

Alkyne Hydroheteroarylation: Enantioselective Coupling of Indoles and Alkynes via Rh-Hydride Catalysis

Faben A. Cruz,⁺ Yamin Zhu,⁺ Quentin D. Tercenio, Zengming Shen* and Vy M. Dong*

[⁺]These authors contributed equally to this work.

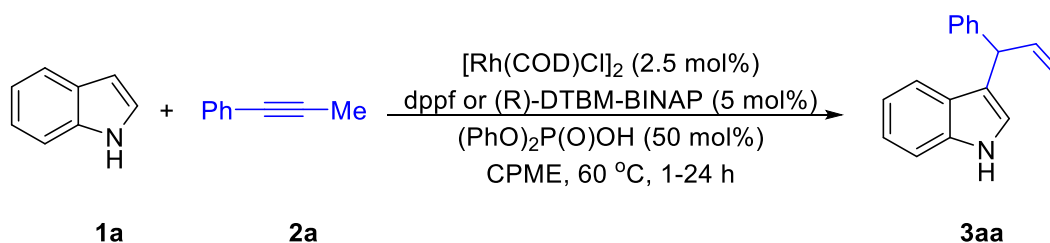
Supporting Information

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1. General Information

All reactions were run in oven-dried or flame-dried glassware under an atmosphere of N₂. Tetrahydrofuran, dichloromethane, toluene, dimethylformamide and diethyl ether were purified using an Innovative Technologies Pure Solv system, degassed by three freeze-pump-thaw cycles, and stored over 3 Å MS within an N₂ filled glove box. Dimethylsulfoxide were refluxed with CaH₂ and distilled prior to use. The molarity of organolithium reagents was determined by titration with *iso*-propanol/1,10-phenanthroline. Reactions were monitored either *via* gas chromatography using an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD or by analytical thin-layer chromatography on EMD Silica Gel 60 F₂₅₄ plates. Visualization of the developed plates was performed under UV light (254 nm) or using either KMnO₄ or *p*-anisaldehyde stain. Column chromatography was performed with Silicycle Silia-P Flash Silica Gel using glass columns. Automated column chromatography was performed using either a Biotage SP1 or Teledyne Isco CombiFlash Rf 200 purification system. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a Bruker DRX-400 (400 MHz ¹H, 100 MHz ¹³C, 376.5 MHz ¹⁹F, 161.9 MHz), GN-500 (500 MHz ¹H, 125.7 MHz ¹³C), CRYO-500 (500 MHz ¹H, 125.7 MHz ¹³C) or AVANCE-600 (600 MHz ¹H, 151 MHz ¹³C, 565 MHz ¹⁹F) 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). Infrared spectra were obtained on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. High resolution mass spectra (HRMS) was performed by the University of California, Irvine Mass Spectrometry Center. Enantiomeric excesses for stereoselective reactions were determined by chiral SFC analysis using an Agilent Technologies HPLC (1200 series) system and Aurora A5 Fusion.

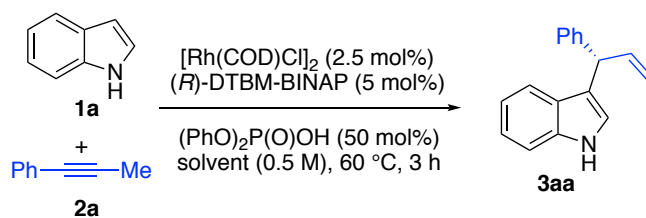
2. Typical procedure for the Rh-catalyzed allylation of indoles



In a N_2 -filled glovebox, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (1.2 mg, 0.0025 mmol), dppf (2.8 mg, 0.005 mmol) or (*R*)-DTBM-BINAP (6.0 mg, 0.005 mmol), diphenyl hydrogen phosphate (12.5 mg, 0.05 mmol), indole **1** (0.10 mmol), alkyne **2** (0.12 mmol) and CPME (0.2 mL) were added to a 1 dram vial. After heating the reaction mixture at 60 °C for 1-24 hours, the resulting solution was cooled to rt. The selectivity was determined by ^1H NMR analysis of the crude reaction mixture. The product **3** was isolated by flash column chromatography or preparatory TLC using hexanes/EtOAc.

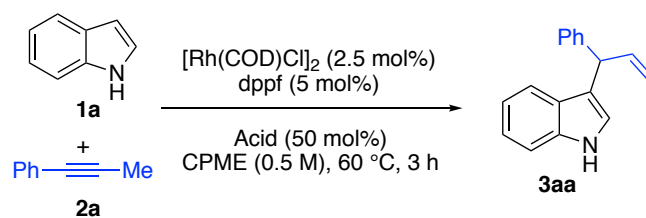
Preparative Scale Reaction: In a N_2 -filled glovebox, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (12.3 mg, 0.025 mmol), (*R*)-DTBM-BINAP (59.6 mg, 0.05 mmol), diphenyl hydrogen phosphate (125.1 mg, 0.5 mmol), *N*-methyl indole **1b** (131.2 mg, 1.0 mmol), alkyne **2a** (151 μL , 0.12 mmol) and CPME (2 mL) were added to a 1 dram vial. After heating the reaction mixture at 60 °C for 24 hours, the resulting solution was cooled to rt. The selectivity was determined by ^1H NMR analysis of the crude reaction mixture. The product **3ba** was isolated by flash column chromatography using 2% ethyl acetate in hexanes as a yellow oil (228.8 mg, 0.93 mmol, 93% yield, 91% *ee*).

Evaluation of Solvents



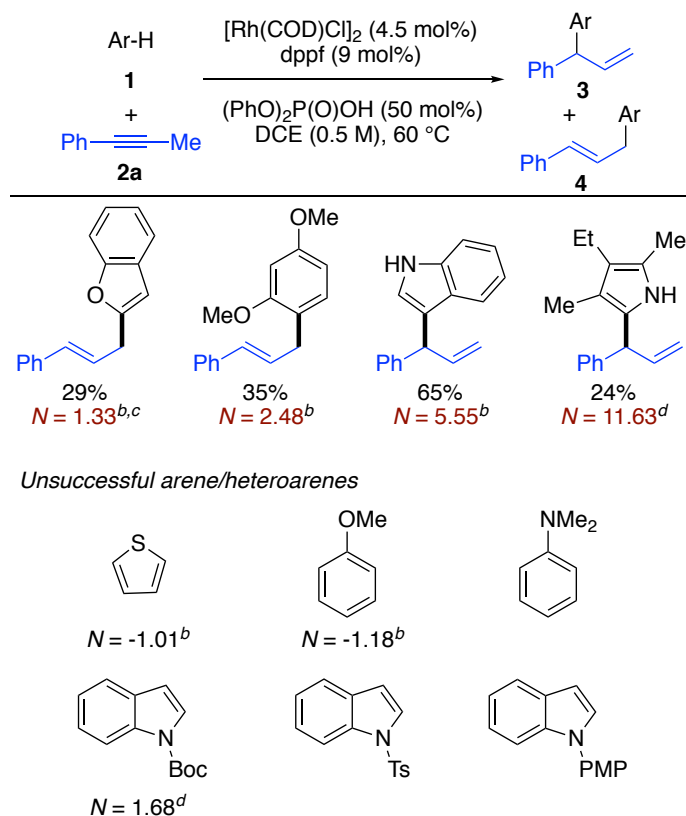
Solvent	NMR yield	ee	Solvent	NMR yield	ee
1,2-DCE	24%	nd	Ethyl acetate	74%	91%
Toluene	11%	nd	THF	52%	91%
Acetone	16%	nd	1,4-dioxane	73%	90%
MeOH	28%	nd	2-Me-THF	80%	92%
MeCN	24%	nd	1,2-DME	50%	92%
MeNO ₂	42%	nd	CPME	92%	91%

Evaluation of Acids



Acid	NMR yield
TFA	6%
Benzoic Acid	< 5%
PTSA	60%
$(\text{PhO})_2\text{P}(\text{O})\text{OH}$	90%
$(\text{BuO})_2\text{P}(\text{O})\text{OH}$	27%

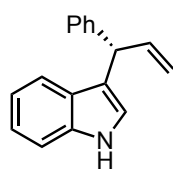
Alkyne Hydroarylation with Arenes of Various Nucleophilicities^a



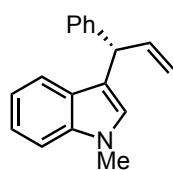
^a**1** (0.1 mmol), **2a** (0.12 mmol), [Rh(COD)Cl]₂ (4.5 mol%), dppf (9.0 mol%), (PhO)₂P(O)OH (50 mol%), DCE (0.2 mL), 60 °C, ^bNucleophilicity in DCM. ^cNucleophilicity of furan. ^dNucleophilicity in MeCN.

In a N₂-filled glovebox, [Rh(COD)Cl]₂ (2.2 mg, 0.0045 mmol), dppf (5.0 mg, 0.009 mmol), diphenyl hydrogen phosphate (12.5 mg, 0.05 mmol), arene/heteroarene **1** (0.10 mmol), alkyne **2a** (25 μL, 0.12 mmol) and DCE (0.2 mL) were added to a 1 dram vial. After heating the reaction mixture at 60 °C, the resulting solution was cooled to rt. The selectivity was determined by ¹H NMR analysis of the crude reaction mixture. The product **3** was isolated by flash column chromatography or preparatory TLC using hexanes/EtOAc.

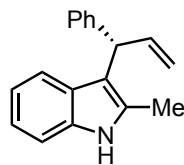
3. Characterization data



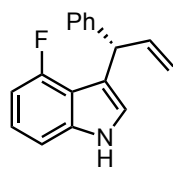
(S)-3-(1-Phenylallyl)-1H-indole (3aa): yellow oil, isolated *via* preparatory TLC using 8% ethyl acetate in hexanes, $R_f = 0.15$, 19.7 mg, 86% yield, 91% ee, $[\alpha]_D^{25} = -16.8$ ($c = 0.42$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.¹ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.93 (s, 1H), 7.41 – 7.09 (m, 8H), 7.00 (t, $J = 6.4$ Hz, 1H), 6.85 (s, 1H), 6.32 (ddd, $J = 16.8, 9.2, 6.8$ Hz, 1H), 5.17 (d, $J = 9.2$ Hz, 1H), 5.05 (d, $J = 16.8$ Hz, 1H), 4.94 (d, $J = 6.8$ Hz, 1H). **Chiral SFC:** 91% ee, AD-H column, 220 nm, 2% 2-propanol in CO_2 , 2 mL/min, retention time 30.7 min and 33.6 min (major).



(S)-1-Methyl-3-(1-phenylallyl)-1H-indole (3ba): yellow oil, isolated *via* preparatory TLC using 2% ethyl acetate in hexanes, $R_f = 0.1$, 22.2 mg, 90% yield, 92% ee, $[\alpha]_D^{25} = -0.5$ ($c = 0.76$, CHCl_3). This compound was also prepared on a 1 mmol scale to afford **3ba** in 93% yield and 91% ee (see Preparative Scale Reaction). The $^1\text{H NMR}$ spectrum is in accordance with literature.² $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (dt, $J = 8.0, 0.8$ Hz, 1H), 7.31 – 7.28 (m, 5H), 7.27 – 7.18 (m, 2H), 7.07 – 6.99 (m, 1H), 6.73 (s, 1H), 6.36 (ddd, $J = 17.2, 10.0, 6.8$ Hz, 1H), 5.20 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.09 (dt, $J = 17.2, 1.6$ Hz, 1H), 4.97 (d, $J = 6.8$ Hz, 1H), 3.75 (s, 3H). **Chiral SFC:** 92% ee, AD-H column, 220 nm, 2% 2-propanol in CO_2 , 2 mL/min, retention time 4.7 min and 5.0 min (major).

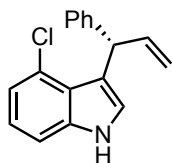


(S)-2-Methyl-3-(1-phenylallyl)-1H-indole (3ca): yellow oil, isolated *via* preparatory TLC using 8% ethyl acetate in hexanes, $R_f = 0.25$, 23.4 mg, 95% yield, 69% ee, $[\alpha]_D^{24} = +76.5$ ($c = 0.68$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.² $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (s, 1H), 7.38 – 7.24 (m, 6H), 7.22 – 7.15 (m, 1H), 7.08 (ddd, $J = 8.0, 7.2, 1.2$ Hz, 1H), 6.97 (ddd, $J = 8.0, 7.2, 1.2$ Hz, 1H), 6.46 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.21 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.07 (dt, $J = 17.2, 1.6$ Hz, 1H), 4.99 (d, $J = 7.2$ Hz, 1H), 2.34 (s, 3H). Impurities at approx. δ 1.50 (s), 1.30 (s), and 1.10 (s) could not be removed after several attempts at purification. **Chiral SFC:** 69% ee, OJ-H column, 220 nm, 9% 2-propanol in CO_2 , 2 mL/min, retention time 11.1 min (major) and 12.1 min.

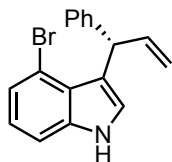


(S)-4-Fluoro-3-(1-phenylallyl)-1H-indole (3da): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.4$, 20.0mg, 80% yield, 90% ee, $[\alpha]_D^{25} = -17.4$ ($c = 0.33$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.32 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 7.15 – 7.02 (m, 2H), 6.85 (d, $J = 2.4$ Hz, 1H), 6.69 (ddd, $J = 11.2, 7.6,$

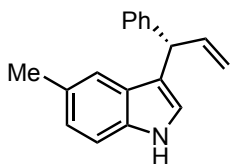
0.8 Hz, 1H), 6.37 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.21 – 5.15 (m, 2H), 5.00 (dt, $J = 17.2, 1.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.4, 140.8, 128.4, 128.2, 126.2, 122.7, 122.6, 122.4, 122.4, 115.3, 107.1, 107.1, 105.0, 104.8, 47.0. ^{19}F NMR (565 MHz, CDCl_3) δ -121.3. IR (ATR): 1503, 1345, 1223, 1031, 917, 776, 731, 699, 684, 608 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{14}\text{NF}$ $[\text{M}]^+$ 251.1110, found 251.1115. Chiral SFC: 90% ee, OJ-H column, 220 nm, 10% 2-propanol in CO_2 , 3 mL/min, retention time 10.3 min and 11.3 min (major).



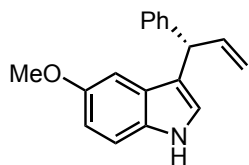
(S)-4-Chloro-3-(1-phenylallyl)-1H-indole (3ea): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 27.0 mg, 99% yield, 93% ee, $[\alpha]_D^{25} = -8.6$ ($c = 0.47$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 1H), 7.32 – 7.17 (m, 6H), 7.10 – 7.01 (m, 2H), 6.90 (dd, $J = 2.4, 0.8$ Hz, 1H), 6.36 (ddd, $J = 17.2, 10.0, 6.4$ Hz, 1H), 5.63 (d, $J = 6.4$ Hz, 1H), 5.20 (dt, $J = 10.0, 1.6$ Hz, 1H), 4.88 (dt, $J = 17.2, 1.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.6, 141.5, 137.9, 128.8, 128.1, 126.1, 124.3, 122.6, 118.7, 115.5, 109.8, 46.0. IR (ATR): 1337, 1190, 925, 776, 757, 738, 705, 625, 587, 578, 572 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{14}\text{NCl}$ $[\text{M}]^+$ 267.0815, found 267.0808. Chiral SFC: 93% ee, AD-H column, 220 nm, 10% 2-propanol in CO_2 , 2 mL/min, retention time 10.2 min (major) and 11.4 min.



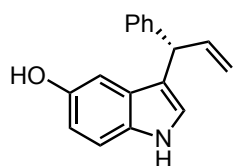
(S)-4-Bromo-3-(1-phenylallyl)-1H-indole (3fa): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 29.1 mg, 93% yield, 89% ee, $[\alpha]_D^{25} = -15.0$ ($c = 0.88$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 8.13 (s, 1H), 7.33 – 7.18 (m, 7H), 7.00 (t, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 2.4$ Hz, 1H), 6.37 (ddd, $J = 17.2, 10.0, 6.0$ Hz, 1H), 5.76 (d, $J = 6.0$ Hz, 1H), 5.21 (dt, $J = 10.0, 1.6$ Hz, 1H), 4.87 (dt, $J = 17.2, 1.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.6, 141.5, 137.8, 128.9, 128.1, 126.1, 124.9, 124.8, 124.4, 122.9, 119.0, 115.7, 114.4, 110.4, 45.5. IR (ATR): 1418, 1332, 1183, 1030, 995, 909, 811, 792, 735, 699, 674, 623, 574 cm^{-1} . HRMS calculated for $\text{C}_{17}\text{H}_{14}\text{NBr}$ $[\text{M}]^+$ 311.0310, found 311.0312. Chiral SFC: 89% ee, OJ-H column, 220 nm, 10% 2-propanol in CO_2 , 3 mL/min, retention time 16.1 min and 18.5 min (major).



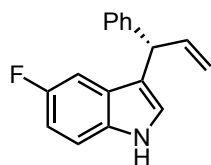
(S)-5-Methyl-3-(1-phenylallyl)-1H-indole (3ga)³: yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.4$, 21.9 mg, 87% yield, 89% ee, $[\alpha]_D^{25} = -17.1$ ($c = 1.05$, CHCl_3). The ^1H NMR spectrum is in accordance with literature.³ ^1H NMR (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.34 – 7.18 (m, 7H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.83 (s, 1H), 6.36 (ddd, $J = 17.2, 10.0, 7.0$ Hz, 1H), 5.19 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.07 (dt, $J = 17.2, 1.6$ Hz, 1H), 4.95 (d, $J = 7.0$ Hz, 1H), 2.39 (s, 3H). Chiral SFC: 89% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 5.0 min and 13.5 min (major).



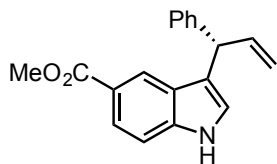
(S)-5-Methoxy-3-(1-phenylallyl)-1H-indole (3ha): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 21.3 mg, 81% yield, 90% ee, $[\alpha]_D^{25} = -18.0$ ($c = 0.42$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.¹ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.34 – 7.18 (m, 6H), 6.84 (d, $J = 7.6$ Hz, 3H), 6.35 (ddd, $J = 17.0, 10.0, 7.2$ Hz, 1H), 5.21 (dd, $J = 10.0, 0.8$ Hz, 1H), 5.09 (dd, $J = 17.0, 0.8$ Hz, 1H), 4.92 (d, $J = 7.2$ Hz, 1H), 3.75 (s, 3H). **Chiral SFC:** 90% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 5.8 min and 13.2 min (major).



(S)-3-(1-Phenylallyl)-1H-indol-5-ol (3ia): yellow oil, isolated *via* preparatory TLC using 20% ethyl acetate in hexanes, $R_f = 0.25$, 22.4 mg, 90% yield, 90% ee, $[\alpha]_D^{26} = -12.1$ ($c = 0.25$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 (s, 1H), 7.34 – 7.18 (m, 6H), 6.88 (d, $J = 2.4$ Hz, 1H), 6.80 – 6.72 (m, 2H), 6.34 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.2 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.07 (dt, $J = 17.2, 1.6$ Hz, 1H), 4.88 (d, $J = 7.2$ Hz, 1H), 4.52 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.1, 143.0, 140.3, 131.9, 128.4, 128.3, 127.5, 126.3, 123.6, 117.8, 115.5, 111.8, 111.7, 104.4, 47.0. **IR** (ATR): 1488, 1452, 1217, 1178, 917, 846, 796, 751, 728, 699, 673, 600 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{15}\text{NO}$ $[\text{M}]^+$ 249.1154, found 249.1149. **Chiral SFC:** 90% ee, OJ-H column, 220 nm, 20% 2-propanol in CO_2 , 3 mL/min, retention time 9.8 min (major) and 10.5 min.

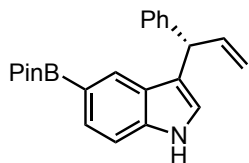


(S)-5-Fluoro-3-(1-phenylallyl)-1H-indole (3ja): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.4$, 17.9 mg, 71% yield, 85% ee, $[\alpha]_D^{25} = +1.1$ ($c = 0.71$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.³ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.33 – 7.19 (m, 6H), 7.03 (dd, $J = 10.0, 2.4$ Hz, 1H), 6.95 – 6.84 (m, 2H), 6.33 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.21 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.07 (dt, $J = 17.2, 1.6$ Hz, 1H), 4.89 (d, $J = 7.2$ Hz, 1H). **Chiral SFC:** 85% ee, OJ-H column, 220 nm, 20% 2-propanol in CO_2 , 3 mL/min, retention time 4.3 min and 7.4 min (major).

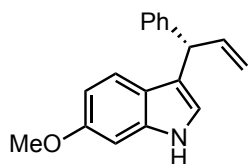


(S)-Methyl 3-(1-phenylallyl)-1H-indole-5-carboxylate (3ka): yellow oil, isolated *via* preparatory TLC using 20% ethyl acetate in hexanes, $R_f = 0.3$, 18.7 mg, 64% yield, 96% ee, $[\alpha]_D^{25} = -55.3$ ($c = 0.58$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (s, 1H), 8.2 (s, 1H), 7.88 (dd, $J = 8.8, 1.6$ Hz, 1H), 7.35 (dd, $J = 8.8, 0.4$ Hz, 1H), 7.33 – 7.20 (m, 5H), 6.91 (dd, $J = 2.4, 0.8$ Hz, 1H), 6.35 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.22 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.06 (dt, $J = 17.0, 1.6$ Hz, 1H), 5.01 (dd, $J = 7.2, 0.8$ Hz, 1H), 3.89 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.1, 142.7, 140.1, 139.2, 128.4, 128.4, 126.5, 126.5, 123.8, 123.5, 122.7, 121.5, 120.0, 115.8, 110.8, 51.8, 46.5. **IR** (ATR): 1687, 1611, 1434, 1260, 1243, 1216, 1111, 988, 917, 766,

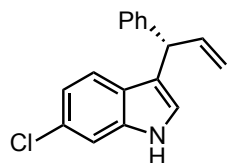
753, 748, 700 cm^{-1} . **HRMS** calculated for $\text{C}_{19}\text{H}_{17}\text{NO}_2$ $[\text{M}]^+$ 291.1259, found 291.1254. **Chiral SFC**: 86% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 5.4 min and 13.2 min (major).



(S)-3-(1-Phenylallyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (3la): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.4$, 24.6 mg, 69% yield, 94% ee, $[\alpha]_D^{23} = -35.7$ ($c = 0.28$, CHCl_3). **^1H NMR** (400 MHz, CDCl_3) δ 8.07 (s, 1H), 8.03 (d, $J = 0.8$ Hz, 1H), 7.65 (dd, $J = 8.2$, 0.8 Hz, 1H), 7.34 (dd, $J = 8.2$, 0.8 Hz, 1H), 7.30 (d, $J = 4.4$ Hz, 4H), 7.25 – 7.18 (m, 1H), 6.81 (dd, $J = 2.4$, 0.8 Hz, 1H), 6.35 (ddd, $J = 17.2$, 10.0, 7.2 Hz, 1H), 5.19 (dt, $J = 10.0$, 1.6 Hz, 1H), 5.06 (d, $J = 7.2$ Hz, 1H), 5.03 (dt, $J = 17.2$, 1.6 Hz, 1H), 1.35 (s, 12H). **^{13}C NMR** (101 MHz, CDCl_3) δ 143.2, 140.5, 138.5, 128.4, 128.4, 128.3, 127.1, 126.7, 126.2, 122.6, 119.1, 115.5, 110.5, 83.4, 46.1, 24.9. **IR** (ATR): 1371, 1351, 1142, 1097, 908, 856, 730, 690 cm^{-1} . **HRMS** calculated for calculated for $\text{C}_{23}\text{H}_{27}\text{BNO}_2$ $[\text{M}+\text{H}]^+$ 360.2139, found 360.2155. **Chiral SFC**: 94% ee, OJ-H column, 220 nm, 10% 2-propanol in CO_2 , 3 mL/min, retention time 12.6 min and 14.5 min (major).

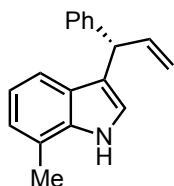


(S)-6-Methoxy-3-(1-phenylallyl)-1H-indole (3ma): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 14.0 mg, 53% yield, 91% ee, $[\alpha]_D^{24} = -2.5$ ($c = 0.24$, CHCl_3). **^1H NMR** (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.32 – 7.19 (m, 6H), 6.84 (d, $J = 2.4$ Hz, 1H), 6.77 (dd, $J = 2.4$, 1.2 Hz, 1H), 6.70 (dd, $J = 8.8$, 2.4 Hz, 1H), 6.34 (ddd, $J = 17.2$, 10.0, 7.2 Hz, 1H), 5.19 (dt, $J = 10.0$, 1.6 Hz, 1H), 5.07 (dt, $J = 17.2$, 1.6 Hz, 1H), 4.91 (dd, $J = 7.2$, 1.2 Hz, 1H), 3.82 (s, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 156.5, 143.2, 140.5, 137.4, 128.4, 128.3, 126.2, 121.2, 121.2, 120.4, 118.4, 115.4, 109.2, 94.6, 55.6, 47.0. **IR** (ATR): 1451, 1154, 1013, 925, 839, 888, 756, 749, 700, 629, 612 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{17}\text{NO}$ $[\text{M}]^+$ 263.1310, found 263.1302. **Chiral SFC**: 91% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 9.8 min (major) and 10.7 min.

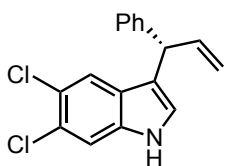


(S)-6-Chloro-3-(1-phenylallyl)-1H-indole (3na): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.5$, 19.1 mg, 72% yield, 92% ee, $[\alpha]_D^{25} = -1.4$ ($c = 0.28$, CHCl_3). **^1H NMR** (400 MHz, CDCl_3) δ 8.00 (s, 1H), 7.35 – 7.21 (m, 7H), 7.00 (dd, $J = 8.4$, 1.6 Hz, 1H), 6.89 (dd, $J = 2.4$, 0.8 Hz, 1H), 6.33 (ddd, $J = 17.2$, 10.0, 7.2 Hz, 1H), 5.2 (dt, $J = 10.0$, 1.6 Hz, 1H), 5.07 (dt, $J = 17.2$, 1.6 Hz, 1H), 4.93 (d, $J = 7.2$ Hz, 1H). **^{13}C NMR** (101 MHz, CDCl_3) δ 142.8, 140.1, 134.0, 128.4, 128.3, 128.0, 126.4, 125.4, 123.1, 120.7, 120.1, 118.7, 115.7, 111.0, 46.8. **IR** (ATR): 1450, 1095, 1060, 905, 844, 804, 753, 699, 591

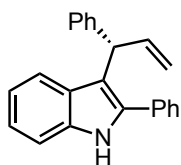
cm⁻¹. **HRMS** calculated for C₁₇H₁₄NCl [M]⁺ 267.0815, found 267.0813. **Chiral SFC**: 92% ee, OJ-H column, 220 nm, 15% 2-propanol in CO₂, 3 mL/min, retention time 6.6 min and 9.3 min (major).



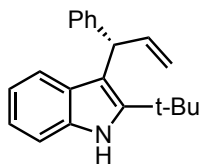
(S)-7-Methyl-3-(1-phenylallyl)-1H-indole (30a): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, R_f = 0.3, 23.6 mg, 96% yield, 91% ee, [α]_D²⁵ = -16.8 (c = 0.73, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.32 – 7.20 (m, 6H), 7.01 – 6.94 (m, 2H), 6.90 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.37 (ddd, *J* = 17.2, 10.0, 7.2, 1H), 5.21 (d, *J* = 10.0 Hz, 1H), 5.09 (dd, *J* = 17.2, 0.8 Hz, 1H), 4.97 (d, *J* = 7.2 Hz, 1H), 2.48 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.2, 140.5, 136.2, 128.4, 128.3, 126.3, 126.2, 122.6, 122.1, 120.2, 119.5, 119.0, 117.6, 115.4, 47.0, 16.6. **IR** (ATR): 1450, 1429, 1063, 994, 916, 779, 744, 699, 665, 611, 600 cm⁻¹. **HRMS** calculated for C₁₈H₁₇N [M]⁺ 247.1361, found 247.1355. **Chiral SFC**: 91% ee, OJ-H column, 220 nm, 15% 2-propanol in CO₂, 3 mL/min, retention time 9.0 min and 16.7 min (major).



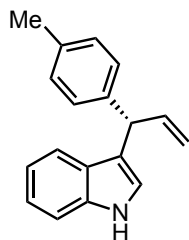
(S)-5,6-Dichloro-3-(1-phenylallyl)-1H-indole (3pa): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, R_f = 0.3, 16.2mg, 54% yield, 85% ee, [α]_D²⁵ = -21.1 (c = 0.34, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (s, 1H), 7.45 (s, 2H), 7.35 – 7.28 (m, 2H), 7.24-7.22 (m, 3H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.30 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.22 (d, *J* = 10.0 Hz, 1H), 5.05 (d, *J* = 17.2 Hz, 1H), 4.87 (d, *J* = 7.2 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.4, 139.8, 135.4, 128.5, 128.3, 126.6, 126.0, 124.4, 123.5, 120.8, 118.4, 116.0, 112.5, 46.6. **IR** (ATR): 1449, 1098, 919, 865, 845, 758, 743, 699, 657 cm⁻¹. **HRMS** calculated for C₁₇H₁₃NCl₂ [M]⁺ 301.0425, found 301.0419. **Chiral SFC**: 91% ee, OJ-H column, 220 nm, 15% 2-propanol in CO₂, 3 mL/min, retention time 5.6 min and 11.6 min (major).



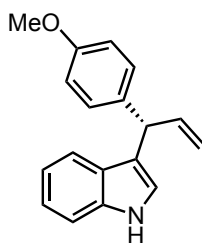
(S)-2-phenyl-3-(1-phenylallyl)-1H-indole (3qa): yellow oil, isolated *via* preparatory TLC using 5% ethyl acetate in hexanes, R_f = 0.25, 22.2 mg, 72% yield, 92% ee, [α]_D²² = -14.9 (c = 2.22, CHCl₃). **¹H NMR** (400 MHz, CDCl₃): δ 8.07 (bs, 1H), 7.55-7.52 (m, 2H), 7.49-7.44 (m, 2H), 7.44-7.38 (m, 3H), 7.38-7.34 (m, 2H), 7.32-7.25 (m, 2H), 7.23-7.17 (m, 2H), 7.02 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.59-6.51 (m, 1H), 5.26 (dt, *J* = 10.1, 1.5 Hz, 1H), 5.15 (d, *J* = 6.8 Hz, 1H), 5.10 (dt, *J* = 17.1, 1.6 Hz, 1H). The ¹H NMR is in accordance with the literature (Chen, S.-J.; Lu, G.-P.; Cai, C. *Synthesis* **2014**, *46*, 1717). **¹³C NMR** (126 MHz, CDCl₃) δ 143.3, 140.2, 136.4, 135.6, 133.1, 128.9, 128.7, 128.37, 128.31, 128.13, 128.01, 126.1, 122.2, 121.5, 119.7, 116.2, 113.9, 111.0, 46.0. **IR** (ATR): 3400, 1682, 1619, 1487, 1459, 1299, 1244, 1089, 1013, 911, 917, 740 cm⁻¹. **Chiral SFC**: 92% ee, AD-H column, 220 nm, 25% 2-propanol in CO₂, 2 mL/min, retention time 5.1 min (major) and 9.7 min (minor).



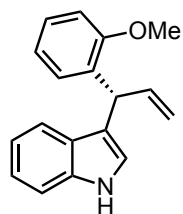
(S)-2-(tert-butyl)-3-(1-phenylallyl)-1H-indole (3ra): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.3$, 19.8 mg, 69% yield, 86% ee, $[\alpha]_D^{22} = -10.9$ ($c = 1.98$, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.99 (d, $J = 0.3$ Hz, 1H), 7.37-7.34 (m, 3H), 7.32-7.26 (m, 3H), 7.23-7.16 (m, 2H), 7.09 (ddd, $J = 8.1, 7.0, 1.1$ Hz, 1H), 6.91 (ddd, $J = 8.0, 7.1, 1.0$ Hz, 1H), 6.55 (ddd, $J = 17.1, 10.0, 7.6$ Hz, 1H), 5.36 (dd, $J = 7.7, 0.2$ Hz, 1H), 5.26 (ddd, $J = 10.1, 1.6, 1.1$ Hz, 1H), 5.16 (dt, $J = 17.1, 1.5$ Hz, 1H), 1.53 (s, 9H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 143.2, 142.7, 140.0, 134.4, 128.4, 128.20, 128.18, 126.0, 120.99, 120.93, 119.0, 116.0, 111.5, 110.6, 46.4, 32.8, 30.7. **IR** (ATR): 3445, 1470, 1458, 1302, 1244, 909, 740, 726, 697 cm^{-1} . **HRMS** calculated for $\text{C}_{21}\text{H}_{23}\text{N}$ $[\text{M}]^+$ 289.1830, found 289.1835. **Chiral SFC:** 86% ee, OD-H column, 220 nm, 3% 2-propanol in CO_2 , 2 mL/min, retention time 7.9 min (major) and 8.8 min (minor).



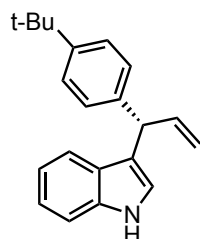
(S)-3-(1-(p-Tolyl)allyl)-1H-indole (3ab): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 18.7 mg, 76% yield, 89% ee, $[\alpha]_D^{26} = -3.1$ ($c = 0.77$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.³ **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.30 – 7.23 (m, 3H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.15 – 7.08 (m, 1H), 6.96 (d, $J = 1.6$ Hz, 1H), 6.43 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.27 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.16 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.02 (d, $J = 7.2$ Hz, 1H), 2.41 (s, 3H). **Chiral SFC:** 89% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 10.3 min and 14.8 min (major).



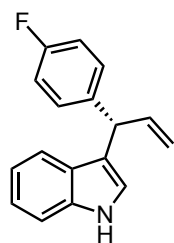
(S)-3-(1-(4-Methoxyphenyl)allyl)-1H-indole (3ac): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 18.4 mg, 70% yield, 82% ee, $[\alpha]_D^{26} = -4.2$ ($c = 0.29$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.¹ **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.42 – 7.31 (m, 2H), 7.22 – 7.14 (m, 3H), 7.06 – 7.00 (m, 1H), 6.88 (dd, $J = 2.4, 0.8$ Hz, 1H), 6.85 – 6.78 (m, 2H), 6.33 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.17 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.05 (dt, $J = 17.2, 1.6$ Hz, 1H), 4.91 (d, $J = 7.2$ Hz, 1H), 3.79 (s, 3H). **Chiral SFC:** 82% ee, OJ-H column, 220 nm, 20% 2-propanol in CO_2 , 3 mL/min, retention time 7.0 min and 9.6 min (major).



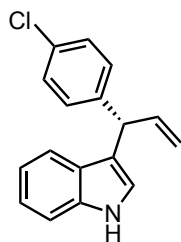
(S)-3-(1-(2-Methoxyphenyl)allyl)-1H-indole (3ad): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 76% yield, 93% ee, $[\alpha]_D^{26} = +4.1$ ($c = 0.30$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.23 – 7.14 (m, 3H), 7.06 – 7.00 (m, 1H), 6.95 – 6.84 (m, 3H), 6.33 (ddd, $J = 17.2, 10.2, 7.2$ Hz, 1H), 5.46 (d, $J = 7.2$ Hz, 1H), 5.17 (dt, $J = 10.2, 1.6$ Hz, 1H), 5.01 (dt, $J = 17.2, 1.6$ Hz, 1H), 3.85 (s, 3H). **Chiral SFC:** 93% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 9.2 min and 13.4 min (major).



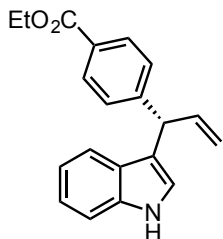
(S)-3-(1-(4-(*tert*-Butyl)phenyl)allyl)-1H-indole (3ae): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.15$, 25.5 mg, 88% yield, 89% ee, $[\alpha]_D^{25} = -3.6$ ($c = 0.45$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.33 (dd, $J = 14.8, 8.0$ Hz, 3H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.04 (t, $J = 7.6$ Hz, 1H), 6.88 (s, 1H), 6.35 (ddd, $J = 17.2, 10.0, 6.8$ Hz, 1H), 5.17 (d, $J = 10.0$ Hz, 1H), 5.08 (d, $J = 17.2$ Hz, 1H), 4.94 (d, $J = 6.8$ Hz, 1H), 1.30 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.0, 140.620, 140.1, 136.6, 127.9, 126.9, 125.2, 122.4, 122.0, 119.9, 119.2, 118.7, 115.2, 111.0, 46.5, 34.4, 31.4. **IR** (ATR): 2961, 1456, 1094, 1010, 915, 816, 794, 764, 739 cm^{-1} . **HRMS** calculated for $\text{C}_{21}\text{H}_{23}\text{N}$ $[\text{M}]^+$ 289.1830, found 289.1828. **Chiral SFC:** 89% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 3.3 min and 9.9 min (major).



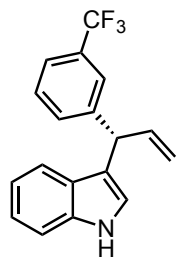
(S)-3-(1-(4-Fluorophenyl)allyl)-1H-indole (3af): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.4$, 23.3 mg, 93% yield, 90% ee, $[\alpha]_D^{26} = +7.5$ ($c = 0.72$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.00 (s, 1H), 7.40 – 7.34 (m, 2H), 7.24 (dd, $J = 6.0, 2.8$ Hz, 2H), 7.19 (t, $J = 7.6$ Hz, 1H), 7.07 – 6.95 (m, 3H), 6.91 – 6.87 (m, 1H), 6.33 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.21 (d, $J = 10.0$ Hz, 1H), 5.06 (d, $J = 17.2$ Hz, 1H), 4.96 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.7, 160.3, 140.3, 138.8, 138.8, 136.7, 129.8, 129.7, 126.6, 122.4, 122.2, 119.7, 119.4, 118.3, 115.6, 115.2, 114.9, 111.1, 46.1. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -117.1. **IR** (ATR): 1504, 1216, 1092, 925, 822, 808, 740, 652, 601, 570 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{14}\text{NF}$ $[\text{M}]^+$ 251.1110, found 251.1105. **Chiral SFC:** 90% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 4.4 min and 6.1 min (major).



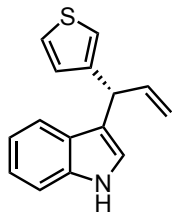
(S)-3-(1-(4-Chlorophenyl)allyl)-1H-indole (3ag): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 22.0 mg, 82% yield, 88% ee, $[\alpha]_D^{26} = -4.1$ ($c = 0.25$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.01 (s, 1H), 7.36 (d, $J = 8.8$ Hz, 2H), 7.26 (dt, $J = 4.4, 2.0$ Hz, 2H), 7.23 – 7.15 (m, 3H), 7.04 (t, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 2.4$ Hz, 1H), 6.32 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.21 (dt, $J = 10.0, 1.2$ Hz, 1H), 5.06 (dt, $J = 17.2, 1.2$ Hz, 1H), 4.94 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.6, 140.0, 136.6, 132.0, 129.8, 128.4, 126.6, 122.4, 122.2, 119.7, 119.4, 118.0, 115.8, 111.1, 46.3. **IR** (ATR): 1487, 1454, 1087, 1014, 998, 919, 846, 811, 795, 764, 753, 740, 726, 577 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{14}\text{NCl}$ $[\text{M}]^+$ 267.0815, found 267.0817. **Chiral SFC:** 88% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 5.6 min and 8.0 min (major).



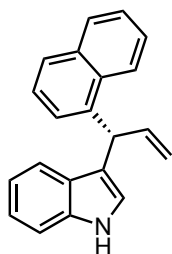
(S)-Ethyl 4-(1-(1H-indol-3-yl)allyl)benzoate (3ah): yellow oil, isolated *via* preparatory TLC using 20% ethyl acetate in hexanes, $R_f = 0.3$, 28.1 mg, 92% yield, 93% ee, $[\alpha]_D^{25} = -1.3$ ($c = 0.48$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.10 (s, 1H), 7.98 (d, $J = 8.4$ Hz, 2H), 7.35 (t, $J = 7.2$ Hz, 4H), 7.21 – 7.13 (m, 1H), 7.02 (ddd, $J = 8.4, 7.2, 0.8$ Hz, 1H), 6.90 (d, $J = 1.6$ Hz, 1H), 6.34 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.23 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.07 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.02 (d, $J = 7.2$ Hz, 1H), 4.36 (q, $J = 7.2$ Hz, 2H), 1.38 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.7, 148.5, 139.6, 136.6, 129.7, 128.6, 128.4, 126.6, 122.5, 122.2, 119.6, 119.4, 117.7, 116.1, 111.1, 60.8, 46.9, 14.3. **IR** (ATR): 1698, 1607, 1366, 1273, 1220, 1176, 1101, 1019, 918, 762, 739, 708, 643 cm^{-1} . **HRMS** calculated for $\text{C}_{20}\text{H}_{19}\text{NO}_2$ $[\text{M}]^+$ 305.1416, found 305.1427. **Chiral SFC:** 81% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 4.0 min and 4.8 min (major).



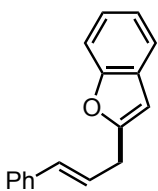
(S)-3-(1-(3-(Trifluoromethyl)phenyl)allyl)-1H-indole (3ai): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.4$, 29.1 mg, 97% yield, 92% ee, $[\alpha]_D^{26} = +4.1$ ($c = 0.58$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.³ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.58 (s, 1H), 7.52 – 7.43 (m, 2H), 7.42 – 7.35 (m, 3H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.05 (t, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 2.4$ Hz, 1H), 6.34 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.25 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.08 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.03 (d, $J = 7.2$ Hz, 1H). **Chiral SFC:** 92% ee, OJ-H column, 220 nm, 12% 2-propanol in CO_2 , 3 mL/min, retention time 2.1 min and 3.1 min (major).



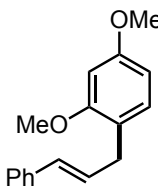
(S)-3-(1-(Thiophen-3-yl)allyl)-1H-indole (3aj): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.25$, 19.4 mg, 81% yield, 88% ee, $[\alpha]_D^{26} = -7.1$ ($c = 0.17$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (s, 1H), 7.47 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.27 – 7.24 (m, 1H), 7.19 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H), 7.06 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H), 7.03 – 6.97 (m, 2H), 6.91 (d, $J = 2.0$ Hz, 1H), 6.34 (ddd, $J = 17.2, 10.0, 7.2$ Hz, 1H), 5.19 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.12 (dt, $J = 17.2, 1.6$ Hz, 1H), 5.03 (d, $J = 7.2$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.1, 140.0, 136.6, 128.2, 126.7, 125.2, 122.1, 122.1, 121.2, 119.7, 119.4, 118.2, 115.2, 111.1, 42.4. **IR** (ATR): 1455, 917, 836, 766, 739, 664, 596, 586 cm^{-1} . **HRMS** calculated for $\text{C}_{15}\text{H}_{13}\text{NS}$ $[\text{M}]^+$ 239.0769, found 239.0765. **Chiral SFC:** 88% ee, OJ-H column, 220 nm, 15% 2-propanol in CO_2 , 3 mL/min, retention time 9.4 min and 10.2 min (major).



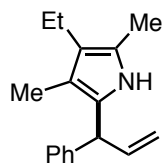
(-)-3-(1-(Naphthalen-1-yl)allyl)-1H-indole (3ak): yellow oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.2$, 27.2 mg, 96% yield, 94% ee, $[\alpha]_D^{25} = -36.0$ ($c = 0.54$, CHCl_3). The $^1\text{H NMR}$ spectrum is in accordance with literature.³ $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.14 (d, $J = 7.6$ Hz, 1H), 7.95 (s, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.78 (dd, $J = 6.4, 3.2$ Hz, 1H), 7.52 – 7.38 (m, 5H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.21 (t, $J = 8.0$ Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 1H), 6.75 (d, $J = 2.4$ Hz, 1H), 6.47 (ddd, $J = 17.2, 10.0, 6.4$ Hz, 1H), 5.78 (d, $J = 6.4$ Hz, 1H), 5.29 (dt, $J = 10.0, 1.6$ Hz, 1H), 5.05 (dt, $J = 17.2, 1.6$ Hz, 1H). Impurities at approx. δ 4.10 (q), 2.05 (s), and 1.30 (t) appears to be ethyl acetate but could not be removed after several attempts at purification and prolonged periods on hi-vac. **Chiral SFC:** 94% ee, OJ-H column, 220 nm, 20% 2-propanol in CO_2 , 3 mL/min, retention time 9.3 min and 17.9 min (major).



1-phenyl-3-(benzofuran-2-yl)-1-propene: yellow oil, isolated *via* preparatory TLC using 2% ethyl acetate in hexanes, $R_f = 0.2$, 6.8 mg, 29% yield. The $^1\text{H NMR}$ spectrum is in accordance with literature.⁴ $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.51 – 7.48 (m, 1H), 7.45 – 7.38 (m, 3H), 7.34 – 7.30 (m, 2H), 7.25 – 7.17 (m, 3H), 6.58 (d, $J = 15.8$ Hz, 1H), 6.48 (q, $J = 0.9$ Hz, 1H), 6.39 (dt, $J = 15.8, 6.8$ Hz, 1H), 3.71 (dt, $J = 6.8, 1.1$ Hz, 2H).



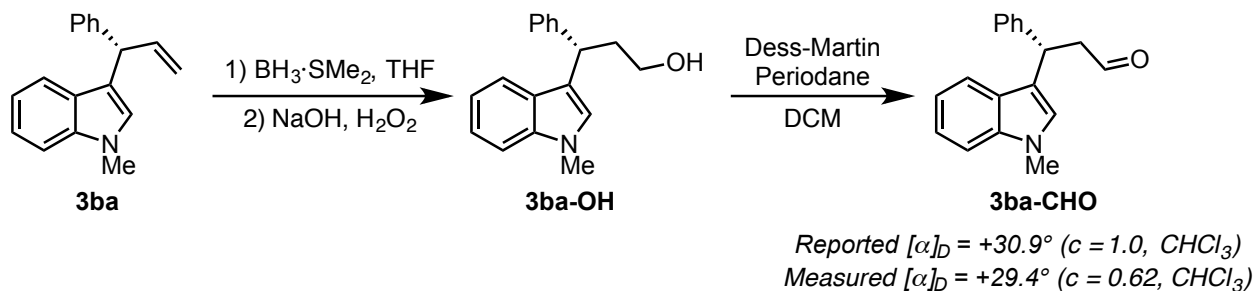
1-phenyl-3-(2,4-dimethoxyphenyl)-1-propene: colorless oil, isolated *via* preparatory TLC using 5% ethyl acetate in hexanes, $R_f = 0.35$, 8.9 mg, 35% yield. The $^1\text{H NMR}$ spectrum is in accordance with literature.⁵ $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.41 – 7.39 (m, 2H), 7.34 (dd, $J = 7.1, 1.6$ Hz, 2H), 7.25 – 7.21 (m, 1H), 7.13 (d, $J = 8.2$ Hz, 1H), 6.53-6.48 (m, 2H), 6.44 – 6.38 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.52 (d, $J = 5.6$ Hz, 2H).



3-ethyl-2,4-dimethyl-5-(1-phenylallyl)-1H-pyrrole: green oil, isolated *via* preparatory TLC using 10% ethyl acetate in hexanes, $R_f = 0.55$, 5.7 mg, 24% yield, $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.34 – 7.30 (m, 2H), 7.25 – 7.20 (m, 3H), 7.14 – 7.12 (bs, 1H), 6.21 (ddd, $J = 17.0, 10.2, 6.7$ Hz, 1H), 5.22 (dt, $J = 10.1, 1.5$ Hz, 1H), 4.98 (dt, $J = 17.1, 1.6$ Hz, 1H), 4.79 (d, $J = 6.6$ Hz, 1H), 2.38 (q, $J = 7.5$ Hz, 2H), 2.12 (d, $J = 5.1$ Hz, 3H), 1.08 (t, $J = 7.5$ Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3): δ 142.3, 139.3, 128.63, 128.49, 126.6, 124.7, 121.19, 121.11, 116.4, 114.0, 46.7, 17.9, 15.9, 11.2, 9.3. **IR** (ATR): 3462, 2958, 2922, 2856, 1634, 1600, 1491, 1382, 1310, 1220, 1062, 1029, 996, 919, 839, 745, 699, 667, 636 cm^{-1} . **HRMS** calculated for $\text{C}_{17}\text{H}_{22}\text{N}$ $[\text{M}+\text{H}]^+$ 240.1752, found 239.1702.

Determination of Absolute Configuration

Absolute configuration was determined by analogy to a compound with known absolute configuration and reported optical rotation.⁶ Indole **3ba** obtained from the described Rh-catalyzed alkyne hydroarylation was derivatized to literature reported aldehyde **3ba-CHO**. The measured optical rotation of **3ba-CHO** ($[\alpha]_D^{22} = +29.4^\circ$, $c = 0.62$, CHCl_3) was compared to the literature reported value ($[\alpha]_D = +30.9^\circ$, $c = 1.0$, CHCl_3) to assign the absolute configuration as (*S*).

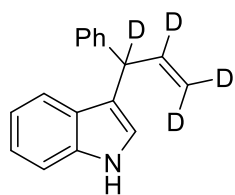
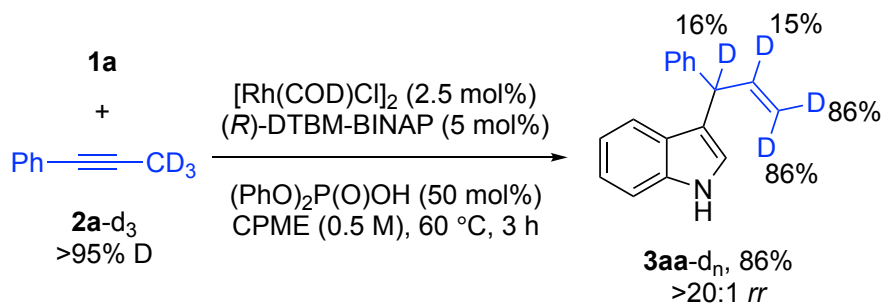


To a flame-dried round bottom was added **3ba** (100 mg, 0.4 mmol, 1 equiv.). After addition of 2 mL of THF, the reaction mixture was cooled to 0 °C. A 2 M $\text{BH}_3 \cdot \text{SMe}_2$ solution in THF (1 mL, 2.0 mmol, 5 equiv.) was slowly added at 0 °C. After addition, the reaction mixture was warmed to room temperature and allowed to stir for 1 hour. Next, the reaction mixture was cooled to 0 °C and aqueous NaOH (80 mg, 5 equiv.) was slowly added, followed by H_2O_2 (1 mL). The reaction was heated to 60 °C for 2 hours. After cooling to room temperature, the reaction mixture was extracted with Et_2O . The combined organic layers were dried using anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified *via* column chromatography to afford alcohol **3ba-OH** (45.4 mg, 43% yield). The ^1H NMR is in accordance with the literature.⁷ ^1H NMR (400 MHz; CD_2Cl_2): δ 7.44 (ddd, $J = 8.0, 1.1, 0.8$ Hz, 1H), 7.36-7.33 (m, 2H), 7.31-7.26 (m, 3H), 7.20-7.15 (m, 2H), 7.01-6.97 (m, 2H), 4.38 (t, $J = 7.7$ Hz, 1H), 3.62 (tt, $J = 6.7, 3.4$ Hz, 2H), 2.48-2.40 (m, 1H), 2.30-2.23 (m, 1H).

To a flame-dried round bottom was added **3ba-OH** (45 mg, 0.17 mmol, 1 equiv.). After addition of 2 mL of DCM, the reaction mixture was cooled to 0 °C. Dess-Martin Periodane (87 mg, 0.20 mmol, 1.2 equiv.) was added at 0 °C. The reaction was warmed to room temperature and allowed to stir for 15 minutes. The reaction was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and NaHCO_3 and extracted with DCM. The organic layers were dried with anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified *via* column chromatography to afford aldehyde **3ba-CHO** (12.3 mg, 28% yield). The ^1H NMR is in accordance with the literature.⁶ ^1H NMR (400 MHz; CD_2Cl_2): δ 9.74 (t, $J = 2.1$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 1H), 7.33-7.26 (m, 5H), 7.20-7.14 (m, 2H), 7.00-6.96 (m, 1H), 6.92 (s, 1H), 4.84 (t, $J = 7.8$ Hz, 1H), 3.74 (s, 3H), 3.20 (ddd, $J = 16.6, 8.2, 2.5$ Hz, 1H), 3.08 (ddd, $J = 16.6, 7.3, 1.8$ Hz, 1H).

Use of Deuterium Labeled Alkyne

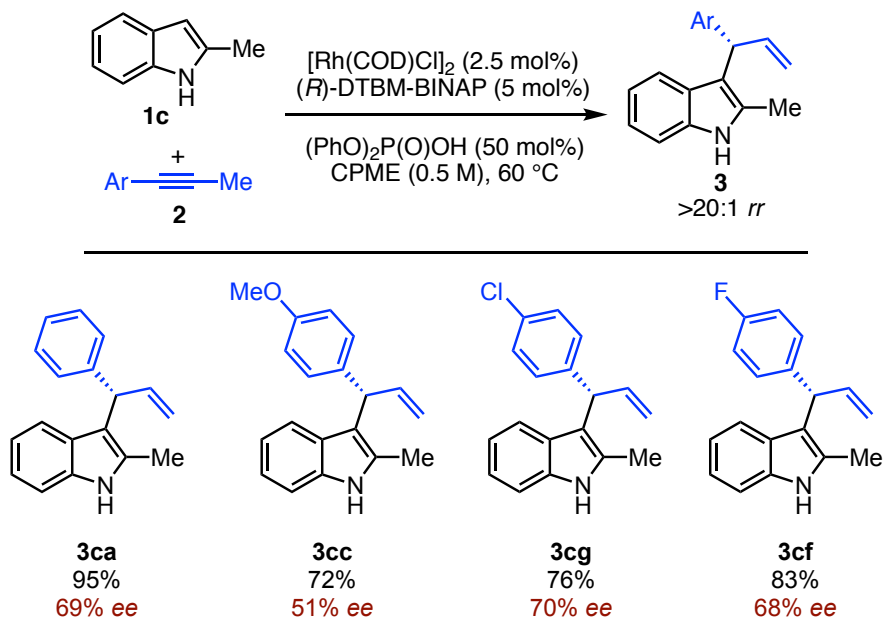
Similar to our previous studies,⁸⁻¹⁰ use of a deuterated alkyne (**2a-d₃**) resulted in deuterium incorporation throughout the allyl fragment. This deuterium-scrambling suggests that β -hydride elimination to generate the corresponding allene is reversible.



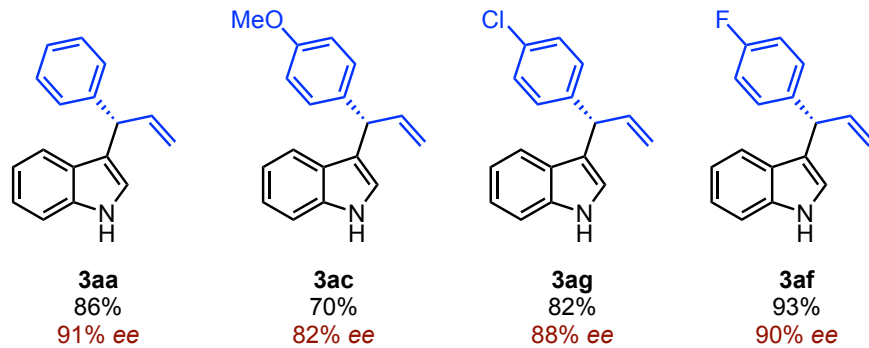
3-(1-Phenylallyl-1,2,3,3-D₄)-1H-indole (3aa-d_n): yellow oil, 20.0 mg, 86% yield.

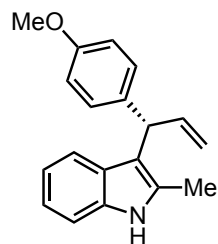
¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.27 (m, 4H), 7.25 – 7.15 (m, 2H), 7.04 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.36-6.34 (m, 0.85H), 5.19 (dd, *J* = 10.2, 1.6 Hz, 0.14H), 5.07 (dd, *J* = 17.2, 1.6 Hz, 0.14H), 4.99 – 4.96 (m, 0.84H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.2, 140.2, 136.6, 128.4, 128.3, 126.8, 126.3, 122.4, 122.0, 119.8, 119.3, 118.5, 111.0, 46.8. **IR** (ATR): 1455, 1416, 1335, 1218, 1093, 1009, 938, 738, 698, 602, 579 cm⁻¹.

Coupling of 2-Methyl Indole and Various Aryl-Alkynes: Observed Lower Enantioselectivity

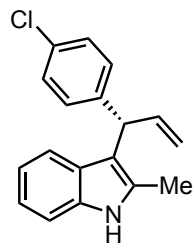


In contrast, higher enantioselectivities are observed when using the same alkynes when indole is used:

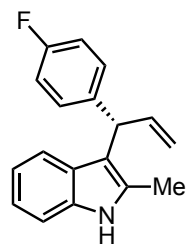




(S)-3-(1-(4-methoxyphenyl)allyl)-2-methyl-1H-indole (3cc): yellow oil, isolated *via* preparatory TLC using 5% ethyl acetate in hexanes, $R_f = 0.05$, 20.0 mg, 72% yield, 51% ee, $[\alpha]_D^{22} = +3.6$ ($c = 0.67$, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.77 (s, 1H), 7.36-7.34 (m, 1H), 7.28-7.21 (m, 3H), 7.09 (ddd, $J = 8.1, 7.1, 1.1$ Hz, 1H), 6.98 (ddd, $J = 8.0, 7.0, 1.0$ Hz, 1H), 6.83-6.81 (m, 2H), 6.44 (ddd, $J = 17.1, 10.1, 7.0$ Hz, 1H), 5.19 (dt, $J = 10.1, 1.6$ Hz, 1H), 5.07 (dt, $J = 17.0, 1.6$ Hz, 1H), 4.94 (d, $J = 7.0$ Hz, 1H), 3.78 (s, 3H), 2.34 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 158.0, 140.4, 135.47, 135.39, 131.5, 129.3, 128.1, 121.0, 119.6, 119.2, 115.4, 113.7, 113.1, 110.3, 55.4, 45.2, 12.5. **IR** (ATR): 3400, 1682, 1608, 1507, 1459, 1299, 1241, 1175, 1031, 910, 825, 740, 644 cm^{-1} . **HRMS** $\text{C}_{19}\text{H}_{19}\text{NO}$ $[\text{M}]^+$ 277.1466, found 277.1463. **Chiral SFC:** 51% ee, OJ-H column, 220 nm, 10% 2-propanol in CO_2 , 3 mL/min, retention time 7.7 min and 9.11 min (major).



(S)-3-(1-(4-chlorophenyl)allyl)-2-methyl-1H-indole (3cg): yellow oil, isolated *via* preparatory TLC using 5% ethyl acetate in hexanes, $R_f = 0.1$, 21.4 mg, 76% yield, 70% ee, $[\alpha]_D^{22} = +46.4$ ($c = 2.14$, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.87 (s, 1H), 7.37-7.32 (m, 2H), 7.28 (m, 4H), 7.15 (ddd, $J = 8.1, 7.1, 1.1$ Hz, 1H), 7.04 (ddd, $J = 8.0, 7.0, 1.0$ Hz, 1H), 6.46 (ddd, $J = 17.1, 10.1, 7.0$ Hz, 1H), 5.27 (dt, $J = 10.1, 1.5$ Hz, 1H), 5.12 (dt, $J = 17.1, 1.6$ Hz, 1H), 4.99 (dt, $J = 7.0, 1.3$ Hz, 1H), 2.40 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 141.8, 139.6, 135.5, 131.9, 130.2, 129.7, 128.8, 128.4, 127.9, 121.2, 119.4, 116.0, 112.4, 110.4, 45.4, 12.5. **IR** (ATR): 3400, 1682, 1618, 1487, 1459, 1299, 1244, 1089, 1013, 911, 817, 740 cm^{-1} . **HRMS** $\text{C}_{18}\text{H}_{16}\text{NCl}$ $[\text{M}]^+$ 281.0971, found 281.0977. **Chiral SFC:** 70% ee, AD-H column, 220 nm, 12% 2-propanol in CO_2 , 2 mL/min, retention time 7.2 min (major) and 8.7 min.

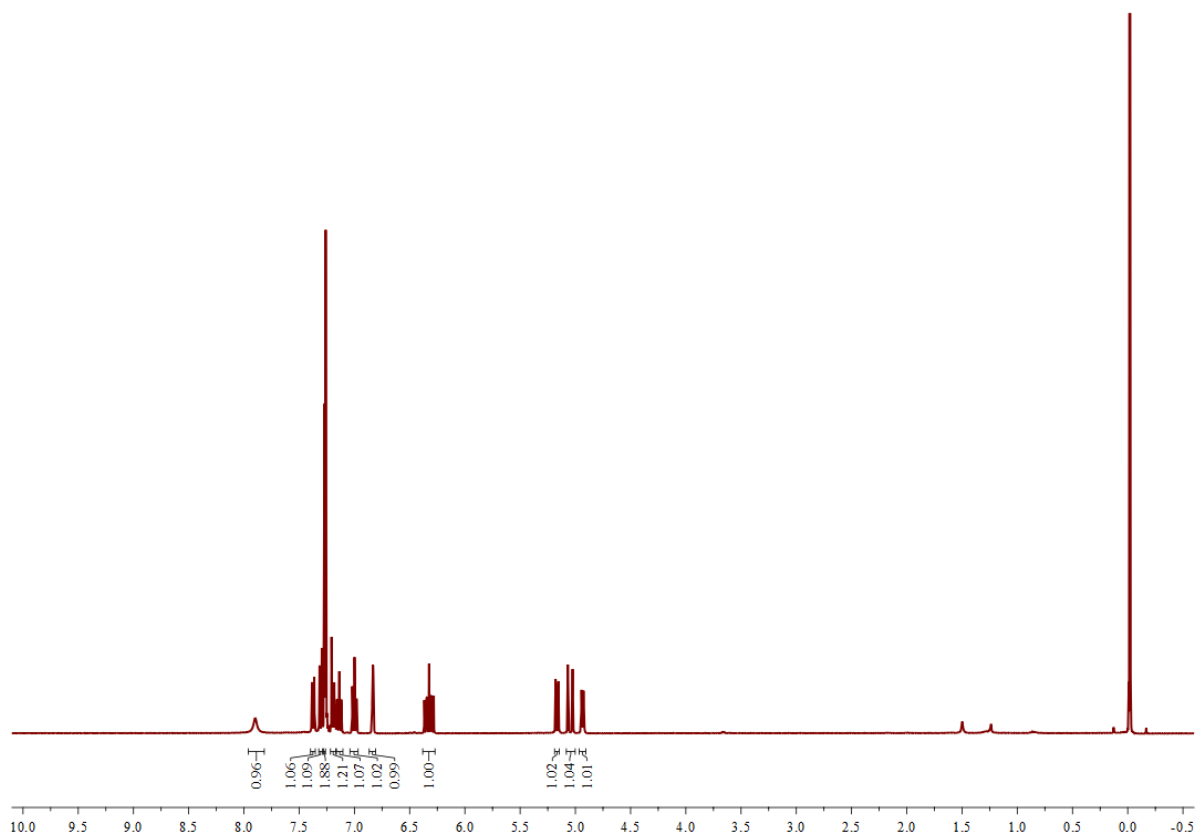
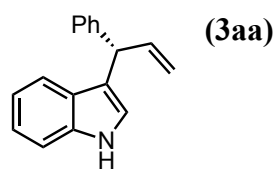


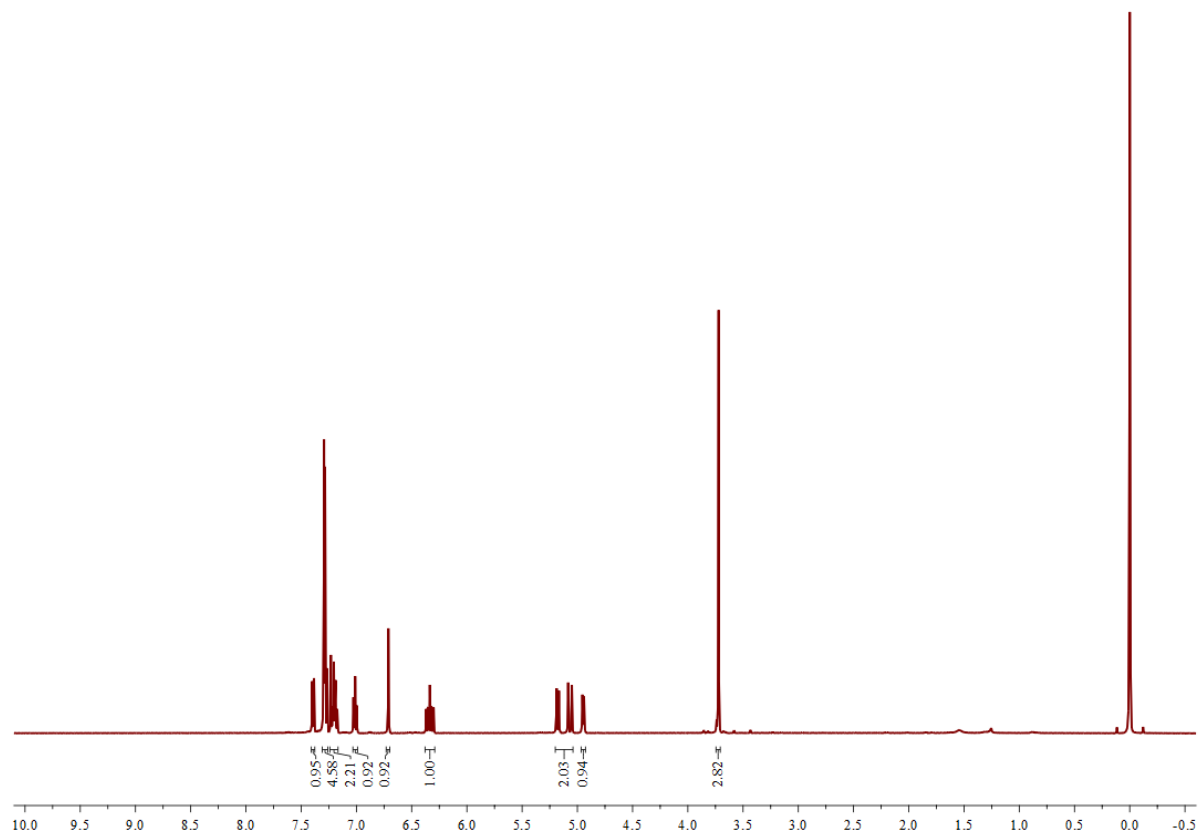
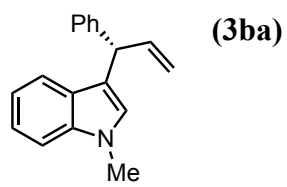
(S)-3-(1-(4-fluorophenyl)allyl)-2-methyl-1H-indole (3cf): yellow oil, isolated *via* preparatory TLC using 5% ethyl acetate in hexanes, $R_f = 0.1$, 22.1 mg, 83% yield, 68% ee, $[\alpha]_D^{22} = +45.5$ ($c = 2.21$, CHCl_3). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.79 (bs, 1H), 7.33-7.31 (m, 1H), 7.29-7.25 (m, 3H), 7.11 (ddd, $J = 8.1, 7.1, 1.1$ Hz, 1H), 7.02-6.94 (m, 3H), 6.44 (ddd, $J = 17.1, 10.1, 7.0$ Hz, 1H), 5.22 (dt, $J = 10.1, 1.5$ Hz, 1H), 5.08 (dt, $J = 17.0, 1.6$ Hz, 1H), 4.97-4.95 (m, 1H), 2.35 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 162.4, 160.5, 139.9, 138.89, 138.87, 135.5, 131.6, 129.77, 129.71, 127.9, 121.1, 119.41, 119.33, 115.8, 115.06, 114.89, 112.6, 110.4, 45.3, 12.4. **$^{19}\text{F NMR}$** (376 MHz, CDCl_3) δ -118.0. **IR** (ATR): 3400, 1682, 119, 1487, 1459, 1299, 1244, 1089, 1013, 911, 818, 740, 637 cm^{-1} . **HRMS** calculated for $\text{C}_{18}\text{H}_{16}\text{NF}$ $[\text{M}]^+$ 265.1267, found 265.1279. **Chiral SFC:** 68% ee, AD-H column, 220 nm, 10% 2-propanol in CO_2 , 2 mL/min, retention time 5.6 min (major) and 6.8 min.

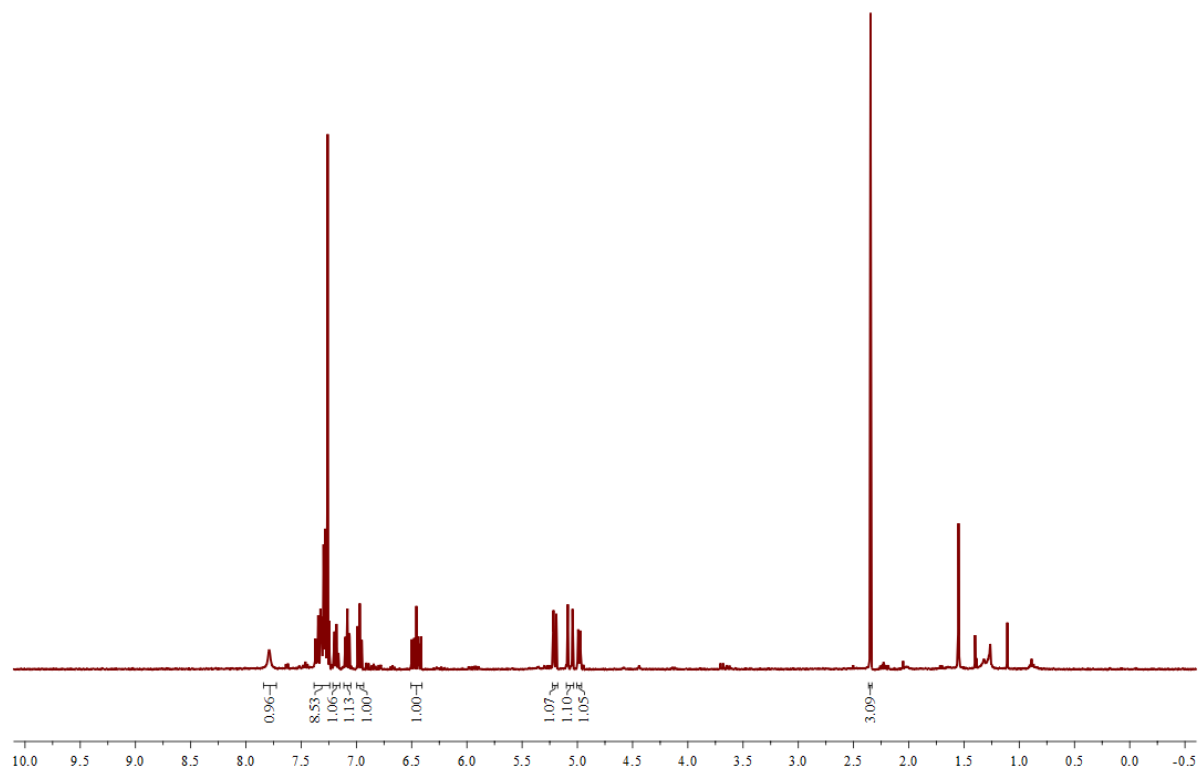
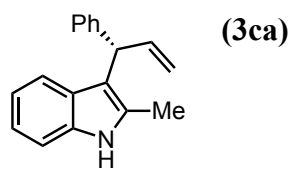
4. References

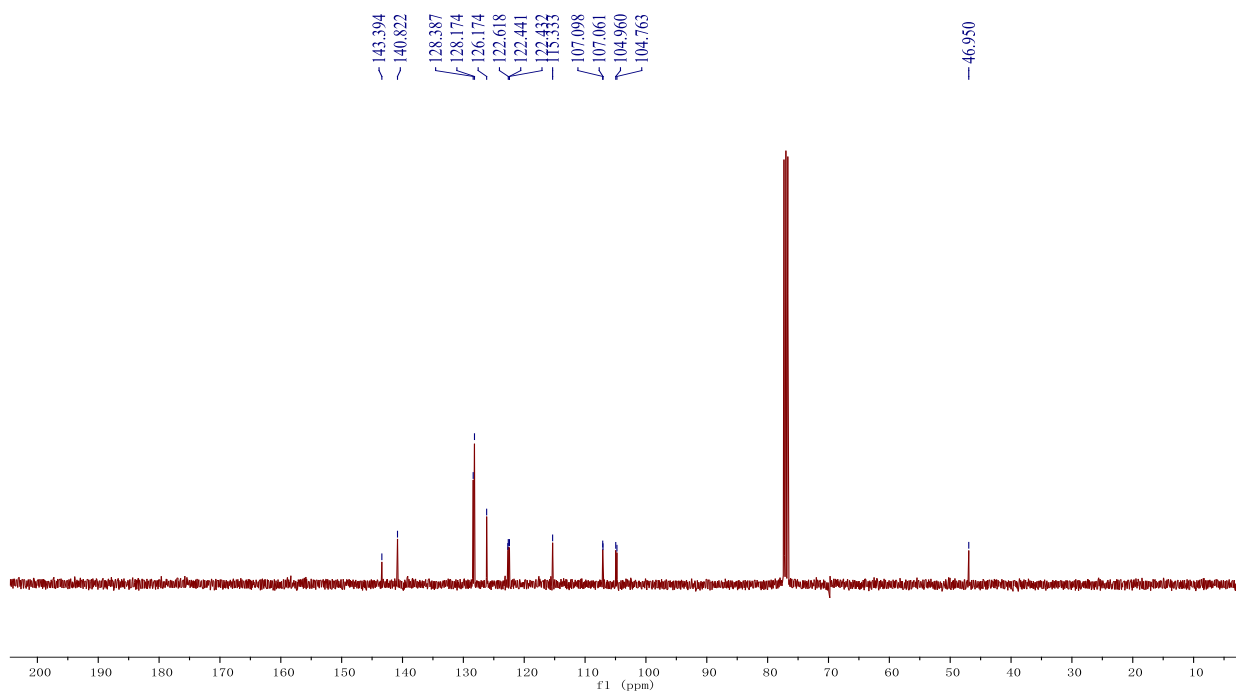
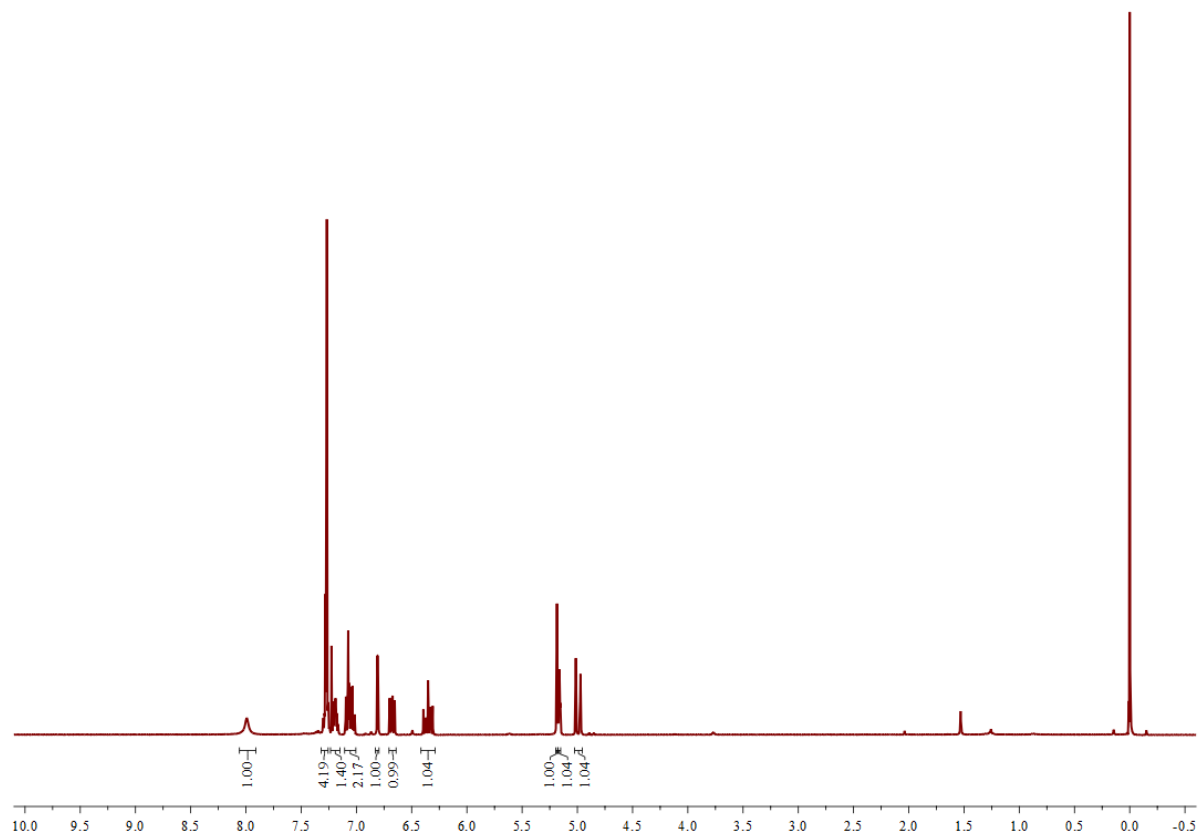
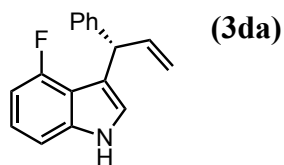
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- (10) F. A. Cruz, Z. Chen, S. I. Kurtoic, V. M. Dong, *Chem. Commun.* **2016**, *52*, 5836

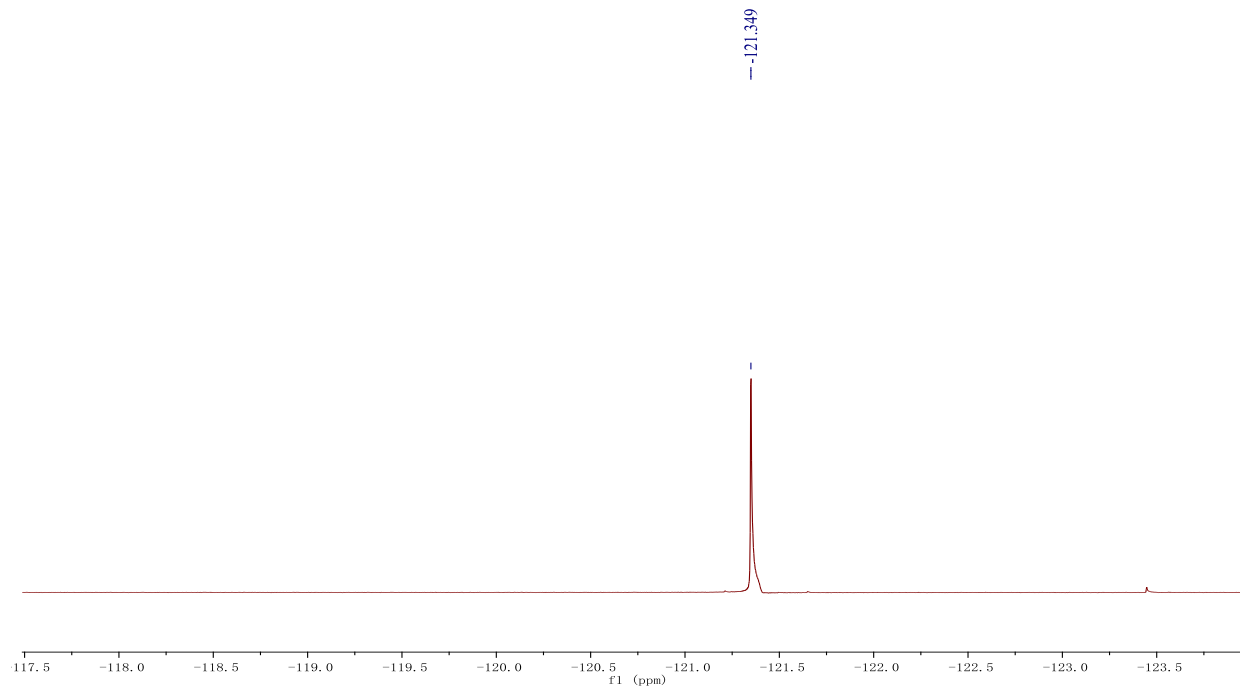
5. NMR Spectra

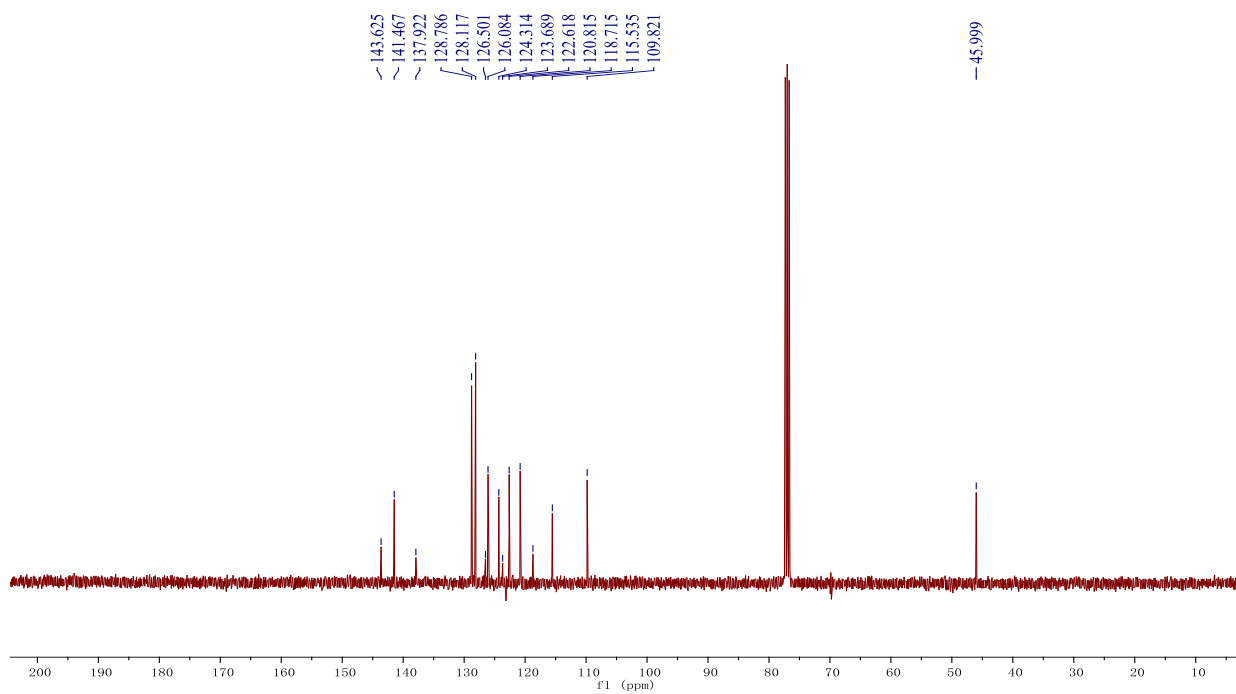
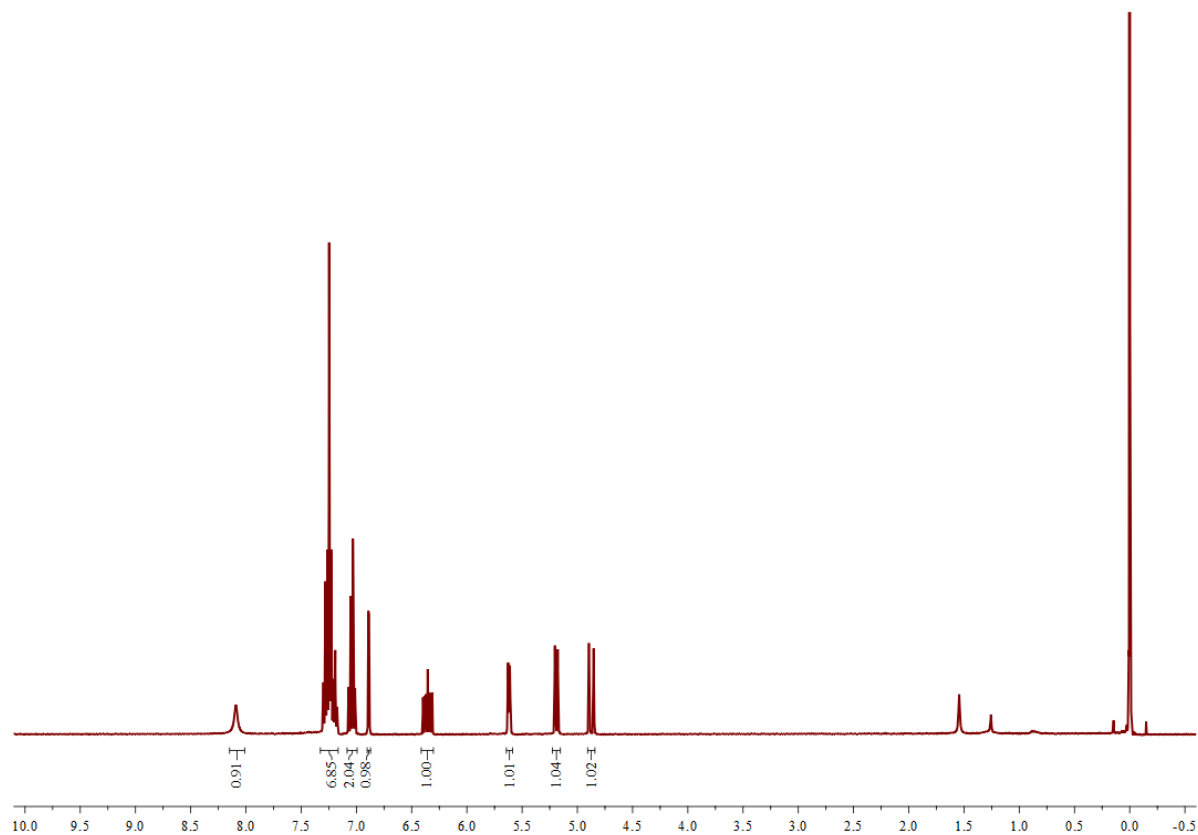
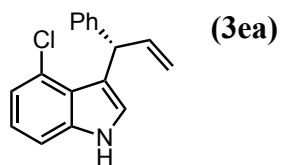


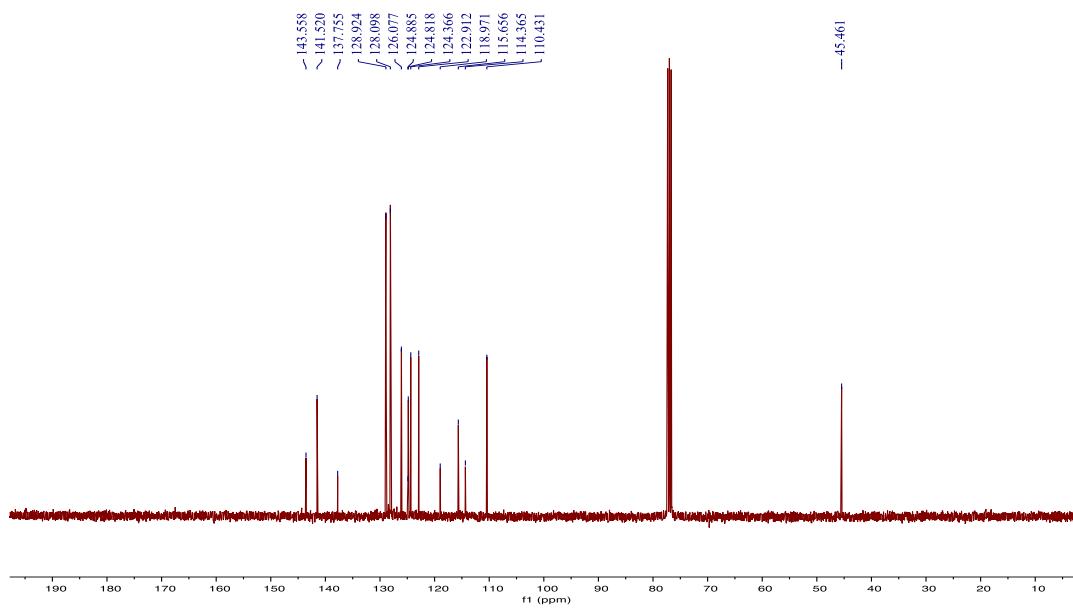
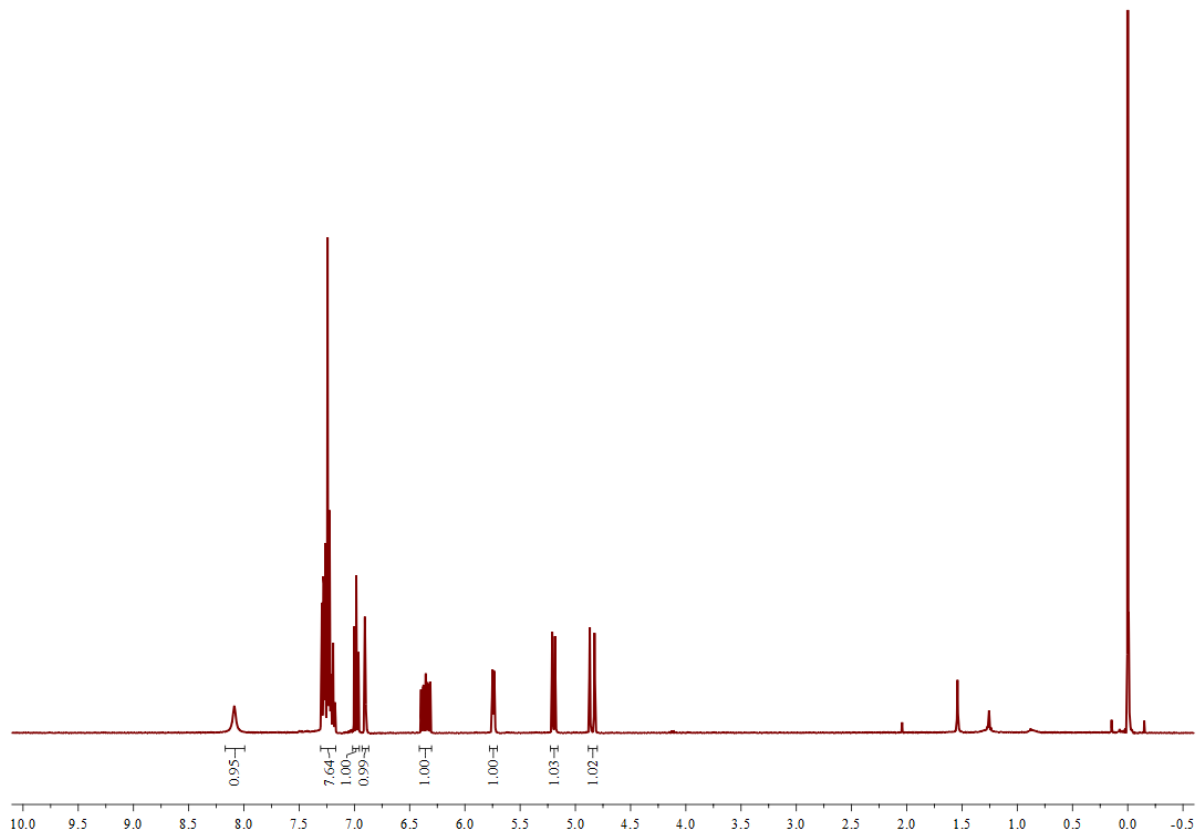
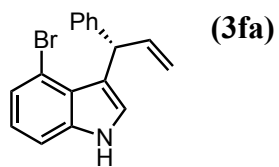


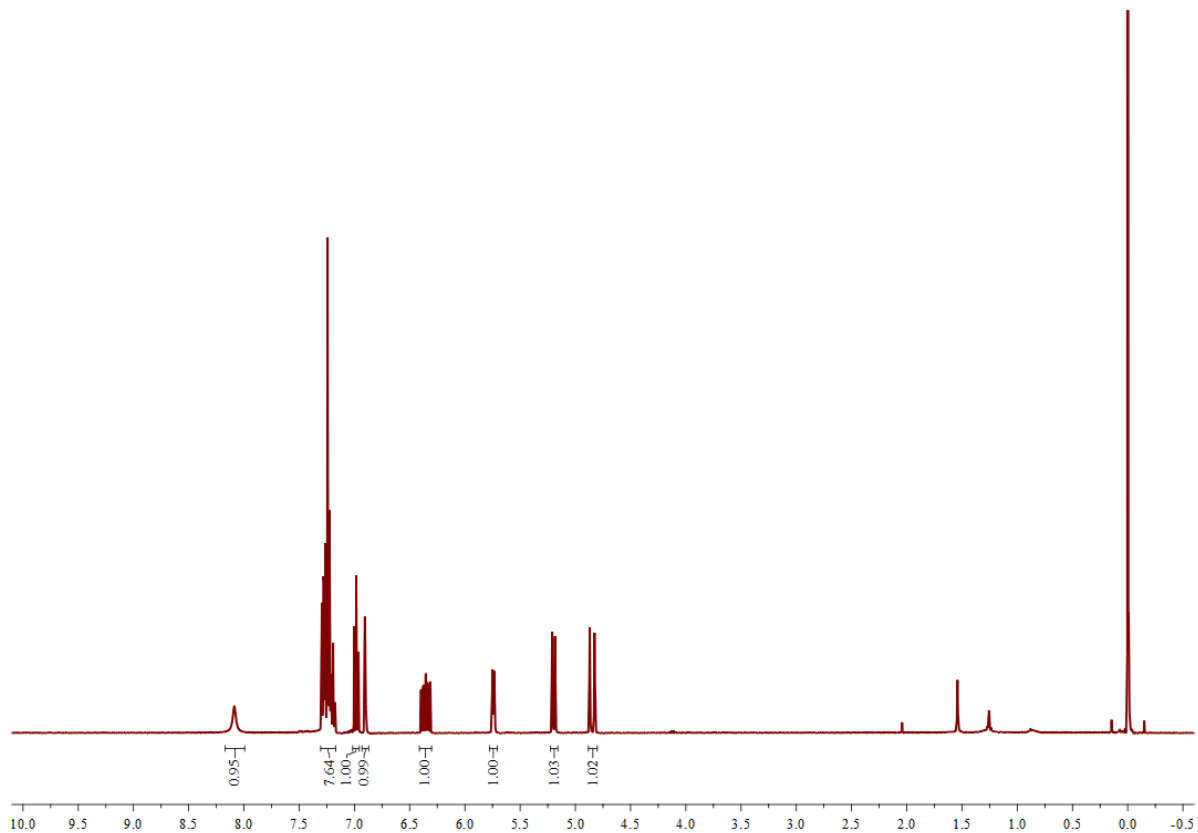
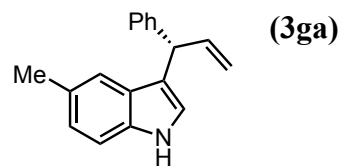


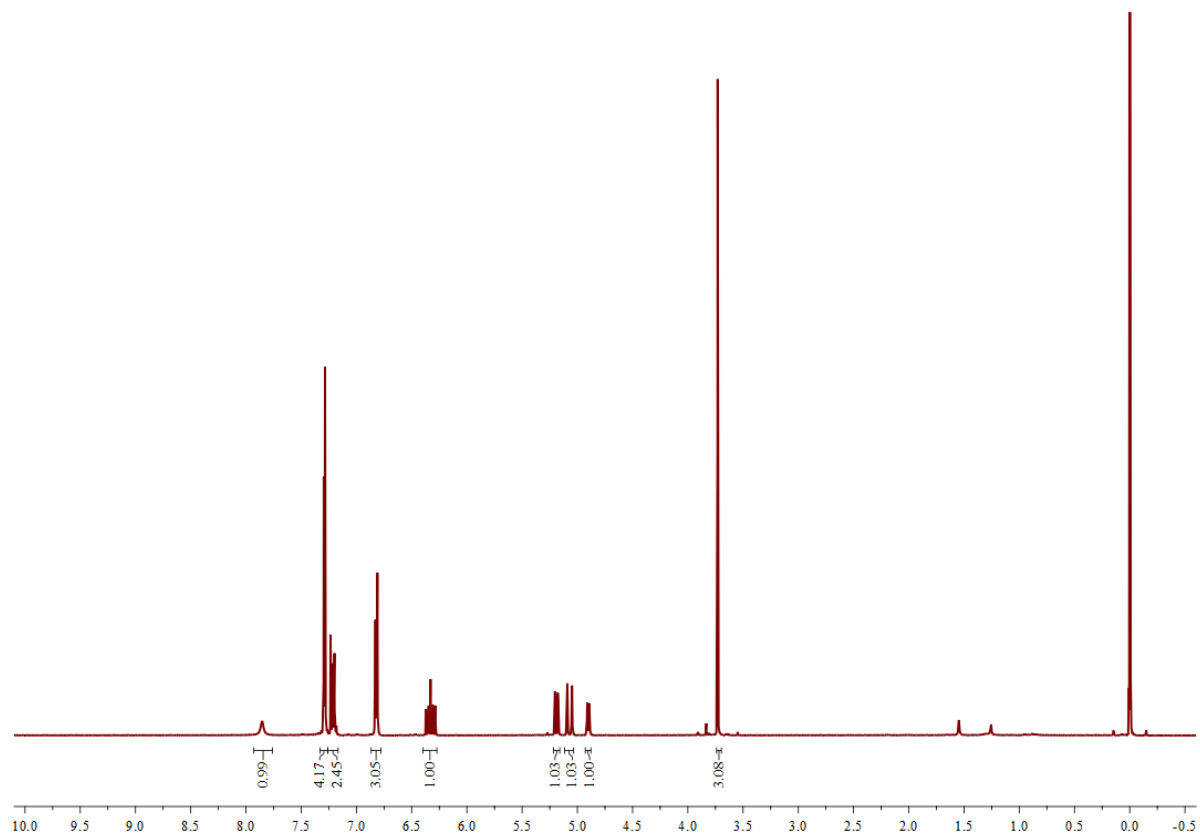
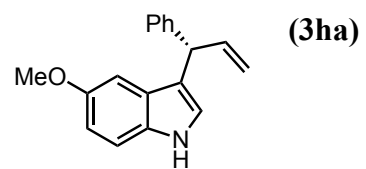


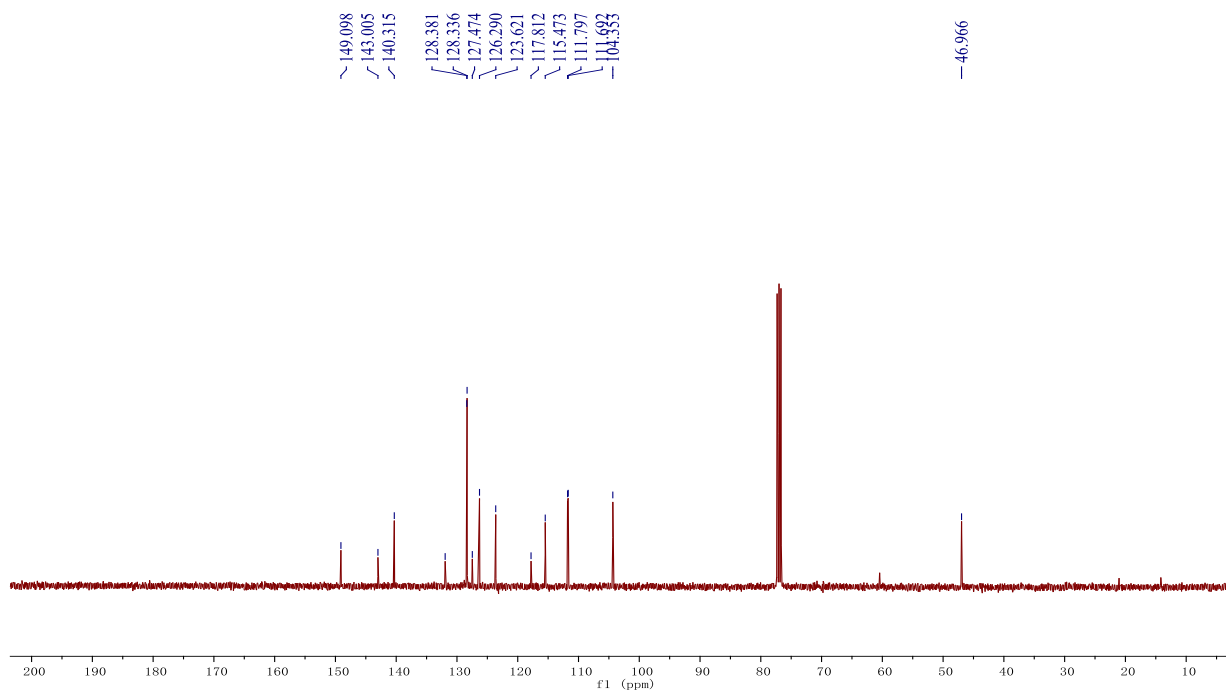
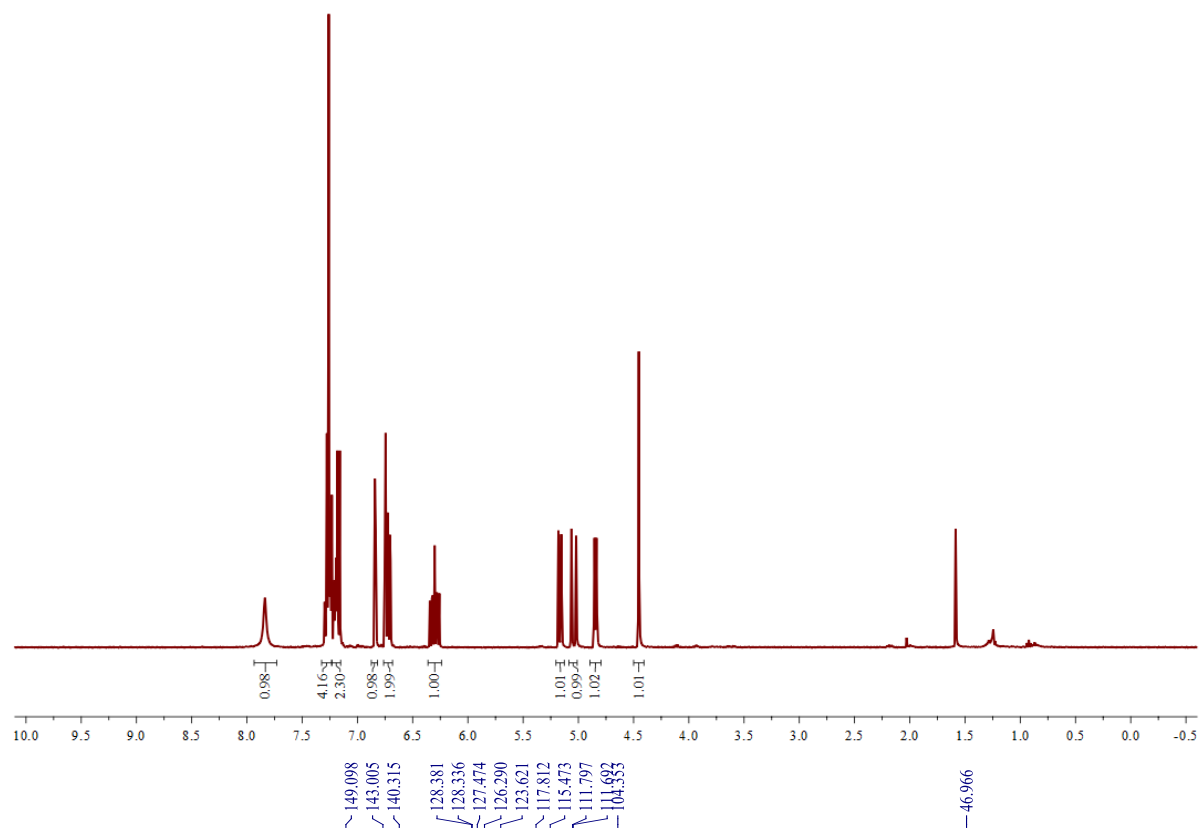
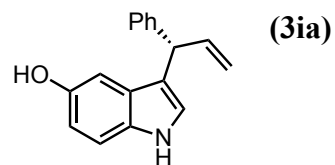


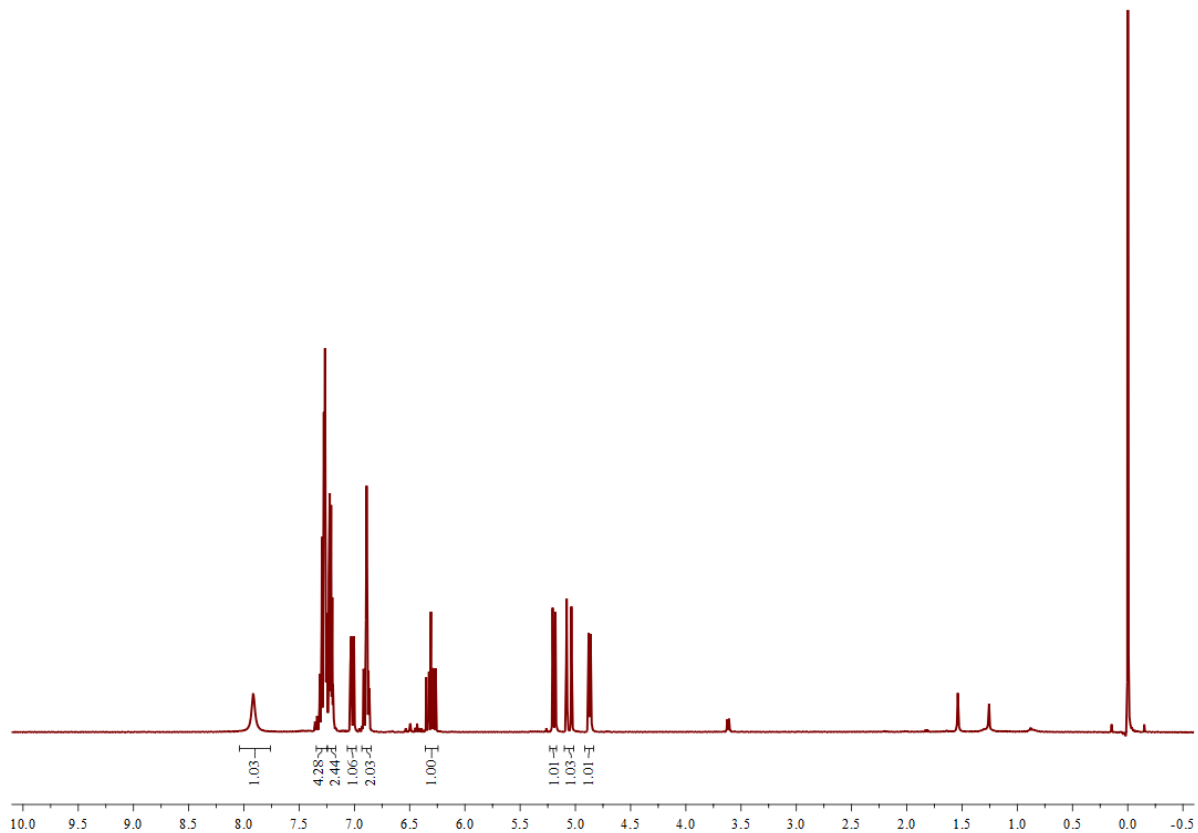
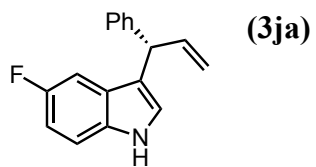


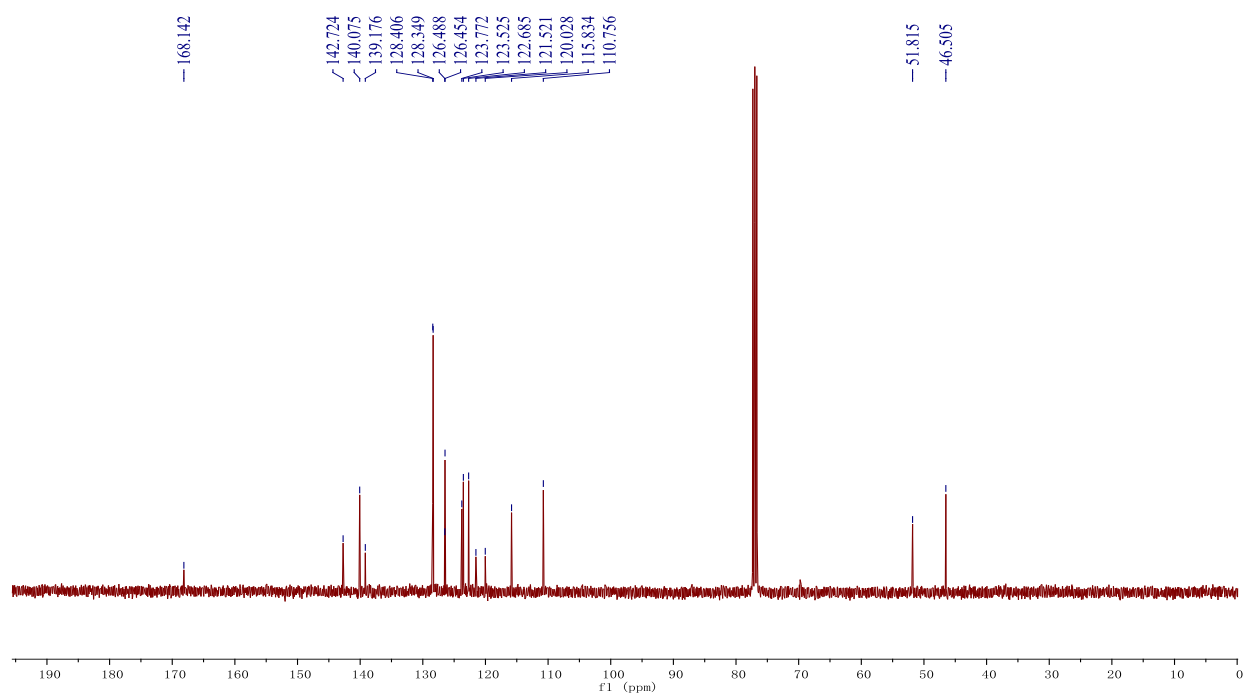
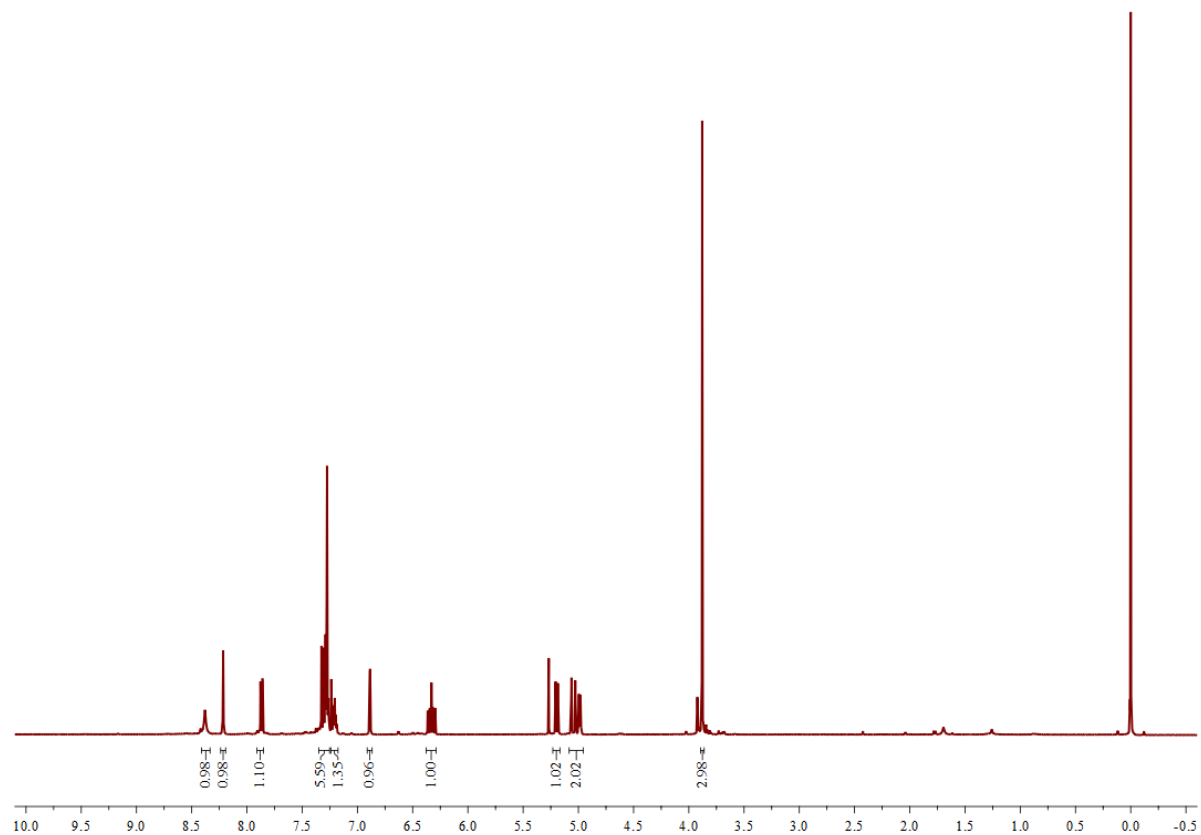
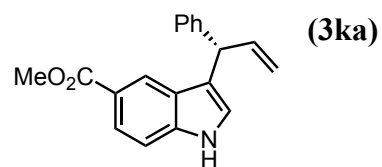


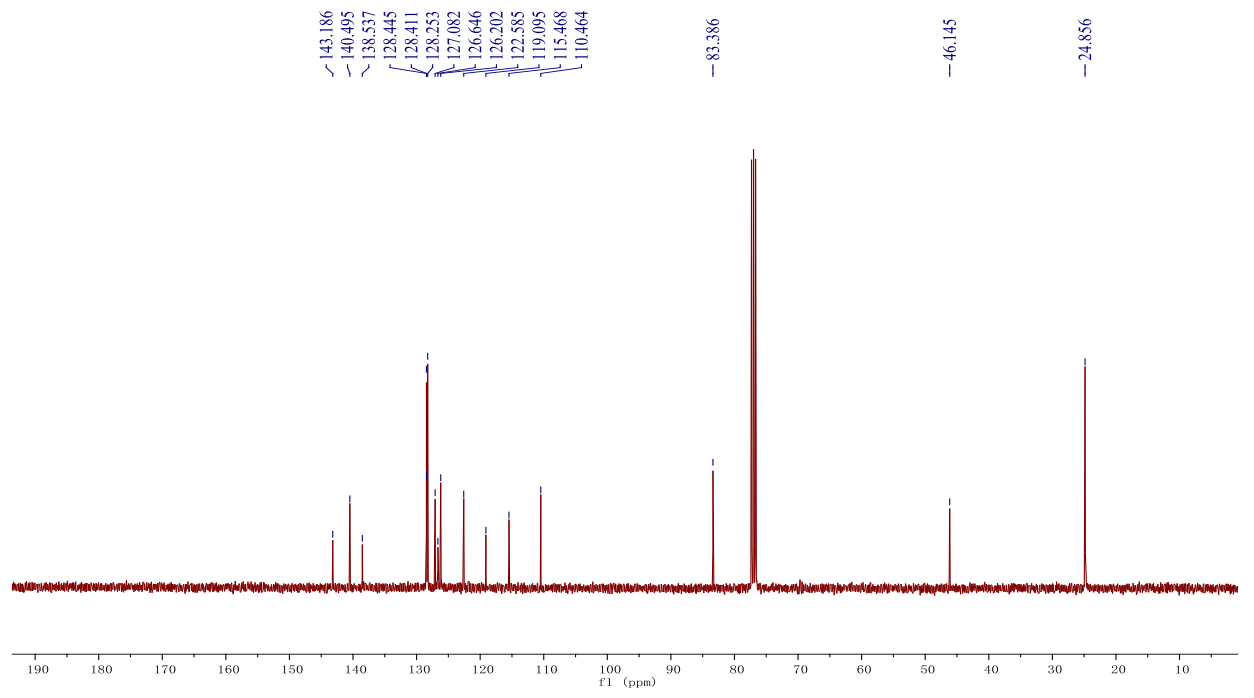
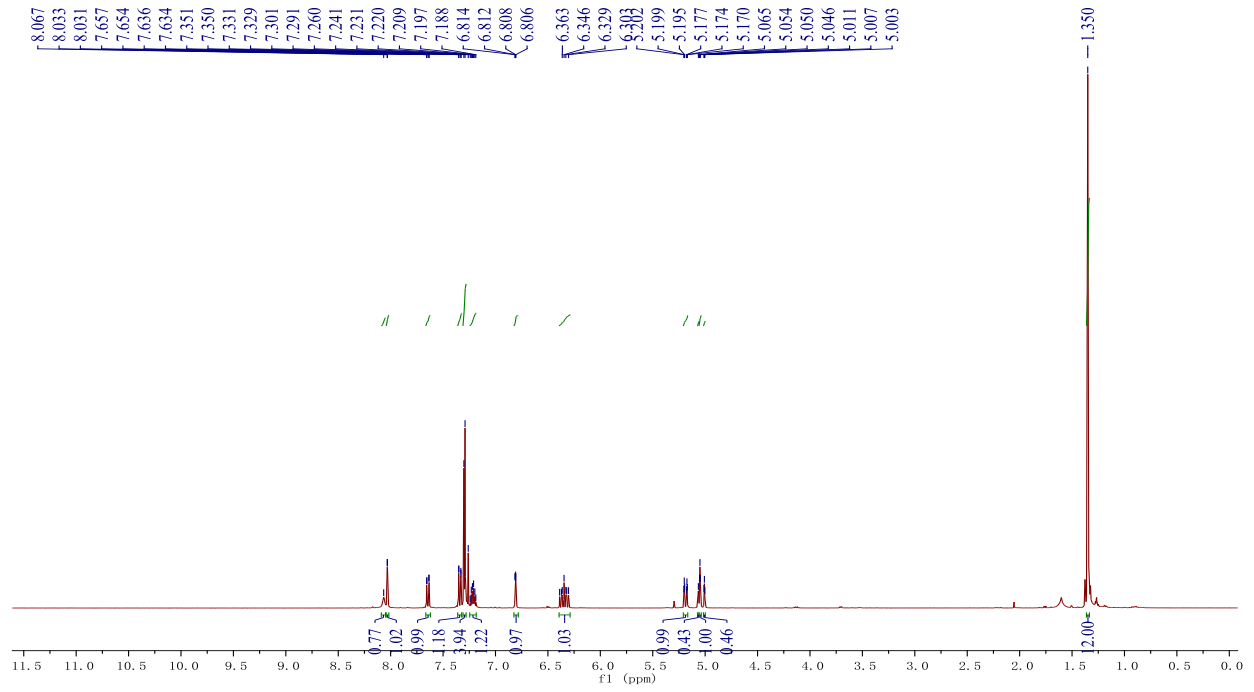
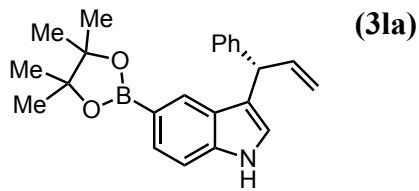


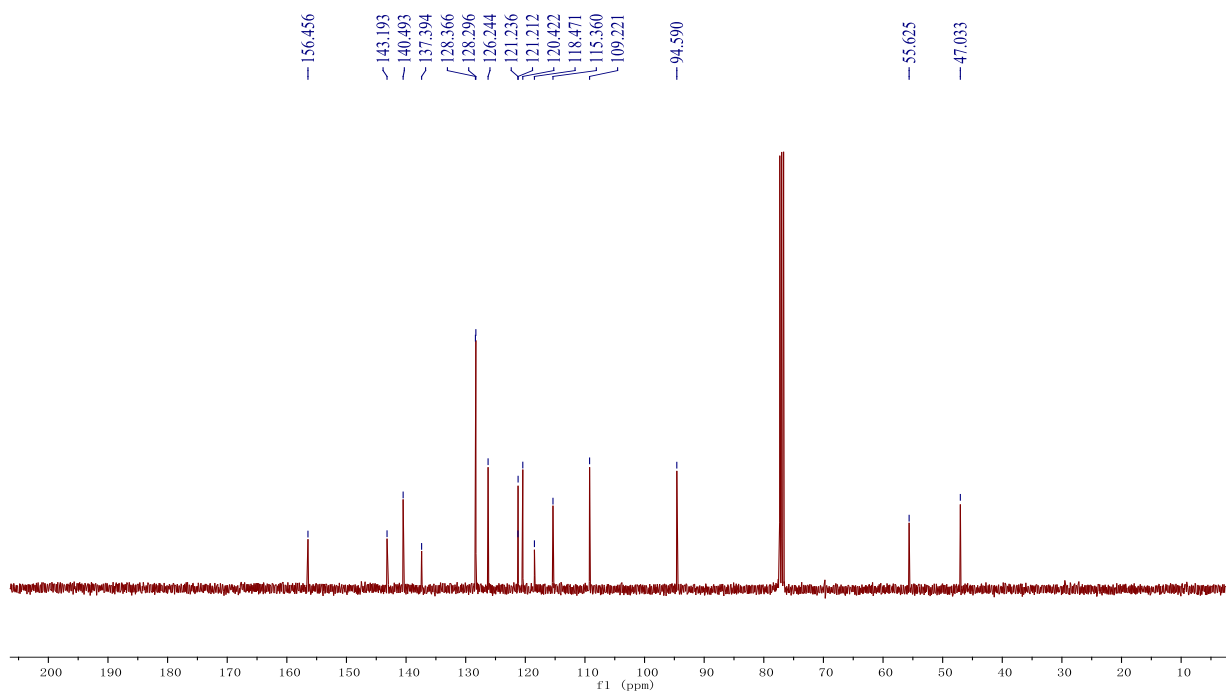
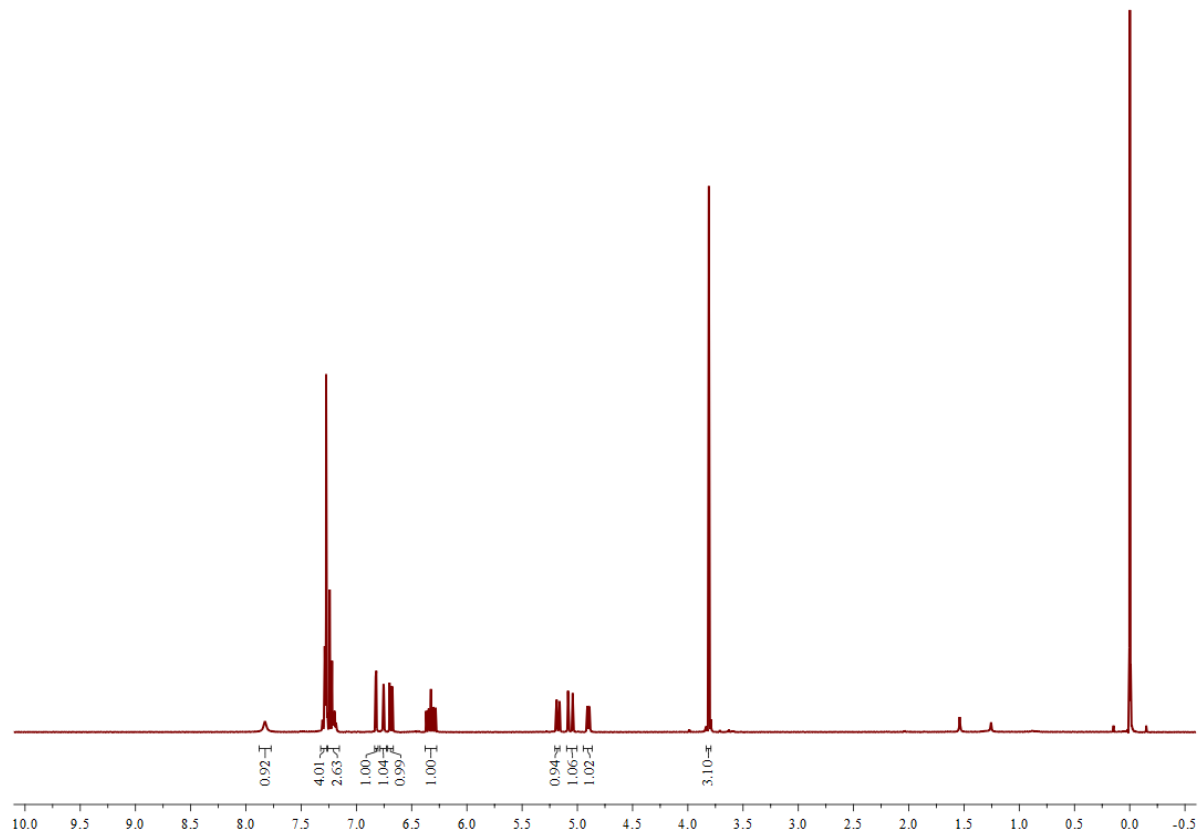
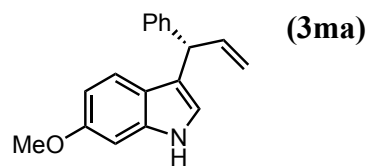


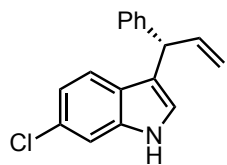




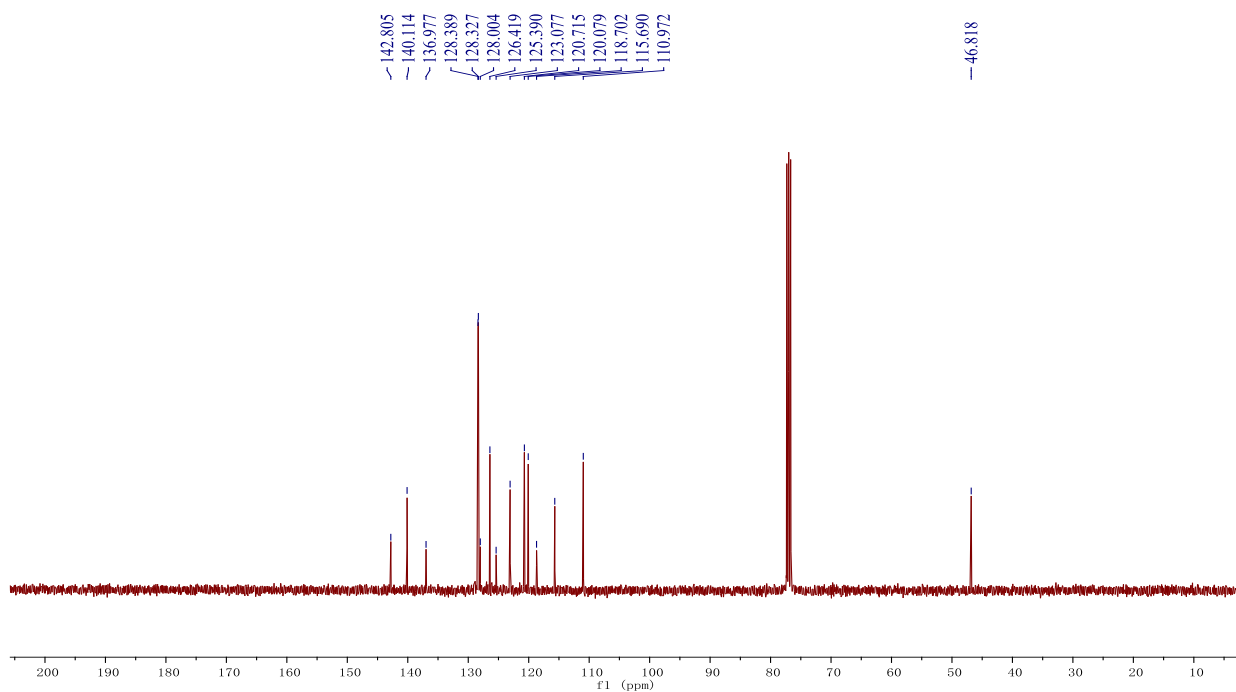
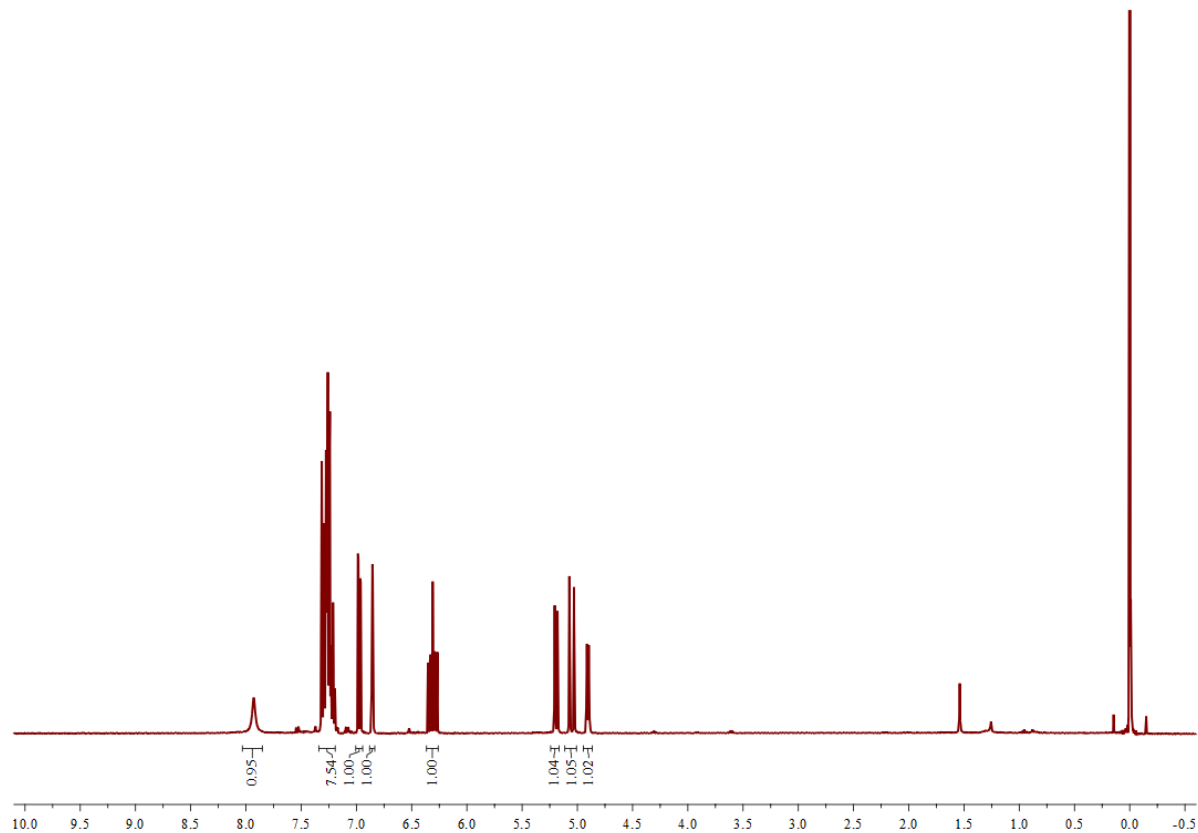


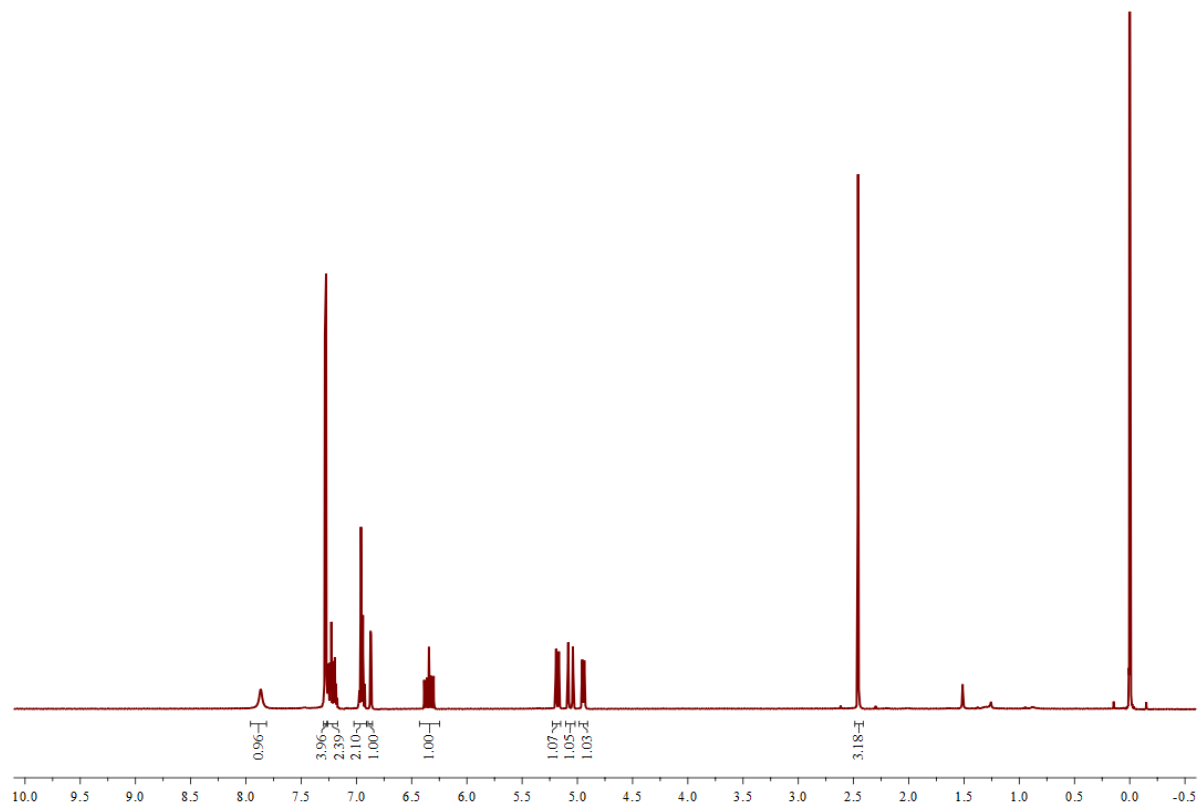
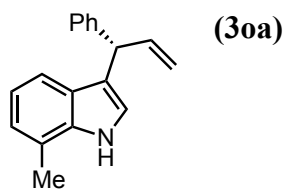




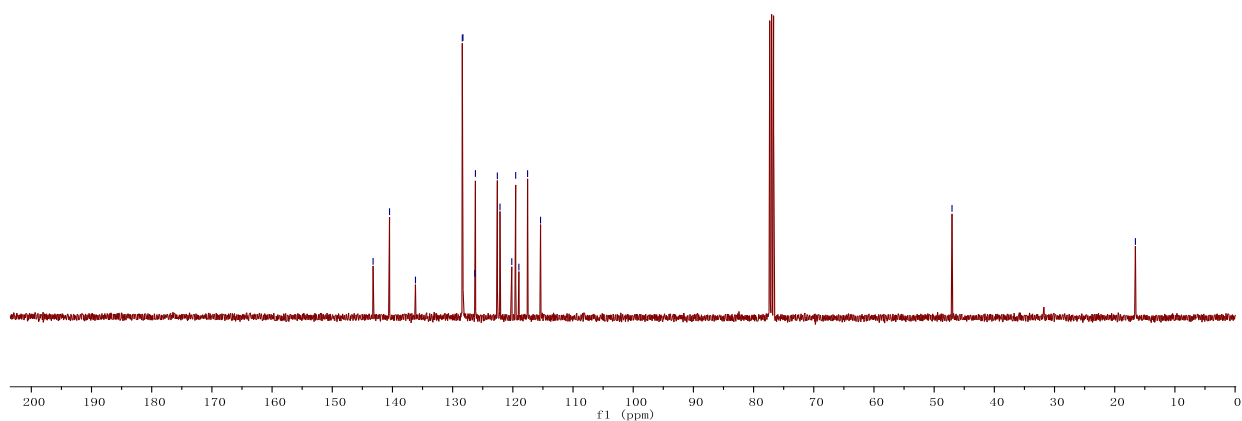


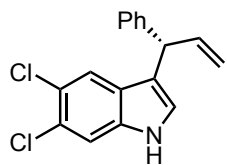
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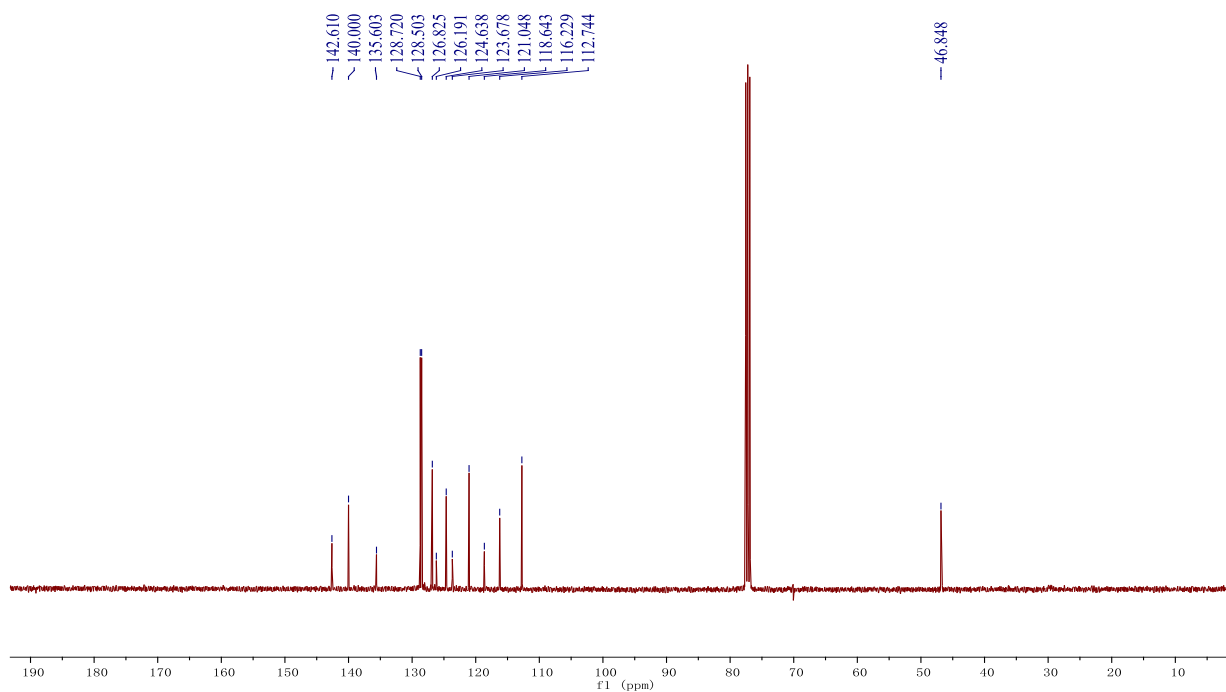
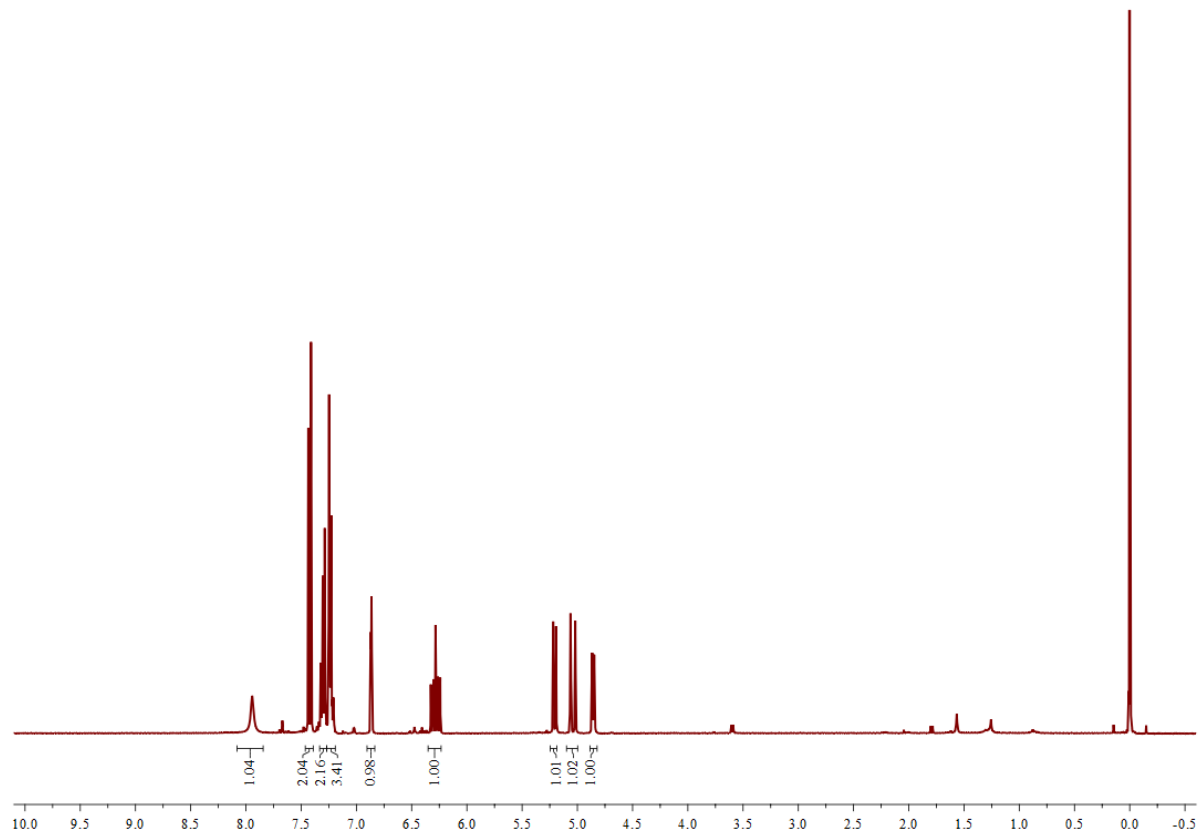


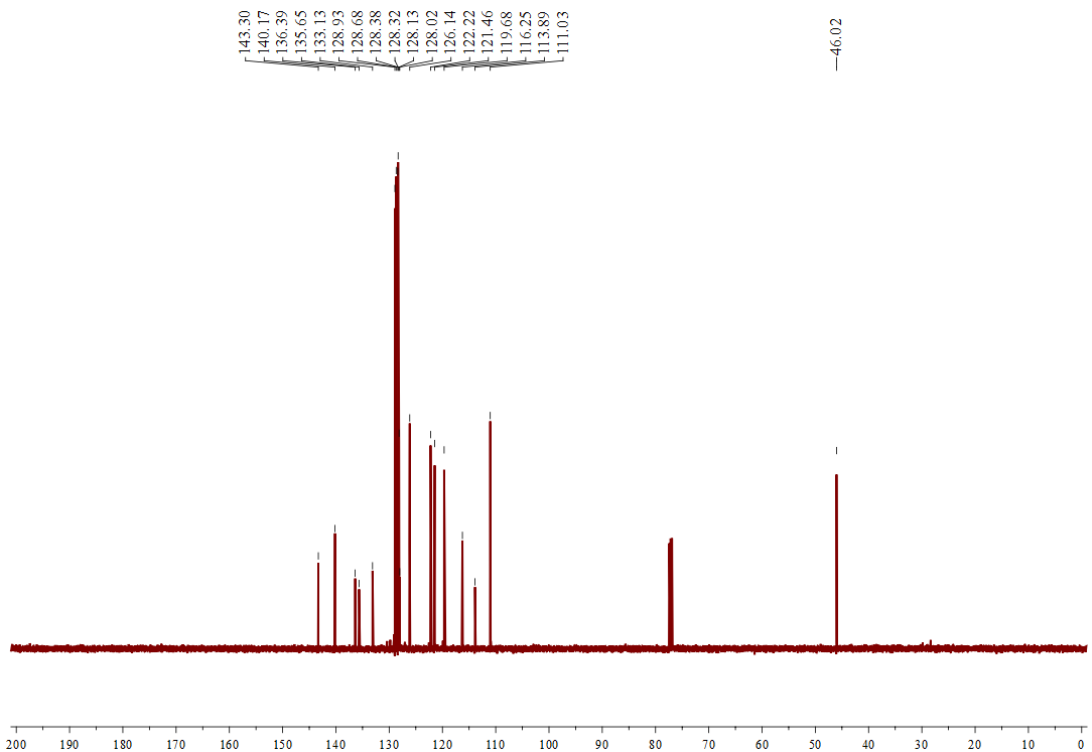
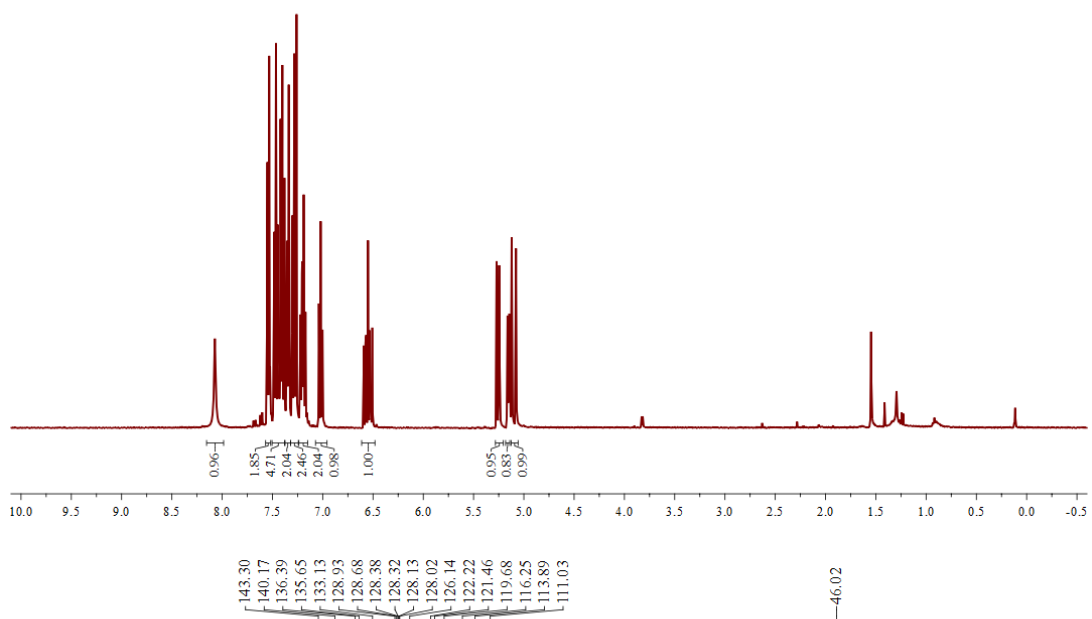
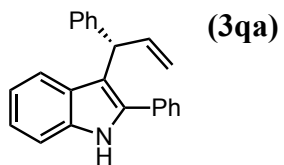
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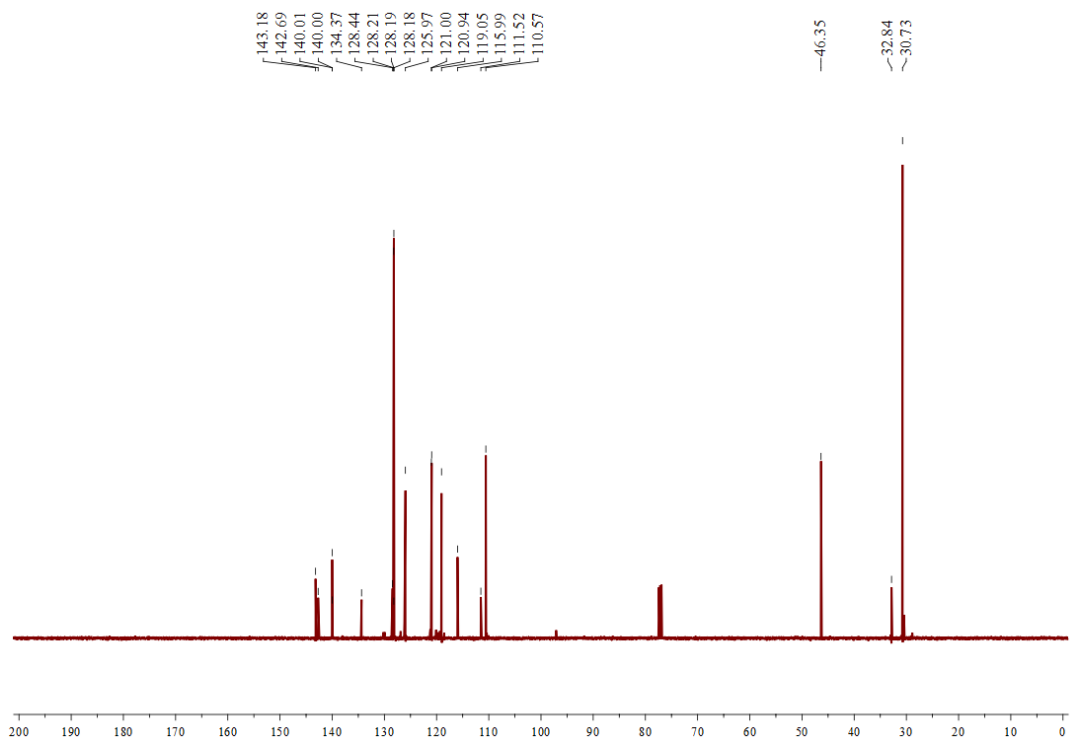
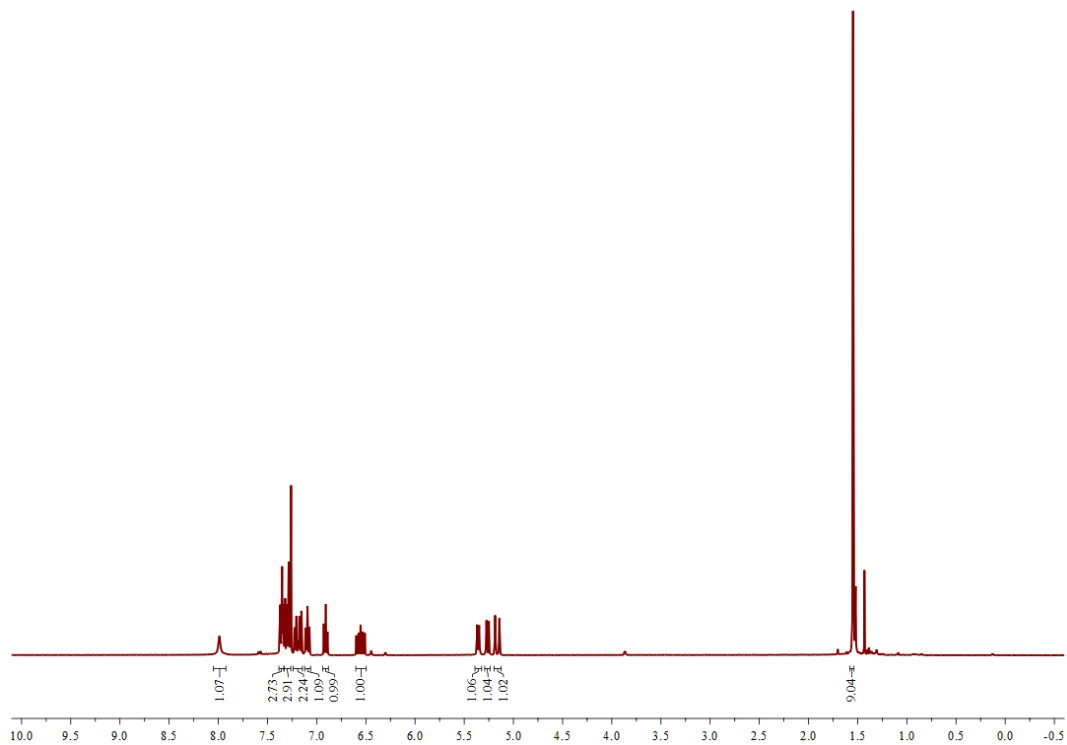
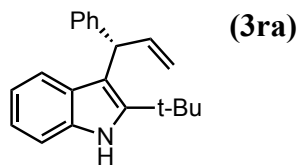


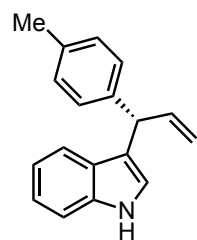


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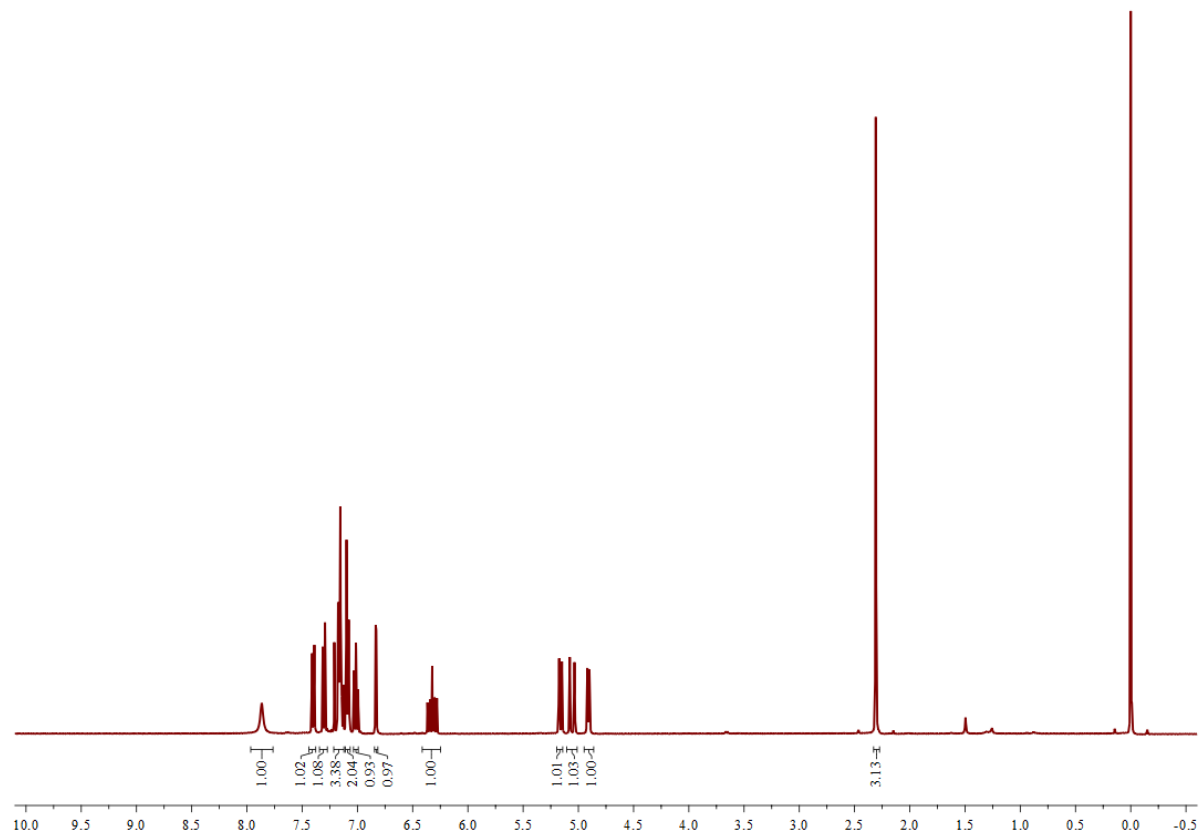


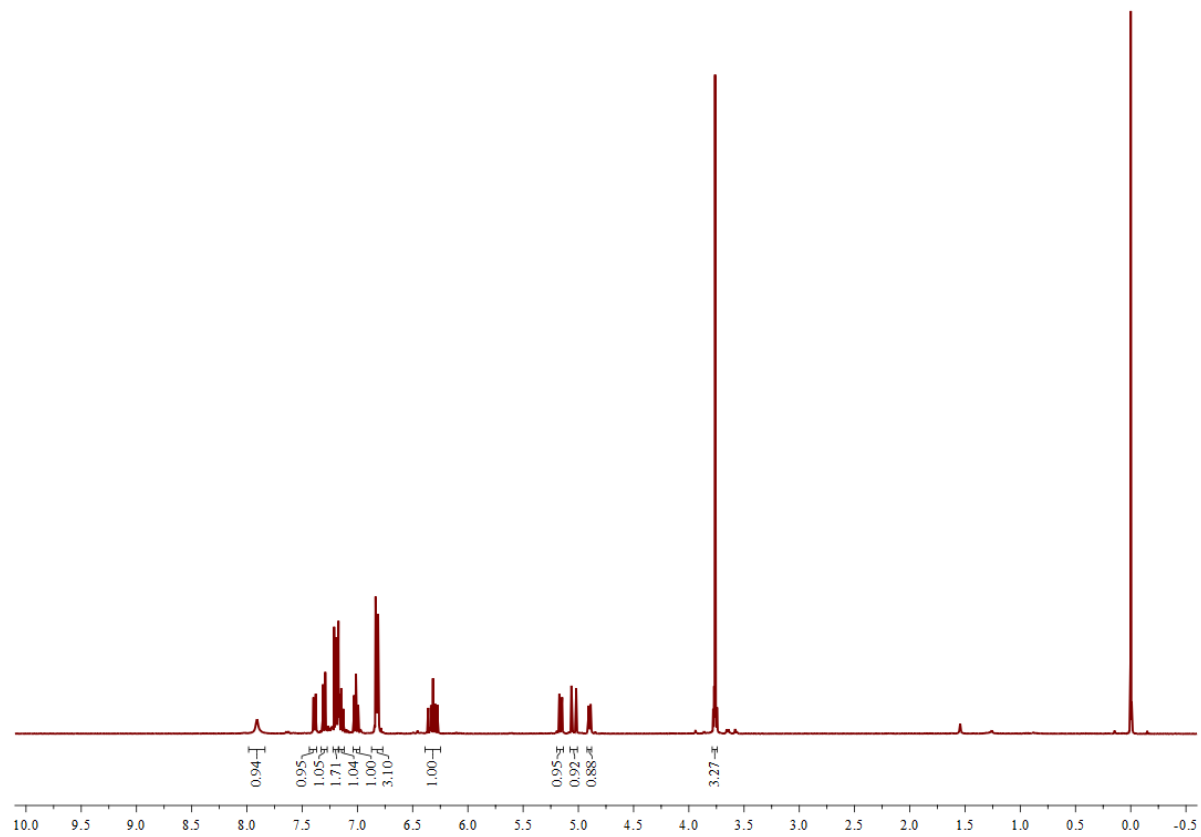
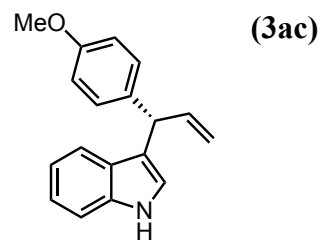


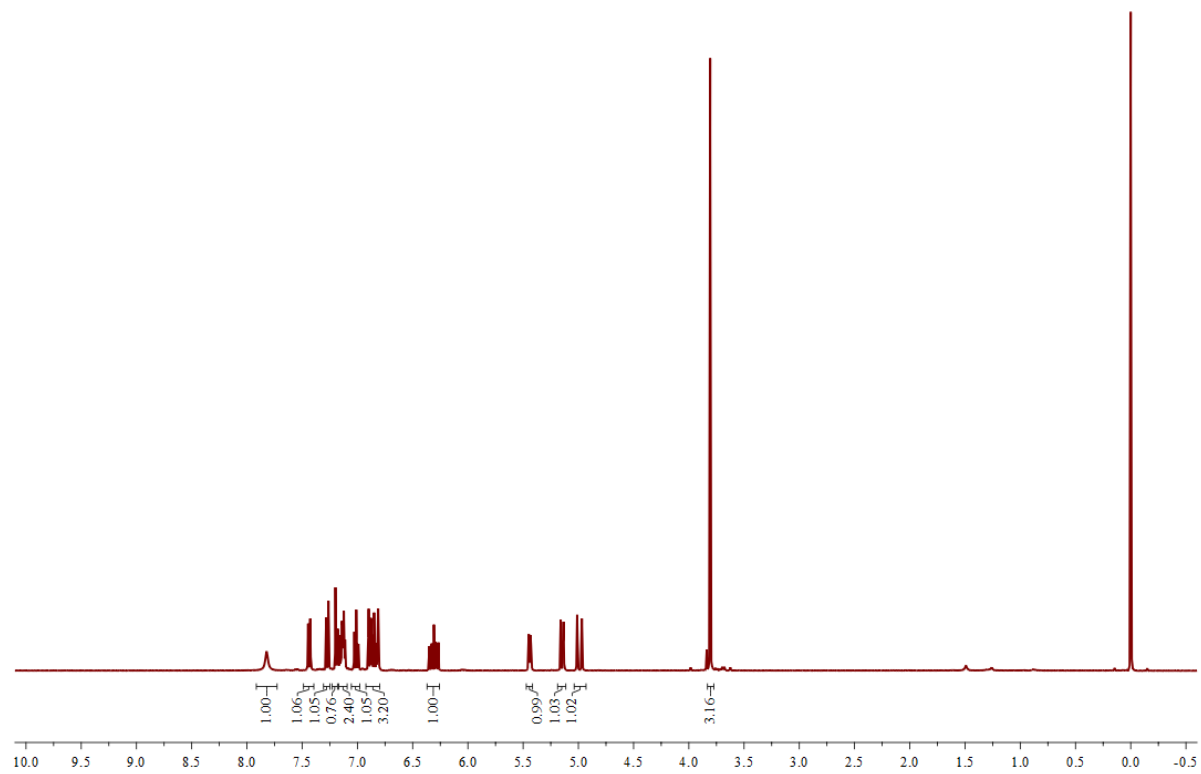
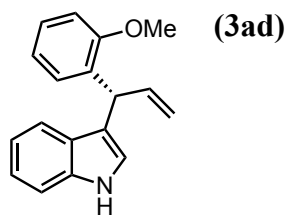


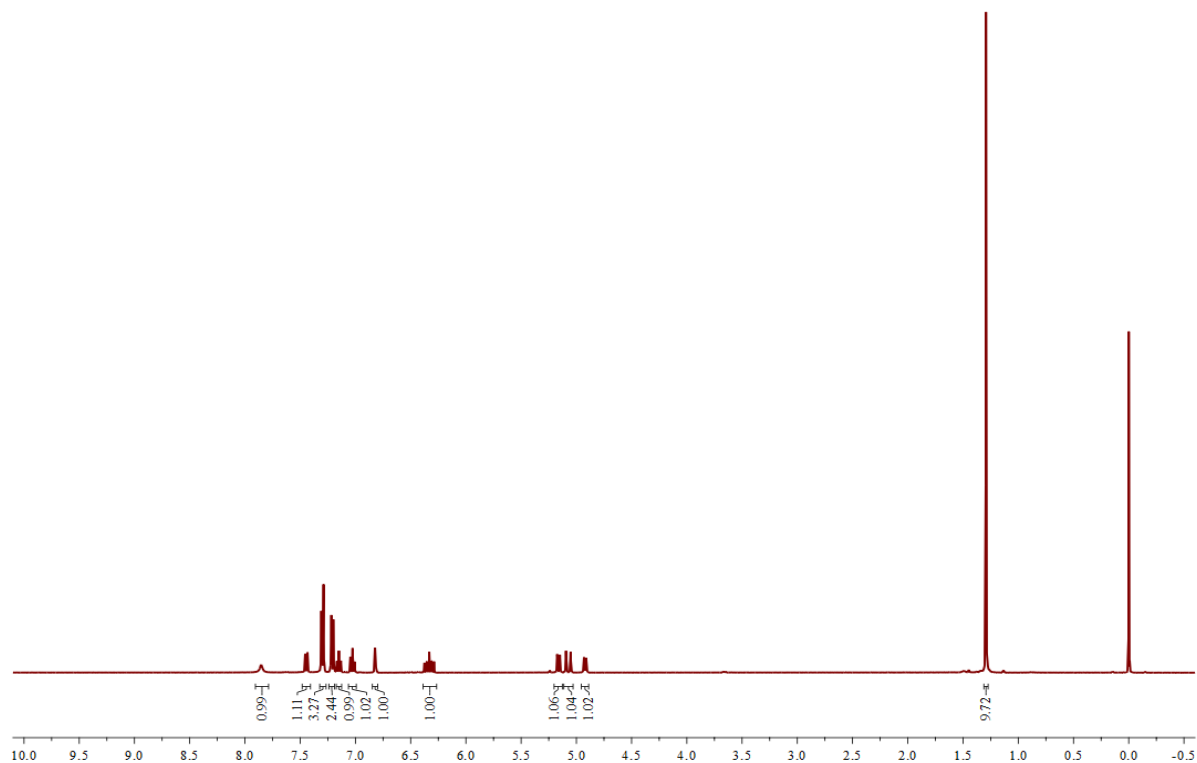
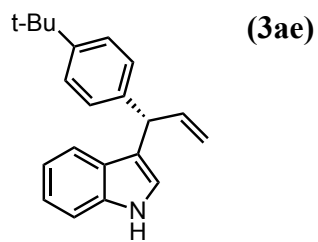


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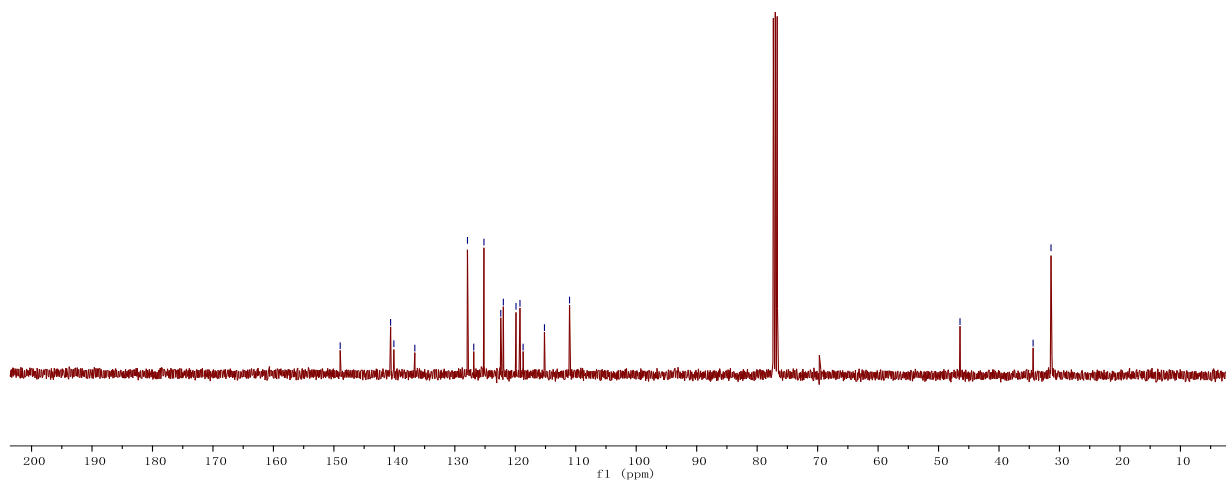


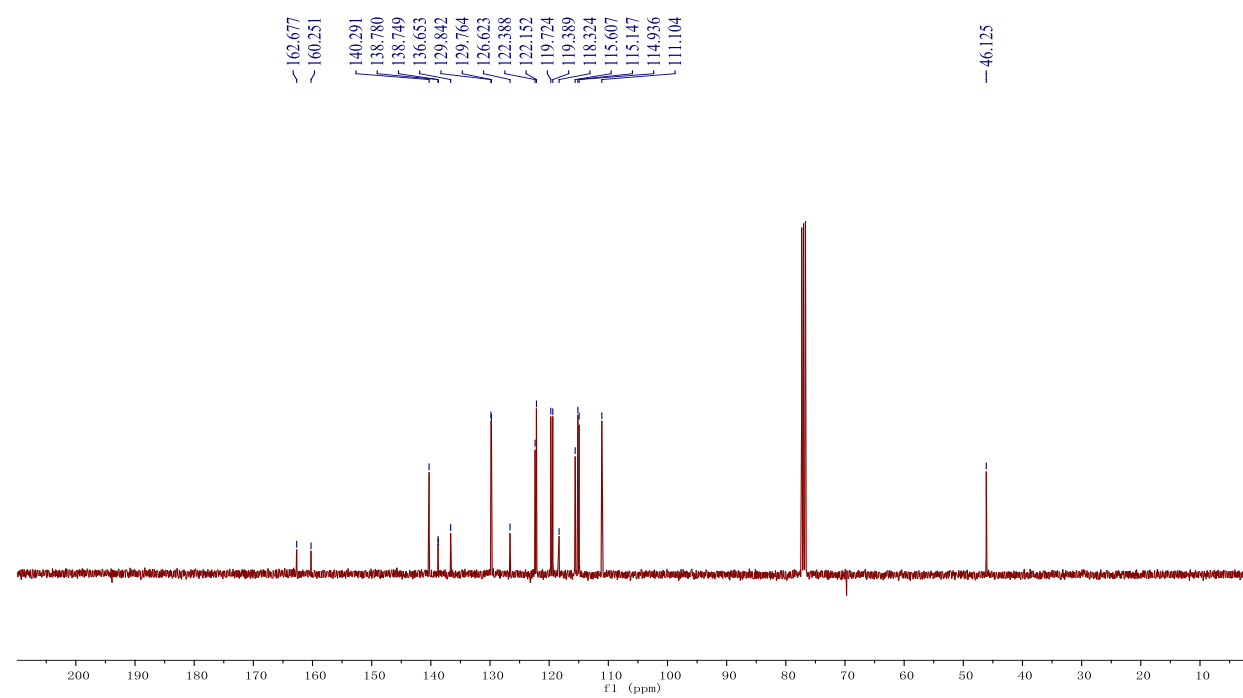
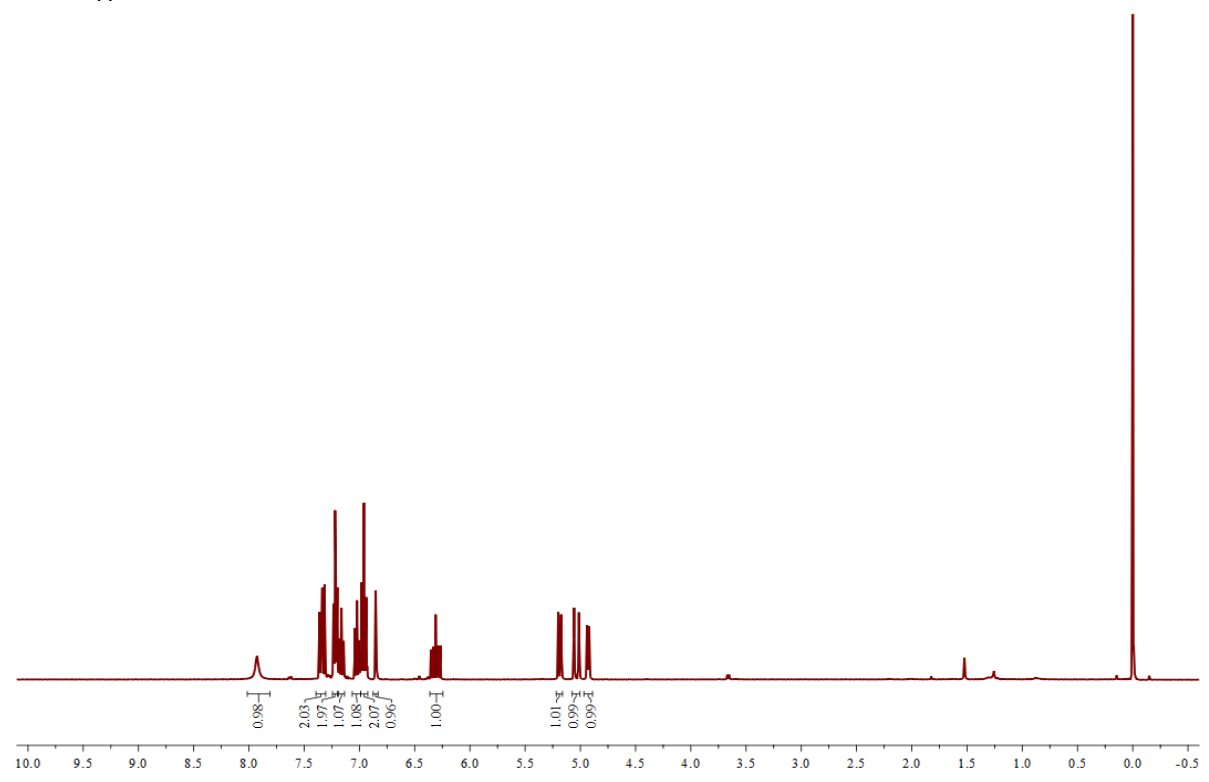
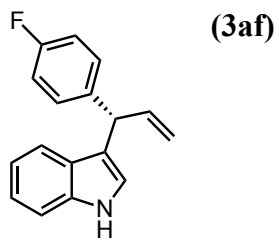


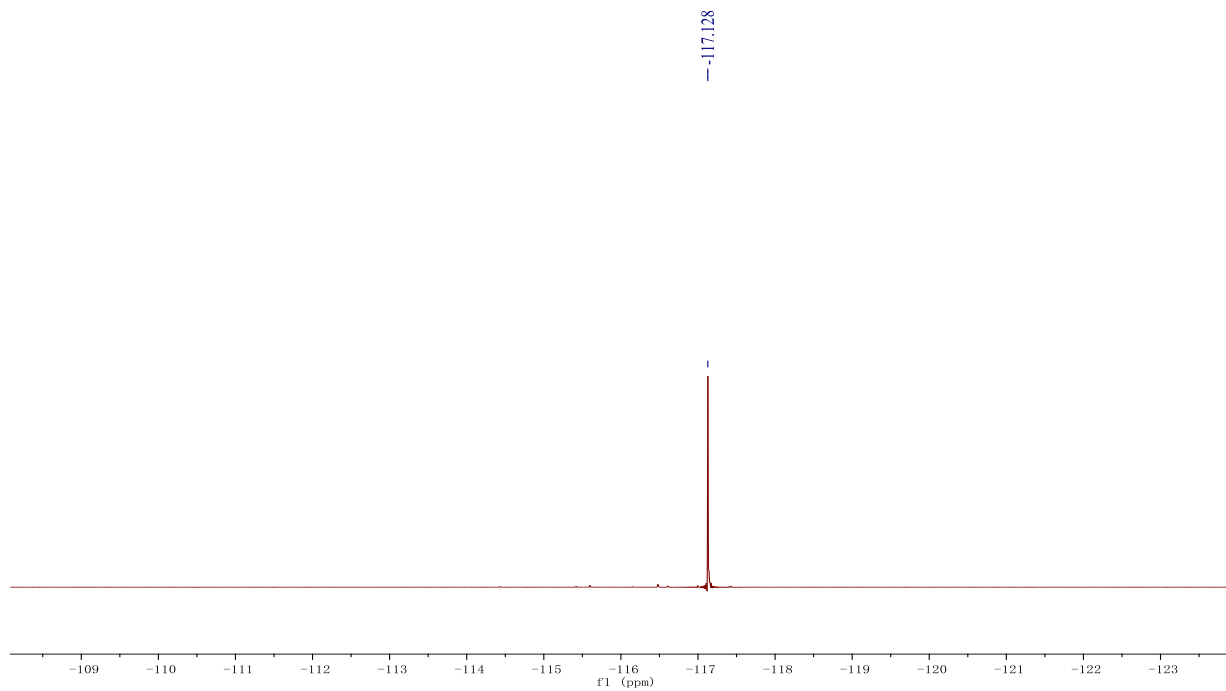


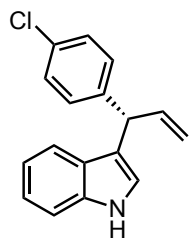
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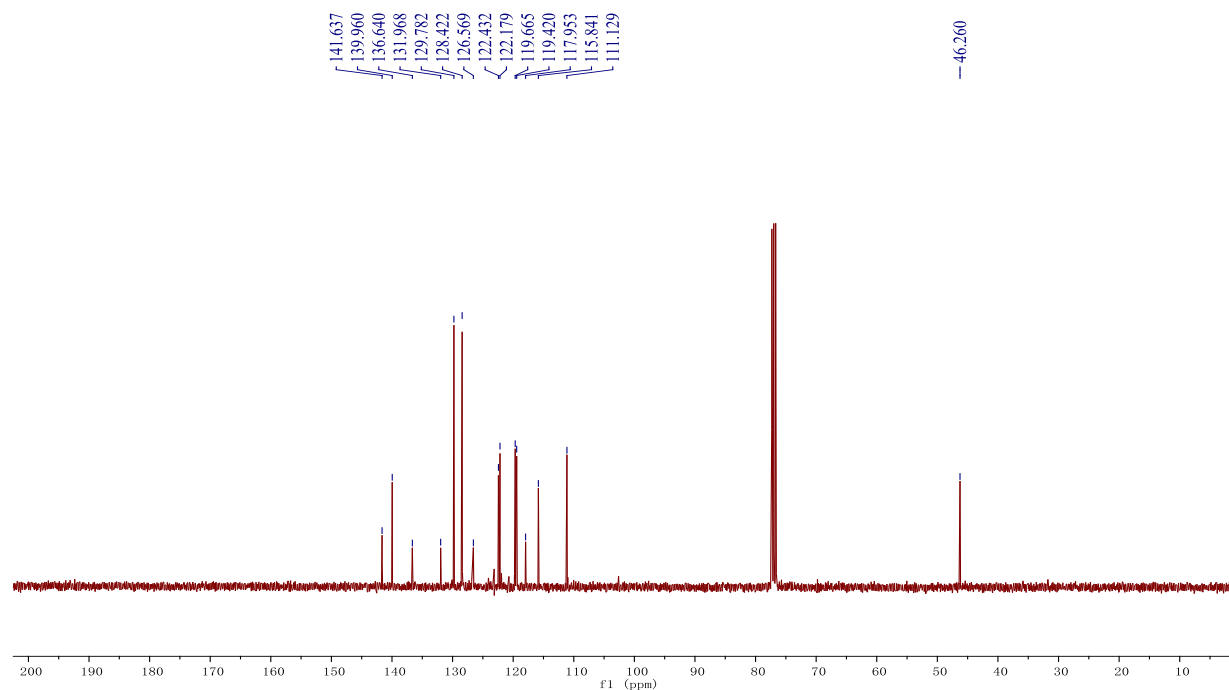
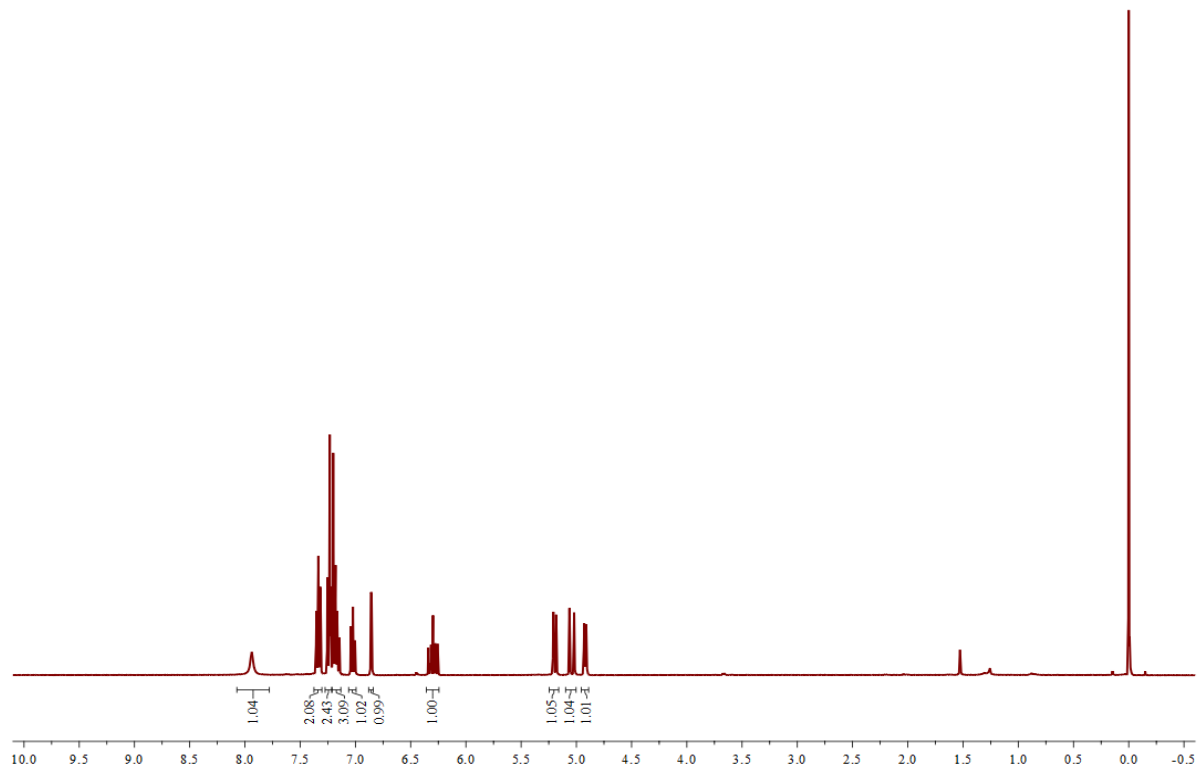


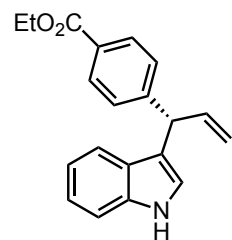




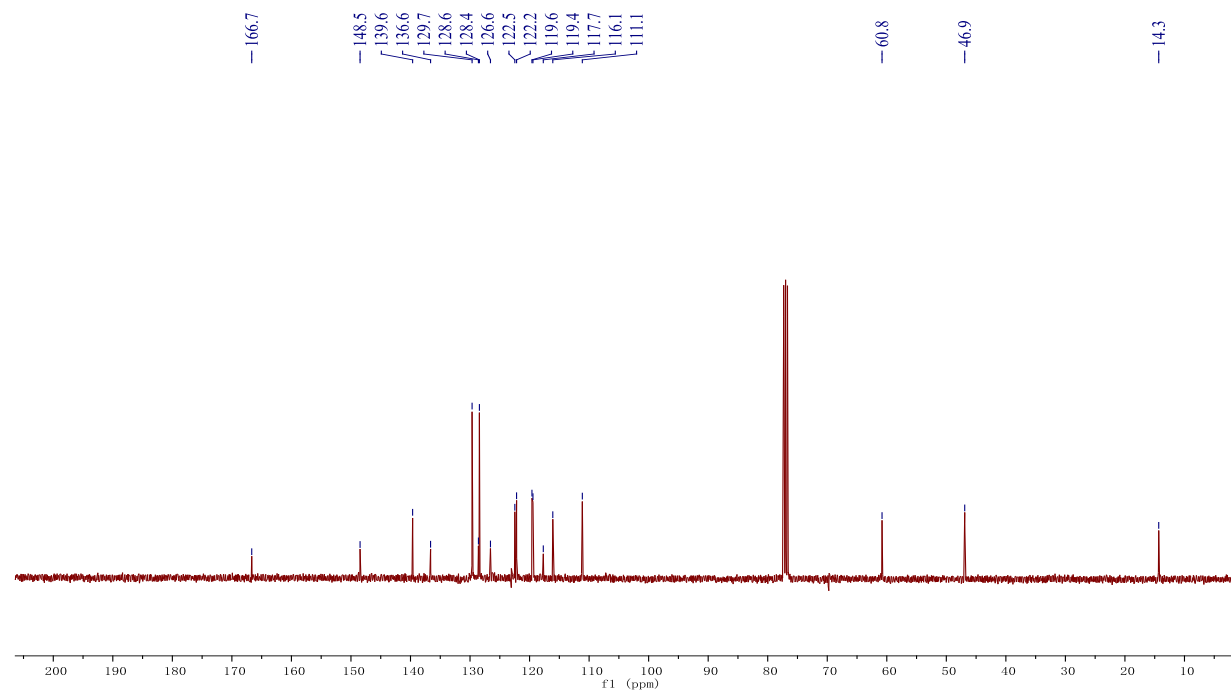
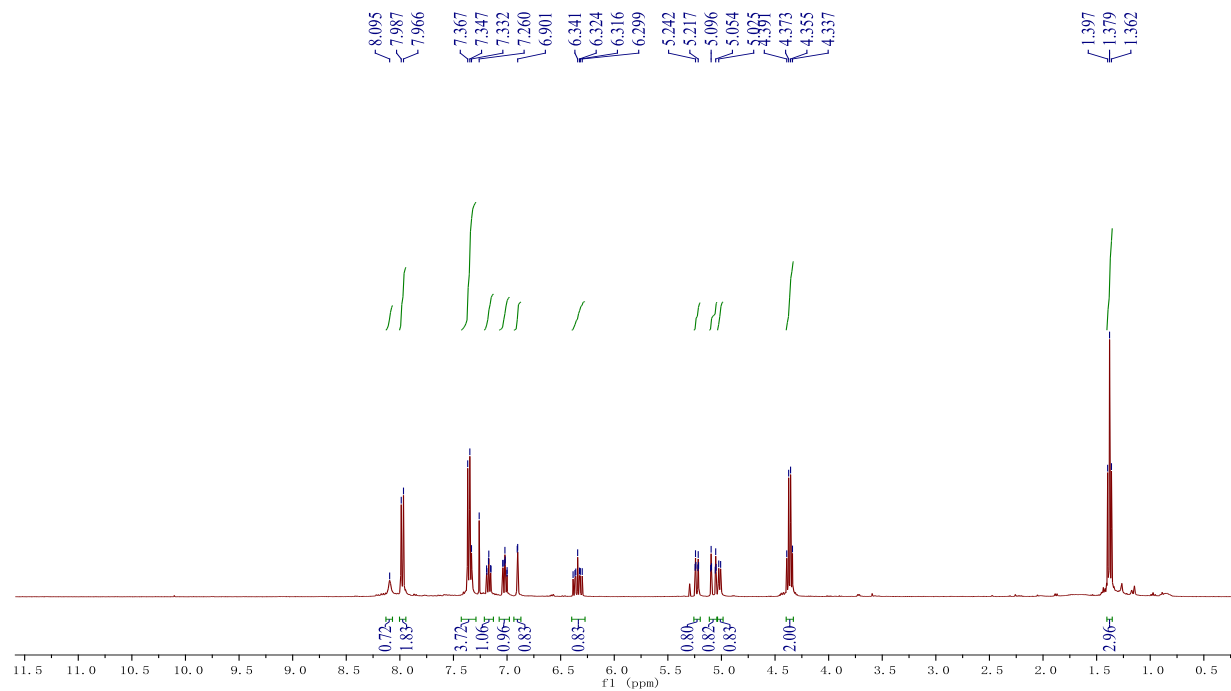


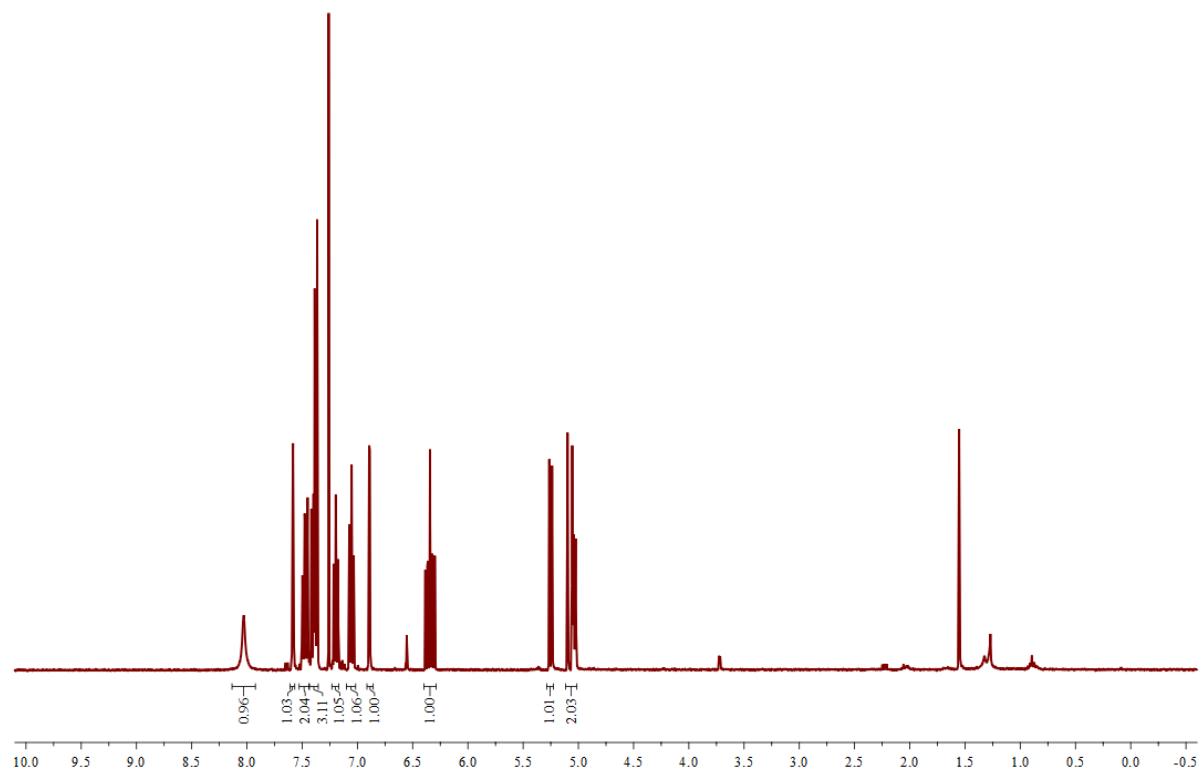
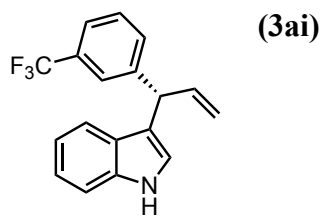
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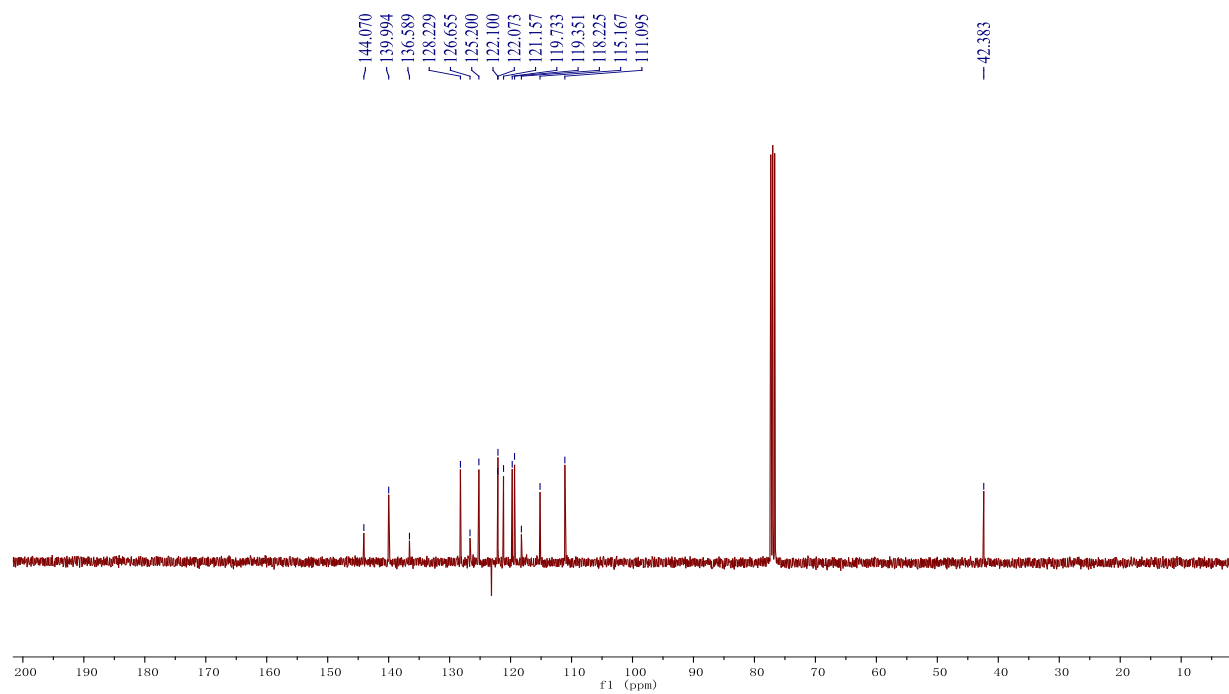
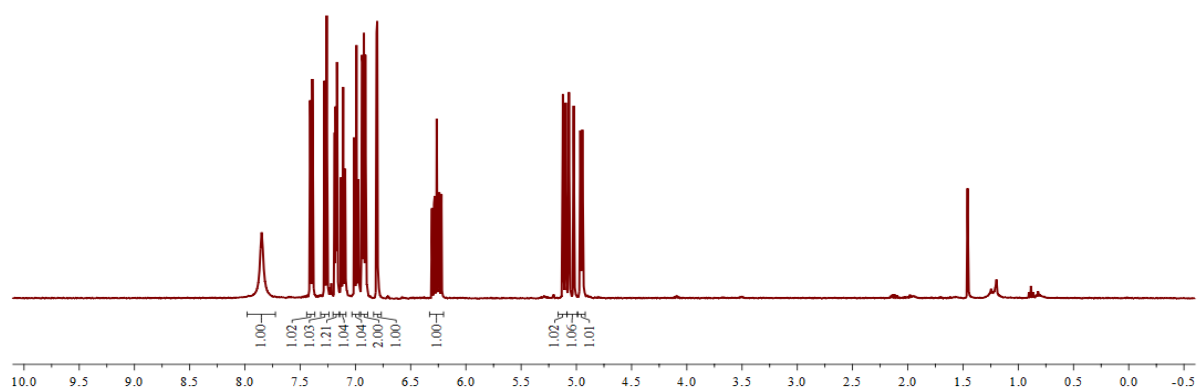
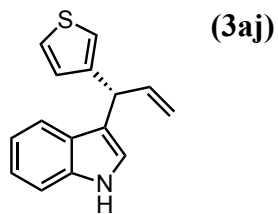


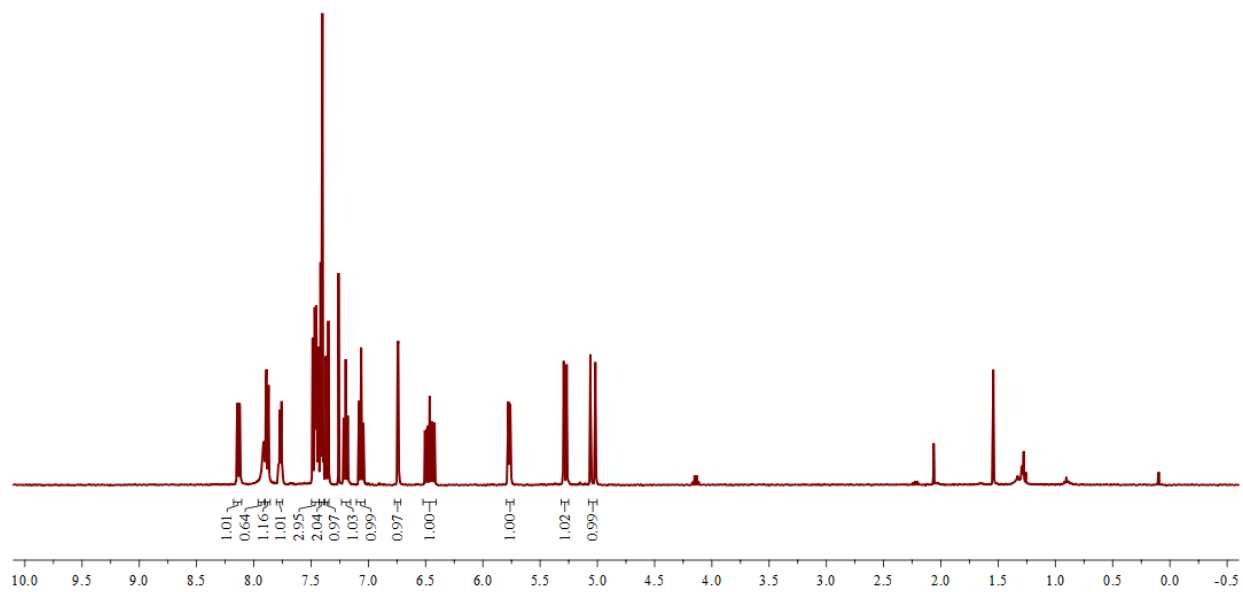
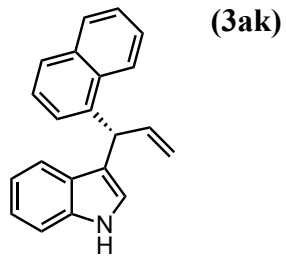


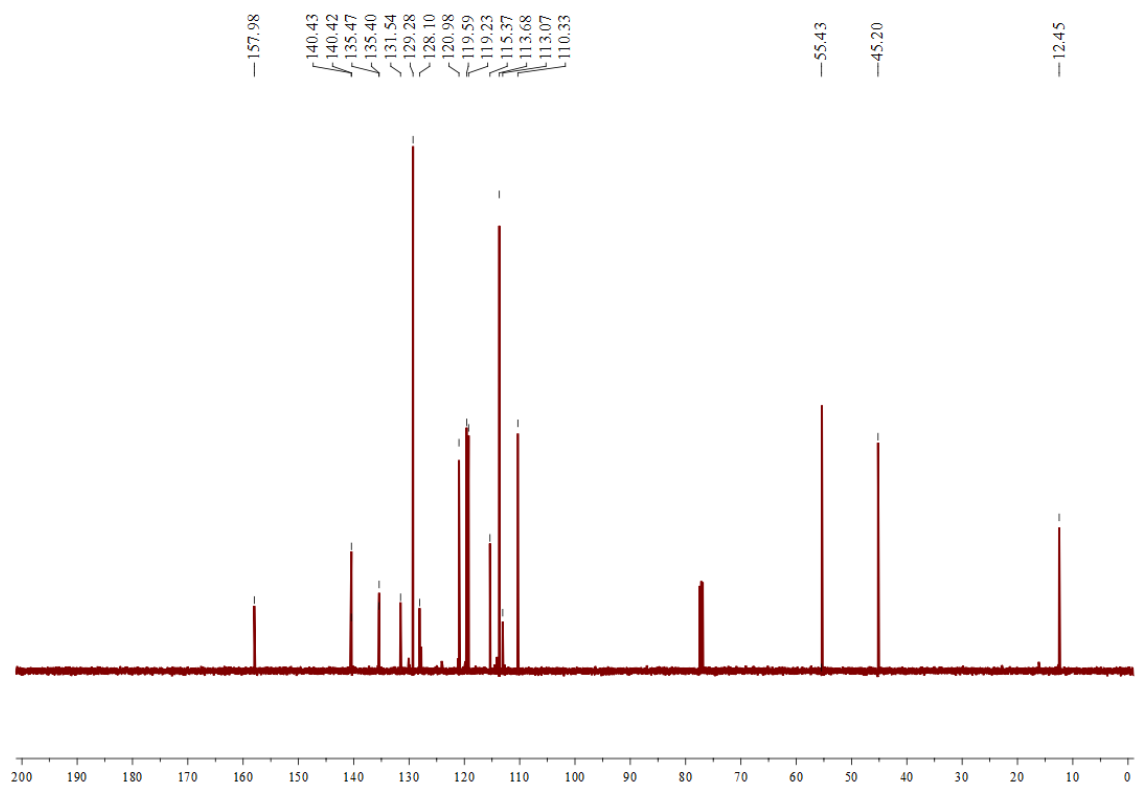
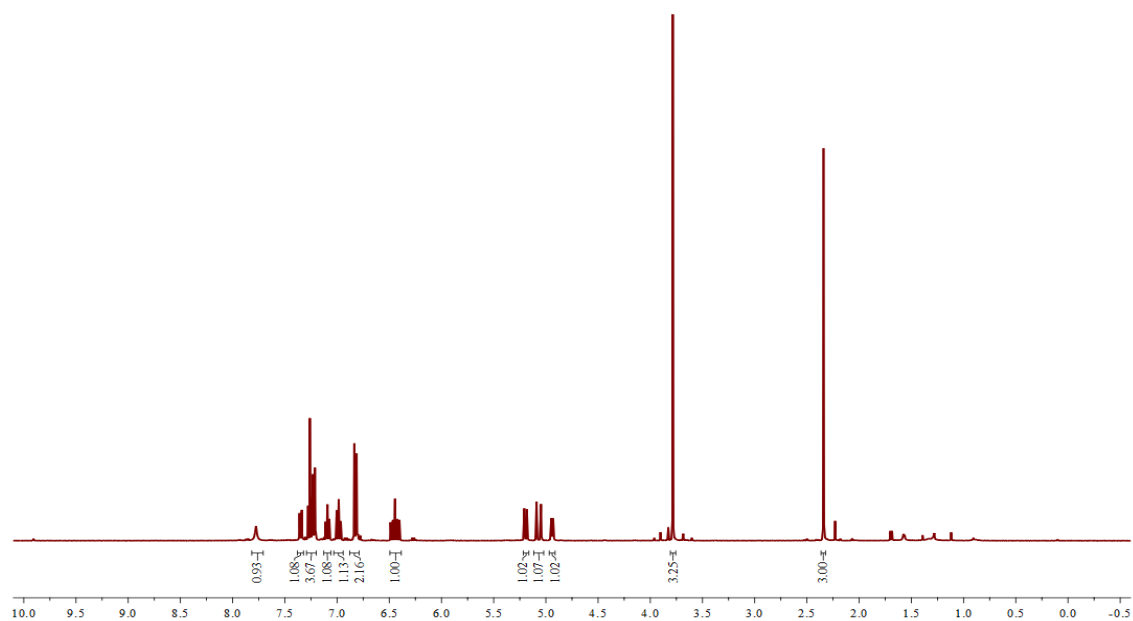
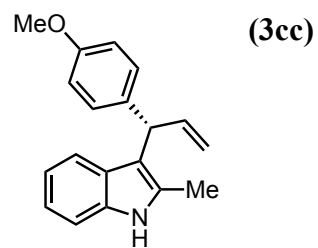
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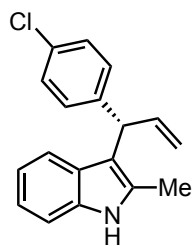




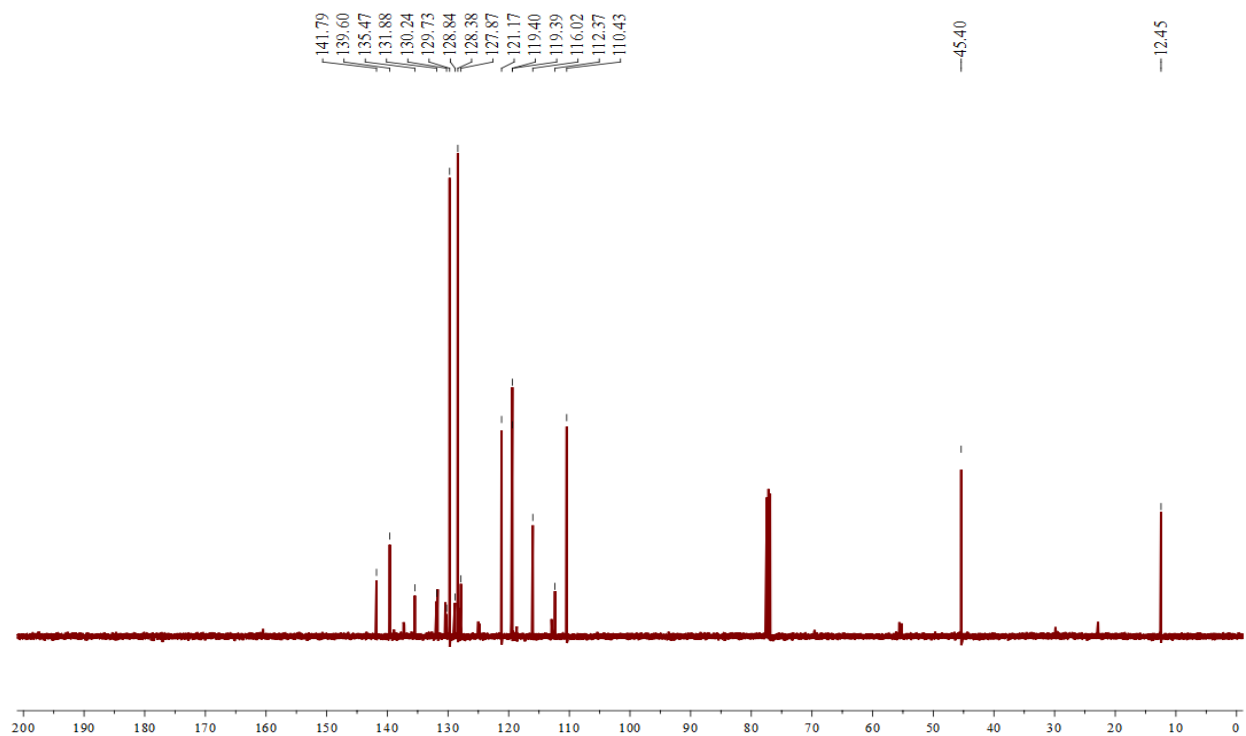
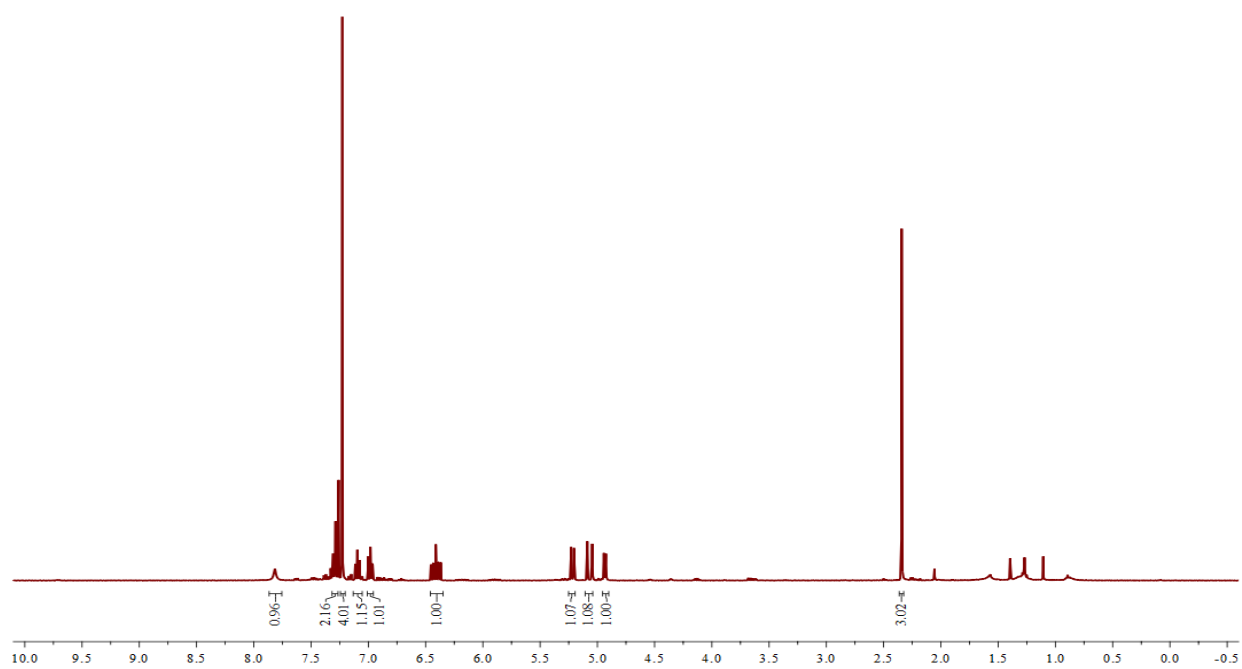


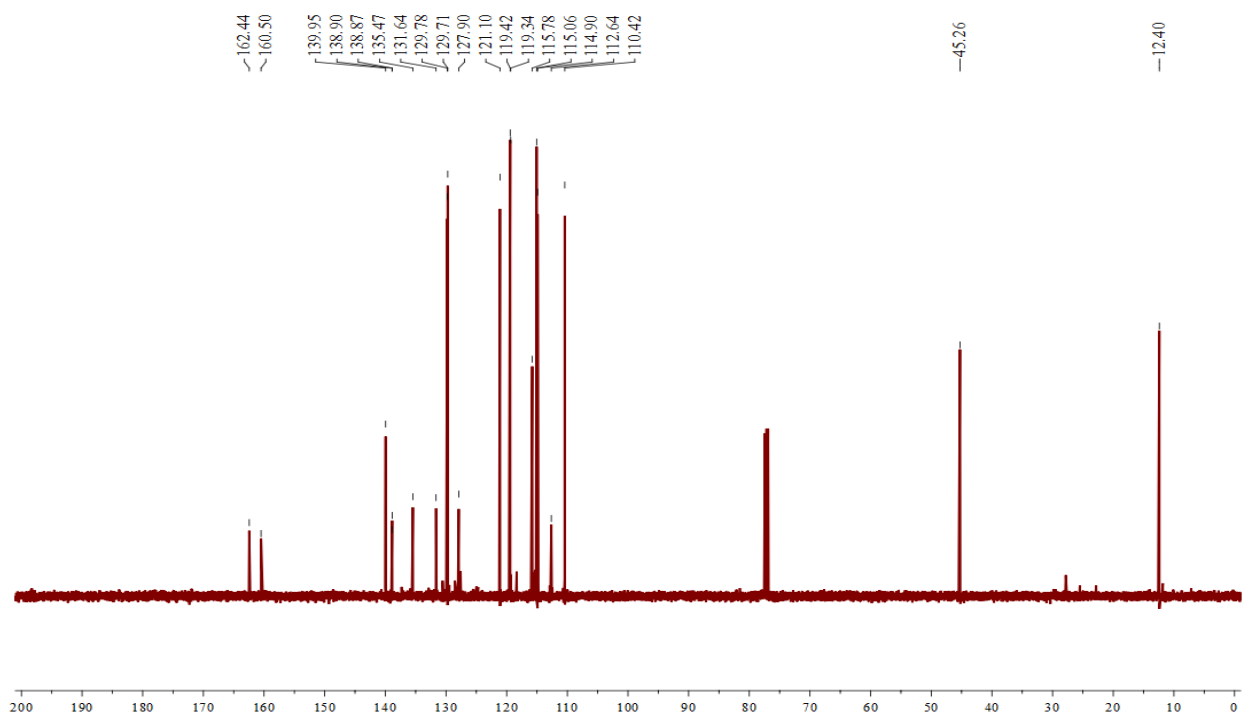
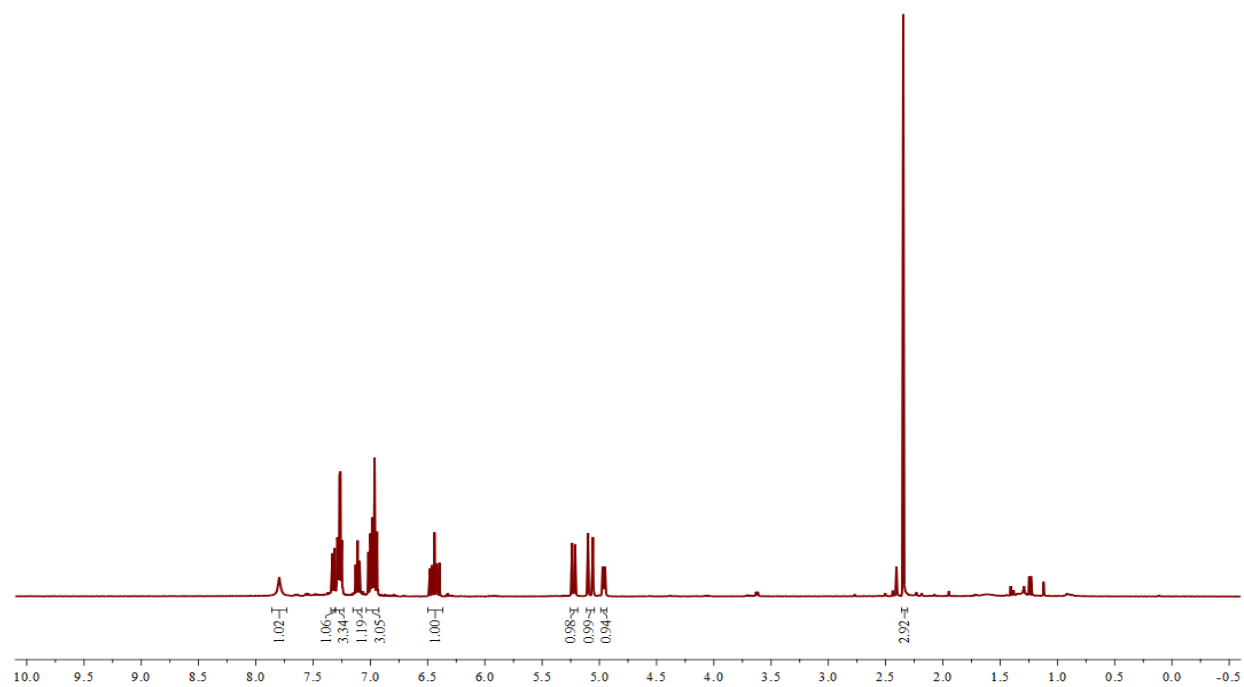
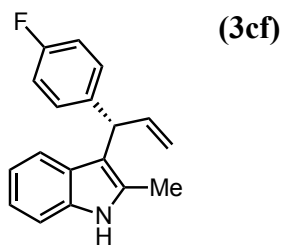


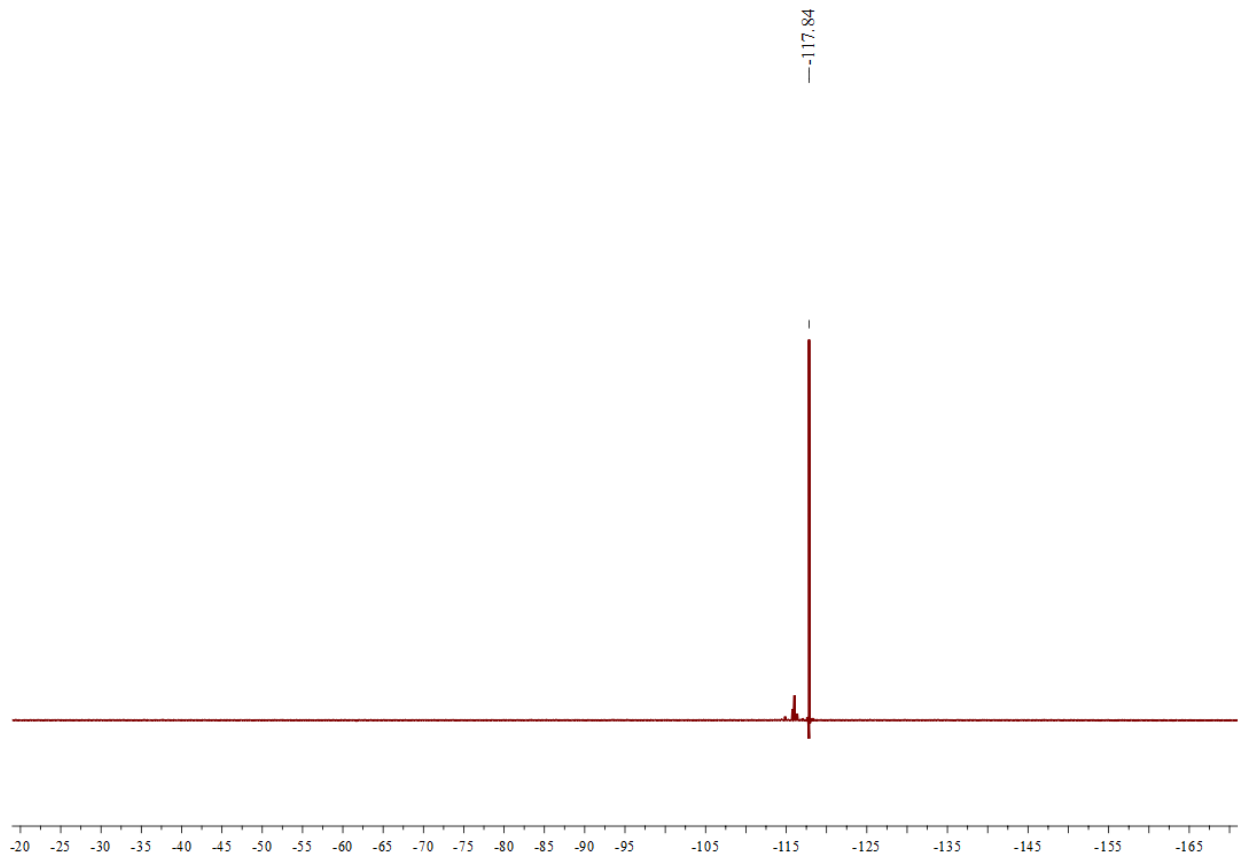


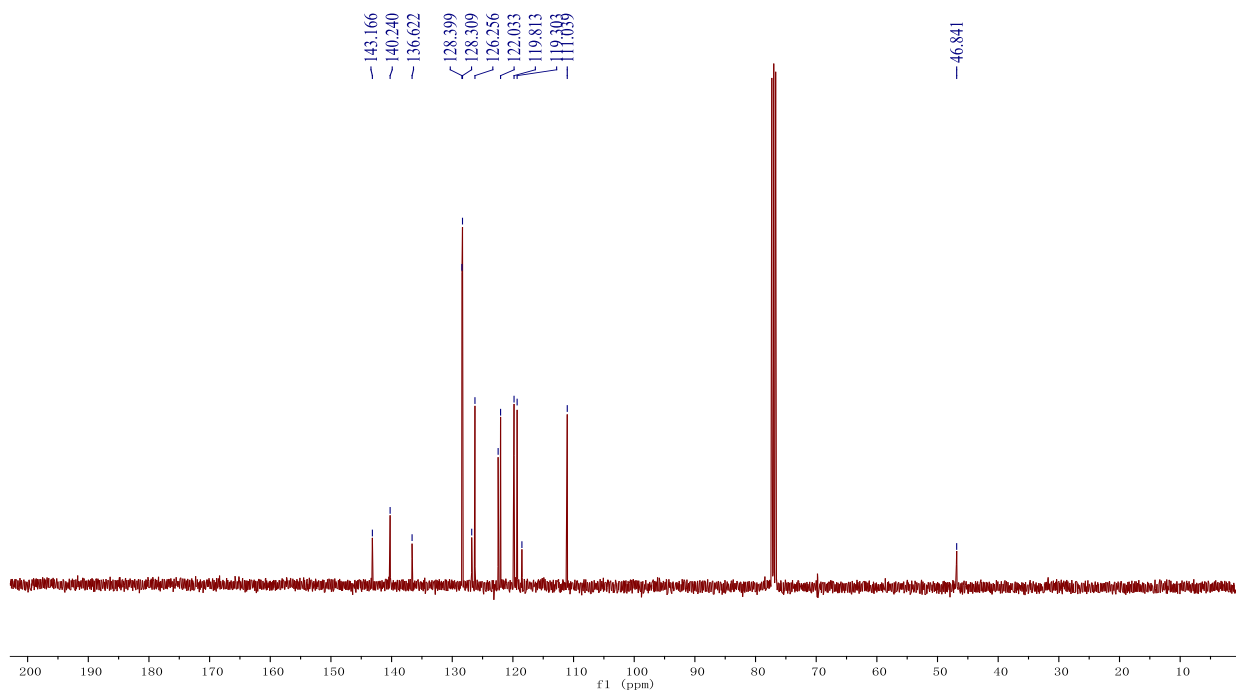
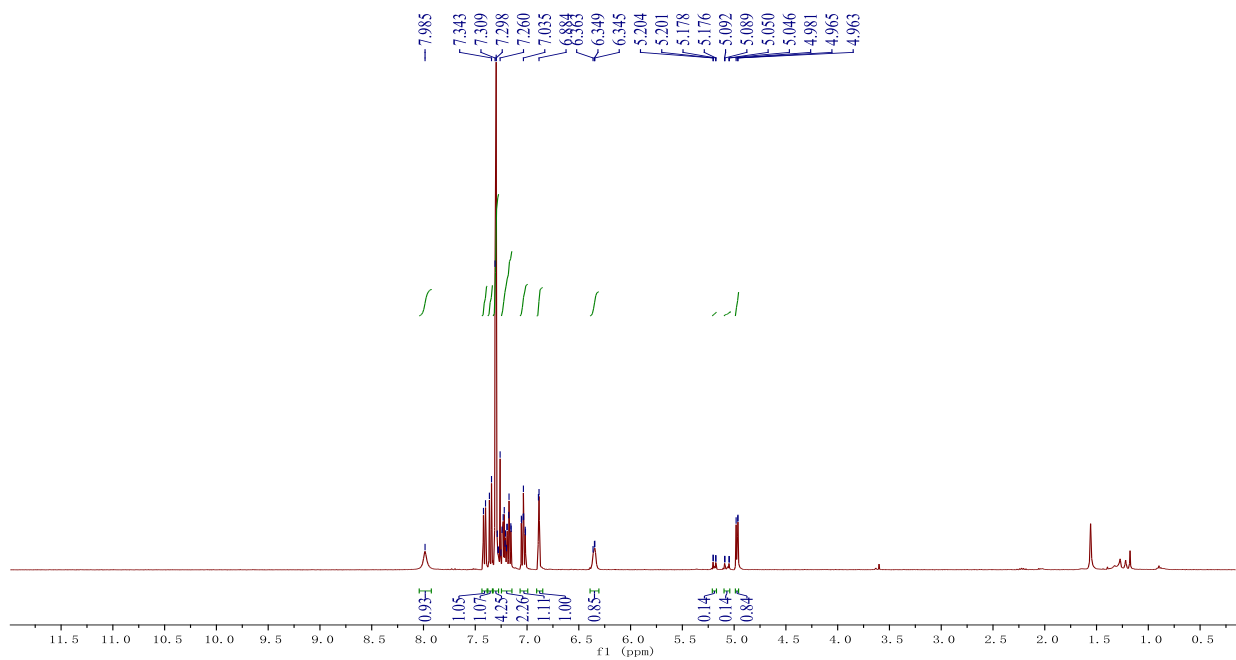
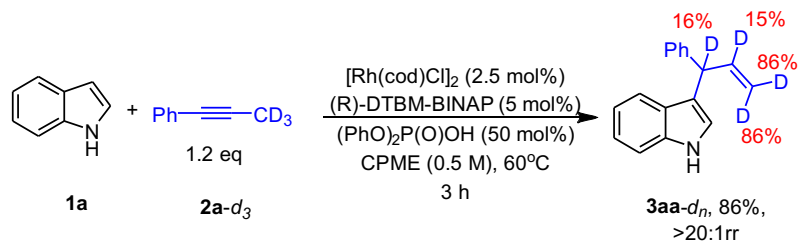


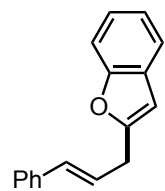
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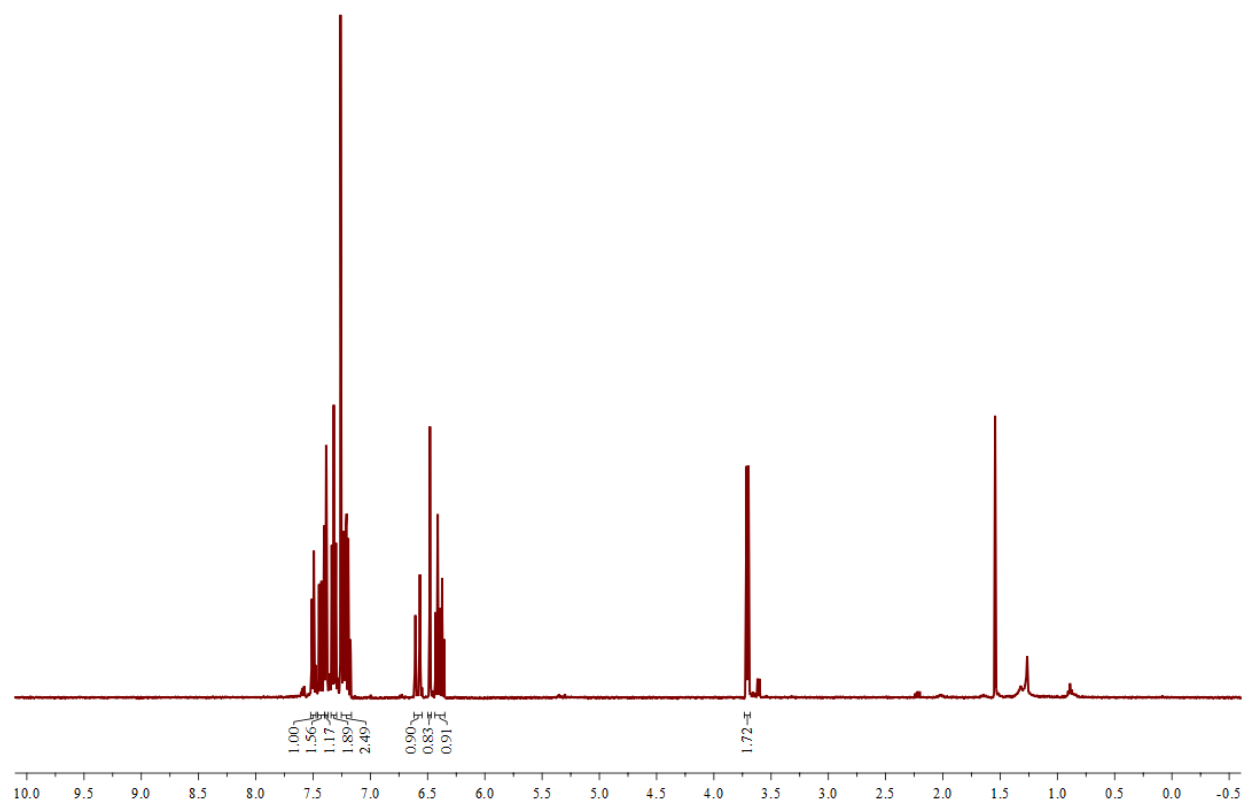


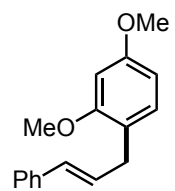




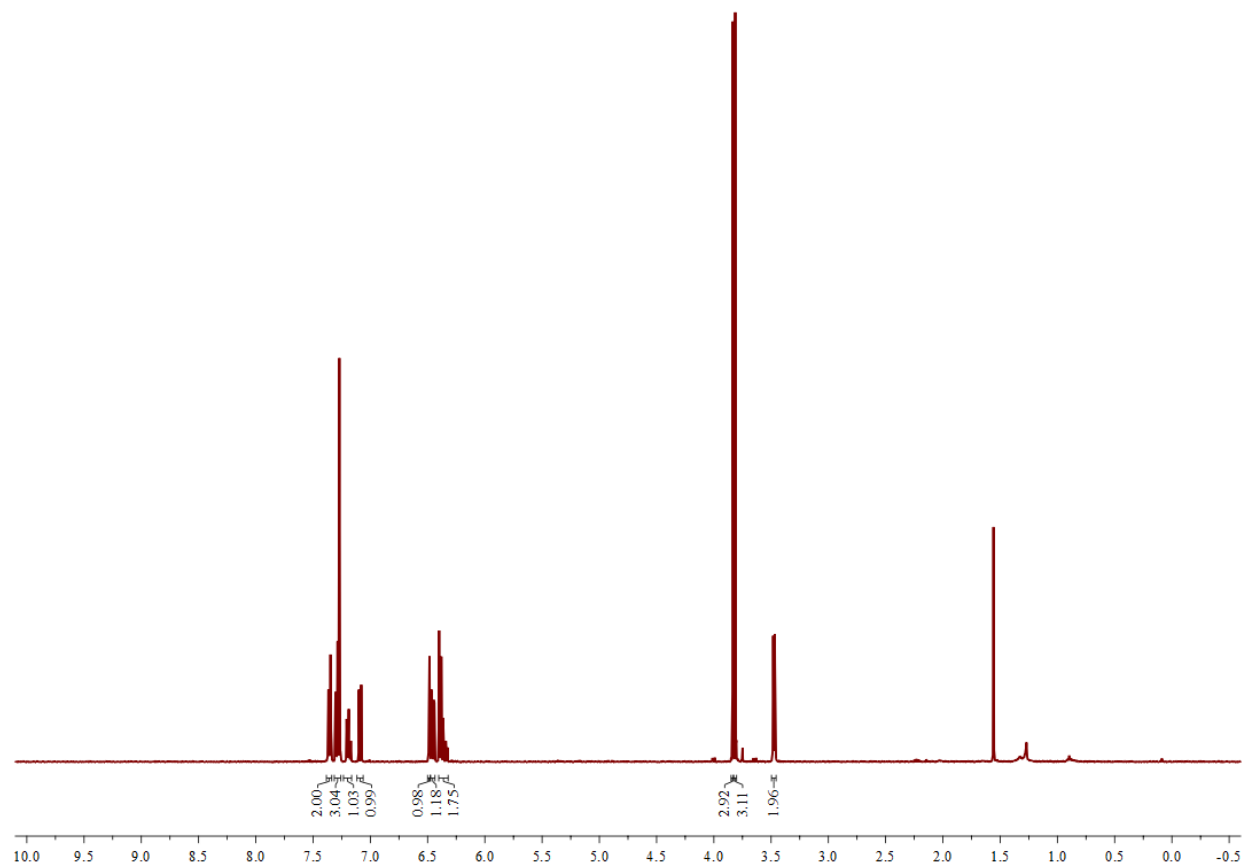


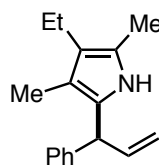
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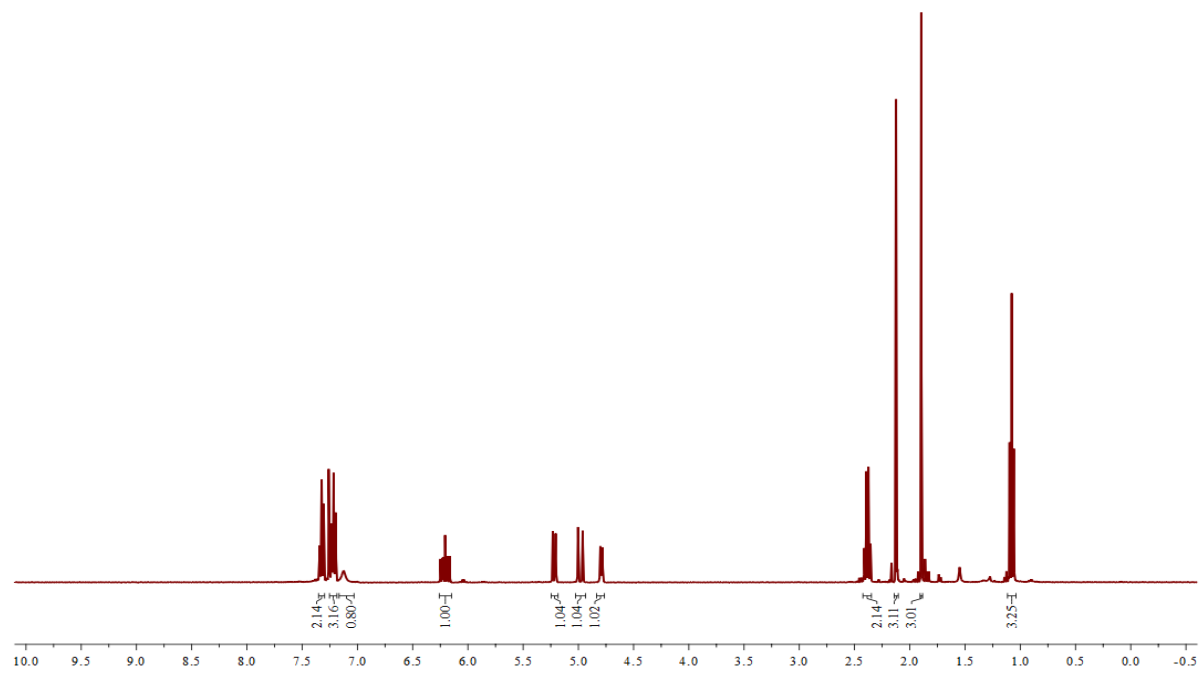


1-phenyl-3-(2,4-dimethoxyphenyl)-1-propene

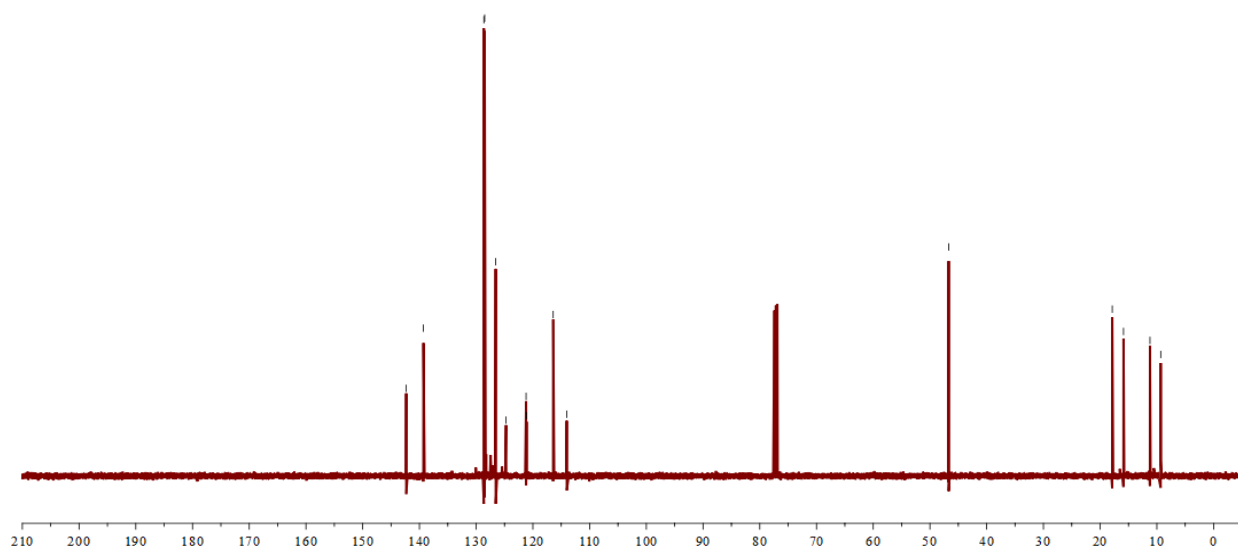




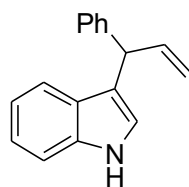
3-ethyl-2,4-dimethyl-5-(1-phenylallyl)-1H-pyrrole



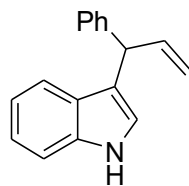
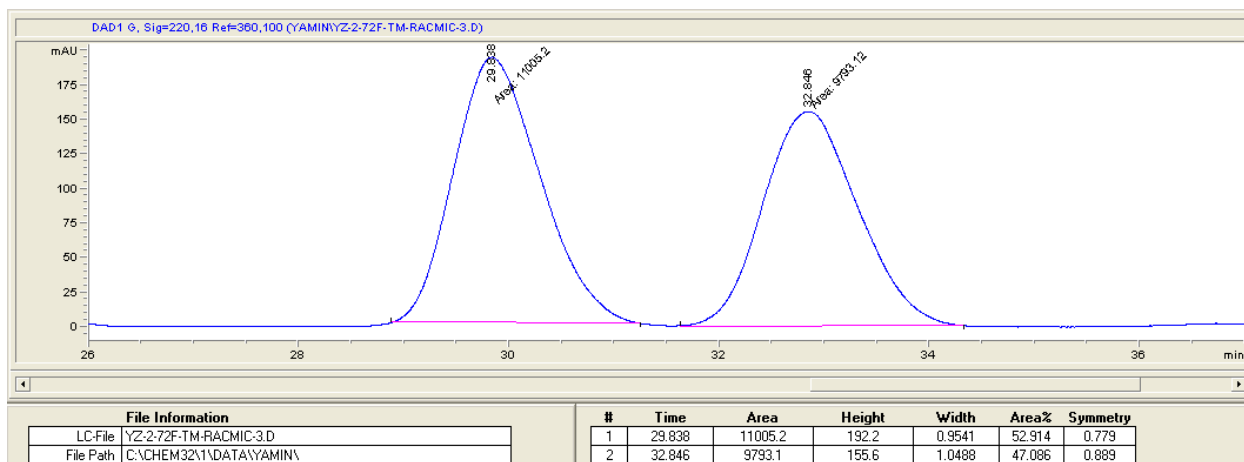
142.33
 139.29
 128.63
 128.50
 126.56
 124.74
 121.20
 121.12
 116.42
 114.03
 -46.70
 17.86
 15.88
 11.21
 9.31



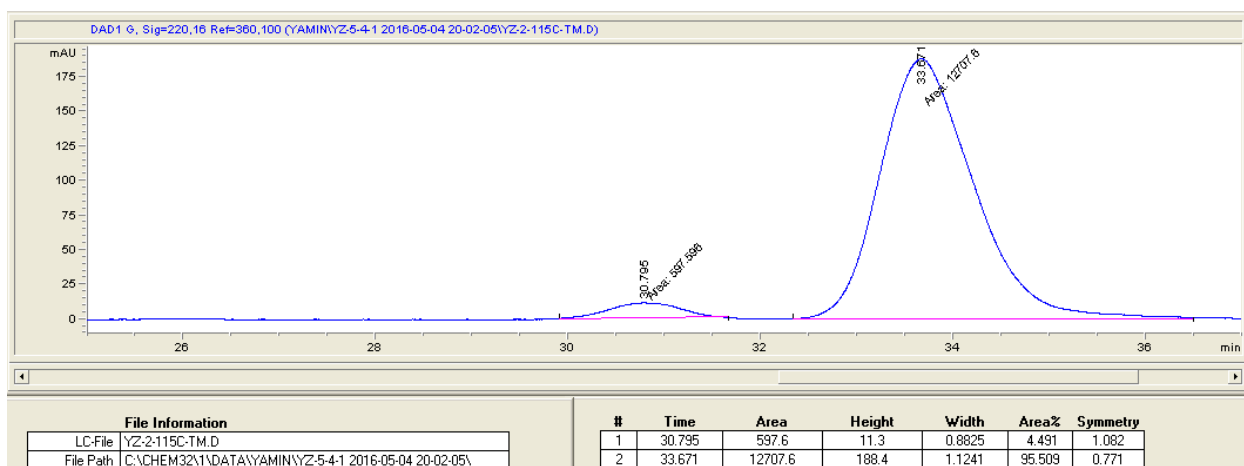
6. SFC Spectra

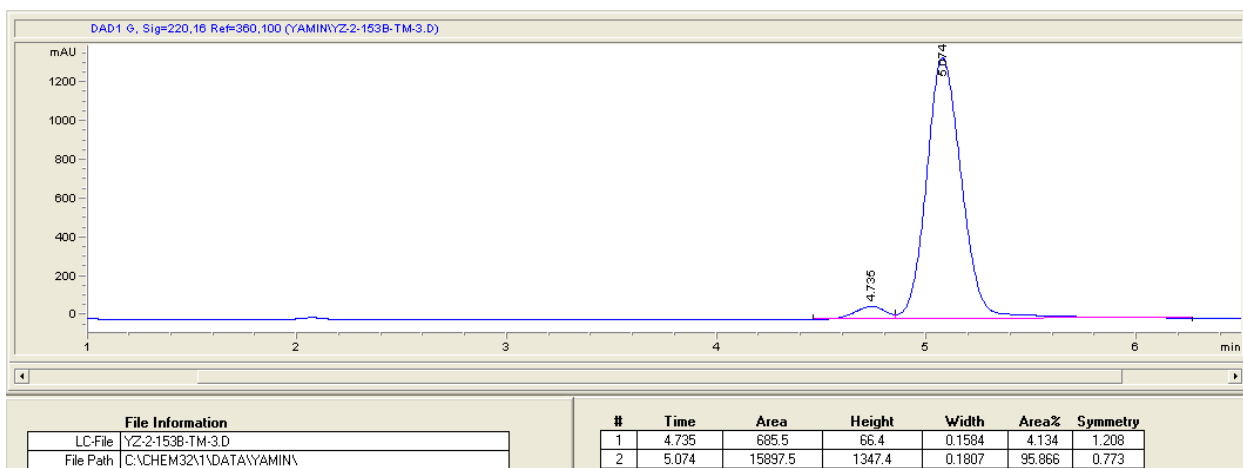
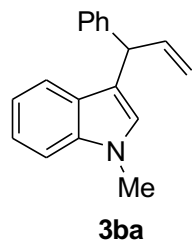
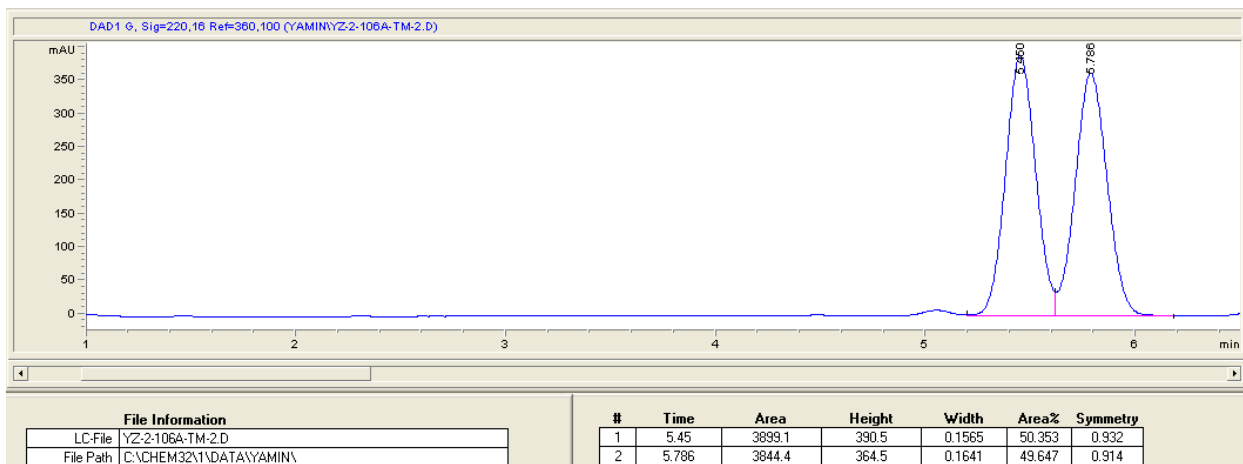
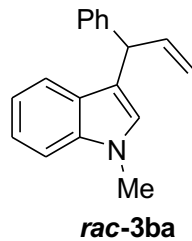


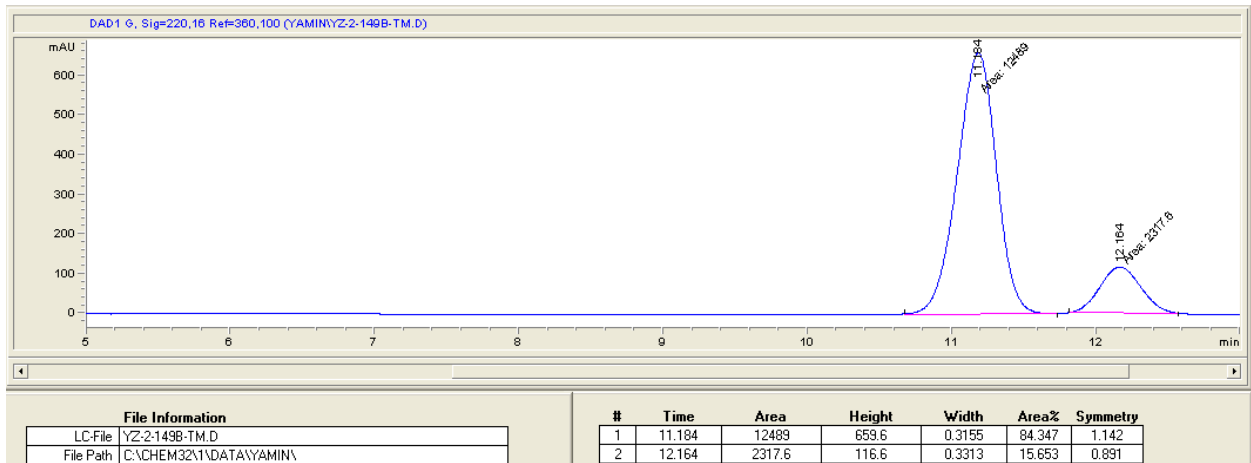
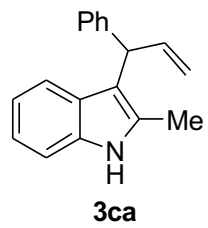
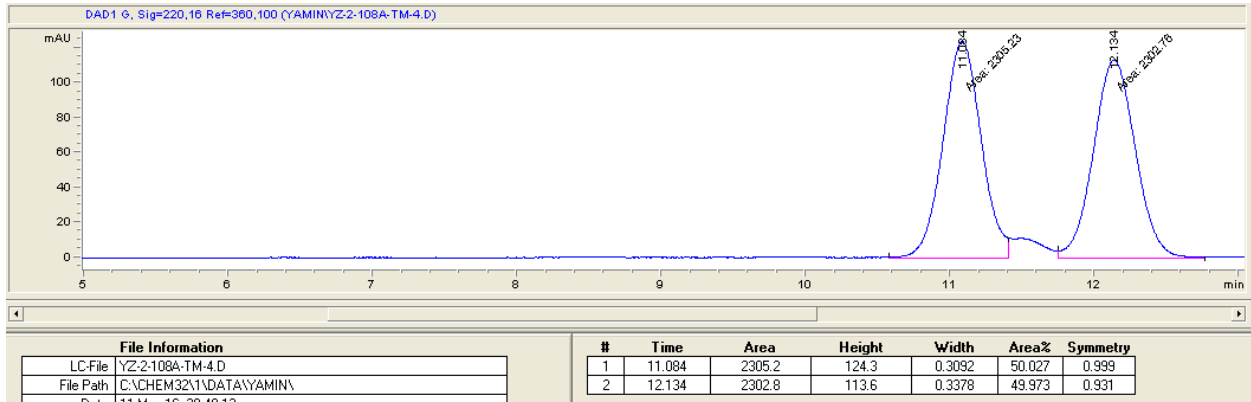
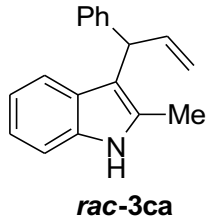
rac-3aa

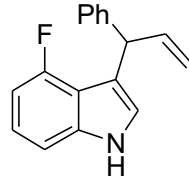


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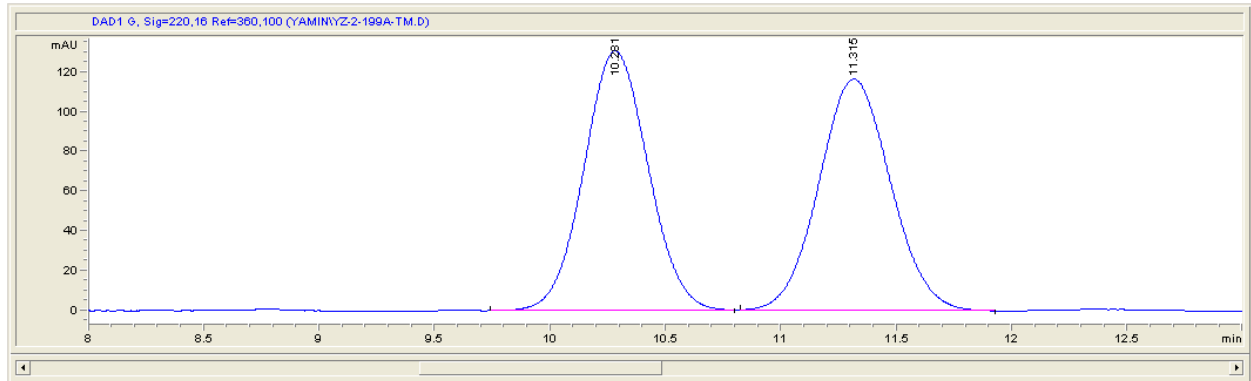




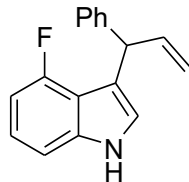




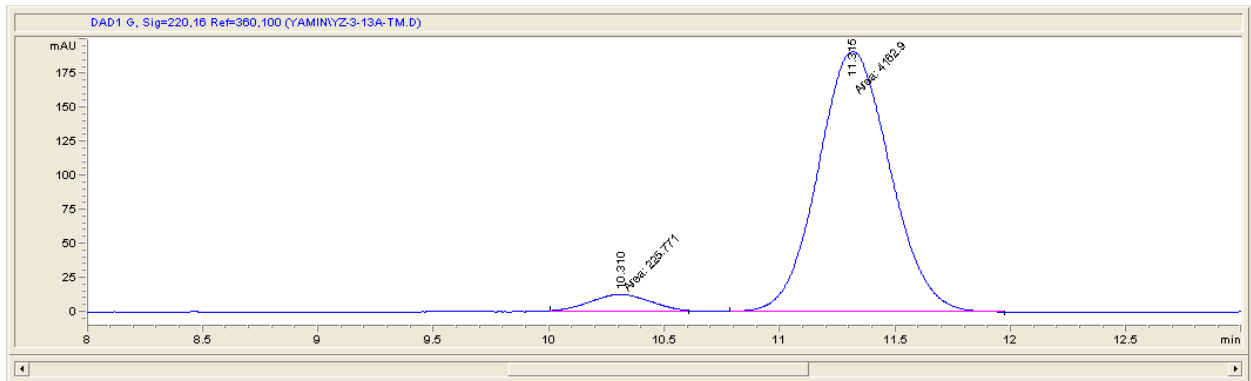
rac-3da



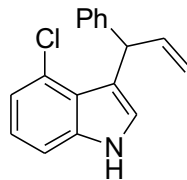
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File Path	C:\CHEM32\1\DATA\YAMIN\	2	11.315	2530.5	116.7	0.331	49.892	0.931



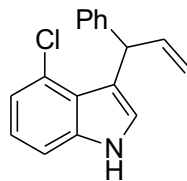
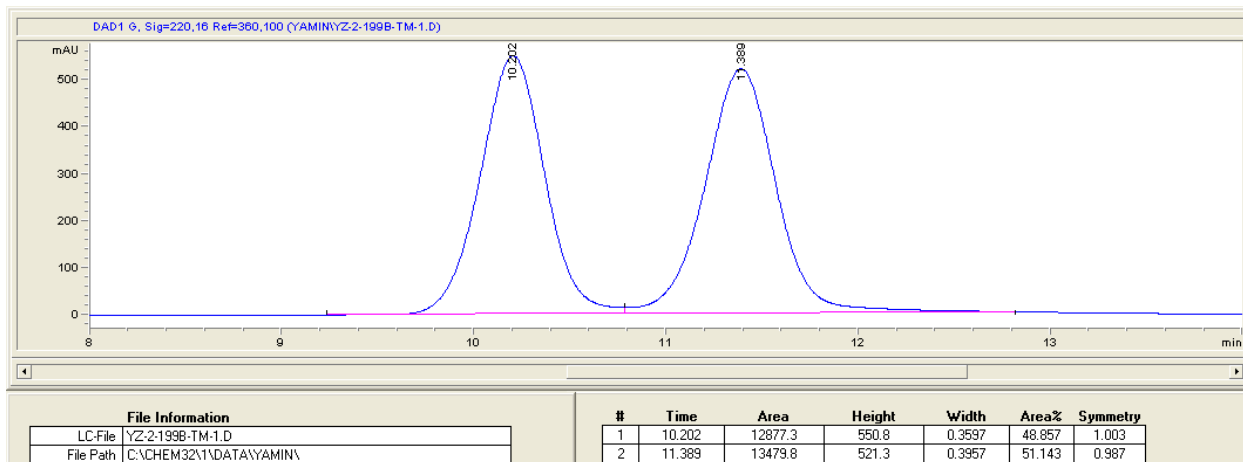
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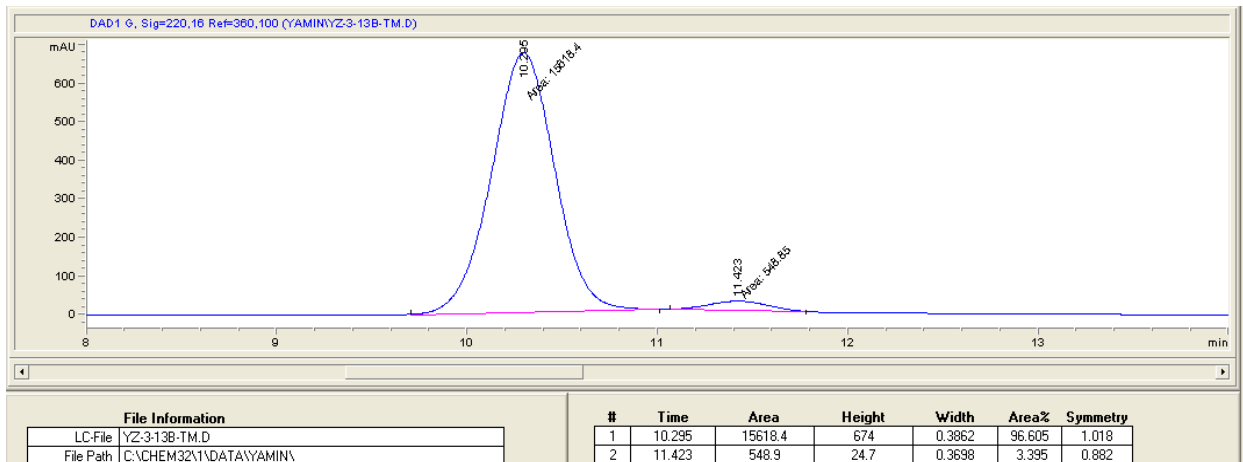
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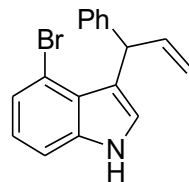


rac-3ea

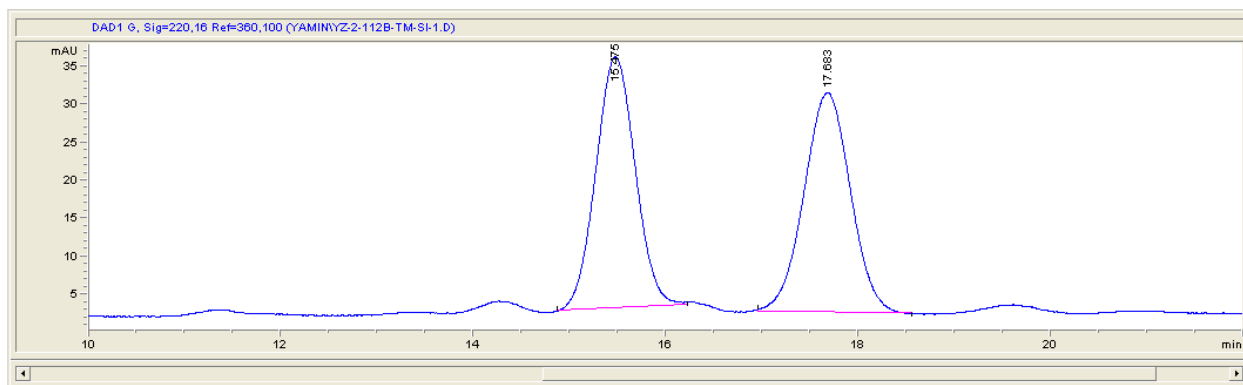


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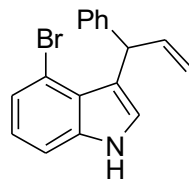




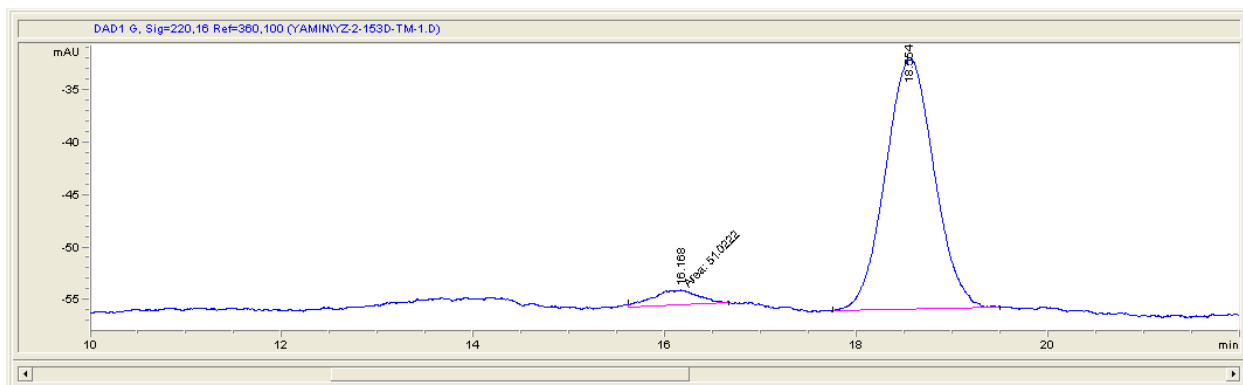
rac-3fa



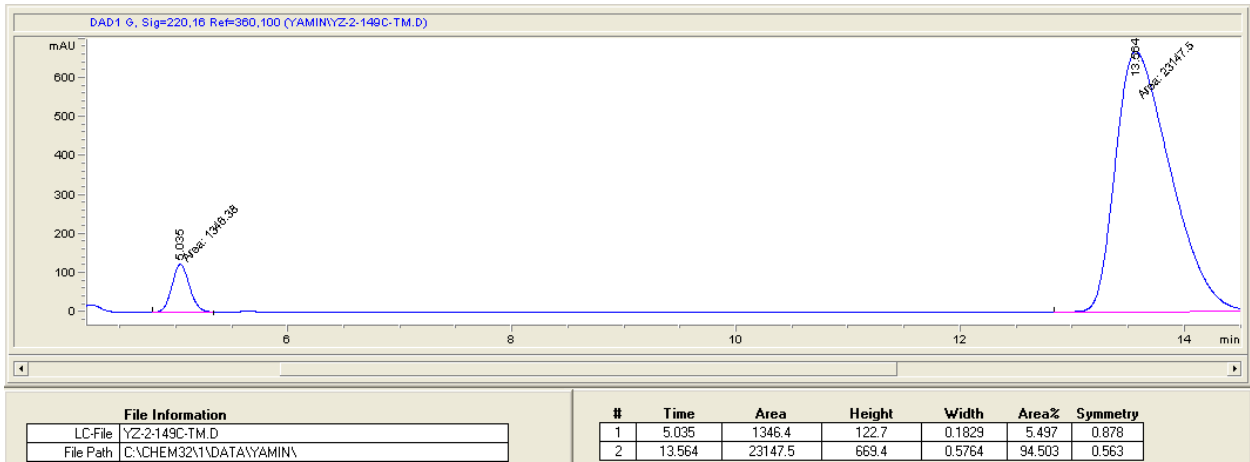
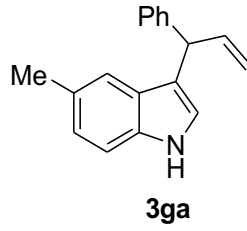
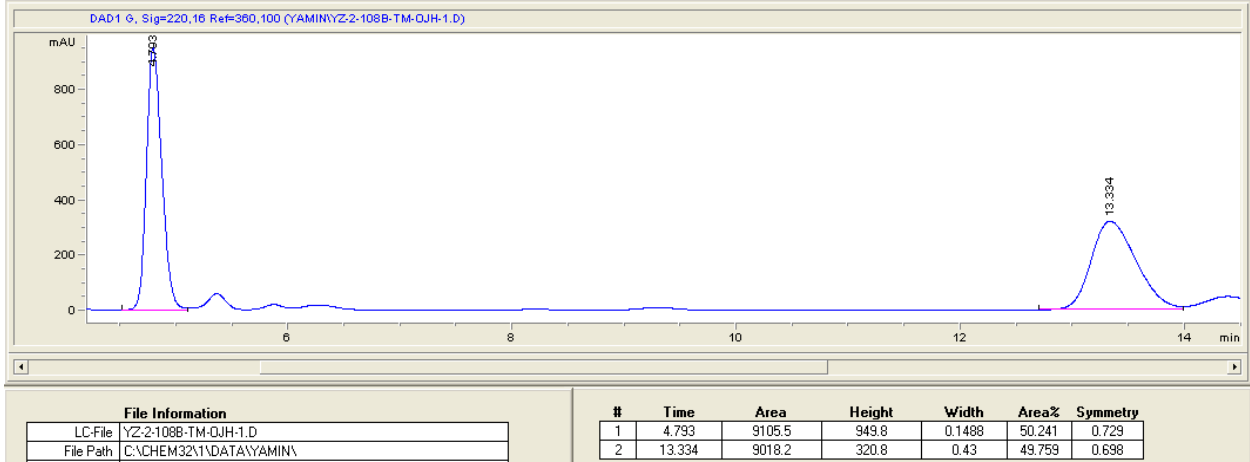
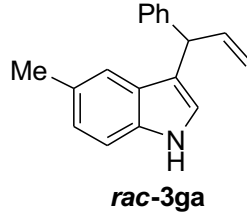
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File Path	C:\CHEM32\1\DATA\YAMIN\	2	17.683	969.5	28.9	0.4598	50.583	1.008

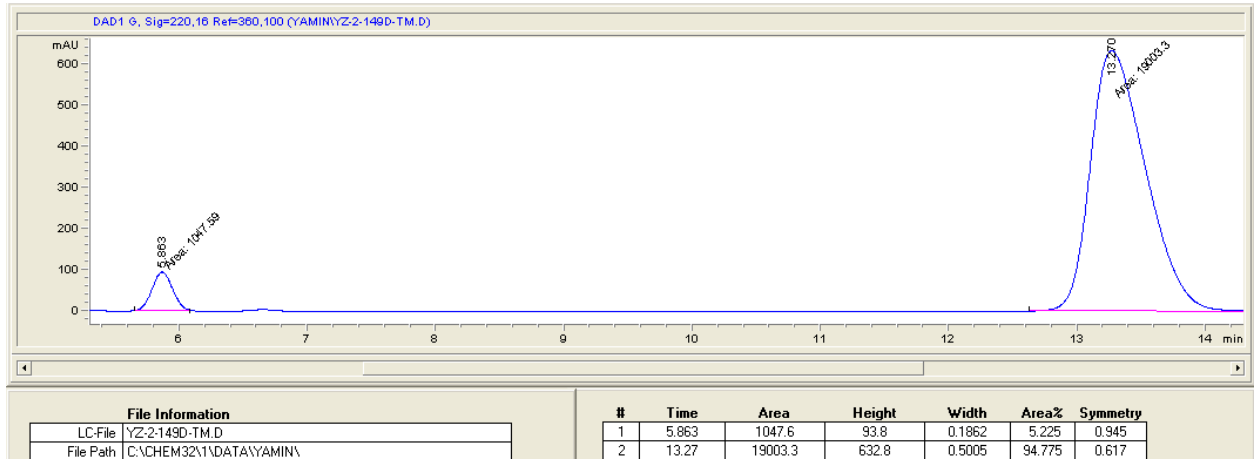
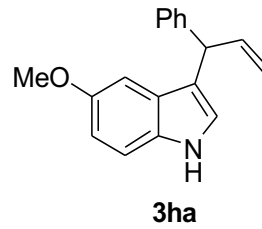
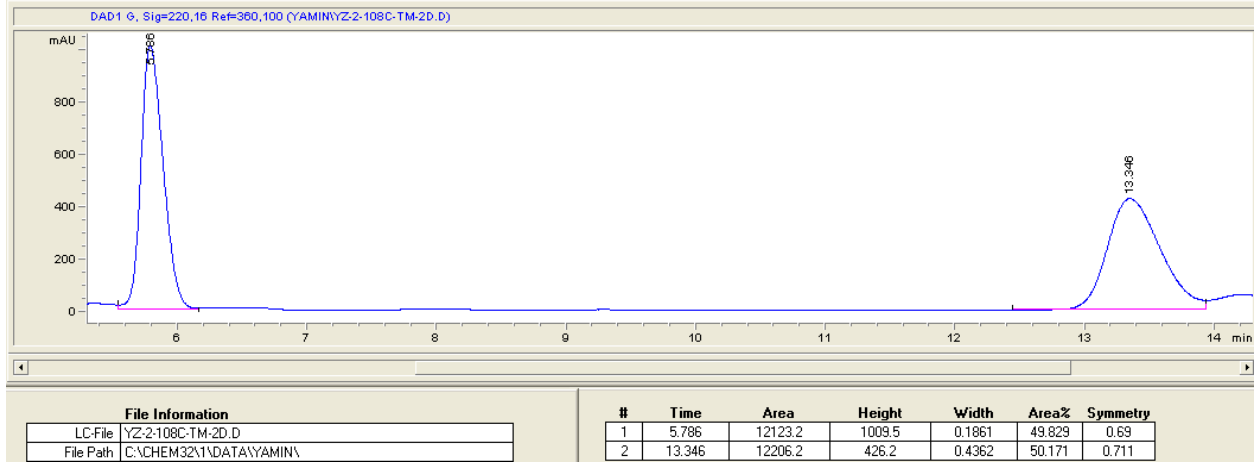
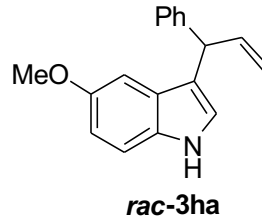


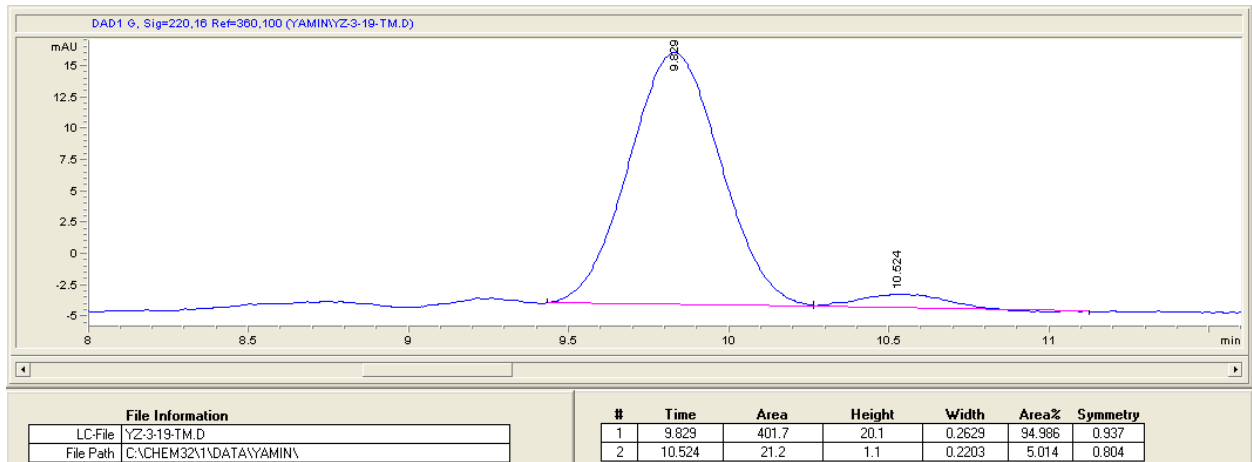
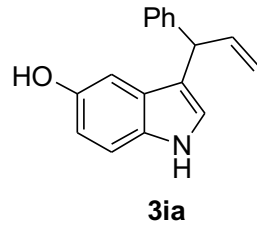
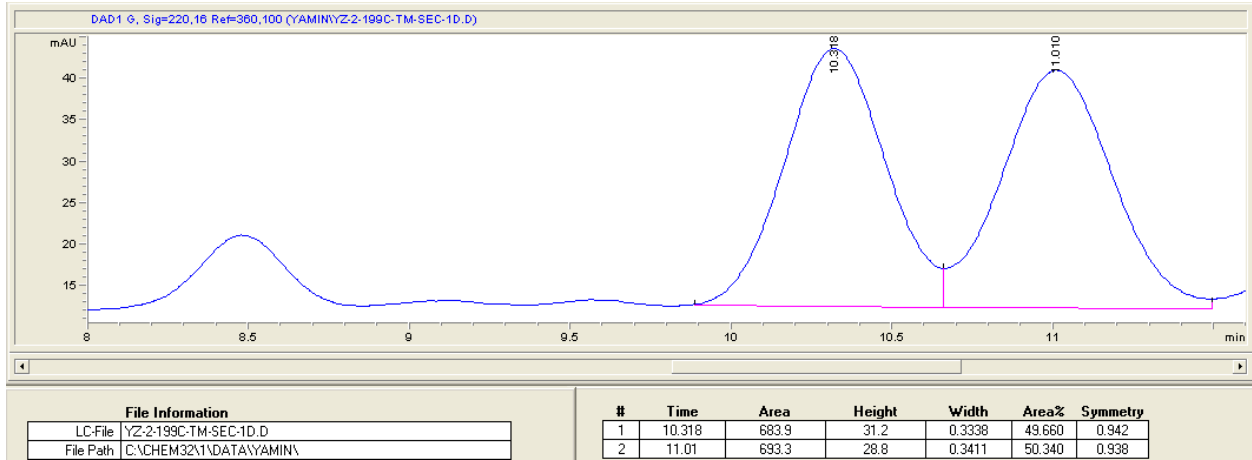
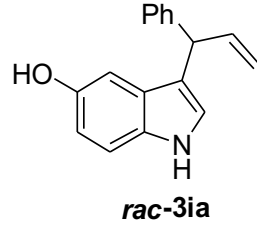
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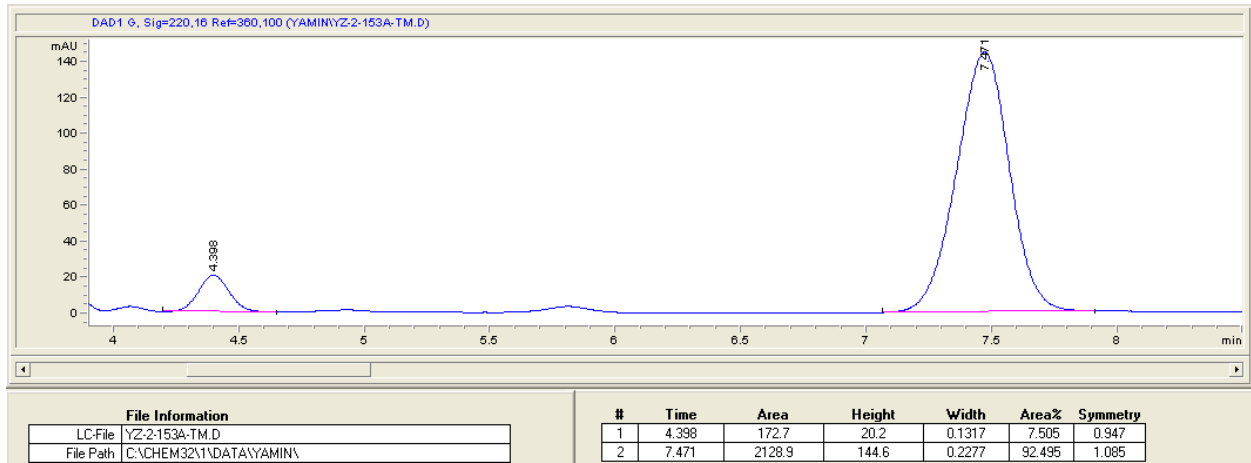
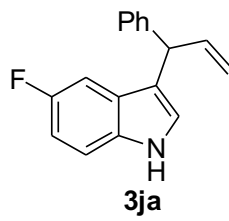
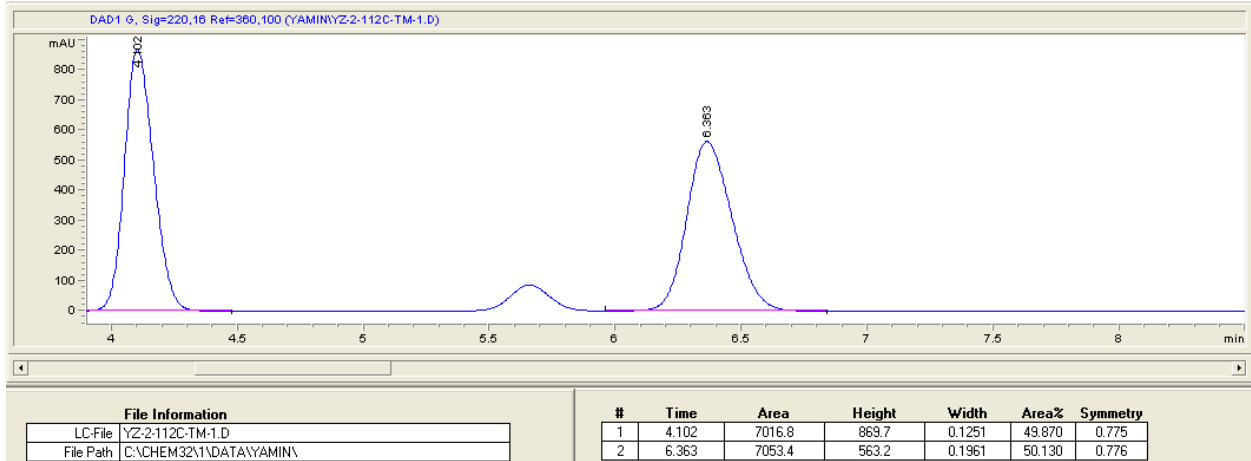
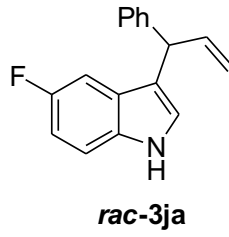


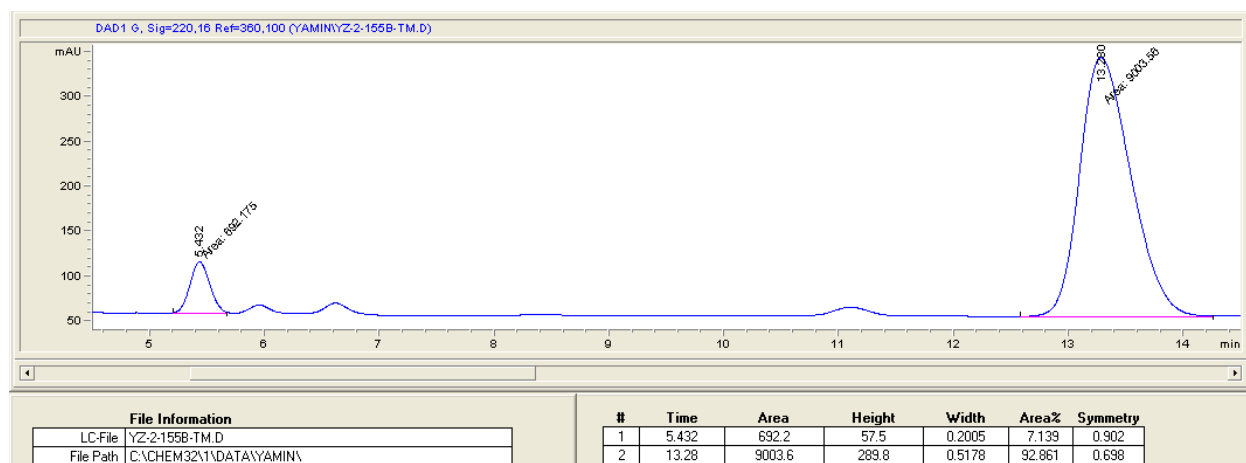
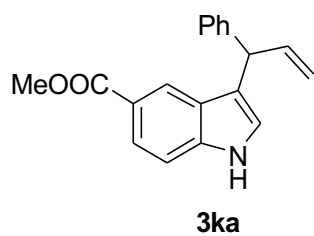
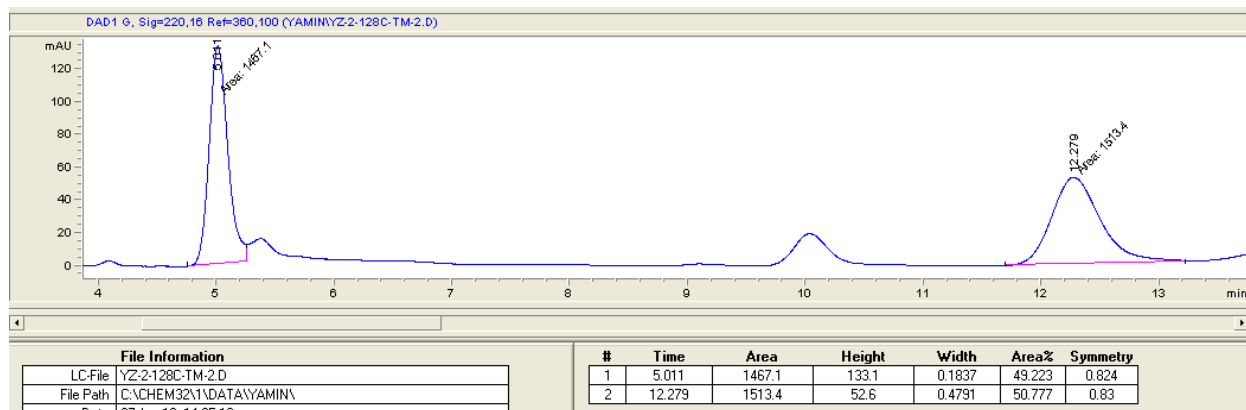
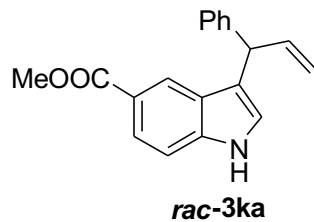
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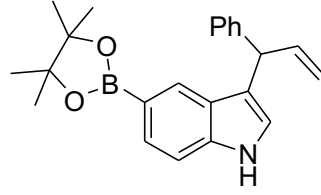




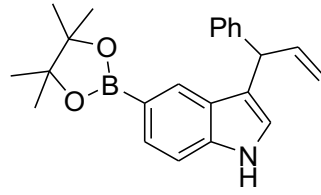
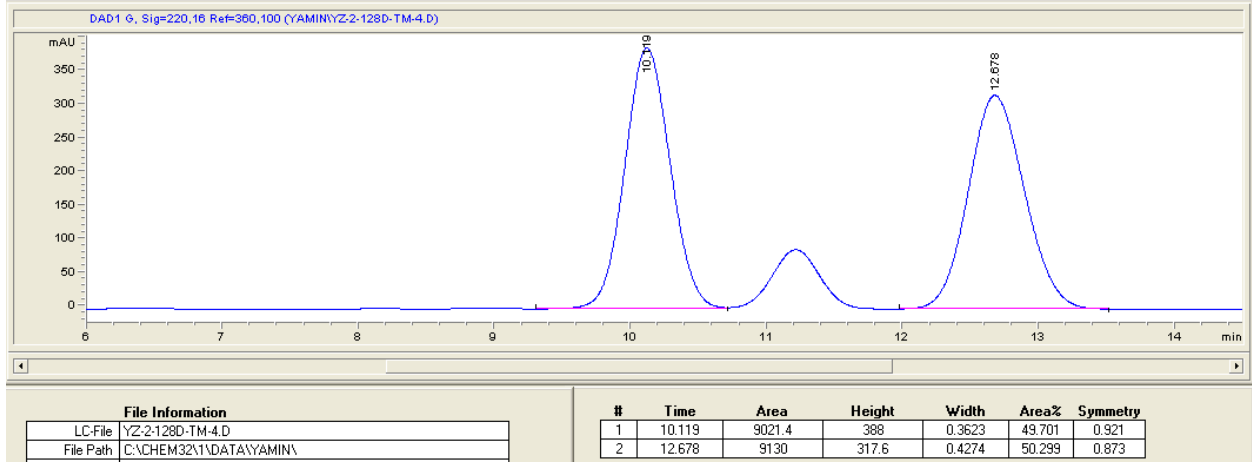




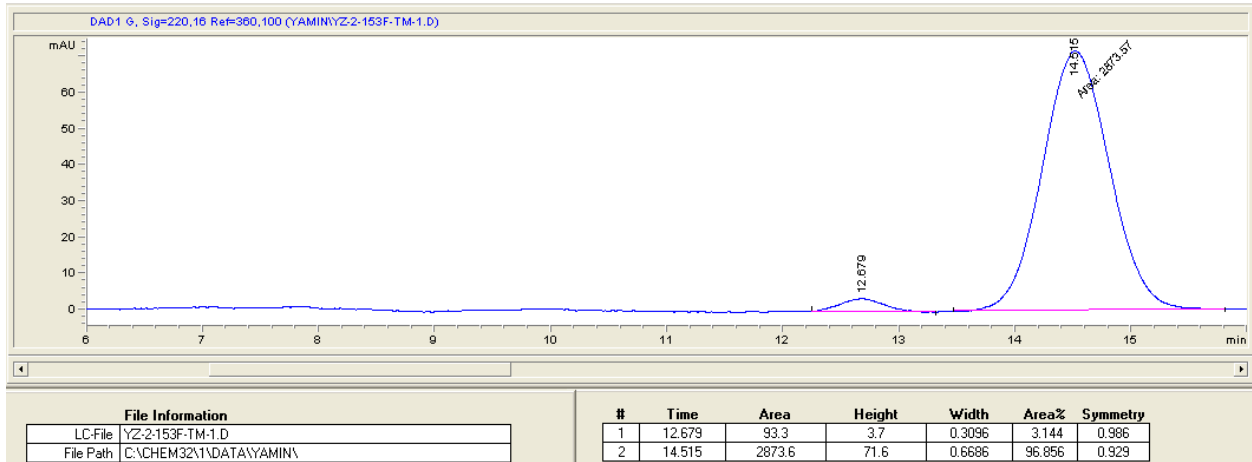


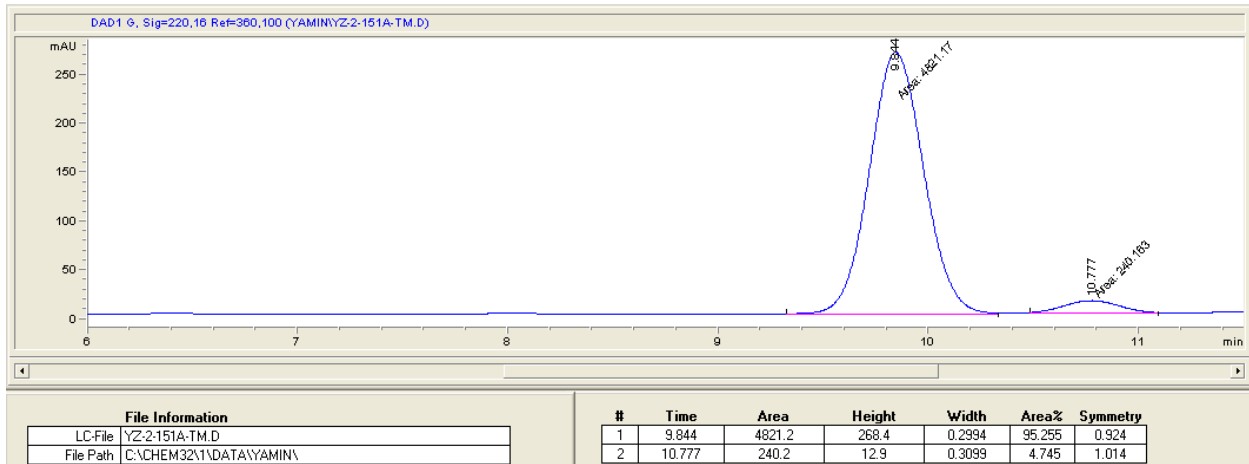
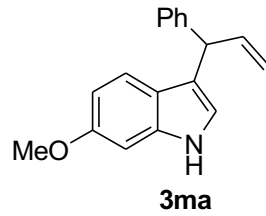
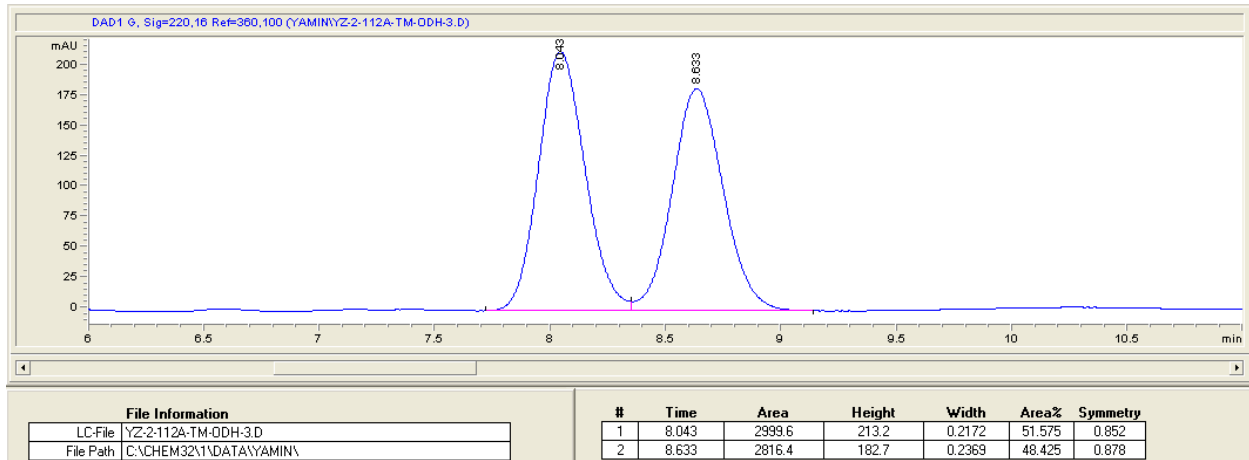
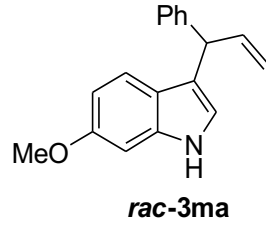


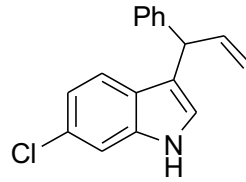
rac-3la



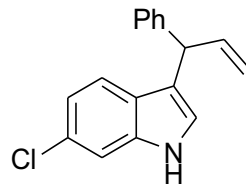
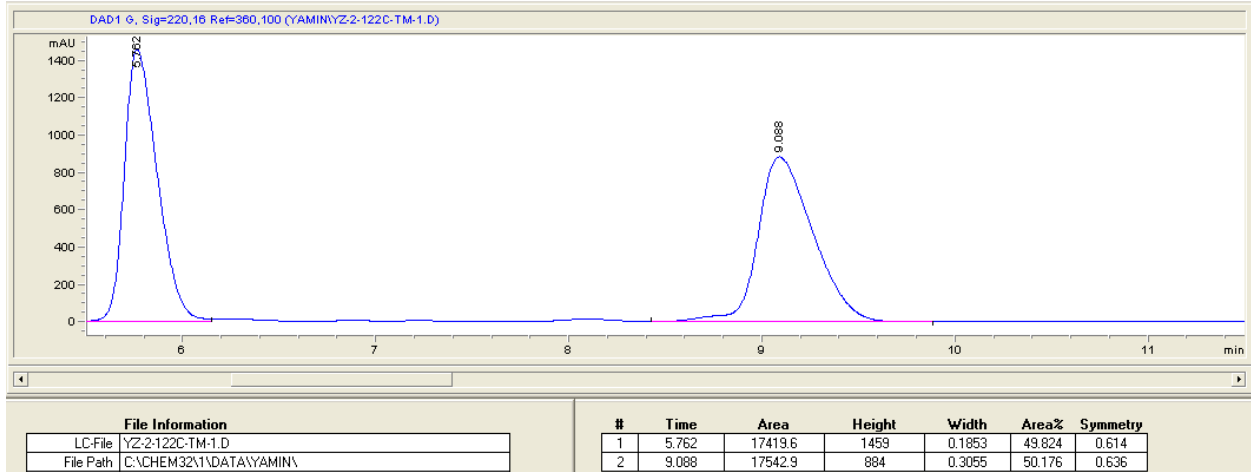
3la



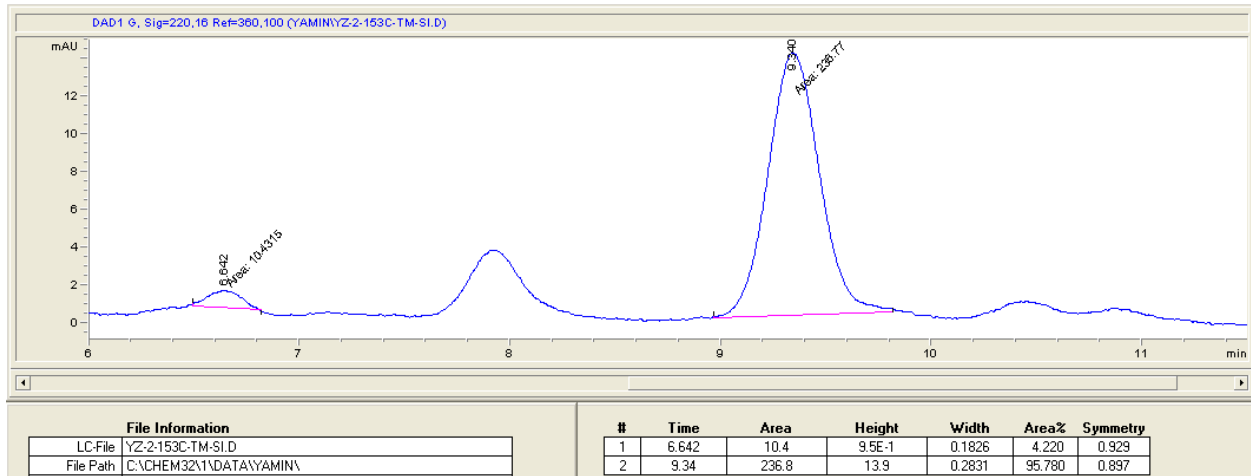


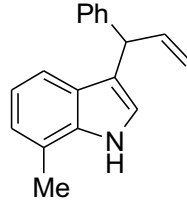


rac-3na

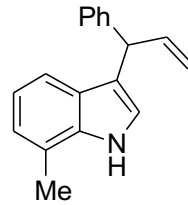
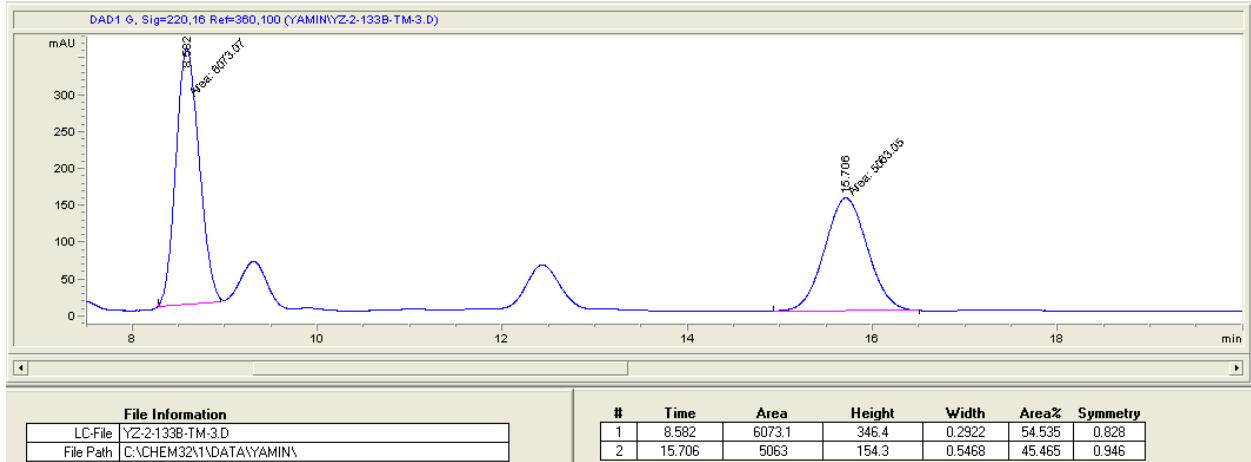


3na

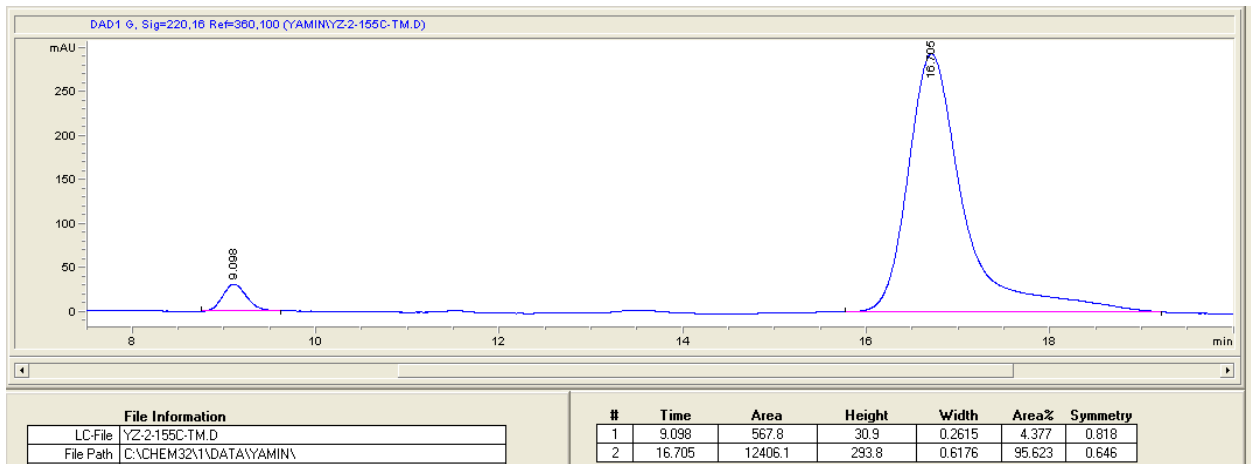


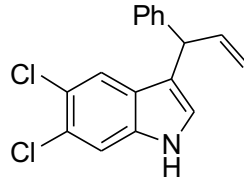


rac-30a

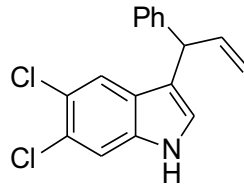
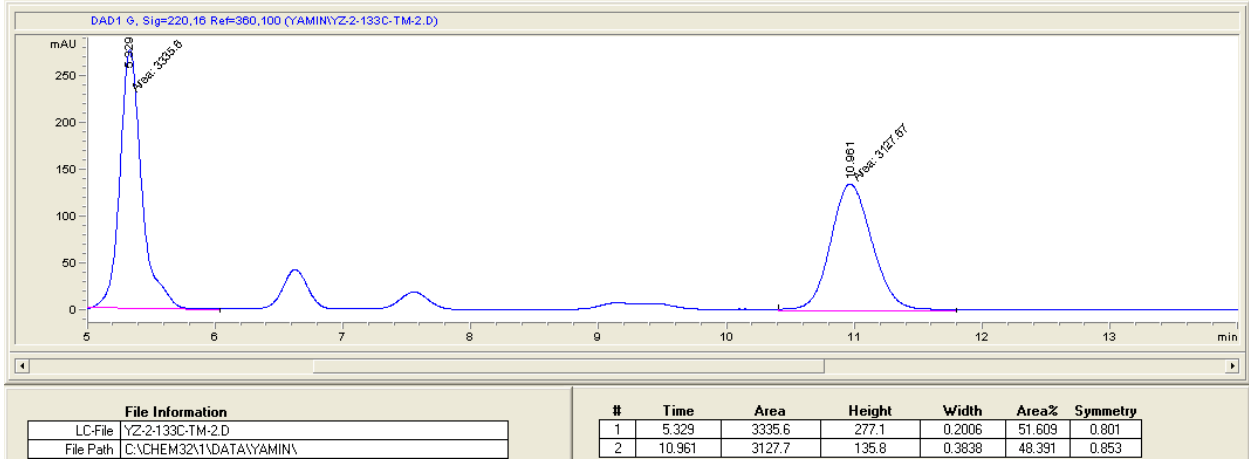


30a

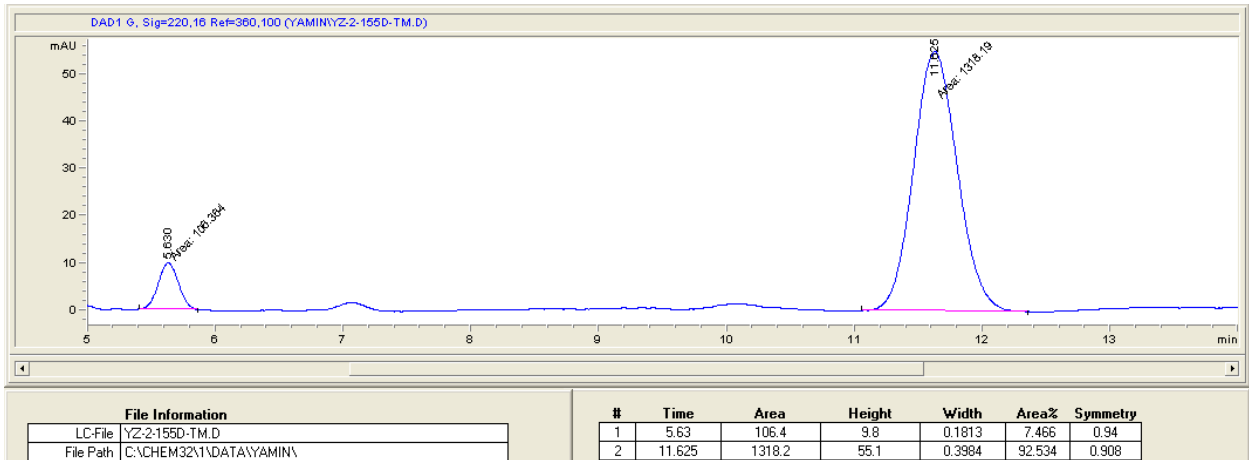


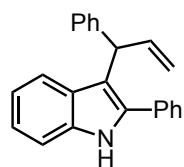


rac-3pa

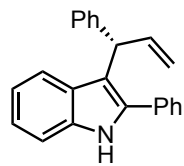
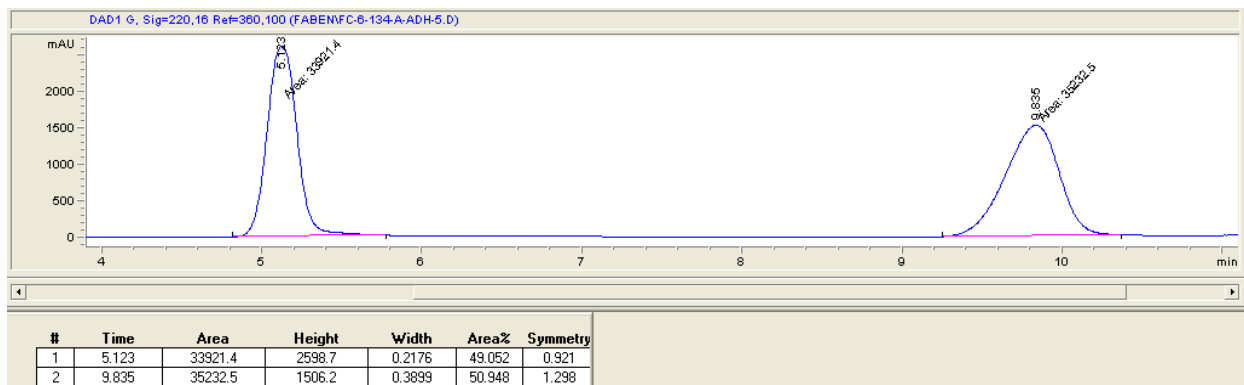


3pa

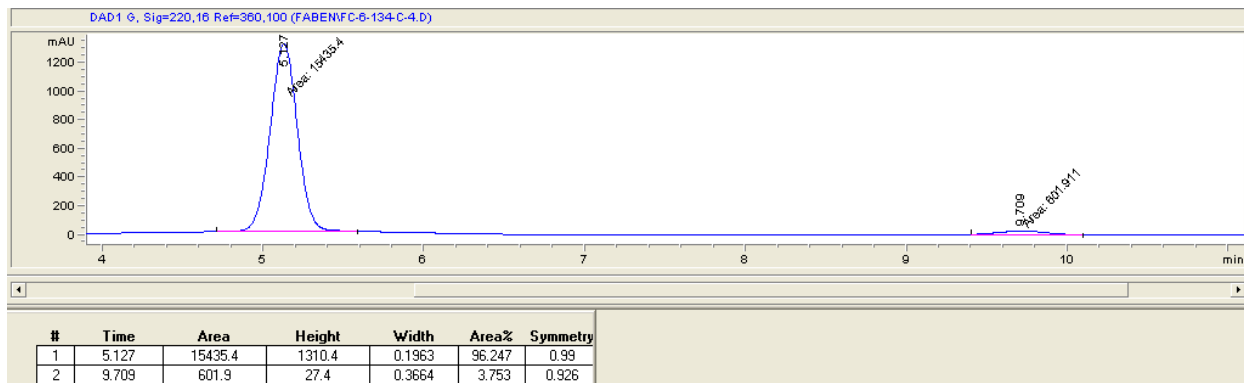


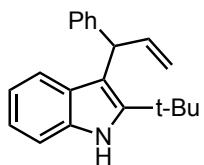


rac-3qa

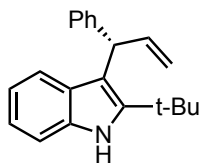
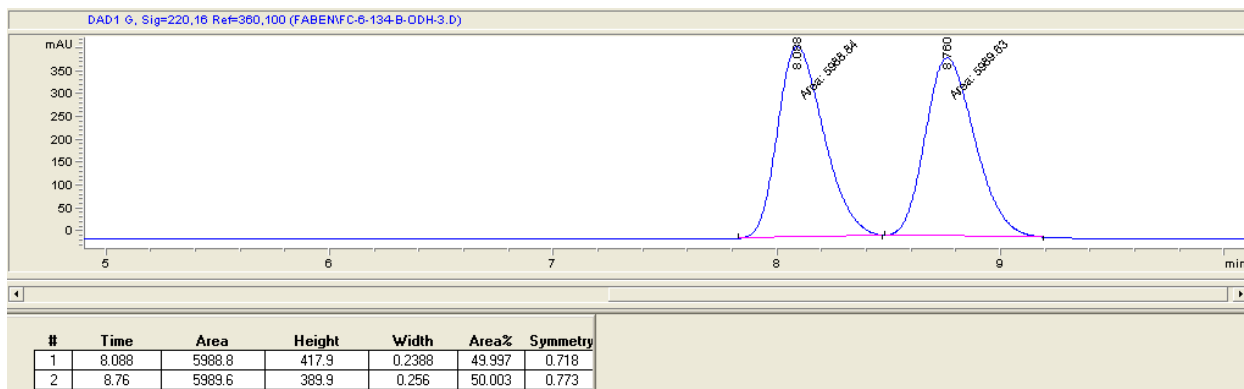


3qa

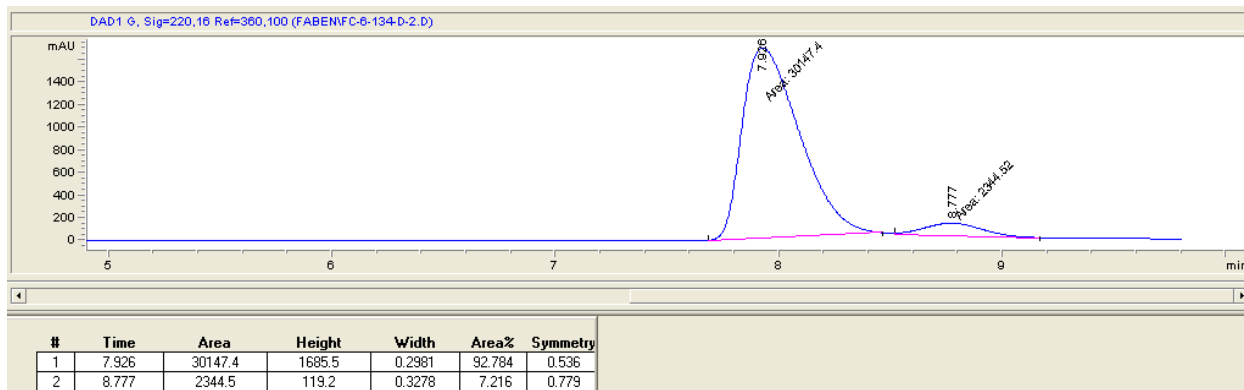


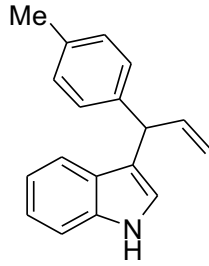


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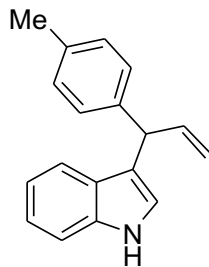
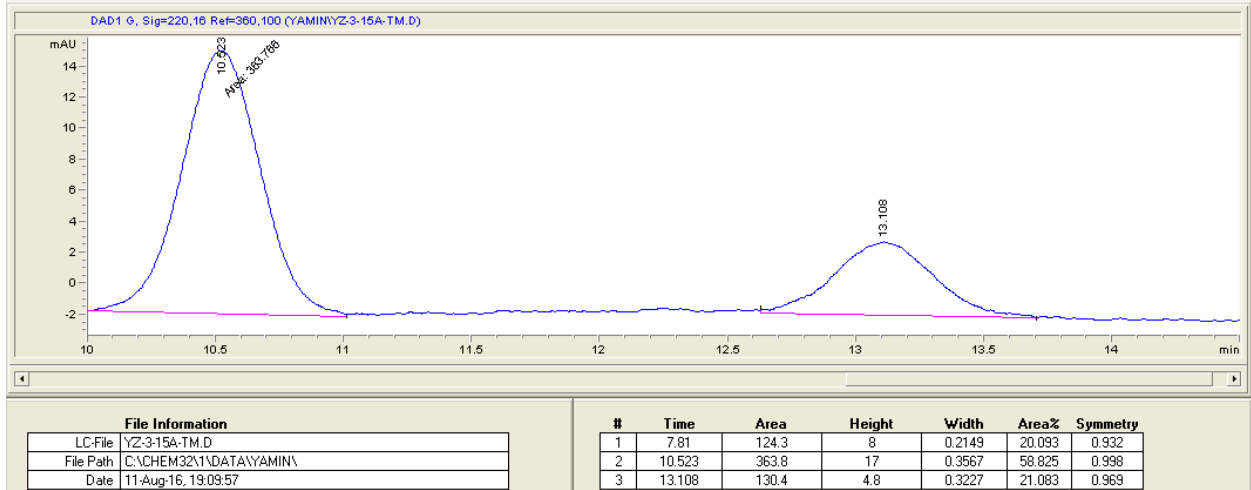


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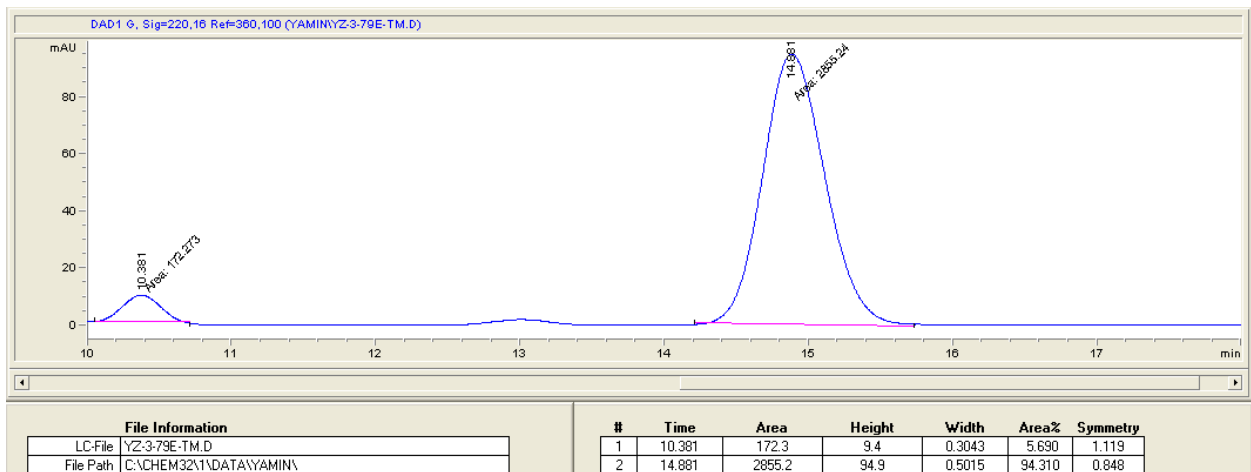


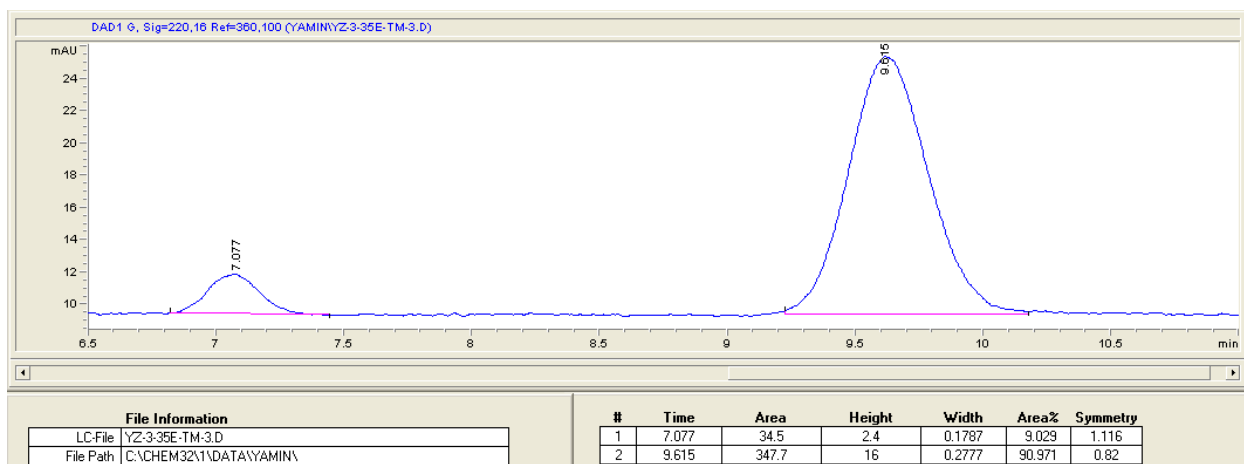
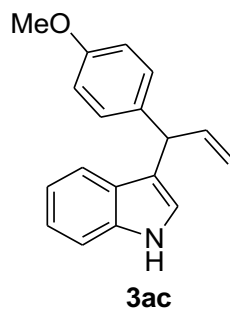
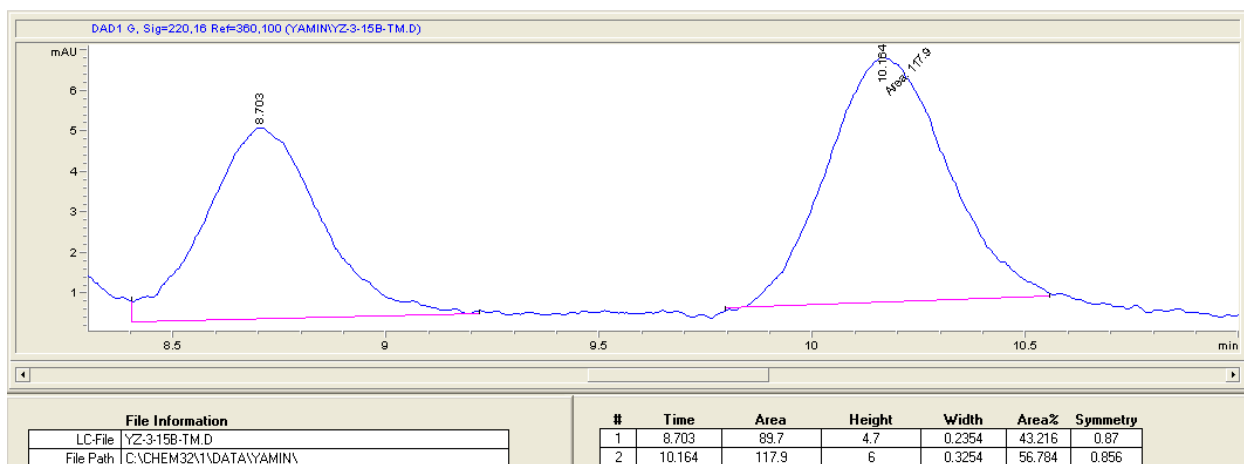
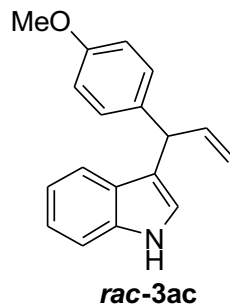


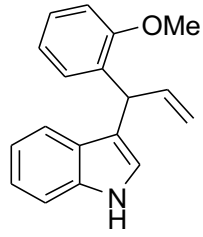
rac-3ab



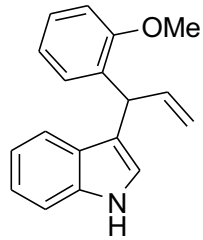
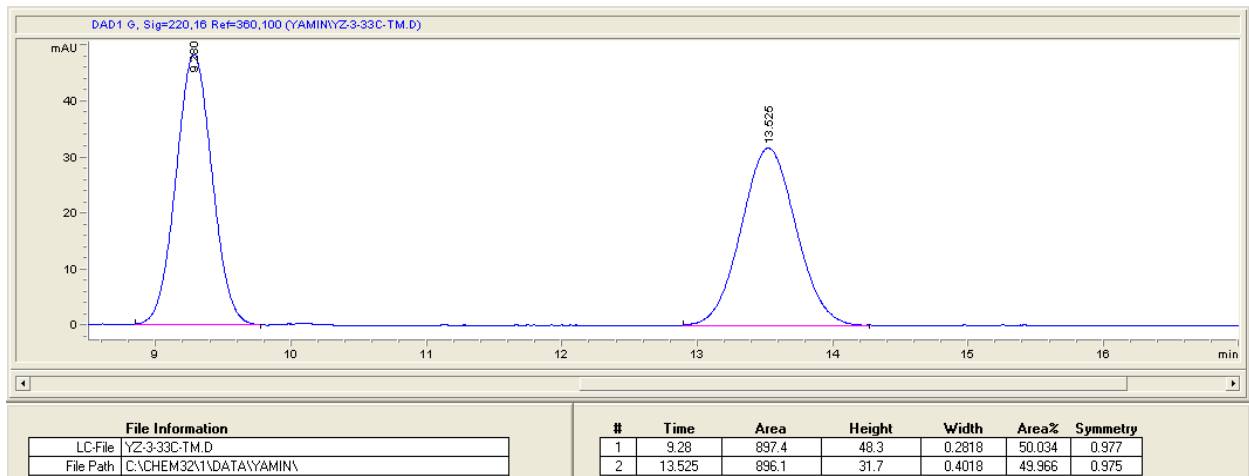
3ab



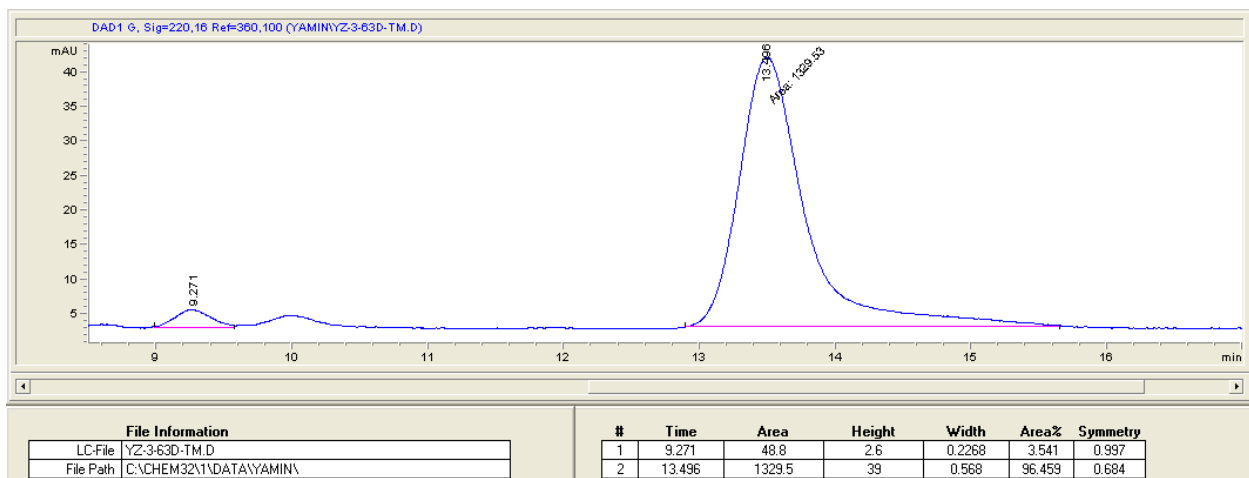


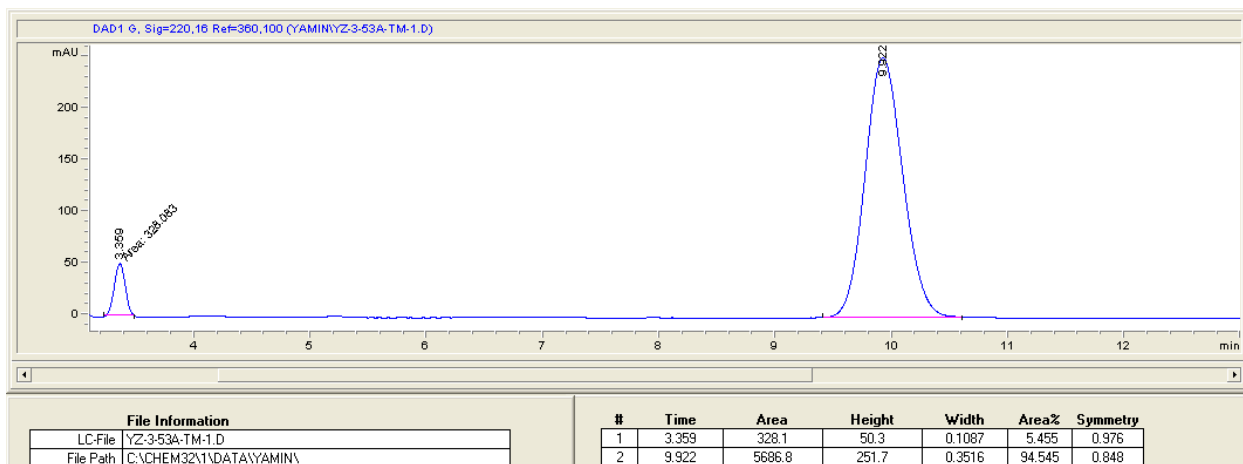
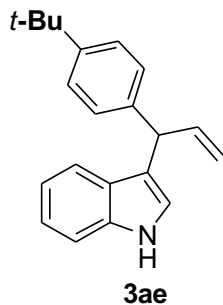
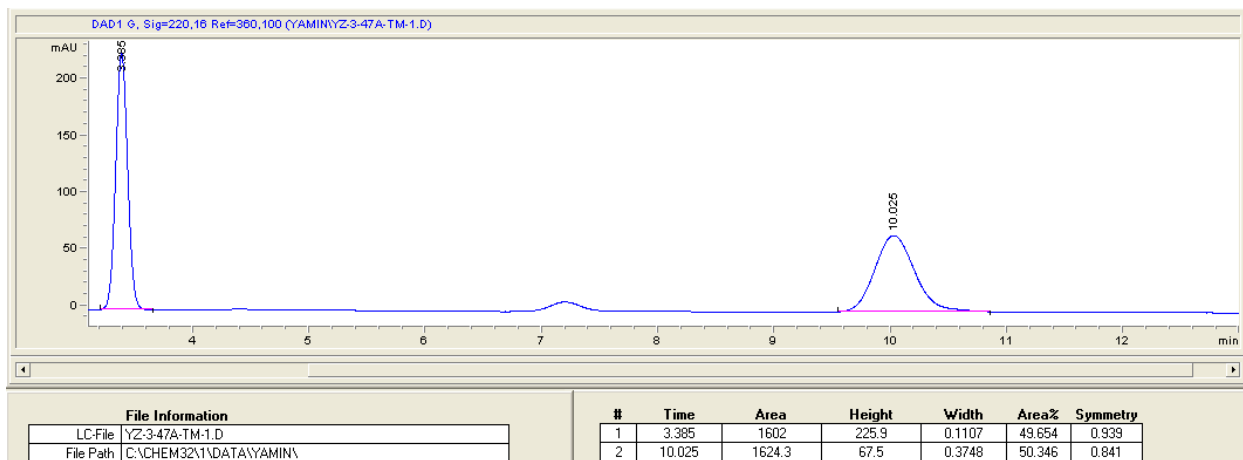
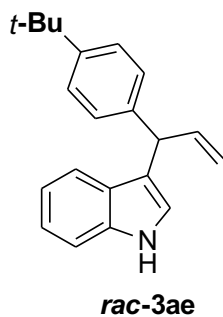


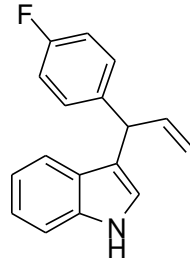
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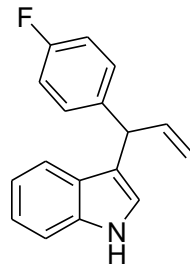
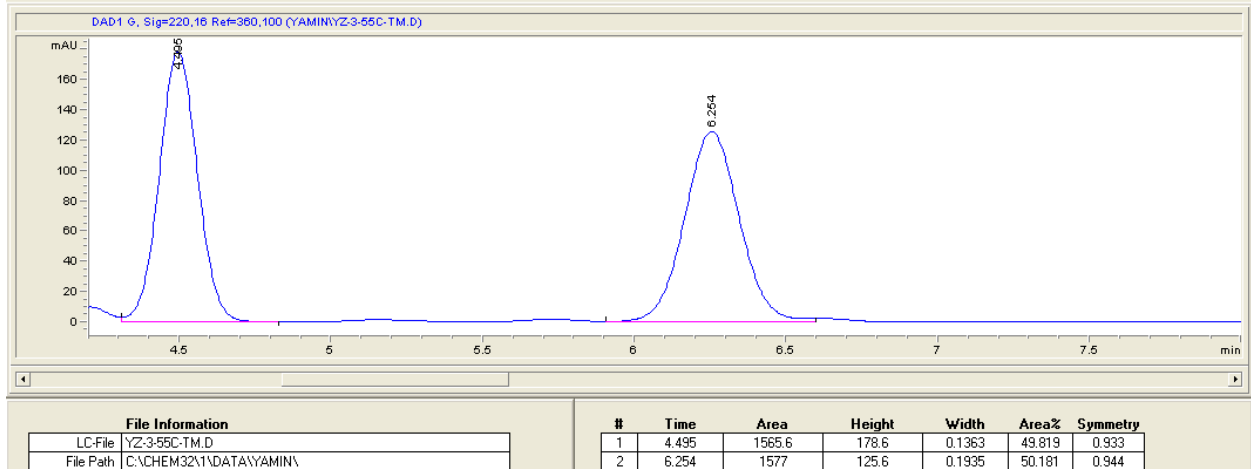
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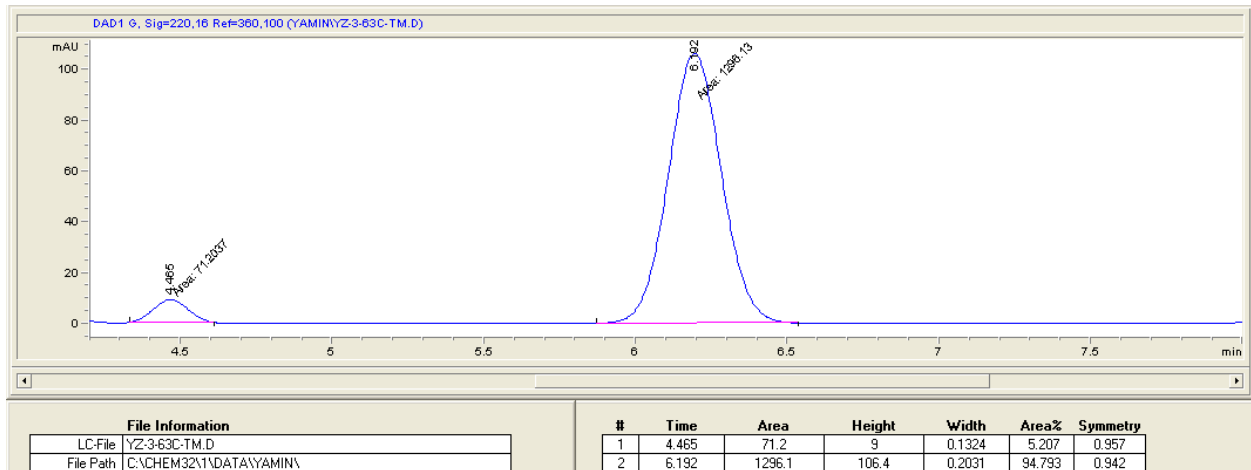


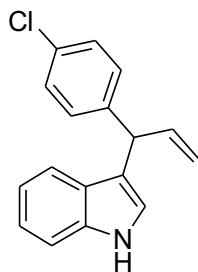


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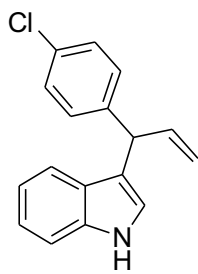
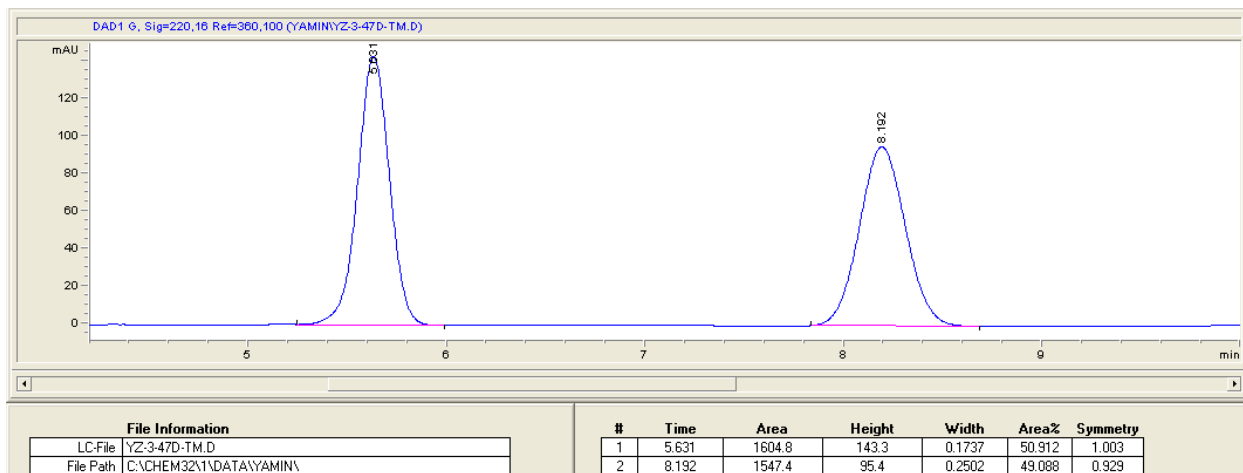


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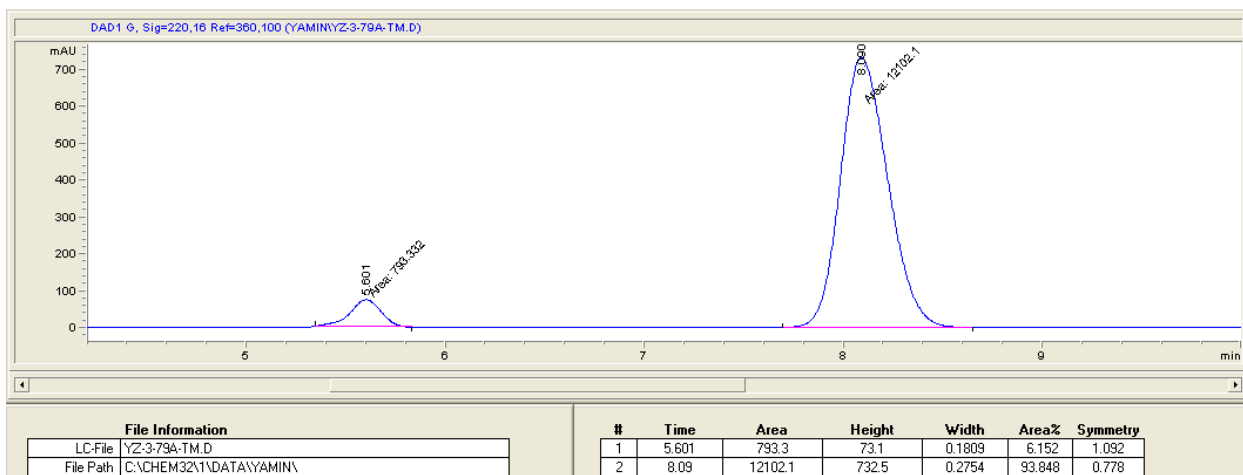


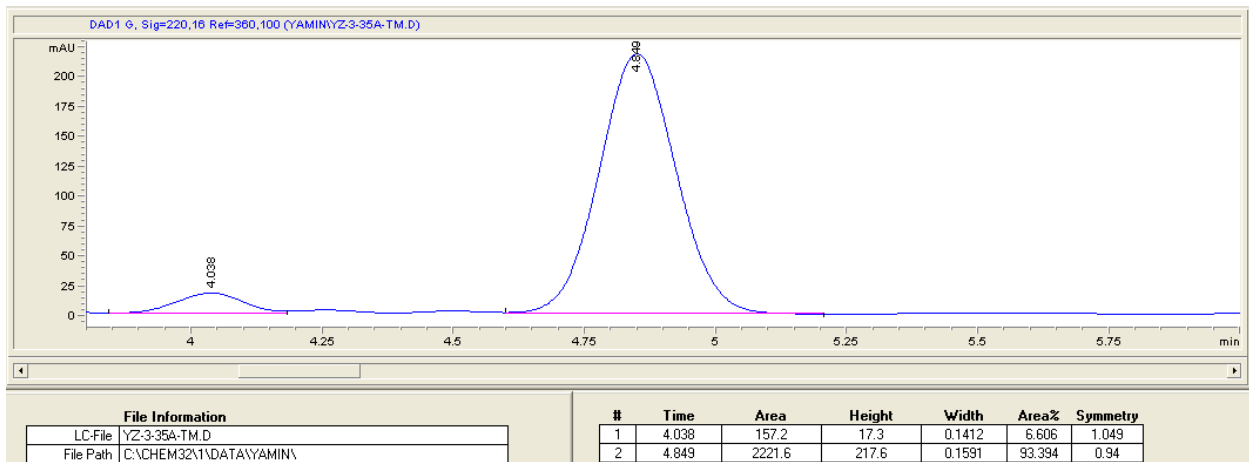
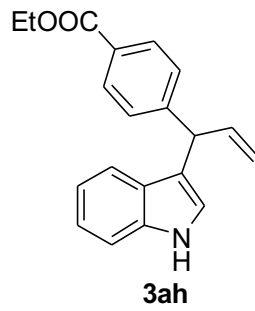
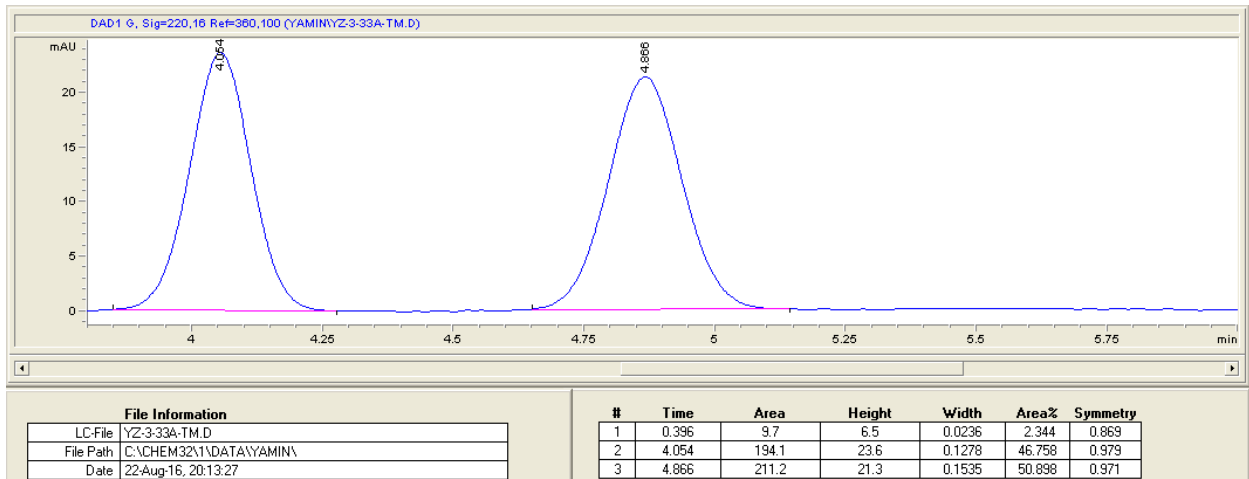
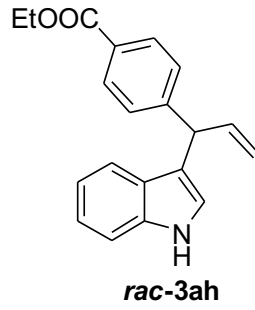


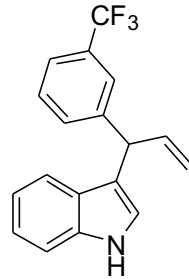
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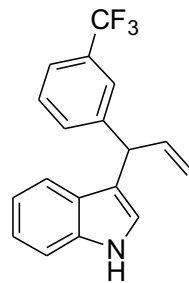
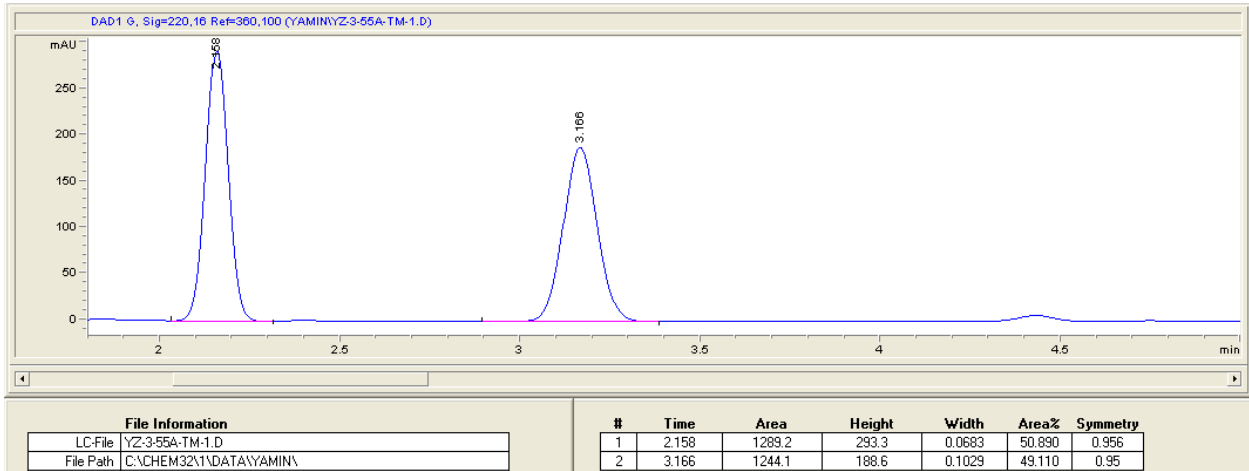
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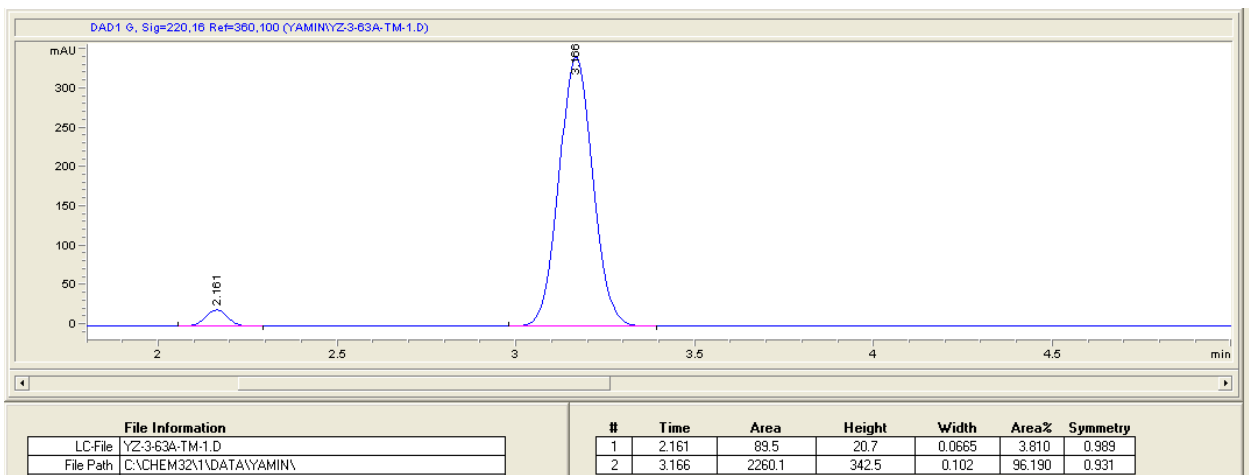


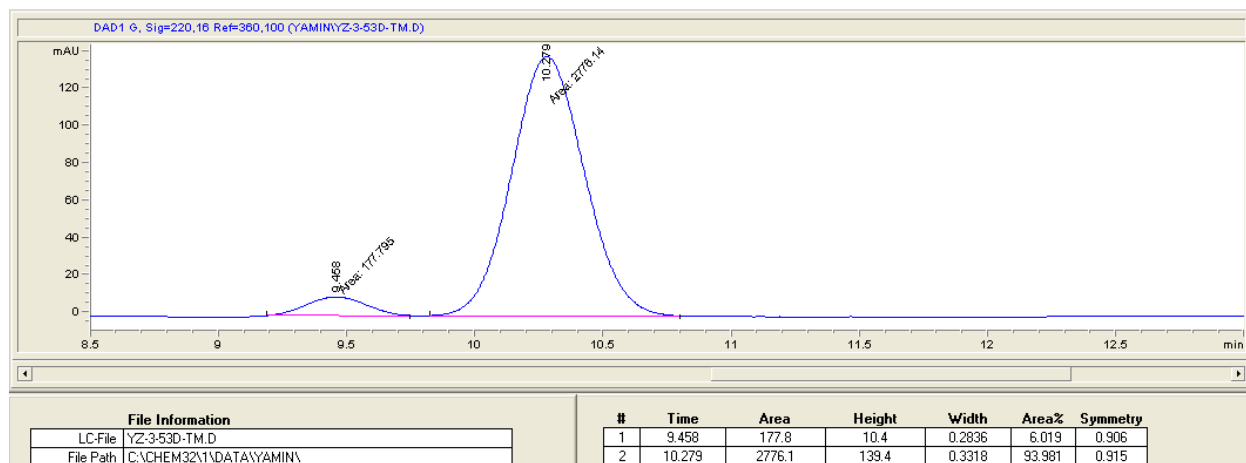
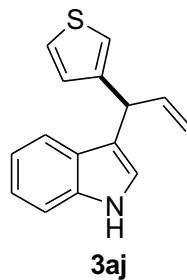
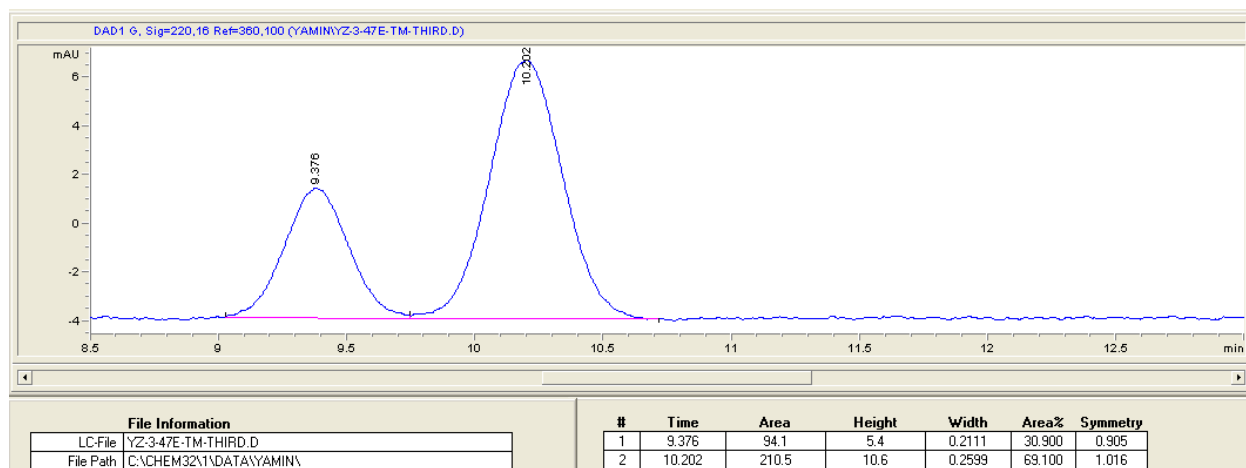
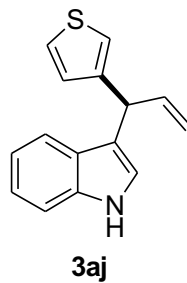


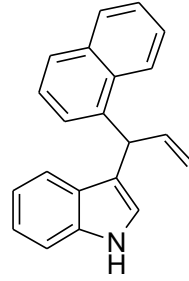
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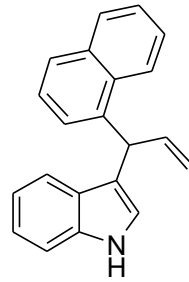
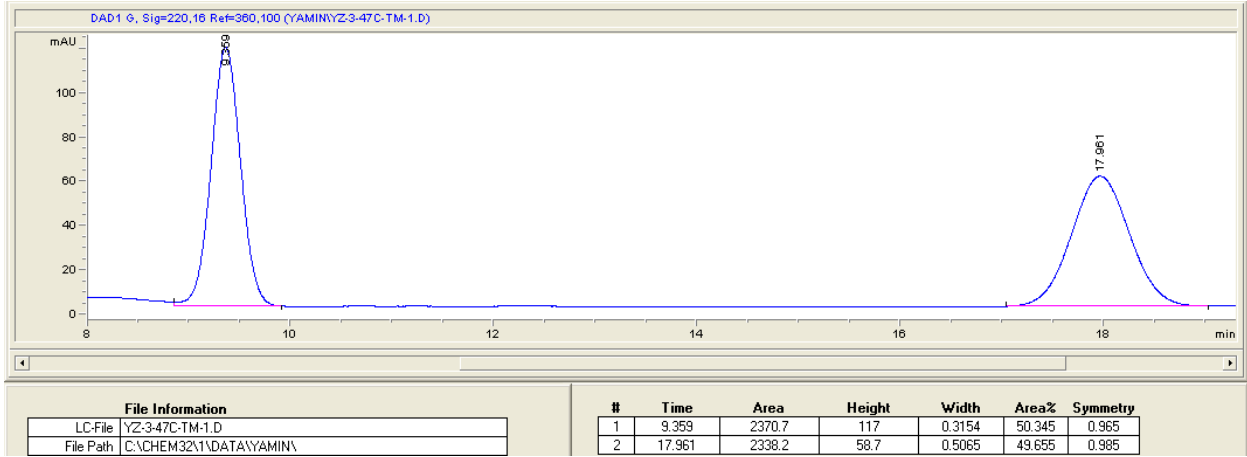
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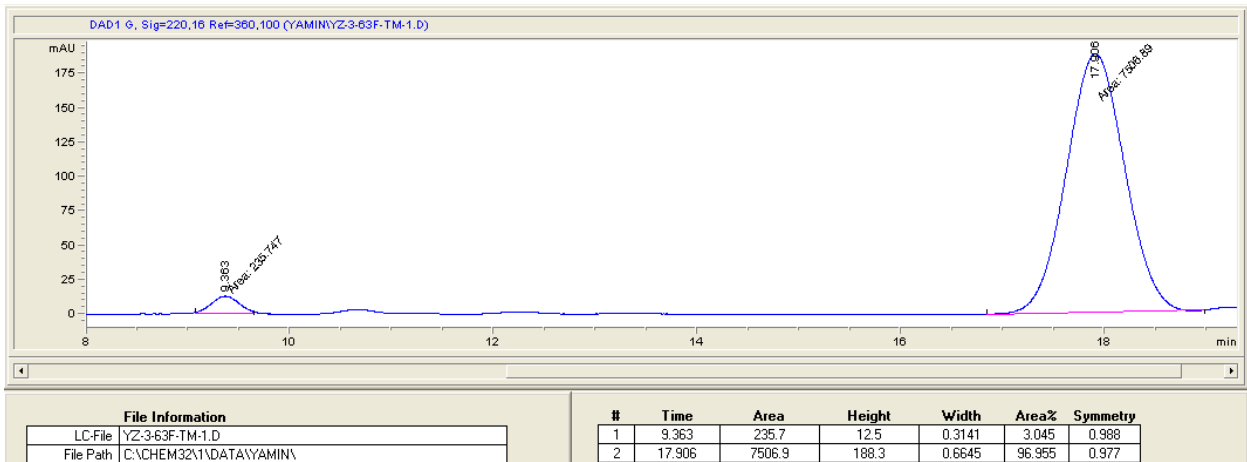


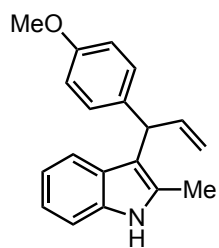


rac-3ak

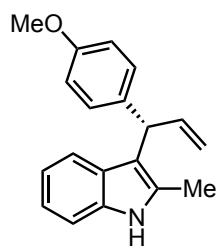
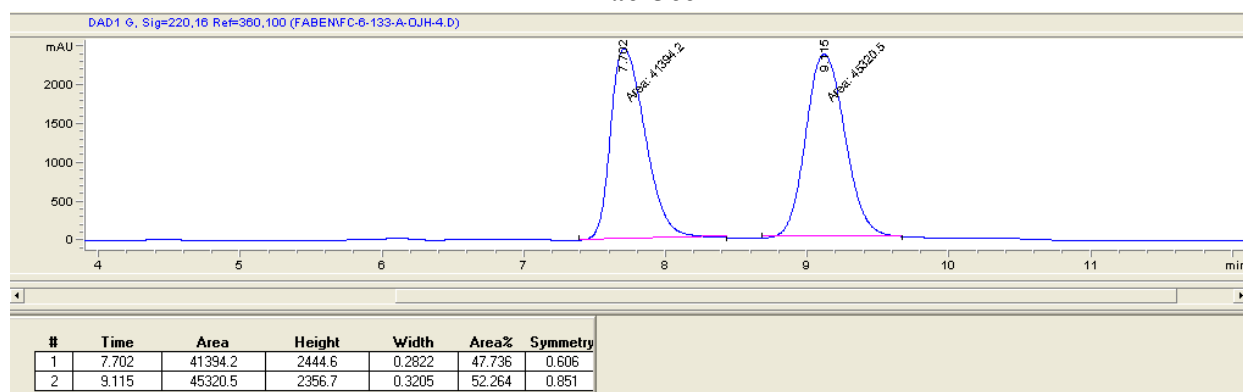


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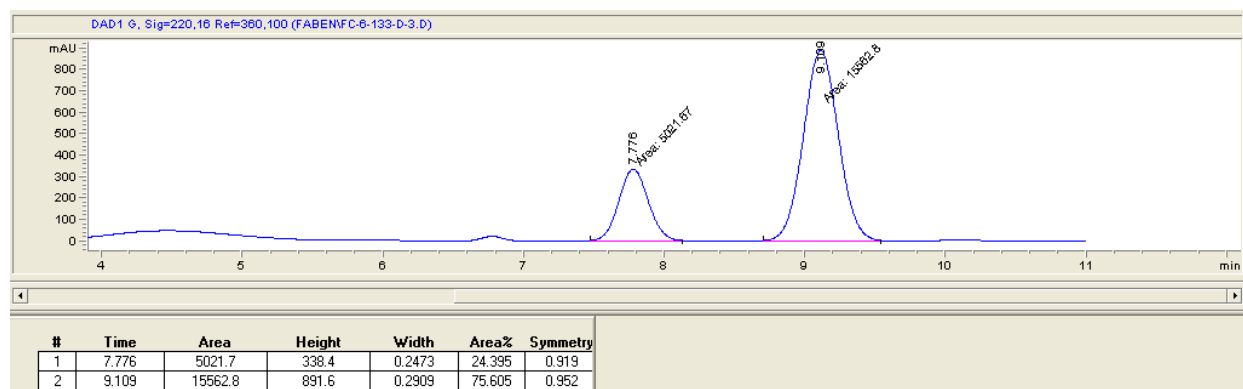


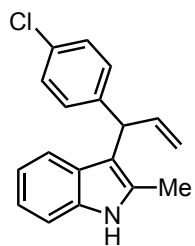


rac-3cc

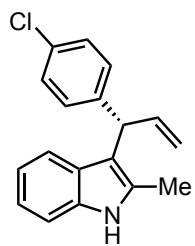
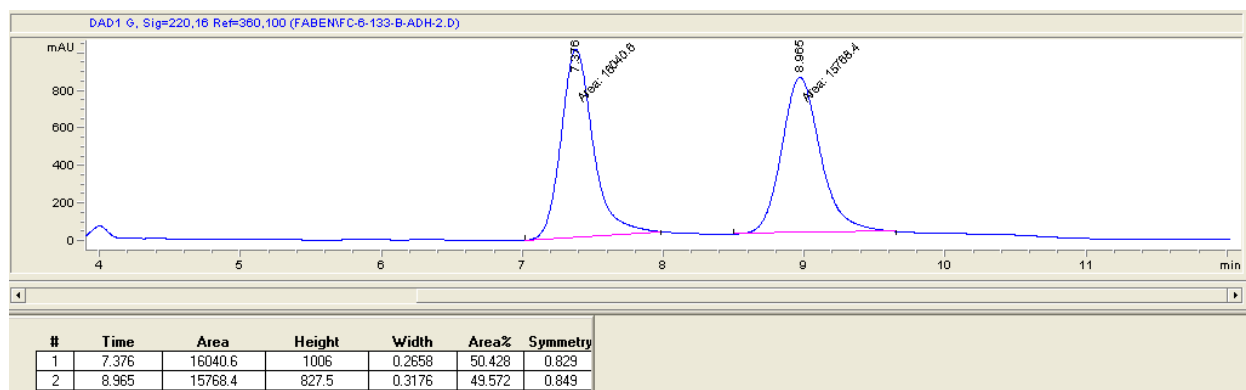


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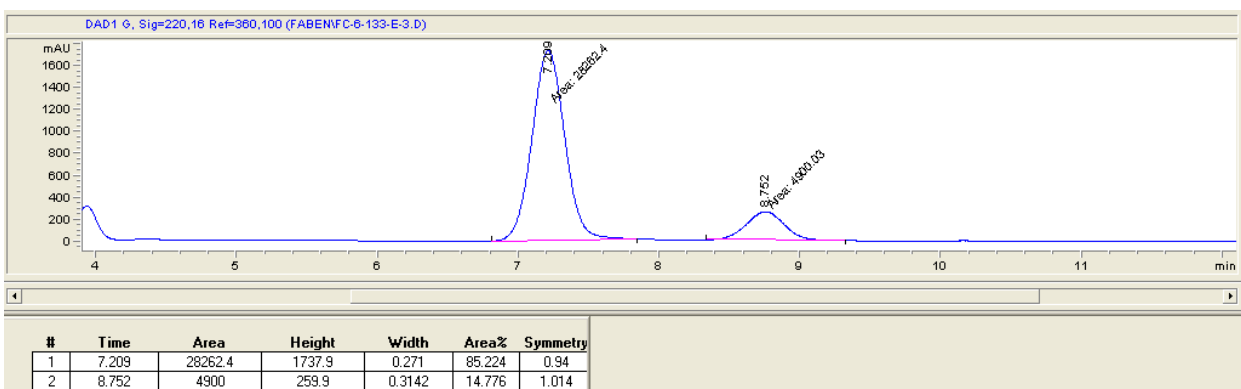


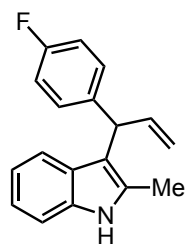


rac-3cg

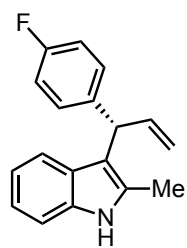
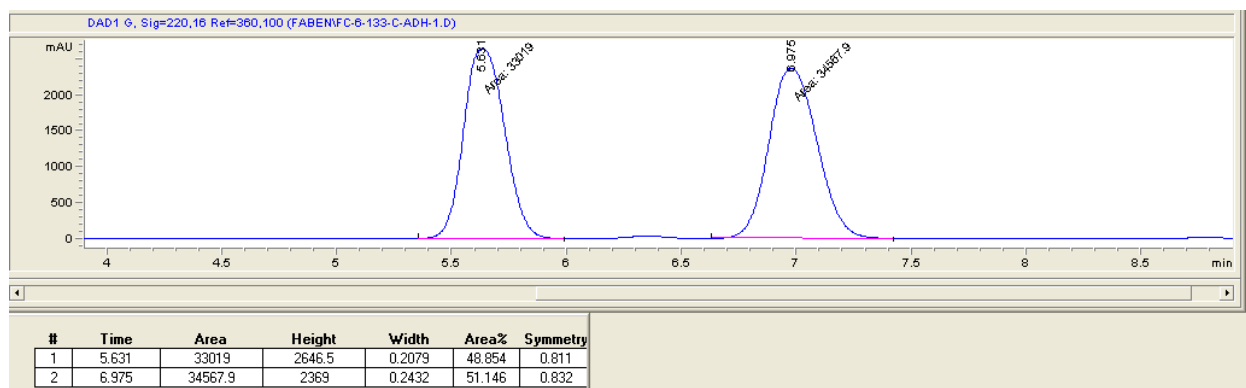


3cg





rac-3cf



3cf

