Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

1,2-Amino alcohol-dependent Petasis allylboration for racemic and chiral homoallylamines

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Contents

General information

All reactions involving air-sensitive compounds were performed in oven-dried glassware by using standard Schlenk techniques. All reactions were monitored by TLC, TLC analysis was performed by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the stationary phase. ^{1}H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm). ^{13}C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.2 ppm). ^{19}F NMR (471 MHz) spectra were recorded on a Bruker Avance 500 instrument. Optical rotations were measured on a Hanon Automatic Polarimeter P850. Infrared spectra were recorded on a NICOLET FT/IR-200 spectrometer. High resolution MS (ESI-orbitrap) were obtained on Thermo Fisher Q Exactive Mass Spectrometer. Melting points were recorded on a X-4 series microscope melting point apparatus at ambient pressure.

General procedure for the racemic homoallylamines

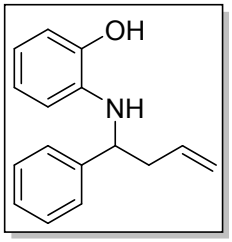
A mixture of 2-aminophenol (0.24 mmol), aldehyde (0.20 mmol) and 4Å MS (100 mg) was stirred in MeOH (0.4 mL) at rt for 2 h. Allylboronate (0.24 mmol) was added, then the mixture was stirred at rt for the time indicated in the table. Finally, the reaction mixture was subjected to the preparative thin layer chromatography to give desired product.

General procedure for the chiral homoallylamines

A mixture of chiral amino alcohol (0.24 mmol), aldehyde (0.2 mmol) and methanol (1.0 mmol) was stirred in DMSO (0.4 mL) at rt for 2 h. Allylboronate (0.24 mmol) was added, then the reaction mixture was stirred at rt for the time indicated in the table. Finally, the reaction mixture was subjected to the preparative thin layer chromatography to give desired product.

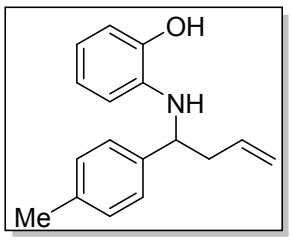
Characterization data of the reaction products

***rac*-2-((1-phenylbut-3-en-1-yl)amino)phenol (4ac)[1]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 82% yield as a brown oil, Rf = 0.48 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 - 7.35 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.24 - 7.20 (m, 1H), 6.69 - 6.65 (m, 2H), 6.56 - 6.55 (m, 1H), 6.38 (d, *J* = 7.5 Hz, 1H), 5.82 - 5.74 (m, 1H), 5.20 - 5.12 (m, 2H), 4.36 (t, *J* = 7.0 Hz, 1H), 2.64 - 2.52 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6 (d, *J* = 25.2 Hz), 136.1,

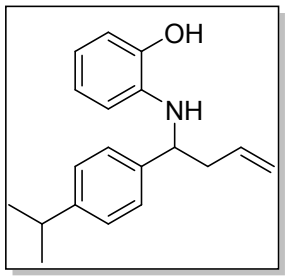


134.7, 128.5, 127.0, 126.4, 121.5, 118.2, 117.7, 114.2, 113.7, 57.8, 43.2.

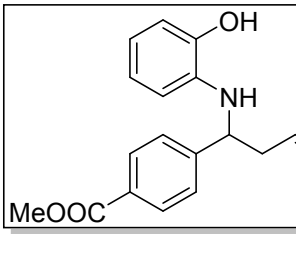
***rac*-2-((1-(*p*-tolyl)but-3-en-1-yl)amino)phenol (4bc)[1]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 83% yield as a brown oil, Rf = 0.47 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.67 - 6.65 (m, 2H), 6.56 - 6.53 (m, 1H), 6.41 (d, *J* = 7.5 Hz, 1H), 5.83 - 5.74 (m, 1H), 5.19 - 5.11 (m, 2H), 4.33 (t, *J* = 5.5 Hz, 1H), 2.62 - 2.51 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 140.5, 136.5, 136.1, 134.8, 129.3, 126.3, 121.5, 118.1, 114.1, 113.9, 57.6, 43.2, 21.1 .

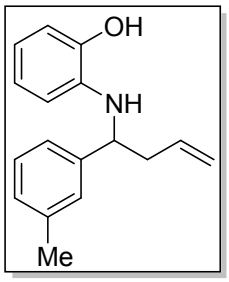


***rac*-2-((1-(4-isopropylphenyl)but-3-en-1-yl)amino)phenol (4cc):** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 85% yield as a brown oil, Rf = 0.47 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 - 7.37 (m, 2H), 7.18 -7.16 (d, *J* = 8.0 Hz, 2H), 6.71 - 6.69 (m, 2H), 6.58 - 6.56 (m, 1H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.84 - 5.76 (m, 1H), 5.21 - 5.12 (m, 2H), 4.35 (t, *J* = 6.0 Hz, 1H), 2.91 - 2.85 (m, 1H), 2.64 - 2.52 (m, 2H), 1.24 (d, *J* = 1.5 Hz, 3H), 1.23 (d, *J* = 1.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 143.7, 140.8, 136.2, 134.9, 126.6, 126.3, 121.5, 118.0, 117.6, 114.1, 113.8, 57.5, 43.2, 33.7, 24.0; IR (KBr): 3419, 2959, 1608, 1509, 1457, 1268, 1195, 1103, 739 cm^{-1}; HRMS calcd. for $[M+H]^+$: 280.1702, found: 280.1706.



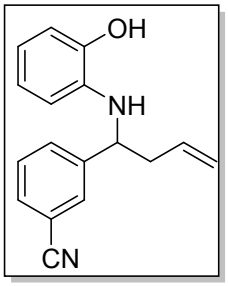
***rac*-methyl-4-(1-((2-hydroxyphenyl)amino)but-3-en-1-yl)benzoate (4gc):** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 80% yield as a brown oil, Rf = 0.48 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 7.5 Hz), 6.64 (t, *J* = 7.0 Hz, 1H), 6.55 (t, *J* = 7.0 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 5.81 - 5.73 (m, 1H), 5.21 - 5.14 (m, 2H), 4.44 (t, *J* = 6.0 Hz, 1H), 3.91 (s, 3H), 2.66 - 2.54 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 149.3, 143.5, 135.8, 134.0, 129.8, 128.8, 126.5, 125.8, 121.3, 118.7, 117.6, 114.2, 113.0, 57.5, 52.5, 42.9; IR (KBr): 3409, 2974, 1701, 1523, 1440, 1298, 1159, 1102, 734 cm^{-1}; HRMS calcd. for $[M+H]^+$: 296.1286, found: 296.1292.



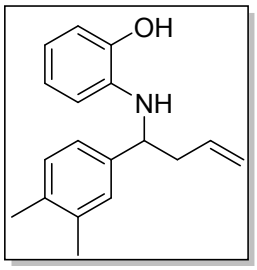


***rac*-2-((1-(m-tolyl)but-3-en-1-yl)amino)phenol (4hc)[1]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 83% yield as a brown oil, Rf = 0.49 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 - 7.16 (m, 3H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.69 - 6.57 (m, 3H), 6.42 (d, *J* = 7.0 Hz, 1H), 5.84 - 5.76 (m, 1H), 5.22 - 5.17 (m, 2H), 4.33 (s, 1H), 2.64 - 2.52 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 138.1, 136.2, 134.8, 128.4, 127.8, 127.0, 123.5, 121.5, 118.1, 117.6, 114.1, 113.7, 57.8, 43.2, 21.6.

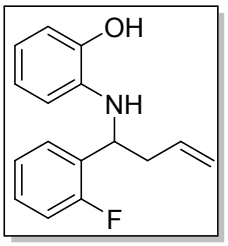
***rac*-3-(1-((2-hydroxyphenyl)amino)but-3-en-1-yl)benzonitrile (4lc):** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 86% yield as a brown oil, Rf = 0.47 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.58 (t, *J* = 7.5 Hz, 1H), 5.79 - 5.70 (m, 1H), 5.21 - 5.16 (m, 2H), 4.41 (t, *J* = 6.0 Hz, 1H), 2.63 - 2.51 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 143.4, 135.5, 133.5, 131.1, 130.9, 130.2, 129.4, 121.4, 119.1, 119.0, 117.8, 114.3, 112.7, 112.5, 57.0, 43.0; IR (KBr): 3408, 3075, 1610, 1514, 1445, 1271, 1196, 1100, 741 cm^{-1}; HRMS calcd. for $[M+H]^+$: 263.1185, found: 263.1189.



***rac*-2-((1-(3,4-dimethylphenyl)but-3-en-1-yl)amino)phenol (4mc):** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 85% yield as a brown oil, Rf = 0.45 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.13 - 7.06 (m, 2H), 6.70 - 6.69 (m, 2H), 6.58 - 6.56 (m, 1H), 6.45 - 6.43 (m, 1H), 5.84 - 5.76 (m, 1H), 5.20 - 5.12 (m, 2H), 4.29 (t, *J* = 6.0 Hz, 1H), 2.62 - 2.50 (m, 2H), 2.24 (d, *J* = 7.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 141.0, 136.7, 136.2, 135.2, 135.0, 129.8, 127.6, 123.7, 121.5, 118.0, 117.6, 57.6, 43.3, 19.9, 19.4; IR (KBr): 3689, 2923, 1610, 1509, 1445, 1267, 1195, 1100, 741 cm^{-1}; HRMS calcd. for $[M+H]^+$: 266.1546, found: 266.1550.

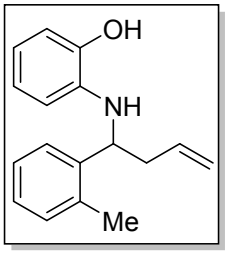


***rac*-2-((1-(2-fluorophenyl)but-3-en-1-yl)amino)phenol (4nc):** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 84 % yield as a brown oil, Rf = 0.49 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.22 - 7.18 (m, 1H), 7.08 - 7.06 (m, 2H), 6.70 - 6.68 (m, 2H), 6.59 - 6.57 (m, 1H), 6.52 (d, *J* = 7.5 Hz, 1H), 5.85 - 5.77 (m, 1H), 5.21 - 5.13 (m, 2H), 4.76 (t, *J* = 6.0 Hz, 1H), 2.71 - 2.57 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.5, 159.6, 143.6, 135.6, 134.3, 128.5, (d, *J* = 7.6 Hz), 127.8 (d, *J* = 5.0 Hz), 124.3 (d, *J* = 2.5 Hz), 121.6 (d, *J* = 21.4 Hz), 118.4, 117.8, 115.5, 114.2, 113.3,

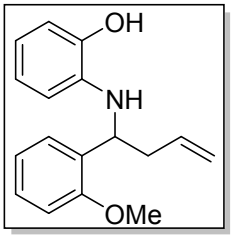


51.3, 41.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -120.0 (s, 1F); IR (KBr): 3421, 3076, 2925, 1610, 1513, 1265, 1221, 1096, 740 cm^{-1}; HRMS calcd. for $[M+H]^+$: 256.1138, found: 256.1143.

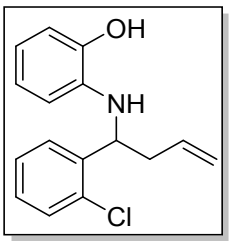
***rac*-2-((1-(o-tolyl)but-3-en-1-yl)amino)phenol (4oc)[1]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 84% yield as a brown oil, Rf = 0.46 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 - 7.42 (m, 1H), 7.19 - 7.13 (m, 3H), 6.68 - 6.55 (m, 3H), 6.26 (d, *J* = 6.5 Hz, 1H), 5.88 - 5.80 (m, 1H), 5.25 - 5.15 (m, 2H), 4.60 (s, 1H), 2.63 - 2.48 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 141.2, 136.2, 134.8, 134.6, 130.6, 126.7, 126.5, 125.5, 121.6, 118.2, 117.5, 114.2, 113.1, 53.8, 41.4, 19.2.



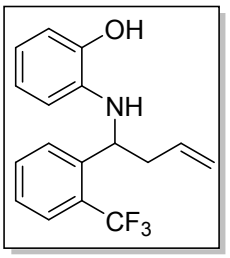
***rac*-2-((1-(2-methoxyphenyl)but-3-en-1-yl)amino)phenol (4pc)[2]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 82% yield as a brown oil, Rf = 0.45 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.21 (td, *J* = 8.0 Hz, 1.5 Hz, 1H), 6.92 - 6.87 (m, 2H), 6.69 - 6.57 (m, 3H), 6.40 (d, *J* = 7.0 Hz, 1H), 5.85 - 5.77 (m, 1H), 5.19 - 5.09 (m, 2H), 4.75 (s, 1H), 3.91 (s, 3H), 2.70 - 2.51 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 144.1, 136.0, 135.4, 130.9, 127.8, 127.2, 121.4, 127.2, 121.4, 120.7, 117.8, 117.6, 114.2, 110.5, 55.4, 52.2, 40.5.



***rac*-2-((1-(2-chlorophenyl)but-3-en-1-yl)amino)phenol (4qc)[1]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 83% yield as a brown oil, Rf = 0.47 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 - 7.43 (m, 1H), 7.39 - 7.37 (m, 1H), 7.20 - 7.15 (m, 2H), 6.70 - 6.68 (m, 1H), 6.56 - 6.55 (m, 1H), 6.27 - 6.26 (m, 1H), 5.88 - 5.80 (m, 1H), 5.25 - 5.16 (m, 2H), 4.87 (s, 1H), 2.74 - 2.69 (m, 1H), 2.52 - 2.46 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 140.4, 135.7, 134.3, 132.7, 129.7, 128.1, 127.6, 127.2, 121.7, 118.5, 117.4, 114.1, 112.9, 53.8, 40.8.

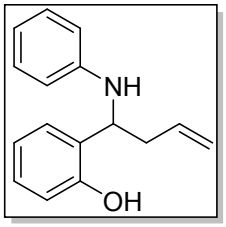


***rac*-2-((1-(2-(trifluoromethyl)phenyl)but-3-en-1-yl)amino)phenol (4rc):** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 90% yield as a brown oil, Rf = 0.46 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72（d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.69 - 6.64 (m, 2H), 6.56 - 6.53 (t, *J* = 7.5 Hz, 1H), 6.36 (d, *J* = 7.5 Hz, 1H), 5.92 - 5.84 (m, 1H), 4.83 (d, *J* = 7.0 Hz, 1H), 2.72 -

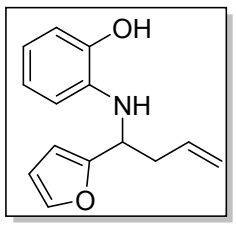


2.67 (m, 1H), 2.42 - 2.36 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 143.2, 135.6, 134.4, 132.4, 127.4, 127.1, 126.0 (q, *J* = 6.1 Hz), 125.8, 123.7, 121.6, 118.6, 117.7, 114.1, 113.1, 53.2, 43.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.3 (s, 3F); IR (KBr): 3423, 2970, 1609, 1513, 1311, 1117, 1036, 740 cm^{-1}; HRMS calcd. for $[M+H]^+$: 306.1107, found: 306.1111.

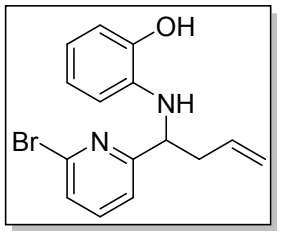
***rac*-2-(1-(phenylamino)but-3-en-1-yl)phenol (4sg)[2]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 87% yield as a brown oil, Rf = 0.48 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 - 7.14 (m, 4H), 6.92 - 6.87 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 2H), 5.89 - 5.81 (m, 1H), 5.31 - 5.27 (m, 2H), 4.33 (t, *J* = 7.0 Hz, 1H), 2.68 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.6, 146.8, 134.3, 129.3, 128.6, 127.8, 126.2, 59.9, 41.4.



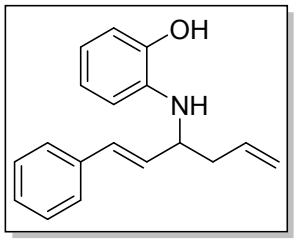
***rac*-2-((1-(furan-2-yl)but-3-en-1-yl)amino)phenol (4tc)[3]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 80% yield as a brown oil, Rf = 0.48 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 - 7.35 (m, 1H), 6.78 - 6.76 (td, *J* = 7.5 Hz, 1.5 Hz, 1H), 6.75 - 6.74 (m, 1H), 6.67 (td, *J* = 7.5 Hz, 1.0 Hz), 6.64 (dd, *J* = 8.0 Hz, 1.0 Hz, 1H), 5.20 - 5.12 (m, 2H), 4.45 (t, *J* = 6.5Hz, 1H), 2.69 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 145.0, 141.6, 135.3, 134.1, 121.3, 119.3, 118.3, 115.2, 114.5, 110.1, 106.3, 52.5, 39.2.



***rac*-2-((1-(6-bromopyridin-2-yl)but-3-en-1-yl)amino)phenol (4uc):** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 80% yield as a brown oil, Rf = 0.46 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.75 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.70 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.61 (td, *J* = 7.5 Hz, 1.0 Hz, 1H), 6.39 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 5.82 - 5.74 (m, 1H), 5.21 - 5.13 (m, 2H), 4.48 - 4.46 (m, 1H), 2.79 - 2.74 (m, 1H), 2.60 - 2.54 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 144.2, 141.7, 139.1, 135.7, 134.0, 126.4, 121.5, 119.8, 118.7, 118.6, 114.7, 114.3, 59.0, 41.3; IR (KBr): 3076, 2926, 1639, 1514, 1433, 1266, 1160, 993, 740 cm^{-1}; HRMS calcd. for $[M+H]^+$: 317.0290, found: 317.0295.

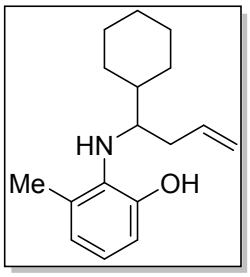


rac-(*E*)-2-((1-phenylhexa-1,5-dien-3-yl)amino)phenol (4vc)[1]: According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 80% yield as a brown oil, Rf = 0.47 (PE/EA = 5:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz), 6.83 - 6.73

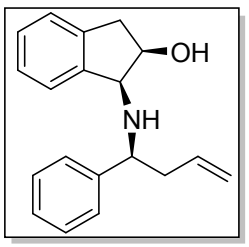


(m, 3H), 6.66 - 6.63 (m, 1H), 6.61 - 6.57 (m, 1H), 6.21 (dd, *J* = 16.0 Hz, 6.0 Hz, 1H), 5.94 - 5.86 (m, 1H), 5.23 - 5.16 (m, 2H), 4.06 - 4.01 (m, 1H), 2.53 - 2.50 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 137.0, 135.9, 134.5, 131.6, 130.5, 128.5, 127.4, 126.4, 121.5, 118.3, 114.3, 55.8, 40.5.

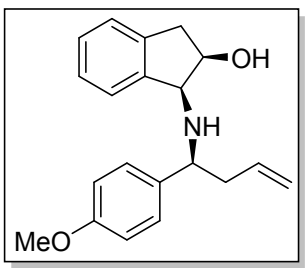
***rac*-2-((1-cyclohexylbut-3-en-1-yl)amino)-3-methylphenol (4wh)[3]:** According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 60% yield as a brown oil, Rf = 0.48 (PE/EA = 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 2H), 5.88 - 5.79 (m, 1H), 5.15 - 5.10 (m, 2H), 2.90 - 2.87 (m, 1H), 2.28-2.23 (m, 3H), 2.10 - 2.04 (m, 1H), 1.83 - 1.62 (m, 5H), 1.28 - 1.14 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 136.2, 133.5, 131.9, 125.0, 121.9, 117.8, 112.1, 62.0, 40.5, 35.6, 28.8 (d, *J* = 8.8 Hz), 26.6 (d, *J* = 2.9 Hz), 18.1.



(1*S*,2*R*)-1-(((*S*)-1-phenylbut-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6ae)[4]: According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 95% yield as a brown oil, Rf = 0.40 (PE/DCM = 1:1), dr = 13.6:1, $[\alpha]_D^{25}$ = -15.7 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 4.5 Hz, 4H), 7.31 - 7.28 (m, 1H), 7.20 - 7.15 (m, 3H), 7.06 (d, *J* = 7.0 Hz, 1H), 5.82 - 5.74 (m, 1H), 5.12 - 5.06 (m, 2H), 4.42 - 4.40 (m, 1H), 4.01 (d, *J* = 5.0 Hz, 1H), 3.86 (t, *J* = 7.0 Hz, 1H), 2.97 - 2.96 (m, 2H), 2.58 - 2.51 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4 , 142.3, 141.0, 135.0, 128.7, 128.0, 127.5, 127.0, 126.7, 125.5, 125.4, 123.6, 117.8, 70.7, 63.5, 61.5, 42.6, 39.8; IR (KBr): 3334, 2915, 1640, 1456, 1156, 1050, 916, 810, 702 cm^{-1}; HRMS calcd. for $[M+H]^+$: 280.1696, found: 280.1696.



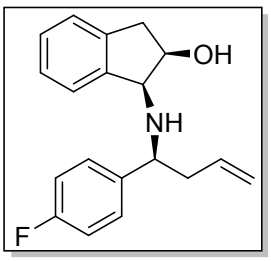
(1*S*,2*R*)-1-(((*S*)-1-(*p*-tolyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6be) : According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 95% yield as a brown oil, Rf = 0.38 (PE/DCM = 1:1), dr = 14.3:1, $[\alpha]_D^{25}$ = 12.0 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 - 7.27 (m, 2H), 7.21 - 7.16 (m, 5H), 7.08 (d, *J* = 7.0 Hz, 1H), 5.83 - 5.75 (m, 1H), 5.13 - 5.06 (m, 2H), 4.41 - 4.39 (m, 1H), 4.01 (d, *J* = 5.0 Hz, 1H), 3.82 (t, *J* = 7.0 Hz, 1H), 2.98 - 2.96 (m, 2H), 2.57 - 2.51 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 141.1, 140.4, 137.1, 135.1, 129.4, 127.9, 126.9, 126.7, 125.5, 123.5, 117.6, 70.7, 63.5, 61.2, 42.6, 39.8, 21.1; IR (KBr): 3331, 2918, 1640, 1459, 1160, 1050, 915, 817, 730 cm^{-1}; HRMS calcd. for $[M+H]^+$: 294.1853, found: 294.1852.



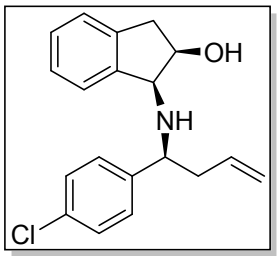
(1*S*,2*R*)-1-(((*S*)-1-(4-methoxyphenyl)but-3-en-1-yl)amino)-

2,3-dihydro-1*H*-inden-2-ol (6ce): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 92% yield as a brown oil, Rf = 0.39 (PE/DCM = 1:1), dr = 12.3:1, $[\alpha]_D^{25}$ = 17.0 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 - 7.26 (m, 2H), 7.16 - 7.11 (m, 3H), 7.02 (d, *J* = 6.5 Hz, 1H), 6.89 - 6.88 (m, 2H), 5.78 - 5.69 (m, 1H), 5.07 - 5.04 (m, 2H), 4.36 (m, 1H), 3.97 (d, *J* = 5.0 Hz, 1H), 3.78 (s, 3H), 2.93 (d, *J* = 3.0 Hz, 2H), 2.52 - 2.44 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 142.4, 141.1, 135.5, 135.1, 128.0, 127.9, 126.6, 125.5, 123.5, 117.6, 114.1, 70.7, 63.5, 60.9, 55.3, 42.6, 39.8; IR (KBr): 3339, 2913, 1610, 1511, 1174, 1036, 916, 831, 746 cm^{-1}; HRMS calcd. for $[M+H]^+$: 310.1801, found: 310.1802.

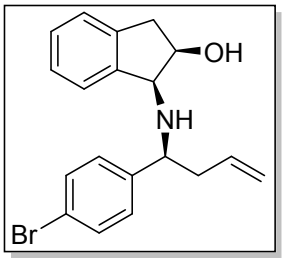
(1*S*,2*R*)-1-(((*S*)-1-(4-fluorophenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6de): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 93% yield as a brown oil, Rf = 0.36 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 17.0 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 - 7.36 (m, 2H), 7.21 - 7.17 (m, 3H), 7.11 - 7.08 (m, 3H), 5.80 - 5.72 (m, 1H), 5.12 - 5.06 (m, 2H), 4.42 - 4.40 (m, 1H), 3.97 (d, *J* = 5.0 Hz, 1H), 3.88 (t, *J* = 7.0 Hz, 1H), 2.97 (d, *J* = 3.5 Hz, 2H), 2.57 - 2.46 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 161.1, 142.2, 140.9, 139.2, 134.7, 128.5 (d, *J* = 8.0 Hz), 128.0, 126.7, 125.5, 123.6, 118.0, 115.6, 115.4, 70.8, 63.5, 60.7, 42.7, 39.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.2 (s, 1F); IR (KBr): 3333, 2914, 1603, 1508, 1157, 1050, 917, 834, 744 cm^{-1}; HRMS calcd. for $[M+H]^+$: 298.1601, found: 298.1602.



(1*S*,2*R*)-1-(((*S*)-1-(4-chlorophenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6ee): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 88% yield as a brown oil, Rf = 0.38 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 21.7 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 - 7.32 (m, 4H), 7.21 - 7.17 (m, 3H), 7.10 (d, *J* = 6.5 Hz, 1H), 5.79 - 5.70 (m, 1H), 5.11 - 5.06 (m, 2H), 4.41 (q, *J* = 3.6 Hz, 1H), 3.95 (d, *J* = 5.0 Hz, 1H), 3.85 (t, *J* = 6.5 Hz, 1H), 2.96 (d, *J* = 3.5 Hz, 2H), 2.55 - 2.46 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 142.0, 140.9, 134.6, 133.1, 128.8, 128.4, 128.0, 126.8, 125.5, 123.6, 118.1, 70.9, 63.5, 60.7, 42.6, 39.8; IR (KBr): 3404, 2921, 1640, 1486, 1160, 1088, 916, 826, 740 cm^{-1}; HRMS calcd. for $[M+H]^+$: 314.1305, found: 314.1306.

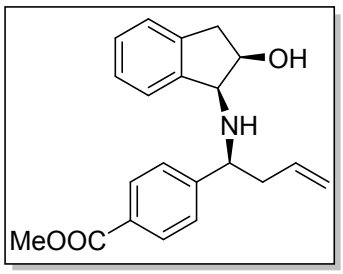


(1*S*,2*R*)-1-(((*S*)-1-(4-bromophenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6fe): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 94% yield as a brown oil, Rf =

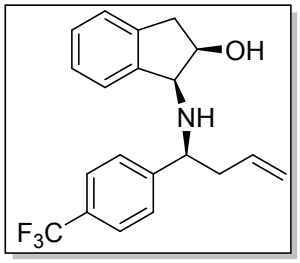


0.41 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 11.3 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.21 - 7.17 (m, 3H), 7.12 (d, *J* = 6.0 Hz, 2H), 5.80 - 5.72 (m, 1H), 5.12 - 5.07 (m, 2H), 4.13 (q, *J* = 3.5Hz, 1H), 3.95 (d, *J* = 5.0 Hz, 1H), 3.85 (t, *J* = 7.0 Hz, 1H), 2.55-2.45 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 142.2, 140.8, 134.6, 131.8, 128.8, 128.0, 126.8, 125.5, 123.6, 121.1, 118.2, 70.9, 63.6, 60.8, 42.6, 39.8; IR (KBr): 3328, 2917, 1640, 1477, 1158, 1101, 917, 826, 746 cm^{-1}; HRMS calcd. for $[M+H]^+$: 358.0800, found: 358.0801.

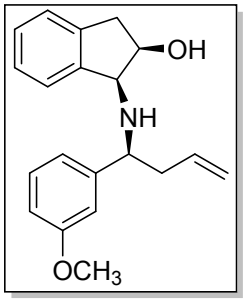
Methyl4-((*S*)-1-(((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)amino) but-3-en-1-yl)benzoate (6ge): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 90% yield as a brown oil, Rf = 0.38 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 29.7 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.20 - 7.15 (m, 3H), 7.09 (d, *J* = 6.5 Hz, 1H), 5.79 - 5.71 (m, 1H), 5.11 - 5.06 (m, 2H), 4.43 - 4.40 (m, 1H), 3.95 - 3.91 (m, 5H), 2.95 (d, *J* = 3.5 Hz, 2H), 2.57 - 2.47 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 148.9, 142.1, 140.8, 134.4, 130.0, 129.4, 128.0, 127.1, 126.8, 125.5, 123.6, 118.2, 70.9, 63.6, 61.1, 52.1, 42.5, 39.8; IR (KBr): 3421, 2911, 1719, 1609, 1435, 1169, 1111, 917, 856, 746 cm^{-1}; HRMS calcd. for $[M+H]^+$: 338.1750, found: 338.1751.



(1*S*,2*R*)-1-(((S)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6he): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 93% yield as a brown oil, Rf = 0.40 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 24.0 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.21 - 7.17 (m, 3H), 7.13 (d, *J* = 5.0 Hz, 1H), 5.81 - 5.72 (m, 1H), 5.14 - 5.09 (m, 2H), 4.45 - 4.43 (m, 1H), 3.98 - 3.94 (m, 2H), 2.96 (d, *J* = 3.5 Hz, 2H), 2.56 - 2.49 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 142.1, 140.8, 134.3, 129.9, 129.6, 128.1, 127.4, 126.8, 125.6 (q, *J* = 3.8 Hz), 125.6 , 71.0, 63.6, 60.9, 42.7, 39.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ - 62.5 (s, 3F); IR (KBr): 3404, 2913, 1617, 1416, 1325, 1163, 1123, 1066, 913, 840, 730, 607 cm^{-1}; HRMS calcd. for $[M+H]^+$: 348.1569, found: 348.1570.

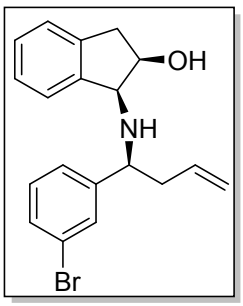


(1*S*,2*R*)-1-(((S)-1-(3-methoxyphenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6ie): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 94% yield as a brown oil, Rf = 0.36 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 14.7 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 1H), 7.20 - 7.16 (m, 3H), 7.10 - 7.08 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.95 - 6.94 (m, 1H),

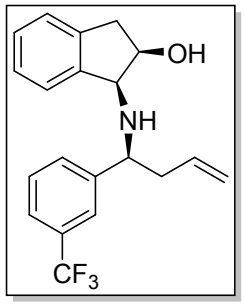


6.82 (dd, J = 8.0, 2.5 Hz, 1H), 5.83 - 5.75 (m, 1H), 5.13 - 5.06 (m, 2H), 4.42 - 4.40 (m, 1H), 4.01 (d, J = 4.5 Hz, 1H), 3.83 - 3.80 (m, 4H), 2.97 - 2.96 (m, 2H), 2.52 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 145.2, 142.3, 141.1, 135.0, 129.7, 127.9, 126.7, 125.5, 123.6, 119.3, 117.7, 113.0, 112.5, 70.7, 63.5, 61.4, 55.2, 42.6, 39.8; IR (KBr): 3386, 2915, 1600, 1465, 1156, 1044, 918, 875, 742 cm^{-1}; HRMS calcd. for $[M+H]^+$: 310.1800, found: 310.1802.

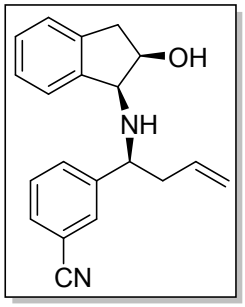
(1*S*,2*R*)-1-(((*S*)-1-(3-bromophenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6je): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 95% yield as a brown oil, Rf = 0.38 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 30.7 (c = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.26 - 7.23 (m, 1H), 7.19 - 7.16 (m, 3H), 7.11 - 7.10 (m, 1H), 5.79 - 5.77 (m, 1H), 5.11 - 5.06 (m, 2H), 4.42 - 4.40 (m, 1H), 3.95 (d, J = 4.5 Hz, 1H), 3.83 (t, J = 7.0 Hz, 1H), 2.96 - 2.95 (m, 2H), 2.50 - 2.47 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 142.1, 140.9, 134.5, 130.6, 130.3, 130.2, 128.1, 126.8, 125.6, 125.5, 123.7, 122.9, 118.2, 70.9, 63.6, 60.9, 42.7, 39.8; IR (KBr): 3337, 2913, 1722, 1569, 1426, 1161, 1051, 916, 834, 745 cm^{-1}; HRMS calcd. for $[M+H]^+$: 358.0800, found: 358.0810.



(1*S*,2*R*)-1-(((*S*)-1-(3-(trifluoromethyl)phenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6ke): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 92% yield as a brown oil, Rf = 0.40 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 10.0 (c = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.21 - 7.19 (m, 3H), 7.14 - 7.12 (m, 1H), 5.81 - 5.73 (m, 1H), 5.14 - 5.09 (m, 2H), 4.46 - 4.43 (m, 1H), 3.98 - 3.94 (m, 2H), 2.98 - 2.97 (m, 2H), 2.54 - 2.51 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 142.1, 140.7, 134.3, 131.2, 130.9, 130.5, 129.1, 128.1, 126.8, 125.5, 124.3 (q, J = 3.7 Hz), 123.7, 118.4, 71.0, 63.6, 60.9, 42.8, 39.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.2 (s, 3F); IR (KBr): 3333, 2916, 1641, 1444, 1327, 1164, 1072, 918, 805, 744 cm^{-1}; HRMS calcd. for $[M+H]^+$: 348.1570, found: 348.1570.

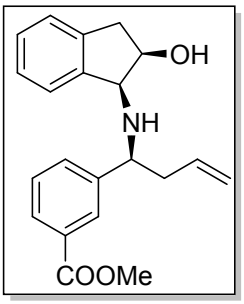


3-((*S*)-1-(((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)amino)but-3-en-1-yl)benzonitrile (6le): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 92% yield as a brown oil, Rf = 0.41 (PE/DCM = 1:1) , dr > 20:1, $[\alpha]_D^{25}$ = 16.0 (c = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 - 7.72 (m, 1H), 7.70 -7.68 (m, 1H), 7.59 - 7.57 (m, 1H), 7.49 (t, J = 8.0 Hz, 1H), 7.21 - 7.17 (m, 4H), 5.78 - 5.70 (m, 1H), 5.12 - 5.08 (m, 2H), 4.46 - 4.44 (m,

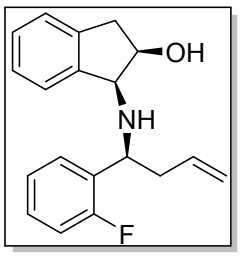


1H), 3.95 (t, *J* = 7.0 Hz, 1H), 3.89 (d, *J* = 5.0 Hz, 1H), 3.00 - 2.92 (m, 2H), 2.52 - 2.46 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 142.0, 140.5, 134.1, 131.6, 131.2, 130.9, 129.5, 128.1, 126.9, 125.3, 123.9, 118.8, 118.6, 112.7, 71.1, 63.7, 60.5, 42.8, 39.9; IR (KBr): 3340, 2914, 1640, 1473, 1158, 1050, 917, 825, 747 cm^{-1}; HRMS calcd. for $[M+H]^+$: 305.1648, found: 305.1648.

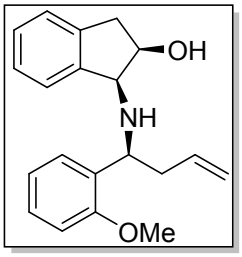
methyl 3-((*S*)-1-(((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1*H*-inden-1-yl)amino) but-3-en-1-yl)benzoate (6me): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 93% yield as a brown oil, Rf = 0.39 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 22.3 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.20 - 7.17 (m, 3H), 7.12 (d, *J* = 6.0 Hz, 1H), 5.80 - 5.72 (m, 1H), 5.12 - 5.06 (m, 2H), 4.43 - 4.41 (m, 1H), 3.96 (m, 5H), 2.96 (d, *J* = 3.2 Hz, 2H), 2.59 - 2.49 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 144.1, 142.1, 140.9, 134.6, 131.6, 130.6, 128.8 (d, *J* = 6.5 Hz), 128.2, 128.0, 126.8, 125.5, 123.7, 70.8, 63.6, 61.1, 52.2, 42.7, 39.8; IR (KBr): 3422, 2911, 1640, 1437, 1197, 1106, 916, 823, 751 cm^{-1}; HRMS calcd. for $[M+H]^+$: 338.1750, found: 338.1751.



(1*S*,2*R*)-1-(((*S*)-1-(2-fluorophenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6ne): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 95% yield as a brown oil, Rf = 0.38 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 30.3 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.5 Hz, 1H), 7.28 - 7.24 (m, 1H), 7.19 - 7.14 (m, 4H), 7.10 - 7.03 (m, 2H), 5.83 - 5.75 (m, 1H), 5.11 - 5.05 (m, 2H), 4.42 - 4.40 (m, 1H), 4.07 (t, *J* = 7.0 Hz, 1H), 3.96 (d, *J* = 5.0 Hz, 1H), 3.00 - 2.91 (m, 2H), 2.66 - 2.52 (m, 2H);^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2, 160.3, 142.0, 141.2, 134.8, 130.1, 130.0, 129.1 - 128.7 (m), 128.0, 126.7, 125.6, 124.4 (d, *J* = 3.4 Hz), 123.4, 117.9, 116.0, 115.8, 70.5, 63.7, 56.6, 41.1, 39.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -119.0 (s, 1F); IR (KBr): 3334, 2912, 1640, 1584, 1483, 1218, 1051, 917, 826, 752 cm^{-1}; HRMS calcd. for $[M+H]^+$: 298.1602, found: 298.1602.

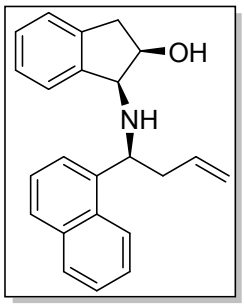


(1*S*,2*R*)-1-(((*S*)-1-(2-methoxyphenyl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6oe): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 86% yield as a brown oil, Rf = 0.38 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 26.3 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 - 7.24 (m, 2H), 7.17 - 7.11 (m, 3H), 6.97 - 6.91 (m, 3H), 5.84 - 5.76 (m, 1H), 5.08 - 5.00 (m, 2H), 4.37 - 4.35 (m, 1H), 3.97 - 3.94 (m, 2H), 3.88 (s, 3H), 3.00 - 2.91 (m,

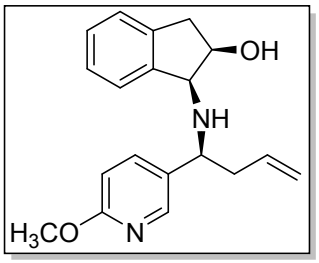


2H), 2.67 - 2.55 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 142.5, 141.4, 136.0, 130.7, 129.0, 128.4, 127.8, 126.5, 125.5, 123.4, 120.7, 117.0, 111.0, 70.2, 63.7, 59.1, 55.2, 40.4, 39.8; IR (KBr): 3365, 2910, 1639, 1462, 1239, 1051, 915, 820, 642 cm^{-1}; HRMS calcd. for $[M+H]^+$: 310.1801, found: 310.1802.

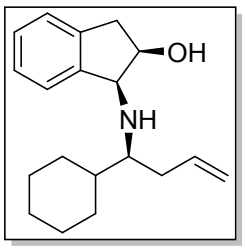
(1*S*,2*R*)-1-(((*S*)-1-(naphthalen-1-yl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6pe): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 93% yield as a brown oil, Rf = 0.39 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 61.3 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.82 (s, 1H), 7.60 - 7.58 (m, 1H), 7.54 - 7.48 (m, 2H), 7.21 - 7.17 (m, 4H), 7.12 (d, *J* = 7.0 Hz, 1H), 5.88 - 5.79 (m, 1H), 5.17 - 5.08 (m, 2H),4.47 - 4.46 (m, 1H), 4.06 - 4.03 (m, 2H), 3.02 - 2.94 (m, 2H), 2.70 - 2.60 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 141.0, 140.7, 135.0, 133.4, 133.0, 128.7, 128.0, 127.78 (d, *J* = 3.5 Hz), 126.7, 126.3 (d, *J* = 3.4 Hz), 125.9, 125.5, 124.5, 123.6, 117.9, 70.8, 63.6, 61.6, 42.6, 39.8; IR (KBr): 3339, 2909, 1633, 1434, 1264, 1160, 1051, 915, 821, 720 cm^{-1}; HRMS calcd. for $[M+H]^+$: 330.1852, found: 330.1852.



(1*S*,2*R*)-1-(((*S*)-1-(6-methoxypyridin-3-yl)but-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6qe): According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 95% yield as a brown oil, Rf = 0.36 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 24.0 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.0 Hz, 1H), 7.66 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.20 - 7.16 (m, 3H), 7.11 (d, *J* = 6.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 5.80 - 5.71 (m, 1H), 5.12 - 5.06 (m, 2H), 4.43 - 4.41 (m, 1H), 3.97 - 3.94 (m, 4H), 3.86 (t, *J* = 7.0 Hz, 1H), 3.00 - 2.92 (m, 2H), 2.57 - 2.45 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 145.8, 142.2, 140.8, 137.1, 134.5, 131.3, 128.0, 126.8, 125.5, 123.7, 118.2, 111.2, 70.9, 63.5, 58.3, 53.5, 42.5, 39.8; IR (KBr): 3330, 2906, 1606, 1395, 1161, 1025, 914, 831, 740 cm^{-1}; HRMS calcd. for $[M+H]^+$: 311.1753, found: 311.1754.

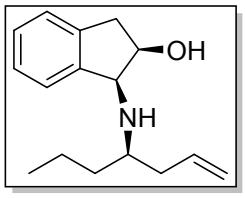


(1*S*,2*R*)-1-(((*S*)-1-cyclohexylbut-3-en-1-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6re) : According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 92 % yield as a brown oil, Rf = 0.38 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 14.7 (*c* = 0.3, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 - 7.21 (m, 4H), 5.91 - 5.83 (m, 1H), 5.11 - 5.03 (m, 2H), 4.33 - 4.30 (m, 1H), 4.16 (d, *J* = 5.0 Hz, 1H), 3.04 - 2.95 (m, 2H), 2.69 - 2.66 (m, 1H), 2.32 - 2.27 (m, 1H), 2.13 - 2.07 (m, 1H), 1.85 - 1.64 (m, 6H), 1.30 - 1.10 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$)



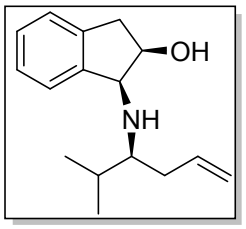
δ 143.0, 141.4, 136.5, 128.0, 126.8, 125.7, 123.5, 117.1, 71.0, 64.9, 62.4, 41.0, 39.6, 36.5, 29.4, 28.5, 26.7 (d, *J* = 10.1 Hz). IR (KBr): 3382, 2852, 1638, 1449, 1264, 1054, 911, 746 cm^{-1}; HRMS calcd. for $[M+H]^+$: 286.2166, found: 286.2165.

(1*S*,2*R*)-1-(((*R*)-hept-1-en-4-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6se): According



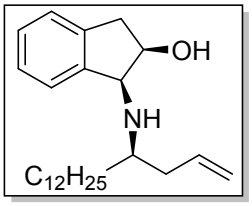
to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 86% yield as a brown oil, Rf = 0.40 (PE/DCM = 1:1) , dr > 20:1, $[\alpha]_D^{25}$ = 22.0 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 - 7.20 (m, 4H), 5.90 - 5.82 (m, 1H), 5.13 - 5.09 (m, 2H), 4.33 - 4.31 (m, 1H), 4.17 (d, *J* = 5.5 Hz, 3H), 3.06 - 2.96 (m, 2H), 2.88 - 2.84 (m, 1H), 2.31 - 2.22 (m, 2H), 1.59 - 1.40 (m, 4H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 141.4, 135.4, 128.0, 126.8, 125.7, 123.5, 117.5, 71.1, 64.3, 57.1, 39.6 (d, *J* = 13.6 Hz), 36.8, 19.2, 14.3; IR (KBr): 3042, 2957, 1640, 1458, 1264, 1049, 913, 700 cm^{-1}; HRMS calcd. for $[M+H]^+$: 246.1853, found: 246.1852.

(1*S*,2*R*)-1-(((*S*)-2-methylhex-5-en-3-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6te):



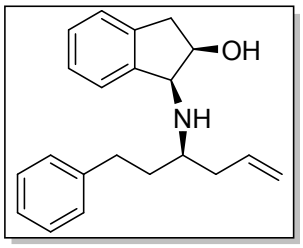
According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 92% yield as a brown oil, Rf = 0.36 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 16.7 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 - 7.20 (m, 4H), 5.91 - 5.83 (m, 1H), 5.12 - 5.08 (m, 2H), 4.33 - 4.31 (m, 1H), 4.16 (d, *J* = 5.0 Hz, 1H), 3.04 - 2.96 (m, 2H), 2.71 - 2.68 (m, 1H), 2.29 - 2.24 (m, 1H), 2.12 - 2.02 (m, 2H), 1.01 (t, *J* = 6.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 141.4, 136.4, 128.0, 126.8, 125.7, 123.5, 117.2, 71.0, 64.8, 62.7, 39.6, 35.9, 30.3, 18.6, 17.7; IR (KBr): 3200, 2982, 1644, 1435, 1153, 1022, 951, 744 cm^{-1}; HRMS calcd. for $[M+H]^+$: 246.1852, found: 246.1854.

(1*S*,2*R*)-1-(((R)-hexadec-1-en-4-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6ue):



According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 86% yield as a brown oil, Rf = 0.39 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 15.5 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 4H), 5.82 - 5.74 (m, 1H), 5.05 - 5.02 (m, 2H), 4.25 - 4.23 (m, 1H), 4.09 (d, *J* = 5.0 Hz, 1H), 2.98 - 2.89 (m, 2H), 2.79 - 2.74 (m, 1H), 2.24 - 2.12 (m, 2H), 1.52 - 1.46 (m, 1H), 1.21-1.19 (m, 20H), 0.81 (t, *J* = 6.8 Hz, 3H)**;** ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 140.4, 134.4, 127.0, 125.7, 124.7, 122.4, 116.4, 70.0, 63.3, 56.2, 38.6, 38.4, 33.5, 30.9, 28.8, 28.7 - 28.6 (m), 28.3, 24.9, 21.7, 13.1; IR (KBr): 3410, 2922, 2853, 1640, 1437, 1407, 1024, 952, 744 cm^{-1}; HRMS calcd. for $[M+H]^+$: 372.3261, found: 372.3261.

(1*S*,2*R*)-1-(((*R*)-1-phenylhex-5-en-3-yl)amino)-2,3-dihydro-1*H*-inden-2-ol (6ve):



According to the general procedure of Petasis-type allylation reactions for the synthesis of racemic homoallylamines, the title compound was obtained in 90% yield as a brown oil, Rf = 0.39 (PE/DCM = 1:1), dr > 20:1, $[\alpha]_D^{25}$ = 9.9 (*c* = 0.3, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 - 7.11 (m, 10H), 5.84 - 5.76 (m, 1H), 5.08 - 5.05 (m, 2H), 4.23 - 4.20 (m, 1H), 4.08 (d, 5.5 Hz, 1H), 2.96 - 2.81 (m, 3H), 2.72 - 2.60 (m, 3H), 2.23 - 2.19 (m, 2H), 1.87 - 1.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 141.8, 141.3, 135.2, 128.6, 128.3, 128.1, 126.8, 126.0, 125.7, 123.6, 117.8, 71.2, 64.1, 56.6, 39.6, 39.3, 36.3, 32.4; IR (KBr): 3388, 2976, 2917, 1639, 1436, 1263, 1026, 1026, 951, 746 cm^{-1}; HRMS calcd. for $[M+H]^+$: 308.2009, found: 308.2009.

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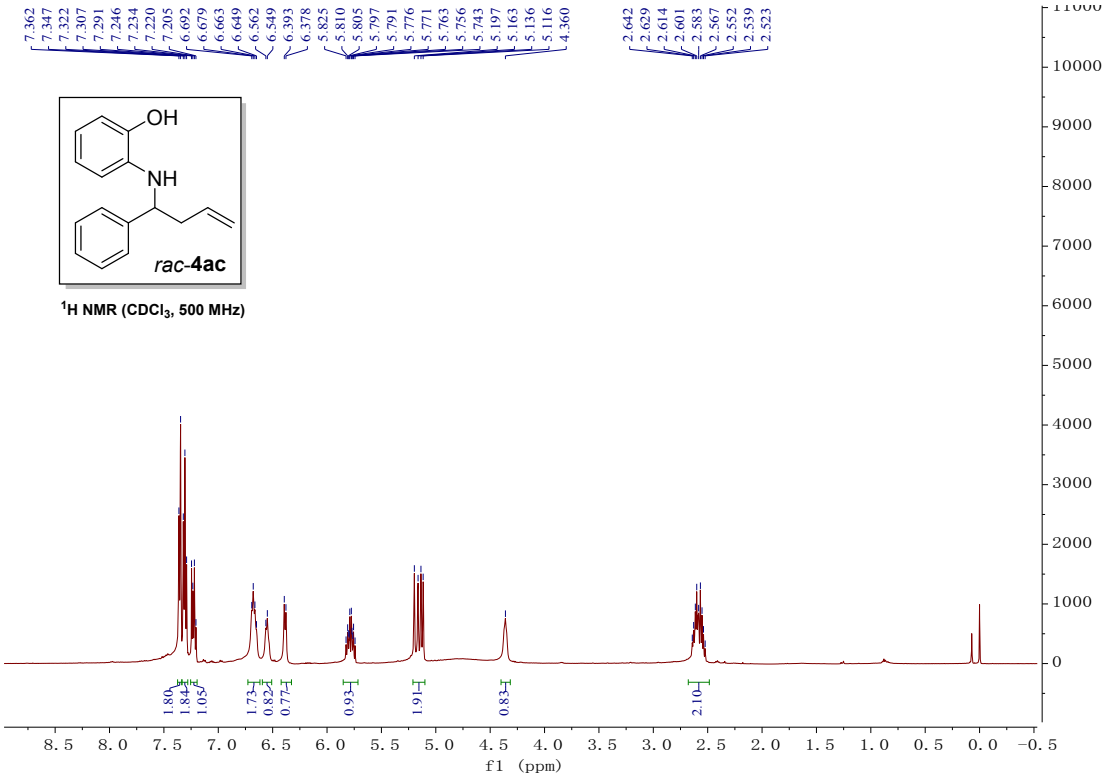
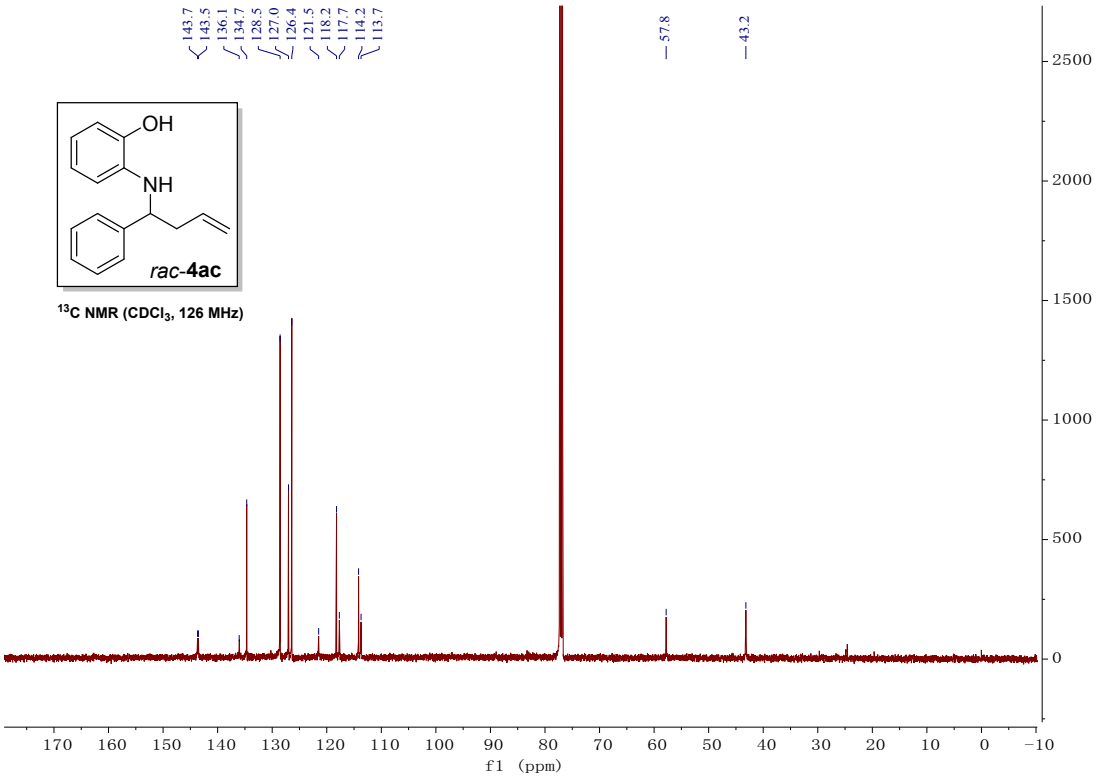
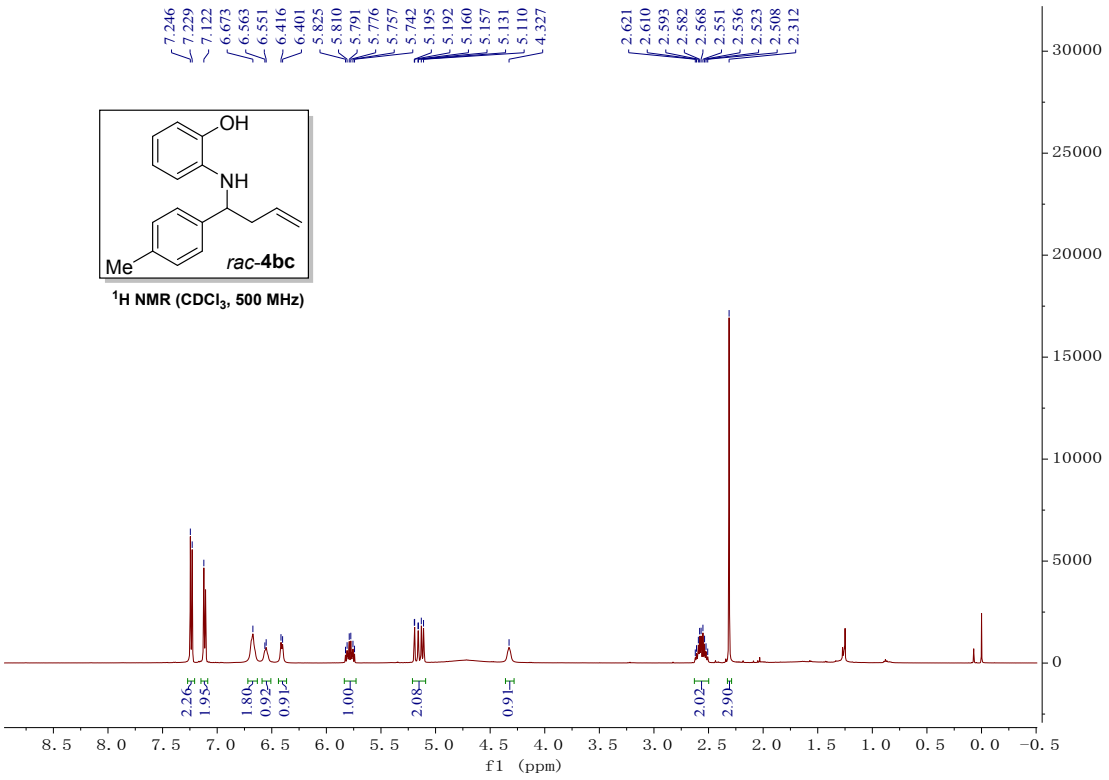
^{1}H, ^{13}C, and ^{19}F NMR spectra copies



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7.229
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6.551
6.416
6.401
5.825
5.810
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5.776
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5.742
5.195
5.192
5.160
5.157
5.131
5.110
4.327
2.621
2.610
2.593
2.582
2.568
2.551
2.536
2.523
2.508
2.312
OH
NH
Me
rac-4bc
1H NMR (CDCl3, 500 MHz)
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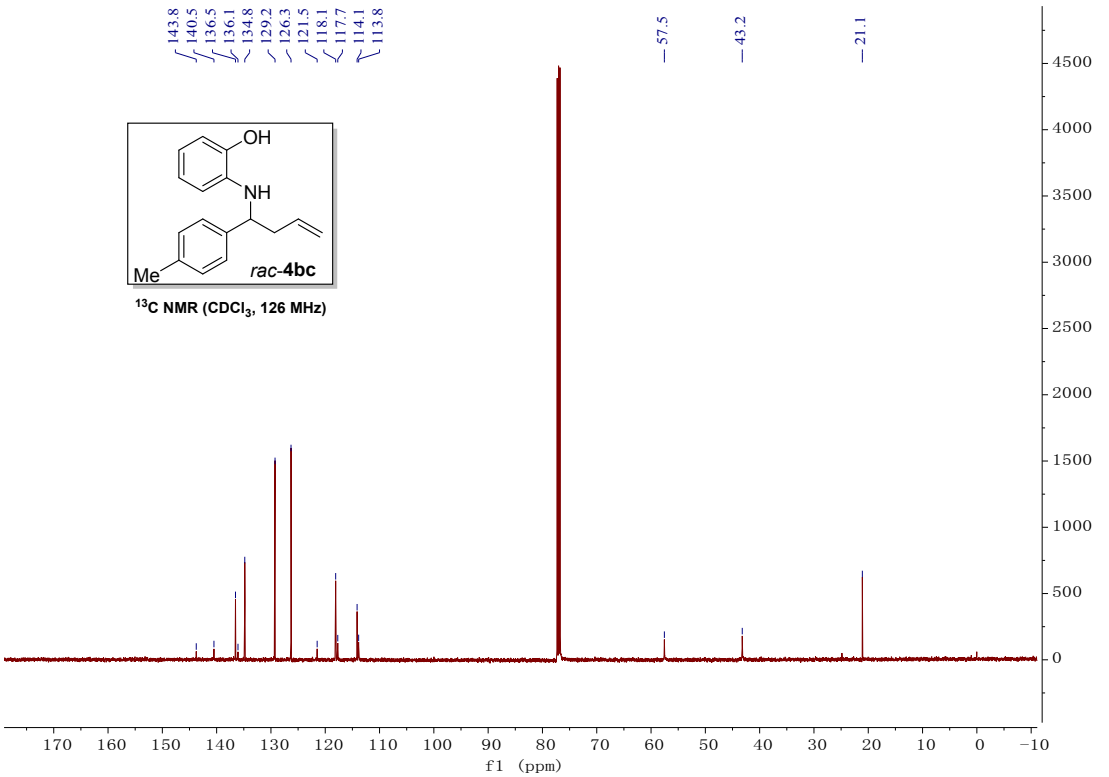
1.80
0.92
0.91
1.00
2.08
0.91
2.02
2.90
f1 (ppm)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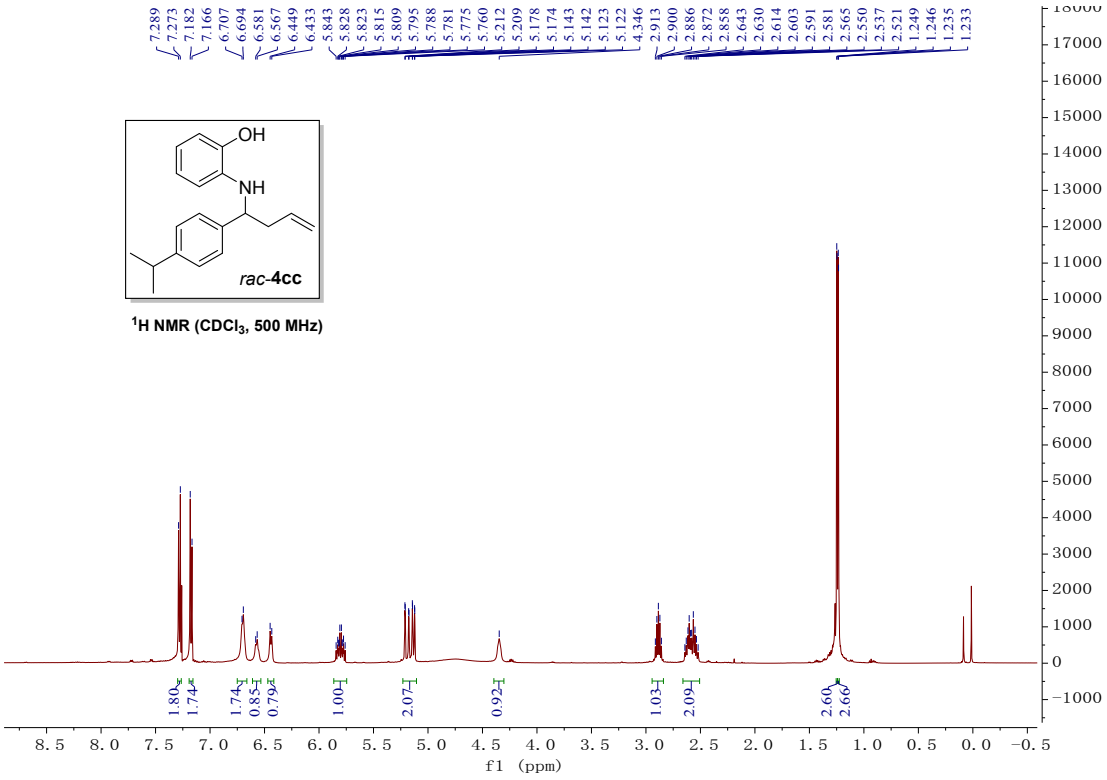
OH
NH
Me
rac-4bc
13C NMR (CDCl3, 126 MHz)
f1 (ppm)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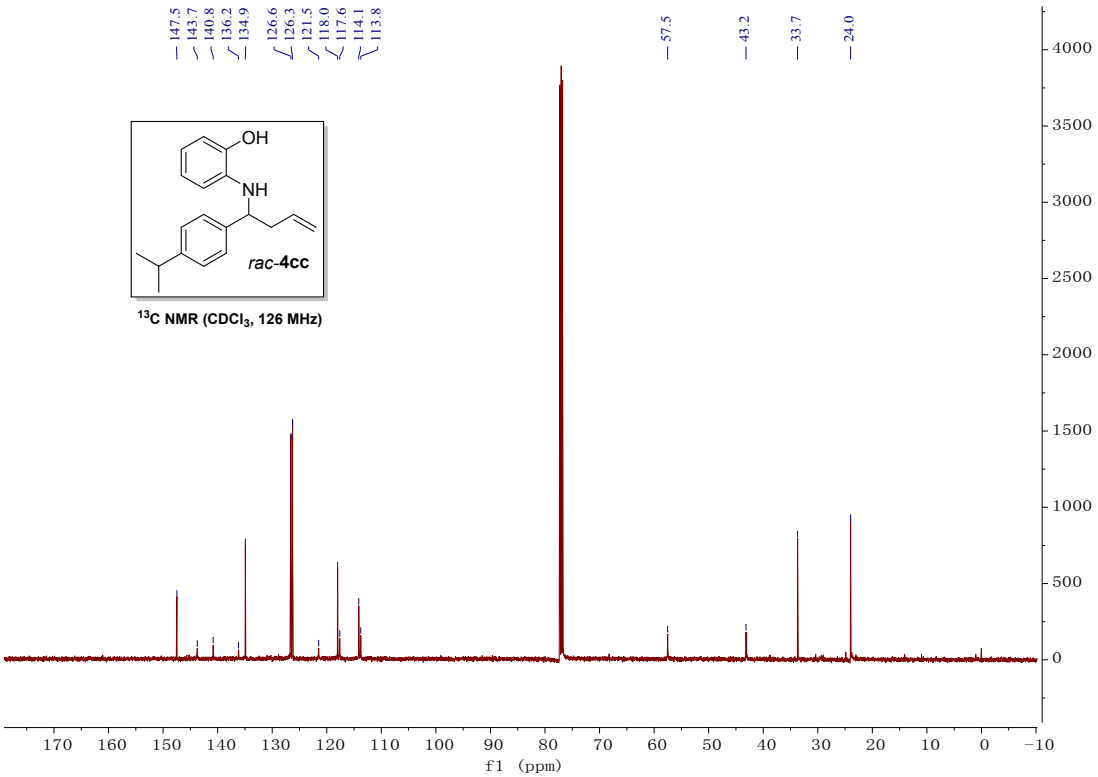
rac-4cc
1H NMR (CDCl3, 500 MHz)
f1 (ppm)


OH
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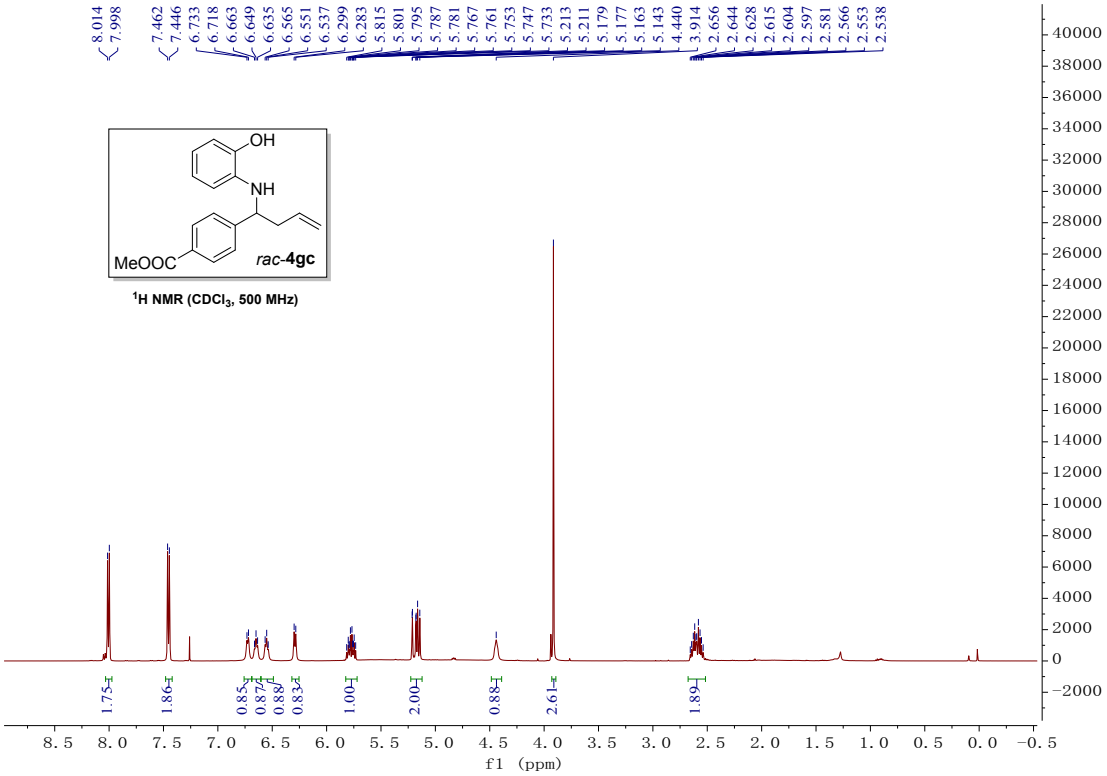
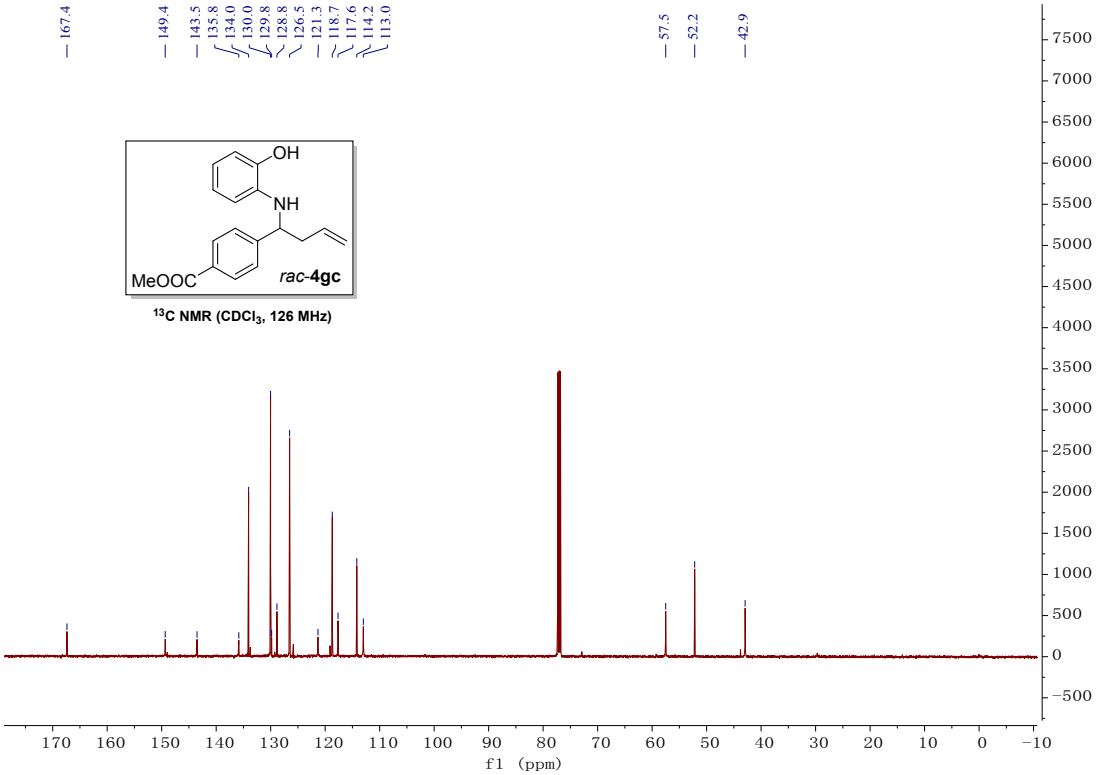
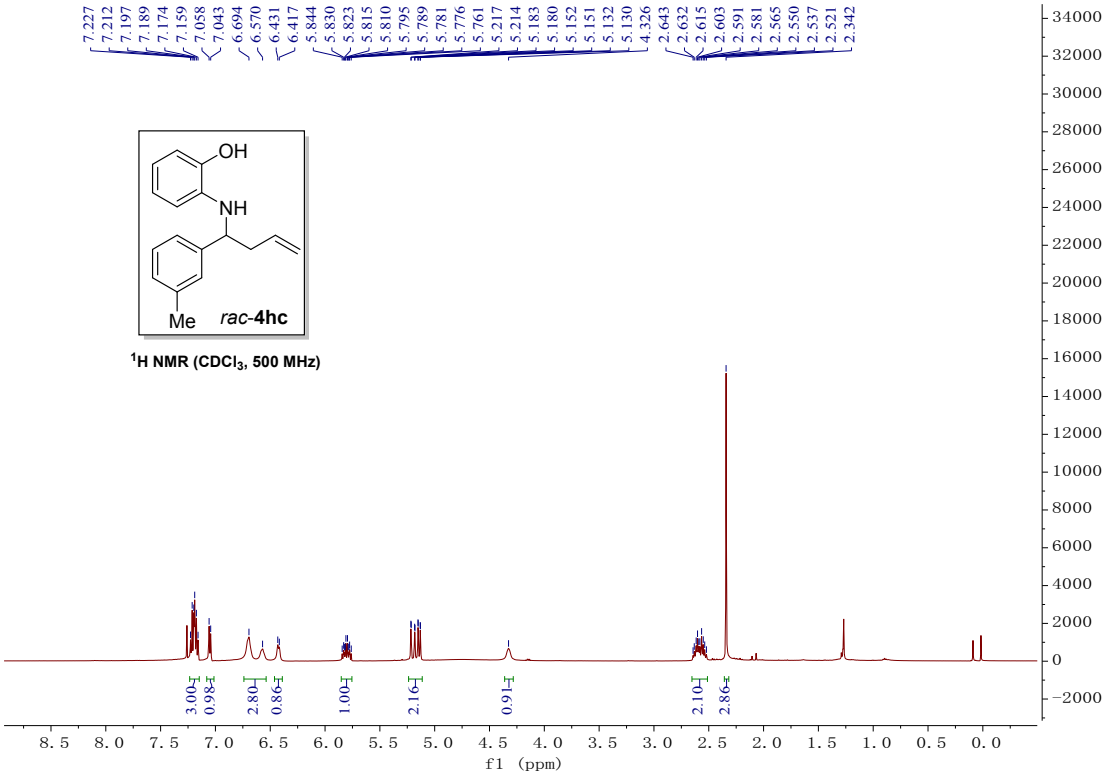
rac-4cc
13C NMR (CDCl3, 126 MHz)
f1 (ppm)



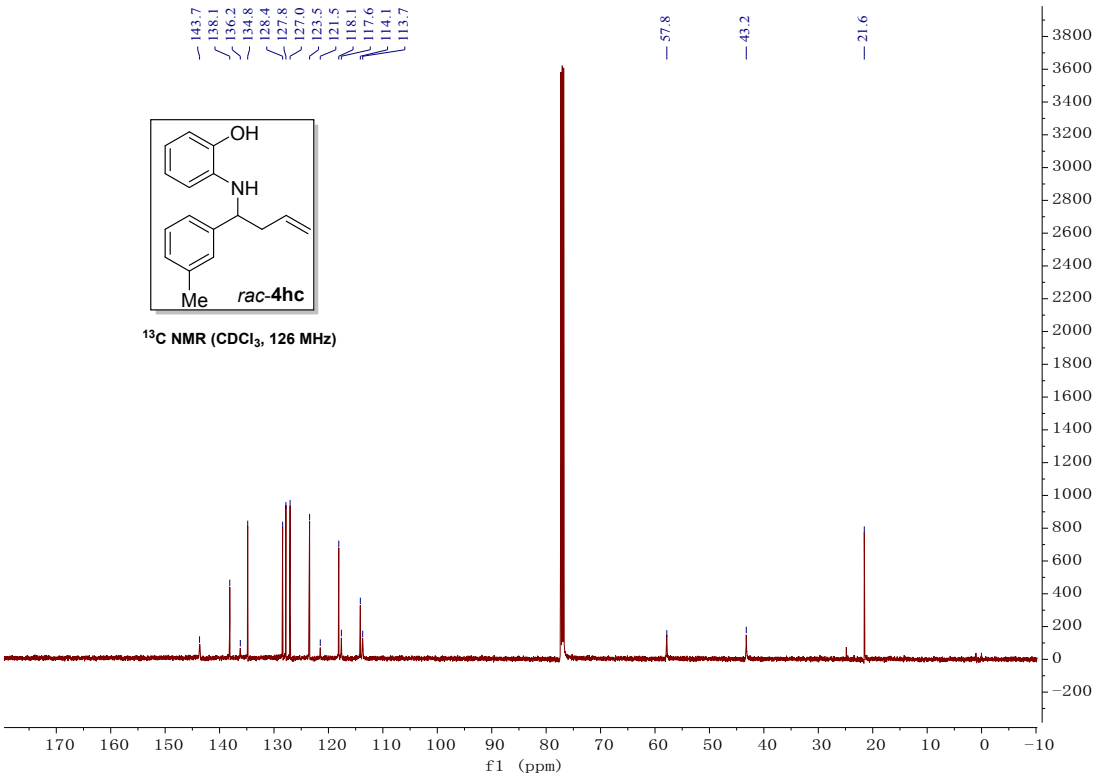
^{1}H NMR ($CDCl_3$, 500 MHz)



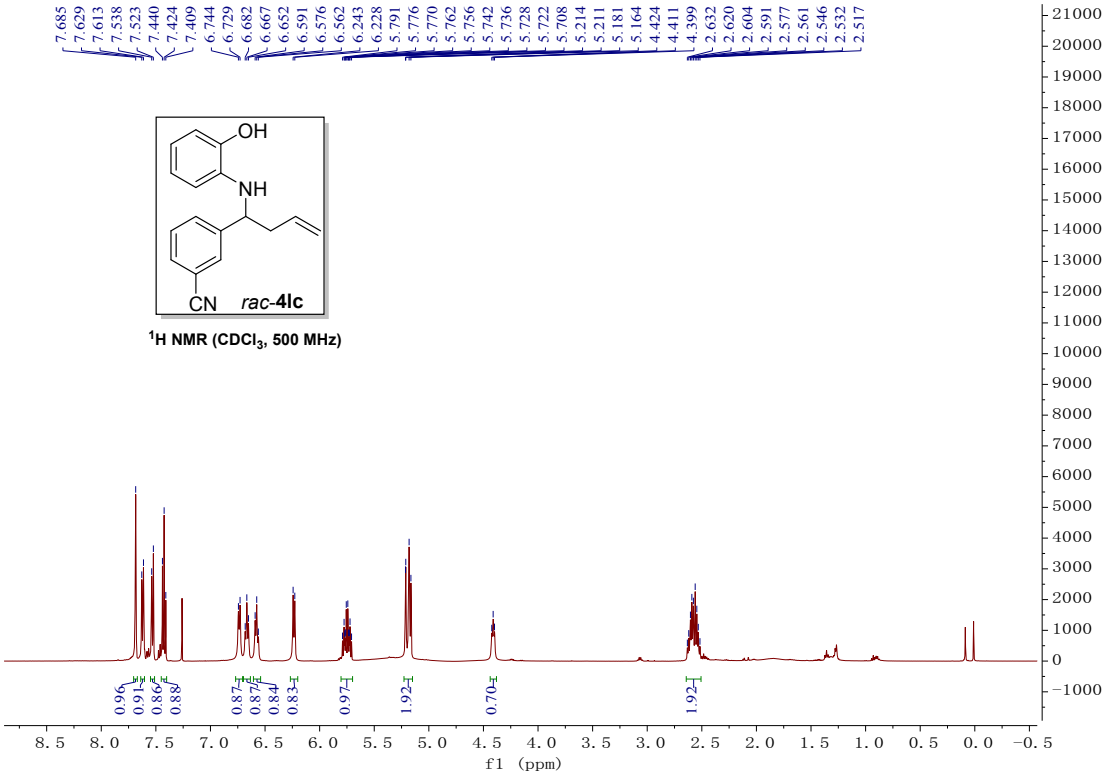
^{13}C NMR ($CDCl_3$, 126 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)



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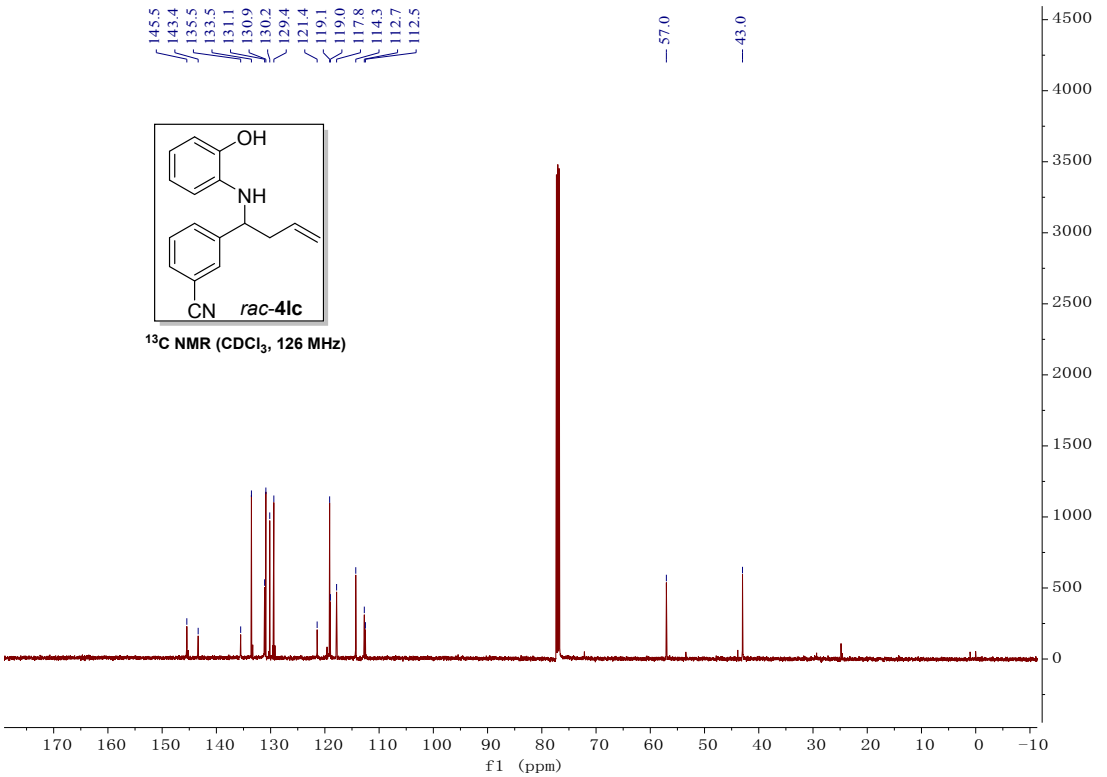

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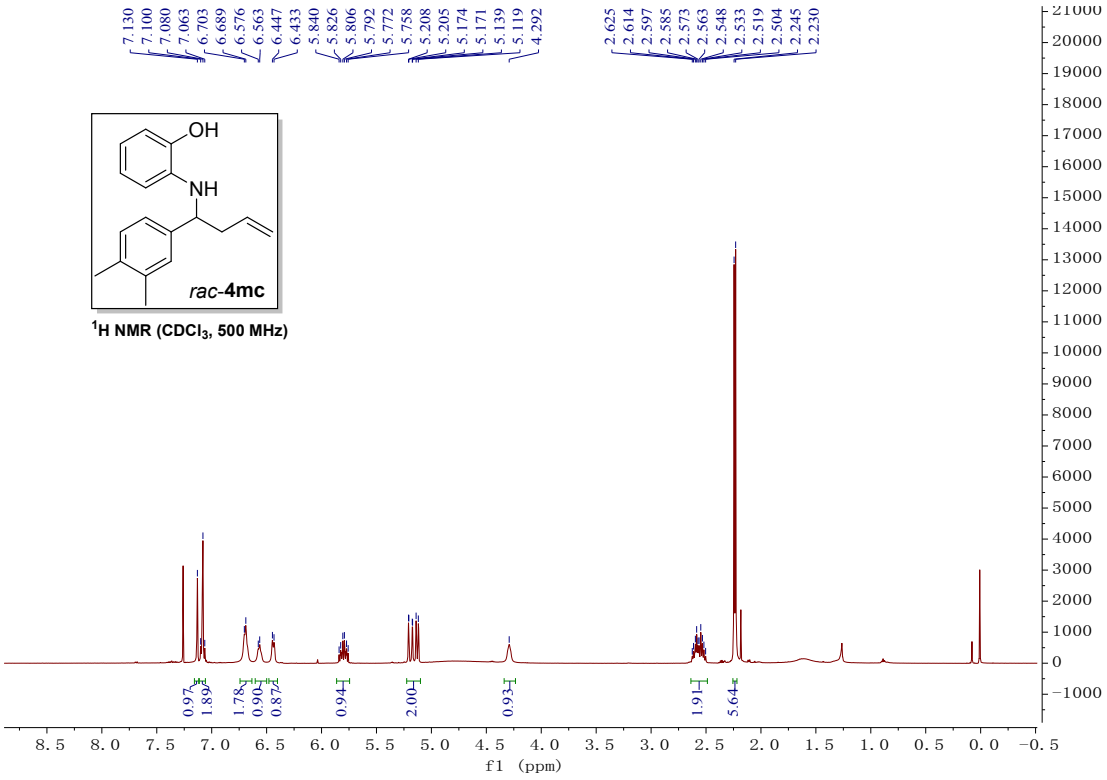

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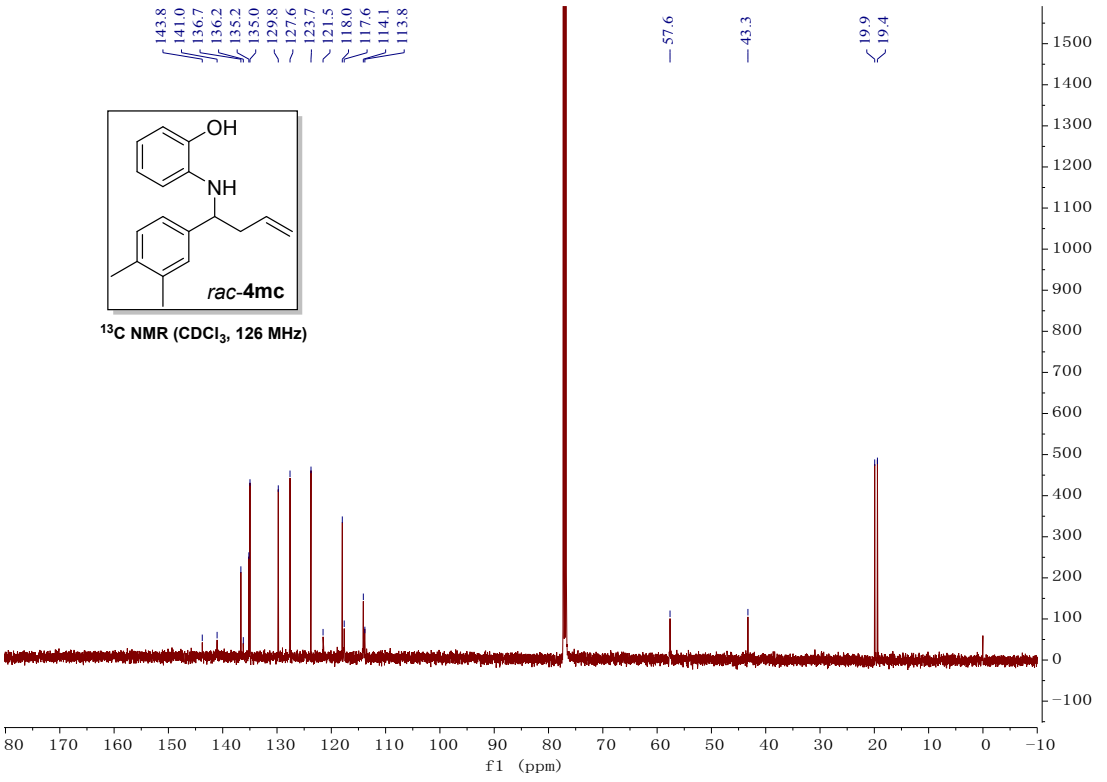
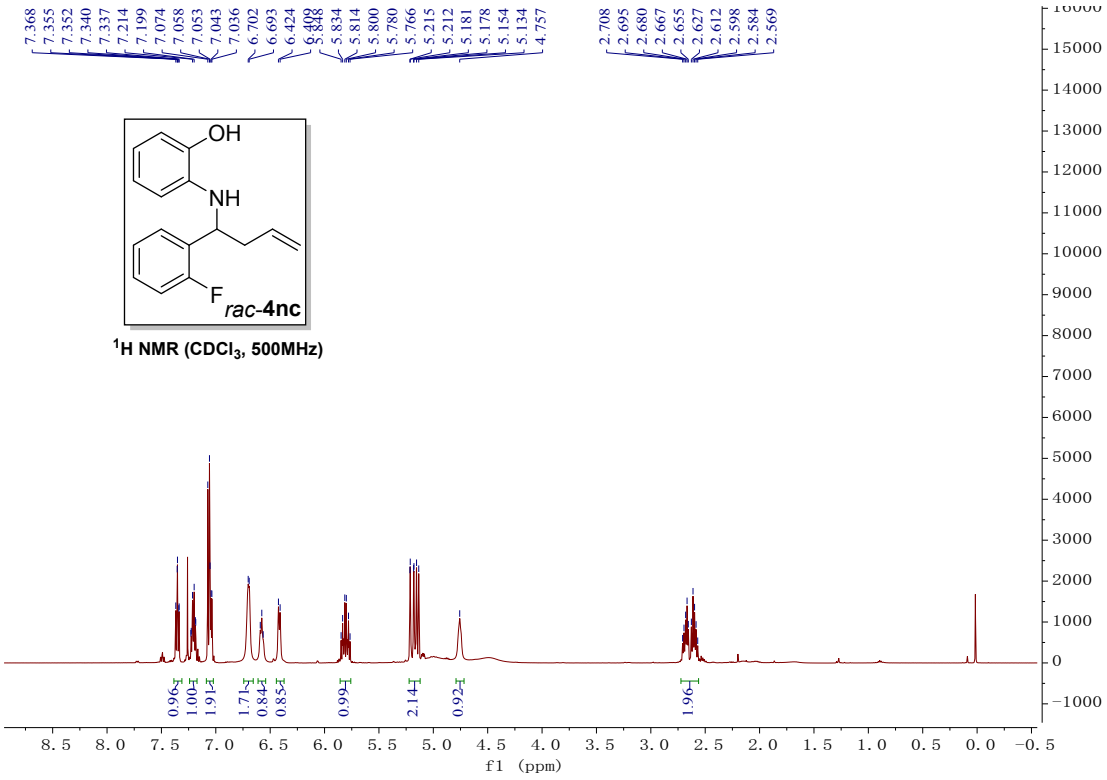
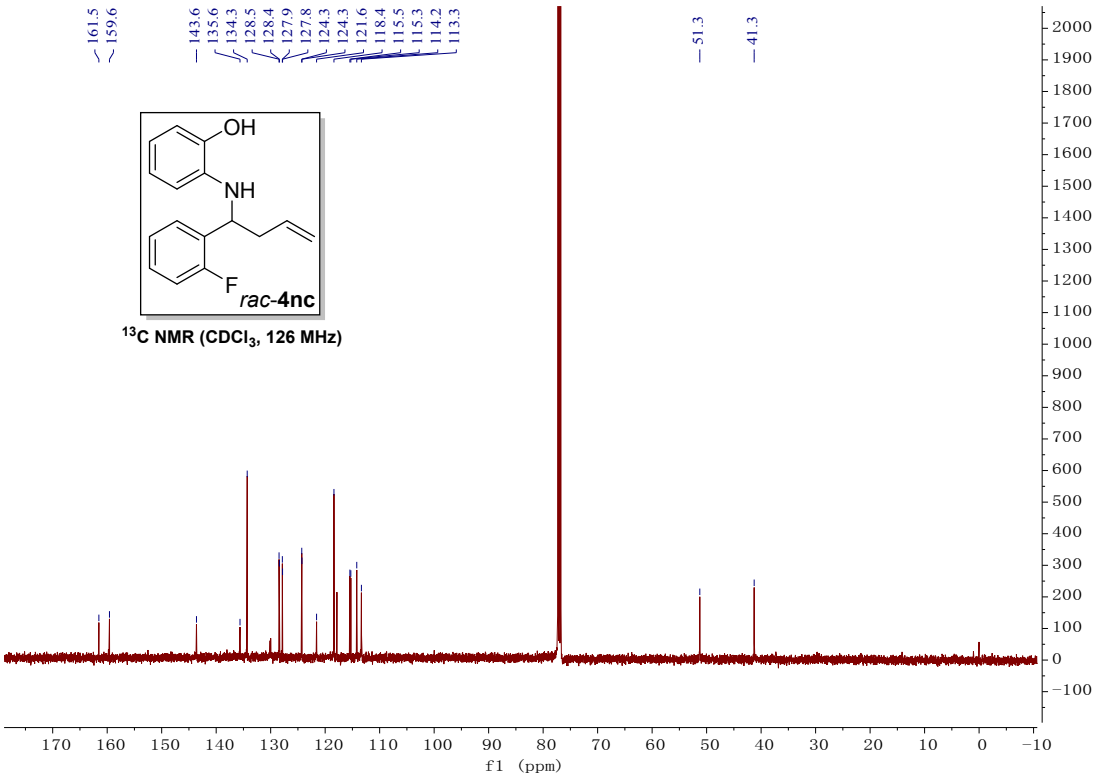


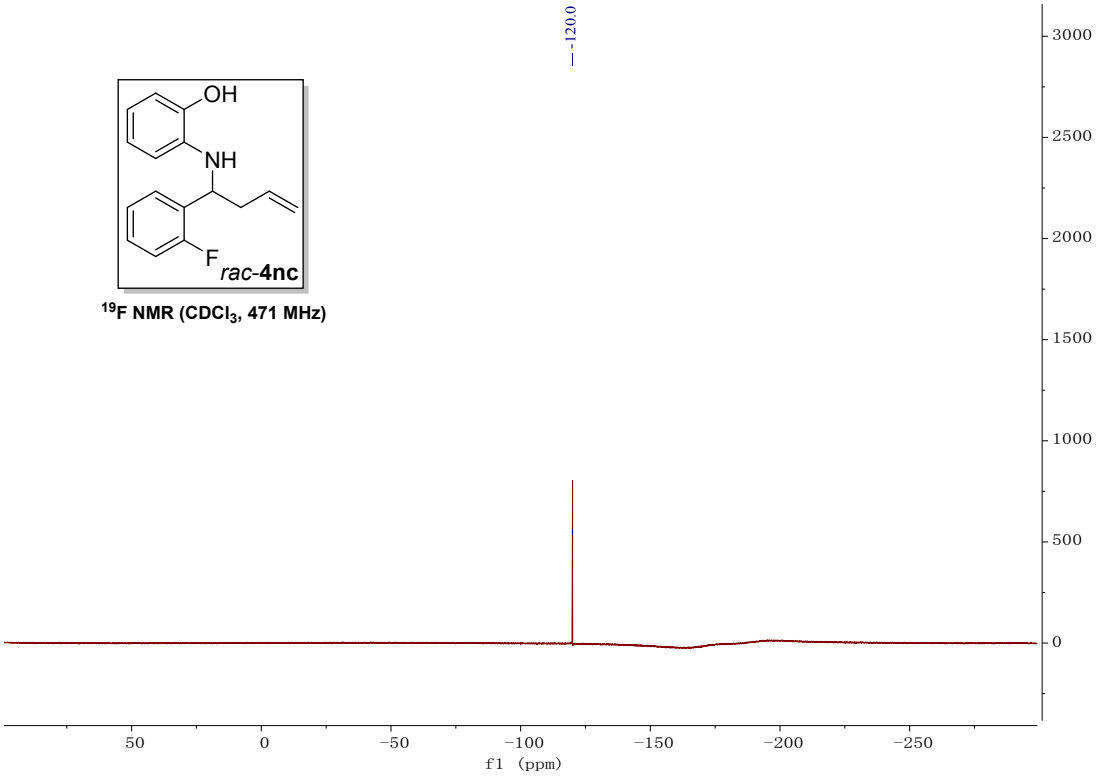
^{13}C NMR ($CDCl_3$, 126 MHz)



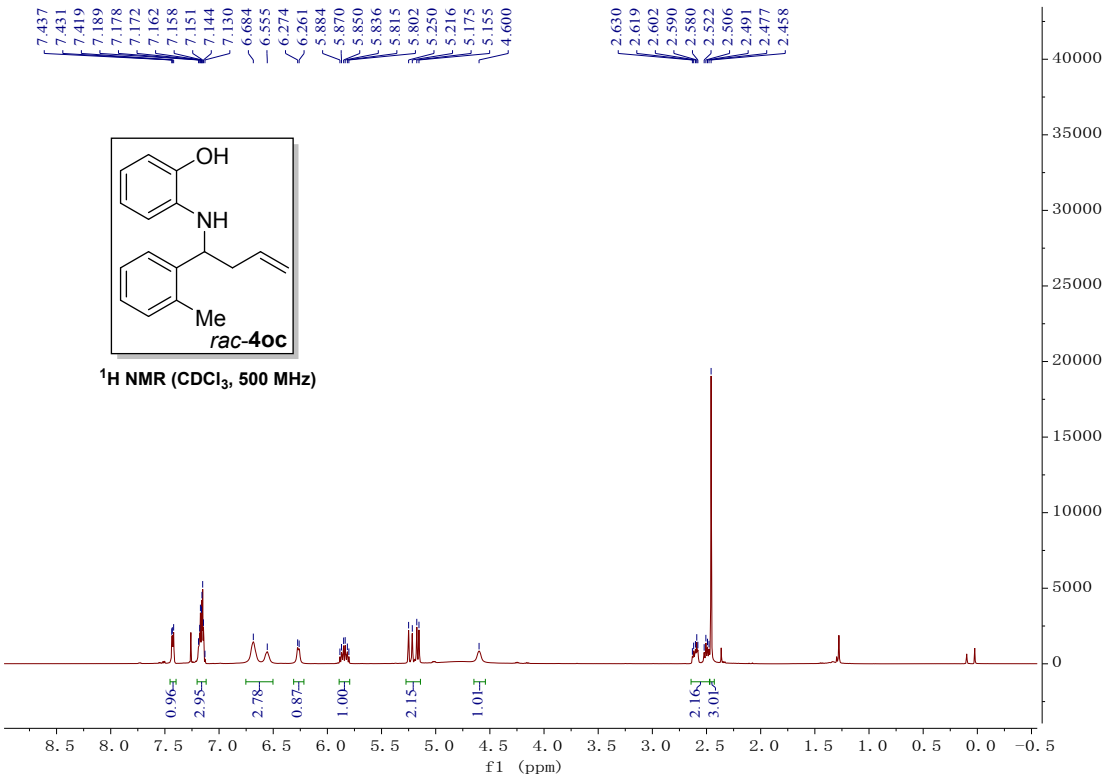
^{1}H NMR ($CDCl_3$, 500MHz)



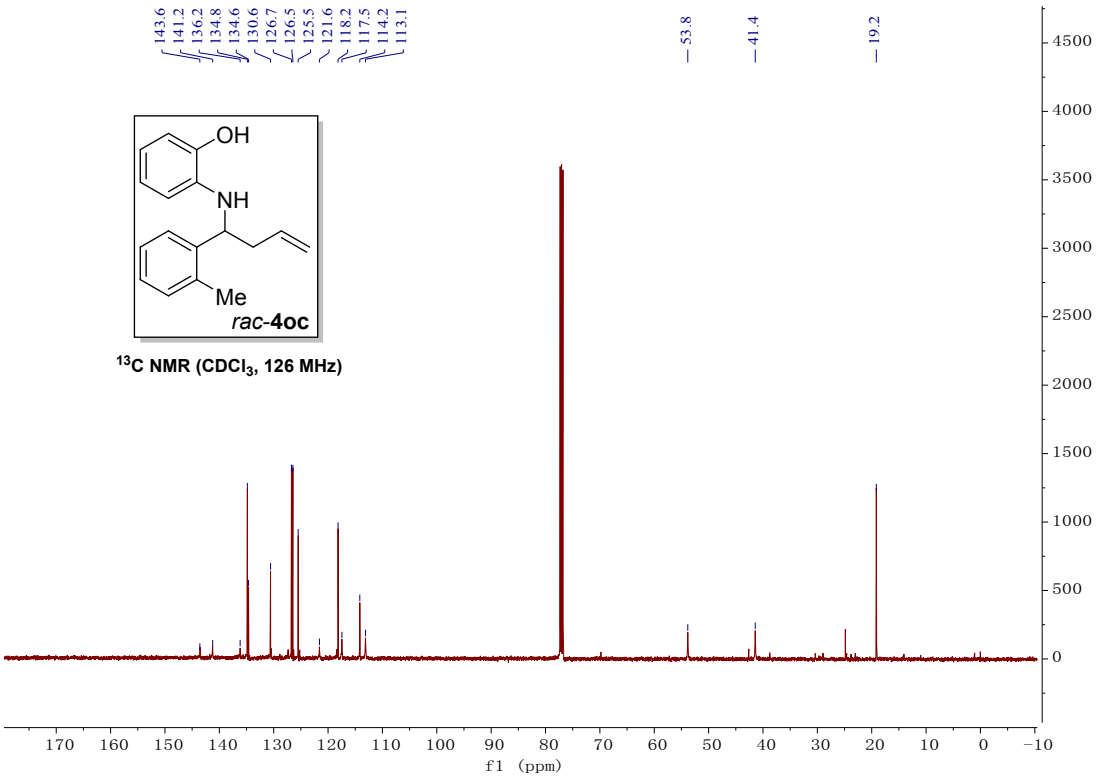
^{13}C NMR ($CDCl_3$, 126 MHz)



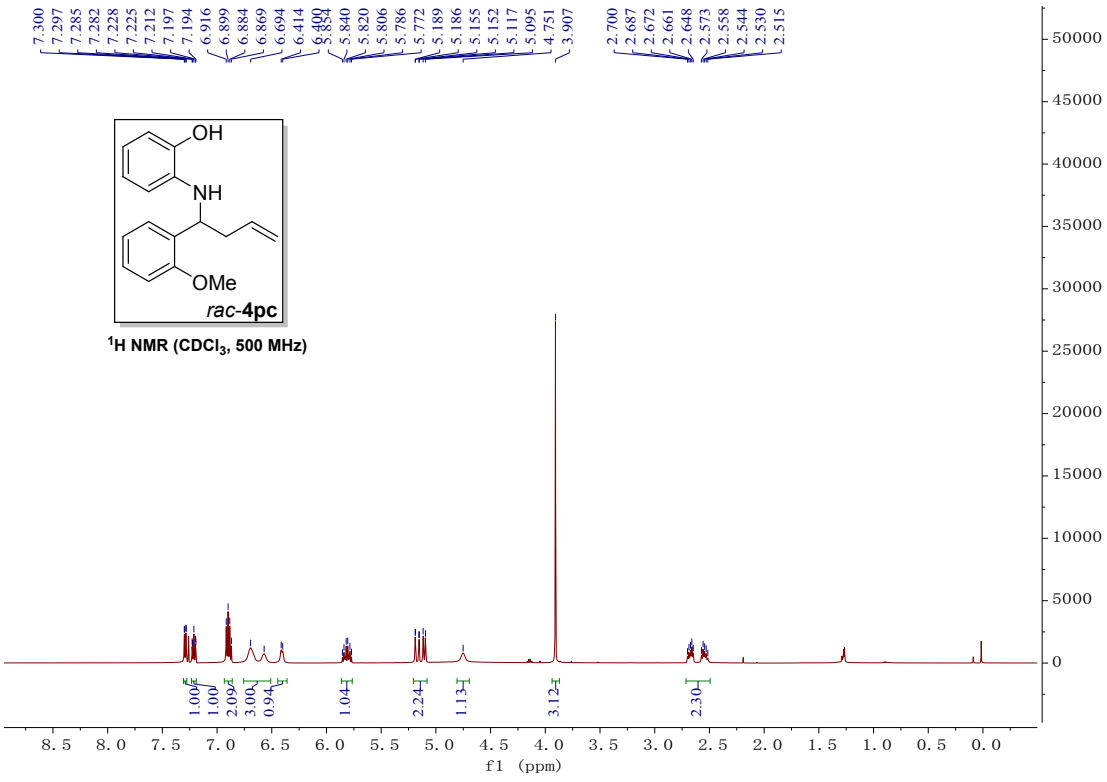
^{19}F NMR ($CDCl_3$, 471 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)



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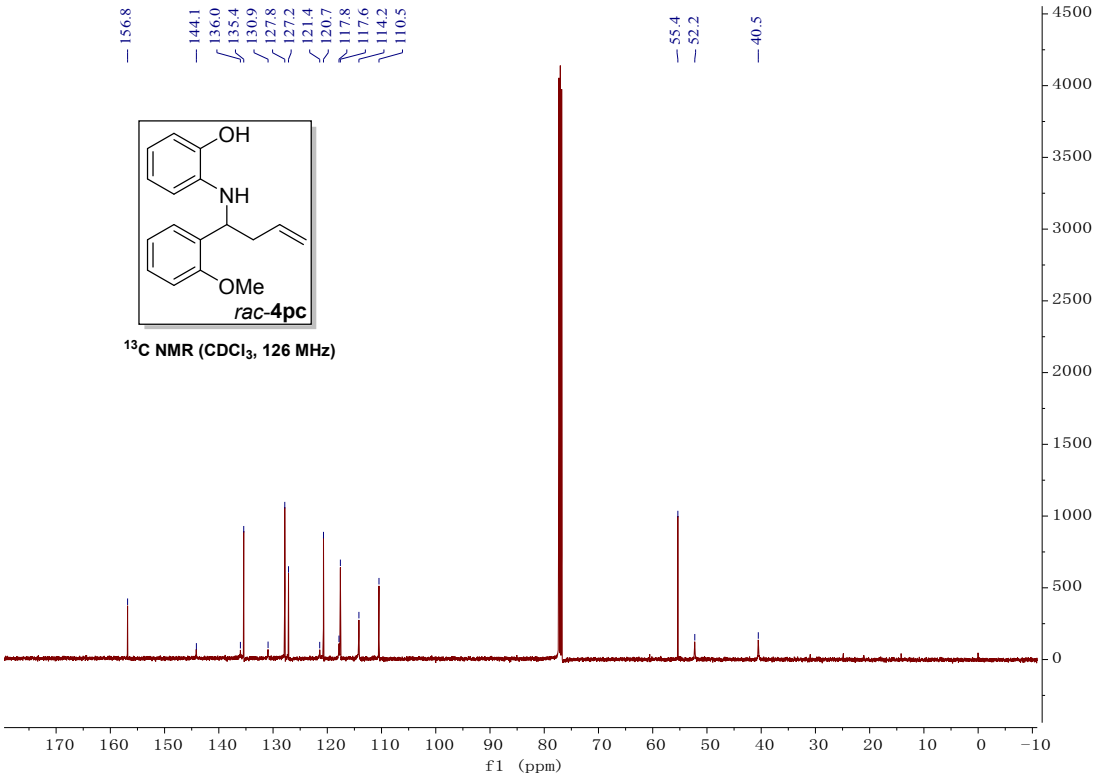
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110.5
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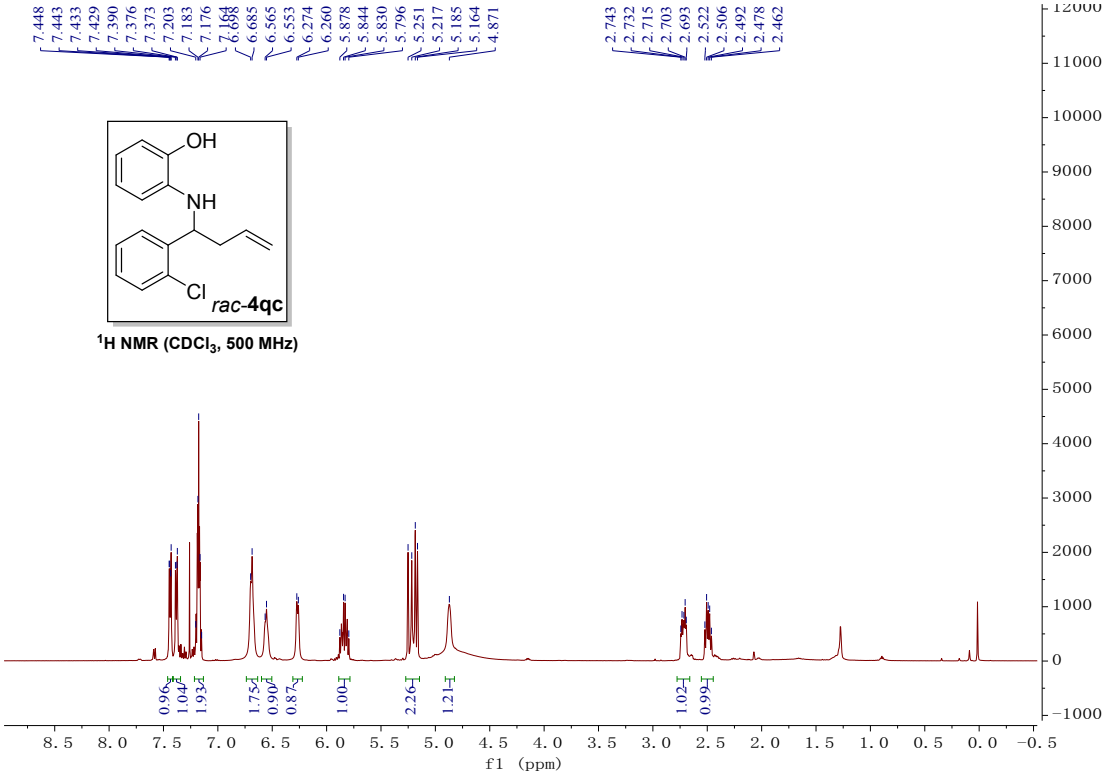
OH
NH
OMe
rac-4pc
13C NMR (CDCl3, 126 MHz)
f1 (ppm)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6.685
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6.553
6.274
6.260
5.878
5.844
5.830
5.796
5.251
5.217
5.185
5.164
4.871
2.743
2.732
2.715
2.703
2.693
2.522
2.506
2.492
2.478
2.462
OH
NH
Cl
rac-4qc
1H NMR (CDCl3, 500 MHz)
0.96
1.04
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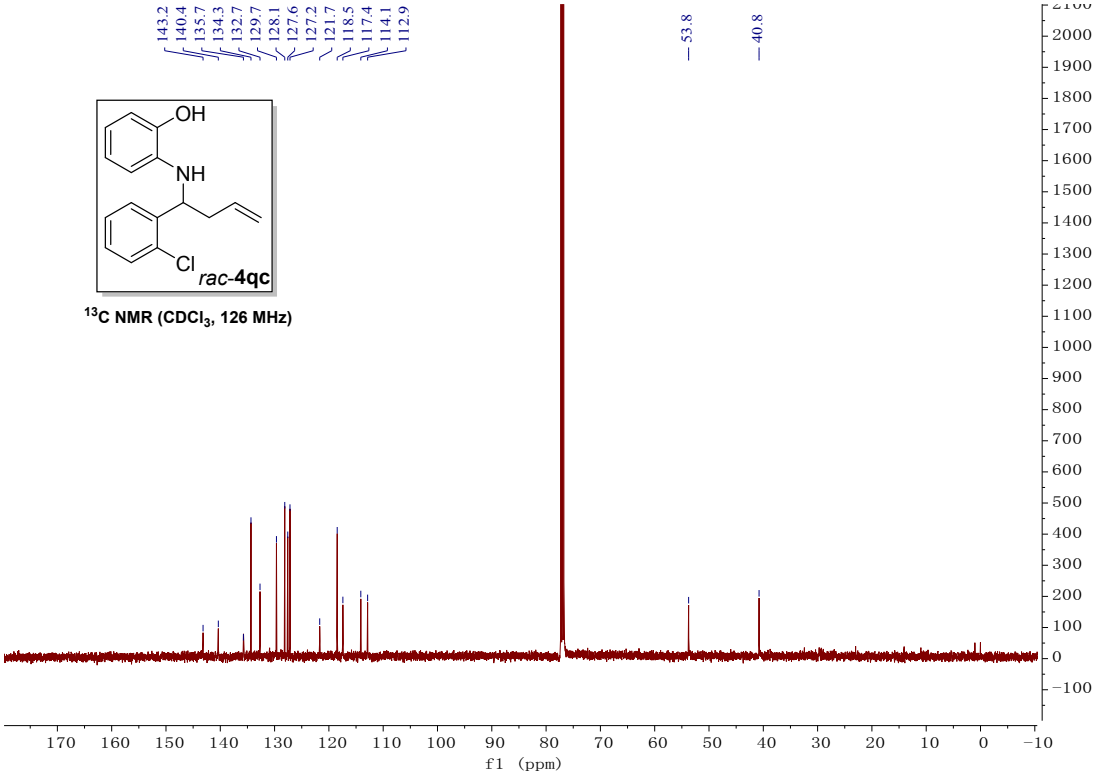
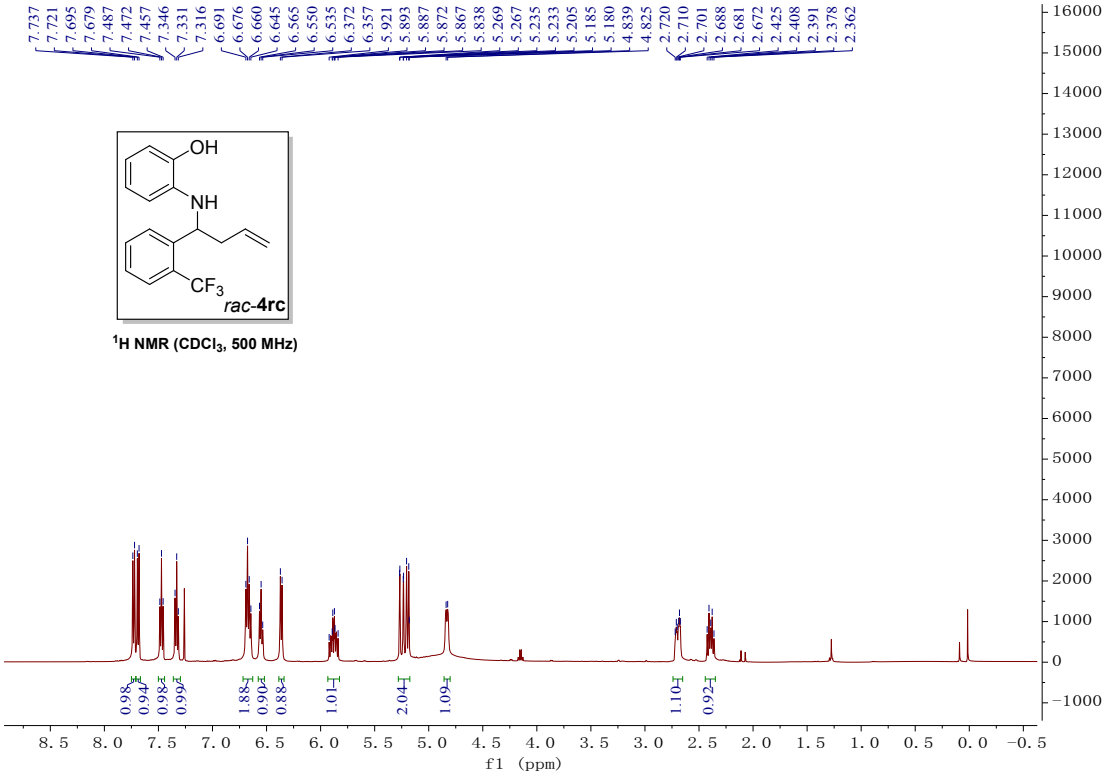
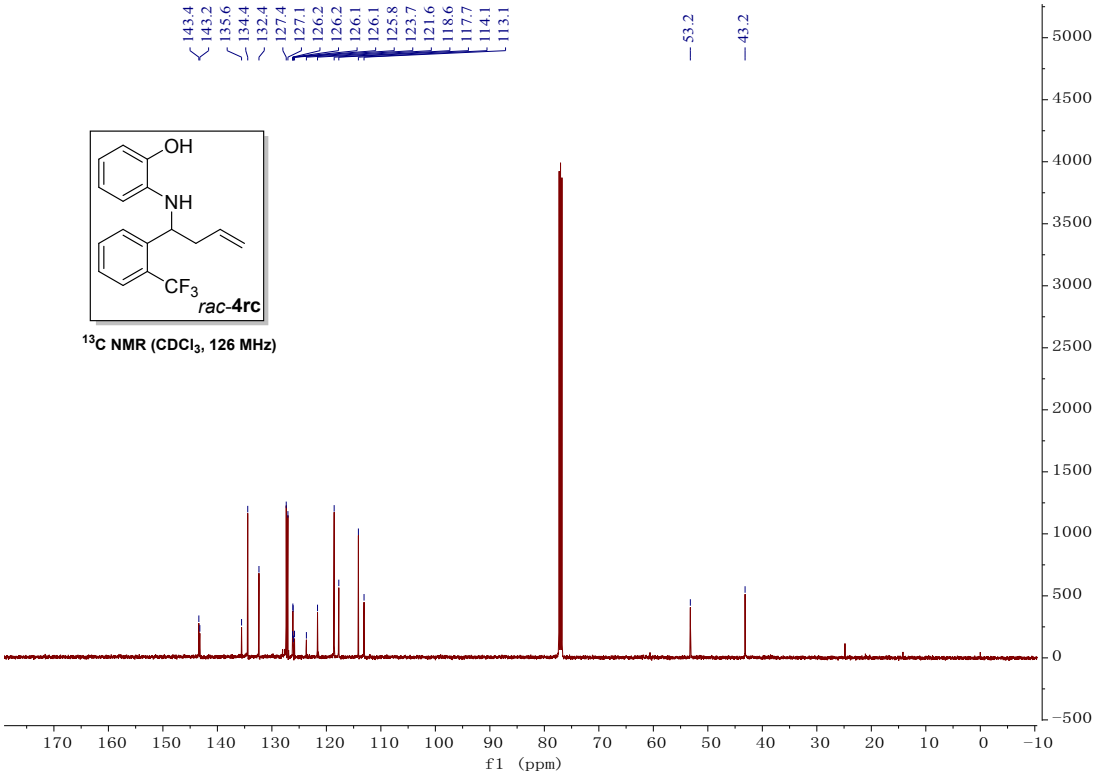
1.75
0.90
0.87
1.00
2.26
1.21
1.02
0.99
f1 (ppm)



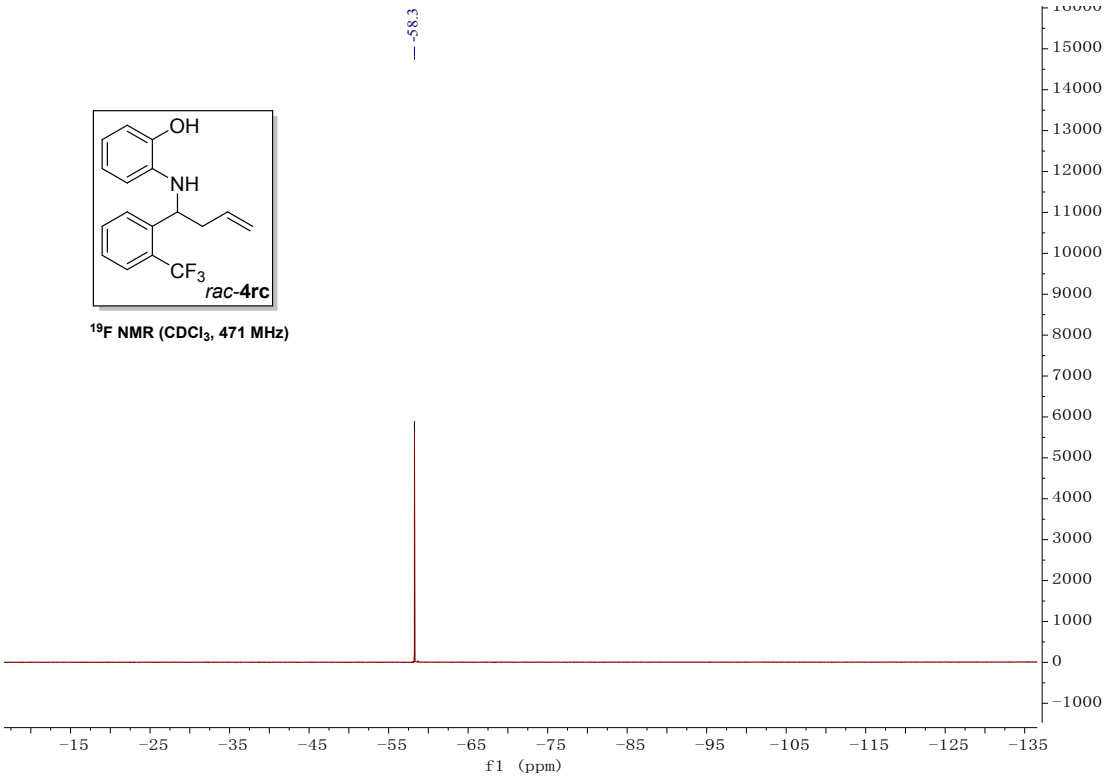
^{13}C NMR ($CDCl_3$, 126 MHz)



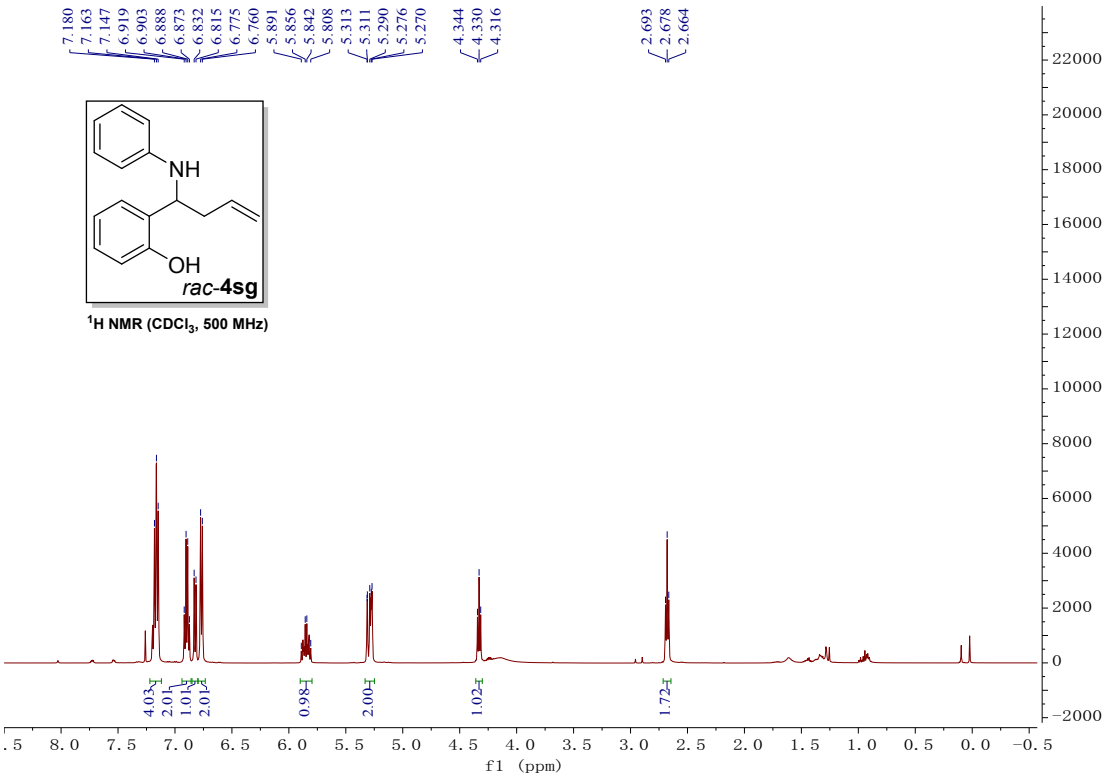
^{1}H NMR ($CDCl_3$, 500 MHz)



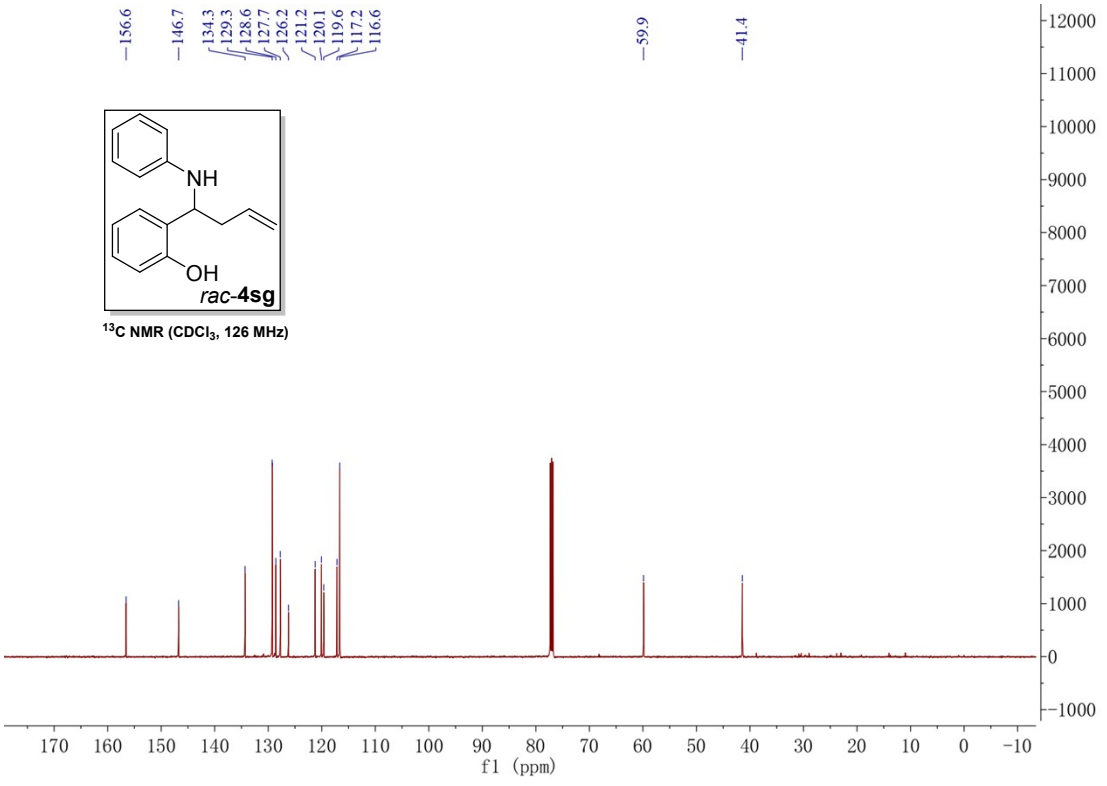
^{13}C NMR ($CDCl_3$, 126 MHz)



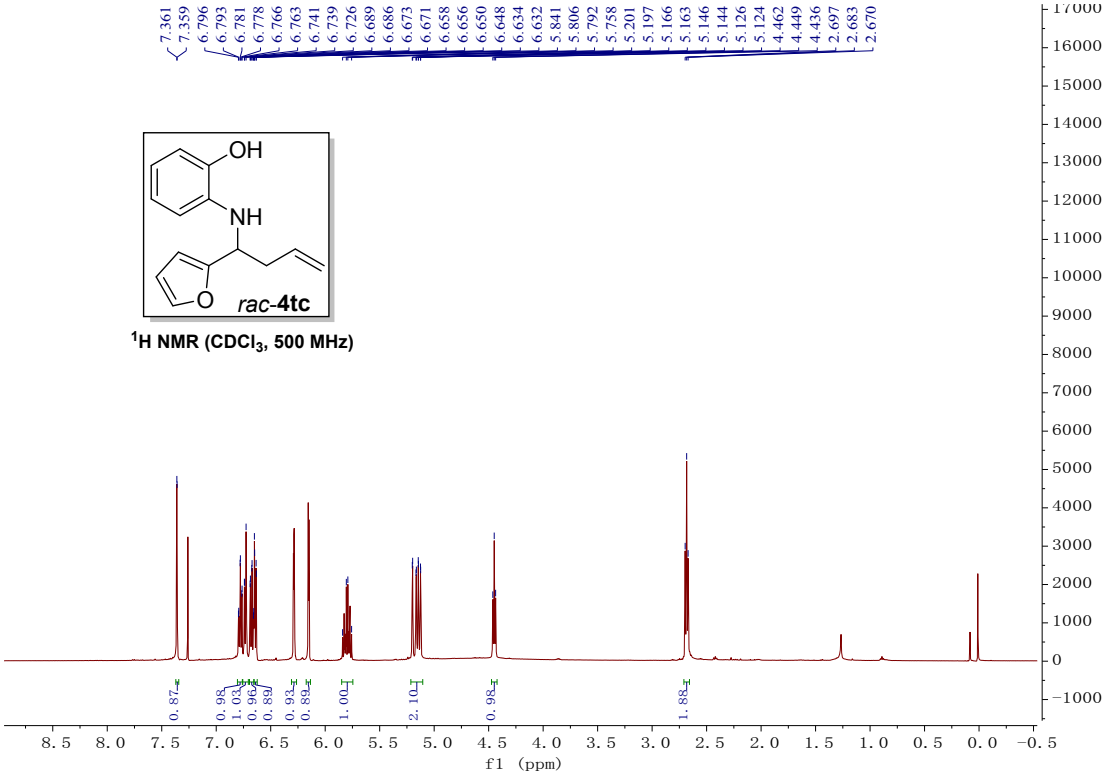
^{19}F NMR ($CDCl_3$, 471 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)



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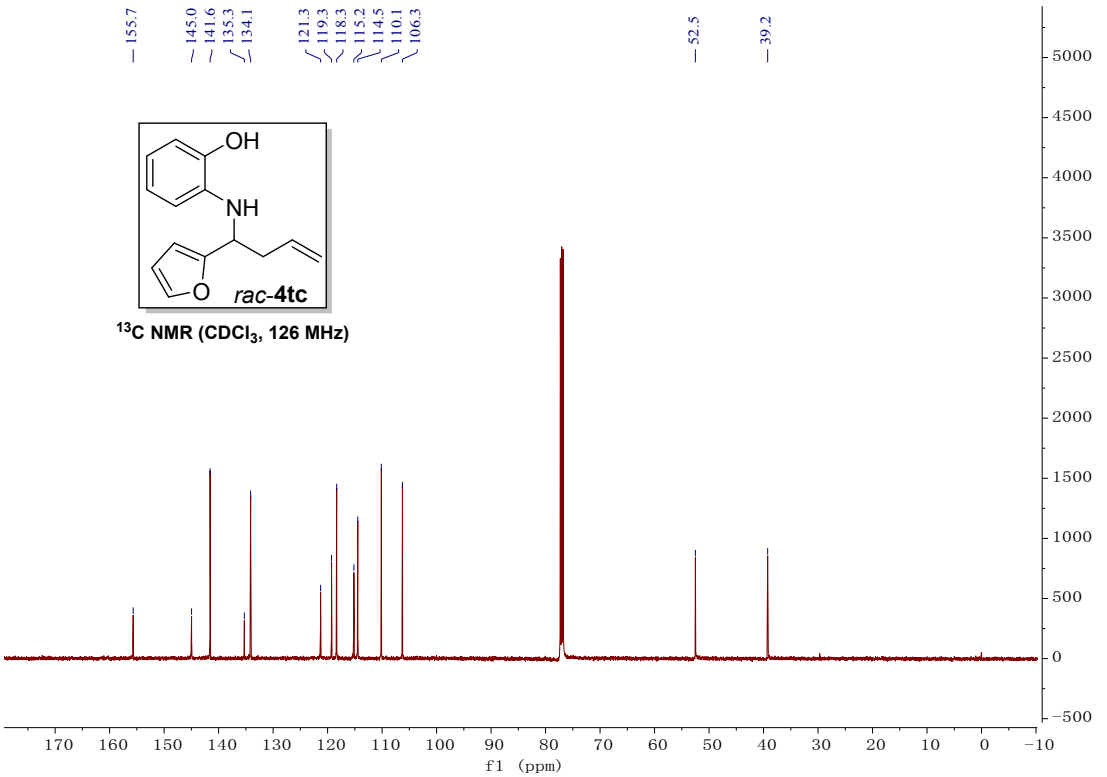

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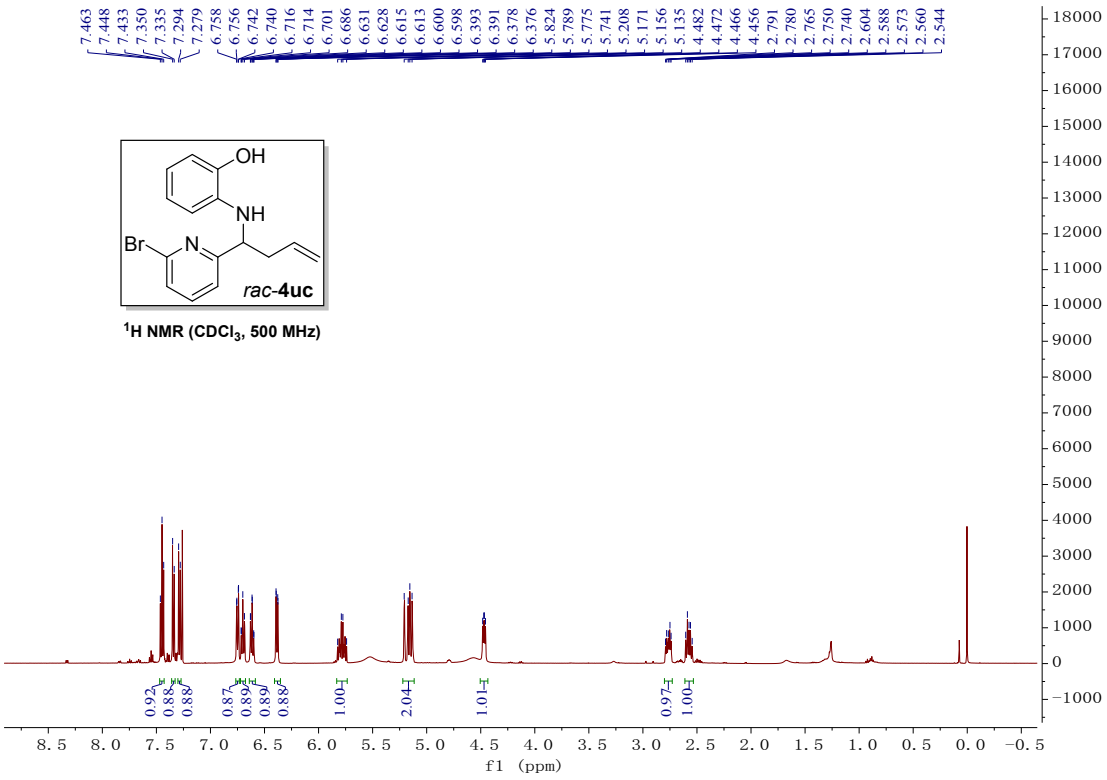

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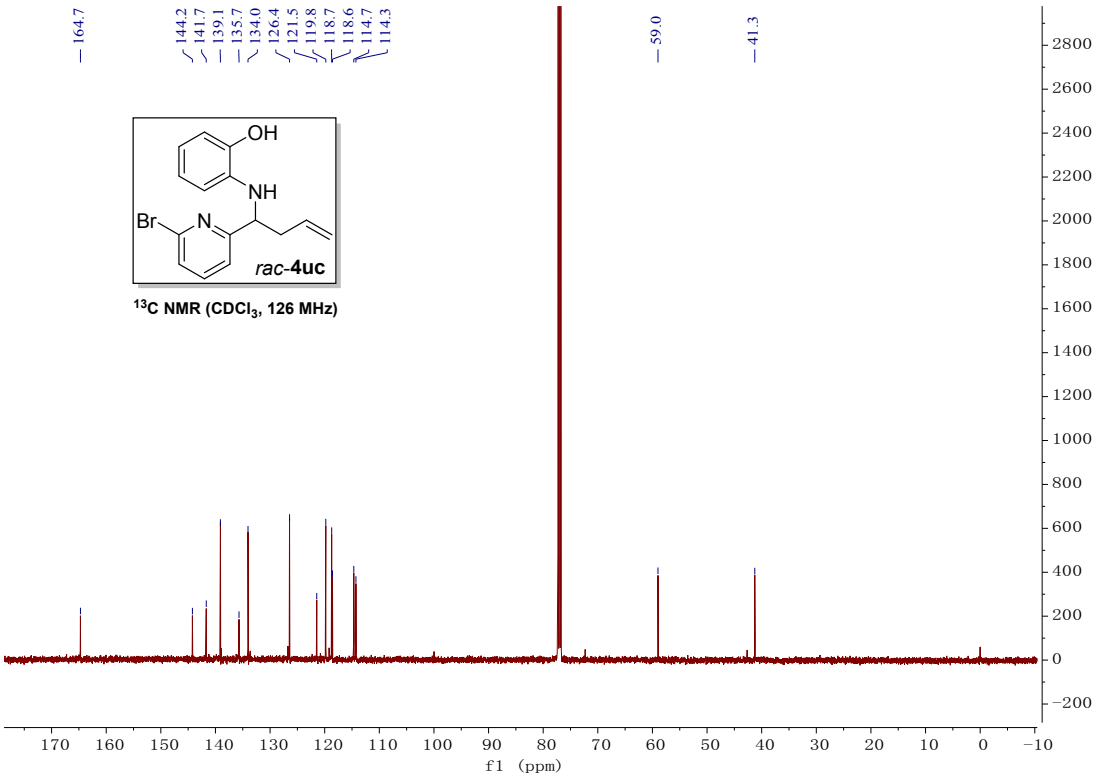

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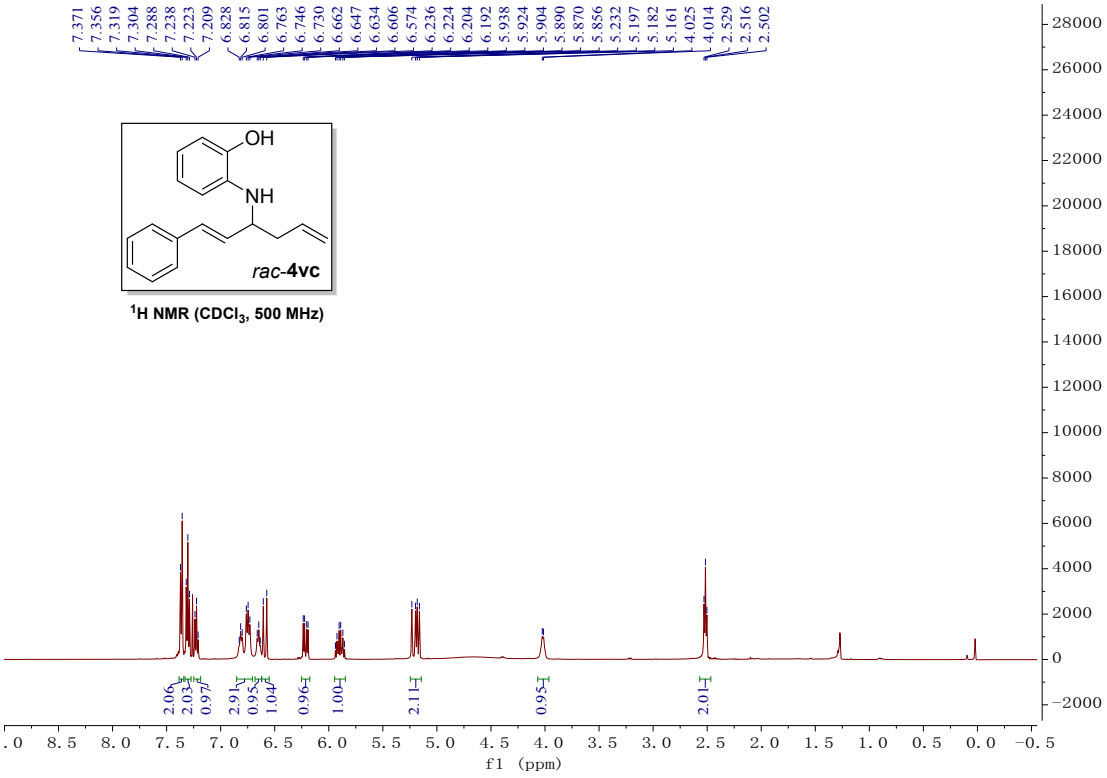

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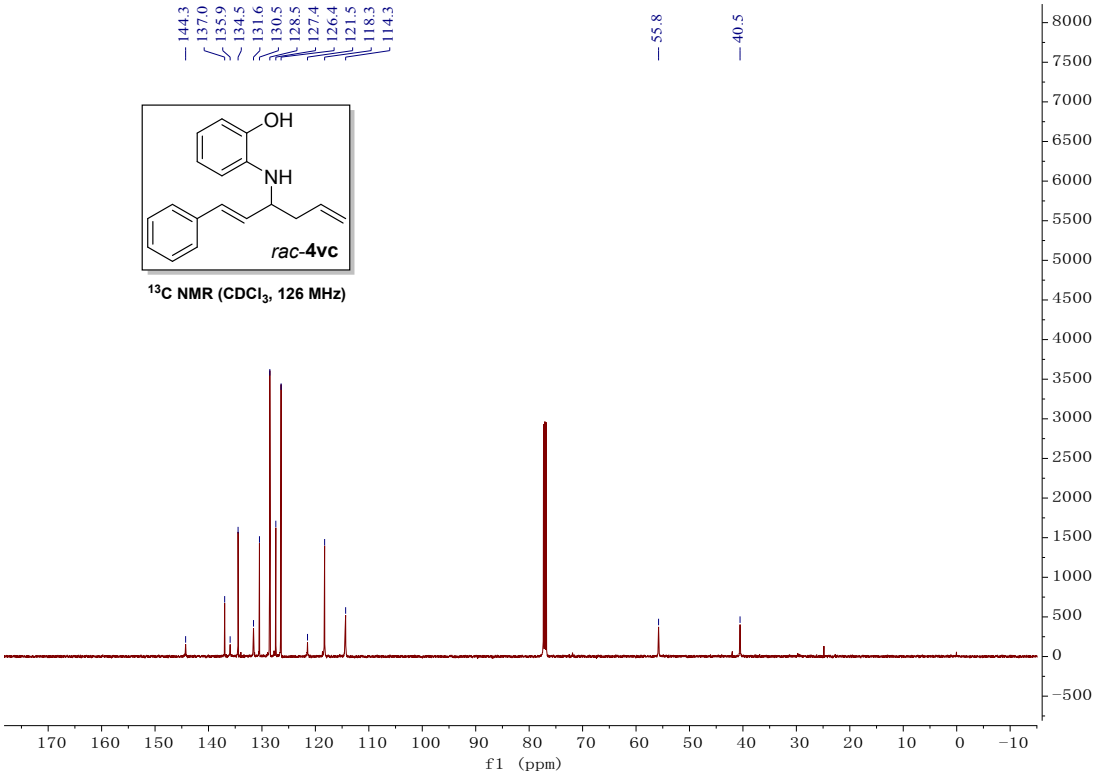

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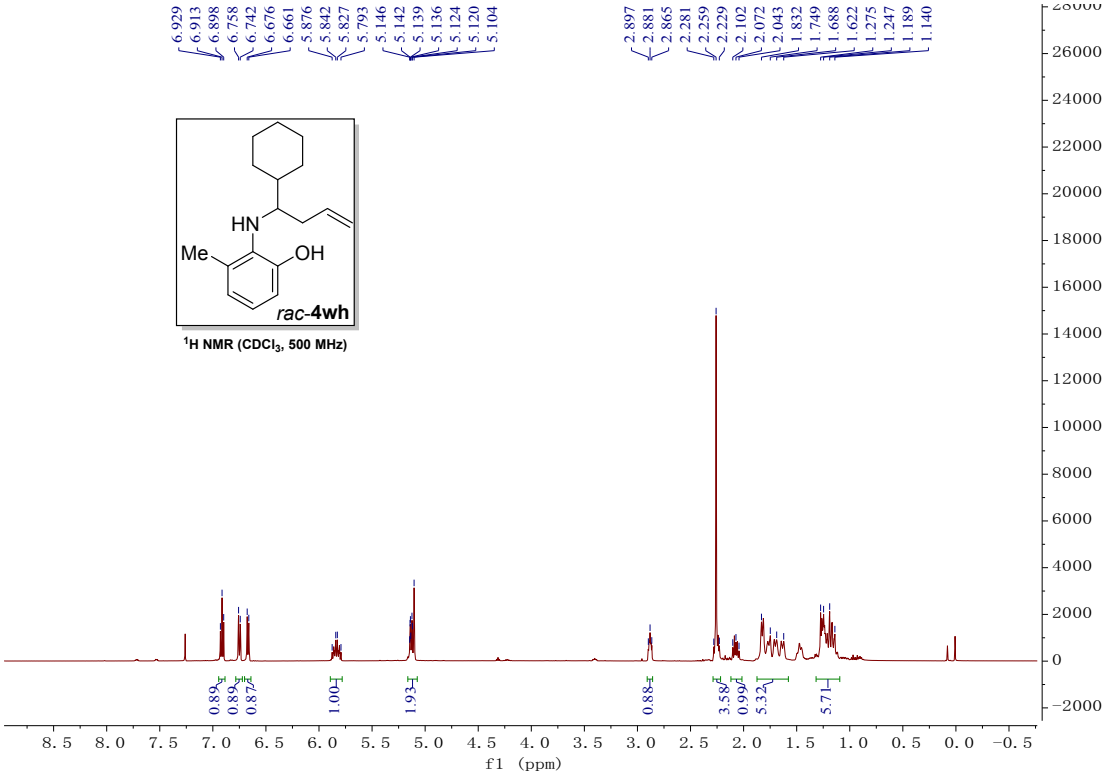

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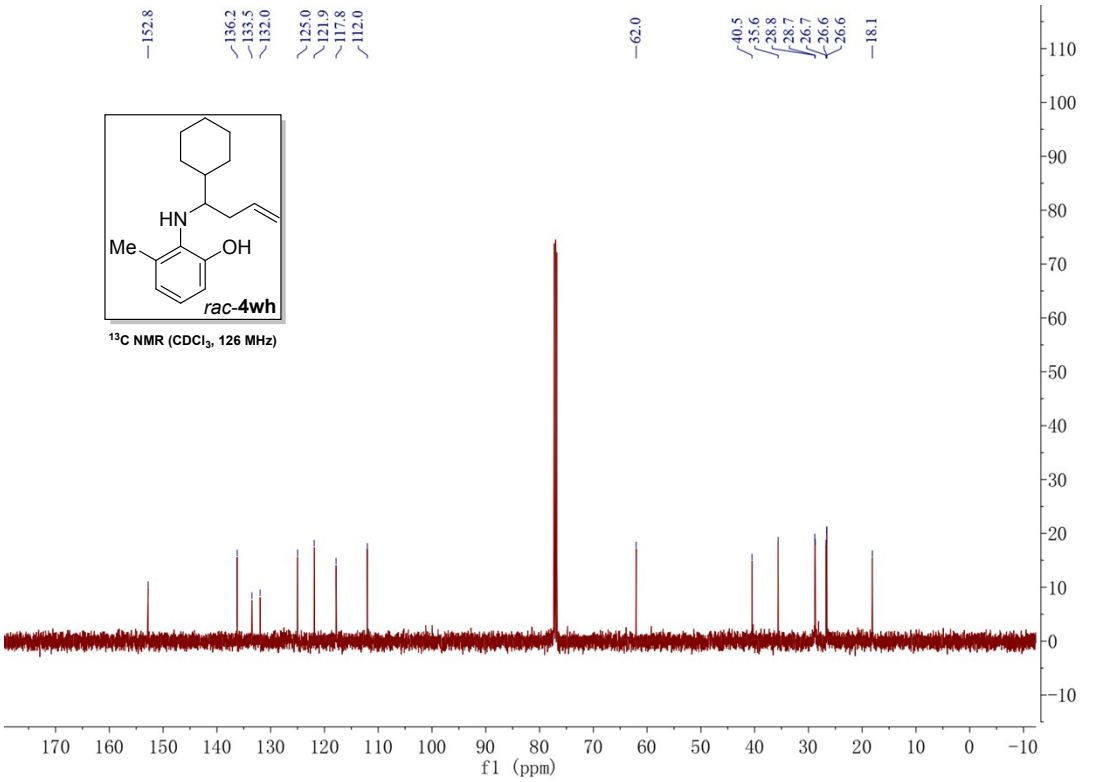
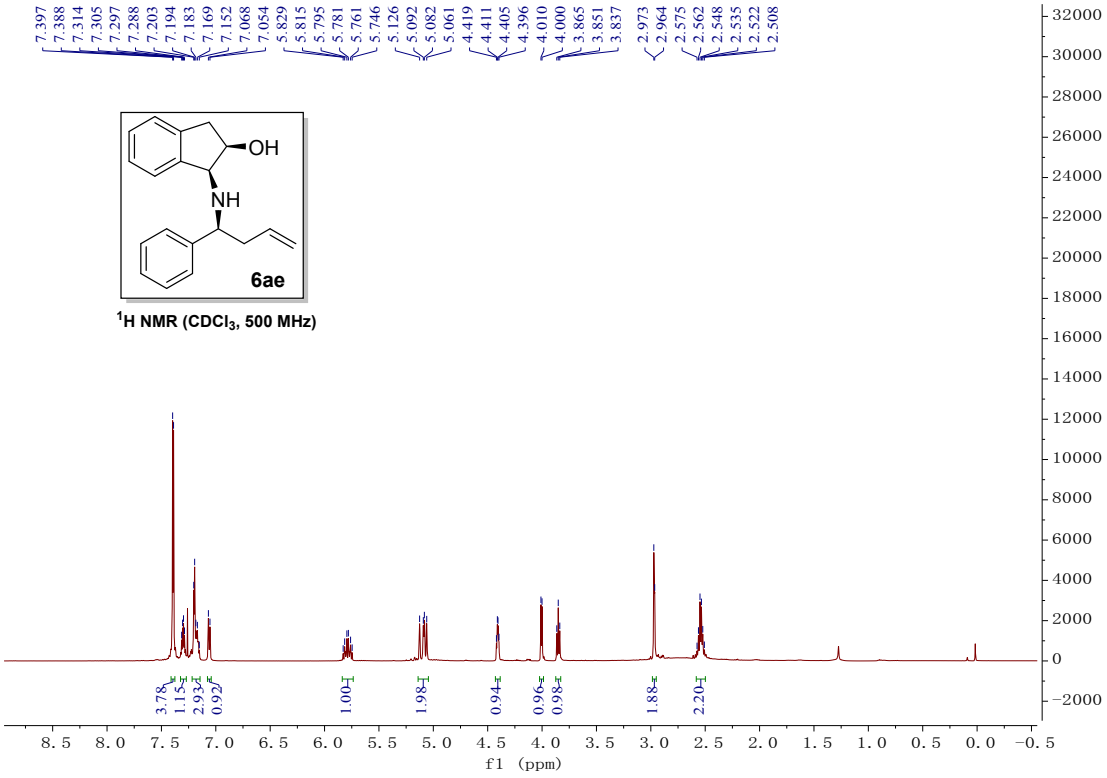


^{13}C NMR ($CDCl_3$, 126 MHz)



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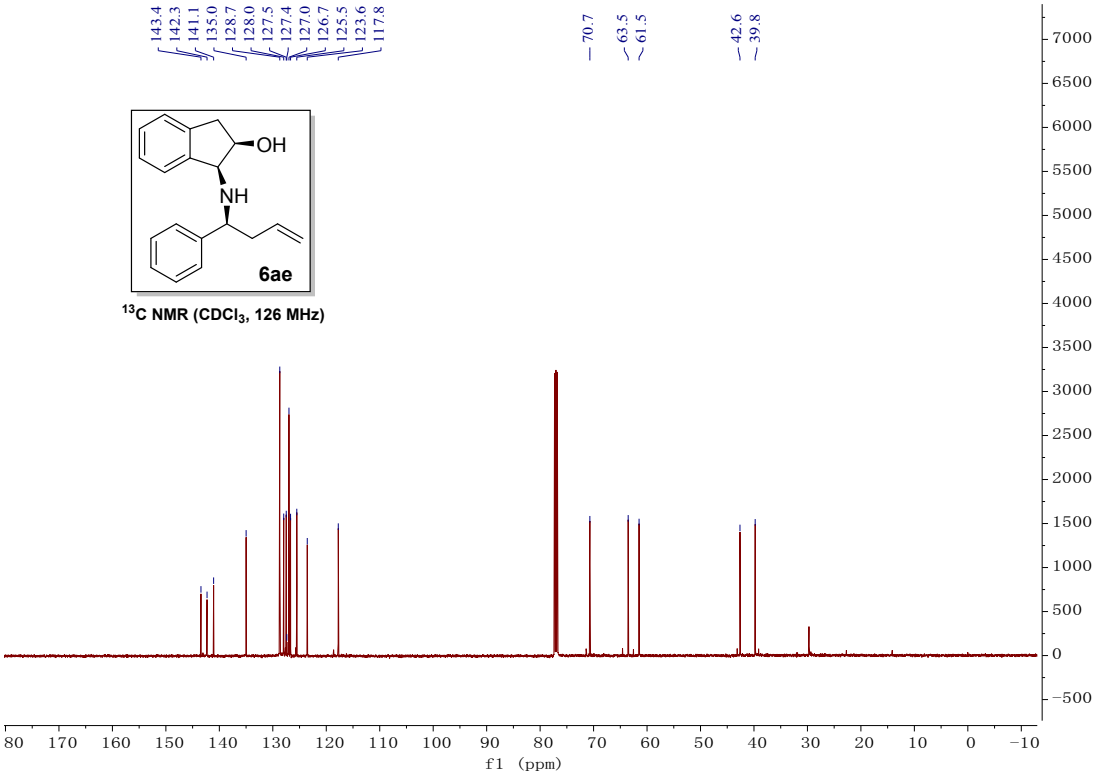

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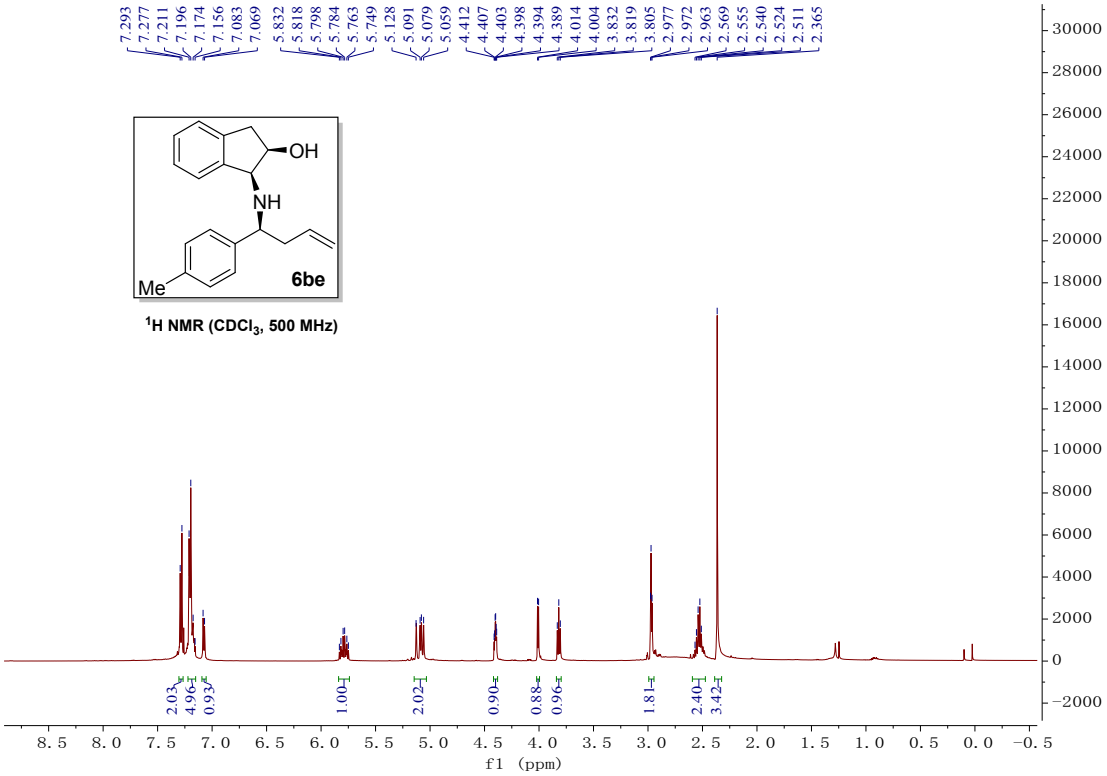

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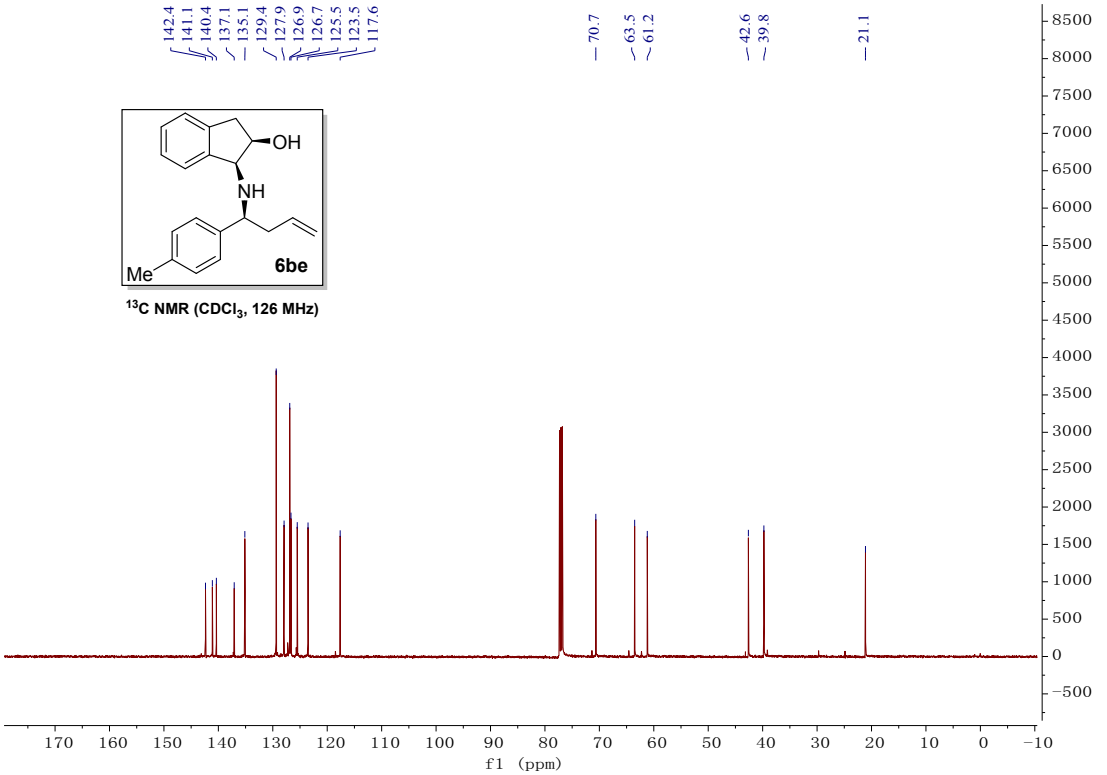

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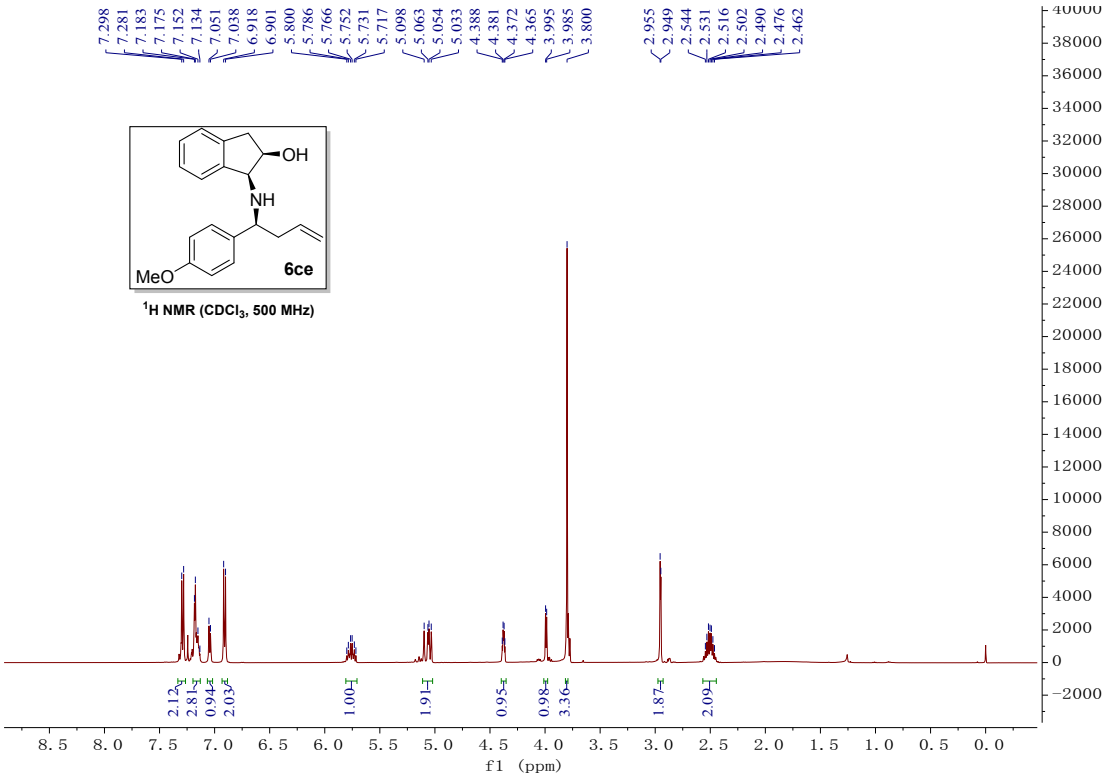

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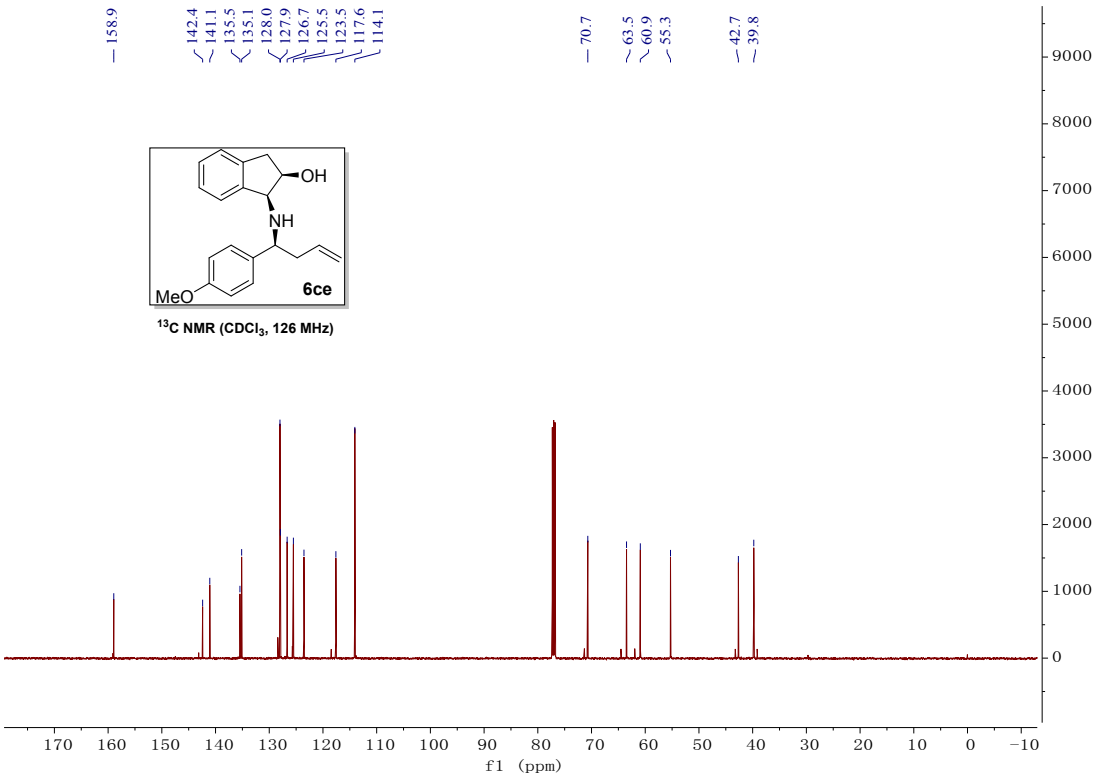

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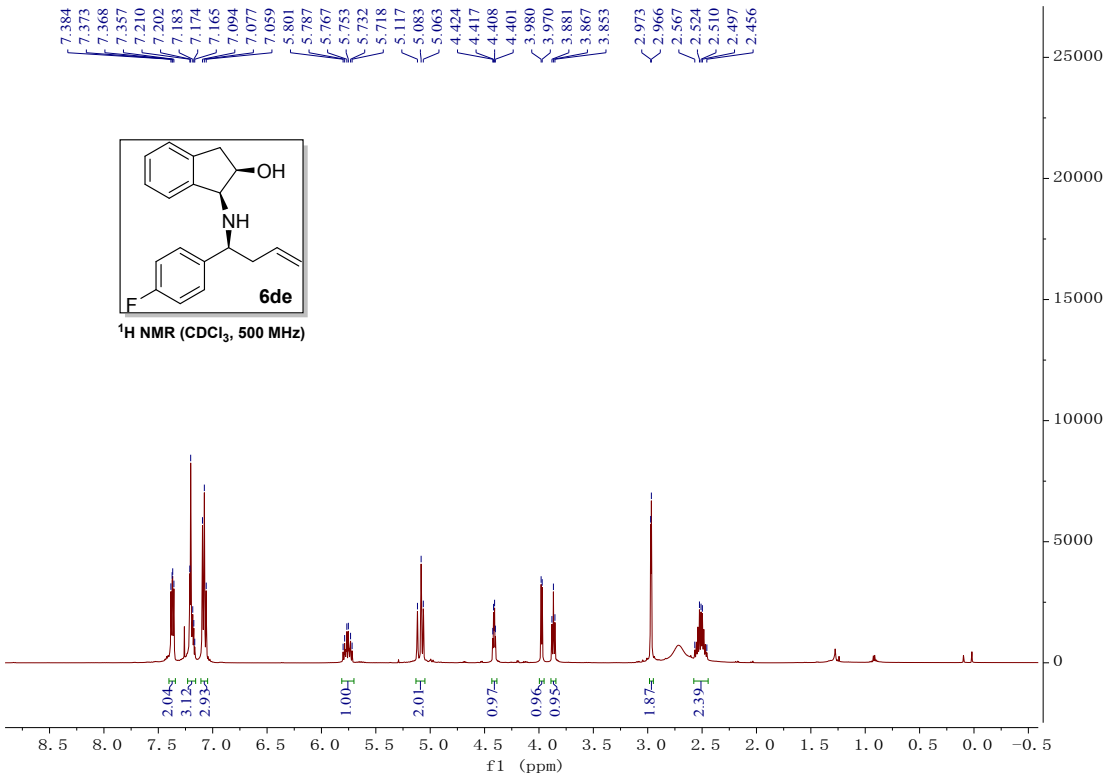

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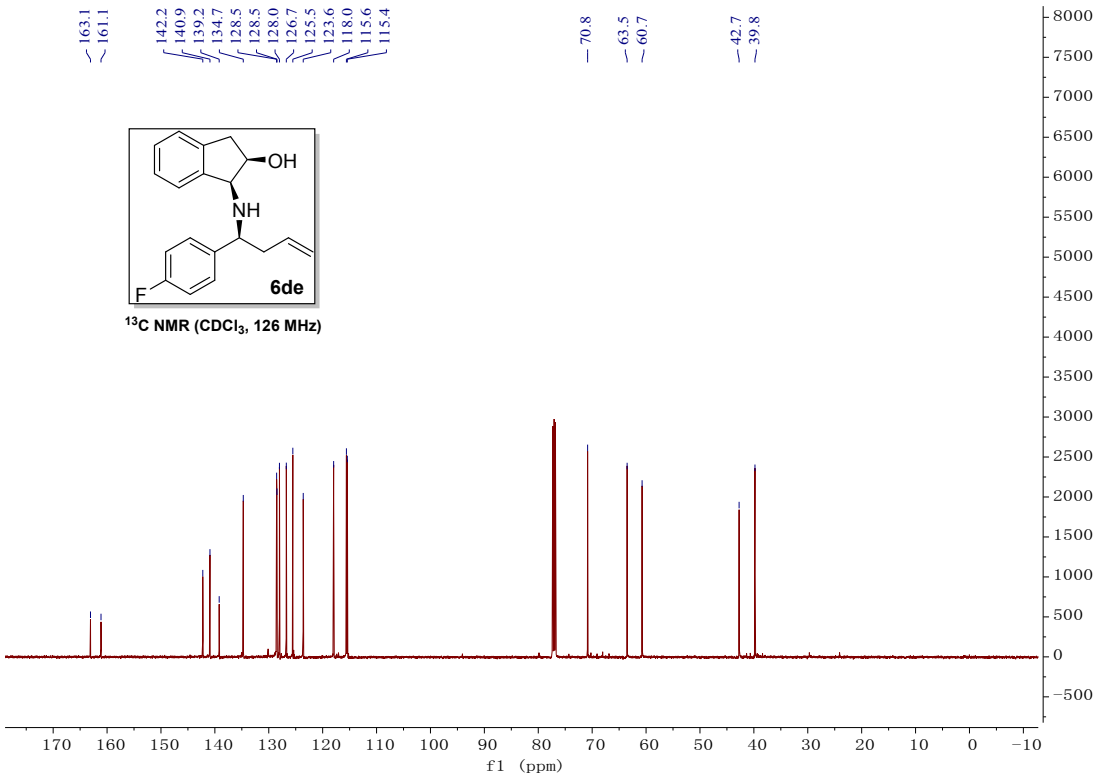

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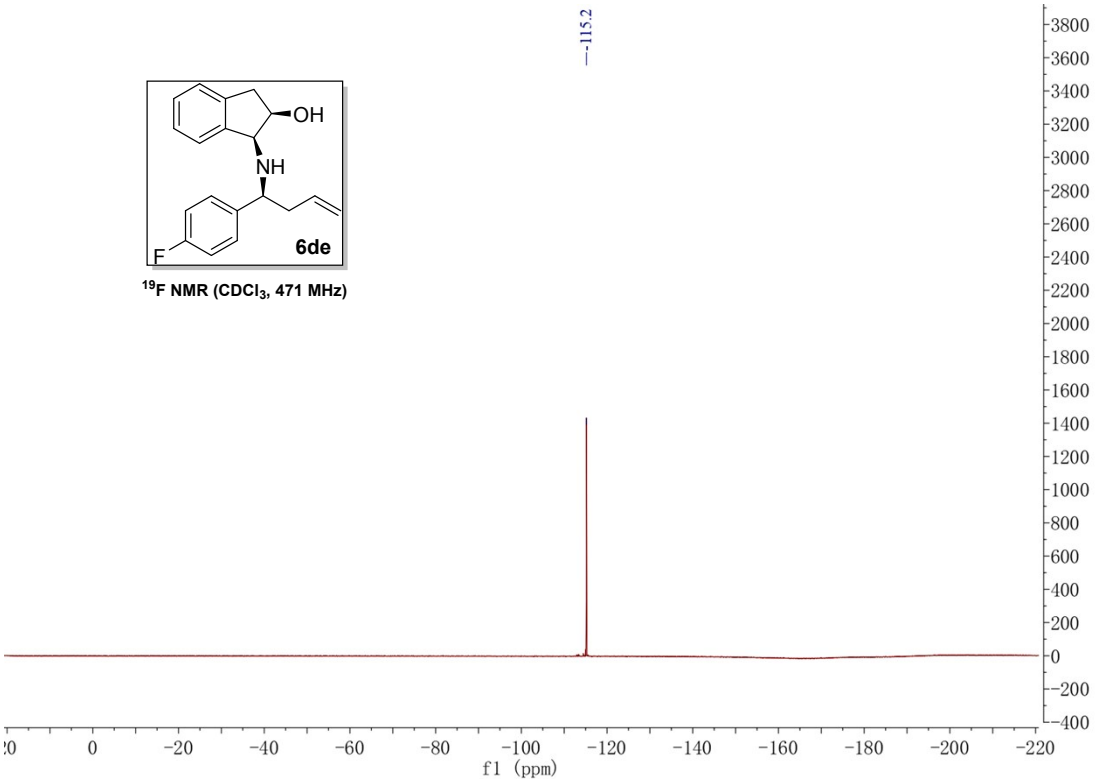
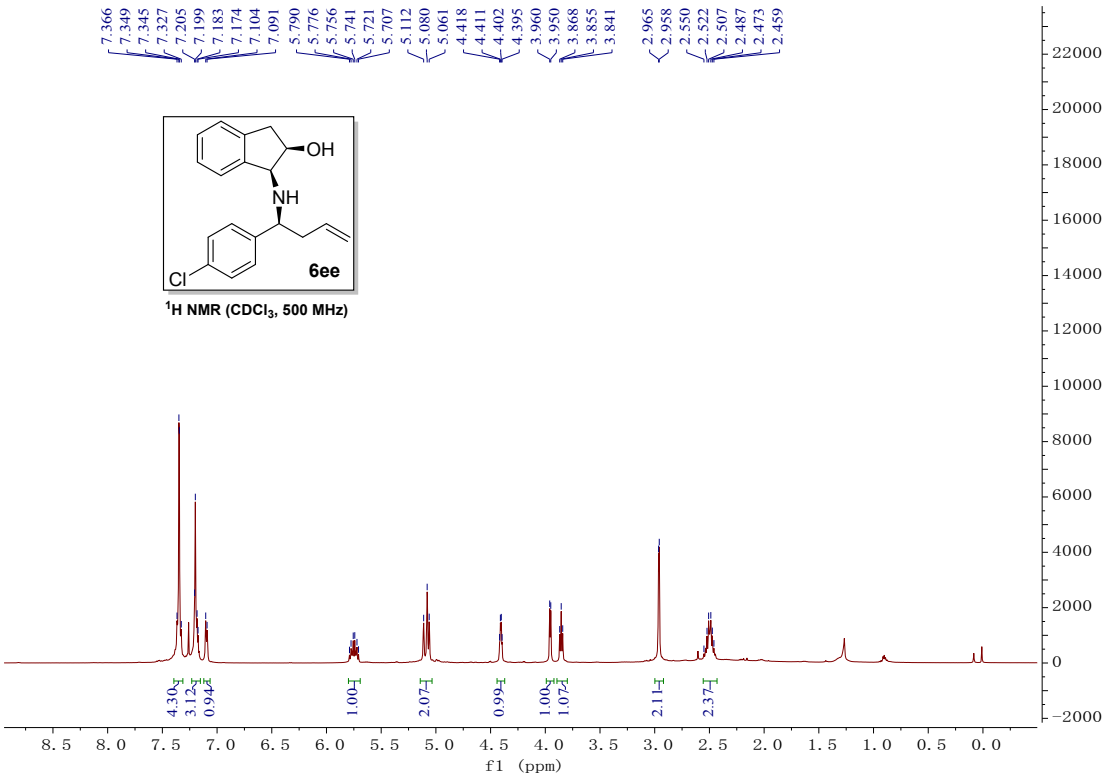


^{19}F NMR ($CDCl_3$, 471 MHz)



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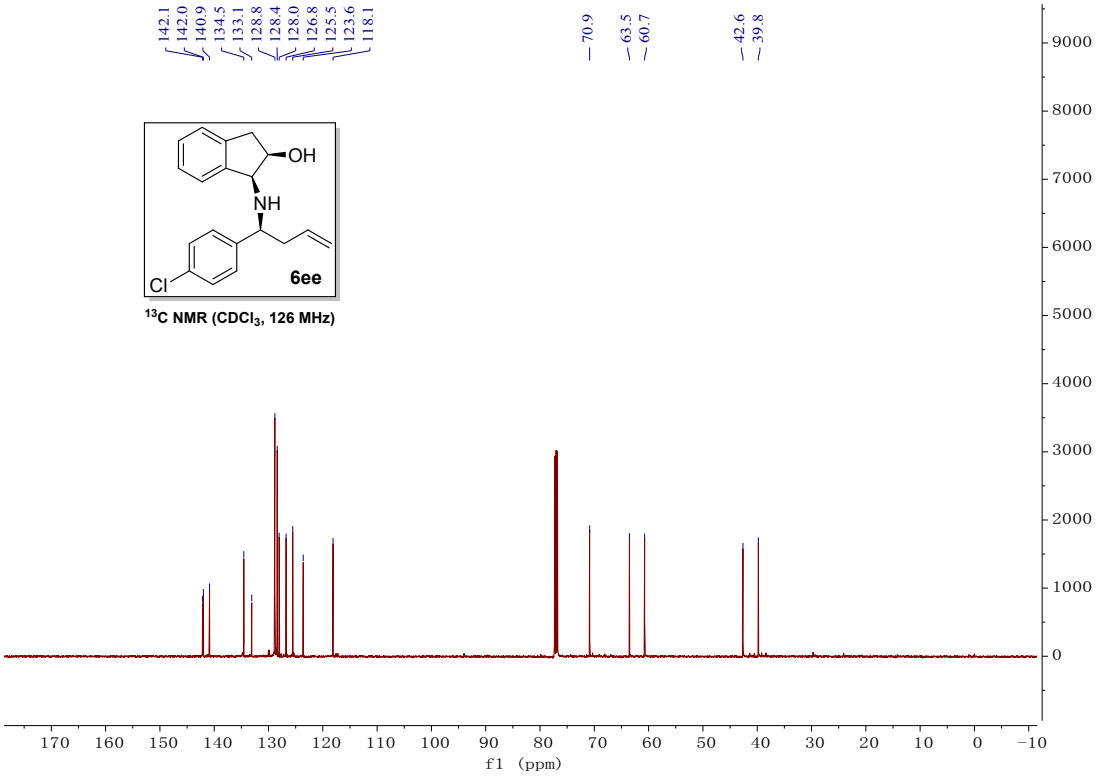
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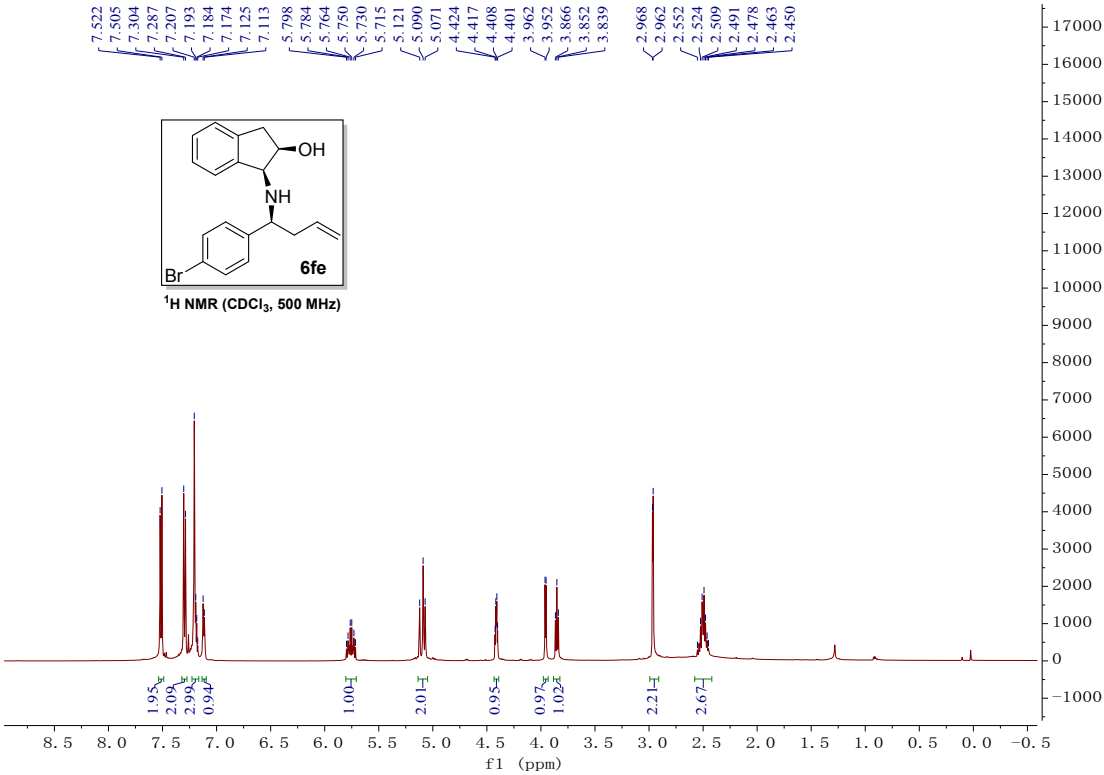
Cl
6ee
13C NMR (CDCl3, 126 MHz)
f1 (ppm)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OH
NH
Br
6fe
1H NMR (CDCl3, 500 MHz)
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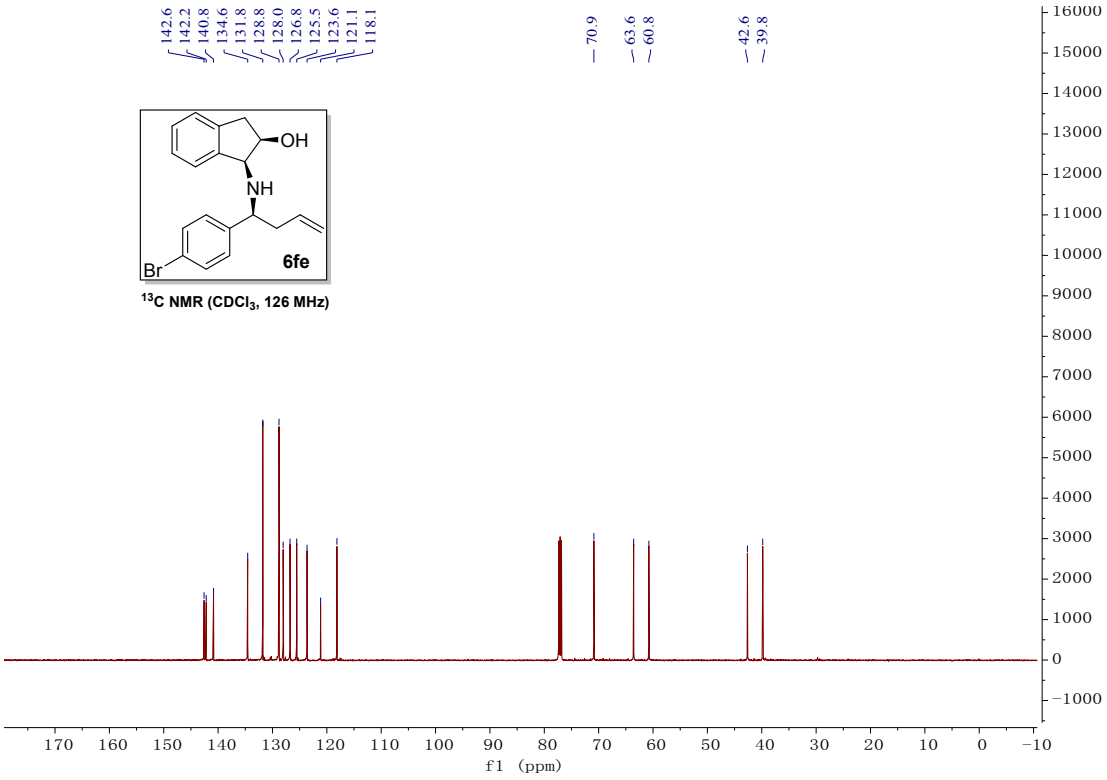
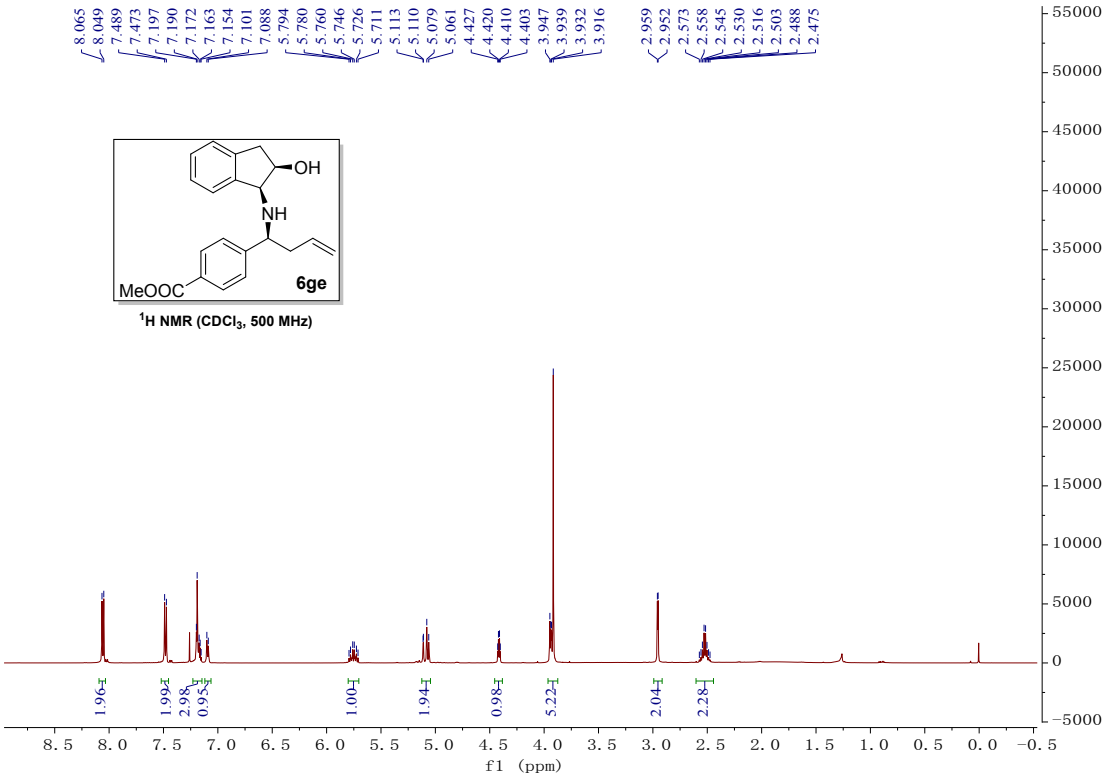
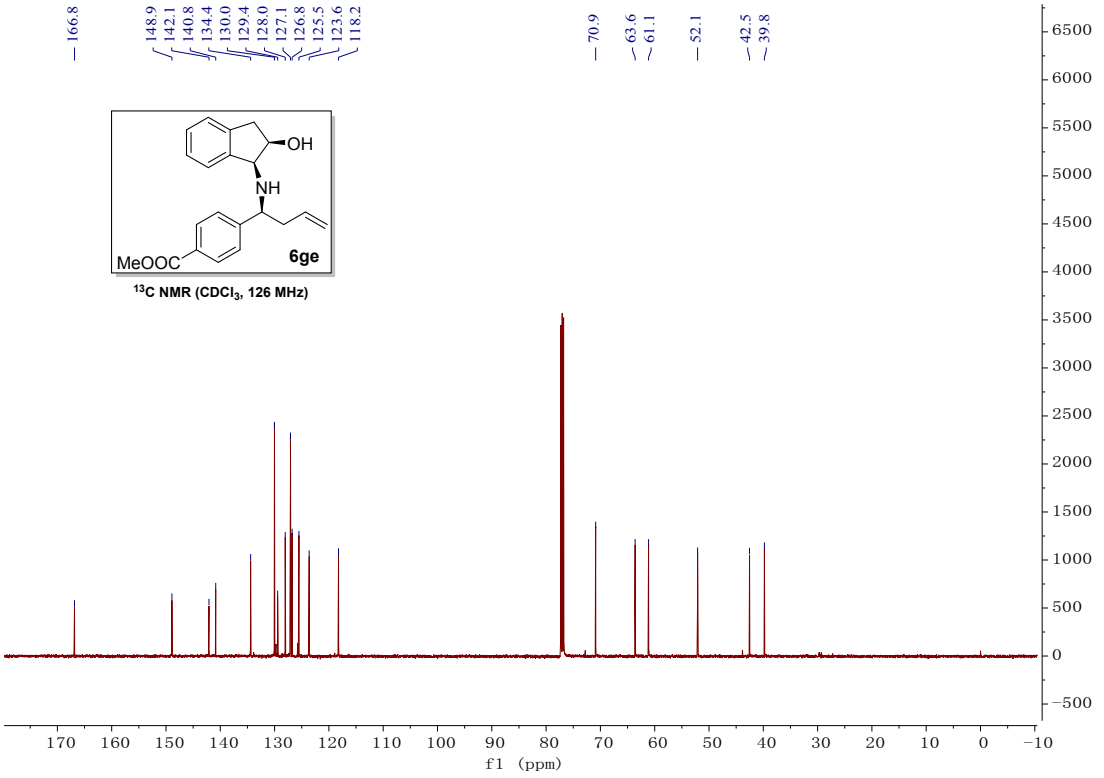
2.67
f1 (ppm)



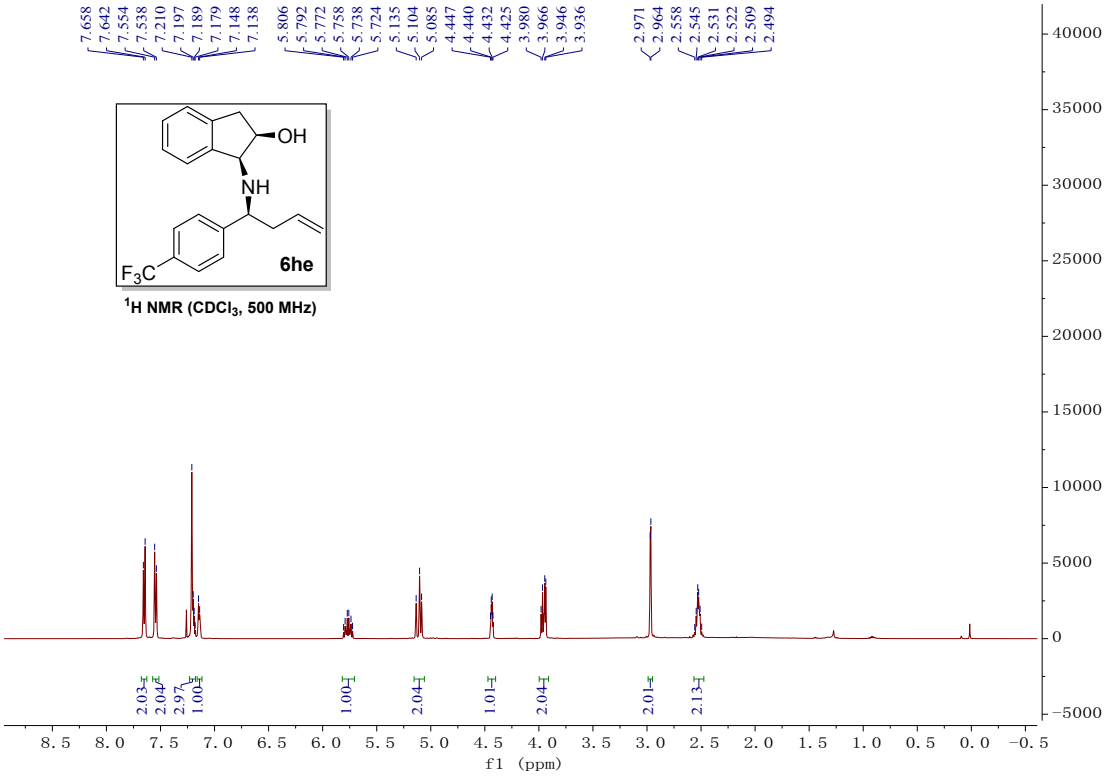
^{13}C NMR ($CDCl_3$, 126 MHz)



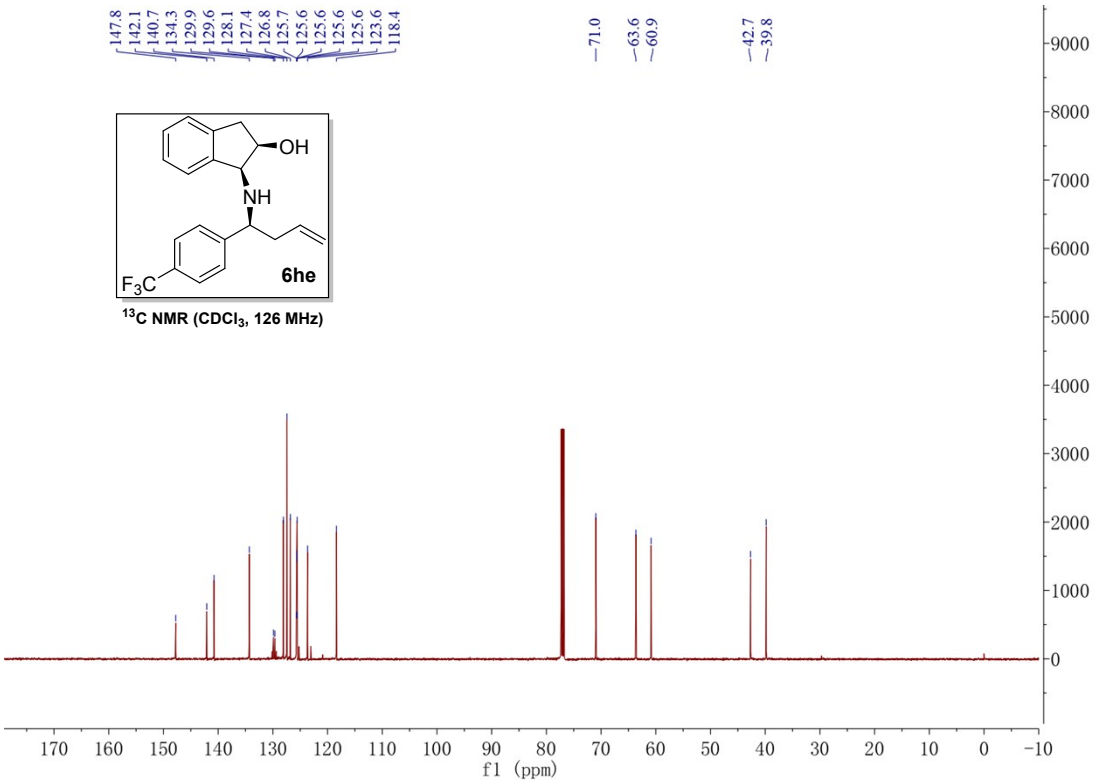
^{1}H NMR ($CDCl_3$, 500 MHz)



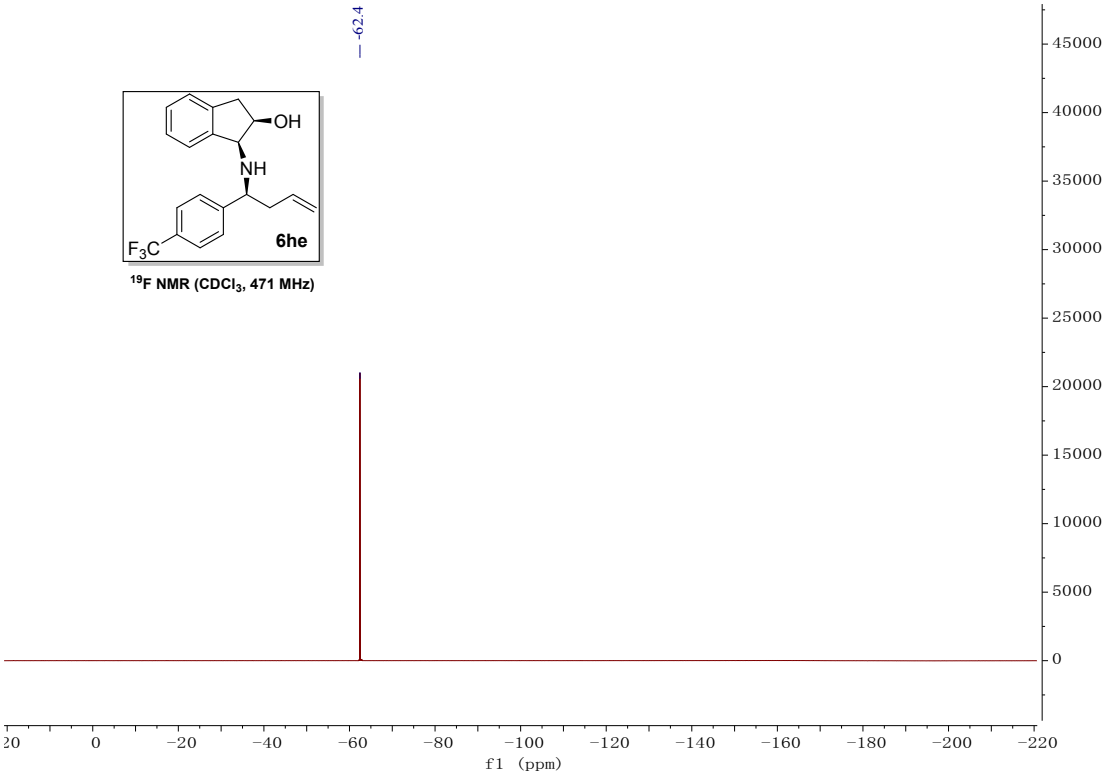
^{13}C NMR ($CDCl_3$, 126 MHz)



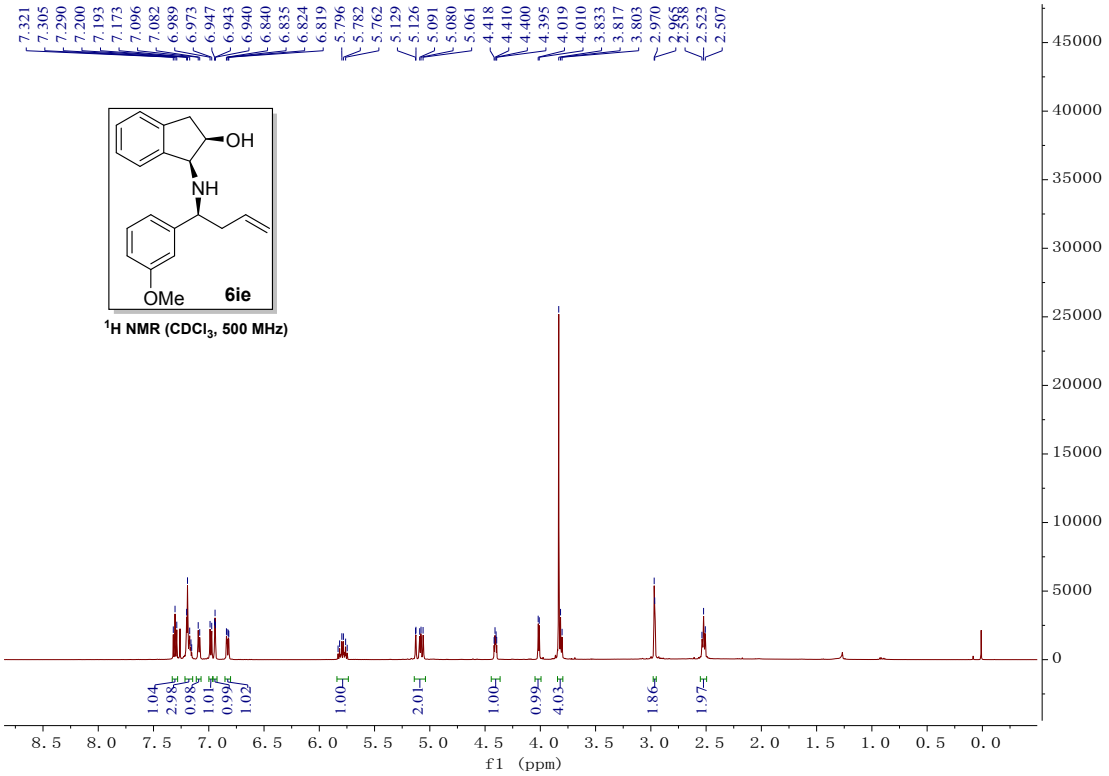
^{1}H NMR ($CDCl_3$, 500 MHz)



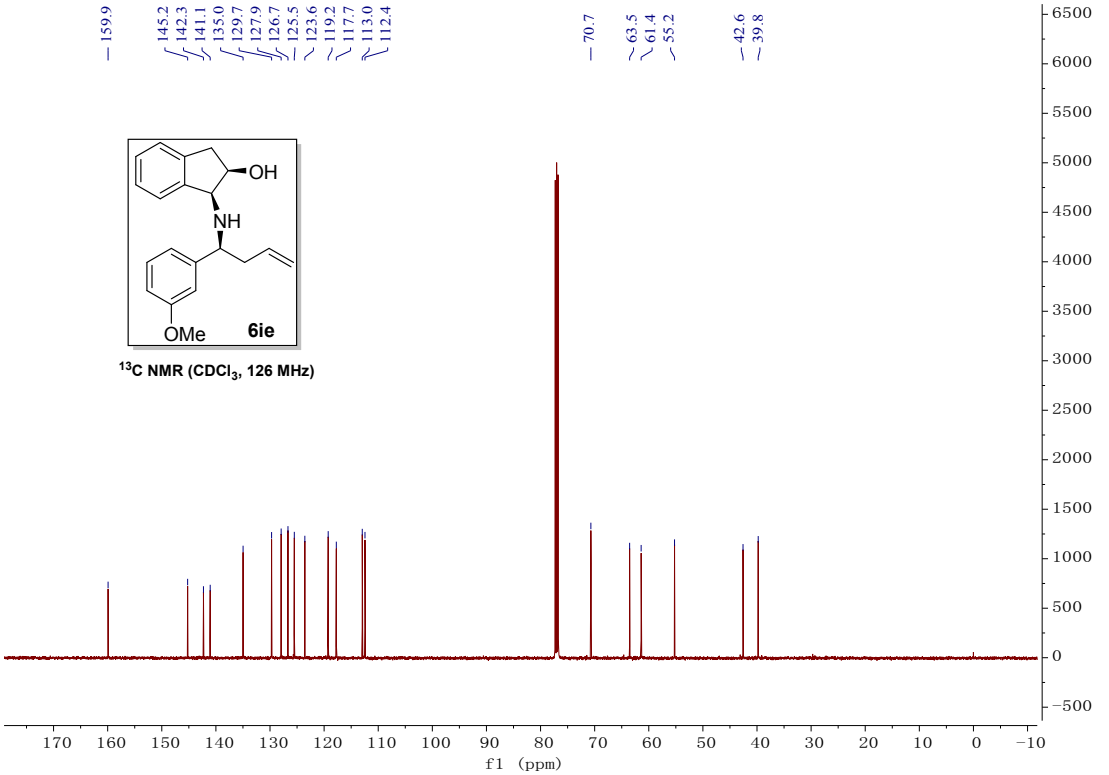
^{13}C NMR ($CDCl_3$, 126 MHz)



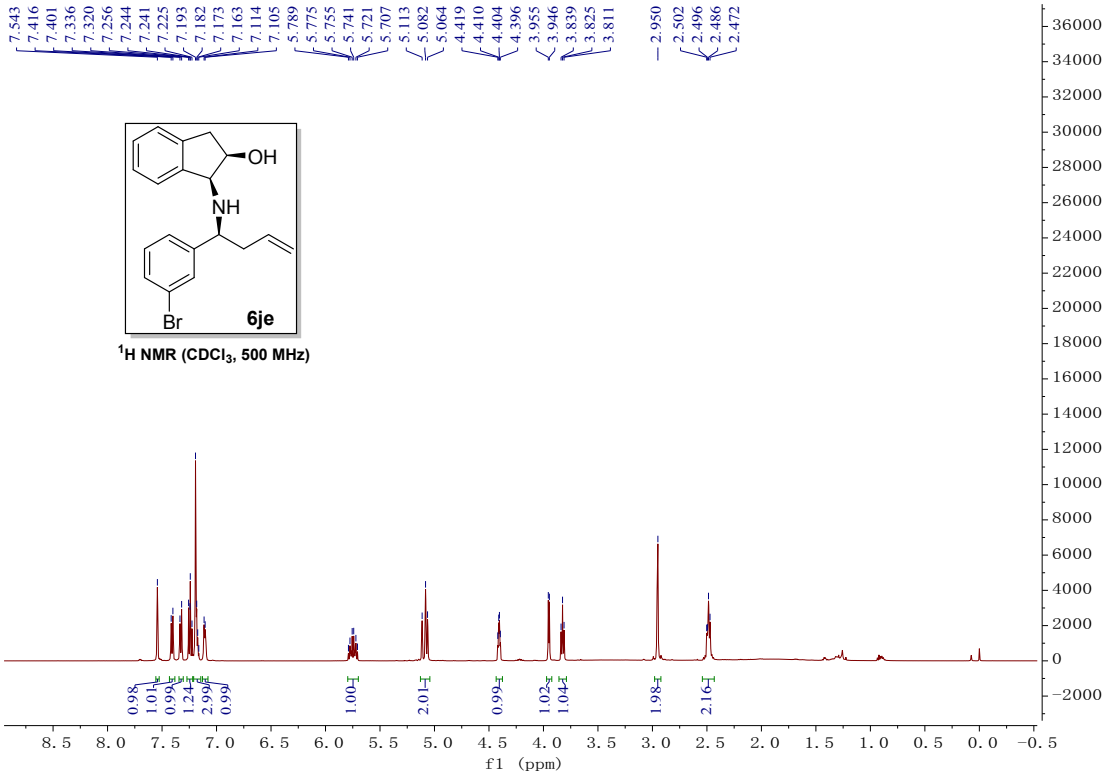
^{19}F NMR ($CDCl_3$, 471 MHz)



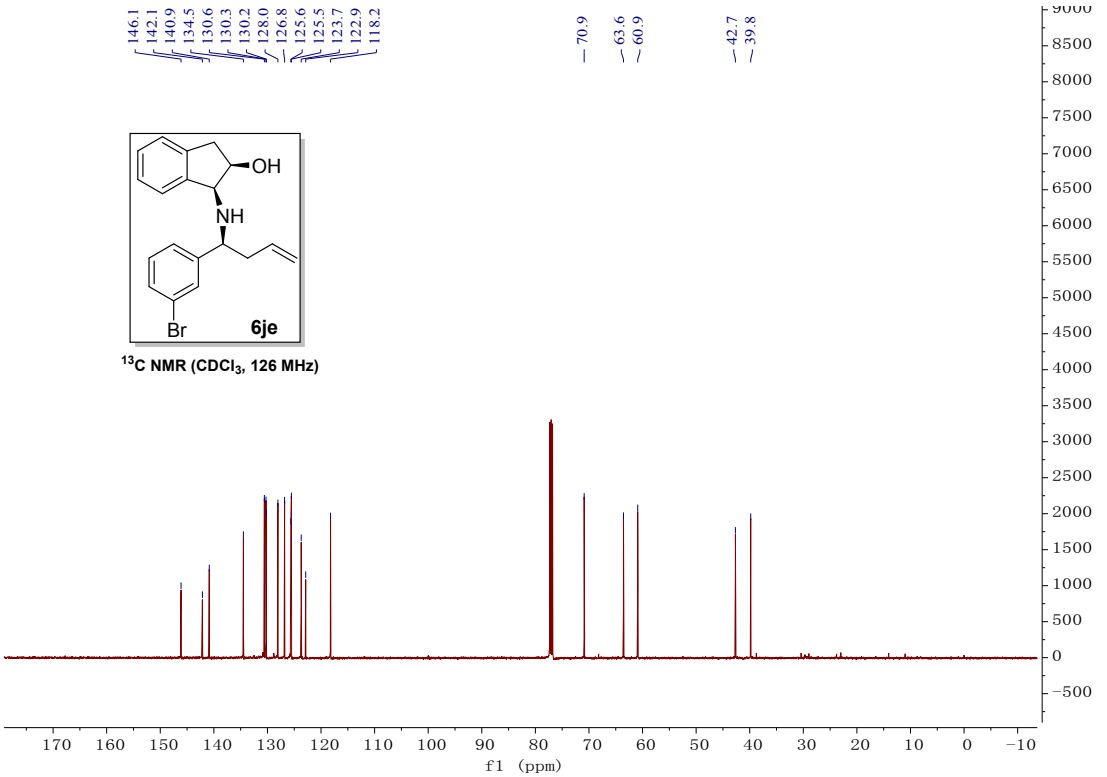
^{1}H NMR ($CDCl_3$, 500 MHz)



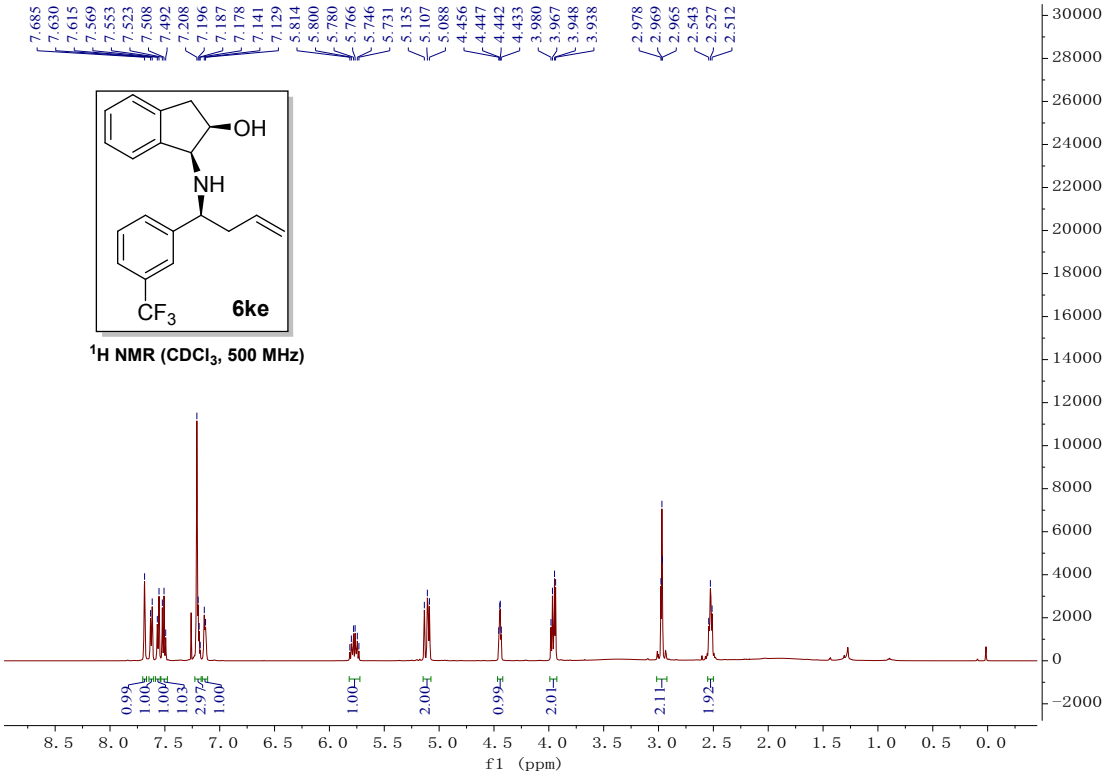
^{13}C NMR ($CDCl_3$, 126 MHz)



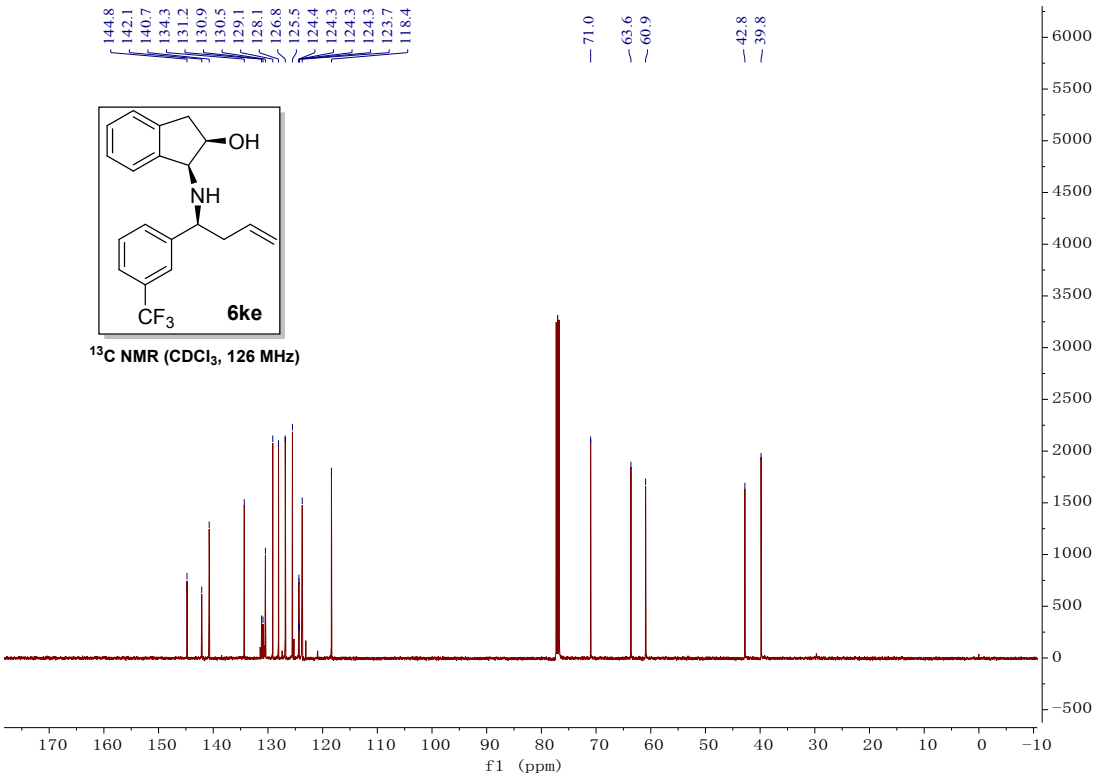
^{1}H NMR ($CDCl_3$, 500 MHz)



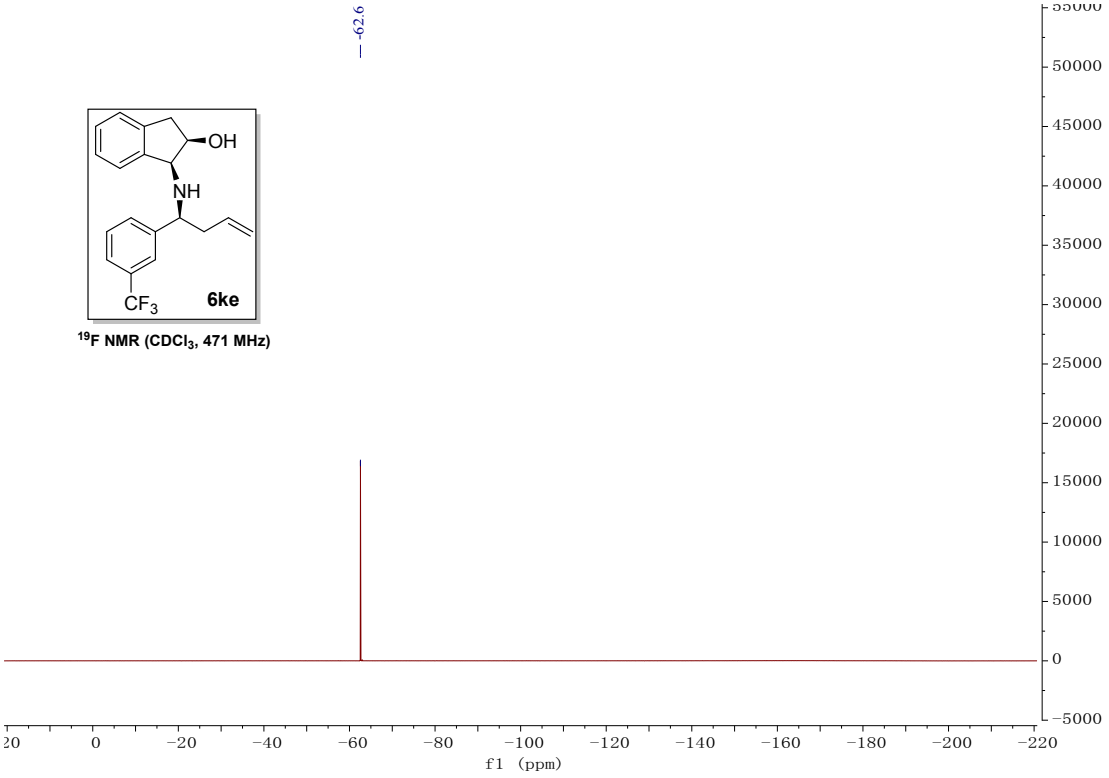
^{13}C NMR ($CDCl_3$, 126 MHz)



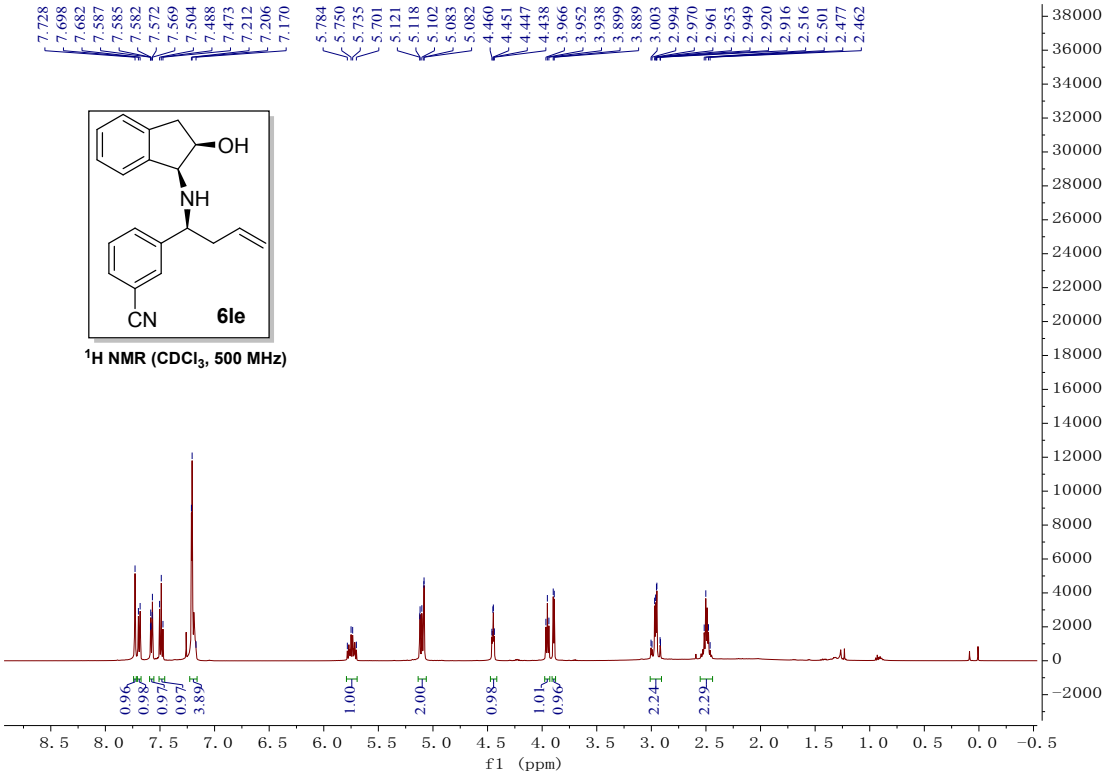
^{1}H NMR ($CDCl_3$, 500 MHz)



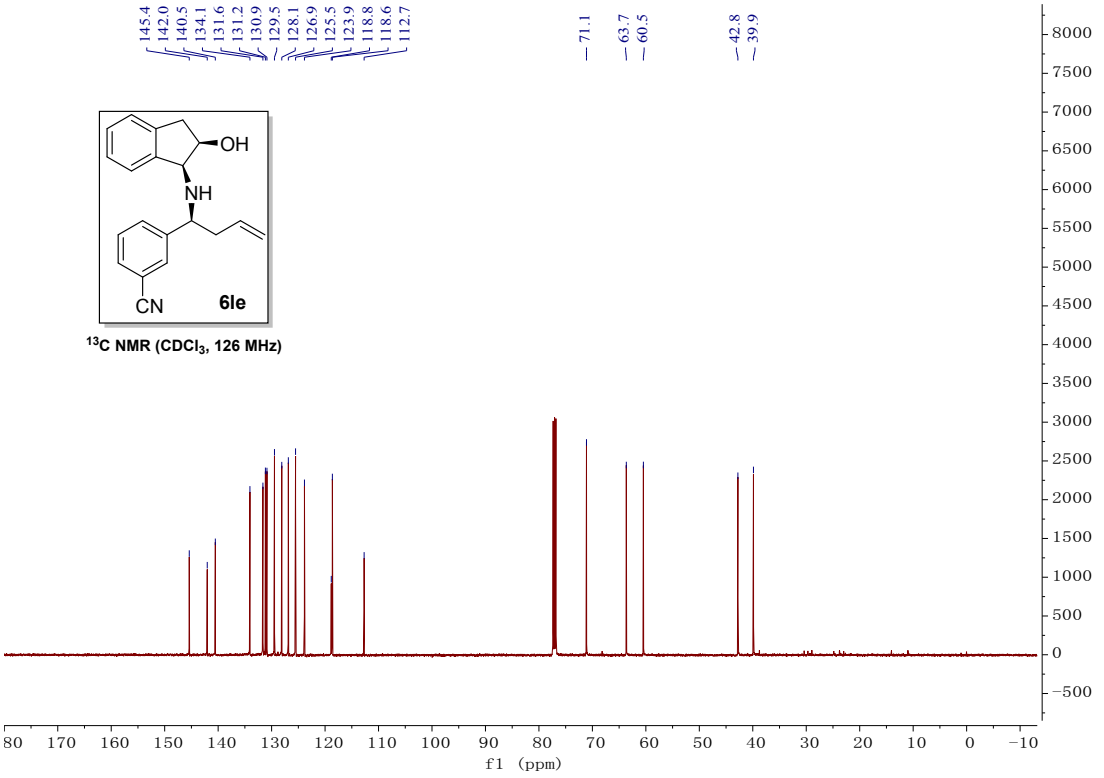
^{13}C NMR ($CDCl_3$, 126 MHz)



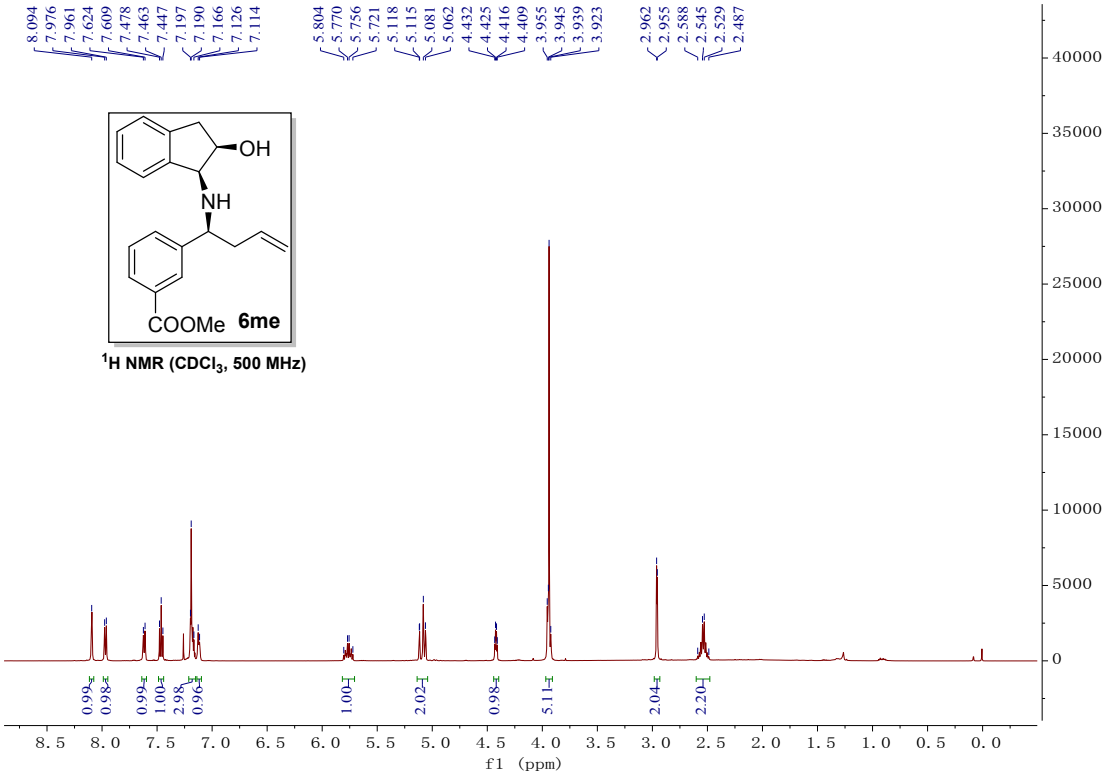
^{19}F NMR ($CDCl_3$, 471 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)



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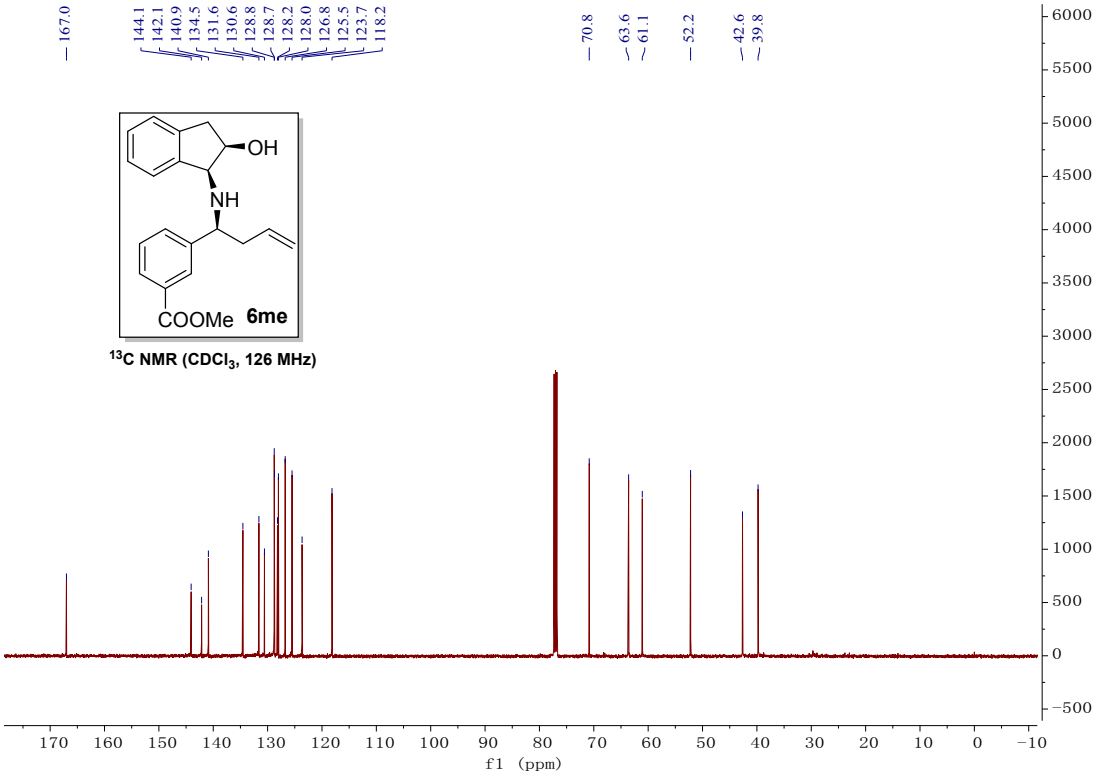
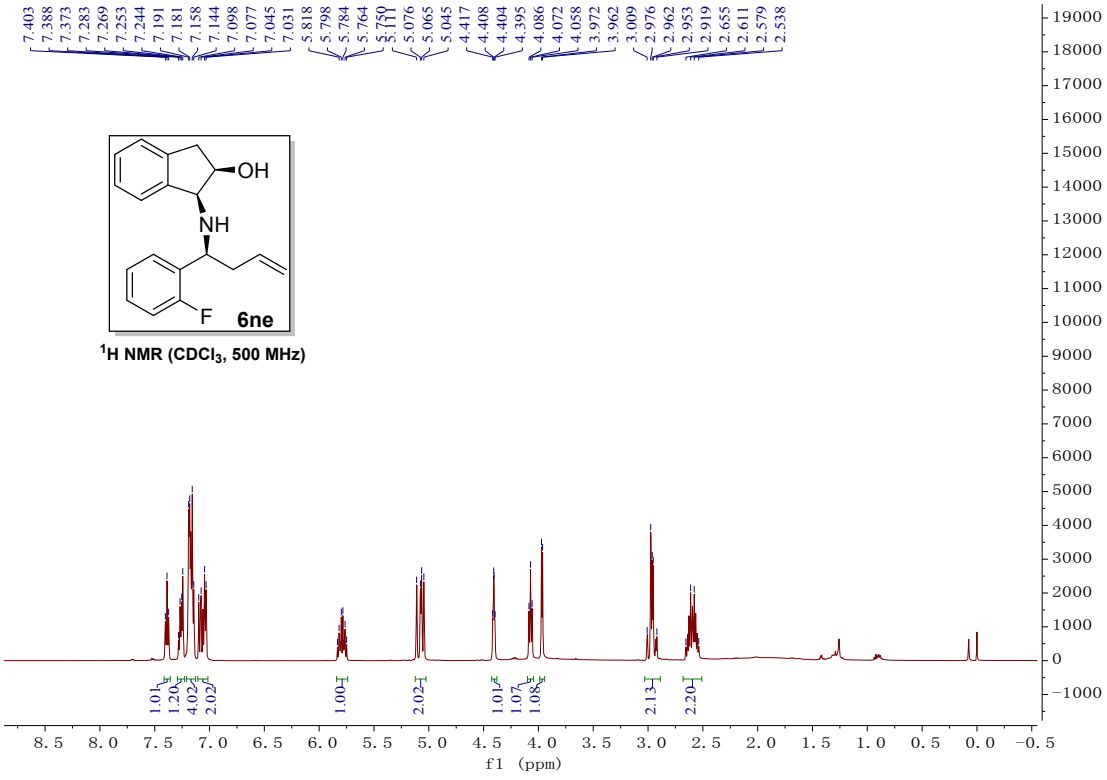
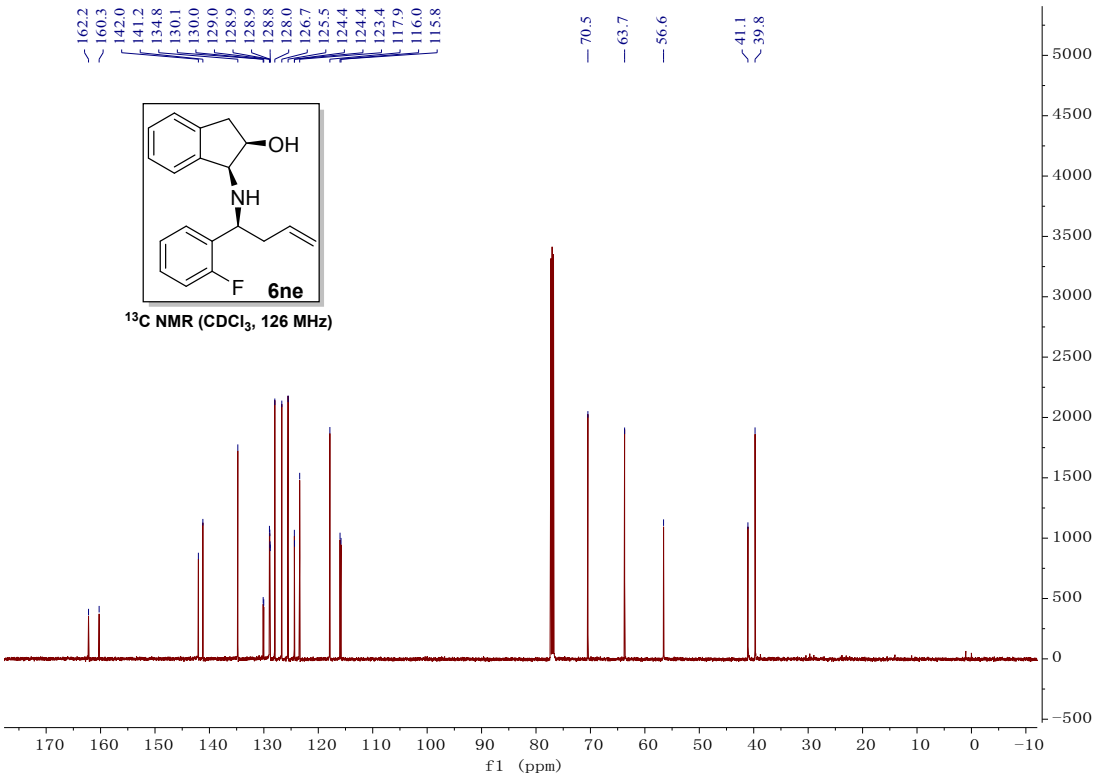


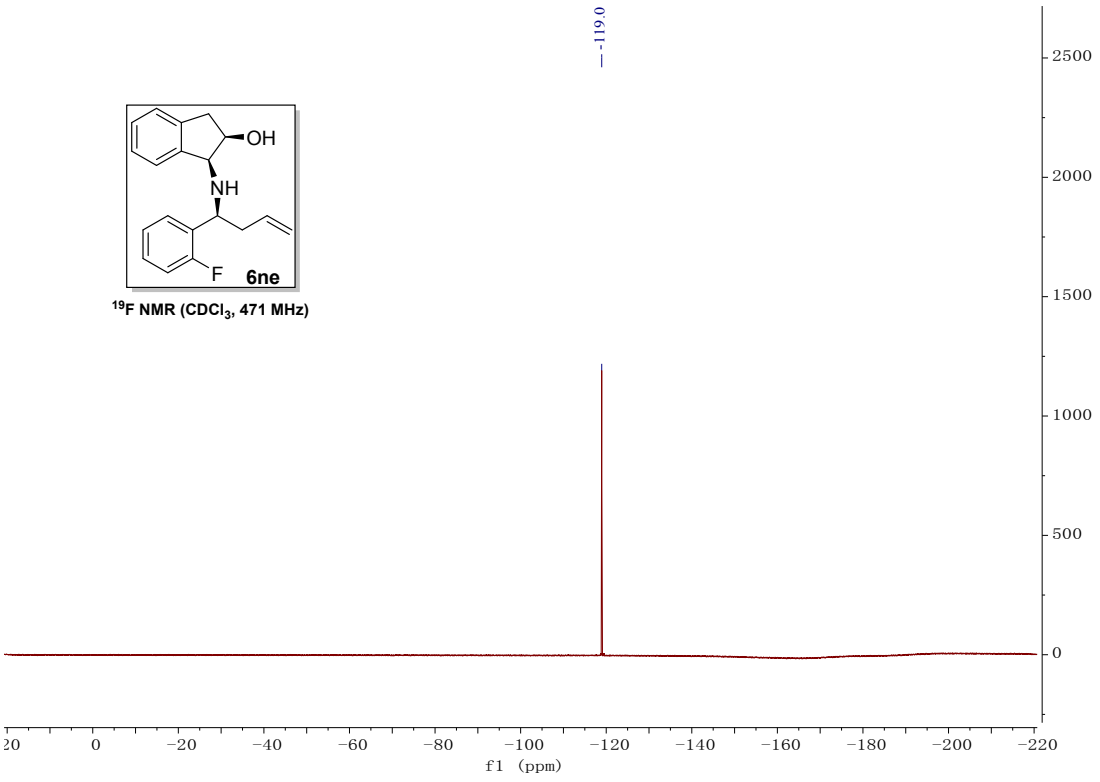
^{13}C NMR ($CDCl_3$, 126 MHz)



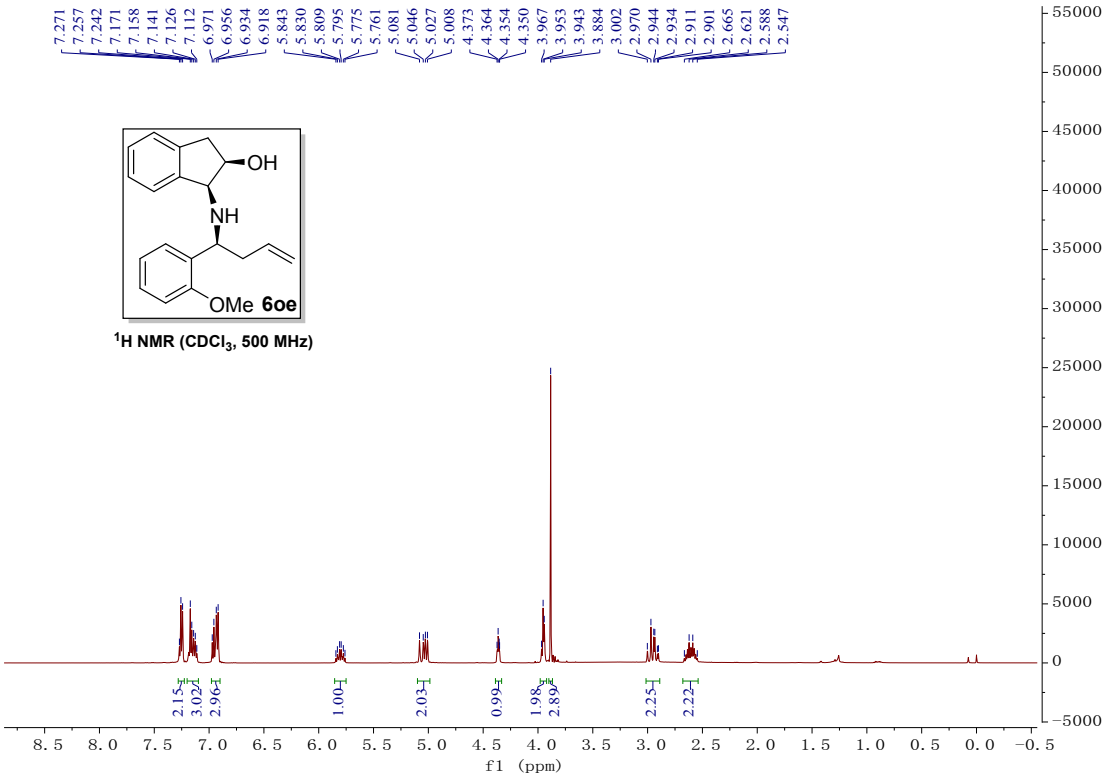
^{1}H NMR ($CDCl_3$, 500 MHz)



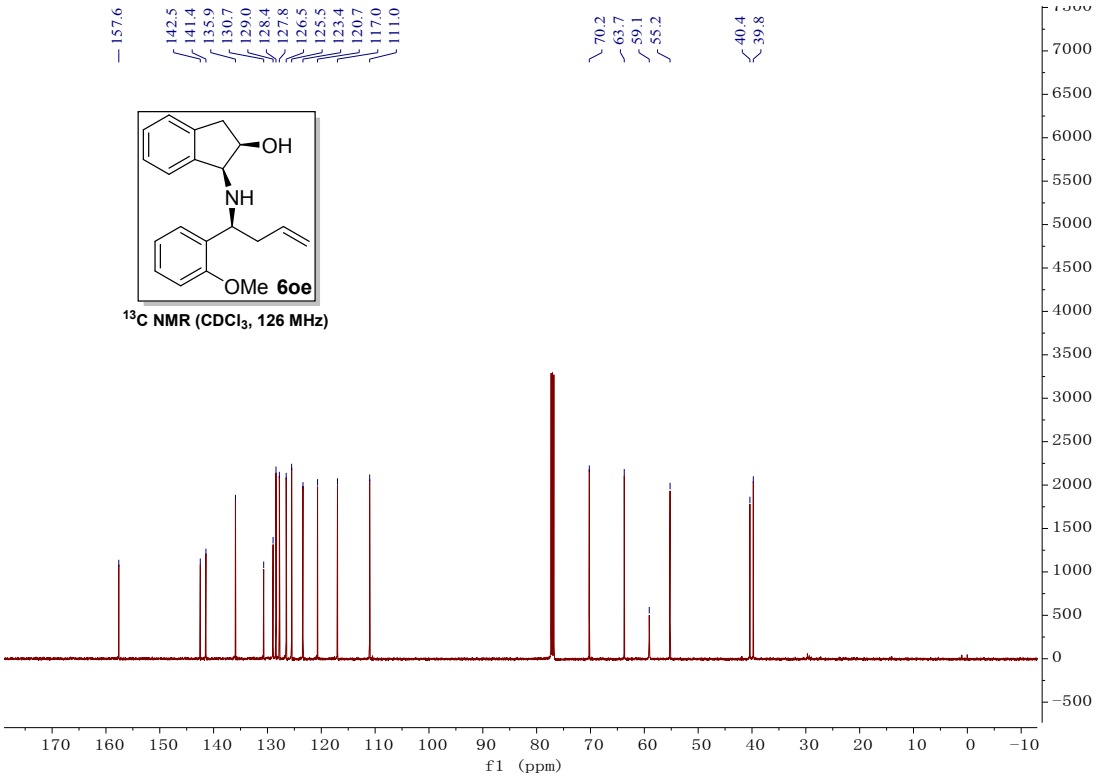
^{13}C NMR ($CDCl_3$, 126 MHz)



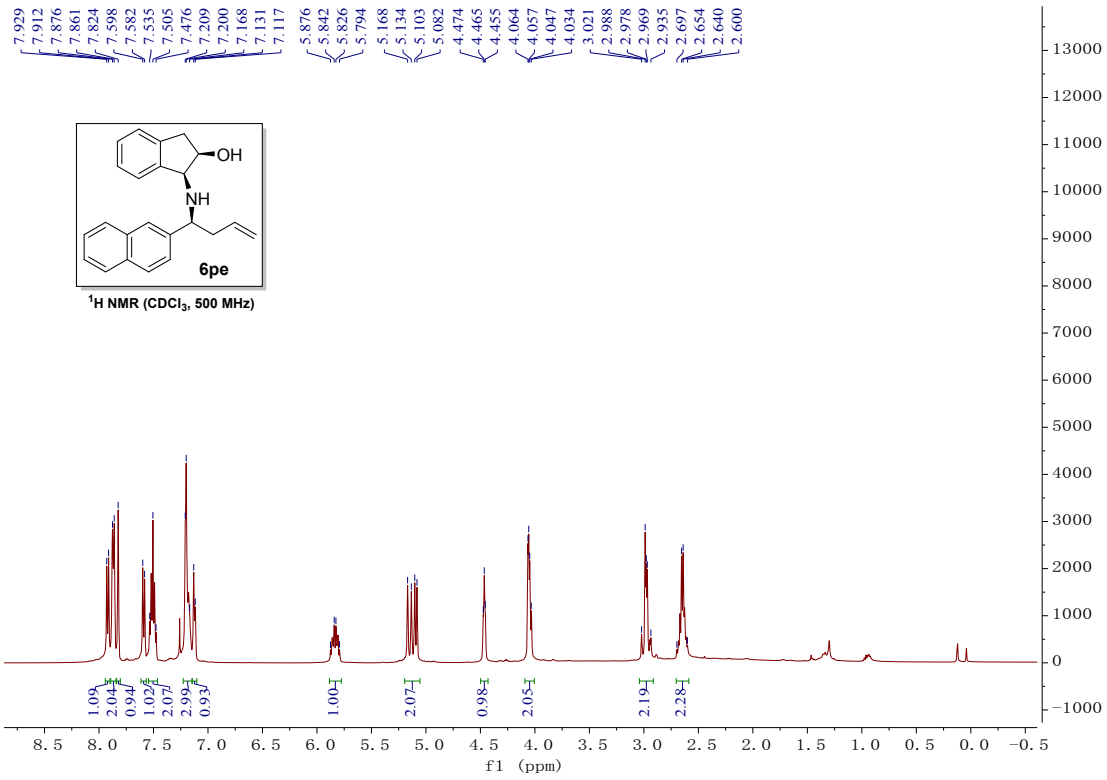
^{19}F NMR ($CDCl_3$, 471 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)



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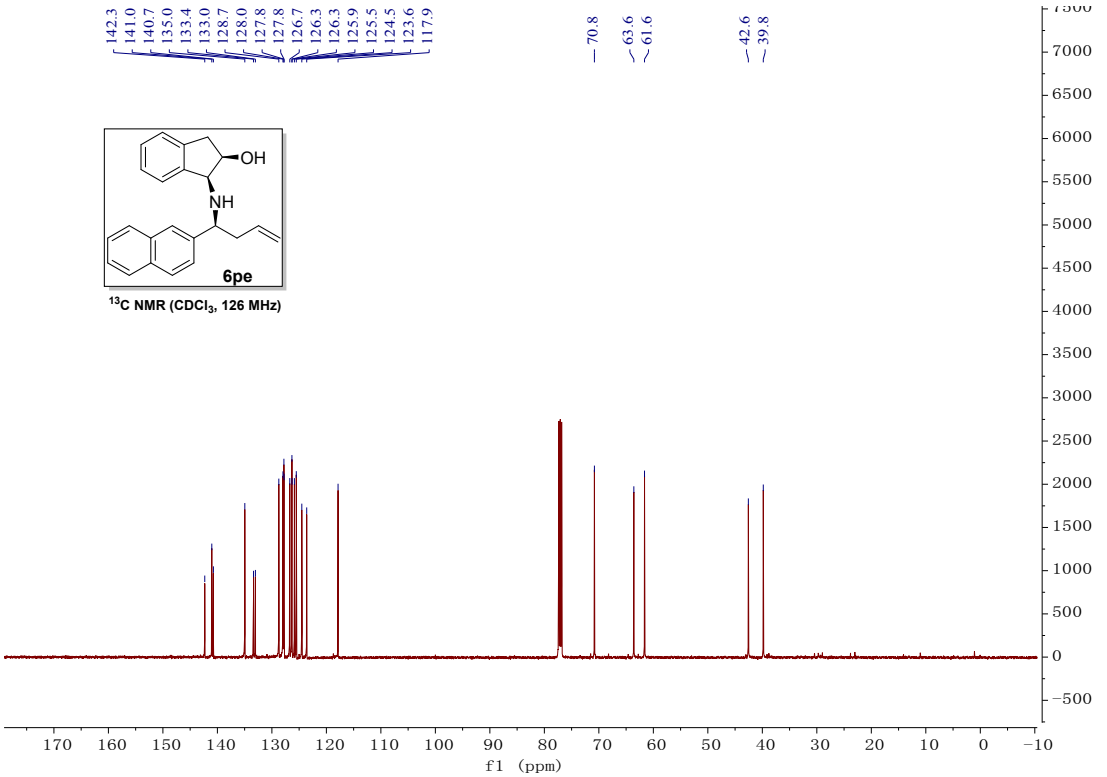
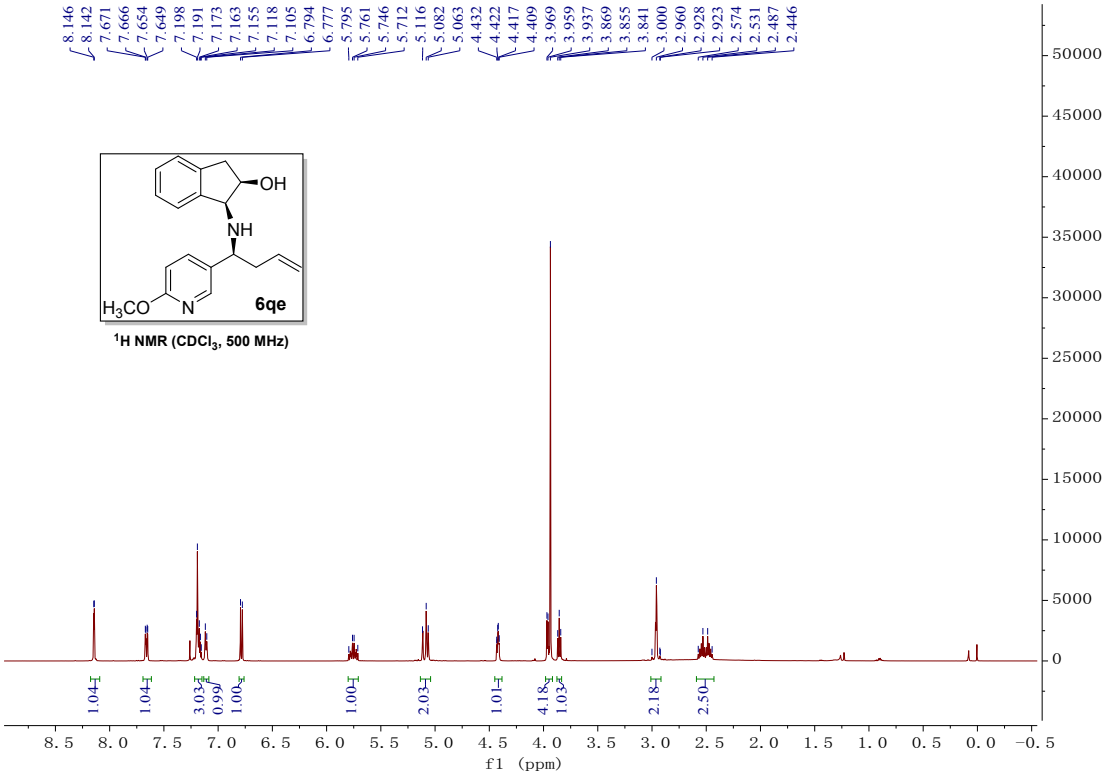
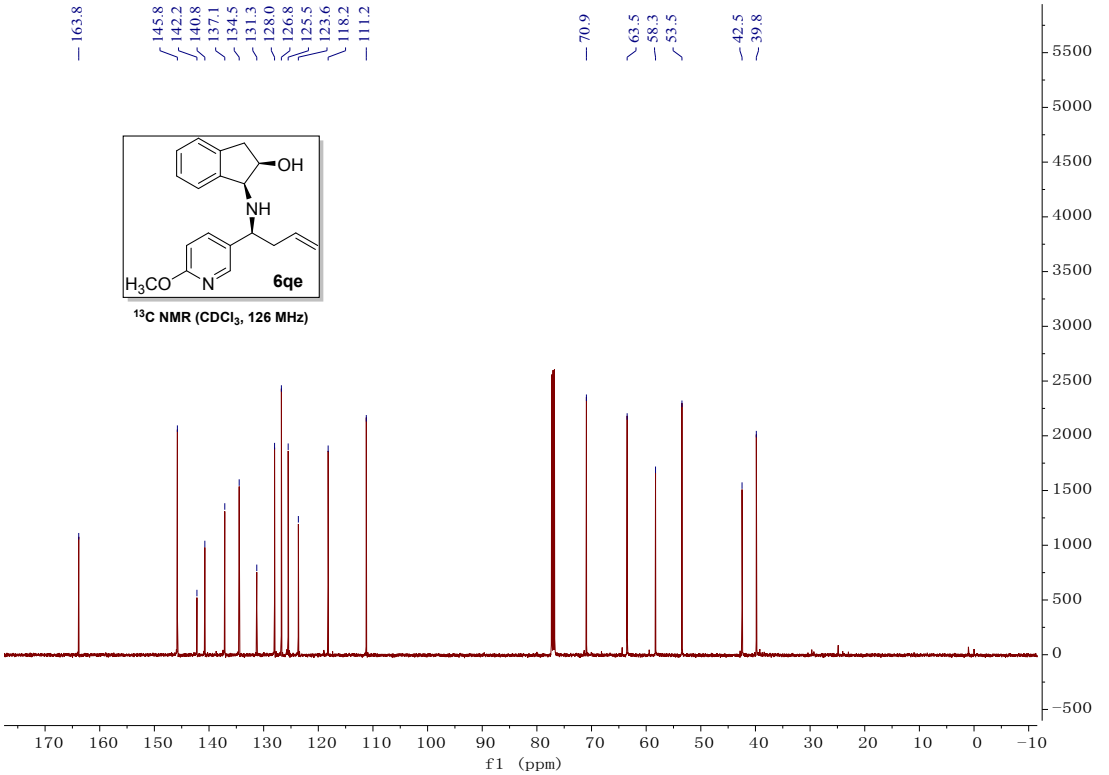
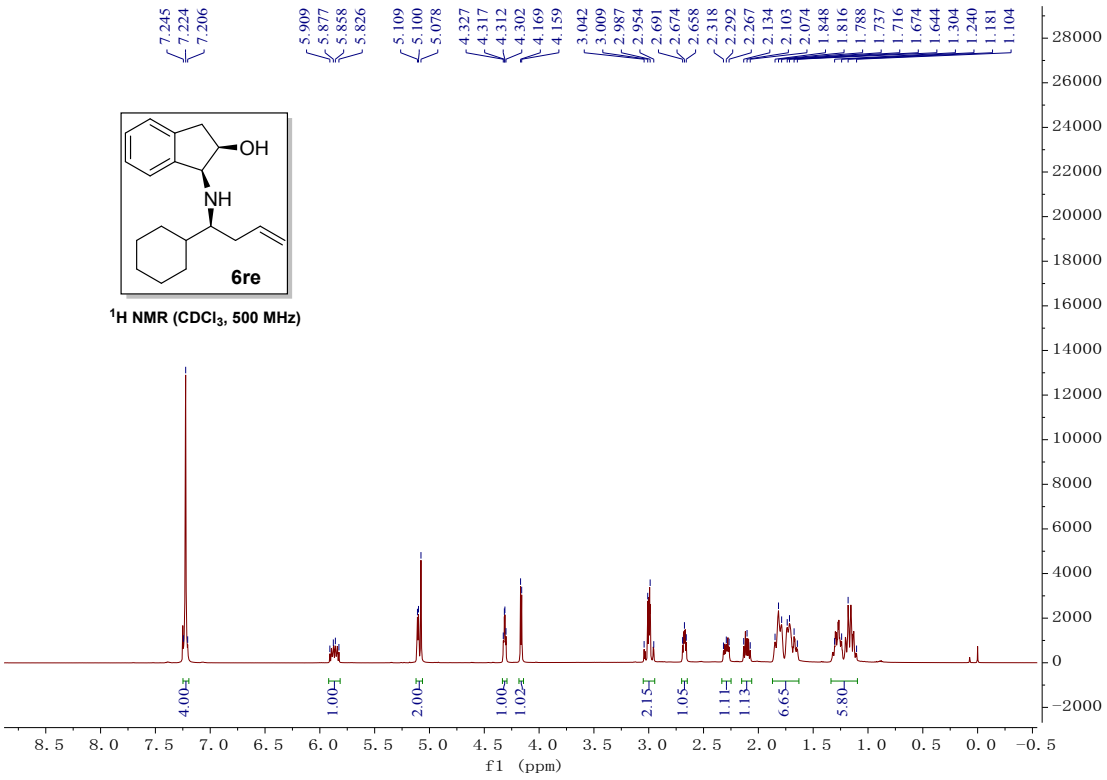


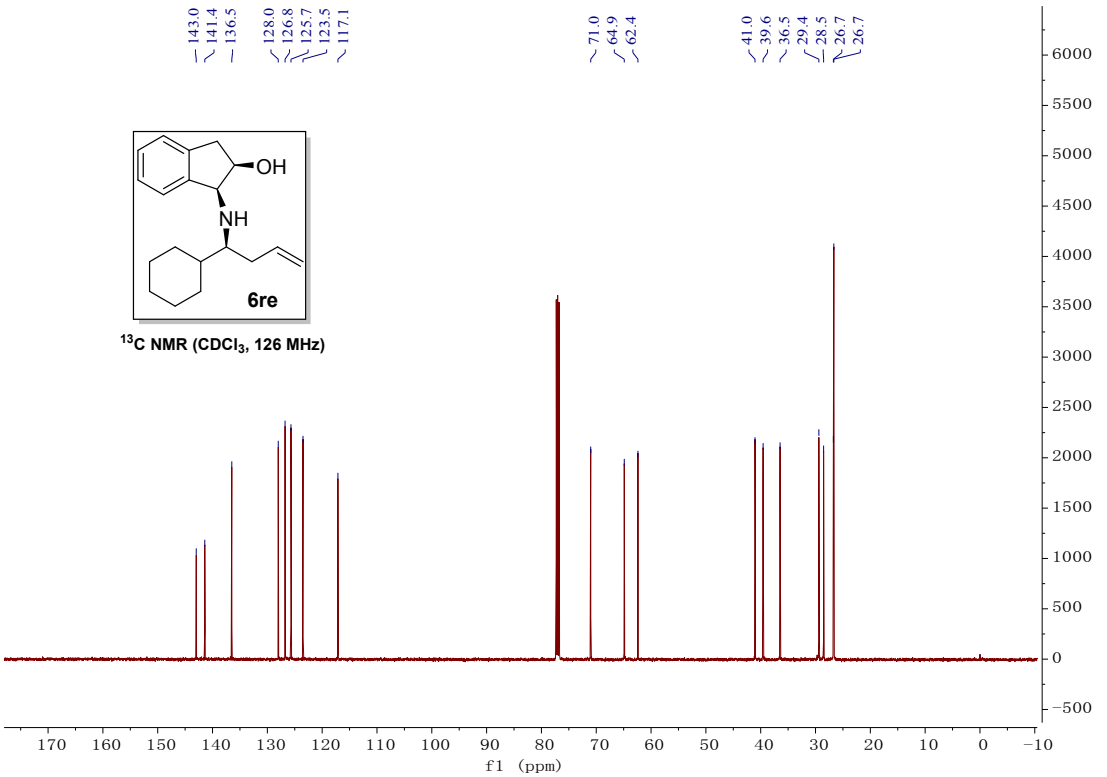
^{13}C NMR ($CDCl_3$, 126 MHz)


8.146
8.142
7.671
7.666
7.654
7.649
7.198
7.191
7.173
7.163
7.155
7.118
7.105
6.794
6.777
5.795
5.761
5.746
5.712
5.116
5.082
5.063
4.432
4.422
4.417
4.409
3.969
3.959
3.937
3.869
3.855
3.841
3.000
2.960
2.928
2.923
2.574
2.531
2.487
2.446
OH
NH
H3CO
N
6qe
1H NMR (CDCl3, 500 MHz)
1.04
1.04
3.03
0.99
1.00
1.00
2.03
1.01
4.18
1.03
2.18
2.50
f1 (ppm)

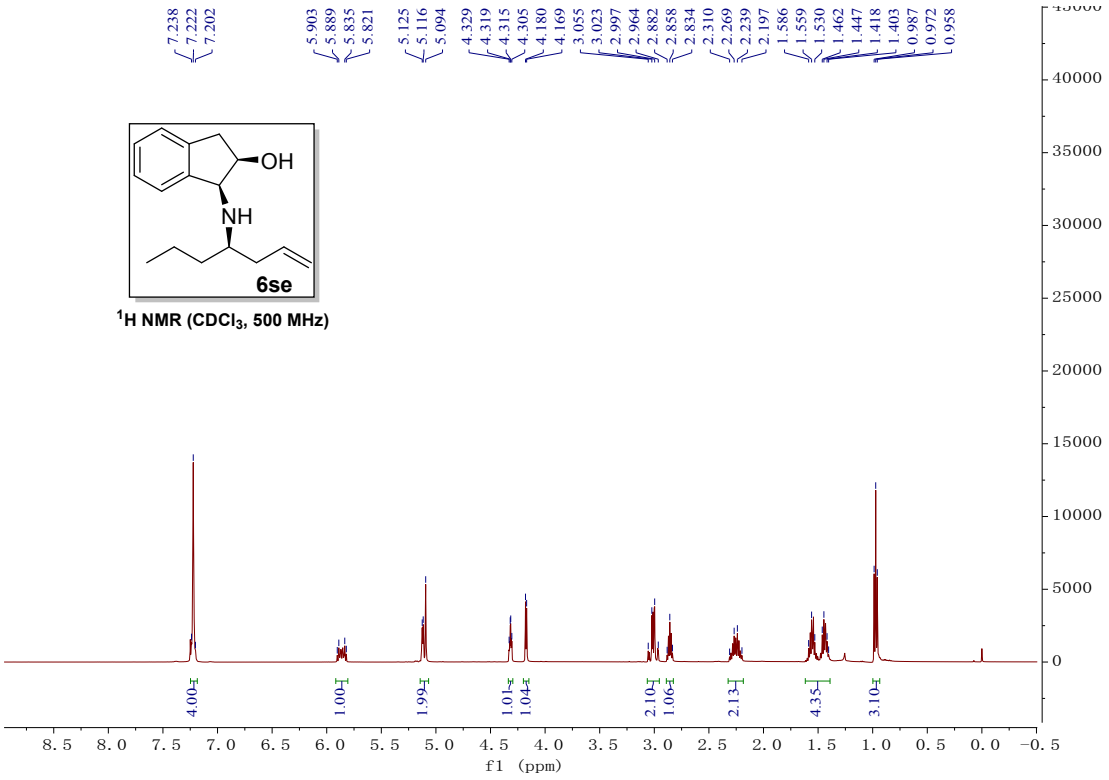

163.8
145.8
142.2
140.8
137.1
134.5
131.3
128.0
126.8
125.5
123.6
118.2
111.2
70.9
63.5
58.3
53.5
42.5
39.8
OH
NH
H3CO
N
6qe
13C NMR (CDCl3, 126 MHz)
f1 (ppm)



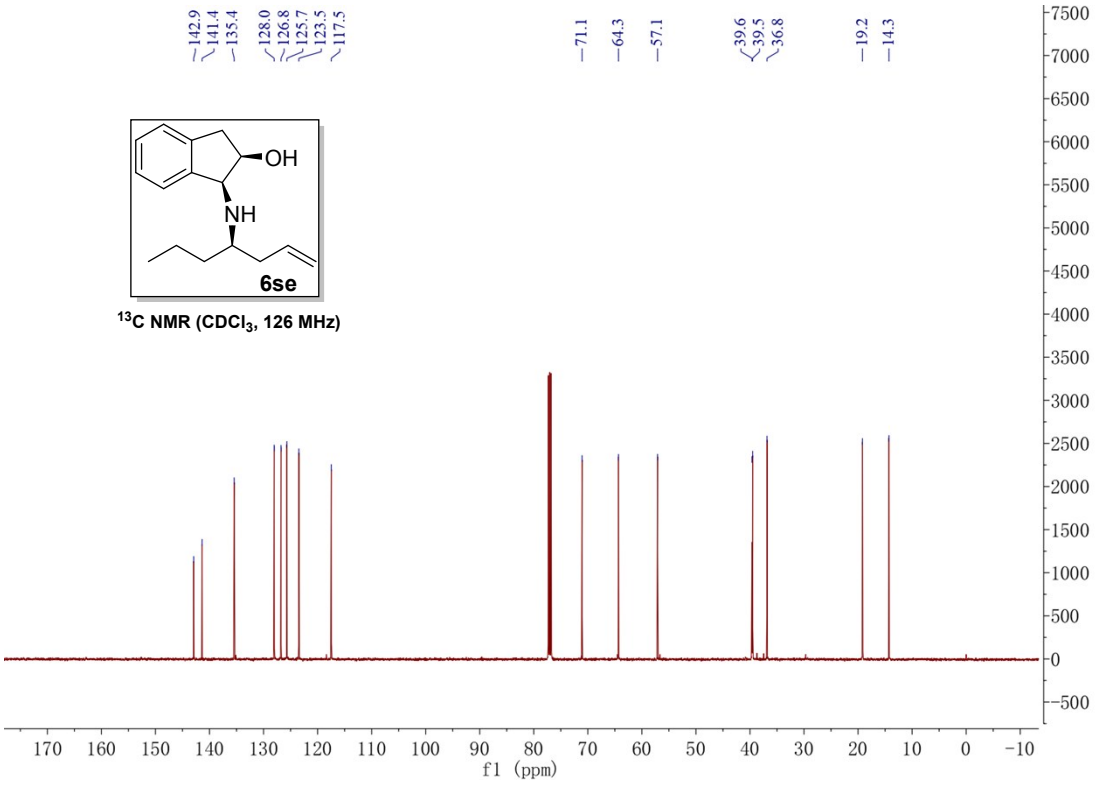
^{1}H NMR ($CDCl_3$, 500 MHz)



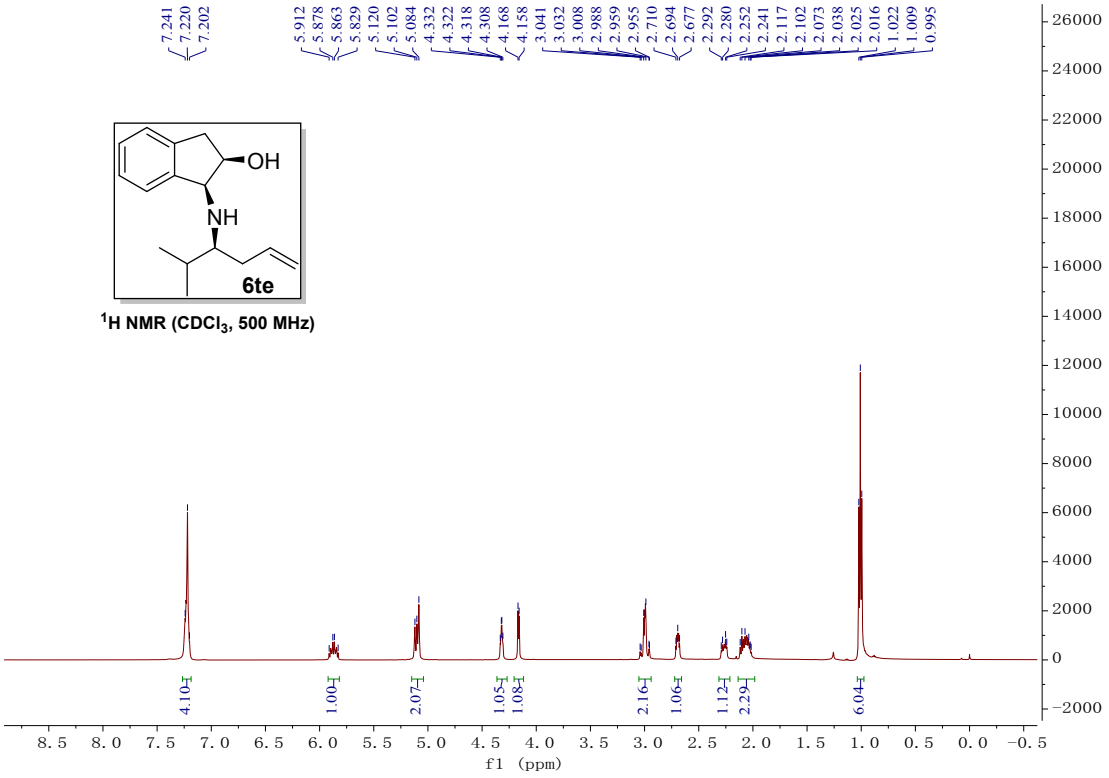
^{13}C NMR ($CDCl_3$, 126 MHz)



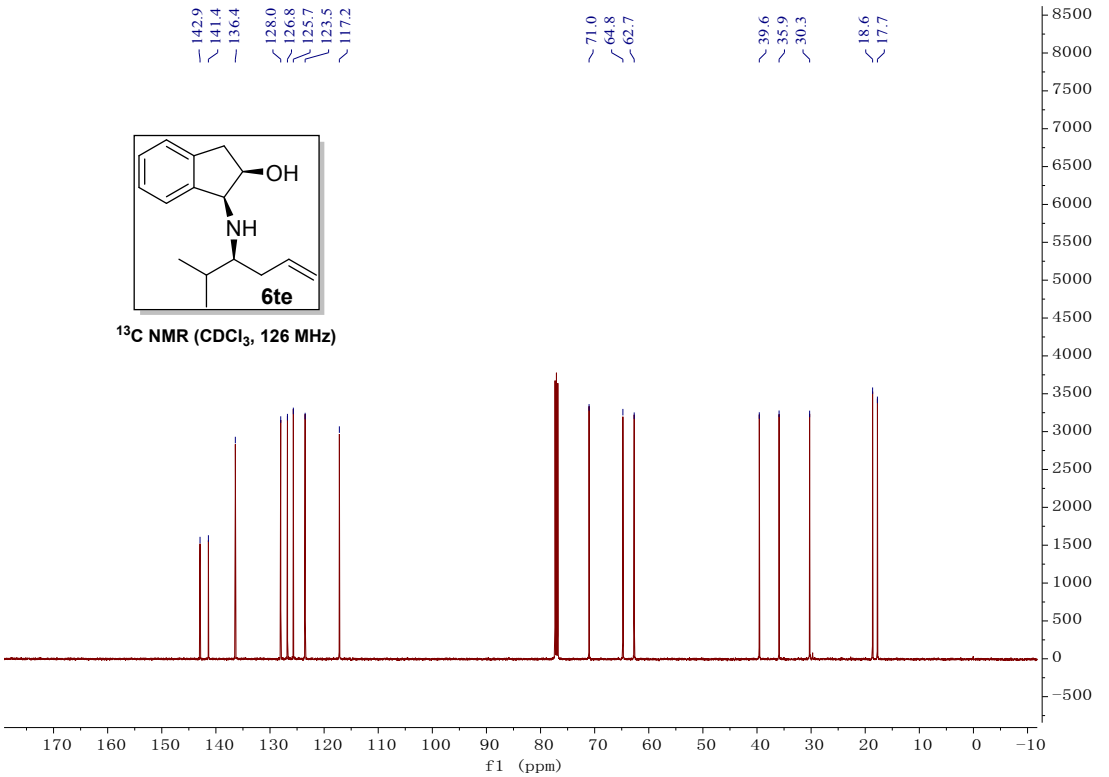
^{1}H NMR ($CDCl_3$, 500 MHz)



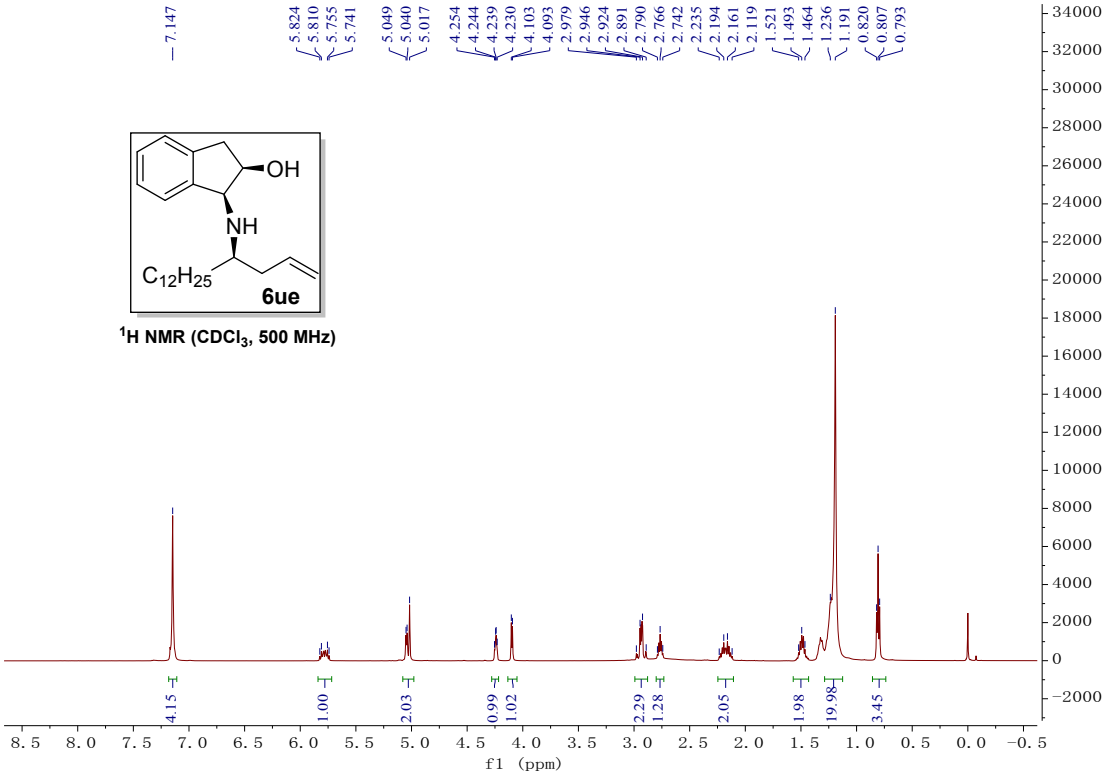
^{13}C NMR ($CDCl_3$, 126 MHz)



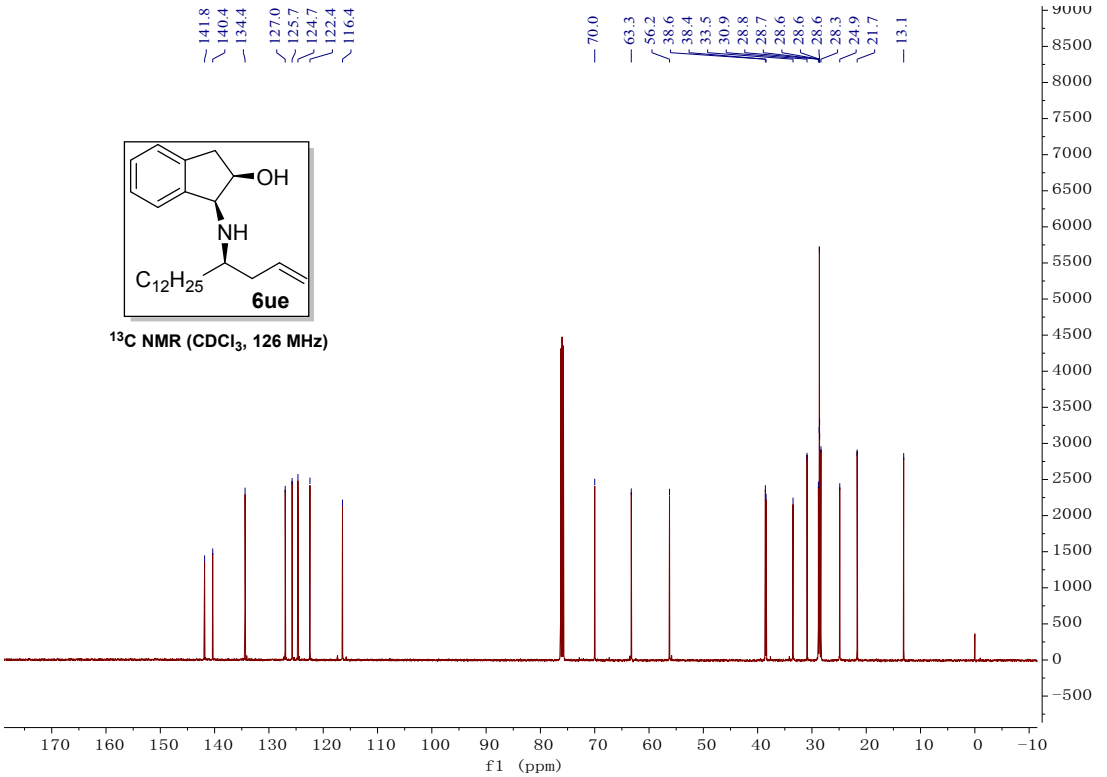
^{1}H NMR ($CDCl_3$, 500 MHz)



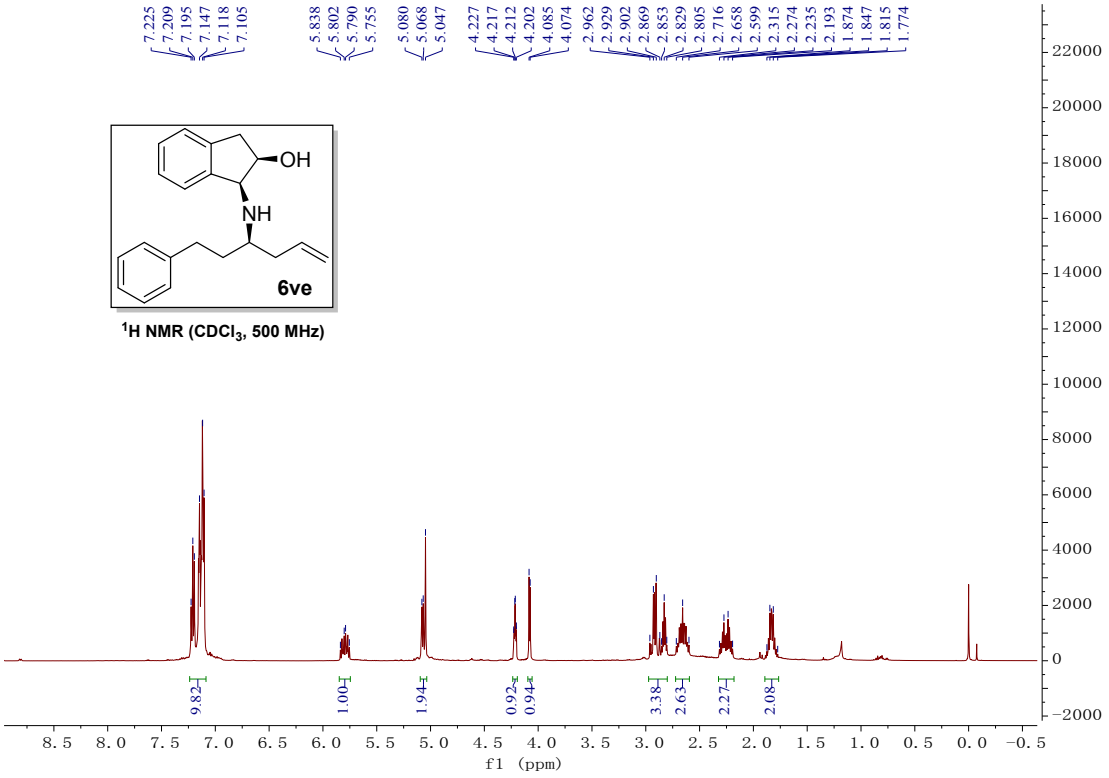
^{13}C NMR ($CDCl_3$, 126 MHz)



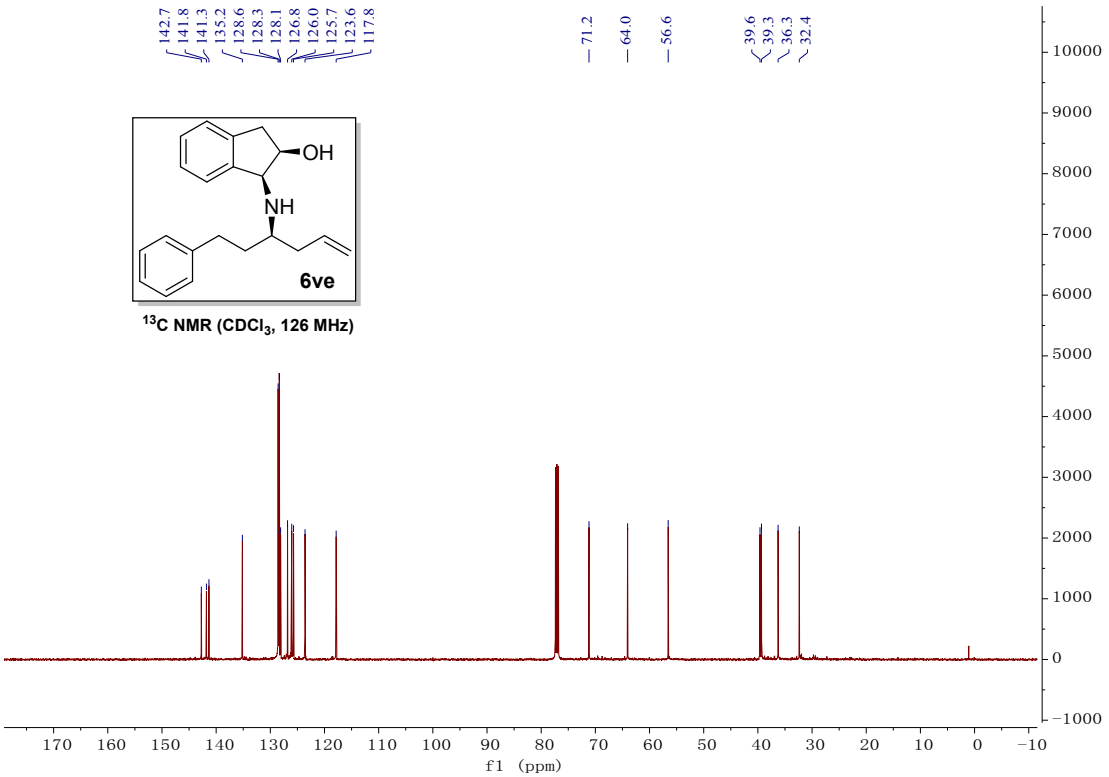
^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)



^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)