

Supplementary Information for

Redox-Neutral Synthesis of π -Allylcobalt Complexes from Alkenes for Aldehyde Allylation via Photoredox Catalysis

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KEYWORDS: cobalt, photoredox catalysis, alkene, allylation, alcohol

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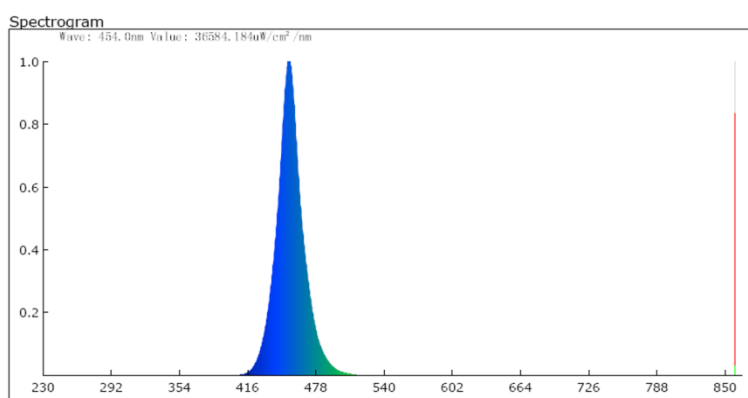
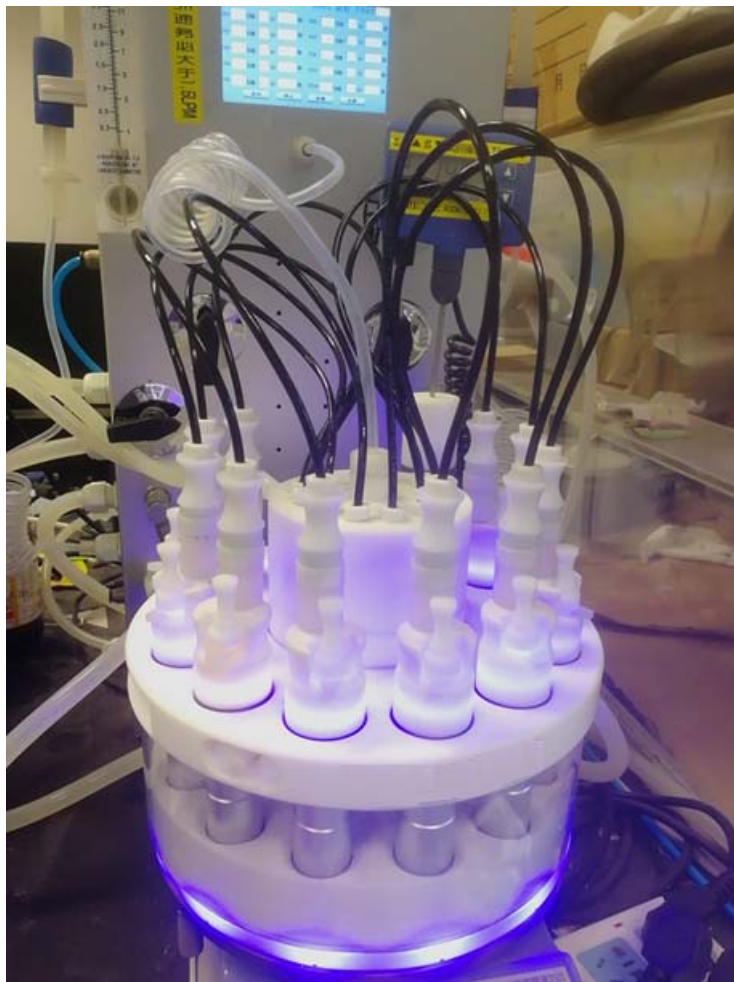
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S1 General Information

Unless otherwise noted, all reactions of substrates preparation were conducted in flame – dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP – TEC – 1020L) with 10W LED. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker 400M spectrometer. Chemical shifts in ^1H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual CDCl_3 (7.26 ppm). Data for ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of CDCl_3 (77.00 ppm). ESI mass spectra were obtained from an HPLC – Q – Tof mass spectrometer using acetonitrile as the mobile phase. UV – vis spectra were collected on an HP 8453 spectrometer. The fluorescence emission spectra were collected on an Edinburgh FS920.

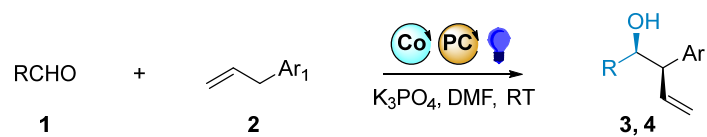
S2 Picture of Reaction Set – Up

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP – TEC – 1020L).



Emission spectra of the 10 W blue LED lamp (maximum emission at $\lambda = 455$ nm). Wavelength: 450 nm-455 nm Quartz glass was used as a reaction vessel. Distance between the light source and quartz tube was approximately 0.5 cm and no filter was used for the reaction.

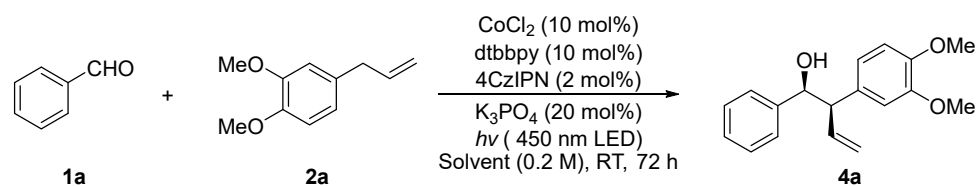
S3 General Procedure of Allylation



Following the standard procedure, a solution of **1** (0.5 mmol, 1 eq.), alkene **2** (1.5 mmol, 3 eq.), CoCl₂ (10 mol%), dtbbpy (10 mol%), K₃PO₄ (20 mol%) and 4CzIPN (2 mol%) in DMF (0.2 M). The reaction mixture was stirred at room temperature with irradiation of 10 W 450 nm LED for 72 h. After completing, the reaction mixture was concentrated under vacuum rotary evaporation. The obtained residue crude reaction mixture was purified by column chromatography on Silica gel (PE/EtOAc) to afford the corresponding compounds. The ¹H NMR analysis of the crude product was calculated using dimethyl terephthalate as the internal standard.

S4 Reaction Optimizations

Table S1. Screening of solvent ^{a, b}



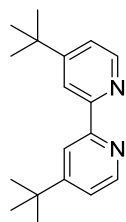
Entry	Solvent	Yield (%)	d.r.
1	DMF	91	8:1
2	THF	trace	-
3	DCM	7	1.6:1
4	CH_3CN	16	5:1
5	DMSO	20	1.2:1
6	DCE	12	4:1
7	CH_3OH	trace	-

^a The reaction of aldehyde **1a** (53.1 mg) was conducted on 0.2 mmol (0.2 M) scale. ^b Yields were determined by $^1\text{H-NMR}$ spectroscopy of the crude mixture with dimethyl terephthalate as internal standard.

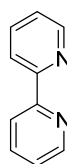
Table S2. Screen of ligand ^{a, b}

Entry	Ligand	Yield (%)	d.r.
1	-	trace	-
2	L1	91	8:1
3	L2	89	8:1
4	L3	trace	-
5	L4	trace	-
6	L8	trace	-
7	L6	trace	-
8	L7	trace	-
9	L8	trace	-
10	L9	trace	-

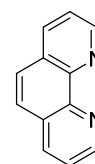
^a The reaction of aldehyde **1a** (53.1 mg) was conducted on 0.2 mmol (0.2 M) scale. ^b Yields were determined by ¹H-NMR spectroscopy of the crude mixture with dimethyl terephthalate as internal standard.



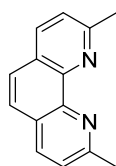
L1



L2



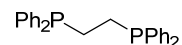
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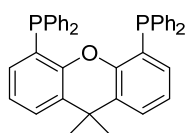
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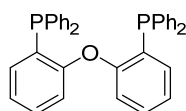
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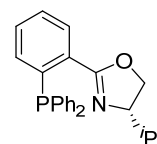
L6



XantPhos **L7**

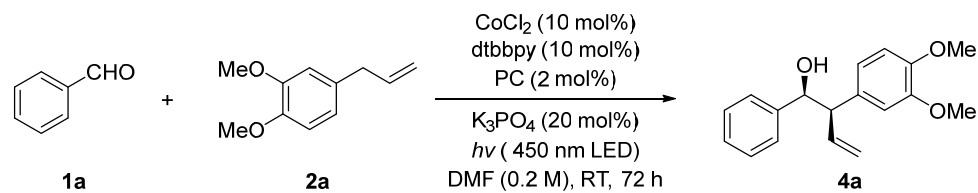


DPEPhos **L8**



L9

Table S3. Screening of photocatalyst ^{a, b}



Entry	PC	Yield (%)	d.r.
1	4CzIPN	91	8:1
2	Ru-1	trace	-
3	Ir-1	48	4:1
4	Ir-2	74	6:1

^a The reaction of aldehyde **1a** (53.1 mg) was conducted on 0.2 mmol (0.2 M) scale. ^b Yields were determined by ¹H-NMR spectroscopy of the crude mixture with dimethyl terephthalate as internal standard.

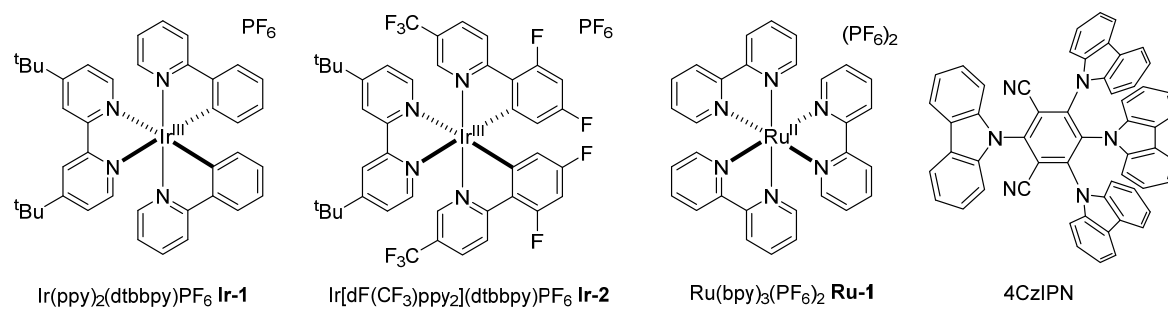
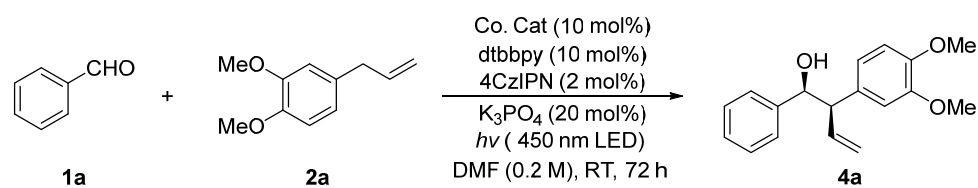
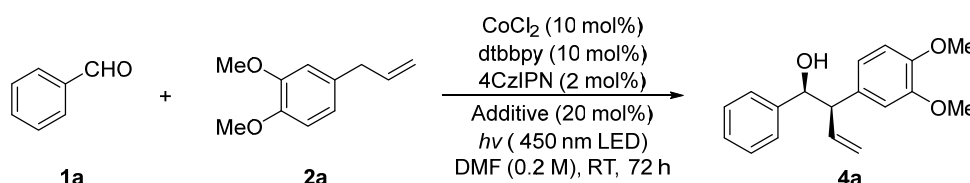


Table S4. Screen of various cobalt salt ^{a, b}

Entry	Cobalt Salt	Yield (%)	d.r.
1	-	15	1:1
2	CoCl ₂	91	8:1
3	CoBr ₂	76	5:1
4	CoSO ₄ •H ₂ O	0	-
5	Co(OAc) ₂ •4H ₂ O	0	-
6	Co(NO ₃) ₂ •6H ₂ O	0	-
7	Co(acac) ₂	0	-
8	Co(acac) ₃	0	-

^a The reaction of aldehyde **1a** (53.1 mg) was conducted on 0.2 mmol (0.2 M) scale. ^b Yields were determined by ¹H-NMR spectroscopy of the crude mixture with dimethyl terephthalate as internal standard.

Table S5. Screen of additive ^{a, b}



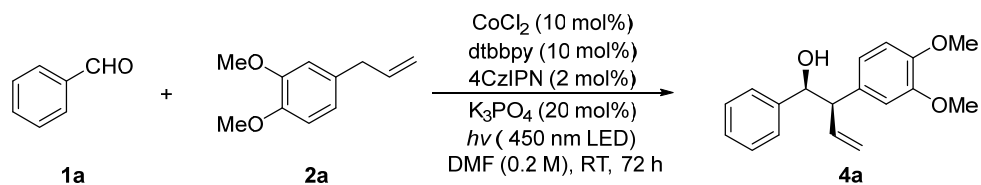
Entry	Additive	Yield (%)	d.r.
1	-	60	4:1
2	2,4,6-collidine	81	9:1
3	K ₂ CO ₃	62	7:1
4	KHCO ₃	85	8:1
5	K ₃ PO ₄	91	8:1
6	Li ₂ CO ₃	88	9:1

^a The reaction of aldehyde **1a** (53.1 mg) was conducted on 0.2 mmol (0.2 M) scale. ^b Yields were determined by ¹H-NMR spectroscopy of the crude mixture with dimethyl terephthalate as internal standard.

S5 Condition-based Sensitivity Screen

Reference: *Angew. Chem. Int. Ed.* **2019**, *58*, 8572-8576.

Procedure and results of sensitivity assessment of reaction:



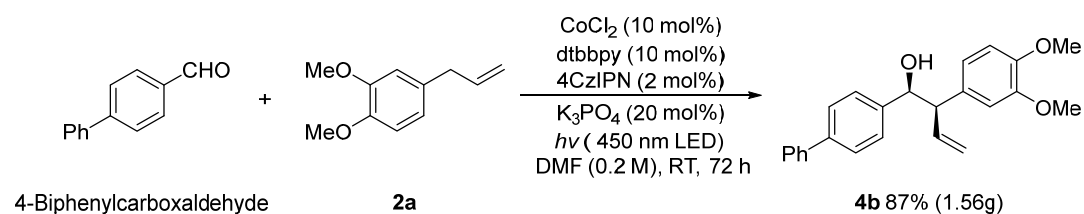
Standard conditions: n (**1a**) = 0.5 mmol (53.1 mg), c = 0.2 M, V = 2.5 mL, inert atmosphere, T = 25 °C, I = 10 W

Stock solution: n (**1a**) = 0.5 mmol (53.1 mg), c = 0.2 M, V = 2.25 mL, benzaldehyde (**1a**): 53.0 mg, 4-allyl-1,2-dimethoxybenzene (**2a**): 267.3 mg, 4CzIPN: 7.9 mg, CoCl_2 : 6.5 mg, dtbbpy: 13.4 mg, K_3PO_4 : 21.2 mg, DMF: 2.25 mL

Table S6: Description of experiments included in the sensitivity assessment

Entry	Experiment	Preparation
1	High c	2.25 mL stock sol.
2	Low c	2.25 mL stock sol. + 0.5 mL DMF
3	High H ₂ O	2.25 mL stock sol. + 0.25 mL DMF + 25 μL H ₂ O
4	Low O ₂	2.25 mL stock sol. + 0.25 mL DMF + degas
5	High O ₂	2.25 mL stock sol. + 0.25 mL DMF + 25 mL air
6	Low T	2.25 mL stock sol. + 0.25 mL DMF, T = 15 °C
7	High T	2.25 mL stock sol. + 0.25 mL DMF, T = 35 °C
8	Low I	2.25 mL stock sol. + 0.25 mL DMF, I = 1 W
9	High I	2.25 mL stock sol. + 0.25 mL DMF, I = 10 W
10	Control	2.25 mL stock sol. + 0.25 mL DMF
11	Big scale	25 mL stock solution 'big scale'

Big scale synthesis of **4b**



In a flame-dried 100 mL Schlenk flask equipped with a magnetic stirrer bar was charged sequentially with CoCl_2 (65.0 mg, 0.5 mmol), ligand L_1 (134.0 mg, 0.5 mmol). The Schlenk flask was transferred to an argon-filled glovebox and followed by the addition of DMF (25 mL). Then the mixture was stirred at room temperature for 2 h. To the resulting mixture were added 4-Biphenylcarboxaldehyde (911.1 mg, 5 mmol), **2a** (2.67 g, 15 mmol), 4CzIPN (78.8mg, 0.1 mmol) and K_3PO_4 (212.2 mg, 1.0 mmol). Next, the resulting mixture was removed out the glovebox. At last, the reaction mixture was stirred at a distance of ~5 cm from 10 W LEDs (450 nm) at room temperature about 4 d, the crude material was purified by flash column chromatography to furnish the desired product (87%, 1.56 g).

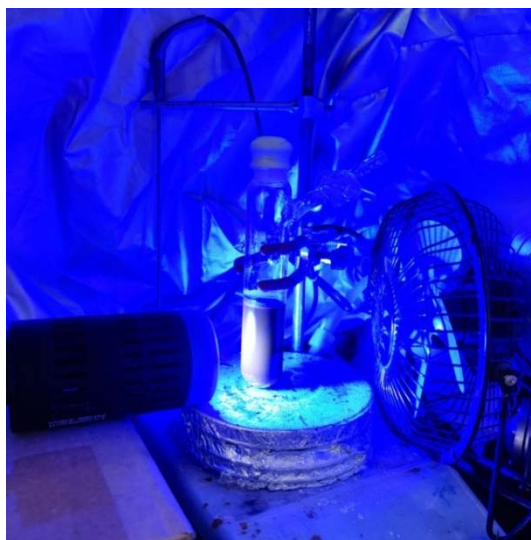
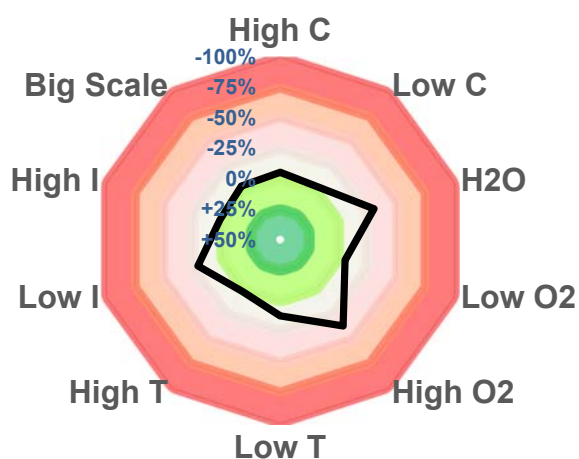


Figure S1. large scale reaction set-up

Table S7: Results of condition-based-sensitivity assessment

Number	Experiment	Yield (%)	Deviation (%)
1	High c	86	-5
2	Low c	88	-3
3	High H ₂ O	60	-31
4	Low O ₂	85	-6
5	High O ₂	53	-38
6	Low T	78	-13
7	High T	88	-3
8	Low I	70	-21
9	High I	89	-2
10	Control	91	-
11	Big scale	87	-4

**Figure S2.** Condition-based-sensitivity radar diagram

The obtained results for the condition-based sensitivity assessment showed that this reaction was sensitive to the presence of oxygen and water and low irradiation intensity. Significant inhibition of reactivity was observed when the air was injected directly into the reaction mixture (Table **S6**, entry 5).

S6 Stern-Volmer Luminescence Quenching Analysis

All samples used in the luminescence quenching-based screening studies were prepared under oxygen-free conditions. The photosensitizer 4CzIPN and potential quenchers were weighed into vials and placed inside a glovebox under a positive pressure of nitrogen. DMF was degassed by nitrogen sparging for one hour and also placed inside along with micropipettes and their tips, cuvettes, empty vials, waste containers, and parafilm. Stern-Volmer luminescence quenching studies were carried out using 1.0×10^{-5} M solution of 4CzIPN and variable concentrations of 4-allyl-1,2-dimethoxybenzene and CoCl_2 / dtbbpy in degassed and dried DMF at room temperature under a nitrogen atmosphere. The samples were prepared in screw-top 4.5 cm quartz cuvettes, equipped with PTFE stopper, and sealed with parafilm inside a nitrogen-filled glovebox. The solutions were irradiated at 440 nm and the luminescence was measured at 520 nm. The ratio of I_0/I was plotted as a function of the quencher concentration (I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed emission intensity of the photocatalyst with added quencher). The results verify that 4-allyl-1,2-dimethoxybenzene and CoCl_2 / dtbbpy quench the 4CzIPN effectively.

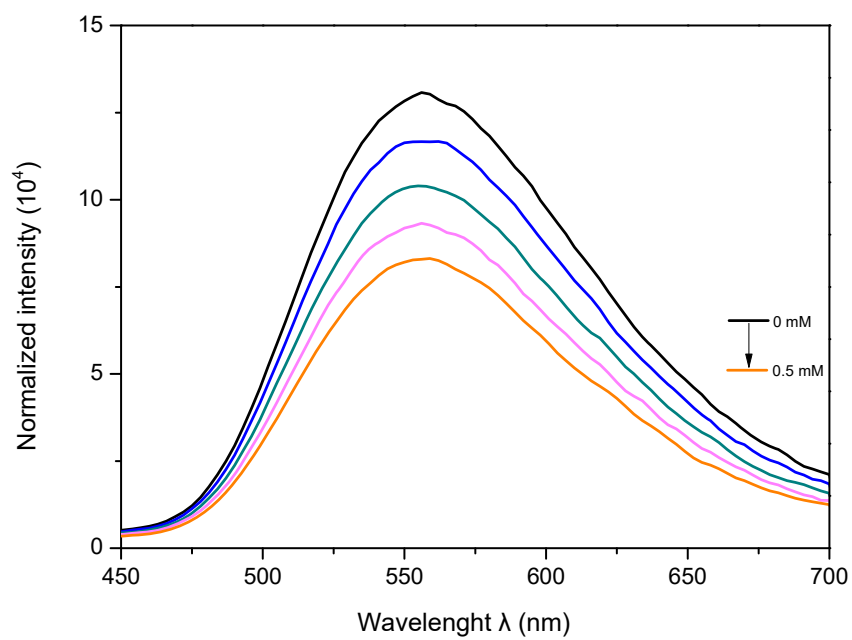


Figure S3. 4CzIPN emission quenching by CoCl₂ and dtbbpy.

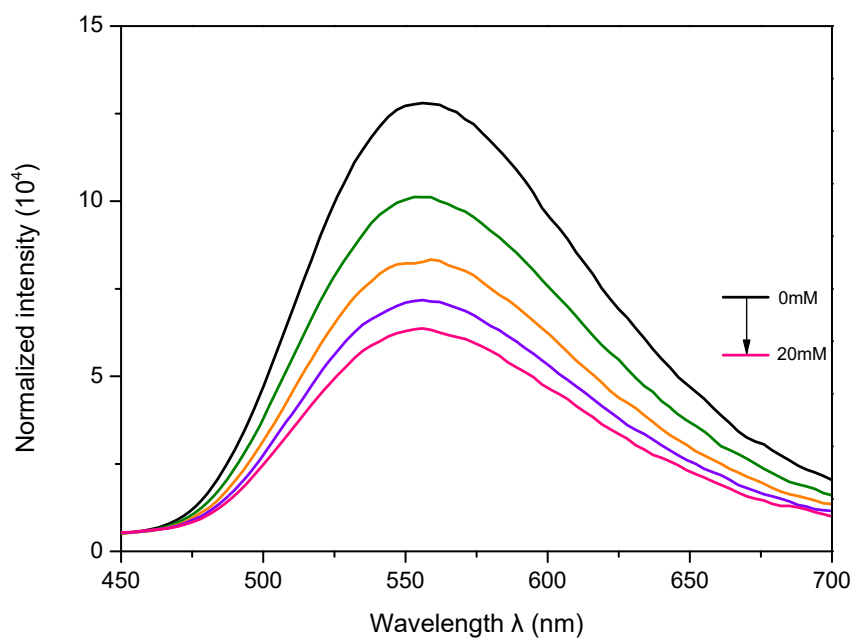
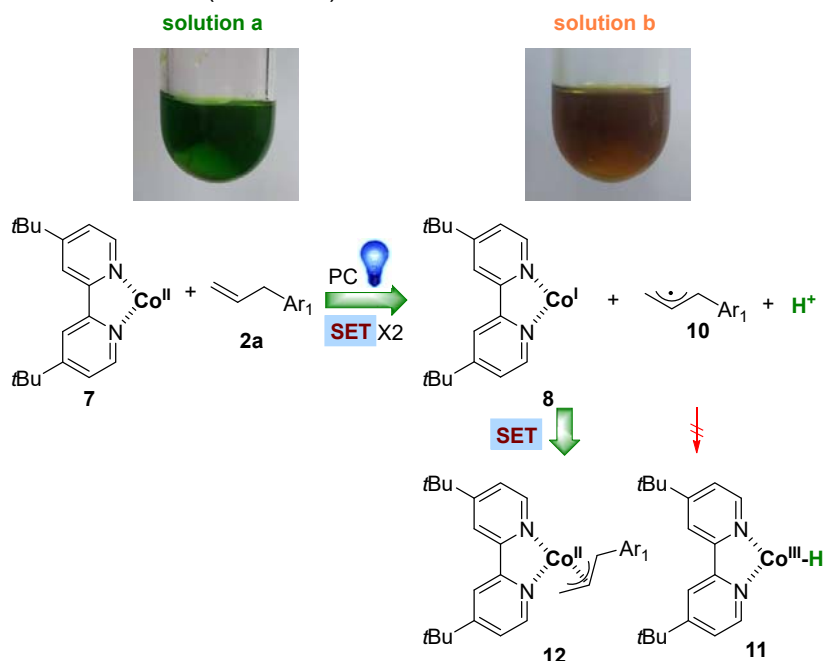


Figure S4. 4CzIPN emission quenching by 4-allyl-1,2-dimethoxybenzene.

S7 UV-Vis Studies

Firstly, CoBr_2 (10 mol%), L_1 (10 mol%), and 4CzIPN (2 mol%) were added to DMF (2.5 mL, 0.2 M) resulting in a green mixture (solution a). Then, the alkene (3 eq.) was added. The reaction mixture was stirred at room temperature under irradiation of 10W 450 nm LED for 5h. The mixture was turned to brown (solution b).



In a glove-box, to a 20 mL oven-dried glass vial CoBr_2 (2.4 mg, 10^{-3} M), dtbbpy (2.6 mg, 10^{-3} M) and DMF (10 mL) were added. The solution was allowed to stir for 2 h in the glove-box. Then, take out 3 ml of this solution from the dried glass vial and put it into a cuvette with a spiral cap. 4CzIPN (1.1 mg, $5 \cdot 10^{-4}$ M) and K_3PO_4 (1.3 mg, $5 \cdot 10^{-4}$ M) were added. Finally, **2a** (16.0 mg, $3 \cdot 10^{-2}$ M) was added to the solution. The cuvette was removed from the glove box and illuminated with a 450 nm LED light. The cuvette was placed in uv-vis and scanned at wavelengths ranging from 800nm to 200nm over time.

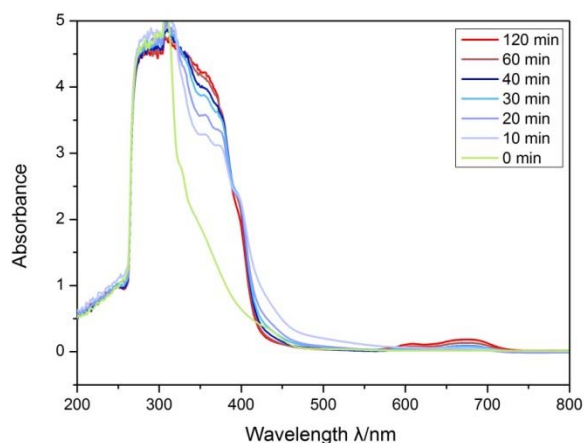
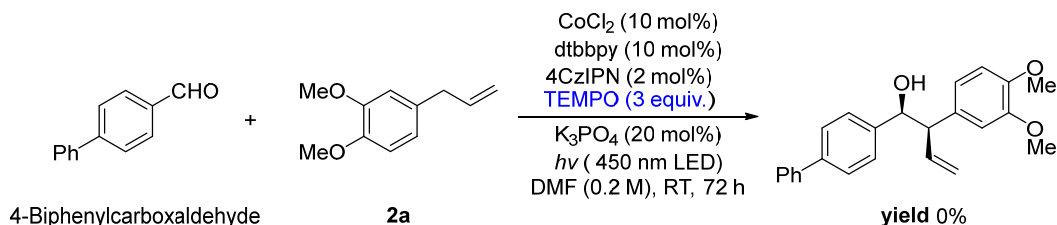


Figure S5. UV-vis spectroscopy studies of cobalt species in the reaction

S8 TEMPO Trapping Experiment

Verification of the formation of allyl radical, generated through reductive quenching of the photocatalyst, was tried via a radical trapping experiment by addition of TEMPO (2,2,6,6-tetramethyl- 1-piperidinyloxy, free radical).



CoCl₂ (6.5 mg, 0.05 mmol, 10 mol%) and dtbbpy (13.4 mg, 0.05 mmol, 10 mol%) in DMF were pre-stirred for two hours in an argon-filled glovebox. Then to an oven-dried screw-cap 10 mL reaction tube was added 4CzIPN (7.9 mg, 0.01 mmol, 2 mol%), K₃PO₄ (21.2 mg, 0.1 mmol, 20 mol%), 4-Biphenylcarboxaldehyde (91.1 mg, 0.5 mmol, 1.0 equiv) and TEMPO (234.4 mg, 1.5 mmol, 3.0 equiv.). The vial was transferred to an argon-filled glovebox, and the above CoCl₂ and dtbbpy in DMF was added. After sealing with Teflon-lined septa and removing the tube from the glovebox, 4-allyl-1,2-dimethoxybenzene (267.2 mg, 1.5 mmol, 3.0 equiv) was added. The reaction mixture was stirred and irradiated with 10 W blue LED for 24 h. The reaction mixture was analyzed by HRMS.

HRMS (ESI) [M+H]⁺ calculated for C₂₀H₃₂NO₃⁺: 334.2377, found: 334.2375.

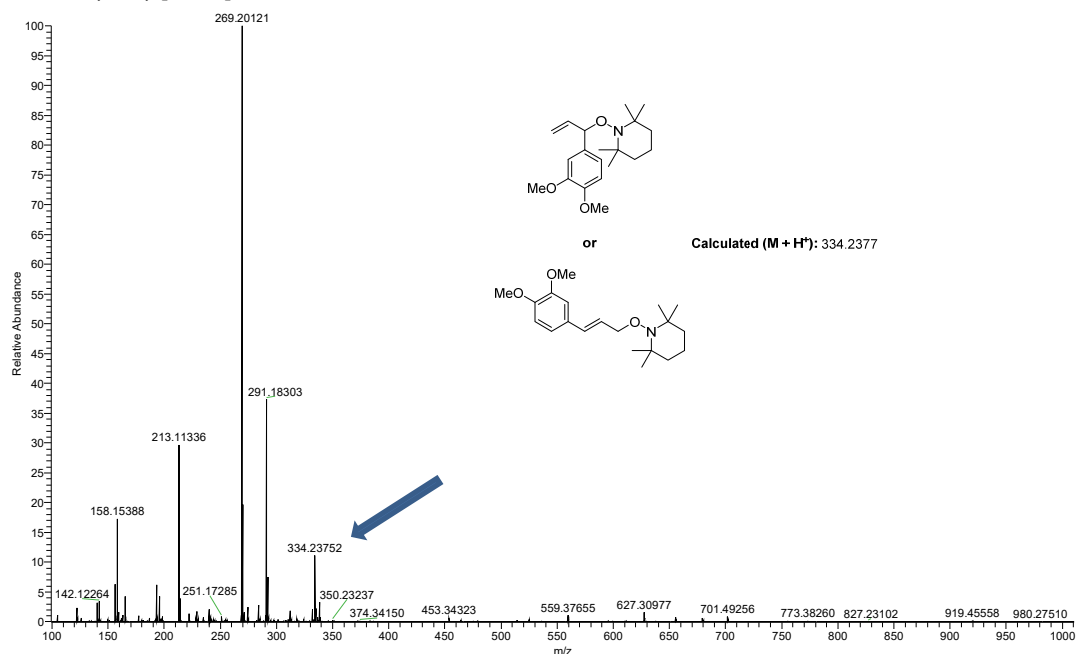
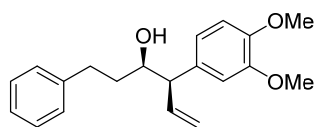


Figure S6. HRMS (ESI) spectra of the crude reaction mixture

S9 Characterization of Products



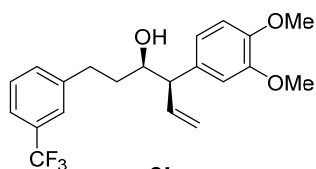
3a

3a, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 109.2 mg, 70%, d.r. = 10:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.16 (d, *J* = 6.9 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 6.12 (dt, *J* = 16.8, 9.8 Hz, 1H), 5.28 – 5.19 (m, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.80 (td, *J* = 8.1, 3.5 Hz, 1H), 3.25 (t, *J* = 8.2 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.74 – 2.63 (m, 1H), 1.97 (s, 1H), 1.80 – 1.63 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 148.9, 147.6, 141.9, 138.2, 133.8, 128.3, 128.1, 125.6, 119.7, 117.6, 111.2, 110.8, 72.9, 56.8, 55.7, 55.6, 35.8, 31.8.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₀H₂₃O₂⁺, 295.1693, found: 295.1696.



3b

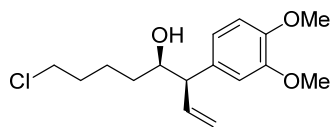
3b, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 133.0 mg, 70%, d.r. = 9:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.73 – 6.66 (m, 1H), 6.65 (s, 1H), 6.07 (dt, *J* = 16.7, 9.8 Hz, 1H), 5.28 – 5.17 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.76 – 3.69 (m, 1H), 3.20 (t, *J* = 8.3 Hz, 1H), 2.89 (ddd, *J* = 14.3, 9.2, 5.4 Hz, 1H), 2.70 (ddd, *J* = 13.9, 9.2, 7.4 Hz, 1H), 1.90 (s, 1H), 1.75 – 1.59 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 149.0, 147.8, 142.9, 138.1, 133.6, 131.8, 130.5 (q, *J* = 32.1 Hz), 128.6, 125.1 (q, *J* = 3.4 Hz), 124.2 (d, *J* = 275.7 Hz), 122.6 (q, *J* = 3.7 Hz), 119.7, 118.0, 111.4, 110.9, 72.7, 57.0, 55.8, 55.8, 35.6, 31.7.

¹⁹F NMR (377 MHz, CDCl₃): δ -62.53.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₁H₂₂F₃O₂⁺, 363.1566, found: 363.1571.



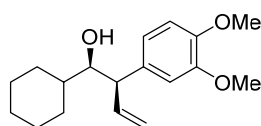
3c

3c, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 74.5 mg, 50%, d.r. = 13:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.84 – 6.80 (m, 1H), 6.77 – 6.68 (m, 2H), 6.08 (ddd, *J* = 17.2, 9.6 Hz, 1H), 5.26 – 5.15 (m, 2H), 3.91 – 3.82 (m, 6H), 3.74 (s, 1H), 3.51 – 3.45 (m, 2H), 3.17 (t, *J* = 7.9 Hz, 1H), 1.84 (s, 1H), 1.78 – 1.57 (m, 3H), 1.52 – 1.27 (m, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 148.9, 147.7, 138.1, 133.9, 119.7, 117.8, 111.3, 111.0, 73.6, 56.8, 55.8, 44.9, 33.4, 32.4, 23.0.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₆H₂₂ClO₂⁺, 281.1303, found: 281.1306.



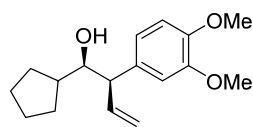
3d

3d, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 97.2 mg, 67%, d.r. = 15:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.82 (d, *J* = 8.1 Hz, 1H), 6.77 – 6.71 (m, 2H), 6.12 (ddd, *J* = 17.1, 10.3, 9.0 Hz, 1H), 5.24 – 5.12 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.54 – 3.49 (m, 1H), 3.44 – 3.35 (m, 1H), 1.90 – 1.79 (m, 1H), 1.70 (d, *J* = 16.3 Hz, 3H), 1.64 – 1.55 (m, 2H), 1.23 (d, *J* = 13.8 Hz, 2H), 1.11 (t, *J* = 8.1 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 148., 147.5, 138.3, 134.6, 119.7, 117.4, 111.3, 111.1, 78.1, 55.8, 55.8, 53.0, 39.5, 30.1, 26.7, 26.4, 26.3, 25.9.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₈H₂₅O₂⁺, 273.1849, found: 273.1850.



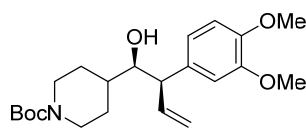
3e

3e, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 88.3 mg, 64%, d.r. = 10:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.84 – 6.81 (m, 1H), 6.82 – 6.73 (m, 2H), 6.16 (ddd, *J* = 17.1, 10.2, 9.2 Hz, 1H), 5.23 – 5.14 (m, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.65 (t, *J* = 6.2 Hz, 1H), 3.29 (dd, *J* = 9.2, 5.8 Hz, 1H), 1.94 – 1.79 (m, 1H), 1.79 – 1.68 (m, 2H), 1.66 – 1.55 (m, 3H), 1.53 – 1.40 (m, 3H), 1.37 – 1.28 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.9, 147.6, 137.8, 134.8, 119.7, 117.4, 111.3, 111.2, 77.8, 55.8, 54.9, 42.6, 29.2, 27.4, 25.6, 25.6.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₇H₂₃O₂⁺, 259.1693, found: 259.1694.



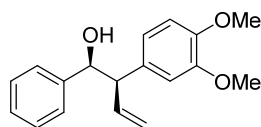
3f

3f, R_f = 0.2 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 130.4 mg, 67%, d.r. = 7:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.82 (d, *J* = 8.2 Hz, 1H), 6.77 – 6.70 (m, 1H), 6.70 (s, 1H), 6.11 (dt, *J* = 17.1, 9.7 Hz, 1H), 5.25 – 5.12 (m, 2H), 4.09 (s, 2H), 3.86 (s, 3H), 3.85 (s, 3H), 3.56 – 3.50 (m, 1H), 3.41 – 3.31 (m, 1H), 2.64 – 2.45 (m, 2H), 1.85 – 1.72 (m, 2H), 1.56 – 1.48 (m, 1H), 1.42 (s, 11H), 1.34 – 1.20 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 154.7, 149.0, 147.7, 137.6, 134.0, 119.7, 117.9, 111.4, 110.9, 79.1, 77.1, 55.8, 55.8, 52.9, 43.7, 43.6, 38.1, 28.8, 28.4, 26.3.

HRMS-ESI (m/z) [M+Na]⁺ calculated for C₂₂H₃₃NNaO₅⁺, 414.2251, found: 414.2251.



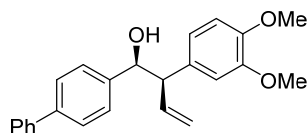
4a

4a, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 124.9 mg, 88%, d.r. = 8:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.26 – 7.15 (m, 3H), 7.17 – 7.10 (m, 2H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.65 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 6.23 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1H), 5.31 – 5.18 (m, 2H), 4.78 (d, *J* = 7.7 Hz, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.49 (t, *J* = 8.3 Hz, 1H), 2.35 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.4, 147.4, 141.8, 137.7, 132.9, 127.8, 127.2, 126.6, 120.0, 118.1, 111.7, 110.8, 77.2, 58.4, 55.6, 55.6.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₈H₁₉O₂⁺, 267.1380, found: 267.1382.



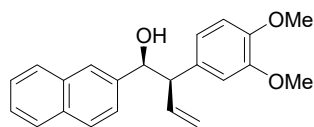
4b

4b, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 165.6 mg, 92%, d.r. = 8:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.60 – 7.55 (m, 1H), 7.58 – 7.52 (m, 1H), 7.51 – 7.43 (m, 2H), 7.43 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.24 – 7.19 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.46 (d, *J* = 2.0 Hz, 1H), 6.27 (ddd, *J* = 17.0, 10.3, 8.8 Hz, 1H), 5.34 – 5.23 (m, 2H), 4.83 (d, *J* = 7.7 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.54 (t, *J* = 8.3 Hz, 1H), 2.45 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.4, 147.5, 140.9, 140.6, 140.0, 137.7, 132.8, 128.6, 127.1, 127.0, 126.8, 126.5, 120.0, 118.2, 111.8, 110.8, 77.0, 58.4, 55.6, 55.5.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₄H₂₃O₂⁺, 343.1693, found: 343.1691.



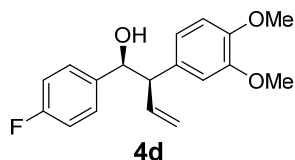
4c

4c, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 150.3 mg, 90%, d.r. = 10:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.81 – 7.67 (m, 3H), 7.62 (s, 1H), 7.48 – 7.39 (m, 2H), 7.28 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.73 – 6.65 (m, 2H), 6.49 (d, *J* = 1.9 Hz, 1H), 6.26 (ddd, *J* = 17.1, 10.3, 8.8 Hz, 1H), 5.31 – 5.19 (m, 2H), 4.97 (d, *J* = 7.4 Hz, 1H), 3.80 (s, 3H), 3.62 (m, 4H), 2.46 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.5, 147.6, 139.3, 137.6, 132.9, 132.8, 127.8, 127.4, 125.8, 125.6, 125.6, 124.7, 120.2, 118.2, 111.7, 111.0, 77.3, 58.3, 55.7, 55.6.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₂H₂₁O₂⁺, 317.1536, found: 317.1539.



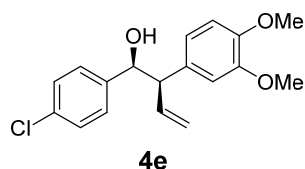
4d, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 75.5 mg, 50%, d.r. = 7:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.08 (dd, *J* = 8.6, 5.6 Hz, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.43 (d, *J* = 2.0 Hz, 1H), 6.20 (ddd, *J* = 17.1, 10.3, 8.8 Hz, 1H), 5.31 – 5.18 (m, 2H), 4.74 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.41 (t, *J* = 8.4 Hz, 1H), 2.44 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 161.9 (d, *J* = 245.2 Hz), 148.5, 147.6, 137.6, 137.5 (d, *J* = 2.9 Hz), 132.6, 128.1 (d, *J* = 8.0 Hz), 120.0, 118.3, 114.6 (d, *J* = 21.2 Hz), 111.6, 110.9, 76.5, 58.7, 55.7, 55.6.

¹⁹F NMR (377 MHz, CDCl₃): δ -115.17.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₈H₁₈FO₂⁺, 285.1285, found: 285.1287.

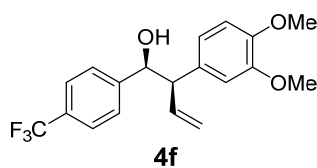


4e, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 144.7 mg, 91%, d.r. = 5.6:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.20 – 7.12 (m, 2H), 7.07 – 7.00 (m, 2H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.42 (d, *J* = 2.0 Hz, 1H), 6.17 (ddd, *J* = 17.0, 10.3, 8.8 Hz, 1H), 5.29 – 5.15 (m, 2H), 4.72 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.40 (t, *J* = 8.2 Hz, 1H), 2.49 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.5, 147.6, 140.3, 137.4, 132.8, 132.5, 127.9, 127.8, 120.0, 118.3, 111.6, 110.9, 76.5, 58.5, 55.6, 55.6.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₈H₁₈ClO₂⁺, 301.0990, found: 301.0992.



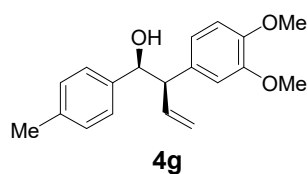
4f, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 96.8 mg, 55%, d.r. = 4:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.65 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 6.21 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 5.33 – 5.21 (m, 2H), 4.84 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.44 (t, *J* = 8.3 Hz, 1H), 2.42 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.6, 147.8, 145.8, 137.1, 132.2, 129.4 (d, *J* = 32.5 Hz), 126.9, 124.0 (d, *J* = 272.7), 124.7 (q, *J* = 4.0 Hz), 120.0, 118.9, 111.6, 111.0, 76.7, 58.7, 55.7, 55.6.

¹⁹F NMR (376 MHz, CDCl₃): δ -62.44.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₉H₁₈F₃O₂⁺, 335.1253, found: 335.1257.

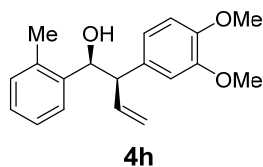


4g, R_f = 0.6(EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 111.8 mg, 75%, d.r. = 10:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.02 (s, 4H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.65 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 6.22 (ddd, *J* = 17.0, 10.3, 8.7 Hz, 1H), 5.30 – 5.15 (m, 2H), 4.75 (d, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.48 (t, *J* = 8.2 Hz, 1H), 2.37 (s, 1H), 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 148.3, 147.3, 138.8, 137.9, 136.7, 133.0, 128.4, 126.4, 119.9, 117.8, 111.7, 110.7, 77.0, 58.2, 55.5, 55.4, 20.9.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₉H₂₁O₂⁺, 281.1536, found: 281.1536.

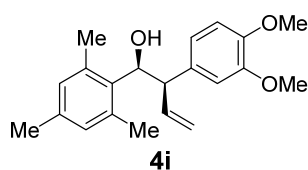


4h, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 129.6 mg, 87%, d.r. = 8:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 2H), 6.39 (s, 1H), 6.32 (dt, *J* = 17.1, 9.5 Hz, 1H), 5.37 – 5.19 (m, 2H), 5.04 (d, *J* = 7.5 Hz, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 3.53 (t, *J* = 8.2 Hz, 1H), 2.19 (s, 1H), 1.98 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 148.3, 147.5, 140.3, 137.4, 135.3, 132.9, 129.9, 127.1, 126.3, 125.8, 119.8, 118.4, 111.8, 110.7, 73.0, 57.4, 55.7, 55.5, 19.0.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₉H₂₁O₂⁺, 281.1536, found: 281.1538.

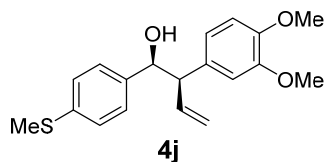


4i, R_f = 0.6 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 88.0 mg, 54%, d.r. = 13:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.69 (s, 2H), 6.66 (s, 2H), 6.37 (dt, *J* = 18.2, 9.3 Hz, 1H), 6.19 (s, 1H), 5.43 – 5.32 (m, 2H), 5.10 (d, *J* = 10.1 Hz, 1H), 3.92 (t, *J* = 9.6 Hz, 1H), 3.79 (s, 3H), 3.55 (s, 3H), 2.18 (s, 10H).

¹³C NMR (101 MHz, CDCl₃): δ 147.9, 147.4, 138.3, 136.7, 136.4, 133.9, 132.9, 129.8, 119.4, 118.2, 111.9, 110.3, 73.6, 55.6, 55.3, 54.5, 20.8, 20.5.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₁H₂₅O₂⁺, 309.1849, found: 309.1852.

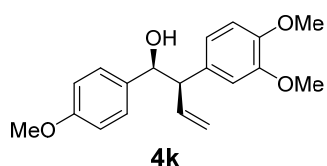


4j, R_f = 0.4 (EA:PE = 1:2), column solvent: hexane/EtOAc = 5:1, 105.6 mg, 64%, d.r. = 9.3:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.10 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.63 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.43 (d, *J* = 2.0 Hz, 1H), 6.20 (ddd, *J* = 17.1, 10.3, 8.8 Hz, 1H), 5.32 – 5.18 (m, 2H), 4.74 (d, *J* = 7.8 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.45 (t, *J* = 8.3 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.4, 147.5, 138.7, 137.7, 137.2, 132.7, 127.1, 126.0, 120.0, 118.2, 111.7, 110.9, 76.8, 58.5, 55.7, 55.6, 15.7.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₉H₂₁O₂S⁺, 313.1257, found: 313.1258.

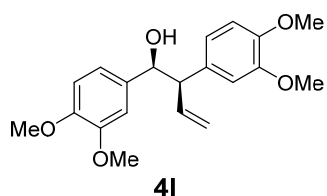


4k, R_f = 0.4 (EA:PE = 1:2), column solvent: hexane/EtOAc = 5:1, 122.5 mg, 78%, d.r. = 9.7:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.04 (d, *J* = 8.3 Hz, 2H), 6.78 – 6.67 (m, 3H), 6.62 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.44 (s, 1H), 6.21 (ddd, *J* = 17.2, 10.3, 8.8 Hz, 1H), 5.31 – 5.17 (m, 2H), 4.72 (d, *J* = 7.8 Hz, 1H), 3.80 (s, 3H), 3.72 (d, *J* = 6.9 Hz, 6H), 3.45 (t, *J* = 8.3 Hz, 1H), 2.38 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 158.7, 148.3, 147.3, 138.0, 133.9, 133.0, 127.7, 120.0, 117.9, 113.1, 111.6, 110.8, 76.7, 58.5, 55.6, 55.6, 55.0.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₉H₂₁O₃⁺, 297.1485, found: 297.1486.

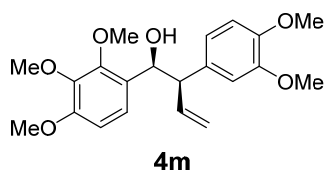


4l, R_f = 0.4 (EA:PE = 1:2), column solvent: hexane/EtOAc = 5:1, 91.2 mg, 53%, d.r. = 8:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.72 – 6.63 (m, 3H), 6.62 – 6.56 (m, 2H), 6.46 (s, 1H), 6.20 (dt, *J* = 16.8, 9.6 Hz, 1H), 5.29 – 5.16 (m, 2H), 4.71 (d, *J* = 7.8 Hz, 1H), 3.79 (s, 6H), 3.74 (s, 3H), 3.71 (s, 3H), 3.43 (t, *J* = 8.3 Hz, 1H), 2.37 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.4, 148.2, 148.0, 147.4, 138.0, 134.3, 133.0, 120.1, 118.9, 117.9, 111.6, 110.8, 110.2, 109.5, 76.9, 58.5, 55.6, 55.6.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₀H₂₃O₄⁺, 327.1591, found: 327.1591.

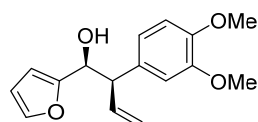


4m, R_f = 0.3 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 104.7 mg, 56%, d.r. = 5:1, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.90 (d, *J* = 8.6 Hz, 1H), 6.73 – 6.64 (m, 2H), 6.62 (d, *J* = 1.9 Hz, 1H), 6.55 (d, *J* = 8.6 Hz, 1H), 6.24 (ddd, *J* = 17.1, 10.2, 8.5 Hz, 1H), 5.20 (dd, *J* = 10.3, 1.7 Hz, 1H), 5.17 – 5.10 (m, 1H), 5.02 (d, *J* = 7.5 Hz, 1H), 3.81 – 3.74 (m, 15H), 3.62 (t, *J* = 8.0 Hz, 1H), 2.50 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 152.8, 151.0, 148.4, 147.3, 141.4, 138.1, 133.8, 127.5, 122.2, 120.0, 117.4, 111.5, 110.8, 106.7, 72.7, 60.8, 60.5, 56.8, 55.7, 55.6, 55.6.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₁H₂₅O₅⁺, 357.1697, found: 357.1698.



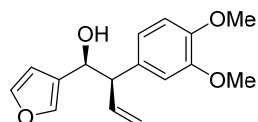
4n

4n, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 123.3 mg, 90%, d.r. = 7:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.32 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.70 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.57 (d, *J* = 2.0 Hz, 1H), 6.27 – 6.13 (m, 2H), 6.05 (d, *J* = 3.2 Hz, 1H), 5.31 – 5.18 (m, 2H), 4.83 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.77 – 3.73 (m, 1H), 2.33 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 154.1, 148.5, 147.6, 141.6, 137.4, 132.7, 119.8, 118.2, 111.3, 110.8, 110.0, 107.4, 71.0, 55.6, 55.2.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₆H₁₇O₃⁺, 257.1172, found: 257.1174.



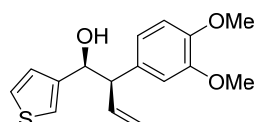
4o

4o, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 127.4 mg, 93%, d.r. = 10:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.27 (s, 1H), 7.15 (s, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.71 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 6.23 – 6.11 (m, 2H), 5.30 – 5.20 (m, 2H), 4.82 (d, *J* = 7.6 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.46 (t, *J* = 8.2 Hz, 1H), 2.11 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.6, 147.7, 142.6, 139.6, 137.9, 133.0, 126.5, 120.1, 118.2, 111.6, 111.0, 108.8, 70.1, 57.5, 55.7.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₆H₁₇O₃⁺, 257.1172, found: 257.1174.



4p

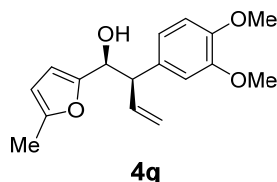
4p, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 116.0 mg, 80%, d.r. = 4:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.17 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.84 (d, *J* = 5.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.68 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.48 (d, *J* = 1.9 Hz, 1H),

6.20 (ddd, $J = 17.1, 10.3, 8.7$ Hz, 1H), 5.31 – 5.19 (m, 2H), 4.90 (d, $J = 7.5$ Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.50 (t, $J = 8.1$ Hz, 1H), 2.26 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3): δ 148.5, 147.6, 143.3, 137.7, 132.9, 125.9, 125.1, 121.4, 120.0, 118.1, 111.6, 110.8, 73.6, 57.9, 55.7, 55.6.

HRMS-ESI (m/z) [M-OH] $^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{S}^+$, 273.0944, found: 273.0948.

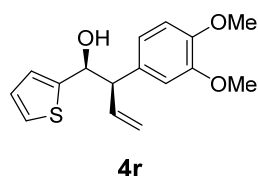


4q, $R_f = 0.4$ (EA:PE = 1:2), column solvent: hexane/EtOAc = 5:1, 113.8 mg, 79%, d.r. = 10:1, colorless oil.

^1H NMR (400 MHz, CDCl_3): δ 6.73 (q, $J = 8.4$ Hz, 2H), 6.59 (s, 1H), 6.19 (dt, $J = 17.1, 9.4$ Hz, 1H), 5.91 (s, 1H), 5.78 (s, 1H), 5.31 – 5.20 (m, 2H), 4.75 (d, $J = 7.9$ Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.76 (d, $J = 8.6$ Hz, 1H), 2.27 (s, 1H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3): δ 152.1, 151.3, 148.4, 147.5, 137.7, 132.9, 119.8, 118.2, 111.3, 110.8, 108.5, 105.9, 70.9, 55.6, 55.6, 55.1, 13.5.

HRMS-ESI (m/z) [M-OH] $^+$ calculated for $\text{C}_{17}\text{H}_{19}\text{O}_3^+$, 271.1329, found: 271.1329.

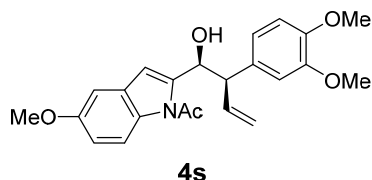


4r, $R_f = 0.4$ (EA:PE = 1:2), column solvent: hexane/EtOAc = 5:1, 76.8 mg, 53%, d.r. = 5:1, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.15 (dd, $J = 5.1, 1.3$ Hz, 1H), 6.81 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.76 (d, $J = 8.2$ Hz, 1H), 6.70 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.64 (d, $J = 3.6$ Hz, 1H), 6.55 (d, $J = 2.0$ Hz, 1H), 6.22 (ddd, $J = 17.0, 10.4, 8.7$ Hz, 1H), 5.32 – 5.21 (m, 2H), 5.07 (d, $J = 7.7$ Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.55 (t, $J = 8.2$ Hz, 1H), 2.54 (s, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.5, 147.6, 145.7, 137.6, 132.7, 126.2, 124.5, 124.2, 120.0, 118.4, 111.6, 110.9, 73.4, 58.7, 55.6.

HRMS-ESI (m/z) [M-OH] $^+$ calculated for $\text{C}_{16}\text{H}_{17}\text{O}_2\text{S}^+$, 273.0944, found: 273.0945.

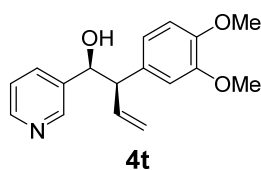


4s, $R_f = 0.4$ (EA:PE = 1:2), column solvent: hexane/EtOAc = 5:1, 144.2 mg, 73%, d.r. = 12:1, colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 9.0$ Hz, 1H), 7.06 (s, 1H), 6.96 (d, $J = 2.5$ Hz, 1H), 6.93 – 6.88 (m, 1H), 6.76 – 6.68 (m, 2H), 6.59 (s, 1H), 6.25 (dt, $J = 18.7, 9.5$ Hz, 1H), 5.35 – 5.18 (m, 2H), 5.03 (d, $J = 7.1$ Hz, 1H), 3.88 – 3.75 (m, 8H), 3.68 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.1, 156.1, 148.7, 147.8, 137.2, 133.2, 130.6, 129.6, 123.5, 123.1, 120.0, 118.5, 117.3, 113.1, 111.5, 111.1, 103.0, 71.4, 56.2, 55.8, 55.7, 55.5, 23.5.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₃H₂₄NO₄⁺, 378.1700, found: 378.1703.



4t, R_f = 0.2 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 116.8 mg, 82%, d.r. = 4:1, colorless oil.

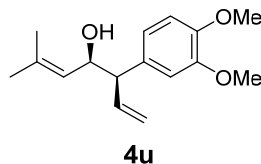
¹H NMR (400 MHz, CDCl₃): δ 8.39 – 8.33 (m, 2H), 7.51 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.18 (dd, *J* = 7.9, 4.9 Hz, 1H), 6.71 (s, 1H), 6.61 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.49 (d, *J* = 2.0 Hz, 1H), 6.20 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1H), 5.30 – 5.15 (m, 2H), 4.86 (d, *J* = 7.7 Hz, 1H), 4.41 (s, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.44 (t, *J* = 8.2 Hz, 1H).

¹H NMR (400 MHz, CDCl₃): δ 8.51 – 8.44 (m, 2H), 7.67 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.33 – 7.29 (m, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 5.92 (ddd, *J* = 17.1, 10.4, 8.2 Hz, 1H), 5.05 (dt, *J* = 10.2, 1.2 Hz, 1H), 4.96 (s, 0.5H), 4.94 (m, *J* = 1.8 Hz, 1H), 4.90 (m, *J* = 1.5 Hz, 0.5H), 4.44 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.54 (t, *J* = 8.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 148.8, 147.9, 147.6, 147.0, 138.5, 137.1, 135.6, 132.2, 123.1, 120.2, 118.6, 111.7, 111.2, 74.9, 58.4, 55.8, 55.7.

¹³C NMR (101 MHz, CDCl₃): δ 149.1, 148.2, 147.6, 147.0, 138.3, 137.0, 135.6, 131.7, 123.3, 120.6, 118.6, 111.8, 111.4, 74.9, 58.0, 55.8, 55.7.

HRMS-ESI (m/z) [M+H]⁺ calculated for C₁₇H₂₀NO₃⁺, 286.1438, found: 286.1435.

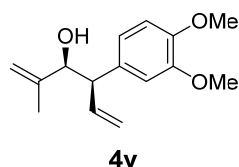


4u, R_f = 0.4 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 72.1 mg, 55%, d.r. = 4:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.79 (d, *J* = 8.2 Hz, 1H), 6.78 – 6.72 (m, 1H), 6.71 (s, 1H), 6.14 (ddd, *J* = 17.0, 10.4, 8.8 Hz, 1H), 5.26 – 5.16 (m, 2H), 5.11 (d, *J* = 9.0 Hz, 1H), 4.49 (t, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.26 (t, *J* = 8.1 Hz, 1H), 1.77 (s, 1H), 1.62 (s, 3H), 1.50 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 148.5, 147.5, 138.2, 136.3, 133.5, 125.2, 120.2, 117.6, 111.6, 110.9, 70.9, 56.8, 55.7, 25.7, 18.2.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₆H₂₁O₂⁺, 245.1536, found: 245.1537.

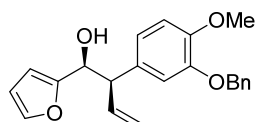


4v, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 93 mg, 75%, d.r. = 13:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 6.79 (d, *J* = 8.1 Hz, 1H), 6.74 (d, *J* = 11.1 Hz, 2H), 6.10 (ddd, *J* = 17.1, 10.3, 8.6 Hz, 1H), 5.23 – 5.11 (m, 2H), 4.84 (s, 1H), 4.80 – 4.75 (m, 1H), 4.24 (d, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.38 (t, *J* = 8.0 Hz, 1H), 2.01 (s, 1H), 1.66 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 148.6, 147.5, 144.6, 138.0, 133.5, 120.0, 117.5, 113.2, 111.2, 111.0, 78.1, 55.7, 55.6, 54.2, 17.9.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₁₅H₁₉O₂⁺, 231.1380, found: 231.1380.



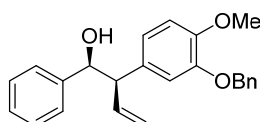
5a

5a, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 162.8 mg, 93%, d.r. = 14:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.39 (m, 2H), 7.40 – 7.25 (m, 4H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.68 – 6.61 (m, 1H), 6.60 (s, 1H), 6.27 – 6.13 (m, 2H), 6.05 (d, *J* = 2.8 Hz, 1H), 5.34 – 5.20 (m, 2H), 5.10 (s, 2H), 4.83 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 3.76 (d, *J* = 8.3 Hz, 1H), 2.28 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 154.0, 149.2, 146.8, 141.7, 137.4, 137.1, 133.2, 128.4, 127.7, 127.2, 119.8, 118.3, 113.7, 111.8, 110.1, 107.5, 71.0, 70.8, 55.8, 55.3.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₂H₂₁O₃⁺, 333.1485, found: 333.1486.



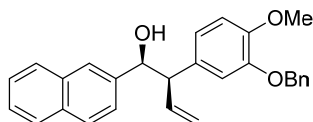
5b

5b, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 133.2 mg, 74%, d.r. = 6:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.43 – 7.39 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.25 – 7.18 (m, 3H), 7.16 – 7.10 (m, 2H), 6.75 (d, *J* = 8.3 Hz, 1H), 6.59 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.46 (d, *J* = 2.1 Hz, 1H), 6.22 (ddd, *J* = 17.0, 10.3, 8.8 Hz, 1H), 5.31 – 5.20 (m, 2H), 5.09 (s, 2H), 4.78 (d, *J* = 7.7 Hz, 1H), 3.72 (s, 3H), 3.48 (t, *J* = 8.3 Hz, 1H), 2.32 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 149.2, 146.7, 141.8, 137.7, 137.1, 133.5, 128.4, 127.8, 127.7, 127.3, 127.2, 126.6, 120.0, 118.2, 113.8, 112.3, 76.6, 70.9, 58.6, 55.8.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₄H₂₃O₂⁺, 343.1693, found: 343.1696.



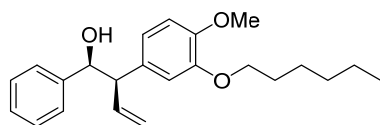
5c

5c, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 192.7 mg, 94%, d.r. = 7:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.80 – 7.76 (m, 1H), 7.75 – 7.67 (m, 2H), 7.61 (s, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.37 (m, 2H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.61 (d, *J* = 6.2 Hz, 1H), 6.51 (d, 1H), 6.25 (dt, *J* = 17.2, 9.5 Hz, 1H), 5.31 – 5.18 (m, 2H), 5.07 (s, 2H), 4.97 (d, *J* = 5.2 Hz, 1H), 3.63 (s, 3H), 3.59 (d, *J* = 8.2 Hz, 1H), 2.40 (d, *J* = 2.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 149.2, 146.7, 139.3, 137.6, 137.1, 133.5, 132.9, 132.7, 128.4, 127.9, 127.7, 127.5, 127.4, 127.2, 125.8, 125.6, 125.5, 124.6, 120.1, 118.3, 113.9, 112.3, 77.3, 70.9, 58.3, 55.7.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₈H₂₅O₂⁺, 393.1849, found: 393.1851.



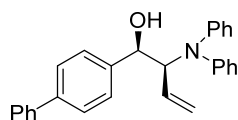
5d

5d, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 192.7 mg, 62%, d.r. = 7:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.24 – 7.17 (m, 3H), 7.17 – 7.11 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.42 (s, 1H), 6.23 (dt, *J* = 18.1, 9.6 Hz, 1H), 5.30 – 5.19 (m, 2H), 4.78 (d, *J* = 7.7 Hz, 1H), 3.94 (t, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 3.48 (t, *J* = 8.4 Hz, 1H), 2.34 (s, 1H), 1.89 – 1.71 (m, 2H), 1.48 – 1.38 (m, 2H), 1.37 – 1.27 (m, 4H), 0.90 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 148.8, 147.0, 141.8, 137.8, 132.7, 127.8, 127.2, 126.6, 120.0, 118.1, 112.5, 112.1, 77.2, 68.8, 58.5, 55.7, 31.5, 29.0, 25.5, 22.5, 13.9.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₂₃H₂₉O₂⁺, 337.2162, found: 337.2164.



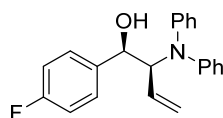
5e

5e, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 99.7 mg, 51%, d.r. = 7:1, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.57 (m, 1H), 7.58 (s, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 7.49 – 7.40 (m, 2H), 7.39 – 7.30 (m, 3H), 7.26 – 7.17 (m, 4H), 6.97 (t, *J* = 7.3 Hz, 2H), 6.88 – 6.83 (m, 2H), 6.86 – 6.80 (m, 2H), 6.23 (ddd, *J* = 17.4, 10.6, 7.1 Hz, 1H), 5.37 – 5.27 (m, 2H), 5.22 (d, *J* = 7.0 Hz, 1H), 4.73 (t, *J* = 7.1 Hz, 1H), 2.13 (s, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 147.1, 140.7, 140.6, 133.7, 129.0, 128.7, 127.2, 127.2, 127.0, 126.9, 122.9, 121.9, 119.7, 73.6, 69.1.

HRMS-ESI (m/z) [M+H]⁺ calculated for C₂₈H₂₆NO⁺, 392.2009, found: 392.2002.



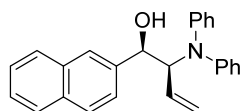
5f

5f, R_f = 0.5 (EA:PE =1:4), column solvent: hexane/EtOAc = 5:1, 108.6 mg, 65%, d.r. = 3:1, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.17 (m, 6H), 6.99 – 6.93 (m, 4H), 6.83 – 6.77 (m, 4H), 6.19 (ddd, *J* = 17.5, 10.5, 7.2 Hz, 1H), 5.33 – 5.24 (m, 2H), 5.15 (d, *J* = 7.1 Hz, 1H), 4.62 (t, *J* = 7.2 Hz, 1H), 2.10 (s, 1H).

¹³C NMR (101 MHz, DMSO-*D*₆) δ 161.75 (d, *J* = 242.6 Hz), 147.37, 140.32 (d, *J* = 3.2 Hz), 135.34, 129.38, 128.94 (d, *J* = 8.0 Hz), 122.68, 121.70, 118.36, 114.86 (d, *J* = 21.0 Hz), 71.94, 69.21.

¹⁹F NMR (377 MHz, DMSO-*D*₆) δ -115.71.

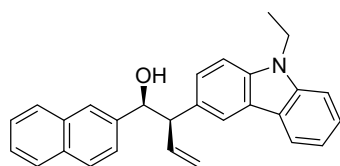


5g

5g, Rf = 0.6 (EA:PE =1:4), column solvent: hexane/EtOAc = 5:1, 118.6 mg, 63%, d.r. = 5:1, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.75 (m, 2H), 7.75 – 7.70 (m, 1H), 7.63 (s, 1H), 7.50 – 7.41 (m, 3H), 7.23 – 7.16 (m, 4H), 6.96 (t, *J* = 7.3 Hz, 2H), 6.87 – 6.81 (m, 4H), 6.23 (ddd, *J* = 17.4, 10.5, 7.1 Hz, 1H), 5.36 – 5.23 (m, 3H), 4.82 (t, *J* = 6.9 Hz, 1H), 2.18 (d, *J* = 2.9 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 147.40, 141.62, 135.42, 133.02, 132.82, 129.35, 128.15, 127.92, 127.68, 126.39, 126.05, 125.83, 125.45, 122.83, 121.72, 118.38, 72.60, 68.89.



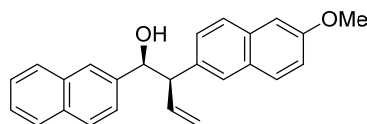
5h

5h, Rf = 0.4 (EA:PE =1:4), column solvent: hexane/EtOAc = 5:1, 172.0 mg, 87%, d.r. = 14:1, colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.96 (s, 1H), 7.80 – 7.72 (m, 3H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.43 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.25 – 7.16 (m, 3H), 6.45 (ddd, *J* = 16.9, 10.3, 8.7 Hz, 1H), 5.35 – 5.26 (m, 2H), 5.19 (d, *J* = 7.2 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.93 (t, *J* = 8.0 Hz, 1H), 2.32 (s, 1H), 1.39 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 140.1, 139.6, 138.8, 138.3, 133.0, 132.7, 131.0, 127.9, 127.5, 127.4, 126.2, 125.7, 125.5, 125.5, 124.8, 122.9, 122.7, 120.3, 119.7, 118.6, 118.0, 108.3, 108.3, 77.5, 58.7, 37.4, 13.7.

HRMS-ESI (m/z) [M+H]⁺ calculated for C₂₈H₂₆NO⁺, 392.2009, found: 392.2000.



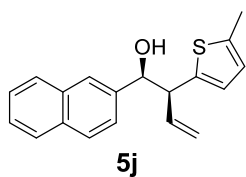
5i

5i, Rf = 0.5 (EA:PE =1:4), column solvent: hexane/EtOAc = 5:1, 153.9 mg, 86%, d.r. = 10:1, colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (ddd, *J* = 13.5, 6.1, 3.3 Hz, 2H), 7.70 – 7.66 (m, 2H), 7.59 (t, *J* = 9.2 Hz, 2H), 7.52 (s, 1H), 7.42 (dt, *J* = 6.3, 3.4 Hz, 2H), 7.31 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.21 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.09 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.37 (ddd, *J* = 17.0, 10.2, 8.7 Hz, 1H), 5.33 – 5.20 (m, 2H), 5.15 (dd, *J* = 7.3, 2.3 Hz, 1H), 3.88 (s, 3H), 3.84 (t, *J* = 8.0 Hz, 1H), 2.45 (d, *J* = 2.6 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 157.4, 139.4, 137.7, 135.8, 133.3, 133.0, 132.8, 129.1, 128.8, 127.9, 127.5, 127.5, 127.1, 126.8, 126.8, 125.8, 125.6, 125.6, 124.7, 118.7, 118.4, 105.5, 77.1, 58.6, 55.2.

HRMS-ESI (m/z) [M-OH]⁻ calculated for C₂₅H₂₁O⁻, 337.1598, found: 337.1583.

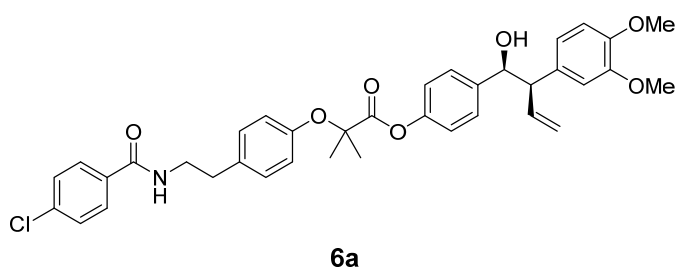


5j, R_f = 0.6 (EA:PE =1:4), column solvent: hexane/EtOAc = 5:1, 58.8 mg, 40%, d.r. = 5:1, colorless oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.78 (m, 3H), 7.78 – 7.73 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 – 7.37 (m, 1H), 6.51 (s, 2H), 6.14 (ddd, *J* = 16.9, 10.1, 8.7 Hz, 1H), 5.26 – 5.13 (m, 2H), 5.05 (d, *J* = 6.3 Hz, 1H), 3.98 – 3.90 (m, 1H), 2.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 141.0, 139.1, 138.4, 136.7, 133.0, 132.9, 128.0, 127.7, 127.6, 125.9, 125.7, 125.6, 124.8, 124.7, 124.5, 118.6, 77.3, 53.7, 15.2.

HRMS-ESI (m/z) [M-OH]⁻ calculated for C₁₉H₁₇S⁻, 277.1056, found: 277.1045.

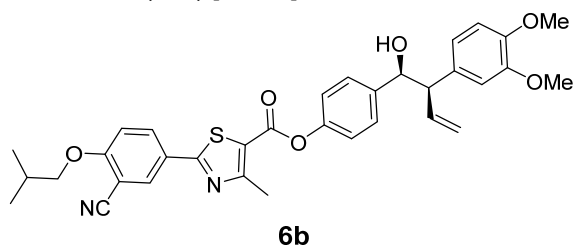


6a, R_f = 0.5 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 241.1 mg, 75%, d.r. = 8:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 6.40 (s, 1H), 6.30 – 6.24 (m, 1H), 6.19 (dd, *J* = 17.3, 9.0 Hz, 1H), 5.30 – 5.18 (m, 2H), 4.77 (d, *J* = 7.7 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.62 (q, *J* = 6.4 Hz, 2H), 3.42 (t, *J* = 8.2 Hz, 1H), 2.85 (t, *J* = 6.8 Hz, 2H), 2.31 (s, 1H), 1.71 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 172.7, 166.3, 153.9, 149.6, 148.4, 147.5, 139.9, 137.5, 137.4, 132.8, 132.6, 132.6, 129.5, 128.7, 128.2, 127.6, 120.5, 120.0, 119.2, 118.3, 111.7, 110.9, 79.1, 76.6, 58.6, 55.7, 55.6, 41.2, 34.6, 25.3, 25.3.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₃₇H₃₇ClNO₆⁺, 626.2304, found: 626.2309.

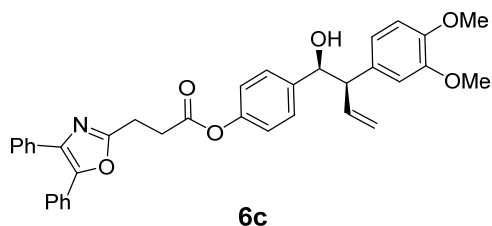


6b, R_f = 0.2 (EA:PE =1:2), column solvent: hexane/EtOAc = 5:1, 299.1 mg, 70%, d.r. = 8:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 8.21 (d, *J* = 2.2 Hz, 1H), 8.12 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.05 (dd, *J* = 13.6, 8.6 Hz, 3H), 6.76 (d, *J* = 8.3 Hz, 1H), 6.70 – 6.64 (m, 1H), 6.47 – 6.42 (m, 1H), 6.23 (ddd, *J* = 17.1, 10.3, 8.8 Hz, 1H), 5.34 – 5.21 (m, 2H), 4.83 (d, *J* = 7.7 Hz, 1H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 3.47 (t, *J* = 8.3 Hz, 1H), 2.80 (s, 3H), 2.37 (s, 1H), 2.27 – 2.14 (m, 1H), 1.10 (s, 3H), 1.08 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 168.0, 162.9, 162.6, 160.2, 149.3, 148.5, 147.6, 139.9, 137.5, 132.6, 132.1, 127.7, 125.7, 121.0, 120.5, 120.0, 118.5, 115.3, 112.6, 111.6, 110.9, 102.9, 77.2, 76.7, 75.6, 58.7, 55.7, 28.1, 19.0, 17.6.

HRMS-ESI (m/z) [M-OH]⁺ calculated for C₃₄H₃₃N₂O₅S⁺, 581.2105, found: 581.2110.



6c, R_f = 0.2 (EA:PE = 1:2), column solvent: hexane/EtOAc = 5:1, 253.0 mg, 88%, d.r. = 8:1, colorless oil.

¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, *J* = 6.8 Hz, 2H), 7.58 (d, *J* = 6.4 Hz, 2H), 7.41 – 7.29 (m, 6H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.67 – 6.60 (m, 1H), 6.42 (d, *J* = 1.9 Hz, 1H), 6.21 (dt, *J* = 17.1, 9.5 Hz, 1H), 5.33 – 5.17 (m, 2H), 4.79 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.45 (t, *J* = 8.2 Hz, 1H), 3.28 (t, *J* = 7.3 Hz, 2H), 3.14 (t, *J* = 7.3 Hz, 2H), 2.68 (s, 1H).

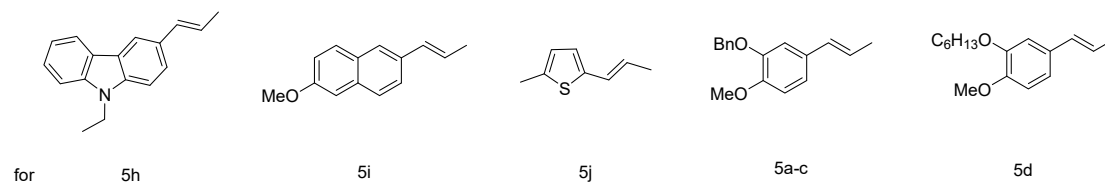
¹³C NMR (101 MHz, CDCl₃): δ 170.4, 161.5, 149.7, 148.5, 147.5, 145.5, 139.6, 137.5, 134.8, 132.6, 132.0, 128.6, 128.6, 128.5, 128.1, 127.8, 127.6, 126.4, 120.8, 120.0, 118.3, 111.6, 110.8, 76.7, 58.6, 55.6, 31.1, 23.3.

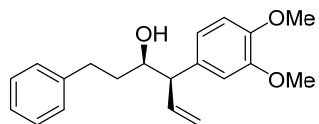
HRMS-ESI (m/z) [M-OH]⁺ calculated for C₃₆H₃₂NO₅⁺, 558.2275, found: 558.2287.

S10 NMR Spectrum

Diastereomeric ratios were determined by ^1H NMR spectroscopy of crude products. The two diastereoisomers are difficult to completely separate by column chromatography, but the partially pure major product can be isolated for characterization.

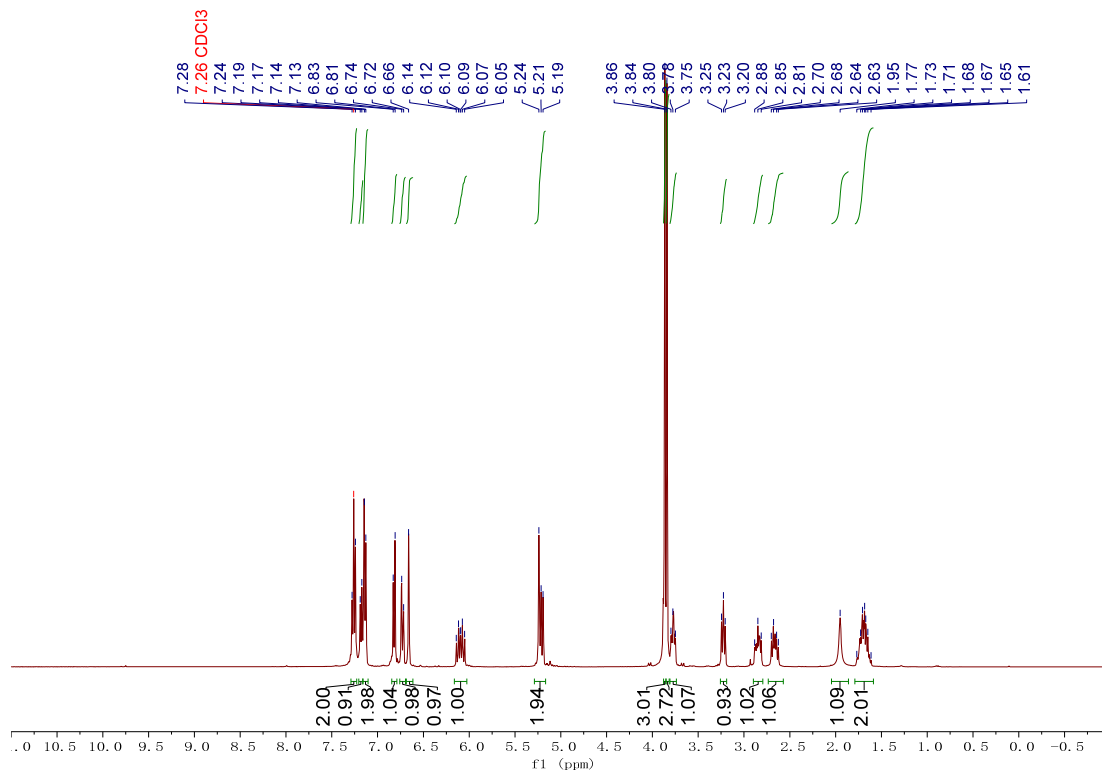
The following substrates were used for the products of 5h, 5i, 5j, 5a-c, and 5d.



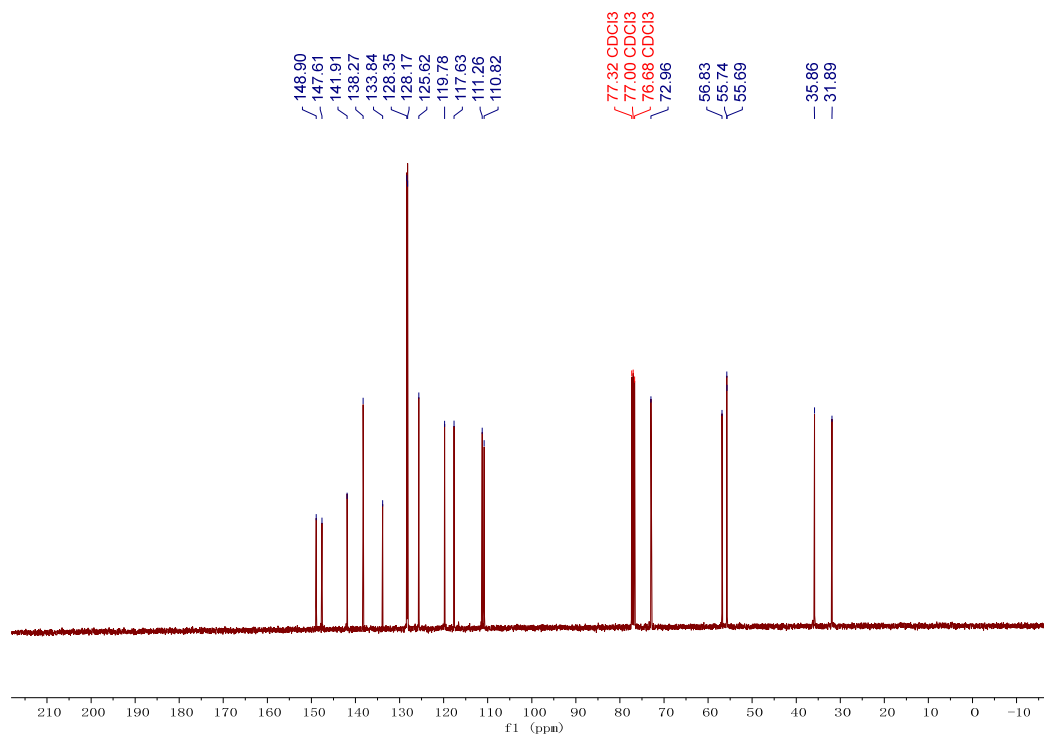


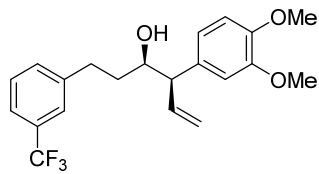
3a, 70% yield

¹H NMR (400 MHz, CDCl₃)



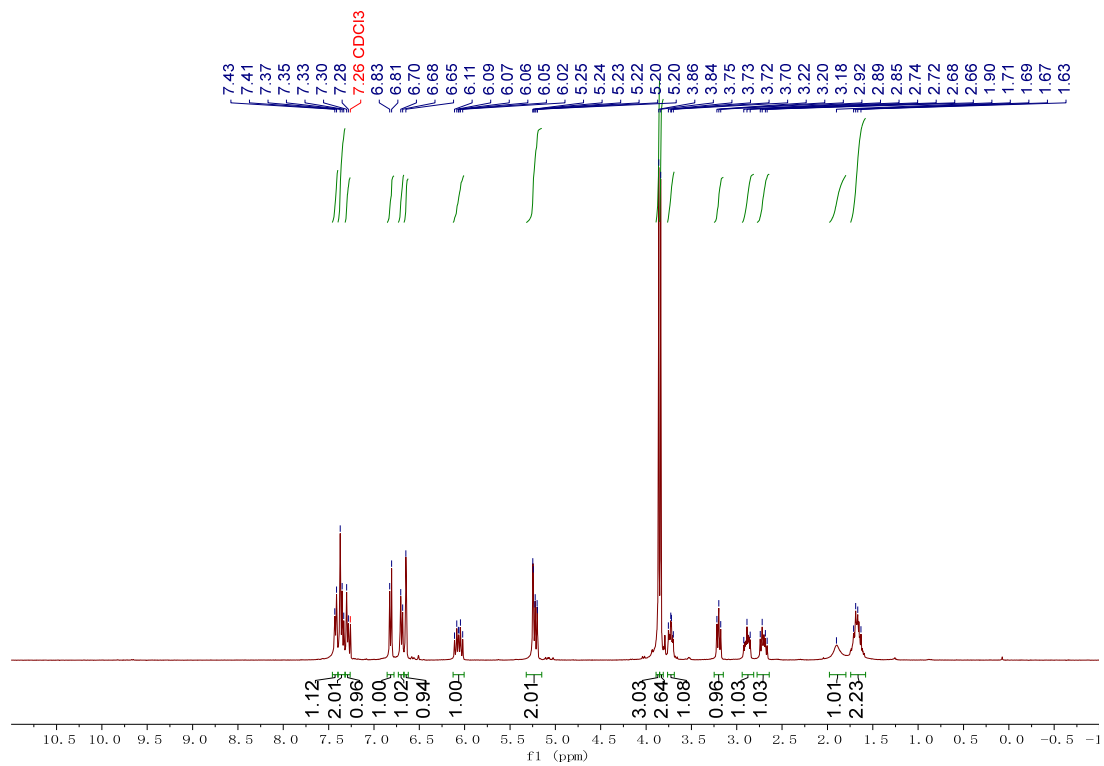
¹³C NMR (101 MHz, CDCl₃)



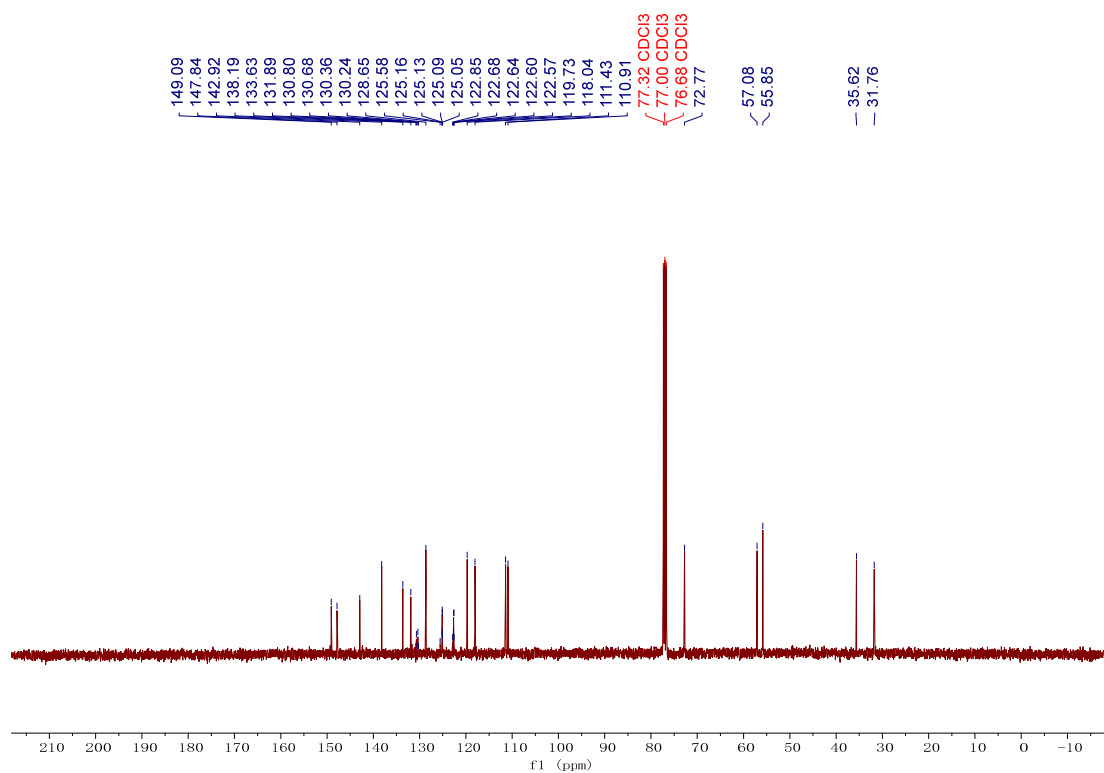


3b, 64% yield

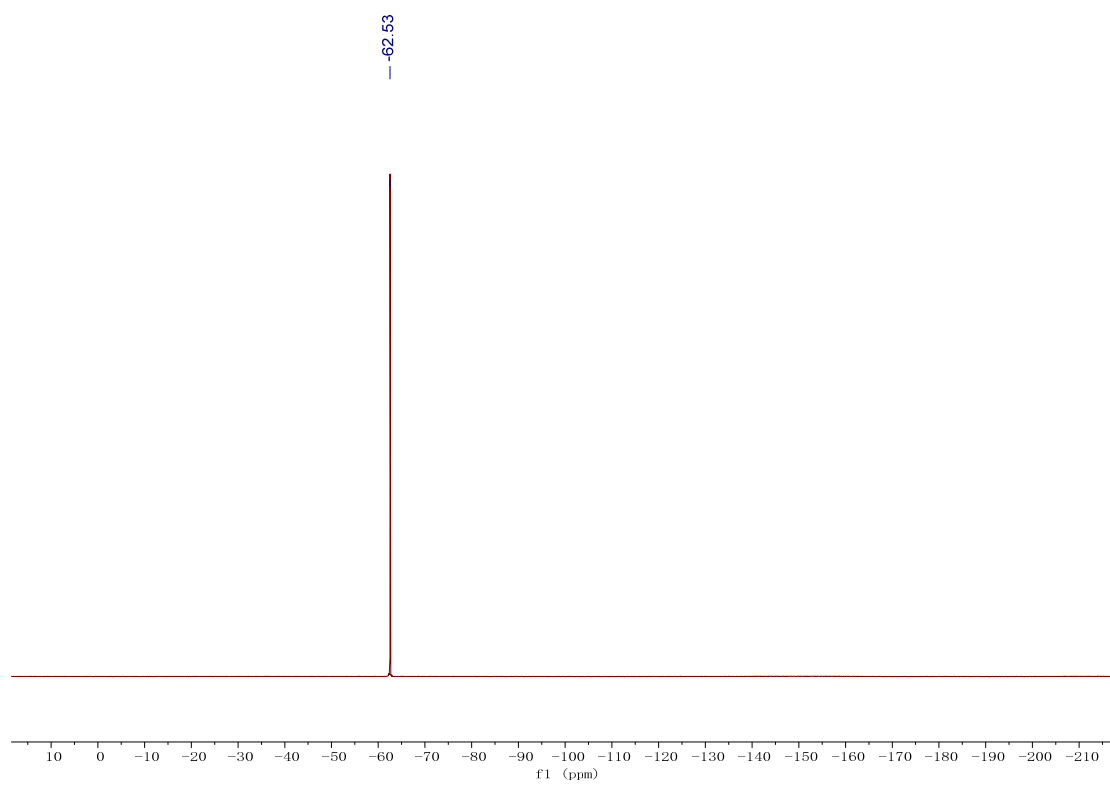
$^1\text{H NMR}$ (400 MHz, CDCl_3)

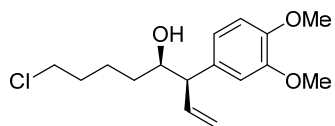


$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



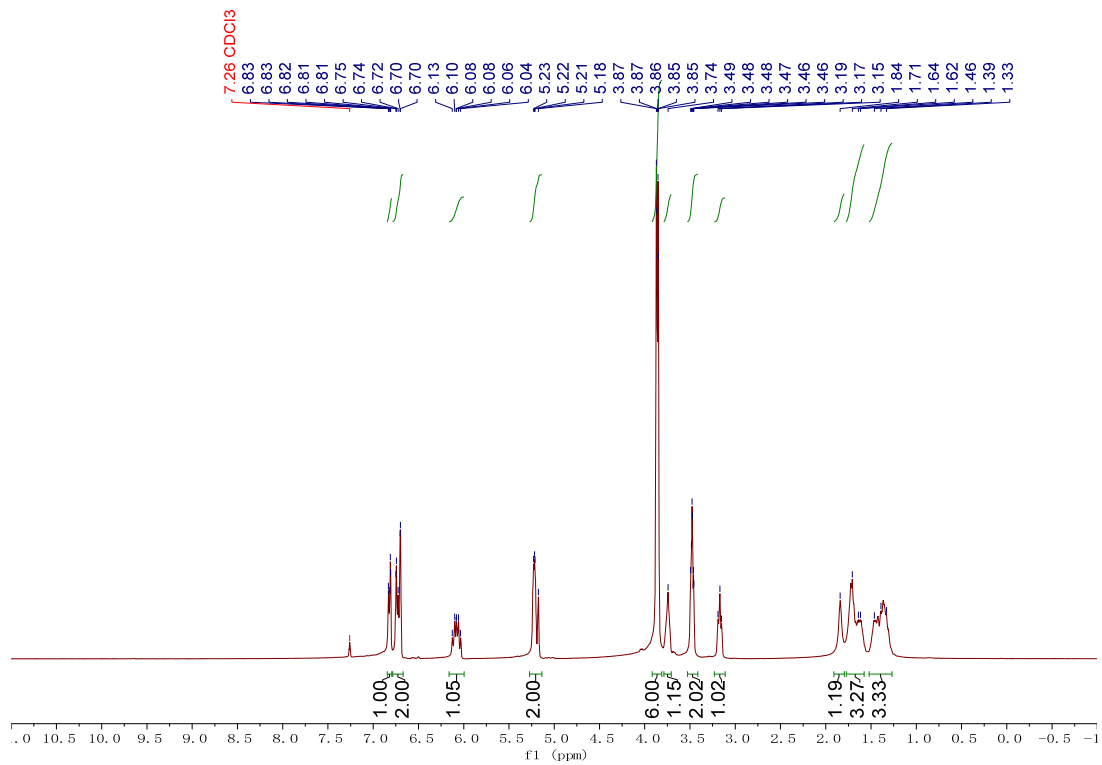
^{19}F NMR (377 MHz, CDCl_3)



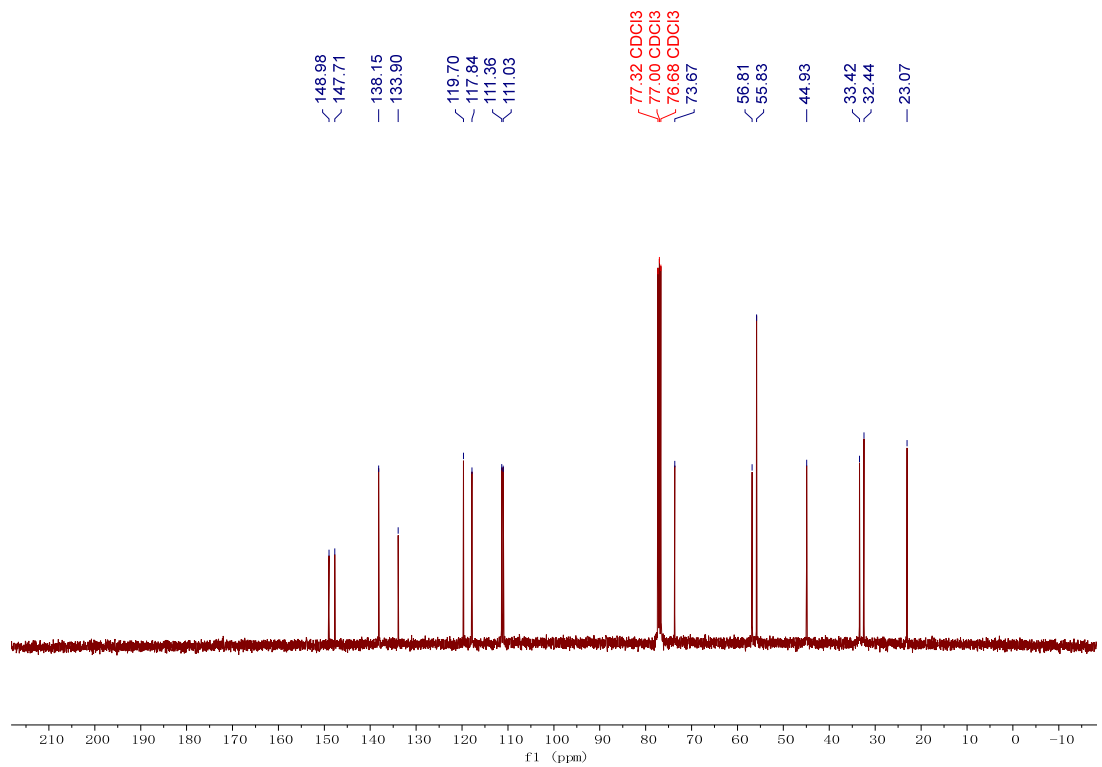


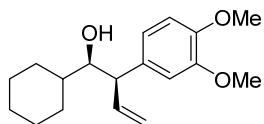
3c, 50% yield

¹H NMR (400 MHz, CDCl₃)



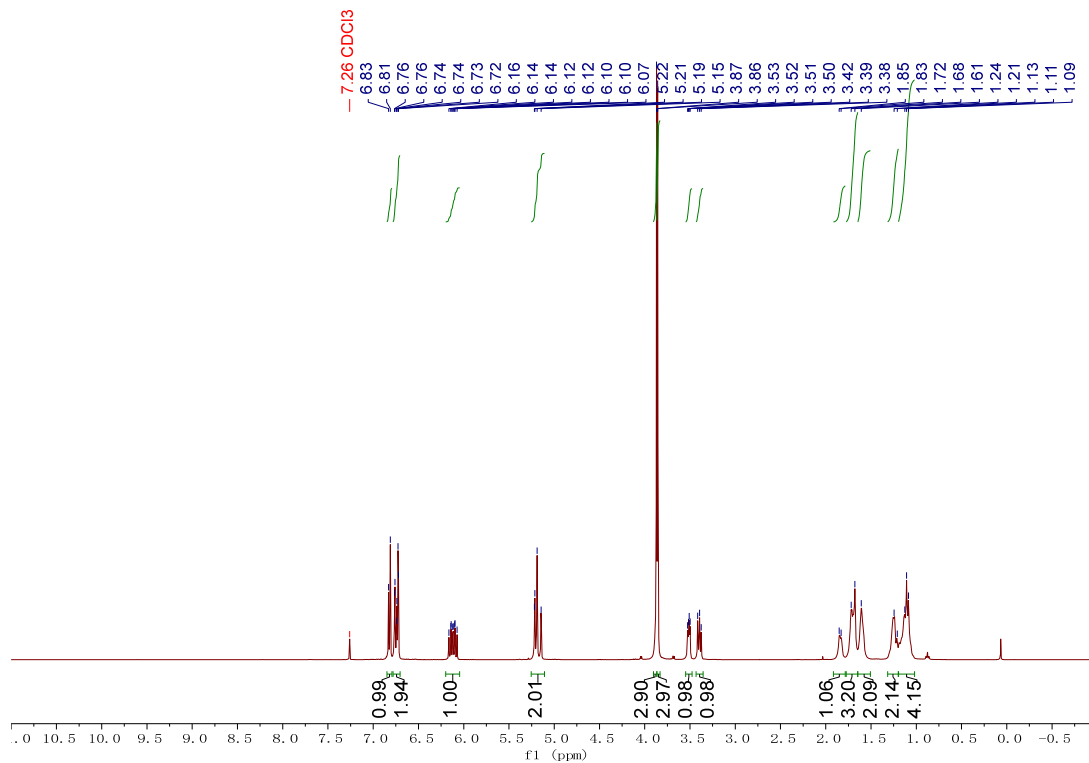
¹³C NMR (101 MHz, CDCl₃)



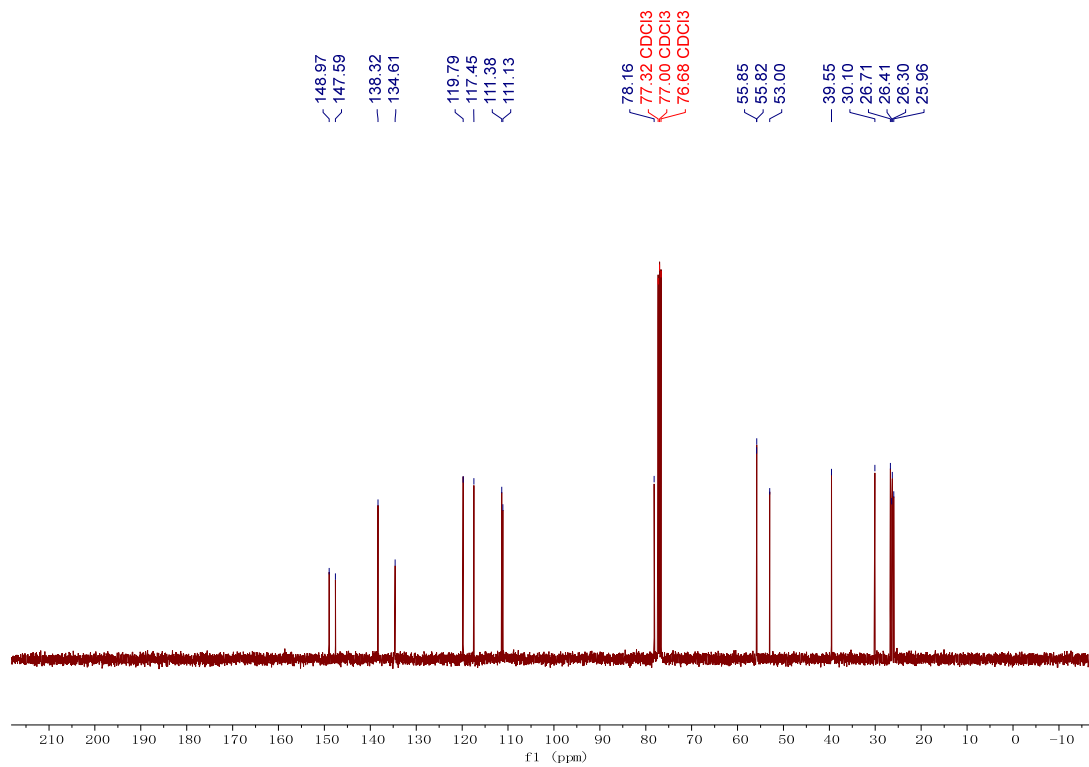


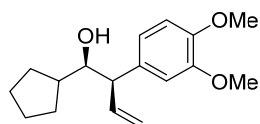
3d, 67%, yield

¹H NMR (400 MHz, CDCl₃)



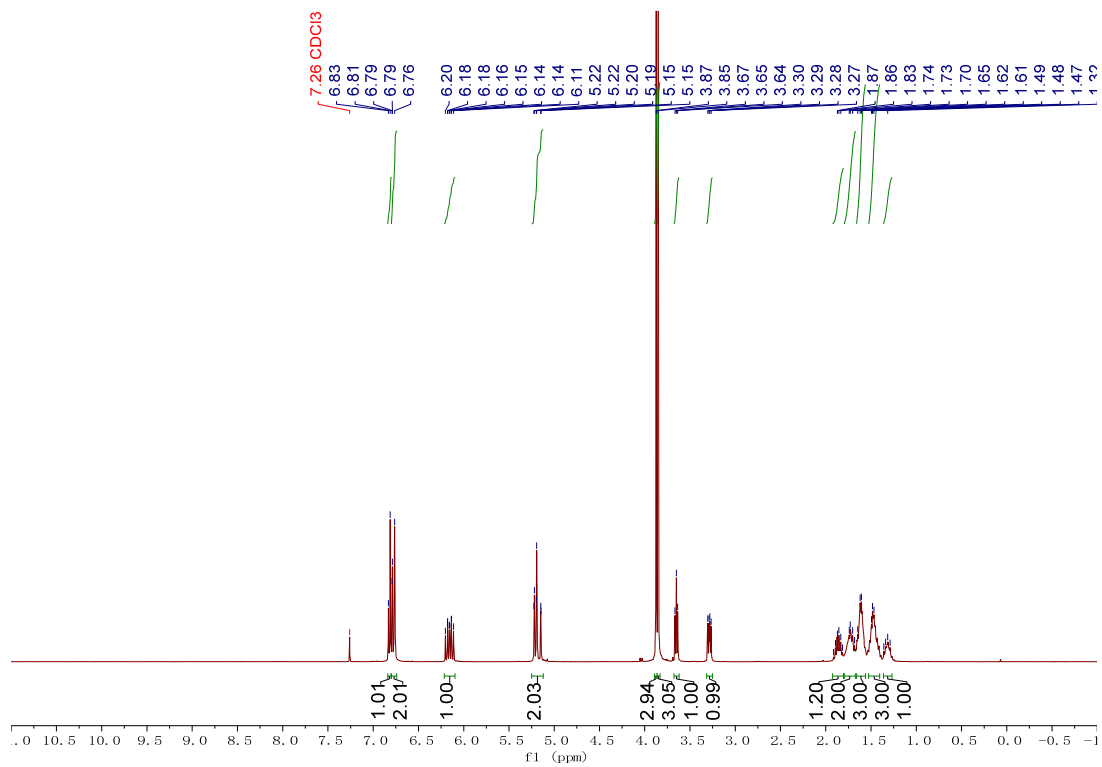
¹³C NMR (101 MHz, CDCl₃)



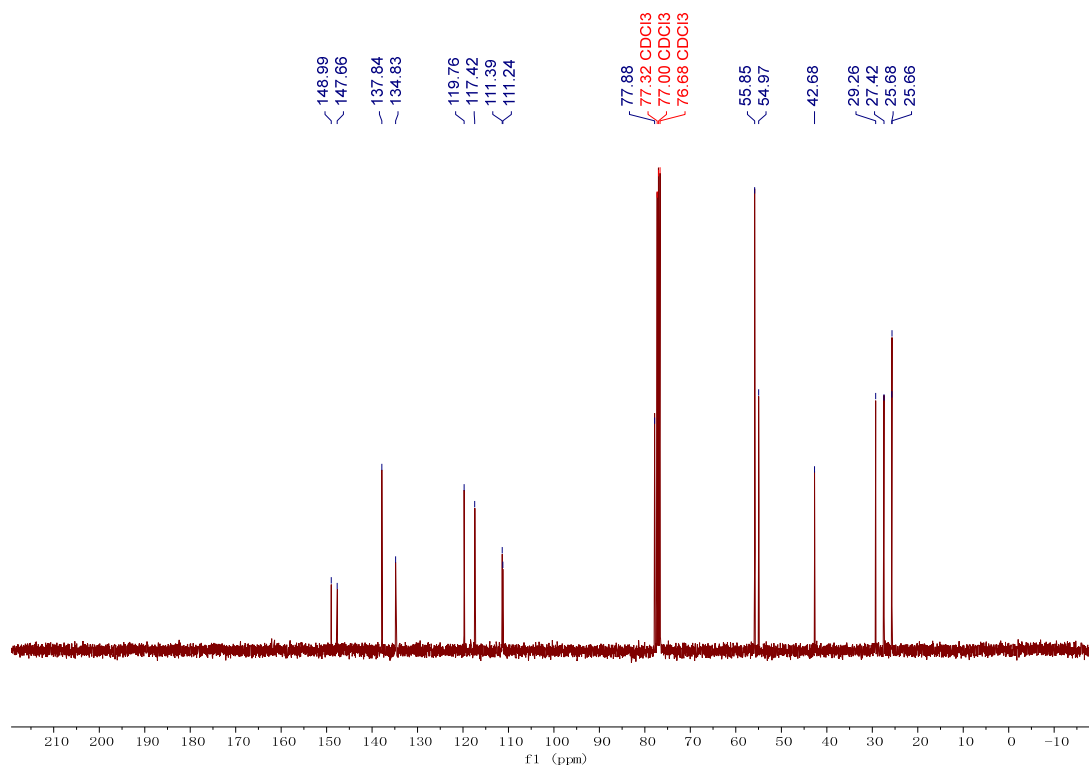


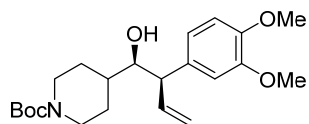
3e, 64% yield

¹H NMR (400 MHz, CDCl₃)



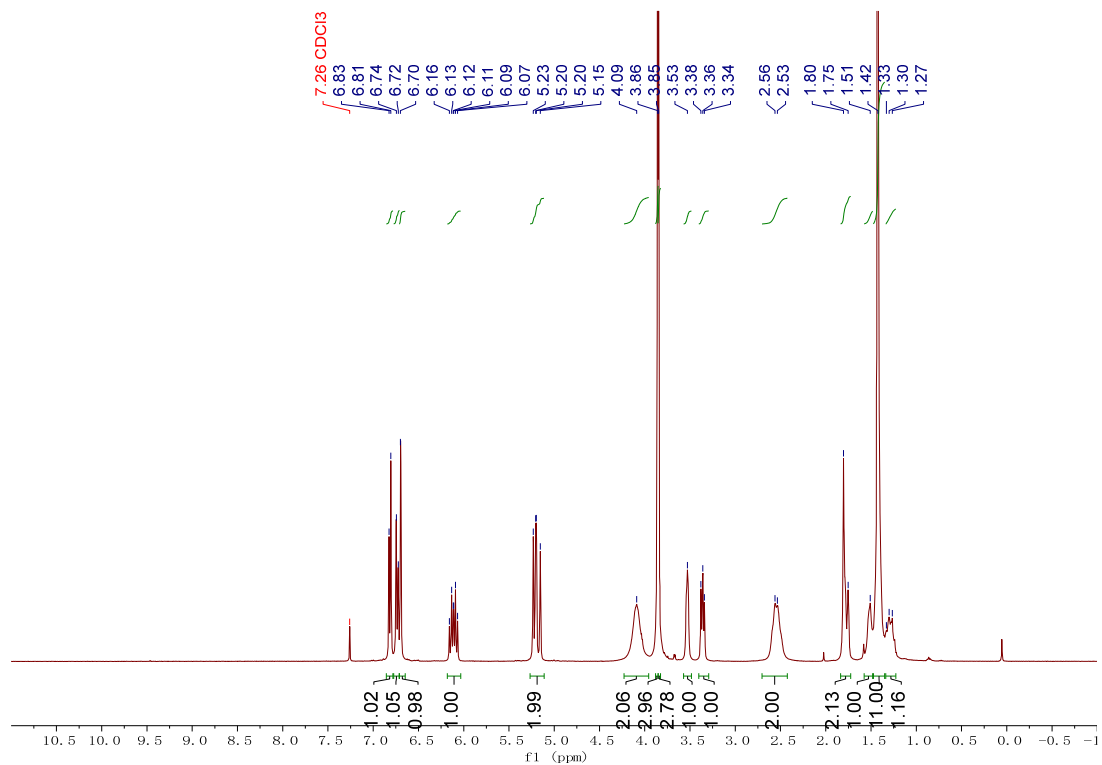
¹³C NMR (101 MHz, CDCl₃)



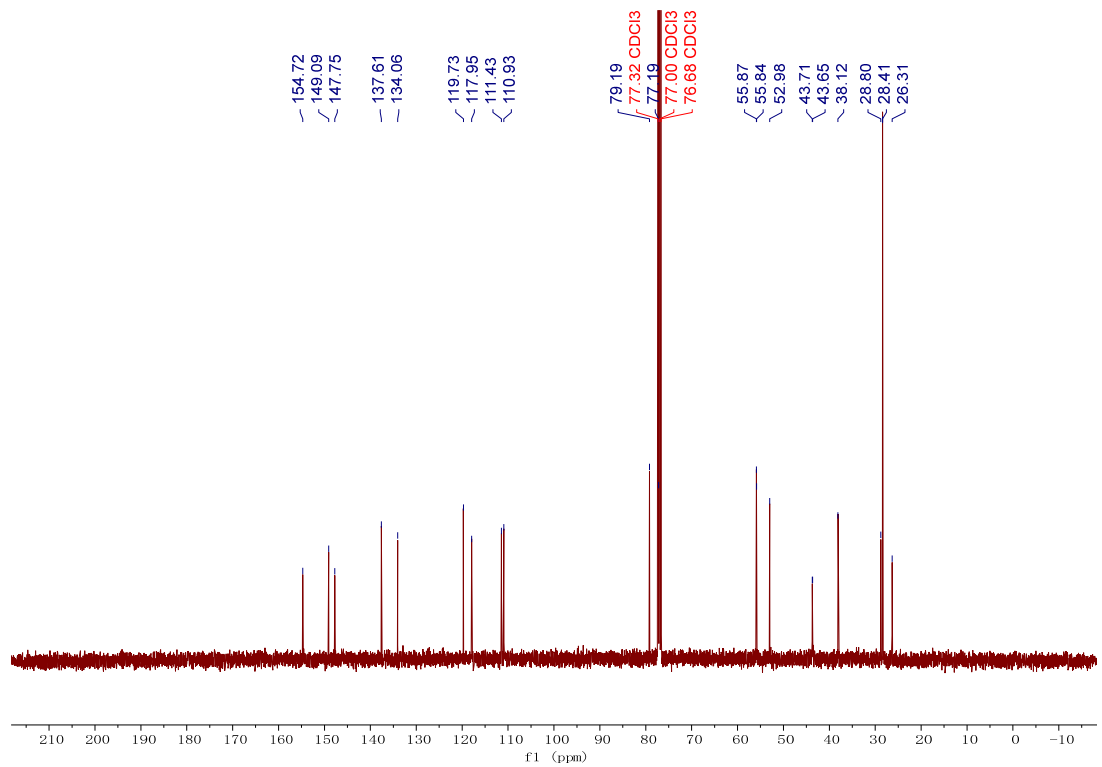


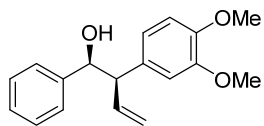
3f, 67% yield

¹H NMR (400 MHz, CDCl₃)

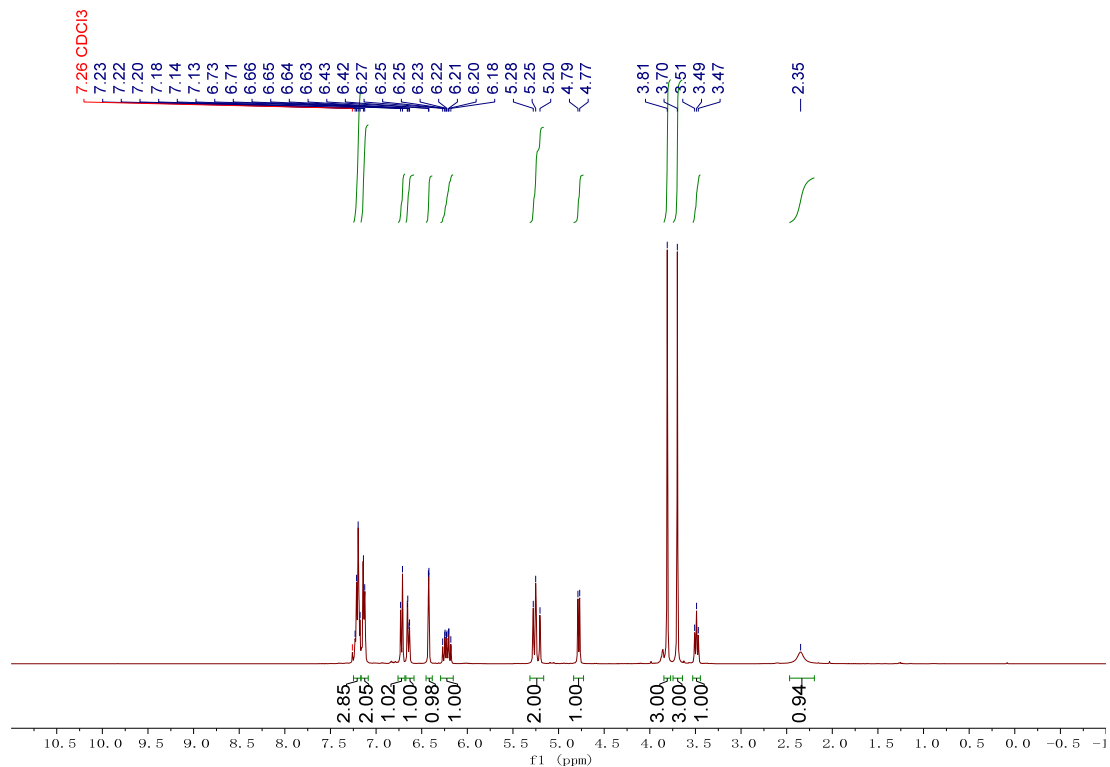


¹³C NMR (101 MHz, CDCl₃)

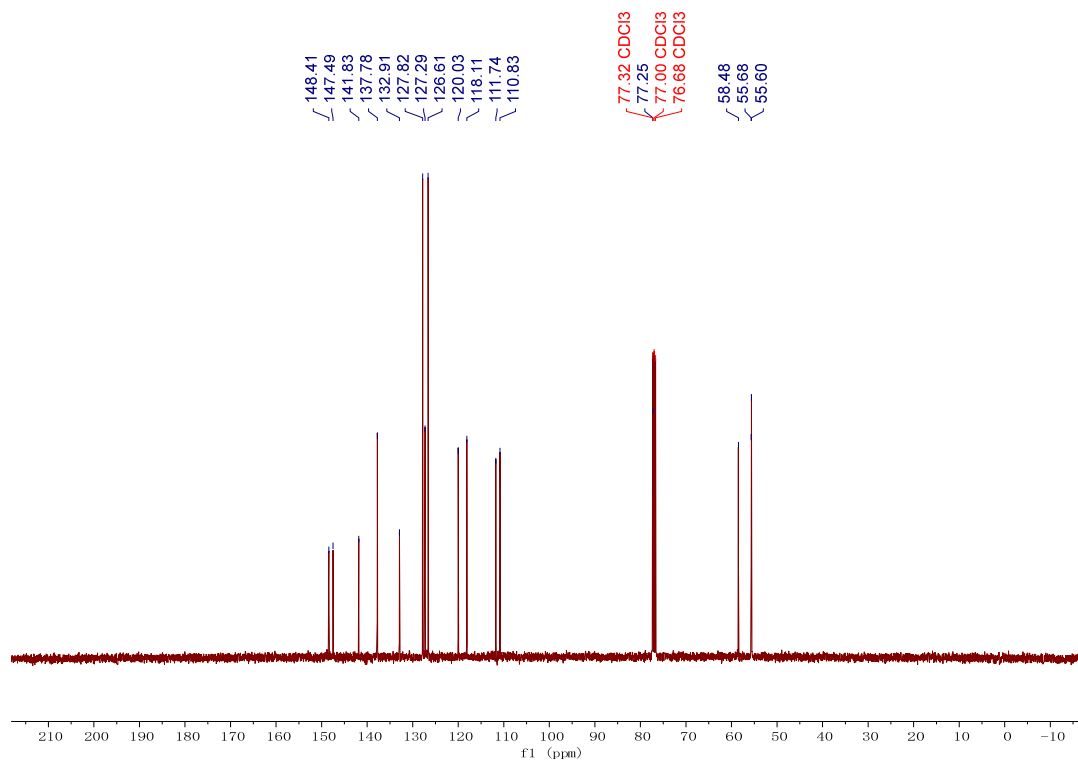


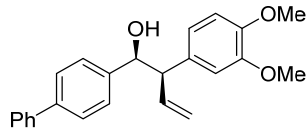


4a, 88% yield $^1\text{H NMR}$ (400 MHz, CDCl_3)



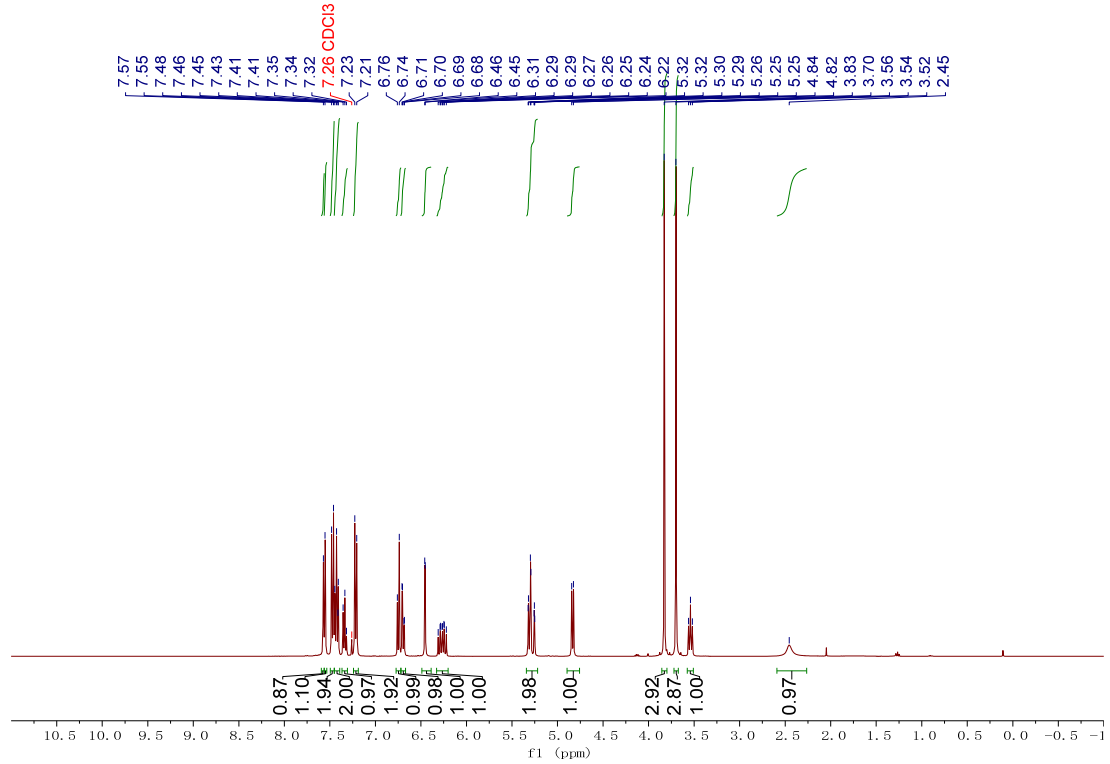
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



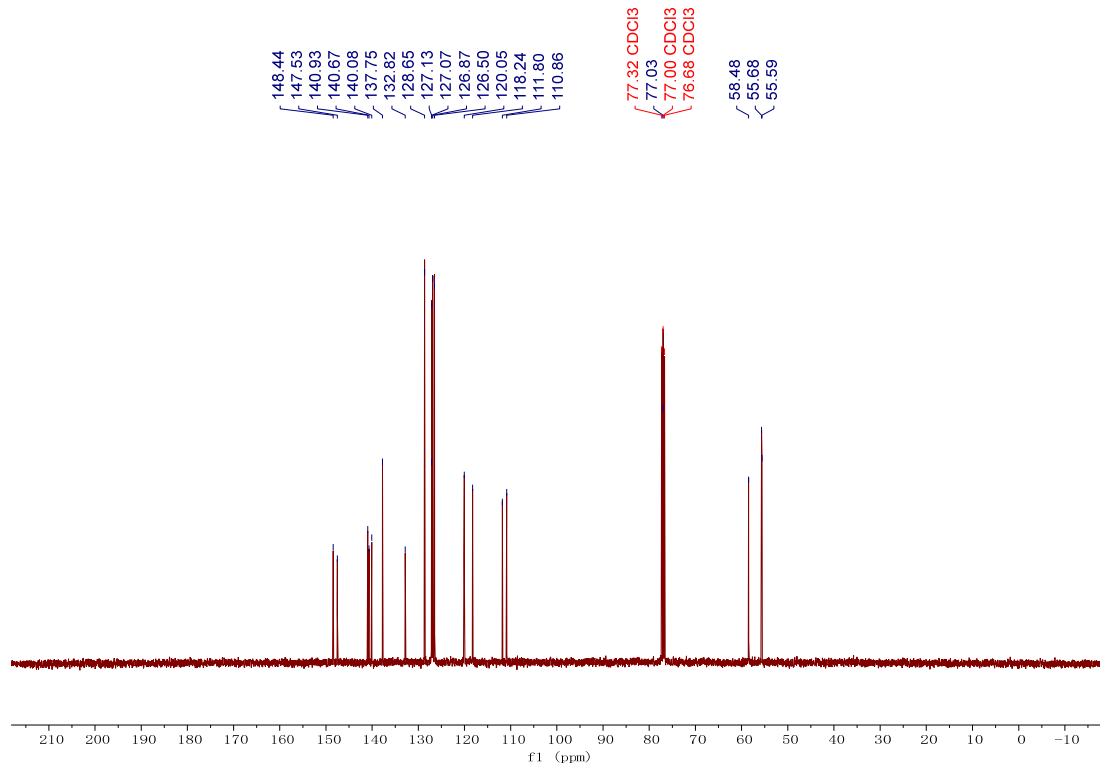


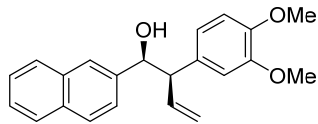
4b, 92% yield

¹H NMR (400 MHz, CDCl₃)



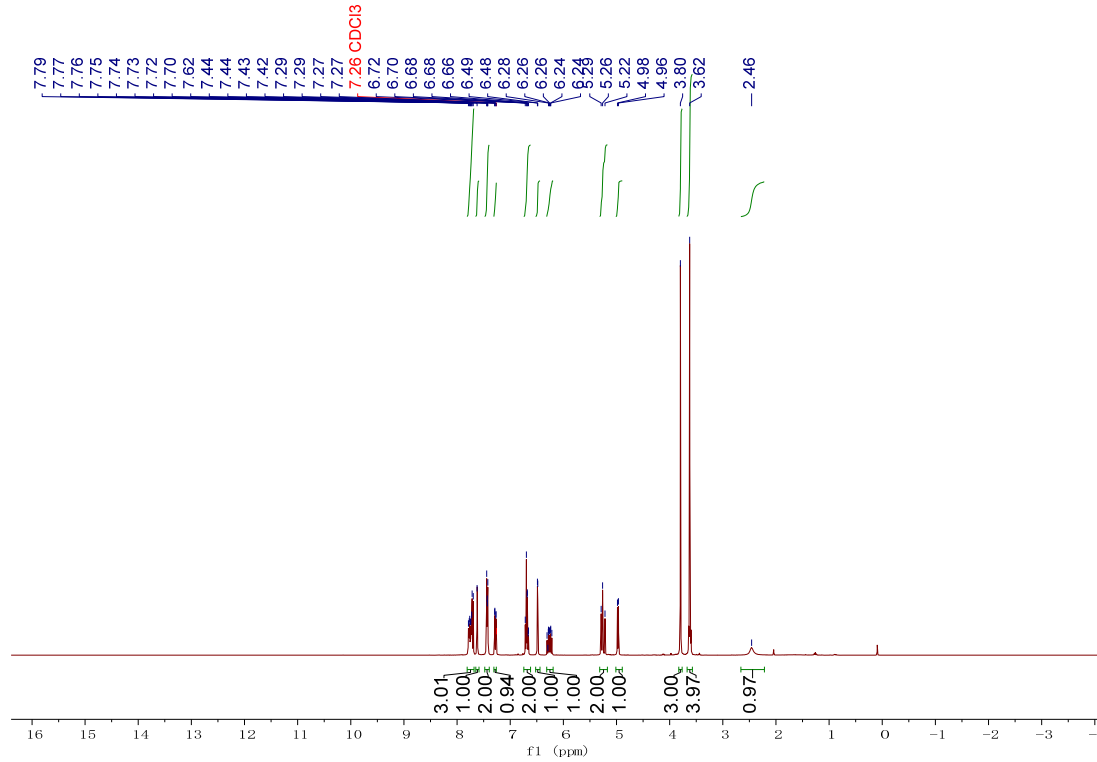
¹³C NMR (101 MHz, CDCl₃)



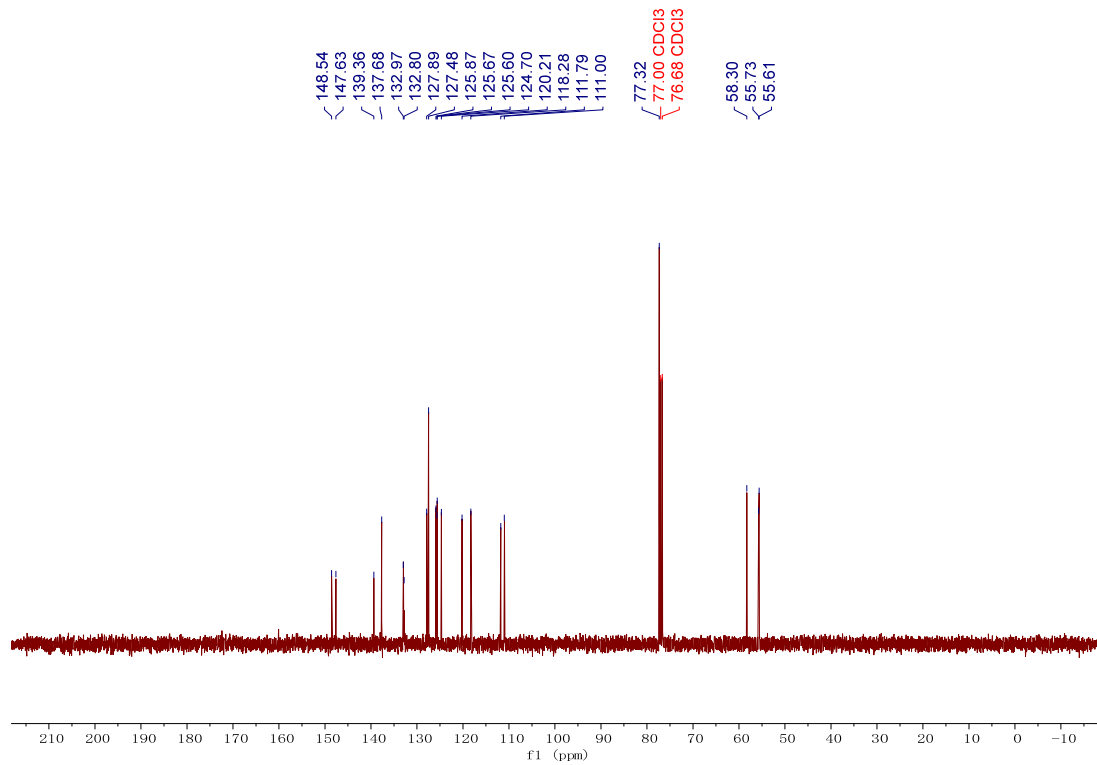


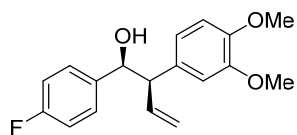
4c, 90% yield

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



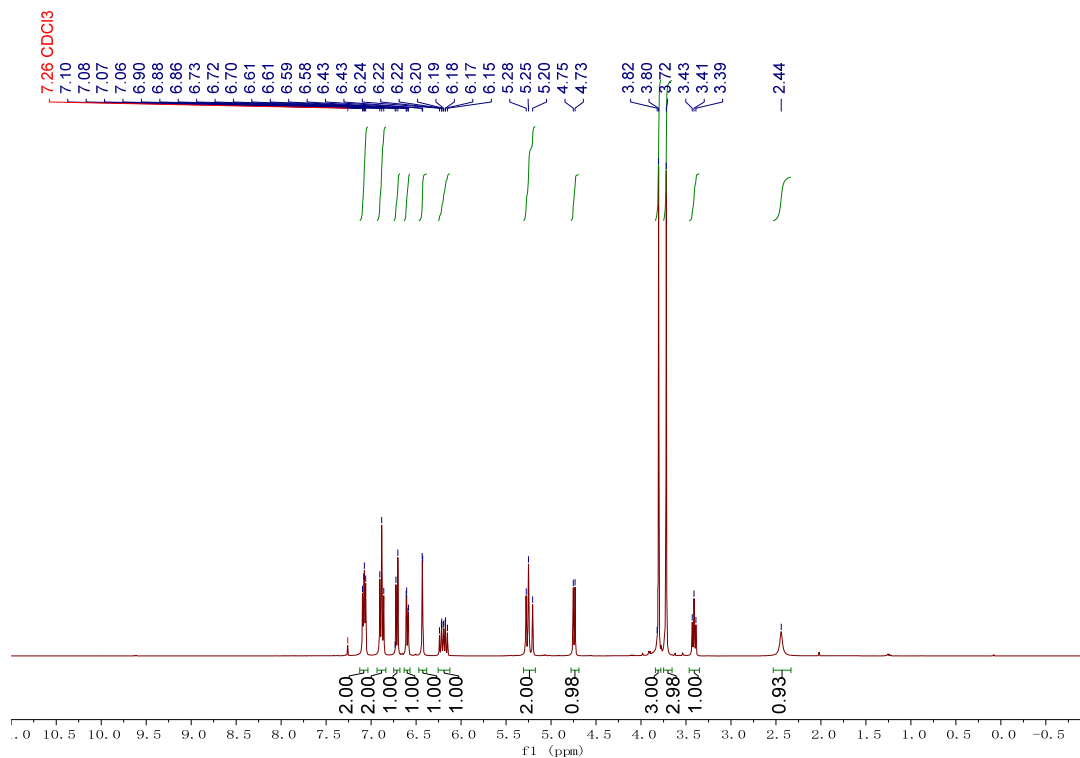
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



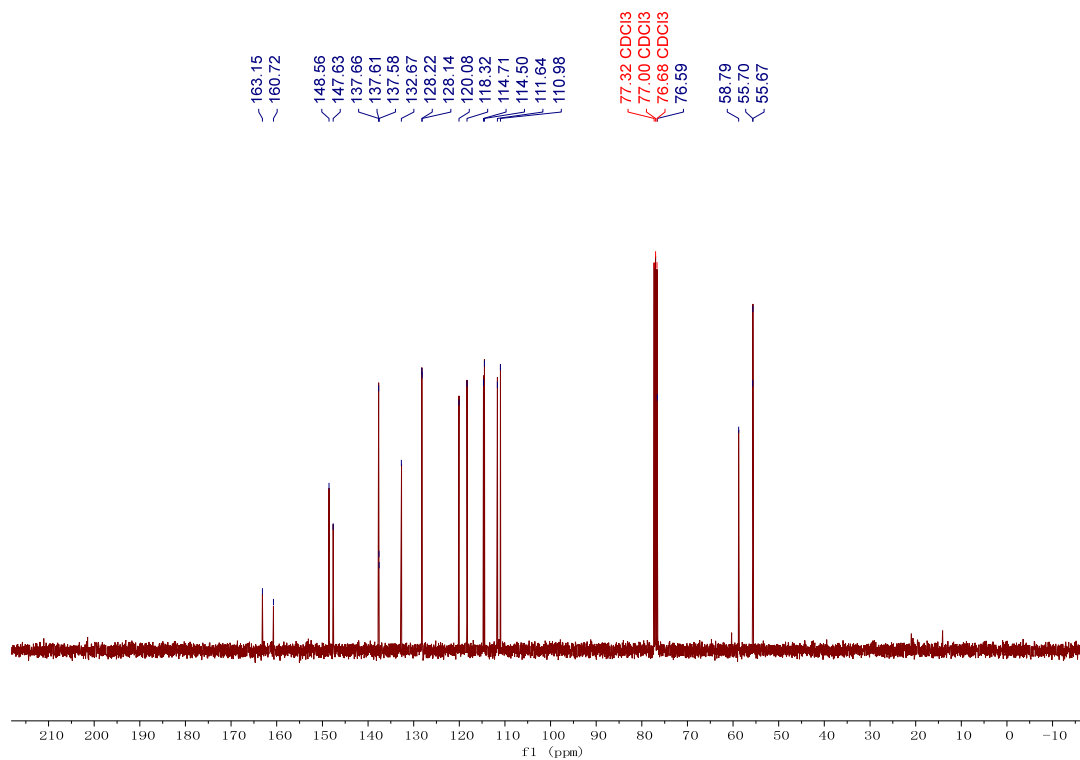


4d, 50% yield

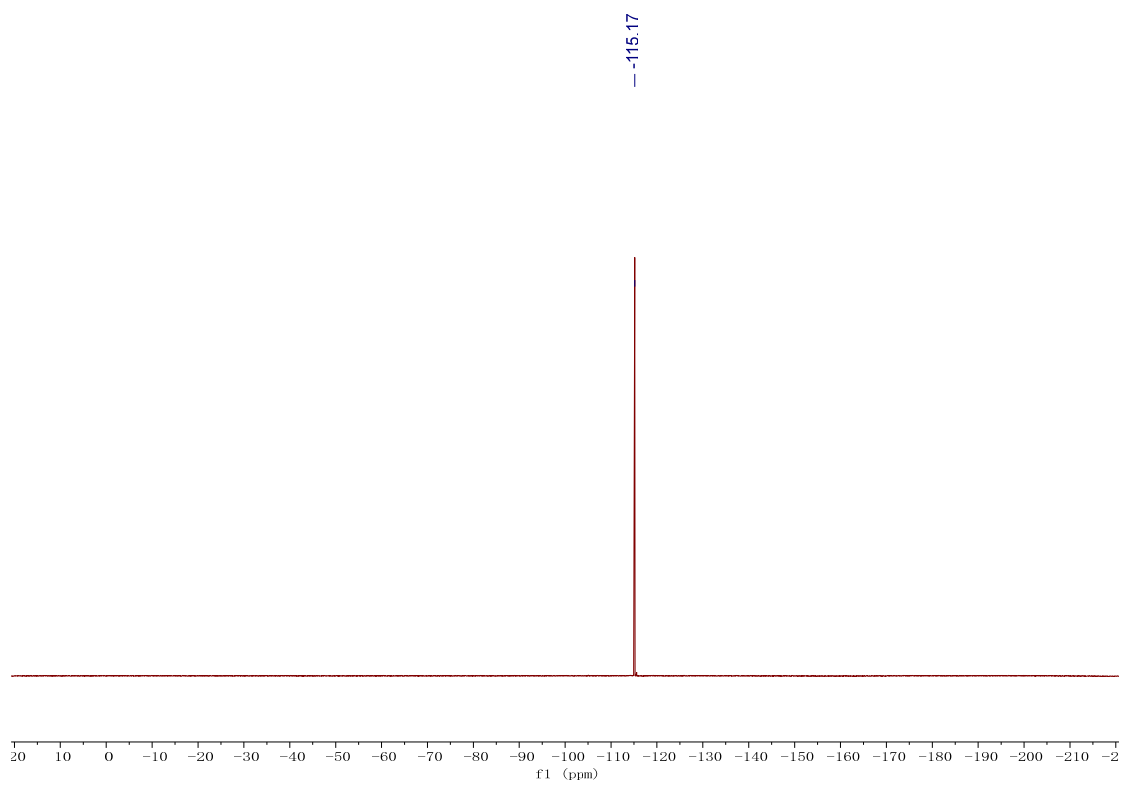
¹H NMR (400 MHz, CDCl₃)

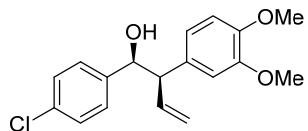


¹³C NMR (101 MHz, CDCl₃)



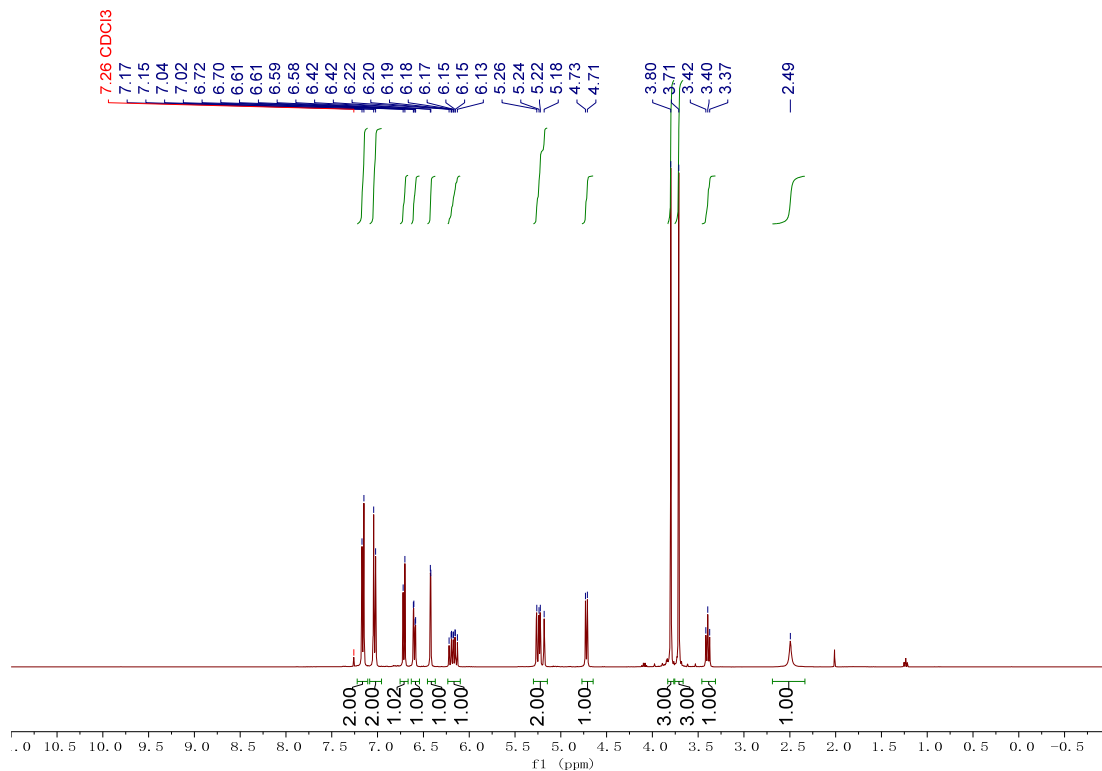
^{19}F NMR (377 MHz, CDCl_3)



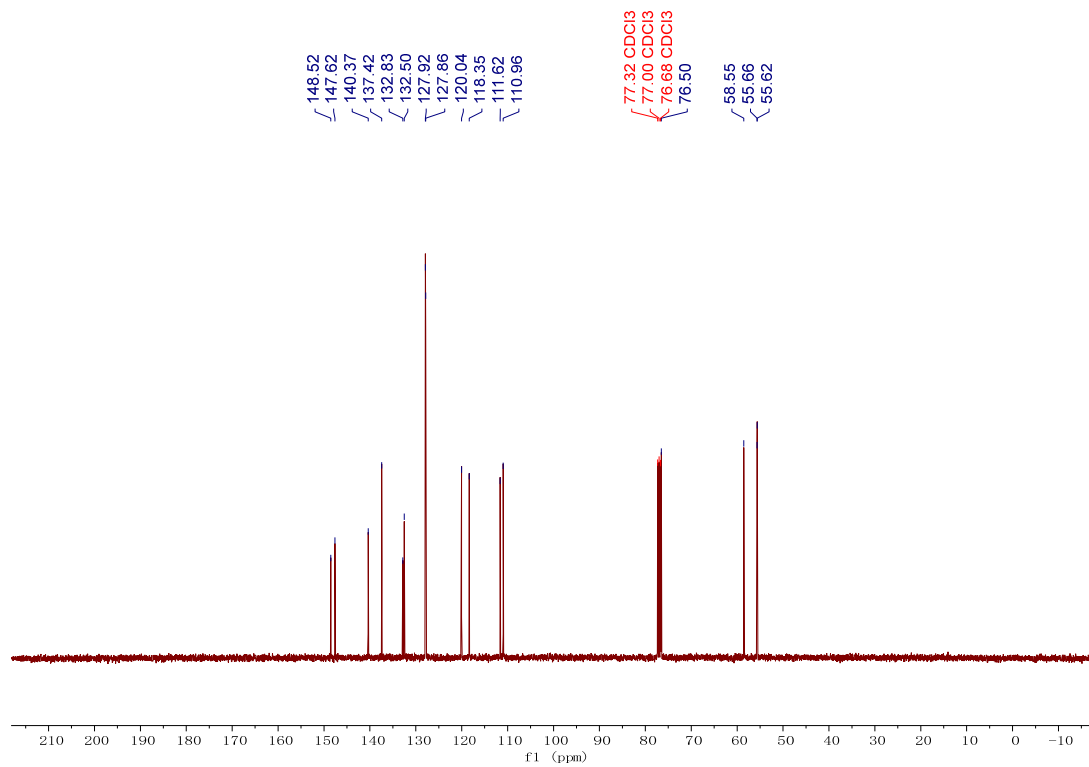


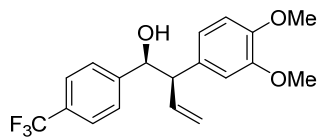
4e, 91% yield

^1H NMR (400 MHz, CDCl_3)



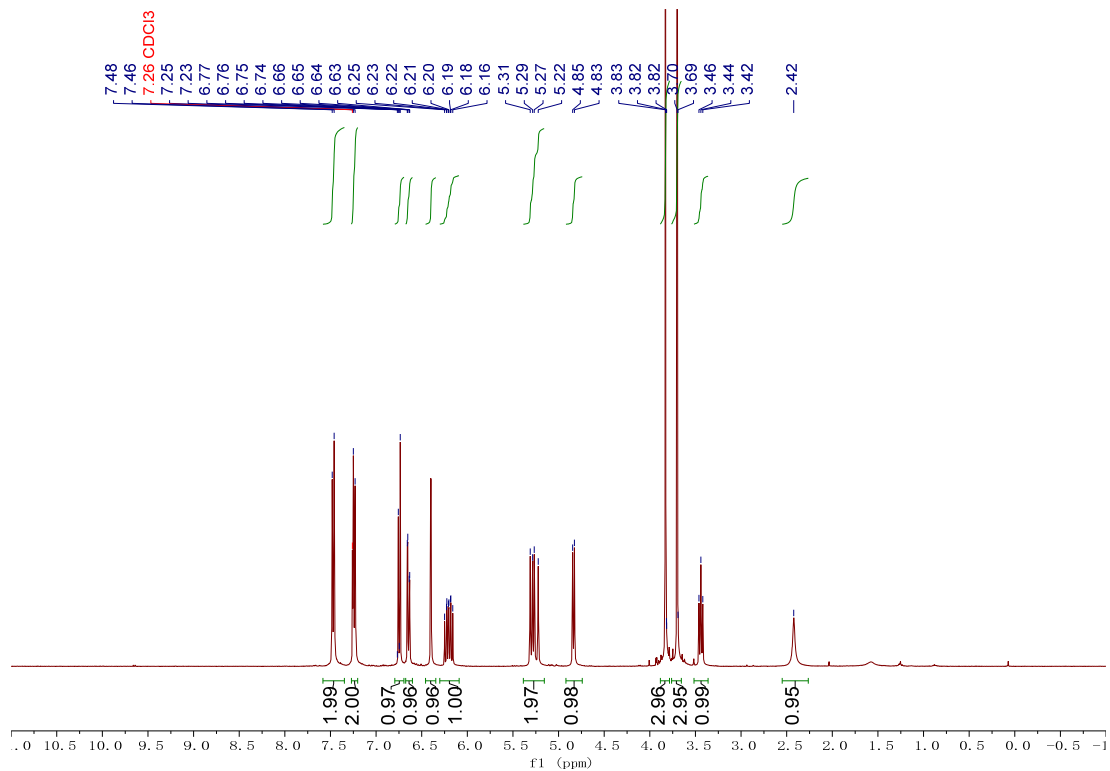
^{13}C NMR (101 MHz, CDCl_3)



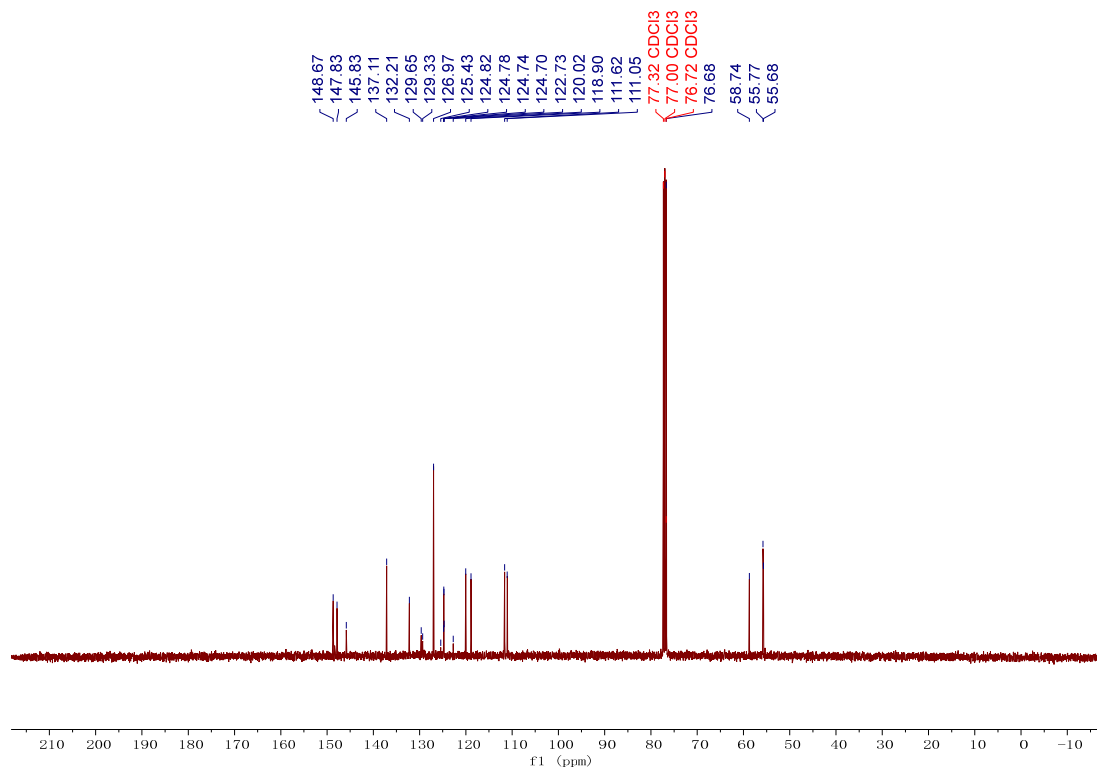


4f, 55% yield

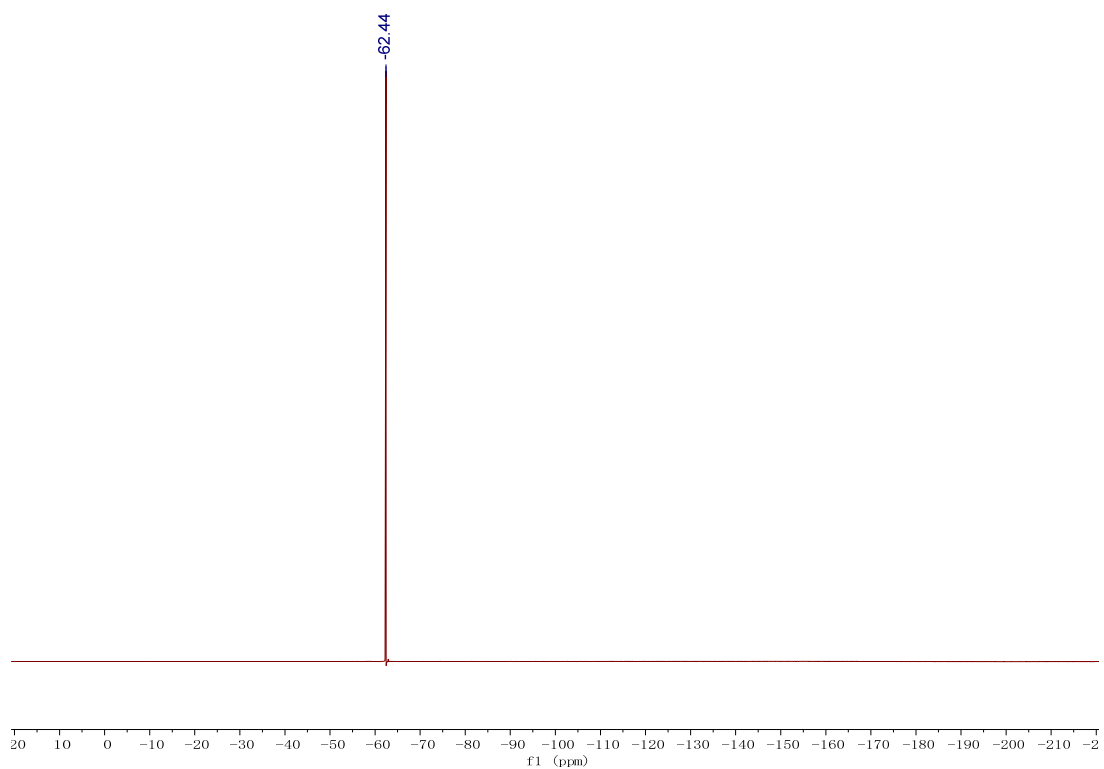
$^1\text{H NMR}$ (400 MHz, CDCl_3)

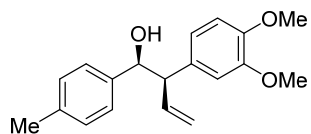


$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



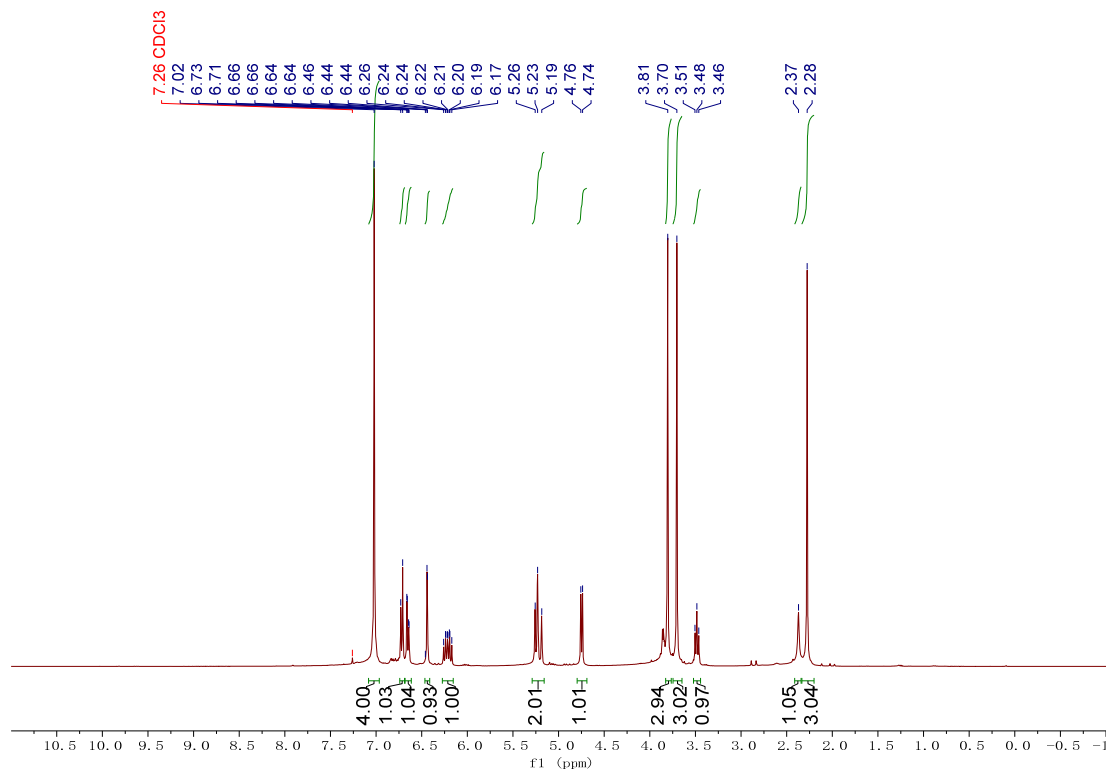
¹⁹F NMR (377 MHz, CDCl₃)



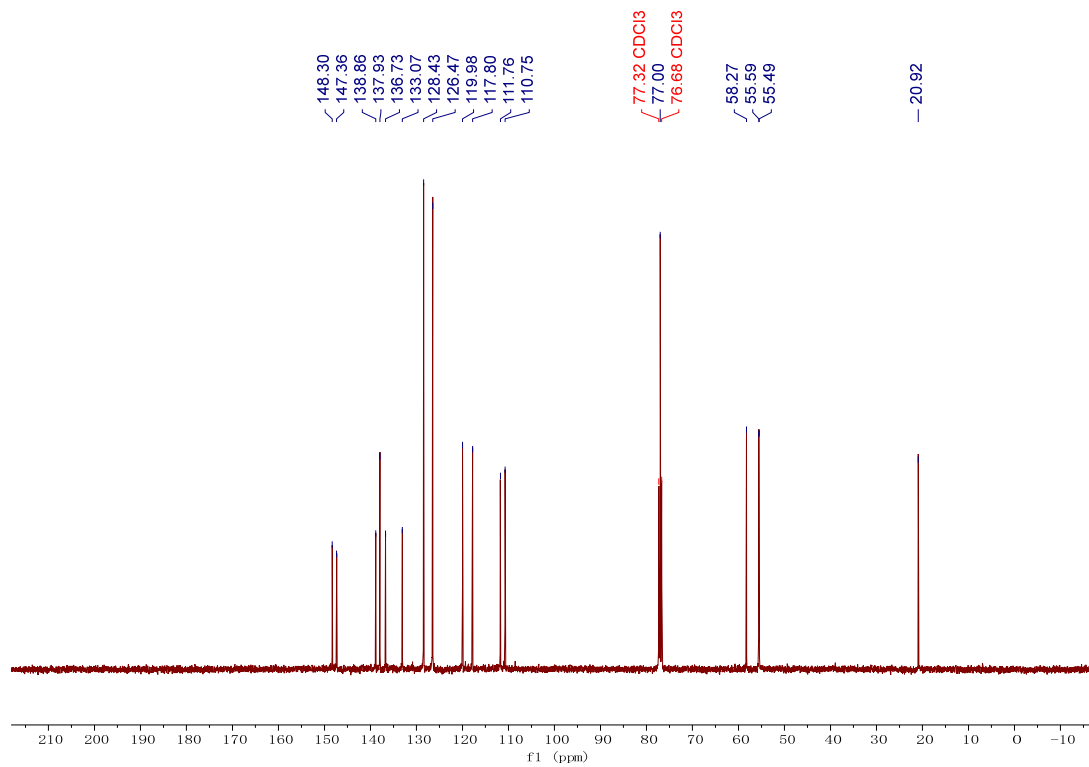


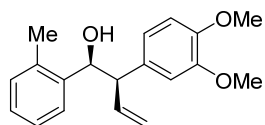
4g, 75% yield

¹H NMR (400 MHz, CDCl₃)



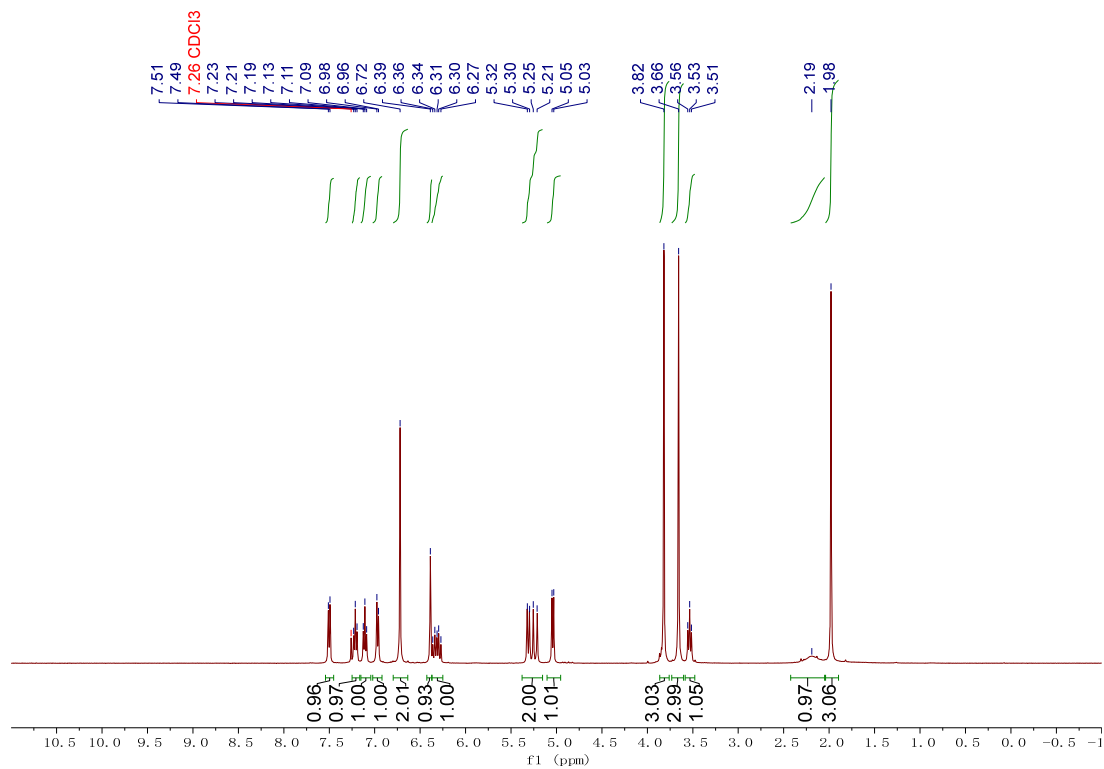
¹³C NMR (101 MHz, CDCl₃)



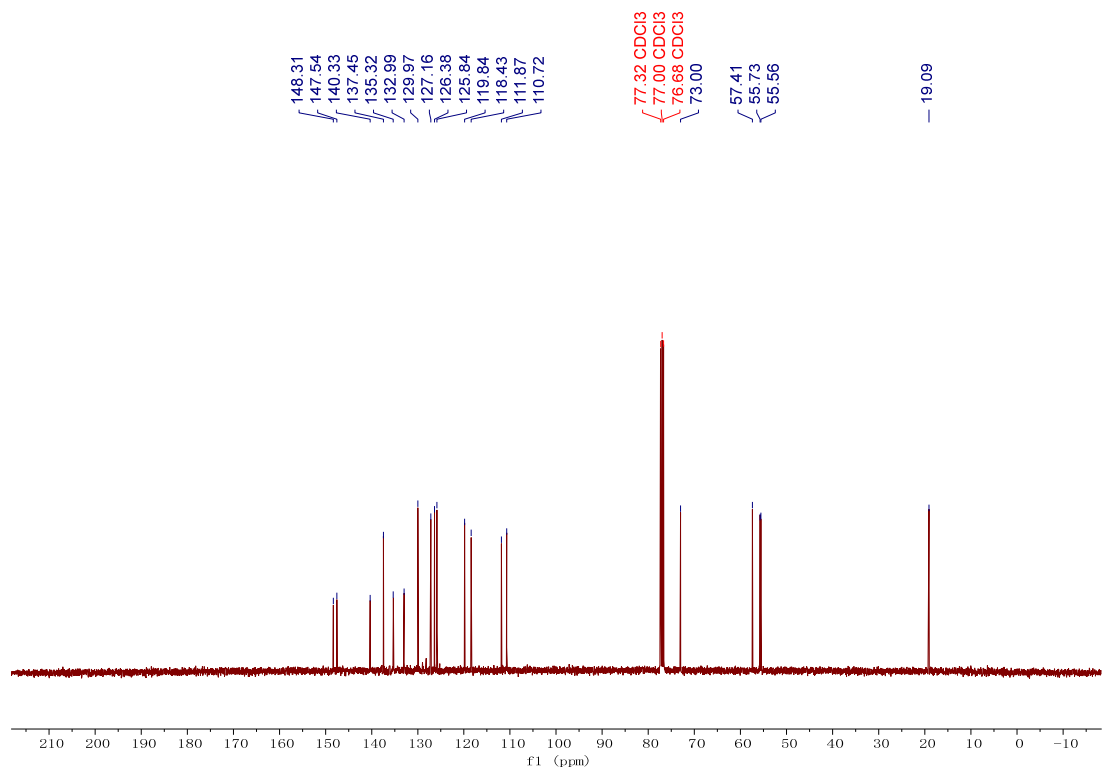


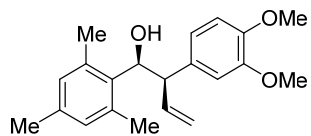
4h, 87% yield

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



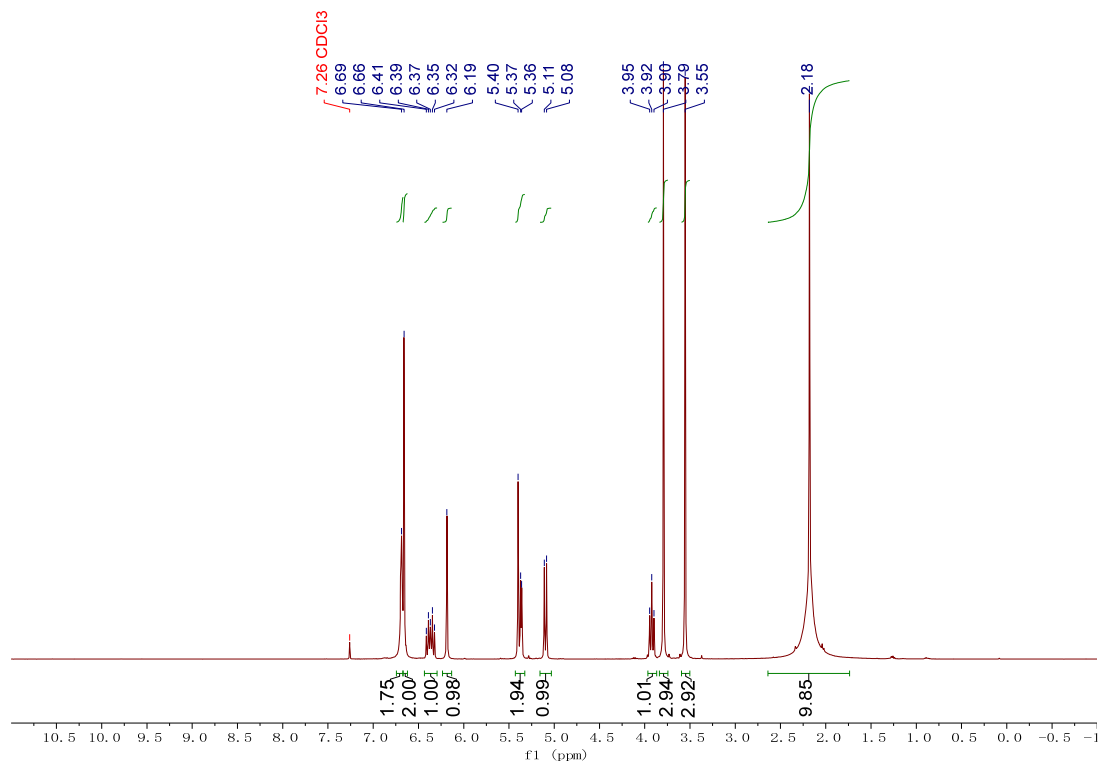
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



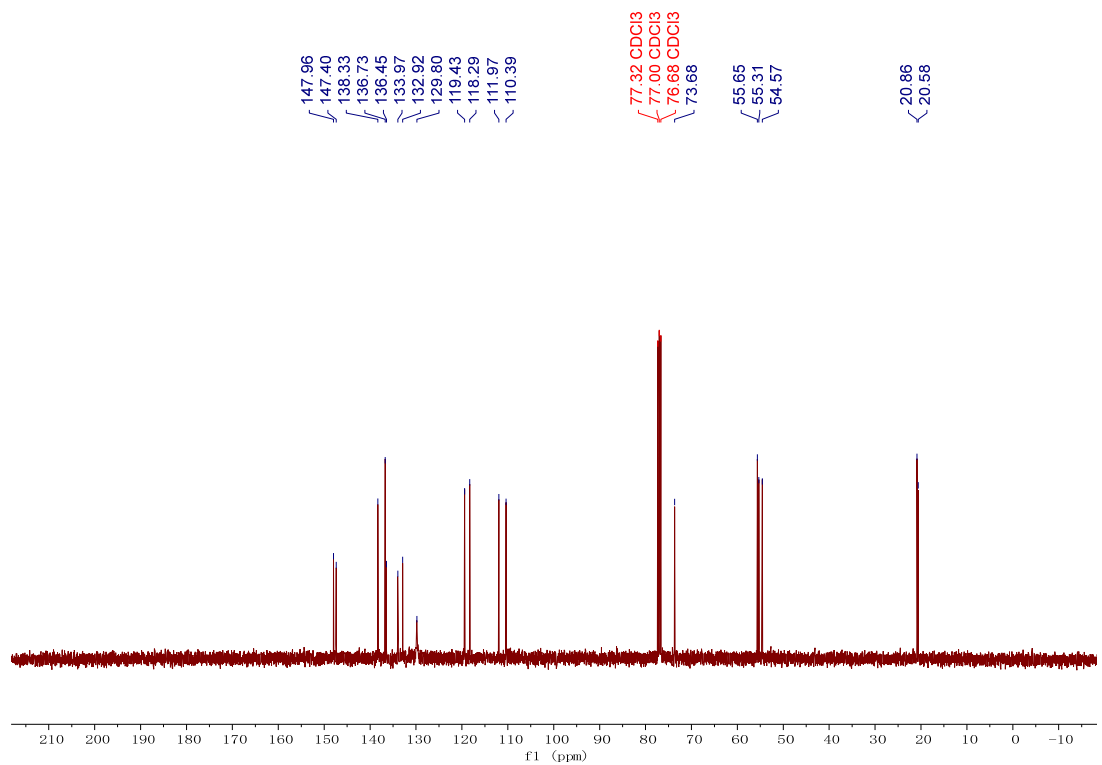


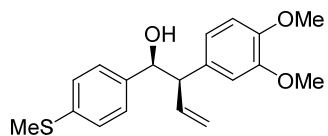
4i, 54% yield

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



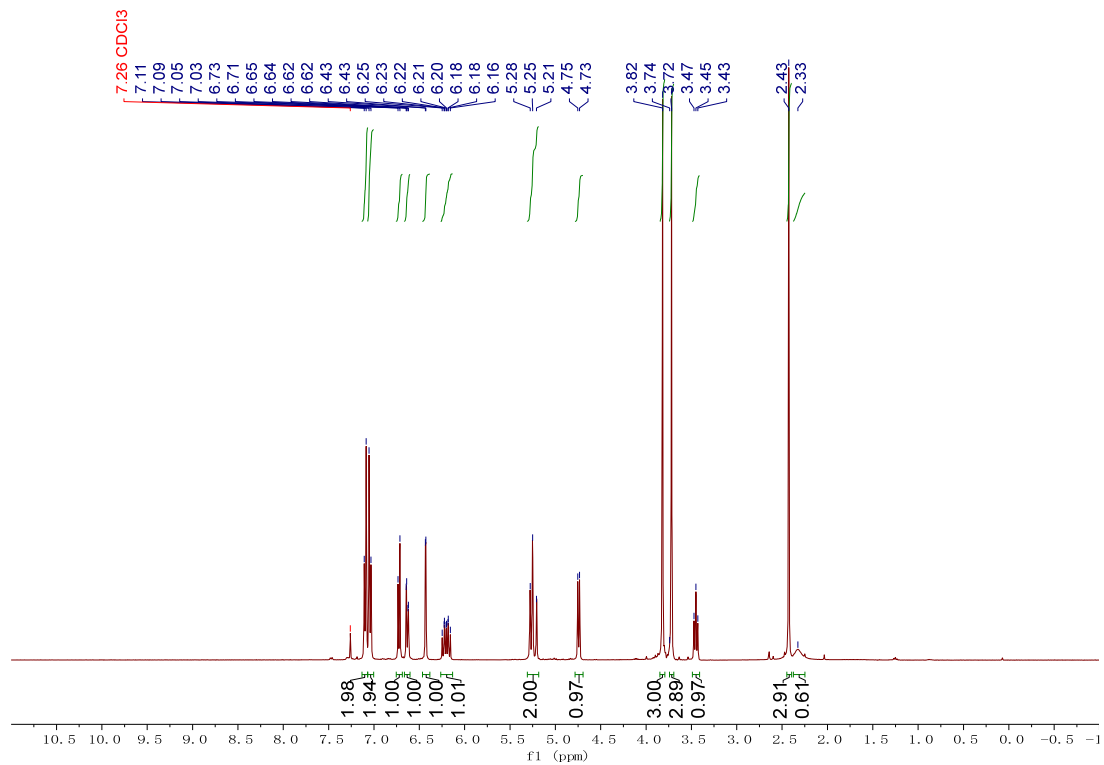
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



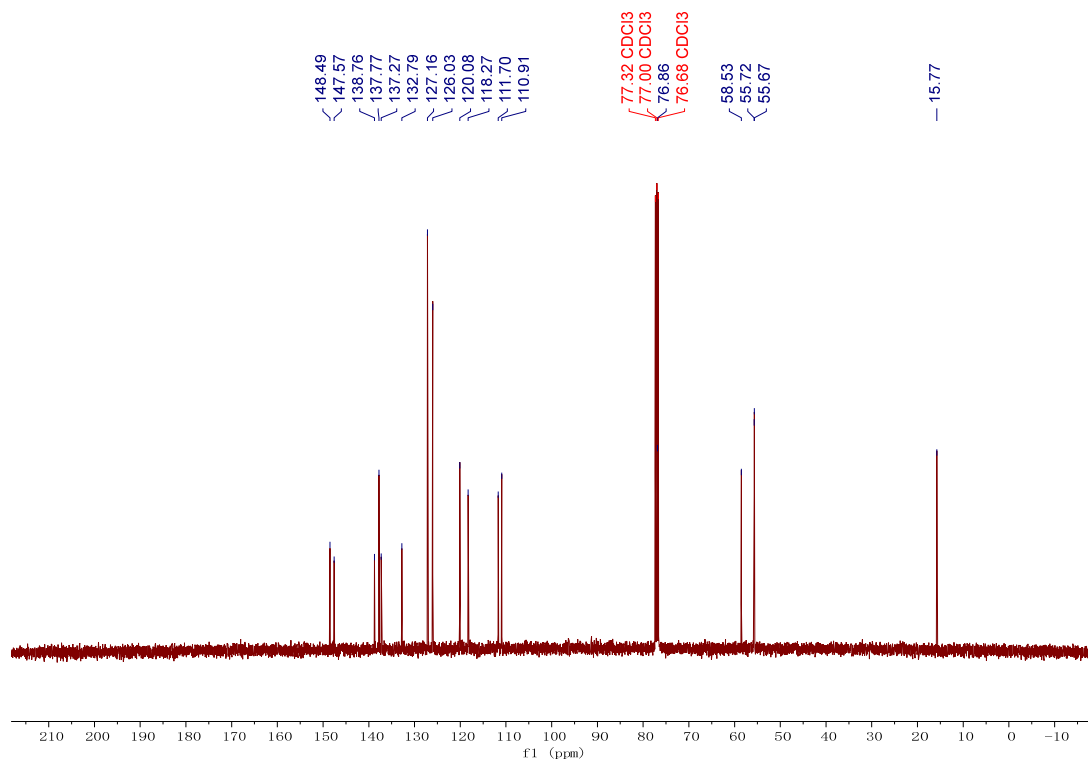


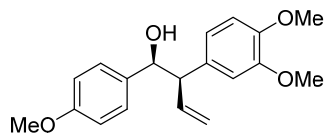
4j, 64% yield

¹H NMR (400 MHz, CDCl₃)



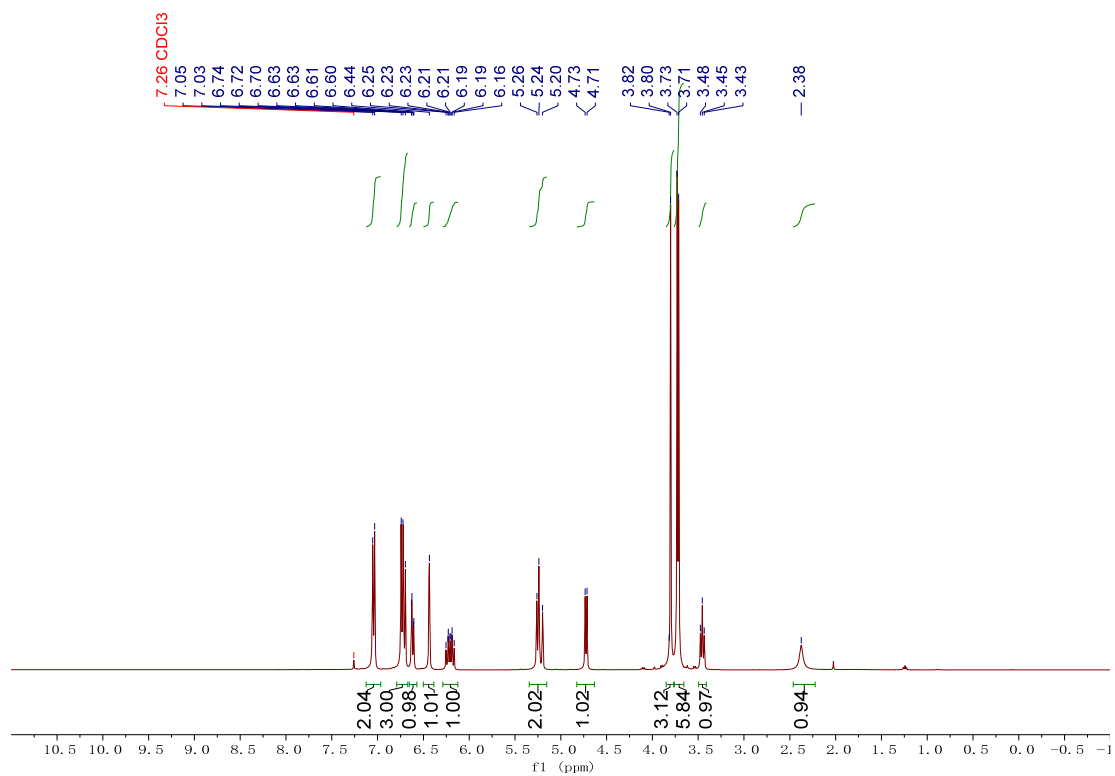
¹³C NMR (101 MHz, CDCl₃)



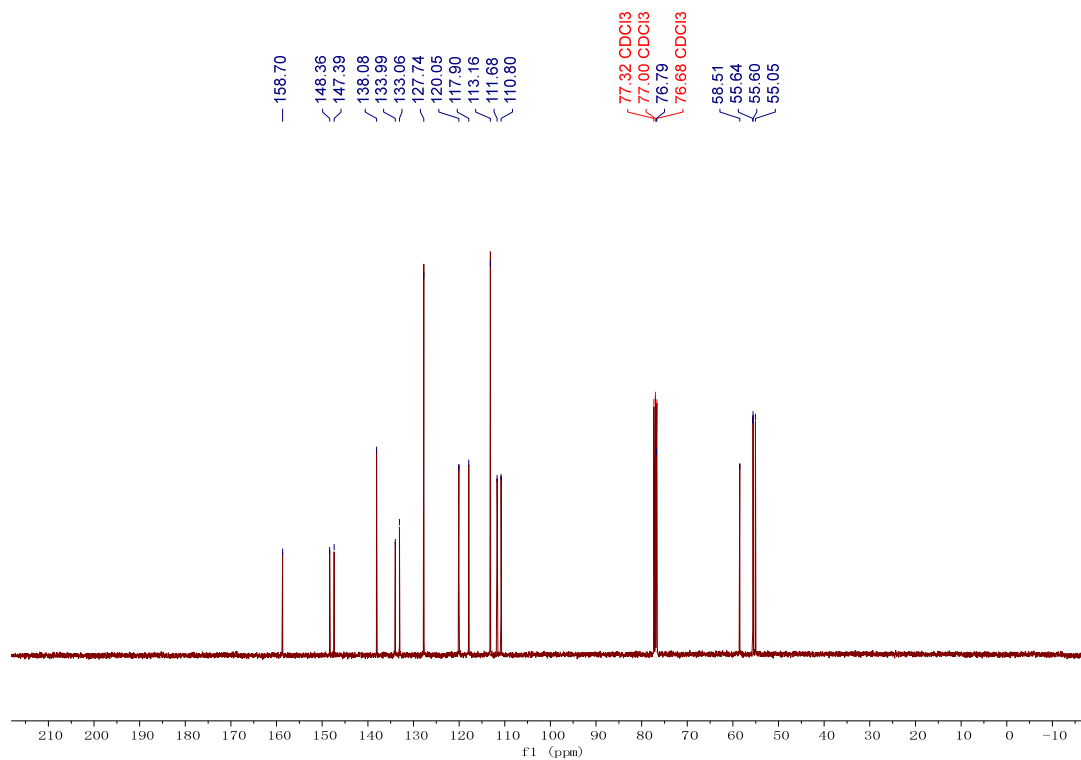


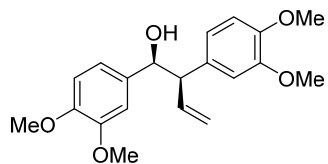
4k, 78% yield

¹H NMR (400 MHz, CDCl₃)



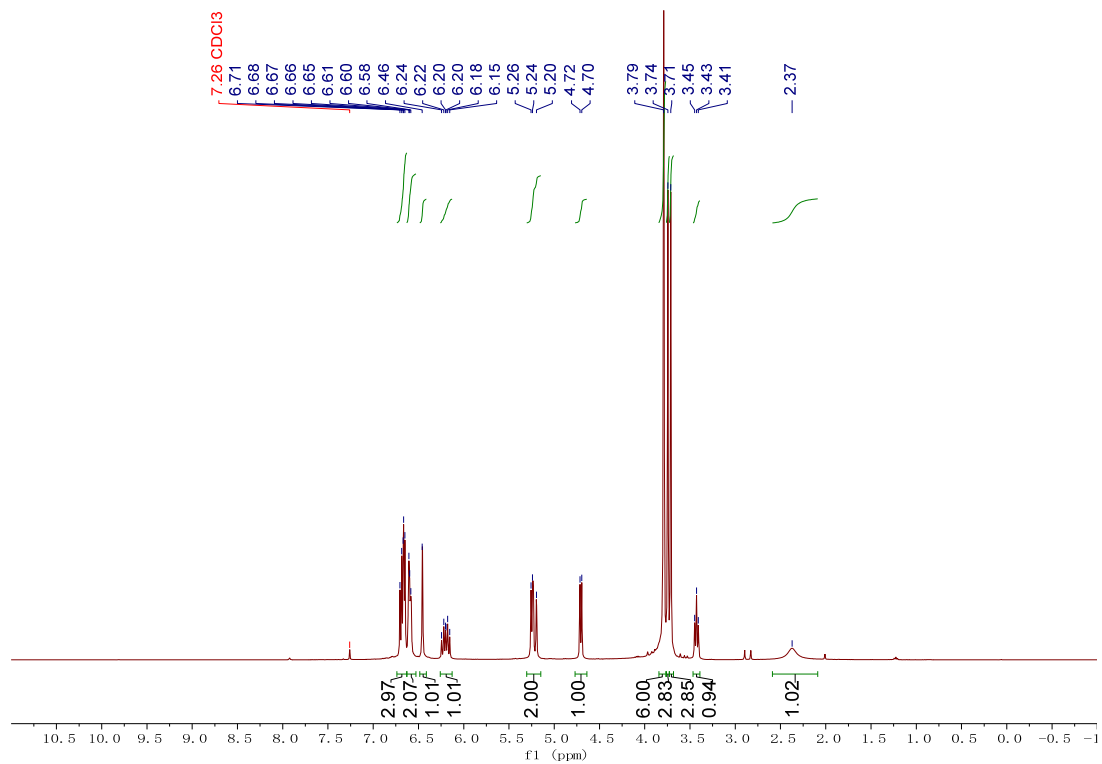
¹³C NMR (101 MHz, CDCl₃)



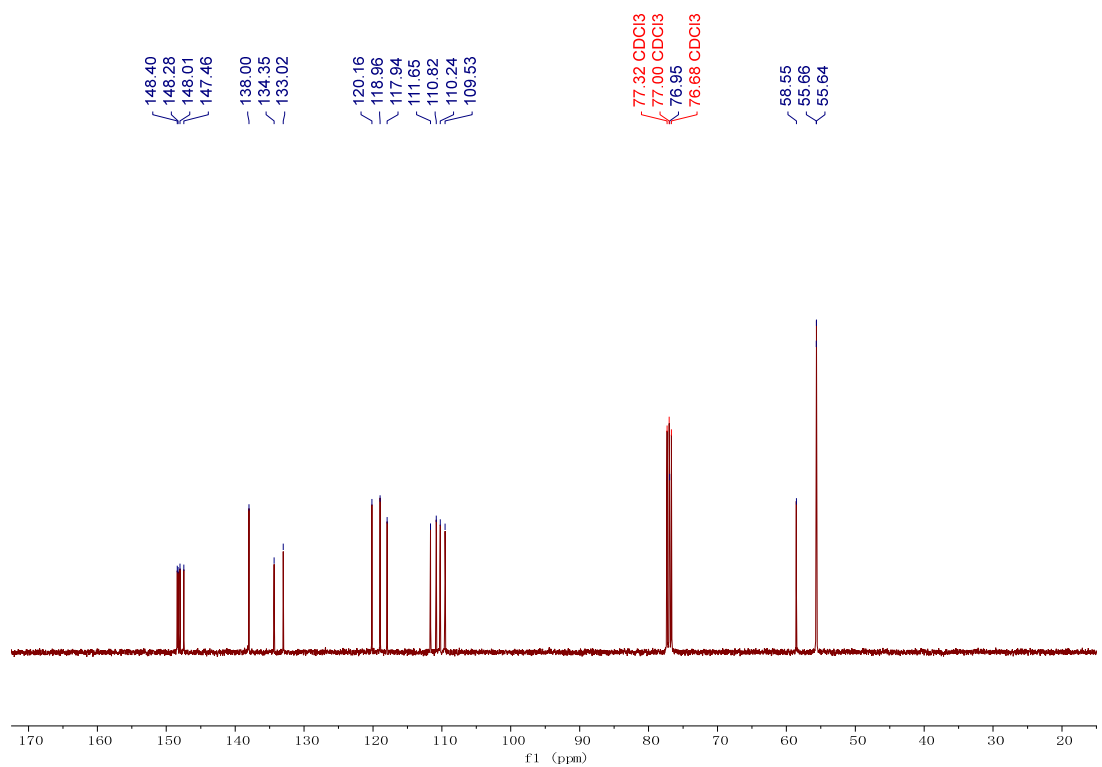


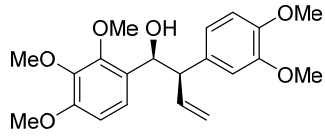
4i, 53% yield

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



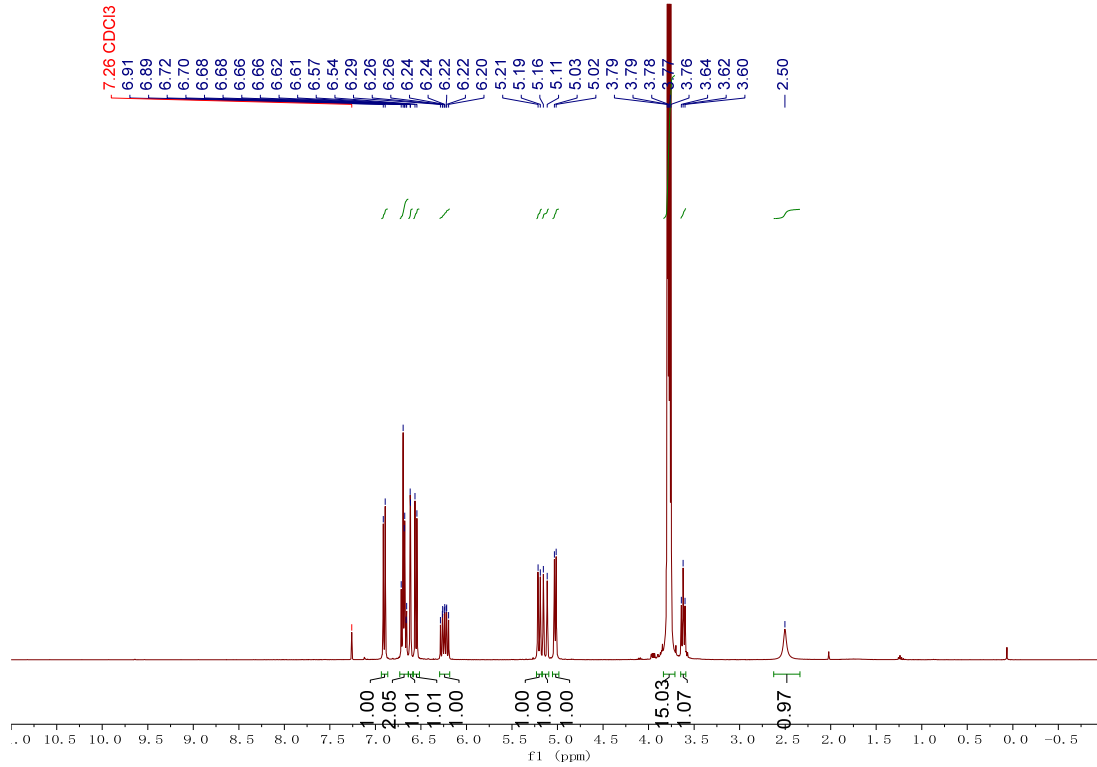
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



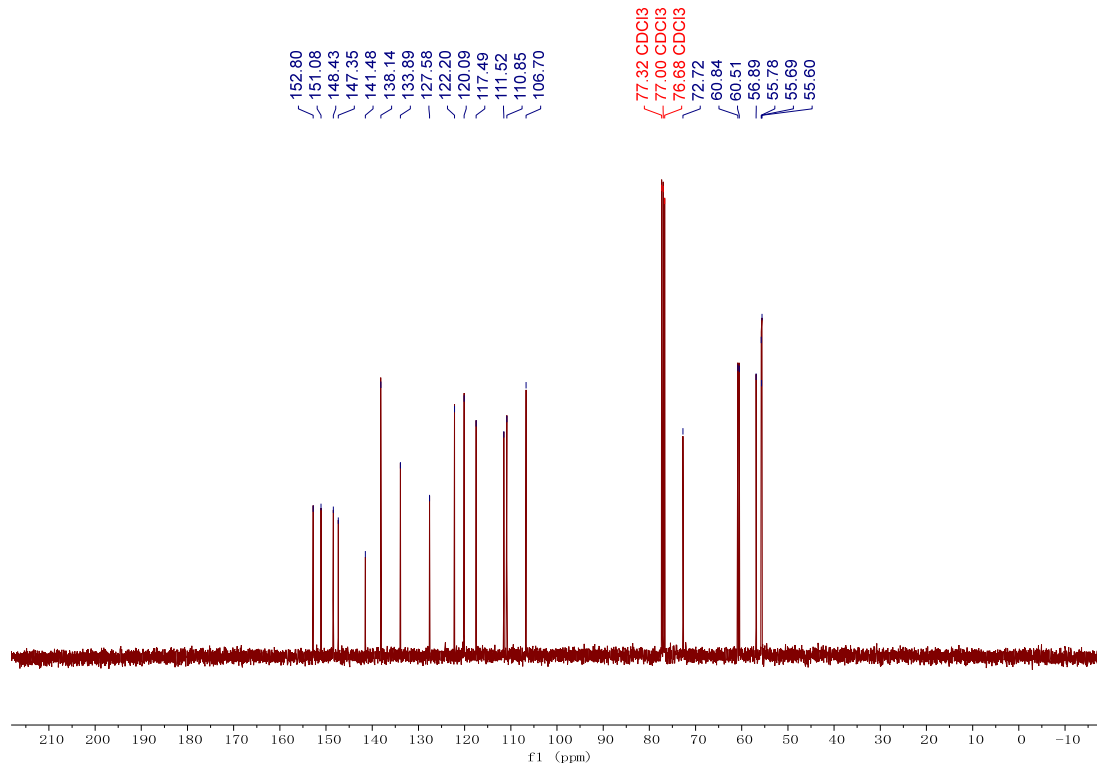


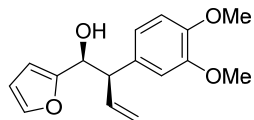
4m, 56% yield

¹H NMR (400 MHz, CDCl₃)



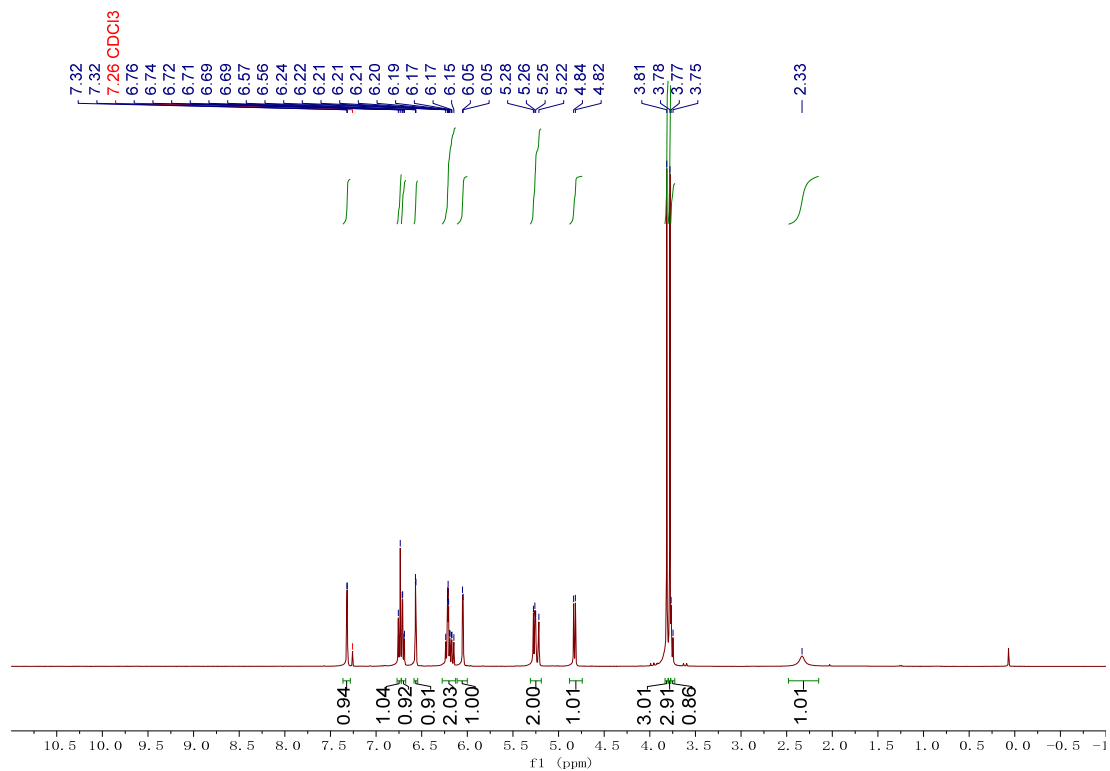
¹³C NMR (101 MHz, CDCl₃)



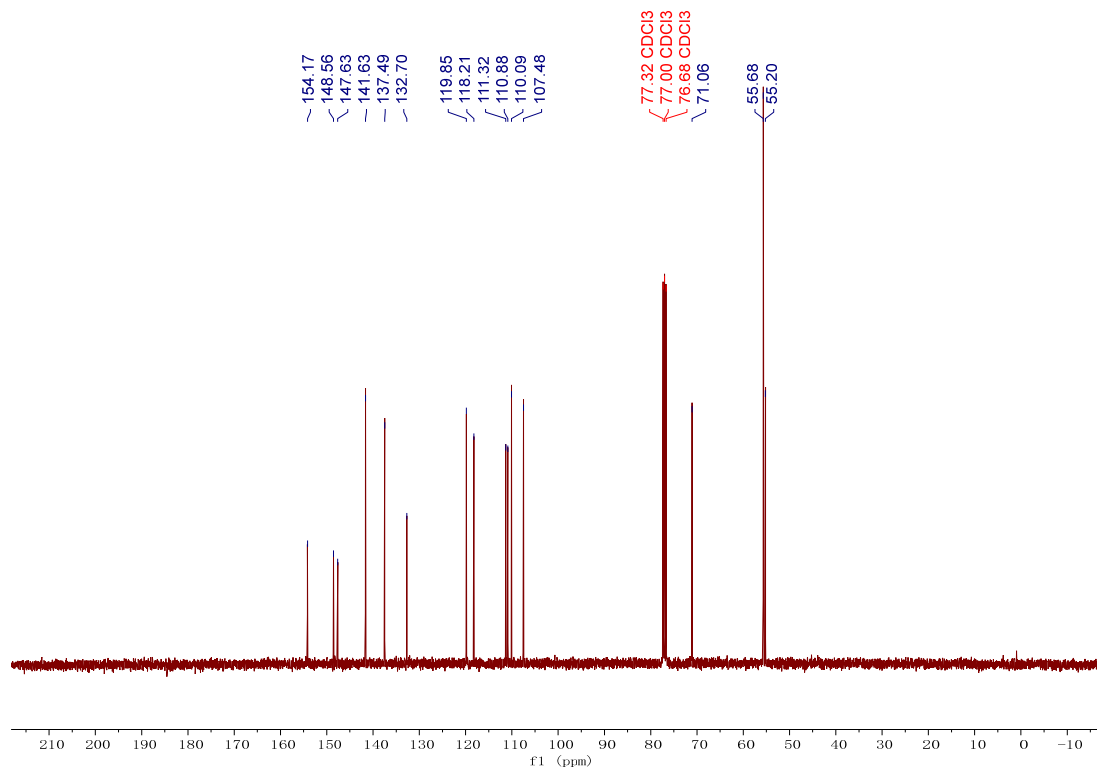


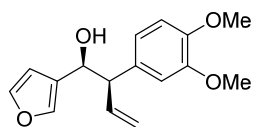
4n, 90% yield

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



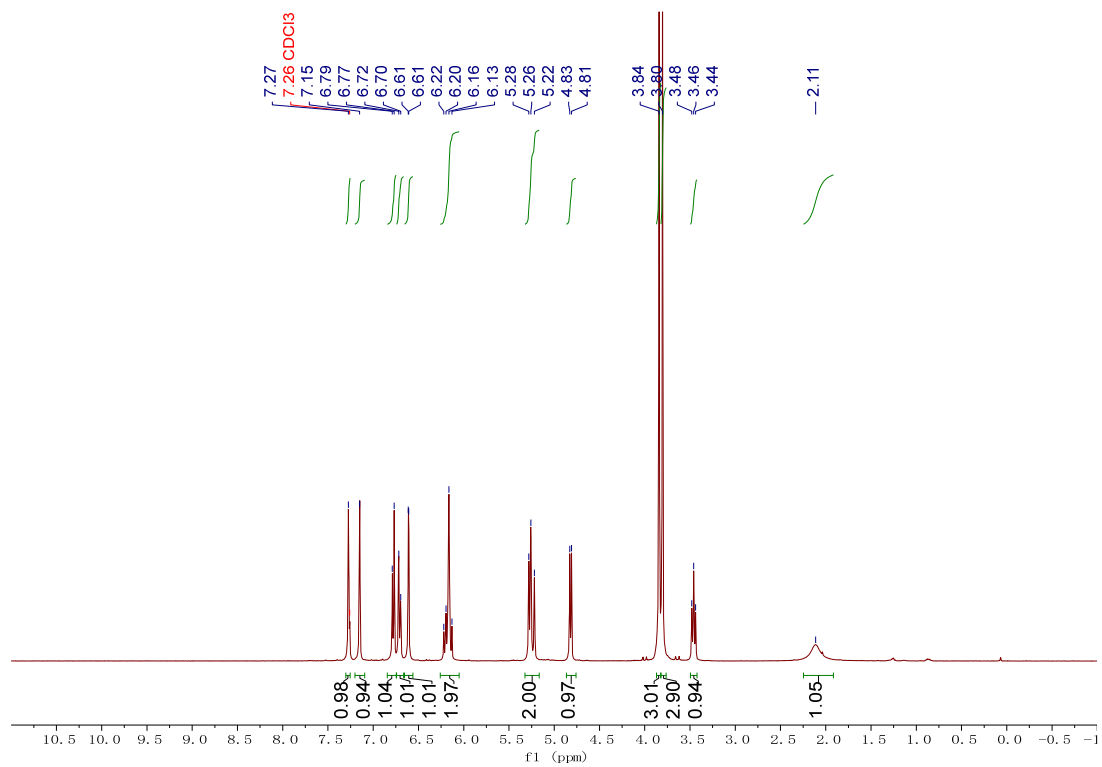
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



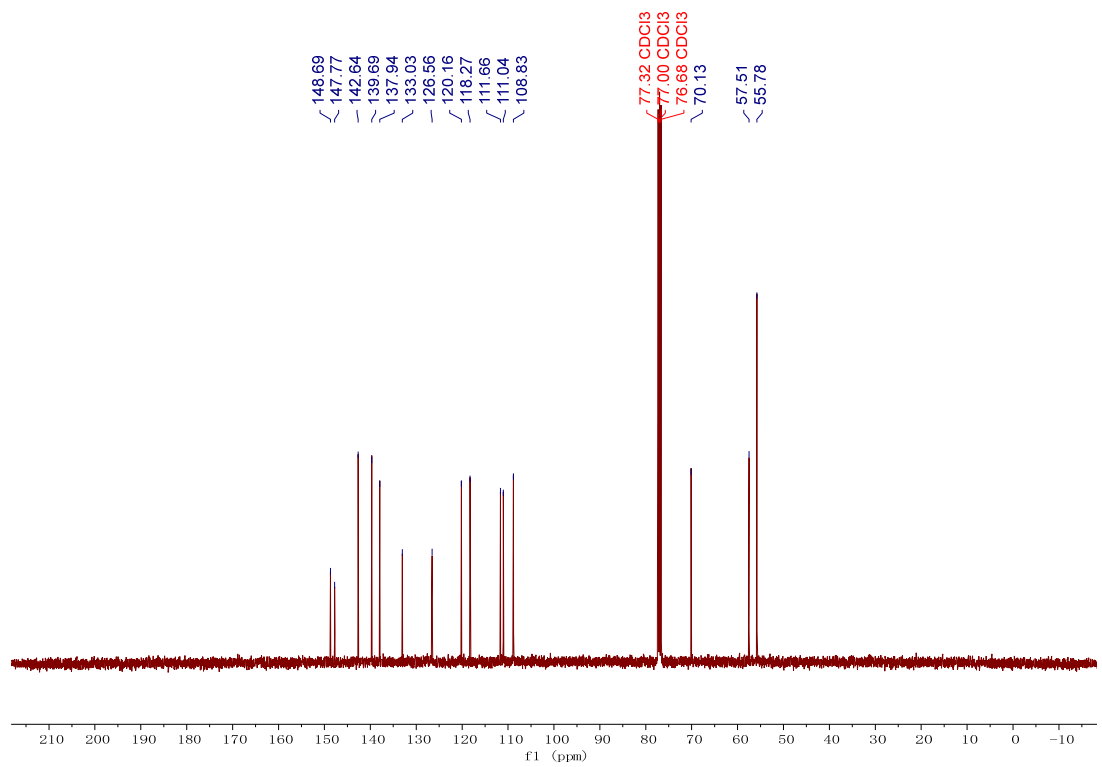


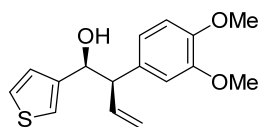
4o, 93% yield

^1H NMR (400 MHz, CDCl_3)



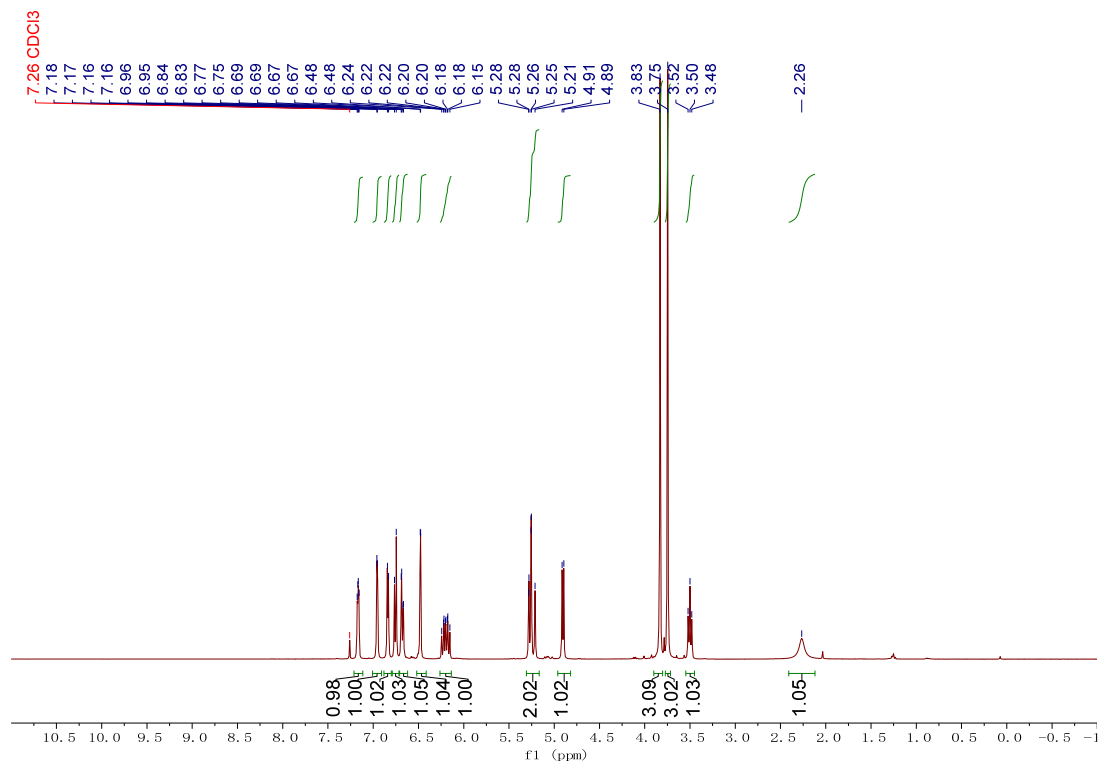
^{13}C NMR (101 MHz, CDCl_3)



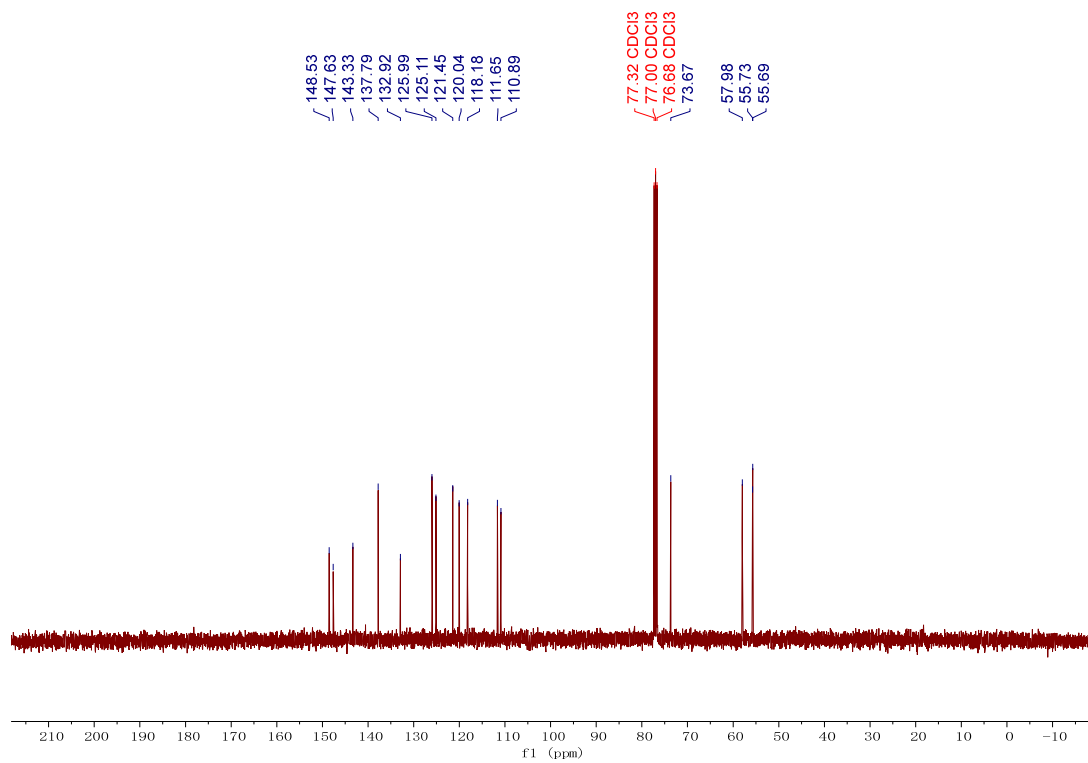


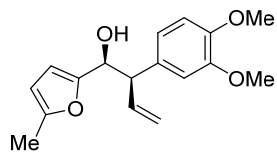
4p, 80% yield

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



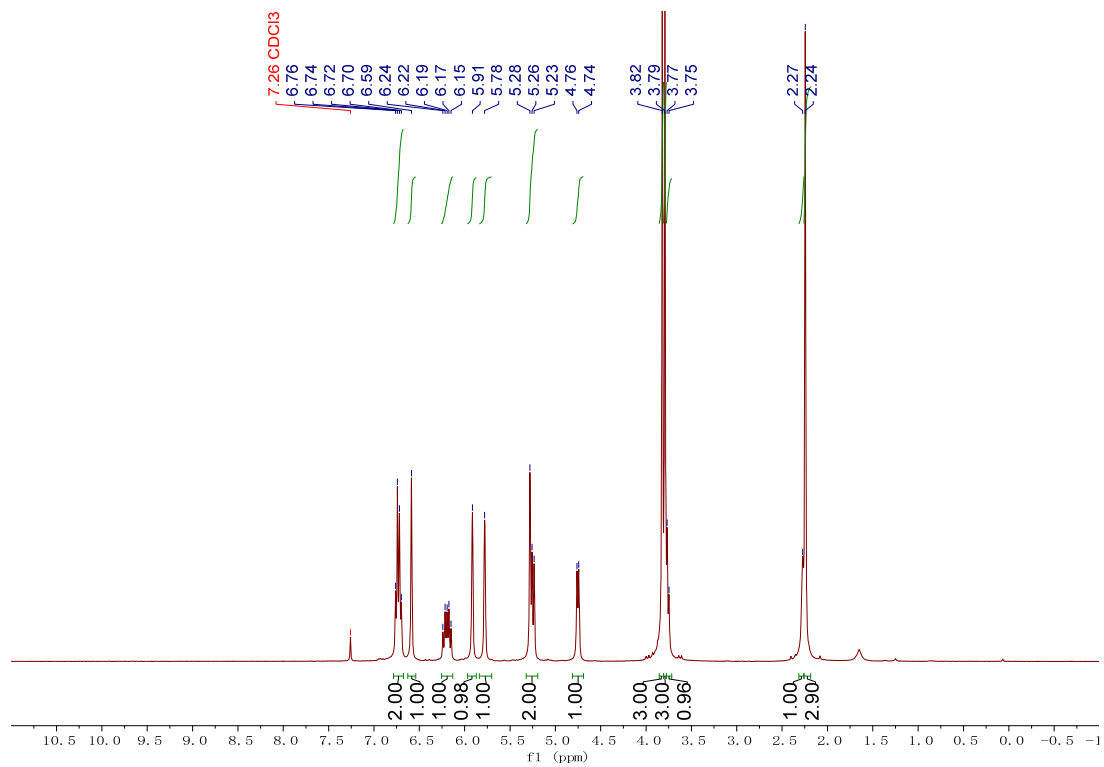
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



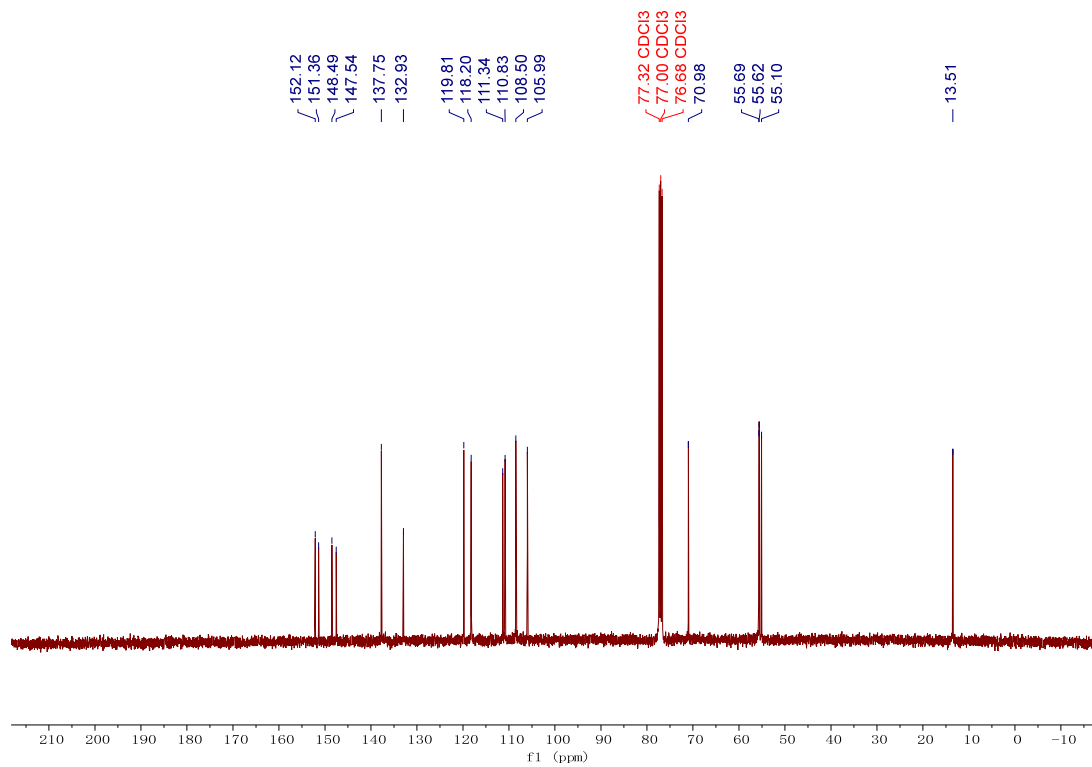


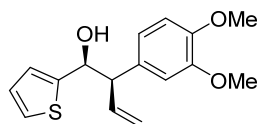
4q, 79% yield

¹H NMR (400 MHz, CDCl₃)



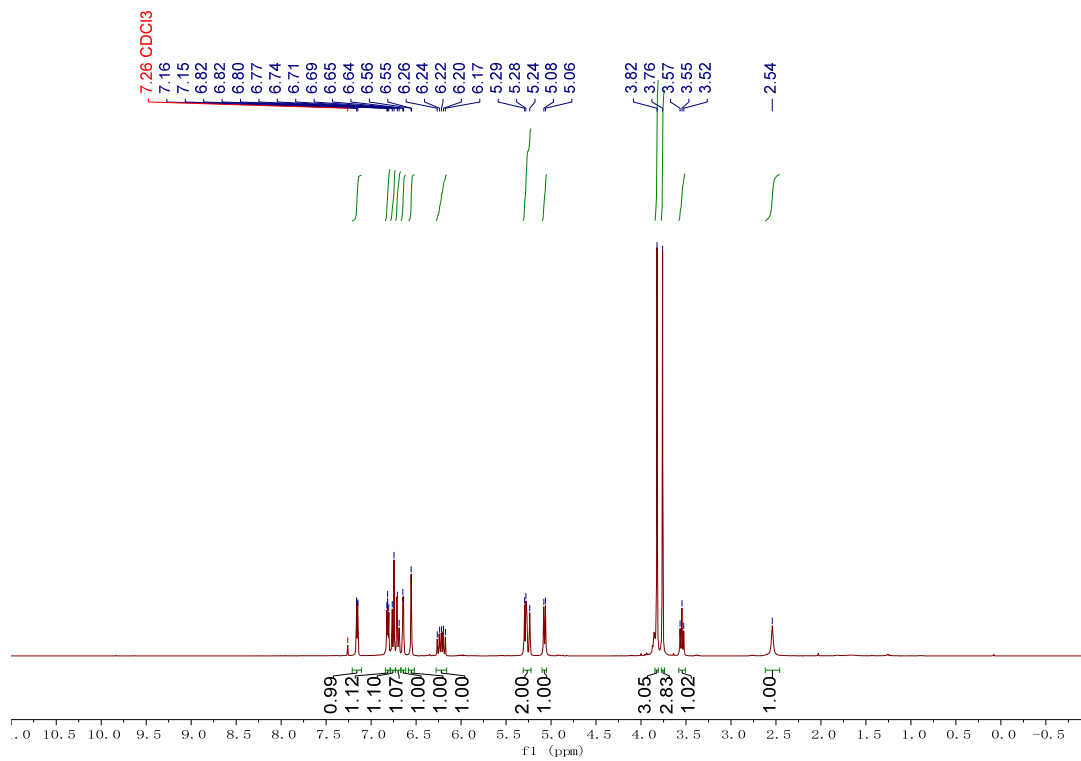
¹³C NMR (101 MHz, CDCl₃)



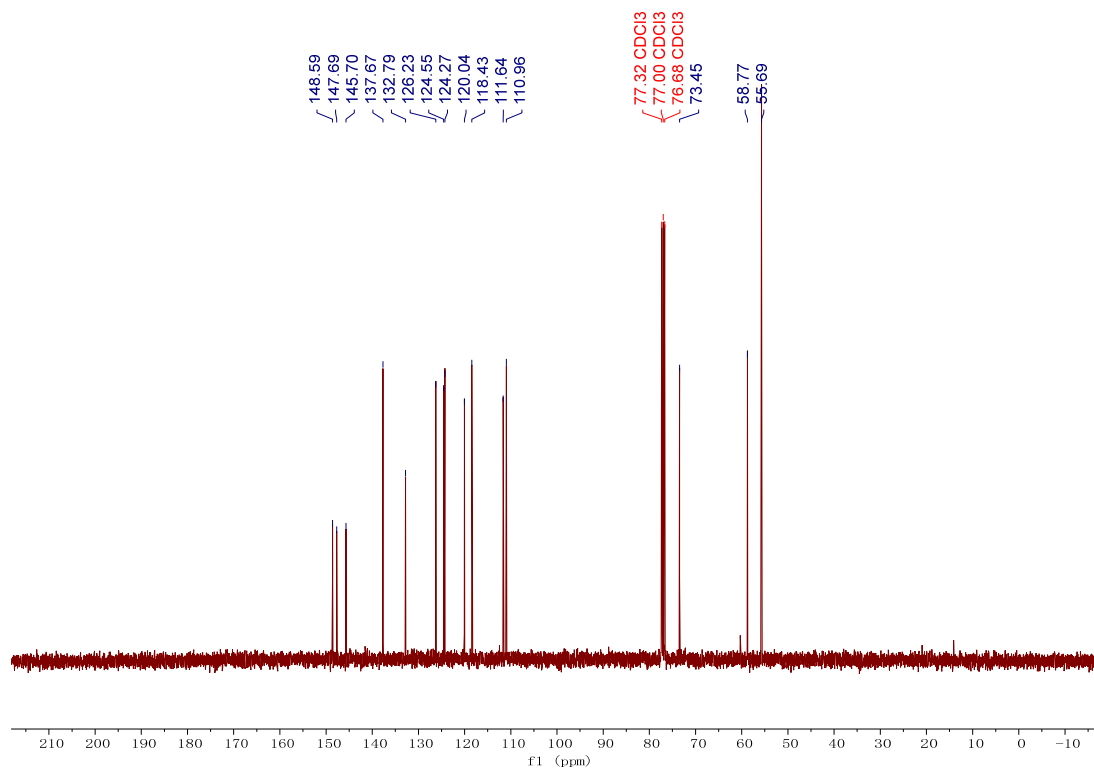


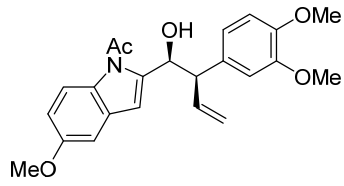
4r, 53% yield

¹H NMR (400 MHz, CDCl₃)



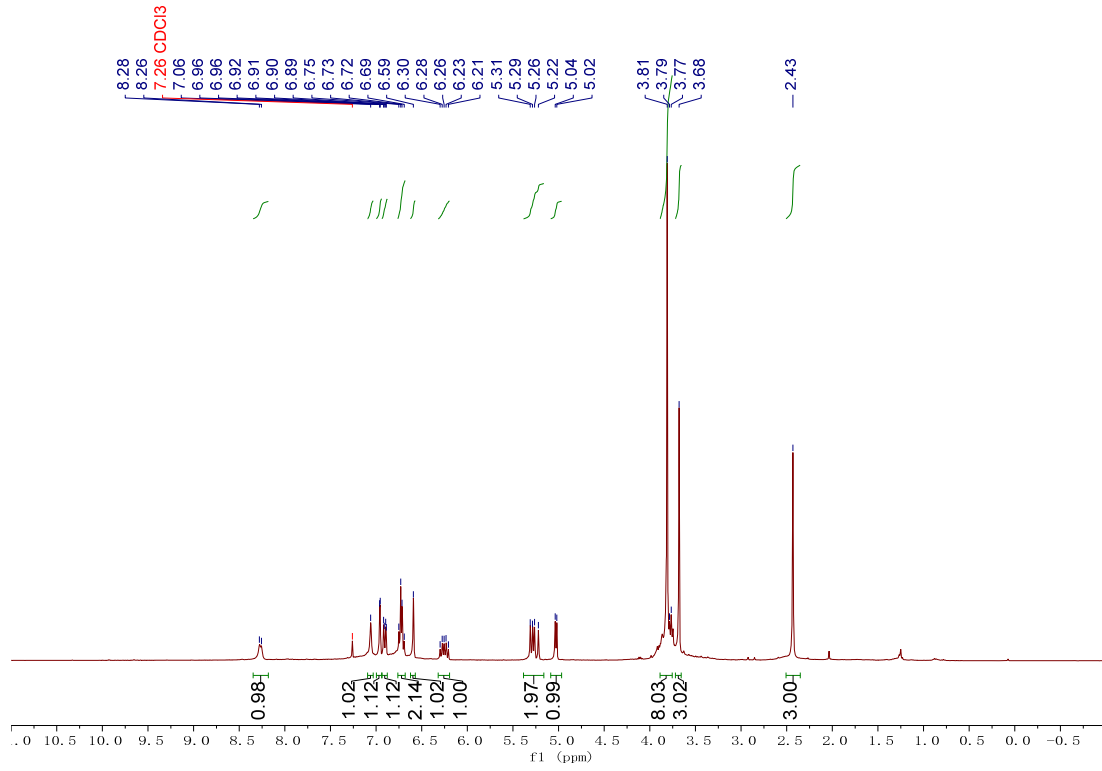
¹³C NMR (101 MHz, CDCl₃)



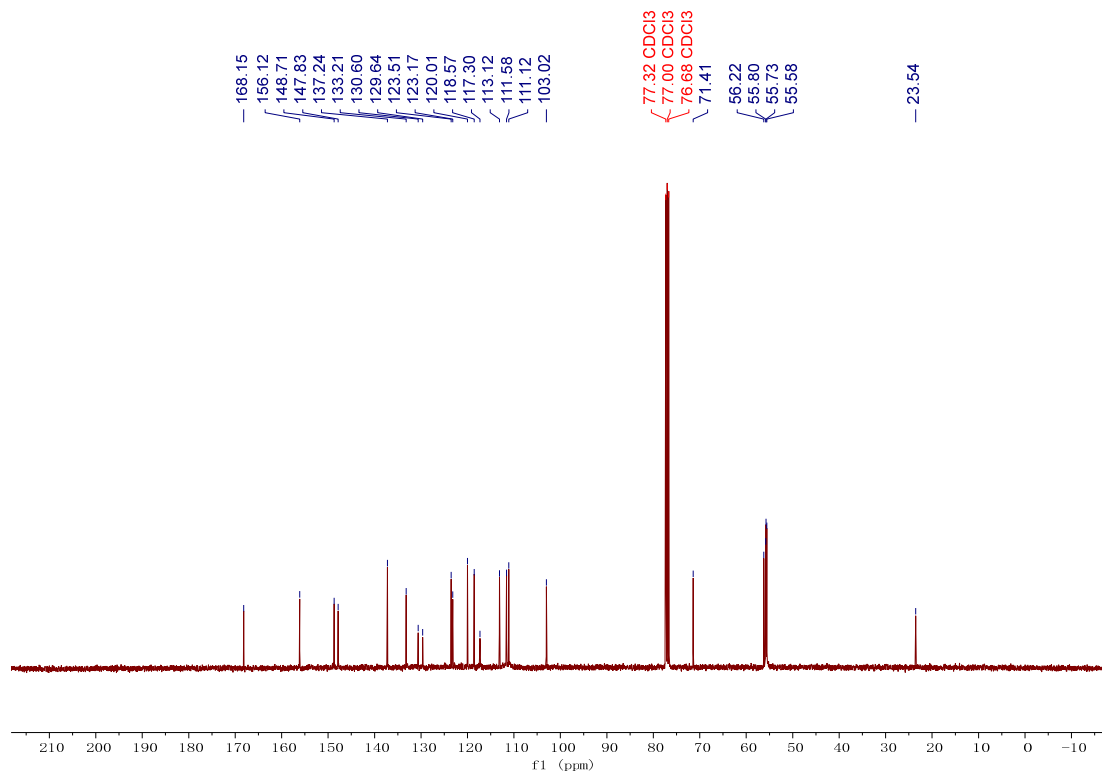


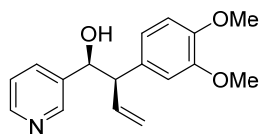
4s, 73% yield

¹H NMR (400 MHz, CDCl₃)



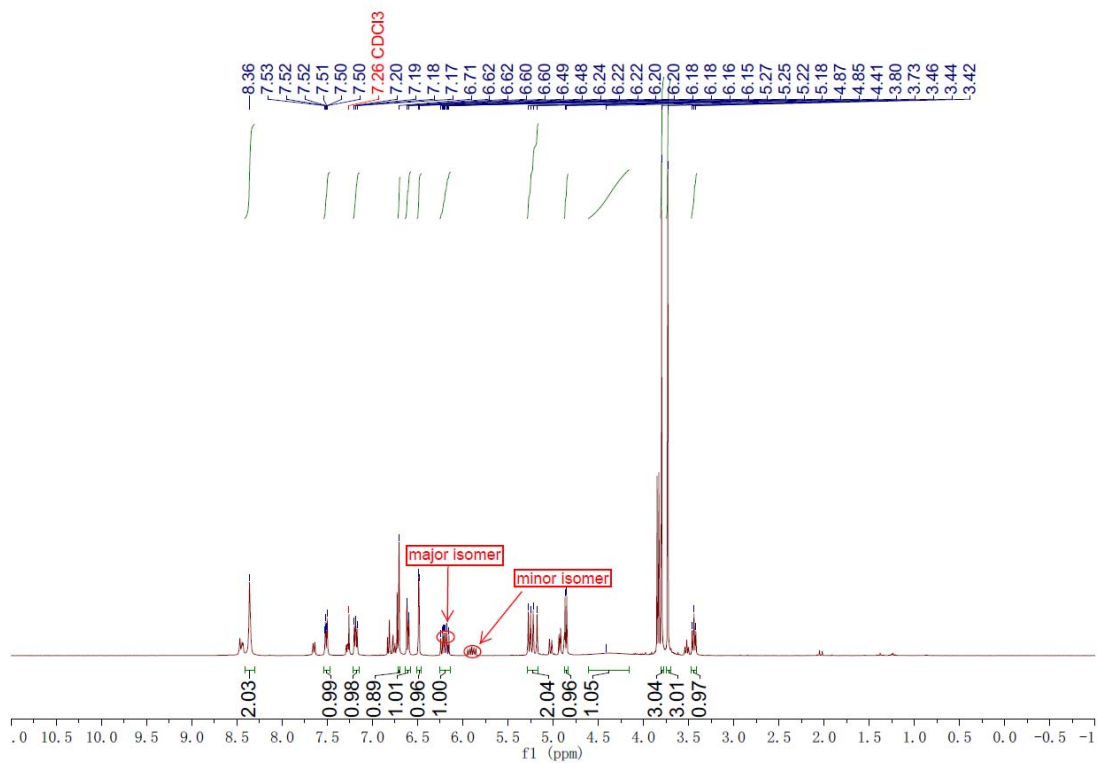
¹³C NMR (101 MHz, CDCl₃)



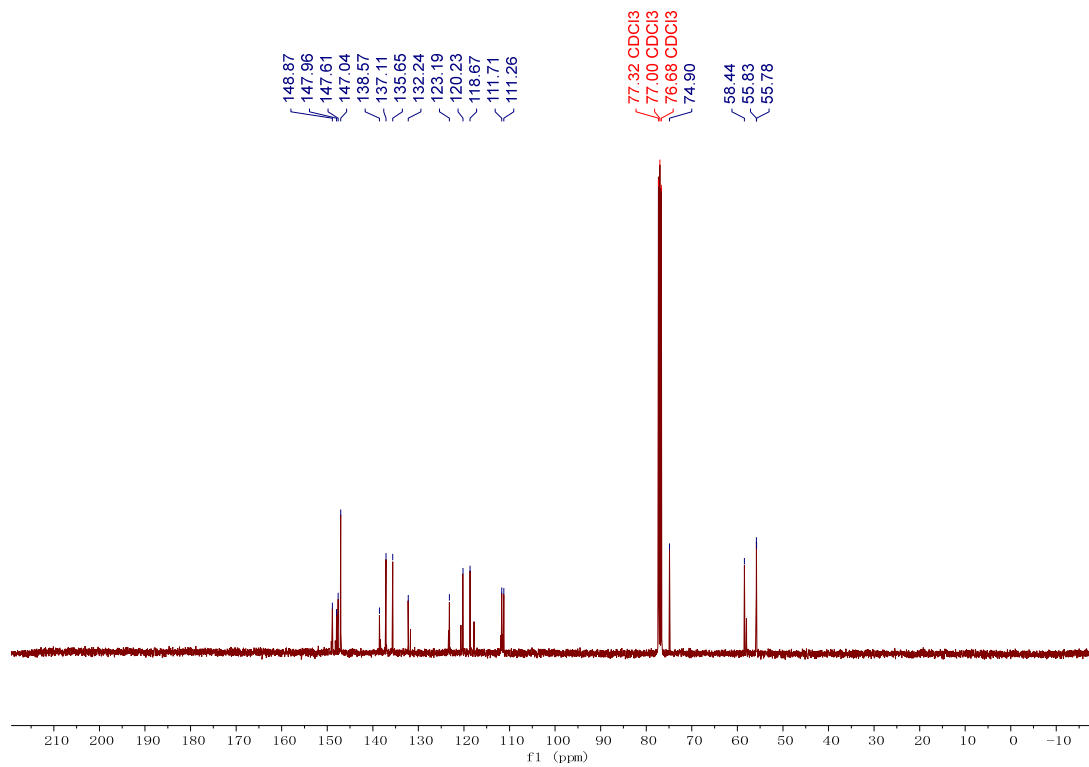


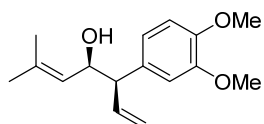
4t, 82% yield

¹H NMR (400 MHz, CDCl₃)



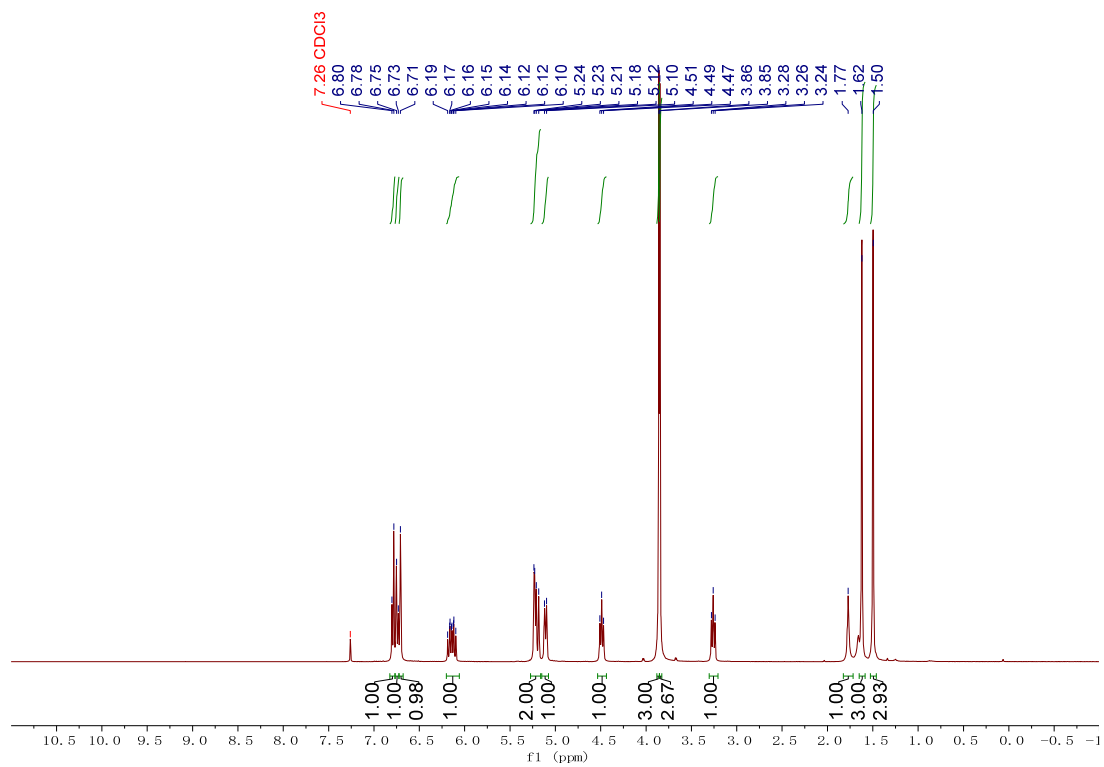
¹³C NMR (101 MHz, CDCl₃)



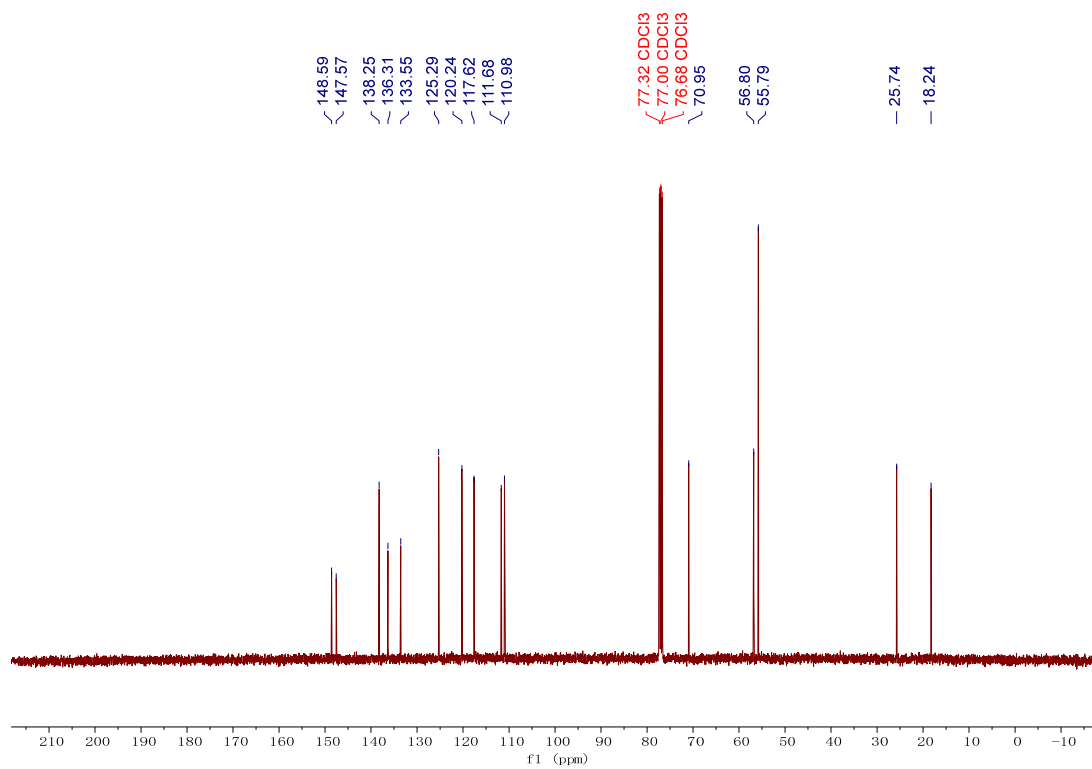


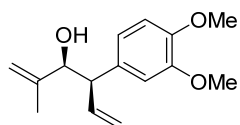
4u, 55% yield

¹H NMR (400 MHz, CDCl₃)

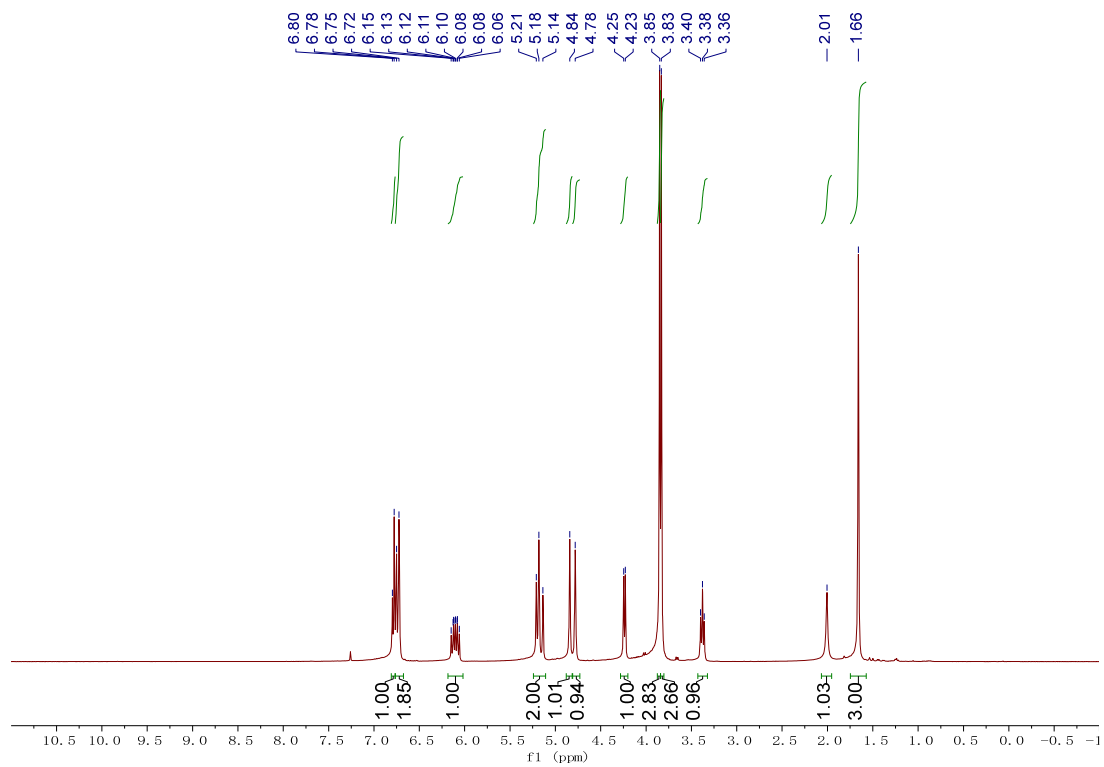


¹³C NMR (101 MHz, CDCl₃)

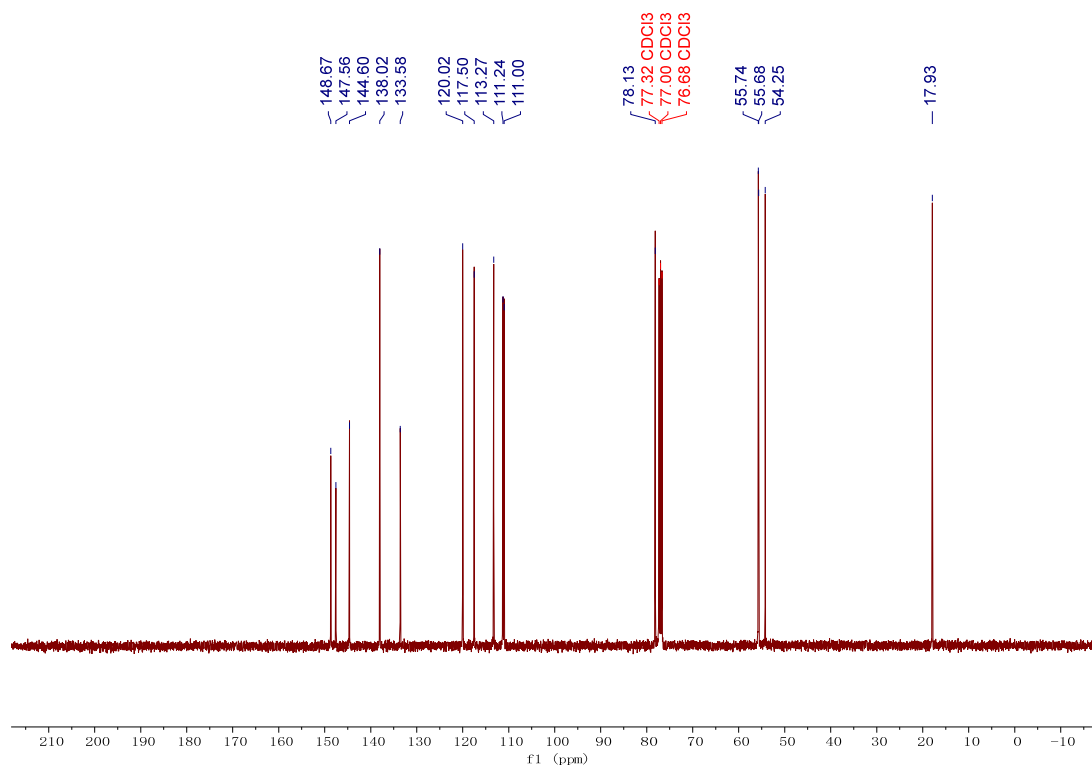


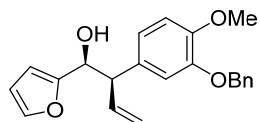


4v, 75% yield $^1\text{H NMR}$ (400 MHz, CDCl_3)



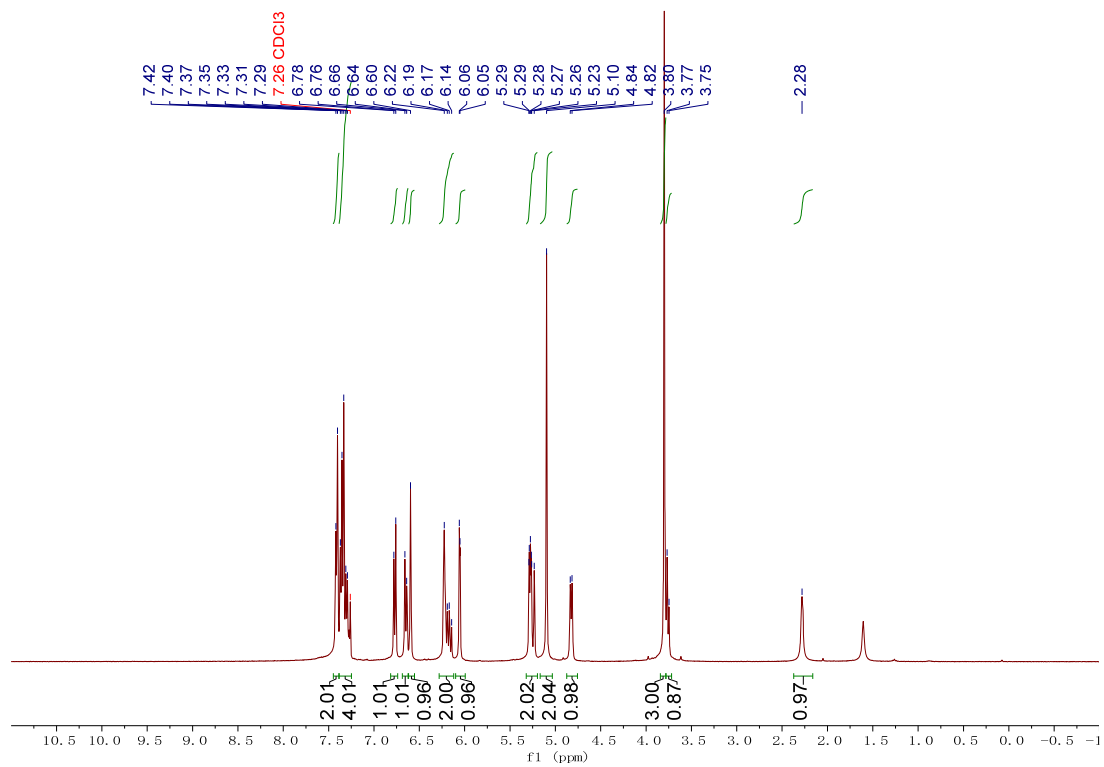
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



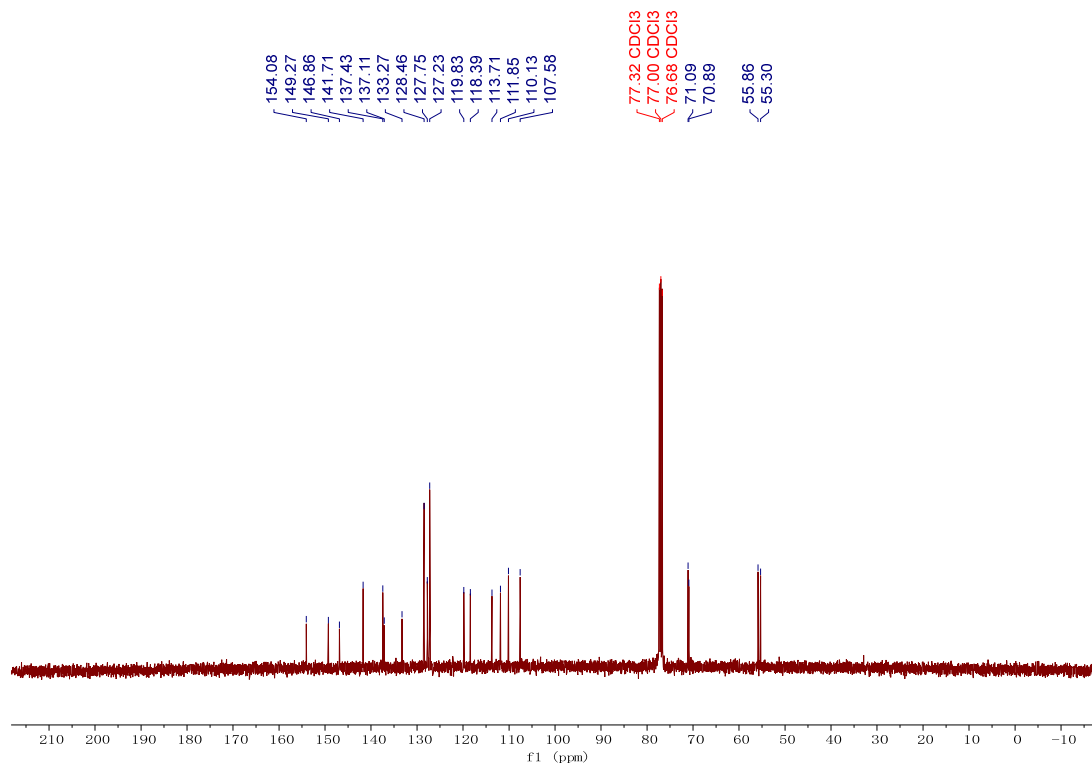


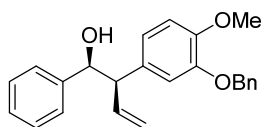
5a, 93% yield

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

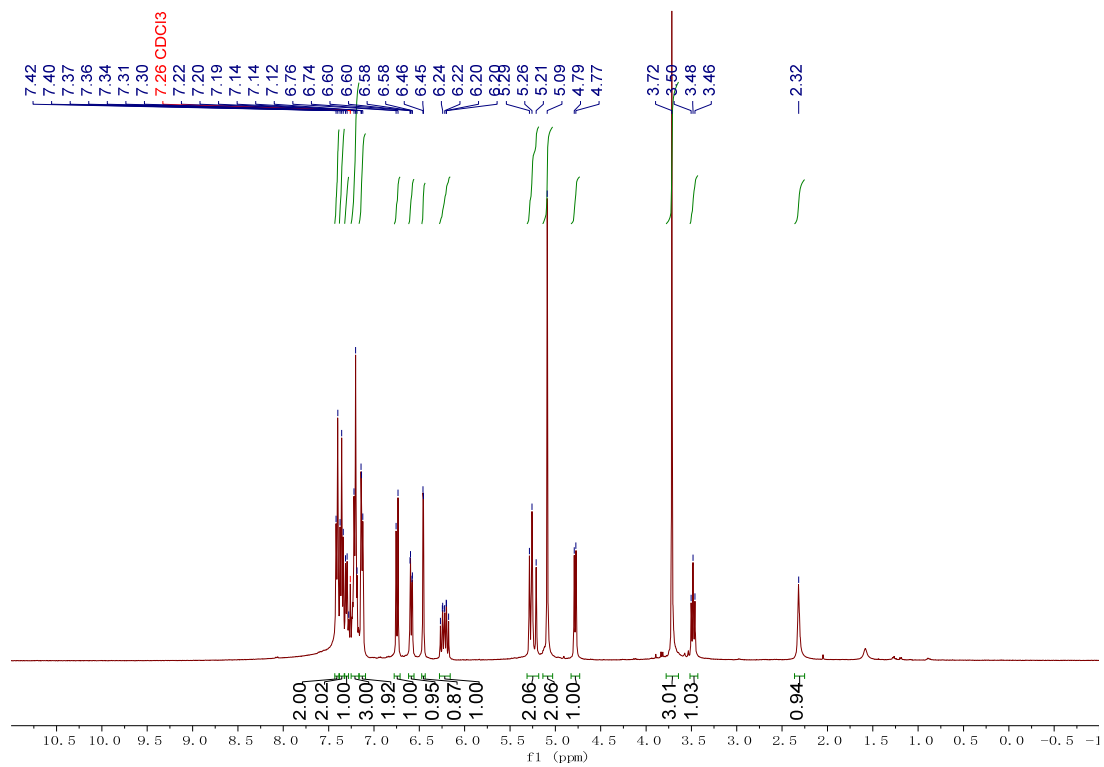


$^{13}\text{C NMR}$ (101 MHz, CDCl_3)

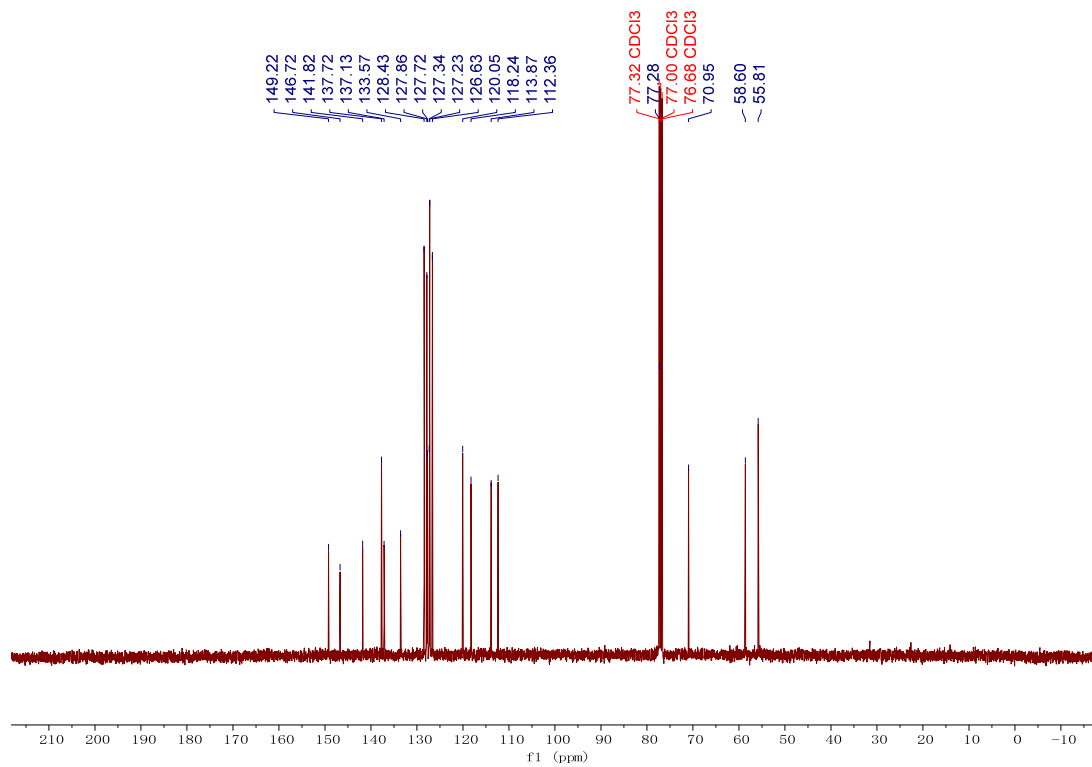


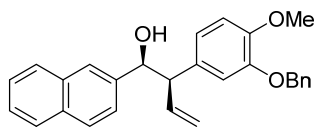


5b, 74% yield $^1\text{H NMR}$ (400 MHz, CDCl_3)



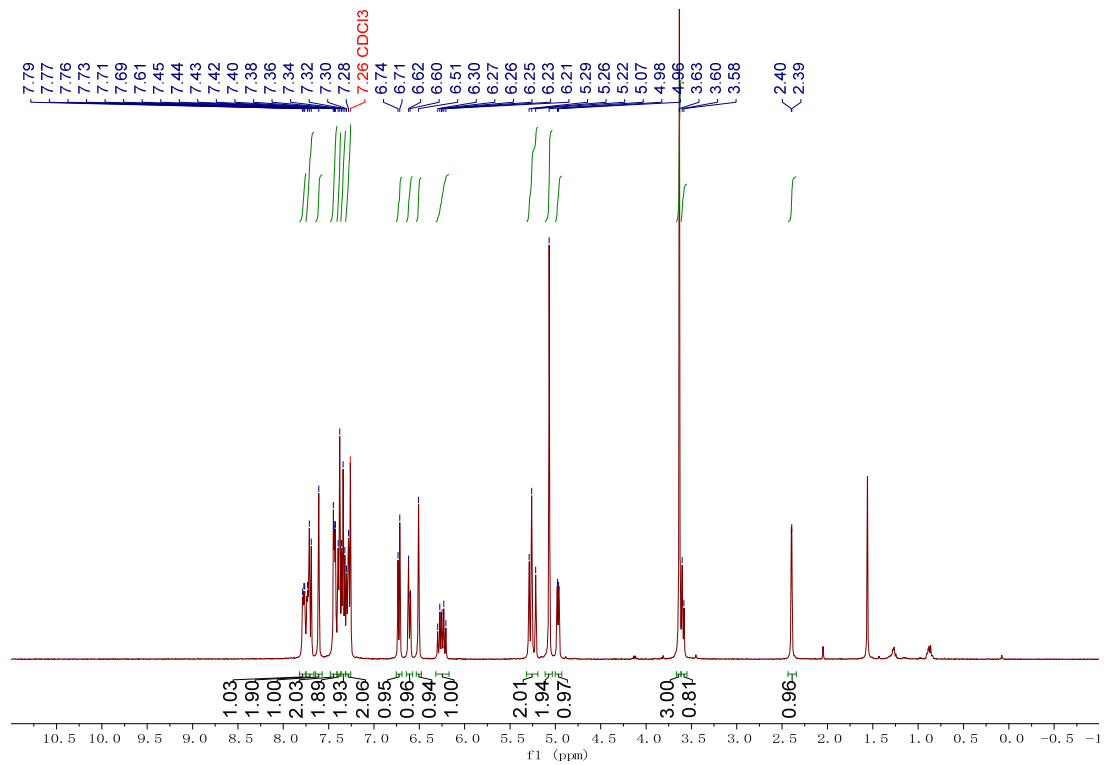
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



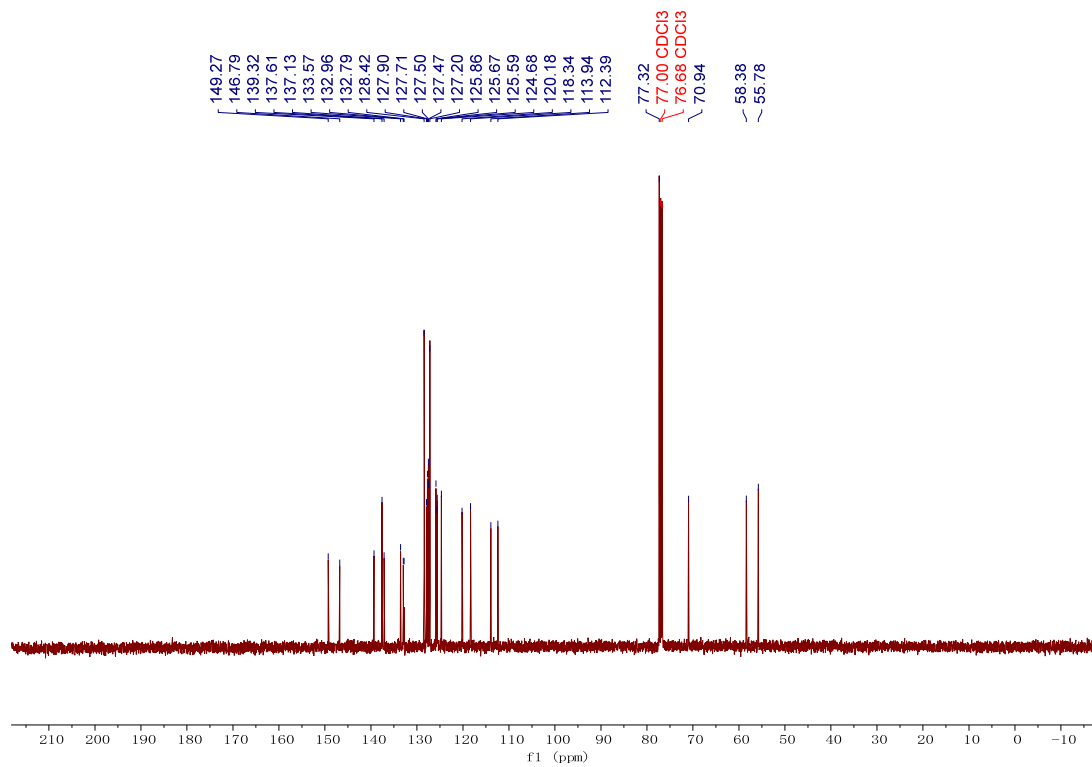


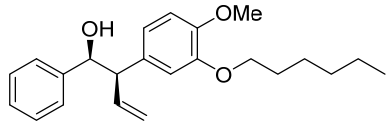
5c, 94% yield

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



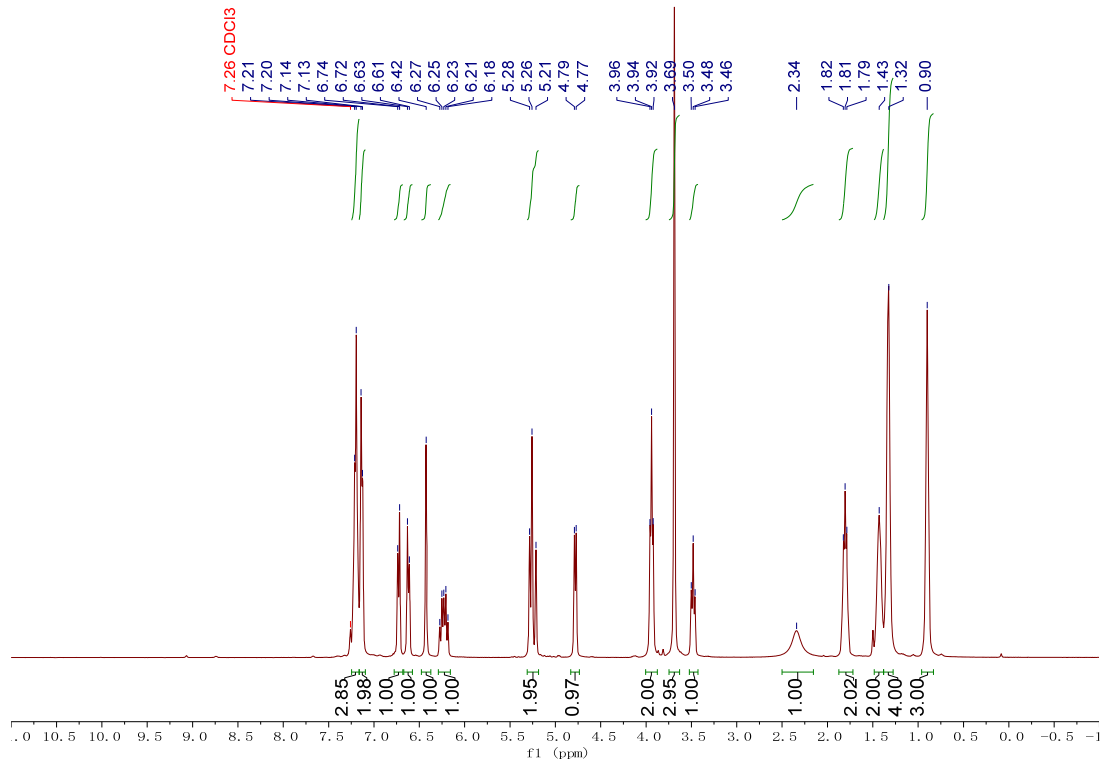
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



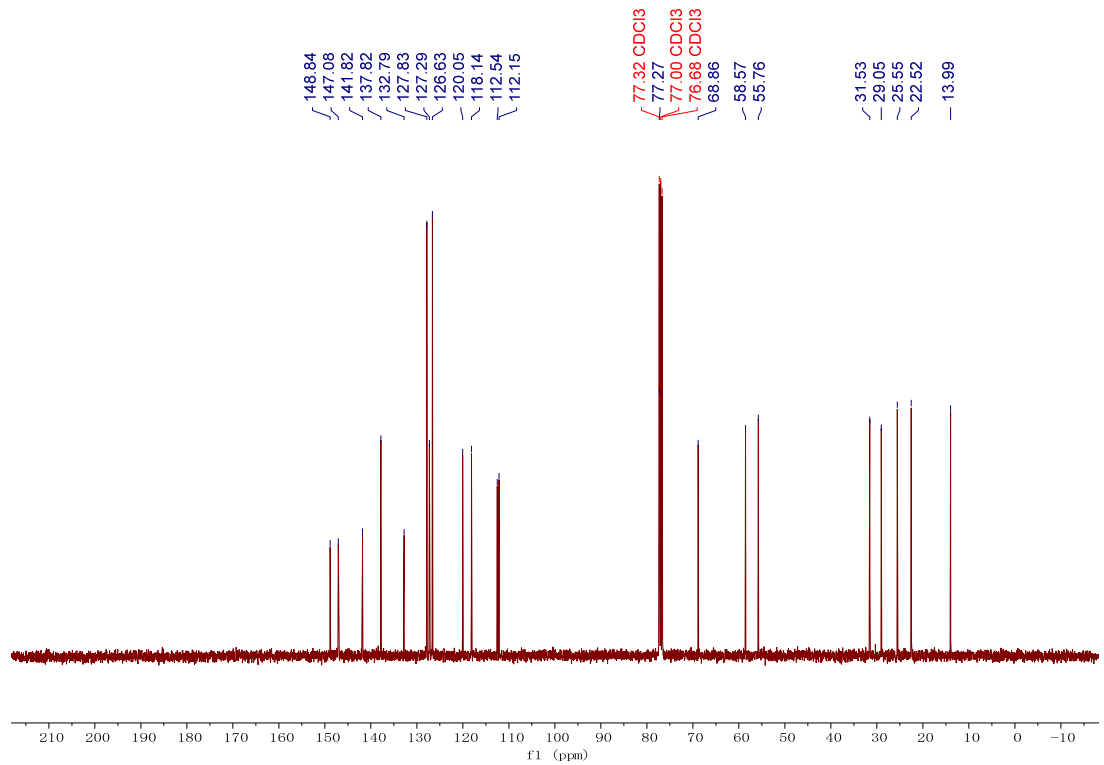


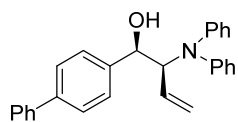
5d, 62% yield

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



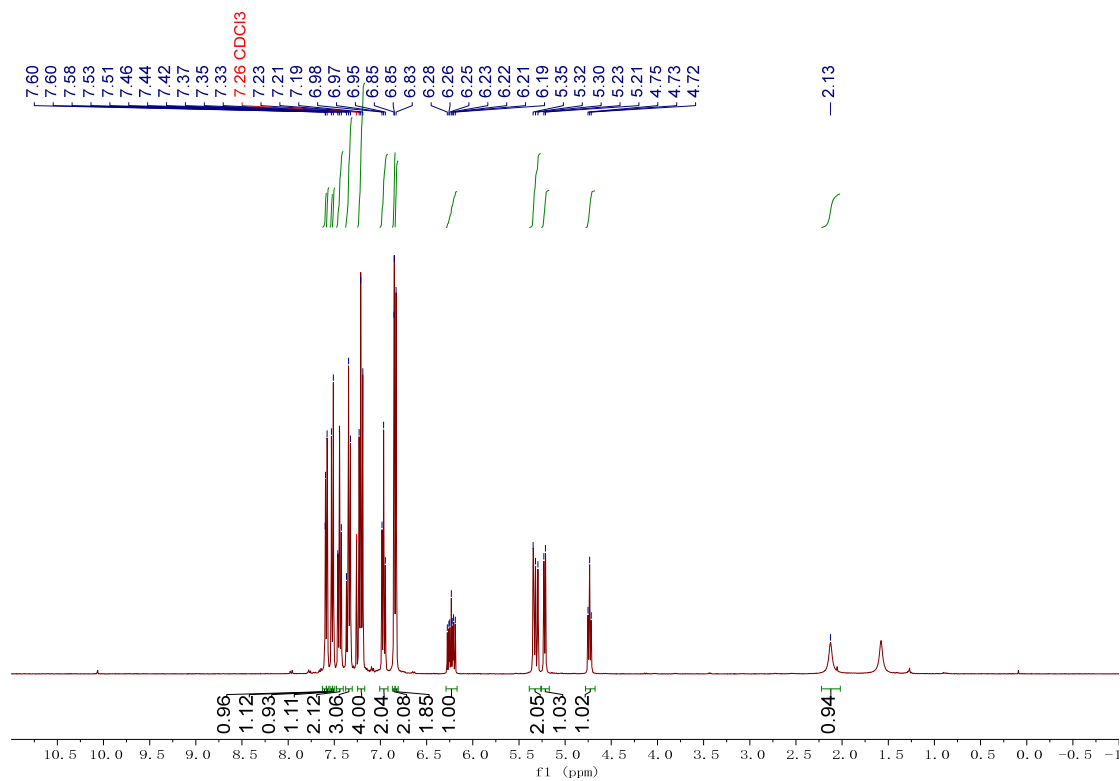
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



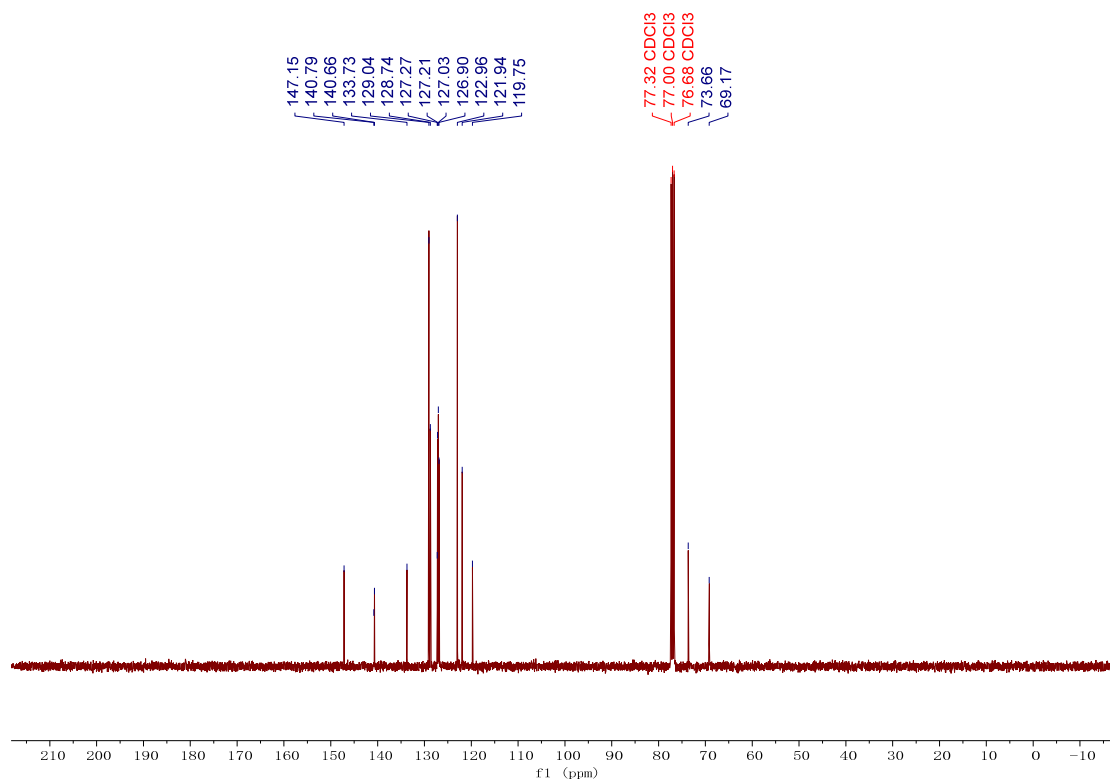


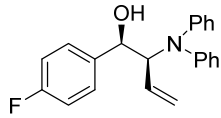
5e, 51% yield

¹H NMR (400 MHz, CDCl₃)



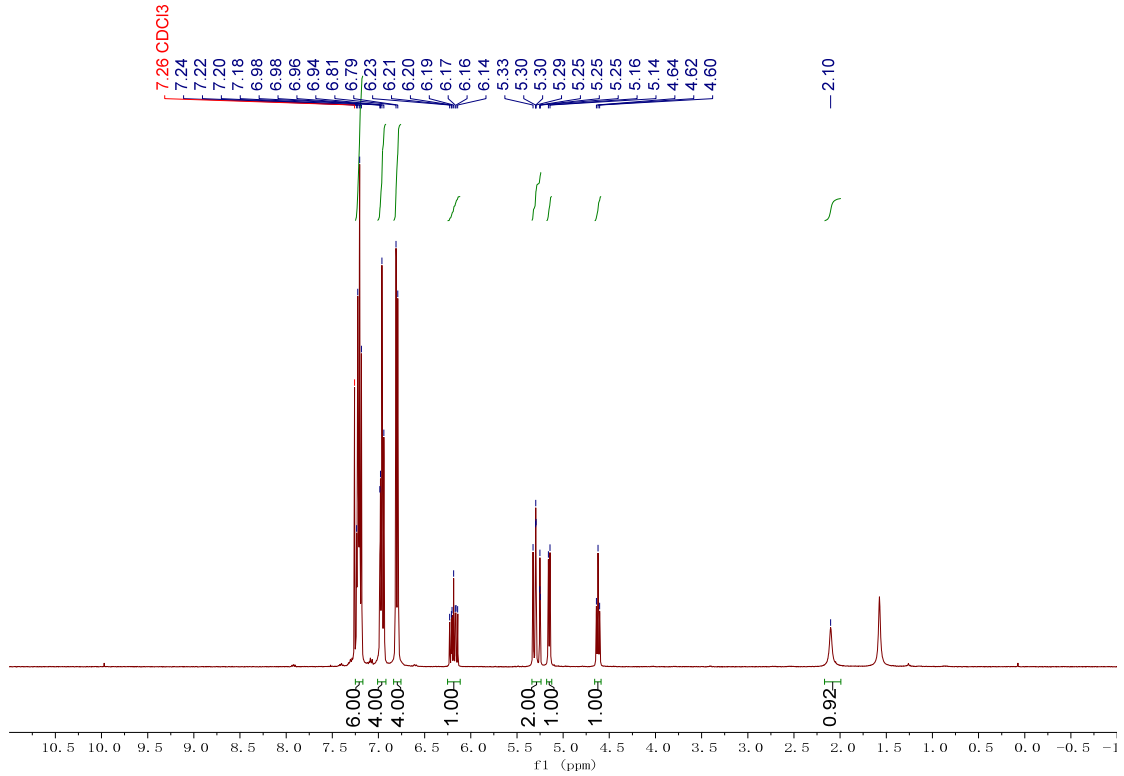
¹³C NMR (101 MHz, CDCl₃)



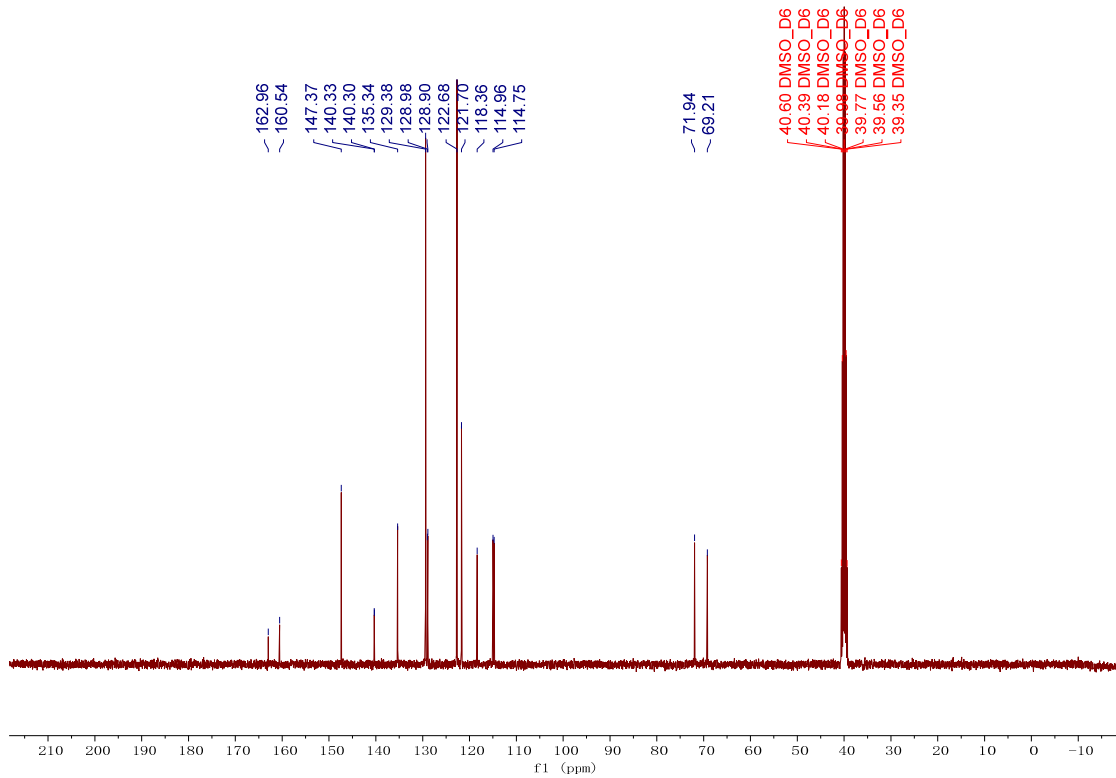


5f, 65% yield

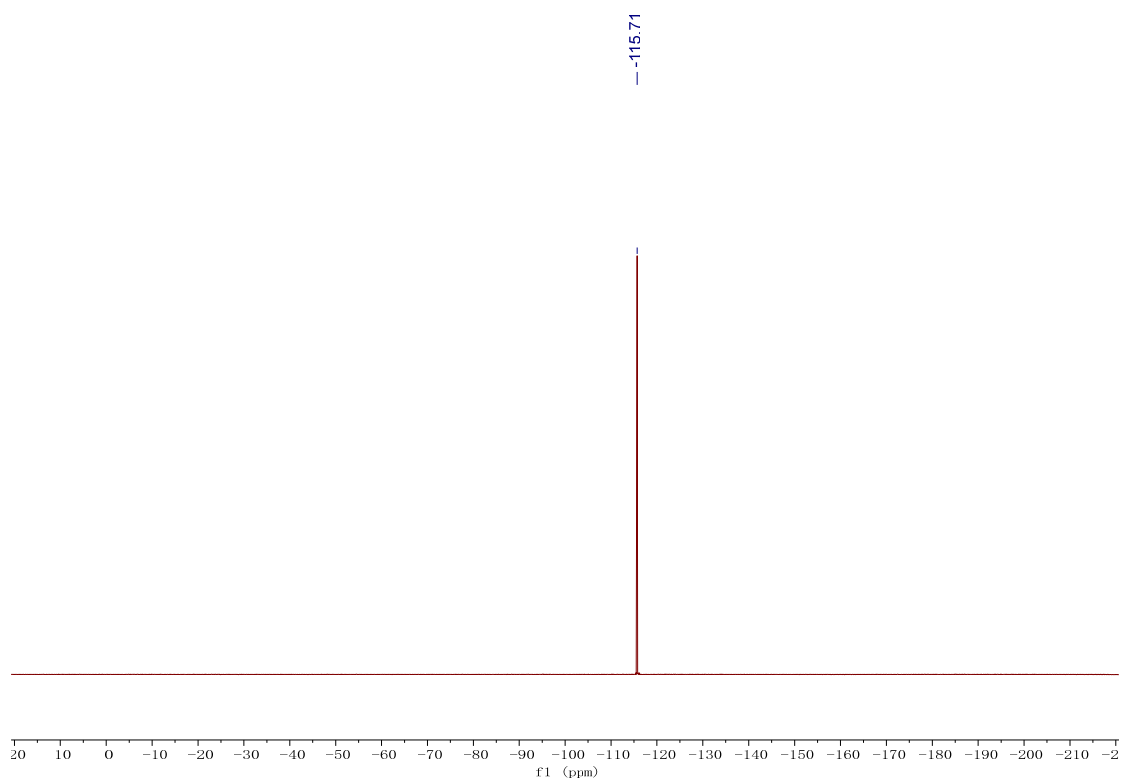
^1H NMR (400 MHz, CDCl_3)

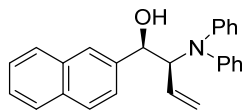


^{13}C NMR (101 MHz, DMSO_d6)



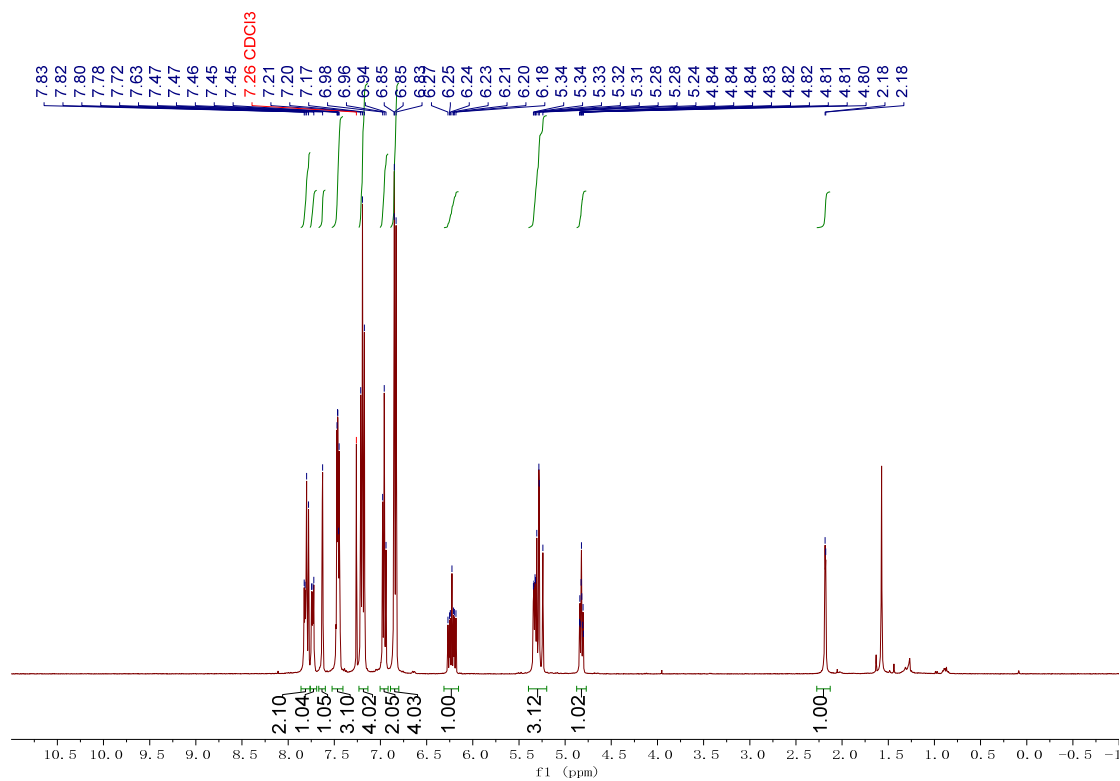
¹⁹F NMR (377 MHz, DMSO-_D₆)



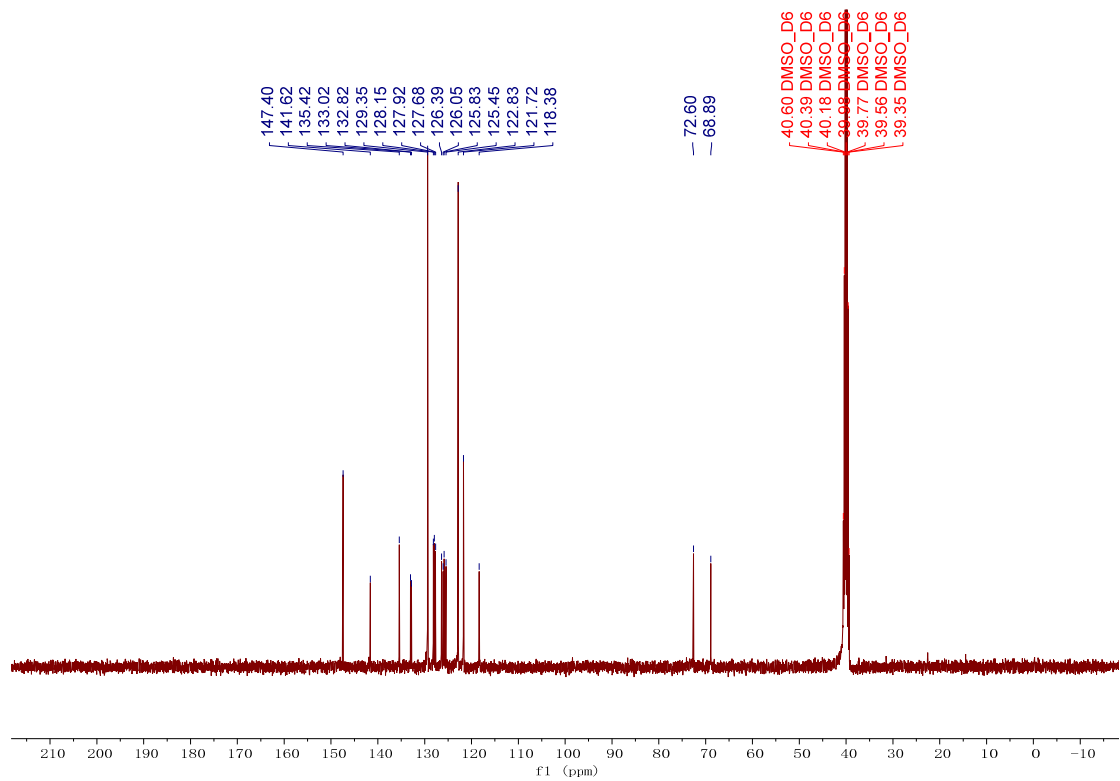


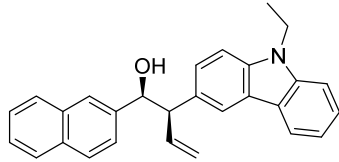
5g, 63% yield

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



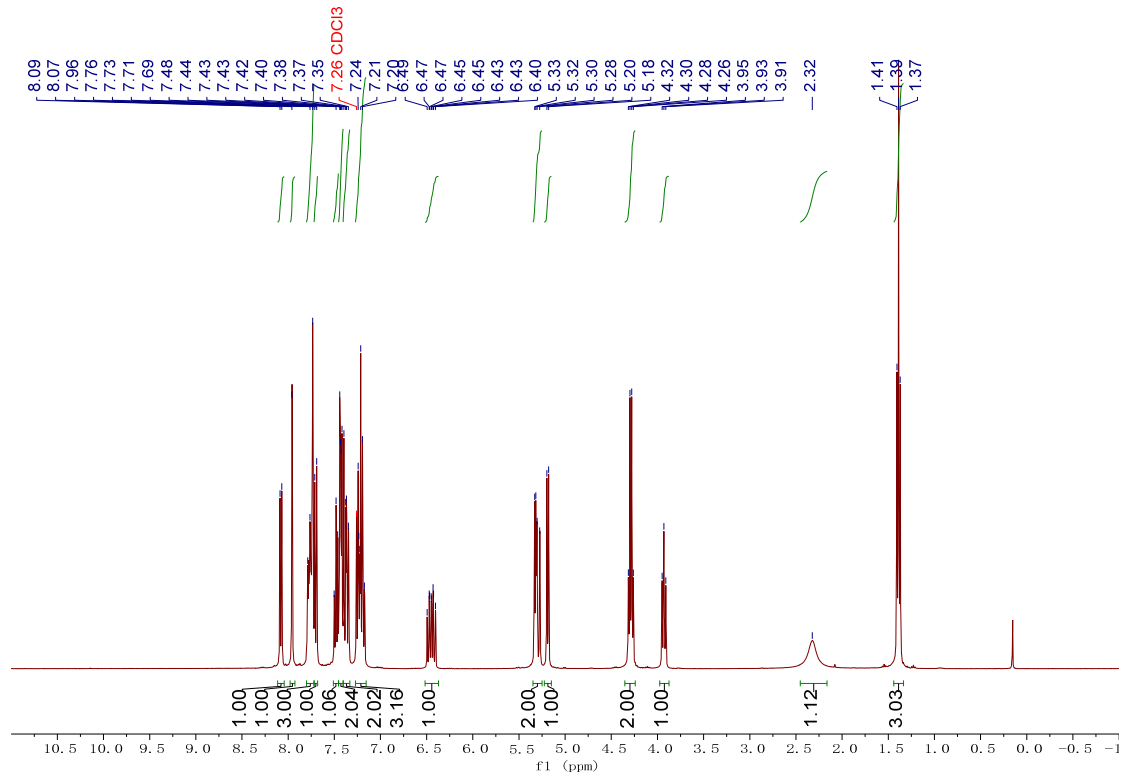
$^{13}\text{C NMR}$ (101 MHz, DMSO_d6)



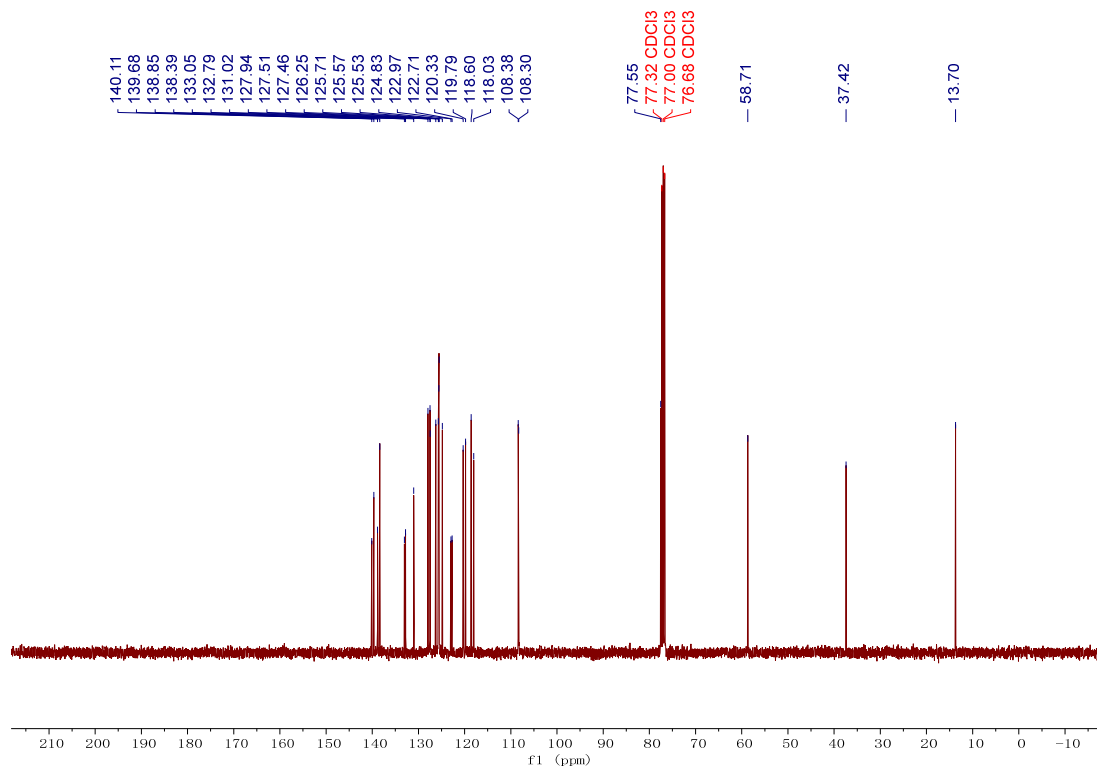


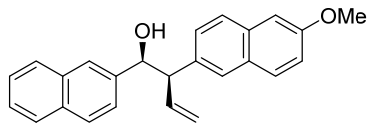
5h, 87% yield

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



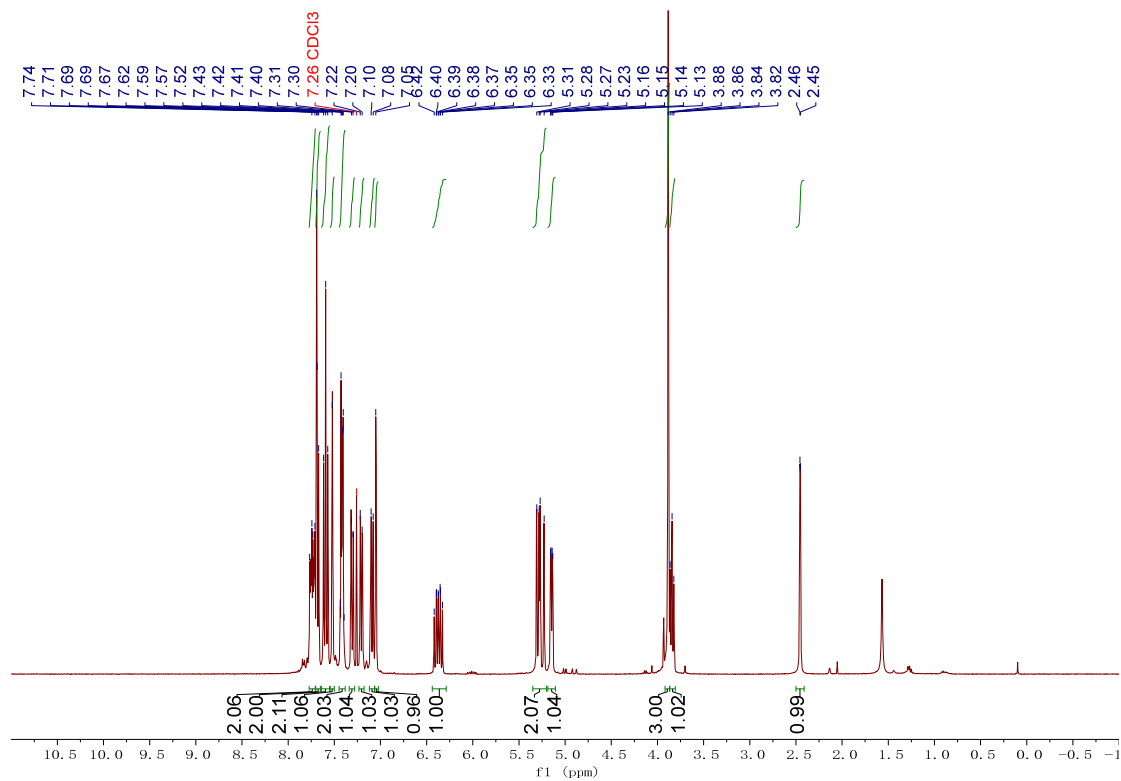
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



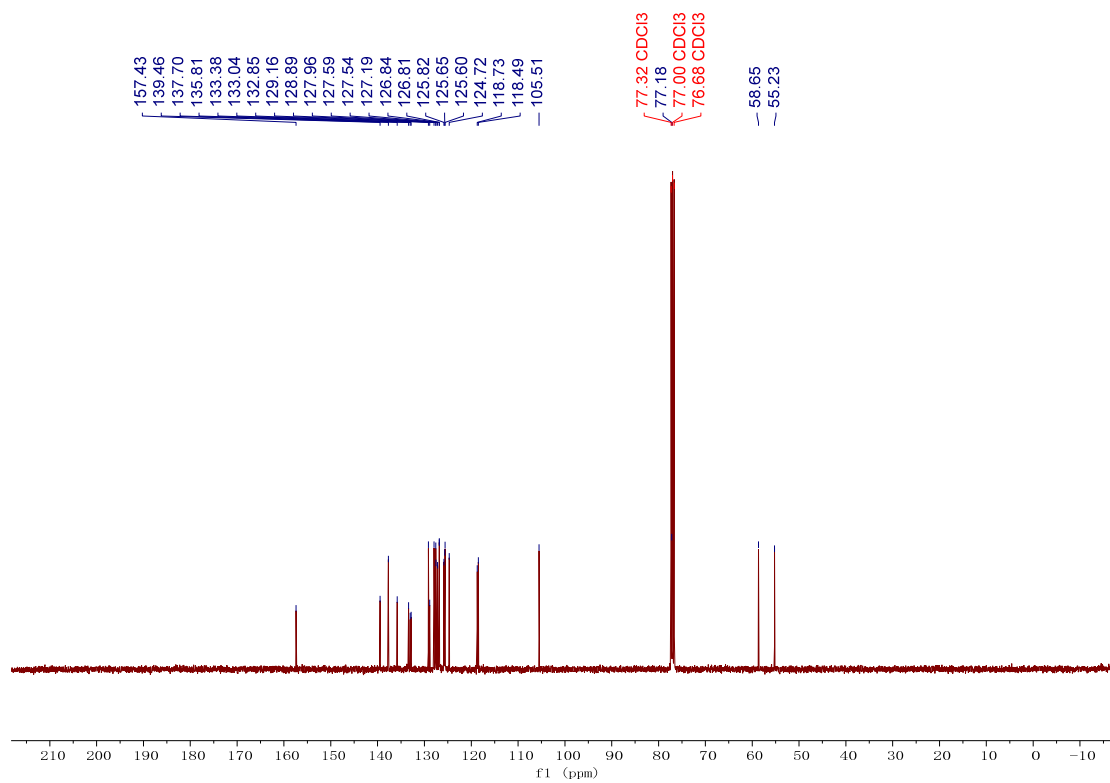


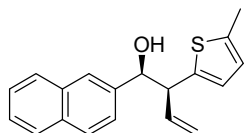
5i, 86% yield

¹H NMR (400 MHz, CDCl₃)

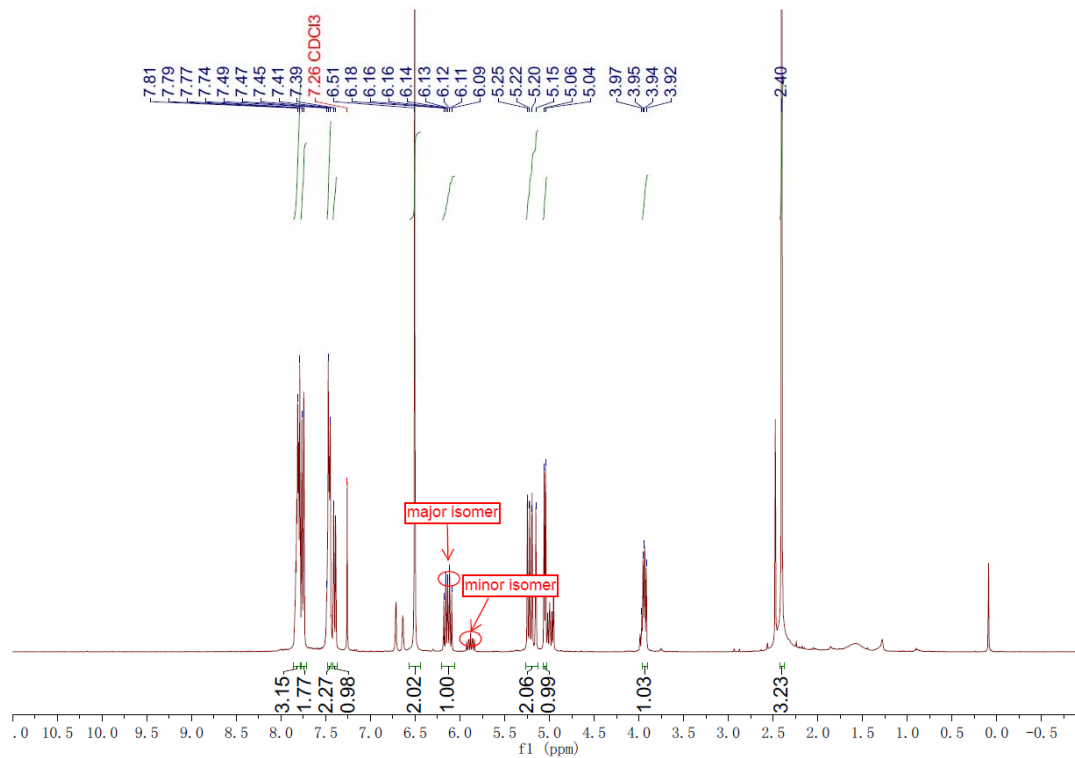


¹³C NMR (101 MHz, CDCl₃)

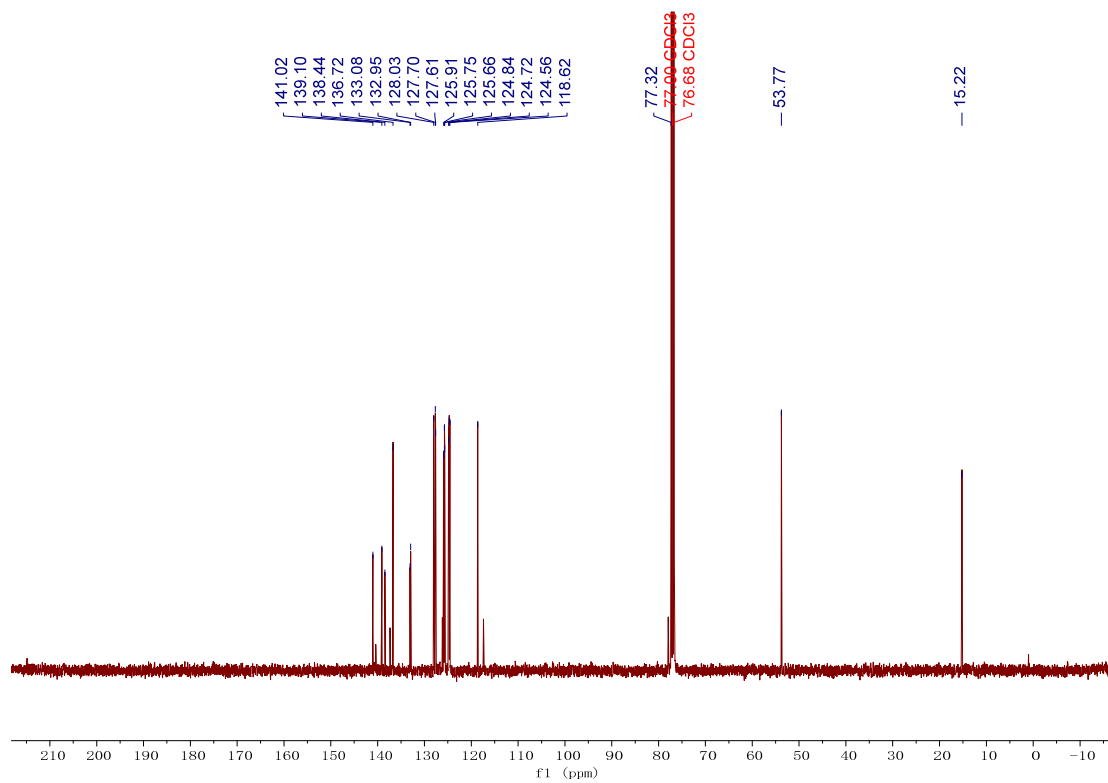


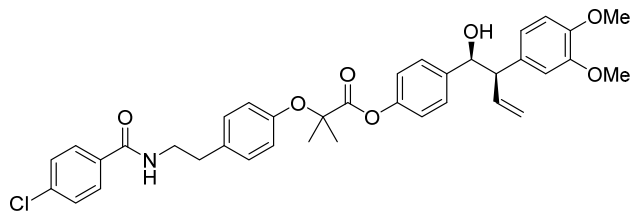


5j 40% yield $^1\text{H NMR}$ (400 MHz, CDCl_3)



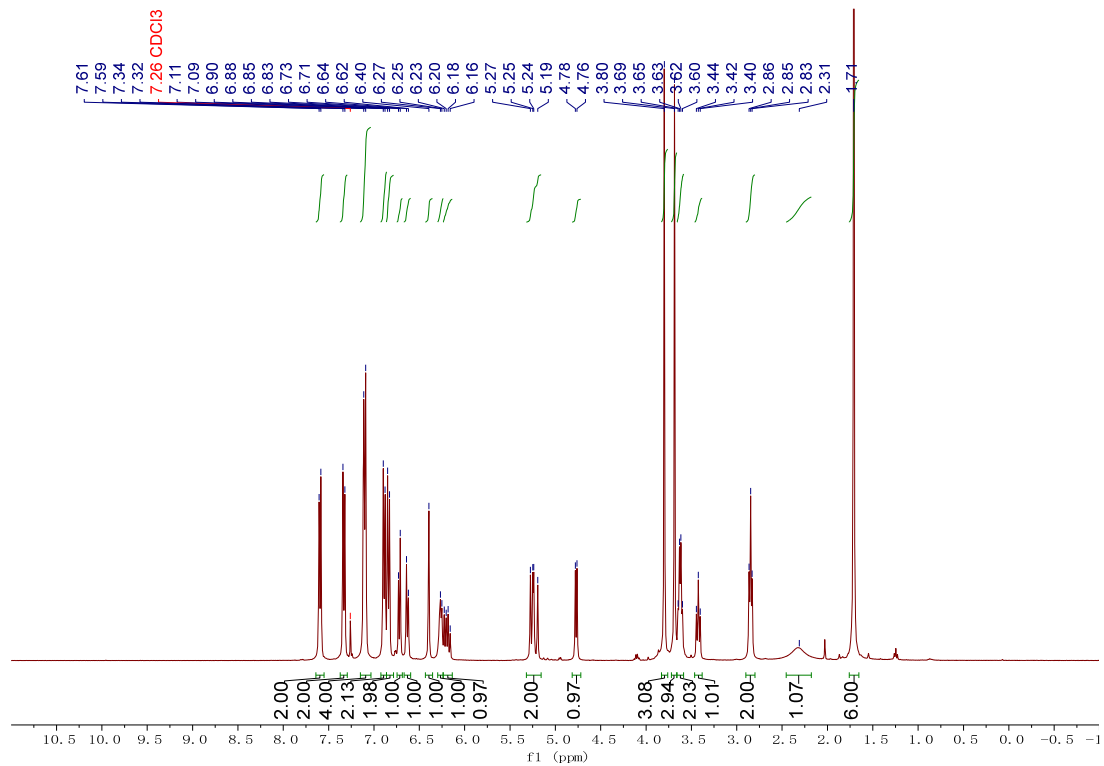
$^{13}\text{C NMR}$ (101 MHz, CDCl_3)



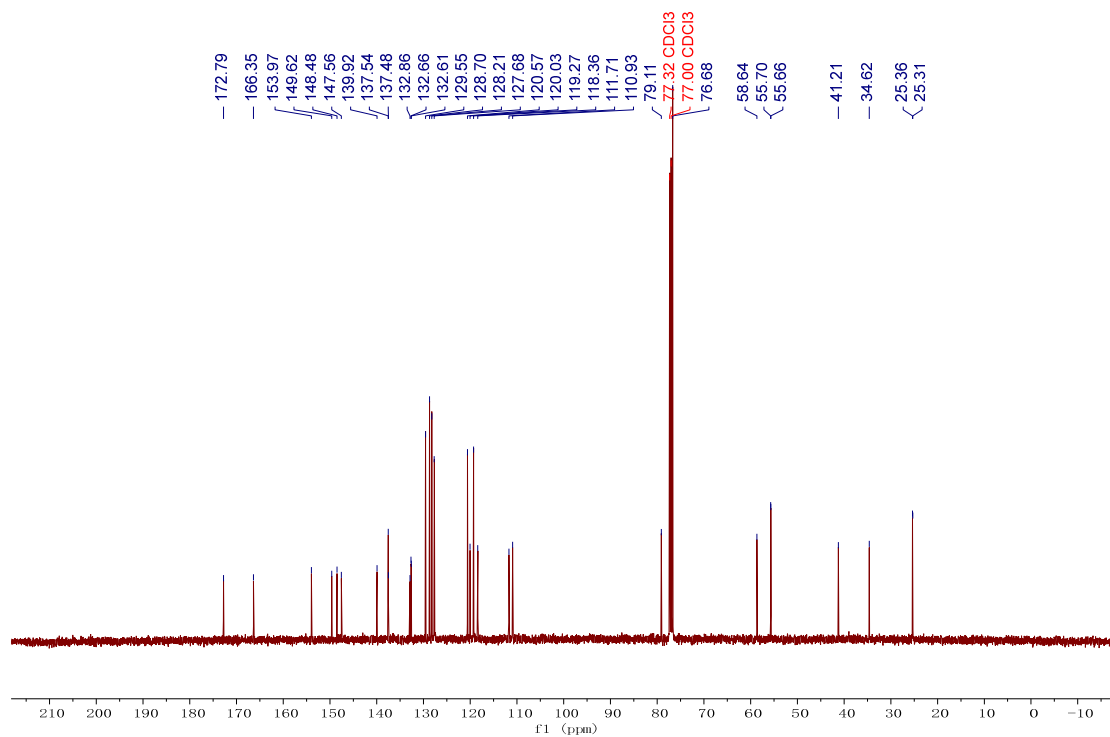


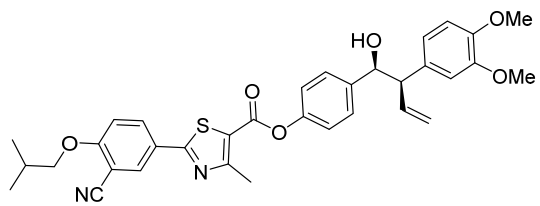
6a, 75% yield

¹H NMR (400 MHz, CDCl₃)



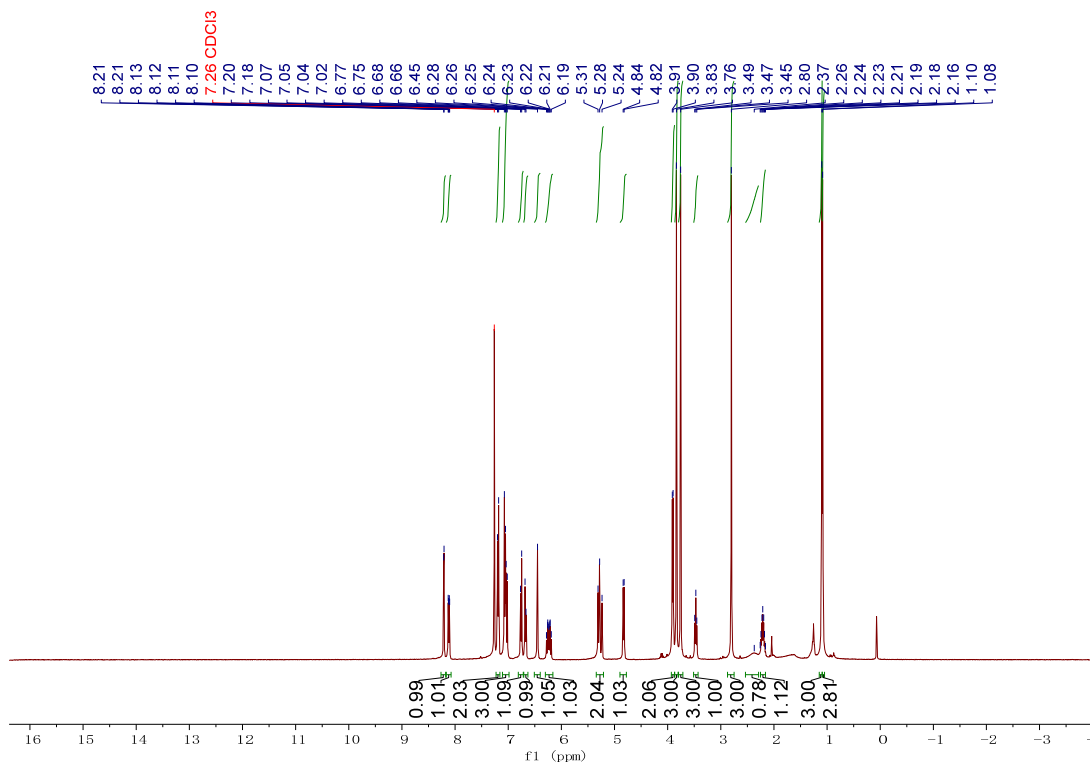
¹³C NMR (101 MHz, CDCl₃)



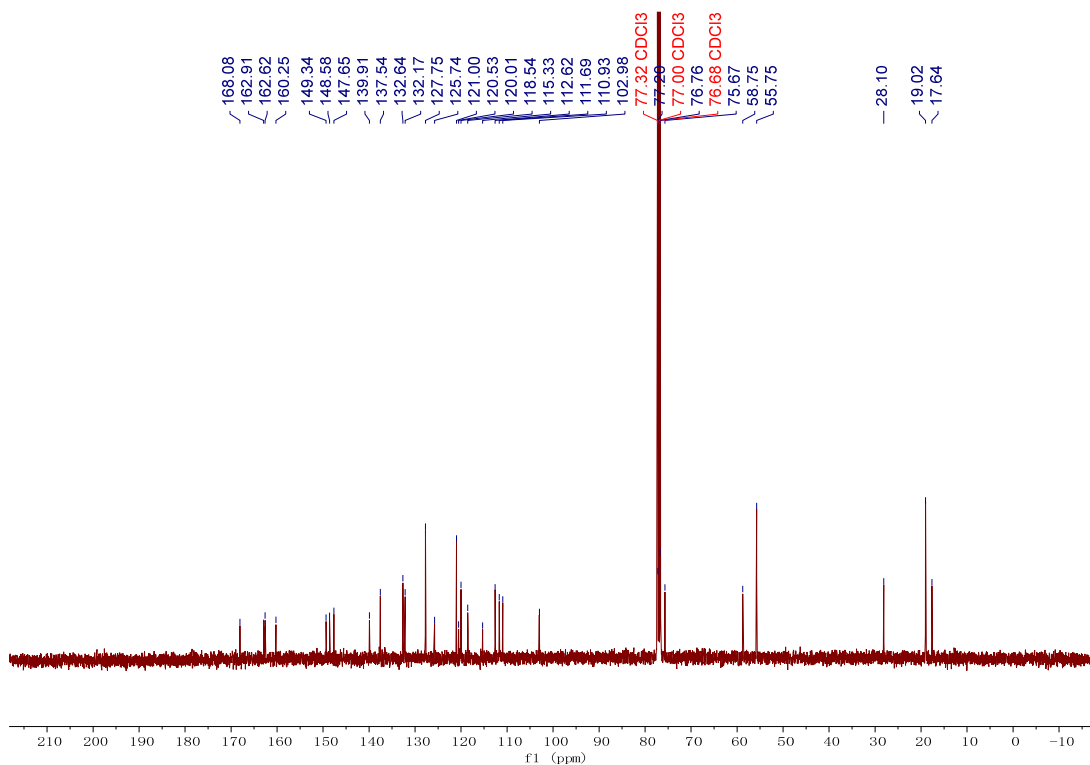


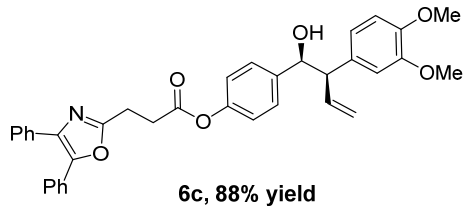
6b, 70% yield

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

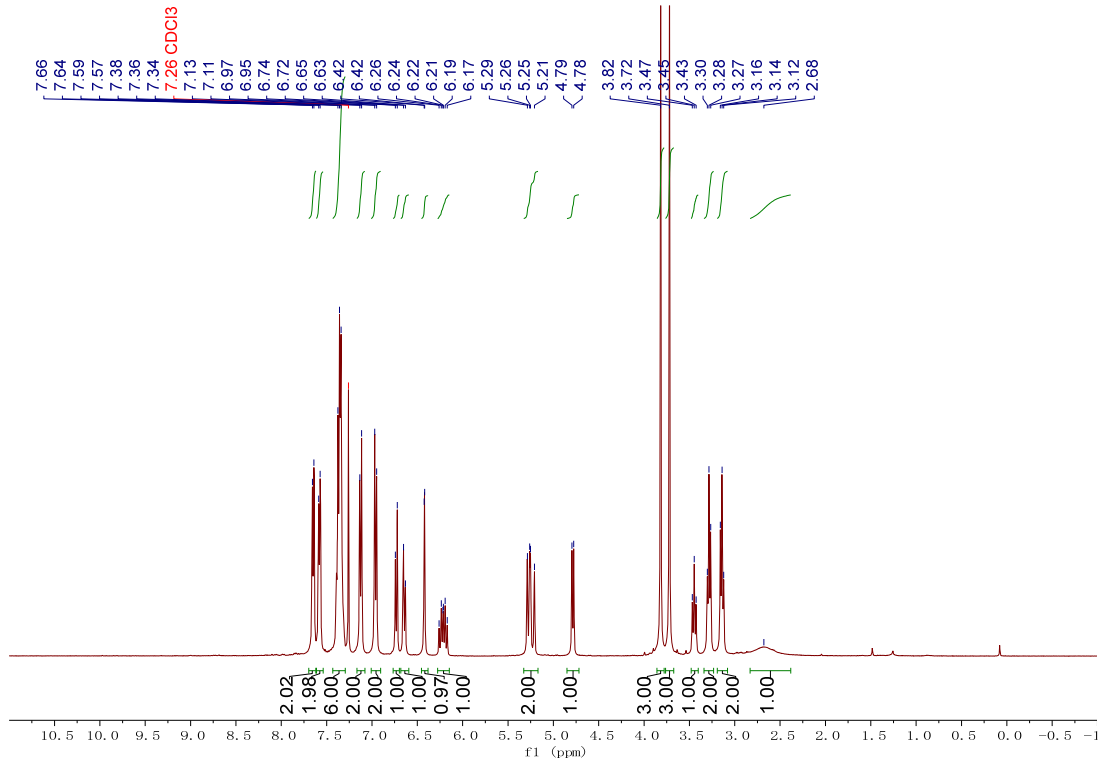


$^{13}\text{C NMR}$ (101 MHz, CDCl_3)





¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

