Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Phenolate Anion-Catalyzed Direct Activation of Inert Alkyl Chlorides Driven by Visible Light

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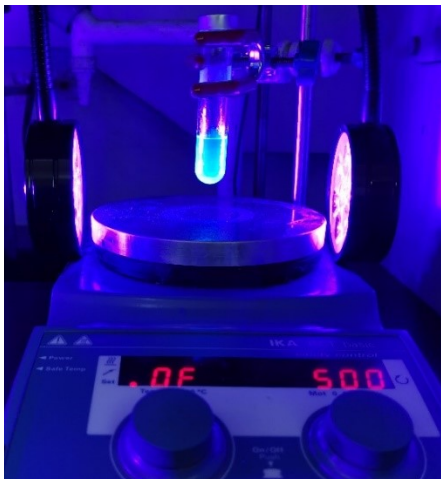
General Information

All reactions were performed under argon atmosphere using flame-dried glassware unless otherwise noted. DMF was distilled over CaH_2 and rigorously degassed by freeze/pump/thaw. All reagents were commercially available and used without further purification unless indicated otherwise. Thin layer chromatographies were carried out on GF254 plates (0.25 mm layer thickness). Flash chromatography was performed with 200-300 mesh silica gels. Visualization of the developed chromatogram was performed by fluorescence quenching or by ceric ammonium molybdate, or $KMnO_4$ stain. Yields reported were for isolated, spectroscopically pure compounds.

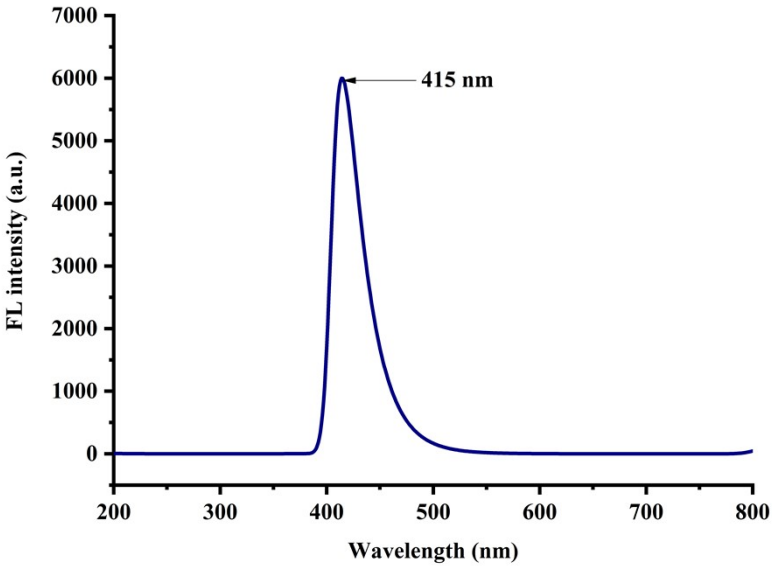
^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 600 MHz spectrophotometers. Chemical shifts (δ) are expressed in ppm., and *J*-values are given in Hz. The residual solvent protons (^1H) or the solvent carbons (^{13}C) were used as internal standards. ESIMS and HRESIMS were taken on AB QSTAR Pulsar mass spectrometer or Aglient LC/MSD TOF mass spectrometer. UV-Vis measurements were carried out on a Hitachi UV-1900 UV-Visible spectrophotometer. The emission spectra were recorded in a Hitachi F-7000 fluorescence spectrometer.

General Procedure for Radical C−O Bond Formation (Procedure A)

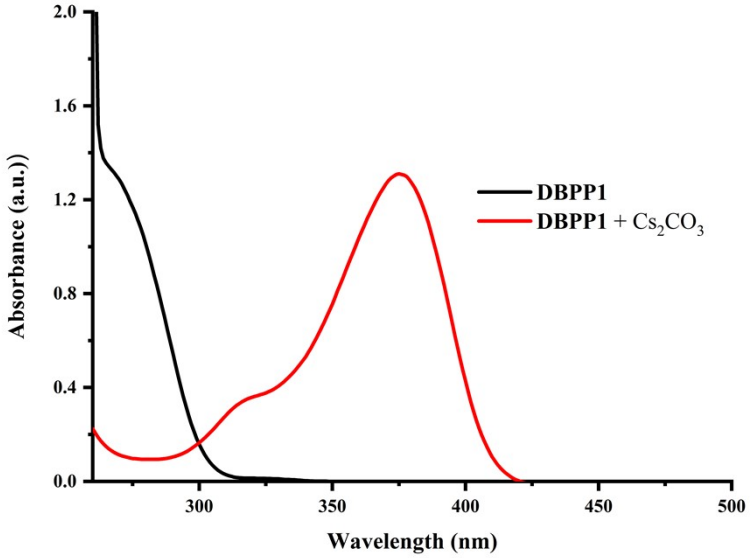
To an oven dried 10 mL glass tube with a magnetic stirring bar was added **DBPP1** (0.03 mmol, 10 mol%), Cs_2CO_3 (0.60 mmol, 2.0 equiv) and TEMPOH (0.36 mmol, 1.2 equiv). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMF (3.0 mL) and alkyl chloride (0.30 mmol) were carefully added under Argon. The reaction mixture was stirred under two 415 nm light emitting diode (LED) lamps (7 W) (the distance was about 7.5 cm) irradiation for the indicated time at room temperature. Irradiation was stopped and the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether) on silica gel to afford the product.



Supplementary Figure 1. Experimental setup for photocatalytic activation of alkyl chlorides.



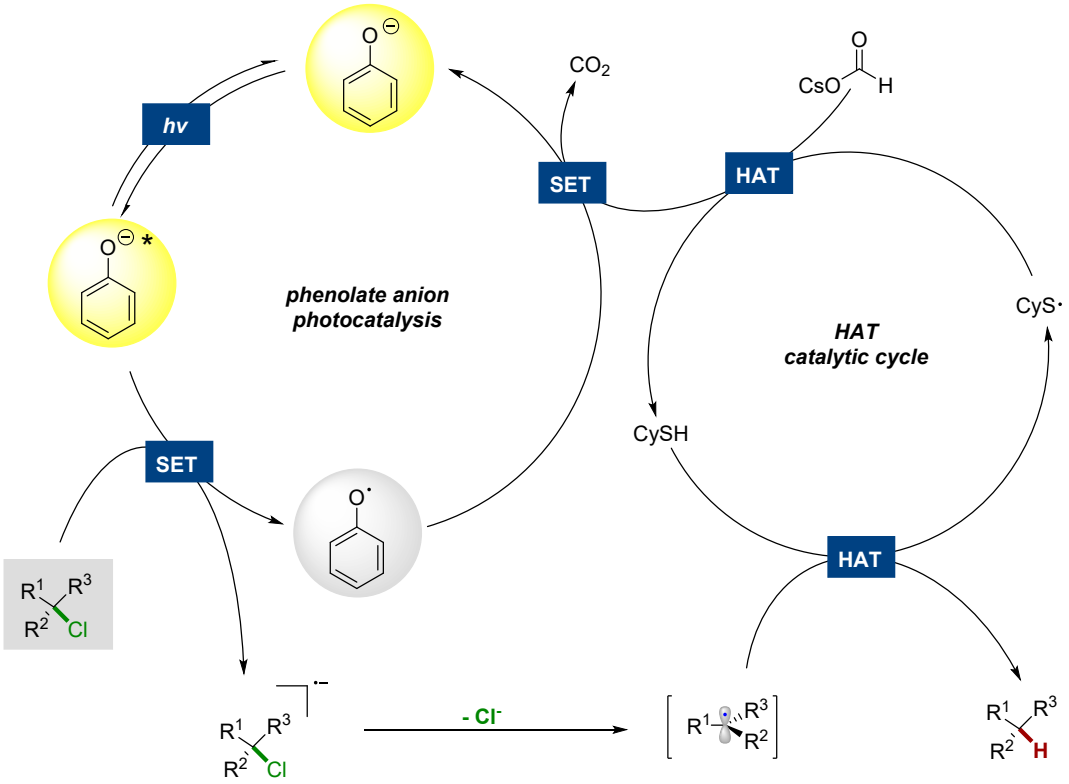
Supplementary Figure 2. Emission spectra of the 415 nm LED lamp.



Supplementary Figure 3. Absorption spectra of the catalyst **DBPP1** (5×10^{-4} M) with and without base Cs_2CO_3. Dry degassed DMF was used as solvent.

General Procedure for Radical Dehalogenation (Procedure B)

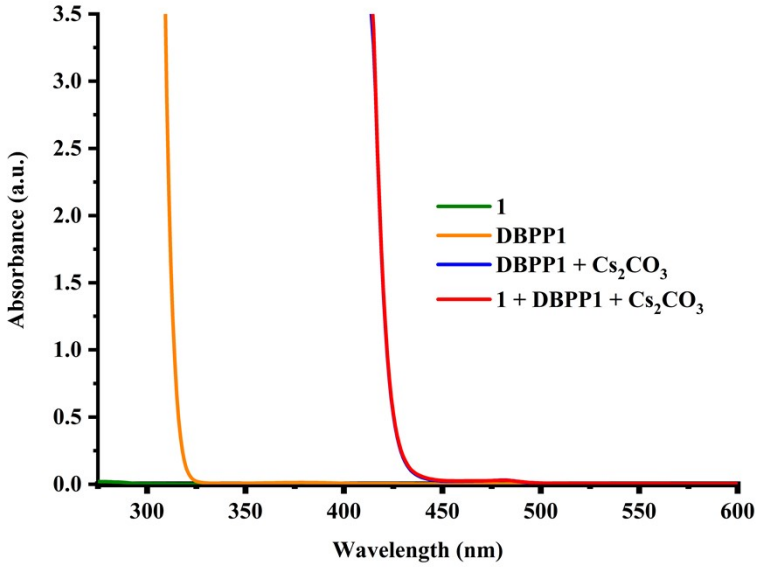
To an oven dried 10 mL glass tube with a magnetic stirring bar was added **DBPP1** (0.03 mmol, 10 mol%), Cs_2CO_3 (0.60 mmol, 2.0 equiv) and HCOOCs (0.90 mmol, 3.0 equiv). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMF (3.0 mL), CySH (0.06 mmol, 20 mol%) and alkyl chloride (0.30 mmol, 1.0 equiv) were carefully added under Argon. The reaction mixture was stirred under two 415 nm LED lamps (7 W) (the distance was about 7.5 cm) irradiation for the indicated time at room temperature. Irradiation was stopped and the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (acetone/petroleum ether) on silica gel to afford the product.



Supplementary Figure 4. Proposed mechanistic pathway radical dehalogenation.

Supplementary Note 1. UV-Vis Spectroscopic Measurements

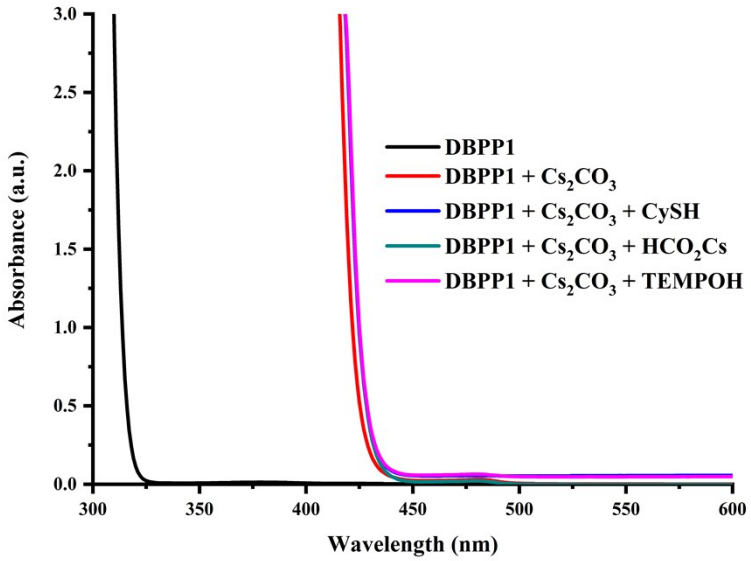
The UV-Vis absorption spectra of DMF solutions (0.1 M) of **1**, **DBPP1**, mixtures of **DBPP1** and Cs_2CO_3, and mixtures of **1**, **DBPP1** and Cs_2CO_3 were recorded on Hitachi UV-1900 UV-Visible spectrophotometer (1 mm short light path cuvettes have been employed in order to avoid fast signal saturation). The colorless solution of **DBPP1** (orange line) was immediately turned to a primrose yellow color upon addition of Cs_2CO_3 (blue line) and no new color change after the 1-chlorohexane **1** was added to the solution of the phenolate anion of **DBPP1** (red line). These observations excluded the formation of a ground-state electron-donor acceptor (EDA) complex between the phenolate anion and alkyl chloride and supported the SET process form the direct photoexcited phenolate anion to alkyl chloride for the generation of alkyl radical.



Supplementary Figure 5. UV-Vis absorption spectra of mixtures of **1**, **DBPP1**, and Cs_2CO_3 in DMF at concentrations of 0.1M.

Supplementary Note 2. UV-Vis Spectroscopic Measurements with Additives

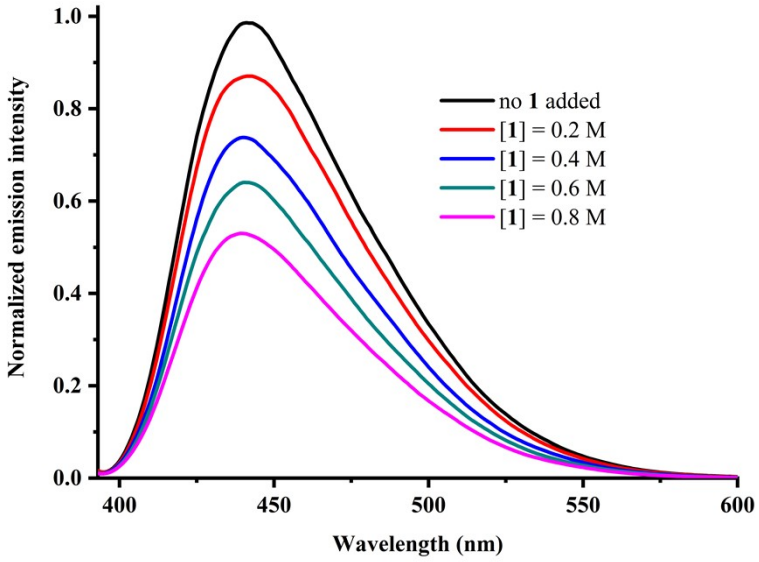
The UV-Vis absorption spectra of DMF solutions (0.1 M) of **DBPP1**, mixtures of **DBPP1** and Cs_2CO_3, and mixtures of **DBPP1** with different additives (CySH, HCO_2Na, and TMPOH) in the presence of Cs_2CO_3 were recorded on Hitachi UV-1900 UV-Visible spectrophotometer (1 mm short light path cuvettes have been employed in order to avoid fast signal saturation). The results showed that the additives did not change the UV-Vis absorption and excluded the formatino of EDA complex of **DBPP1** with additives.



Supplementary Figure 6. Absorption spectra of the catalyst **DBPP1** (0.1 M) with different additives. Dry degassed DMF was used as solvent.

Supplementary Note 3. Stern-Volmer Experiments

The samples were prepared mixing the phenolate anion of **DBPP1** (5×10^{-5} M, freshly prepared *in situ* by the deprotonation of **DBPP1** with 1.1 equiv Cs_2CO_3) with the required amount of **1** in a total volume of 1 mL of dry DMF (rigorously degassed by freeze/pump/thaw) in a 10 × 10 mm light path quartz fluorescence cuvette under an argon atmosphere. The samples were vigorously bubbled with dry argon for 5 minutes prior to the measurement. The excitation wavelength was fixed at 372 nm, the emission light was acquired from 392 nm to 600 nm.

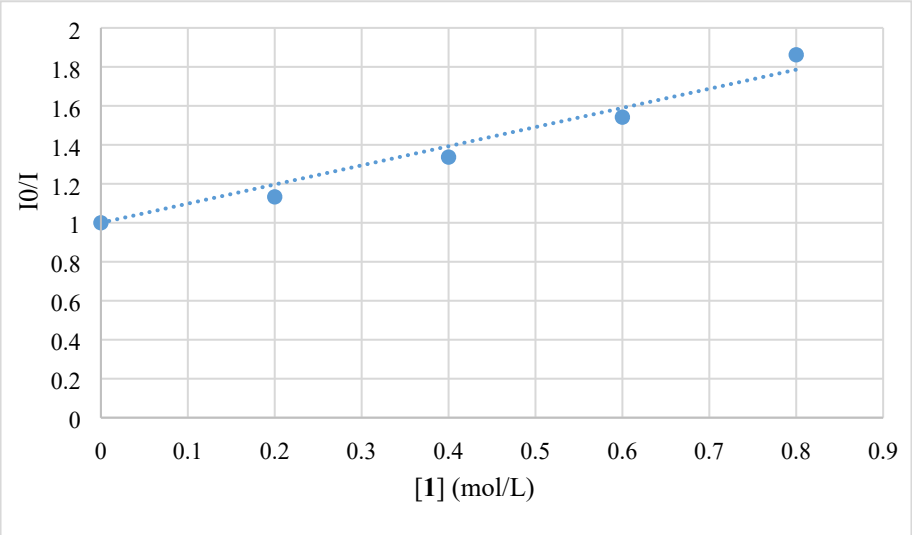


Supplementary Figure 7. Quenching of the phenolate anion of **DBPP1** emission (5×10^{-5} M in DMF) in the presence of increasing amounts of **1**.

The Stern-Volmer plot shows a linear correlation between the amounts of **1** and the ratio I_0/I. The quenching of excited-state photosensitizer with externally added quencher (Q) follows Stern-Volmer relationship: [1]

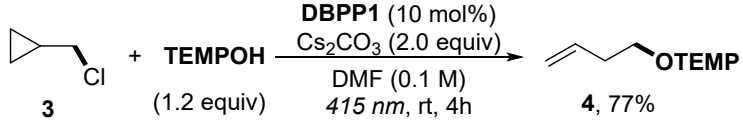
$$I_0/I = 1 + k_q\tau_0[Q] = K_{SV}[Q] \quad \text{Eq. S1}$$

Where I_0 is the intensity at emission maximum in the absence of quencher; I is the intensity at the emission maximum in the presence of quencher at a concentration of [Q]; τ_0 is the lifetime of the photosensitizer in the absence of quencher; k_q is the rate constant for the quenching process by the quencher; K_{SV} ($= k_q\tau_0$) is directly obtained from Stern-Volmer plots as 0.98 M^{-1}. Based on the fluorescence lifetime of the phenolate anion of **DBPP1** (τ_0 = 7.08 ns), [2] the quenching rate constant $k_q = K_{SV}/\tau_0 = 1.4 \times 10^8$ M^{-1} s^{-1} can be calculated for 1-chlorohexane **1**.



Supplementary Figure 8. Stern-Volmer quenching plot.

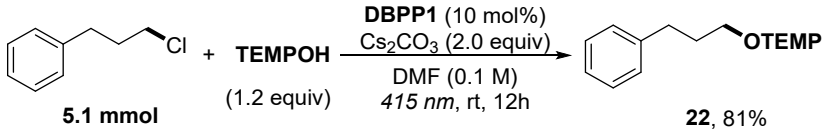
Supplementary Note 4. Radical Clock Experiments



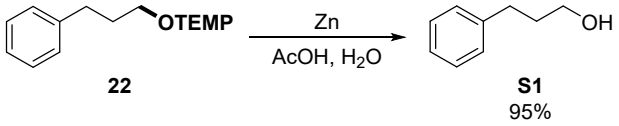
To an oven dried 10 mL glass tube with a magnetic stirring bar was added **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMF (3.0 mL) and (chloromethyl)cyclopropane **3** (27.0 mg, 0.30 mmol) were carefully added under Argon. The reaction mixture was stirred under two 415 nm LED lamps (7 W) (the distance was about 7.5 cm) irradiation for the indicated time at room temperature. Irradiation was stopped and the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (ethyl acetate/petroleum ether = 1:200) on silica gel to afford **4** a colorless oil (48.8 mg, 77% yield).

1-(but-3-en-1-yloxy)-2,2,6,6-tetramethylpiperidine (4): ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.86 (ddt, *J* = 17.1, 10.2, 6.8, 1H), 5.07 (dd, *J* = 17.1, 1.4, 1H), 5.00 (d, *J* = 10.2, 1H), 3.78 (t, *J* = 6.8, 2H), 2.28 (q, *J* = 6.8, 2H), 1.57 – 1.31 (m, 6H), 1.16 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.8, 115.8, 76.0, 59.7, 39.6, 33.3, 33.1, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{26}ON$ $[M + H]^+$, 212.2009, found 212.2012.

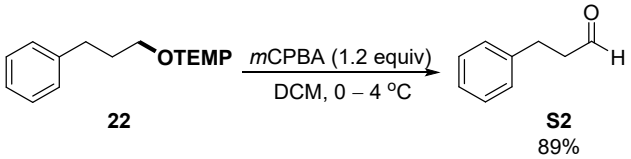
Supplementary Note 5. Scale up Experiment and Chemical Manipulation of Products



To an oven dried 100 mL eggplant shaped flask with a magnetic stirring bar was added **DBPP1** (143.8 mg, 0.51 mmol, 10 mol%), Cs_2CO_3 (3.32 g, 10.2 mmol), TEMPOH (960.8 mg, 6.12 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. DMF (51.0 mL) and (3-chloropropyl)benzene (788.7 mg, 5.1 mmol) were carefully added under Argon. The reaction mixture was stirred under four 415 nm LED lamps (7 W) (the distance was about 7.5 cm) irradiation for 12 h. Irradiation was stopped and the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (ethyl acetate/petroleum ether = 1:200) on silica gel to afford **22** a colorless oil (1.14 g, 81% yield).

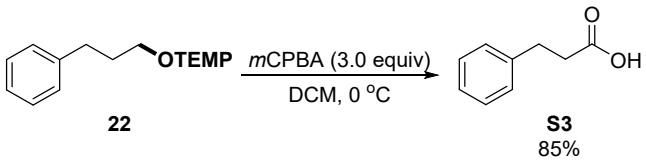


2,2,6,6-Tetramethyl-1-(3-phenylpropoxy)piperidine (**22**) (82.6 mg, 0.30 mmol) was dissolved in HOAc/H_2O (1.0 mL : 3.0 mL) under argon. Then activated zinc powder (117.0 mg, 1.80 mmol) was added to the mixture in one portion and the solution was stirred over night at room temperature. NaOH (10 mL, 0.5 M) was added to quench the reaction. The mixture was extracted with DCM. The combined organic layers were washed with brine and dried over Na_2SO_4. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether 1:10) to afford the product 3-phenylpropan-1-ol **S1** as a colorless oil (38.8 mg, 95% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (t, *J* = 7.5, 2H), 7.26 – 7.15 (m, 3H), 3.70 (t, *J* = 6.4, 2H), 2.75 (t, *J* = 7.6, 2H), 1.93 (tt, *J* = 7.6, 6.4, 2H). Analytical data are in agreement with those reported in the literarure[3].



To a solution of the 2,2,6,6-tetramethyl-1-(3-phenylpropoxy)piperidine (**22**) (82.6 mg, 0.30 mmol) in DCM (1.5 mL) was added portionwise *m*CPBA (62.13 mg, 0.36 mmol) over 10 min at 0 – 4 °C. The mixture was stirred at the same temperature for 30 min. H_2O was added to quench the reaction. The mixture was extracted with DCM. The combined organic layers were washed with brine and dried over Na_2SO_4. The crude mixture was purified by silica gel chromatography (ethyl acetate/petroleum ether

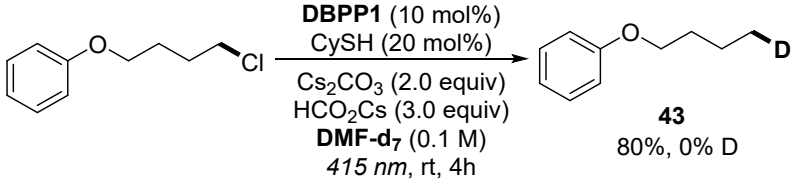
1:30) to afford the product 3-phenylpropanal **S2** as a yellow oil (35.8 mg, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.29 (t, *J* = 7.4, 2H), 7.24 – 7.19 (m, 3H), 2.96 (t, *J* = 7.5, 2H), 2.77 (t, *J* = 7.5, 2H). Analytical data are in agreement with those reported in the literarure[4].



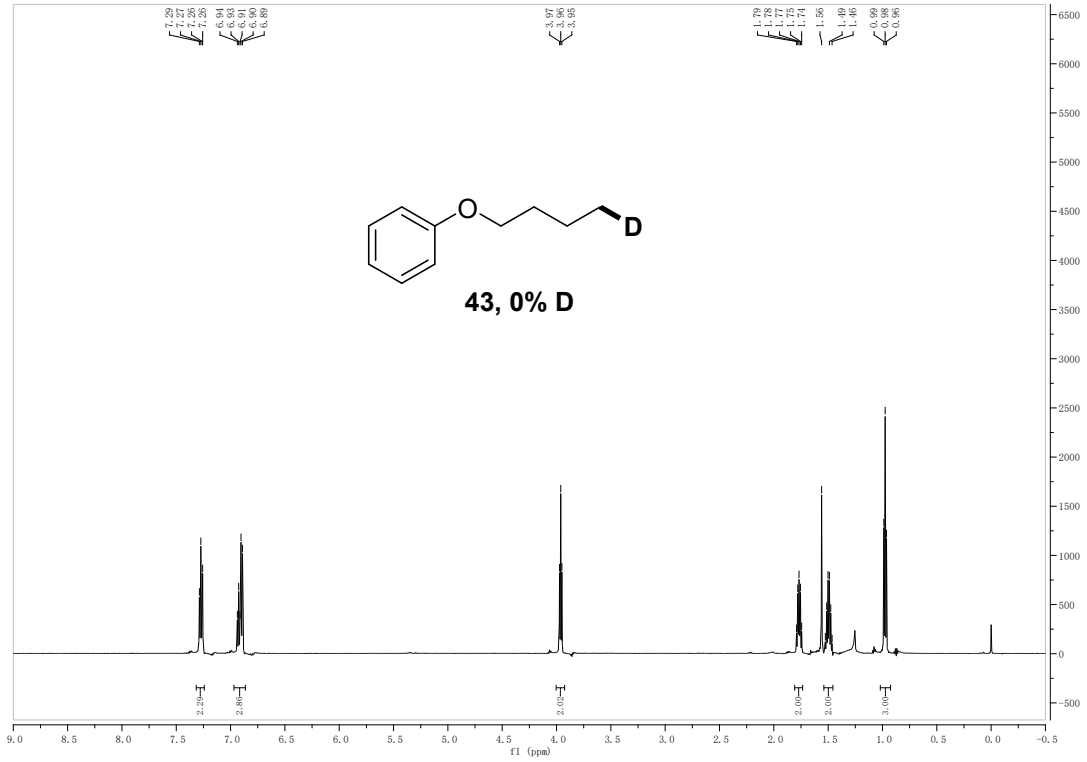
22 **S3** 85%

To a solution of the 2,2,6,6-tetramethyl-1-(3-phenylpropoxy)piperidine (**22**) (82.6 mg, 0.30 mmol) in DCM (10 mL) was added portionwise *m*CPBA (155.3 mg, 0.75 mmol) over 5 min at 0 °C. The mixture was stirred at the same temperature for 30 min. After removing the solvent under vacuo, the residue was purified with TLC (DCM/CH_3Cl/ethyl acetate 1:1:1) to afford the product 3-phenylpropanoic acid **S3** as a colorless oil (38.3 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.22 (m, 5H), 2.99 (t, *J* = 7.8, 2H), 2.71 (t, *J* = 7.8, 1H). Analytical data are in agreement with those reported in the literarure[8].

Supplementary Note 6. Deuterium labeling experiments

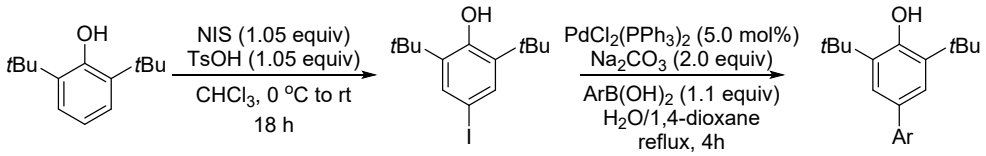


To an oven dried 10 mL glass tube with a magnetic stirring bar was added **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol) and HCOOCs (160.2 mg, 0.90 mmol). Then the reaction tube was allowed to be vacuumed and purged with Argon for three times. CySH (7.0 mg, 0.06 mmol, 20 mol%), (4-chlorobutoxy)benzene (55.2 mg, 0.30 mmol) and DMF-d7 (3.0 mL) were carefully added under Argon. The reaction mixture was stirred under two 415 nm LED lamps (7 W) (the distance was about 7.5 cm) irradiation for 4 hours at room temperature. Irradiation was stopped and the reaction was diluted with water. The aqueous phase was extracted with ethyl acetate (15 mL × 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **43** as a colorless oil (36.0 mg, 80% yield, 0% D). These results ruled out the possibility of hydrogen atom abstraction from the solvent in the alkyl halide reduction reaction.

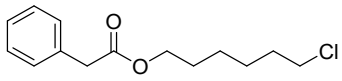


Synthesis of Catalysts

Catalysts **DBPP1, DBPP2, DBPP3, DBPP4** were prepared following the general procedure reported by our own group and all spectral data were in accordance with the literature.[2]



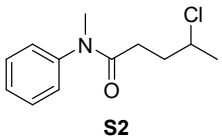
Synthesis of Starting Materials



S1

6-Chlorohexyl 2-phenylacetate (S1)

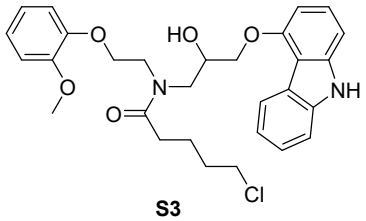
Phenylacetyl chloride (1.56 g, 10.1 mmol) was added dropwise to a solution of 6-chloro-1-hexanol (1.36 g, 10.0 mmol) and triethylamine (1.03 g, 10.1 mol) in DCM (20.0 mL) at 0 °C. After stirring at ambient temperature, the solution was washed with water. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The crude product was subjected to column chromatography (petroleum ether as an eluent) on silica gel to give **S1** (2.41 g, 95% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 – 7.22 (m, 5H), 4.08 (t, *J* = 6.6, 2H), 3.60 (s, 2H), 3.48 (t, *J* = 6.7, 2H), 1.82 – 1.63 (m, 2H), 1.69 – 1.53 (m, 2H), 1.49 – 1.42 (m, 2H), 1.39 – 1.27 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.6, 134.2, 129.3, 128.6, 128.3, 64.7, 44.9, 41.5, 32.4, 28.4, 26.4, 25.2; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{19}ClO_2Na$ $[M + Na]^+$, 277.0966, found 277.0968.



S2

4-Chloro-*N*-methyl-*N*-phenylpentanamide (S2)

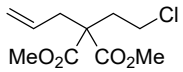
4-Chloropentanoyl chloride (1.56 g, 10.1 mmol) was added dropwise to an ice-cooled stirred solution of *N*-methylaniline (1.07 g, 10.0 mmol) and triethylamine (1.03 g, 10.1 mmol) in DCM (20 mL). After 10 min at 0 °C, the solution was stirred at room temperature for 3 h. The reaction was quenched with 1 N HCl (10 mL), extracted with DCM (5 x 5 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was subjected to column chromatography (petroleum ether/acetone = 10 : 1) on silica gel to give **S2** (2.09 g, 93% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (t, *J* = 7.5, 2H), 7.35 (t, *J* = 7.2, 1H), 7.20 (d, *J* = 7.5, 2H), 4.06 – 3.98 (m, 1H), 3.27 (s, 3H), 2.28 – 2.20 (m, 2H), 2.14 – 2.07 (m, 1H), 1.85 – 1.78 (m, 1H), 1.46 (d, *J* = 6.4, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.0, 143.9, 129.9, 127.9, 127.3, 58.4, 37.3, 35.7, 31.2, 25.5; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{17}ClON$ $[M + H]^+$, 226.0993, found 226.0994.



S3

***N*-(3-((9*H*-Carbazol-4-yl)oxy)-2-hydroxypropyl)-5-chloro-*N*-(2-(2-methoxyphenoxy)ethyl)pentanamide (S3)**

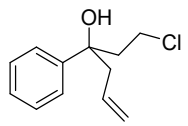
Carvedilol (2.03 g, 5.0 mmol) was dissolved in anhydrous DCM (50.0 mL). Anhydrous pyridine (1.86 g, 23.5 mmol) was added, the solution was cooled to 0 °C, and 5-chlorovaleroyl chloride (0.79 g, 5.1 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h, whereupon it was diluted with DCM (25 mL) and washed with sat. aq. $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated to dryness under reduced pressure. The crude product was subjected to column chromatography (petroleum ether/acetone = 3 : 1) on silica gel to give **S3** (2.10 g, 80% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 – 8.15 (m, 2H), 7.39 – 7.29 (m, 3H), 7.23 – 7.15 (m, 1H), 7.06 (t, *J* = 8.1, 1H), 6.97 – 6.79 (m, 3.5H), 6.75 – 6.65 (m, 1.5H), 4.62 (s, 0.5H), 4.43 (d, *J* = 4.9, 0.5H), 4.42 – 4.22 (m, 3H), 4.15 – 3.96 (m, 2H), 3.94 – 3.87 (m, 1H), 3.86 – 3.67 (m, 5H), 3.55 (t, *J* = 5.7, 1H), 3.35 (t, *J* = 6.7, 1H), 2.63 (d, *J* = 6.7, 1H), 2.52 – 2.39 (m, 1H), 1.89 – 1.79 (m, 2H), 1.75 – 1.60 (m, 1H), 1.58 – 1.48 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 176.3, 173.8, 154.9, 154.8, 149.7, 148.8, 147.8, 147.7, 141.0, 138.8, 126.8, 126.7, 125.2, 125.1, 122.7, 122.6, 122.4, 122.1, 121.5, 121.2, 120.8, 119.7, 119.6, 113.8, 113.0, 112.6, 111.9, 111.4, 110.2, 104.1, 104.0, 101.4, 101.1, 100.0, 70.5, 69.6, 69.3, 68.5, 66.7, 55.7, 55.6, 54.0, 51.7, 49.4, 48.4, 44.8, 44.7, 32.7, 32.3, 32.2, 31.9, 22.5, 22.4; HR-ESI-MS (*m/z*): calcd. for $C_{29}H_{34}ClO_5N_2$ $[M + H]^+$, 525.2151, found 525.2156.



57a

Dimethyl 2-allyl-2-(2-chloroethyl)malonate (57a)

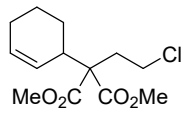
A solution of dimethyl allylmalonate (1.72 g, 10.0 mmol) in THF (10.0 mL) was added dropwise to a suspension of NaH (264.0 mg, 11.0 mmol) in DMF (10.0 mL) at 0 °C. The cooling bath was removed and the mixture was stirred for 1 h at room temperature. 1-Bromo-2-chloroethane (4.38 g, 30.0 mmol) was added over 15 min and the resulting mixture was stirred for 48 h at rt. The reaction was quenched with saturated aqueous NH_4Cl. The aqueous solution was extracted with DCM and the combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography (petroleum ether/acetone = 80 : 1) on silica gel to give **51a** (1.40 g, 60% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.69 – 5.59 (m, 1H), 5.21 – 5.10 (m, 2H), 3.74 (s, 6H), 3.60 – 3.49 (m, 2H), 2.68 (d, *J* = 7.4, 2H), 2.46 – 2.34 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 131.7, 119.7, 56.6, 52.6, 39.8, 37.9, 35.9; HR-ESI-MS (*m/z*): calcd. for $C_{10}H_{15}ClO_4Na$ $[M + Na]^+$, 257.0551, found 257.0549.



57b

1-Chloro-3-phenylhex-5-en-3-ol (57b)

Allylmagnesium bromide (10.0 mL 1 M in Et_2O, 10.0 mmol) was slowly added (over 10 min) to a stirred solution of 3-chloro-1-phenylpropan-1-one (833.3 mg, 5.0 mmol) in anhydrous THF (10 mL) at 0 °C. The reaction mixture was allowed to warm up to rt. After 1 h at rt, the reaction was quenched with an aqueous solution of NH_4Cl (10.0 mL). The mixture was extracted with Et_2O and dried over anhydrous Na_2SO_4. The crude product was subjected to column chromatography (petroleum ether/acetone = 10 : 1) on silica gel to give **51b** (0.89 g, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 – 7.23 (m, 5H), 5.60 – 5.45 (m, 1H), 5.25 – 5.11 (m, 2H), 3.57 (td, *J* = 10.3, 6.4, 1H), 3.21 (td, *J* = 10.4, 5.9, 1H), 2.73 (dd, *J* = 13.7, 6.0, 1H), 2.51 (dd, *J* = 13.7, 8.8, 1H), 2.43 – 2.27 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.4, 132.6, 128.4, 127.0, 125.0, 120.5, 75.2, 47.8, 45.5, 40.1; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{15}ClONa$ [M + Na]$^+$, 233.0704, found 233.0704.



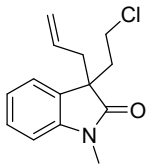
57c

Dimethyl 2-(2-chloroethyl)-2-(cyclohex-2-en-1-yl)malonate (57c)

The mixture was cooled to 0 °C, and to the mixture was added dimethyl propanedioate (1.32 g, 10.0 mmol) dropwise. The reaction was stirred at 0 °C for 1 h, and then, 3-bromocyclohexene (1.77 g, 11.0 mmol) was added. The reaction mixture was refluxed overnight. The crude reaction was quenched with saturated aqueous NH_4Cl, extracted with Et_2O, washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was carried onto the next step without further purification. The crude product was subjected to column chromatography (petroleum ether/acetone = 30 : 1) on silica gel to give dimethyl 2-(cyclohex-2-en-1-yl)malonate (1.65 g, 78% yield).

Sodium hydride (288.0 mg, 7.2 mmol, 60% dispersion in mineral oil) was added to DMSO (6.0 mL) and allowed to stir for 10 min at rt. Next dimethyl 2-(cyclohex-2-en-1-yl)malonate (1.27 g, 6.0 mmol, in 2 mL DMF) was added drop wise and reaction mixture was stirred for 1.0 h. 1-Bromo-2-chloroethane (876.0 mg, 6.0 mmol) was added and the reaction mixture stirred for 30 min, then at 60 °C for 8 h. The reaction mixture was quenched with sat. NH_4Cl (10.0 mL) and extracted with Et_2O. The organic layer was washed with deionized water, dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude product was subjected to column chromatography (petroleum ether/acetone = 60 : 1) on silica gel to give **51c** (1.12 g, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.84 – 5.71 (m, 1H), 5.60 (d, *J* = 10.3, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 3.64 – 3.53 (m, 2H), 2.97 – 2.93 (m, 1H), 2.47 – 2.30 (m, 2H), 2.01 – 1.91 (m, 2H),

1.87 – 1.77 (m, 1H), 1.76 – 1.68 (m, 1H), 1.59 – 1.48 (m, 1H), 1.36 – 1.27 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.5, 129.5, 127.1, 60.4, 52.5, 52.3, 40.7, 35.5, 24.8, 24.5, 22.3; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{20}ClO_4$ $[M + H]^+$, 275.1045, found 275.1050.



57d

3-Allyl-3-(2-chloroethyl)-1-methylindolin-2-one (57d)

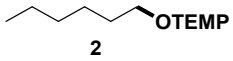
To a solution of indolin-2-one (2.67 g, 20.0 mmol) in 60 mL dry THF at –78 °C was added *n*-BuLi (16 mL, 2.5 M in hexane) and tetramethylethylenediamine (TMEDA, 6.0 mL, 20 mmol). The resulting solution was stirred for 2 h at –78 °C, followed by dropwise addition of allyl bromide (1.9 mL, 22.0 mmol, 1.1 equiv), and the solution was slowly warmed up to –20 °C with stirring for 1 h. The reaction was quenched by the addition of aqueous saturated NH_4Cl (100 ml) solution, and the reaction mixture was extracted with EtOAc. The organic solution was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to give a crude residue. The crude product was subjected to column chromatography (petroleum ether/acetone = 5 : 1) on silica gel to give 3-allylindolin-2-one (2.8 g, 81% yield).

To a suspension of NaH (440.0 mg, 11.0 mmol, 60% dispersion in mineral oil) in toluene (50 mL) at 100 °C under nitrogen atmosphere was slowly added a pre-heated solution of 3-allylindolin-2-one (1.73 g, 10.0 mmol) in toluene (10 mL), and the resulting mixture was allowed to stir at 100 °C for 1 h. To the former solution was slowly added dimethyl sulfate (0.95 mL, 10.0 mmol), and the corresponding reaction mixture was stirred at 100 °C for 1 h until completion of the reaction, monitored by TLC. The reaction was quenched by the addition of an aqueous saturated NH_4Cl solution at 0 °C, and the corresponding solution was stirred at room temperature for 30 minutes. The reaction mixture was extracted with EtOAc, and the organic solution was washed with brine, dried over $MgSO_4$ and concentrated in *vacuo* to give a crude residue. The crude product was subjected to column chromatography (petroleum ether/acetone = 8 : 1) on silica gel to give 3-allyl-1-methylindolin-2-one (1.31 g, 70% yield).

A solution of 3-allyl-1-methylindolin-2-one (0.94 g, 5.0 mmol) in THF (5.0 mL) was added dropwise to a suspension of NaH (132.0 mg, 5.5 mmol) in DMF (5.0 mL) at 0 ºC. The cooling bath was removed and the mixture was stirred for 1 h at room temperature. Freshly distilled 1-bromo-2-chloroethane (2.19 g, 15.0 mmol) was added over 15 min and the resulting mixture was stirred for 48 h at rt. The reaction was quenched with saturated aqueous NH_4Cl. The aqueous solution was extracted with DCM and the combined organic extracts were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was subjected to column chromatography (petroleum ether/acetone = 6 : 1) on silica gel to give **57d** (0.92 g, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.25 (m, 1H), 7.20 (d, J = 7.3,

1H), 7.09 (t, *J* = 7.5, 1H), 6.85 (d, *J* = 7.7, 1H), 5.47 – 5.36 (m, 1H), 5.00 (dd, *J* = 17.0, 1.3, 1H), 4.99 – 4.91 (m, 1H), 3.28 – 3.15 (m, 4H), 3.10 (td, *J* = 10.6, 4.8, 1H), 2.52 (t, *J* = 10.2, 2H), 2.46 (ddd, *J* = 13.7, 10.5, 6.3, 1H), 2.26 (ddd, *J* = 13.7, 10.5, 4.8, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 178.3, 143.7, 131.5, 128.4, 123.2, 122.6, 119.3, 108.2, 51.7, 42.1, 39.8, 39.3, 26.2; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{17}ClON$ $[M + H]^+$, 250.0993, found 250.0997.

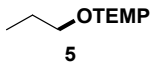
Identification of Compounds



2

1-(Hexyloxy)-2,2,6,6-tetramethylpiperidine (2)

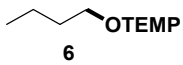
Prepared according to the general procedure A using 1-chlorohexane **1** (38.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **2** as a colorless oil (67.2 mg, 93% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.74 (t, *J* = 6.7, 2H), 1.62 – 1.43 (m, 6H), 1.43 – 1.29 (m, 8H), 1.17 (s, 6H), 1.11 (s, 6H), 0.91 (t, *J* = 6.9, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.9,
59.6, 39.6, 33.1, 31.9, 28.7, 26.1, 22.6, 20.1, 17.2, 14.0; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{32}ON$ $[M + H]^+$, 242.2478, found 242.2475.



5

2,2,6,6-Tetramethyl-1-propoxypiperidine (5)

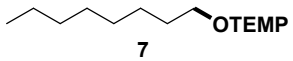
Prepared according to the general procedure A using 1-chloropropane (23.4 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **5** as a colorless oil (47.7 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.69 (t, *J* = 6.7, 2H), 1.62 – 1.29 (m, 8H), 1.15 (s, 6H), 1.10 (s, 6H), 0.97 – 0.90 (t, *J* = 7.3, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 78.3, 59.6, 39.7, 33.1, 22.0, 20.1, 17.2, 10.9; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{26}ON$ $[M + H]^+$, 200.2009, found 200.2011.



6

1-Butoxy-2,2,6,6-tetramethylpiperidine (6)

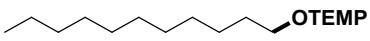
Prepared according to the general procedure A using 1-chlorobutane (27.6 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **6** as a colorless oil (53.0 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.73 (t, *J* = 6.6, 2H), 1.57 – 1.29 (m, 10H), 1.15 (s, 6H), 1.11 (s, 6H), 0.92 (t, *J* = 7.3, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.6, 59.6, 39.6, 33.1, 30.9, 20.1, 19.7, 17.2, 14.2; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{28}ON$ $[M + H]^+$, 214.2165, found 214.2165.



7

2,2,6,6-Tetramethyl-1-(octyloxy)piperidine (7)

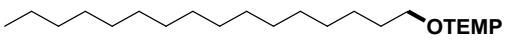
Prepared according to the general procedure A using 1-chlorooctane (44.4 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **7** as a colorless oil (70.3 mg, 87% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.71 (t, J = 6.7, 2H), 1.52 – 1.27 (m, 18H), 1.15 (s, 6H), 1.09 (s, 6H), 0.88 (t, J = 6.9, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.9, 59.6, 39.6, 33.1, 31.9, 29.7, 29.3, 28.7, 26.5, 22.7, 20.1, 17.2, 14.1; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{36}ON$ $[M + H]^+$, 270.2791, found 270.2788.



8

2,2,6,6-Tetramethyl-1-(undecyloxy)piperidine (8)

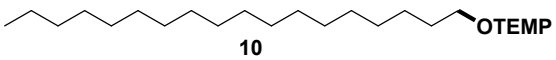
Prepared according to the general procedure A using 1-chloroundecane (57.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **8** as a colorless oil (86.9 mg, 93% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.71 (t, J = 6.7, 2H), 1.55 – 1.41 (m, 6H), 1.40 – 1.20 (m, 18H), 1.14 (s, 6H), 1.09 (s, 6H), 0.88 (t, J = 7.0, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.9, 59.6, 39.6, 33.1, 31.9, 29.7, 29.6, 29.3, 28.7, 26.5, 22.7, 20.1, 17.2, 14.1; HR-ESI-MS (*m/z*): calcd. for $C_{20}H_{42}ON$ $[M + H]^+$, 312.3261, found 312.3261.



9

1-(Hexadecyloxy)-2,2,6,6-tetramethylpiperidine (9)

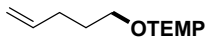
Prepared according to the general procedure A using 1-chlorohexadecane (78.1 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **9** as a colorless oil (103.0 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.71 (t, J = 6.7, 2H), 1.54 – 1.25 (m, 34H), 1.15 (s, 6H), 1.09 (s, 6H), 0.88 (t, J = 7.0, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.9, 59.6, 39.6, 33.1, 31.9, 29.7, 29.6, 29.4, 28.7, 26.5, 22.7, 20.1, 17.2, 14.1; HR-ESI-MS (*m/z*): calcd. for $C_{25}H_{52}ON$ $[M + H]^+$, 382.4043, found 382.4043.



10

2,2,6,6-Tetramethyl-1-(octadecyloxy)piperidine (10)

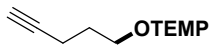
Prepared according to the general procedure A using 1-chlorooctadecane (86.5 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **10** as a colorless oil (110.5 mg, 88% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.71 (t, *J* = 6.7, 2H), 1.57 – 1.43 (m, 6H), 1.39 – 1.21 (m, 32H), 1.15 (s, 6H), 1.09 (s, 6H), 0.88 (t, *J* = 7.0, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.9, 59.6, 39.6, 33.1 31.9, 29.7, 29.6, 29.4, 28.7, 26.5, 22.7, 20.1, 17.2, 14.1; HR-ESI-MS (*m/z*): calcd. for $C_{27}H_{56}ON$ $[M + H]^+$, 410.4356, found 410.4355.



11

2,2,6,6-Tetramethyl-1-(pent-4-en-1-yloxy)piperidine (11)

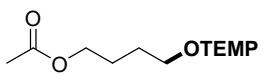
Prepared according to the general procedure A using 5-chloropent-1-ene (31.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **11** as a colorless oil (52.7 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.84 (ddt, *J* = 16.9, 10.2, 6.6, 1H), 5.03 (dd, *J* = 17.1, 1.7, 1H), 4.95 (d, *J* = 10.2, 1H), 3.74 (t, *J* = 6.6, 2H), 2.14 (dd, *J* = 14.7, 7.0, 2H), 1.68 – 1.59 (m, 2H), 1.60 – 1.27 (m, 6H), 1.15 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.8, 114.4, 76.1, 59.6, 39.6, 33.0, 30.7, 28.1, 20.1, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{28}ON$ $[M + H]^+$, 226.2165, found 226.2161.



12

2,2,6,6-Tetramethyl-1-(pent-4-yn-1-yloxy)piperidine (12)

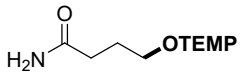
Prepared according to the general procedure A using 5-chloropent-1-yne (30.6 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **12** as a colorless oil (56.2 mg, 84% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.81 (t, *J* = 6.1, 2H), 2.31 (td, *J* = 7.2, 2.6, 2H), 1.94 (t, *J* = 2.6, 1H), 1.80 – 1.71 (m, 2H), 1.62 – 1.28 (m, 6H), 1.15 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 84.4, 74.7, 68.2, 59.7, 39.6, 33.1, 28.0, 20.1, 17.1, 15.6; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{26}ON$ $[M + H]^+$, 224.2009, found 224.2010.



13

4-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)butyl acetate (13)

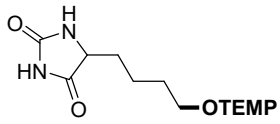
Prepared according to the general procedure A using 4-chlorobutyl acetate (45.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **13** as a colorless oil (72.4 mg, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.09 (t, *J* = 6.7, 2H), 3.76 (t, *J* = 6.4, 2H), 2.05 (s, 3H), 1.79 – 1.67 (m, 2H), 1.68 – 1.55 (m, 2H), 1.56 – 1.29 (m, 6H), 1.14 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.2, 76.1, 64.6, 59.7, 39.6, 33.1, 25.8, 25.3, 21.0, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{30}O_3N$ $[M + H]^+$, 272.2220, found 272.2217.



14

4-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)butanamide (14)

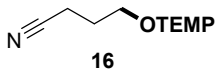
Prepared according to the general procedure A using 4-chlorobutanamide (36.3 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:30) to afford the product **14** as a colorless oil (50.9 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.89 (s, 1H), 5.76 (s, 1H), 3.79 (t, *J* = 6.1, 2H), 2.36 (t, *J* = 7.6, 2H), 1.93 – 1.81 (m, 2H), 1.59 – 1.30 (m, 6H), 1.14 (s, 6H), 1.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.6, 75.6, 59.7, 39.6, 33.1, 24.7, 20.2, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{27}O_2N_2$ $[M + H]^+$, 243.2067, found 243.2069.



15

5-(4-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)butyl)imidazolidine-2,4-dione (15)

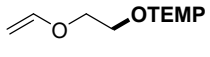
Prepared according to the general procedure A using 5-(4-chlorobutyl)imidazolidine-2,4-dione (57.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:10) to afford the product **15** as a colorless oil (72.8 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.73 (s, 1H), 6.37 (s, 1H), 4.03 (dd, *J* = 7.6, 4.6, 1H), 3.67 (t, *J* = 6.1, 2H), 1.88 – 1.80 (m, 1H), 1.73 – 1.62 (m, 1H), 1.56 – 1.22 (m, 10H), 1.07 (s, 6H), 1.01 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.8, 157.6, 76.1, 59.7, 58.8, 39.6, 33.1, 31.8, 28.2, 22.1, 20.2, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{30}O_3N_3$ $[M + H]^+$, 312.2282, found 312.2284.



16

4-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)butanenitrile (16)

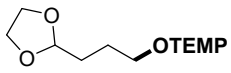
Prepared according to the general procedure A using 4-chlorobutanenitrile (30.9 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **16** as a colorless oil (56.5 mg, 84% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.84 (t, *J* = 5.8, 2H), 2.48 (t, *J* = 7.2, 2H), 1.90 (d, *J* = 7.0, 2H), 1.61 – 1.29 (m, 6H), 1.15 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 119.6, 73.7, 59.8, 39.6, 33.1, 25.1, 20.1, 17.1, 14.4; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{25}ON_2$ $[M + H]^+$, 225.1961, found 225.1961.



17

2,2,6,6-Tetramethyl-1-(2-(vinyloxy)ethoxy)piperidine (17)

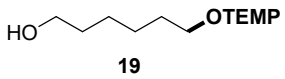
Prepared according to the general procedure A using (2-chloroethoxy)ethene (31.8 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **17** as a colorless oil (60.0 mg, 88% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.48 (dd, *J* = 14.3, 6.7, 1H), 4.20 (dd, *J* = 14.3, 1.8, 1H), 4.01 – 3.96 (m, 3H), 3.88 – 3.77 (m, 2H), 1.62 – 1.29 (m, 6H), 1.20 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 152.2, 86.5, 75.4, 67.0, 59.9, 39.7, 32.9, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{26}O_2N$ $[M + H]^+$, 228.1958, found 228.1964.



18

1-(3-(1,3-Dioxolan-2-yl)propoxy)-2,2,6,6-tetramethylpiperidine (18)

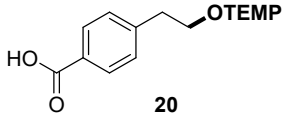
Prepared according to the general procedure A using 2-(3-chloropropyl)-1,3-dioxolane (45.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **18** as a colorless oil (73.2 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.89 (t, *J* = 4.0, 1H), 3.97 (td, *J* = 6.3, 1.5, 2H), 3.85 (t, *J* = 6.1, 2H), 3.76 (t, *J* = 6.4, 2H), 1.81 – 1.72 (m, 2H), 1.69 – 1.61 (m, 2H), 1.62 – 1.28 (m, 6H), 1.14 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 104.6, 76.2, 64.9, 59.7, 39.6, 33.1, 31.0, 23.3, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{30}O_3N$ $[M + H]^+$, 272.2220, found 272.2224.



19

6-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)hexan-1-ol (19)

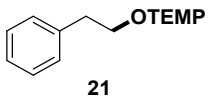
Prepared according to the general procedure A using 6-chlorohexan-1-ol (40.8 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:50) to afford the product **19** as a colorless oil (65.2 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.73 (t, *J* = 6.6, 2H), 3.65 (t, *J* = 6.6, 2H), 1.64 – 1.31 (m, 14H), 1.14 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.7, 62.9, 59.7, 39.6, 33.0, 32.8, 28.7, 26.3, 25.8, 20.1, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{32}O_2N$ $[M + H]^+$, 258.2428, found 258.2427.



20

4-(2-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)ethyl)benzoic acid (20)

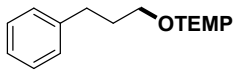
Prepared according to the general procedure A using 4-(2-chloroethyl)benzoic acid (55.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (293.3 mg, 0.90 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 8 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **20** as a colorless oil (69.6 mg, 76% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.1, 2H), 7.34 (d, *J* = 8.1, 2H), 3.97 (t, *J* = 6.6, 2H), 2.89 (t, *J* = 6.6, 2H), 1.46 – 1.32 (m, 6H), 1.04 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.1, 130.0, 129.3, 127.5, 76.7, 59.8, 39.6, 35.6, 32.9, 20.2, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{28}O_3N$ $[M + H]^+$, 306.2064, found 306.2061.



21

2,2,6,6-Tetramethyl-1-phenethoxypiperidine (21)

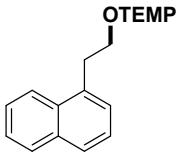
Prepared according to the general procedure A using (2-chloroethyl)benzene (42.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **21** as a colorless oil (53.3 mg, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.20 (m, 5H), 3.98 (t, *J* = 7.0, 2H), 2.86 (t, *J* = 7.0, 2H), 1.63 – 1.27 (m, 6H), 1.11 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.6, 129.1, 128.1, 125.9, 77.5, 59.7, 39.7, 35.4, 33.0, 20.1, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{17}H_{28}ON$ $[M + H]^+$, 262.2465, found 262.2165.



22

2,2,6,6-Tetramethyl-1-(3-phenylpropoxy)piperidine (22)

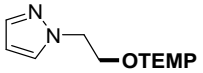
Prepared according to the general procedure A using (3-chloropropyl)benzene (46.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **22** as a colorless oil (75.1 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 – 7.19 (m, 5H), 3.77 (td, *J* = 6.5, 1.4, 2H), 2.74 – 2.66 (m, 2H), 1.90 – 1.82 (m, 2H), 1.58 – 1.31 (m, 6H), 1.13 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 142.4, 128.4, 128.3, 125.7, 76.2, 59.7, 39.7, 33.1, 32.8, 30.5, 20.1, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{30}ON$ $[M + H]^+$, 276.2322, found 276.2325.



23

2,2,6,6-Tetramethyl-1-(2-(naphthalen-1-yl)ethoxy)piperidine (23)

Prepared according to the general procedure A using 1-(2-chloroethyl)naphthalene (57.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **23** as a colorless oil (74.7 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4, 1H), 7.82 (d, *J* = 8.0, 1H), 7.70 (d, *J* = 7.4, 1H), 7.49 (t, *J* = 7.1, 1H), 7.44 (t, *J* = 7.3, 1H), 7.42 – 7.36 (m, 2H), 4.08 (t, *J* = 7.2, 2H), 3.30 (t, *J* = 7.2, 2H), 1.58 – 1.22 (m, 6H), 1.05 (s, 6H), 1.04 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 135.6, 133.8, 132.3, 128.6, 126.9, 126.8, 125.7, 125.4, 125.4, 124.0, 77.1, 59.7, 39.6, 33.0, 32.2, 20.2, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{21}H_{30}ON$ $[M + H]^+$, 312.2322, found 312.2325.

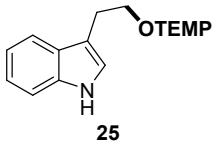


24

1-(Hexyloxy)-2,2,6,6-tetramethylpiperidine (24)

Prepared according to the general procedure A using 1-(2-chloroethyl)-1H-pyrazole (39.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:20) to afford the product **24** as a colorless oil (64.8 mg,

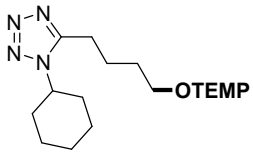
86% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 – 7.46 (m, 2H), 6.24 (s, 1H), 4.27 (t, *J* = 5.1, 2H), 4.06 (t, *J* = 5.1, 2H), 1.57 – 1.24 (m, 6H), 1.04 (s, 6H), 0.98 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 139.2, 130.3, 105.2, 75.1, 59.8, 51.4, 39.6, 32.7, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{26}ON_3$ $[M + H]^+$, 252.2070, found 252.2070.



25

3-(2-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)ethyl)-1H-indole (25)

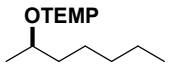
Prepared according to the general procedure A using 3-(2-chloroethyl)-1H-indole (53.7 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:100) to afford the product **25** as a colorless oil (82.9 mg, 92% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.62 (d, *J* = 7.9, 1H), 7.33 (d, *J* = 8.1, 1H), 7.17 (t, *J* = 7.4, 1H), 7.11 (t, *J* = 7.4, 1H), 7.03 (s, 1H), 4.04 (t, *J* = 7.3, 2H), 2.99 (t, *J* = 7.3, 2H), 1.60 – 1.29 (m, 6H), 1.14 (s, 6H), 1.11 (s, 6H): ^{13}C NMR (150 MHz, $CDCl_3$): δ 136.2, 127.8, 121.8, 119.2, 119.0, 113.6, 111.0, 77.1, 59.7, 39.7, 33.1, 24.5, 20.2, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{29}ON_2$ $[M + H]^+$, 301.2274, found 301.2271.



26

1-(4-(1-Cyclohexyl-1H-tetrazol-5-yl)butoxy)-2,2,6,6-tetramethylpiperidine (26)

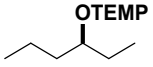
Prepared according to the general procedure A using 5-(4-chlorobutyl)-1-cyclohexyl-1H-tetrazole (72.6 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:60) to afford the product **26** as a colorless oil (88.3 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.20 – 4.10 (m, 1H), 3.79 (t, *J* = 6.1, 2H), 2.97 – 2.82 (m, 2H), 2.15 – 1.85 (m, 8H), 1.78 (d, *J* = 12.9, 1H), 1.70 – 1.62 (m, 2H), 1.60 – 1.30 (m, 9H), 1.14 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.8, 76.0, 59.7, 57.5, 39.6, 33.1, 32.9, 28.4, 25.3, 24.8, 24.7, 23.5, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{20}H_{38}ON_5$ $[M + H]^+$, 364.3071, found 364.3075.



27

1-(Heptan-2-yloxy)-2,2,6,6-tetramethylpiperidine (27)

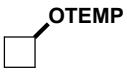
Prepared according to the general procedure A using 2-chloroheptane (40.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **27** as a colorless oil (62.0 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.80 – 3.70 (m, 1H), 1.66 – 1.32 (m, 6H), 1.32 – 1.16 (m, 8H), 1.09 – 0.99 (m, 15H), 0.82 (t, J = 7.0, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 78.4, 77.2, 60.0, 59.1, 40.3, 36.3, 34.4, 32.2, 25.6, 22.7, 20.4, 19.8, 17.4, 14.0; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{34}ON$ $[M + H]^+$, 256.2635, found 256.2636.



28

1-(Hexan-3-yloxy)-2,2,6,6-tetramethylpiperidine (28)

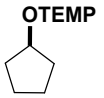
Prepared according to the general procedure A using 3-chlorohexane (36.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **28** as a colorless oil (68.7 mg, 95% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.72 – 3.65 (m, 1H), 1.81 – 1.71 (m, 1H), 1.69 – 1.61 (m, 1H), 1.52 – 1.28 (m, 10H), 1.12 (s, 12H), 0.92 (t, J = 7.2, 3H), 0.86 (t, J = 7.5, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 82.9, 40.4, 34.6, 25.3, 18.9, 17.4, 14.5, 9.9; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{32}ON$ $[M + H]^+$, 242.2478, found 242.2483.



29

1-Cyclobutoxy-2,2,6,6-tetramethylpiperidine (29)

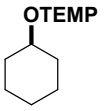
Prepared according to the general procedure A using chlorocyclobutane (27.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **29** as a colorless oil (47.5 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.23 – 4.07 (m, 1H), 2.34 – 2.23 (m, 2H), 1.92 (qd, J = 9.6, 2.9, 2H), 1.55 – 1.18 (m, 8H), 1.08 (s, 6H), 1.05 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 81.1, 58.7, 39.7, 33.3, 32.4, 20.1, 17.2, 11.1; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{26}ON$ $[M + H]^+$, 212.2009, found 212.2007.



30

1-(Cyclopentyloxy)-2,2,6,6-tetramethylpiperidine (30)

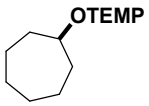
Prepared according to the general procedure A using chlorocyclopentane (31.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **30** as a colorless oil (61.5 mg, 91% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.26 – 4.20 (m, 1H), 1.98 – 1.86 (m, 2H), 1.70 – 1.50 (m, 4H), 1.49 – 1.27 (m, 8H), 1.18 (s, 6H), 1.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 88.2, 59.4, 40.2, 34.1, 32.7, 29.7, 23.4, 20.3, 17.3; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{28}ON$ $[M + H]^+$, 226.2165, found 226.2163.



31

1-(Cyclohexyloxy)-2,2,6,6-tetramethylpiperidine (31)

Prepared according to the general procedure A using chlorocyclohexane (35.4 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **31** as a colorless oil (63.1 mg, 88% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.55 – 3.48 (m, 1H), 1.97 (d, *J* = 7.7, 2H), 1.69 – 1.61 (m, 2H), 1.52 – 1.23 (m, 6H), 1.19 – 0.92 (m, 18H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 81.7, 59.6, 40.3, 34.5, 32.9, 26.0, 25.1, 20.3, 17.3; HR-ESI-MS (*m/z*): calcd. for $C_{15}H_{30}ON$ $[M + H]^+$, 240.2322, found 240.2325.

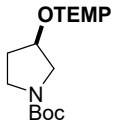


32

1-(Cycloheptyloxy)-2,2,6,6-tetramethylpiperidine (32)

Prepared according to the general procedure A using chlorocycloheptane (39.6 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **32** as a colorless oil (72.2 mg, 95% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.82 (tt, *J* = 8.5, 4.4, 1H), 2.09 – 1.98 (m, 2H), 1.69 – 1.39 (m, 13H), 1.39 – 1.28

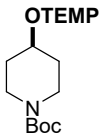
(m, 3H), 1.11 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 83.9, 59.7, 40.4, 34.4, 33.5, 28.6, 23.4, 20.4, 17.3; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{32}ON$ $[M + H]^+$, 254.2478, found 254.2478.



33

***tert*-Butyl 3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pyrrolidine-1-carboxylate (33)**

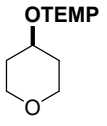
Prepared according to the general procedure A using tert-butyl 3-chloropyrrolidine-1-carboxylate (61.5 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **33** as a colorless oil (81.2 mg, 83% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.50 – 4.40 (m, 1H), 3.69 – 3.17 (m, 4H), 2.17 – 2.02 (m, 1H), 1.98 – 1.90 (m, 1H), 1.63 – 1.29 (m, 15H), 1.21 – 1.01 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.7, 83.6, 83.2, 79.0, 59.7, 50.4, 50.2, 44.2, 43.8, 40.2, 34.3, 33.5, 31.8, 31.1, 29.7, 28.5, 20.3, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{18}H_{35}O_3N_2$ $[M + H]^+$, 327.2642, found 327.2644.



34

***tert*-Butyl 4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)piperidine-1-carboxylate (34)**

Prepared according to the general procedure A using tert-butyl 4-chloropiperidine-1-carboxylate (65.7 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **34** as a colorless oil (84.7 mg, 83% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.95 (brs, 2H), 3.82 – 3.71 (m, 1H), 2.88 – 3.81 (m, 2H), 1.99 – 1.91 (m, 2H), 1.65 – 1.25 (m, 17H), 1.17 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.8, 79.6, 79.3, 59.7, 42.4, 40.2, 34.5, 31.9, 28.4, 20.2, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{37}O_3N_2$ $[M + H]^+$, 341.2799, found 341.2797.



35

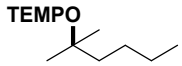
2,2,6,6-Tetramethyl-1-((tetrahydro-2H-pyran-4-yl)oxy)piperidine (35)

Prepared according to the general procedure A using 4-chlorotetrahydro-2*H*-pyran (36.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **35** as a colorless oil (62.2 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.92 – 3.86 (m, 2H), 3.80 – 3.69 (m, 1H), 3.29 (td, *J* =11.5, 1.9, 2H), 2.00 – 1.86 (m, 2H), 1.59 – 1.45 (m, 3H), 1.44 – 1.18 (m, 4H), 1.08 (s, 6H), 1.04 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 78.8, 66.8, 59.6, 40.2, 34.5, 33.4, 20.3, 17.3; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{37}O_3N_2$ $[M + H]^+$, 242.2115, found 242.2112.

36

1-(*tert*-Butoxy)-2,2,6,6-tetramethylpiperidine (36)

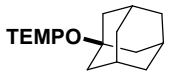
Prepared according to the general procedure A using 2-chloro-2-methylpropane (27.6 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **36** as a colorless oil (41.6 mg, 65% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.57 – 1.39 (m, 6H), 1.28 (s, 9H), 1.12 (s, 6H), 1.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 59.1, 40.9, 34.8, 29.4, 20.4, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{28}ON$ $[M + H]^+$, 214.2165, found 214.2165.



37

2,2,6,6-Tetramethyl-1-((2-methylhexan-2-yl)oxy)piperidine (37)

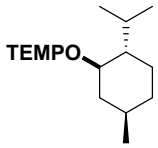
Prepared according to the general procedure A using 2-chloro-2-methylhexane (40.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **37** as a colorless oil (64.3 mg, 84% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.65 – 1.53 (m, 3H), 1.52 – 1.40 (m, 6H), 1.36 – 1.24 (m, 9H), 1.14 (s, 6H), 1.11 (s, 6H), 0.95 (t, *J* = 7.3, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 78.7, 59.1, 43.3, 40.9, 34.8, 26.9, 26.5, 23.5, 20.7, 17.2, 14.2; HR-ESI-MS (*m/z*): calcd. for $C_{16}H_{34}ON$ $[M + H]^+$, 256.2635, found 256.2631.



38

1-((Adamantan-1-yl)oxy)-2,2,6,6-tetramethylpiperidine (38)

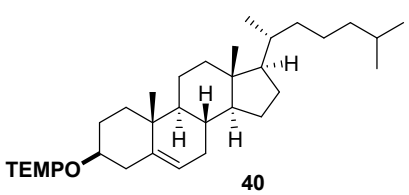
Prepared according to the general procedure A using 1-chloroadamantane (51.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **38** as a colorless oil (70.7 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.13 – 2.10 (m, 3H), 1.92 – 1.89 (m, 6H), 1.63 – 1.37 (m, 11H), 1.31 – 1.23 (m, 1H), 1.18 (s, 6H), 1.08 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 76.4, 59.1, 42.5, 41.0, 36.6, 35.5, 31.5, 20.6, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{34}ON$ $[M + H]^+$, 292.2635, found 292.2637.



39

1-(((*2S,5R*)-2-Isopropyl-5-methylcyclohexyl)oxy)-2,2,6,6-tetramethylpiperidine (39)

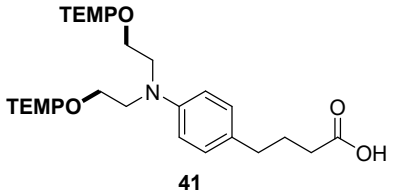
Prepared according to the general procedure A using menthyl chloride (52.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **39** as a colorless oil (73.5 mg, 83% yield, d.r. = 8.1:1). Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.58 (td, *J* = 10.7, 3.5, 1H), 2.43 (dd, *J* = 12.2, 2.1, 1H), 2.35 (dtd, *J* = 13.9, 6.9, 2.6, 1H), 1.66 – 1.36 (m, 7H), 1.29 – 1.19 (m, 3H), 1.17 – 1.13 (m, 6H), 1.10 – 0.96 (m, 7H), 0.97 – 0.74 (m, 11H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 80.6, 60.5, 58.5, 48.8, 40.7, 40.2, 40.0, 35.1, 34.4, 34.2, 31.7, 25.9, 23.8, 22.6, 21.0, 20.6, 17.5, 16.9; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{38}ON$ $[M + H]^+$, 296.2948, found 296.2947. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.23 – 4.20 (m, 1H), 2.38 – 2.32 (m, 1H), 2.03 (td, *J* = 13.2, 6.5, 1H), 1.87 (td, *J* = 11.0, 6.5, 1H), 1.76 – 1.69 (m, 1H), 1.53 – 1.37 (m, 8H), 1.24 – 1.11 (m, 14H), 0.98 – 0.81 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 78.8, 48.8, 41.4, 37.0, 34.7, 28.1, 27.2, 23.2, 23.1, 22.1, 20.7, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{38}ON$ $[M + H]^+$, 296.2948, found 296.2951.



40

1-(((*8S,9S,10R,13R,14S,17R*)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)oxy)-2,2,6,6-tetramethylpiperidine (40)

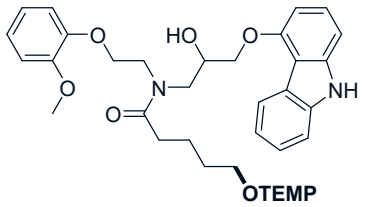
Prepared according to the general procedure A using cholesteryl chloride (121.3 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF:THF (1:1, 3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **40** as a colorless oil (126.1 mg, 80% yield, d.r. = 3.0:1). Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.33 (d, *J* = 4.9, 1H), 3.58 – 3.51 (m, 1H), 2.48 – 2.40 (m, 1H), 2.20 – 2.10 (m, 1H), 2.06 – 1.93 (m, 3H), 1.88 – 1.78 (m, 2H), 1.53 – 1.21 (m, 18H), 1.21 – 1.03 (m, 17H), 1.03 – 0.81 (m, 16H), 0.67 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.9, 121.0, 82.8, 56.8, 56.2, 50.2, 42.4, 40.3, 39.9, 39.5, 39.4, 37.8, 36.8, 36.2, 35.8, 32.0, 28.8, 28.2, 28.0, 24.3, 23.8, 22.8, 22.5, 21.1, 19.4, 18.7, 17.3, 11.9; HR-ESI-MS (*m/z*): calcd. for $C_{36}H_{64}ON$ [M + H]$^+$, 526.4982, found 526.4984. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.33 – 5.24 (m, 1H), 3.90 (brs, 1H), 2.43 (d, *J* = 14.7, 1H), 2.30 (d, *J* = 14.7, 1H), 2.05 – 1.94 (m, 3H), 1.86 – 1.79 (m, 1H), 1.61 – 1.41 (m, 14H), 1.39 – 1.25 (m, 6H), 1.22 – 1.02 (m, 22H), 0.97 – 0.83 (m, 10H), 0.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.0, 121.2, 79.0, 59.7, 56.9, 56.3, 50.2, 42.4, 40.4, 39.9, 39.5, 37.3, 37.0, 36.2, 35.8, 33.9, 31.9, 28.3, 28.0, 26.8, 24.3, 23.9, 22.8, 22.6, 20.8, 19.3, 18.7, 17.2, 11.9; HR-ESI-MS (*m/z*): calcd. for $C_{36}H_{64}ON$ [M + H]$^+$, 526.4982, found 526.4981.



41

4-(4-(Bis(2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)amino)phenyl)butanoic acid (41)

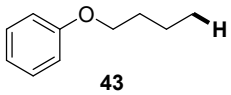
Prepared according to the general procedure A using chlorambucil (90.9 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (293.3 mg, 0.90 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 12 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **41** as a colorless oil (111.3 mg, 68% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.98 (d, *J* = 8.5, 2H), 6.64 (d, *J* = 8.5, 2H), 3.94 (t, *J* = 6.0, 4H), 3.52 (t, *J* = 6.0, 4H), 2.54 (t, *J* = 7.5, 2H), 2.33 (t, *J* = 7.5, 2H), 1.98 – 1.85 (m, 2H), 1.61 – 1.28 (m, 12H), 1.11 (s, 12H), 1.08 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.7, 129.0, 128.1, 111.9, 75.0, 59.7, 49.7, 39.6, 34.0, 33.5, 33.0, 26.8, 20.2, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{32}H_{56}O_4N_3$ [M + H]$^+$, 546.4265, found 546.4265.



42

***N*-(3-((9*H*-Carbazol-4-yl)oxy)-2-hydroxypropyl)-*N*-(2-(2-methoxyphenoxy)ethyl)-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentanamide (42)**

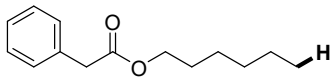
Prepared according to the general procedure A using N-(3-((9H-carbazol-4-yl)oxy)-2-hydroxypropyl)-5-chloro-N-(2-(2-methoxyphenoxy)ethyl)pentanamide (157.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 12 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **42** as a colorless oil (158.6 mg, 82% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 – 8.20 (m, 2H), 7.42 – 7.27 (m, 3H), 7.23 – 7.17 (m, 1H), 7.10 – 7.01 (m, 1H), 6.96 – 6.88 (m, 2H), 6.88 – 6.62 (m, 3H), 4.90 (d, *J* = 3.9, 0.54H), 4.62 (s, 44H), 4.43 (s, 56H), 4.40 – 4.18 (m, 2.46H), 4.18 – 3.97 (m, 2H), 3.95 – 3.91 (m, 1H), 3.86 – 3.69 (m, 6H), 3.65 (t, *J* = 6.5, 1H), 2.64 – 2.60 (m, 1H), 2.52 – 2.45 (m, 1H), 1.85 – 1.72 (m, 2H), 1.72 – 1.64 (m, 2H), 1.64 – 1.27 (m, 6H), 1.20 – 0.98 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 176.9, 174.4, 155.0, 154.8, 149.7, 148.9, 147.9, 147.8, 141.1, 141.0, 138.8, 126.8, 126.7, 125.1, 125.0, 122.8, 122.7, 122.5, 122.0, 121.5, 121.1, 120.8, 119.7, 119.6, 113.8, 113.1, 112.7, 112.6, 111.9, 111.4, 110.2, 104.1, 104.0, 101.4, 101.1, 76.6, 70.6, 69.8, 69.3, 68.6, 66.8, 59.7, 59.6, 55.7, 55.6, 54.1, 51.8, 49.4, 48.4, 39.6, 33.8, 33.4, 33.1, 28.7, 28.5, 22.4, 22.2, 20.2, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{38}H_{52}O_6N_3$ $[M + H]^+$, 646.3851, found 646.3854.



43

Butoxybenzene (43)

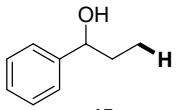
Prepared according to the general procedure B using (4-chlorobutoxy)benzene (55.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **43** as a colorless oil (36.0 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 – 7.26 (m, 2H), 7.03 – 6.80 (m, 3H), 3.96 (t, *J* = 6.5, 2H), 1.89 – 1.73 (m, 2H), 1.52 – 1.48 (m, 2H), 0.98 (t, *J* = 7.4, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.2, 129.4, 120.4, 114.5, 67.6, 31.4, 19.3, 13.9; HR-ESI-MS (*m/z*): calcd. for $C_{10}H_{15}O$ $[M + H]^+$, 151.1116, found 151.1117.



44

Hexyl 2-phenylacetate (44)

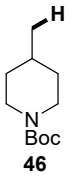
Prepared according to the general procedure B using 6-chlorohexyl 2-phenylacetate (76.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **44** as a colorless oil (56.1 mg, 85% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50 – 7.03 (m, 5H), 4.08 (t, *J* = 6.7, 2H), 3.61 (s, 2H), 1.74 – 1.52 (m, 2H), 1.43 – 1.16 (m, 6H), 0.87 (t, *J* = 6.9, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.7, 134.2, 129.2, 128.5, 127.0, 65.0, 41.5, 31.4, 28.5, 25.5, 22.5, 13.9; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{20}O_2Na$ $[M + Na]^+$, 243.1356, found 243.1356.



45

1-Phenylpropan-1-ol (45)

Prepared according to the general procedure B using 3-chloro-1-phenylpropan-1-ol (51.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:30) to afford the product **45** as a colorless oil (27.4 mg, 67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.41 – 7.25 (m, 5H), 4.60 (t, *J* = 6.5, 1H), 1.87 (s, 1H), 1.85 – 1.70 (m, 2H), 0.92 (t, *J* = 7.4, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 128.4, 127.5, 126.0, 76.0, 31.9, 10.1; HR-ESI-MS (*m/z*): calcd. for $C_9H_{12}ONa$ $[M + Na]^+$, 159.0780, found 159.0780.

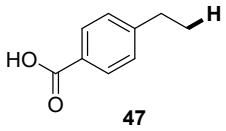


46

***tert*-Butyl 4-methylpiperidine-1-carboxylate (46)**

Prepared according to the general procedure B using tert-butyl 4-(chloromethyl)piperidine-1-carboxylate (69.9 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:50) to afford the product **46** as a colorless oil (55.5 mg, 93% yield). The product gives two sets of NMR signals,

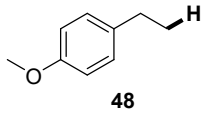
owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.05 (brs, 2H), 2.68 (brs, 2H), 1.61 – 1.58 (m, 2H), 1.54 – 1.41 (m, 10H), 1.12 – 1.06 (m, 2H), 0.93 (d, *J* = 6.6, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.9, 79.1, 44.0, 34.0, 31.0, 28.5, 21.8; HR-ESI-MS (*m/z*): calcd. for $C_{11}H_{21}O_2NNa$ $[M + Na]^+$, 222.1465, found 222.1466.



47

4-Ethylbenzoic acid (47)

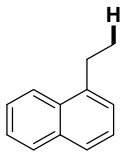
Prepared according to the general procedure B using 4-(2-chloroethyl)benzoic acid (55.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (293.3 mg, 0.90 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **47** as a colorless oil (35.1 mg, 78% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.1, 2H), 7.30 (d, *J* = 8.1, 2H), 2.73 (q, *J* = 7.6, 2H), 1.27 (t, *J* = 7.6, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 150.7, 130.4, 128.0, 126.8, 29.0, 15.2; HR-ESI-MS (*m/z*): calcd. for $C_9H_9O_2$ $[M - H]^-$, 149.0608, found 149.0609.



48

1-Ethyl-4-methoxybenzene (48)

Prepared according to the general procedure B using 1-(2-chloroethyl)-4-methoxybenzene (51.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **48** as a colorless oil (33.9 mg, 83% yield). Spectra are consistent with reported literature values.[9] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.6, 2H), 6.84 (d, *J* = 8.6, 2H), 3.79 (s, 3H), 2.59 (q, *J* = 7.6, 2H), 1.21 (t, *J* = 7.6, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 157.6, 136.4, 128.7, 113.8, 55.3, 28.0, 15.9.

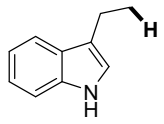


49

1-Ethylnaphthalene (49)

Prepared according to the general procedure B using 1-(2-chloroethyl)naphthalene (57.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90

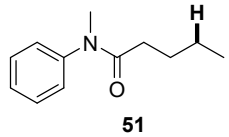
mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **49** as a colorless oil (39.8 mg, 85% yield). Spectra are consistent with reported literature values.[7] ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4, 1H), 7.74 (d, *J* = 8.2, 1H), 7.59 (d, *J* = 8.2, 1H), 7.45 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.23 (d, *J* = 6.9, 1H), 3.00 (q, *J* = 7.5, 2H), 1.28 (t, *J* = 7.5, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 140.3, 133.9, 131.9, 128.8, 126.5, 125.7, 125.5, 124.9, 123.8, 26.0, 15.1.



50

3-Ethyl-1*H*-indole (50)

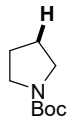
Prepared according to the general procedure B using 3-(2-chloroethyl)-1H-indole (53.7 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:100) to afford the product **50** as a colorless oil (39.2 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.61 (d, *J* = 7.9, 1H), 7.31 (d, *J* = 8.1, 1H), 7.18 (t, *J* = 7.5, 1H), 7.11 (t, *J* = 7.4, 1H), 6.93 (s, 1H), 2.78 (q, *J* = 7.5, 2H), 1.33 (t, *J* = 7.5, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 136.5, 127.5, 121.9, 120.5, 119.1, 119.0, 118.9, 111.1, 18.4, 14.5; HR-ESI-MS (*m/z*): calcd. for $C_{10}H_{12}N$ $[M + H]^+$, 146.0964, found 146.0962.



51

***N*-Methyl-*N*-phenylpentanamide (51)**

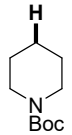
Prepared according to the general procedure B using 4-chloro-N-methyl-N-phenylpentanamide (67.5 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:50) to afford the product **51** as a colorless oil (55.0 mg, 96% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.6, 2H), 7.34 (t, *J* = 7.3, 1H), 7.18 (d, *J* = 7.6, 2H), 3.26 (s, 3H), 2.07 (t, *J* = 7.3, 2H), 1.59 – 1.49 (m, 2H), 1.24 – 1.18 (m, 2H), 0.80 (t, *J* = 7.2, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.3, 144.4, 129.7, 127.6, 127.3, 37.3, 33.8, 27.7, 22.4, 13.7; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{18}NO$ $[M + H]^+$, 192.1383, found 192.1386.



52

***tert*-Butyl pyrrolidine-1-carboxylate (52)**

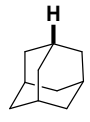
Prepared according to the general procedure B using tert-butyl (R)-3-chloropyrrolidine-1-carboxylate (61.5 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:100) to afford the product **52** as a colorless oil (43.6 mg, 85% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.39 – 3.21 (m, 4H), 1.83 (brs, 4H), 1.50 – 1.45 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.7, 78.8, 45.9, 45.6, 34.0, 28.5, 28.5, 26.0, 25.7, 25.0; HR-ESI-MS (*m/z*): calcd. for $C_9H_{17}O_2NNa$ $[M + Na]^+$, 194.1151, found 194.1152.



53

***tert*-Butyl piperidine-1-carboxylate (53)**

Prepared according to the general procedure B using tert-butyl 4-chloropiperidine-1-carboxylate (65.7 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:100) to afford the product **53** as a colorless oil (48.9 mg, 88% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.43 – 3.30 (m, 4H), 1.61 – 1.55 (m, 2H), 1.52 – 1.48 (m, 4H), 1.45 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 155.0, 79.1, 28.5, 25.7, 24.5; HR-ESI-MS (*m/z*): calcd. for $C_{10}H_{19}O_2NNa$ $[M + Na]^+$, 208.1308, found 208.1312.

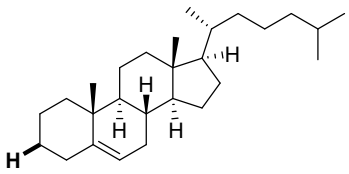


54

Adamantane (54)

Prepared according to the general procedure B using 1-chloroadamantane (51.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was

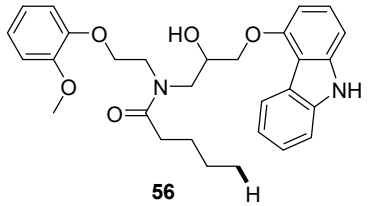
purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **54** as a colorless oil (32.6 mg, 80% yield). Spectra are consistent with reported literature values.[8] ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.87 (s, 4H), 1.75 (s, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 37.8, 28.7.7.



55

(*8S,9S,10R,13R,14S,17R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthrene (55)

Prepared according to the general procedure B using cholesteryl chloride (121.3 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF:THF (1:1, ZZ3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **55** as a colorless oil (99.9 mg, 90% yield). Spectra are consistent with reported literature values.[6] ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.29 – 5.24 (m, 1H), 2.26 – 2.20 (m, 1H), 2.05 – 1.89 (m, 3H), 1.87 – 1.77 (m, 2H), 1.78 – 1.67 (m, 1H), 1.62 – 1.29 (m, 9H), 1.29 – 0.79 (m, 26H), 0.67 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 143.7, 119.0, 56.9, 56.2, 50.6, 42.3, 39.9, 39.6, 37.5, 36.2, 35.8, 32.9, 31.9, 31.2, 28.3, 28.1, 28.0, 24.3, 23.9, 22.8, 22.6, 20.8, 19.5, 18.7, 11.9.

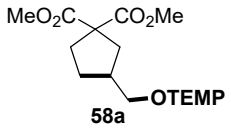


56

***N*-(3-((9*H*-Carbazol-4-yl)oxy)-2-hydroxypropyl)-*N*-(2-(2-methoxyphenoxy)ethyl)pentanamide (56)**

Prepared according to the general procedure B using N-(3-((9H-carbazol-4-yl)oxy)-2-hydroxypropyl)-5-chloro-N-(2-(2-methoxyphenoxy)ethyl)pentanamide (157.3 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:5) to afford the product **56** as a colorless oil (117.6 mg, 80% yield). The product gives two sets of NMR signals, owing to the presence of rotamers around the amide. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.28 – 8.20 (m, 1H), 7.40 – 7.26 (m, 3H), 7.20 – 7.10 (m, 1H), 7.03 (t, *J* = 8.8, 1H), 6.96 – 6.61 (m, 5H), 4.61 (d, *J* = 4.9, 0.49H), 4.48 – 4.40 (m, 0.51H), 4.40 – 4.19 (m, 2.49H), 4.15 – 3.96 (m, 2.51H), 3.95 – 3.87 (m, 1H), 3.83 – 3.66 (m, 7H), 2.60 – 2.40 (m, 2H), 1.73 – 1.52 (m, 2H), 1.42 – 1.15 (m, 2H), 0.93 (t, *J* = 7.4, 1.59H), 0.80 (t, *J* = 7.4, 1.41H); ^{13}C NMR

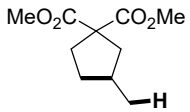
(150 MHz, $CDCl_3$): δ 177.2, 174.7, 155.0, 154.8, 149.7, 148.9, 147.8, 141.1, 141.0, 138.8, 126.8, 126.7, 125.1, 125.0, 122.8, 122.6, 122.4, 122.1, 121.5, 121.1, 120.8, 119.6, 113.9, 113.1, 112.6, 112.0, 111.4, 110.2, 110.2, 104.1, 104.0, 101.3, 101.1, 70.6, 69.8, 69.3, 68.5, 66.8, 55.7, 55.6, 54.1, 51.8, 49.4, 48.3, 33.5, 33.0, 27.4, 27.3, 22.6, 22.4, 14.0, 13.9; HR-ESI-MS (*m/z*): calcd. for $C_{29}H_{35}O_5N_2$ $[M + H]^+$, 491.2540, found 491.2549.



58a

Dimethyl 3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)cyclopentane-1,1 -dicarboxylate (58a)

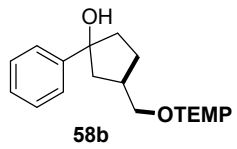
Prepared according to the general procedure A using dimethyl 2-allyl-2-(2-chloroethyl)malonate (70.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:100) to afford the product **58a** as a colorless oil (86.3 mg, 81% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.65 (s, 3H), 3.61 (d, *J* = 6.5, 2H), 2.40 (dd, *J* = 13.5, 7.9, 1H), 2.31 – 2.18 (m, 2H), 2.09 (dt, *J* = 13.4, 8.0, 1H), 1.86 (dd, *J* = 13.5, 9.5, 1H), 1.79 (dt, *J* = 7.4, 2.3, 1H), 1.53 – 1.21 (m, 7H), 1.05 (dd, *J*=22.6, 10.0, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.0, 172.9, 79.4, 60.2, 59.8, 52.6, 39.6, 38.7, 37.6, 34.0, 33.1, 29.0, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{19}H_{34}O_5N$ $[M + H]^+$, 356.2431, found 356.2435.



59a

Dimethyl 3-methylcyclopentane-1,1-dicarboxylate (59a)

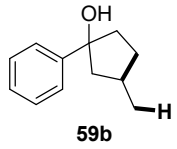
Prepared according to the general procedure B using dimethyl 2-allyl-2-(2-chloroethyl)malonate (70.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:100) to afford the product **59a** as a colorless oil (49.8 mg, 83% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.72 (s, 6H), 2.46 (dd, *J* = 13.3, 7.1, 1H), 2.33 (ddd, *J* = 12.7, 8.5, 3.8, 1H), 2.15 (ddd, *J* = 13.6, 9.1, 7.9, 1H), 2.04 (tdd, *J* = 13.5, 8.3, 5.0, 1H), 1.86 (ddd, *J* = 11.7, 7.4, 4.2, 1H), 1.67 (dd, *J* = 13.3, 10.2, 1H), 1.25 (dq, *J* = 12.4, 9.4, 1H), 1.01 (d, *J* = 6.6, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.3, 60.3, 52.6, 42.7, 34.4, 34.2, 34.1, 19.5; HR-ESI-MS (*m/z*): calcd. for $C_{10}H_{17}O_4$ $[M + H]^+$, 201.1121, found 201.1123.



58b

1-Phenyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)cyclopentan-1-ol (58b)

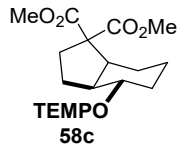
Prepared according to the general procedure A using 1-chloro-3-phenylhex-5-en-3-ol (63.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:50) to afford the product **58b** as a colorless oil (79.5 mg, 80% yield, d.r. > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.7, 2H), 7.34 (t, *J* = 7.3, 2H), 7.28 – 7.22 (m, 1H), 3.77 (dt, *J* = 14.9, 8.2, 2H), 2.72 – 2.62 (m, 1H), 2.20 – 2.12 (m, 3H), 2.06 – 1.96 (m, 1H), 1.86 (dd, *J* = 13.3, 10.2, 1H), 1.74 – 1.26 (m, 7H), 1.22 – 1.06 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.8, 128.3, 128.0, 126.9, 125.0, 83.7, 80.3, 59.9, 45.7, 41.0, 39.7, 37.3, 33.2, 27.4, 20.2, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{21}H_{34}O_2N$ $[M + H]^+$, 332.2584, found 332.2582.



59b

3-Methyl-1-phenylcyclopentan-1-ol (59b)

Prepared according to the general procedure B using 1-chloro-3-phenylhex-5-en-3-ol (63.0 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:50) to afford the product **59b** as a colorless oil (39.6 mg, 75% yield, d.r. > 20:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.3, 2H), 7.34 (t, *J* = 7.7, 1H), 7.26 – 7.22 (m, 1H), 2.49 (ddt, *J* = 14.4, 10.3, 7.3, 1H), 2.22 – 2.14 (m, 2H), 2.11 (ddd, *J* = 13.2, 6.6, 1.6, 1H), 1.98 (tdd, *J* = 9.2, 6.4, 2.9, 1H), 1.65 – 1.60 (m, 1H), 1.44 – 1.37 (m, 1H), 1.09 (d, *J* = 6.7, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.3, 128.2, 126.8, 125.0, 84.0, 51.0, 41.5, 32.8, 32.6, 20.9; HR-ESI-MS (*m/z*): calcd. for $C_{12}H_{17}O$ $[M + H]^+$, 177.1274, found 177.1274.

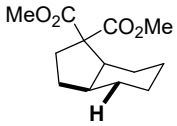


58c

Dimethyl 4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)octahydro-1*H*-indene-1,1- dicarboxylate (58c)

Prepared according to the general procedure A using dimethyl 2-(2-chloroethyl)-2-(cyclohex-2-en-1-yl)malonate (82.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude

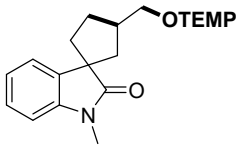
mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **58c** as a colorless oil (104.3 mg, 88% yield, d.r. = 6.2:1). Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.81 (d, *J* = 2.5, 1H), 3.70 (s, 3H), 3.69 (s, 3H), 2.91 – 2.81 (m, 1H), 2.72 – 2.61 (m, 2H), 2.12 – 2.03 (m, 1H), 1.90 – 1.84 (m, 1H), 1.73 – 1.65 (m, 1H), 1.65 – 1.52 (m, 3H), 1.49 – 1.31 (m, 7H), 1.19 – 0.99 (m, 13H), 1.09 – 0.98 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.0, 171.1, 64.9, 59.7, 52.5, 52.2, 43.0, 42.4, 40.4, 34.2, 29.7, 25.8, 25.6, 23.4, 20.2, 19.6, 17.2; HR-ESI-MS (*m/z*): calcd. for $C_{22}H_{38}O_5N$ $[M + H]^+$, 396.2744, found 396.2745. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.98 – 3.91 (m, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 2.72 (ddd, *J* = 14.7, 10.8, 3.9, 1H), 2.68 – 2.59 (m, 2H), 2.12 – 2.01 (m, 2H), 1.79 – 1.68 (m, 3H), 1.57 – 1.25 (m, 7H), 1.19 – 0.99 (m, 14H), 0.91 (dt, *J* = 12.4, 11.0, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.1, 170.9, 81.3, 64.1, 52.5, 52.2, 46.0, 43.1, 40.3, 30.0, 26.9, 23.7, 23.2, 21.6, 20.2, 17.3; HR-ESI-MS (*m/z*): calcd. for $C_{22}H_{38}O_5N$ $[M + H]^+$, 396.2744, found 396.2742.



59c

Dimethyl octahydro-1*H*-indene-1,1-dicarboxylate (59c)

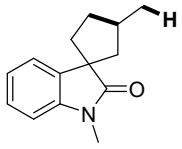
Prepared according to the general procedure B dimethyl 2-(2-chloroethyl)-2-(cyclohex-2-en-1-yl)malonate (82.2 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:200) to afford the product **59c** as a colorless oil (64.8 mg, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.70 (s, 3H), 3.69 (s, 3H), 2.70 (ddd, *J* = 14.8, 11.1, 3.8, 1H), 2.61 – 2.50 (m, 1H), 2.31 (ddd, *J* = 12.1, 7.9, 4.3, 1H), 2.04 (ddd, *J* = 14.8, 9.3, 7.5, 1H), 1.80 – 1.70 (m, 1H), 1.70 – 1.63 (m, 1H), 1.63 – 1.51 (m, 3H), 1.49 – 1.41 (m, 1H), 1.36 – 1.13 (m, 3H), 1.03 (qd, *J* = 12.7, 3.3, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 173.3, 171.1, 64.8, 52.5, 52.2, 44.8, 38.3, 30.5, 26.2, 25.5, 25.2, 23.5, 20.4; HR-ESI-MS (*m/z*): calcd. for $C_{13}H_{20}O_4Na$ $[M + Na]^+$, 263.1254, found 263.1257.



58d

1'-Methyl-3-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)spiro[cyclopentane-1,3'-indolin]-2'-one (58d)

Prepared according to the general procedure A using 3-allyl-3-(2-chloroethyl)-1-methylindolin-2-one (74.7 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), TEMPOH (56.6 mg, 0.36 mmol), and DMF (3.0 mL). Time of irradiation: 6 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:50) to afford the product **58d** as a colorless oil (92.2 mg, 83% yield, d.r. = 1.5:1). Major diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ7.32 – 7.20 (m, 2H), 7.06 (t, *J* = 7.5, 1H), 6.82 (d, *J* = 7.7, 1H), 3.92 – 3.85 (m, 1H), 3.85 – 3.77 (m, 1H), 3.21 (s, 3H), 2.62 (dt, *J* = 16.0, 8.0, 1H), 2.23 (dt, *J* = 12.8, 6.1, 1H), 2.14 (dd, *J* = 13.7, 6.1, 1H), 2.02 – 1.92 (m, 2H), 1.91 – 1.80 (m, 2H), 1.57 – 1.29 (m, 6H), 1.19 – 1.05 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 181.4, 142.8, 137.0, 127.4, 122.5, 122.4, 107.7, 80.1, 59.8, 54.1, 42.0, 40.3, 39.7, 37.3, 33.2, 29.9, 26.3, 20.1, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{35}O_2N_2$ $[M + H]^+$, 371.2693, found 371.2695. Minor diastereoisomer: ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.20 (m, 2H), 7.05 (t, *J* = 7.5, 1H), 6.81 (d, *J* = 7.7, 1H), 3.84 (dt, *J* = 14.6, 8.4, 2H), 3.21 (s, 3H), 2.81 – 2.65 (m, 1H), 2.29 (dd, *J* = 13.3, 8.1, 1H), 2.25 – 2.11 (m, 2H), 1.95 – 1.88 (m, 1H), 1.85 – 1.81 (m, 1H), 1.76 (dd, *J* = 13.3, 9.8, 1H), 1.68 – 1.42 (m, 4H), 1.38 – 1.21 (m, 2H), 1.17 (s, 6H), 1.12 (s 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 182.1, 143.1, 136.6, 127.4, 122.6, 122.3, 107.6, 79.3, 59.9, 53.7, 41.3, 40.1, 39.7, 38.1, 33.2, 30.5, 26.2, 20.2, 17.1; HR-ESI-MS (*m/z*): calcd. for $C_{23}H_{35}O_2N_2$ $[M + H]^+$, 371.2693, found 371.2692.



59d

1',3-Dimethylspiro[cyclopentane-1,3'-indolin]-2'-one (59d)

Prepared according to the general procedure B using 3-allyl-3-(2-chloroethyl)-1-methylindolin-2-one (74.7 mg, 0.30 mmol), **DBPP1** (8.5 mg, 0.03 mmol, 10 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol), HCOOCs (160.2 mg, 0.90 mmol), CySH (7.0 mg, 0.06 mmol, 20 mol%) and DMF (3.0 mL). Time of irradiation: 4 hours. The crude mixture was purified by silica gel chromatography (acetone/petroleum ether 1:50) to afford the product **59d** as a colorless oil (56.8 mg, 88% yield). The product gives two sets of NMR signals, owing to the presence of diastereoisomers (1.5:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.19 (m, 2H), 7.09 – 7.00 (m, 1H), 6.84 – 6.78 (m, 1H), 3.20 (s, 1.2H), 3.19 (s, 1.8H), 2.60 – 2.40 (m, 1H), 2.29 – 2.19 (m, 1H), 2.15 – 2.05 (m, 1H), 1.98 – 1.89 (m, 1H), 1.89 – 1.76 (m, 1H), 1.71 – 1.63 (m, 1H), 1.59 – 1.42 (m, 1H), 1.16 (d, *J* = 6.5, 1.2H), 1.13 (d, *J* = 6.6, 1.8H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 182.4, 181.9, 143.0, 142.8, 137.5, 137.0, 127.3, 122.6, 122.5, 122.3, 122.2, 107.7, 107.6, 54.4, 54.0, 46.7, 46.6, 38.3, 37.9, 36.0, 35.4, 35.1, 26.3, 26.2, 19.7; HR-ESI-MS (*m/z*): calcd. for $C_{14}H_{18}ON$ $[M + H]^+$, 216.1383, found 216.1386.

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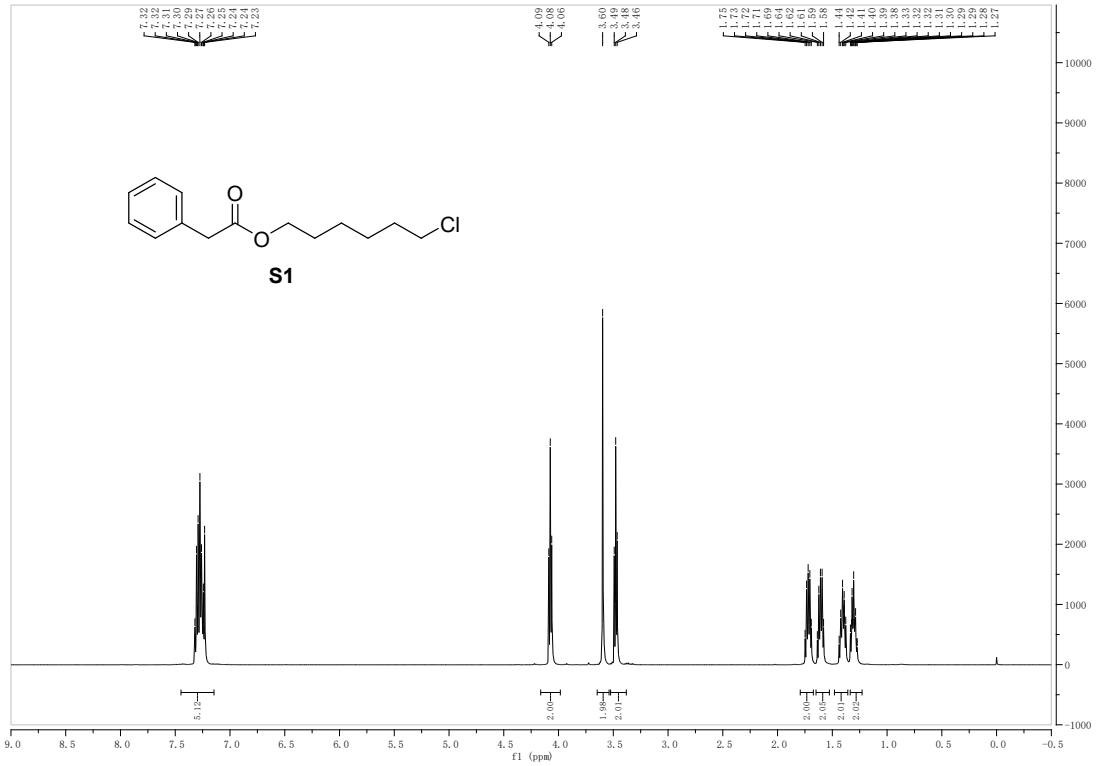
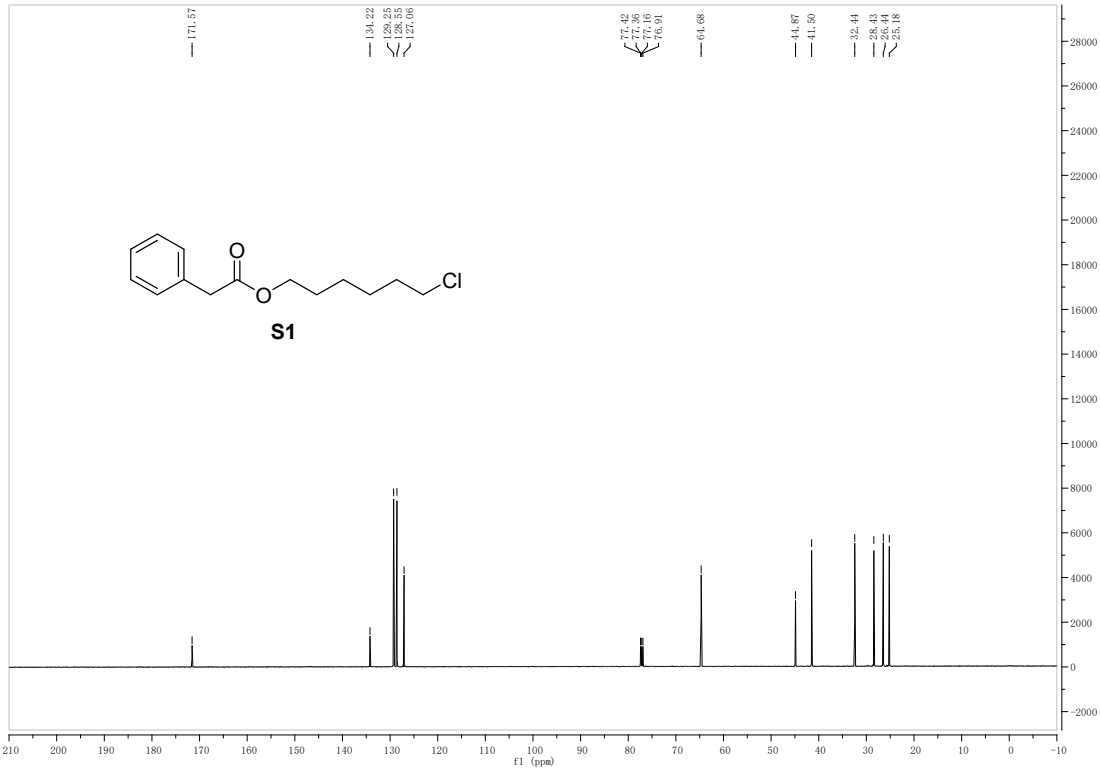
NMR Spectral Data



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2.10
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O
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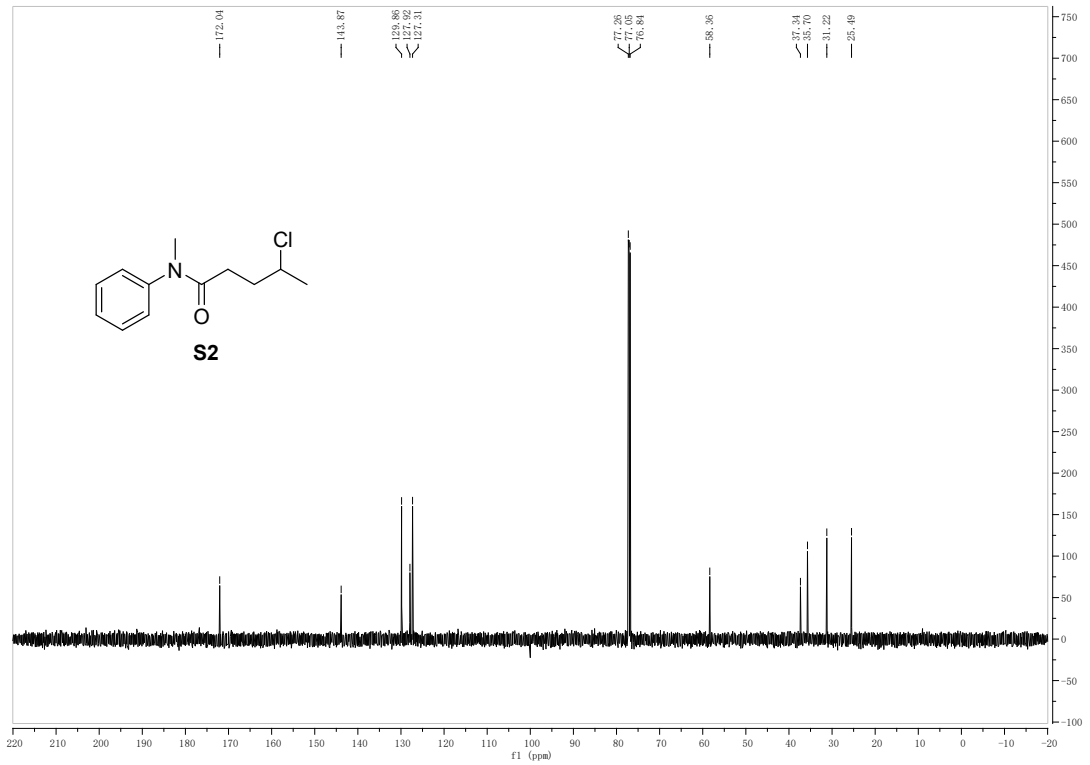
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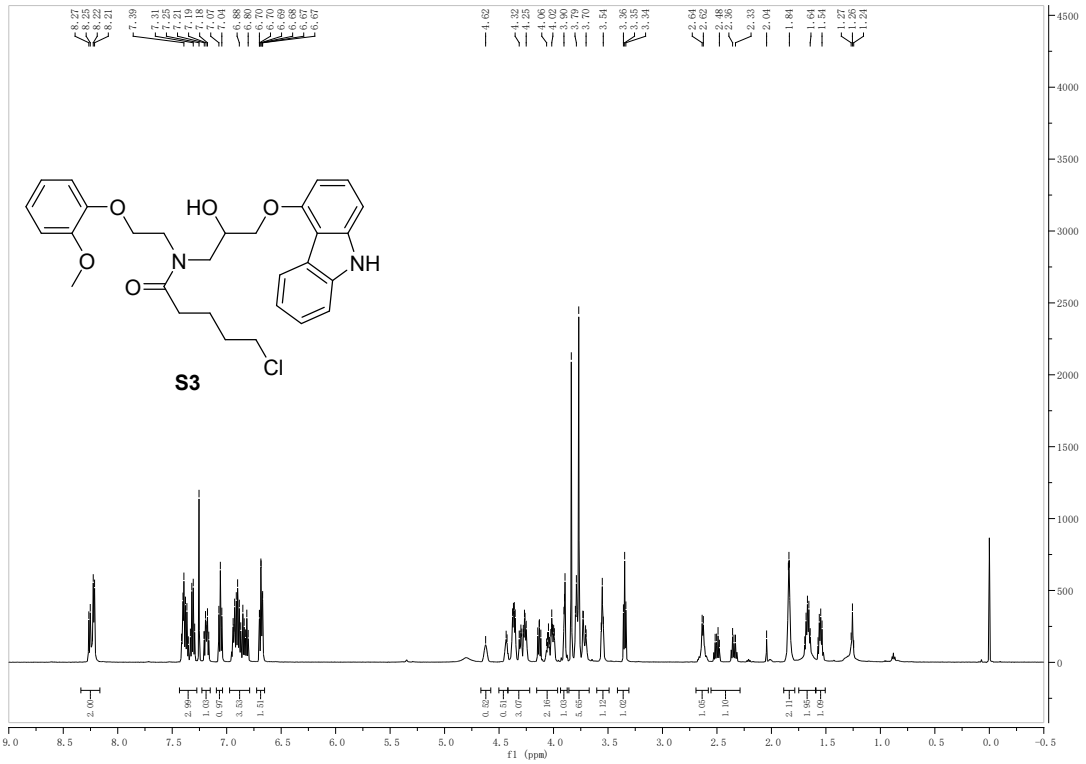
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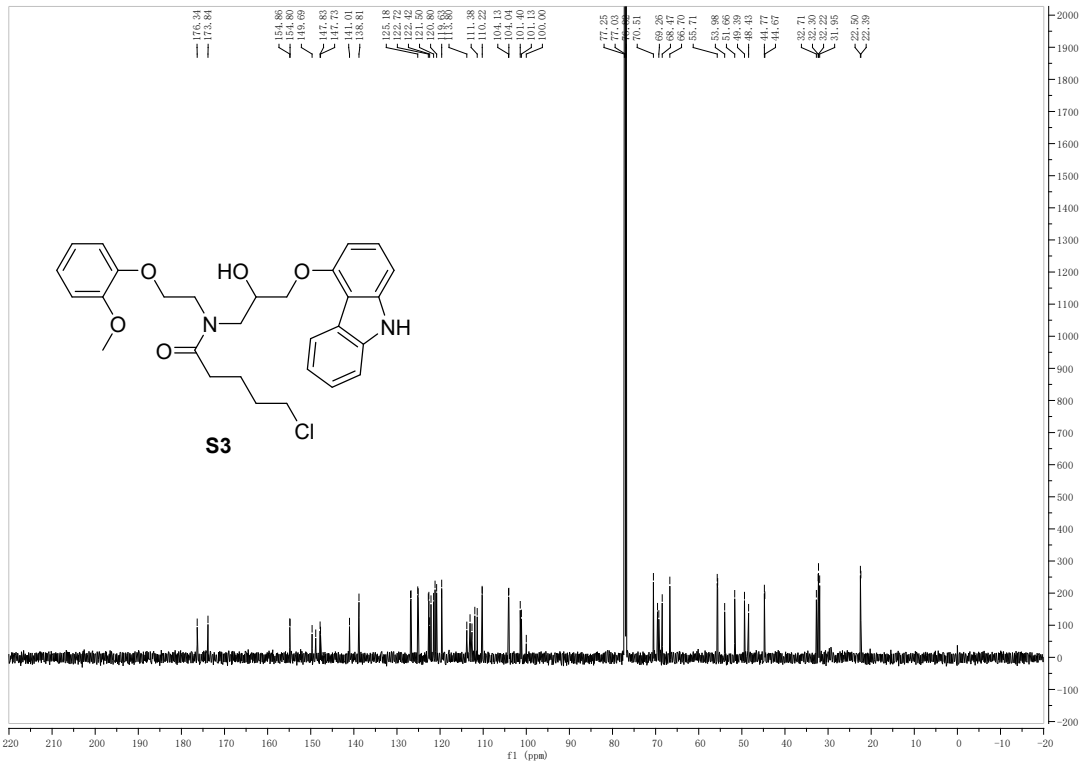
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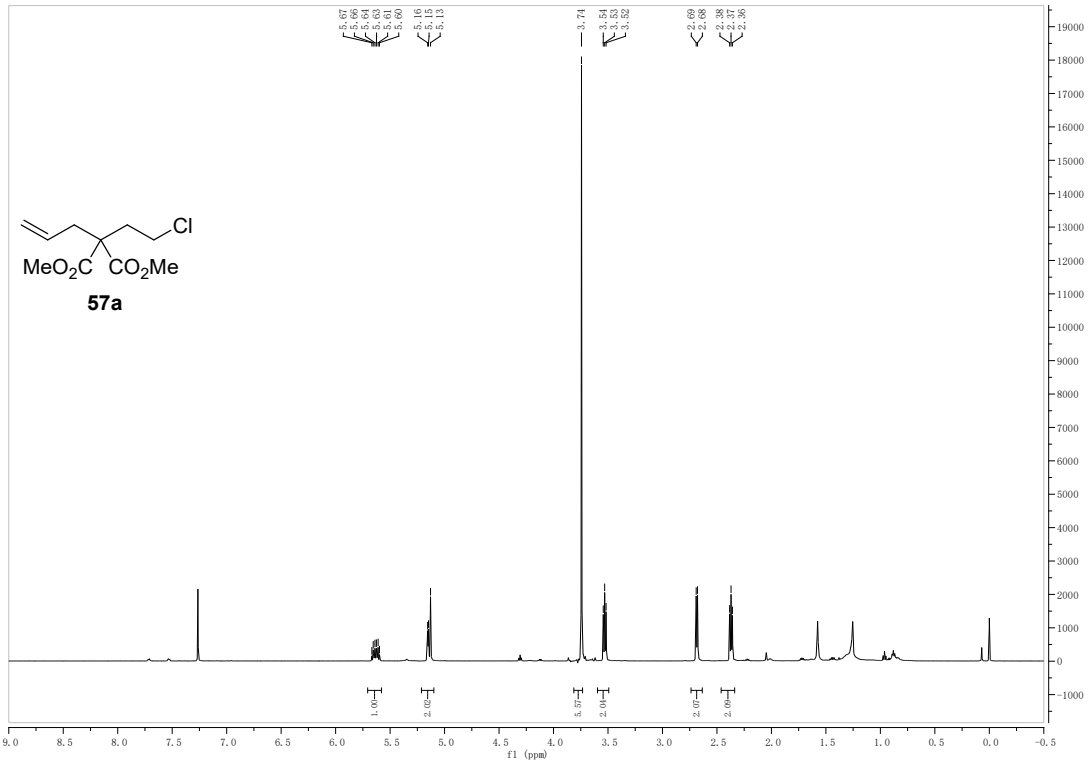
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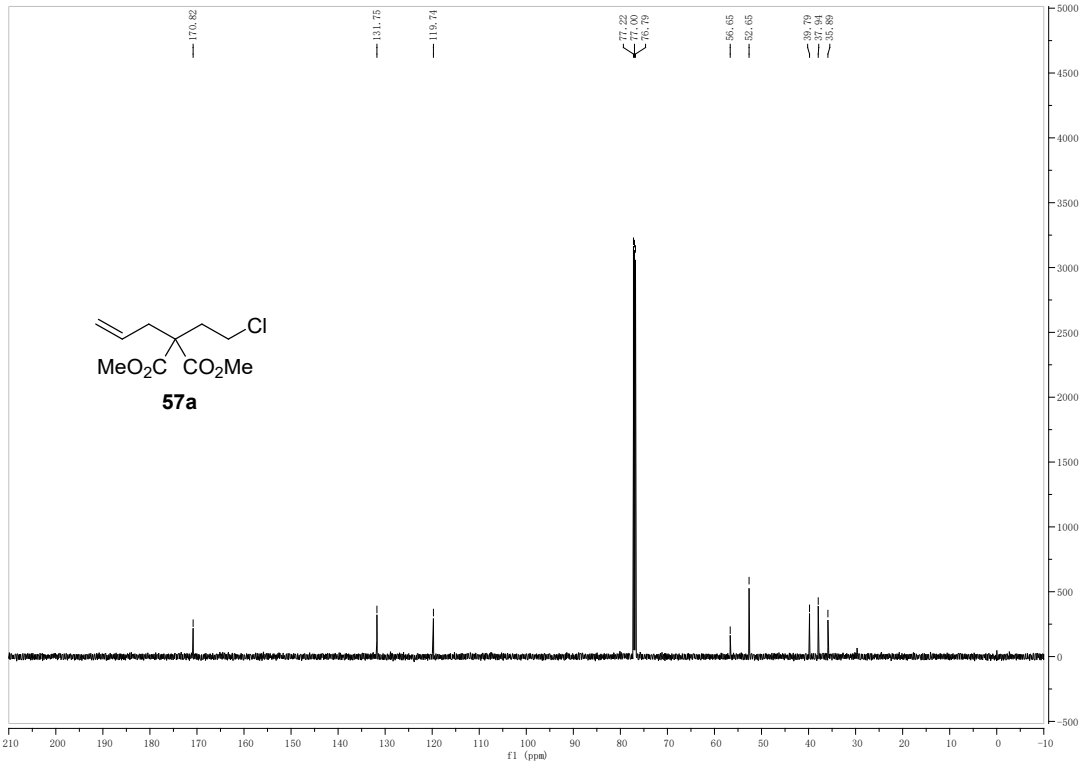
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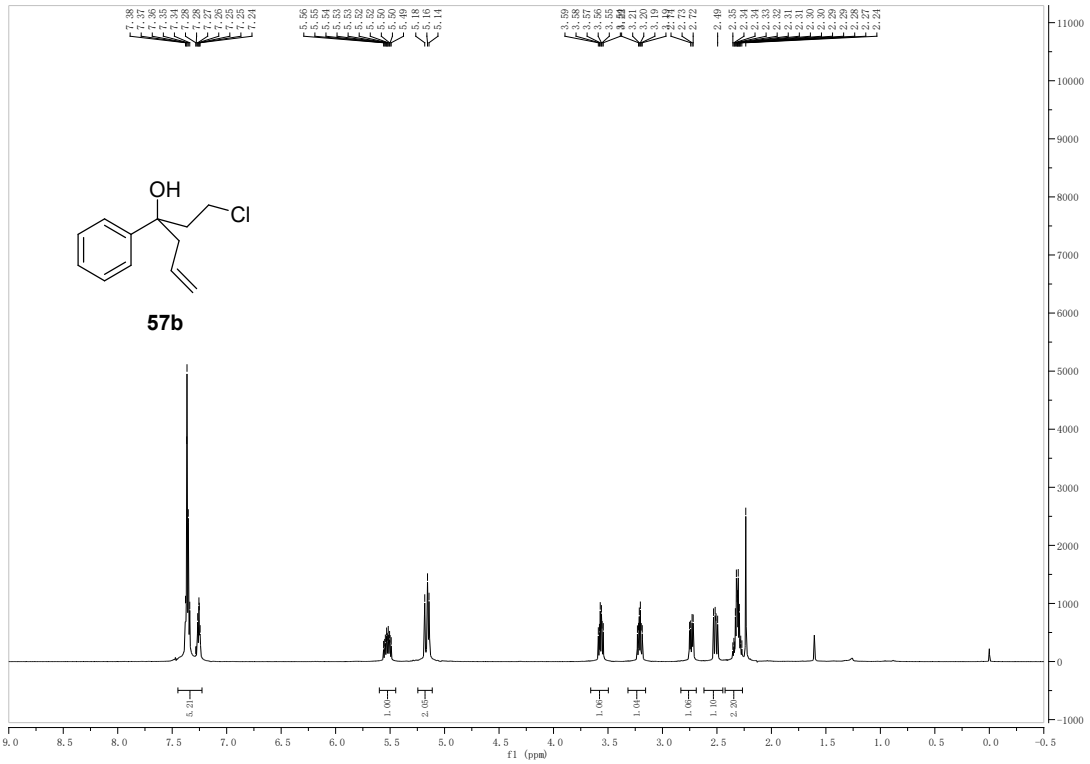
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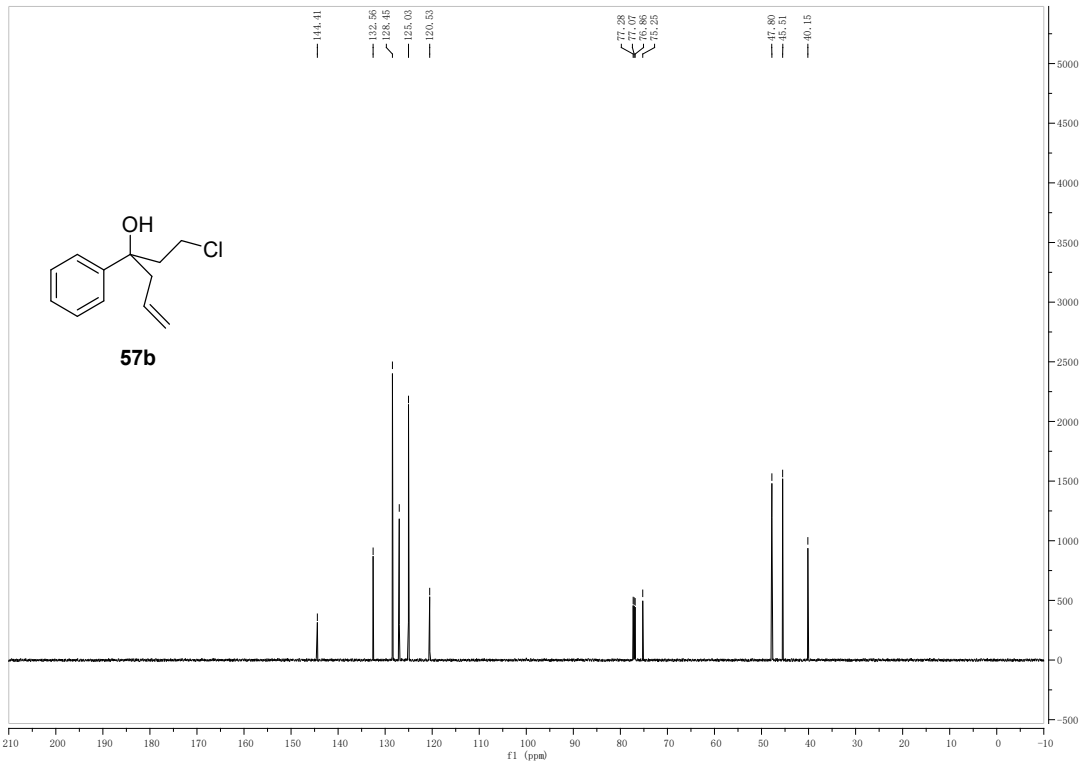
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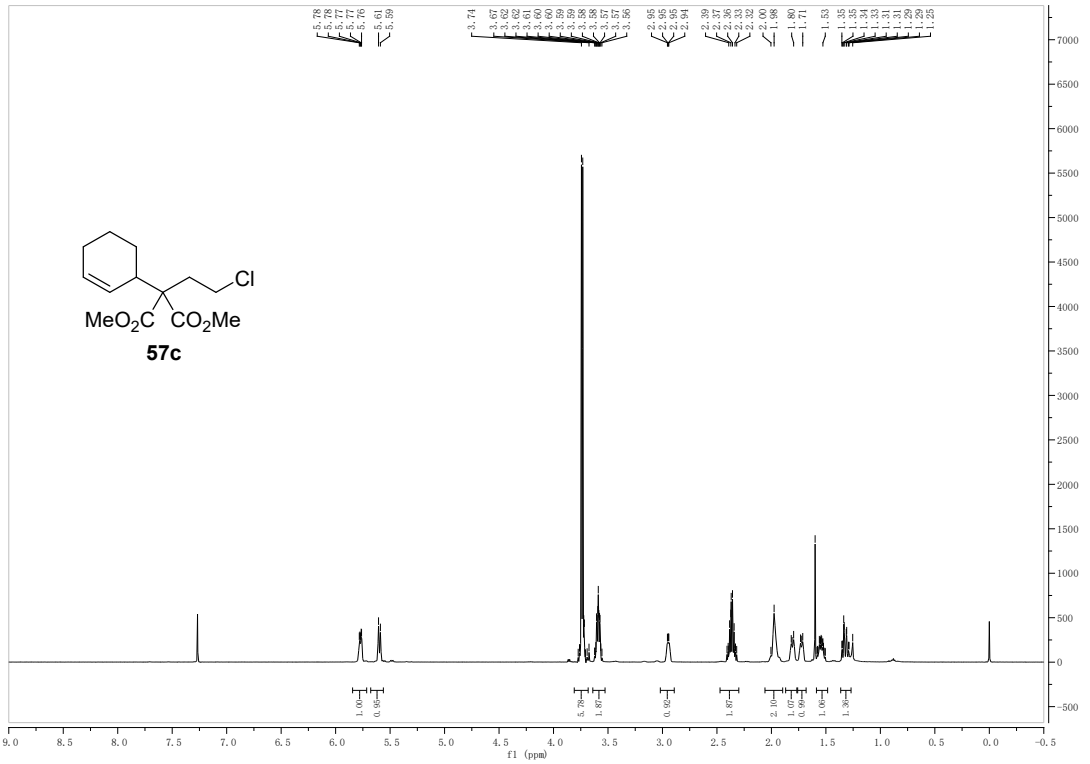
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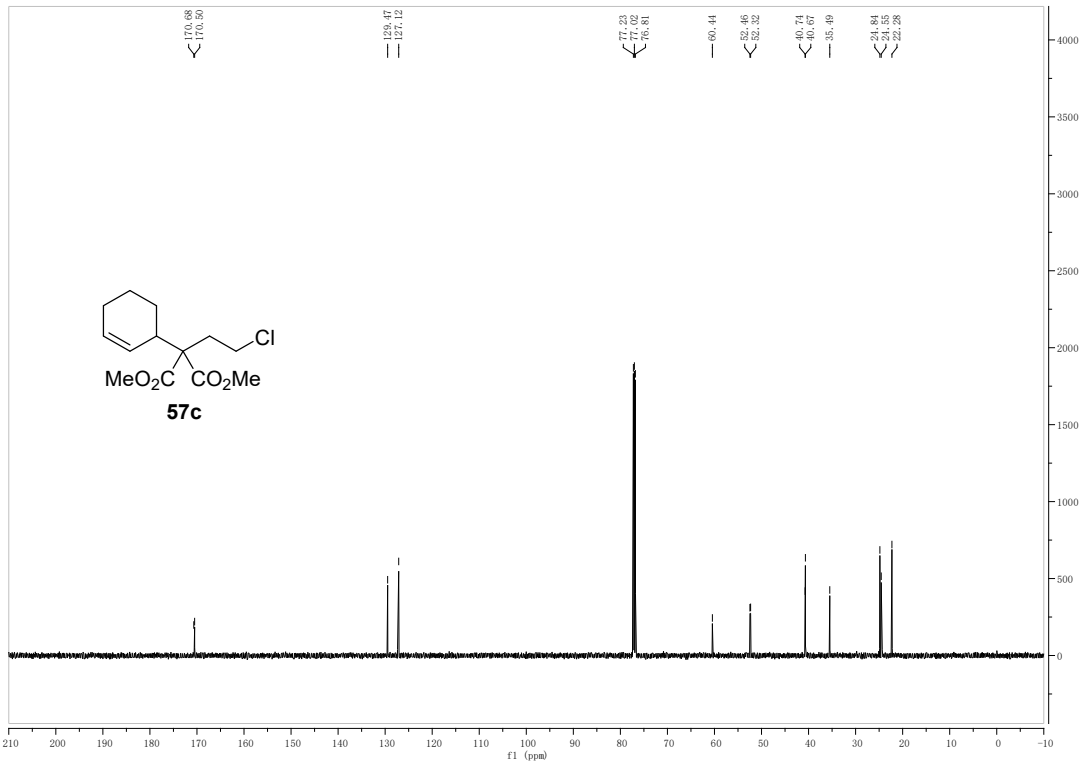
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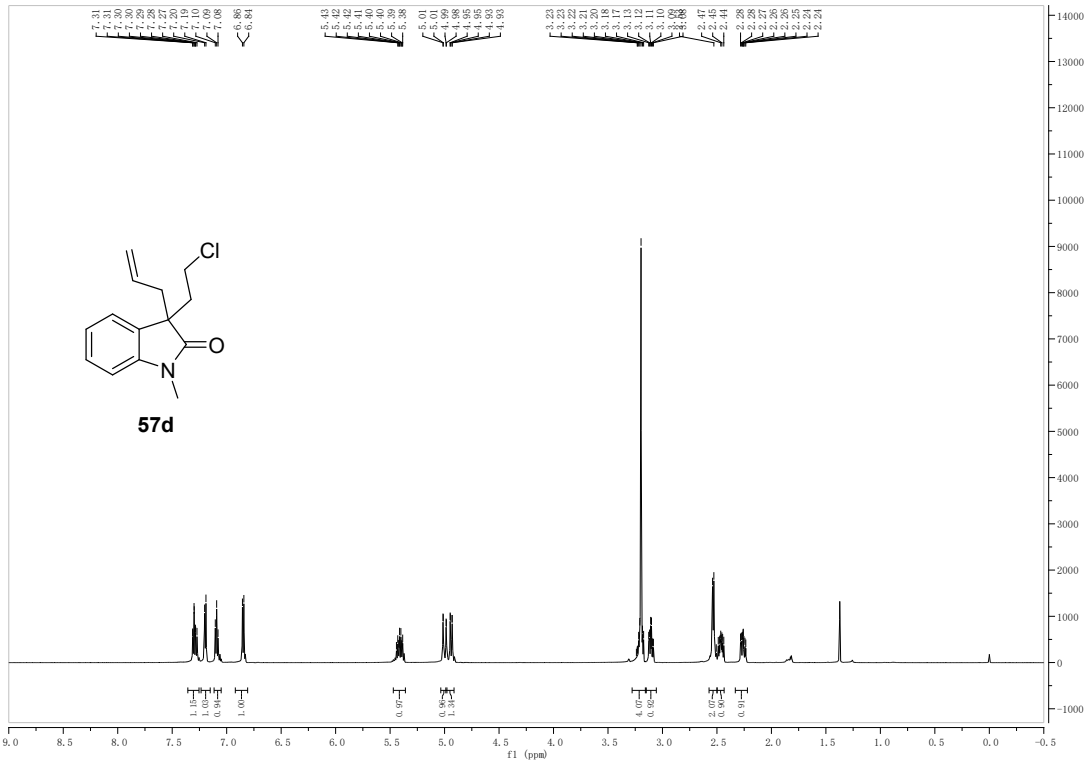
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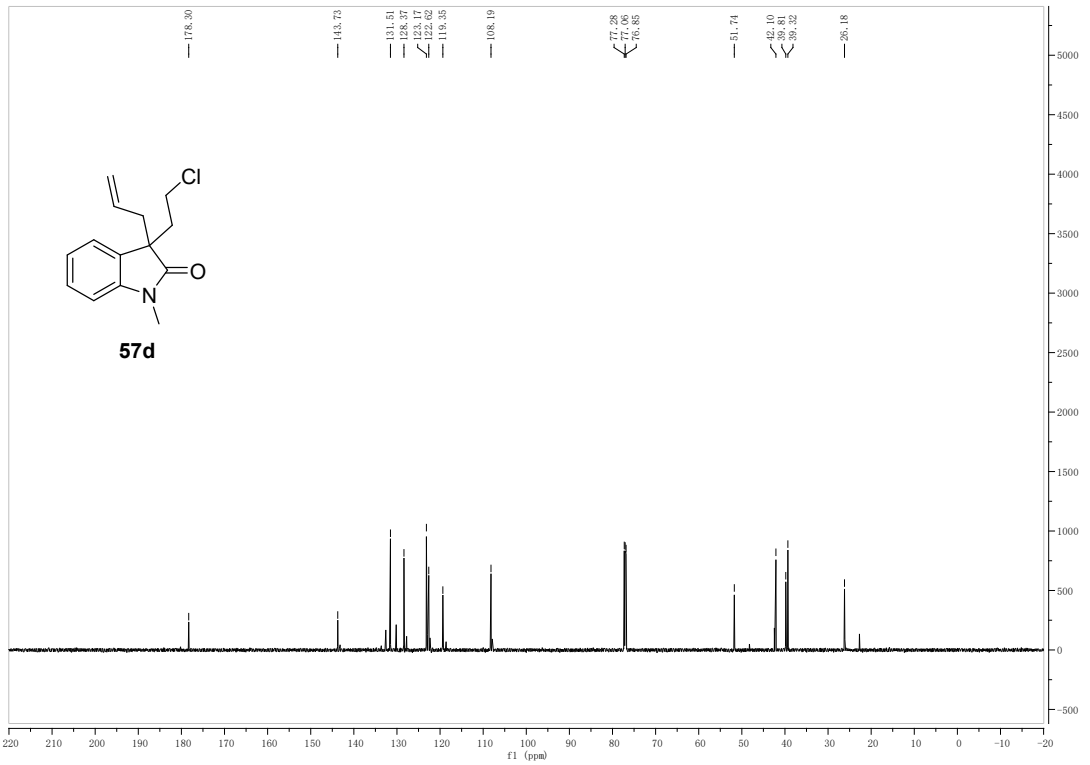
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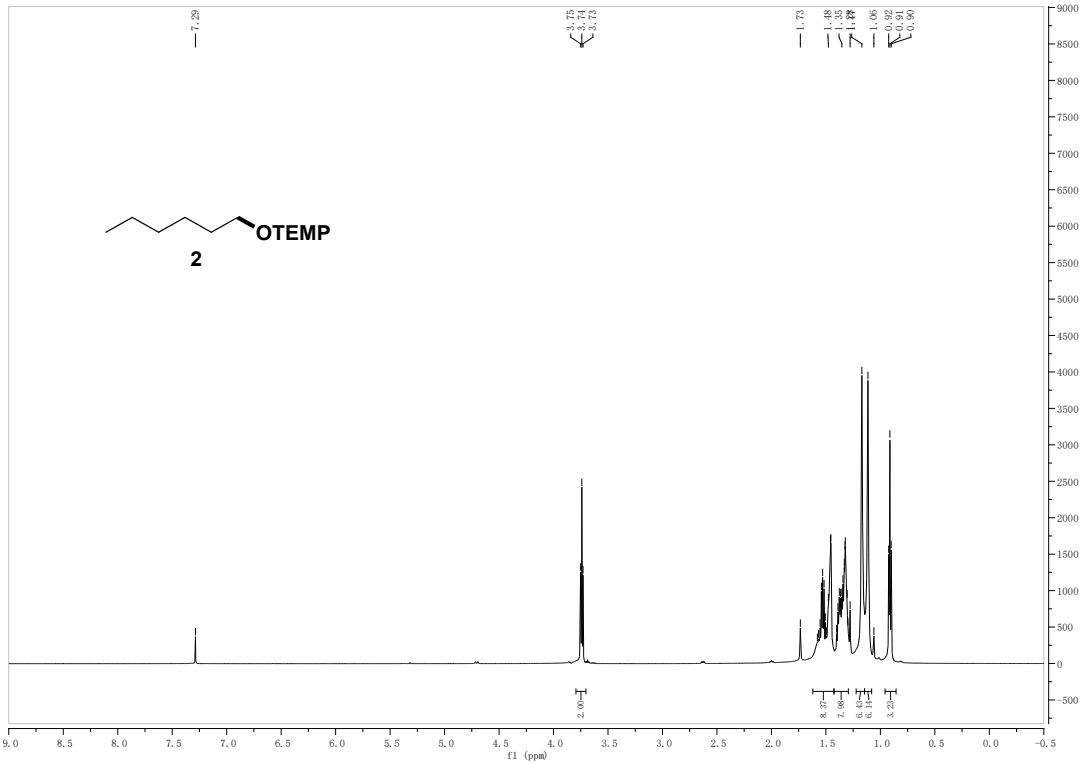
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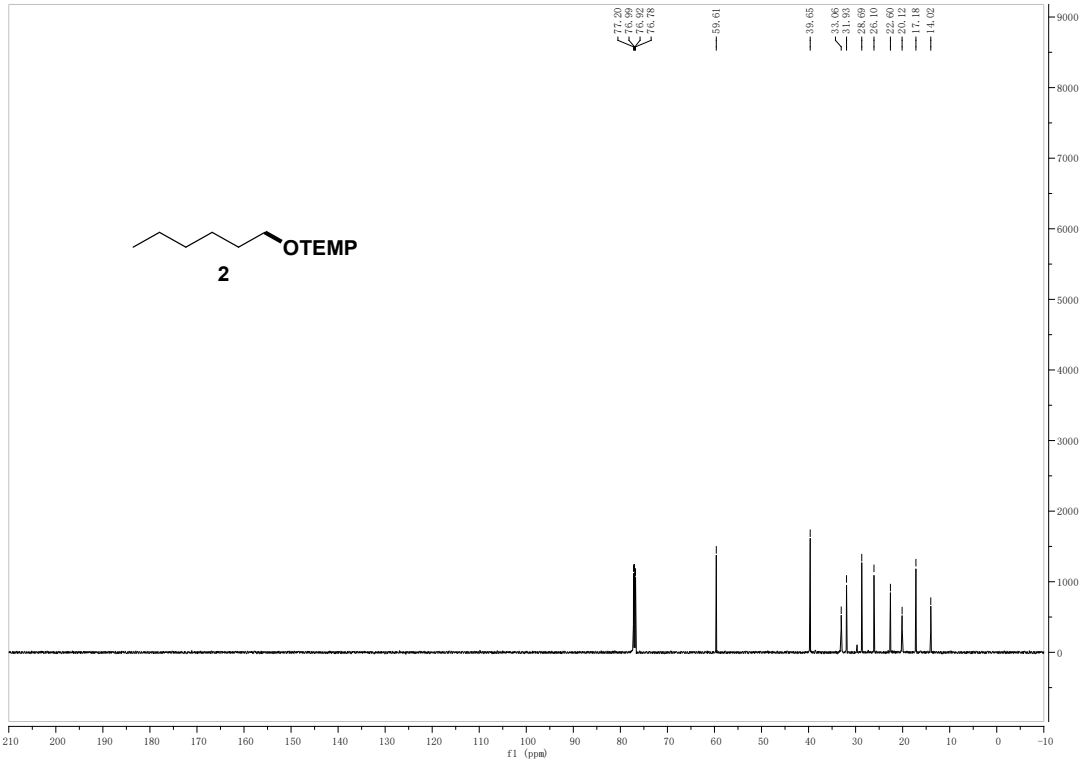
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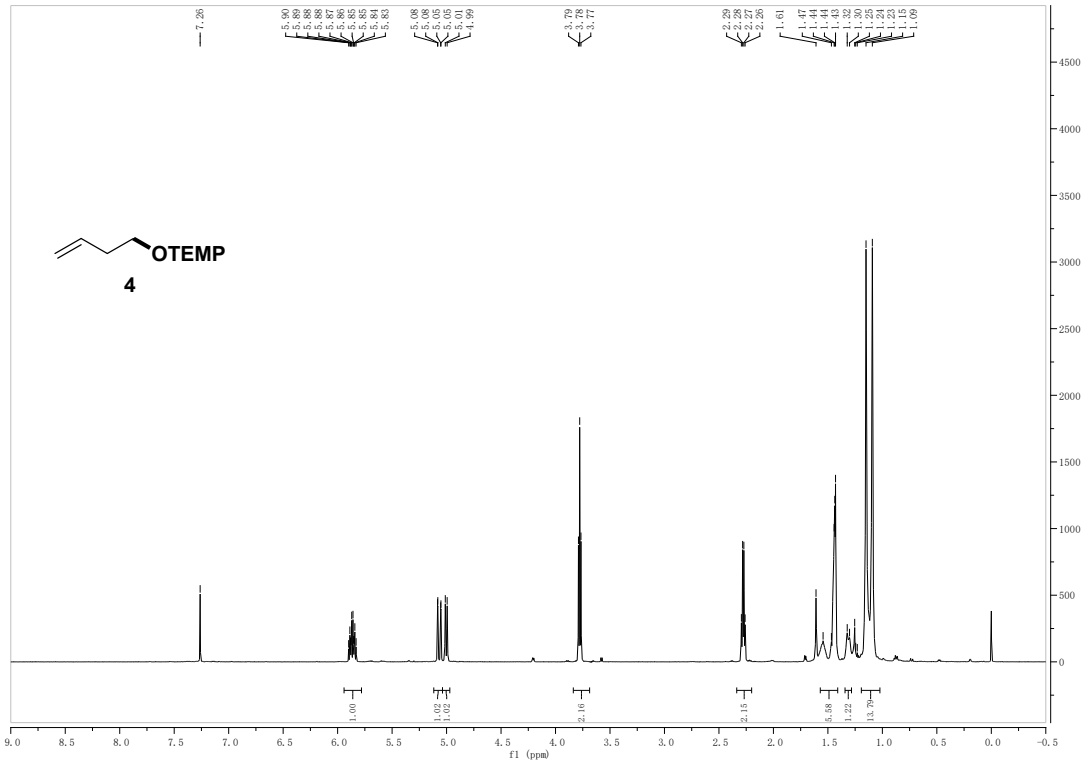
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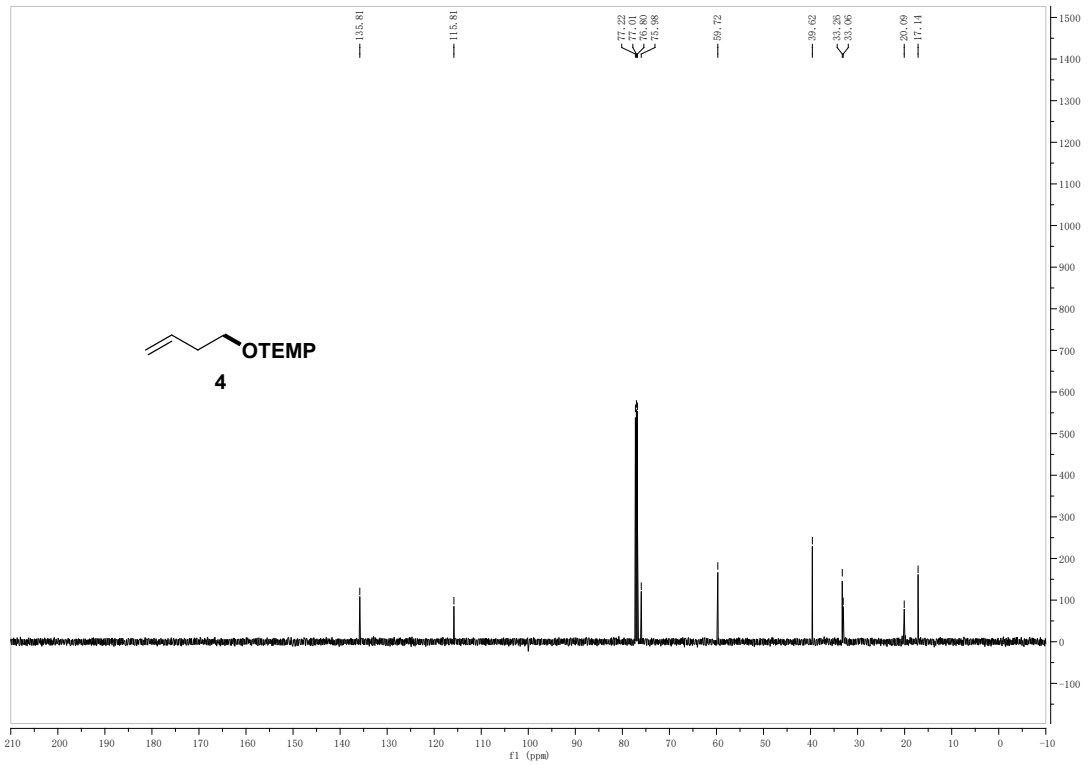
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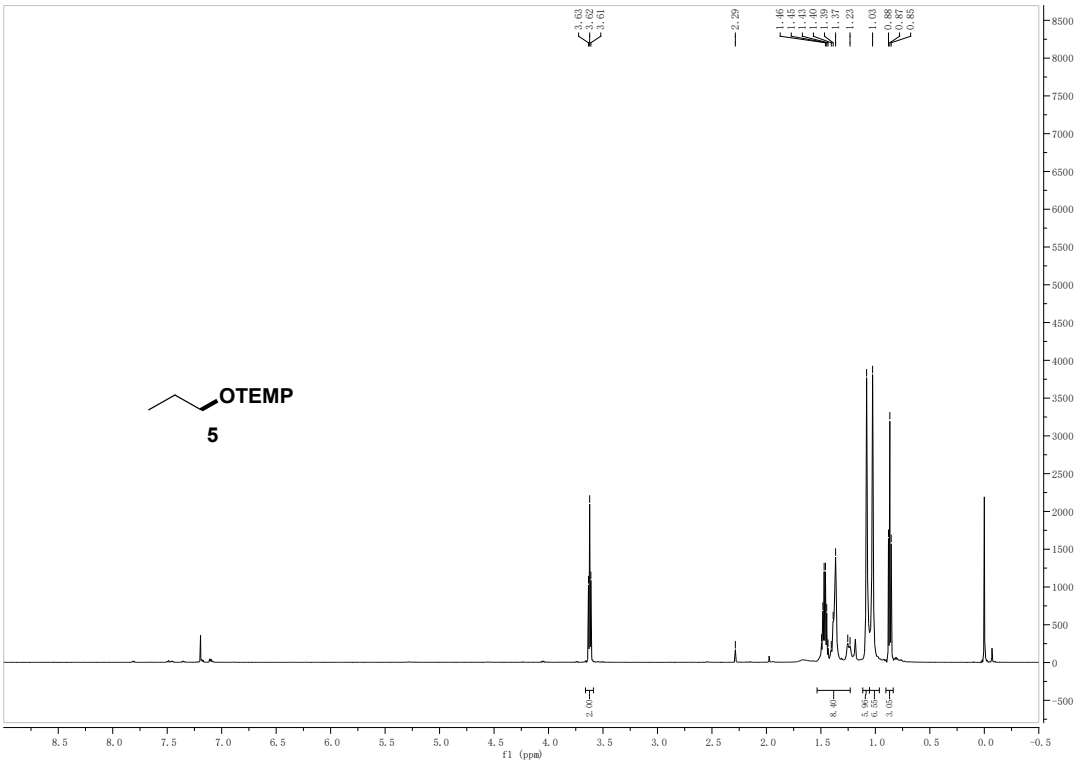
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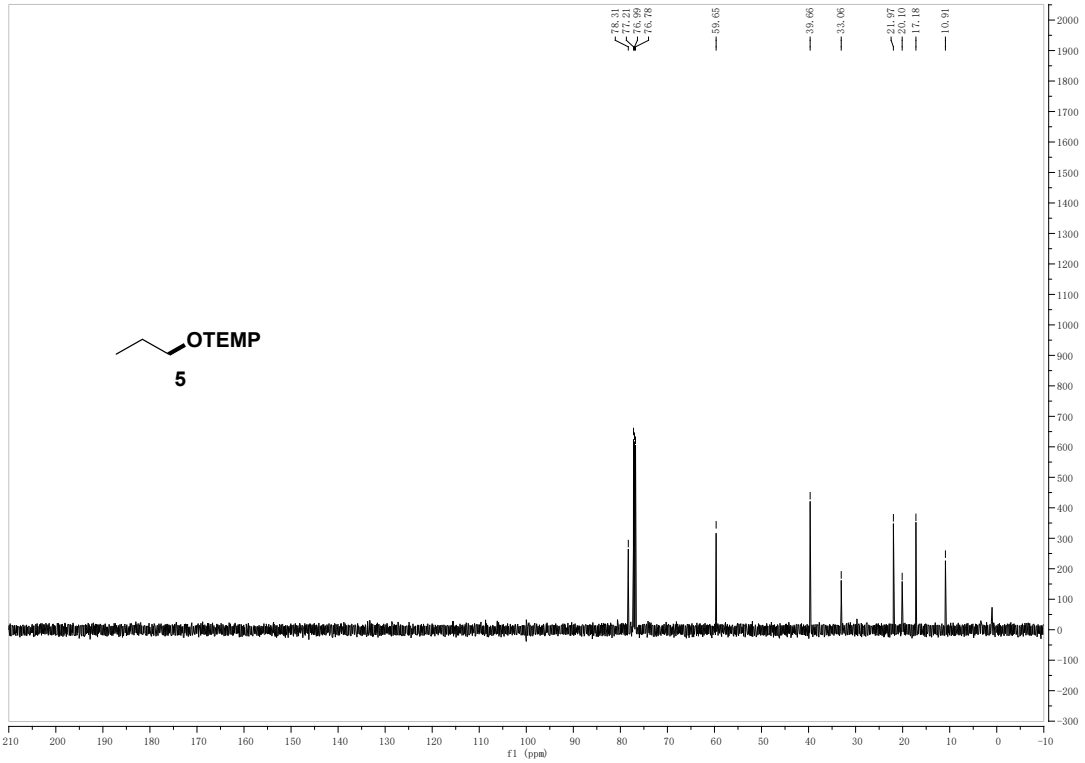
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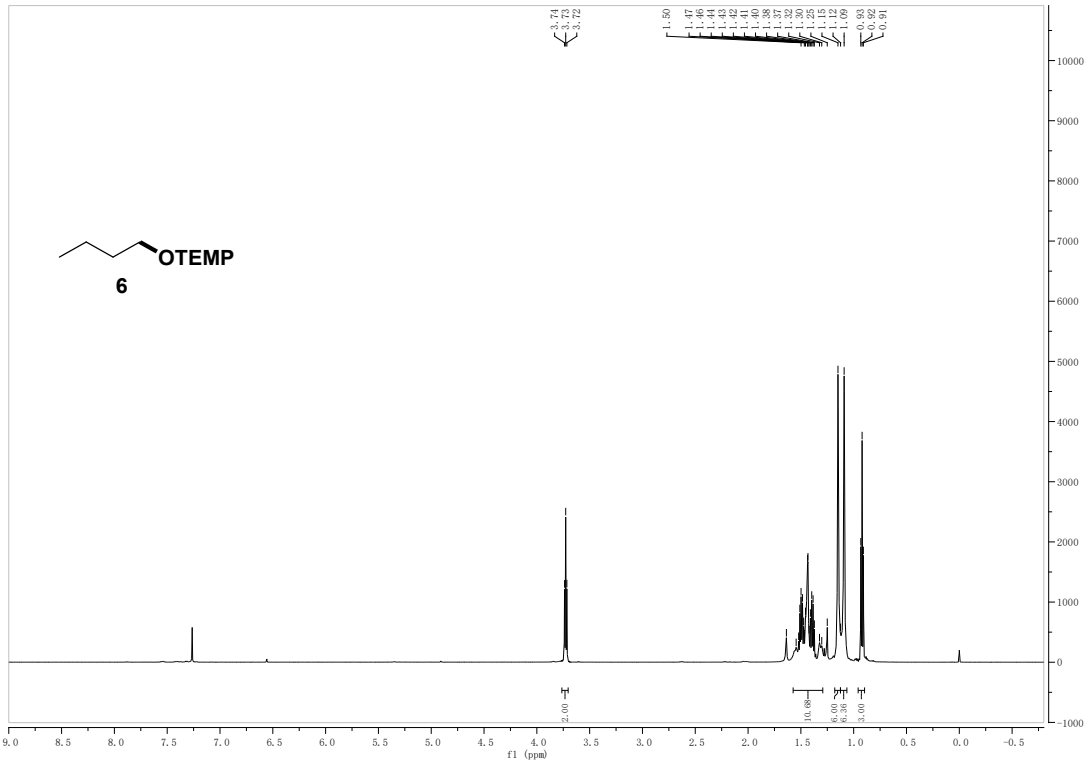
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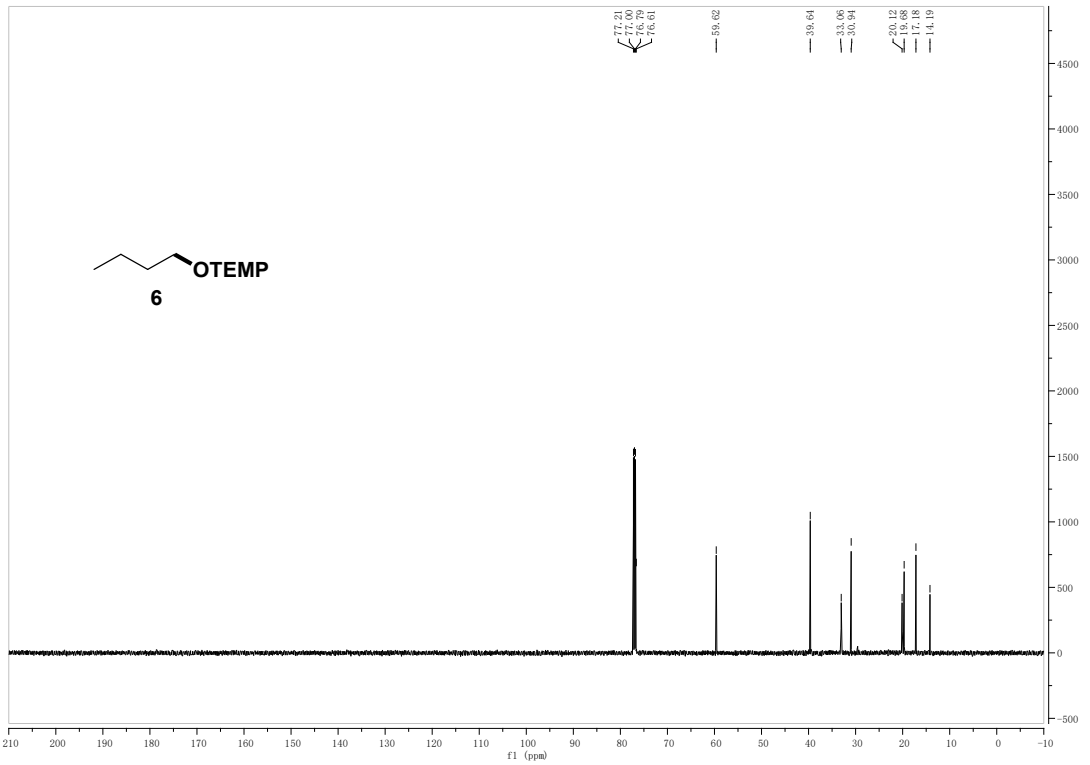
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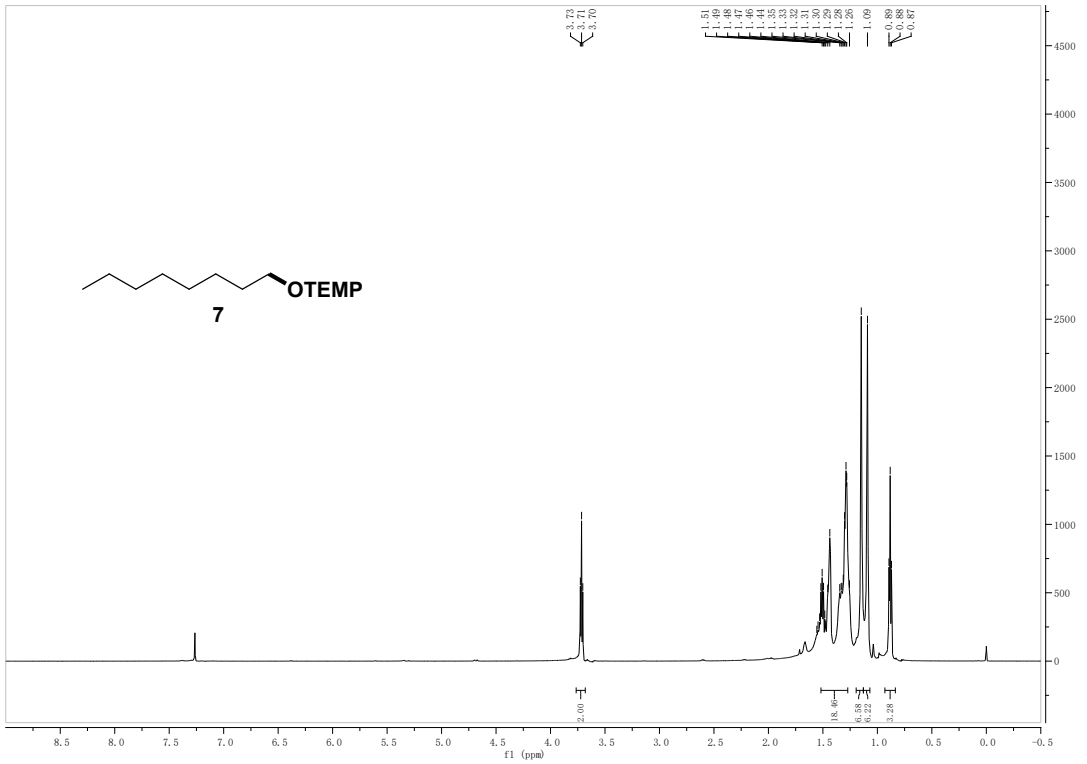
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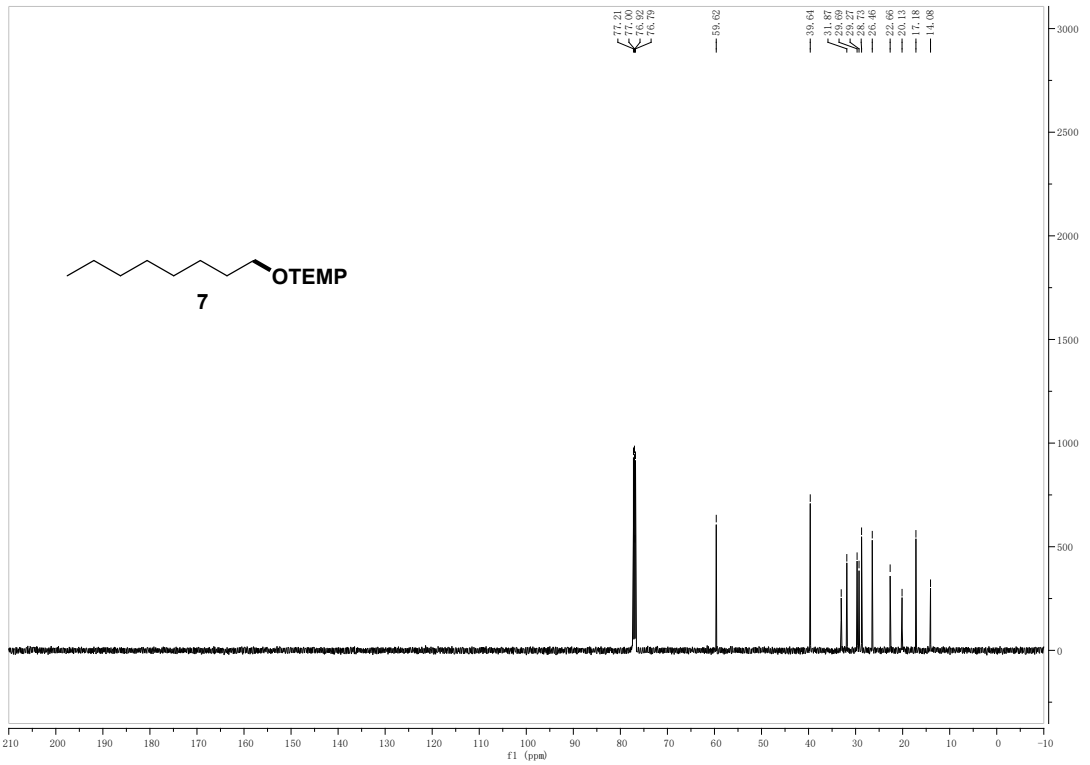
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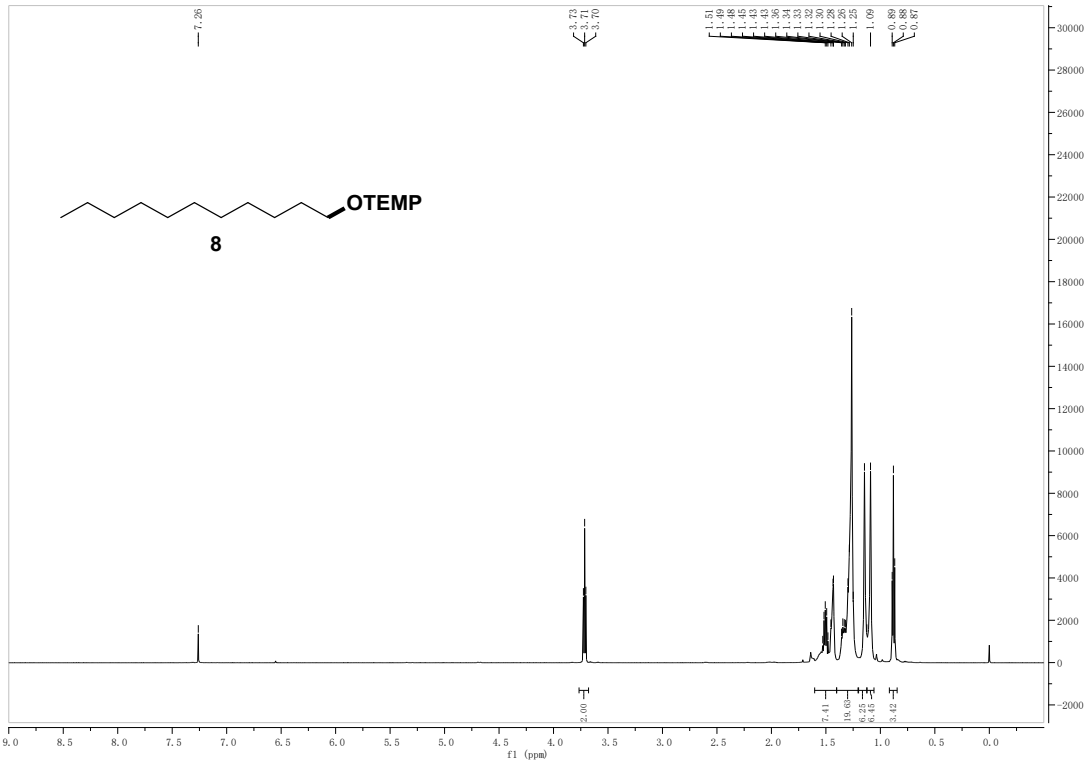
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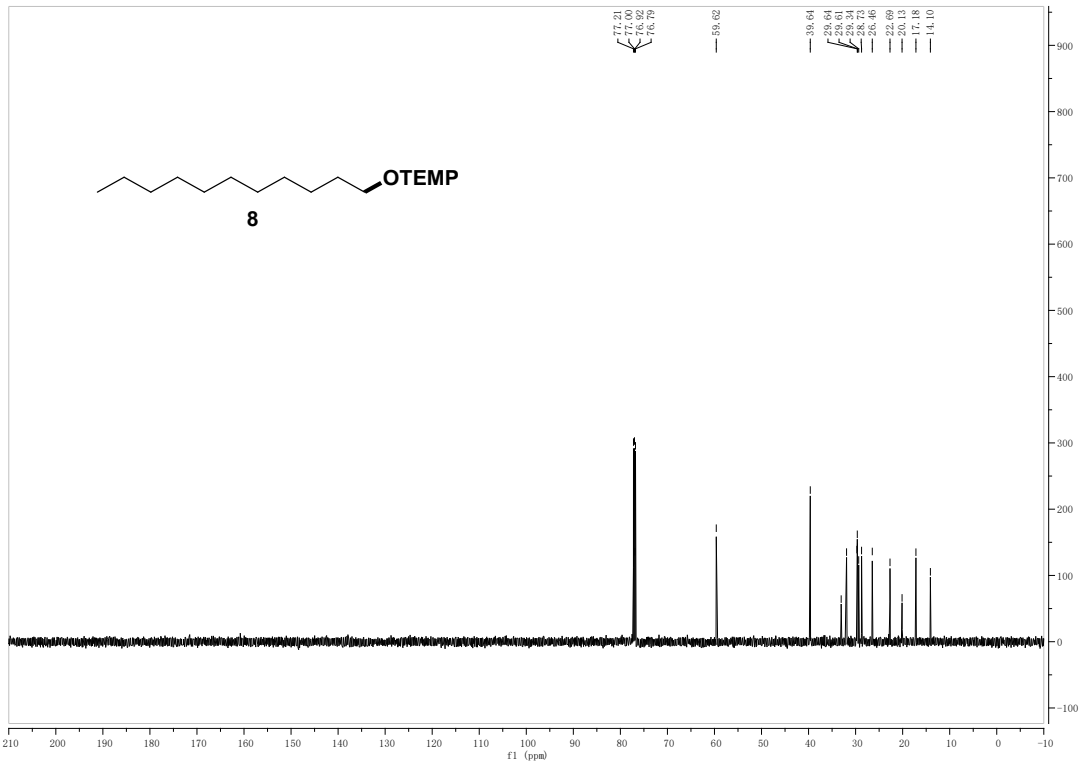
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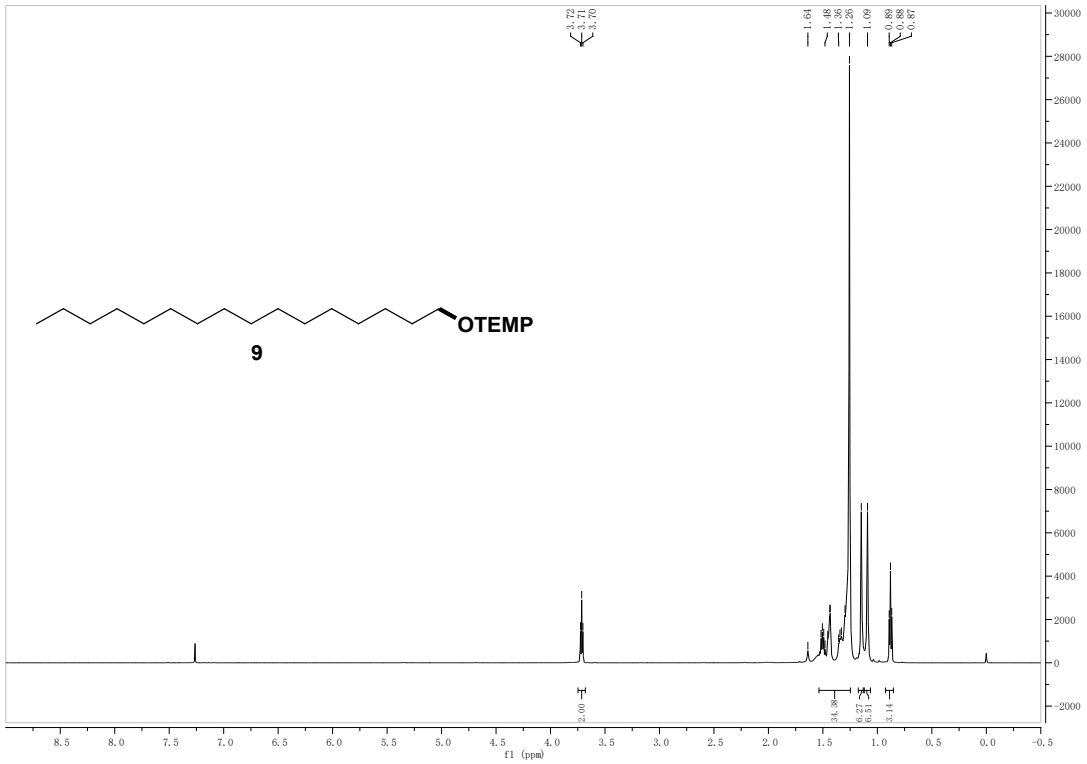
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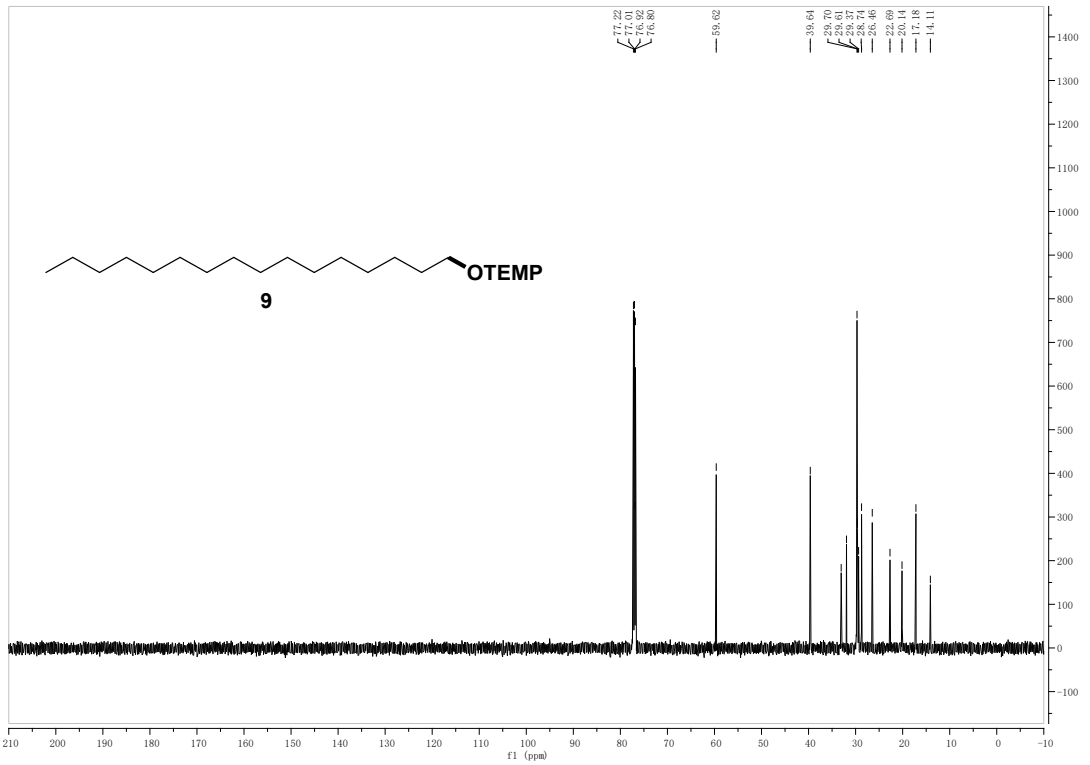
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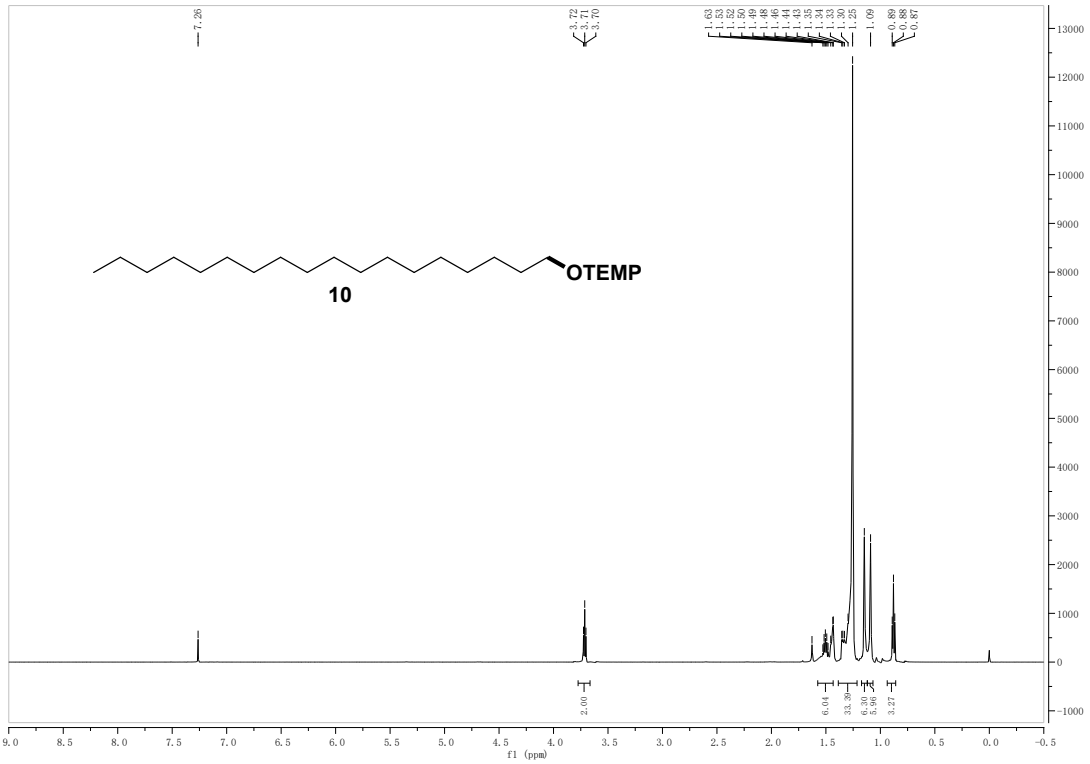
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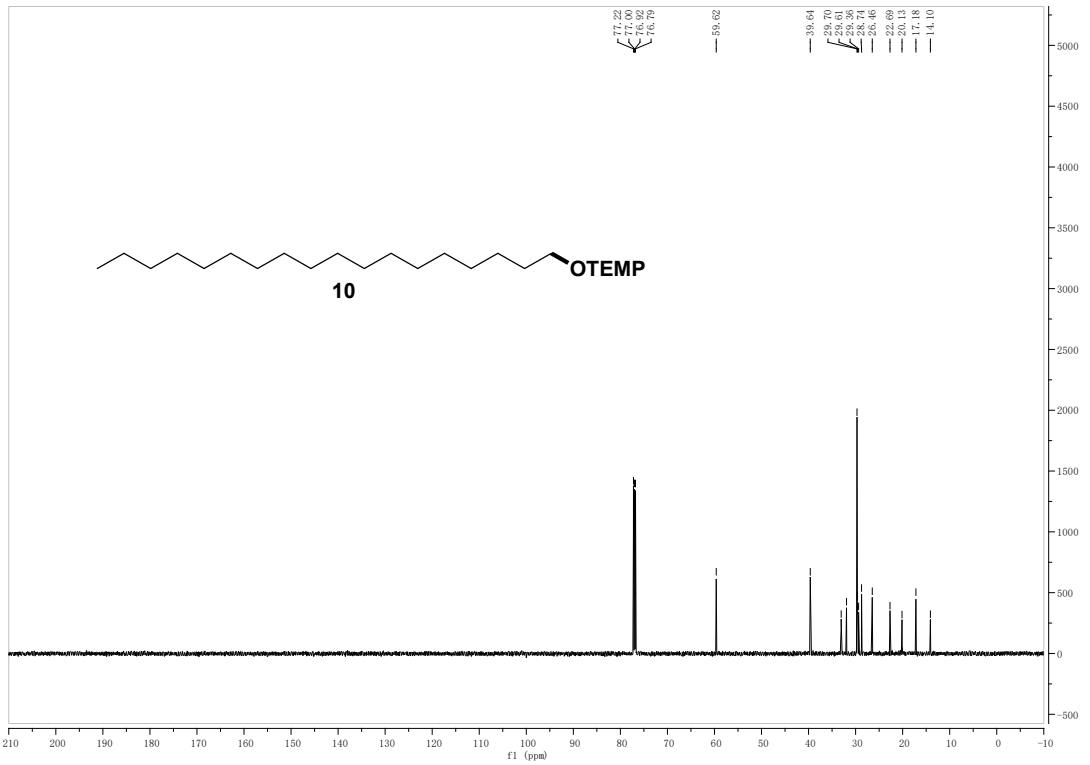
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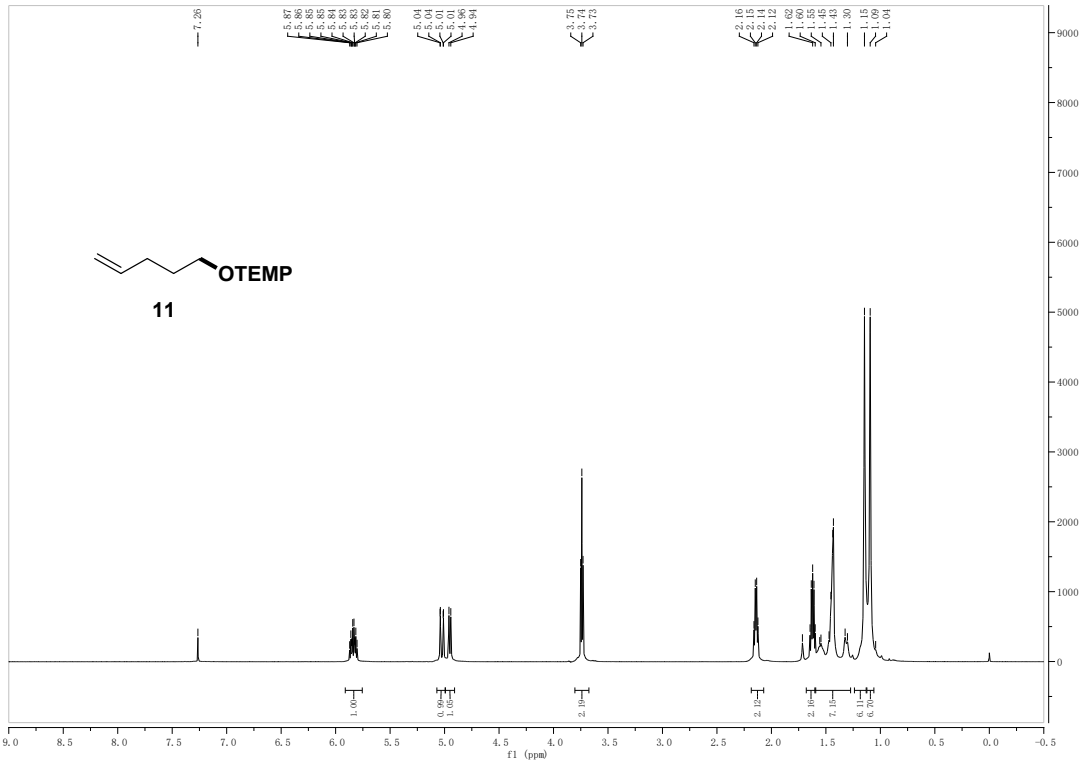
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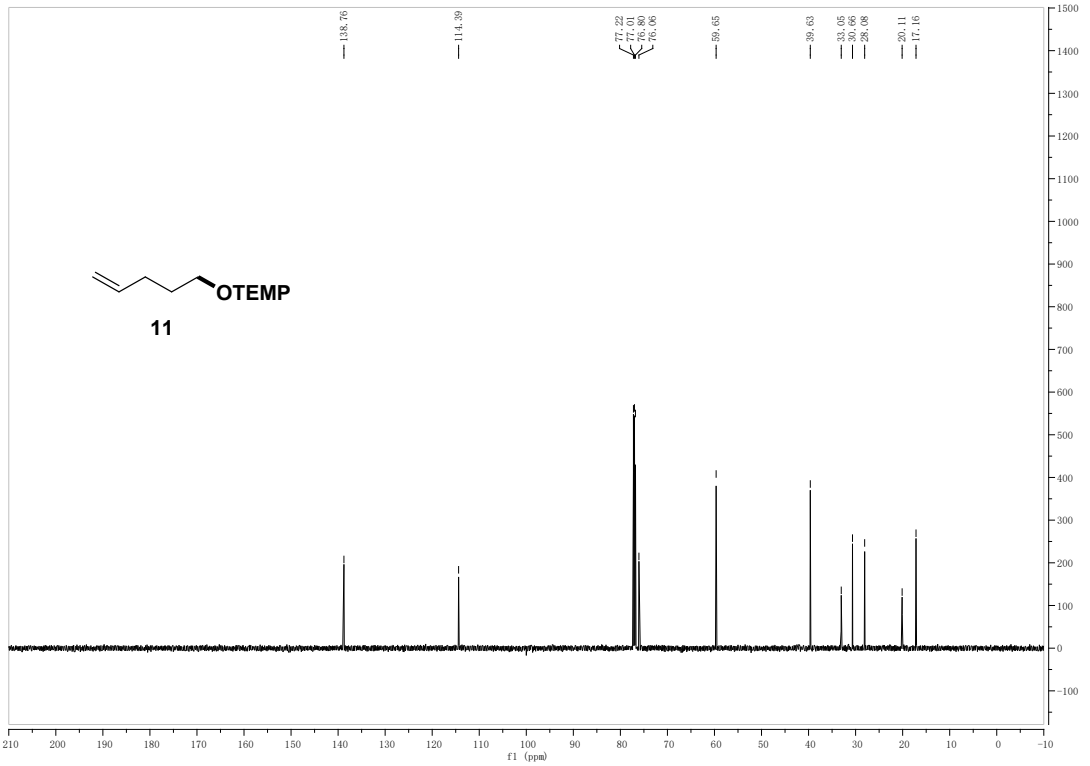
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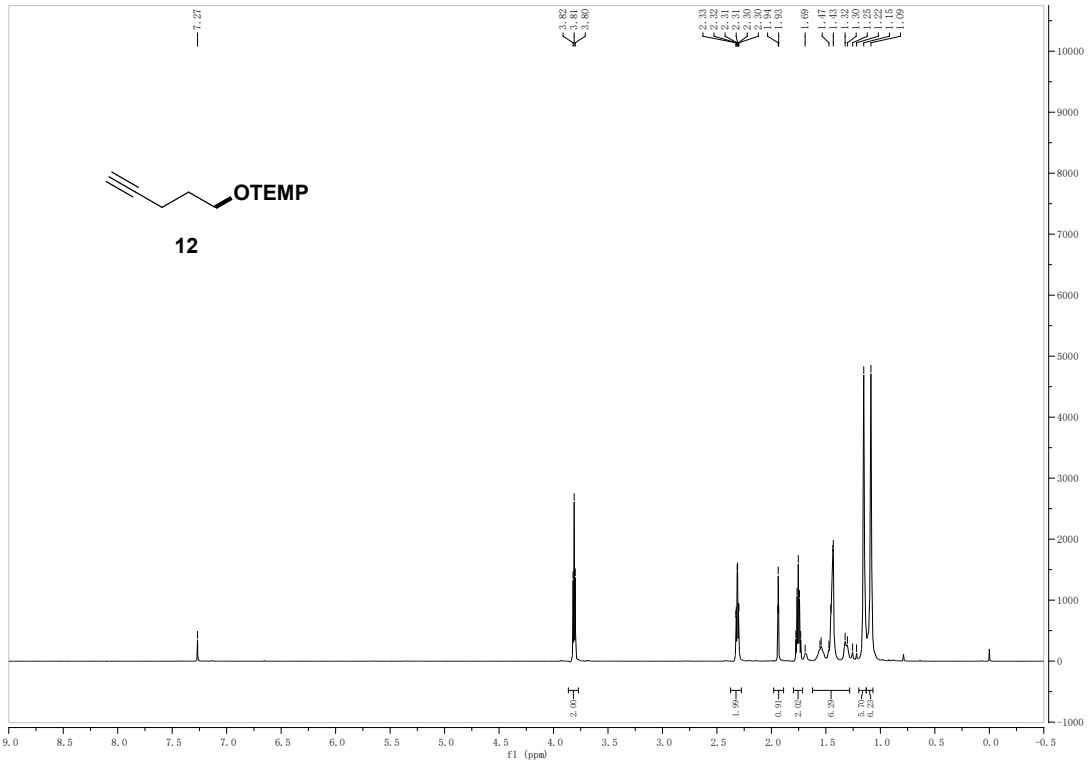
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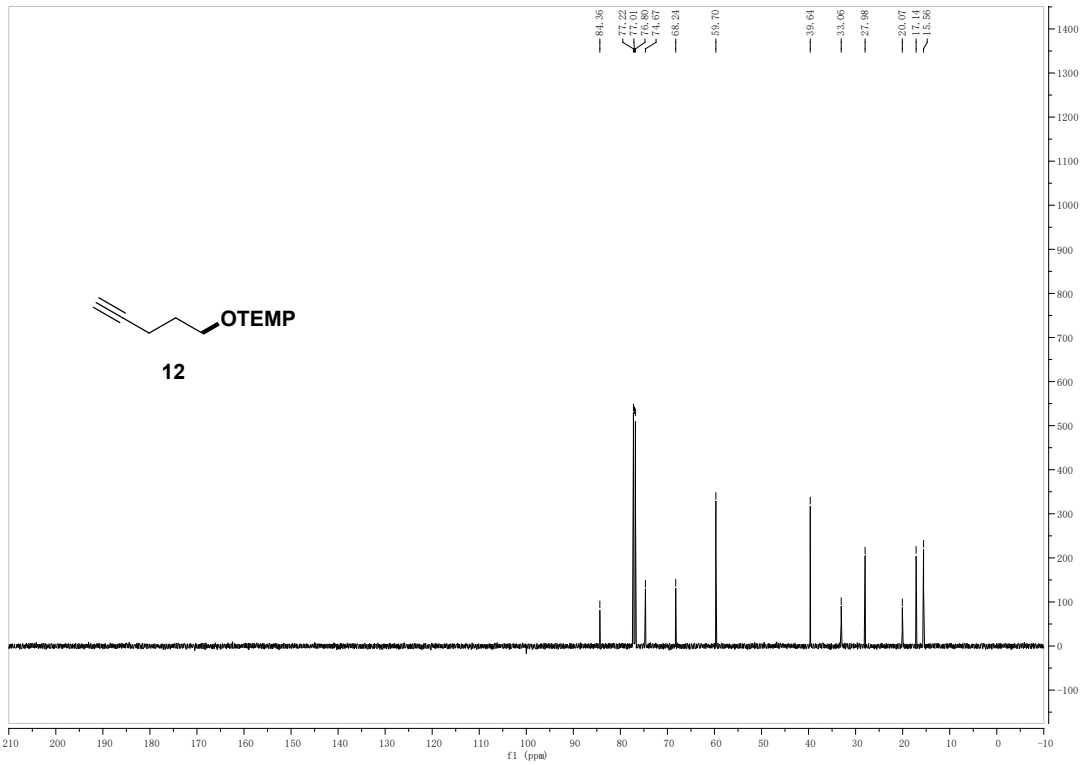
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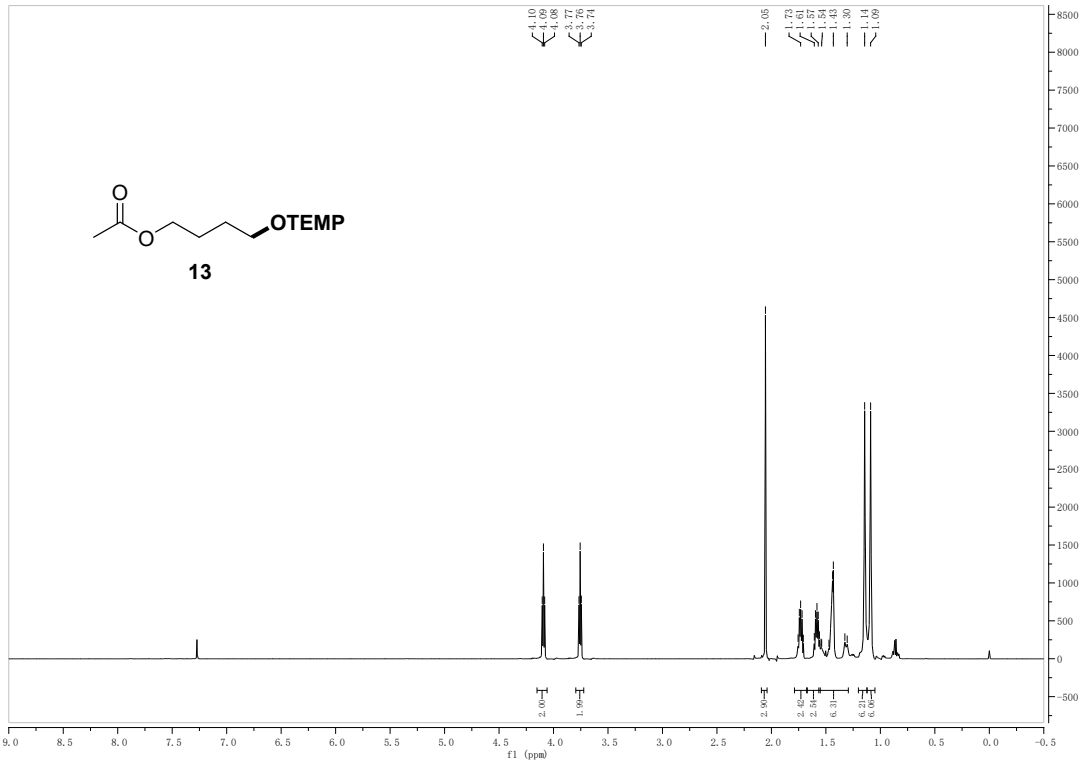
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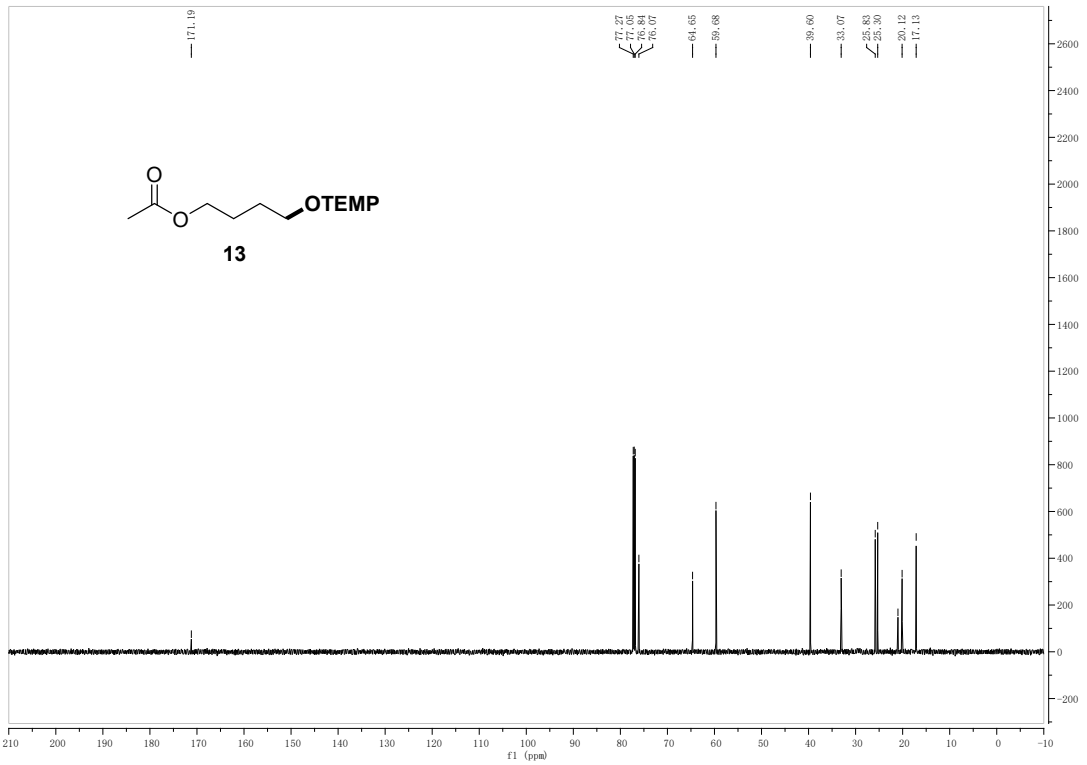
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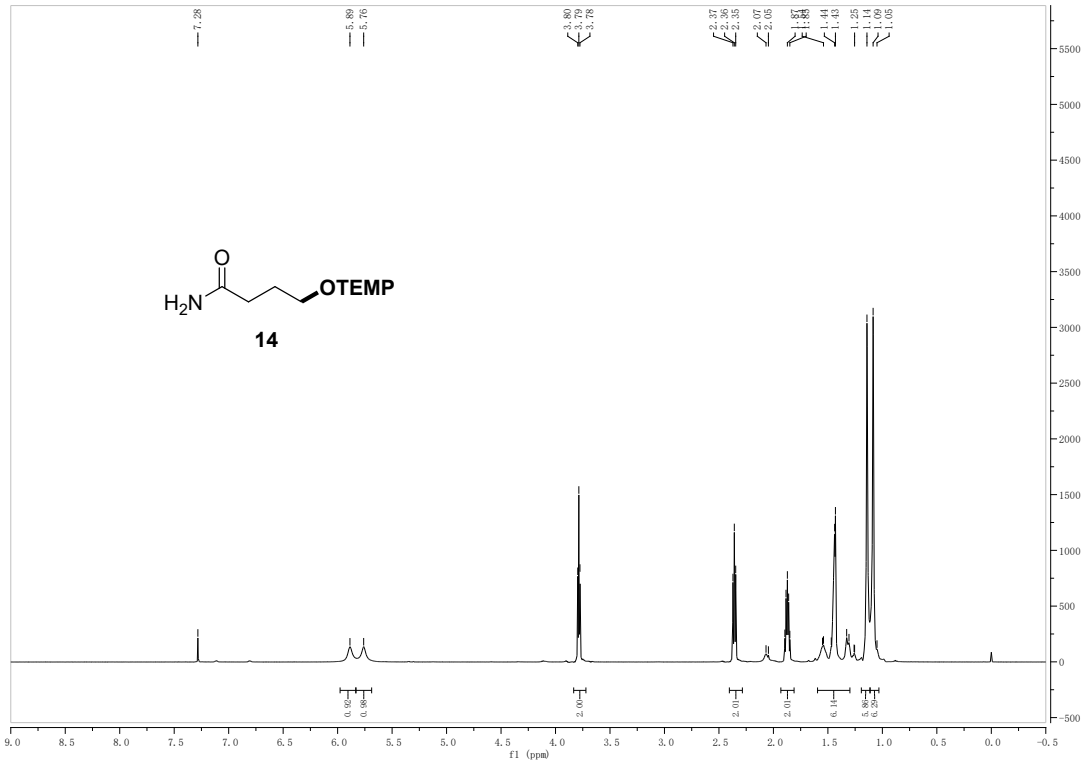
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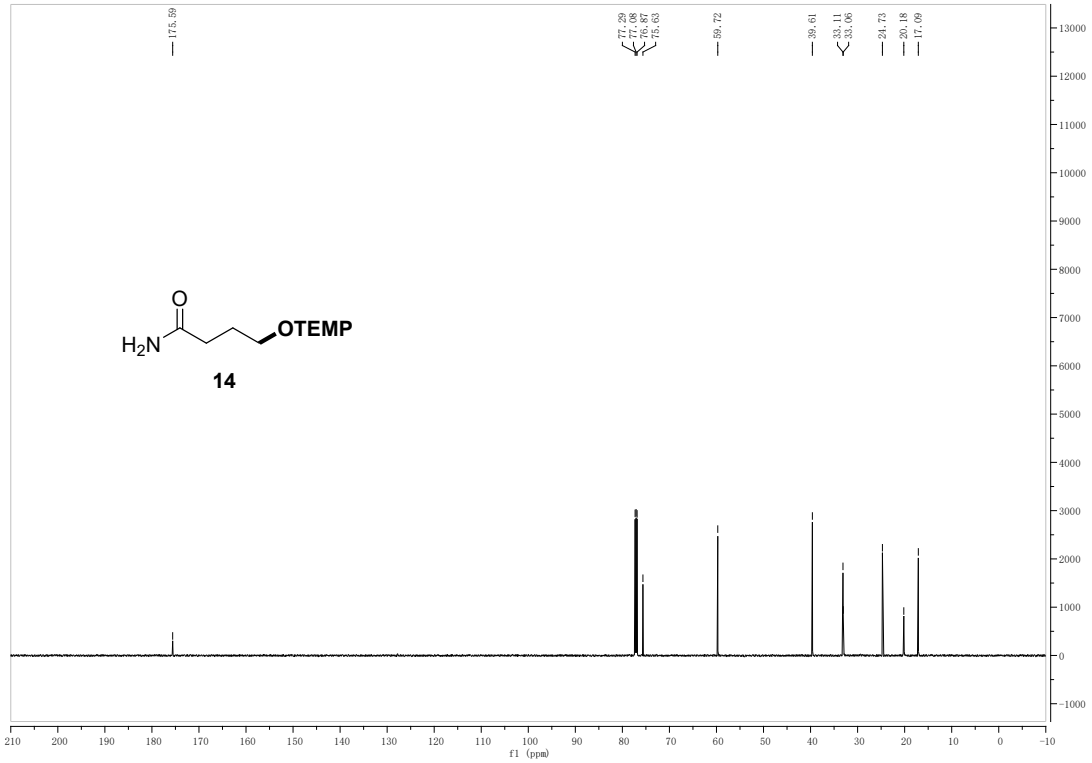
5.89
5.76
3.80
3.79
3.78
2.37
2.36
2.35
2.07
2.05
1.87
1.85
1.44
1.43
1.25
1.14
1.09
1.05
O
H2N
OTEMP
14
0.92
0.98
2.00
2.01
2.01
6.14
5.88
6.29
f1 (ppm)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77.08
76.87
76.63
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33.11
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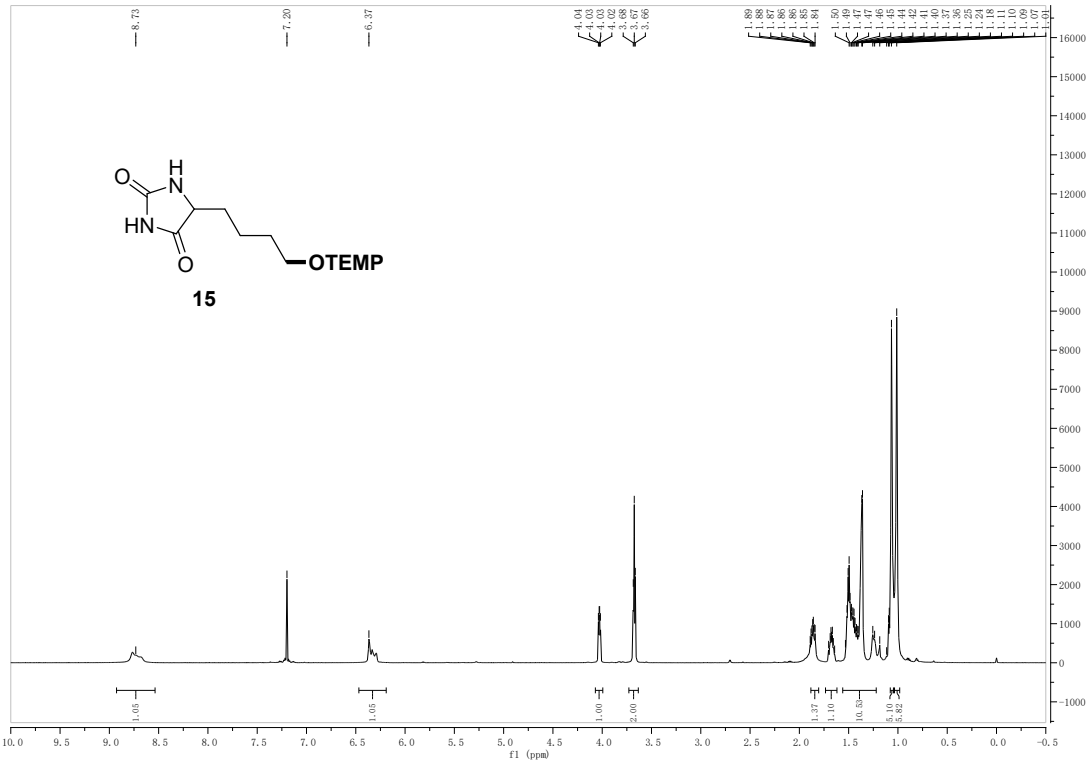
24.73
20.18
17.09
O
H2N
OTEMP
14
f1 (ppm)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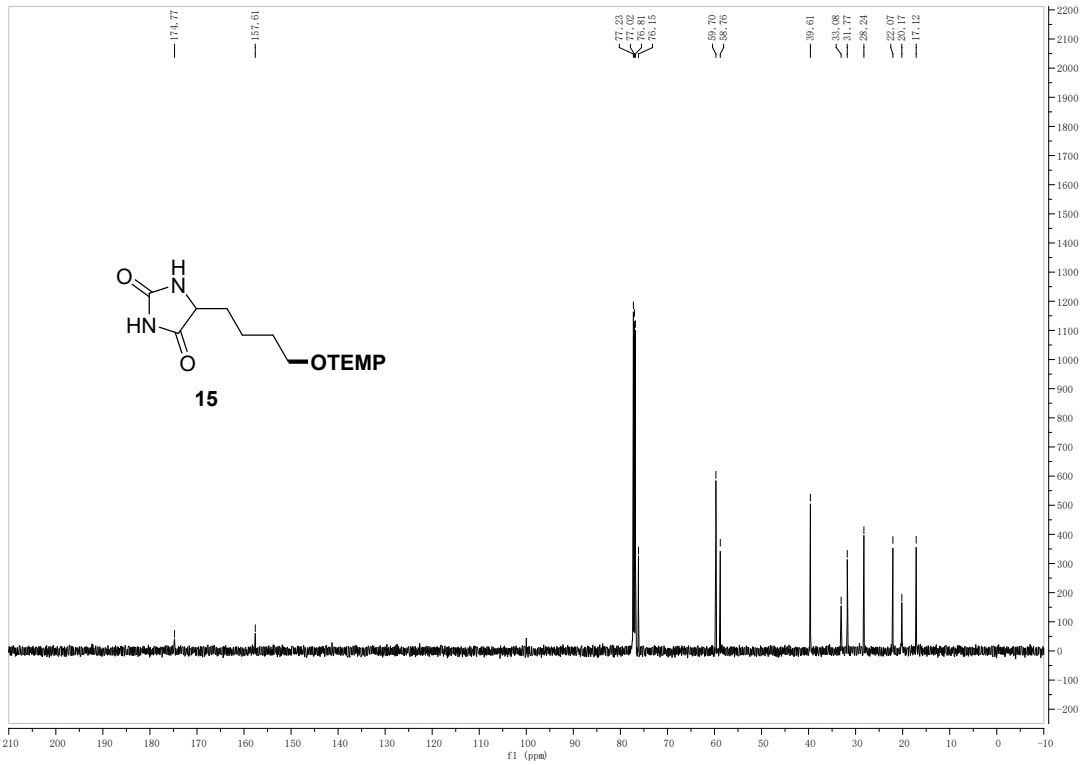
4.03
4.02
4.02
3.68
3.67
3.66
1.89
1.88
1.87
1.86
1.86
1.85
1.84
1.50
1.49
1.47
1.47
1.46
1.45
1.44
1.42
1.41
1.40
1.37
1.36
1.25
1.24
1.18
1.11
1.10
1.09
1.07
1.01
1.05
1.05
1.00
2.00
1.37
1.10
10.53
5.10
5.82
f1 (ppm)
O
H
N
HN
O
OTEMP
15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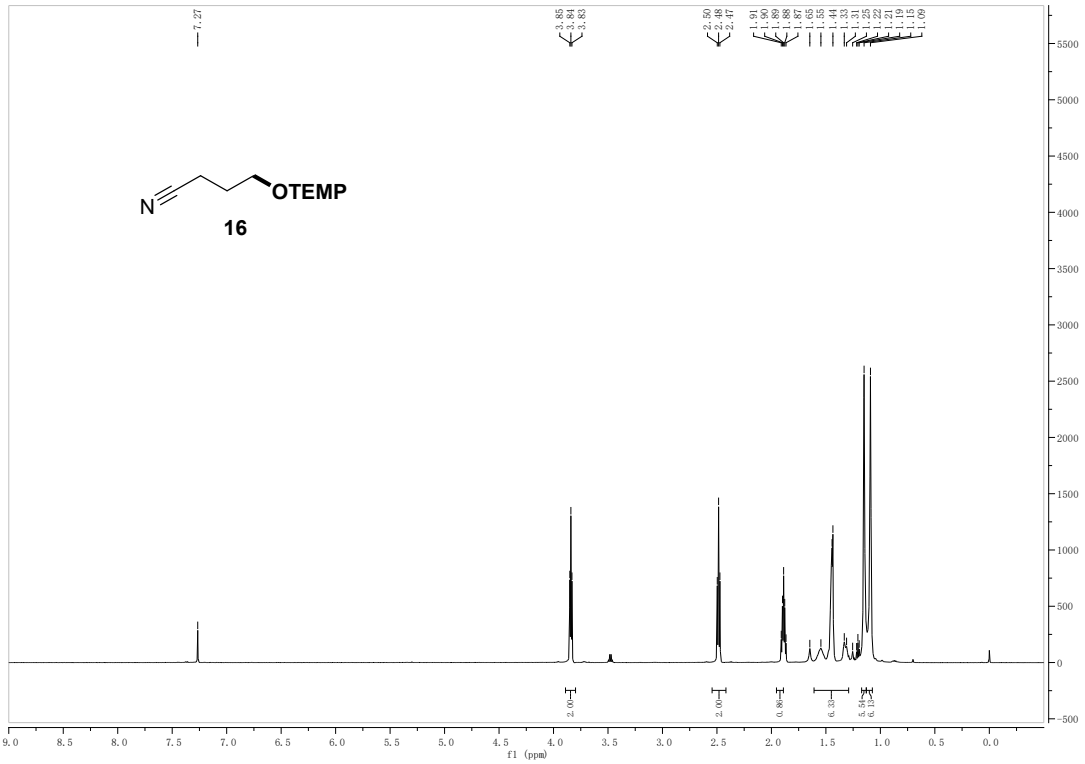
76.15
59.70
58.76
39.61
33.08
31.77
28.24
22.07
20.17
17.12
f1 (ppm)
O
H
N
HN
O
OTEMP
15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3.84
3.83
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2.47
1.91
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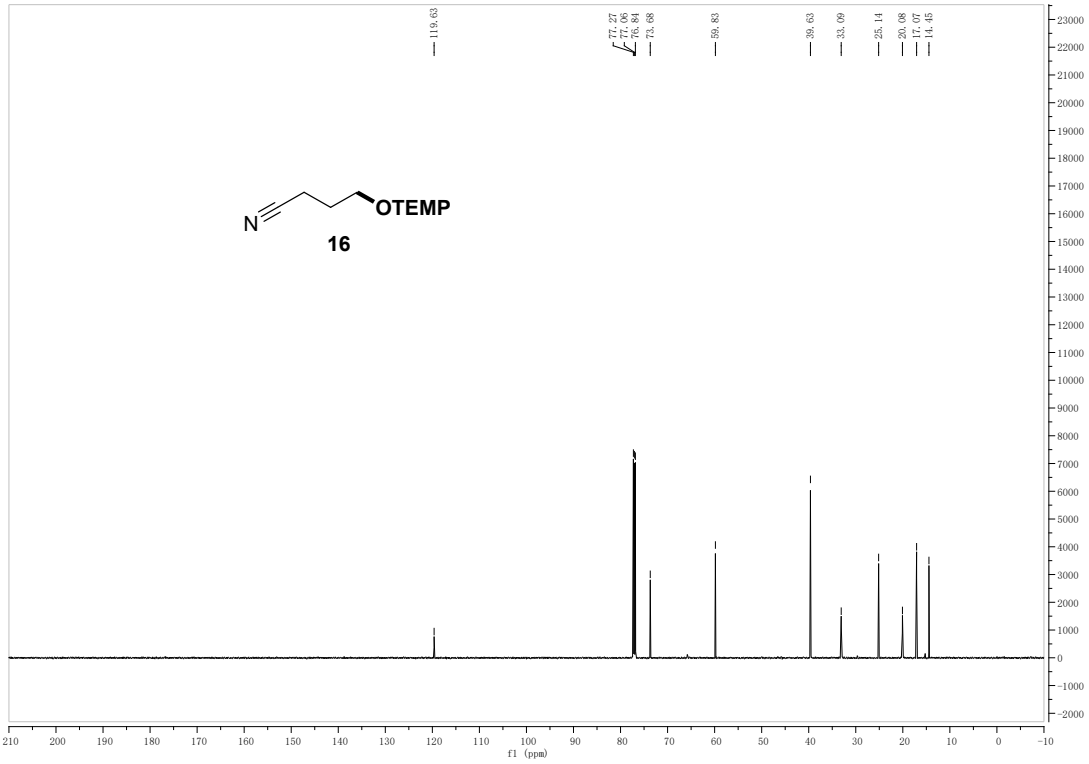
1.89
1.88
1.87
1.65
1.55
1.44
1.33
1.31
1.25
1.22
1.21
1.19
1.15
1.09
N
OTEMP
16
2.00
2.00
0.86
6.33
5.54
6.13
f1 (ppm)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77.27
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73.68
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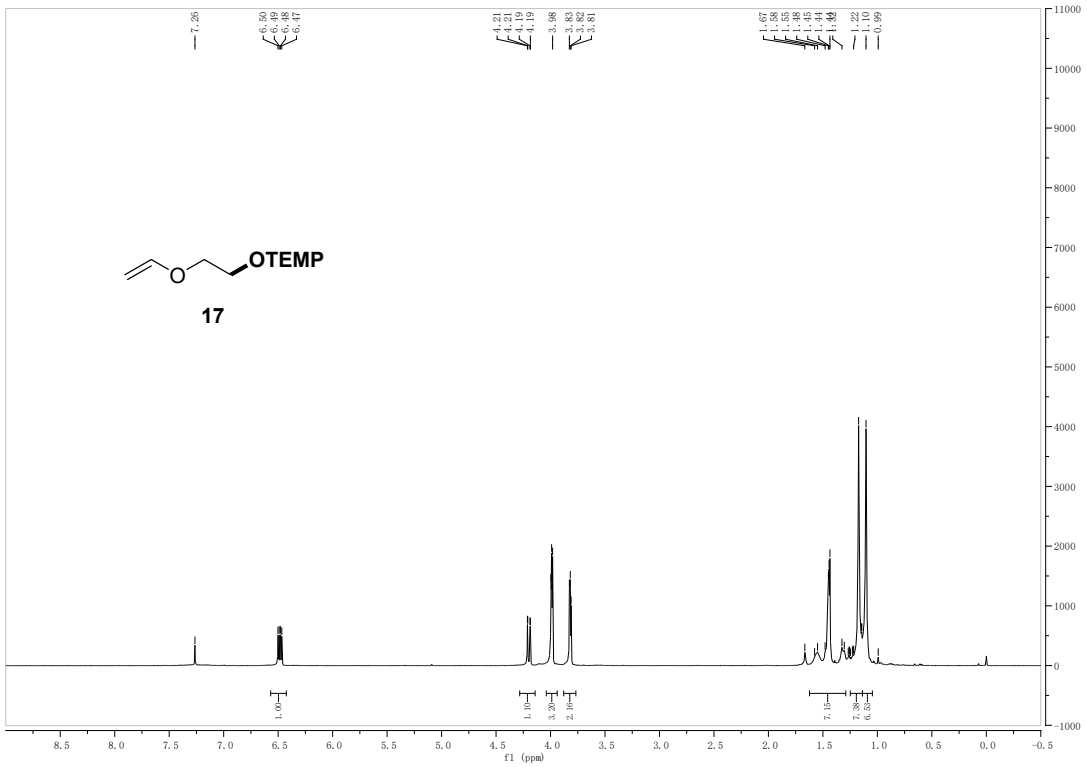
33.09
25.14
20.08
17.07
14.45
N
OTEMP
16
f1 (ppm)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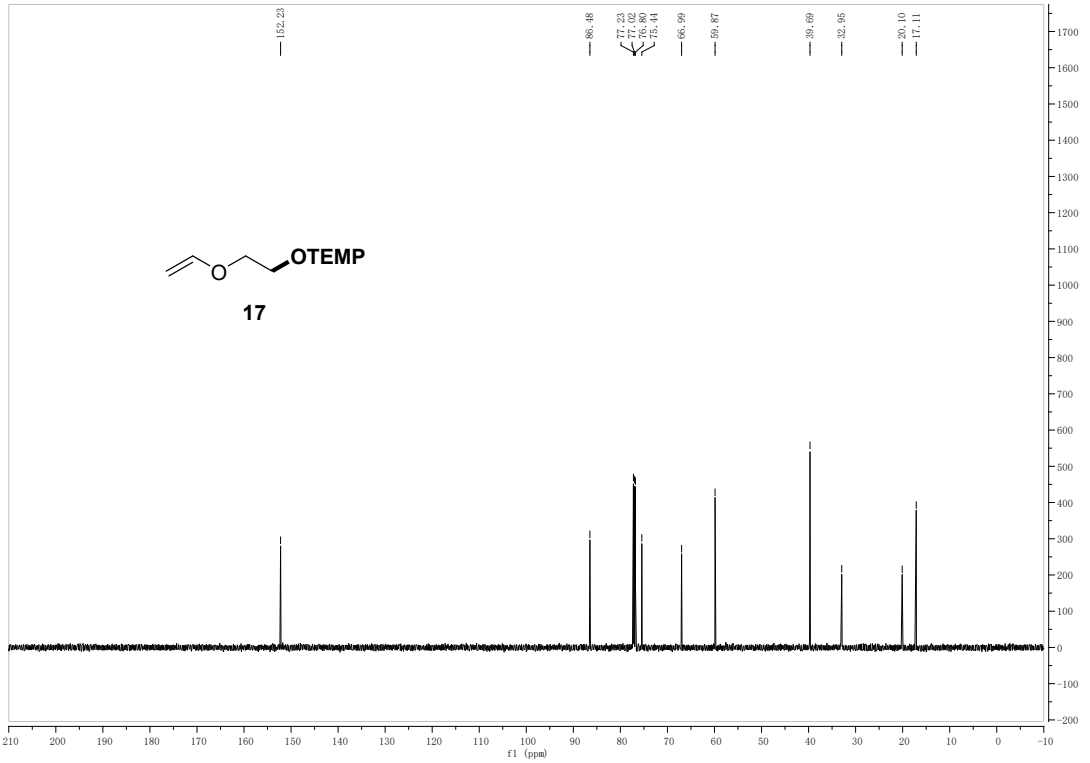
6.50
6.49
6.48
6.47
4.21
4.21
4.19
4.19
3.98
3.83
3.82
3.81
1.67
1.58
1.55
1.48
1.45
1.44
1.42
1.22
1.10
0.99
OTEMP
17
1.00
1.10
3.20
2.16
7.15
7.38
6.53
f1 (ppm)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86.48
77.23
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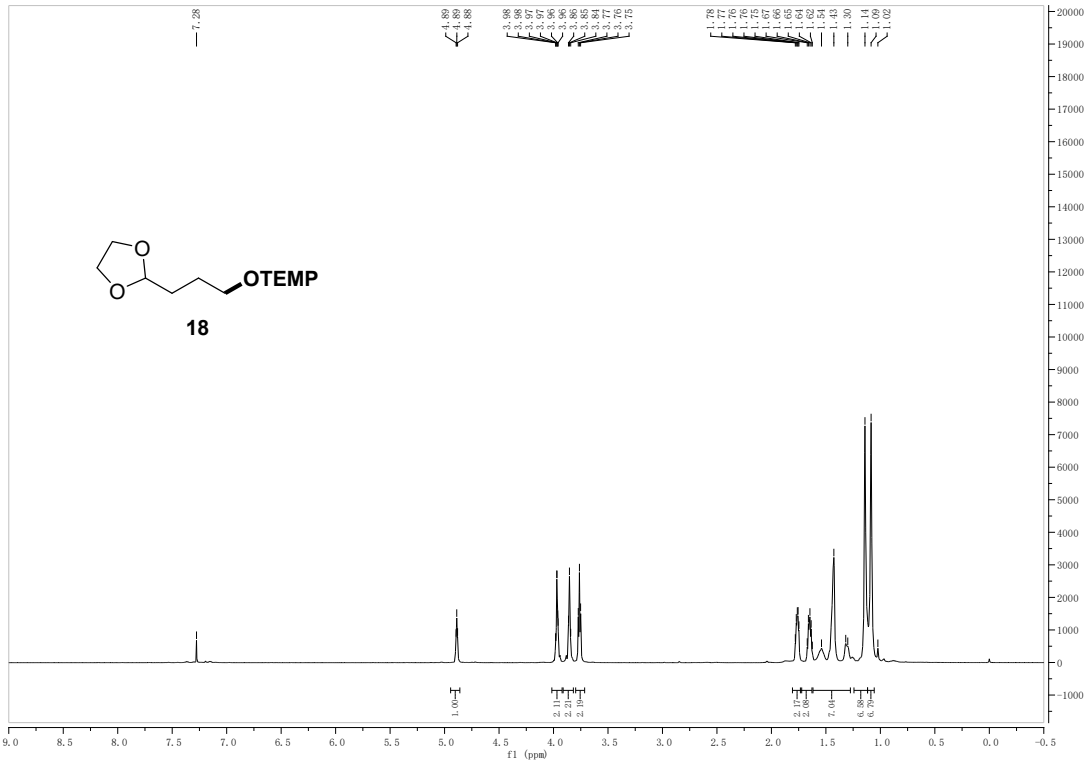
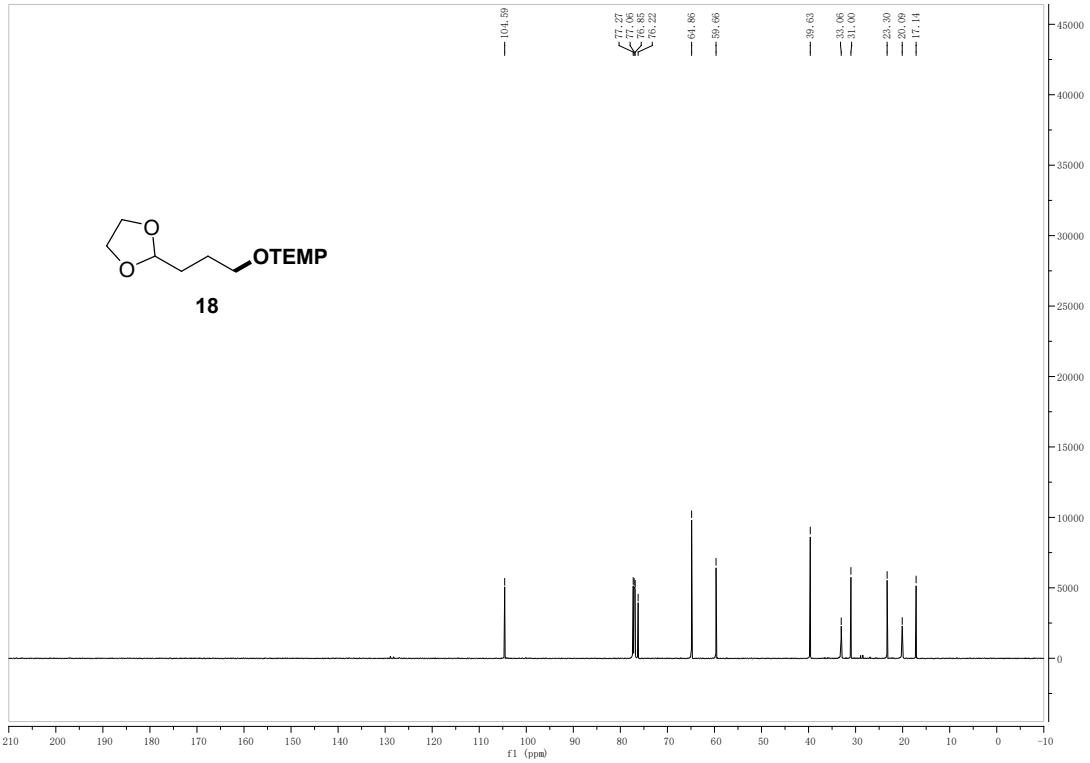
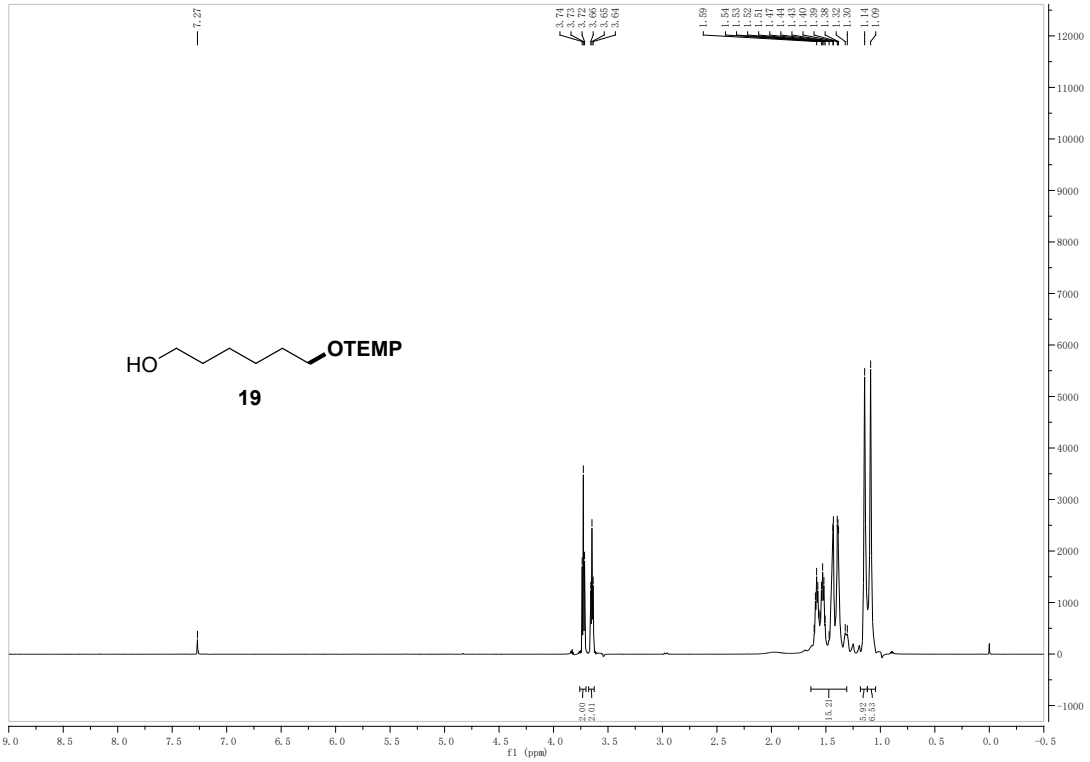
76.80
76.44
66.99
59.87
39.69
32.95
20.10
17.11
OTEMP
17
f1 (ppm)


OTEMP
18
f1 (ppm)


OTEMP
18
f1 (ppm)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3.65
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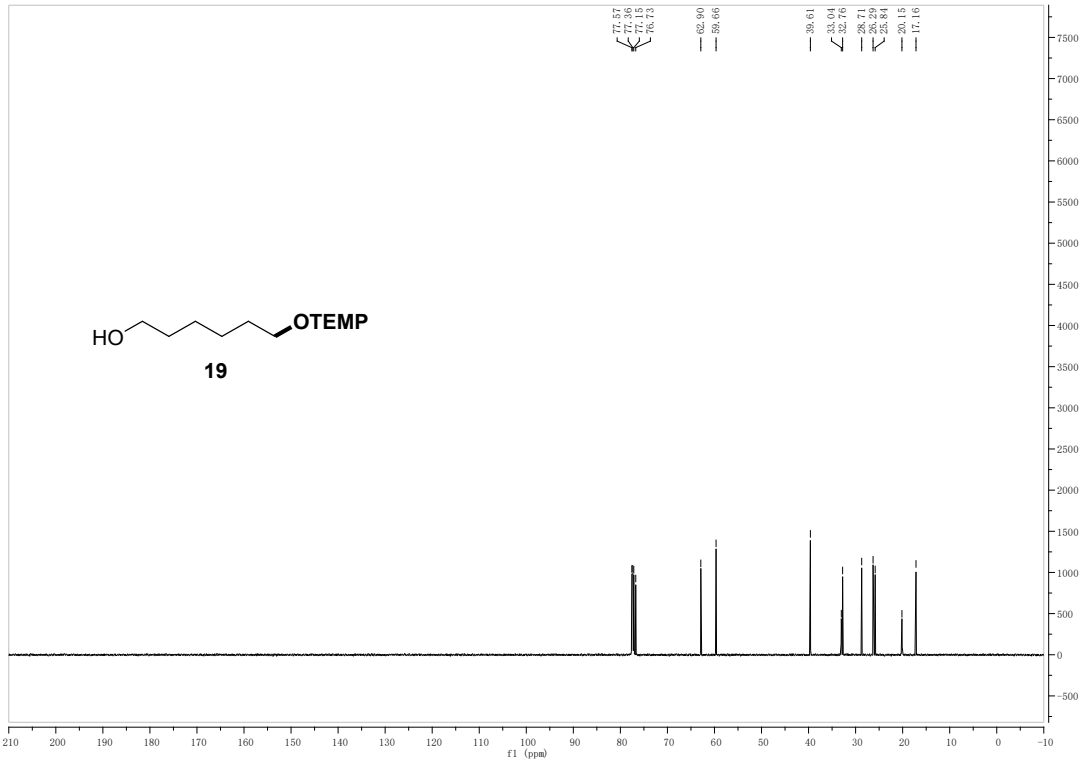
1.59
1.54
1.53
1.52
1.51
1.47
1.44
1.43
1.40
1.39
1.38
1.32
1.30
1.14
1.09
HO
OTEMP
19
2.00
2.01
15.21
5.92
6.53
f1 (ppm)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77.36
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76.73
62.90
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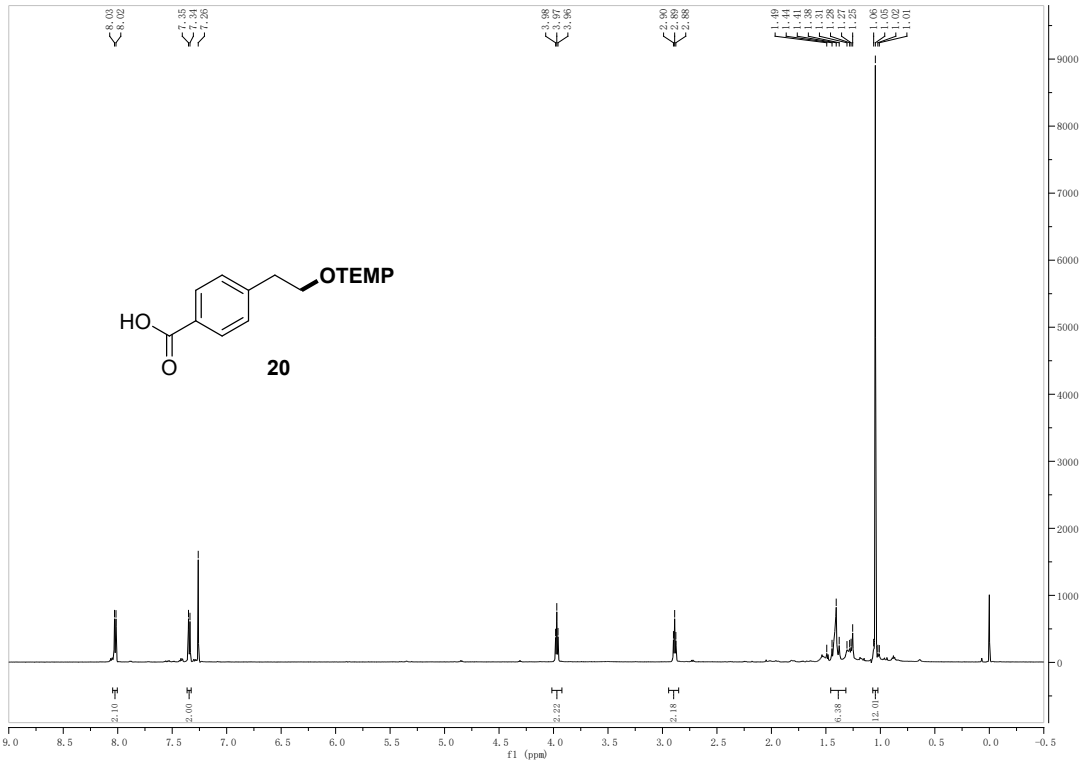
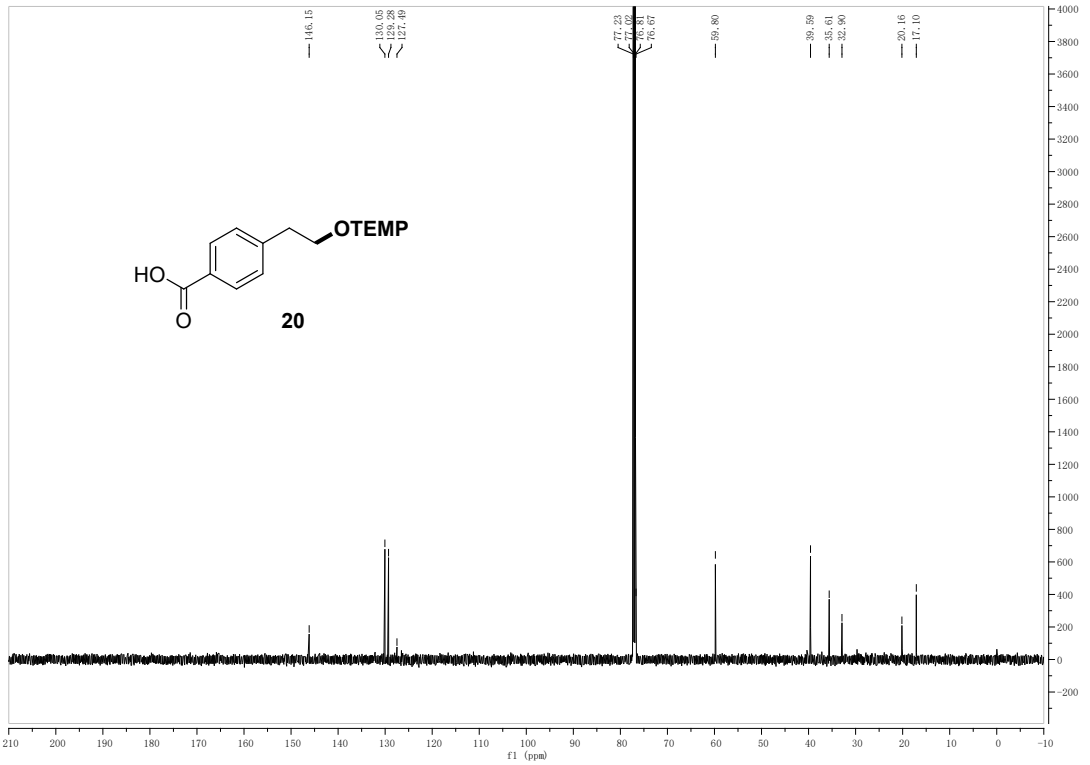
39.61
33.04
32.76
28.71
26.29
25.84
20.15
17.16
HO
OTEMP
19
f1 (ppm)


8.03
8.02
7.35
7.34
7.26
3.98
3.97
3.96
2.90
2.89
2.88
1.49
1.44
1.41
1.38
1.31
1.28
1.27
1.25
1.06
1.05
1.02
1.01
OTEMP
HO
O
20
2.10
2.00
2.22
2.18
6.38
12.01
f1 (ppm)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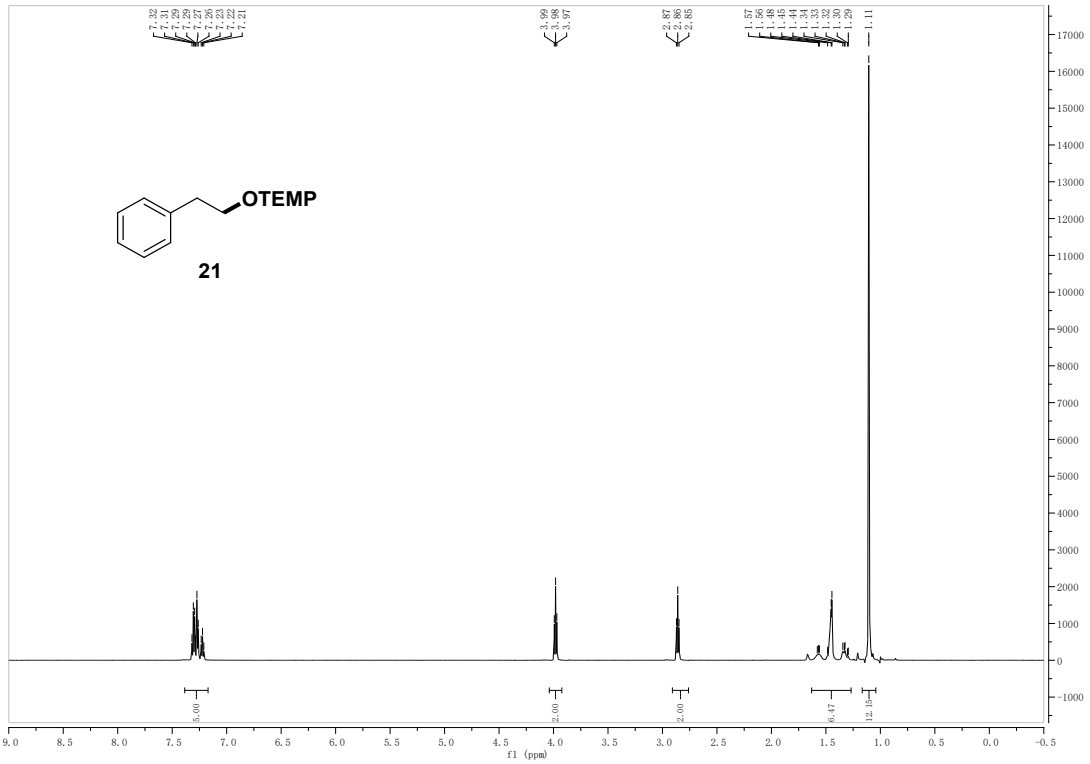
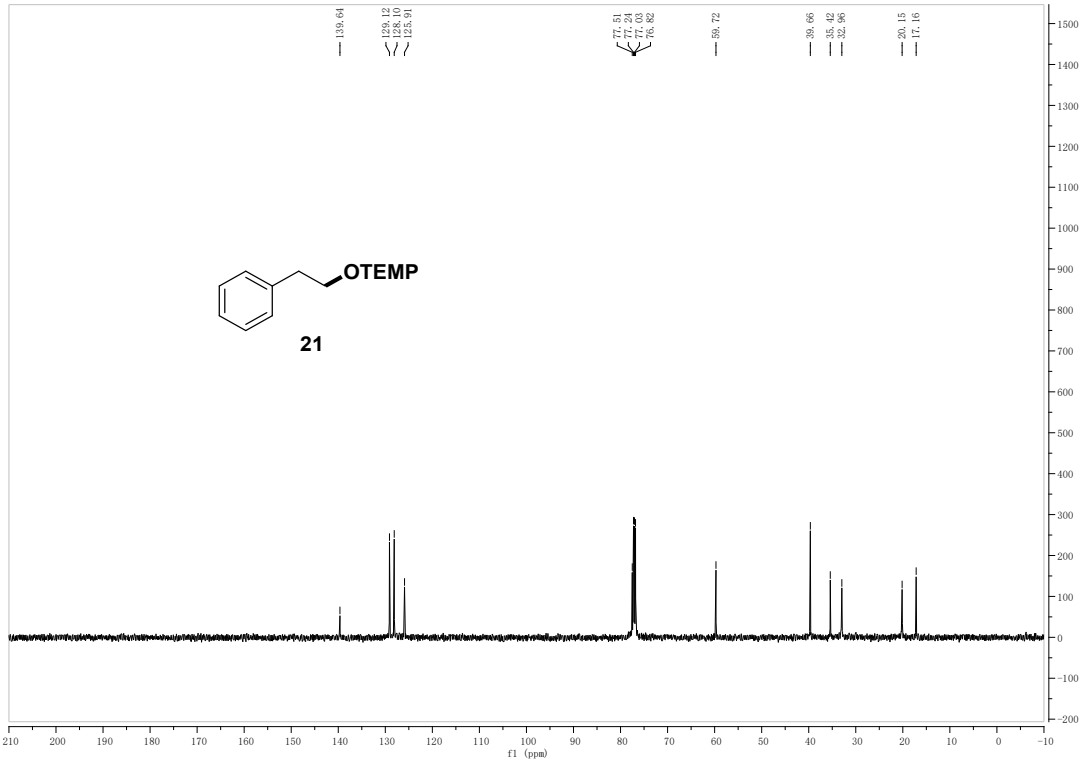
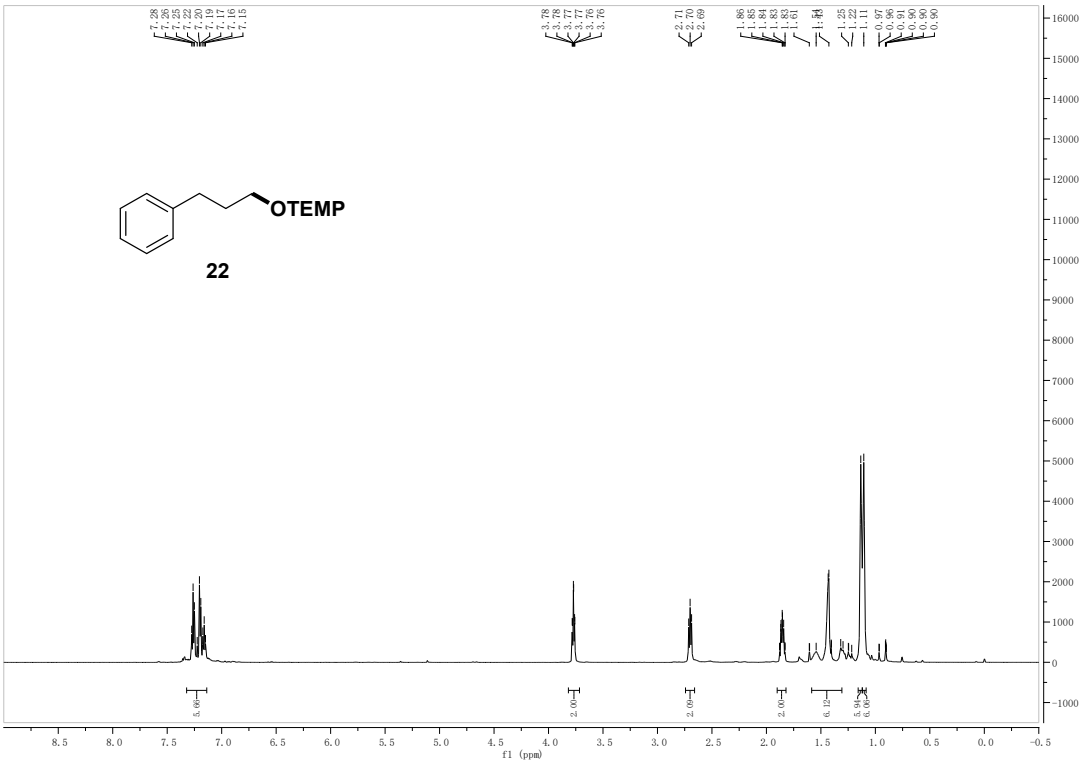
130.05
129.28
127.49
77.23
77.00
76.80
76.67
59.80
39.59
35.61
32.90
20.16
17.10
OTEMP
HO
O
20
f1 (ppm)


OTEMP
21
f1 (ppm)


OTEMP
21
f1 (ppm)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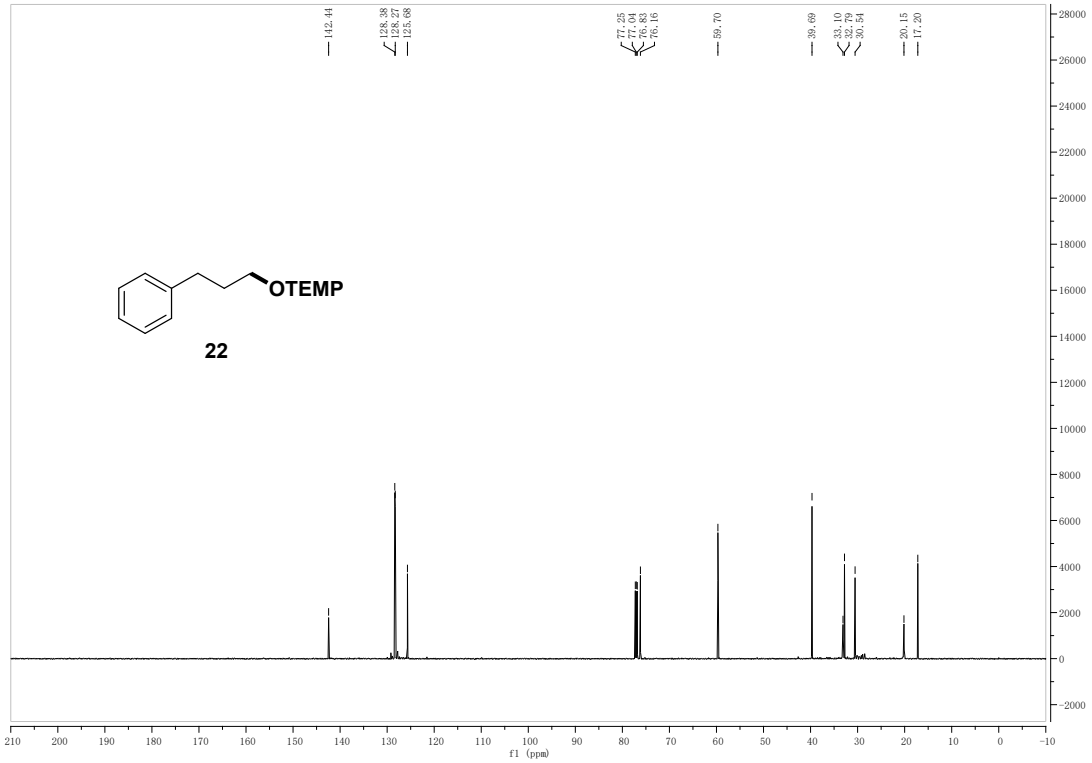
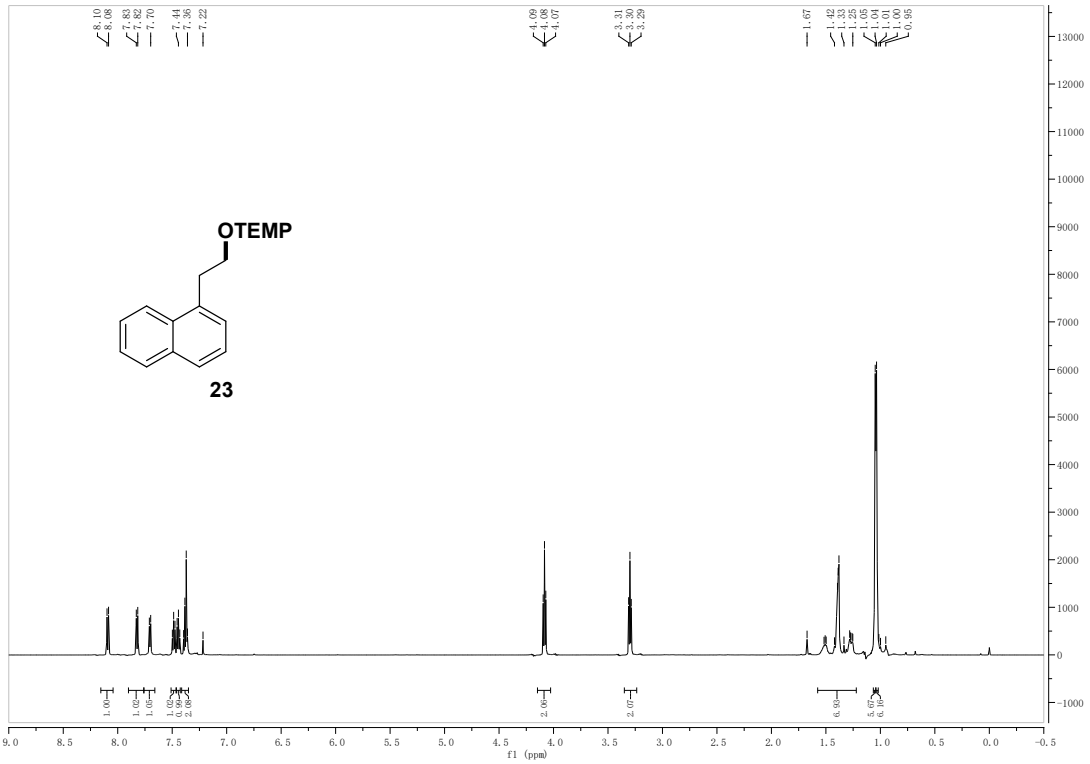
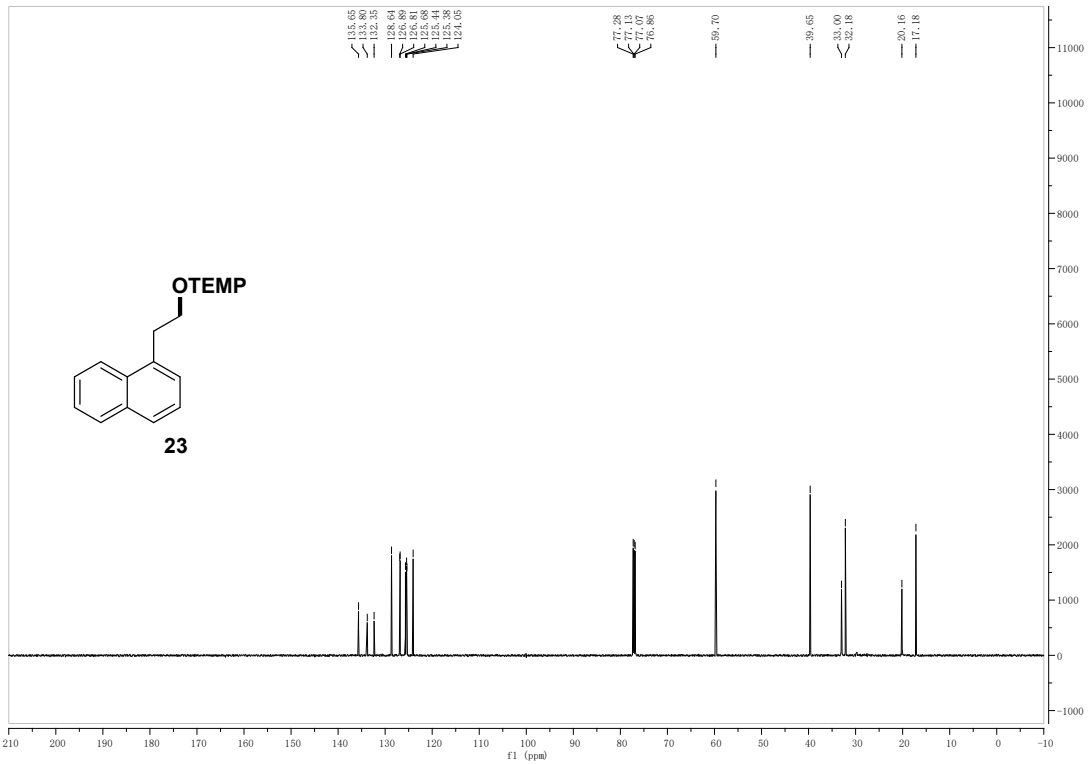
22
f1 (ppm)


OTEMP
22
f1 (ppm)


8.10
8.08
7.83
7.82
7.70
7.44
7.36
7.22
4.09
4.08
4.07
3.31
3.30
3.29
1.67
1.42
1.33
1.25
1.05
1.04
1.01
1.00
0.95
OTEMP
23
f1 (ppm)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133.80
132.35
128.64
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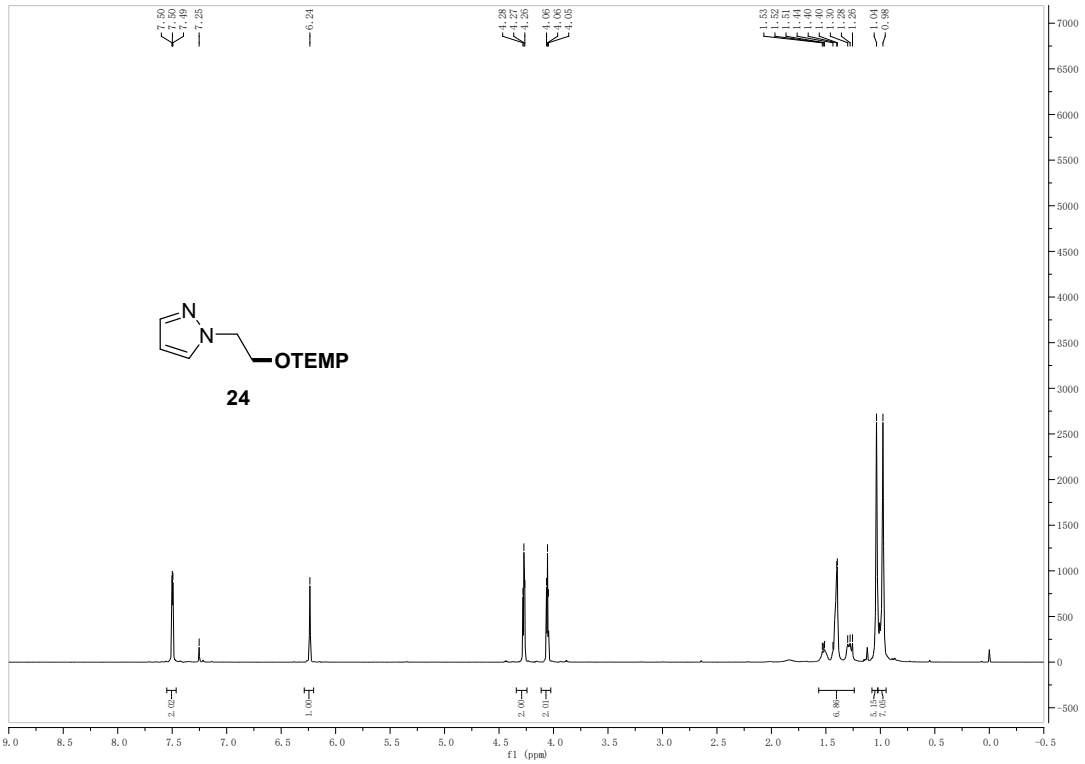
125.81
125.68
125.44
125.38
124.05
77.28
77.13
77.07
76.86
59.70
39.65
33.00
32.18
20.16
17.18
OTEMP
23
f1 (ppm)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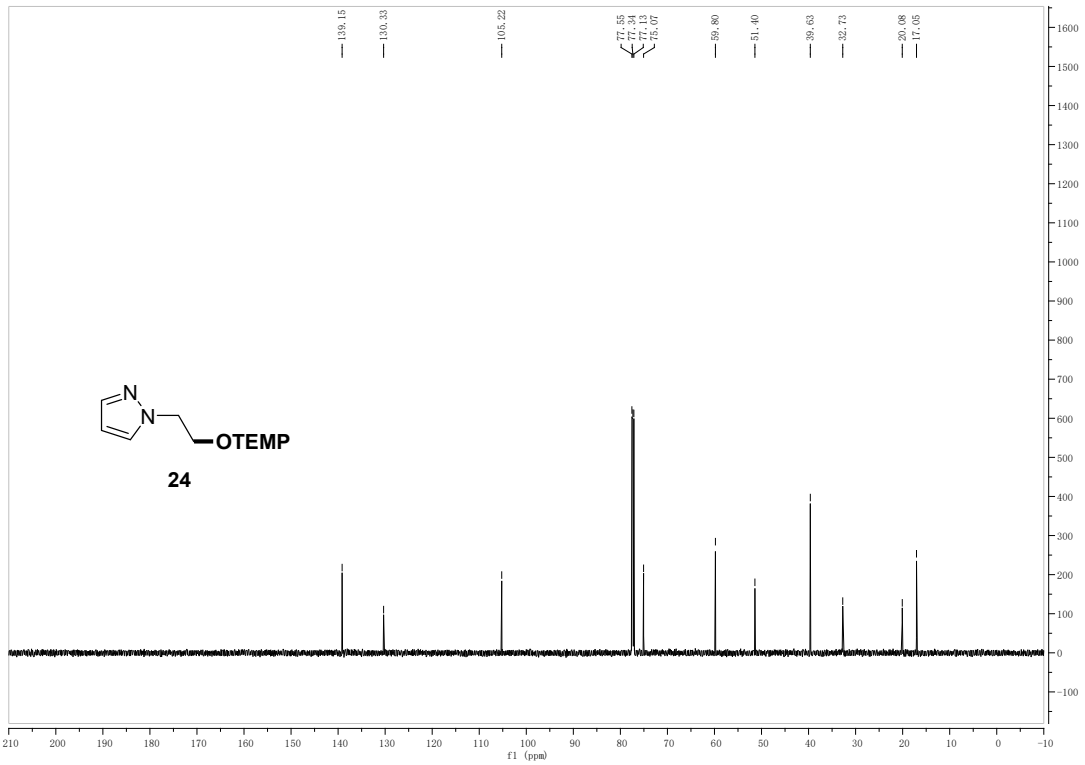
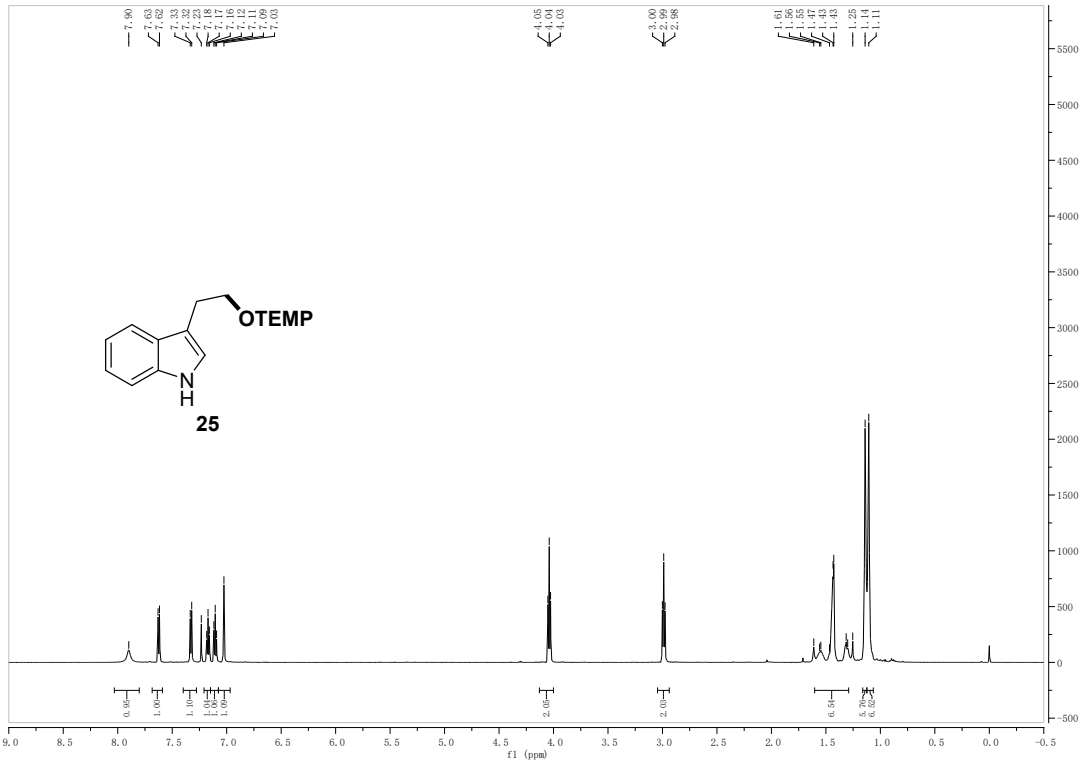
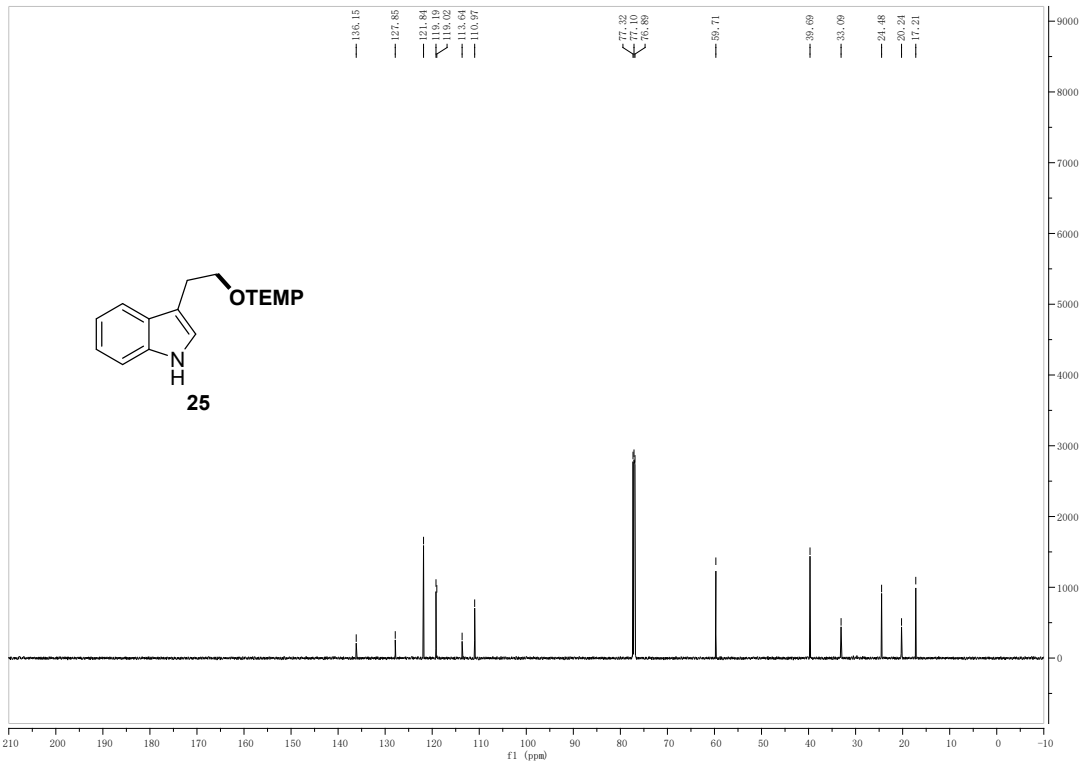
7.50
7.49
7.25
6.24
4.28
4.27
4.26
4.05
4.05
4.05
1.53
1.52
1.51
1.44
1.40
1.40
1.30
1.28
1.25
1.04
0.98
OTEMP
24
2.02
1.00
2.00
2.01
6.86
5.15
7.05
f1 (ppm)


139.15
130.33
105.22
77.55
77.34
77.13
76.07
59.80
51.40
39.63
32.73
20.08
17.05
OTEMP
24
f1 (ppm)


OTEMP
N
H
25
f1 (ppm)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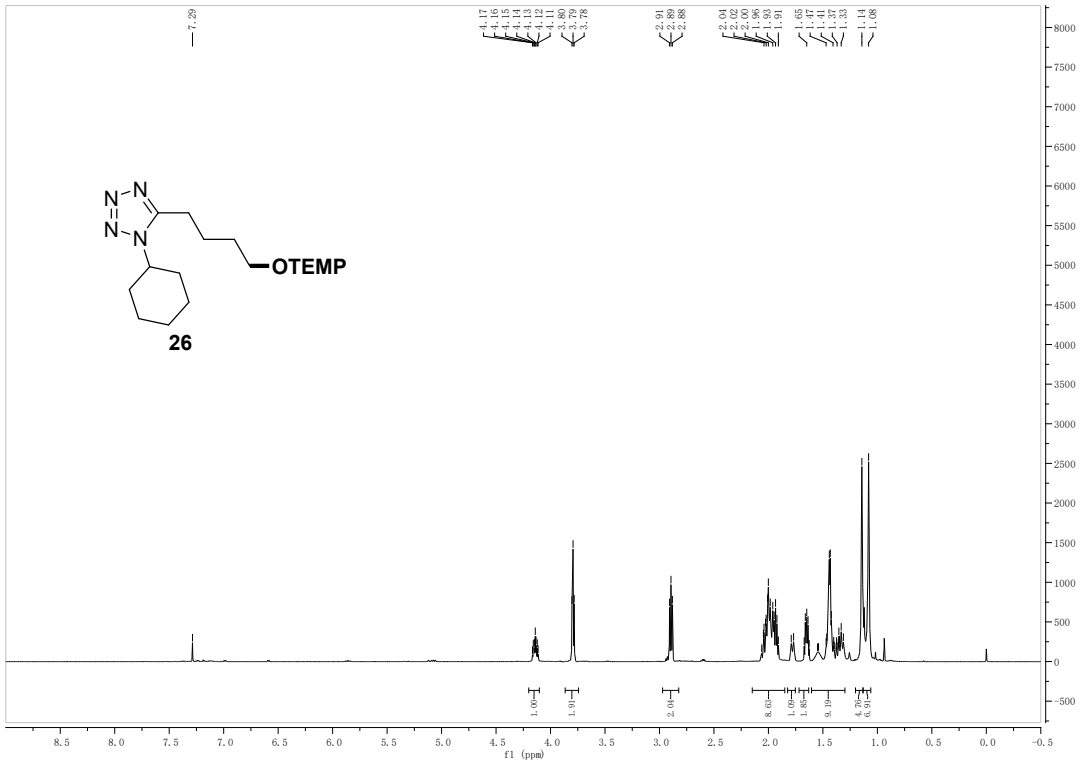
N
H
25
f1 (ppm)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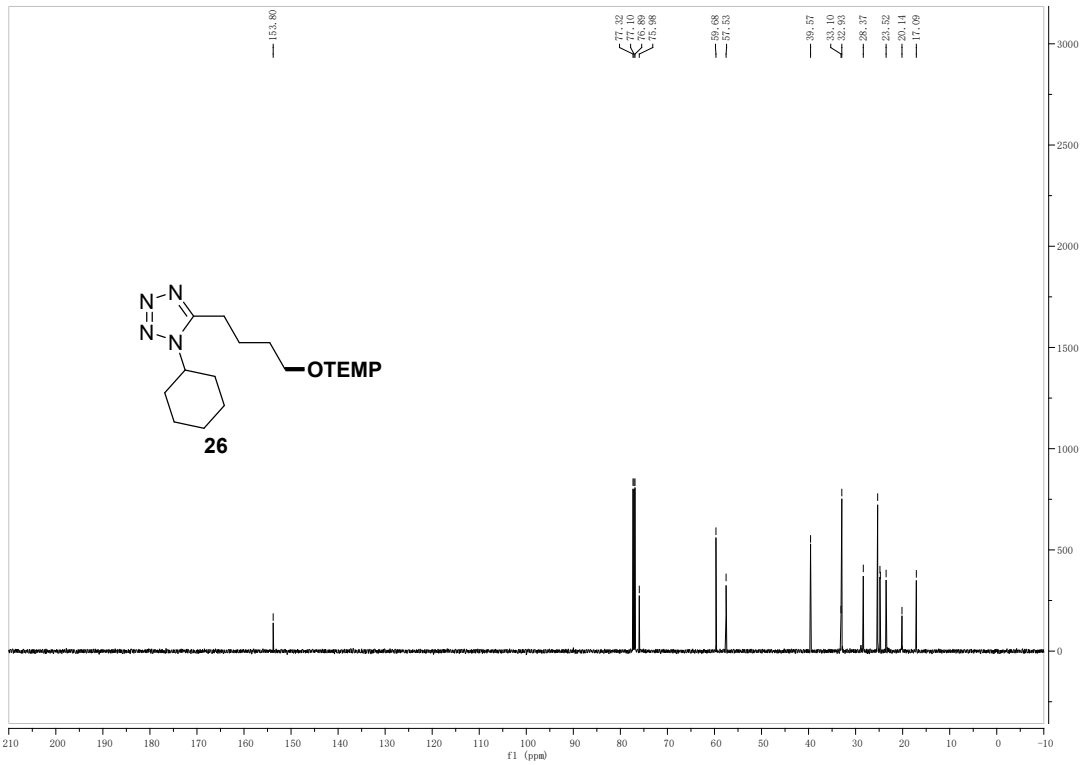
26
f1 (ppm)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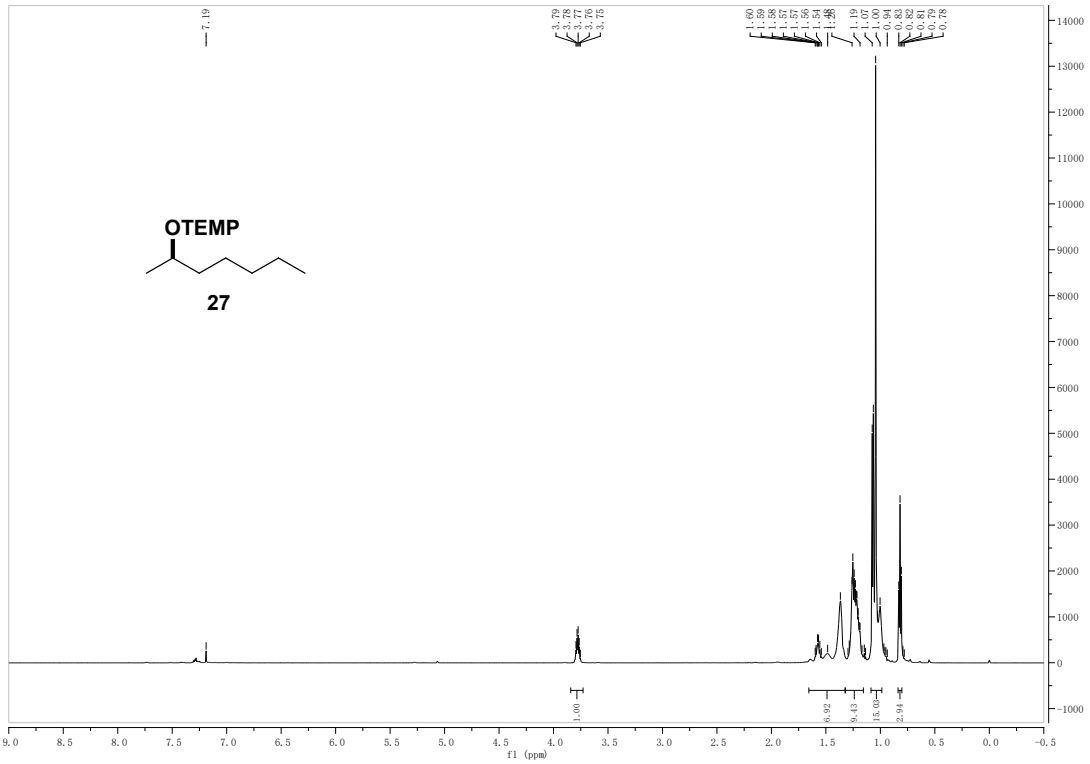
26
f1 (ppm)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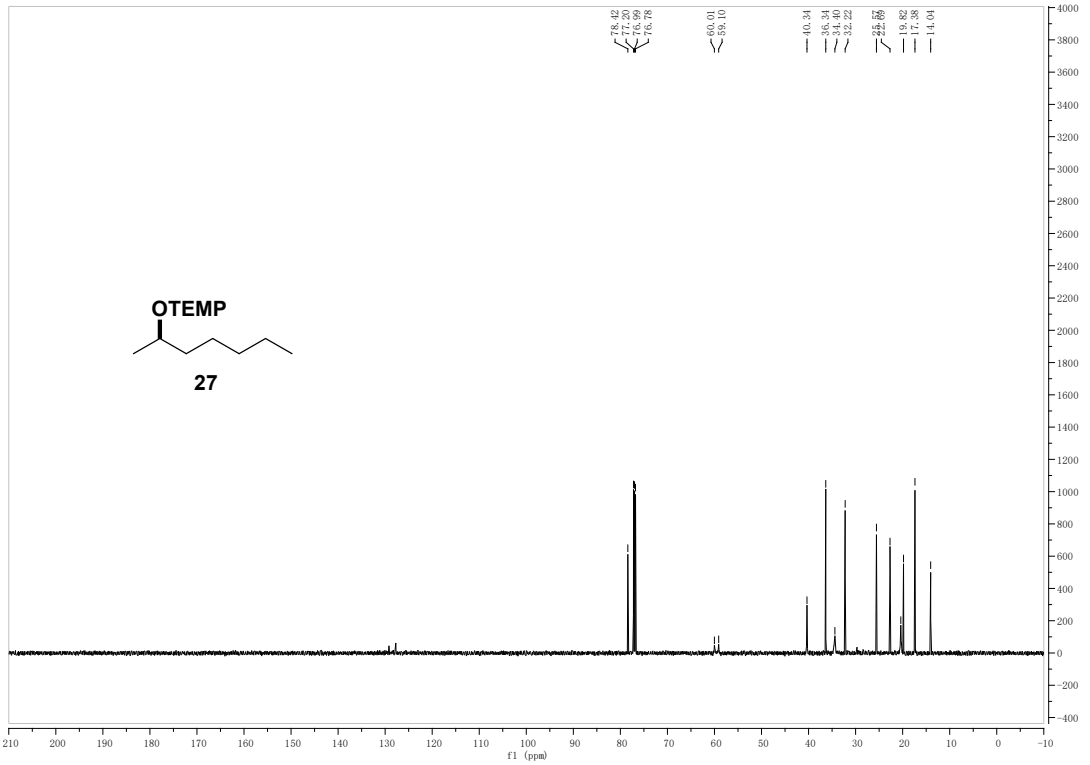
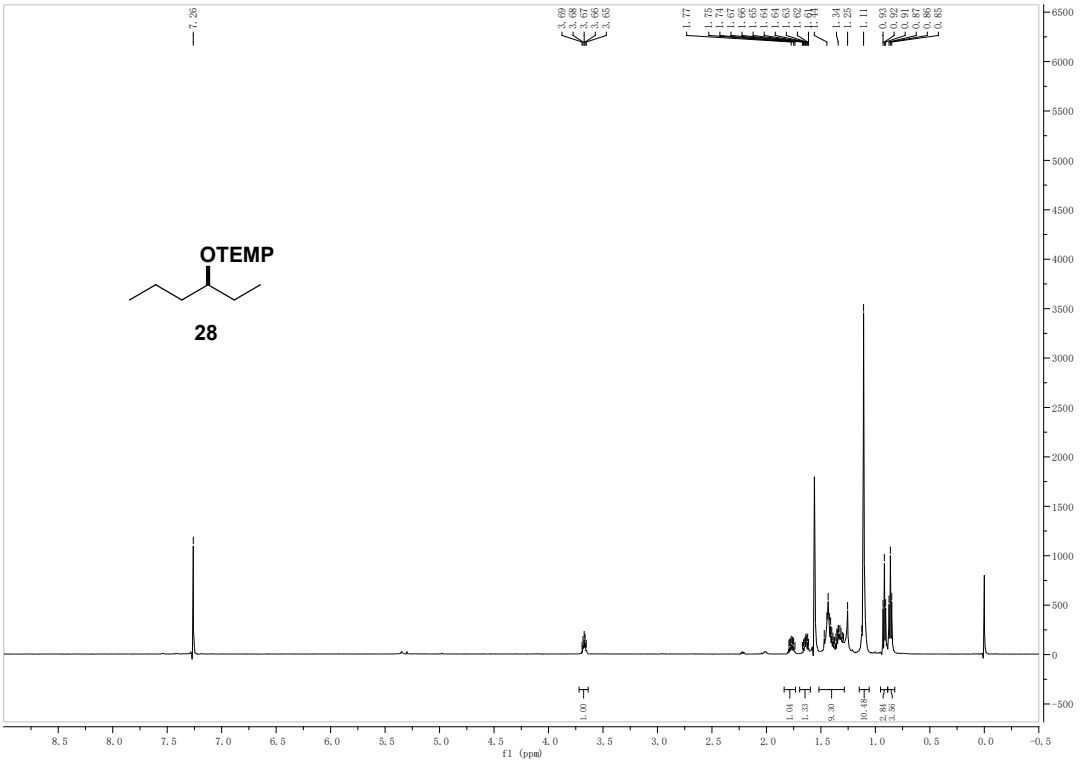
f1 (ppm)


OTEMP
27
f1 (ppm)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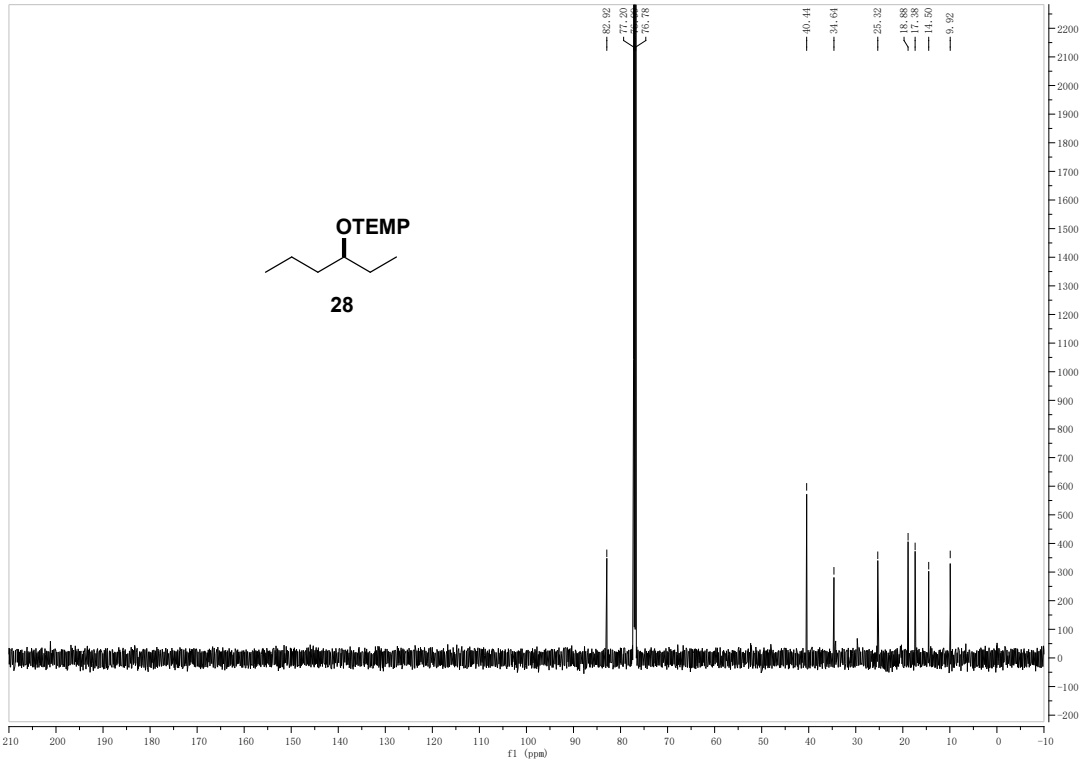
28
f1 (ppm)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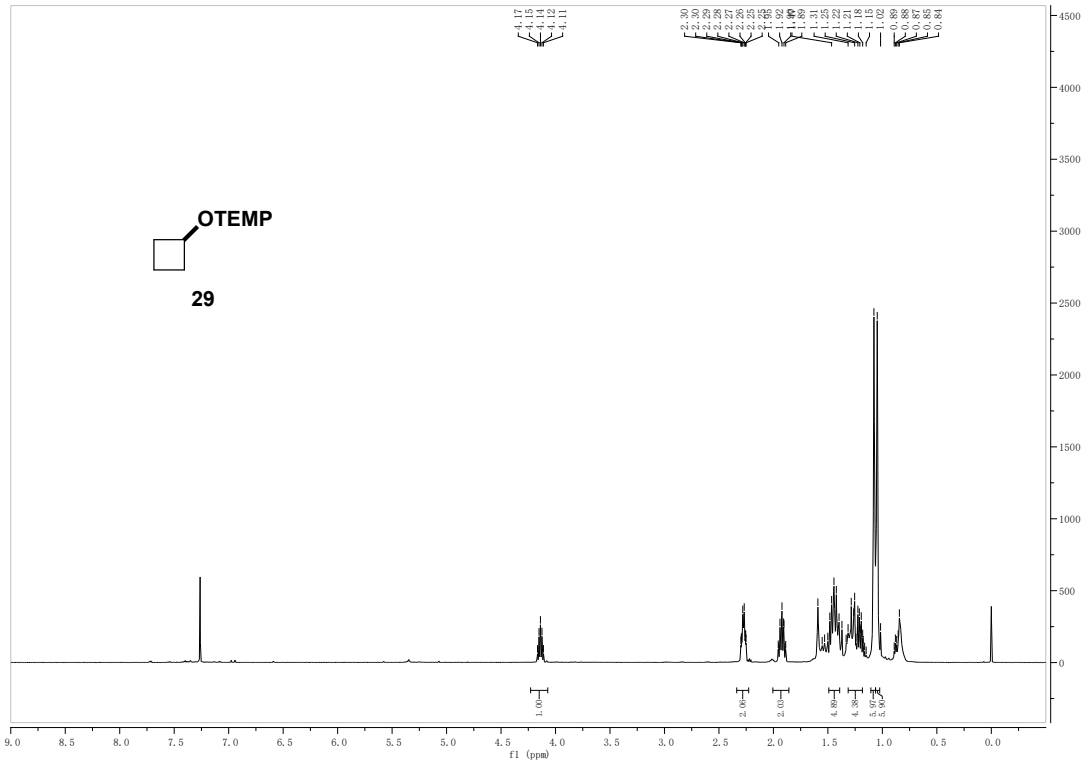
28
f1 (ppm)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29
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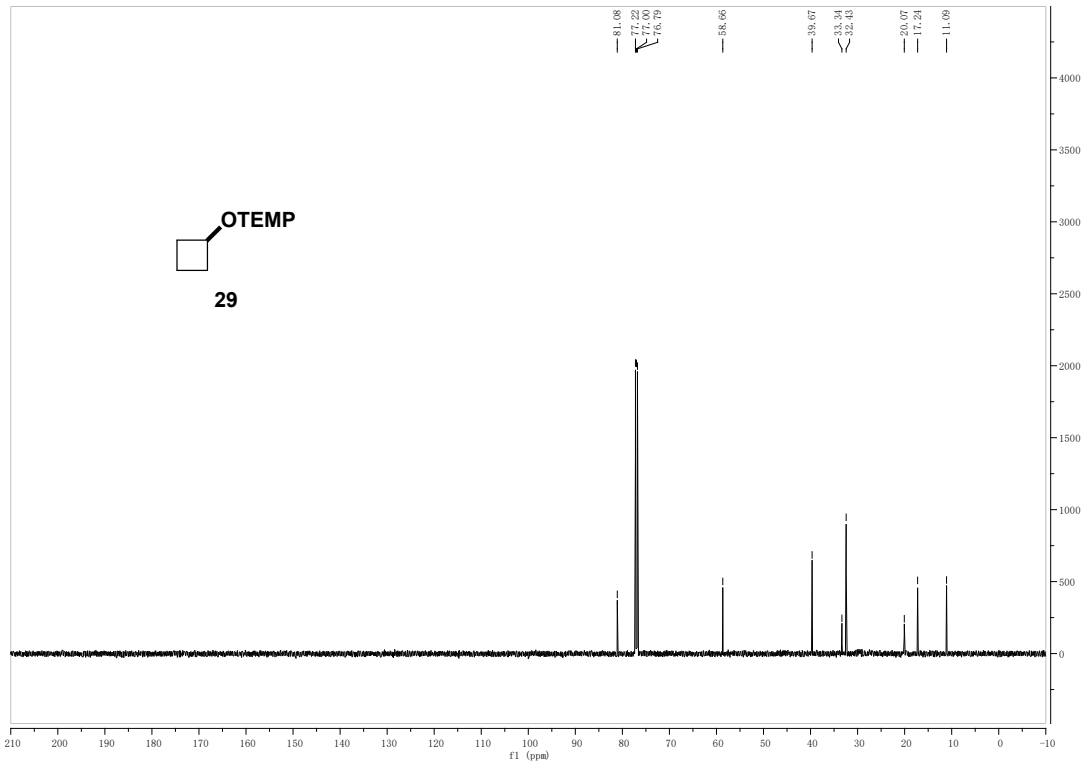
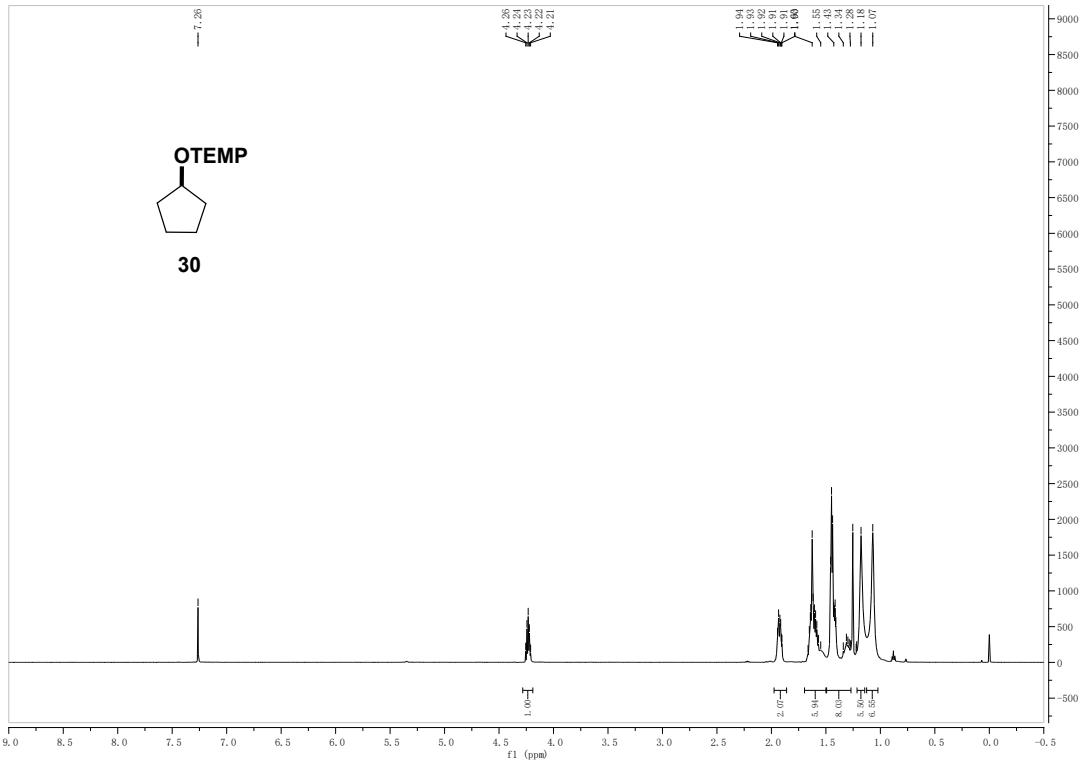

OTEMP
29
f1 (ppm)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4.23
4.22
4.21
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1.92
1.91
1.91
1.55
1.43
1.34
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1.18
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OTEMP
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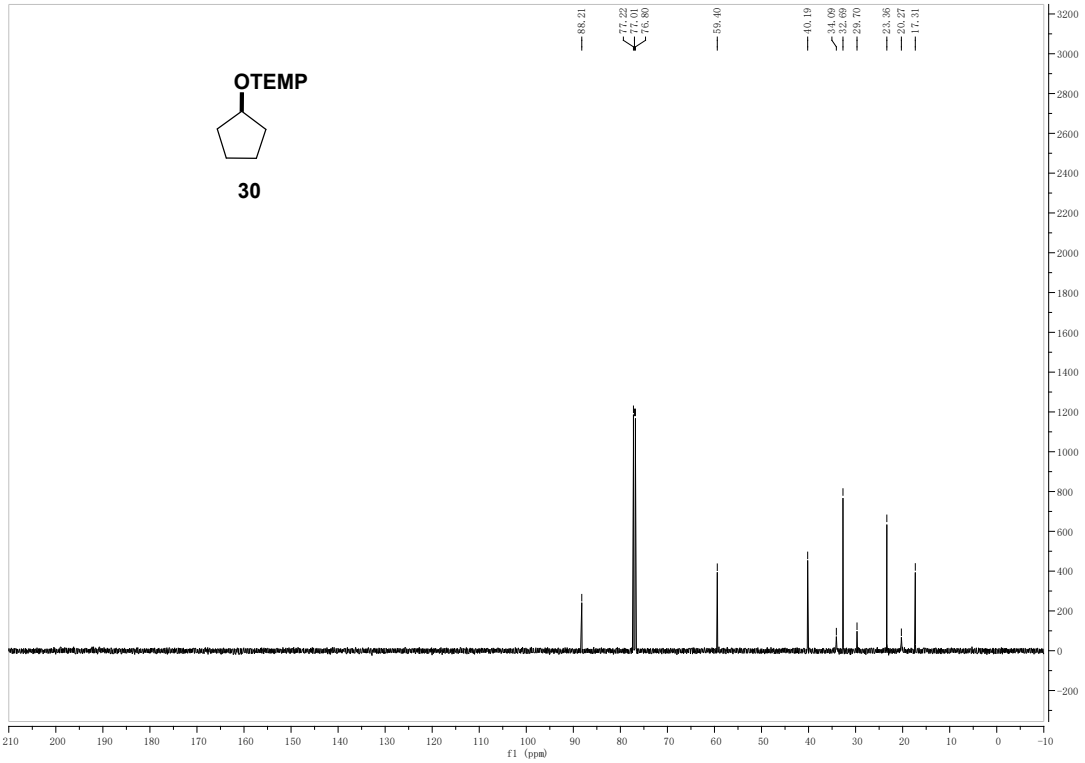
1.00
2.07
5.94
8.03
5.90
6.55
f1 (ppm)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40.19
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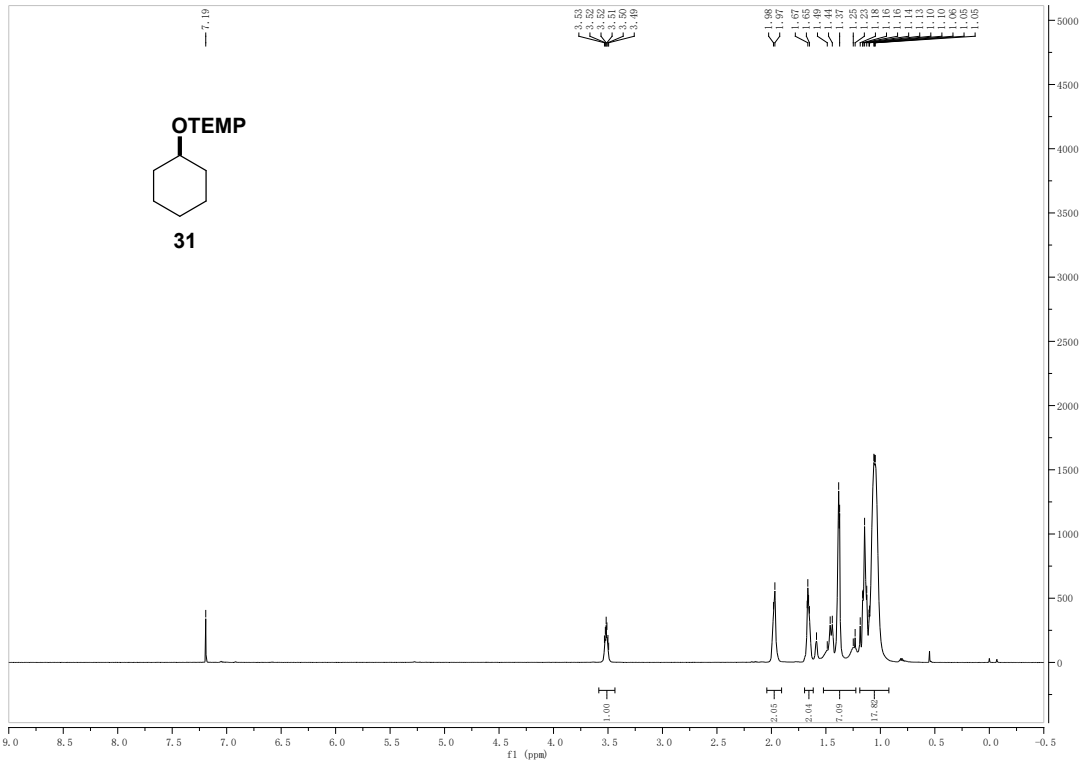
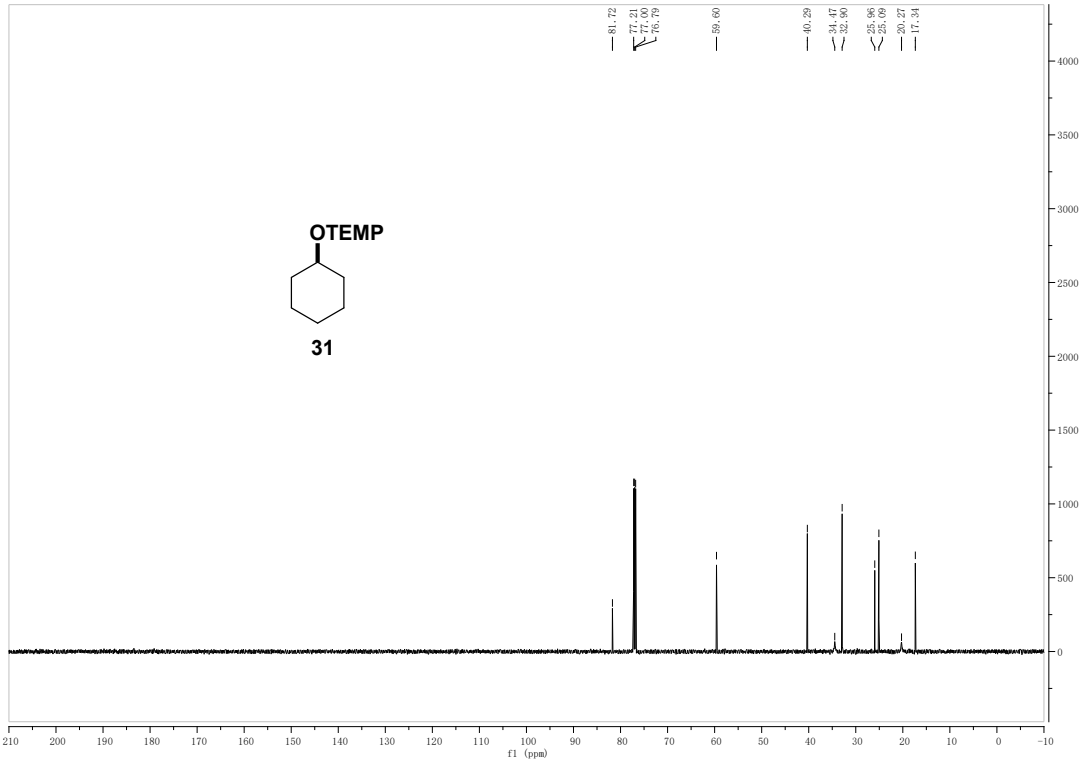
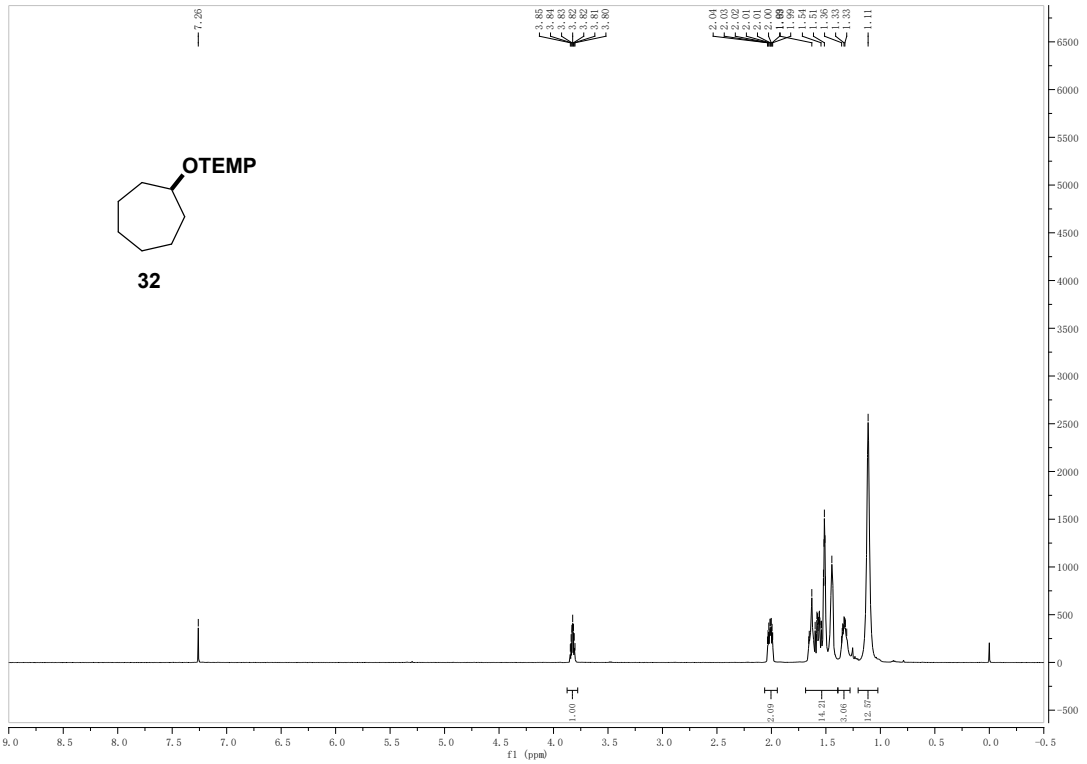
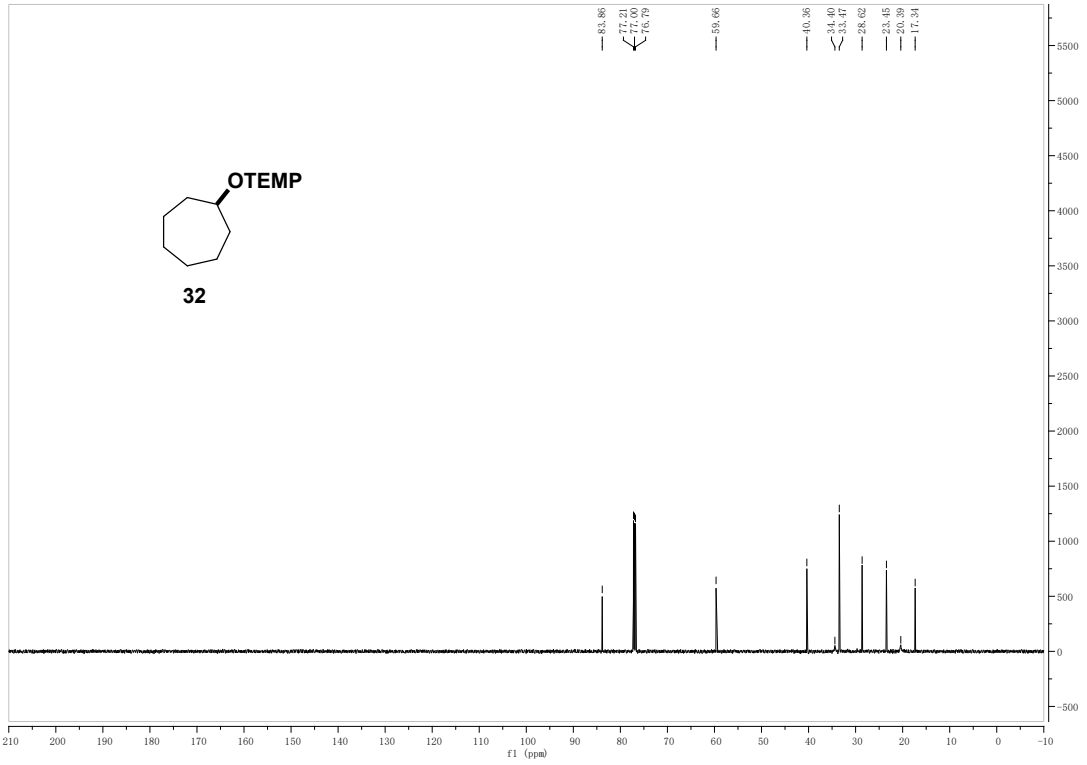
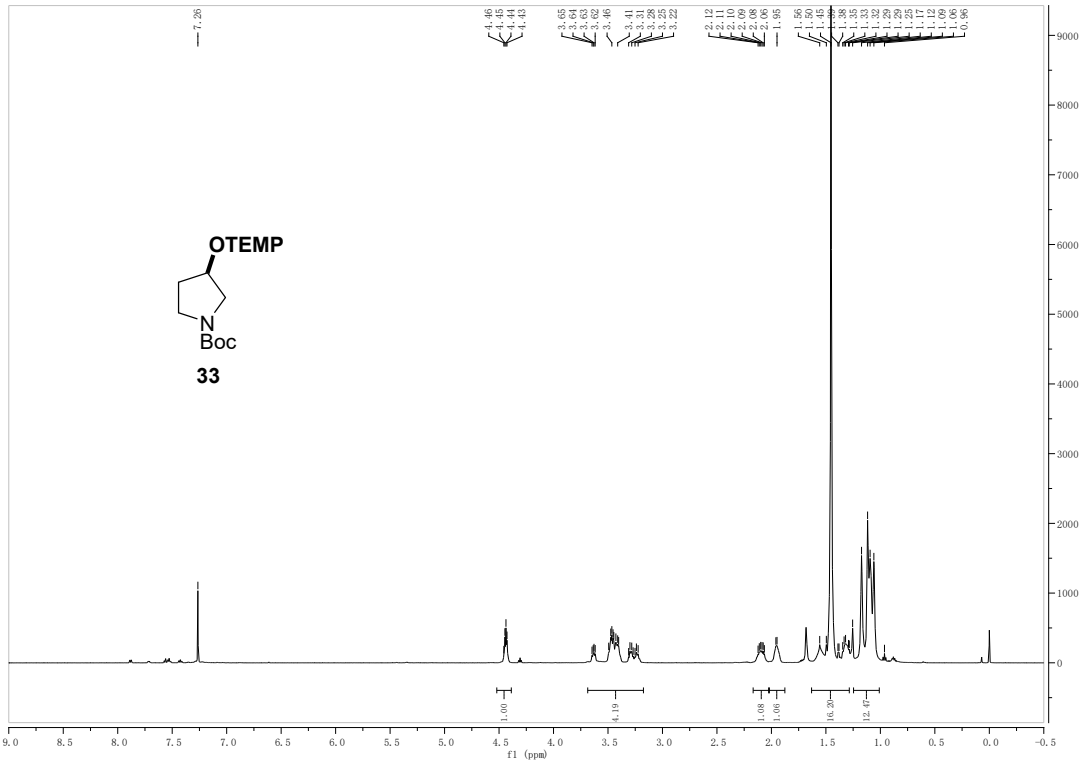
29.70
23.36
20.27
17.31
OTEMP
30
f1 (ppm)


OTEMP
31
f1 (ppm)


OTEMP
31
f1 (ppm)


OTEMP
32
f1 (ppm)


OTEMP
32
f1 (ppm)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N
Boc
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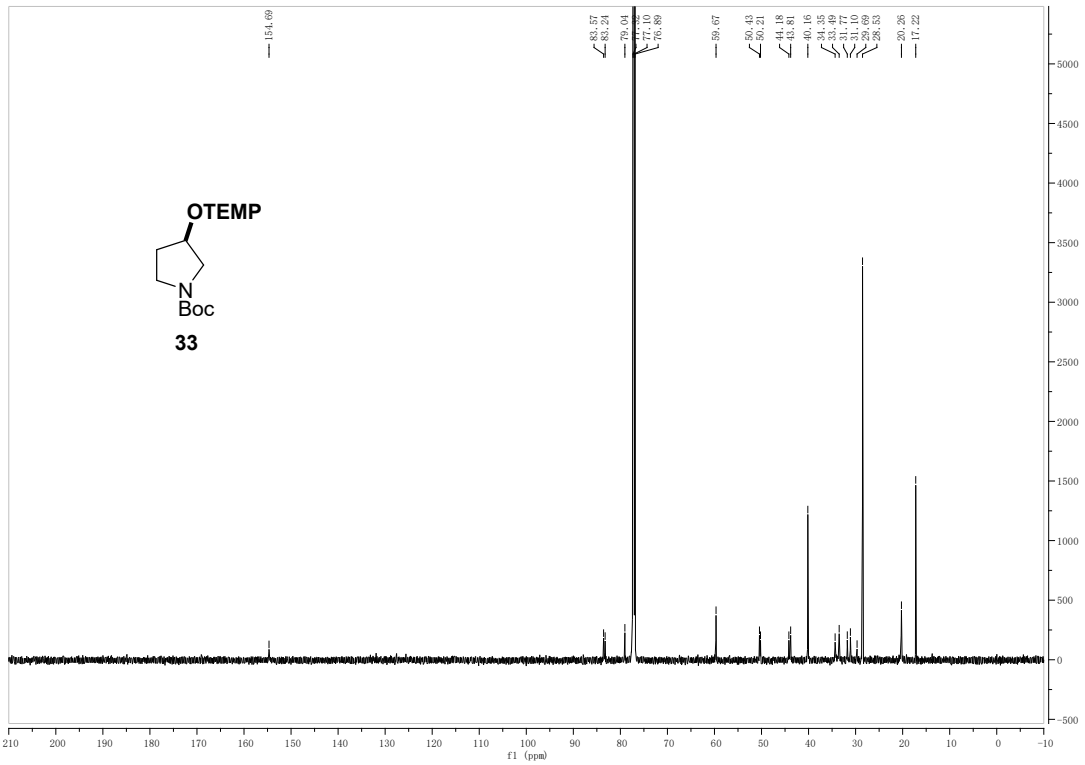
f1 (ppm)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Boc
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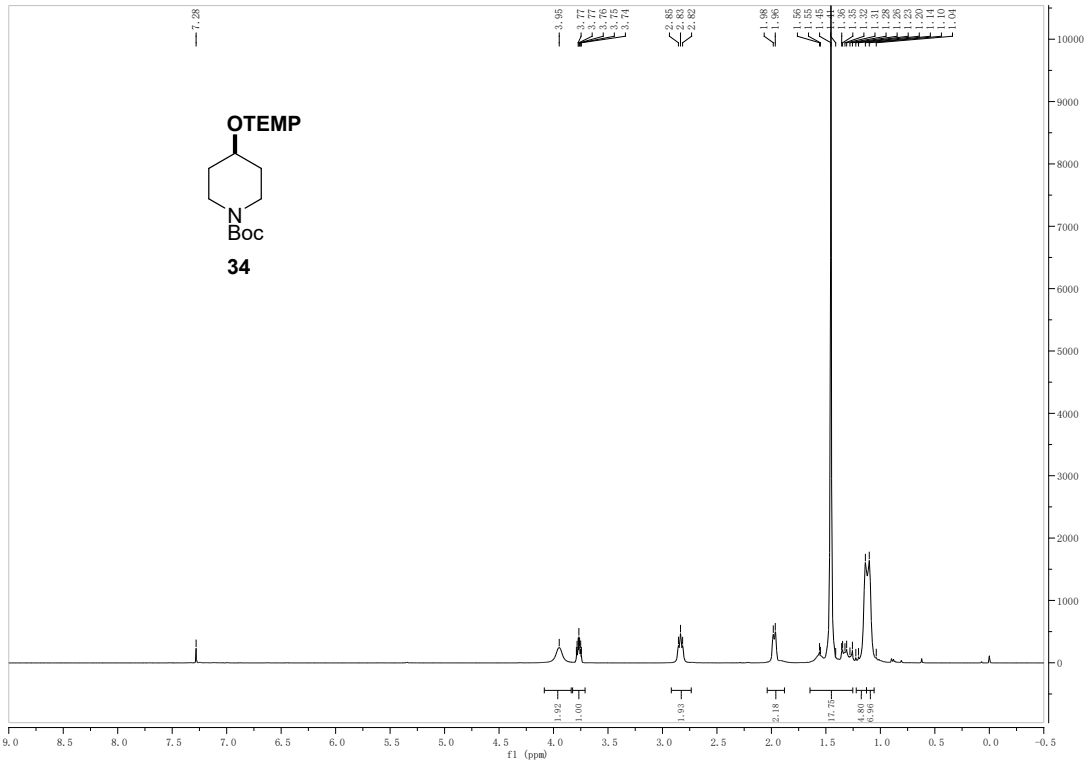
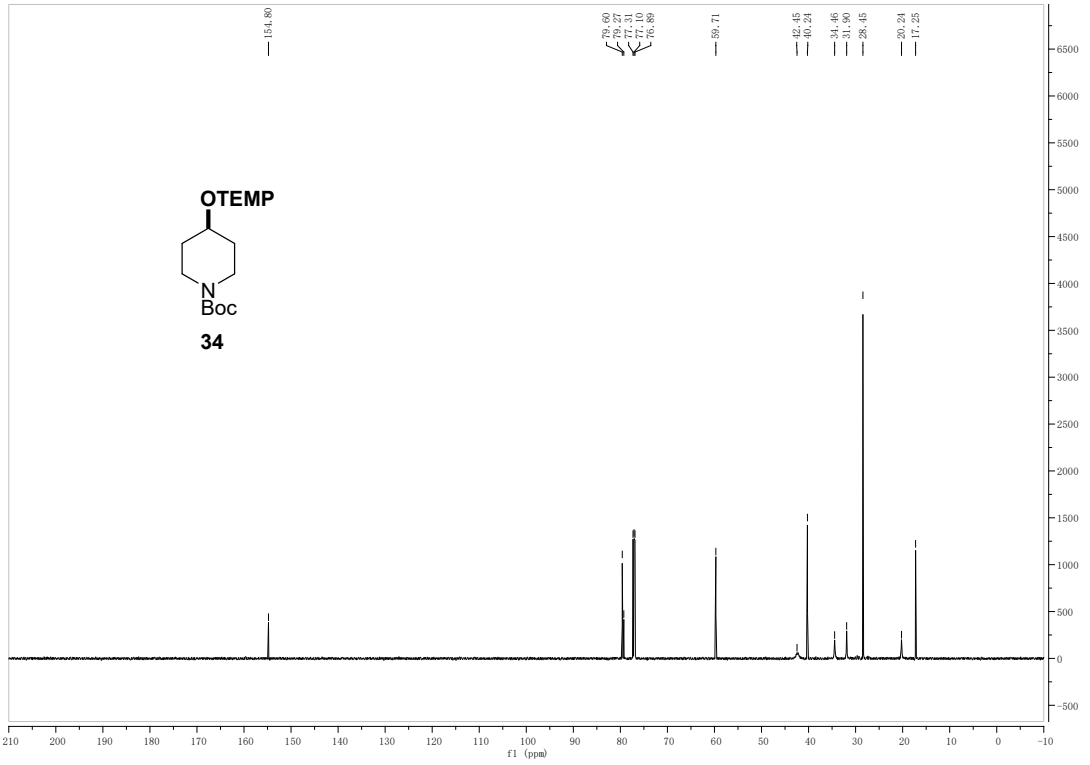
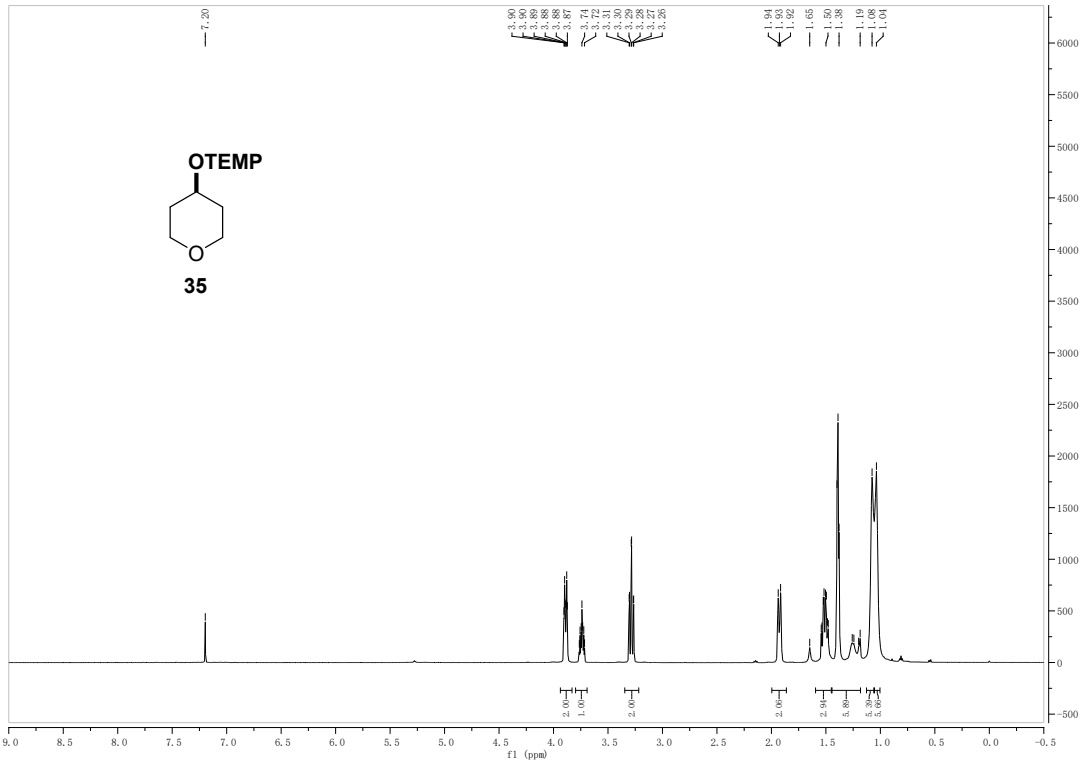
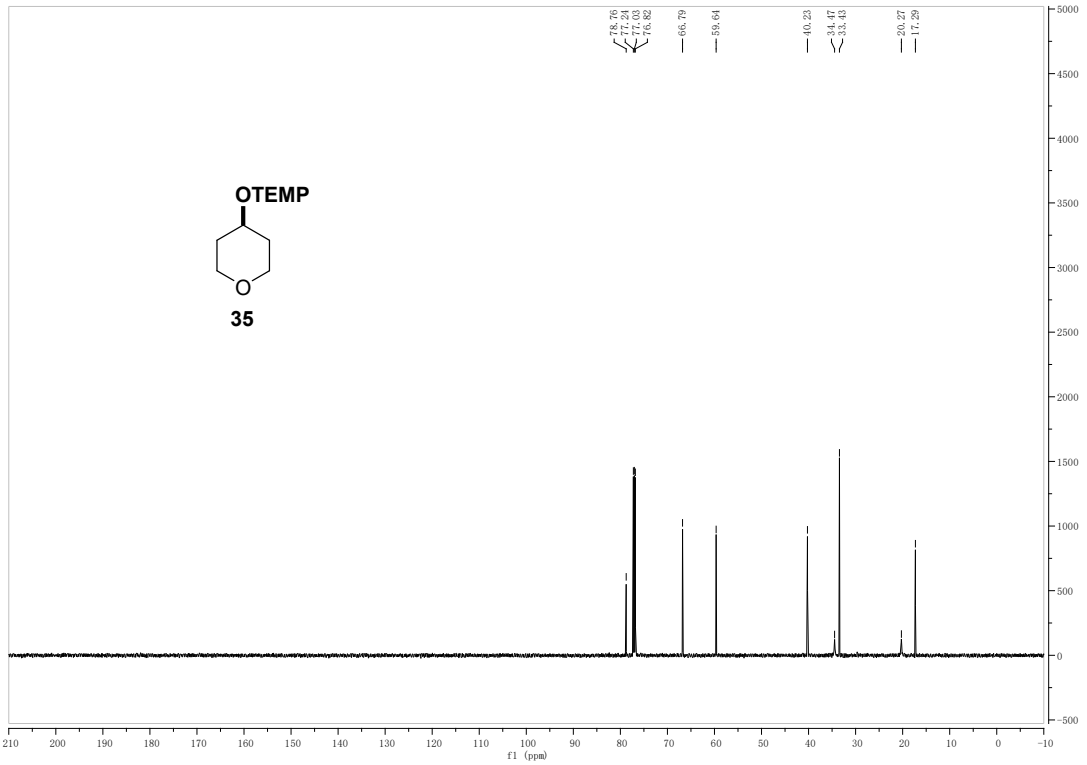
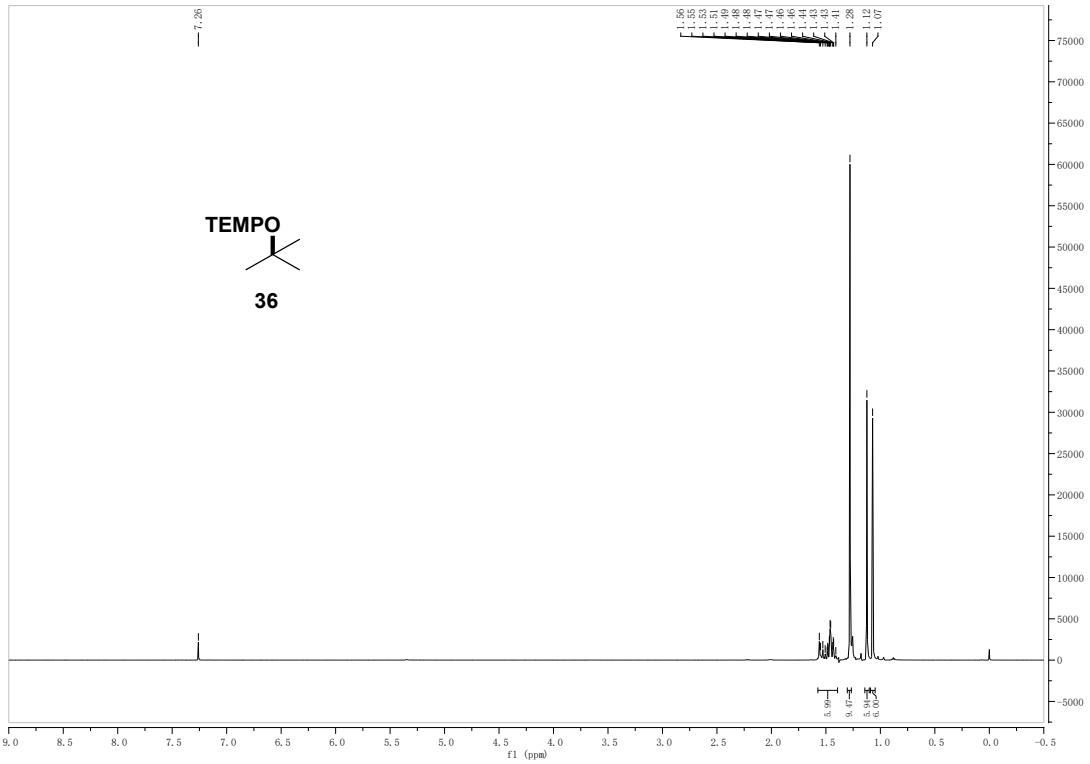
f1 (ppm)

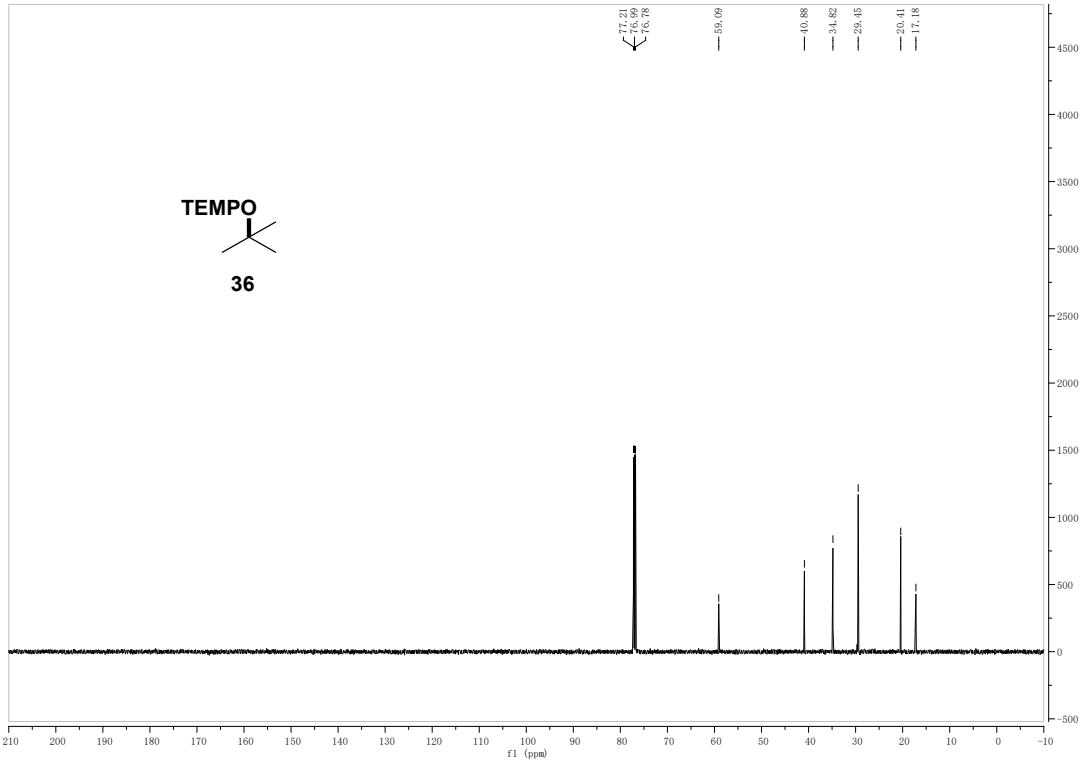

OTEMP
N
Boc
34
f1 (ppm)

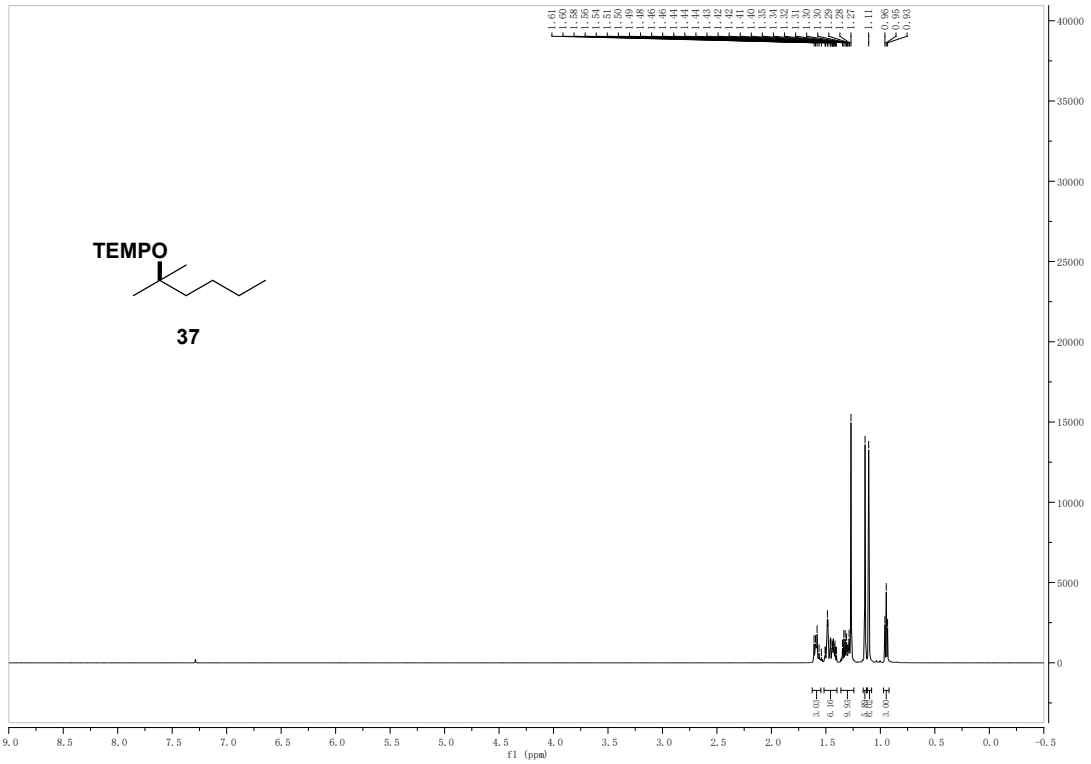

OTEMP
N
Boc
34
f1 (ppm)

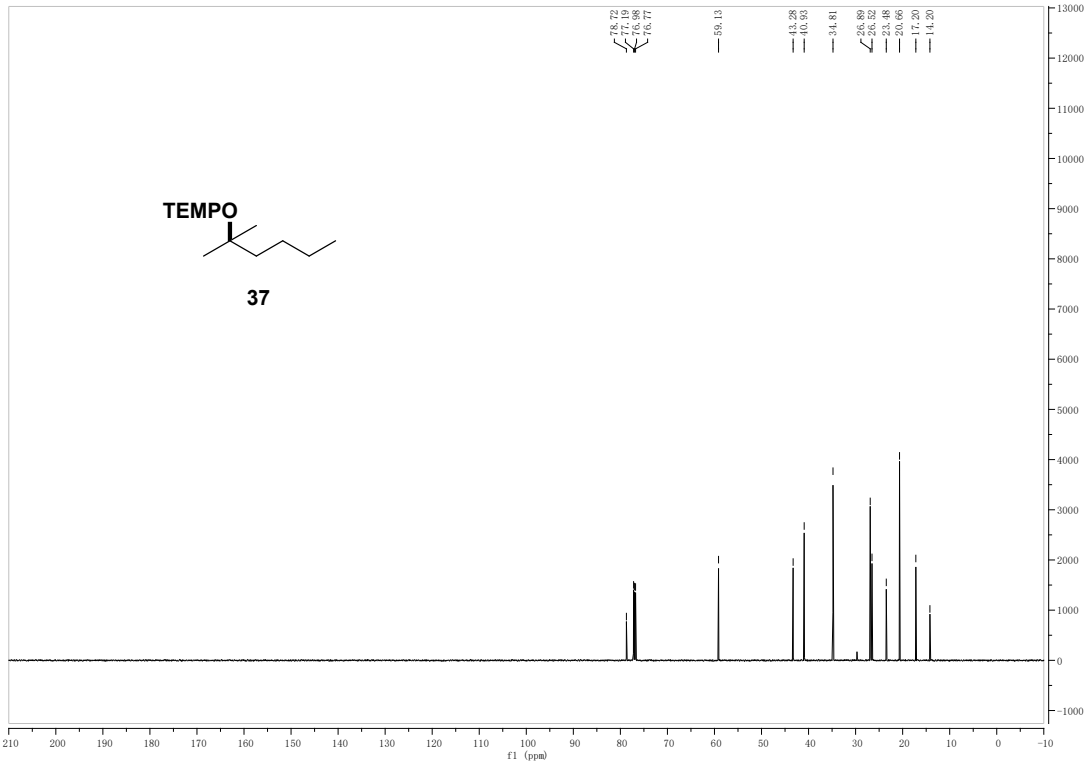

OTEMP
O
35
f1 (ppm)

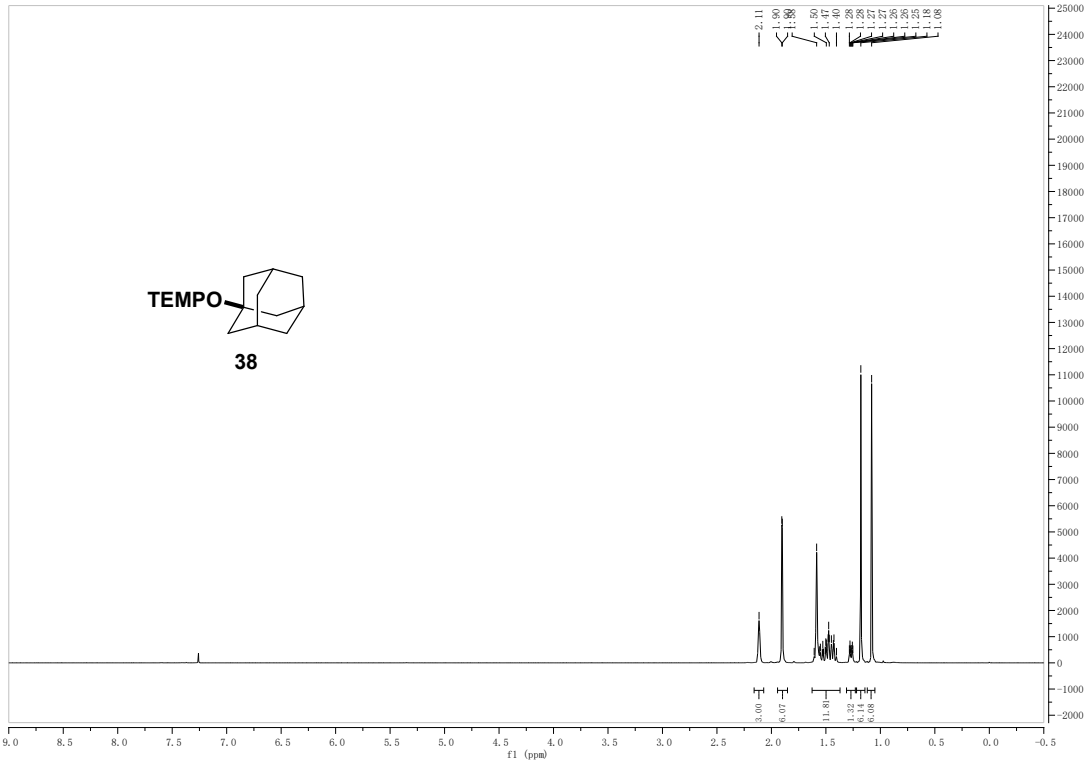

OTEMP
O
35
f1 (ppm)

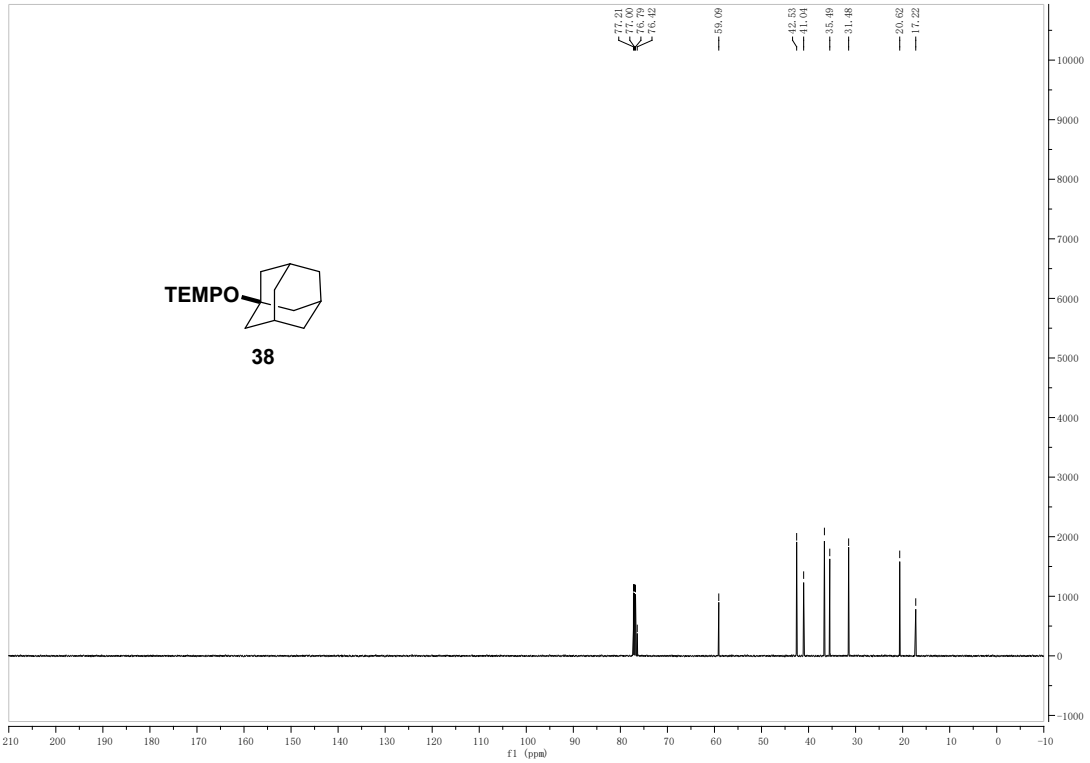

7.26
1.56
1.55
1.53
1.51
1.49
1.48
1.47
1.46
1.44
1.43
1.41
1.28
1.12
1.07
TEMPO
36
5.99
9.47
5.90
5.00
f1 (ppm)

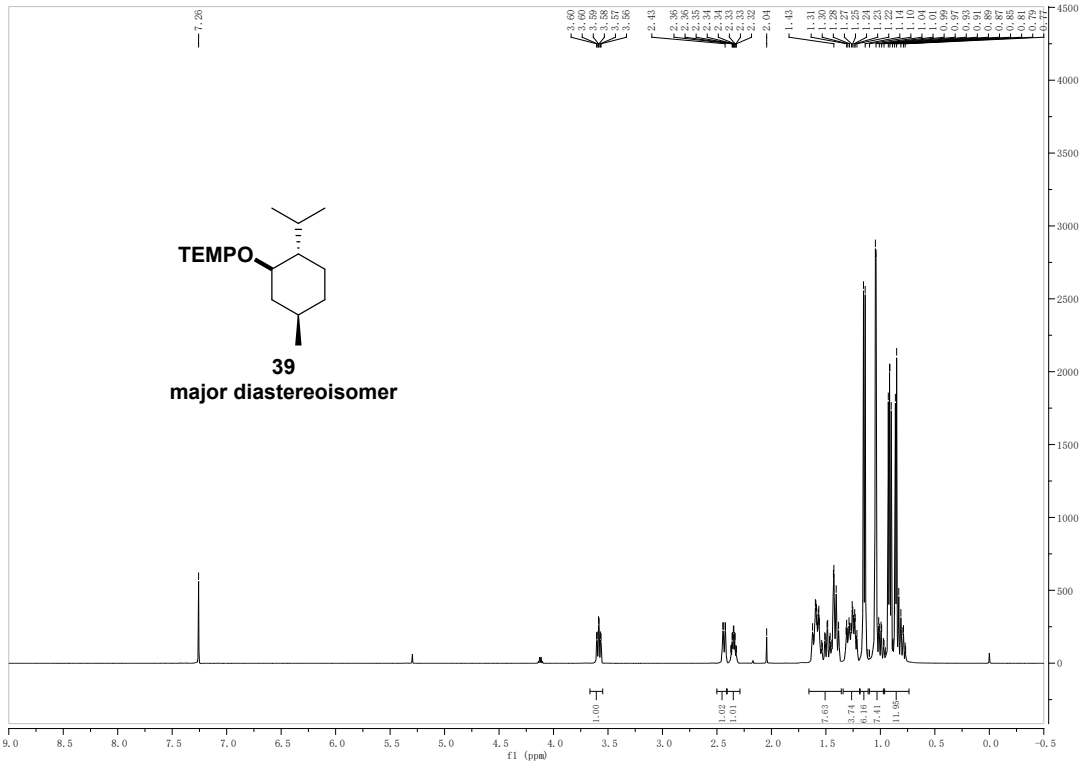

77.21
76.99
76.78
59.09
40.88
34.82
29.45
20.41
17.18
TEMPO
36
f1 (ppm)

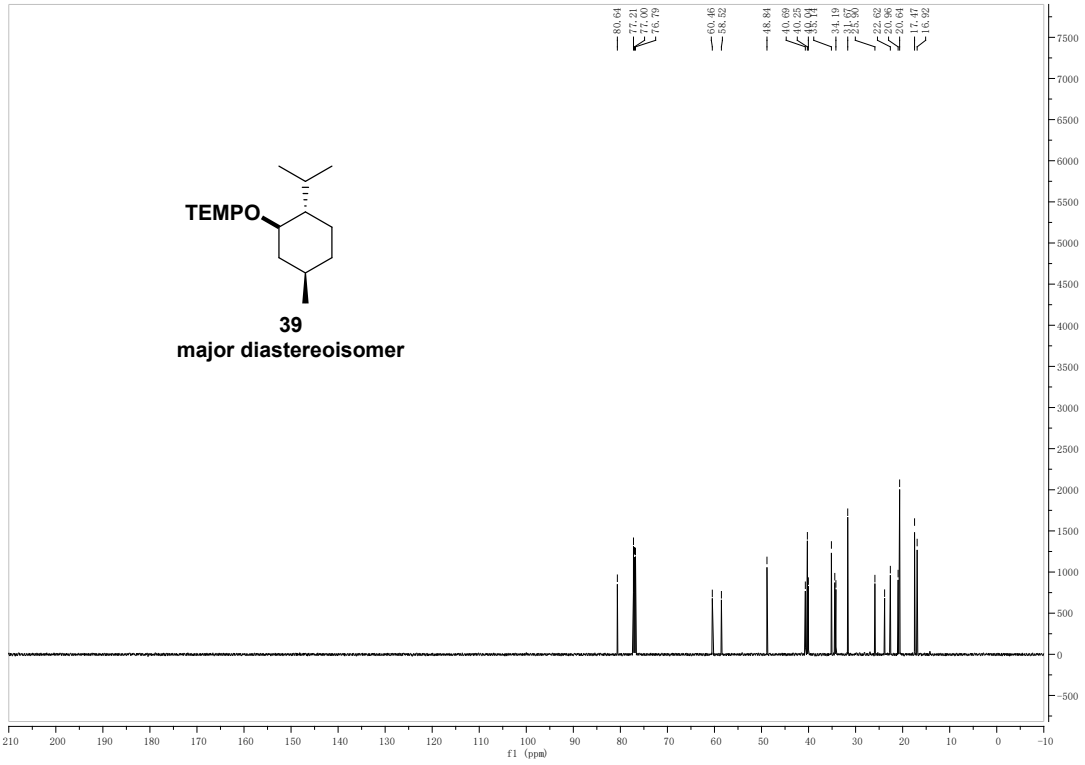

TEMPO
37
f1 (ppm)

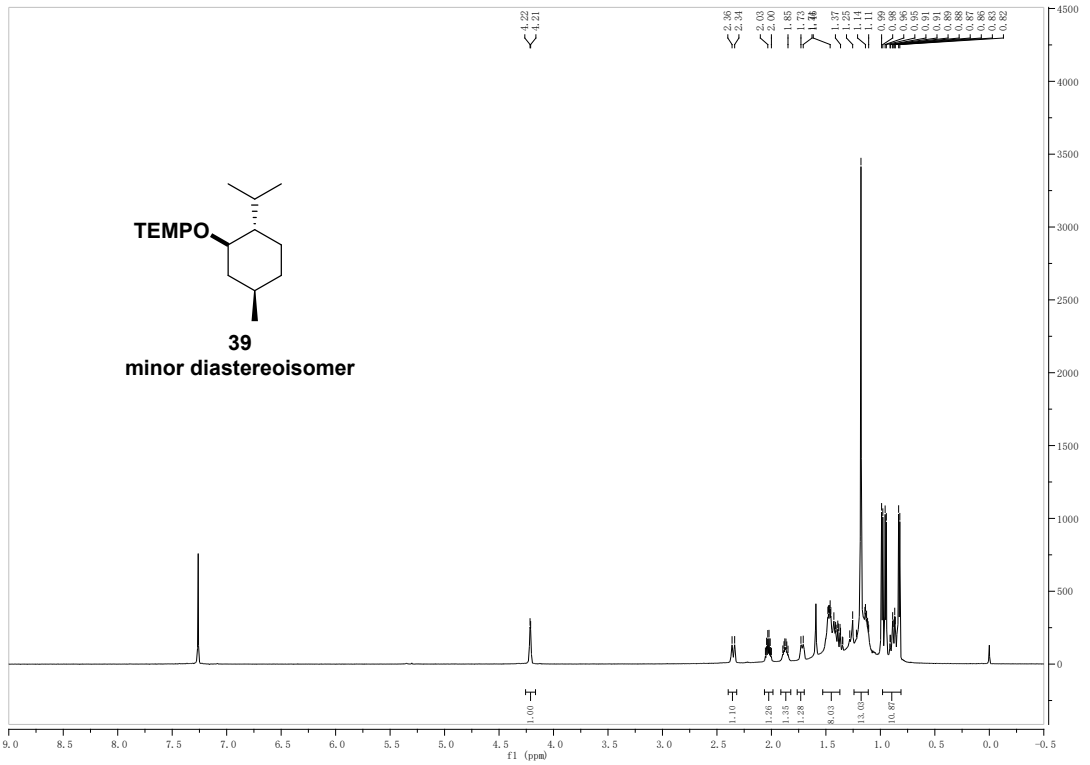

TEMPO
37
f1 (ppm)

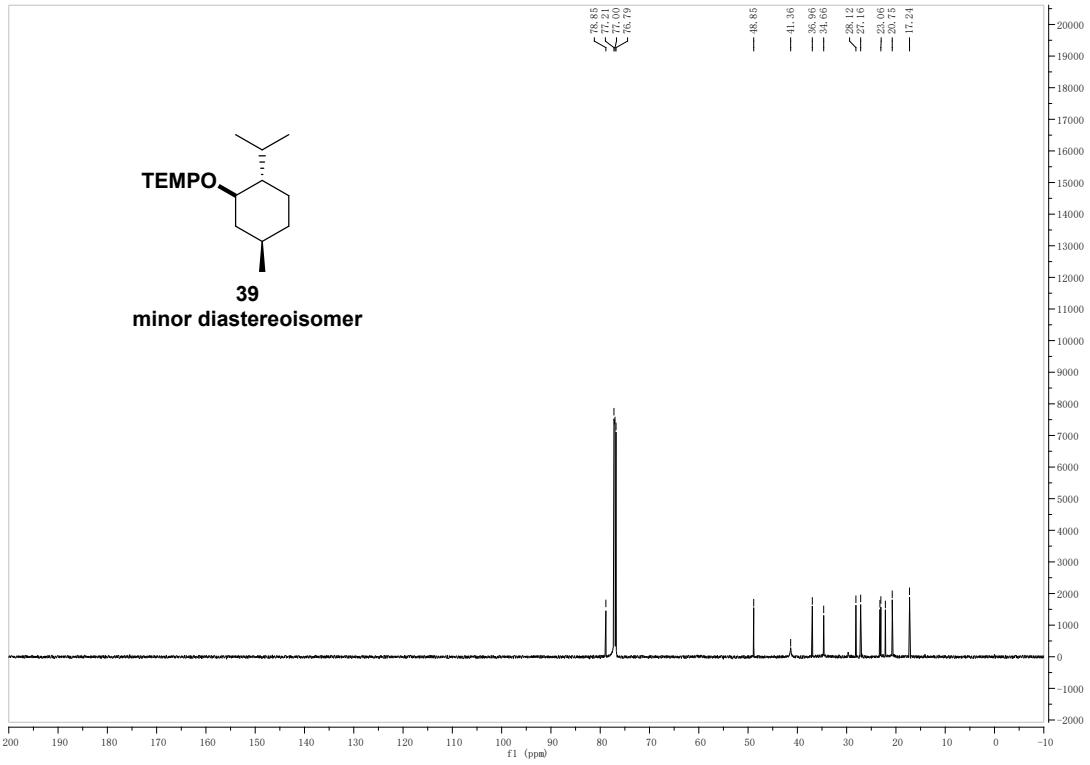

TEMPO
38
f1 (ppm)

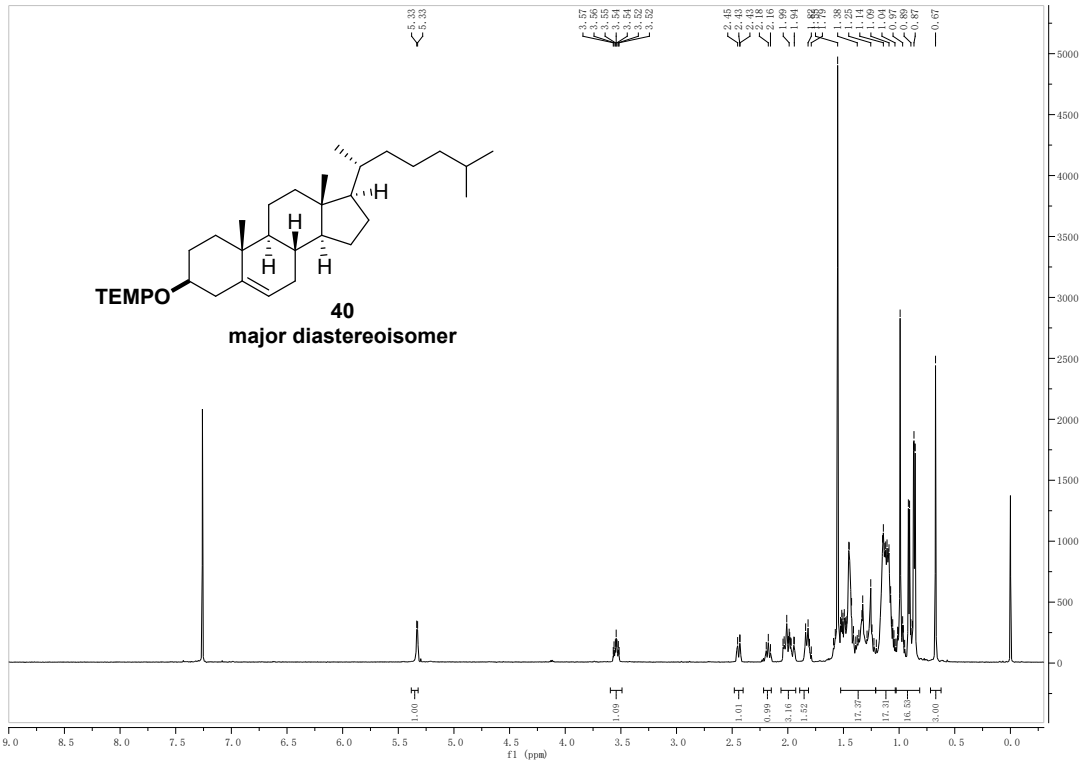

TEMPO
38
f1 (ppm)

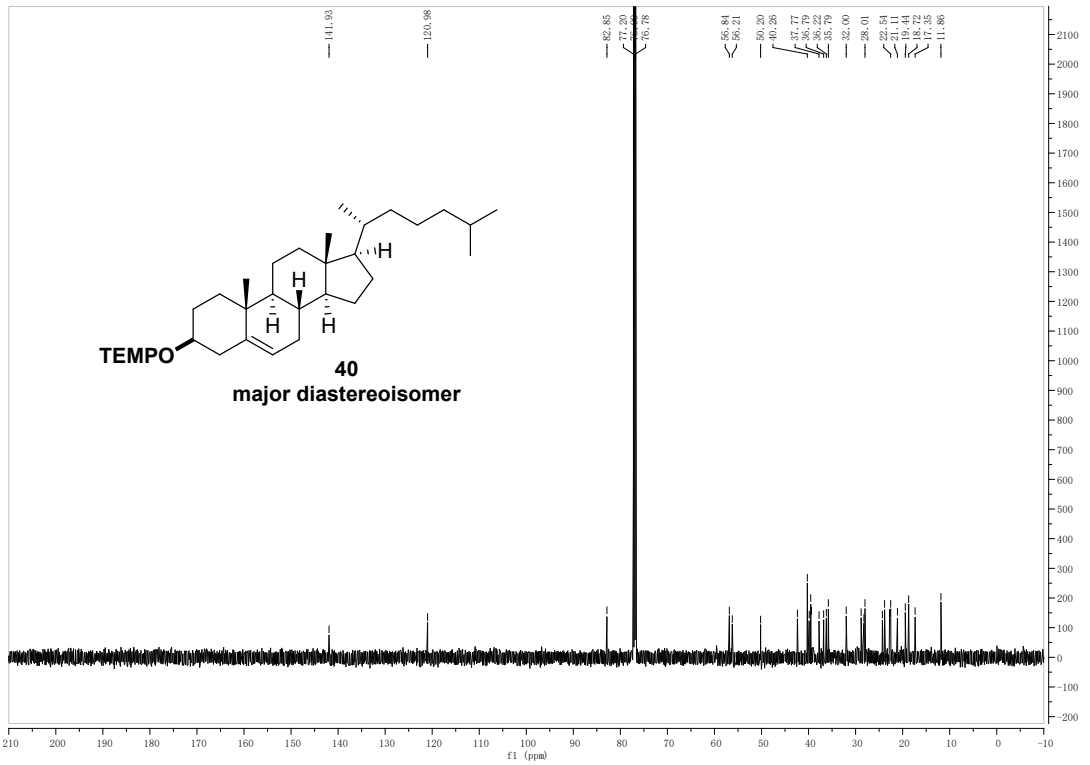

TEMPO
39
major diastereoisomer
f1 (ppm)

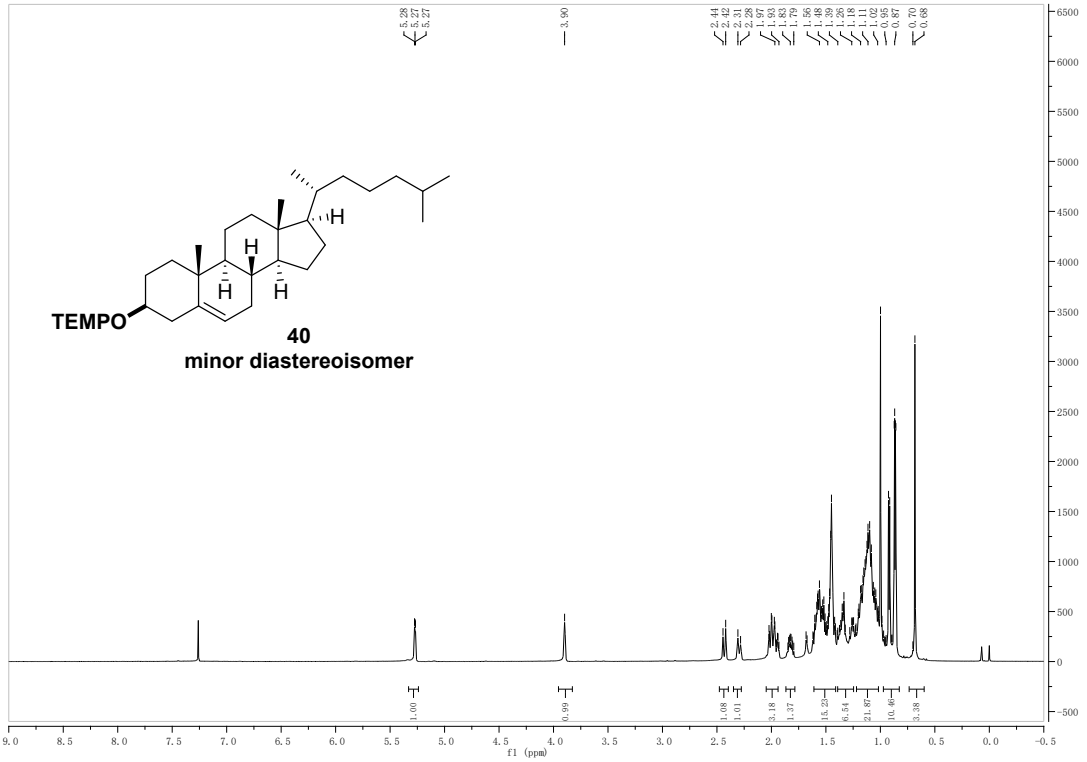

TEMPO
39
major diastereoisomer
f1 (ppm)

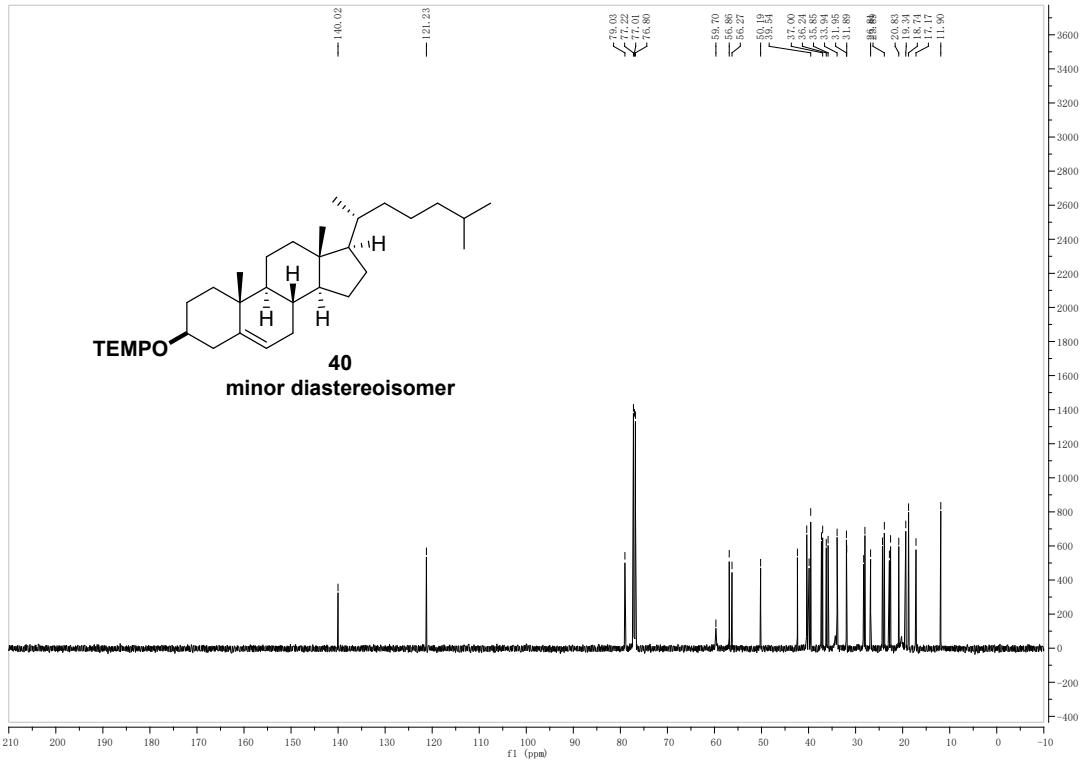

TEMPO
39
minor diastereoisomer
f1 (ppm)

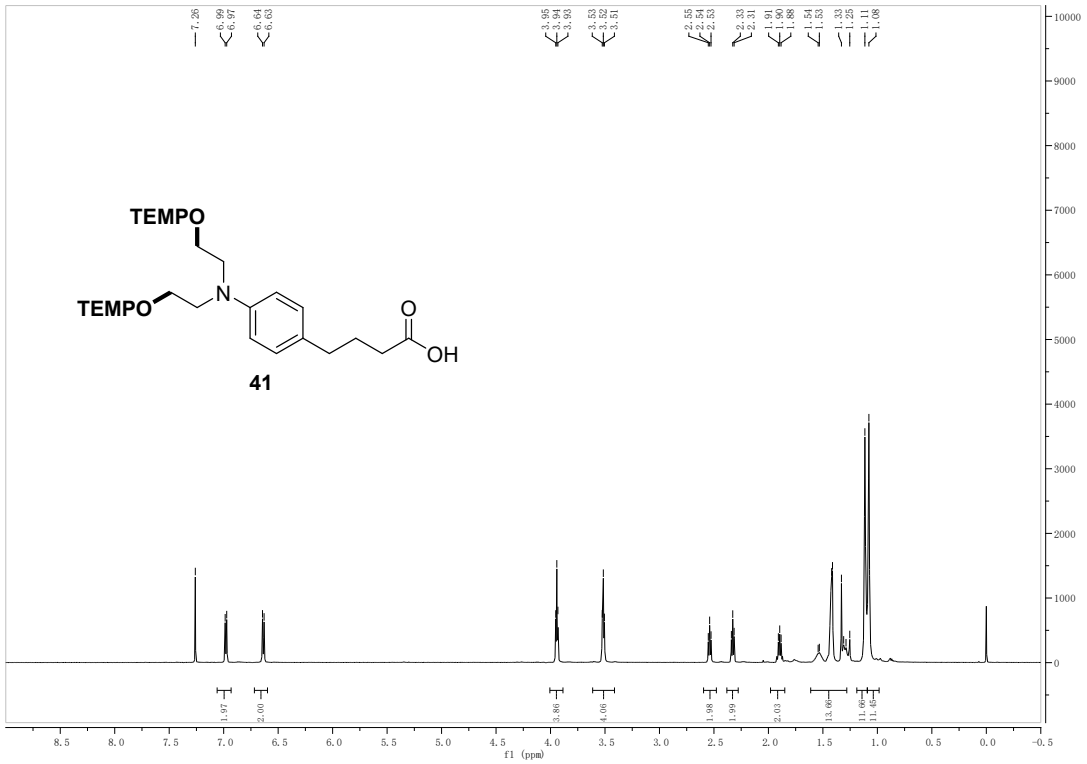

TEMPO
39
minor diastereoisomer
f1 (ppm)

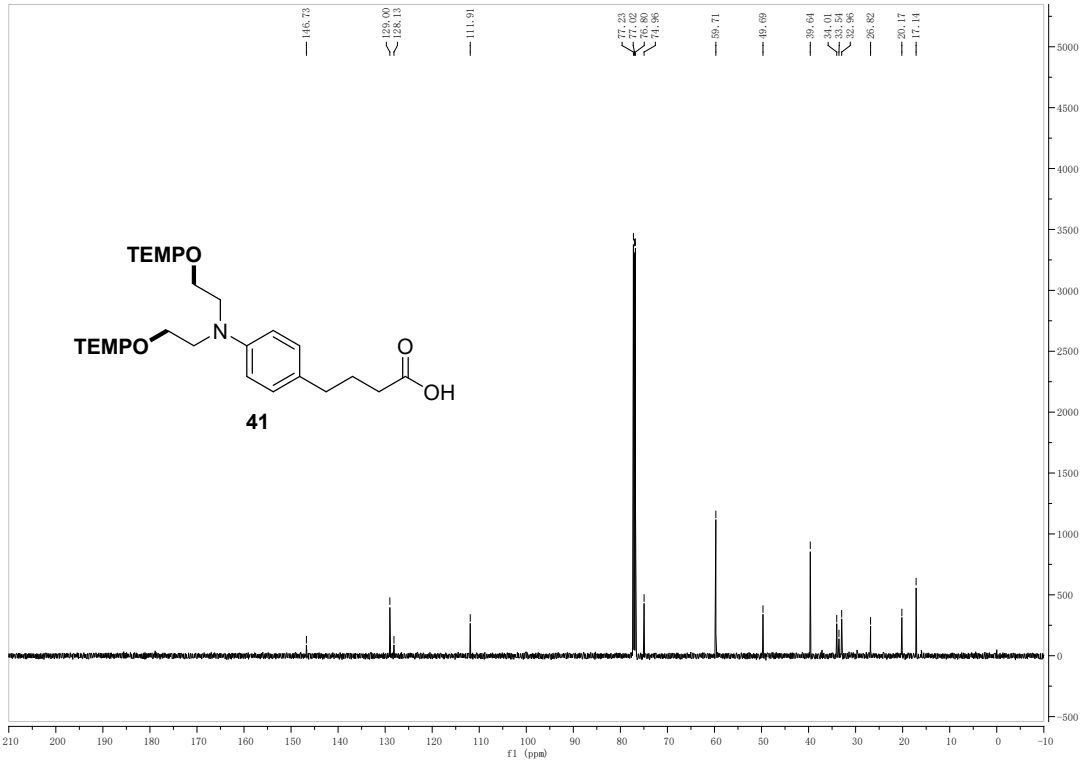

TEMPO
40
major diastereoisomer
f1 (ppm)

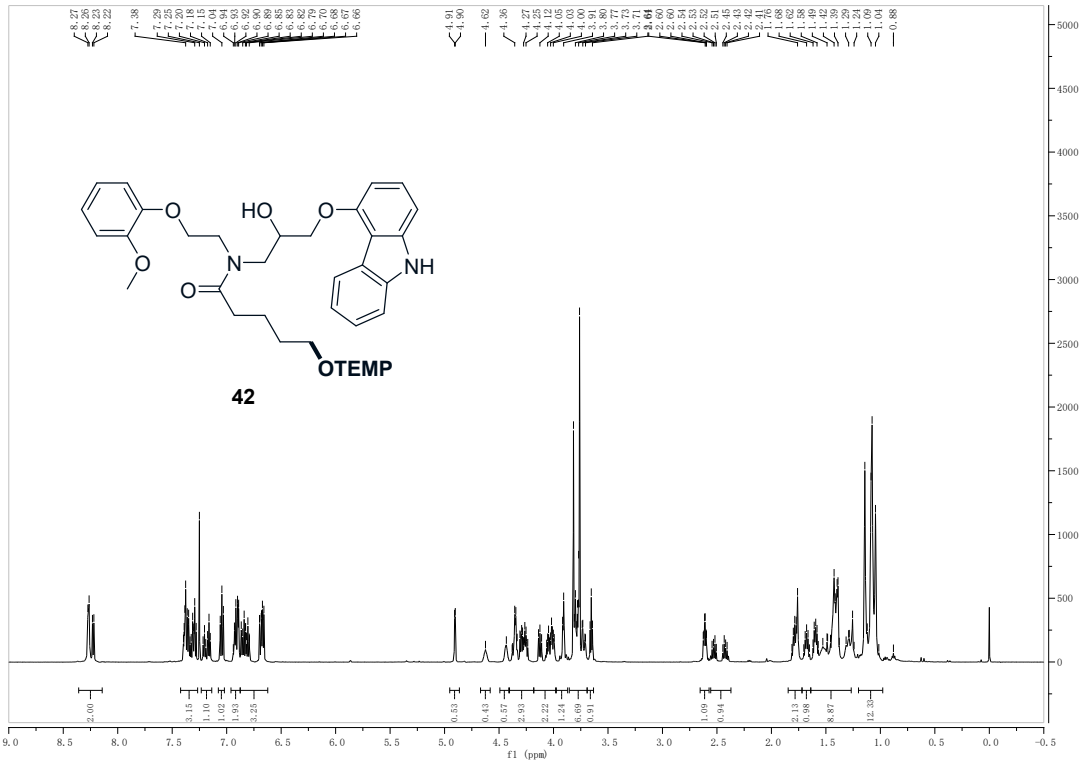

TEMPO
40
major diastereoisomer
f1 (ppm)


TEMPO
40
minor diastereoisomer
f1 (ppm)

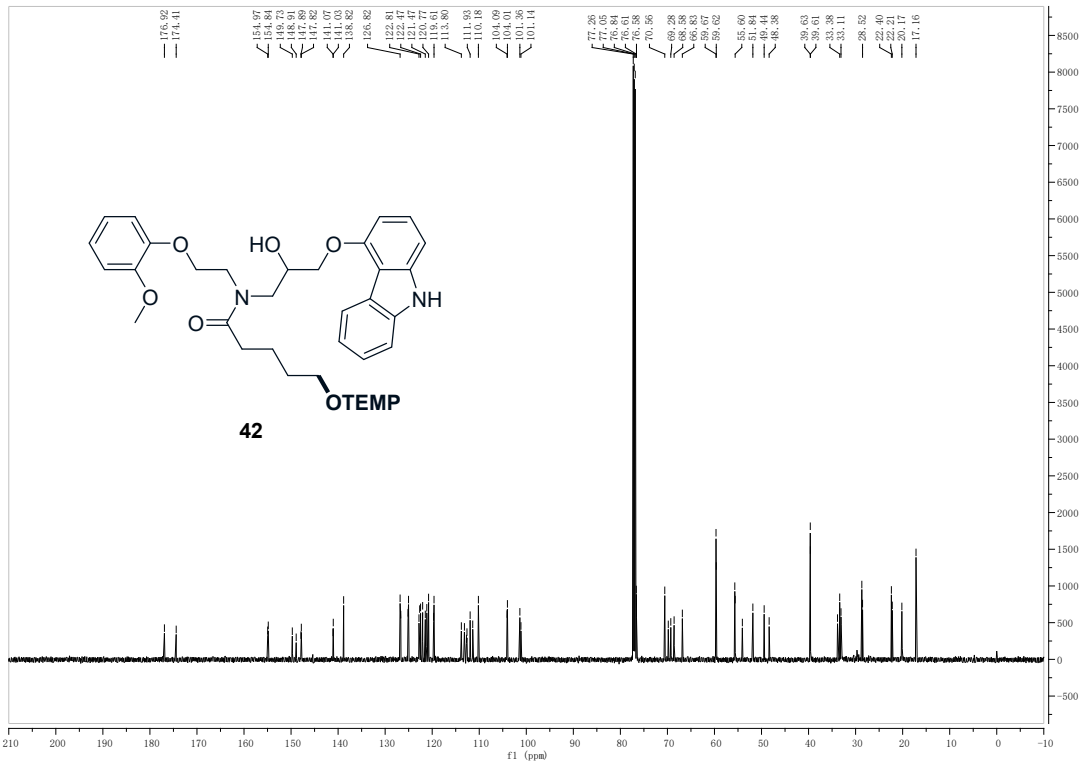

TEMPO
40
minor diastereoisomer
f1 (ppm)


7.26
6.99
6.97
6.64
6.63
3.95
3.94
3.93
3.53
3.52
3.51
2.55
2.54
2.53
2.33
2.31
1.91
1.90
1.88
1.54
1.53
1.33
1.25
1.11
1.08
TEMPO
TEMPO
N
O
OH
41
1.97
2.00
3.86
4.06
1.98
1.99
2.03
13.69
11.66
11.65
f1 (ppm)

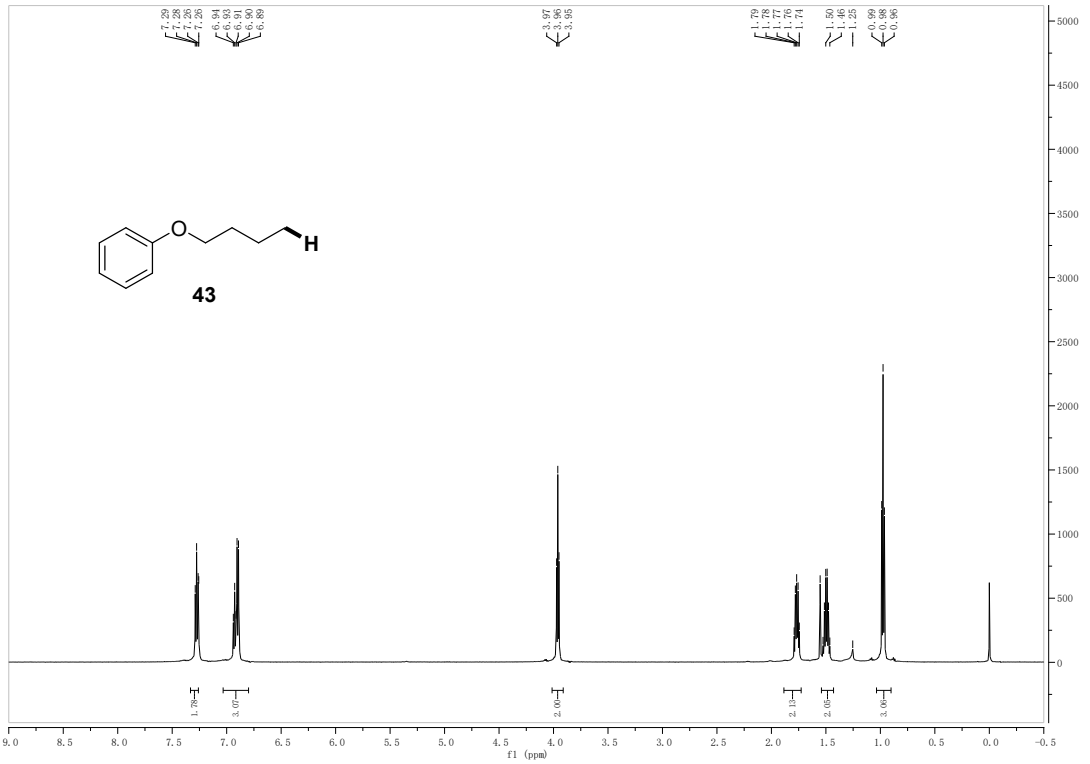

146.73
129.00
128.13
111.91
77.23
77.02
76.80
74.96
59.71
49.69
39.64
34.01
33.54
32.96
25.82
20.17
17.14
TEMPO
TEMPO
N
O
OH
41
f1 (ppm)

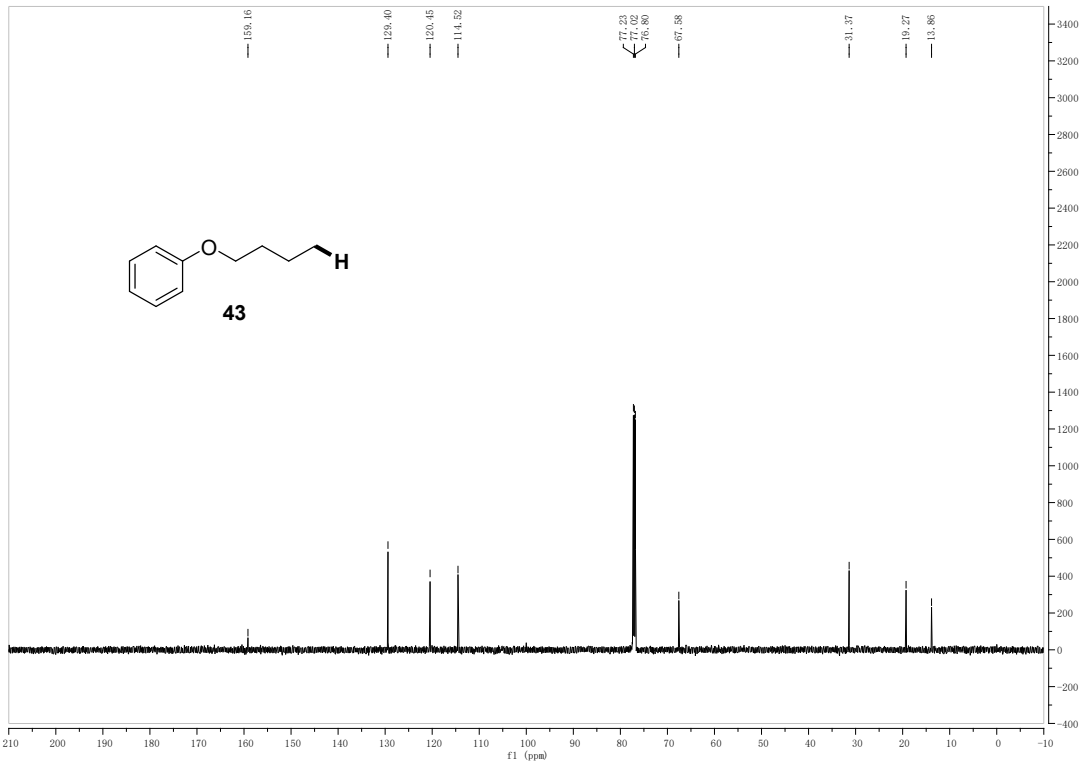


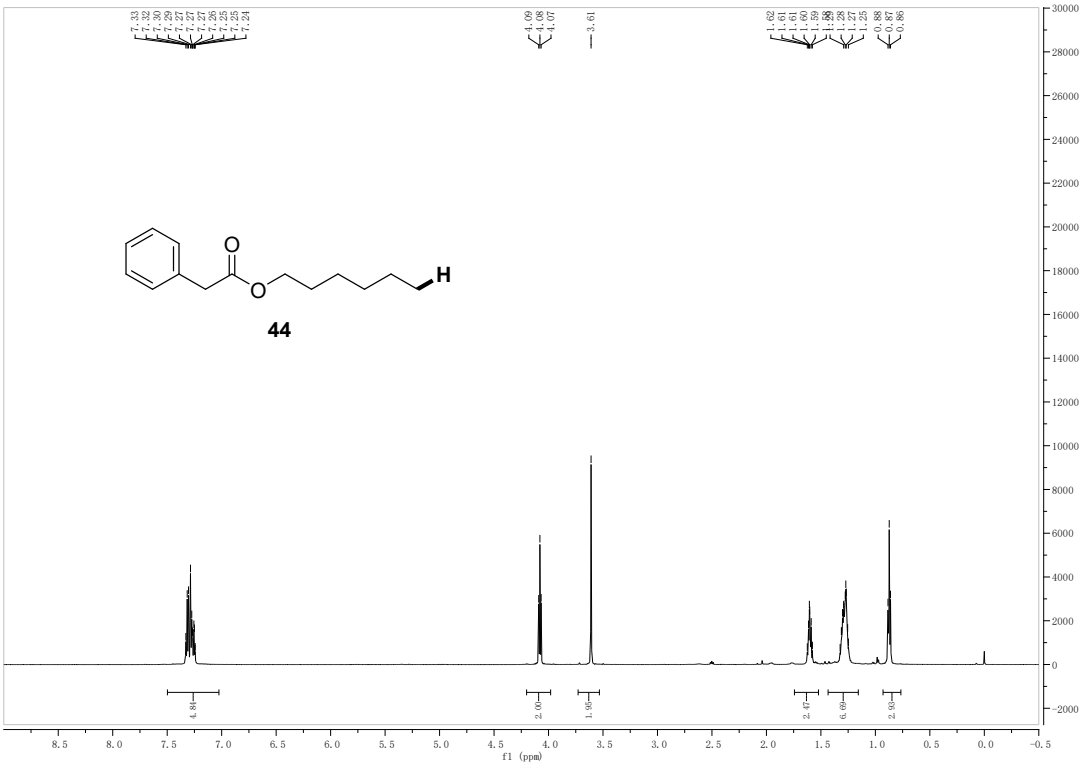
42

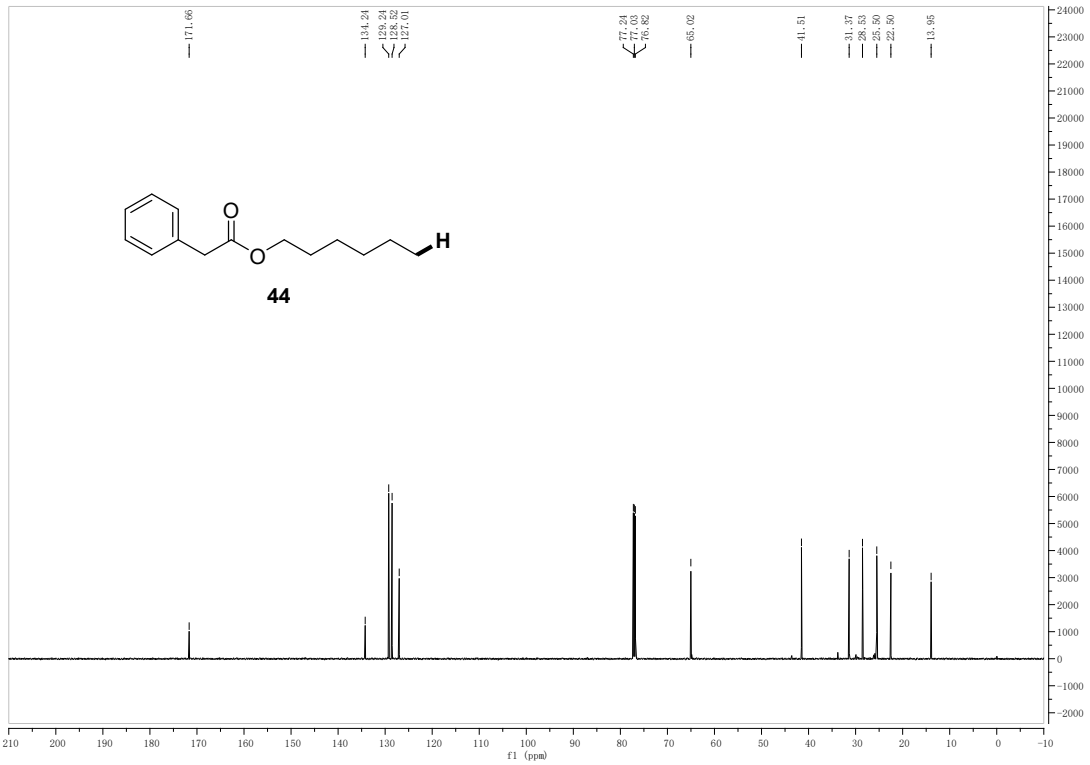


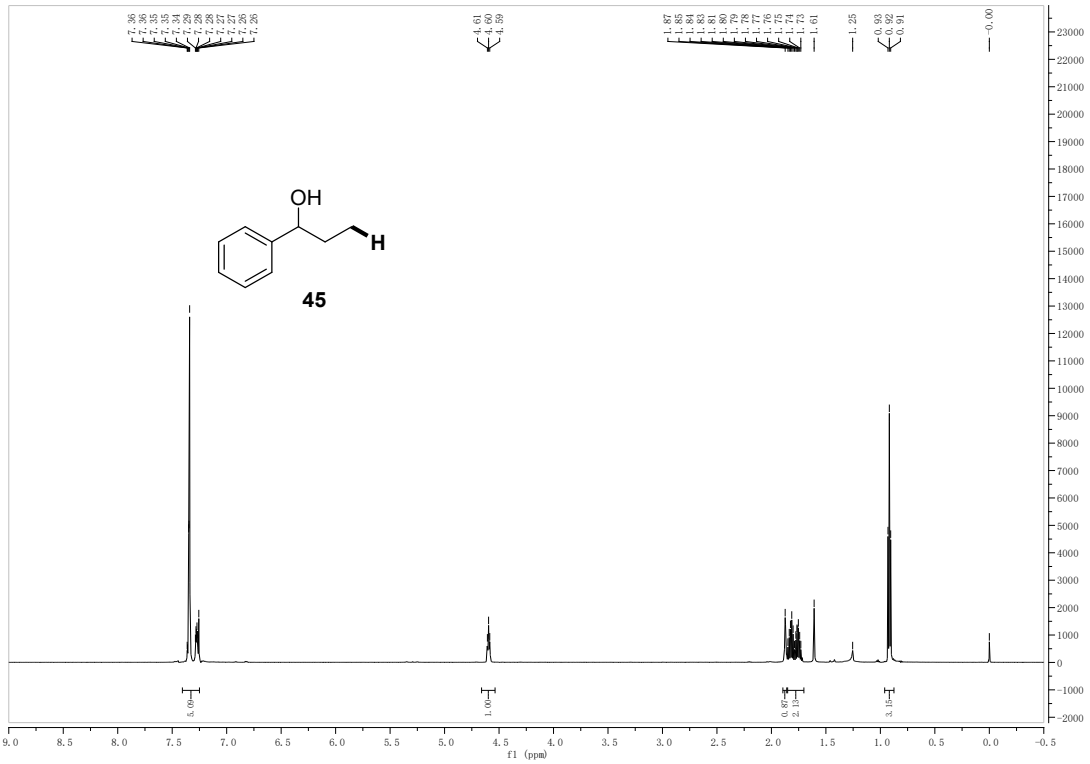
42

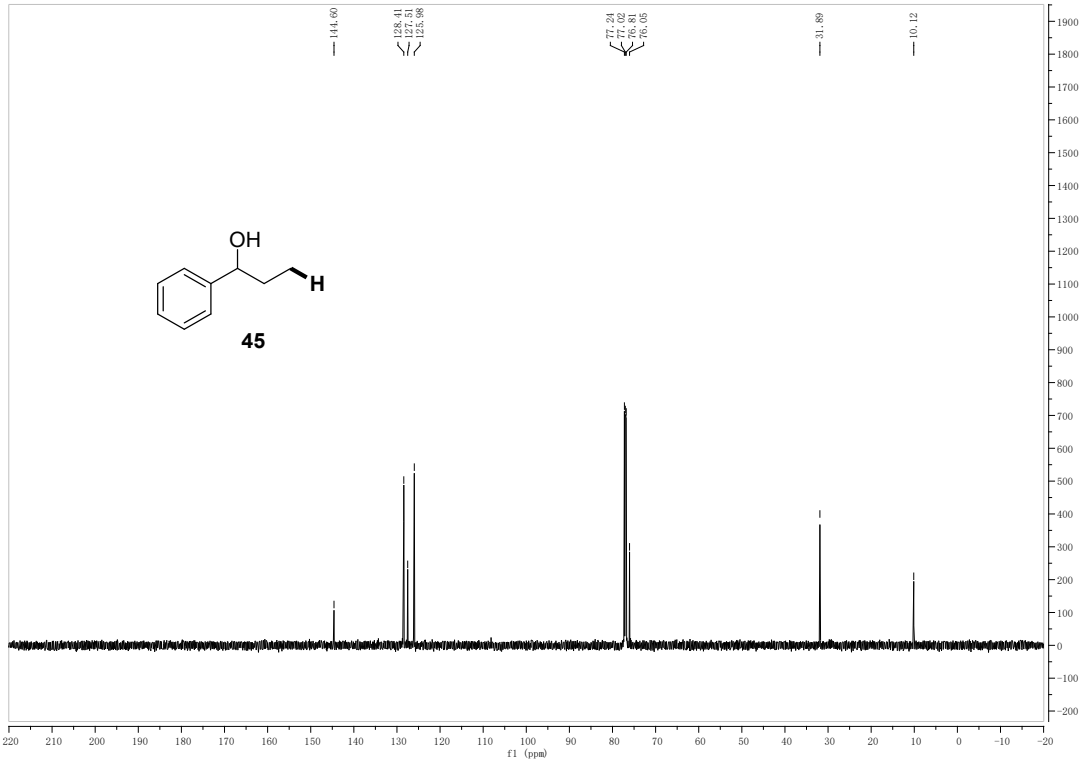

7.29
7.28
7.26
7.26
6.94
6.93
6.91
6.90
6.89
3.97
3.96
3.95
1.79
1.78
1.77
1.76
1.74
1.50
1.46
1.25
0.99
0.98
0.96
O
H
43
1.78
3.07
2.00
2.13
2.05
3.06
f1 (ppm)

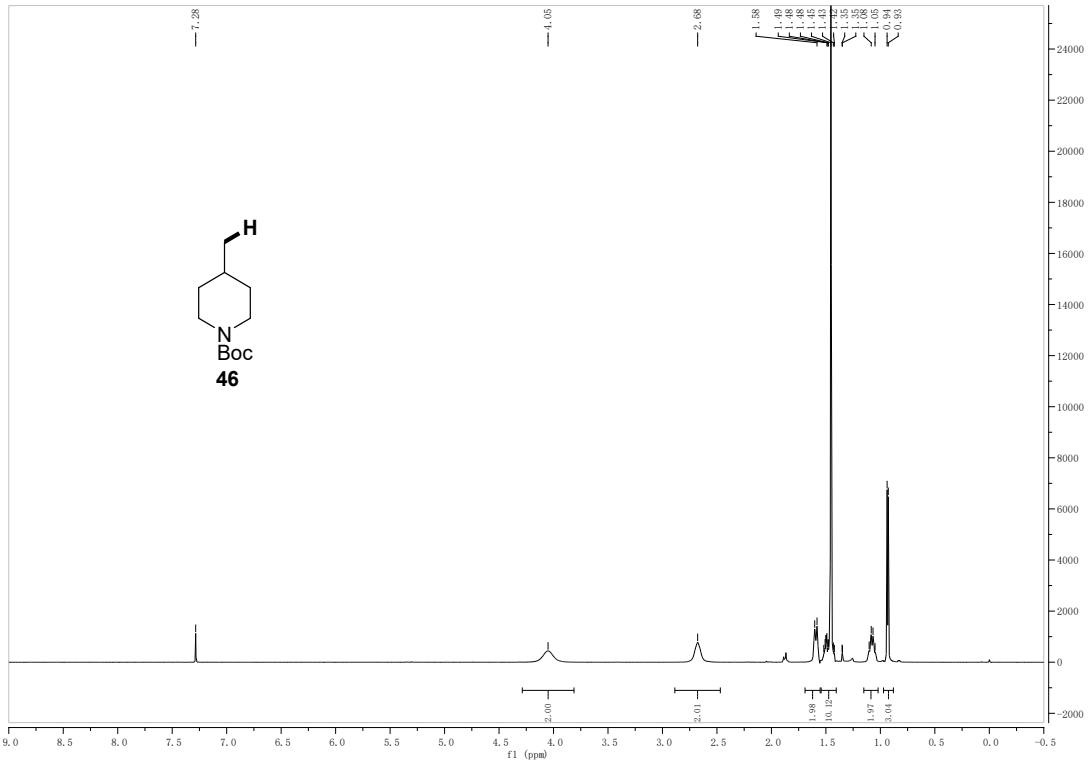

159.16
129.40
120.45
114.52
77.23
77.02
76.80
67.58
31.37
19.27
13.86
O
H
43
f1 (ppm)

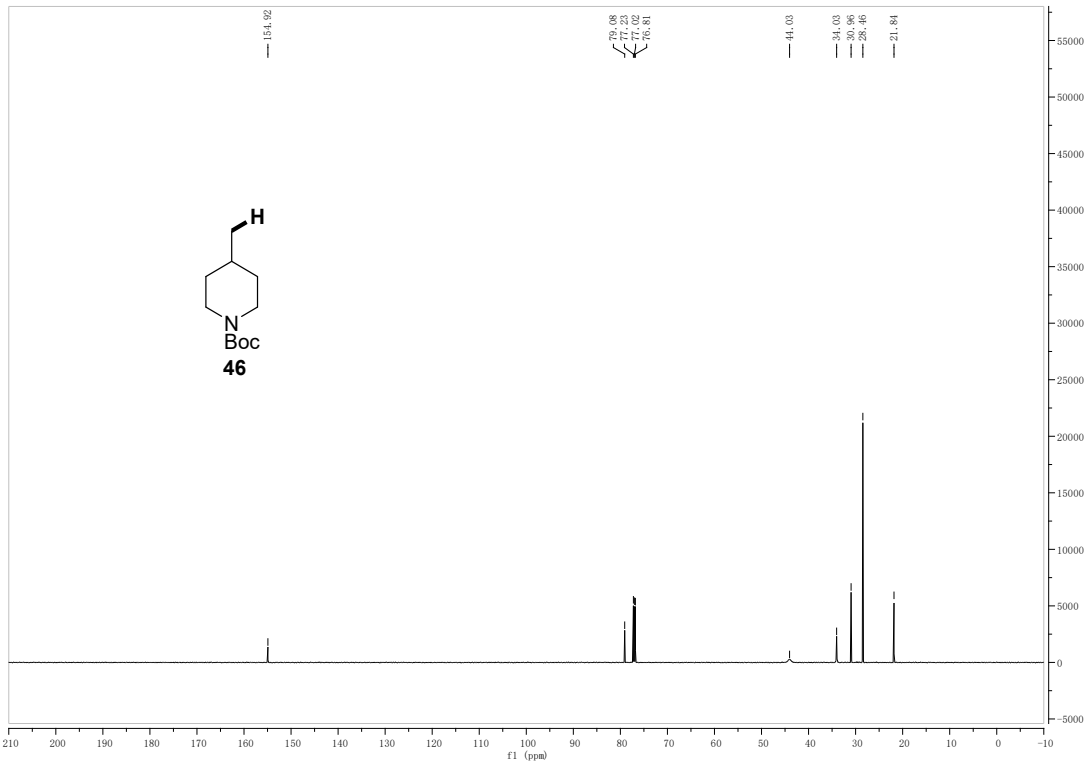

7.33
7.32
7.30
7.29
7.27
7.27
7.27
7.26
7.25
7.25
7.24
4.09
4.08
4.07
3.61
1.62
1.61
1.61
1.60
1.59
1.58
1.58
1.28
1.27
1.25
0.88
0.87
0.86
O
O
H
44
4.84
2.00
1.95
2.47
6.69
2.93
f1 (ppm)

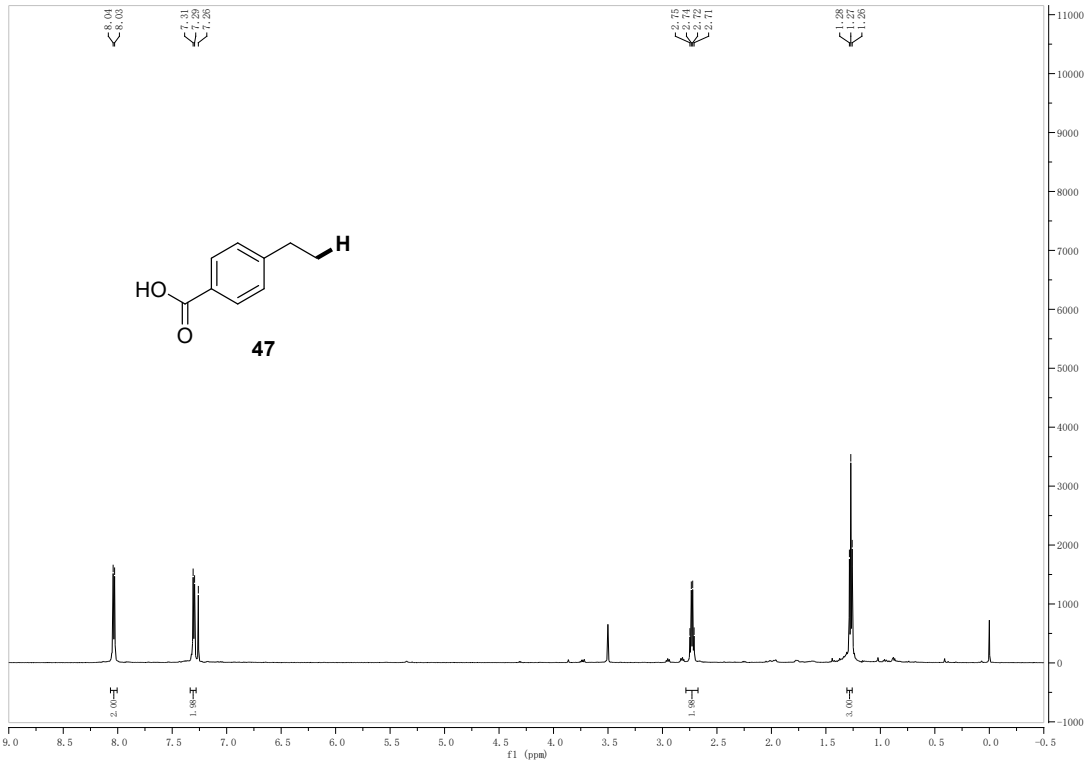

171.66
134.24
129.24
128.52
127.01
77.24
77.03
76.82
65.02
41.51
31.37
28.53
25.50
22.50
13.95
O
O
H
44
f1 (ppm)

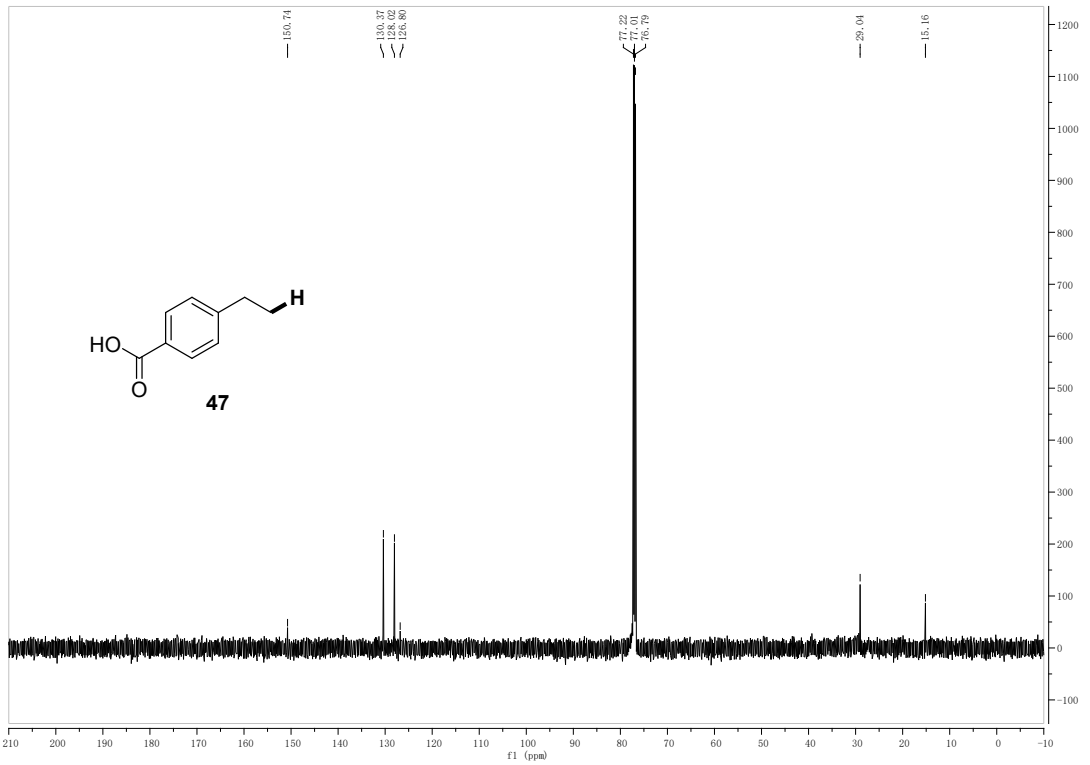

7.36
7.36
7.35
7.35
7.34
7.29
7.28
7.28
7.27
7.27
7.26
7.25
4.61
4.60
4.59
1.87
1.85
1.84
1.83
1.81
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.61
1.25
0.93
0.92
0.91
0.00
OH
H
45
5.09
1.00
0.87
2.13
3.15
f1 (ppm)

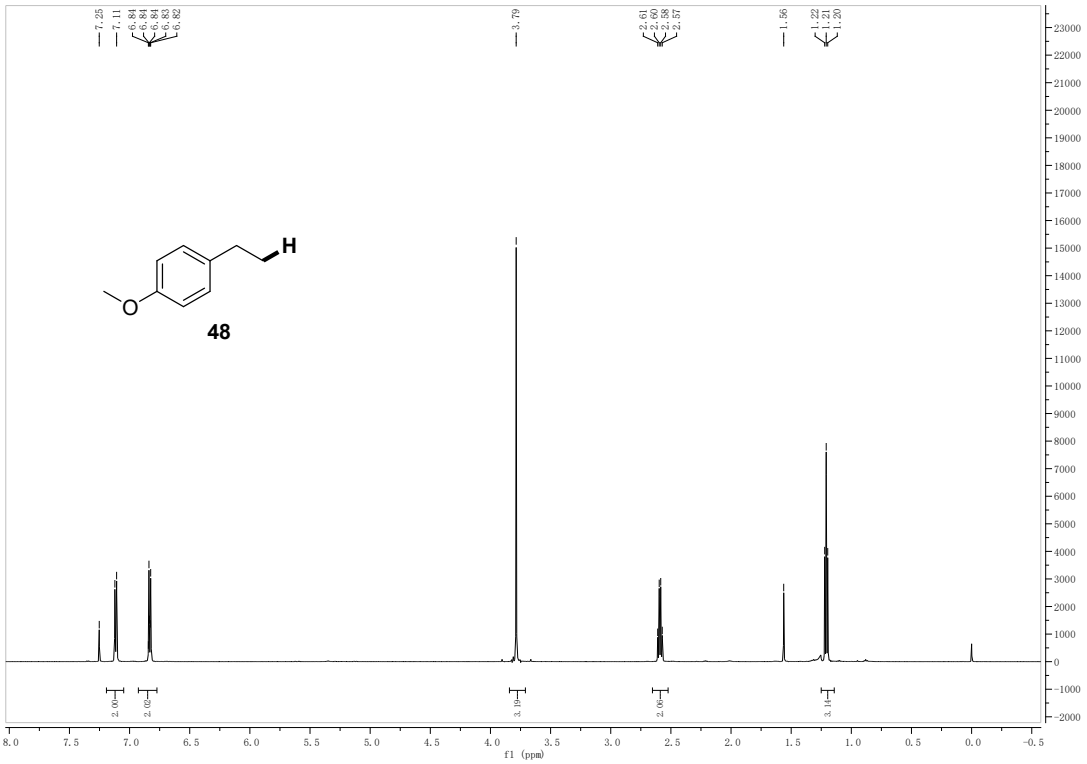

144.60
128.41
127.51
125.98
77.24
77.02
76.81
76.05
31.89
10.12
OH
H
45
f1 (ppm)

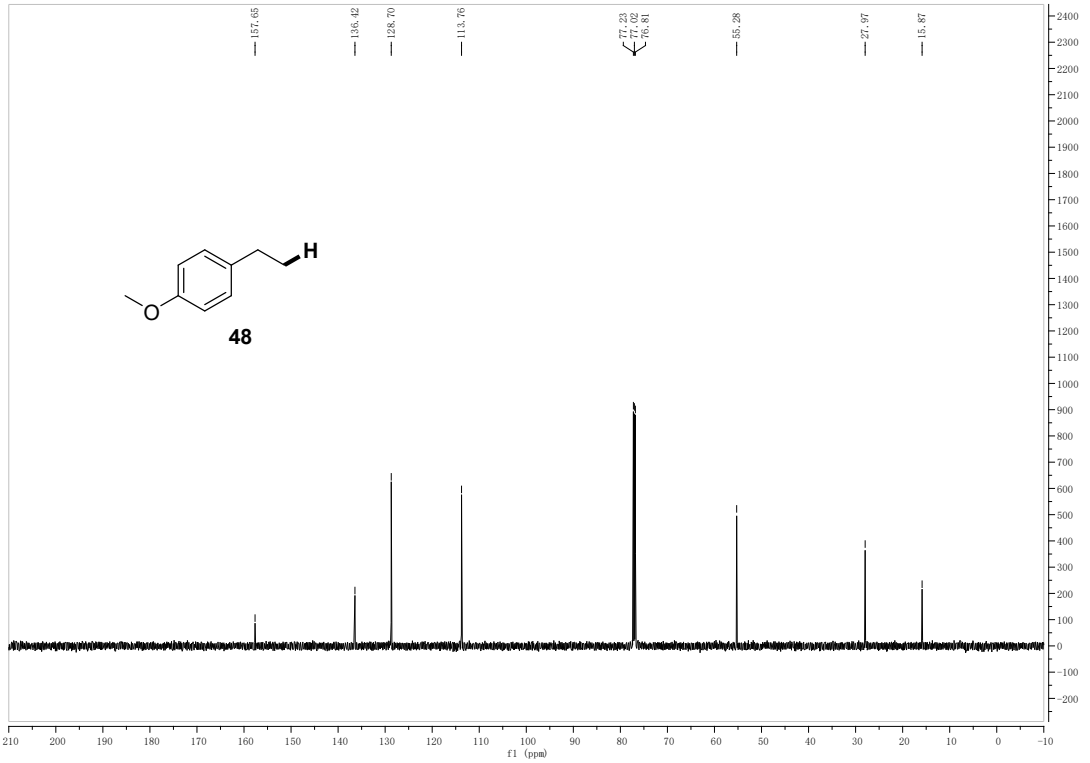

7.28
4.05
2.68
1.58
1.49
1.48
1.48
1.45
1.43
1.42
1.35
1.35
1.06
1.05
0.94
0.93
H
N
Boc
46
2.00
2.01
1.98
10.12
1.97
3.04
f1 (ppm)


154.92
79.08
77.23
77.02
76.81
44.03
34.03
30.96
28.46
21.84
H
N
Boc
46
f1 (ppm)


8.04
8.03
7.31
7.29
7.26
2.75
2.74
2.72
2.71
1.28
1.27
1.26
HO
O
H
47
2.00
1.98
1.98
3.00
f1 (ppm)


150.74
130.37
128.02
126.80
77.22
77.01
76.79
29.04
15.16
HO
O
H
47
f1 (ppm)


7.25
7.11
6.84
6.84
6.84
6.83
6.82
3.79
2.61
2.60
2.59
2.57
1.56
1.22
1.21
1.20
H
O
48
2.00
2.02
3.19
2.06
3.14
f1 (ppm)


157.65
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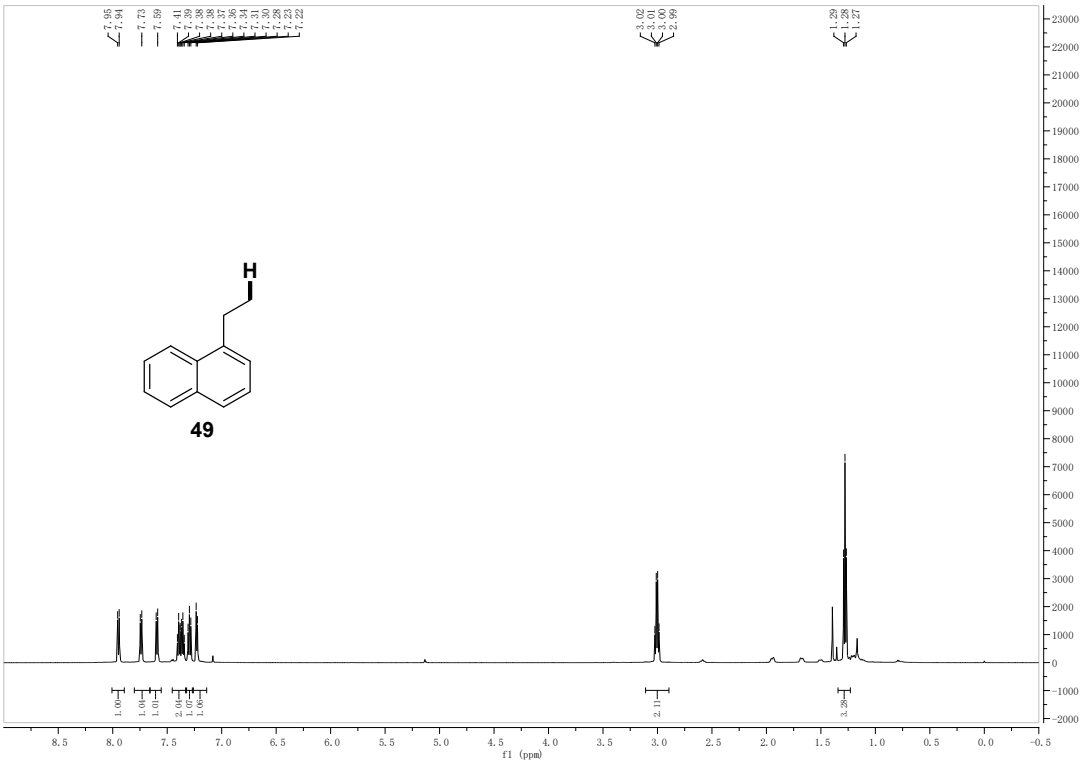
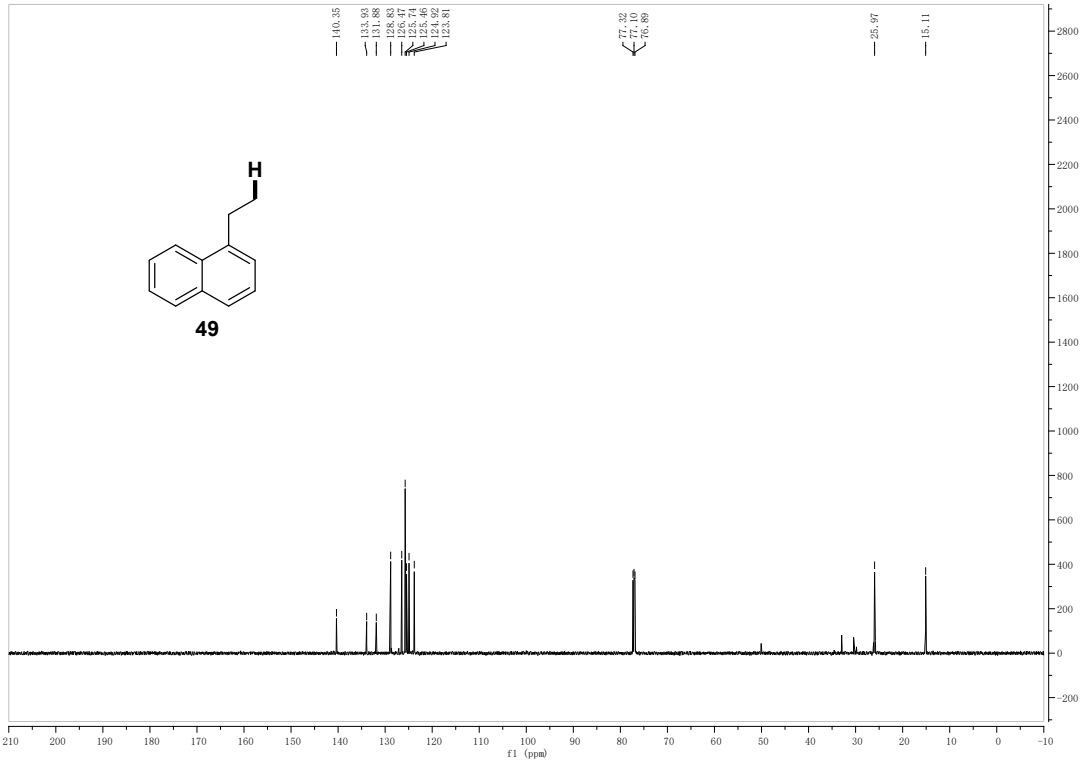
113.76
77.23
77.02
76.81
55.28
27.97
15.87
H
O
48
f1 (ppm)


7.95
7.94
7.73
7.59
7.41
7.39
7.38
7.38
7.37
7.36
7.34
7.31
7.30
7.28
7.23
7.22
3.02
3.01
3.00
2.99
1.29
1.28
1.27
H
49
1.00
1.04
1.01
2.04
1.07
1.06
2.11
3.28
f1 (ppm)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131.88
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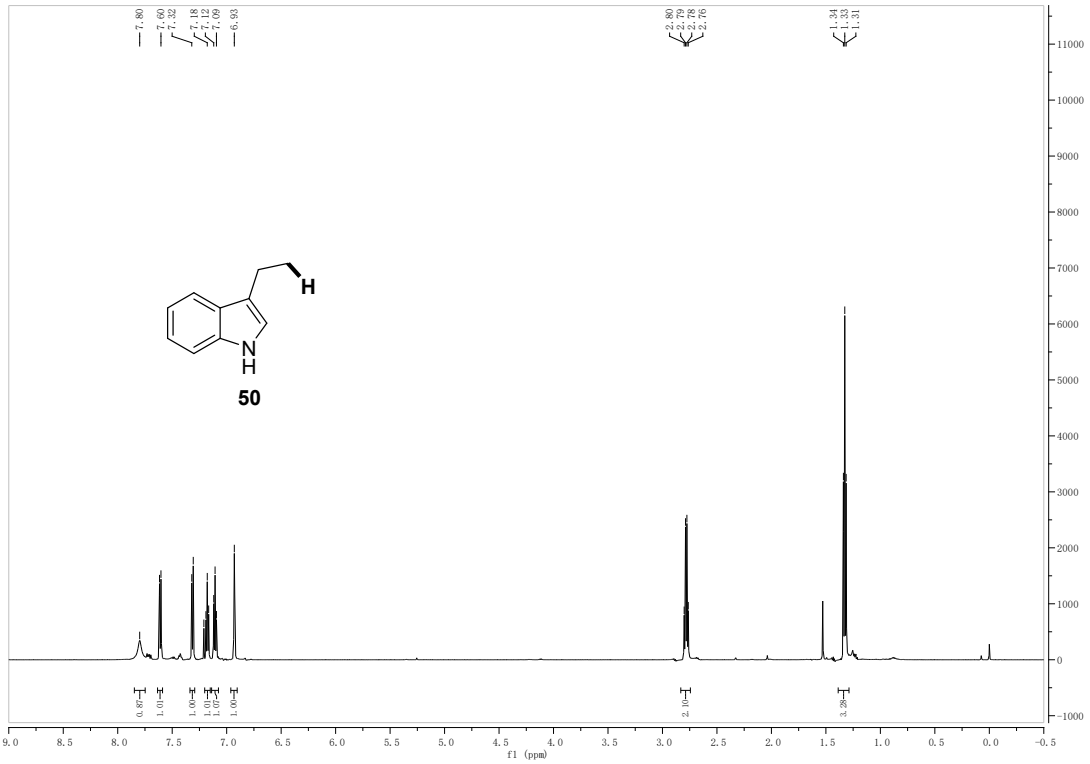
126.47
125.74
125.46
124.92
123.81
77.32
77.10
76.89
25.97
15.11
H
49
f1 (ppm)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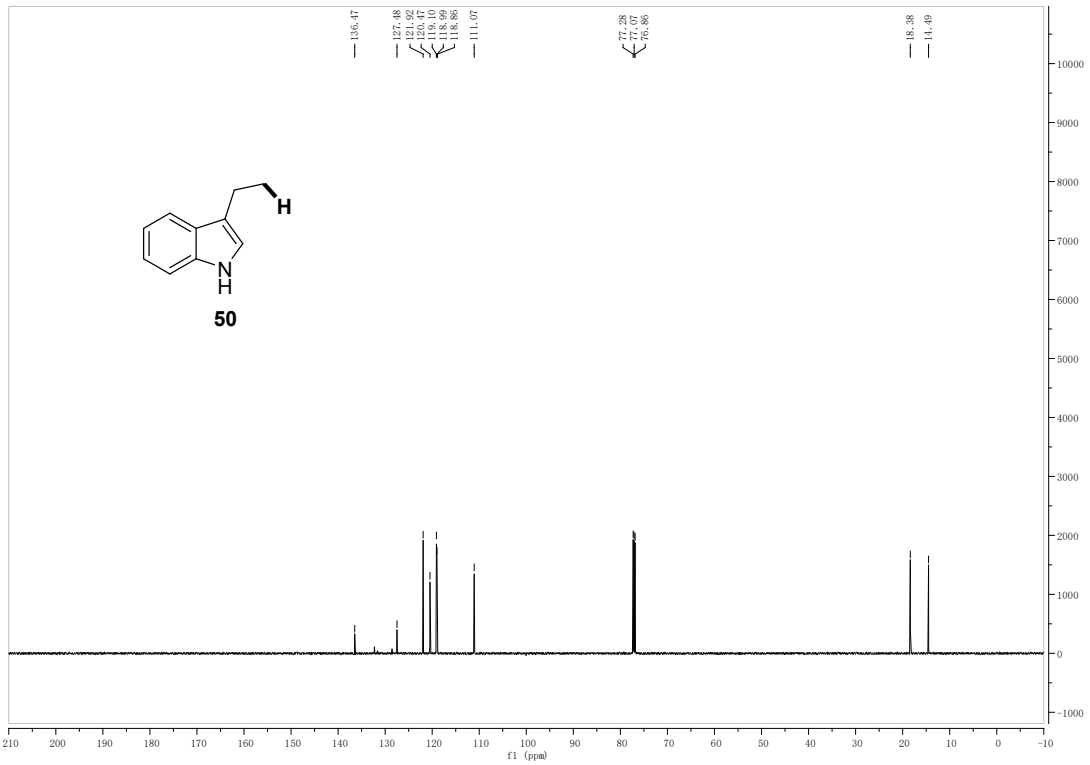
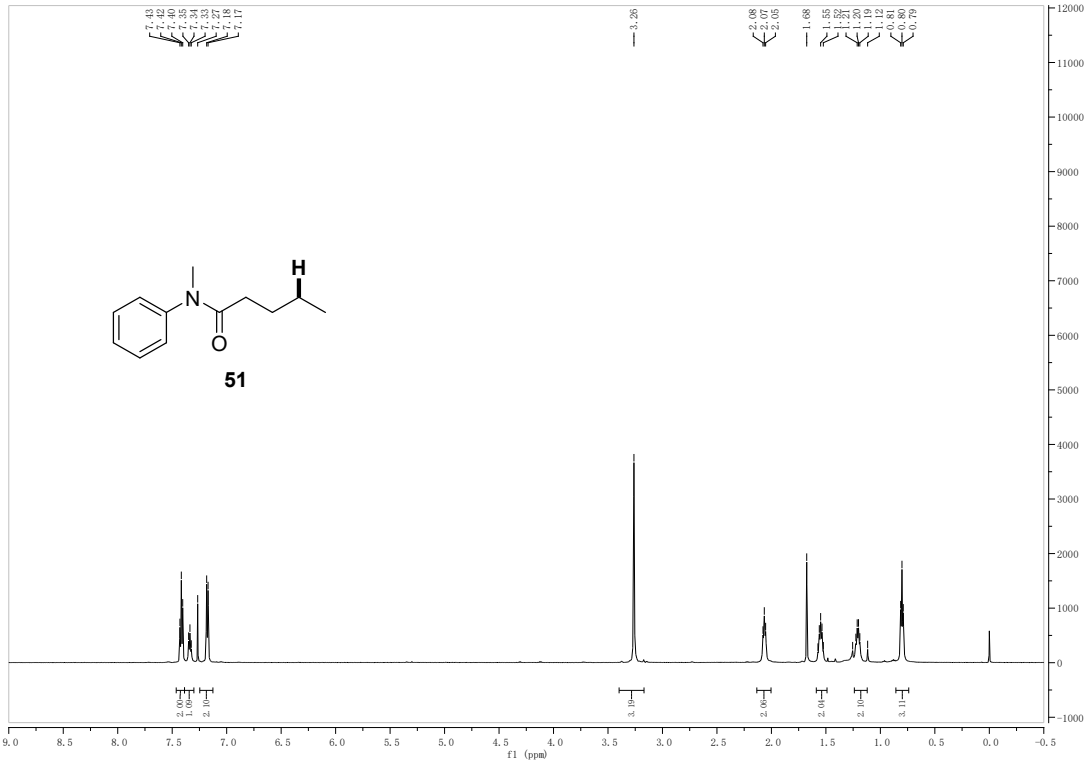
7.60
7.32
7.18
7.12
7.09
6.93
2.80
2.79
2.78
2.76
1.34
1.33
1.31
0.87
1.01
1.00
1.01
1.07
1.06
2.10
3.28
f1 (ppm)

50


136.47
127.48
121.92
120.47
119.10
118.98
118.86
111.07
77.28
77.07
76.86
18.38
14.49
f1 (ppm)

50


7.43
7.42
7.40
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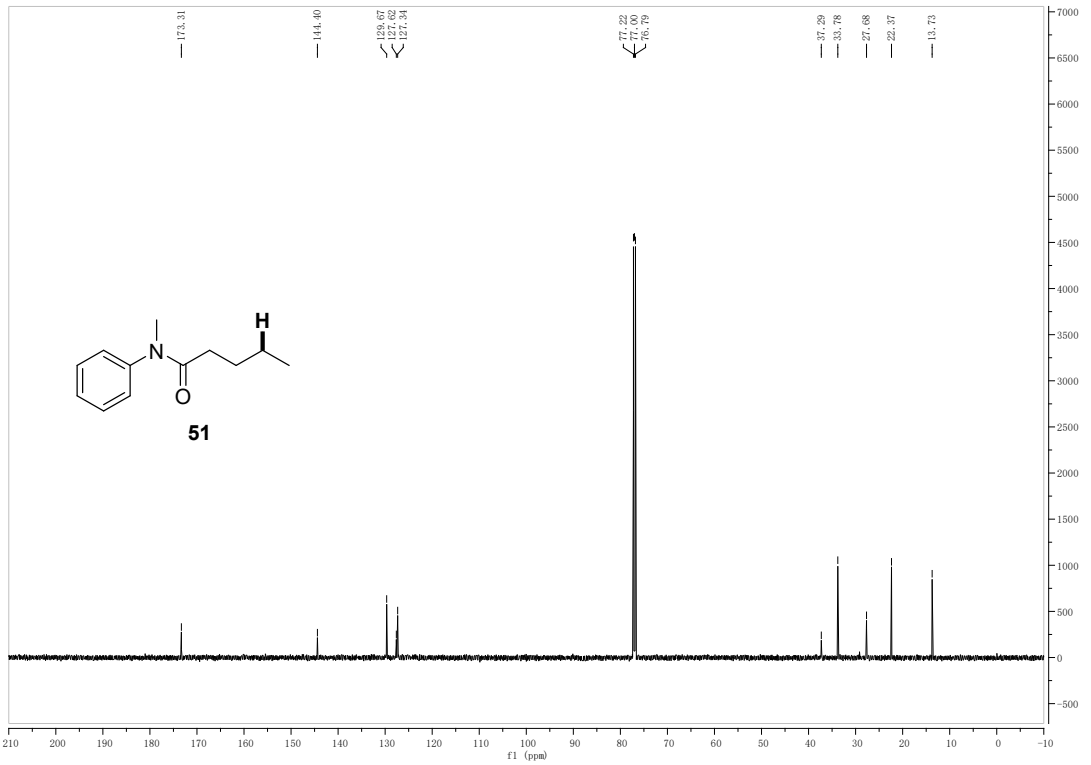
7.34
7.33
7.27
7.18
7.17
3.26
2.08
2.07
2.05
1.68
1.55
1.52
1.27
1.20
1.19
1.12
0.81
0.80
0.79
N
O
H
51
f1 (ppm)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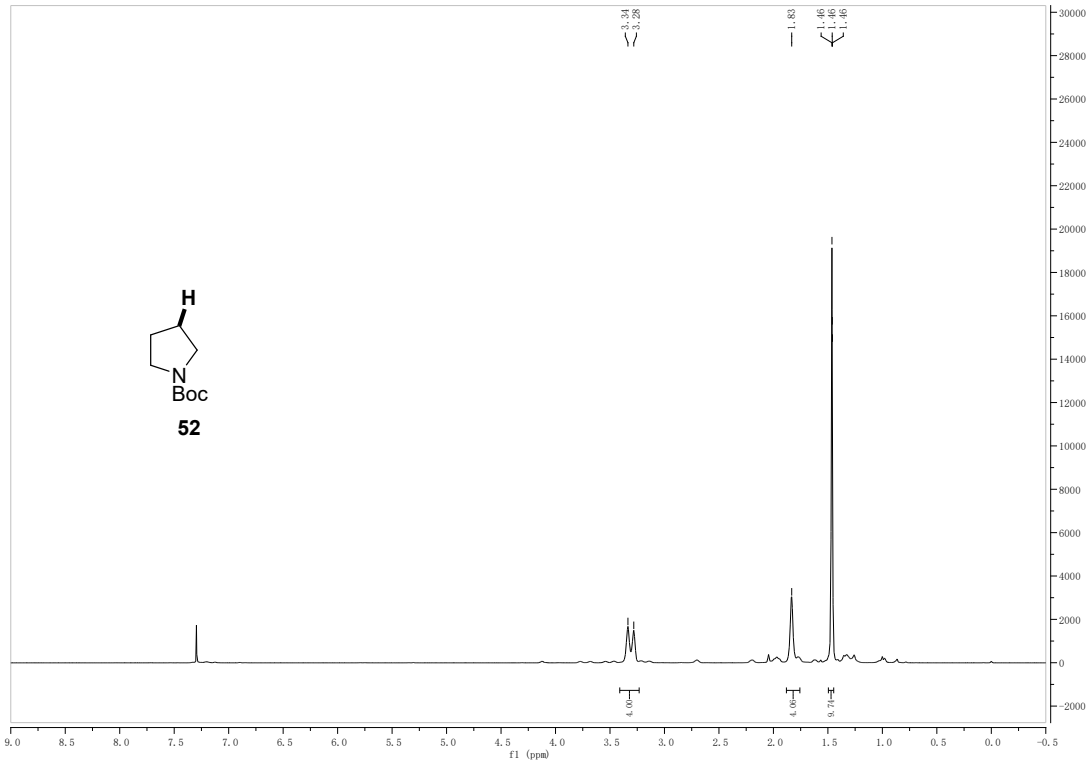
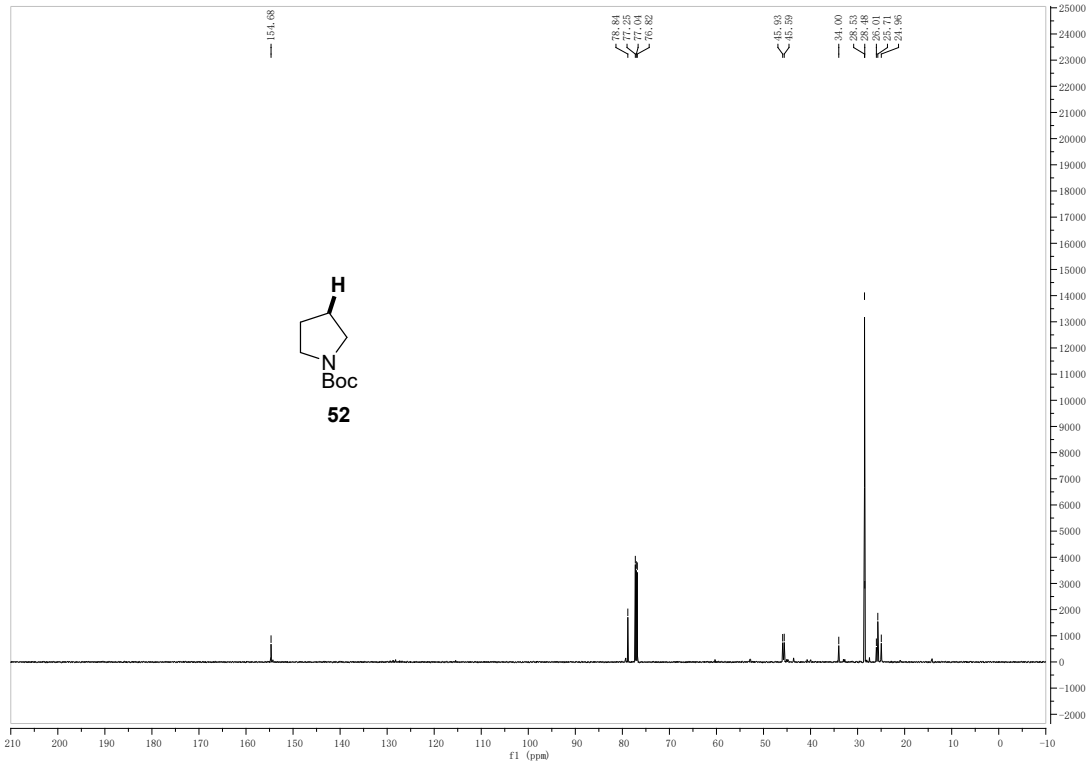
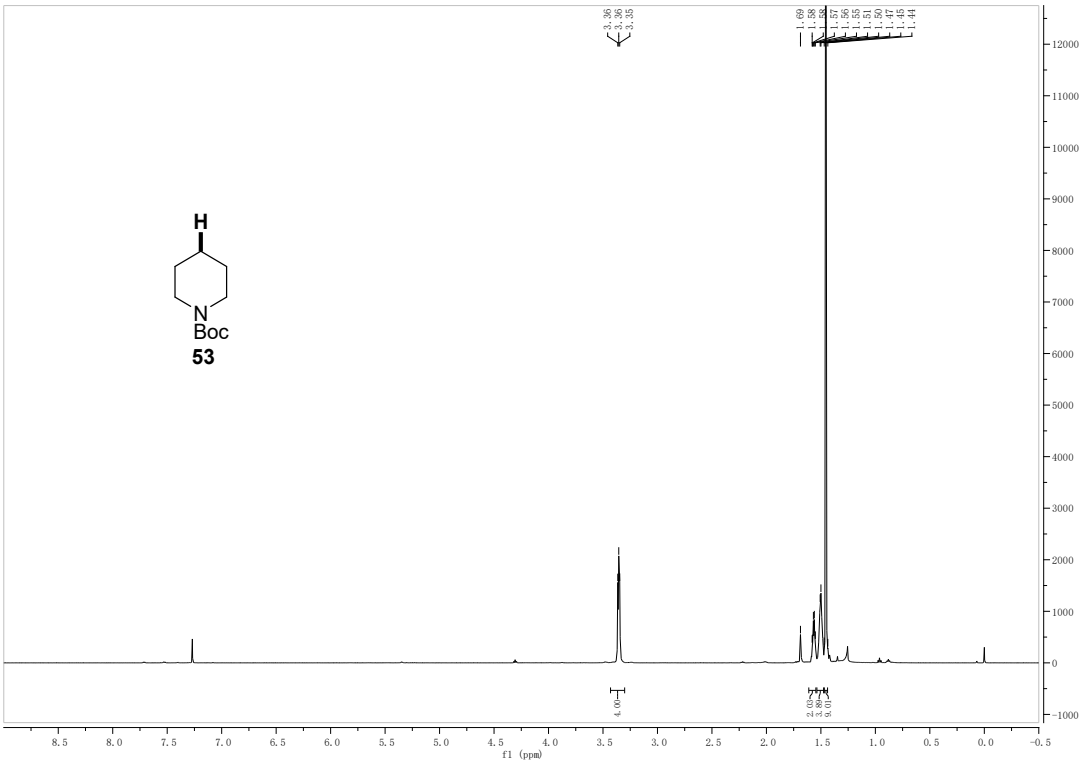
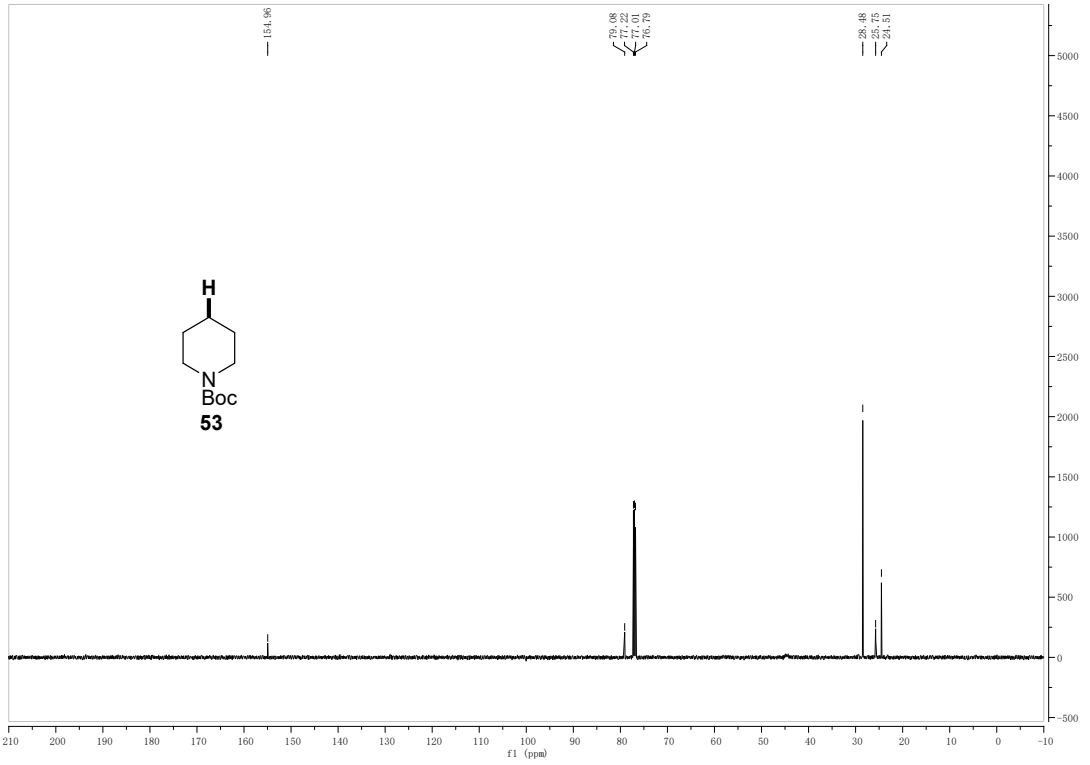
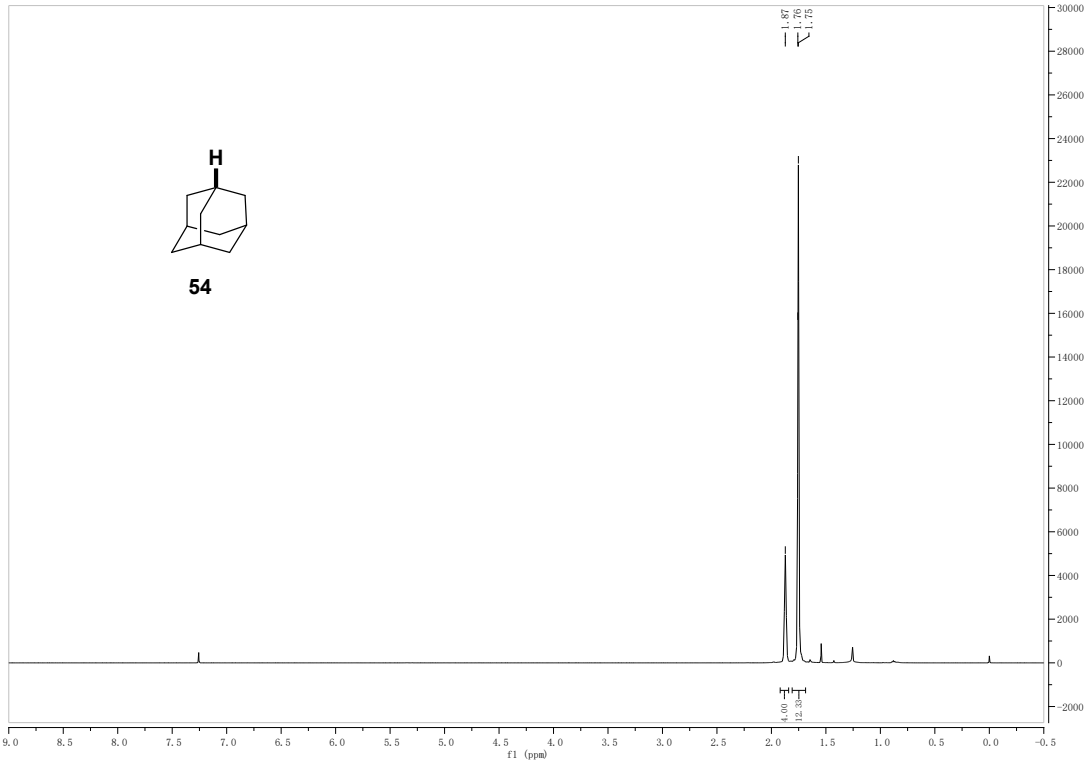
144.40
129.67
127.62
127.34
77.22
77.00
76.79
37.29
33.78
27.68
22.37
13.73
N
O
H
51
f1 (ppm)


3.34
3.28
1.83
1.46
1.46
1.46
H
N
Boc
52
4.00
4.06
9.74
f1 (ppm)

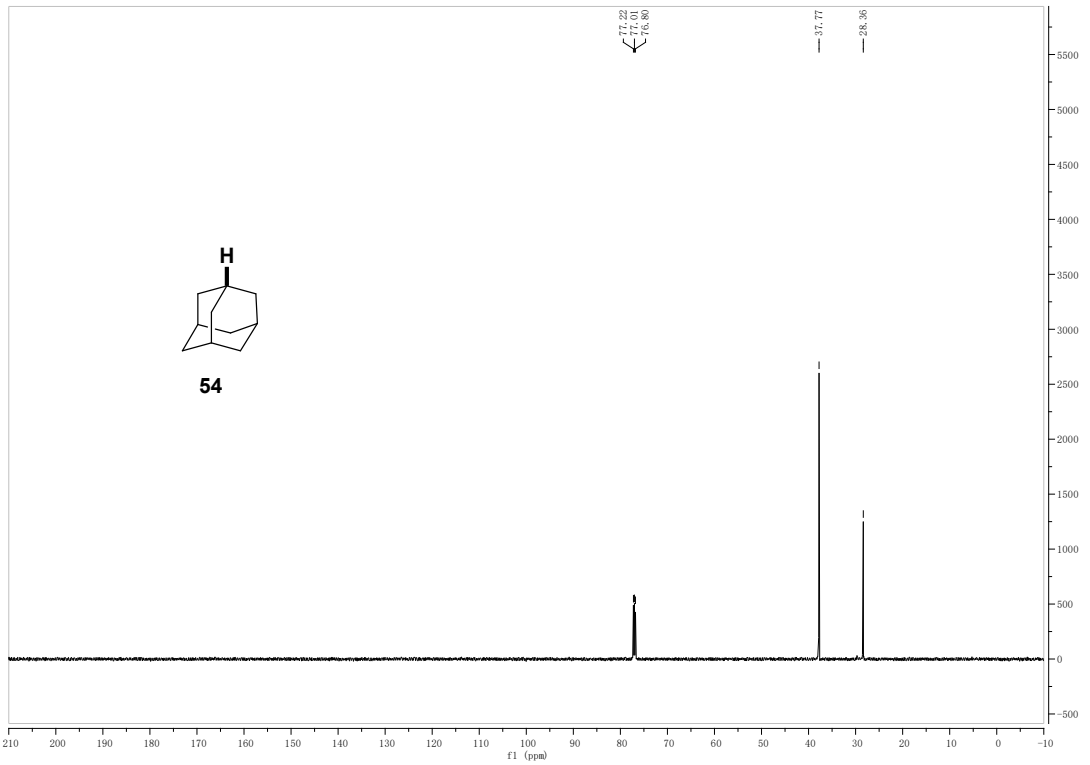

154.68
79.84
77.25
77.04
76.82
45.93
45.59
34.00
28.53
28.48
26.01
25.71
24.96
H
N
Boc
52
f1 (ppm)


3.36
3.36
3.35
1.69
1.58
1.58
1.57
1.56
1.55
1.51
1.50
1.47
1.45
1.44
H
N
Boc
53
4.00
2.03
9.01
f1 (ppm)

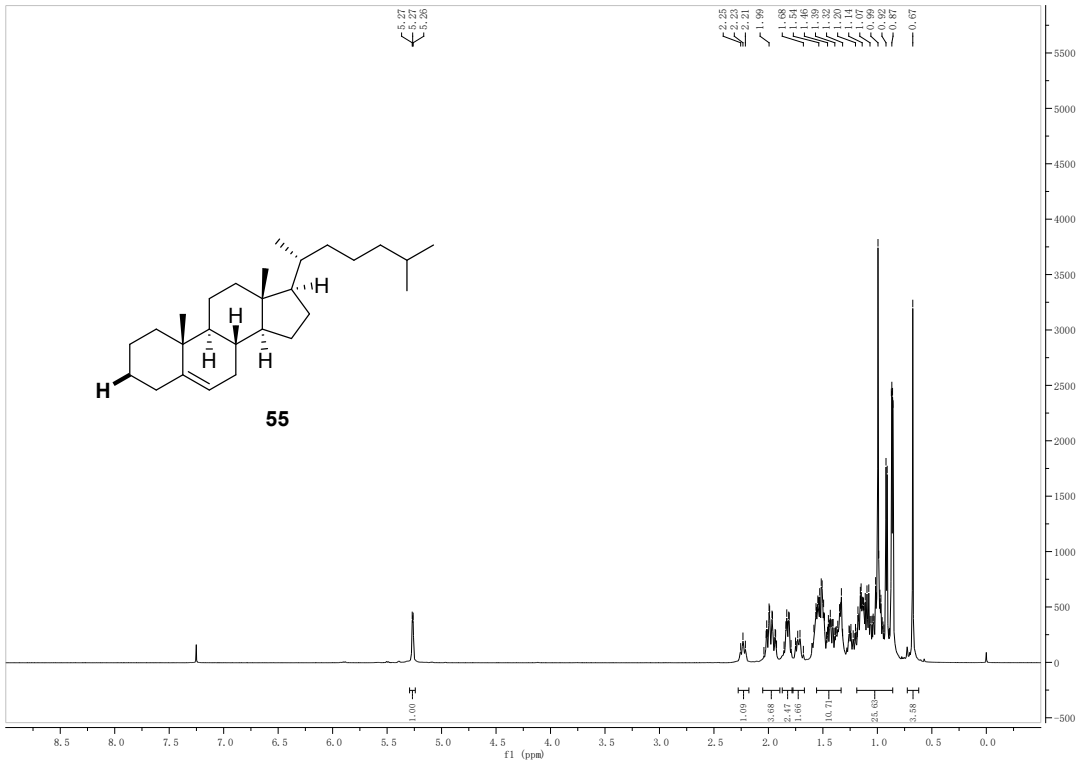

154.96
79.08
77.22
77.01
76.79
28.48
25.75
24.51
H
N
Boc
53
f1 (ppm)

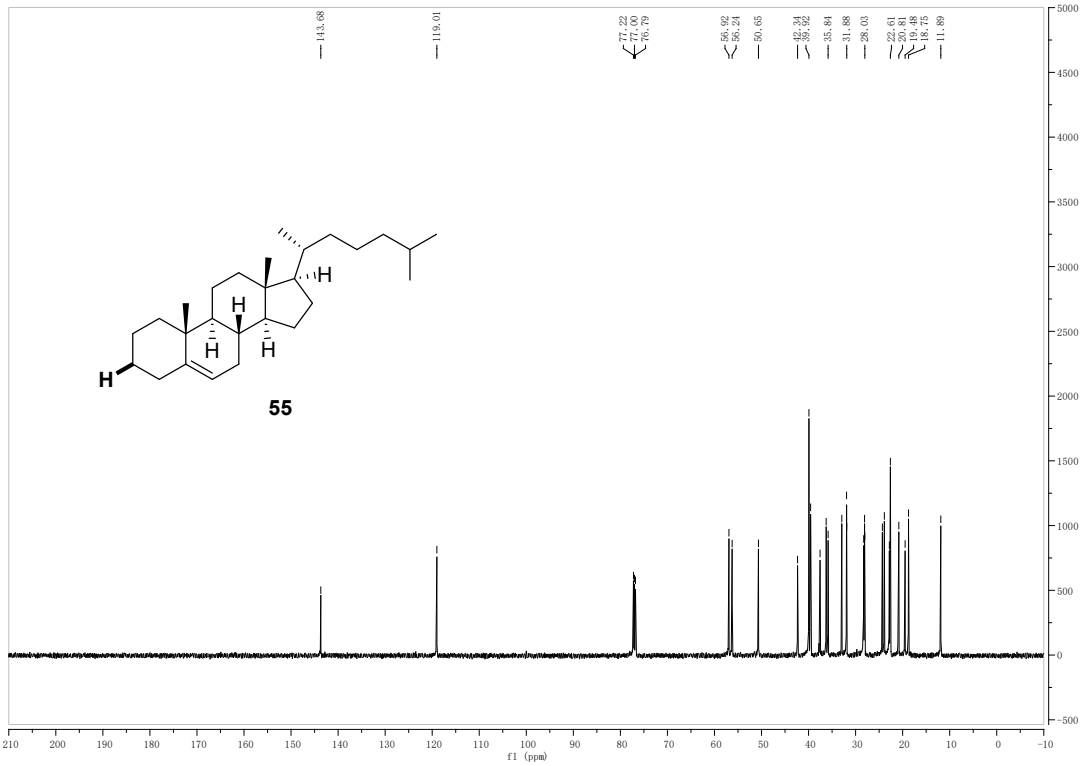


54



54


5.27
5.27
5.26
2.25
2.23
2.21
1.99
1.68
1.54
1.46
1.39
1.32
1.20
1.14
1.07
0.99
0.92
0.87
0.67
55
1.00
1.09
3.68
2.47
1.66
10.71
25.63
3.58
f1 (ppm)


143.68
119.01
77.22
77.00
76.79
56.92
56.24
50.65
42.34
39.92
35.84
31.88
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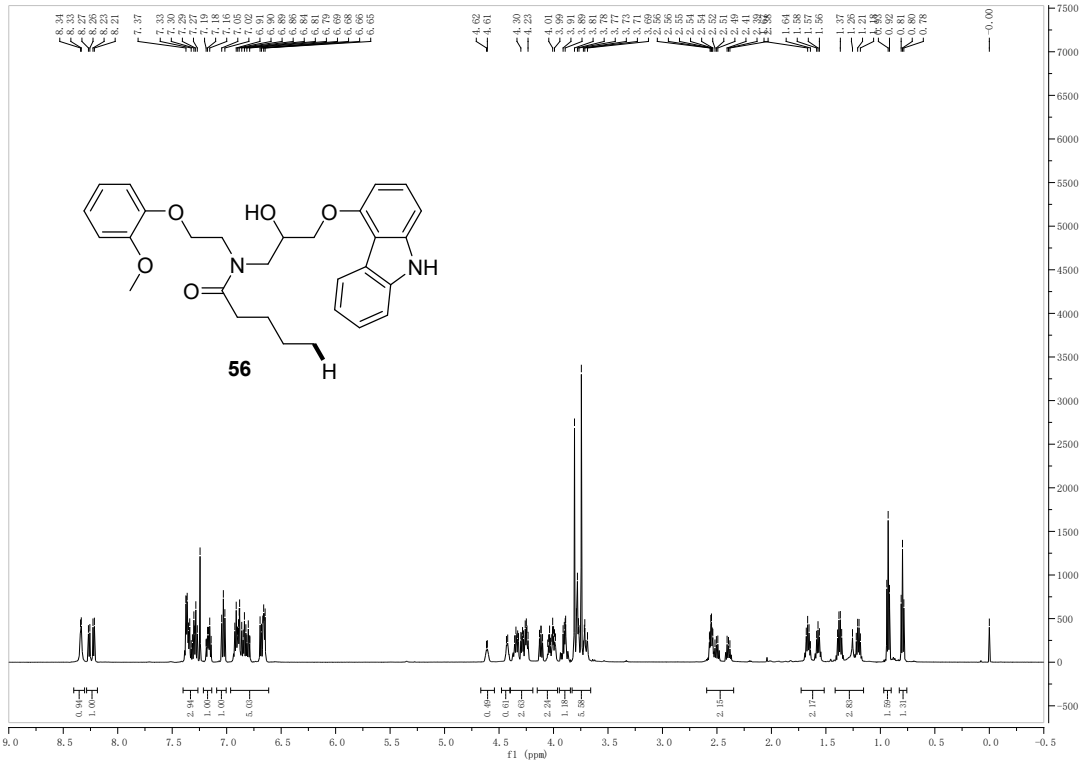
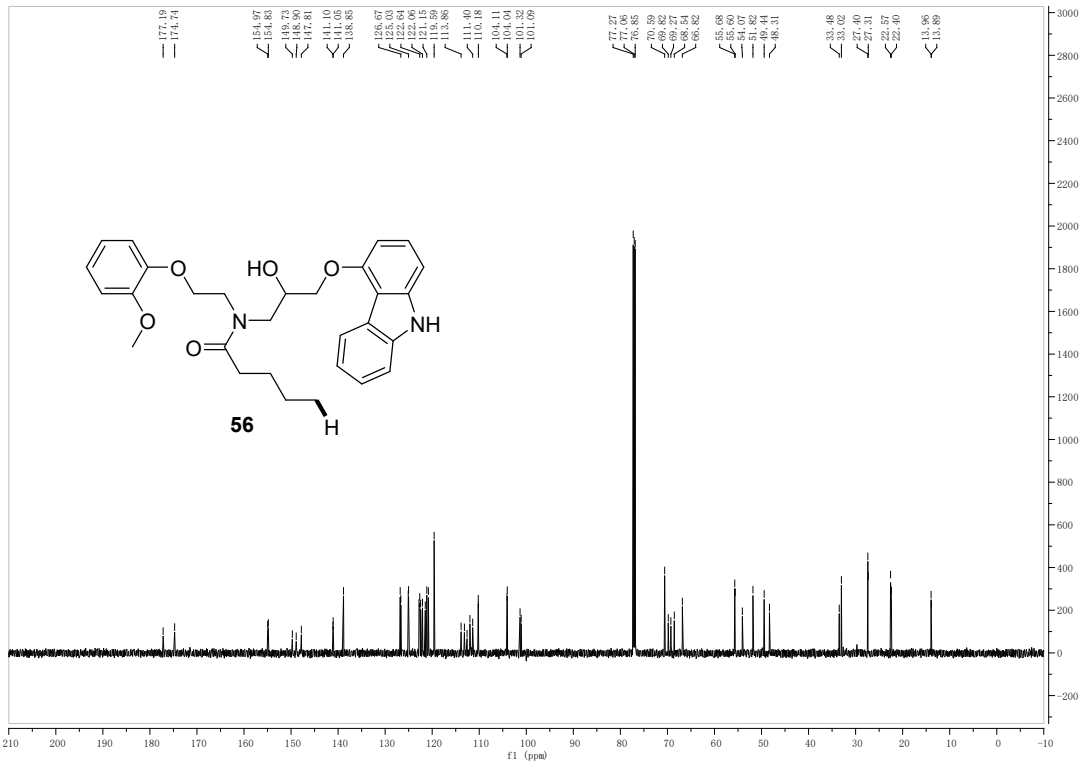
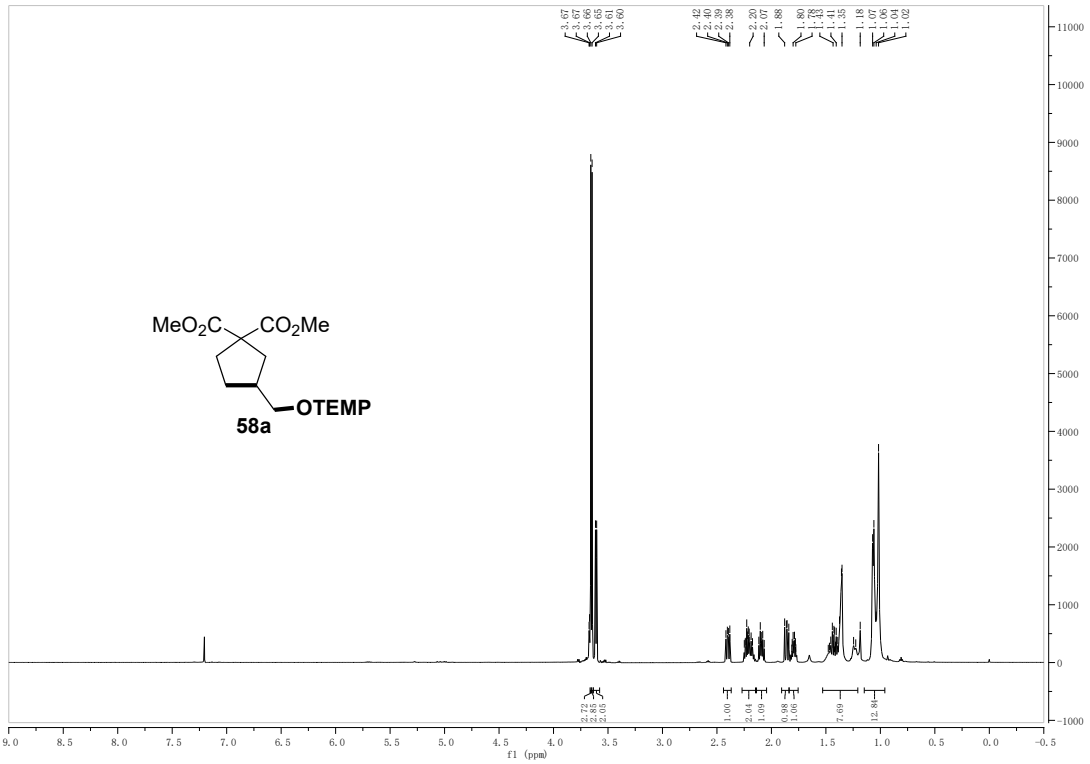
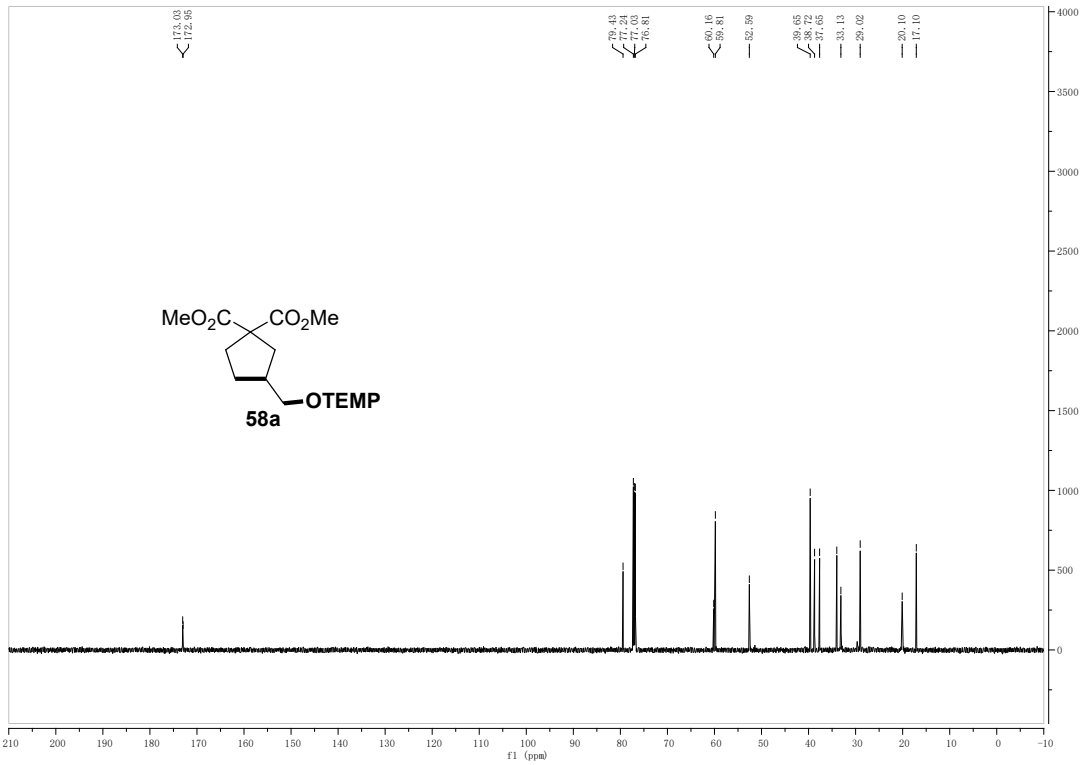
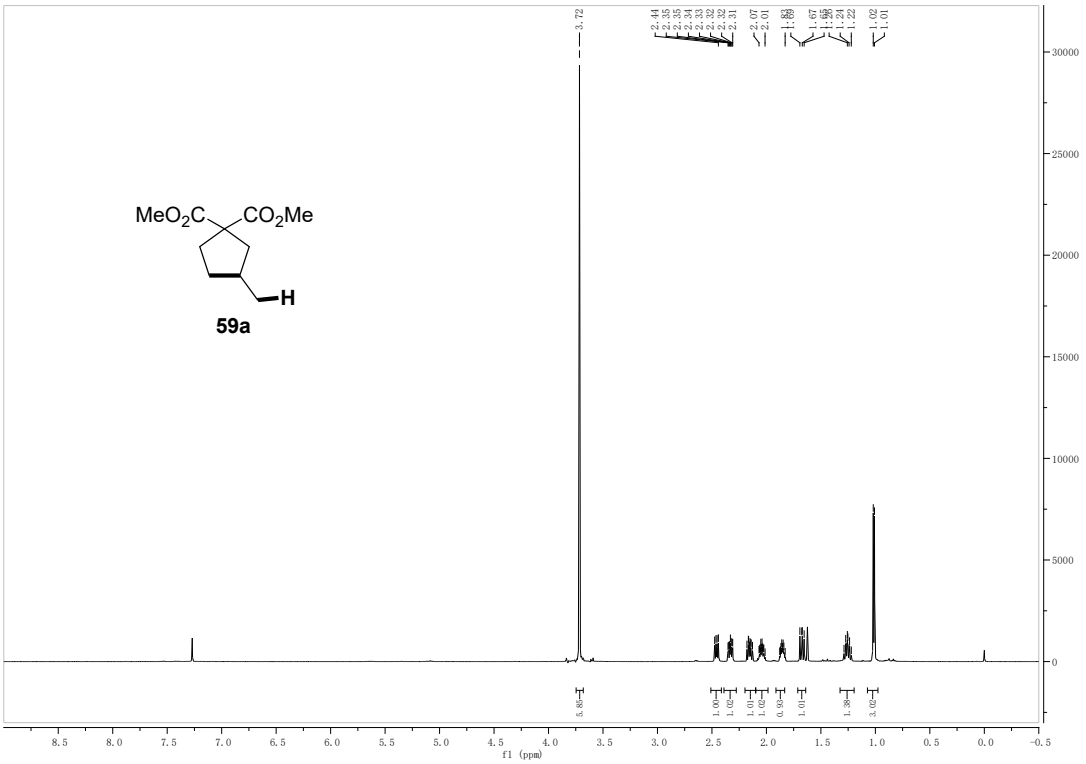
20.81
19.48
18.75
11.89
55
f1 (ppm)

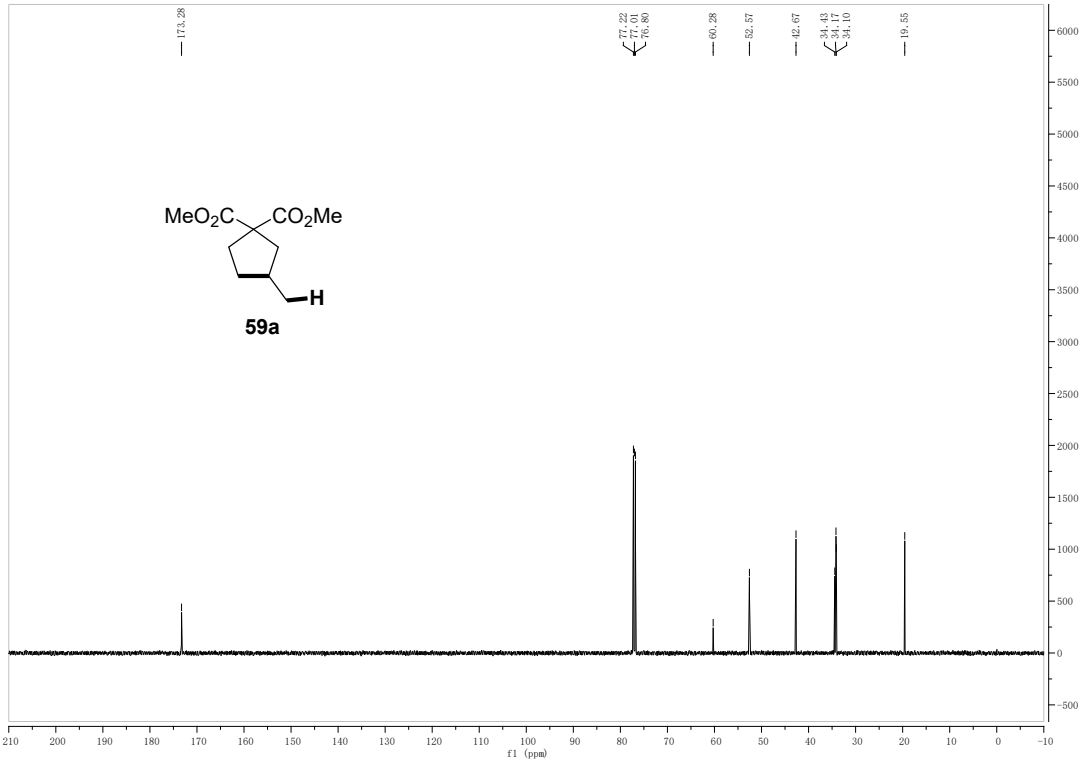

HO
O
N
NH
O
56
H
f1 (ppm)

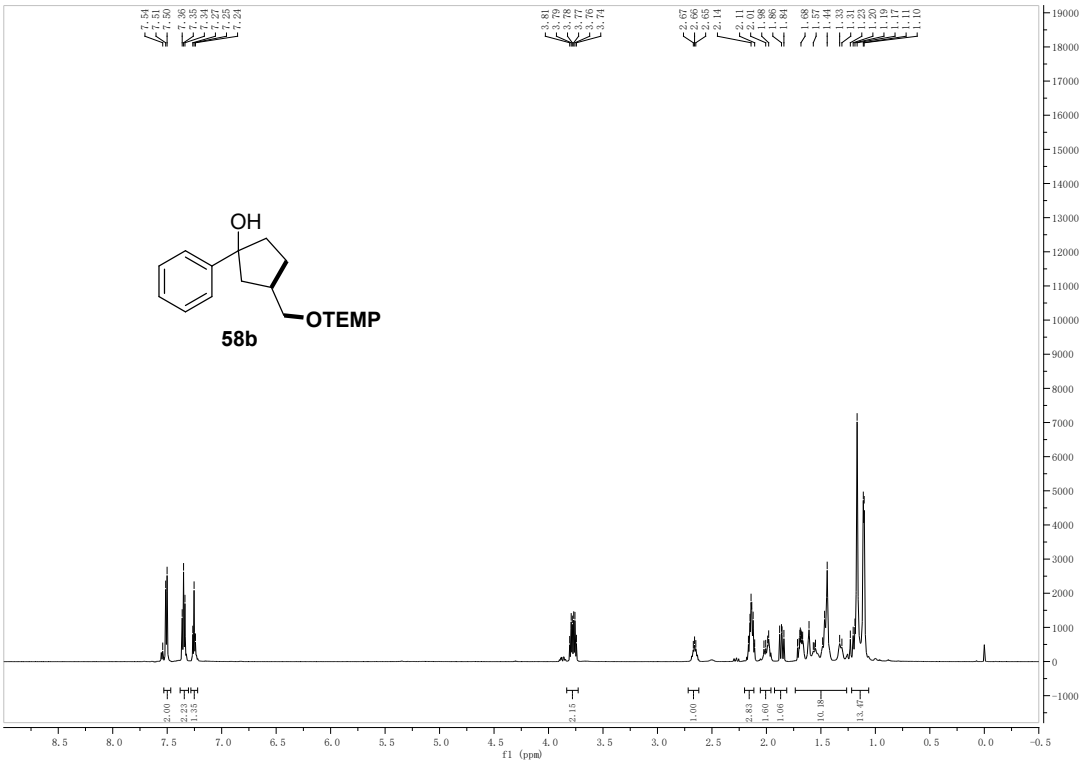

HO
O
N
NH
O
56
H
f1 (ppm)

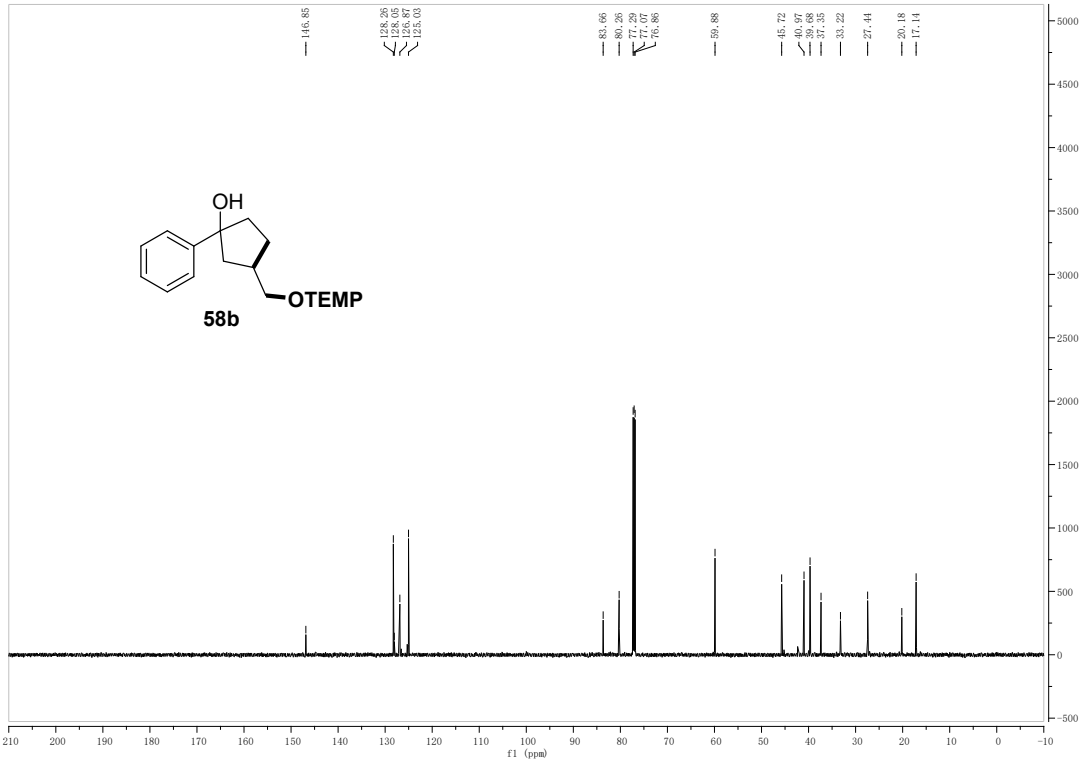

MeO2C
CO2Me
OTEMP
58a
f1 (ppm)

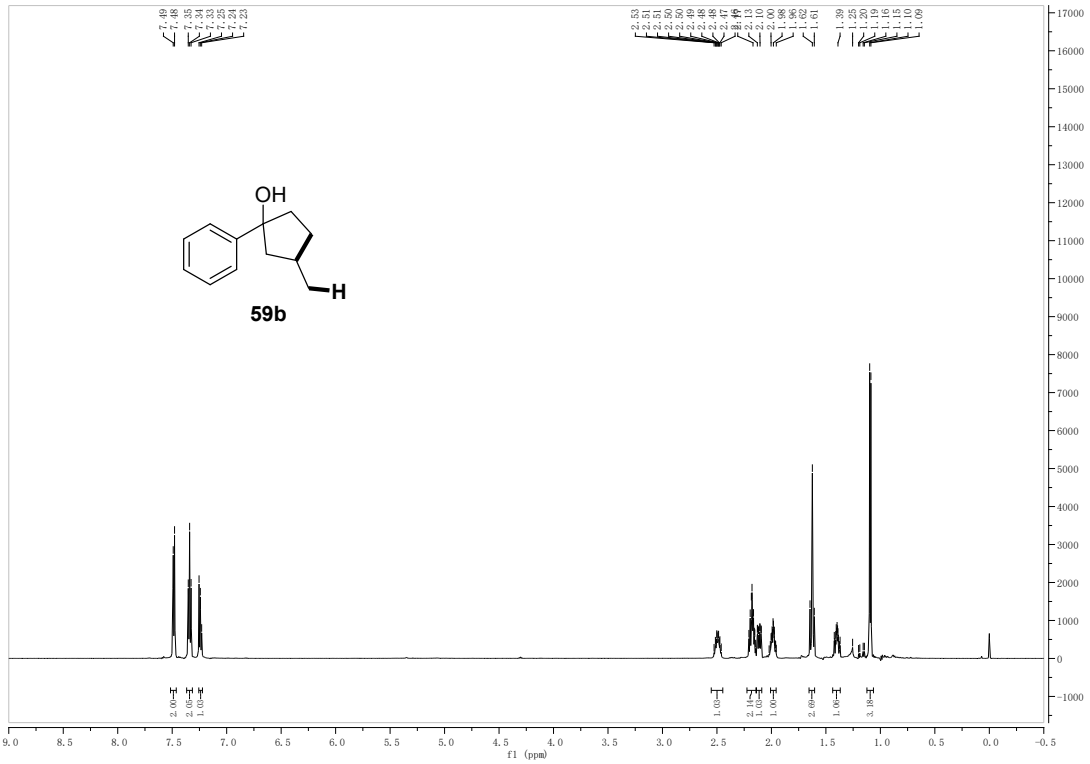

MeO2C
CO2Me
OTEMP
58a
f1 (ppm)

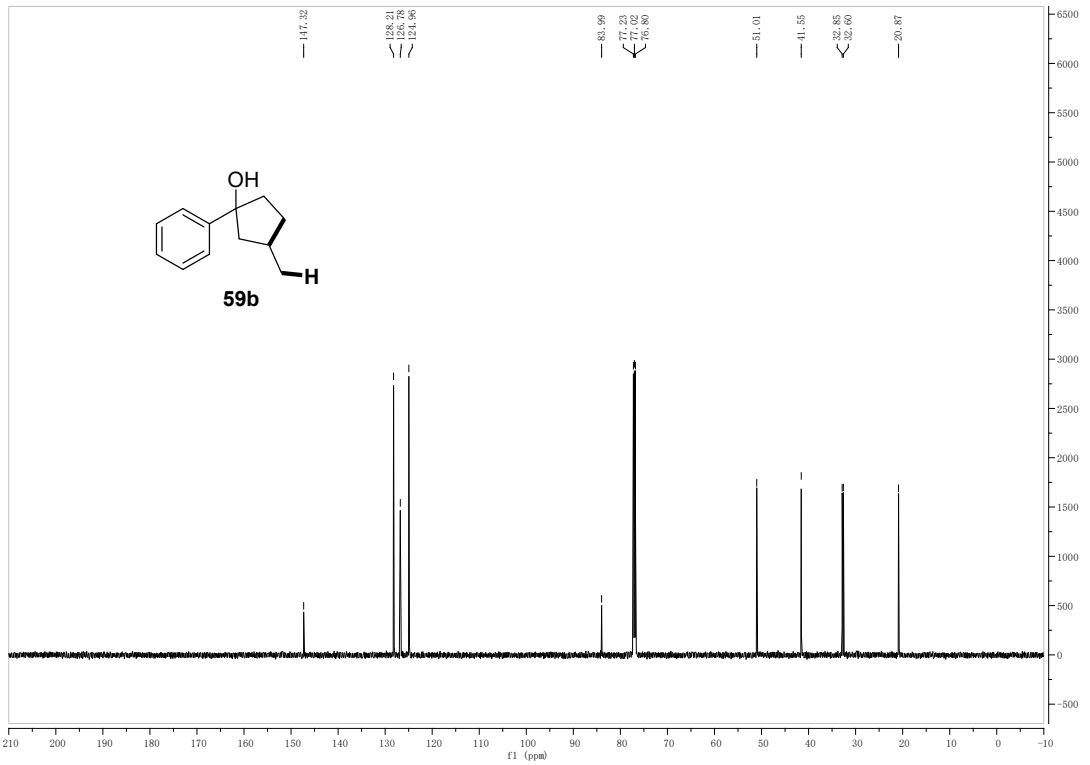

MeO2C
CO2Me
H
59a
f1 (ppm)

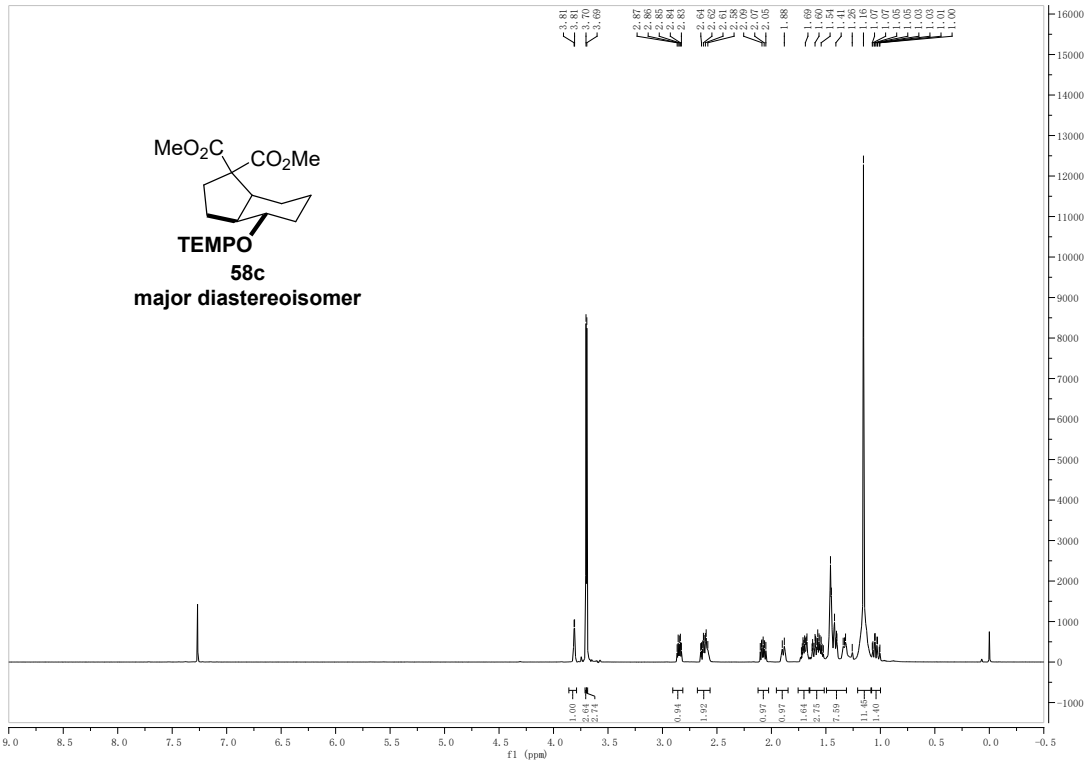

MeO2C
CO2Me
H
59a
f1 (ppm)

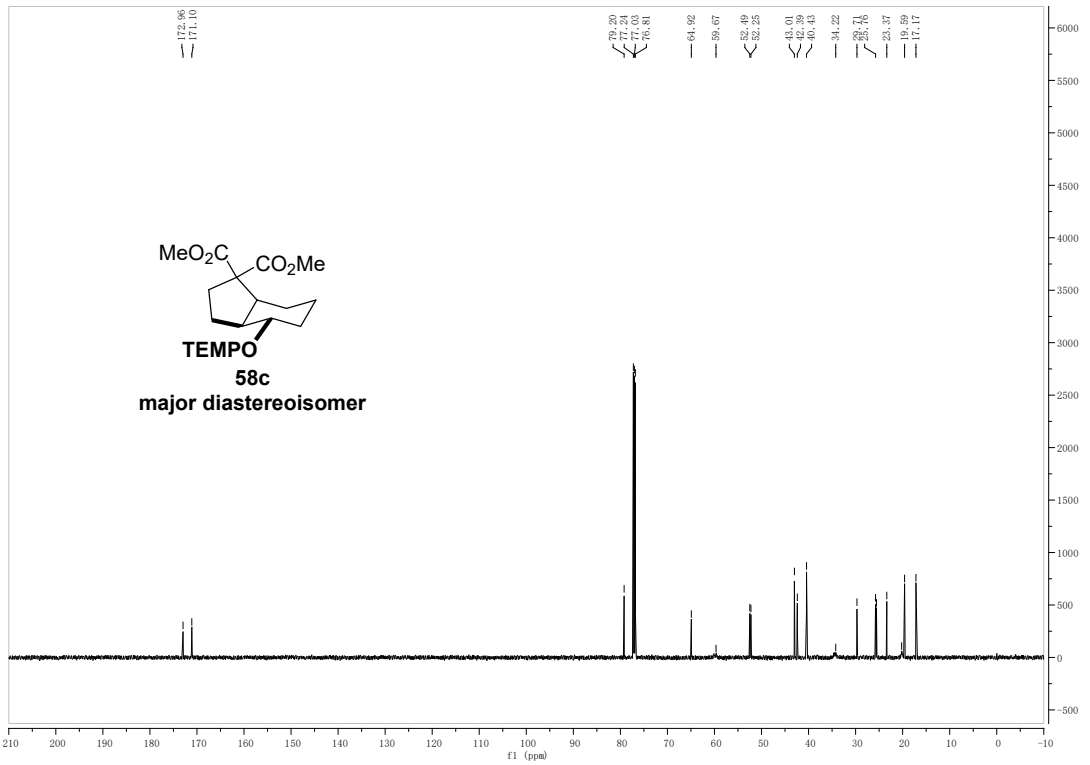

OH
OTEMP
58b
f1 (ppm)

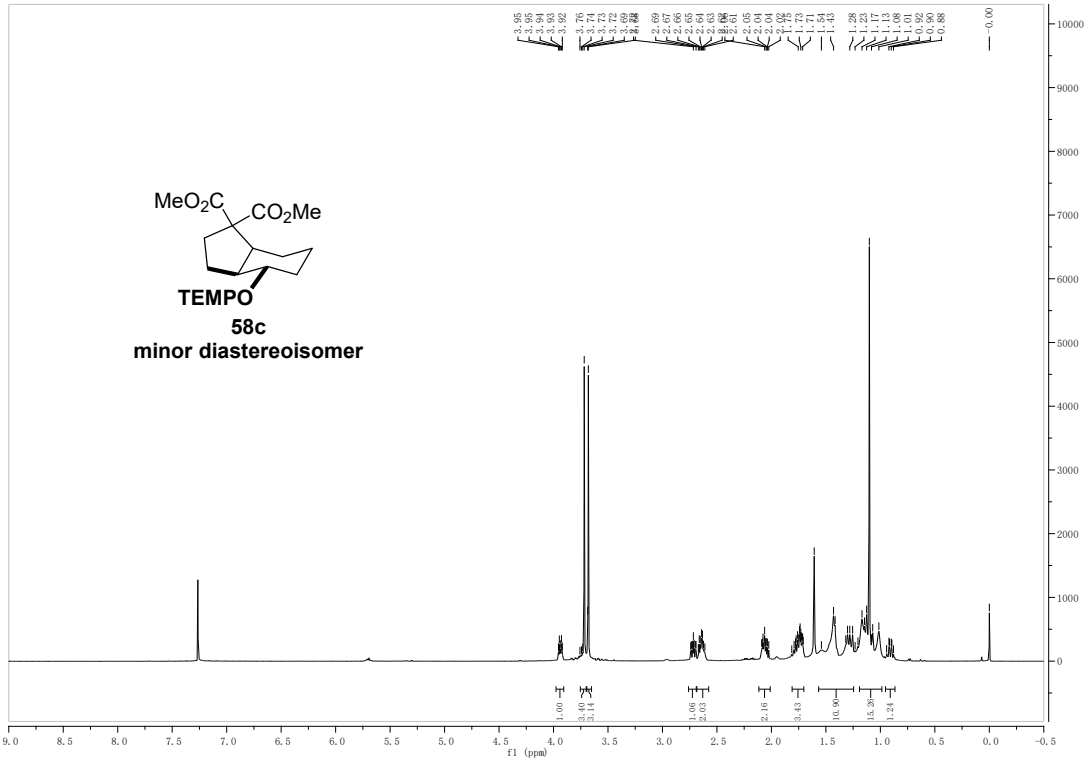

OH
OTEMP
58b
f1 (ppm)

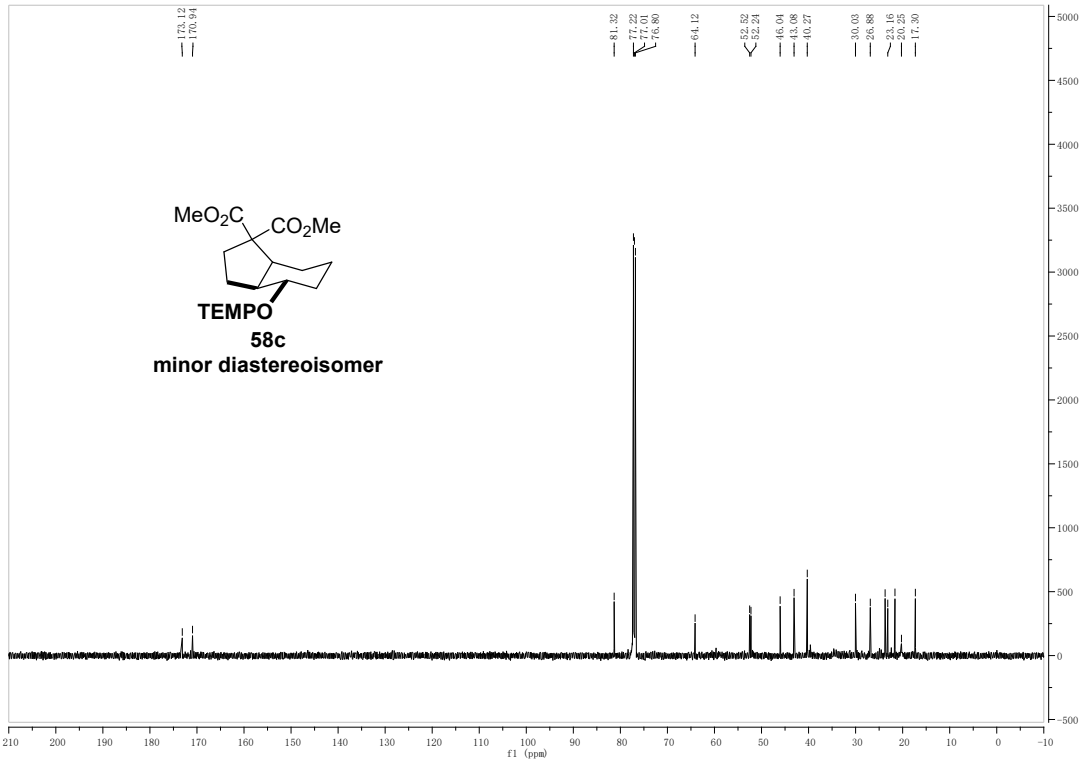

OH
H
59b
f1 (ppm)

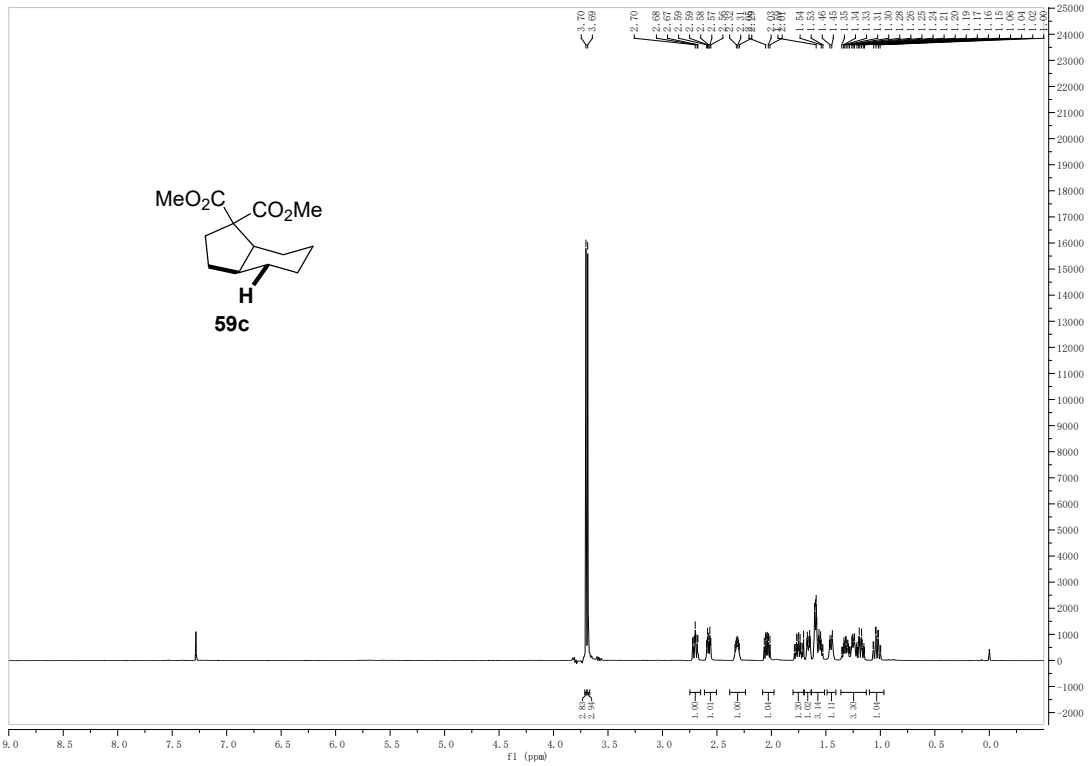

OH
H
59b
f1 (ppm)

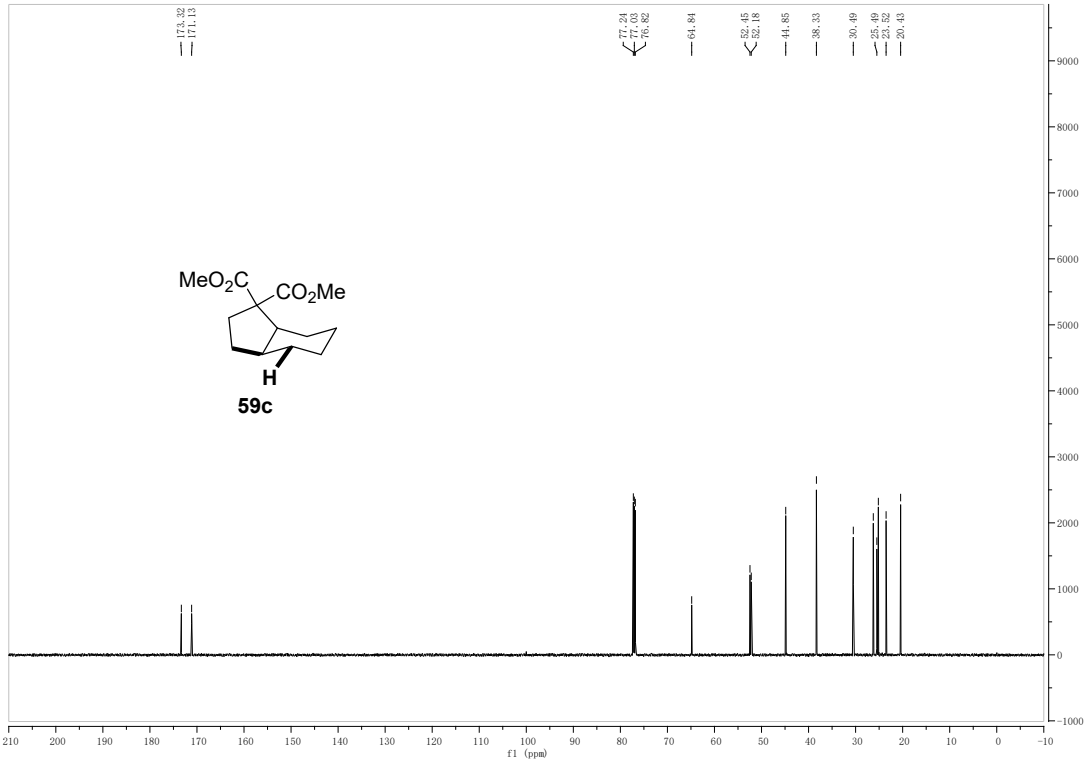

MeO2C
CO2Me
TEMPO
58c
major diastereoisomer
f1 (ppm)

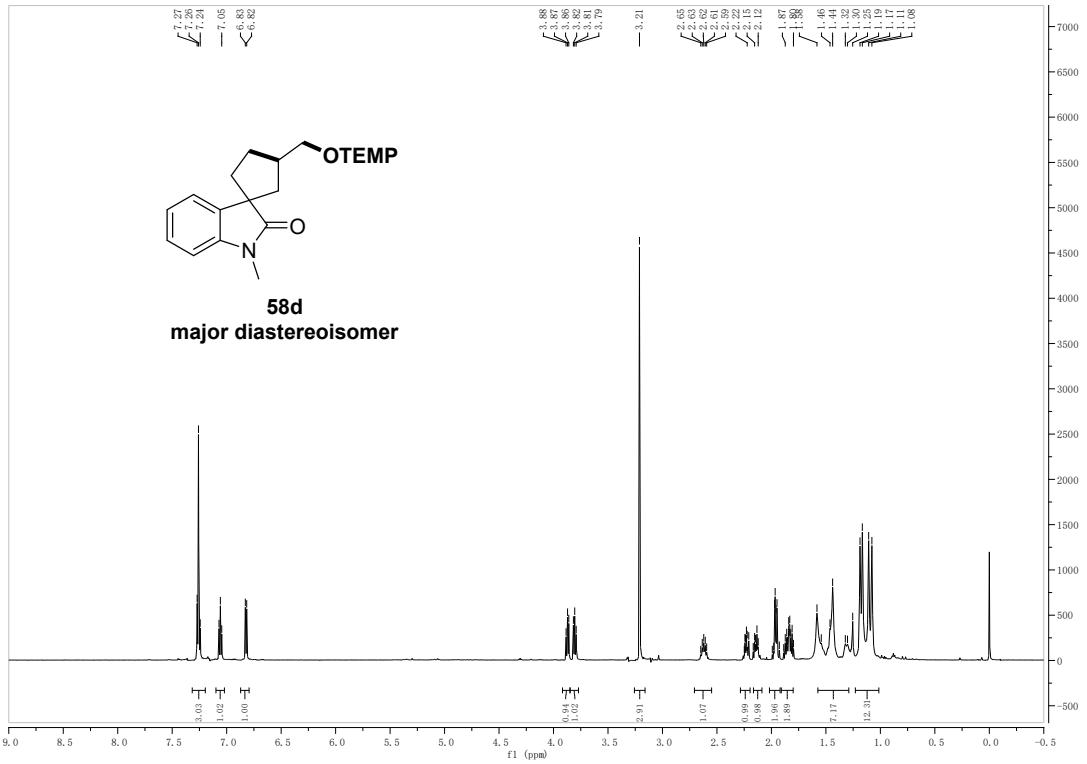

MeO2C
CO2Me
TEMPO
58c
major diastereoisomer
f1 (ppm)

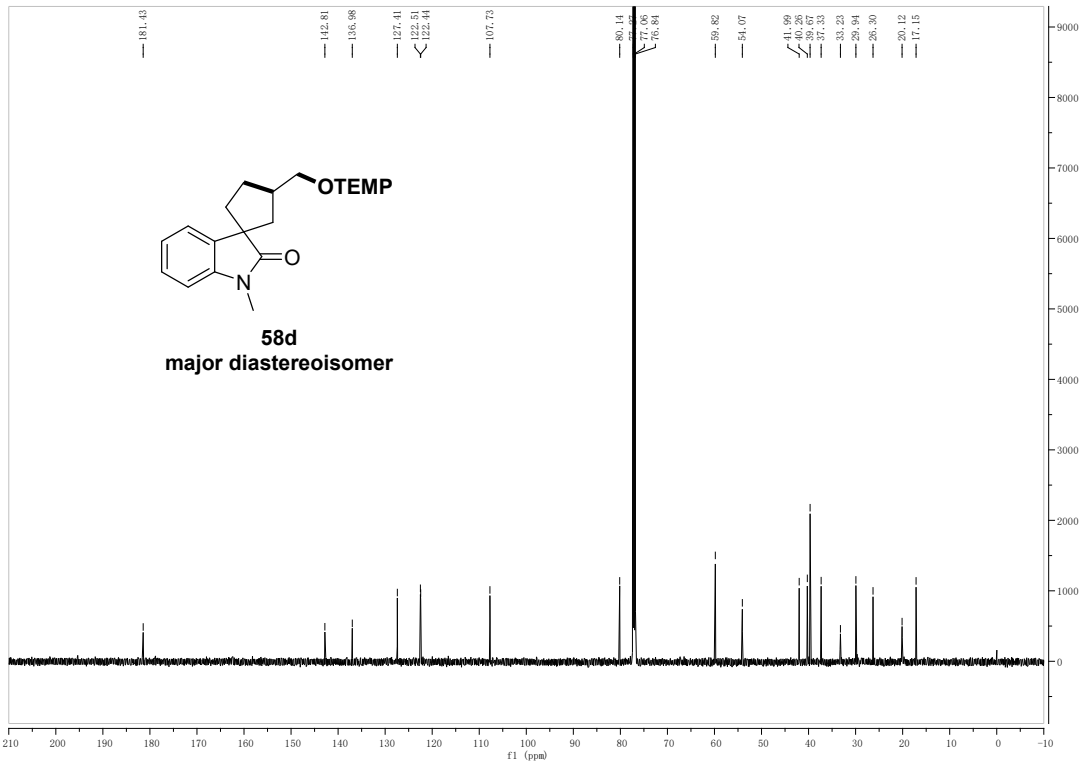

MeO2C
CO2Me
TEMPO
58c
minor diastereoisomer
f1 (ppm)

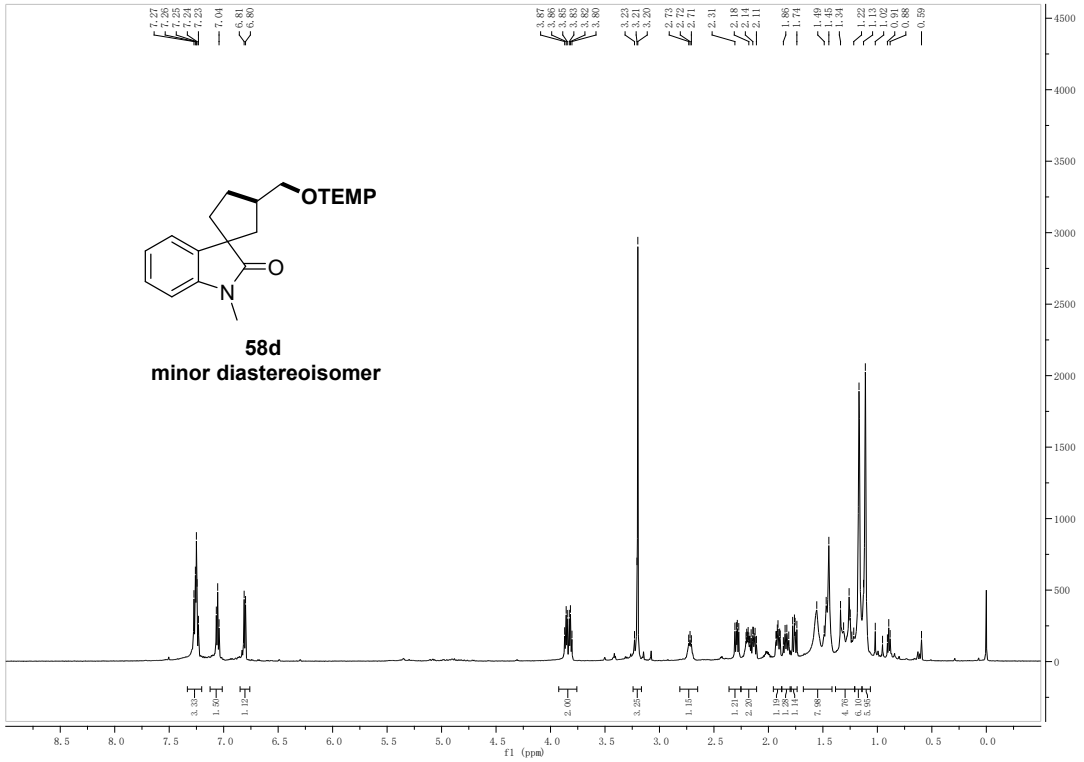

MeO2C
CO2Me
TEMPO
58c
minor diastereoisomer
f1 (ppm)

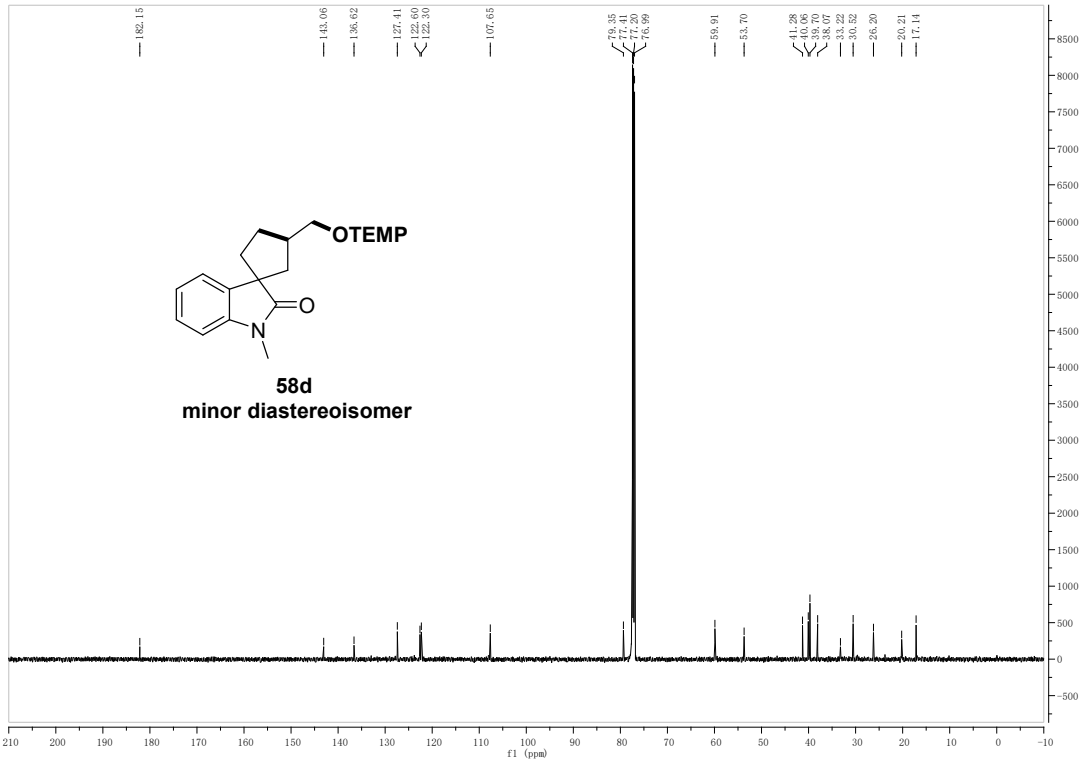

MeO2C
CO2Me
H
59c
f1 (ppm)

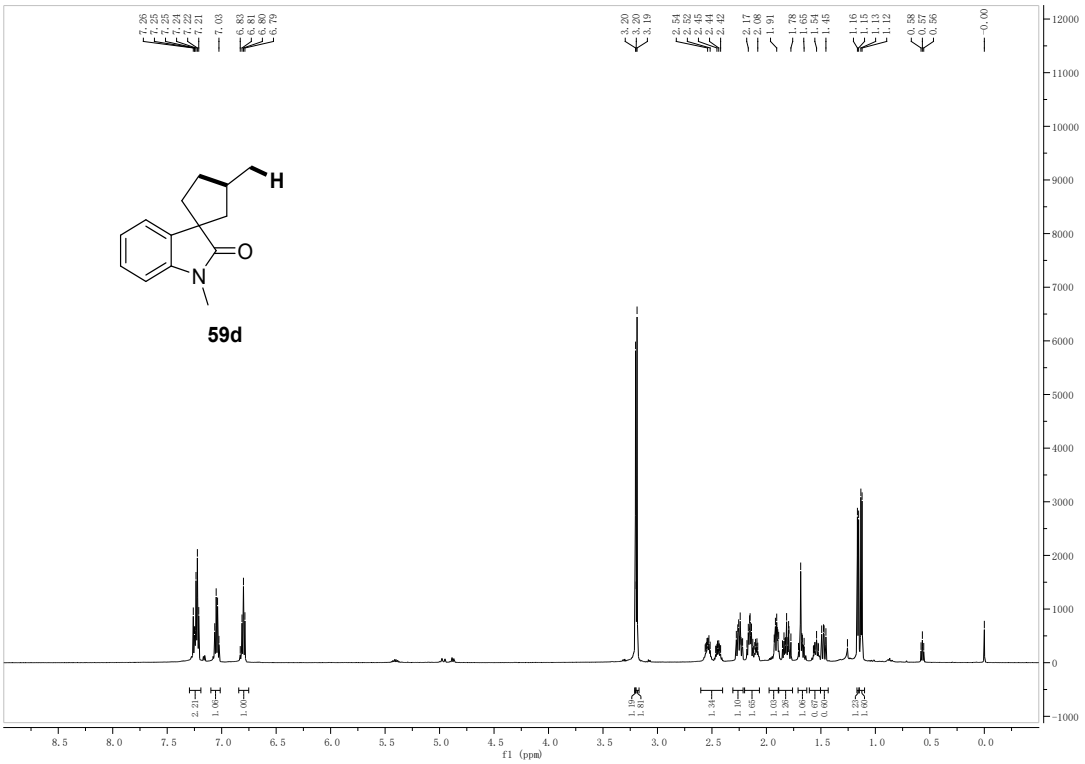

MeO2C
CO2Me
H
59c
f1 (ppm)

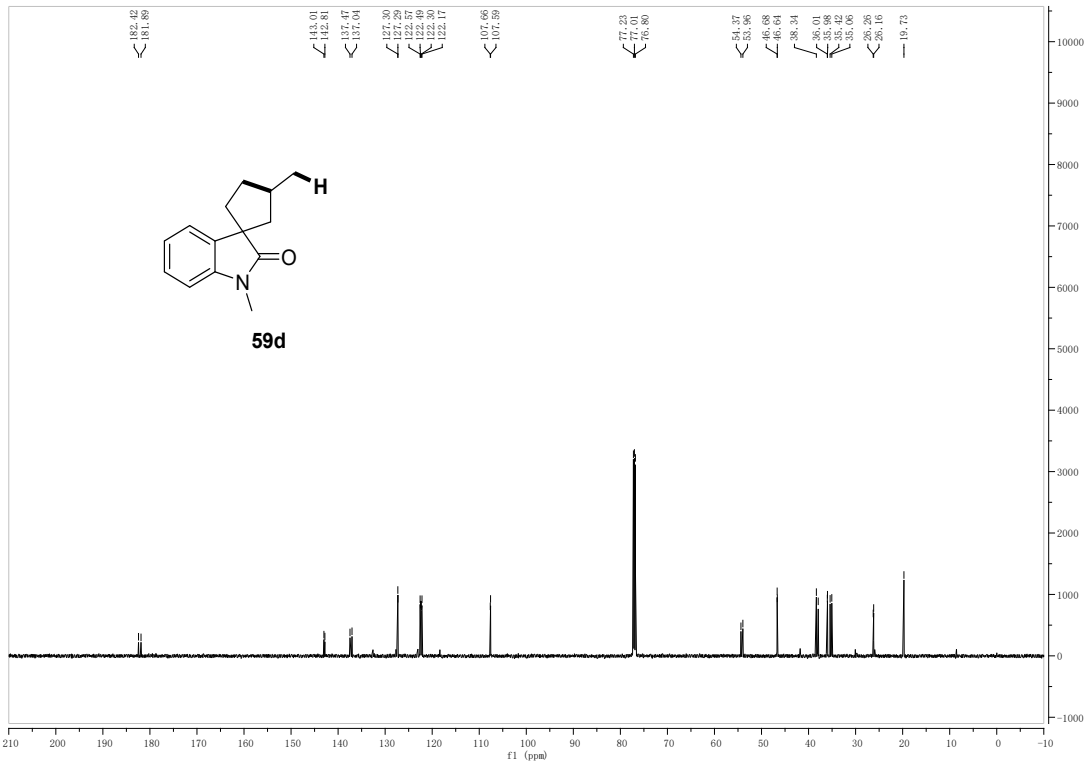

OTEMP
O
N
58d
major diastereoisomer
f1 (ppm)


OTEMP
O
N
58d
major diastereoisomer
f1 (ppm)


OTEMP
O
N
58d
minor diastereoisomer
f1 (ppm)


OTEMP
O
N
58d
minor diastereoisomer
f1 (ppm)


59d
f1 (ppm)


59d
f1 (ppm)