Supporting information for

Visible-Light-Driven Decarboxylative C(sp³)-H Alkylation of Glycine Derivatives via in situ formation of NHPI Esters

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Supporting Information

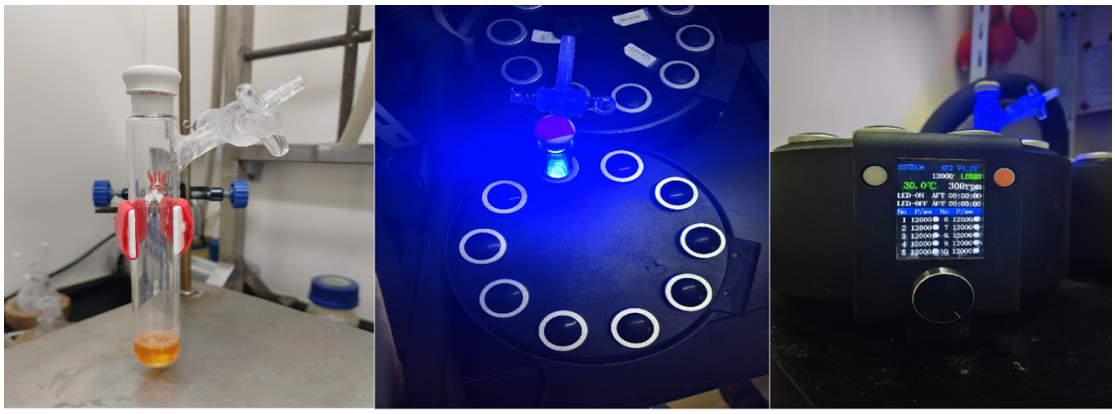
1. Experimental Section

1.1 General Considerations

All manipulations were conducted with Schlenk tube. ^{1}H NMR spectra were recorded on Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. Data were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, td = doublet of triplets, m = multiplet, br = broad signal), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm). High resolution mass spectrometry (HRMS) data were obtained on a QTOF mass analyzer with electrospray ionization (ESI) through a Bruker Daltonicmior OTOF-QII. All anhydrous solvents were commercially supplied from Energy-Chemical. Substrates were purchased from Bidepharm, Aladdin, Energy, or synthesized according to the procedures outlined below. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

1.2 Reaction setup

The optimization of reaction conditions was using parallel photoreactor (Purchasing from Shanghai 3STechnology Co., Ltd, AF2 type) irradiated with 12 W blue-light-emitting diodes (LEDs, 450-455 nm), 25 mL schlenk tubes were used for all 0.2 mmol scale reactions, the temperature was maintained at 30 °C.



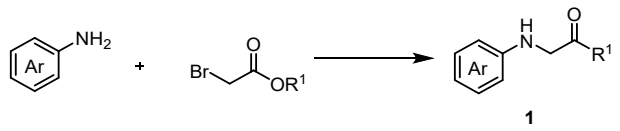
(1) (2)

(1) Reaction sealing tubes and the manual bottle capping tools for 0.2 mmol reactions.

(2) Parallel reaction setups under a photoreactor for 0.2 mmol reactions.

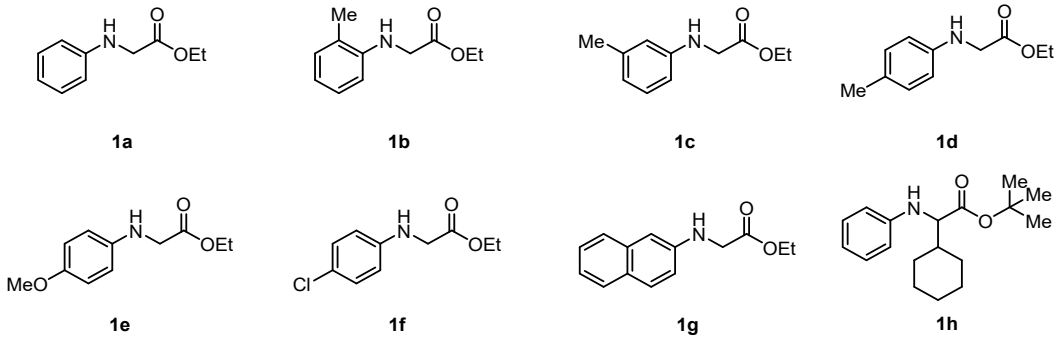
1.3 Starting Materials

(a) Preparation of glycine esters



1

Different glycine esters

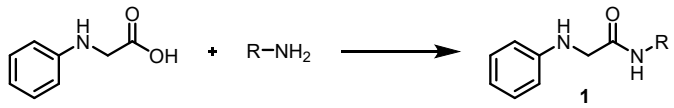


1a **1b** **1c** **1d**

1e **1f** **1g** **1h**

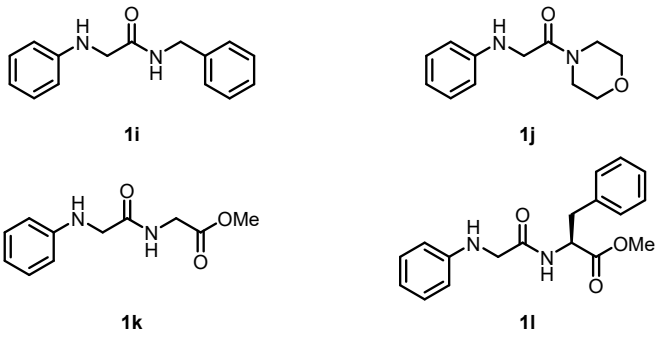
According to literature reports,[1] the following substrates **1a-1h** were prepared.

(b) Preparation of glycine dipeptides



1

Different dipeptides



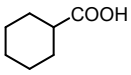
1i **1j**

1k **1l**

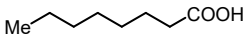
According to literature reports,[2] **1i-1l** were prepared.

(c) Carboxylic acid

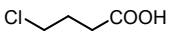
The substrates **2a**-**2u** are commercially available and were used as received.



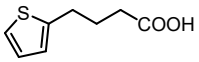
2a: cyclohexanecarboxylic acid



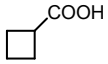
2b: octanoic acid



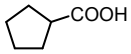
2c: 4-chlorobutanoic acid



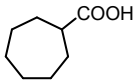
2d: 4-(thiophen-2-yl)butanoic acid



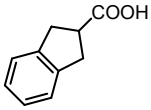
2e: cyclobutanecarboxylic acid



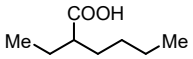
2f: cyclopentanecarboxylic acid



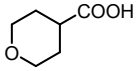
2g: cycloheptanecarboxylic acid



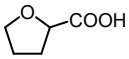
2h: 2,3-dihydro-1*H*-indene-2-carboxylic acid



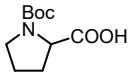
2i: 2-ethylhexanoic acid



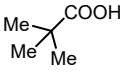
2j: tetrahydro-2*H*-pyran-4-carboxylic acid



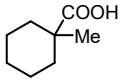
2k: tetrahydrofuran-2-carboxylic acid



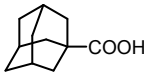
2l: (*tert*-butoxycarbonyl)proline



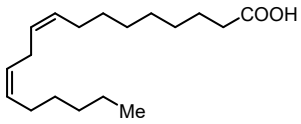
2m: pivalic acid



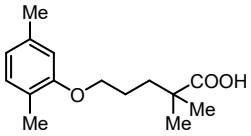
2n: 1-methylcyclohexane-1-carboxylic acid



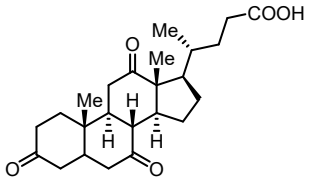
2o: (3*r*,5*r*,7*r*)-adamantane-1-carboxylic acid



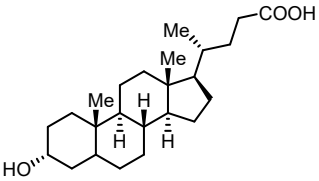
2p: (9*Z*,12*Z*)-octadeca-9,12-dienoic acid



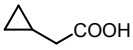
2q: 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid



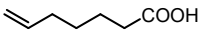
2r: (4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid



2s: (4*R*)-4-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoic acid

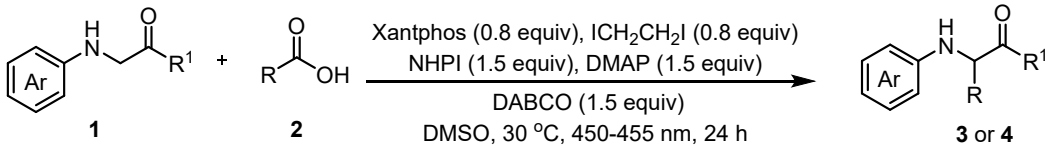


2t: 2-cyclopropylacetic acid



2u: hept-6-enoic acid

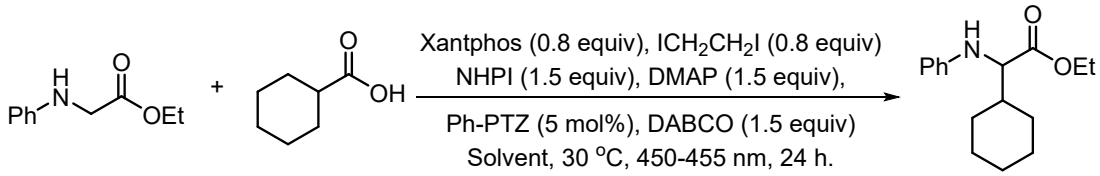
1.4 General procedure for the reaction



In an oven dried 25 mL Schlenk tube was charged with **1** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C under irradiation of Blue LEDs (450-455 nm). After stirring for 24 h, t the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases was removed under vacuo. The residue was purified by silica gel column chromatography to afford the product **3** or **4**.

1.5 The effect of different reaction conditions

Table S1. The effect of different solvents [a,b]

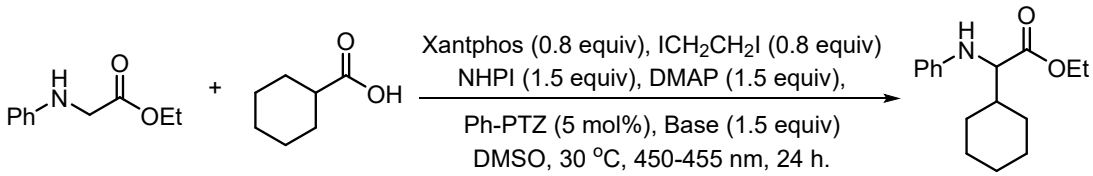


1a **2a** **3a**

Entry	Solvents	Yield (%)[b]
1	DMSO	56
2	CH_3CN	11
3	DCE	15
4	1,4-Dioxane	21
5	Acetone	9
6	DMA	15
7	EA	10
8	$PhCF_3$	5

[a] Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Xantphos (0.16 mmol, 0.8 equiv), ICH_2CH_2I (0.16 mmol, 0.8 equiv), NHPI (0.3 mmol, 1.5 equiv), DMAP (0.3 mmol, 1.5 equiv), Ph-PTZ (0.01 mmol, 5 mol%), DABCO (0.3 mmol, 1.5 equiv), Solvent (2 mL), 450-455 nm, at 30 °C for 24 h. [b] Isolated yield.

Table S2. The effect of different bases [a,b]

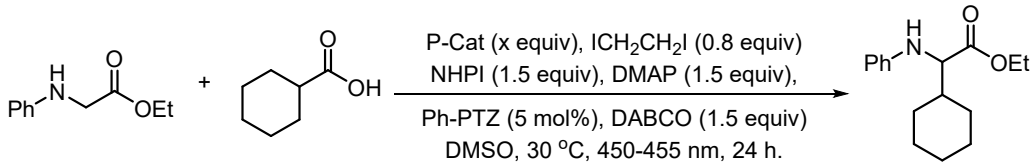


1a **2a** **3a**

Entry	Bases	Yield (%)[b]
1	DABCO	56
2	BTMG	30
3	NEt_3	43
6	DIPEA	10
9	DBU	43
4	K_2CO_3	53
7	$KHCO_3$	22
8	$NaHCO_3$	21

[a] Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Xantphos (0.16 mmol, 0.8 equiv), ICH_2CH_2I (0.16 mmol, 0.8 equiv), NHPI (0.3 mmol, 1.5 equiv), DMAP (0.3 mmol, 1.5 equiv), Ph-PTZ (0.01 mmol, 5 mol%), Base (0.3 mmol, 1.5 equiv), DMSO (2 mL), 450-455 nm, at 30 °C for 24 h. [b] Isolated yield.

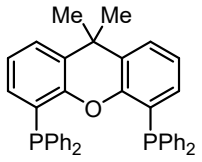
Table S3. The effect of different phosphines [a,b]



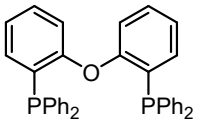
1a **2a** **3a**

Entry	Phosphines	Yield (%)[b]
1	Xantphos (0.8 equiv)	56
2	DPEphos (0.8 equiv)	55
3	*Rac*-BINAP (0.8 equiv)	0
4	dppp (0.8 equiv)	48
5	dppf (0.8 equiv)	0
6	PPh_3 (1.6 equiv)	46
7	PCy_3 (1.6 equiv)	23

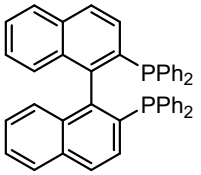
[a] Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Phosphines (x mmol, x equiv), ICH_2CH_2I (0.16 mmol, 0.8 equiv), NHPI (0.3 mmol, 1.5 equiv), DMAP (0.3 mmol, 1.5 equiv), Ph-PTZ (0.01 mmol, 5 mol%), DABCO (0.3 mmol, 1.5 equiv), DMSO (2 mL), 450-455 nm, at 30 °C for 24 h. [b] Isolated yield.



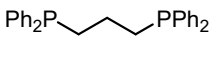
Xantphos



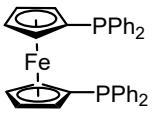
DPEphos



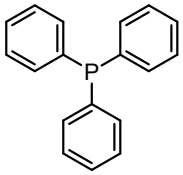
***Rac*-BINAP**



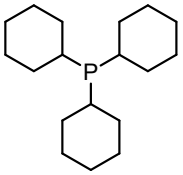
dppp



dppf

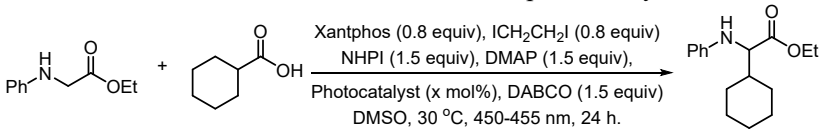


PPh_3



PCy_3

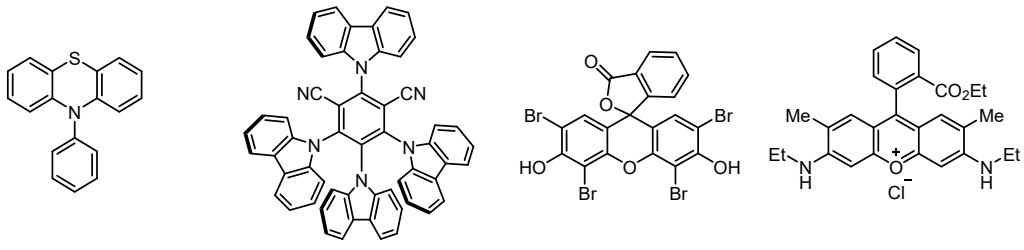
Table S4. The effect of different photocatalyst [a,b]



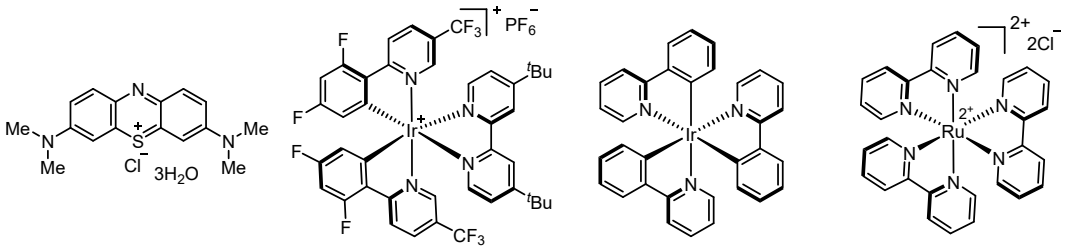
1a **2a** **3a**

Entry	Photocatalyst	Yield (%)[b]
1	Ph-PTZ (5 mol%)	56
2	4CzIPN (5 mol%)	32
3	Eosin Y (5 mol%)	44
4	Rhodamine 6G (5 mol%)	71
5	Methylene Blue (5 mol%)	20
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol%)	53
7	$Ir(ppy)_3$ (2 mol%)	54
8	$[Ru(bpy)_3]Cl_2$ (2 mol%)	48

[a] Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Xantphos (0.16 mmol, 0.8 equiv), ICH_2CH_2I (0.16 mmol, 0.8 equiv), NHPI (0.3 mmol, 1.5 equiv), DMAP (0.3 mmol, 1.5 equiv), Photocatalyst (x mmol, x mol%), DABCO (0.3 mmol, 1.5 equiv), DMSO (2 mL), 450-455 nm, at 30 °C for 24 h. [b] Isolated yield.

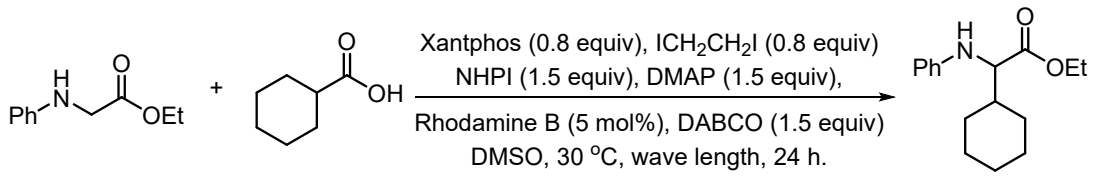


Ph-PTZ **4CzIPN** **Eosin Y** **Rhodamine 6G**



Methylene blue trihydrate **$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$** **$Ir(ppy)_3$** **$[Ru(bpy)_3]Cl_2$**

Table S5. The effect of different wave length [a,b]

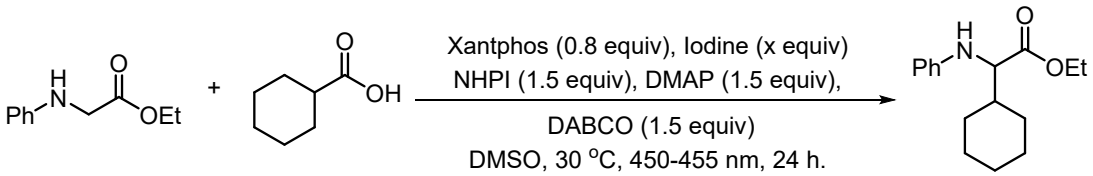


1a **2a** **3a**

Entry	wave lengths	Yield (%)[b]
1	520~525 nm	55
2	460~465 nm	65
3	450~455 nm	71
4	440~445 nm	62
5	420~425 nm	56
6	390~395 nm	34
7	360~365 nm	32
8	Dark	0

[a] Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Xantphos (0.16 mmol, 0.8 equiv), ICH_2CH_2I (0.16 mmol, 0.8 equiv), NHPI (0.3 mmol, 1.5 equiv), DMAP (0.3 mmol, 1.5 equiv), Rhodamine 6G (0.01 mmol, 5 mol%), DABCO (0.3 mmol, 1.5 equiv), DMSO (2 mL), wave length LED, at 30 °C for 24 h. [b] Isolated yield.

Table S6. The effect of different iodines [a,b]

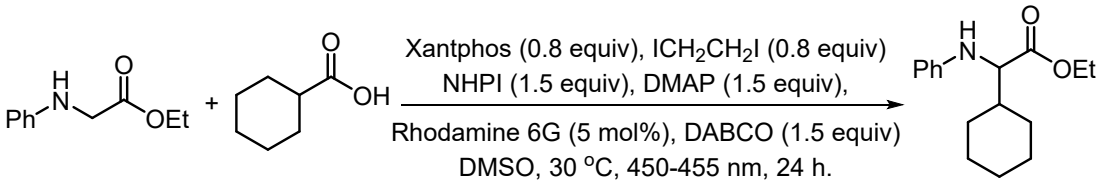


1a **2a** **3a**

Entry	Iodines	Yield (%)[b]
1	ICH_2CH_2I (0.8 equiv)	72
2	CH_3I (1.6 equiv)	0
3	*n*-Bu_4NI (1.6 equiv)	0
4	NaI (1.6 equiv)	0

[a] Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Xantphos (0.16 mmol, 0.8 equiv), Iodine (x mmol, x equiv), NHPI (0.3 mmol, 1.5 equiv), DMAP (0.3 mmol, 1.5 equiv), DABCO (0.3 mmol, 1.5 equiv), DMSO (2 mL), 450-455 nm, at 30 °C for 24 h. [b] Isolated yield.

Table S7. Control experiments [a,b]

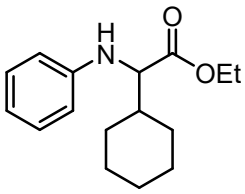


1a 2a 3a

Entry	Variations from standard coniditions	Yield (%) [b]
1	without Rhodamine 6G	72
2	without Xantphos	0
3	without ICH2CH2I	0
4	without NHPI	0
5	without DMAP	0
6	without DABCO	0
7	Dark	0

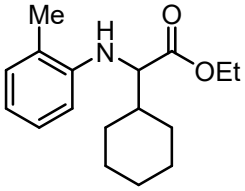
[a] Standard conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Xantphos (0.16 mmol, 0.8 equiv), ICH_2CH_2I (0.16 mmol, 0.8 equiv), NHPI (0.3 mmol, 1.5 equiv), DMAP (0.3 mmol, 1.5 equiv), Rhodamine 6G (0.01 mmol, 5 mol%), DABCO (0.3 mmol, 1.5 equiv), DMSO (2 mL), wave length LED, at 30 °C for 24 h. [b] Isolated yield.

1.6 Analytical data for compounds



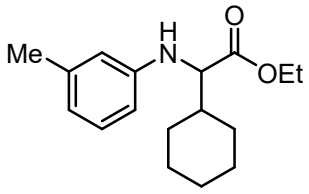
3a

ethyl 2-cyclohexyl-2-(phenylamino)acetate (3a): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3a** as a white solid (37.8 mg, 72% yield): Rf = 0.8 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.18-7.15 (m, 2H), 6.74-6.70 (m, 1H), 6.64-6.62 (m, 2H), 4.20-4.13 (m, 3H), 3.89-3.85 (m, 1H), 1.85-1.67 (m, 6H), 1.27-1.15 (m, 8H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.6, 147.4, 129.2, 118.0, 113.5, 62.0, 60.8, 41.3, 29.6, 29.2, 26.2, 26.1, 26.0, 14.3 ppm; These data are in agreement with literature.[2]



3b

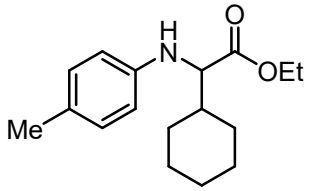
ethyl 2-cyclohexyl-2-(*o*-tolylamino)acetate (3b): The general procedure was followed using ethyl *o*-tolylglycinate (**1b**, 39 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3b** as a colorless oil (21.6 mg, 39% yield): Rf = 0.7 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.10-7.04 (m, 2H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.05-4.03 (m, 1H), 3.92-3.89 (m,1H), 2.21 (s, 3H), 1.91-1.70 (m, 6H), 1.27-1.23 (m, 8H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.8, 145.4, 130.3, 127.0, 122.7, 117.6, 110.4, 61.9, 60.8, 41.4, 29.6, 29.3, 26.2, 26.13, 26.07, 17.5, 14.3 ppm; These data are in agreement with literature.[7]



3c

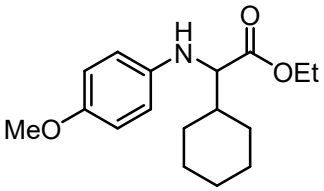
ethyl 2-cyclohexyl-2-(*m*-tolylamino)acetate (3c): The general procedure was followed using ethyl *m*-tolylglycinate (**1c**, 39 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3c** as a white solid (38.6 mg, 70% yield): Rf = 0.7 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.05 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 7.2 Hz, 1H), 6.47-6.43 (m, 2H), 4.21-4.15 (m, 2H), 4.09 (br, 1H), 3.86 (d, *J* = 6.0 Hz, 1H), 2.27 (s, 3H), 1.89-1.66 (m, 6H), 1.29-1.17 (m, 8H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.7, 147.5, 139.0, 129.1, 119.0, 114.4, 110.5, 62.0, 60.7, 41.3, 29.6, 29.2, 26.2, 26.1, 26.0, 21.6,

14.3 ppm; These data are in agreement with literature.[2]



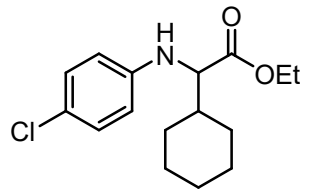
3d

ethyl 2-cyclohexyl-2-(*p*-tolylamino)acetate (3d): The general procedure was followed using ethyl *p*-tolylglycinate (**1d**, 39 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3d** as a colorless oil (41.3 mg, 75% yield): Rf = 0.7 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.98 (d, *J* = 7.6 Hz, 2H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.01 (br, 1H), 3.83 (d, *J* = 6.4 Hz, 1H), 2.23 (s, 3H), 1.88-1.66 (m, 6H), 1.30-1.14 (m, 8H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.8, 145.2, 129.7, 127.3, 113.7, 62.4, 60.7, 41.3, 29.6, 29.2, 26.2, 26.07, 26.03, 20.3, 14.3 ppm; These data are in agreement with literature.[2]



3e

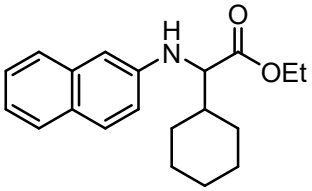
ethyl 2-cyclohexyl-2-((4-methoxyphenyl)amino)acetate (3e): The general procedure was followed using ethyl (4-methoxyphenyl)glycinate (**1e**, 42 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 20:1) afforded product **3e** as a colorless oil (32.6 mg, 56% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 6.77-6.73 (m, 2H), 6.62-6.58 (m, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.87 (br, 1H), 3.77-3.73 (m, 4H), 1.88-1.65 (m, 6H), 1.29-1.14 (m, 8H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 174.0, 152.6, 141.6, 115.2, 114.8, 63.4, 60.7, 55.7, 41.3, 29.6, 29.2, 26.2, 26.1, 26.0, 14.3 ppm; These data are in agreement with literature.[3]



3f

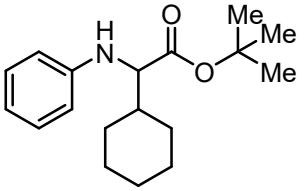
ethyl 2-((4-chlorophenyl)amino)-2-cyclohexylacetate (3f): The general procedure was followed using ethyl (4-chlorophenyl)glycinate (**1f**, 43 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3f** as a colorless oil (19.9 mg, 34% yield): Rf = 0.6 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.11-7.09 (m, 2H), 6.56-6.52 (m, 2H), 4.19-4.13 (m, 3H), 3.80 (d, *J* = 6.4 Hz, 1H), 1.85-1.66 (m, 6H), 1.26-1.18 (m, 8H);

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 173.4, 146.0, 129.1, 122.7, 114.6, 62.2, 60.9, 41.2, 29.7, 29.6, 29.1, 26.1, 26.03, 26.00, 14.3 ppm; These data are in agreement with literature.[4]



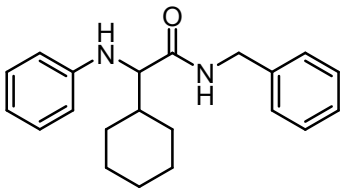
3g

ethyl 2-cyclohexyl-2-(naphthalen-2-ylamino)acetate (3g): The general procedure was followed using ethyl naphthalen-2-ylglycinate (**1g**, 46 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3g** as a colorless oil (32.6 mg, 52% yield): Rf = 0.6 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.68-7.60 (m, 3H), 7.38-7.34 (m, 1H), 7.23-7.19 (m, 1H), 6.94 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 4.34 (br, 1H), 4.24-4.15 (m, 2H), 4.03 (d, *J* = 6.0 Hz, 1H), 1.95-1.69 (m, 6H), 1.32-1.20 (m, 8H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 173.6, 145.0, 135.0, 129.0, 127.8, 127.6, 126.3, 126.0, 122.2, 118.2, 105.5, 62.0, 60.9, 41.2, 29.6, 29.3, 26.2, 26.1, 26.0, 14.3 ppm; These data are in agreement with literature.[2]



3h

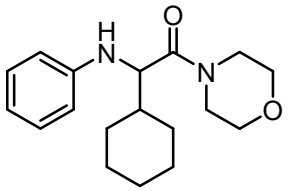
***tert*-butyl 2-cyclohexyl-2-(phenylamino)acetate (3h):** The general procedure was followed using ethyl naphthalen-2-ylglycinate (**1h**, 58 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3h** as a colorless oil (23.2 mg, 40% yield): Rf = 0.6 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17-7.13 (m, 2H), 6.70 (t, *J* = 7.2, 1H), 6.62 (d, *J* = 8.0, 2H), 4.13-4.12 (m, 1H), 3.77-3.74 (m, 1H), 1.79-1.65 (m, 5H), 1.42 (s, 9H), 1.29-1.21 (m, 5H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 172.8, 147.7, 129.2, 117.8, 113.6, 81.4, 62.4, 41.3, 29.5, 29.2, 28.1, 26.3, 26.2, 26.1 ppm; These data are in agreement with literature.[3]



3i

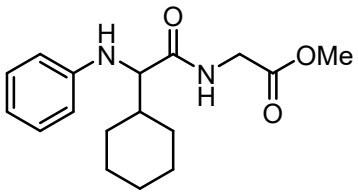
***N*-benzyl-2-cyclohexyl-2-(phenylamino)acetamide (3i):** The general procedure was followed using *N*-benzyl-2-(phenylamino)acetamide (**1i**, 48 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum

ether : ethyl acetate = 20:1 to 5:1) afforded product **3i** as a white solid (44.5 mg, 69% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.26-7.15 (m, 6H), 7.08-7.05 (m, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.51 (dd, *J* = 14.8, 6.0 Hz, 1H), 4.39 (dd, *J* = 14.8, 5.6 Hz, 1H), 3.94-3.93 (m, 1H), 3.65-3.63 (m, 1H), 2.07-2.03 (m, 1H), 1.81-1.69 (m, 5H), 1.32-1.21 (m, 5H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 172.6, 147.3, 138.2, 129.3, 128.5, 127.6, 127.3, 119.0, 113.7, 64.9, 43.2, 41.1, 30.3, 28.2, 26.21, 26.18, 26.1 ppm; These data are in agreement with literature.[1]



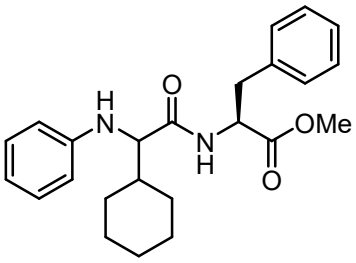
3j

2-cyclohexyl-1-morpholino-2-(phenylamino)ethan-1-one (3j): The general procedure was followed using 1-morpholino-2-(phenylamino)ethan-1-one (**1j**, 44 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3j** as a white solid (33.4 mg, 55% yield): Rf = 0.8 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17-7.13 (m, 2H), 6.73-6.69 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.46 (br, 1H), 4.09 (d, *J* = 6.0 Hz, 1H), 3.64-3.57 (m, 8H), 1.90-1.66 (m, 6H), 1.24-1.13 (m, 5H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 171.8, 148.1, 129.3, 118.1, 113.9, 67.0, 66.6, 58.4, 46.3, 42.4, 42.0, 30.3, 29.7, 28.7, 26.2, 26.1 ppm; These data are in agreement with literature.[1]



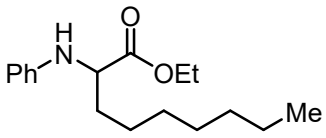
3k

methyl (2-cyclohexyl-2-(phenylamino)acetyl)glycinate (3k): The general procedure was followed using methyl phenylglycylglycinate (**1k**, 44 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 10:1 to 2:1) afforded product **3k** as a yellow oil (34.7 mg, 57% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 2:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21-7.17 (m, 2H), 6.79 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.17 (dd, *J* = 18.4, 6.4 Hz, 1H), 3.96-3.87 (m, 2H), 3.71 (s, 3H), 3.62 (d, *J* = 4.0 Hz, 1H), 2.07-2.00 (m, 1H), 1.81-1.68 (m, 5H), 1.35-1.13 (m, 6H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.2, 170.1, 147.3, 129.4, 119.0, 113.7, 64.7, 52.2, 41.2, 40.8, 30.2, 28.0, 26.24, 26.20, 26.1 ppm; These data are in agreement with literature.[4]



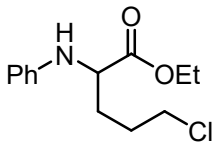
3l

methyl (2-cyclohexyl-2-(phenylamino)acetyl)-*L*-phenylalaninate (3l): The general procedure was followed using methyl phenylglycyl-*L*-phenylalaninate (**1l**, 62 mg, 0.2 mmol) and cyclohexanecarboxylic acid (**2a**, 38 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 10:1 to 6:1) afforded product **3l** as a white solid (41.8 mg, 53% yield, 1:1 d.r.): Rf = 0.7 (petroleum ether : ethyl acetate = 2:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.25-7.00 (m, 7H), 6.84-6.75 (m, 2H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.55 (d, *J* = 7.6 Hz, 1H), 5.00-4.97 (m, 0.5H), 4.94-4.89 (m, 0.5H), 3.91-3.82 (m, 1H), 3.70-3.49 (m, 4H), 3.23-2.91 (m, 2H), 1.79-1.65 (m, 4H), 1.32-1.12 (m, 7H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 172.6, 172.4, 171.8, 171.6, 147.4, 147.1, 136.1, 135.3, 129.4, 129.2, 129.14, 129.08, 128.5, 126.94, 126.91, 119.1, 118.9, 114.0, 113.5, 65.1, 64.4, 52.8, 52.2, 52.1, 41.1, 41.0, 38.0, 37.9, 30.2, 30.0, 28.0, 27.9, 26.24, 26.19, 26.16, 26.1, 26.0 ppm; These data are in agreement with literature.[2]



4a

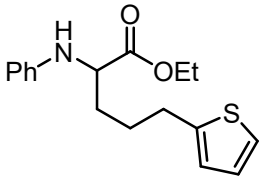
ethyl 2-(phenylamino)nonanoate (4a): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and octanoic acid (**2b**, 43 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **4a** as a colorless oil (26.2 mg, 47% yield): Rf = 0.6 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.07-4.03 (m, 1H), 1.87-1.74 (m, 2H), 1.35-1.23 (m, 13H), 0.90-0.87 (m, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 174.3, 147.0, 129.3, 118.1, 113.4, 60.9, 56.6, 33.1, 31.7, 29.3, 29.1, 25.5, 22.6, 14.2, 14.0 ppm; These data are in agreement with literature.[3]



4b

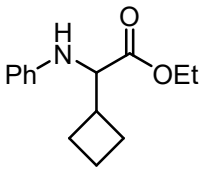
ethyl 5-chloro-2-(phenylamino)pentanoate (4b): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and 4-chlorobutanoic acid (**2c**, 37 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 20:1) afforded product **4b** as a colorless oil (25 mg, 49% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24-7.20 (m, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.56-6.54 (m, 2H), 4.25-4.13 (m, 3H), 3.60-3.55 (m, 1H), 3.46-3.34 (m, 1H), 2.30-2.04 (m, 4H),

1.24 (t, *J* = 6.8 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 174.5, 146.7, 129.2, 116.6, 111.9, 60.9, 60.8, 48.2, 30.9, 23.8, 14.2 ppm; These data are in agreement with literature.[3]



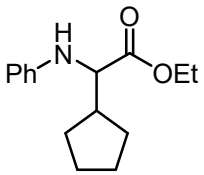
4c

ethyl 2-(phenylamino)-5-(thiophen-2-yl)pentanoate (4c): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and 4-(thiophen-2-yl)butanoic acid (**2d**, 51 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 20:1) afforded product **4c** as a colorless oil (41 mg, 68% yield): Rf = 0.6 (petroleum ether : ethyl acetate = 2:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17 (t, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 5.2 Hz, 1H), 6.93-6.90 (m, 1H), 6.79 (s, 1H), 6.7 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.11-4.08 (m, 2H), 2.96-2.86 (m, 2H), 1.93-1.86 (m, 4H), 1.24 (t, *J* = 7.6 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 173.9, 146.8, 144.5, 129.3, 126.7, 124.3, 123.1, 118.3, 113.5, 61.1, 56.4, 32.3, 29.5, 27.6, 14.2 ppm; These data are in agreement with literature. [8]



4d

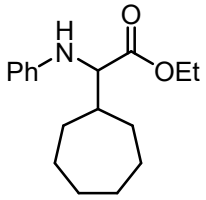
ethyl 2-cyclobutyl-2-(phenylamino)acetate (4d): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and cyclobutanecarboxylic acid (**2e**, 30 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 20:1) afforded product **4d** as a colorless oil (28.4 mg, 61% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.19-4.12 (m, 2H), 4.04 (br, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 2.75-2.64 (m, 1H), 2.08-1.86 (m, 6H), 1.23 (t, *J* = 7.2 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 173.4, 147.3, 129.2, 118.2, 113.5, 61.0, 60.8, 38.3, 25.3, 24.7, 18.0, 14.3 ppm; These data are in agreement with literature. [4]



4e

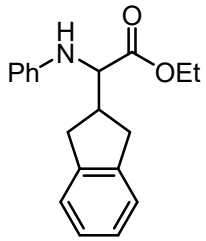
ethyl 2-cyclopentyl-2-(phenylamino)acetate (4e): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and cyclopentanecarboxylic acid (**2f**, 34 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 20:1) afforded product **4e** as a colorless oil (31.7 mg, 64% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.18-7.14 (m, 2H), 6.75-

6.71 (m, 1H), 6.65-6.63 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.12-4.09 (m, 1H), 3.87 (t, *J* = 8.0 Hz, 1H), 2.28-2.20 (m, 1H), 1.86-1.81 (m, 1H), 1.77-1.64 (m, 3H), 1.62-1.56 (m, 2H), 1.52-1.43 (m, 2H), 1.26-1.22 (m, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 174.1, 147.3, 129.2, 118.2, 113.5, 60.84, 60.76, 43.2, 29.3, 29.0, 25.3, 25.1, 14.2 ppm; These data are in agreement with literature. [4]



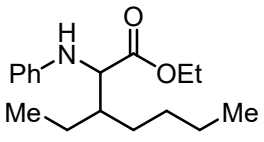
4f

ethyl 2-cycloheptyl-2-(phenylamino)acetate (4f): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and cycloheptanecarboxylic acid (**2g**, 43 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **4f** as a colorless oil (38 mg, 69% yield): Rf = 0.7 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.18-7.14 (m, 2H), 6.74-6.70 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.20-4.14 (m, 3H), 3.91-3.87 (m, 1H), 1.96 (s, 1H), 1.86-1.68 (m, 4H), 1.60-1.41 (m, 8H), 1.26-1.23 (m, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 173.7, 147.3, 129.3, 118.1, 113.5, 62.3, 60.8, 42.7, 31.1, 30.0, 28.4, 27.9, 26.7, 26.6, 14.3 ppm; These data are in agreement with literature.[5]



4g

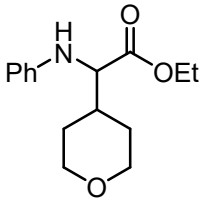
ethyl 2-(2,3-dihydro-1*H*-inden-2-yl)-2-(phenylamino)acetate (4g): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and 2,3-dihydro-1*H*-indene-2-carboxylic acid (**2h**, 49 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **4g** as a colorless oil (29.6 mg, 50% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.21-7.16 (m, 6H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.22-4.09 (m, 4H), 3.14 (dd, *J* = 15.6, 7.6 Hz, 1H), 3.06-2.88 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$):** δ 173.5, 147.0, 142.2, 142.0, 129.3, 126.5, 124.4, 118.4, 113.6, 61.0, 60.2, 42.6, 35.9, 35.6, 14.2 ppm; These data are in agreement with literature.[5]



4h

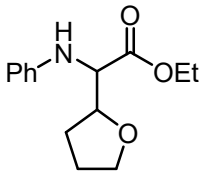
ethyl 3-ethyl-2-(phenylamino)heptanoate (4h): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and 2-ethylhexanoic acid (**2i**, 43 mg, 0.3 mmol).

Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **4h** as a colorless oil (24.1 mg, 43% yield): Rf = 0.8 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.23-4.13 (m, 2H), 4.08 (s, 2H), 1.80-1.74 (m, 1H), 1.46-1.23 (m, 11H), 0.98-0.88 (m, 6H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 174.0, 147.5, 147.4, 129.3, 118.1, 113.5, 60.8, 58.8, 42.7, 29.5, 29.3, 29.1, 23.1, 22.90, 22.87, 22.5, 14.3, 14.0, 11.6, 11.4 ppm; These data are in agreement with literature.[3]



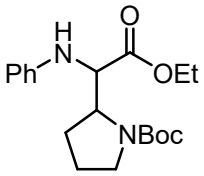
4i

ethyl 2-(phenylamino)-2-(tetrahydro-2H-pyran-4-yl)acetate (4i): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and tetrahydro-2*H*-pyran-4-carboxylic acid (**2j**, 39 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 to 3:1) afforded product **4i** as a colorless oil (40.5 mg, 77% yield): Rf = 0.3 (petroleum ether : ethyl acetate = 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.21-4.14 (m, 3H), 4.04-3.98 (m, 2H), 3.92-3.90 (m, 1H), 3.42-3.35 (m, 2H), 2.05-1.95 (m, 1H), 1.79-1.74 (m, 1H), 1.60-1.53 (m, 3H), 1.25 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.0, 147.1, 129.3, 118.4, 113.6, 67.8, 67.5, 61.4, 61.0, 38.7, 29.32, 29.28, 14.3 ppm; These data are in agreement with literature.[5]



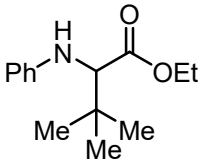
4j

ethyl 2-(phenylamino)-2-(tetrahydrofuran-2-yl)acetate (4j): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and tetrahydrofuran-2-carboxylic acid (**2k**, 35 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 to 5:1) afforded product **4j** as a colorless oil (22 mg, 44% yield): Rf = 0.3 (petroleum ether : ethyl acetate = 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.19-7.15 (m, 2H), 6.77-6.69 (m, 2H), 6.64 (d, *J* = 8.0 Hz, 1H), 4.44-4.31 (m, 1H), 4.24-4.19 (m, 2H), 4.13-4.05 (m, 1H), 3.97-3.85 (m, 1H), 3.83-3.75 (m, 1H), 2.04-1.89 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 172.5, 172.1, 147.4, 146.9, 129.3, 129.2, 118.5, 118.4, 113.9, 113.7, 79.8, 79.3, 69.2, 68.7, 61.3, 61.2, 60.7, 59.8, 28.4, 27.9, 26.0, 25.6, 14.20, 14.16 ppm; These data are in agreement with literature.[6]



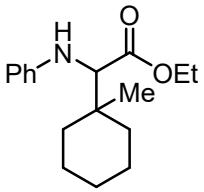
4k

tert-butyl 2-(2-ethoxy-2-oxo-1-(phenylamino)ethyl)pyrrolidine-1-carboxylate (4k): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and (*tert*-butoxycarbonyl)proline (**2l**, 65 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 to 10:1) afforded product **4k** as a colorless oil (33.3 mg, 48% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.18-7.10 (m, 2H), 6.72-6.63 (m, 3H), 5.36-5.28 (m, 0.31H), 4.75 (br, 0.33H), 4.66 (br, 0.27H), 4.55 (br, 0.52H), 4.40-4.36 (m, 0.44H), 4.32-4.29 (m, 0.37H), 4.25-4.10 (m, 2.76H), 3.52-3.13 (m, 2.09H), 2.01-1.74 (m, 4H), 1.60-1.48 (m, 9H), 1.28-1.24 (m, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 172.7, 172.5, 156.0, 155.0, 154.1, 147.9, 147.1, 129.3, 129.1, 118.0, 117.5, 113.6, 113.1, 112.9, 79.8, 79.6, 61.4, 61.2, 60.3, 59.8, 58.7, 58.0, 57.7, 47.1, 28.7, 28.5, 27.3, 26.6, 24.3, 23.7, 14.2, 14.1 ppm; These data are in agreement with literature.[3]



4l

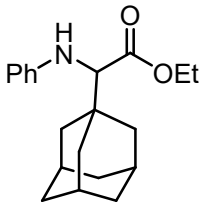
ethyl 3,3-dimethyl-2-(phenylamino)butanoate (4l): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and pivalic acid (**2m**, 31 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 3s0:1) afforded product **4l** as a colorless oil (29.7 mg, 63% yield): Rf = 0.7 (petroleum ether : ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.19-7.15 (m, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.19-4.10 (m, 3H), 3.80-3.78 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.08 (s, 9H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.3, 147.7, 129.2, 118.3, 113.8, 65.5, 60.5, 34.5, 26.8, 14.3 ppm; These data are in agreement with literature.[3]



4m

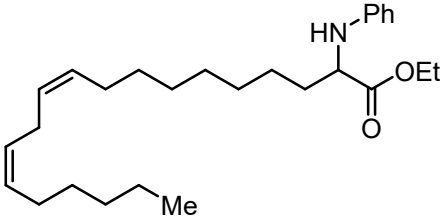
ethyl 2-(1-methylcyclohexyl)-2-(phenylamino)acetate (4m): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and 1-methylcyclohexane-1-carboxylic acid (**2n**, 43 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **4m** as a colorless oil (35.8 mg, 65% yield): Rf = 0.8 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ

7.16 (t, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.20-4.09 (m, 3H), 3.95 (s, 1H), 1.66-1.46 (m, 8H), 1.35-1.30 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.05 (s, 3H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$):** δ 173.3, 147.8, 129.3, 118.2, 113.8, 64.5, 60.5, 37.1, 34.91, 34.87, 26.1, 21.8, 21.7, 20.3, 14.3 ppm; These data are in agreement with literature.[3]



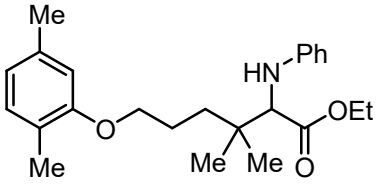
4n

ethyl 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-(phenylamino)acetate (4n): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and (3*r*,5*r*,7*r*)-adamantane-1-carboxylic acid (**2o**, 54 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **4n** as a colorless oil (40.3 mg, 64% yield): Rf = 0.7 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.16 (t, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.19-4.10 (m, 3H), 3.66 (s, 1H), 2.04-2.01 (m, 3H), 1.83-1.57 (m, 12H), 1.24 (t, *J* = 7.2 Hz, 3H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$):** δ 172.8, 147.9, 129.2, 118.1, 113.8, 66.4, 60.5, 39.0, 36.9, 36.4, 28.4, 14.3 ppm; These data are in agreement with literature.[3]



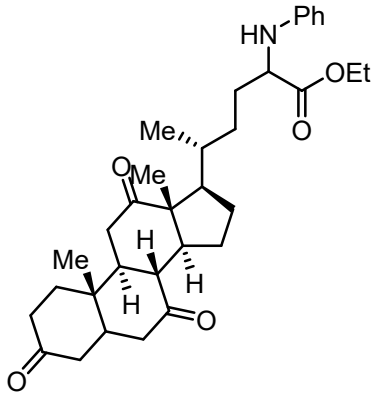
4o

ethyl (10*Z*,13*Z*)-2-(phenylamino)nonadeca-10,13-dienoate (4o): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and (9*Z*,12*Z*)-octadeca-9,12-dienoic acid (**2p**, 84 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **4o** as a colorless oil (39.2 mg, 47% yield): Rf = 0.7 (petroleum ether : ethyl acetate = 10:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.19-7.15 (m, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 2H), 5.42-5.30 (m, 4H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.06-4.03 (m, 1H), 2.79-2.76 (m, 2H), 2.08-2.02 (m, 4H), 1.84-1.71 (m, 2H), 1.32-1.23 (m, 19H), 0.91-0.88 (m, 3H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$):** δ 174.3, 147.0, 130.2, 130.0, 129.3, 128.0, 127.9, 118.2, 113.4, 61.0, 56.7, 33.1, 31.5, 29.7, 29.6, 29.34, 29.31, 29.2, 27.2, 25.6, 25.5, 22.7, 22.6, 14.2, 14.1 ppm. HRMS (ESI-TOF) m/z calcd for $C_{27}H_{44}NO_2$ $(M + H)^+$: 414.3372, found 414.3388.



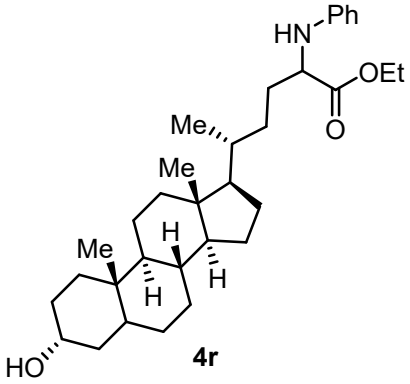
4p

ethyl 6-(2,5-dimethylphenoxy)-3,3-dimethyl-2-(phenylamino)hexanoate (4p): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid (**2q**, 75 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 10:1 to 4:1) afforded product **4p** as a colorless oil (52.3 mg, 68% yield): Rf = 0.8 (petroleum ether : ethyl acetate = 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):**δ 7.26-7.17 (m, 2H), 7.07-6.96 (m, 1H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.71-6.67 (m, 3H), 6.63 (s, 1H), 4.20-4.15 (m, 3H), 3.96-3.92 (m, 3H), 2.33 (s, 3H), 2.19 (s, 3H), 1.97-1.79 (m, 2H), 1.64-1.57 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 6H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 173.2, 156.9, 147.6, 136.4, 130.3, 129.3, 123.5, 120.7, 118.4, 113.9, 112.0, 68.2, 64.1, 60.6, 36.8, 36.0, 24.1, 24.0, 23.5, 21.4, 15.7, 14.3 ppm. HRMS (ESI-TOF) m/z calcd for $C_{24}H_{32}NO_3$ $(M - H)^-$: 382.2382, found 382.2365.



4q

ethyl(5*R*)-5-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)-2-(phenylamino)hexanoate (4q): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and (4*R*)-4-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl) pentanoic acid (**2r**, 121 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 10:1 to 3:1) afforded product **4q** as a colorless oil (47.1 mg, 44% yield): Rf = 0.9 (petroleum ether : ethyl acetate = 1:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.15 (t, *J* = 7.6 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 2H), 4.17-4.10 (m, 3H), 4.00 (br, 1H), 2.92-2.79 (m, 3H), 2.35-2.11 (m, 8H), 2.03-2.01 (m, 2H), 1.99 (br, 1H), 1.97-1.92 (m, 2H), 1.86-1.76 (m, 2H), 1.64-1.52 (m, 2H), 1.38 (s, 3H), 1.27-1.21 (m, 7H), 1.05 (d, *J* = 8.0 Hz, 3H), 0.87-0.83 (m, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 211.93, 211.91, 209.0, 208.7, 174.2, 174.1, 146.9, 146.8, 129.2, 118.2, 118.1, 113.42, 113.35, 61.0, 60.9, 60.3, 57.0, 56.8, 56.7, 51.7, 48.9, 46.8, 45.5, 45.4, 44.9, 42.7, 38.6, 36.4, 35.9, 35.7, 35.6, 35.2, 31.0, 30.9, 29.9, 29.8, 27.6, 25.1, 21.8, 18.9, 18.8, 14.2, 14.1, 11.8 ppm. HRMS (ESI-TOF) m/z calcd for $C_{33}H_{46}NO_5$ $(M + H)^+$: 536.3376, found 536.3394.

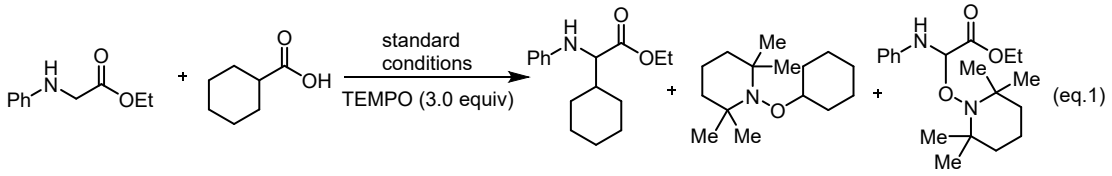


4r

ethyl(5*R*)-5-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)-2-(phenylamino)hexanoate (4r): The general procedure was followed using ethyl phenylglycinate (**1a**, 36 mg, 0.2 mmol) and (4*R*)-4-((3*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl) pentanoic acid (**2s**, 113 mg, 0.3 mmol). Purification of this material by chromatography on silica gel (petroleum ether : ethyl acetate = 10:1 to 2:1) afforded product **4r** as a colorless oil (43.6 mg, 43% yield): Rf = 0.5 (petroleum ether : ethyl acetate = 2:1). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.16 (t, *J* = 7.6 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.01-3.98 (m, 1H), 3.65-3.58 (m, 1H), 1.97-1.93 (m, 1H), 1.85-1.64 (m, 7H), 1.57-1.48 (m, 3H), 1.40-0.99 (m, 21H), 0.92-0.91 (m, 6H), 0.63 (d, *J* = 5.6 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 174.3, 174.2, 147.0, 146.9, 129.2, 118.12, 118.09, 113.43, 113.41, 71.8, 60.92, 60.90, 57.1, 57.0, 56.43, 56.42, 55.8, 42.7, 42.0, 40.4, 40.1, 36.4, 35.8, 35.5, 35.4, 35.3, 34.5, 31.5, 30.5, 29.62, 29.56, 28.14, 28.10, 27.2, 26.4, 24.1, 23.3, 20.8, 18.6, 18.5, 14.2, 12.0 ppm. HRMS (ESI-TOF) m/z calcd for $C_{33}H_{52}NO_3$ $(M + H)^+$: 510.3947, found 510.3959.

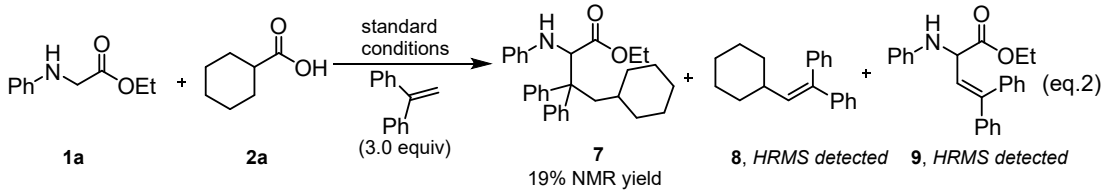
1.7 Mechanistic studies

1.7.1 Radical-trapping experiments



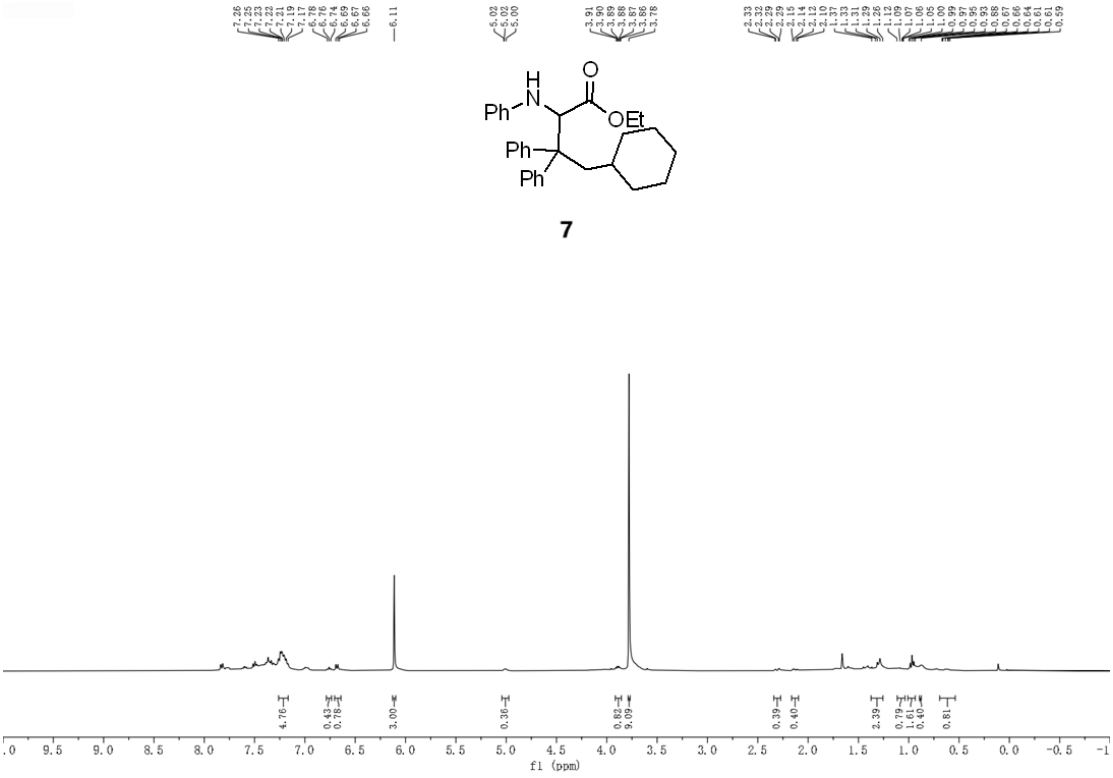
1a **2a** **3a**, 0% **5**, *HRMS detected* **6**, *HRMS detected*

Procedure of **eq. 1**: To an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1 equiv), **2a** (38 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv), DABCO (34 mg, 0.3 mmol, 1.5 equiv) and TEMPO (94 mg, 0.6 mmol, 3.0 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C under irradiation of Blue LEDs (450-455 nm). After stirring for 24 h, the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases were removed under vacuo. The resulting mixture was analyzed by HRMS. TEMPO-adduct **5** and **6** were detected. TEMPO-adduct **5** HRMS (ESI-TOF) m/z calcd for $C_{15}H_{30}NO$ $(M + H)^+$: 240.2327, found 240.2346. TEMPO-adduct **6** HRMS (ESI-TOF) m/z calcd for $C_{19}H_{31}N_2O_3$ $(M + H)^+$: 335.2335, found 335.2353.



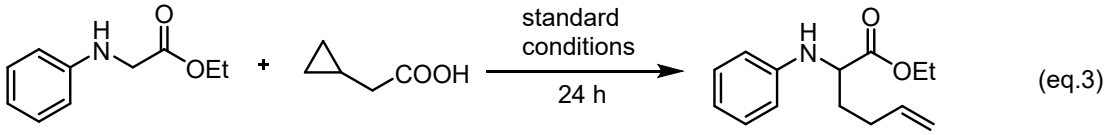
1a **2a** **7** 19% NMR yield **8**, *HRMS detected* **9**, *HRMS detected*

Procedure of **eq. 2**: To an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1 equiv), **2a** (38 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) and ethene-1,1-diyldibenzene (108 mg, 0.6 mmol, 3 equiv) were added in turn under Ar. The tube was screw capped and heated to 30 °C under irradiation of Blue LEDs (450-455 nm). After stirring for 24 h, the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases were removed under vacuo. 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) was added as an internal standard before the mixturewas transferred to an NMR tube and diluted with $CDCl_3$. ^1H NMR analysis showed the yield of **7** was 19%. These data are in agreement with literature.[3] The resulting mixture was analyzed by HRMS. **7**, **8** and **9** were detected. **7** HRMS (ESI-TOF) m/z calcd for $C_{30}H_{36}NO_2$ $(M + H)^+$: 442.2746, found 442.2747. **8** HRMS (ESI-TOF) m/z calcd for $C_{20}H_{23}$ $(M + H)^+$: 263.1800, found 263.1829. **9** HRMS (ESI-TOF) m/z calcd for $C_{24}H_{24}NO_2$ $(M + H)^+$: 358.1807, found 358.1836.



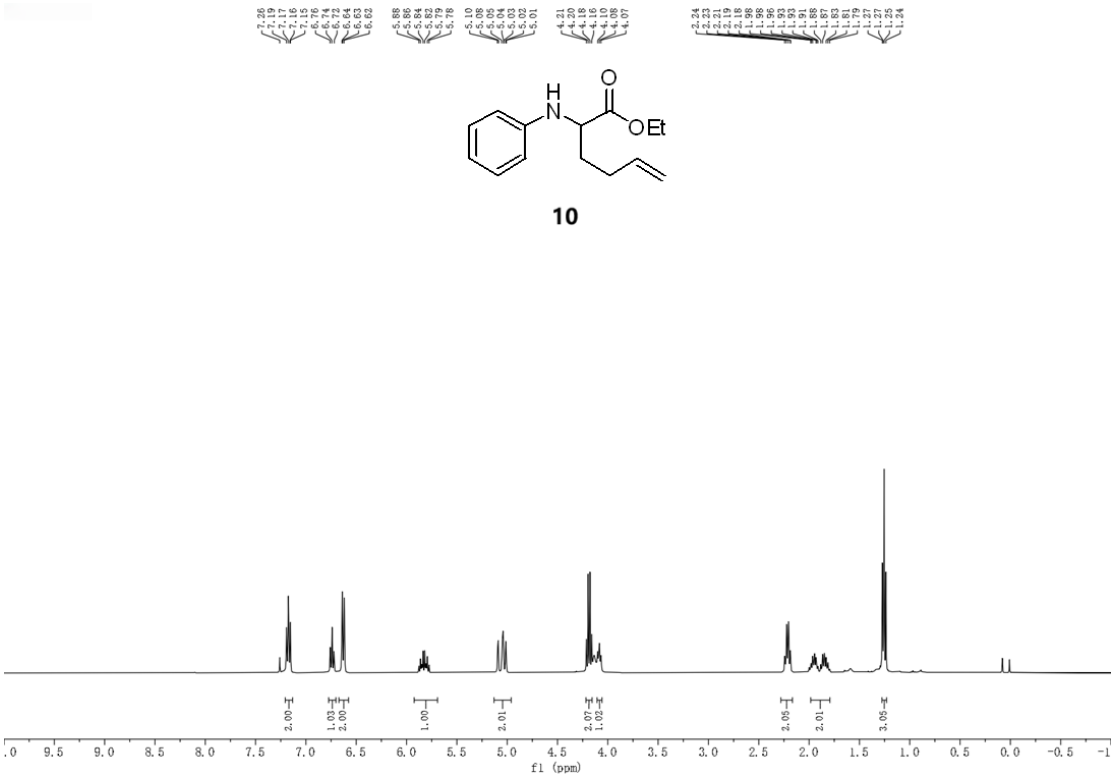
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **7**

1.7.2 Radical clock experiments

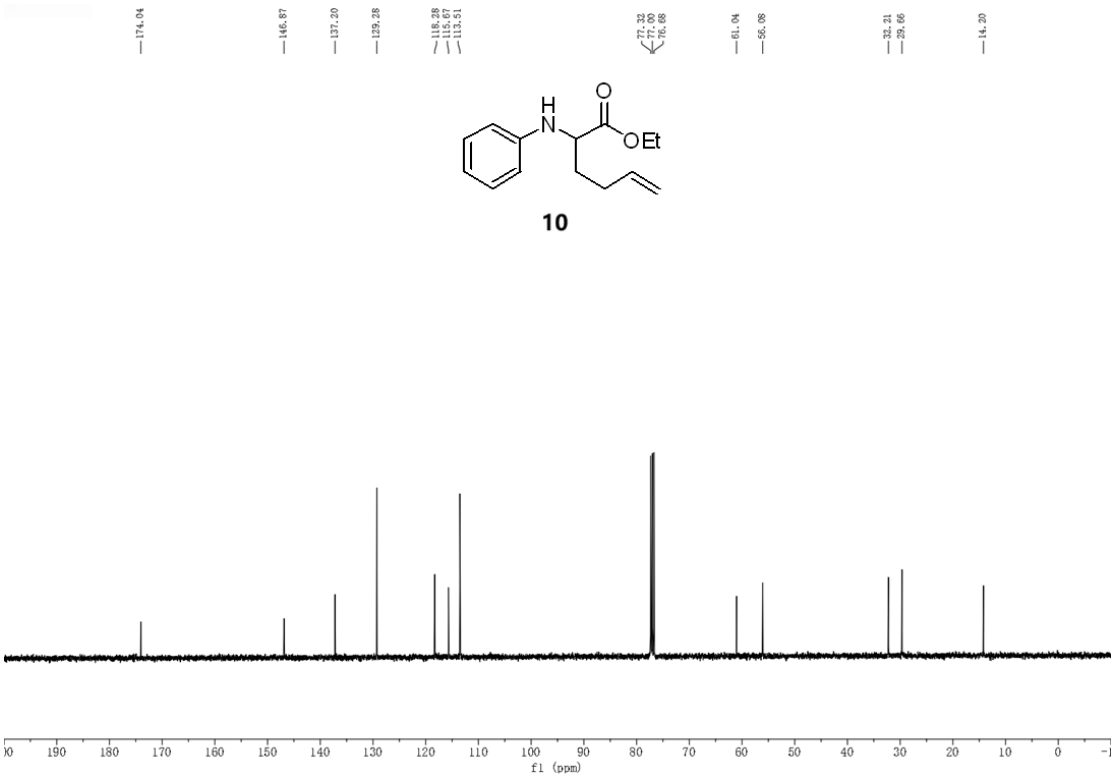


1a **2t** **10**, 66% (eq.3)

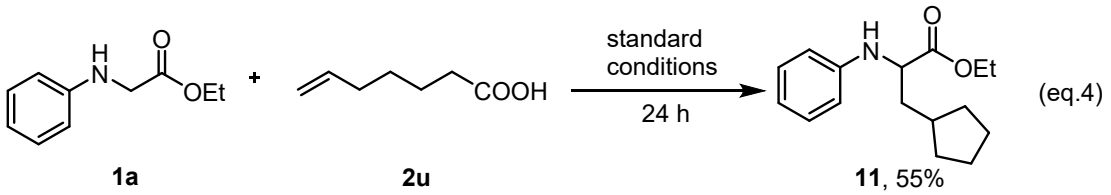
Procedure of **eq. 3**: In an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1.0 equiv), **2t** (30 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C under irradiation of Blue LEDs (450-455 nm). After stirring for 24 h, the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases was removed under vacuo. The residue was purified by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 10:1) afforded product **10** as a colorless oil (30.6 mg, 66% yield): Rf = 0.6 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.19-7.15 (m, 2H), 6.76-6.72 (m, 1H), 6.64-6.62 (m, 2H), 5.88-5.78 (m, 1H), 5.10-5.01 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.08 (t, *J* = 6.4 Hz, 1H), 2.24-2.18 (m, 2H), 1.98-1.80 (m, 2H), 1.27-1.23 (m, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 174.0, 146.9, 137.2, 129.3, 118.3, 115.7, 113.5, 61.0, 56.1, 32.2, 29.7, 14.2 ppm. These data are in agreement with literature.[4]



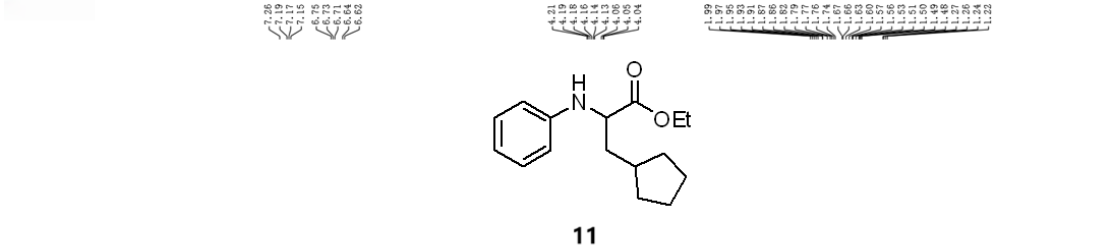
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **10**

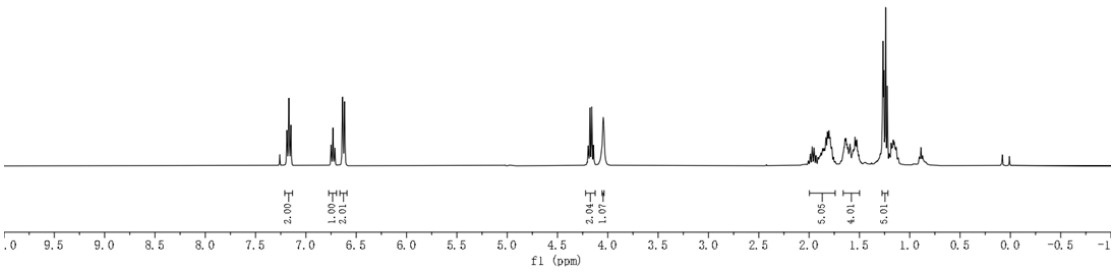


^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **10**

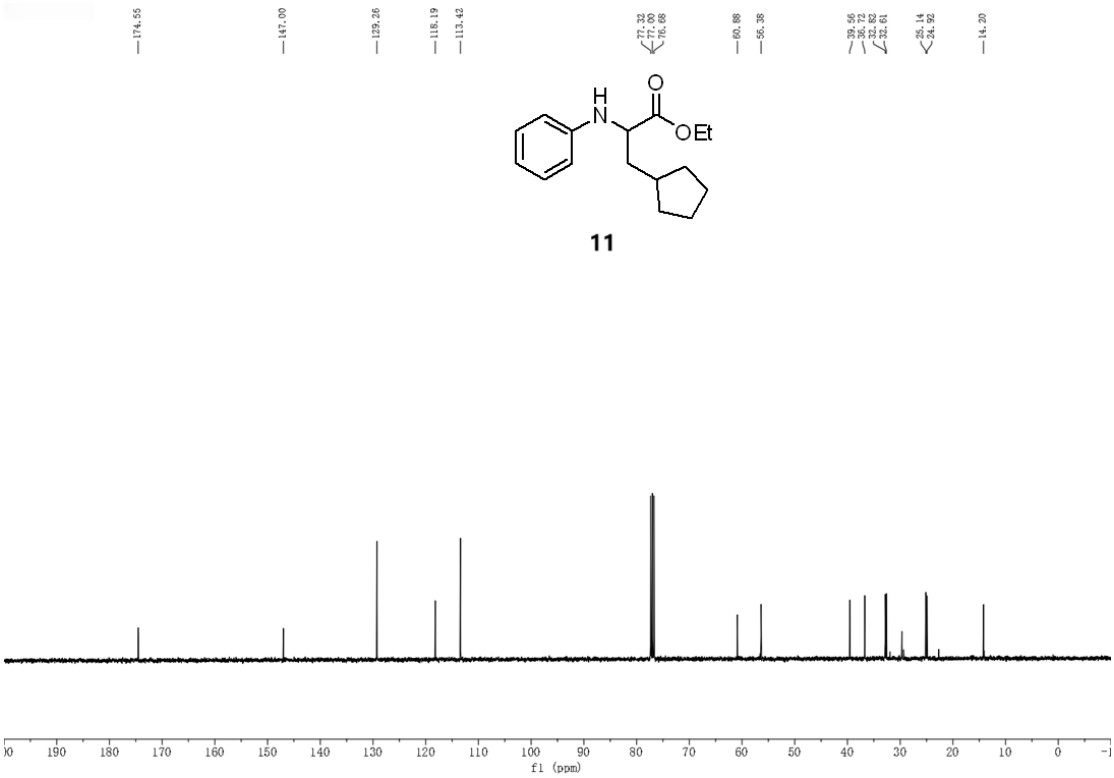


Procedure of **eq. 4**: In an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1.0 equiv), **2u** (38 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C under irradiation of Blue LEDs (450-455 nm). After stirring for 24 h, the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases was removed under vacuo. The residue was purified by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 10:1) afforded product **11** as a colorless oil (28.7 mg, 55% yield): Rf = 0.6 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.17 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.21-4.13 (m, 2H), 4.06-4.04 (m, 1H), 1.99-1.74 (m, 5H), 1.67-1.48 (m, 4H), 1.27-1.22 (m, 5H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 174.6, 147.0, 129.3, 118.2, 113.4, 60.9, 56.4, 39.6, 36.7, 32.8, 32.6, 25.1, 24.9, 14.2 ppm. These data are in agreement with literature.[4]



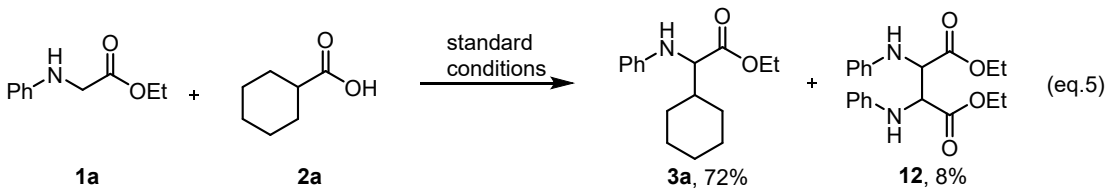


^{1}H NMR spectra (400 MHz, $CDCl_3$) of **11**

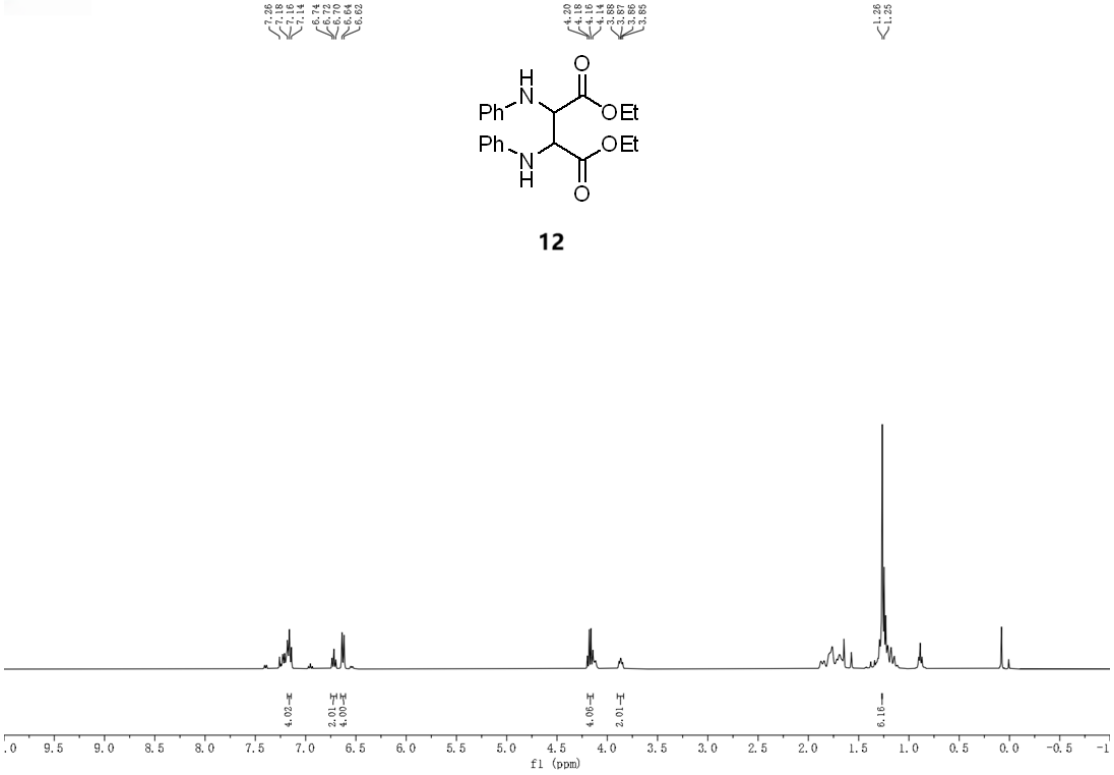


$^{13}C\{^{1}H\}$ NMR spectra (100 MHz, $CDCl_3$) of **11**

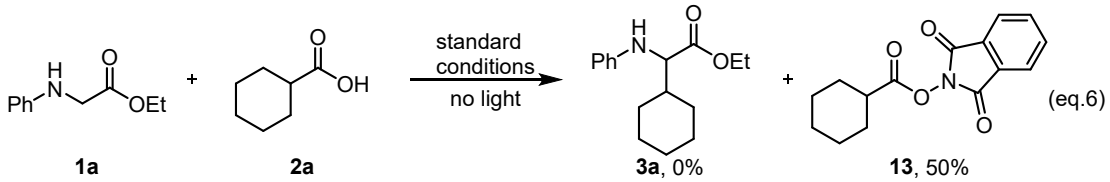
1.7.3 Control experiments



Procedure of **eq. 5**: In an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1.0 equiv), **2a** (38 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C. After stirring for 24 h, the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases was removed under vacuo. The residue was purified by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 10:1) afforded product **3a** as a white solid (37.8 mg, 72% yield): Rf = 0.8 (petroleum ether : ethyl acetate = 10:1) and **12** as a white solid (5.7 mg, 8% yield): Rf = 0.2 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.18-7.14 (m, 4H), 6.74-6.70 (m, 2H), 6.63 (d, *J* = 8.0 Hz, 4H), 4.20-4.14 (m, 4H), 3.88-3.85 (m, 2H), 1.26-1.25 (m, 6H); These data are in agreement with literature.[7] HRMS (ESI-TOF) m/z calcd for $C_{20}H_{25}N_2O_4$ $(M + H)^+$: 357.1814, found 357.1826.

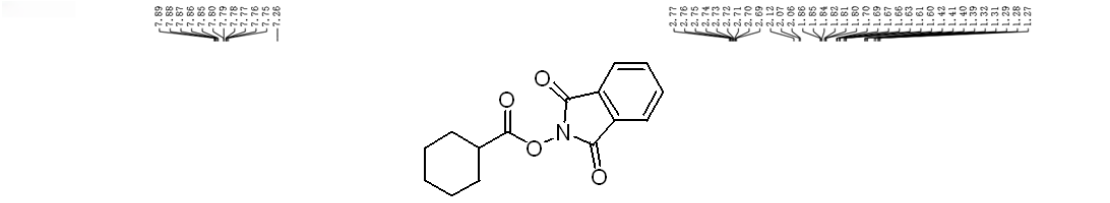


^{1}H NMR spectra (400 MHz, $CDCl_3$) of **12**

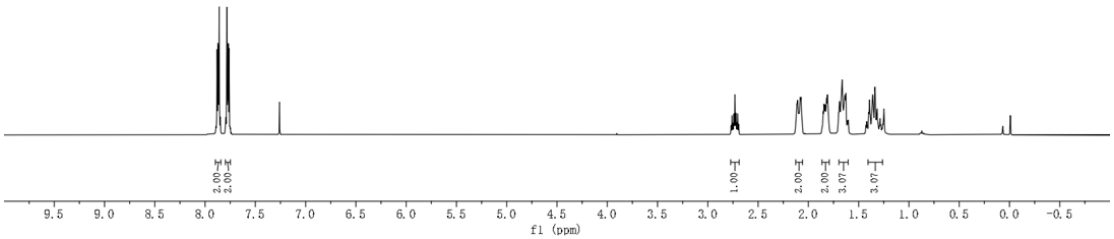


1a **2a** **3a**, 0% **13**, 50%

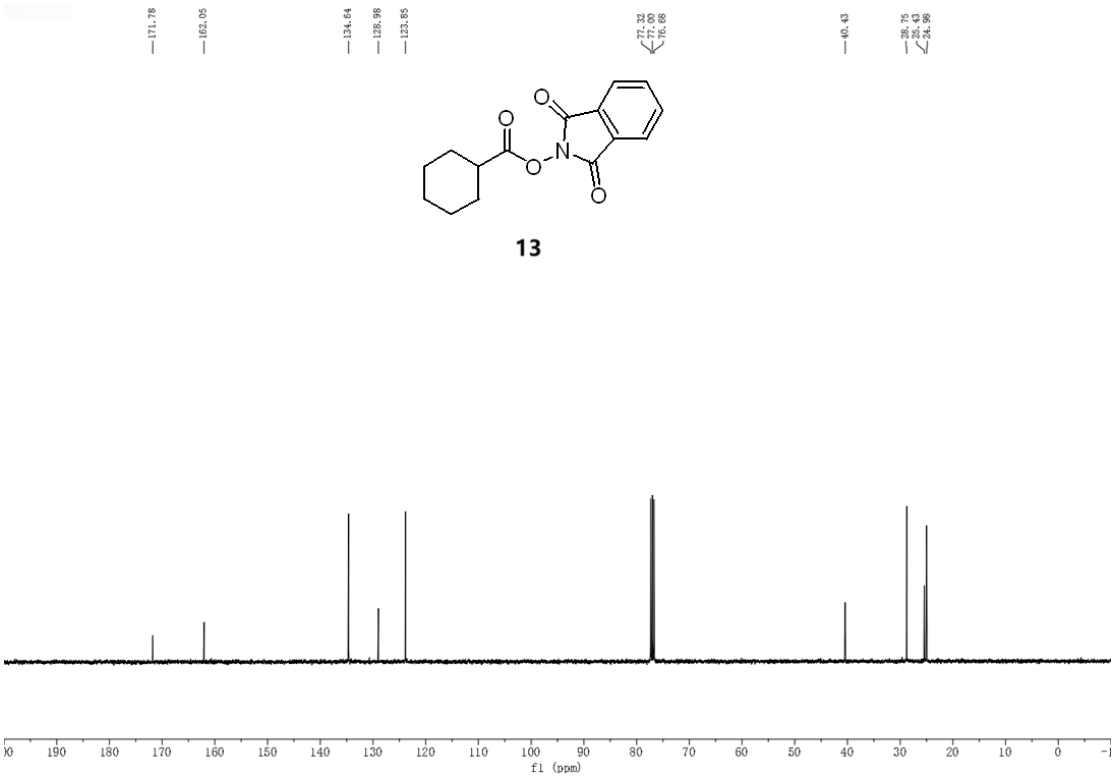
Procedure of **eq. 6**: In an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1.0 equiv), **2a** (38 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C in dark. After stirring for 24 h, the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases was removed under vacuo. The residue was purified by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 10:1) afforded product **13** as a white solid (27.3 mg, 50% yield): Rf = 0.4 (petroleum ether : ethyl acetate = 10:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.89-7.85 (m, 2H), 7.80-7.75 (m, 2H), 2.77-2.69 (m, 1H), 2.12-2.06 (m, 2H), 1.86-1.80 (m, 2H), 1.70-1.60 (m, 3H), 1.42-1.27 (m, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):** δ 171.8, 162.1, 134.6, 129.0, 123.9, 40.4, 28.8, 25.4, 25.0 ppm. These data are in agreement with literature.[10]



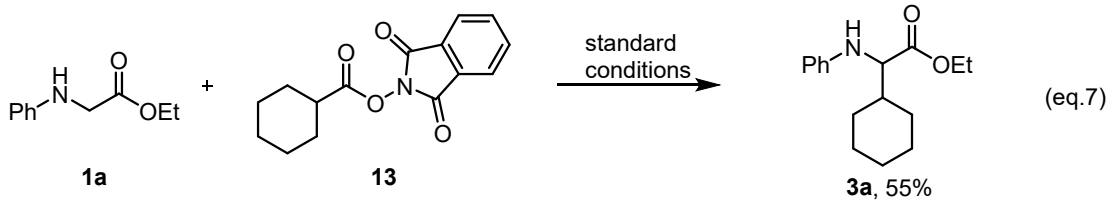
13



^{1}H NMR spectra (400 MHz, $CDCl_3$) of **13**



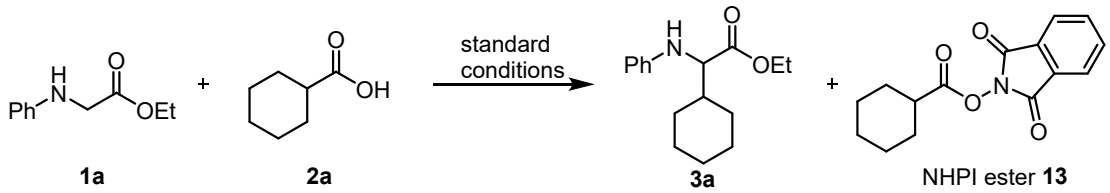
$^{13}C\{^{1}H\}$ NMR spectra (100 MHz, $CDCl_3$) of **13**



(eq.7)

Procedure of **eq. 7**: In an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1.0 equiv), **13** (82 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C. After stirring for 24 h, the reaction mixture was quenched by water and extracted with EtOAc three times. The combined organic phases was removed under vacuo. The residue was purified by chromatography on silica gel (petroleum ether : ethyl acetate = 40:1 to 30:1) afforded product **3a** as a white solid (28.8 mg, 55% yield): Rf = 0.8 (petroleum ether : ethyl acetate = 10:1).

1.7.4 Kinetic monitoring experiment



Time/yield %	0 h	0.5h	1h	2h	4h	8h	12h	16h	20h	24h
3a	0	5	15	22	37	42	52	56	66	73
NHPI ester **13**	0	26	29	25	8	0	0	0	0	0

In an oven-dried 25 mL Schlenk tube was charged with **1a** (36 mg, 0.2 mmol, 1.0 equiv), **2a** (38 mg, 0.3 mmol, 1.5 equiv), Xantphos (93 mg, 0.16 mmol, 0.8 equiv), ICH_2CH_2I (45 mg, 0.16 mmol, 0.8 equiv), NHPI (49 mg, 0.3 mmol, 1.5 equiv), DMAP (37 mg, 0.3 mmol, 1.5 equiv) and DABCO (34 mg, 0.3 mmol, 1.5 equiv). The tube was then evacuated and back-filled under argon flow (this sequence was repeated three times), anhydrous DMSO (2.0 mL) was added under Ar. The tube was screw capped and heated to 30 °C under irradiation of Blue LEDs (450-455 nm). 100 μL of reaction mixture was taken by a syringe at indicated time (0.5 h, 1 h, 2 h, 4 h, 8 h, 12 h, 16 h, 20h, 24h), the resulting mixture was quenched by water and extracted with EtOAc three times. The combined organic phases was removed under vacuo. ^{1}H NMR of the crude mixture using 1,3,5-trimethylbenzene as internal standard (Figure S1).

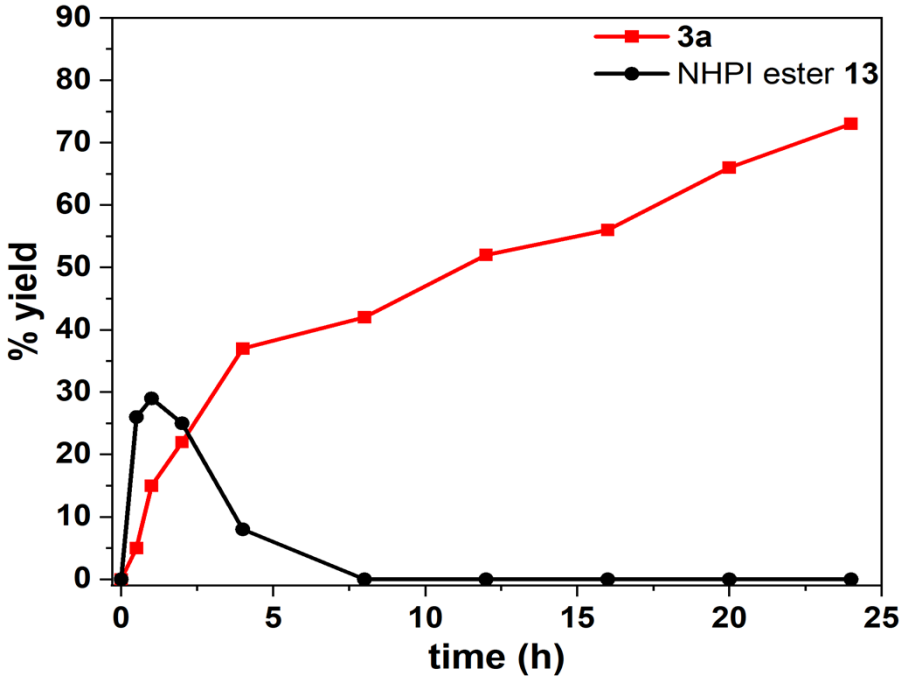


Figure S1. Kinetic monitoring experiment

1.7.5 UV-Vis absorption spectra

UV-Vis absorption spectra of NHPI ester **13**, **1a**, ICH_2CH_2I, Xantphos, a mixture of Xantphos and ICH_2CH_2I, a mixture of **1a**, ICH_2CH_2I and Xantphos, a mixture of NHPI ester **13**, ICH_2CH_2I and Xantphos, a mixture of NHPI ester **13**, **1a**, ICH_2CH_2I and Xantphos were provided respectively. The UV-vis absorption spectra of DMSO solutions of NHPI ester **13** (1×10^{-3} M), **1a** (1×10^{-3} M), Xantphos (1×10^{-4} M), ICH_2CH_2I (1×10^{-4} M), a mixture of Xantphos (1×10^{-4} M) and ICH_2CH_2I (1×10^{-4} M), a mixture of **1a** (1×10^{-3} M), ICH_2CH_2I (1×10^{-4} M) and Xantphos (1×10^{-4} M), a mixture of NHPI ester **13** (1×10^{-3} M), Xantphos (1×10^{-4} M) and ICH_2CH_2I (1×10^{-4} M), a mixture of NHPI ester **13** (1×10^{-3} M), **1a** (1×10^{-3} M), Xantphos (1×10^{-4} M) and ICH_2CH_2I (1×10^{-4} M) were recorded in 1 cm path quartz cuvettes using a UV-2700 ultraviolet-visible spectrophotometer. As shown in Figure S1, when mixture of NHPI ester **13** (1×10^{-3} M), Xantphos (1×10^{-4} M) and ICH_2CH_2I (1×10^{-4} M) in DMSO, visible red shift was observed in UV/vis absorption spectrum. This indicates the formation of an electron donor-acceptor (EDA) complex between the NHPI ester **13**, Xantphos and ICH_2CH_2I.

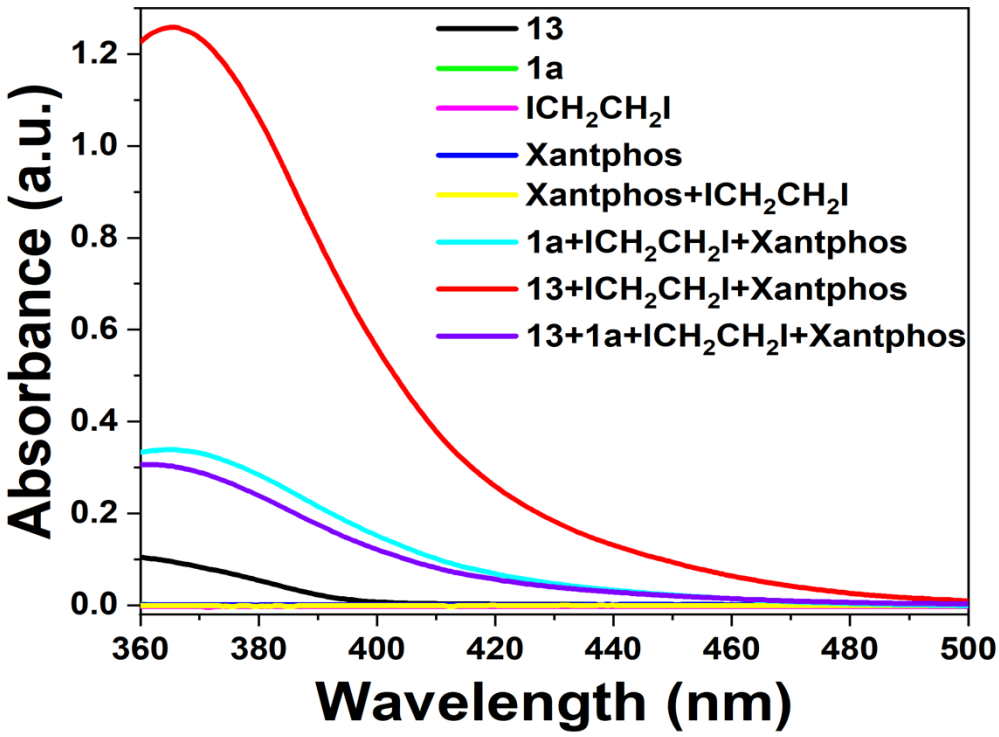


Figure S2. UV-Vis studies about the EDA complex

1.8 References

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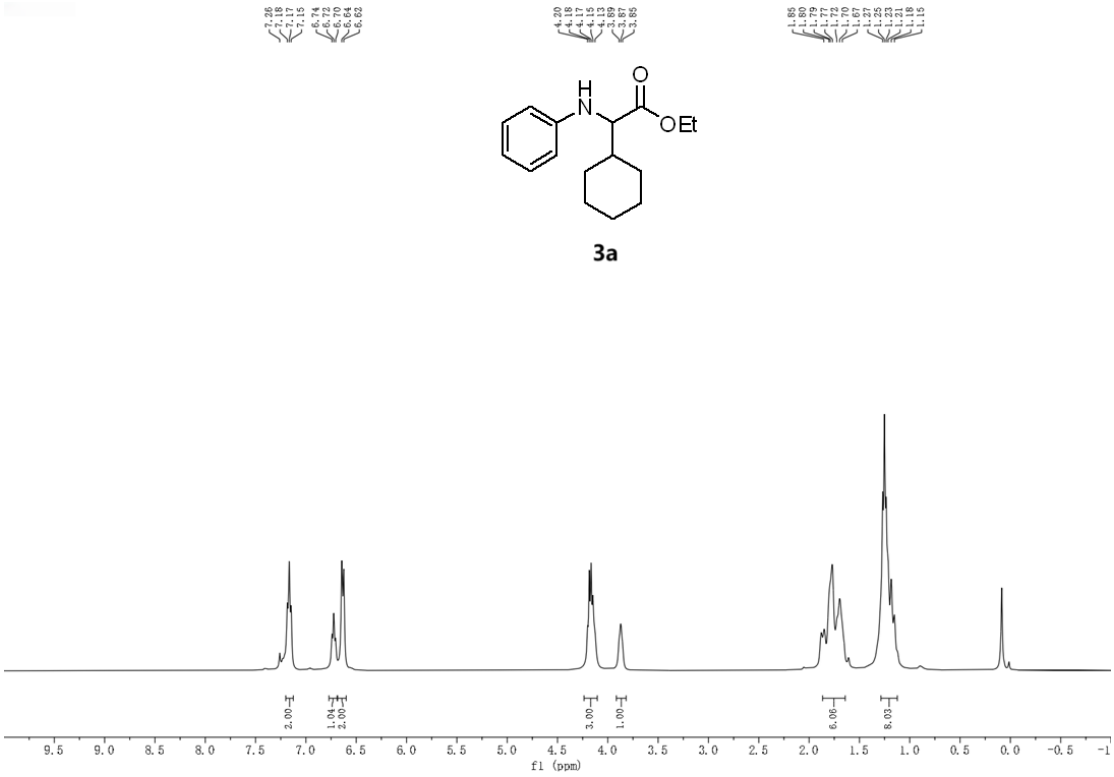
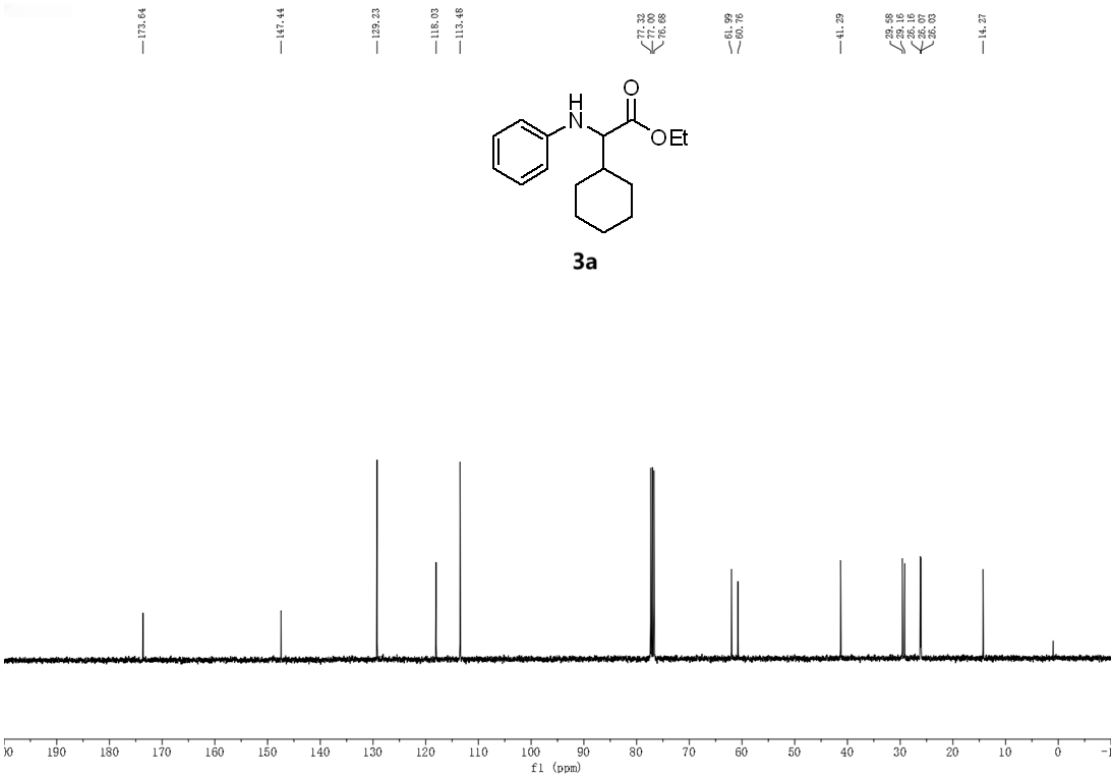
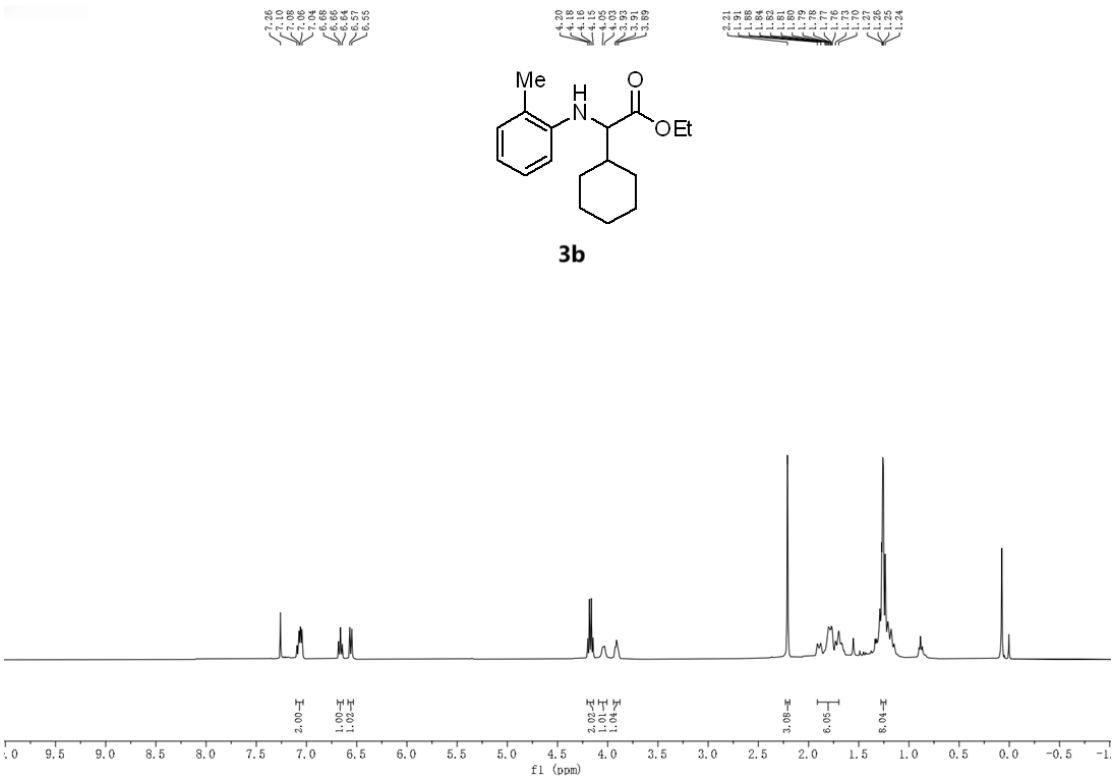
2. NMR spectra of products



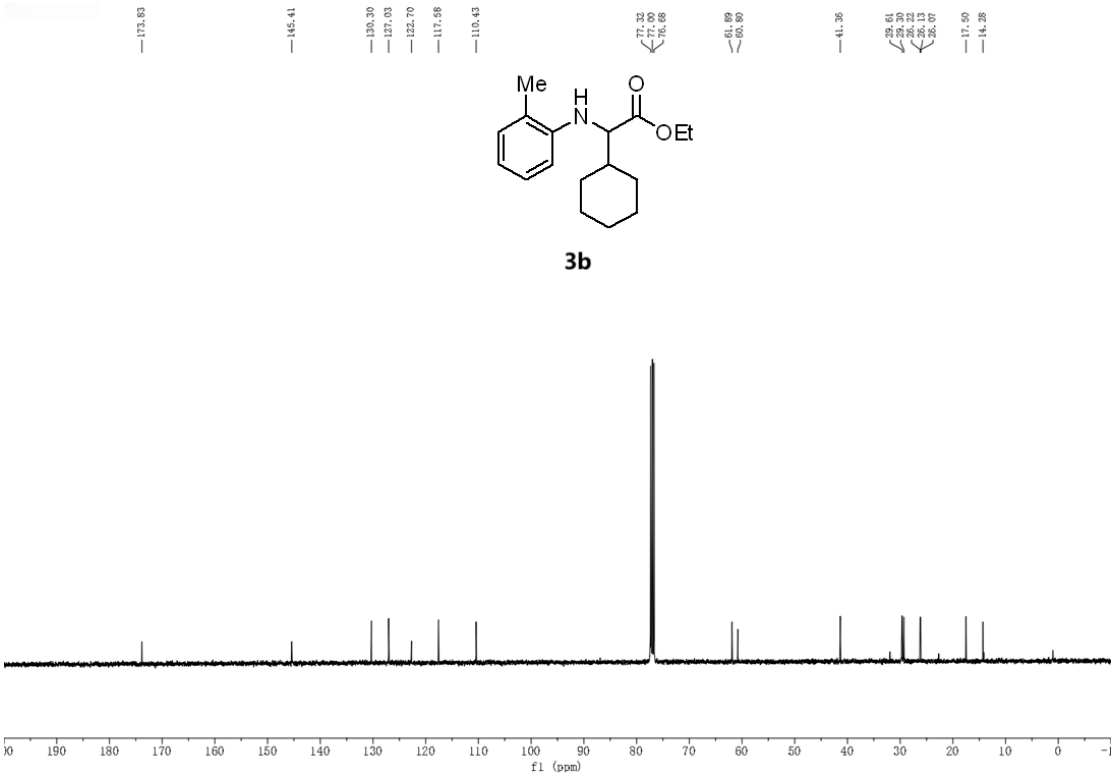
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3a**



$^{13}C\{^{1}H\}$ NMR spectra (100 MHz, $CDCl_3$) of **3a**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3b**



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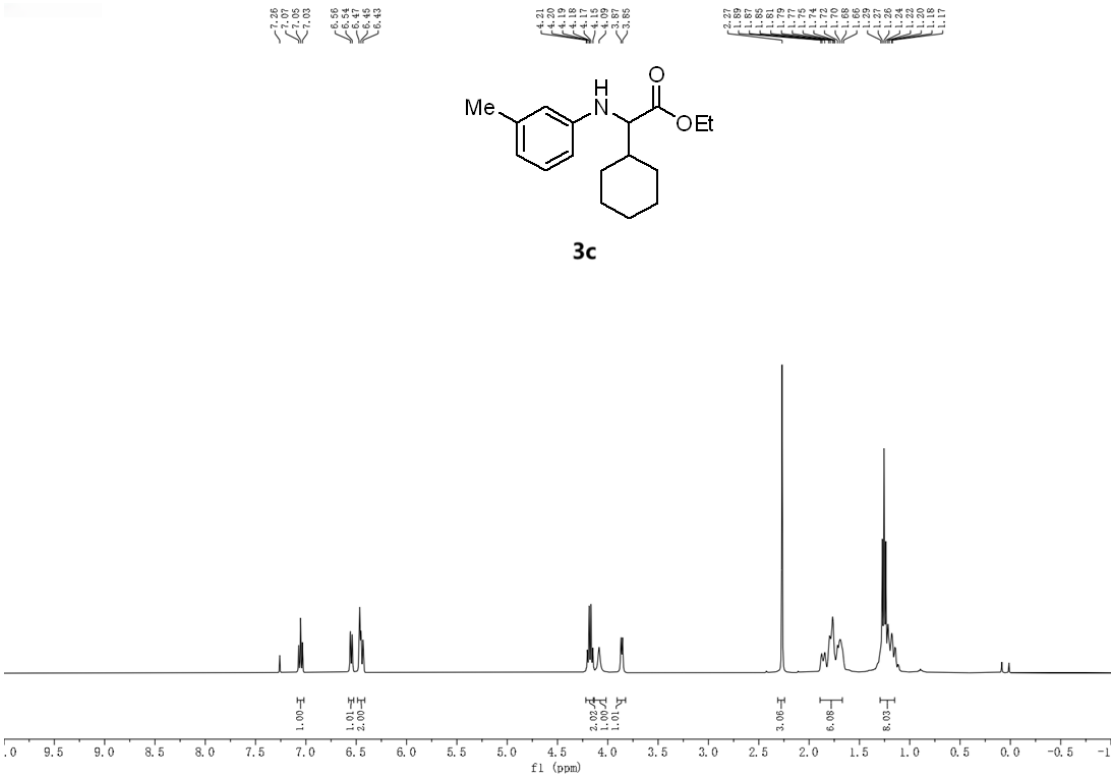

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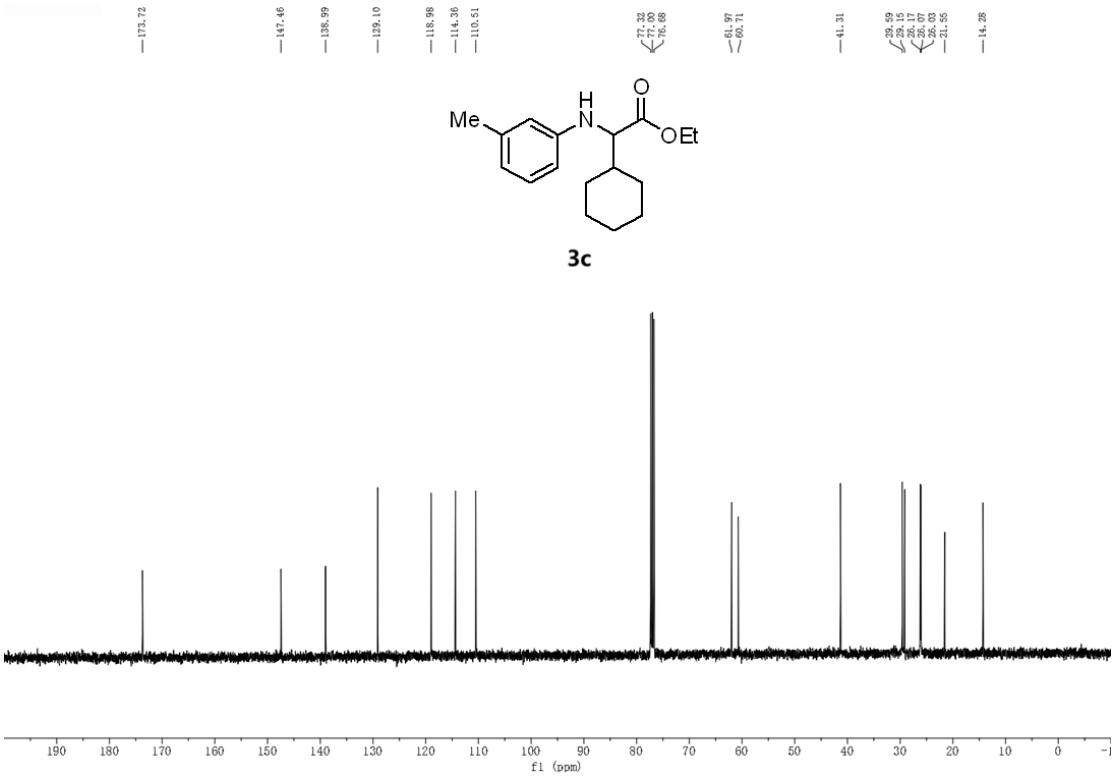

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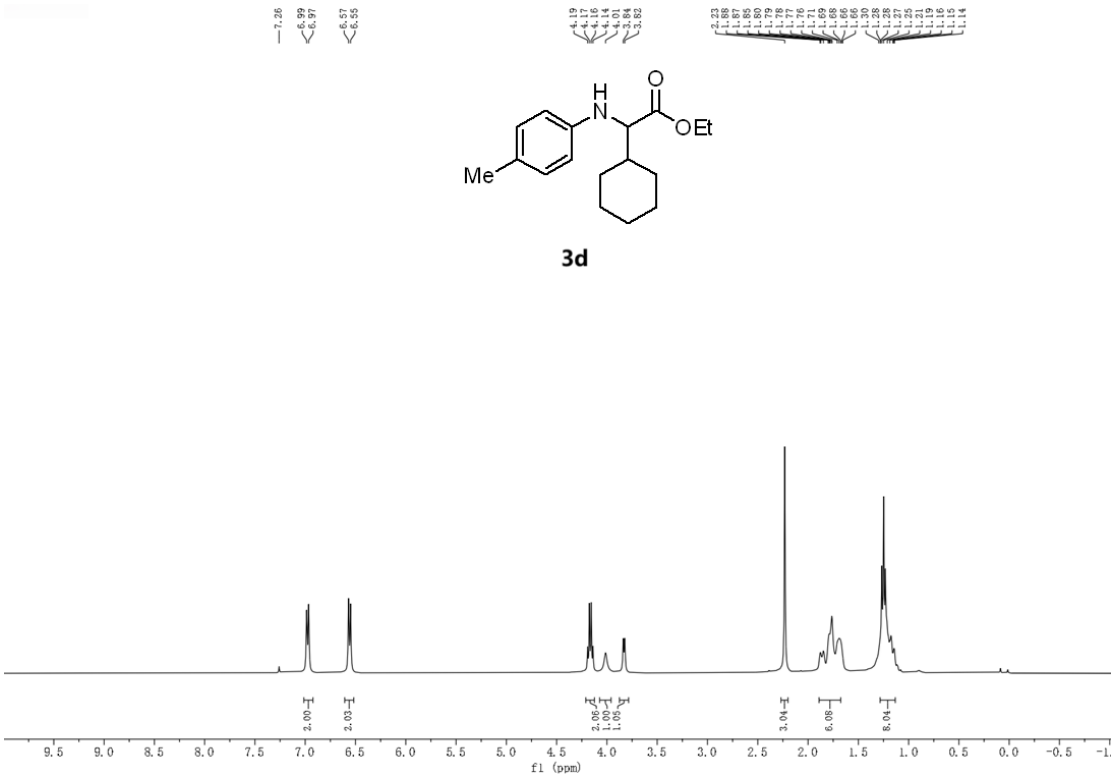

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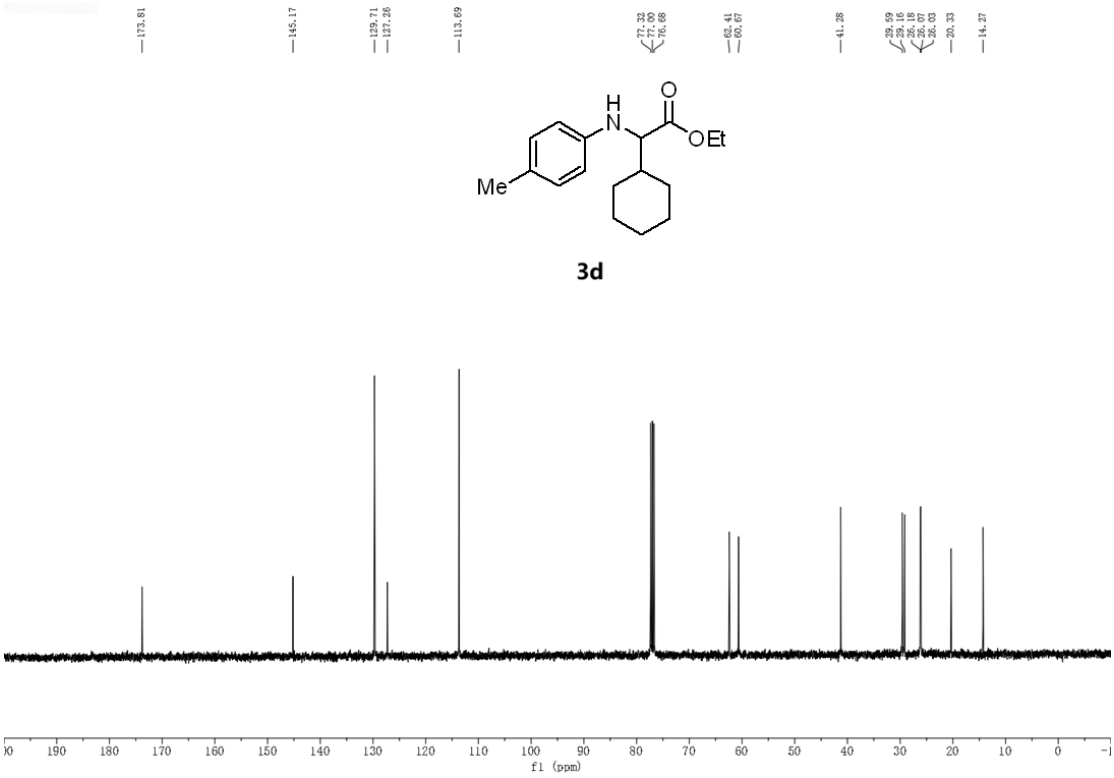

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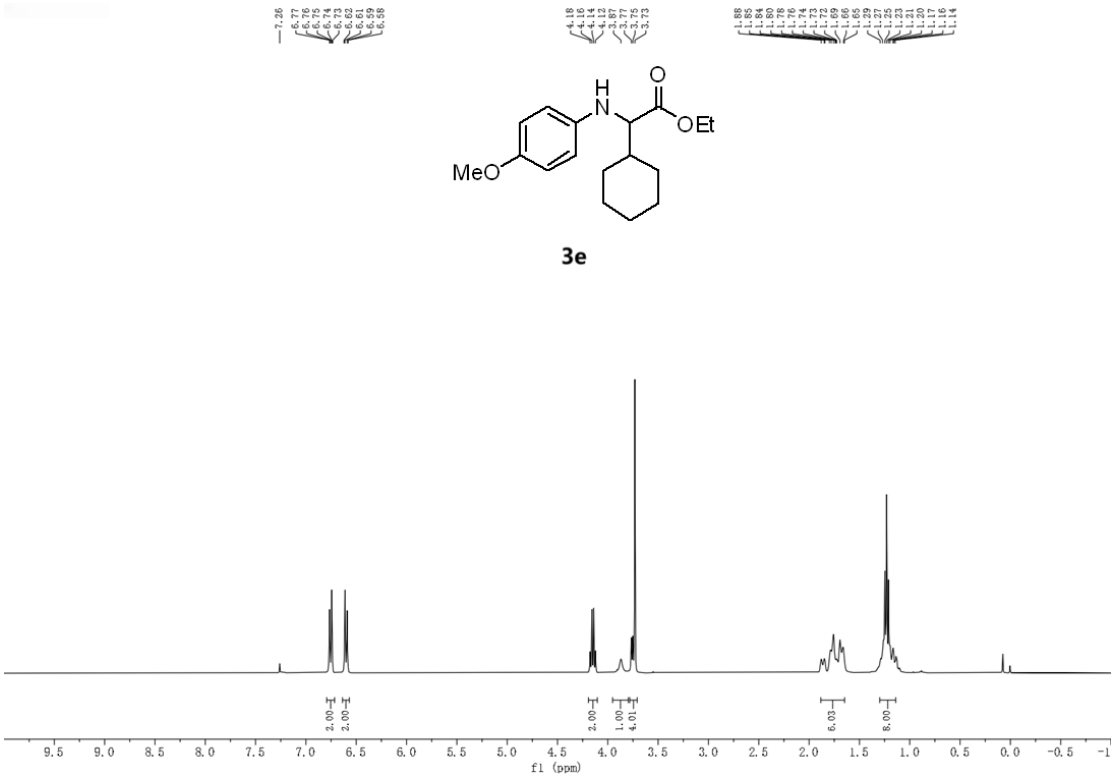

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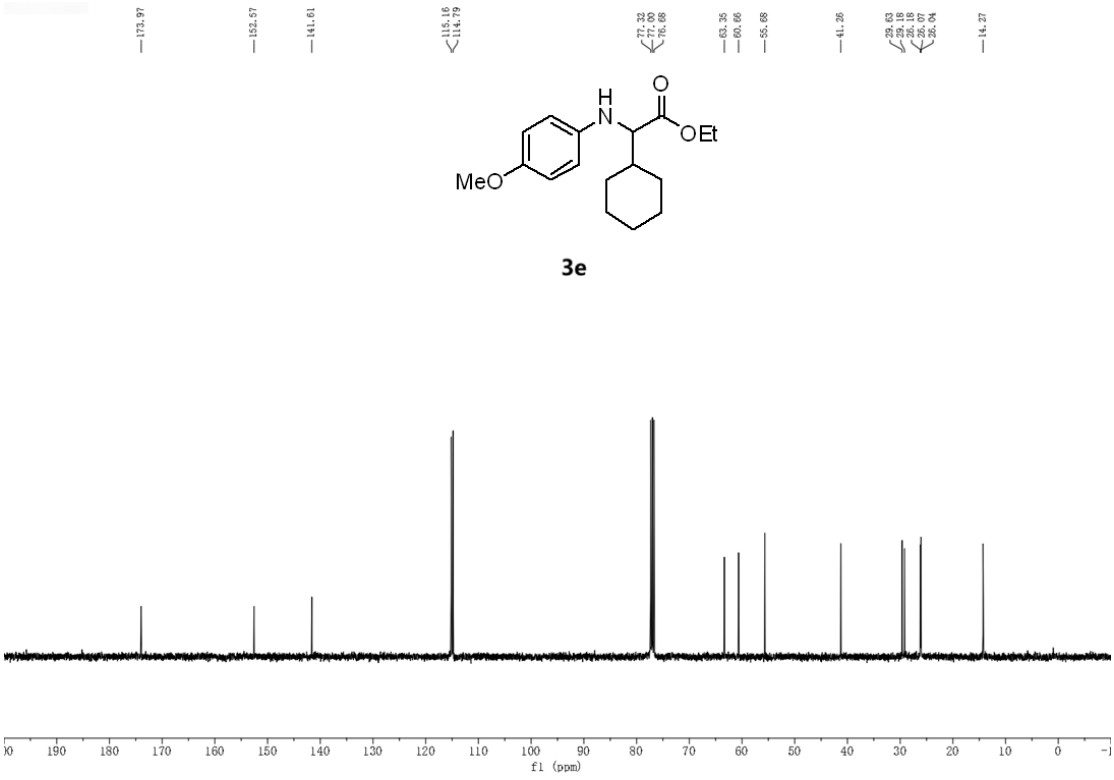

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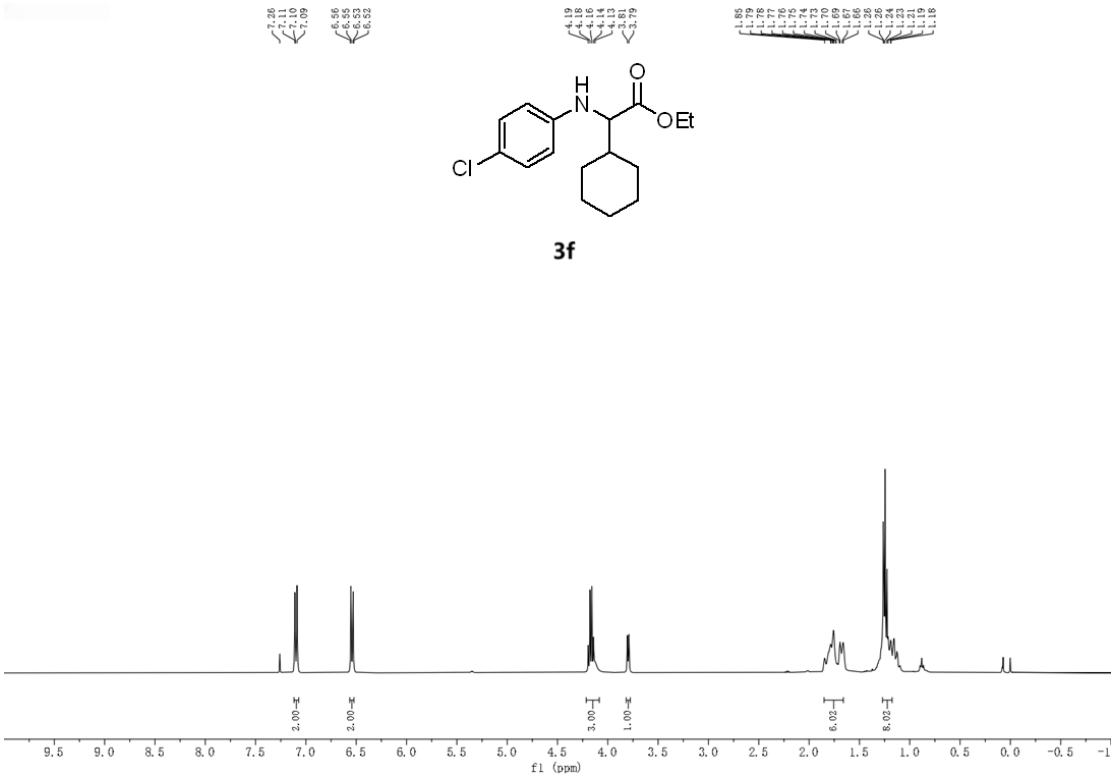

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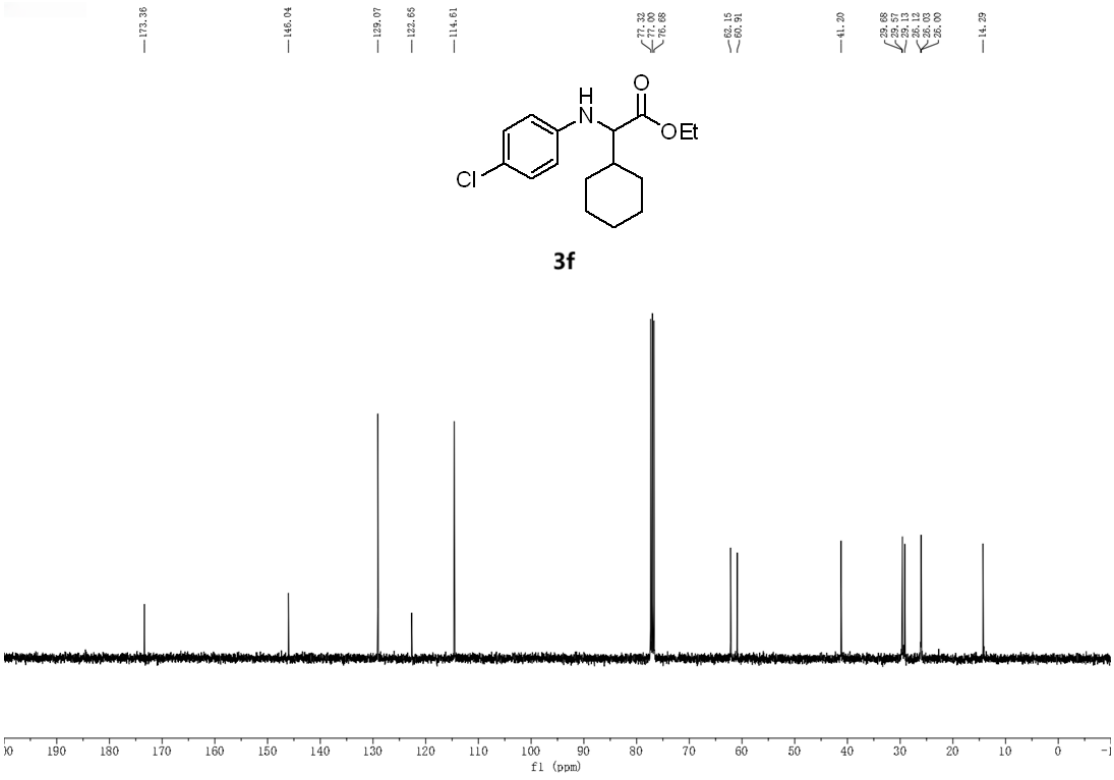

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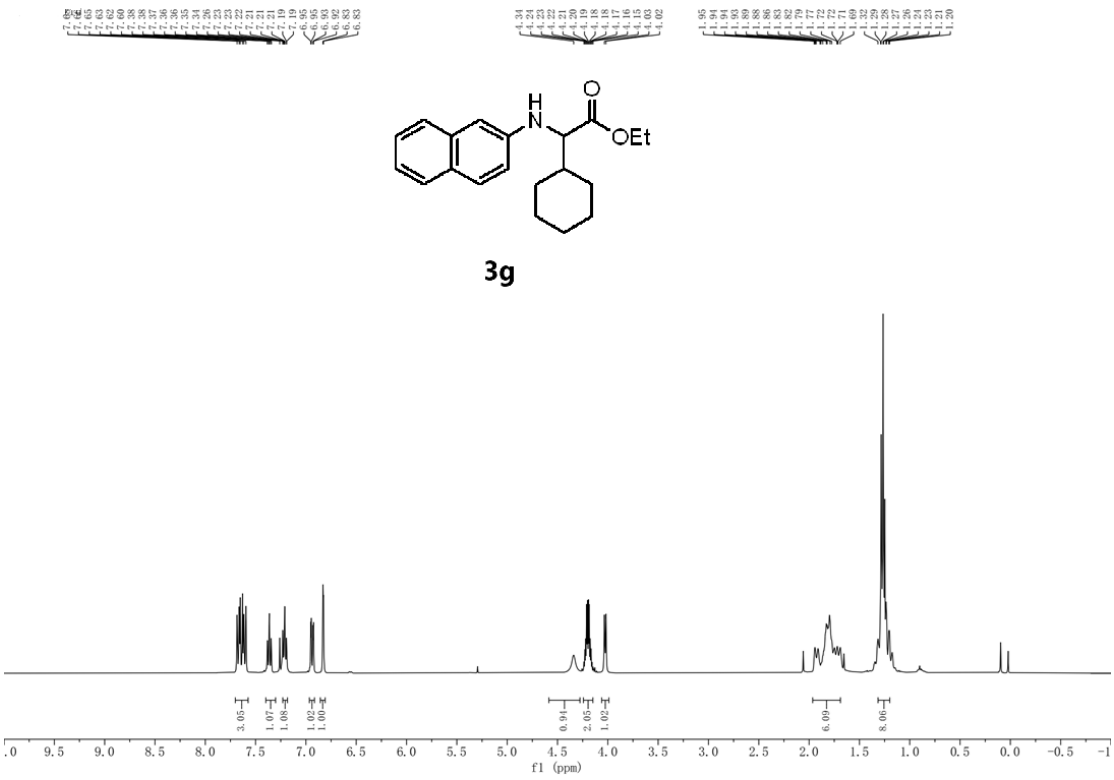

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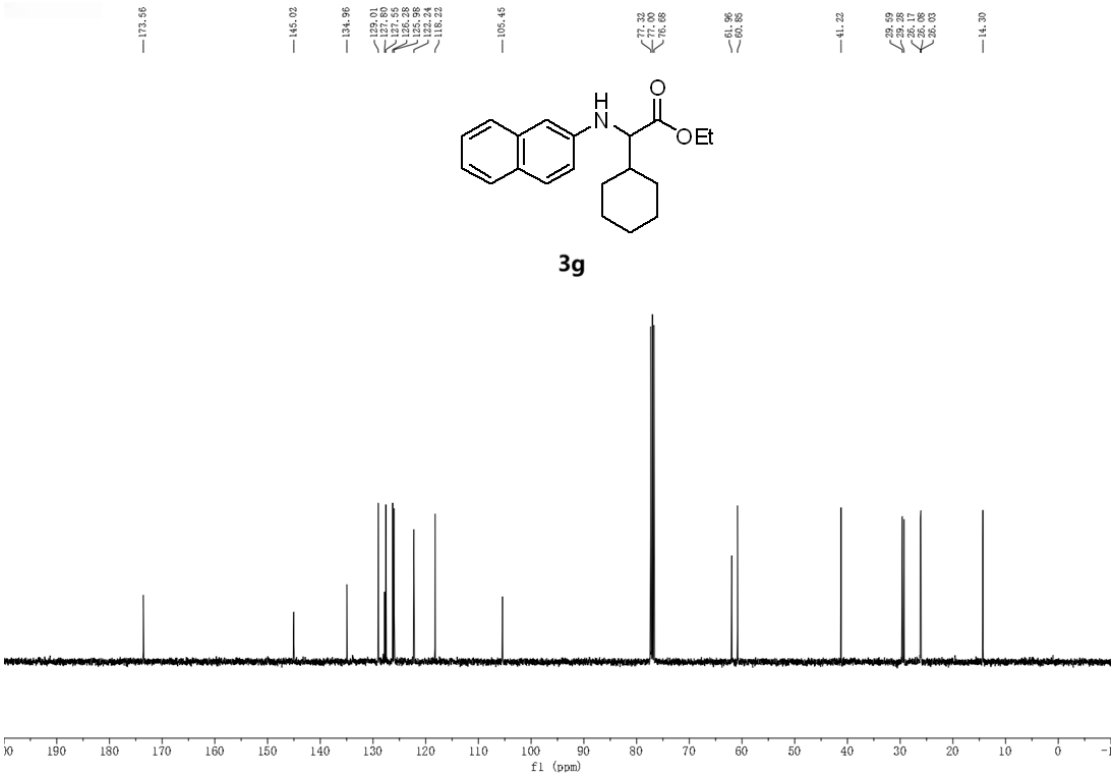

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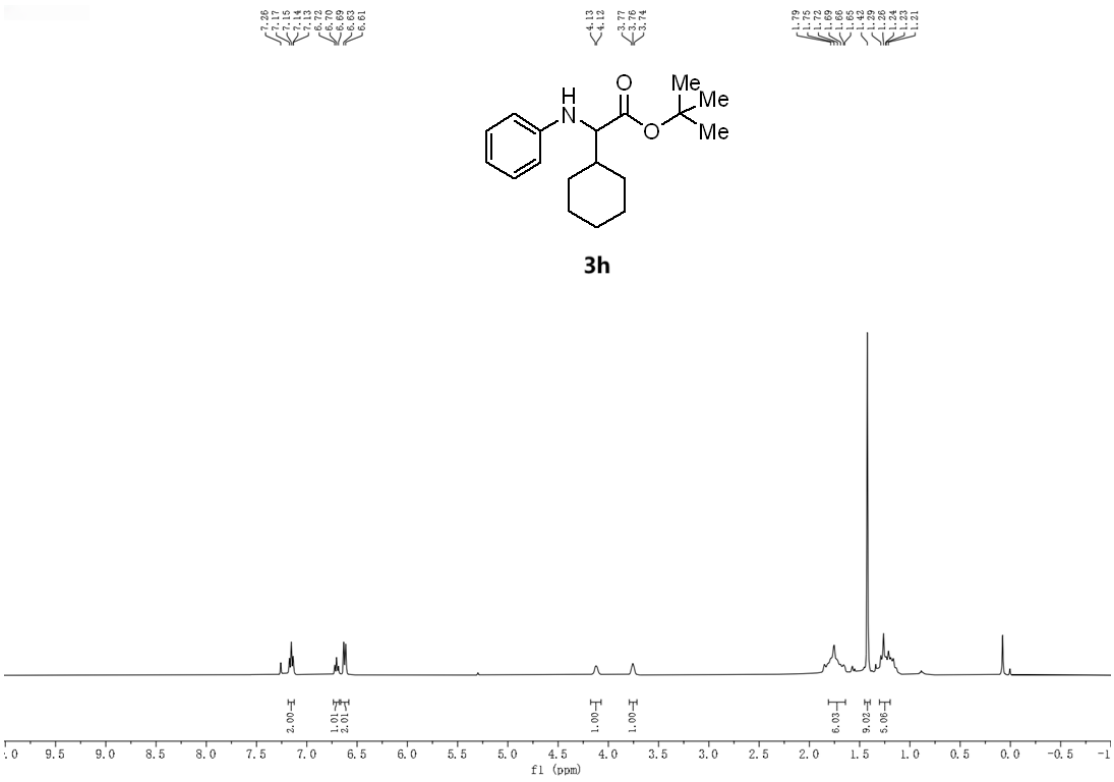

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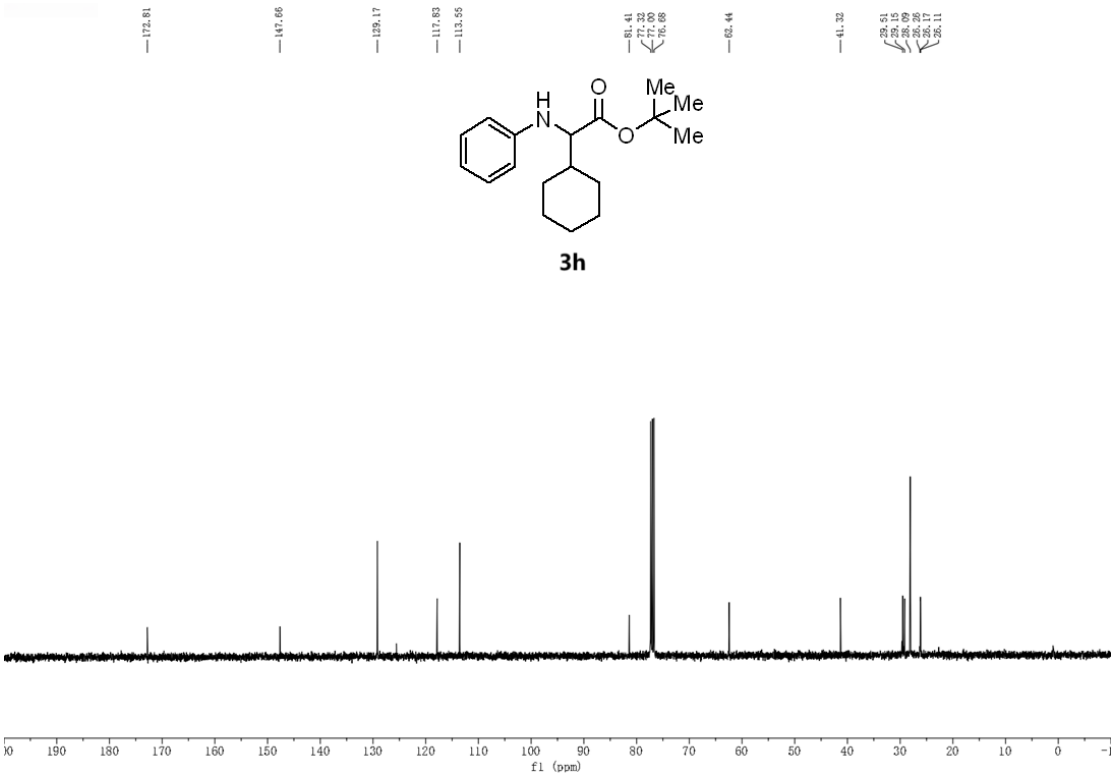

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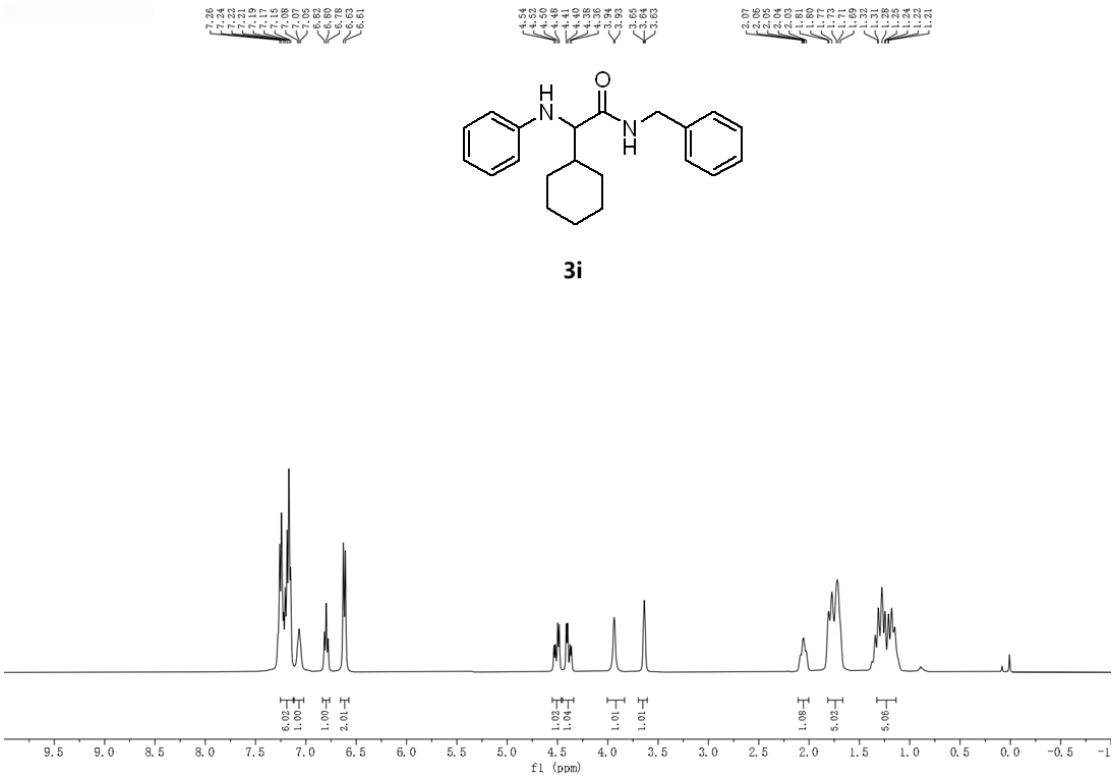
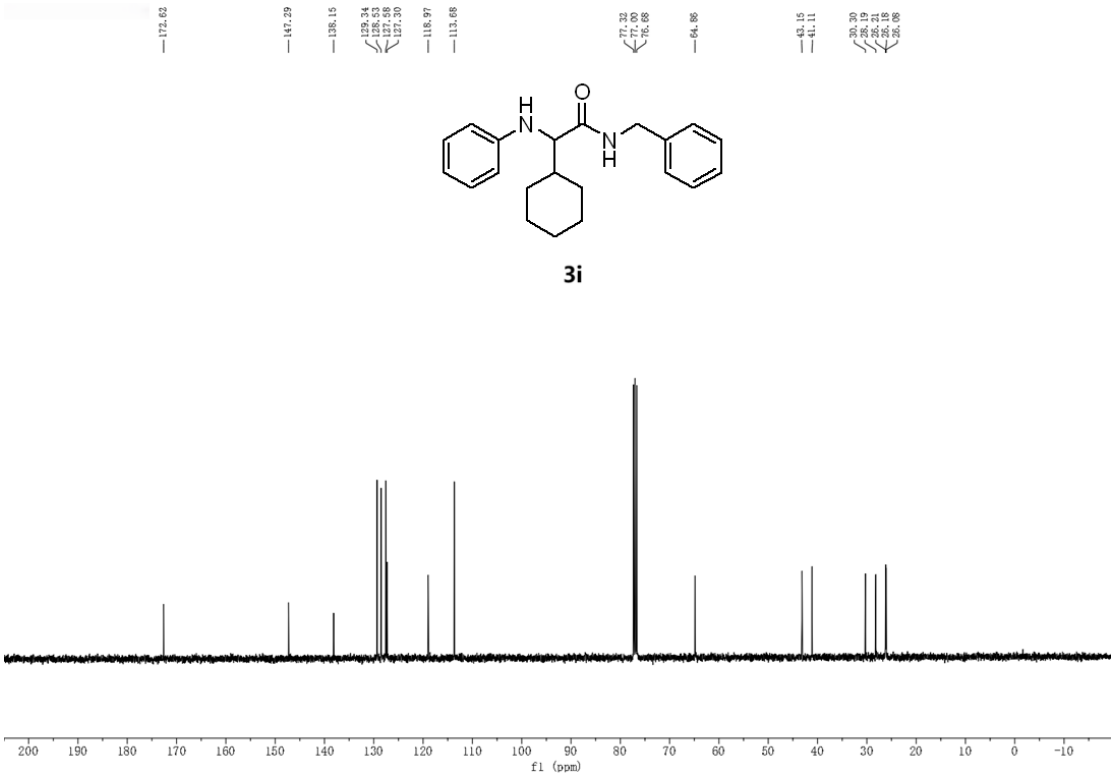


3i

^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3i**



3i

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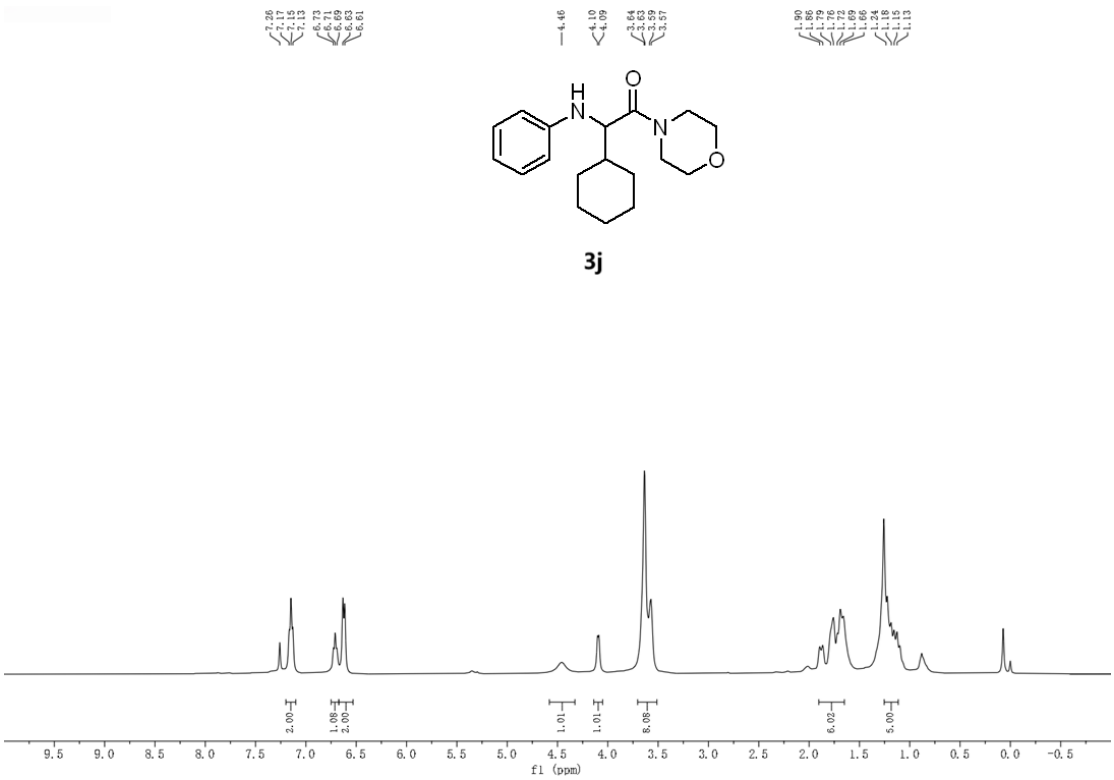

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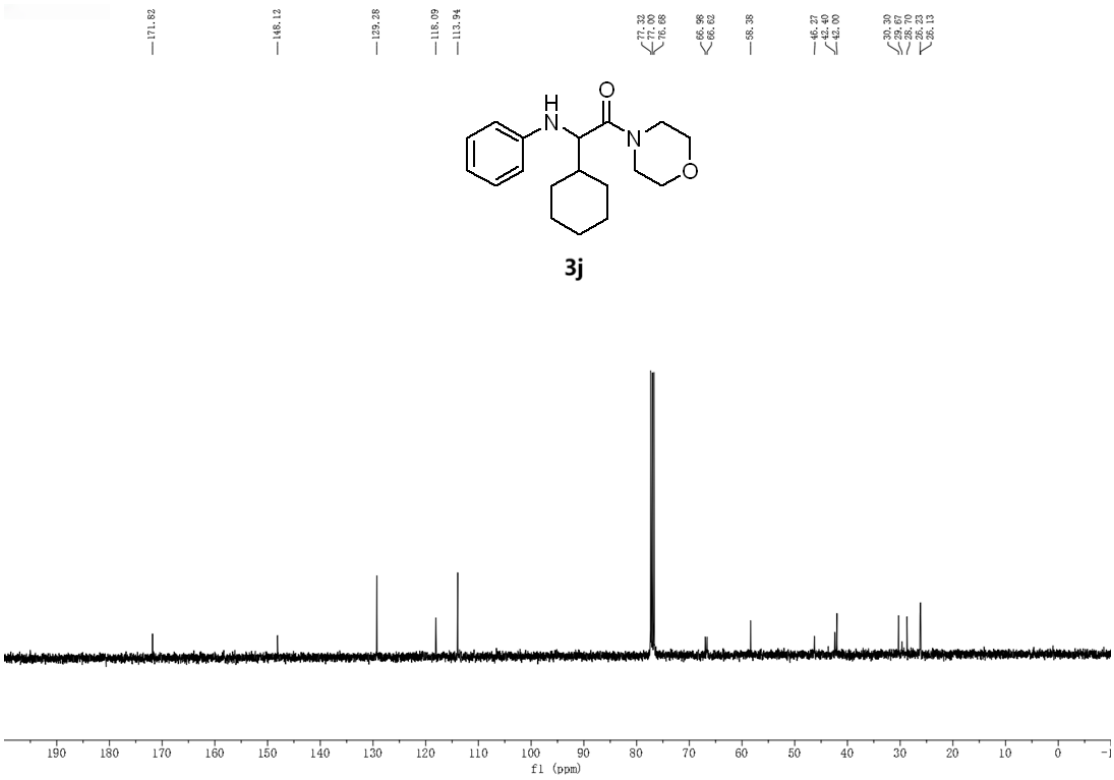

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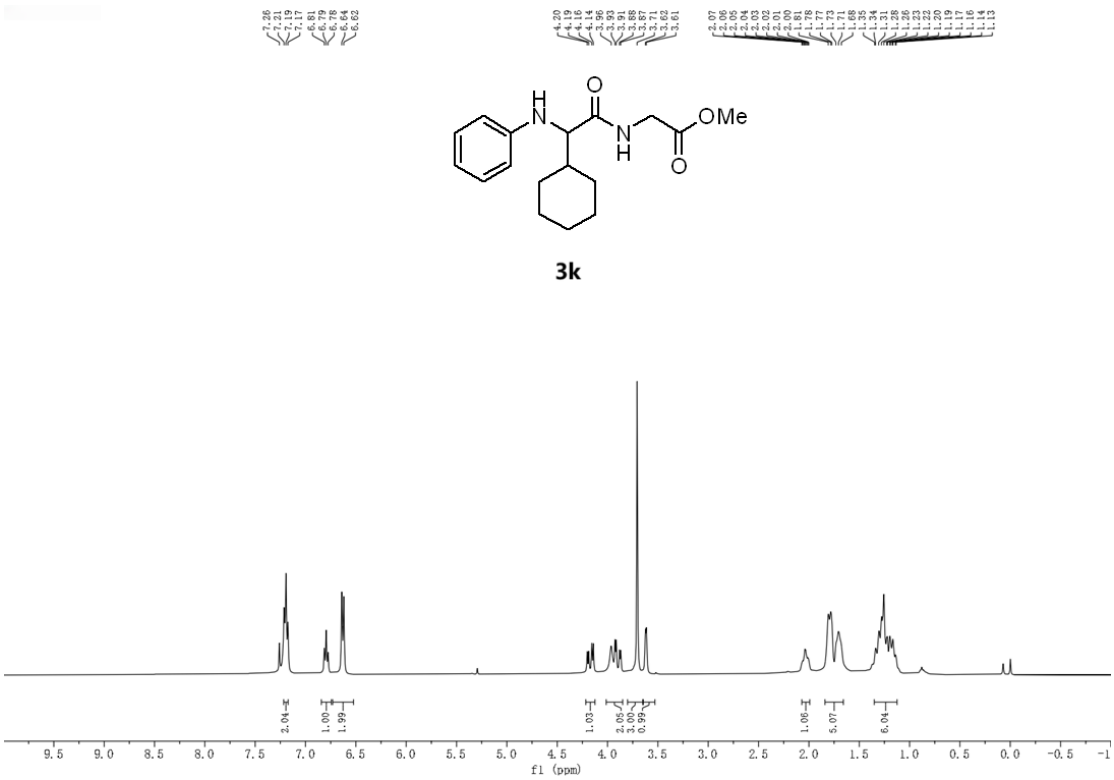

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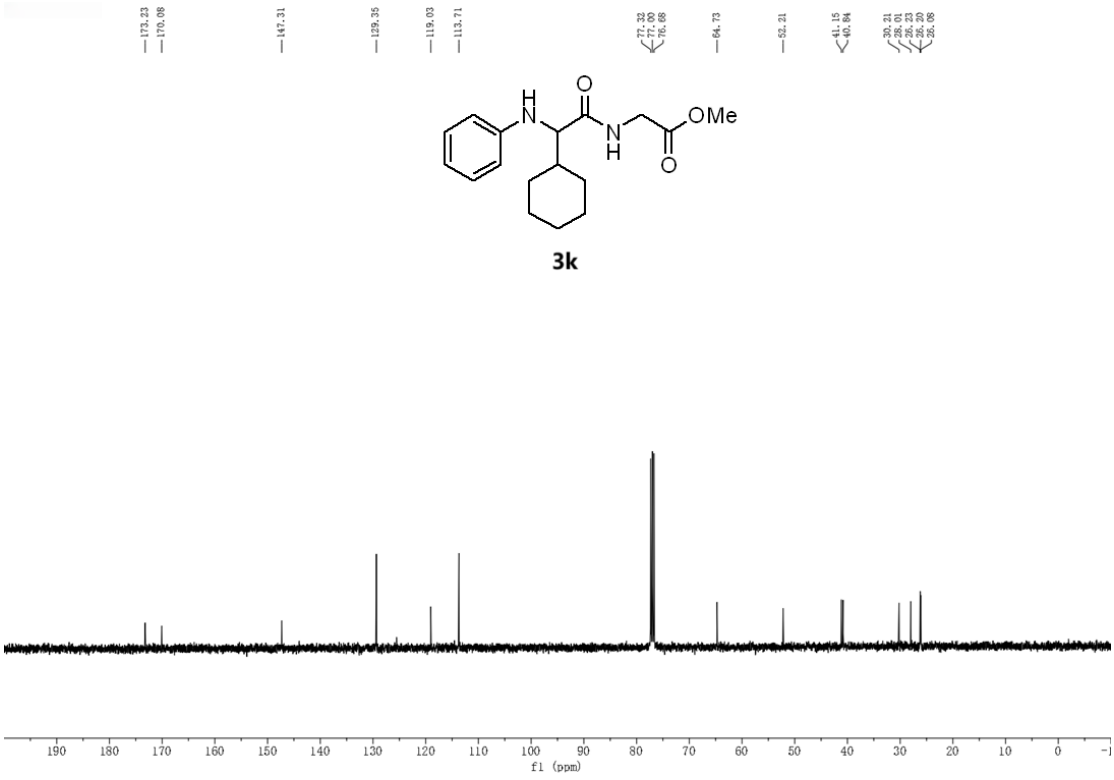

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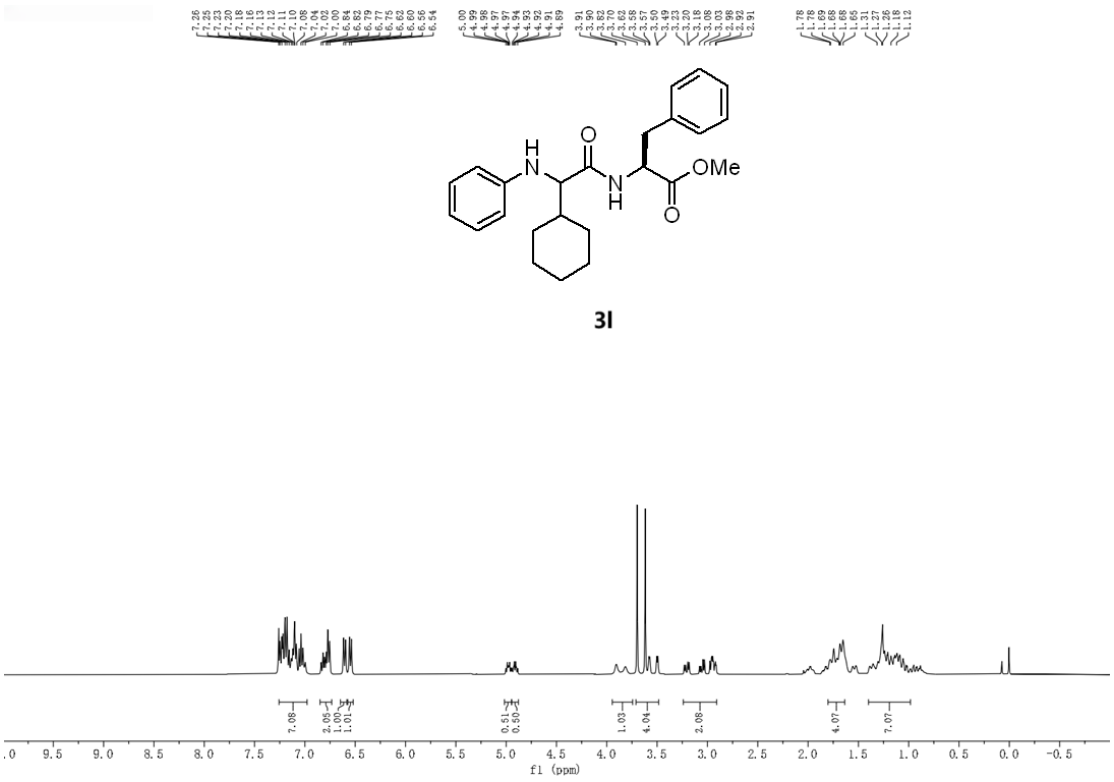
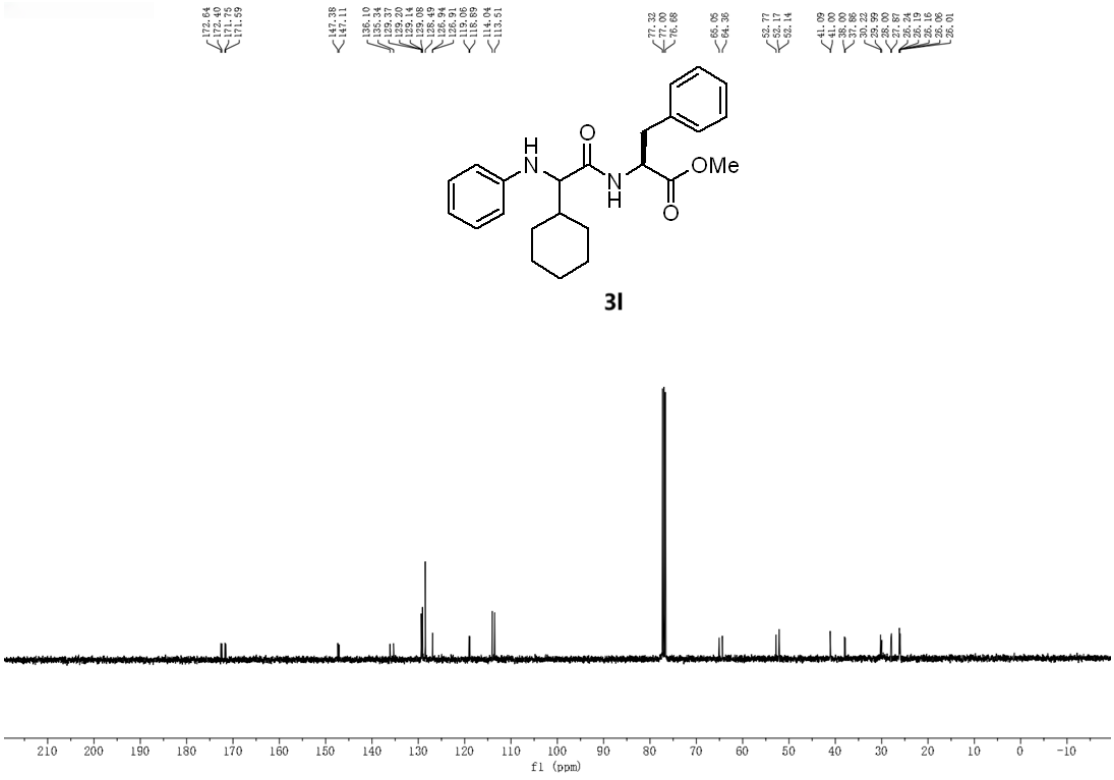


3l

^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3l**



3l

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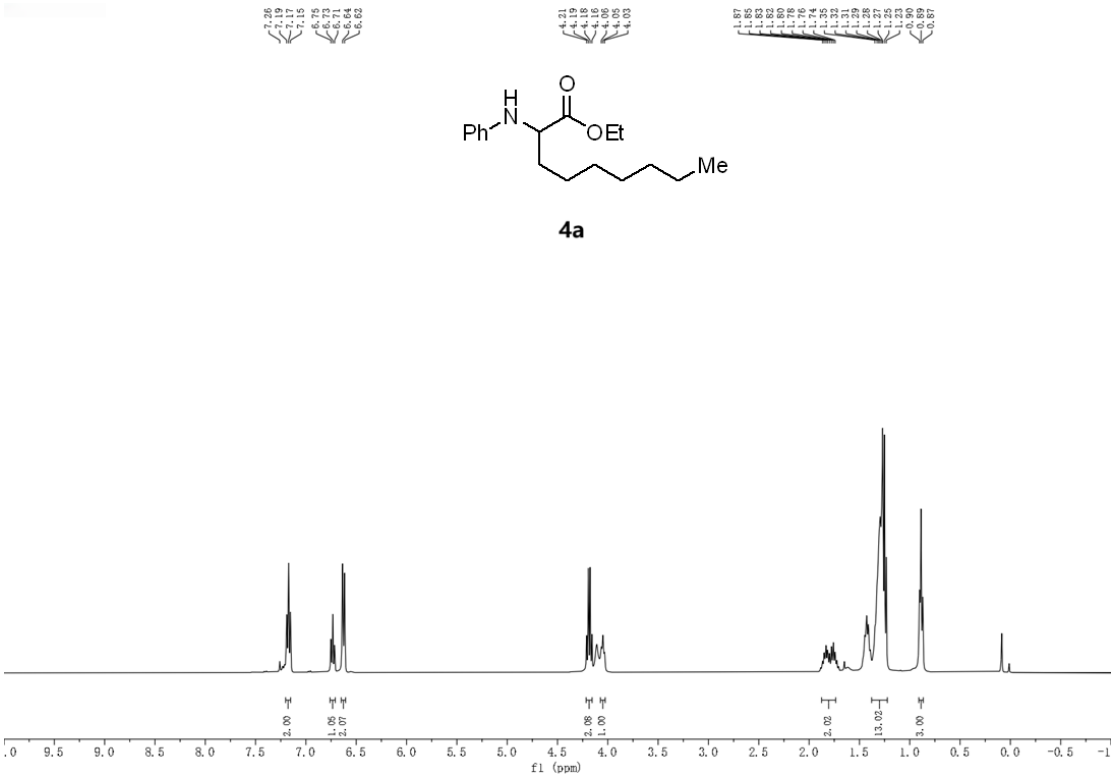
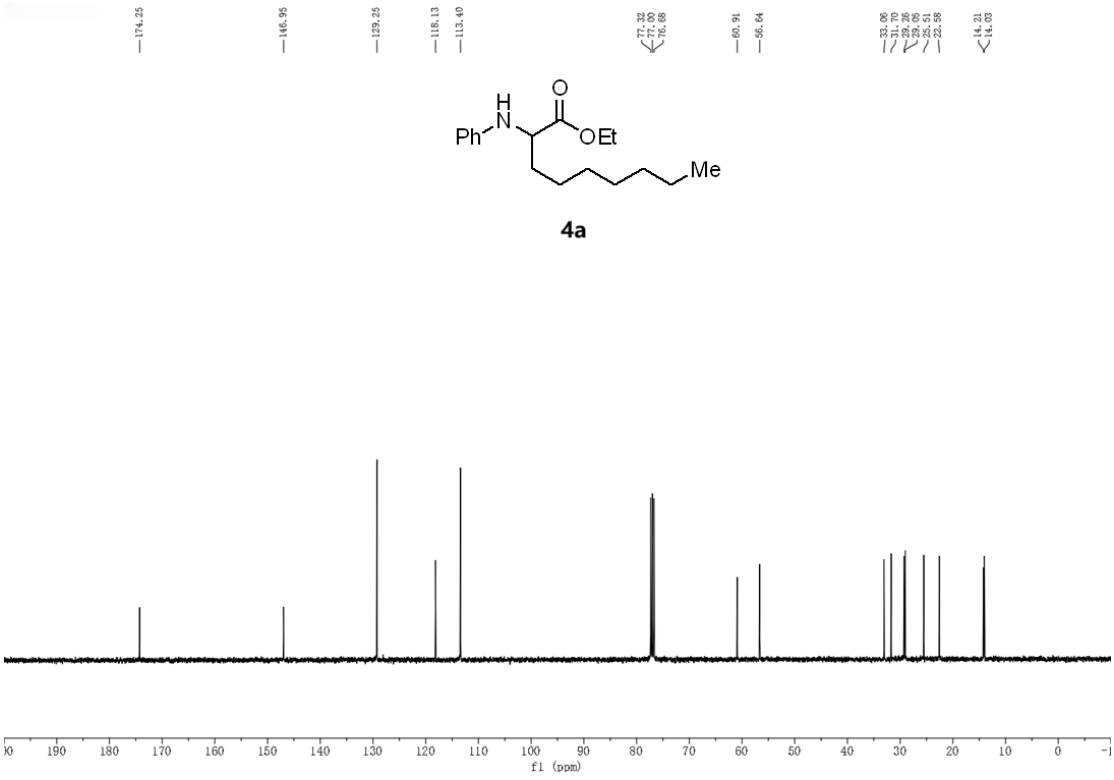


^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4a**



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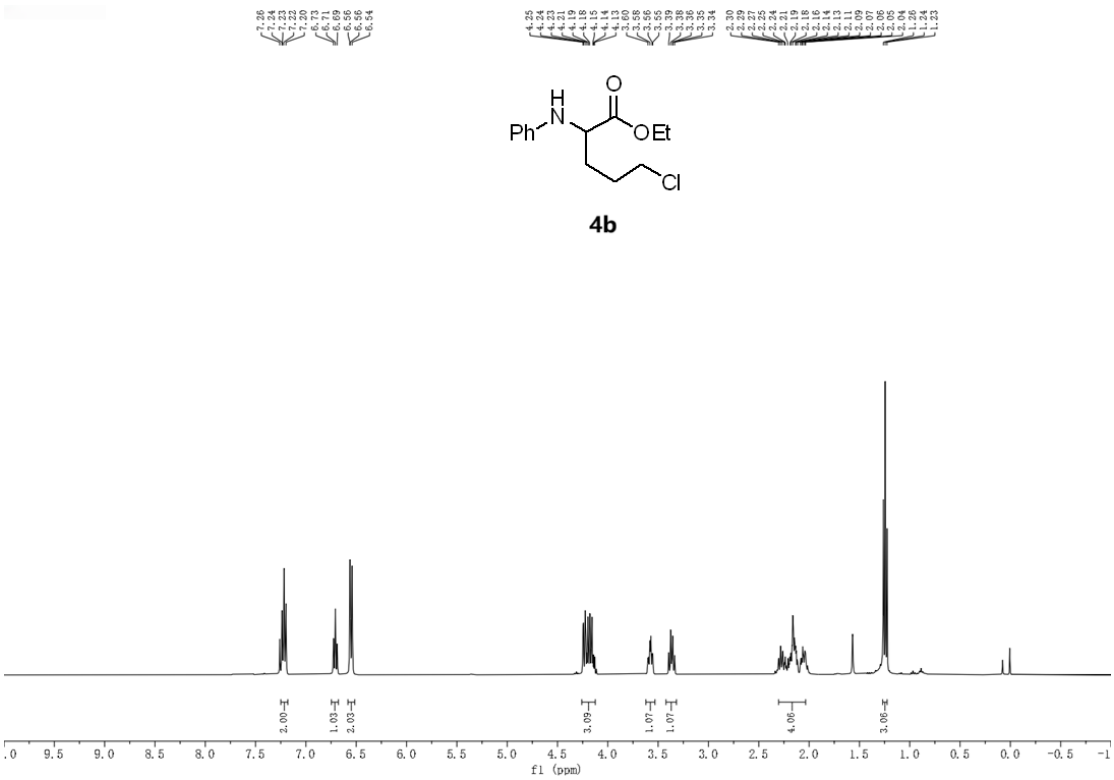

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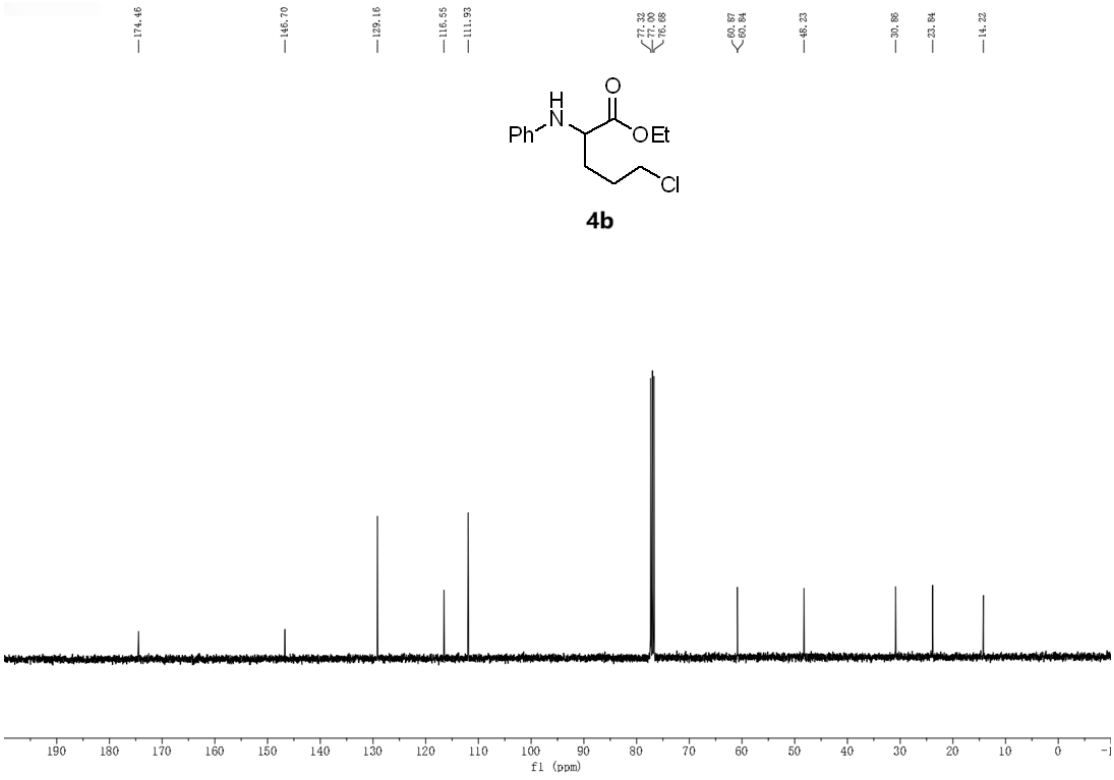

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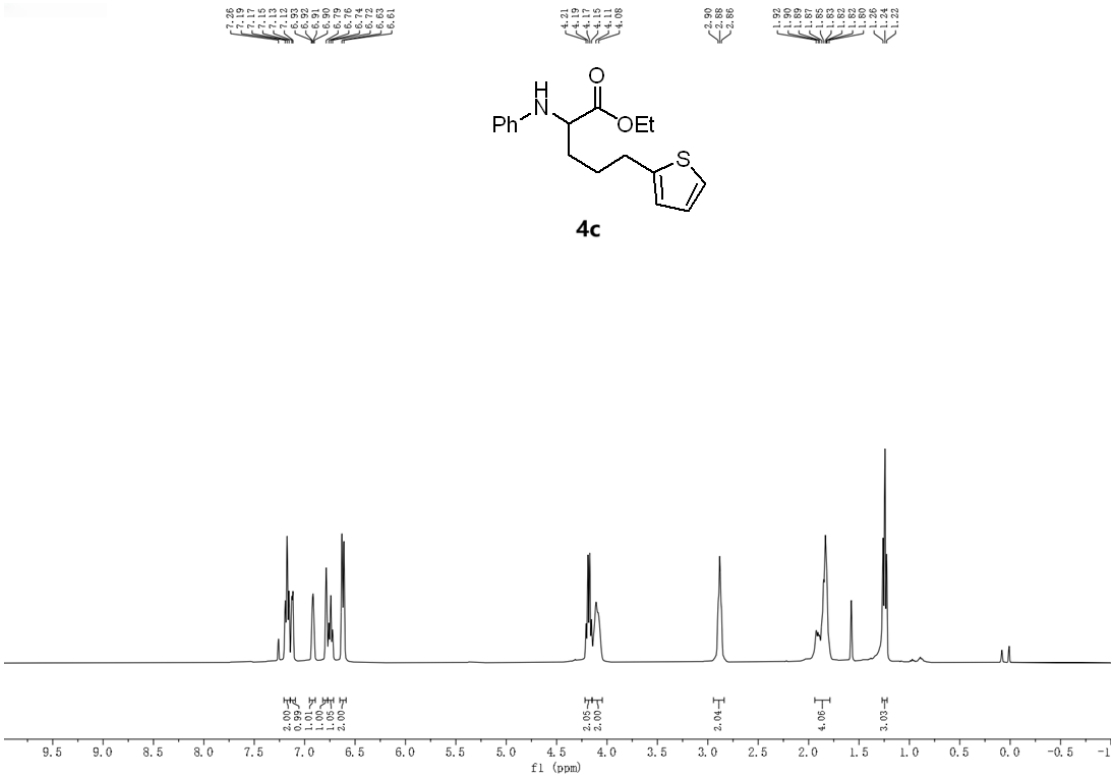
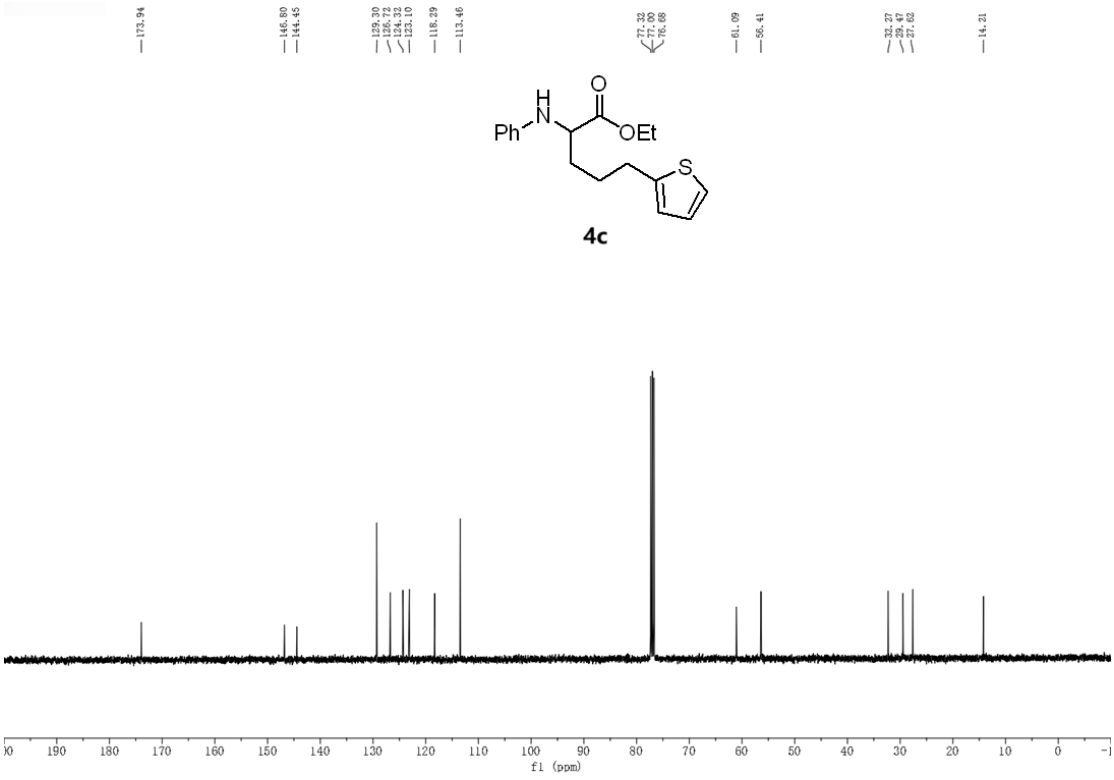


^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4c**



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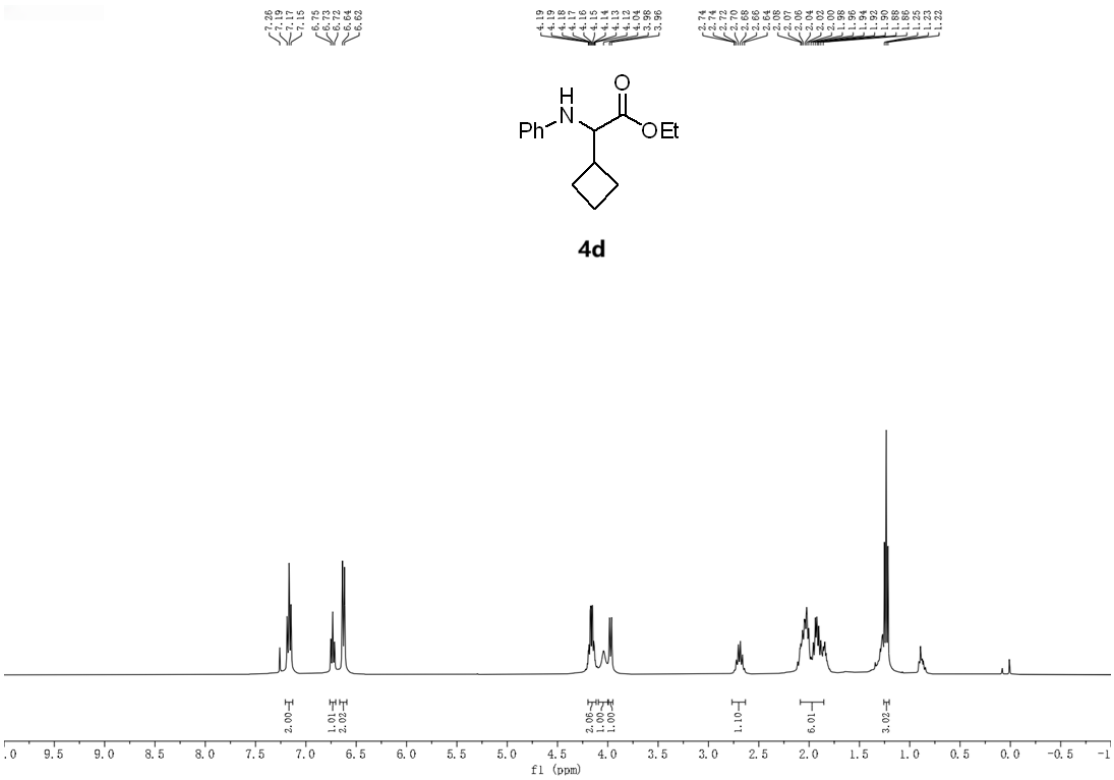

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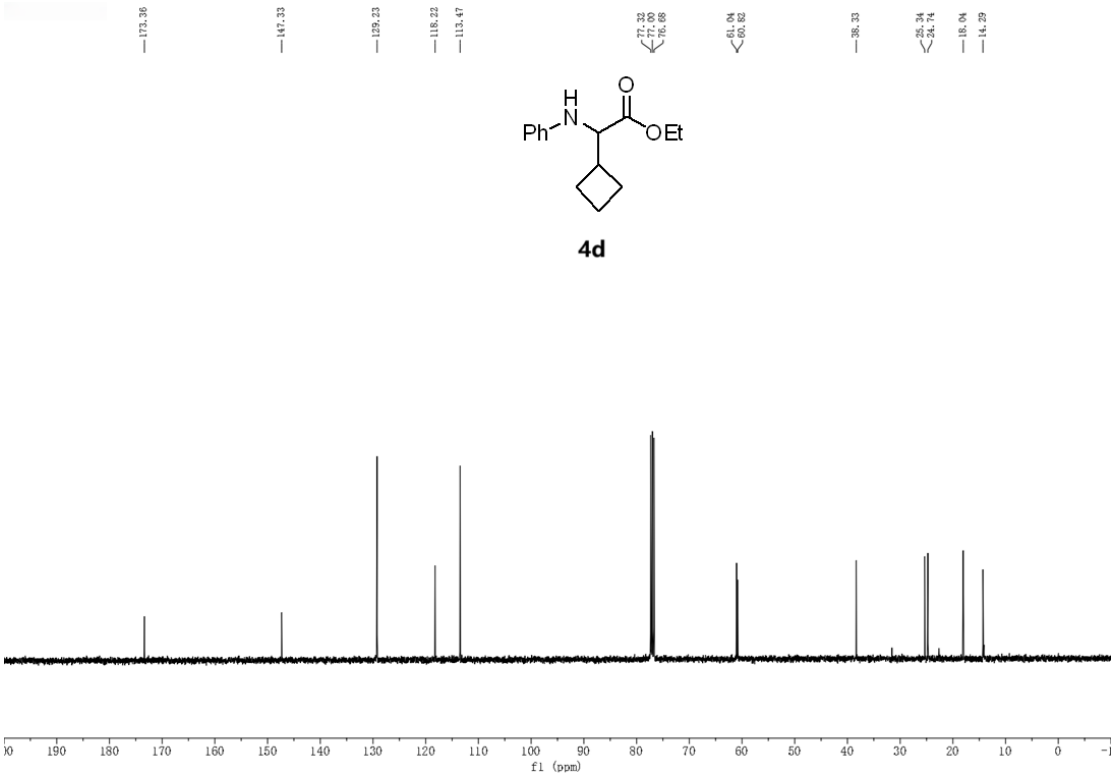

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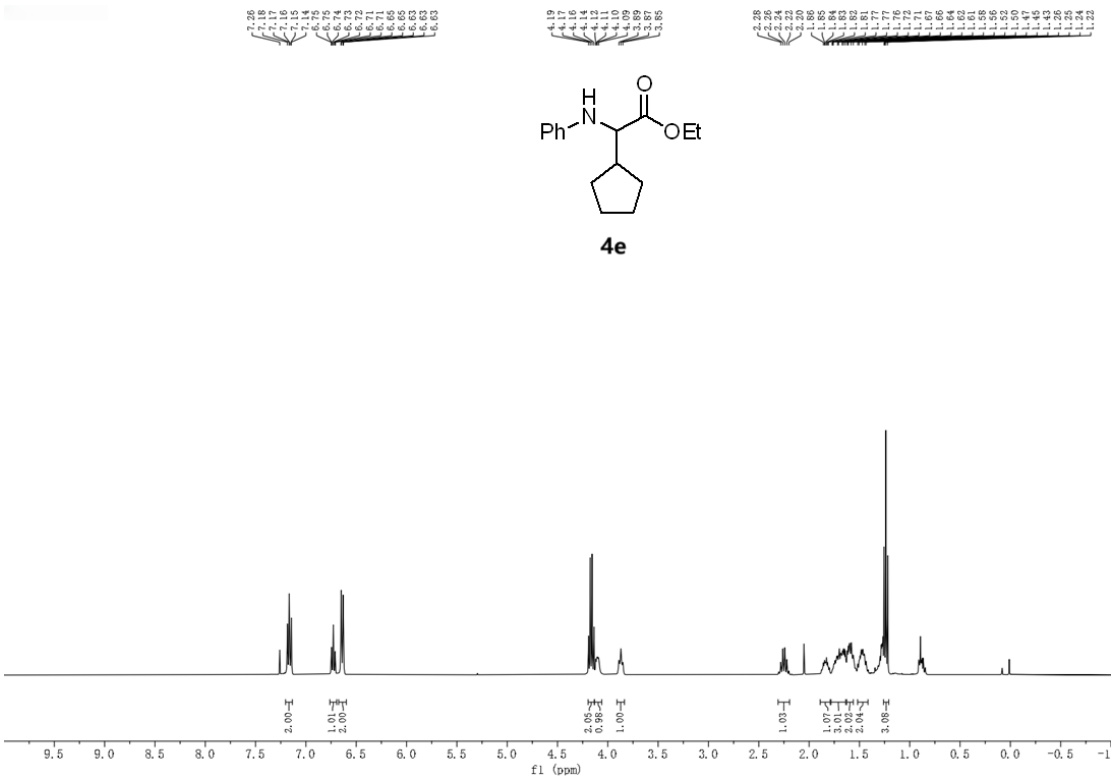

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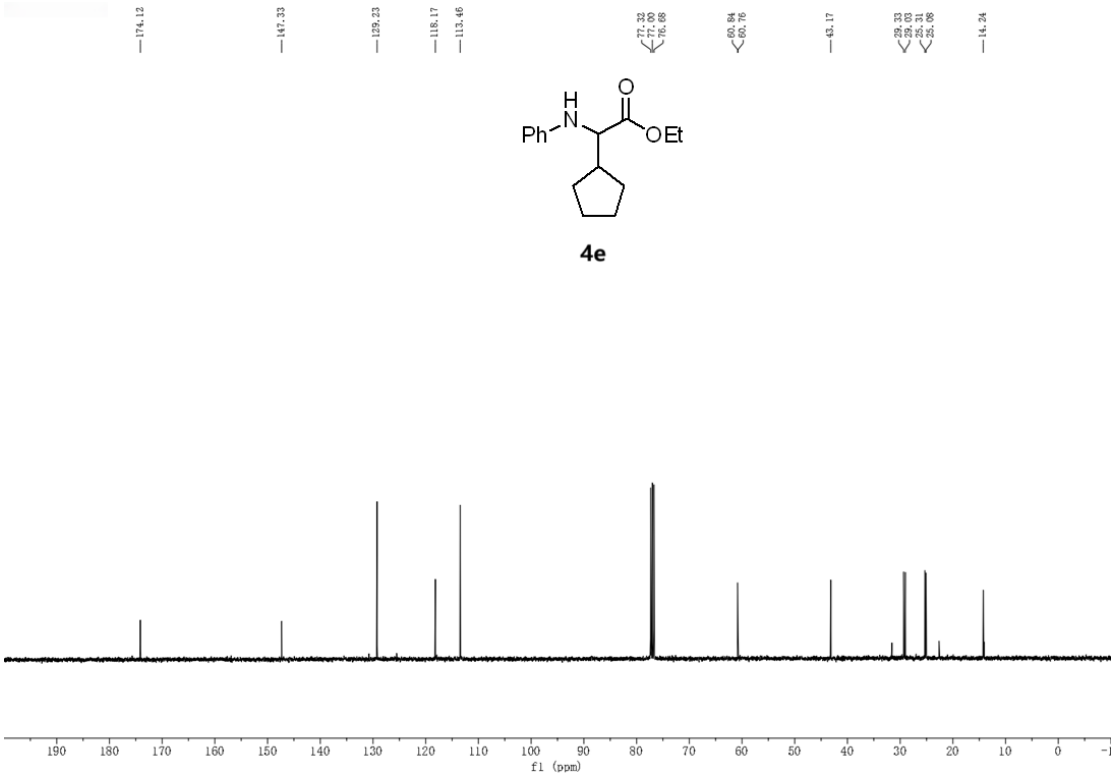

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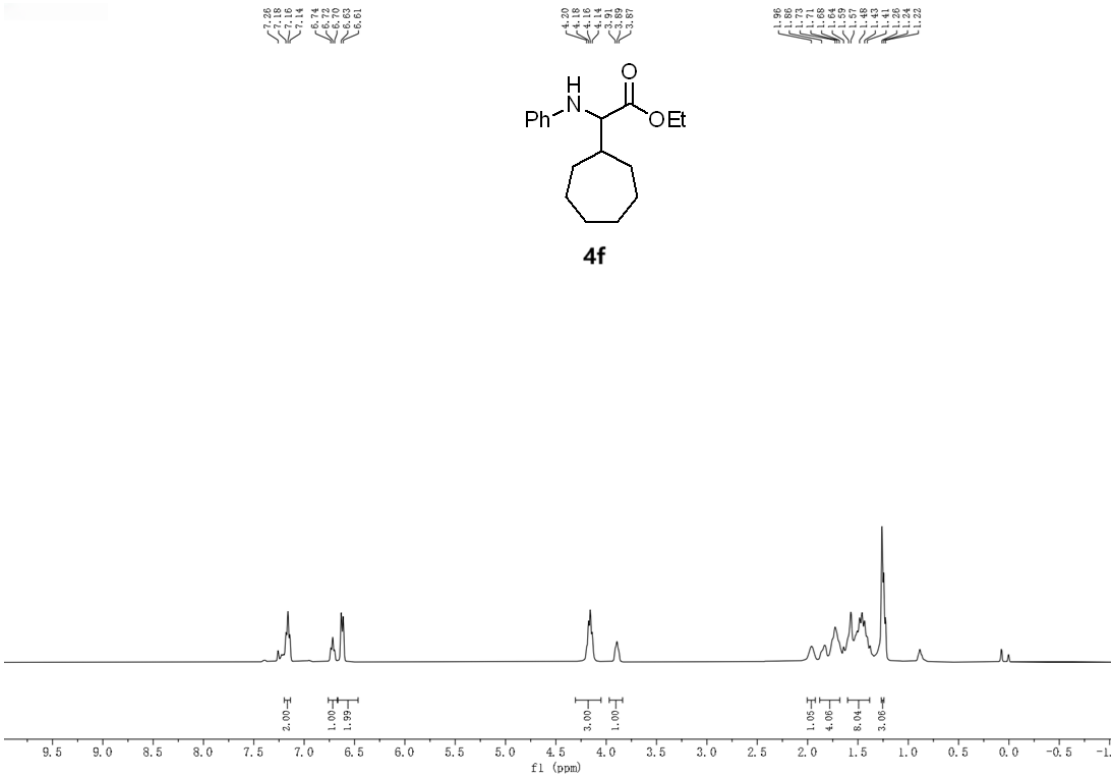

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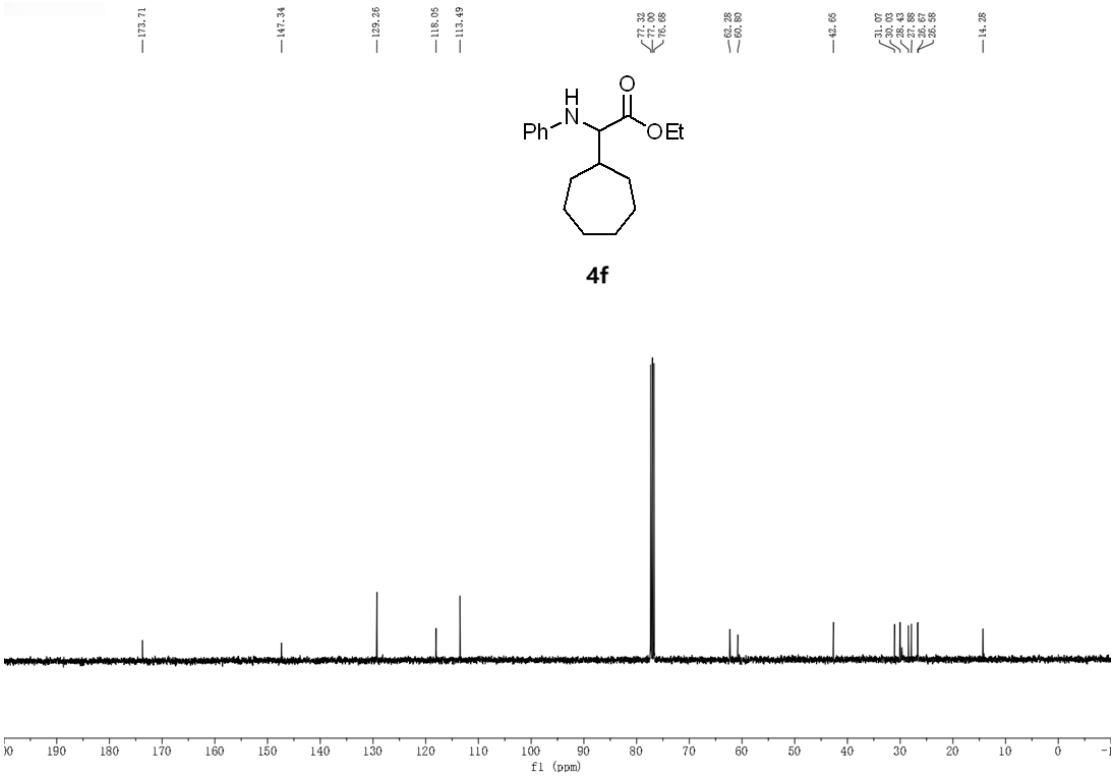

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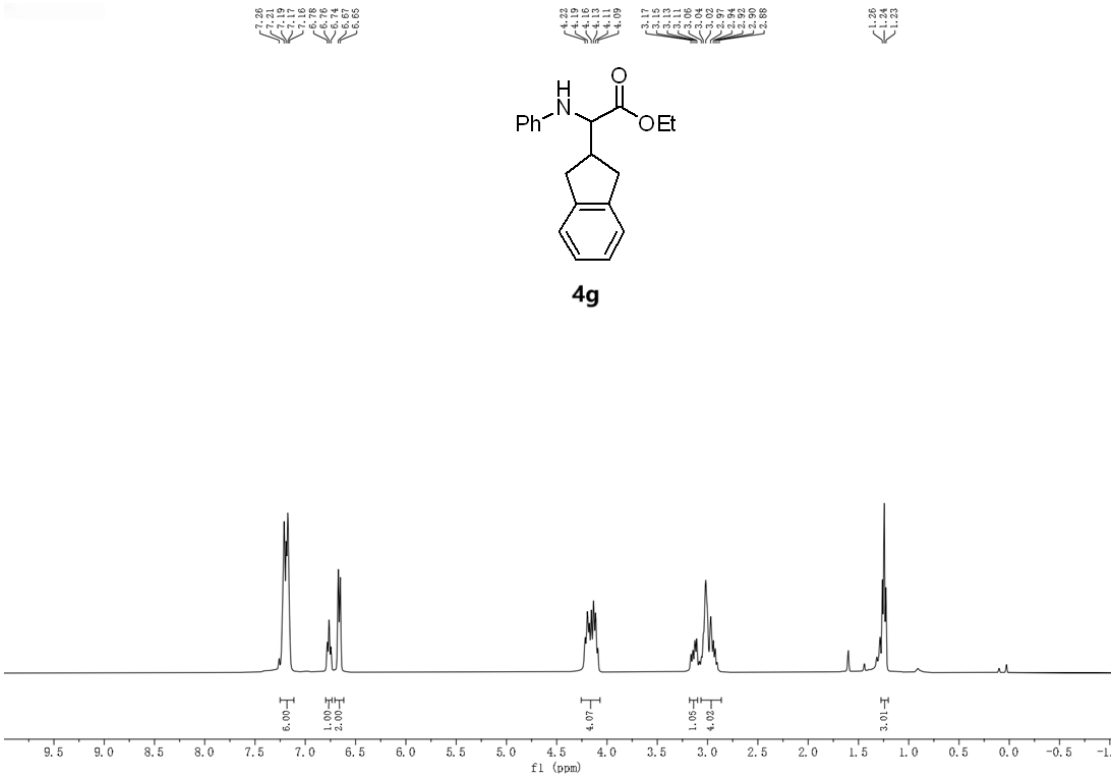

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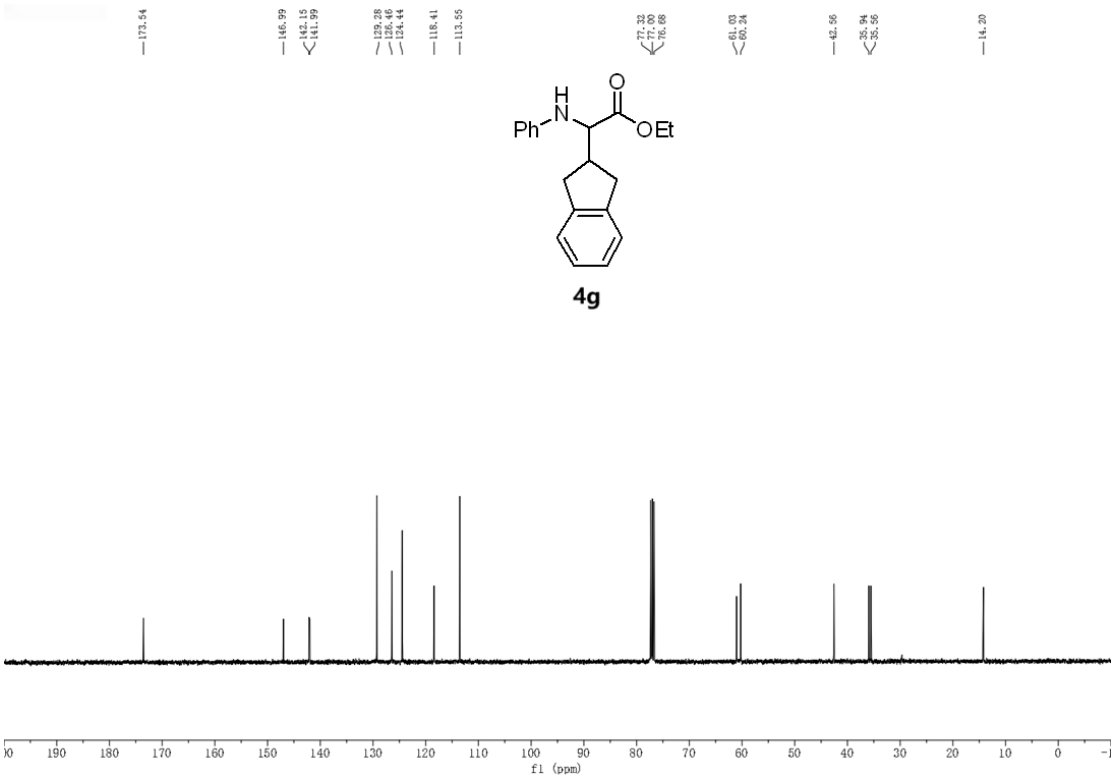

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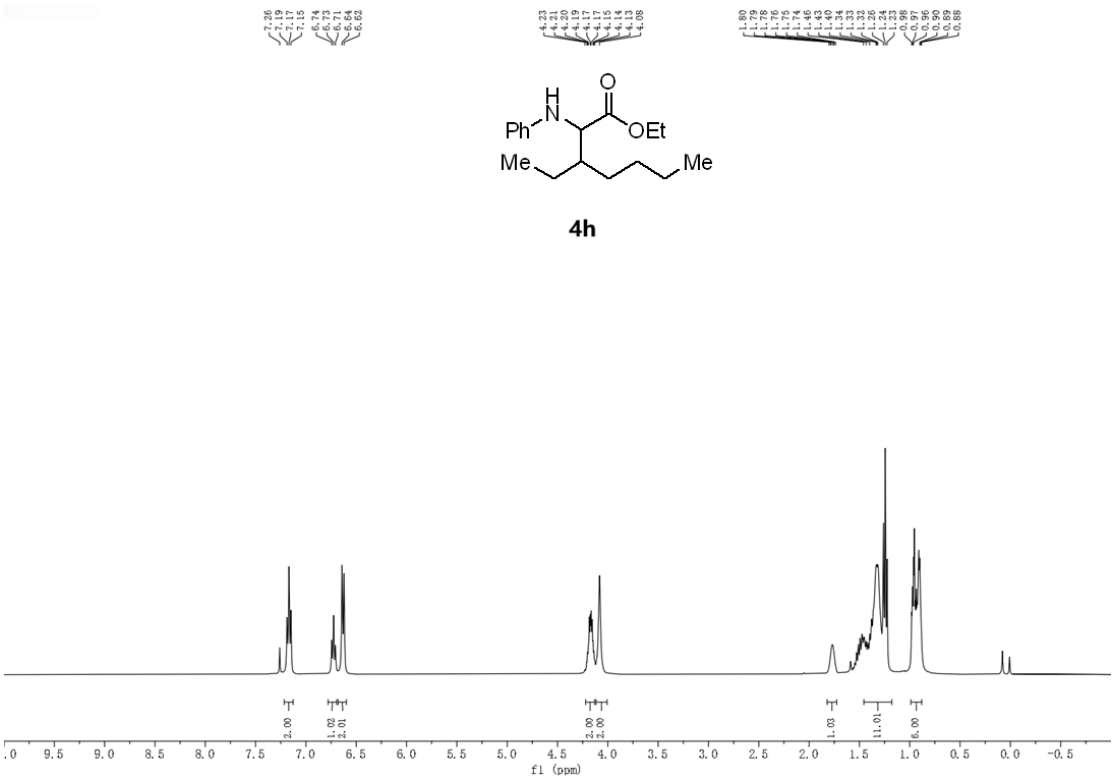

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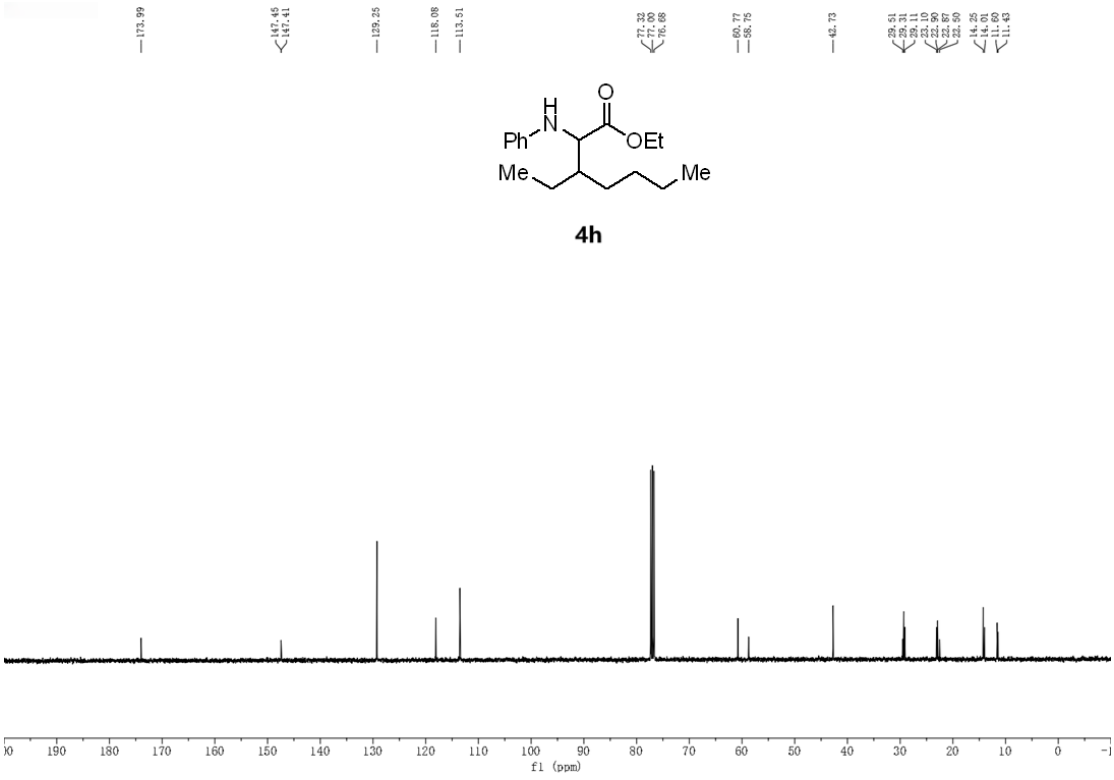

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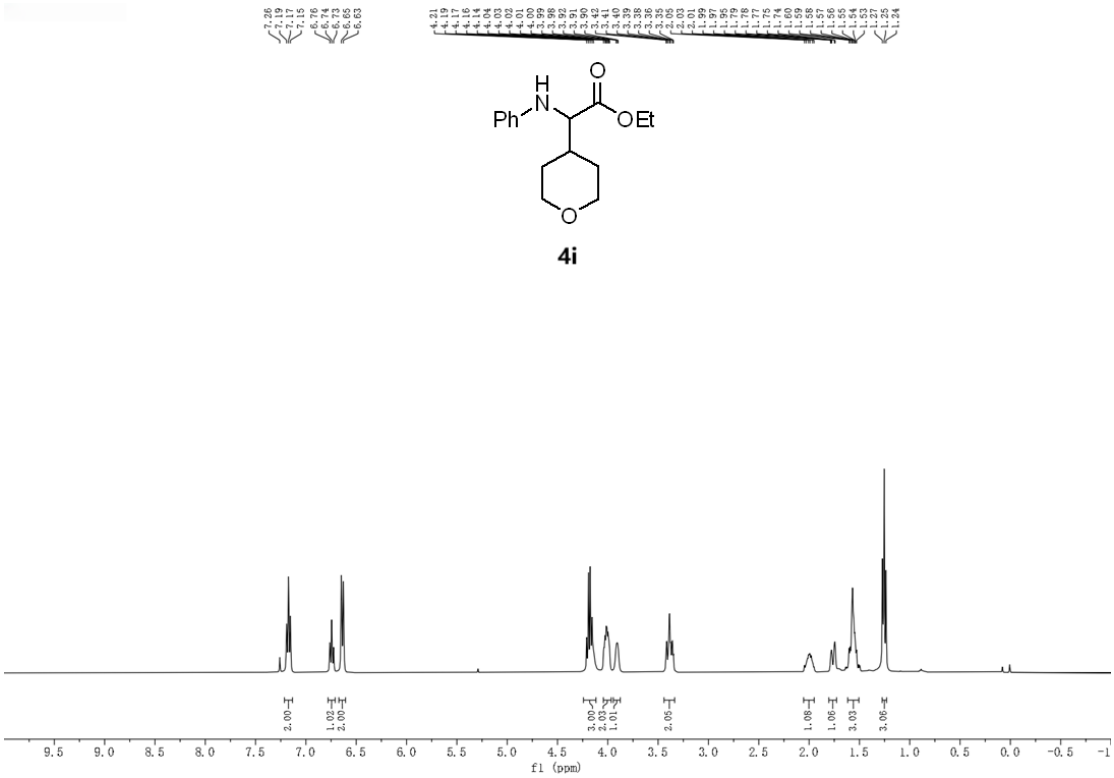
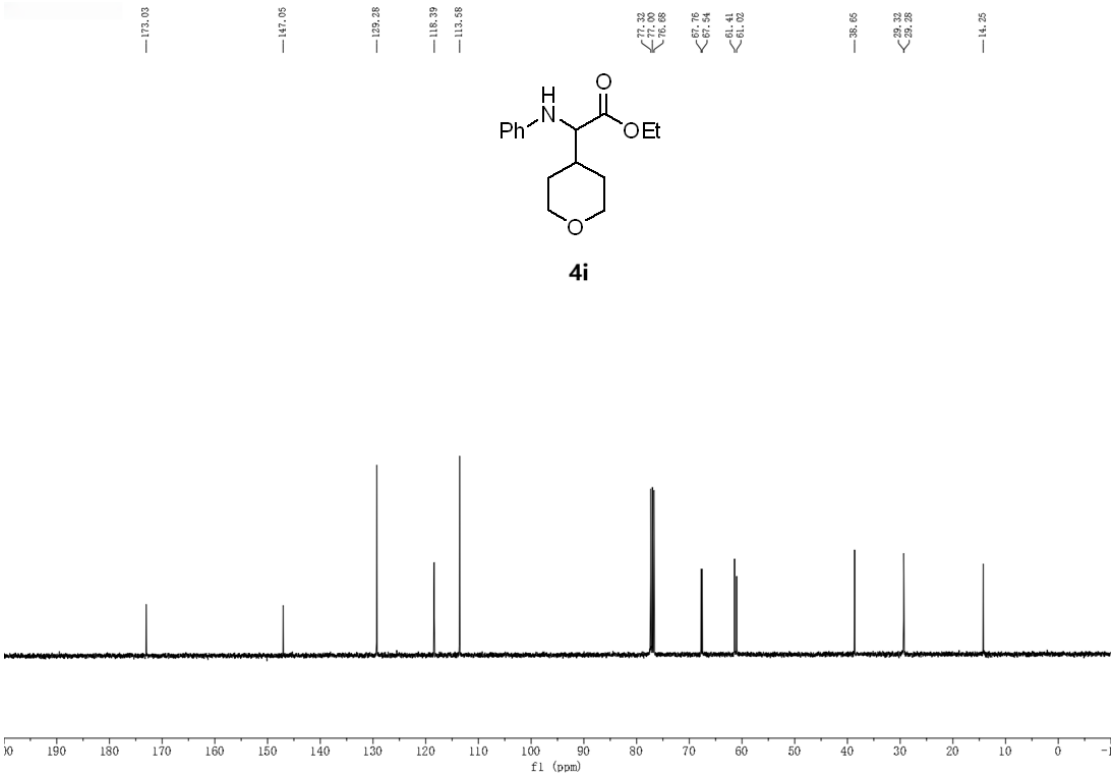
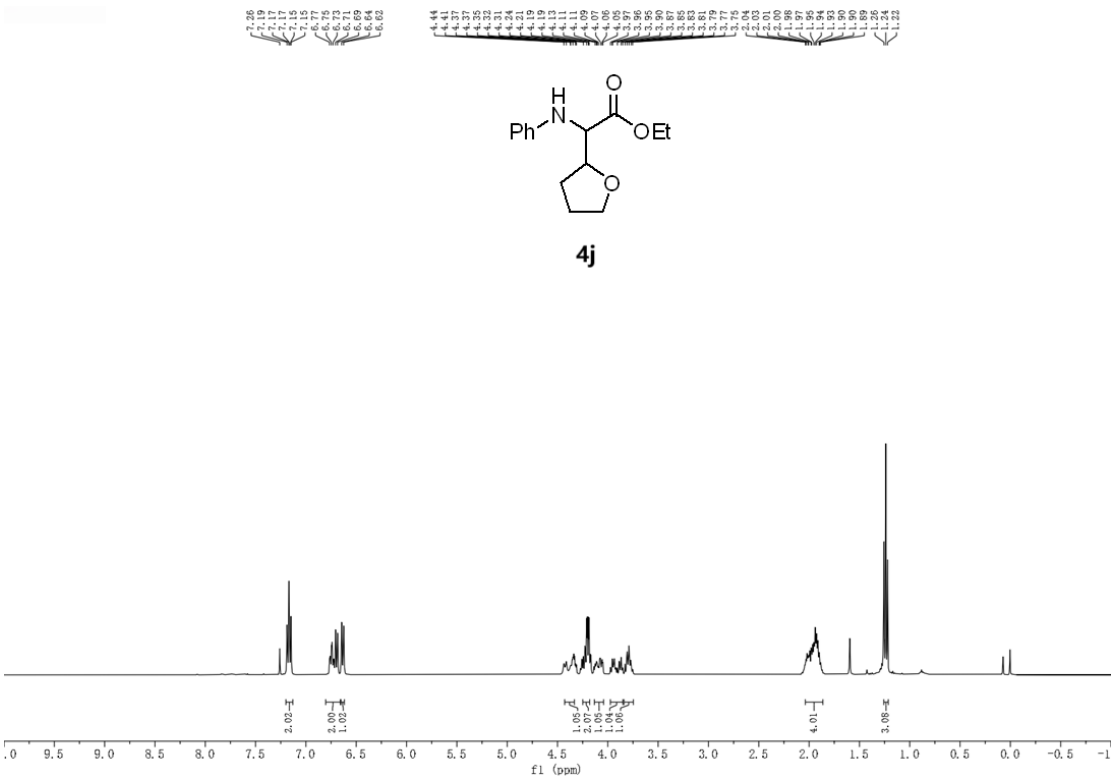


^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4i**

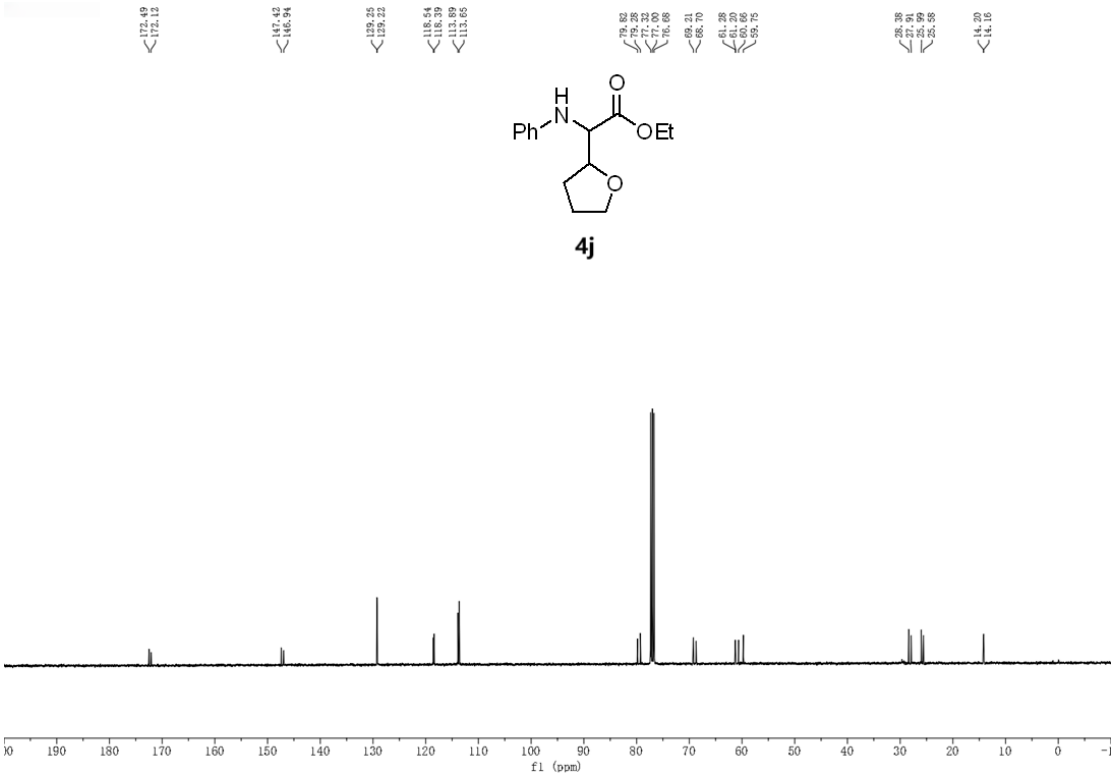


^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **4i**



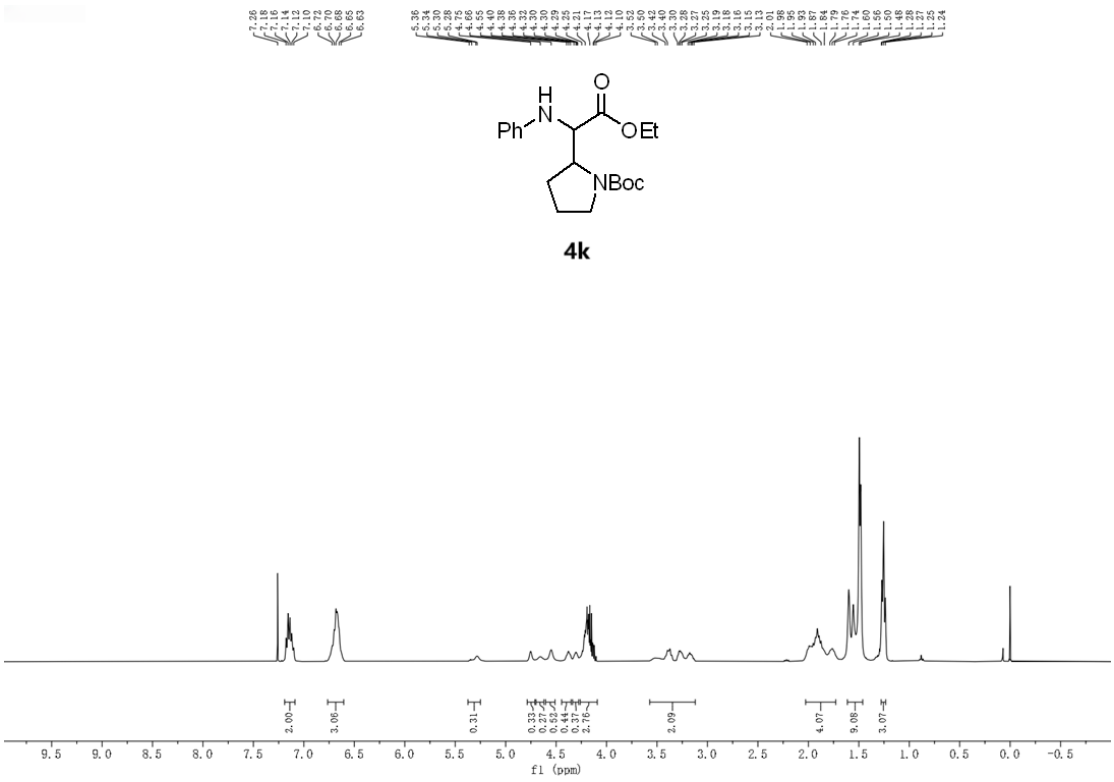
4j

^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4j**



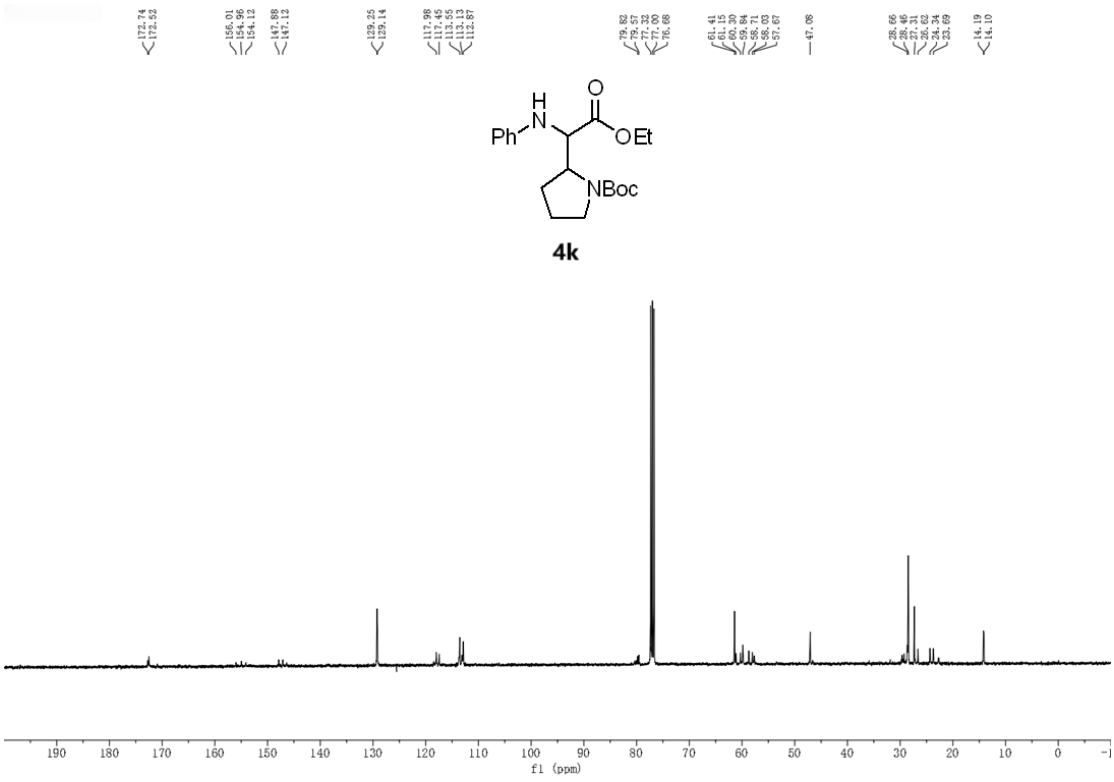
4j

^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **4j**



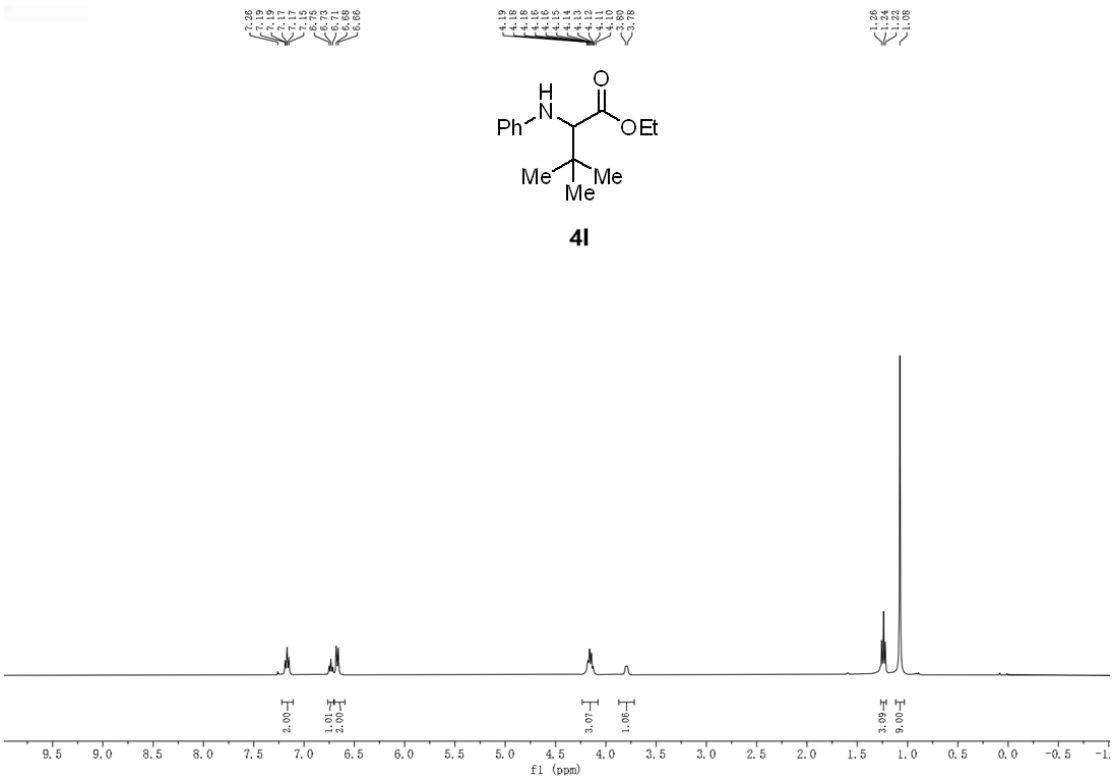
4k

^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4k**



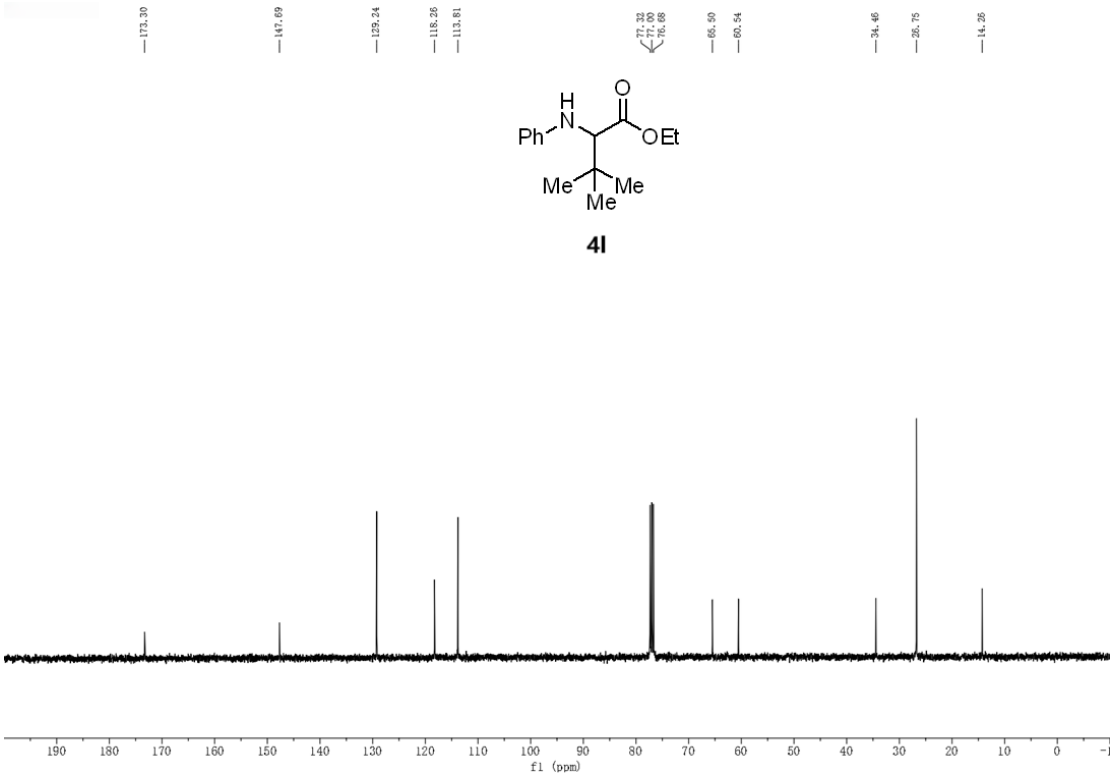
4k

^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **4k**



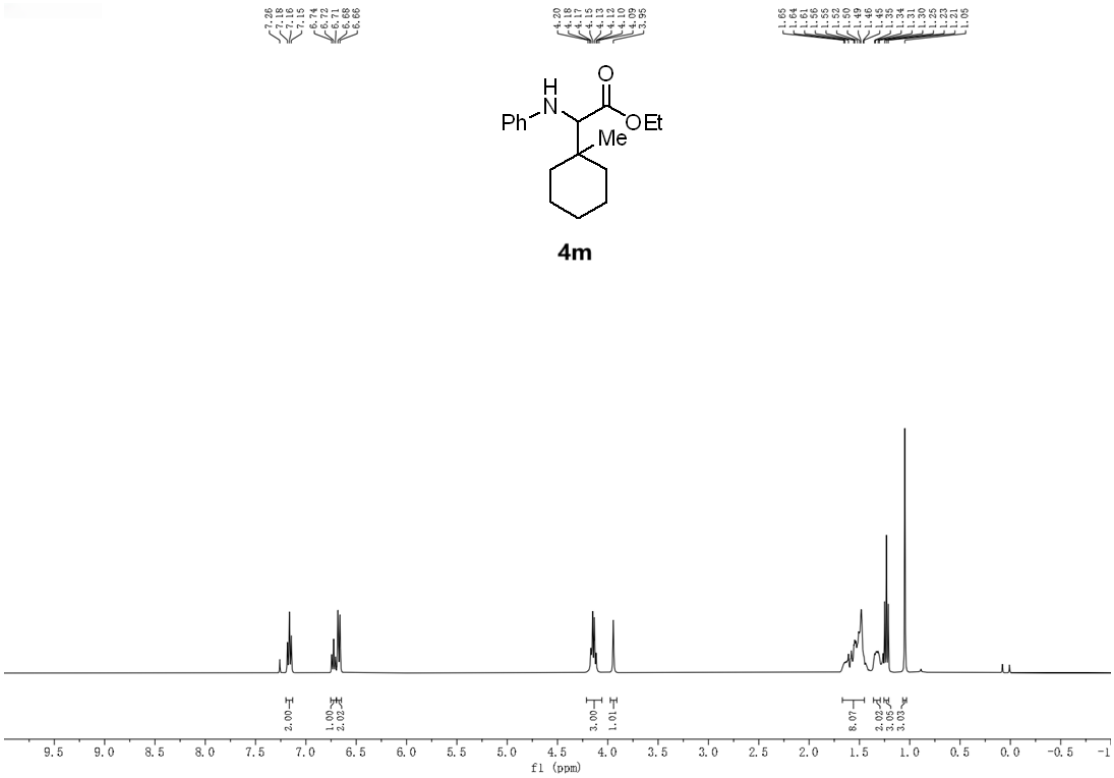
4l

^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4l**

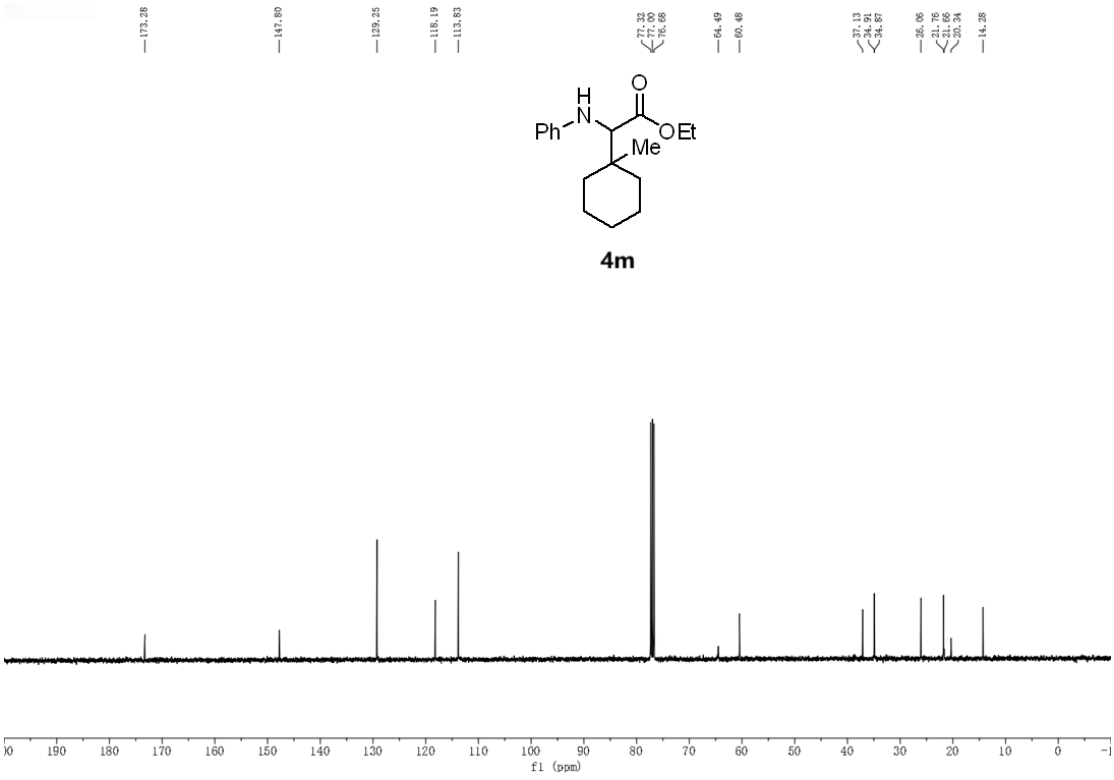


4l

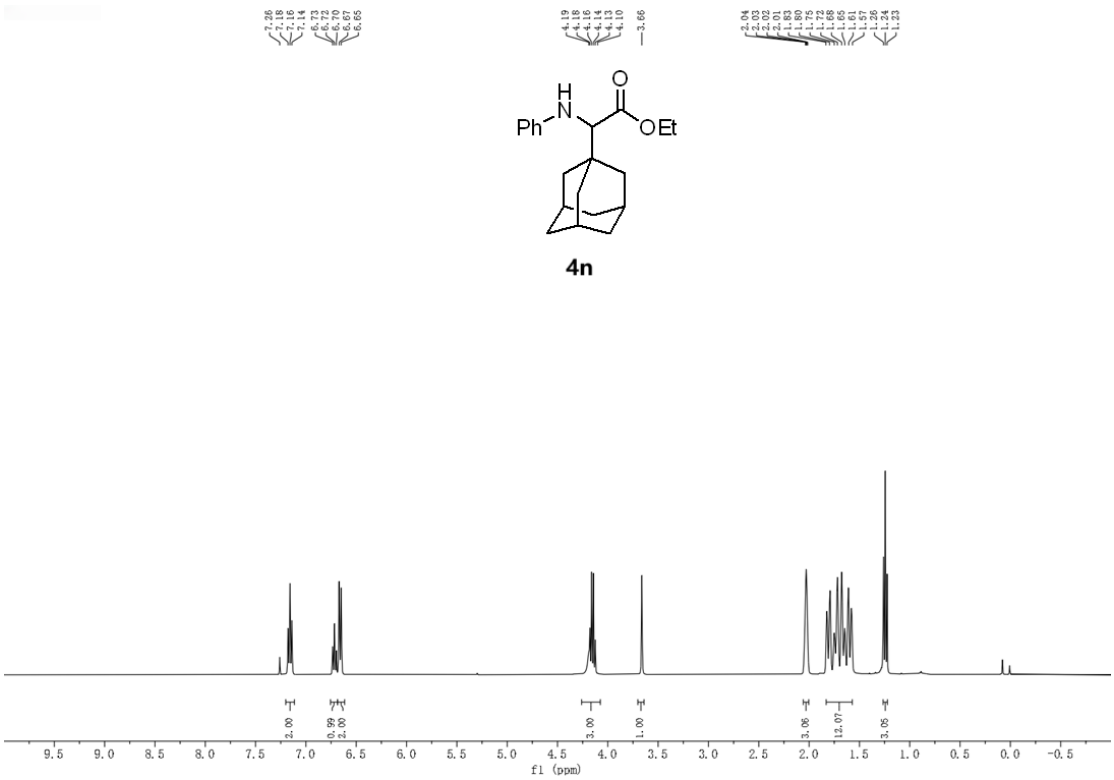
$^{13}C\{^{1}H\}$ NMR spectra (100 MHz, $CDCl_3$) of **4l**



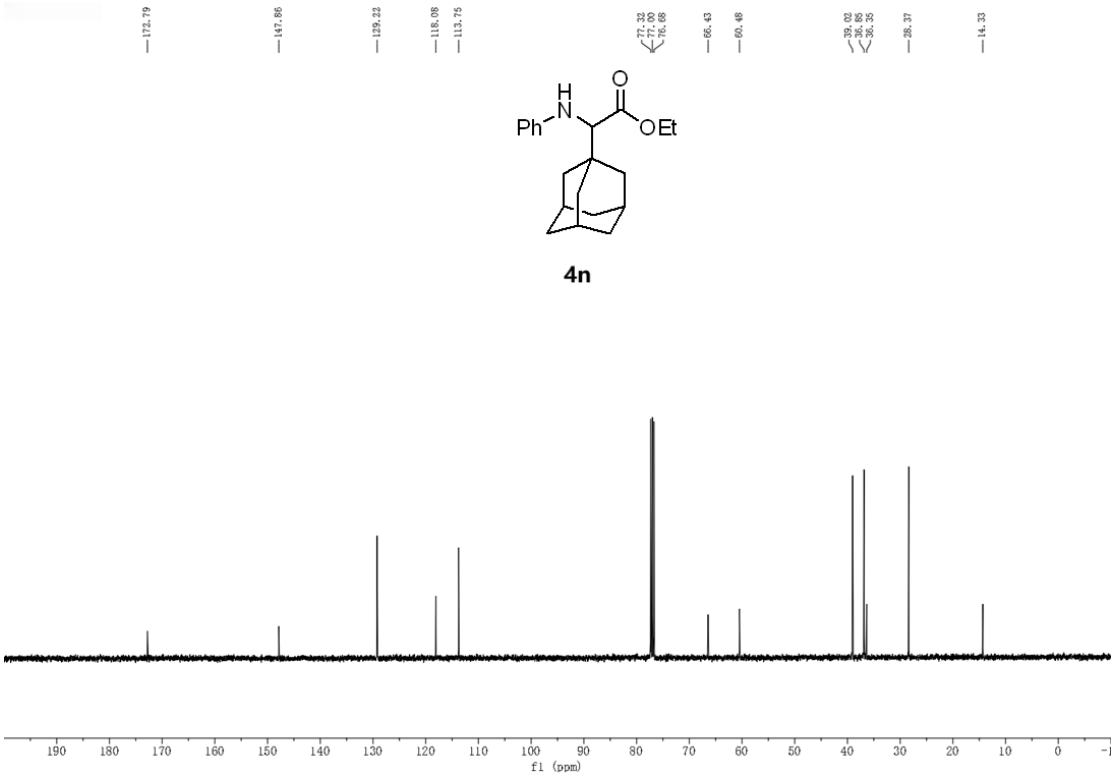
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4m**



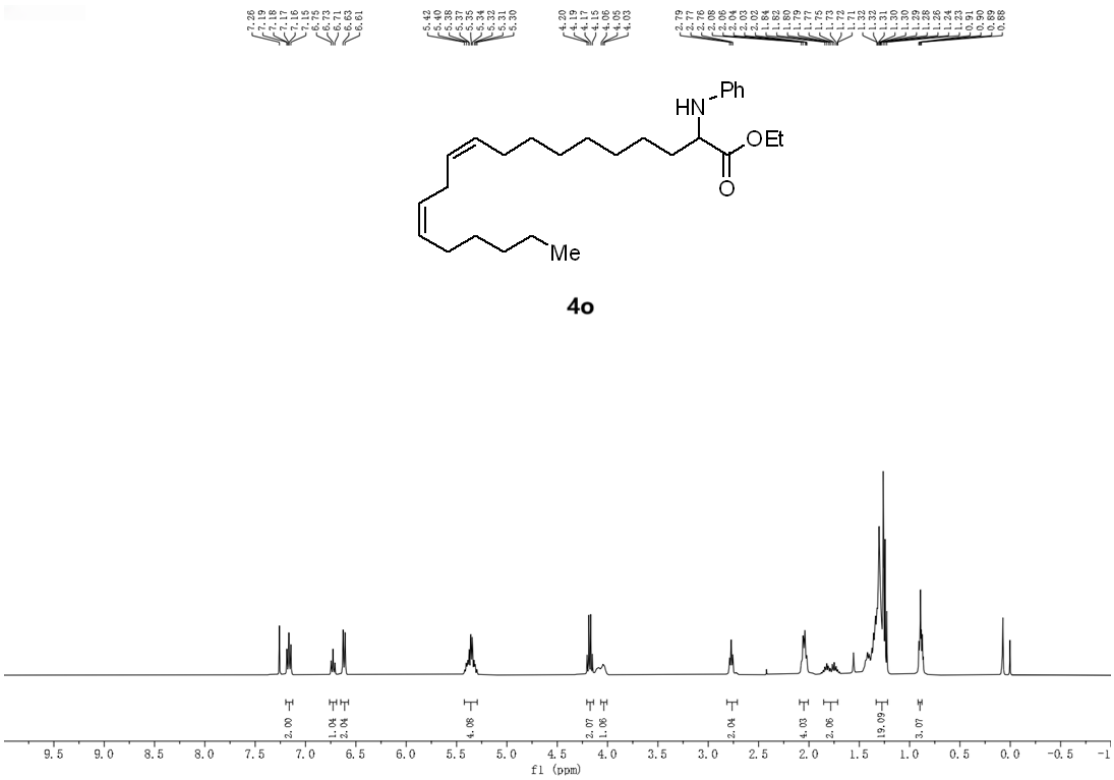
^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **4m**



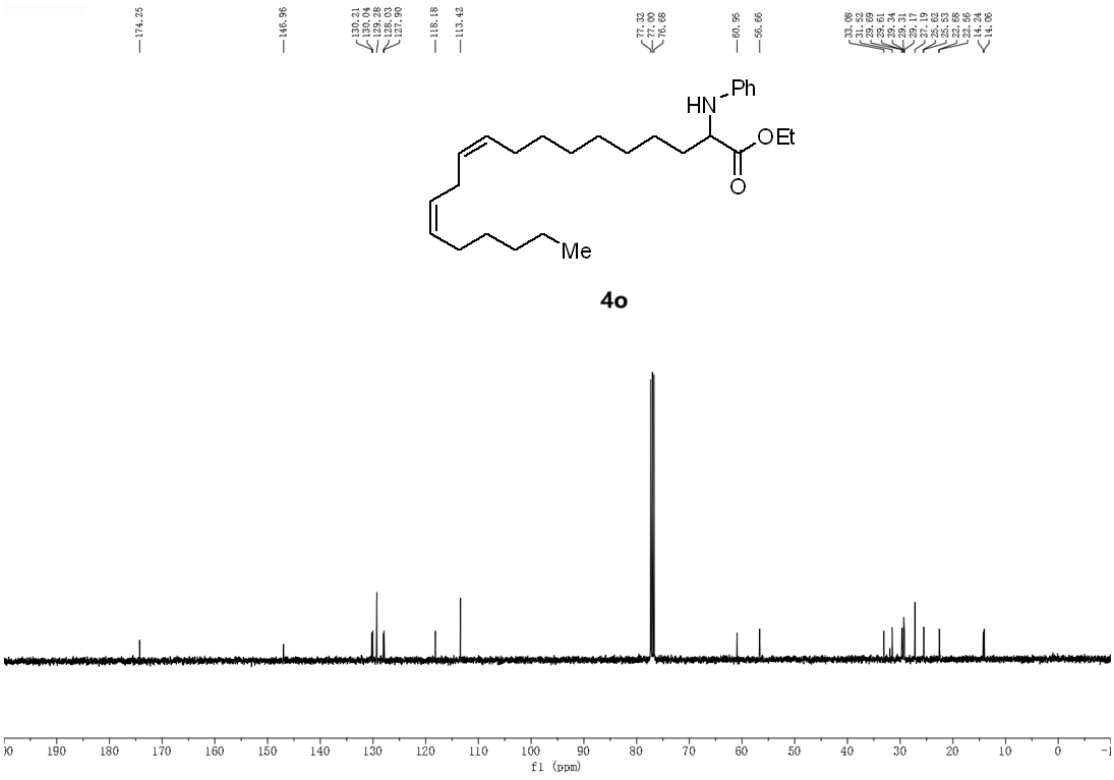
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4n**



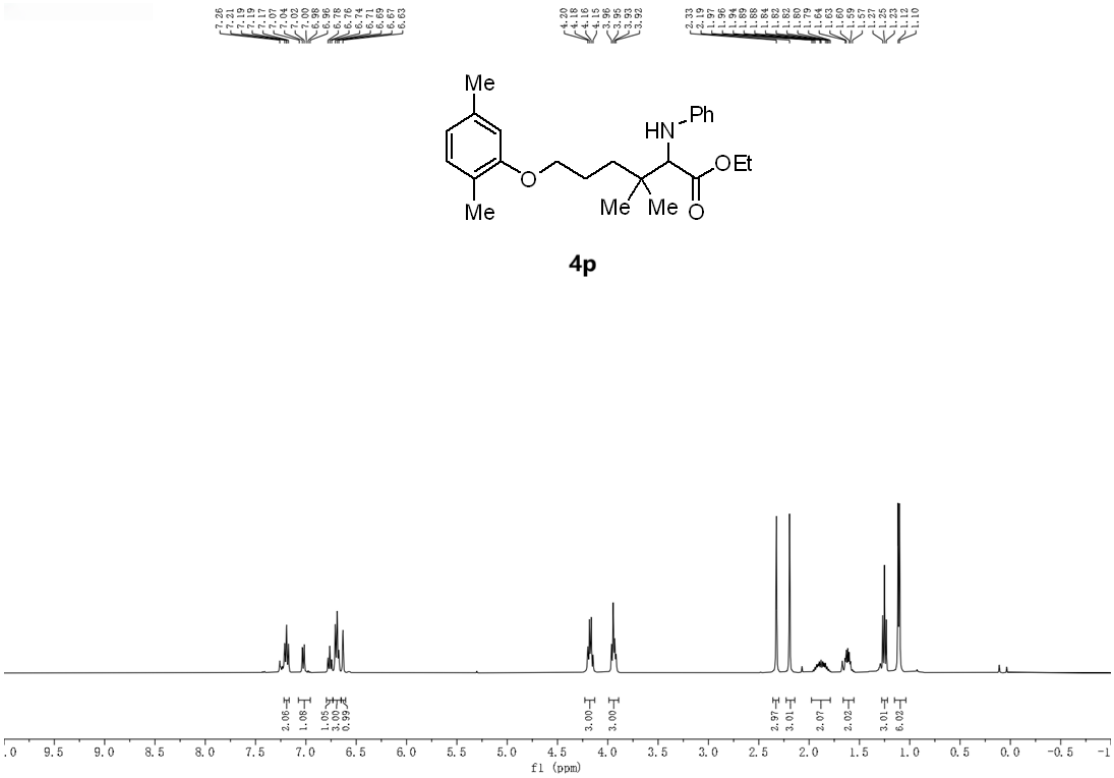
^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **4n**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4o**

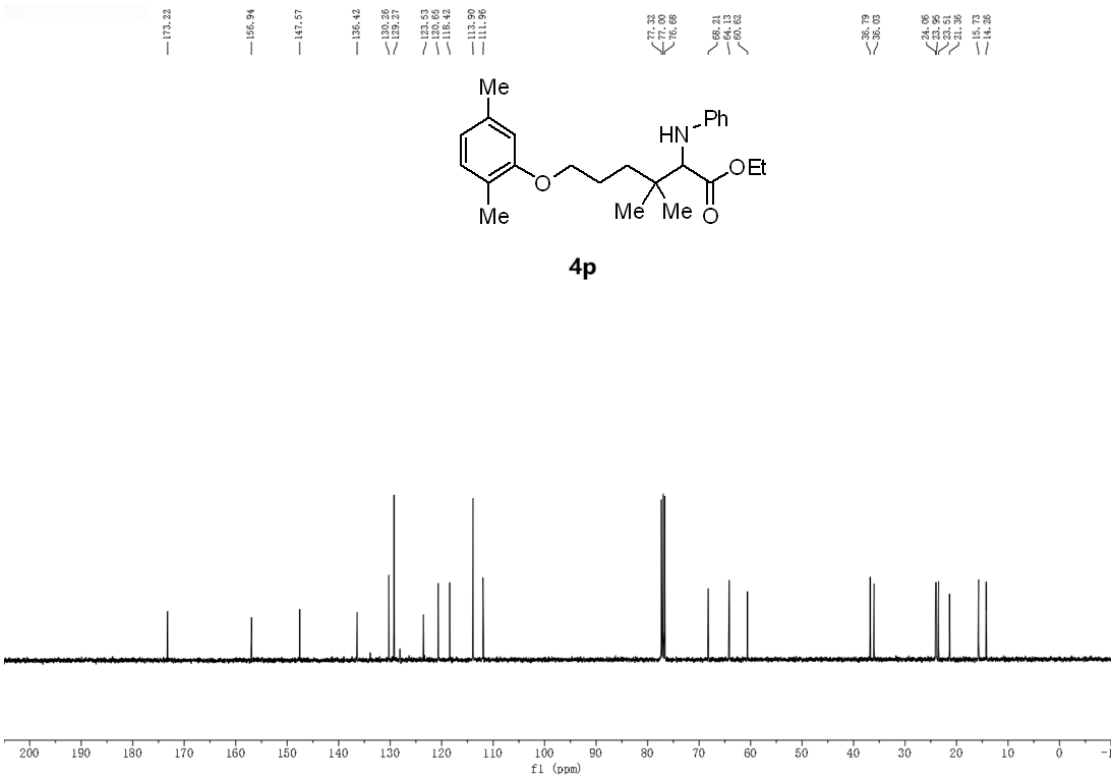


$^{13}C\{^{1}H\}$ NMR spectra (100 MHz, $CDCl_3$) of **4o**



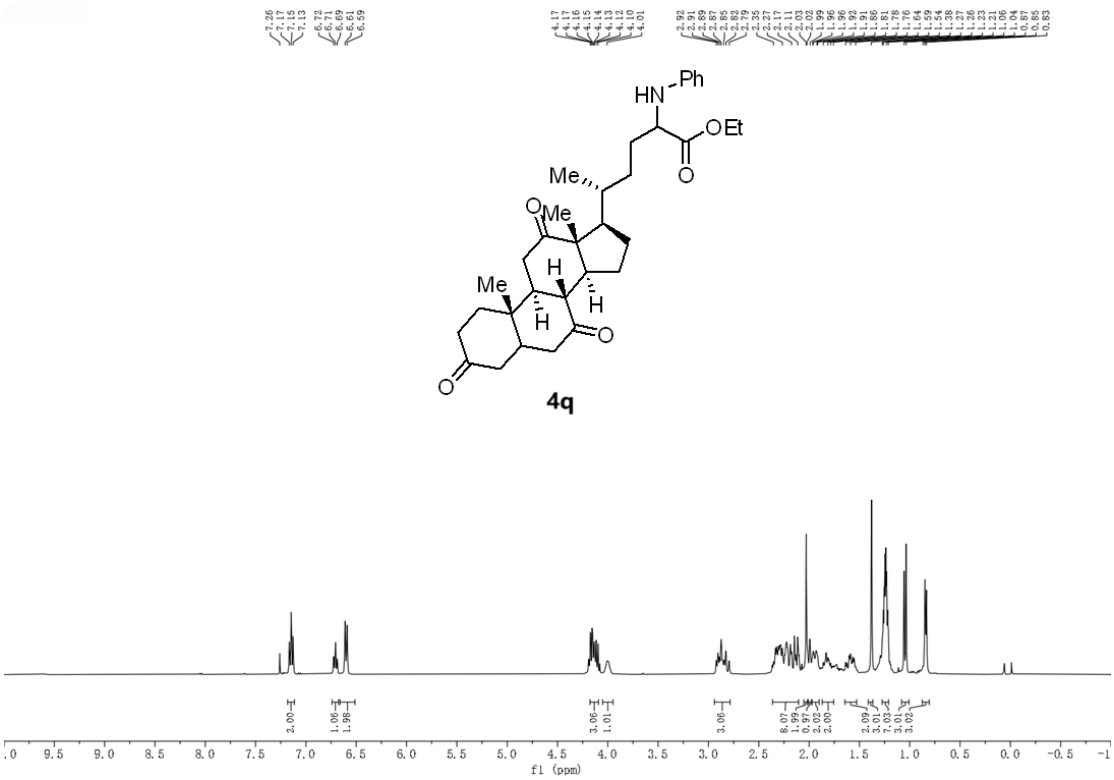
4p

^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4p**

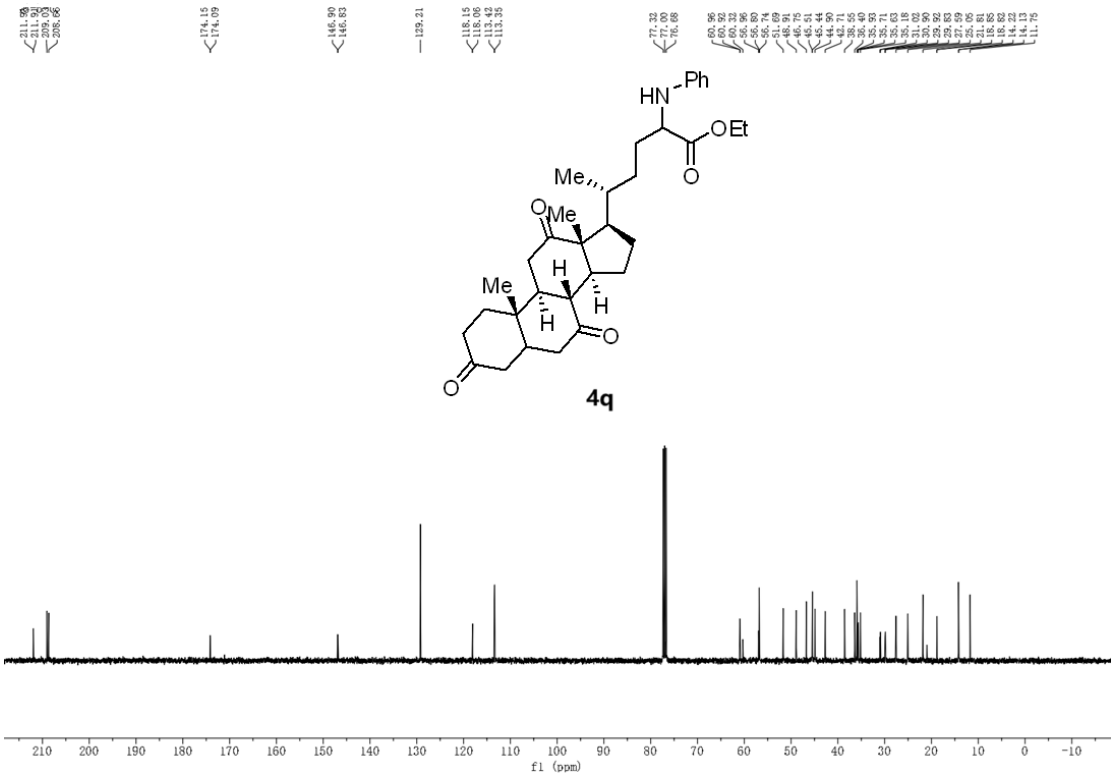


4p

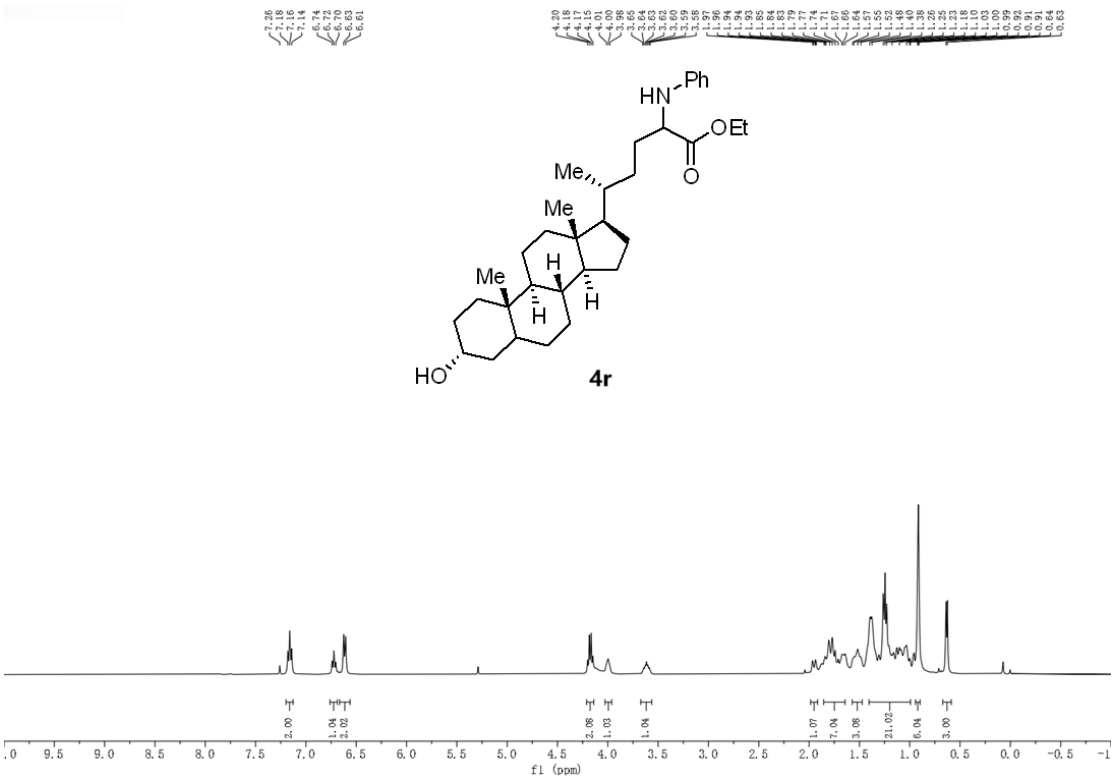
$^{13}C\{^{1}H\}$ NMR spectra (100 MHz, $CDCl_3$) of **4p**



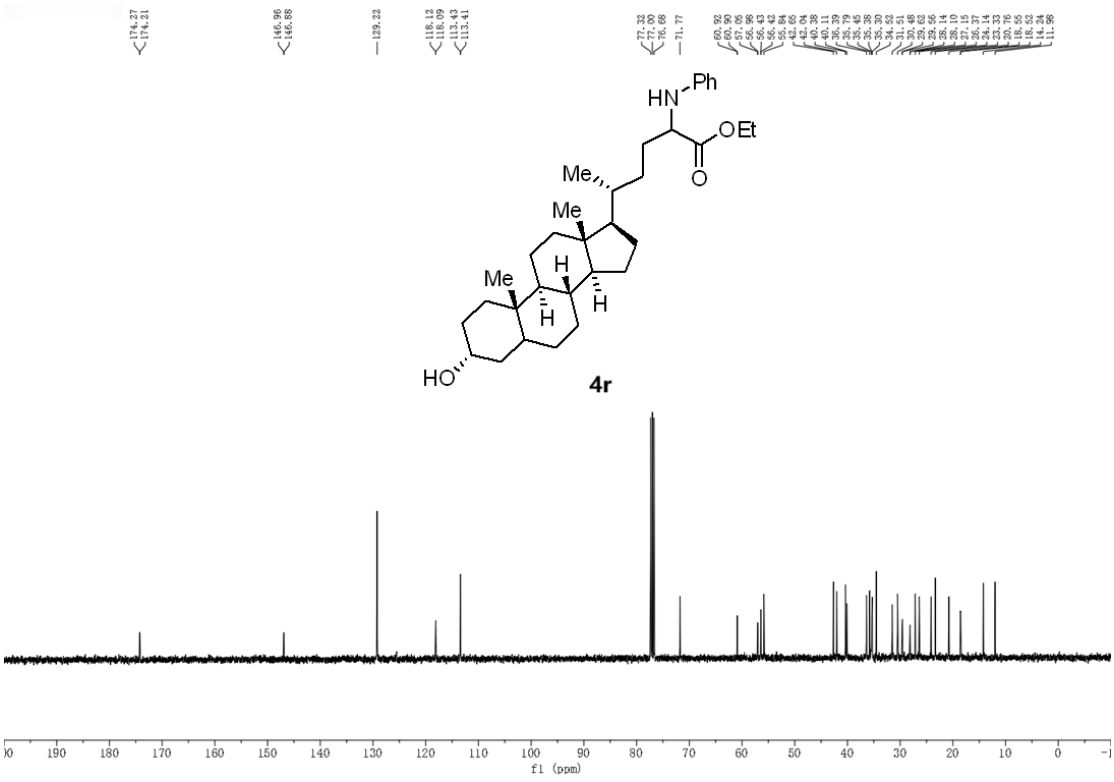
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4q**



^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **4q**



^{1}H NMR spectra (400 MHz, $CDCl_3$) of **4r**



^{13}C{^{1}H} NMR spectra (100 MHz, $CDCl_3$) of **4r**