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Electronic Supplementary Information

Radical 1,4-aryl remote migration enables nickel-catalyzed cross-electrophile coupling of β-bromo-α-benzylamino acid esters with vinyl triflates

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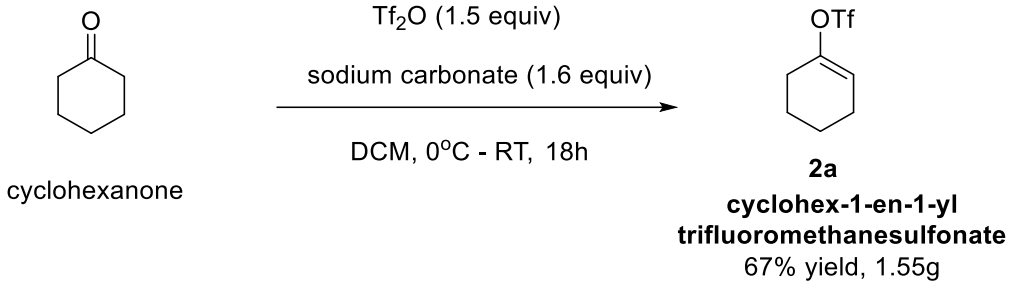
General Information

All manipulations of oxygen- and moisture-sensitive materials were conducted with a Schlenk technique under a nitrogen atmosphere. Solvents were purified and dried in a standard manner, and DMA was continuously refluxed and freshly distilled from dried over CaH_2 before we use it. All commercially available reagents were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd and Anhui Senrise Technology Co., Ltd. Flash column chromatography was performed using EM Silica gel 60 (CCIS, 200-400 mesh). Visualization was accomplished with UV light (254 nm) and/or an aqueous alkaline $KMnO_4$ solution followed by heating. Conversion was monitored by thin layer chromatography (TLC) using TLC silica gel 60 F254 from Hailang. Zinc powder (Aladdin) was activated with hydrochloric acid before used. Amino acid esters bromides were prepared according to literature procedures.[1-3]

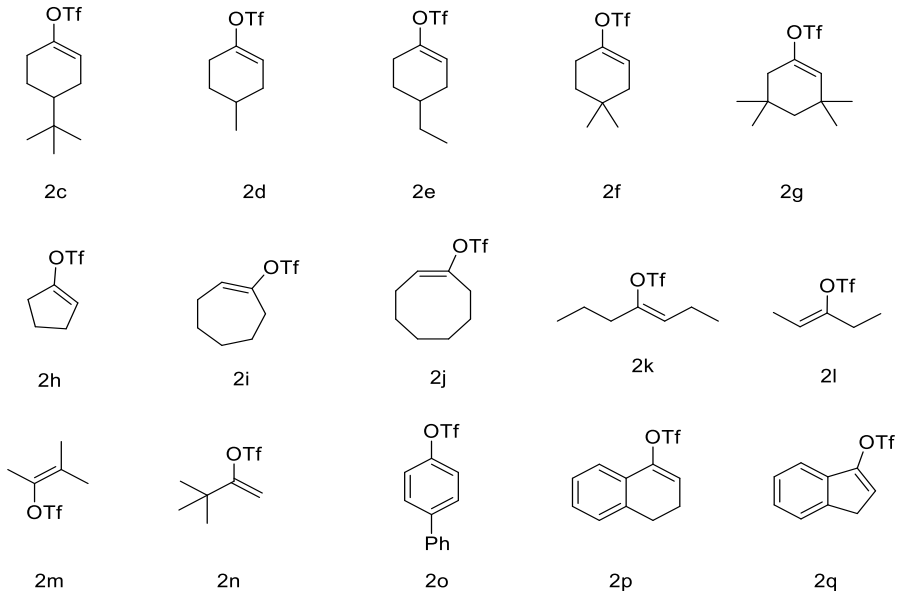
^1H NMR, ^{13}C NMR spectra were recorded at 25 ^oC on Bruker 400 or 500 MHz NMR spectrometer with trimethylsilane resonance as the internal standard. Chemical shifts are given in ppm. The spectra are calibrated to the residual 1H and 13C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). Infrared spectra were recorded on a MAGNA-IR550 spectrometer. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometer.

General procedure

Synthesis of vinyl triflates (2a – 2p).[4]



All glassware and reagents are dry. Transfering DCM (30mL) to Schlenk tube with scratch cap (200 mL), and weighing 1.696g of sodium carbonate (1.6 equiv) floating in it, cyclohexanone (10mmol 1 equiv) is transferred to the Schlenk tube. **Note: After the above operation is completed, sealing it tightly and injecting nitrogen gas.** Adding the trifluoromethanesulfonic anhydride dropwise into the reaction tube under vigorous stirring for ten minutes at 0 °C, subsequently, placeing the reaction tube in an ice water bath, the reaction mixture was slowly warmed to rt and stirred for 18 hours, followed by dilution with DCM (10 mL), quenching with water (10 mL) and extraction with DCM (3 × 10 mL). The combined organic phases were washed with saturated aqueous solution of NaHCO3 (2 × 10 mL) and brine (2 × 10 mL). The organic phase was dried over anhydrous MgSO4, concentrated in vacuo. Purified by column chromatography (SiO2, n-hexane) afforded **2a** (67% yield, 1.55g) as a pale - chartreuse oil. (**2c-2q** are shown in the following figure).

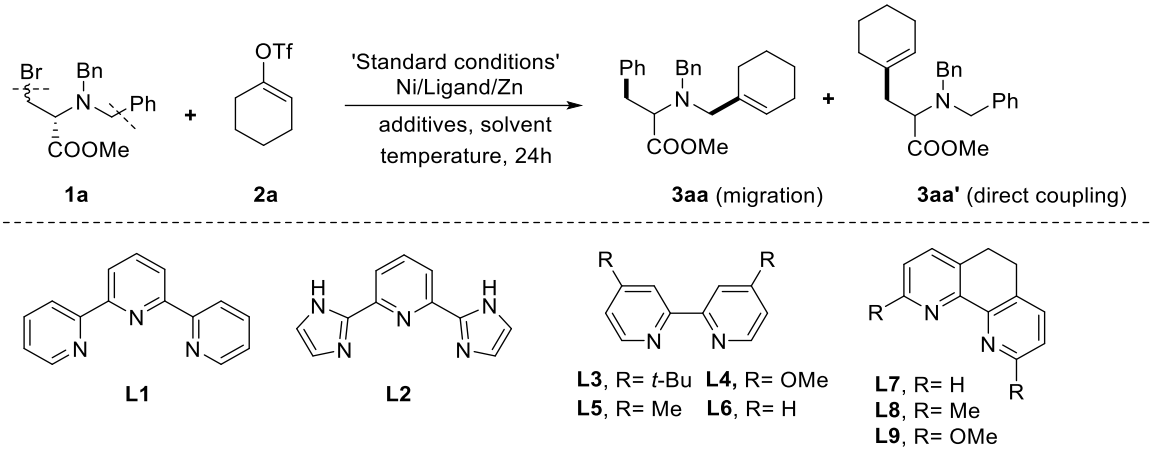


General procedure for sequential rearrangement and cross-electrophile coupling by using vinyl triflates.

To a Schlenk tube with screw-cap was added amino acid ester bromide 1 (0.3 mmol, if solid), vinyl triflates 2 (0.2 mmol, if solid), $NiBr_2$(dme) (10% mmol), 2,2':6',2''-Terpyridine (12mmol%), $MgCl_2$ (2 equiv), Zn power (2 equiv), DABCO (1 equiv), and melamine (0.5 equiv). The tube was evacuated and back-filled with nitrogen (this process was repeated three times), DMA (2.5mL) were added consecutively via syringe with amino acid ester bromides 1 (0.2 mmol, if liquid) and vinyl triflates 2 (0.3 mmol, if liquid). The resulting mixture was bubbled with nitrogen to degas for 1 min and stirred at 35 ^oC temperature for 24 h (heating by oil bath). Note: a stirring speed above 800 rpm is highly important for reproducibility. The resulted mixture was filtered through a short plug of silica gel to remove metal salts, and diluted with Et_2O (50 mL). The filtrate was poured into a separatory funnel and partitioned with brine (30 mL). The aqueous layer was then extracted with diethyl ether (3 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (eluent: n-Hex/ethyl acetate) to afford the corresponding compounds (**3aa**-**3az**).

Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions[a]



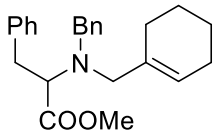
Entry	Change from the standard conditions	3aa **yield (%)**[b]	3aa' **yield (%)**[b]
1	None	72	trace
2	**L2** instead of **L1**	18	trace
3	**L3** instead of **L1**	55	trace
4	**L4** instead of **L1**	53	trace
5	**L5** instead of **L1**	57	trace
6	**L6** instead of **L1**	48	trace
7	**L7** instead of **L1**	60	trace
8	**L8** instead of **L1**	21	trace
9	**L9** instead of **L1**	28	trace
10	CH_3CN instead of DMA	36	trace
11	NMP instead of DMA	38	trace

12	1,4-Dioxane instead of DMA	11	trace
13	DMSO instead of DMA	32	trace
14	THF instead of DMA	18	trace
15	DIPA instead of DABCO	66	trace
16	K_3PO_4 instead of DABCO	20	trace
17	K_2CO_3 instead of DABCO	12	trace
18	Et_3N instead of DABCO	10	trace
19	$NiCl_2$(dme) instead of $NiBr_2$(dme)	54	trace
20	$NiCl_2(PPh_3)_2$ instead of $NiBr_2$(dme)	46	trace
21	Ni(dppf)Cl_2 instead of $NiBr_2$(dme)	38	trace
22	$PdCl_2(PPh_3)_2$ instead of $NiBr_2$(dme)	23	trace
23	$Pd(OAc)_2$ instead of $NiBr_2$(dme)	24	trace
24	25 ^oC instead of 35 ^oC	63	trace
25	55 ^oC instead of 35 ^oC	44	trace
26	without $MgCl_2$	13	trace
27	without melamine	52	trace

[a]Standard conditions : **1a** (0.3 mmol), **2a** (0.2 mmol), $NiBr_2$(dme) (10 mol %), **L1** (12 mol %), Zn (2 equiv), $MgCl_2$ (2 equiv), DACBO (1 equiv), melamine **4a** (0.5 equiv) and DMA (2.5 mL) at 35 ^oC under a N_2 atmosphere for 24 h. The yields were determined by GC analysis using an internal standard and isolated yield in parentheses. DMA= dimethyl acetamide, DIAP = diisopropylamine, NMP = N-methylpyrrolidone, DMF = dimethyllformamide. The diastereomeric ratio (dr) and regioselective ratio (rr) were determined using ^1H NMR analysis.

Characterization of new compounds

Generation of New compounds via cross-electrophile coupling of β-bromo amino acid esters with cyclohex-1-en-1-yl trifluoromethanesulfonate.



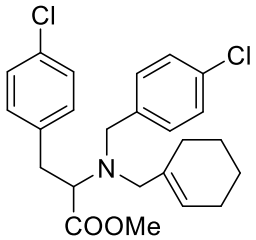
Methyl N-benzyl-N-(cyclohex-1-en-1-ylmethyl)phenylalaninate (3aa):

Yield = 72% (52.46 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 60/1). R_f: 0.45

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, J = 7.1 Hz, 4H), 7.25 – 7.20 (m, 4H), 7.19 – 7.13 (m, 2H), 5.33 (t, 1H), 3.86 (d, J = 13.8 Hz, 2H), 3.67 (s, 3H), 3.47 – 3.39 (m, 3H), 2.40 – 2.23 (m, 2H), 2.02 – 1.83 (m, 1H), 1.60 – 1.14 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5, 139.8, 133.7, 129.0, 128.1, 126.9, 124.3, 58.9, 54.3, 51.0, 38.4, 27.3, 25.4, 22.8, 22.4.

HRMS: calcd for $C_{24}H_{29}NO_2$; $[M+H]^+$ 364.2271, found: 364.2273



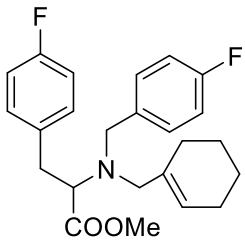
Methyl 2-((4-chlorobenzyl)(cyclohex-1-en-1-ylmethyl)amino)-3-(4-chlorophenyl)propanoate (3ab):

Yield = 50% (43.11 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 60/1). R_f: 0.42

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (d, J = 2.0 Hz, 1H), 7.24 – 7.20 (m, 4H), 7.15 (dd, J = 8.5, 2.1 Hz, 2H), 7.07 (td, J = 8.1, 2.1 Hz, 1H), 5.41 (s, 1H), 4.10 (d, J = 2.0 Hz, 2H), 3.93 (d, J = 14.7 Hz, 1H), 3.77 (s, 3H), 3.60 (td, J = 7.7, 2.1 Hz, 1H), 2.50 (ddd, J = 68.4, 14.2, 7.8 Hz, 2H), 1.97 (s, 2H), 1.77 (s, 2H), 1.63 – 1.53 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.4, 138.5, 137.2, 134.2, 133.7, 132.1, 129.9, 129.0, 128.4, 127.7, 124.2, 61.7, 53.2, 51.2, 51.1, 38.3, 27.6, 25.4, 22.9, 22.3.

HRMS: calcd for $C_{24}H_{27}Cl_2NO_2$; $[M+H]^+$ 432.1492, found: 432.1490



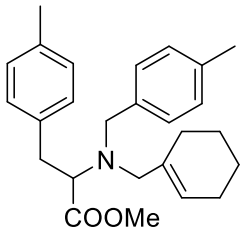
Methyl 2-((cyclohex-1-en-1-ylmethyl)(4-fluorobenzyl)amino)-3-(4-fluorophenyl)propanoate (3ac):

Yield = 85% (68 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.48

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (ddd, *J* = 9.3, 5.7, 2.9 Hz, 4H), 6.94 – 6.87 (m, 4H), 5.31 (d, *J* = 3.7 Hz, 1H), 3.77 (d, *J* = 13.8 Hz, 2H), 3.67 (s, 3H), 3.42 – 3.35 (m, 3H), 2.37 – 2.22 (m, 2H), 1.90 (dd, *J* = 6.9, 3.5 Hz, 2H), 1.53 – 1.45 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 163.2, 160.8, 135.3, 135.2, 133.6, 130.4, 130.3, 124.4, 115.0, 114.8, 58.8, 53.4, 51.1, 38.3, 27.3, 27.3, 25.3, 22.8, 22.4.

HRMS: calcd for $C_{24}H_{27}F_2NO_2$; $[M+H]^+$ 400.2083, found: 400.2083



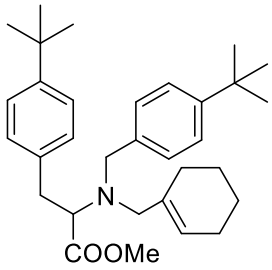
Methyl 2-((cyclohex-1-en-1-ylmethyl)(4-methylbenzyl)amino)-3-(p-tolyl)propanoate (3ad):

Yield = 86% (67.3 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.41

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 4H), 7.15 (d, *J* = 7.7 Hz, 4H), 5.44 (s, 1H), 3.93 (d, *J* = 13.8 Hz, 2H), 3.78 (s, 3H), 3.57 (dd, *J* = 8.9, 6.7 Hz, 1H), 3.48 (d, *J* = 13.8 Hz, 2H), 2.37 (s, 6H), 2.04 (t, *J* = 15.2 Hz, 2H), 1.68 – 1.64 (m, 2H), 1.61 (s, 1H), 1.39 (s, 1H), 1.32 (d, *J* = 14.6 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.8, 136.4, 136.3, 133.7, 129.0, 128.8, 125.1, 57.8, 54.1, 52.1, 51.7, 26.4, 25.4, 22.8, 22.2, 21.2.

HRMS: calcd for $C_{26}H_{33}NO_2$; $[M+H]^+$ 392.2584, found: 392.2583



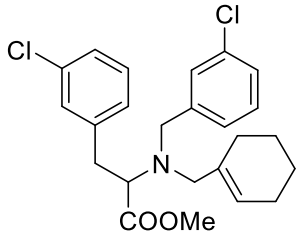
Methyl 2-((4-(tert-butyl)benzyl)(cyclohex-1-en-1-ylmethyl)amino)-3-(4-(tert-butyl)phenyl)propanoate (3ae):

Yield = 56% (52.8 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.43

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 1.7 Hz, 1H), 7.35 (d, J = 4.1 Hz, 6H), 7.31 (d, J = 11.5 Hz, 1H), 5.46 (t, J = 3.8 Hz, 1H), 3.96 (s, 1H), 3.93 (s, 1H), 3.79 (s, 3H), 3.62 – 3.53 (m, 1H), 3.52 (d, J = 1.3 Hz, 1H), 3.48 (s, 1H), 2.49 – 2.41 (m, 1H), 2.40 – 2.32 (m, 1H), 2.06 (d, 1H), 2.03 (d, 1H), 1.68 – 1.52 (m, 6H), 1.36 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.7, 149.7, 136.8, 133.9, 128.7, 125.0, 124.3, 58.8, 53.8, 51.0, 38.4, 34.5, 31.5, 27.3, 25.4, 22.9, 22.4.

HRMS: calcd for $C_{32}H_{45}NO_2$; $[M+H]^+$ 476.3523, found: 476.3521



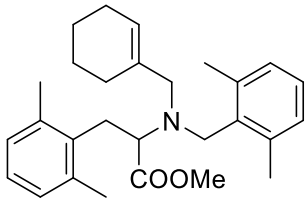
Methyl 2-((3-chlorobenzyl)(cyclohex-1-en-1-ylmethyl)amino)-3-(3-chlorophenyl)propanoate (3af):

Yield = 67% (116 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 63/1). R_f: 0.39

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 2.3 Hz, 2H), 7.30 (d, J = 6.4 Hz, 4H), 7.29 – 7.26 (m, 2H), 5.49 (s, 1H), 3.97 (s, 1H), 3.95 (s, 1H), 3.83 (s, 3H), 3.59 (d, J = 1.9 Hz, 1H), 3.56 (d, J = 3.9 Hz, 2H), 2.54 – 2.49 (m, 1H), 2.43 (d, J = 6.0 Hz, 1H), 2.14 (s, 1H), 2.08 (s, 1H), 1.71 – 1.67 (m, 4H), 1.67 – 1.63 (m, 3H), 1.34 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 141.7, 134.2, 133.5, 129.4, 129.2, 127.3, 127.1, 125.0, 58.9, 53.9, 51.2, 38.4, 27.3, 25.4, 22.8, 22.4.

HRMS: calcd for $C_{24}H_{27}Cl_2NO_2$; $[M+H]^+$ 432.1492, found: 432.1493



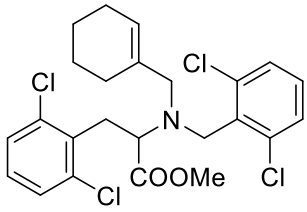
Methyl 2-((cyclohex-1-en-1-ylmethyl)(2,6-dimethylbenzyl)amino)-3-(2,6-dimethylphenyl)propanoate (3ag):

Yield = 45% (37.8 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 60/1). R_f: 0.39

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (s, 1H), 7.08 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 7.5 Hz, 4H), 5.25 (s, 1H), 3.91 (d, J = 12.5 Hz, 2H), 3.77 (s, 3H), 3.49 (t, J = 7.3 Hz, 1H), 2.58 (dd, J = 14.5, 8.1 Hz, 1H), 2.32 (s, 12H), 1.90 (s, 2H), 1.60 (d, J = 17.8 Hz, 2H), 1.50 – 1.41 (m, 4H), 1.30 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5, 138.8, 134.6, 134.0, 128.2, 127.1, 123.2, 59.4, 51.0, 47.8, 36.6, 27.8, 25.3, 22.9, 22.3, 20.1.

HRMS: calcd for $C_{28}H_{37}NO_2$; $[M+H]^+$ 420.2897, found: 420.2895



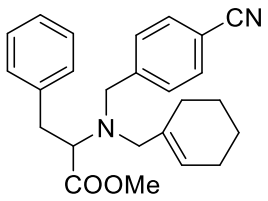
Methyl 2-((cyclohex-1-en-1-ylmethyl)(2,6-dichlorobenzyl)amino)-3-(2,6-dichlorophenyl)propanoate (3ah):

Yield = 47% (47.12 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 60/1). R_f: 0.45

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 3.2 Hz, 4H), 7.16 (t, J = 8.0 Hz, 2H), 5.34 (s, 1H), 4.30 (d, J = 12.7 Hz, 2H), 4.03 (d, J = 12.7 Hz, 2H), 3.76 (s, 3H), 3.45 (dd, J = 8.3, 5.9 Hz, 1H), 2.64 – 2.50 (m, 2H), 1.90 (s, 2H), 1.47 (h, J = 5.4 Hz, 4H), 1.32 – 1.29 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 137.8, 134.1, 134.0, 129.0, 128.4, 123.2, 60.5, 51.2, 49.0, 36.6, 28.2, 25.4, 23.0, 22.3.

HRMS: calcd for $C_{24}H_{25}Cl_4NO_2$; $[M+H]^+$ 502.0683, found: 502.0681



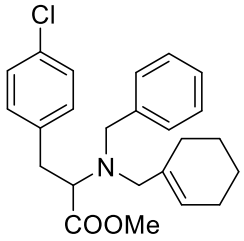
Methyl N-(4-cyanobenzyl)-N-(cyclohex-1-en-1-ylmethyl)phenylalaninate (3ai):

Yield = 72% (84 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 58/1). R_f: 0.29

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (td, J = 7.3, 6.3, 1.8 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.48 – 7.43 (m, 4H), 7.42 – 7.36 (m, 1H), 5.54 (d, J = 4.3 Hz, 1H), 4.15 (d, J = 14.6 Hz, 1H), 4.01 (dd, J = 14.3, 4.6 Hz, 1H), 3.90 (s, 3H), 3.78 (dd, J = 15.7, 5.2 Hz, 1H), 3.70 – 3.60 (m, 2H), 2.52 (dt, J = 14.7, 8.8 Hz, 2H), 2.13 (s, 2H), 1.73 (d, J = 14.2 Hz, 5H), 1.41 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 145.9, 138.9, 133.5, 132.0, 129.4, 129.0, 128.3, 127.3, 124.7, 119.1, 110.8, 59.3, 54.9, 53.9, 51.2, 38.4, 27.4, 25.4, 22.8, 22.4.

HRMS: calcd for $C_{25}H_{28}N_2O_2$; $[M+H]^+$ 389.2224, found: 389.2220



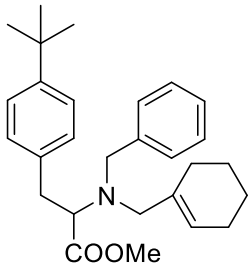
Methyl 2-(benzyl(cyclohex-1-en-1-ylmethyl)amino)-3-(4-chlorophenyl)propanoate (3aj):

Yield = 76% (60.1 mg), white solid oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.37

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.32 (m, 6H), 7.32 – 7.28 (m, 3H), 5.43 (s, *J* = 3.7 Hz, 1H), 3.92 (dd, *J* = 13.9, 2.1 Hz, 2H), 3.78 (s, 3H), 3.55 – 3.49 (m, 3H), 2.47 – 2.34 (m, 2H), 2.07 – 1.97 (m, 2H), 1.68 – 1.63 (m, 2H), 1.62 – 1.59 (m, 2H), 1.30 (d, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5, 139.5, 138.4, 133.7, 132.6, 130.3, 129.0, 128.3, 128.2, 127.1, 124.5, 58.9, 54.4, 53.5, 51.2, 38.4, 27.3, 25.4, 22.8, 22.4.

HRMS: calcd for $C_{24}H_{28}ClNO_2$; $[M+H]^+$ 398.1881, found: 398.1881



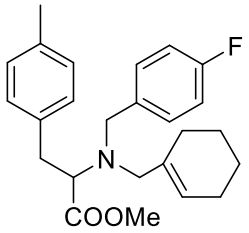
Methyl 2-(benzyl(cyclohex-1-en-1-ylmethyl)amino)-3-(4-(tert-butyl)phenyl)propanoate (3ak):

Yield = 61% (101.4 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.38

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.37 – 7.35 (m, 2H), 7.30 – 7.27 (m, 2H), 5.44 (s, 1H), 4.03 (d, J = 14.5 Hz, 1H), 3.88 (d, J = 13.7 Hz, 1H), 3.79 (s, 3H), 3.63 (d, J = 14.4 Hz, 1H), 3.58 – 3.51 (m, 2H), 2.49 – 2.35 (m, 2H), 2.03 (s, 2H), 1.65 – 1.57 (m, 6H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5, 150.1, 144.4, 136.1, 133.7, 129.1, 128.7, 125.1, 125.1, 125.0, 124.5, 59.1, 54.3, 53.8, 51.2, 38.4, 34.5, 31.5, 27.3, 25.4, 22.9, 22.4.

HRMS: calcd for $C_{28}H_{37}NO_2$; $[M+H]^+$ 420.2897, found: 420.2894



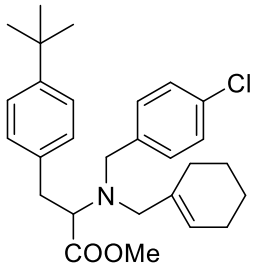
Methyl 2-((cyclohex-1-en-1-ylmethyl)(4-fluorobenzyl)amino)-3-(p-tolyl)propanoate (3al):

Yield = 71% (56.2 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 60/1). R_f: 0.42

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 – 7.20 (m, 2H), 7.18 – 7.12 (m, 2H), 7.03 (d, *J* = 7.8 Hz, 2H), 6.93 – 6.87 (m, 2H), 5.32 (d, *J* = 3.6 Hz, 1H), 3.79 (dd, *J* = 13.8, 5.4 Hz, 2H), 3.66 (s, 3H), 3.41 (d, *J* = 9.2 Hz, 2H), 3.38 – 3.33 (m, 2H), 2.25 (s, 3H), 1.94 – 1.85 (m, 2H), 1.51 – 1.45 (m, 5H), 1.27 – 1.16 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.4, 163.1, 136.5, 135.5, 135.5, 133.7, 130.3, 128.9, 128.8, 124.3, 114.7, 58.8, 53.9, 53.4, 51.0, 38.3, 27.3, 25.4, 22.8, 22.4, 21.1.

HRMS: calcd for $C_{25}H_{30}FNO_2$; $[M+H]^+$ 396.5259, found: 396.5253



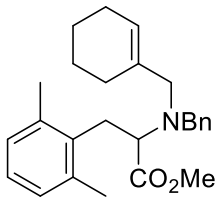
Methyl 3-(4-(tert-butyl)phenyl)-2-((4-chlorobenzyl)(cyclohex-1-en-1-ylmethyl)amino)propanoate (3am):

Yield = 76% (69 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 60/1). R_f: 0.42

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 3H), 7.30 (s, 1H), 7.28 (d, J = 7.7 Hz, 4H), 5.42 (t, J = 4.5 Hz, 1H), 3.90 (td, J = 13.1, 4.5 Hz, 2H), 3.77 (s, 3H), 3.70 – 3.66 (m, 1H), 3.54 – 3.46 (m, 3H), 2.48 – 2.32 (m, 2H), 2.01 (s, 2H), 1.58 (s, 2H), 1.39 (d, J = 4.7 Hz, 2H), 1.34 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5, 149.9, 138.5, 136.4, 133.7, 132.5, 130.3, 128.7, 128.2, 125.1, 124.4, 58.9, 54.0, 53.6, 51.1, 38.4, 34.5, 31.4, 29.8, 27.3, 25.4, 22.4.

HRMS: calcd for $C_{28}H_{36}ClNO_2$; $[M+H]^+$ 454.2507, found: 454.2505



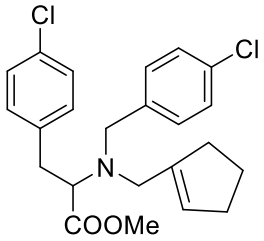
Methyl 2-(benzyl(cyclohex-1-en-1-ylmethyl)amino)-3-(2,6-dimethylphenyl)propanoate (3an):

Yield = 80 % (63 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.46

^{1}H NMR (500 MHz, Chloroform-d) δ 7.31 – 7.26 (m, 5H), 7.08 – 7.02 (m, 1H), 6.98 (d, J = 7.4 Hz, 2H), 5.43 (s, 1H), 3.92 (dd, J = 12.6, 2.5 Hz, 1H), 3.84 (d, J = 2.3 Hz, 1H), 3.77 (s, 3H), 3.62 – 3.55 (m, 2H), 3.52 (d, J = 7.5 Hz, 1H), 2.33 (d, J = 2.4 Hz, 6H), 1.98 (s, 2H), 1.54 – 1.49 (m, 5H), 1.32 – 1.29 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.6, 139.8, 138.7, 134.8, 134.1, 129.6, 128.3, 127.9, 127.1, 126.8, 123.9, 59.5, 53.9, 51.0, 48.3, 38.0, 27.3, 25.4, 22.8, 22.3, 20.3.

HRMS: calcd for $C_{26}H_{33}NO_2$; $[M+H]^+$ 392.2584, found: 392.2586



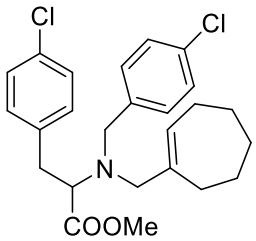
Methyl 2-((4-chlorobenzyl)(cyclopent-1-en-1-ylmethyl)amino)-3-(4-chlorophenyl)propanoate (3ao):

Yield = 74% (122.9 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 63/1). R_f: 0.33

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (t, *J* = 8.7 Hz, 8H), 5.35 (s, 1H), 3.86 (d, *J* = 14.0 Hz, 2H), 3.78 (s, 3H), 3.52 (d, *J* = 7.2 Hz, 2H), 3.49 (d, *J* = 5.7 Hz, 1H), 2.62 – 2.51 (m, 2H), 2.34 – 2.30 (m, 2H), 2.06 – 1.94 (m, 2H), 1.88 – 1.82 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.0, 140.3, 138.0, 132.8, 130.2, 128.4, 126.7, 59.4, 53.7, 51.2, 34.4, 32.5, 31.6, 23.4.

HRMS: calcd for $C_{23}H_{25}Cl_2NO_2$; $[M+H]^+$ 417.1262, found: 417.1258



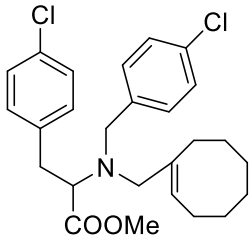
Methyl 2-((4-chlorobenzyl)(cyclohept-1-en-1-ylmethyl)amino)-3-(4-chlorophenyl)propanoate (3ap):

Yield = 55% (98 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 63/1). R_f: 0.38

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.28 (m, 8H), 5.55 (t, *J* = 6.4 Hz, 1H), 3.86 (dt, *J* = 14.1, 3.0 Hz, 2H), 3.76 (dd, *J* = 5.4, 2.1 Hz, 3H), 3.68 – 3.58 (m, 1H), 3.50 – 3.45 (m, 2H), 2.50 – 2.34 (m, 2H), 2.05 (q, *J* = 5.7 Hz, 2H), 1.92 – 1.79 (m, 2H), 1.63 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 140.0, 138.0, 132.7, 130.2, 129.5, 128.4, 59.5, 53.8, 51.1, 40.6, 32.3, 32.2, 28.4, 27.1, 26.5.

HRMS: calcd for $C_{25}H_{29}Cl_2NO_2$; $[M+H]^+$ 446.1648, found: 446.1647



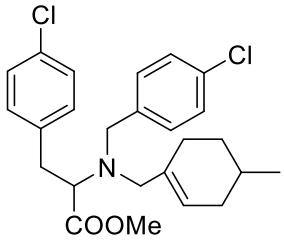
Methyl (E)-2-((4-chlorobenzyl)(cyclooct-1-en-1-ylmethyl)amino)-3-(4-chlorophenyl)propanoate (3aq):

Yield = 50% (91.6 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 63/1). R_f: 0.36

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 8H), 5.56 (t, J = 6.4 Hz, 1H), 3.89 (s, 1H), 3.85 (s, 1H), 3.76 (s, 3H), 3.52 (s, 1H), 3.49 – 3.44 (m, 2H), 2.50 – 2.46 (m, 1H), 2.44 – 2.37 (m, 2H), 2.07 (dq, J = 6.6, 3.6, 2.6 Hz, 2H), 1.92 – 1.82 (m, 2H), 1.80 – 1.71 (m, 1H), 1.67 (dd, J = 9.1, 4.2 Hz, 1H), 1.62 (s, 1H), 1.45 (dd, J = 8.0, 4.9 Hz, 1H), 1.41 (dd, J = 8.4, 4.0 Hz, 1H), 1.29 (d, J = 4.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.0, 138.0, 136.9, 136.3, 132.7, 130.7, 130.1, 130.0, 128.4, 128.3, 127.4, 59.4, 56.3, 53.8, 51.1, 37.3, 29.9, 28.4, 28.2, 26.5, 26.4, 26.1.

HRMS: calcd for $C_{26}H_{31}Cl_2NO_2$; $[M+H]^+$ 460.1805, found: 460.1807



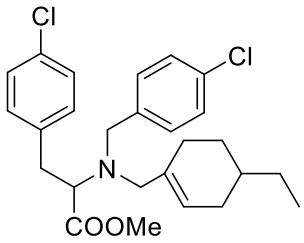
Methyl 2-((4-chlorobenzyl)((4-methylcyclohex-1-en-1-yl)methyl)amino)-3-(4-chlorophenyl)propanoate (3ar):

Yield = 62% (55.3 mg), light green oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.42

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (s, 8H), 5.40 (s, 1H), 3.90 (s, 1H), 3.87 (s, 1H), 3.78 (s, 3H), 3.55 – 3.50 (m, 1H), 3.50 (d, J = 1.9 Hz, 2H), 2.47 – 2.41 (m, 1H), 2.44 – 2.39 (m, 1H), 2.09 (t, J = 11.7 Hz, 1H), 1.71 – 1.67 (m, 2H), 1.65 (s, 2H), 1.32 – 1.29 (m, 1H), 1.20 (td, J = 11.3, 4.1 Hz, 1H), 1.01 (t, J = 5.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.3, 138.1, 133.2, 132.8, 130.3, 128.4, 124.1, 59.0, 53.6, 51.2, 37.8, 34.1, 31.2, 28.4, 27.4, 21.8.

HRMS: calcd for $C_{25}H_{29}Cl_2NO_2$; $[M+H]^+$ 446.1648, found: 446.1652



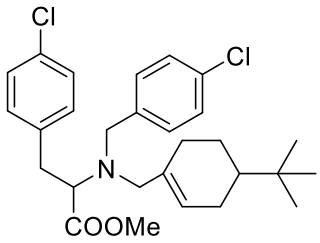
Methyl 2-((4-chlorobenzyl)((4-ethylcyclohex-1-en-1-yl)methyl)amino)-3-(4-chlorophenyl)propanoate (3as):

Yield = 68% (62.61mg), chartreuse oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.38

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, *J* = 1.1 Hz, 8H), 5.40 (s, 1H), 3.90 (d, *J* = 2.0 Hz, 1H), 3.87 (d, *J* = 2.0 Hz, 1H), 3.78 (s, 3H), 3.52 (s, 1H), 3.49 (s, 1H), 2.48 – 2.43 (m, 1H), 2.42 – 2.38 (m, 1H), 2.16 – 2.09 (m, 1H), 1.77 – 1.73 (m, 1H), 1.67 (s, 1H), 1.65 (s, 2H), 1.38 – 1.35 (m, 2H), 1.33 (d, *J* = 3.9 Hz, 1H), 1.32 – 1.29 (m, 1H), 1.21 – 1.16 (m, 1H), 0.98 – 0.95 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 138.1, 133.5, 133.4, 132.7, 130.8, 130.3, 130.3, 128.4, 124.3, 124.1, 59.0, 53.7, 51.2, 38.2, 35.2, 31.9, 29.2, 28.8, 28.7, 27.6, 11.6.

HRMS: calcd for $C_{25}H_{29}Cl_2NO_2$; $[M+H]^+$ 460.1805, found: 460.1805



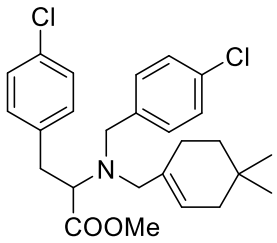
Methyl 2-(((4-(tert-butyl)cyclohex-1-en-1-yl)methyl)(4-chlorobenzyl)amino)-3-(4-chlorophenyl)propanoate (3at):

Yield = 53% (102.9 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 63/1). R_f: 0.3

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 2.3 Hz, 8H), 5.42 (d, *J* = 5.2 Hz, 1H), 3.89 (d, *J* = 4.2 Hz, 1H), 3.86 (d, *J* = 4.2 Hz, 1H), 3.78 (s, 3H), 3.52 (d, *J* = 3.2 Hz, 1H), 3.49 (d, *J* = 2.7 Hz, 1H), 2.47 – 2.41 (m, 1H), 2.07 – 1.98 (m, 1H), 1.82 – 1.73 (m, 3H), 1.69 (d, *J* = 4.0 Hz, 1H), 1.63 (s, 1H), 1.29 (s, 1H), 1.28 – 1.20 (m, 1H), 1.13 (dq, *J* = 18.7, 6.7, 5.8 Hz, 1H), 0.93 (d, *J* = 4.6 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 138.1, 138.1, 133.5, 133.2, 132.8, 132.7, 130.4, 130.2, 128.3, 124.7, 59.0, 53.6, 51.2, 44.4, 44.0, 38.0, 37.6, 32.2, 29.0, 27.3, 24.1.

HRMS: calcd for $C_{28}H_{35}Cl_2NO_2$; $[M+H]^+$488.2118, found: 488.2121



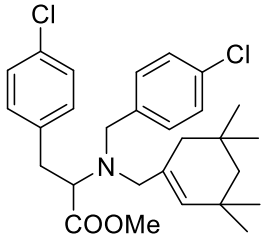
Methyl 2-((4-chlorobenzyl)((4,4-dimethylcyclohex-1-en-1-yl)methyl)amino)-3-(4-chlorophenyl)propanoate (3au):

Yield = 56% (102.7 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.33

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 1.4 Hz, 8H), 5.34 (s, 1H), 3.89 (d, J = 14.0 Hz, 2H), 3.77 (s, 3H), 3.55 – 3.52 (m, 1H), 3.49 (s, 2H), 2.50 – 2.39 (m, 2H), 1.85 – 1.77 (m, 2H), 1.35 – 1.29 (m, 4H), 0.97 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 138.0, 132.8, 132.0, 130.3, 128.4, 123.6, 59.2, 53.7, 51.2, 39.4, 38.0, 35.6, 28.9, 28.5, 27.8, 25.3.

HRMS: calcd for $C_{26}H_{31}Cl_2NO_2$; $[M+H]^+$460.1805, found:460.1803



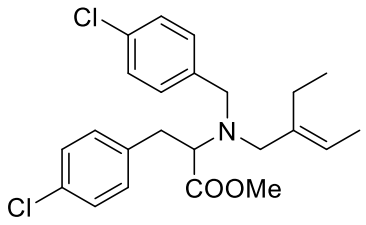
Methyl 2-((4-chlorobenzyl)((3,3,5,5-tetramethylcyclohex-1-en-1-yl)methyl)amino)-3-(4-chlorophenyl)propanoate (3av):

Yield = 55% (108 mg), yellow oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.38

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (s, 8H), 5.18 (s, 1H), 3.89 (s, 1H), 3.86 (s, 1H), 3.78 (s, 3H), 3.53 (s, 1H), 3.50 (s, 1H), 3.47 (d, J = 7.4 Hz, 1H), 2.39 (d, J = 7.4 Hz, 2H), 1.63 (s, 2H), 1.32 (d, J = 4.0 Hz, 2H), 1.05 (s, 3H), 0.99 (s, 3H), 0.87 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 138.1, 133.5, 132.8, 130.4, 129.5, 128.4, 59.1, 53.9, 51.1, 49.6, 41.5, 39.0, 32.4, 31.1, 30.7, 28.9.

HRMS: calcd for $C_{28}H_{35}Cl_2NO_2$; $[M+H]^+$488.2118, found: 488.2115



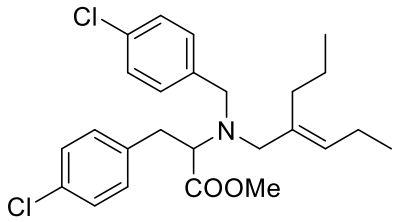
Methyl 2-((4-chlorobenzyl)((3,5,5-trimethylcyclohex-1-en-1-yl)methyl)amino)-3-(4-chlorophenyl)propanoate (3aw):

Yield = 88% (74.1 mg), colorless oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.5

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 – 7.29 (m, 4H), 7.27 (d, J = 8.6 Hz, 4H), 5.17 (t, J = 6.8 Hz, 1H), 3.88 (s, 1H), 3.86 (s, 1H), 3.76 (s, 3H), 3.51 (s, 1H), 3.48 (d, J = 3.5 Hz, 1H), 3.45 (d, J = 7.7 Hz, 1H), 2.56 – 2.51 (m, 1H), 2.37 (d, J = 6.2 Hz, 1H), 1.97 (d, J = 6.7 Hz, 1H), 1.71 – 1.66 (m, 1H), 1.29 (s, 3H), 0.86 (t, J = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.1, 138.0, 137.4, 132.7, 130.2, 128.4, 121.5, 59.5, 53.8, 51.2, 36.6, 22.0, 13.1, 12.6.

HRMS: calcd for $C_{23}H_{27}Cl_2NO_2$; $[M+H]^+$ 420.1492, found: 420.1495



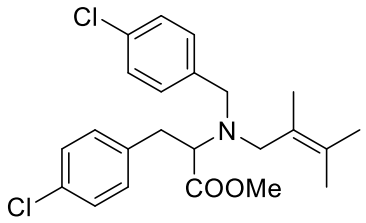
Methyl (E)-2-((4-chlorobenzyl)(2-propylpent-2-en-1-yl)amino)-3-(4-chlorophenyl)propanoate (3ax):

Yield = 80% (68.8 mg), yellowish oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.47

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, J = 1.4 Hz, 8H), 5.16 (t, J = 7.2 Hz, 1H), 3.89 (s, 1H), 3.86 (s, 1H), 3.77 (s, 3H), 3.52 (s, 1H), 3.49 (s, 1H), 3.48 – 3.46 (m, 1H), 2.55 – 2.48 (m, 1H), 2.37 (dd, J = 14.2, 8.1 Hz, 1H), 2.05 – 2.01 (m, 1H), 1.92 -1.86 (m, 1H), 1.66 – 1.60 (m, 1H), 1.26 (ddd, J = 9.1, 7.3, 4.0 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H), 0.82 (d, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.2, 138.0, 134.2, 132.7, 130.4, 130.3, 128.4, 59.3, 53.8, 51.2, 37.0, 31.1, 21.3, 21.2, 14.6, 14.1.

HRMS: calcd for $C_{25}H_{31}Cl_2NO_2$; $[M+H]^+$ 448.1805, found: 448.1801



Methyl 2-((4-chlorobenzyl)(2,3-dimethylbut-2-en-1-yl)amino)-3-(4-chlorophenyl)propanoate (3ay):

Yield = 83% (69.9 mg), yellowish oil. Purified by flash silica gel column chromatography through silica gel (n-Hex /ethyl acetate, 65/1). R_f: 0.5

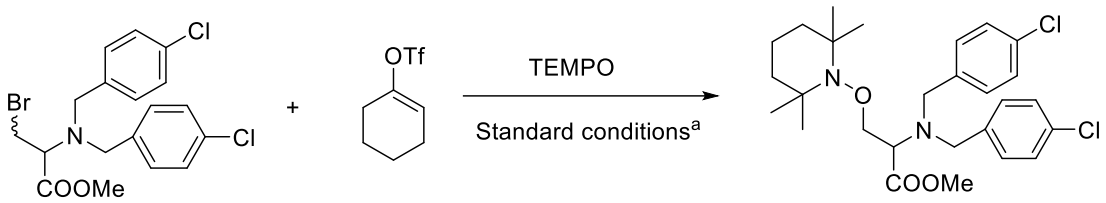
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 7.32 (m, 1H), 7.31 (s, 3H), 7.31 (s, 3H), 7.29 (d, J = 2.7 Hz, 1H), 3.90 (s, 1H), 3.87 (s, 1H), 3.79 (s, 3H), 3.55 (d, J = 7.6 Hz, 1H), 3.53 (d, J = 3.2 Hz, 2H), 3.50 (s, 1H), 2.01 – 1.95 (m, 1H), 1.01 (d, J = 6.8 Hz, 4H), 0.96 (d, J = 6.8 Hz, 5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 151.3, 137.9, 132.8, 130.2, 128.4, 109.5, 59.6, 53.9, 51.3, 35.0, 32.6, 21.8, 21.4.

HRMS: calcd for $C_{23}H_{27}Cl_2NO_2$; $[M+H]^+$ 420.1492, found: 420.1495

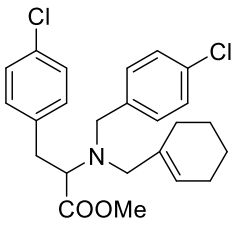
Control experiments

Following the general procedure 2.2 : Using ethyl methyl 2-(bis(4-chlorobenzyl)amino)-3-bromopropanoate (128.7 mg, 0.3 mmol), cyclohex-1-en-1-yl trifluoromethanesulfonate (69 mg, 0.2mmol) and TEMPO reagents (62.5 mg, 0.4mmol), the compound **4** was obtained after purification by flash chromatography. (n-Hex/ethyl acetate = 63:1, 40.58 mg, Yield = 40%, white solid, R_f:)



4 (Observeed by ^{1}H NMR)

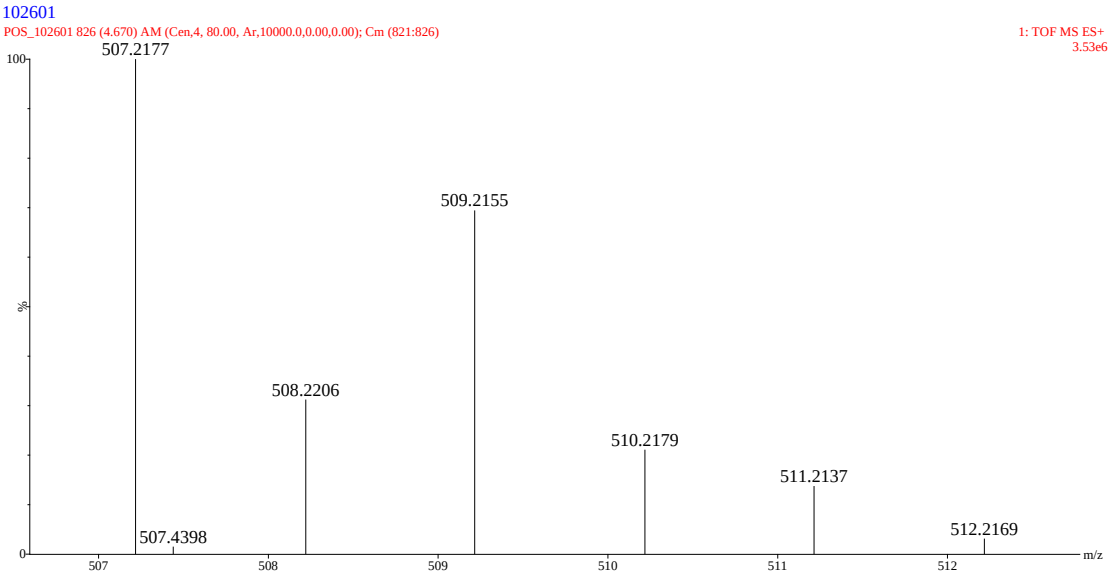
+

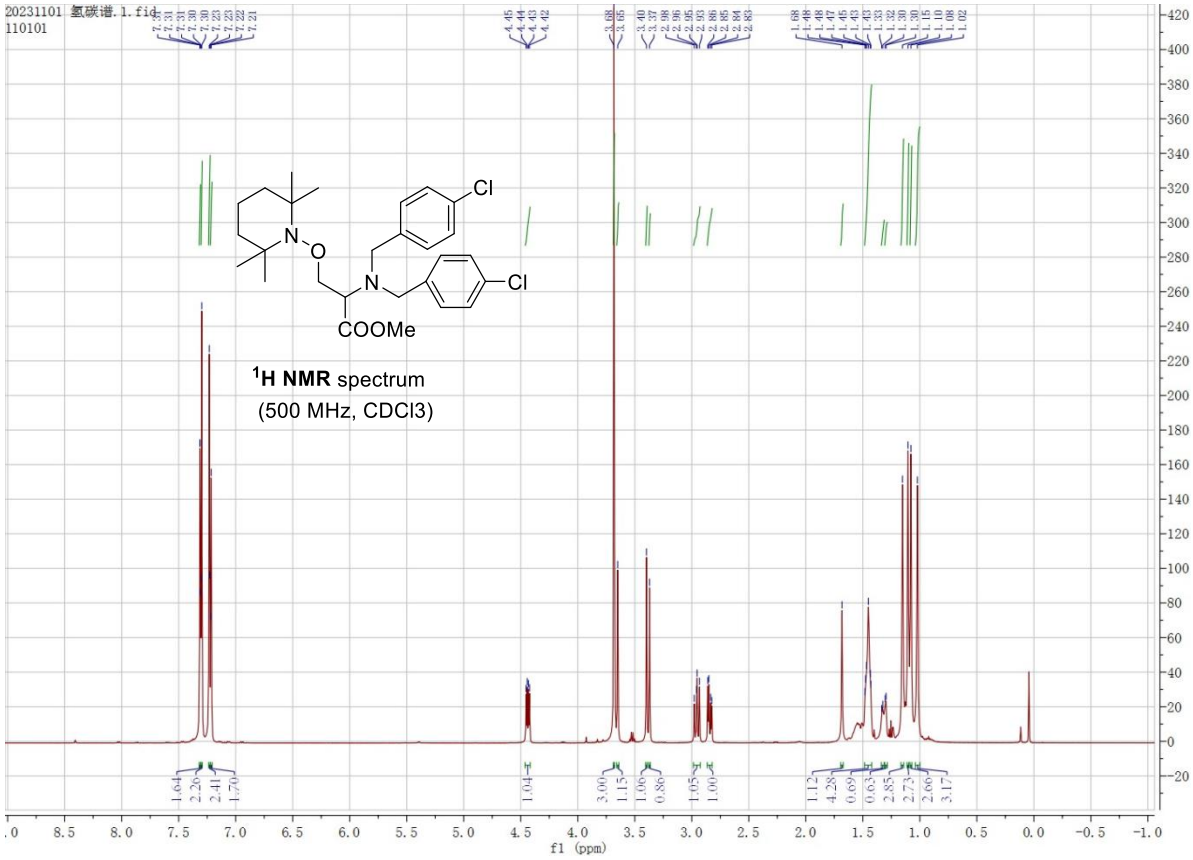


2af (not observed)

HIGH RESLUTION MASS SPECTROMETRY REPORT

Sample No.	Formula (M)	Ion Formula	Measured m/z	Calc m/z	Diff (ppm)
102601	C27H37Cl2N2O3	$[M]^+$	507.2177	507.2176	0.19
		[M-H]-			





^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (s, 2H), 7.30 (s, 2H), 7.23 (d, *J* = 2.1 Hz, 2H), 7.22 (d, *J* = 2.0 Hz, 2H), 4.44 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.68 (s, 3H), 3.65 (s, 1H), 3.40 (s, 1H), 3.37 (s, 1H), 2.96 (dd, *J* = 12.5, 10.3 Hz, 1H), 2.84 (dd, *J* = 12.5, 4.9 Hz,

1H), 1.68 (s, 1H), 1.48 – 1.42 (m, 4H), 1.32 (s, 1H), 1.30 (d, *J* = 3.8 Hz, 1H), 1.15 (s, 3H), 1.10 (s, 3H), 1.08 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.9, 137.3, 132.8, 130.4, 128.4, 59.5, 58.1, 54.6, 51.3, 40.2, 33.3, 20.0, 17.1.

References

1. R. Appel, Angew. Chem., Int. Ed., 1975, 14, 801-811.

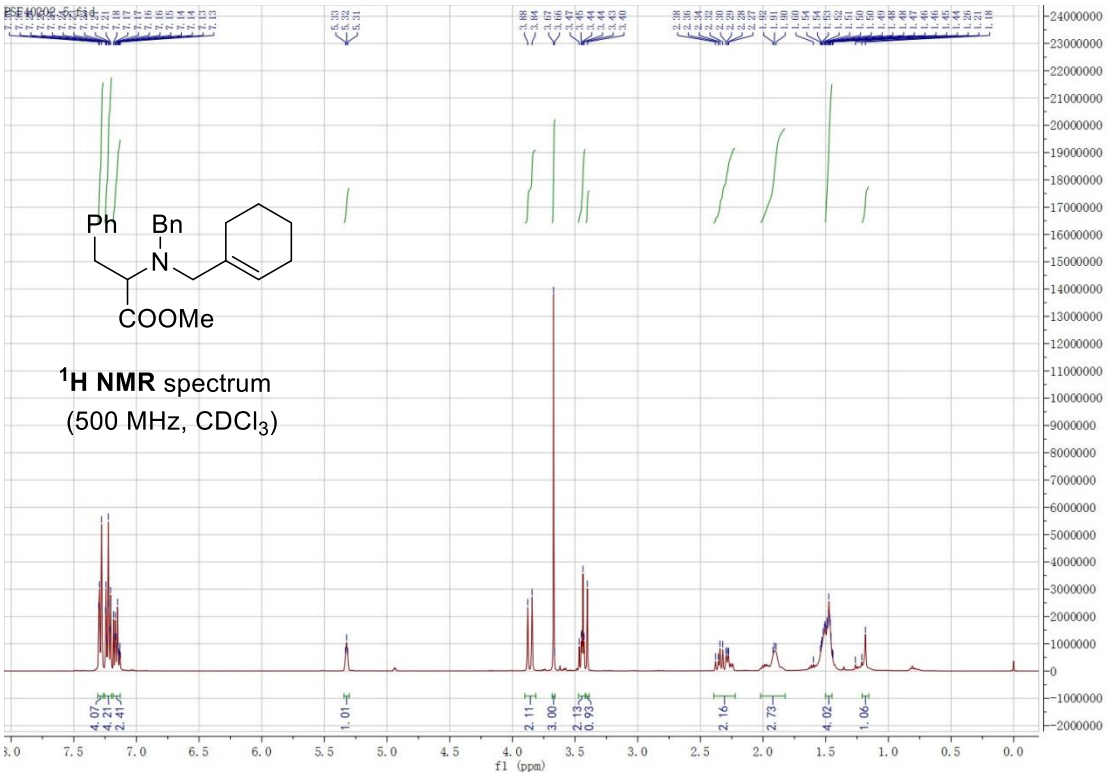
2. H. Xu, C. Zhao, Q. Qian, W. Deng and H. Gong, Chem. Sci., 2013, 4, 4022-4029.

3. S. Tang, Z.-H. Xu, T. Liu, S.-W. Wang, J. Yu, J. Liu, Y. Hong, S.-L. Chen, J. Heand J.-H. Li, Angew. Chem., Int. Ed., 2021, 60, 21360-21367.

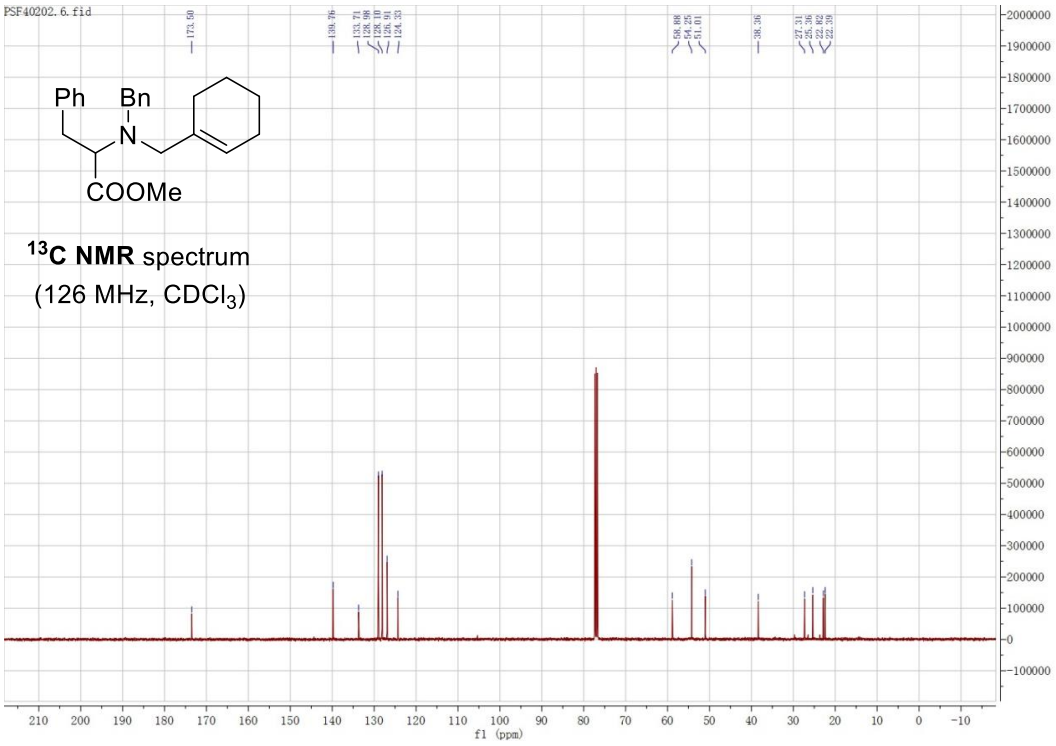
4. R. M. Oechsner, I. H. Lindenmaier and I. Fleischer, Org.Lett., 2023, 25, 1655-1660.

NMR Spectra

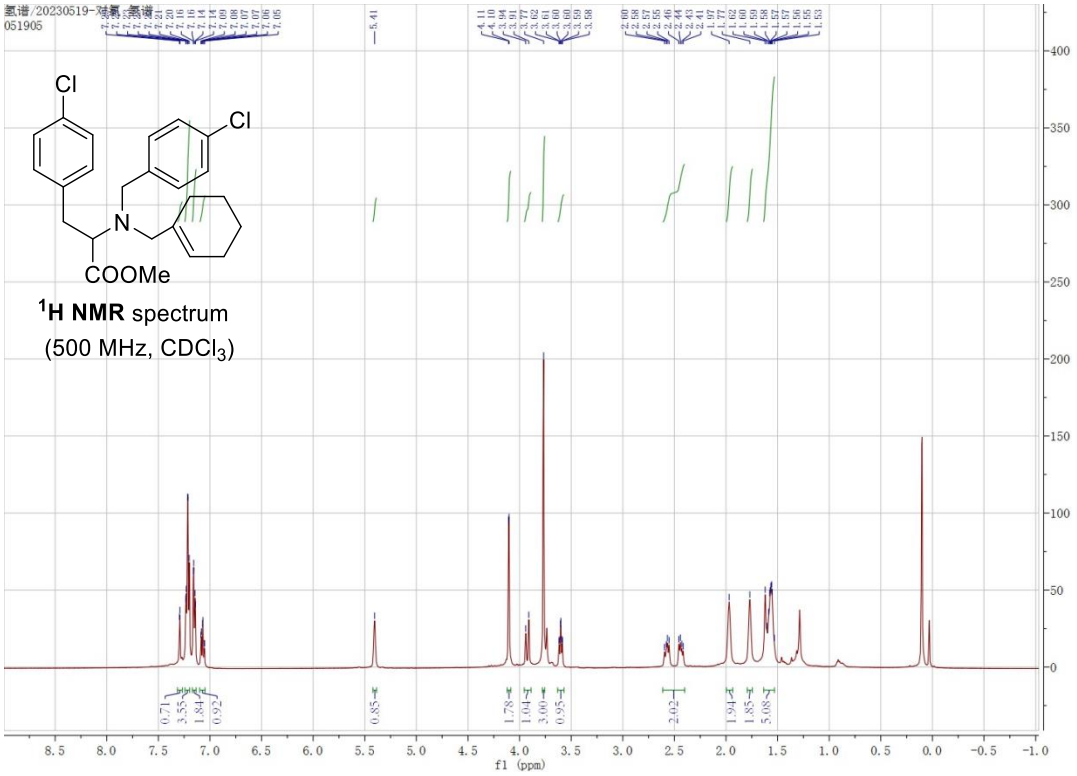
^{1}H NMR spectra of the product **3aa**:



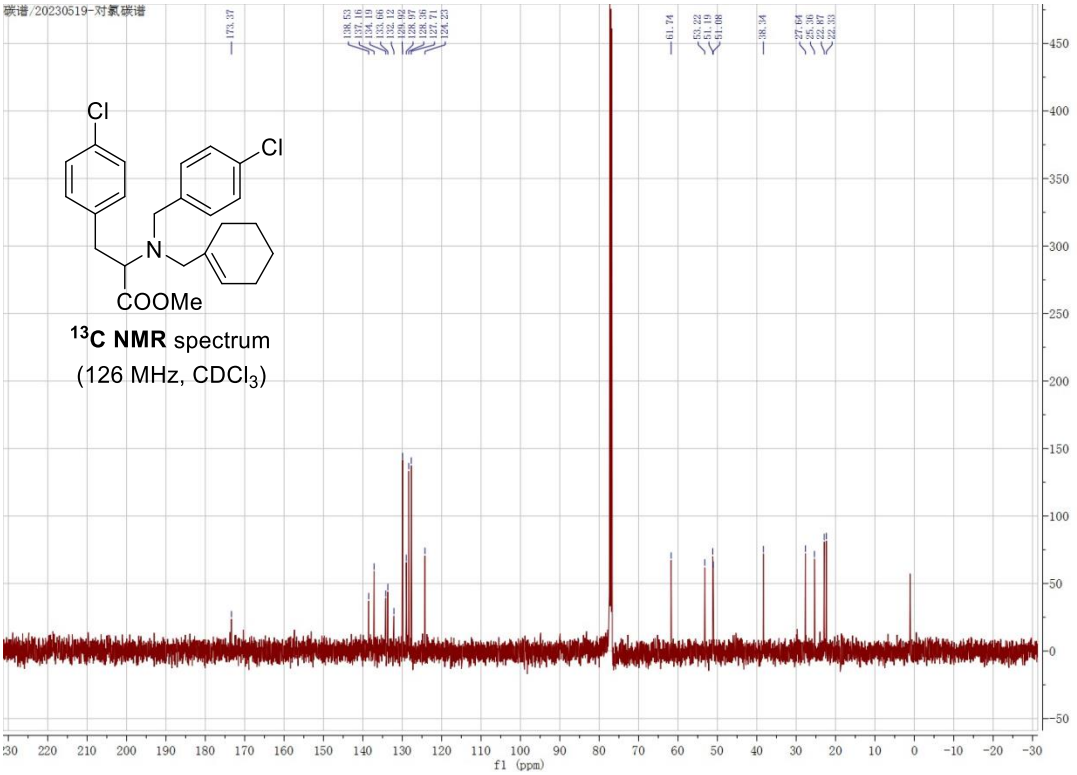
^{13}C NMR spectra of the product **3aa**:



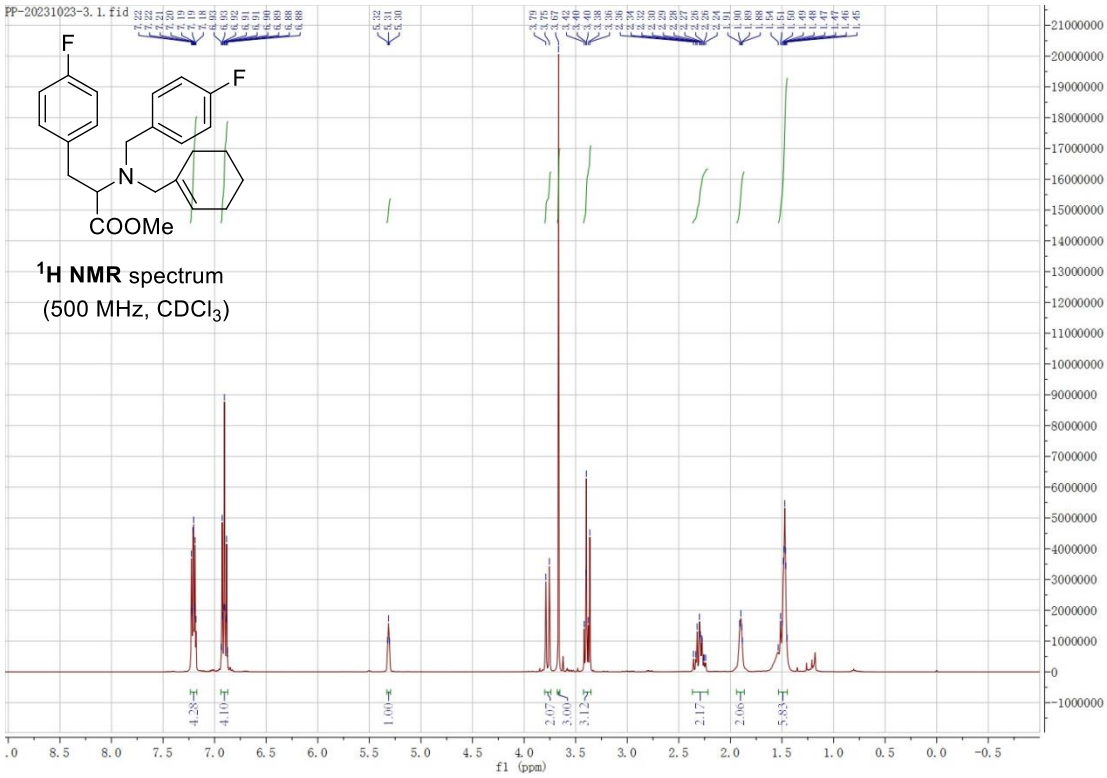
^{1}H NMR spectra of the product **3ab**:



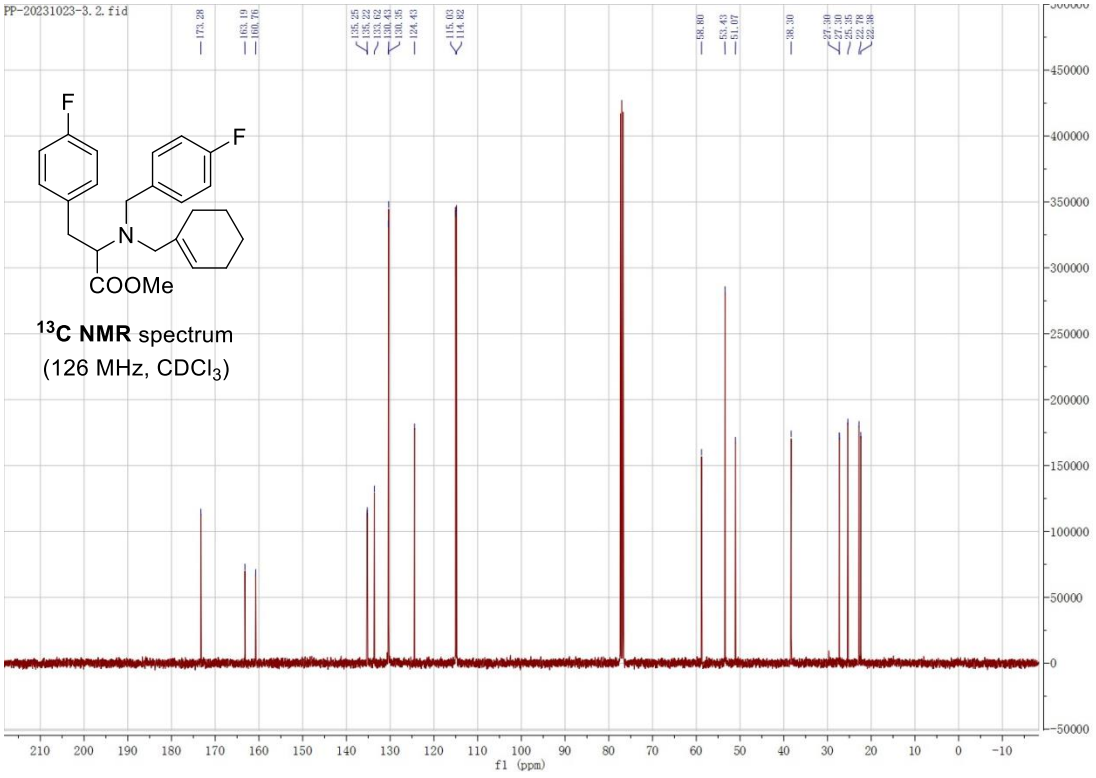
^{13}C NMR spectra of the product **3ab**:



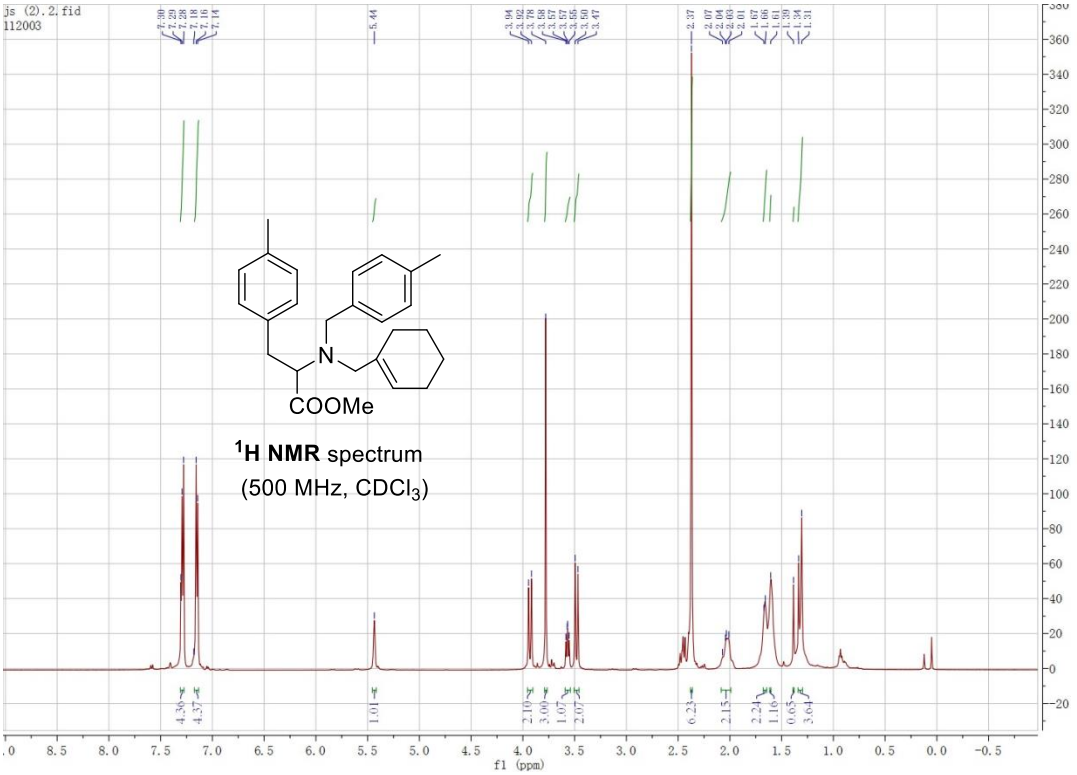
^{1}H NMR spectra of the product **3ac**:



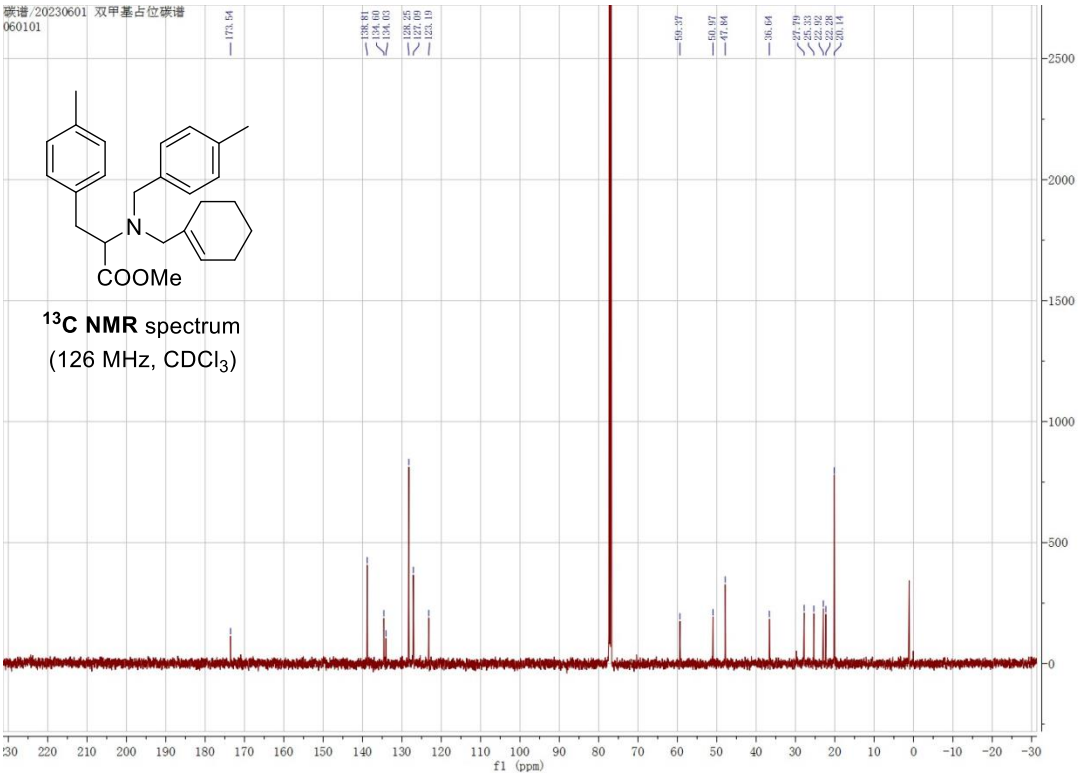
^{13}C NMR spectra of the product **3ac**:



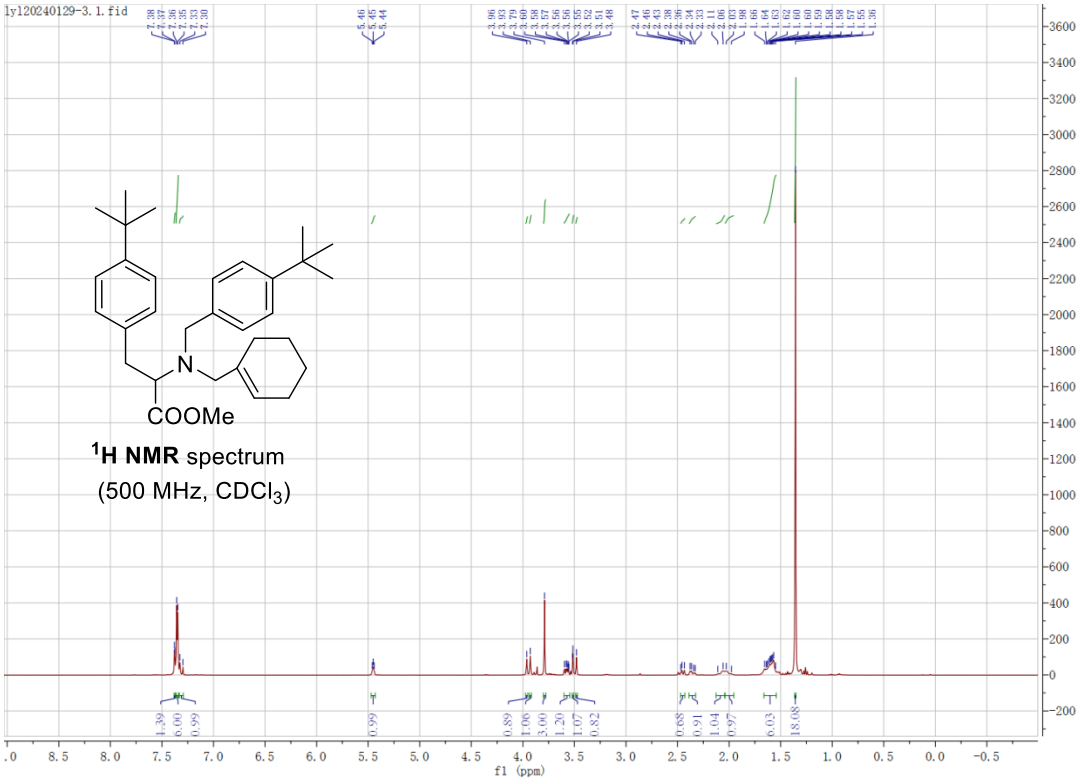
^{1}H NMR spectra of the product **3ad**:



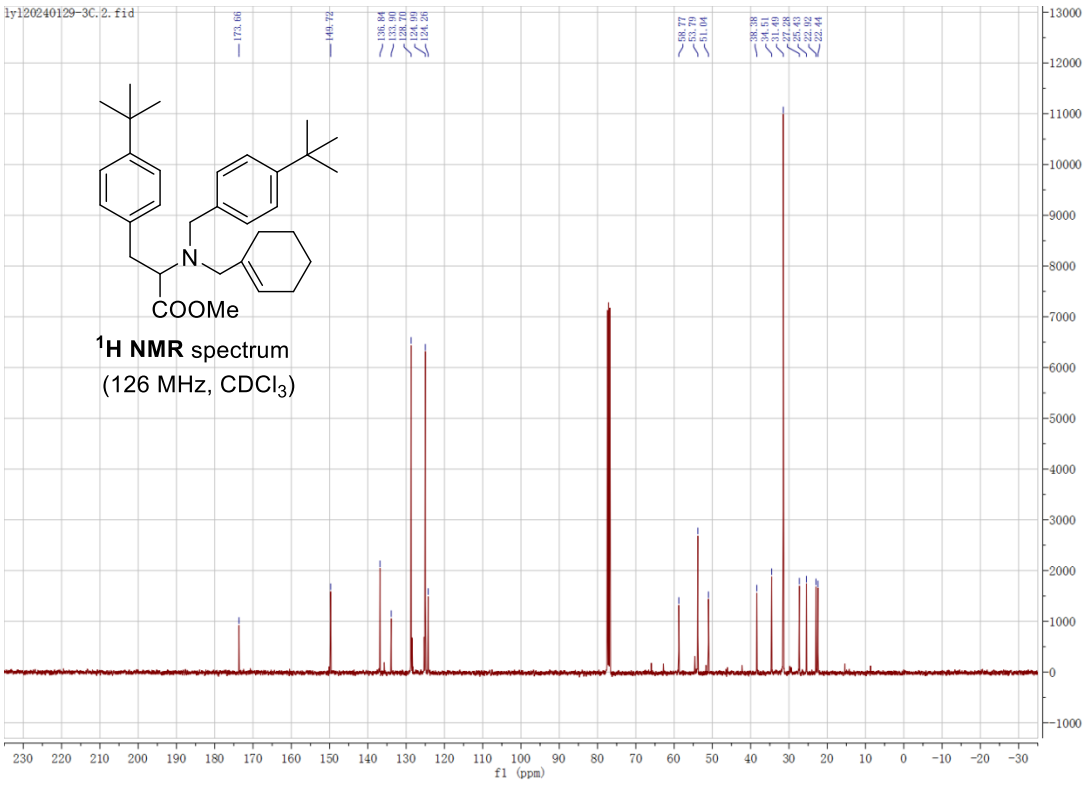
^{13}C NMR spectra of the product **3ad**:



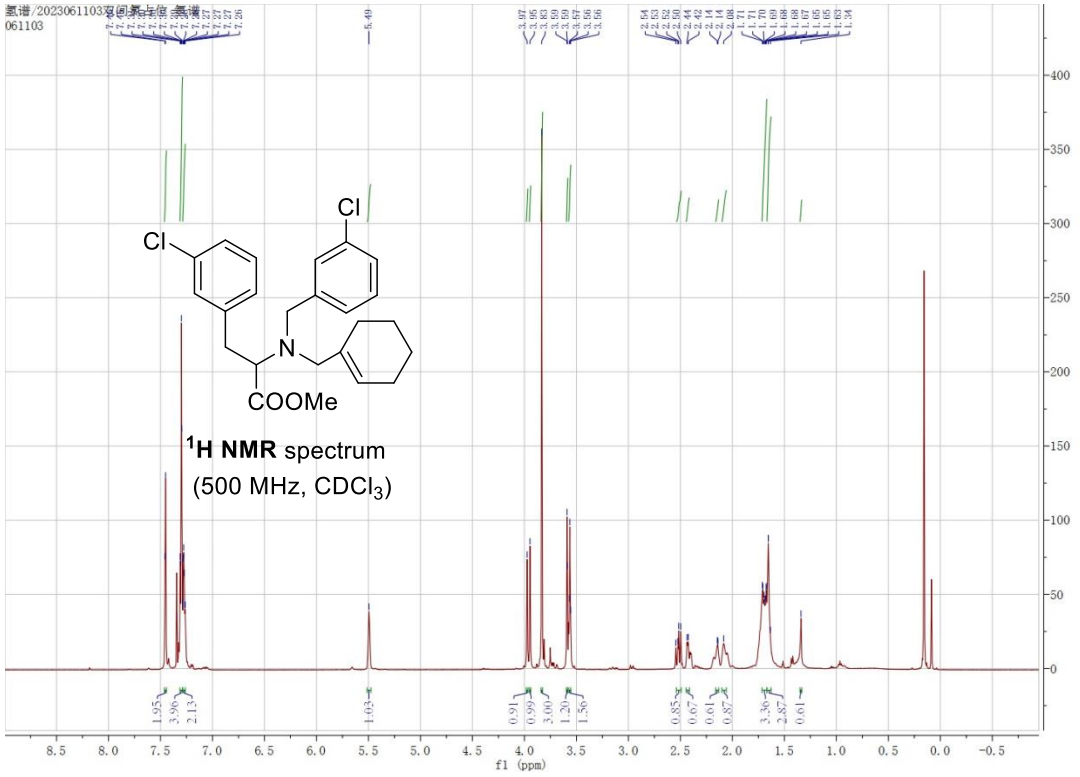
^{1}H NMR spectra of the product **3ae**:



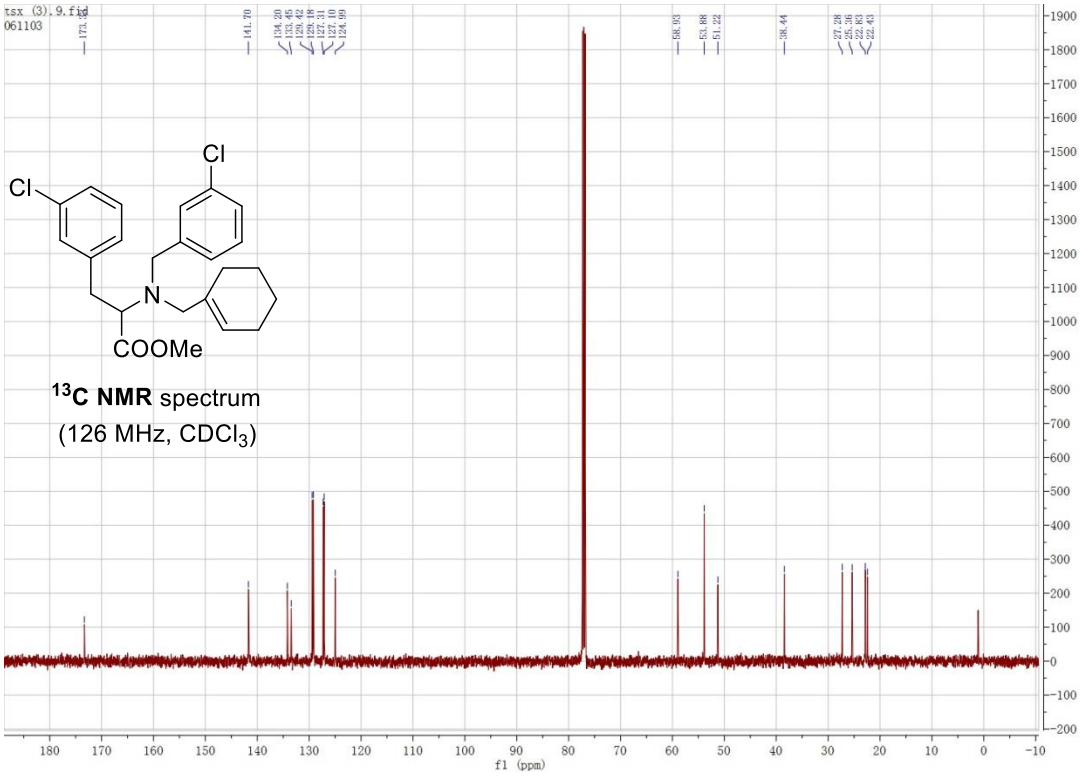
^{13}C NMR spectra of the product **3ae**:



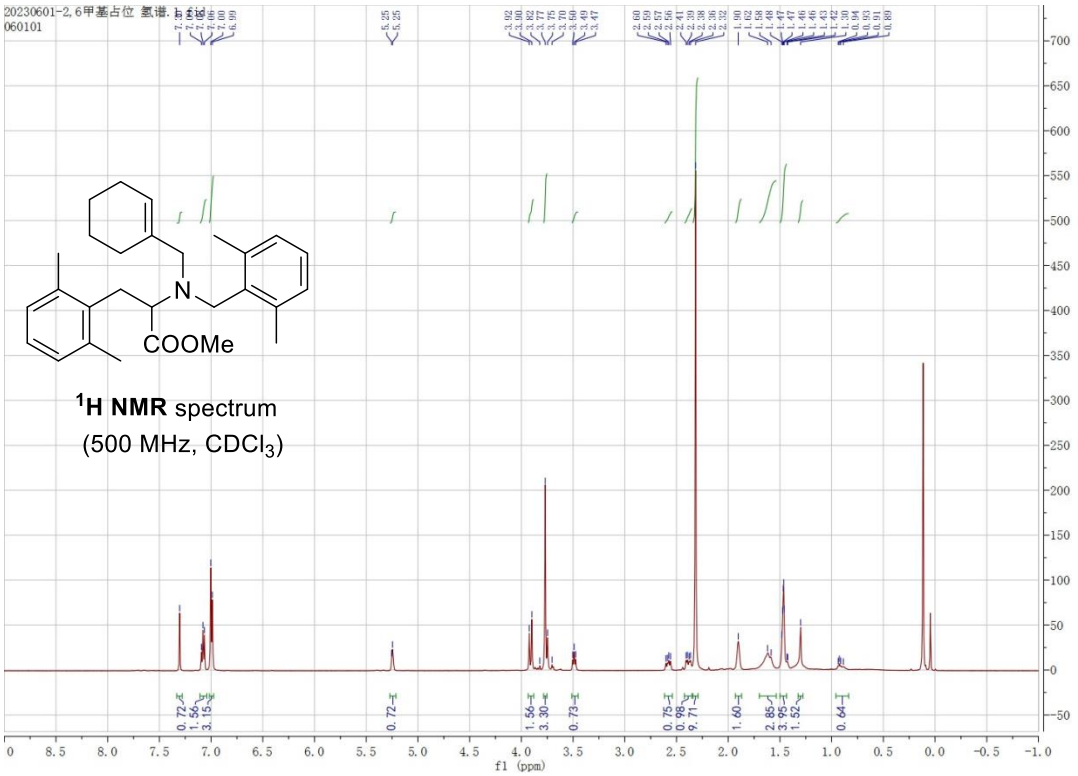
^{1}H NMR spectra of the product **3af**:



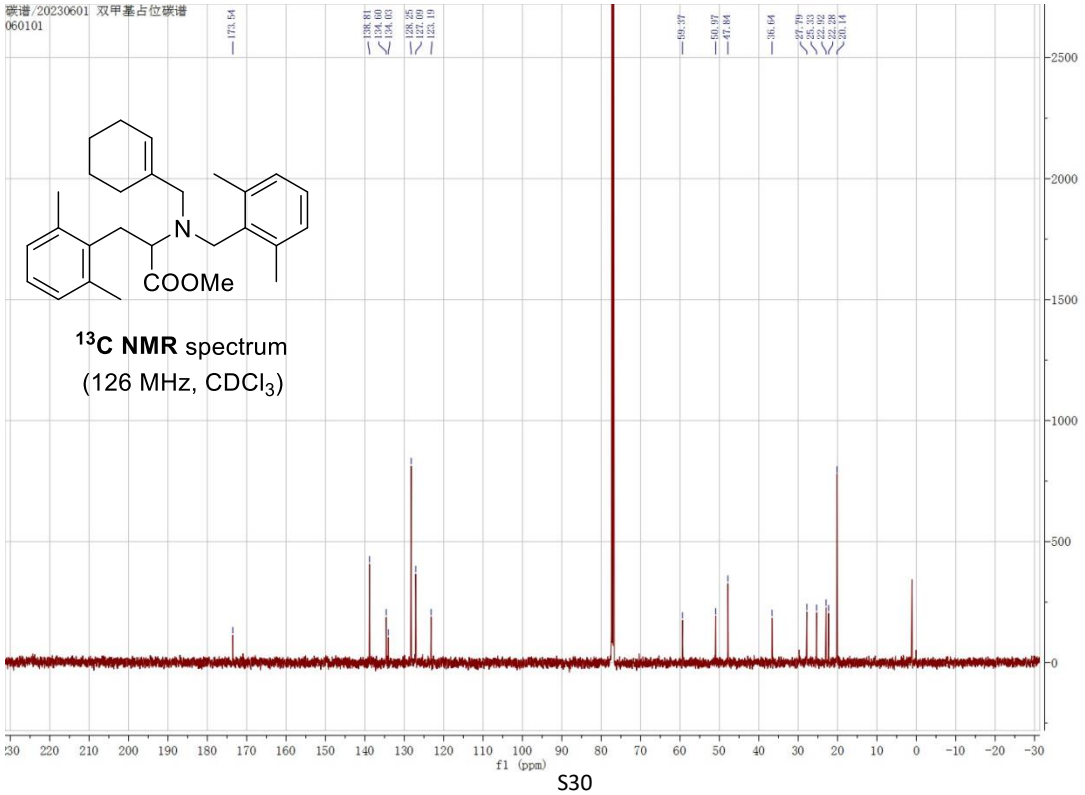
^{13}C NMR spectra of the product **3af**:



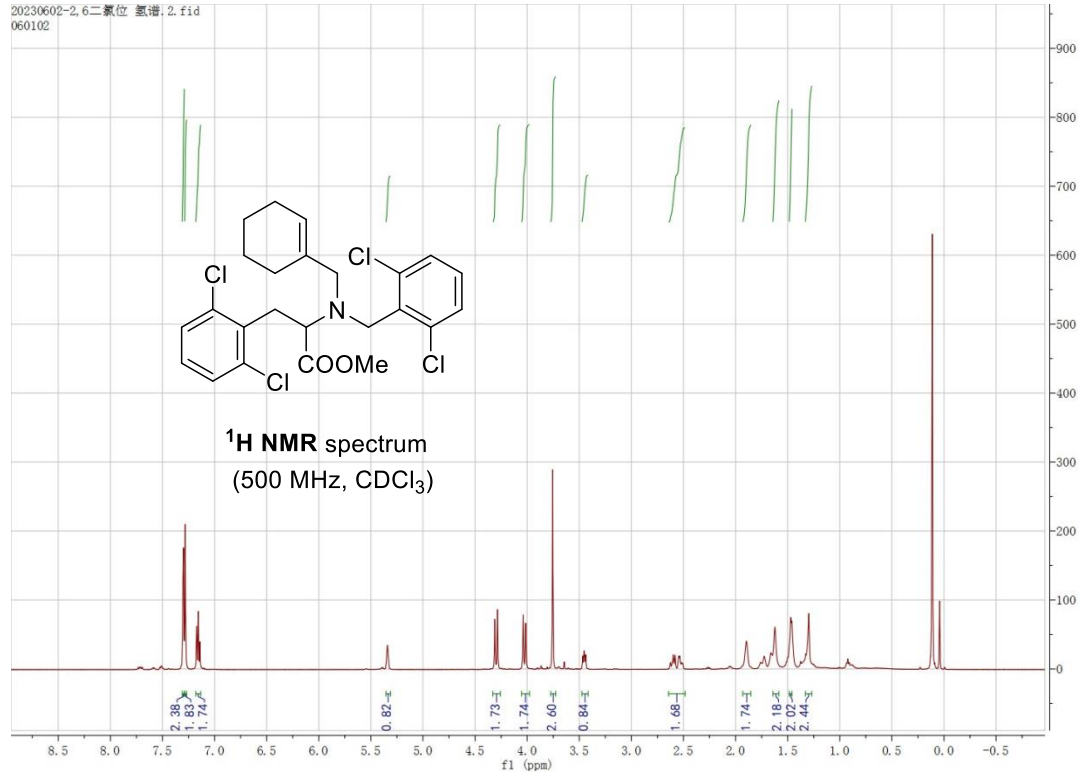
^{1}H NMR spectra of the product **3ag**:



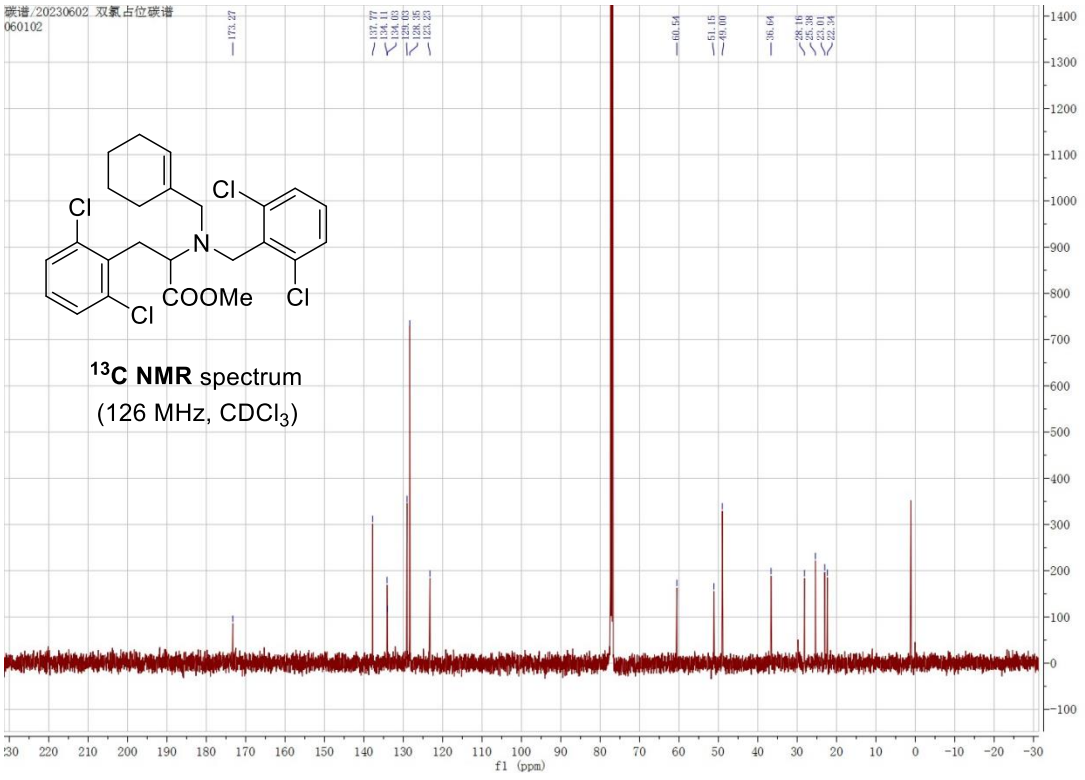
^{13}C NMR spectra of the product **3ag**:



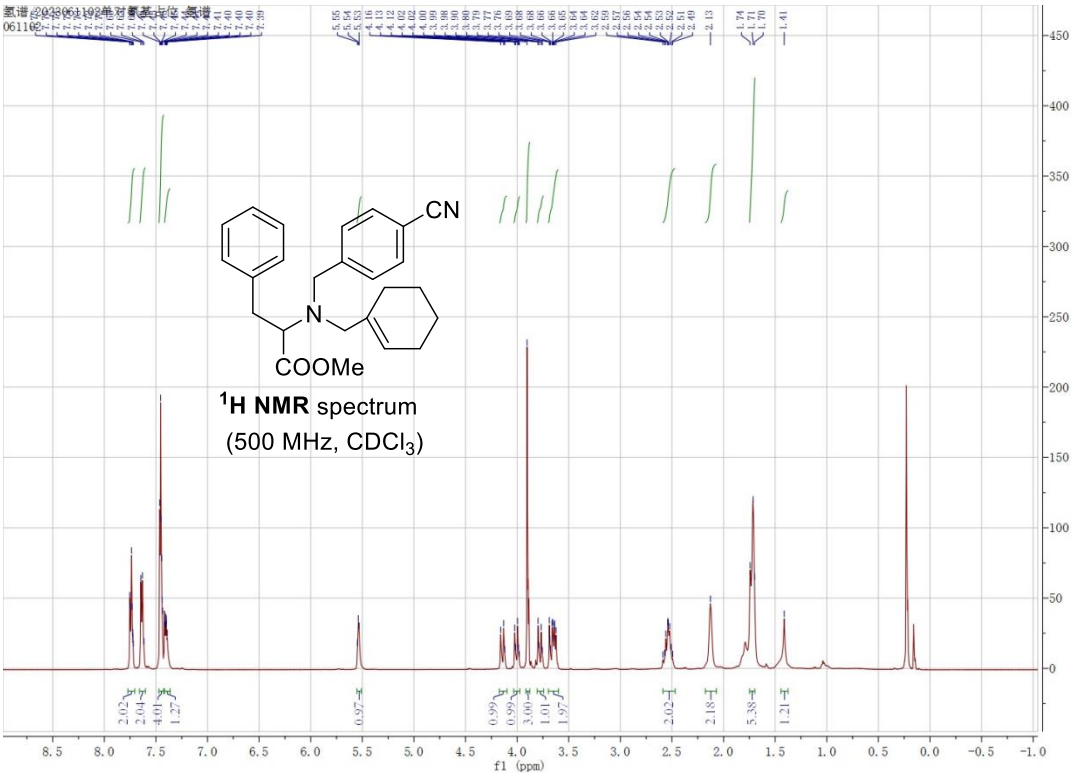
^{1}H NMR spectra of the product **3ah**:



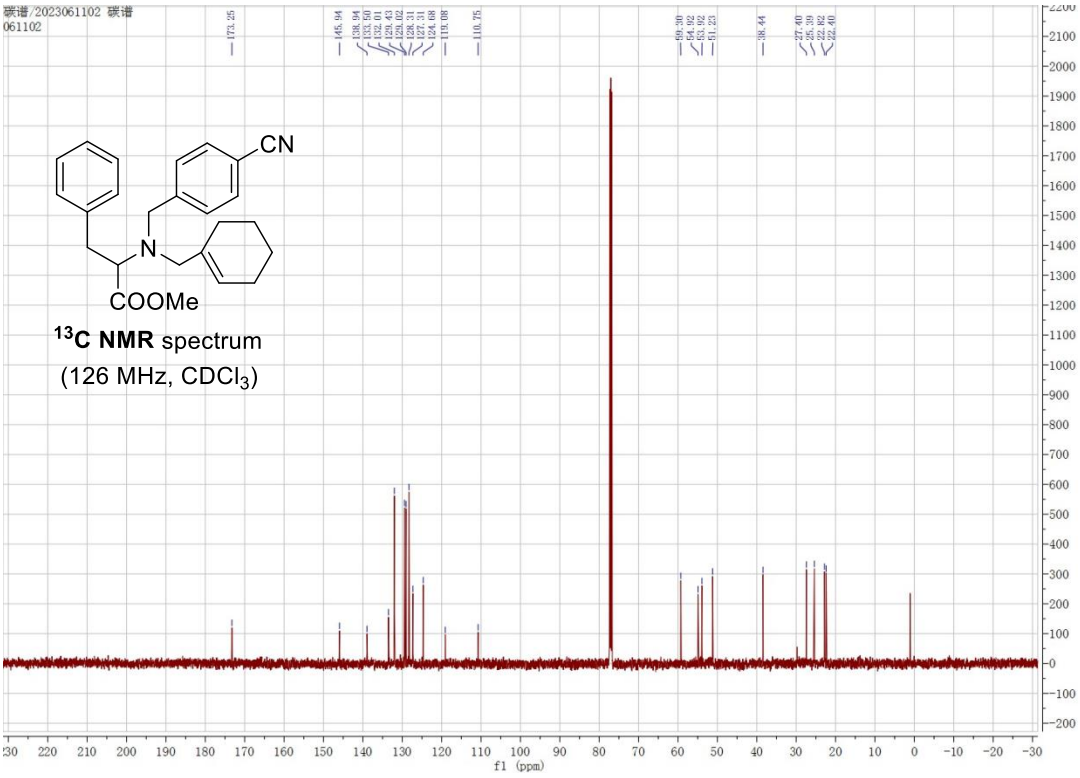
^{13}C NMR spectra of the product **3ah**:



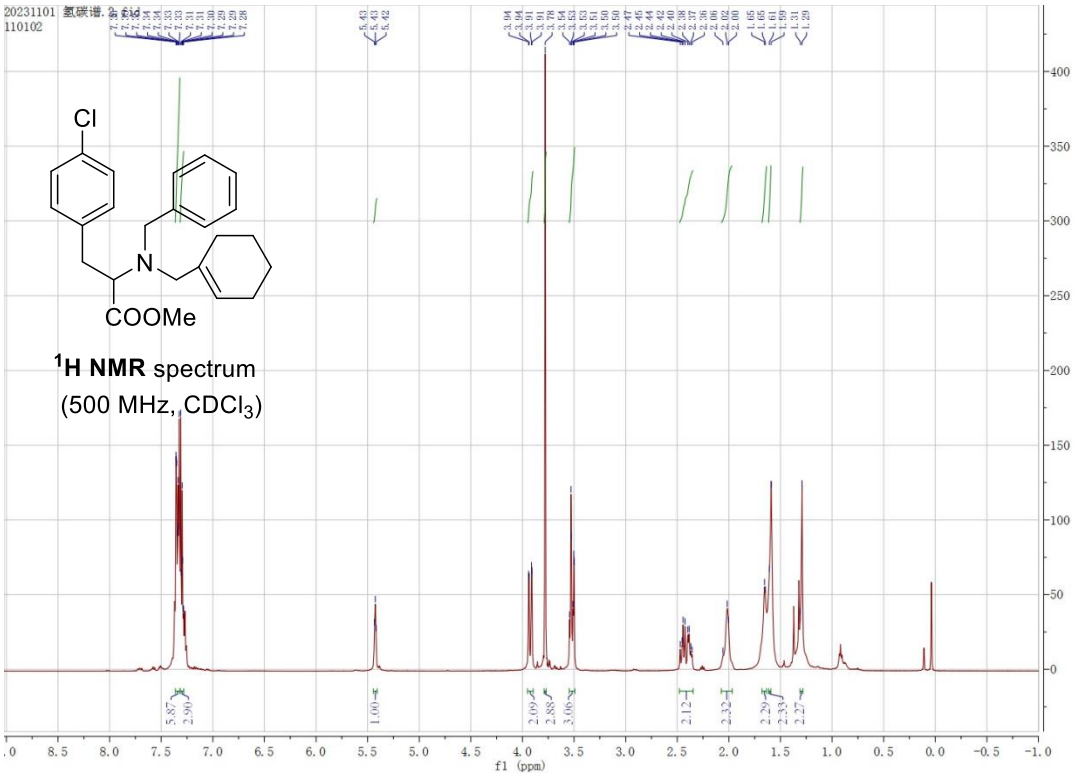
^{1}H NMR spectra of the product **3ai**:



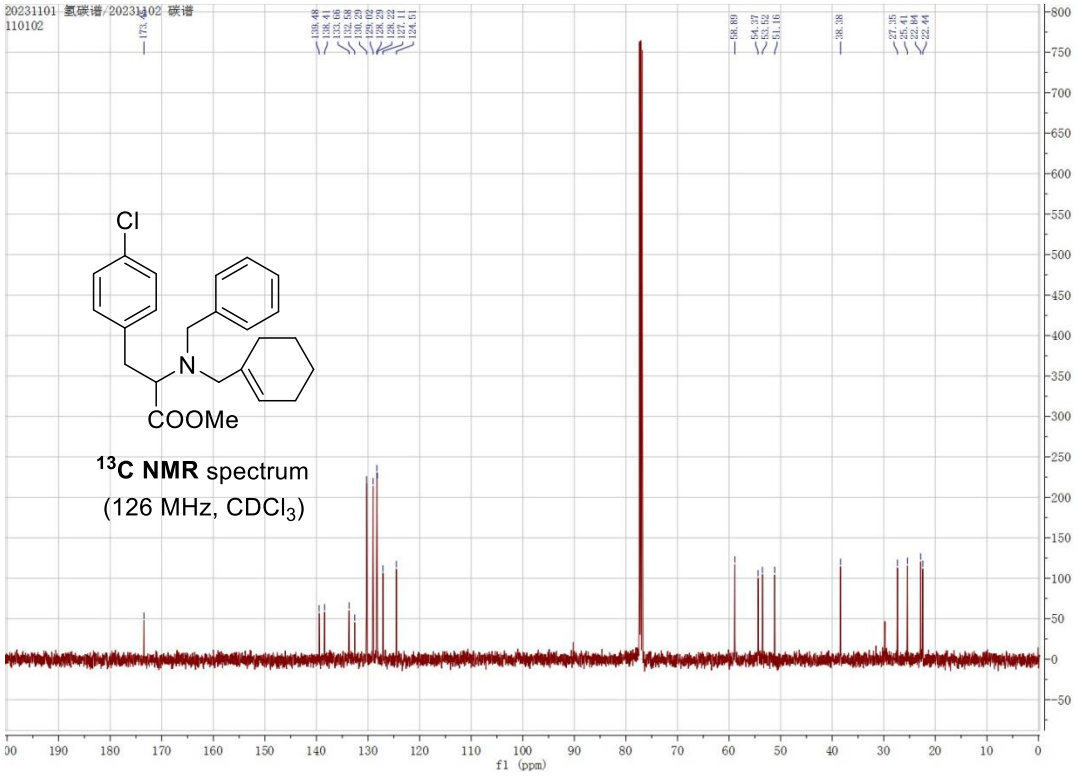
^{13}C NMR spectra of the product **3ai**:



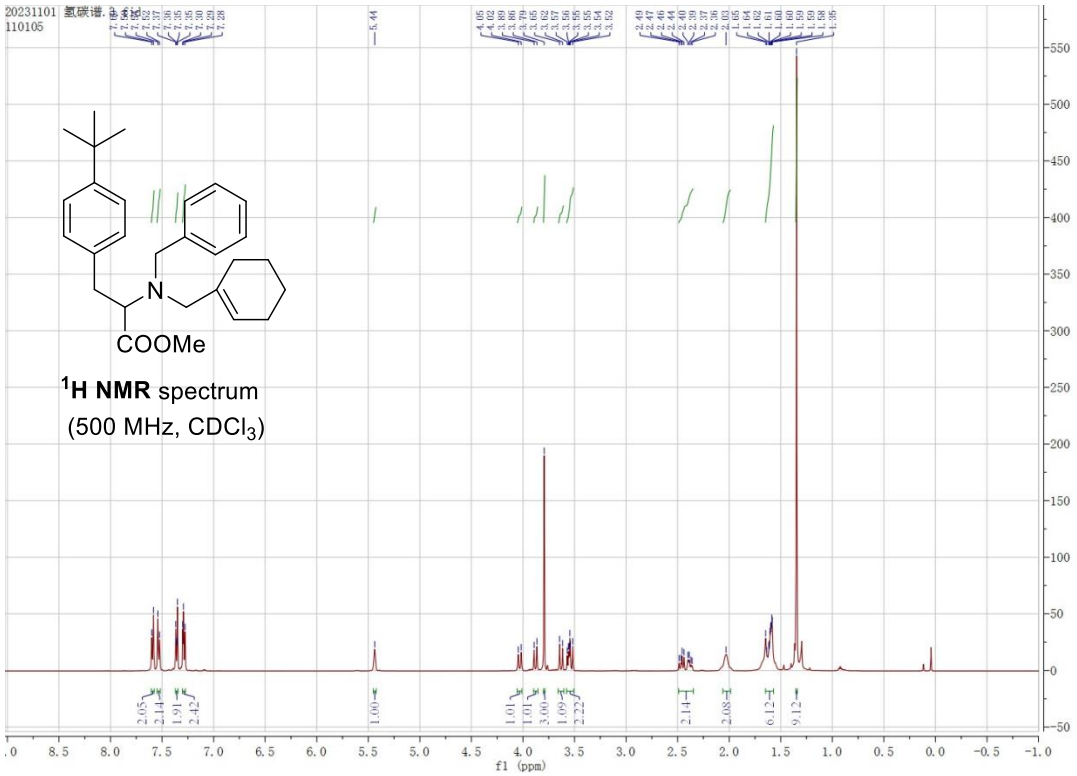
^{1}H NMR spectra of the product **3aj**:



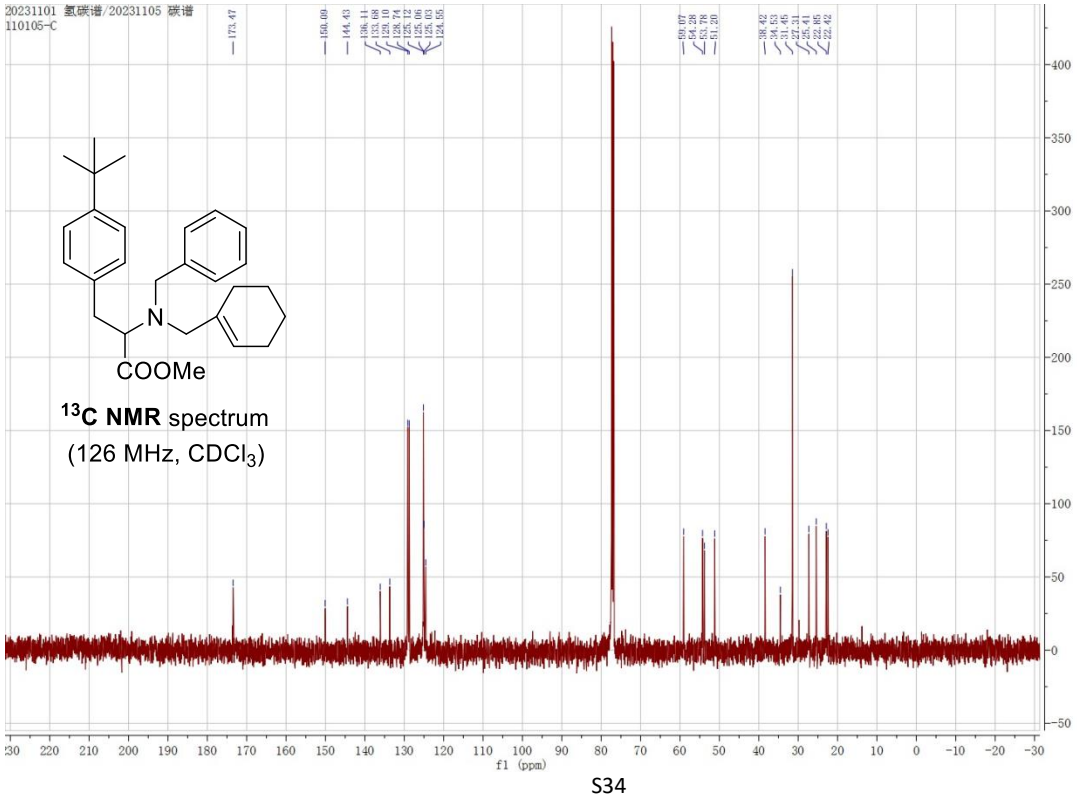
^{13}C NMR spectra of the product **3aj**:



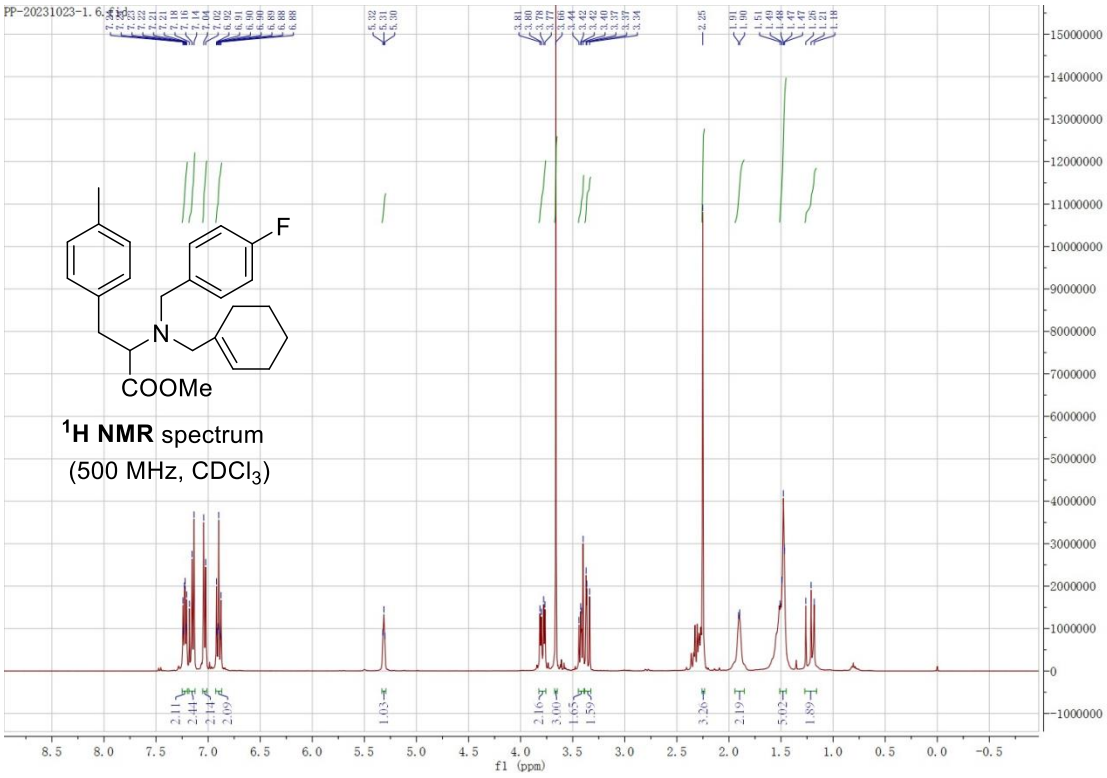
^{1}H NMR spectra of the product **3ak**:



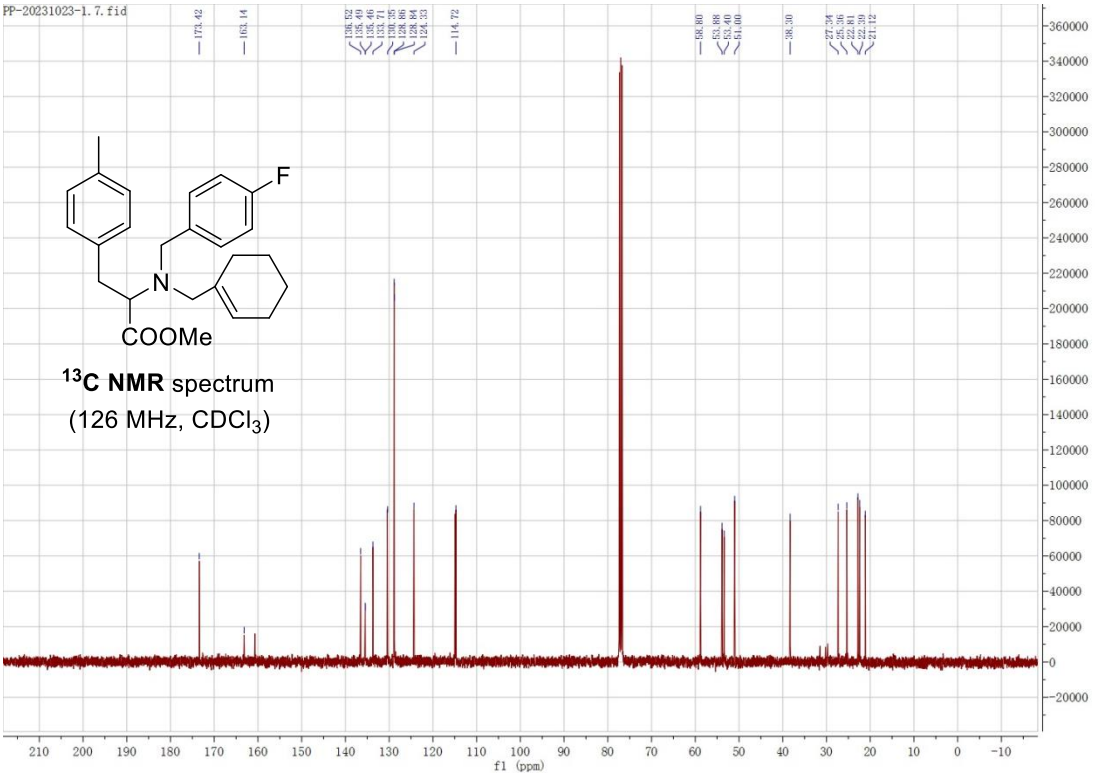
^{13}C NMR spectra of the product **3ak**:



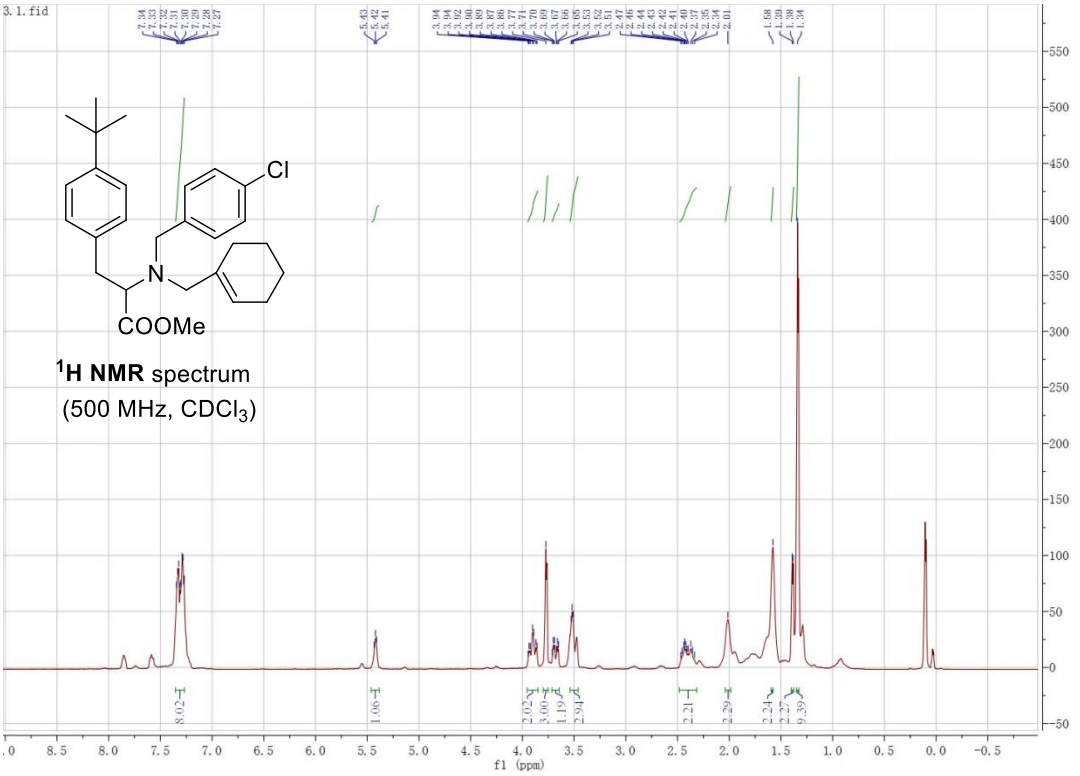
^{1}H NMR spectra of the product **3al**:



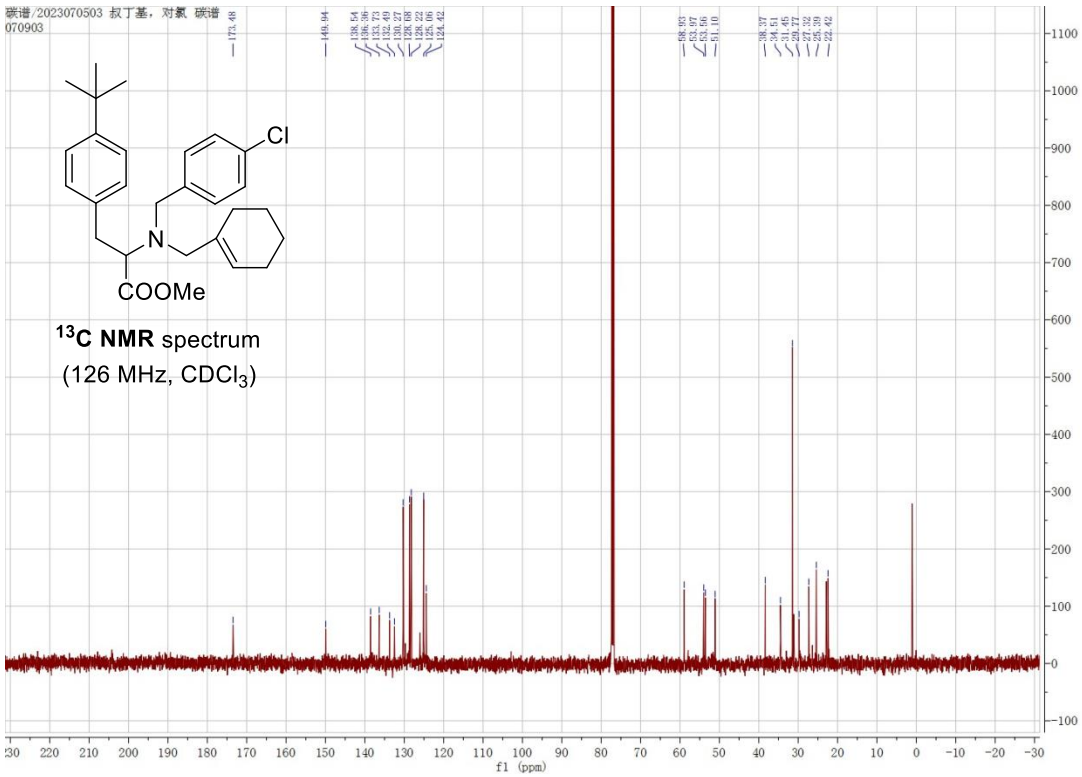
^{13}C NMR spectra of the product **3al**:



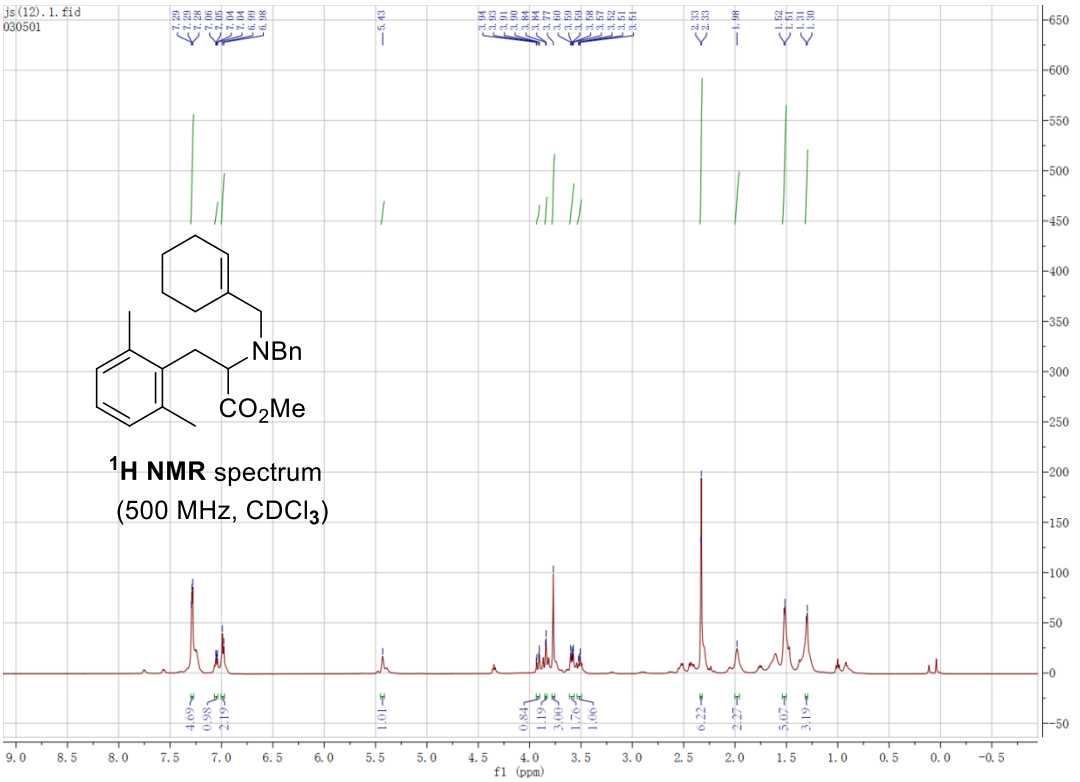
^{1}H NMR spectra of the product **3am**:



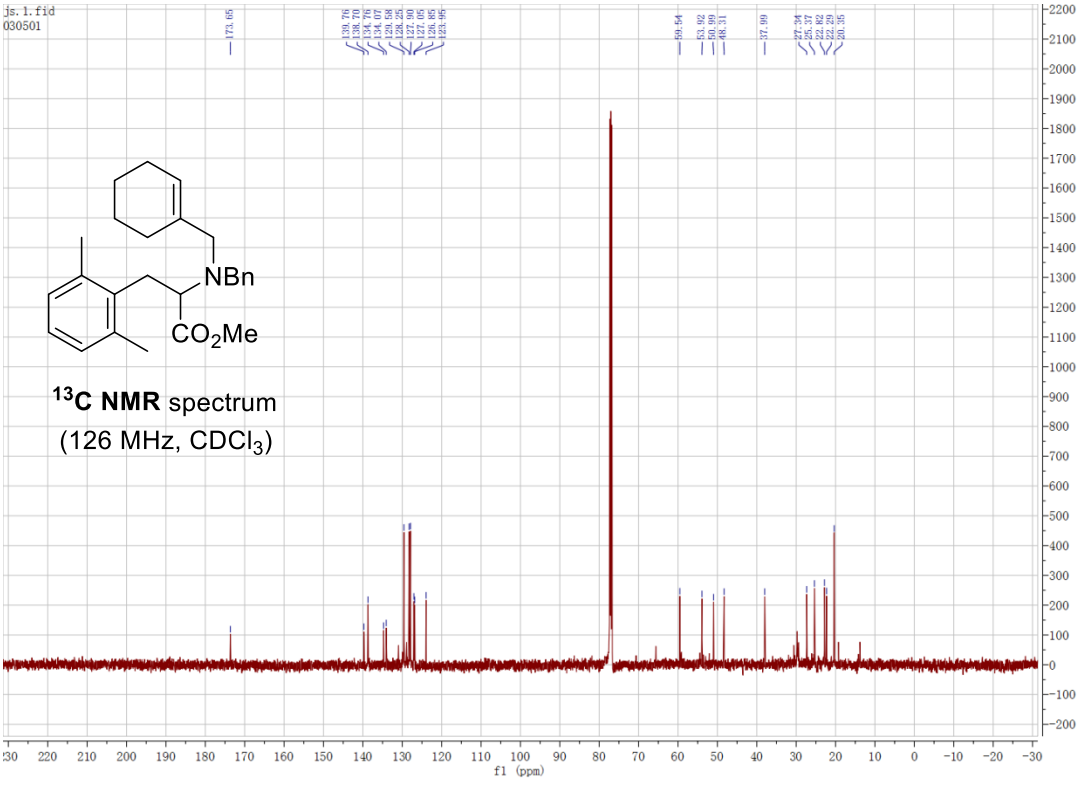
^{13}C NMR spectra of the product **3am**:



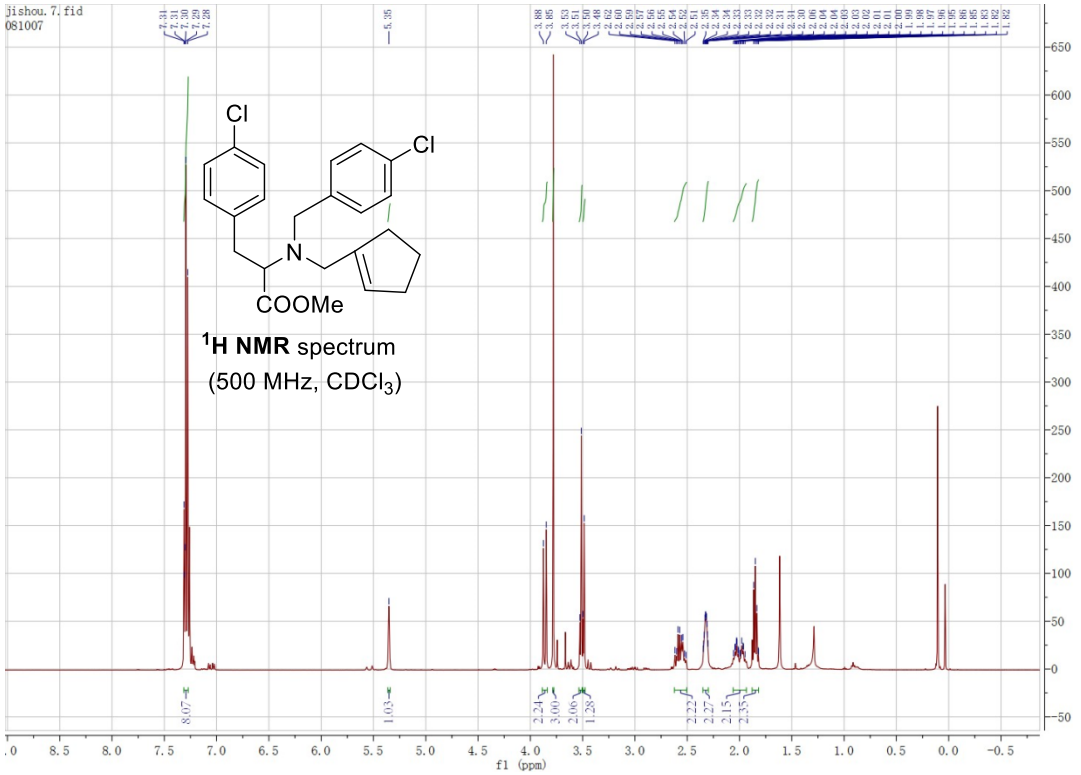
^{1}H NMR spectra of the product **3an:**



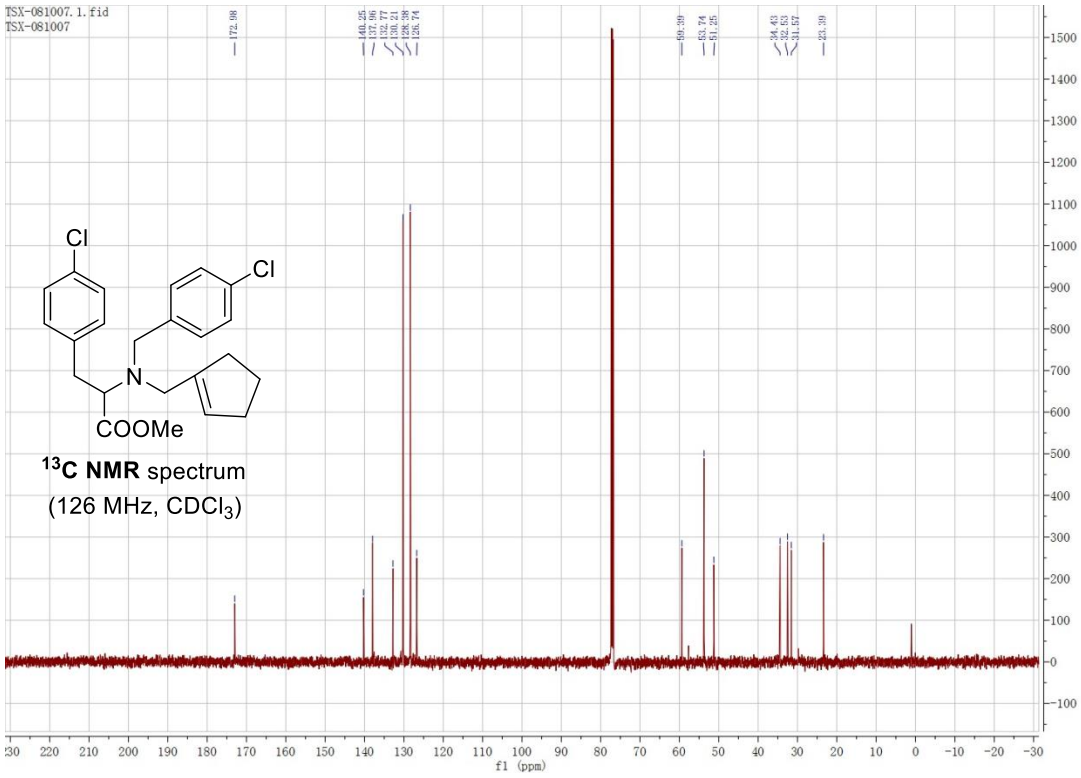
^{13}C NMR spectra of the product **3an**:



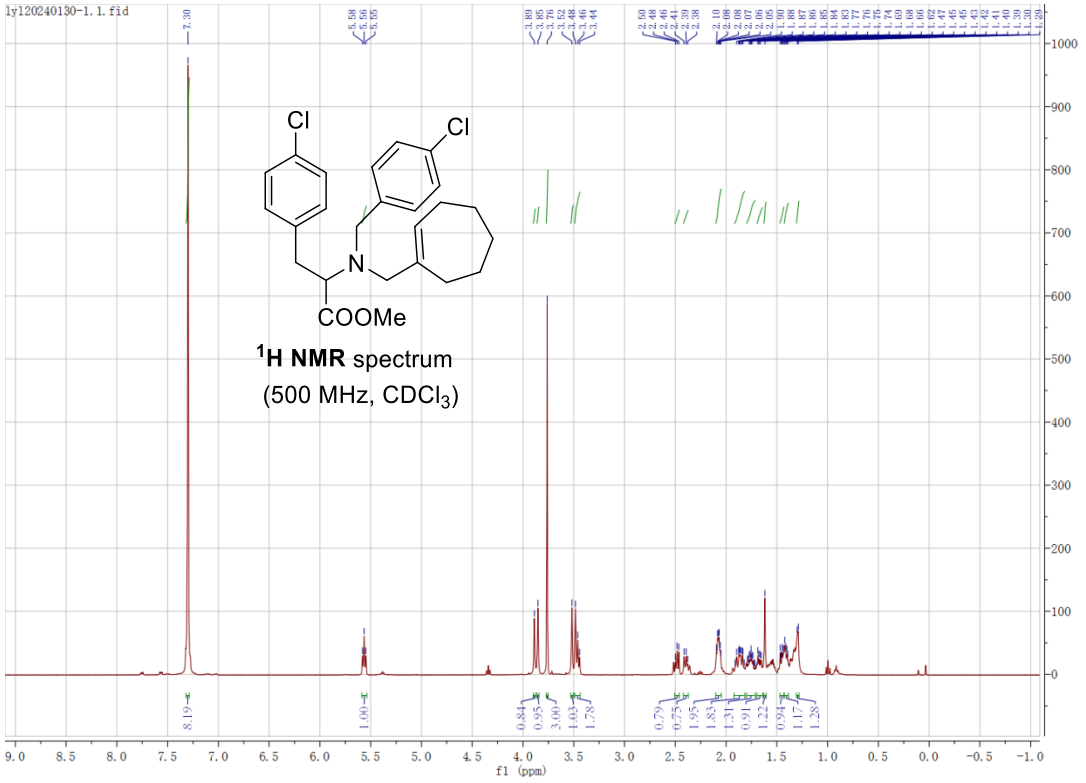
^{1}H NMR spectra of the product **3ao**:



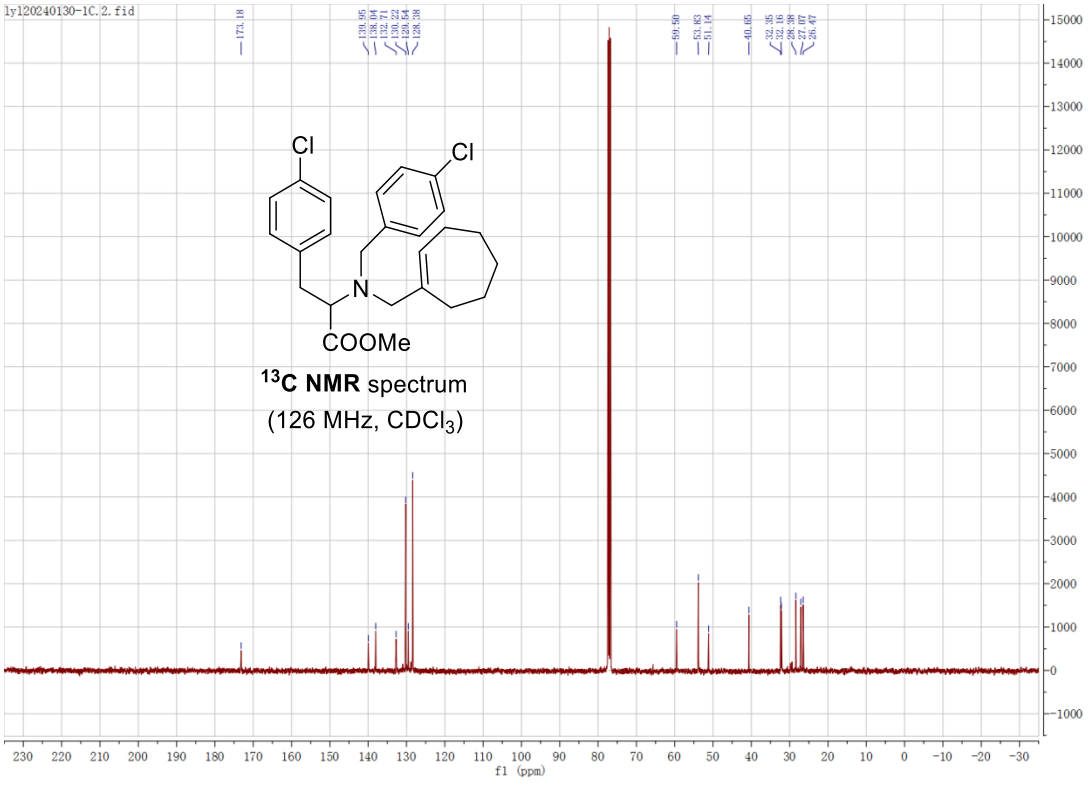
^{13}C NMR spectra of the product **3ao**:



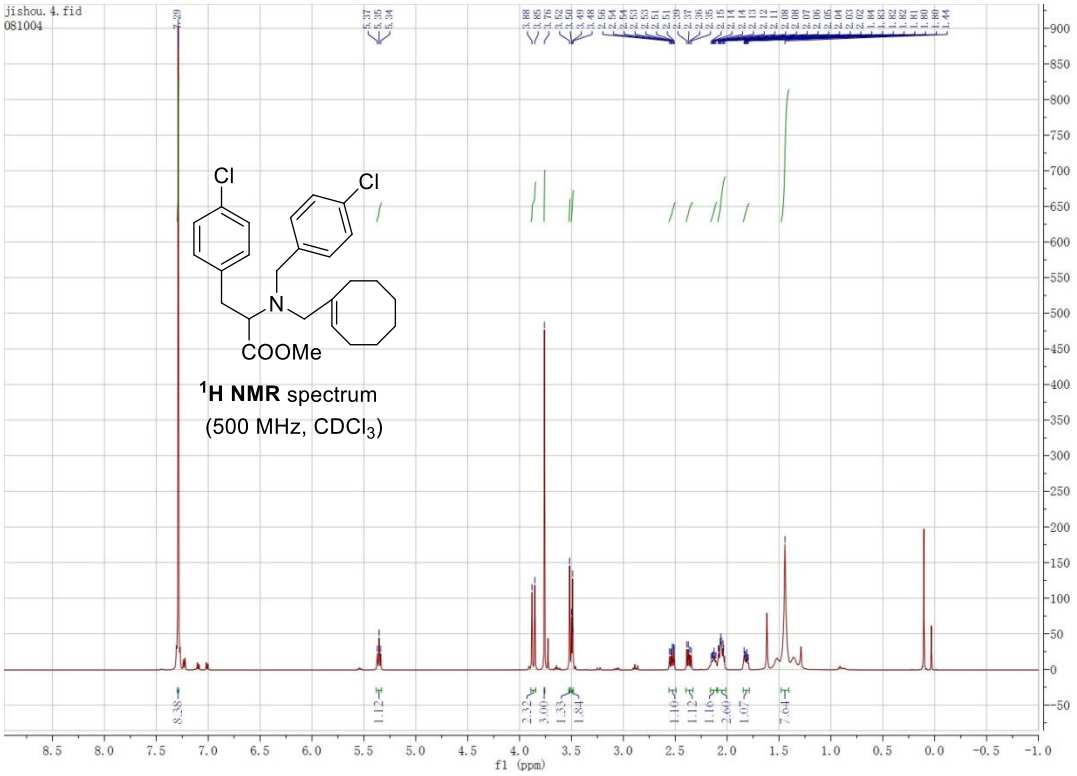
^{1}H NMR spectra of the product **3ap**:



^{13}C NMR spectra of the product **3ap**:



^{1}H NMR spectra of the product **3aq**:



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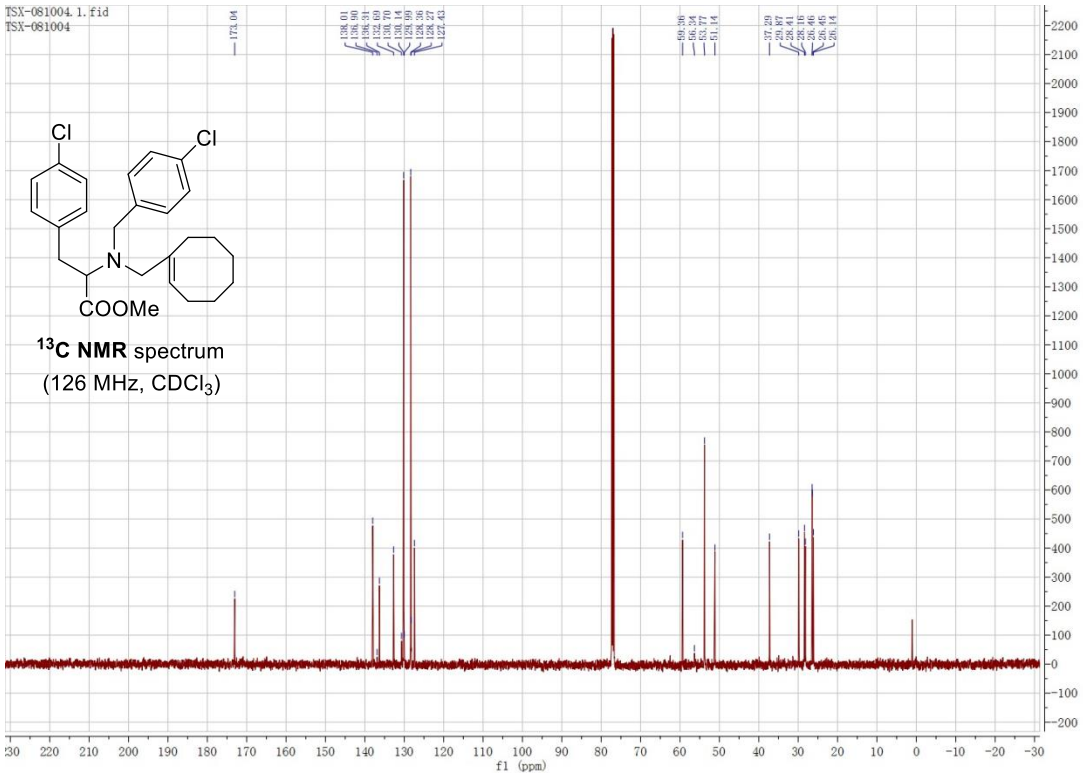
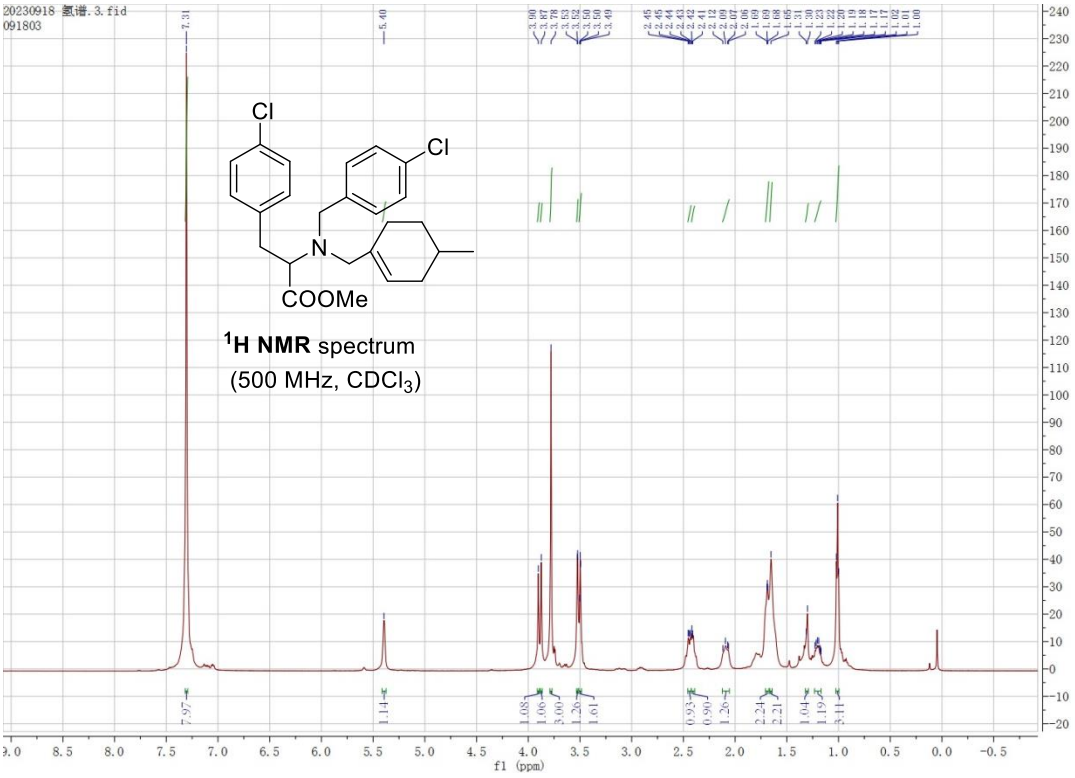
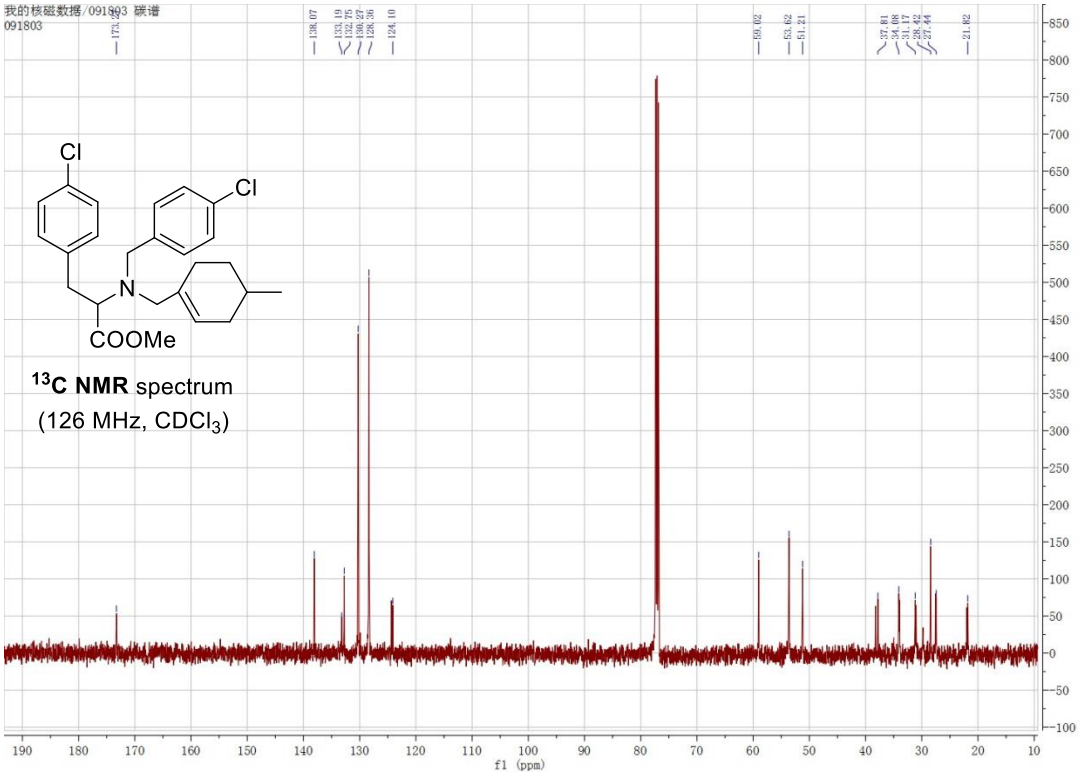


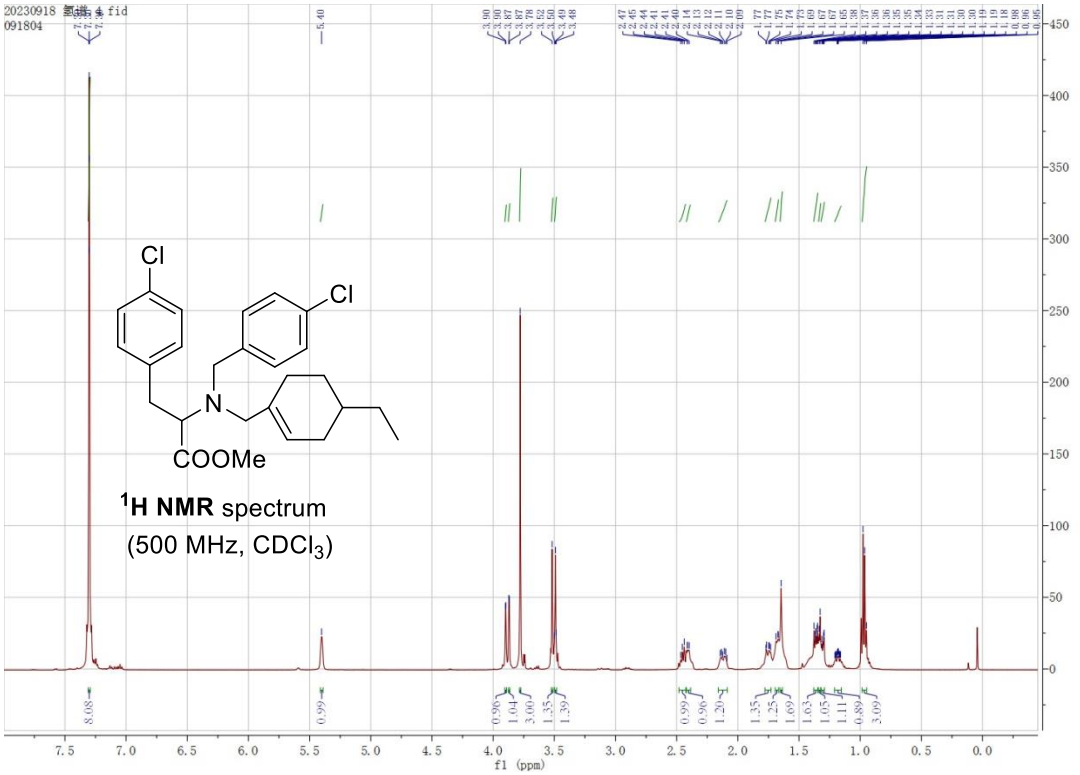
^{1}H NMR spectra of the product **3ar**:



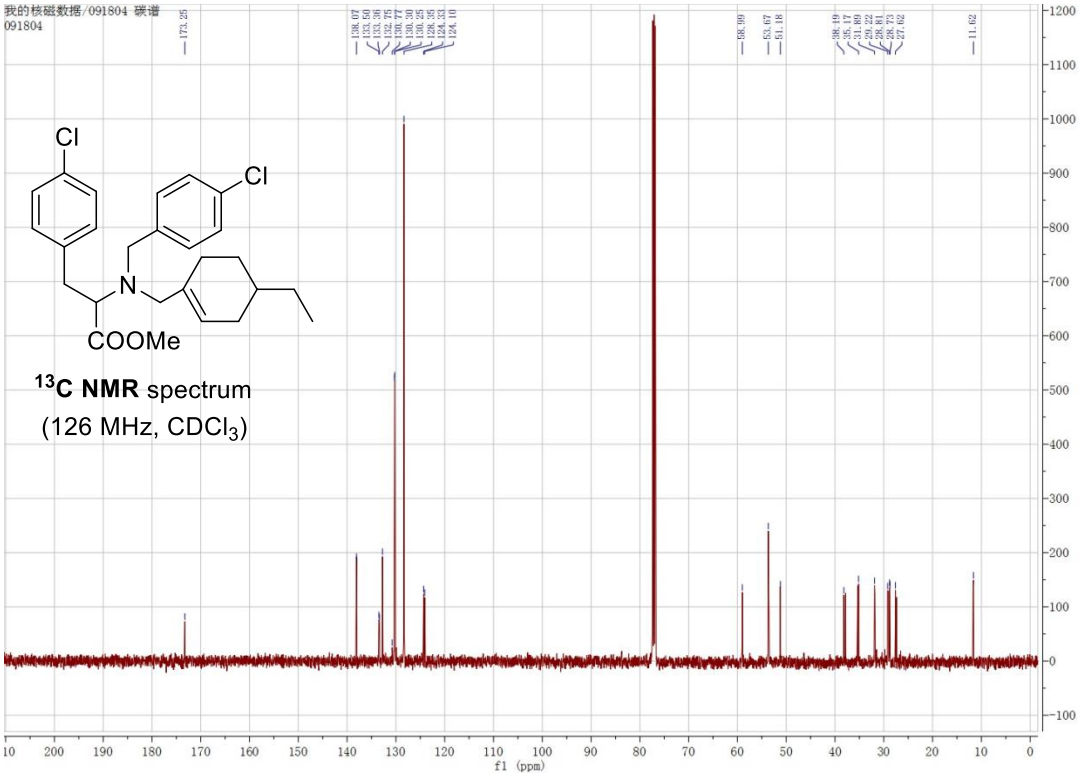
^{13}C NMR spectra of the product **3ar**:



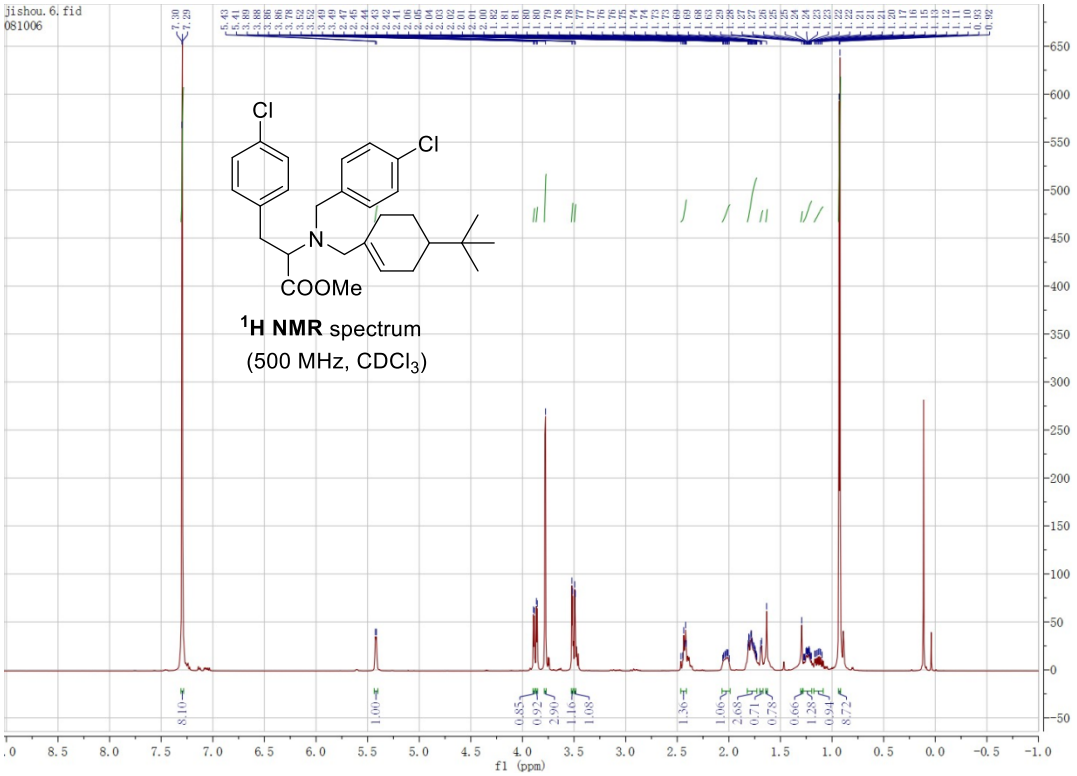
^{1}H NMR spectra of the product **3as**:



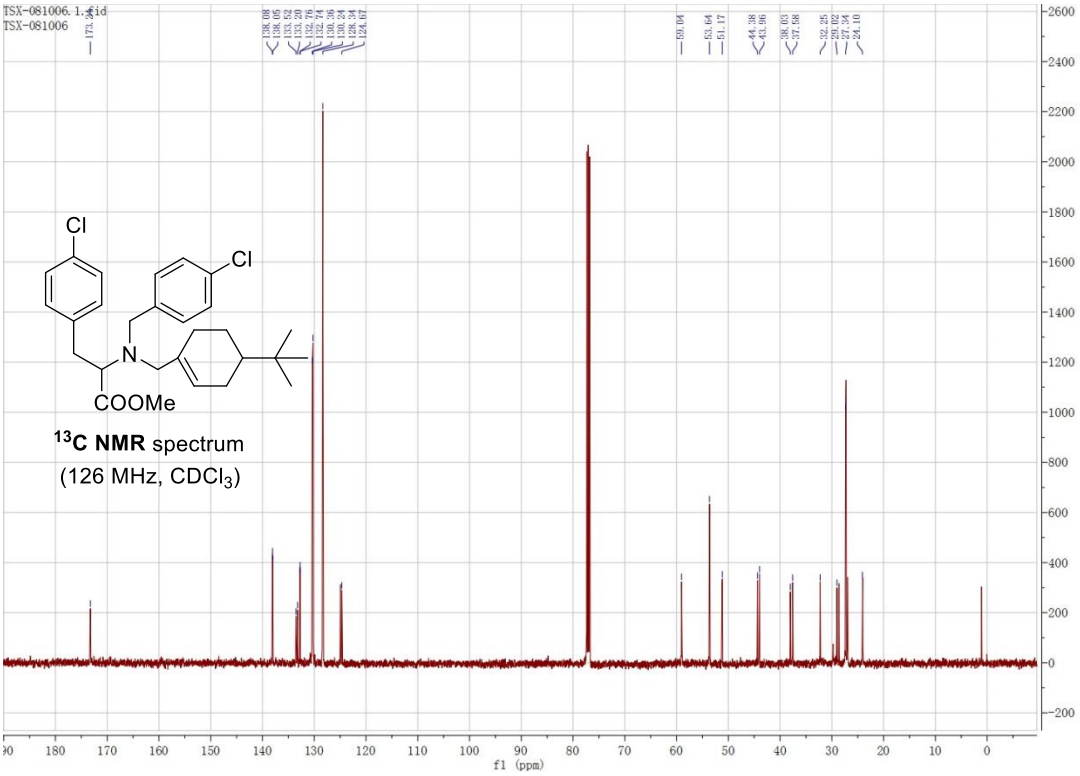
^{13}C NMR spectra of the product **3as**:



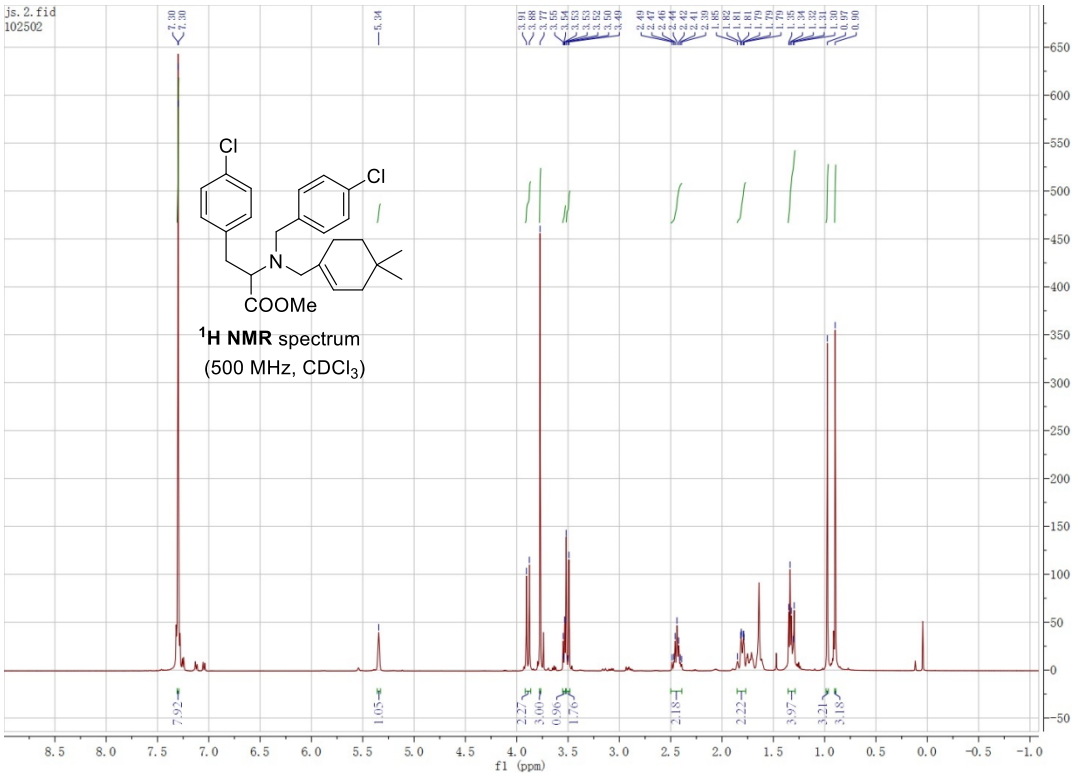
^{1}H NMR spectra of the product **3at**:



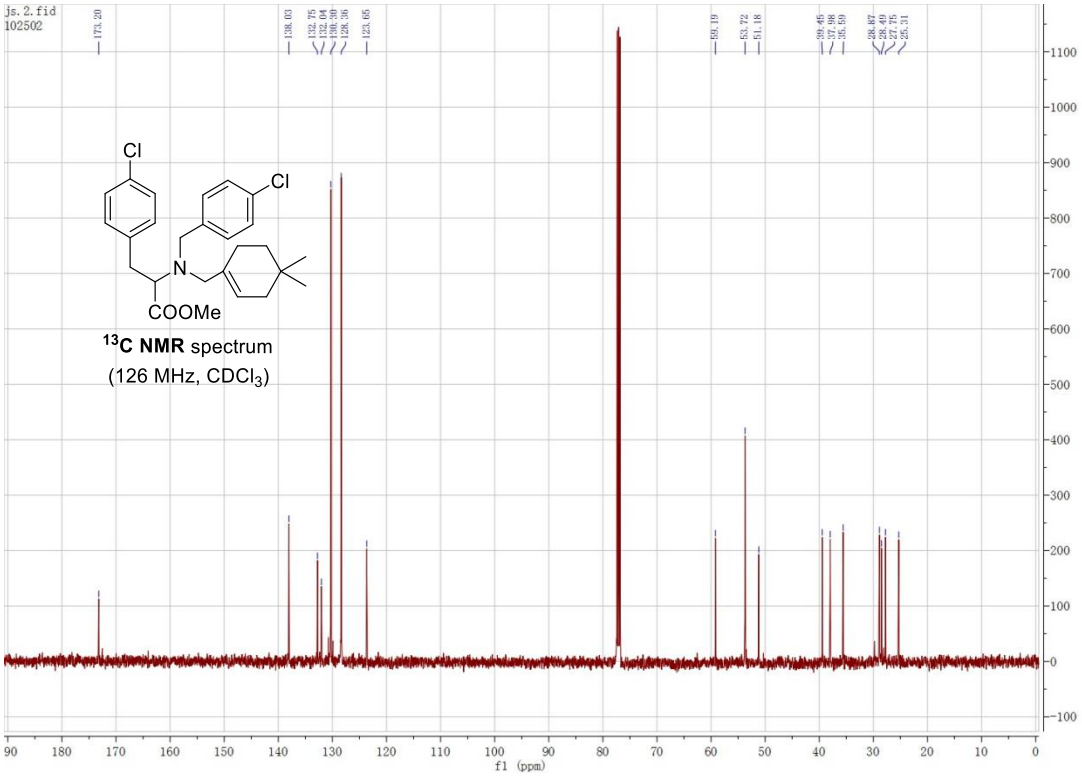
^{13}C NMR spectra of the product **3at**:



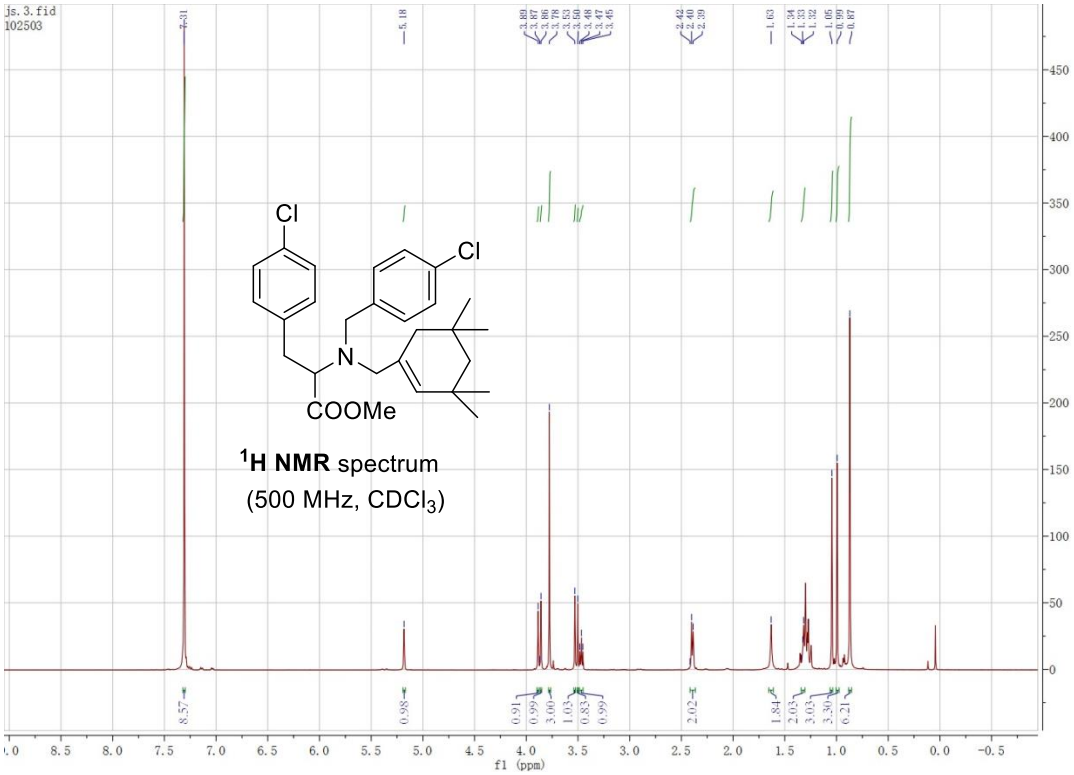
^{1}H NMR spectra of the product **3au**:



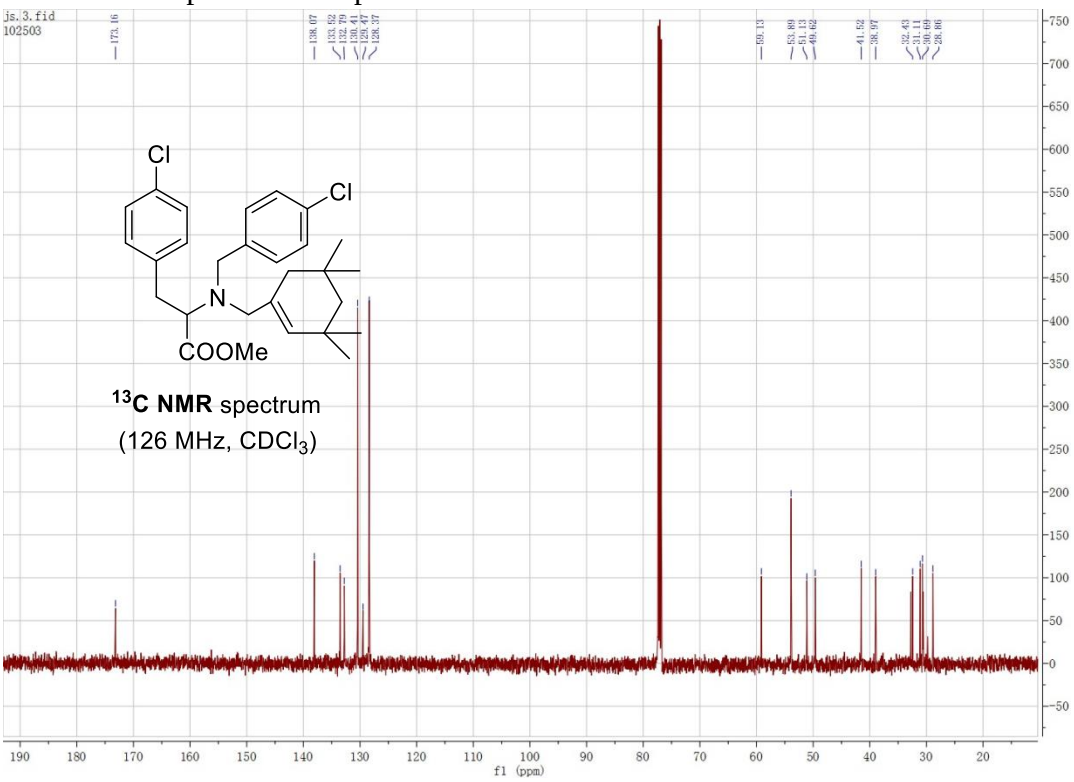
^{13}C NMR spectra of the product **3au**:



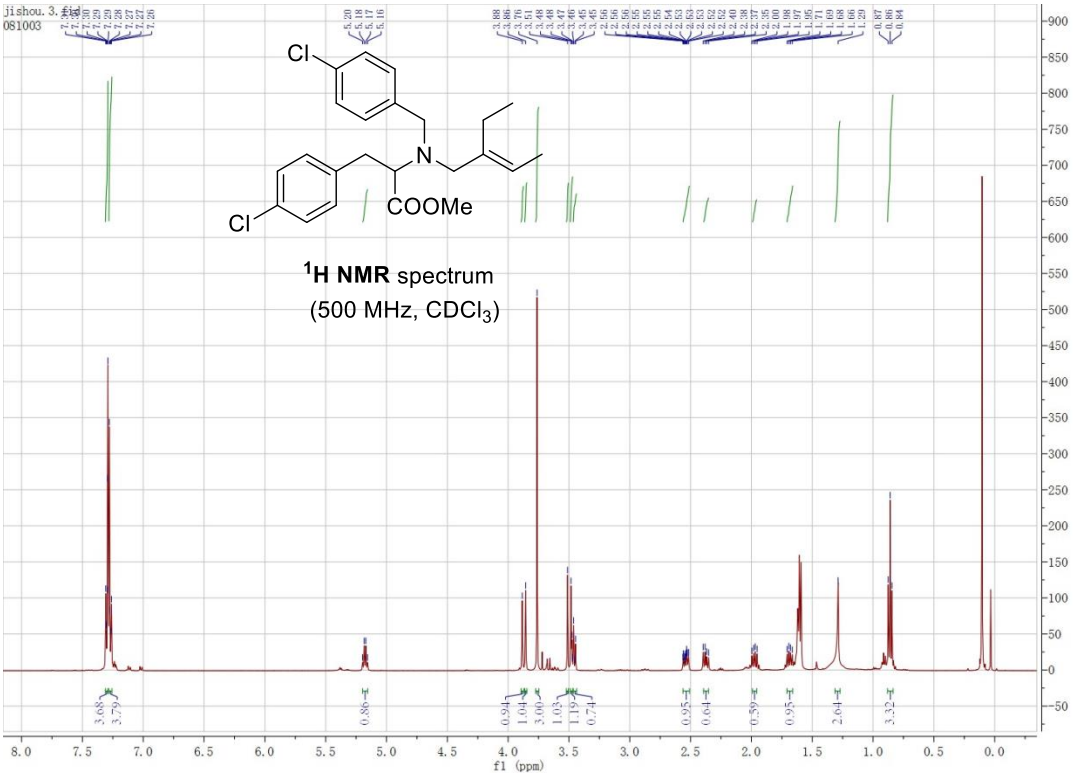
^{1}H NMR spectra of the product **3av**:



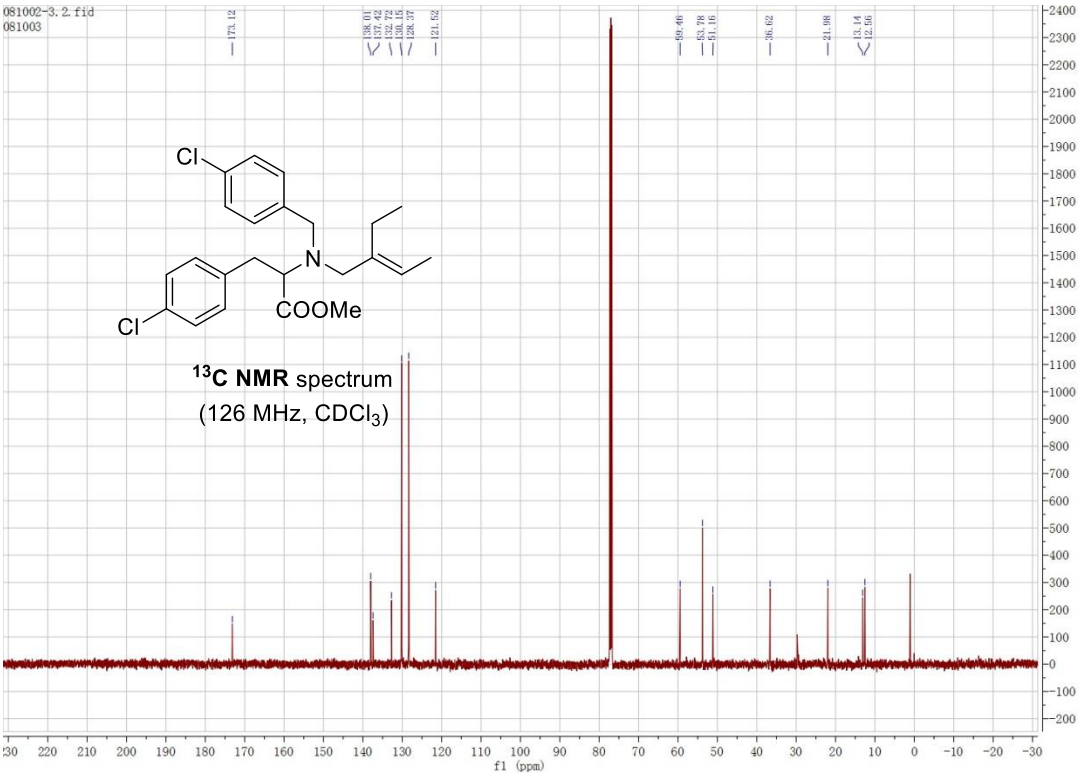
^{13}C NMR spectra of the product **3av**:



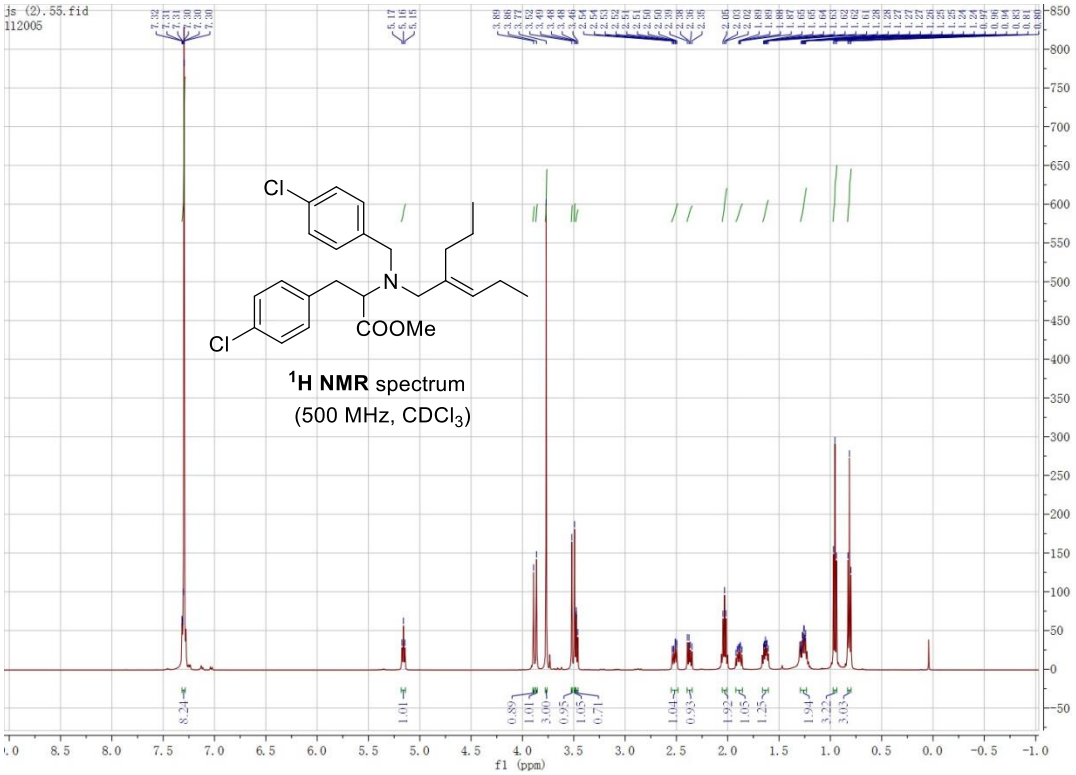
^{1}H NMR spectra of the product **3aw**:



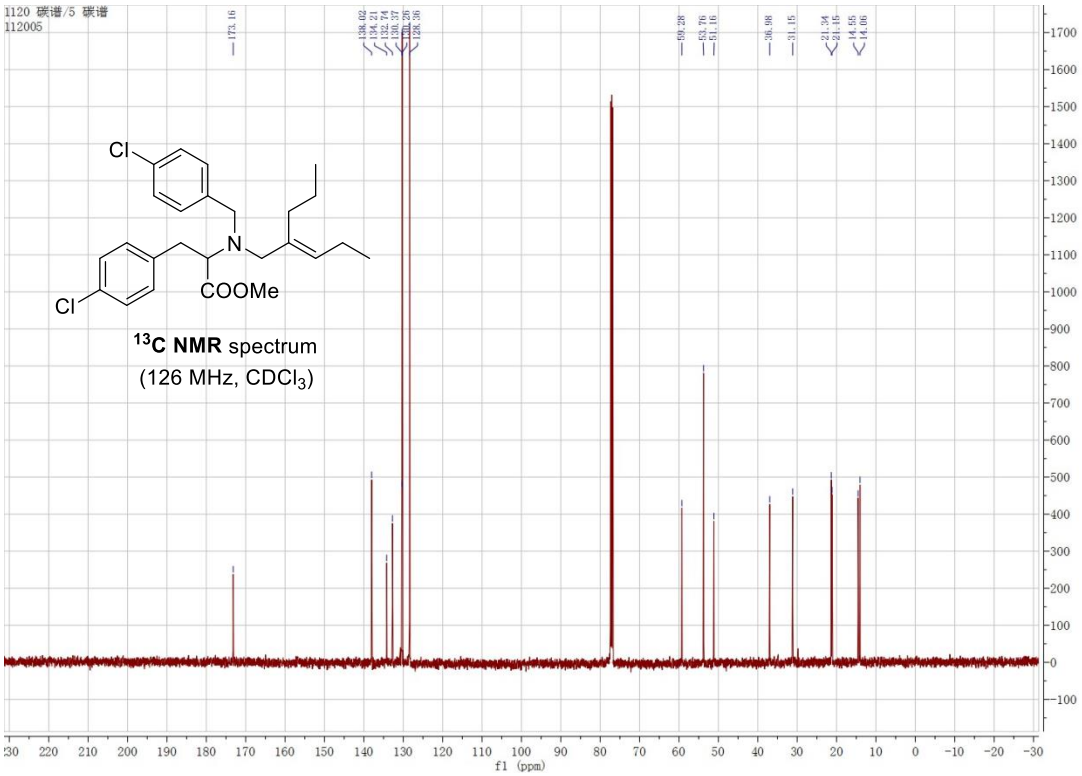
^{13}C NMR spectra of the product **3aw**:



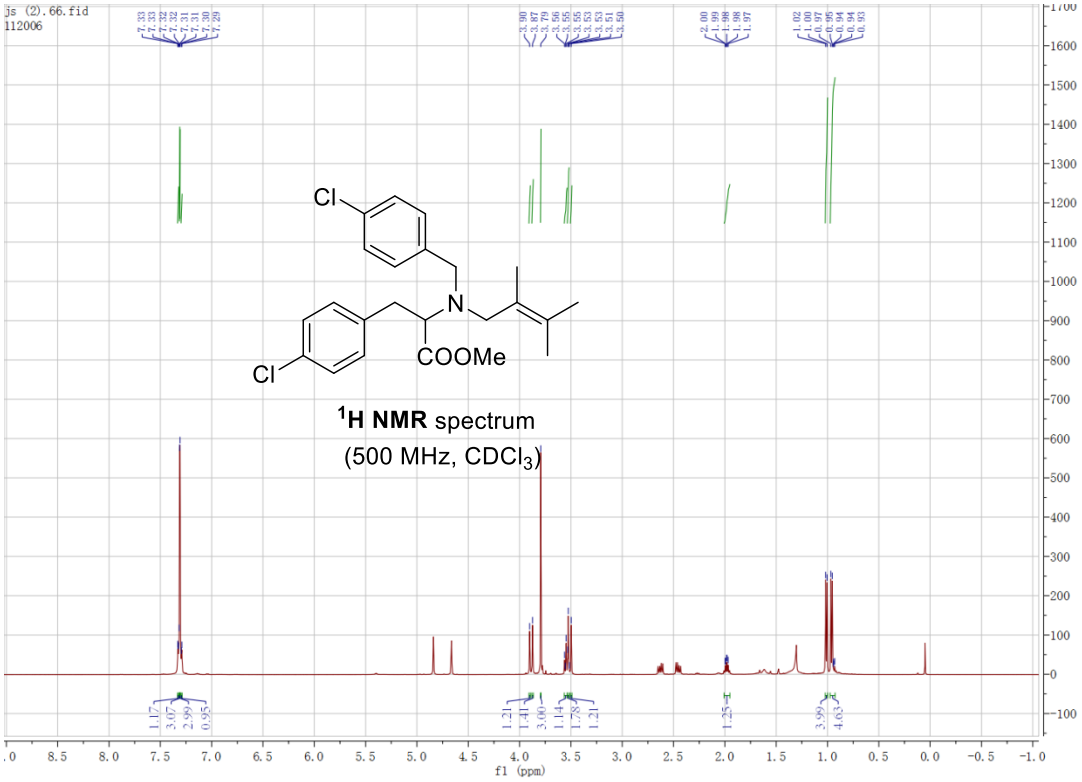
^{1}H NMR spectra of the product **3ax**:



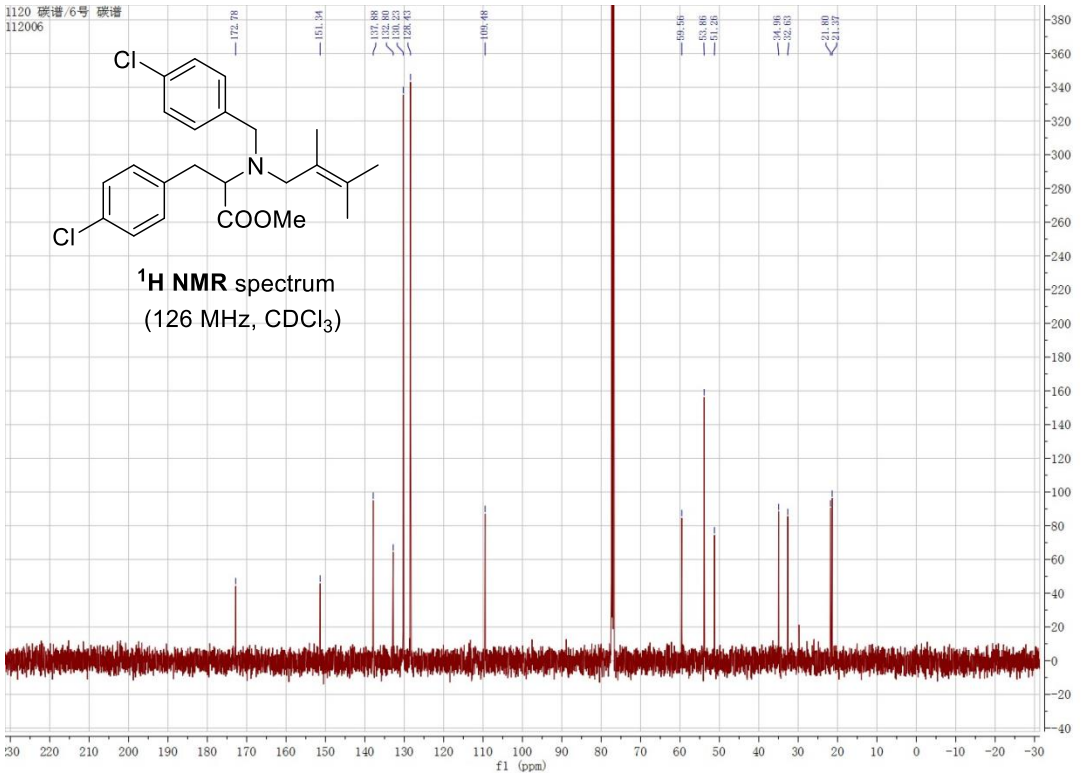
^{13}C NMR spectra of the product **3aw**:



^{1}H NMR spectra of the product **3ay**:



^{13}C NMR spectra of the product **3ay**:



H-H COSY spectra of 3an: