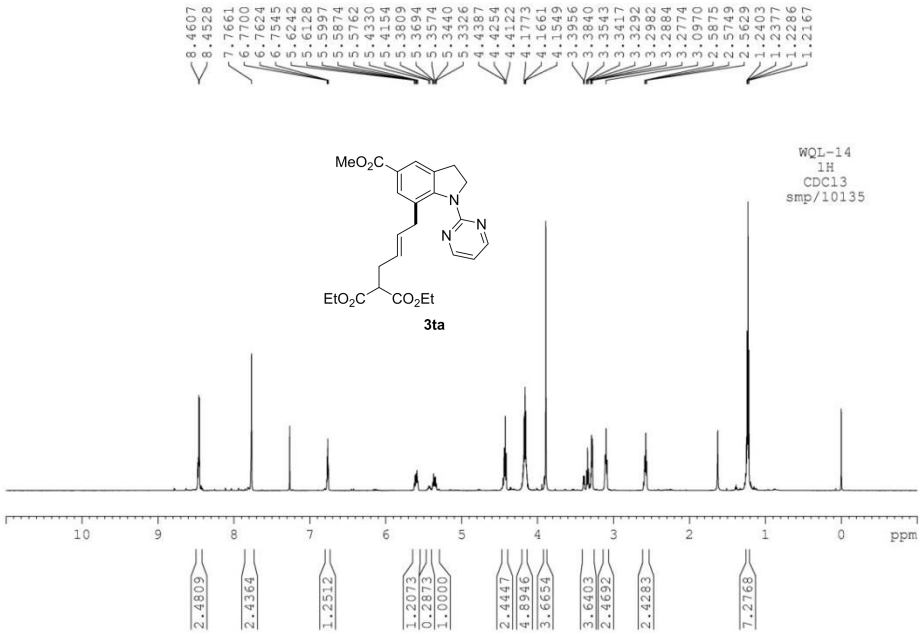


Figure S43. ^{1}H NMR spectrum of compound **3ta**

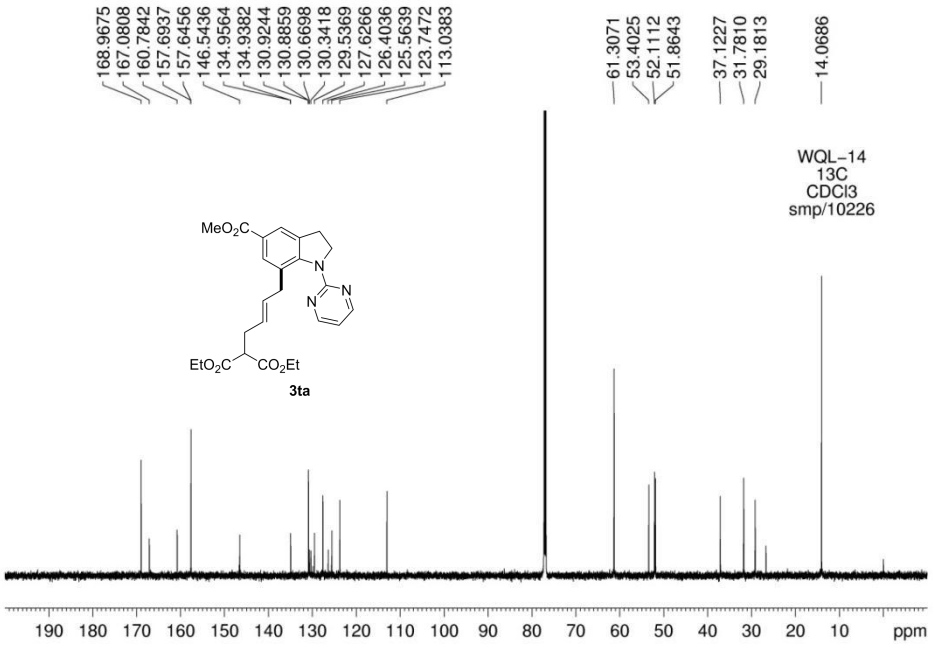


Figure S44. ^{13}C NMR spectrum of compound **3ta**

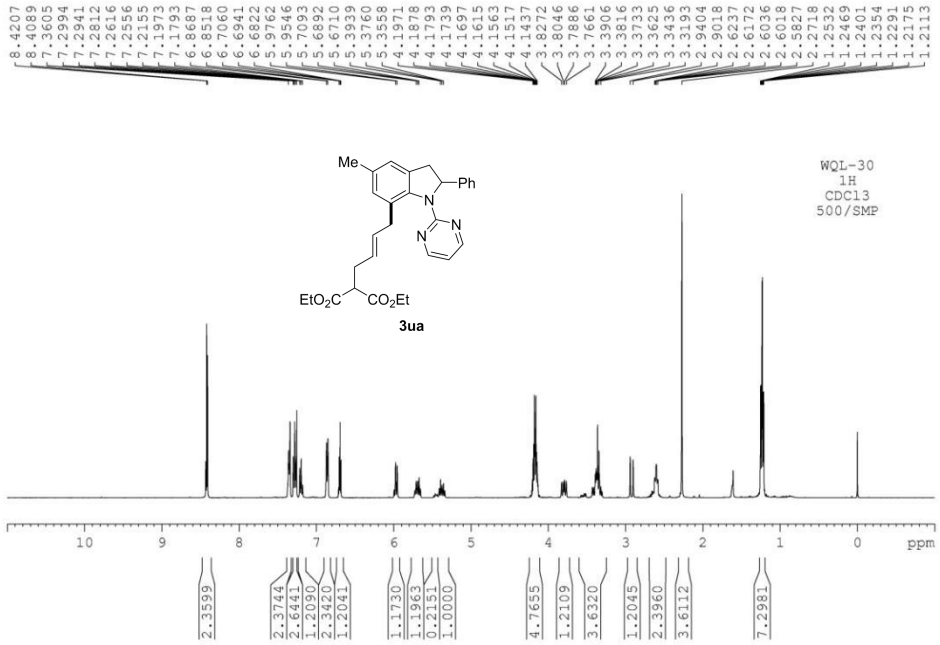


Figure S45. [1]H NMR spectrum of compound **3ua**

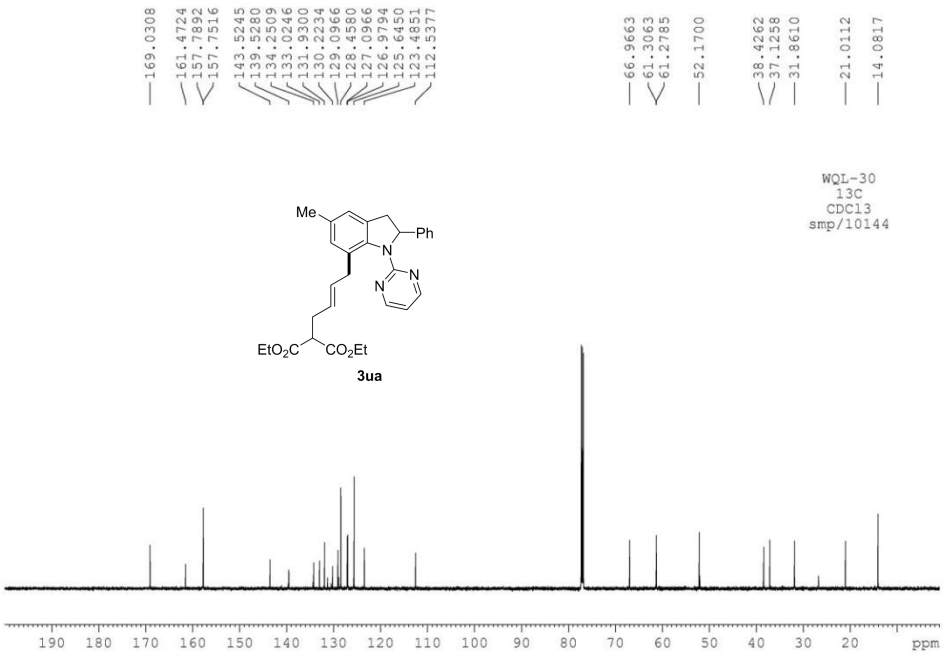


Figure S46. [13]C NMR spectrum of compound **3ua**

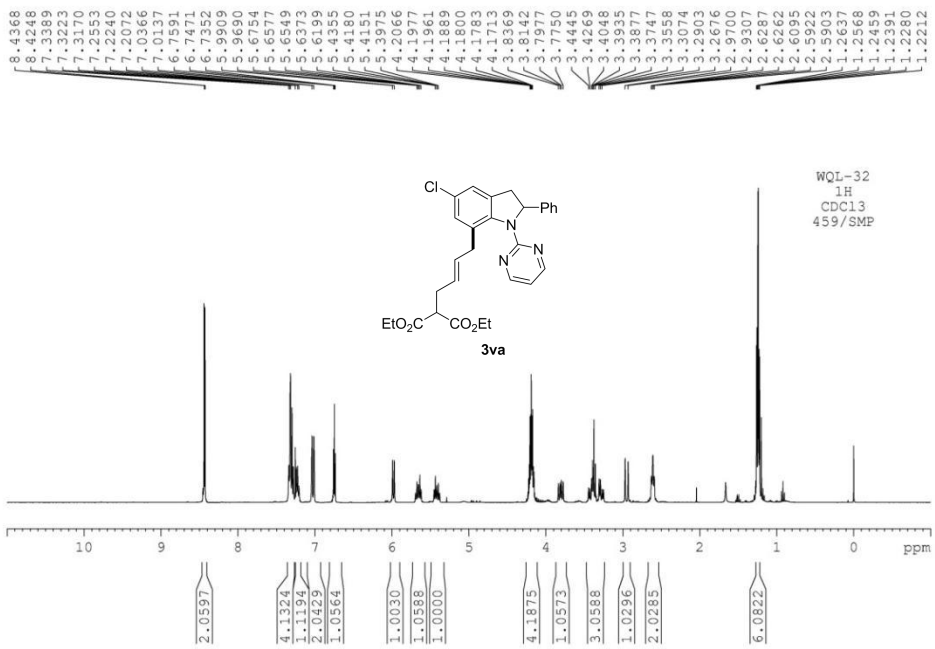


Figure S47. ^{1}H NMR spectrum of compound **3va**

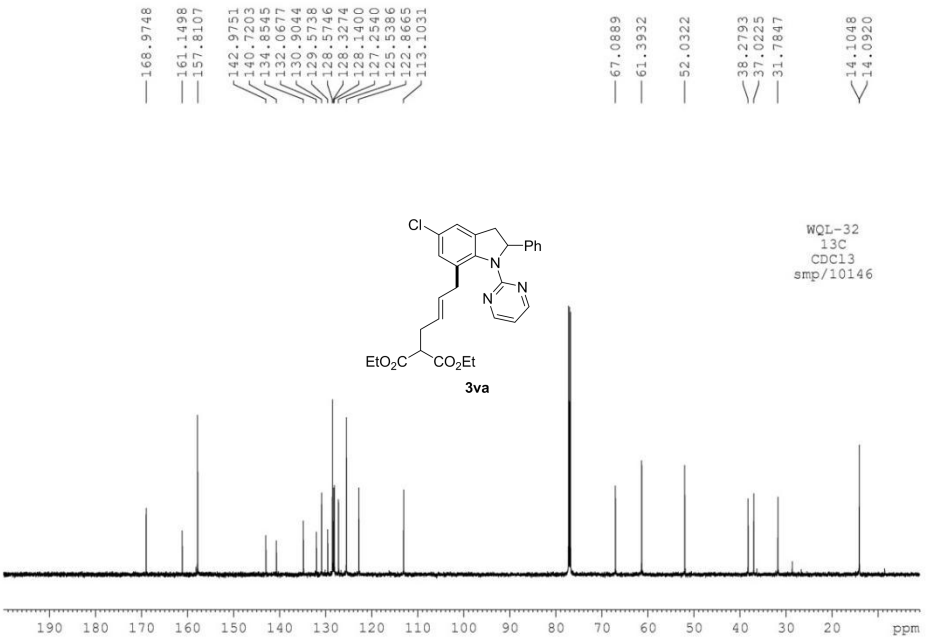


Figure S48. ^{13}C NMR spectrum of compound **3va**

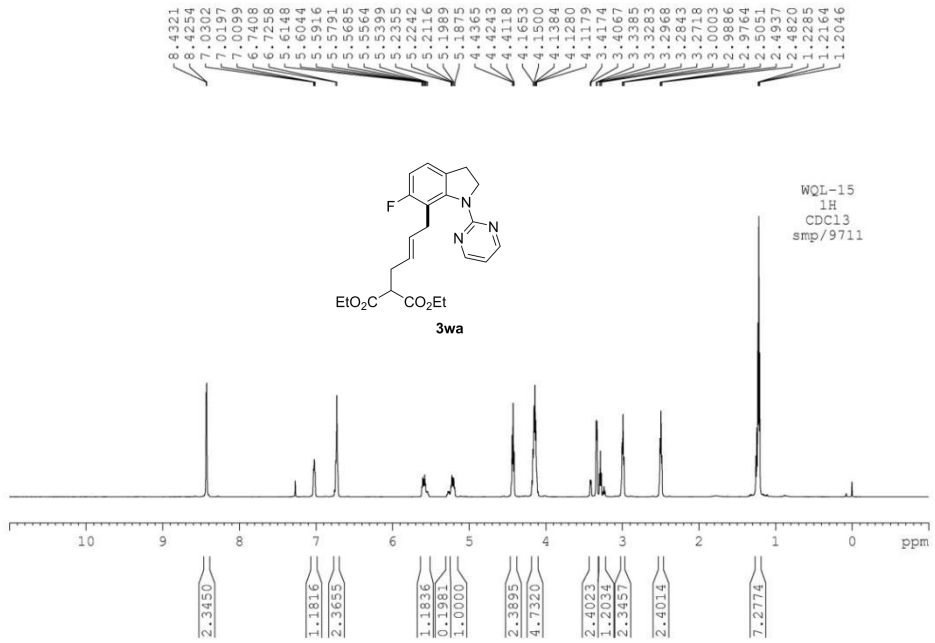


Figure S49. ^{1}H NMR spectrum of compound **3wa**

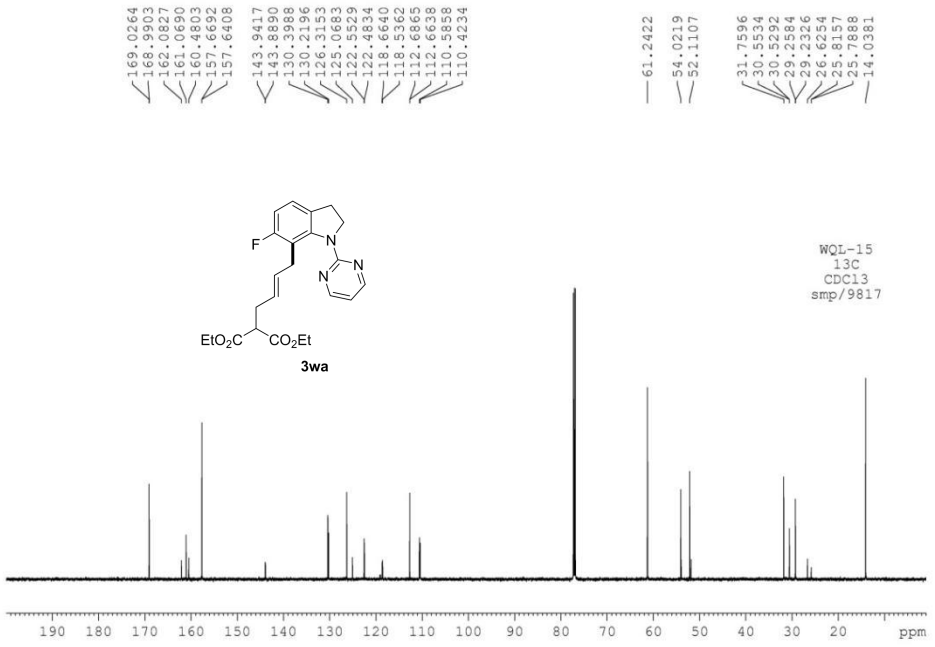


Figure S50. ^{13}C NMR spectrum of compound **3wa**

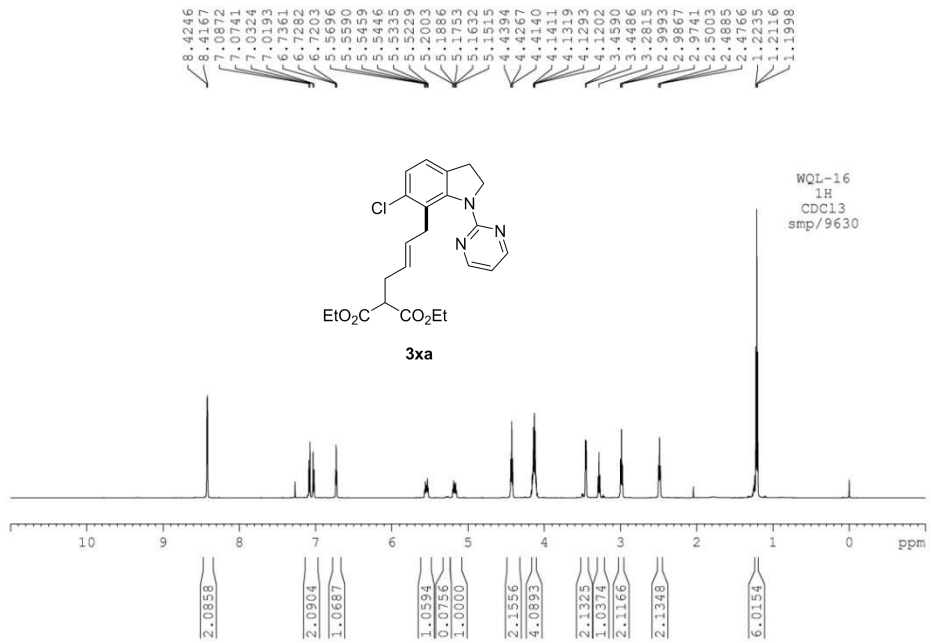


Figure S51. ^{1}H NMR spectrum of compound **3xa**

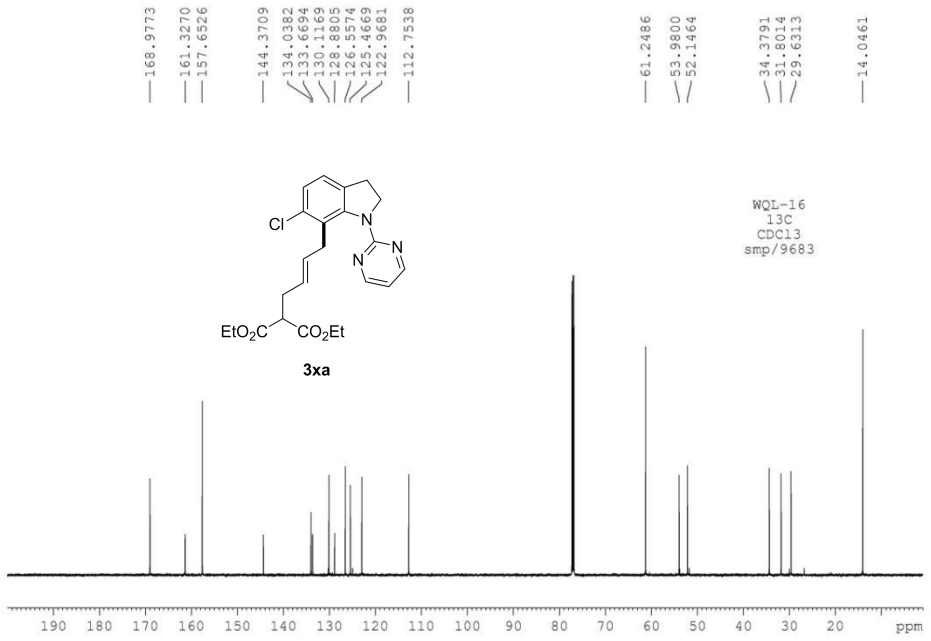


Figure S52. ^{13}C NMR spectrum of compound **3xa**

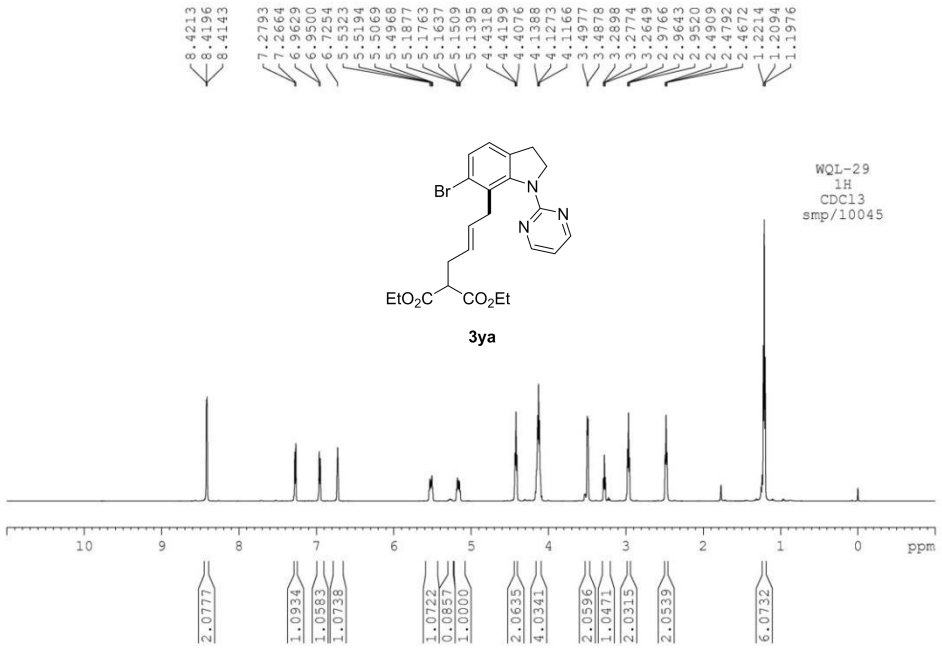


Figure S53. ^{1}H NMR spectrum of compound **3ya**

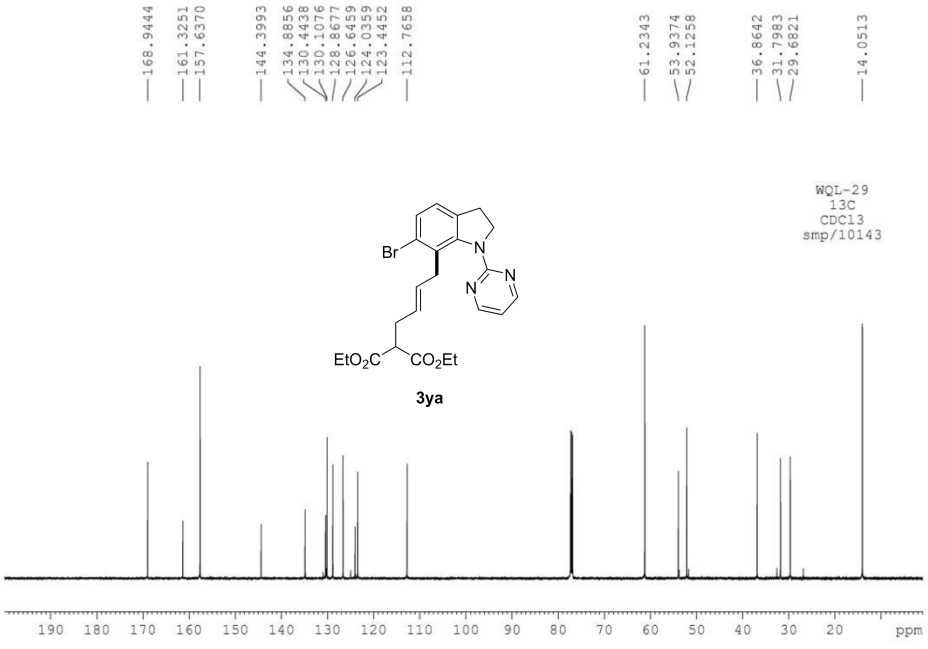


Figure S54. ^{13}C NMR spectrum of compound **3ya**

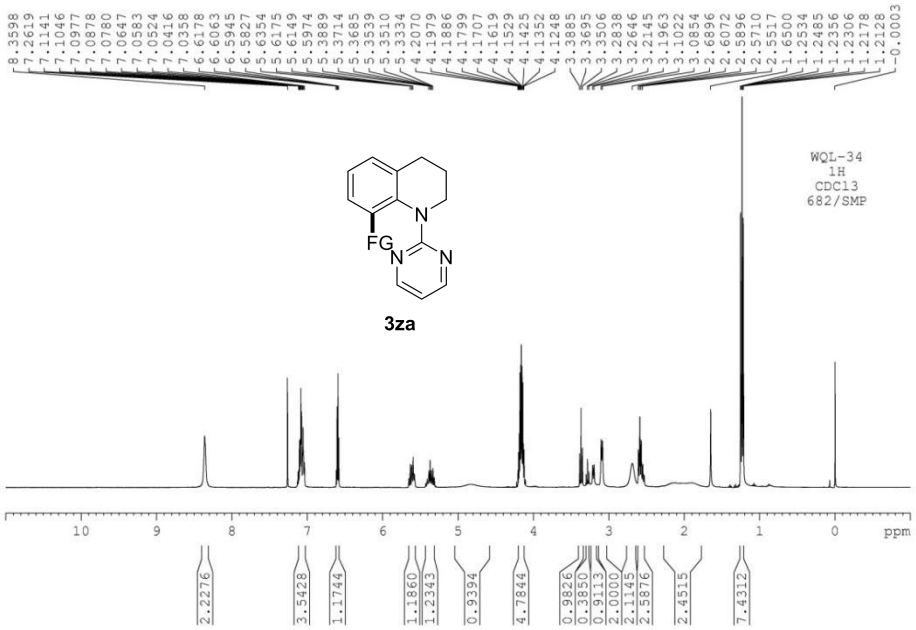


Figure S55. ^{1}H NMR spectrum of compound **3za**

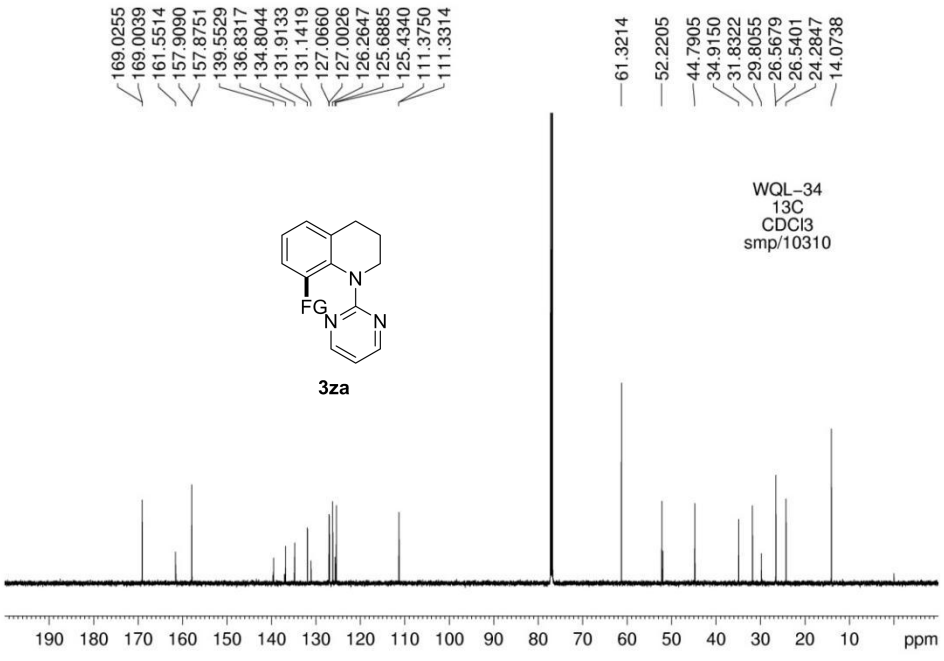


Figure S56. ^{13}C NMR spectrum of compound **3za**

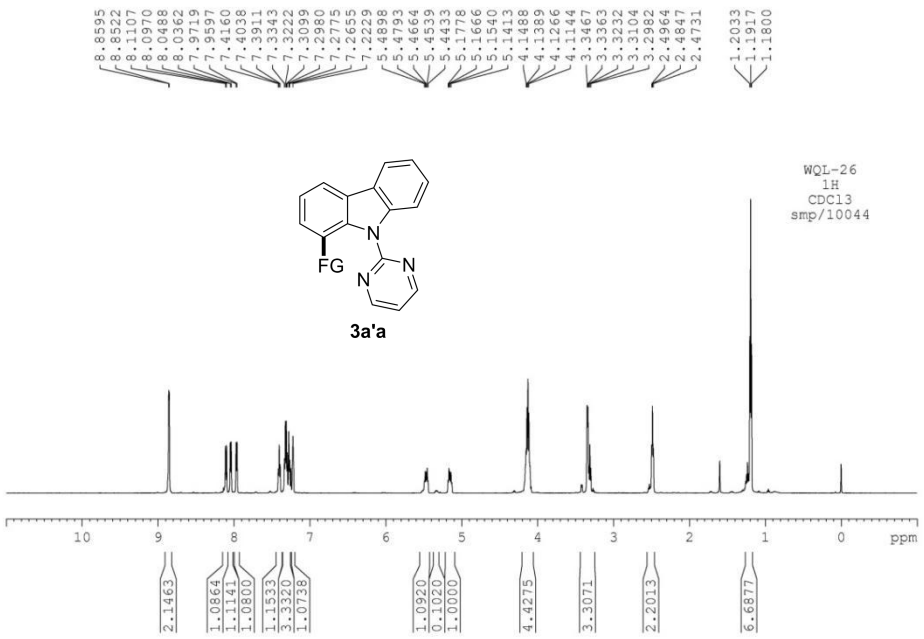


Figure S57. ^{1}H NMR spectrum of compound **3a'a**

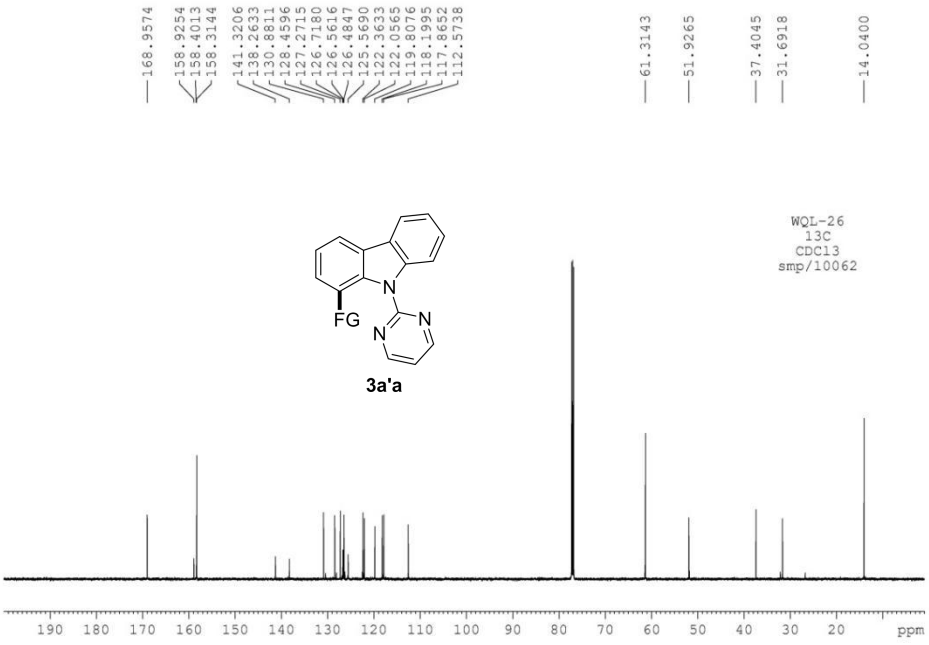


Figure S58. ^{13}C NMR spectrum of compound **3a'a**

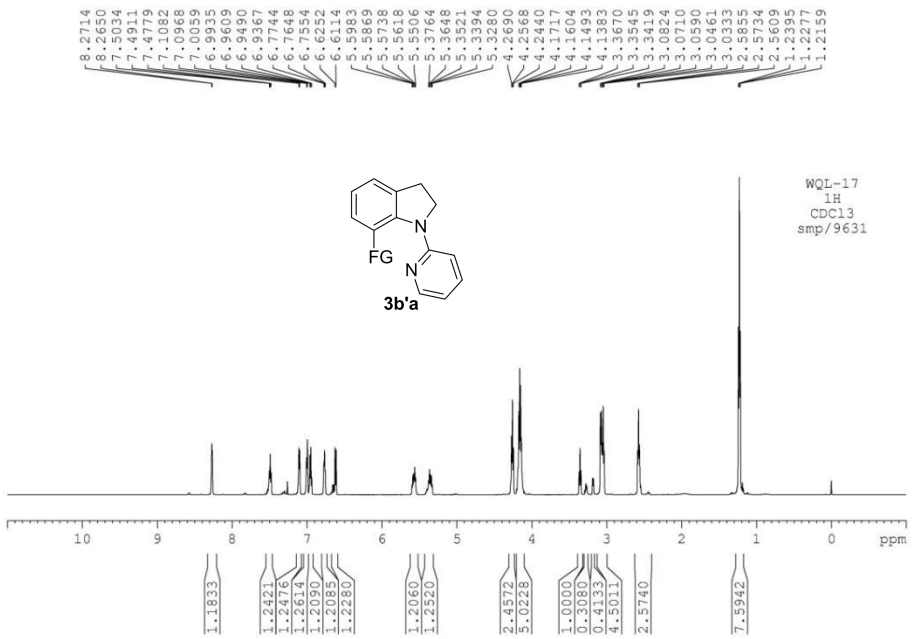


Figure S59. ^{1}H NMR spectrum of compound **3b'a**

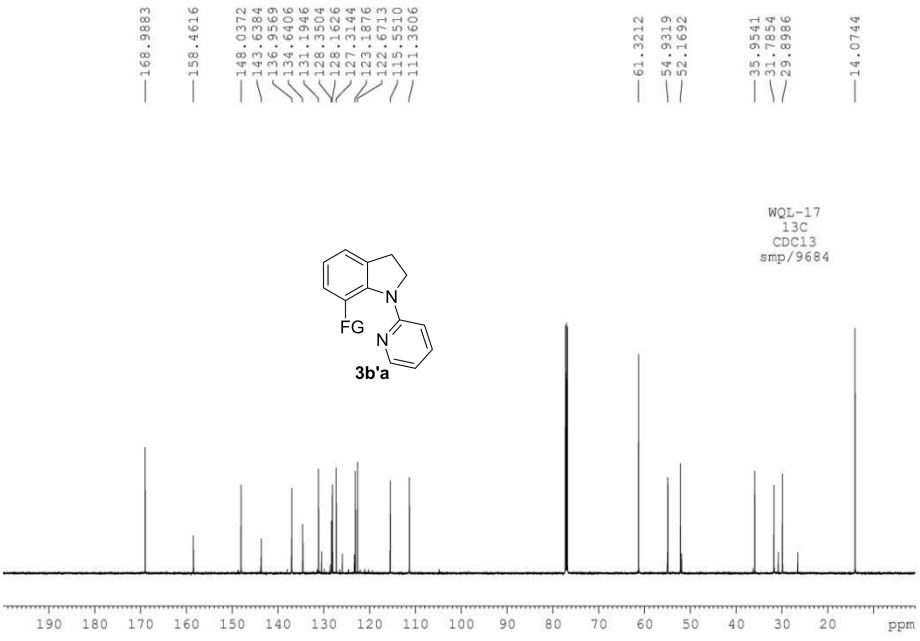


Figure S60. ^{13}C NMR spectrum of compound **3b'a**

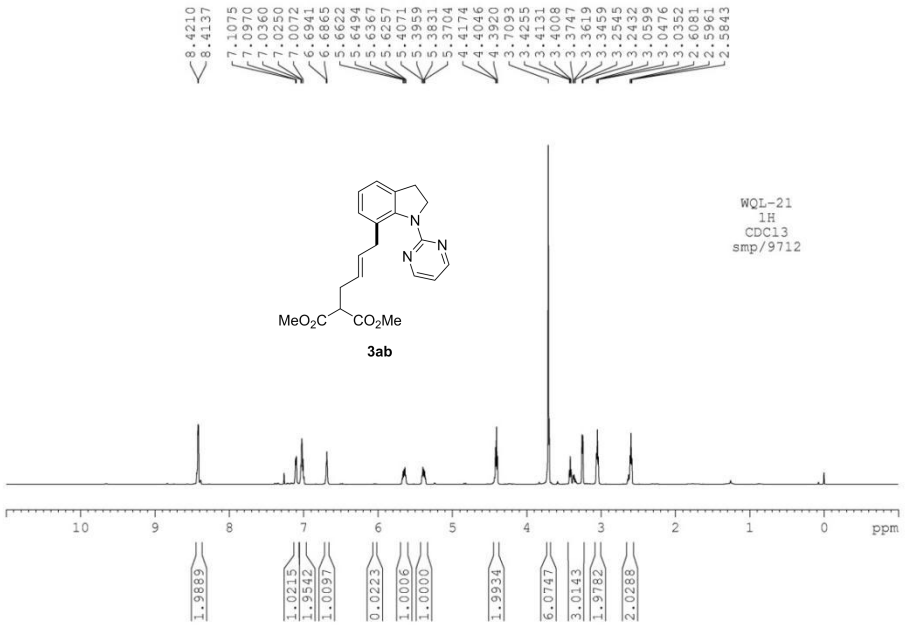


Figure S61. ^{1}H NMR spectrum of compound **3ab**

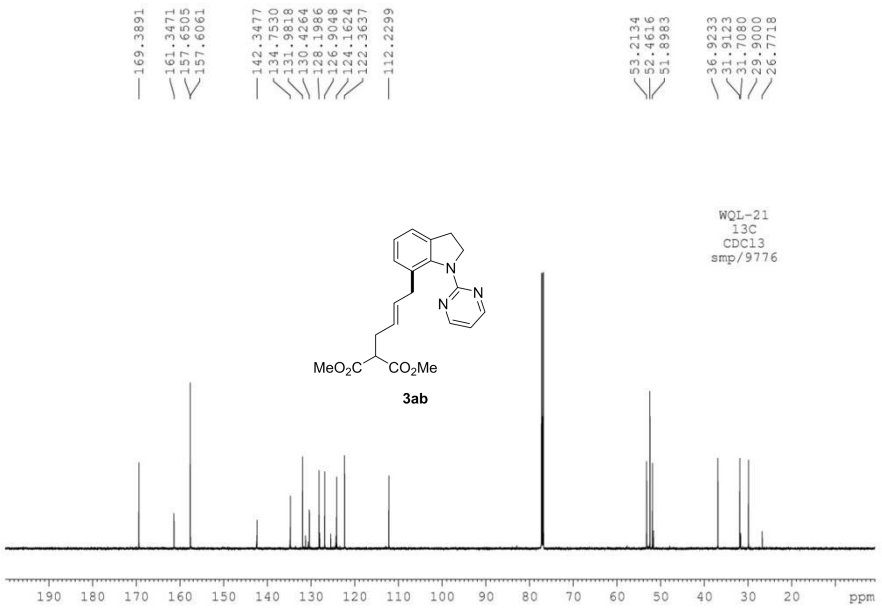


Figure S62. ^{13}C NMR spectrum of compound **3ab**

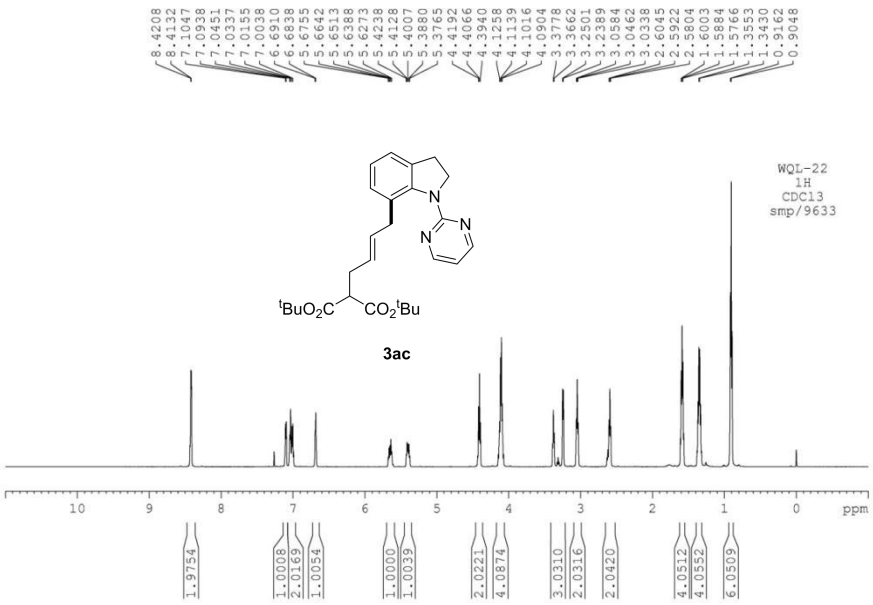


Figure S63. ^{1}H NMR spectrum of compound **3ac**

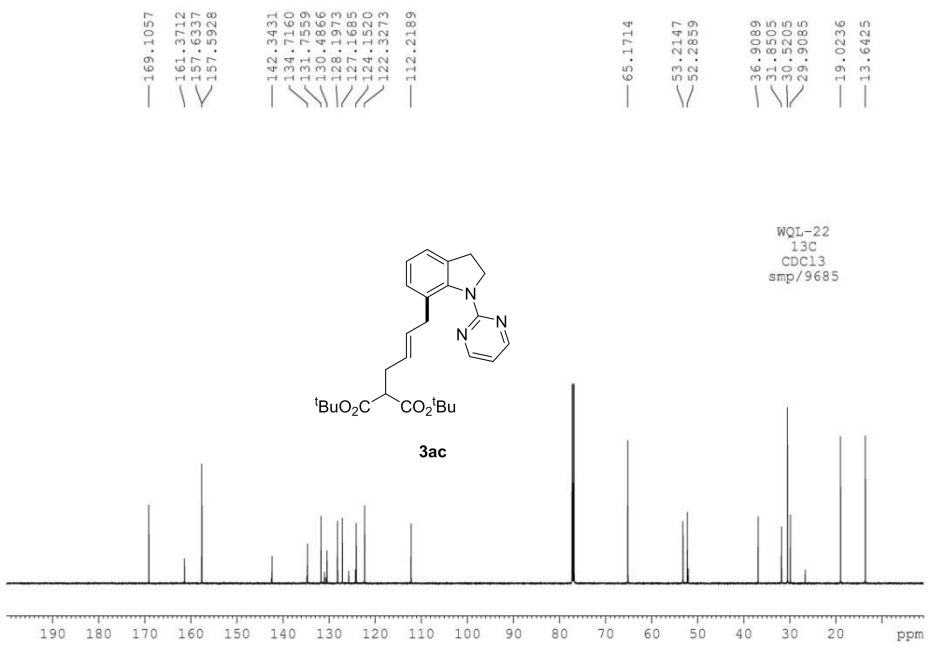


Figure S64. ^{13}C NMR spectrum of compound **3ac**

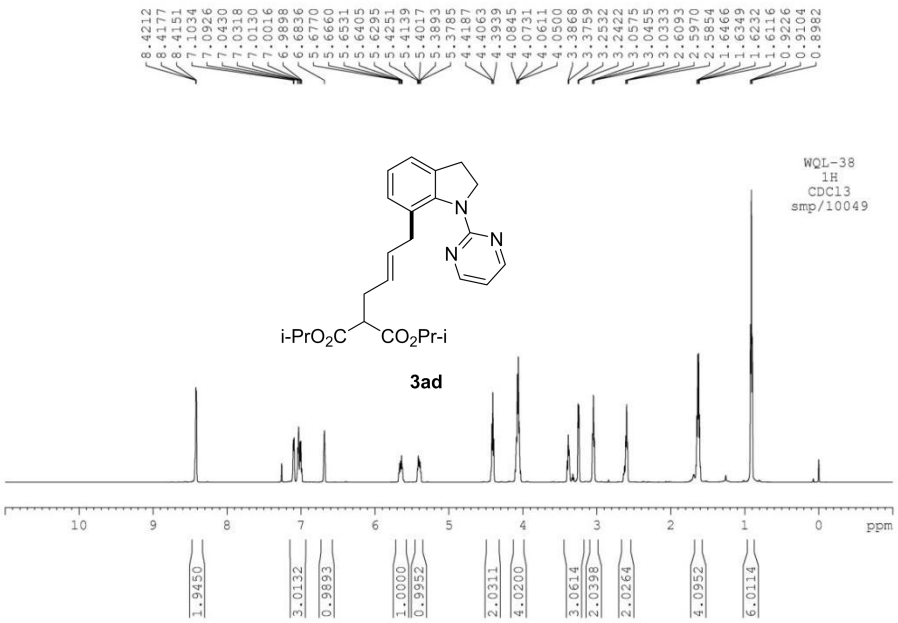


Figure S65. ^{1}H NMR spectrum of compound **3ad**

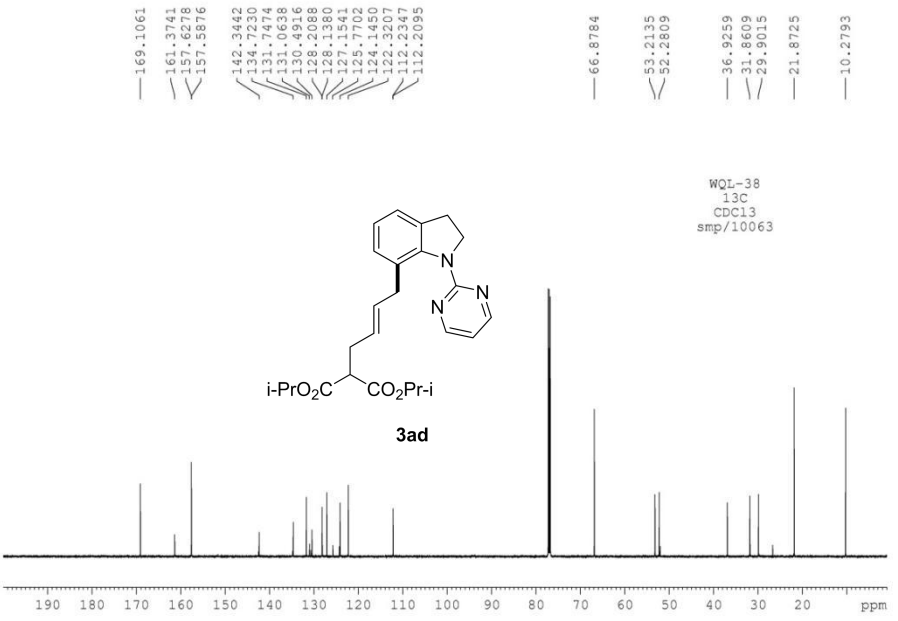


Figure S66. ^{13}C NMR spectrum of compound **3ad**

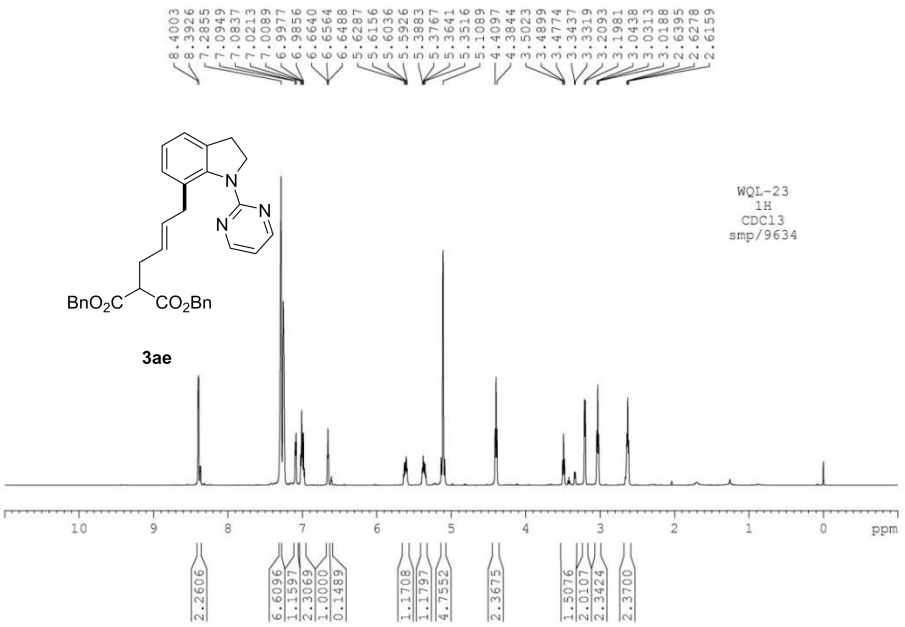


Figure S67. ^{1}H NMR spectrum of compound **3ae**

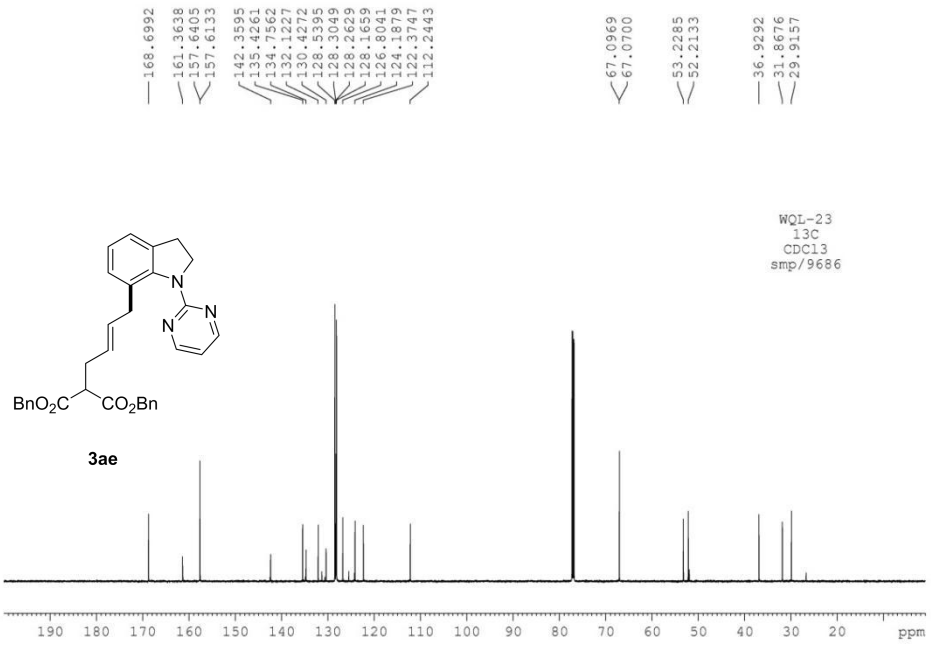


Figure S68. ^{13}C NMR spectrum of compound **3ae**

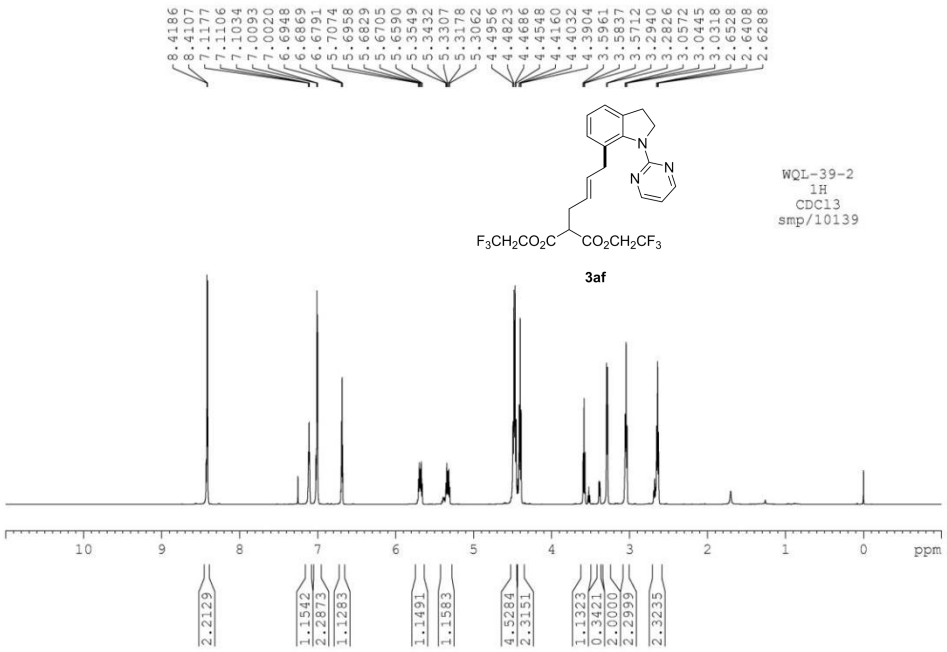


Figure S69. [1]H NMR spectrum of compound **3af**

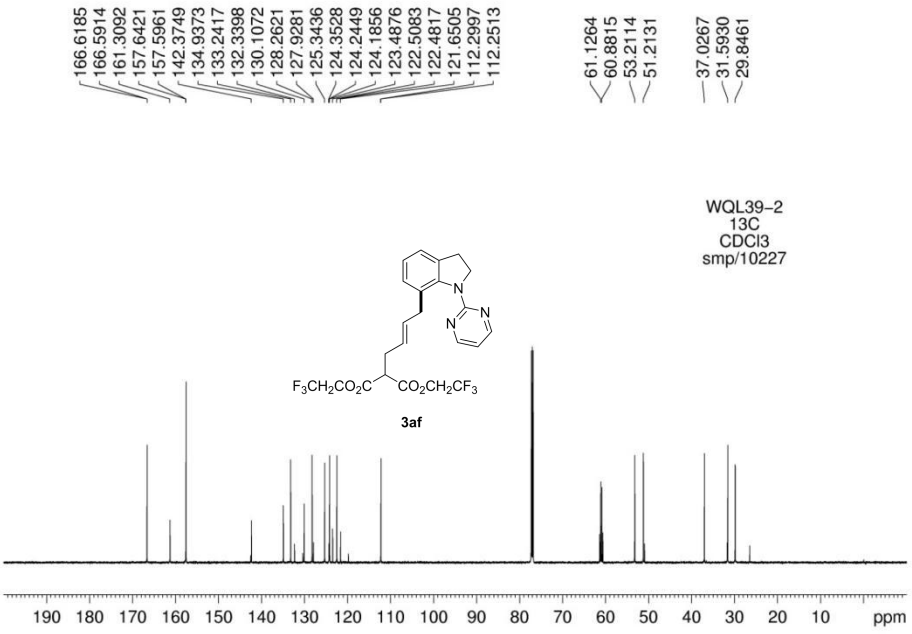


Figure S70. [13]C NMR spectrum of compound **3af**

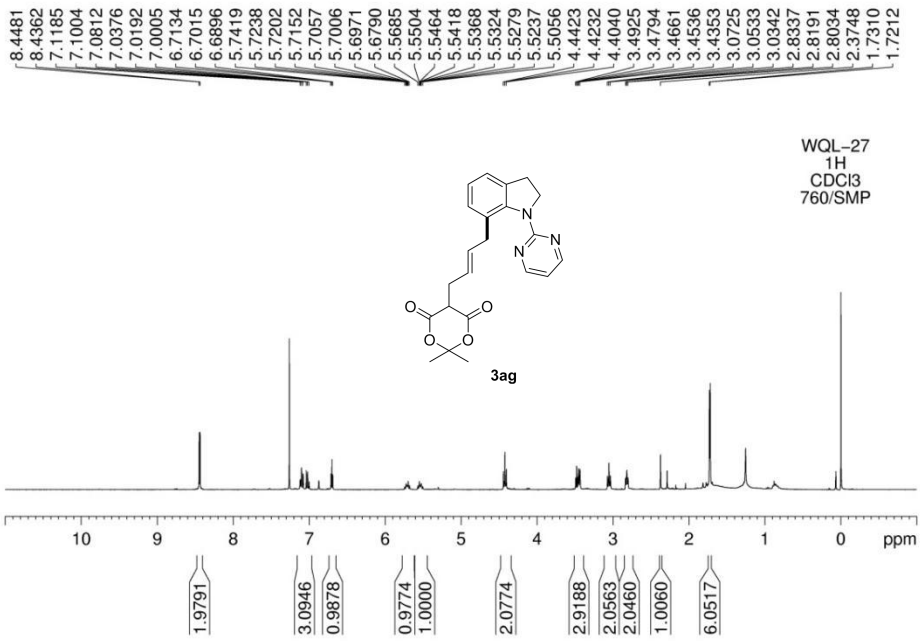


Figure S71. ^{1}H NMR spectrum of compound **3ag**

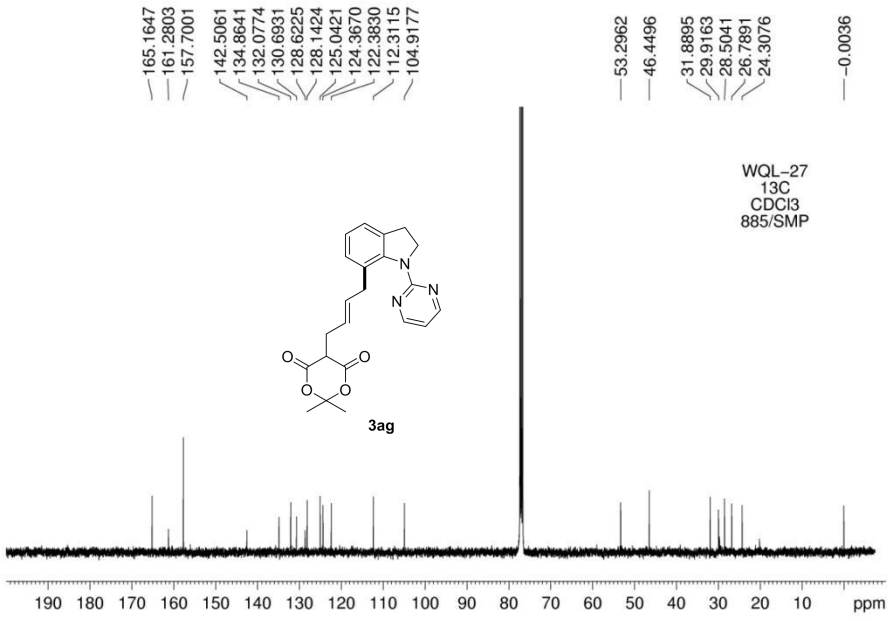


Figure S72. ^{13}C NMR spectrum of compound **3ag**

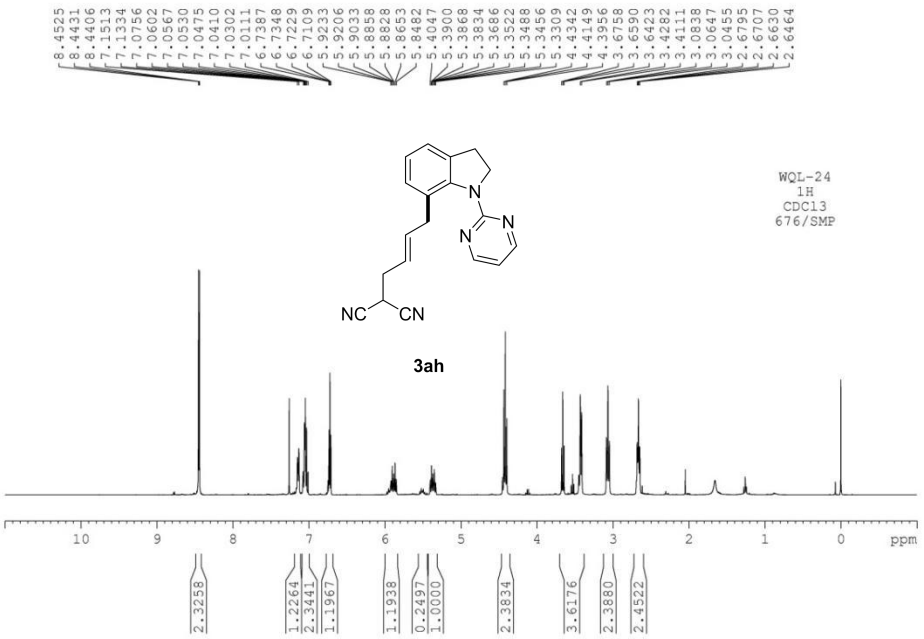


Figure S73. ^{1}H NMR spectrum of compound **3ah**

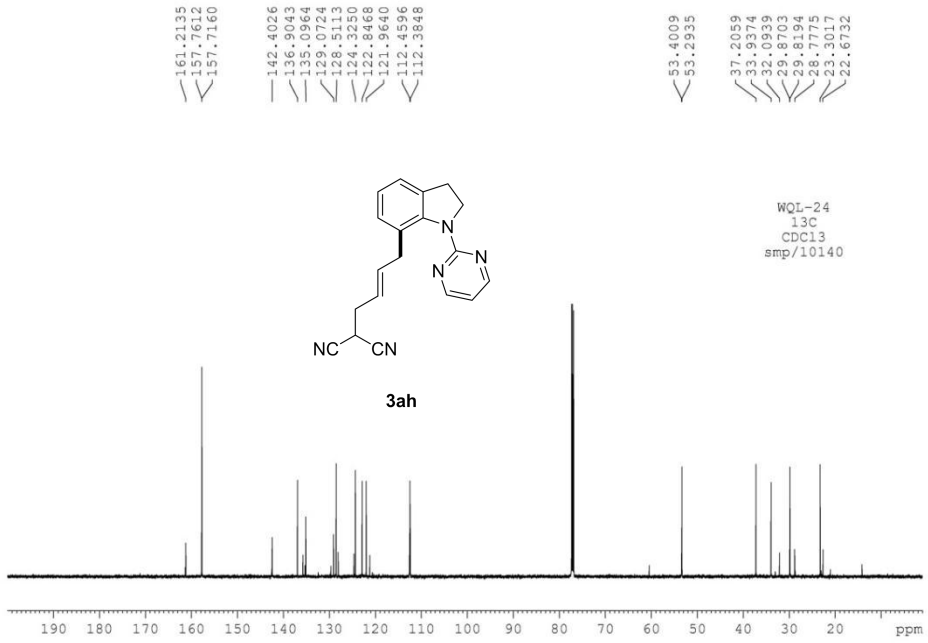


Figure S74. ^{13}C NMR spectrum of compound **3ah**

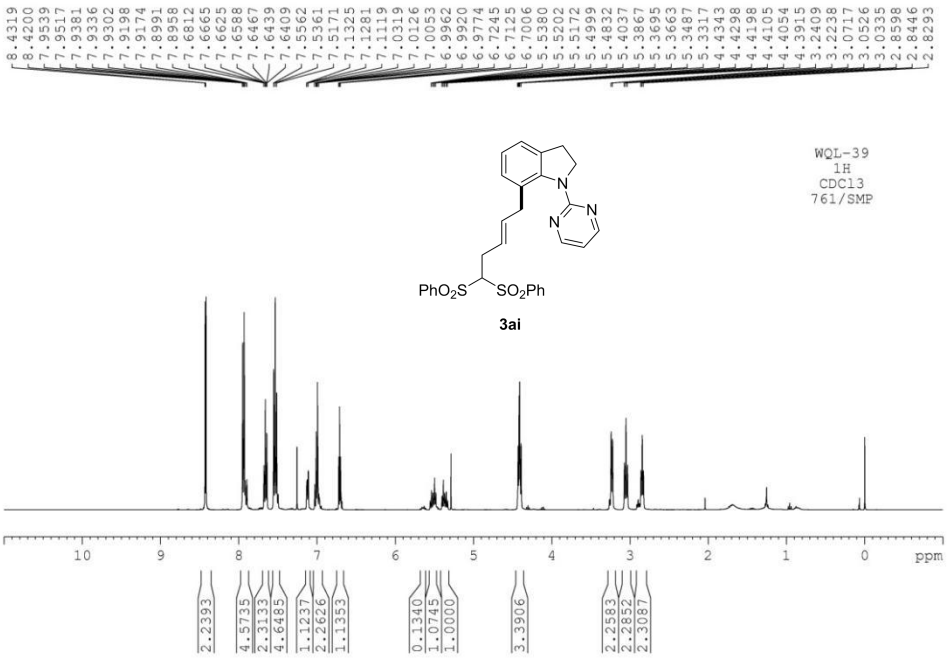


Figure S75. ^{1}H NMR spectrum of compound **3ai**

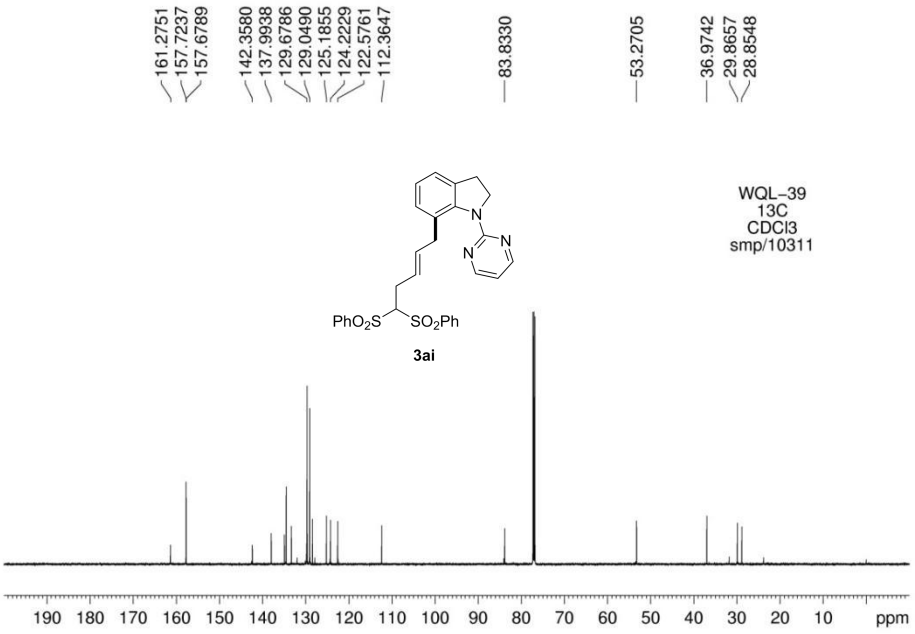


Figure S76. ^{13}C NMR spectrum of compound **3ai**

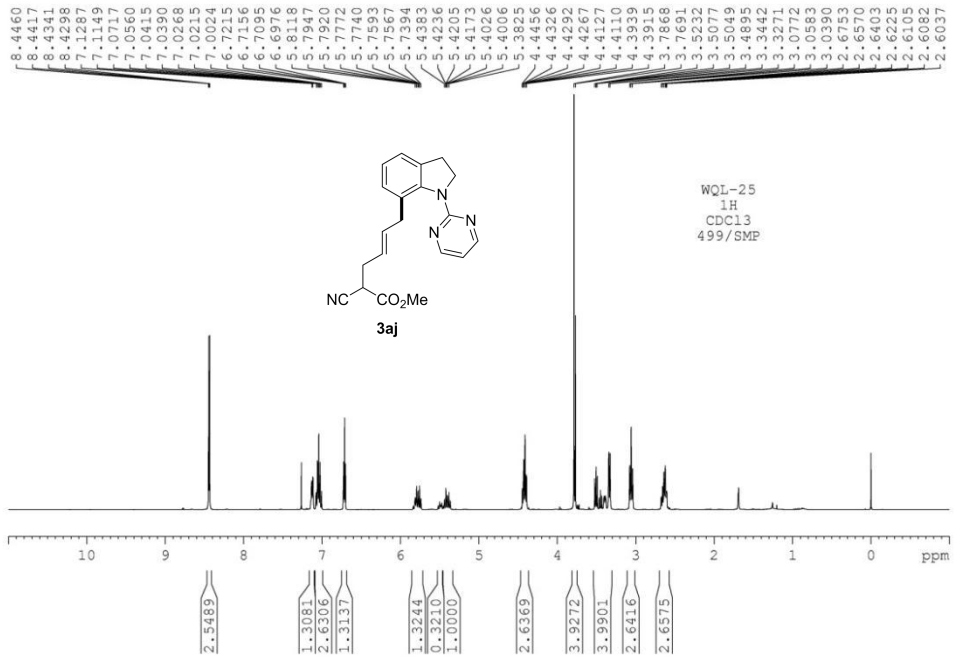


Figure S77. ^{1}H NMR spectrum of compound **3aj**

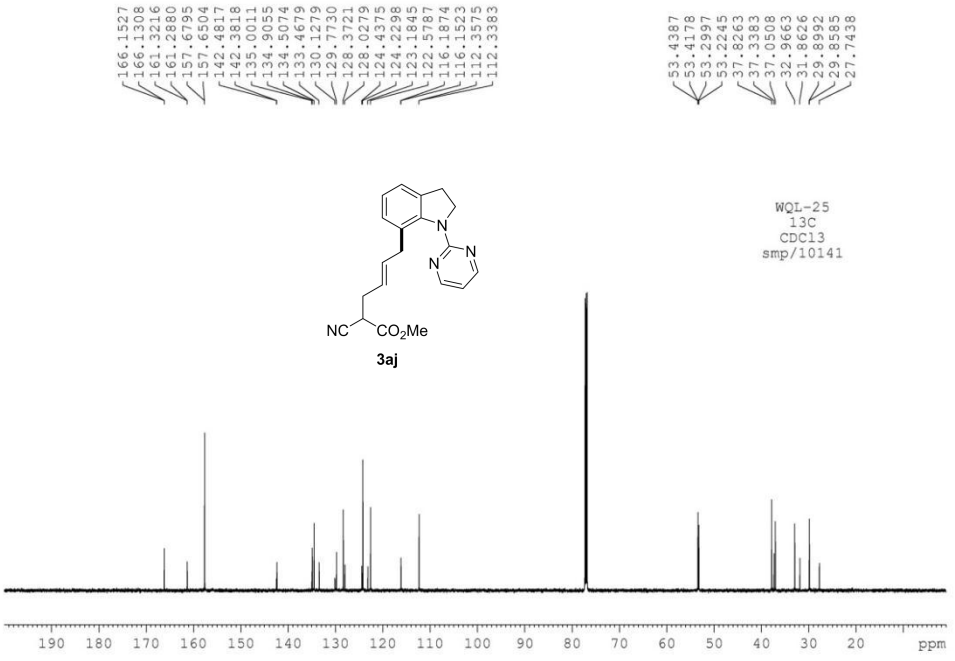


Figure S78. ^{13}C NMR spectrum of compound **3aj**

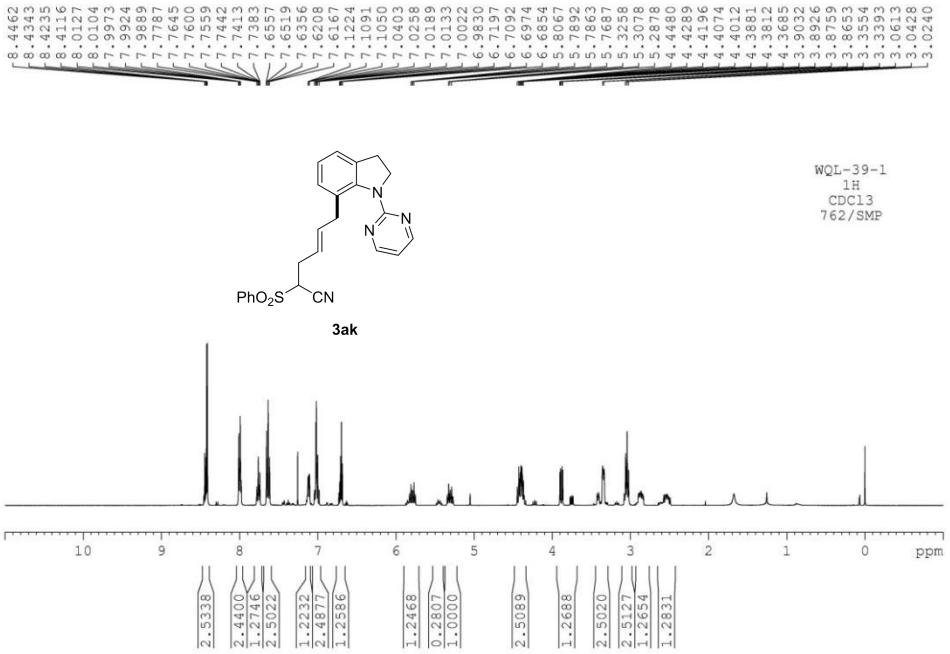


Figure S79. ^{1}H NMR spectrum of compound **3ak**

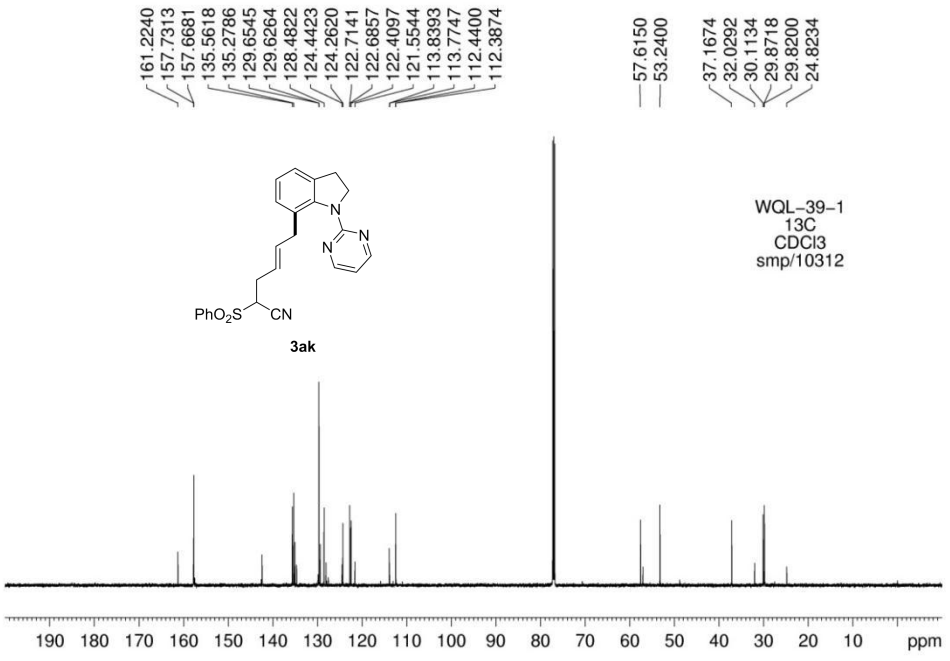


Figure S80. ^{13}C NMR spectrum of compound **3ak**

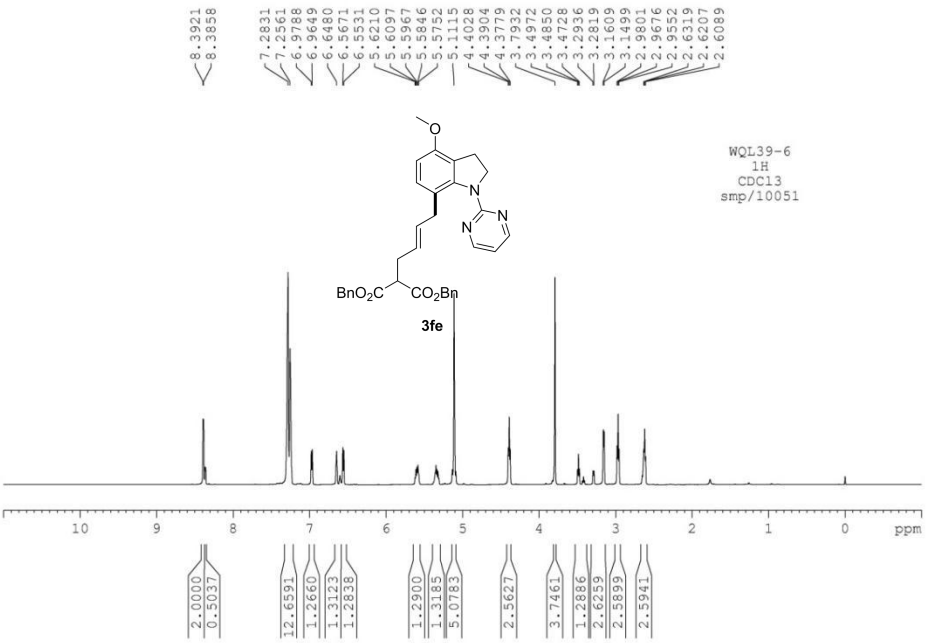


Figure S81. ^{1}H NMR spectrum of compound **3fe**

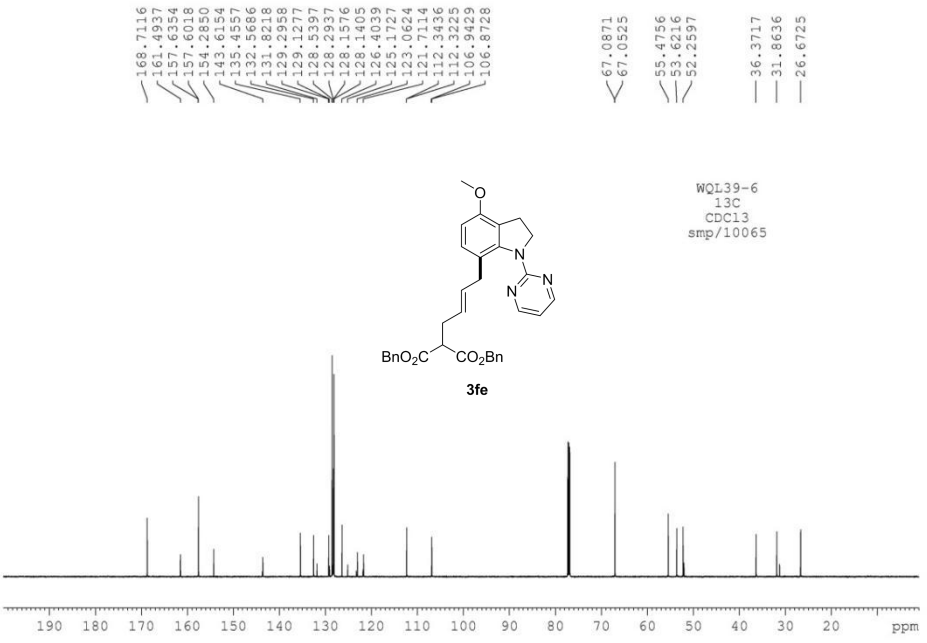


Figure S82. ^{13}C NMR spectrum of compound **3fe**

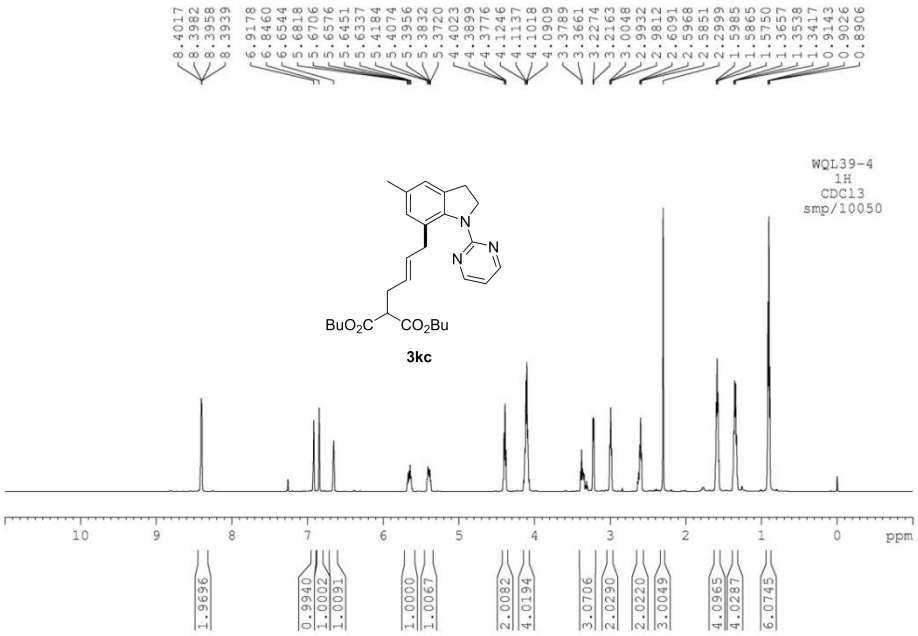


Figure S83. ^{1}H NMR spectrum of compound **3kc**

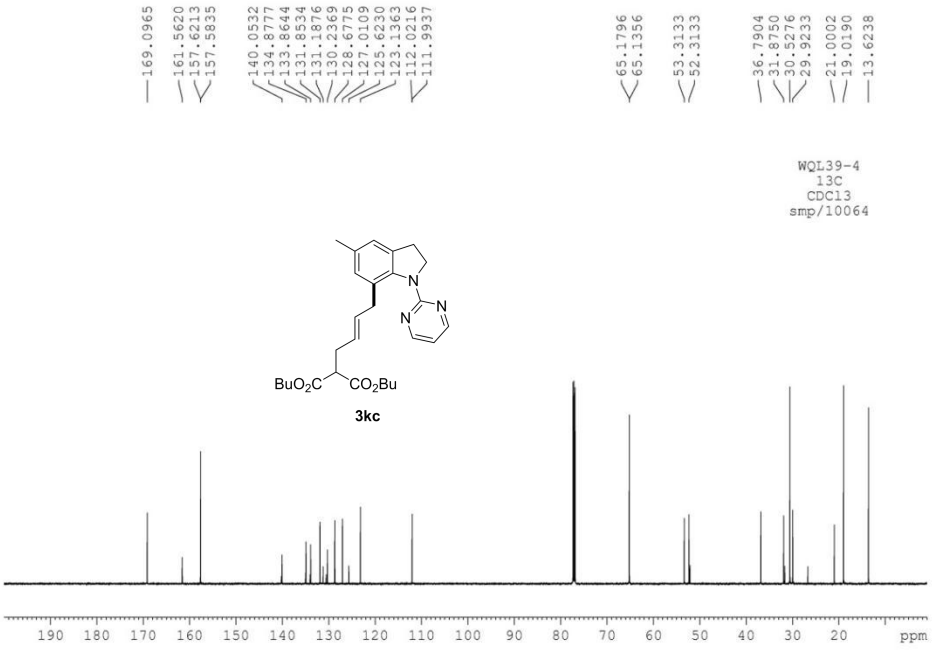


Figure S84. ^{13}C NMR spectrum of compound **3kc**

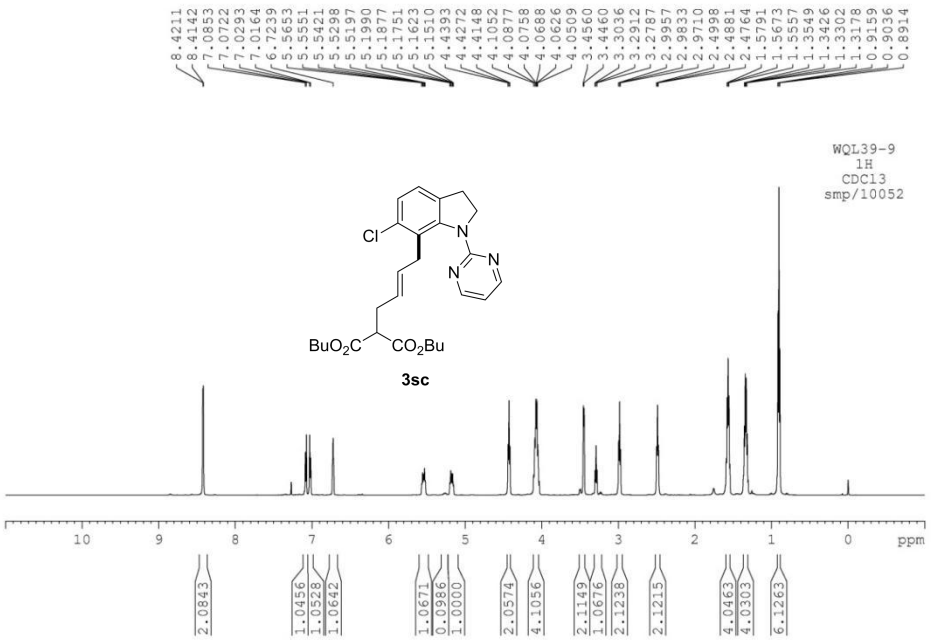


Figure S85. [1]H NMR spectrum of compound **3sc**

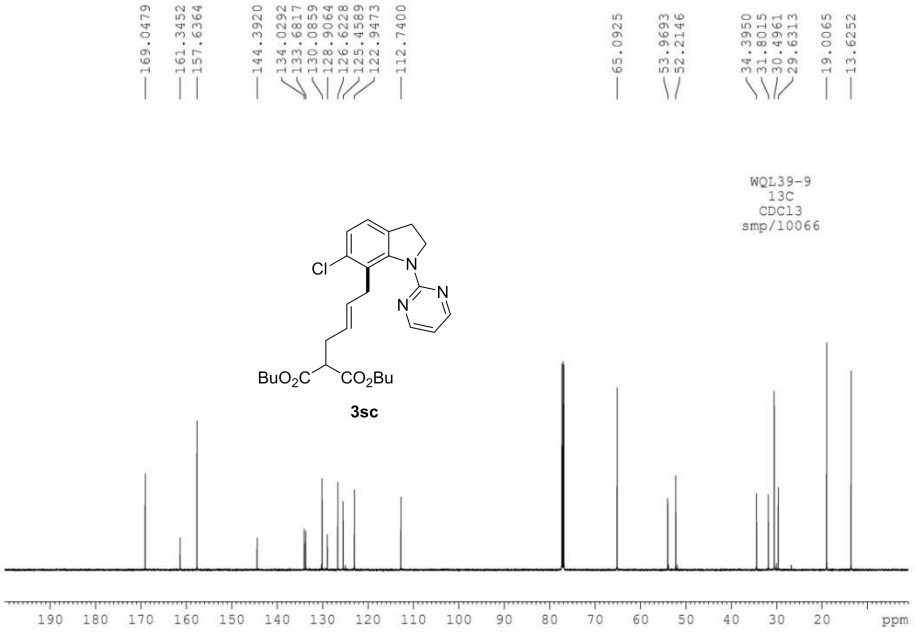


Figure S86. [13]C NMR spectrum of compound **3sc**

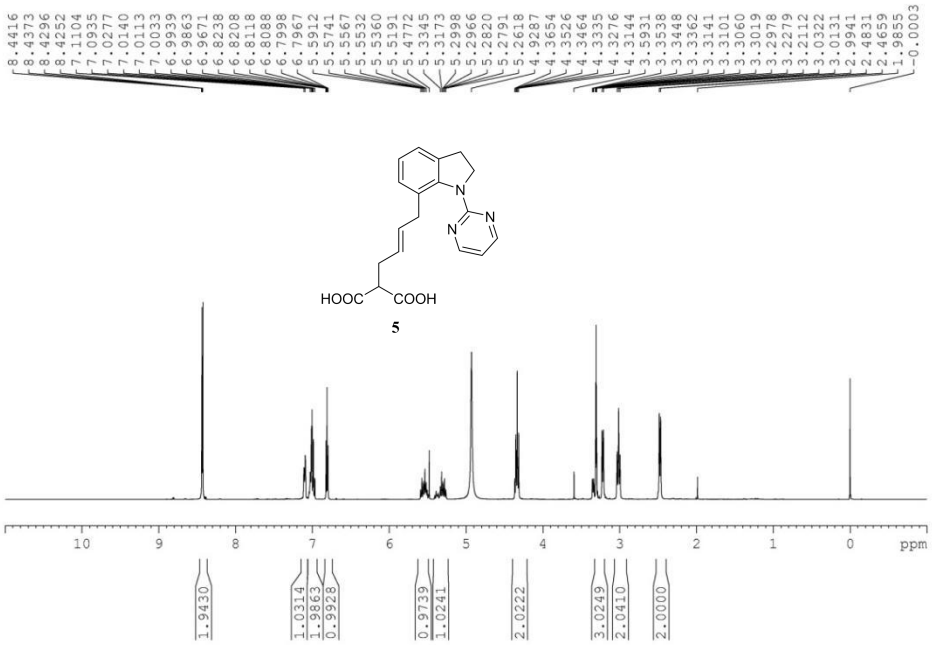


Figure S87. ^{1}H NMR spectrum of compound **5**

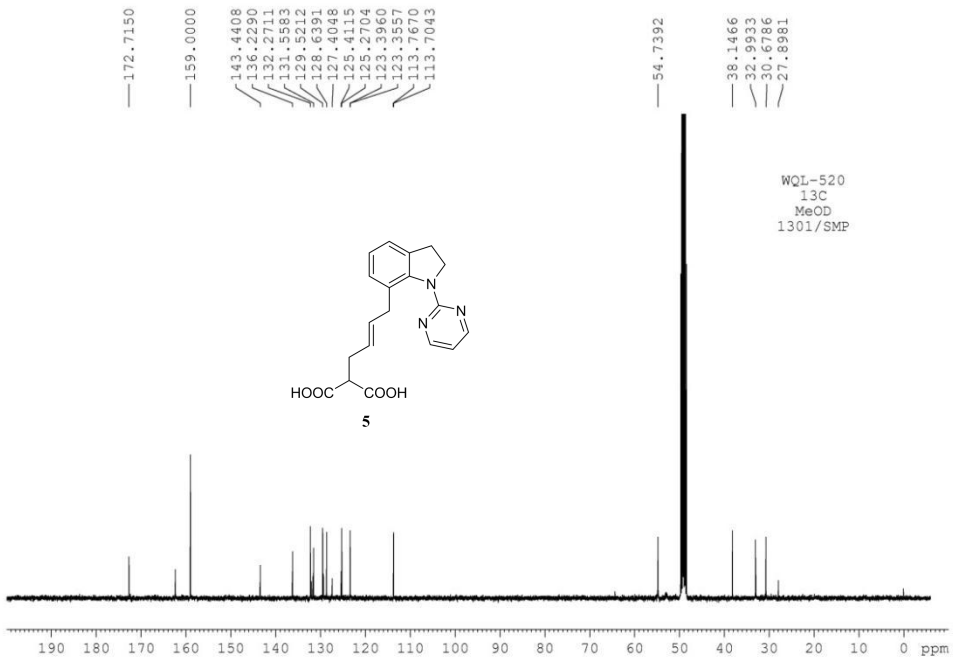


Figure S88. ^{13}C NMR spectrum of compound **5**

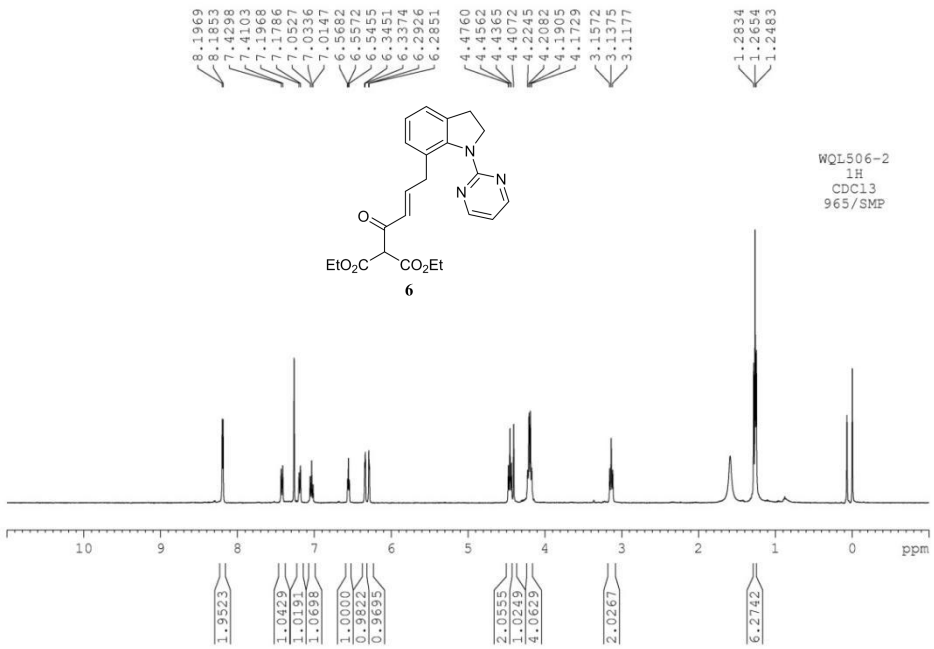


Figure S89. ^{1}H NMR spectrum of compound **6**

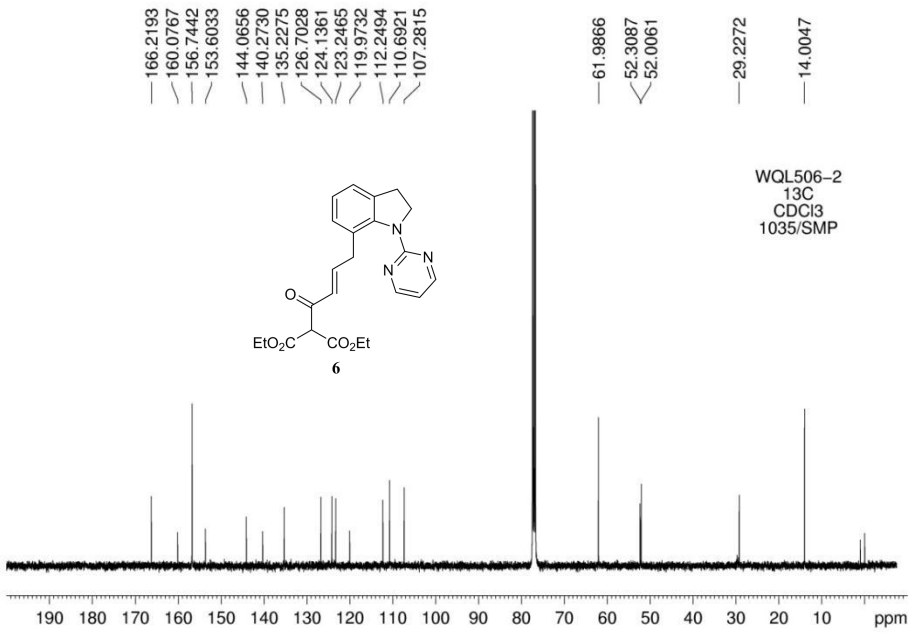


Figure S90. ^{13}C NMR spectrum of compound **6**

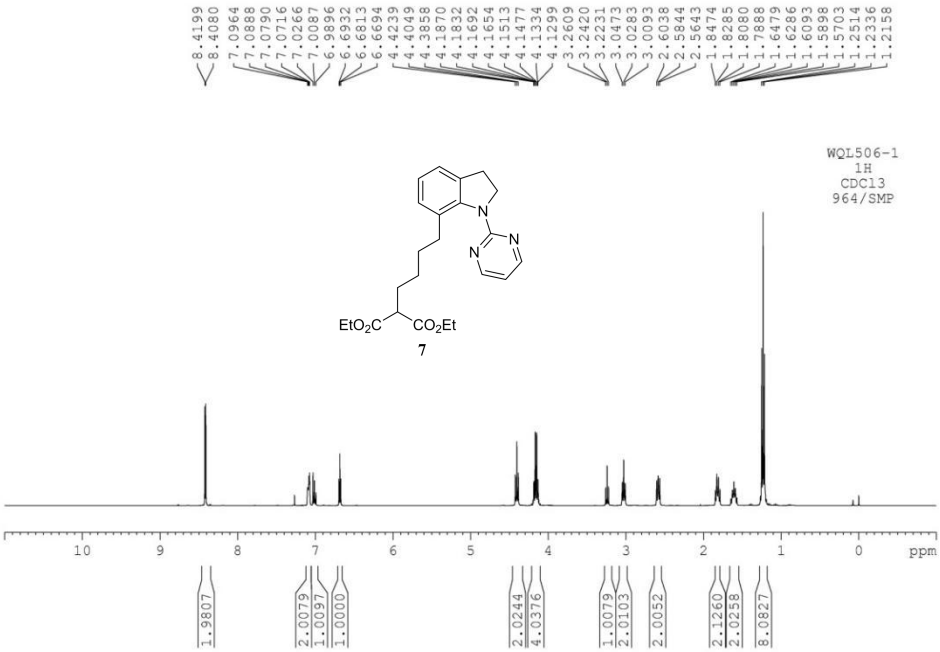


Figure S91. ^{1}H NMR spectrum of compound **7**

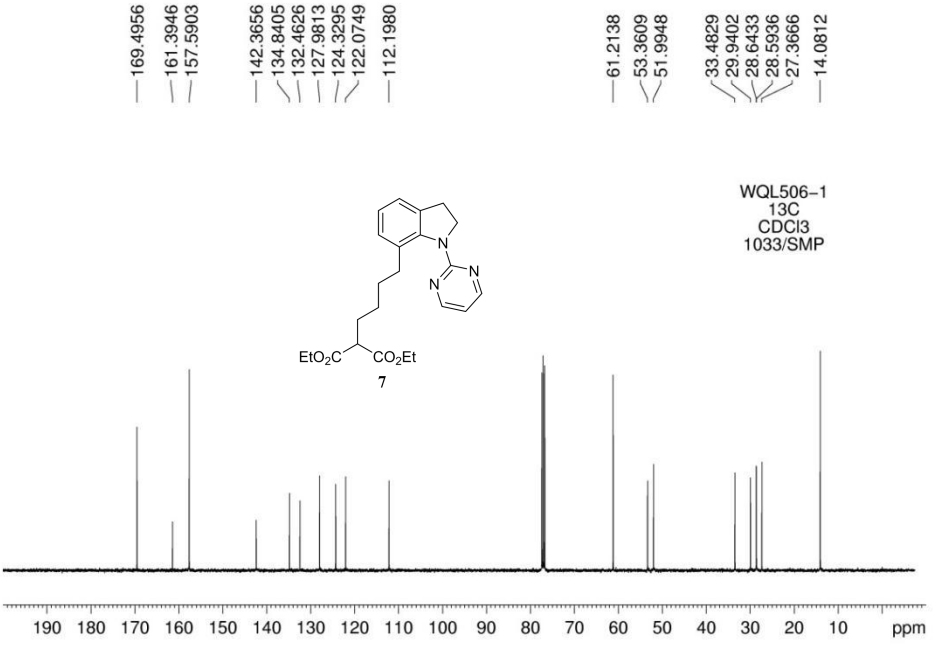


Figure S92. ^{13}C NMR spectrum of compound **7**

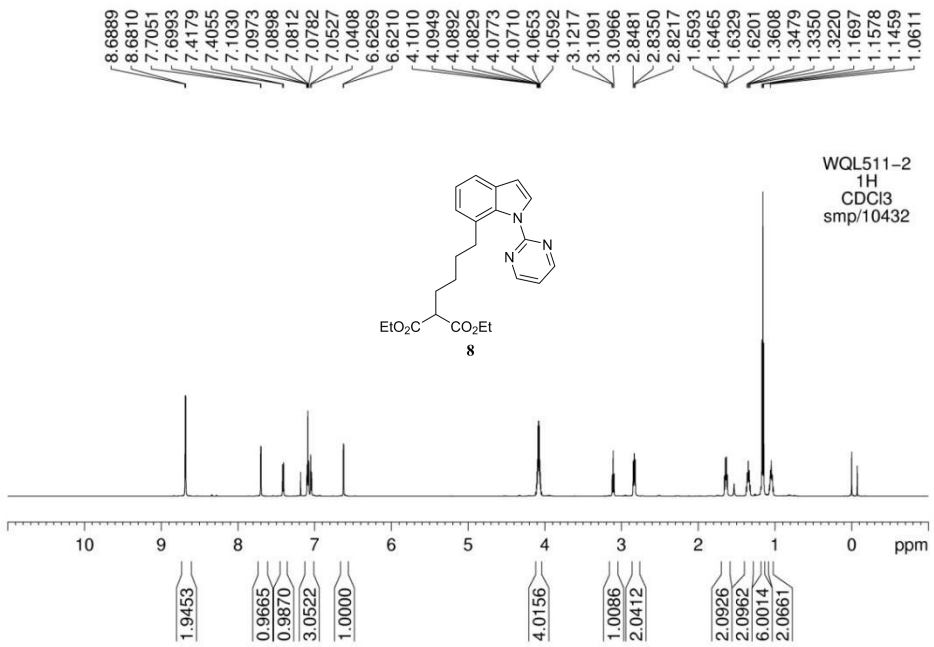


Figure S93. ^{1}H NMR spectrum of compound **8**

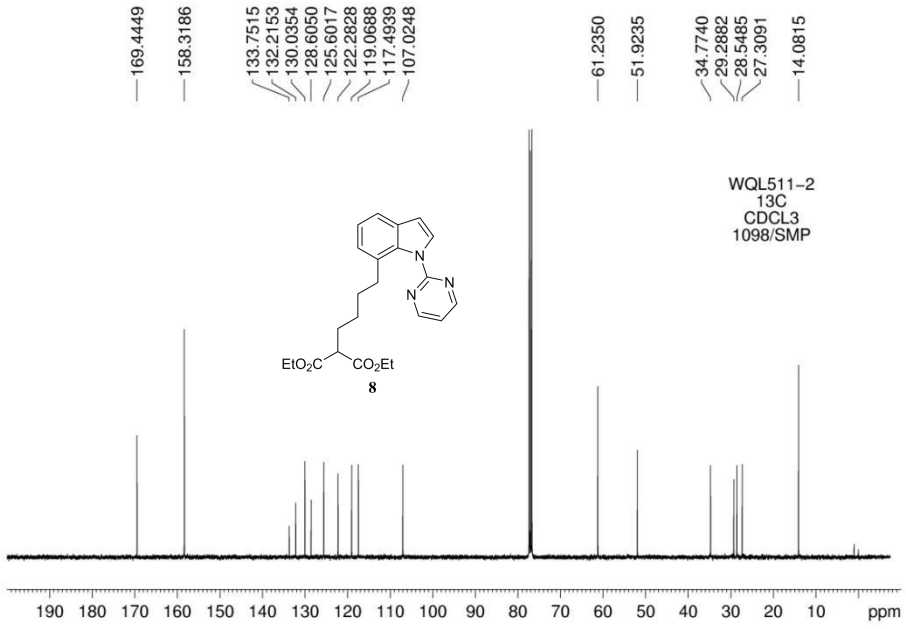


Figure S94. ^{13}C NMR spectrum of compound **8**

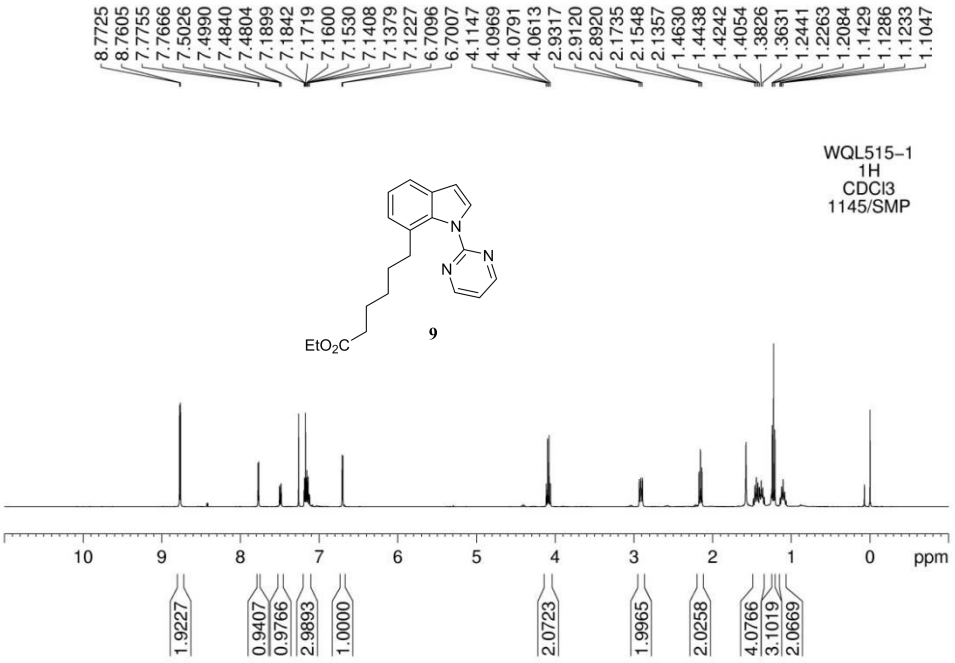


Figure S95. ^{1}H NMR spectrum of compound **9**

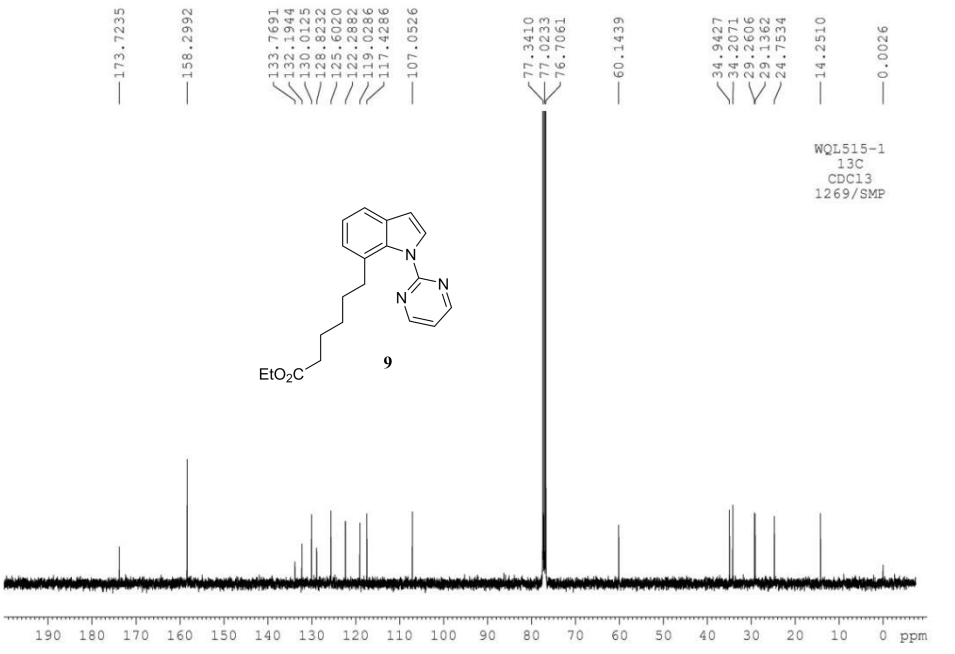


Figure S96. ^{13}C NMR spectrum of compound **9**