Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Asymmetric Diels–Alder Cycloadditions of Benzofulvene-Based 2,4-Dienal via Trienamine Activation

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Supplementary Information

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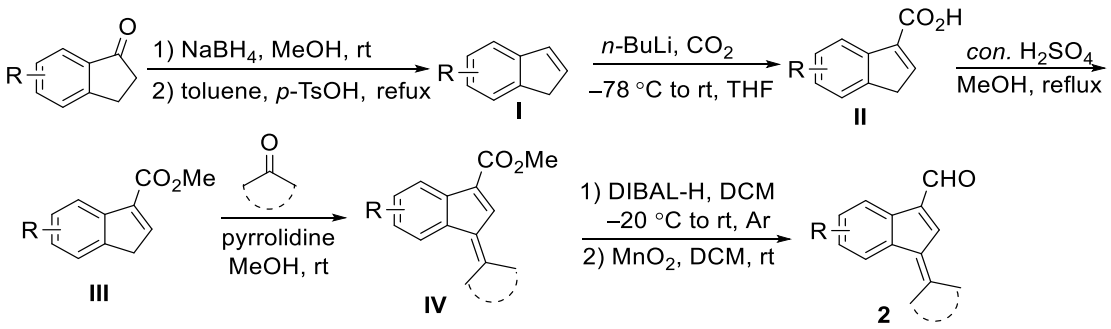
1. General method

NMR data were obtained for ^{1}H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz or 150 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI-HRMS was recorded on a Waters SYNAPT G2. In each case, diastereomeric ratio was determined by ^{1}H-NMR analysis and enantiomeric ratio was determined by HPLC analysis on a chiral stationary phase in comparison with authentic racemate, using a Daicel Chiralpak AD-H Column (250 × 4.6 mm), Chiralcel OD-H Column (250 × 4.6 mm), Chiralpak IC Column (250 × 4.6 mm) or Chiralpak ID Column (250 × 4.6 mm). UV detection was monitored at 254 nm. Optical rotation was measured in $CHCl_3$ solution at 25 ℃. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate and petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, 2,4-dinitrophenylhydrazine and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and ethyl acetate (EtOAc) were distilled. Oxindoles derivatives **3** were prepared according to the literature procedures.[1] Catalysts **C1**–**C3** were synthesized according to the literature procedures.[2]

1. S.-W. Duan, Y. Li, Y.-Y. Liu, Y.-Q. Zou, D.-Q. Shi and W.-J. Xiao, *Chem. Commun.*, 2012, **48**, 5160.
2. (*a*) Y. Hayashi, H. Gotoh, T. Hayashi and M. Shoji, *Angew. Chem., Int. Ed.*, 2005, **44**, 4212; (*b*) M Marigo, T. C. Wabnitz, D. Fielenbach and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2005, **44**, 794; (*c*) Y. Wang, P. Li, X. Liang and J. Ye, *Adv. Synth. Catal.*, 2008, **350**, 1383.

2. General procedure for the preparation of α-substituted 2,4-dienals



$NaBH_4$ (1.2 equiv) was added in portions to the solution of the indanone in MeOH at 0 °C. Then the solution was stirred at room temperature for 1 h. The mixture was poured into the ice-water.

EtOAc (2 × 30 mL) were added to the mixture, and the organic layers were separated and dried over by anhydrous Na_2SO_4. The solvent was removed under reduced pressure, yielding the crude product without further purification.

A solution of the indanol (1.0 equiv) and *p*-TsOH (0.1 equiv) in toluene was refluxed using a Dean-Stark water trap overnight. The solution was cooled to room temperature and washed with saturated aqueous $NaHCO_3$ solution, dried over by Na_2SO_4 and filtered. The crude product was purified by flash chromatography (pure petroleum) to provide the substituted indene **I**.

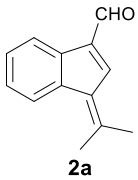
The mixture of **I** in dry THF was cooled to −78 °C and *n*-BuLi (2.4 M solution in THF, 1.0 equiv) was added dropwise over 20 min. The resulting mixture was stirred for 30 min at −40 °C and cooled to −78 °C, followed by dry CO_2 gas was placed directly into the mixture. The reaction mixture was allowed to warm to room temperature for 2 h. After quenching by 1 M HCl, water (30 mL) and EtOAc (2 × 30 mL) were added to the solution and the organic layers were separated. The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. Purification by flash column chromatography on silica gel eluting with EtOAc/petroleum ether (25/100) yielded the compound **II** as a white solid.

To a solution of **II** in MeOH, catalytic amounts of concentrated H_2SO_4 was added and the mixture was stirred overnight under reflux. The solution was cooled to room temperature and washed with saturated $NaHCO_3$ solution and extracted with DCM (3 × 30 mL). After removal of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel eluted with EtOAc/petroleum ether (10/100) to give the product **III**.

In a 50 mL Schlenk flask, the corresponding ketone (1.2 equiv) and **III** (1.0 equiv) were dissolved in MeOH (25 mL). Pyrrolidine (0.05 equiv) was added slowly. The mixture was stirred at room temperature, and the yellow solution was formed. Then water (30 mL) and EtOAc (2 × 30 mL) were added and the organic layer was separated. The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure and purification by flash column chromatography on silica gel [EtOAc/petroleum ether (1/100)] yielded the title compound **IV** as a yellow solid.

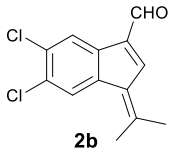
To a solution of **IV** (1.0 equiv) in DCM, DIBAL-H (2.4 M solution in THF, 2.0 equiv)) was added dropwise under an argon atmosphere at −20 ℃ and the mixture was stirred for 5 h at room temperature. After completion, the reaction was quenched with HCl (1M) solution at 0 ℃ and the

mixture was extracted with DCM (3 × 30 mL). The combined organic phases were washed with brine (20 mL) before being dried (Na_2SO_4) and concentrated *in vacuo.* Under an argon atmosphere, a mixture of the intermediate and MnO_2 (5.0 equiv) was stirred at room temperature for 8 h. Then the mixture was filtered through a thin plug of celite and the residue was eluted with DCM. The filtrate was concentrated and purified by flash column chromatography on silica gel eluting with EtOAc/petroleum ether (1/30) yielded substrate **2** as a yellow solid.



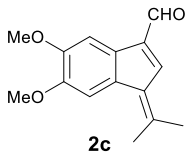
2a

Synthesis of 2a: yellow solid; 46% yield for 7 steps; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.11 (s, 1H), 8.17 (d, *J* = 5.2 Hz, 1H), 7.82-7.72 (m, 1H), 7.60 (s, 1H), 7.34-7.32 (m, 2H), 2.53 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.9, 153.9, 141.7, 138.6, 138.1, 136.2, 136.0, 126.7, 126.2, 123.5, 122.7, 25.7, 23.9. ESI-HRMS: calcd. for $C_{13}H_{12}O$+Na^+ 207.0780, found 207.0785.



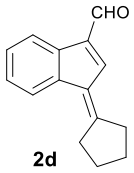
2b

Synthesis of 2b: yellow solid; 39% yield for 7 steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.06 (s, 1H), 8.28 (s, 1H), 7.83 (s, 1H), 7.65 (s, 1H), 2.53 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.2, 156.7, 142.4, 138.0, 136.5, 135.3, 134.7, 130.6, 129.9, 125.0, 124.0, 26.0, 24.0



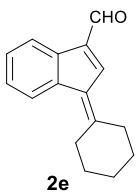
2c

Synthesis of 2c: yellow solid; 42% yield for 7 steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.05 (s, 1H), 7.77 (s, 1H), 7.51 (s, 1H), 7.30 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 2.50 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 189.0, 152.2, 148.4, 147.7, 140.9, 138.0, 136.3, 132.3, 128.7, 108.1, 105.8, 56.4, 56.1, 25.6, 23.6.



2d

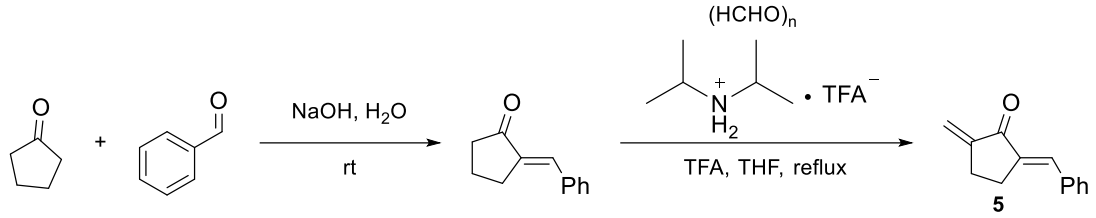
Synthesis of 2d: yellow solid; 38% yield for 7 steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.11 (s, 1H), 8.19 (d, *J* = 6.8 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.48 (s, 1H), 7.34-7.30 (m, 2H), 3.08-2.99 (m, 4H), 2.03-1.96 (m, 2H), 1.94-1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.9, 165.7, 142.3, 138.5, 138.1, 136.2, 132.7, 126.7, 126.2, 122.8, 35.3, 34.2, 26.6, 25.8.



2e

Synthesis of 2e: yellow solid; 40% yield for 7 steps. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.11 (s, 1H), 8.20 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.68 (s, 1H), 7.32-7.28 (m, 2H), 3.14-3.03 (m, 2H), 2.88-2.74 (m, 2H), 1.86 (d, *J* = 2.4 Hz, 4H), 1.80-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.9, 163.3, 141.8, 139.2, 137.9, 136.2, 133.2, 126.7, 126.2, 123.7, 122.7, 35.3, 33.2, 29.1, 28.2, 26.1. ESI-HRMS: calcd. for $C_{16}H_{16}O$+Na^+ 247.1093, found 247.1094.

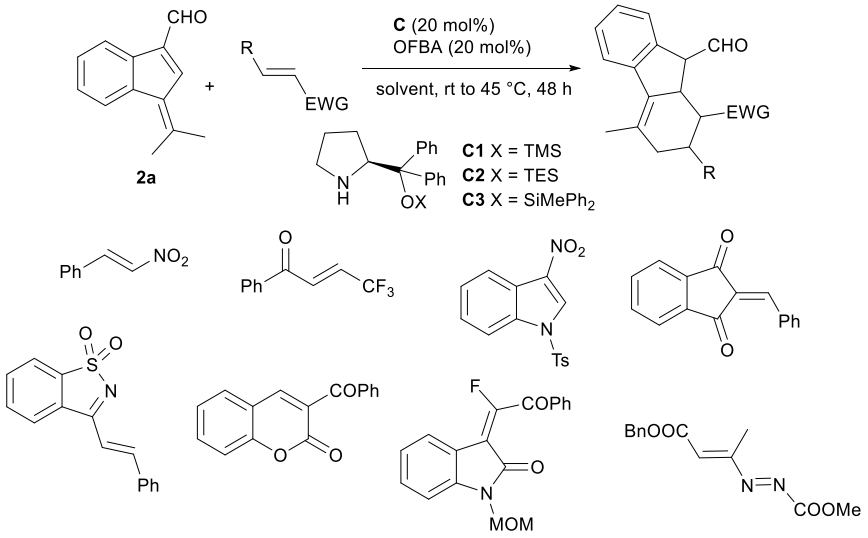
3. General procedure for the preparation of dienone 5



The dienone **5** was prepared using a straightforward two-step procedure. The first step is a base-catalyzed cross-aldol condensation reaction using benzaldehyde and cyclopentanone. Cyclopentanone (0.81 mL, 3 equiv) was added to a solution of NaOH (180 mg, 1.5 equiv) in water (50 mL) and stirred at room temperature for 5 min, followed by the addition of benzaldehyde (0.3 mL, 3 mmol). After 3 days of stirring, the product was extracted with EtOAc (3 × 20 mL) and purified by flash column chromatography on silica gel eluting with EtOAc/petroleum ether (1/100) yielded (*E*)-2-benzylidenecyclopentan-1-one as a yellow solid (465 mg, 90% yield).

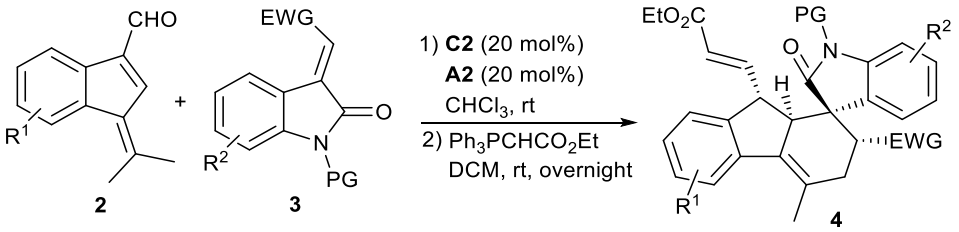
Then the enone (465 mg, 2.7 mmol) was dissolved in THF, followed by the addition of obtained salt (TFA was added to the solution of diisopropylamine in Diethyl ether to give a white salt (580 mg, 1.0 equiv), $(HCHO)_n$ (324 mg, 4.0 equiv), and catalytic amounts of TFA (30 mg, 0.1 equiv). The mixture was heated under reflux overnight. The solution was cooled to room temperature and washed with saturated aqueous $NaHCO_3$ solution. The product was extracted with EtOAc (3 × 20 mL) and purified by flash chromatography to provide dienone **5** as a yellow solid (298 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60-7.54 (m, 3H), 7.42-7.32 (m, 3H), 6.19 (s, 1H), 5.48 (s, 1H), 3.08-2.91 (m, 2H), 2.89-2.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.7, 145.5, 137.4, 135.6, 134.4, 130.7, 129.5, 128.7, 118.5, 26.4, 26.1.

4. More screening studies on diverse electrophiles

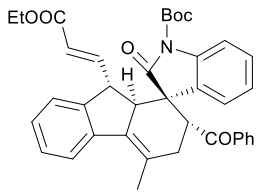


An array of dienophiles outlined above were screened under the optimized conditions but failed to give the desired cycloadducts.

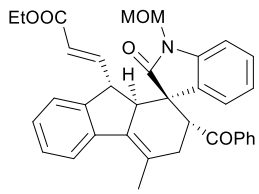
5. General procedure for amine-catalysed asymmetric Diels–Alder cycloaddition reactions



1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde **2** (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of 3-olefinic oxindoles **3** (0.1 mmol). Then the mixture was stirred at room temperature for the indicated time. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give aldehyde cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4**.

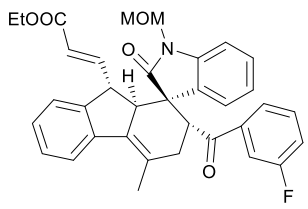


Synthesis of 4a: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CDCl_3$ (1.0 mL), followed by the addition of *tert*-butyl (*E*)-2-oxo-3-(2-oxo-2-phenylethylidene)indoline-1-carboxylate (0.1 mmol). Then the mixture was stirred at room temperature for 30 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4a (**isolated as a pure diastereomer): 37.4 mg as a light yellow solid, 57% yield; $[\alpha]_D^{20}$ = –10.0 (*c* = 0.25 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 13.59 min, t (major) = 27.27 min];^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01 (d, *J* = 8.2 Hz, 1H), 7.85-7.78 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.35-7.31 (m, 1H), 7.30-7.25 (m, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.06-7.02 (m, 1H), 6.93 (dd, *J* = 12.0, 4.2 Hz, 2H), 6.78 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.60 (d, *J* = 15.6 Hz, 1H), 4.44 (dd, *J* = 12.4, 6.0 Hz, 1H), 4.21-4.06 (m, 2H), 3.61-3.52 (m, 1H), 3.59-3.53 (m, 1H), 3.03 (t, *J* = 9.6 Hz, 1H), 2.90 (dd, *J* = 18.8, 5.6 Hz, 1H), 2.67-2.63 (m, 1H), 2.17 (s, 3H), 1.54 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 199.7, 177.0, 165.6, 148.8, 148.0, 144.9, 140.3, 138.9, 136.5, 133.2, 133.1, 128.6, 128.5, 128.2, 128.2, 127.6, 127.5, 127.0, 124.8, 124.8, 124.3, 124.2, 123.8, 114.9, 83.8, 60.3, 56.8, 50.8, 50.3, 46.9, 34.9, 27.9, 19.0, 14.1. ESI-HRMS: calcd. for $C_{38}H_{27}NO_4$+Na^+ 626.2513, found 626.2494.



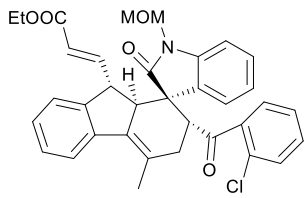
Synthesis of 4b: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-3-(2-oxo-2-phenylethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 24 h. After completion, the crude product was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give

the desired product **4b**: 45.4 mg as a light yellow solid, 83% yield; $[\alpha]_D^{20}$ = –157.5 (*c* = 0.24 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 14.99 min, t (major) = 23.42 min]; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.71 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.15-7.07 (m, 3H), 6.94 (t, *J* = 8.4 Hz, 2H), 6.79 (t, *J* = 7.8 Hz, 1H), 6.38 (dd, *J* = 15.6, 9.6 Hz, 1H), 5.21 (d, *J* = 15.6 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 4.15 (d, *J* = 7.8 Hz, 1H), 4.06-3.97 (m, 3H), 3.46-3.37 (m, 4H), 3.19 (dd, *J* = 18.6, 7.8 Hz, 1H), 2.40 (d, *J* = 18.6 Hz, 1H), 2.14 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 200.5, 177.3, 165.5, 148.3, 143.7, 141.7, 140.4, 137.2, 133.1, 131.3, 129.8, 128.6, 128.5, 128.4, 127.4, 126.7, 125.9, 125.3, 124.4, 124.3, 123.0, 121.4, 109.0, 71.4, 59.8, 56.8, 51.9, 50.3, 49.1, 44.2, 33.3, 19.4, 14.2. ESI-HRMS: calcd. for $C_{35}H_{33}NO_5$+Na^+ 570.2251, found 570.2250.

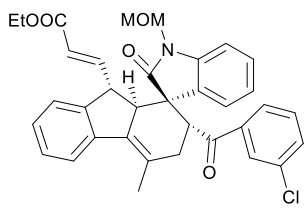


Synthesis of 4c: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-3-(2-(3-fluorophenyl)-2-oxoethylidene)-1-(methoxymethyl)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 20 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give aldehyde of **4c**. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4c**: 46.2 mg as a light yellow solid, 81% yield; $[\alpha]_D^{20}$ = –203.1 (*c* = 0.72 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.93 min, t (major) = 15.59 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.23-7.27 (m, 1H), 7.12 (dd, *J* = 14.0, 7.2 Hz, 2H), 7.03 (dd, *J* = 16.1, 7.8 Hz, 3H), 6.94 (t, *J* = 8.8Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.37 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.21 (d, *J* = 15.6 Hz, 1H), 5.11(dd, *J* = 26.8, 10.8 Hz, 2H), 4.10 (d, *J* = 9.0 Hz, 1H), 4.02 (dd, *J* = 14.0, 6.8 Hz, 2H), 3.94 (d, *J* = 7.5 Hz, 1H), 3.48-3.34 (m, 4H), 3.17 (dd, *J* = 18.5, 7.5 Hz, 1H), 2.38 (d, *J* = 18.5 Hz, 1H), 2.14 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.8, 177.1, 165.5 (J_{CF}^1 = 254.2 Hz), 165.4, 148.1, 143.6, 141.6, 140.3, 131.2, 131.1 (J_{CF}^3

= 9.1 Hz), 129.5, 128.6, 127.3, 126.7, 125.8, 125.2, 124.4, 124.3, 122.9, 121.4, 115.6 (J_{CF}^2 = 21.7 Hz), 109.1, 71.4, 59.8, 56.8, 56.8, 51.8, 50.3, 49.1, 44.1, 33.3, 19.3, 14.2. ESI-HRMS: calcd. for $C_{35}H_{32}FNO_5$+Na^+ 588.2157, found 588.2164.

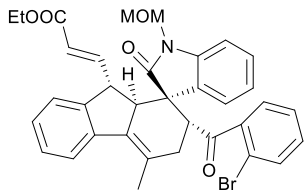


Synthesis of 4d: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CDCl_3$ (1.0 mL), followed by the addition of (*E*)-3-(2-(2-chlorophenyl)-2-oxoethylidene)-1-(methoxymethyl)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 22h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4d** [a mixture (10:1 dr) of diastereomers]: 43.5 mg as a light yellow solid, 75% yield; $[\alpha]_D^{20}$ = –68.2 (*c* = 0.54 in $CHCl_3$); 96% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 10.56 min, t (major) = 11.67 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, *J* = 7.6 Hz, 1H), 7.40-7.30 (m, 2H), 7.31-7.22 (m, 3H), 7.22-7.15 (m, 2H), 7.16-7.09 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.41 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.25 (d, *J* = 15.6 Hz, 1H), 5.16-5.06 (m, *J* = 13.2Hz, 10.8 Hz, 2H), 4.19 (d, *J* = 7.6 Hz, 1H), 4.09-3.98 (m, 2H), 3.85 (d, *J* = 7.6 Hz, 1H), 3.46-3.33 (m, 4H), 3.12 (dd, *J* = 18.8, 7.8 Hz, 1H), 2.45 (d, *J* = 18.8 Hz, 1H), 2.15 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.9, 176.9, 165.5, 148.2, 143.7, 141.7, 140.3, 139.1, 131.8, 131.5, 131.4, 130.7, 130.1, 129.5, 128.7, 127.3, 126.7, 126.6, 126.0, 124.6, 124.3, 123.1, 121.6, 121.5, 109.1, 71.3, 59.8, 56.6, 51.8, 50.4, 49.1, 48.8, 32.1, 19.3, 14.2. ESI-HRMS: calcd. for $C_{35}H_{32}{}^{35}ClNO_5$+$Na^+$ 604.1861, found 604.1865.



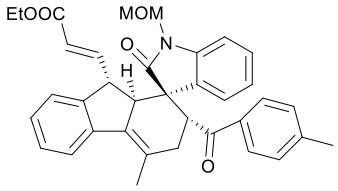
Synthesis of 4e: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-3-(2-(3-chlorophenyl)-2-oxoethylidene)-1-(methoxymethyl)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 21 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct.

Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4e**: 41.0 mg as a light yellow solid, 71% yield; $[\alpha]_D^{20}$ = –127.3 (*c* = 0.22 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.55 min, t (major) = 17.78 min]; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.70 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 7.12 (dd, *J* = 13.8, 7.2 Hz, 2H), 7.07 (d, *J* = 7.2Hz, 1H), 6.94 (dd, *J* = 11.4, 7.8 Hz, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.38 (dd, *J* = 15.6, 9.6 Hz, 1H), 5.22 (d, *J* = 15.6 Hz, 1H), 5.13 (dd, *J* = 16.8Hz, 10.8 Hz, 2H), 4.10 (d, *J* = 7.8 Hz, 1H), 4.02 (dd, *J* = 13.9, 7.2 Hz, 2H), 3.91 (d, *J* = 7.2 Hz, 1H), 3.48-3.36 (m, 4H), 3.19 (dd, *J* = 18.6, 7.2 Hz, 1H), 2.38 (d, *J* = 18.6 Hz, 1H), 2.14 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 199.0, 177.0, 165.4, 148.1, 143.6, 141.7, 140.3, 138.6, 134.9, 132.9, 131.3, 129.8, 129.5, 128.7, 128.4, 127.4, 126.7, 126.4, 125.7, 125.0, 124.4, 124.3, 123.0, 121.5, 109.1, 71.4, 59.8, 56.8, 51.8, 50.3, 49.1, 44.5, 33.1, 19.3, 14.2. ESI-HRMS: calcd. for $C_{35}H_{32}{}^{35}ClNO_5$+$Na^+$ 604.1861, found 604.1865.

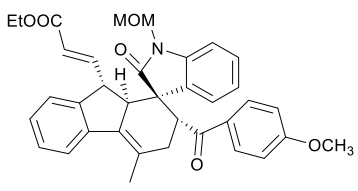


Synthesis of 4f: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-3-(2-(2-bromophenyl)-2-oxoethylidene)-1-(methoxymethyl)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 22 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4f** [a mixture (10:1 dr) of diastereomers]: 49.1 mg as a light yellow solid, 78% yield; $[\alpha]_D^{20}$ = –72.2 (*c* = 0.54 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 26.23 min, t (major) = 31.56 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (d, *J* = 7.6 Hz, 1H), 7.58-7.53 (m, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.28-7.20 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.04-6.97 (m, 2H), 6.93 (m, 2H), 6.42 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.27 (d, *J* = 15.6 Hz, 1H), 5.11 (d, *J* = 6.0 Hz, 2H),

4.22 (m, 1H), 4.04 (dt, *J* = 6.9, 5.4 Hz, 2H), 3.82 (d, *J* = 7.6 Hz, 1H), 3.47-3.35 (m, 4H), 3.12 (dd, *J* = 18.8, 8.0 Hz, 1H), 2.46 (d, *J* = 18.8 Hz, 1H), 2.15 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, CDCl3): δ (ppm) 201.9, 176.8, 165.4, 148.2, 143.7, 141.7, 140.9, 140.2, 133.9, 131.8, 131.5, 130.1, 129.1, 128.7, 127.2, 127.1, 126.7, 126.1, 124.4, 124.3, 123.1, 121.6, 121.5, 119.6, 109.0, 71.2, 59.8, 56.6, 51.7, 50.4, 49.1, 48.8, 31.8, 19.2, 14.1. ESI-HRMS: calcd. for $C_{35}H_{32}{}^{79}BrNO_5$+$Na^+$ 648.1356, found 648.1354.

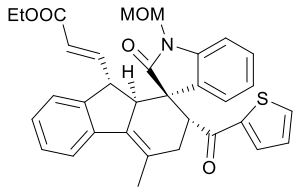


Synthesis of 4g: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-3-(2-oxo-2-(p-tolyl)ethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 24h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4g**: 43.4 mg as a light yellow solid, 77% yield; $[\alpha]_D^{20}$ = –362.1 (*c* = 0.28 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 14.33 min, t (major) = 19.52 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.61 (t, *J* = 8.2 Hz, 3H), 7.24(t, *J* = 7.6 Hz ,1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.12-7.06 (m, 3H), 6.93 (t, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.38 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.21 (d, *J* = 15.6 Hz, 1H), 5.13 (dd, *J* = 25.6, 10.8 Hz, 2H), 4.17 (d, *J* = 8.8 Hz, 1H), 4.02 (dd, *J* = 14.0, 6.8 Hz, 2H), 3.96 (d, *J* = 7.6 Hz, 1H), 3.45-3.34 (m, 4H), 3.18 (dd, *J* = 18.8, 7.6 Hz, 1H), 2.40 (d, *J* = 18.8 Hz, 1H), 2.35 (s, 3H), 2.13 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.0, 177.3, 165.5, 148.3, 143.9, 143.6, 141.6, 140.5, 134.7, 131.1, 129.8, 129.2, 128.5, 127.3, 126.6, 126.0, 125.3, 124.3, 123.0, 121.4, 121.3, 109.0, 71.4, 59.8, 56.8, 51.9, 50.3, 49.1, 43.9, 43.8, 33.4, 21.5, 19.3, 14.2. ESI-HRMS: calcd. for $C_{36}H_{35}NO_5$+Na^+ 584.2407, found 584.2410.



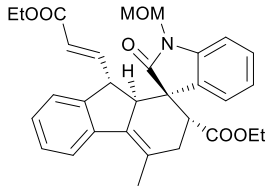
Synthesis of 4h: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of

(*E*)-1-(methoxymethyl)-3-(2-(4-methoxyphenyl)-2-oxoethylidene) indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 26 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4h**: 41.2 mg as a light yellow solid, 70% yield; $[\alpha]_D^{20}$ = –264.4 (*c* = 0.50 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 17.16 min, t (major) = 21.78 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.97-6.89 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.77 (t, *J* = 7.6 Hz, 1H), 6.37 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.20 (d, *J* = 15.6 Hz, 1H), 5.12 (dd, *J* = 23.2, 10.8 Hz, 2H), 4.16 (d, *J* = 8.8 Hz, 1H), 4.04-4.02 (m, 2H), 3.94 (d, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.45-3.34 (m, 4H), 3.17 (dd, *J* = 18.4, 7.6 Hz, 1H), 2.38 (d, *J* = 18.8 Hz, 1H), 2.14 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 198.9, 177.3, 165.4, 163.4, 148.3, 143.6, 141.6, 140.5, 131.0, 130.7, 130.1, 129.7, 128.5, 127.3, 126.6, 126.0, 125.5, 124.3, 122.9, 121.3, 113.7, 108.9, 71.4, 59.8, 56.8, 55.4, 51.8, 50.4, 49.1, 43.5, 33.5, 19.3, 14.2. ESI-HRMS: calcd. for $C_{36}H_{35}NO_6$+Na^+ 600.2357, found 600.2358.

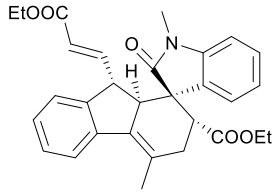


Synthesis of 4i: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-3-(2-oxo-2-(thiophen-2-yl)ethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4i**: 48.0 mg as a light yellow solid, 87% yield; $[\alpha]_D^{20}$ = –222.0 (*c* = 0.50 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.31 min, t (major) = 18.59 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.64-7.57 (m, 2H), 7.42 (d, *J* = 3.6 Hz, 1H), 7.23 (m, *J* = 7.6 Hz, 1H), 7.16-7.05 (m, 3H), 7.02-6.88 (m, 3H), 6.79

(t, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.16-5.14 (m, 3H), 4.08 (d, *J* = 8.8 Hz, 1H), 4.05-3.95 (m, 2H), 3.75 (d, *J* = 7.6 Hz, 1H), 3.45-3.32 (m, 4H), 3.21 (dd, *J* = 18.6, 7.4 Hz, 1H), 2.47 (d, *J* = 18.6 Hz, 1H), 2.15 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 193.0, 176.9, 165.4, 148.1, 144.8, 143.5, 141.5, 140.4, 134.7, 132.2, 130.9, 129.4, 128.7, 128.2, 127.3, 126.6, 125.7, 125.4, 124.3, 122.9, 121.4, 109.0, 71.4, 59.8, 56.8, 56.7, 51.7, 50.2, 49.1, 45.9, 33.6, 19.2, 14.2. ESI-HRMS: calcd. for $C_{33}H_{31}SNO_5$+Na^+ 576.1815, found 576.1830.

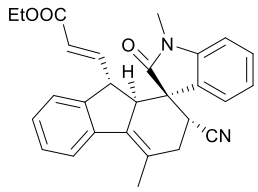


Synthesis of 4j: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of ethyl (*E*)-2-(1-(methoxymethyl)-2-oxoindolin-3-ylidene)acetate (0.1 mmol). Then the mixture was stirred at room temperature for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4j**: 37.0 mg as a light yellow solid, 72% yield; $[\alpha]_D^{20}$ = –69.7 (*c* = 0.80 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 8.52 min, t (major) = 12.89 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 7.6 Hz, 1H), 7.21 (m, 2H), 7.18-7.07 (m, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 7.00-6.94 (m, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.35 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.20 (d, *J* = 15.6 Hz, 1H), 5.11 (s, 2H), 4.11 (q, *J* = 7.2Hz, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.88-3.79 (m, 1H), 3.43-3.34 (m, 4H), 3.06 (dd, *J* = 18.4, 6.8 Hz, 1H), 2.93 (dd, *J* = 7.6, 2.0 Hz, 1H), 2.47 (d, *J* = 18.4 Hz, 1H), 2.16 (d, *J* = 2.0 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.9, 172.9, 165.5, 148.2, 143.6, 141.7, 140.3, 130.7, 129.9, 128.8, 127.4, 126.7, 125.9, 124.5, 124.4, 124.3, 122.9, 121.5, 109.3, 71.3, 60.6, 59.9, 56.7, 51.5, 49.8, 49.0, 44.7, 33.4, 19.3, 14.2, 14.0. ESI-HRMS: calcd. for $C_{31}H_{33}NO_6$+Na^+ 538.2200, found 538.2203



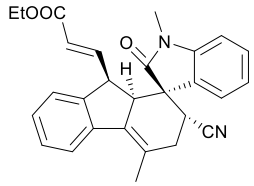
Synthesis of 4k: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of ethyl (*E*)-2-(1-methyl-2-oxoindolin-3-ylidene) acetate (0.1 mmol). Then the

mixture was stirred at room temperature for 26 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4k**: 32.5 mg as a light yellow solid, 67% yield; $[\alpha]_D^{20}$ = –66.5 (*c* = 0.49 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 6.83 min, t (minor) = 8.01 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (d, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 15.6, 8.0 Hz, 2H), 7.11 (dd, *J* = 16.8, 7.6 Hz, 2H), 6.97-6.87 (m, 2H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.32 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.16 (d, *J* = 15.6 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.80 (d, *J* = 8.0 Hz, 1H), 3.34 (t, *J* = 10.0 Hz, 1H), 3.22 (s, 3H), 3.09 (dd, *J* = 18.4, 6.8 Hz, 1H), 2.91 (d, *J* = 6.0 Hz, 1H), 2.45 (d, *J* = 18.4 Hz, 1H), 2.16 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.2, 173.0, 165.4, 148.2, 143.6, 143.4, 140.2, 130.6, 130.4, 128.7, 127.2, 126.6, 125.9, 124.3, 124.2, 122.4, 121.4, 107.8, 60.4, 59.8, 51.5, 49.3, 49.1, 44.3, 33.2, 25.9, 19.3, 14.2, 14.0. ESI-HRMS: calcd. for $C_{30}H_{31}NO_5$+Na^+ 508.2094, found 508.2096.

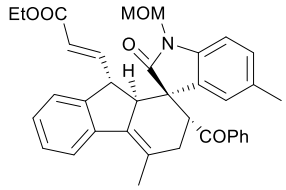


Synthesis of 4l: 1-(propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-2-(1-(methoxymethyl)-2-oxoindolin-3-ylidene) acetonitrile (0.1 mmol). Then the mixture was stirred at room temperature for 28 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4l**: 19 mg as a light yellow solid, 44% yield; $[\alpha]_D^{20}$ = –241.6 (*c* = 0.12 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 18.07 min, t (minor) = 20.50 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.33-7.21 (m, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.33 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.19 (d, *J* = 15.6 Hz, 1H), 4.07-4.03

(m, 2H), 3.61 (d, *J* = 9.2 Hz, 1H), 3.37-3.33 (m, 2H), 3.23 (s, 3H), 3.09 (d, *J* = 6.4 Hz, 1H), 2.62 (d, *J* = 18.0 Hz, 1H), 2.16 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.0, 165.1, 147.1, 143.3, 143.0, 139.6,130.2, 129.4, 128.9, 127.6, 127.2, 125.1, 124.6, 124.4, 124.3, 123.0, 122.1, 120.3, 108.0, 60.0, 52.5, 48.7, 47.3, 33.3, 32.6, 26.2, 18.9, 14.2. ESI-HRMS: calcd. for $C_{28}H_{26}N_2O_3$+Na^+ 461.1836, found 461.1833.

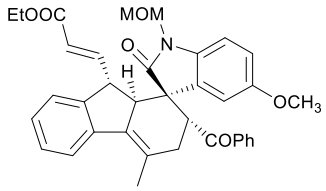


diastereomer 4l′: 18 mg as a light yellow solid, 42% yield; $[\alpha]_D^{20}$ = +12.0 (*c* = 0.20 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 13.12 min, t (minor) = 15.18 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 7.6 Hz, 1H), 7.43-7.36 (m, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 4.0 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.71 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.38 (d, *J* = 15.6 Hz, 1H), 4.20-4.16 (m, 2H), 3.47 (dd, *J* = 12.0, 6.8 Hz, 1H), 3.38 (d, *J* = 8.4 Hz, 1H), 3.21 (s, 3H), 3.01 (t, *J* = 9.6 Hz, 1H), 2.96-2.73 (m, 2H), 2.18 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 175.9, 165.4, 147.2, 144.5, 144.0, 138.6, 132.8, 129.7, 127.9, 127.6, 125.7, 125.6, 124.4, 124.4, 124.3, 124.1, 123.0, 118.2, 108.9, 60.4, 53.3, 50.7, 48.3, 33.3, 32.9, 26.2, 18.6, 14.2. ESI-HRMS: calcd. for $C_{28}H_{26}N_2O_3$+Na^+ 461.1836, found 461.1833.



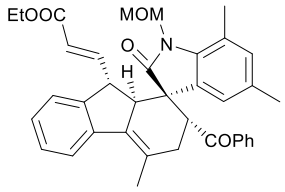
Synthesis of 4m: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-5-methyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 25 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4m**: 45.3 mg as a light yellow solid, 80% yield; $[\alpha]_D^{20}$ = –227.3 (*c* = 0.6 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) =9.58 min, t (major) =13.59 min]; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.72 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.88-6.84 (m, 3H), 6.39 (dd, *J* = 15.6, 10.0

Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 5.10 (dd, *J* = 39.6, 10.2 Hz, 2H), 4.11 (d, *J* = 9.0 Hz, 1H), 4.07-3.96 (m, 3H), 3.44-3.35 (m, 4H), 3.18 (dd, *J* = 18.6, 7.8 Hz, 1H), 2.40 (d, *J* = 18.6 Hz, 1H), 2.14 (s, 3H), 2.05 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 200.6, 177.2, 165.5, 148.3, 143.7, 140.5, 139.2, 137.4, 133.0, 132.5, 131.2, 129.7, 128.8, 128.5, 128.4, 127.3, 126.7, 126.7, 125.4, 124.4, 124.3, 121.1, 108.8, 71.4, 59.8, 56.7, 51.8, 50.4, 49.1, 44.2, 33.4, 20.8, 19.3, 14.2. ESI-HRMS: calcd. for $C_{36}H_{35}NO_5$+Na^+ 584.2407, found 584.2410.

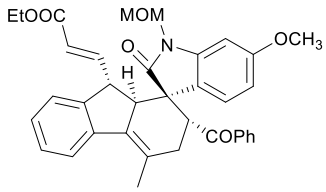


Synthesis of 4n: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CDCl_3$ (1.0 mL), followed by the addition of (*E*)-5-methoxy-1-(methoxymethyl)-3-(2-oxo-2-phenylethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 25 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4n**: 47.3 mg as a light yellow solid, 82% yield; $[\alpha]_D^{20}$ = –249.5 (*c* = 0.38 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) =11.25 min, t (major) =16.35 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.43 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.22 (d, *J* = 15.6 Hz, 1H), 5.10 (dd, *J* = 28.0, 10.4 Hz, 2H), 4.12(d, *J* = 8.0 Hz, 1H), 4.05-3.99 (m, 3H), 3.52 (s, 3H), 3.46-3.34 (m, 4H), 3.19 (dd, *J* = 18.8, 7.2 Hz, 1H), 2.39 (d, *J* = 19.2 Hz, 1H), 2.14 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.4, 177.0, 165.5, 156.1, 148.2, 143.6, 140.4, 137.2, 135.1, 133.1, 131.1, 130.8, 128.6, 128.4, 127.3, 126.7, 125.3, 124.4, 124.3, 121.4, 114.5, 112.2, 109.7, 71.5, 59.9, 56.7, 55.6, 51.8, 50.8, 49.1, 44.0, 33.4, 19.3, 14.0. ESI-HRMS: calcd. for $C_{36}H_{35}NO_6$+Na^+ 600.2357, found 600.2356.

Synthesis of 4o: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-5,7-dimethyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (0.1

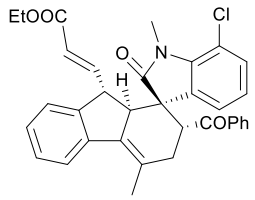


mmol). Then the mixture was stirred at room temperature for 28 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4o** [a mixture (10:1 dr) of diastereomer]: 45.2 mg as a white solid, 85% yield; $[\alpha]_D^{20}$ = –129.2 (*c* = 0.26 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 8.08 min, t (minor) = 12.80 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 6.68 (s, 1H), 6.63 (s, 1H), 6.35 (dd, *J* = 15.4, 10.0 Hz, 1H), 5.20 (q, *J* = 10.9 Hz, 3H), 4.06-3.97 (m, 4H), 3.47-3.34 (m, 4H), 3.24-3.12 (m, 1H), 2.46 (s, 3H), 2.37 (d, *J* = 18.6 Hz, 1H), 2.15 (s, 3H), 1.99 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.0, 178.3, 165.5, 148.1, 143.8, 140.5, 137.7, 137.4, 132.8, 132.6, 132.4, 131.3, 130.4, 128.5, 128.3, 127.1, 126.6, 125.5, 124.3, 124.3, 124.2, 121.3, 120.1, 71.9, 59.8, 56.5, 52.3, 49.6, 49.1, 44.3, 33.6, 20.5, 19.3, 18.1, 14.2. ESI-HRMS: calcd. for $C_{37}H_{37}NO_5$+Na^+ 598.2564, found 598.2574.

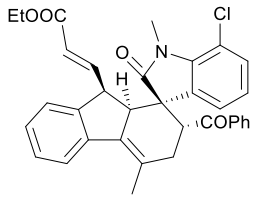


Synthesis of 4p: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-6-methoxy-1-(methoxymethyl)-3-(2-oxo-2-phenylethylidene)indolin -2-one (0.1 mmol). Then the mixture was stirred at room temperature for 27 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4p**: 41.2 mg as a light yellow solid, 74% yield; $[\alpha]_D^{20}$ = –353.2 (*c* = 0.68 in $CHCl_3$); 98% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 12.52 min, t (major) = 23.31 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72-7.64 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.20-7.14 (m, 1H),

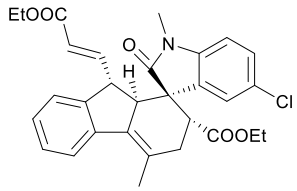
7.05 (t, *J* = 7.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.32 (dd, *J* = 15.6, 10.0 Hz, 1H), 6.22 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.16 (d, *J* = 15.6 Hz, 1H), 5.03 (dd, *J* = 26.4, 10.8 Hz, 2H), 4.06 (d, *J* = 9.6 Hz, 1H), 4.01-3.88 (m, 3H), 3.64 (s, 3H), 3.34 (s, 3H), 3.29 (t, *J* = 9.6 Hz, 1H), 3.12 (dd, *J* = 19.6, 8.0 Hz, 1H), 2.31 (d, *J* = 18.8 Hz, 1H), 2.05 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 200.6, 177.8, 165.6, 160.5, 148.2, 143.7, 143.0, 140.5, 137.2, 133.1, 131.2, 128.6, 128.4, 127.3, 126.8, 126.7, 125.2, 124.4, 124.4, 121.7, 121.2, 107.7, 96.3, 59.9, 56.9, 55.3, 52.4, 49.9, 49.2, 44.2, 33.4, 19.3, 14.1. ESI-HRMS: calcd. for $C_{36}H_{35}NO_6$+Na^+ 600.2357, found 600.2361.



Synthesis of 4q: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-7-chloro-1-methyl-3-(2-oxo-2-phenylethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 22 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4q**: 27 mg as a light yellow solid, 49% yield; $[\alpha]_D^{20}$ = −188.4 (*c* = 0.36 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak OD, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 7.13 min, t (major) = 10.65 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)7.68 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.68 (t, *J* = 8.0 Hz, 1H), 6.37 (dd, *J* = 15.2, 10.0 Hz, 1H), 5.32 (d, *J* = 15.2 Hz, 1H), 4.05 (dd, *J* = 7.2, 6.4 Hz, 2H), 3.97-3.95 (m, 2H), 3.59 (s, 3H), 3.37 (t, *J* = 9.6 Hz, 1H), 3.17 (dd, *J* = 18.0, 6.8 Hz, 1H), 2.41 (d, *J* = 18.4 Hz, 1H), 2.15 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.5, 176.9, 165.4, 148.4, 143.6, 140.1, 139.3, 137.2, 133.3, 133.0, 131.3, 130.6, 128.6, 128.31, 127.3, 126.7, 125.5, 124.3, 124.2, 123.2, 121.8, 121.8, 115.2, 59.9, 52.4, 50.0, 49.2, 44.4, 33.3, 29.5, 19.4, 14.2. ESI-HRMS: calcd. for $C_{34}H_{30}{}^{35}ClNO_4$+$Na^+$ 574.1756, found 574.1758.

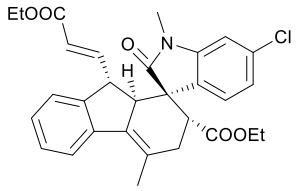


diastereomer 4q′: 18 mg as a light yellow solid, 32% yield; $[\alpha]_D^{20}$ = –35.7 (*c* = 0.30 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 9.74 min, t (minor) = 18.91 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 7.6 Hz, 2H), 7.63-7.51 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.29-7.23 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.90-6.83 (m, 2H), 6.74 (dd, *J* = 15.4, 10.0 Hz, 1H), 5.58 (d, *J* = 15.4 Hz, 1H), 4.44 (dd, *J* = 12.8, 6.4 Hz, 1H), 4.21-4.18 (m, 2H), 3.52 (d, *J* = 7.6 Hz, 1H), 3.42 (s, 3H), 2.99 (t, *J* = 9.6 Hz, 1H), 2.84 (dd, *J* = 18.4, 5.6 Hz, 1H), 2.72-2.58 (m, 1H), 2.16 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 199.7, 178.3, 165.6, 147.8, 144.9, 140.0, 138.9, 136.4, 133.1, 132.9, 132.1, 130.4, 128.5, 128.4, 127.6, 127.4, 126.9, 124.6, 124.2, 123.9, 123.6, 123.1, 115.7, 60.3, 56.1, 50.1, 49.2, 47.1, 34.7, 29.4, 18.9, 14.2. ESI-HRMS: calcd. for $C_{34}H_{30}{}^{35}ClNO_4$+$Na^+$ 574.1756, found 574.1758.

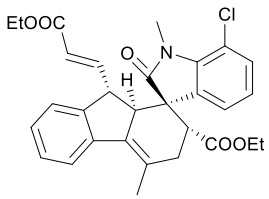


Synthesis of 4r: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of ethyl (*E*)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (0.1 mmol). Then the mixture was stirred at room temperature for 20 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4r**: 43.3 mg as a white solid, 83% yield; $[\alpha]_D^{20}$ = –340.3 (*c* = 1.05 in $CHCl_3$); 97% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 5.62 min, t (minor) = 7.03 min]; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.59 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.13 (d, *J* = 1.8 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.39 (dd, *J* = 15.0, 9.6 Hz, 1H), 5.17 (d, *J* = 15.6 Hz, 1H), 4.28-4.13 (m, 2H), 4.13-4.05 (m, 2H), 3.78 (d, *J* = 9.6 Hz, 1H), 3.32 (t, *J* = 9.8 Hz, 1H), 3.23 (s, 3H), 3.09 (dd, *J* = 17.4, 6.0 Hz, 1H), 2.89 (d, *J* = 6.6 Hz, 1H), 2.46 (d, *J* = 17.4 Hz, 1H), 2.16 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 175.7, 172.9, 165.3, 148.1, 143.4, 142.0, 140.2, 132.1, 130.3, 128.7, 127.9, 127.4, 126.8, 125.8, 125.0, 124.3, 121.9,

108.8, 60.8, 60.2, 51.2, 49.5, 49.1, 44.0, 33.1, 26.2, 19.3, 14.1, 14.1. ESI-HRMS: calcd. for $C_{30}H_{30}{}^{35}ClNO_5$+$Na^+$ 542.1705, found 542.1713.

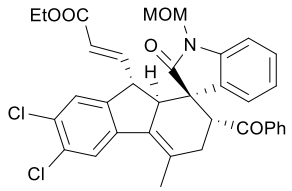


Synthesis of 4s: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of ethyl (*E*)-2-(6-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (0.1 mmol). Then the mixture was stirred at room temperature for 20 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4s**: 35.2 mg as a light yellow solid, 68% yield; $[\alpha]_D^{20}$ = –157.8 (*c* = 0.90 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 9.80 min, t (major) = 12.33 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.94-6.87 (m, 2H), 6.82 (d, *J* = 1.6 Hz, 1H), 6.35 (dd, *J* = 15.4, 10.0 Hz, 1H), 5.20 (d, *J* = 15.4 Hz, 1H), 4.18-4.03 (m, 4H), 3.79 (d, *J* = 9.6 Hz, 1H), 3.32 (t, *J* = 9.6 Hz, 1H), 3.20 (s, 3H), 3.09 (dd, *J* = 18.8, 6.4 Hz, 1H), 2.88 (dd, *J* = 7.6, 1.6 Hz, 1H), 2.44 (d, *J* = 18.8 Hz, 1H), 2.15 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.1, 172.9, 165.4, 148.1, 144.7, 143.4, 140.2, 134.7, 130.3, 128.9, 127.4, 126.8, 125.8, 125.5, 124.3, 124.3, 122.2, 121.8, 108.5, 60.7, 60.3, 51.5, 49.2, 49.1, 44.0, 33.1, 26.1, 19.3, 14.2, 14.1. ESI-HRMS: calcd. for $C_{30}H_{30}{}^{35}ClNO_5$+$Na^+$ 542.1705, found 542.1720.



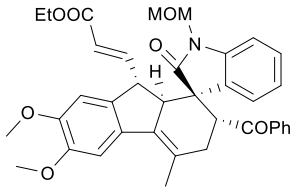
Synthesis of 4t: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of ethyl (*E*)-2-(7-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (0.1 mmol). Then the mixture was stirred at room temperature for 20 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash

chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4t**: 36.5 mg as a white solid, 69% yield; $[\alpha]_D^{20}$ = –25.0 (*c* = 1.00 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak IC, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (major) = 6.27 min, t (minor) = 8.08 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (d, *J* = 8.0 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.14-7.11 (m, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.2 Hz, 1H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.35 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.34 (d, *J* = 15.6 Hz, 1H), 4.15-4.02 (m, 4H), 3.70 (d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.38 (t, *J* = 10.0 Hz, 1H), 3.06 (dd, *J* = 18.4, 6.8 Hz, 1H), 2.90 (d, *J* = 18.4 Hz, 1H), 2.45 (d, *J* = 18.4 Hz, 1H), 2.16 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 176.5, 172.8, 165.4, 148.2, 143.5, 140.1, 139.4, 133.4, 130.9, 130.6, 127.4, 126.8, 126.0, 124.3, 123.2, 122.8, 122.0, 115.5, 60.6, 60.0, 51.8, 49.2, 49.2, 44.5, 33.3, 29.5, 19.4, 14.2, 14.1. ESI-HRMS: calcd. for $C_{30}H_{30}{}^{35}ClNO_5$+$Na^+$ 542.1705, found 542.1712.

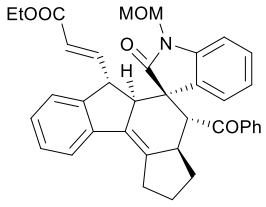


Synthesis of 4u: 5,6-Dichloro-1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-3-(2-oxo-2-phenylethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 19 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4u**: 47 mg as a white solid, 77% yield; $[\alpha]_D^{20}$ = –286.7 (*c* = 0.85 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 12.07 min, t (major) = 17.35 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71 (d, *J* = 7.6 Hz, 2H), 7.65 (s, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.15-7.04 (m, 2H), 7.00-6.91 (m, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.31 (dd, *J* = 15.2, 10.0 Hz, 1H), 5.27-5.03 (m, 3H), 4.17 (d, *J* = 8.4 Hz, 1H), 4.11-3.91 (m, 3H), 3.42 (s, 3H), 3.33 (t, *J* = 9.6 Hz, 1H), 3.19 (dd, *J* = 18.8, 7.2 Hz, 1H), 2.39 (d, *J* = 18.8 Hz, 1H), 2.12 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 200.4, 177.0, 165.2, 146.6, 143.7, 141.6, 140.3, 137.1, 133.2, 131.4, 130.4, 129.6, 129.2, 128.8, 128.6, 128.4, 127.9, 126.2, 125.9, 125.7, 123.1, 122.3, 109.2, 71.4, 60.0, 56.9, 52.0, 50.2, 48.6, 44.0, 33.4, 19.4, 14.2. ESI-HRMS: calcd. for $C_{35}H_{31}{}^{35}Cl_2NO_5$+$Na^+$ 638.1471, found

638.1472.

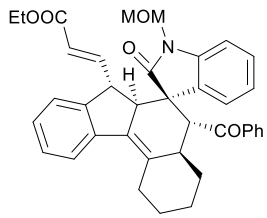


Synthesis of 4v: 5,6-Dimethoxy-1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of ethyl (*E*)-2-(7-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (0.1 mmol). Then the mixture was stirred at room temperature for 25 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4v**: 49.4 mg as a white solid, 81% yield; $[\alpha]_D^{20}$ = –72.7 (*c* = 3.00 in $CHCl_3$); >99% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 26.83 min, t (major) = 59.81 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.17 (s, 1H), 7.12-7.06 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.44-5.32 (m, 2H), 5.22-5.03 (m, 3H), 4.11 (d, *J* = 8.4 Hz, 1H), 4.03-3.97 (m, 3H), 3.90 (s, 3H), 3.79 (s, 3H), 3.41 (s, 3H), 3.35 (t, *J* = 9.6 Hz, 1H), 3.15 (dd, *J* = 18.4, 7.6 Hz, 1H), 2.39 (d, *J* = 18.6 Hz, 1H), 2.13 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 200.6, 177.3, 165.6, 148.6, 148.6, 148.5, 141.7, 137.3, 136.39, 133.0, 131.3, 129.8, 128.6, 128.4, 126.0, 123.0, 122.5, 121.3, 109.1, 107.8, 107.3, 71.5, 59.9, 56.9, 56.2, 56.0, 52.3, 50.6, 49.1, 44.3, 33.3, 30.9, 19.2, 14.2. ESI-HRMS: calcd. for $C_{37}H_{37}NO_7$+Na^+ 630.2462, found 630.2464.



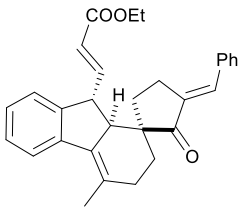
Synthesis of 4w: 1-Cyclopentylidene-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-3-(2-oxo-2-phenylethylidene) indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired

product **4w**: 45.4 mg as a white solid, 80% yield; $[\alpha]_D^{20}$ = –185.1 (*c* = 0.74 in $CHCl_3$); 95% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (major) = 12.38 min, t (minor) = 15.83 min];^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.50 (d, *J* = 7.6 Hz, 1H), 7.39-7.32 (m, 3H), 7.31-7.25 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 3H), 7.13 (d, *J* = 7.6Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 2H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.41 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.25 (d, *J* = 15.6 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.03 (dd, *J* = 14.0, 7.2 Hz, 2H), 3.86 (d, *J* = 10.4 Hz, 1H), 3.67 (t, *J* = 8.0 Hz, 1H), 3.40-3.35 (m, 1H), 3.21-3.08 (m, 4H), 2.95-2.88 (m, 1H), 2.86-2.73 (m, 1H), 2.30-2.18 (m, 1H), 2.06-2.01 (m, 1H), 1.98-1.82 (m, 1H), 1.34-2.23 (m, 1H), 1.17 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 200.9, 179.1, 165.8, 148.4, 144.1, 141.2, 139.5, 138.8, 138.2, 132.5, 130.4, 128.3, 128.0, 127.8, 127.7, 127.0, 125.4, 125.1, 123.3, 123.0, 121.7, 108.8, 71.8, 60.0, 57.0, 56.6, 55.9, 54.8, 48.8, 43.6, 32.9, 30.2, 26.1, 14.2. ESI-HRMS: calcd. for $C_{37}H_{35}NO_5$+Na^+ 596.2407, found 596.2409.



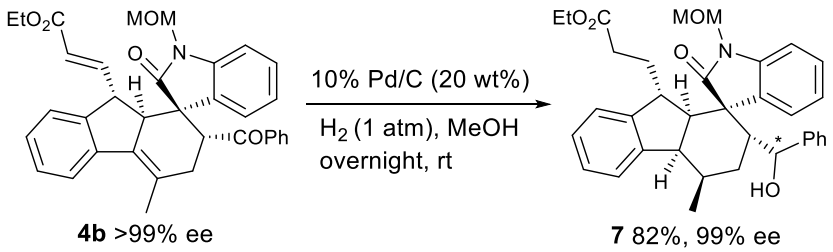
Synthesis of 4x: 1-Cyclohexylidene-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*E*)-1-(methoxymethyl)-3-(2-oxo-2-phenylethylidene)indolin-2-one (0.1 mmol). Then the mixture was stirred at room temperature for 24 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **4x**: 45.7 mg as a white solid, 79% yield; $[\alpha]_D^{20}$ = –171.3 (*c* = 0.58 in $CHCl_3$); 96% ee, determined by HPLC analysis [Chiralpak ID, *n*-hexane/*i*-PrOH = 60/40, 1.0 mL/min, λ = 254 nm, t (minor) = 10.33 min, t (major) = 11.43 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71-7.62 (m, 3H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.95-6.88 (m, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.37 (dd, *J* = 15.6, 10.0 Hz, 1H), 5.19 (d, *J* = 15.6 Hz, 1H), 5.18-5.07 (m, 2H), 4.05-3.95 (m, 3H), 3.73 (s, 1H), 3.52-3.43 (m, 2H), 3.39 (s, 3H), 2.57 (d, *J* = 10.8 Hz, 1H), 2.29-2.16 (m, 1H), 2.16-2.07 (m, 1H), 1.80 (t, *J* = 13.6 Hz, 3H), 1.60-1.37 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 201.5, 177.8, 165.5, 148.5, 144.2, 141.4, 140.4, 137.9, 133.0, 132.3,

129.7, 129.2, 128.5, 128.5, 128.3, 127.2, 126.7, 126.1, 124.8, 124.5, 122.7, 121.5, 108.9, 71.4, 59.8, 56.7, 52.2, 51.4, 50.3, 49.6, 41.5, 34.5, 29.4, 26.5, 25.9, 14.2. ESI-HRMS: calcd. for $C_{38}H_{37}NO_5$+Na^+ 610.2564, found 610.2565.



Synthesis of 6: 1-(Propan-2-ylidene)-1*H*-indene-3-carbaldehyde (0.12 mmol), catalyst **C2** (7.2 mg, 0.02 mmol), acid **A2** (2.7 mg, 0.02 mmol) were dissolved in $CHCl_3$ (1.0 mL), followed by the addition of (*Z*)-2-benzylidene-5-methylenecyclopentan-1-one (0.1 mmol). Then the mixture was stirred at room temperature for 20 h. After completion, purification by flash chromatography on silica gel (EtOAc/petroleum ether) to give the cycloadduct. Subsequently, Wittig reaction of the cycloadduct with Ph_3PCHCO_2Et (35 mg, 0.1 mmol) was conducted in DCM (1.0 mL) at room temperature overnight. Then the mixture was concentrated, and purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the desired product **6**: 45.2 mg as a white solid, 67% yield; $[\alpha]_D^{20}$ = +88.0 (*c* = 0.40 in $CHCl_3$); 85% ee, determined by HPLC analysis [Chiralpak IE, *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, λ = 254 nm, t (minor) = 24.59 min, t (major) = 29.26 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (dd, *J* = 7.6, 3.2 Hz, 3H), 7.47-7.36 (m, 4H), 7.32-7.24 (m, 1H), 7.20-7.13 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.77 (dd, *J* = 15.6, 9.6 Hz, 1H), 5.77 (d, *J* = 15.6 Hz, 1H), 4.08-4.02 (m, 2H), 3.64 (t, *J* = 9.6 Hz, 1H), 3.24-3.17 (m, 1H), 3.06-2.89 (m, 2H), 2.41-2.21 (m, 2H), 2.15-2.12 (m, 1H), 2.04 (d, *J* = 2.0 Hz, 3H), 1.94-1.87 (m, 2H), 1.69-1.64 (m, 1H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 210.6, 165.7, 148.8, 144.3, 140.1, 136.2, 135.6, 133.4, 132.6, 130.6, 129.3, 128.6, 127.8, 127.3, 126.8, 124.6, 124.0, 123.2, 60.1, 54.3, 49.8, 48.2, 31.5, 30.2, 26.5, 26.0, 19.3, 14.0. ESI-HRMS: calcd. for $C_{30}H_{30}O_3$+Na^+ 461.2087, found 461.2085.

6. Transformation of cycloadduct 4b



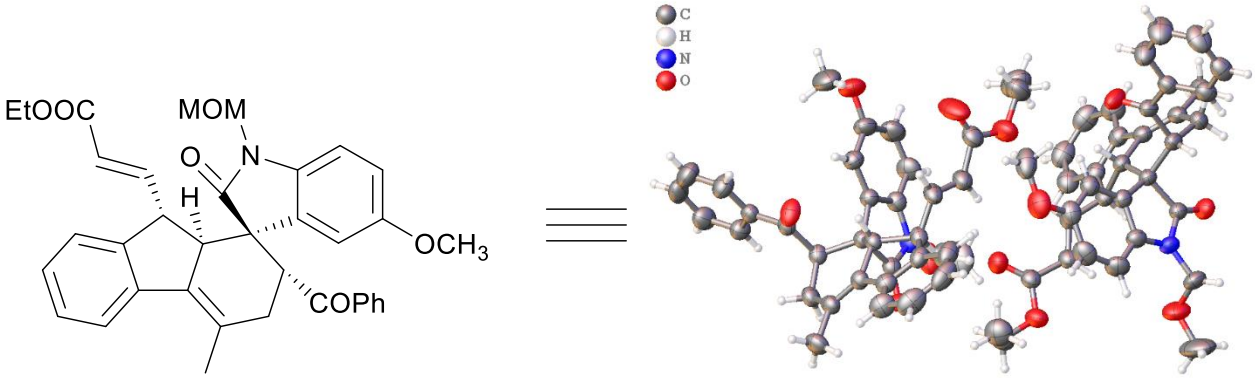
4b >99% ee

7 82%, 99% ee

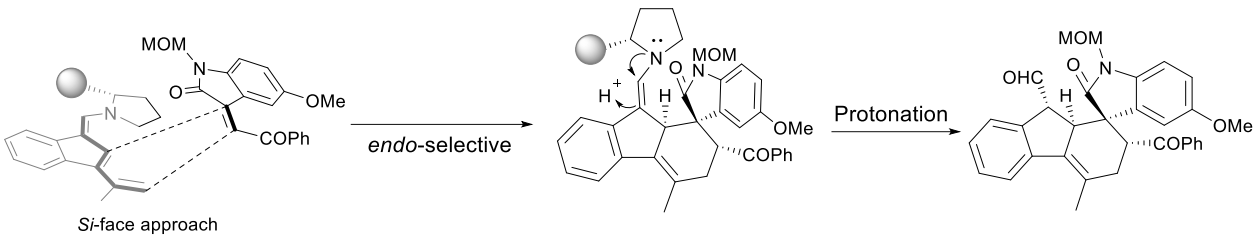
Synthesis of 7: The cycloadduct **4b** (0.1 mmol) and 20% Pd/C was dissolved in MeOH (1.0 mL).

The suspension stirred under an atmosphere of hydrogen overnight. The mixture was filtered and the solvent evaporated. The product **7** was isolated by flash chromatography on silica gel (EtOAc/petroleum ether): 45.1 mg as a white solid, 82% yield; $[\alpha]_D^{20}$ = +59.5 (*c* = 0.75 in $CHCl_3$); 99% ee, determined by HPLC analysis [Chiralpak IB, *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, λ = 254 nm, t (minor) = 6.40 min, t (major) = 8.31 min]; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66 (d, *J* = 7.2 Hz, 1H), 7.35-7.23 (m, 6H), 7.15-7.03 (m, 6H), 5.20 (dd, *J* = 24.4, 10.8 Hz, 2H), 4.10-3.99 (m, 3H), 3.72 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.58-3.49 (t, *J* = 7.2 Hz, 1H), 3.42 (s, 3H), 3.06-2.95 (m, 1H), 2.25-2.13 (m, 3H), 2.07 (dd, *J* = 10.8, 8.0 Hz, 1H), 2.04-1.96 (m, 1H), 1.92 (dd, *J* = 13.2, 4.0 Hz, 1H), 1.83-1.78 (m, 1H), 1.47 (d, *J* = 6.4 Hz, 1H), 1.27-1.24 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.41 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 181.7, 173.7, 145.5, 144.9, 143.2, 141.9, 134.8, 128.6, 128.0, 127.7, 127.0, 126.7, 123.7, 123.3, 123.3, 122.3, 110.0, 78.4, 72.5, 60.1, 56.9, 51.5, 51.0, 45.5, 44.4, 39.9, 32.1, 31.5, 29.3, 15.3, 14.2. ESI-HRMS: calcd. for $C_{35}H_{39}NO_5$+Na^+ 576.2720, found 576.2719. *The absolute configuration of the newly formed tertiary alcohol has not been assigned yet*.

7. Crystal data and structural refinement for enantiopure 4n

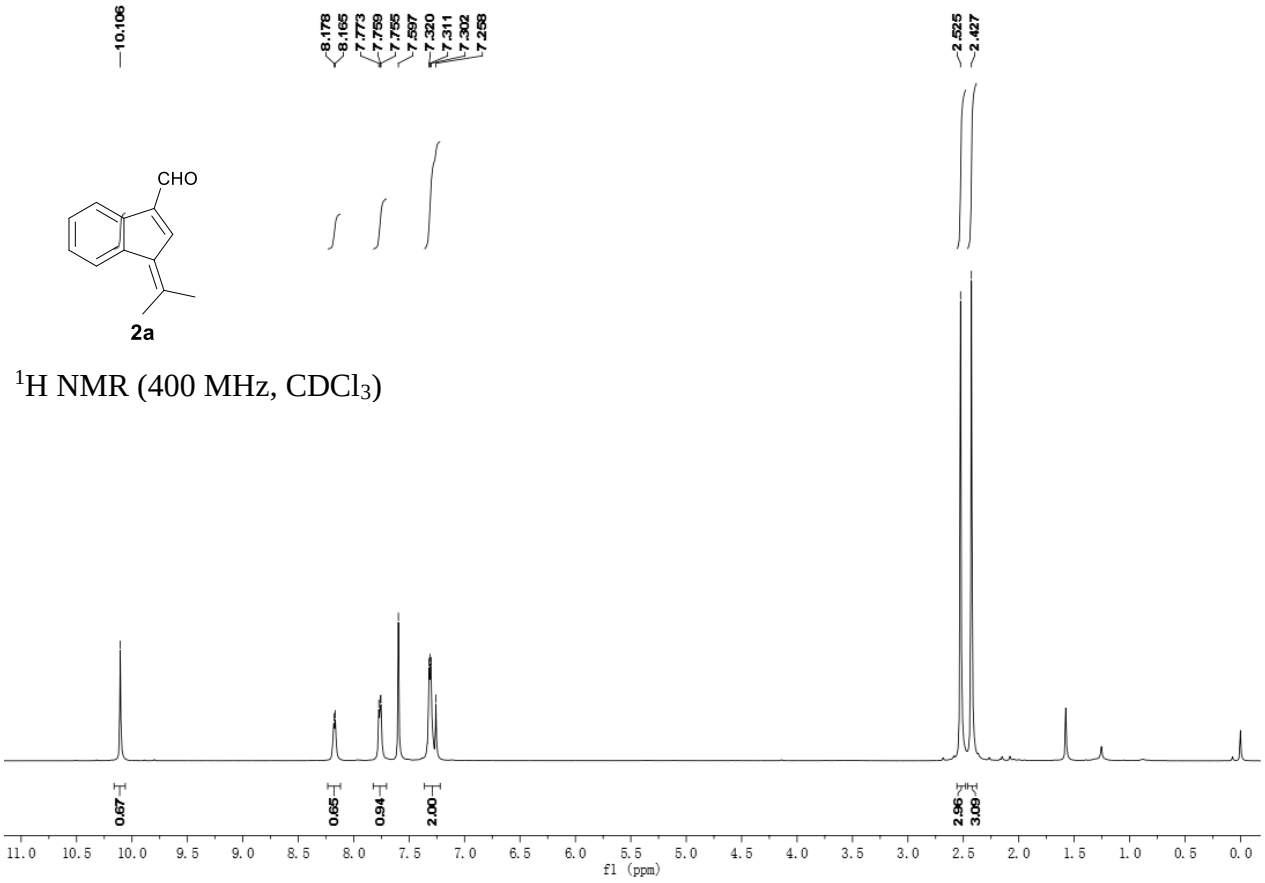


Identification code	**4n**
Empirical formula	$C_{72}H_{68}N_2O_{12}$
Formula weight	1153.28
Temperature/K	296.31(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.0672(2)
b/Å	24.0508(5)
c/Å	11.3892(2)
α/ °	90
β/ °	91.3083(19)
γ/ °	90
Volume/Å^3	3030.72(11)
Z	2
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	0.694
F(000)	1220.0
Crystal size/mm^3	0.7 × 0.5 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/	10.7 to 145.528
Index ranges	-13 ≤ h ≤ 13, -29 ≤ k ≤ 29, -9 ≤ l ≤ 13
Reflections collected	33123
Independent reflections	11836 [R_{int} = 0.0366, R_{sigma} = 0.0346]
Data/restraints/parameters	11836/1/783
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0538, wR_2 = 0.1400
Final R indexes [all data]	R_1 = 0.0565, wR_2 = 0.1450
Largest diff. peak/hole / e Å^{-3}	0.33/-0.38
Flack parameter	0.00(6)



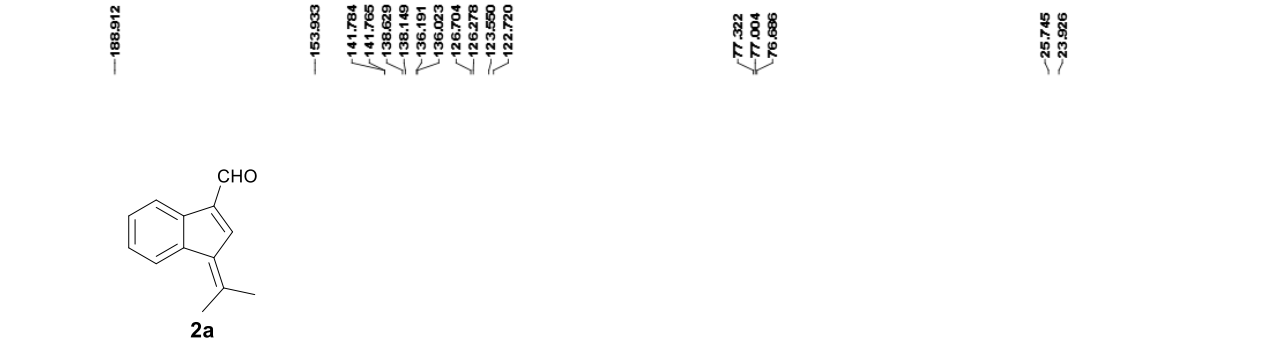
The absolute configuration of the Diels–Alder product **4n** was unambiguously determined by X-ray crystallographic analysis. Based on these results, we proposed that the product was formed through an *endo*-selective cycloaddition after the final protonation process.

8. NMR spectra and HPLC chromatograms



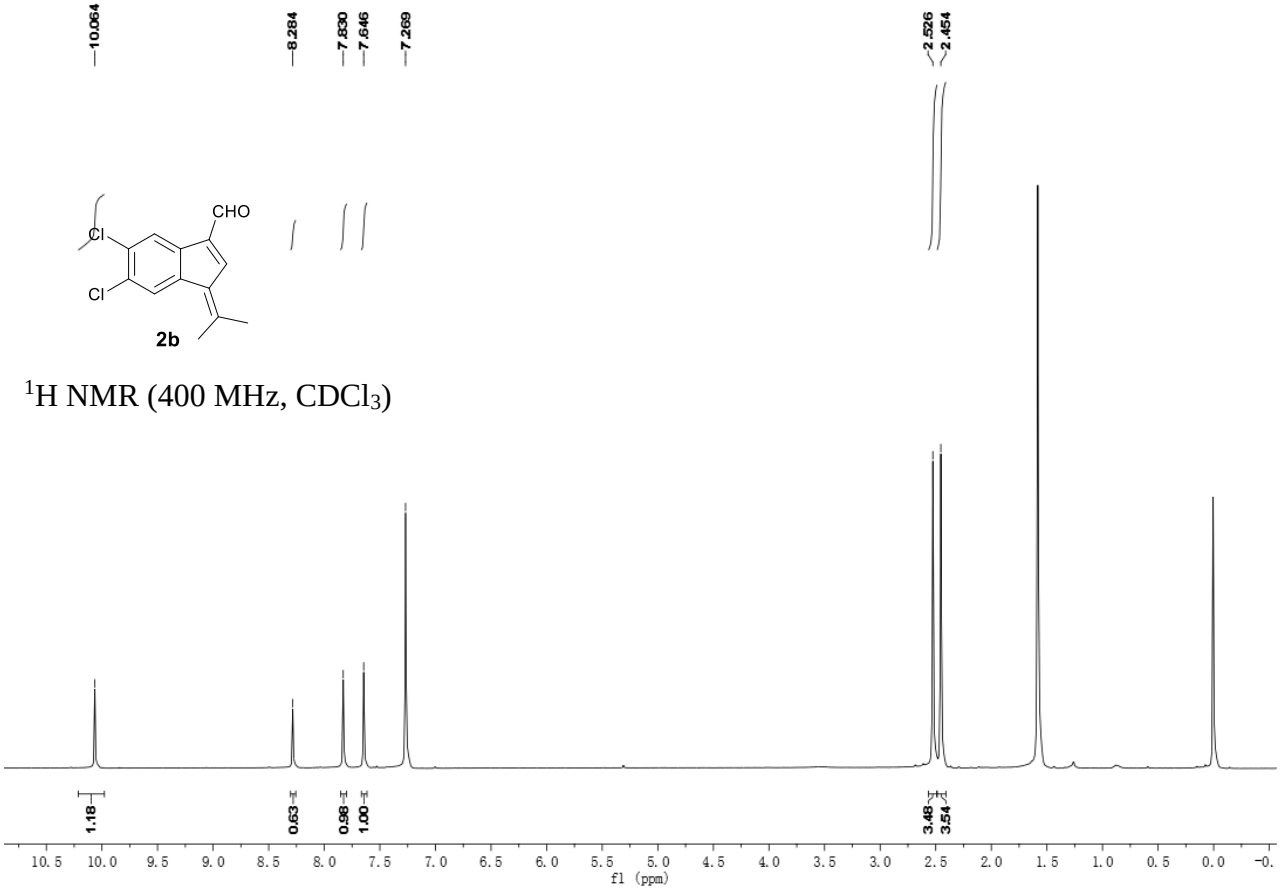
2a

^{1}H NMR (400 MHz, $CDCl_3$)

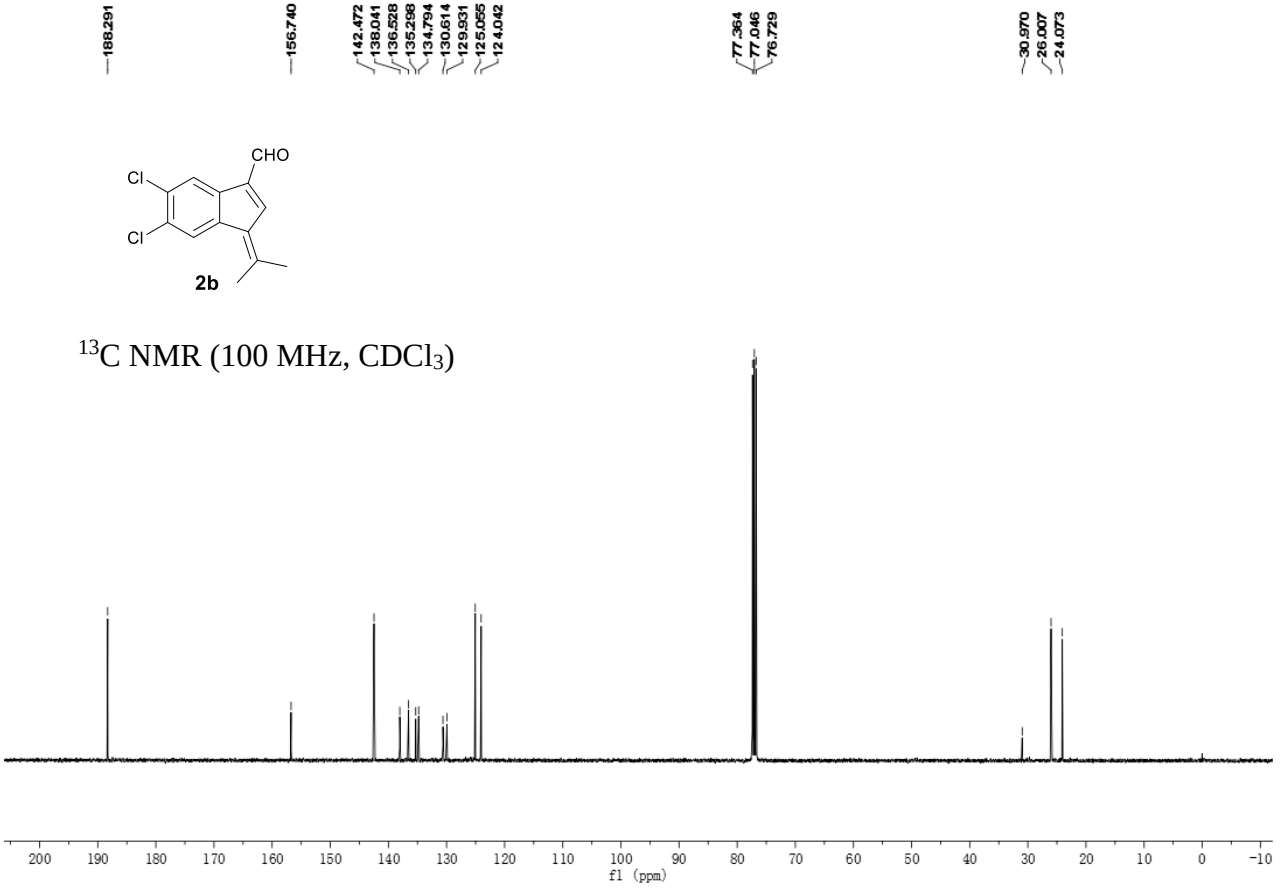


2a

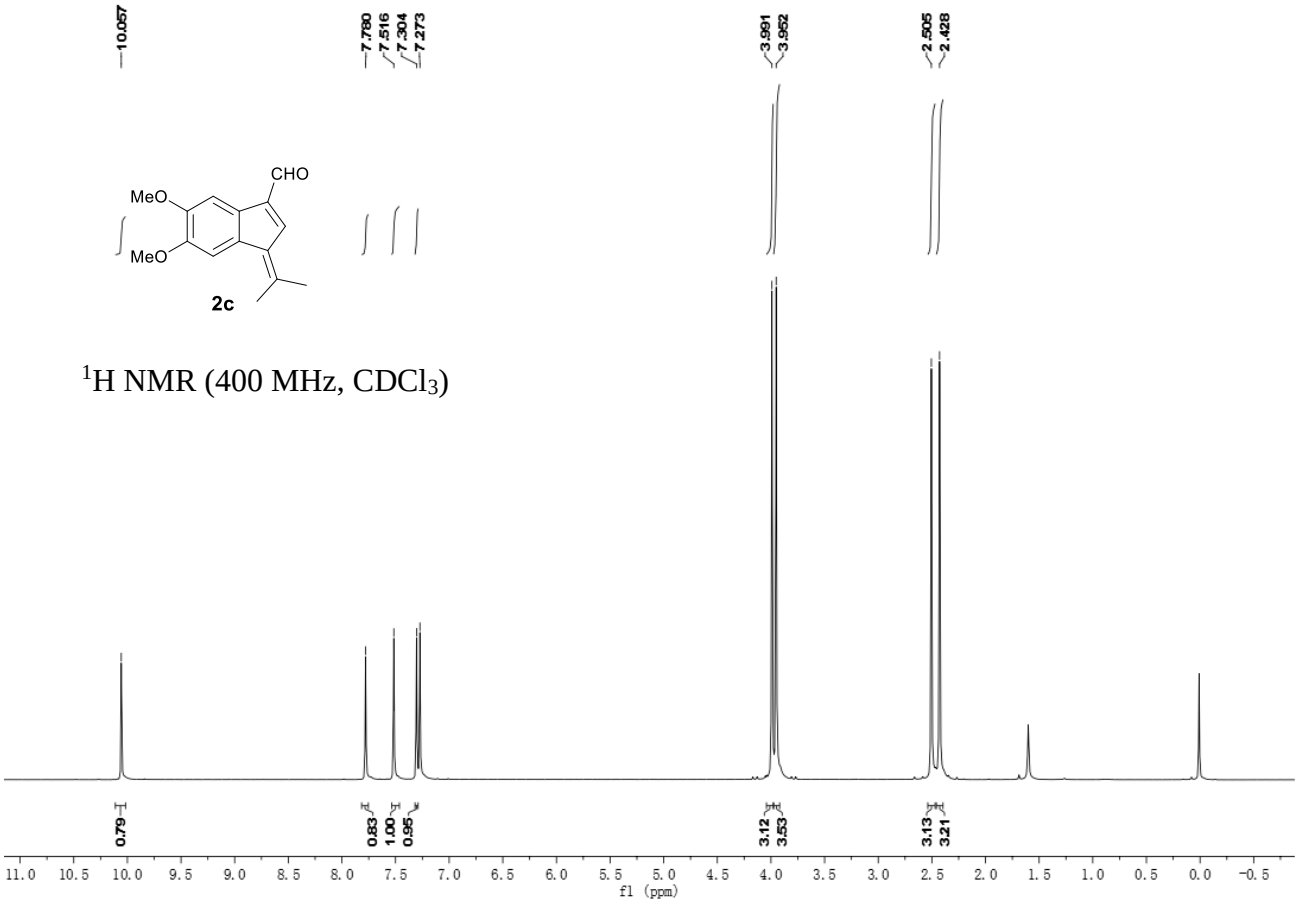
^{13}C NMR (100 MHz, $CDCl_3$)



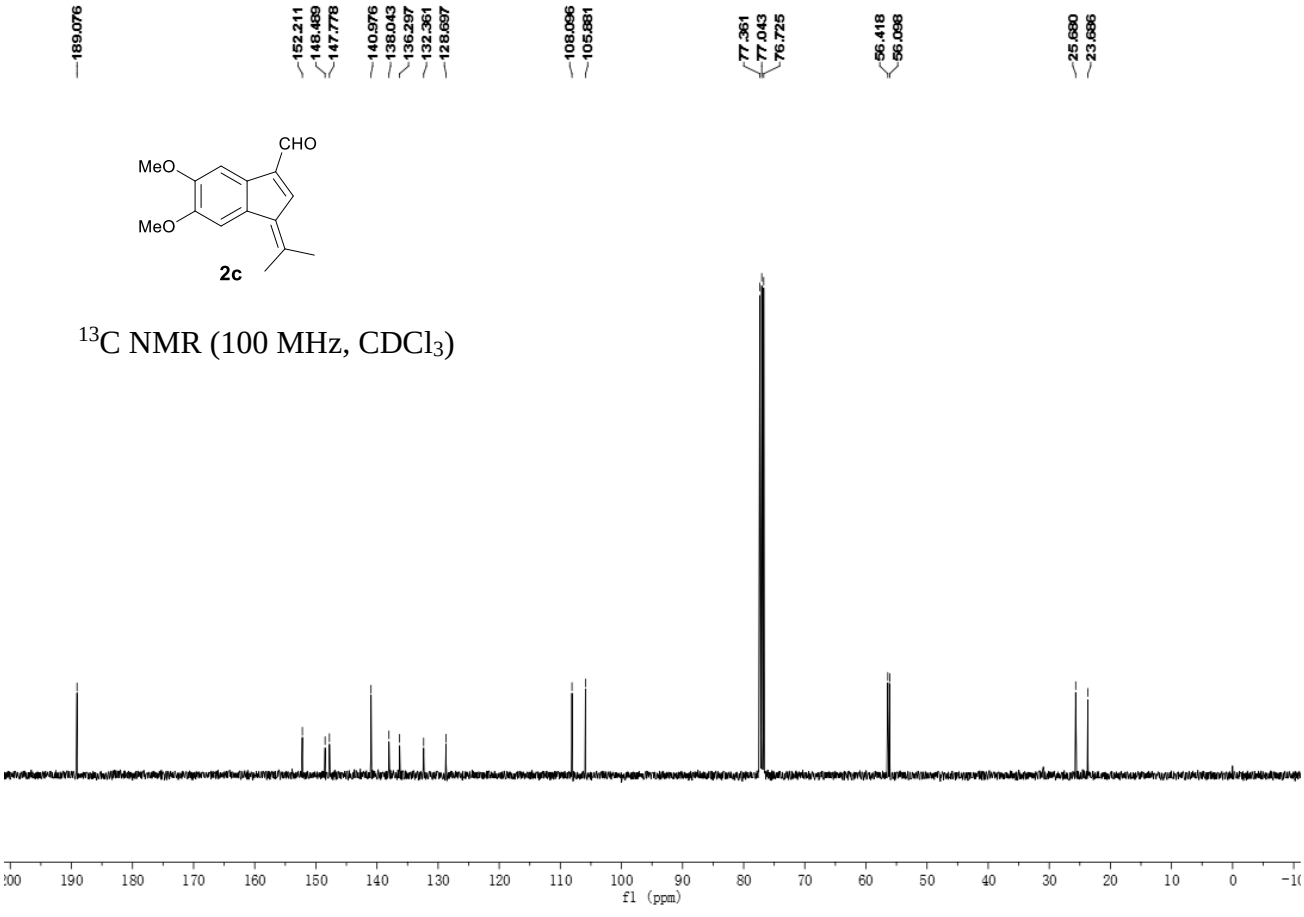
^{1}H NMR (400 MHz, $CDCl_3$)



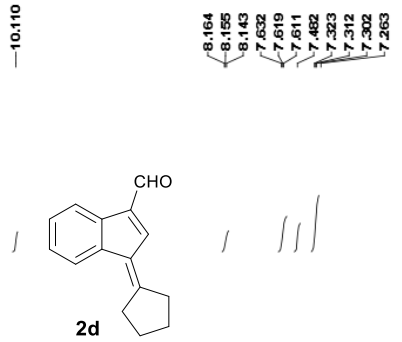
^{13}C NMR (100 MHz, $CDCl_3$)



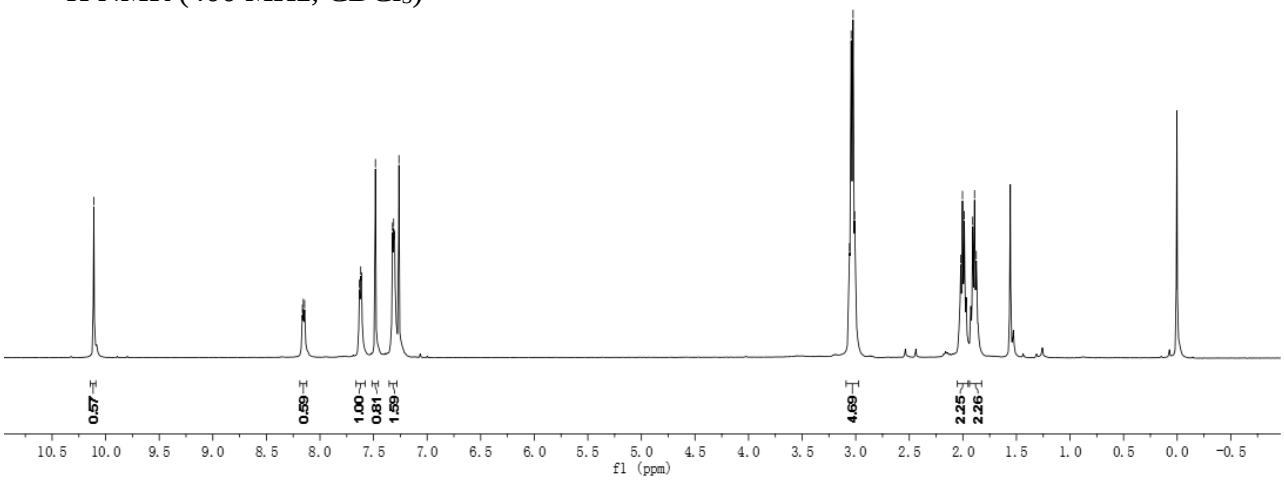
^{1}H NMR (400 MHz, $CDCl_3$)

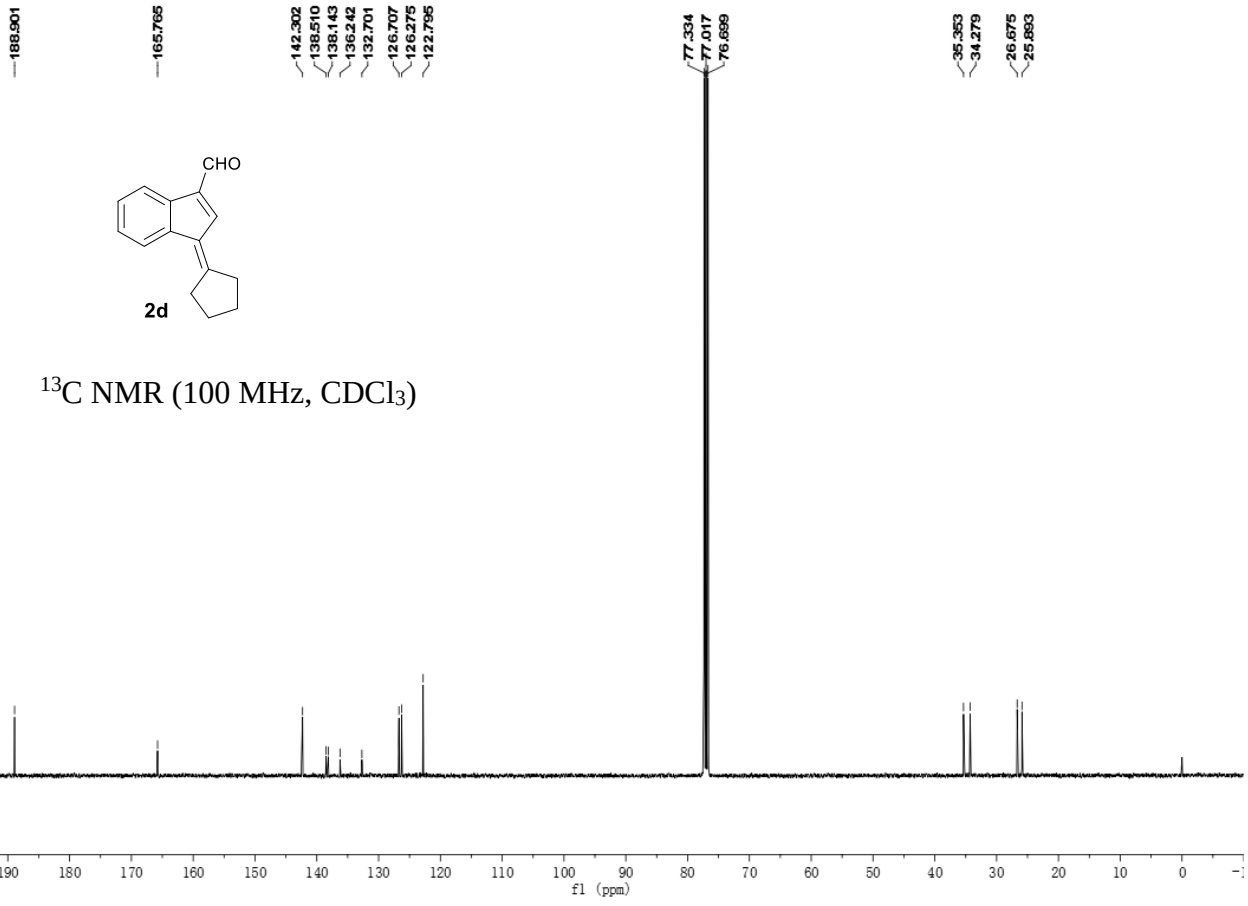


^{13}C NMR (100 MHz, $CDCl_3$)

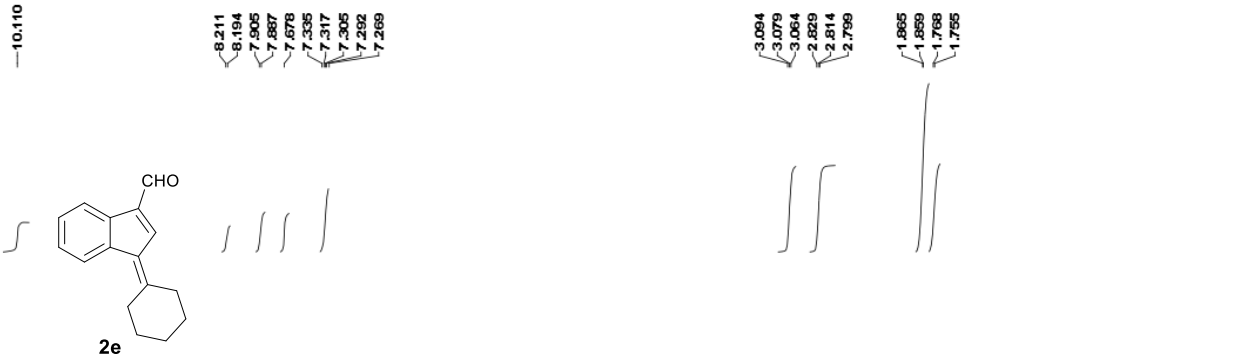


^{1}H NMR (400 MHz, $CDCl_3$)



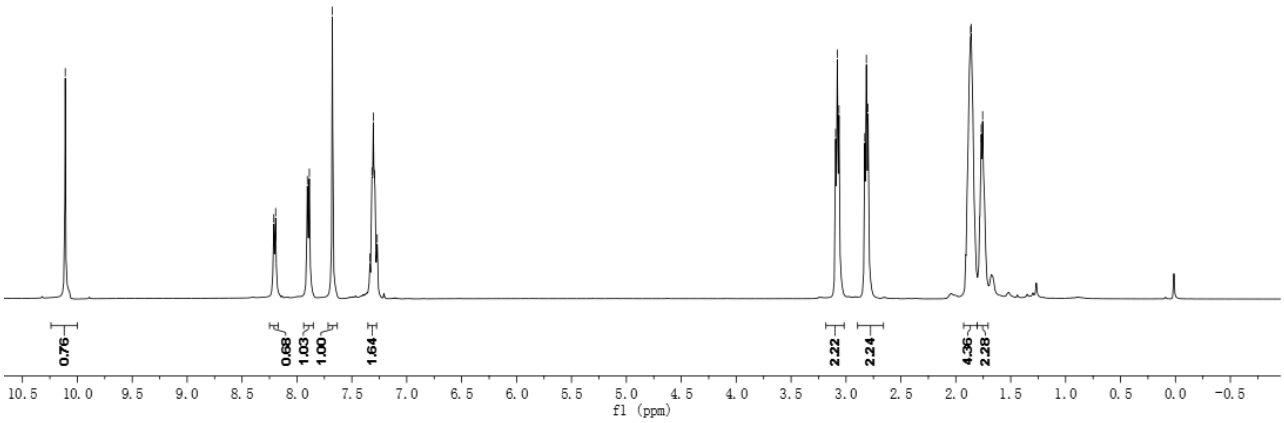


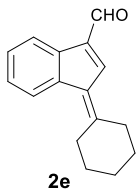
^{13}C NMR (100 MHz, $CDCl_3$)



2e

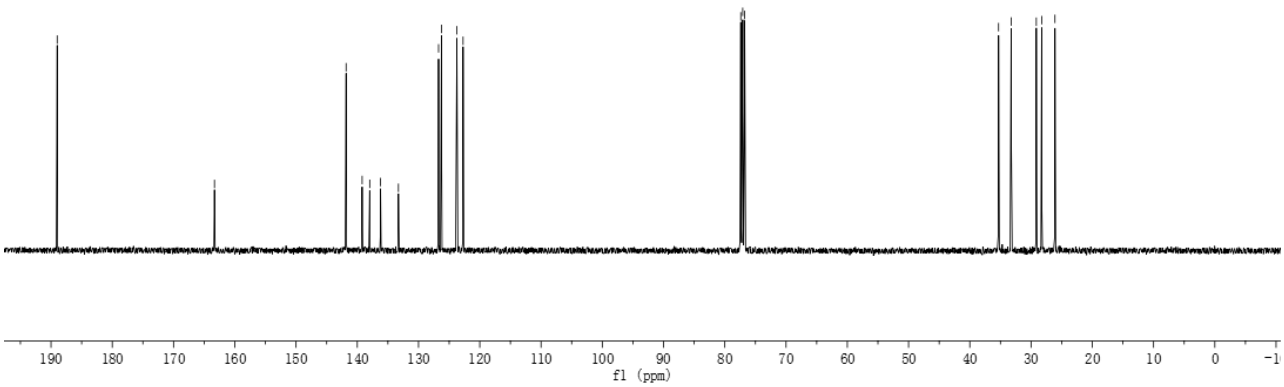
^{1}H NMR (400 MHz, $CDCl_3$)

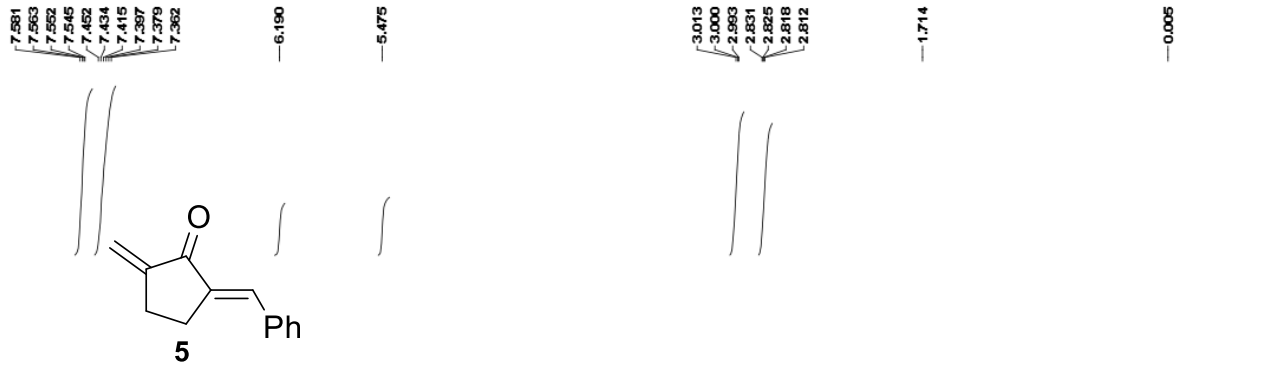




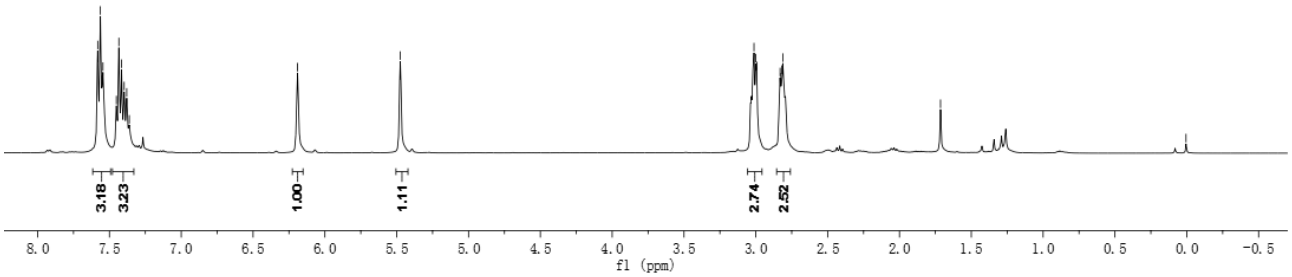
2e

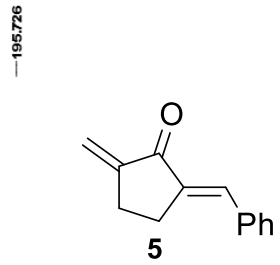
^{13}C NMR (100 MHz, $CDCl_3$)



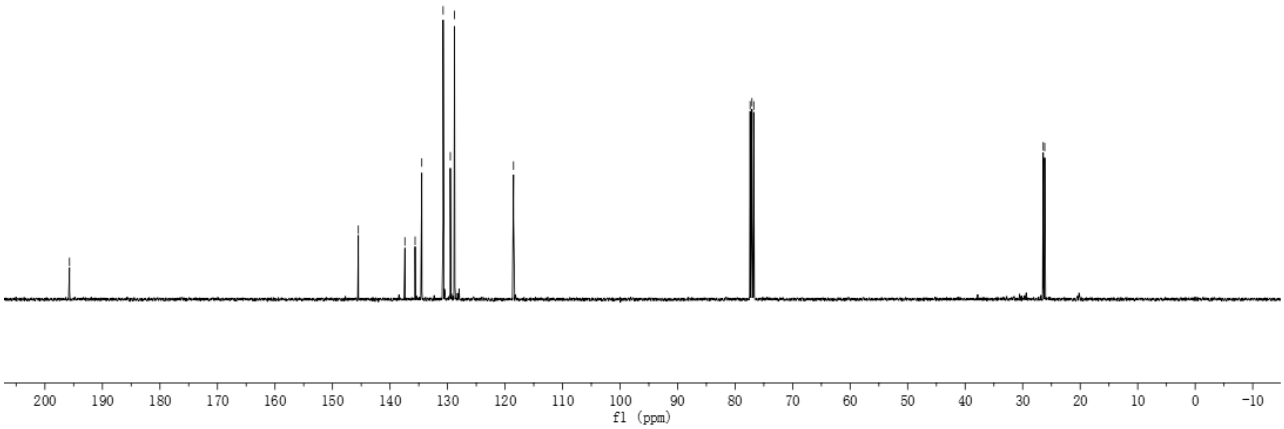


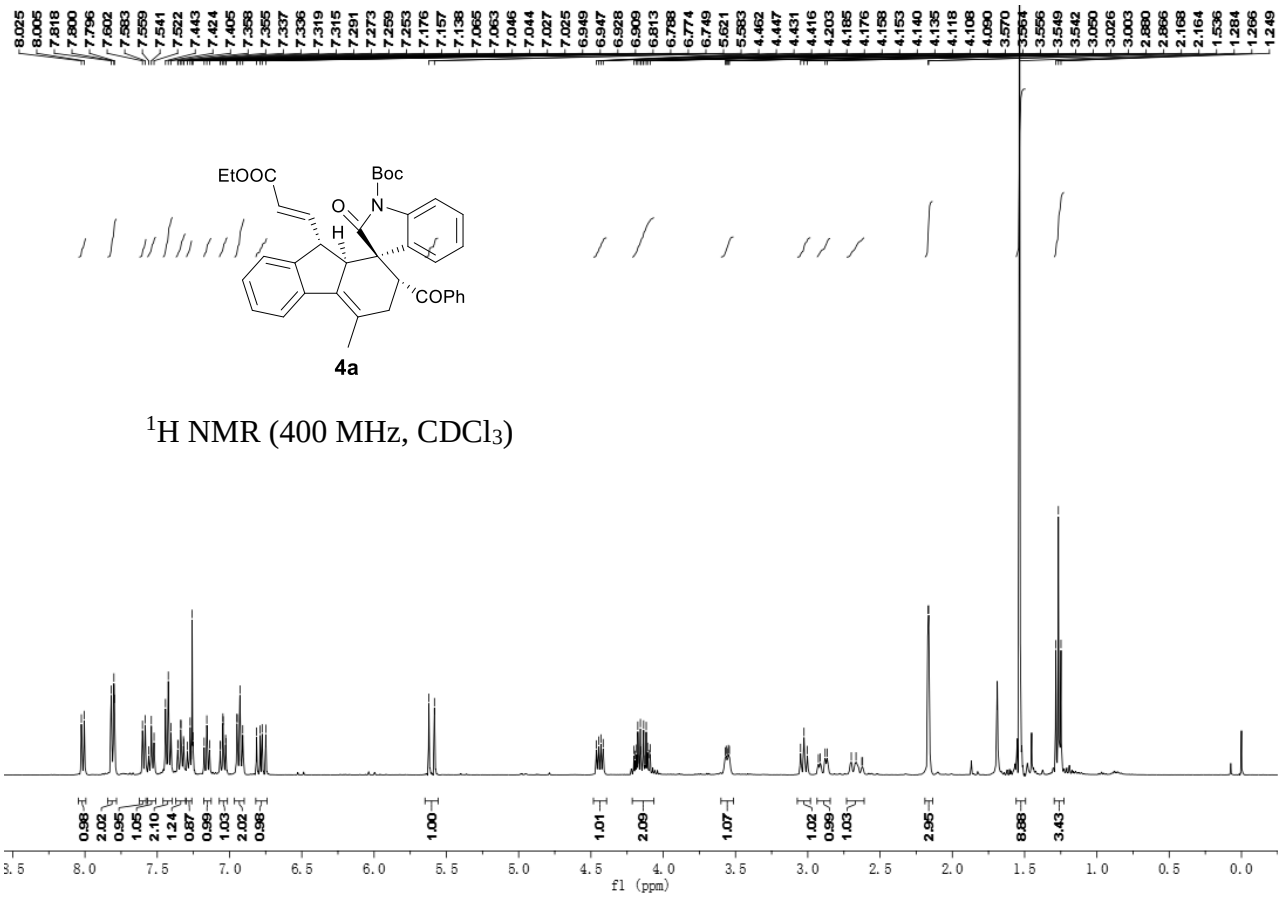
^{1}H NMR (400 MHz, $CDCl_3$)





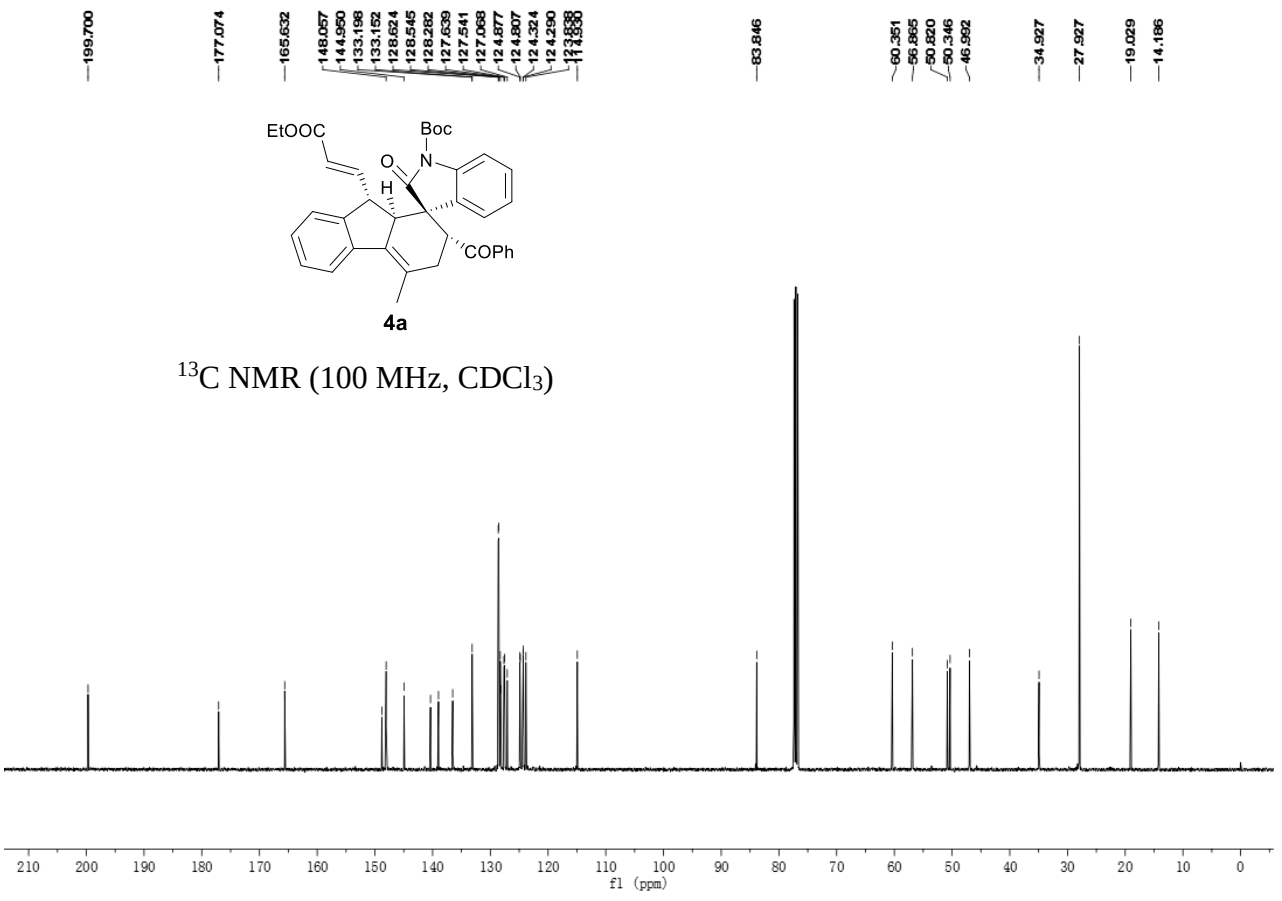
^{13}C NMR (100 MHz, $CDCl_3$)





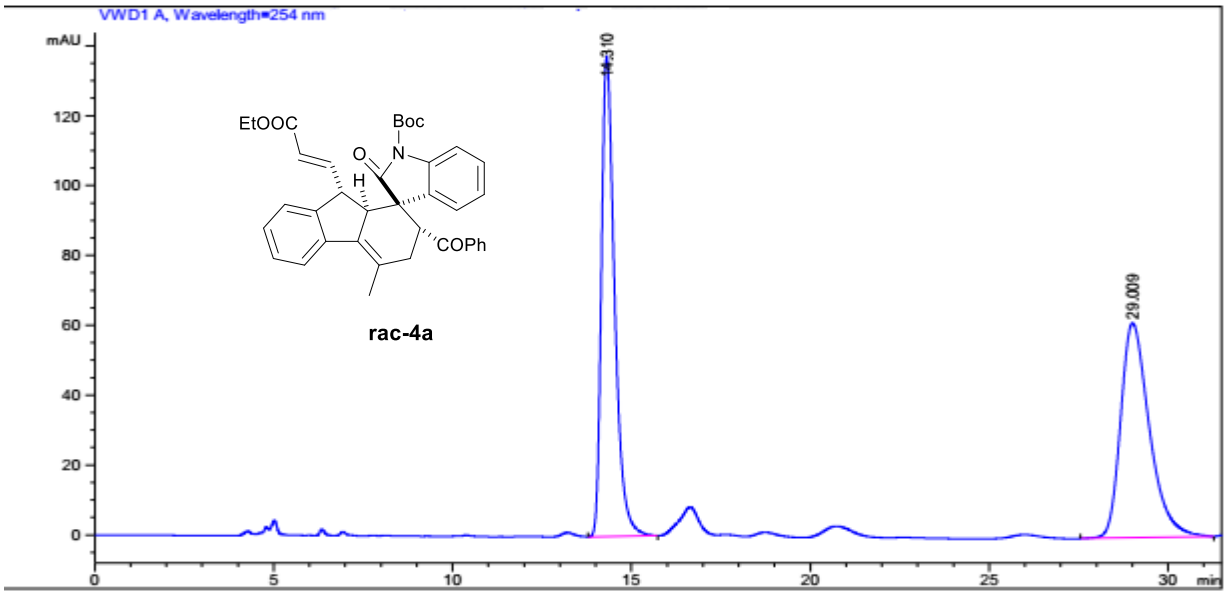
4a

^{1}H NMR (400 MHz, $CDCl_3$)

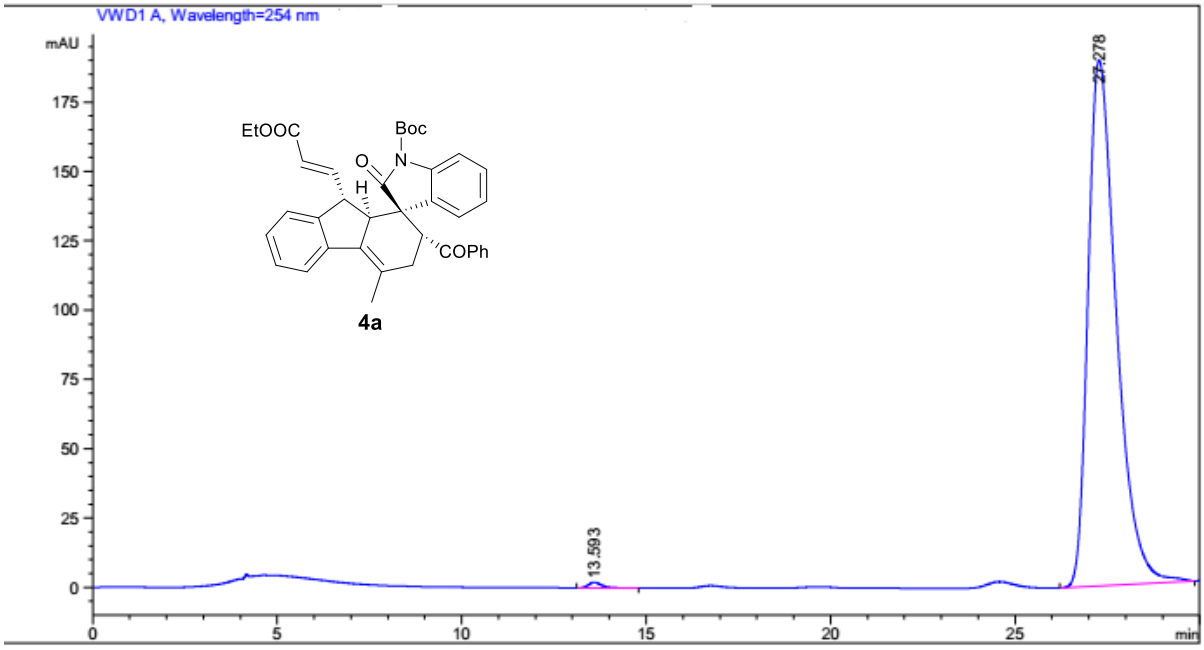


4a

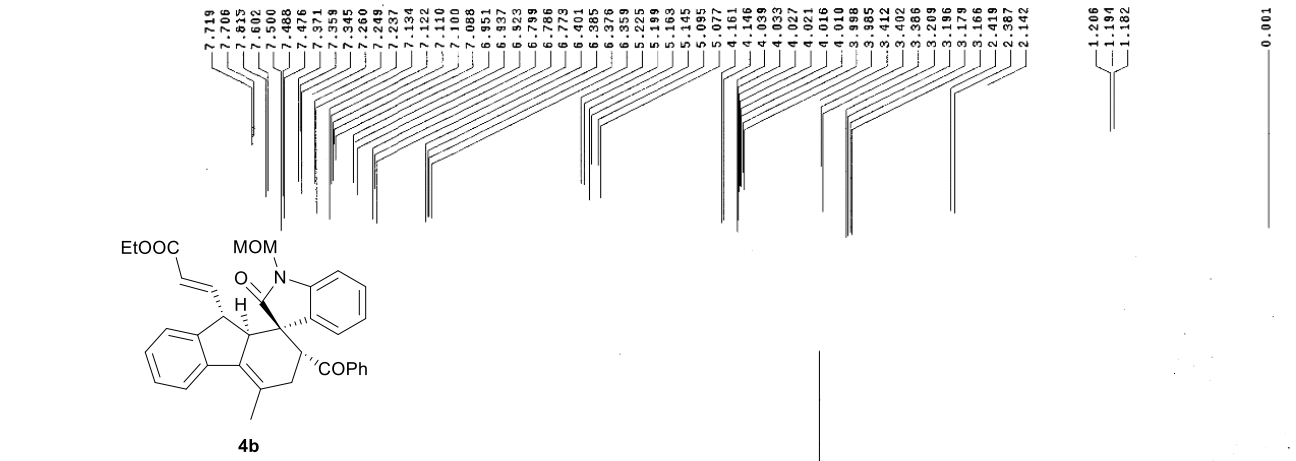
^{13}C NMR (100 MHz, $CDCl_3$)



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
14.310	BBA	0.39	137.3809	3519.2876	50.6964
29.009	BBA	0.85	61.4001	3422.5952	49.3036
			Totals:	6941.8828	100.0000

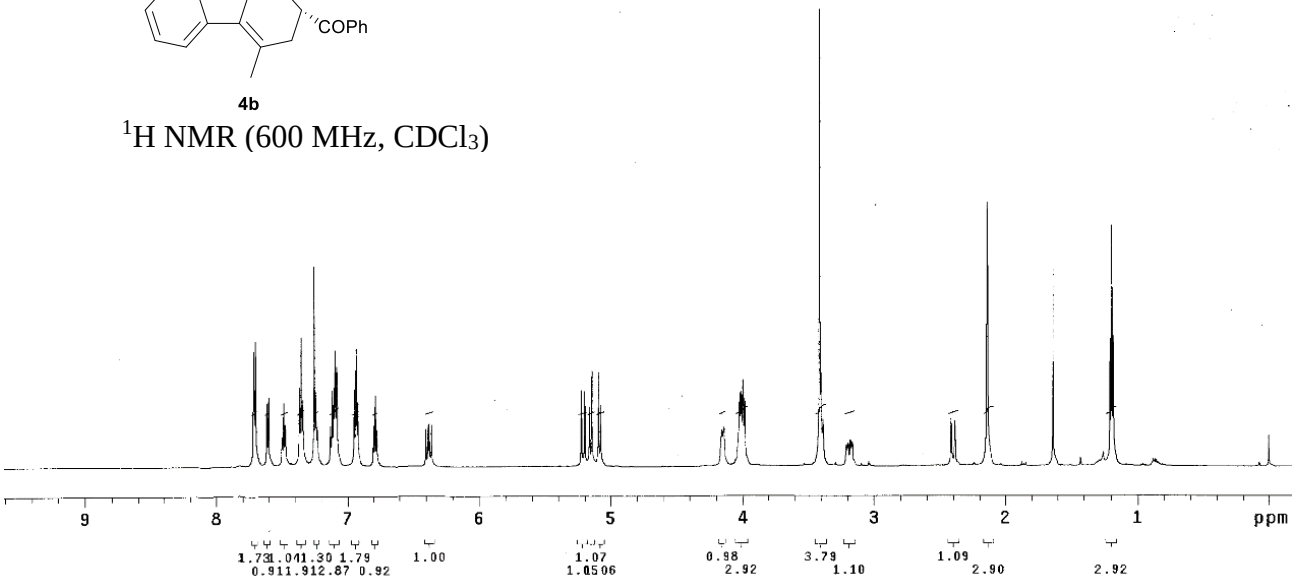


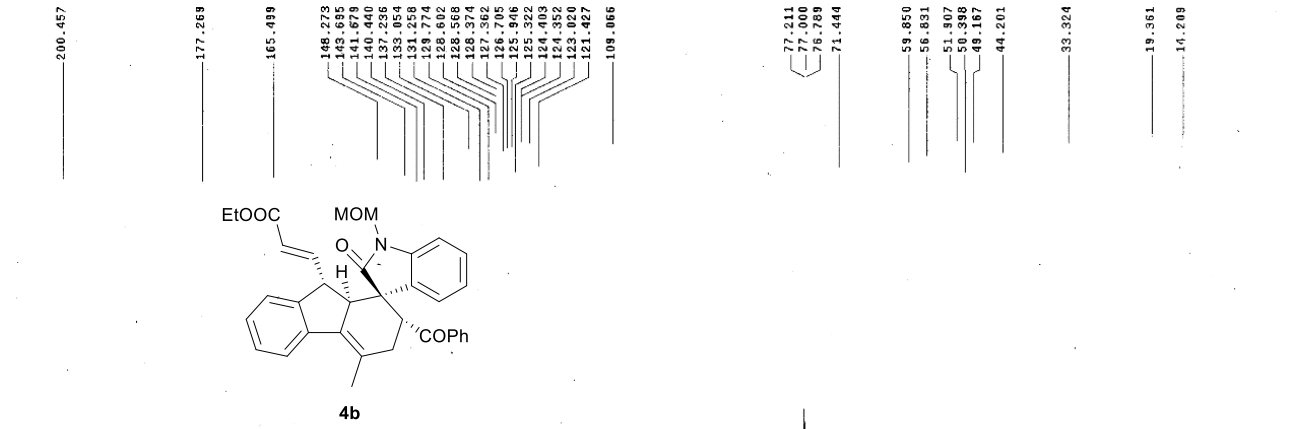
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
13.593	BB	0.38	2.0199	50.9763	0.5021
27.278	BBA	0.80	189.4639	10101.0859	99.4979
			Totals:	10152.0623	100.0000



4b

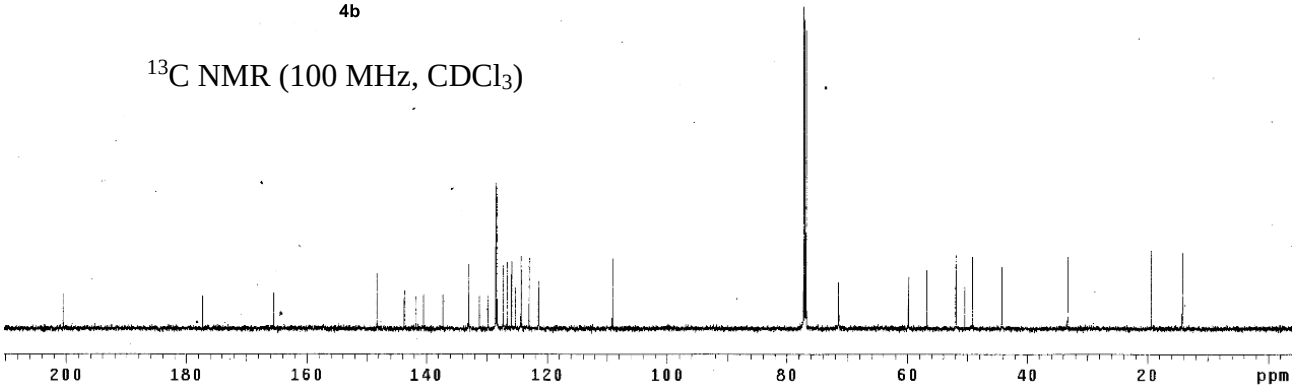
^{1}H NMR (600 MHz, $CDCl_3$)

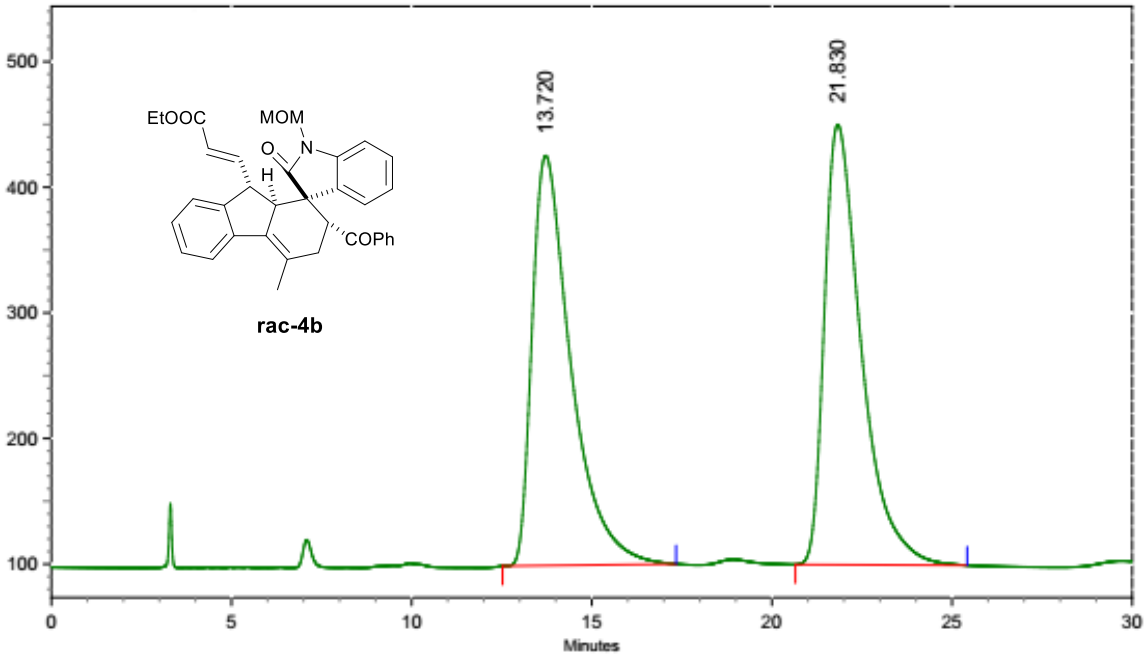




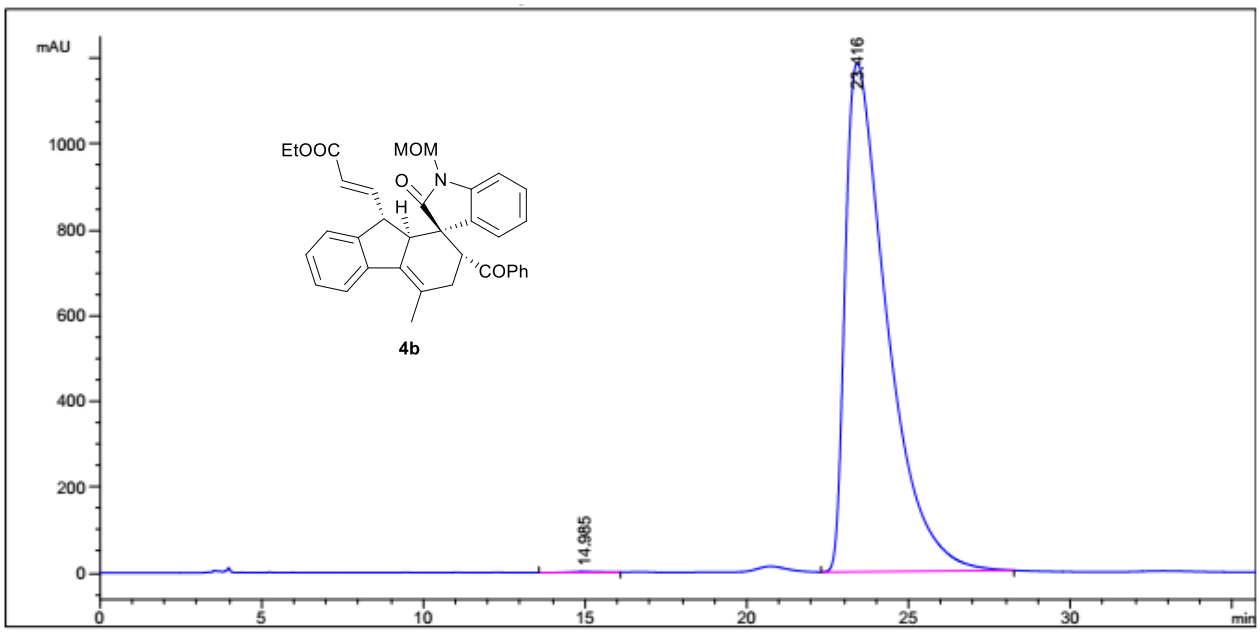
4b

^{13}C NMR (100 MHz, $CDCl_3$)

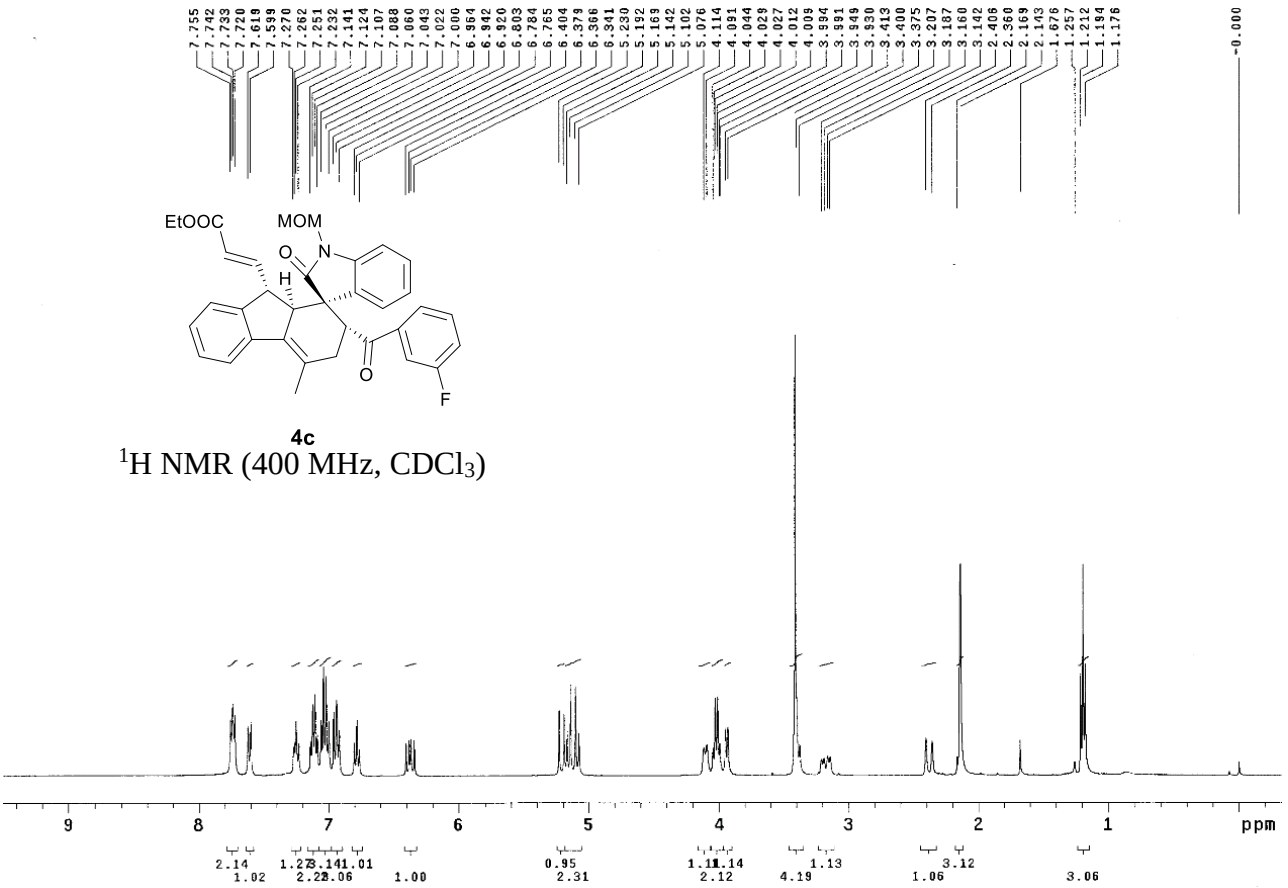




Peak No.	Ret Time	Width	Height	Area	Area [%]
1	13.720	4.817	5474406	411068476	49.5395
2	21.830	4.770	5879505	418710274	50.4605

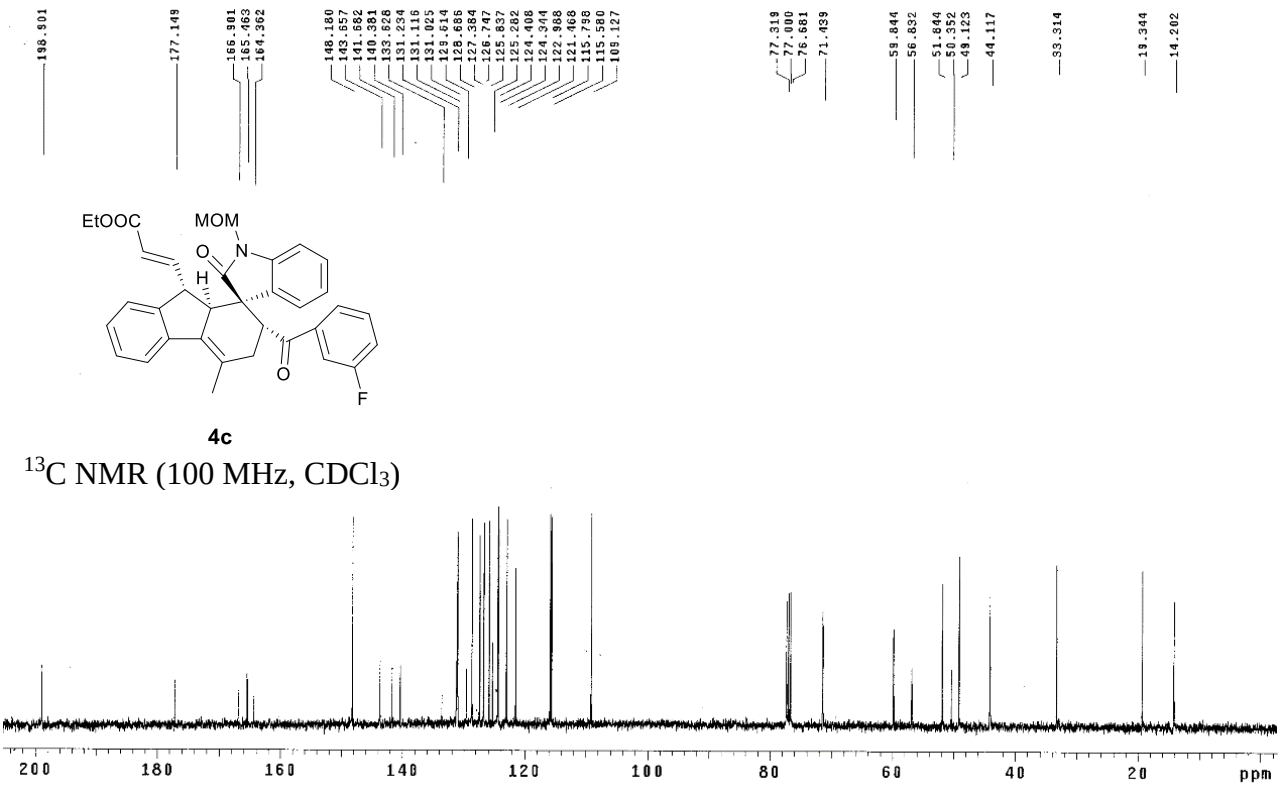


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.985	BV	0.8212	128.28226	1.86890	0.1205
2	23.416	BBA	1.3330	1.06313e5	1187.18970	99.8795



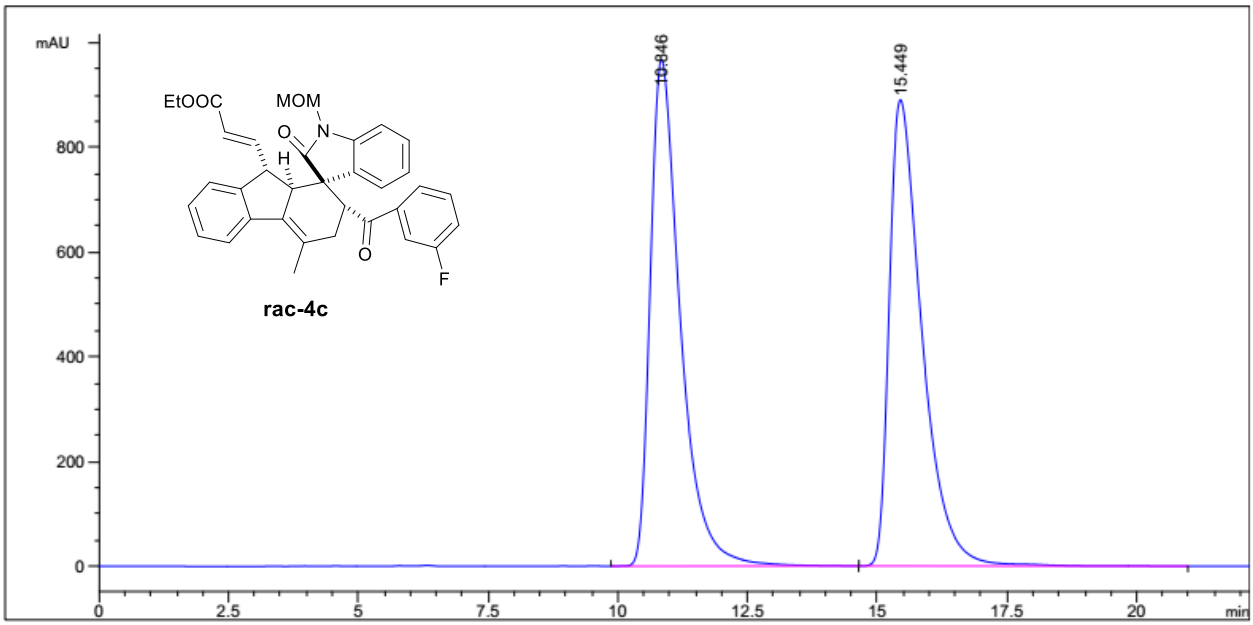
4c

^{1}H NMR (400 MHz, $CDCl_3$)

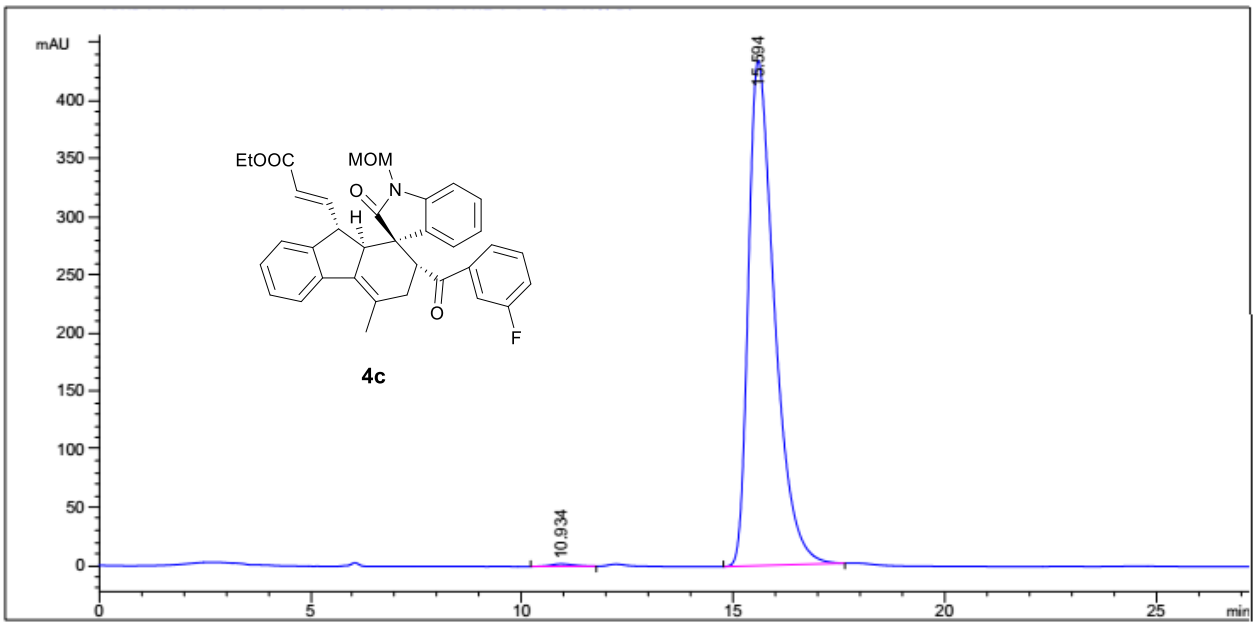


4c

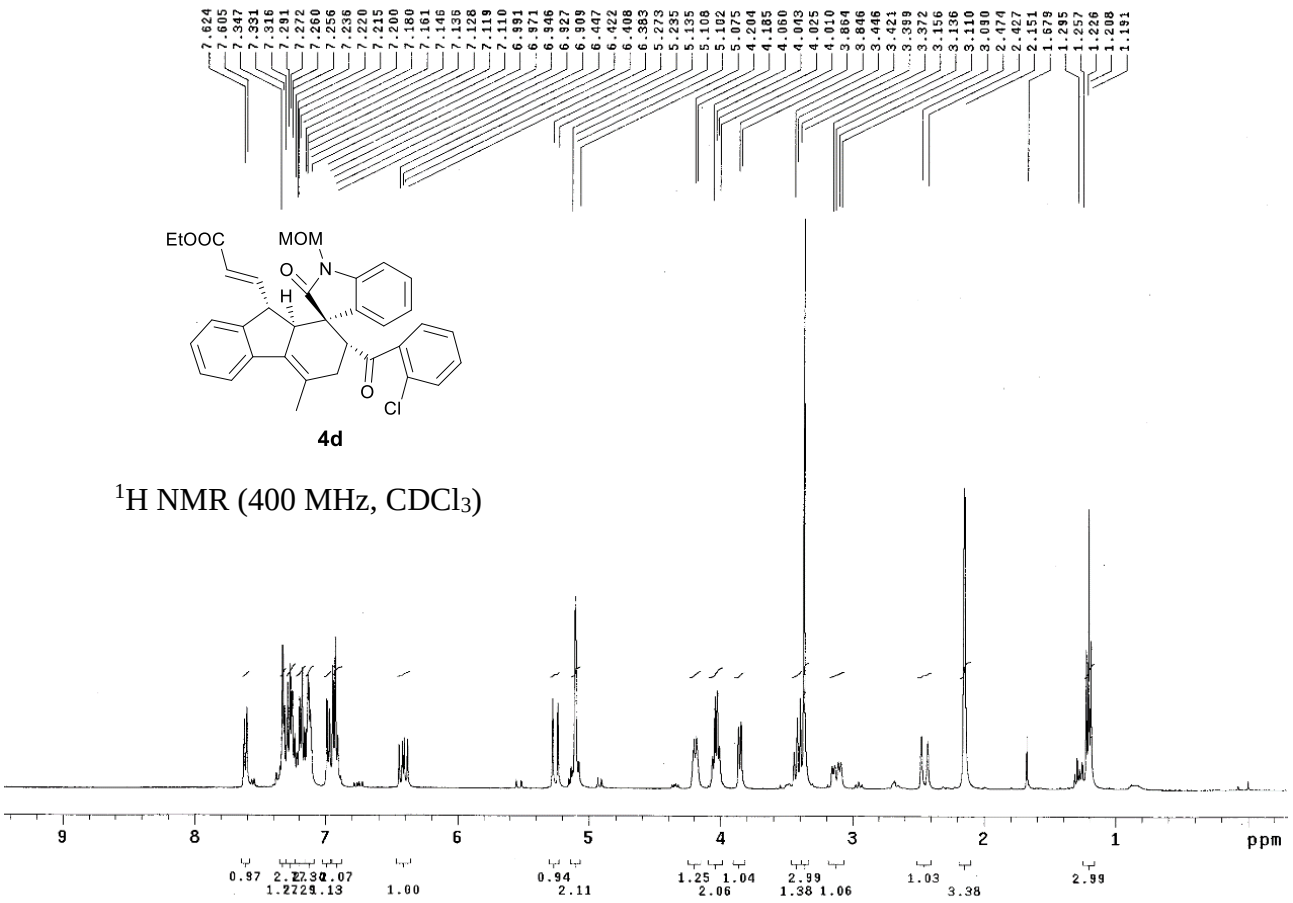
^{13}C NMR (100 MHz, $CDCl_3$)



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.846	BB	0.6053	3.89558e4	967.11115	50.0083
2	15.449	BB	0.6603	3.89428e4	890.21875	49.9917

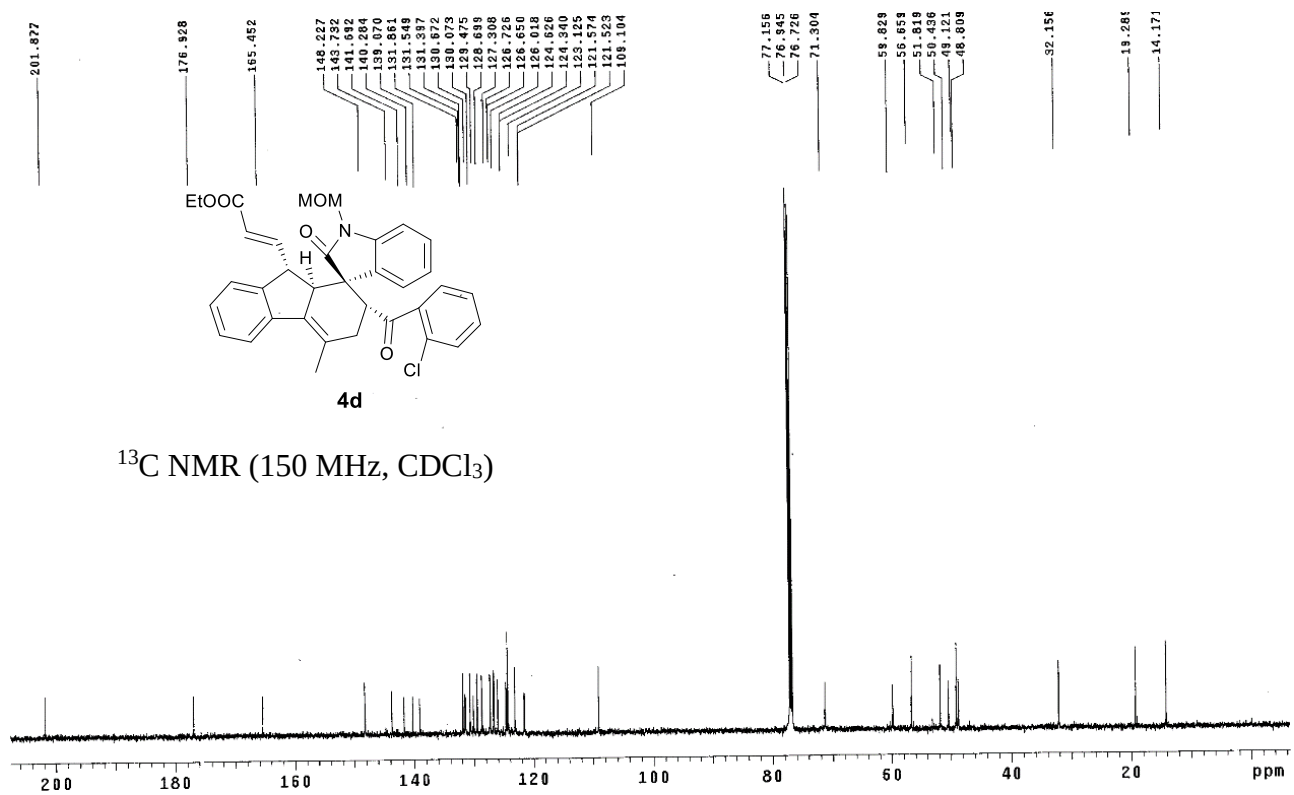


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.934	BB	0.5655	80.13419	2.12324	0.4286
2	15.594	BB	0.6487	1.86144e4	434.16769	99.5714



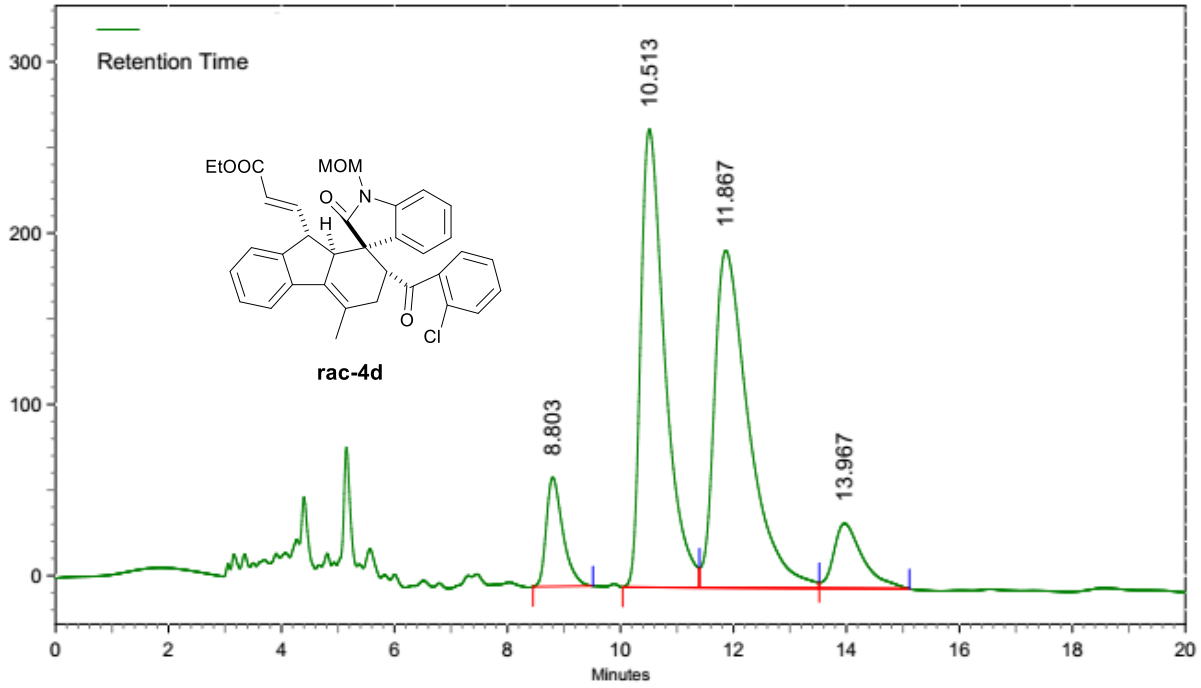
4d

^{1}H NMR (400 MHz, $CDCl_3$)

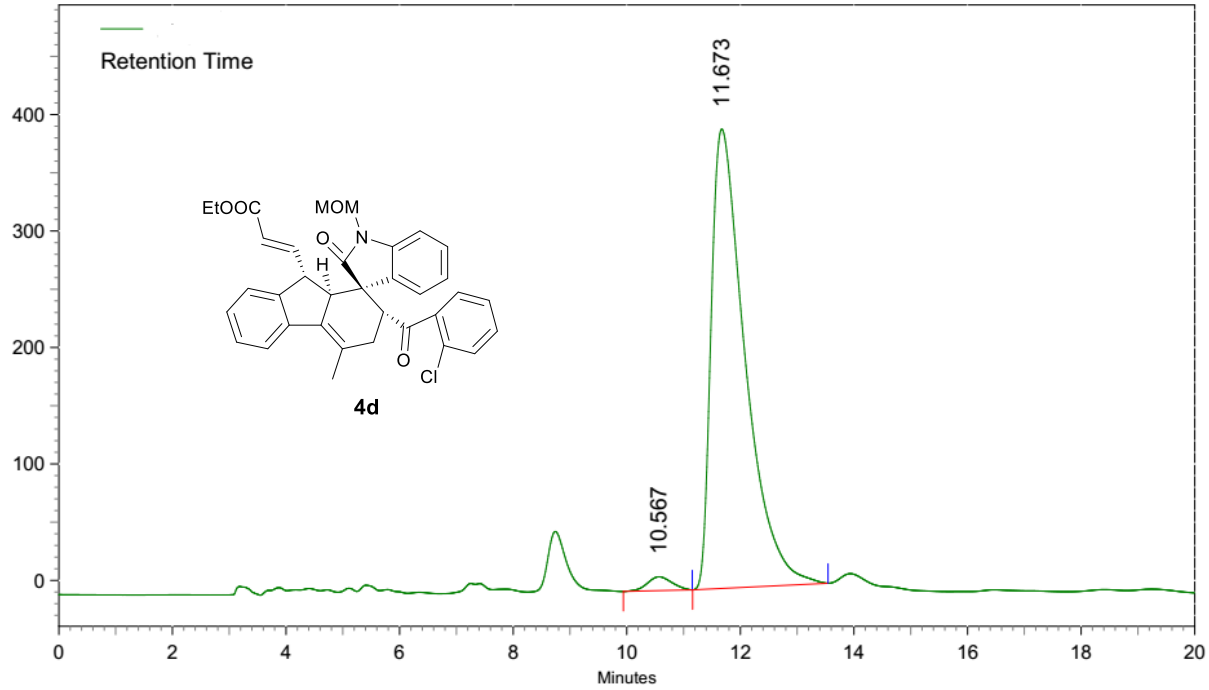


4d

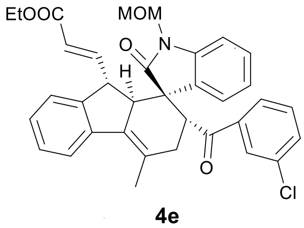
^{13}C NMR (150 MHz, $CDCl_3$)



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.803	1.060	1067271	21773737	6.8567
2	10.513	1.357	4485820	133100131	41.9139
3	11.867	2.123	3303133	139903668	44.0564
4	13.967	1.597	637401	22778227	7.1730

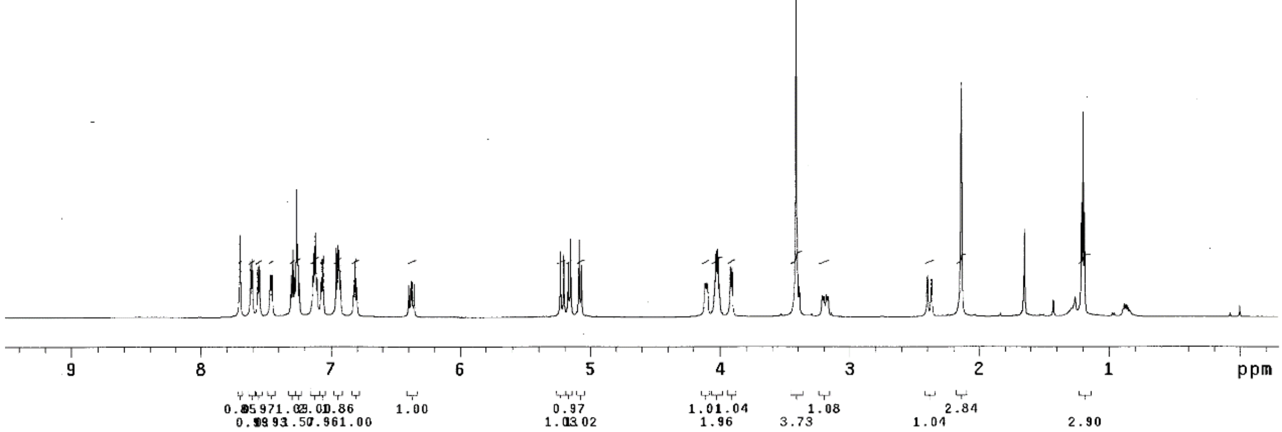


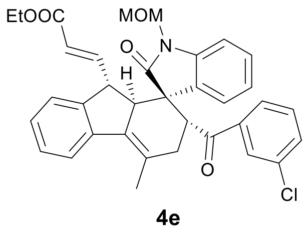
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.567	1.213	199136	5995839	2.1389
2	11.673	2.383	6617208	274325472	97.8611



4e

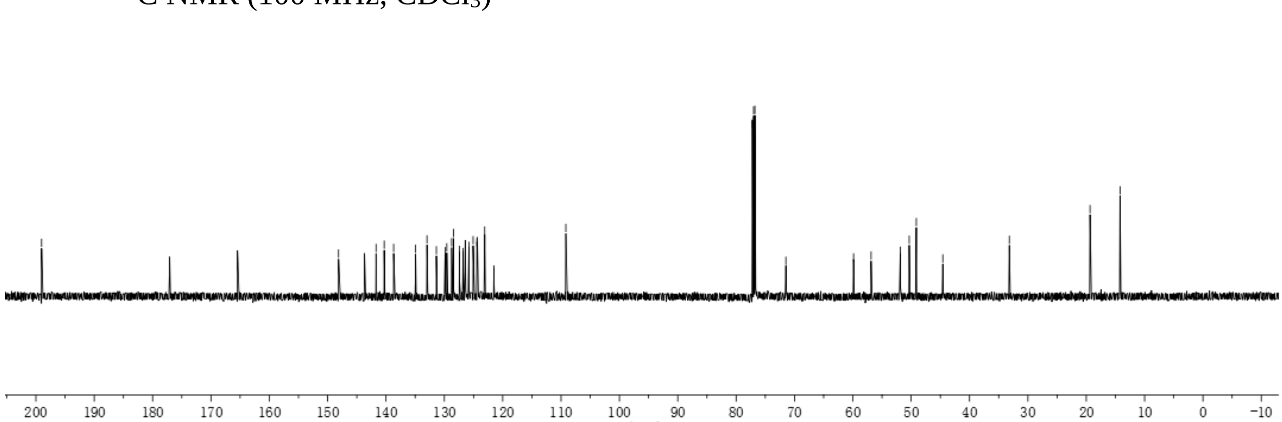
^{1}H NMR (600 MHz, $CDCl_3$)

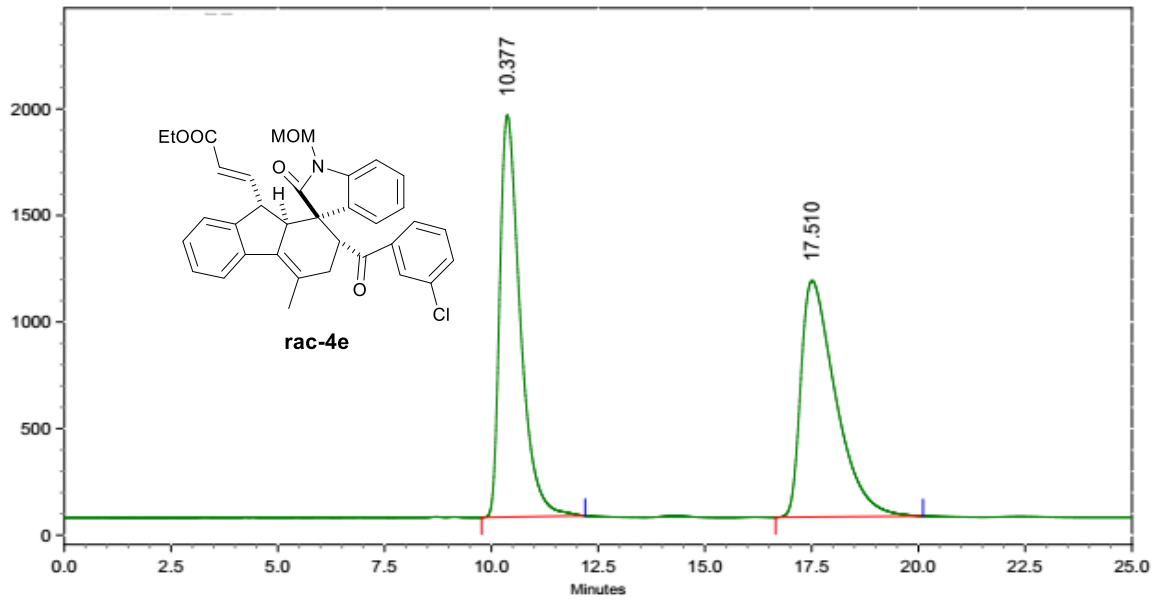




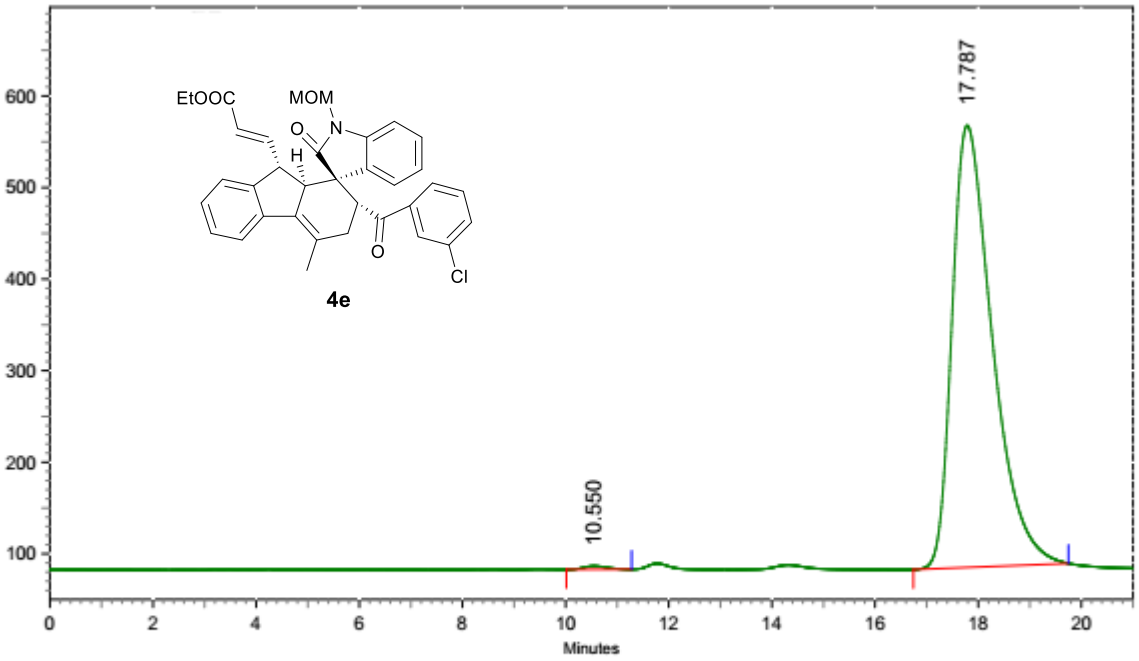
4e

^{13}C NMR (100 MHz, $CDCl_3$)

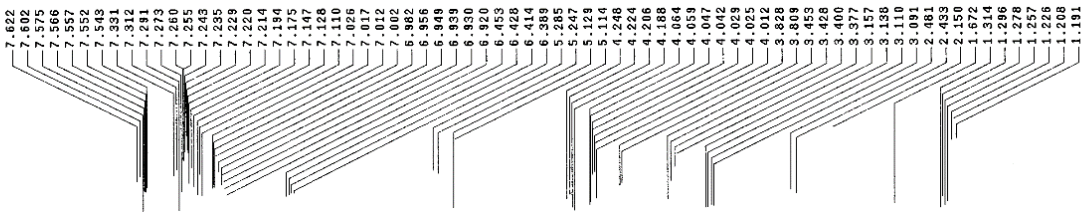


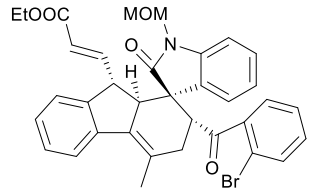


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.377	2.427	31626566	1052964590	50.0127
2	17.510	3.453	18617201	1052429386	49.9873



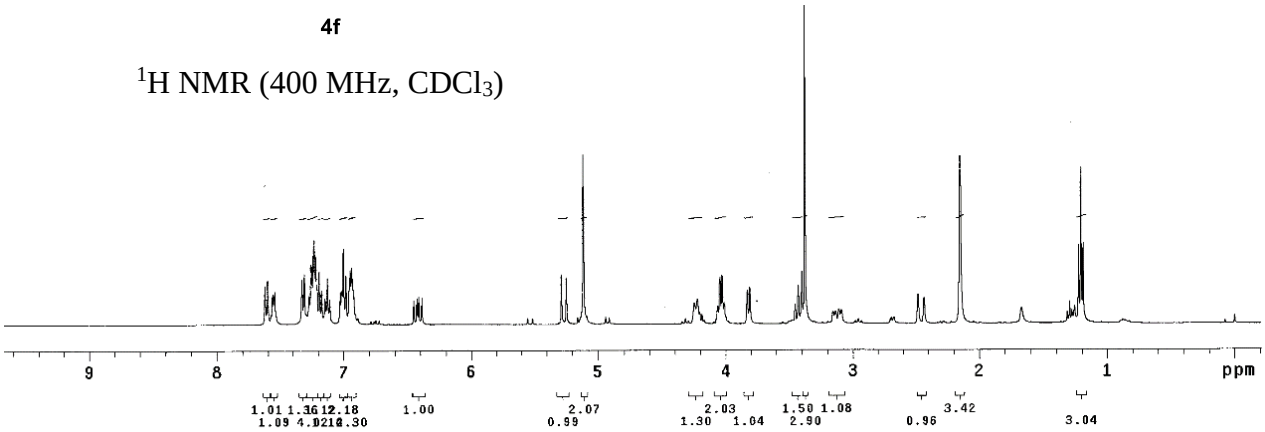
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.550	1.267	62266	1929538	0.4378
2	17.787	3.007	8098286	438831453	99.5622

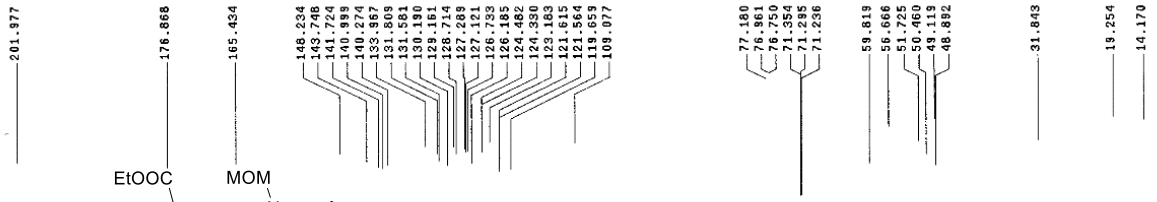


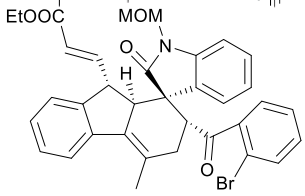


4f

^{1}H NMR (400 MHz, $CDCl_3$)

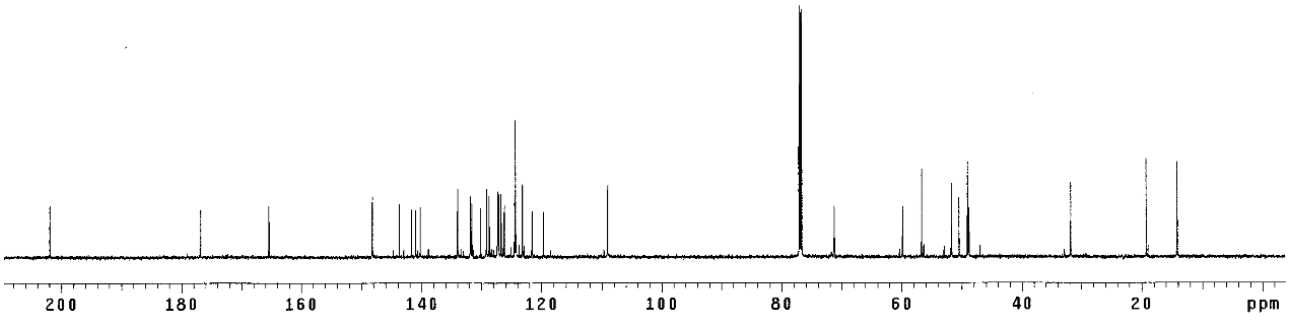


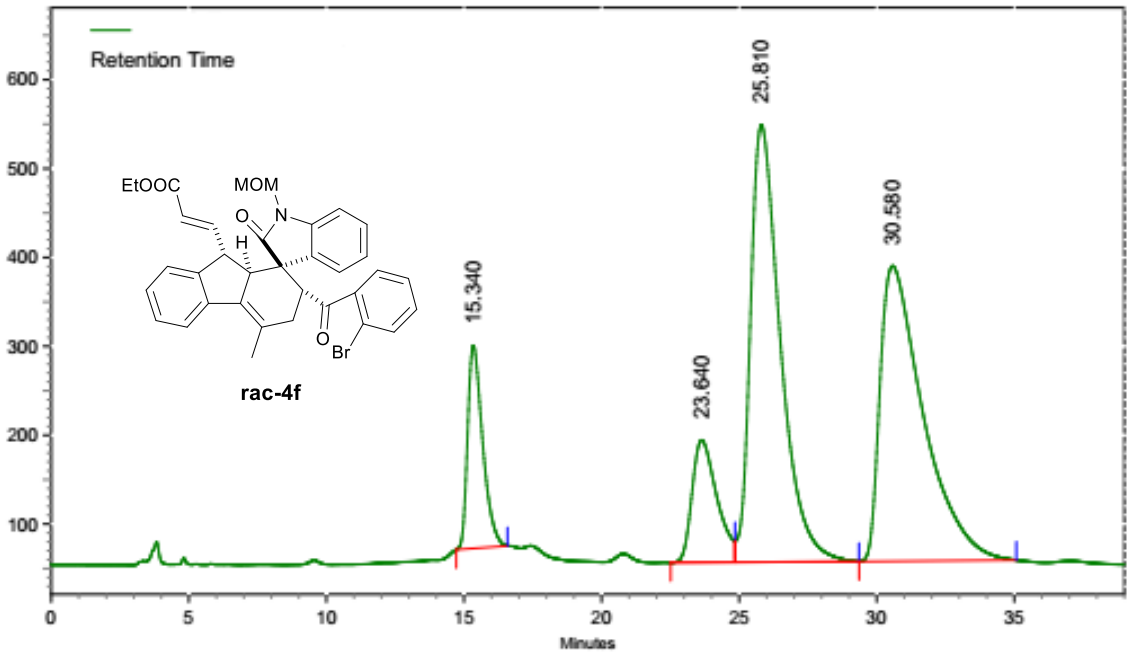




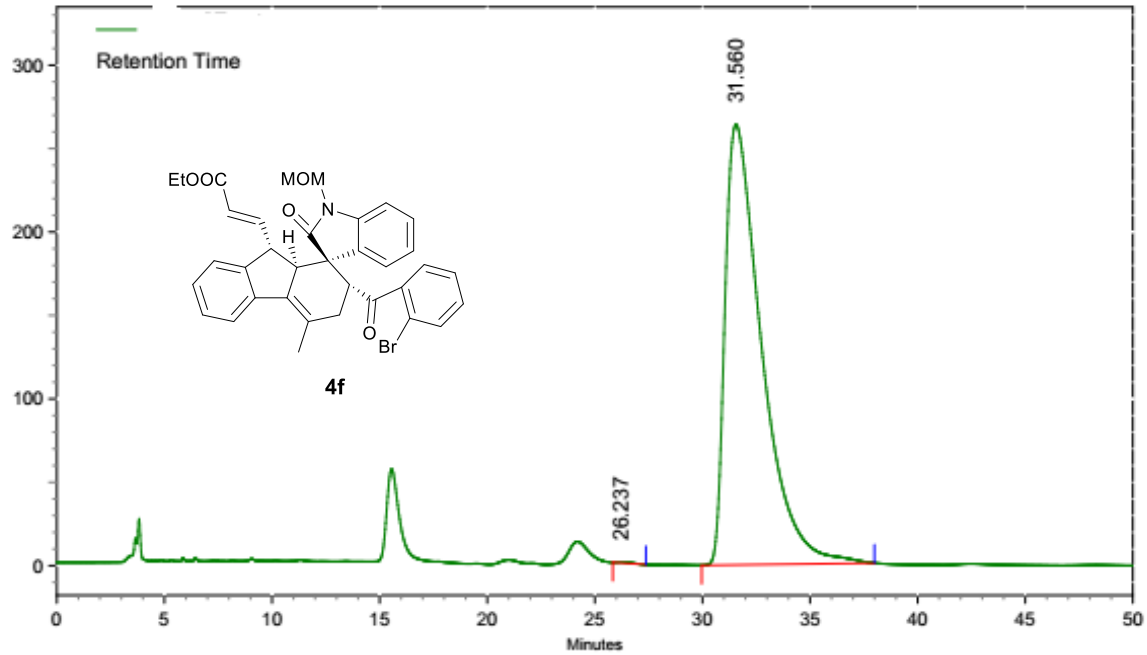
4f

^{13}C NMR (150 MHz, $CDCl_3$)

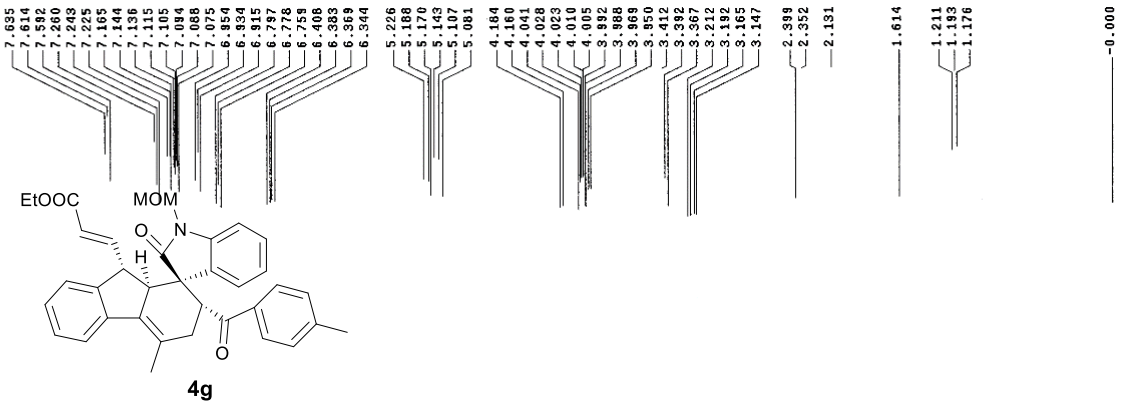




Peak No.	Ret Time	Width	Height	Area	Area [%]
1	15.340	1.860	3830251	145463260	9.5542
2	23.640	2.337	2308111	144907648	9.5178
3	25.810	4.503	8252464	625461447	41.0813
4	30.580	5.713	5573797	606665681	39.8467

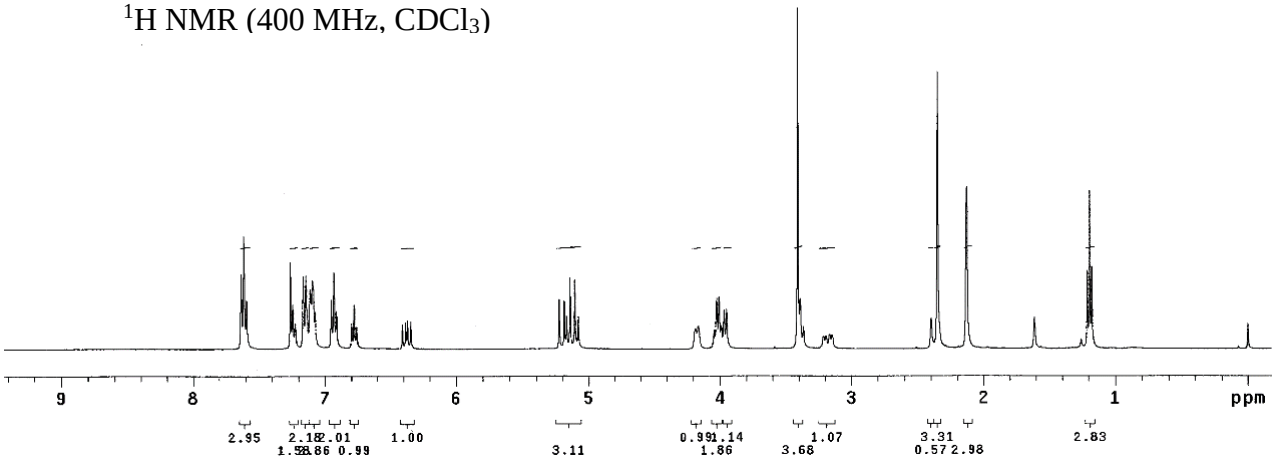


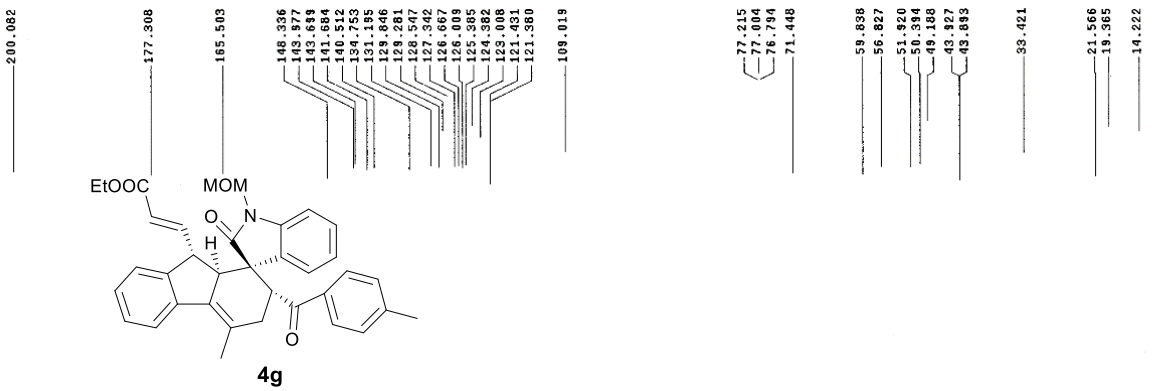
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	26.237	1.543	8866	464260	0.0889
2	31.560	8.027	4427700	522001923	99.9111



4g

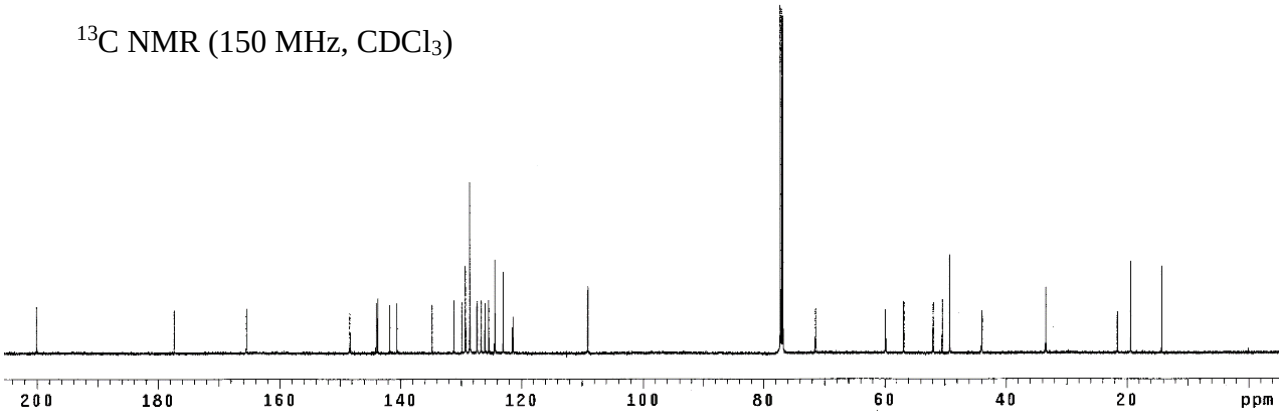
^{1}H NMR (400 MHz, $CDCl_3$)

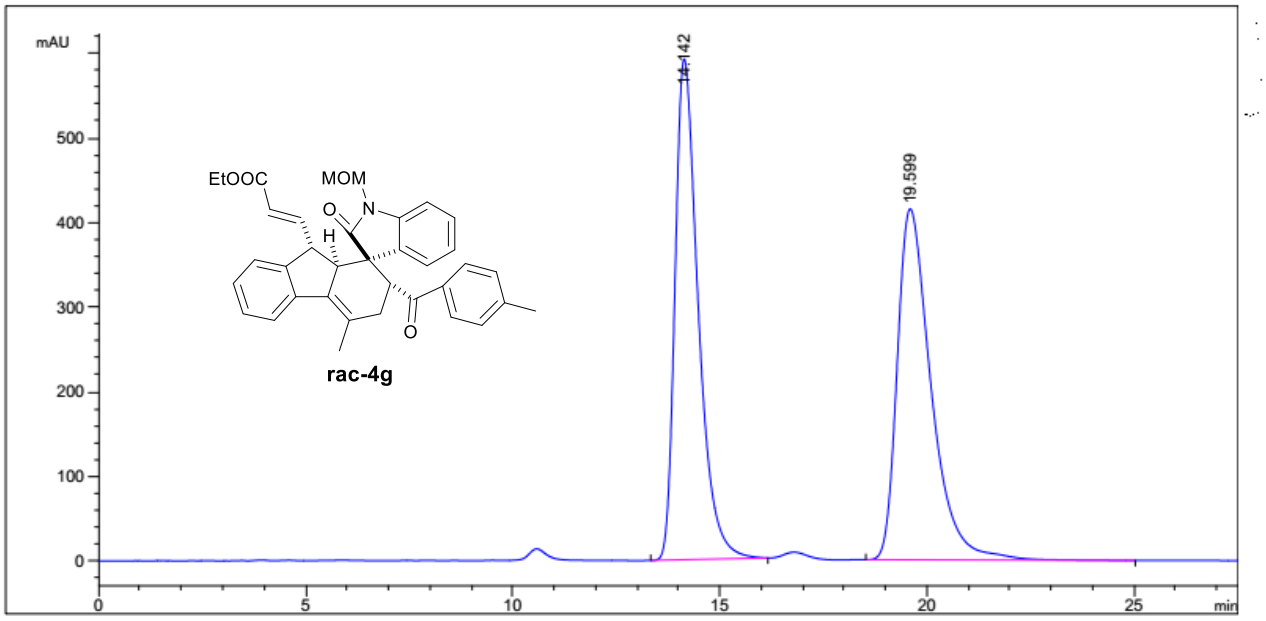




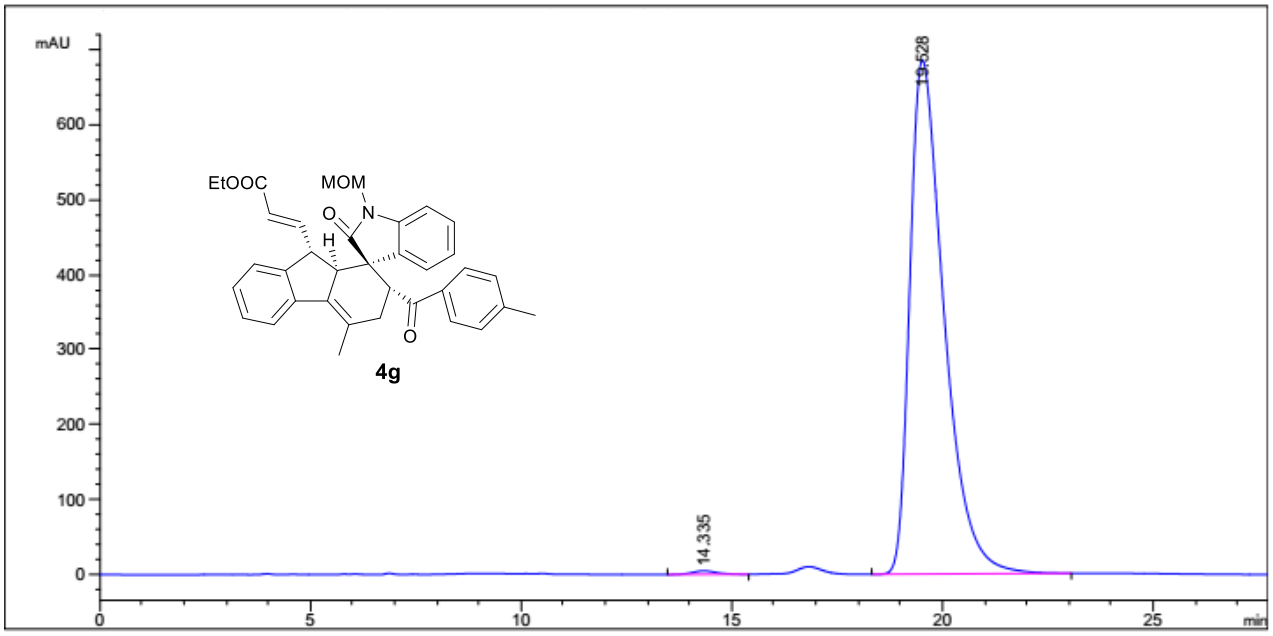
4g

^{13}C NMR (150 MHz, $CDCl_3$)

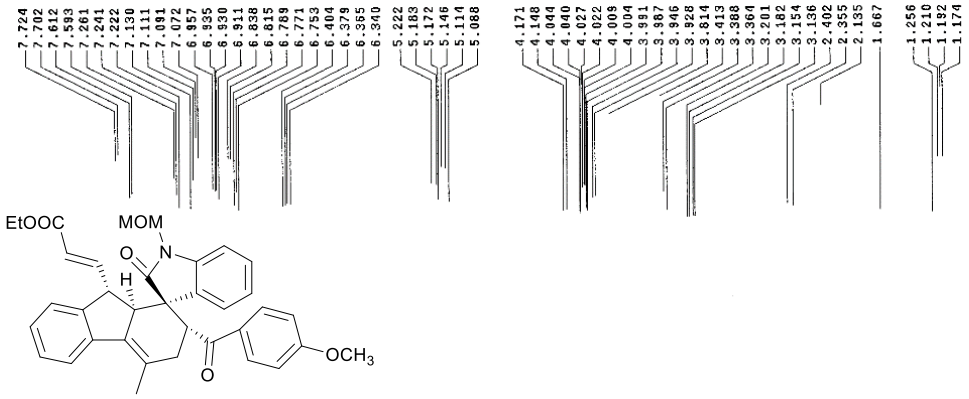




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.142	BBA	0.5903	2.30098e4	592.06836	49.4155
2	19.599	BB	0.8616	2.35541e4	414.99280	50.5845

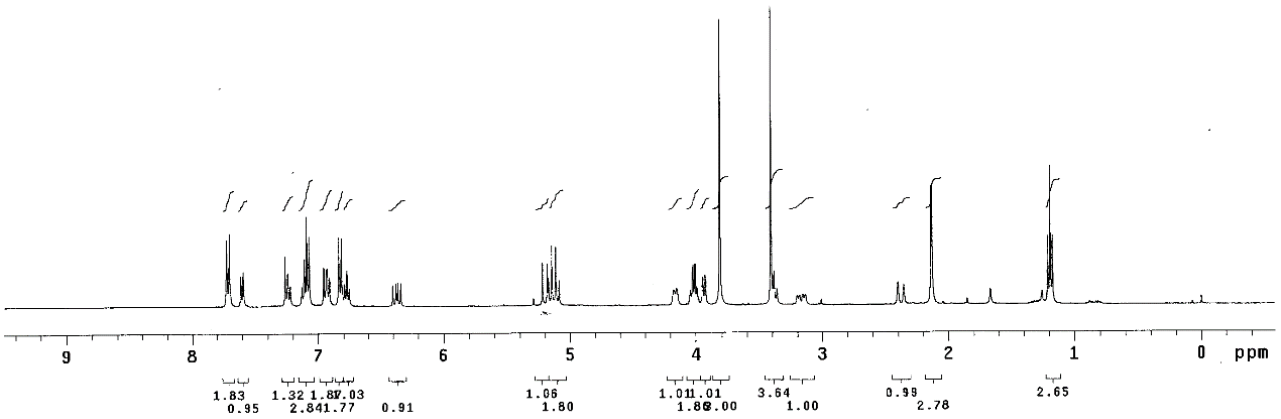


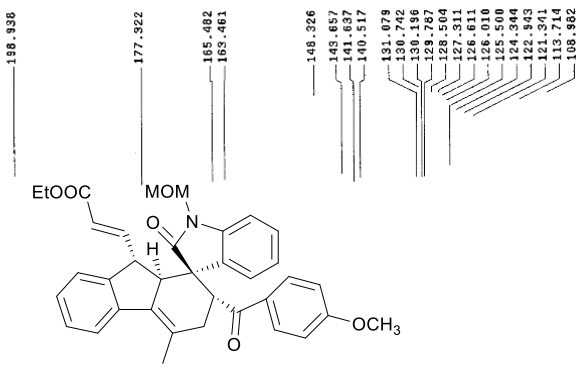
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.335	BBA	0.6047	189.55951	4.71272	0.4870
2	19.528	BB	0.8517	3.87316e4	685.11749	99.5130



4h

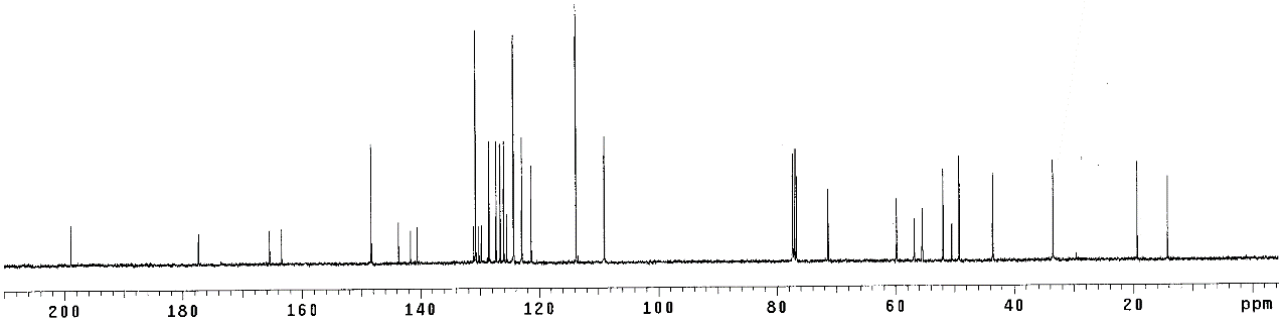
^{1}H NMR (400 MHz, $CDCl_3$)

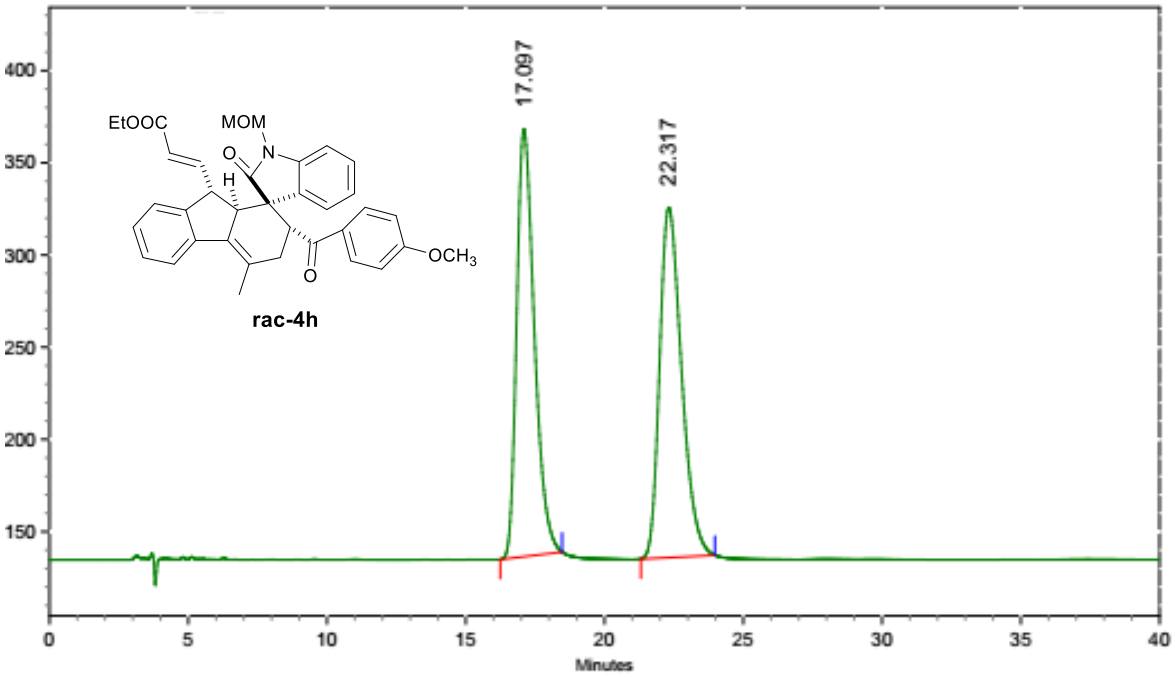




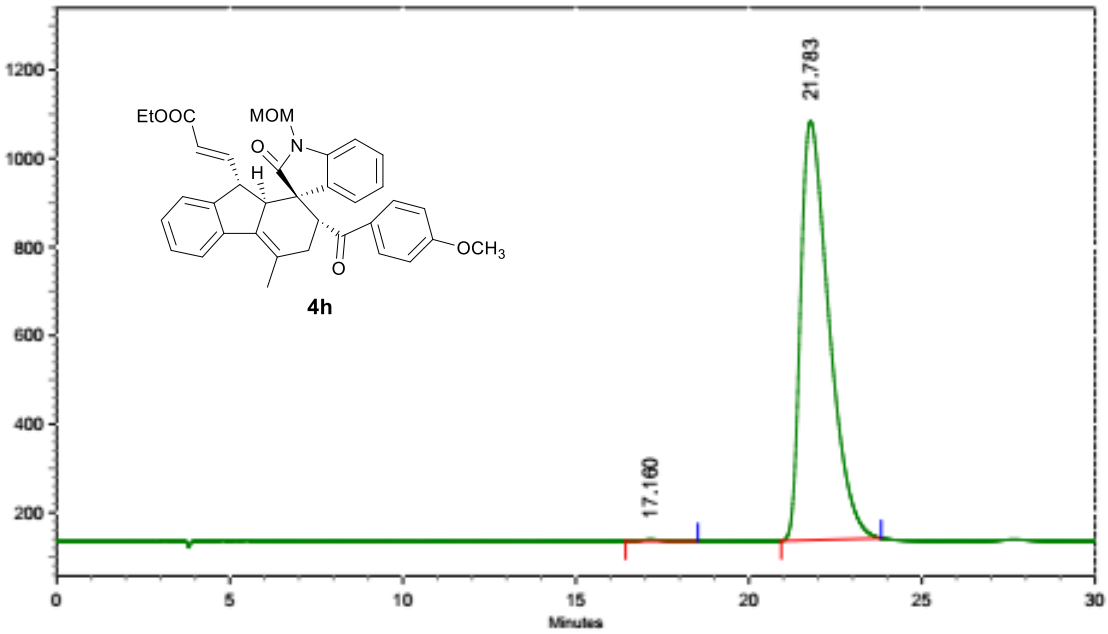
4h

^{13}C NMR (100 MHz, $CDCl_3$)

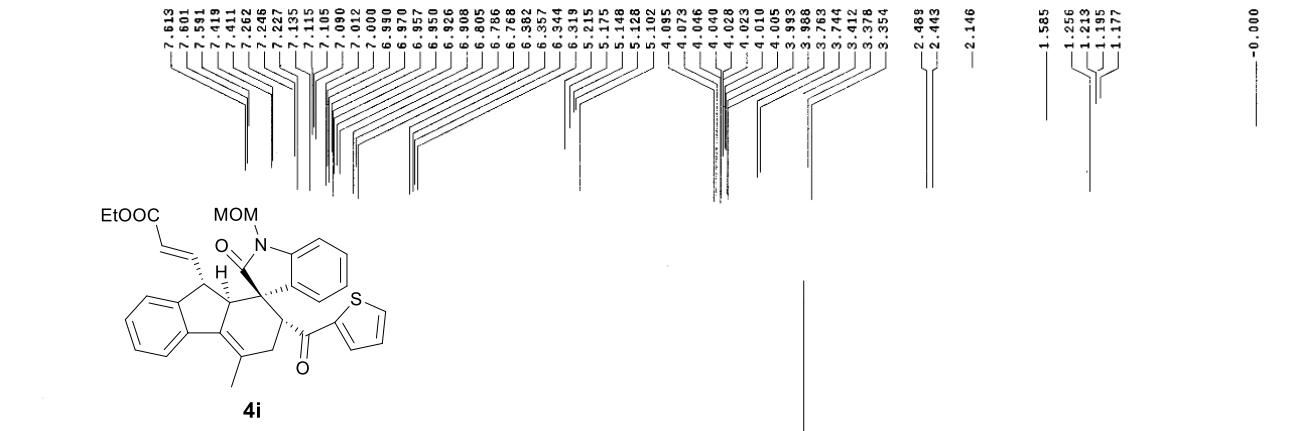




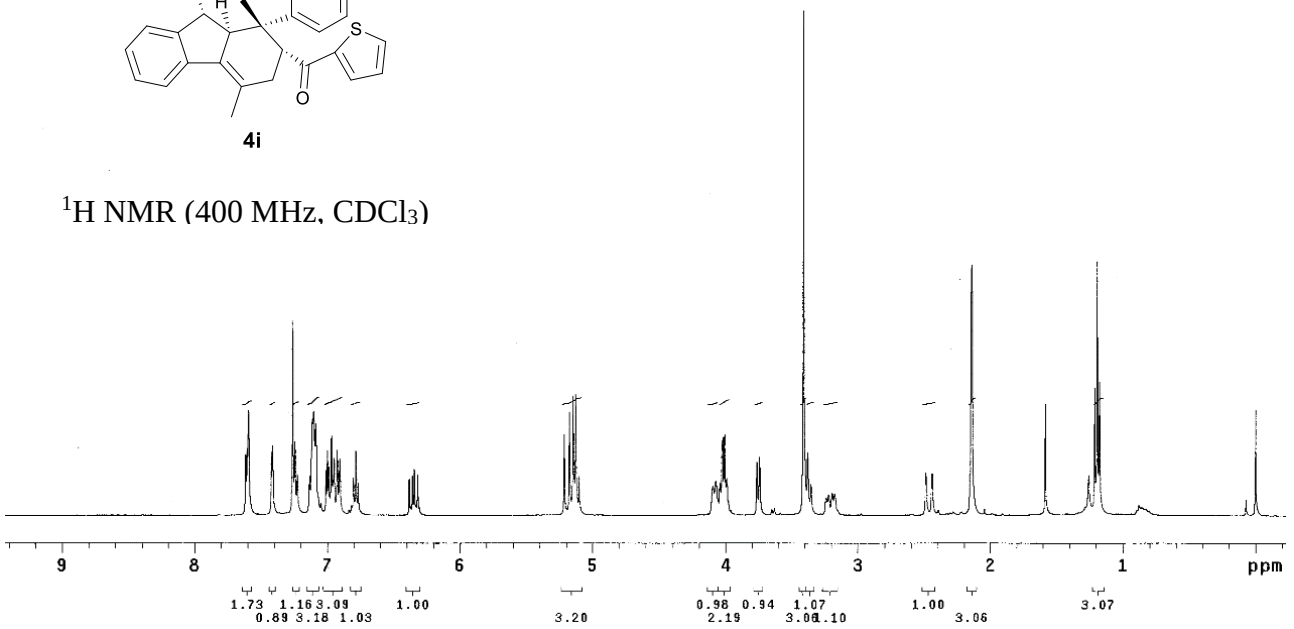
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	17.097	2.230	3890699	172012320	49.6147
2	22.317	2.667	3185644	174684051	50.3853

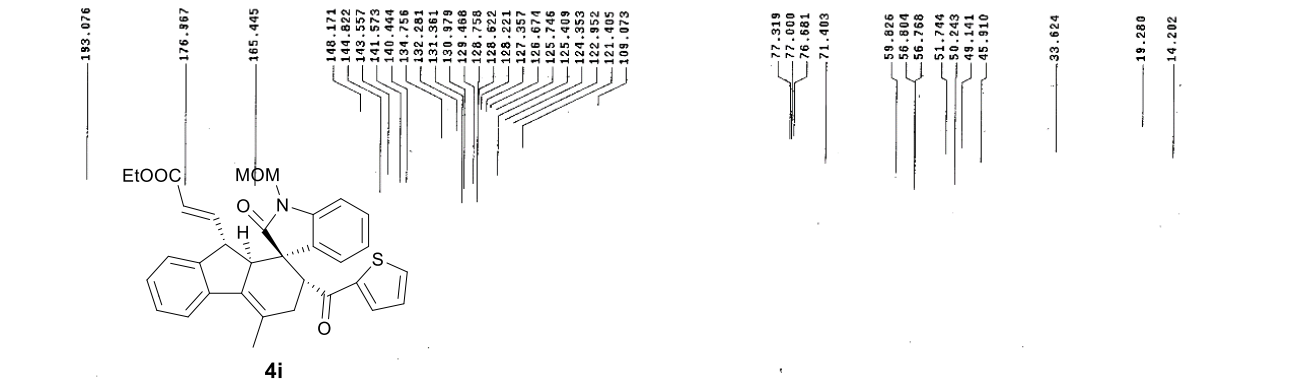


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	17.160	2.090	64367	2761103	0.3051
2	21.783	2.890	15871805	902139573	99.6949

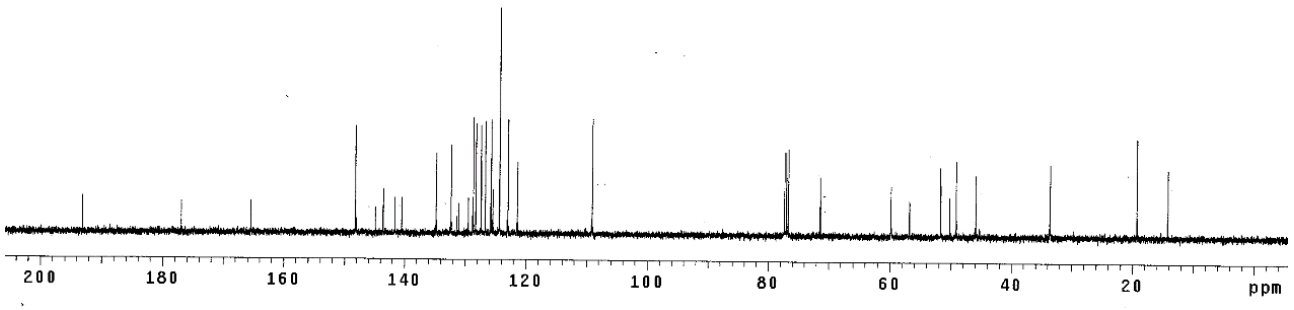


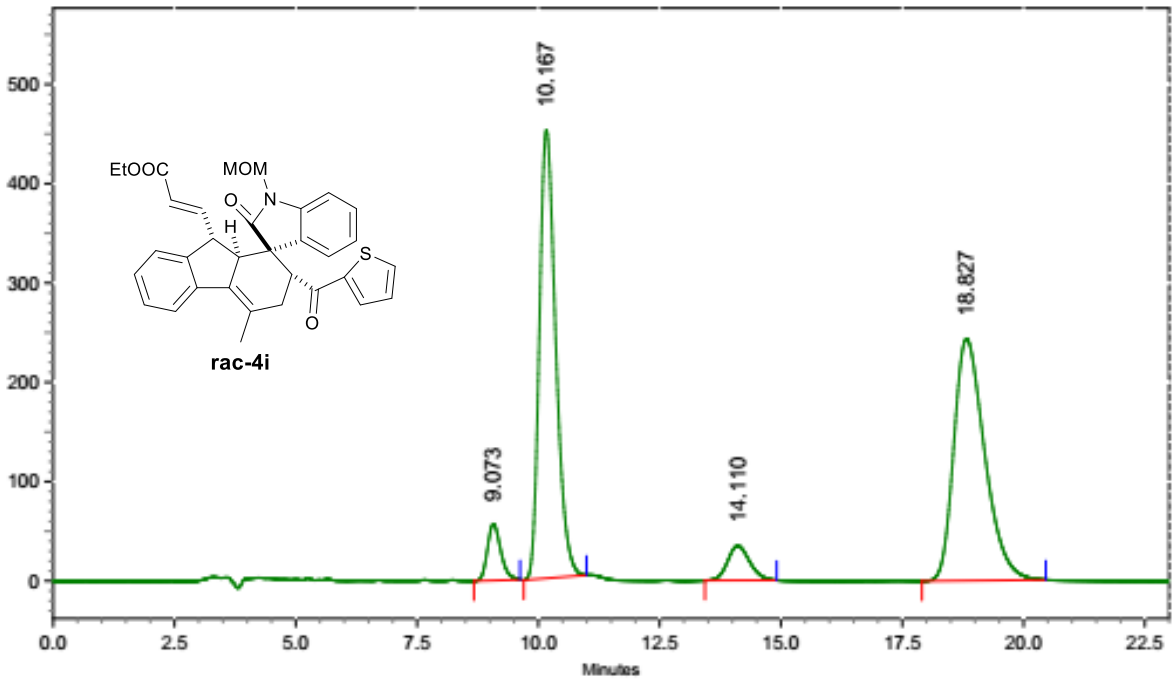
^{1}H NMR (400 MHz, $CDCl_3$)



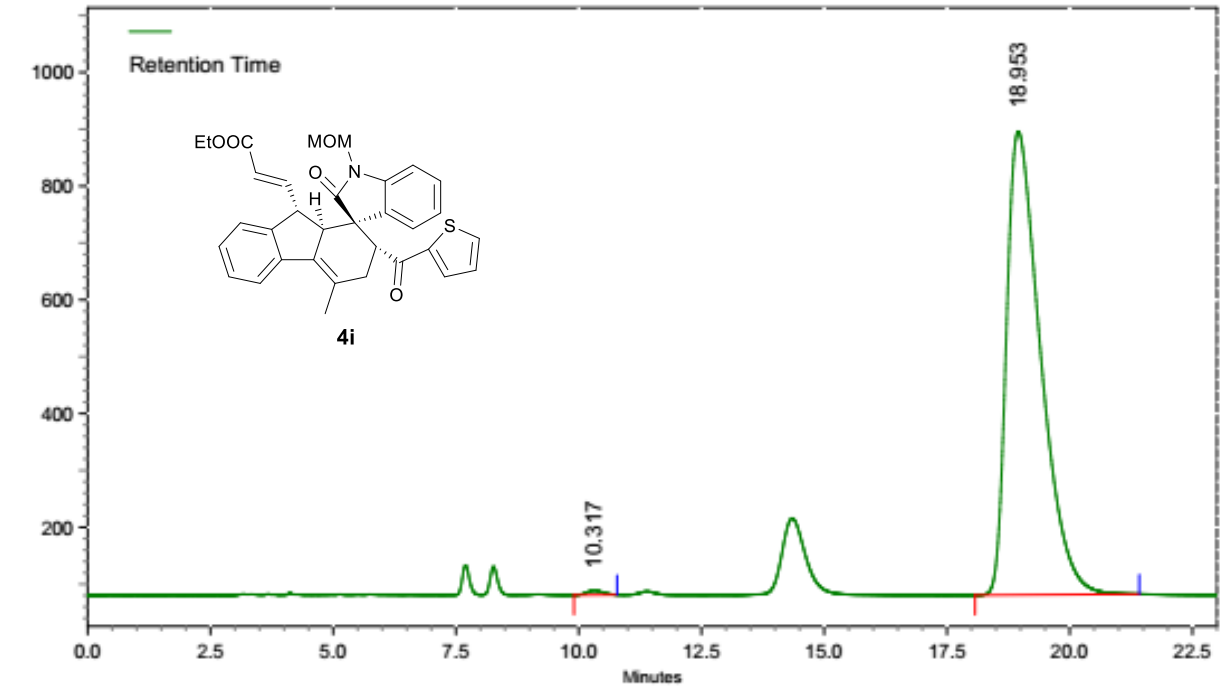


^{13}C NMR (100 MHz, $CDCl_3$)

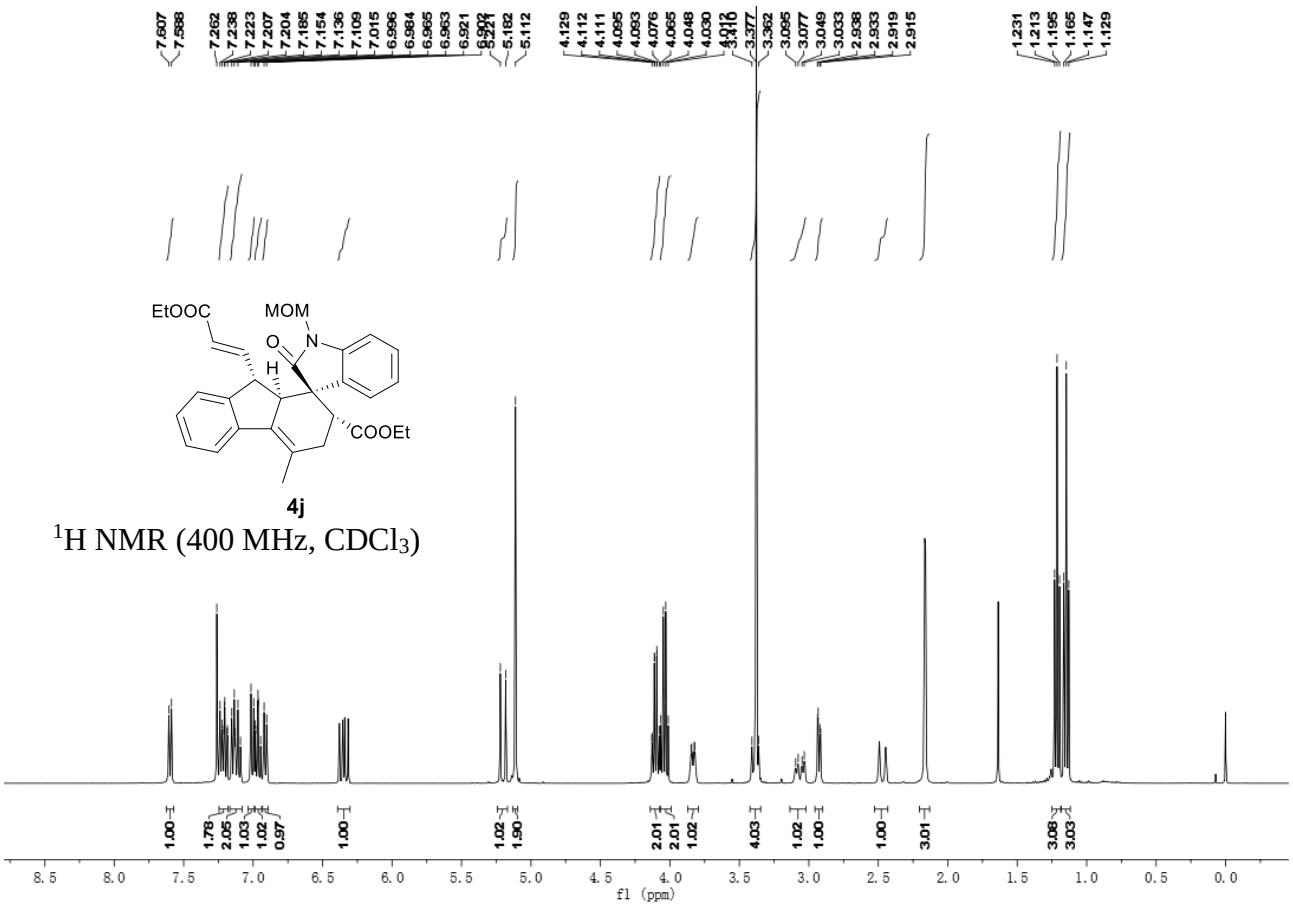




Peak No.	Ret Time	Width	Height	Area	Area [%]
1	9.073	0.950	957302	18326723	4.6382
2	10.167	1.293	7569941	177253302	44.8599
3	14.110	1.480	585920	18560543	4.6974
4	18.827	2.553	4086064	180985456	45.8045

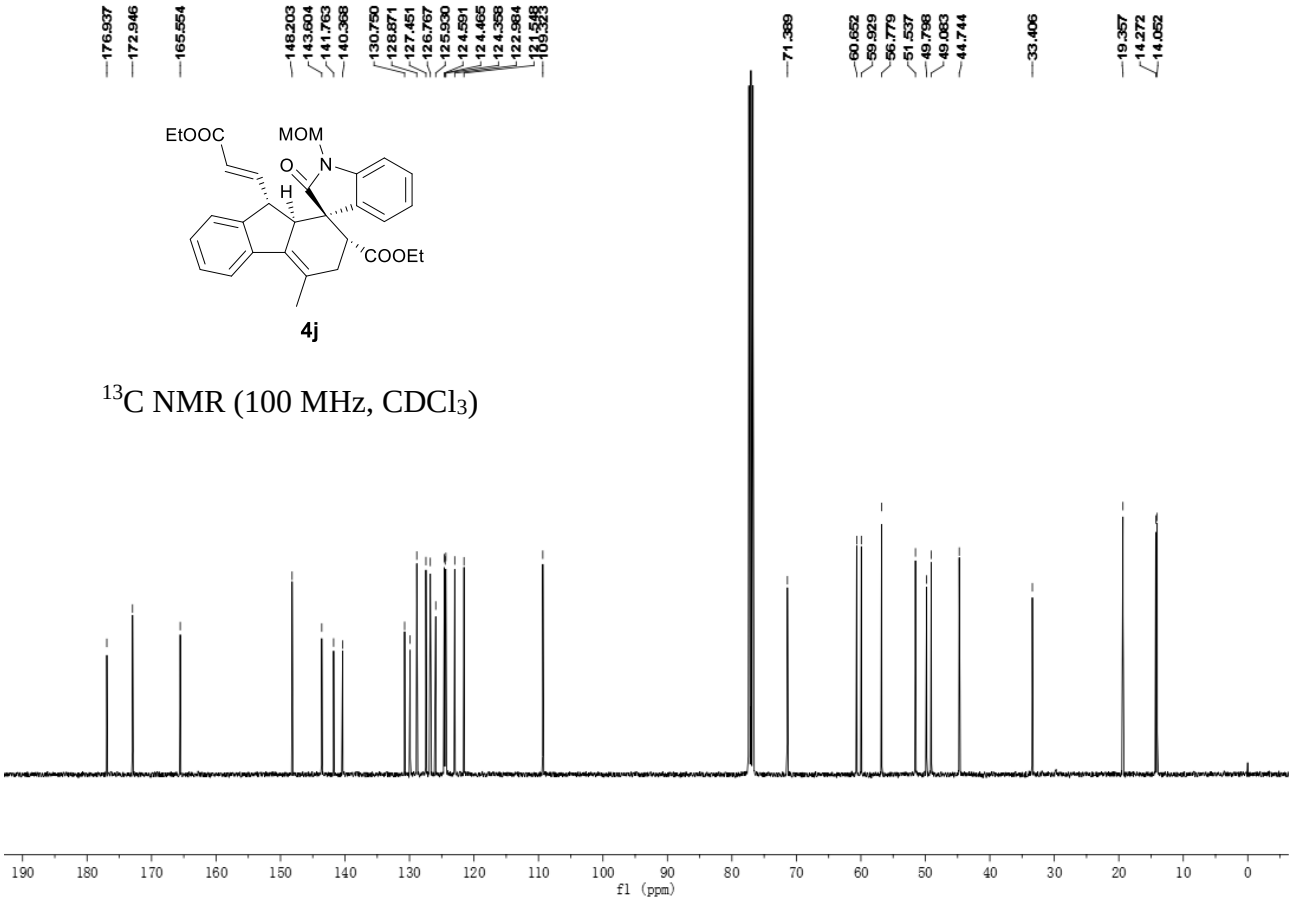


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	10.317	0.880	130381	2939071	0.4450
2	18.953	3.343	13673756	657563592	99.5550



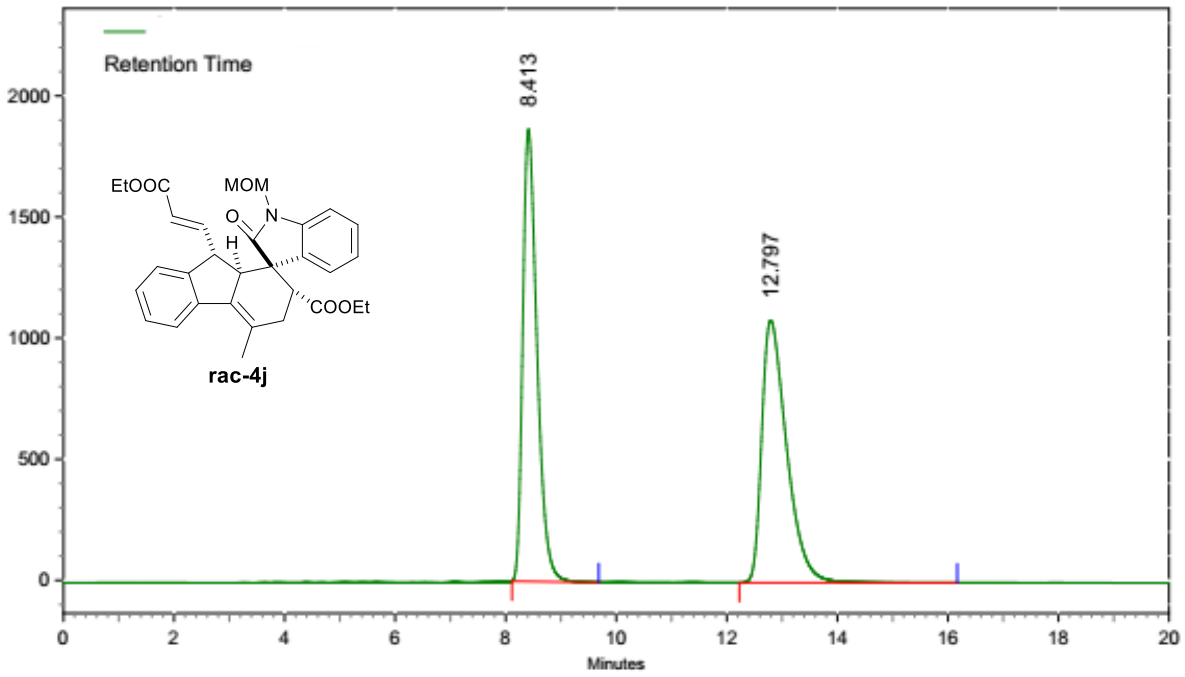
4j

^{1}H NMR (400 MHz, $CDCl_3$)

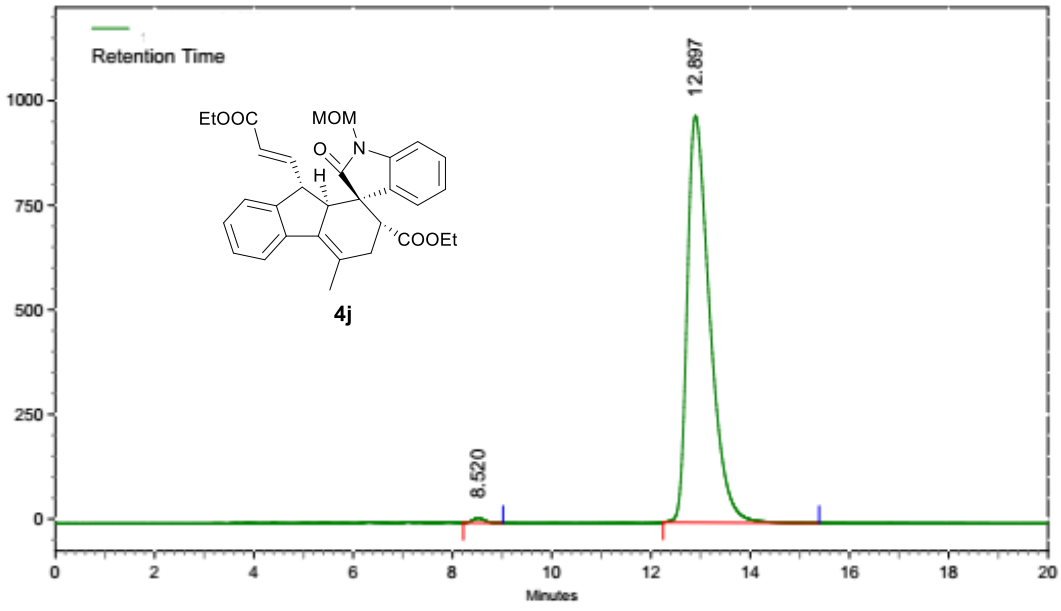


4j

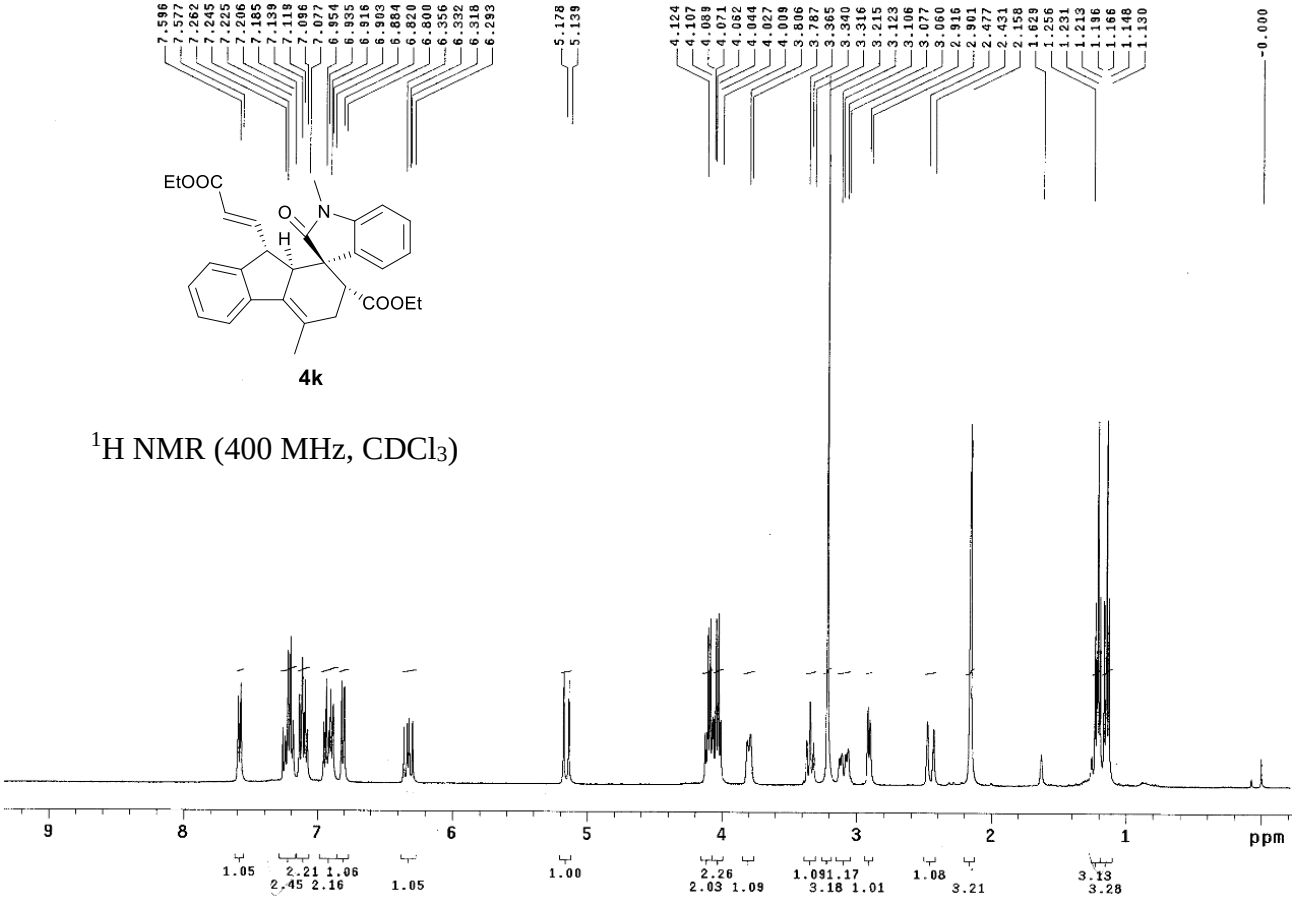
^{13}C NMR (100 MHz, $CDCl_3$)



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.413	1.570	31319875	561166785	49.6430
2	12.797	3.943	18174987	569238799	50.3570

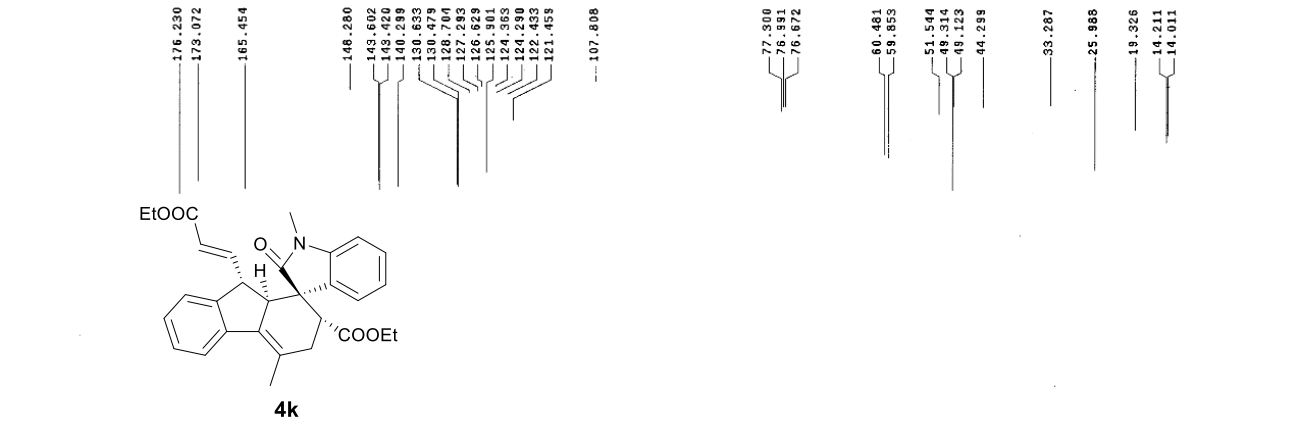


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	8.520	0.800	191374	3211005	0.6217
2	12.897	3.143	16305025	513314387	99.3783



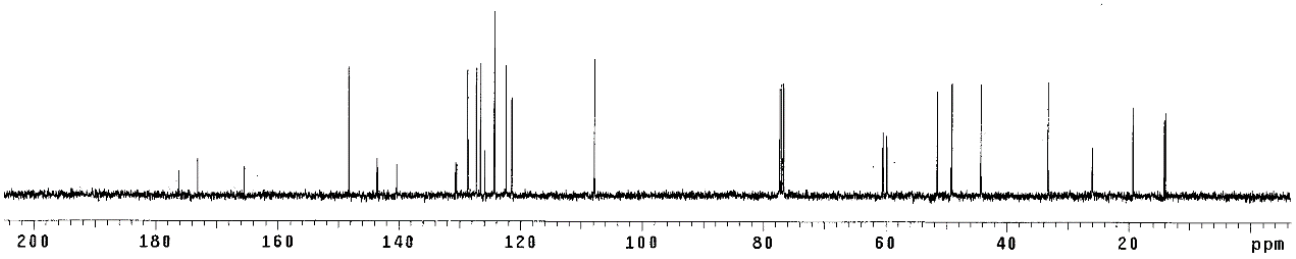
4k

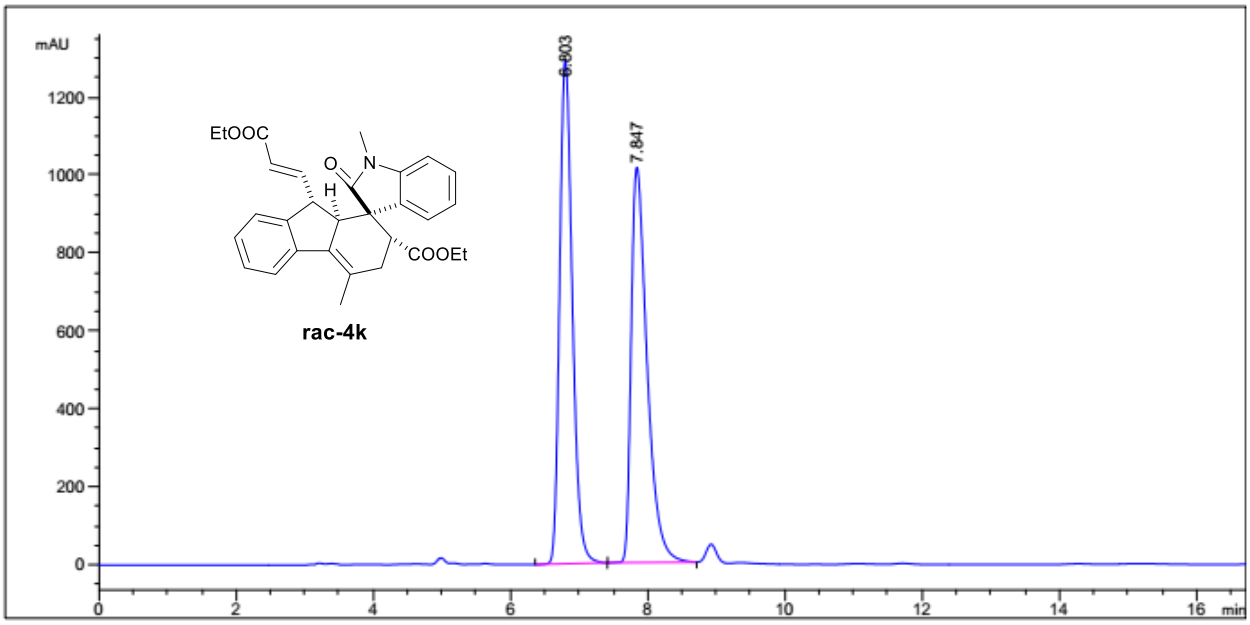
^{1}H NMR (400 MHz, $CDCl_3$)



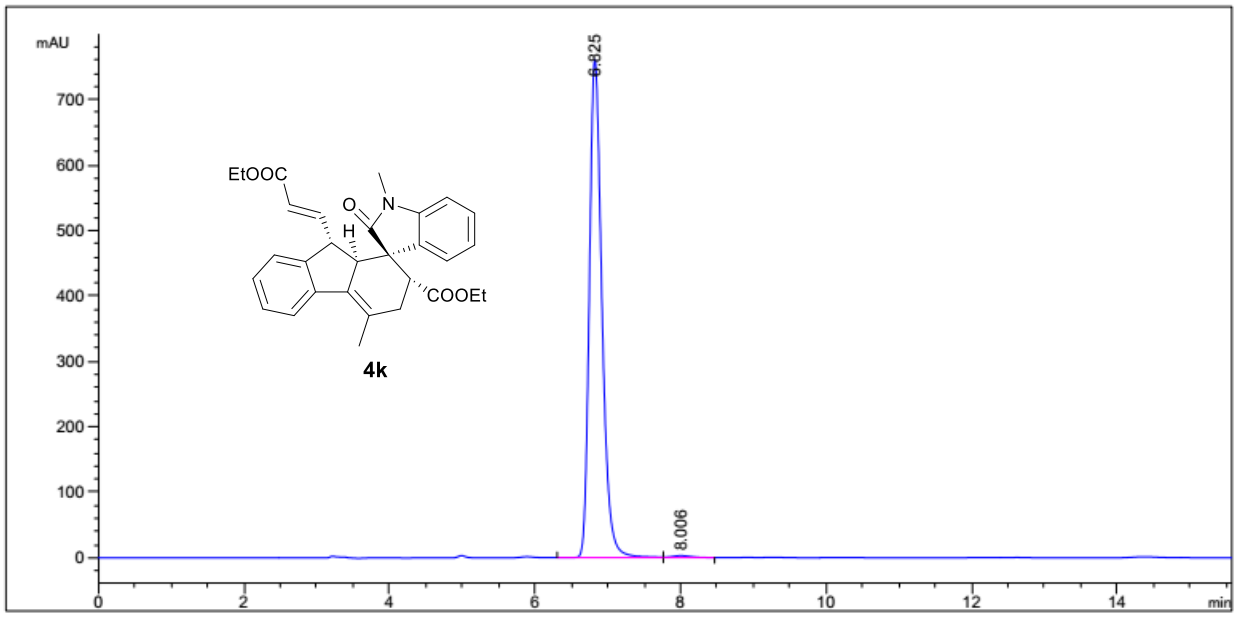
4k

^{13}C NMR (100 MHz, $CDCl_3$)

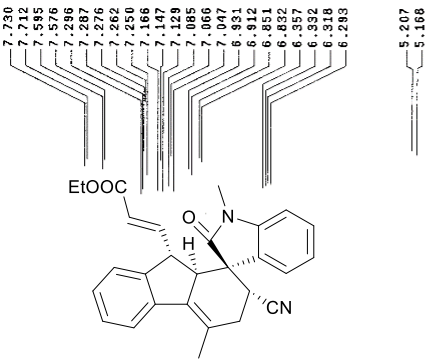




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.803	BB	0.1996	1.66339e4	1292.90198	50.4659
2	7.847	BB	0.2447	1.63267e4	1013.70160	49.5341

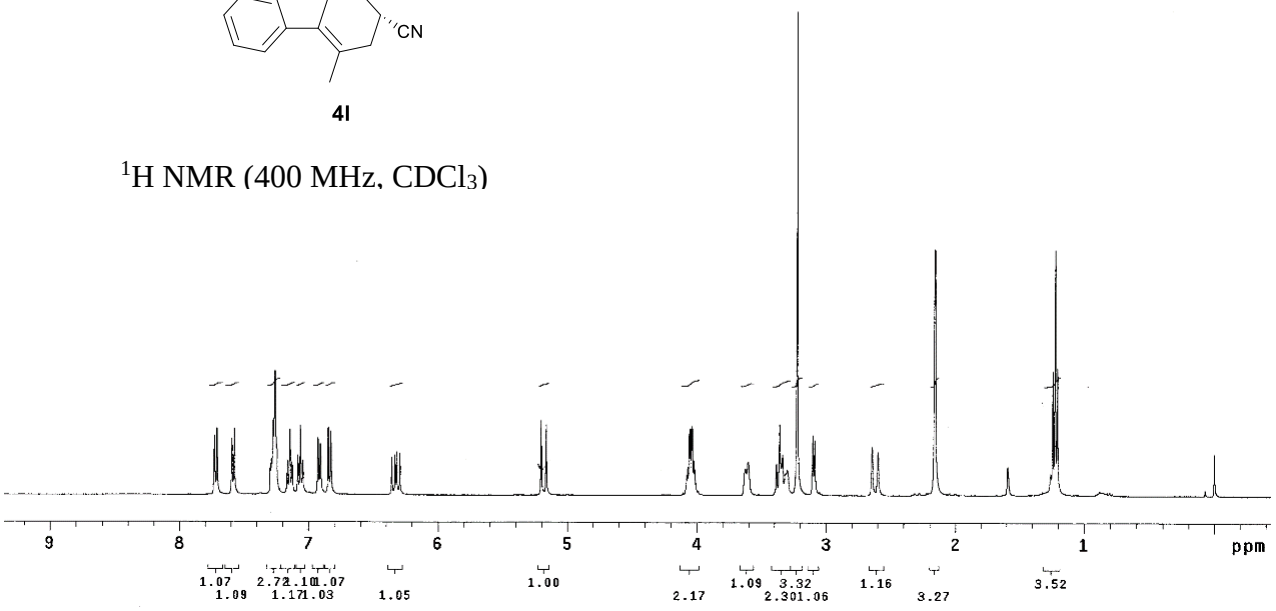


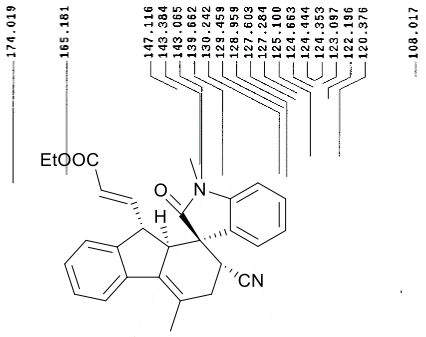
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.825	BV	0.1834	9115.91211	761.12036	99.3991
2	8.006	VBA	0.2760	55.10472	2.99273	0.6009



4l

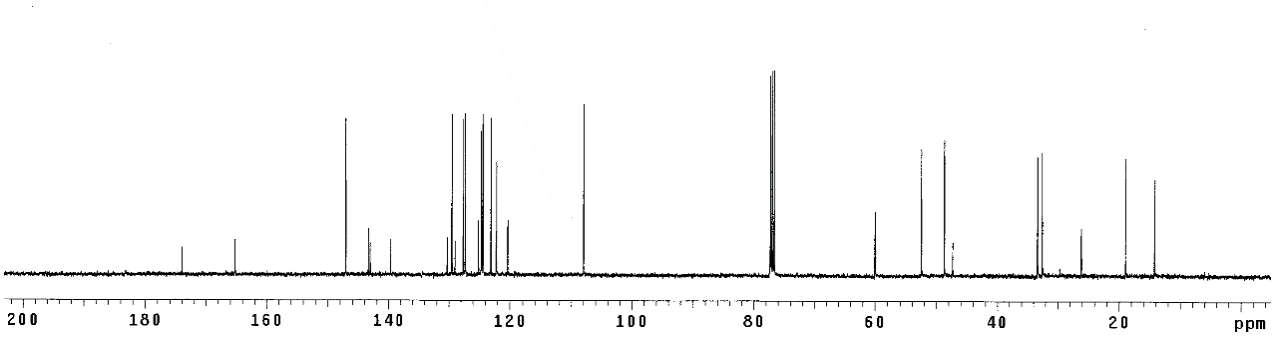
^{1}H NMR (400 MHz, $CDCl_3$)

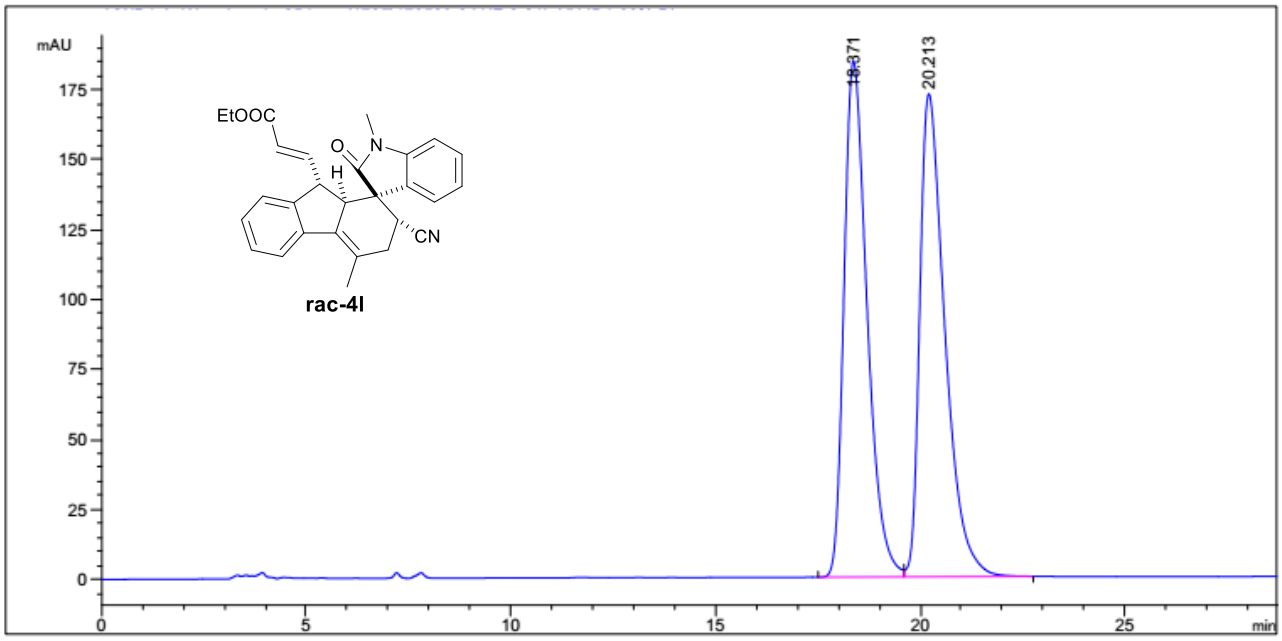




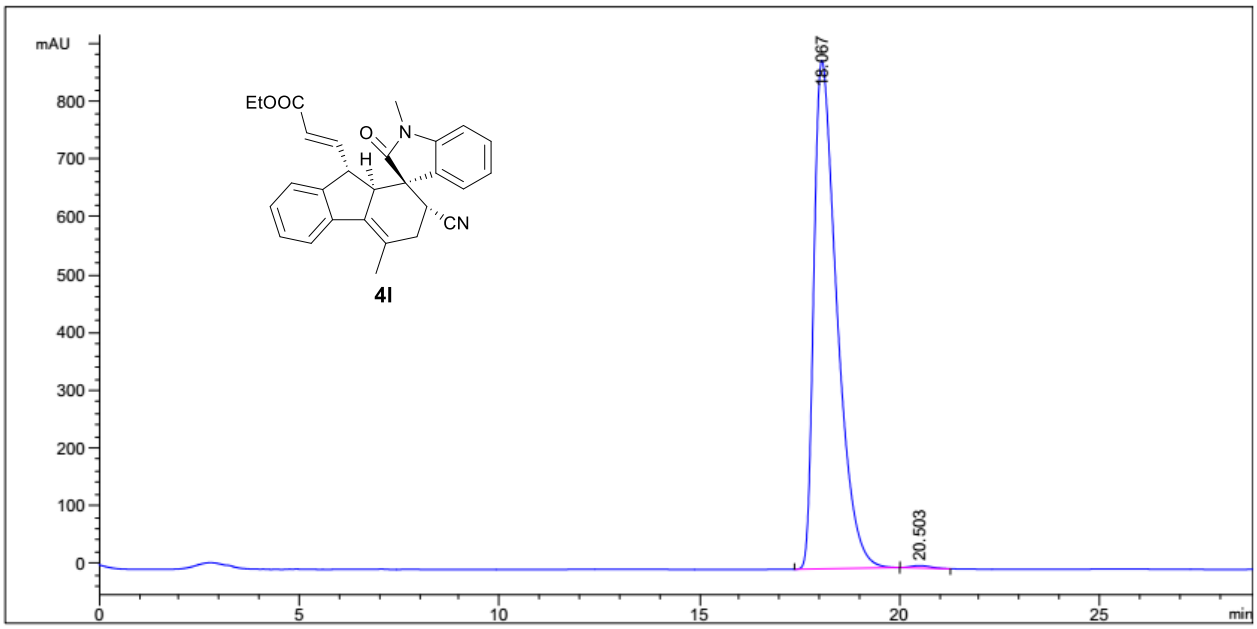
4l

^{13}C NMR (100 MHz, $CDCl_3$)

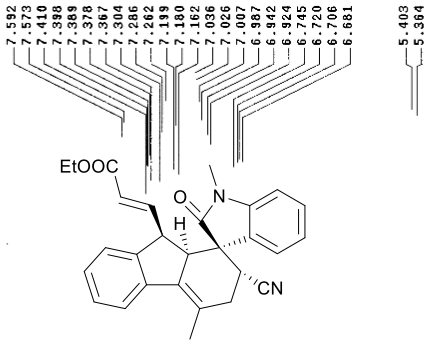




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.371	BV	0.5987	7204.63232	184.33412	49.5392
2	20.213	VB	0.6434	7338.66260	172.49057	50.4608

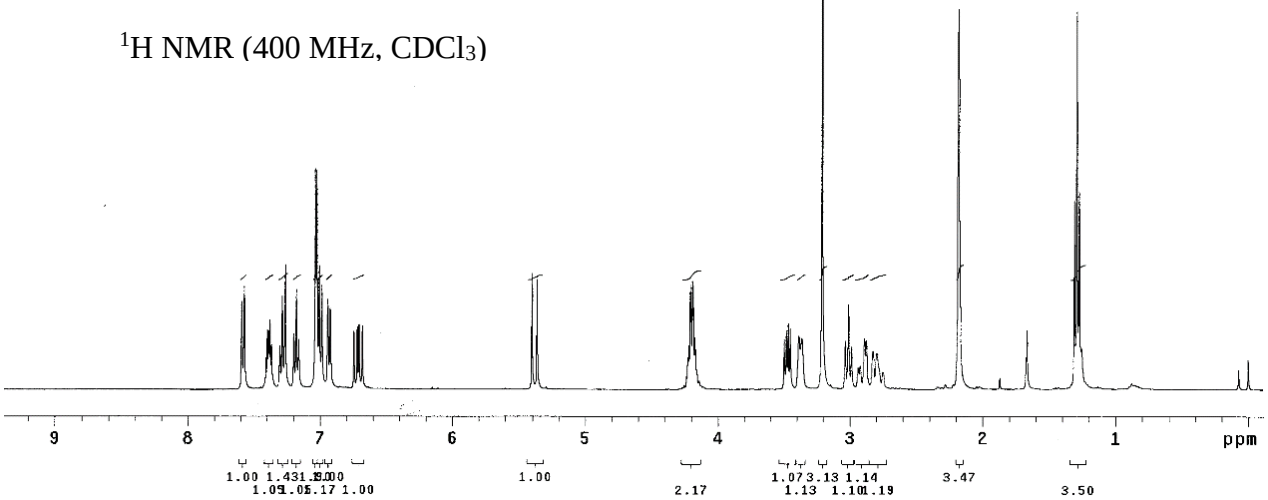


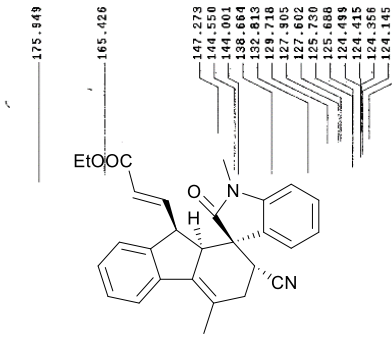
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.067	BB	0.6058	3.51719e4	880.47894	99.6041
2	20.503	BB	0.5106	139.80815	4.20091	0.3959



4l′

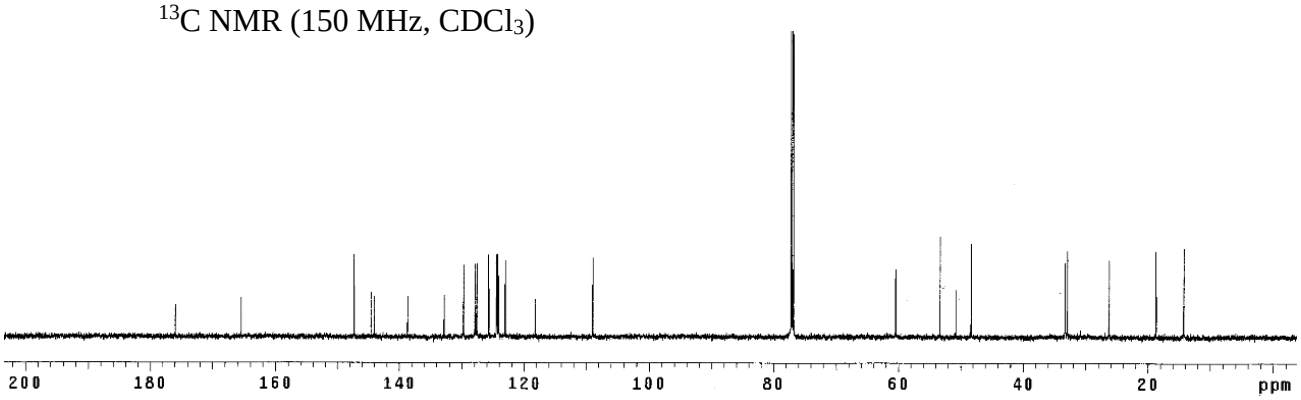
^{1}H NMR (400 MHz, $CDCl_3$)

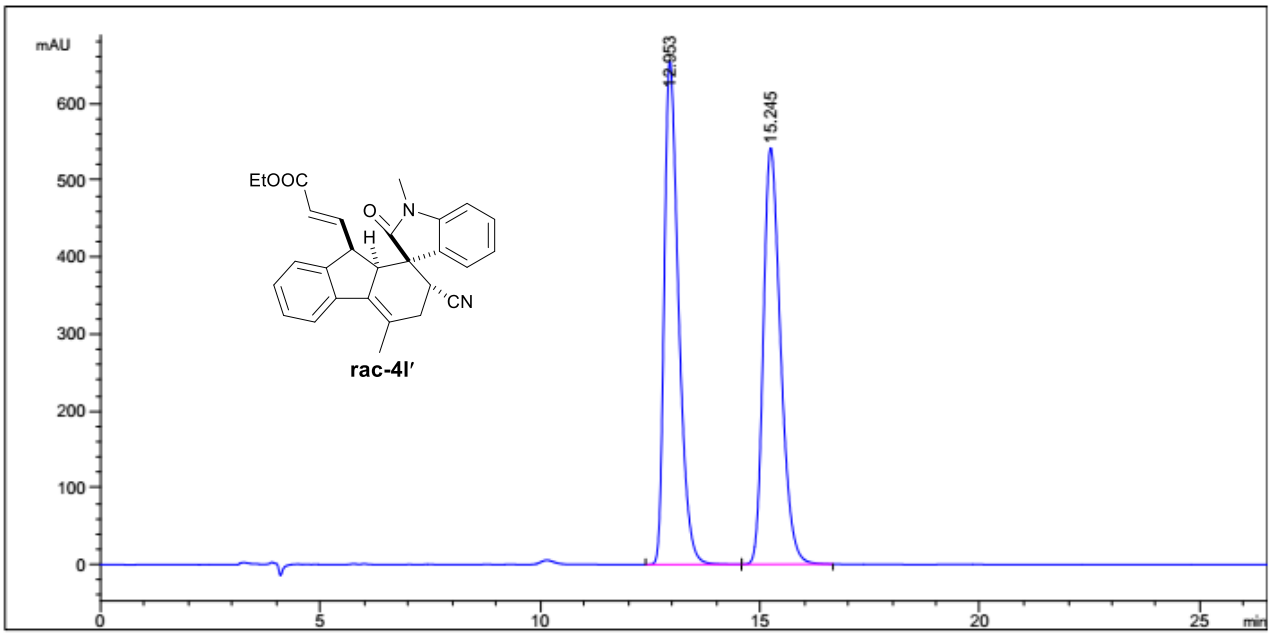




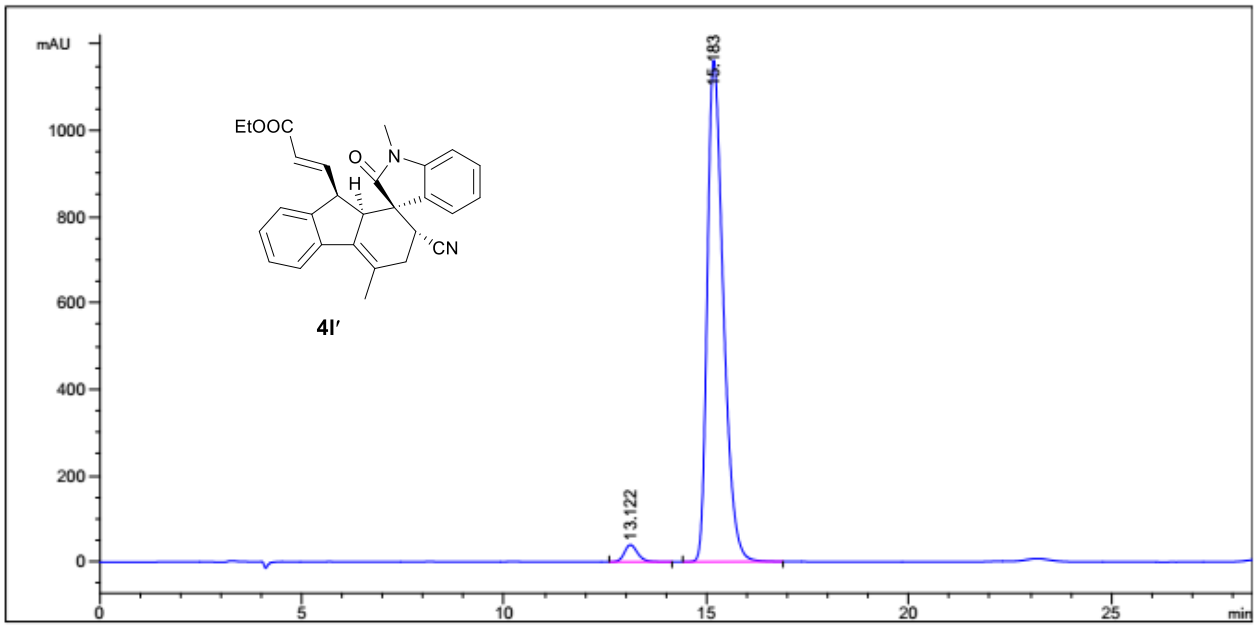
4l′

^{13}C NMR (150 MHz, $CDCl_3$)

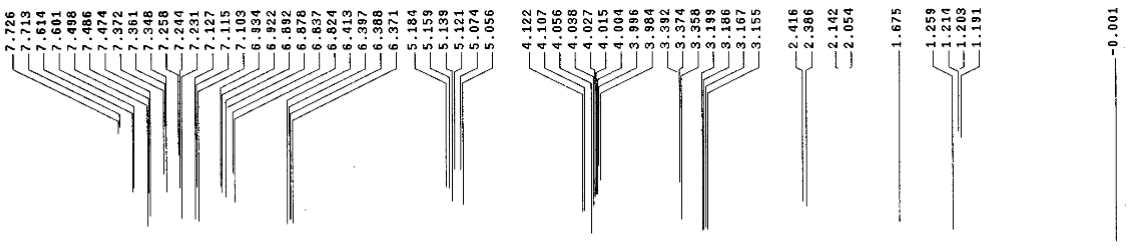


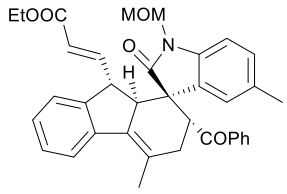


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.953	BB	0.3450	1.47930e4	654.96460	50.0581
2	15.245	BBA	0.4185	1.47587e4	541.37323	49.9419



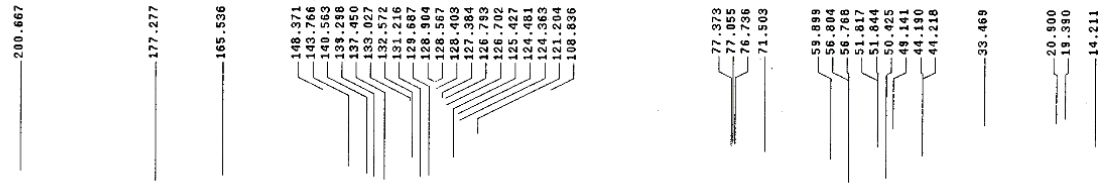
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.122	BB	0.3507	890.36652	39.22332	2.7078
2	15.183	BB	0.4216	3.19914e4	1162.37769	97.2922

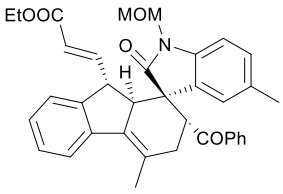




4m

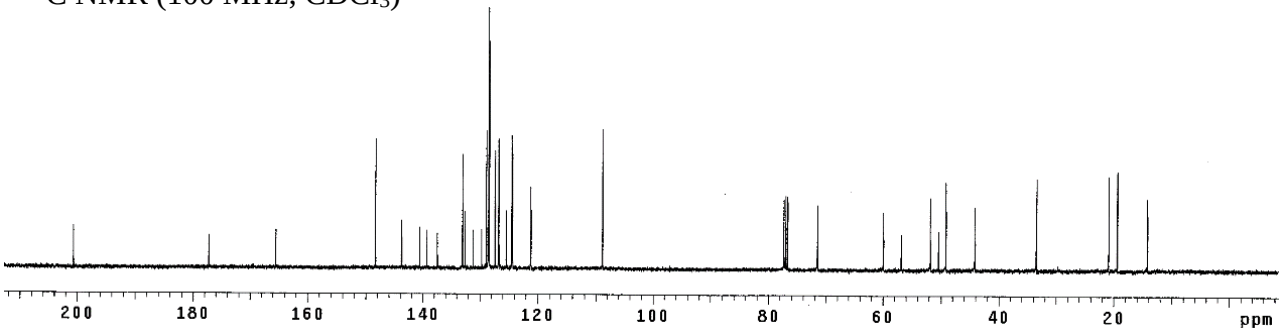
^{1}H NMR (600 MHz, $CDCl_3$)

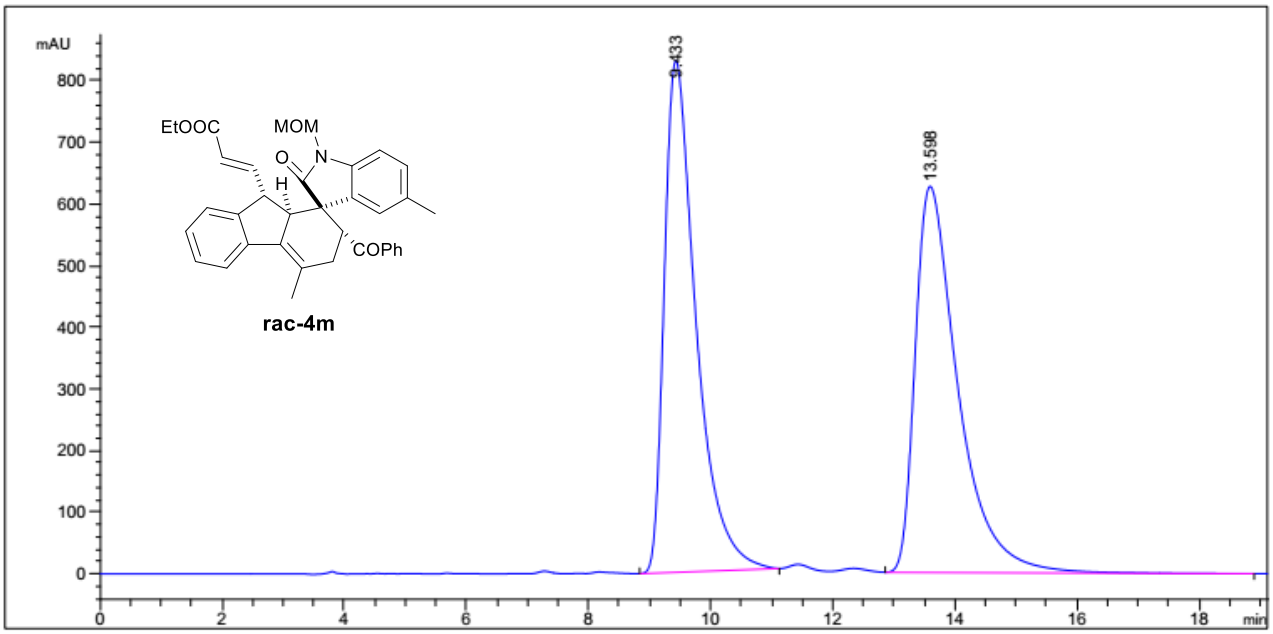




4m

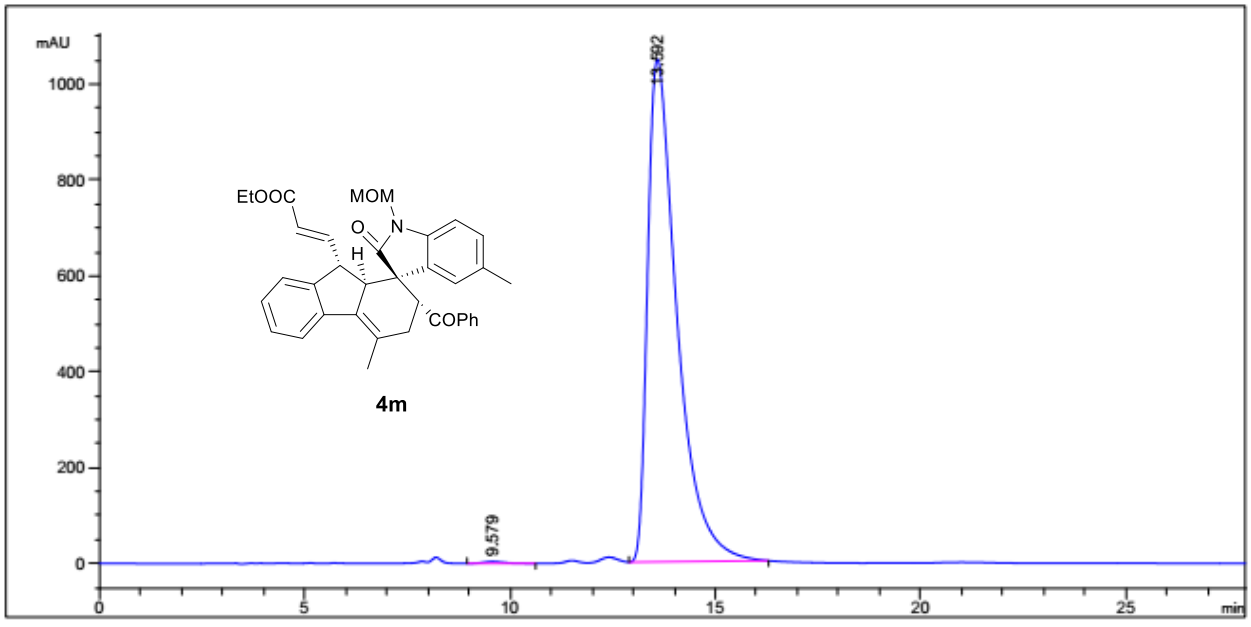
^{13}C NMR (100 MHz, $CDCl_3$)





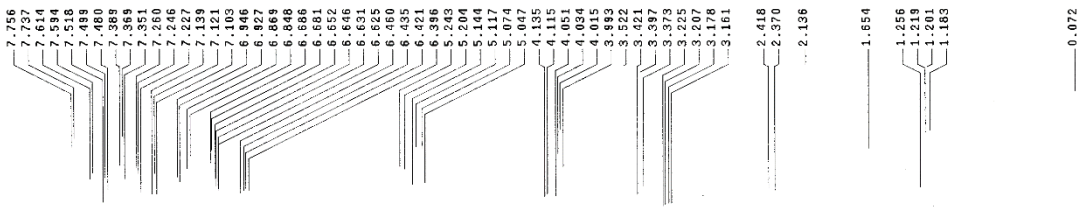
rac-4m

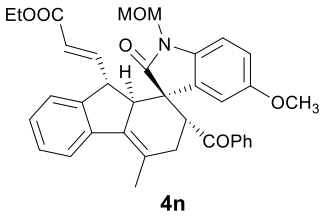
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.433	BBA	0.5411	2.99966e4	829.95923	49.6005
2	13.598	BBA	0.7295	3.04797e4	626.14923	50.3995



4m

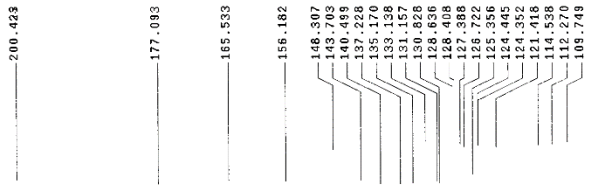
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.579	BBA	0.5182	141.30280	4.00253	0.2703
2	13.592	BBA	0.7445	5.21384e4	1048.84778	99.7297

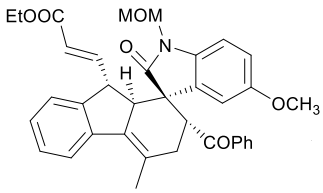




4n

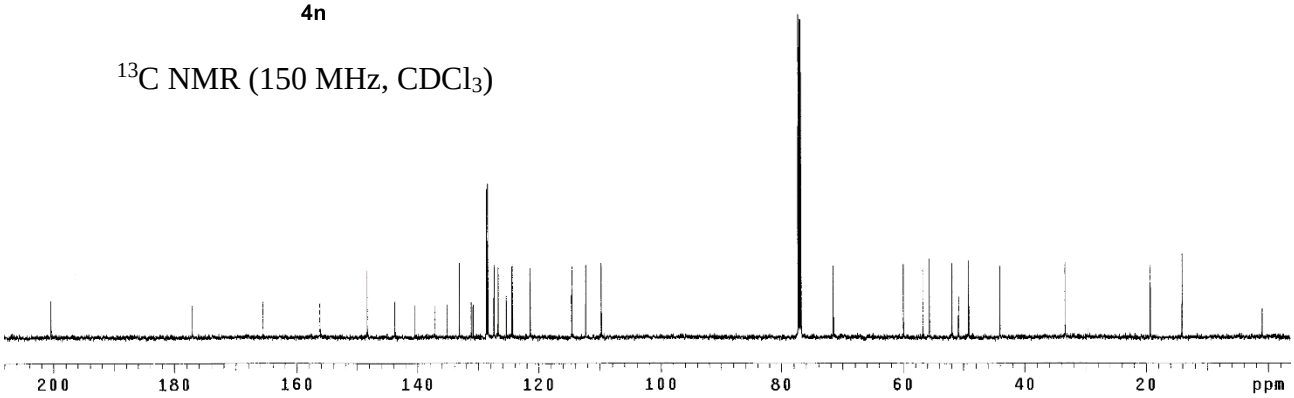
^{1}H NMR (400 MHz, $CDCl_3$)

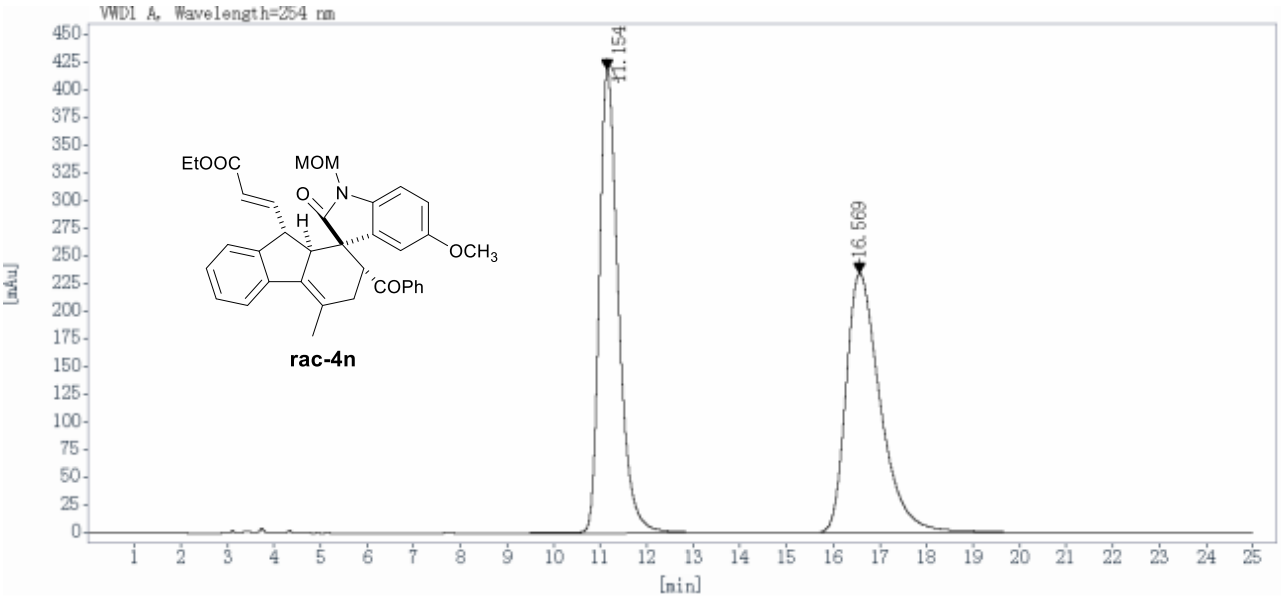




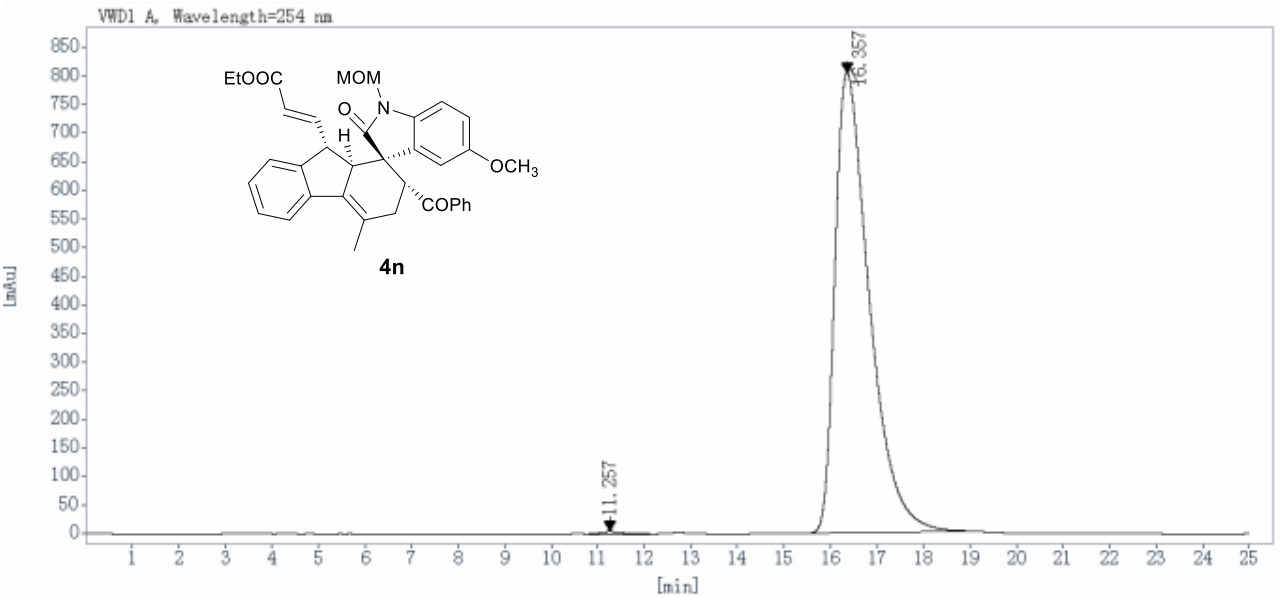
4n

^{13}C NMR (150 MHz, $CDCl_3$)

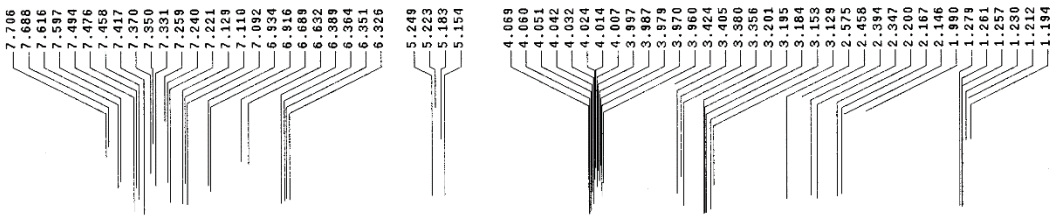


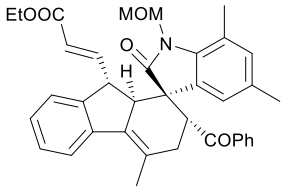


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
11.154	BBA	0.43	418.6285	11937.6221	49.6361
16.569	BBA	0.78	234.2753	12112.6621	50.3639



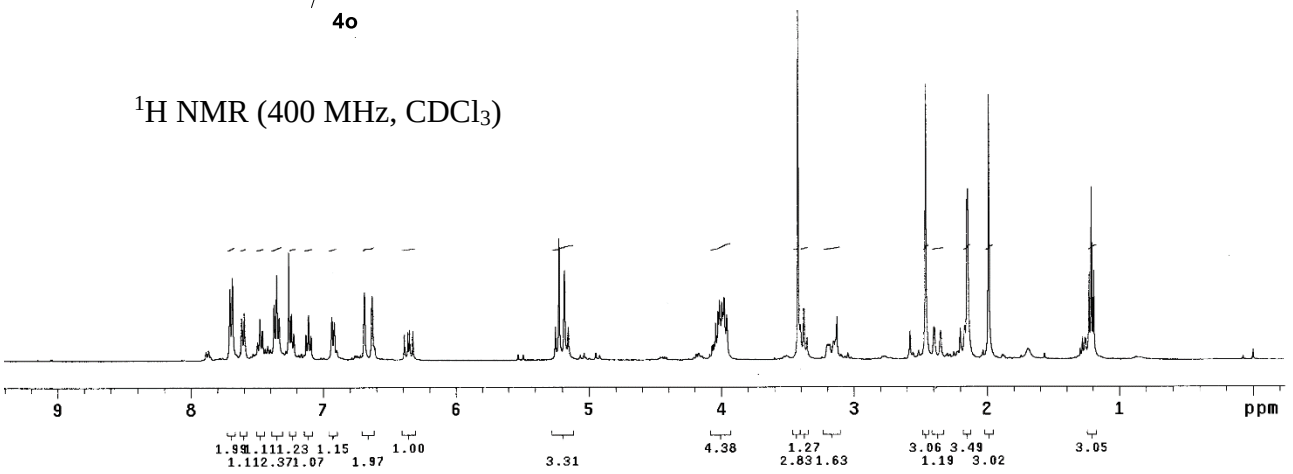
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
11.257	BB	0.48	3.9697	127.5939	0.3083
16.357	BBA	0.78	803.5150	41263.2500	99.6917

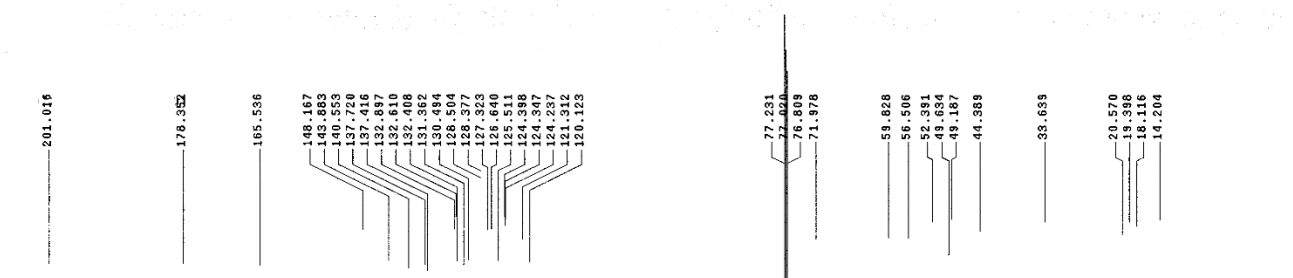


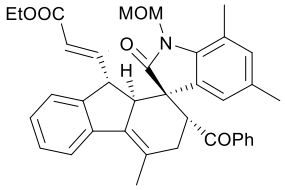


4o

^{1}H NMR (400 MHz, $CDCl_3$)

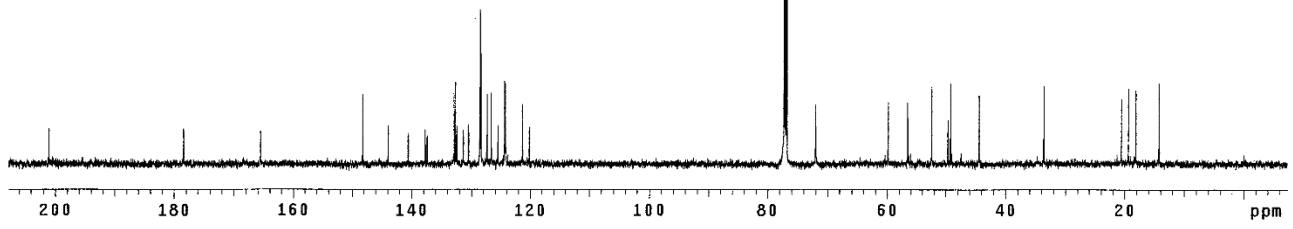


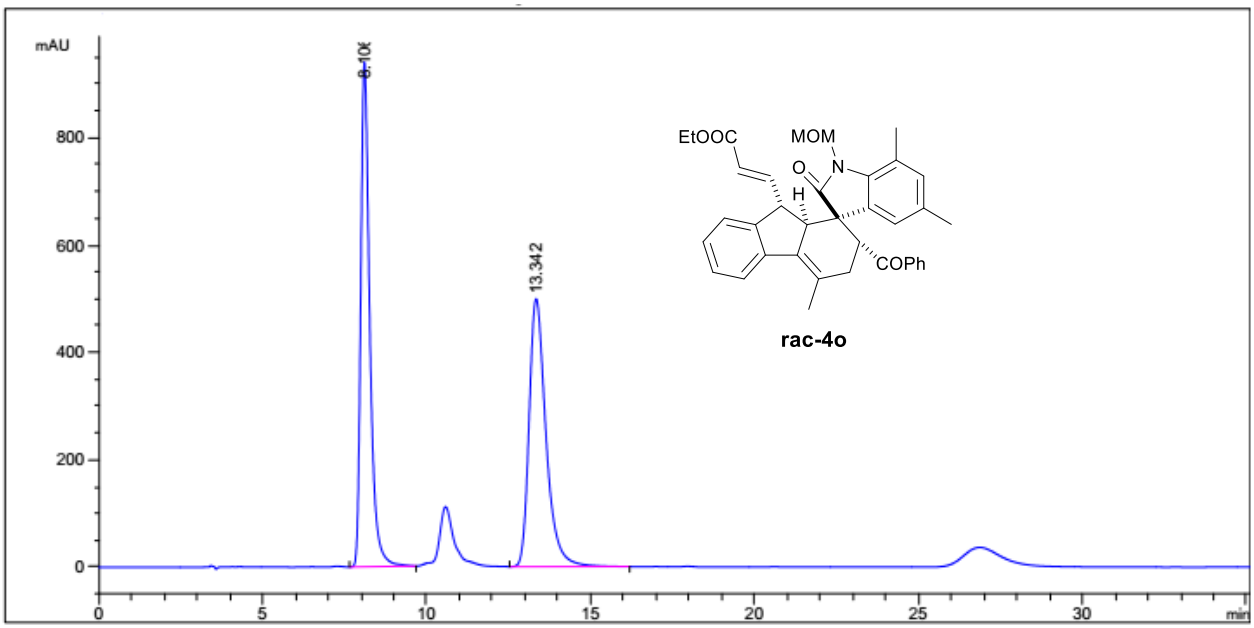




4o

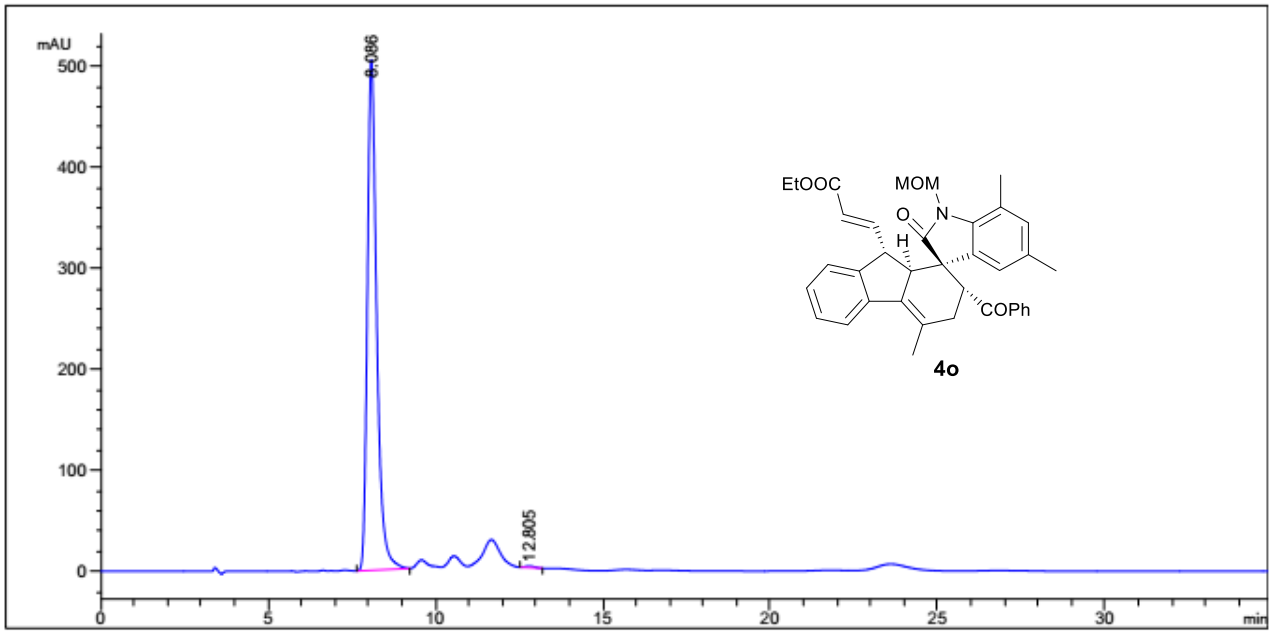
^{13}C NMR (150 MHz, $CDCl_3$)





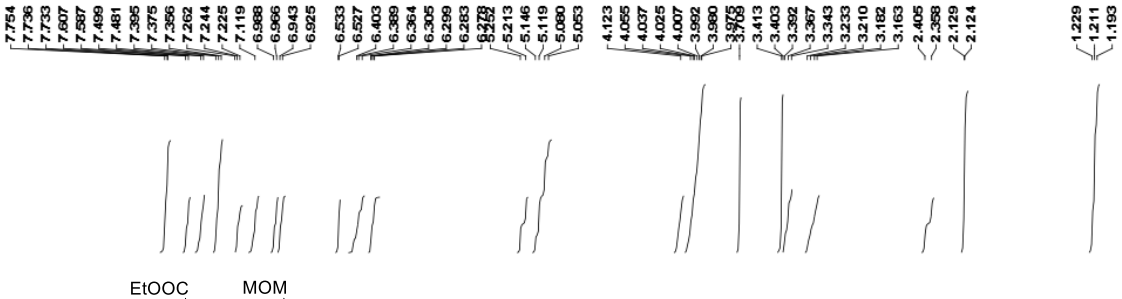
rac-4o

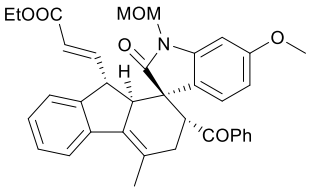
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.106	BB	0.2872	1.79759e4	939.95587	50.1794
2	13.342	BBA	0.5408	1.78473e4	499.23419	49.8206



4o

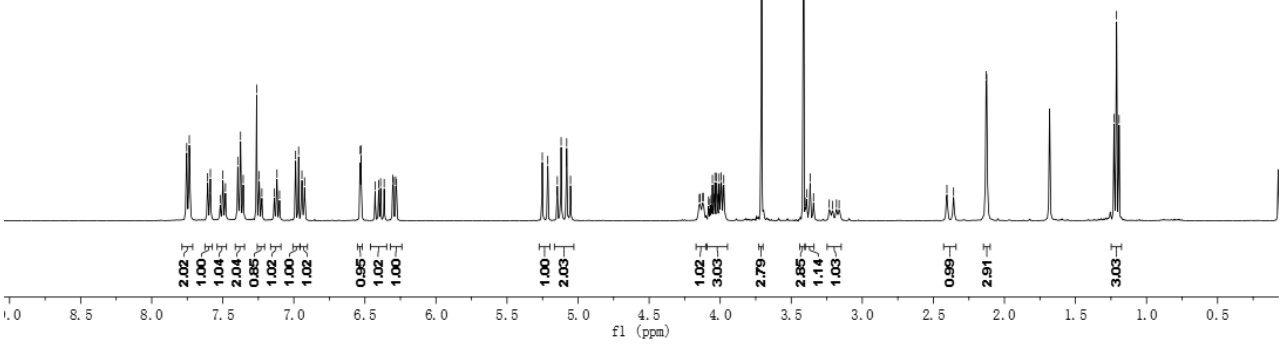
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.086	BB	0.2958	9853.25488	505.47781	99.6912
2	12.805	BB	0.3172	30.51867	1.59996	0.3088

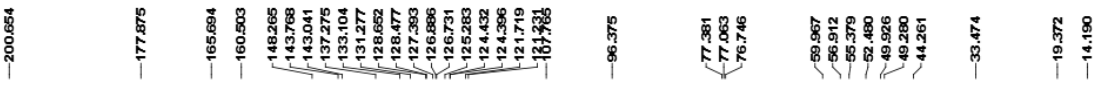


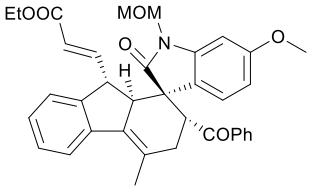


4p

^{1}H NMR (400 MHz, $CDCl_3$)

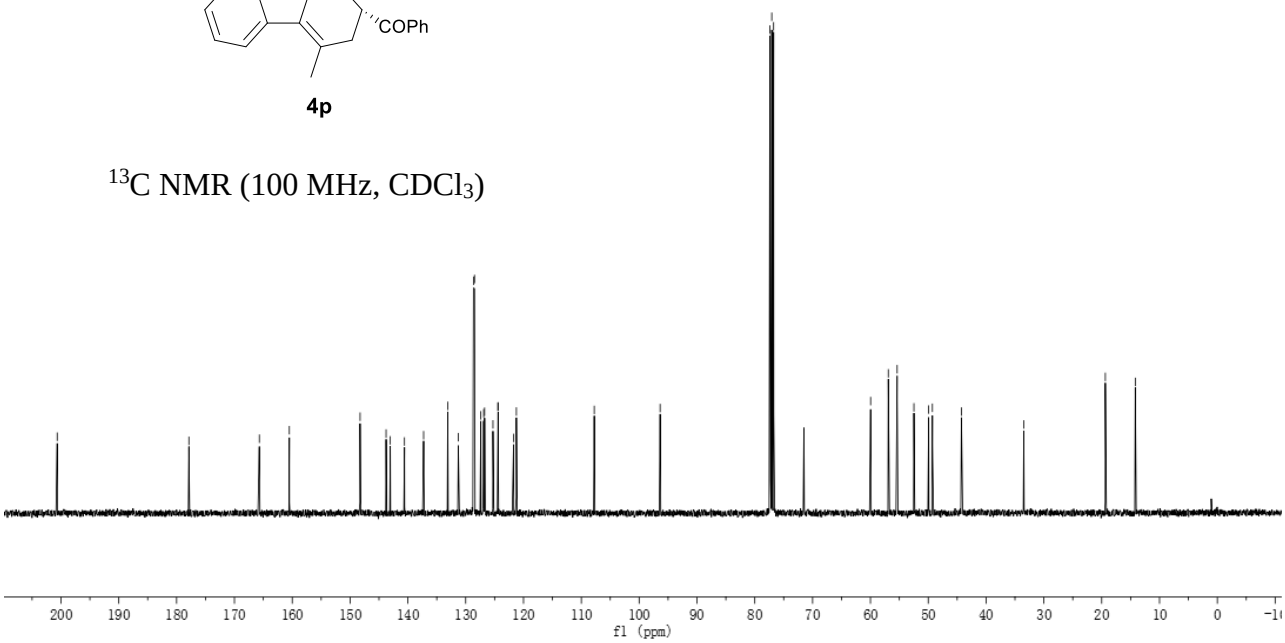


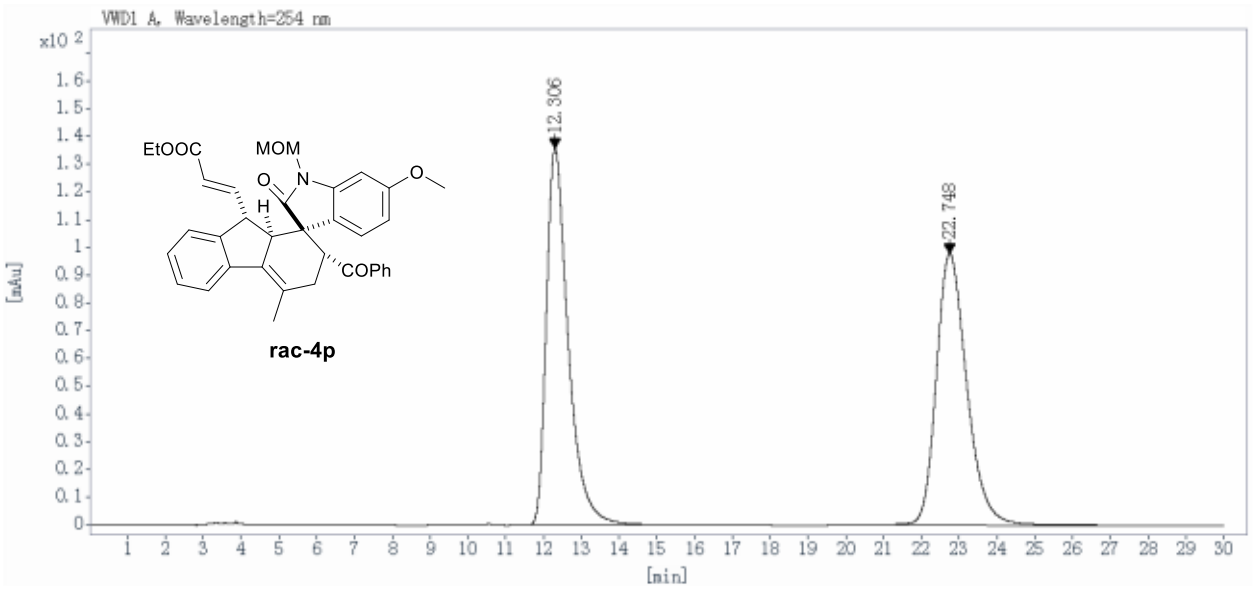




4p

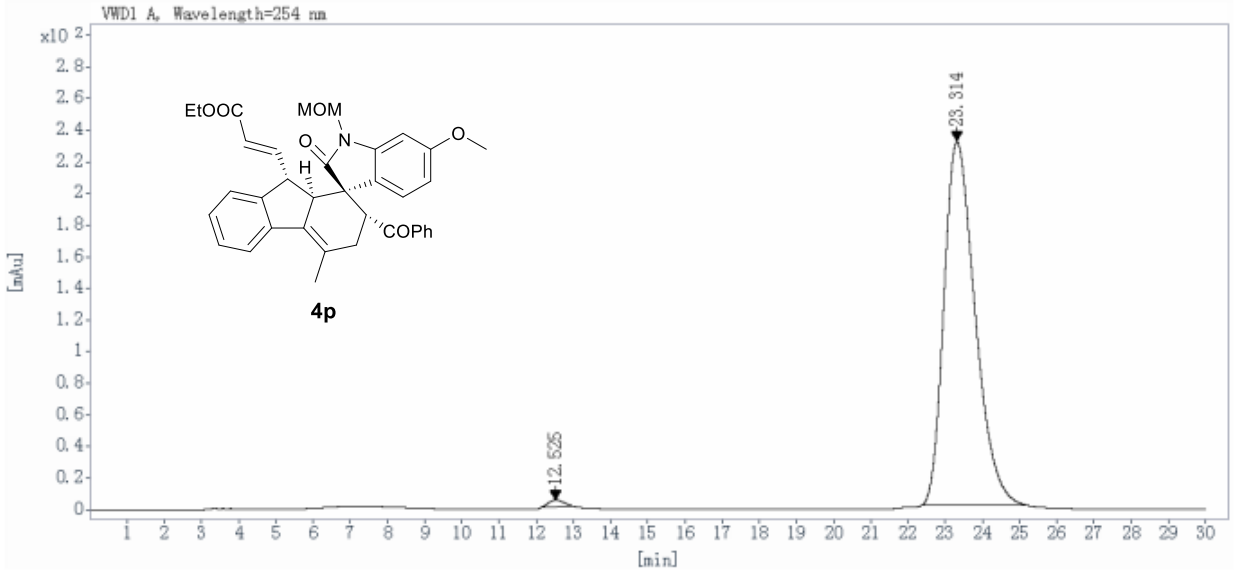
^{13}C NMR (100 MHz, $CDCl_3$)





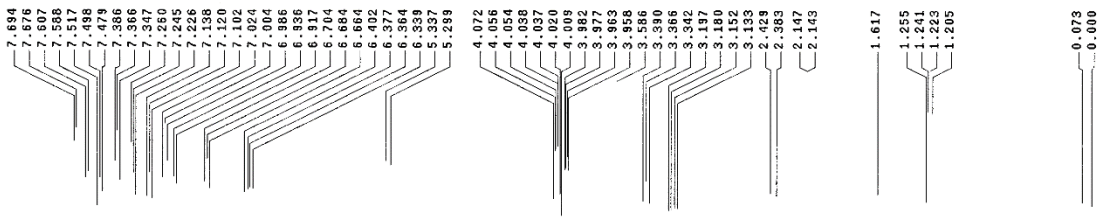
rac-4p

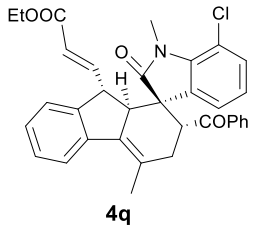
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.306	BB	0.61	135.5940	5467.3462	49.8823
22.748	BB	0.86	97.9341	5493.1543	50.1177
			Totals:	10960.5005	100.0000



4p

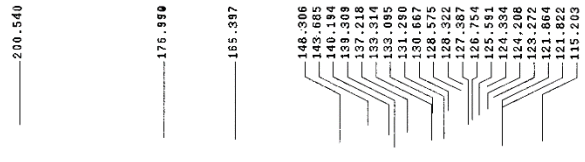
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.525	BBA	0.47	4.0115	111.8718	0.8290
23.314	BBA	0.90	230.0665	13382.2666	99.1710
			Totals:	13494.1385	100.0000

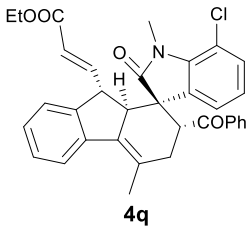




4q

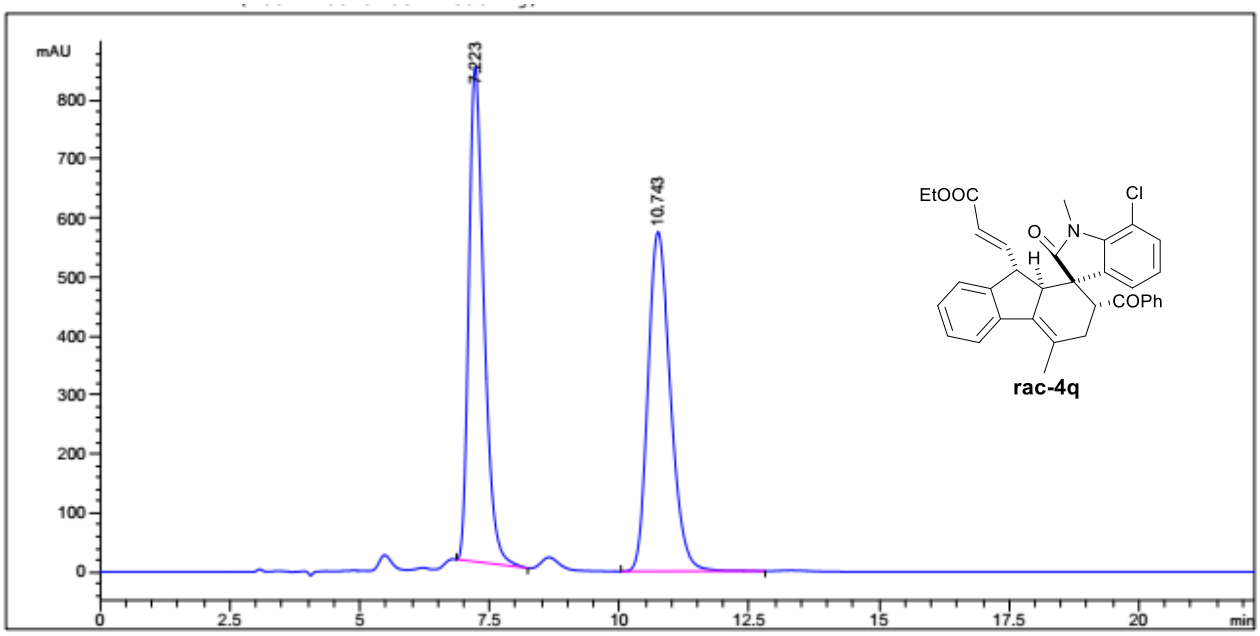
^{1}H NMR (400 MHz, $CDCl_3$)



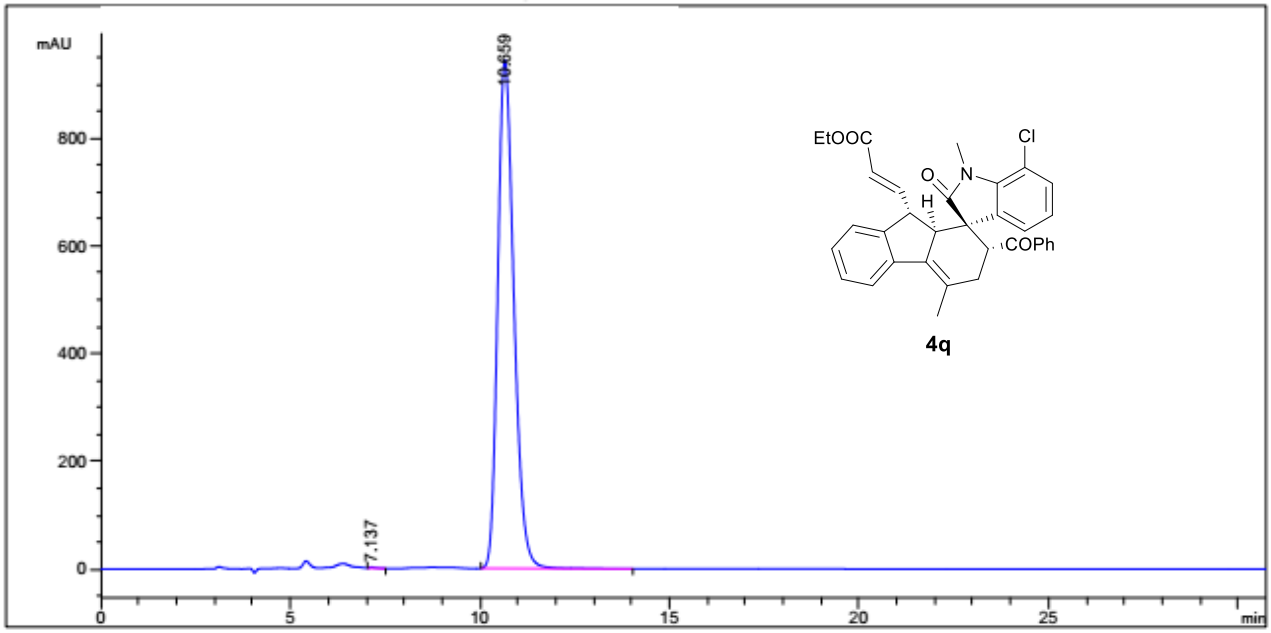


4q

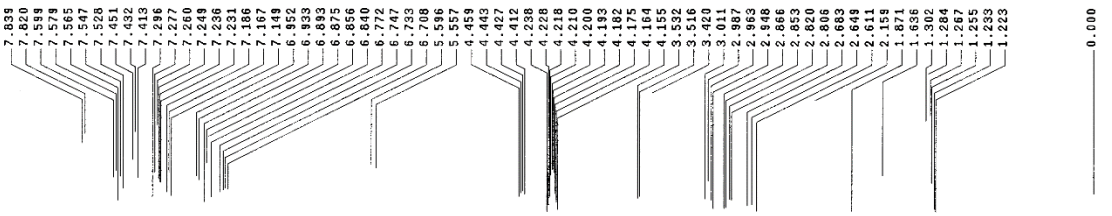
^{13}C NMR (150 MHz, $CDCl_3$)

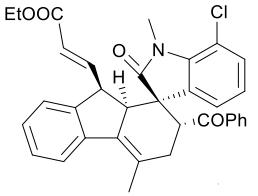


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.223	BB	0.3101	1.70646e4	839.01501	49.7071
2	10.743	BB	0.4633	1.72657e4	575.97101	50.2929



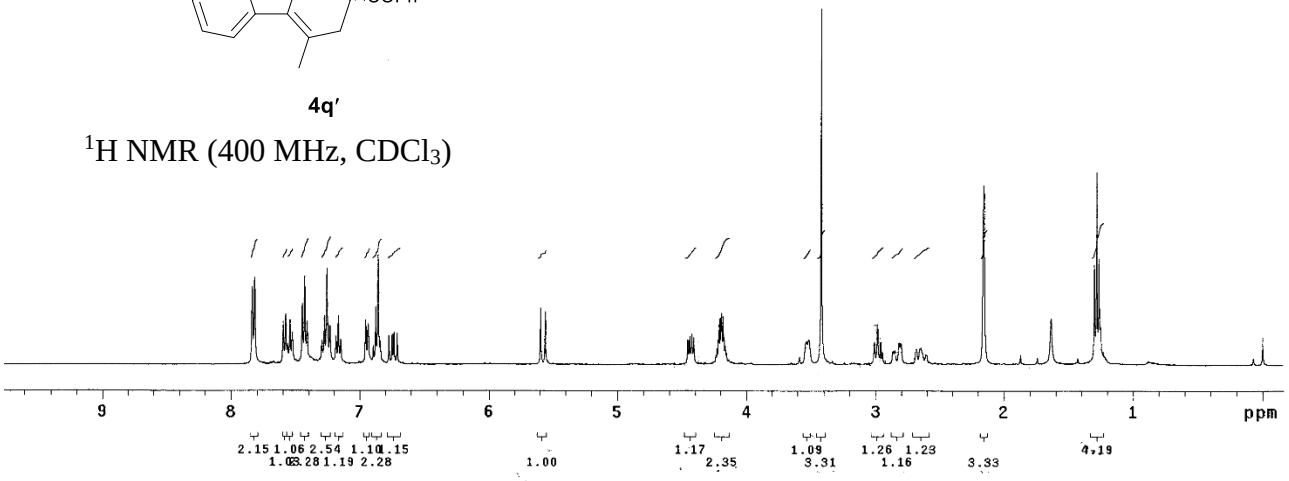
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.137	BB	0.1199	19.66145	2.20822	0.0700
2	10.659	BB	0.4600	2.80584e4	944.97076	99.9300

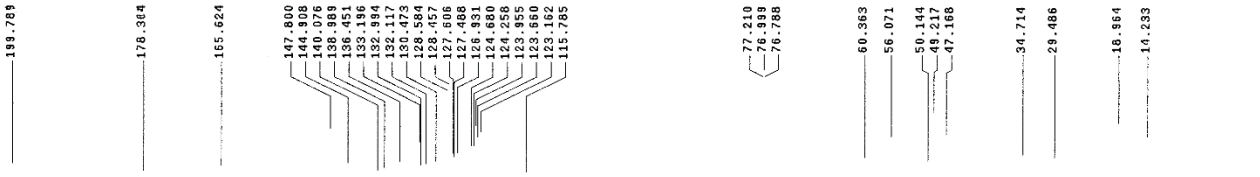


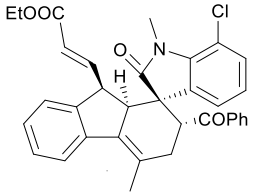


4q′

^{1}H NMR (400 MHz, $CDCl_3$)

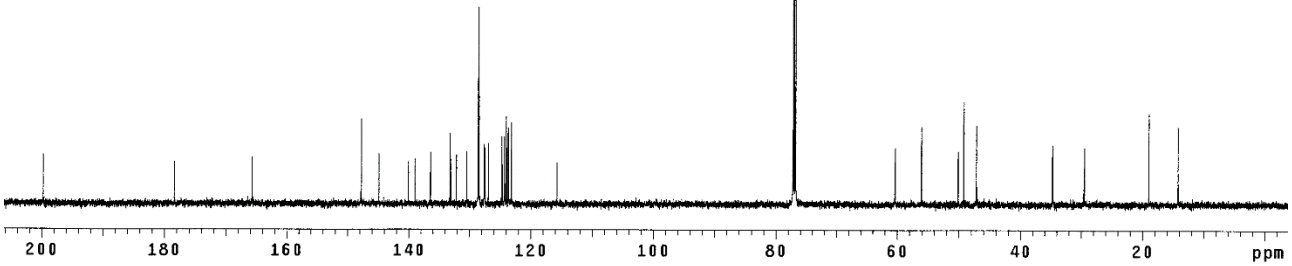


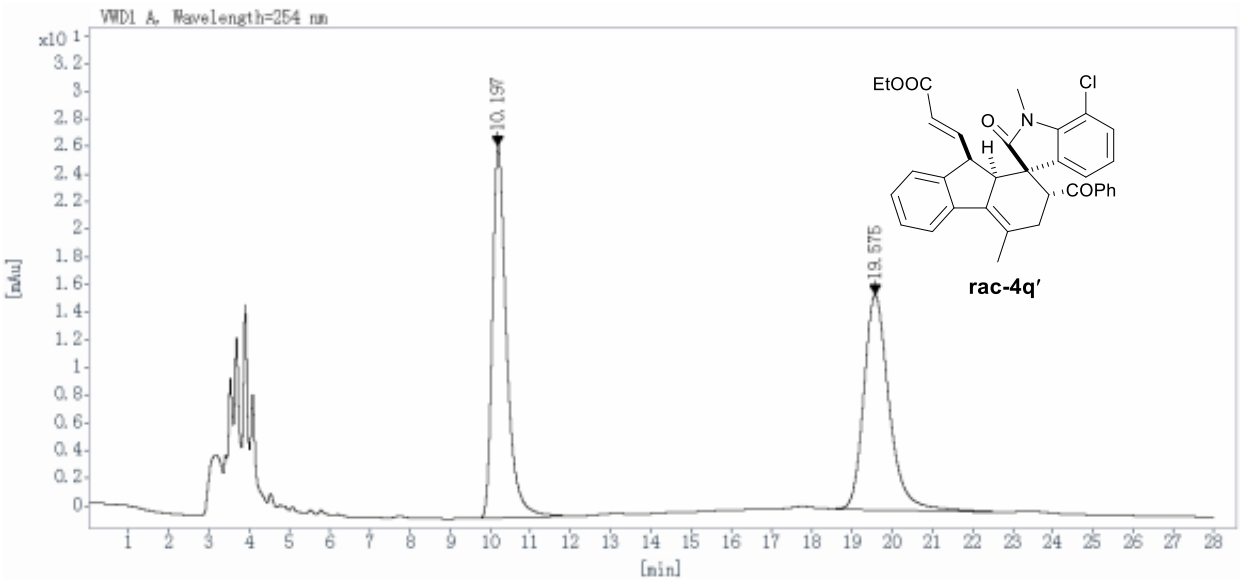




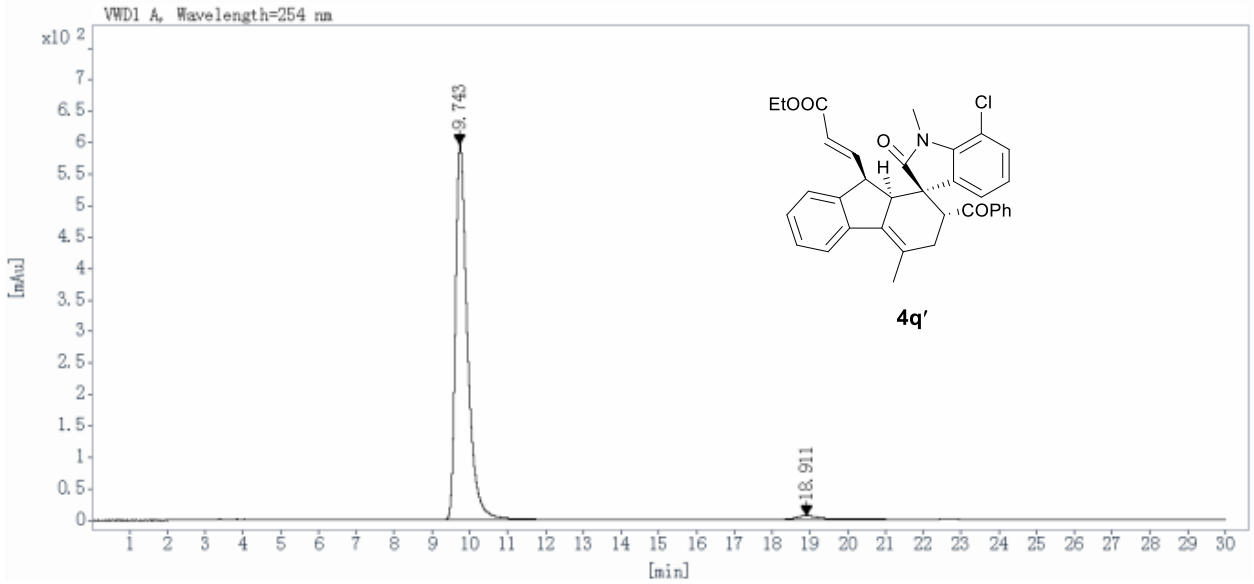
4q′

^{13}C NMR (150 MHz, $CDCl_3$)

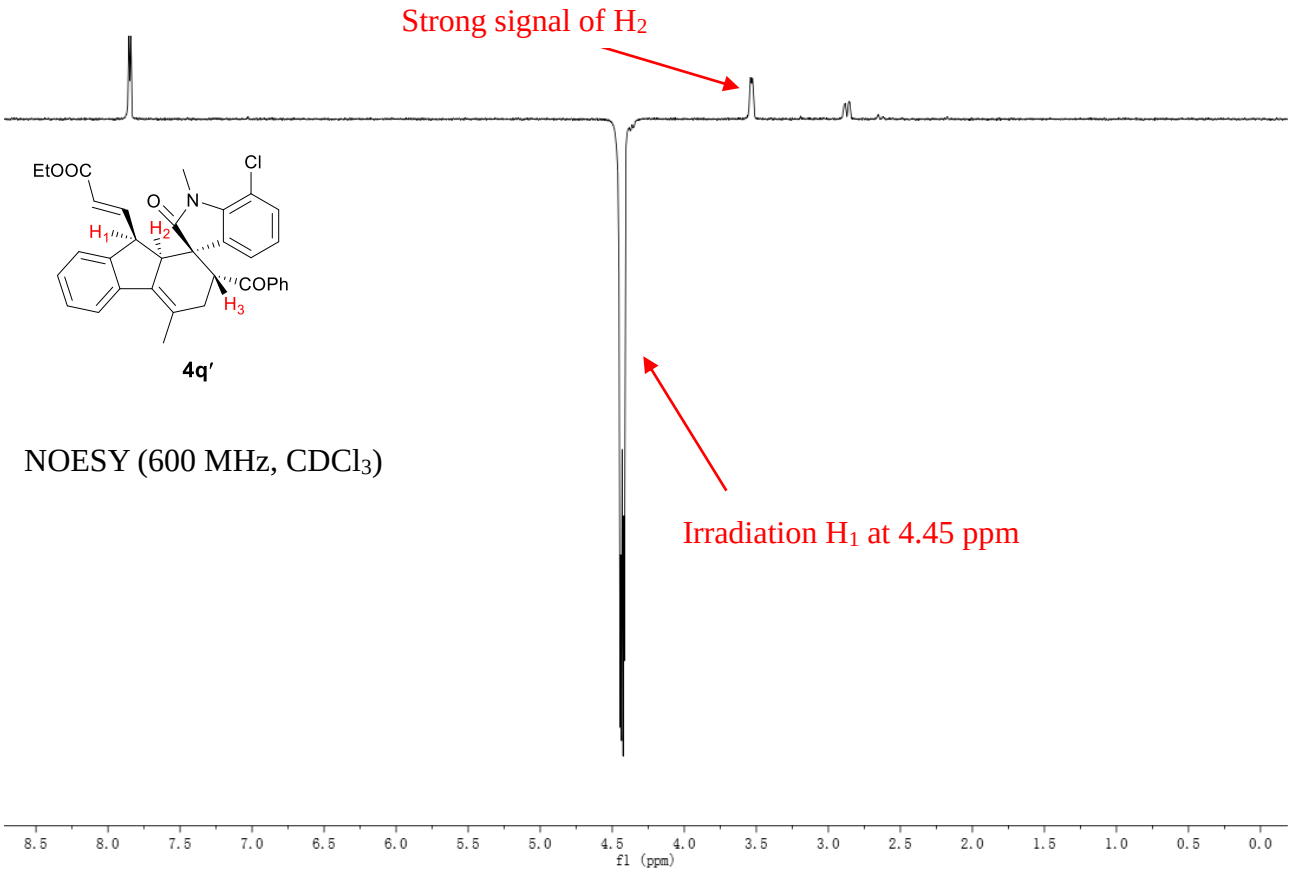


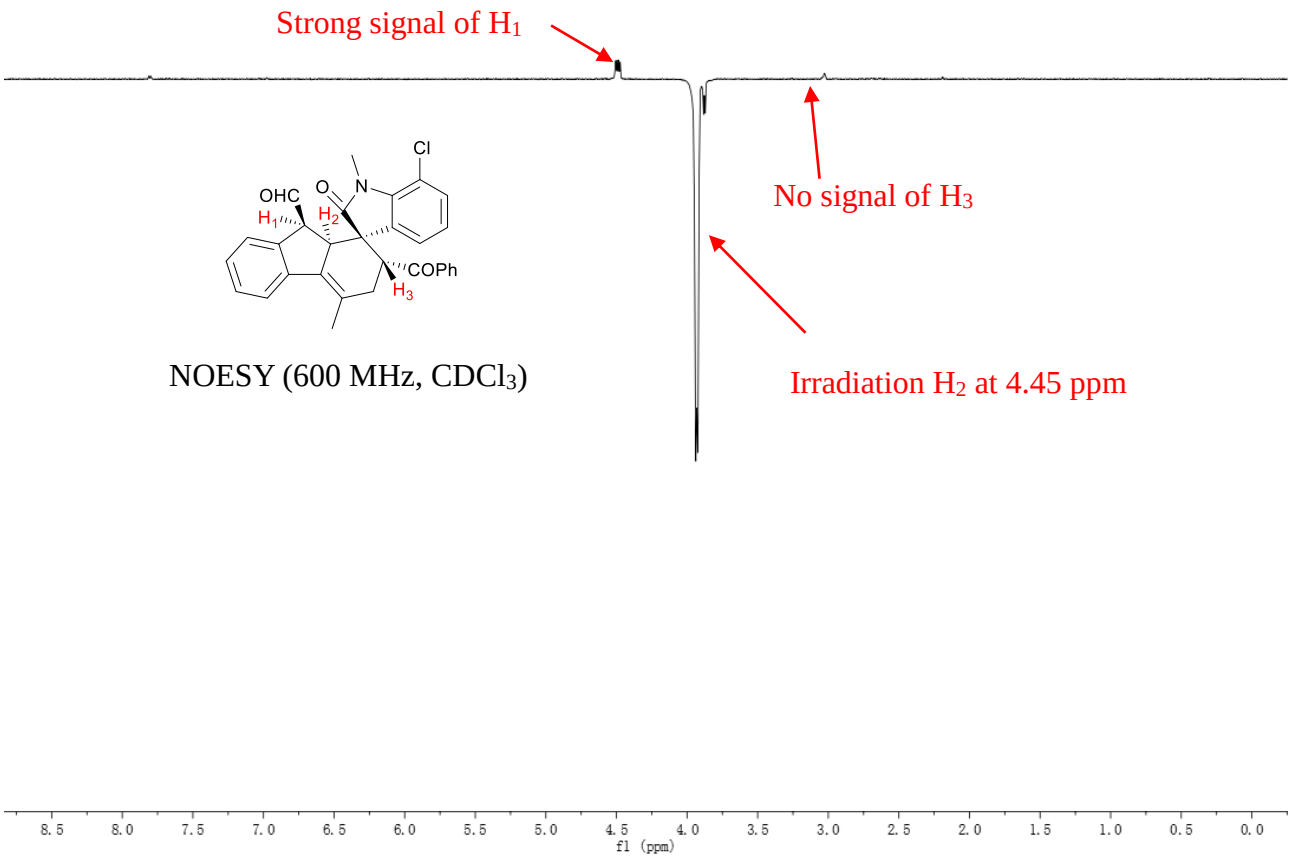


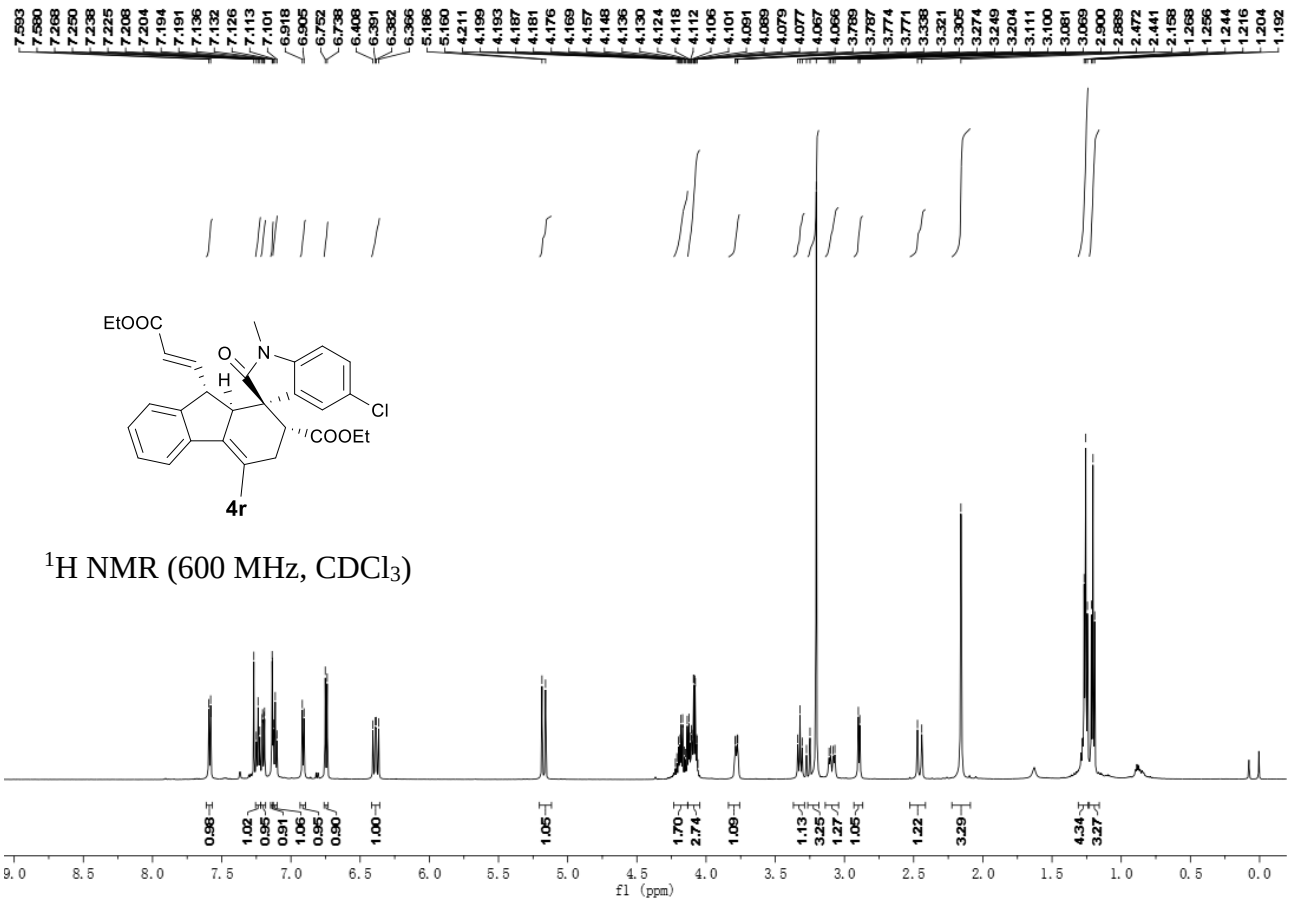
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.197	BB	0.37	26.8940	659.8615	49.2612
19.575	BB	0.67	15.5346	679.6548	50.7388
			Totals:	1339.5163	100.0000



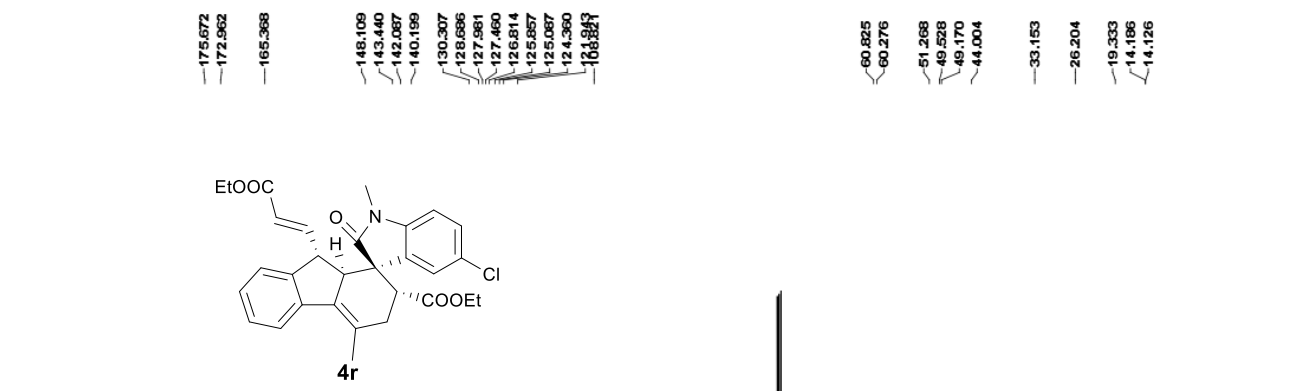
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.743	BB	0.33	595.4728	13152.7148	97.5997
18.911	BB	0.78	5.9313	323.4661	2.4003
			Totals:	13476.1810	100.0000


Strong signal of H2
EtOOC
Cl
O
N
H1
H2
COPh
H3
4q′
NOESY (600 MHz, CDCl3)
Irradiation H1 at 4.45 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

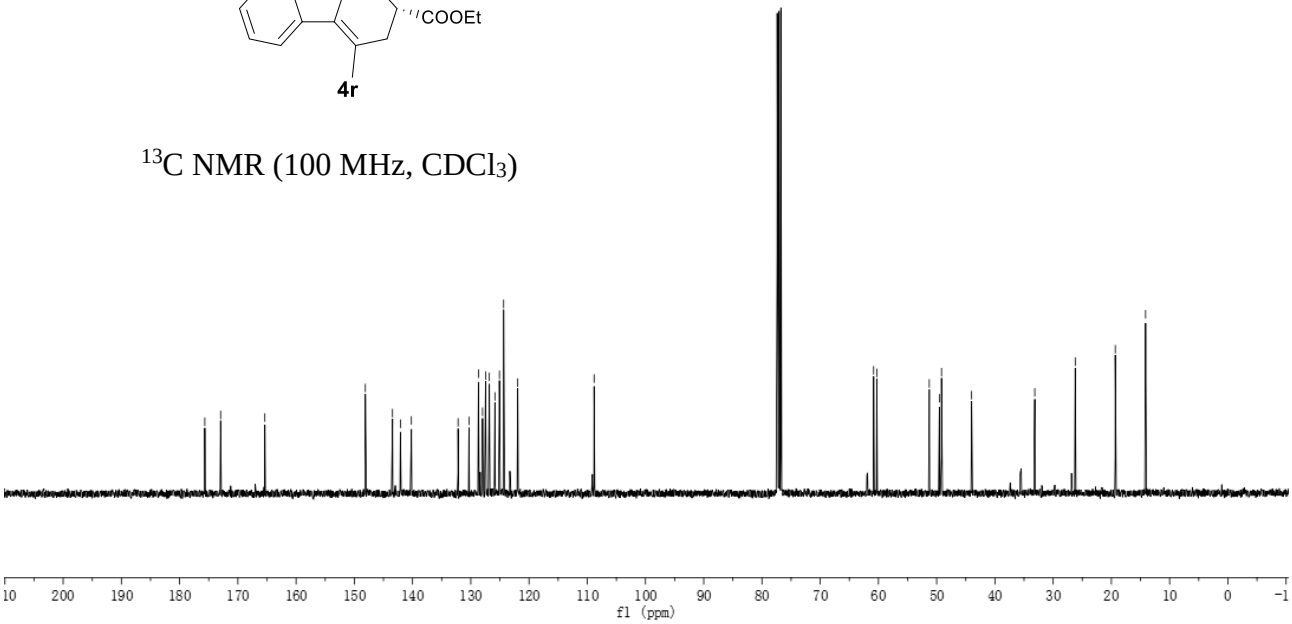

Strong signal of H1
Cl
OHC
O
N
H1
H2
COPh
H3
NOESY (600 MHz, CDCl3)
No signal of H3
Irradiation H2 at 4.45 ppm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

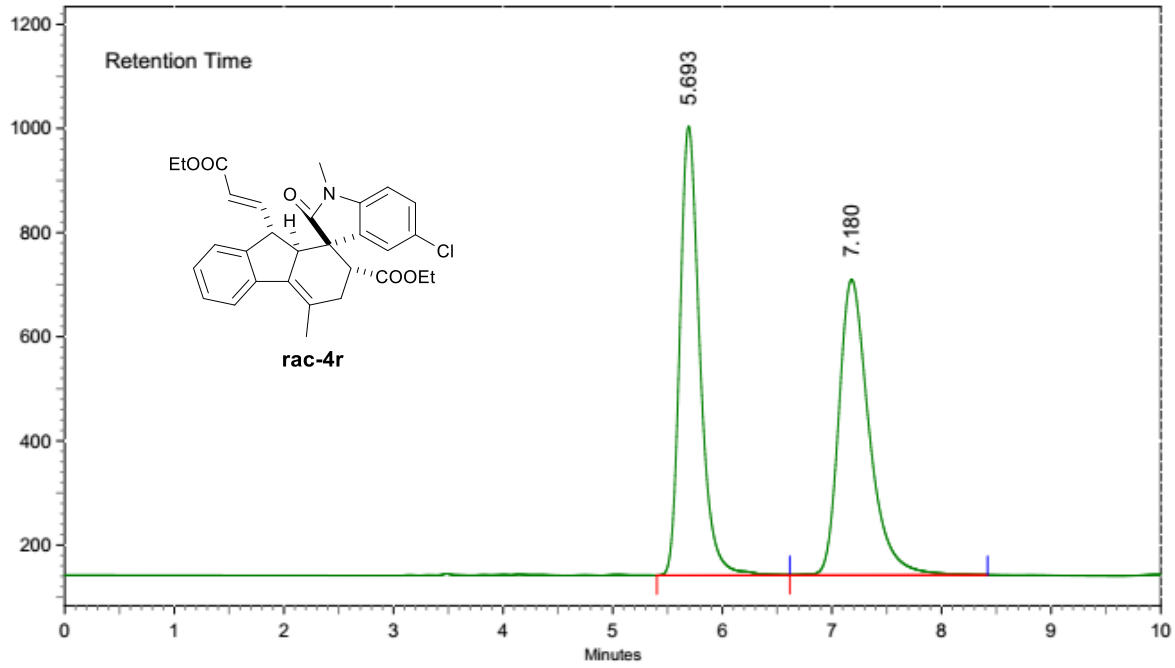


^{1}H NMR (600 MHz, $CDCl_3$)

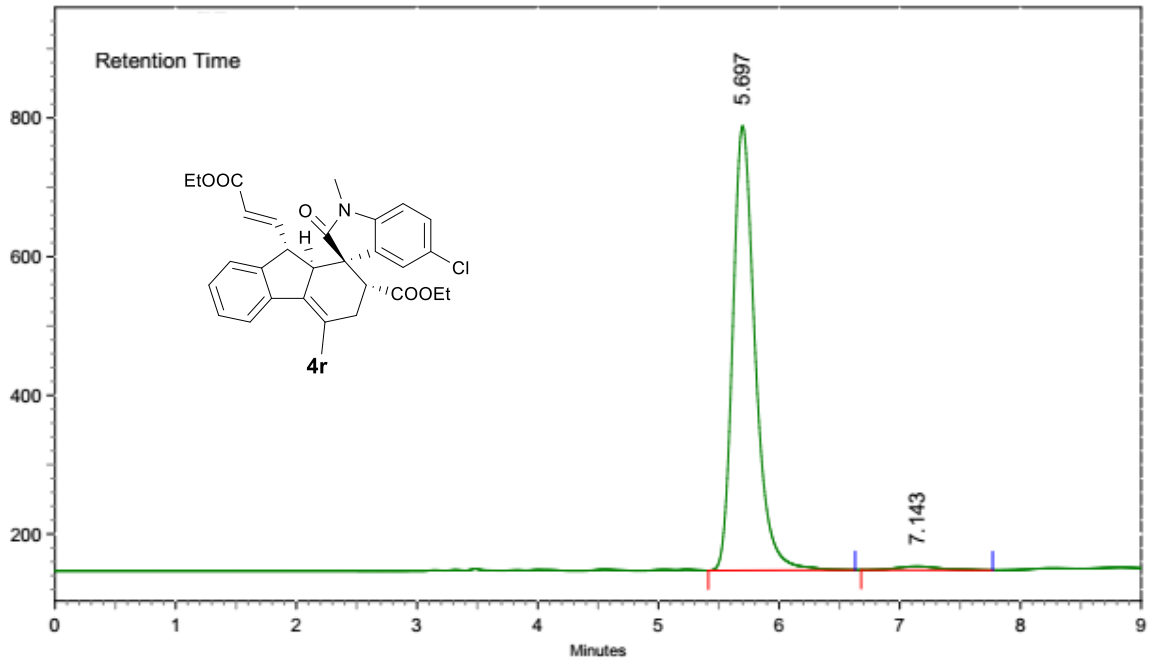


^{13}C NMR (100 MHz, $CDCl_3$)

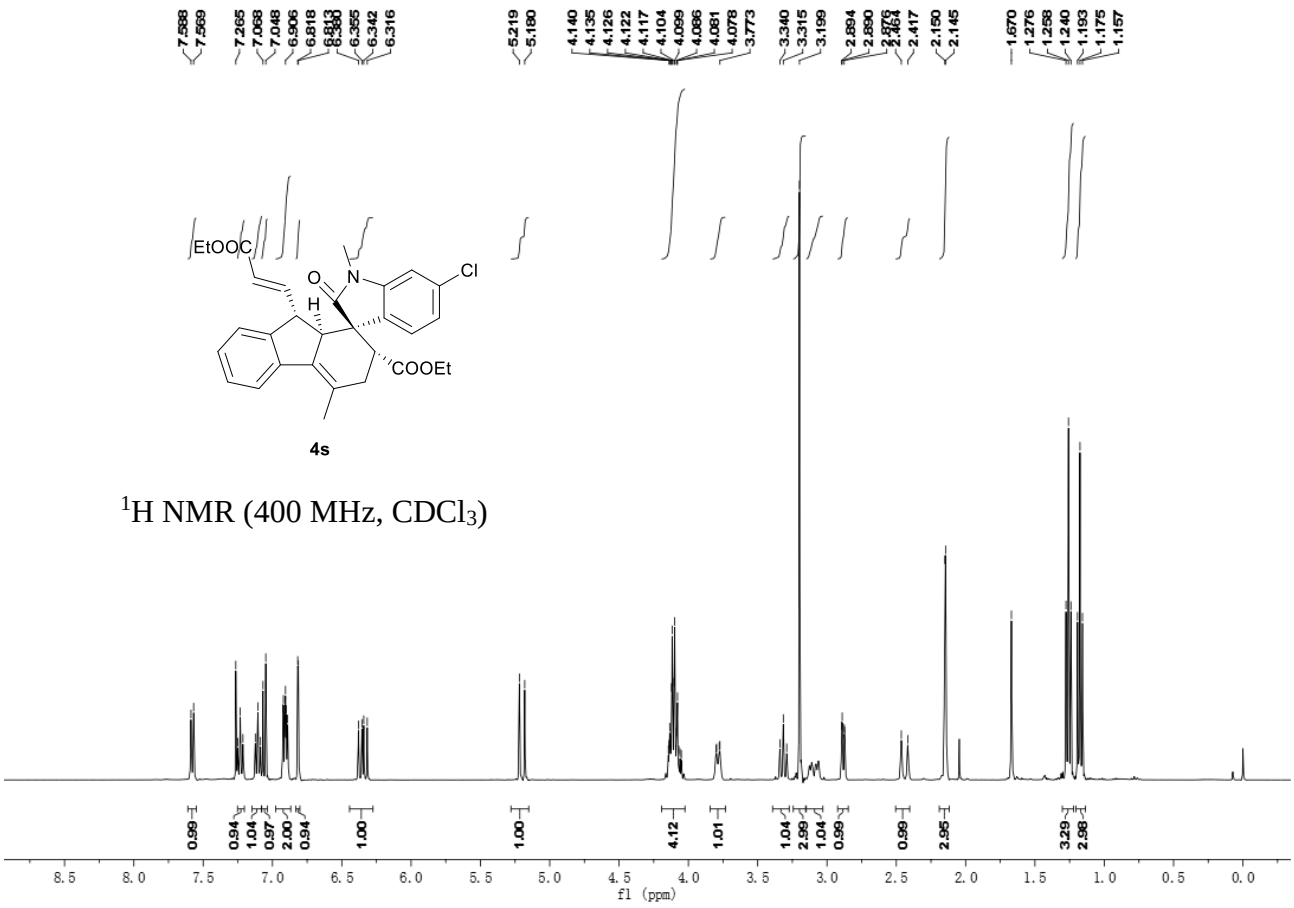




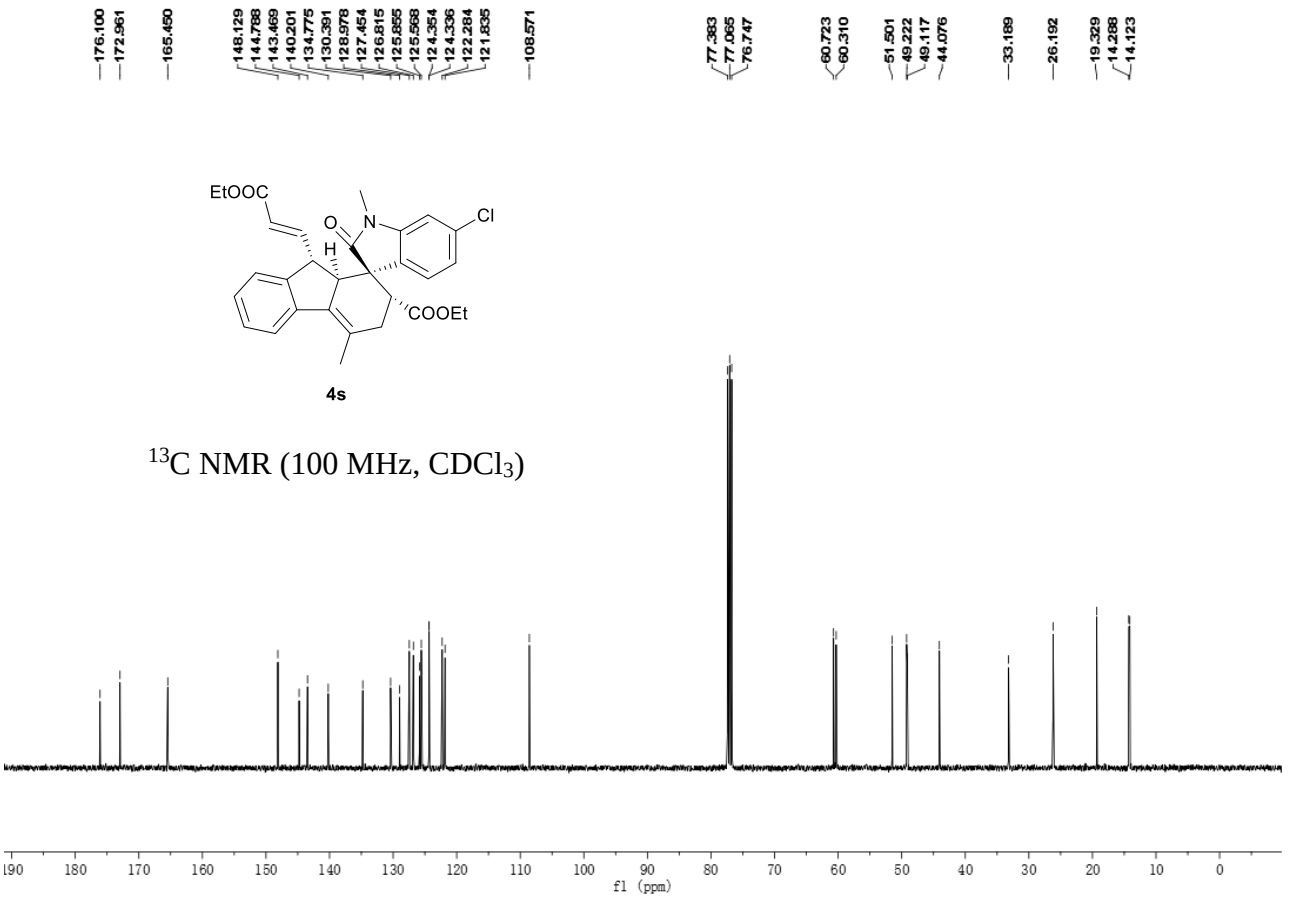
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.693	1.213	14464891	183219474	50.1067
2	7.180	1.803	9526157	182439085	49.8933



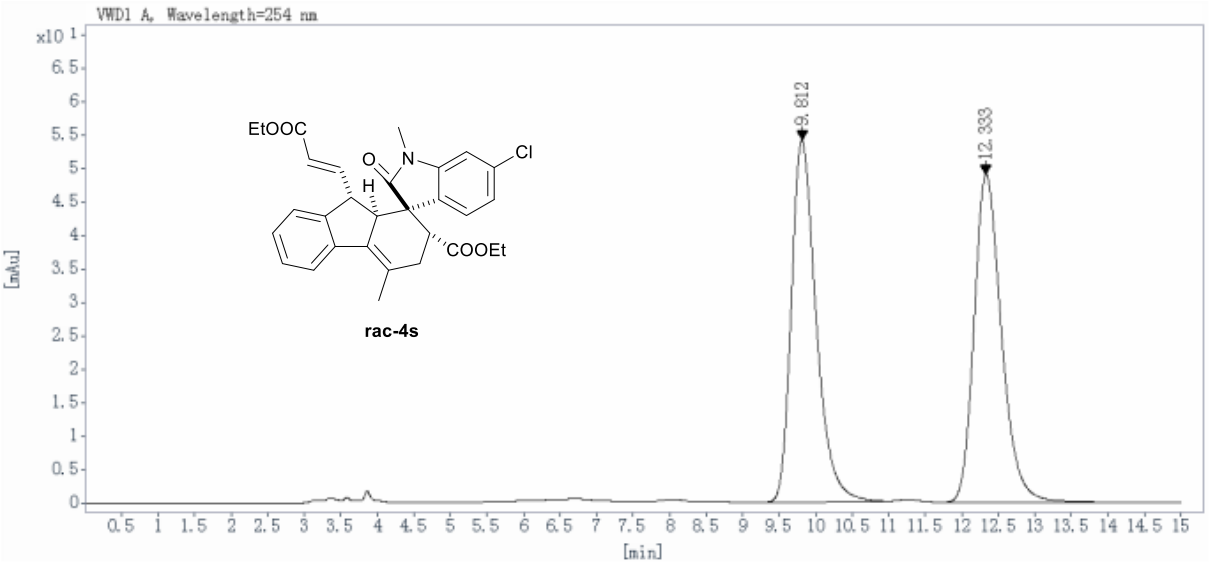
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	5.697	1.217	10753666	138070998	98.4075
2	7.143	1.090	88143	2234421	1.5925



^{1}H NMR (400 MHz, $CDCl_3$)

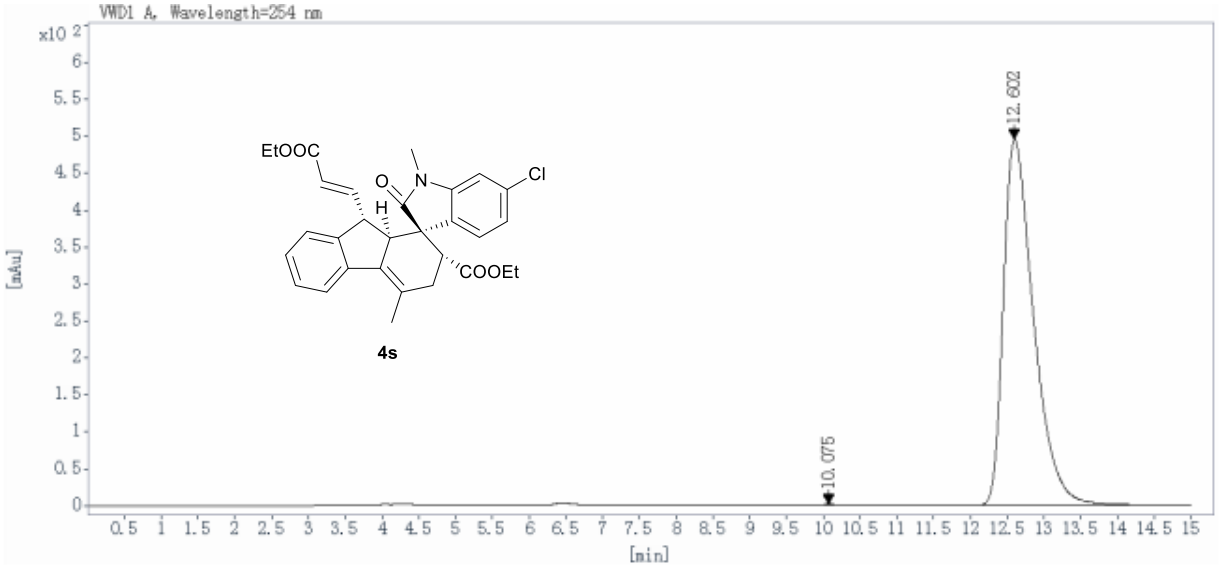


^{13}C NMR (100 MHz, $CDCl_3$)



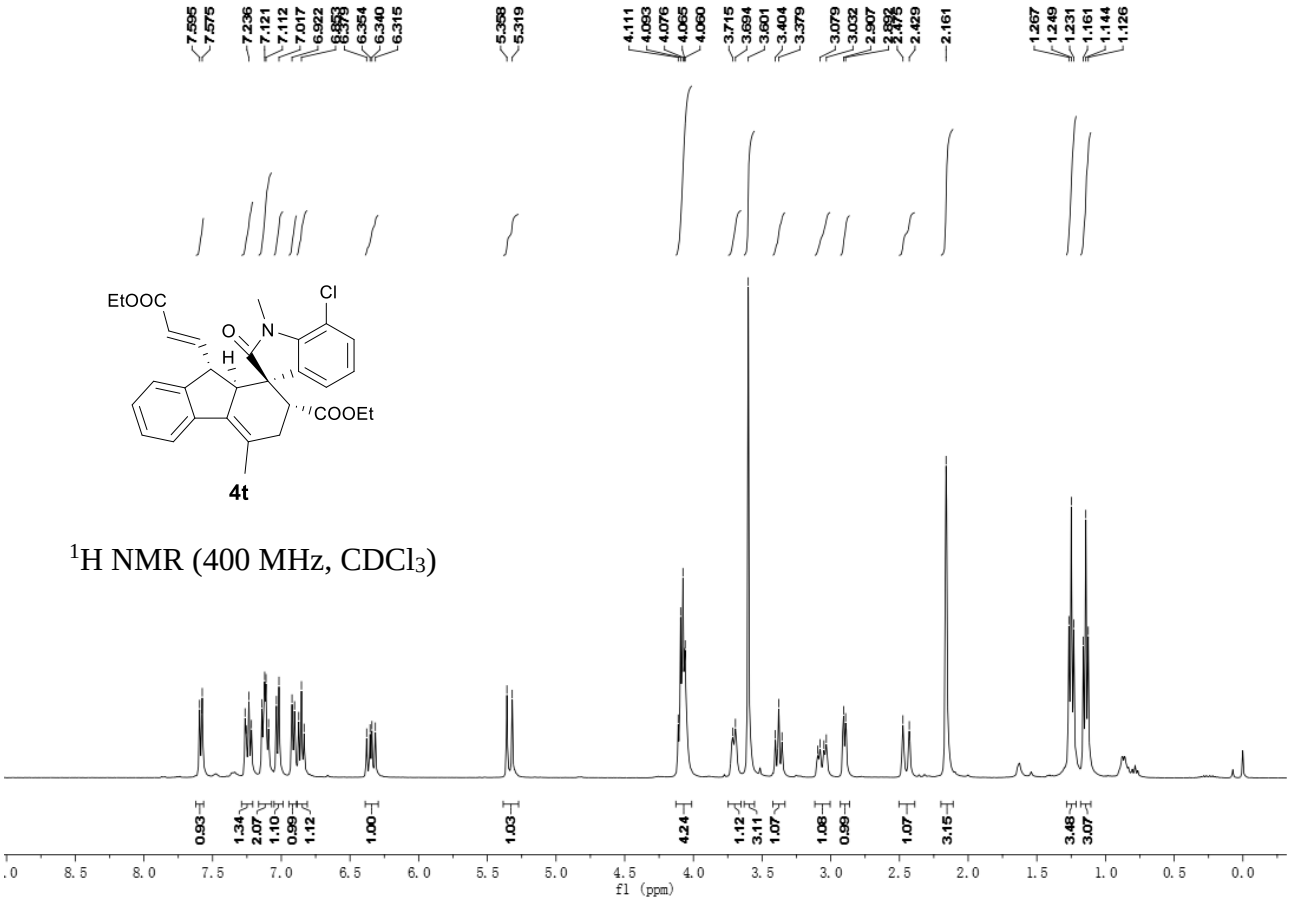
rac-4s

Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
9.812	BB	0.36	54.0320	1277.2461	49.9248
12.333	BB	0.40	49.0530	1281.0914	50.0752
			Totals:	2558.3375	100.0000

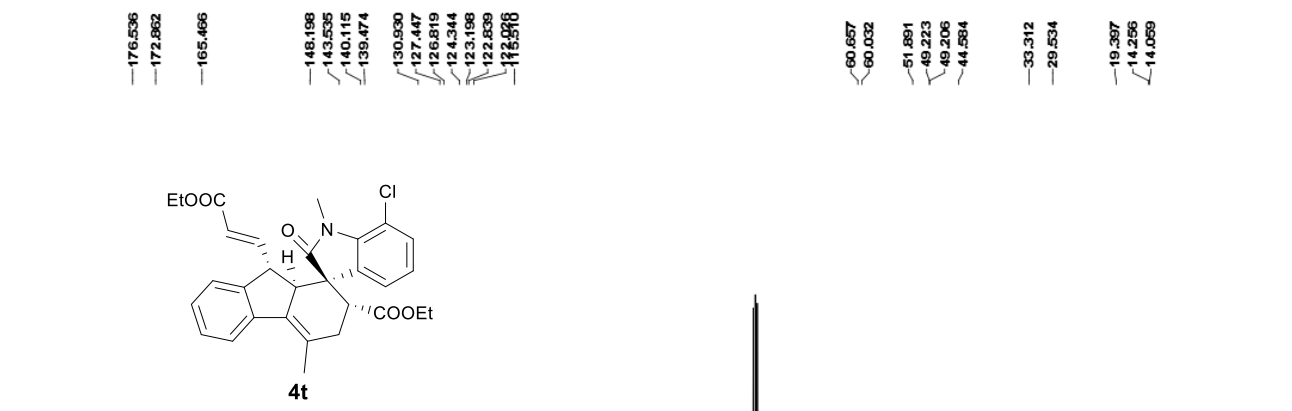


4s

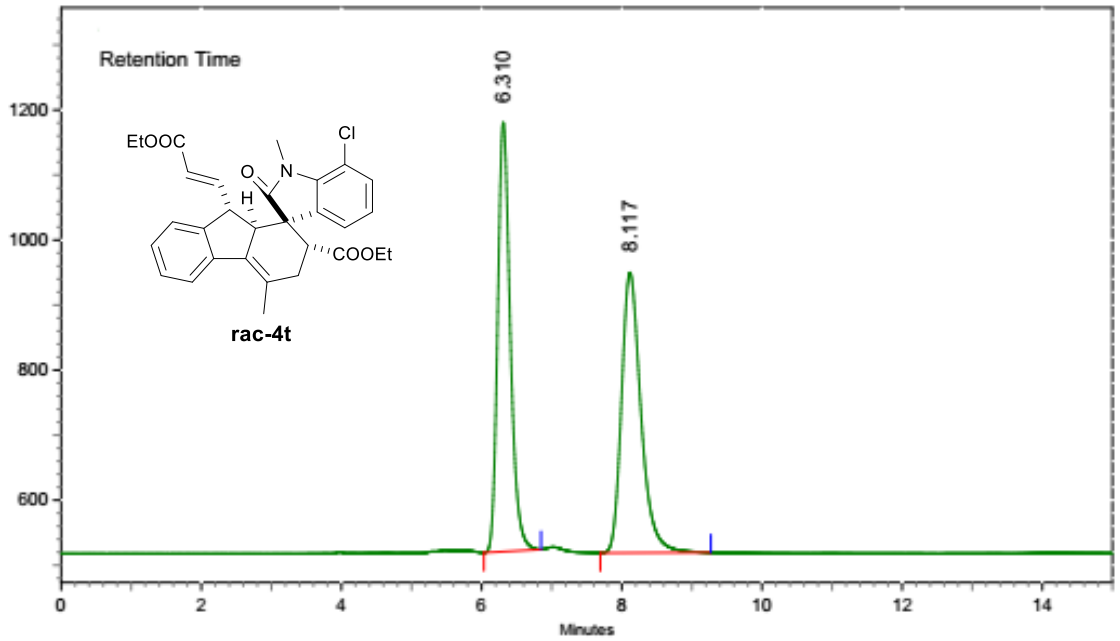
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.075	BB	0.34	0.8595	19.2545	0.1360
12.602	BB	0.43	495.2272	14140.1621	99.8640
			Totals:	14159.4166	100.0000



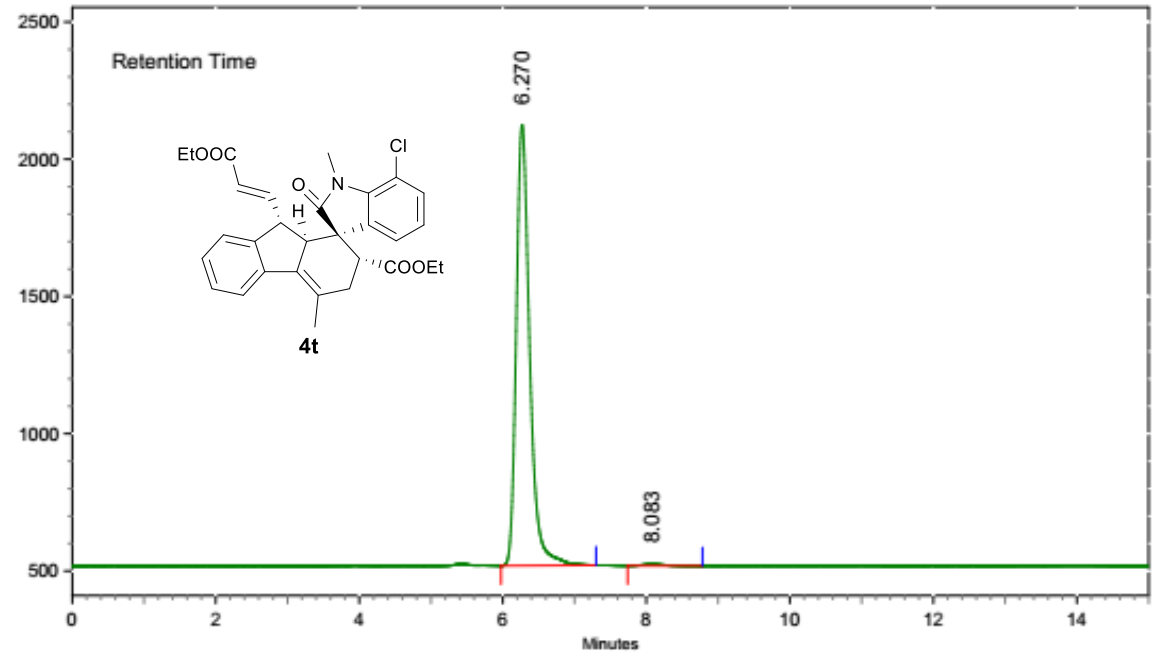
^{1}H NMR (400 MHz, $CDCl_3$)



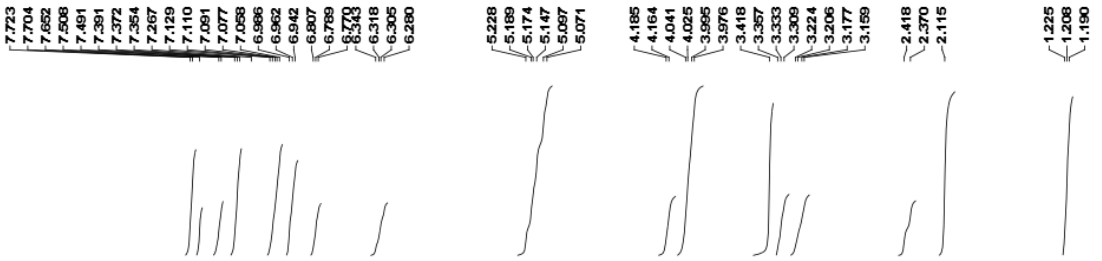
^{1}H NMR (100 MHz, $CDCl_3$)

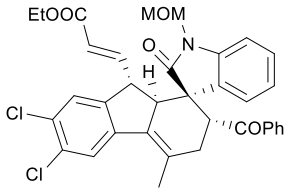


Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.310	0.813	11065298	137989679	49.7453
2	8.117	1.577	7230675	139402753	50.2547



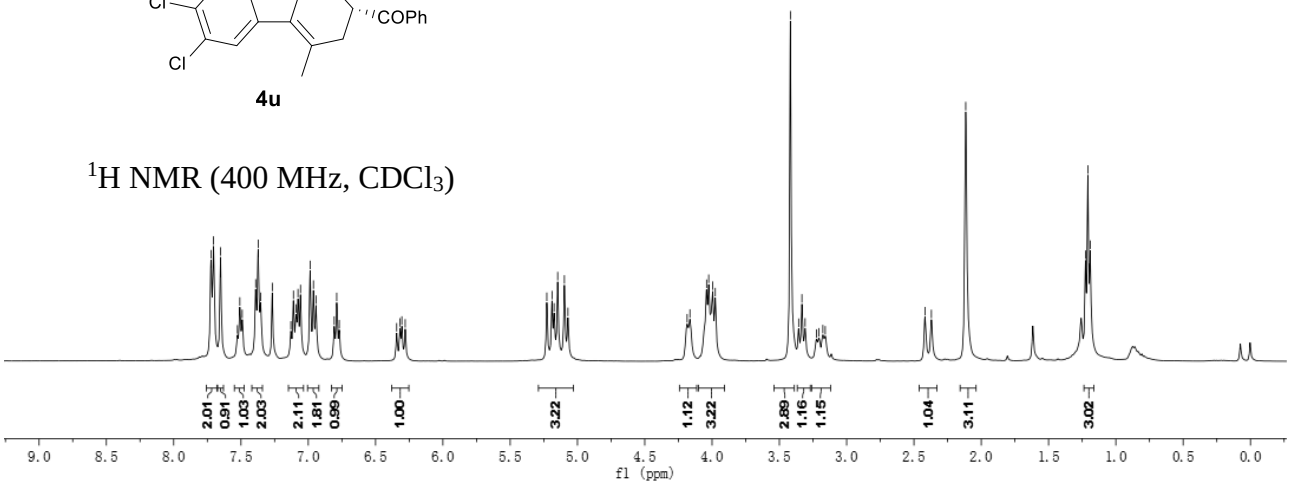
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.270	1.323	26942497	349591703	99.4474
2	8.083	1.043	100432	1942678	0.5526

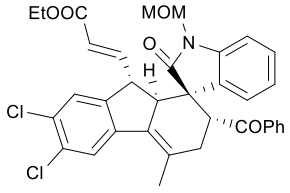




4u

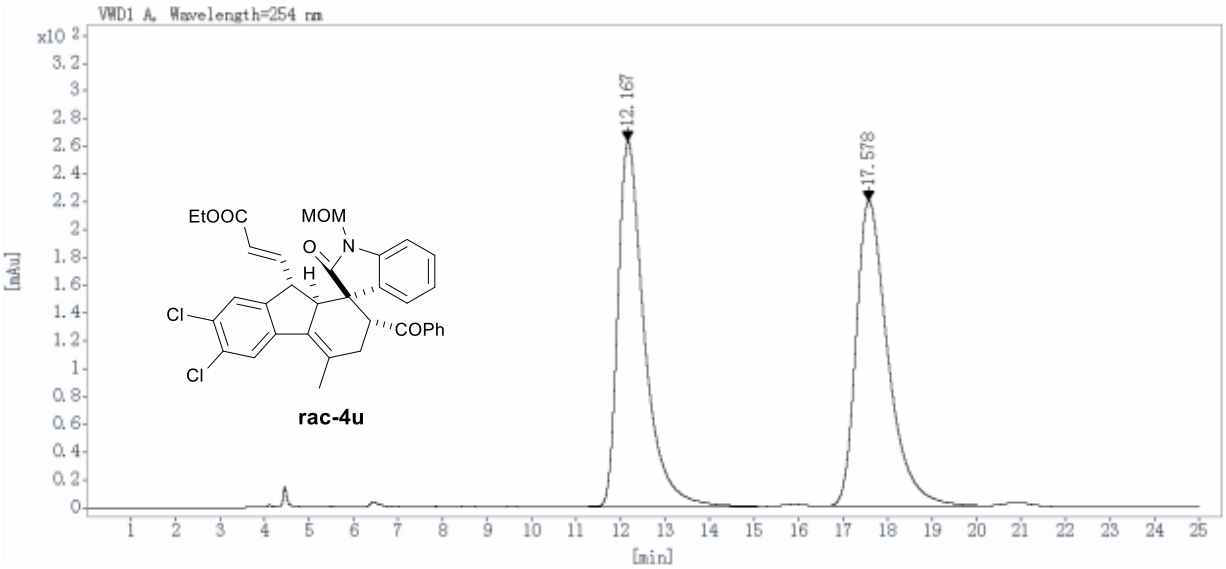
^{1}H NMR (400 MHz, $CDCl_3$)



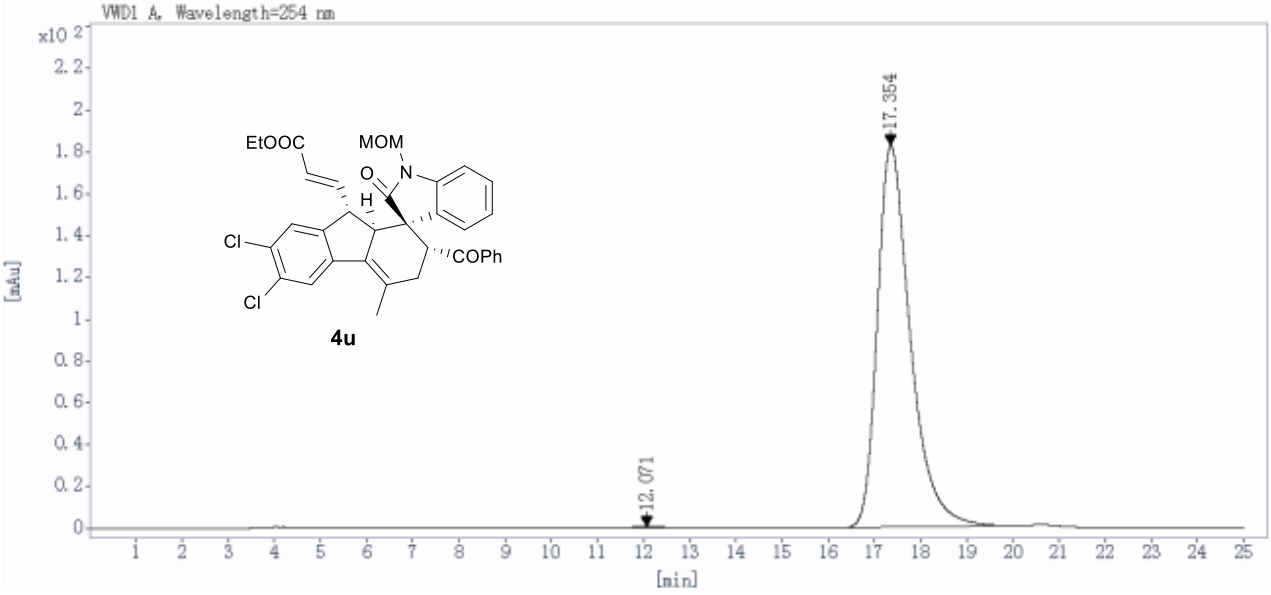


4u

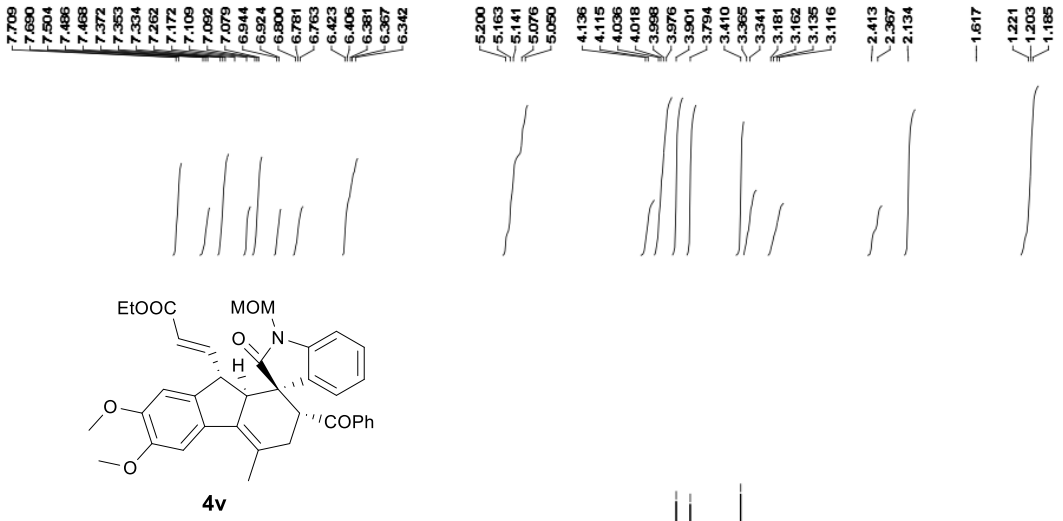
^{13}C NMR (100 MHz, $CDCl_3$)



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.167	BB	0.62	263.1772	10872.4014	49.9683
17.578	BBA	0.75	219.8274	10886.2080	50.0317

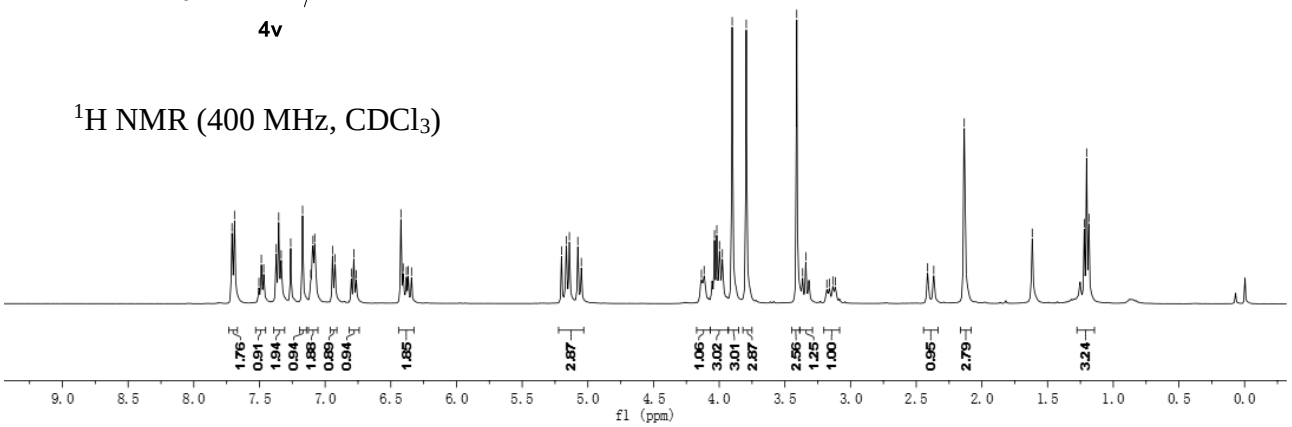


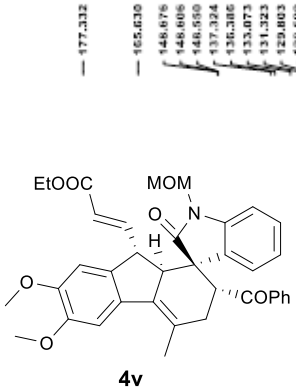
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.071	BB	0.50	0.8650	35.4365	0.3884
17.354	BB	0.75	182.7152	9088.3379	99.6116



4v

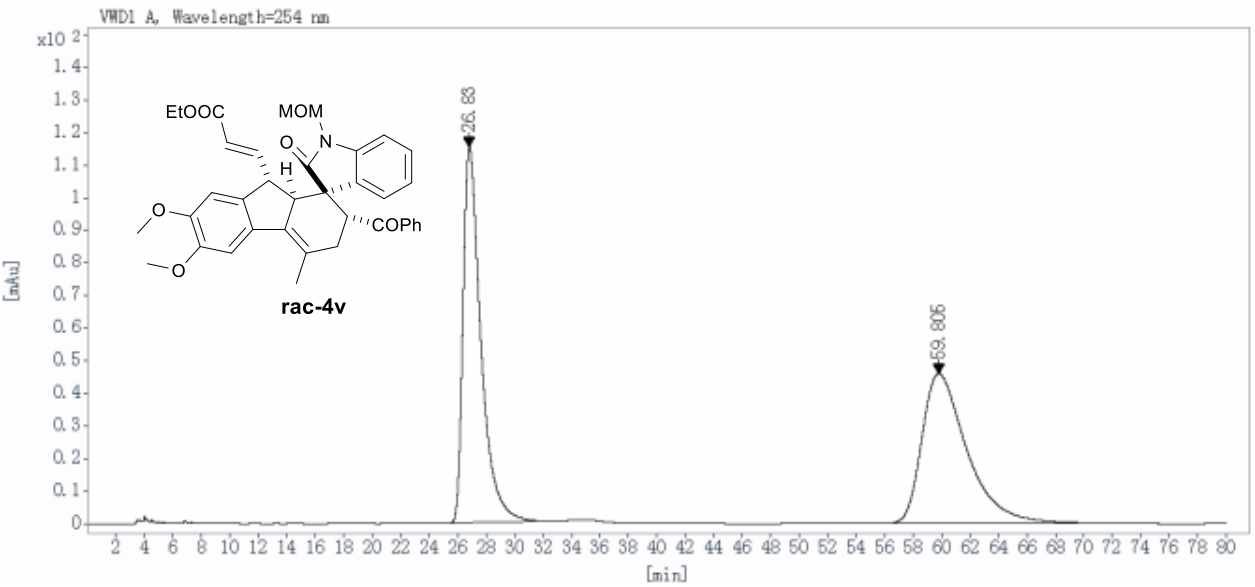
^{1}H NMR (400 MHz, $CDCl_3$)



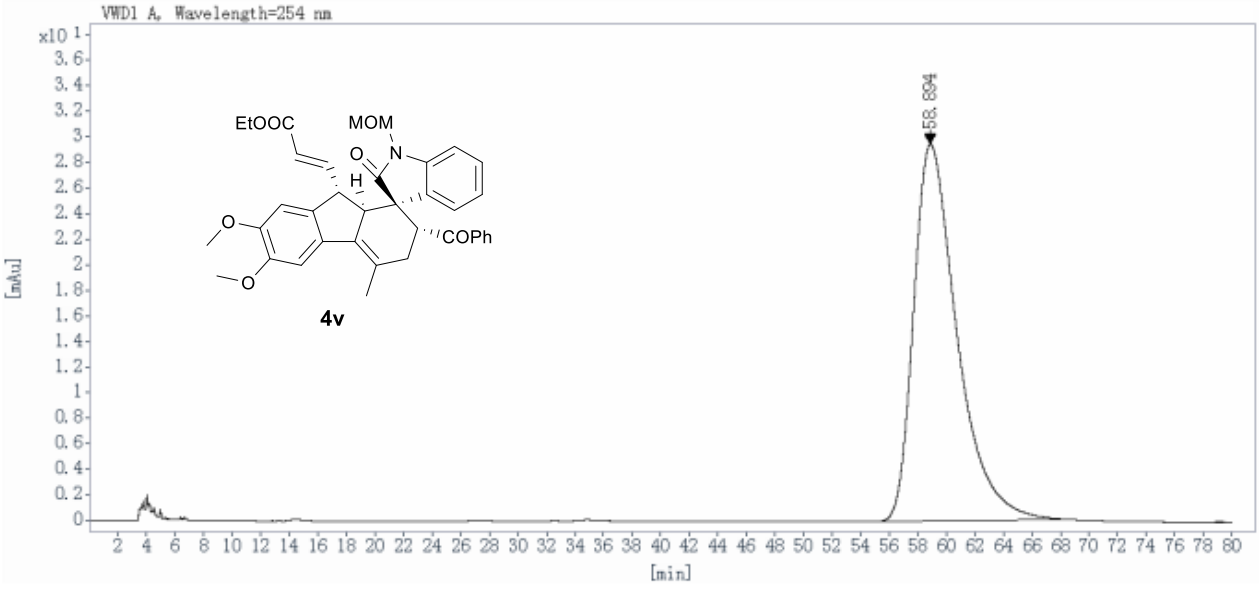


4v

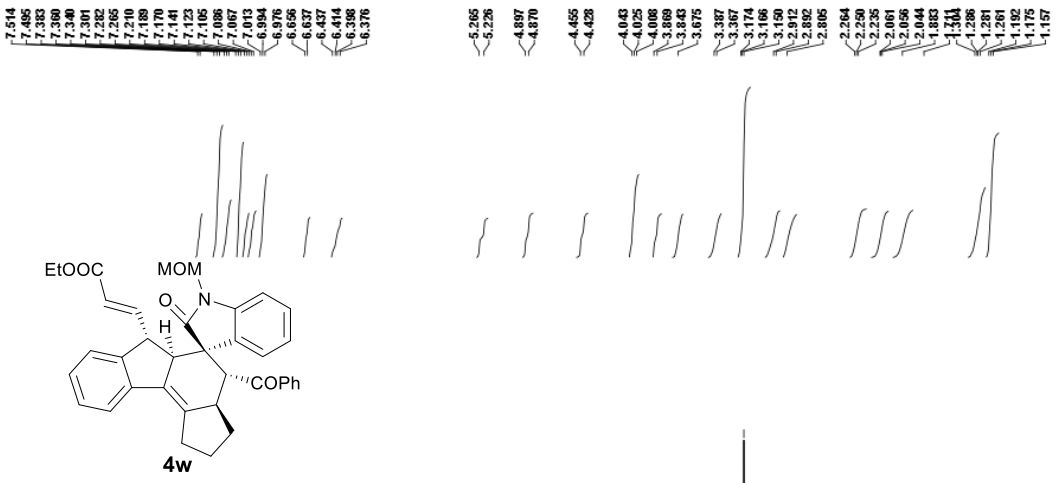
^{13}C NMR (100 MHz, $CDCl_3$)



Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
26.830	BB	1.30	115.2181	10073.3213	50.0101
59.805	BB	3.08	45.8727	10069.2617	49.9899

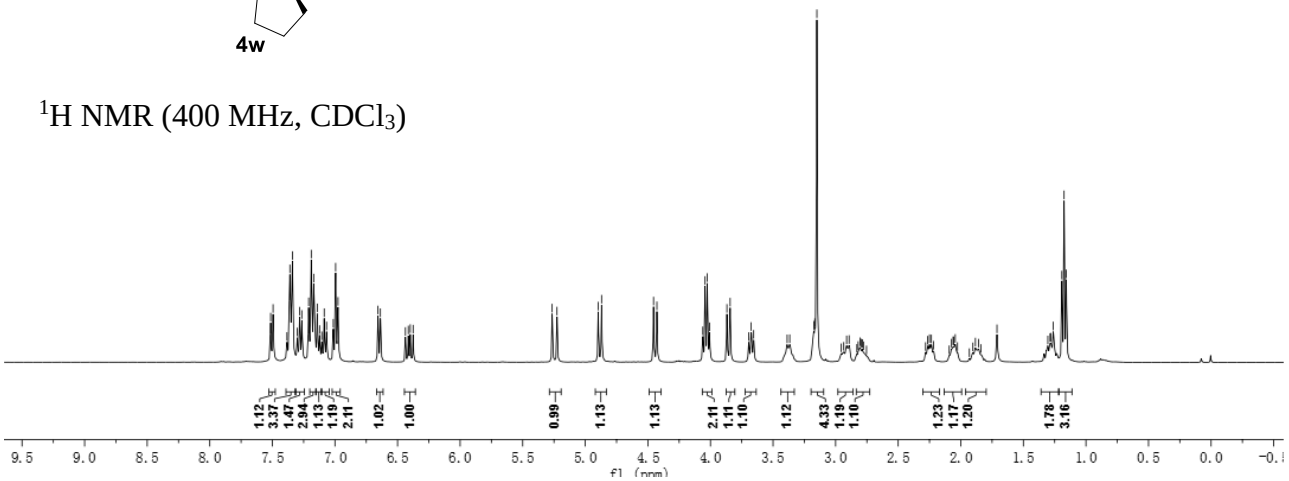


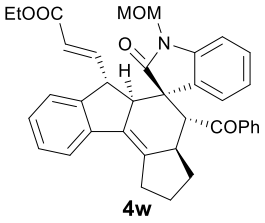
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
58.894	BB	2.83	29.4700	6222.8101	100.0000
			Totals:	6222.8101	100.0000



4w

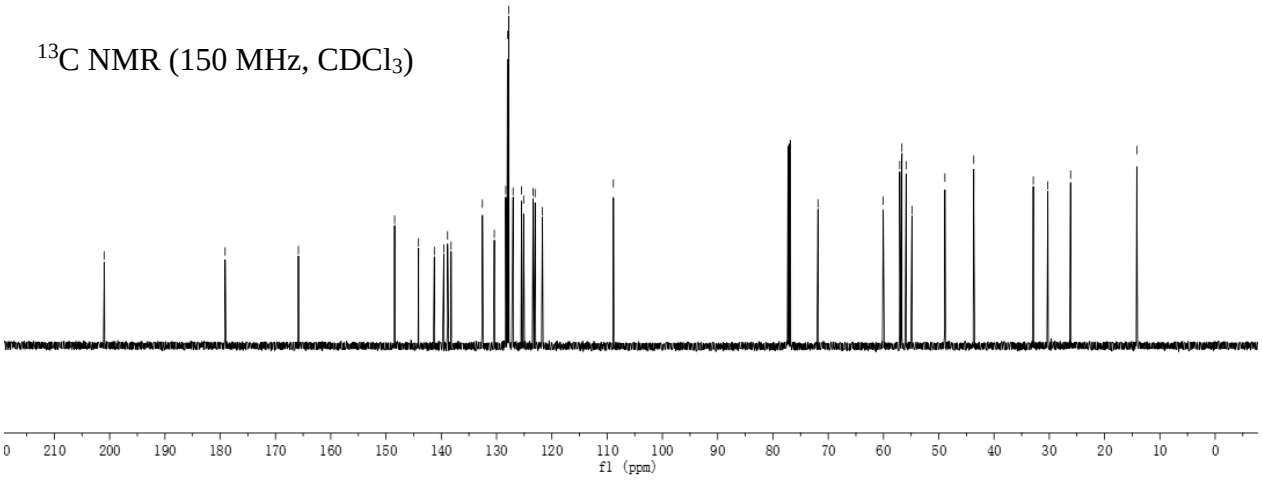
^{1}H NMR (400 MHz, $CDCl_3$)

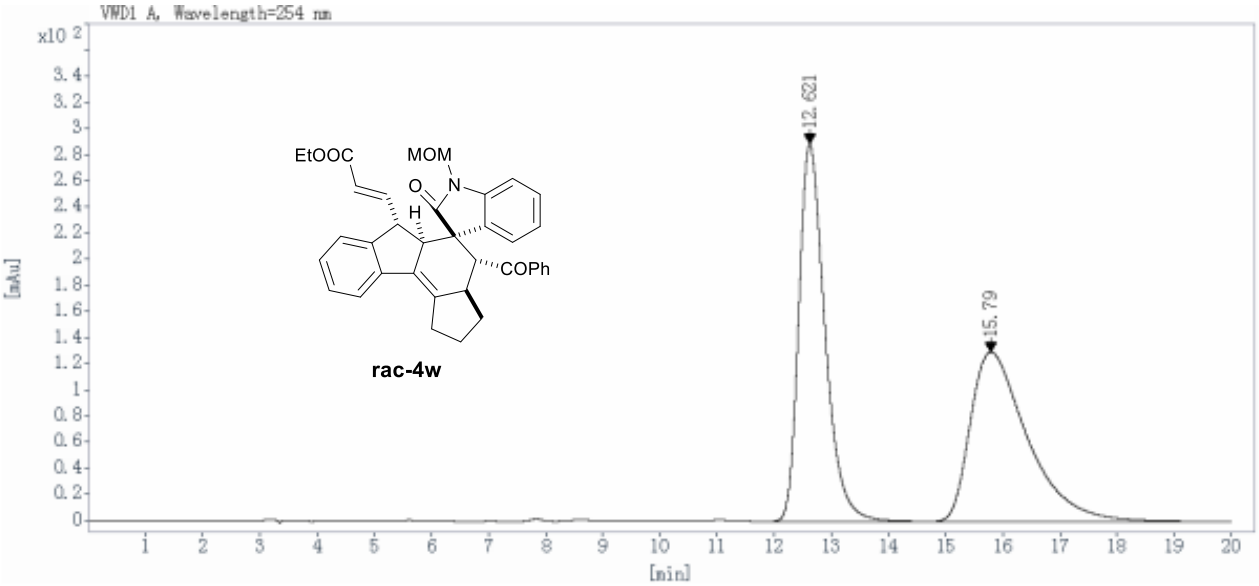




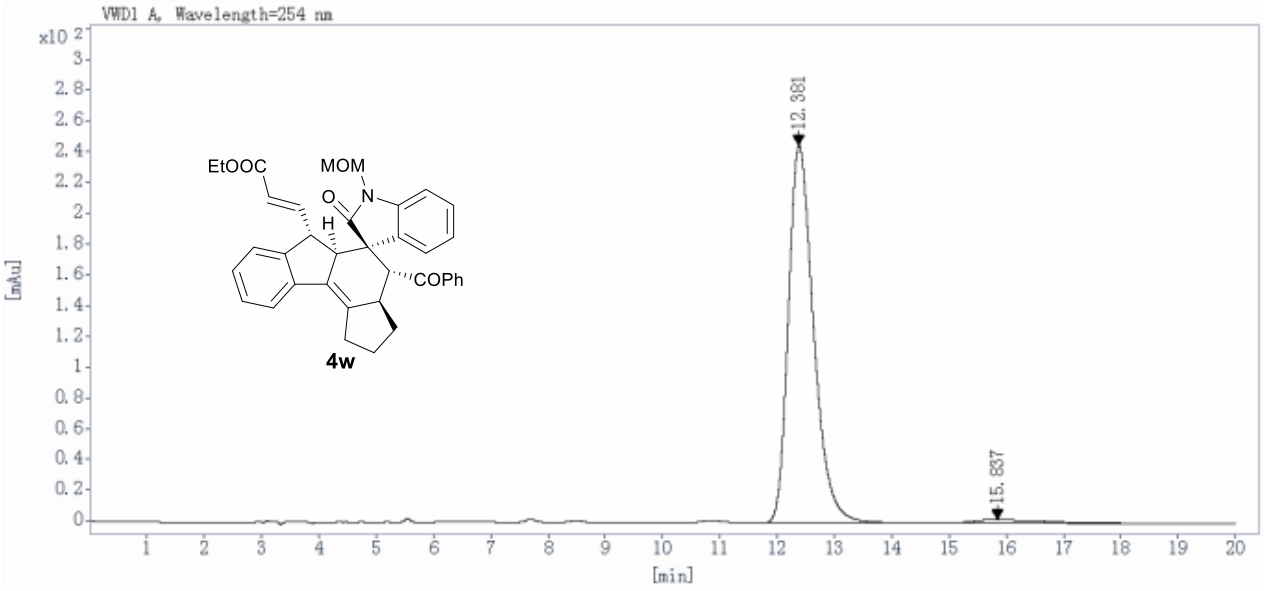
4w

^{13}C NMR (150 MHz, $CDCl_3$)

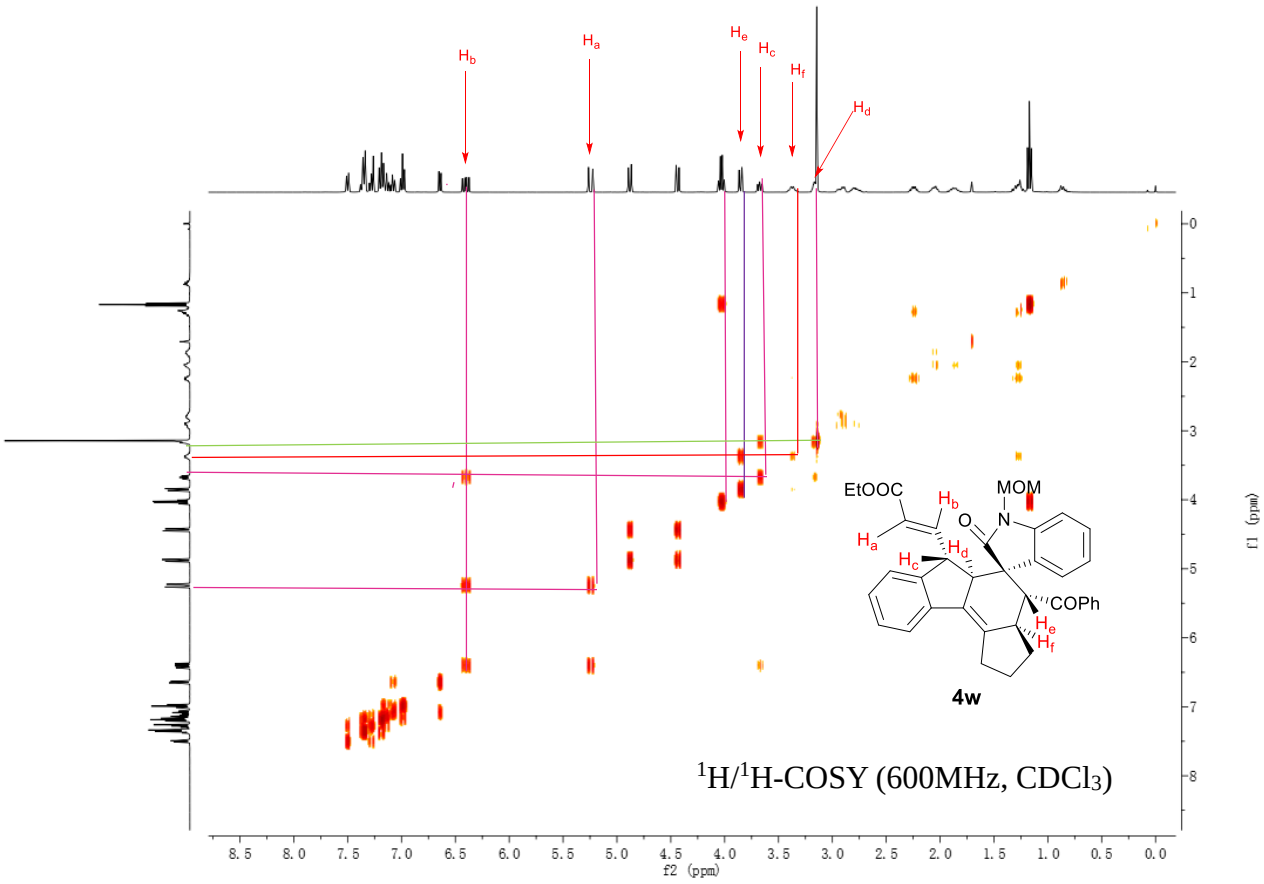




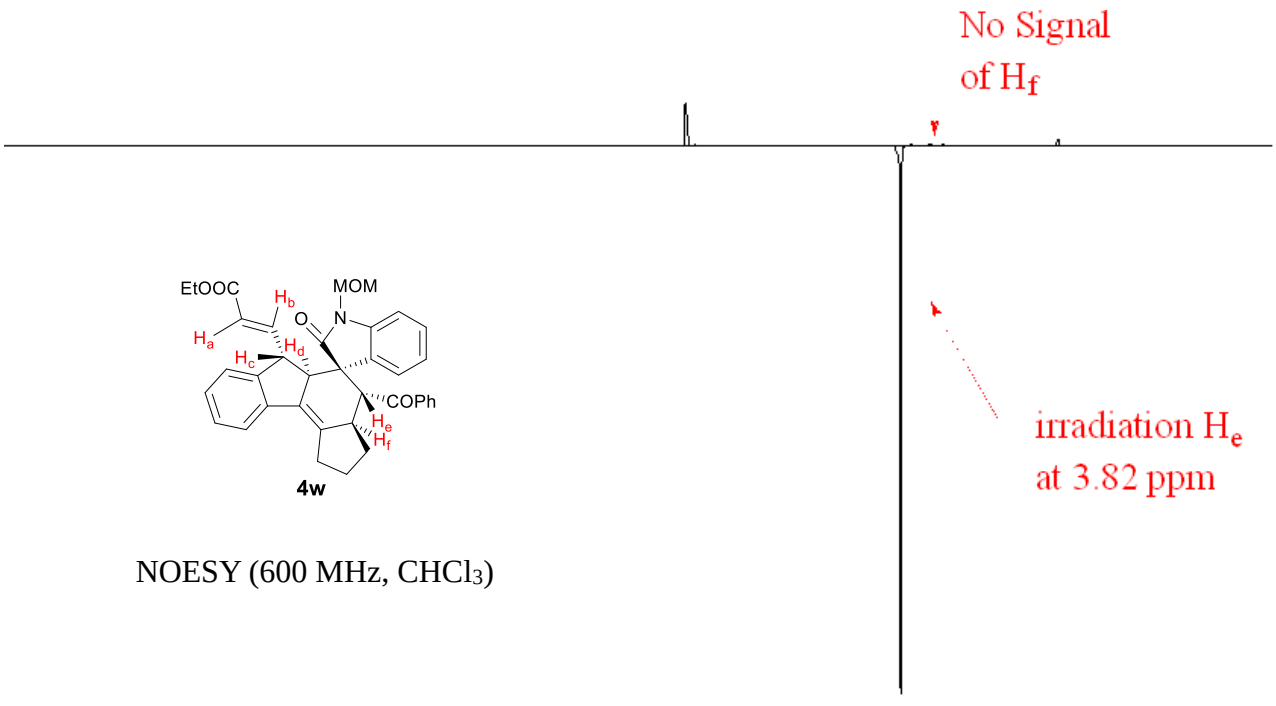
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.621	BB	0.49	288.8666	9202.3896	50.3087
15.790	BB	1.06	129.8929	9089.4590	49.6913



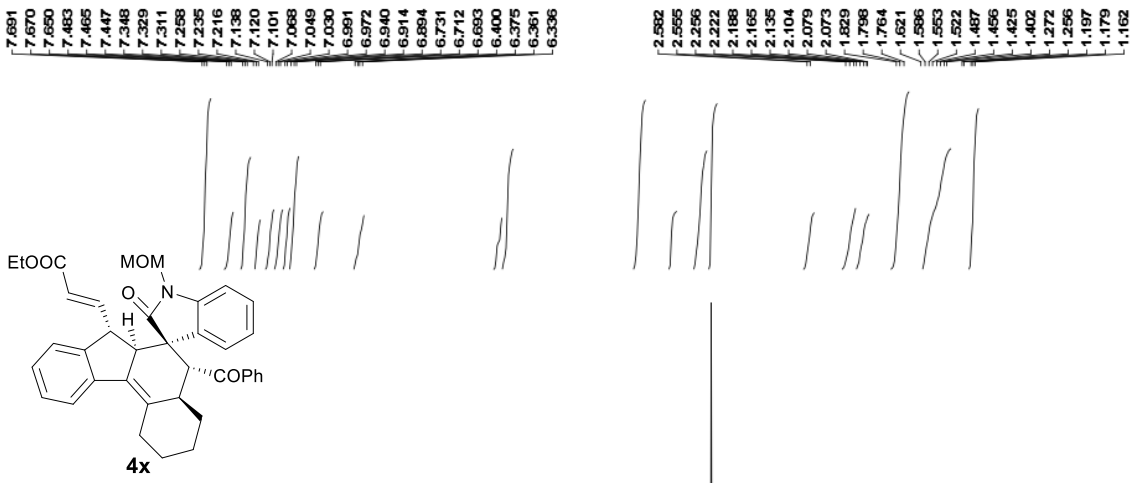
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
12.381	BB	0.47	245.2301	7514.2607	97.4887
15.837	BB	1.04	2.3553	193.5698	2.5113



$^1H/^1H$-COSY (600MHz, $CDCl_3$)

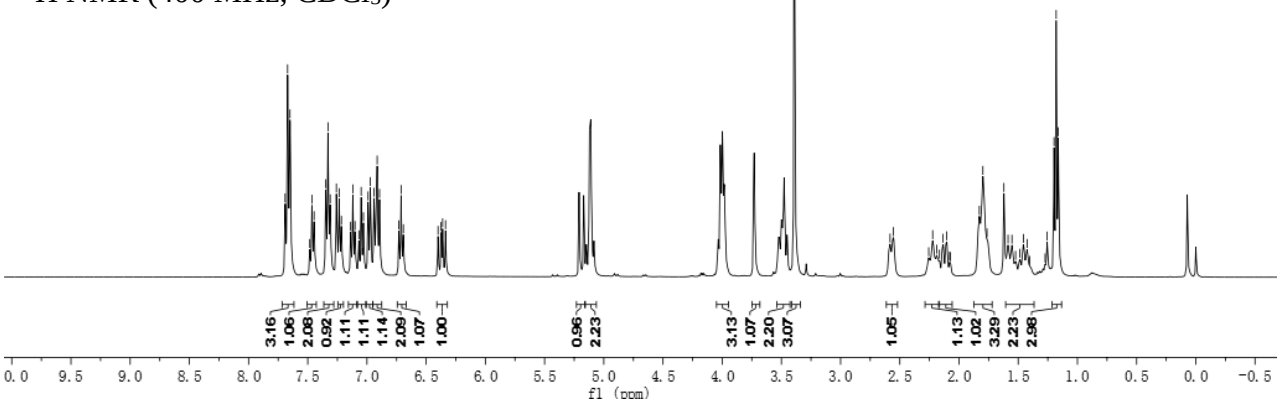


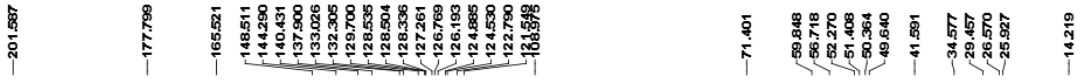
NOESY (600 MHz, $CHCl_3$)

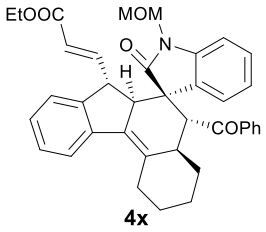


4x

^{1}H NMR (400 MHz, $CDCl_3$)

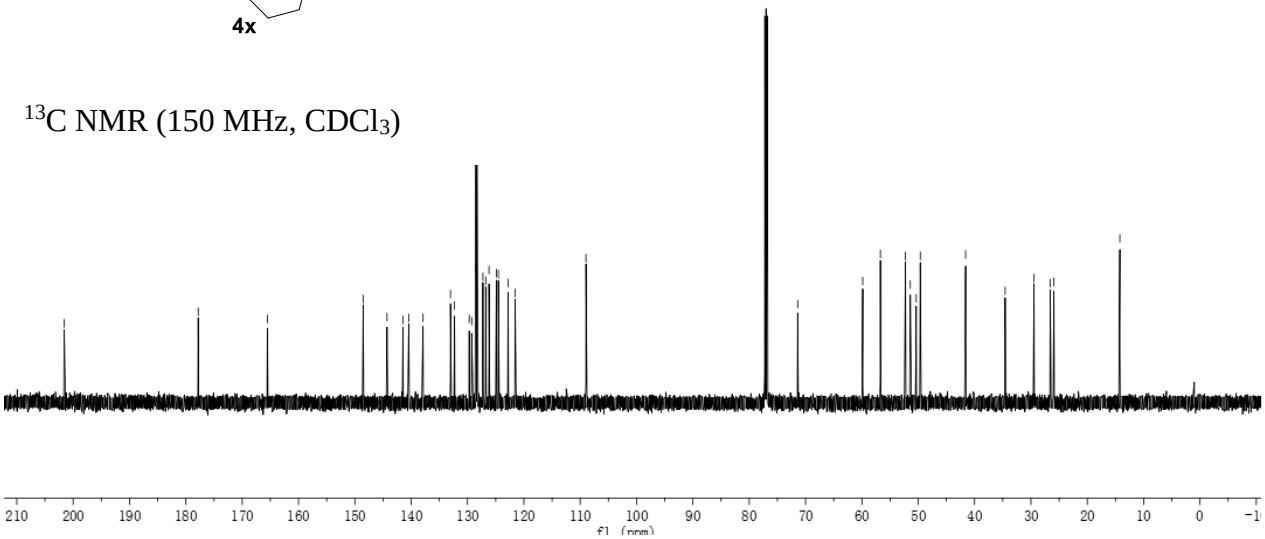


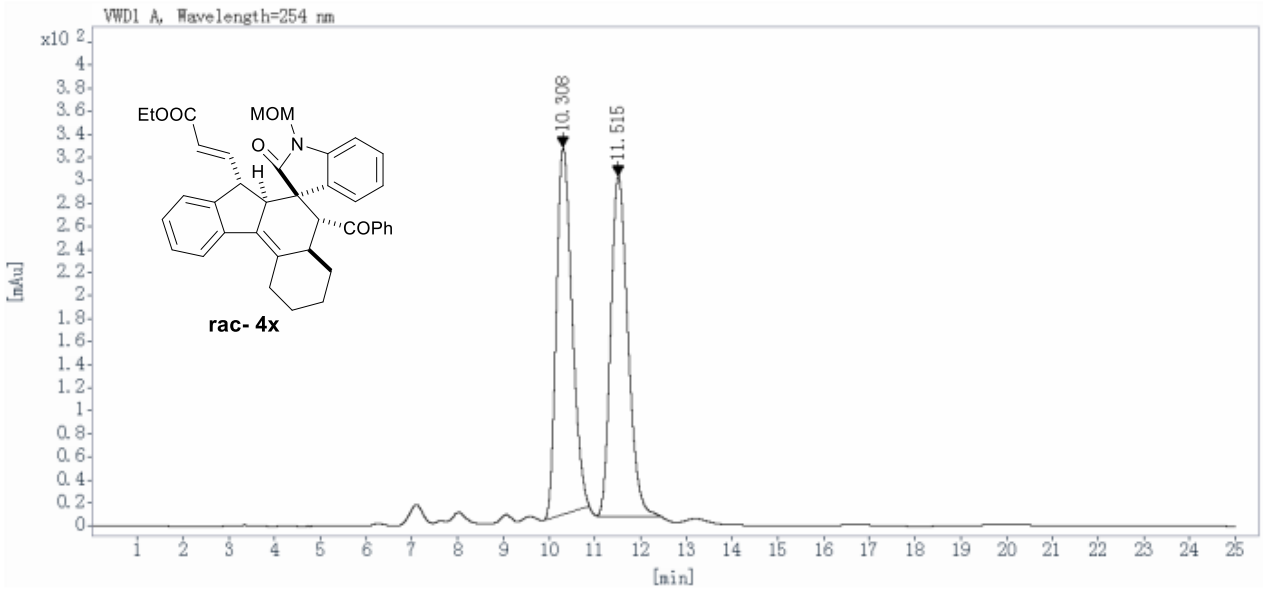




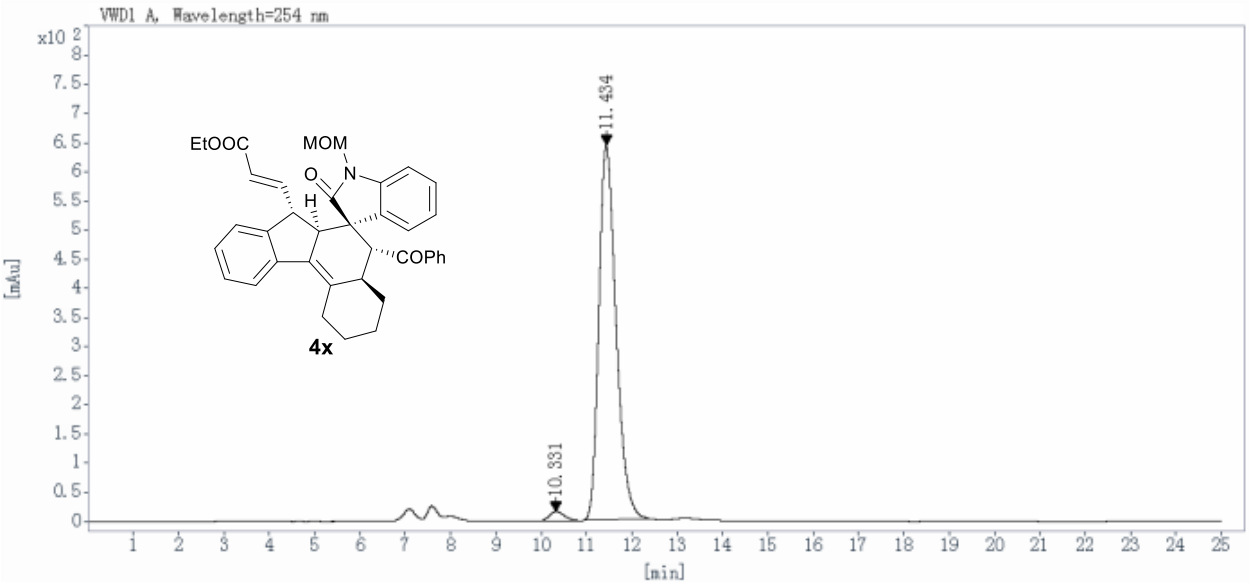
4x

^{13}C NMR (150 MHz, $CDCl_3$)

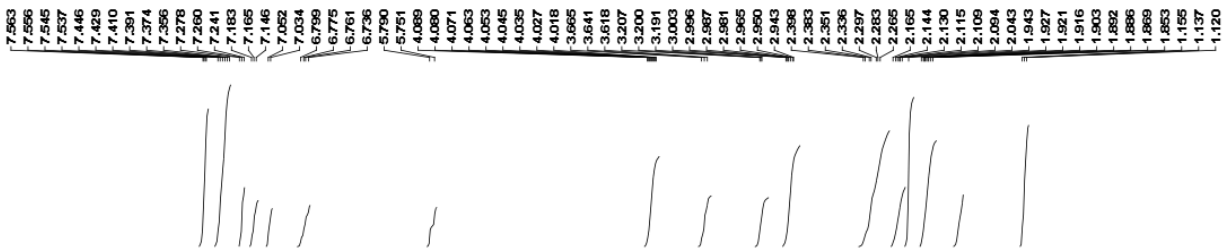


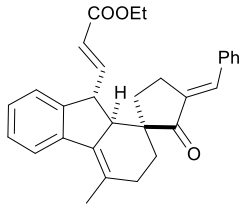


Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.308	BBA	0.37	318.6765	7581.0928	49.5645
11.515	BBA	0.40	295.5233	7714.3203	50.4355



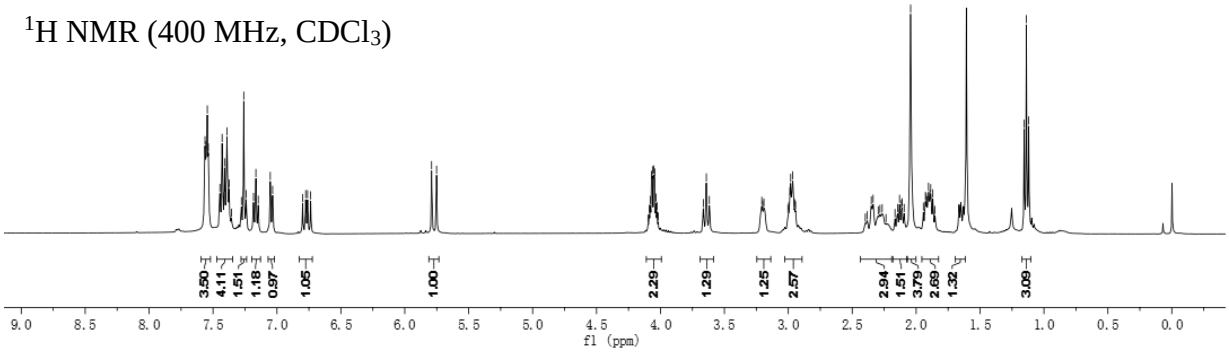
Ret Time [min]	Peak Type	Width [min]	Height [mAU]	Area [mAU*s]	Area [%]
10.331	BBA	0.36	16.5310	385.1845	2.2244
11.434	BBA	0.41	642.1149	16931.0605	97.7756

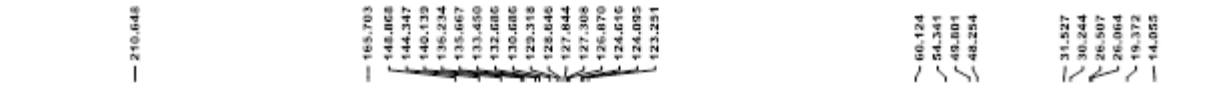


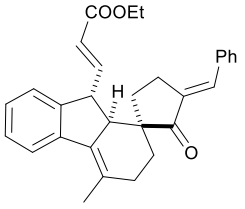


6

^{1}H NMR (400 MHz, $CDCl_3$)

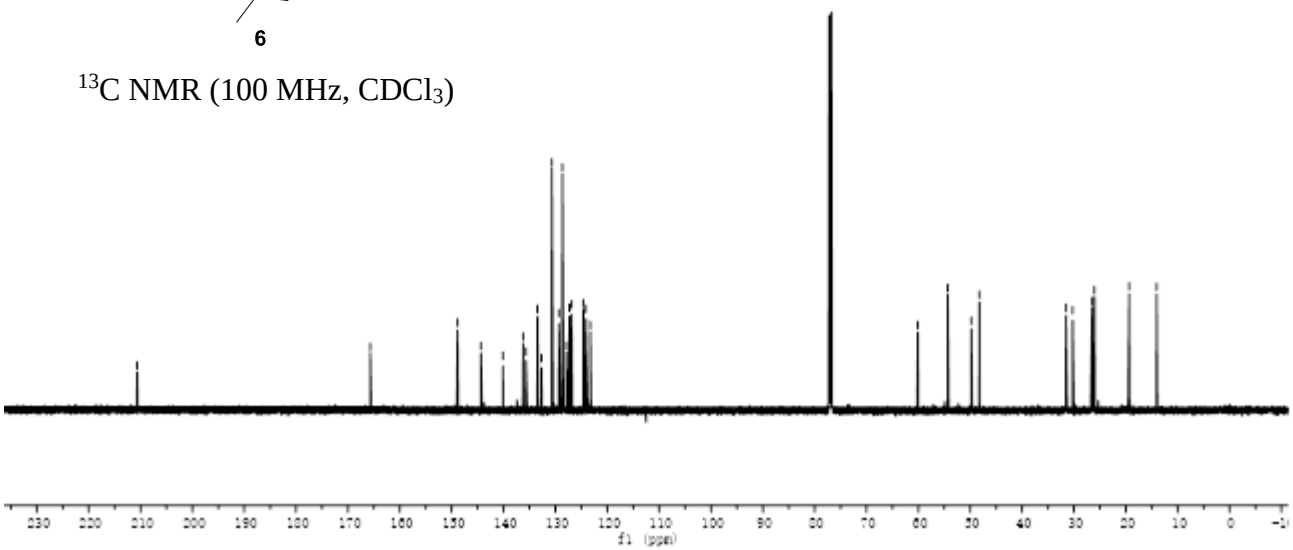


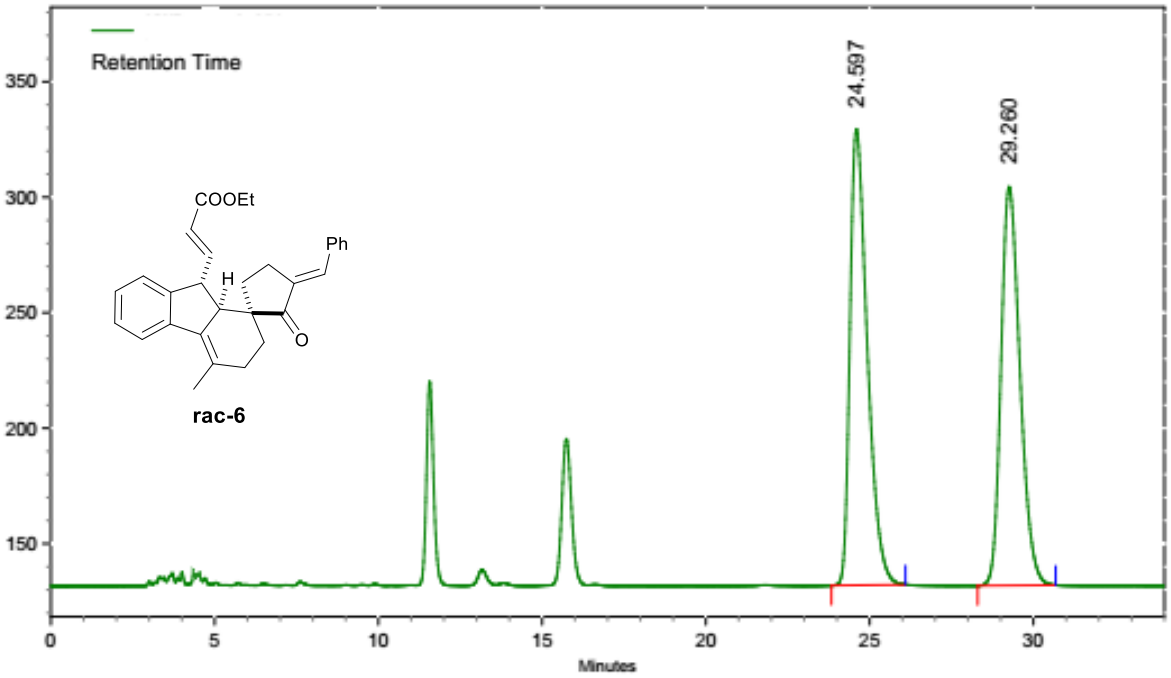




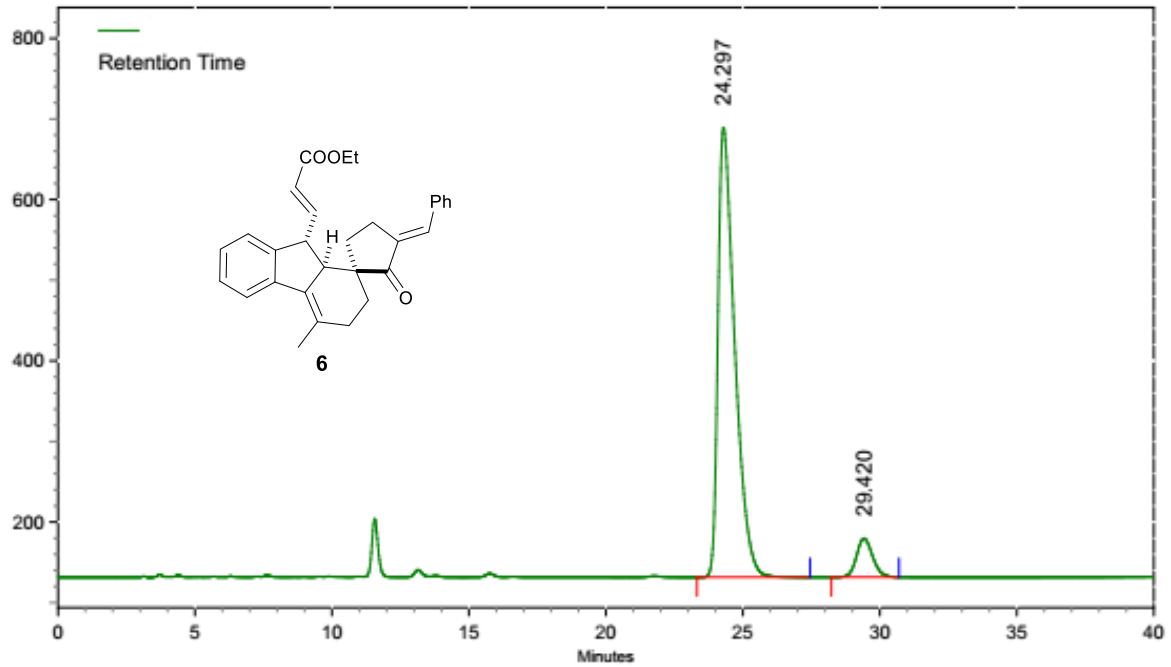
6

^{13}C NMR (100 MHz, $CDCl_3$)

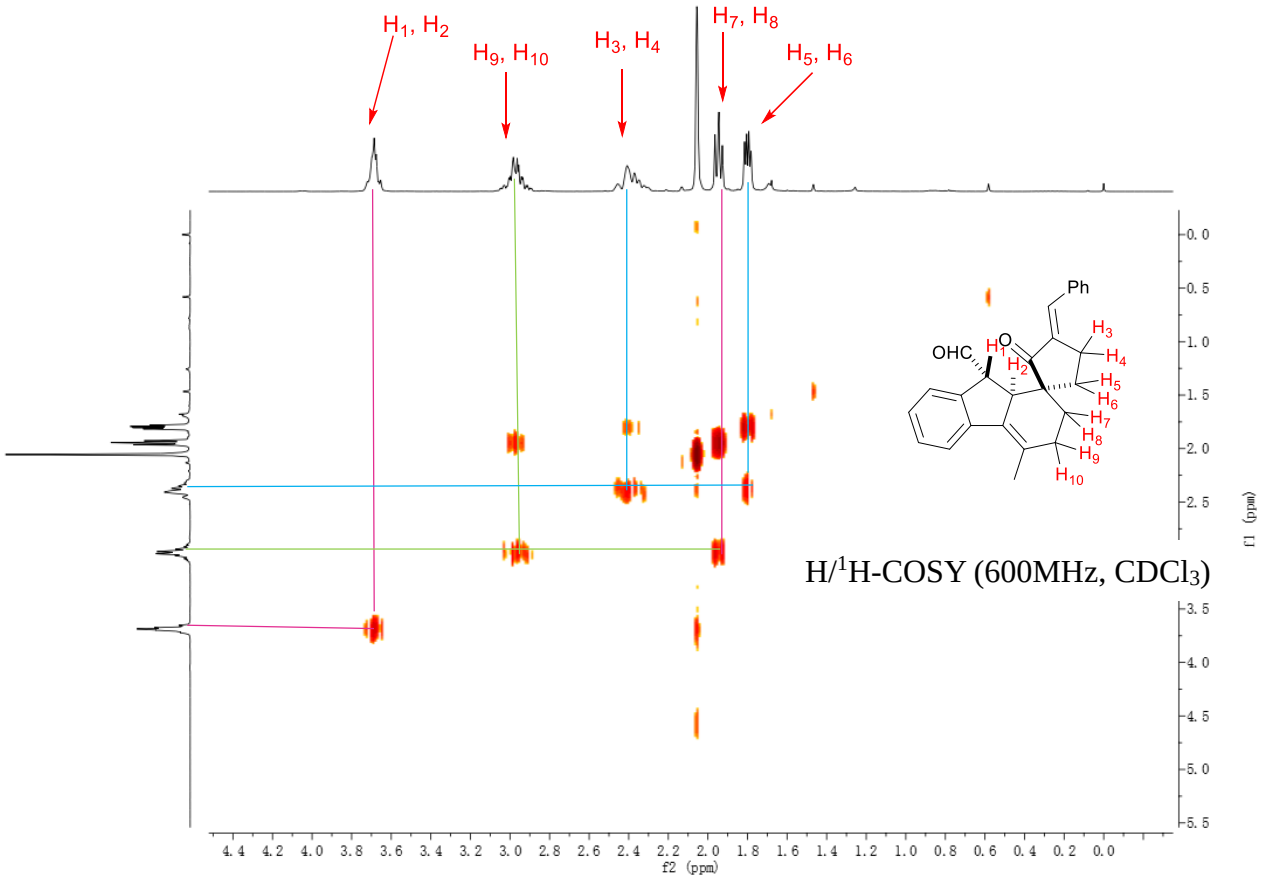




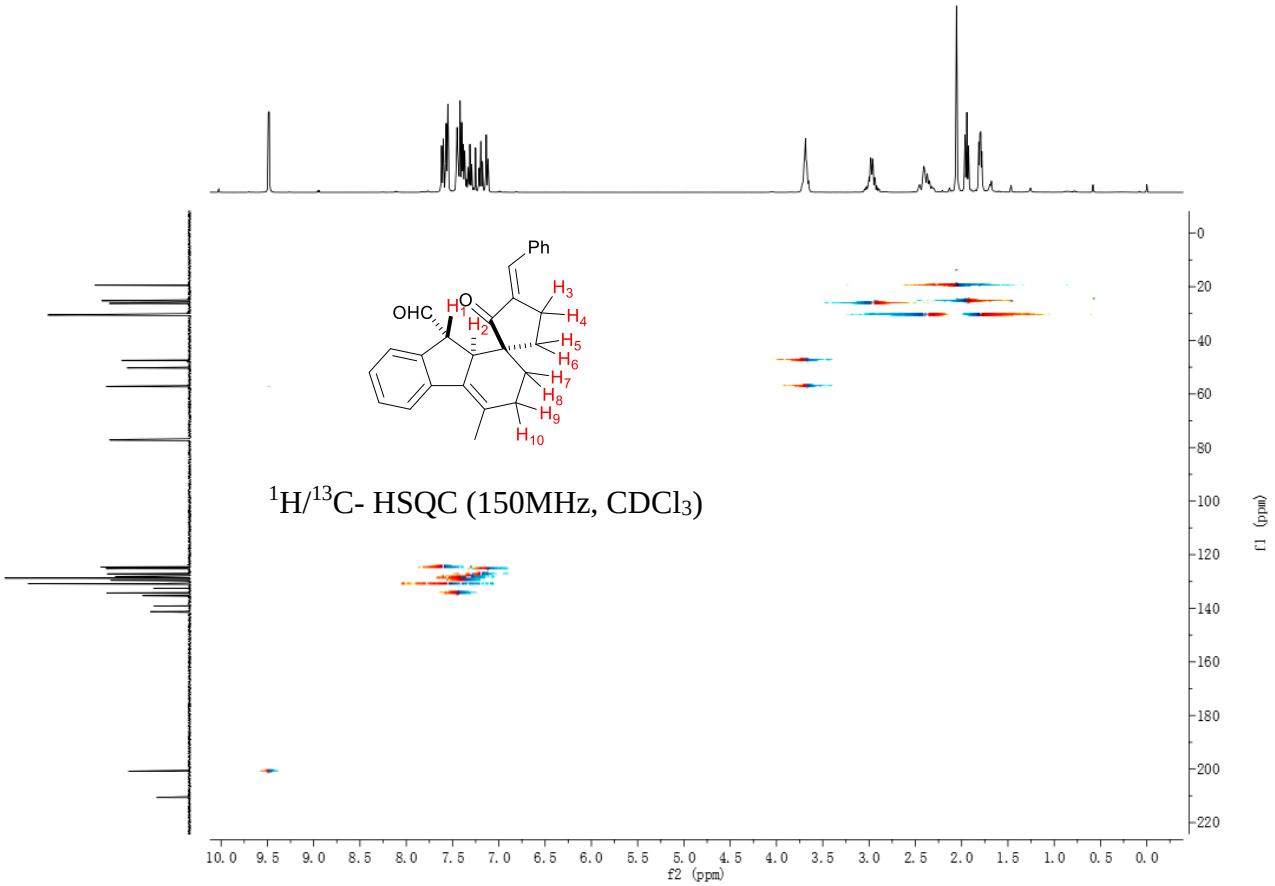
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	24.597	2.260	3314362	122061654	51.0861
2	29.260	2.380	2896191	116871753	48.9139



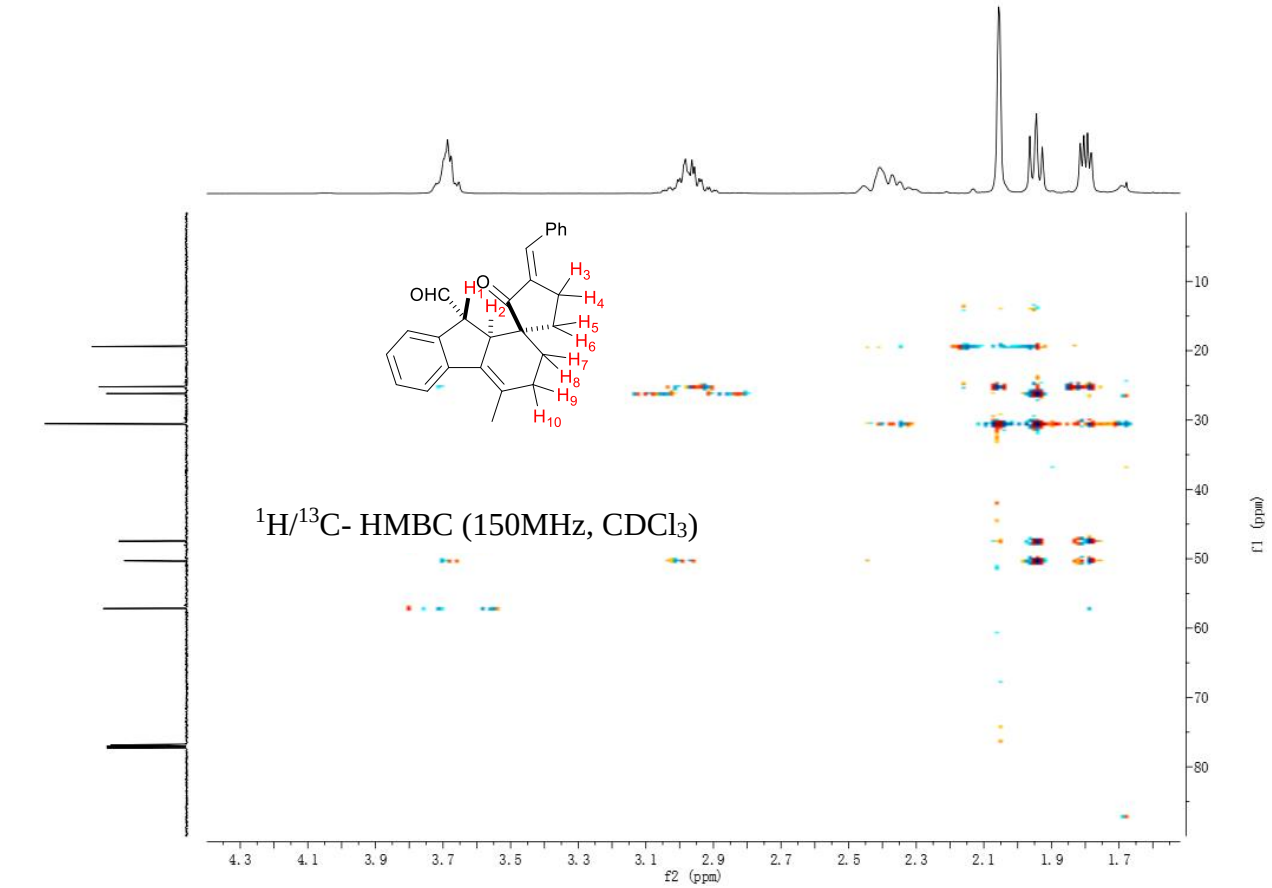
Peak No.	Ret Time	Width	Height	Area	Area [%]
1	24.297	4.127	9358994	397328578	92.3585
2	29.420	2.470	807043	32873792	7.6415



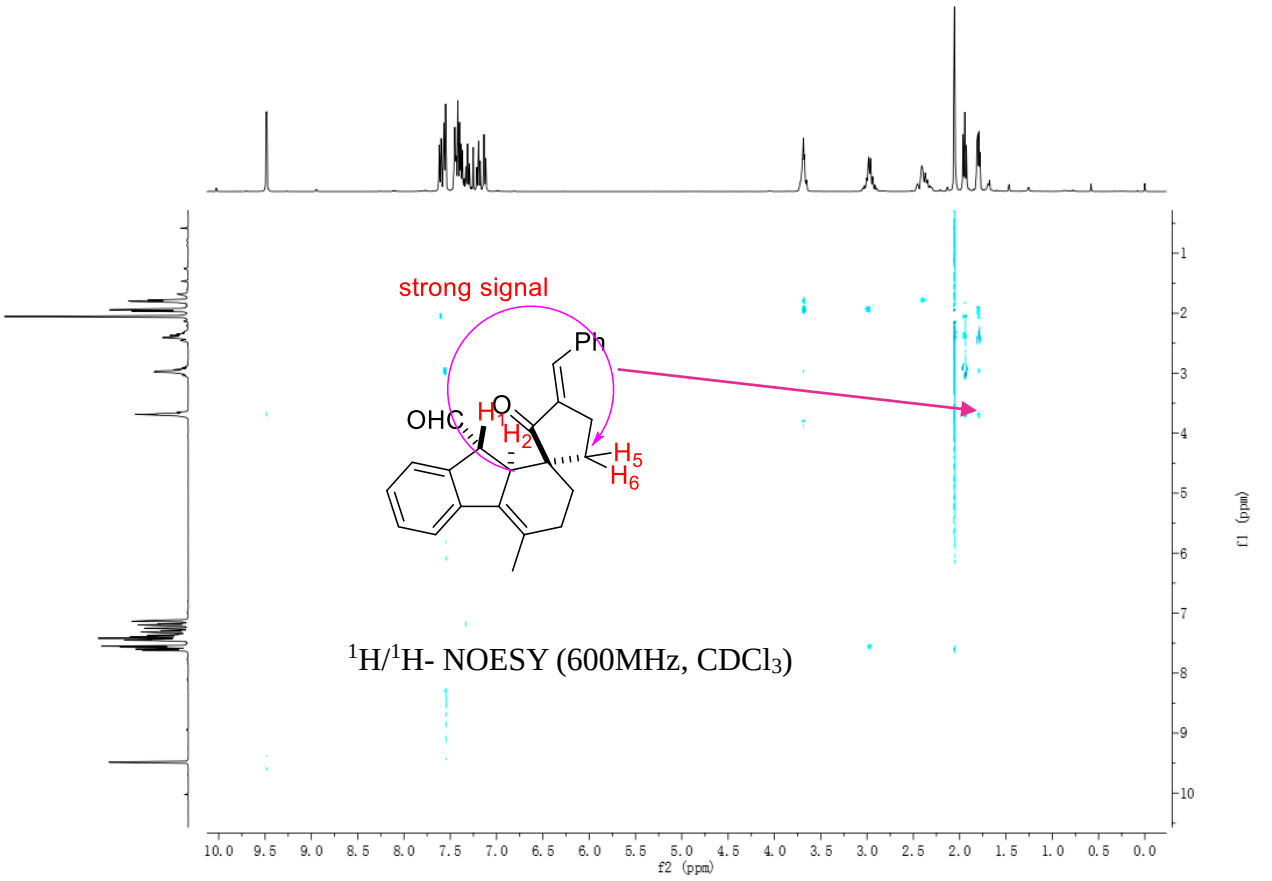
H/^{1}H-COSY (600MHz, $CDCl_3$)



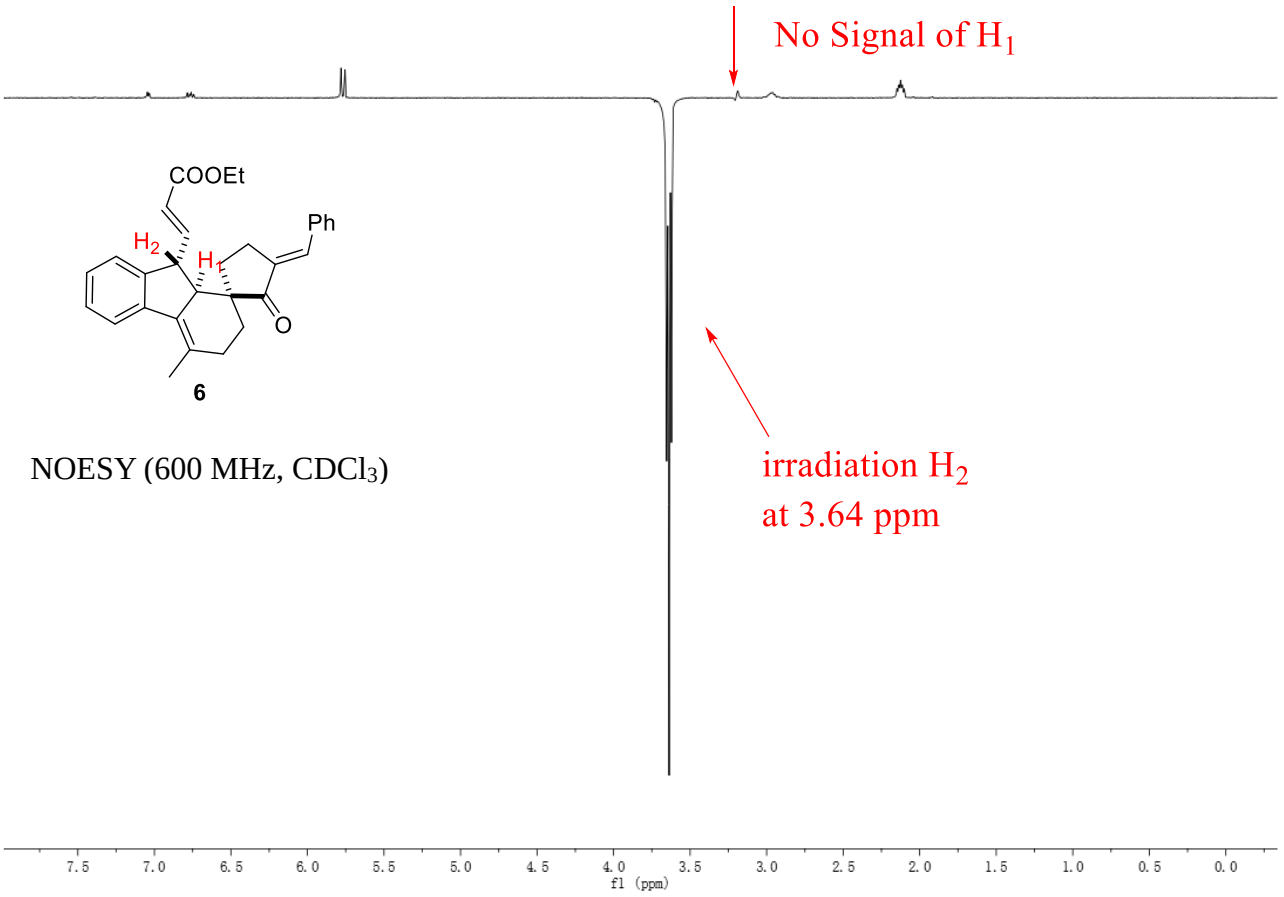
^{1}H/^{13}C- HSQC (150MHz, $CDCl_3$)



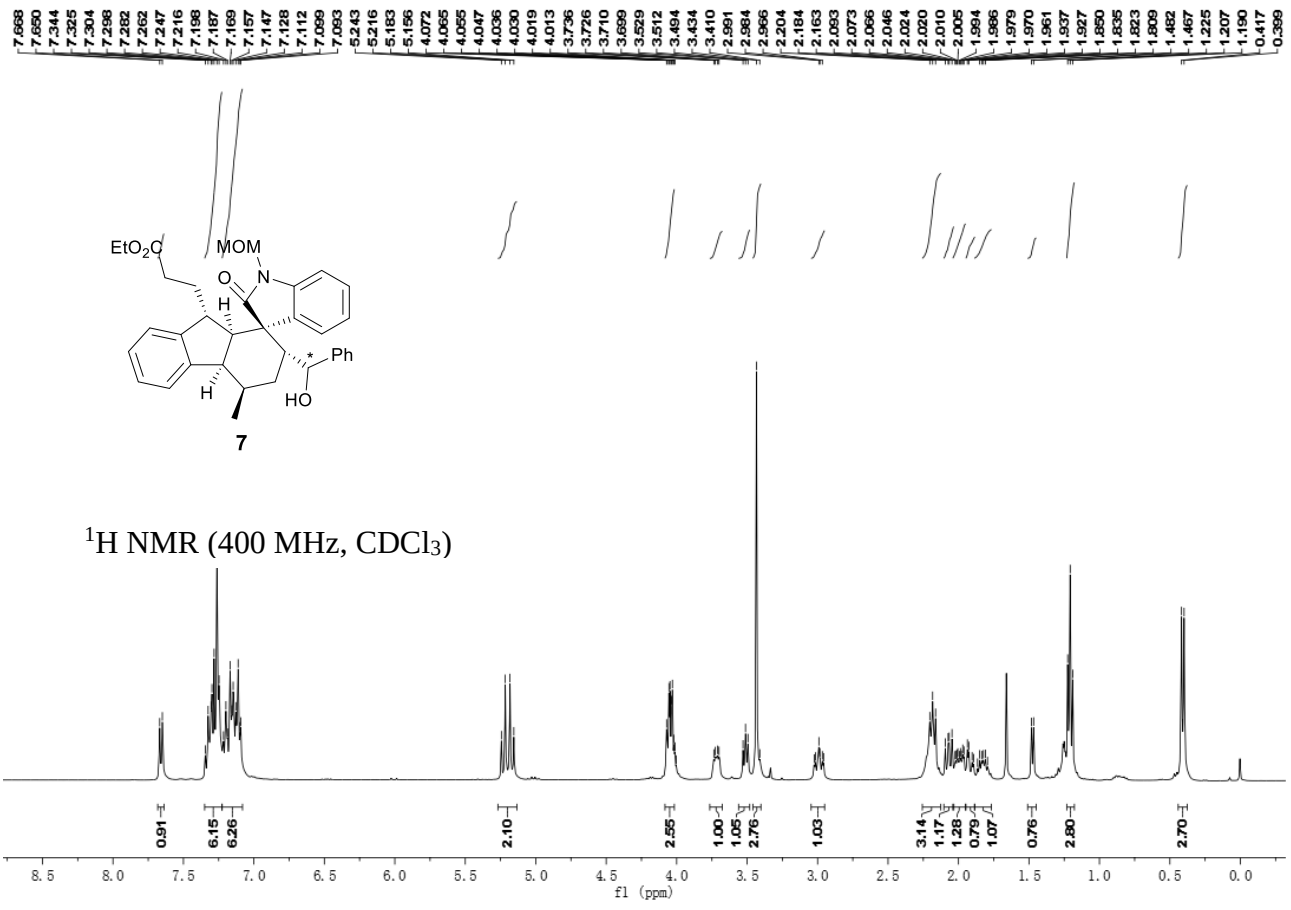
$^{1}H/^{13}C$- HMBC (150MHz, $CDCl_3$)



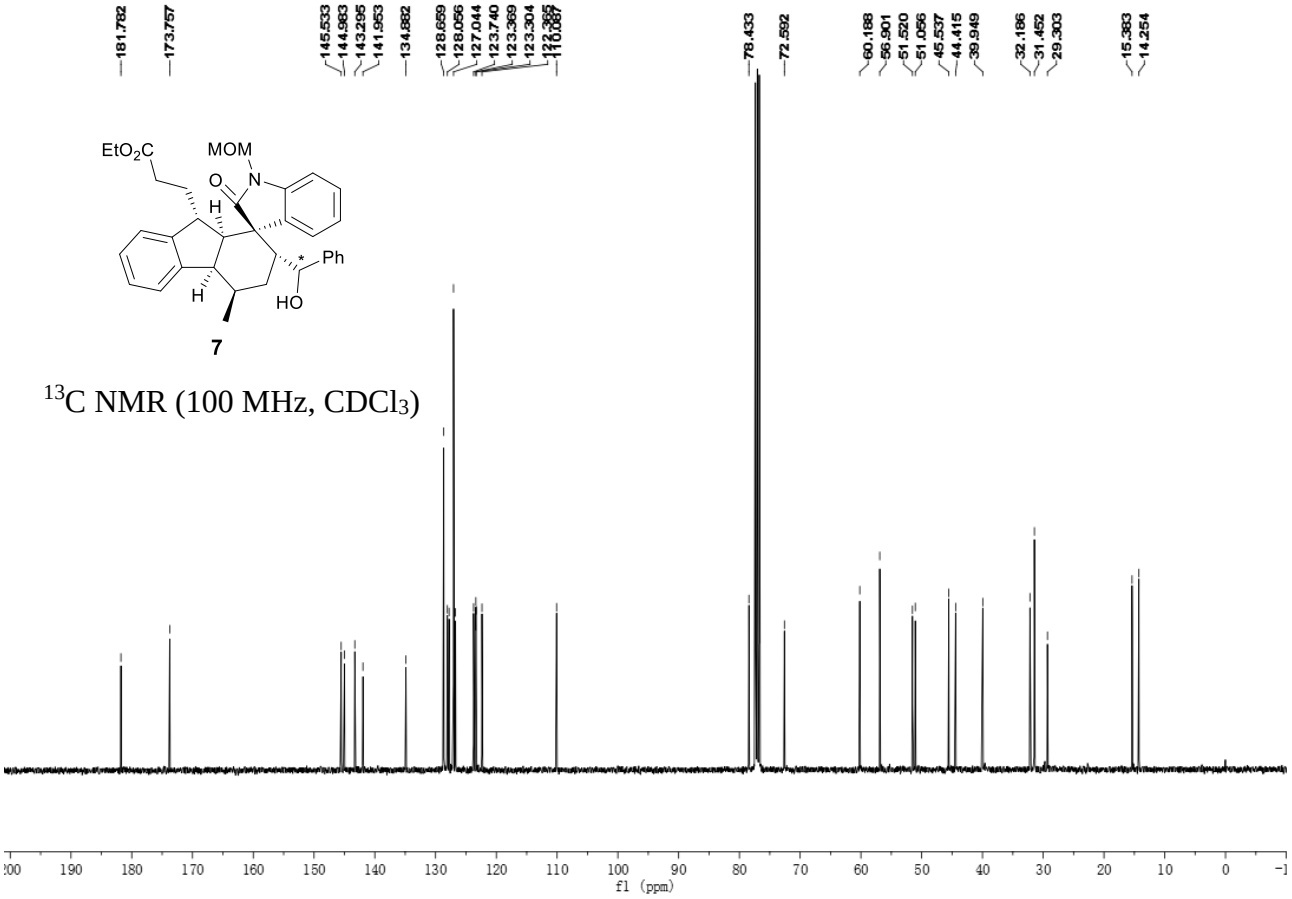
$^{1}H/^{1}H$- NOESY (600MHz, $CDCl_3$)

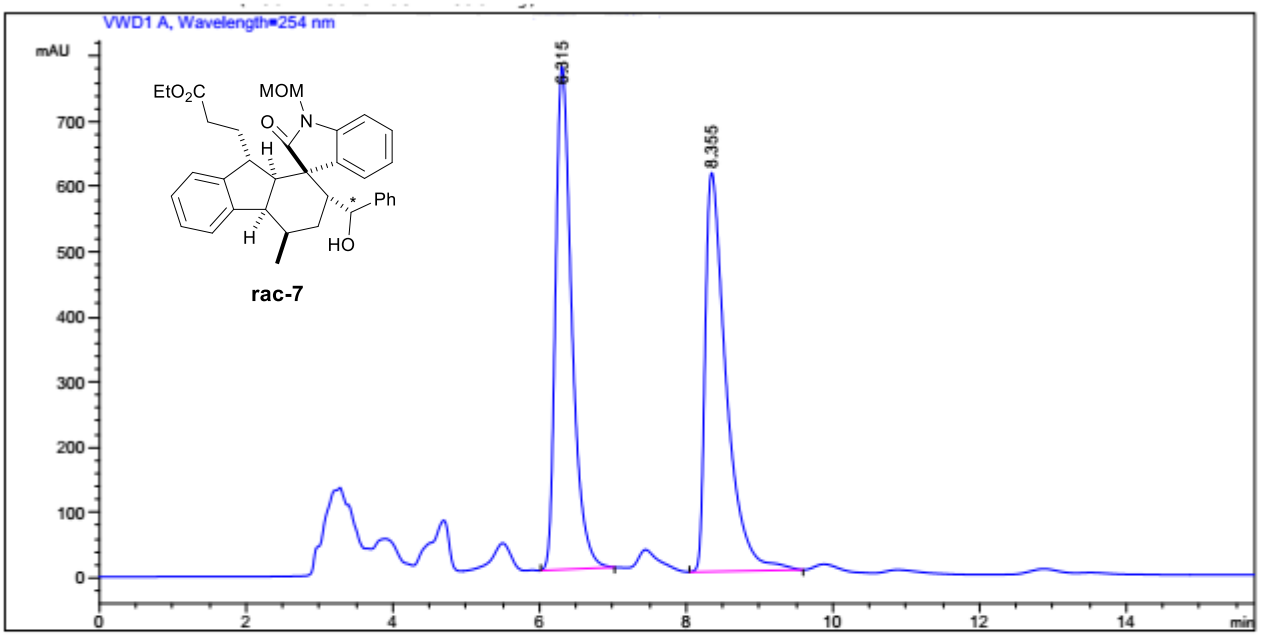


NOESY (600 MHz, $CDCl_3$)

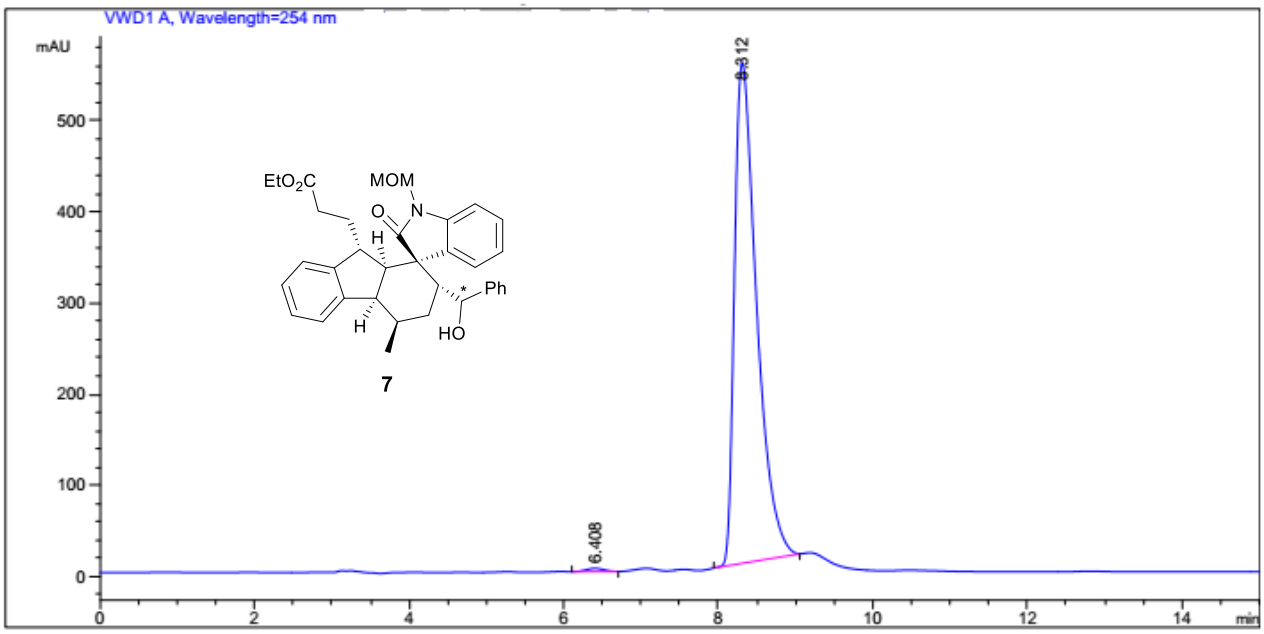


^1H NMR (400 MHz, $CDCl_3$)





Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.315	BBA	0.2352	1.18909e4	771.19019	49.4617
2	8.355	BBA	0.2956	1.21497e4	612.11926	50.5383



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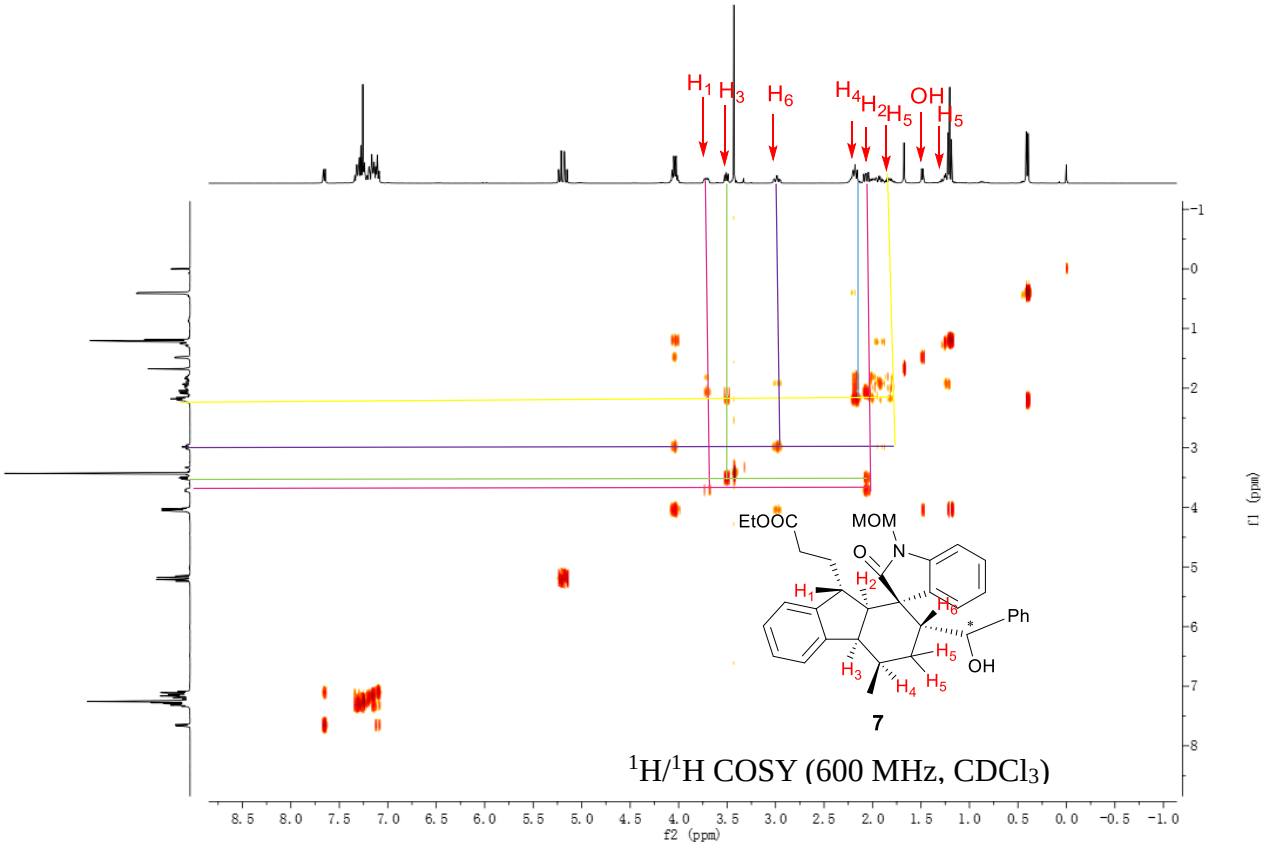
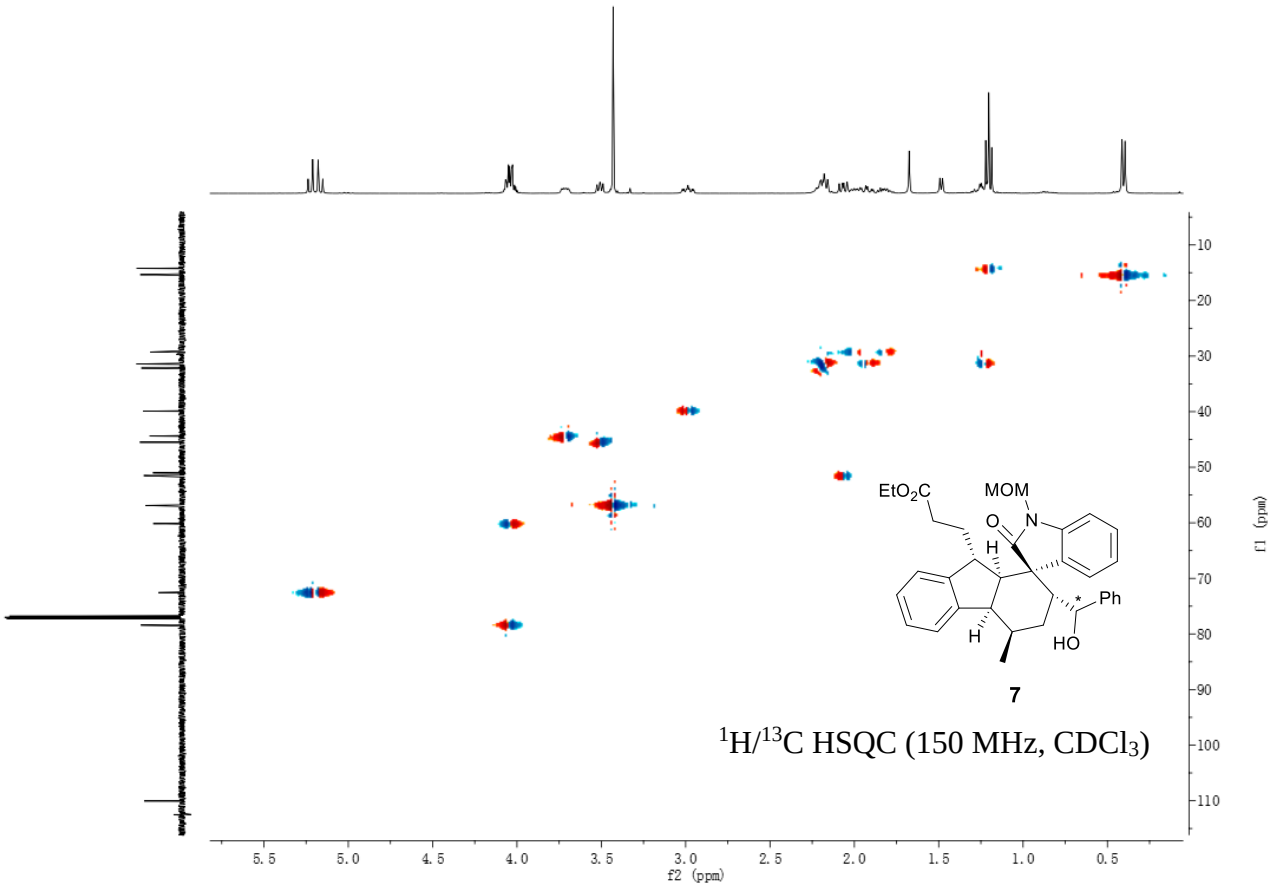
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.408	BB	0.2513	55.07197	3.48640	0.5015
2	8.312	BB	0.3020	1.09266e4	549.11676	99.4985

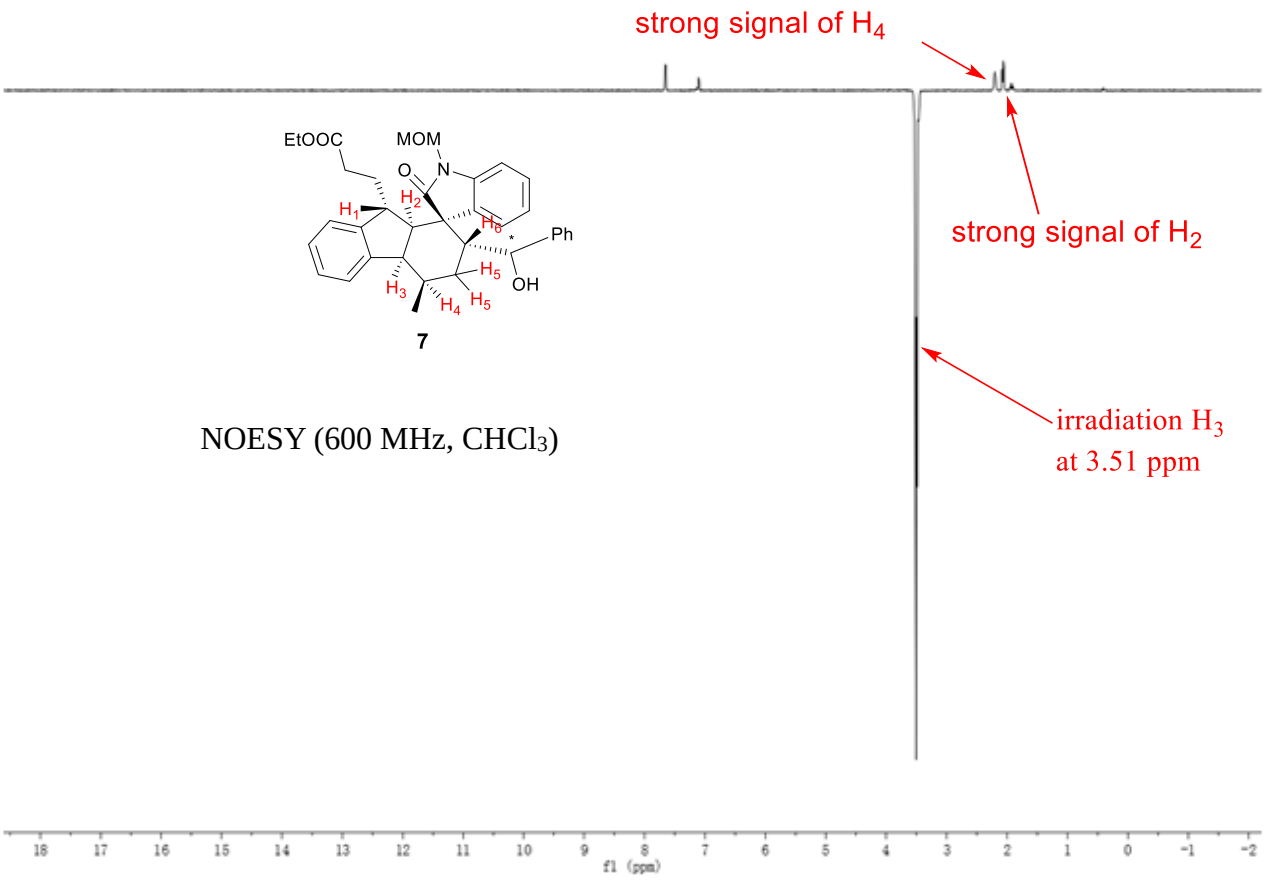


7

$^1H/^1H$ COSY (600 MHz, $CDCl_3$)



$^{1}H/^{13}C$ HSQC (150 MHz, $CDCl_3$)



NOESY (600 MHz, $CHCl_3$)