Supporting Information

Highly Enantioselective Allylic Amination Reaction through Aerobic Oxidative Organo-Organo Dual Catalytic System

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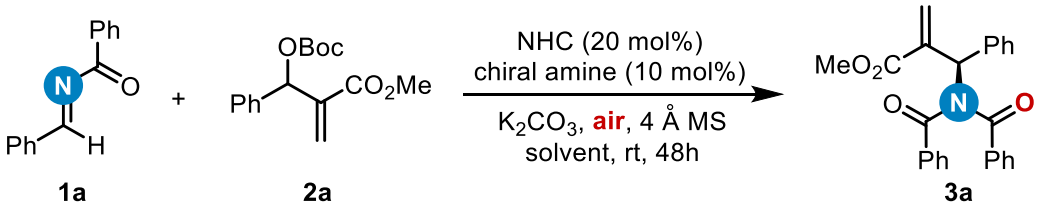
1. General information

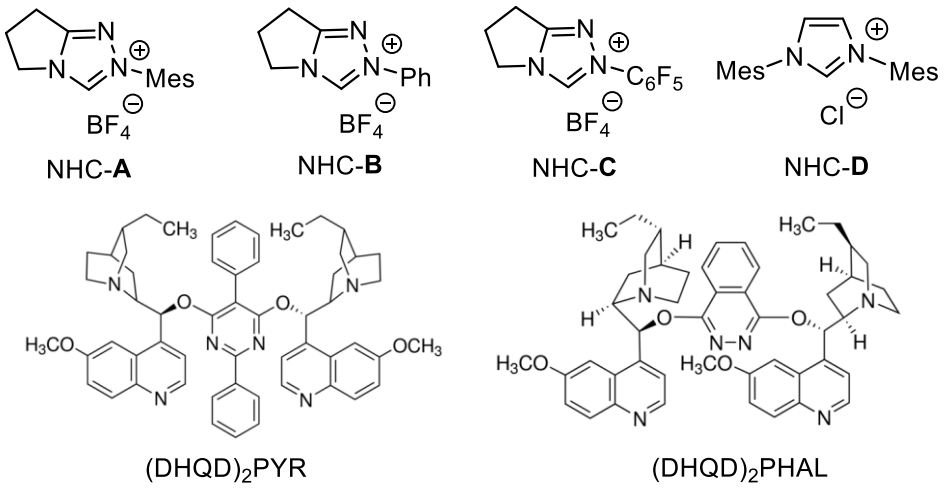
Commercially available materials purchased from Alfa Aesar or Sigma-Aldrich were used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker BBFO (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets); m (multiplet), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as m (multiplet) or br (broad). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker BBFO (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). The determination of ee was performed via chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Jasco P-1030 polarimeter and are reported as follows: $[\alpha]_D^{25}$ (*c* in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

2. Screening of reaction conditions[a]



Entry	NHC	Chiral amine	Solvent	Yield (%)[b]	ee (%)[c]
1	NHC-**A**	quinine	DCE	45	28
2	NHC-**A**	cinchonine	DCE	40	8
3	NHC-**A**	quinidine	DCE	37	3
4	NHC-**A**	cinchonidine	DCE	65	67
5	NHC-**A**	$(DHQD)_2PYR$	DCE	72	94
6	NHC-**A**	$(DHQD)_2PHAL$	DCE	63	30
7	NHC-**B**	$(DHQD)_2PYR$	DCE	56	94
8	NHC-**C**	$(DHQD)_2PYR$	DCE	48	94
9	NHC-**D**	$(DHQD)_2PYR$	DCE	62	94
10	NHC-**A**	$(DHQD)_2PYR$	CH_2Cl_2	68	93
11	NHC-**A**	$(DHQD)_2PYR$	CHCl3	70	78
12	NHC-**A**	$(DHQD)_2PYR$	Toluene	67	88
13	NHC-**A**	$(DHQD)_2PYR$	THF	70	92
14[d]	NHC-**A**	$(DHQD)_2PYR$	DCE	51	93
15[e]	NHC-**A**	$(DHQD)_2PYR$	DCE	74	81
16[f]	NHC-**A**	$(DHQD)_2PYR$	DCE	**90**	**94**
17[g]	NHC-**A**	$(DHQD)_2PYR$	DCE	0	-

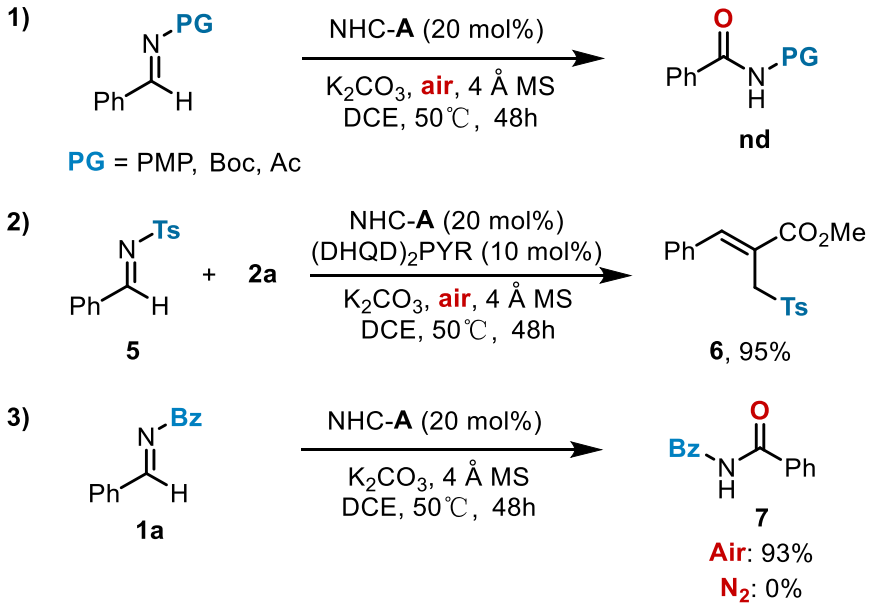
[a] General conditions (unless otherwise specified): **1a** (0.1 mmol), **2a** (0.15 mmol), NHC pre-cat. (20 mol%), chiral amine(10 mol%), 4 Å MS (50 mg), K_2CO_3 (1.0 equiv), solvent (1.0 mL), rt, open to air, 48 h. [b] Isolated yield. [c] Determined by chiral HPLC. [d] 0.5 eq. K_2CO_3. [e] 1.5 eq. K_2CO_3. [f] Run at 50 ℃. [g] Under N_2 atmosphere

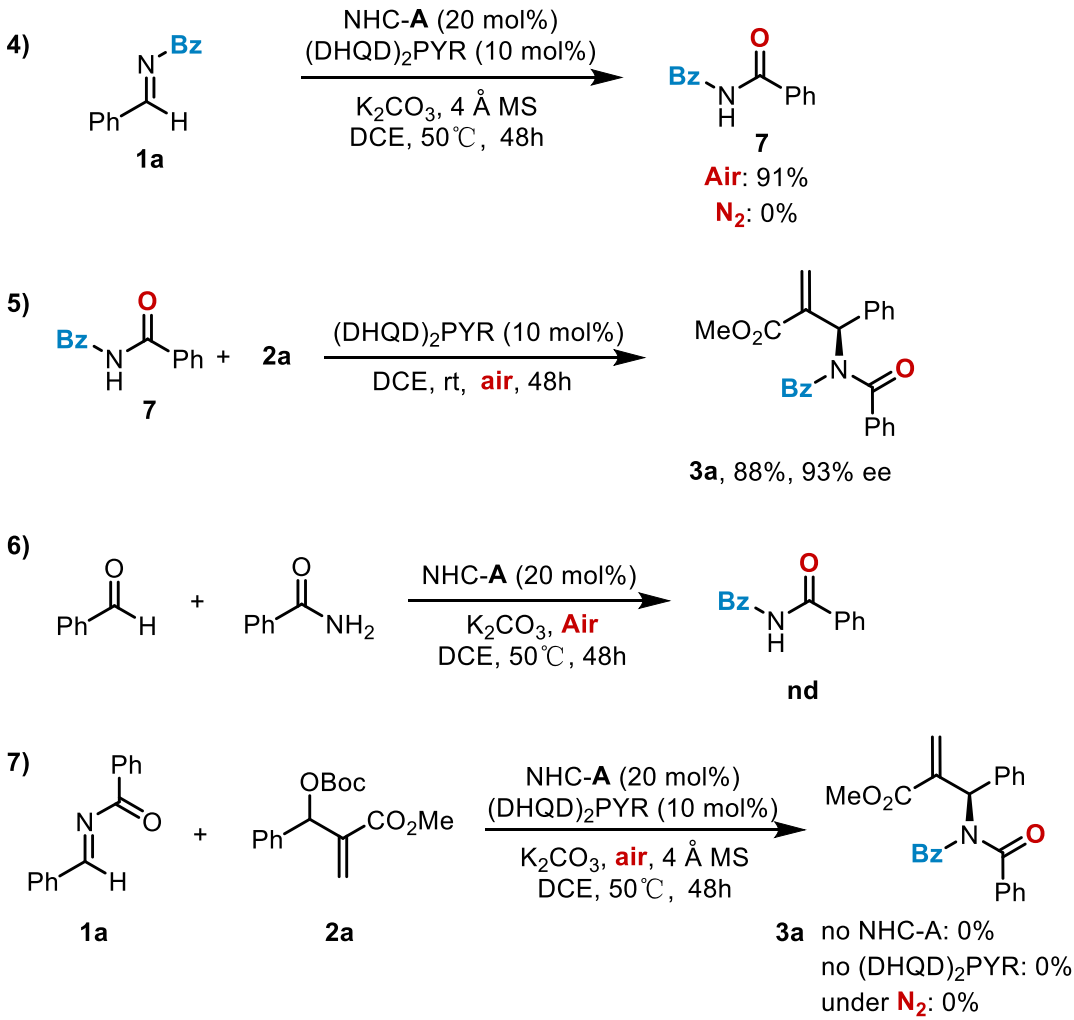


3. General procedure for the synthesis of 3 and 4

To a dry tube equipped with a magnetic stirring bar, was added **1** (0.1 mmol), **2** (0.15 mmol), NHC precatalyst salt **A** (0.02 mmol), 4 Å MS (50 mg), K_2CO_3 (1.0 equiv) and DCE (1 mL). The reaction was opened to air and stirred at 50 ℃ for 48 h till **1a** was completely consumed (monitored by TLC). After that, the crude residue were purified by flash chromatography to afford the desired products **3** or **4**, which were confirmed by ^{1}H NMR, ^{13}C NMR spectrum.

4. Control experiments[1]

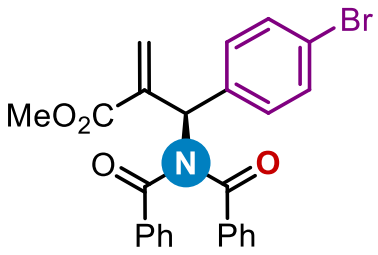
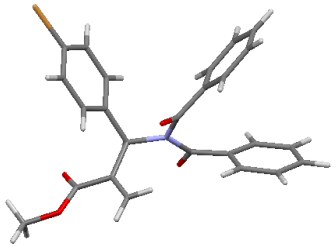




All reactions performed on a 0.1 mmol scale, general conditions: K_2CO_3 (1.0 equiv), DCE (0.1 M), 4 Å MS (50 mg).

5. Stereochemistry determination and X-ray structures

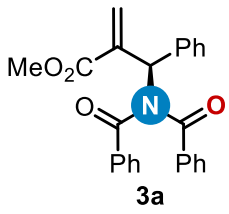
Absolute configurations of the products **3 and 4** were assigned based on the crystal X-ray structures of **4j** (CCDC number 2287548) which was obtained as colorless needles *via* evaporation of a hexane/CH_2Cl_2 solution. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

 **4j**	 CCDC 2287548

6. Compound characterization

Methyl (*R*)-2-((N-benzoylbenzamido)(phenyl)methyl)acrylate (3a)

Product **3a** was obtained 35.9 mg in 90 % yield as white solid. mp: 111- 112℃, $[\alpha]_D^{25}$ = + 74.1 (c = 1.0 in $CHCl_3$).



3a

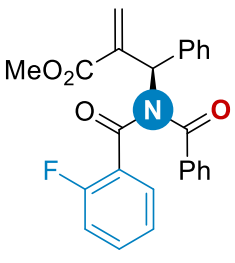
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.57 (m, 2H), 7.38-7.35 (m, 6H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.11-7.07 (m, 4H), 6.93 (t, *J* = 1.8 Hz, 1H), 6.54 (d, *J* = 0.9 Hz, 1H), 5.71 (d, *J* = 1.5 Hz, 1H), 3.73 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 166.5, 139.1, 137.7, 137.4, 131.7, 129.5, 129.1, 128.8, 128.6, 128.1, 128.0, 61.6, 52.1.

HRMS (ESI, m/z): calcd. For $C_{25}H_{22}NO_4$ $[M+H]^+$: 400.1543, found: 400.1542; **HPLC analysis**: 94% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 24.2 min (minor), 41.6 min (major)].

Methyl (*R*)-2-((N-benzoyl-2-fluorobenzamido)(phenyl)methyl)acrylate (3b)

Product **3b** was obtained 37.1 mg in 89 % yield as colorless oil. $[\alpha]_D^{25}$ = + 40.3 (*c* = 1.0 in $CHCl_3$)



3b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61-7.53 (m, 2H), 7.44-7.19 (m, 7H), 7.17-7.07 (m, 3H), 6.97-6.86 (m, 2H), 6.71-6.64 (m, 1H), 6.56 (t, *J* = 0.9 Hz, 1H), 5.78 (d, *J* = 1.4 Hz, 1H), 3.73 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 168.2, 166.5, 160.0, 157.5, 138.8, 137.3, 136.7, 133.1, 133.0, 132.0, 129.9, 129.9, 129.6, 129.1, 128.7, 128.5, 128.1, 128.0, 125.8, 125.6, 123.9, 123.9, 115.9, 115.7, 61.2, 52.1.

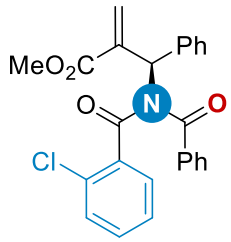
^{19}F NMR (376 MHz, $CDCl_3$): δ – 111.5.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}FNO_4$ $[M+H]^+$: 418.1449, found: 418.1451;

HPLC analysis: 92% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 26.0 min (minor), 35.4 min (major)].

Methyl (*R*)-2-((N-benzoyl-2-chlorobenzamido)(phenyl)methyl)acrylate (3c)

Product **3c** was obtained 37.2 mg in 86 % yield as colorless oil. $[\alpha]_D^{25}$ = + 62.4 (*c* = 1.0 in $CHCl_3$)



3c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.39-7.35 (m, 4H), 7.32-7.28 (m, 1H), 7.25-7.19 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 2H), 7.05-7.02 (m, 2H), 6.99-6.95 (m, 1H), 6.90 (t, *J* = 1.9 Hz, 1H), 6.55 (d, *J* = 1.1 Hz, 1H), 5.74 (s, 1H), 3.74 (s, 3H).

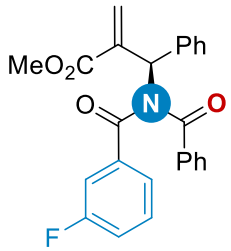
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 169.1, 166.5, 138.7, 137.3, 137.1, 136.1, 132.5, 131.8, 131.4, 130.4, 129.5, 129.3, 129.1, 128.6, 128.4, 128.2, 128.1, 126.2, 61.2, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}ClNO_4$ $[M+H]^+$: 434.1154, found: 434.1155;

HPLC analysis: 92% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 17.1 min (minor), 20.5 min (major)].

Methyl (*R*)-2-((N-benzoyl-3-fluorobenzamido)(phenyl)methyl)acrylate (3d)

Product **3d** was obtained 35.9 mg in 86 % yield as colorless oil. $[\alpha]_D^{25}$ = + 126.7 (*c* = 1.0 in $CHCl_3$)



3d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.42-7.20 (m, 6H), 7.18-7.00 (m, 5H), 6.90-6.84 (m, 2H), 6.54 (d, *J* = 1.1 Hz, 1H), 5.68 (d, *J* = 1.6 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 172.1, 172.1, 166.4, 163.22, 160.7, 139.4, 139.4, 138.9, 137.5, 137.1, 132.0, 129.8, 129.7, 129.6, 129.0, 128.9, 128.7, 128.3, 128.1, 124.4, 124.4, 118.7, 118.5, 115.9, 115.6, 61.7, 52.2.

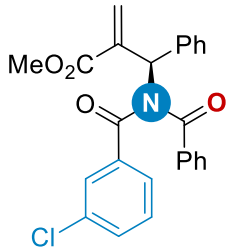
^{19}F NMR (376 MHz, $CDCl_3$): δ – 112.0.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}FNO_4$ $[M+H]^+$: 418.1449, found: 418.1451;

HPLC analysis: 91% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 15.1 min (minor), 20.7 min (major)].

Methyl (*R*)-2-((N-benzoyl-3-chlorobenzamido)(phenyl)methyl)acrylate (3e)

Product **3e** was obtained 38.1 mg in 88% yield as white solid. mp: 124-125℃. $[\alpha]_D^{25}$ = + 101.9 (*c* = 1.0 in $CHCl_3$)



3e

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.29 (m, 6H), 7.25-7.20 (m, 2H), 7.14-7.10 (m, 3H), 7.01 (t, *J* = 7.9 Hz, 1H), 6.89 (s, 1H), 6.54 (d, *J* = 1.2 Hz, 1H), 5.67 (d, *J* = 1.7 Hz, 1H), 3.72 (s, 3H).

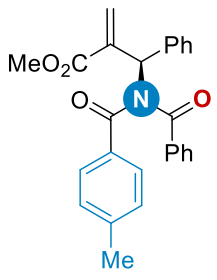
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 172.0, 166.4, 138.9, 138.9, 137.5, 137.1, 134.1, 132.0, 131.5, 129.6, 129.4, 129.0, 128.8, 128.8, 128.7, 128.3, 128.2, 126.7, 61.7, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}ClNO_4$ $[M+H]^+$: 434.1154, found: 434.1155;

HPLC analysis: 91% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 14.0 min (minor), 29.6 min (major)].

Methyl (*R*)-2-((N-benzoyl-4-methylbenzamido)(phenyl)methyl)acrylate (3f)

Product **3f** was obtained 35.1 mg in 85 % yield as colorless oil. $[\alpha]_D^{25}$ = + 72.1 (*c* = 1.0 in $CHCl_3$)



3f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 2H), 7.39-7.23 (m, 7H), 7.18-7.14 (m, 1H), 7.09-7.04 (m, 2H), 6.94-6.86 (m, 3H),

6.53-6.51 (m, 1H), 5.71 (d, *J* = 1.4 Hz, 1H), 3.69 (s, 3H), 2.15 (s, 3H).

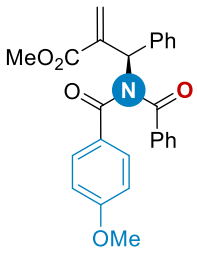
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 173.4, 166.5, 142.5, 139.3, 137.8, 137.4, 134.6, 131.6, 129.4, 129.1, 129.0, 128.8, 128.8, 128.6, 128.1, 128.0, 61.5, 52.1, 21.4.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1702;

HPLC analysis: 93% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 23.8 min (minor), 37.4 min (major)].

Methyl (*R*)-2-((N-benzoyl-4-methoxybenzamido)(phenyl)methyl)acrylate (3g)

Product **3g** was obtained 37.8 mg in 88 % yield as colorless oil. $[\alpha]_D^{25}$ = + 43.8 (*c* = 1.0 in $CHCl_3$)



3g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.55 (m, 2H), 7.41-7.33 (m, 6H), 7.29-7.25 (m, 1H), 7.22-7.17 (m, 1H), 7.13-7.09 (m, 2H), 6.92-6.91 (m, 1H), 6.60-6.57 (m, 2H), 6.53 (d, *J* = 0.8 Hz, 1H), 5.70 (d, *J* = 1.4 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H).

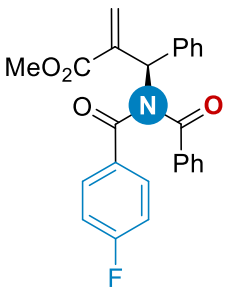
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 173.0, 166.5, 162.4, 139.3, 137.7, 137.4, 131.5, 131.3, 129.7, 129.3, 129.1, 128.6, 128.6, 128.1, 127.9, 113.4, 61.5, 55.3, 52.1.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_5$ $[M+H]^+$: 430.1649, found: 430.1652;

HPLC analysis: 99% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 31.6 min (minor), 54.0 min (major)].

Methyl (*R*)-2-((N-benzoyl-4-fluorobenzamido)(phenyl)methyl)acrylate (3h)

Product **3h** was obtained 37.5 mg in 90 % yield as colorless oil. $[\alpha]_D^{25}$ = + 98.6 (*c* = 1.0 in $CHCl_3$)



3h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.55 (m, 2H), 7.42-7.34 (m, 6H), 7.31-7.28 (m, 1H), 7.23-7.18 (m, 1H), 7.12-7.07 (m, 2H), 6.91-6.90 (m, 1H), 6.80-6.74 (m, 2H), 6.53 (d, *J* = 1.1 Hz, 1H), 5.68 (d, *J* = 1.6 Hz, 1H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 172.4, 166.4, 165.6, 163.1, 139.0, 137.6, 137.2, 133.7, 133.6, 131.8, 131.4, 131.3, 131.2, 129.5, 129.0, 128.7, 128.7, 128.2, 128.1, 115.6, 115.4, 115.2, 61.7, 52.1.

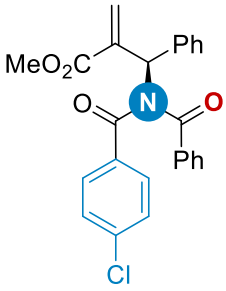
^{19}F NMR (376 MHz, $CDCl_3$): δ – 106.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}FNO_4$ $[M+H]^+$: 418.1449, found: 418.1451;

HPLC analysis: 95% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 24.0 min (minor), 34.8 min (major)].

Methyl (*R*)-2-((N-benzoyl-4-chlorobenzamido)(phenyl)methyl)acrylate (3i)

Product **3i** was obtained 39.5 mg in 91% yield as colorless oil. $[\alpha]_D^{25}$ = + 88.0 (*c* = 1.0 in $CHCl_3$)



3i

^{1}H NMR (400 MHz, CDCl3): δ 7.58-7.55 (m, 2H), 7.38-7.27 (m, 7H), 7.25-7.20 (m, 1H), 7.14-7.05 (m, 4H), 6.88 (s, 1H), 6.53 (d, *J* = 1.0 Hz, 1H), 5.67 (d, *J* = 1.6 Hz, 1H), 3.72 (s, 3H).

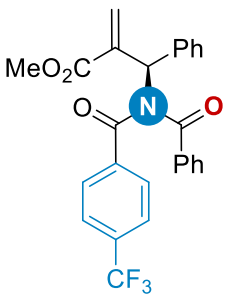
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 172.5, 166.4, 139.0, 137.9, 137.5, 137.2, 135.8, 132.0, 130.2, 129.6, 129.0, 128.8, 128.7, 128.4, 128.3, 128.1, 61.7, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}ClNO_4$ $[M+H]^+$: 434.1154, found: 434.1157;

HPLC analysis: 94% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 16.1 min (minor), 21.1 min (major)].

Methyl (*R*)-2-((N-benzoyl-4-(trifluoromethyl)benzamido)(phenyl)methyl)acrylate (3j)

Product **3j** was obtained 31.8 mg in 68 % yield as colorless oil. $[\alpha]_D^{25}$ = +103.6 (*c* = 1.0 in $CHCl_3$)



3j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.40-7.31 (m, 7H), 7.25-7.20 (m, 1H), 7.12-7.09 (m,

2H), 6.87 (t, *J* = 1.9 Hz, 1H), 6.55 (d, *J* = 1.4 Hz, 1H), 5.66 (d, *J* = 1.8 Hz, 1H), 3.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 172.3, 166.4, 140.6, 138.8, 137.4, 137.1, 132.9, 132.6, 132.1, 129.7, 129.0, 128.9, 128.9, 128.8, 128.3, 128.2, 125.2, 125.1, 125.0, 125.0, 124.6, 121.9, 61.8, 52.2.

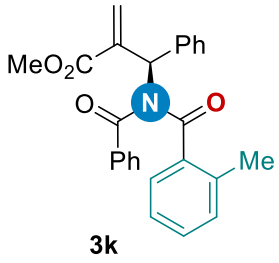
^{19}F NMR (376 MHz, $CDCl_3$): δ – 63.4.

HRMS (ESI, m/z): calcd. For $C_{26}H_{21}F_3NO_4$ $[M+H]^+$: 468.1417, found: 468.1420;

HPLC analysis: 93% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 13.4 min (minor), 16.2 min (major)].

Methyl (*R*)-2-((N-(2-methylbenzoyl)benzamido)(phenyl)methyl)acrylate (3k)

Product **3k** was obtained 33.9 mg in 82% yield as colorless oil. $[\alpha]_D^{25}$ = + 88.2 (*c* = 1.0 in $CHCl_3$)



3k

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.4 Hz, 2H), 7.39-7.35 (m, 2H), 7.31-7.27 (m, 3H), 7.20-7.15 (m, 2H), 7.11-7.07 (m, 2H), 7.03-6.94 (m, 2H), 6.89 (t, *J* = 1.8 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H), 6.53 (d, *J* = 1.0 Hz, 1H), 5.70 (s, 1H), 3.73 (s, 3H), 2.19 (s, 3H).

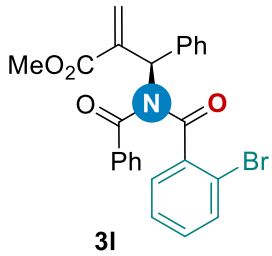
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 172.6, 166.5, 139.1, 138.2, 138.0, 137.7, 136.6, 131.4, 131.0, 130.8, 129.3, 128.7, 128.1, 128.0, 127.9, 127.9, 125.2, 61.2, 52.2, 19.8.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1700;

HPLC analysis: 89% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 19.7 min (minor), 23.3 min (major)].

Methyl (*R*)-2-((N-(2-bromobenzoyl)benzamido)(phenyl)methyl)acrylate (3l)

Product **3l** was obtained 40.5 mg in 85 % yield as colorless oil. $[\alpha]_D^{25}$ = + 66.8 (*c* = 1.0 in $CHCl_3$)



3l

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.4 Hz, 2H), 7.41-7.35 (m, 4H), 7.34-7.28 (m, 1H), 7.26-7.13 (m, 5H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 6.95 (td, *J* = 7.8, 1.7 Hz, 1H), 6.89 (s, 1H), 6.55 (d, *J* = 1.1 Hz, 1H), 5.74 (s, 1H), 3.74 (s, 3H).

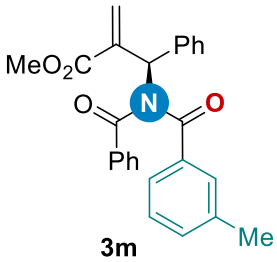
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 169.5, 166.5, 138.7, 137.7, 137.3, 137.2, 133.8, 131.8, 131.4, 129.3, 129.2, 128.7, 128.4, 128.2, 128.1, 126.7, 121.8, 61.3, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}BrNO_4$ $[M+H]^+$: 478.0648, found: 478.0649;

HPLC analysis: 92% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 28.8 min (minor), 32.8 min (major)].

Methyl (*R*)-2-((N-(3-methylbenzoyl)benzamido)(phenyl)methyl)acrylate (3m)

Product **3m** was obtained 31.4 mg in 76 % yield as colorless oil. $[\alpha]_D^{25}$ = + 71.5 (*c* = 1.0 in $CHCl_3$)



3m

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.54 (m, 2H), 7.37-7.33 (m, 4H), 7.29-7.25 (m, 1H), 7.19-7.14 (m, 3H), 7.09-7.05 (m, 2H), 6.97-6.93 (m, 3H), 6.53 (d, *J* = 0.9 Hz, 1H), 5.71 (d, *J* = 1.4 Hz, 1H), 3.71 (s, 3H), 2.14 (s, 3H).

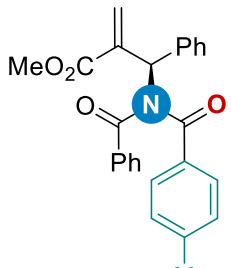
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 173.6, 166.5, 139.2, 137.8, 137.7, 137.4, 137.2, 132.4, 131.5, 129.5, 129.3, 129.1, 128.7, 128.6, 128.1, 128.0, 128.0, 126.0, 61.5, 52.1, 21.0.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1699;

HPLC analysis: 93% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 19.1 min (minor), 43.9 min (major)].

Methyl (*R*)-2-((N-(4-methylbenzoyl)benzamido)(phenyl)methyl)acrylate (3n)

Product **3n** was obtained 30.6 mg in 74 % yield as colorless oil. $[\alpha]_D^{25}$ = + 61.0 (*c* = 1.0 in $CHCl_3$)



3n

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.54 (m, 2H), 7.39-7.24 (m, 7H), 7.19-7.15 (m, 1H), 7.10-7.05 (m, 2H), 6.94-6.87 (m, 3H), 6.54-6.52 (m, 1H), 5.71 (d, *J* = 1.4 Hz, 1H), 3.70 (s, 3H), 2.16 (s, 3H).

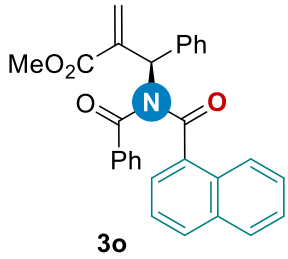
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 173.4, 166.5, 142.5, 139.2, 137.7, 137.4, 134.5, 131.6, 129.4, 129.1, 129.0, 128.9, 128.8, 128.6, 128.1, 128.0, 61.5, 52.1, 21.3.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1701;

HPLC analysis: 91% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 23.5 min (minor), 37.9 min (major)].

Methyl (*R*)-2-((N-benzoyl-1-naphthamido)(phenyl)methyl)acrylate (3o)

Product **3o** was obtained 41.8 mg in 93% yield as white solid. mp: 66 - 67℃. $[\alpha]_D^{25}$ = + 87.0 (*c* = 1.0 in $CHCl_3$)



3o

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.58 (dd, *J* = 14.6, 8.2 Hz, 2H), 7.49-7.28 (m, 6H), 7.23-7.13 (m, 3H), 7.04 (s, 1H), 6.81-6.67 (m, 3H), 6.57 (d, *J* = 0.9 Hz, 1H), 5.76 (s, 1H), 3.77 (s, 3H).

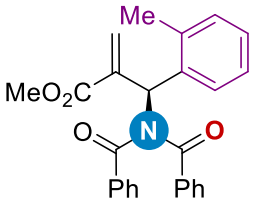
^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 172.0, 166.6, 139.2, 137.7, 137.1, 135.1, 133.1, 131.9, 130.5, 130.1, 129.4, 129.3, 128.7, 128.1, 127.9, 127.9, 127.6, 127.1, 127.0, 126.4, 125.4, 123.9, 61.1, 52.2.

HRMS (ESI, m/z): calcd. For $C_{29}H_{24}NO_4$ $[M+H]^+$: 450.1700, found: 450.1702;

HPLC analysis: 92% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 34.23 min (minor), 50.8 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(o-tolyl)methyl)acrylate (4a)

Product **4a** was obtained 33.1 mg in 80% yield as colorless oil. $[\alpha]_D^{25}$ = + 182.8 (*c* = 1.0 in $CHCl_3$)



4a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.4 Hz, 1H), 7.42-7.40 (m, 4H), 7.27-7.14 (m, 5H), 7.11-7.04 (m, 5H), 6.48 (d, *J* = 0.5 Hz, 1H), 5.52 (d, *J* = 1.2 Hz, 1H), 3.70 (s, 3H), 2.42 (s, 3H).

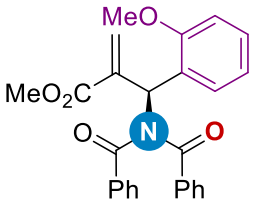
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 166.4, 138.2, 137.4, 136.4, 136.3, 131.6, 130.5, 129.6, 129.0, 128.9, 128.1, 128.0, 126.4, 58.6, 52.1, 19.2.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1703;

HPLC analysis: 87 % ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 13.2 min (minor), 23. 1 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(2-methoxyphenyl)methyl)acrylate (4b)

Product **4b** was obtained 39.1 mg in 91 % yield as white solid. mp: 65 - 66℃. $[\alpha]_D^{25}$ = + 6.1 (*c* = 1.0 in $CHCl_3$)



4b

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.44-7.42 (m, 4H), 7.28-7.17 (m, 4H), 7.12-7.08 (m, 4H), 6.98 (td, *J* = 7.5, 0.9 Hz, 1H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.54 (s, 1H), 5.84 (d, *J* = 1.0 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H).

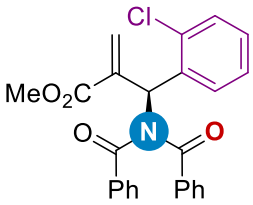
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 166.4, 156.7, 138.5, 137.4, 131.5, 130.5, 129.3, 128.9, 128.4, 128.0, 125.7, 120.6, 110.5, 56.3, 55.3, 52.1.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_5$ $[M+H]^+$: 430.1649, found: 430.1650;

HPLC analysis: 94% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 13.1 min (minor), 34.4 min (major)].

Methyl (*S*)-2-((N-benzoylbenzamido)(2-chlorophenyl)methyl)acrylate (4c)

Product **4c** was obtained 27.8 mg in 64 % yield as colorless oil. $[\alpha]_D^{25}$ = + 65.5 (*c* = 1.0 in $CHCl_3$)



4c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.50-7.15 (m, 10H), 7.12-7.08 (m, 4H), 6.60 (s, 1H), 5.79 (d, *J* = 1.3 Hz, 1H), 3.70 (s, 3H).

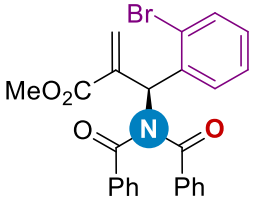
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 166.0, 137.4, 137.0, 135.3, 133.8, 131.8, 131.2, 129.7, 129.7, 129.4, 129.0, 128.1, 126.9, 58.5, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}ClNO_4$ $[M+H]^+$: 434.1154, found: 434.1154;

HPLC analysis: 82% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 12.6 min (minor), 23.3 min (major)].

Methyl (S)-2-((N-benzoylbenzamido)(2-bromophenyl)methyl)acrylate (4d)

Product **4d** was obtained 43.0 mg in 90% yield as white solid. mp: 126-127℃, $[\alpha]_D^{25}$ = + 122.4 (*c* = 1.0 in $CHCl_3$)



4d

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.48-7.45 (m, 4H), 7.37-7.33 (m, 2H), 7.21-7.08 (m, 7H), 6.59 (s, 1H), 5.71 (d, *J* = 1.4 Hz, 1H), 3.69 (s, 3H).

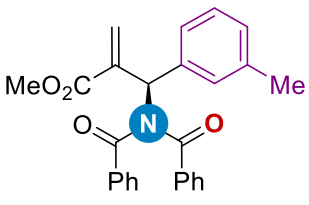
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 166.0, 137.4, 137.2, 137.0, 133.1, 131.8, 131.2, 130.0, 129.6, 129.0, 128.1, 127.6, 124.3, 61.2, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}BrNO_4$ $[M+H]^+$: 478.0648, found: 478.0647;

HPLC analysis: 91% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 15:85; retention times: 14.8 min (minor), 32.8 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(m-tolyl)methyl)acrylate (4e)

Product **4e** was obtained 33.9 mg in 82% yield as colorless oil. $[\alpha]_D^{25}$ = + 78.9 (*c* = 1.0 in $CHCl_3$)



4e

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.33 (m, 6H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.19-7.15(m, 2H), 7.10-7.08 (m, 5H), 6.89

(t, *J* = 1.7 Hz, 1H), 6.53 (s, 1H), 5.71 (s, 1H), 3.72 (s, 3H), 2.33 (s, 3H).

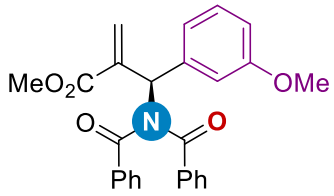
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 166.5, 139.2, 138.2, 137.6, 137.4, 131.6, 129.8, 129.4, 128.9, 128.8, 128.5, 128.1, 126.1, 61.6, 52.1, 21.5.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1704;

HPLC analysis: 77% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 14.1 min (minor), 25.9 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(3-methoxyphenyl)methyl)acrylate (4f)

Product **4f** was obtained 39.5 mg in 92% yield as colorless oil. $[\alpha]_D^{25}$ = + 81.8 (*c* = 1.0 in $CHCl_3$)



4f

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.36 (m, 4H), 7.29-7.25 (m, 1H), 7.19-7.13 (m, 8H), 6.91 (s, 1H), 6.85-6.79 (m, 1H), 6.54 (d, *J* = 0.8 Hz, 1H), 5.74 (d, *J* = 1.4 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H).

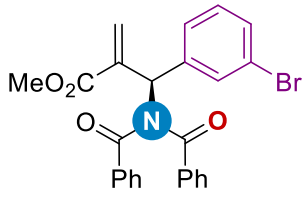
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 166.5, 159.7, 139.2, 139.0, 137.3, 131.7, 129.6, 129.6, 128.9, 128.1, 121.4, 114.6, 113.6, 61.5, 55.2, 52.1.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_5$ $[M+H]^+$: 430.1649, found: 430.1648;

HPLC analysis: 89% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 19.5 min (minor), 32.2 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(3-bromophenyl)methyl)acrylate (4g)

Product **4g** was obtained 35.8 mg in 75 % yield as colorless oil. $[\alpha]_D^{25}$ = + 66.2 (*c* = 1.0 in $CHCl_3$)



4g

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 1.7 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.44-7.42 (m, 1H), 7.38-7.35 (m, 4H), 7.24-7.17 (m, 3H), 7.12-7.08 (m, 4H), 6.93 (s, 1H), 6.58 (d, *J* = 1.2 Hz, 1H), 5.75 (d, *J* = 1.7 Hz, 1H), 3.72 (s, 3H).

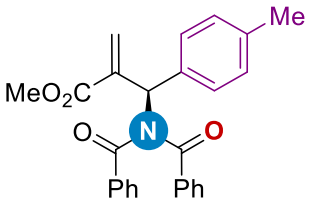
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 166.2, 140.0, 138.3, 137.1, 132.2, 131.8, 131.2, 130.2, 130.1, 128.8, 128.2, 127.7, 122.7, 60.7, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}BrNO_4$ $[M+H]^+$: 478.0648, found: 478.0649;

HPLC analysis: 80% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 15.6 min (minor), 21.6 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(p-tolyl)methyl)acrylate (4h)

Product **4h** was obtained 33.5 mg in 81% yield as white solid. mp: 175-176℃. $[\alpha]_D^{25}$ = + 63.9 (*c* = 1.0 in $CHCl_3$)



4h

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.37-7.34 (m, 4H), 7.20-7.15 (m, 4H), 7.10-7.06 (m, 4H), 6.89 (s, 1H), 6.53 (d, *J* = 0.7 Hz, 1H), 5.74 (d, *J* = 1.4 Hz, 1H), 3.72 (s, 3H), 2.31 (s, 3H).

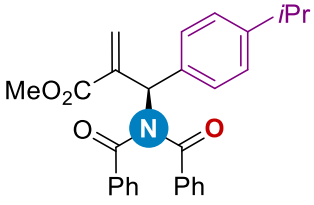
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 166.5, 139.3, 137.7, 137.4, 134.6, 131.6, 129.3, 129.1, 129.0, 128.8, 128.1, 61.4, 52.1, 21.1.

HRMS (ESI, m/z): calcd. For $C_{26}H_{24}NO_4$ $[M+H]^+$: 414.1700, found: 414.1702;

HPLC analysis: 99% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 27.8 min (minor), 30.5 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(4-isopropylphenyl)methyl)acrylate (4i)

Product **4i** was obtained 35.8 mg in 81% yield as colorless oil. $[\alpha]_D^{25}$ = + 75.2 (*c* = 1.0 in $CHCl_3$)



4i

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.38-7.35 (m, 4H), 7.22-7.14 (m, 5H), 7.09-7.05 (m, 4H), 6.90 (s, 1H), 6.52 (s, 1H), 5.70 (d, *J* = 1.3 Hz, 1H), 3.71 (s, 3H), 1.22 (s, 3H), 1.21 (s, 3H).

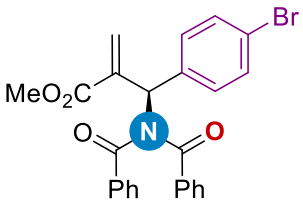
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 166.6, 148.5, 139.4, 137.5, 134.9, 131.6, 129.4, 129.0, 128.9, 128.1, 126.7, 61.4, 52.1, 33.7, 23.9, 23.8.

HRMS (ESI, m/z): calcd. For $C_{28}H_{28}NO_4$ $[M+H]^+$: 442.2013, found: 442.2015;

HPLC analysis: 97% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 21.5 min (minor), 28.9 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(4-bromophenyl)methyl)acrylate (4j)

Product **4j** was obtained 33.9 mg in 71% yield as white solid. mp: 170-171℃ $[\alpha]_D^{25}$ = + 40.2 (*c* = 1.0 in $CHCl_3$)



4j

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, 4H), 7.37-7.34 (m, 4H), 7.21-7.16 (m, 2H), 7.11-7.07 (m, 4H), 6.92 (t, *J* = 1.6 Hz, 1H), 6.56 (d, *J* = 1.3 Hz, 1H), 5.75 (d, *J* = 1.7 Hz, 1H), 3.71 (s, 3H).

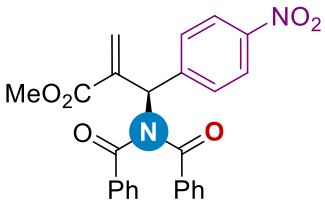
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 166.2, 138.6, 137.1, 136.7, 131.8, 131.8, 130.9, 129.6, 128.8, 128.2, 122.2, 60.8, 52.2.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}BrNO_4$ $[M+H]^+$: 478.0648, found: 478.0644;

HPLC analysis: 93% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 28.7 min (minor), 34.3 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(4-nitrophenyl)methyl)acrylate (4k)

Product **4k** was obtained 33.8 mg in 76 % yield as colorless oil. $[\alpha]_D^{25}$ = + 22.0 (*c* = 1.0 in $CHCl_3$)



4k

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26-8.21 (m, 2H), 7.81-7.77 (m, 2H), 7.39-7.36 (m, 4H), 7.24-7.19 (m, 2H), 7.13-7.10 (m, 5H), 6.65 (d, *J* = 1.2 Hz, 1H), 5.81 (d, *J* = 1.7 Hz, 1H), 3.73 (s, 3H).

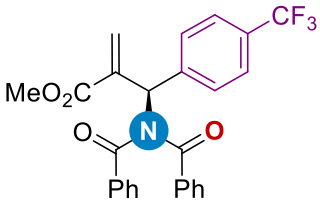
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 165.9, 147.6, 145.0, 137.7, 136.7, 132.1, 130.4, 130.0, 128.8, 128.3, 123.8, 60.4, 52.4.

HRMS (ESI, m/z): calcd. For $C_{25}H_{21}N_2O_6$ $[M+H]^+$: 445.1394, found: 445.1394;

HPLC analysis: 99% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 5:95; retention times: 73.9 min (minor), 78.4 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(4-(trifluoromethyl)phenyl)methyl)acrylate (4l)

Product **4l** was obtained 36.0 mg in 77 % yield as colorless oil. $[\alpha]_D^{25}$ = + 55.2 (*c* = 1.0 in $CHCl_3$)



4l

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.39-7.36 (m, 4H), 7.22-7.18 (m, 2H), 7.12-7.05 (m, 5H), 6.60 (d, *J* = 1.2 Hz, 1H), 5.74 (d, *J* = 1.7 Hz, 1H), 3.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 166.2, 141.8, 138.3, 137.0, 131.9, 130.3, 130.1, 129.5, 128.8, 128.2, 125.6, 125.6, 60.8, 52.3.

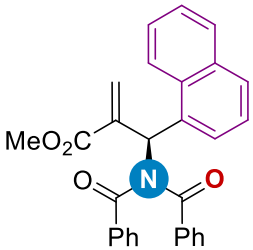
^{19}F NMR (376 MHz, $CDCl_3$): δ – 62.6.

HRMS (ESI, m/z): calcd. For $C_{26}H_{21}F_3NO_4$ $[M+H]^+$: 468.1417, found: 468.1420;

HPLC analysis: 94% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 10:90; retention times: 16.5 min (minor), 22.7 min (major)].

Methyl (*R*)-2-((N-benzoylbenzamido)(naphthalen-1-yl)methyl)acrylate e (4m)

Product **4m** was obtained 31.9 mg in 71% yield as colorless oil. $[\alpha]_D^{25}$ = + 61.8 (*c* = 1.0 in $CHCl_3$)



4m

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.6 Hz, 1H), 7.97 (s, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.63-7.58 (m, 1H), 7.49-7.44 (m, 2H), 7.39-7.36 (m, 4H), 7.15-7.10 (m, 2H), 7.05-7.01 (m, 4H), 6.65 (s, 1H), 6.00 (s, 1H), 3.68 (s, 3H).

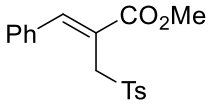
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.4, 166.4, 138.5, 137.2, 133.8, 132.7, 131.7, 131.2, 130.2, 129.0, 128.9, 128.1, 128.1, 126.7, 125.7, 125.1, 123.2, 57.7, 52.2.

HRMS (ESI, m/z): calcd. For $C_{29}H_{24}NO_4$ $[M+H]^+$: 450.1700, found: 450.1702;

HPLC analysis: 76% ee, [CHIRALPAK ODH column; 0.5 mL/min; solvent system: *i*-PrOH/hexane = 20:80; retention times: 13.3 min (minor), 37.2 min (major)].

Methyl (*Z*)-3-phenyl-2-(tosylmethyl)acrylate (6)

Product **6** was obtained in 95 % yield as white solid. mp: 124-125℃.

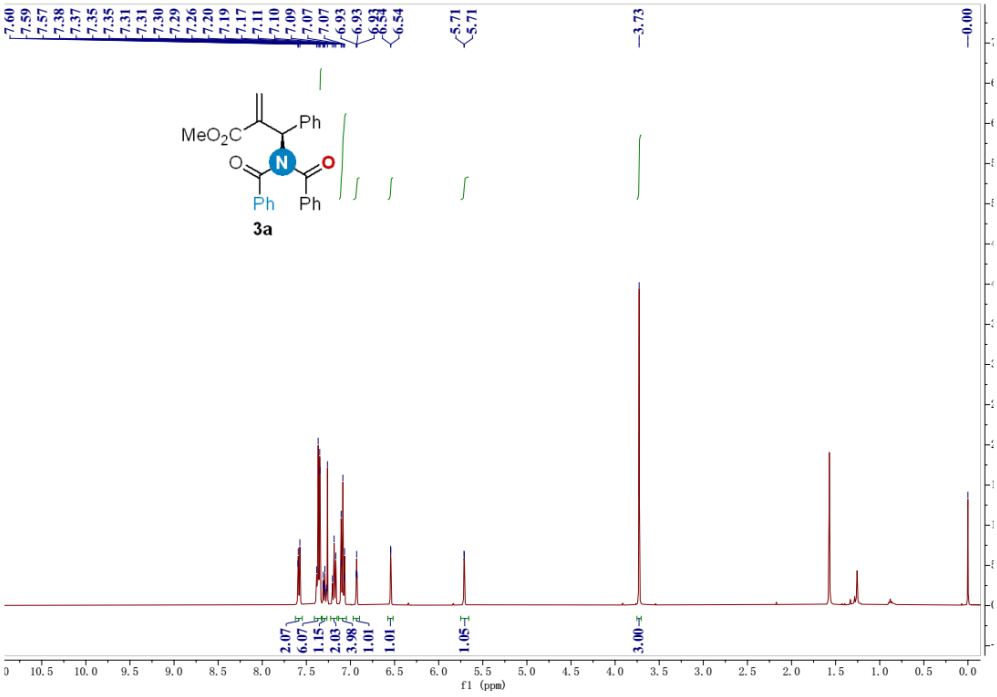


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.75-7.72 (m, 2H), 7.49-7.47 (m, 2H), 7.40-7.37 (m, 3H), 7.30-7.28 (m, 2H), 4.50 (s, 2H), 3.64 (s, 3H), 2.44 (s, 3H).

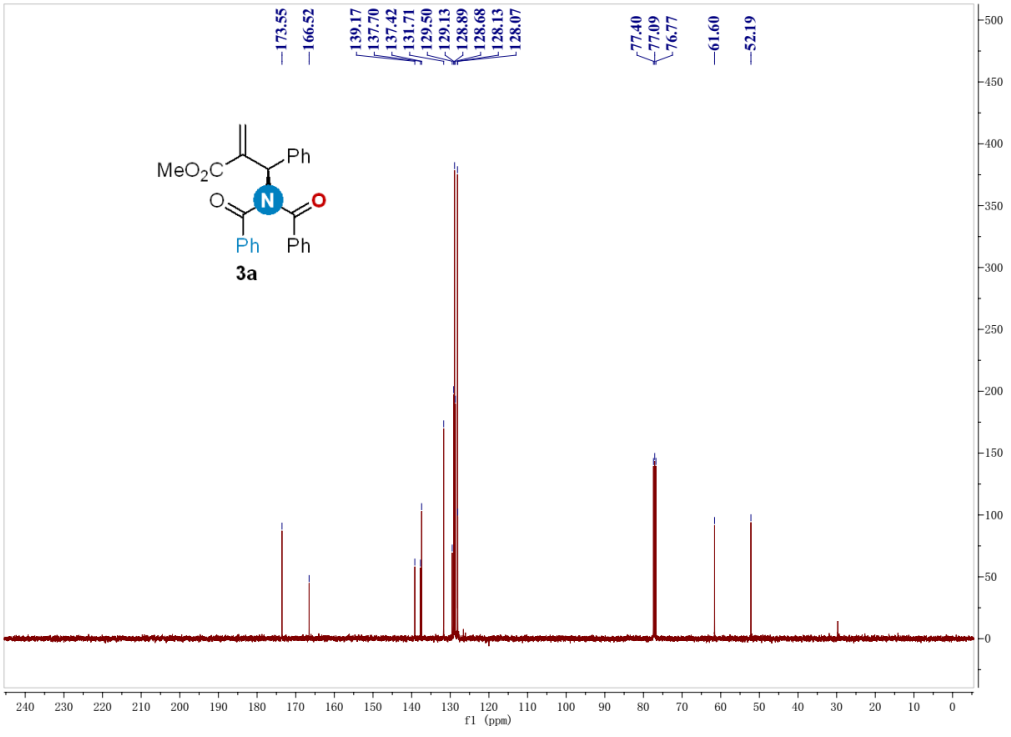
^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 146.1, 144.7, 136.3, 133.7, 129.6, 129.6, 129.1, 128.7, 128.5, 121.1, 55.1, 52.3, 21.6.

HRMS (ESI, m/z): calcd. For $C_{18}H_{19}O_4S$ $[M+H]^+$: 331.0999, found: 331.1000;

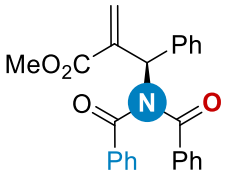
7. ^{1}H, ^{13}C NMR and HPLC data



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



^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



3a

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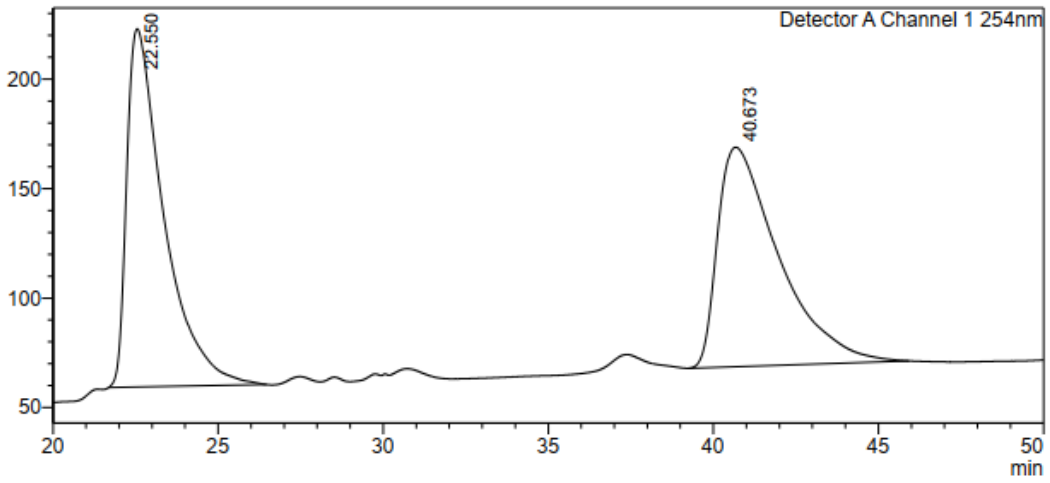
mV



Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.550	12792380	163595	49.776	62.014
2	40.673	12907436	100206	50.224	37.986
Total		25699815	263801	100.000	100.000

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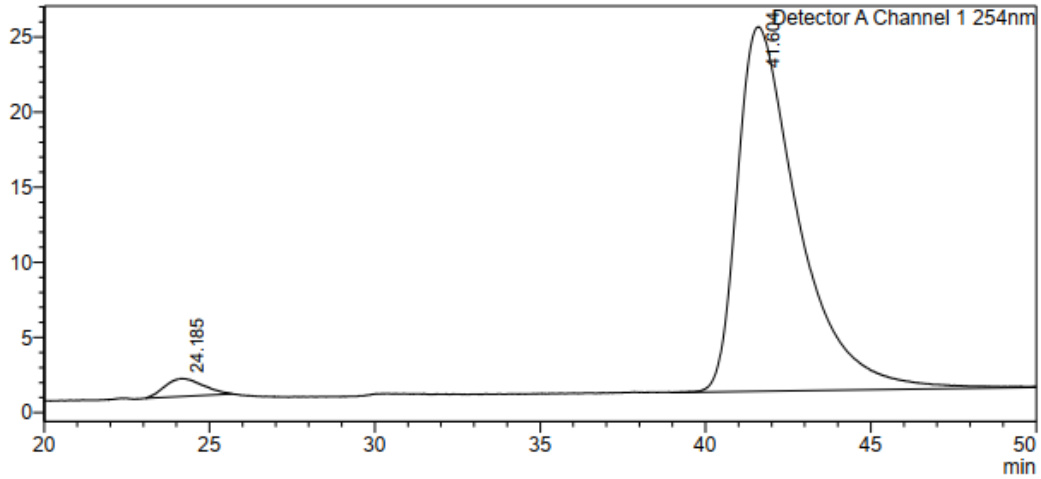
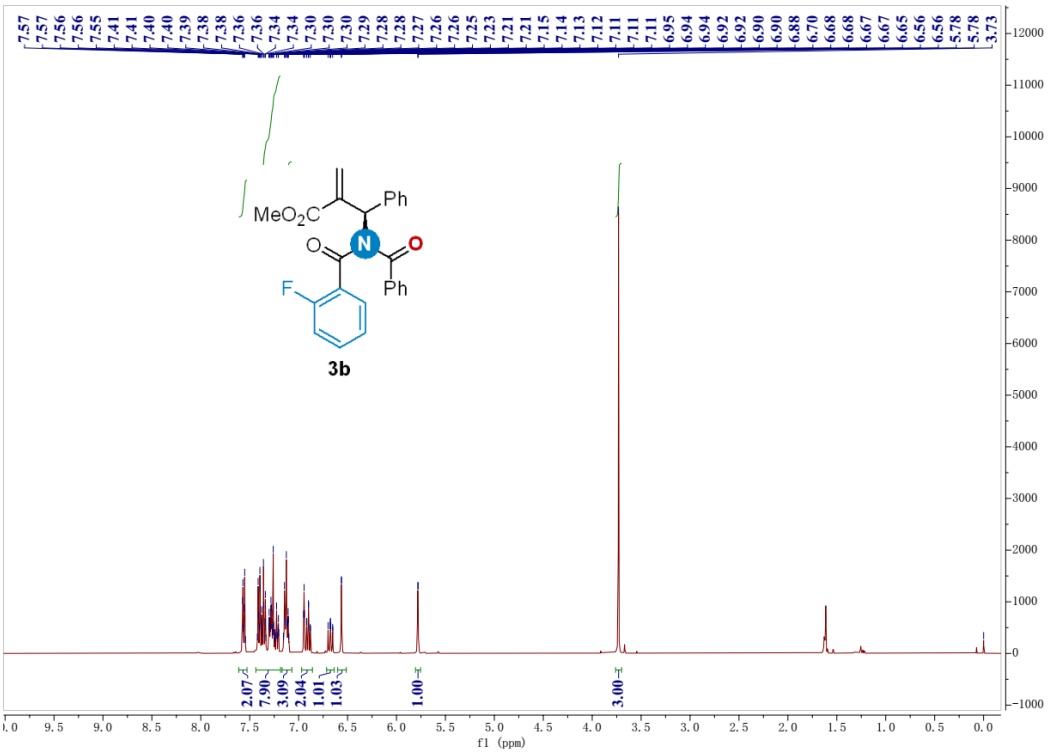
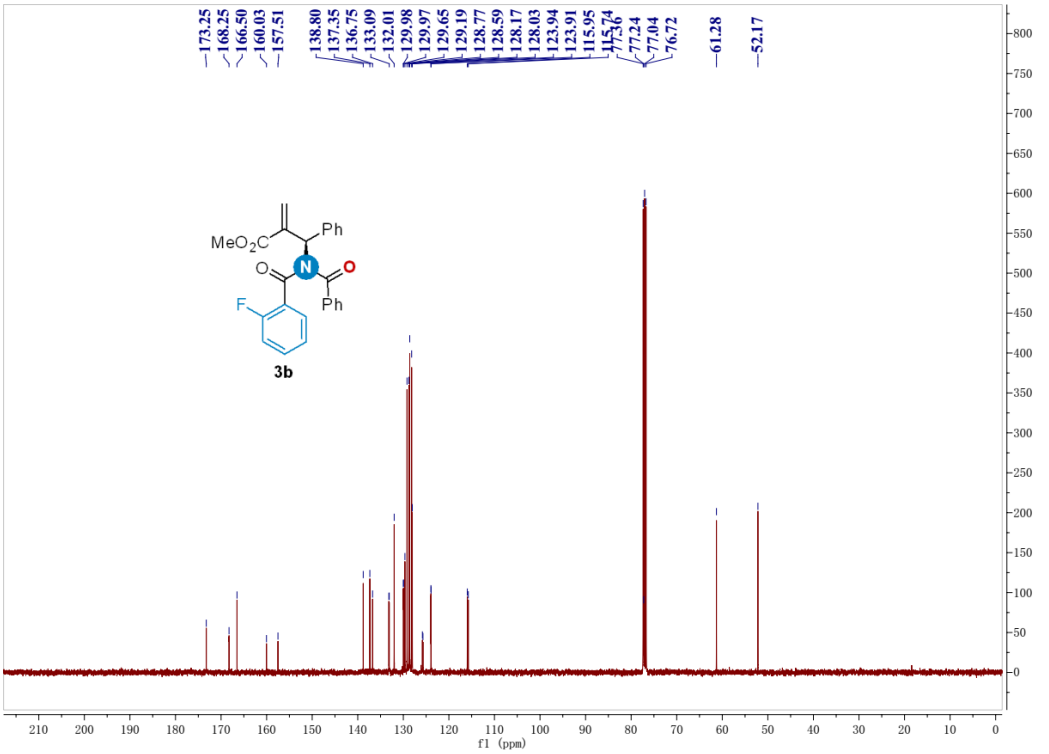
mV



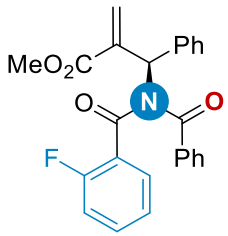
Peak#	Ret. Time	Area	Height	Area%	Height%
1	24.185	94494	1179	2.951	4.637
2	41.604	3107990	24242	97.049	95.363
Total		3202484	25421	100.000	100.000



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



^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



3b

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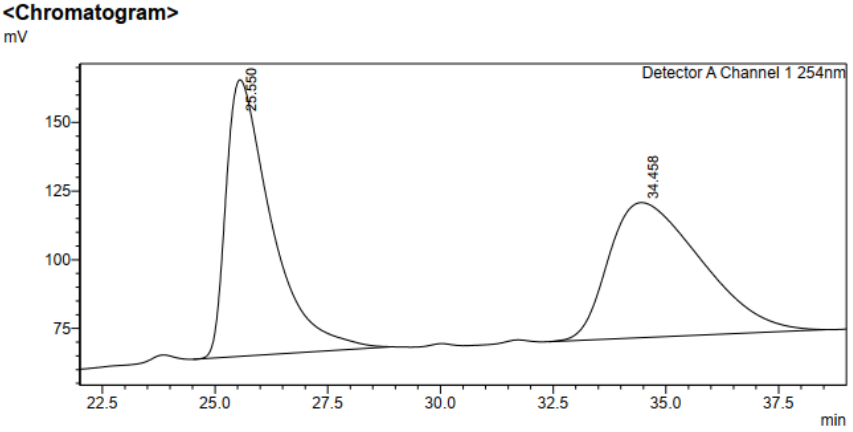

Peak#	Ret. Time	Area	Height	Area%	Height%
1	25.550	7078578	100702	50.181	67.192
2	34.458	7027532	49170	49.819	32.808
Total		14106109	149872	100.000	100.000

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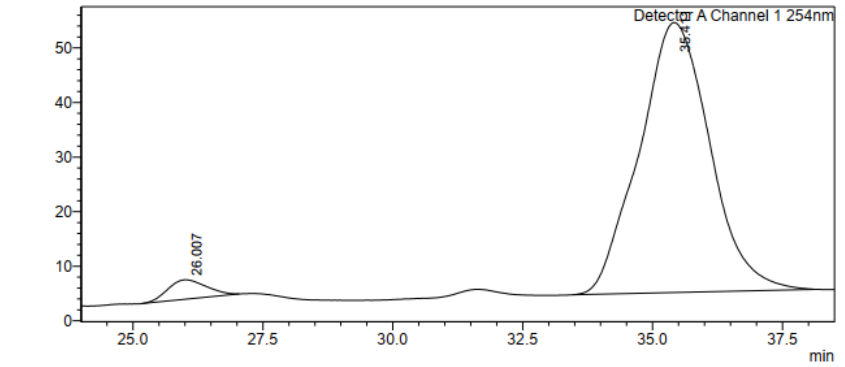
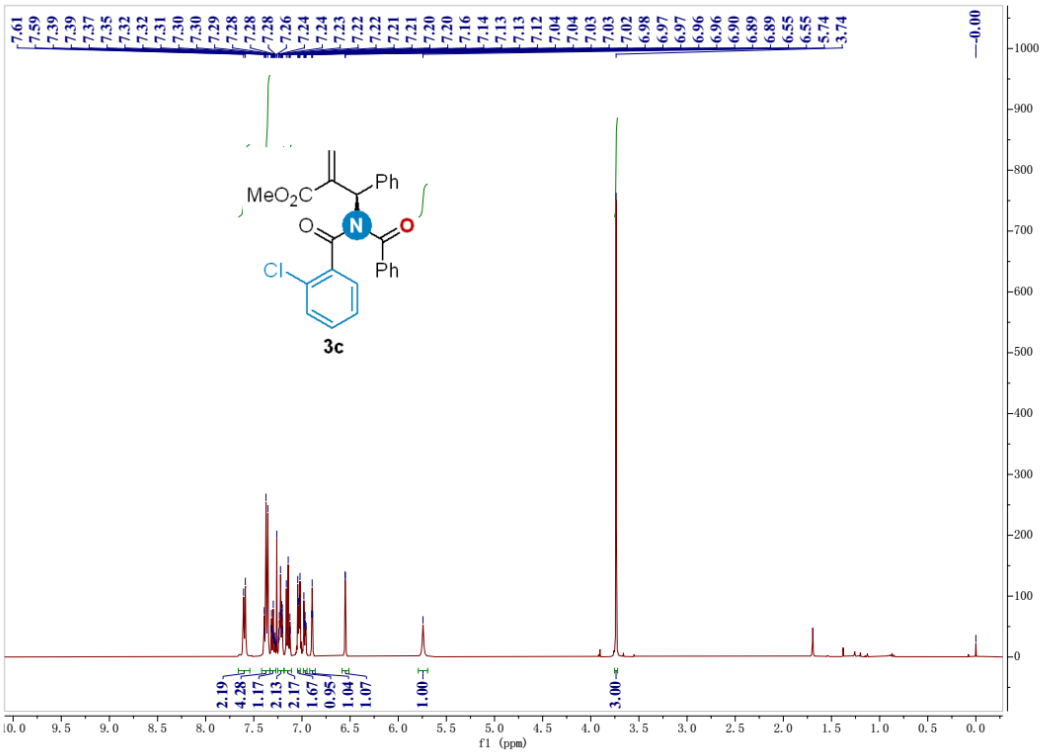
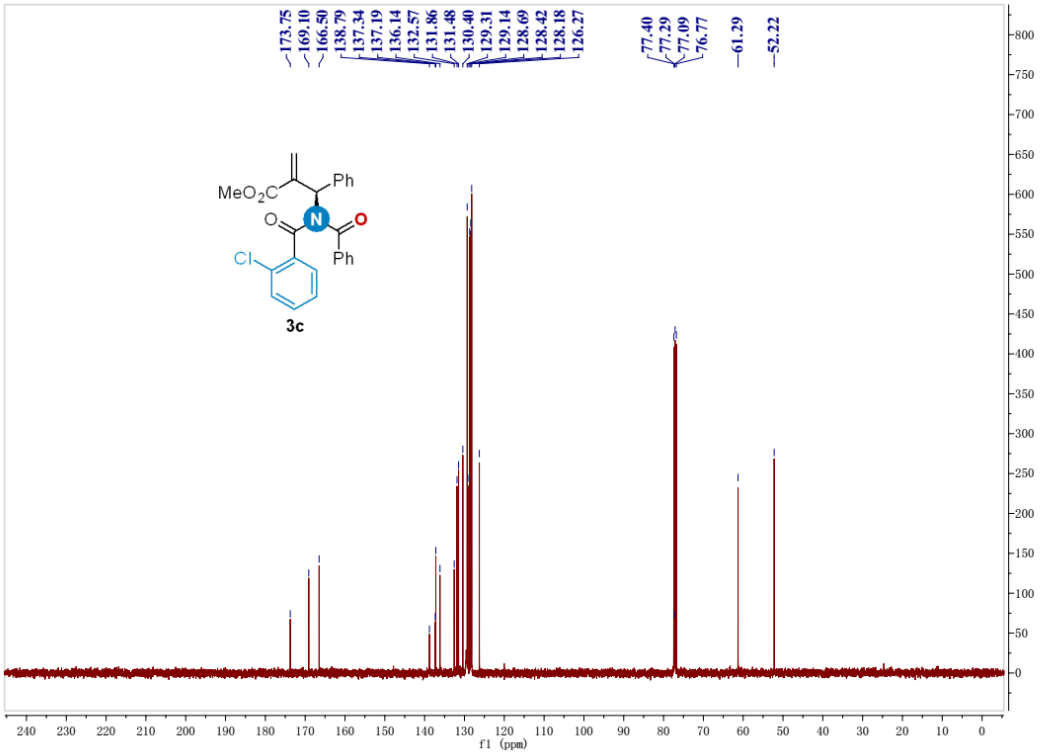


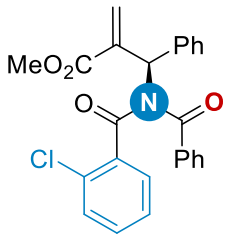
Peak#	Ret. Time	Area	Height	Area%	Height%
1	26.007	183446	3565	3.780	6.724
2	35.411	4669165	49460	96.220	93.276
Total		4852611	53025	100.000	100.000



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

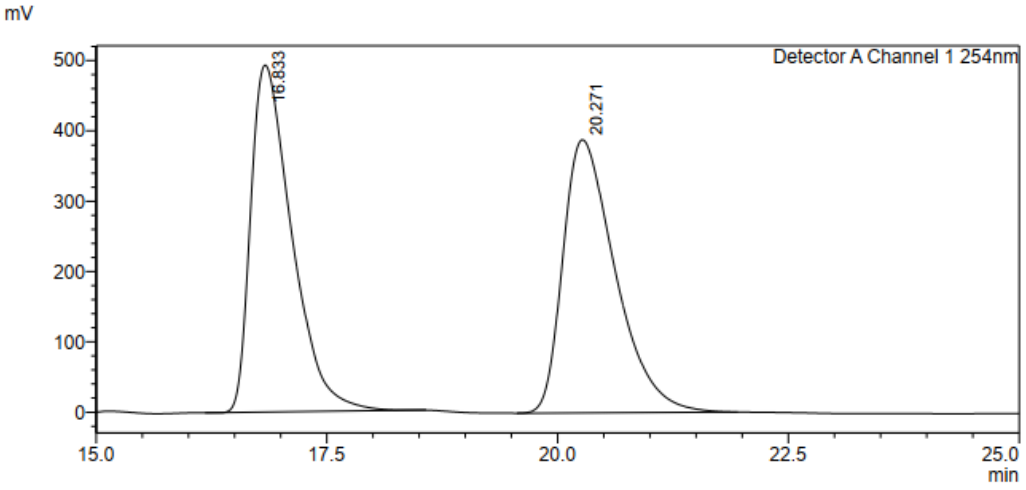


^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)



3c

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.833	15276082	493258	49.870	55.957
2	20.271	15355946	388230	50.130	44.043
Total		30632028	881487	100.000	100.000

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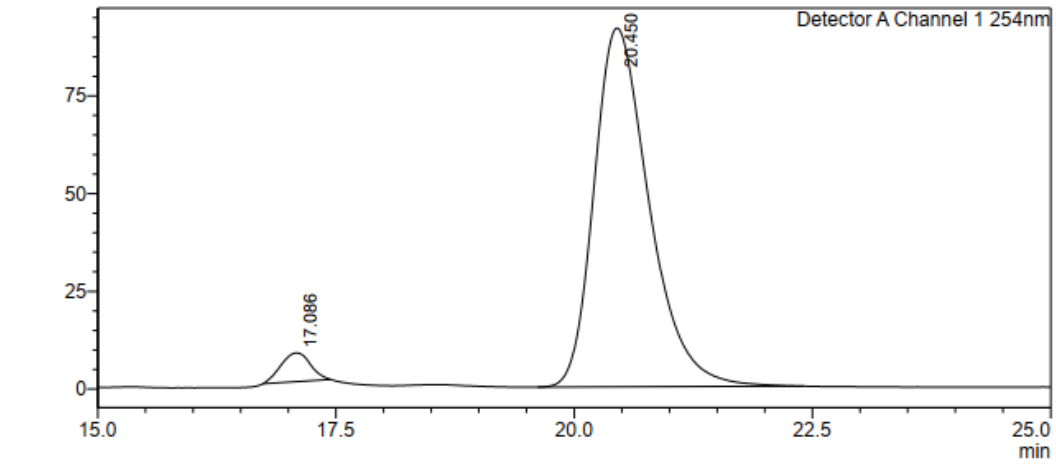
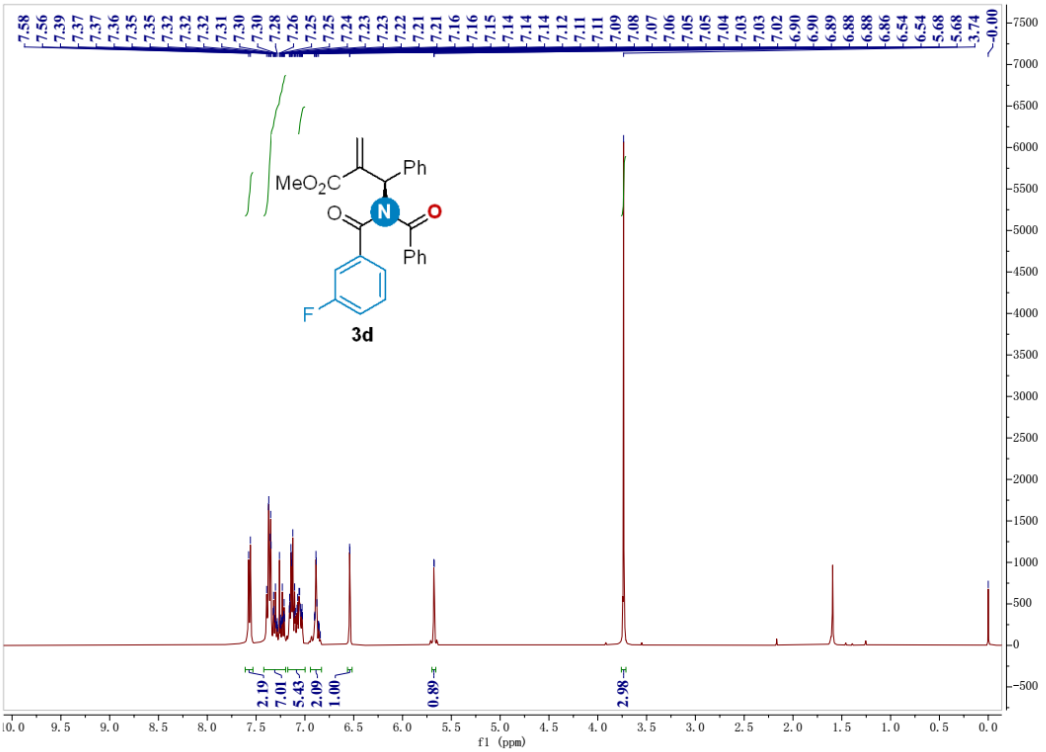
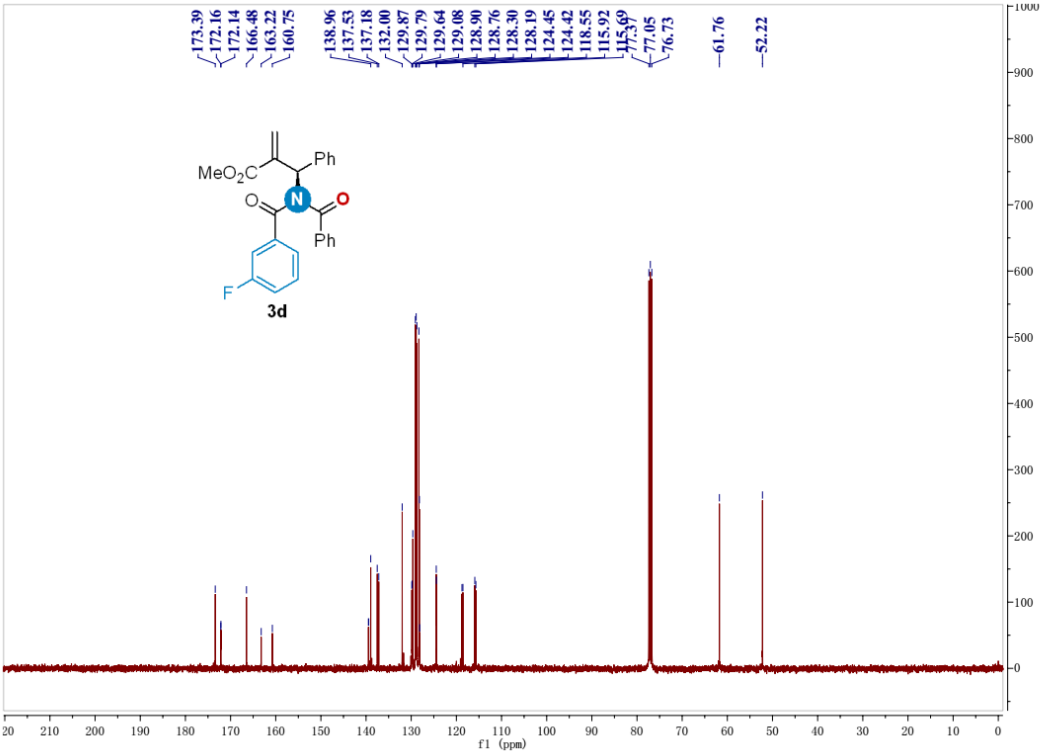


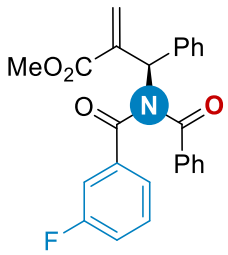
Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.086	158336	7316	4.112	7.387
2	20.450	3692356	91721	95.888	92.613
Total		3850693	99037	100.000	100.000



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



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



3d

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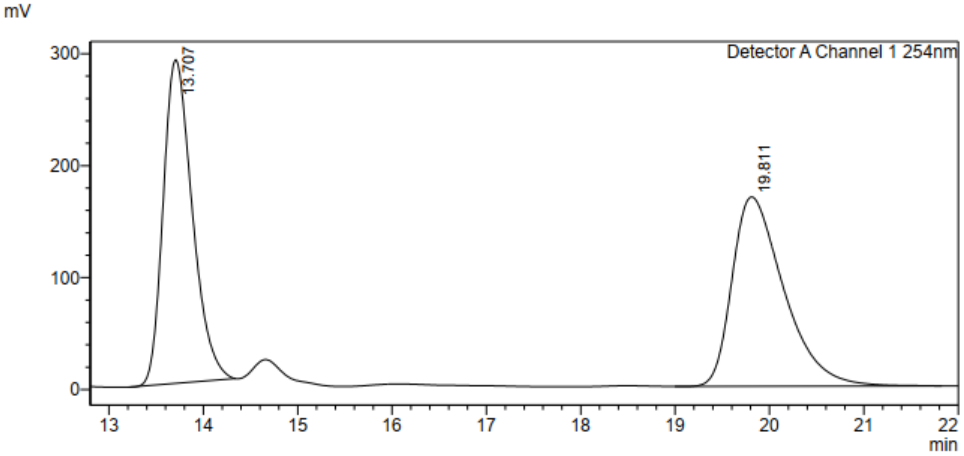

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.707	6210828	289024	48.975	63.073
2	19.811	6470860	169214	51.025	36.927
Total		12681687	458239	100.000	100.000

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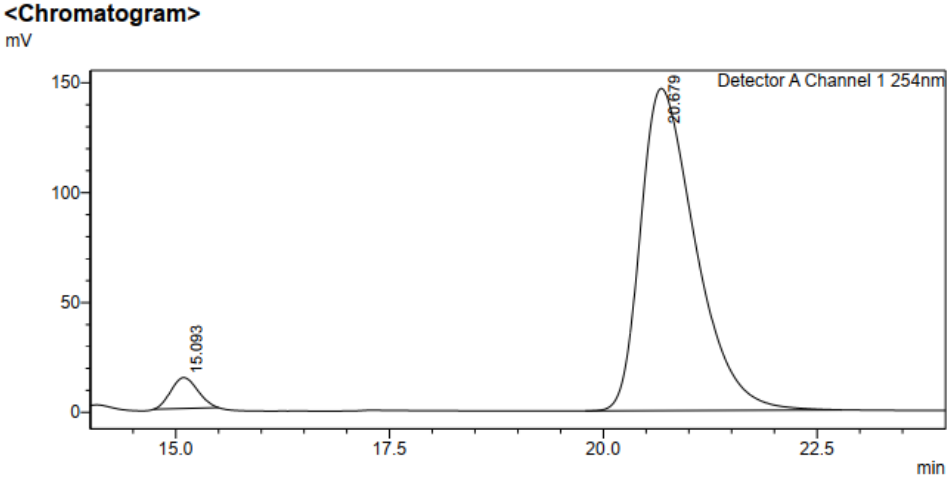
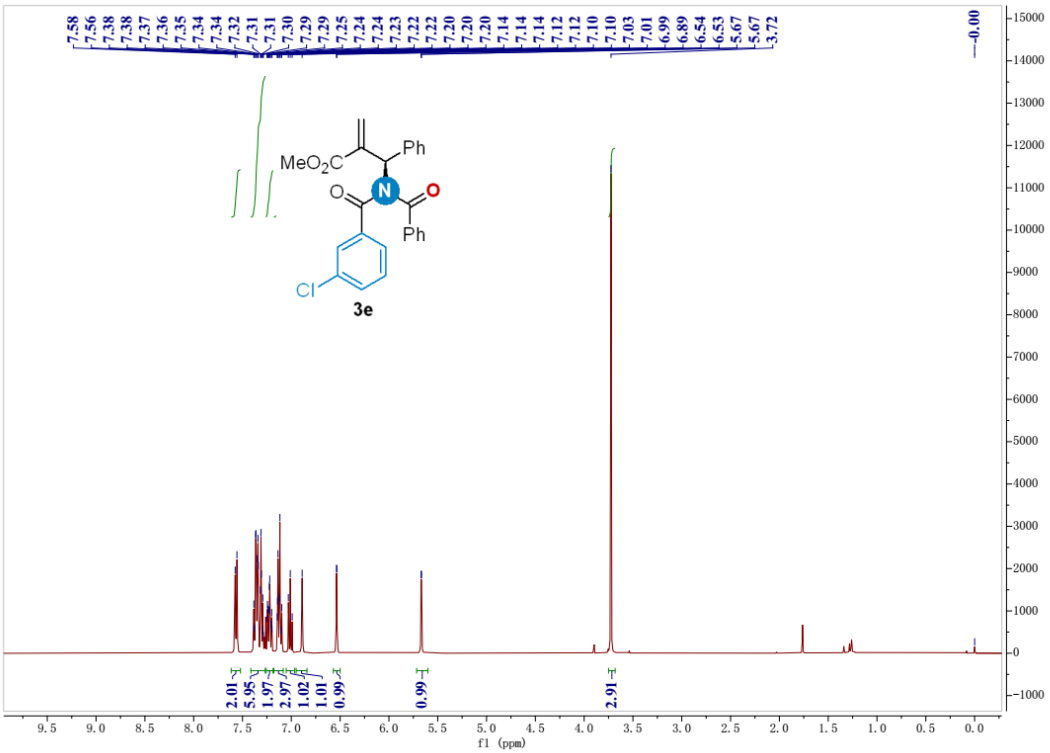
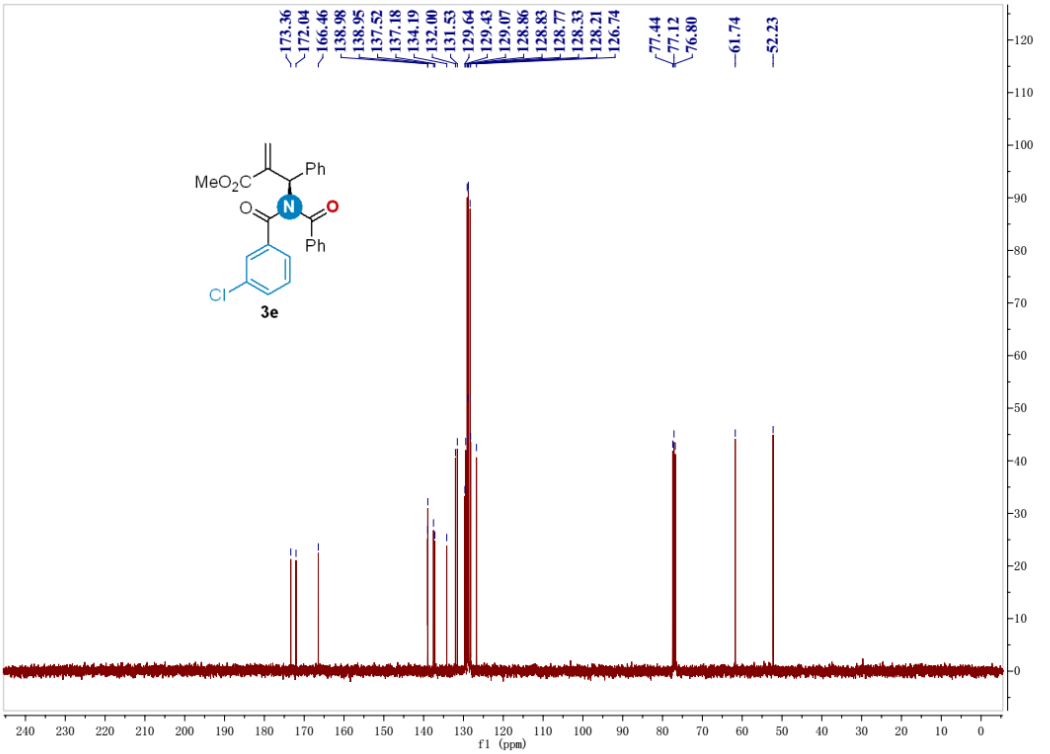


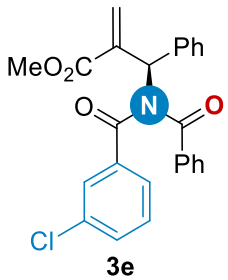
Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.093	309451	14094	4.510	8.774
2	20.679	6552019	146547	95.490	91.226
Total		6861469	160641	100.000	100.000



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

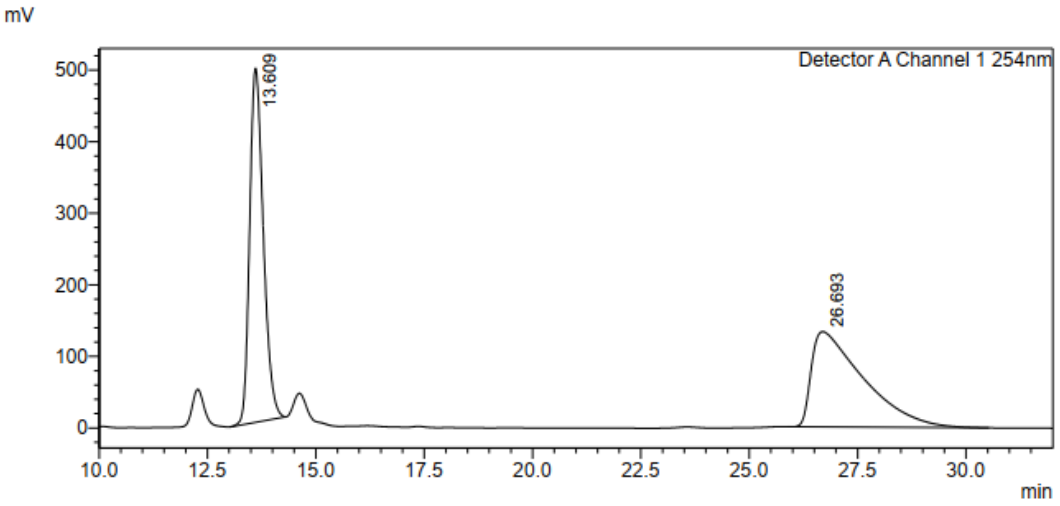


^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)



3e

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.609	10848949	494141	49.396	78.791
2	26.693	11114208	133009	50.604	21.209
Total		21963157	627150	100.000	100.000

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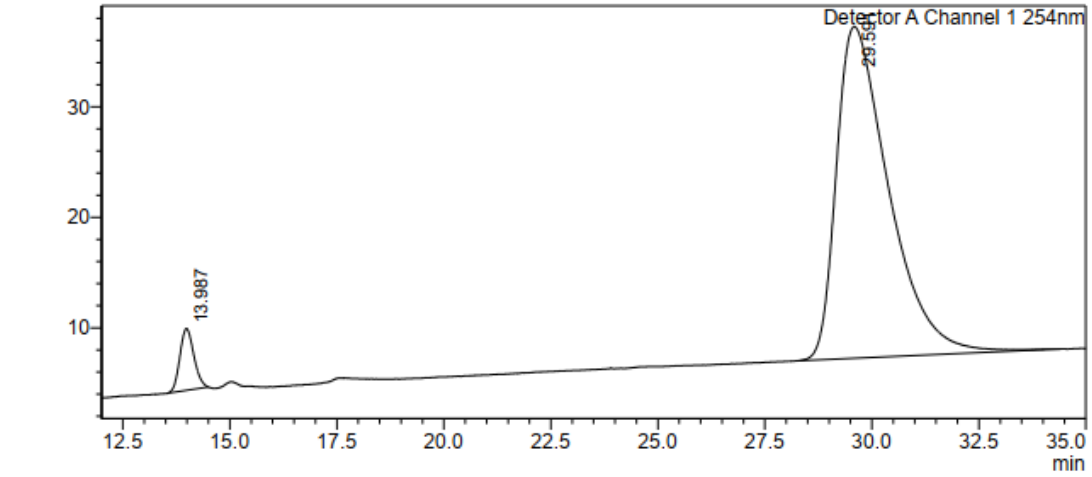
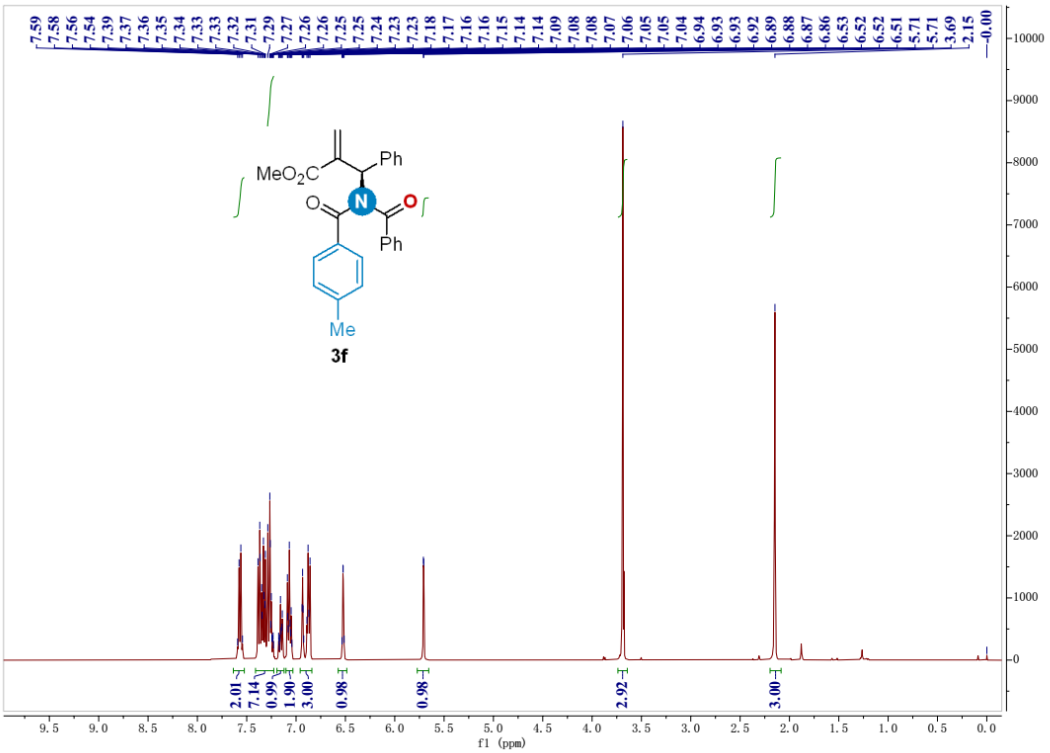
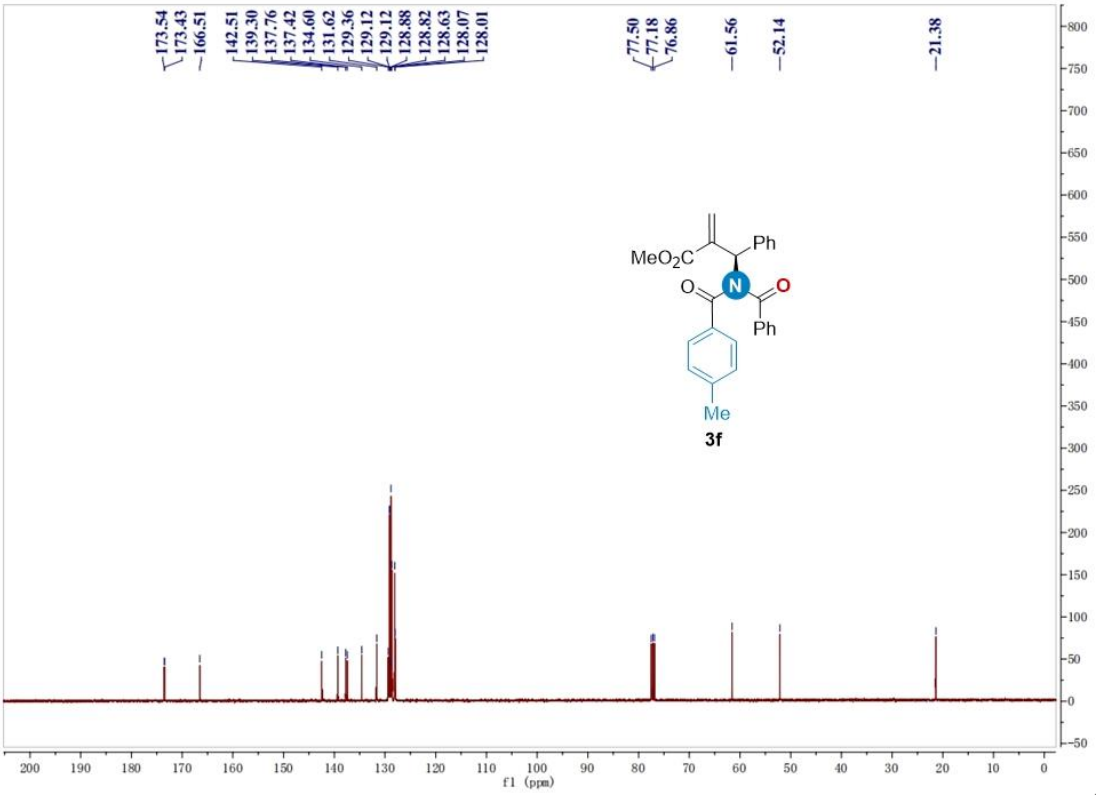


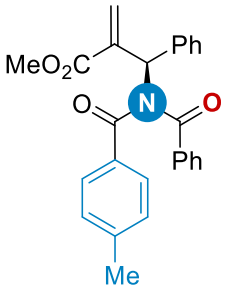
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.987	127349	5585	4.747	15.687
2	29.591	2555204	30018	95.253	84.313
Total		2682554	35603	100.000	100.000



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



^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



3f

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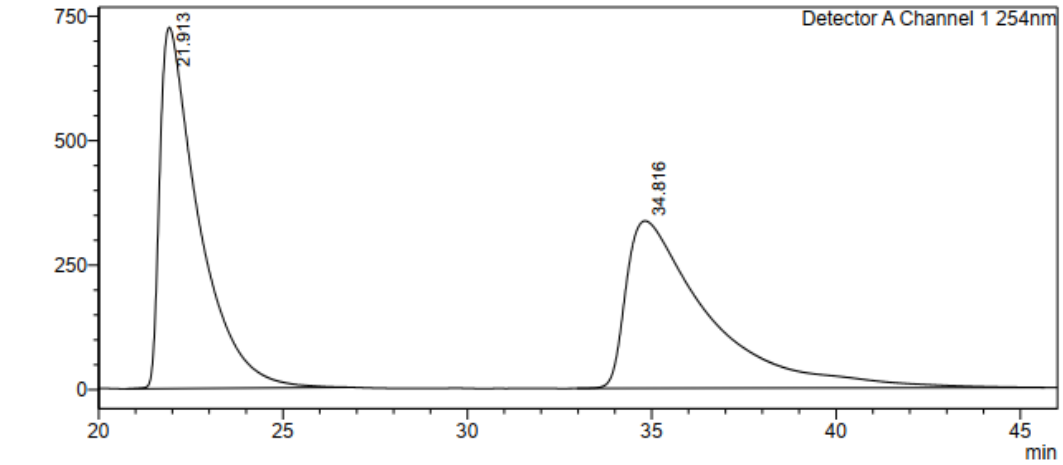

Peak#	Ret. Time	Area	Height	Area%	Height%
1	21.913	53062547	724979	50.394	68.331
2	34.816	52232534	336008	49.606	31.669
Total		105295081	1060987	100.000	100.000

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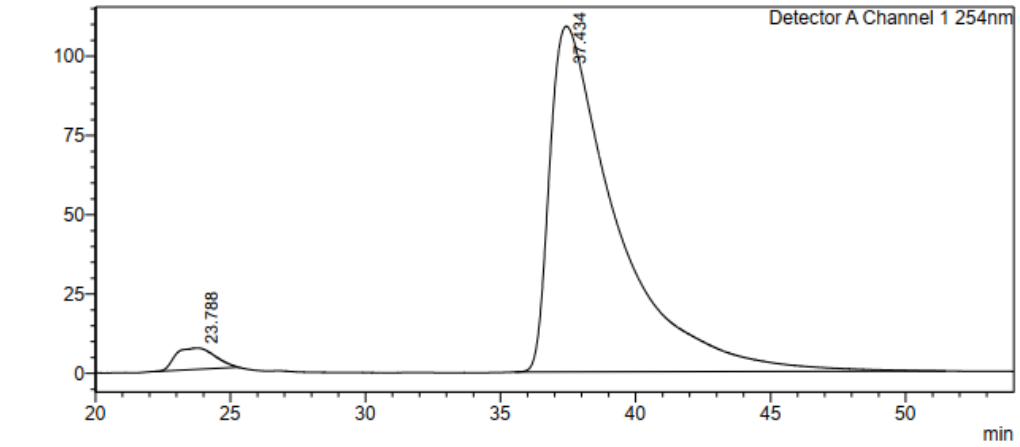
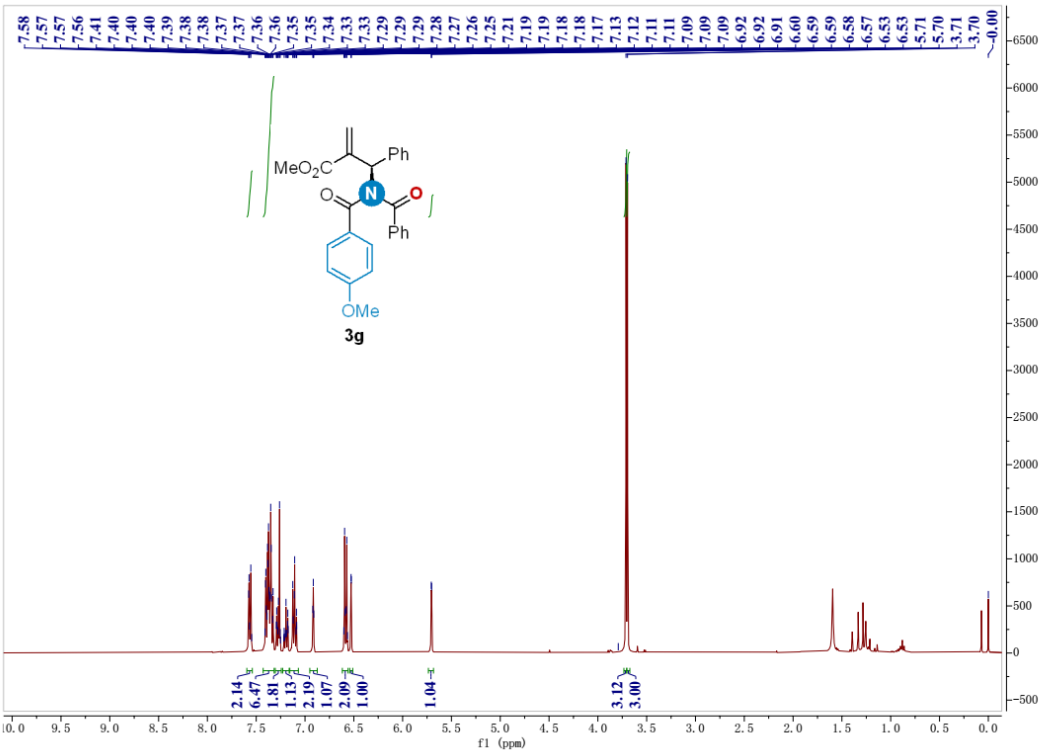
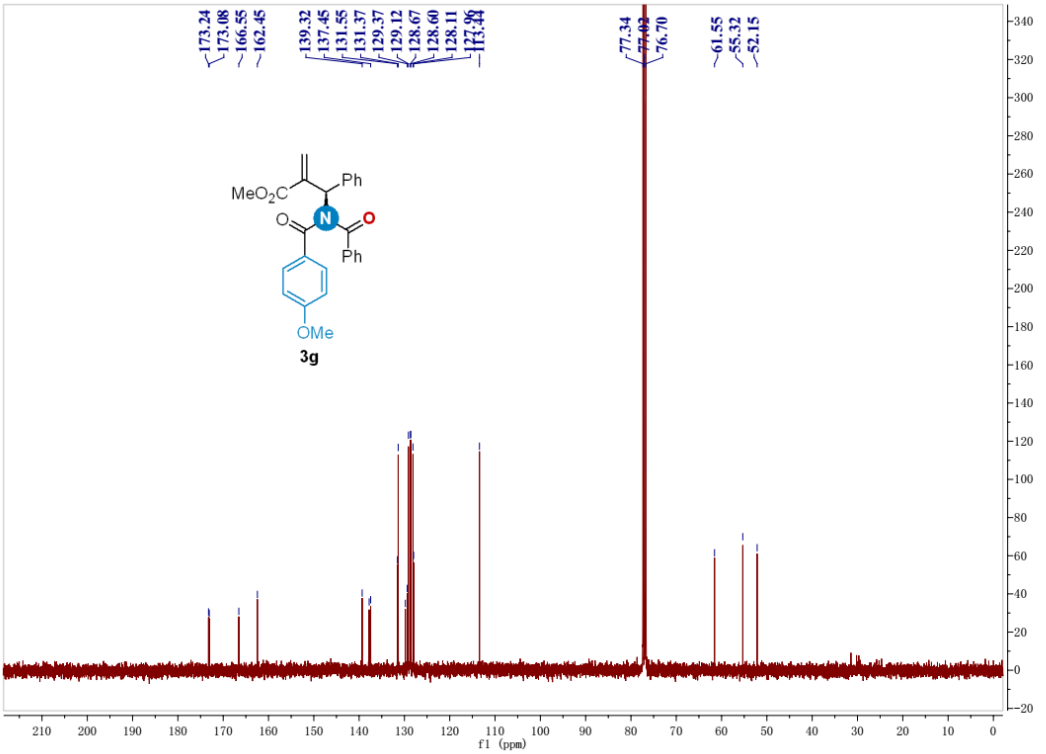


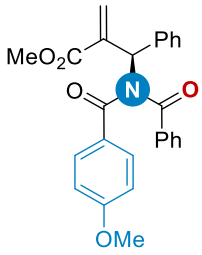
Peak#	Ret. Time	Area	Height	Area%	Height%
1	23.788	676889	6695	3.475	5.787
2	37.434	18803711	109005	96.525	94.213
Total		19480600	115700	100.000	100.000



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

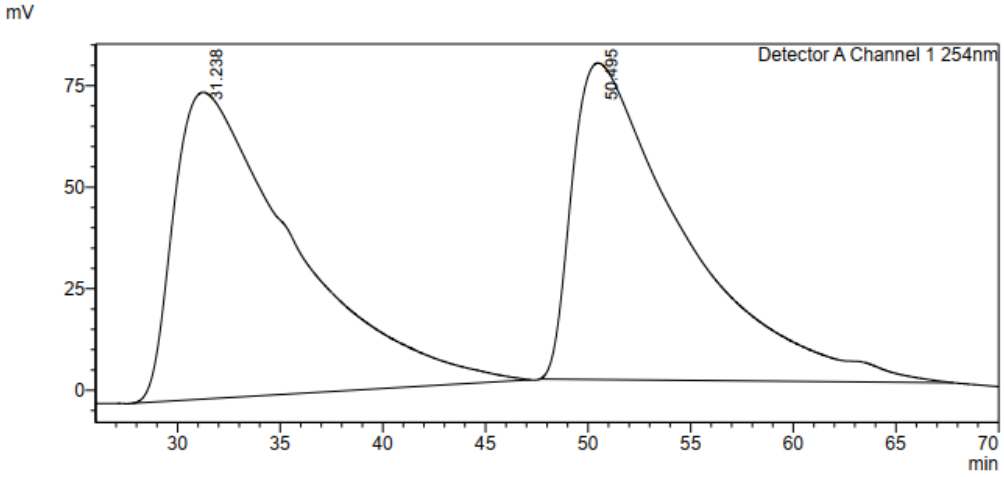


^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



3g

<Chromatogram>



Peak#	Ret. Time	Area	Height	Area%	Height%
1	31.238	30989283	75531	51.229	49.217
2	50.495	29501933	77935	48.771	50.783
Total		60491216	153467	100.000	100.000

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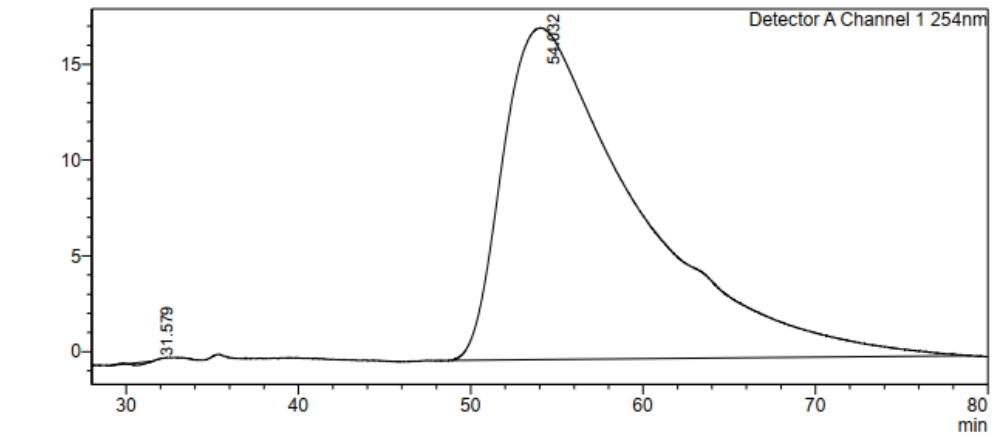
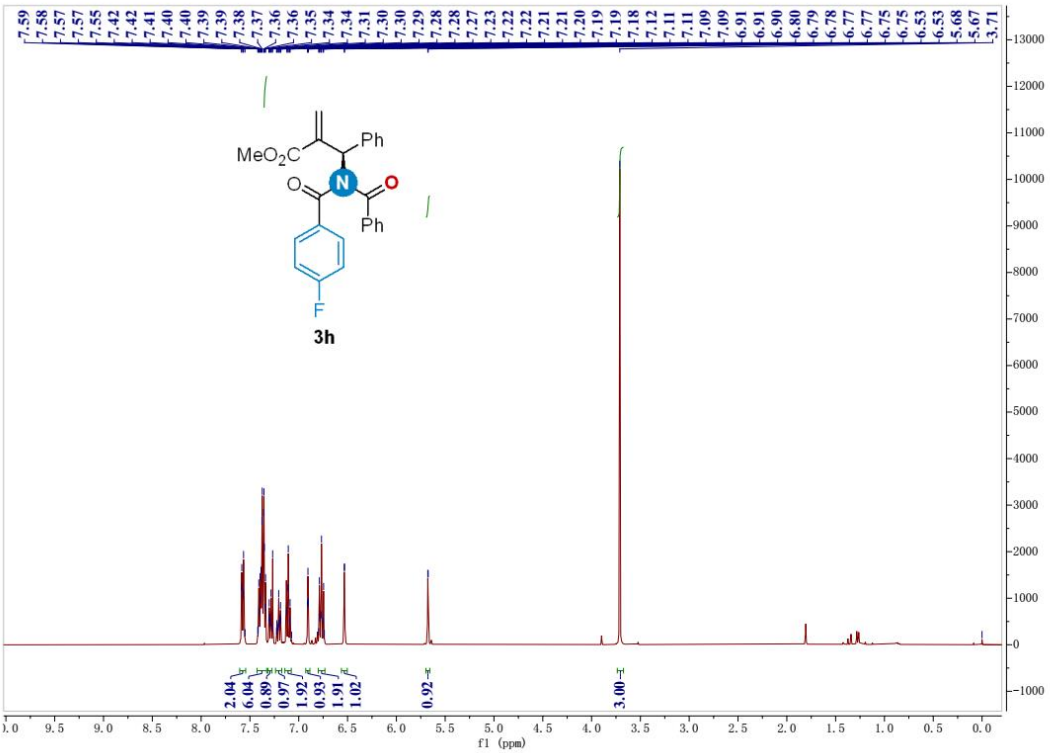
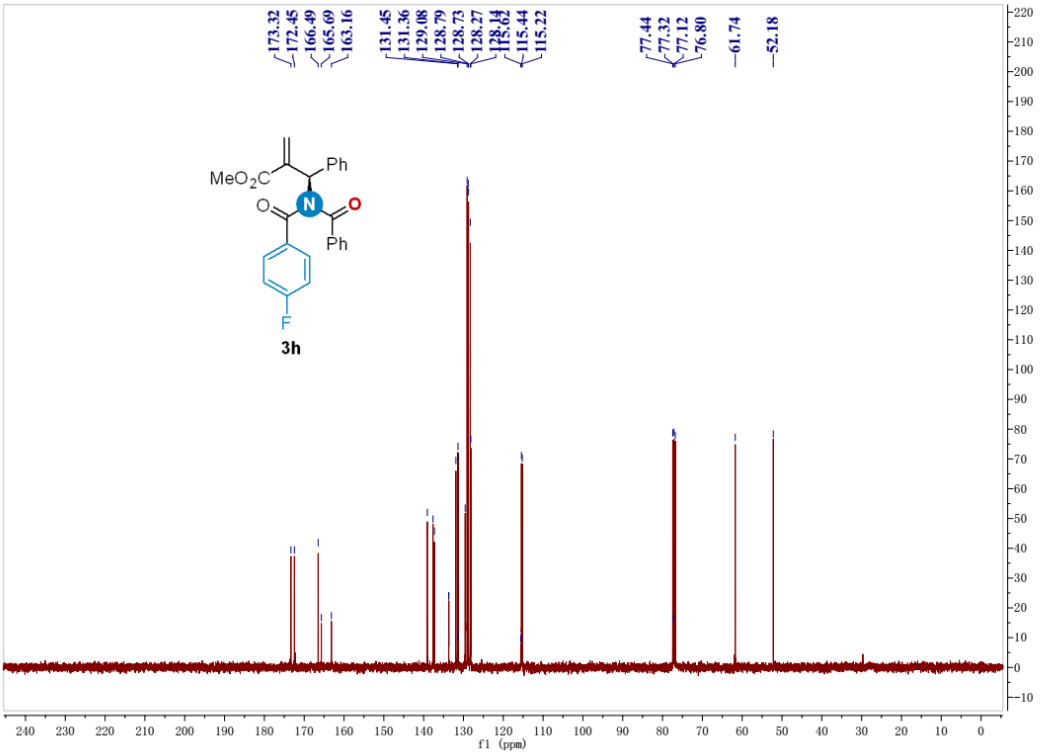


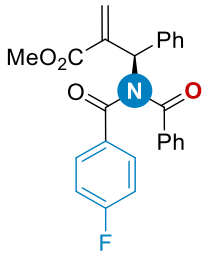
Peak#	Ret. Time	Area	Height	Area%	Height%
1	31.579	-5538	-3	-0.058	-0.017
2	54.032	9484316	17322	100.058	100.017
Total		9478779	17319	100.000	100.000



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



^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



3h

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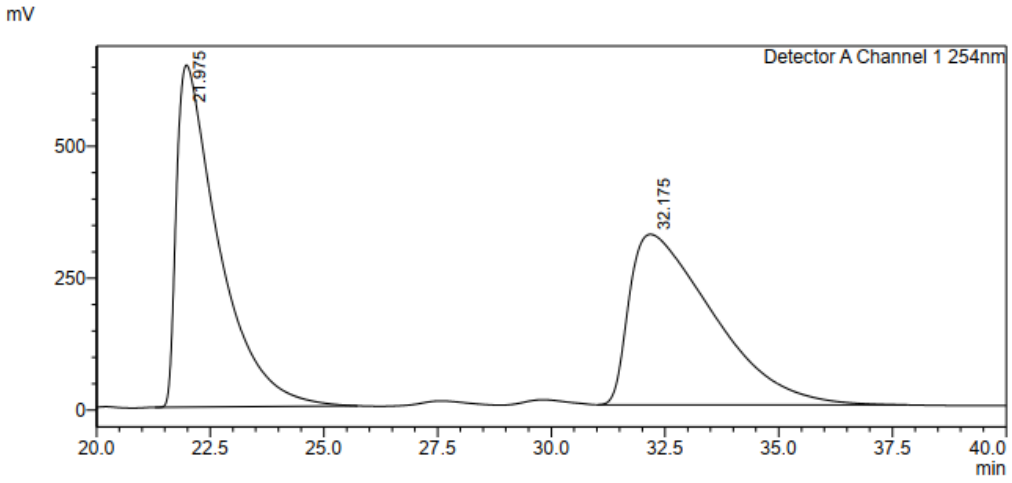

Peak#	Ret. Time	Area	Height	Area%	Height%
1	21.975	41955879	647761	50.270	66.726
2	32.175	41505314	323011	49.730	33.274
Total		83461193	970772	100.000	100.000

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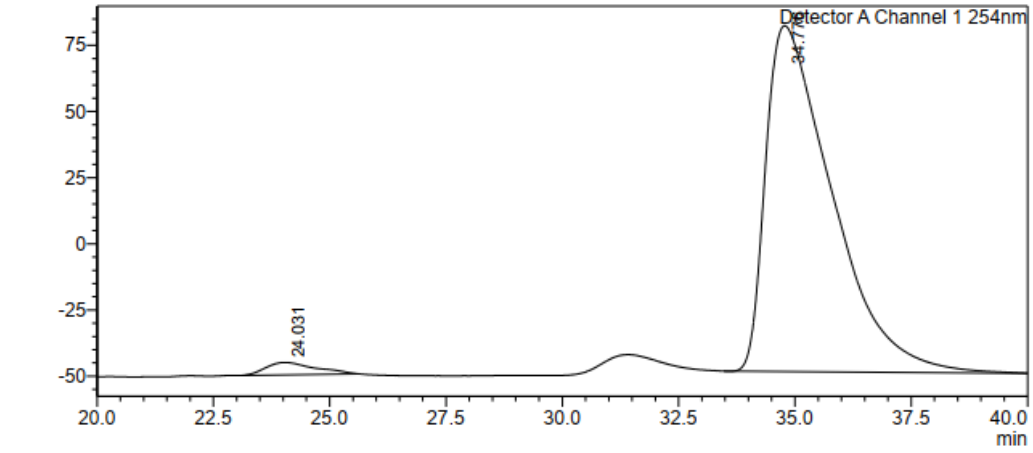
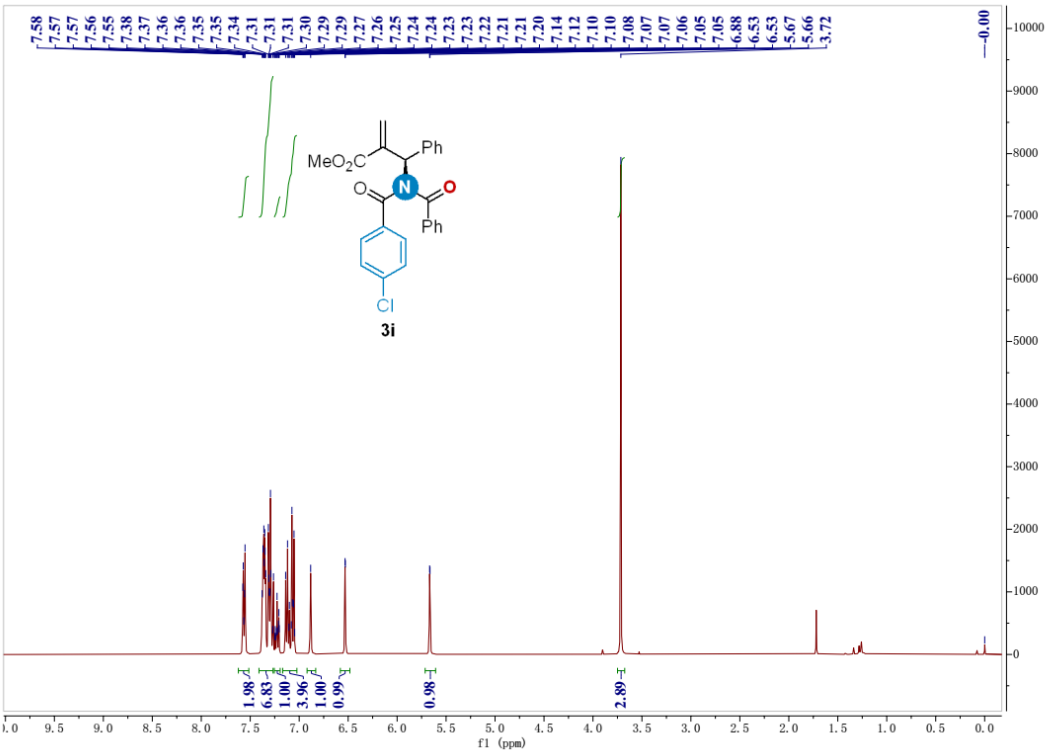
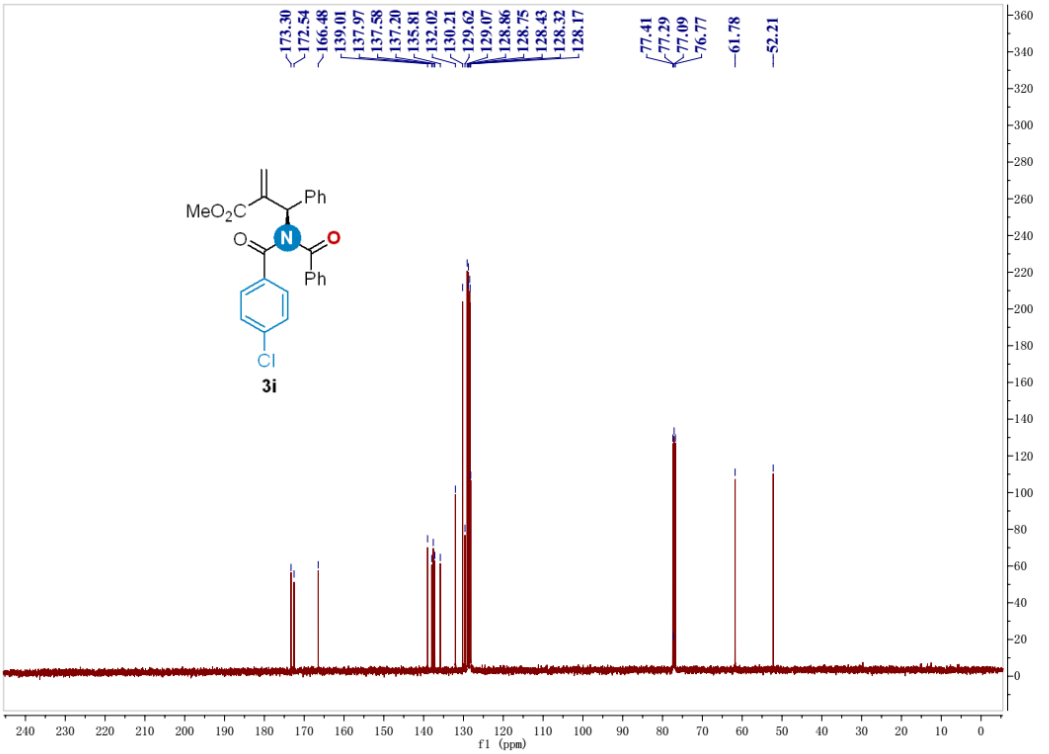


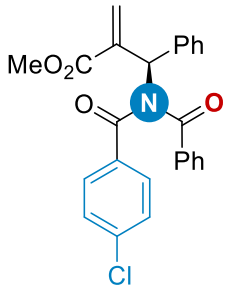
Peak#	Ret. Time	Area	Height	Area%	Height%
1	24.031	345051	4674	2.586	3.453
2	34.776	12996546	130660	97.414	96.547
Total		13341597	135334	100.000	100.000



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



^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



3i

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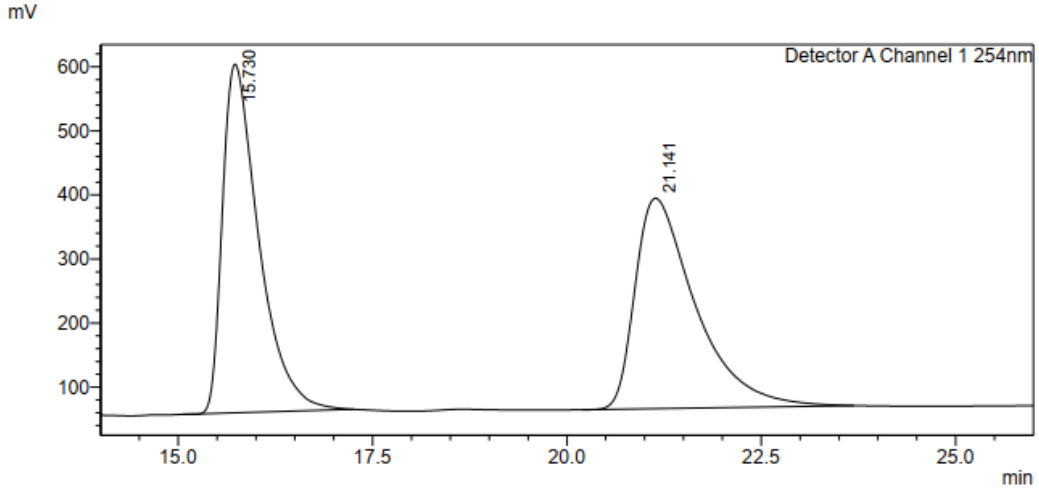

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.730	17698368	543951	49.861	62.353
2	21.141	17797362	328420	50.139	37.647
Total		35495730	872370	100.000	100.000

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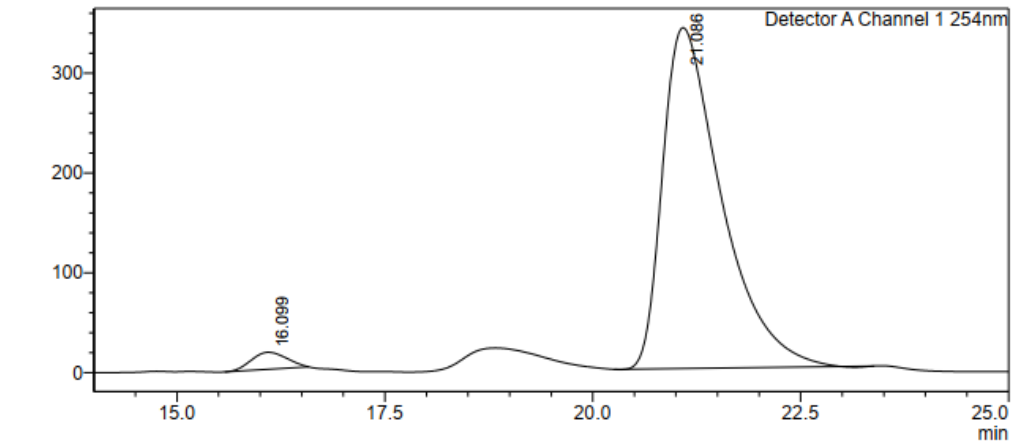
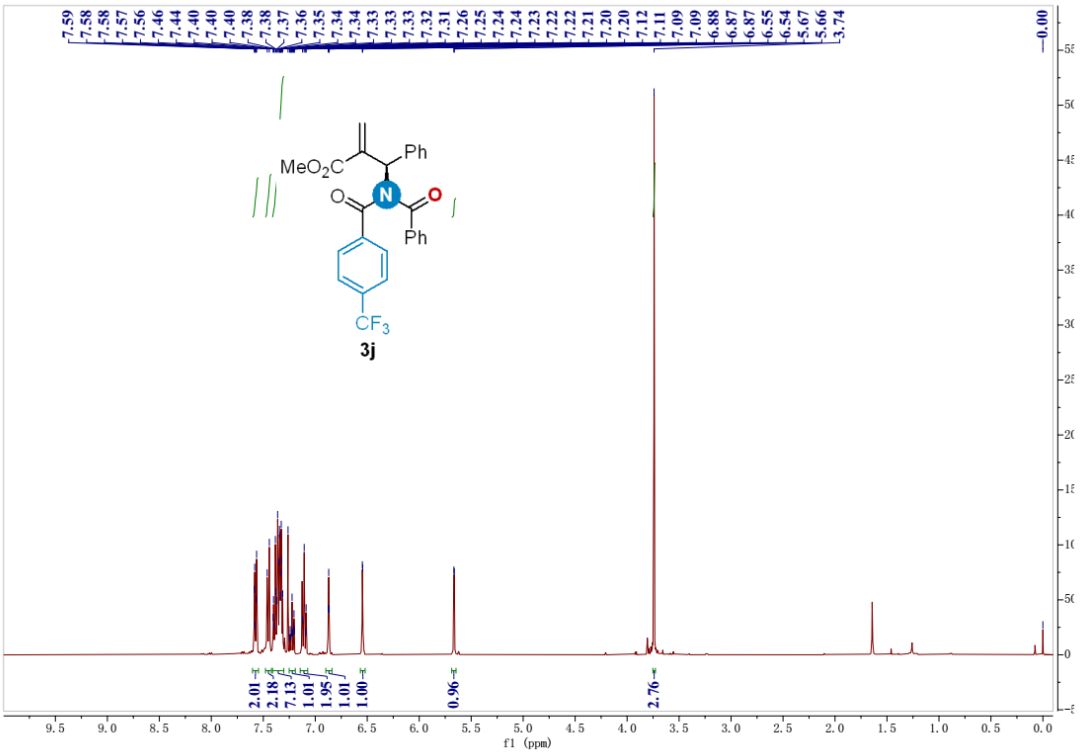
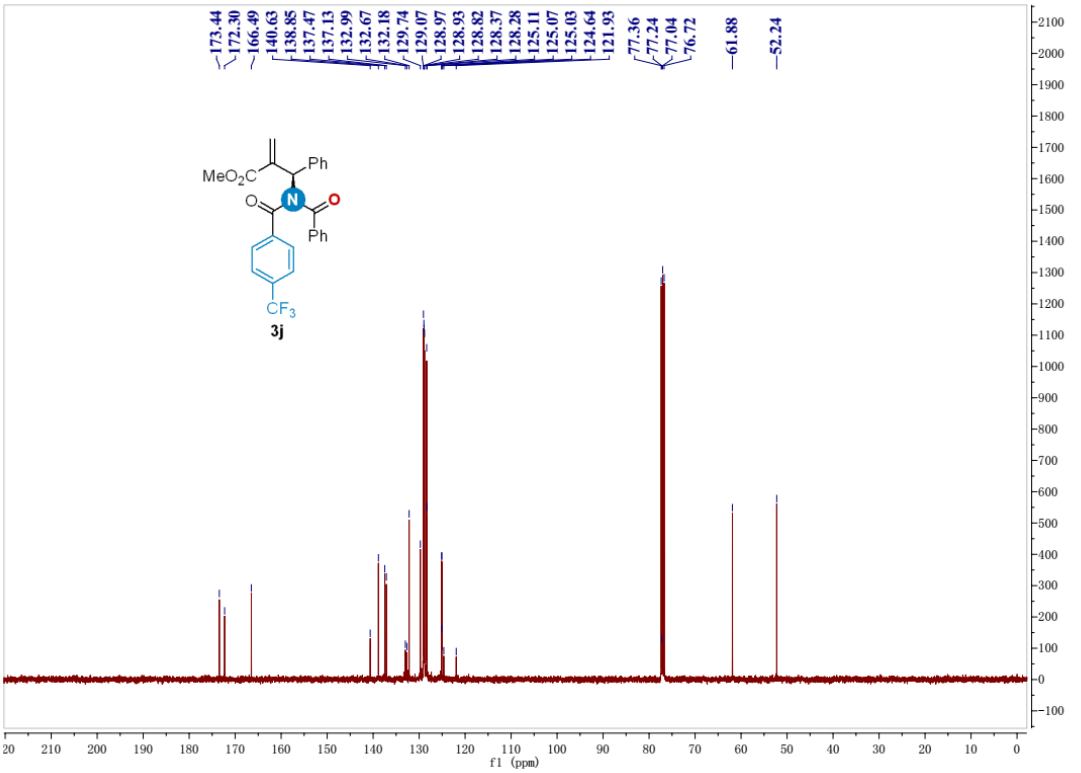


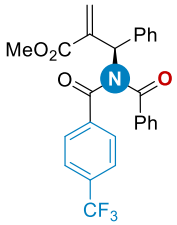
Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.099	505001	17060	2.916	4.761
2	21.086	16813746	341266	97.084	95.239
Total		17318747	358327	100.000	100.000



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



^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$)



3j

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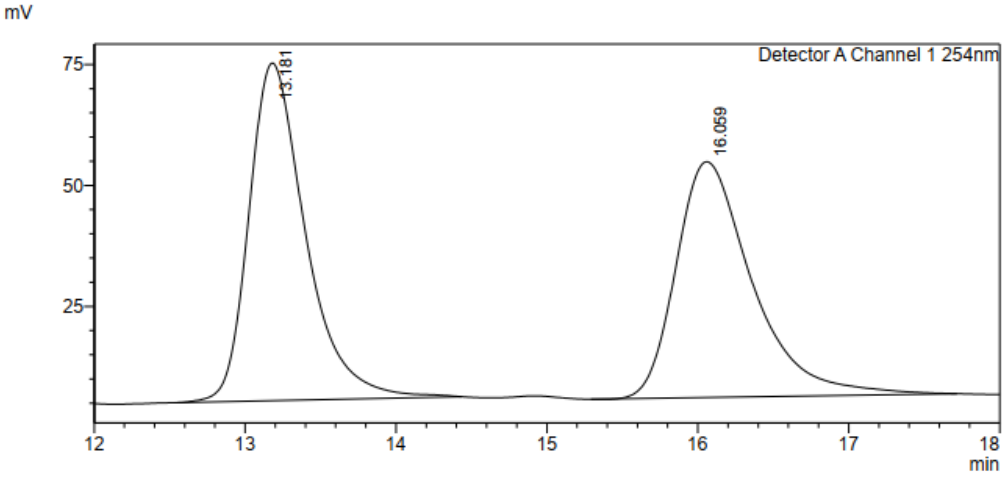

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.181	1824913	69771	51.526	58.873
2	16.059	1716837	48741	48.474	41.127
Total		3541750	118512	100.000	100.000

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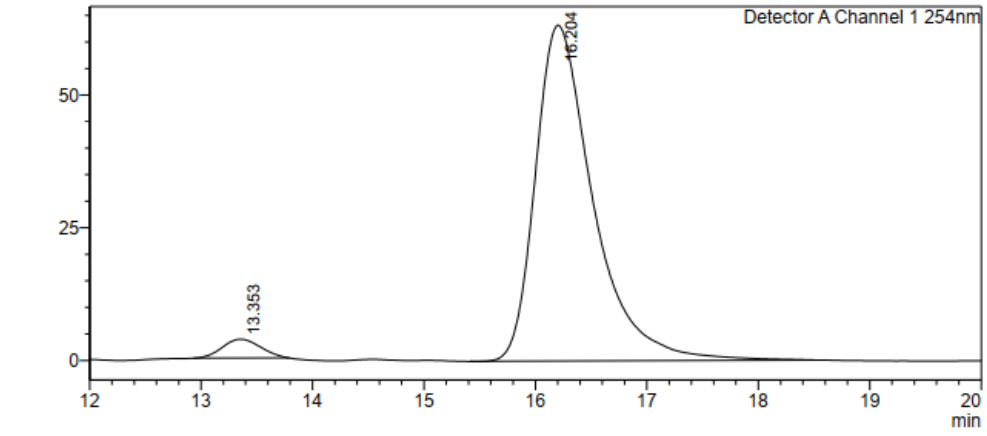
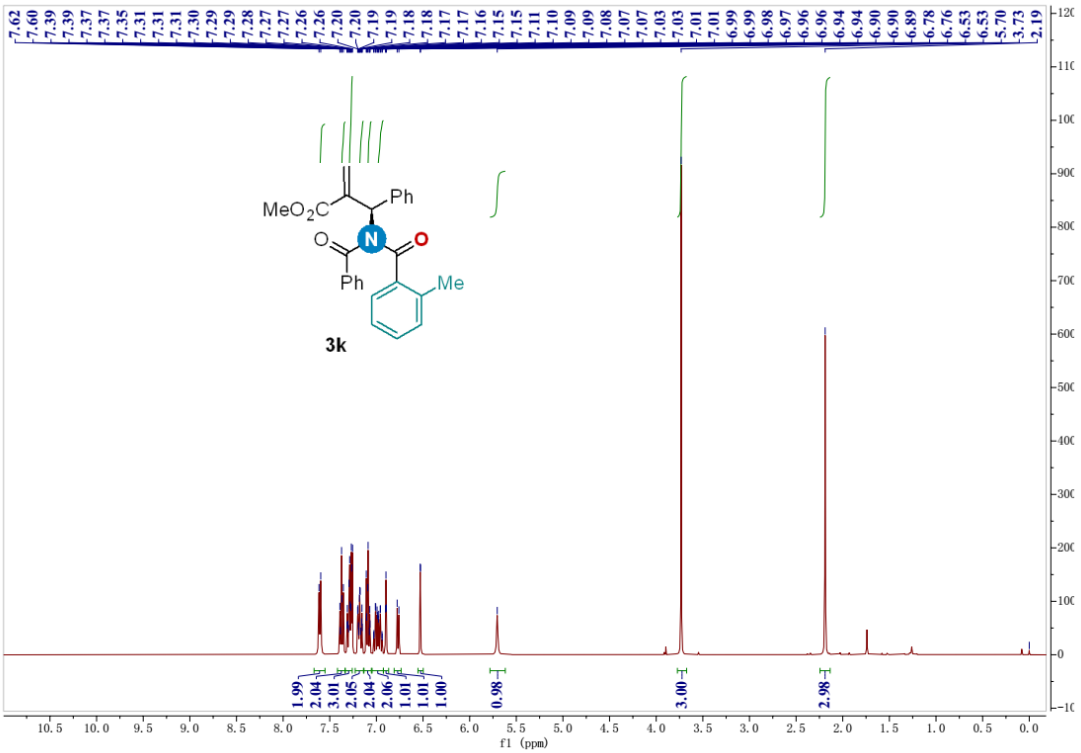
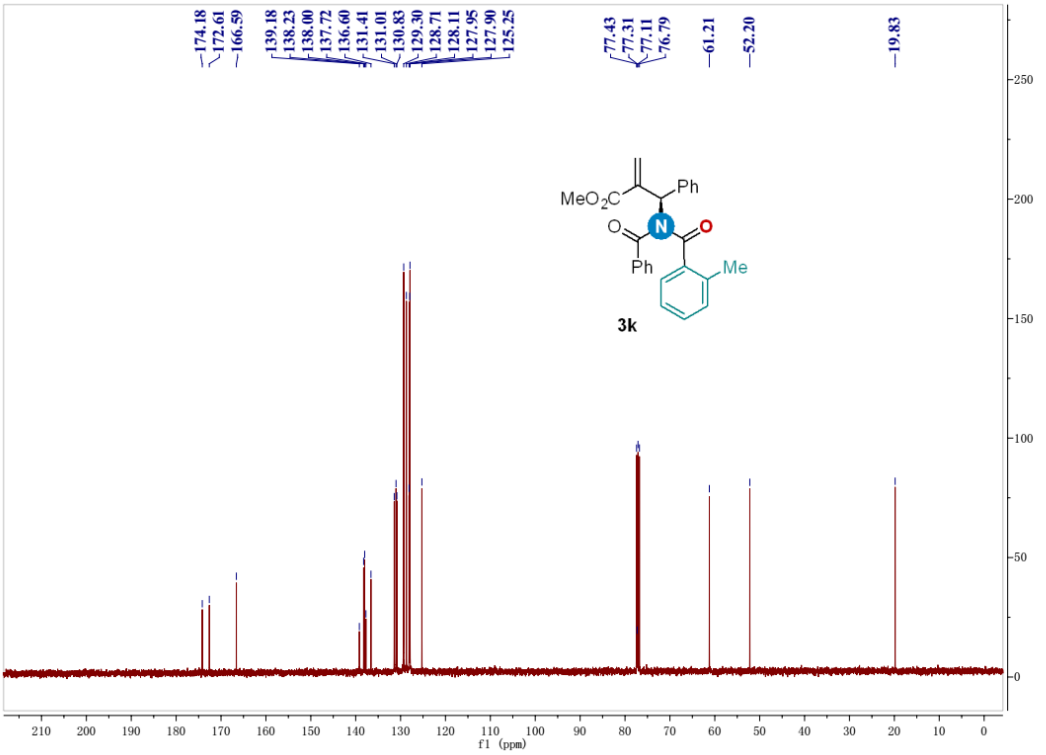


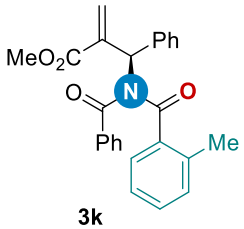
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.353	85089	3545	3.598	5.307
2	16.204	2279789	63258	96.402	94.693
Total		2364877	66803	100.000	100.000



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



^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



3k

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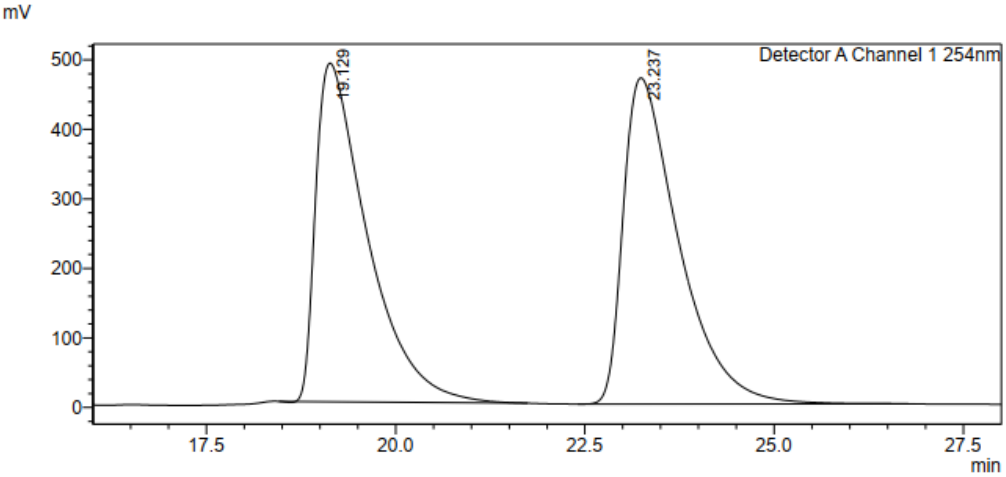

Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.129	23080541	487129	49.035	50.938
2	23.237	23989058	469196	50.965	49.062
Total		47069599	956325	100.000	100.000

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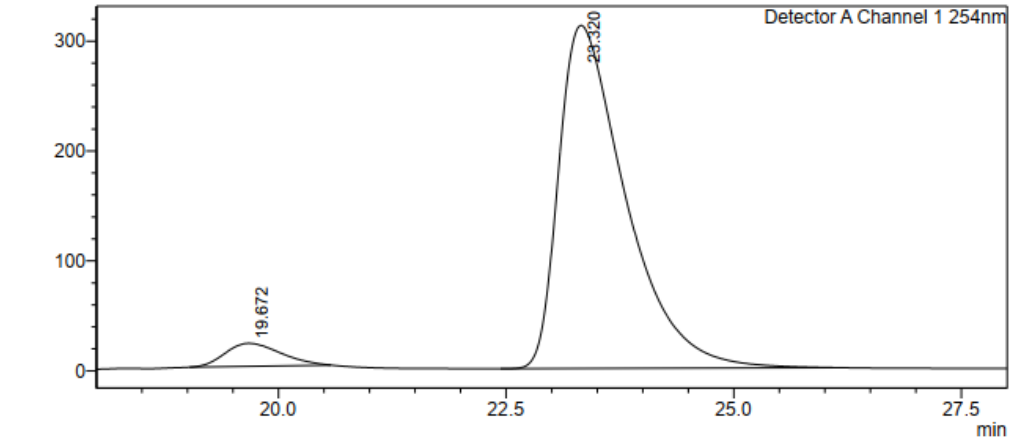
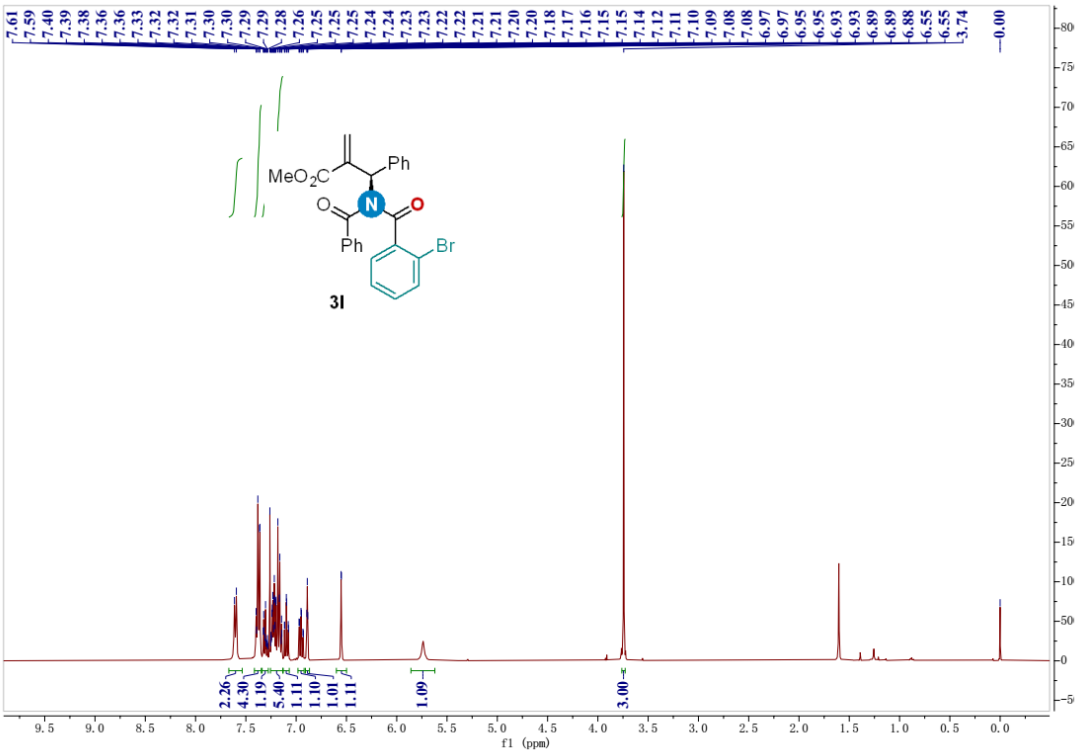
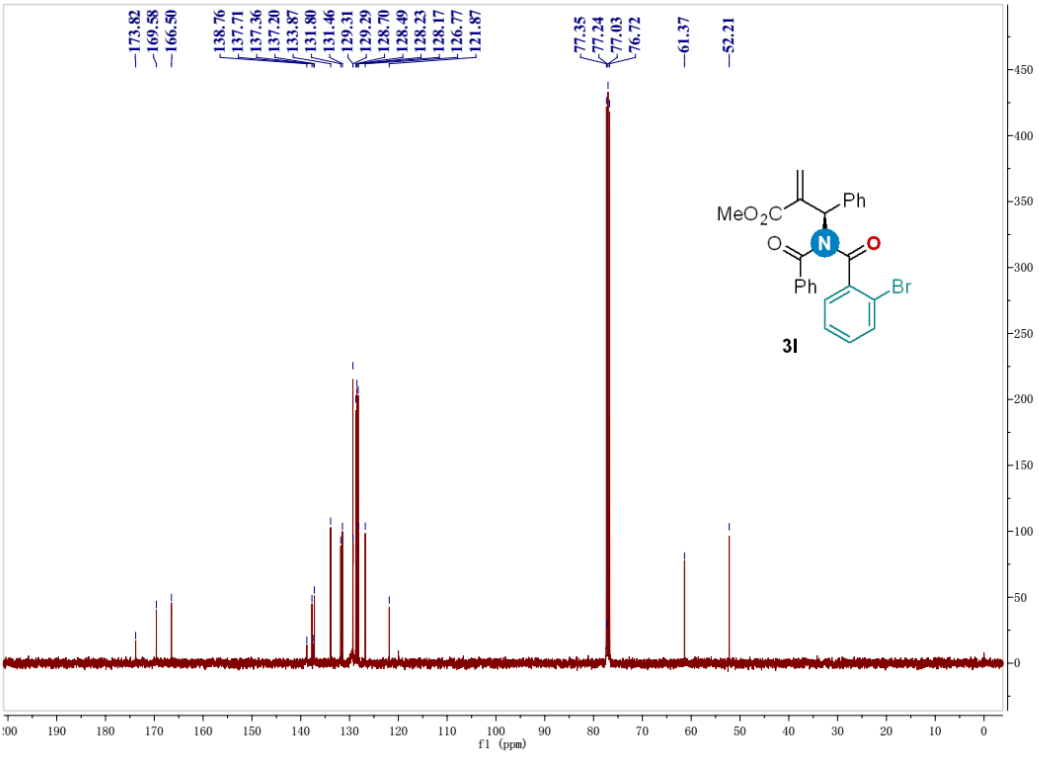


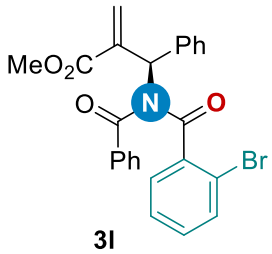
Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.672	889150	20892	5.268	6.274
2	23.320	15989155	312097	94.732	93.726
Total		16878305	332989	100.000	100.000



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



^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



3l

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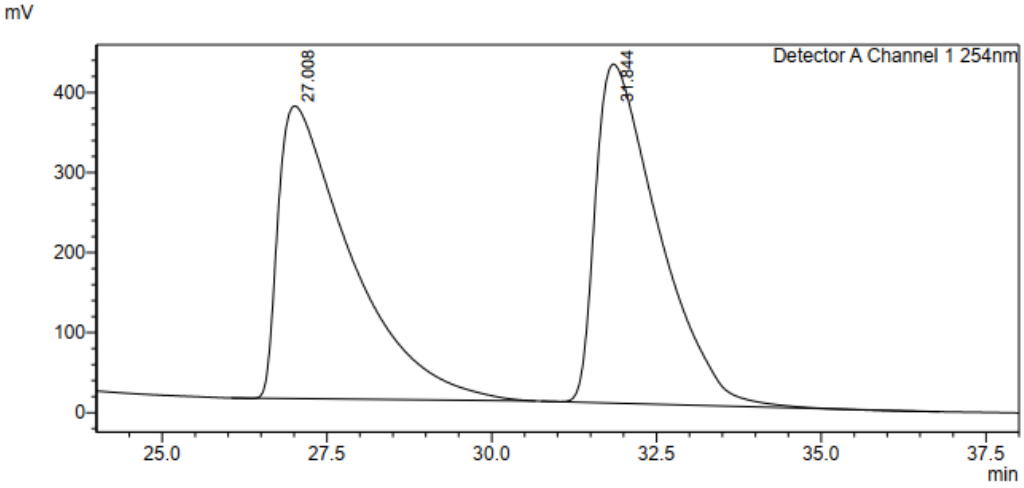

Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.008	28129907	365510	49.901	46.333
2	31.844	28242083	423361	50.099	53.667
Total		56371990	788872	100.000	100.000

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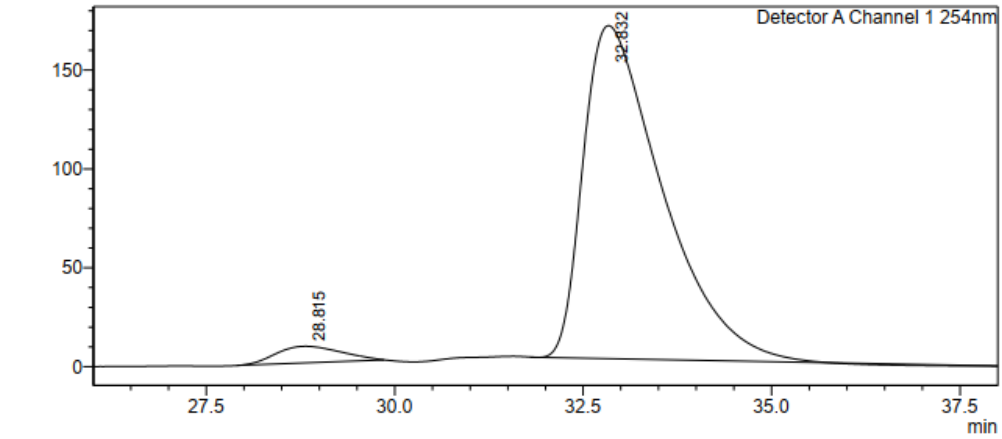
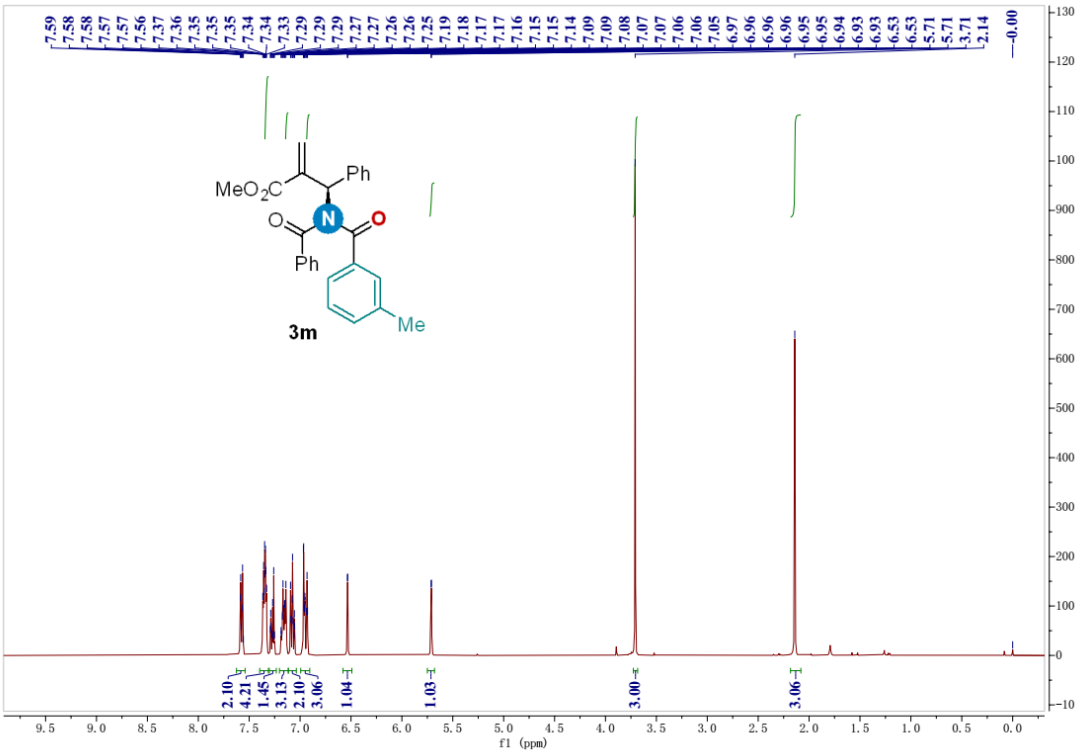
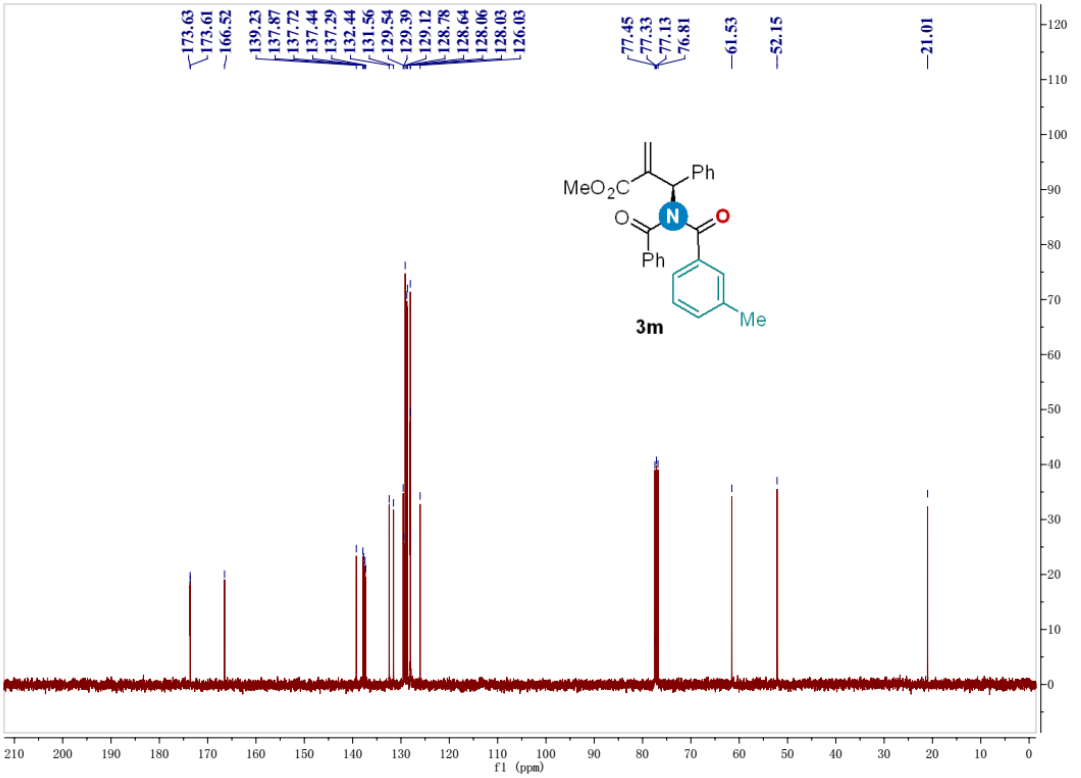


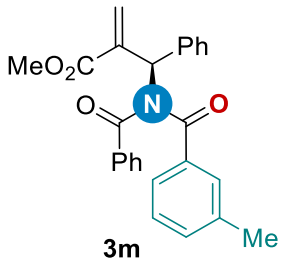
Peak#	Ret. Time	Area	Height	Area%	Height%
1	28.815	502595	8382	3.943	4.742
2	32.832	12245353	168395	96.057	95.258
Total		12747948	176777	100.000	100.000



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



^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



3m

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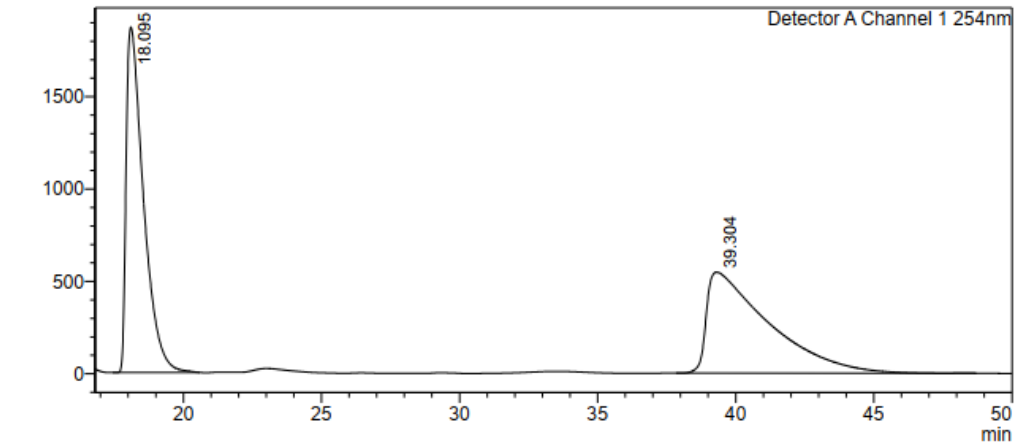

Peak#	Ret. Time	Area	Height	Area%	Height%
1	18.095	81561545	1868425	48.880	77.386
2	39.304	85299609	546003	51.120	22.614
Total		166861153	2414428	100.000	100.000

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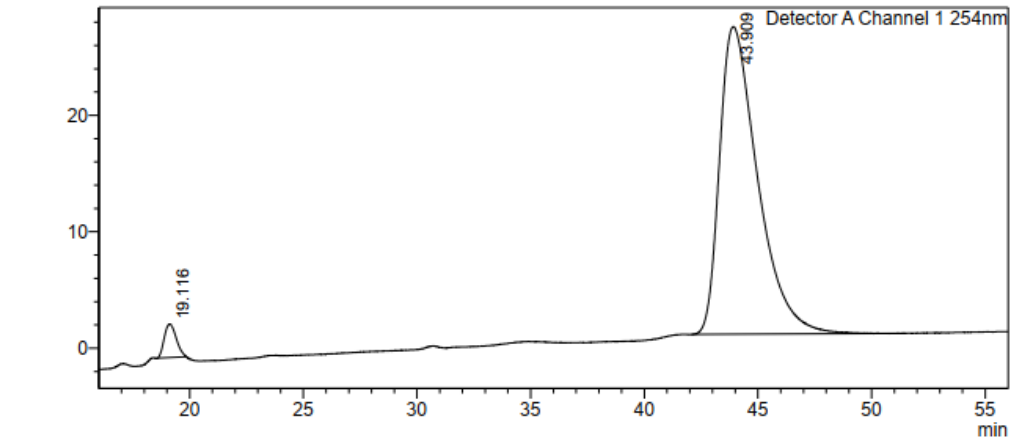
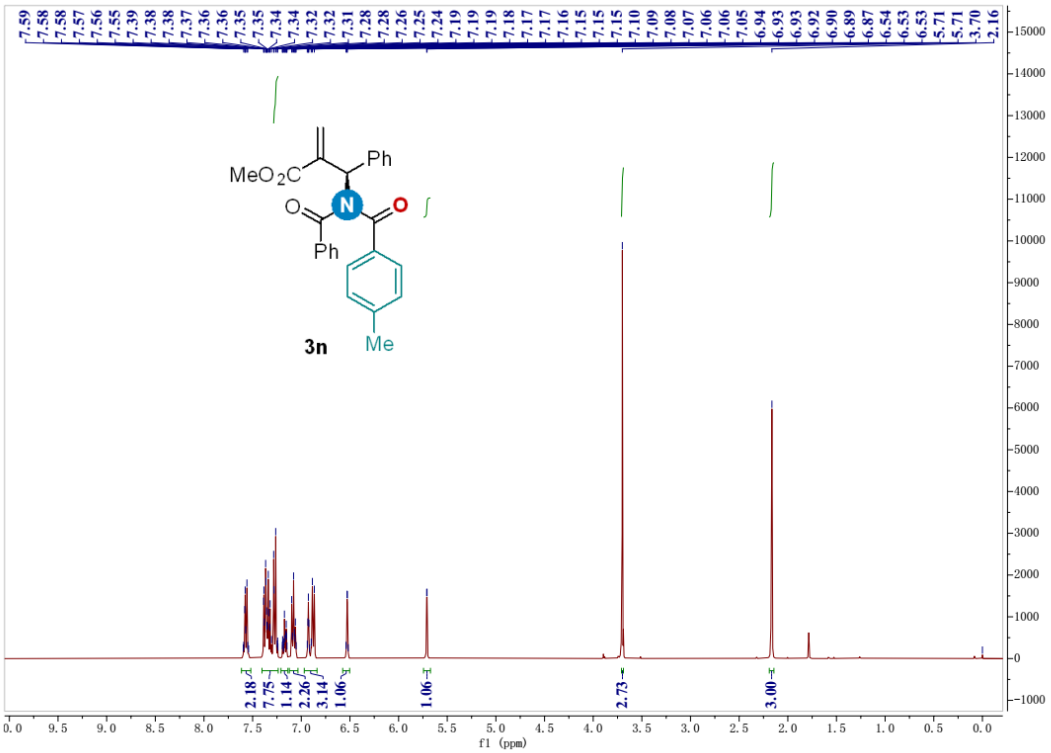
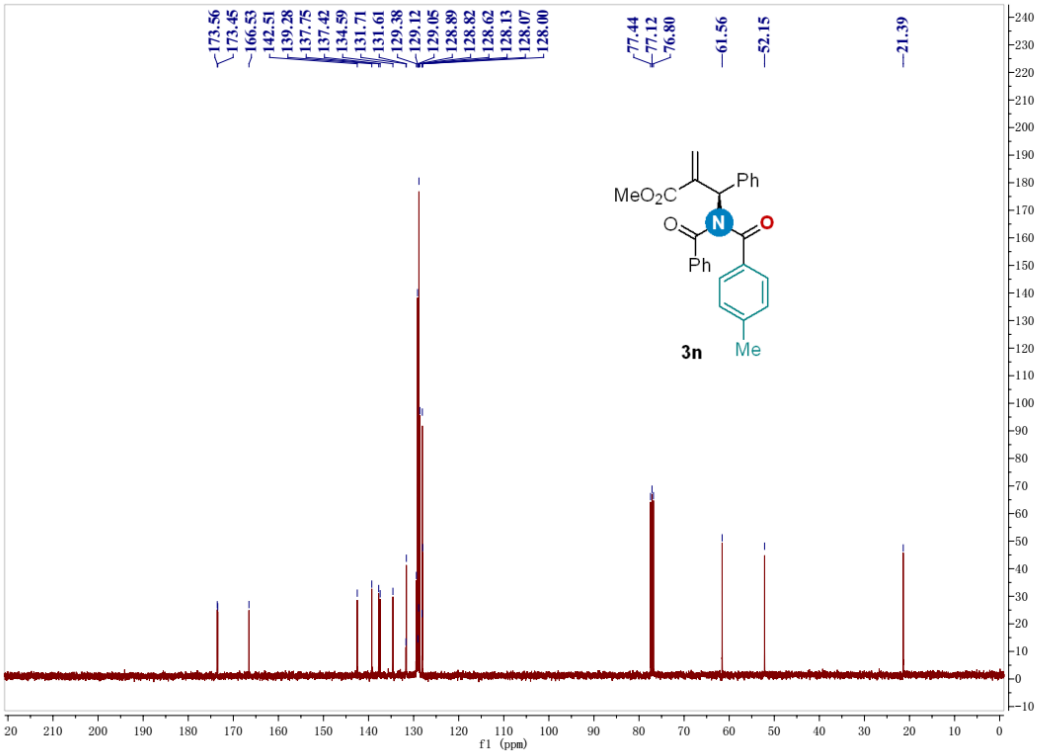


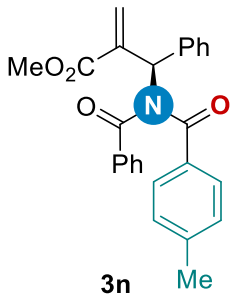
Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.116	104457	2867	3.279	9.793
2	43.909	3080955	26408	96.721	90.207
Total		3185411	29274	100.000	100.000



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



^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$)



3n

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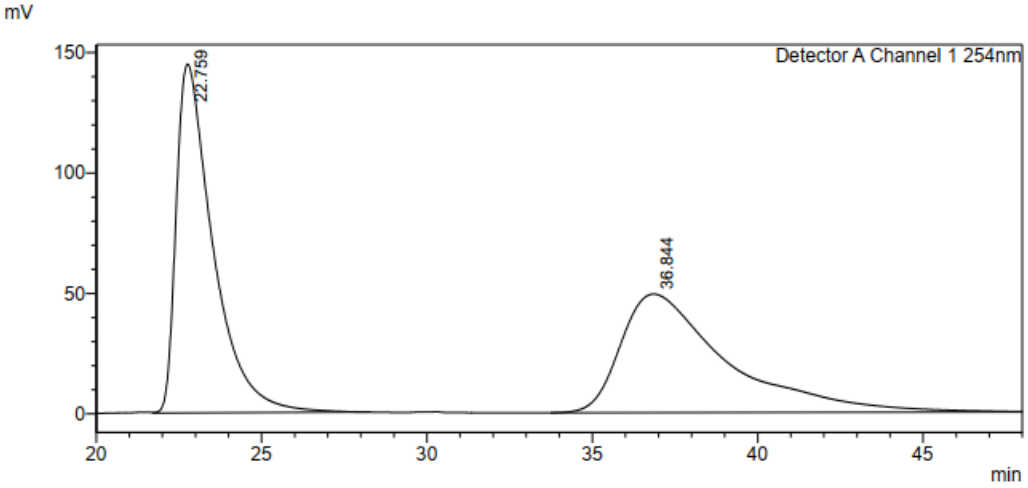

Peak#	Ret. Time	Area	Height	Area%	Height%
1	22.759	11215341	144777	50.516	74.613
2	36.844	10986016	49259	49.484	25.387
Total		22201357	194036	100.000	100.000

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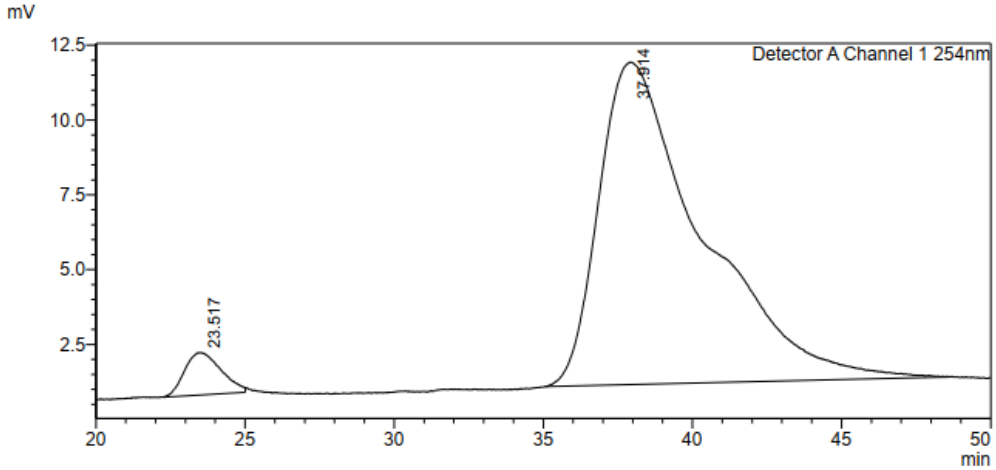
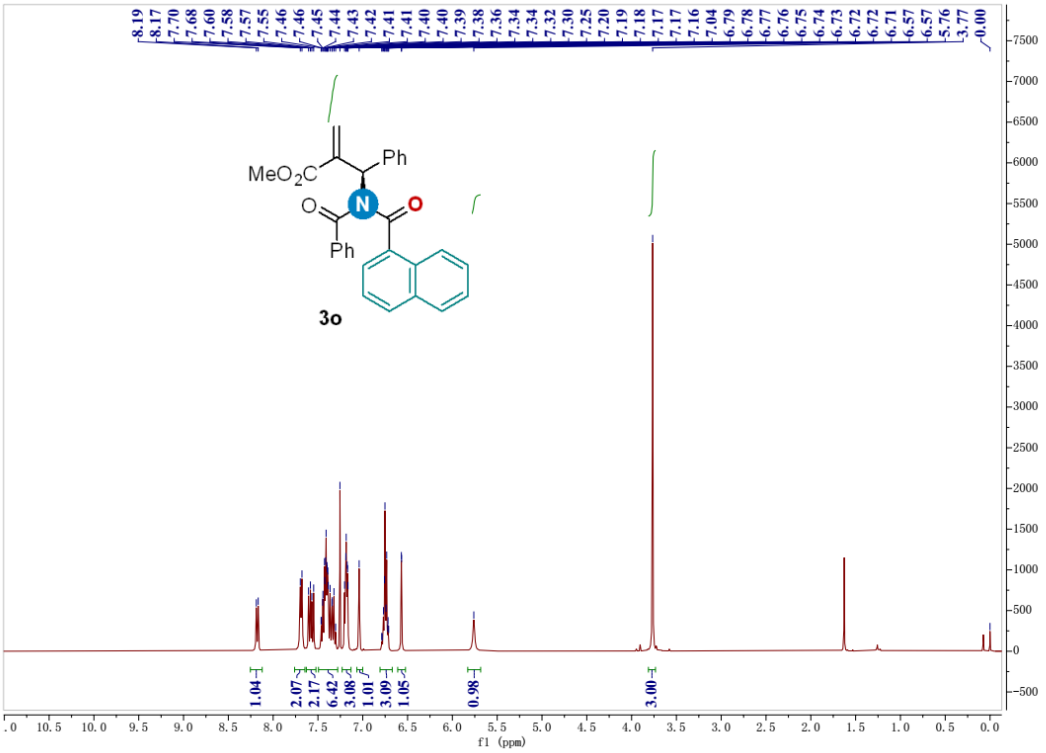
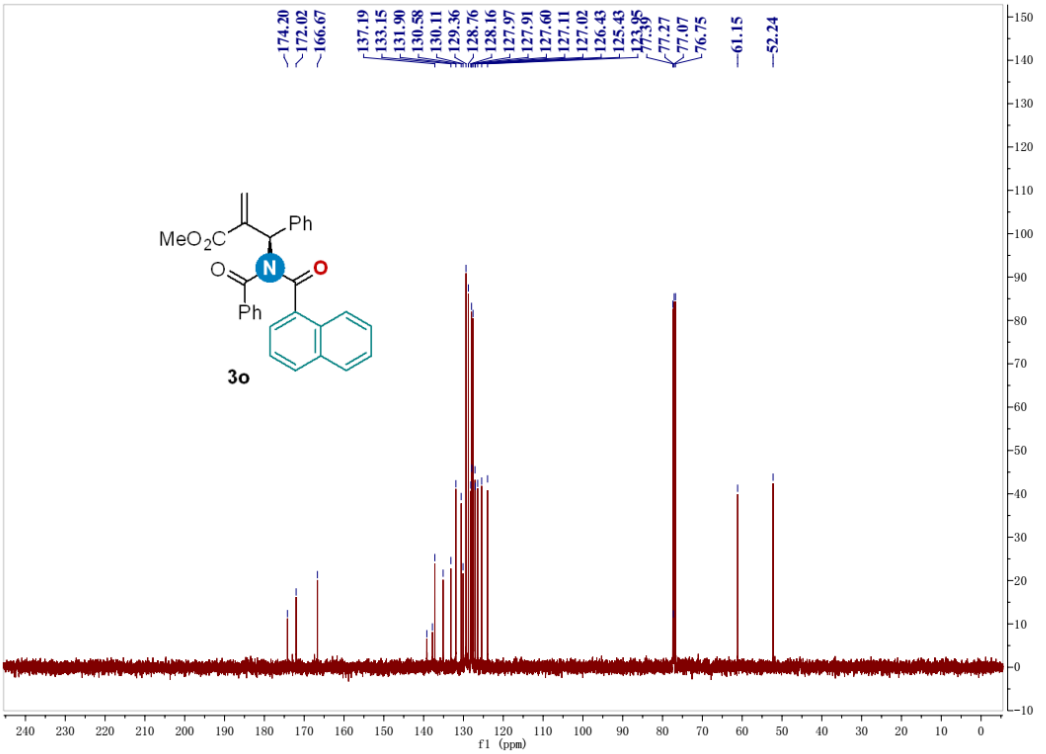


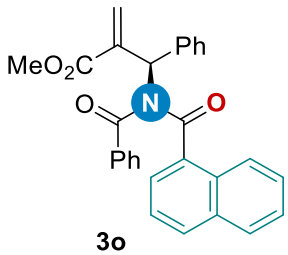
Peak#	Ret. Time	Area	Height	Area%	Height%
1	23.517	120211	1410	4.428	11.578
2	37.914	2594871	10767	95.572	88.422
Total		2715082	12177	100.000	100.000



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



^{13}C NMR spectrum of **3o** (100 MHz, $CDCl_3$)



3o

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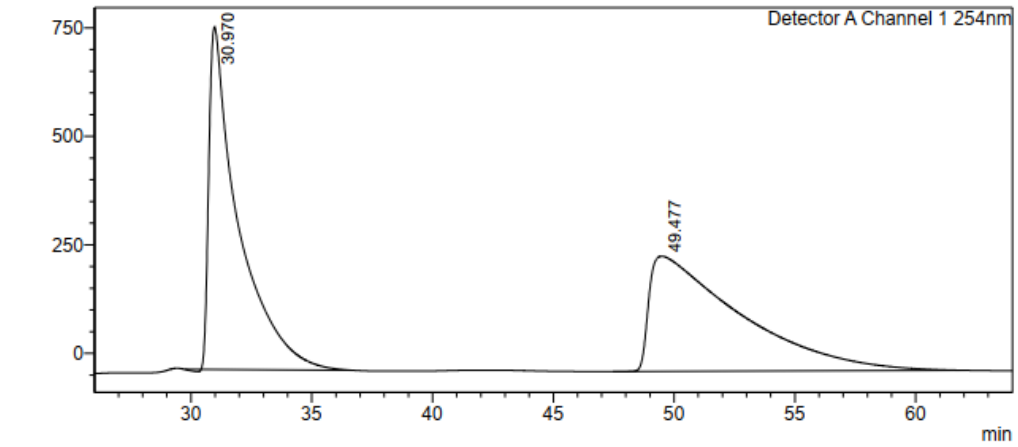

Peak#	Ret. Time	Area	Height	Area%	Height%
1	30.970	66614868	789340	49.029	74.834
2	49.477	69253194	265451	50.971	25.166
Total		135868062	1054791	100.000	100.000

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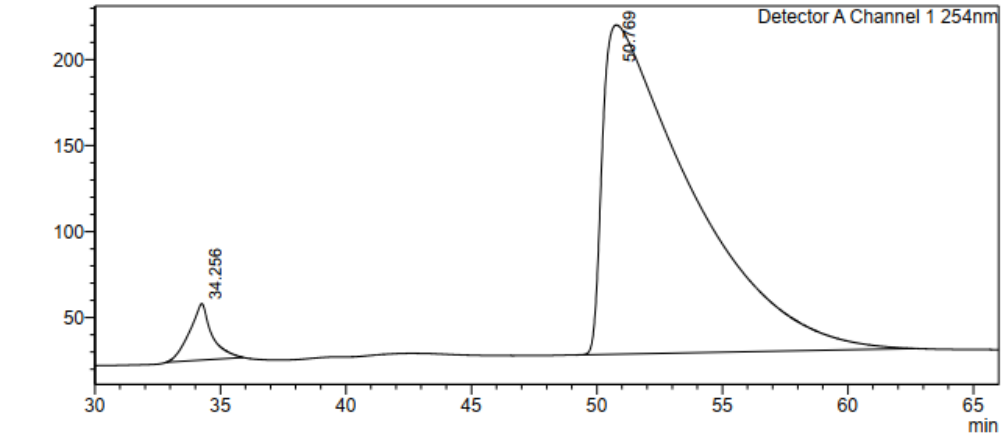
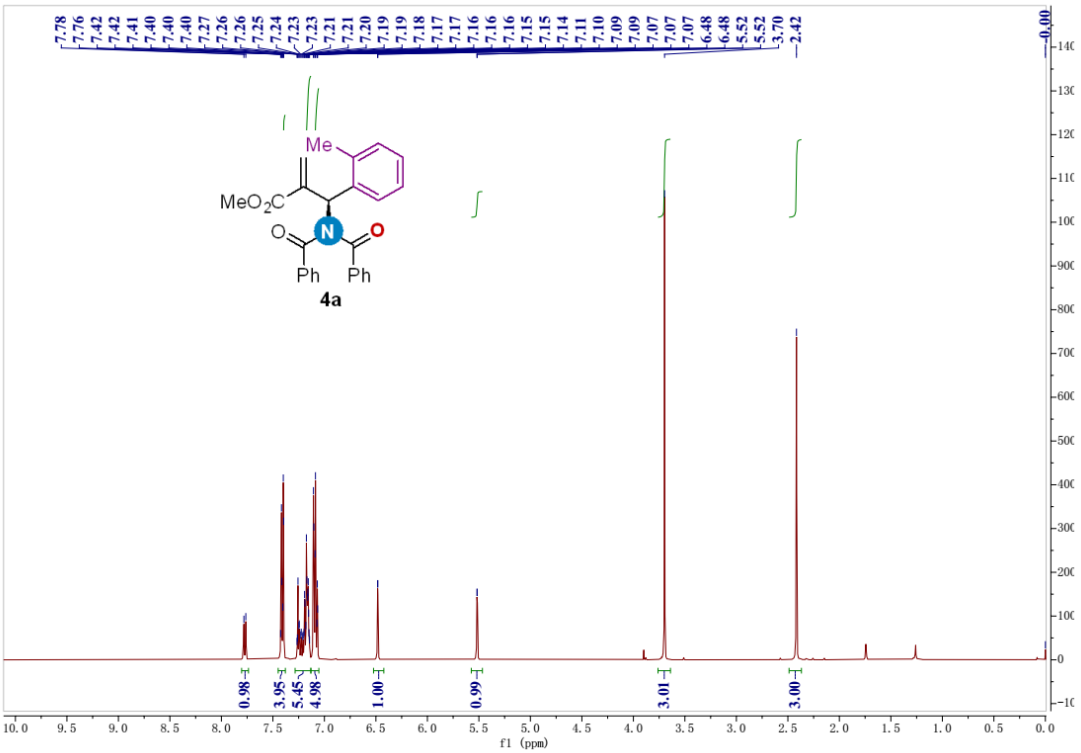
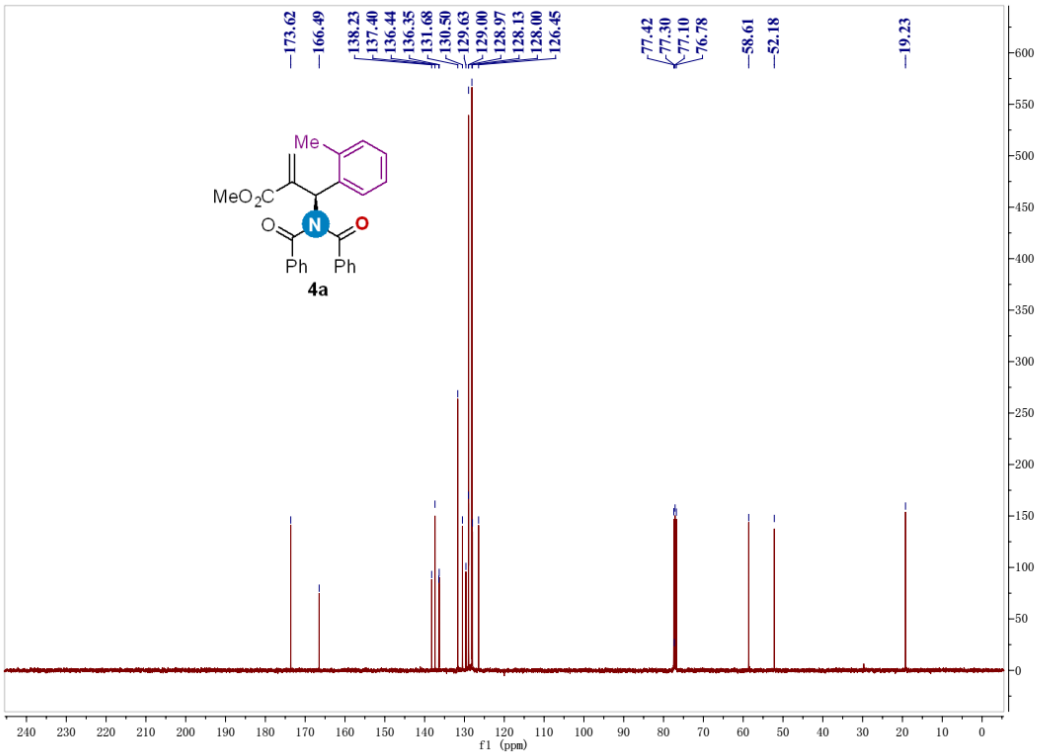


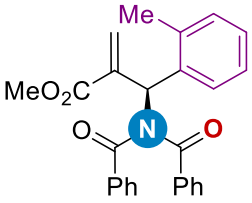
Peak#	Ret. Time	Area	Height	Area%	Height%
1	34.256	2024517	32815	4.120	14.632
2	50.769	47114549	191450	95.880	85.368
Total		49139067	224264	100.000	100.000



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

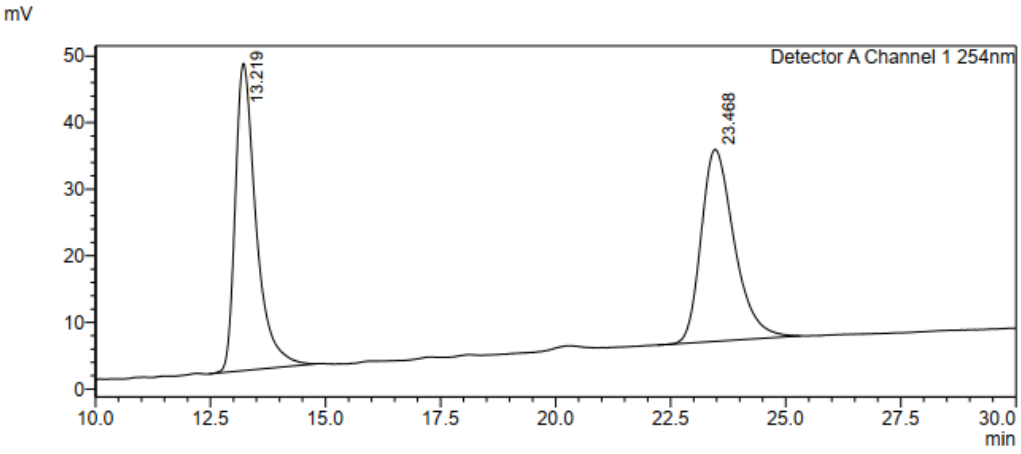


^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



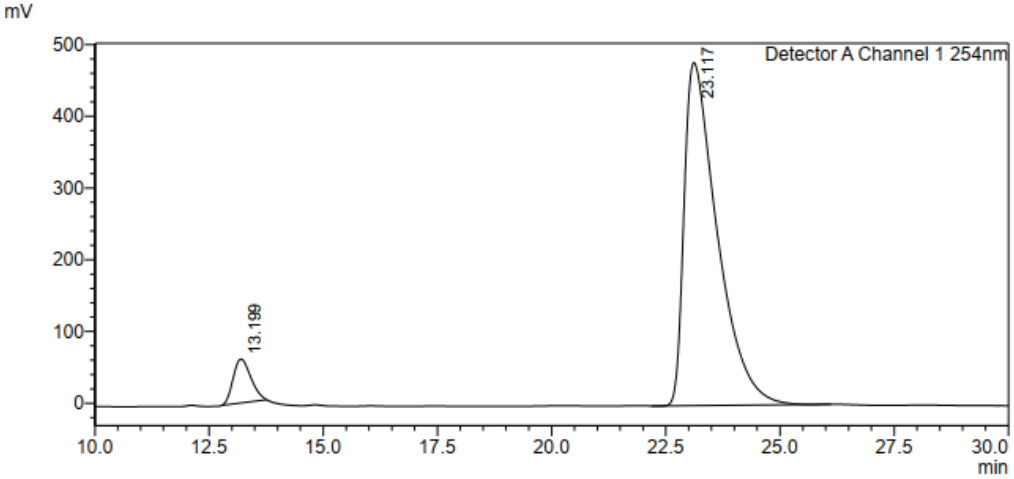
4a

<Chromatogram>

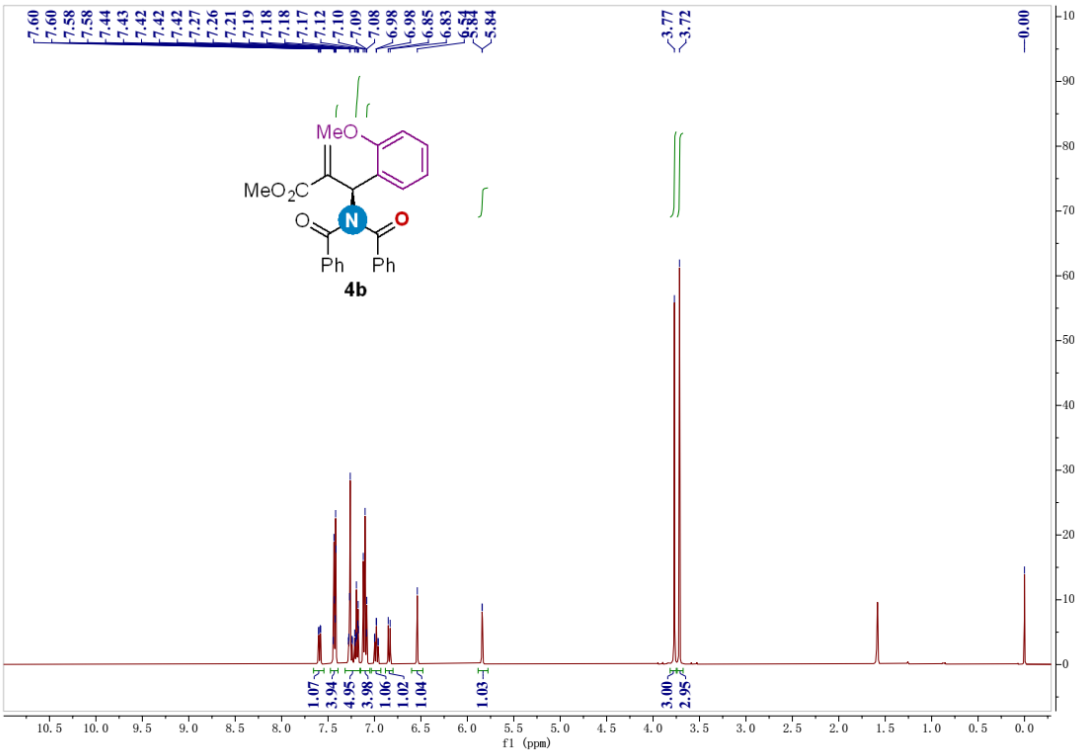


Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.219	1455370	46113	50.207	61.537
2	23.468	1443364	28822	49.793	38.463
Total		2898734	74935	100.000	100.000

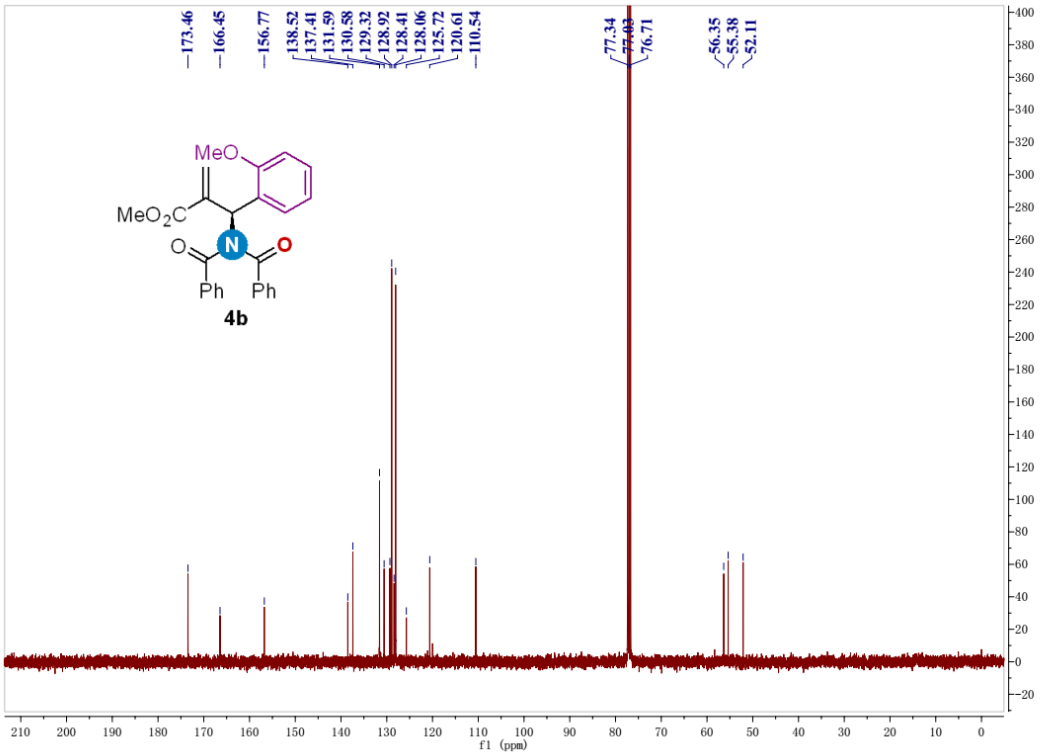
<Chromatogram>



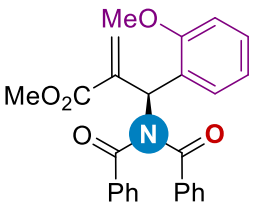
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.199	1639542	60953	6.366	11.307
2	23.117	24114414	478129	93.634	88.693
Total		25753956	539083	100.000	100.000



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



^{13}C NMR spectrum of **4b** (100 MHz, $CDCl_3$)



4b

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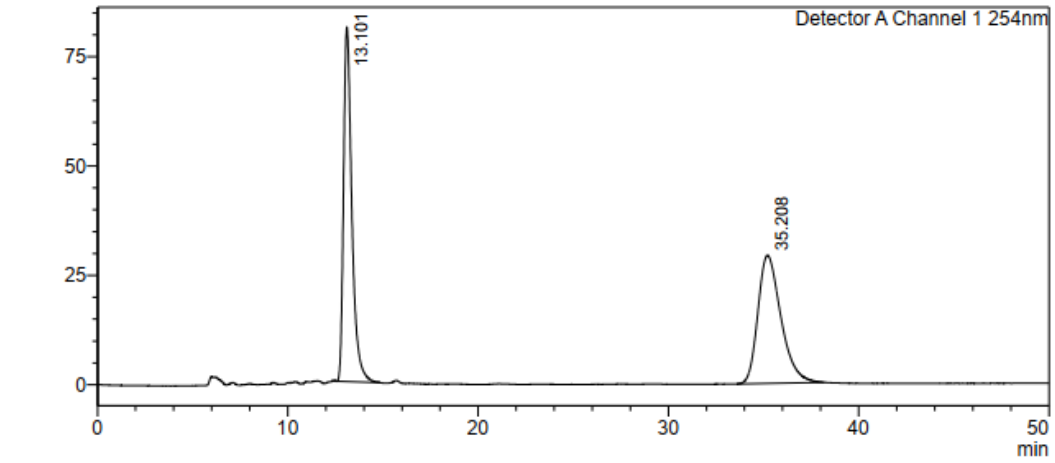
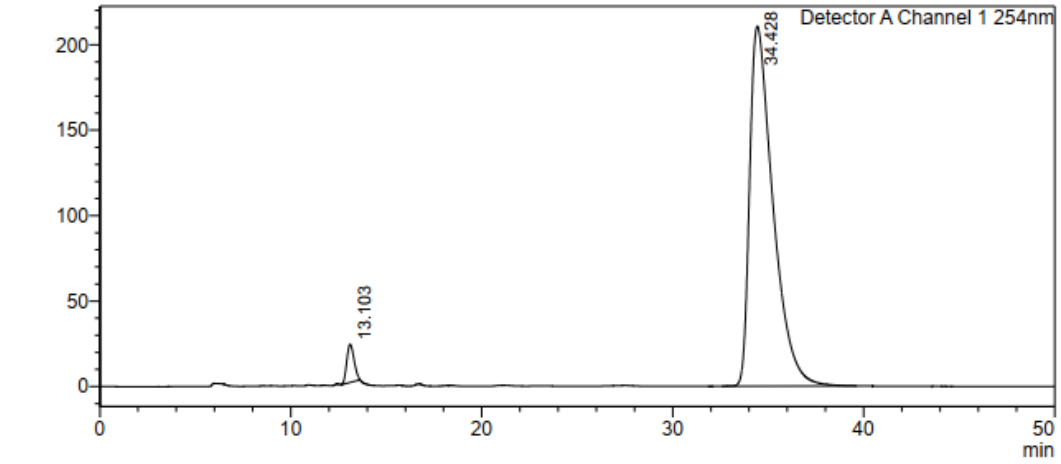
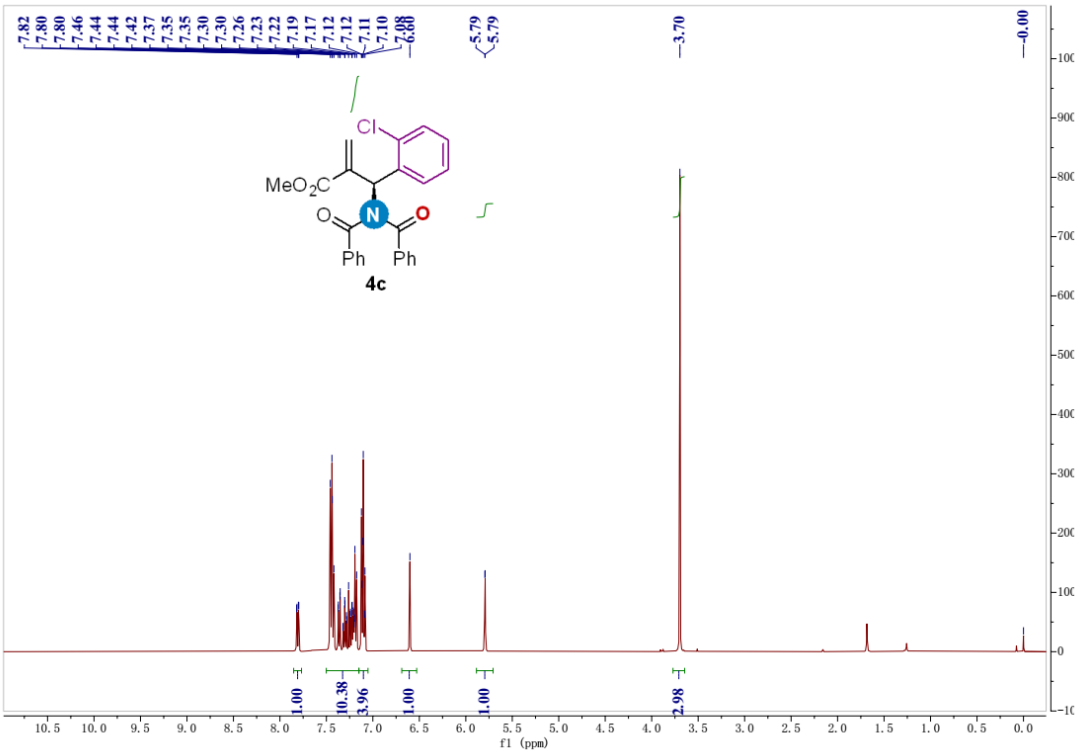


Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.101	2462164	81019	50.045	73.462
2	35.208	2457780	29268	49.955	26.538
Total		4919944	110287	100.000	100.000

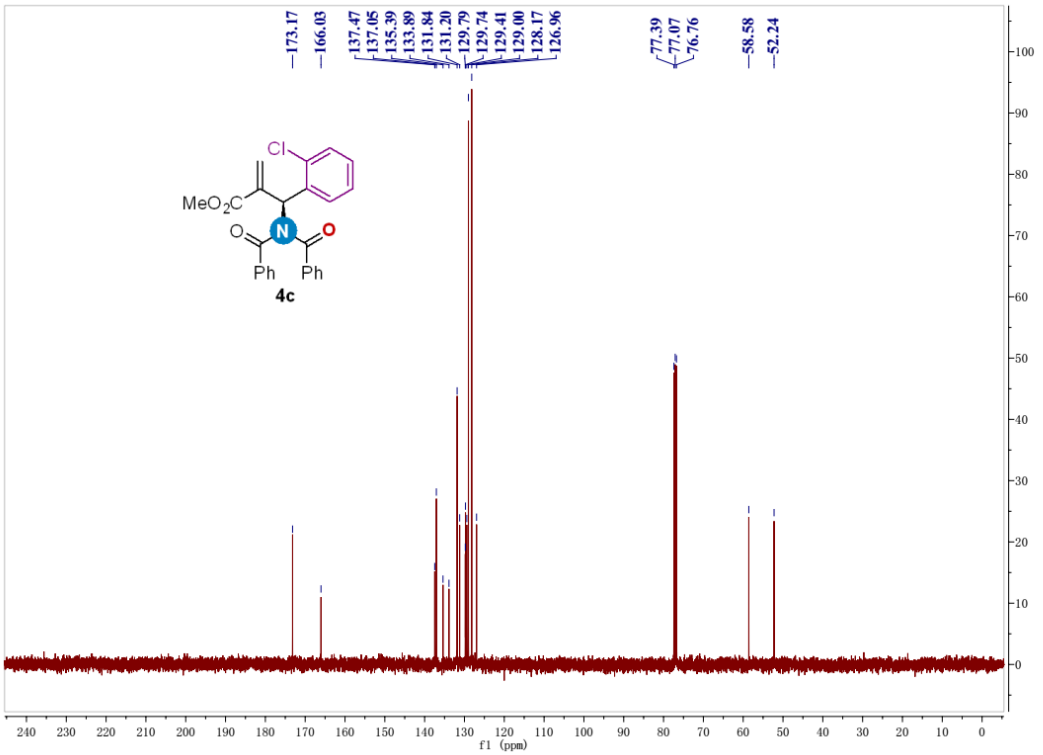
<Chromatogram>



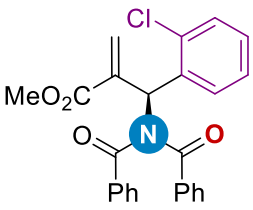
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.103	594538	22332	3.220	9.591
2	34.428	17871988	210514	96.780	90.409
Total		18466525	232847	100.000	100.000



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

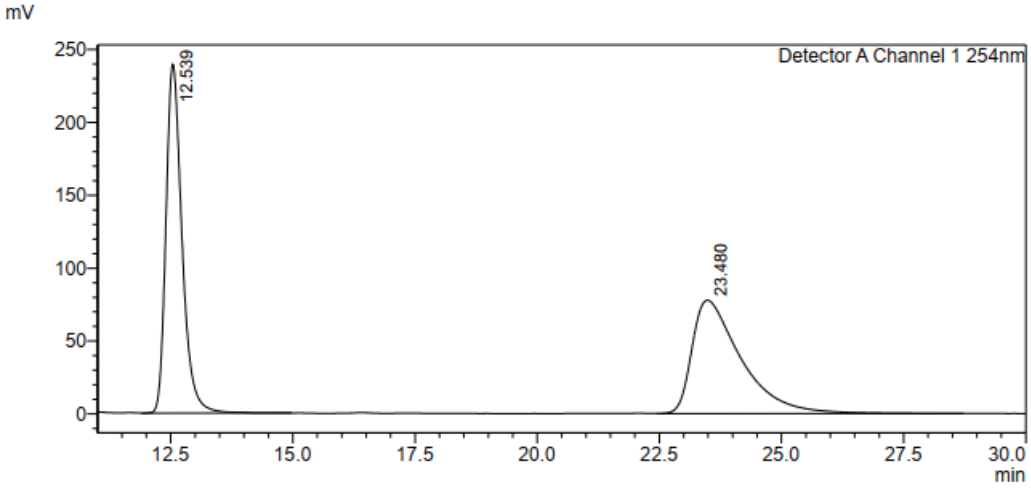


^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



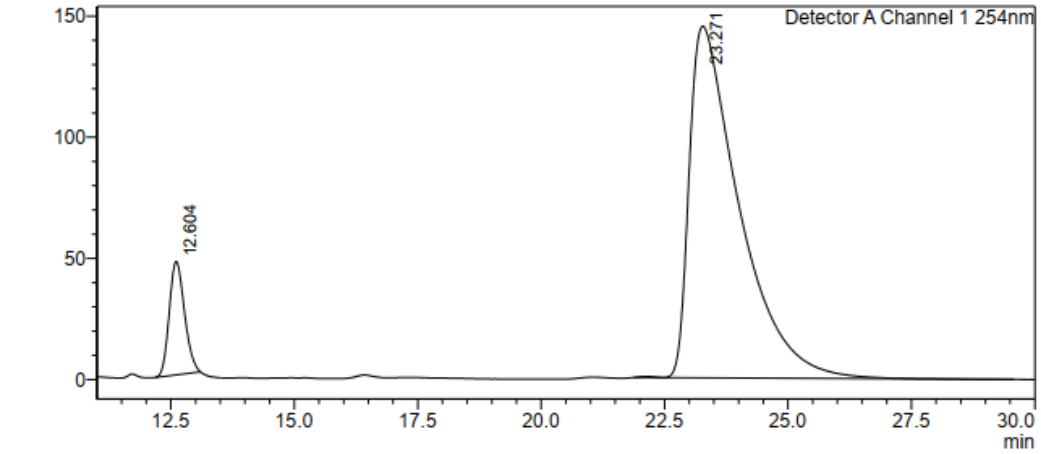
4c

<Chromatogram>

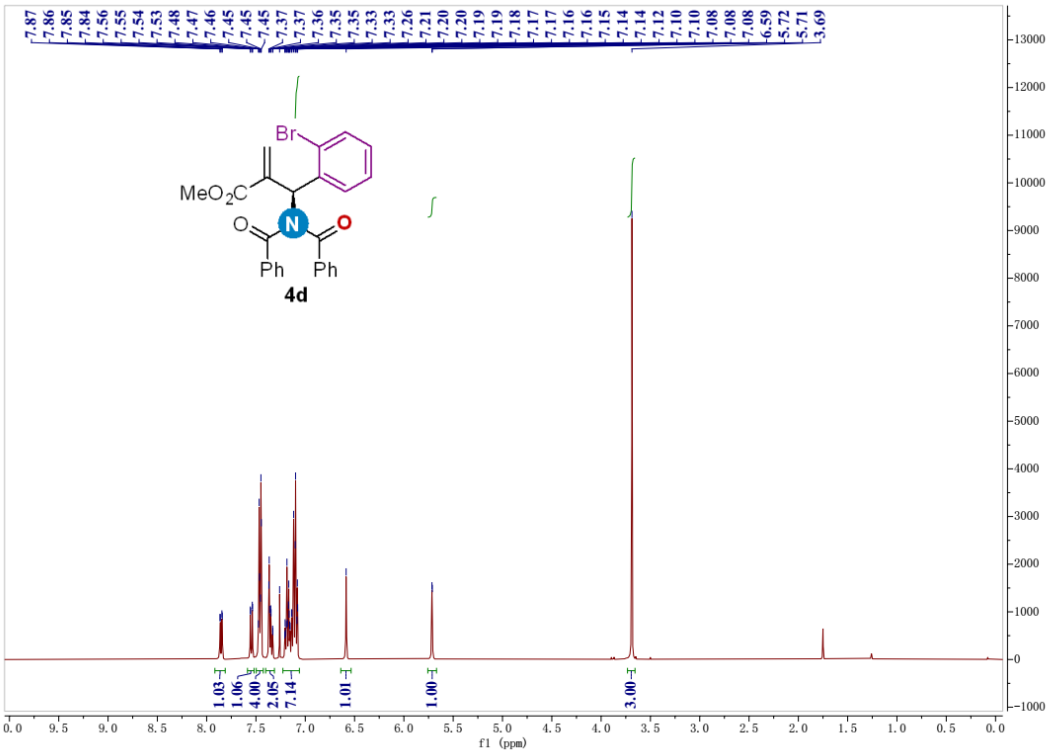


Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.539	5462502	239173	50.143	75.473
2	23.480	5431377	77726	49.857	24.527
Total		10893880	316898	100.000	100.000

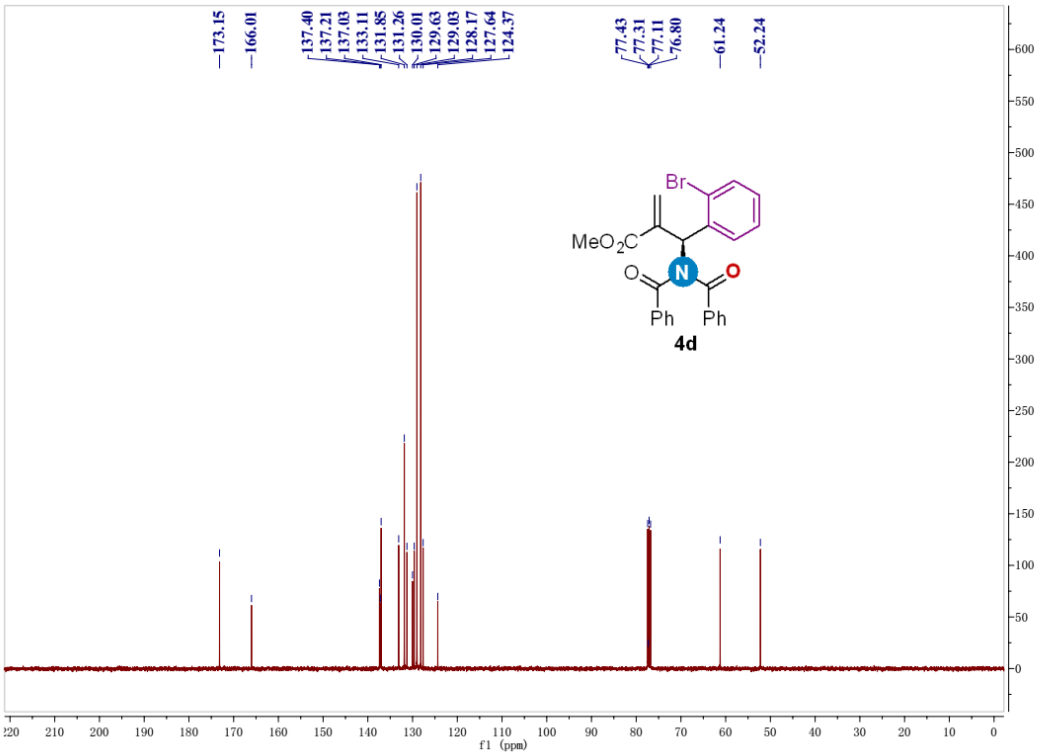
<Chromatogram>



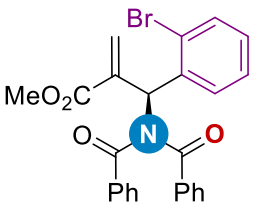
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.604	1007948	46860	8.982	24.395
2	23.271	10213817	145228	91.018	75.605
Total		11221765	192088	100.000	100.000



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

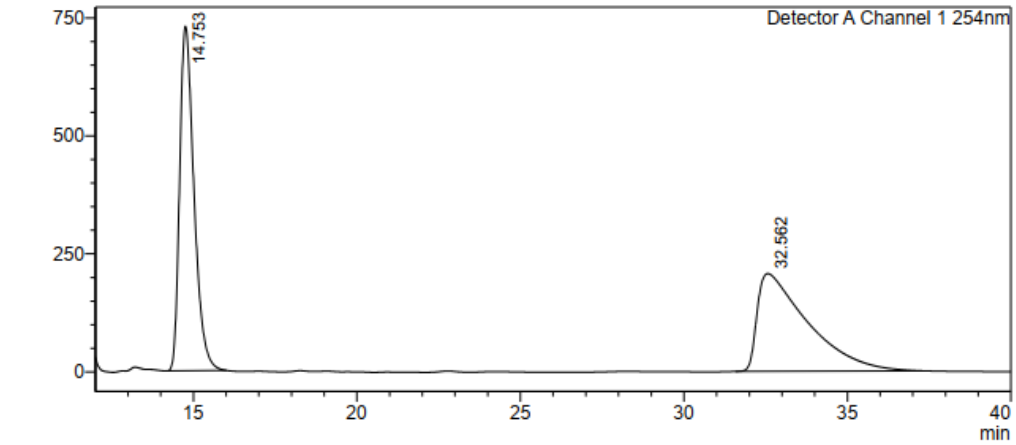


^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



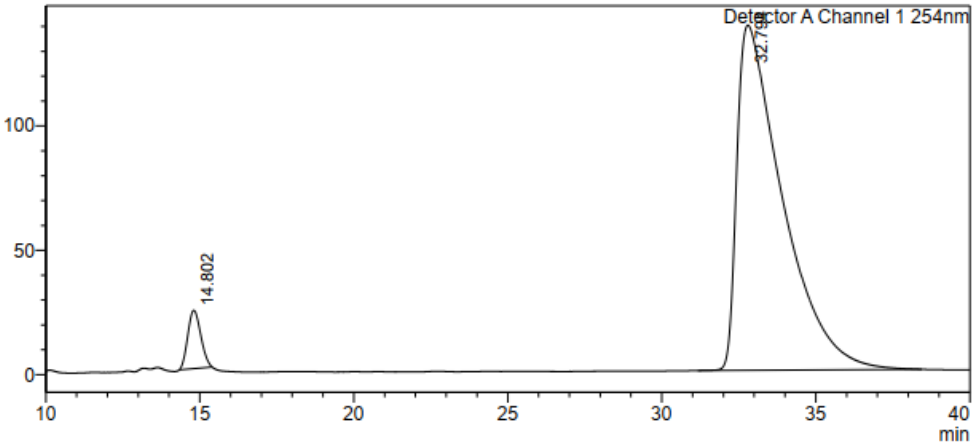
4d

<Chromatogram>

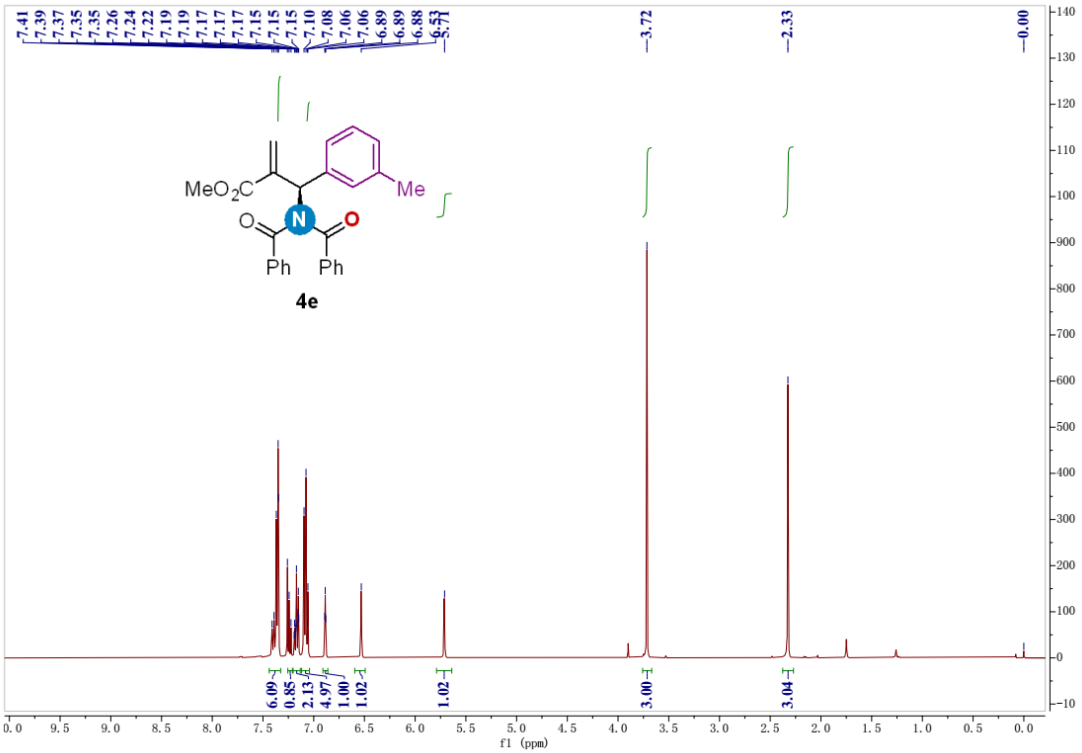


Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.753	22242144	729834	50.069	77.901
2	32.562	22180536	207037	49.931	22.099
Total		44422680	936871	100.000	100.000

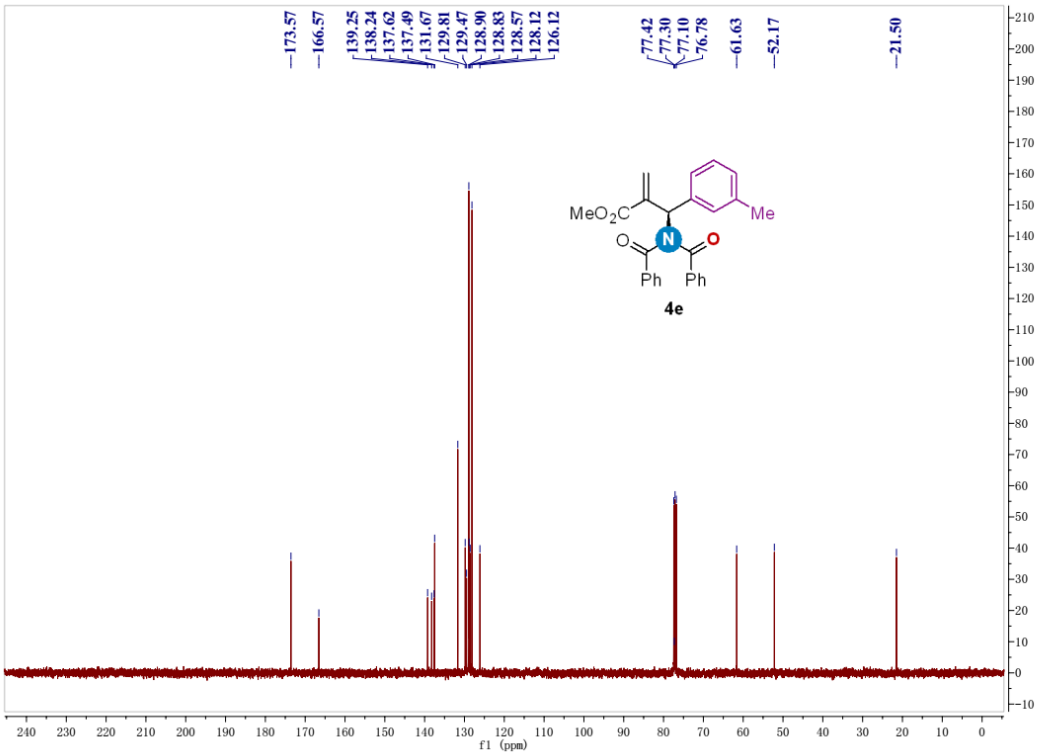
<Chromatogram>



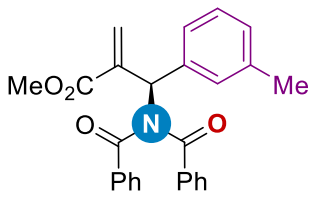
Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.802	693570	23449	4.631	14.456
2	32.794	14281945	138762	95.369	85.544
Total		14975515	162211	100.000	100.000



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



^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



4e

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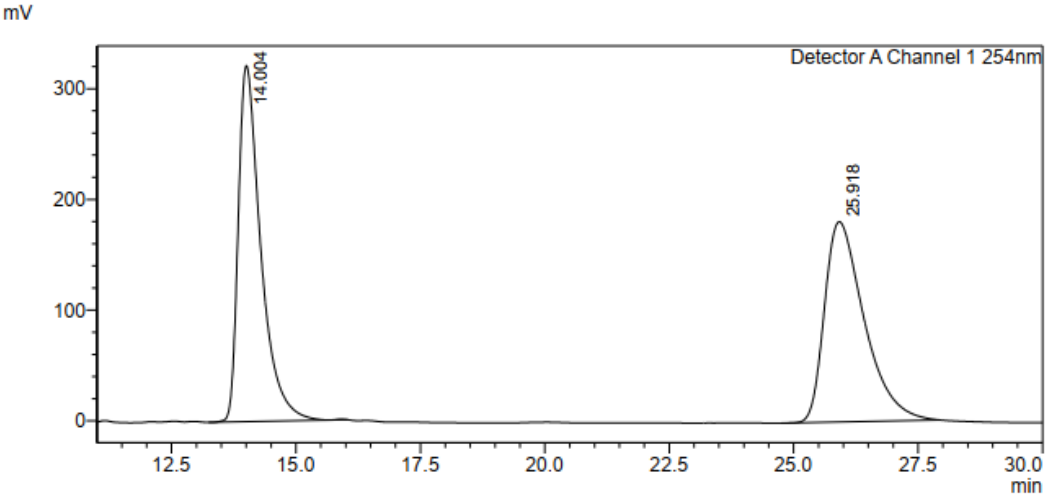

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.004	10131474	321399	50.234	63.987
2	25.918	10037171	180893	49.766	36.013
Total		20168645	502292	100.000	100.000

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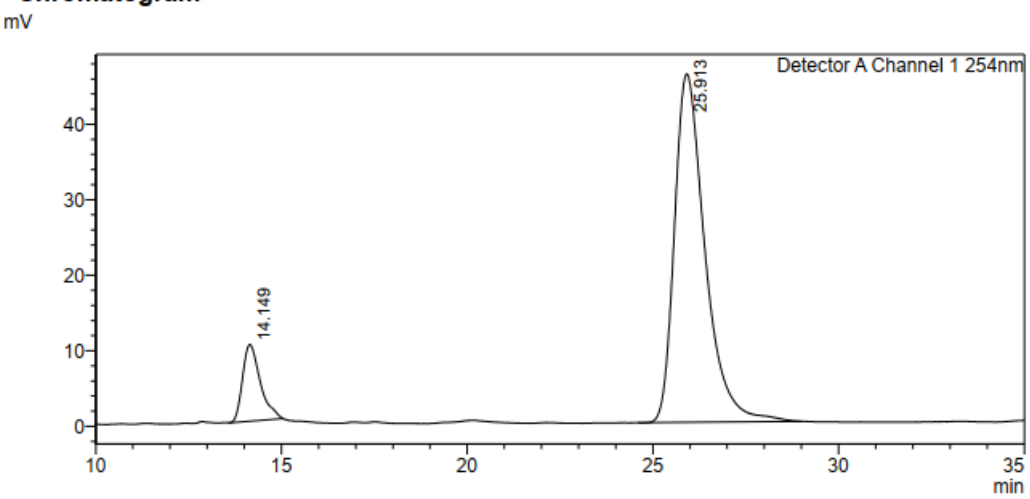
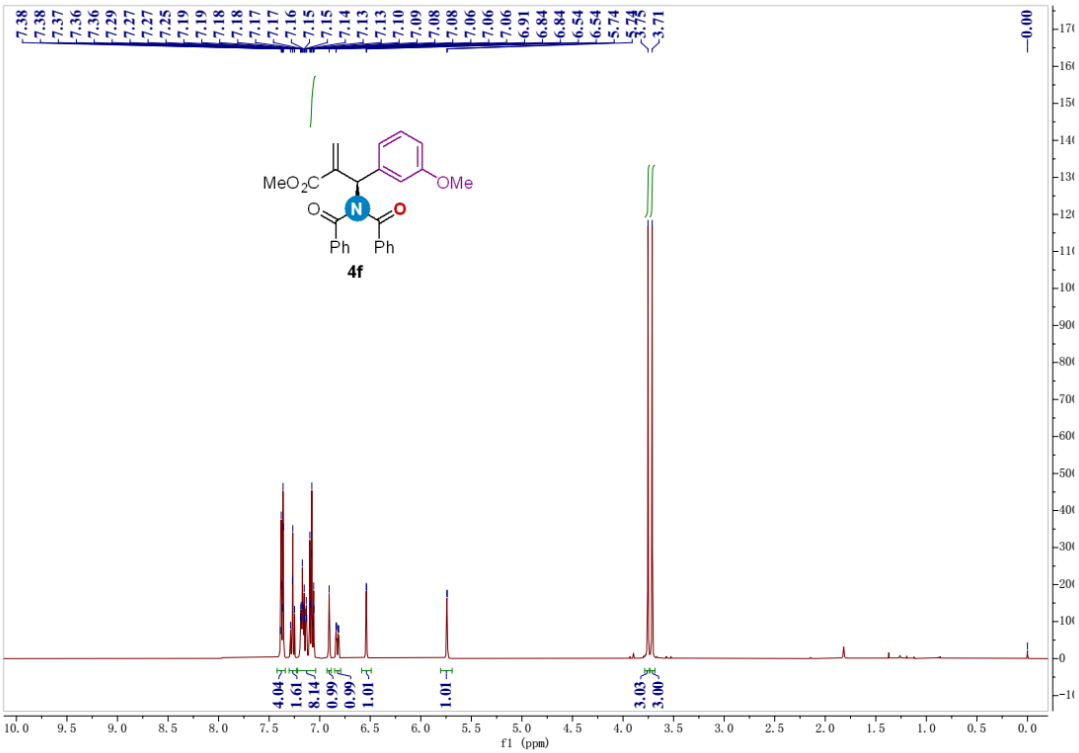
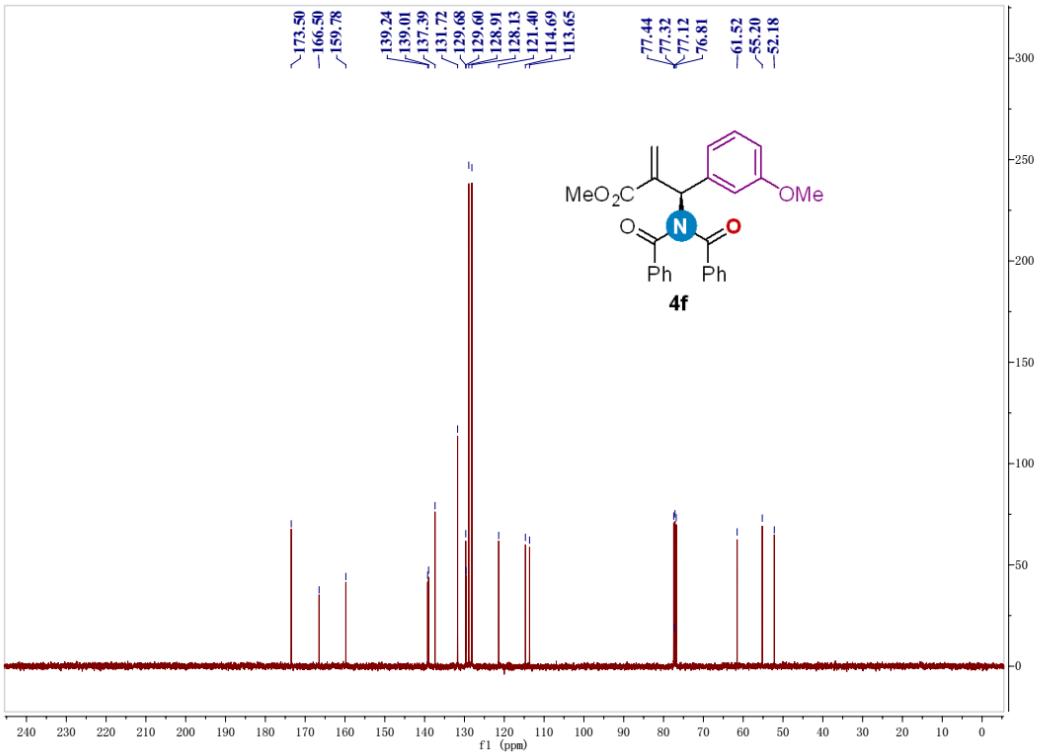


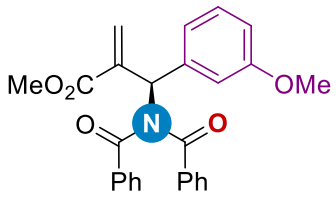
Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.149	337000	10134	11.312	18.009
2	25.913	2642041	46135	88.688	81.991
Total		2979041	56268	100.000	100.000



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



^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



4f

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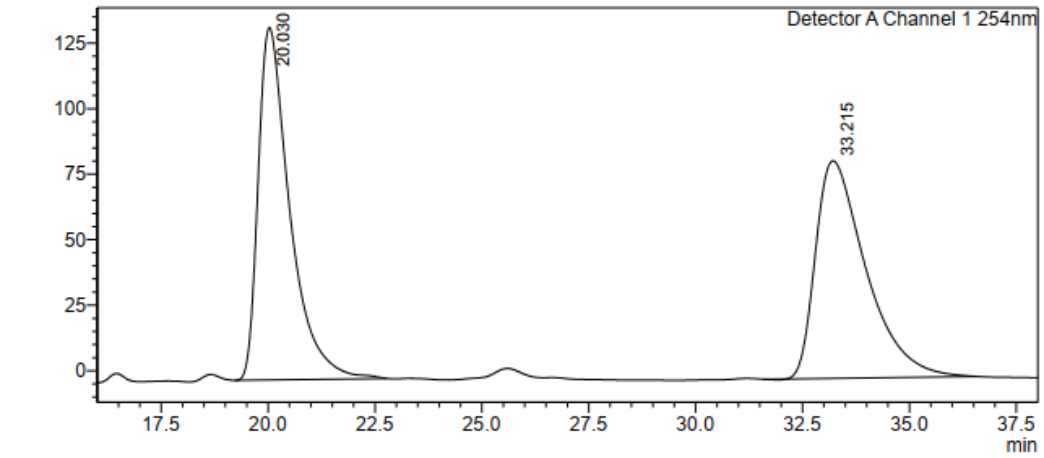

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.030	6929434	134414	50.498	61.827
2	33.215	6792655	82989	49.502	38.173
Total		13722089	217404	100.000	100.000

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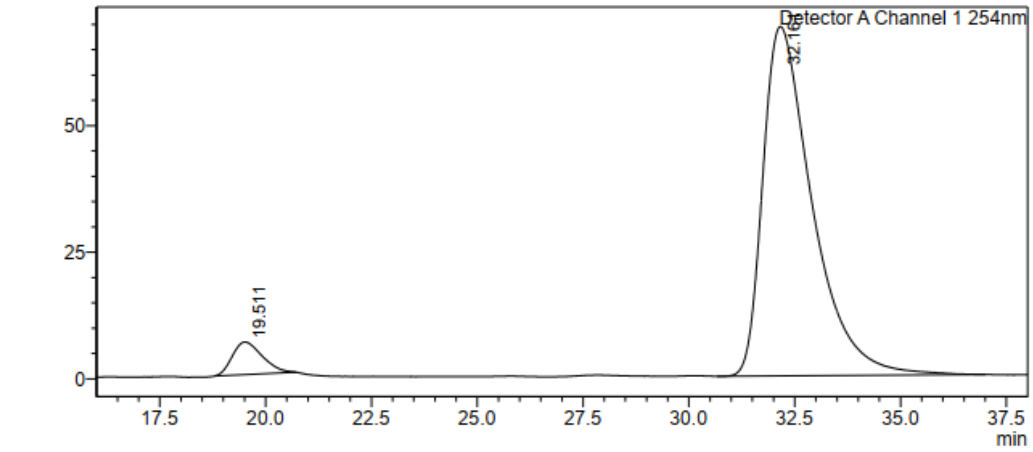
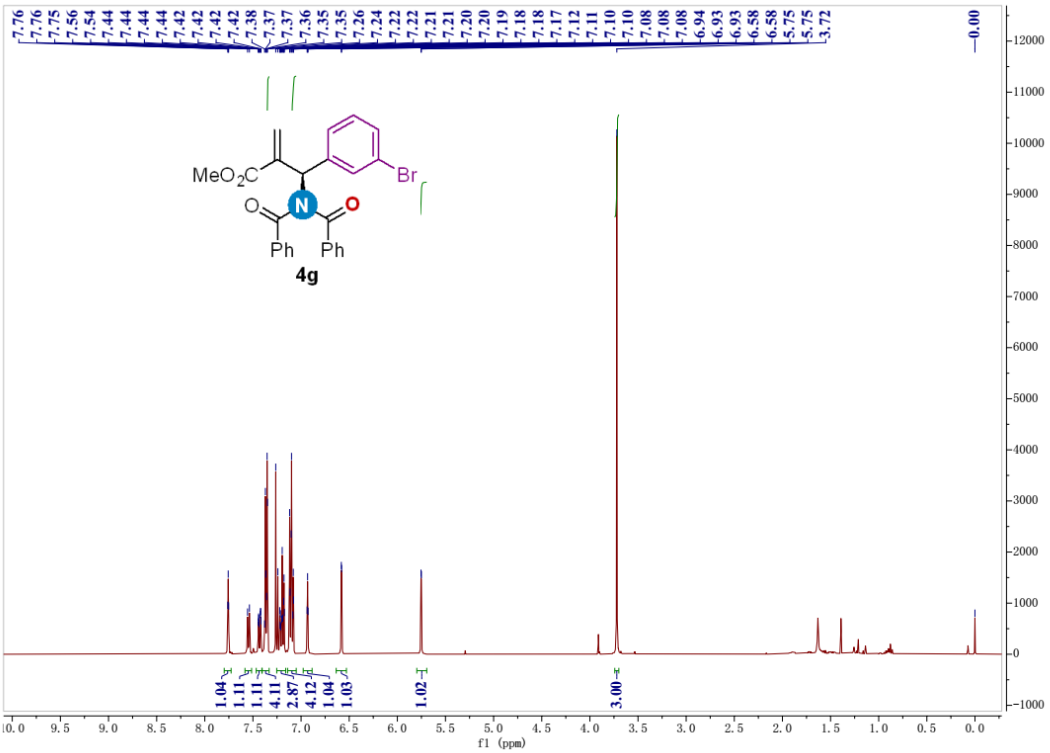
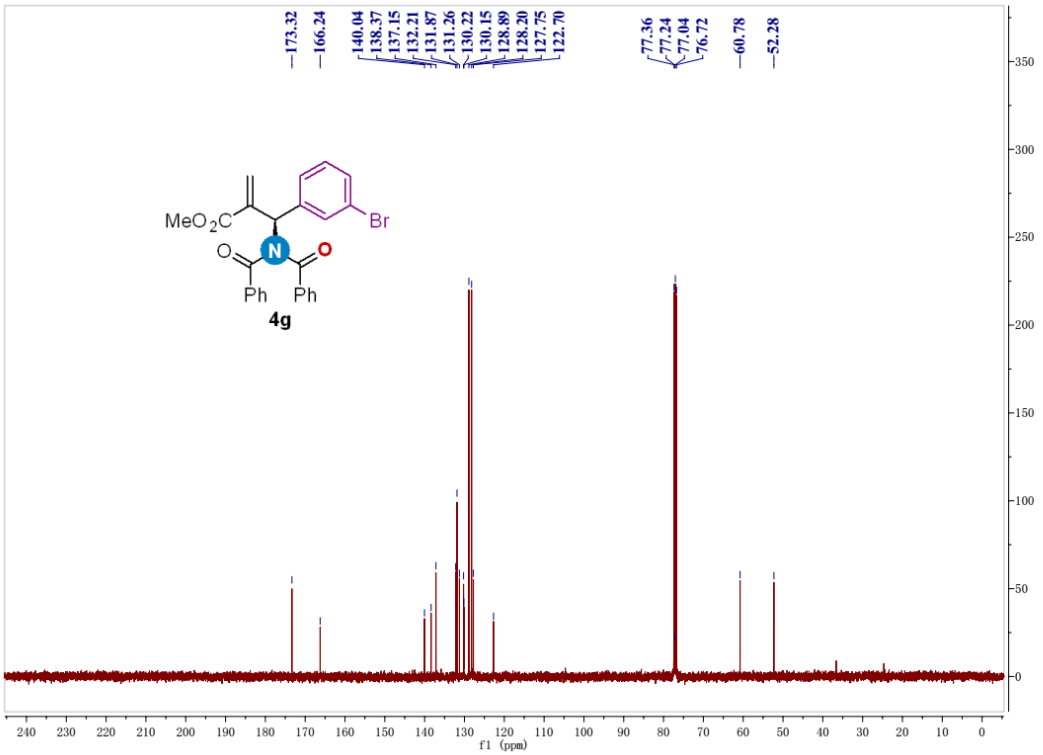


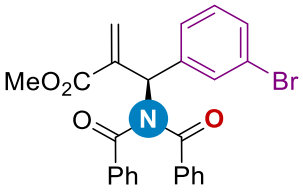
Peak#	Ret. Time	Area	Height	Area%	Height%
1	19.511	316898	6439	5.359	8.535
2	32.161	5596122	69006	94.641	91.465
Total		5913020	75445	100.000	100.000



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



^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



4g

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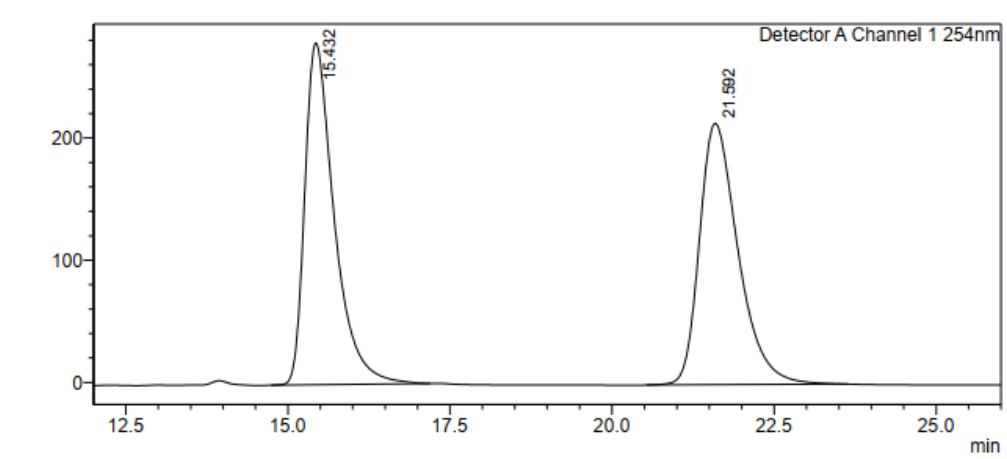

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.432	8856006	279518	49.904	56.655
2	21.592	8890080	213850	50.096	43.345
Total		17746086	493368	100.000	100.000

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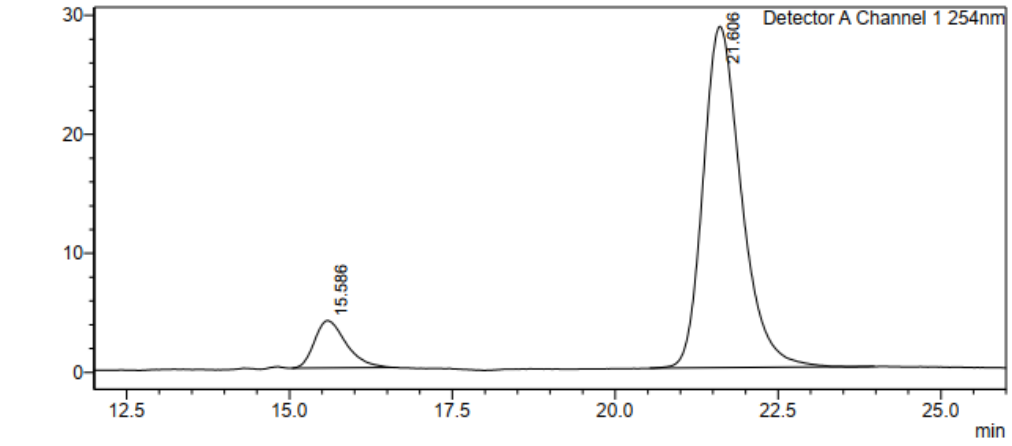
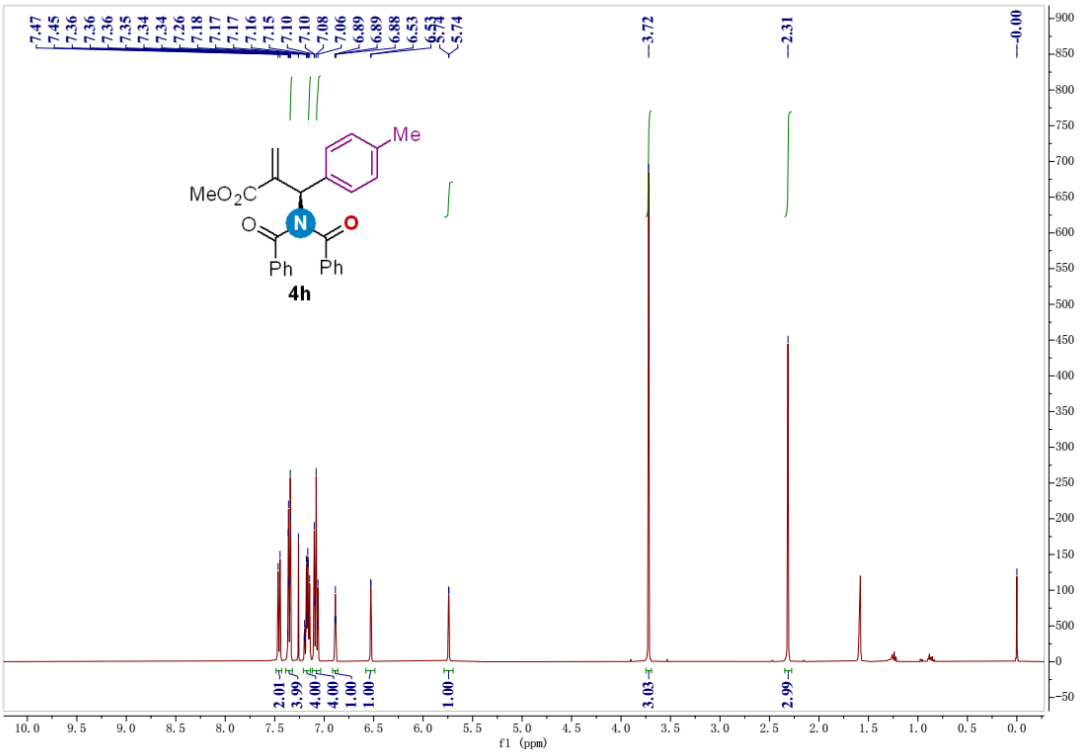
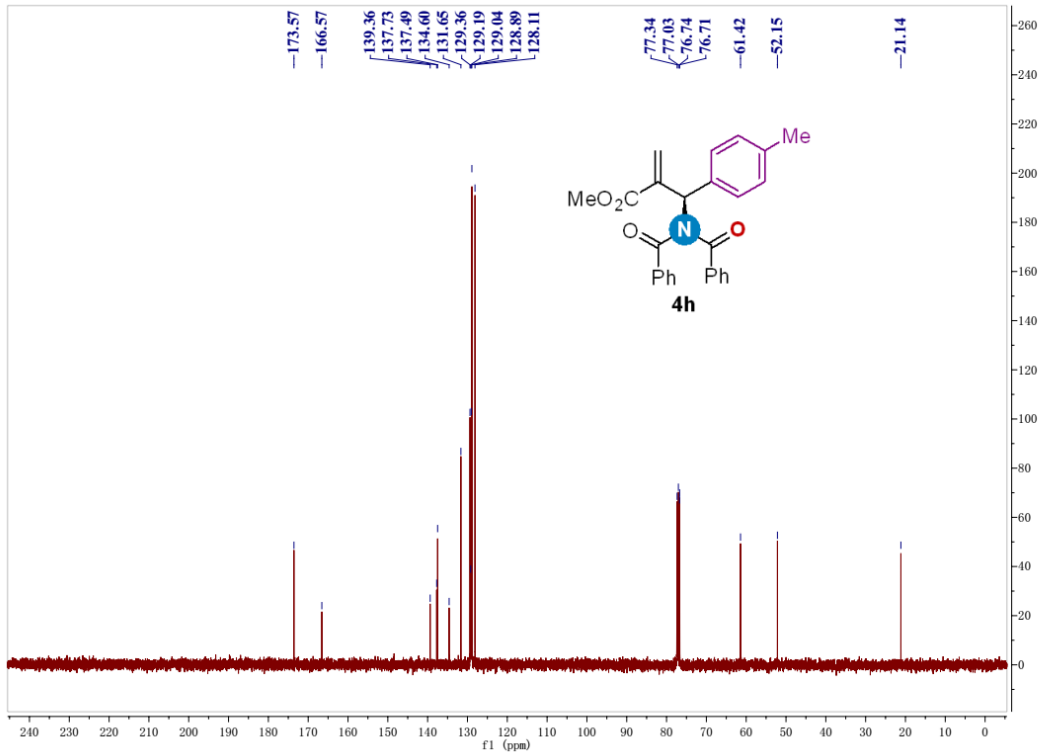


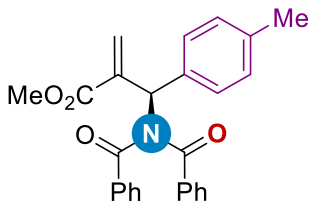
Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.586	134825	3978	10.313	12.183
2	21.606	1172525	28677	89.687	87.817
Total		1307350	32655	100.000	100.000



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



^{13}C NMR spectrum of **4h** (100 MHz, $CDCl_3$)



4h

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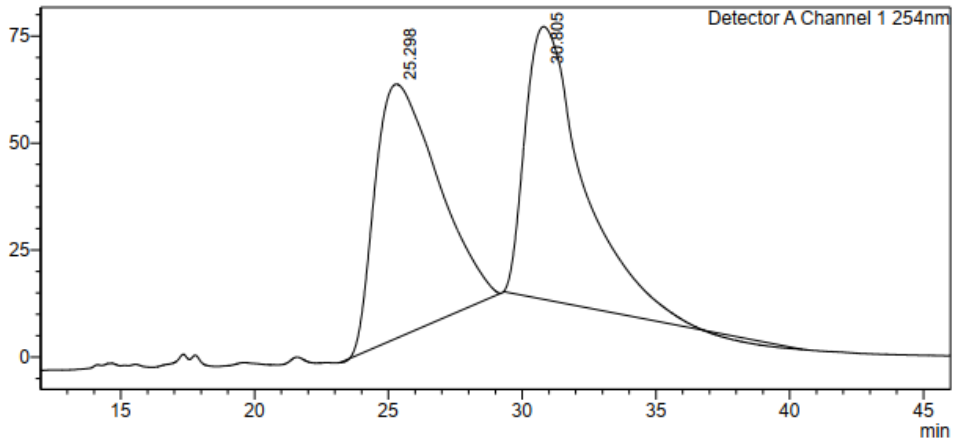
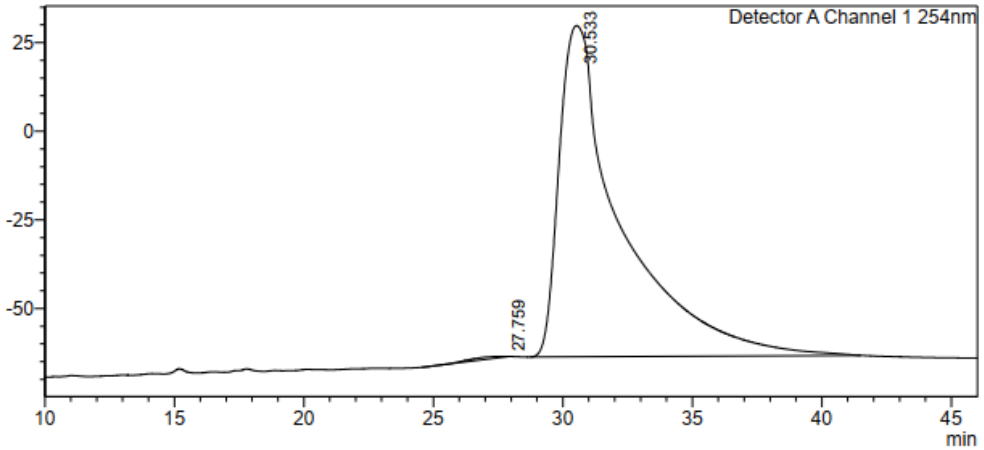
mV



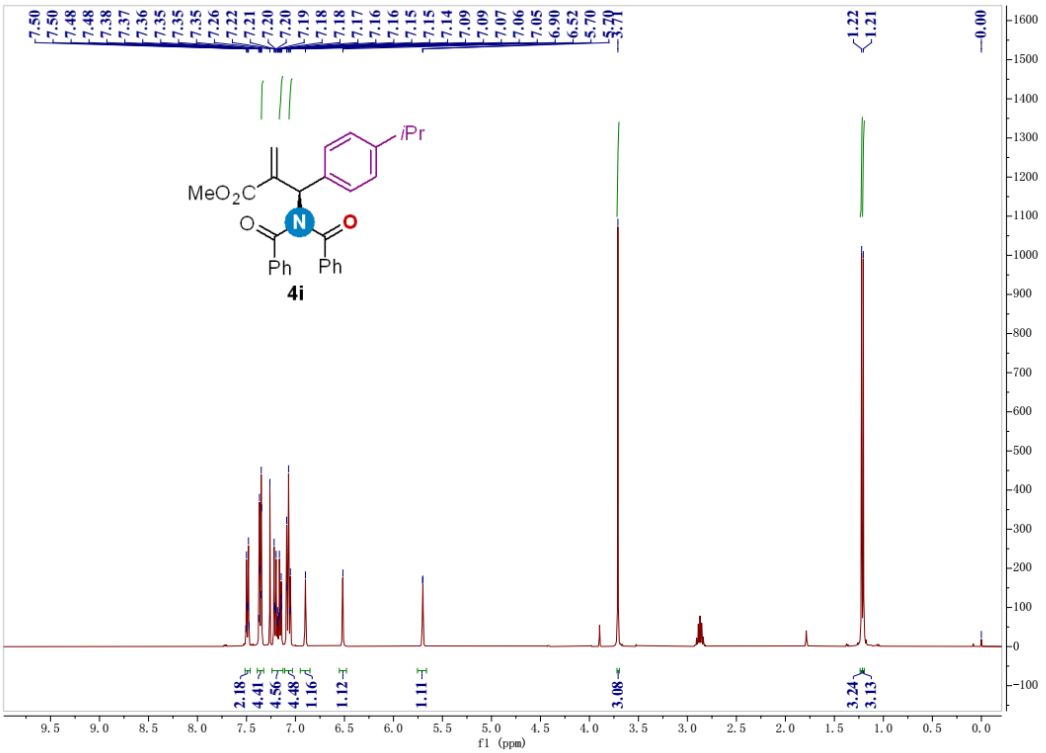
Peak#	Ret. Time	Area	Height	Area%	Height%
1	25.298	9702050	59401	50.183	48.245
2	30.805	9631349	63723	49.817	51.755
Total		19333399	123124	100.000	100.000

<Chromatogram>

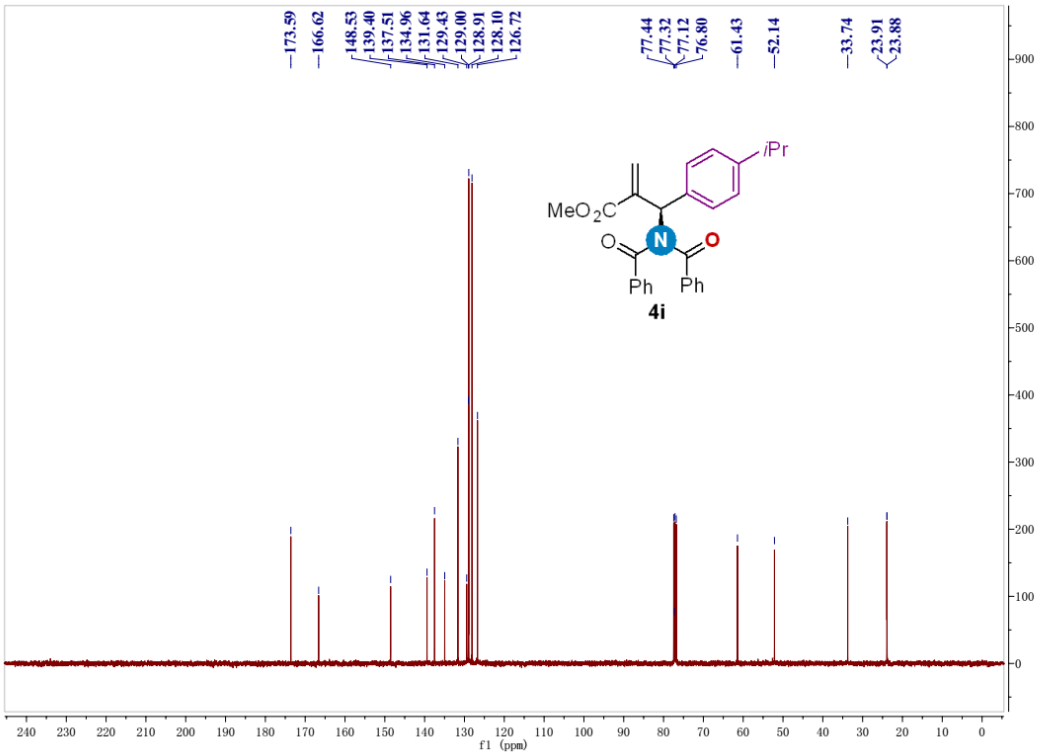
mV



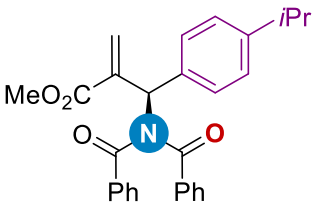
Peak#	Ret. Time	Area	Height	Area%	Height%
1	27.759	55200	196	0.354	0.209
2	30.533	15532652	93412	99.646	99.791
Total		15587852	93608	100.000	100.000



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



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



4i

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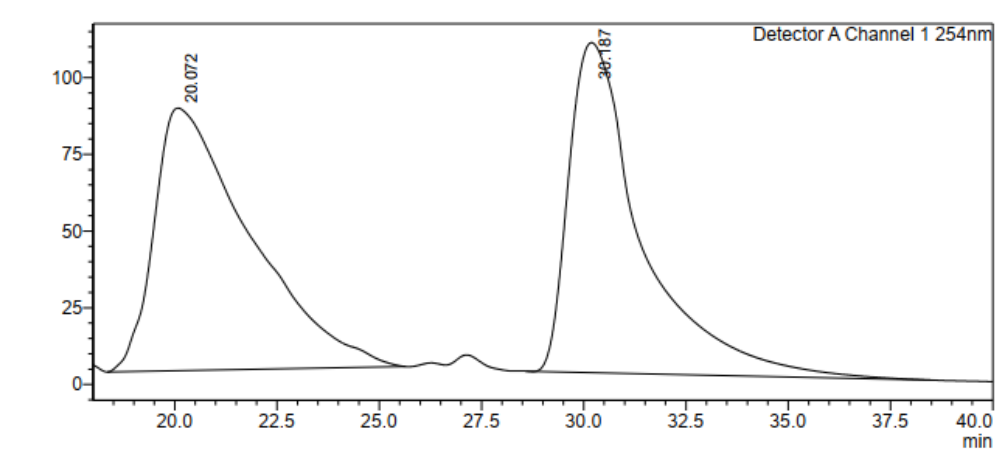

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.072	14028211	85594	51.191	44.325
2	30.187	13375364	107512	48.809	55.675
Total		27403576	193106	100.000	100.000

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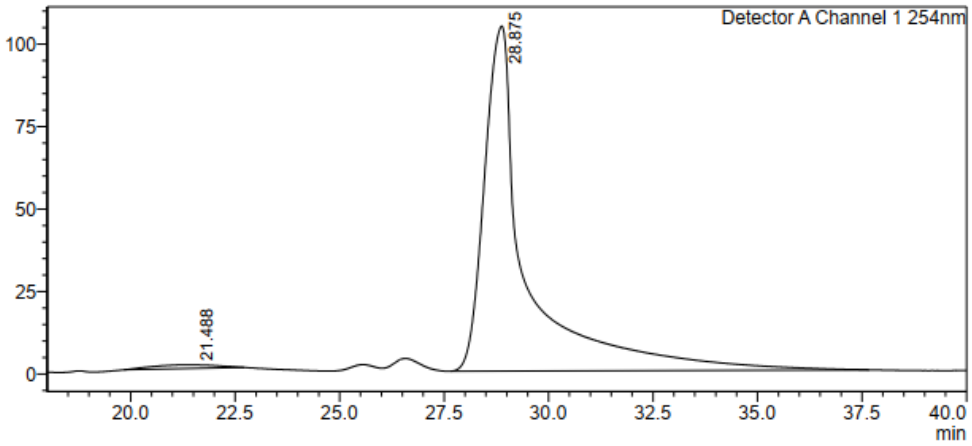
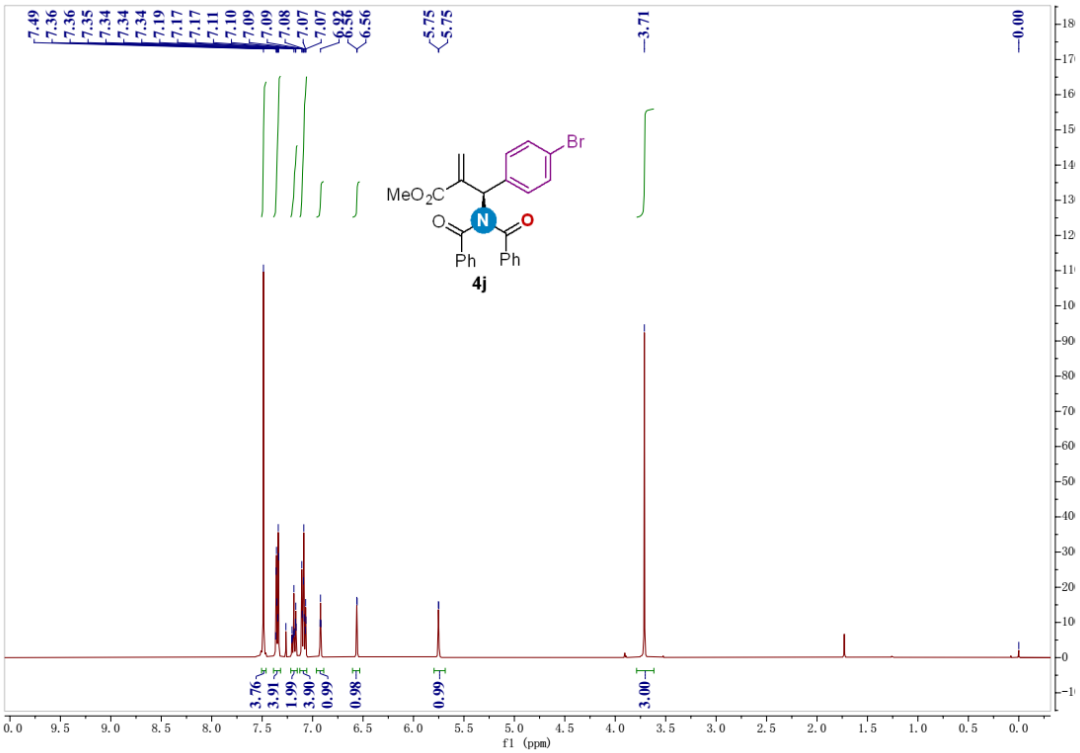
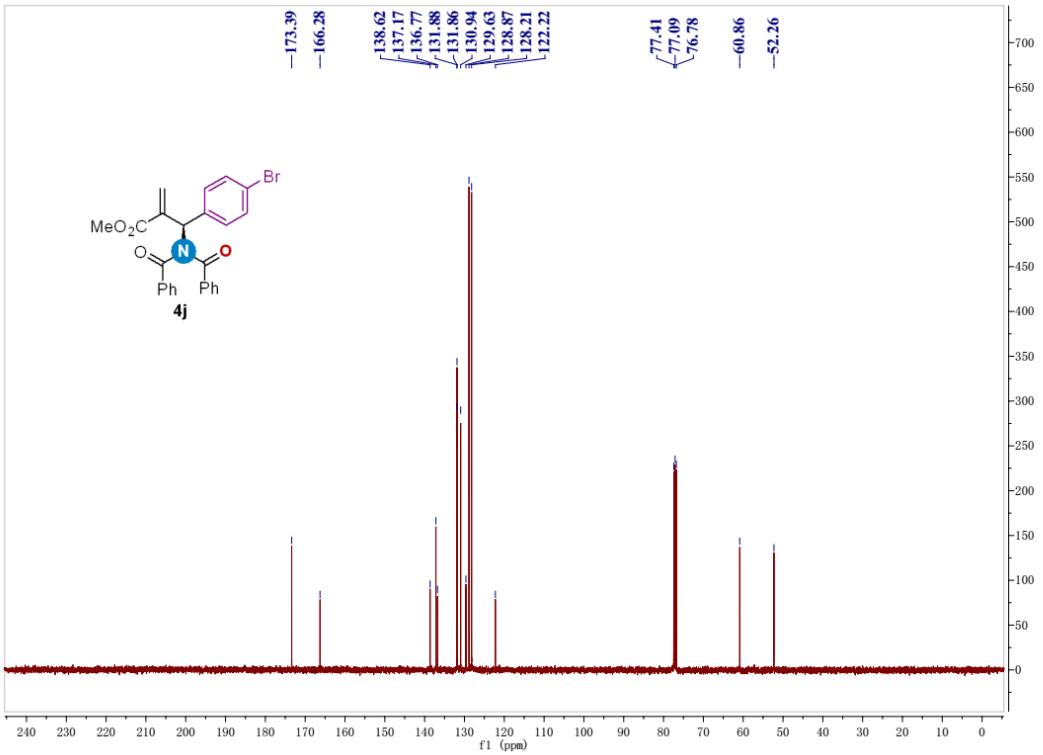


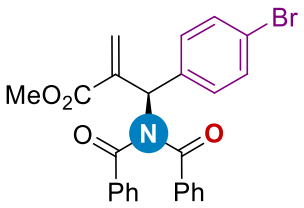
Peak#	Ret. Time	Area	Height	Area%	Height%
1	21.488	124797	1106	1.648	1.047
2	28.875	7447024	104587	98.352	98.953
Total		7571821	105693	100.000	100.000



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



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



4j

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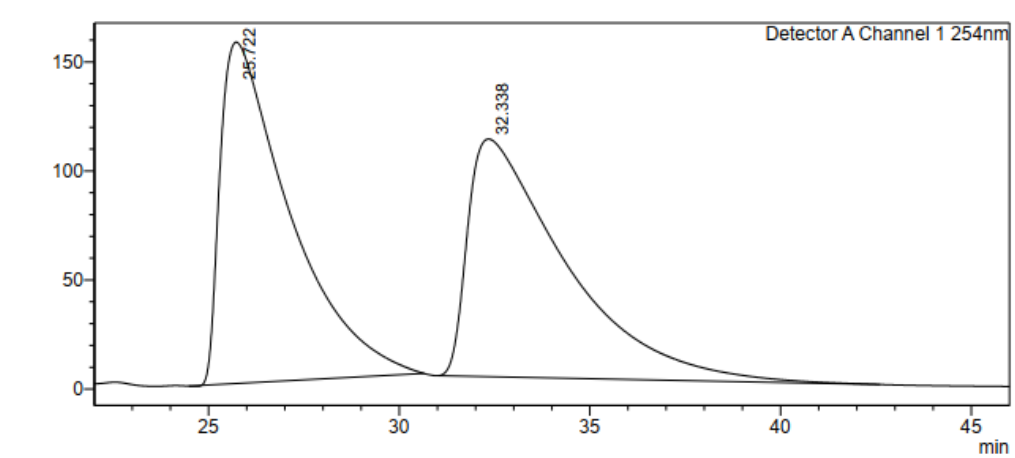

Peak#	Ret. Time	Area	Height	Area%	Height%
1	25.722	19874500	156558	50.484	58.961
2	32.338	19493523	108972	49.516	41.039
Total		39368023	265530	100.000	100.000

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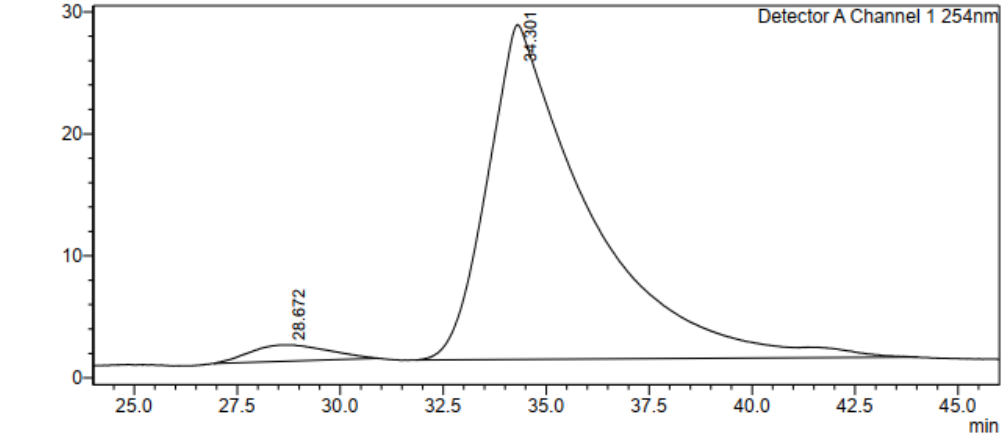
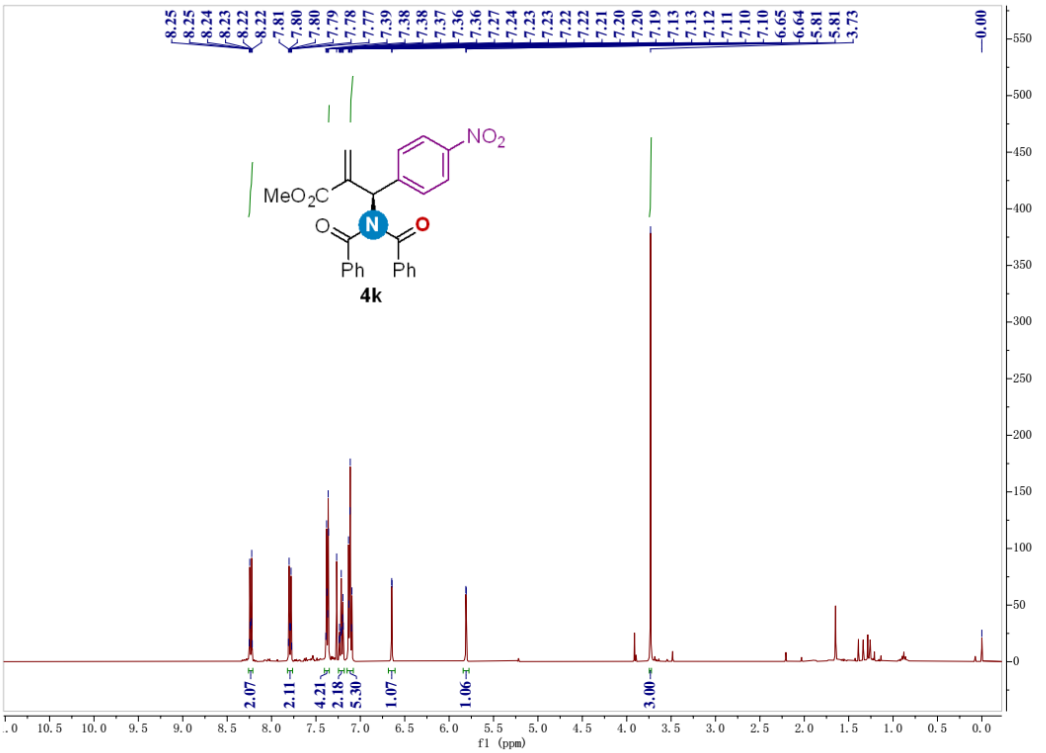
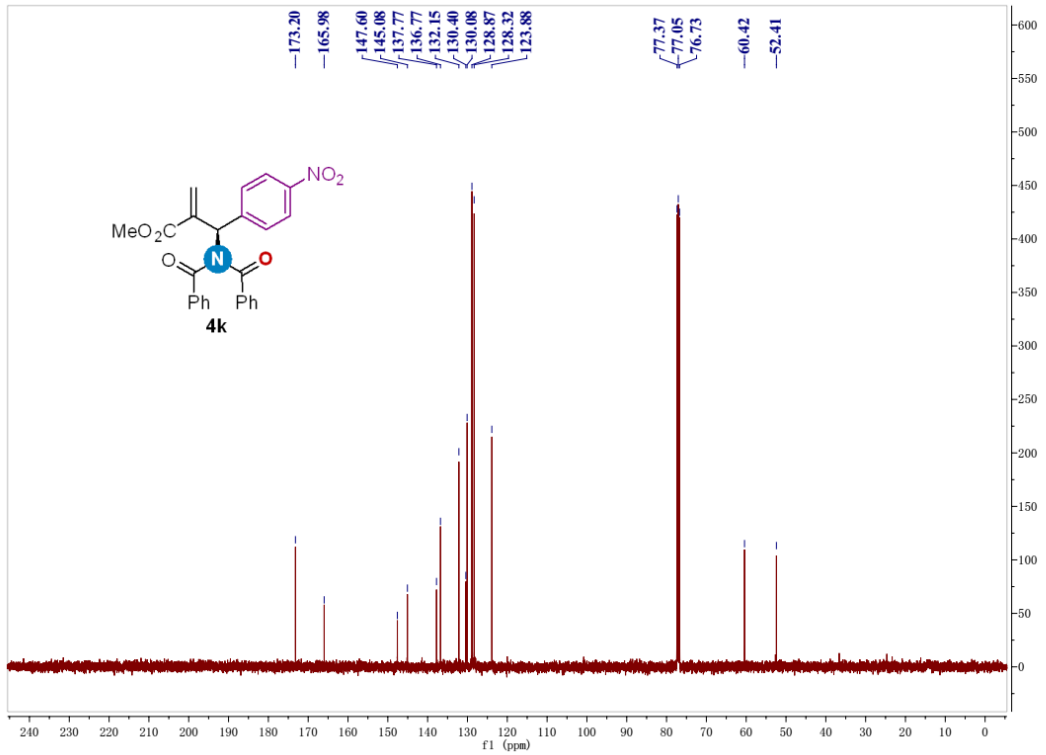


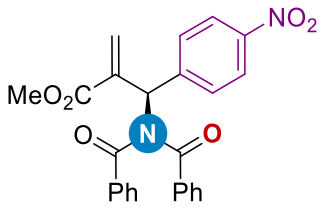
Peak#	Ret. Time	Area	Height	Area%	Height%
1	28.672	174803	1336	3.578	4.643
2	34.301	4710292	27437	96.422	95.357
Total		4885095	28773	100.000	100.000



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



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



4k

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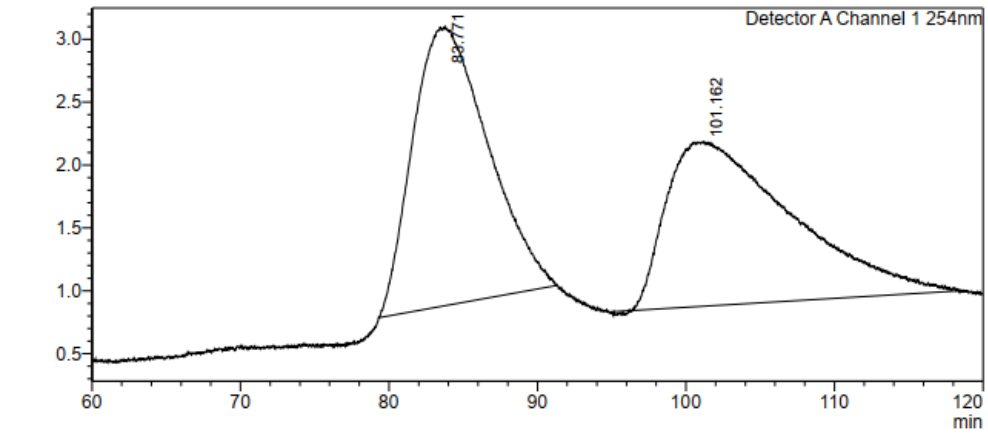

Peak#	Ret. Time	Area	Height	Area%	Height%
1	83.771	781858	2217	50.440	62.855
2	101.162	768232	1310	49.560	37.145
Total		1550091	3527	100.000	100.000

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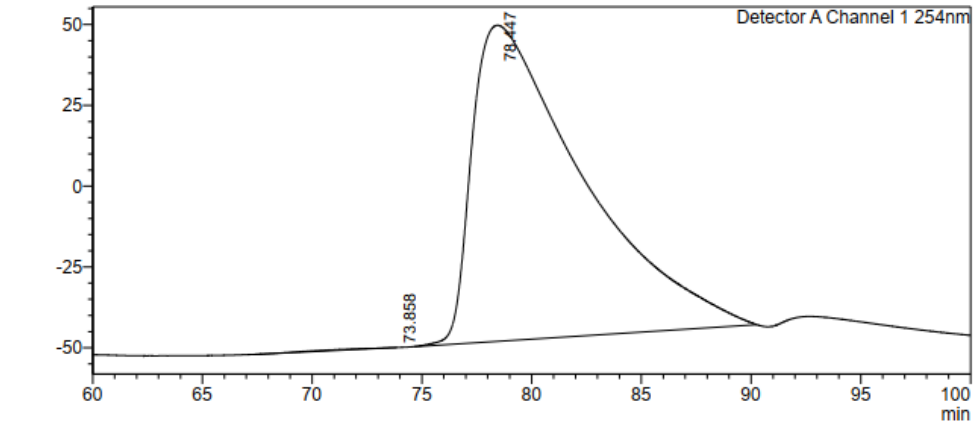
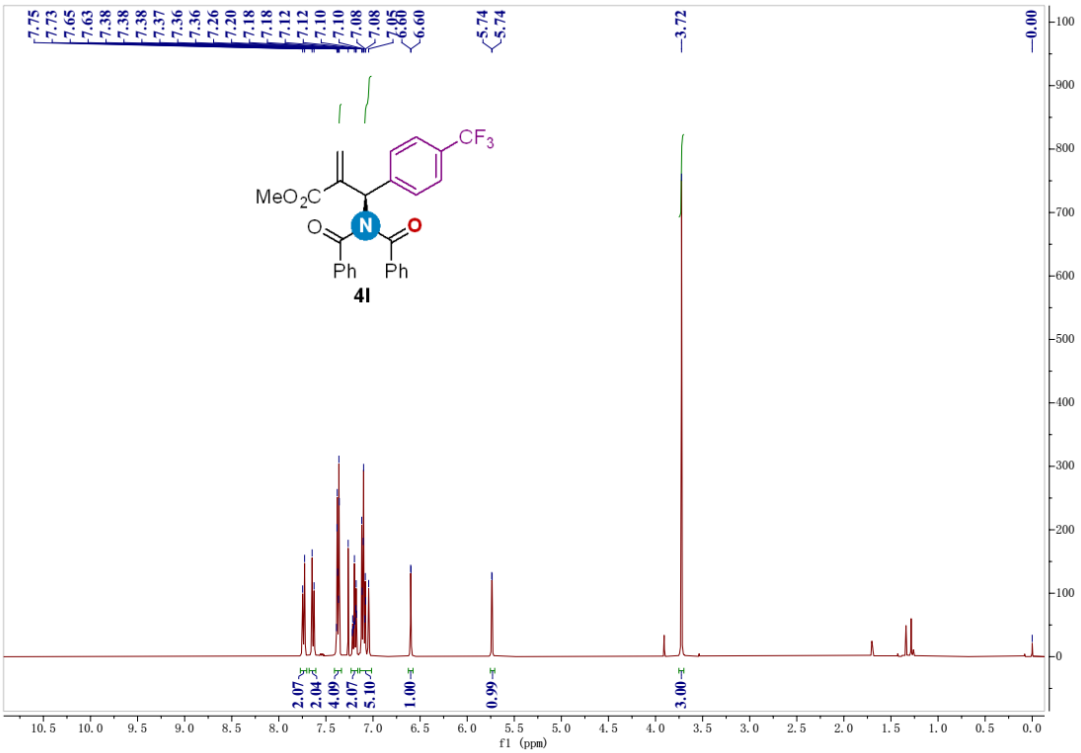
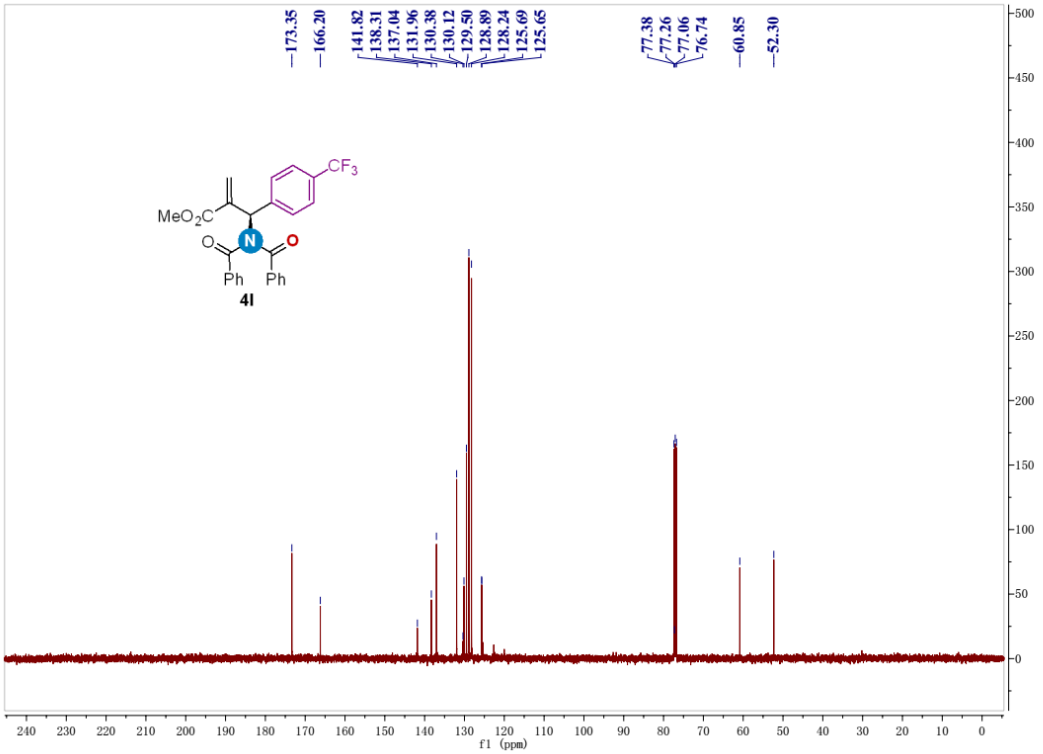


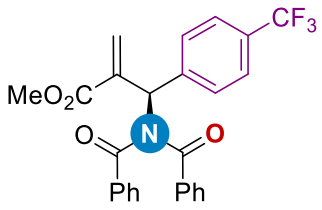
Peak#	Ret. Time	Area	Height	Area%	Height%
1	73.858	51176	1	0.149	0.001
2	78.447	34283398	97786	99.851	99.999
Total		34334574	97787	100.000	100.000



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



^{13}C NMR spectrum of **4l** (100 MHz, $CDCl_3$)



4l

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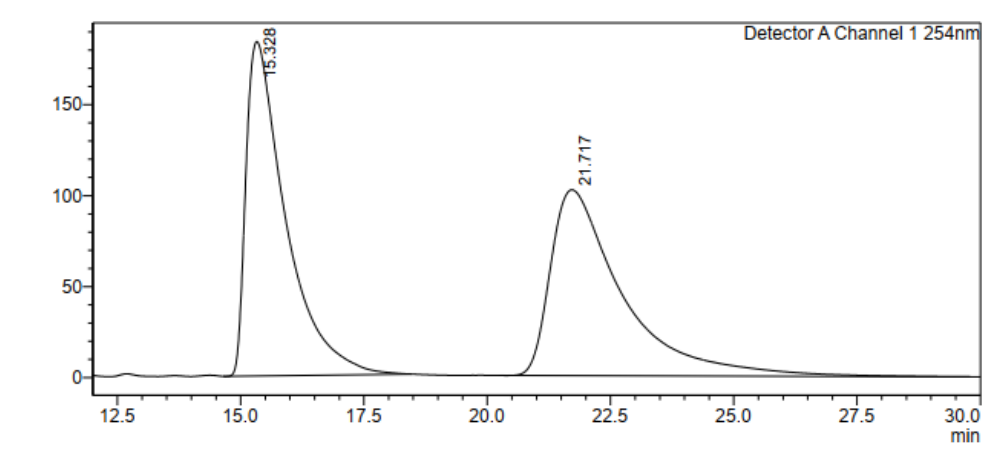

Peak#	Ret. Time	Area	Height	Area%	Height%
1	15.328	10281638	183843	49.790	64.281
2	21.717	10368290	102156	50.210	35.719
Total		20649928	285999	100.000	100.000

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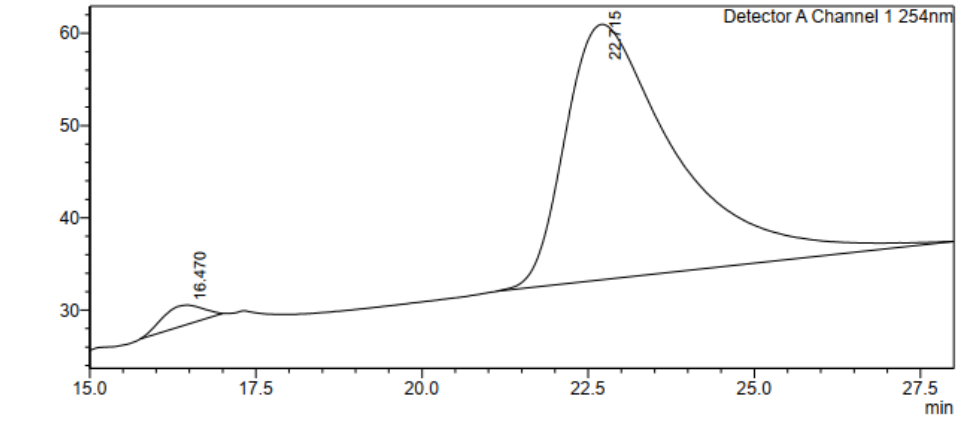
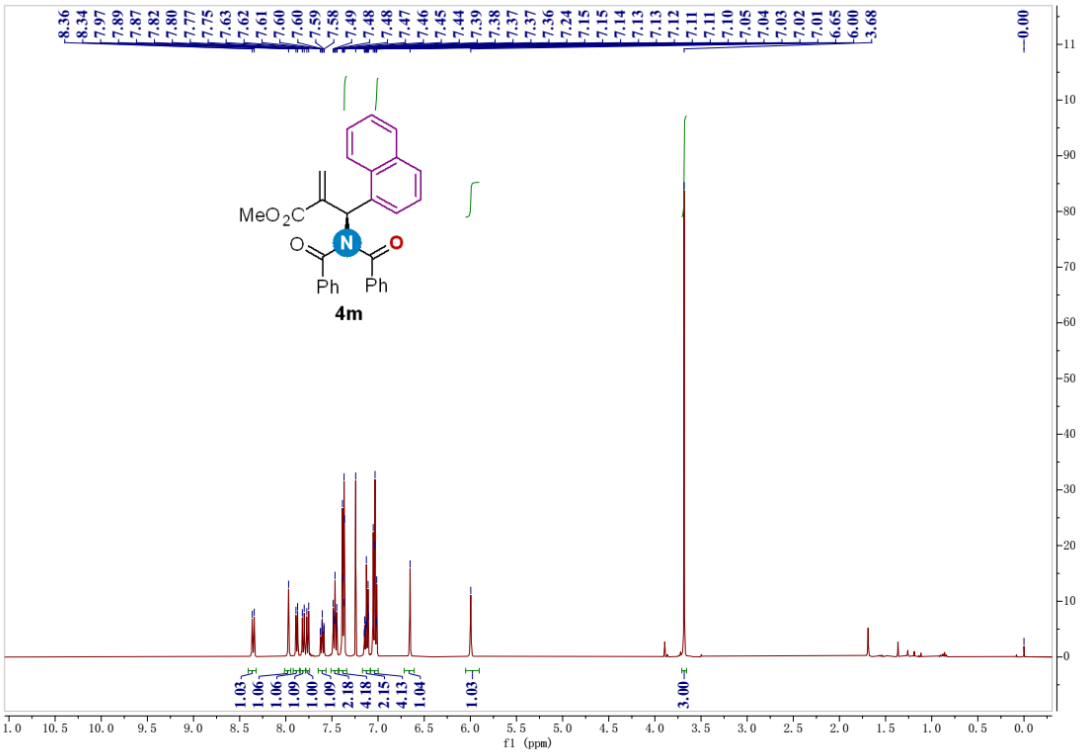
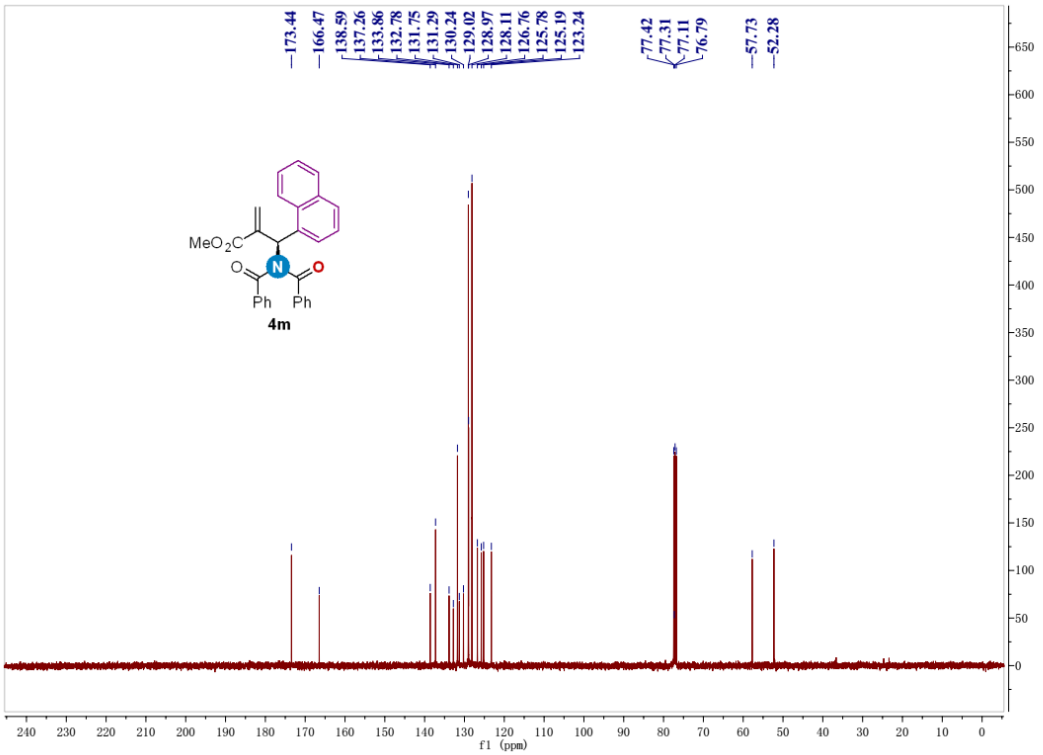


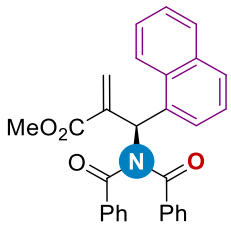
Peak#	Ret. Time	Area	Height	Area%	Height%
1	16.470	94051	2089	2.839	7.023
2	22.715	3218687	27658	97.161	92.977
Total		3312738	29747	100.000	100.000



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



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



4m

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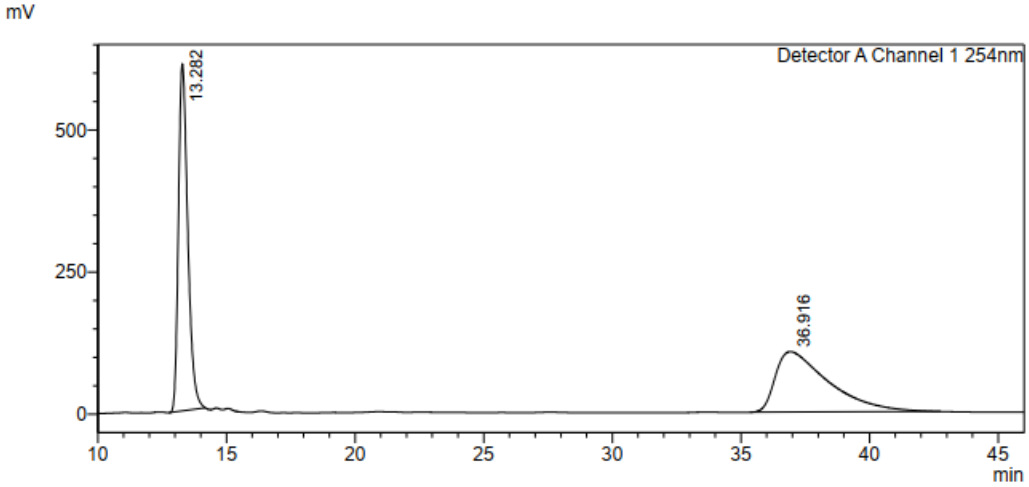

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.282	15377595	610311	50.146	85.159
2	36.916	15287834	106358	49.854	14.841
Total		30665429	716668	100.000	100.000

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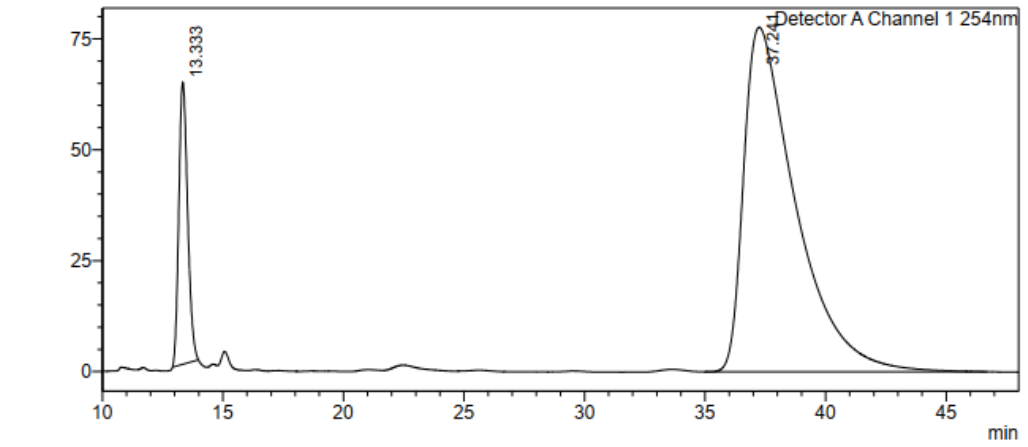
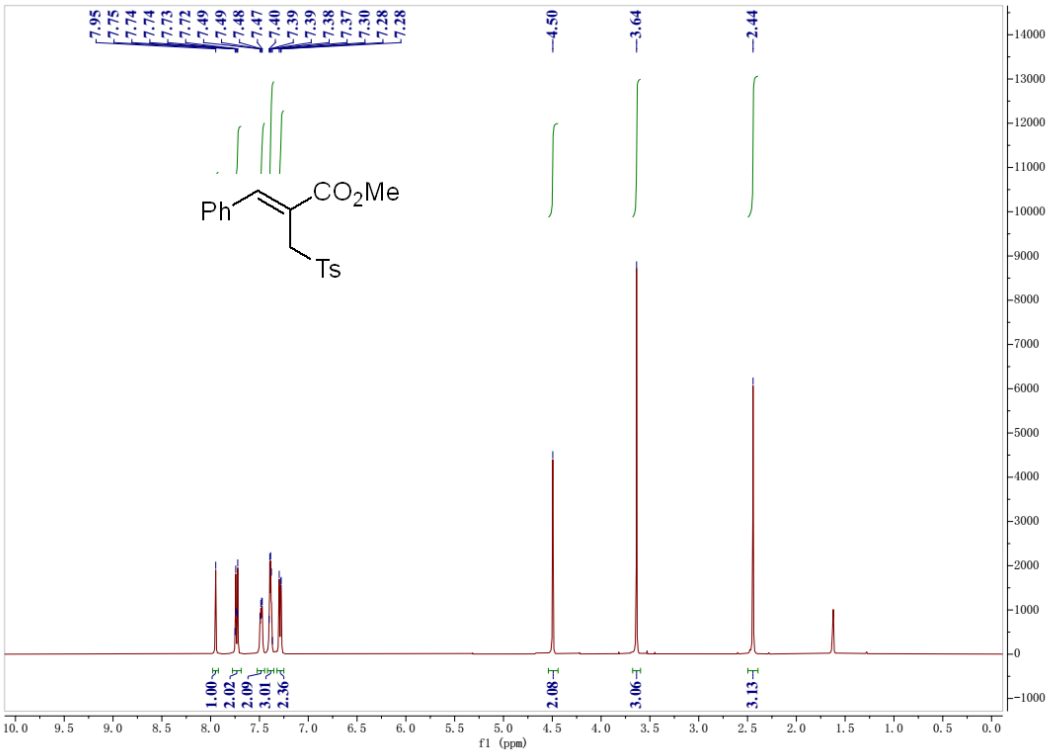
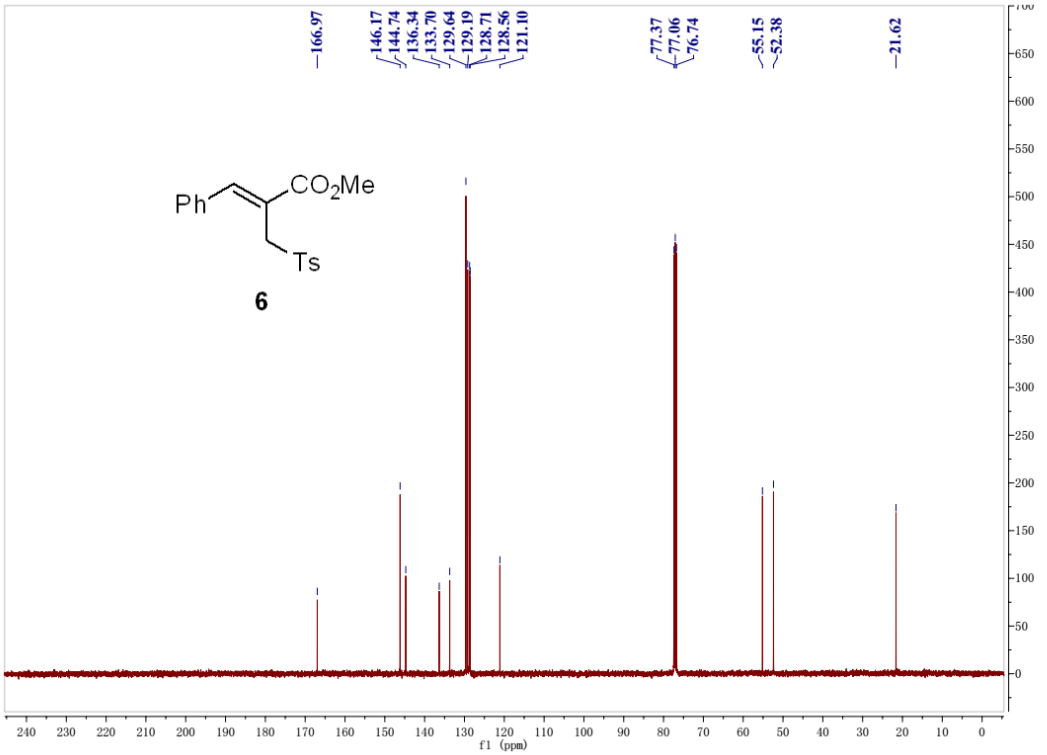


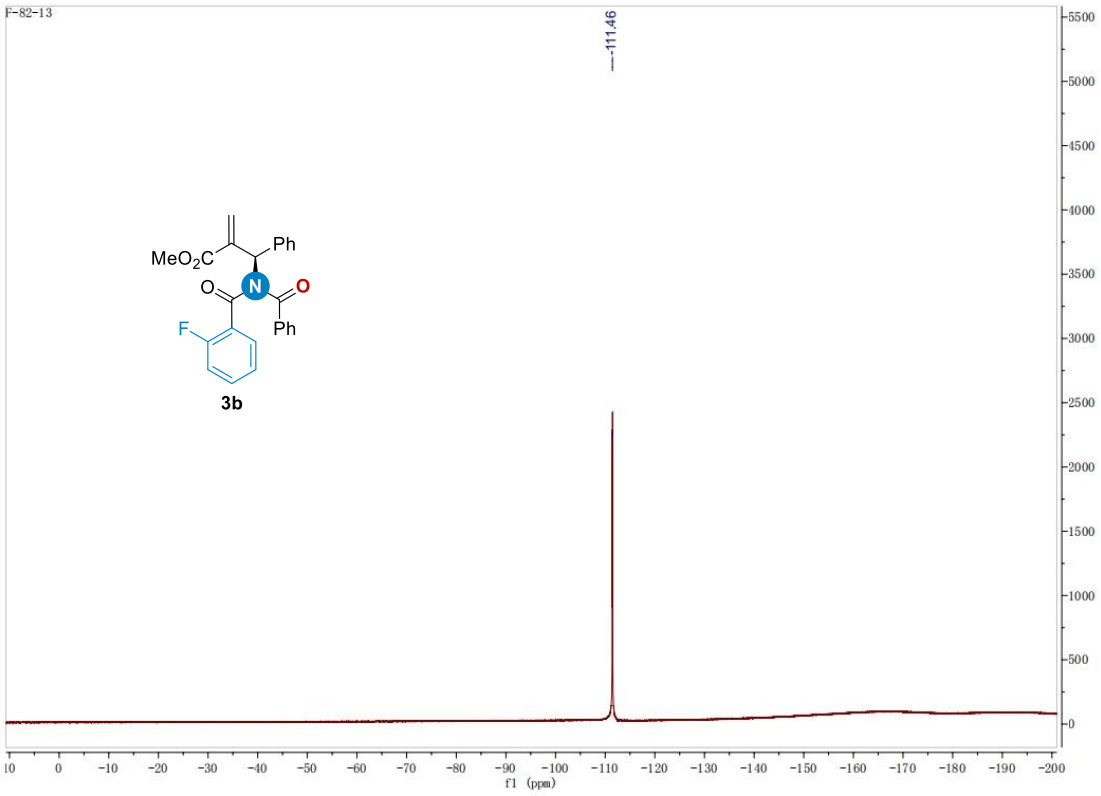
Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.333	1615006	63635	12.179	45.034
2	37.241	11645369	77669	87.821	54.966
Total		13260374	141304	100.000	100.000



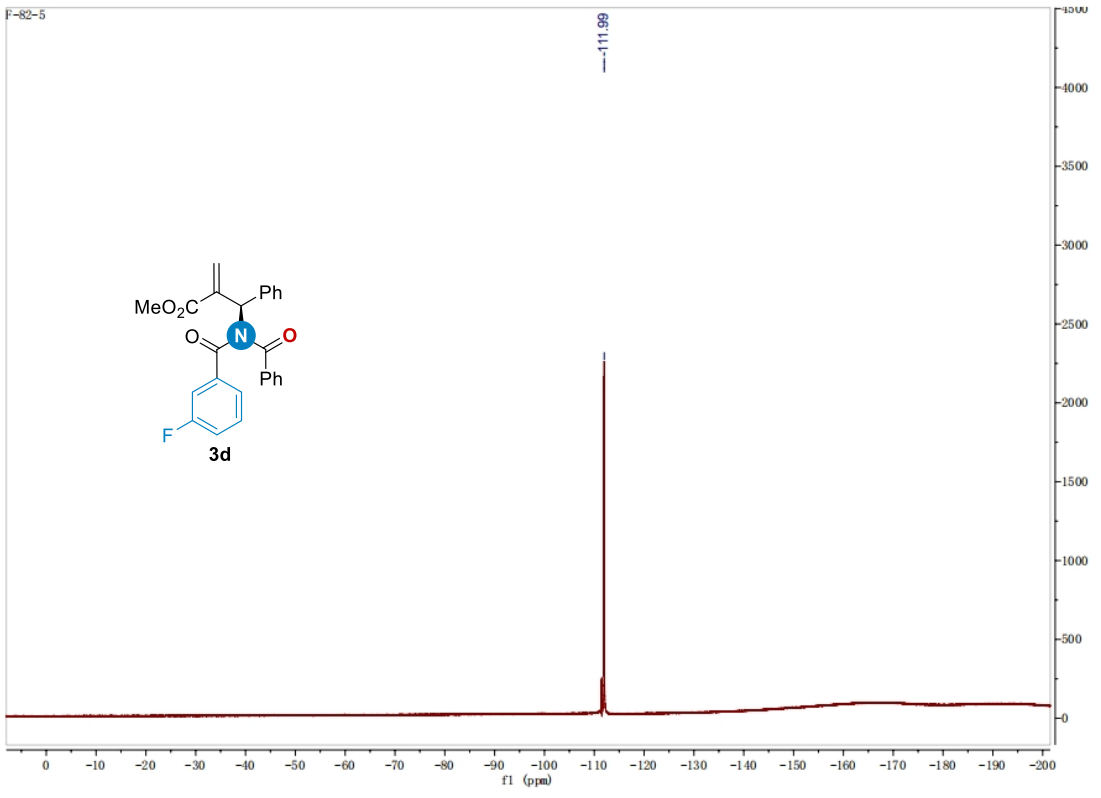
^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$)



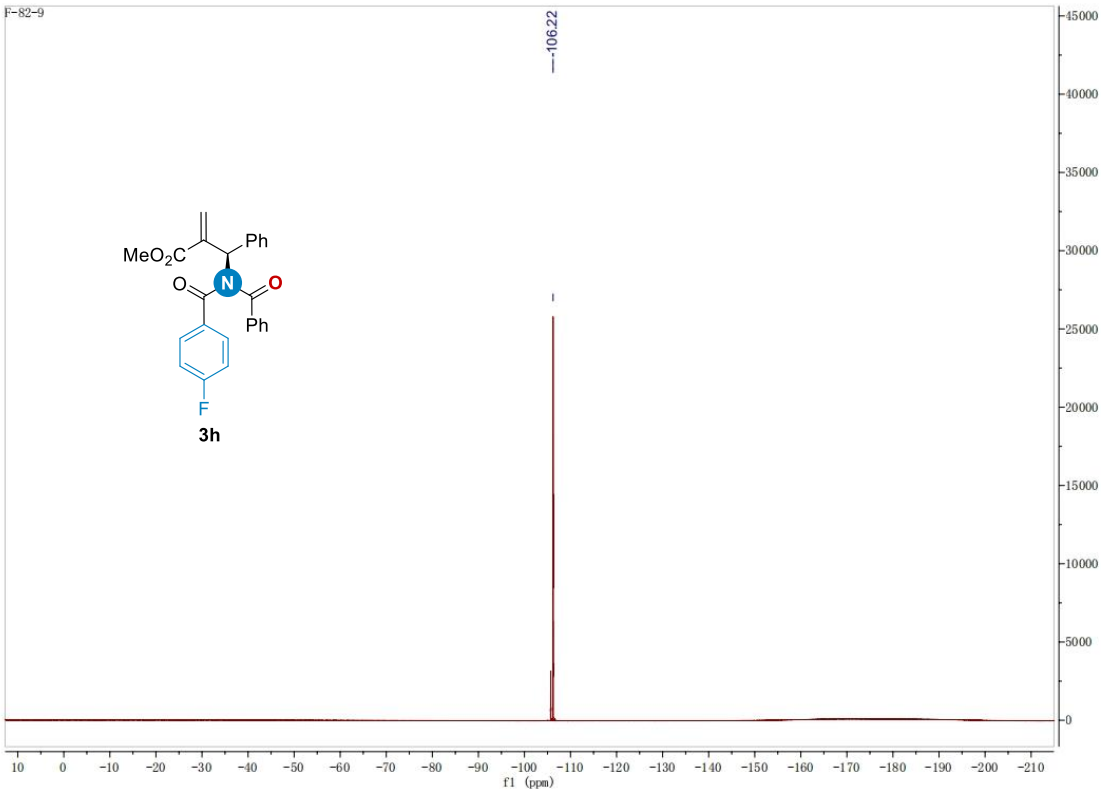
^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$)



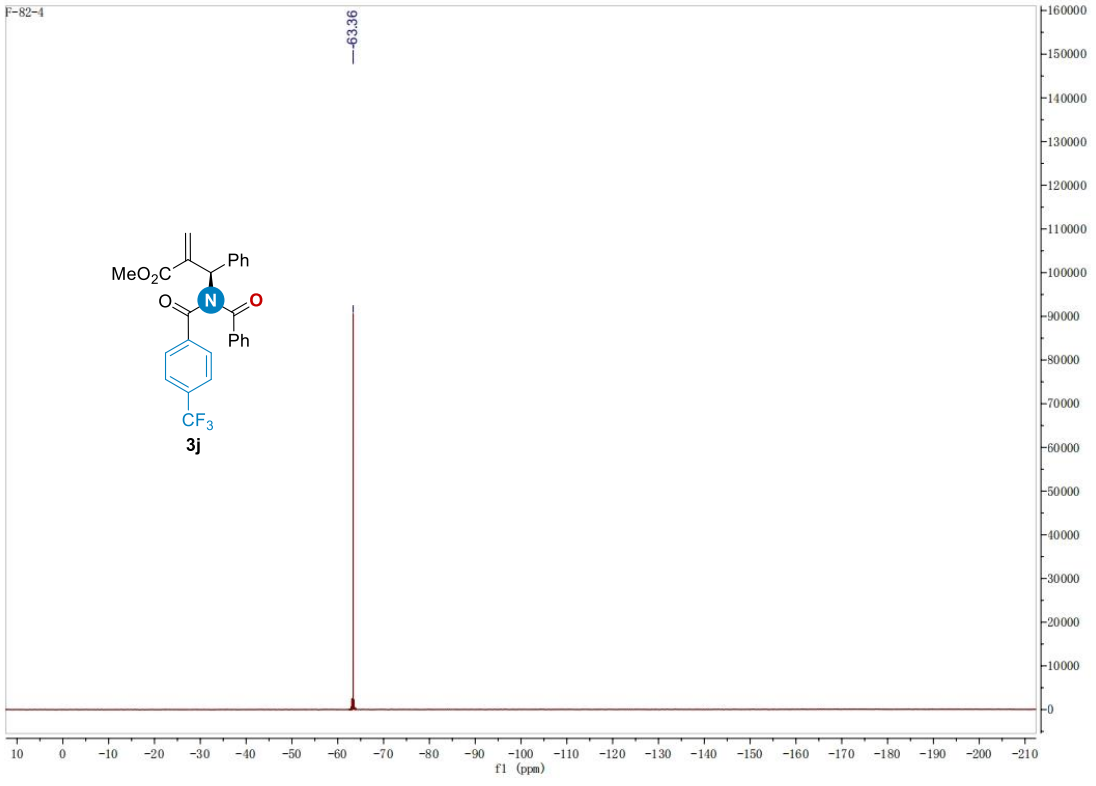
^{19}F NMR spectrum of **3b** (376 MHz, CDCl3)



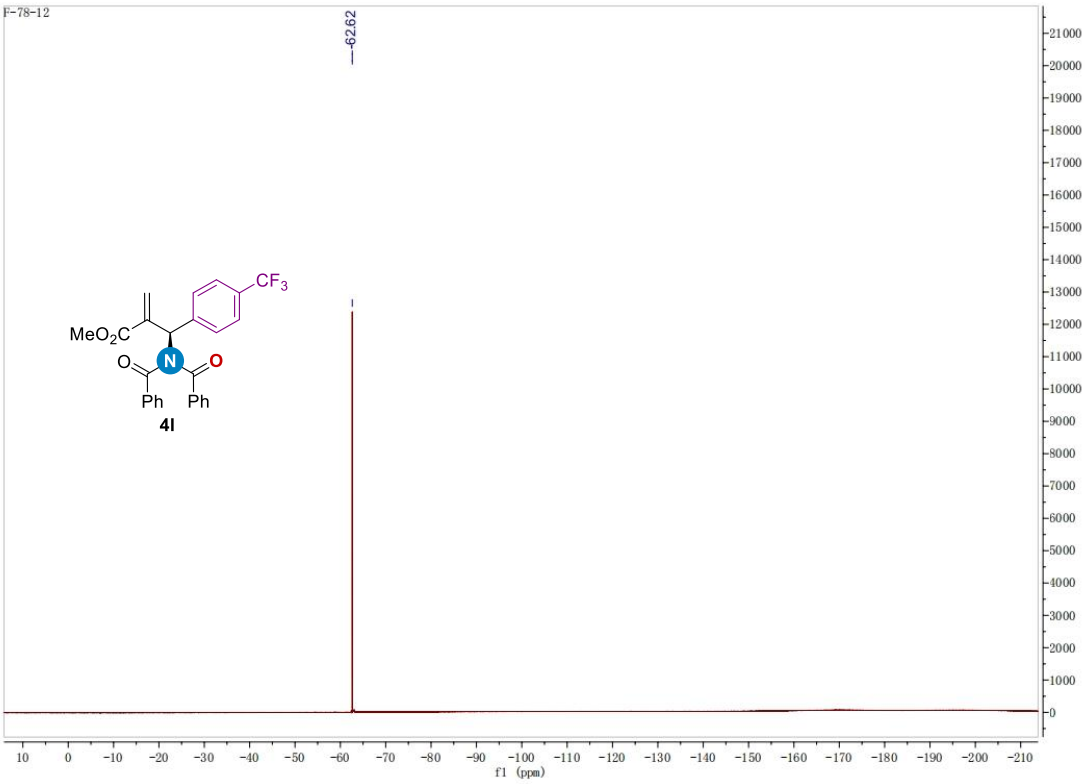
^{19}F NMR spectrum of **3d** (376 MHz, CDCl3)



^{19}F NMR spectrum of **3h** (376 MHz, CDCl3)



^{19}F NMR spectrum of **3j** (376 MHz, CDCl3)



^{19}F NMR spectrum of **4l** (376 MHz, CDCl3)

8. References

[1] (a) Bortolini, O.; Chiappe, C.; Fogagnolo, M.; Giovannini, P. P.; Massi, A.; Pomelli, C. S.; Ragno, D. An Insight into the Mechanism of the Aerobic Oxidation of Aldehydes Catalyzed by N-Heterocyclic Carbenes. *Chem. Commun.* **2014**, *50*, 2008. (b) Bortolini, O.; Chiappe, C.; Fogagnolo, M.; Massi, A.; Pomelli, C. S. Formation, Oxidation, and Fate of the Breslow Intermediate in the N-Heterocyclic Carbene-Catalyzed Aerobic Oxidation of Aldehydes. *J. Org. Chem.* **2017**, *82*, 302. (c) Jin, Z.; Xu, J.; Yang, S.; Song, B.-A.; Chi, Y. R. Enantioselective Sulfonation of Enones with Sulfonyl Imines by Cooperative N-Heterocyclic-Carbene/Thiourea /Tertiary-Amine Multicatalysis. *Angew. Chem. Int. Ed.* **2013**, *52*, 12354.