

Supporting Information For:

**Rhodium-Catalyzed Enantioselective
Hydroamination of Alkynes with Indolines**

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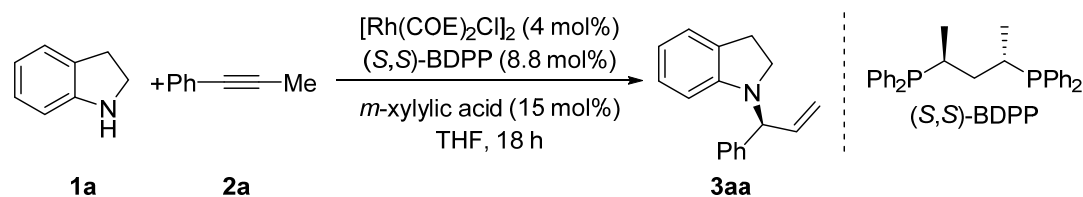
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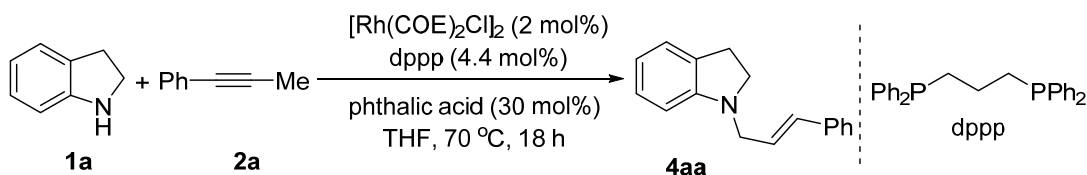
1. General: Commercial reagents were purchased from Sigma Aldrich, Strem, or Alfa Aesar and used without further purification. Reactions were monitored using thin-layer chromatography (TLC) or GC-FID. Visualization of the developed plates was performed under UV light (254 nm) or KMnO₄ stain. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. ¹H and ¹³C NMR spectra were recorded on Bruker CRYO500 or DRX400 spectrometer. ¹H NMR spectra were internally referenced to the residual solvent signal or TMS. ¹³C NMR spectra were internally referenced to the residual solvent signal. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were obtained on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex QStar Mass Spectrometer (ESI). Infrared (IR) spectra were obtained on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR, and are reported in terms of frequency of absorption (cm⁻¹). Column chromatography was performed with Silicycle Silia-P Flash Silica Gel using glass columns. Solvents were purchased from Fisher. Enantiomeric excesses for stereoselective reactions were determined by chiral SFC analysis using an Agilent Technologies HPLC (1200 series) system and Aurora A5 Fusion. Solvents used in hydroaminations were degassed by three freeze-pump-thaw cycles before being taken into a nitrogen-filled glove box. 1-Phenyl allene was prepared according to literature procedure.¹

2. Typical procedures for the hydroamination of alkynes



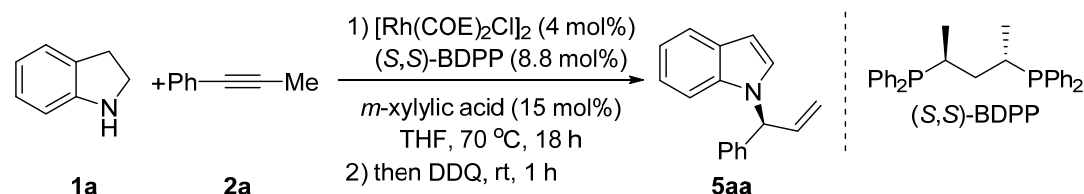
Method A: A mixture of $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (5.7 mg, 0.008 mmol), (S,S)-BDPP (7.8 mg, 0.018 mmol), *m*-xylylic acid (4.5 mg, 0.03 mmol), amine **1** (0.20 mmol), alkyne **2** (0.30 mmol), and THF (0.25 mL) were added to a 1 dram vial in the glove box. After heating the reaction mixture at 70 °C for 18 h, the resulting solution was cooled to rt. The selectivity was determined by ^1H NMR analysis of the crude reaction mixture. The product **3** was purified by column chromatography on silica gel using hexanes/EtOAc (20:1~10:1) or DCM/Hexane (10:1~5:1).

Method B: A mixture of $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (5.7 mg, 0.008 mmol), (S,S)-BDPP (7.8 mg, 0.018 mmol), *m*-xylylic acid (4.5 mg, 0.03 mmol), amine **1** (0.20 mmol), alkyne **2** (0.30 mmol), and THF (0.25 mL) were added to a 1 dram vial in the glove box. After heating the reaction mixture at 60 °C for 18 h, the resulting solution was cooled to rt. The selectivity was determined by ^1H NMR analysis of the crude reaction mixture. The product **3** was purified by column chromatography on silica gel using hexanes/EtOAc (20:1~10:1) or DCM/Hexane (10:1~5:1).



Method C: A mixture of $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (2.9 mg, 0.004 mmol), dppp (3.6 mg, 0.009 mmol), phthalic acid (10.0 mg, 0.06 mmol), amine **1** (0.20 mmol), alkyne **2** (0.30 mmol), and THF (0.25 mL) were added to a 1 dram vial in the glove box. After heating the reaction mixture at 70 °C for 18 h, the resulting solution was cooled to rt. The selectivity was determined by ^1H NMR analysis of the crude reaction mixture. The product **4** was purified by column chromatography on silica gel using hexanes/EtOAc (20:1~10:1).

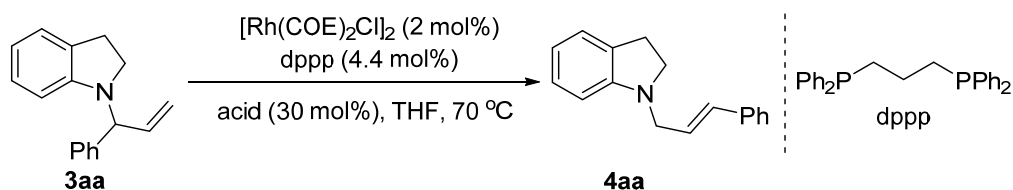
3. Typical procedure for one pot synthesis of *N*-allylic indoles



Method D: A mixture of $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (5.7 mg, 0.008 mmol), (S,S)-BDPP (7.8 mg, 0.018 mmol), *m*-xylylic acid (4.5 mg, 0.03 mmol), amine **1** (0.20 mmol), alkyne **2** (0.30 mmol), and THF (0.25 mL) were added to a 1 dram vial in the glove box. After heating the reaction mixture at

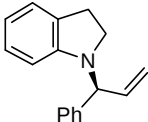
indicated temperature for 18 h, the resulting solution was cooled to rt. Then DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone, 0.30 mmol) was added and the reaction system was stirred for 1 h at room temperature. The THF was removed and DCM was added. Then the dark suspension mixture was filtrated through an aluminum oxide pat, washed with DCM, and the solvent was removed under reduced pressure. The selectivity was determined by ^1H NMR analysis of the crude reaction mixture. The product **5** was purified by column chromatography on silica gel using DCM/Hexane (20:1~10:1).

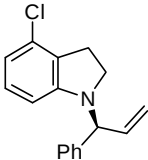
4. Typical procedure for isomerization of *N*-allylic indoline **3aa**

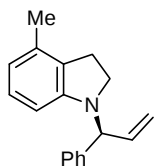


Method E: A mixture of $[\text{Rh}(\text{COE})_2\text{Cl}]_2$ (2.9 mg, 0.004 mmol), dppp (3.6 mg, 0.009 mmol), acid (0.06 mmol), racemic branched amine **3aa** (0.20 mmol), and THF (0.25 mL) were added to a 1 dram vial in the glove box. Then the reaction mixture was heated at 70 °C. The reaction progress was monitored by GC. The selectivity (**4aa/3aa**) was determined by ^1H NMR analysis of the crude reaction mixture.

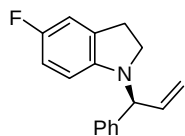
5. Characterization data

 1-(1-Phenyl-2-propenyl)-2,3-dihydroindole **3aa**: (Method **A**) colorless oil, 80% yield, 90% ee, $[\alpha]_D^{26} = -27.4$ (c 1.26, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.43 – 7.40 (m, 2H), 7.35 – 7.32 (m, 2H), 7.27 (t, $J = 7.3$ Hz, 1H), 7.06 (d, $J = 7.2$ Hz, 1H), 6.94 (t, $J = 7.7$ Hz, 1H), 6.62 (t, $J = 7.3$ Hz, 1H), 6.31 (d, $J = 7.9$ Hz, 1H), 6.13 – 6.06 (m, 1H), 5.32 (s, 1H), 5.29 (d, $J = 6.9$ Hz, 1H), 4.96 (d, $J = 7.7$ Hz, 1H), 3.41 – 3.28 (m, 2H), 2.94 (t, $J = 8.3$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.42, 140.59, 135.86, 130.55, 128.62, 127.87, 127.35, 127.11, 124.52, 118.13, 117.57, 108.42, 64.50, 50.38, 28.45. IR (ATR): 2844, 1605, 1484, 1458, 1246, 922, 741, 699 cm^{-1} . Chiral SFC: IC column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 4.0 min and 4.3 min (major).

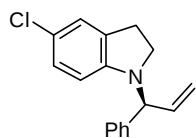
 1-(1-Phenyl-2-propenyl)-4-chloro-2,3-dihydroindole **3ba**: (Method **B**) colorless oil, 72% yield, 90% ee, $[\alpha]_D^{28} = -28.8$ (c 1.30, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.34 (m, 4H), 7.30 (t, $J = 7.1$ Hz, 1H), 6.89 (t, $J = 8.0$ Hz, 1H), 6.60 (d, $J = 8.0$ Hz, 1H), 6.19 (d, $J = 7.9$ Hz, 1H), 6.15 – 6.05 (m, 1H), 5.35 (dd, $J = 10.3, 0.9$ Hz, 1H), 5.32 (dd, $J = 17.1, 1.3$ Hz, 1H), 5.00 (d, $J = 7.5$ Hz, 1H), 3.50 – 3.36 (m, 2H), 3.08 – 2.94 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 152.65, 139.94, 135.26, 130.57, 128.71, 128.69, 128.35, 127.85, 127.56, 118.47, 117.46, 106.22, 64.10, 49.63, 27.66. IR (ATR): 2846, 1598, 1451, 1253, 1122, 925, 752, 718, 698 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{17}\text{ClN}$ $[\text{M}+\text{H}]^+$ 270.1044, found 270.1040. Chiral SFC: OJ-H column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 4.5 min (major) and 5.9 min.



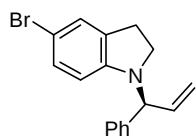
1-(1-Phenyl-2-propenyl)-4-methyl-2,3-dihydroindole **3ca**: (Method **A**) colorless oil, 81% yield, 90% ee, $[\alpha]_D^{26} = -29.6$ (c 1.34, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.46 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 7.31 – 7.28 (m, 1H), 6.90 (t, $J = 7.7$ Hz, 1H), 6.49 (d, $J = 7.6$ Hz, 1H), 6.20 (d, $J = 7.9$ Hz, 1H), 6.17 – 6.08 (m, 1H), 5.36 – 5.30 (m, 2H), 4.99 (d, $J = 7.7$ Hz, 1H), 3.46 – 3.34 (m, 2H), 2.96 – 2.84 (m, 2H), 2.21 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 151.14, 140.61, 135.82, 133.96, 129.02, 128.60, 127.90, 127.33, 127.22, 119.02, 118.16, 105.96, 64.45, 50.04, 27.12, 18.71. **IR** (ATR): 2843, 1593, 1461, 1257, 1154, 994, 921, 755, 727, 698 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 250.1590, found 250.1588. **Chiral SFC**: OJ-H column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 5.1 min and 6.6 min (major).



1-(1-Phenyl-2-propenyl)-5-fluoro-2,3-dihydroindole **3da**: (Method **B**) colorless oil, 82% yield, 89% ee, $[\alpha]_D^{28} = -12.4$ (c 1.38, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.42 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.25 (m, 1H), 6.79 (ddt, $J = 8.3, 2.3, 1.0$ Hz, 1H), 6.65 – 6.58 (m, 1H), 6.15 (dd, $J = 8.6, 4.3$ Hz, 1H), 6.07 (ddd, $J = 16.5, 10.9, 7.8$ Hz, 1H), 5.33 – 5.23 (m, 2H), 4.84 (d, $J = 7.8$ Hz, 1H), 3.34 (td, $J = 8.2, 1.0$ Hz, 2H), 2.91 (t, $J = 8.4$ Hz, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 156.46 (d, $J = 234.7$ Hz), 147.66, 140.59, 135.97, 132.42 (d, $J = 8.0$ Hz), 128.70, 127.81, 127.47, 118.22, 112.69 (d, $J = 22.7$ Hz), 112.19 (d, $J = 23.8$ Hz), 108.68 (d, $J = 7.9$ Hz), 65.53, 51.26, 28.58 (d, $J = 1.7$ Hz). $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -127.8. **IR** (ATR): 2845, 1602, 1486, 1470, 1230, 1177, 1126, 929, 799, 741, 699 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{17}\text{FN}$ $[\text{M}+\text{H}]^+$ 254.1340, found 254.1341. **Chiral SFC**: OJ-H column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 3.5 min and 4.1 min (major).

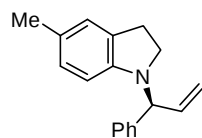


1-(1-Phenyl-2-propenyl)-5-chloro-2,3-dihydroindole **3ea**: (Method **B**) colorless oil, 78% yield, 90% ee, $[\alpha]_D^{28} = -39.5$ (c 1.41, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.41 – 7.37 (m, 2H), 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.02 – 6.98 (m, 1H), 6.88 (dd, $J = 8.4, 2.2$ Hz, 1H), 6.19 (d, $J = 8.4$ Hz, 1H), 6.07 (ddd, $J = 17.6, 10.2, 7.6$ Hz, 1H), 5.34 – 5.27 (m, 2H), 4.91 (d, $J = 7.6$ Hz, 1H), 3.43 – 3.32 (m, 2H), 2.93 (t, $J = 8.4$ Hz, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.92, 140.06, 135.44, 132.57, 128.73, 127.84, 127.58, 126.79, 124.74, 118.47, 109.17, 64.71, 50.65, 28.28. **IR** (ATR): 2843, 1601, 1485, 1466, 1247, 925, 797, 734, 699 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{15}\text{ClN}$ $[\text{M}-\text{H}]^-$ 268.0893, found 268.0889. **Chiral SFC**: OJ-H column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 6.2 min and 6.7 min (major).

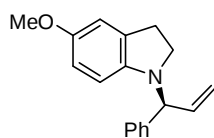


1-(1-Phenyl-2-propenyl)-5-bromo-2,3-dihydroindole **3fa**: (Method **B**) colorless oil, 85% yield, 88% ee, $[\alpha]_D^{28} = -38.3$ (c 1.78, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.42 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 7.15 – 7.14 (m, 1H), 7.04 – 7.01 (m, 1H), 6.16 (d, $J = 8.4$ Hz, 1H), 6.08 (ddd, $J = 17.7, 10.2, 7.6$ Hz, 1H), 5.36 – 5.27 (m, 2H), 4.93 (d, $J = 7.6$ Hz, 1H), 3.44 – 3.31 (m, 2H), 2.95 (t, $J = 8.5$ Hz, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 150.46, 140.04, 135.38, 132.98, 129.70, 128.72, 127.82, 127.56, 127.48, 118.45, 109.60, 109.13, 64.43, 50.50, 28.23. **IR** (ATR): 2843, 1596, 1483, 1468, 1246, 925, 795, 733, 699 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{15}\text{BrN}$ $[\text{M}-\text{H}]^-$ 312.0388, found 312.0399. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 6.9 min and

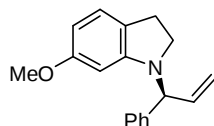
7.7 min (major).



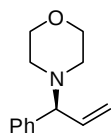
1-(1-Phenyl-2-propenyl)-5-methyl-2,3-dihydroindole **3ga**: (Method **B**) colorless oil, 83% yield, 89% ee, $[\alpha]_D^{28} = -27.4$ (c 1.37, CHCl_3). **^1H NMR** (500 MHz, CDCl_3) δ 7.48 – 7.44 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.28 (m, 1H), 6.96 – 6.92 (m, 1H), 6.80 – 6.76 (m, 1H), 6.24 (d, $J = 8.0$ Hz, 1H), 6.18 – 6.08 (m, 1H), 5.36 – 5.31 (m, 2H), 4.93 (d, $J = 7.9$ Hz, 1H), 3.36 (t, $J = 8.3$ Hz, 2H), 2.95 (t, $J = 8.3$ Hz, 2H), 2.25 (s, 3H). **^{13}C NMR** (126 MHz, CDCl_3) δ 149.17, 140.82, 136.09, 131.06, 128.61, 127.86, 127.31, 127.24, 125.51, 118.08, 108.67, 65.24, 50.92, 28.53, 20.79. **IR** (ATR): 2844, 1619, 1491, 1449, 1248, 1151, 994, 922, 799, 699 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 250.1590, found 250.1591. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 4.3 min and 5.0 min (major).



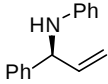
1-(1-Phenyl-2-propenyl)-5-methoxy-2,3-dihydroindole **3ha**: (Method **B**) colorless oil, 80% yield, 77% ee, $[\alpha]_D^{24} = -16.9$ (c 1.42, CHCl_3). **^1H NMR** (500 MHz, CD_2Cl_2) δ 7.44 (d, $J = 7.6$ Hz, 2H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.27 (t, $J = 7.3$ Hz, 1H), 6.72 – 6.70 (m, 1H), 6.45 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.16 (d, $J = 8.5$ Hz, 1H), 6.10 (ddd, $J = 17.5, 10.2, 8.1$ Hz, 1H), 5.32 – 5.28 (m, 2H), 4.82 (d, $J = 8.0$ Hz, 1H), 3.68 (s, 3H), 3.35 – 3.25 (m, 2H), 2.89 (t, $J = 8.1$ Hz, 2H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 153.11, 146.07, 141.58, 136.94, 132.80, 128.83, 128.07, 127.52, 117.87, 112.20, 111.43, 109.28, 66.17, 56.13, 51.56, 29.04. **IR** (ATR): 2829, 1593, 1487, 1450, 1433, 1234, 1179, 1136, 1034, 922, 796, 699 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$ 266.1539, found 266.1543. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 11.3 min and 13.8 min (major).

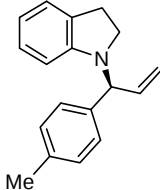


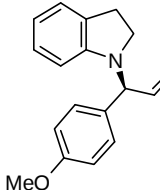
1-(1-Phenyl-2-propenyl)-6-methoxy-2,3-dihydroindole **3ia**: (Method **A**) colorless oil, 84% yield, 83% ee, $[\alpha]_D^{24} = -40.0$ (c 1.48, CHCl_3). **^1H NMR** (500 MHz, CDCl_3) δ 7.47 – 7.42 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 6.97 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.24 – 6.08 (m, 2H), 5.97 (d, $J = 2.1$ Hz, 1H), 5.37 – 5.31 (m, 2H), 4.98 (d, $J = 7.6$ Hz, 1H), 3.69 (s, 3H), 3.46 – 3.33 (m, 2H), 2.91 (t, $J = 8.5$ Hz, 2H). **^{13}C NMR** (126 MHz, CDCl_3) δ 159.81, 152.69, 140.35, 135.69, 128.63, 127.91, 127.42, 124.40, 122.94, 118.20, 101.28, 96.20, 64.34, 55.37, 50.93, 27.61. **IR** (ATR): 2832, 1618, 1592, 1493, 1450, 1288, 1264, 1208, 1157, 1035, 919, 821, 764, 699 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{20}\text{NO}$ $[\text{M}+\text{H}]^+$ 266.1539, found 266.1542. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 10.2 min and 13.9 min (major).

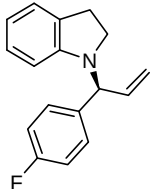


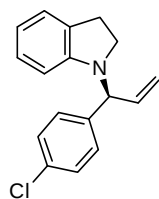
1-(1-Phenyl-2-propenyl)morphine **3ja**: (Method **A**, *m*-xylylic acid (50 mol%)) colorless oil, 47% yield, 26% ee, $[\alpha]_D^{25} = -20.3$ (c 0.64, CHCl_3). **^1H NMR** (500 MHz, CD_2Cl_2) δ 7.37 – 7.29 (m, 4H), 7.23 (t, $J = 6.8$ Hz, 1H), 5.96 – 5.85 (m, 1H), 5.24 (d, $J = 17.1$ Hz, 1H), 5.09 (d, $J = 10.1$ Hz, 1H), 3.71 – 3.57 (m, 5H), 2.51 – 2.40 (m, 2H), 2.34 – 2.26 (m, 2H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 142.34, 140.48, 128.90, 128.34, 127.53, 116.60, 75.77, 67.45, 52.37. **IR** (ATR): 2956, 2852, 2803, 1717, 1450, 1303, 1276, 1208, 1116, 1069, 1011, 993, 873, 758, 700, 679 cm^{-1} . **Chiral SFC**: OD-H column, 230 nm, 1.5% 2-propanol in CO_2 , 2.5 mL/min, retention time 1.9 min and 2.2 min (major).


N-Phenyl-1-phenyl-2-propenylamine 3ka: (Method **A**) colorless oil, 32% yield, 76% ee, $[\alpha]_D^{25} = -7.4$ (c 0.44, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 7.41 – 7.35 (m, 4H), 7.31 – 7.26 (m, 1H), 7.13 – 7.09 (m, 2H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.61 – 6.58 (m, 2H), 6.06 (ddd, $J = 17.1, 10.2, 6.0$ Hz, 1H), 5.27 (dt, $J = 17.1, 1.4$ Hz, 1H), 5.23 (dt, $J = 10.2, 1.3$ Hz, 1H), 4.97 (d, $J = 6.0$ Hz, 1H), 4.17 (brs, 1H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 147.63, 142.50, 139.73, 129.39, 129.06, 127.76, 127.45, 117.85, 116.03, 113.88, 61.03. **IR** (ATR): 2922, 2845, 1600, 1501, 1452, 1313, 1075, 992, 924, 746, 691 cm⁻¹. **Chiral SFC:** OJ-H column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 6.7 min and 7.2 min (major).

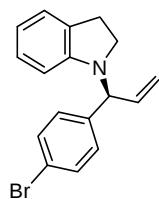

1-(1-(4-Methylphenyl)-2-propenyl)-2,3-dihydroindole 3ab: (Method **B**) colorless oil, 73% yield, 91% ee, $[\alpha]_D^{28} = -31.6$ (c 1.21, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 7.31 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 7.2$ Hz, 1H), 6.92 (t, $J = 7.7$ Hz, 1H), 6.59 (t, $J = 7.4$ Hz, 1H), 6.31 (d, $J = 7.9$ Hz, 1H), 6.16 – 6.07 (m, 1H), 5.32 (s, 1H), 5.29 (dd, $J = 4.3, 0.9$ Hz, 1H), 4.96 (d, $J = 7.6$ Hz, 1H), 3.41 – 3.29 (m, 2H), 2.99 – 2.87 (m, 2H), 2.36 (s, 3H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 151.80, 137.95, 137.34, 136.52, 130.95, 129.49, 128.03, 127.19, 124.68, 117.82, 117.64, 108.53, 64.35, 50.48, 28.64, 21.19. **IR** (ATR): 2844, 1605, 1484, 1458, 1329, 1251, 1157, 1024, 919, 741, 698 cm⁻¹. **HRMS** calculated for C₁₈H₂₀N [M+H]⁺ 250.1590, found 250.1604. **Chiral SFC:** IC column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 4.9 min and 5.5 min (major).


1-(1-(4-Methoxyphenyl)-2-propenyl)-2,3-dihydroindole 3ac: (Method **A**) colorless oil, 70% yield, 82% ee, $[\alpha]_D^{28} = -29.6$ (c 1.24, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 7.36 – 7.32 (m, 2H), 7.05 (d, $J = 7.2$ Hz, 1H), 6.94 – 6.88 (m, 3H), 6.59 (t, $J = 7.4$ Hz, 1H), 6.32 (d, $J = 7.9$ Hz, 1H), 6.12 (ddd, $J = 16.6, 10.8, 7.6$ Hz, 1H), 5.32 (d, $J = 0.7$ Hz, 1H), 5.31 – 5.27 (m, 1H), 4.96 (d, $J = 7.6$ Hz, 1H), 3.81 (s, 3H), 3.40 – 3.27 (m, 2H), 2.99 – 2.87 (m, 2H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 159.27, 151.80, 136.53, 132.96, 130.98, 129.25, 127.21, 124.69, 117.74, 117.65, 114.11, 108.56, 63.94, 55.59, 50.43, 28.63. **IR** (ATR): 2834, 1605, 1509, 1484, 1459, 1243, 1173, 1032, 828, 742 cm⁻¹. **HRMS** calculated for C₁₈H₂₀NO [M+H]⁺ 266.1539, found 266.1546. **Chiral SFC:** IC column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 7.9 min and 10.3 min (major).

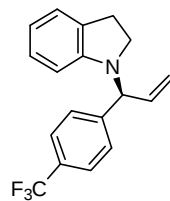

1-(1-(4-Fluorophenyl)-2-propenyl)-2,3-dihydroindole 3ad: (Method **B**) colorless oil, 87% yield, 90% ee, $[\alpha]_D^{28} = -23.4$ (c 1.47, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 7.45 – 7.39 (m, 2H), 7.09 – 7.03 (m, 3H), 6.94 – 6.90 (m, 1H), 6.60 (td, $J = 7.4, 0.7$ Hz, 1H), 6.28 (d, $J = 7.9$ Hz, 1H), 6.10 (ddd, $J = 17.1, 10.3, 7.7$ Hz, 1H), 5.36 – 5.29 (m, 2H), 4.97 (d, $J = 7.8$ Hz, 1H), 3.40 – 3.29 (m, 2H), 3.01 – 2.88 (m, 2H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 162.41 (d, $J = 244.6$ Hz), 151.56, 136.93 (d, $J = 3.1$ Hz), 135.99, 131.02, 129.73 (d, $J = 8.0$ Hz), 127.23, 124.78, 118.45, 117.92, 115.54 (d, $J = 21.3$ Hz), 108.62, 64.03, 50.54, 28.66. **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -116.7. **IR** (ATR): 2844, 1604, 1505, 1484, 1458, 1245, 1220, 1156, 925, 837, 743, 719 cm⁻¹. **HRMS** calculated for C₁₇H₁₇FN [M+H]⁺ 254.1340, found 254.1342. **Chiral SFC:** IC column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 3.5 min and 3.9 min (major).



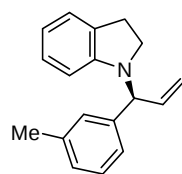
1-(1-(4-Chlorophenyl)-2-propenyl)-2,3-dihydroindole **3ae**: (Method **B**) pale yellow oil, 83% yield, 92% ee, $[\alpha]_D^{28} = -16.0$ (c 1.50, CHCl_3). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ 7.40 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.6$ Hz, 2H), 7.06 (d, $J = 7.2$ Hz, 1H), 6.91 (t, $J = 7.7$ Hz, 1H), 6.61 (t, $J = 7.4$ Hz, 1H), 6.26 (d, $J = 7.9$ Hz, 1H), 6.09 (ddd, $J = 17.2, 10.2, 7.9$ Hz, 1H), 5.35 – 5.30 (m, 2H), 4.95 (d, $J = 7.9$ Hz, 1H), 3.94 – 3.32 (m, 2H), 3.00 – 2.89 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2) δ 151.45, 139.80, 135.71, 133.17, 131.03, 129.52, 128.93, 127.22, 124.79, 118.74, 118.02, 108.69, 64.23, 50.64, 28.67. **IR** (ATR): 2843, 1605, 1483, 1458, 1247, 1089, 1013, 925, 821, 743, 726 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{17}\text{ClN}$ $[\text{M}+\text{H}]^+$ 270.1044, found 270.1058. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 5.1 min and 5.7 min (major).



1-(1-(4-Bromophenyl)-2-propenyl)-2,3-dihydroindole **3af**: (Method **B**) pale yellow oil, 69% yield, 86% ee, $[\alpha]_D^{28} = -10.8$ (c 1.44, CHCl_3). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ 7.49 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.6$ Hz, 2H), 7.05 (d, $J = 7.2$ Hz, 1H), 6.91 (t, $J = 7.7$ Hz, 1H), 6.60 (t, $J = 7.4$ Hz, 1H), 6.25 (d, $J = 7.9$ Hz, 1H), 6.08 (ddd, $J = 18.0, 10.2, 7.9$ Hz, 1H), 5.35 – 5.29 (m, 2H), 4.92 (d, $J = 7.9$ Hz, 1H), 3.39 – 3.31 (m, 2H), 3.00 – 2.88 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 151.43, 140.33, 135.63, 131.89, 131.02, 129.87, 127.21, 124.78, 121.30, 118.77, 118.01, 108.66, 64.29, 50.65, 28.66. **IR** (ATR): 2843, 1605, 1483, 1458, 1247, 1071, 1009, 925, 819, 742, 719 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$ 314.0539, found 314.0543. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 6.5 min and 7.4 min (major).

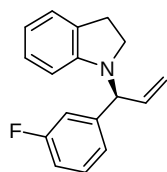


1-(1-(4-Trifluoromethylphenyl)-2-propenyl)-2,3-dihydroindole **3ag**: (Method **B**) pale yellow oil, 70% yield, 91% ee, $[\alpha]_D^{29} = -7.0$ (c 1.41, CHCl_3). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ 7.59 – 7.54 (m, 4H), 7.03 (d, $J = 7.2$ Hz, 1H), 6.86 (t, $J = 7.7$ Hz, 1H), 6.57 (t, $J = 7.4$ Hz, 1H), 6.18 (d, $J = 7.9$ Hz, 1H), 6.06 (ddd, $J = 17.1, 10.2, 8.0$ Hz, 1H), 5.36 – 5.26 (m, 2H), 4.97 (d, $J = 8.0$ Hz, 1H), 3.38 – 3.31 (m, 2H), 2.98 – 2.89 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2) δ 151.35, 145.54, 135.40, 131.05, 129.56 (q, $J = 32.2$ Hz), 128.43, 127.24, 125.78 (q, $J = 3.8$ Hz), 124.85, 119.22, 118.19, 108.69, 64.67, 50.77, 28.70. $^{19}\text{F NMR}$ (376 MHz, CD_2Cl_2) δ -62.9. **IR** (ATR): 2846, 1605, 1485, 1322, 1248, 1161, 1120, 1066, 1017, 929, 831, 743 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{17}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$ 304.1308, found 304.1308. **Chiral SFC**: IB column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 3.5 min and 3.9 min (major).

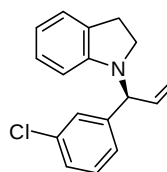


1-(1-(3-Methylphenyl)-2-propenyl)-2,3-dihydroindole **3ah**: (Method **B**) colorless oil, 79% yield, 90% ee, $[\alpha]_D^{28} = -28.4$ (c 1.32, CHCl_3). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ 7.27 – 7.21 (m, 3H), 7.11 (d, $J = 7.0$ Hz, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 6.91 (t, $J = 7.7$ Hz, 1H), 6.59 (t, $J = 7.3$ Hz, 1H), 6.30 (d, $J = 7.9$ Hz, 1H), 6.16 – 6.07 (m, 1H), 5.33 – 5.31 (m, 1H), 5.29 (dd, $J = 2.4, 0.9$ Hz, 1H), 4.93 (d, $J = 7.8$ Hz, 1H), 3.40 – 3.31 (m, 2H), 3.00 – 2.88 (m, 2H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2) δ 151.84, 141.08, 138.60, 136.48, 130.96, 128.76, 128.69, 128.30, 127.21, 125.12, 124.68, 117.89, 117.69, 108.55, 64.80, 50.61, 28.65, 21.63. **IR** (ATR): 2844, 1604, 1484, 1457, 1330, 1250, 993, 922, 773, 741, 717, 700 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 250.1590,

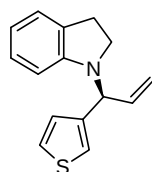
found 250.1591. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 4.3 min and 5.0 min (major).



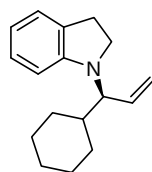
1-(1-(3-Fluorophenyl)-2-propenyl)-2,3-dihydroindole **3ai**: (Method **B**) colorless oil, 82% yield, 94% ee, $[\alpha]_D^{28} = -18.4$ (c 1.38, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 7.38 – 7.31 (m, 1H), 7.24 (d, $J = 7.7$ Hz, 1H), 7.18 (d, $J = 10.3$ Hz, 1H), 7.07 (dd, $J = 7.2, 0.7$ Hz, 1H), 7.02 – 6.97 (m, 1H), 6.95 – 6.89 (m, 1H), 6.61 (td, $J = 7.4, 0.8$ Hz, 1H), 6.26 (d, $J = 7.9$ Hz, 1H), 6.10 (ddd, $J = 17.0, 10.3, 8.0$ Hz, 1H), 5.37 – 5.31 (m, 2H), 4.96 (d, $J = 8.0$ Hz, 1H), 3.38 (t, $J = 8.4$ Hz, 2H), 2.96 (t, $J = 8.3$ Hz, 2H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 163.51 (d, $J = 244.9$ Hz), 151.45, 144.11 (d, $J = 6.6$ Hz), 135.56, 131.02, 130.39 (d, $J = 8.2$ Hz), 127.22, 124.79, 123.69 (d, $J = 2.7$ Hz), 118.90, 118.03, 114.81 (d, $J = 22.1$ Hz), 114.34 (d, $J = 21.3$ Hz), 108.64, 64.45 (d, $J = 1.7$ Hz), 50.66, 28.68. **¹⁹F NMR** (376 MHz, CD₂Cl₂) δ -114.1. **IR** (ATR): 2844, 1604, 1588, 1484, 1458, 1442, 1248, 927, 876, 778, 743, 718, 697 cm⁻¹. **HRMS** calculated for C₁₇H₁₇FN [M+H]⁺ 254.1340, found 254.1349. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 4.2 min and 4.4 min (major).



1-(1-(3-Chlorophenyl)-2-propenyl)-2,3-dihydroindole **3aj**: (Method **B**) pale yellow oil, 81% yield, 93% ee, $[\alpha]_D^{29} = -13.1$ (c 1.45, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 7.45 (s, 1H), 7.36 – 7.26 (m, 3H), 7.06 (d, $J = 7.2$ Hz, 1H), 6.91 (t, $J = 7.7$ Hz, 1H), 6.61 (t, $J = 7.4$ Hz, 1H), 6.25 (d, $J = 7.9$ Hz, 1H), 6.12 – 6.04 (m, 1H), 5.37 – 5.29 (m, 2H), 4.93 (d, $J = 8.0$ Hz, 1H), 3.37 (t, $J = 8.3$ Hz, 2H), 2.96 (t, $J = 8.3$ Hz, 2H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 151.42, 143.57, 135.48, 134.71, 131.03, 130.23, 128.02, 127.69, 127.23, 126.28, 124.80, 118.98, 118.06, 108.64, 64.51, 50.71, 28.68. **IR** (ATR): 2844, 1605, 1594, 1484, 1473, 1249, 1194, 996, 926, 743, 716, 694 cm⁻¹. **HRMS** calculated for C₁₇H₁₇ClN [M+H]⁺ 270.1044, found 270.1049. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 4.5 min and 4.9 min (major).

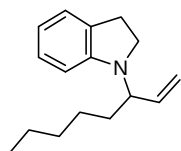


1-(1-(3-Thienyl)-2-propenyl)-2,3-dihydroindole **3ak**: (Method **B** at 50 °C) colorless oil, 80% yield, 65% ee, $[\alpha]_D^{25} = -34.3$ (c 1.29, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 7.36 – 7.31 (m, 1H), 7.20 – 7.17 (m, 1H), 7.11 (d, $J = 5.0$ Hz, 1H), 7.05 (d, $J = 7.2$ Hz, 1H), 6.96 (t, $J = 7.7$ Hz, 1H), 6.60 (t, $J = 7.4$ Hz, 1H), 6.40 (d, $J = 7.9$ Hz, 1H), 6.21 – 6.12 (m, 1H), 5.38 – 5.30 (m, 2H), 5.13 (d, $J = 7.4$ Hz, 1H), 3.42 – 3.36 (m, 1H), 3.33 – 3.26 (m, 1H), 2.98 – 2.87 (m, 2H). **¹³C NMR** (126 MHz, CD₂Cl₂) δ 151.44, 142.05, 135.52, 130.90, 128.01, 127.28, 126.09, 124.81, 122.50, 118.23, 117.78, 108.45, 59.96, 49.79, 28.60. **IR** (ATR): 2844, 1604, 1484, 1458, 1250, 924, 837, 766, 740, 716, 688 cm⁻¹. **HRMS** calculated for C₁₅H₁₆NS [M+H]⁺ 242.0998, found 242.0992. **Chiral SFC**: OJ-H column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 5.5 min (major) and 7.2 min.

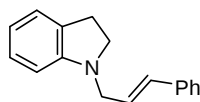


1-(1-(Cyclohexyl)-2-propenyl)-2,3-dihydroindole **3al**: (Method **A**) colorless oil, 15% yield, 27% ee, $[\alpha]_D^{28} = +6.6$ (c 0.24, CHCl₃). **¹H NMR** (500 MHz, CD₂Cl₂) δ 6.99 – 6.94 (m, 2H), 6.50 (t, $J = 7.4$ Hz, 1H), 6.35 (d, $J = 7.9$ Hz, 1H), 5.73 (ddd, $J = 17.1, 10.2, 9.0$ Hz, 1H), 5.17 (dd, $J = 10.3, 1.6$ Hz, 1H), 5.15 – 5.09 (m, 1H), 3.51 (t, $J = 9.5$ Hz, 1H), 3.45 (dd, $J = 15.0, 7.7$ Hz, 1H), 3.36 (dd, $J = 18.8, 9.5$ Hz,

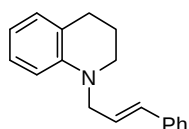
1H), 2.97 – 2.86 (m, 2H), 2.02 (d, $J = 13.0$ Hz, 1H), 1.83 – 1.71 (m, 3H), 1.70 – 1.57 (m, 2H), 1.33 – 1.17 (m, 3H), 1.01 – 0.92 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2) δ 152.13, 134.83, 130.17, 127.30, 124.62, 118.16, 116.67, 107.44, 64.60, 47.28, 39.30, 31.23, 30.77, 28.56, 27.04, 26.52. **IR** (ATR): 2849, 1605, 1487, 1473, 1253, 1157, 917, 740, 719, 696 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 242.1903, found 242.1909. **Chiral SFC**: OJ-H column, 254 nm, 2% 2-propanol in CO_2 , 2.5 mL/min, retention time 2.4 min (major) and 2.7 min.



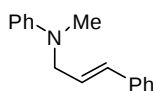
1-(1-Pentyl-2-propenyl)-2,3-dihydroindole **3an**: (Method **A**) colorless oil, 29% yield, 7% ee. $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ 7.04 – 6.93 (m, 2H), 6.53 (t, $J = 7.3$ Hz, 1H), 6.38 (d, $J = 7.9$ Hz, 1H), 5.83 – 5.73 (m, 1H), 5.18 – 5.16 (m, 1H), 5.15 – 5.13 (m, 1H), 3.93 (q, $J = 7.2$ Hz, 1H), 3.41 (dd, $J = 15.3, 8.3$ Hz, 1H), 3.32 (dd, $J = 18.4, 9.3$ Hz, 1H), 2.95 – 2.88 (m, 2H), 1.75 – 1.58 (m, 2H), 1.47 – 1.29 (m, 6H), 0.90 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (126 MHz, CD_2Cl_2) δ 151.97, 136.69, 130.41, 127.36, 124.66, 116.96, 116.75, 107.49, 58.07, 46.98, 32.15, 31.97, 28.50, 26.62, 23.05, 14.24. **IR** (ATR): 2855, 1606, 1487, 1472, 1459, 1255, 1158, 918, 741 cm^{-1} . **HRMS** calculated for $\text{C}_{16}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$ 230.1903, found 230.1903. **Chiral SFC**: OJ-H column, 254 nm, 1.5% *i*-propanol in CO_2 , 2.5 mL/min, retention time 1.5 min and 1.7 min (maj).



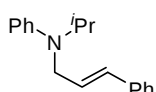
(*E*)-1-(3-Phenyl-2-propenyl)-2,3-dihydroindole **4aa**: (Method **C**) colorless oil, 91% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37 (d, $J = 7.9$ Hz, 2H), 7.29 (t, $J = 7.6$ Hz, 2H), 7.23 – 7.19 (m, 1H), 7.10 – 7.04 (m, 2H), 6.70 – 6.54 (m, 3H), 6.29 (dt, $J = 15.8, 6.2$ Hz, 1H), 3.86 (d, $J = 6.3$ Hz, 2H), 3.37 (t, $J = 8.3$ Hz, 2H), 2.96 (t, $J = 8.3$ Hz, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 152.28, 136.97, 132.43, 130.42, 128.68, 127.62, 127.43, 126.46, 126.03, 124.61, 117.91, 107.54, 53.46, 51.73, 28.67. **IR** (ATR): 3024, 2919, 2815, 1605, 1486, 1266, 965, 714, 735, 691 cm^{-1} .



(*E*)-1-(3-Phenyl-2-propenyl)-1,2,3,4-tetrahydroquinoline **4la**: (Method **C**) colorless oil, 99% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.38 (d, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.07 (t, $J = 7.7$ Hz, 1H), 6.99 (d, $J = 7.3$ Hz, 1H), 6.70 – 6.60 (m, 2H), 6.56 (d, $J = 15.9$ Hz, 1H), 6.28 (dt, $J = 15.8, 5.3$ Hz, 1H), 4.05 (d, $J = 5.5$ Hz, 2H), 3.40 – 3.30 (m, 2H), 2.81 (t, $J = 6.4$ Hz, 2H), 2.04 – 1.99 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 145.44, 137.05, 131.18, 129.18, 128.63, 127.46, 127.28, 126.42, 125.66, 122.71, 116.07, 111.27, 53.60, 49.25, 28.23, 22.43. **IR** (ATR): 3024, 2927, 2840, 1601, 1495, 1344, 1329, 965, 741, 691 cm^{-1} .

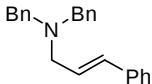


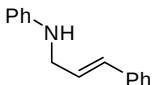
(*E*)-*N*-Methyl-*N*-phenyl-3-phenyl-2-propenylamine **4ma**: (Method **C**) colorless oil, 95% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.19 (m, 5H), 6.78 (d, $J = 8.2$ Hz, 2H), 6.72 (t, $J = 7.3$ Hz, 1H), 6.51 (d, $J = 15.9$ Hz, 1H), 6.24 (dt, $J = 15.9, 5.5$ Hz, 1H), 4.06 (dd, $J = 5.5, 1.5$ Hz, 2H), 2.96 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.64, 136.98, 131.36, 129.31, 128.65, 127.52, 126.43, 125.82, 116.71, 112.74, 55.02, 38.15. **IR** (ATR): 3026, 1597, 1505, 1353, 1200, 1117, 991, 964, 728, 690 cm^{-1} .

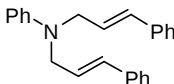


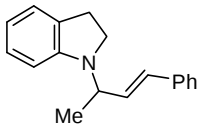
(*E*)-*N*-Isopropyl-*N*-phenyl-3-phenyl-2-propenylamine **4na**: (Method **C**) colorless oil, 85% yield. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.42 (d, $J = 7.9$ Hz, 2H), 7.36 (t, $J =$

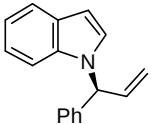
7.4 Hz, 2H), 7.31 – 7.27 (m, 3H), 6.87 (d, $J = 8.1$ Hz, 2H), 6.76 (t, $J = 7.1$ Hz, 1H), 6.63 (d, $J = 15.9$ Hz, 1H), 6.40 – 6.32 (m, 1H), 4.28 – 4.21 (m, 1H), 4.04 (d, $J = 3.8$ Hz, 2H), 1.30 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.25, 137.32, 130.23, 129.29, 128.93, 128.63, 127.30, 126.33, 116.33, 113.09, 48.00, 46.61, 20.08. IR (ATR): 3023, 2969, 1596, 1502, 1390, 1184, 964, 745, 731, 689 cm^{-1} . HRMS calculated for $\text{C}_{18}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 252.1747, found 252.1754.

 (E)-N,N-Dibenzyl-3-phenyl-2-propenylamine **40a**: (Method C) colorless oil, 77% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.28 (m, 12H), 7.26 – 7.19 (m, 3H), 6.54 (d, $J = 15.9$ Hz, 1H), 6.31 (dt, $J = 15.8, 6.5$ Hz, 1H), 3.65 (s, 4H), 3.24 (d, $J = 6.4$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 139.74, 137.31, 132.61, 128.93, 128.64, 128.36, 127.88, 127.44, 126.99, 126.39, 58.06, 55.89. IR (ATR): 3025, 2792, 1599, 1494, 1451, 1364, 1121, 965, 731, 692 cm^{-1} .

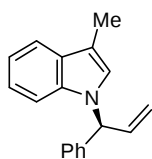
 (E)-N-Phenyl-3-phenyl-2-propenylamine **4ka**: (Method C, aniline (0.30 mmol), alkyne (0.20 mmol)) colorless oil, 55% yield. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 – 7.21 (m, 1H), 7.21 – 7.14 (m, 2H), 6.73 – 6.60 (m, 4H), 6.36 (dt, $J = 15.9, 5.8$ Hz, 1H), 4.05 – 3.85 (m, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 148.64, 137.36, 131.53, 129.54, 128.93, 127.84, 127.69, 126.62, 117.72, 113.29, 46.43. IR (ATR): 3412, 3023, 1600, 1504, 1447, 1316, 1249, 965, 745, 690 cm^{-1} .

 N,N-Bis[(E)-3-phenyl-2-propenyl]benzylamine **4ka'**: (Method C, aniline (0.20 mmol), alkyne (0.50 mmol)) colorless oil, 70% yield. ^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 7.6$ Hz, 4H), 7.30 (t, $J = 7.6$ Hz, 4H), 7.26 – 7.18 (m, 4H), 6.83 (d, $J = 6.7$ Hz, 2H), 6.76 – 6.71 (m, 1H), 6.55 (d, $J = 15.9$ Hz, 2H), 6.29 (dt, $J = 15.9, 5.1$ Hz, 2H), 4.14 (d, $J = 5.3$ Hz, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.94, 137.01, 131.29, 129.39, 128.67, 127.54, 126.45, 125.99, 116.71, 112.70, 52.31. IR (ATR): 3025, 1597, 1504, 1447, 1354, 1218, 1159, 1066, 964, 908 cm^{-1} .

 (E)-1-(4-Phenylbut-3-en-2-yl)-2,3-dihydroindole **4ao**: (Method C) colorless oil, 79% yield. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.37 (d, $J = 7.7$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.21 (t, $J = 7.3$ Hz, 1H), 7.08 – 6.97 (m, 2H), 6.60 – 6.54 (m, 2H), 6.51 (d, $J = 7.9$ Hz, 1H), 6.33 (dd, $J = 16.1, 5.9$ Hz, 1H), 4.39 – 4.33 (m, 1H), 3.47 – 3.37 (m, 2H), 2.94 (t, $J = 8.4$ Hz, 2H), 1.40 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 151.60, 137.46, 131.00, 130.83, 130.72, 128.89, 127.75, 127.44, 126.61, 124.73, 117.42, 107.91, 52.75, 47.61, 28.56, 16.49. IR (ATR): 2971, 2845, 1606, 1486, 1263, 1181, 967, 909, 733, 692 cm^{-1} . HRMS calculated for $\text{C}_{18}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$ 250.1590, found 250.1598.

 1-(1-Phenyl-2-propenyl)-indole **5aa**: (Method D) colorless oil, 77% yield, 90% ee, $[\alpha]_D^{27} = -59.5$ (c 1.19, CHCl_3) [lit.²: $[\alpha]_D^{27} = -58.1$ (c 1.00, CHCl_3) for 95% ee (S)]. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.63 (d, $J = 7.8$ Hz, 1H), 7.38 – 7.27 (m, 4H), 7.24 – 7.18 (m, 3H), 7.17 – 7.07 (m, 2H), 6.55 (d, $J = 3.2$ Hz, 1H), 6.48 – 6.39 (m, 1H), 6.16 (d, $J = 5.9$ Hz, 1H), 5.43 (d, $J = 10.3$ Hz, 1H), 5.07 (d, $J = 17.1$ Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 139.74, 136.62, 136.45, 129.33, 129.05, 128.26, 127.82, 126.60, 121.79, 121.20, 119.97, 119.12, 110.45, 101.74, 62.35. IR (ATR): 3029, 1458, 1308, 1215, 1185, 992, 929, 736,

697 cm⁻¹. **Chiral SFC**: IC column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 5.6 min (major) and 6.0 min.

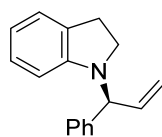
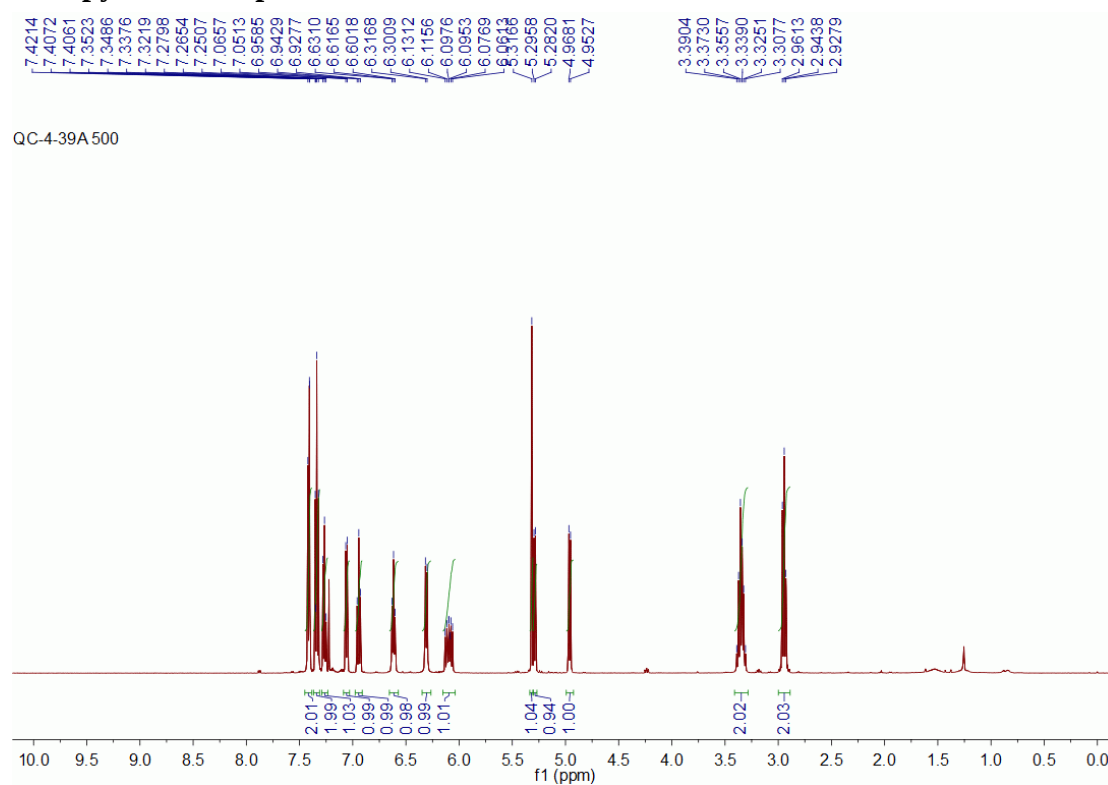


1-(1-Phenyl-2-propenyl)-3-methyl-indole **5ba**: (Method **D**) colorless oil, 72% yield, 85% ee, $[\alpha]_D^{26} = -39.2$ (c 1.19, CHCl₃). **¹H NMR** (500 MHz, CDCl₃) δ 7.57 (d, $J = 7.6$ Hz, 1H), 7.35 – 7.27 (m, 3H), 7.24 – 7.18 (m, 3H), 7.16 – 7.08 (m, 2H), 6.88 (s, 1H), 6.34 (ddd, $J = 17.0, 10.3, 5.9$ Hz, 1H), 6.07 (d, $J = 5.9$ Hz, 1H), 5.37 (dt, $J = 10.3, 1.2$ Hz, 1H), 5.07 – 5.01 (m, 1H), 2.31 (d, $J = 1.0$ Hz, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 139.49, 136.56, 136.47, 129.19, 128.77, 127.92, 127.69, 123.87, 121.57, 119.13, 119.05, 118.77, 110.80, 109.99, 61.79, 9.88. **IR** (ATR): 3028, 2916, 1458, 1354, 1223, 1181, 928, 736, 698 cm⁻¹. **Chiral SFC**: OJ-H column, 254 nm, 2% 2-propanol in CO₂, 2.5 mL/min, retention time 4.7 min (major) and 6.6 min.

6. Reference

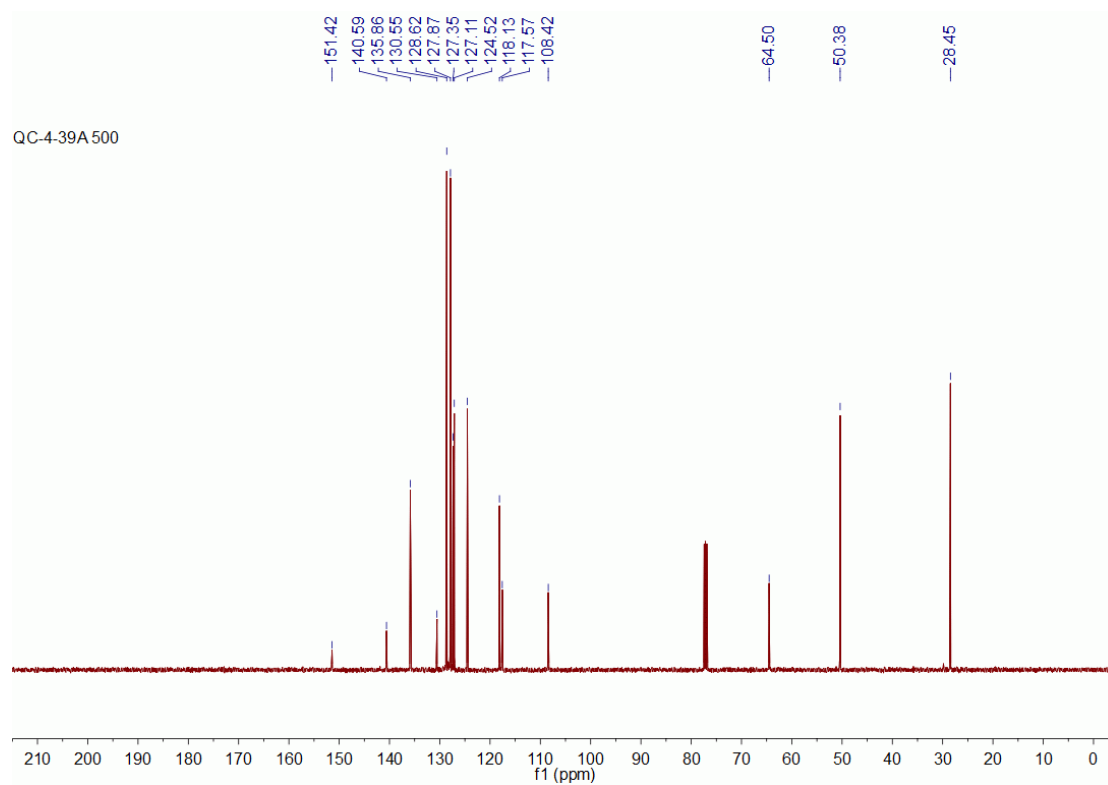
- 1) Kippo, T.; Fukuyama, T.; Ryu, I. *Org. Lett.* **2011**, *13*, 3864.
- 2) Ye, K.-Y.; Dai, L.-X.; You, S.-L. *Chem. Eur. J.* **2014**, *20*, 3040.

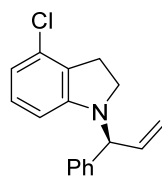
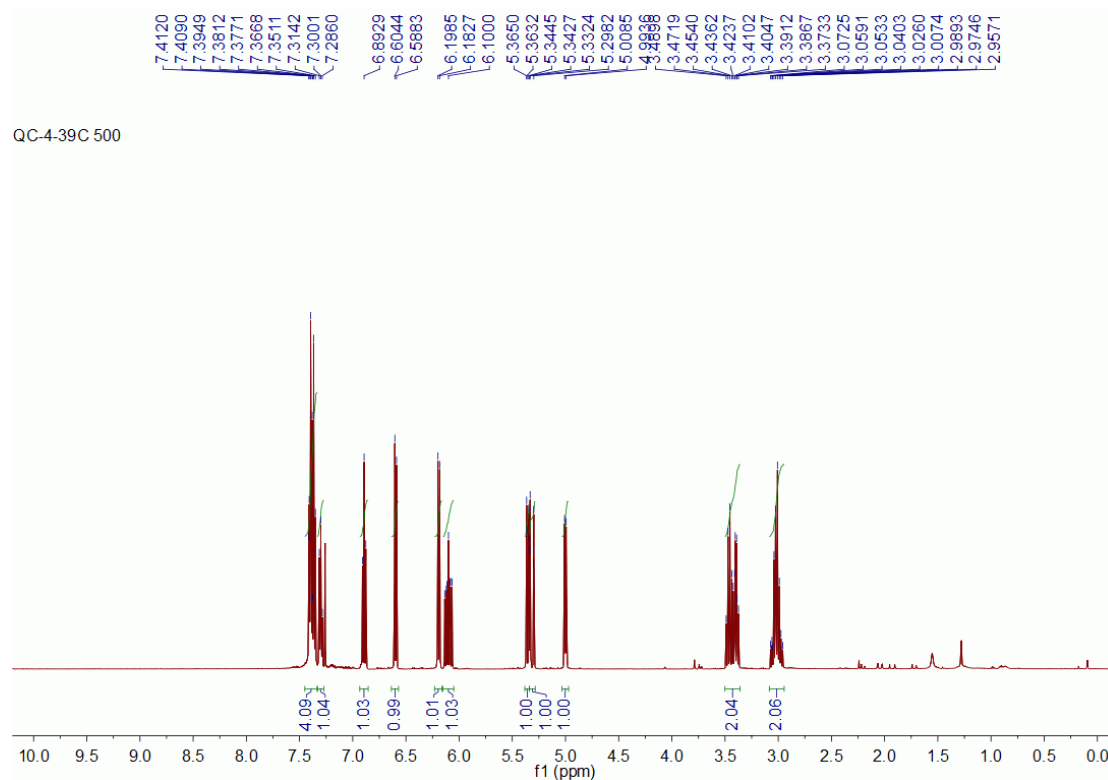
7. Copy of NMR spectra



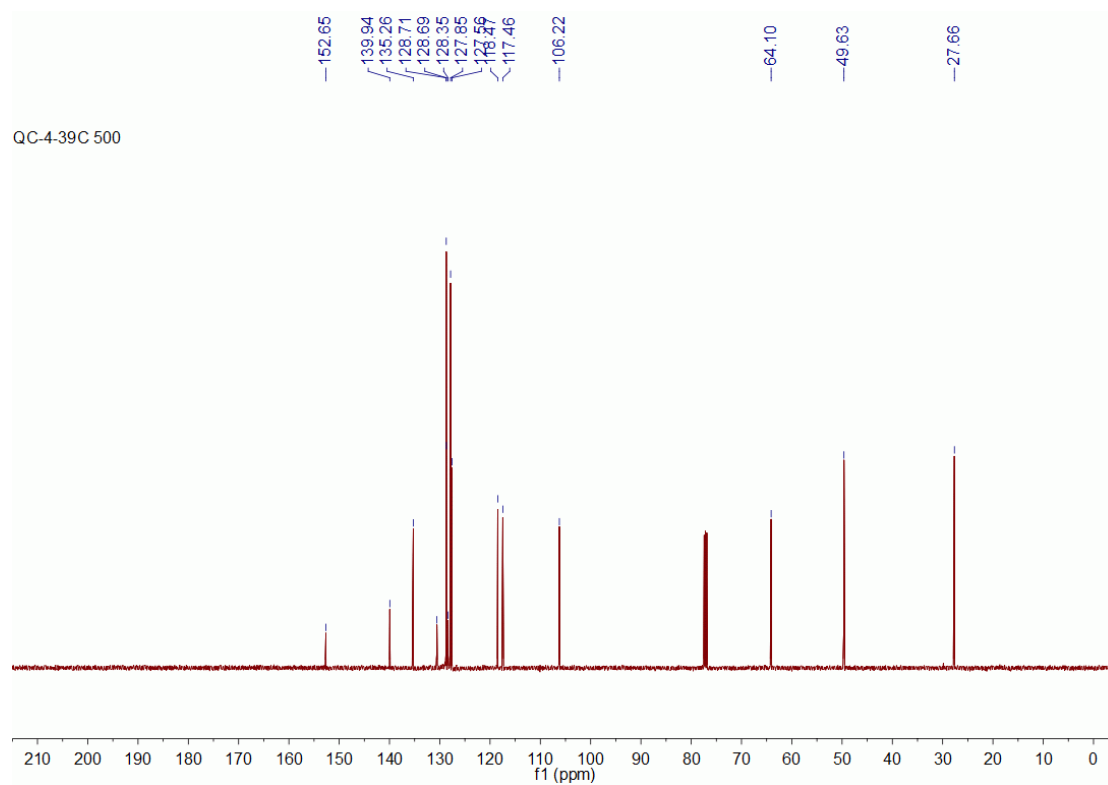
3aa ^1H NMR (500 MHz, CDCl_3)

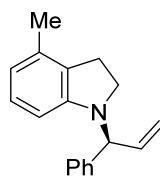
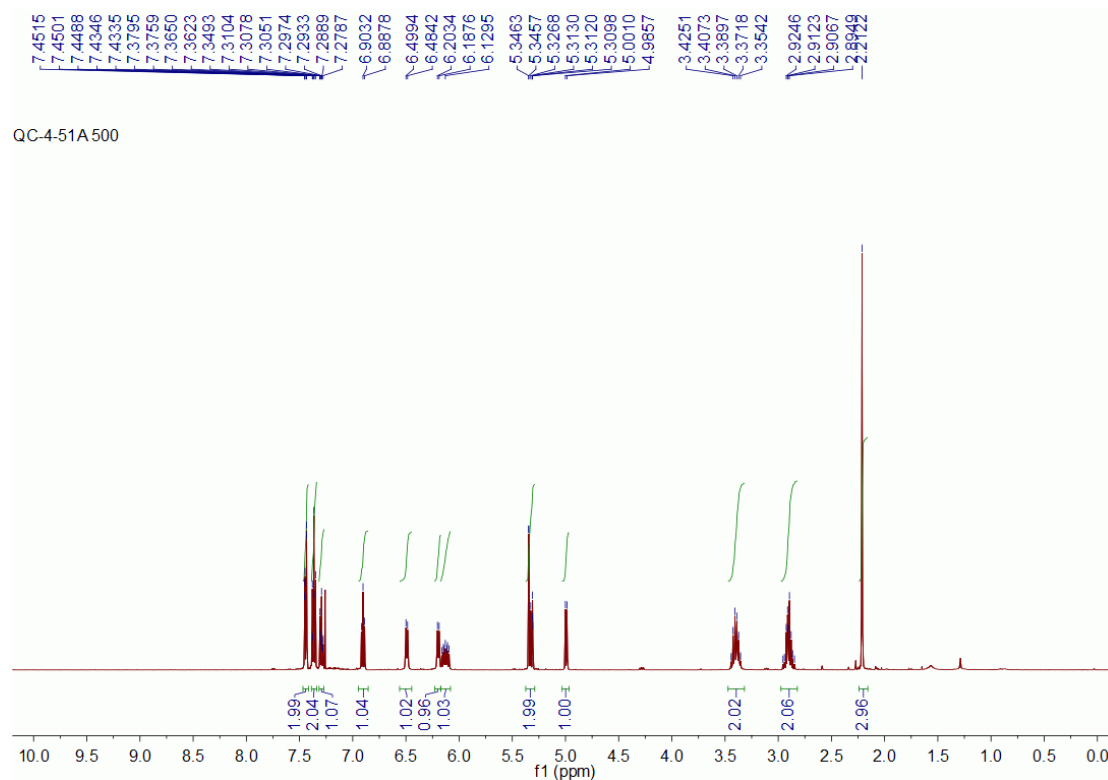
^{13}C NMR (126 MHz, CDCl_3)





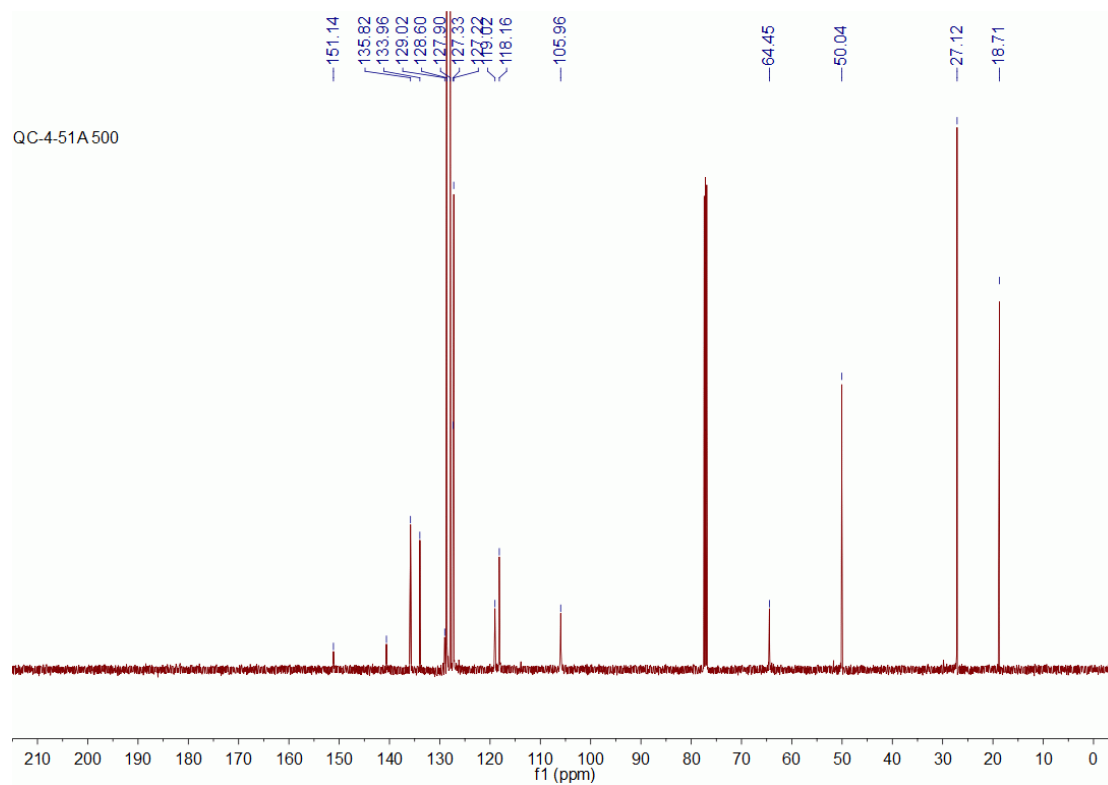
3ba ^1H NMR (500 MHz, CDCl_3)
 ^{13}C NMR (126 MHz, CDCl_3)

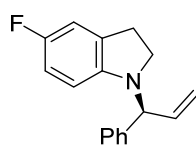
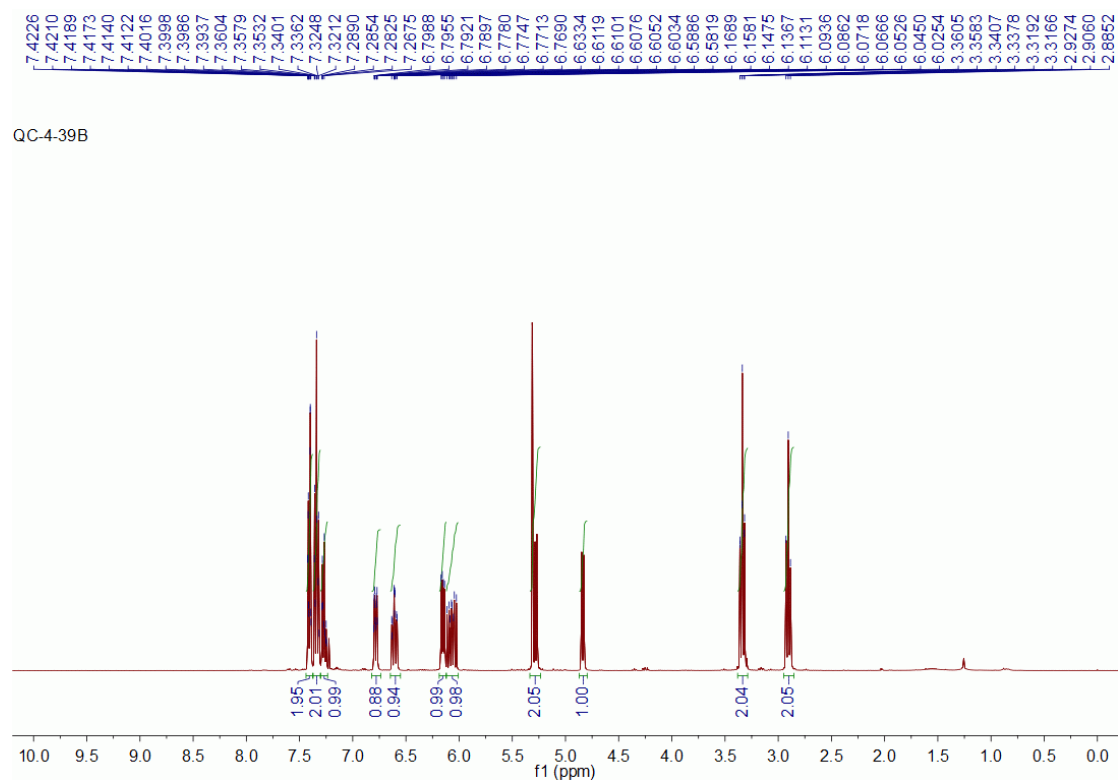




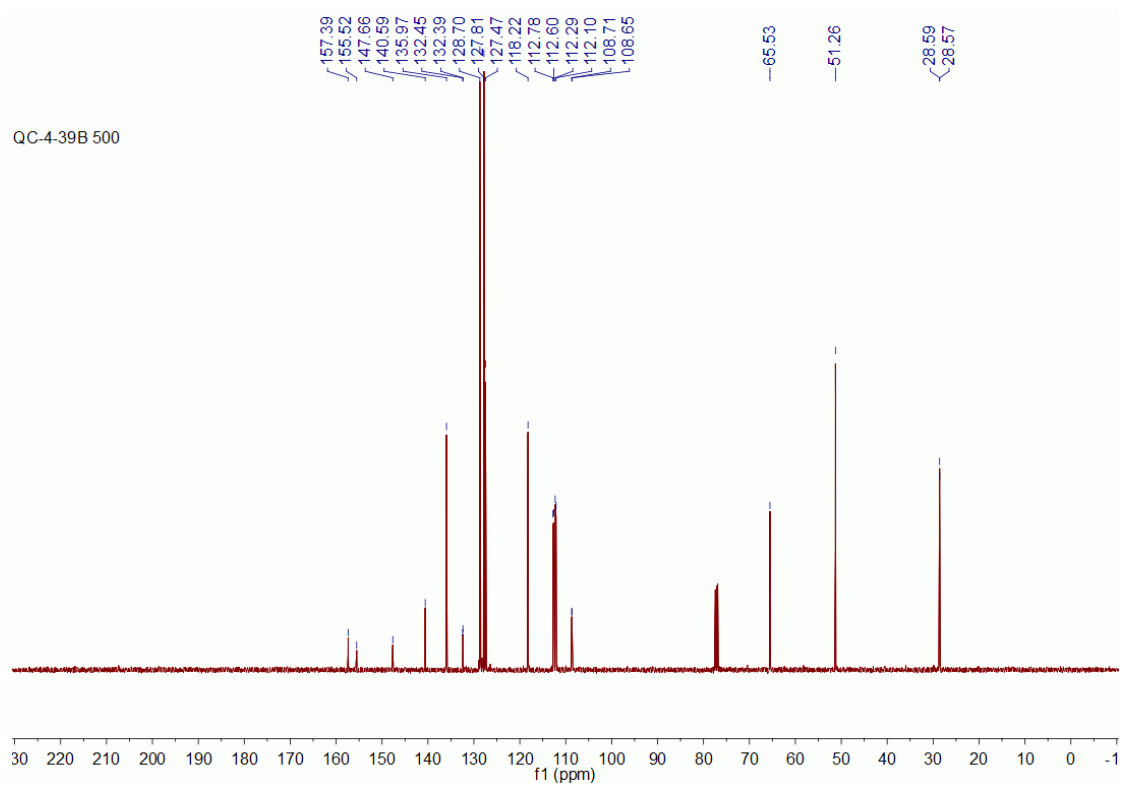
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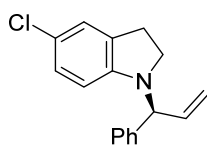
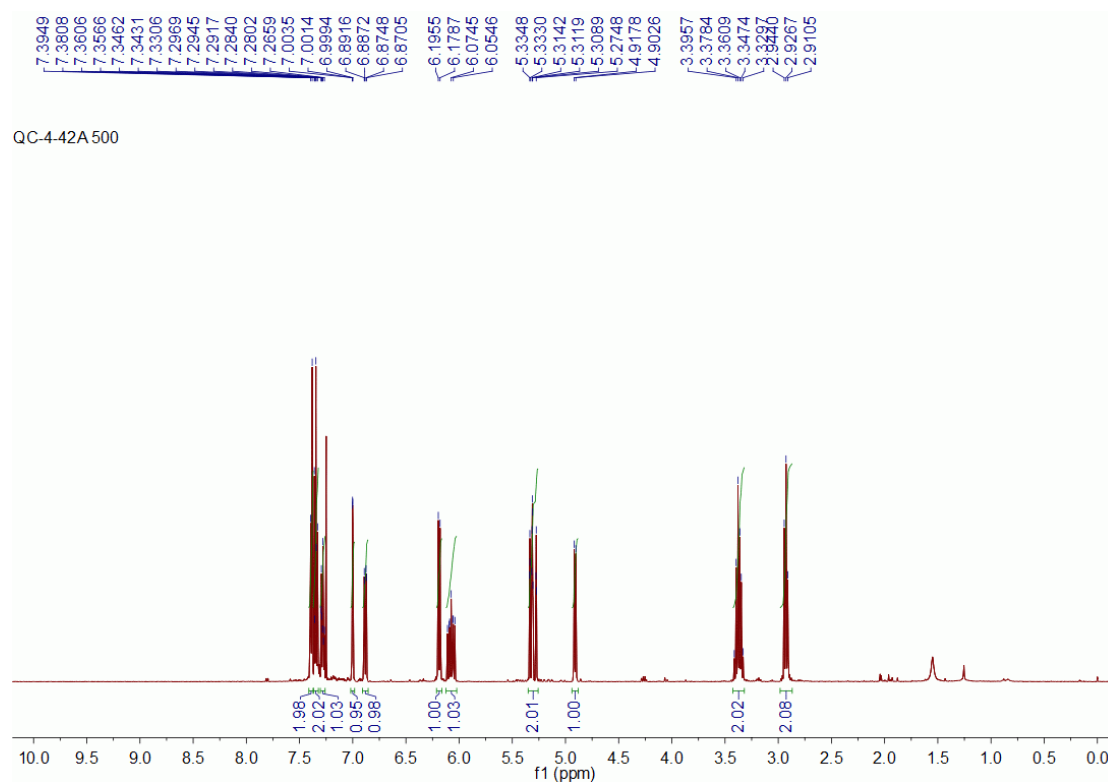
^{13}C NMR (126 MHz, CDCl_3)



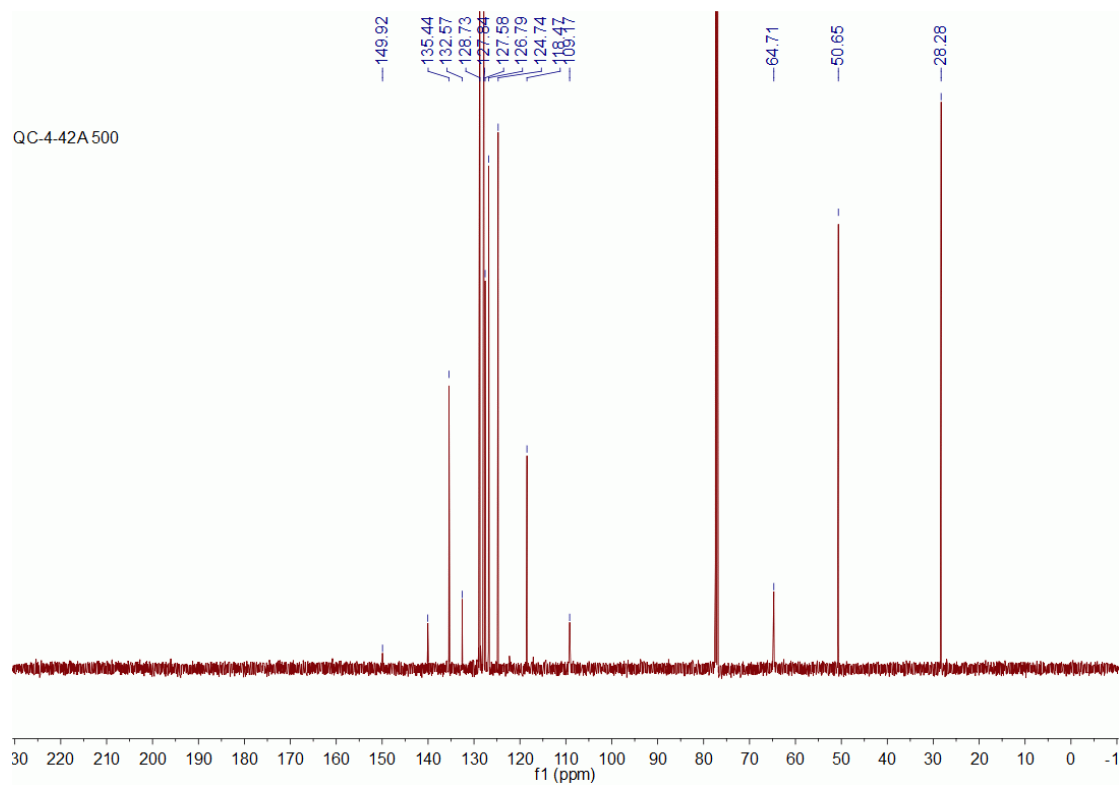


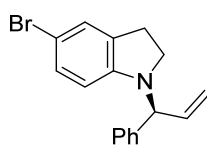
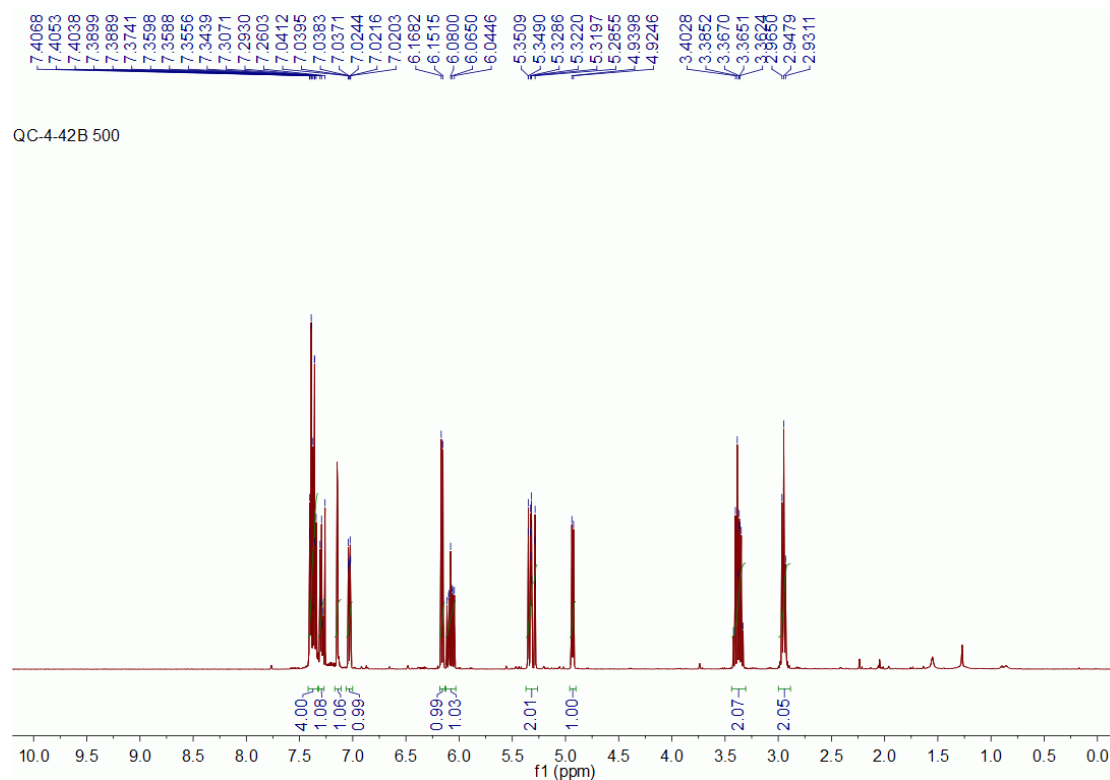
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 ^{13}C NMR (126 MHz, CDCl_3)



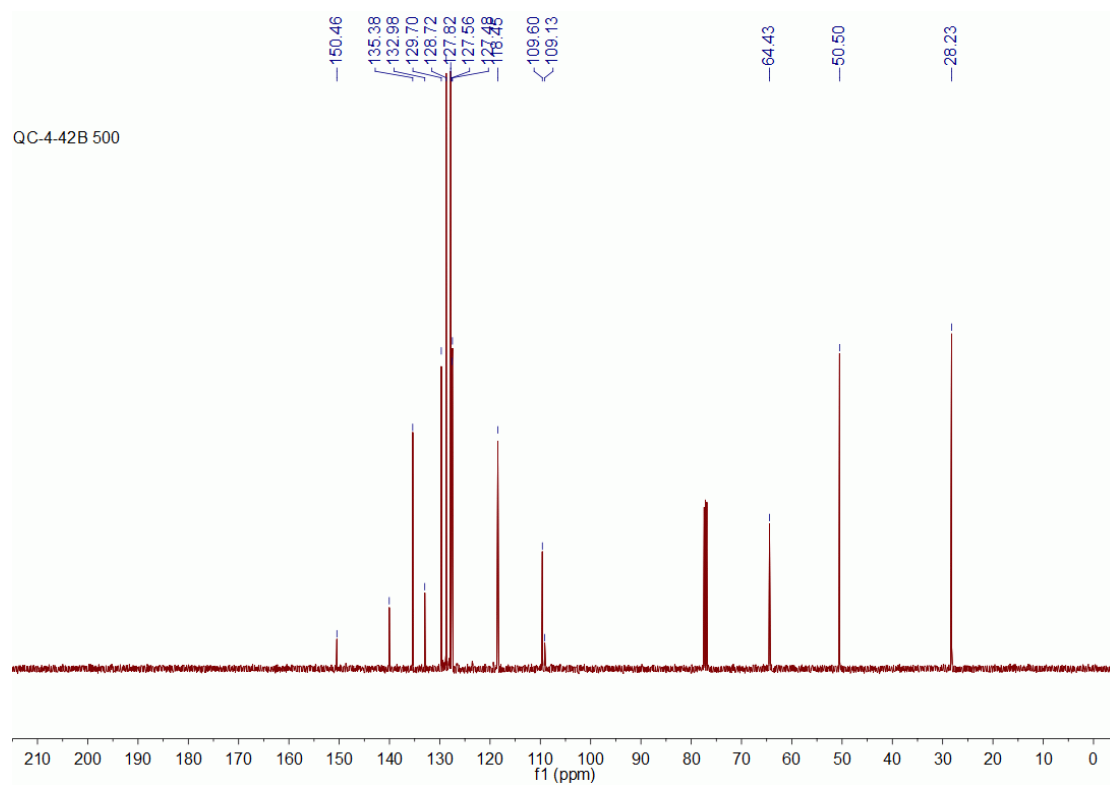


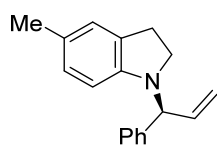
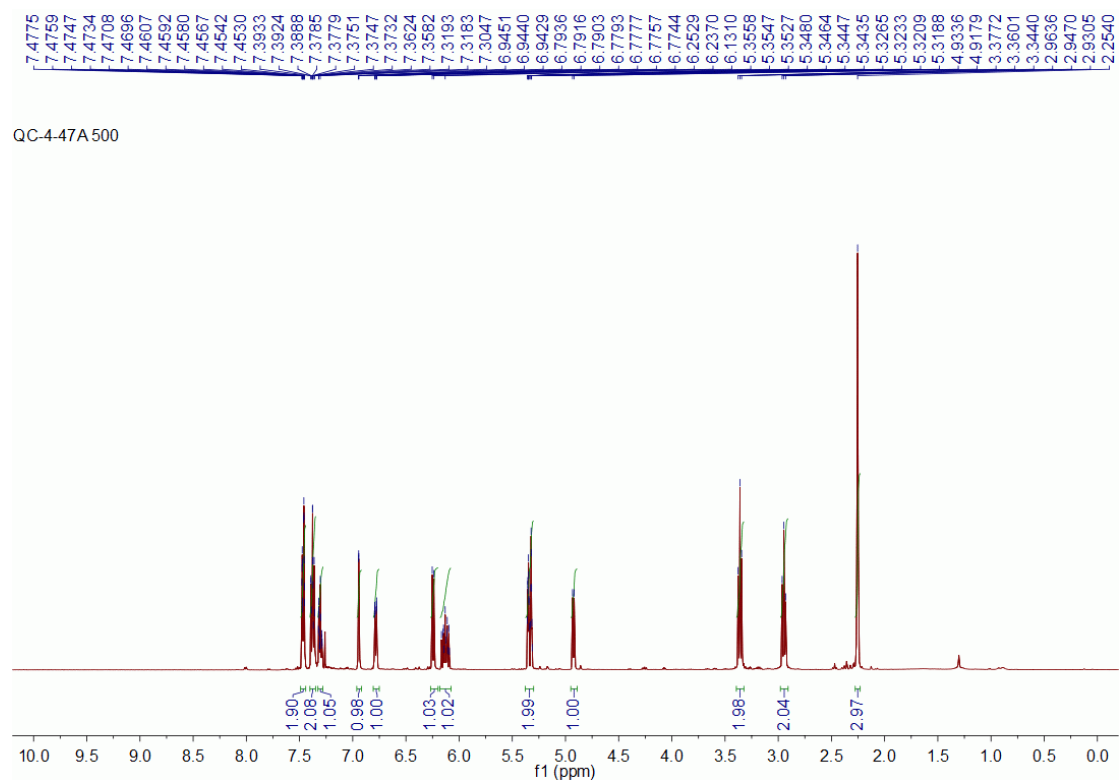
3ea ^1H NMR (500 MHz, CDCl_3)
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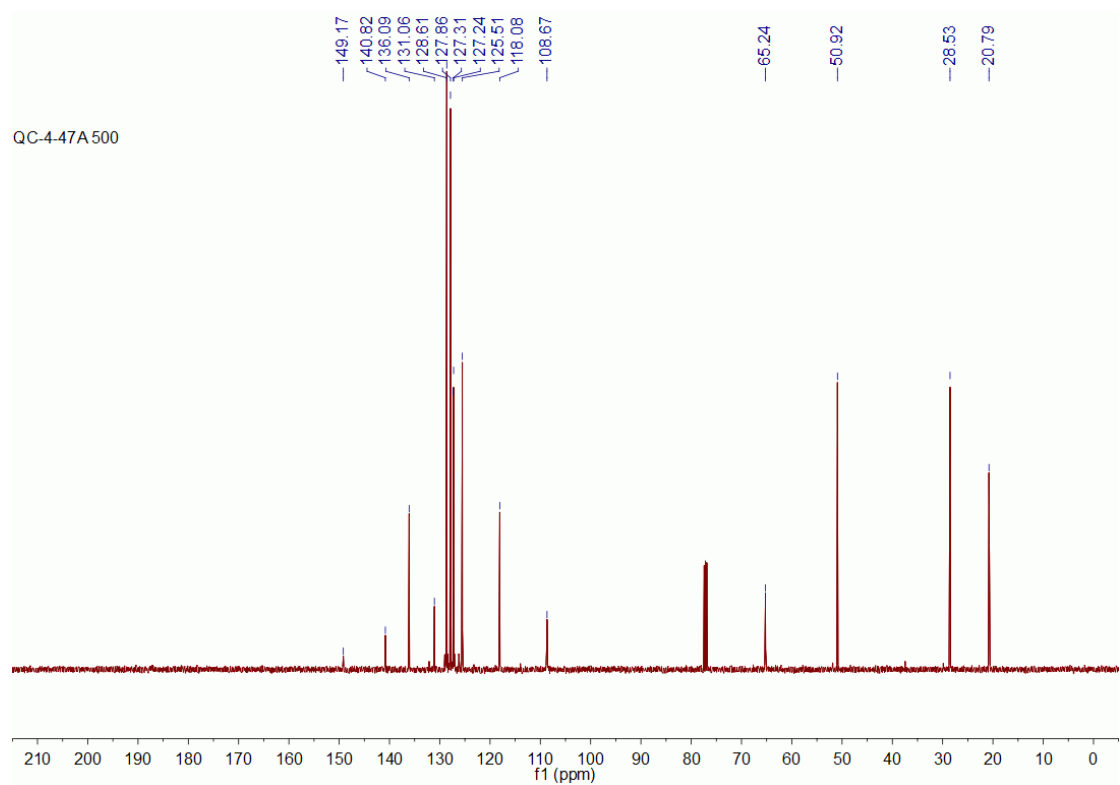


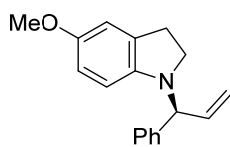
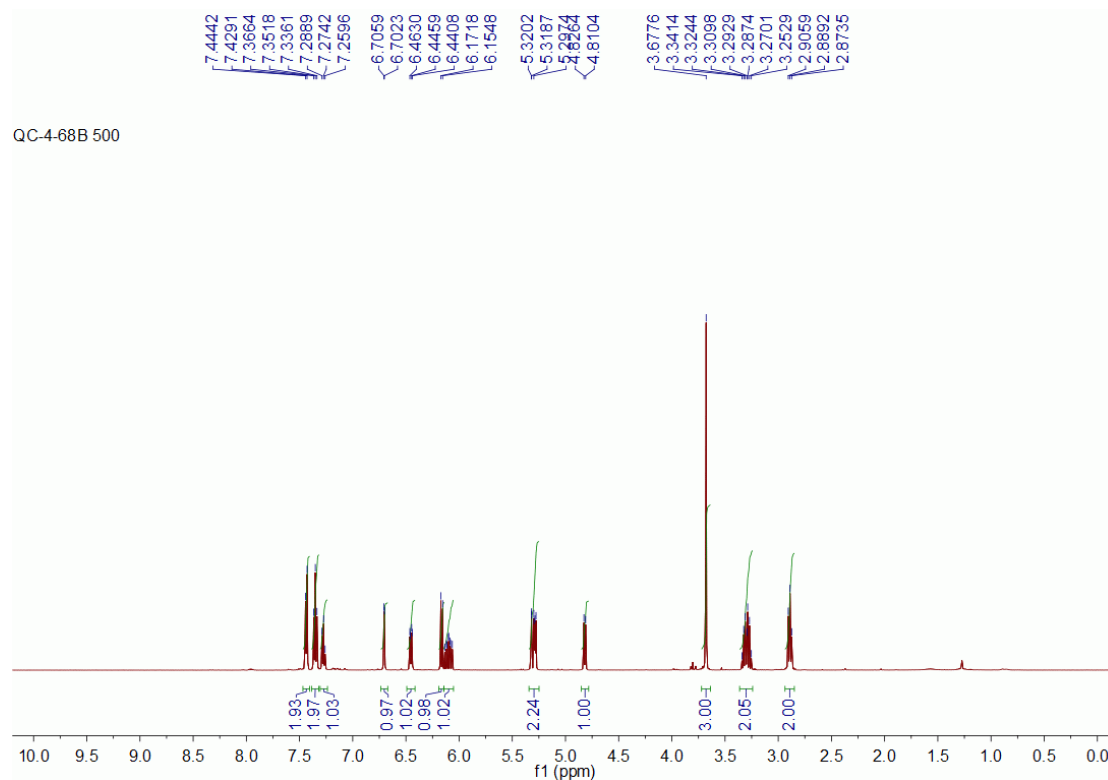
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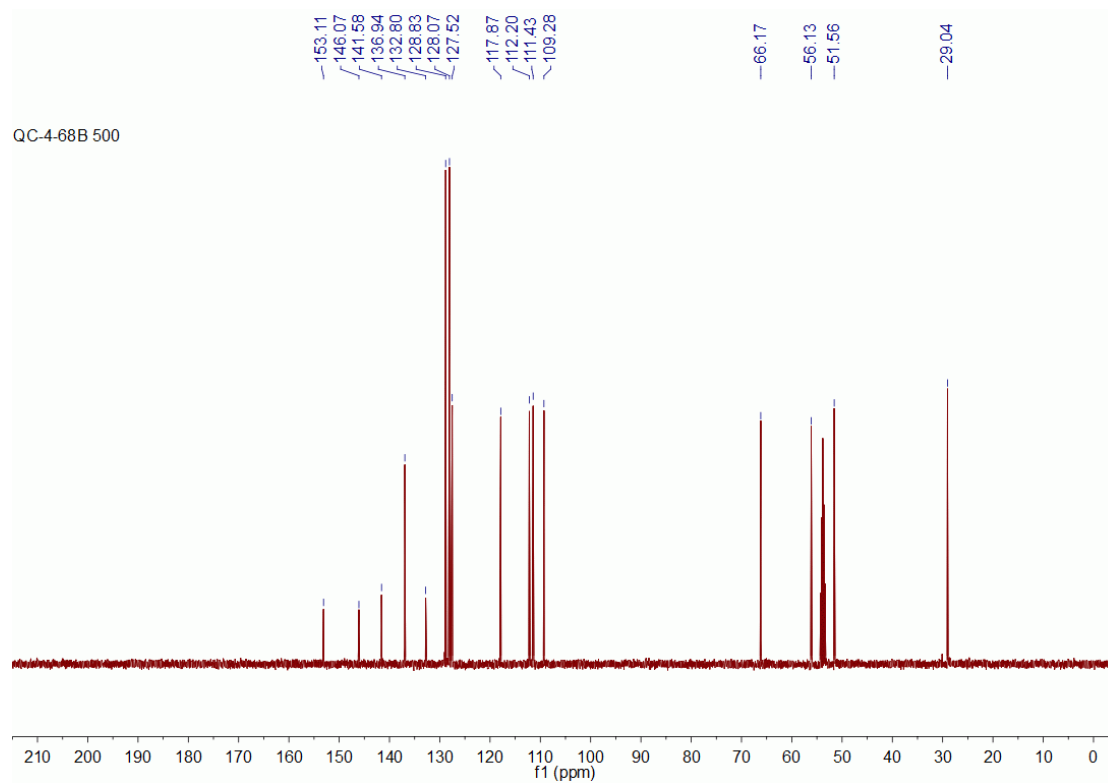


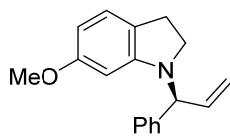
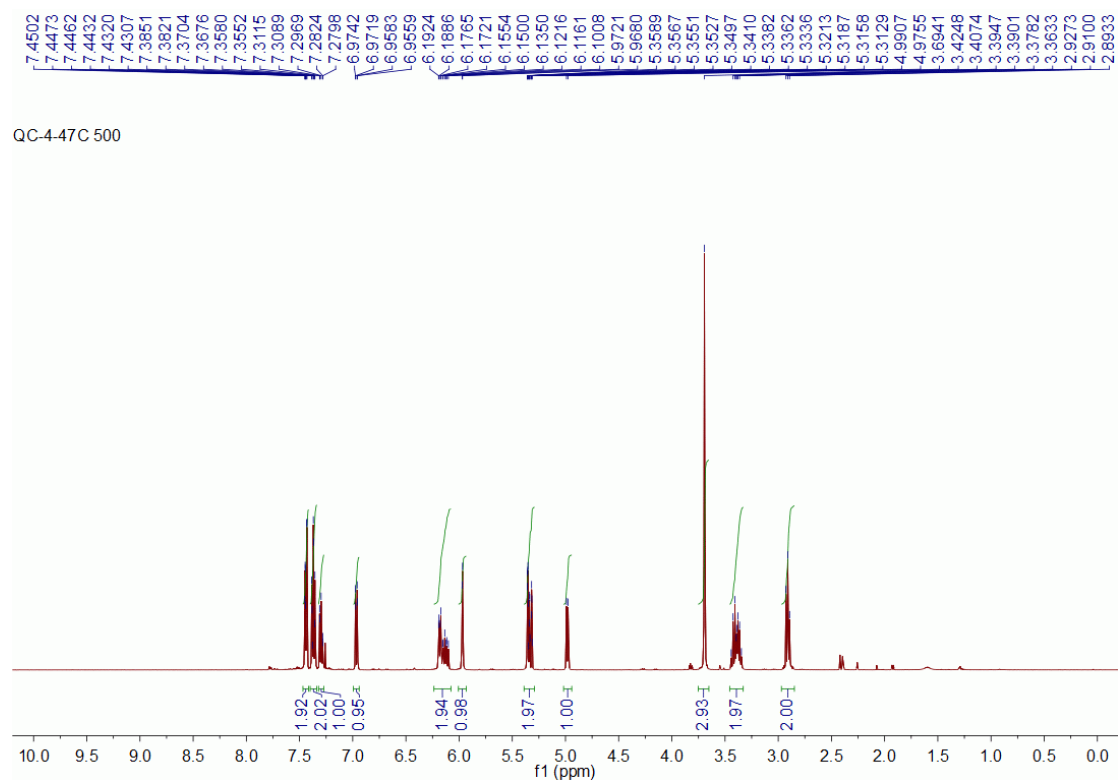
3ga ^1H NMR (500 MHz, CDCl_3)
 ^{13}C NMR (126 MHz, CDCl_3)





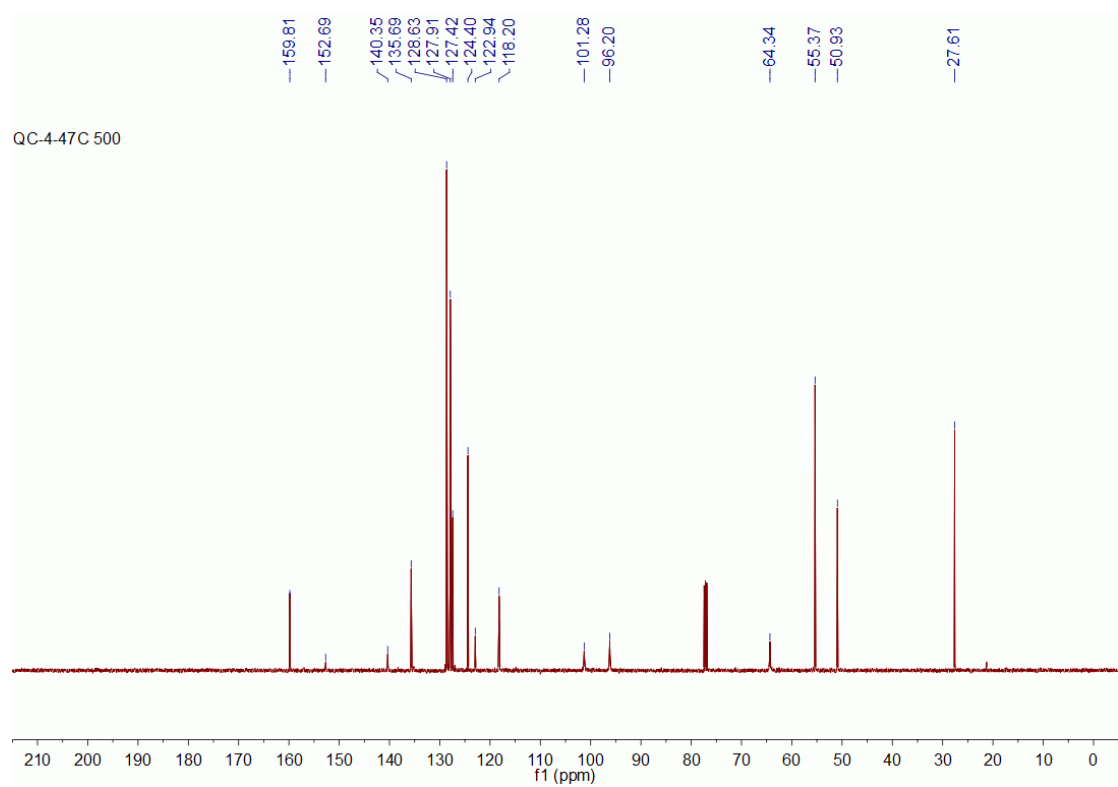
3ha ^1H NMR (500 MHz, CDCl_3)
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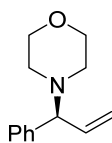
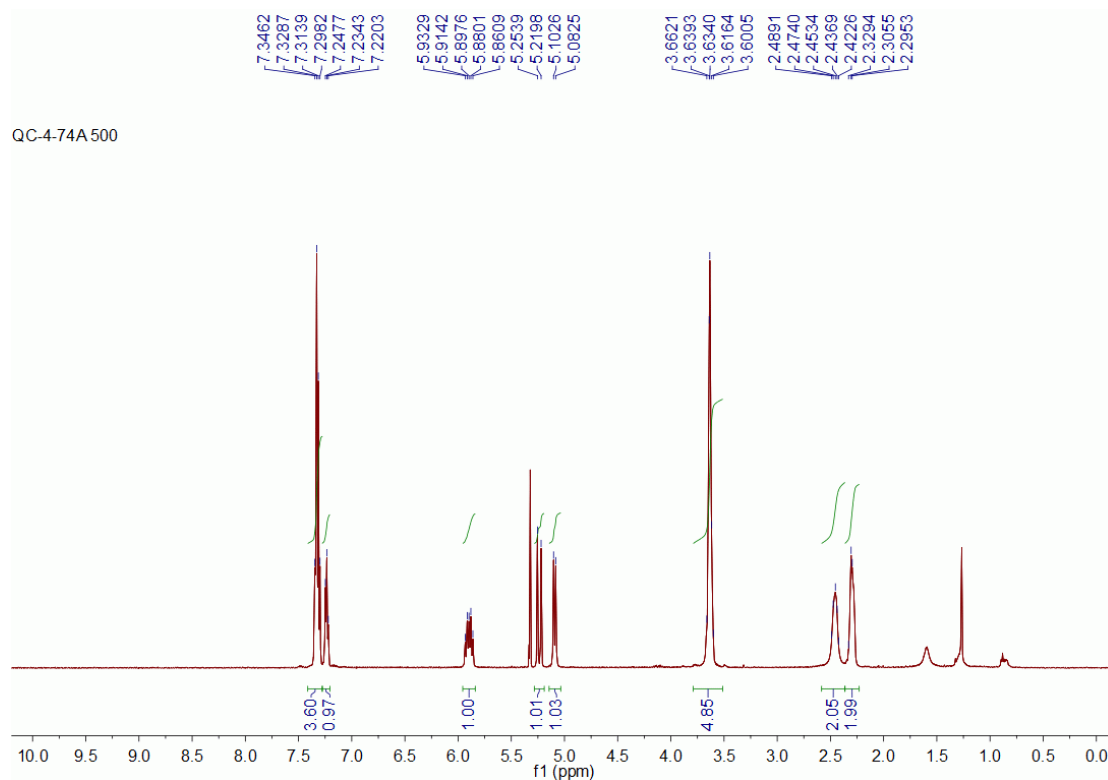




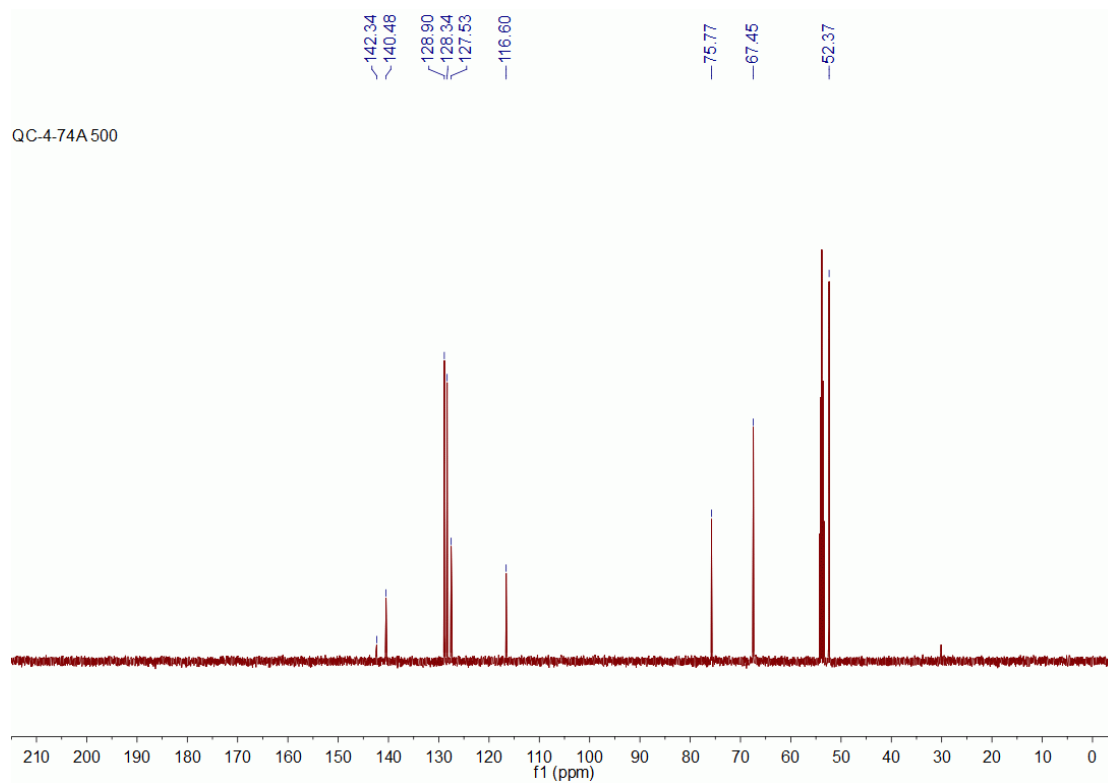
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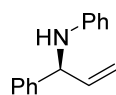
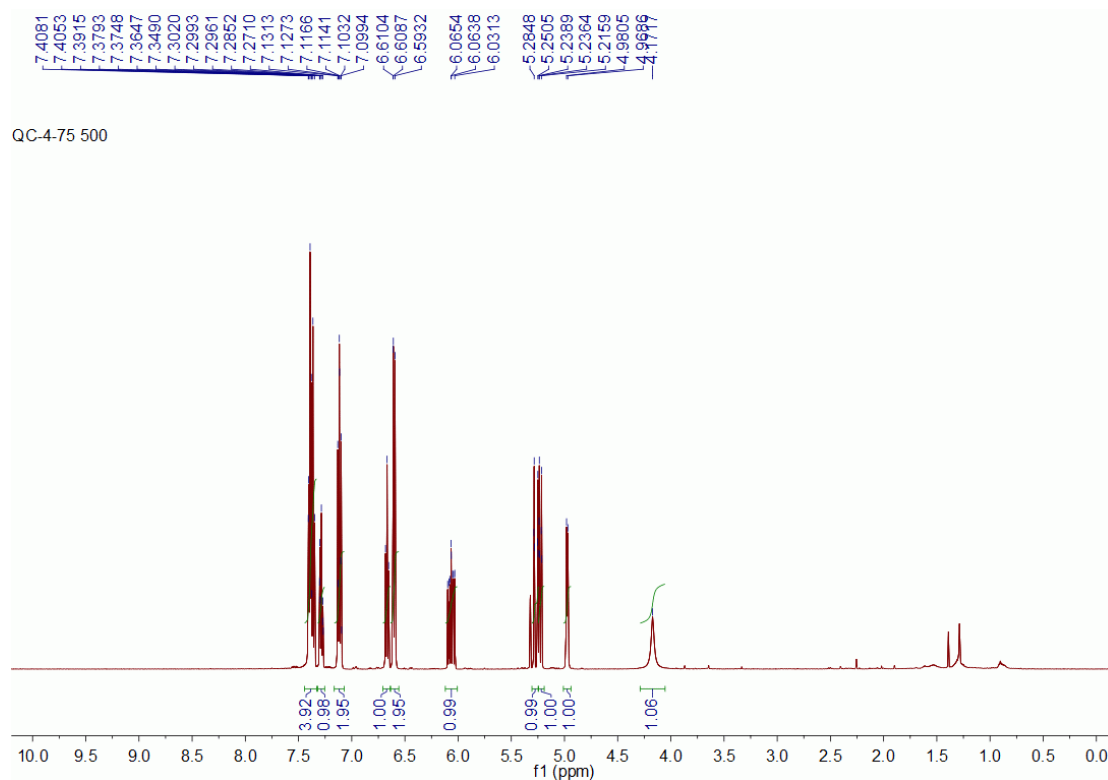
^{13}C NMR (126 MHz, CDCl_3)



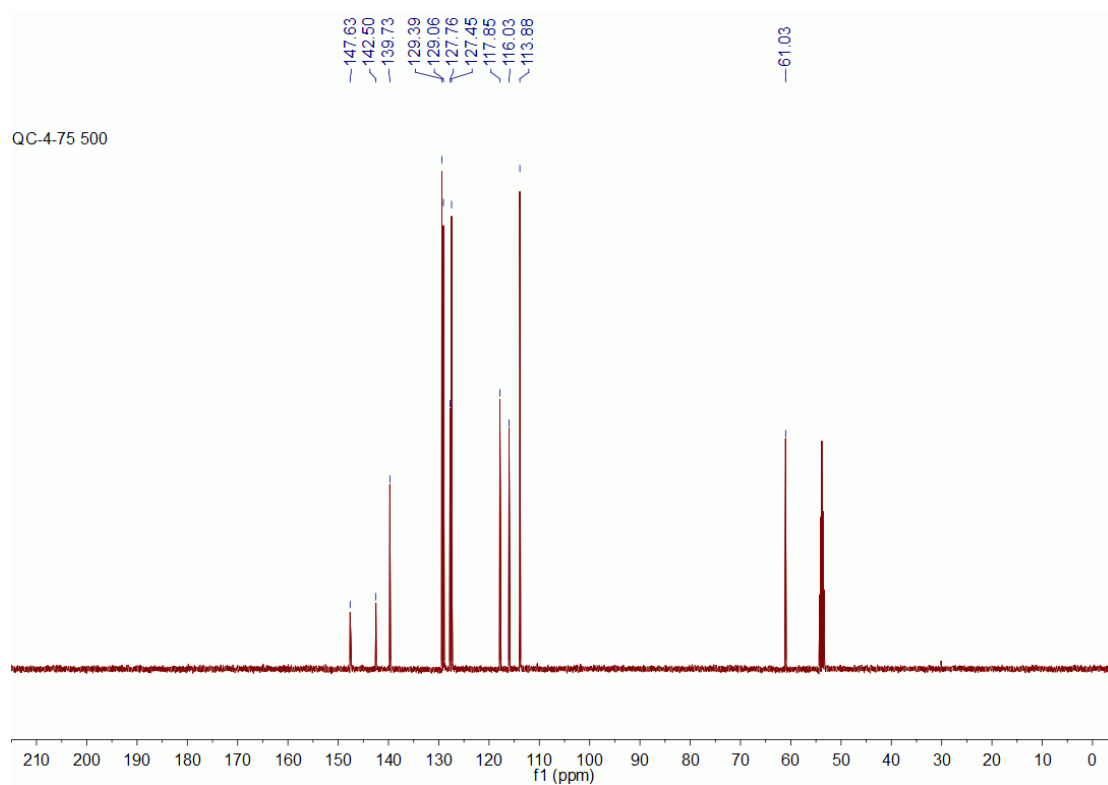


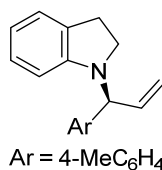
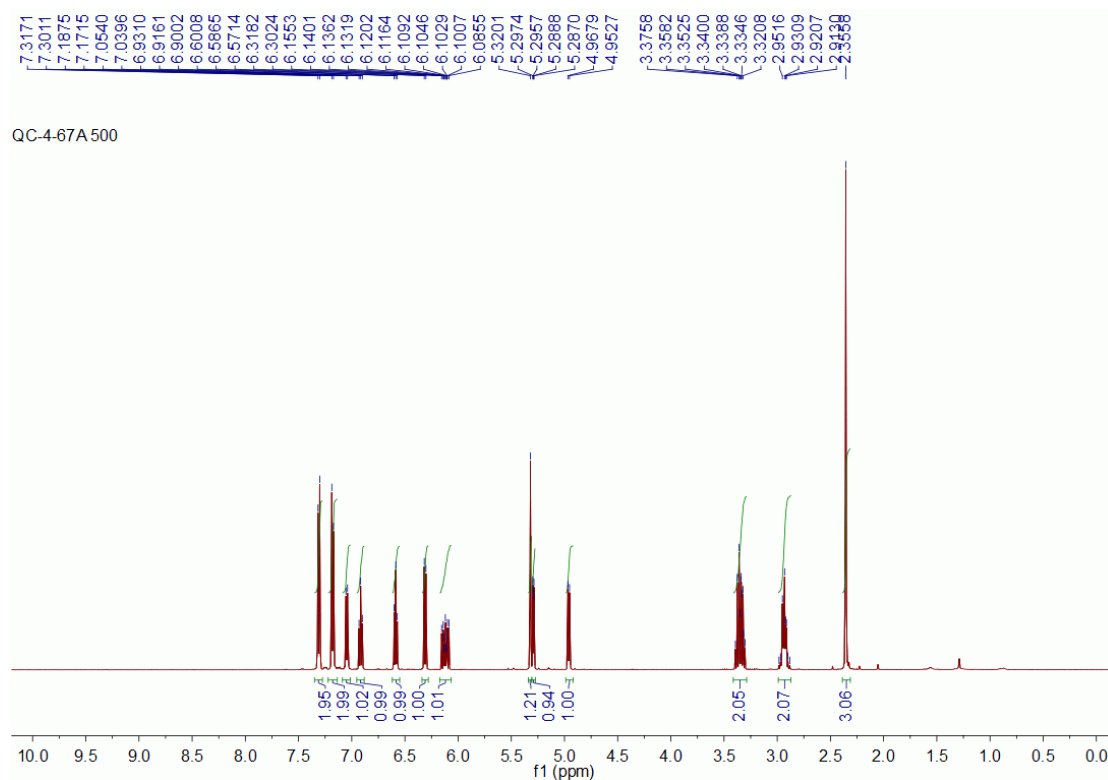
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 ^{13}C NMR (126 MHz, CD_2Cl_2)



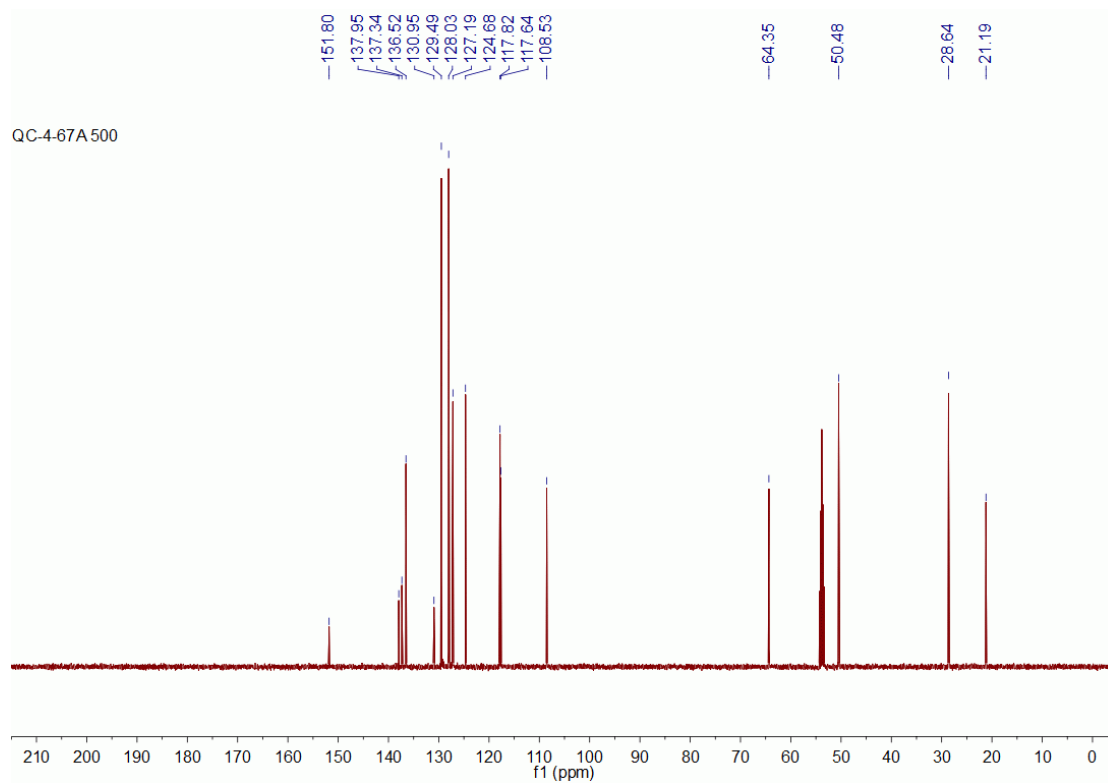


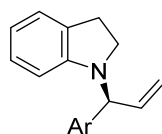
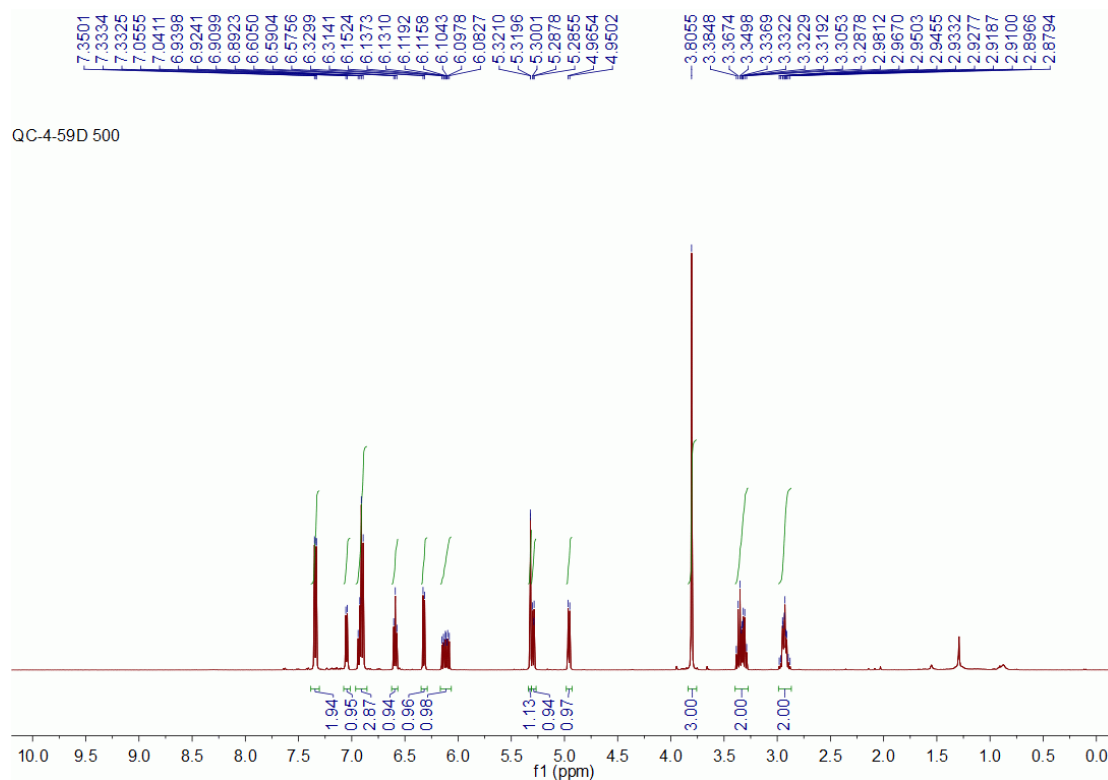
3ka ^1H NMR (500 MHz, CD_2Cl_2)
 ^{13}C NMR (126 MHz, CD_2Cl_2)





3ab ¹H NMR (500 MHz, CD₂Cl₂)
¹³C NMR (126 MHz, CD₂Cl₂)

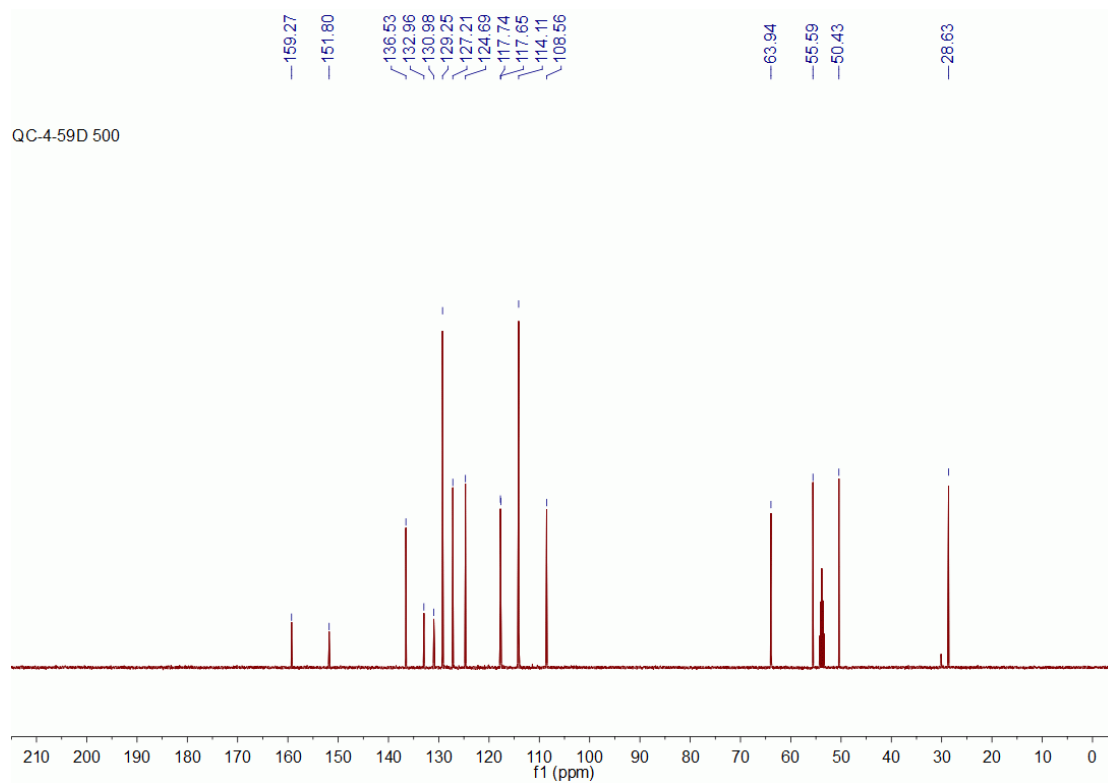


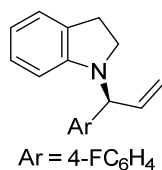
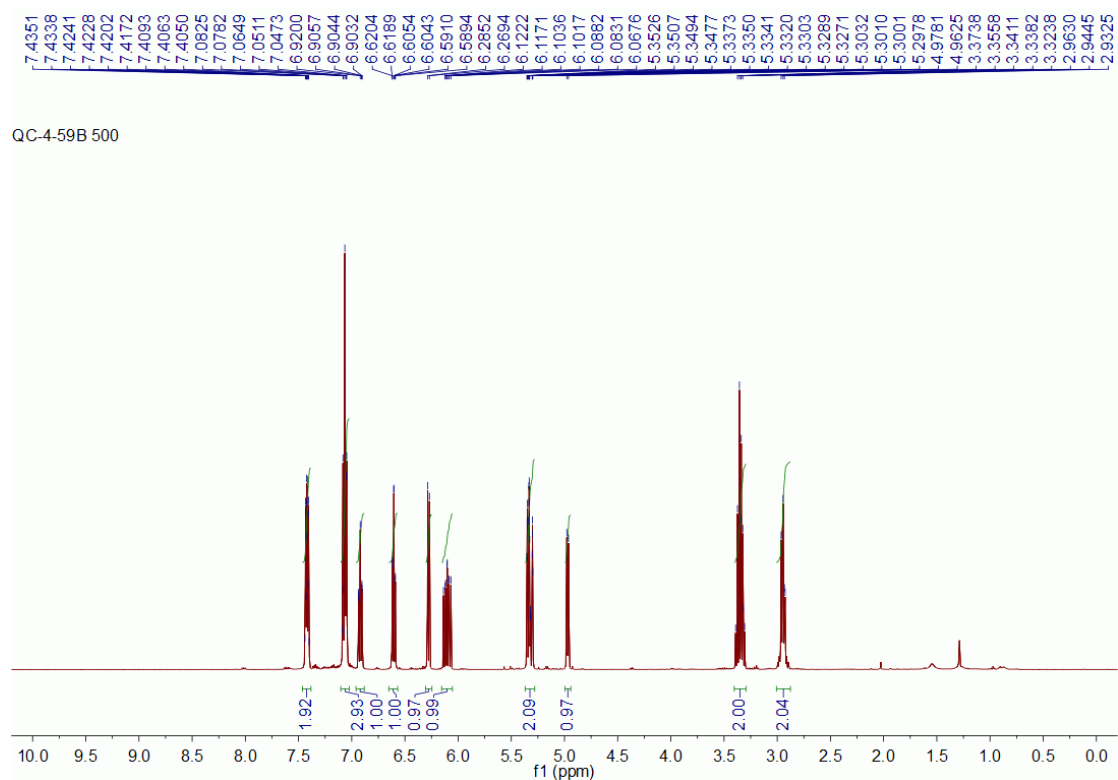


Ar = 4-MeOC₆H₄

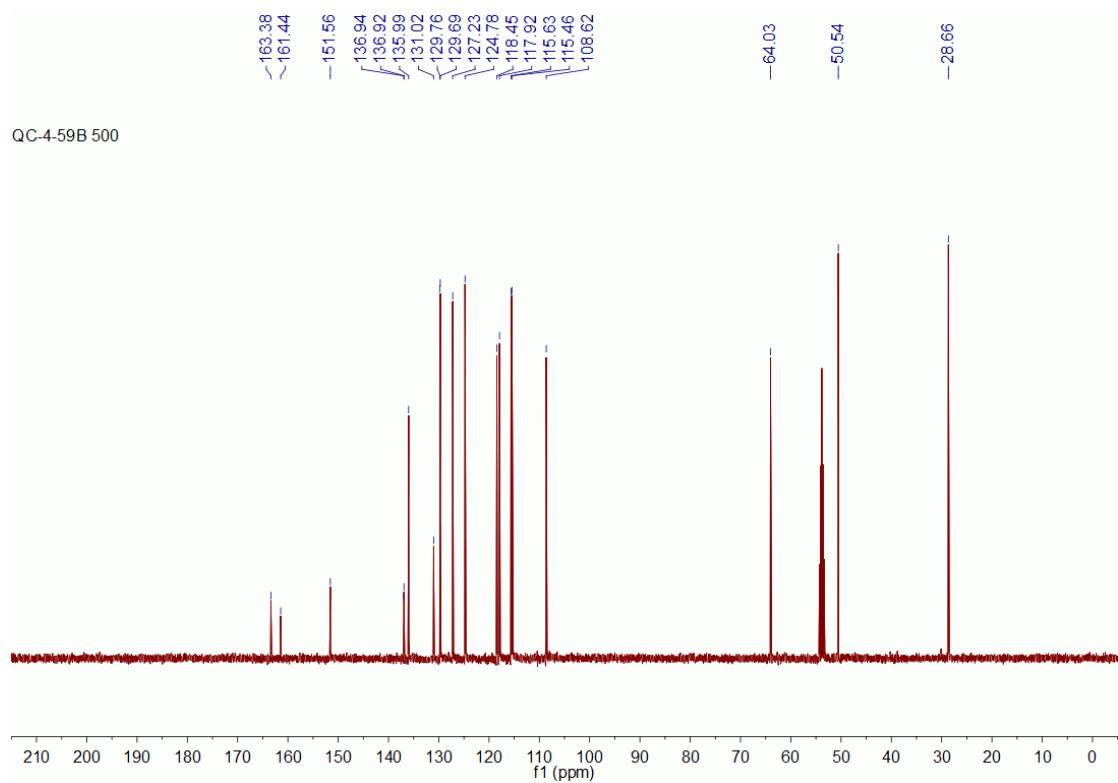
3ac ¹H NMR (500 MHz, CD₂Cl₂)

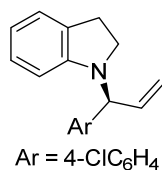
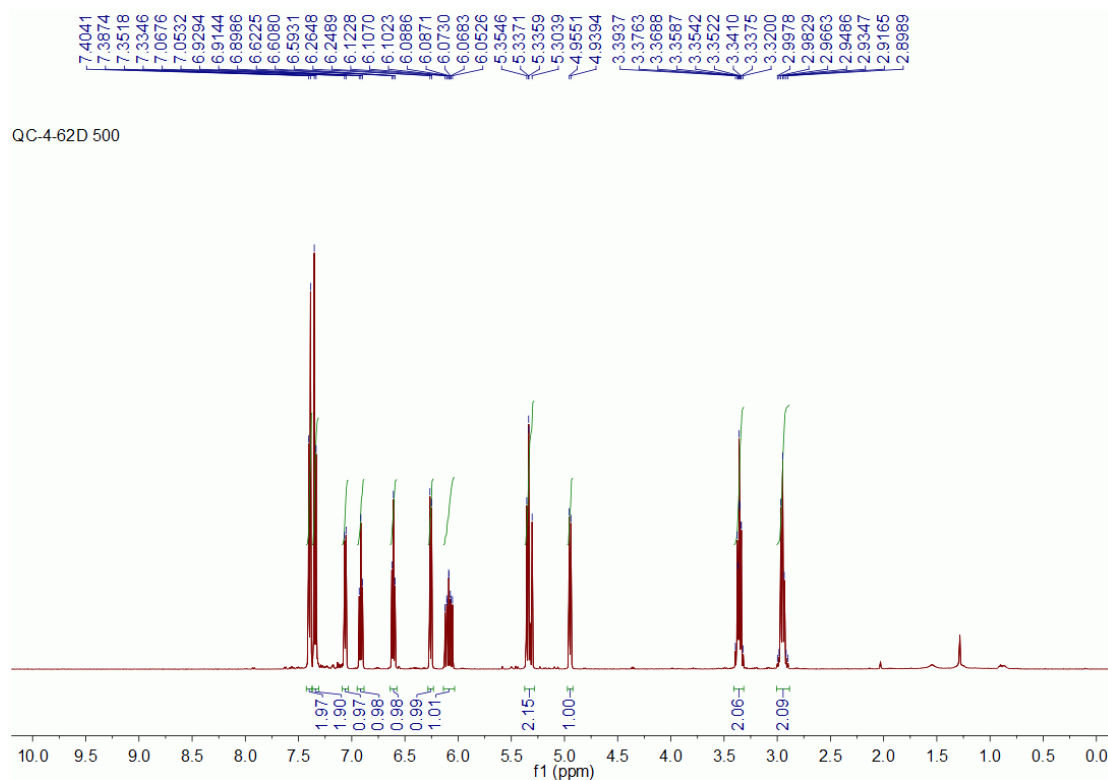
¹³C NMR (126 MHz, CD₂Cl₂)





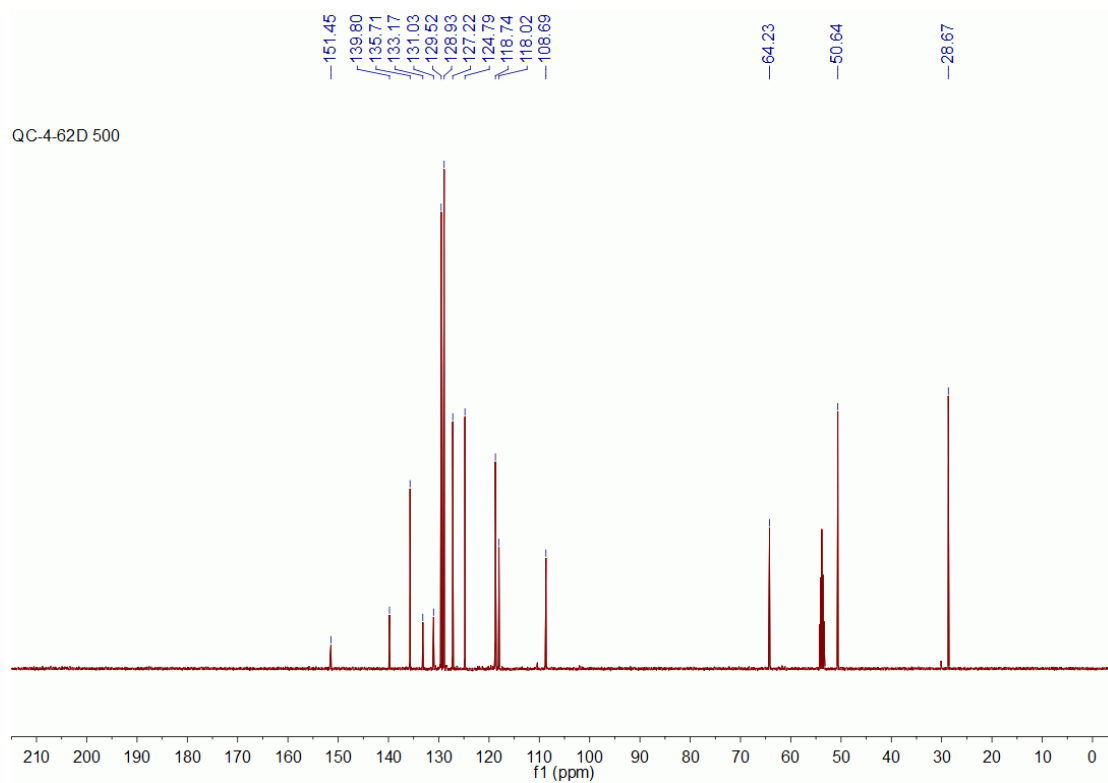
3ad ¹H NMR (500 MHz, CD₂Cl₂)
¹³C NMR (126 MHz, CD₂Cl₂)

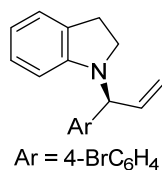
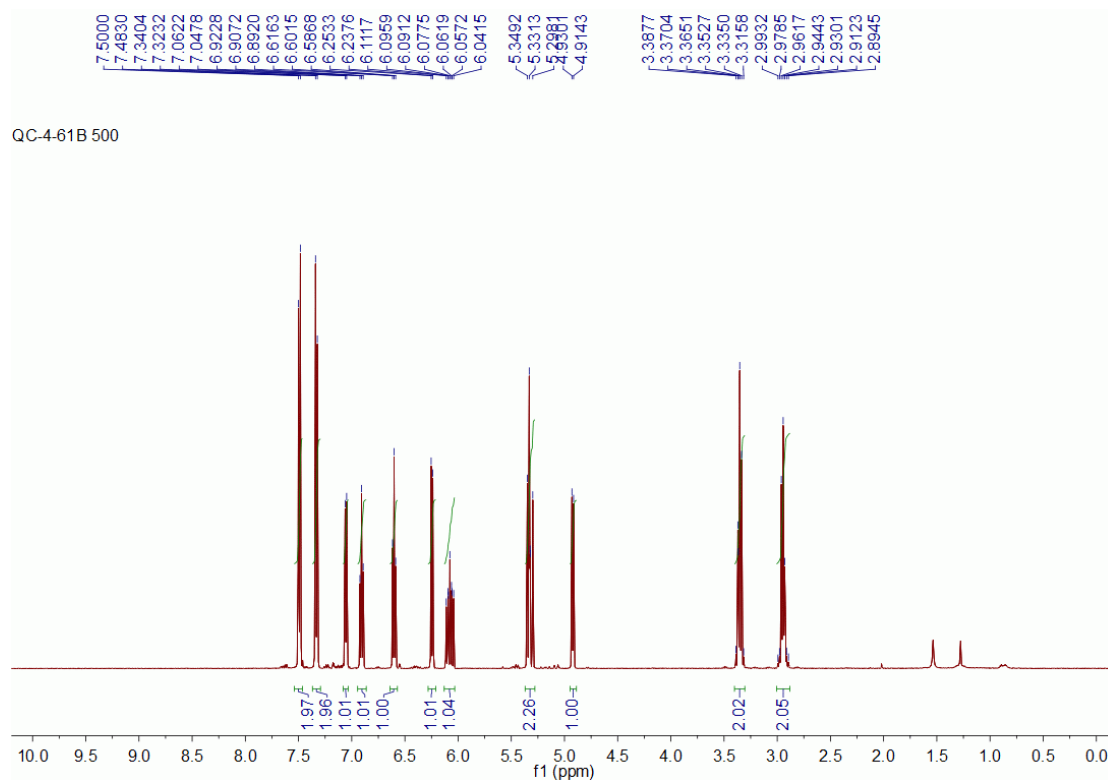




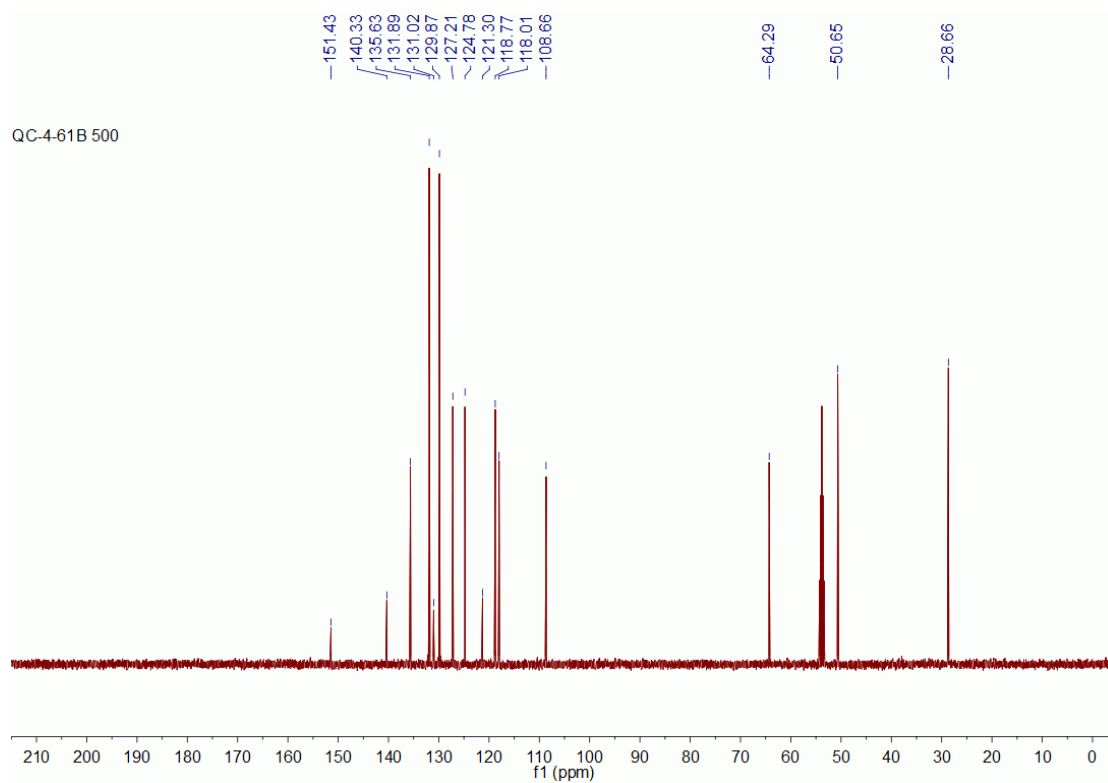
3ae ¹H NMR (500 MHz, CD₂Cl₂)

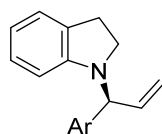
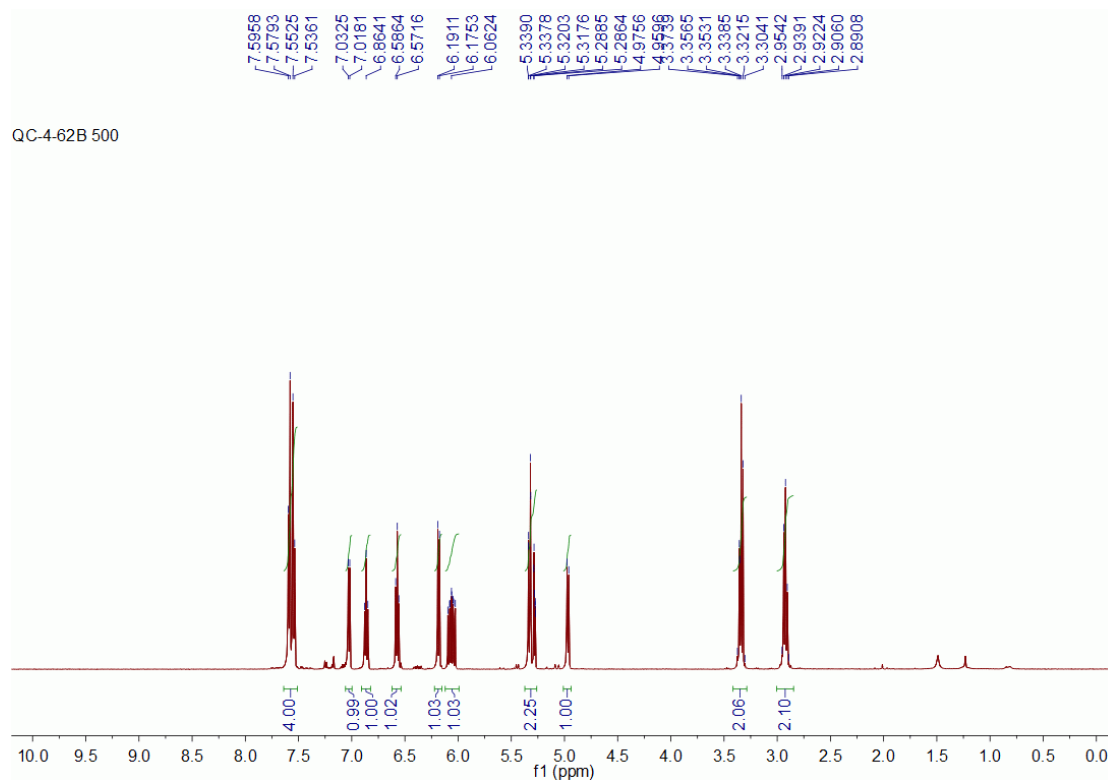
¹³C NMR (126 MHz, CD₂Cl₂)





3af ¹H NMR (500 MHz, CD₂Cl₂)
¹³C NMR (126 MHz, CD₂Cl₂)

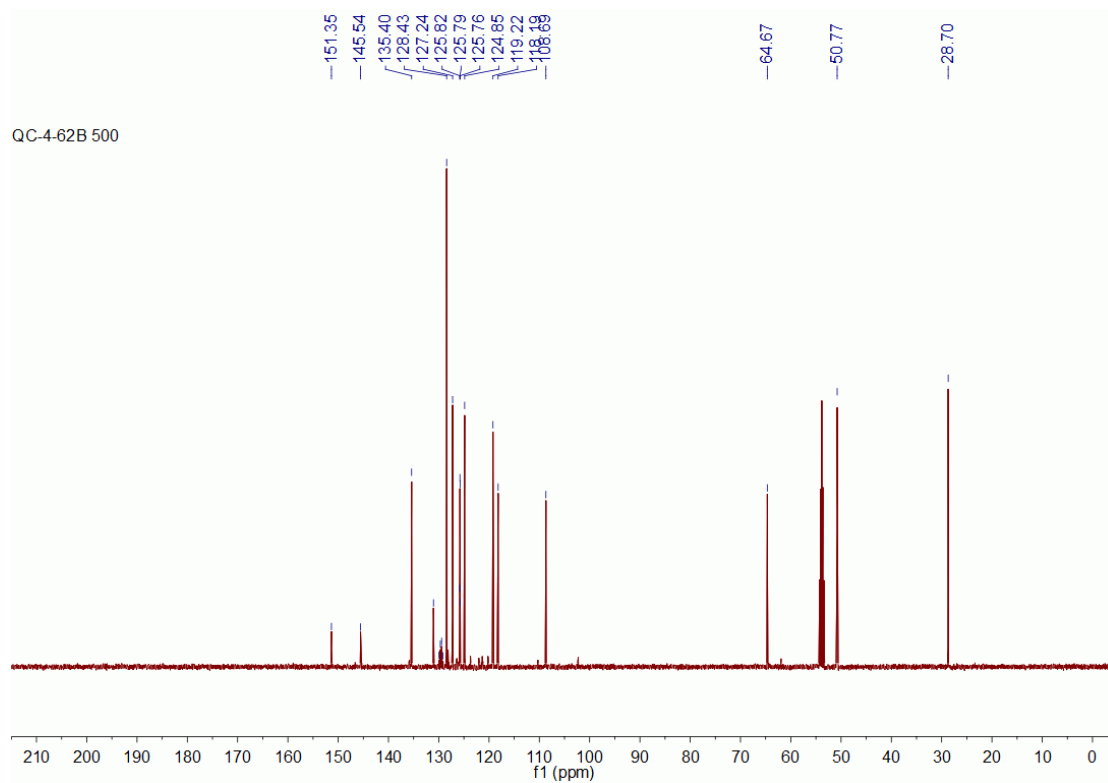


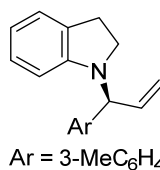
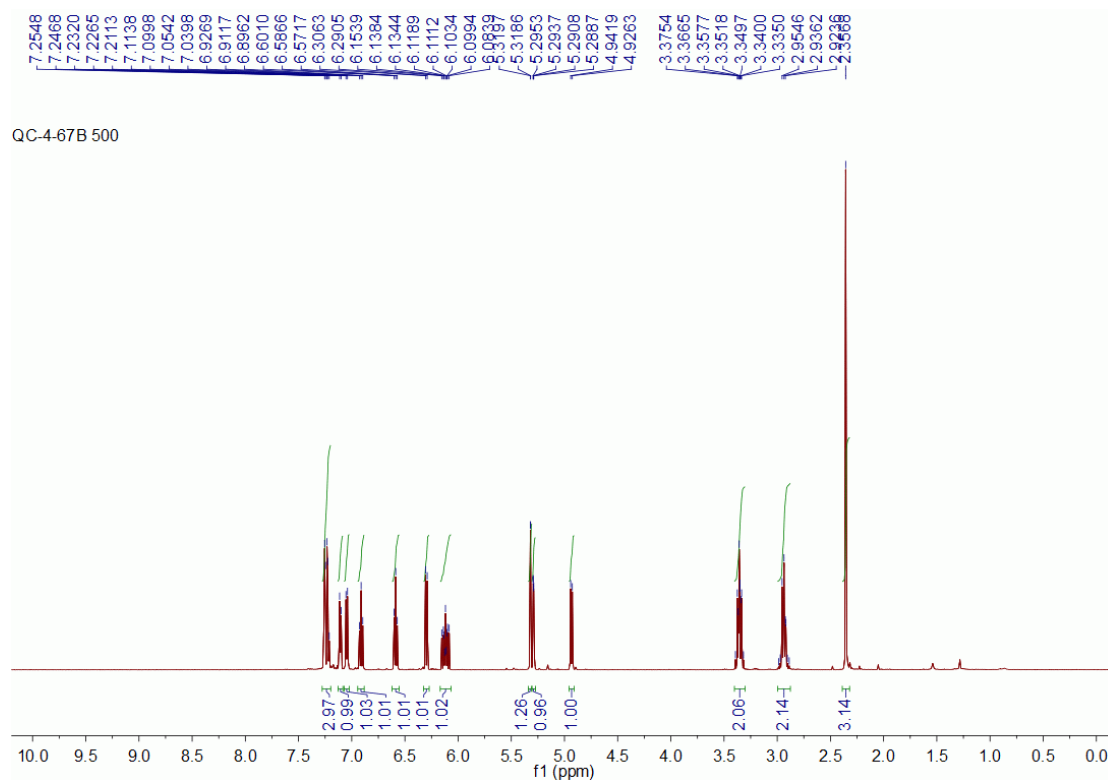


Ar = 4-CF₃C₆H₄

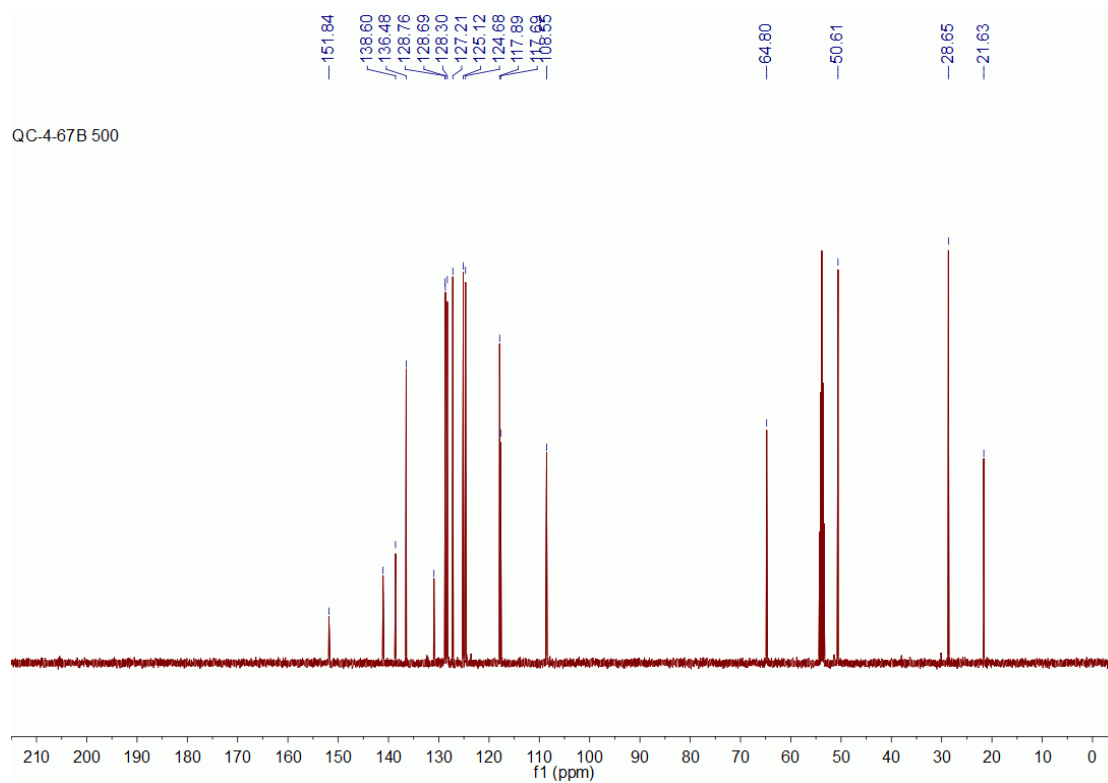
3ag ¹H NMR (500 MHz, CD₂Cl₂)

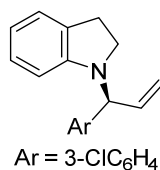
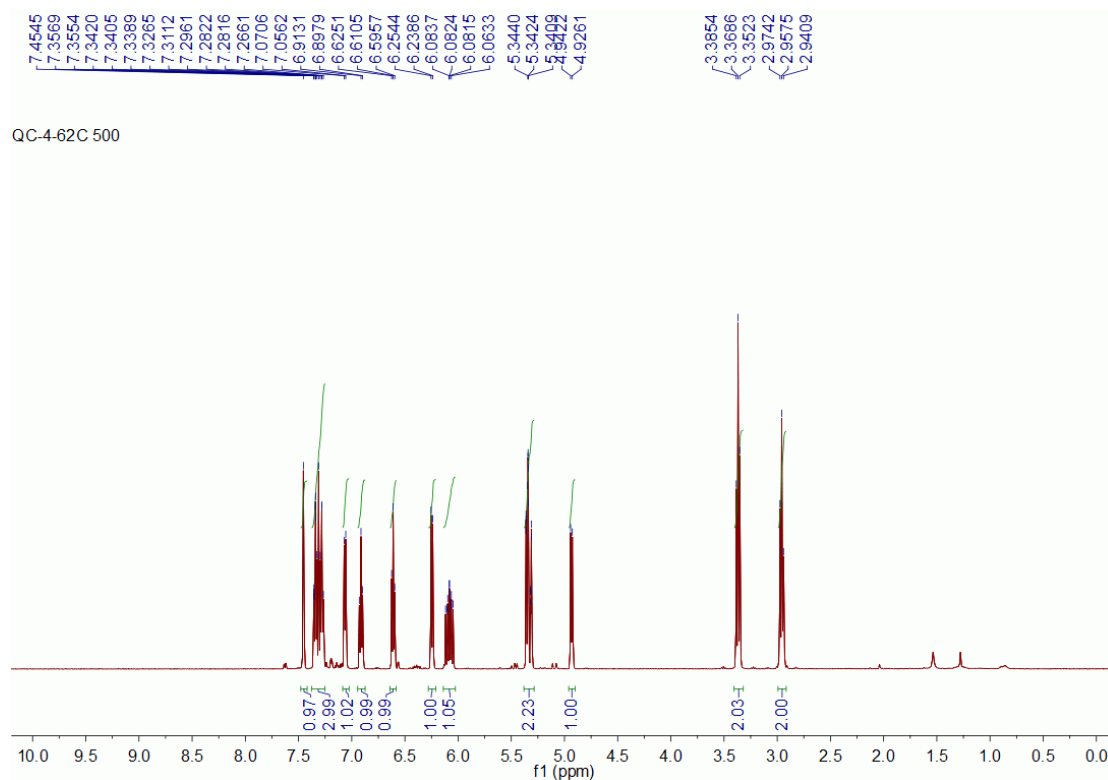
¹³C NMR (126 MHz, CD₂Cl₂)



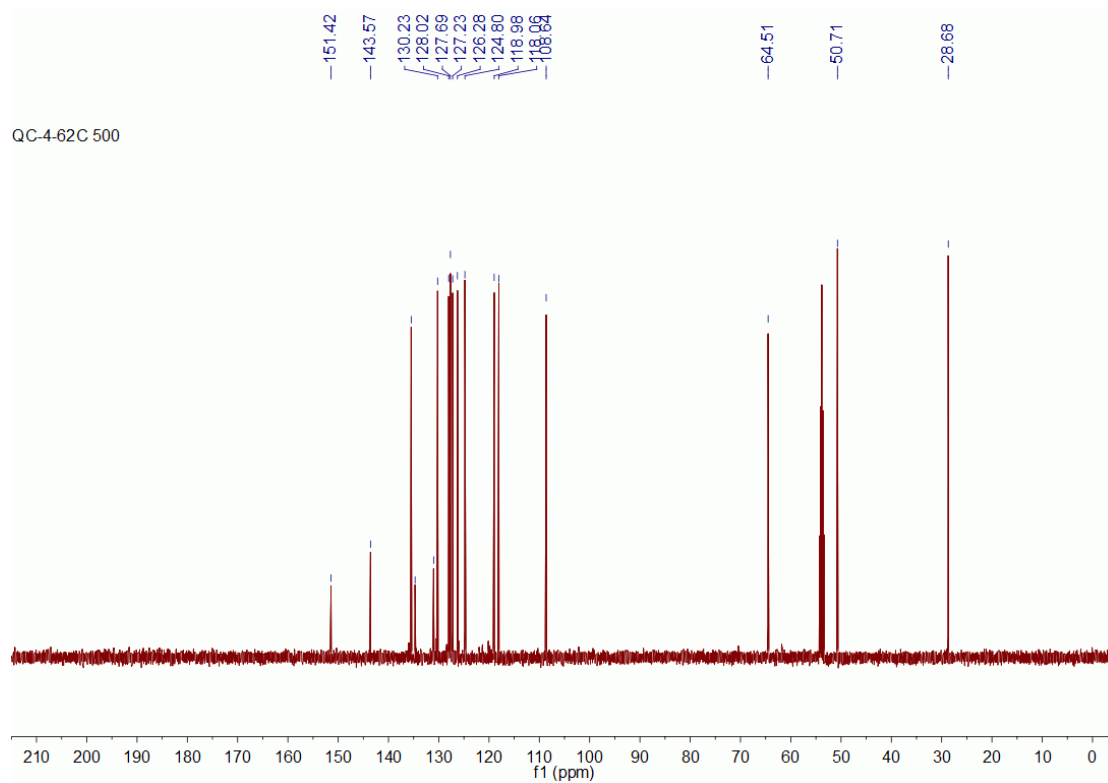


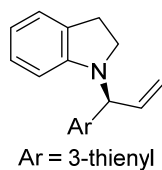
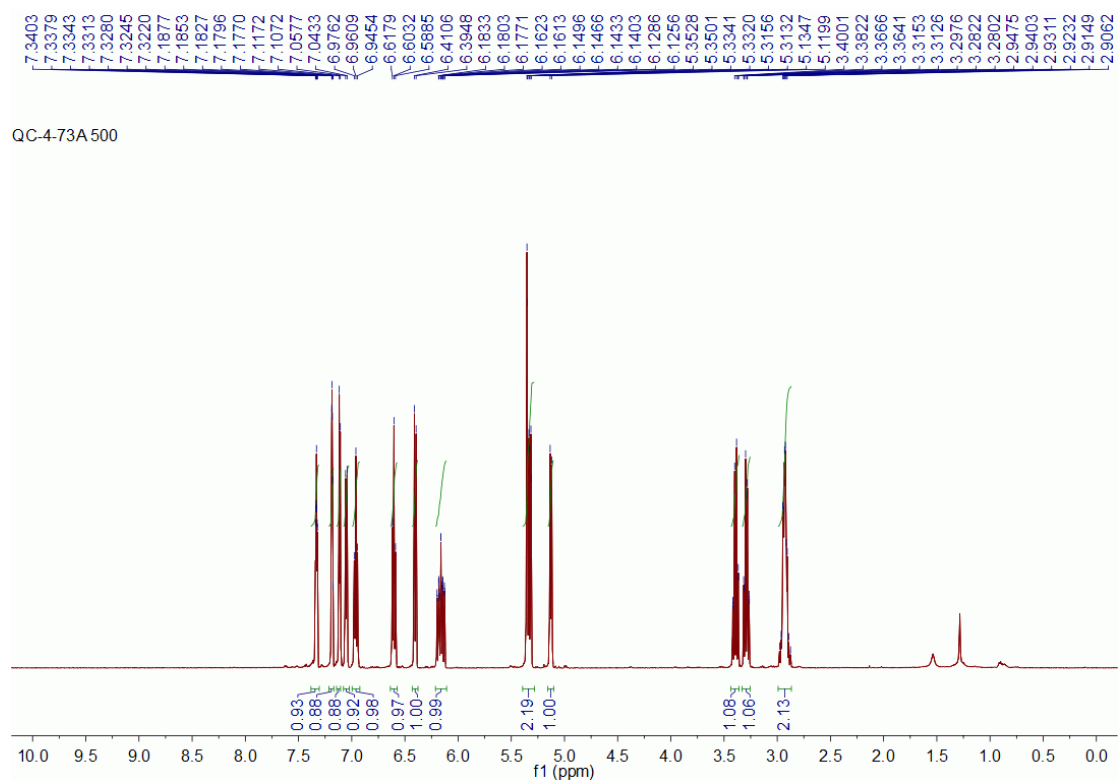
3ah ¹H NMR (500 MHz, CD₂Cl₂)
¹³C NMR (126 MHz, CD₂Cl₂)





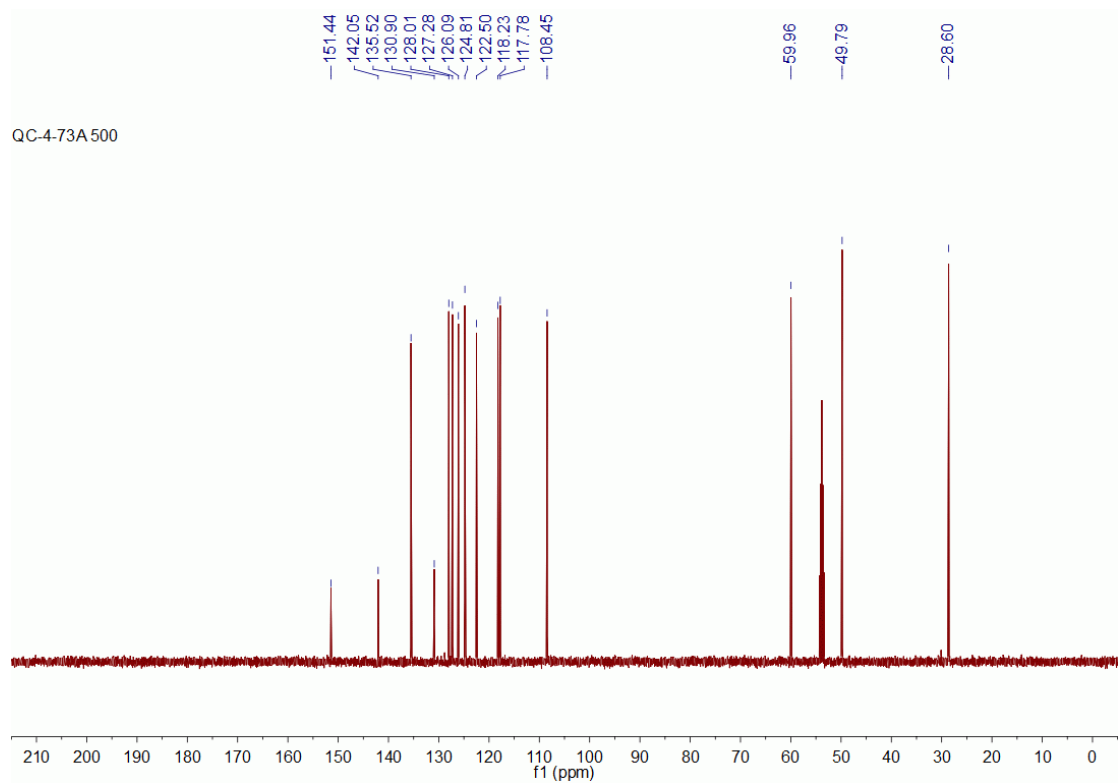
3aj ¹H NMR (500 MHz, CD₂Cl₂)
¹³C NMR (126 MHz, CD₂Cl₂)

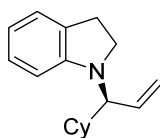
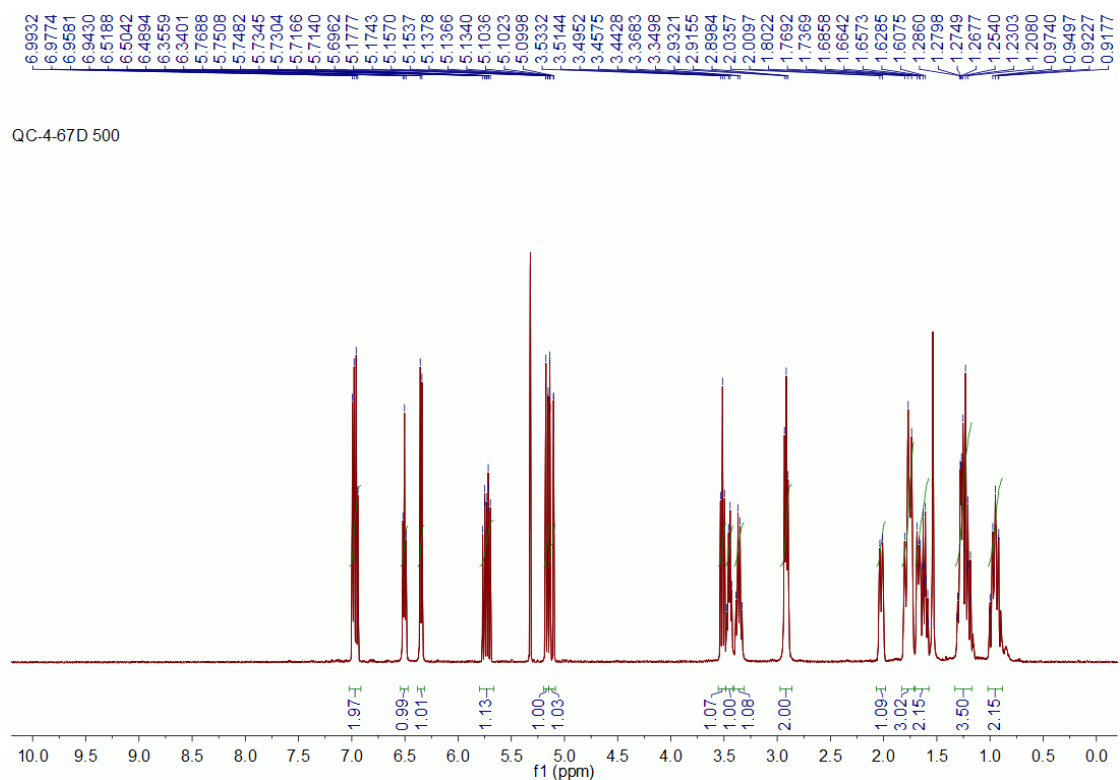




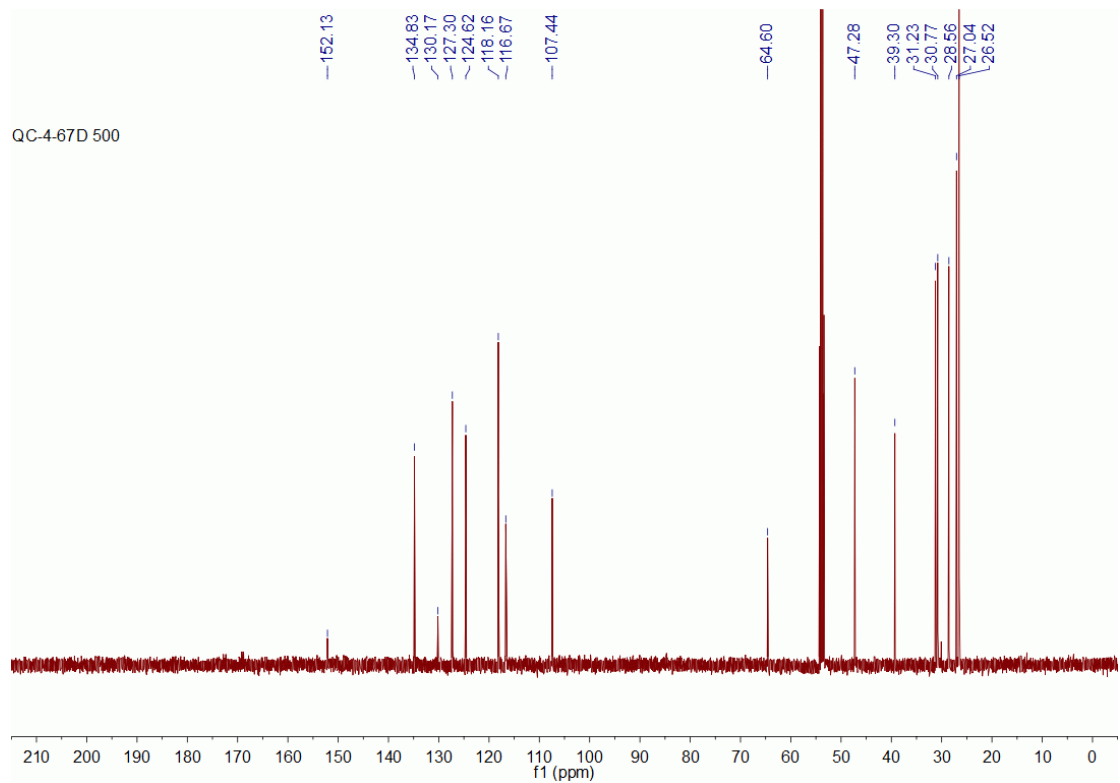
3ak ^1H NMR (500 MHz, CD_2Cl_2)

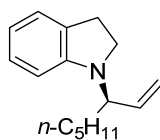
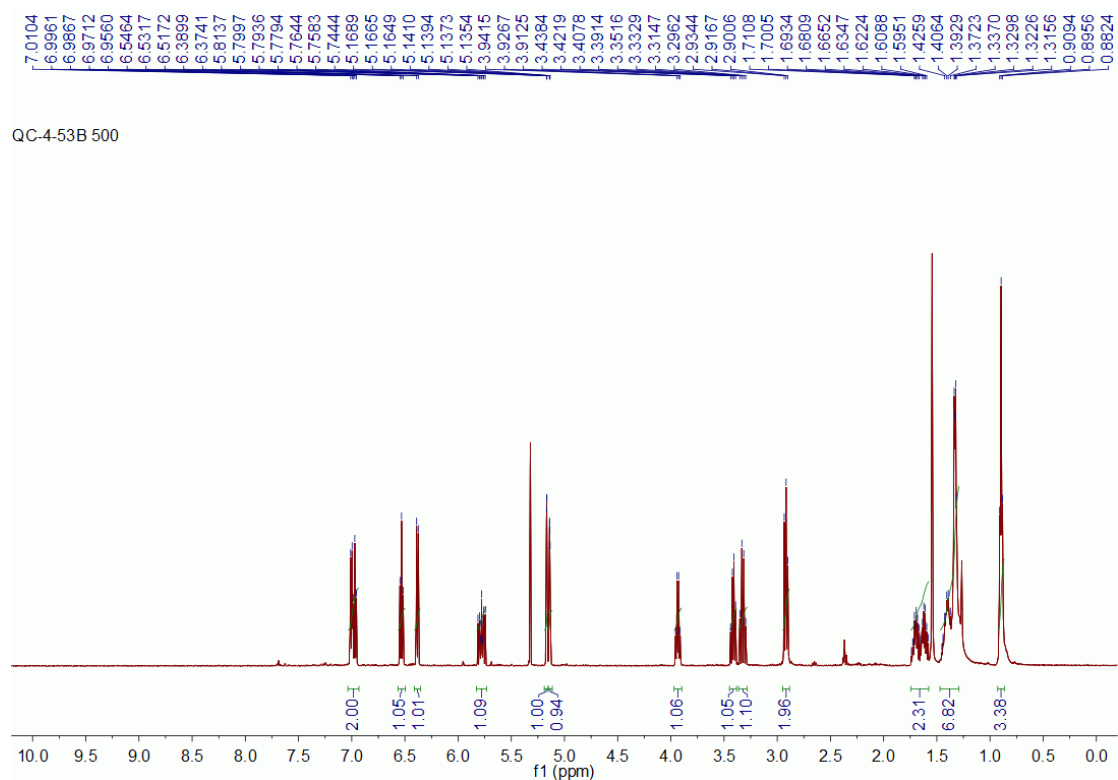
^{13}C NMR (126 MHz, CD_2Cl_2)





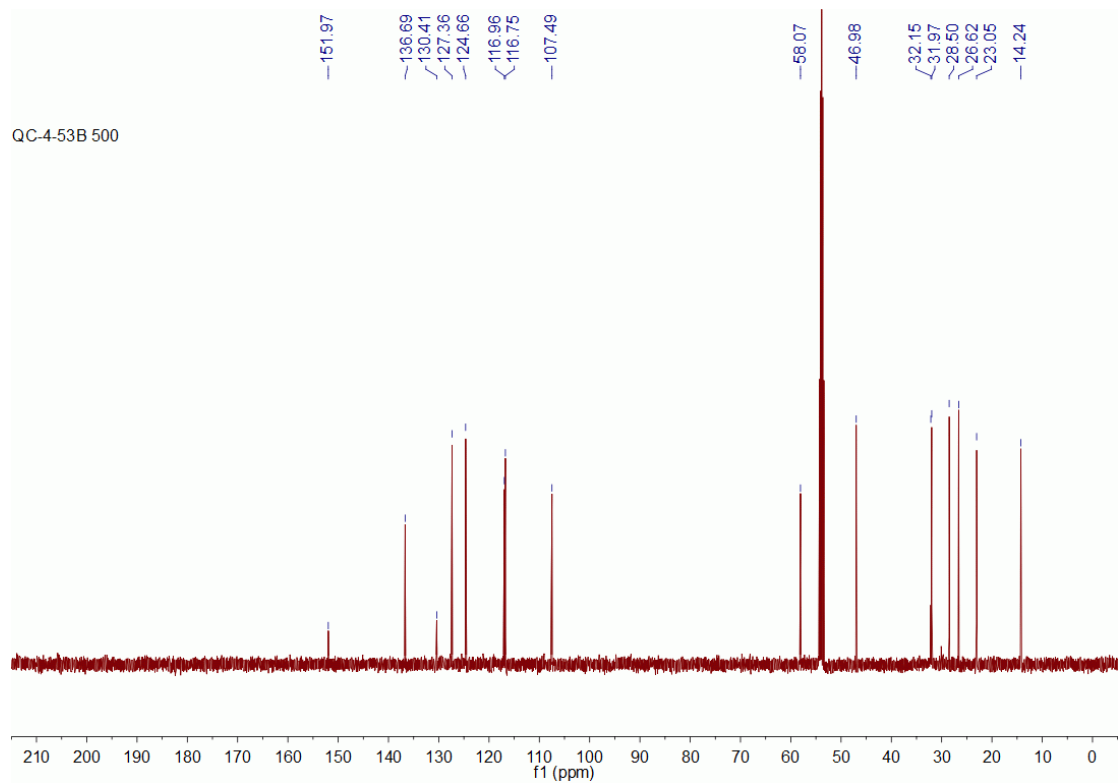
3aI ^1H NMR (500 MHz, CD_2Cl_2)
 ^{13}C NMR (126 MHz, CD_2Cl_2)

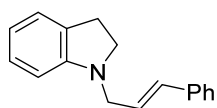
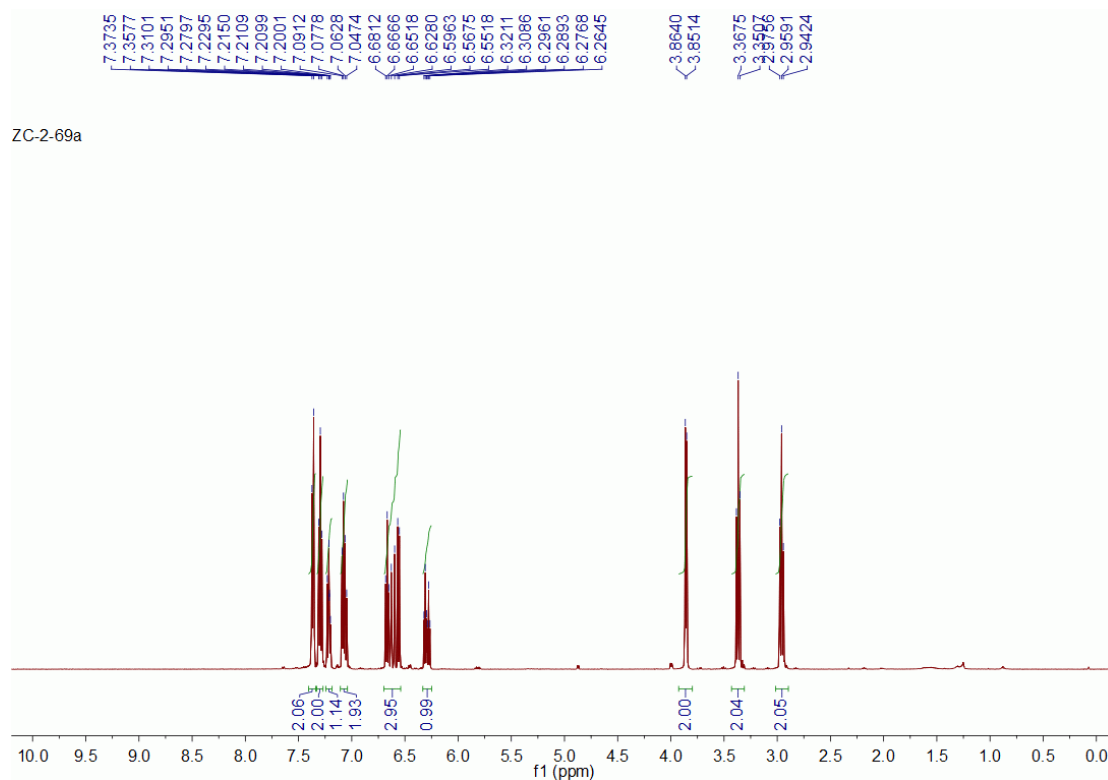




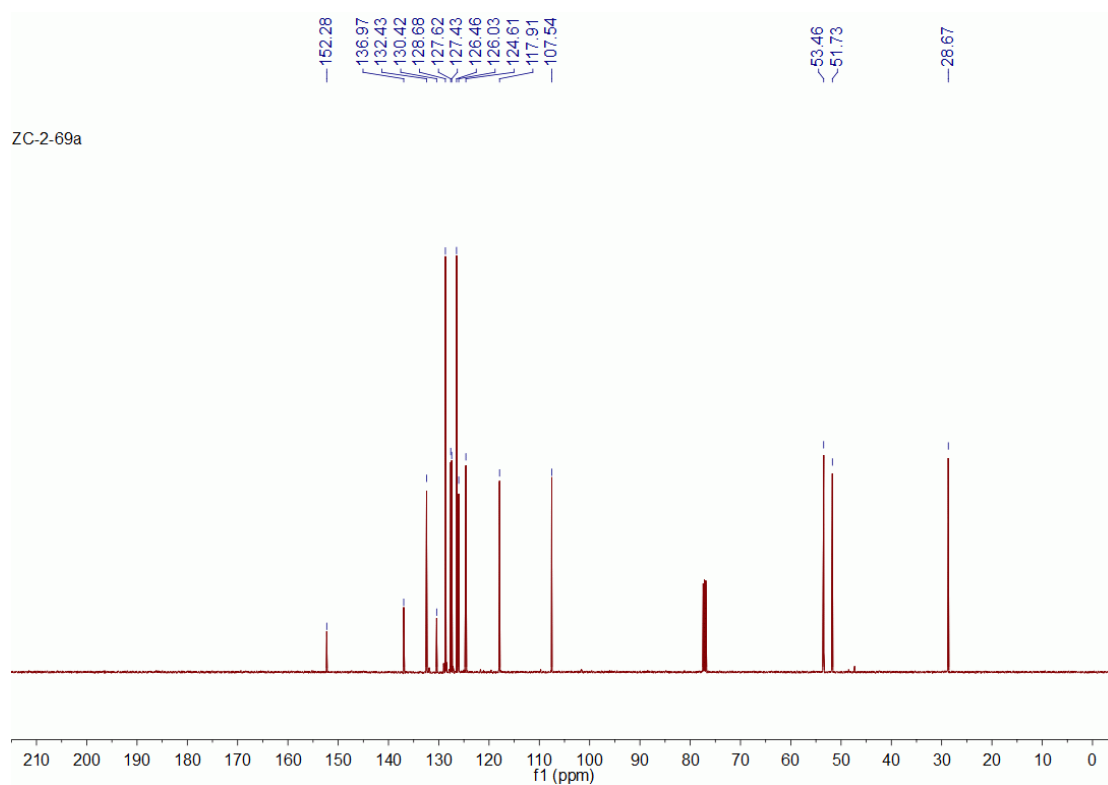
3an ¹H NMR (500 MHz, CD₂Cl₂)

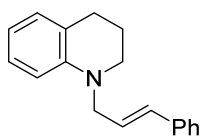
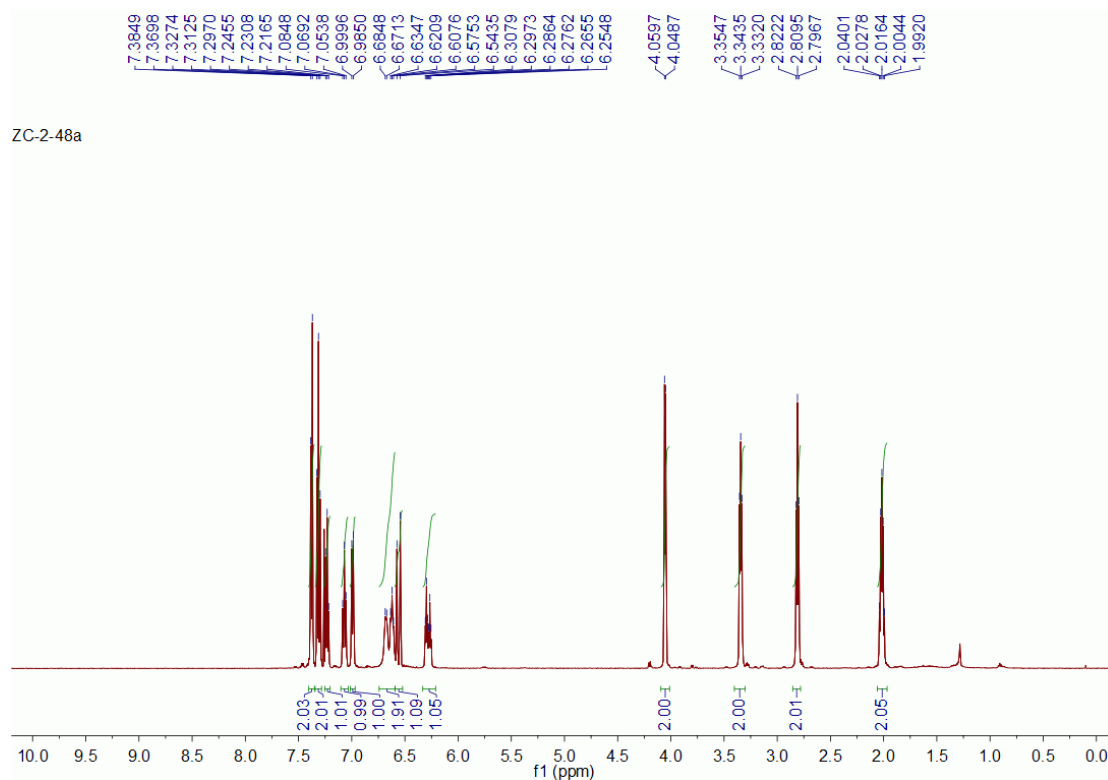
¹³C NMR (126 MHz, CD₂Cl₂)





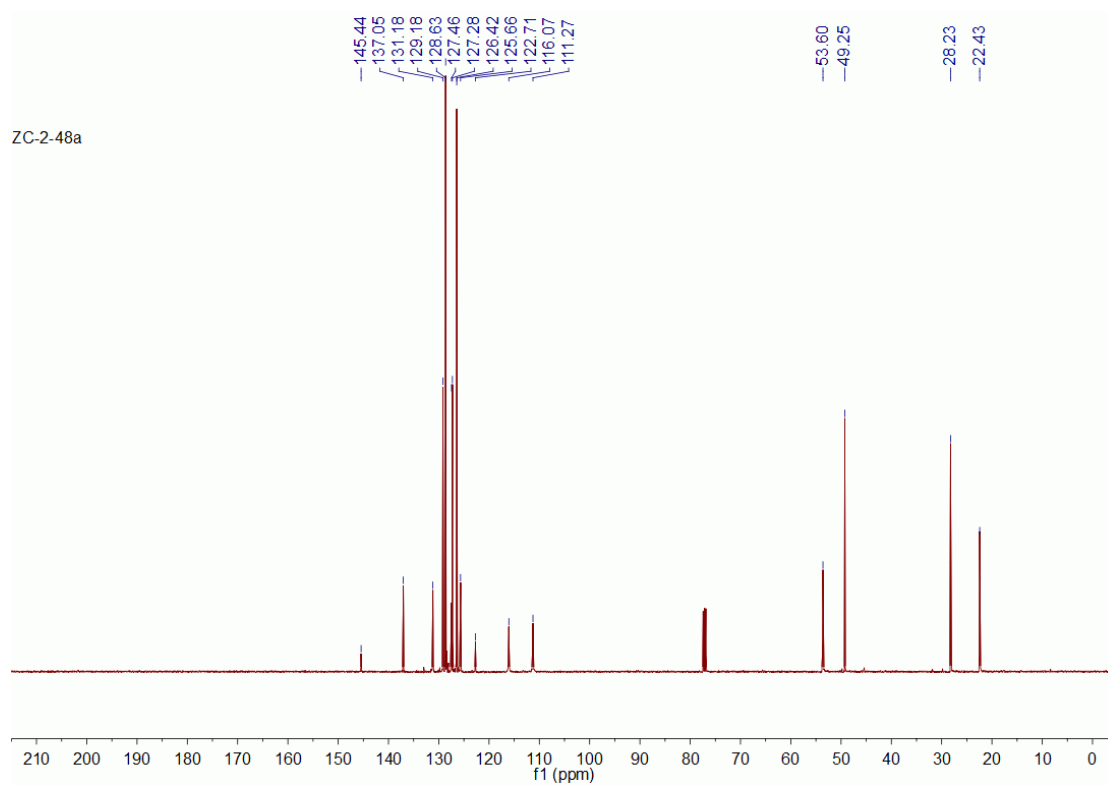
4aa ^1H NMR (500 MHz, CDCl_3)
 ^{13}C NMR (126 MHz, CDCl_3)

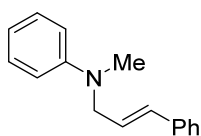
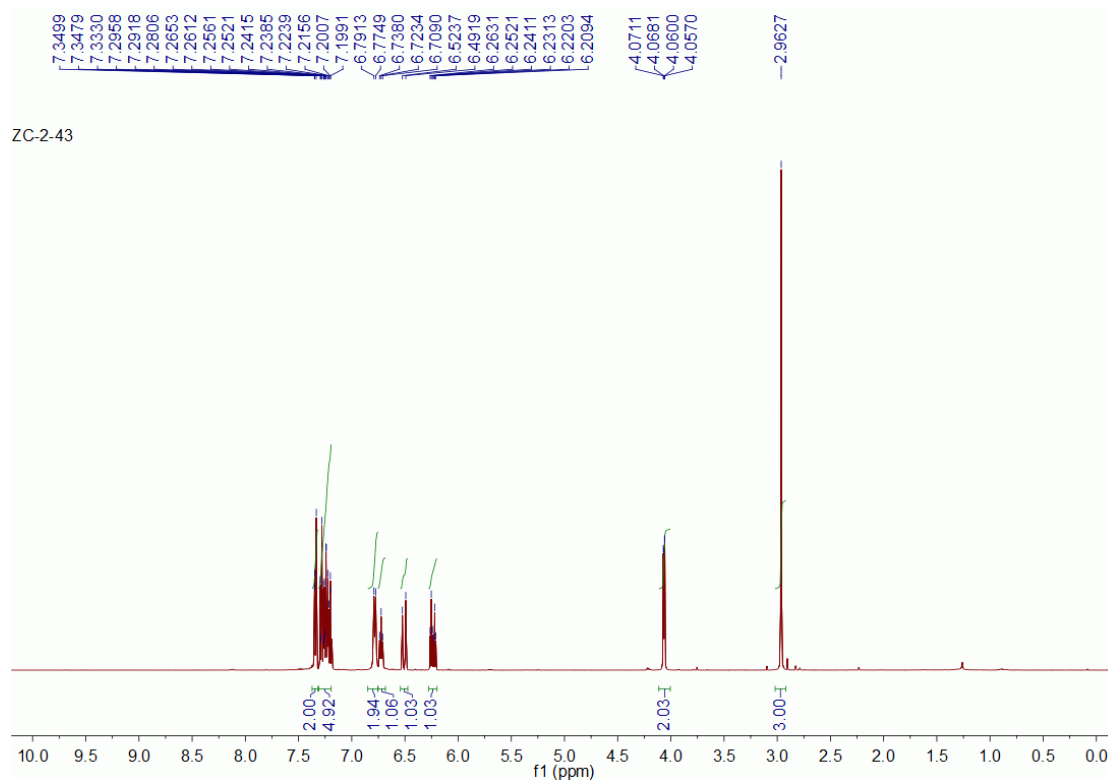




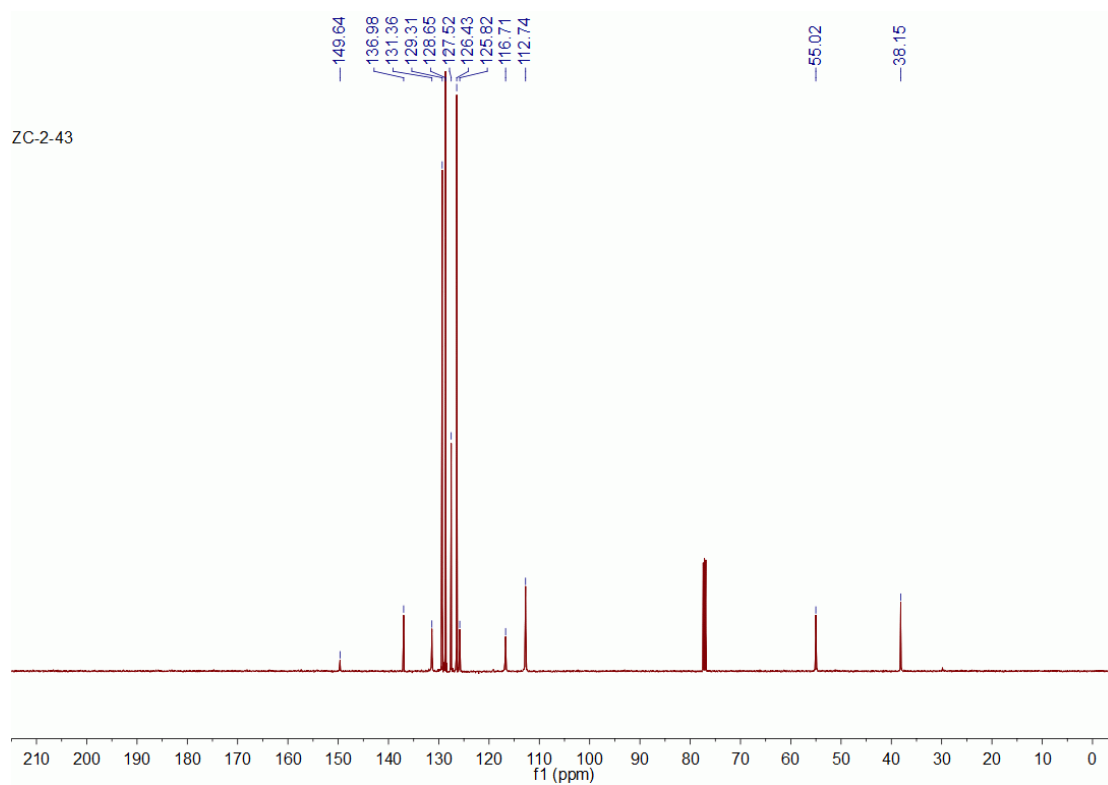
4la ^1H NMR (500 MHz, CDCl_3)

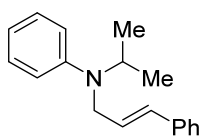
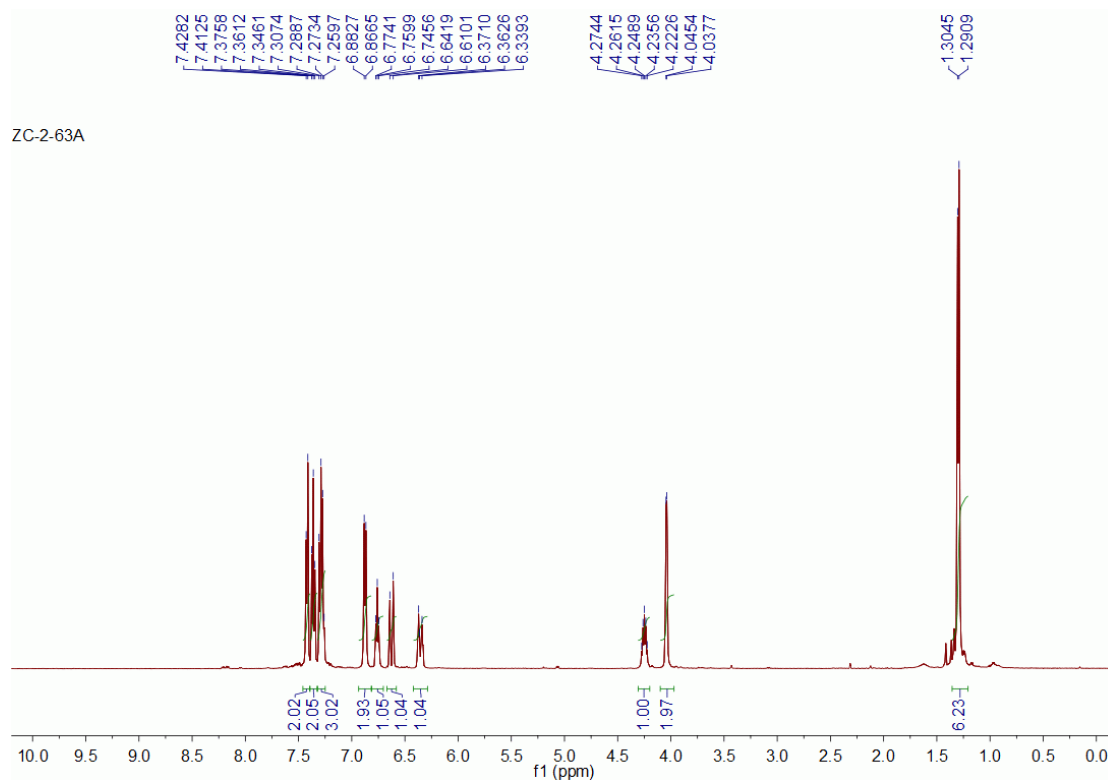
^{13}C NMR (126 MHz, CDCl_3)



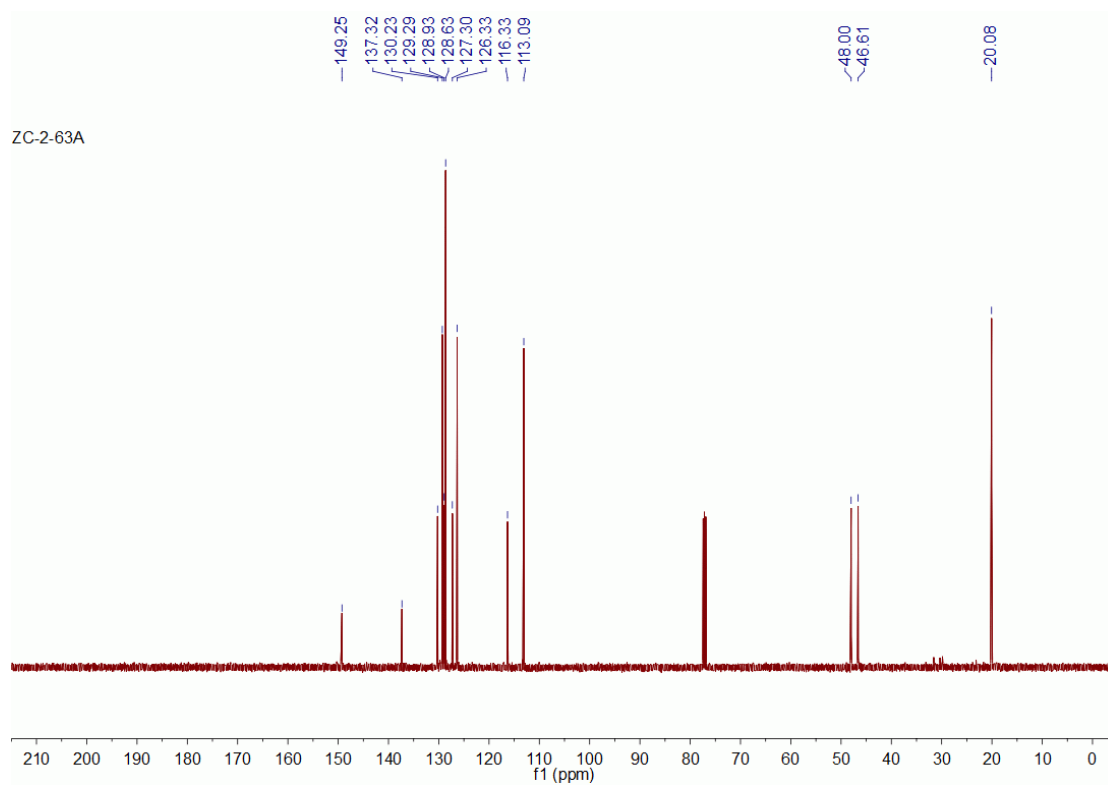


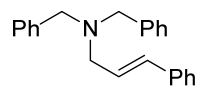
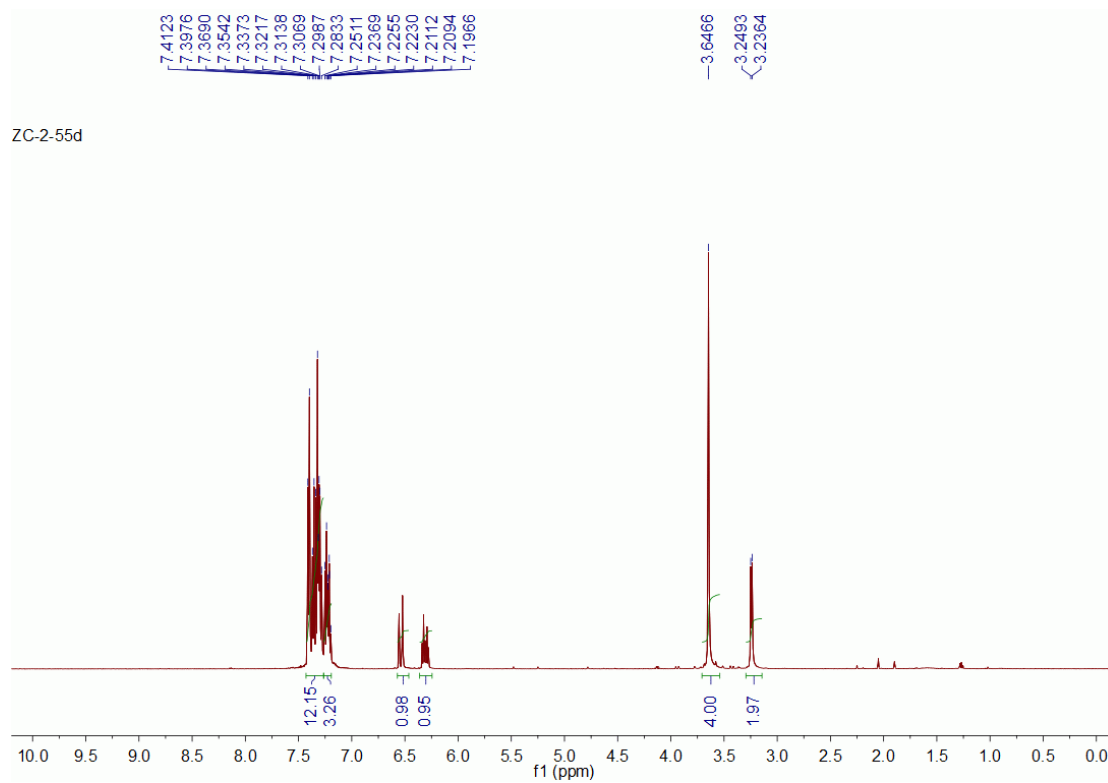
4ma ^1H NMR (500 MHz, CDCl_3)
 ^{13}C NMR (126 MHz, CDCl_3)



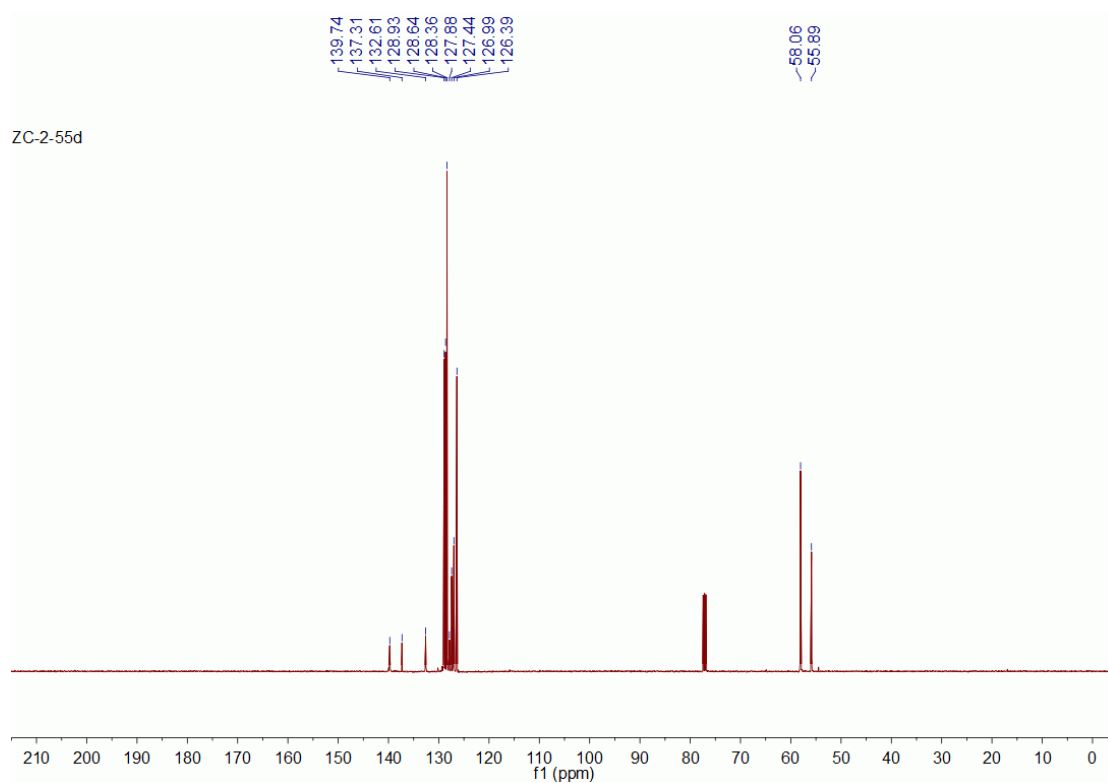


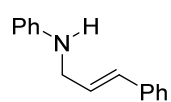
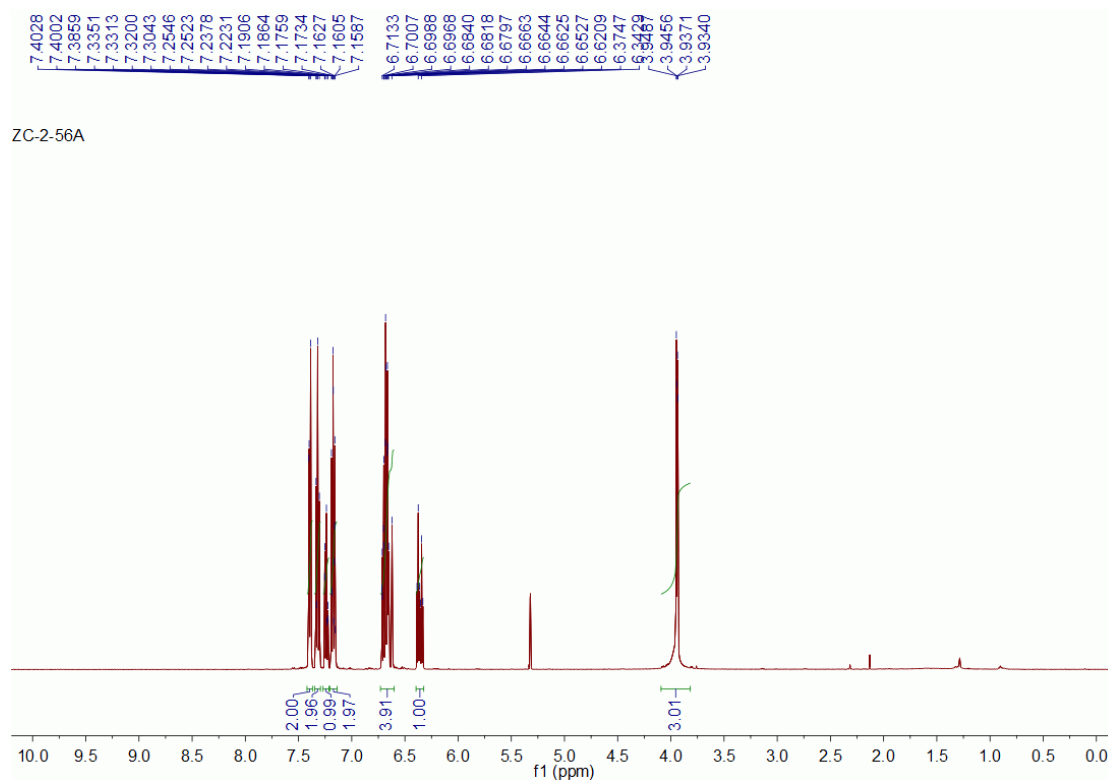
4na ^1H NMR (500 MHz, CDCl_3)
 ^{13}C NMR (126 MHz, CDCl_3)



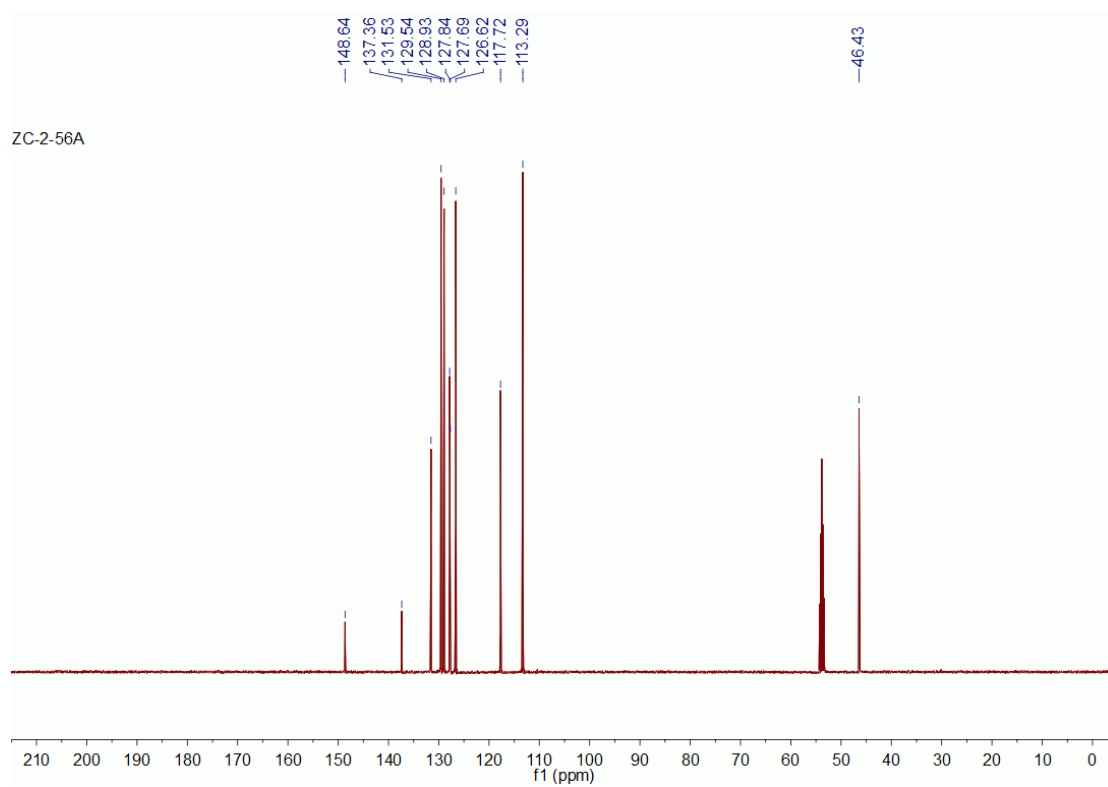


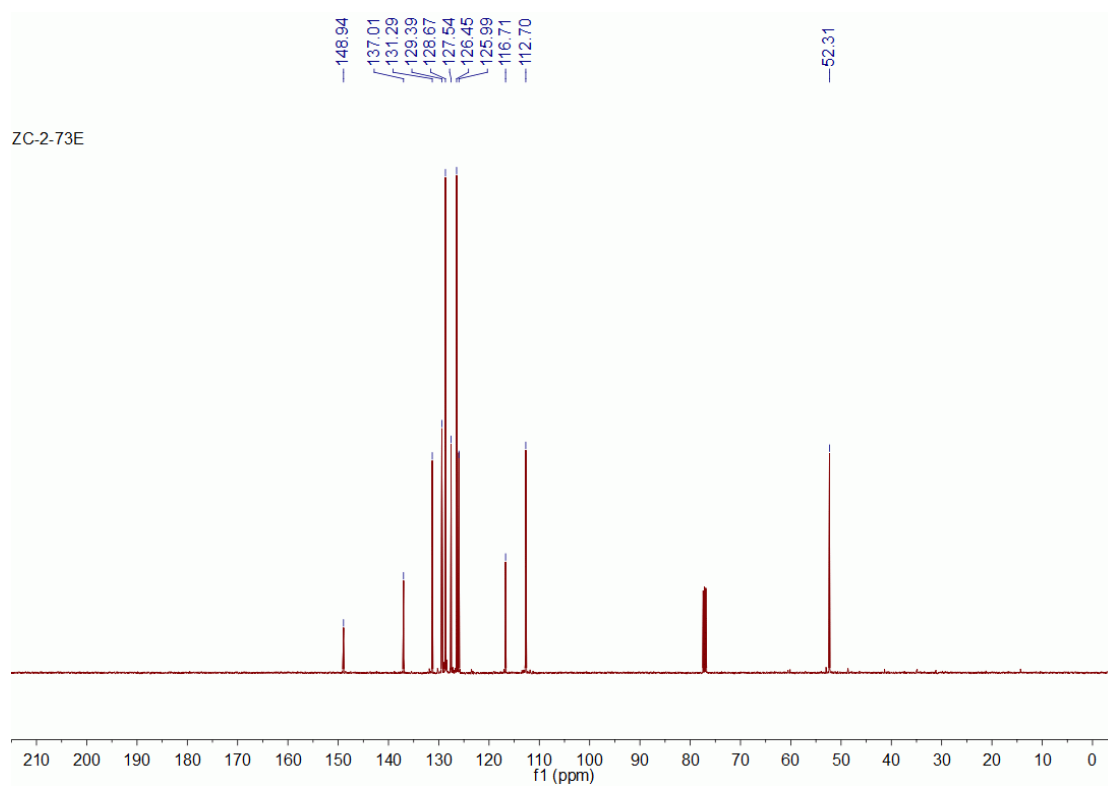
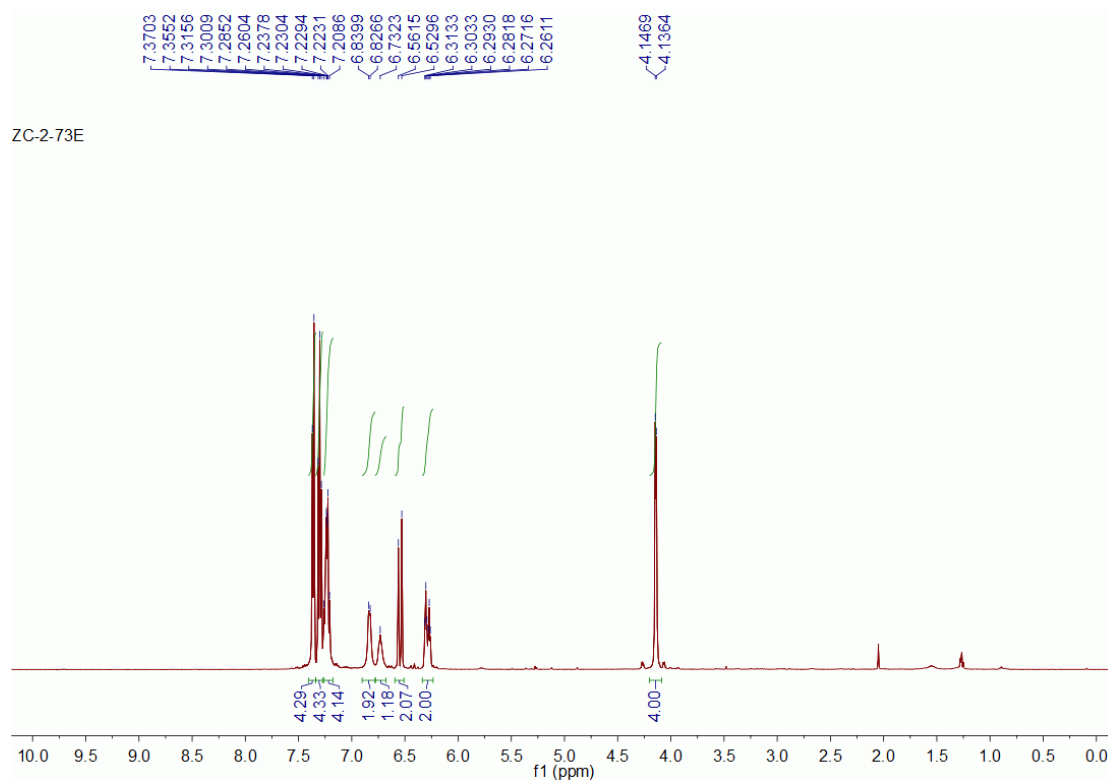
40a ^1H NMR (500 MHz, CDCl_3)
 ^{13}C NMR (126 MHz, CDCl_3)

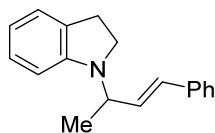
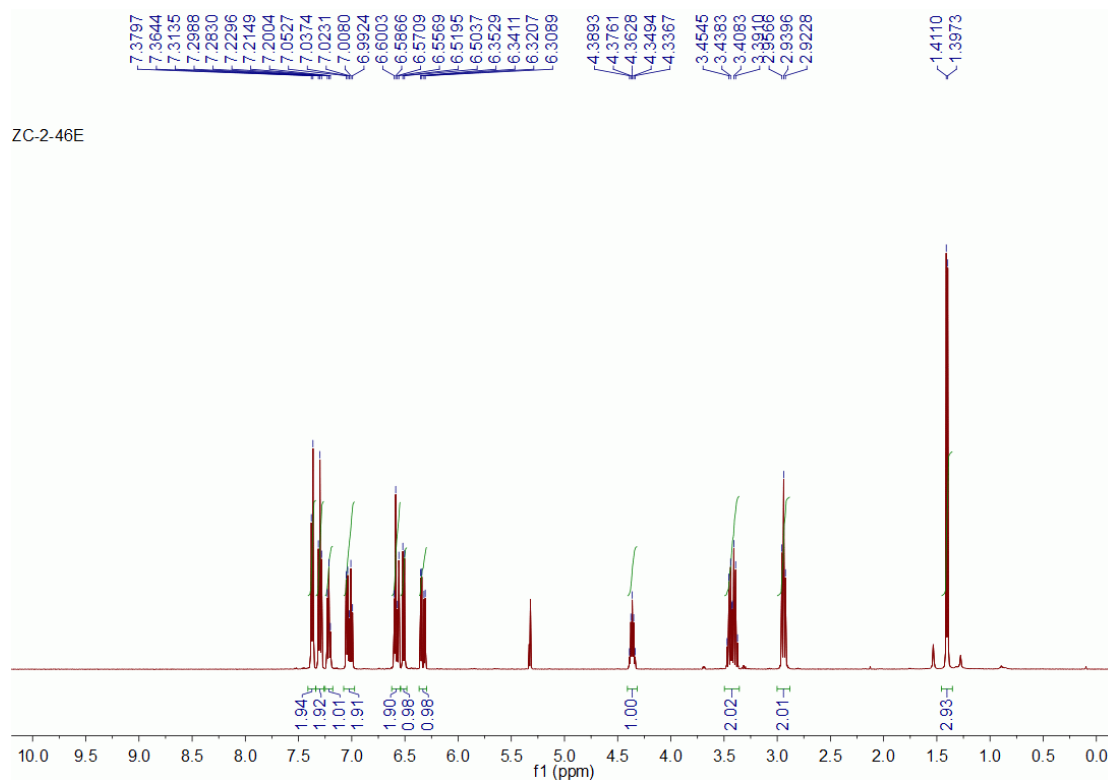




4ka ^1H NMR (500 MHz, CD_2Cl_2)
 ^{13}C NMR (126 MHz, CD_2Cl_2)

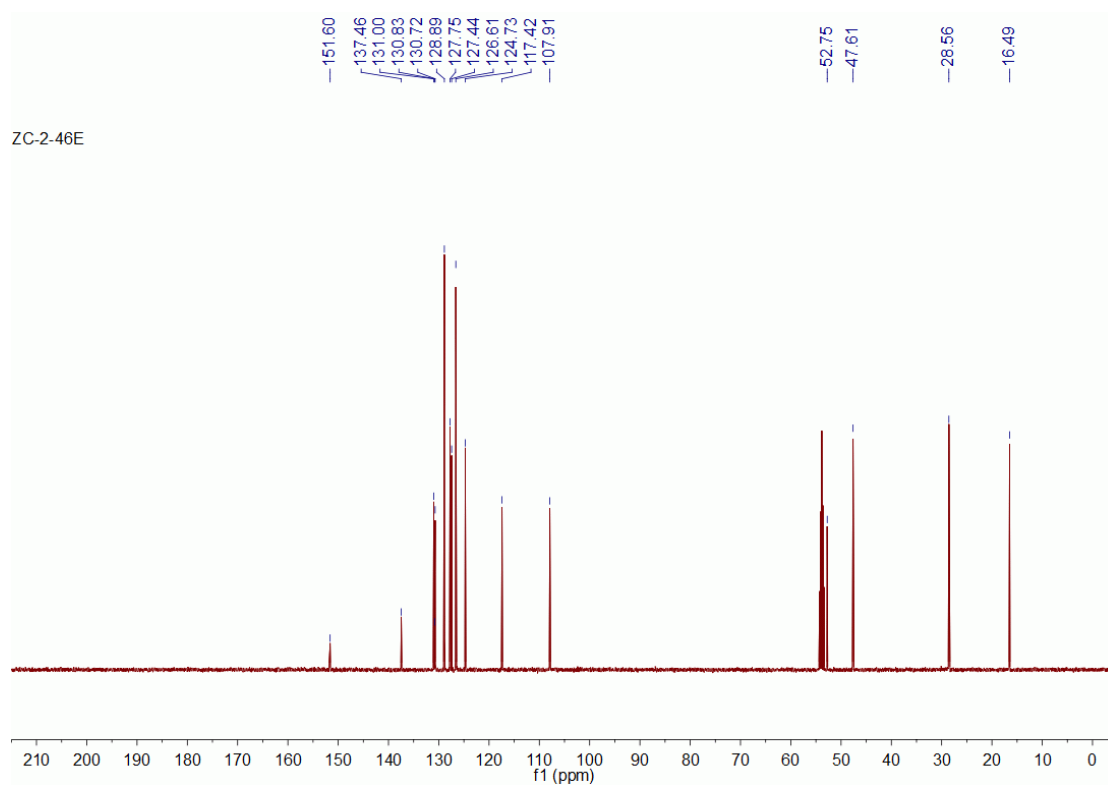


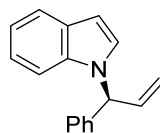
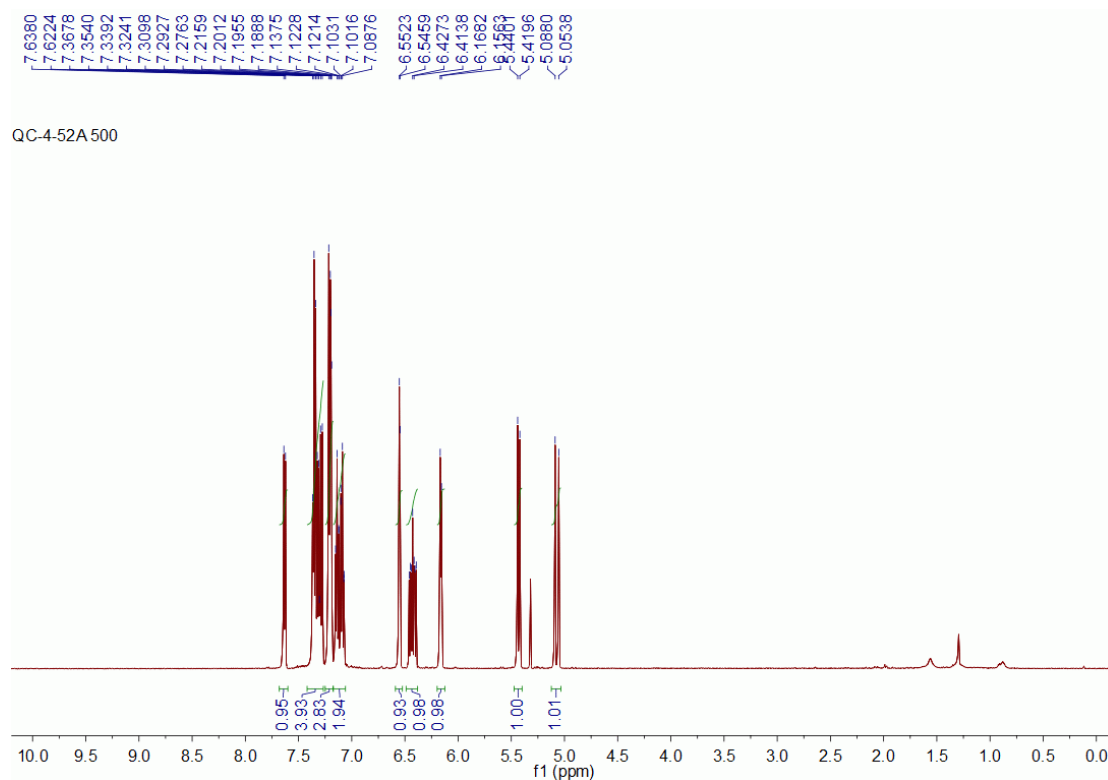




4ao ^1H NMR (500 MHz, CD_2Cl_2)

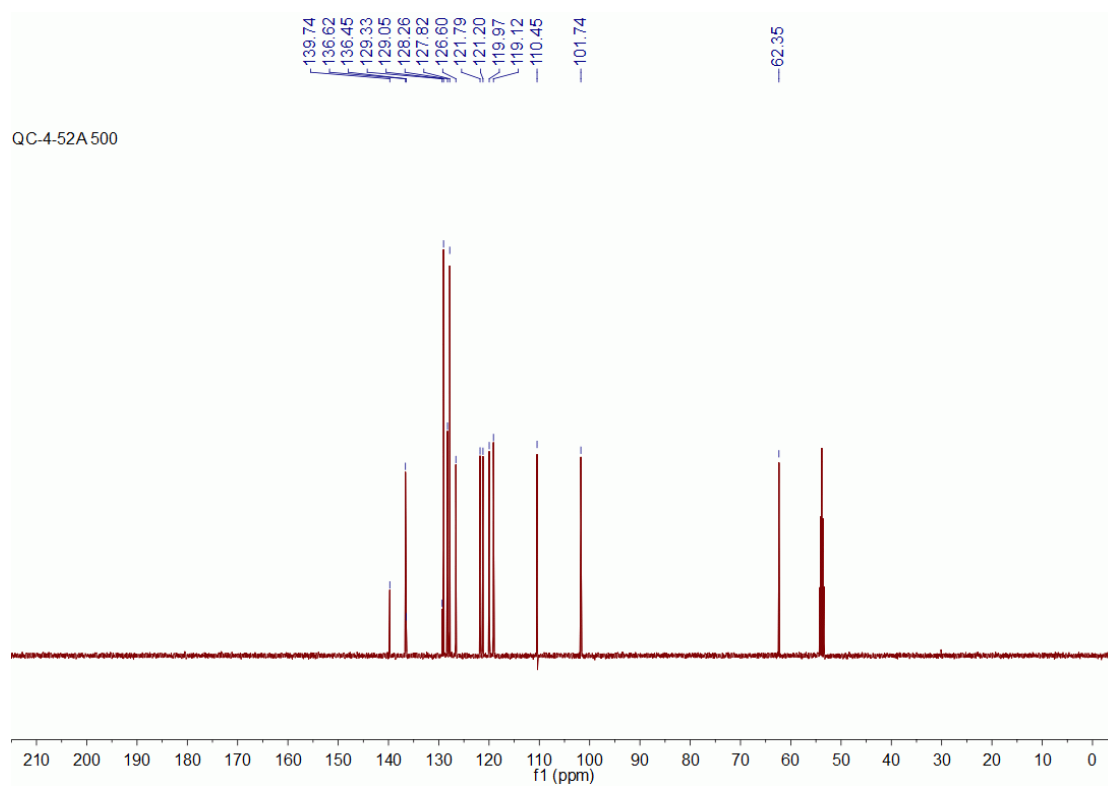
^{13}C NMR (126 MHz, CD_2Cl_2)

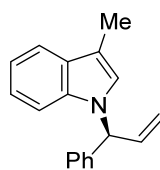
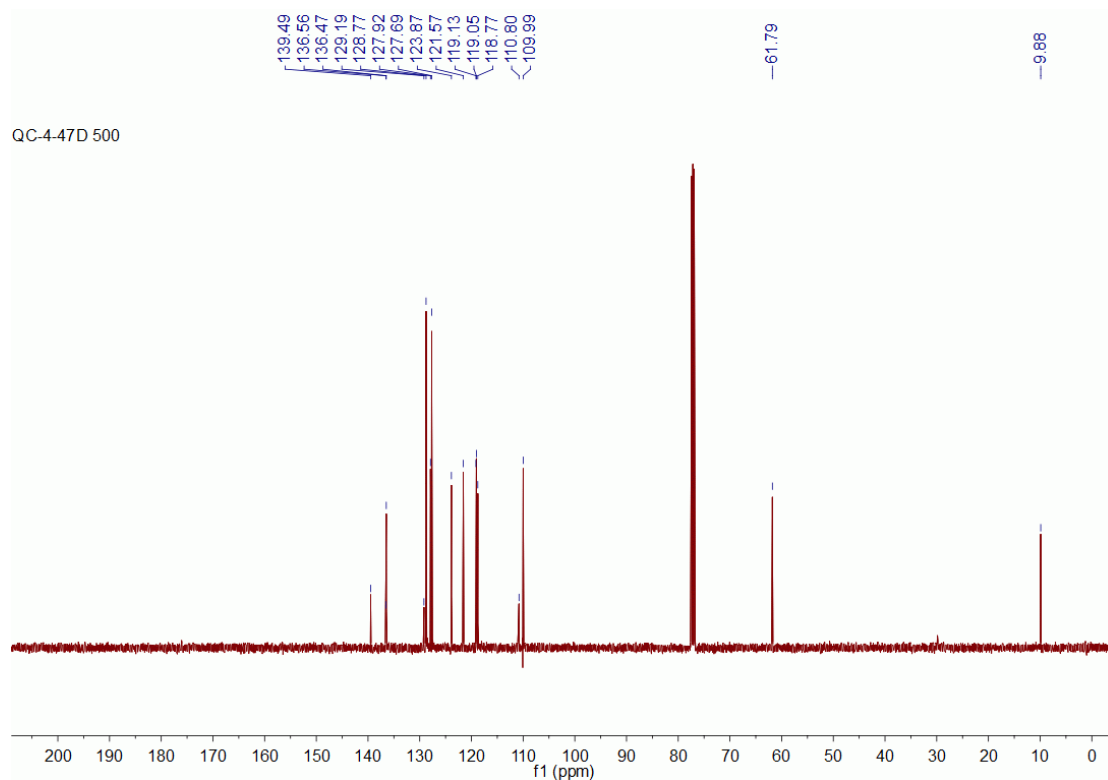




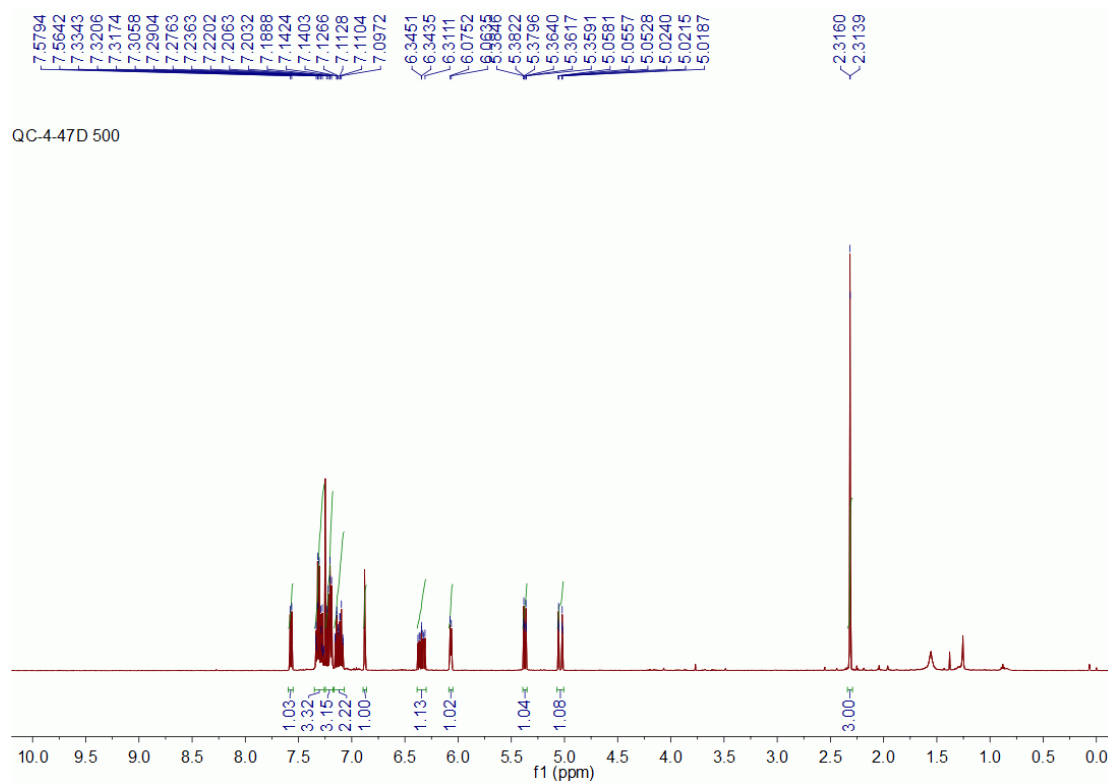
5aa ^1H NMR (500 MHz, CD_2Cl_2)

^{13}C NMR (126 MHz, CD_2Cl_2)





5ba ^1H NMR (500 MHz, CDCl_3)
 ^{13}C NMR (126 MHz, CDCl_3)



8. Copy of SFC spectra

