Supplementary Information

Recyclable *g*-C_3N_4 Catalyzed Decarboxylative Alkenylation of *N*-aryl Glycines with Vinyl Sulfones under Visible-Light Irradiation

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1. General information

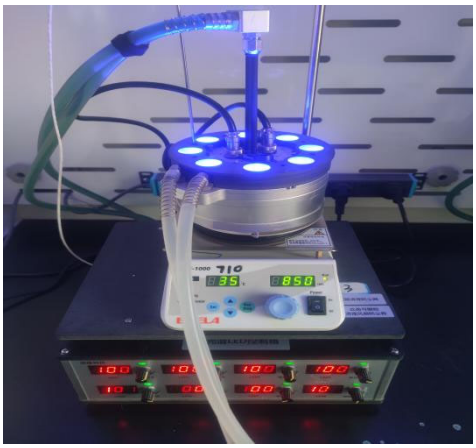
1.1 Materials and instruments.

All the reactions were conducted in 20 mL test tubes unless otherwise noted. All solvents were obtained from commercial suppliers and used without further purification. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on 400 spectrometer and 500 spectrometer in $CDCl_3$ (δH = 7.26 ppm, δC = 77.02 ppm as standard). Data for ^{1}H NMR are reported as follows: chemical shift (ppm, scale), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). High-resolution mass spectra (HRMS) were obtained with a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique.

1.2 The spectrum of the lamp and the visible-light irradiation instrument.

The photochemical reaction was conducted under visible light irradiation using a LED at 35 ℃. The RLH-18CU-C 8-position Photo Reaction System, manufactured by Beijing Roger Tech Ltd., was used in this setup. The photo reactor is equipped with Eight 15 W LEDs. The LEDs have an energy peak wavelength of 460 nm, a peak width at half-height of 20.6 nm, and an irradiance of 126.71 mW/cm^2 at 15 W. The reaction vessel consists of a borosilicate glass tube placed 1.5 cm from the light source, with no filter applied (Figure S1).



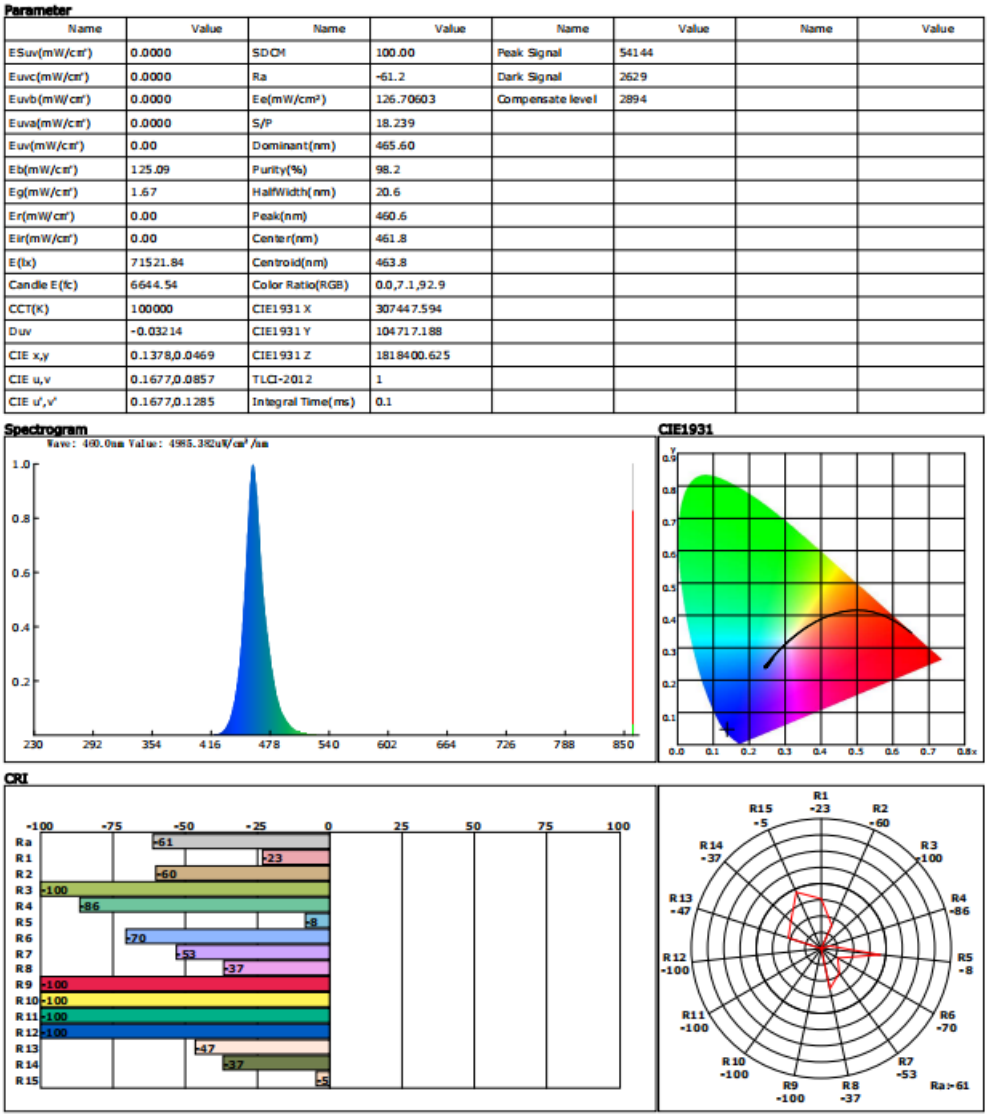
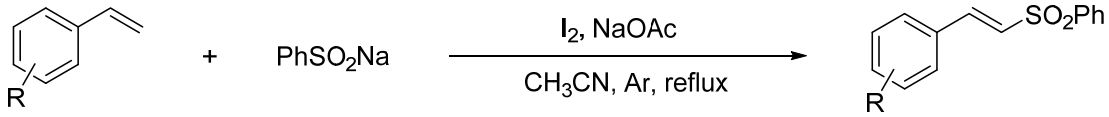


Figure S1. The spectrum of the LED and the visible-light irradiation apparatus.

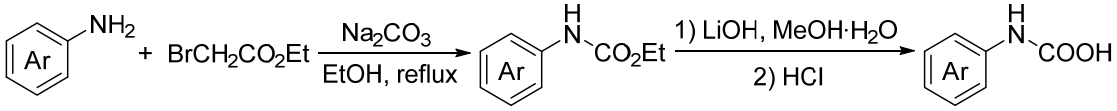
2. Preparation of alkenyl sulfones



Alkenyl sulfones were synthesized according to literature report[1], To a suspension of benzenesulfinic acid sodium salt (3.0 equiv.) and NaOAc (1.5 equiv.) in MeCN (20 mL) was added olefin (5.0 mmol, 1.0 equiv.) followed by iodine (1.5 equiv.). The mixture was heated to reflux for 1 h before being allowed to cool and the excess iodine quenched with 10% aq. sodium thiosulfate. Sat. aq. $NaHCO_3$ was added and the product extracted into DCM (3 x 20 mL). The combined organic phases were washed with H_2O (20 mL), brine (20 mL), dried (MgSO4), filtered, and concentrated

in vacuo. The crude product was purified by flash column chromatography. The spectral data is consistent with the literature data.

3. Preparation of *N*-aryl glycines

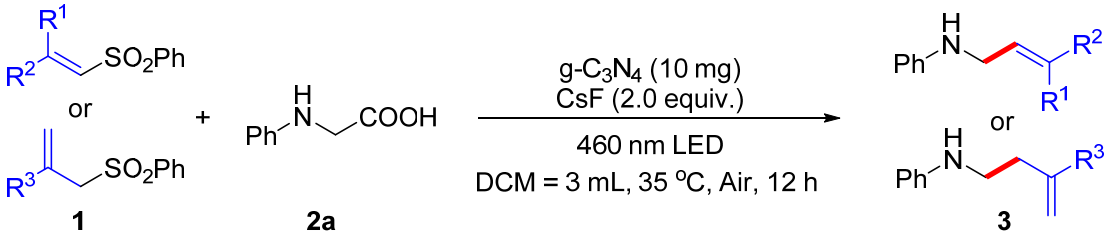


N-aryl glycines are synthesized according to the reported literature.[2] To a solution of aniline (5 mmol, 1.0 equiv.) in ethanol (10 mL) was added sodium carbonate (1.5 equiv.) and ethyl bromoacetate (1.2 equiv.) and the suspension was stirred at reflux for 12 h. After cooling to room temperature, the precipitated salts were removed by filtration. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography to obtain ethyl arylglycinate.

To a solution of ethyl aryl glycinate (3.0 mmol) in MeOH-H_2O (30 mL, MeOH : H_2O = 4:1) at 0 °C was slowly added LiOH (3.0 equiv.). The reaction mixture was allowed to warm to room temperature overnight. Methanol was removed in vacuo and the residual aqueous solution was partitioned with ethyl acetate (20 mL), then the organic phase was extracted with H_2O (5-10 mL, two times). The combined aqueous extracts were acidified to pH 4-5 with 1 mol/L HCl. The aqueous phase was extracted with EA three times. The combined organic extract was dried over Na_2SO_4 and concentrated in vacuo and subjected to chromatography on silica gel to afford the *N*-aryl glycines.

4. General procedure

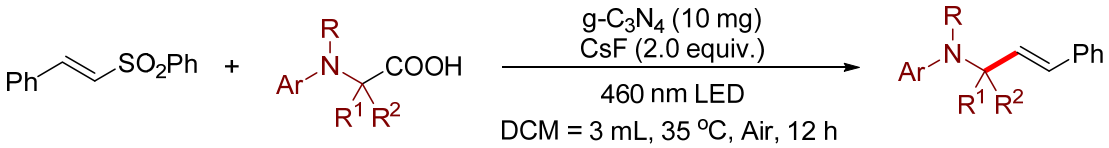
For alkenyl sulfone



Under air atmosphere, to an oven-dried 20 mL test tube equipped with stirring bar, g-C_3N_4 (10 mg), **1** (0.2 mmol), **2a** (2.0 equiv), CsF (2.0 equiv) were sequentially added, and then DCM (3 mL) was added. The reaction mixture was heated at 35 °C in air for 12 h under the irradiation of 15 W 460 nm LED. When the reaction finished, removing of solvent under reduced pressure and the resulting

residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate) to give the desired product **3**.

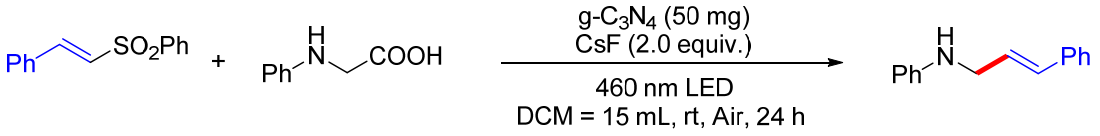
For *N*-aryl Glycines



1a **2** **4**

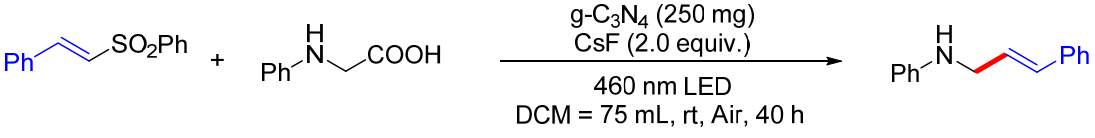
Under air atmosphere, to an oven-dried 20 mL test tube equipped with stirring bar, g-C_3N_4 (10 mg), **1a** (0.2 mmol), **2** (2.0 equiv), CsF (2.0 equiv) were sequentially added, and then DCM (3 mL) was added. The reaction mixture was heated at 35 °C in air for 12 h under the irradiation of 15 W 460 nm LED. When the reaction finished, removing of solvent under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate) to give the desired product **4**.

Scale-up experiment



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

Under air atmosphere, to an oven-dried 50 mL eggplant equipped with stirring bar, g-C_3N_4 (50 mg), **1a** (1 mmol), **2a** (2.0 equiv), CsF (2.0 equiv) were sequentially added, and then DCM (15 mL) was added. The reaction mixture was stirred at room temperature in air for 24 h under the irradiation of 40 W 460 nm LED. When the reaction finished, removing of solvent under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel to give the desired product **3a** in 70% yield (145 mg).

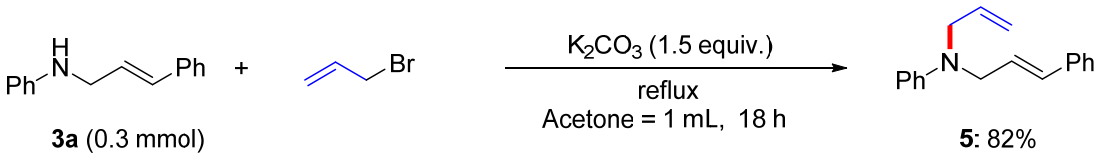


1a **2a** **3a**

Under air atmosphere, to an oven-dried 250 mL eggplant equipped with stirring bar, g-C_3N_4 (250 mg), **1a** (5 mmol), **2a** (2.0 equiv), CsF (2.0 equiv) were sequentially added, and then DCM (75 mL)

was added. The reaction mixture was stirred at room temperature in air for 40 h under the irradiation of 40 W 460 nm LED. When the reaction finished, removing of solvent under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel to give the desired product **3a** in 61% yield (639 mg).

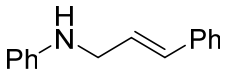
Transformation of product 3a



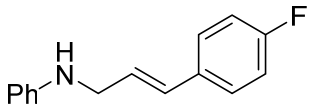
3a (0.3 mmol) **5**: 82%

To an oven-dried 10 mL pressure-resistant tube equipped with stirring bar, **3a** (0.3 mmol, 1.0 equiv.), allyl bromide (1.5 equiv.), K_2CO_3 (1.5 equiv.), were sequentially added, and then Acetone (1 mL) was added. The reaction was stirred and refluxed at 80 ℃ for 18 h. When the reaction finished, removing of solvent under reduced pressure and the resulting residue was purified by flash column chromatography on silica gel to give the desired product **5** in 82% yield (61.2 mg).

5. Characterization of products

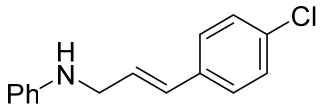


N-cinnamylaniline (**3a**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 35.4 mg. 85%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.25 – 7.20 (m, *2*H), 7.17 – 7.09 (m, 3H), 6.68 – 6.62 (m, 1H), 6.61 – 6.57 (m, 2H), 6.54 (dt, *J* = 16.0, 1.7 Hz, 1H), 6.25 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.85 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.77 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 136.8, 131.5, 129.3, 128.6, 127.5, 127.0, 126.3, 117.6, 113.0, 46.2. HRMS m/z (ESI) calcd for $C_{15}H_{16}N$ $(M + H)^+$: 210.1277; found: 210.1277.

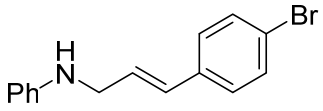


(E)-N-(3-(4-fluorophenyl)allyl)aniline (**3b**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 39.2 mg, 86%, purified by flash

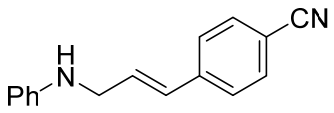
chromatography (petroleum ether/ethyl acetate 50:1), brown solid; Rf = 0.4 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.21 – 7.17 (m, 2H), 7.02 – 6.96 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 6.60 – 6.55 (m, 2H), 6.24 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.92 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.84 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.6 Hz), 147.9, 133.0 (d, *J* = 3.2 Hz), 130.3, 129.3, 127.8 (d, *J* = 8.1 Hz), 126.8 (d, *J* = 2.3 Hz), 117.7, 115.4 (d, *J* = 21.5 Hz), 113.0, 46.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.6. HRMS m/z (ESI) calcd for $C_{15}H_{15}FN$ $(M + H)^+$: 228.1183; found: 228.1186.



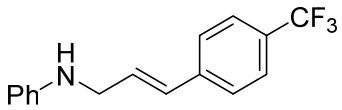
(E)-N-(3-(4-chlorophenyl)allyl)aniline (**3c**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 41.5 mg, 85%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 4H), 7.11 – 7.07 (m, 2H), 6.67 – 6.61 (m, 1H), 6.58 – 6.54 (m, 2H), 6.46 (dt, *J* = 15.9, 1.7 Hz, 1H), 6.19 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.82 (dd, *J* = 5.7, 1.7 Hz, 2H), 3.76 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 135.3, 133.1, 130.2, 129.3, 128.7, 127.8, 127.5, 117.7, 113.0, 46.1. HRMS m/z (ESI) calcd for $C_{15}H_{15}ClN$ $(M + H)^+$: 244.0888; found: 244.0891.



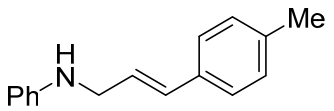
(E)-N-(3-(4-bromophenyl)allyl)aniline (**3d**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 48.4 mg, 84%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.20 (dd, *J* = 18.0, 8.1 Hz, 4H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 2H), 6.55 (d, *J* = 16.1 Hz, 1H), 6.31 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.92 (dd, *J* = 5.7, 1.6 Hz, 2H), 3.86 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 135.8, 131.6, 130.2, 129.3, 127.9, 127.9, 121.2, 117.7, 113.0, 46.1. HRMS m/z (ESI) calcd for $C_{15}H_{15}BrN$ $(M + H)^+$: 288.0382; found: 288.0371.



(E)-4-(3-(phenylamino)prop-1-en-1-yl)benzonitrile (**3e**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 32.6 mg, 70%, purified by flash chromatography (petroleum ether/ethyl acetate 5:1), yellow solid; Rf = 0.2 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.45 – 7.42 (m, 2H), 7.22 – 7.17 (m, 2H), 6.77– 6.72 (m, 1H), 6.68 – 6.61 (m, 3H), 6.46 (dt, *J* = 15.9, 5.4 Hz, 1H), 4.00 (dd, *J* = 5.4, 1.7 Hz, 2H), 3.67 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 141.3, 132.4, 131.5, 129.5, 129.3, 126.8, 119.2, 117.8, 112.3, 110.6, 45.9. HRMS m/z (ESI) calcd for $C_{16}H_{14}N_2Na$ $(M + Na)^+$: 257.1049; found: 257.1055.

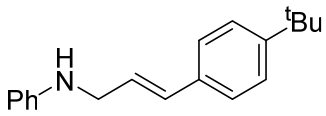


(E)-N-(3-(4-(trifluoromethyl)phenyl)allyl)aniline (**3f**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 44 mg, 79%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), light yellow solid; Rf = 0.4 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.75 – 6.67 (m, 3H), 6.47 (dt, *J* = 15.9, 5.5 Hz, 1H), 4.02 (dd, *J* = 5.5, 1.6 Hz, 2H), 3.93 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 140.3, 129.9, 129.9, 129.3, 129.2 (q, *J* = 25.6 Hz), 126.4, 125.5 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.8 Hz), 117.8, 113.0, 46.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.5. HRMS m/z (ESI) calcd for $C_{16}H_{15}F_3N$ $(M + H)^+$: 278.1151; found: 278.1157.

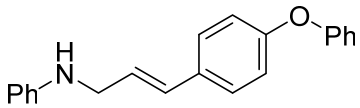


(E)-N-(3-(p-tolyl)allyl)aniline (**3g**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 36.7 mg, 82%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 2H), 7.20 – 7.16 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.74 – 6.69 (m, 1H), 6.68–6.64 (m, 2H), 6.60 – 6.56 (m, 1H), 6.27 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.90 (dd, *J*

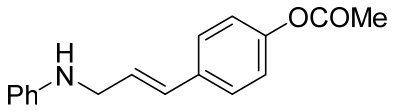
= 5.9, 1.6 Hz, 2H), 3.81 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.1, 137.3, 134.0, 131.4, 129.3, 129.2, 126.2, 125.9, 117.5, 113.0, 46.2, 21.2. HRMS m/z (ESI) calcd for $C_{16}H_{18}N$ $(M + H)^+$: 224.1434; found: 224.1432.



(E)-N-(3-(4-(tert-butyl)phenyl)allyl)aniline (**3h**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 44.4 mg, 84%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 4H), 7.13 – 7.08 (m, 2H), 6.67 – 6.62 (m, 1H), 6.61 – 6.57 (m, 2H), 6.53 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.21 (dt, *J* = 15.8, 5.9 Hz, 1H), 3.85 (dd, *J* = 5.9, 1.6 Hz, 2H), 3.80 (s, 1H), 1.23 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 150.6, 148.0, 134.1, 131.3, 129.4, 126.2, 126.0, 125.5, 117.6, 113.1, 46.3, 34.6, 31.3. HRMS m/z (ESI) calcd for $C_{19}H_{23}NNa$ $(M + Na)^+$: 288.1723; found: 288.1702.

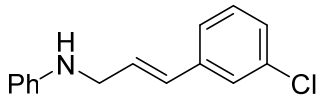


(E)-N-(3-(4-phenoxyphenyl)allyl)aniline (**3i**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 42.8 mg, 71%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.4 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.21 – 7.16 (m, 2H), 7.12 – 7.07 (m, 1H), 7.03 – 6.97 (m, 2H), 6.96 – 6.92 (m, 2H), 6.75 – 6.70 (m, 1H), 6.68 – 6.64 (m, 2H), 6.59 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.24 (dt, *J* = 15.8, 5.8 Hz, 1H), 3.92 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.84 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 156.7, 148.0, 132.1, 130.7, 129.7, 129.3, 127.6, 126.1, 123.3, 118.9, 118.9, 117.6, 113.0, 46.2. HRMS m/z (ESI) calcd for $C_{21}H_{20}N$ $(M + H)^+$: 302.1539; found: 302.1493.

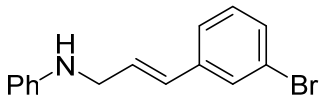


(E)-4-(3-(phenylamino)prop-1-en-1-yl)phenyl acetate (**3j**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 44.3 mg, 83%, purified by

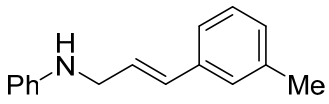
flash chromatography (petroleum ether/ethyl acetate 5:1), yellow solid; Rf = 0.2 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.20 – 7.15 (m, 2H), 7.04 – 7.01 (m, 2H), 6.75 – 6.70 (m, 1H), 6.66 – 6.64 (m, 2H), 6.58 (dt, *J* = 15.8, 1.7 Hz, 1H), 6.26 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.91 (dd, *J* = 5.8, 1.7 Hz, 2H), 3.86 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.6, 150.0, 148.0, 134.7, 130.5, 129.3, 127.4, 127.3, 121.7, 117.7, 113.1, 46.2, 21.2. HRMS m/z (ESI) calcd for $C_{17}H_{17}NO_2Na$ $(M + Na)^+$: 290.1151; found: 290.1148.



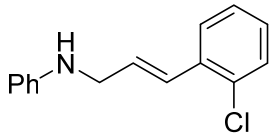
(E)-N-(3-(3-chlorophenyl)allyl)aniline (**3k**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 39 mg, 80%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.4 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 1.6 Hz, 1H), 7.24 – 7.15 (m, 5H), 6.77 – 6.71 (m, 1H), 6.67 – 6.634 (m, 2H), 6.56 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.34 (dt, *J* = 15.9, 5.6 Hz, 1H), 3.95 (dd, *J* = 5.6, 1.7 Hz, 2H), 3.81 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 138.7, 134.5, 130.0, 129.8, 129.3, 128.7, 127.4, 126.3, 124.5, 117.7, 113.0, 46.0. HRMS m/z (ESI) calcd for $C_{15}H_{15}ClN$ $(M + H)^+$: 244.0888; found: 244.0886.



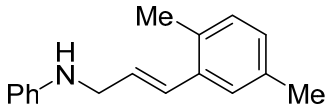
(E)-N-(3-(3-bromophenyl)allyl)aniline (**3l**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 43.2 mg, 77%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 1H), 7.34 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.21 – 7.14 (m, 3H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.6 Hz, 1H), 3.95 – 3.92 (m, 2H), 3.81 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 139.0, 130.3, 130.1, 129.9, 129.3, 129.2, 128.7, 125.0, 122.7, 117.7, 113.0, 46.0. HRMS m/z (ESI) calcd for $C_{15}H_{15}BrN$ $(M + H)^+$: 288.0382; found: 288.0377.



(E)-N-(3-(m-tolyl)allyl)aniline (**3m**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 32.7 mg, 73%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 – 7.07 (m, 5H), 6.99 – 6.95 (m,1H), 6.67 – 6.63 (m, 1H), 6.61 – 6.57 (m, 2H), 6.51 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.23 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.84 (dd, *J* = 5.9, 1.6 Hz, 2H), 3.82 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 138.1, 136.7, 131.6, 129.3, 128.5, 128.3, 127.0, 126.7, 123.4, 117.6, 113.0, 46.2, 21.4. HRMS m/z (ESI) calcd for $C_{16}H_{18}N$ $(M + H)^+$: 224.1434; found: 224.1439.

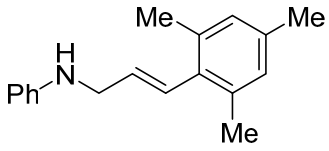


(E)-N-(3-(2-chlorophenyl)allyl)aniline (**3n**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 41.6 mg, 85%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.30 – 7.19 (m, 4H), 7.07 (dt, *J* = 15.8, 1.7 Hz, 1H), 6.80 – 6.77 (m, 1H), 6.75 – 6.71 (m, 2H), 6.35 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.03 (dd, *J* = 5.9, 1.7 Hz, 2H), 3.94 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 135.0, 132.9, 130.1, 129.6, 129.3, 128.5, 127.9, 126.9, 126.8, 117.7, 113.1, 46.3. HRMS m/z (ESI) calcd for $C_{15}H_{15}ClN$ $(M + H)^+$: 244.0888; found: 244.0915.

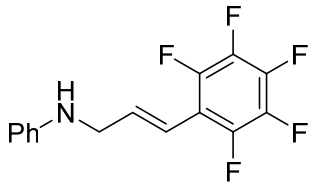


(E)-N-(3-(2,5-dimethylphenyl)allyl)aniline (**3o**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 43 mg, 91%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 1.7 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.96 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.80 (dt, *J* = 15.7, 1.6 Hz, 1H), 6.75 – 6.70 (m, 1H), 6.69 – 6.66 (m, 2H), 6.18 (dt, *J* = 15.7, 5.9 Hz, 1H), 3.94 (dd, *J* = 5.9, 1.6 Hz, 2H), 3.85 (s, 1H),

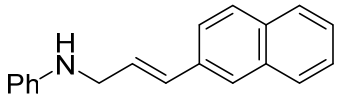
2.30 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 135.7, 135.4, 132.3, 130.2, 129.7, 129.2, 128.2, 128.0, 126.3, 117.6, 113.1, 46.5, 21.0, 19.3. HRMS m/z (ESI) calcd for $C_{16}H_{20}N$ $(M + H)^+$: 238.1590; found: 238.1600.



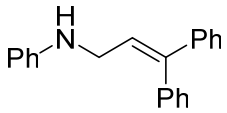
(E)-N-(3-mesitylallyl)aniline (**3p**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 25 mg, 50%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.16 (m, 2H), 6.85 (s, 2H), 6.74 – 6.67 (m, 3H), 6.56 (d, *J* = 16.2 Hz, 1H), 5.76 (dt, *J* = 16.3, 5.6 Hz, 1H), 3.95 (dd, *J* = 5.7, 1.7 Hz, 2H), 3.86 (s, 1H), 2.25 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 136.1, 135.8, 133.7, 131.6, 129.3, 129.2, 128.5, 117.6, 113.2, 46.5, 20.9, 20.9. HRMS m/z (ESI) calcd for $C_{18}H_{22}N$ $(M + H)^+$: 252.1747; found: 252.1767.



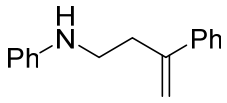
(E)-N-(3-(perfluorophenyl)allyl)aniline (**3q**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 49 mg, 82%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.74 – 6.69 (m, 3H), 6.60 (d, *J* = 16.3 Hz, 1H), 4.05 (d, *J* = 5.2 Hz, 2H), 3.92 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5 , 145.8 – 145.4 (m), 143.8 – 143.4 (m), 140.9 – 140.5 (m), 138.9 – 138.4 (m), 136.91 (td, *J* = 7.4, 2.4 Hz), 136.8 – 136.4 (m), 129.3, 117.9, 115.2, 113.0, 111.7 (td, *J* = 14.1, 4.2 Hz), 46.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -143.0 – -143.1 (m), -156.64 (t, *J* = 20.9 Hz), -163.08 (td, *J* = 21.4, 7.8 Hz). HRMS m/z (ESI) calcd for $C_{15}H_{11}F_5N$ $(M + H)^+$: 300.0806; found: 300.0810.



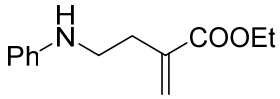
(E)-N-(3-(naphthalen-2-yl)allyl)aniline (**3r**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 40.4 mg, 78%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), brown solid; Rf = 0.4 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 3H), 7.70 (d, *J* = 1.7 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.23 – 7.18 (m, 2H), 6.79 – 6.67 (m, 4H), 6.45 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.98 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.89 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 134.3, 133.6, 132.9, 131.6, 129.3, 128.2, 127.9, 127.6, 127.4, 126.3, 126.2, 125.8, 123.5, 117.6, 113.0, 46.3. HRMS m/z (ESI) calcd for $C_{19}H_{18}N$ $(M + H)^+$: 260.1434; found: 260.1436.



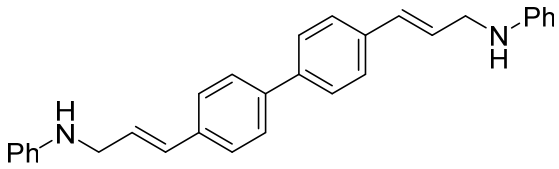
N-(3,3-diphenylallyl)aniline (**3s**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 47.7 mg, 84%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 1H), 7.29 – 7.20 (m, 7H), 7.18 – 7.13 (m, 2H), 6.73– 6.67 (m, 1H), 6.60 – 6.56 (m, 2H), 6.19 (t, *J* = 6.7 Hz, 1H), 3.82 (d, *J* = 6.7 Hz, 2H), 3.69 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 144.2, 141.9, 139.2, 129.7, 129.2, 128.3, 128.2, 127.5, 127.5, 127.5, 126.2, 117.6, 113.1, 43.3. HRMS m/z (ESI) calcd for $C_{21}H_{20}N$ $(M + H)^+$: 286.1590; found: 286.1576.



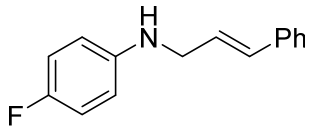
N-(3-phenylbut-3-en-1-yl)aniline (**3t**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 23.1 mg, 52%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40(m, 2H), 7.36 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.18 – 7.13 (m, 2H), 6.71 – 6.66 (m, 1H), 6.60 – 6.54 (m, 2H), 5.40 – 5.38 (m, 1H), 5.16 – 5.14 (m, 1H), 3.69 (s, 1H), 3.23 (t, *J* = 6.9 Hz, 2H), 2.85 – 2.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 145.7, 140.3, 129.2, 128.4, 127.7, 126.1, 117.3, 114.3, 112.9, 42.1, 35.1. HRMS m/z (ESI) calcd for $C_{16}H_{18}N$ $(M + H)^+$: 224.1434; found: 224.1432.



Ethyl 2-methylene-4-(phenylamino)butanoate (**3u**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 15.1 mg, 34%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.3 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 – 7.15 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.65 – 6.60 (m, 2H), 6.25 (d, *J* = 1.3 Hz, 1H), 5.63 (d, *J* = 1.4 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 1H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.66 – 2.60 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 147.9, 138.2, 129.2, 126.7, 117.3, 112.8, 60.9, 42.8, 31.9, 14.2. HRMS m/z (ESI) calcd for $C_{13}H_{18}NO_2$ $(M + H)^+$: 220.1332; found: 220.1337.

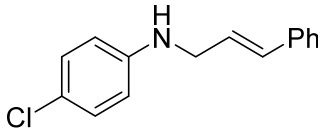


N,N'-((2E,2'E)-[1,1'-biphenyl]-4,4'-diylbis(prop-2-ene-3,1-diyl))dianiline (**3v**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 54.8 mg, 66%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.4 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.21 – 7.14 (m, 4H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.75 – 6.70 (m, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.58 – 6.49 (m, 4H), 6.32 (dt, *J* = 15.9, 5.6 Hz, 1H), 5.83 (dt, *J* = 12.2, 6.5 Hz, 1H), 3.97 (dd, *J* = 6.6, 1.7 Hz, 2H), 3.92 (dd, *J* = 5.7, 1.5 Hz, 2H), 3.83 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 147.7, 137.6, 137.4, 136.3, 136.0, 130.6, 130.6, 130.5, 130.3, 129.3, 129.3, 128.1, 128.1, 117.8, 117.7, 113.0, 113.0, 92.8, 92.7, 46.0, 42.2. HRMS m/z (ESI) calcd for $C_{30}H_{18}N_2K$ $(M + K)^+$: 455.1884; found: 455.1871.

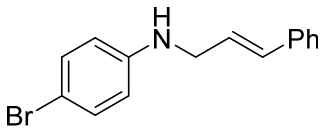


N-cinnamyl-4-fluoroaniline (**4a**). According to the general procedure in 0.2 mmol scale using 2

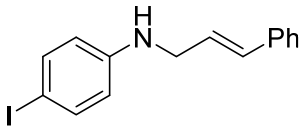
equiv. aryl glycine with reaction time of 12 h; 35 mg, 77%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), brown solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.92 – 6.87 (m, 2H), 6.63 – 6.57 (m, 3H), 6.31 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.89 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.75 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0 (d, *J* = 235.2 Hz), 144.3 (d, *J* = 1.8 Hz), 136.8, 131.7, 128.6, 127.6, 126.8, 126.3, 115.7 (d, *J* = 22.3 Hz), 113.9 (d, *J* = 7.3 Hz), 46.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -127.8. HRMS m/z (ESI) calcd for $C_{15}H_{15}FN$ $(M + H)^+$: 228.1183; found: 228.1183.



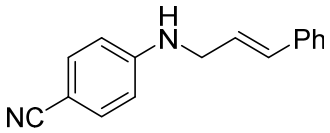
4-chloro-N-cinnamylaniline (**4b**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 36 mg, 75%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.14 – 7.10 (m, 2H), 6.62 – 6.55 (m, 3H), 6.28 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.89 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 136.6, 131.7, 129.1, 128.6, 127.6, 126.4, 126.3, 122.1, 114.1, 46.2. HRMS m/z (ESI) calcd for $C_{15}H_{15}ClN$ $(M + H)^+$: 244.0888; found: 244.0893.



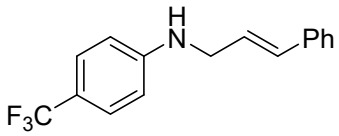
4-bromo-N-cinnamylaniline (**4c**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 40 mg, 71%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.21 (m, 3H), 6.59 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.54 – 6.50 (m, 2H), 6.28 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.89 (dd, *J* = 5.8, 1.7 Hz, 2H), 3.89 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 136.6, 131.9, 131.7, 128.6, 127.6, 126.3, 126.3, 114.6, 109.1, 46.1. HRMS m/z (ESI) calcd for $C_{15}H_{15}BrN$ $(M + H)^+$: 288.0382; found: 288.0378.



N-cinnamyl-4-iodoaniline (**4d**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 47.5 mg, 72%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 2H), 7.37 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 6.62 – 6.57 (m, 1H), 6.47 – 6.43 (m, 2H), 6.28 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.95 (s, 1H), 3.91 (dd, *J* = 5.7, 1.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 137.8, 136.6, 131.7, 128.6, 127.6, 126.3, 126.3, 115.2, 78.2, 45.9. HRMS m/z (ESI) calcd for $C_{15}H_{14}INNa$ $(M + Na)^+$: 358.0063; found: 358.0065.

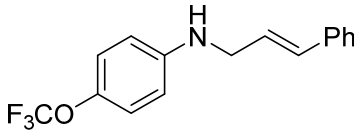


4-(cinnamylamino)benzonitrile (**4e**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 14.5 mg, 32%, purified by flash chromatography (petroleum ether/ethyl acetate 10:1), cyan solid; Rf = 0.3 (petroleum ether/ethyl acetate 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.63 – 6.58 (m, 3H), 6.26 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.45 (s, 1H), 3.98 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 136.3, 133.7, 132.3, 128.6, 127.9, 126.4, 125.1, 120.4, 112.4, 99.0, 45.3. HRMS m/z (ESI) calcd for $C_{16}H_{15}N_2$ $(M + H)^+$: 235.1230; found: 235.1228.

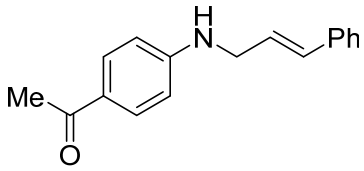


N-cinnamyl-4-(trifluoromethyl)aniline (**4f**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 42.3 mg, 77%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.31

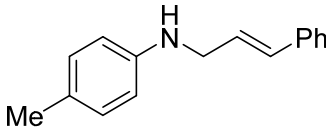
(t, *J* = 7.5 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.67 – 6.58 (m, 3H), 6.28 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.21 (s, 1H), 3.96 (d, *J* = 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 136.5, 132.0, 128.6, 127.7, 126.6 (q, *J* = 3.8 Hz), 126.3, 125.9, 125.0 (q, *J* = 270.4 Hz), 119.0 (q, *J* = 32.4 Hz), 112.0, 45.6. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.9. HRMS m/z (ESI) calcd for $C_{16}H_{15}F_3N$ $(M + H)^+$: 278.1151; found: 278.1173.



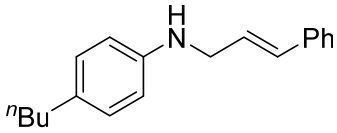
N-cinnamyl-4-(trifluoromethoxy)aniline (**4g**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 46.3 mg, 80%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.24 – 7.19 (m, 2H), 7.16 – 7.11 (m, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.53 – 6.47 (m, 3H), 6.19 (dt, *J* = 15.9, 5.7 Hz, 1H), 3.89 (s, 1H), 3.79 (dd, *J* = 5.8, 1.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 140.5 (q, *J* = 2.1 Hz), 136.6, 131.8, 128.6, 127.7, 126.4, 126.3, 122.4, 120.7 (q, *J* = 255.2 Hz), 113.2, 46.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.4. HRMS m/z (ESI) calcd for $C_{16}H_{14}F_3NONa$ $(M + Na)^+$: 316.0920; found: 316.0947.



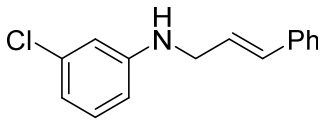
1-(4-(cinnamylamino)phenyl)ethan-1-one (**4h**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 10 mg, 21%, purified by flash chromatography (petroleum ether/ethyl acetate 30:1), white solid; Rf = 0.3 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.38 – 7.35 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.22 (m, 1H), 6.64 – 6.59 (m, 3H), 6.29 (dt, *J* = 15.8, 5.7 Hz, 1H), 4.44 (s, 1H), 4.03 – 3.99 (m, 2H), 2.51 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.4, 151.9, 136.4, 132.1, 130.8, 128.6, 127.8, 126.9, 126.4, 125.6, 111.7, 45.4, 26.1. HRMS m/z (ESI) calcd for $C_{17}H_{18}NO$ $(M + H)^+$: 252.1383; found: 252.1388.



N-cinnamyl-4-methylaniline (**4i**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 32 mg, 72%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow solid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.64 – 6.59 (m, 3H), 6.34 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.91 (dd, *J* = 5.9, 1.5 Hz, 2H), 3.82 (s, 1H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 136.9, 131.4, 129.8, 128.6, 127.5, 127.2, 127.2, 126.3, 113.3, 46.7, 20.4. HRMS m/z (ESI) calcd for $C_{16}H_{18}N$ $(M + H)^+$: 224.1434; found: 224.1434.

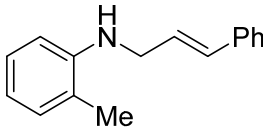


4-butyl-N-cinnamylaniline (**4j**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 44.6 mg, 84%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), brown liquid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.38 – 7.35 (m, 2H), 7.24 – 7.20 (m, 1H), 7.02 – 6.99 (m, 2H), 6.64 – 6.59 (m, 3H), 6.33 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.91 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.73 (s, 1H), 2.52 – 2.48 (m, 2H), 1.58 – 1.51 (m, 2H), 1.37 – 1.30 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 136.9, 132.2, 131.4, 129.1, 128.5, 127.5, 127.2, 126.3, 113.2, 46.6, 34.7, 34.0, 22.3, 14.0. HRMS m/z (ESI) calcd for $C_{19}H_{24}N$ $(M + H)^+$: 266.1903; found: 266.1905.

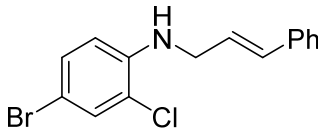


3-chloro-N-cinnamylaniline (**4k**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 22.3 mg, 46%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.22 (m, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.70 – 6.66 (m, 1H), 6.64 – 6.58 (m, 2H), 6.54 – 6.50 (m, 1H), 6.29 (dt, *J* = 15.9,

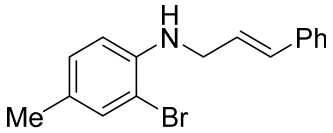
5.8 Hz, 1H), 3.96 (s, 1H), 3.91 (dd, *J* = 5.8, 1.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 136.6, 135.0, 131.8, 130.2, 128.6, 127.7, 126.3, 126.2, 117.4, 112.6, 111.3, 46.0. HRMS m/z (ESI) calcd for $C_{15}H_{15}ClN$ $(M + H)^+$: 244.0888; found: 244.0890.



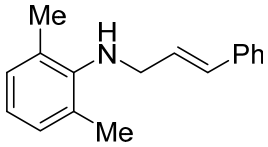
N-cinnamyl-2-methylaniline (**4l**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 30.5 mg, 70%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.15 – 7.11 (m, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.70 – 6.61 (m, 3H), 6.37 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.98 (dd, *J* = 5.8, 1.6 Hz, 2H), 3.67 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 136.8, 131.6, 130.1, 128.6, 127.5, 127.2, 127.1, 126.3, 122.0, 117.2, 110.0, 46.2, 17.6. HRMS m/z (ESI) calcd for $C_{16}H_{18}N$ $(M + H)^+$: 224.1434; found: 224.1431.



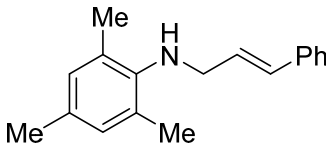
4-bromo-2-chloro-N-cinnamylaniline (**4m**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 23.8 mg, 38%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), light yellow solid; Rf = 0.7 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 2H), 6.63 – 6.56 (m, 2H), 6.28 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.54 (t, *J* = 5.7 Hz, 1H), 4.00 – 3.95 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 136.5, 132.0, 131.3, 130.6, 128.6, 127.8, 126.4, 125.7, 119.8, 112.6, 107.8, 45.7.HRMS m/z (ESI) calcd for $C_{15}H_{14}BrClN$ $(M + H)^+$: 321.9993; found: 321.9989.



2-bromo-N-cinnamyl-4-methylaniline (**4n**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 30.5 mg, 51%, purified by flash chromatography (petroleum ether/ethyl acetate 60:1), light yellow liquid; Rf = 0.8 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.33 – 7.27 (m, 3H), 7.24 – 7.21 (m, 1H), 6.97 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.64 – 6.58 (m, 2H), 6.31 (dt, *J* = 15.9, 5.7 Hz, 1H), 4.38 (s, 1H), 3.96 (dd, *J* = 5.8, 1.7 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 136.8, 132.8, 131.6, 129.1, 128.6, 127.6, 127.6, 126.6, 126.4, 111.8, 109.8, 46.3, 20.1. HRMS m/z (ESI) calcd for $C_{16}H_{16}BrNNa$ $(M + Na)^+$: 324.0358; found: 324.0384.

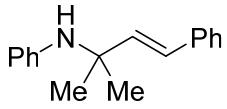


N-cinnamyl-2,6-dimethylaniline (**4o**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 30 mg, 65%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H)), 7.24 – 7.21 (m, 1H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.61 (dt, *J* = 15.7, 1.5 Hz, 1H), 6.36 (dt, *J* = 15.8, 6.4 Hz, 1H), 3.74 (dd, *J* = 6.4, 1.5 Hz, 2H), 2.84 (s, 1H), 2.32 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 136.9, 131.3, 129.7, 128.8, 128.6, 128.1, 127.5, 126.3, 122.1, 50.8, 18.6. HRMS m/z (ESI) calcd for $C_{17}H_{20}N$ $(M + H)^+$: 238.1590; found: 238.1589.

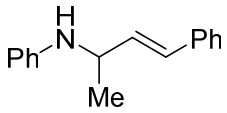


N-cinnamyl-2,4,6-trimethylaniline (**4p**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 22.4 mg, 46%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), yellow liquid; Rf = 0.5 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 6.84 (s, 2H), 6.63 – 6.58 (m, 1H), 6.37 (dt, *J* = 15.8, 6.4 Hz, 1H), 3.70 (dd, *J* = 6.4, 1.5 Hz, 2H), 2.47 (s, 1H), 2.29 (s, 6H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 137.0, 131.6, 131.2, 130.0, 129.4, 128.6, 128.1, 127.5, 126.3, 51.1, 20.6, 18.4. HRMS m/z (ESI) calcd for $C_{18}H_{22}N$ $(M + H)^+$:

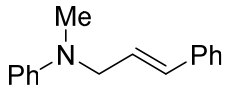
252.1747; found: 252.1745.



(E)-N-(2-methyl-4-phenylbut-3-en-2-yl)aniline (**4q**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 21.6 mg, 47%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), brown solid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.29 (m, 2H), 7.24 – 7.20 (m, 2H), 7.15 – 7.11 (m, 1H), 7.04 – 7.00 (m, 2H), 6.66 – 6.63 (m, 2H), 6.62 – 6.58 (m, 1H), 6.45 (d, *J* = 16.2 Hz, 1H), 6.32 (d, *J* = 16.3 Hz, 1H), 1.40 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 137.9, 137.2, 128.8, 128.5, 127.8, 127.2, 126.3, 117.6, 115.7, 54.5, 28.7. HRMS m/z (ESI) calcd for $C_{17}H_{20}N$ $(M + H)^+$: 238.1590; found: 238.1617.

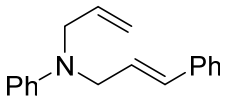


(E)-N-(4-phenylbut-3-en-2-yl)aniline (**4r**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 39.6 mg, 90%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), brown solid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.43– 7.39 (m, 2H), 7.35 – 7.26 (m, 3H), 6.85 – 6.79 (m, 1H), 6.78 – 6.75 (m, 2H), 6.69 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.33 (dd, *J* = 15.9, 5.8 Hz, 1H), 4.28 – 4.21 (m, 1H), 3.79 (s, 1H), 1.51 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 136.9, 133.1, 129.2, 129.1, 128.5, 127.3, 126.3, 117.3, 113.4, 50.8, 22.0. HRMS m/z (ESI) calcd for $C_{16}H_{17}NNa$ $(M + Na)^+$: 246.1253; found: 246.1269.



N-cinnamyl-N-methylaniline (**4t**). According to the general procedure in 0.2 mmol scale using 2 equiv. aryl glycine with reaction time of 12 h; 21.1 mg, 47%, purified by flash chromatography (petroleum ether/ethyl acetate 50:1), light yellow liquid; Rf = 0.6 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.24 – 7.18 (m,

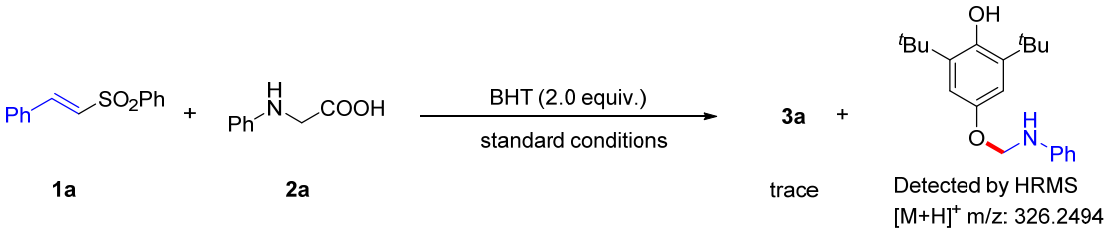
2H), 6.78 (d, J = 8.7 Hz, 2H), 6.74 – 6.70 (m, 1H), 6.51 (d, J = 15.8 Hz, 1H), 6.28 – 6.20 (m, 1H), 4.07 (d, J = 5.4 Hz, 2H), 2.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 136.8, 131.2, 129.2, 128.5, 127.4, 126.3, 125.7, 116.5, 112.6, 54.9, 38.0. HRMS m/z (ESI) calcd for $C_{16}H_{18}N$ $(M + H)^+$: 224.1434; found: 224.1437.



N-allyl-N-cinnamylaniline (**5**). According to the general procedure in 0.3 mmol scale using 1.5 equiv. allyl bromide with reaction time of 18 h; 61.2 mg, 82%, purified by flash chromatography (petroleum ether/ethyl acetate 100:1), light yellow liquid, Rf = 0.7 (petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.18 (m, 3H), 6.78 – 6.74 (m, 2H), 6.69 (tt, J = 7.3, 1.0 Hz, 1H), 6.51 (dt, J = 15.9, 1.8 Hz, 1H), 6.25 (dt, J = 15.9, 5.2 Hz, 1H), 5.93 – 5.83 (m, 1H), 5.23 – 5.15 (m, 2H), 4.08 (dd, J = 5.3, 1.7 Hz, 2H), 3.96 (dt, J = 4.4, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 136.9, 133.9, 131.0, 129.2, 128.5, 127.4, 126.3, 125.9, 116.4, 116.1, 112.4, 52.6, 52.2.

6. Mechanistic studies

6.1 Radical trapping experiment.

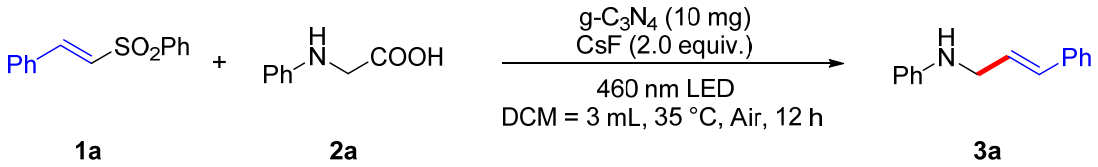


Under the standard conditions, 2.0 equiv. of 2,6-di-tert-butyl-4-methylphenol (BHT) were added to the reaction mixture of alkenyl sulfone **1a** and *N*-aryl glycines **2a**, resulted in complete inhibition of the reaction, only trace yield of **3a** was obtained. The aminomethyl-BHT adduct was detected by high-resolution mass spectrometry, indicating that a radical mechanism is likely involved in the reaction.

6.2 Light on/off experiment.

To determine whether the reaction via radical chain pathway, we performed a light on/off

experiment. We carried out this reaction under optimal conditions, the conversion of **1a** to **3a** was detectable in light conditions, while it halts in the dark, suggesting that the reaction does not proceed through a radical chain pathway (Figure S2).



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

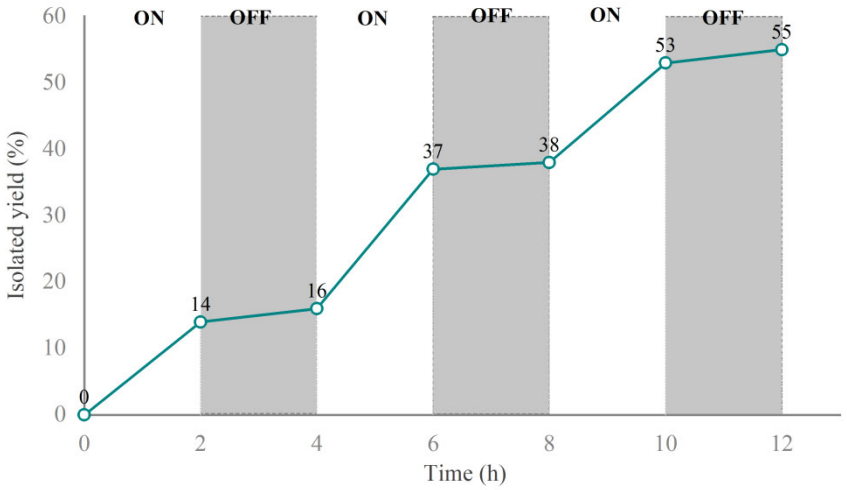


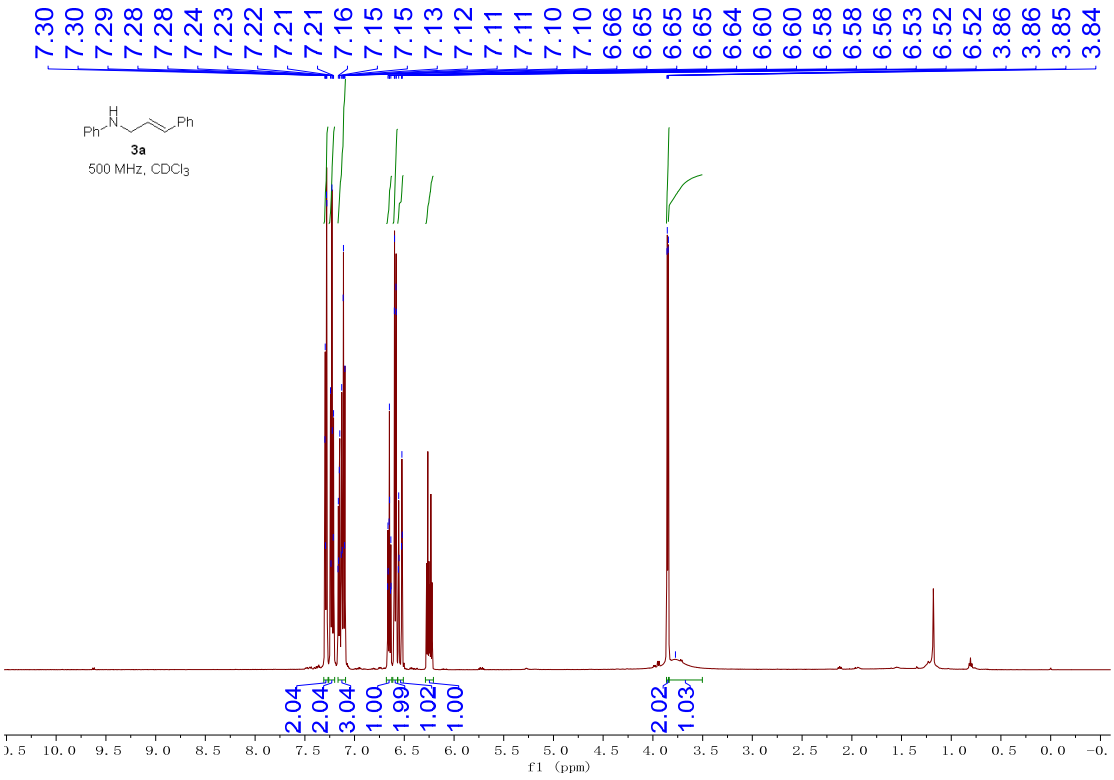
Figure S2. Light on/off experiment.

7. References

1. F. Yue, J. Dong, Y. Liu, Q, Wang, *Org. Lett*., 2021, **23**, 2477.

2. A. Shi, K. Sun, Y. Wu, P. Xiang, I. B. Krylov, A. O. Terent'ev, X. Chen, B. Yu, *J. Catal*., 2022, **415**, 28.

8. NMR spectra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500 MHz, CDCl3
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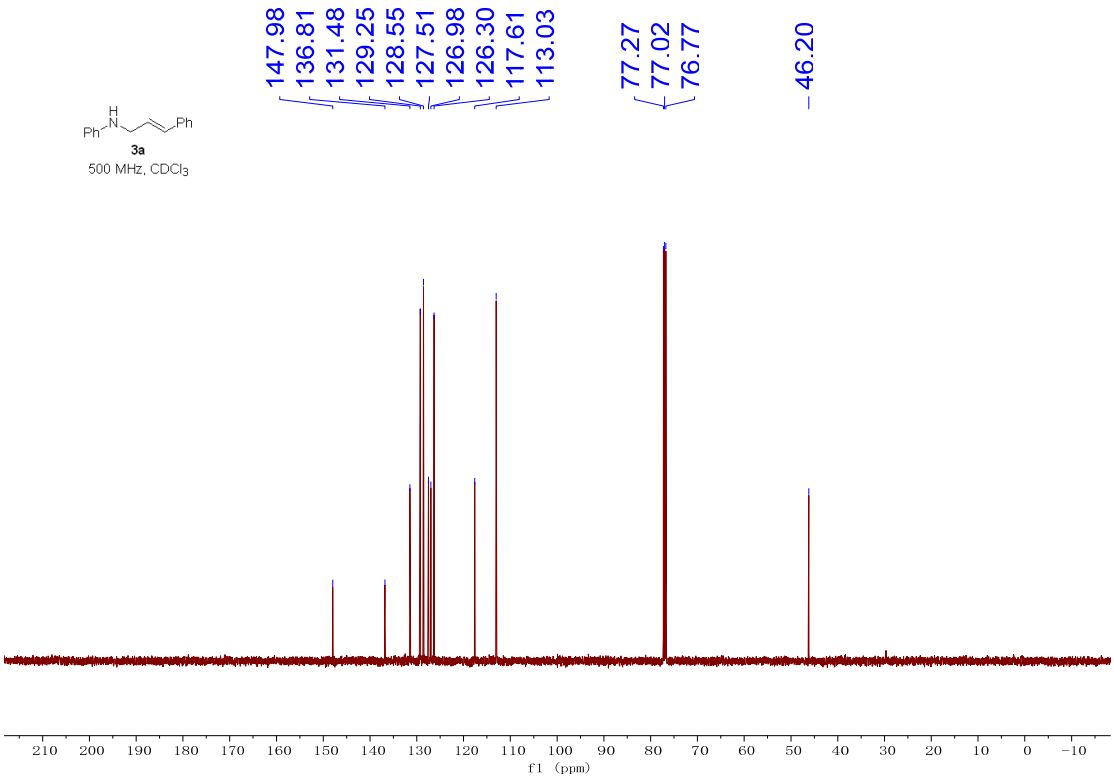
f1 (ppm)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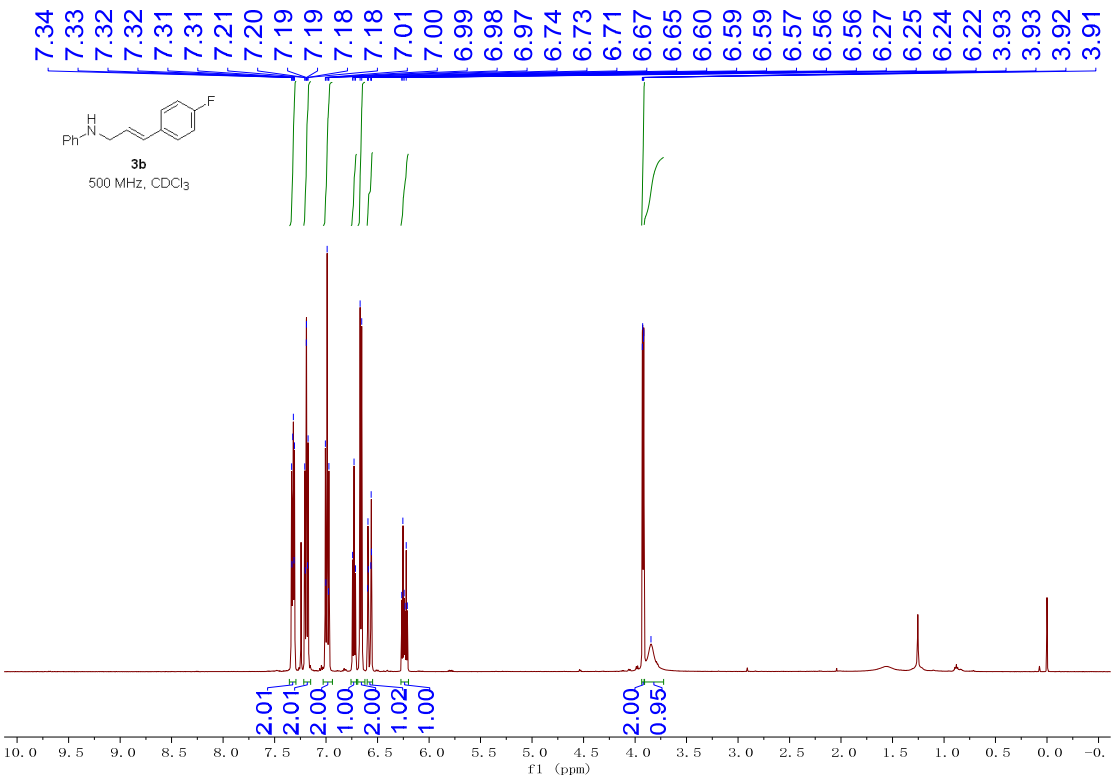
f1 (ppm)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6.60
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6.59
6.57
6.56
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6.27
6.25
6.24
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3.93
3.92
3.91
3b
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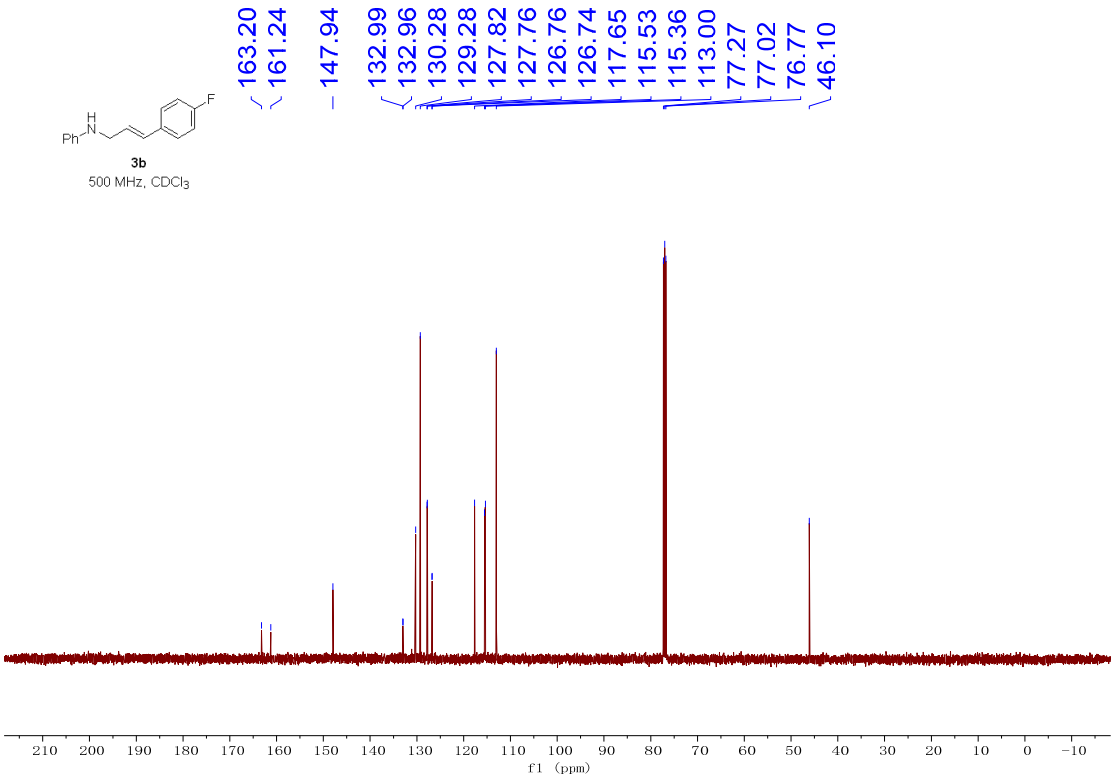
0.95
f1 (ppm)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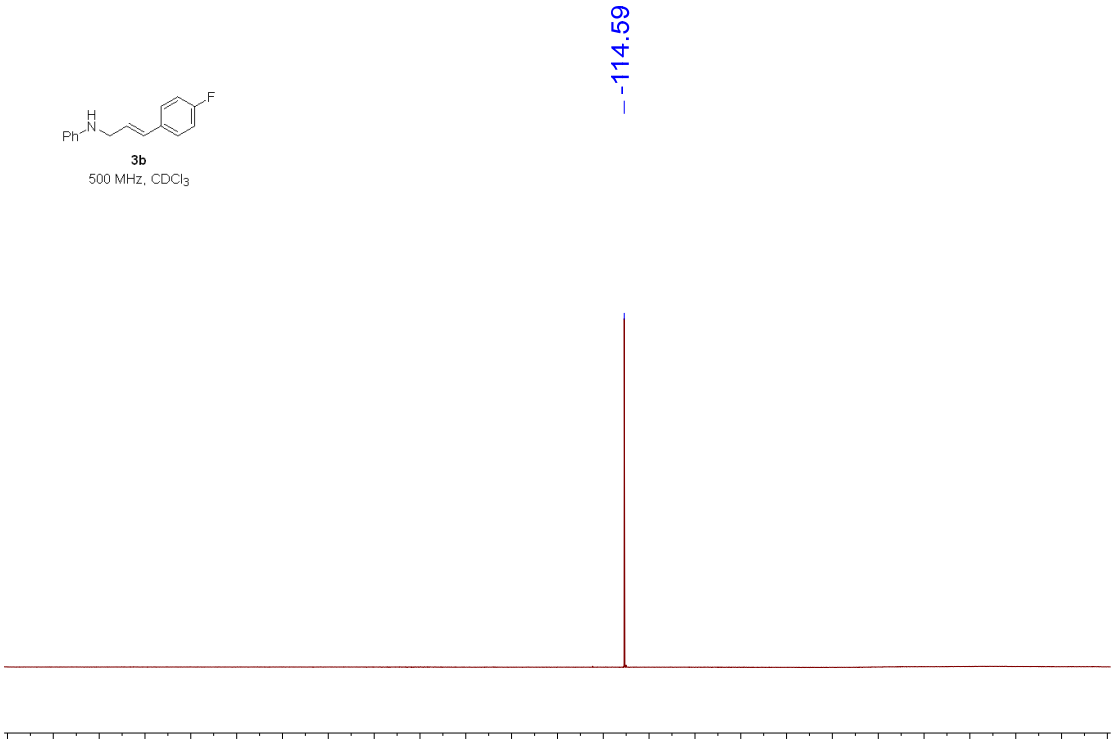
500 MHz, CDCl3
f1 (ppm)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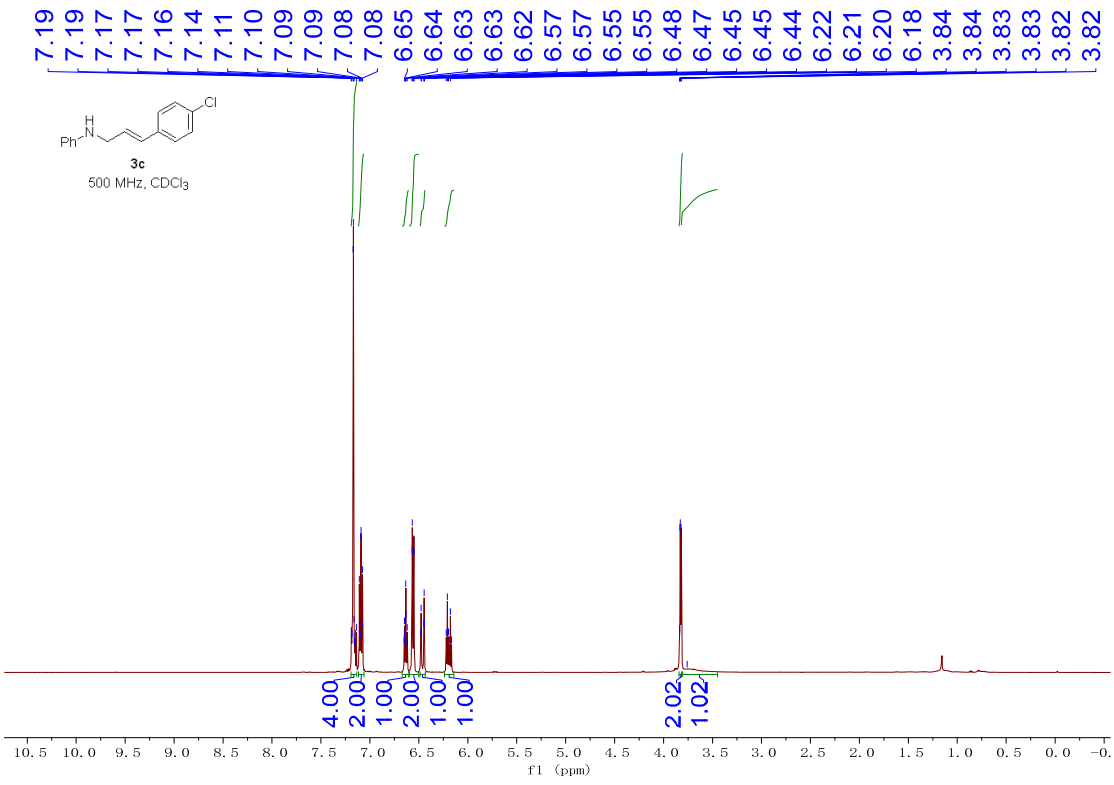
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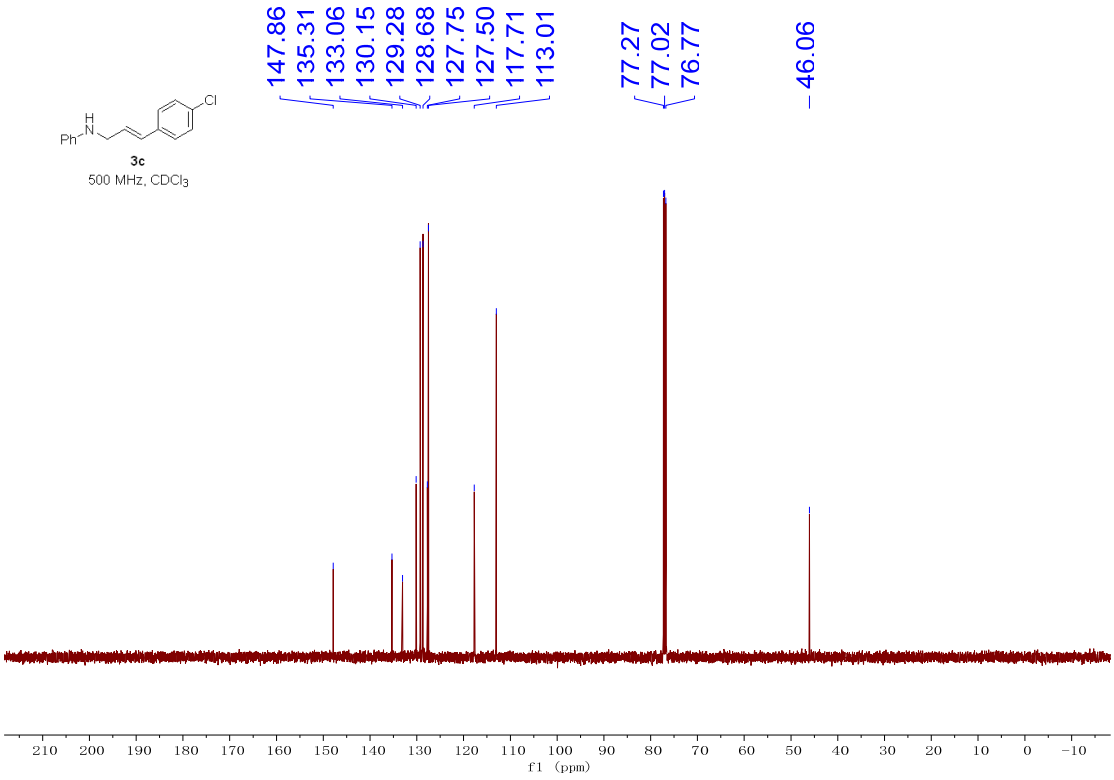
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Ph
H
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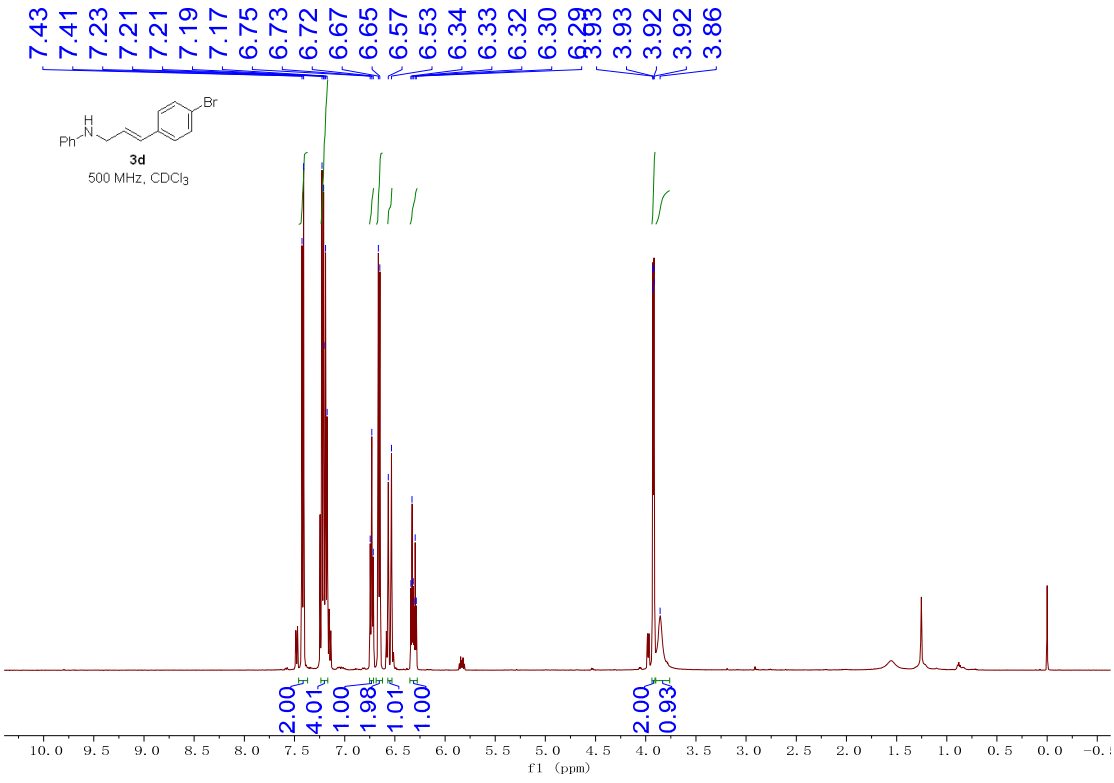
500 MHz, CDCl3
f1 (ppm)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Br
Ph
H
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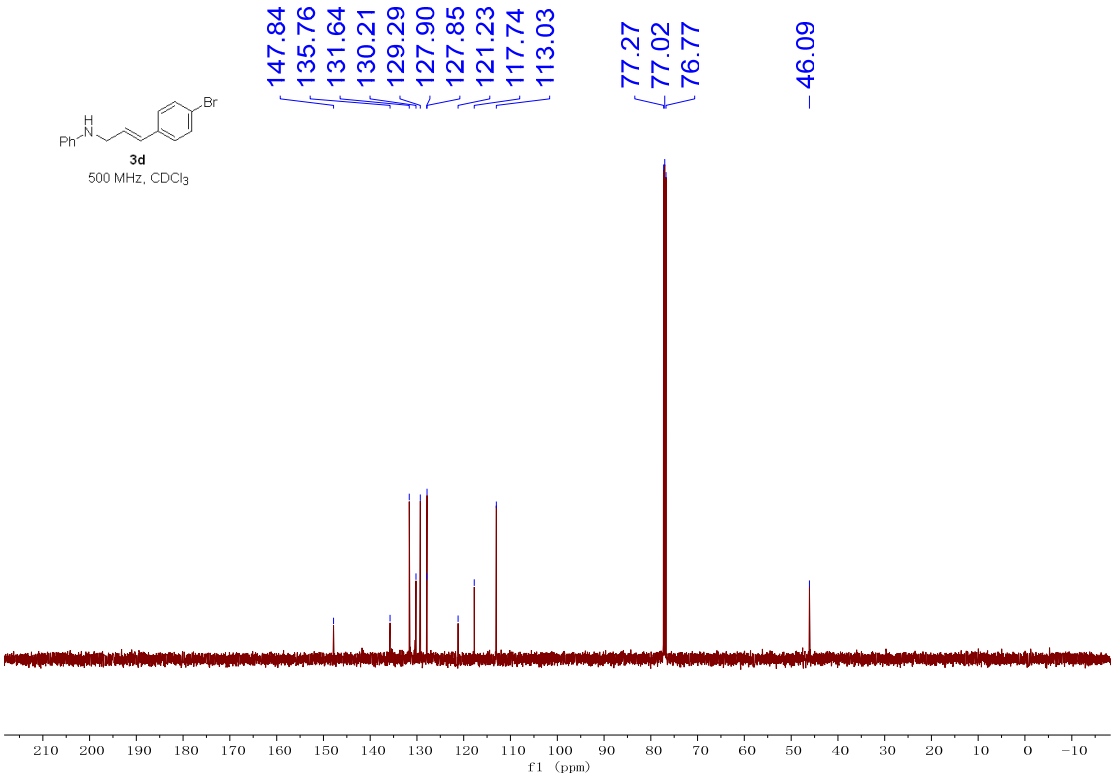
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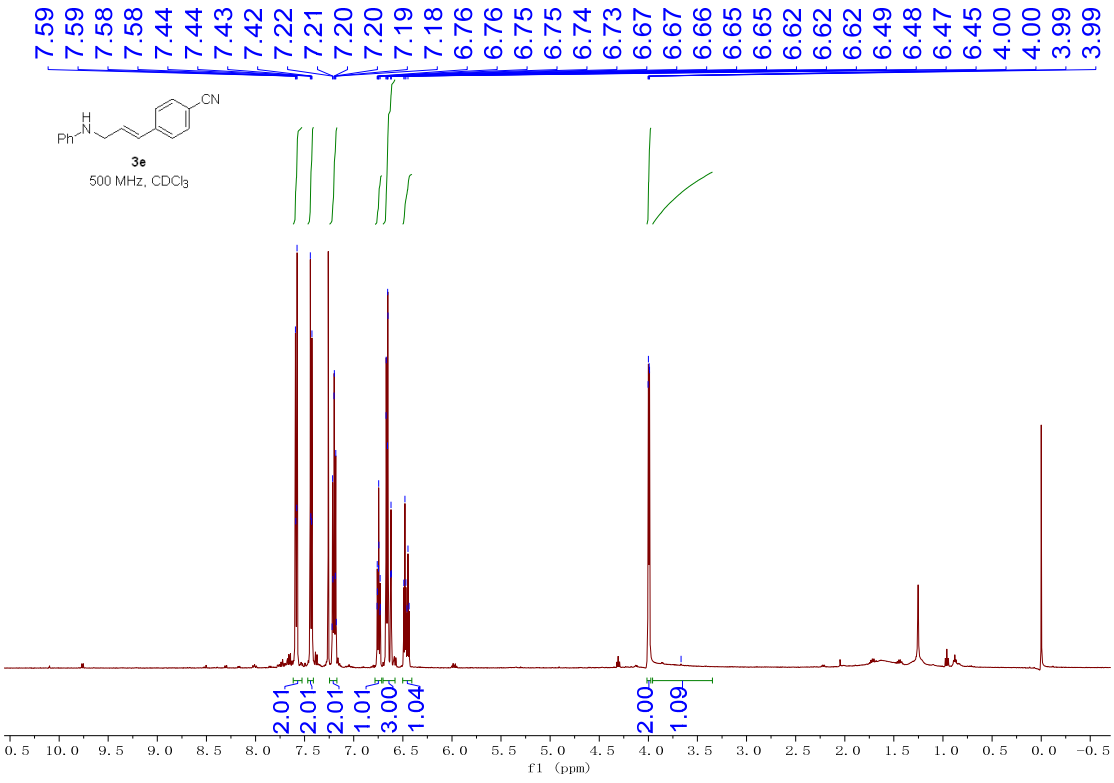
f1 (ppm)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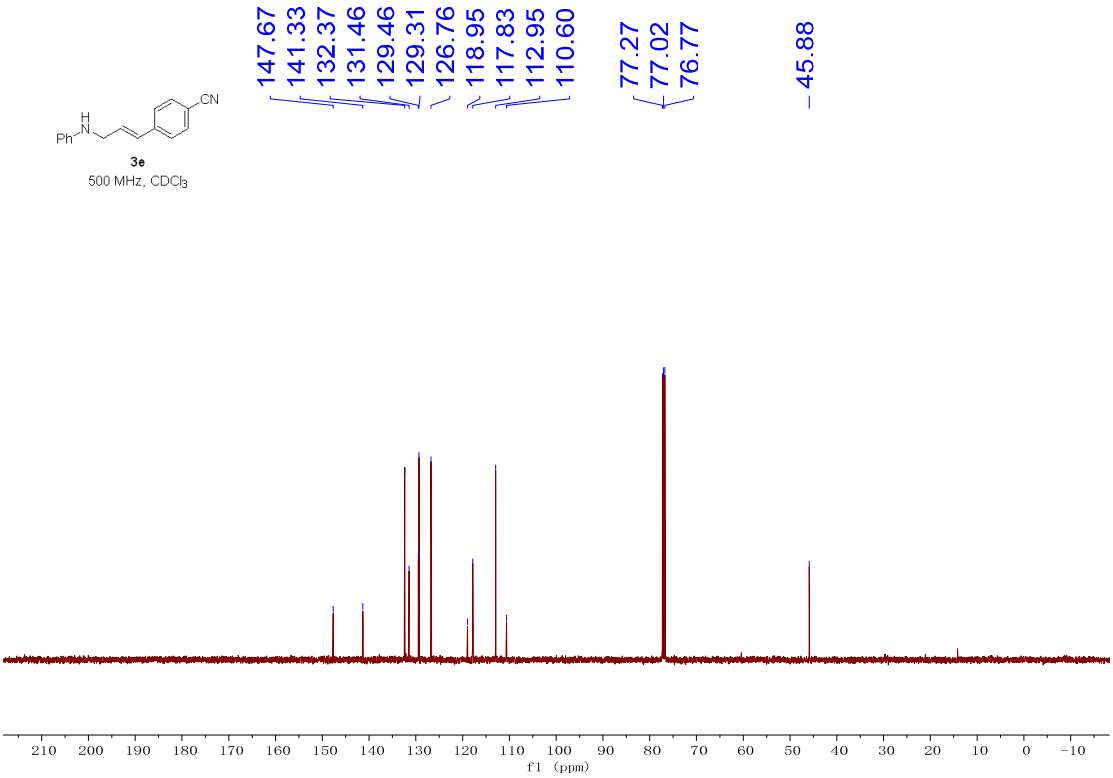
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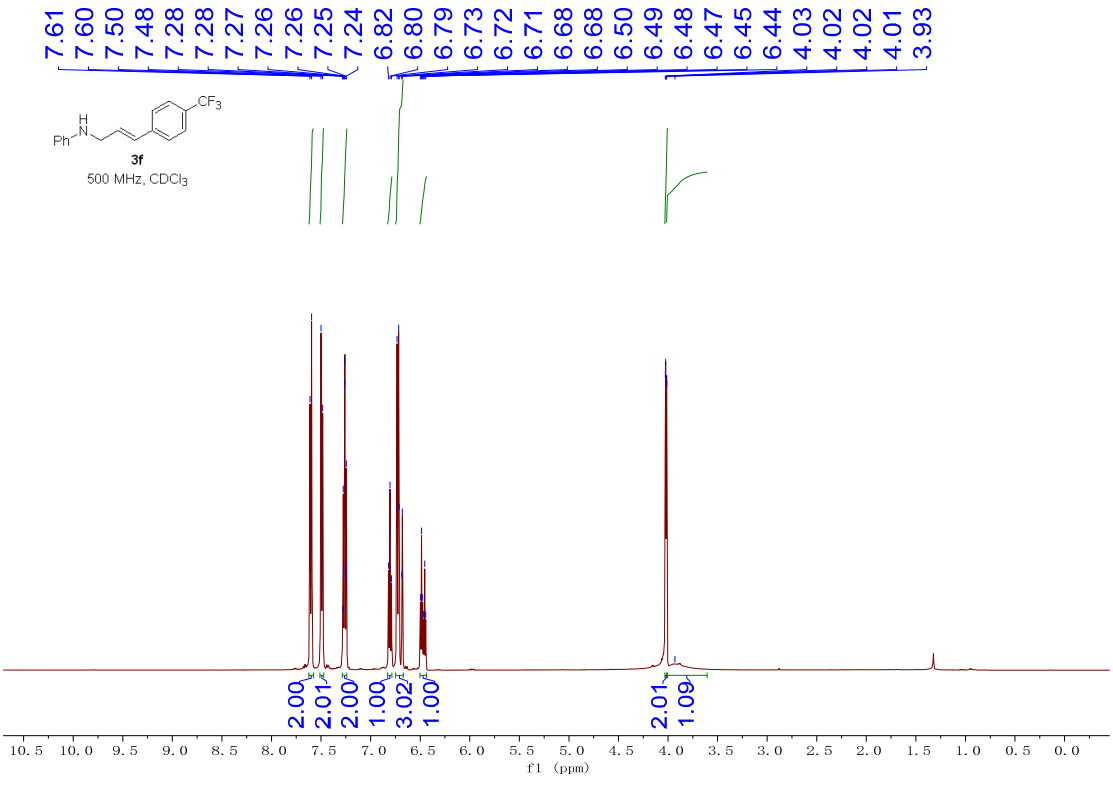
500 MHz, CDCl3
f1 (ppm)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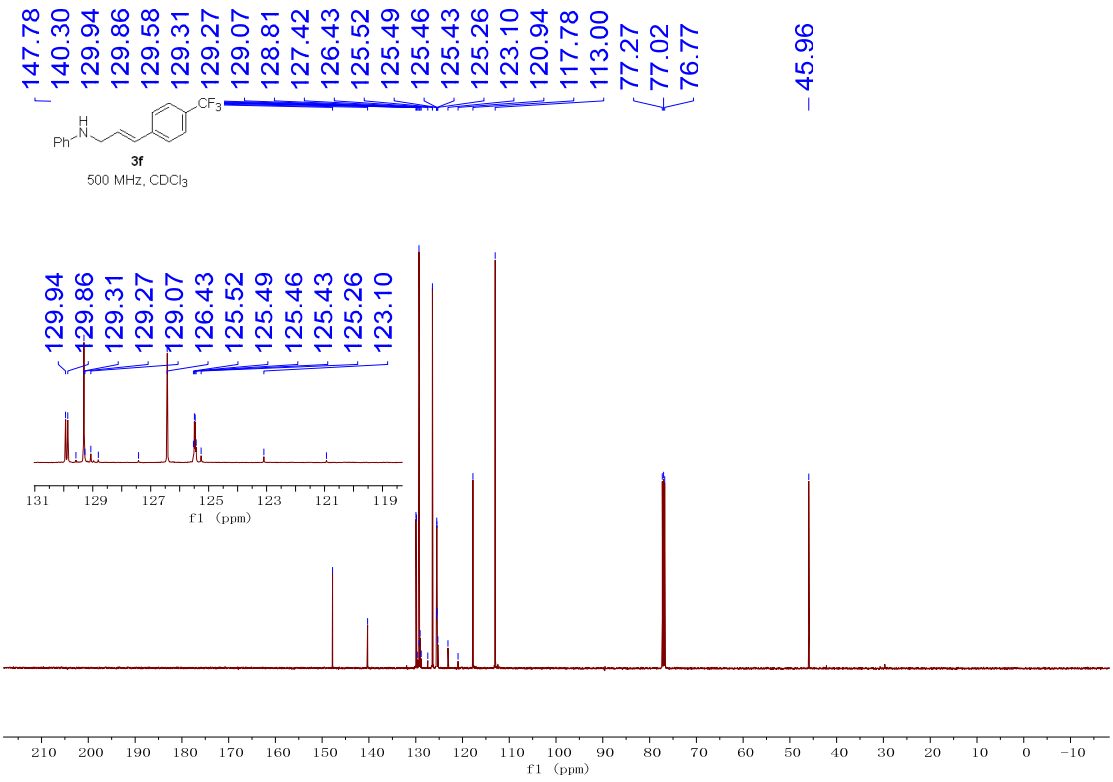
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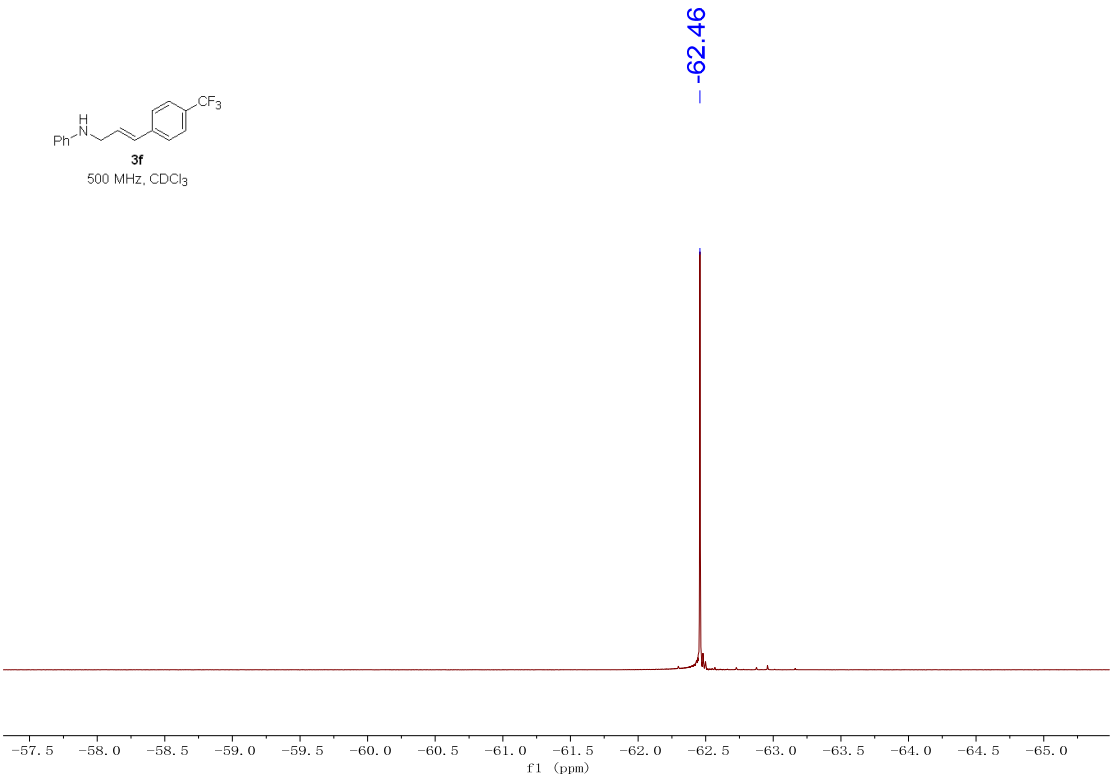
f1 (ppm)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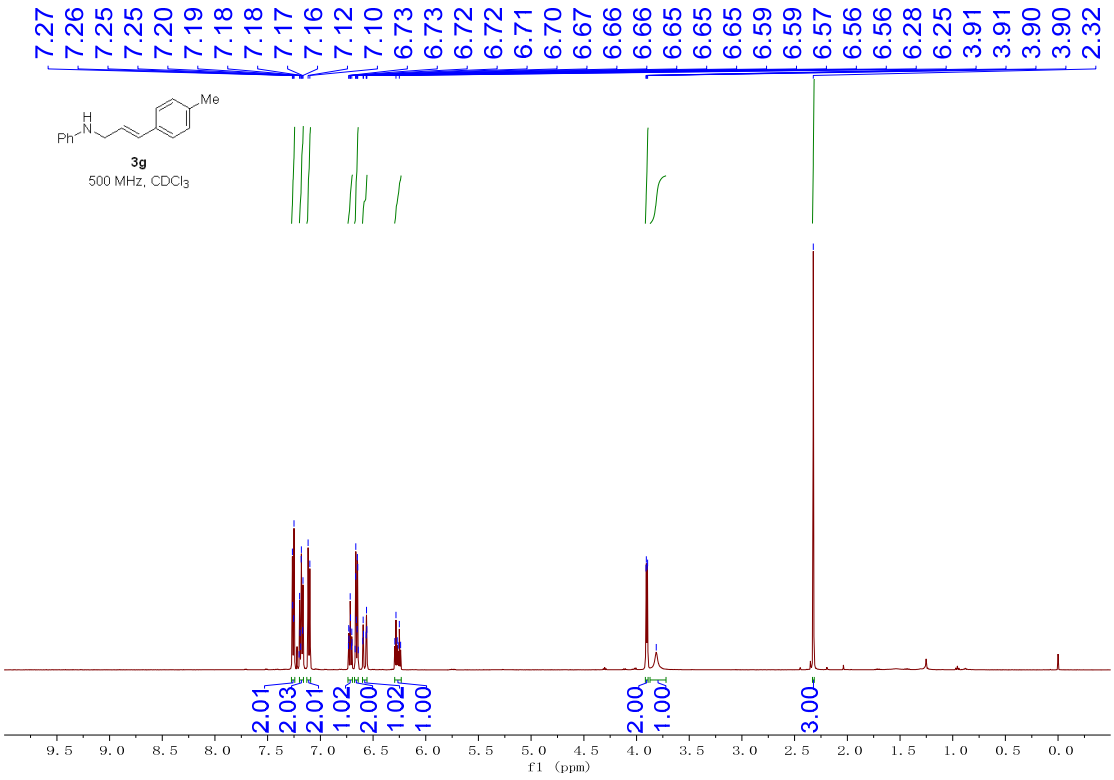
f1 (ppm)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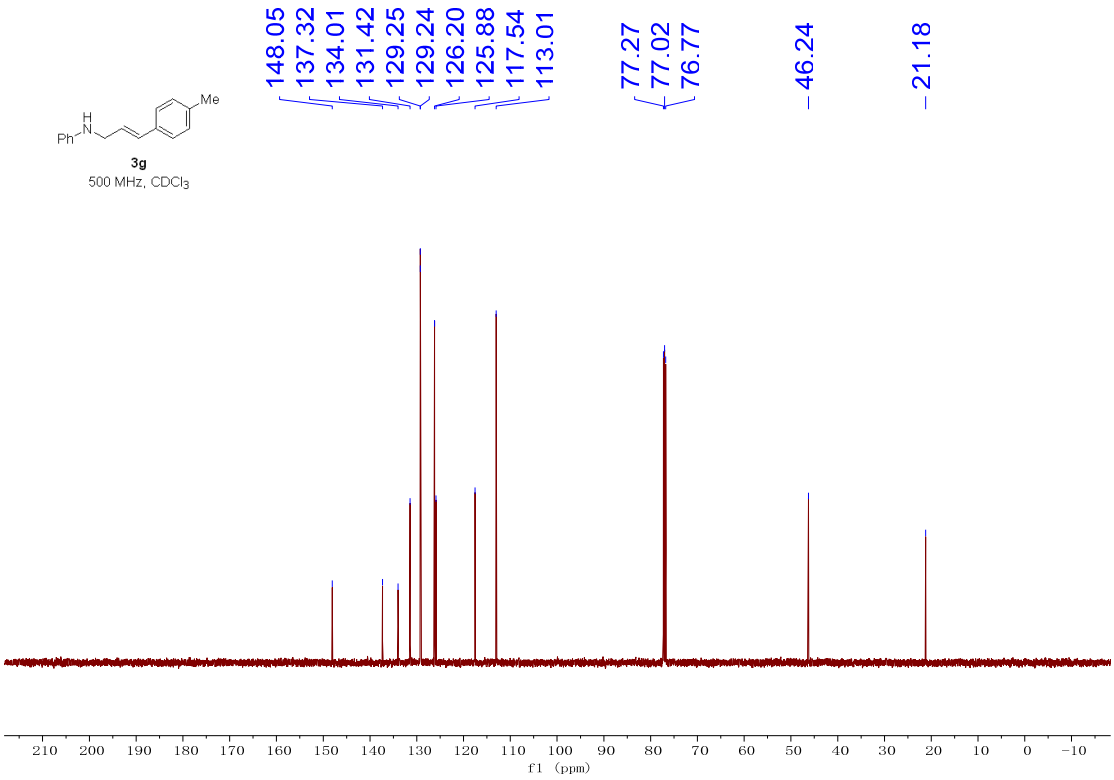
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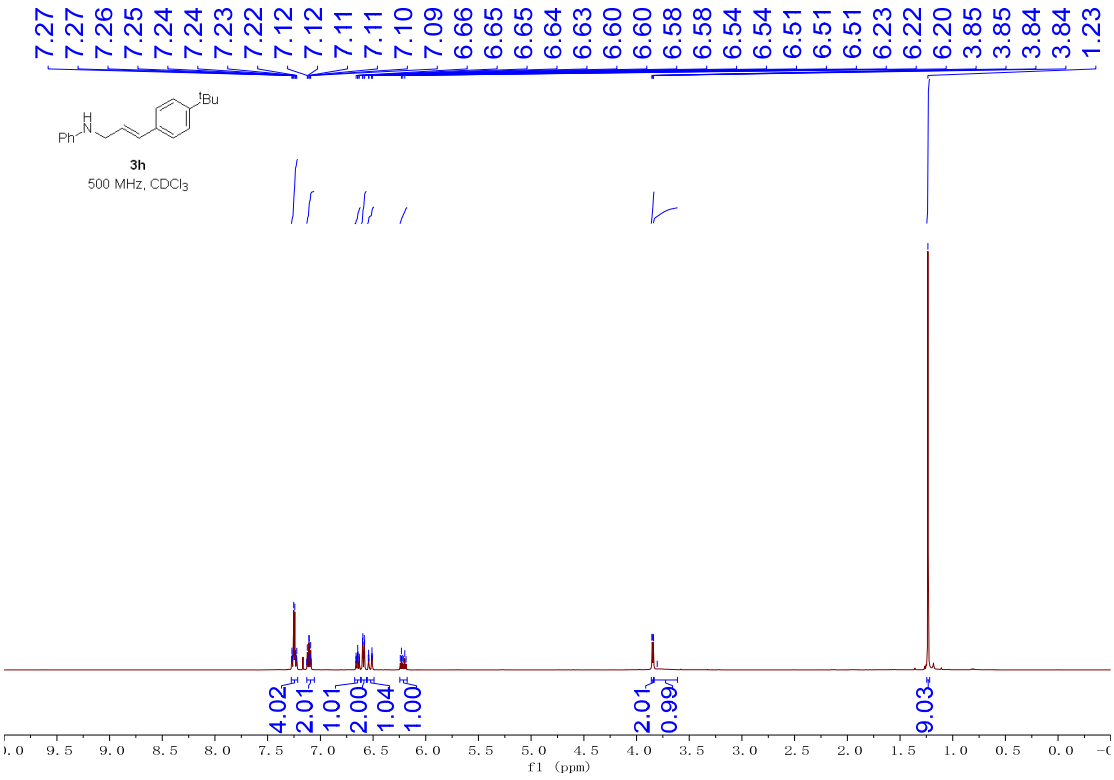
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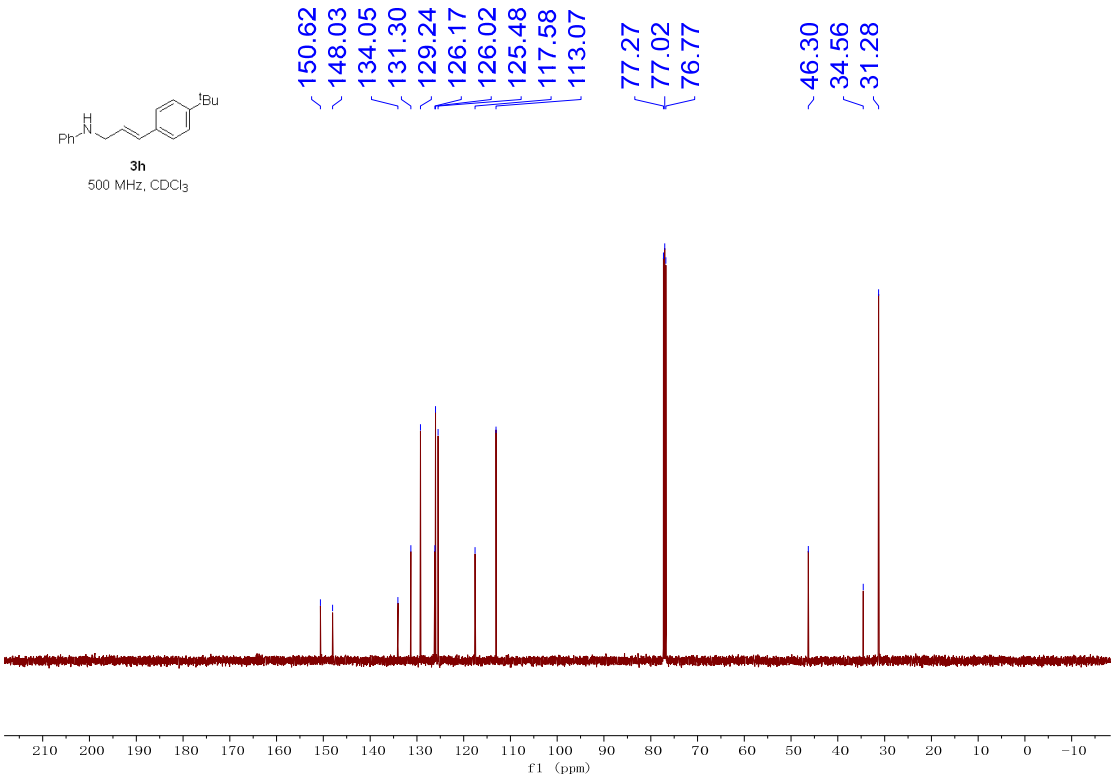
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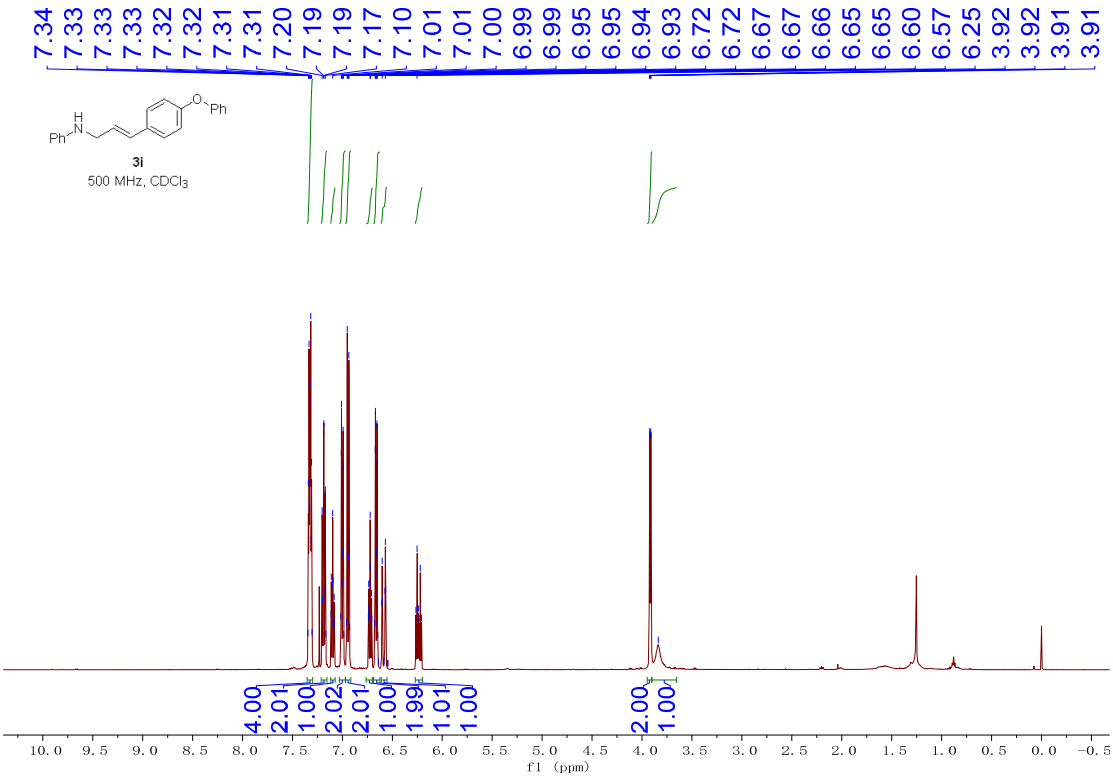
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3.91
Ph
H
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O
Ph
3i
500 MHz, CDCl3
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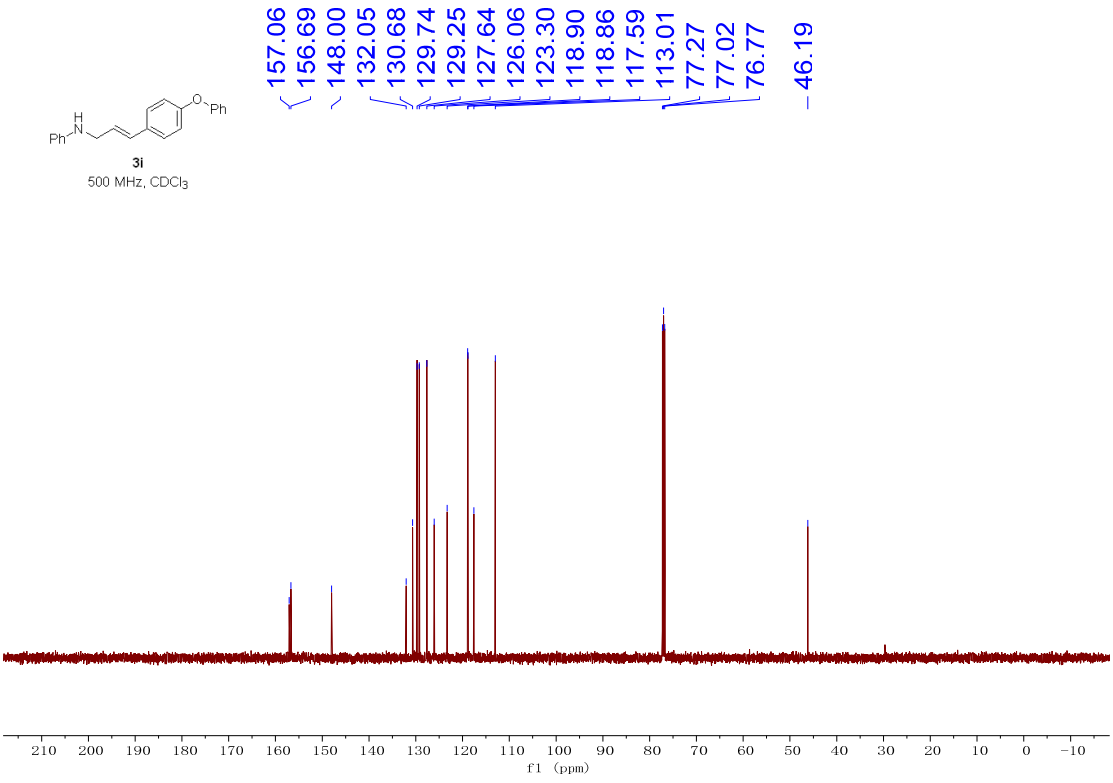
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500 MHz, CDCl3
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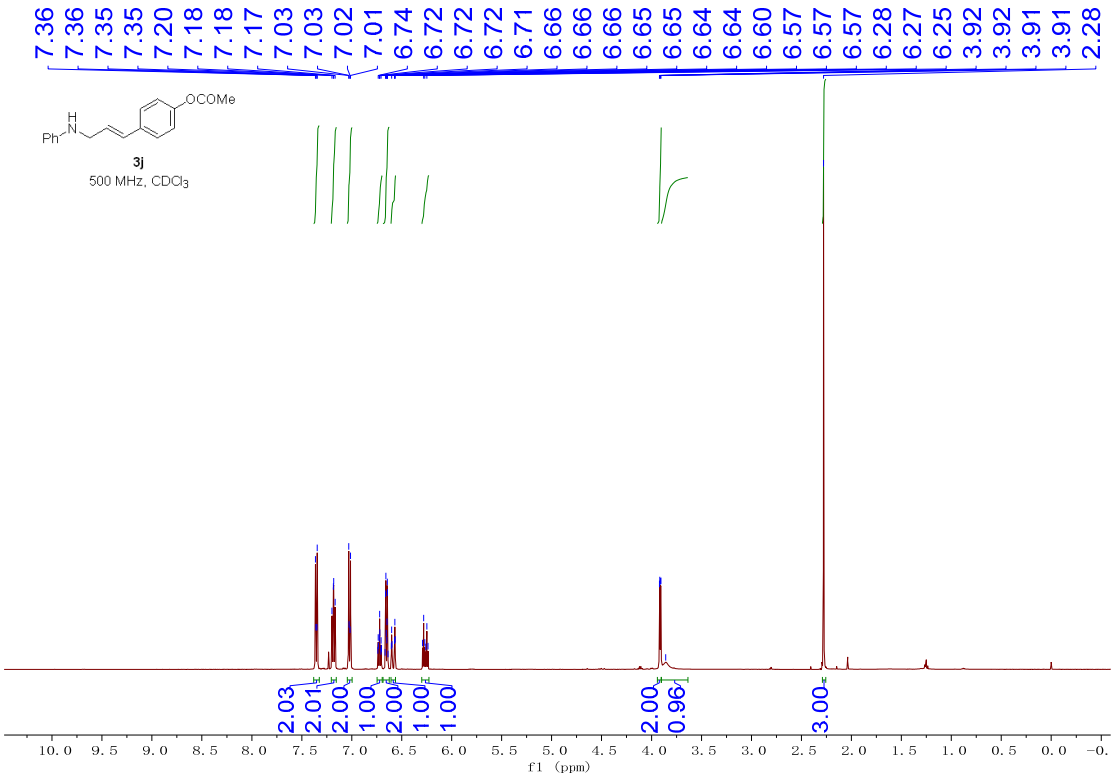
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Ph
H
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3j
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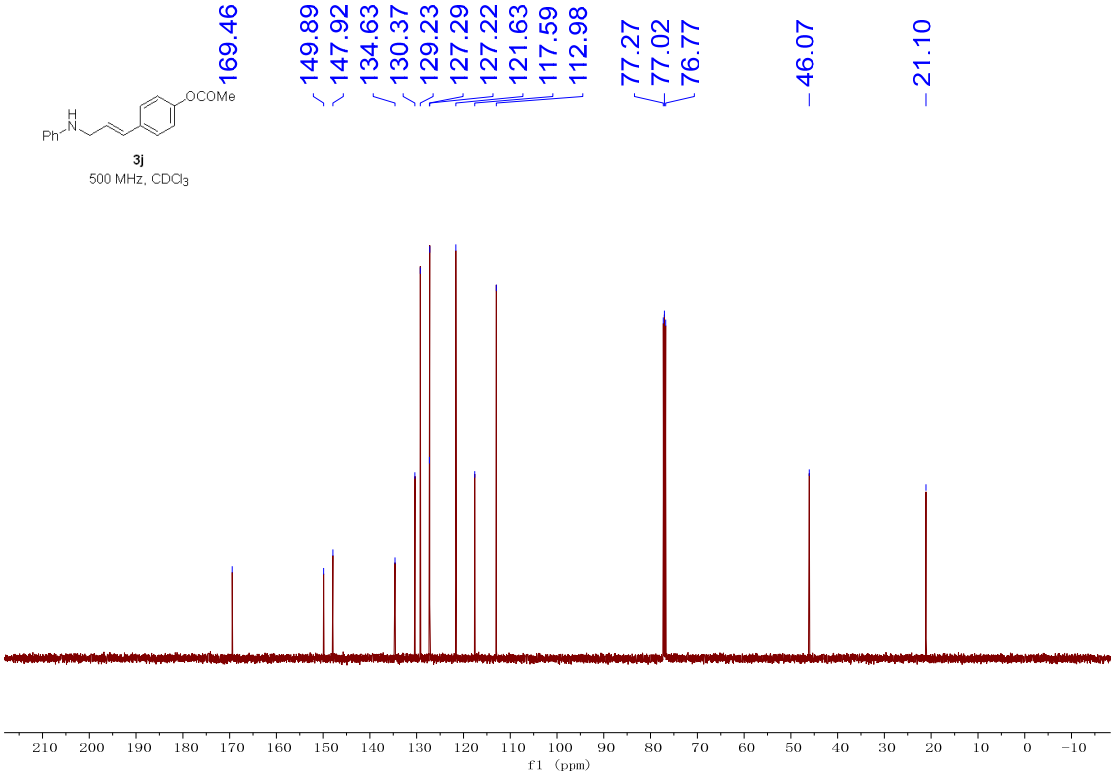
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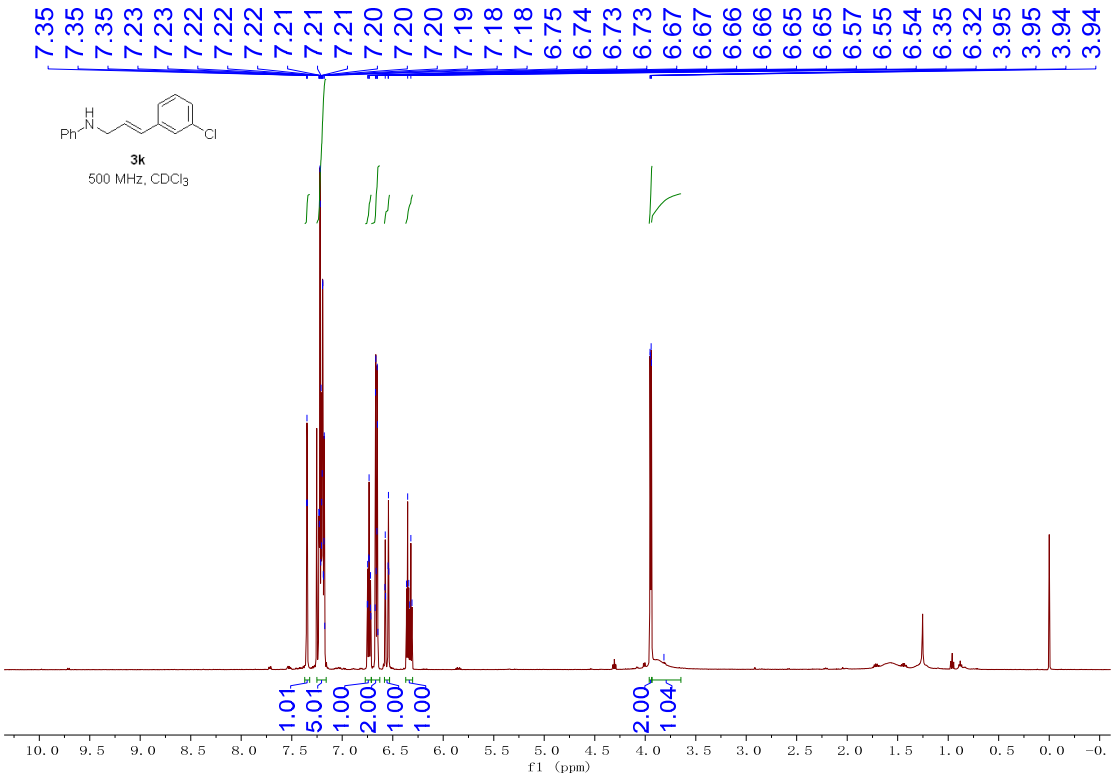
f1 (ppm)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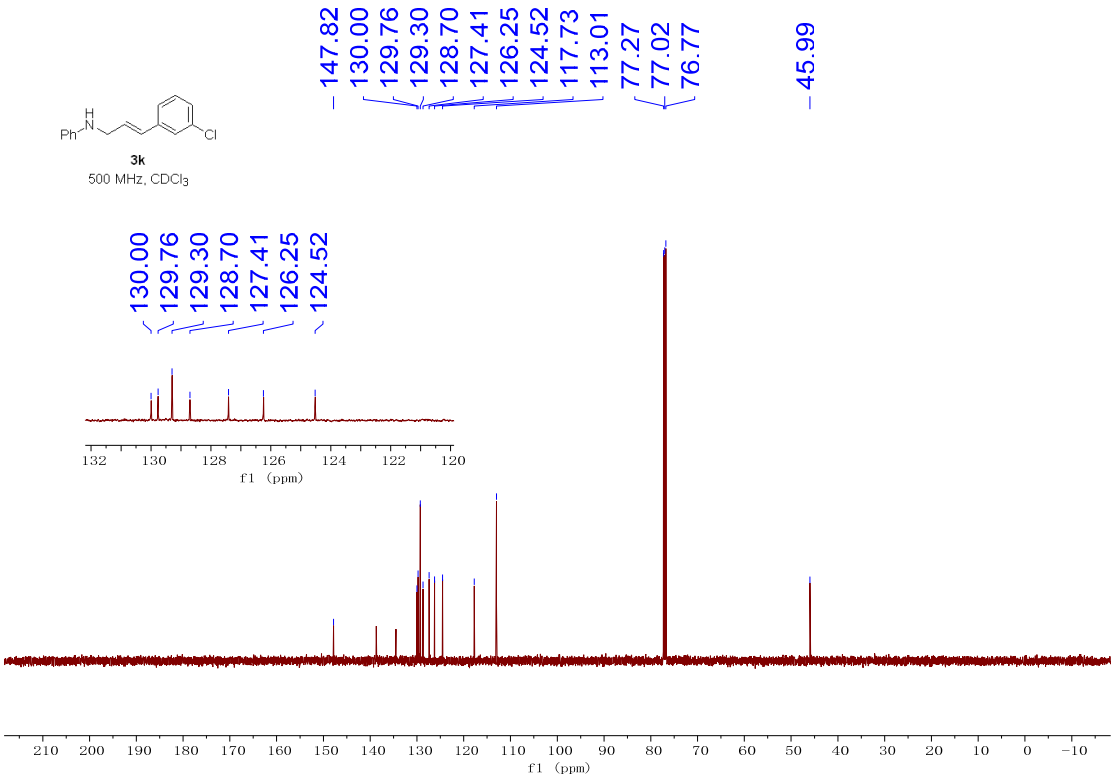
Ph
N
H
Cl
3k
500 MHz, CDCl3
1.01 5.01 1.00 2.00 1.00 1.00 2.00 1.04
f1 (ppm)


147.82 130.00 129.76 129.30 128.70 127.41 126.25 124.52 117.73 113.01 77.27 77.02 76.77 45.99
Ph
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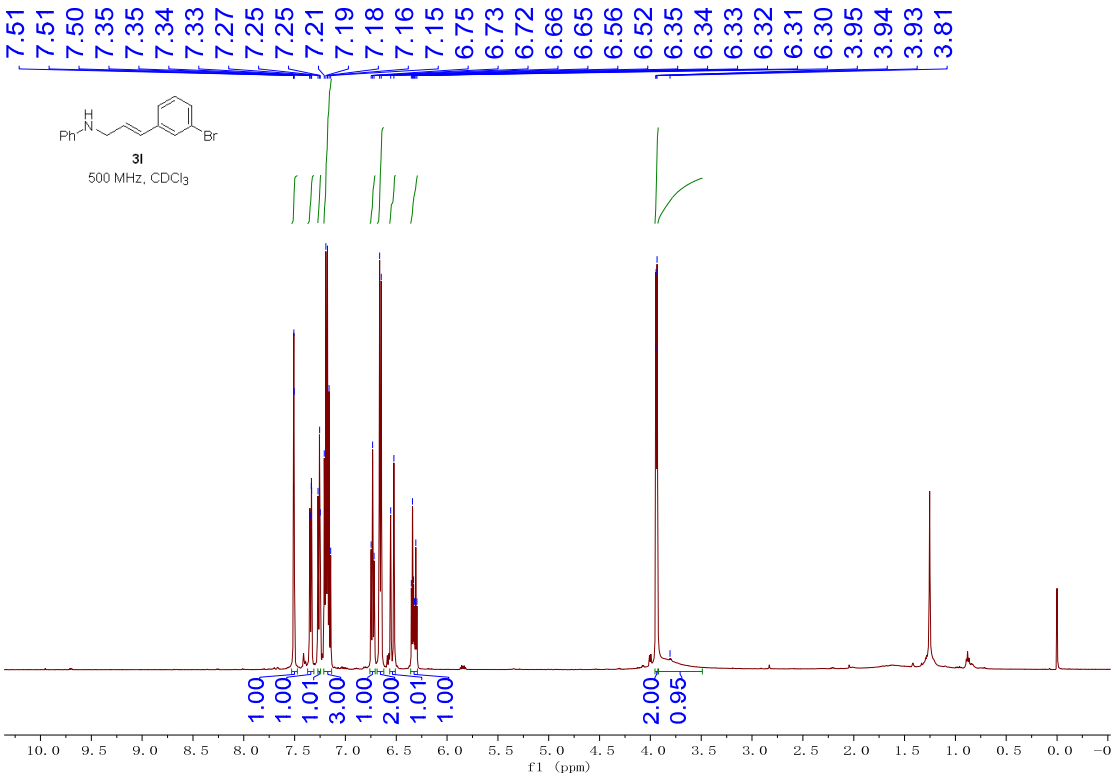
H
Cl
3k
500 MHz, CDCl3
130.00 129.76 129.30 128.70 127.41 126.25 124.52
f1 (ppm)
f1 (ppm)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7.15
6.75
6.73
6.72
6.66
6.65
6.56
6.52
6.35
6.34
6.33
6.32
6.31
6.30
3.95
3.94
3.93
3.81
Ph
H
N
Br
3l
500 MHz, CDCl3
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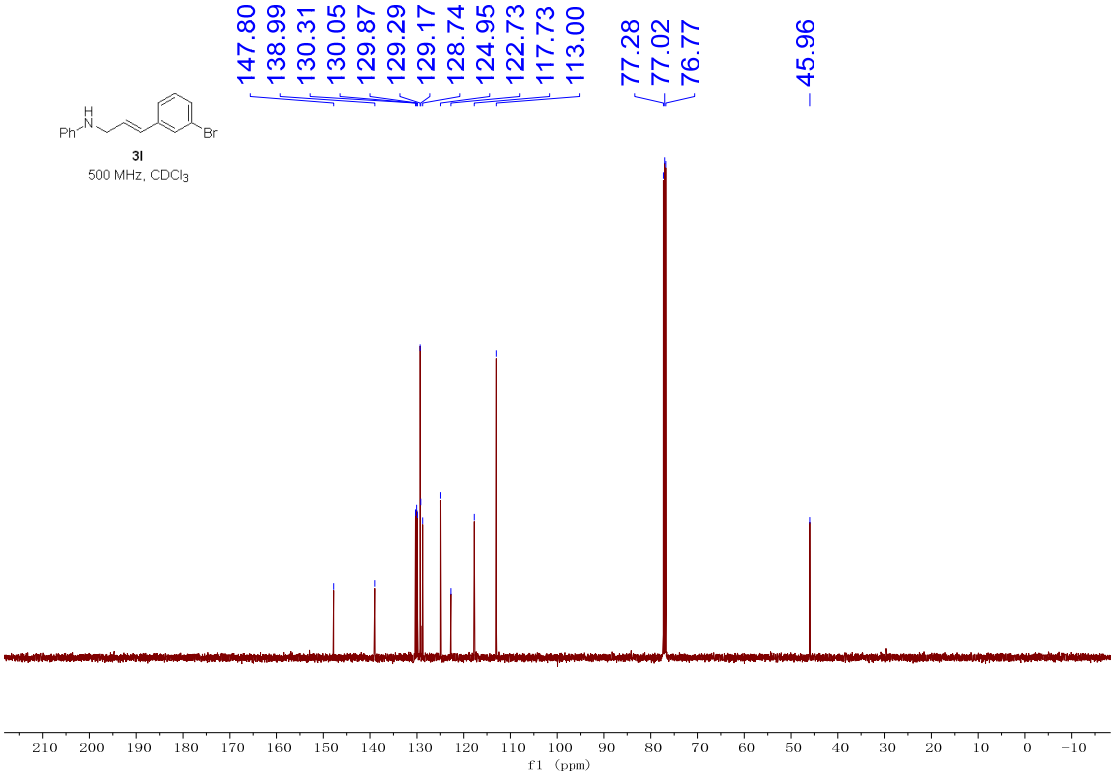
1.01
3.00
1.00
2.00
1.01
1.00
2.00
0.95
f1 (ppm)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128.74
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122.73
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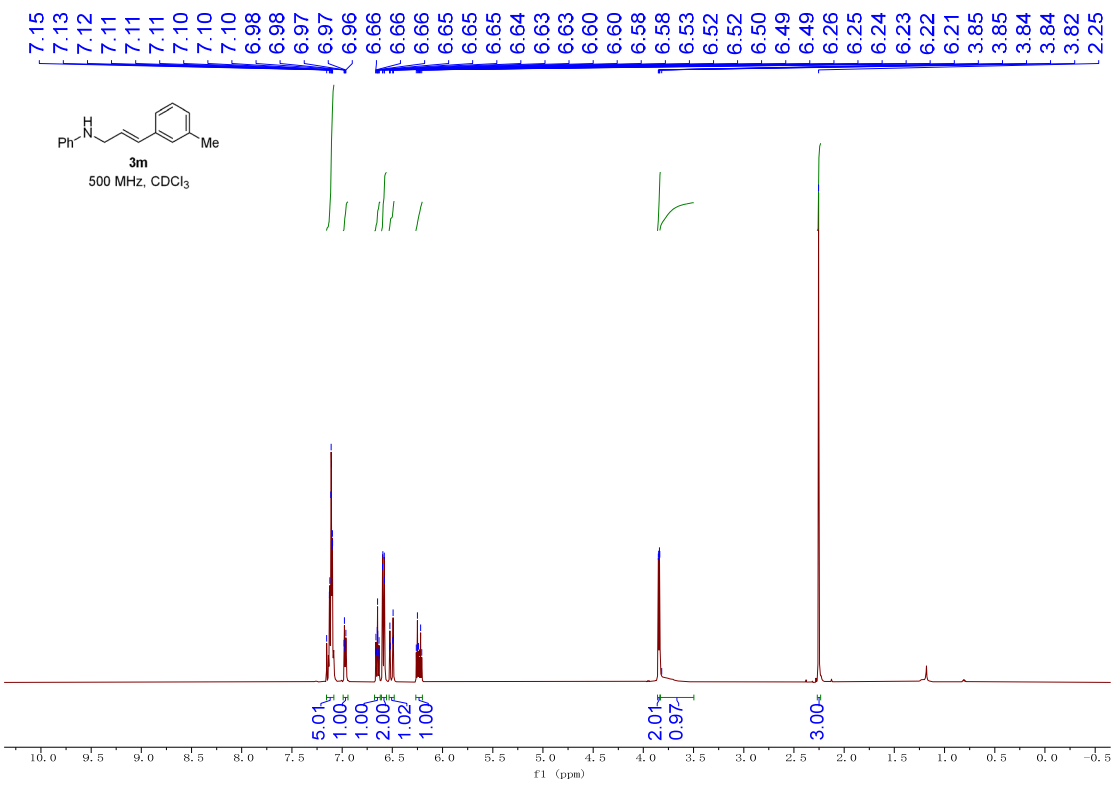
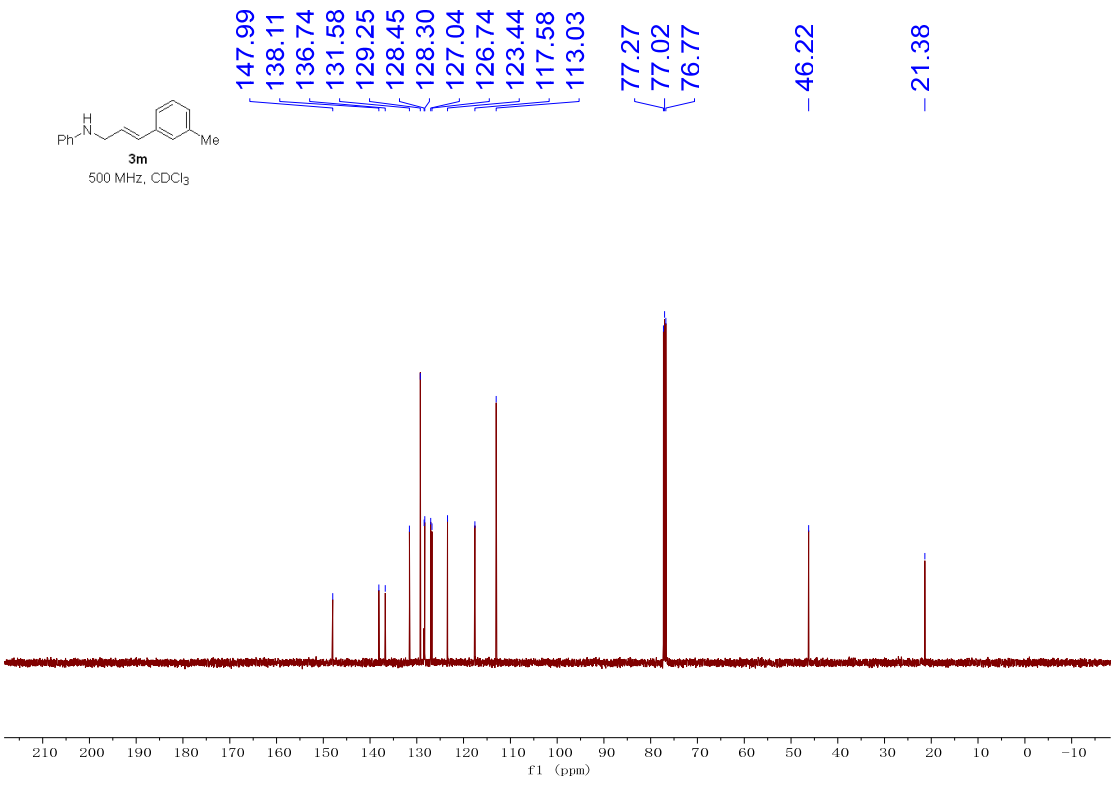
77.02
76.77
45.96
Ph
H
N
Br
3l
500 MHz, CDCl3
f1 (ppm)


7.15 7.13 7.12 7.11 7.11 7.11 7.10 7.10 7.10 6.98 6.98 6.97 6.97 6.96 6.66 6.66 6.66 6.65 6.65 6.65 6.64 6.63 6.63 6.60 6.60 6.58 6.58 6.53 6.52 6.52 6.50 6.49 6.26 6.25 6.24 6.23 6.22 6.21 3.85 3.85 3.84 3.84 3.82 2.25
Ph
N
H
Me
3m
500 MHz, CDCl3
5.01 1.00 1.00 2.00 1.02 1.00 2.01 0.97 3.00
f1 (ppm)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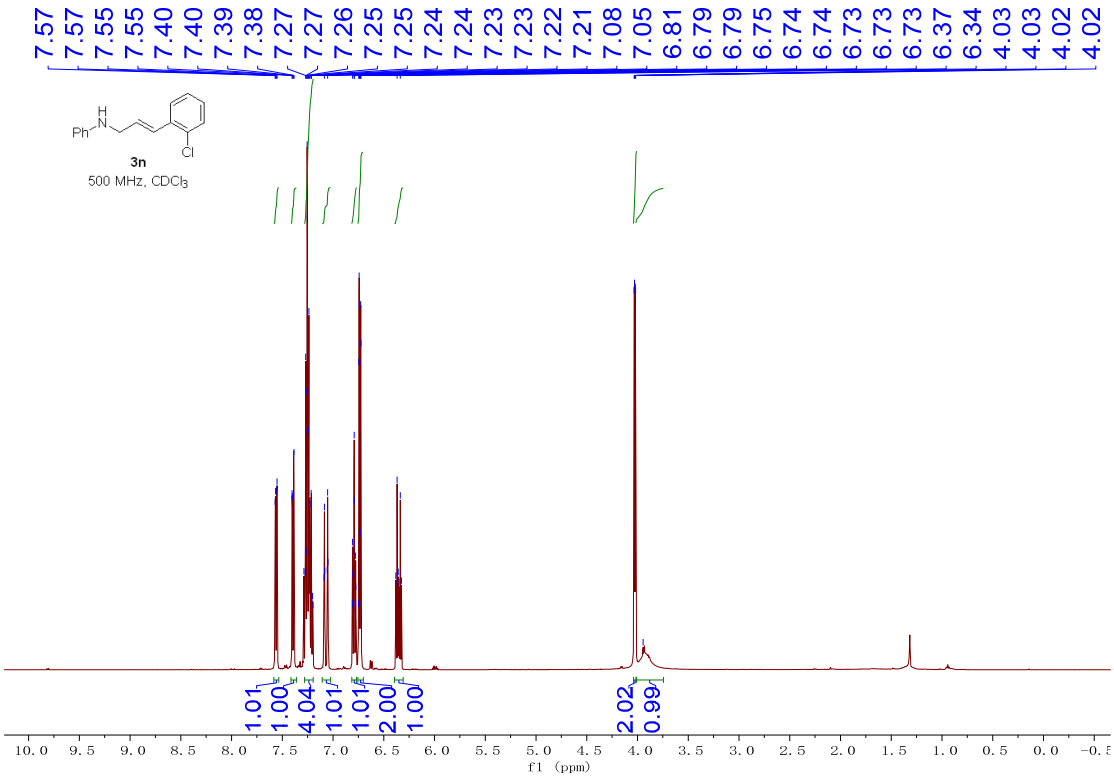
Ph
N
H
Me
3m
500 MHz, CDCl3
f1 (ppm)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7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.08
7.05
6.81
6.79
6.79
6.75
6.74
6.74
6.73
6.73
6.73
6.37
6.34
4.03
4.03
4.02
4.02
Ph
N
H
Cl
3n
500 MHz, CDCl3
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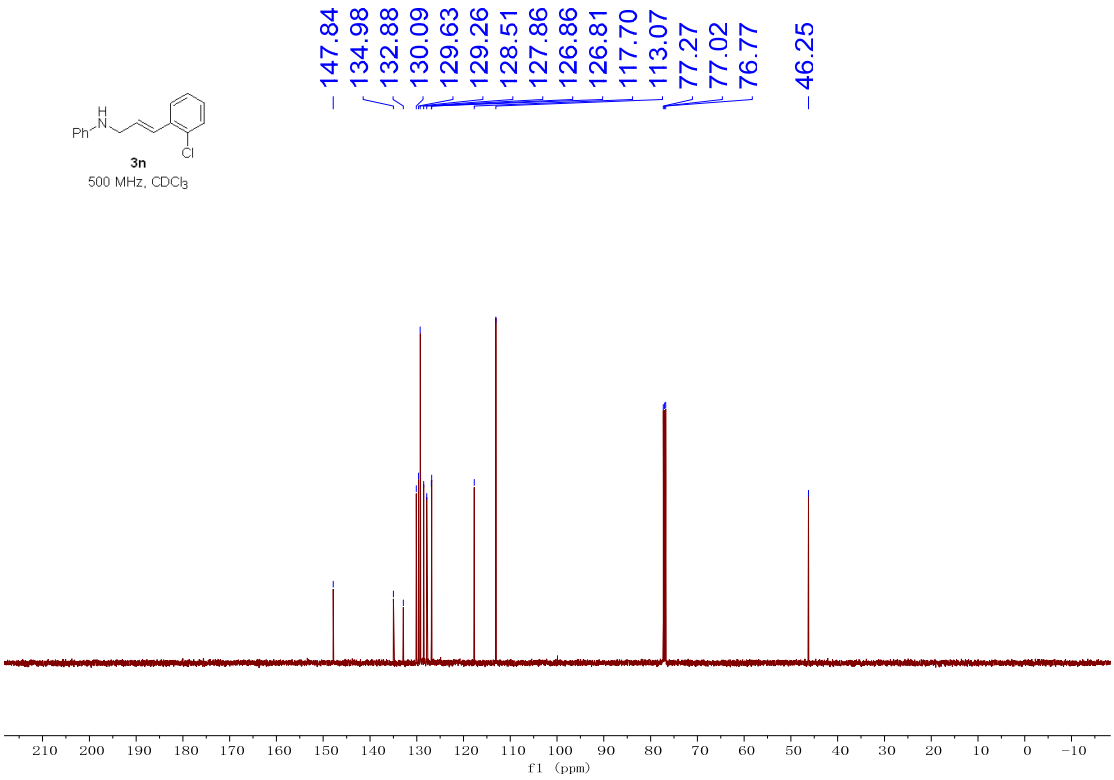
1.00
4.04
1.01
1.01
2.00
1.00
2.02
0.99
f1 (ppm)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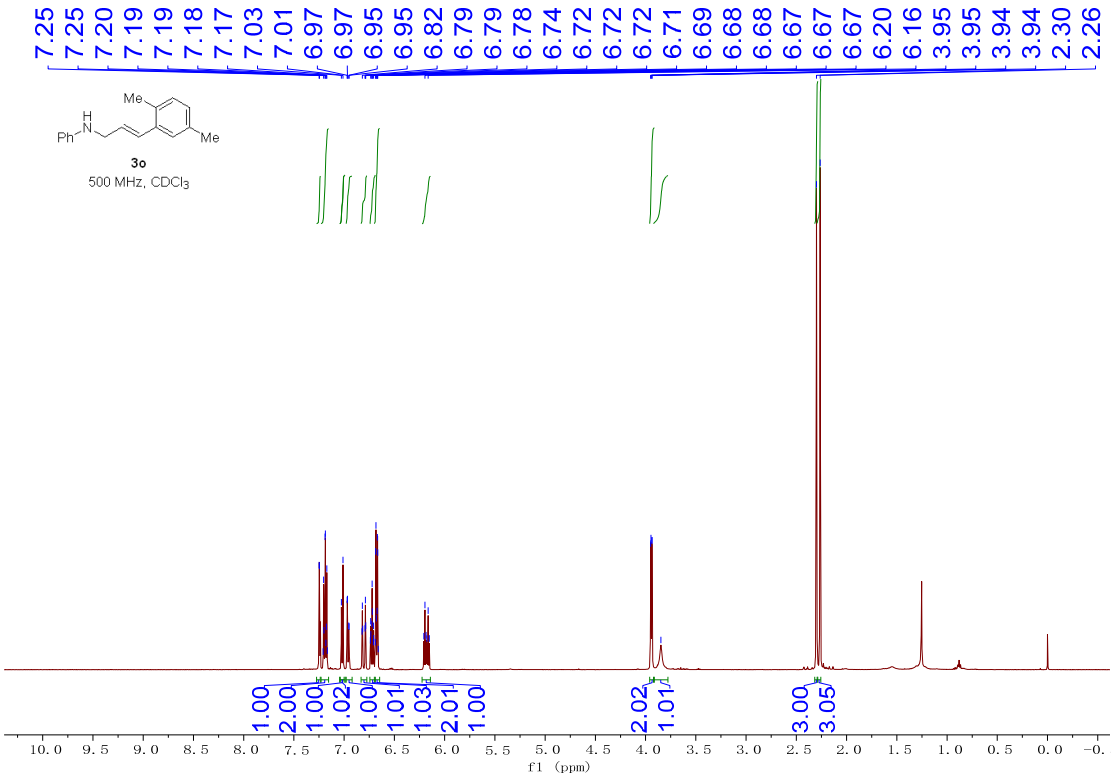
130.09
129.63
129.26
128.51
127.86
126.86
126.81
117.70
113.07
77.27
77.02
76.77
46.25
Ph
N
H
Cl
3n
500 MHz, CDCl3
f1 (ppm)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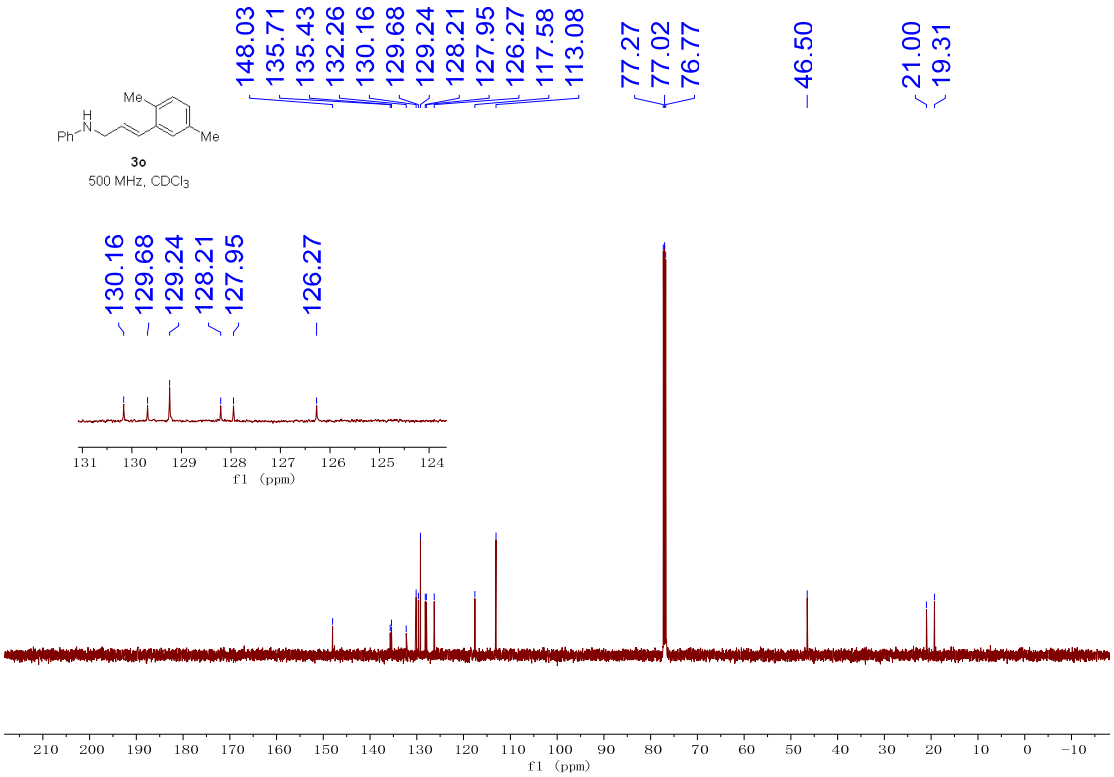
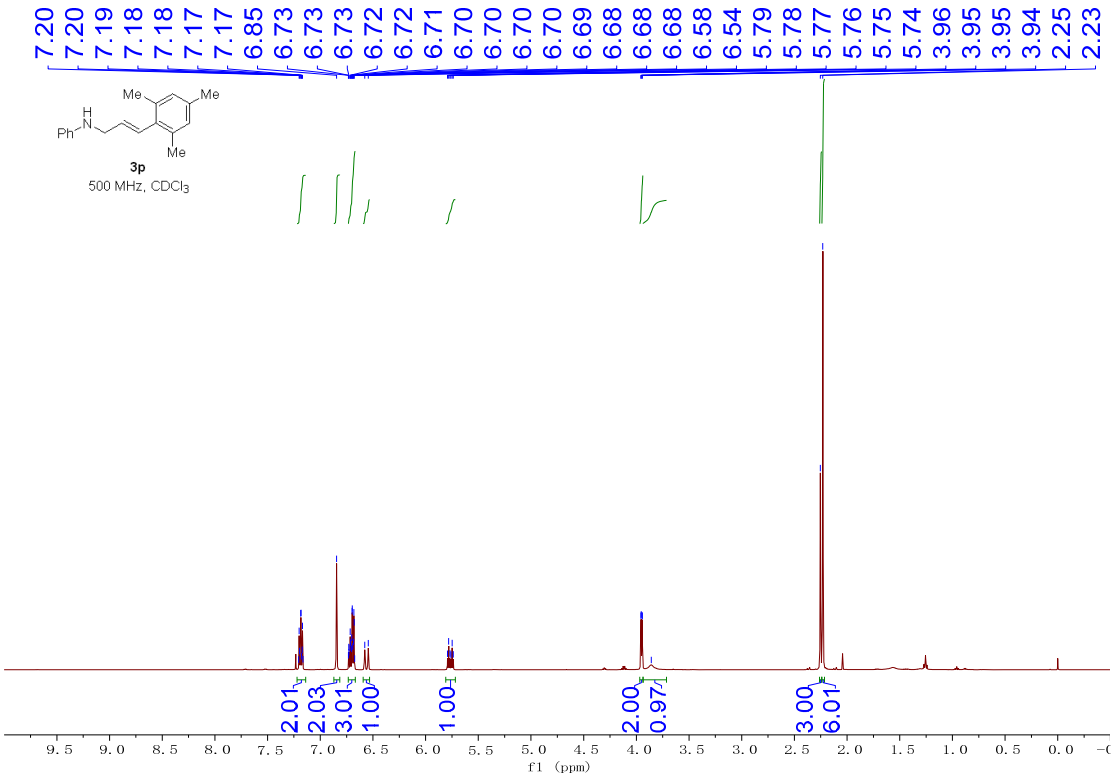
Me
Ph
N
H
Me
3o
500 MHz, CDCl3
1.00 2.00 1.00 1.02 1.00 1.01 1.03 2.01 1.00 2.02 1.01 3.00 3.05
f1 (ppm)


148.03 135.71 135.43 132.26 130.16 129.68 129.24 128.21 127.95 126.27 117.58 113.08 77.27 77.02 76.77 46.50 21.00 19.31
Me
Ph
N
H
Me
3o
500 MHz, CDCl3
130.16 129.68 129.24 128.21 127.95 126.27
f1 (ppm)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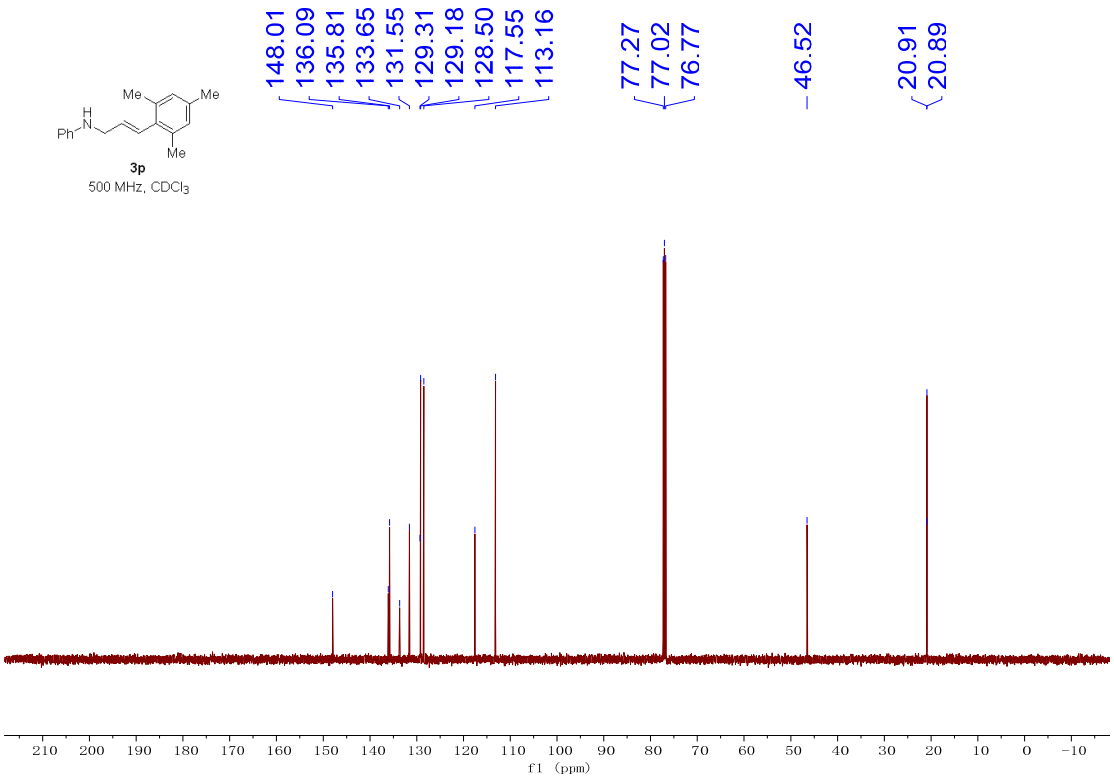
Me
Me
Ph
H
N
Me
3p
500 MHz, CDCl3
2.01 2.03 3.01 1.00 1.00 2.00 0.97 3.00 6.01
f1 (ppm)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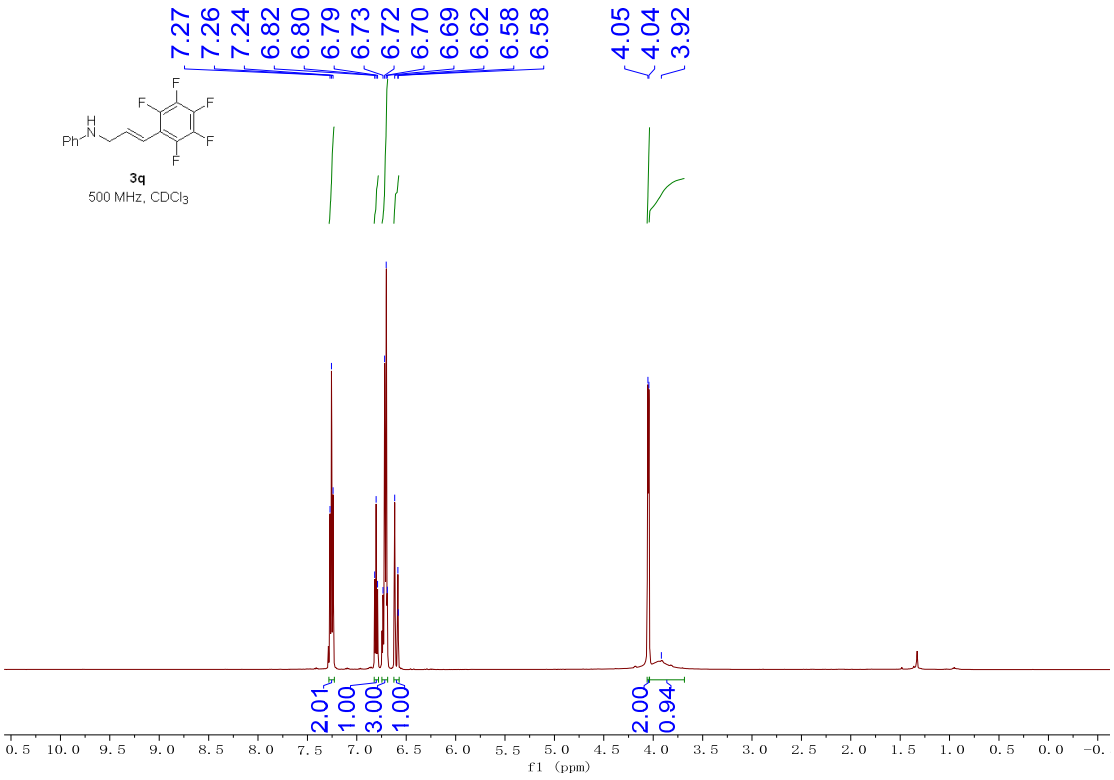
Me
Me
Ph
H
N
Me
3p
500 MHz, CDCl3
f1 (ppm)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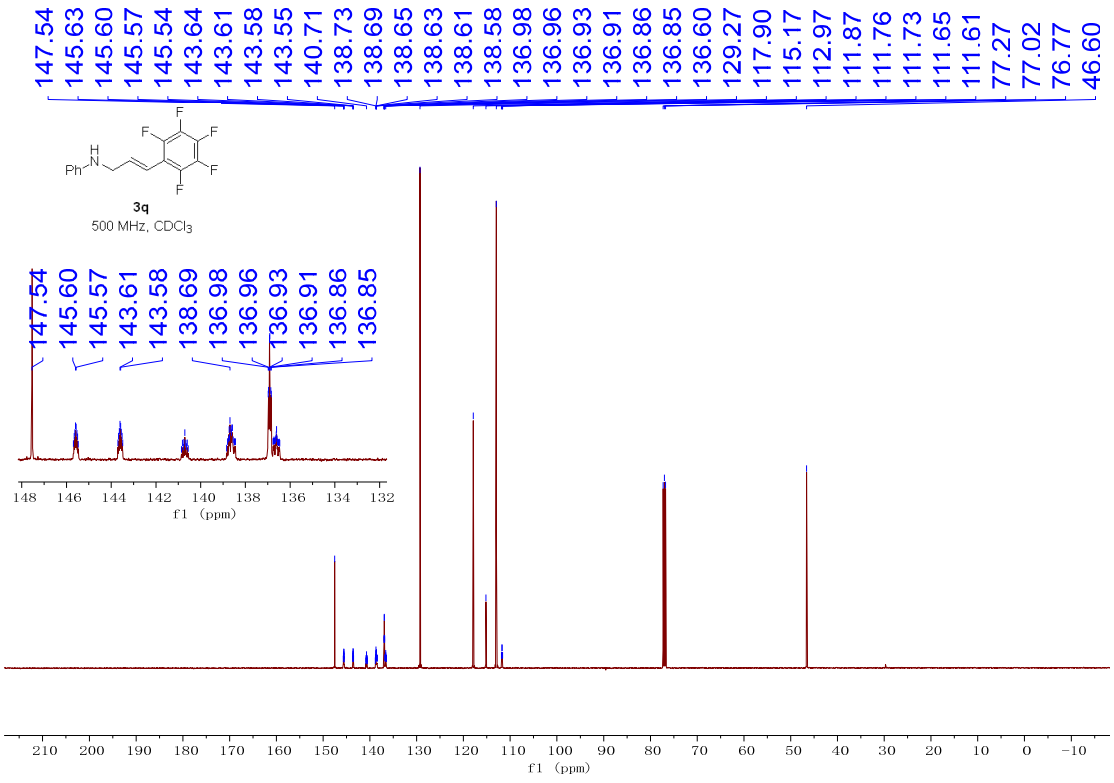
6.79
6.73
6.72
6.70
6.69
6.62
6.58
6.58
4.05
4.04
3.92
3q
500 MHz, CDCl3
2.01
1.00
3.00
1.00
2.00
0.94
f1 (ppm)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138.63
138.61
138.58
136.98
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136.60
129.27
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115.17
112.97
111.87
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77.27
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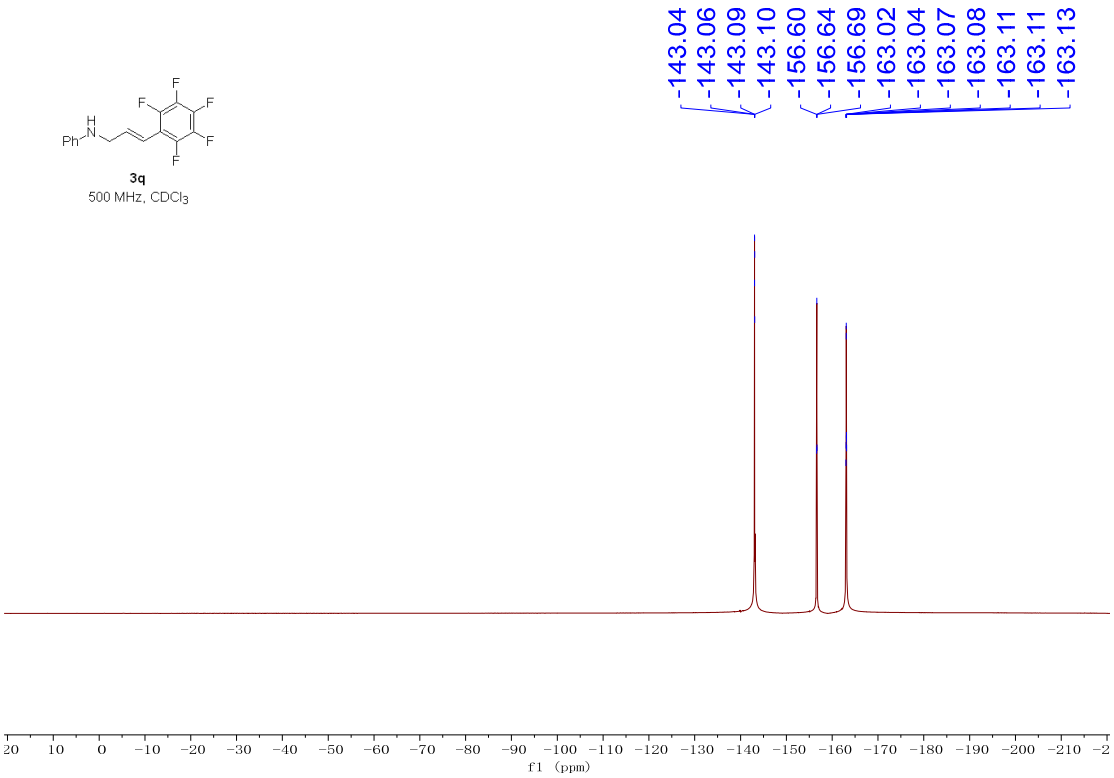
76.77
46.60
3q
500 MHz, CDCl3
f1 (ppm)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-163.04
-163.07
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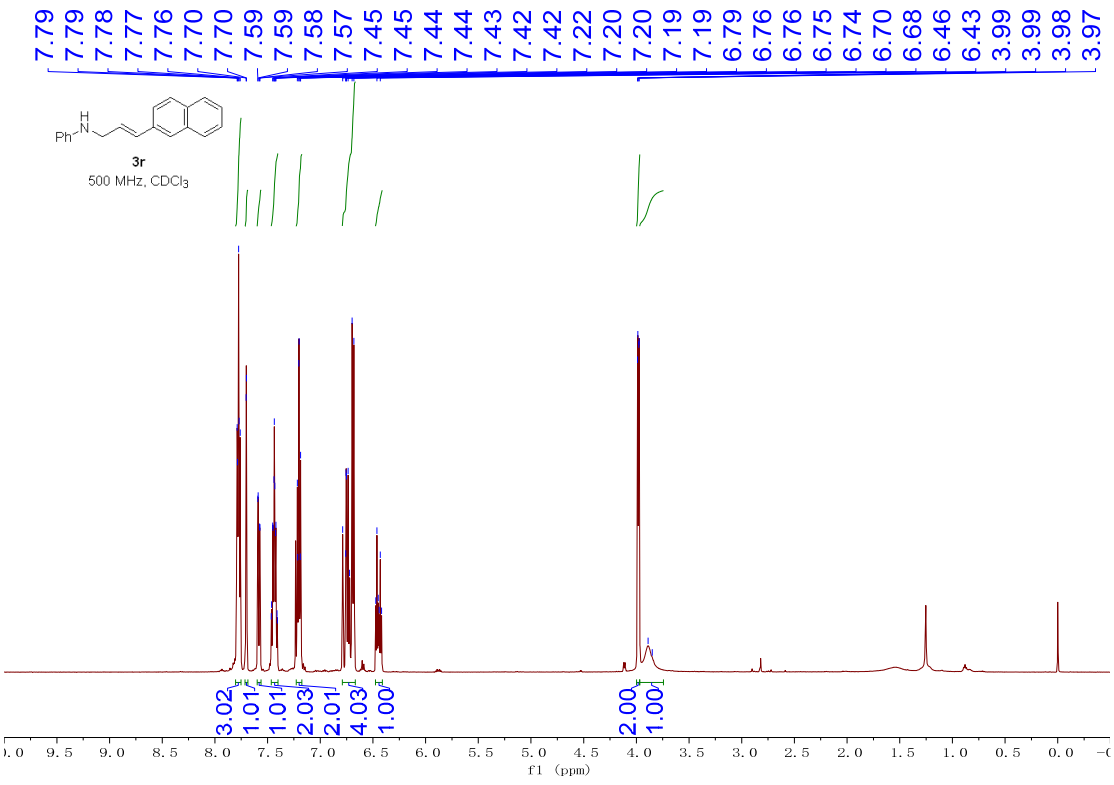
-163.13
3q
500 MHz, CDCl3
f1 (ppm)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7.43
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7.42
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7.20
7.19
7.19
6.79
6.76
6.76
6.75
6.74
6.70
6.68
6.46
6.43
3.99
3.99
3.98
3.97
3r
500 MHz, CDCl3
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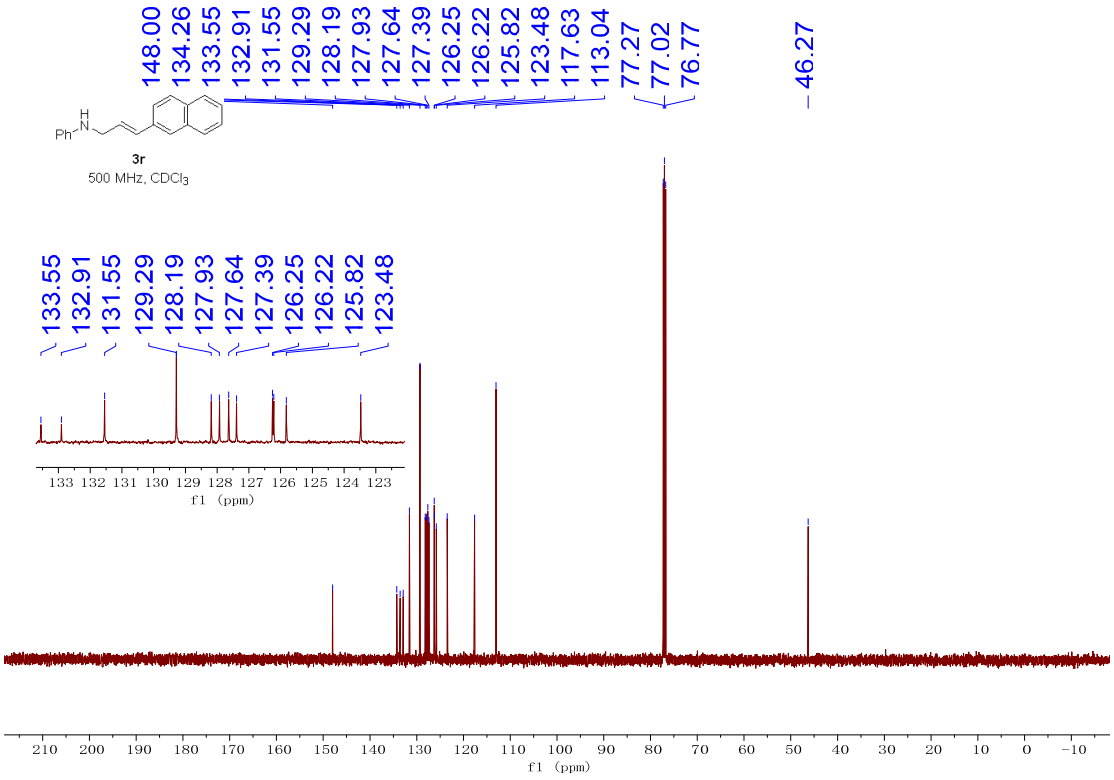
1.01
1.01
2.03
2.01
4.03
1.00
2.00
1.00
f1 (ppm)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126.22
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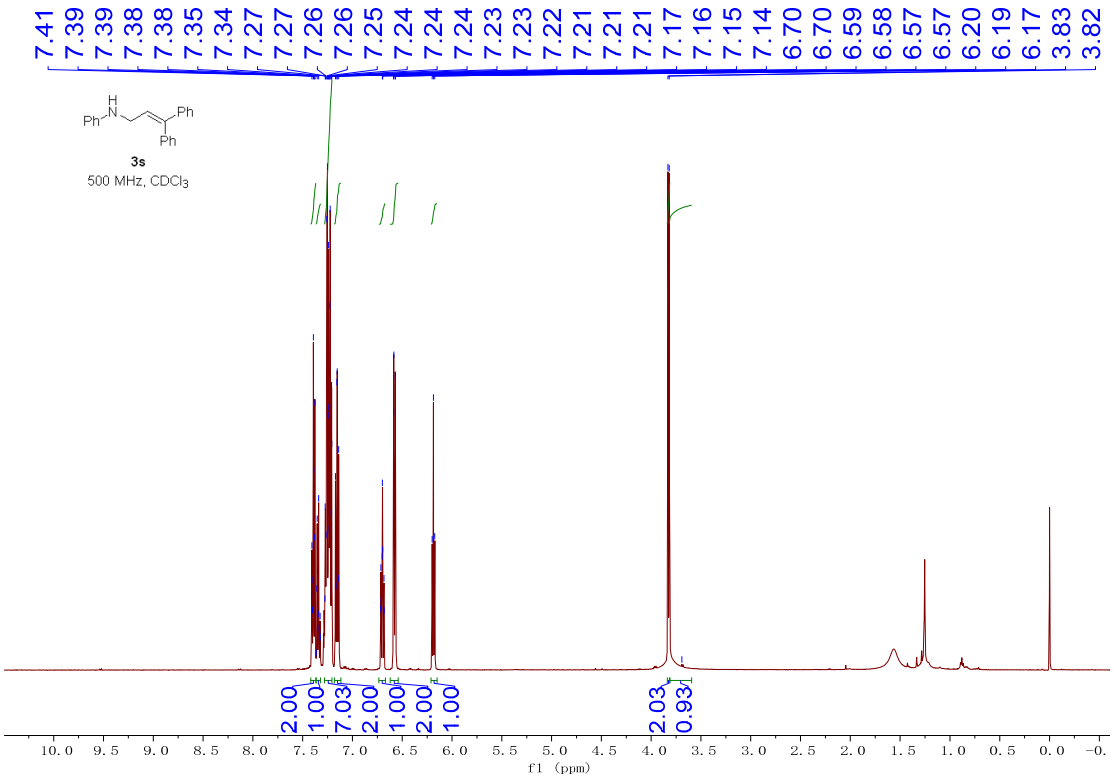
117.63
113.04
77.27
77.02
76.77
46.27
3r
500 MHz, CDCl3
f1 (ppm)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7.21
7.21
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7.14
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6.70
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6.58
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6.57
6.20
6.19
6.17
3.83
3.82
2.00
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2.00
1.00
2.00
1.00
2.03
0.93
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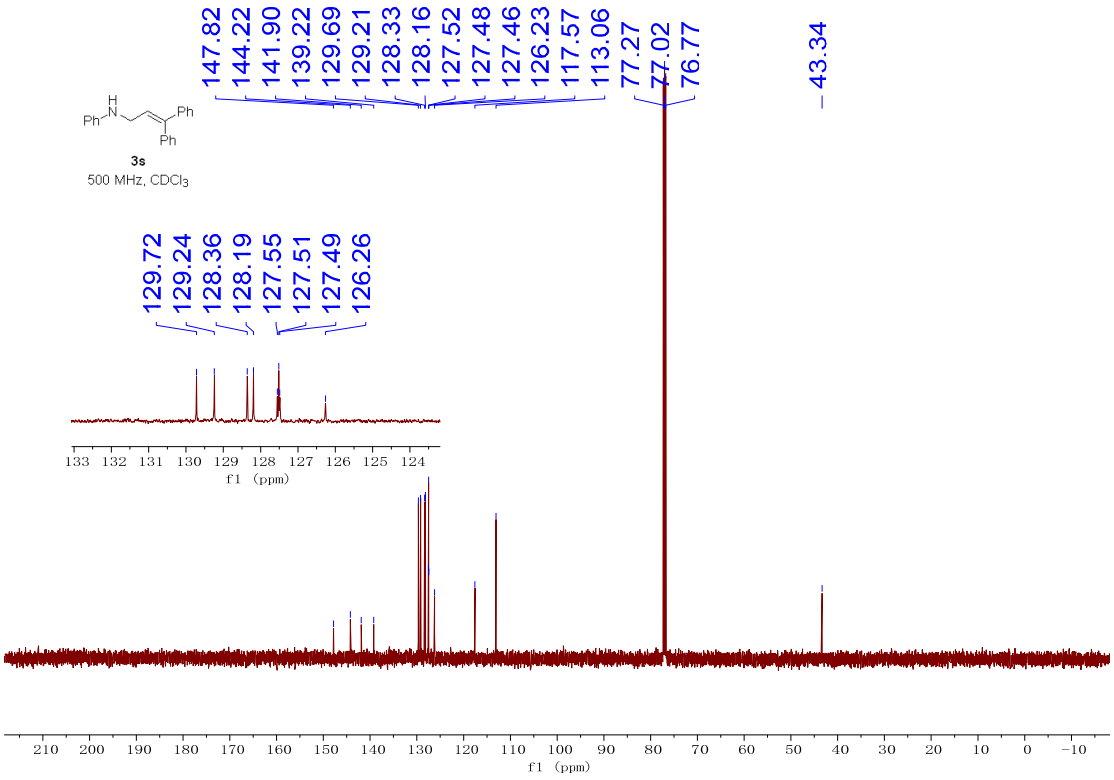
500 MHz, CDCl3
f1 (ppm)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113.06
77.27
77.02
76.77
43.34
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128.36
128.19
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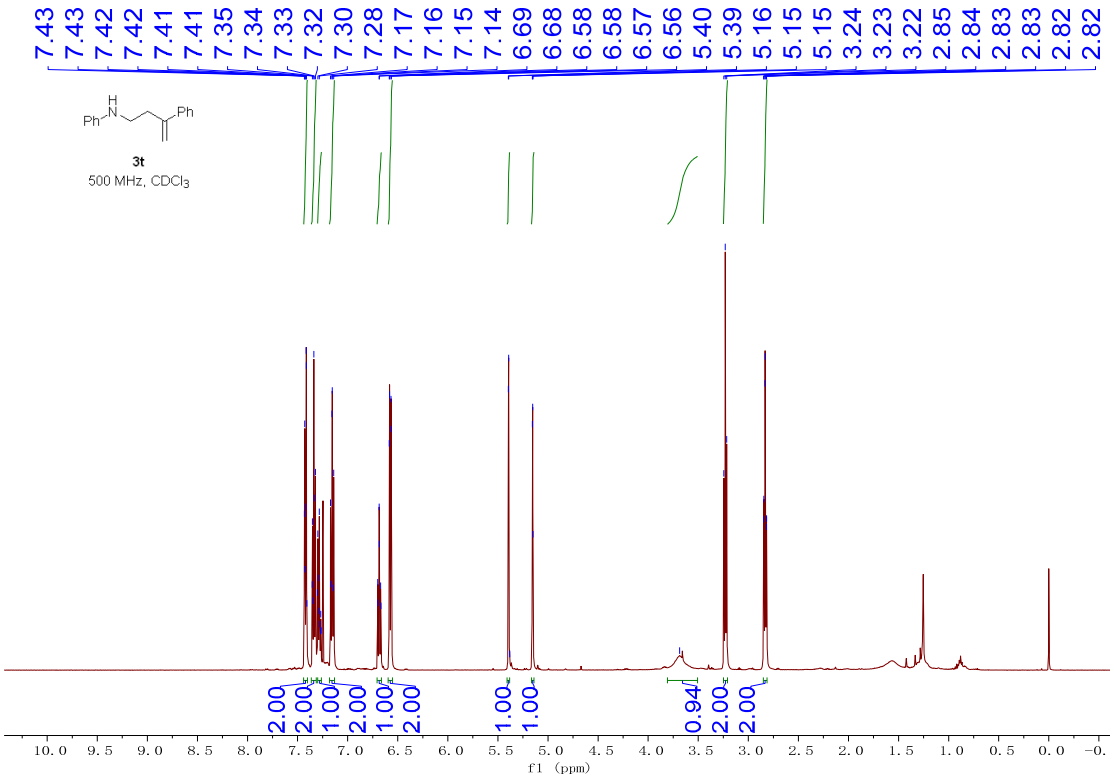
127.51
127.49
126.26
3s
500 MHz, CDCl3
f1 (ppm)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7.16
7.15
7.14
6.69
6.68
6.58
6.58
6.57
6.56
5.40
5.39
5.16
5.15
5.15
3.24
3.23
3.22
2.85
2.84
2.83
2.83
2.82
2.82
3t
500 MHz, CDCl3
2.00
2.00
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2.00
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2.00
1.00
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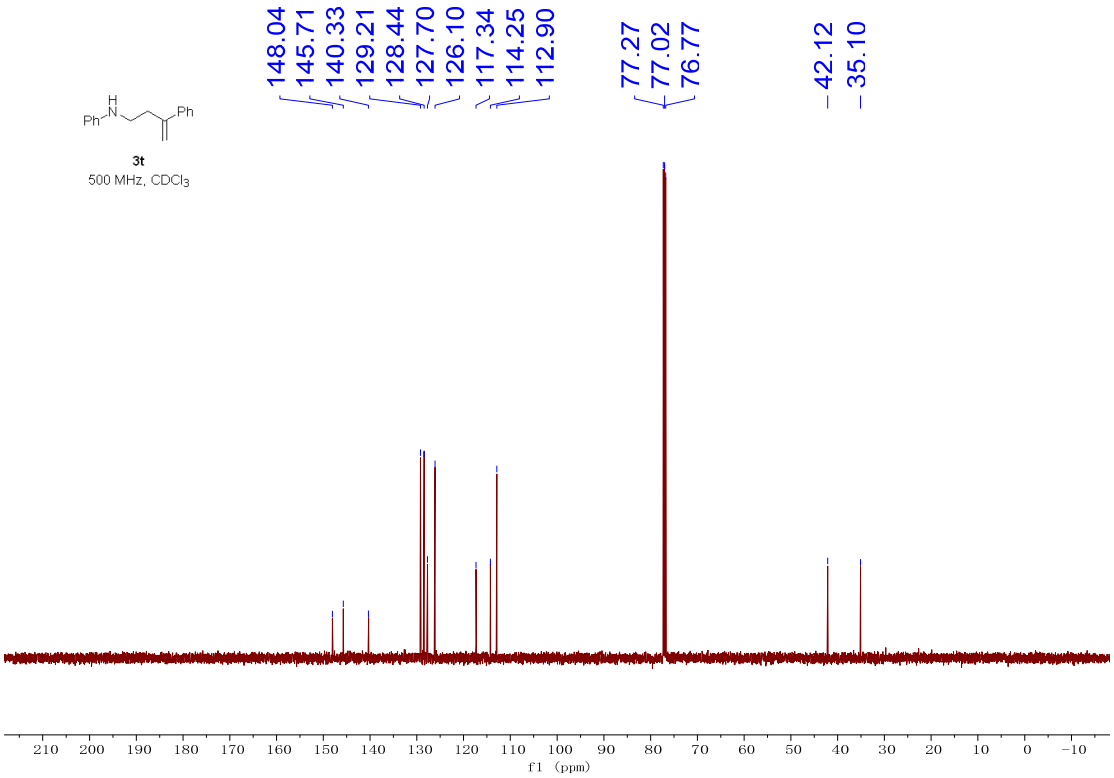
0.94
2.00
2.00
f1 (ppm)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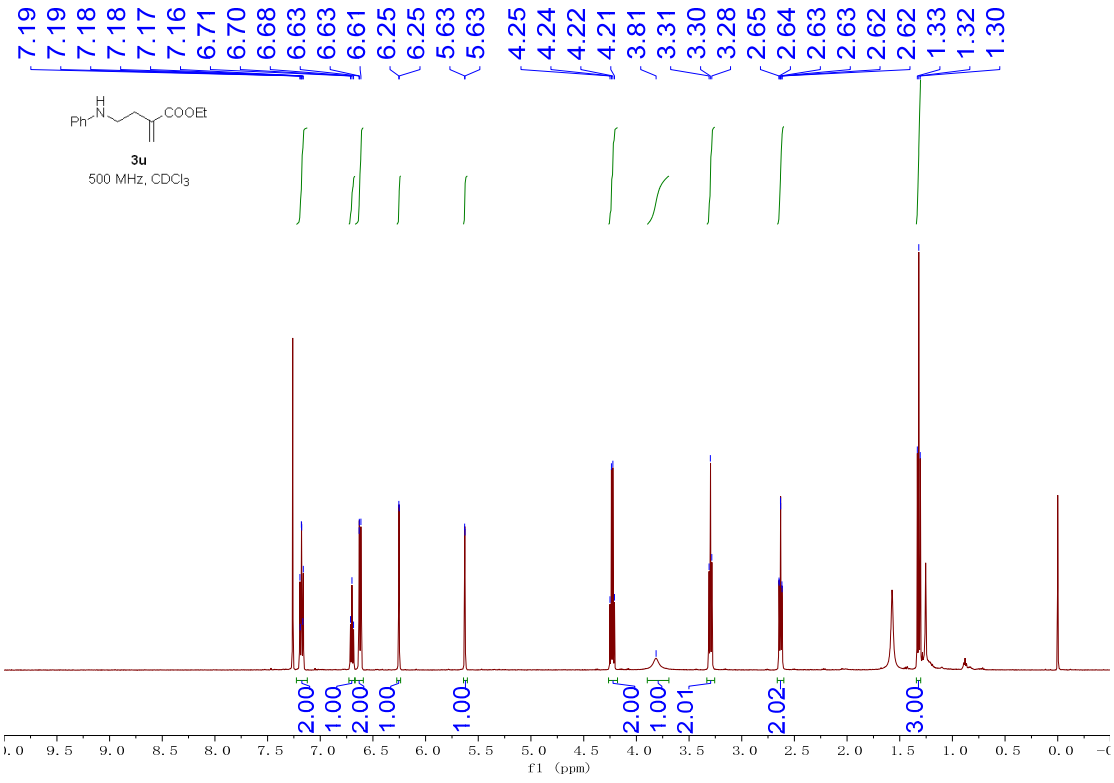
76.77
42.12
35.10
Ph
N
H
Ph
3t
500 MHz, CDCl3
f1 (ppm)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6.25
6.25
5.63
5.63
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4.24
4.22
4.21
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3.30
3.28
2.65
2.64
2.63
2.63
2.62
2.62
1.33
1.32
1.30
Ph
N
H
COOEt
3u
500 MHz, CDCl3
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2.00
1.00
1.00
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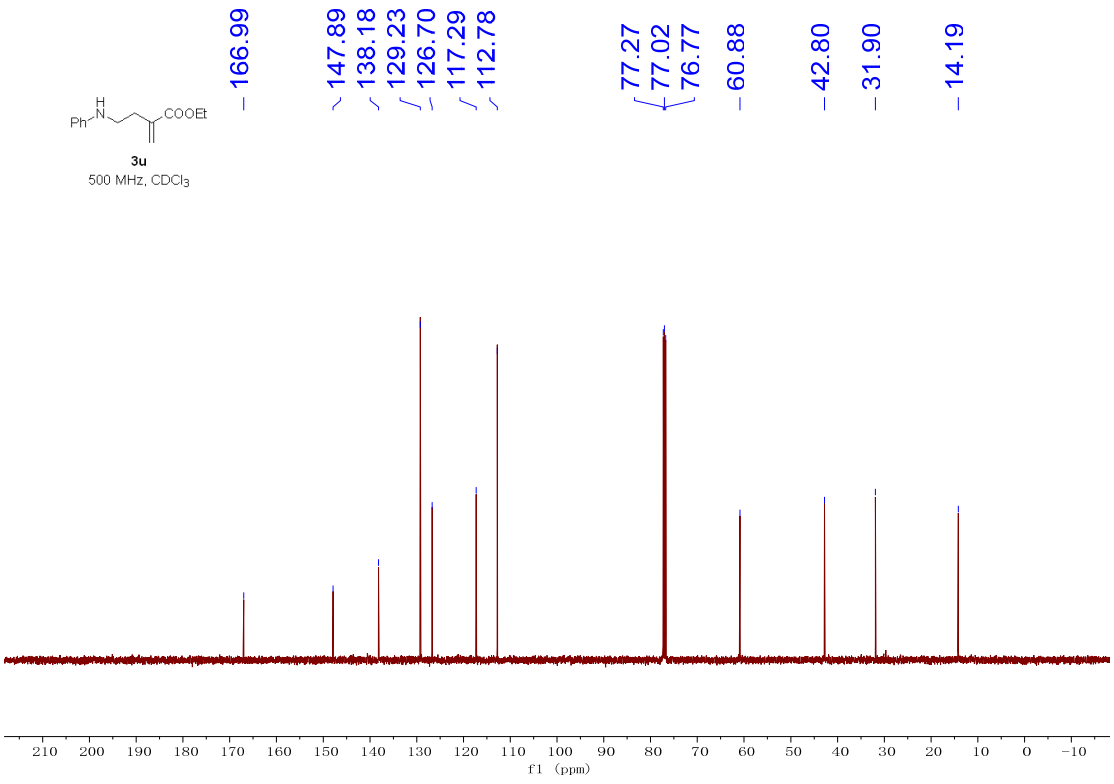
1.00
2.01
2.02
3.00
f1 (ppm)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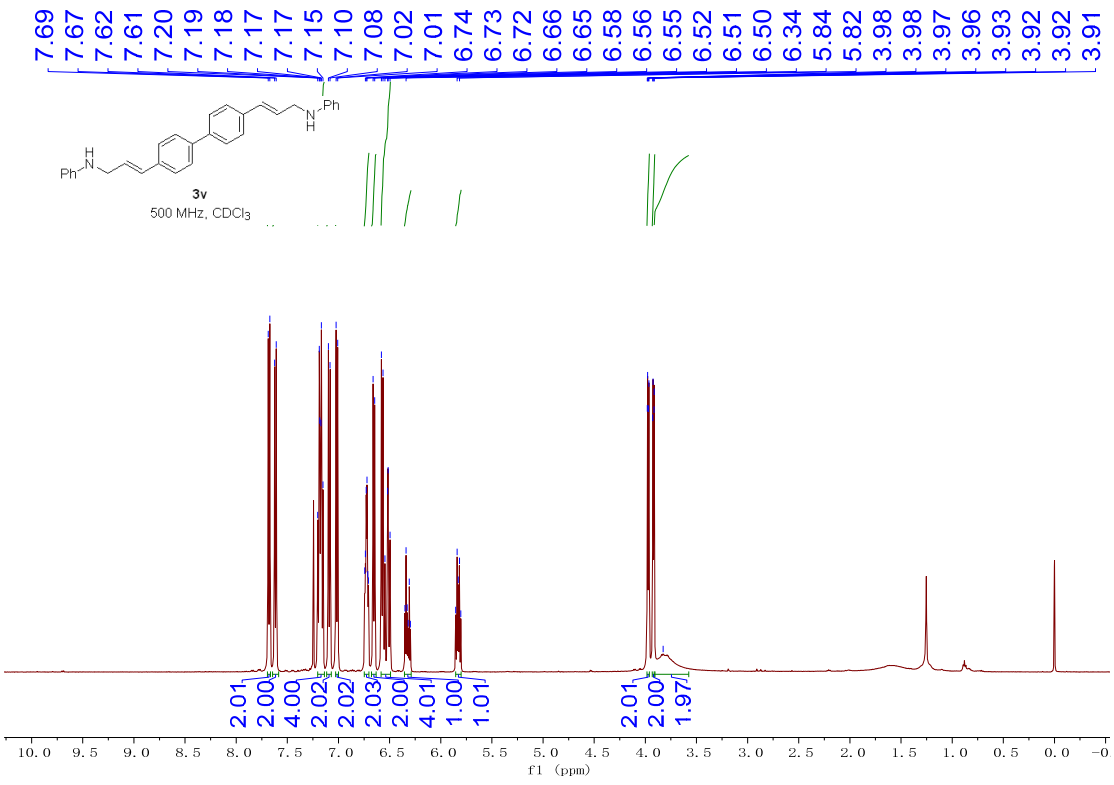
31.90
14.19
Ph
N
H
COOEt
3u
500 MHz, CDCl3
f1 (ppm)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7.10
7.08
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7.01
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6.73
6.72
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6.55
6.52
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5.82
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3.97
3.96
3.93
3.92
3.92
3.91
Ph
N
H
3v
500 MHz, CDCl3
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2.00
4.00
2.02
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2.03
2.00
4.01
1.00
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2.01
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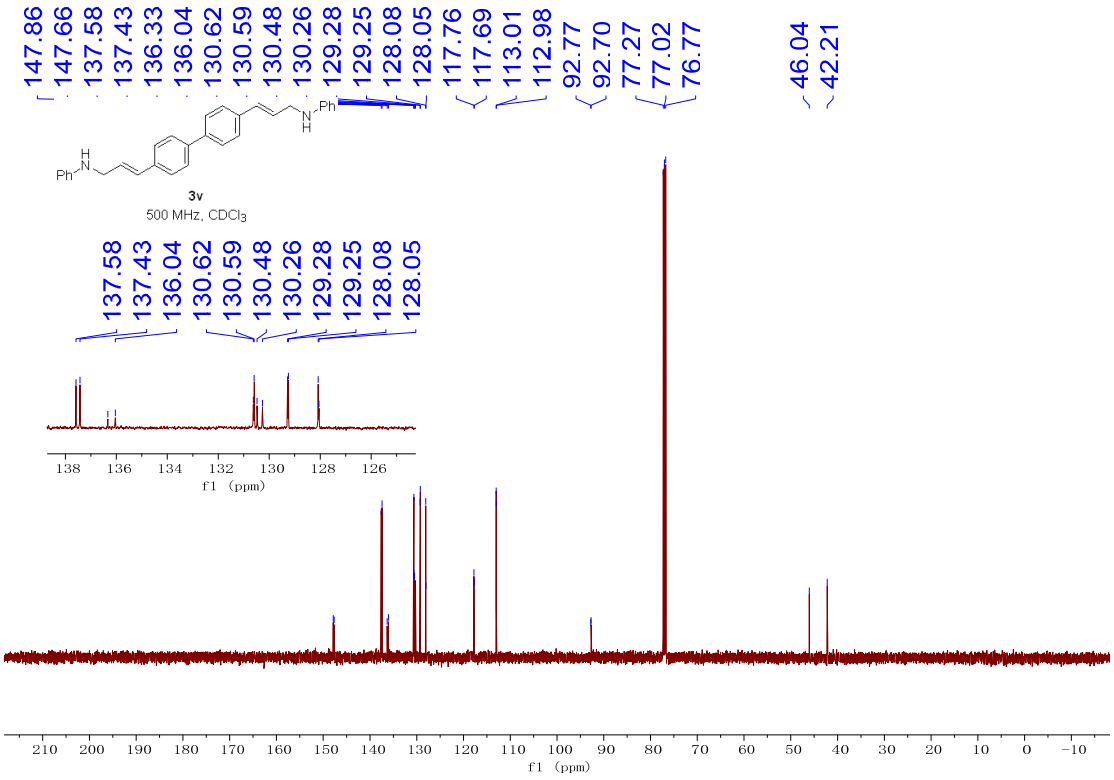
1.97
f1 (ppm)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129.25
128.08
128.05
117.76
117.69
113.01
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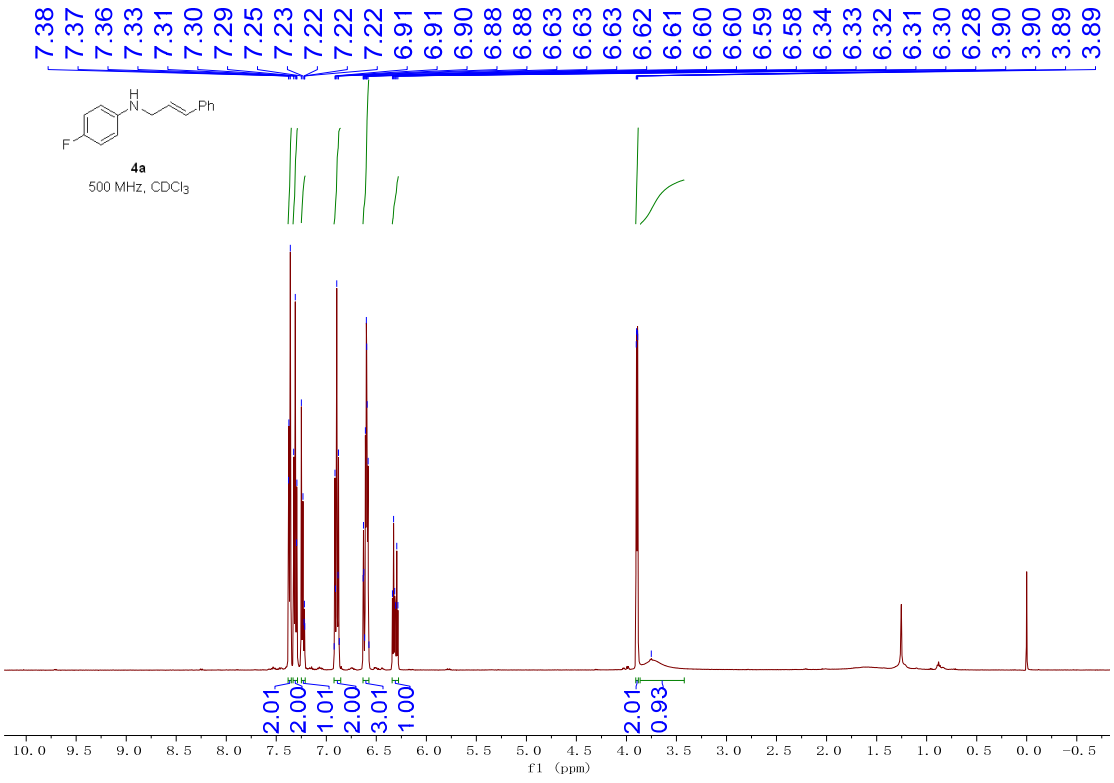
92.70
77.27
77.02
76.77
46.04
42.21
3v
500 MHz, CDCl3
f1 (ppm)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6.28
3.90
3.90
3.89
3.89
4a
500 MHz, CDCl3
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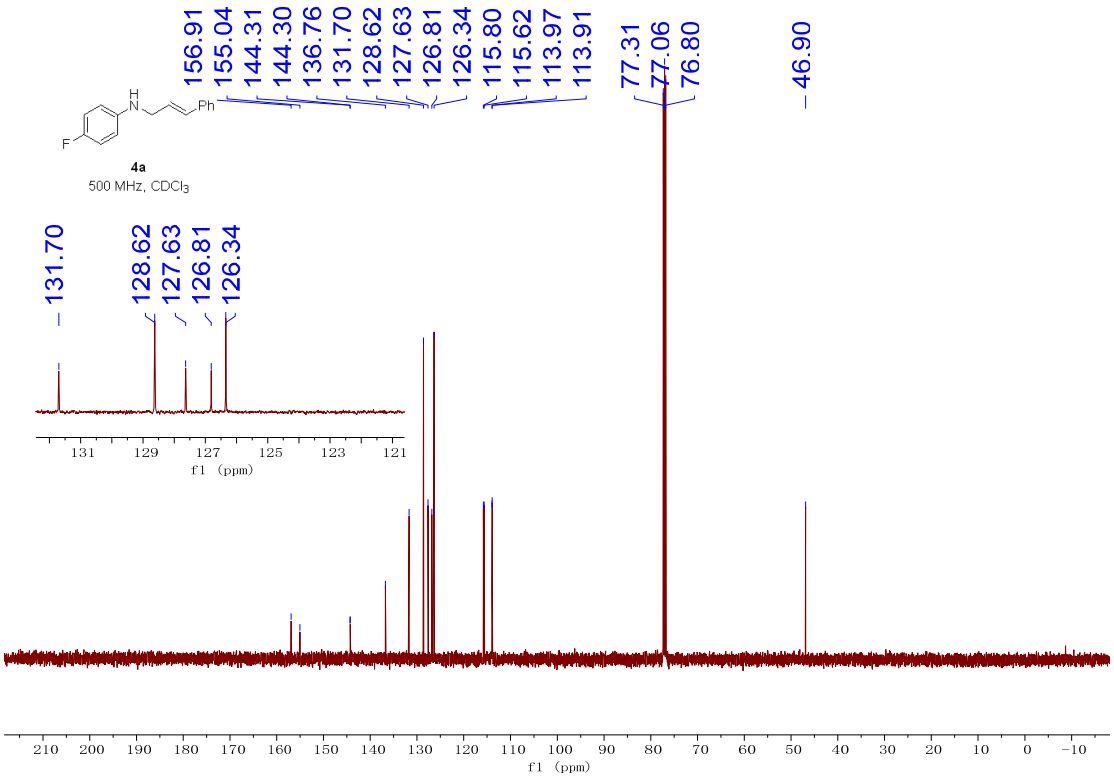
1.01
2.00
3.01
1.00
2.01
0.93
f1 (ppm)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115.80
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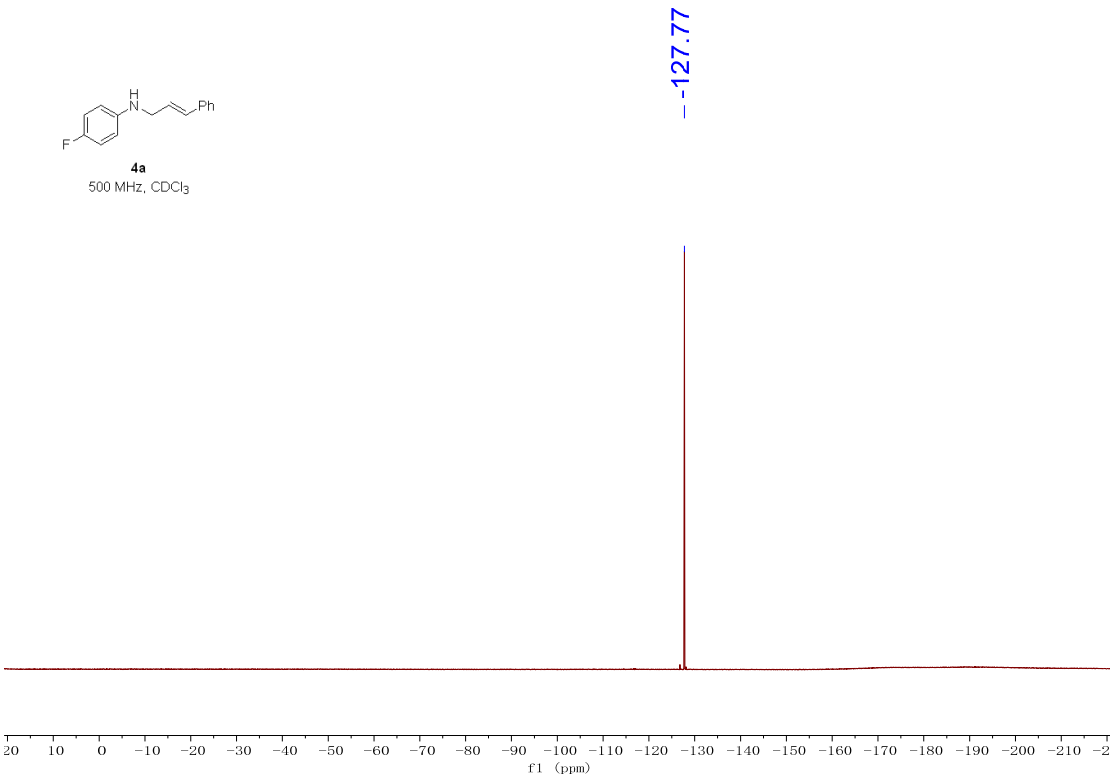
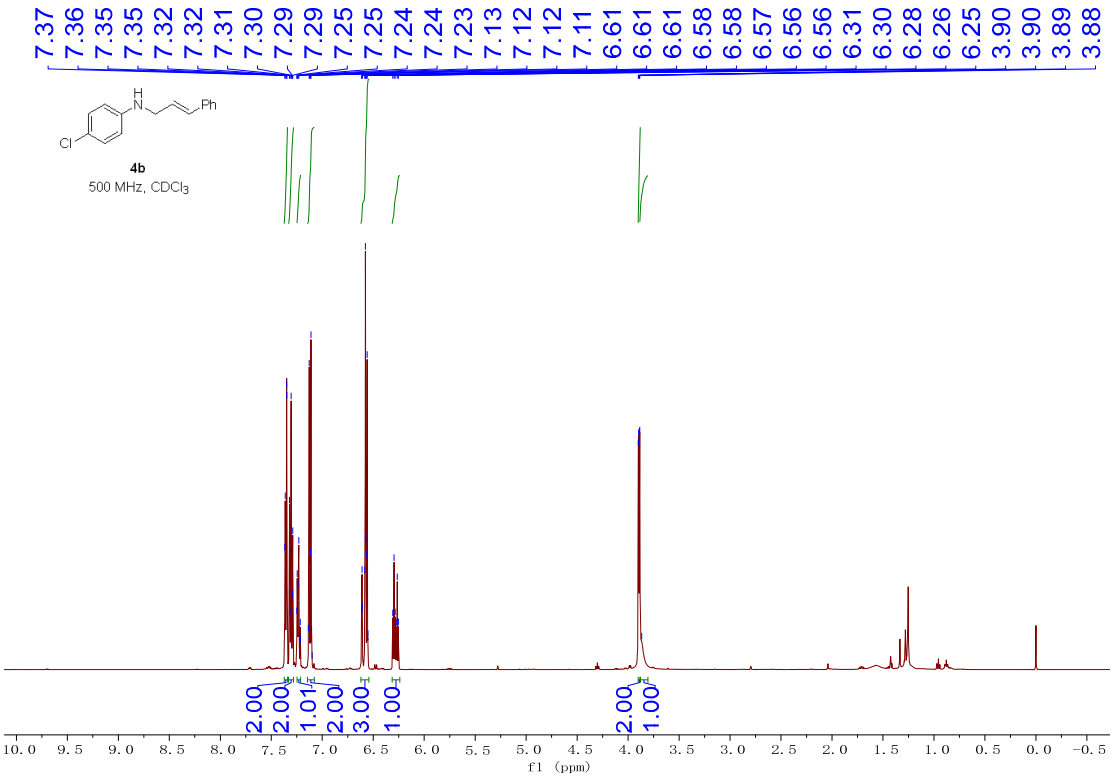
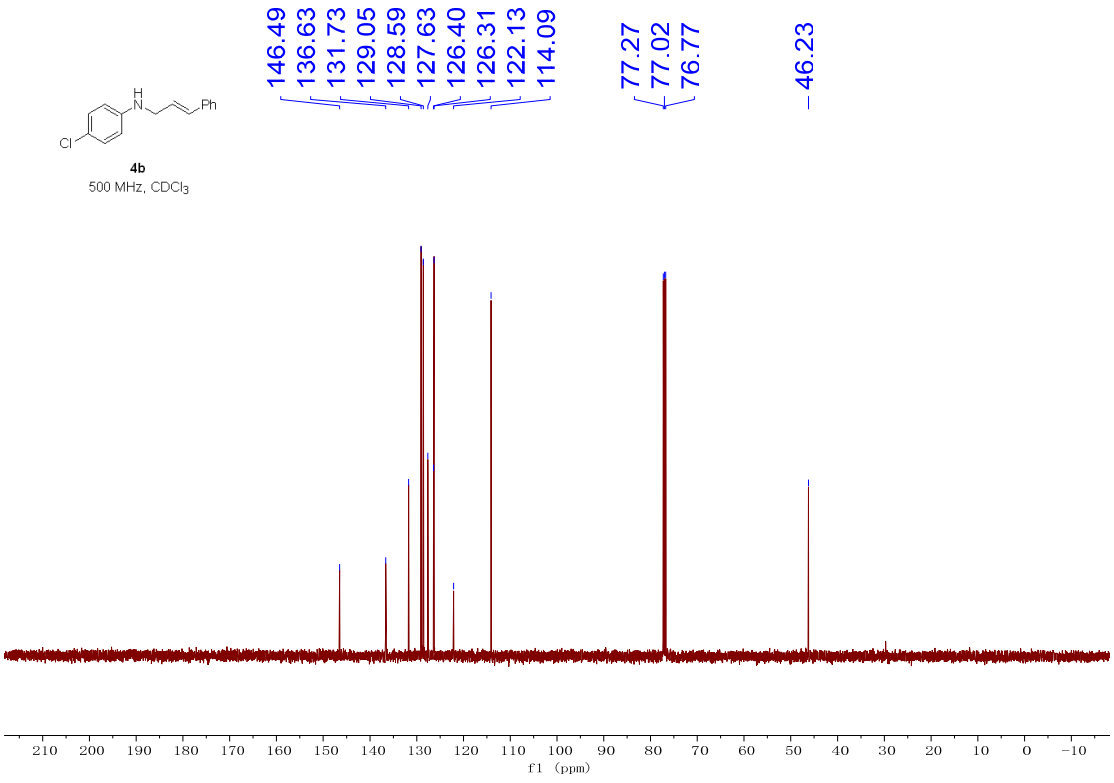
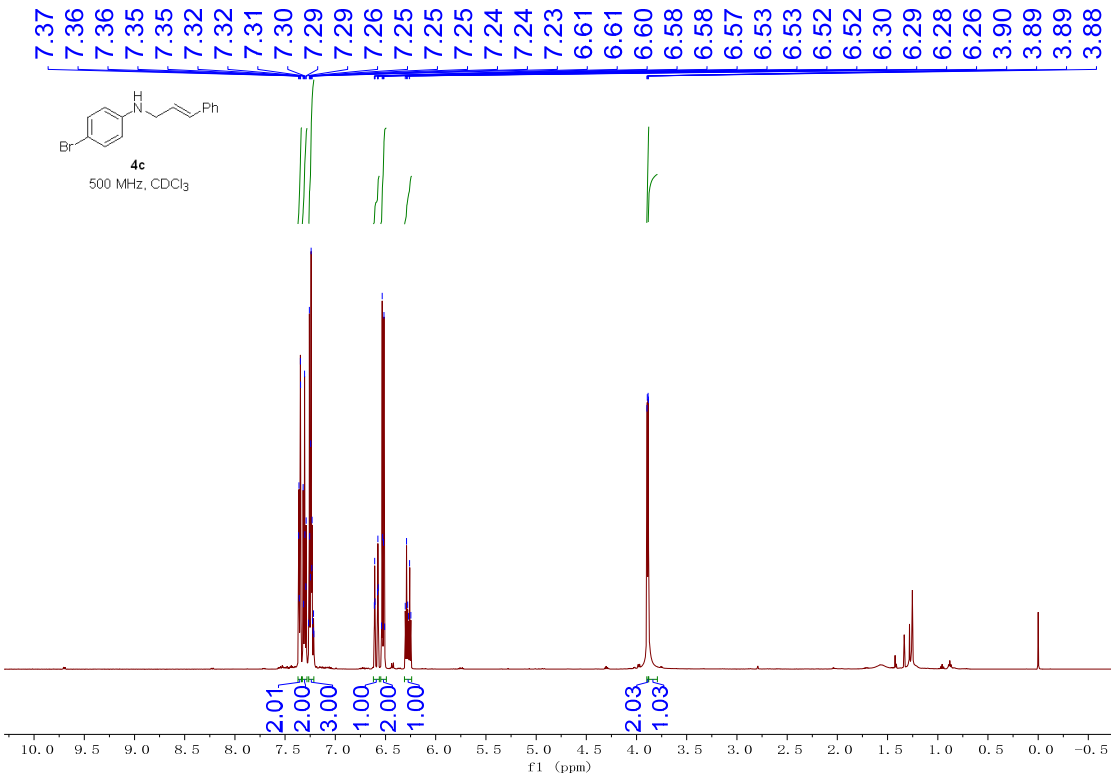
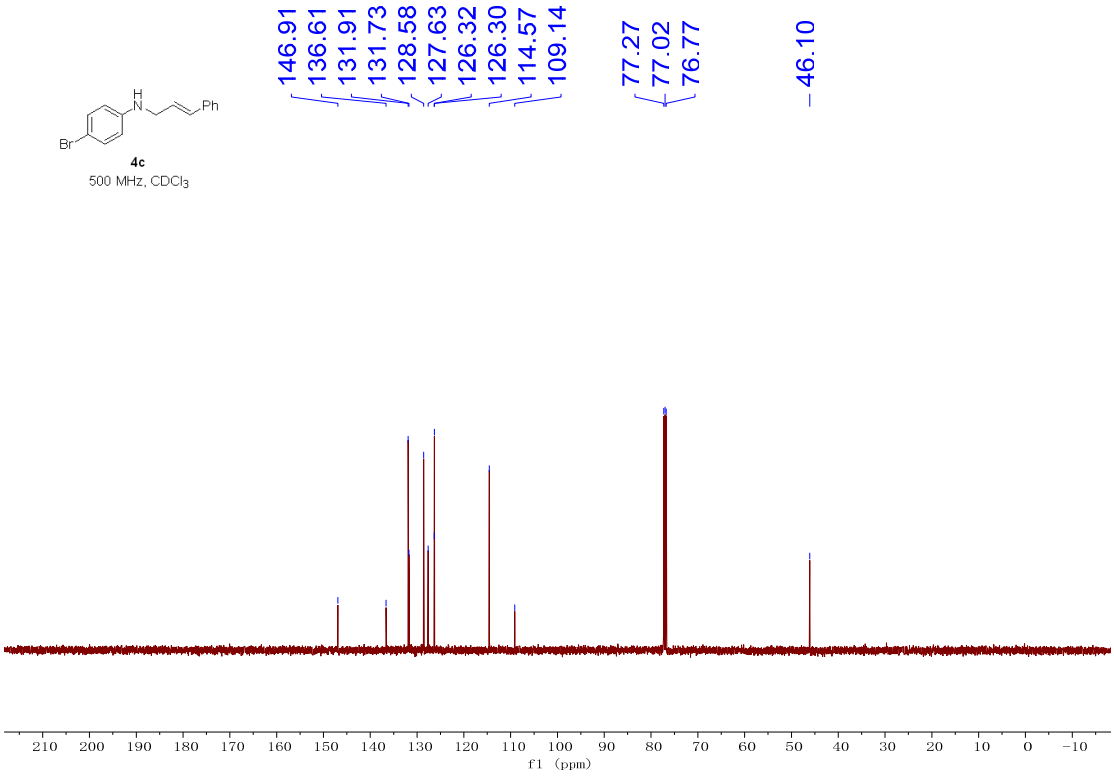
113.97
113.91
77.31
77.06
76.80
46.90
131.70
128.62
127.63
126.81
126.34
131
129
127
125
123
121
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
H
N
Ph
F
4a
500 MHz, CDCl3

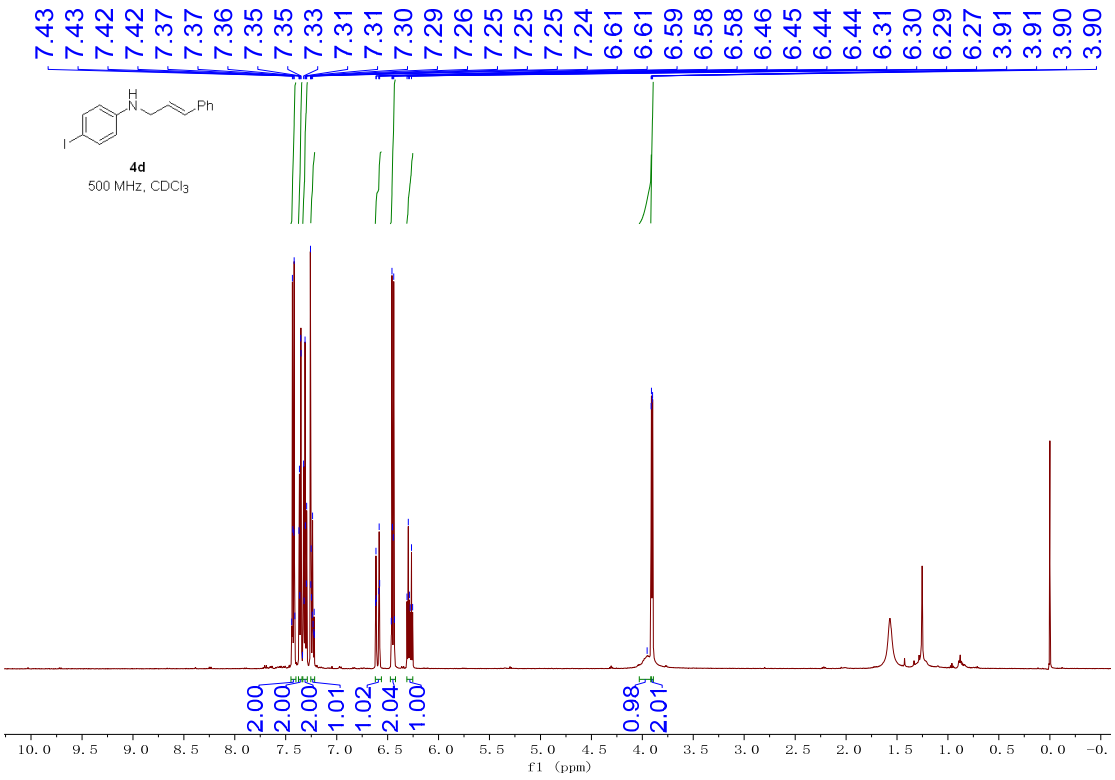

-127.77
H
N
Ph
F
4a
500 MHz, CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

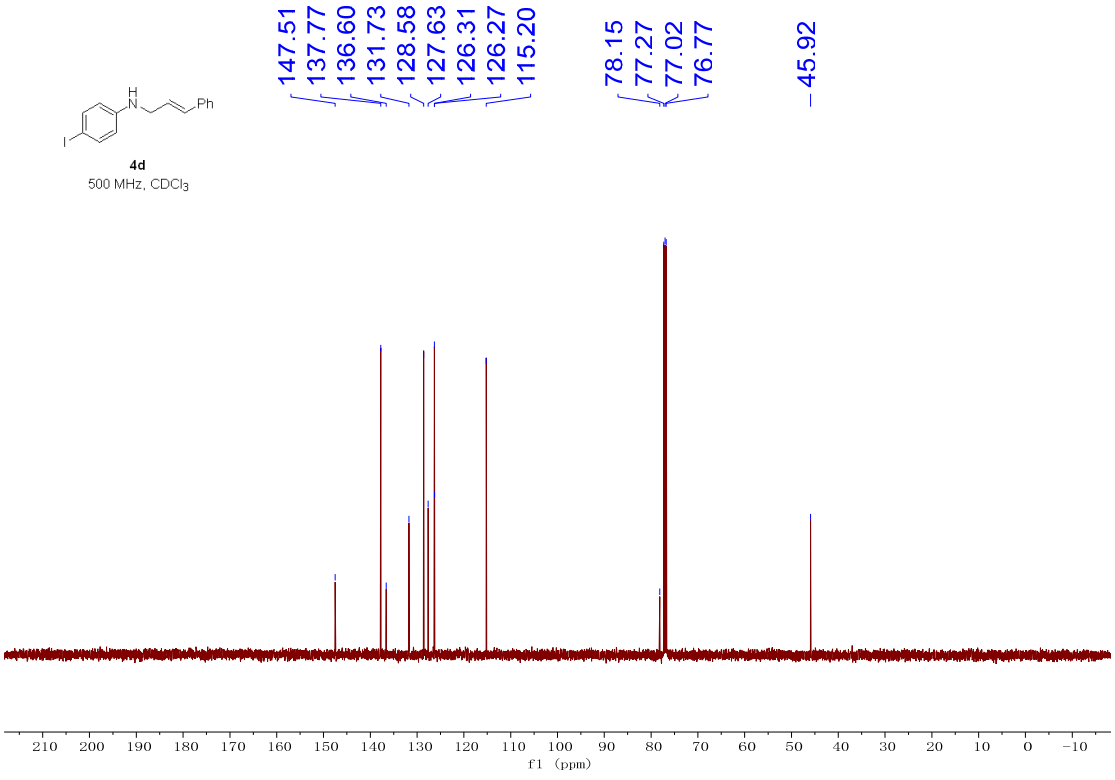

7.37
7.36
7.35
7.35
7.32
7.32
7.31
7.30
7.29
7.29
7.25
7.25
7.24
7.24
7.23
7.13
7.12
7.12
7.11
6.61
6.61
6.61
6.58
6.58
6.57
6.56
6.56
6.31
6.30
6.28
6.26
6.25
3.90
3.90
3.89
3.88
4b
500 MHz, CDCl3
2.00
2.00
1.01
2.00
3.00
1.00
2.00
1.00
f1 (ppm)

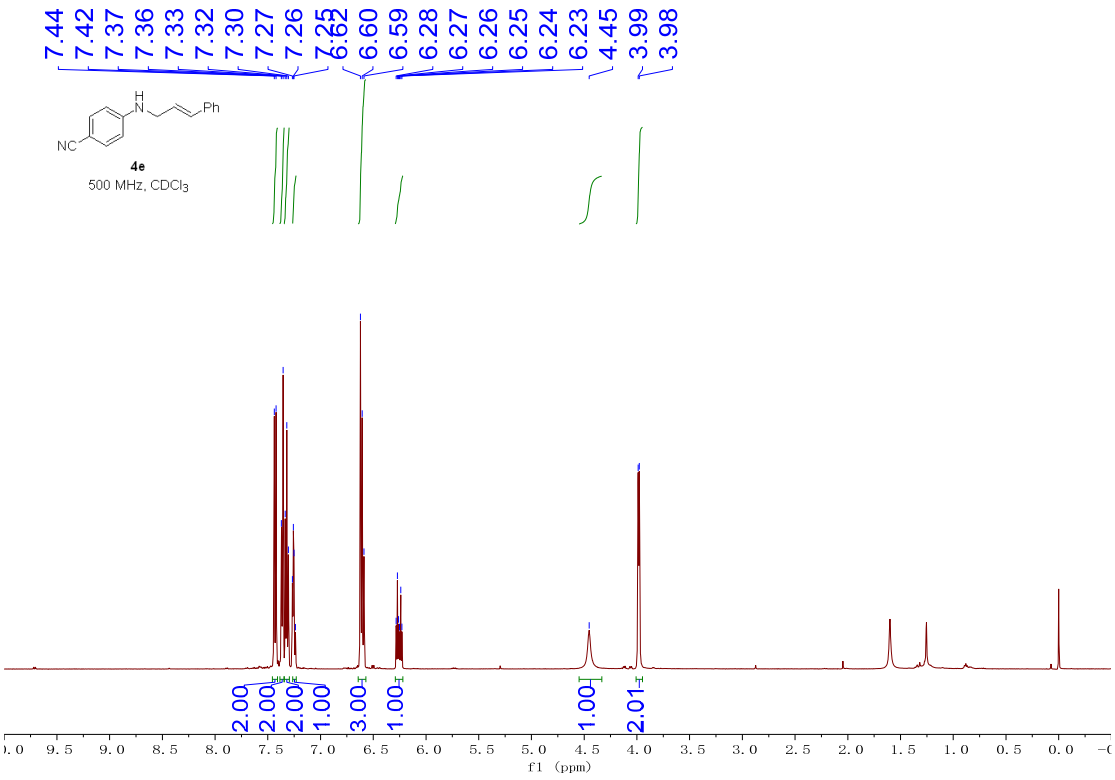

146.49
136.63
131.73
129.05
128.59
127.63
126.40
126.31
122.13
114.09
77.27
77.02
76.77
46.23
4b
500 MHz, CDCl3
f1 (ppm)

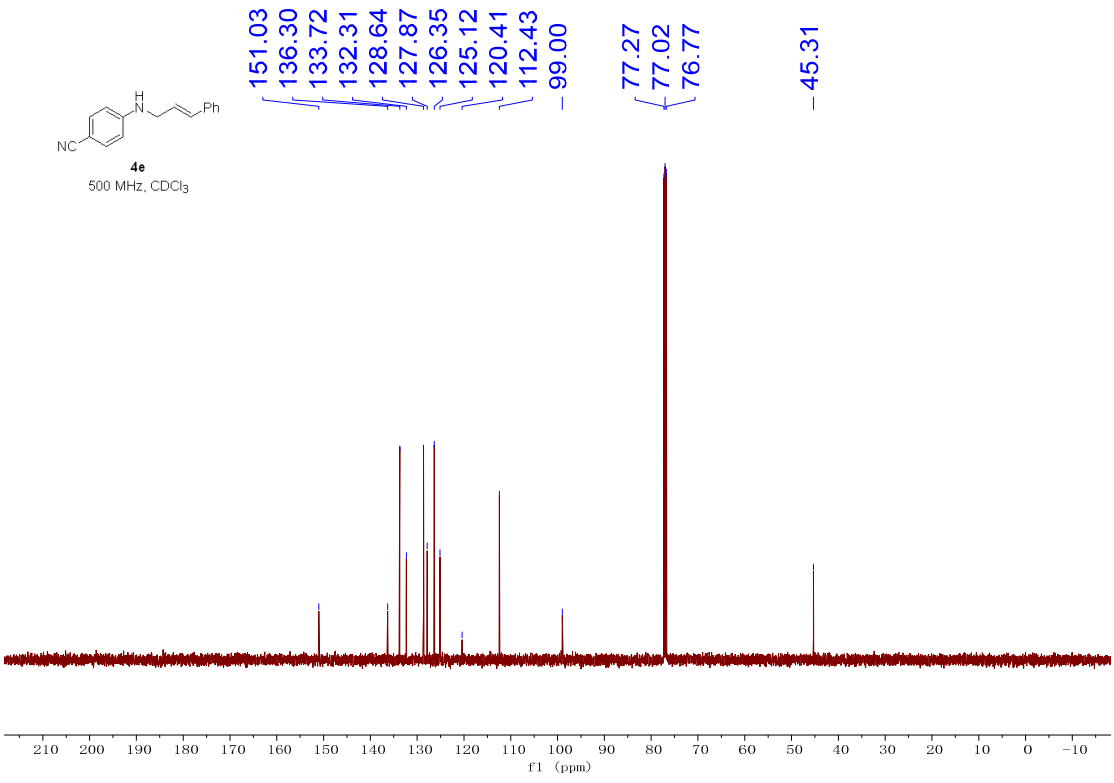

7.37 7.36 7.36 7.35 7.35 7.32 7.32 7.31 7.30 7.29 7.29 7.26 7.25 7.25 7.25 7.24 7.24 7.23 6.61 6.61 6.60 6.58 6.58 6.57 6.53 6.53 6.52 6.52 6.30 6.29 6.28 6.26 3.90 3.89 3.89 3.88
Br
H
N
Ph
4c
500 MHz, CDCl3
2.01 2.00 3.00 1.00 2.00 1.00 2.03 1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

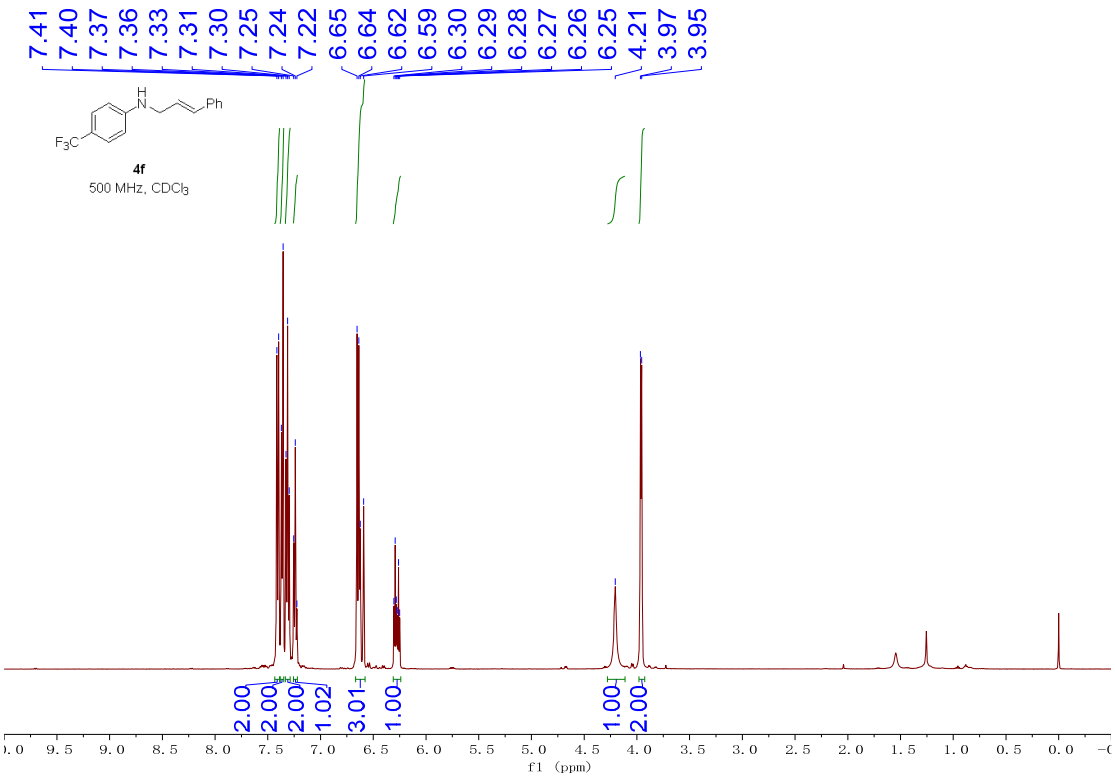

146.91 136.61 131.91 131.73 128.58 127.63 126.32 126.30 114.57 109.14
77.27 77.02 76.77
46.10
Br
H
N
Ph
4c
500 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

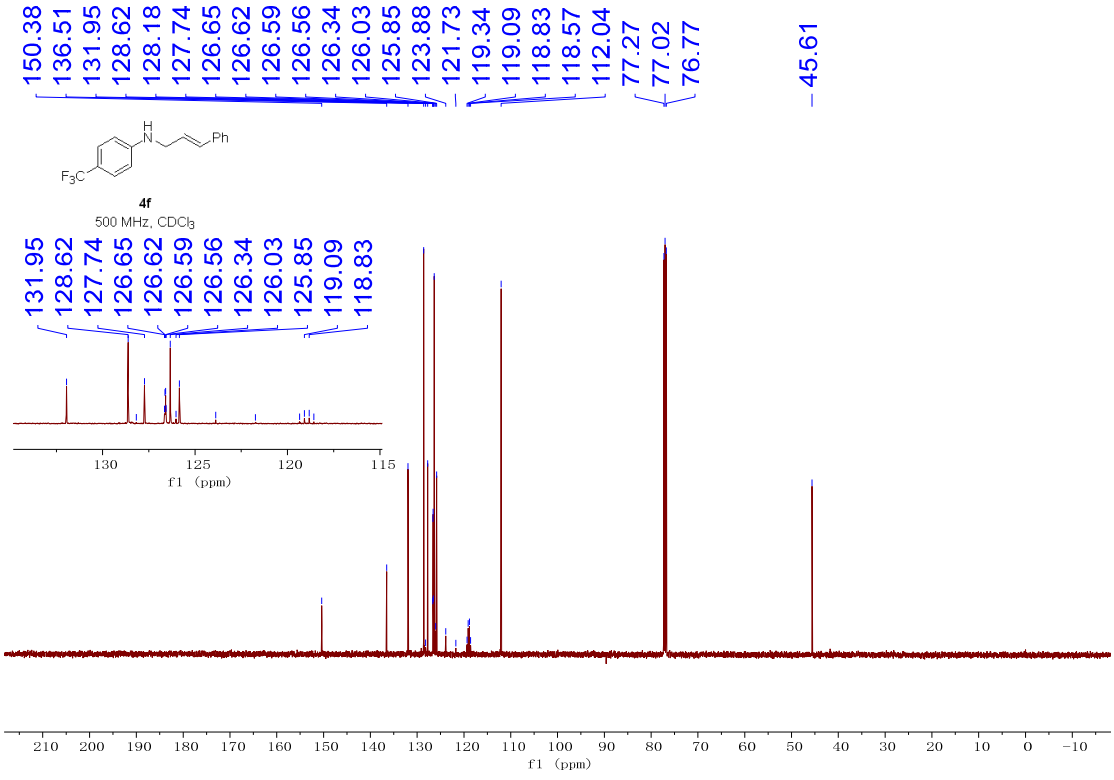

7.43
7.43
7.42
7.42
7.37
7.37
7.36
7.35
7.35
7.33
7.31
7.31
7.30
7.29
7.26
7.25
7.25
7.25
7.24
6.61
6.61
6.59
6.58
6.58
6.46
6.45
6.44
6.44
6.31
6.30
6.29
6.27
3.91
3.91
3.90
3.90
Ph
4d
500 MHz, CDCl3
2.00
2.00
2.00
1.01
1.02
2.04
1.00
0.98
2.01
f1 (ppm)

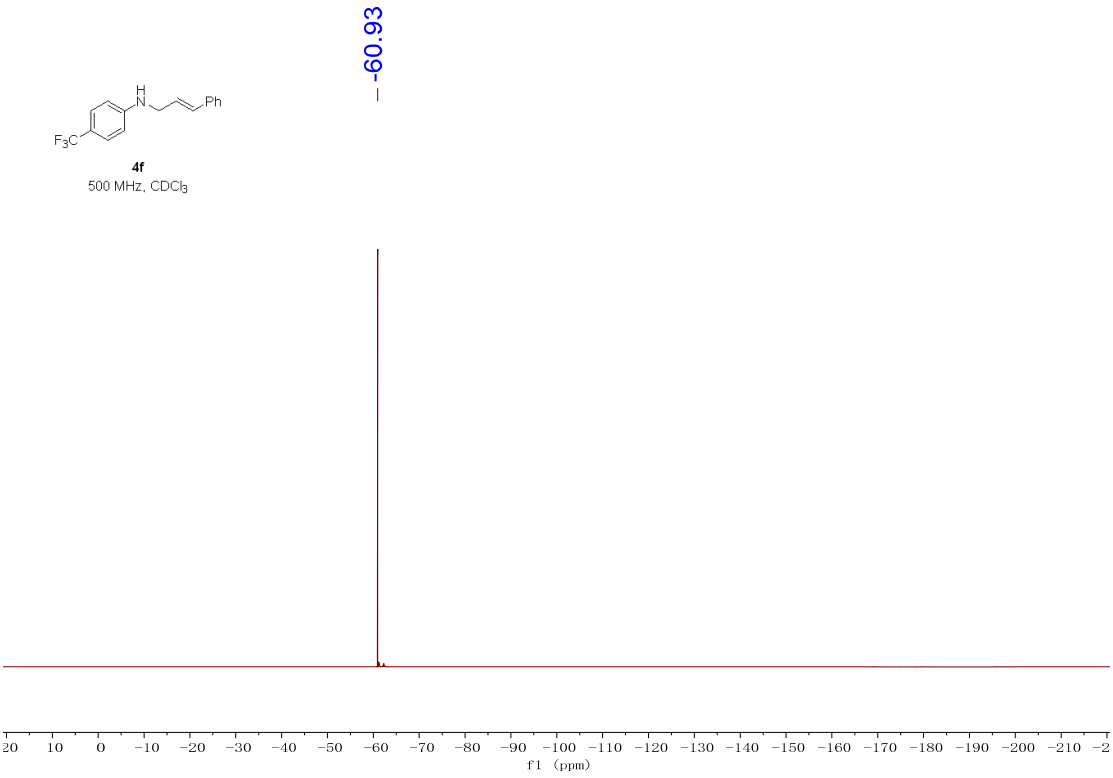

147.51
137.77
136.60
131.73
128.58
127.63
126.31
126.27
115.20
78.15
77.27
77.02
76.77
45.92
Ph
4d
500 MHz, CDCl3
f1 (ppm)

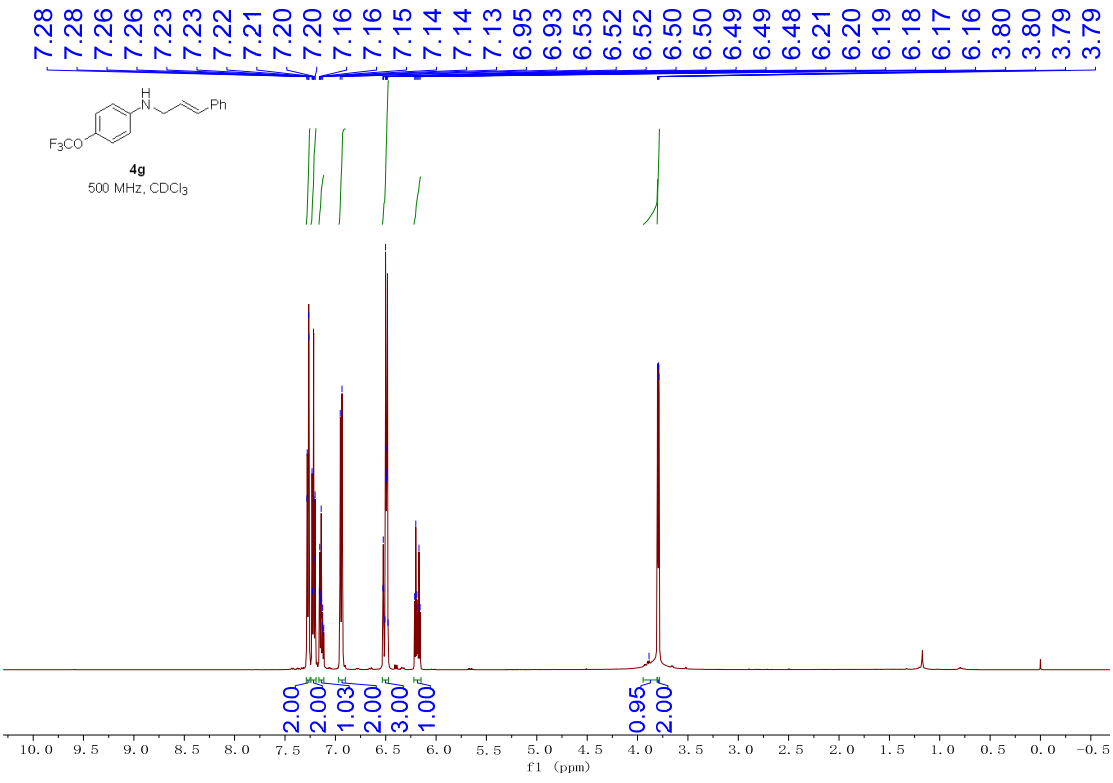

7.44
7.42
7.37
7.36
7.33
7.32
7.30
7.27
7.26
6.62
6.60
6.59
6.28
6.27
6.26
6.25
6.24
6.23
4.45
3.99
3.98
NC
Ph
4e
500 MHz, CDCl3
2.00
2.00
2.00
1.00
3.00
1.00
1.00
2.01
f1 (ppm)

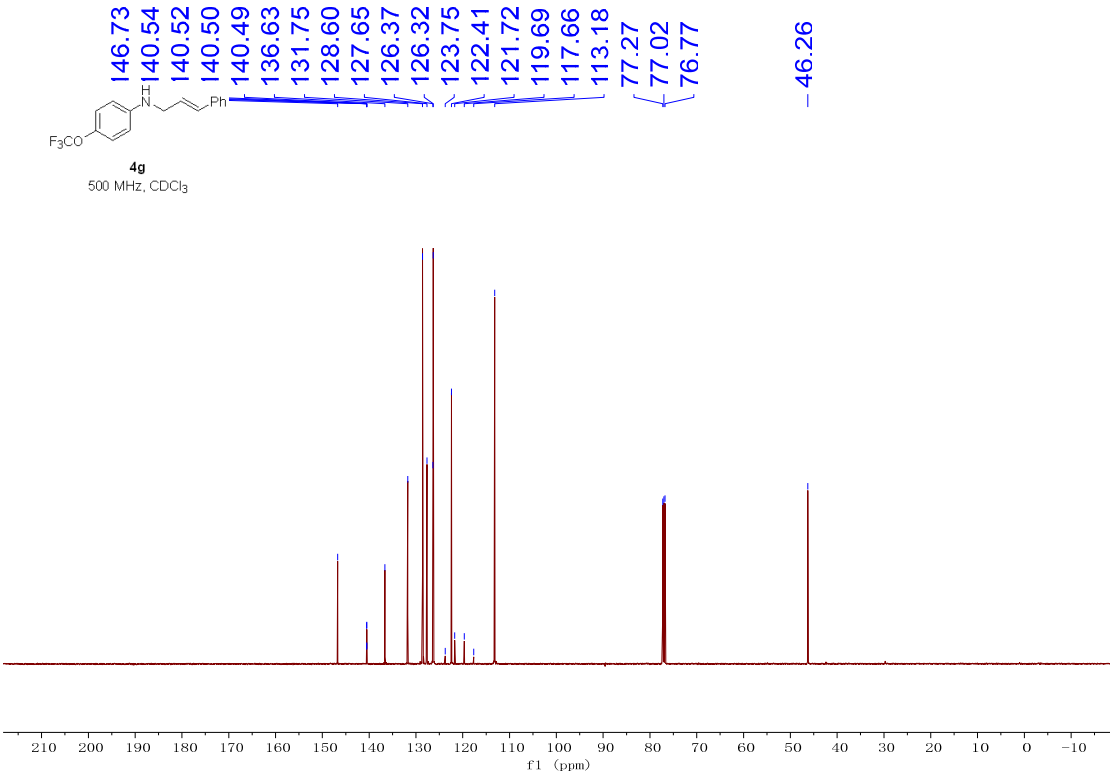

151.03
136.30
133.72
132.31
128.64
127.87
126.35
125.12
120.41
112.43
99.00
77.27
77.02
76.77
45.31
NC
Ph
4e
500 MHz, CDCl3
f1 (ppm)

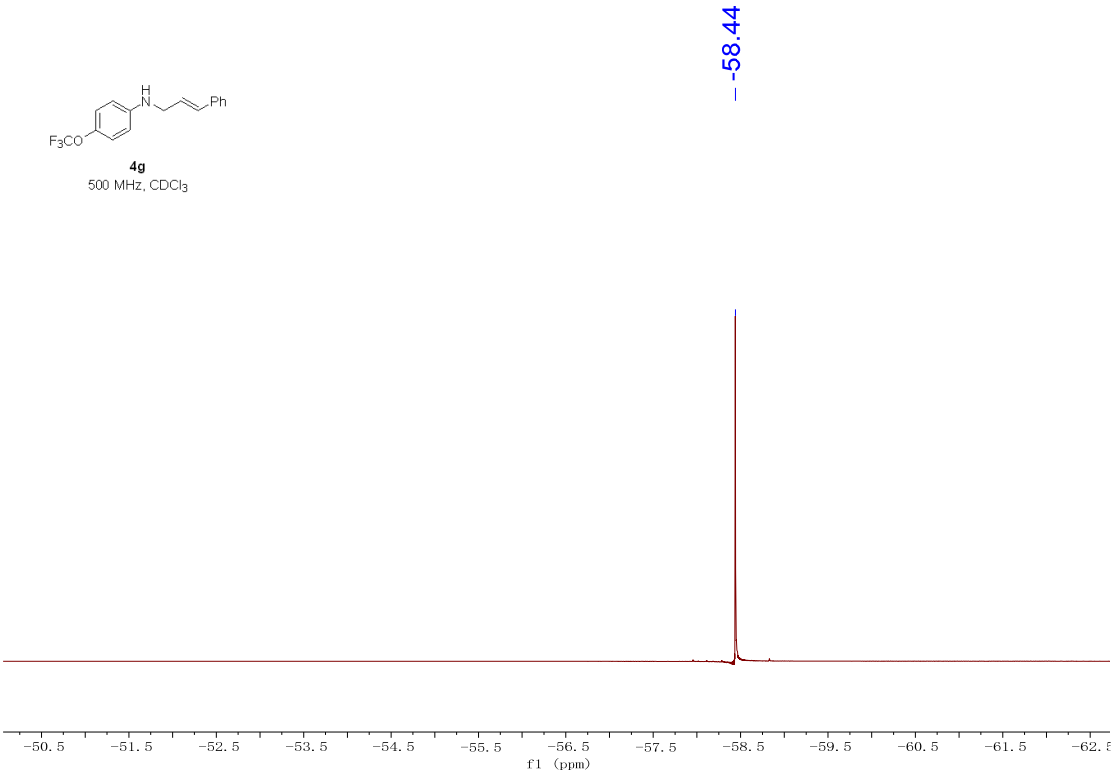

7.41
7.40
7.37
7.36
7.33
7.31
7.30
7.25
7.24
7.22
6.65
6.64
6.62
6.59
6.30
6.29
6.28
6.27
6.26
6.25
4.21
3.97
3.95
4f
500 MHz, CDCl3
2.00
2.00
2.00
1.02
3.01
1.00
1.00
2.00
f1 (ppm)

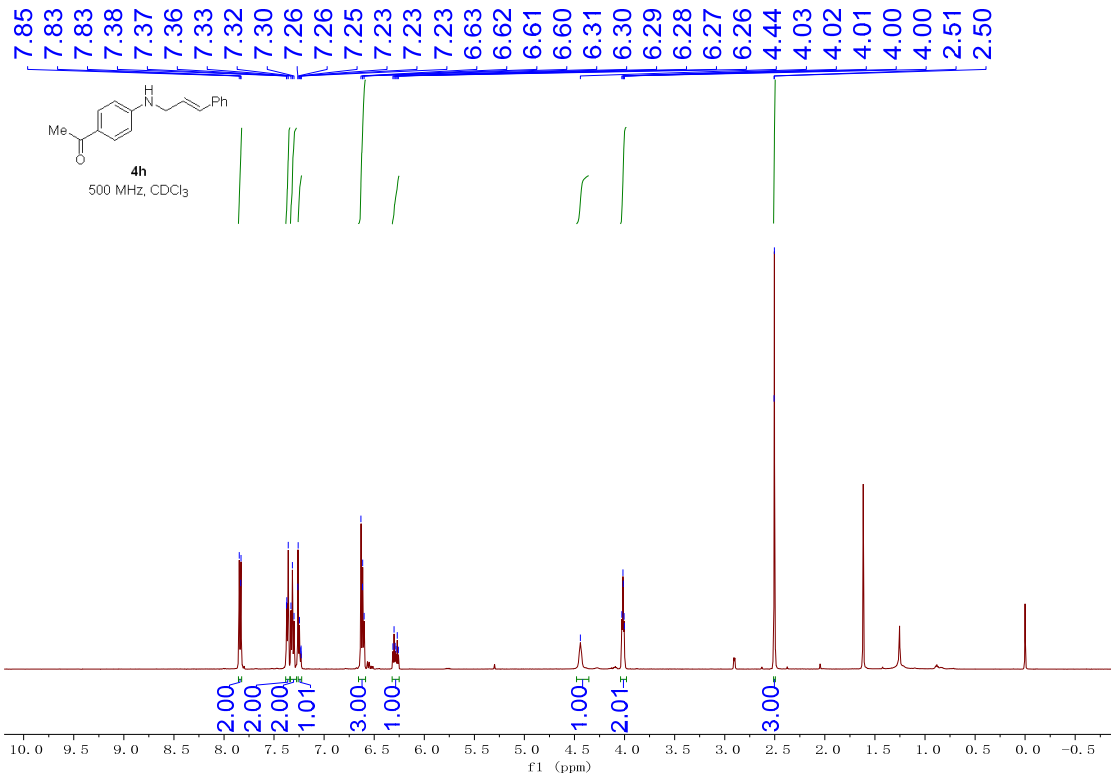

150.38
136.51
131.95
128.62
128.18
127.74
126.65
126.62
126.59
126.56
126.34
126.03
125.85
123.88
121.73
119.34
119.09
118.83
118.57
112.04
77.27
77.02
76.77
45.61
4f
500 MHz, CDCl3
131.95
128.62
127.74
126.65
126.62
126.59
126.56
126.34
126.03
125.85
119.09
118.83
f1 (ppm)
f1 (ppm)

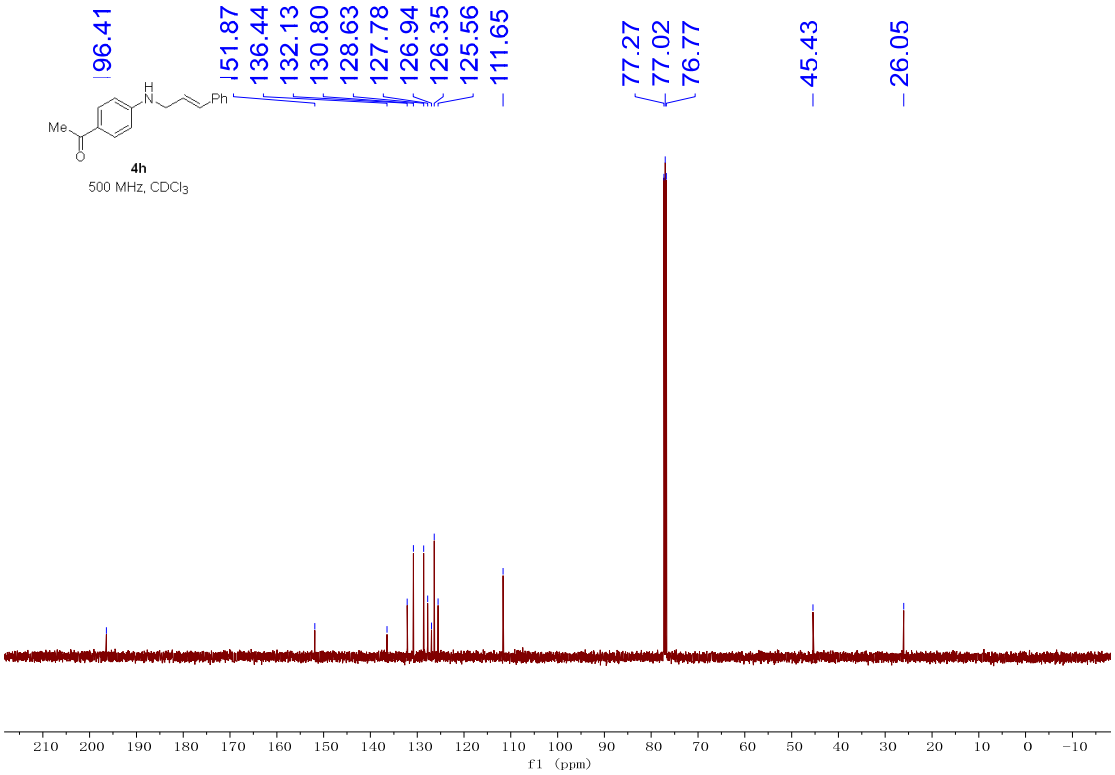

-60.93
4f
500 MHz, CDCl3
f1 (ppm)

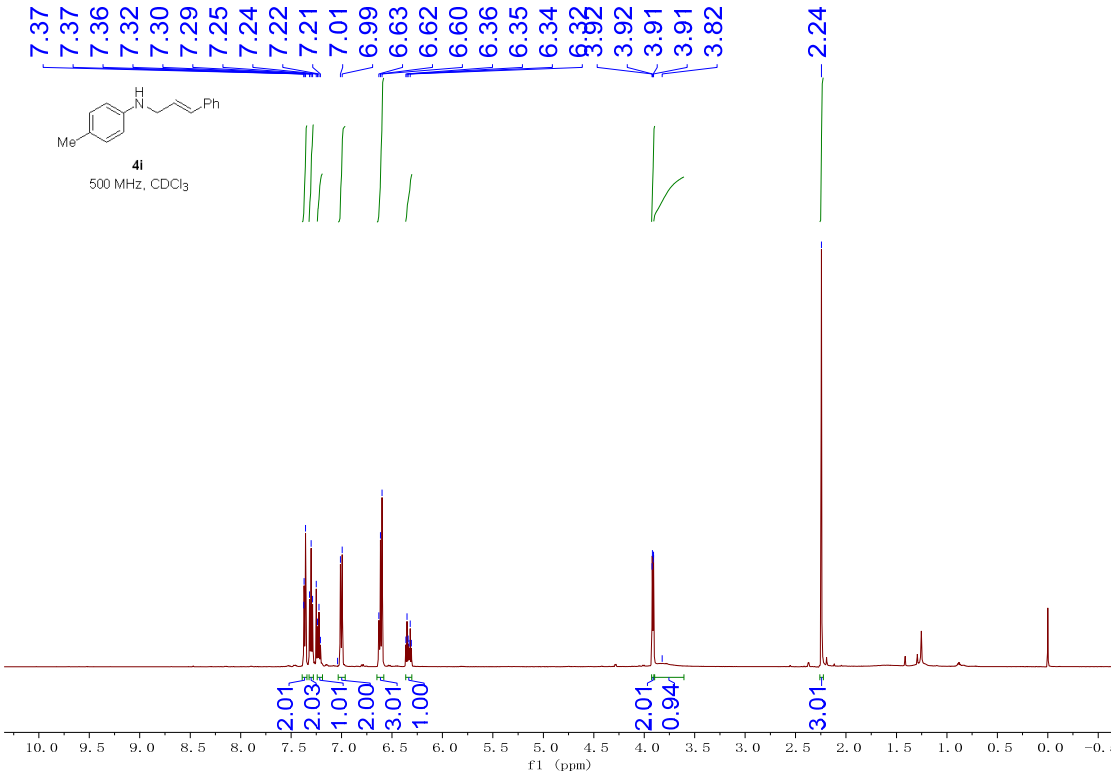

7.28 7.28 7.26 7.26 7.23 7.23 7.22 7.21 7.20 7.20 7.16 7.16 7.15 7.14 7.14 7.13 6.95 6.93 6.53 6.52 6.52 6.50 6.50 6.49 6.49 6.48 6.21 6.20 6.19 6.18 6.17 6.16 3.80 3.80 3.79 3.79
4g
500 MHz, CDCl3
2.00 2.00 1.03 2.00 3.00 1.00 0.95 2.00
f1 (ppm)

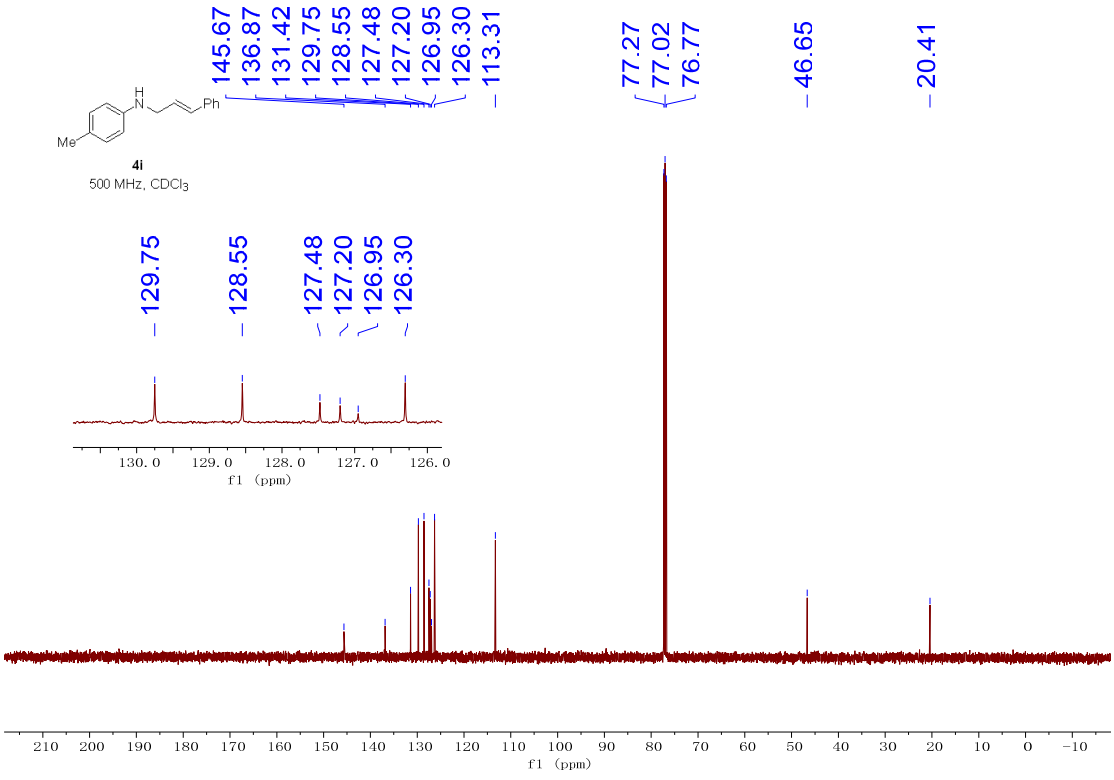

146.73
140.54
140.52
140.50
140.49
136.63
131.75
128.60
127.65
126.37
126.32
123.75
122.41
121.72
119.69
117.66
113.18
77.27
77.02
76.77
46.26
F3CO
Ph
4g
500 MHz, CDCl3
f1 (ppm)

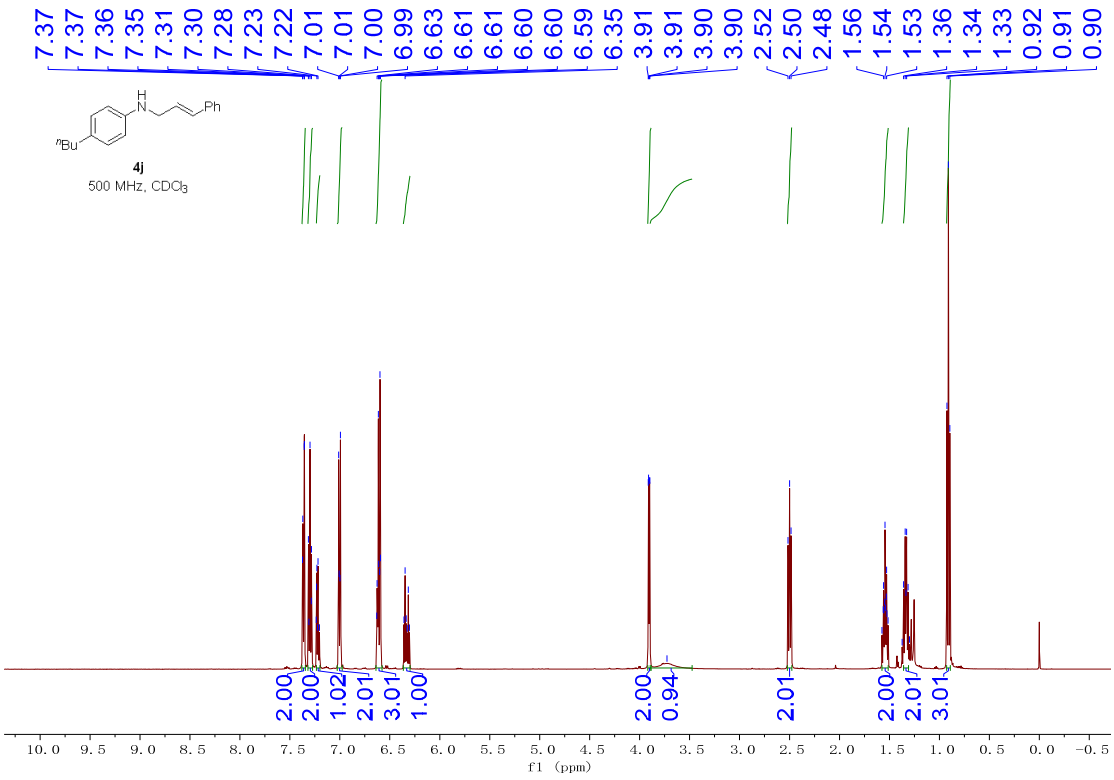

-58.44
F3CO
Ph
4g
500 MHz, CDCl3
f1 (ppm)

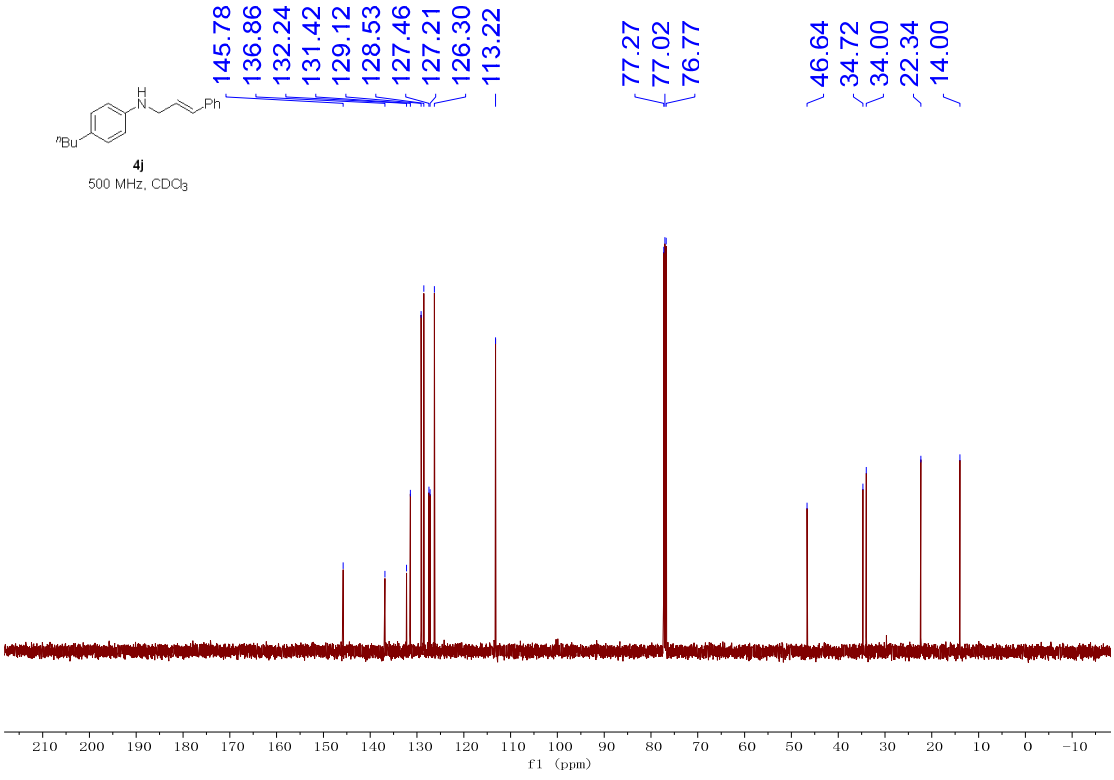

7.85
7.83
7.83
7.38
7.37
7.36
7.33
7.32
7.30
7.26
7.26
7.25
7.23
7.23
7.23
6.63
6.62
6.61
6.60
6.31
6.30
6.29
6.28
6.27
6.26
4.44
4.03
4.02
4.01
4.00
4.00
2.51
2.50
Me
Ph
4h
500 MHz, CDCl3
2.00
2.00
2.00
1.01
3.00
1.00
1.00
2.01
3.00
f1 (ppm)


196.41
151.87
136.44
132.13
130.80
128.63
127.78
126.94
126.35
125.56
111.65
77.27
77.02
76.77
45.43
26.05
Me
Ph
4h
500 MHz, CDCl3
f1 (ppm)


7.37
7.37
7.36
7.32
7.30
7.29
7.25
7.24
7.22
7.21
7.01
6.99
6.63
6.62
6.60
6.36
6.35
6.34
3.92
3.91
3.91
3.82
2.24
Me
Ph
4i
500 MHz, CDCl3
2.01
2.03
1.01
2.00
3.01
1.00
2.01
0.94
3.01
f1 (ppm)


145.67
136.87
131.42
129.75
128.55
127.48
127.20
126.95
126.30
113.31
77.27
77.02
76.77
46.65
20.41
Me
Ph
4i
500 MHz, CDCl3
129.75
128.55
127.48
127.20
126.95
126.30
f1 (ppm)


7.37
7.37
7.36
7.35
7.31
7.30
7.28
7.23
7.22
7.01
7.01
7.00
6.99
6.63
6.61
6.61
6.60
6.60
6.59
6.35
3.91
3.91
3.90
3.90
2.52
2.50
2.48
1.56
1.54
1.53
1.36
1.34
1.33
0.92
0.91
0.90
Ph
nBu
4j
500 MHz, CDCl3
2.00
2.00
1.02
2.01
3.01
1.00
2.00
0.94
2.01
2.00
2.01
3.01
f1 (ppm)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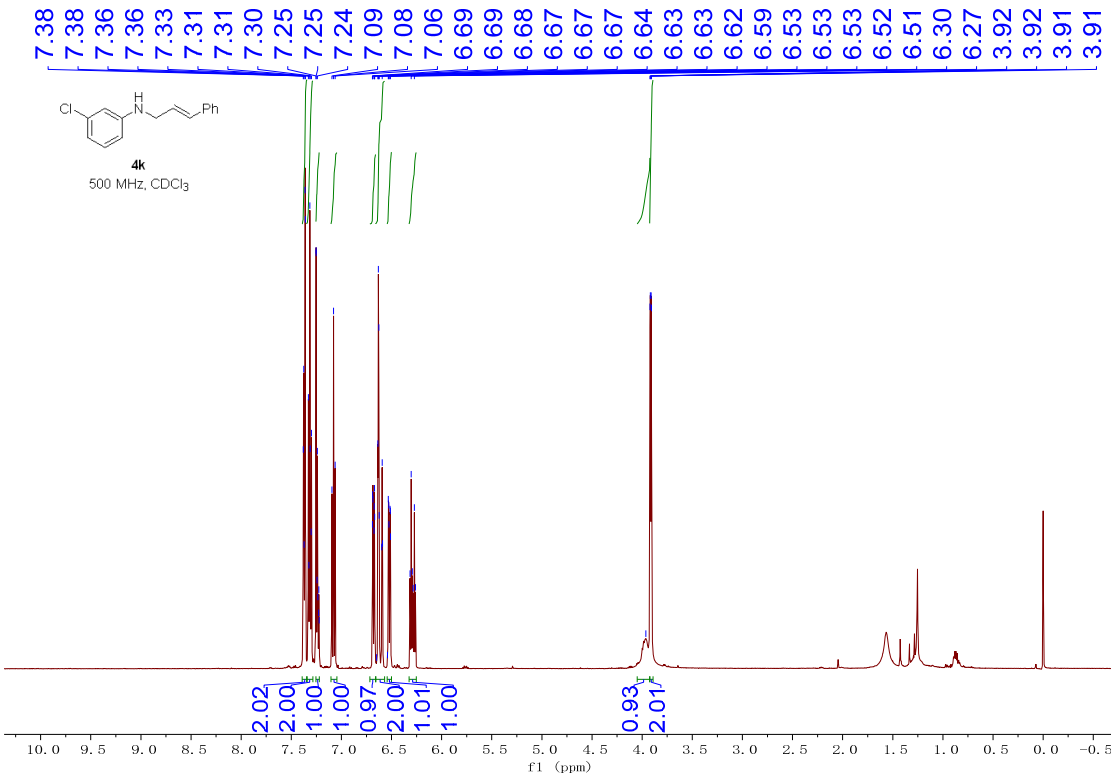
136.86
132.24
131.42
129.12
128.53
127.46
127.21
126.30
113.22
77.27
77.02
76.77
46.64
34.72
34.00
22.34
14.00
Ph
nBu
4j
500 MHz, CDCl3
f1 (ppm)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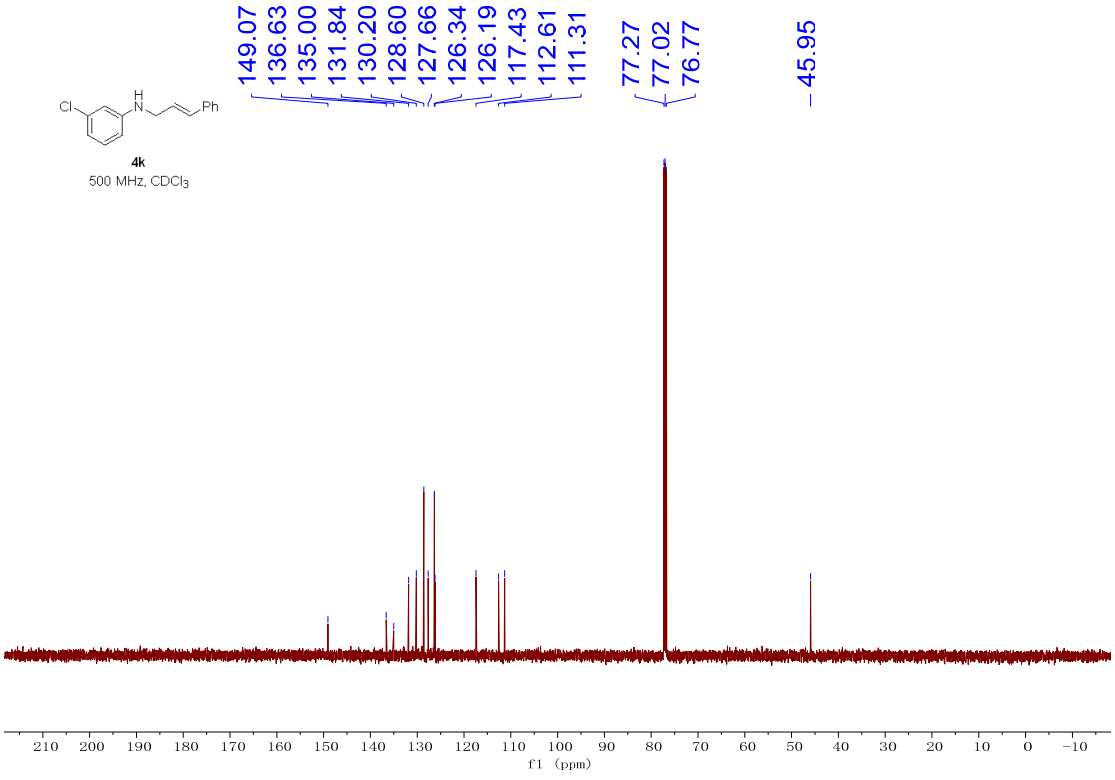
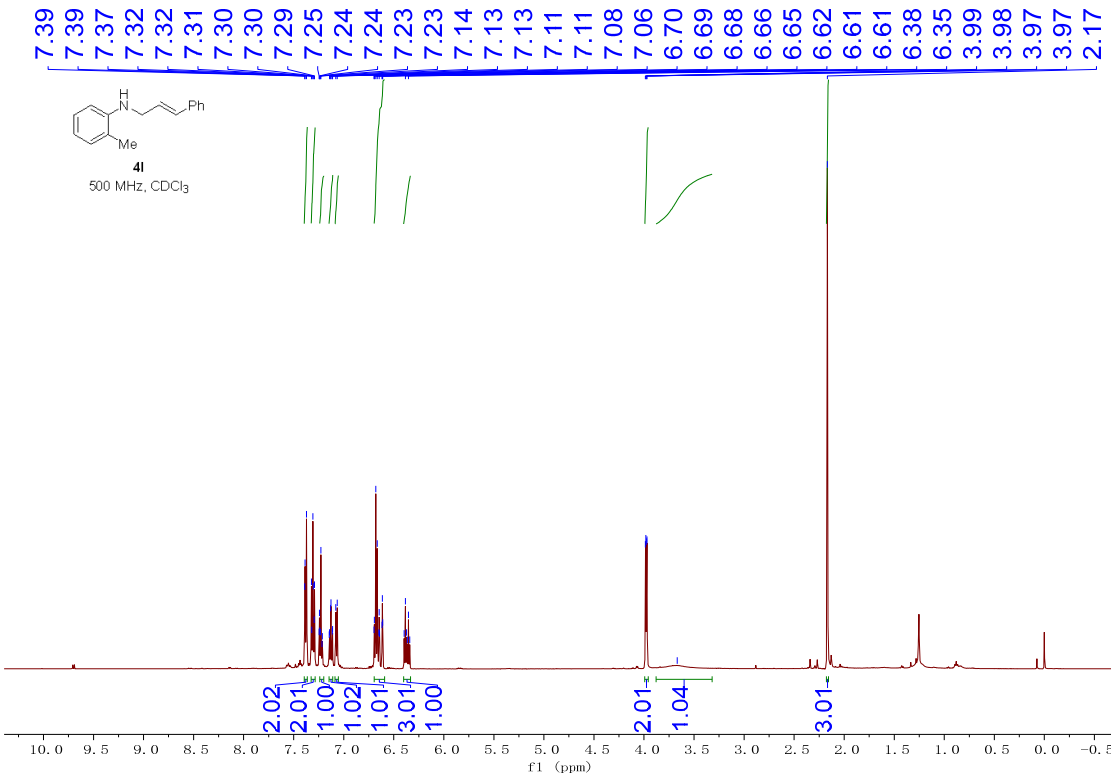
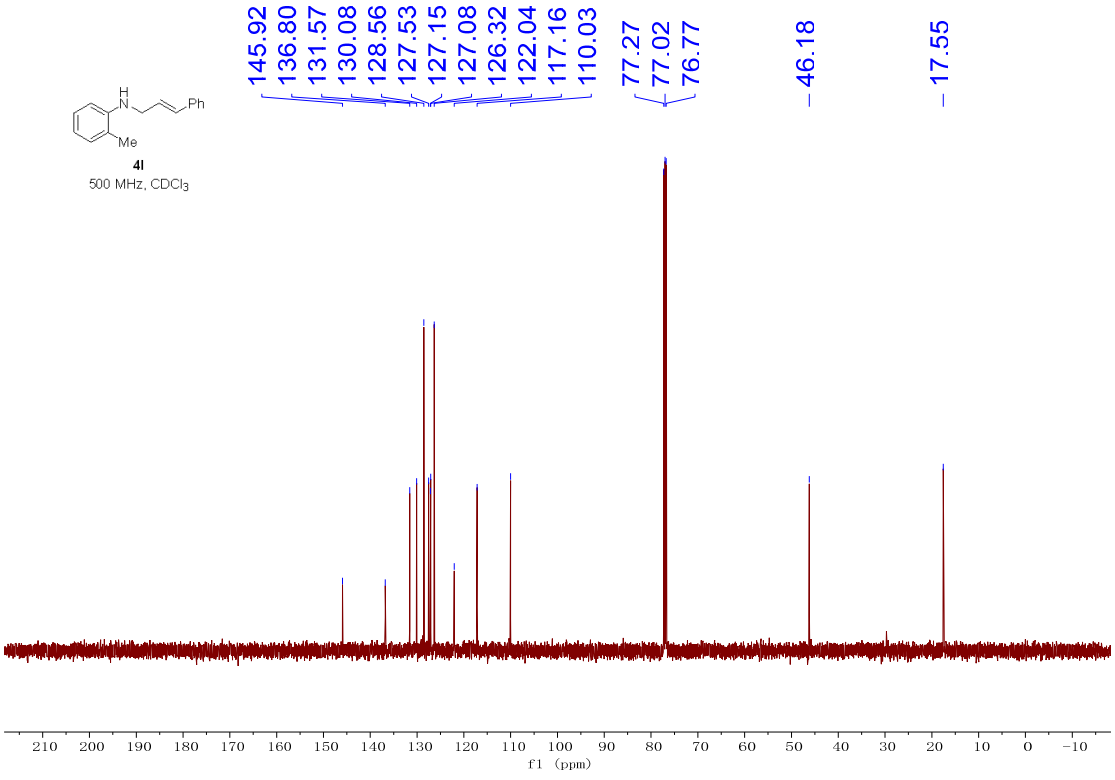
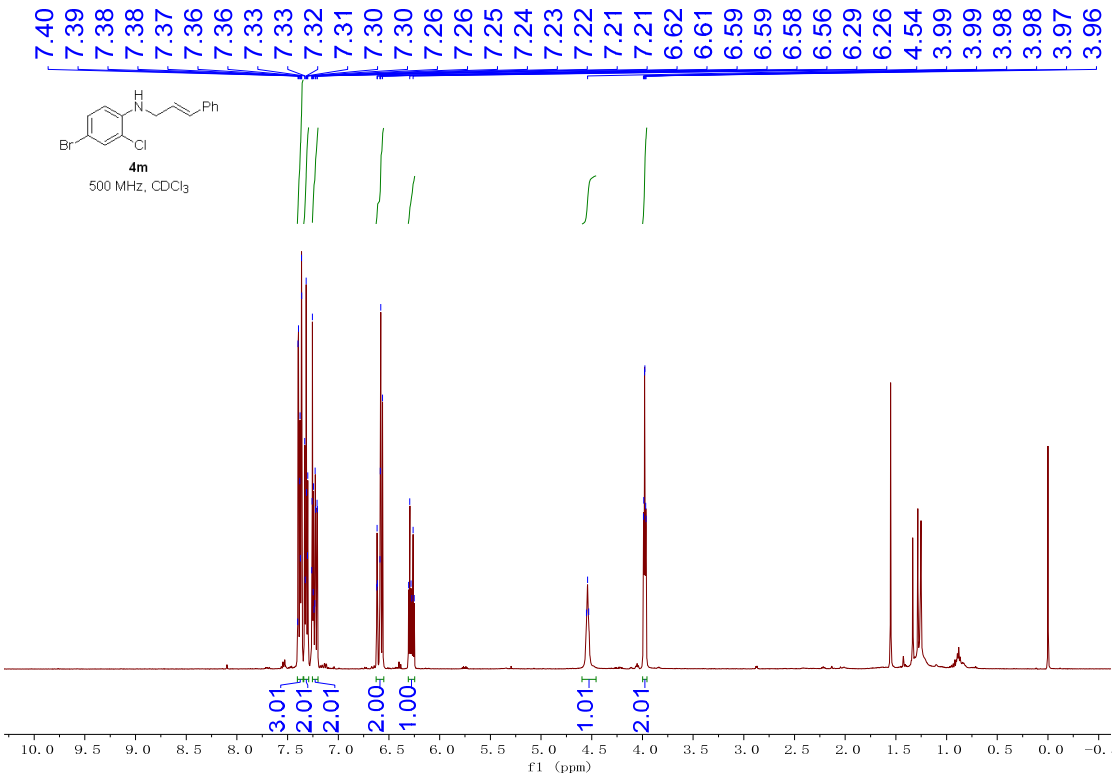
7.38
7.36
7.36
7.33
7.31
7.31
7.30
7.25
7.25
7.24
7.09
7.08
7.06
6.69
6.69
6.68
6.67
6.67
6.67
6.64
6.63
6.63
6.62
6.59
6.53
6.53
6.53
6.52
6.51
6.30
6.27
3.92
3.92
3.91
3.91
Cl
H
N
Ph
4k
500 MHz, CDCl3
2.02
2.00
1.00
1.00
0.97
2.00
1.01
1.00
0.93
2.01
f1 (ppm)


149.07
136.63
135.00
131.84
130.20
128.60
127.66
126.34
126.19
117.43
112.61
111.31
77.27
77.02
76.77
45.95
Cl
H
N
Ph
4k
500 MHz, CDCl3
f1 (ppm)


7.39 7.39 7.37 7.32 7.32 7.31 7.30 7.30 7.29 7.25 7.24 7.24 7.23 7.23 7.14 7.13 7.13 7.11 7.11 7.08 7.06 6.70 6.69 6.68 6.66 6.65 6.62 6.61 6.61 6.38 6.35 3.99 3.98 3.97 3.97 2.17
H
N
Ph
Me
4l
500 MHz, CDCl3
2.02 2.01 1.00 1.02 1.01 3.01 1.00 2.01 1.04 3.01
f1 (ppm)


145.92 136.80 131.57 130.08 128.56 127.53 127.15 127.08 126.32 122.04 117.16 110.03 77.27 77.02 76.77 46.18 17.55
H
N
Ph
Me
4l
500 MHz, CDCl3
f1 (ppm)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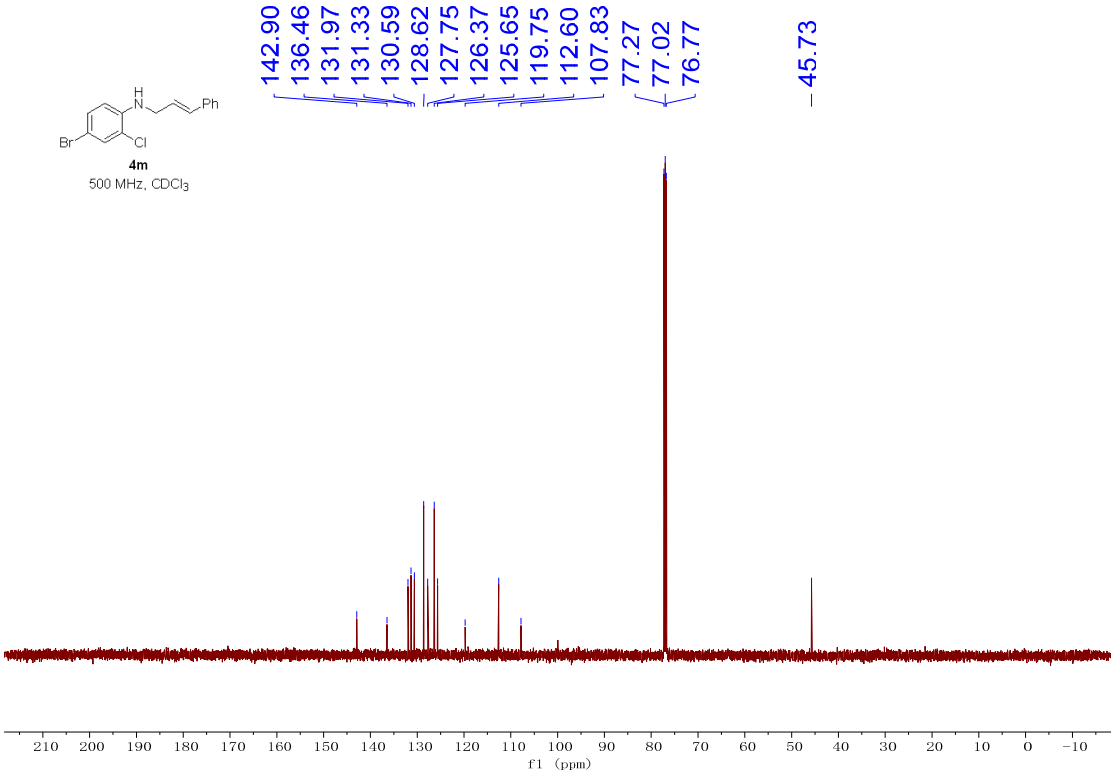
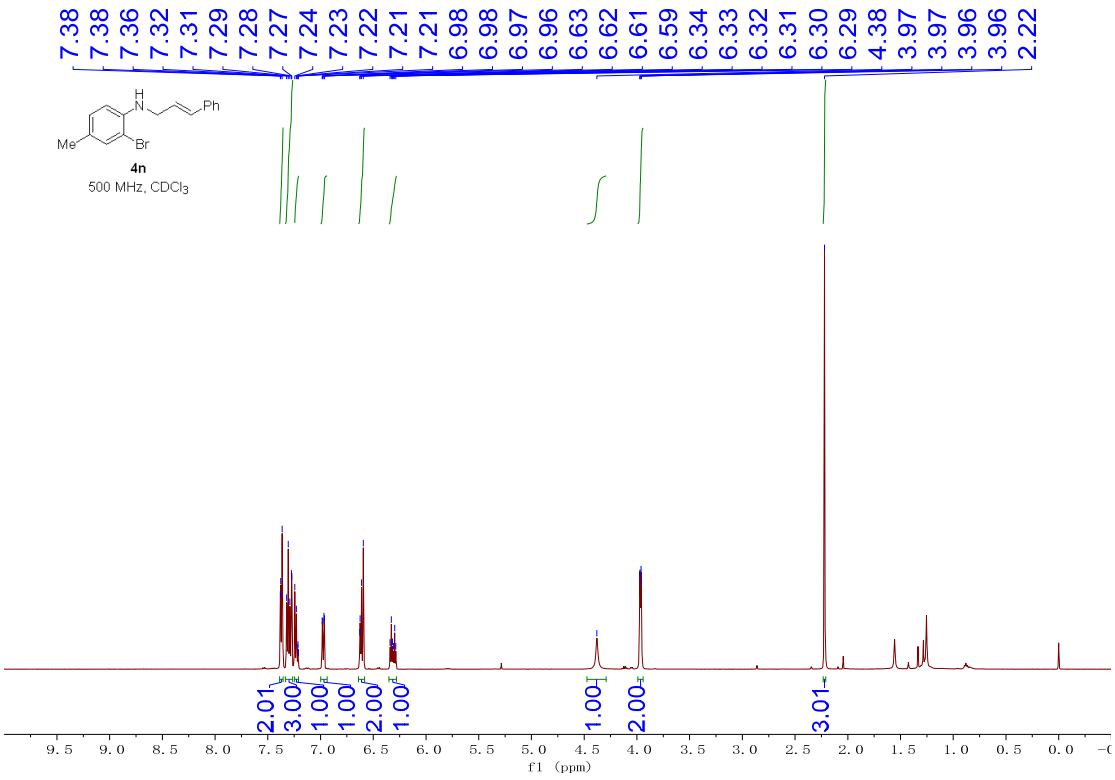
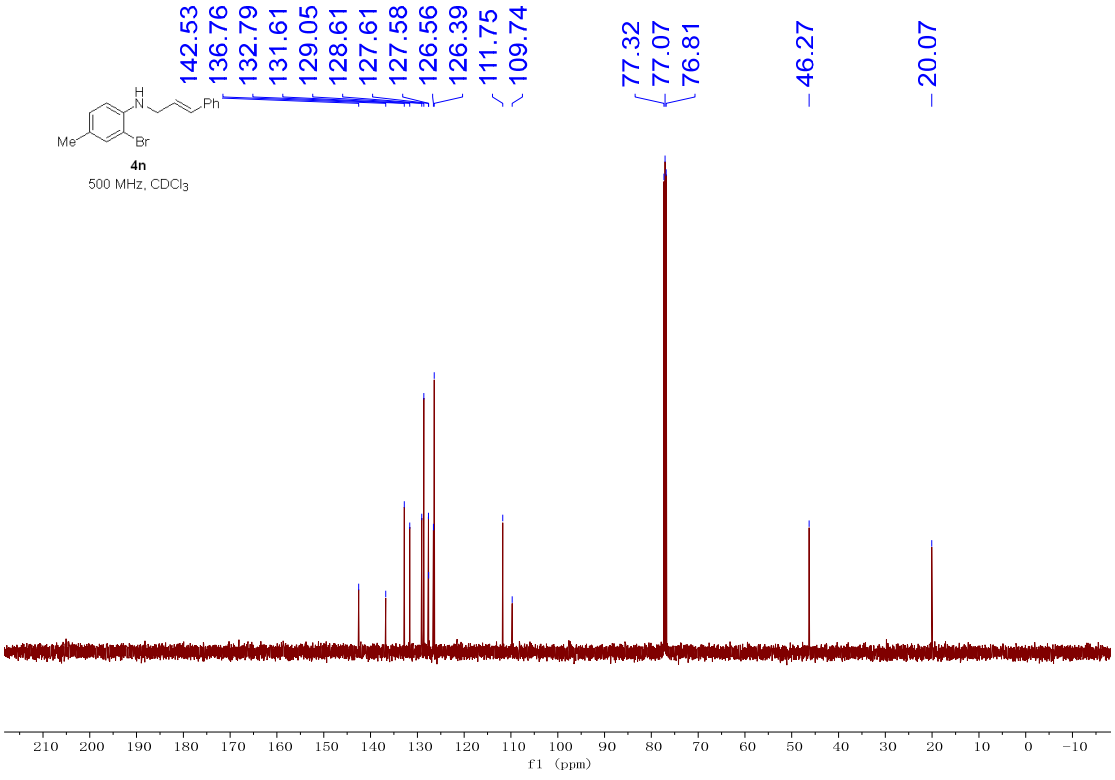
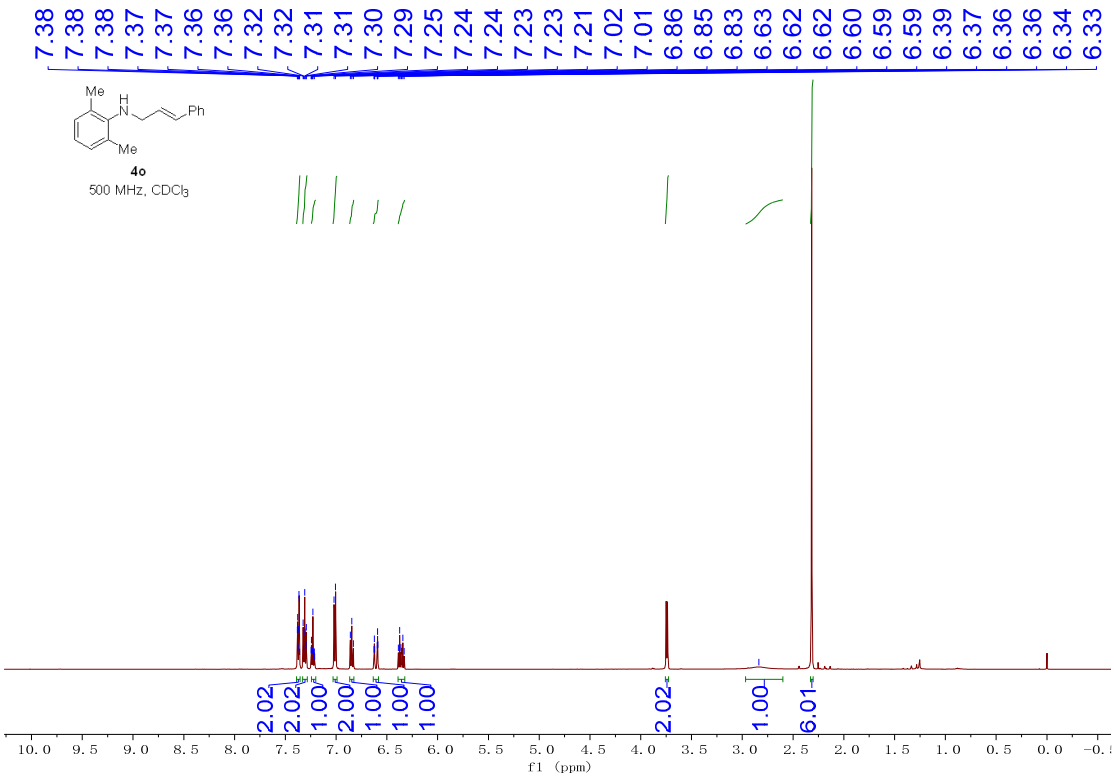
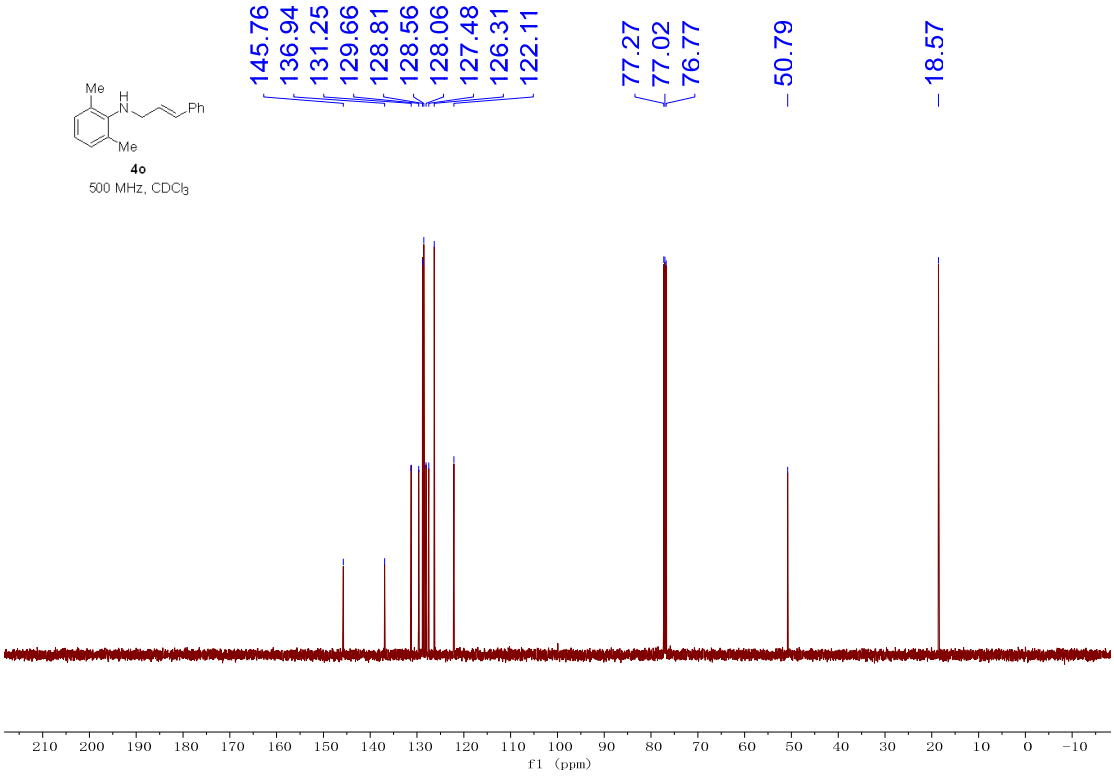
7.39
7.38
7.38
7.37
7.36
7.36
7.33
7.33
7.32
7.31
7.30
7.30
7.26
7.26
7.25
7.24
7.23
7.22
7.21
7.21
6.62
6.61
6.59
6.59
6.58
6.56
6.29
6.26
4.54
3.99
3.99
3.98
3.98
3.97
3.96
H
N
Ph
Br
Cl
4m
500 MHz, CDCl3
3.01
2.01
2.01
2.00
1.00
1.01
2.01
f1 (ppm)

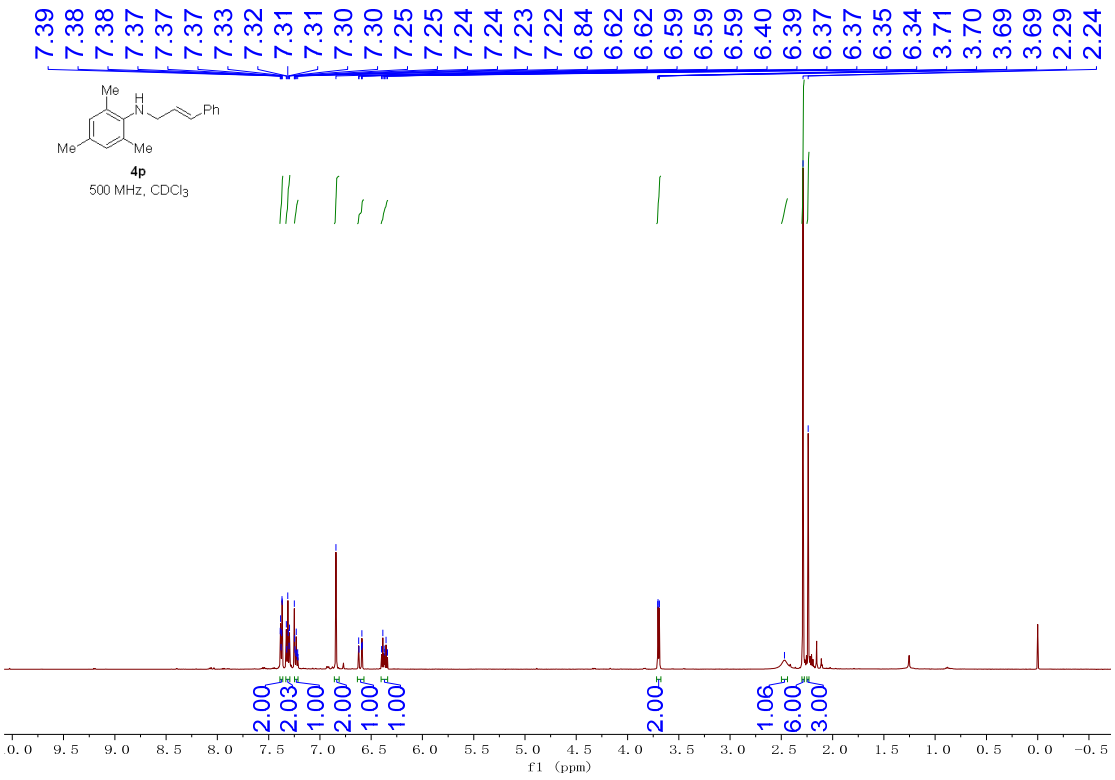

142.90
136.46
131.97
131.33
130.59
128.62
127.75
126.37
125.65
119.75
112.60
107.83
77.27
77.02
76.77
45.73
H
N
Ph
Br
Cl
4m
500 MHz, CDCl3
f1 (ppm)

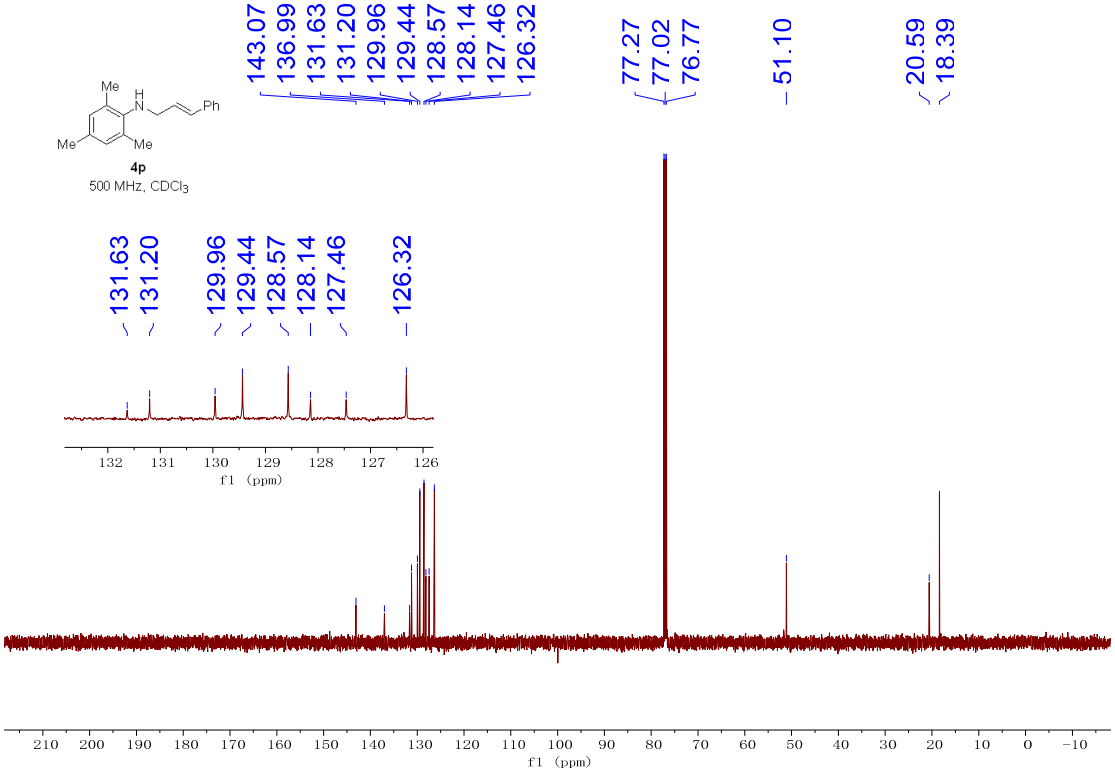

7.38
7.38
7.36
7.32
7.31
7.29
7.28
7.27
7.24
7.23
7.22
7.21
7.21
6.98
6.98
6.97
6.96
6.63
6.62
6.61
6.59
6.34
6.33
6.32
6.31
6.30
6.29
4.38
3.97
3.97
3.96
3.96
2.22
Me
Br
Ph
4n
500 MHz, CDCl3
2.01
3.00
1.00
1.00
2.00
1.00
1.00
2.00
3.01
f1 (ppm)

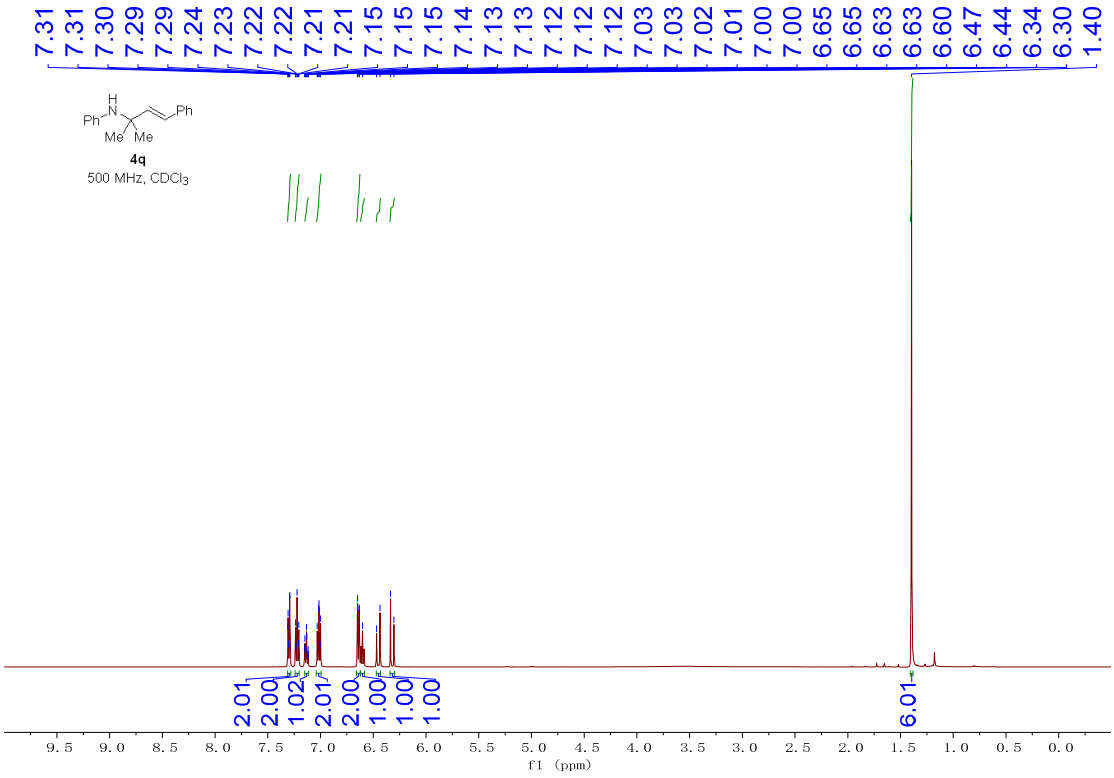

142.53
136.76
132.79
131.61
129.05
128.61
127.61
127.58
126.56
126.39
111.75
109.74
77.32
77.07
76.81
46.27
20.07
Me
Br
Ph
4n
500 MHz, CDCl3
f1 (ppm)

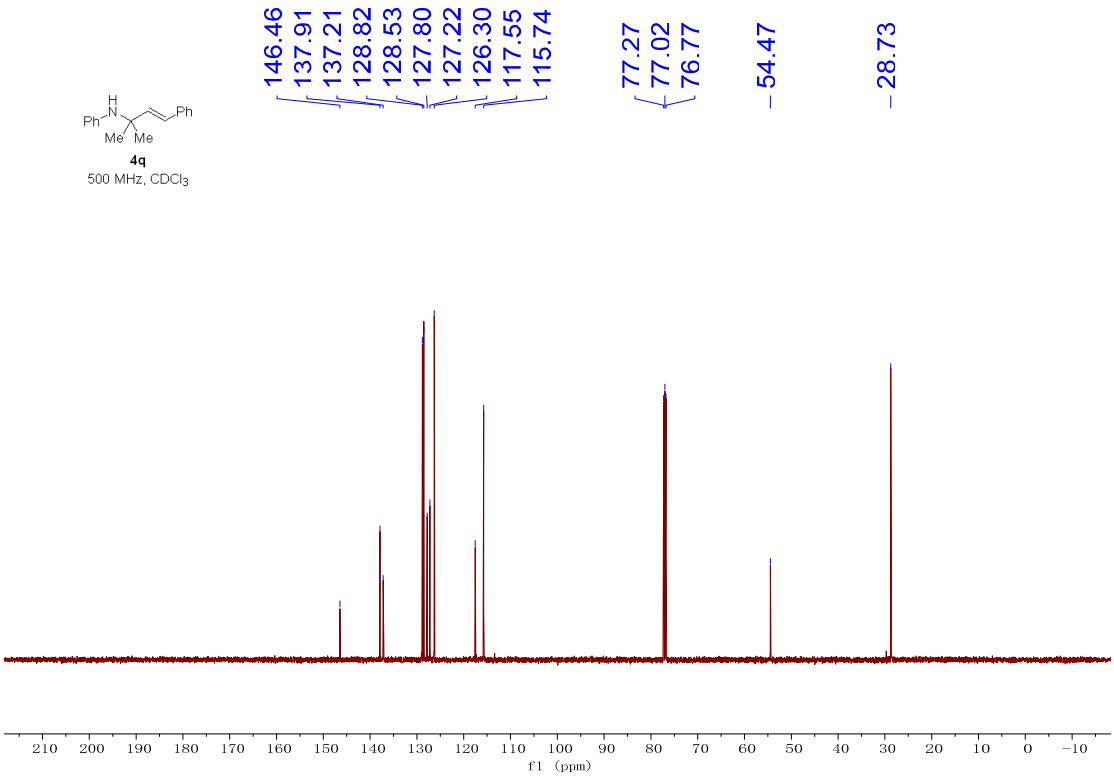

7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.32 7.32 7.31 7.31 7.30 7.29 7.25 7.24 7.24 7.23 7.23 7.21 7.02 7.01 6.86 6.85 6.83 6.63 6.62 6.62 6.60 6.59 6.59 6.39 6.37 6.36 6.36 6.34 6.33
Me
H
N
Ph
Me
4o
500 MHz, CDCl3
2.02 2.02 1.00 2.00 1.00 1.00 1.00 2.02 1.00 6.01
f1 (ppm)

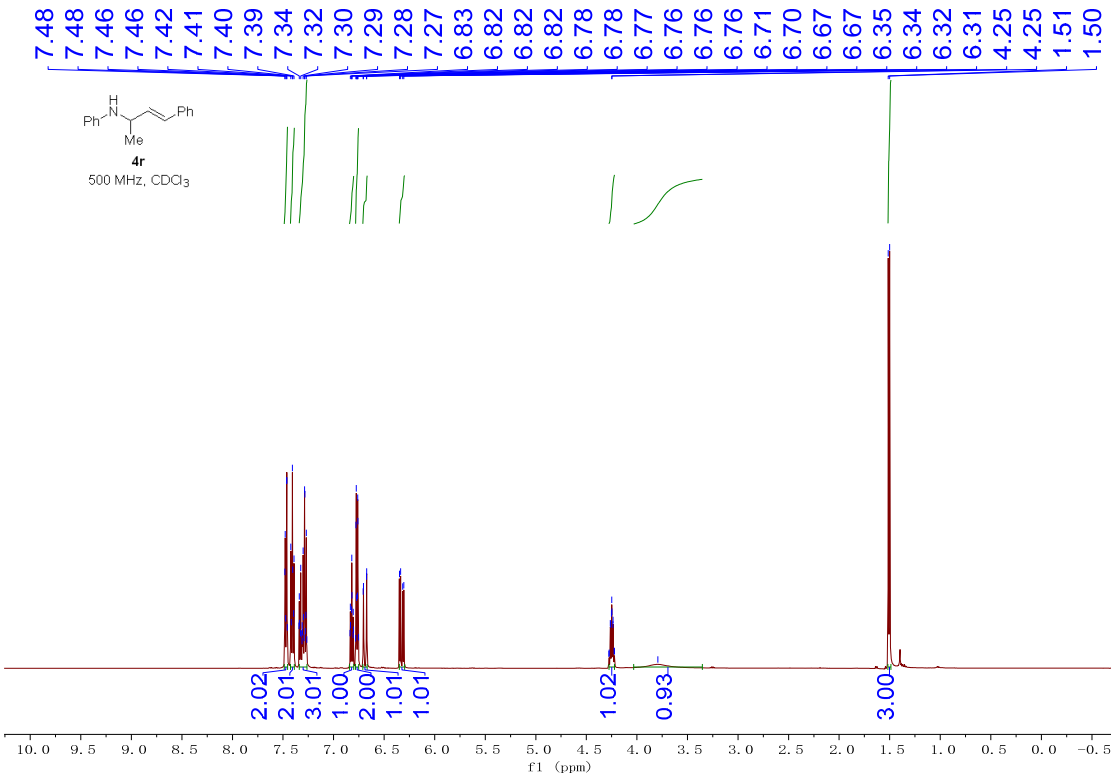

145.76 136.94 131.25 129.66 128.81 128.56 128.06 127.48 126.31 122.11 77.27 77.02 76.77 50.79 18.57
Me
H
N
Ph
Me
4o
500 MHz, CDCl3
f1 (ppm)

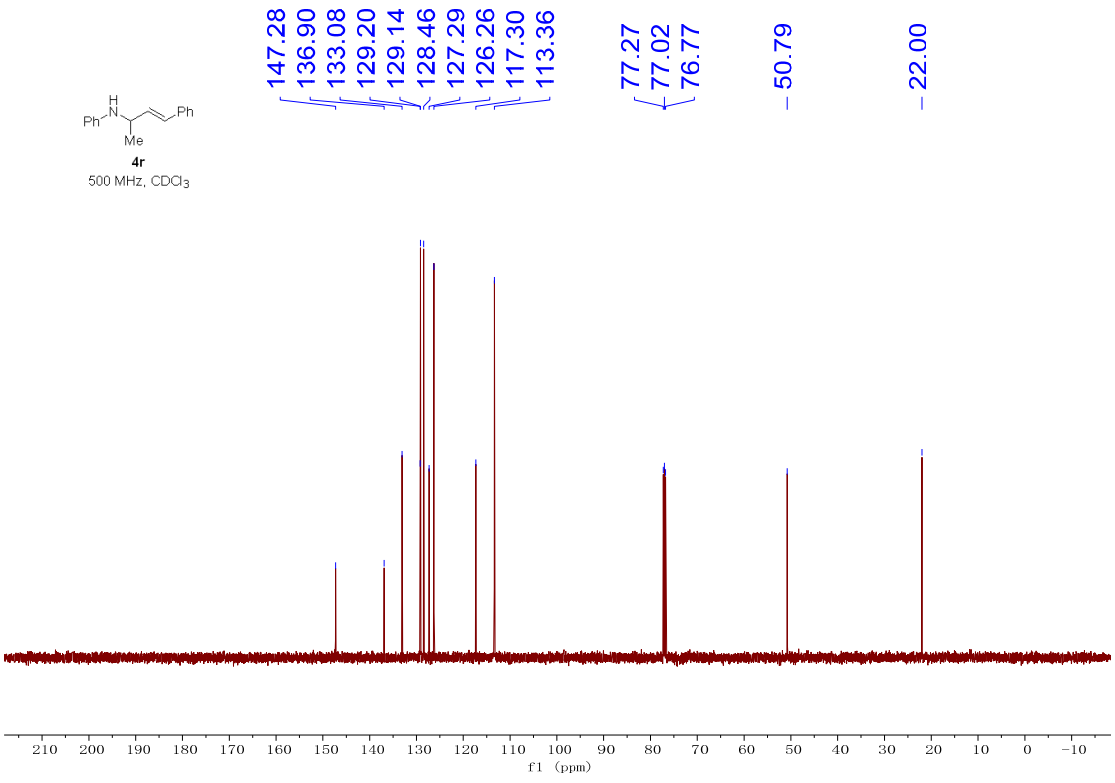

7.39 7.38 7.38 7.37 7.37 7.37 7.33 7.32 7.31 7.31 7.30 7.30 7.25 7.25 7.24 7.24 7.23 7.22 6.84 6.62 6.62 6.59 6.59 6.59 6.40 6.39 6.37 6.37 6.35 6.34 3.71 3.70 3.69 3.69 2.29 2.24
Me
H
N
Ph
Me
Me
4p
500 MHz, CDCl3
2.00 2.03 1.00 2.00 1.00 1.00 2.00 1.06 6.00 3.00
f1 (ppm)

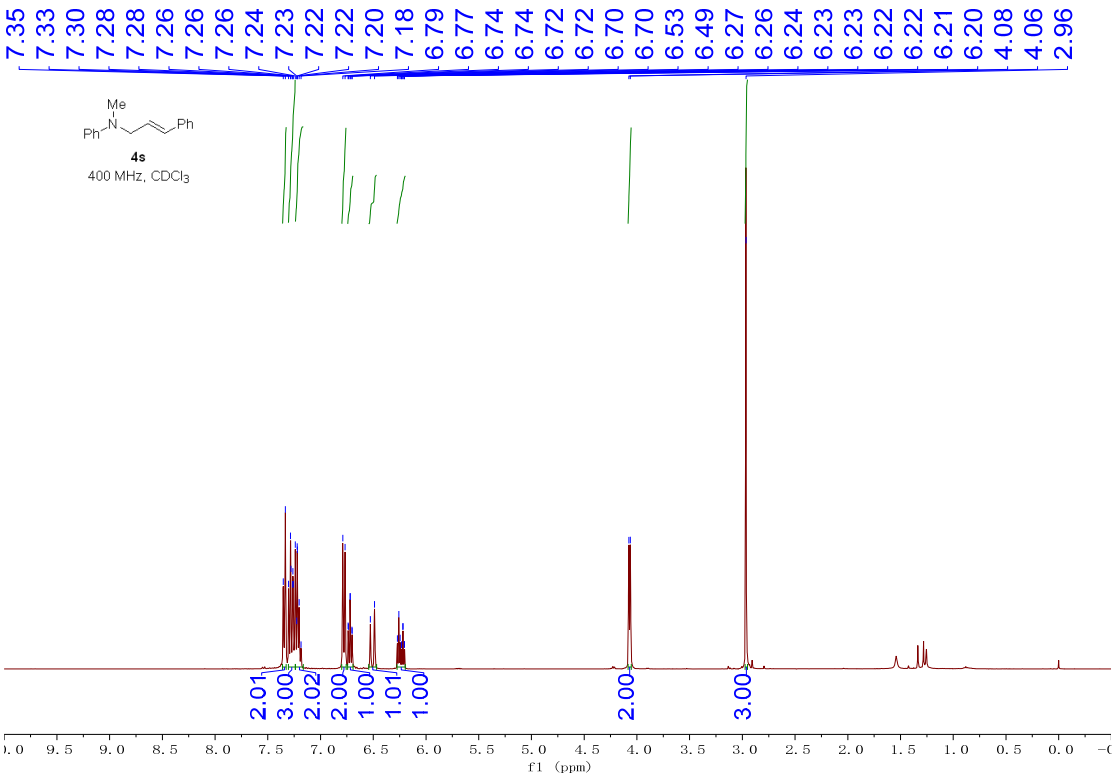

143.07 136.99 131.63 131.20 129.96 129.44 128.57 128.14 127.46 126.32
77.27 77.02 76.77
51.10
20.59 18.39
Me
H
N
Ph
Me
Me
4p
500 MHz, CDCl3
131.63 131.20 129.96 129.44 128.57 128.14 127.46 126.32
f1 (ppm)
f1 (ppm)

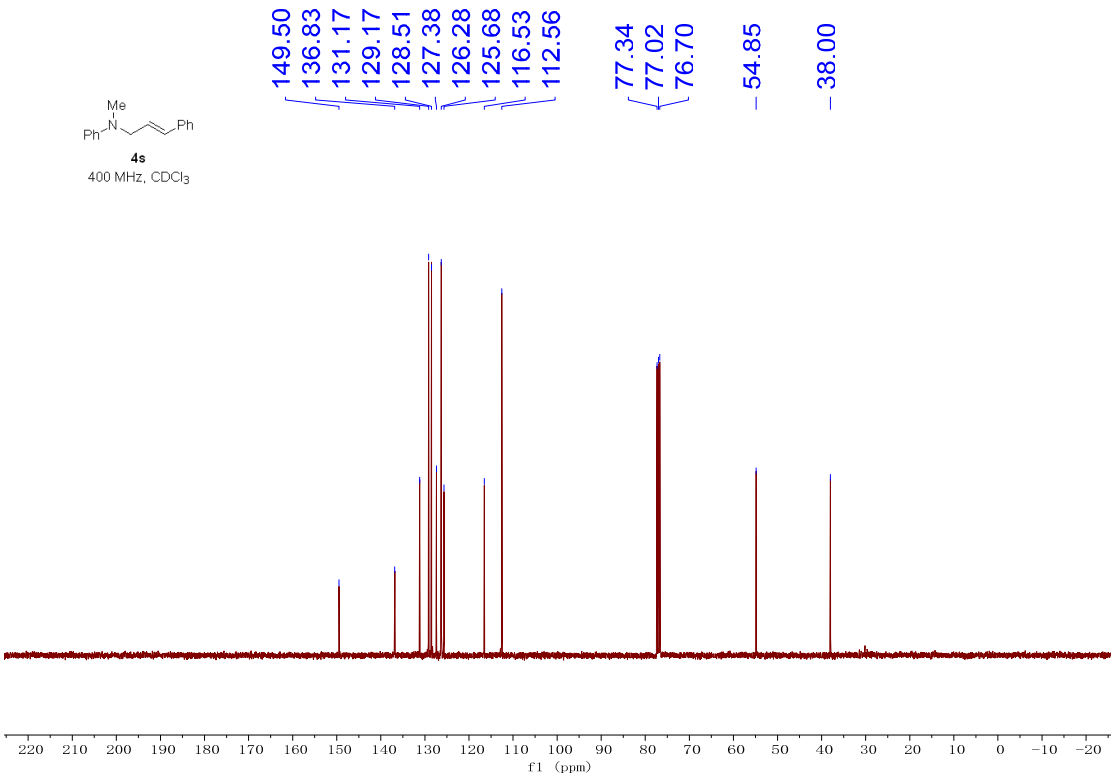

7.31
7.31
7.30
7.29
7.29
7.24
7.23
7.22
7.22
7.21
7.21
7.15
7.15
7.15
7.14
7.13
7.13
7.12
7.12
7.12
7.03
7.03
7.02
7.01
7.00
7.00
6.65
6.65
6.63
6.63
6.60
6.47
6.44
6.34
6.30
1.40
Ph
N
H
Me
Me
Ph
4q
500 MHz, CDCl3
2.01
2.00
1.02
2.01
2.00
1.00
1.00
1.00
6.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

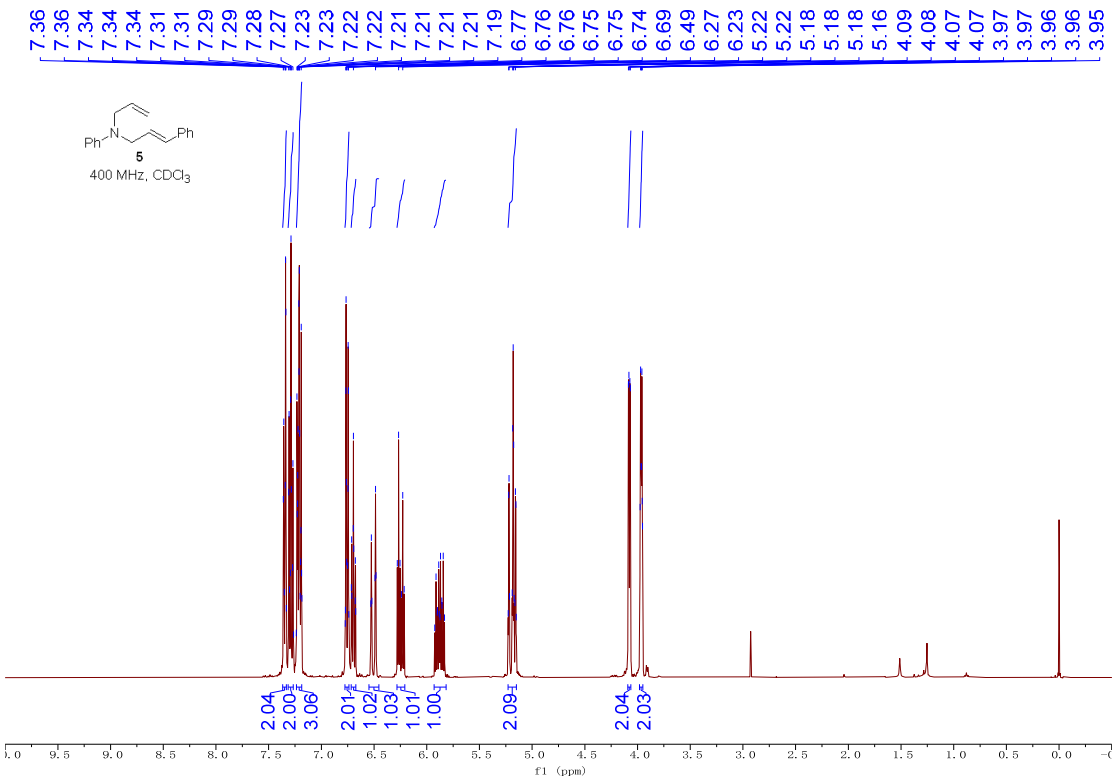

146.46
137.91
137.21
128.82
128.53
127.80
127.22
126.30
117.55
115.74
77.27
77.02
76.77
54.47
28.73
Ph
N
H
Me
Me
Ph
4q
500 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

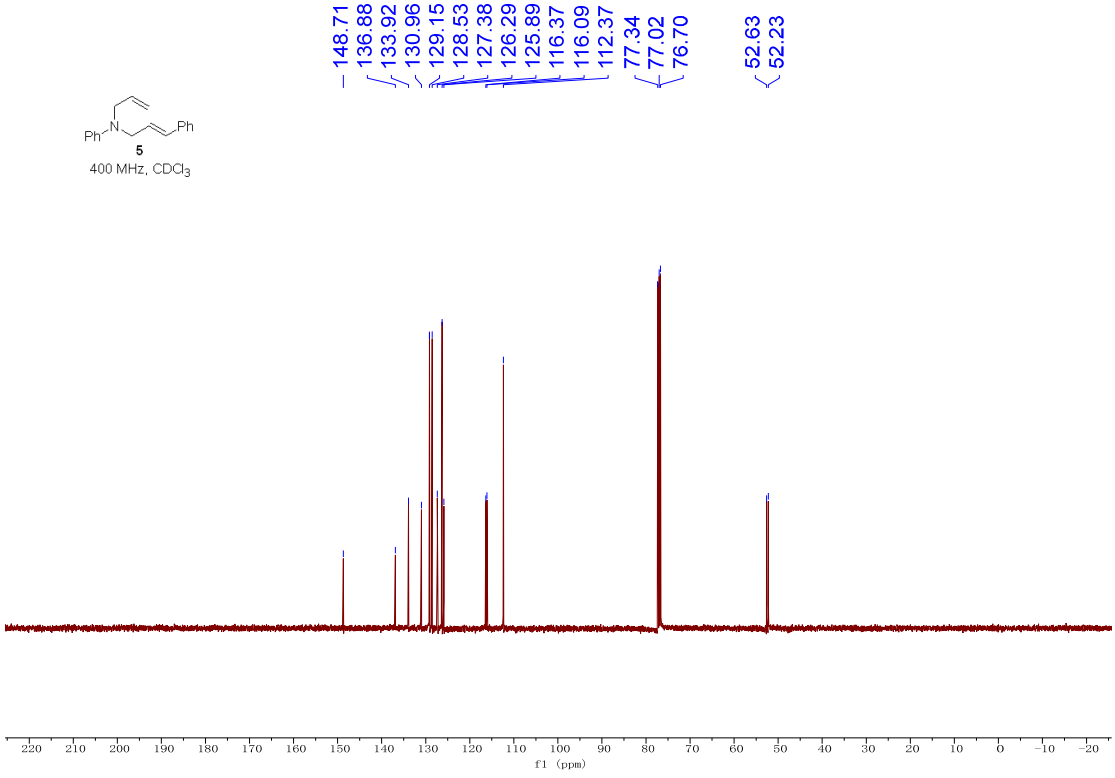

7.48
7.48
7.46
7.46
7.42
7.41
7.40
7.39
7.34
7.32
7.30
7.29
7.28
7.27
6.83
6.82
6.82
6.82
6.78
6.78
6.77
6.76
6.76
6.76
6.71
6.70
6.67
6.67
6.35
6.34
6.32
6.31
4.25
4.25
1.51
1.50
Ph
N
H
Ph
Me
4r
500 MHz, CDCl3
2.02
2.01
3.01
1.00
2.00
1.01
1.01
1.02
0.93
3.00
f1 (ppm)


147.28
136.90
133.08
129.20
129.14
128.46
127.29
126.26
117.30
113.36
77.27
77.02
76.77
50.79
22.00
Ph
N
H
Ph
Me
4r
500 MHz, CDCl3
f1 (ppm)


7.35 7.33 7.30 7.28 7.28 7.26 7.26 7.26 7.24 7.23 7.22 7.22 7.20 7.18 6.79 6.77 6.74 6.74 6.72 6.72 6.70 6.70 6.53 6.49 6.27 6.26 6.24 6.23 6.23 6.22 6.22 6.21 6.20 4.08 4.06 2.96
Me
Ph
N
Ph
4s
400 MHz, CDCl3
2.01 3.00 2.02 2.00 1.00 1.01 1.00 2.00 3.00
f1 (ppm)


149.50 136.83 131.17 129.17 128.51 127.38 126.28 125.68 116.53 112.56 77.34 77.02 76.70 54.85 38.00
Me
Ph
N
Ph
4s
400 MHz, CDCl3
f1 (ppm)


7.36 7.36 7.34 7.34 7.34 7.31 7.31 7.29 7.29 7.28 7.27 7.23 7.23 7.22 7.22 7.21 7.21 7.21 7.19 6.77 6.76 6.76 6.75 6.75 6.74 6.69 6.49 6.27 6.23 5.22 5.22 5.18 5.18 5.16 4.09 4.08 4.07 4.07 3.97 3.97 3.96 3.96 3.95
Ph
N
Ph
5
400 MHz, CDCl3
2.04 2.00 3.06 2.01 1.02 1.03 1.01 1.00 2.09 2.04 2.03
f1 (ppm)


148.71 136.88 133.92 130.96 129.15 128.53 127.38 126.29 125.89 116.37 116.09 112.37 77.34 77.02 76.70 52.63 52.23
Ph
N
Ph
5
400 MHz, CDCl3
f1 (ppm)