Regiodivergent Sulfonylation of Terminal Olefins *via* Dearomative Rearrangement

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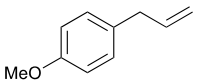
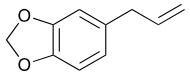
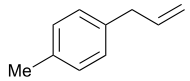
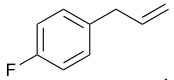
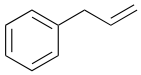
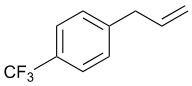
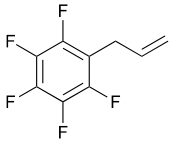
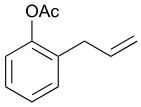
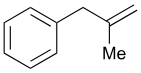
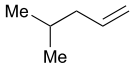
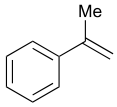
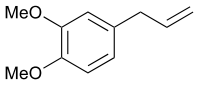
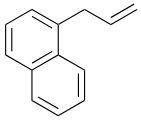
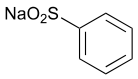
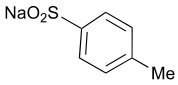
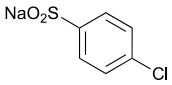
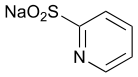
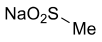
General Information

All reactions were carried out under air in oven-dried glassware with magnetic stirring at room temperature. All commercially obtained reagents were used as received. Solvents were dried and degassed from a JC Meyer company solvent purification system. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). TLC visualization was accompanied with UV light. Concentration in vacuo refers to the removal of volatile solvent using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr).

^{1}H NMR spectra were recorded at either 400 MHZ or 500 MHz, and are reported relative to $CDCl_3$ (δ = 7.26). ^{1}H NMR coupling constants (J) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet). Proton-decoupled ^{13}C NMR spectra were recorded at either 100 MHZ or 125 MHz and reported relative to $CDCl_3$ (δ = 77). IR experiments were recorded with neat samples on a Jasco FT/IR-4700 fitted with diamond ATR sample plate. GCMS data was recorded on a Shimadzu GC-2010 plus System (GCMS-QP2010 SE). High-resolution (HR) mass spectra were recorded at the Shimadzu Center Laboratory for Biological Mass Spectrometry.

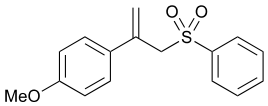
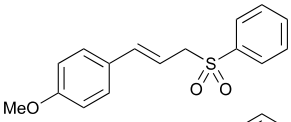
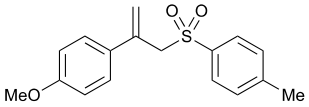
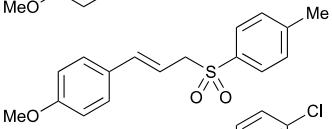
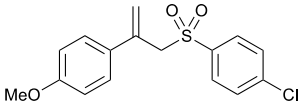
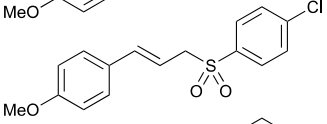
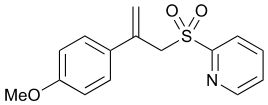
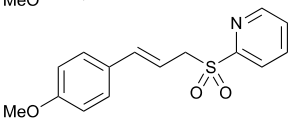
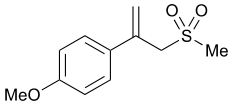
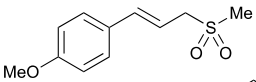
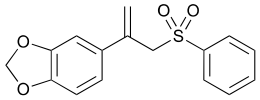
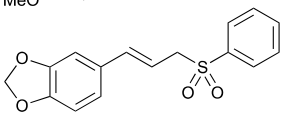
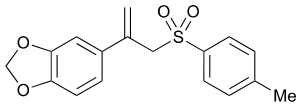
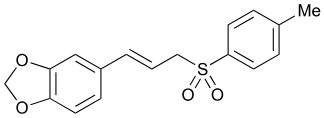
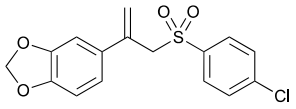
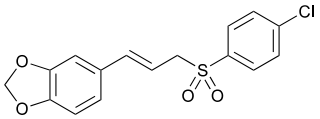
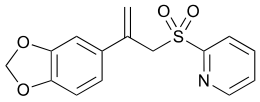
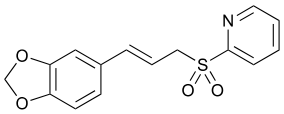
References to Used Allylbenzene Derivatives

Compound No.	Alkene	Ref.
1a		S1
1b		S1
1c		S1
1d		S1
1e		S1
1f		S1
1g		S1
1h		S1
1i		S1
1j		S1
1k		S1
1l		S1
1m		S1

Compound No.	Sulfinate	Ref.
2a		S1
2b		S1
2c		S1
2d		S1
2e		S1

S1) Commercially available (Millipore Sigma)

List and References to Sulfones Adducts (from Scheme **2**)

Compound No.	Expected Product (major)	Ref.	Compound No.	Possible Product (minor or not observed)	Ref.
4a		S2	**4a'**		S3
4b		S4	**4b'**		S5
4c		S6	**4c'**		--
4d		--	**4d'**		--
4e		--	**4e'**		--
4f		S7	**4f'**		--
4g		--	**4g'**		S5
4h		--	**4h'**		--
4i		--	**4i'**		--

S2) Li X.; Xu X.; Zhou C. *Chem. Commun.*, **2012**, *48 (100),* 12240-2. https://pubs.rsc.org/en/content/articlelanding/2012/cc/c2cc36960e

S3) Taniguchi N. *Synlett* **2013**, *24(19),* 2571-4. Disponible en: http://www.thieme-connect.de/DOI/DOI?10.1055/s-0033-1339846

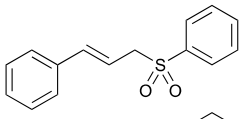
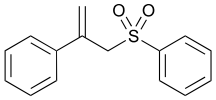
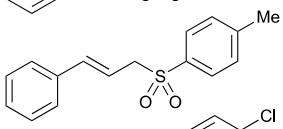
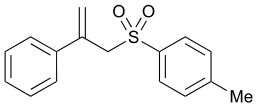
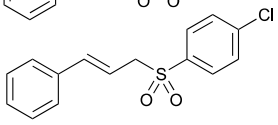
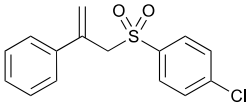
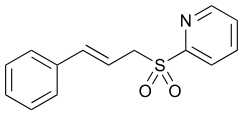
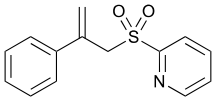
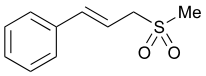
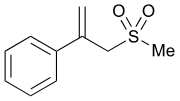
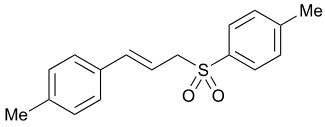
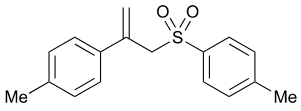
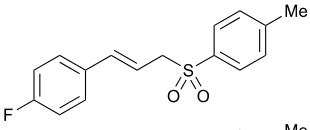
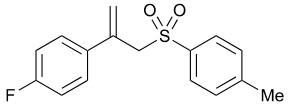
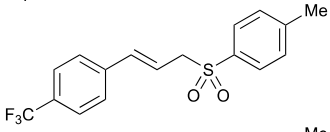
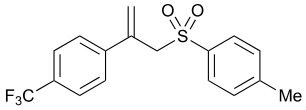
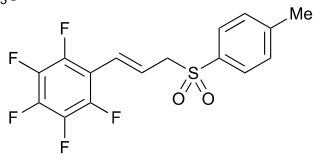
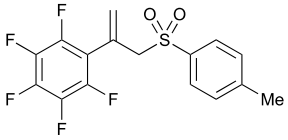
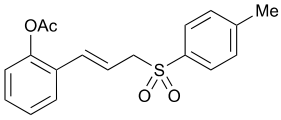
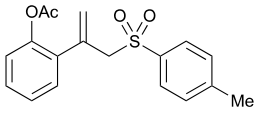
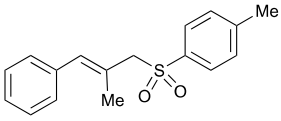
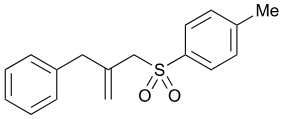
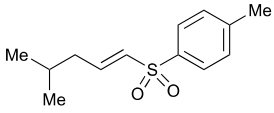
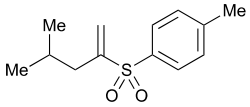
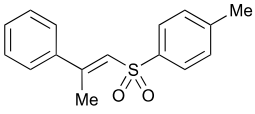
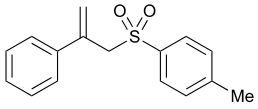
S4) Ermolaeva V.V.; Gerasimova N. P.; Nozhnin N. A.; Moskvichev Y. A.; Alov E. M.; Danilova A. S.; *et al. Mendeleev Commun.* **2005**, *15(2),* 84-6. https://www.sciencedirect.com/science/article/pii/S0959943605701954

S5) Yu J.; Chang X.; Ma R.; Zhou Q.; Wei M.; Cao X:, *et al. Eur. J. Org. Chem.* **2020**, *46*, 7238-42. https://onlinelibrary.wiley.com/doi/abs/10.1002/ejoc.202001306

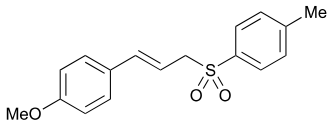
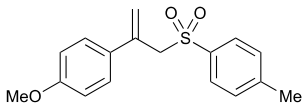
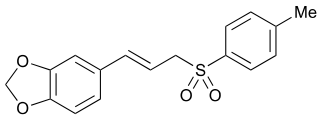
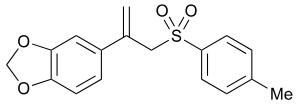
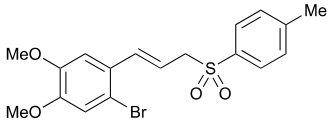
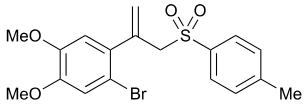
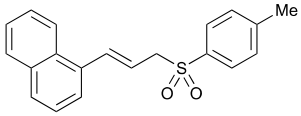
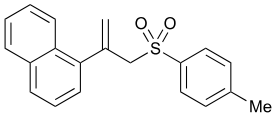
S6) Xu H.; Zhang H.; Tong Q. X.; Zhong J. J. *Org Biomol Chem* **2021**, *19(38),* 8227-31. https://pubs.rsc.org/en/content/articlelanding/2021/ob/d1ob01307f

S7) Karki M.; Magolan J. *J. Org. Chem.* **2015**, *80(7),* 3701-7. https://doi.org/10.1021/acs.joc.5b00211.

List and References to Sulfones Adducts (from Scheme **3**)

Compound No.	Expected Product (major)	Ref.	Compound No.	Possible Product (minor or not observed)	Ref.
3a		S8	**3a'**		S2
3b		S8, S9	**3b**		S4
3c		S9	**3c**		S11
3d		S13	**3d**		S12
3e		S8	**3e**		S14
3f		S10	**3f**		S4
3g		S9	**3g**		S4
3h		S9	**3h**		S4
3i		--	**3i**		--
3j		--	**3j**		--
3k		--	**3k**		--
3l		S16	**3l**		--
3m		S15	**3b**		S4

List and References to Sulfones Adducts (from Scheme **4**)

Compound No.	Expected Product (major)	Ref.	Compound No.	Possible Product (minor or not observed)	Ref.
4b'		S5	**4b**		S4
4g'		S5	**4g**		- -
3n		- -	**3n'**		- -
3o		S9	**3o'**		S2

S8) Chandrasekhar S.; Jagadeshwar V.; Saritha B.; Narsihmulu C. *J. Org. Chem.* **2005**, *70(16),* 6506-7. https://pubs.acs.org/doi/10.1021/jo0505728.

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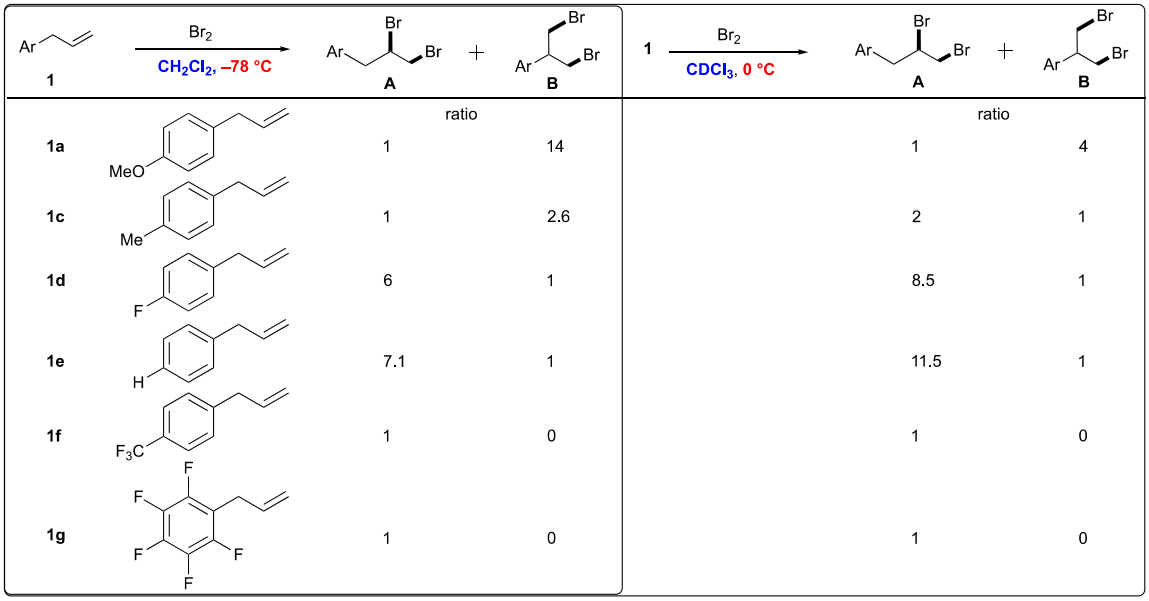
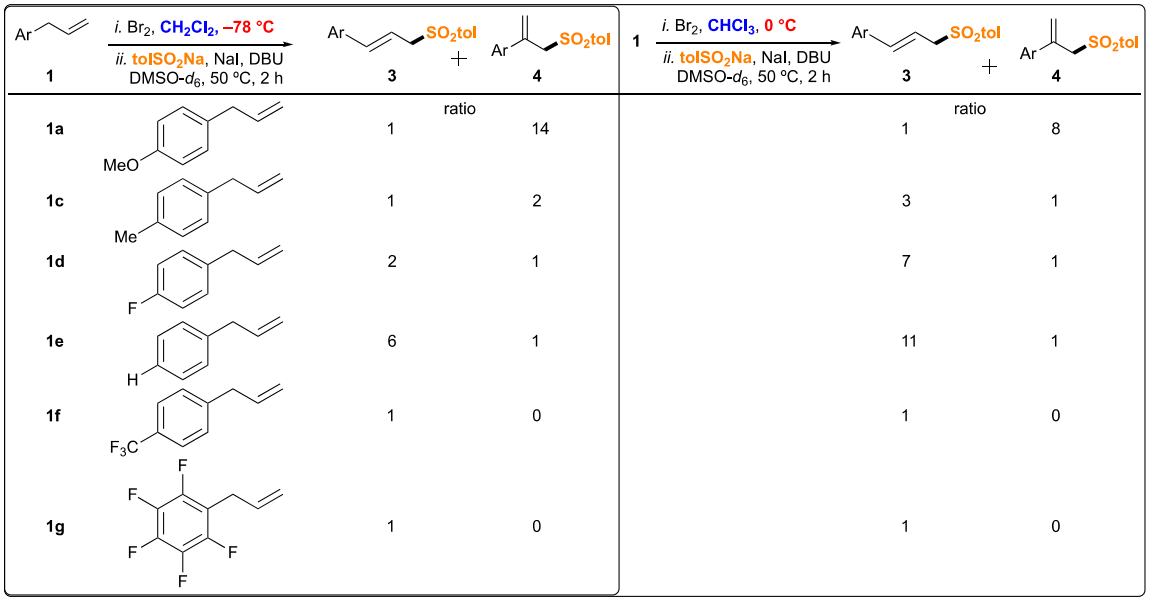
Table S1. Bromination and sulfonylation study (Ratios by ^{1}H NMR)



		ratio			ratio
1a	MeO	1	14	1	4
1c	Me	1	2.6	2	1
1d	F	6	1	8.5	1
1e	H	7.1	1	11.5	1
1f	F_3C	1	0	1	0
1g	F, F, F, F, F	1	0	1	0

Procedure Step 1: To a 10 mL round-bottomed flask, equipped with a stir bar, was added allylaryl (**1**) (0.25 mmol, 1.0 equiv.) and CH_2Cl_2 or $CDCl_3$ (1.0 mL) at room temperature under air. The mixture was cooled down to either –78 °C (*i*PrOH/dry ice) or 0 °C (ice bath), followed by dropwise addition of Br_2 (0.33 mmol, 17 µL, 1.3 equiv.). The reaction was stirred until deemed completed; at either –78 °C for 30 minutes or at 0 °C for 10 minutes. Then, the mixture was analyzed by ^{1}H NMR. Note 1: If $N_{2(liq)}$/MeOH bath (–98 °C) was used, the ratio for **1a** was 1:6 (**A**:**B**), due to freezing of the CH_2Cl_2. On the other hand, when $CHCl_3$ was used instead of $CDCl_3$ under ice bath (0 °C) the ratio for **1a** was 1:10 (**A**:**B**). This indicates the importance of the solvent and temp.

Table S2. Effects on the two-step protocol.



		ratio			ratio
1a	MeO	1	14	1	8
1c	Me	1	2	3	1
1d	F	2	1	7	1
1e	H	6	1	11	1
1f	F_3C	1	0	1	0
1g	F, F, F, F, F	1	0	1	0

Procedure: To a 10 mL round bottom flask was added allylaryl (**1**) (0.40 mmol, 1.0 equiv), solvent (1 mL), at room temperature open to air. The mixture was cooled, followed by the dropwise adding of Br_2 (0.44 mmol, 1.10 equiv). The reaction mixture was stirred. Then, the mixture was concentrated *in vacuo* to afford crude dibromide adduct. To the crude dibromo adduct, DMSO (1 mL), sulfinate nucleophiles (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and DBU (0.48 mmol, 1.20 equiv) were added sequentially. The reaction flask was capped and stirred at 50 °C for 2 h. Then, the mixture was analyzed by ^{1}H NMR (internal std. = mesitylene).

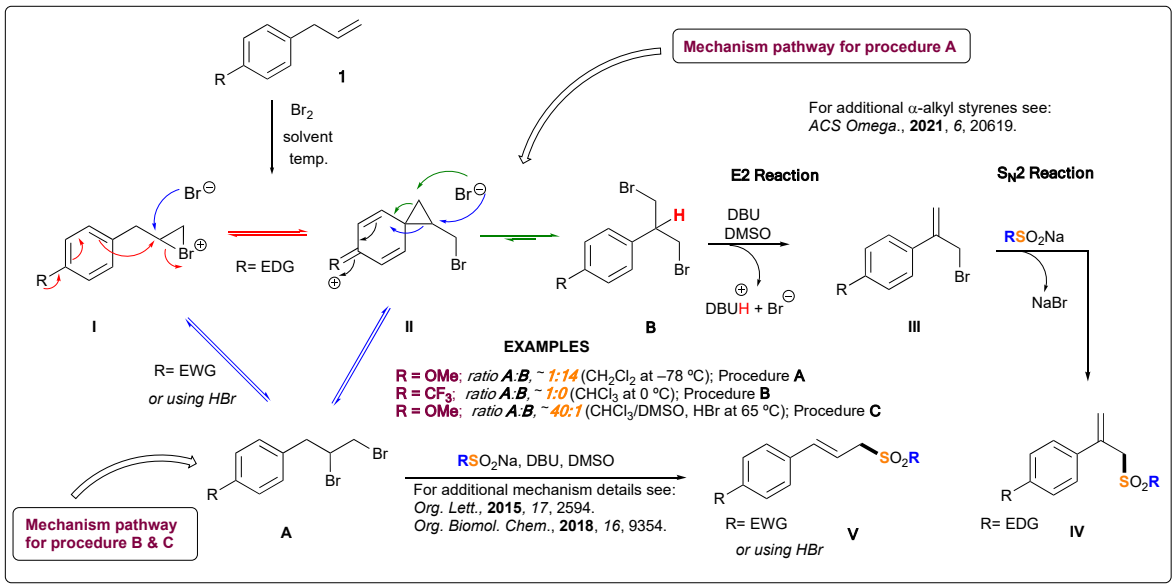
Proposed Mechanism (Scheme ESI-1)

Based on our precedent work and the data previously shown, plausible mechanisms will be as follows:

PROCEDURE A: allylaryl **1** undergoes an alkene bromination to form bromonium ion (**I**), which in turn undergoes an intramolecular attack by the electron-rich benzene to dearomatize the aryl group to form a spiro[2.5] intermediate (**II**). This intermediate, can be ring-opened by bromide ion to produce either a 2,3-dibromo (**A**) or a 1,3-dibromo intermediate (**B**). The 1,3-dibromo adduct is the product of a rearrangement step driven by the formation of the spiro[2.5] intermediate and it is the favored adduct using DCM at –78 ºC. Therefore, it is present in higher ratio. After this dibromination step, an E2 elimination, enabled by DBU produces allyl bromide (**III**), which in turn reacts via a S_N2 displacement to afford the expected α-sulfonylmethyl styrenes (**IV**). It is important to note that intermediates **I**, **II**, **A**, and **B** are in equilibrium and therefore under the correct conditions, we can favor the formation of intermediate **B** to enhance the rearrangement yields. Additional mechanistic details for the formation of adducts like (**IV**) can be found in *ACS Omega* **2021**, *6*, 20619.

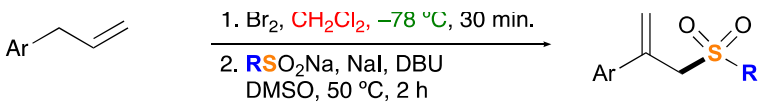
PROCEDURE B: allylaryl **1** undergoes an alkene bromination to form bromonium ion (**I**), which in turn undergoes either a direct bromonium opening by bromide ion to directly form 2,3-dibromo (**A**) (favored using chloroform at 0 ºC) or it can experience an intramolecular attack by benzene to dearomatize the aryl group to form a spiro[2.5] intermediate (**II**). However, the dearomatization is only favored with EDG. Therefore, this unlikely happens when EWG are present, but if it does, this intermediate, can be ring-opened by bromide ion to produce also the 2,3-dibromo intermediate (**A**). After the dibromination step, an E2 elimination, enabled by followed by a S_N2 displacement affords the expected allylsulfones (**V**). Additional mechanistic details for the formation of adducts like (**V**) can be found in *Org. Biomol. Chem.* **2018**, *16*, 9354 and *Org. Lett.* **2015**, *17*, 2594.

PROCEDURE C: This procedure utilizes acidic conditions to synthesize the 2,3-dibromo intermediate (**A**). Therefore, the heteroatoms in the benzene ring get protonated, thus changing their nature from EDG to EWG and therefore it will follow the same mechanistic path as procedure B, giving access to adducts like (**V**).



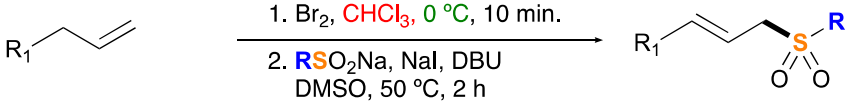
General Procedures and Characterization Data

Procedure A (for electron rich systems**):**



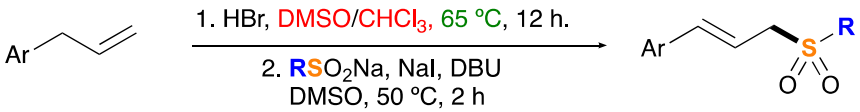
To a 10 mL round bottom flask was added olefin (0.40 mmol, 1.0 equiv), CH_2Cl_2 (1 mL), at room temperature open to air. The mixture was cooled to –78 ˚C, followed by the dropwise adding of Br_2 (0.44 mmol, 1.10 equiv). The reaction mixture was stirred for 30 min. Then, the mixture was concentrated *in vacuo* to afford crude dibromide adduct. To the crude dibromo adduct, DMSO (1 mL), sulfinate nucleophiles (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and DBU (0.48 mmol, 1.20 equiv) were added sequentially. The reaction flask was capped and stirred at 50 °C for 2 h. Purification by flash chromatography [SiO_2, EtOAc/hexanes/Et_3N (85:15:0.5 mixtures)] provided pure products. Ratios were calculated using ^{1}H NMR of crude samples (IS = mes).

Procedure B (for electron weak, electron neutral, and electron poor systems**):**

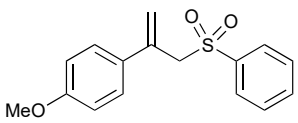


To a 10 mL round bottom flask was added olefin (0.40 mmol, 1.0 equiv), $CHCl_3$ (1 mL), at room temperature open to air. The mixture was cooled to 0 ˚C, followed by the dropwise adding of Br_2 (0.44 mmol, 1.10 equiv). The reaction mixture was stirred for 30 min. Then, the mixture was concentrated *in vacuo* to afford crude dibromide adduct. To the crude dibromo adduct, DMSO (1 mL), sulfinate nucleophiles (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and DBU (0.48 mmol, 1.20 equiv) were added sequentially. The reaction flask was capped and stirred at 50 °C for 2 h. Purification by flash chromatography [SiO_2, EtOAc/hexanes/Et_3N (85:15:0.5 mixtures)] provided pure products. Ratios were calculated using ^{1}H NMR of crude samples (IS = mes).

Procedure C (to access linear adduct with electron rich systems**):**



To a 10 mL round bottom flask was added olefin (0.40 mmol, 1.0 equiv), HBr (48%aq, 5 equiv), DMSO (0.5 mL), $CHCl_3$ (0.5 mL), the reaction was capped and stirred at 65 °C for 12 h. Then the reaction mixture was transferred to a separatory funnel containing water and extracted with Ethyl Acetate (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$, and solvent was removed *in vacuo* to afford crude dibromide adduct.(16)[1] To the crude dibromo adduct, DMSO (1 mL), sulfinate nucleophiles (0.60 mmol, 1.5 equiv), NaI (0.40 mmol, 1.0 equiv), and DBU (0.48 mmol, 1.20 equiv) were added sequentially. The reaction flask was capped and stirred at 50 °C for 2 h. Purification by flash chromatography (SiO_2, EtOAc/hexanes/Et_3N 85:15:0.5 mixtures) provided pure products. Ratios were calculated using ^{1}H NMR of crude samples (IS = mes).

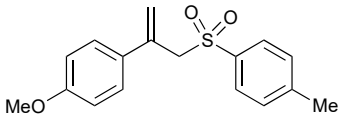


1-methoxy-4-(3-(phenylsulfonyl)prop-1-en-2-yl)benzene (4a). Prepared from 1-allyl-4-methoxybenzene (59 mg, 0.4 mmol) and sodium benzenesulfinate (66 mg, 0.6 mmol, 1.5 equiv) according to procedure A. Colorless liquid (69 mg, 61%), ratio (12.5:1).

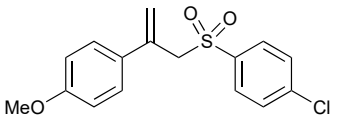
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.79 – 7.75 (m, 2H), 7.58 – 7.51 (m, 1H), 7.43 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.24 – 7.16 (m, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 5.48 (s, 1H), 5.06 (d, *J* = 0.9

[1] M. Karki and J. Magolan, *J. Org. Chem.*, 2015, **80**, 3701–3707.

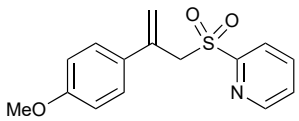
Hz, 1H), 4.23 (d, *J* = 0.8 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 159.57, 138.43, 135.84, 133.74, 131.19, 128.99, 128.75, 127.53, 120.24, 113.85, 62.26, 55.39. IR (neat, cm^{-1}): 3053, 2923, 1604, 1508,1295, 1249, 1141, 516.
LRMS (EI) Calcd for $C_{16}H_{16}O_3S$ [M], 288 Found: 288(M). The spectroscopic data agrees with those reported in the literature (S2).



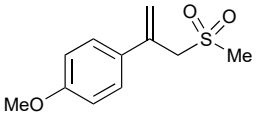
1-methoxy-4-(3-tosylprop-1-en-2-yl)benzene (4b). Prepared from 1-allyl-4-methoxybenzene (59 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to procedure A. Colorless liquid (78 mg, 65%), ratio (25:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 4H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.49 (s, 1H), 5.06 (s, 1H), 4.22 (s, 2H), 3.77 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 159.54, 144.66, 135.96, 135.47, 131.30, 129.58, 128.77, 127.55, 120.10, 113.79, 62.35, 55.38, 21.70. IR (neat, cm^{-1}): 3066, 2927, 1608, 1511,1307, 1253, 1145, 536. LRMS (EI) Calcd for $C_{17}H_{18}O_3S$ [M], 302. Found: 302(M). The spectroscopic data matches the reported literature (S4).



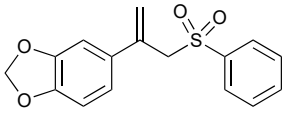
1-chloro-4-((2-(4-methoxyphenyl)allyl)sulfonyl)benzene (4c). Prepared from 1-allyl-4-methoxybenzene (59 mg, 0.4 mmol) and sodium 4-chlorobenzenesulfinate (79 mg, 0.6 mmol, 1.5 equiv) according to procedure A. White solid (80 mg, 63%), melting point: 106 ºC, ratio (20:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 5.51 (s, 1H), 5.10 (s, 1H), 4.25 (s, 2H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 159.70, 140.42, 136.82, 135.81, 130.84, 130.27, 129.22, 127.53, 120.48, 113.89, 62.48, 55.43. **IR** (neat, cm^{-1}): 3050, 2937, 2923, 1592, 1500,1307, 1133, 512. **LRMS (EI)** Calcd for $C_{16}H_{15}ClO_3S$ [M], 322. Found: 322(M). The spectroscopic data agrees with those reported in the literature (S6).
Suitable crystals for X-Ray diffraction were grown as follows: The all sample (59 mg) was dissolved in a minimum amount of ethyl acetate and 3 drops of hexanes were added. It was left to settle, after 24 hours crystals were formed and sent for analysis.



2-((2-(4-methoxyphenyl)allyl)sulfonyl)pyridine (4d). Prepared from 1-allyl-4-methoxybenzene (59 mg, 0.4 mmol) and sodium pyridine-2-sulfinate (66 mg, 0.6 mmol, 1.5 equiv) according to procedure A. Colorless liquid (63 mg, 55%), ratio (10:1).
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.74 – 8.64 (m, 1H), 7.97 – 7.84 (m, 1H), 7.84 – 7.75 (m, 1H), 7.48 – 7.39 (m, 1H), 7.23 (d, J = 8.8 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 5.48 (s, 1H), 5.15 (s, 1H), 4.52 (s, 2H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 159.52, 156.57, 150.24, 137.92, 135.37, 131.16, 127.67, 127.41, 123.40, 120.49, 113.77, 77.51, 77.19, 76.88, 57.95, 55.39. **IR** (neat, cm^{-1}): 3054, 2931, 1600, 1508,1303, 1249, 1160, 528.
HRMS (APCI/ IT-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{15}H_{16}NO_3S$ = 290.0845; found 290.0827.

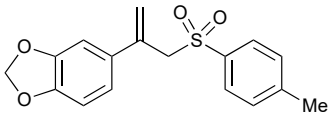


1-methoxy-4-(3-(methylsulfonyl)prop-1-en-2-yl)benzene (4e). Prepared from 1-allyl-4-methoxybenzene (59 mg, 0.4 mmol) and sodium methanesulfinate (41 mg, 0.6 mmol, 1.5 equiv) according to procedure A. White solid (40 mg, 42%), melting point: 73 ºC, ratio (20:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.40 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 5.67 (s, 1H), 5.44 (s, 1H), 4.15 (s, 2H), 3.80 (s, 3H), 2.72 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 159.96, 136.12, 130.96, 127.90, 127.66, 120.51, 114.26, 61.00, 55.43, 40.29. **IR** (neat, cm^{-1}): 3054, 3012, 2927, 1604, 1511,1295, 1241, 1180, 497.
HRMS (APCI/ IT-TOF) *m/z*: [M + H]$^{+}$ calcd for $C_{11}H_{15}O_3S$ = 227.0736; found 227.0699.

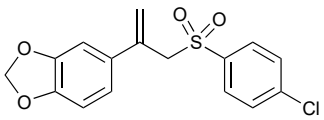


5-(3-(phenylsulfonyl)prop-1-en-2-yl)benzo[*d*][1,3]dioxole (4f). Prepared from 5-allylbenzo[*d*][1,3]dioxole (65 mg, 0.4 mmol) and sodium benzenesulfinate (66 mg, 0.6 mmol, 1.5 equiv) according to general procedure A. White solid (71 mg, 59%), melting point: 78 ºC, ratio (10:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.82 – 7.74 (m, 2H), 7.66 – 7.48 (m, 1H), 7.44 (dd, *J* = 8.4, 7.1 Hz, 2H), 6.74 (dq, *J* = 3.5, 1.9 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 1H), 5.91 (s, 2H), 5.45 (s, 1H), 5.07 (s, 1H), 4.19

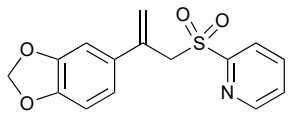
(s, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 147.85, 147.63, 138.43, 136.03, 133.77, 133.10, 129.01, 128.74, 120.88, 120.25, 108.16, 106.84, 101.33, 62.39.
IR (neat, cm^{-1}): 3066, 2923, 1608, 1481,1299, 1234, 1137, 516. **LRMS (EI)** Calcd for $C_{16}H_{14}O_4S$ [M], 302. Found: 302(M).
The spectroscopic data agrees with those reported in the literature (S7).



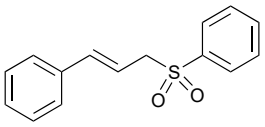
5-(3-tosylprop-1-en-2-yl)benzo[*d*][1,3]dioxole (4g). Prepared from 5-allylbenzo[*d*][1,3]dioxole (65 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure A. Light yellow liquid (80 mg, 63%), ratio (4:1).
^{1}H NMR (400 MHz, ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.65 (d, *J* = 7.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.80 – 6.71 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 5.45 (s, 1H), 5.07 (s, 1H), 4.17 (s, 2H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 147.80, 147.57, 144.75, 136.17, 135.47, 133.24, 129.61, 128.78, 120.77, 120.27, 108.14, 106.91, 101.31, 62.52, 21.71. **IR** (neat, cm^{-1}): 3066, 2919, 1596, 1492,1288, 1234, 1130, 505. **HRMS** (APCI/ IT-TOF) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{17}O_4S$ = 317.0842; found 317.0814.



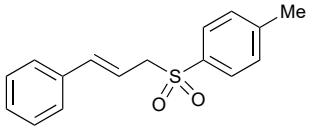
5-(3-((4-chlorophenyl)sulfonyl)prop-1-en-2-yl)benzo[d][1,3]dioxole (4h). Prepared from 5-allylbenzo[*d*][1,3]dioxole (65 mg, 0.4 mmol) and sodium 4-chlorobenzenesulfinate (79 mg, 0.6 mmol, 1.5 equiv) according to general procedure A. Light yellow solid (87 mg, 65%), melting point: 122 ºC, ratio (10:1).
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.67 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.69 – 6.64 (m, 3H), 5.94 (s, 2H), 5.48 (s, 1H), 5.11 (s, 1H), 4.20 (s, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 147.87, 147.73, 140.46, 136.83, 135.99, 132.75, 130.25, 129.23, 121.13, 120.27, 108.21, 106.77, 101.44, 62.62. **IR** (neat, cm^{-1}): 3089, 2915, 1604, 1573, 1481,1303, 1238, 1133, 563, 528.
HRMS (APCI/ IT-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{14}ClO_4S$ = 337.0296; found 337.0251.



2-((2-(benzo[d][1,3]dioxol-5-yl)allyl)sulfonyl)pyridine (4i). Prepared from 5-allylbenzo[*d*][1,3]dioxole (65 mg, 0.4 mmol) and sodium pyridine-2-sulfinate (66 mg, 0.6 mmol, 1.5 equiv) according to general procedure A. Light yellow liquid (67 mg, 55%), ratio (20:1).
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 8.70 (d, *J* = 4.7 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.7 Hz, 1H), 7.51 – 7.43 (m, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.91 (s, 2H), 5.47 (s, 1H), 5.18 (s, 1H), 4.50 (s, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 156.64, 150.24, 147.75, 147.59, 137.89, 135.57, 133.08, 127.40, 123.36, 121.14, 120.44, 108.10, 106.99, 101.30, 58.05.
IR (neat, cm^{-1}): 3066, 2900, 1608, 1492, 1438,1307, 1234, 1160, 532.
HRMS (APCI/ IT-TOF) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{14}NO_4S$ = 304.0638; found 337.0594.

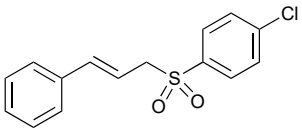


1-(cinnamylsulfonyl)benzene (3a). Prepared from allylbenzene (47 mg, 0.4 mmol) and sodium benzenesulfinate (66 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Light yellow solid (67 mg, 65%), melting point: 109 °C, ratio (1:40).
^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.33-7.25 (m, 5H), 6.38 (d, *J* = 15.3 Hz, 1H), 6.11 (dt, *J* = 15.1, 7.5 Hz, 1H), 3.96 (d, *J* = 7.5 Hz, 2H); **^{13}C NMR** (125 MHz, CHLOROFORM-*D*) δ 139.3, 138.4, 135.8, 133.90, 129.2, 128.7, 128.6, 128.5, 126.7, 115.2, 60.6. **IR** (neat, cm^{-1}): 3028, 2904, 1597, 1317, 1291, 753, 528.
LRMS (EI) Calcd for $C_{15}H_{14}O_2S$ [M], 258.07. Found: 258.07(M).
The spectroscopic data agrees with those reported in the literature (S8)

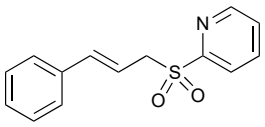


1-(cinnamylsulfonyl)-4-methylbenzene (3b). Prepared from allylbenzene (47 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. White solid, (64 mg, 59%), melting point: 90 °C, ratio (>50:1).
^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.81-7.74 (m, 2H), 7.35-7.28 (m, 7H), 6.41 (dt, *J* = 15.1 Hz, 1H), 6.12 (dt, *J* = 15.1, 7.6 Hz, 1H), 3.96 (dd, *J* = 7.5, 1.2 Hz, 2H), 2.45 (s, 3H); **^{13}C**

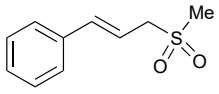
NMR (125 MHz, CHLOROFORM-*D*) δ 144.8, 139.0, 135.9, 135.5, 129.8, 128.7, 128.5, 128.5, 126.7, 115.4, 60.61, 21.7. **IR** (neat, cm^{-1}): 3022, 2920, 1593, 1311, 614, 515.
LRMS (EI) Calcd for $C_{16}H_{16}O_2S$ [M], 272 Found: 272(M).
The spectroscopic data agrees with those reported in the literature (S8, S9)
Suitable crystals for X-Ray diffraction were grown as follows: The all sample (59 mg) was dissolved in a minimum amount of ethyl acetate and 3 drops of hexanes were added. It was left to settle, after 24 hours crystals were formed and sent for analysis.



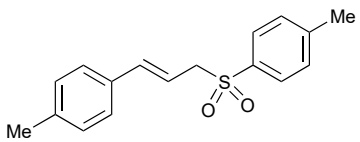
1-chloro-4-(cinnamylsulfonyl)benzene (3c). Prepared from allylbenzene (47 mg, 0.4 mmol) and sodium 4-chlorobenzenesulfinate (79 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Light yellow solid (73 mg, 63%), melting point: 103 °C, ratio (50:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.17 (m, 5H), 6.38 (d, *J* = 16.0, 1.2 Hz, 1H), 6.08 (dt, *J* = 15.8, 7.6 Hz, 1H), 3.94 (dd, *J* = 7.6, 1.2 Hz, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 140.62, 139.54, 136.82, 135.59, 130.10, 129.50, 128.80, 126.70, 114.81, 60.54 ppm. **IR** (neat, cm^{-1}): 3050, 2973, 2923, 1597, 1500, 1307, 1133, 512.
LRMS (EI) Calcd for $C_{15}H_{13}ClO_2S$ [M], 292. Found: 292(M).
The spectroscopic data agrees with those reported in the literature (S9)



2-(cinnamylsulfonyl)pyridine (3d). Prepared from allylbenzene (47 mg, 0.4 mmol) and sodium pyridine-2-sulfinate (66 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Light yellow liquid (53 mg, 52%), ratio (>50:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.78 (dd, *J* = 4.7, 1.6 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.91 (td, *J* = 7.7, 1.7 Hz, 1H), 7.53 (dd, *J* = 7.7, 4.7 Hz, 1H), 7.29 – 7.21 (m, 5H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.09 (dt, *J* = 15.6, 7.6 Hz, 1H), 4.28 (dd, *J* = 7.7, 1.1 Hz, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 156.70, 150.33, 139.67, 138.23, 135.78, 128.72, 128.63, 127.56, 123.01, 114.52, 56.23. **IR** (neat, cm^{-1}): 3050, 2973, 2923, 1592, 1500, 1307, 1133, 513.
LRMS (EI) Calcd for $C_{14}H_{13}NO_2S$ [M], 259. Found: 259(M).
The spectroscopic data agrees with those reported in the literature (S13)

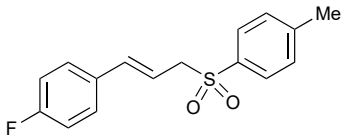


(*E*)-(3-(methylsulfonyl)prop-1-en-1-yl)benzene (3e). Prepared from allylbenzene (47 mg, 0.4 mmol) and sodium methanesulfinate (41 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Light yellow solid (35 mg, 45%), melting point: 120 °C. ratio: single product.
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.44 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.88 (d, *J* = 7.6 Hz, 2H), 2.89 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 139.19, 135.48, 128.94, 128.90, 126.85, 115.66, 59.26, 39.29. **IR** (neat, cm^{-1}): 3043, 3019 2927, 1596, 1492, 1268, 1118, 539.
LRMS (EI) Calcd for $C_{10}H_{12}O_2S$ [M], 196. Found: 196M).
The spectroscopic data agrees with those reported in the literature (S8)



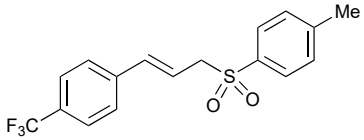
1-methyl-4-[(1*E*)-3-(4-methylbenzene-1-sulfonyl)prop-1-en-1-yl]benzene (3f). Prepared from 1-allyl-4-methylbenzene (53 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. White solid, (70 mg, 62%), melting point: 98 °C. This wsa the only adduct that showed a crude ratio of (3:1), while after purification we were able to enhance the ratio to (>50:1), as shown by the ^{1}H NMR spectrum (see below). This due to having the week electron donating group (Me). See Table S2 above.
^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.75-7.73 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.34 (d, *J* = 15.0 Hz, 1H), 6.04 (dt, *J* = 15.0, 7.5 Hz, 1H), 3.92 (dd, *J* = 7.35, 1.0 Hz, 2H), 2.43 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (125 MHz, CHLOROFORM-*D*) δ 144.8, 139.0, 138.6, 135.6,

133.2, 129.8, 129.4, 128.6, 126.6, 114.3, 60.7, 21.7, 21.3. **IR** (neat, cm^{-1}): 3029, 2917, 1595, 1312, 1288, 759, 514.
LRMS (EI) Calcd for $C_{17}H_{18}O_2S$ [M], 286. Found: 286(M).
The spectroscopic data agrees with those reported in the literature (S10)

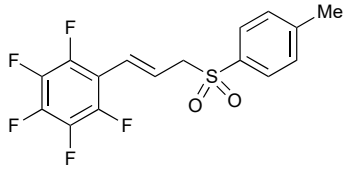


1-fluoro-4-[(1*E*)-3-(4-methylbenzene-1-sulfonyl)prop-1-en-1-yl]benzene (3g). Prepared from 1-allyl-4-fluorobenzene (54 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. White solid, (66 mg, 57%), melting point: 96 °C, ratio (>50:1). **^{1}H NMR** (500 MHz, CHLOROFORM-*D*) δ 7.75-7.73 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28-7.24 (m, 2H), 7.04-6.95 (m, 2H), 6.37 (d, *J* = 15.0 Hz 1H), 6.02 (dt, *J* = 15.0, 7.5 Hz, 1H), 3.92 (dd, *J* = 7.9, 1.0 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, CHLOROFORM-*D*) δ 163.8, 161.9, 144.9, 137.9, 135.6, 132.1, 132.1, 129.8, 128.5, 128.4, 128.3, 115.8, 115.6, 115.1, 115.1, 60.5, 21.7. **IR** (neat, cm^{-1}): 3031, 2925, 1595, 1314, 768, 636, 505.
LRMS (EI) Calcd for $C_{16}H_{15}FO_2S$ [M], 290. Found: 290(M).
The spectroscopic data agrees with those reported in the literature (S9)

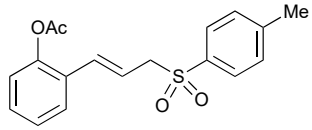
1-methyl-4-{(2*E*)-3-[4-(trifluoromethyl)phenyl]prop-2-ene-1-sulfonylbenzene (3h). Prepared from 1-allyl-4-(trifluoromethyl)benzene (75 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. White solid, (90 mg, 66%) melting point: 107 °C, ratio (>50:1).



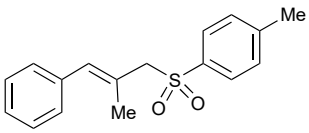
^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 15.2 Hz, 1H), 6.20 (dt, *J* = 15.1, 7.5 Hz, 1H), 3.95 (dd, *J* = 7.5, 1.2 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, CHLOROFORM-*D*) δ 145.1, 139.2, 137.6, 135.5, 130.4, 130.1, 129.9, 128.5, 126.9, 125.7, 125.7, 125.7, 125.6, 125.1, 123.0, 118.3, 60.4, 21.7. **IR** (neat, cm^{-1}): 3044, 2925, 1596, 1323, 1283, 509.
LRMS (EI) Calcd for $C_{17}H_{15}F_3O_2S$ [M], 340. Found: 340(M).
The spectroscopic data agrees with those reported in the literature (S9)



(E)-1,2,3,4,5-pentafluoro-6-(3-tosylprop-1-en-1-yl)benzene (3i). Prepared from 1-allyl-2,3,4,5,6-pentafluorobenzene (83 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. White solid (95 mg, 65%), melting point: 149 ºC, ratio (single adduct)
^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.75 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 6.43 (dt, J = 16.4, 7.3 Hz, 1H), 6.32 (d, J = 16.2 Hz, 1H), 3.96 (d, J = 7.4 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 145.32, 139.01, 135.30, 129.98, 128.57, 125.27, 123.14, 110.79, 77.45, 77.13, 76.81, 61.33, 21.78. **^{19}F NMR** (376 MHz, CHLOROFORM-D) δ 138.37 – 146.23 (m), 153.97 (tt, *J* = 21.0, 1.9 Hz), 158.45 – 166.63 (m). **IR** (neat, cm^{-1}): 3050, 2919, 1592, 1492, 1292, 1126, 509.
HRMS (APCI/ IT-TOF) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{12}F_5O_2S$ = 363.0473; found 337.0471.

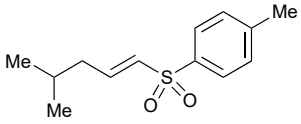


(*E*)-2-(3-tosylprop-1-en-1-yl)phenyl acetate (3j). Prepared from 2-allylphenyl acetate (70 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Light yellow solid (85 mg, 65%), melting point: 111 ºC, ratio (45:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.41 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 – 7.23 (m, 3H), 7.18 (td, *J* = 7.5, 1.3 Hz, 1H), 7.00 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.09 (dt, *J* = 15.6, 7.6 Hz, 1H), 3.92 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.41 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 169.24, 148.08, 144.93, 135.36, 132.71, 129.87, 129.50, 128.62, 127.22, 126.40, 122.88, 118.24, 60.68, 21.76, 20.93. **IR** (neat, cm^{-1}): 3046, 2923, 1754, 1596, 1484, 1295, 1203, 1145, 524.
HRMS (APCI/ IT-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{19}O_4S$ = 331.0999; found 331.0965.



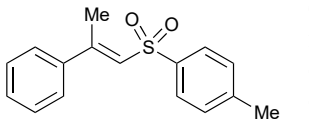
(*E*)-1-methyl-4-((2-methyl-3-phenylprop-1-en-1-yl)sulfonyl)benzene (3k). Prepared from (2-methyl-2-propenyl)benzene (53 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Colorless liquid (56 mg, 49%), ratio (50:1).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.13 (m, 5H), 6.94 – 6.90 (m, 2H), 6.59 (s, 1H), 3.99 (s, 2H), 2.41 (s, 3H), 2.11 (d, *J* = 1.5 Hz, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 144.61, 136.36, 136.32, 134.34, 129.77, 128.29, 128.18, 128.17, 127.07, 126.36, 59.78, 24.26, 21.73. **IR** (neat, cm^{-1}): 3054, 2919, 1596, 1492, 1307, 1145, 512.
HRMS (APCI/ IT-TOF) *m/z*: [M + H]$^+$ calcd for $C_{17}H_{19}O_2S$ = 287.1100; found 287.1076.



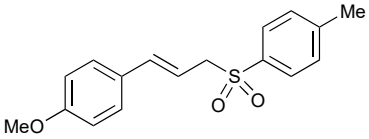
(*E*)-1-methyl-4-((4-methylpent-1-en-1-yl)sulfonyl)benzene (3l). Prepared from 4-methyl-1-pentene (34 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Colorless liquid (40 mg, 43%), ratio (13:1).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.93 (dt, *J* = 15.0, 7.5 Hz, 1H), 6.29 (dt, *J* = 15.0, 1.4 Hz, 1H), 2.43 (s, 3H), 2.10 (td, *J* = 6.9, 1.5 Hz, 2H), 1.77 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 145.64, 144.26, 137.84, 131.56, 129.96, 127.67, 40.62, 27.80, 22.38, 21.72.
IR (neat, cm^{-1}): 3050, 2958, 2923, 1596, 1461, 1303, 1141, 532.
LRMS (EI) Calcd for $C_{13}H_{18}O_2S$ [M], 238. Found: 238(M).
The spectroscopic data agrees with those reported in the literature (S16)



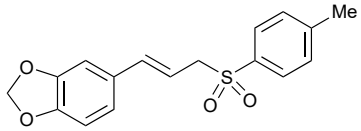
(*E*)-1-methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (3m). Prepared from α-methyl styrene (47 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure B. Light yellow solid (75mg, 70%), melting point: 92 °C, ratio: single product.

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.24 (m, 7H), 6.59 (d, *J* = 1.3 Hz, 1H), 2.51 (d, *J* = 1.3 Hz, 3H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 153.09, 144.26, 140.29, 139.33, 129.95, 129.93, 128.81, 127.86, 127.40, 126.41, 21.73, 17.27. **IR** (neat, cm^{-1}): 3050, 2973, 2915, 1592, 1488, 1292, 1133, 1076, 536.
LRMS (EI) Calcd for $C_{16}H_{16}O_2S$ [M], 272. Found: 272(M).
The spectroscopic data agrees with those reported in the literature (S15)



***E*)-1-methoxy-4-(3-tosylprop-1-en-1-yl)benzene (4b')**. Prepared from 1-allyl-4-methoxybenzene (59 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure C. Light yellow solid (61 mg, 50%), melting point: 106 °C, ratio (40:1).

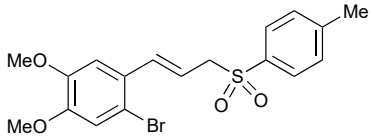
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.95 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.91 (dd, *J* = 7.6, 1.2 Hz, 2H), 3.80 (s, 3H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 159.92, 144.78, 138.59, 135.59, 129.79, 128.70, 128.62, 128.01, 114.11, 112.86, 60.75, 55.40, 21.76. **IR** (neat, cm^{-1}): 3027, 2919, 2846, 1600, 1508, 1299, 1245, 1141, 509.
LRMS (EI) Calcd for $C_{17}H_{18}O_3S$ [M], 302. Found: 302(M).
The spectroscopic data agrees with those reported in the literature (S5)



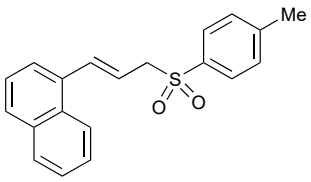
(*E*)-5-(3-tosylprop-1-en-1-yl)benzo[*d*][1,3]dioxole (4g'). Prepared from 5-allylbenzo[*d*][1,3]dioxole (65 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure C. Light yellow solid (62 mg, 49%), melting point: 82 ºC, ratio (>50:1).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 1.5 Hz, 1H), 6.73 – 6.69 (m, 2H), 6.27 (d, *J* = 15.8 Hz, 1H), 5.96 – 5.84 (m, 3H), 3.88 (dd, *J* = 7.6, 1.2 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 148.17, 148.04, 144.85, 138.70, 135.55, 130.34, 129.82, 128.60, 121.83, 113.33, 108.40, 105.78, 101.35, 60.60, 21.77. **IR** (neat, cm^{-1}): 3034, 2900, 1596, 1492, 1442, 1288, 1245, 1130, 509.

LRMS (EI) Calcd for $C_{17}H_{16}O_4S$ [M], 316 Found: 316(M).
The spectroscopic data agrees with those reported in the literature (S5)



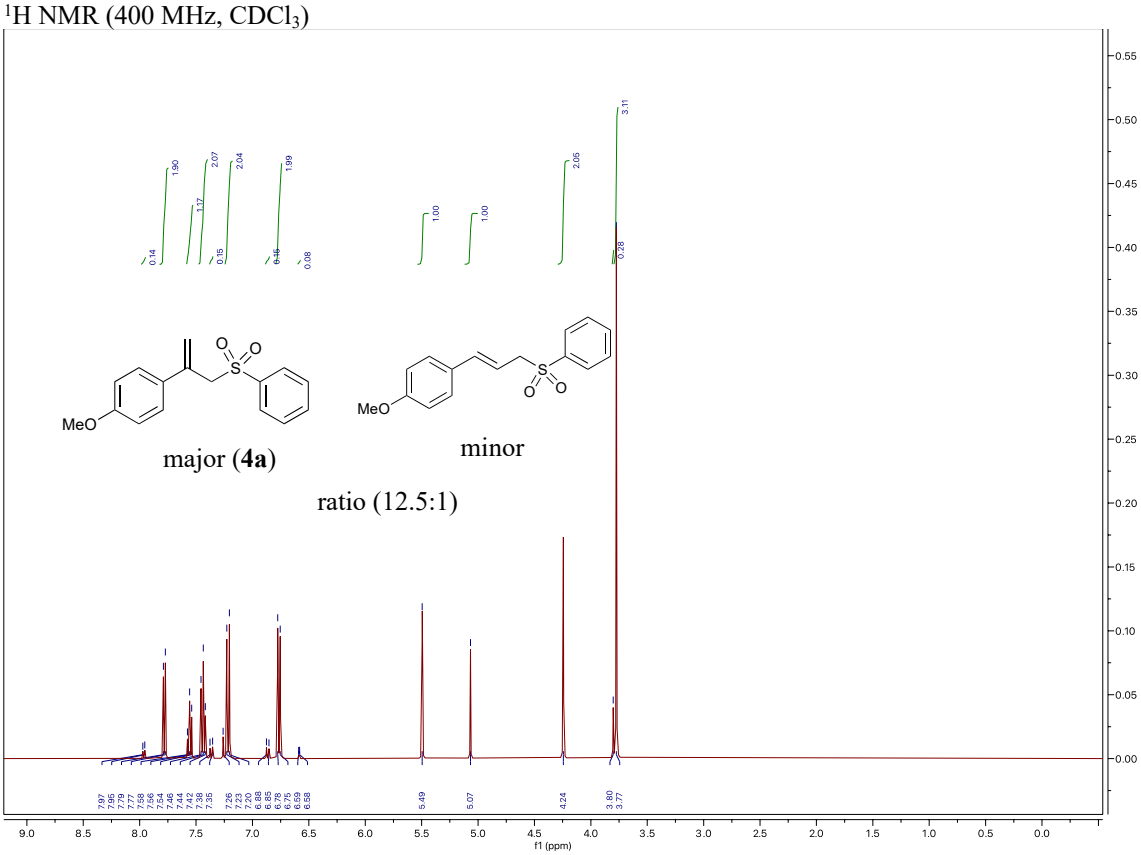
(*E*)-1-bromo-4,5-dimethoxy-2-(3-tosylprop-1-en-1-yl)benzene (3n). Prepared from 4-allyl-1,2-dimethoxybenzene (71 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure C. Light yellow solid (87 mg, 53%), melting point: 60 ºC, ratio (>50:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 15.7 Hz, 1H), 5.99 (dt, *J* = 15.5, 7.6 Hz, 1H), 3.95 (dd, *J* = 7.6, 1.2 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 149.96, 148.65, 144.97, 137.59, 135.34, 129.85, 128.59, 127.76, 116.15, 115.27, 114.59, 109.00, 60.61, 56.26, 56.17, 21.77. **IR** (neat, cm^{-1}): 3054, 2923, 2842, 1596, 1500, 1292, 1257, 1137, 509.
HRMS (APCI/ IT-TOF) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{20}BrO_4S$ = 411.0260; found 411.0215.



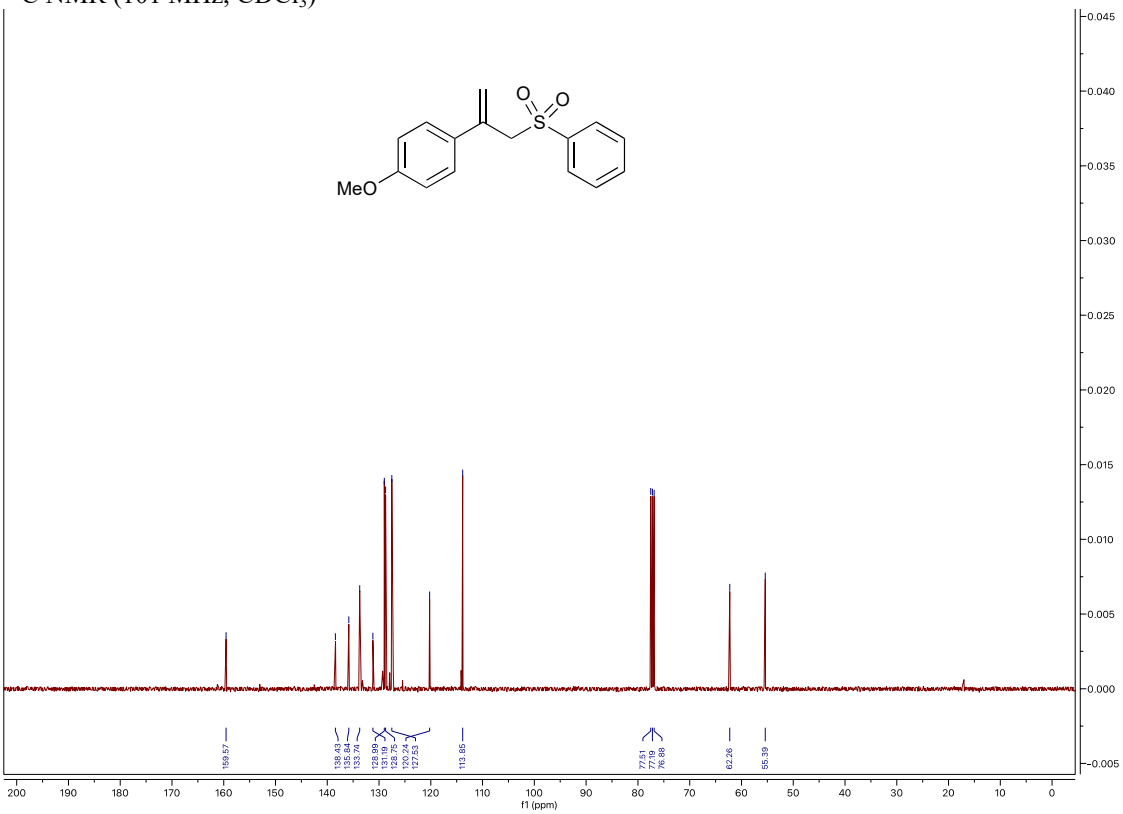
(*E*)-1-(3-tosylprop-1-en-1-yl)naphthalene (3o). Prepared from 1-allylnaphthalene (67 mg, 0.4 mmol) and sodium 4-methylbenzenesulfinate (71 mg, 0.6 mmol, 1.5 equiv) according to general procedure C. Yellow solid (69 mg, 52%). Melting point: 89 ºC, ratio (>50:1).
^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.85 – 7.79 (m, 4H), 7.68 (dd, *J* = 8.5, 1.4 Hz, 1H), 7.54 – 7.40 (m, 4H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.07 (d, *J* = 15.6 Hz, 1H), 6.13 (dt, *J* = 15.5, 7.6 Hz, 1H), 4.06 (dd, *J* = 7.7, 1.2 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 144.91, 136.92, 135.31, 133.70, 133.56, 130.92, 129.93, 128.91, 128.79, 128.67, 126.28, 126.08, 125.71, 124.38, 123.64, 118.83, 60.82, 21.78. **IR** (neat, cm^{-1}): 3050, 2973, 2923, 1592, 1500, 1392, 1307, 1133, 512.
LRMS (EI) Calcd for $C_{20}H_{18}O_2S$ [M], 322. Found: 322(M).
The spectroscopic data agrees with those reported in the literature (S9)

^{1}H and ^{13}C NMR Spectra

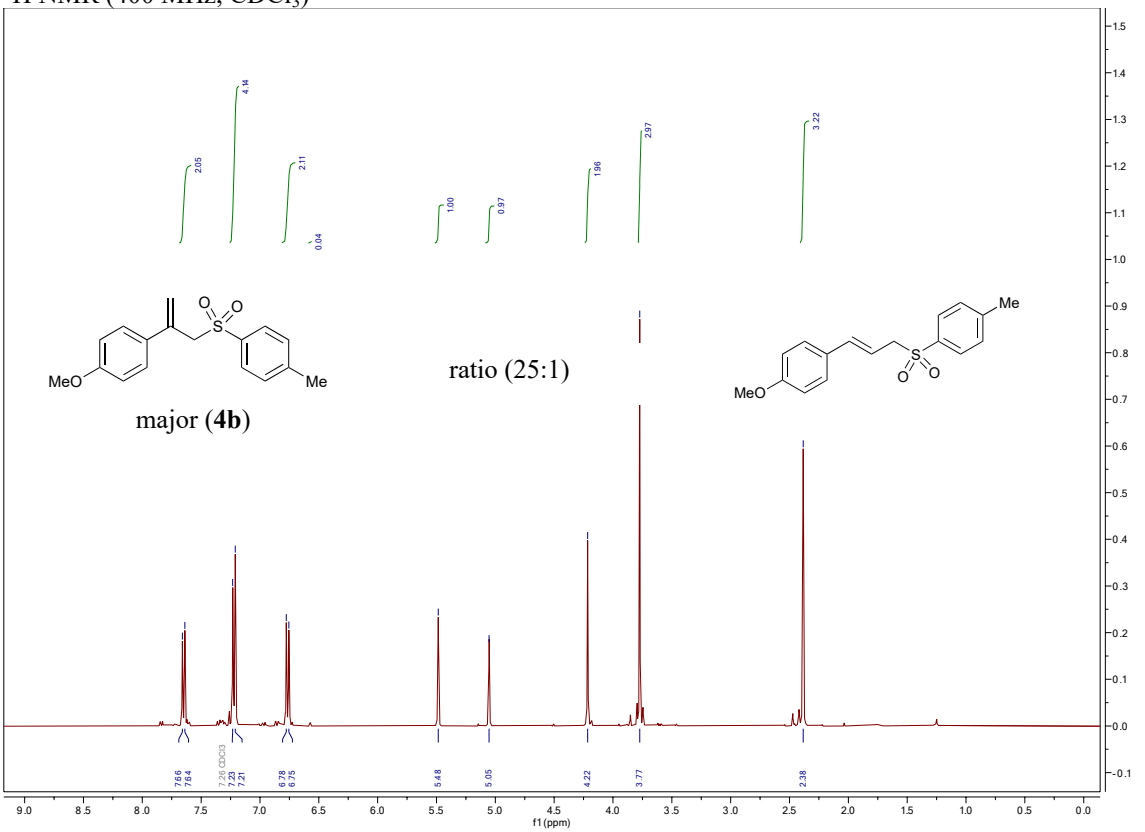
^{1}H NMR (400 MHz, $CDCl_3$)



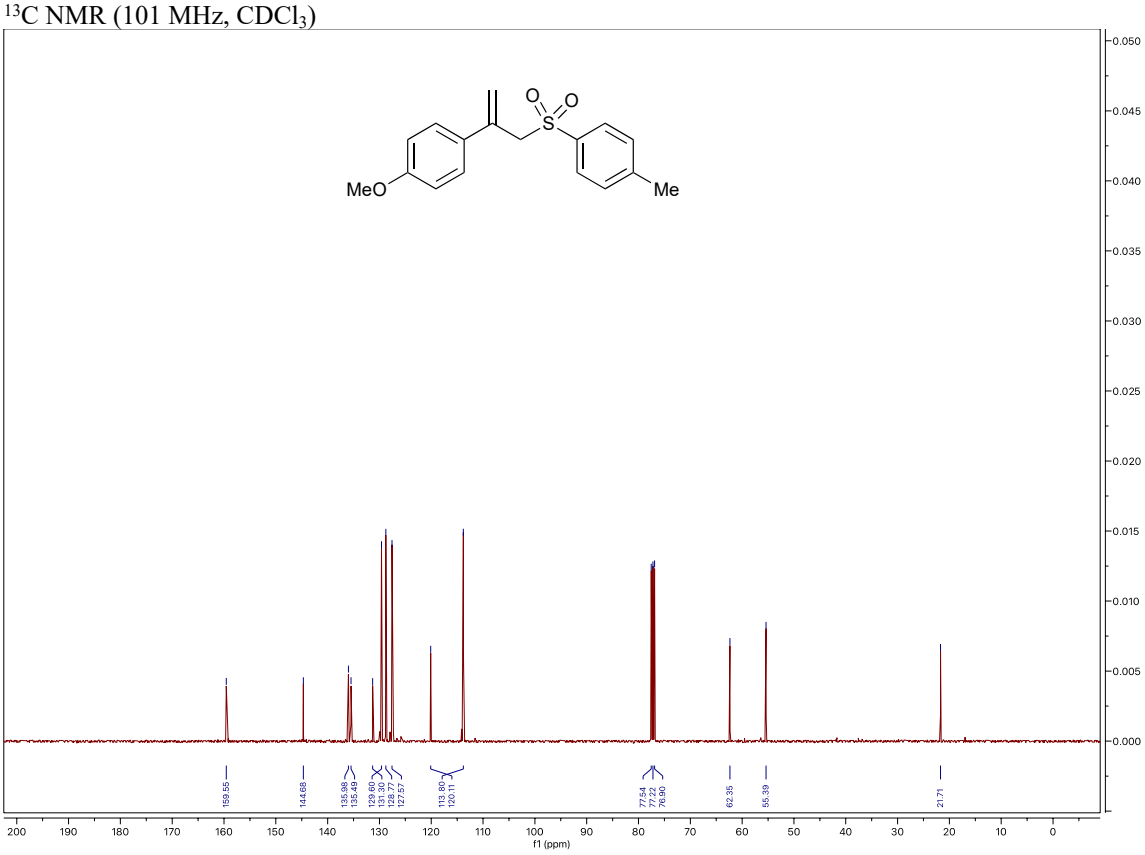
^{13}C NMR (101 MHz, $CDCl_3$)



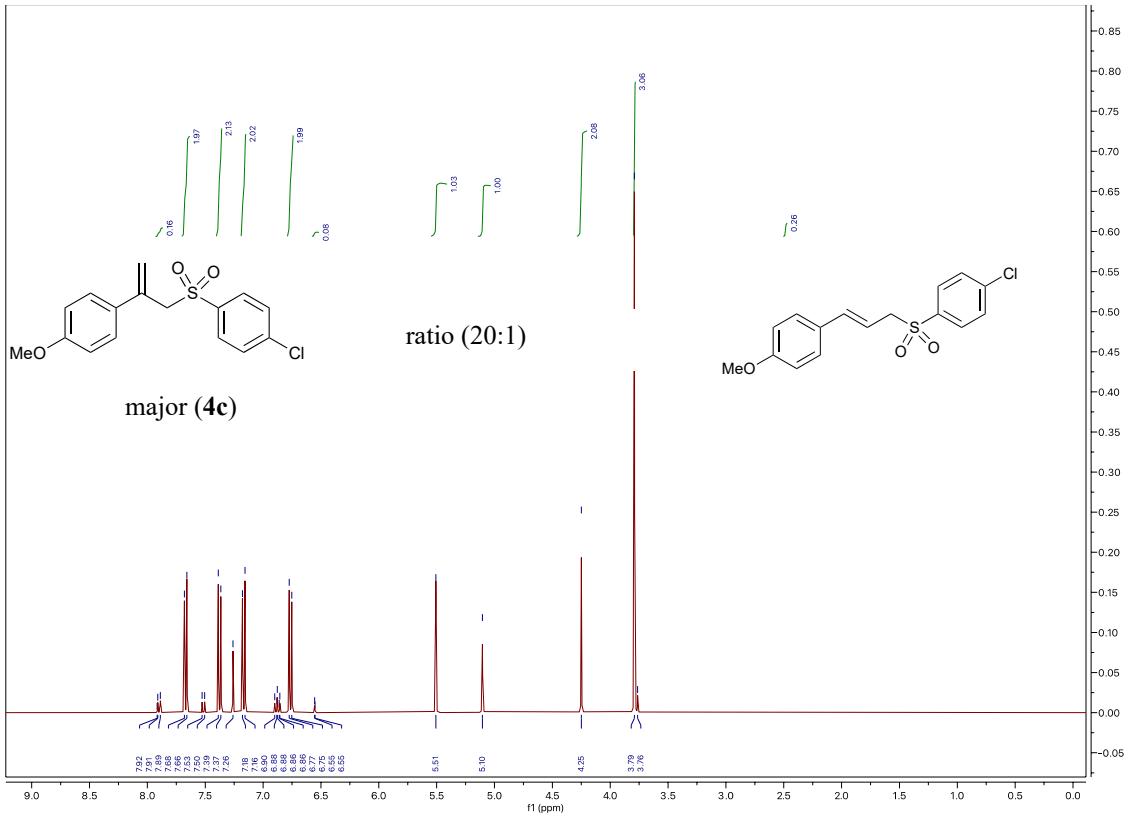
^{1}H NMR (400 MHz, $CDCl_3$)



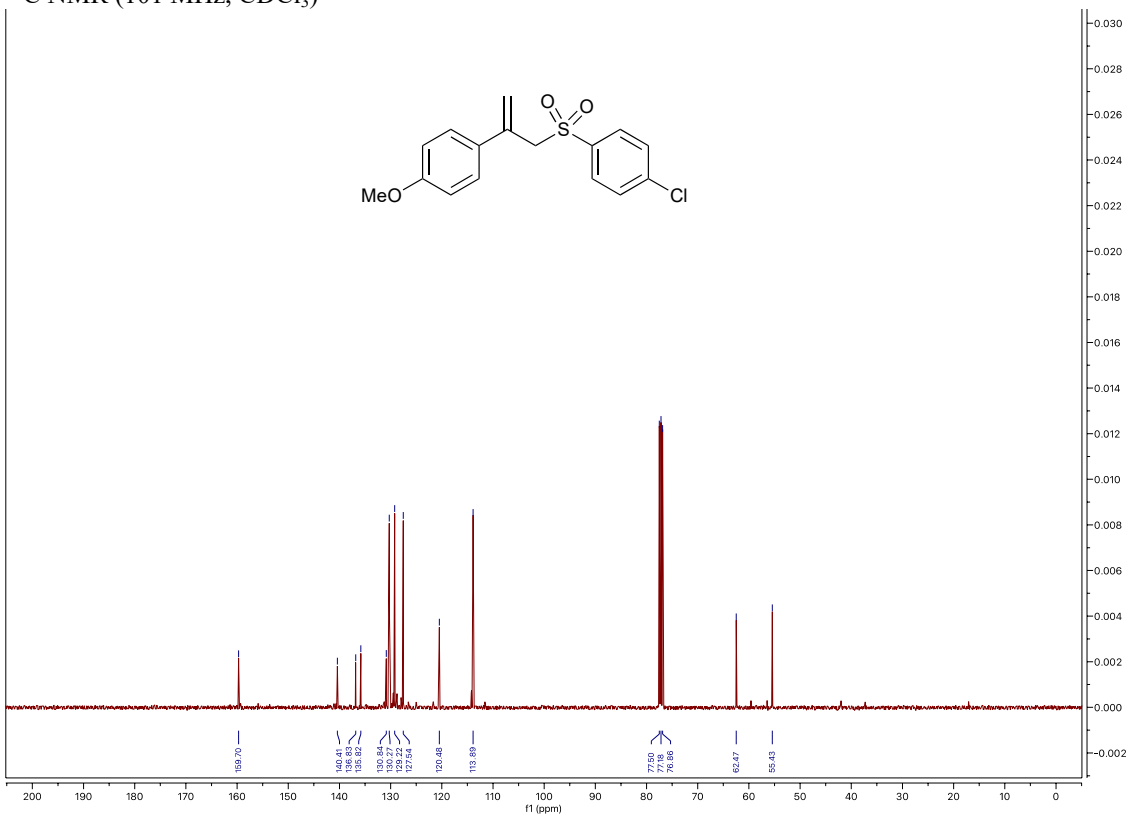
^{13}C NMR (101 MHz, $CDCl_3$)



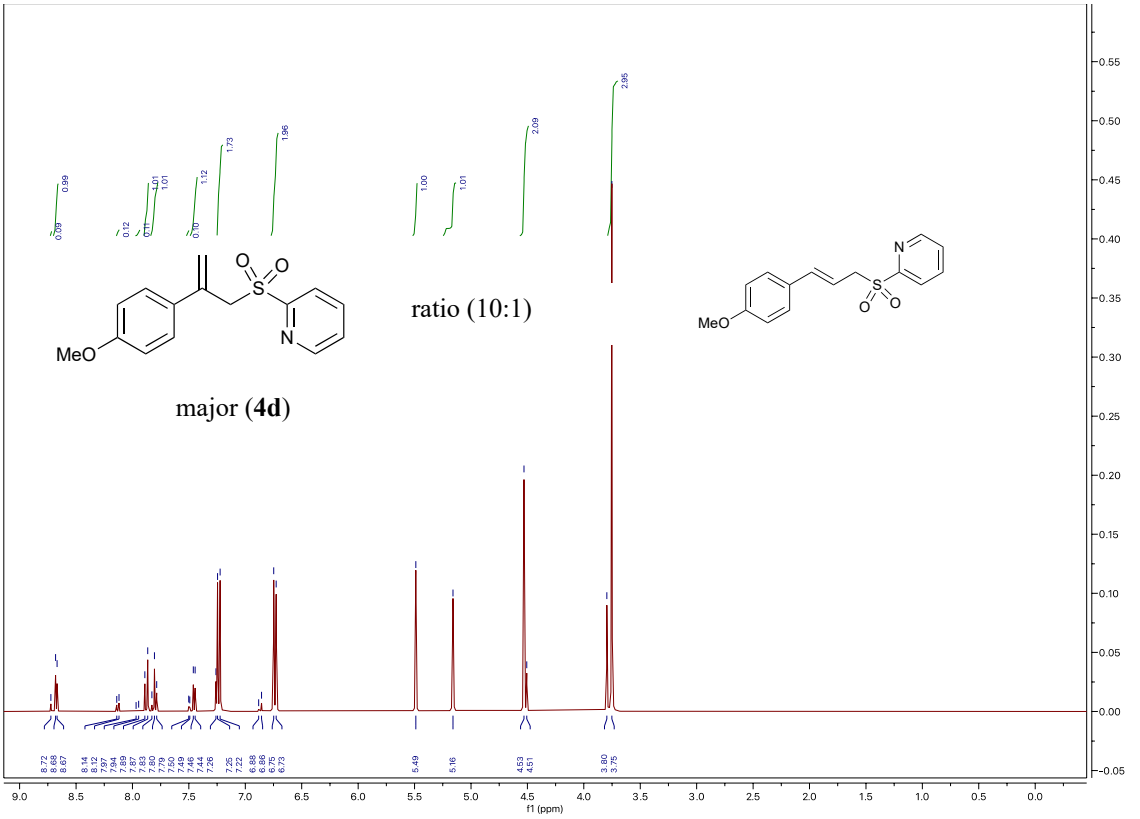
^{1}H NMR (400 MHz, $CDCl_3$)



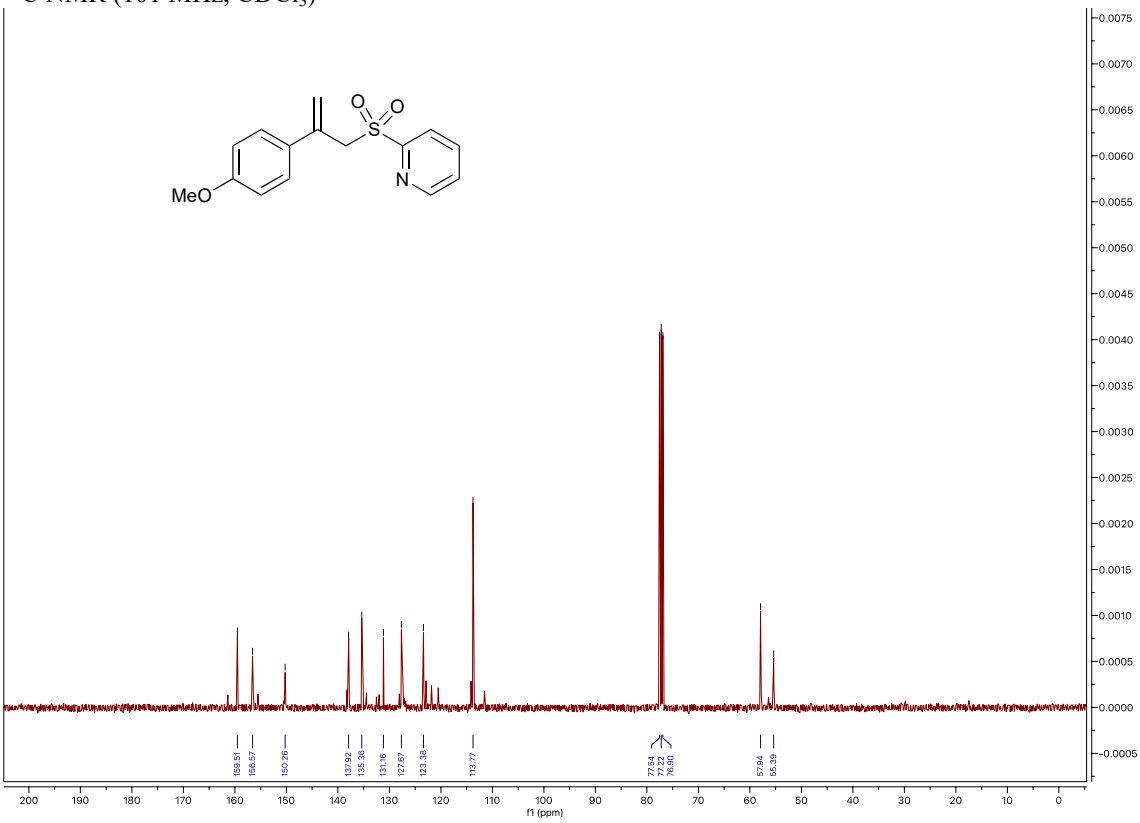
^{13}C NMR (101 MHz, $CDCl_3$)



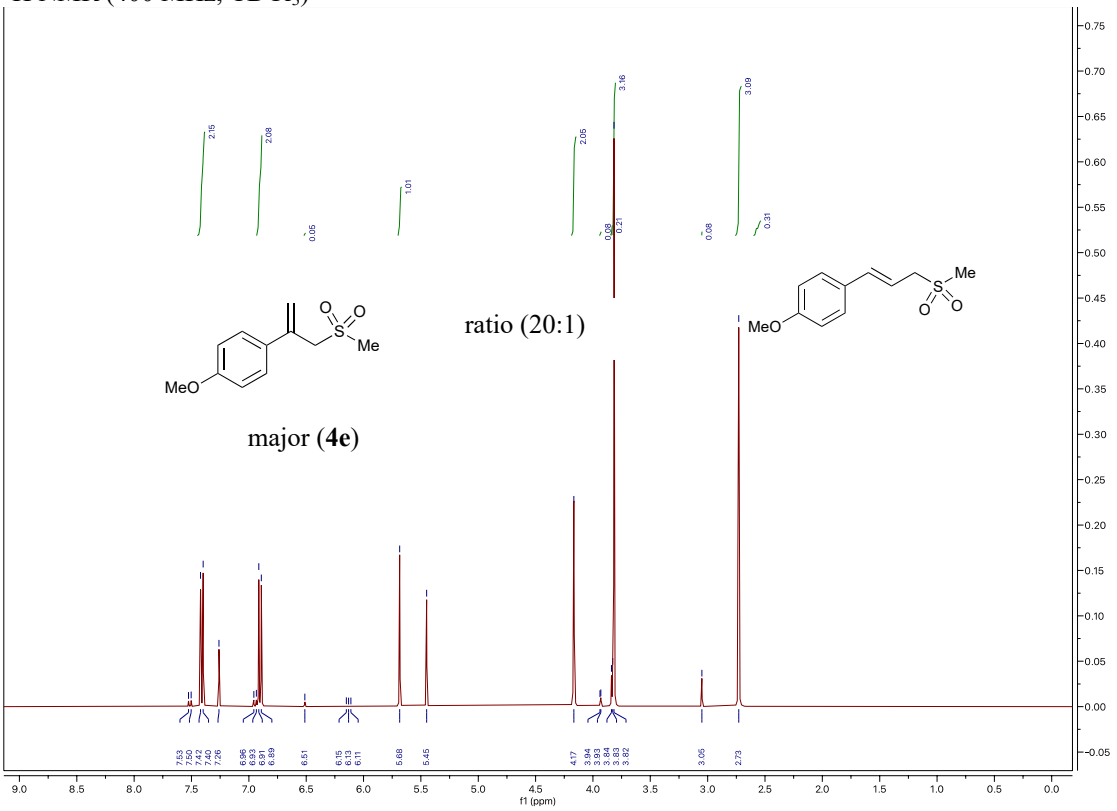
^{1}H NMR (400 MHz, $CDCl_3$)



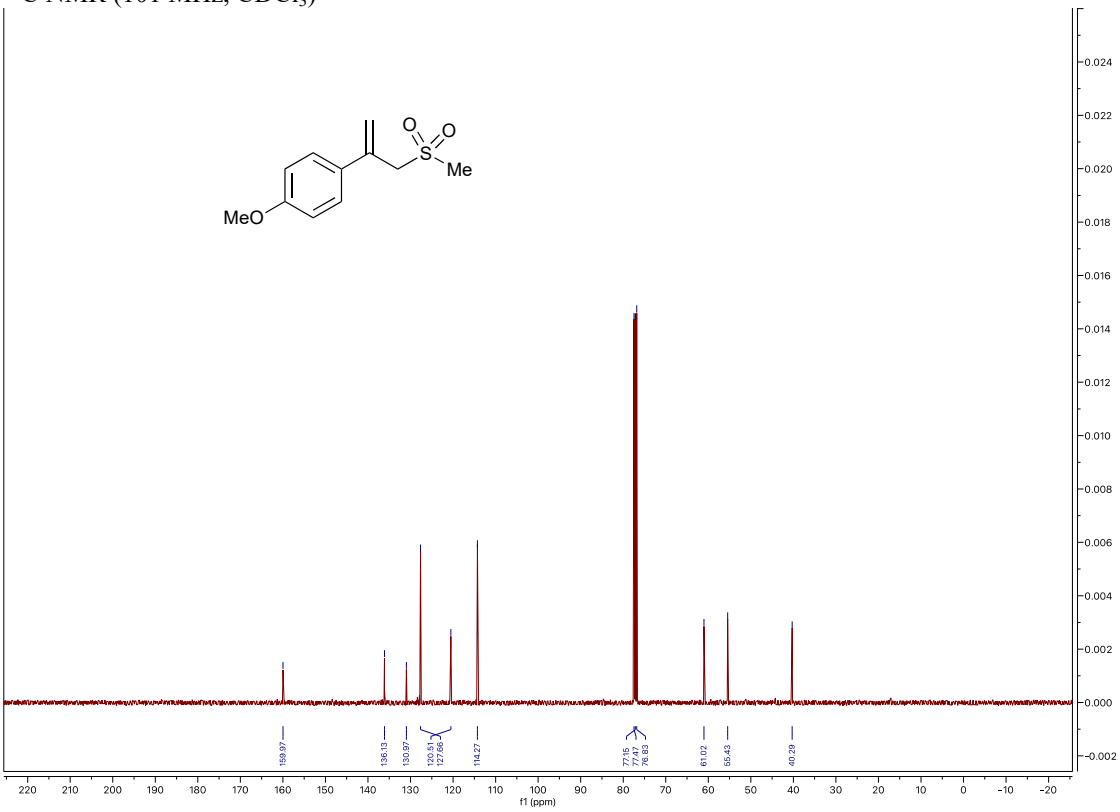
^{13}C NMR (101 MHz, $CDCl_3$)



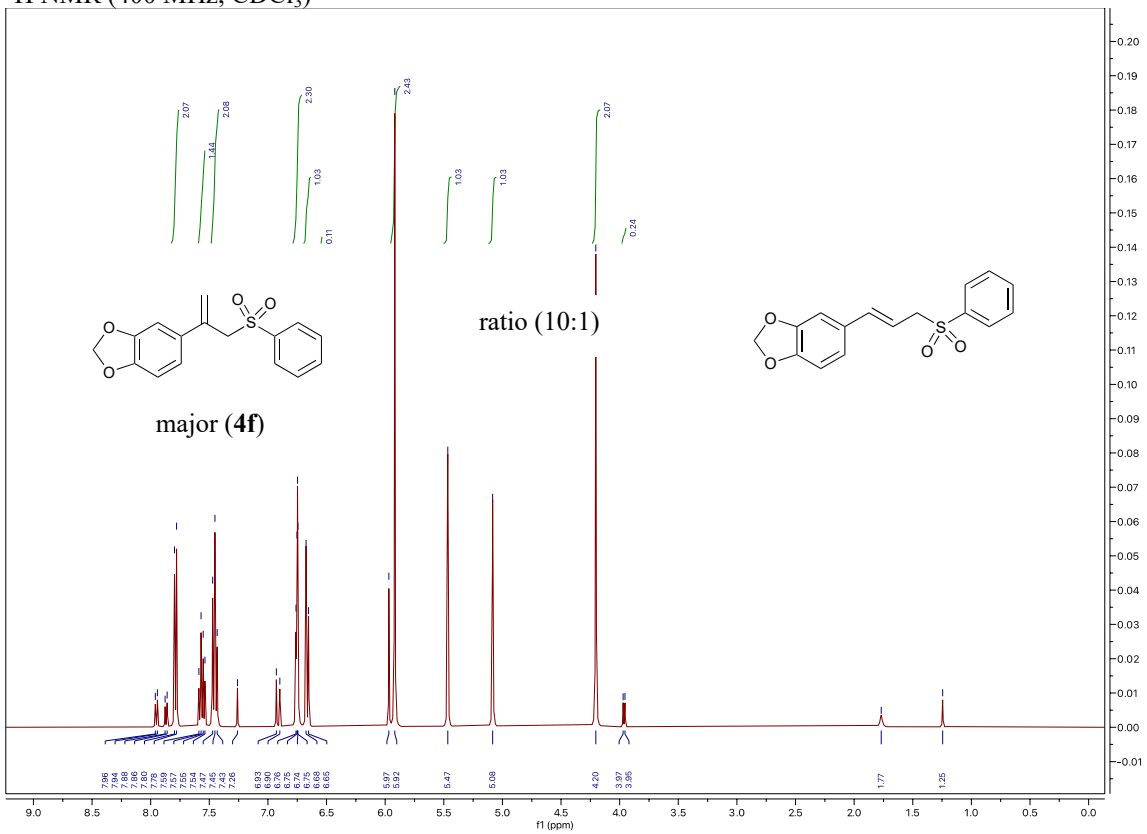
^{1}H NMR (400 MHz, $CDCl_3$)



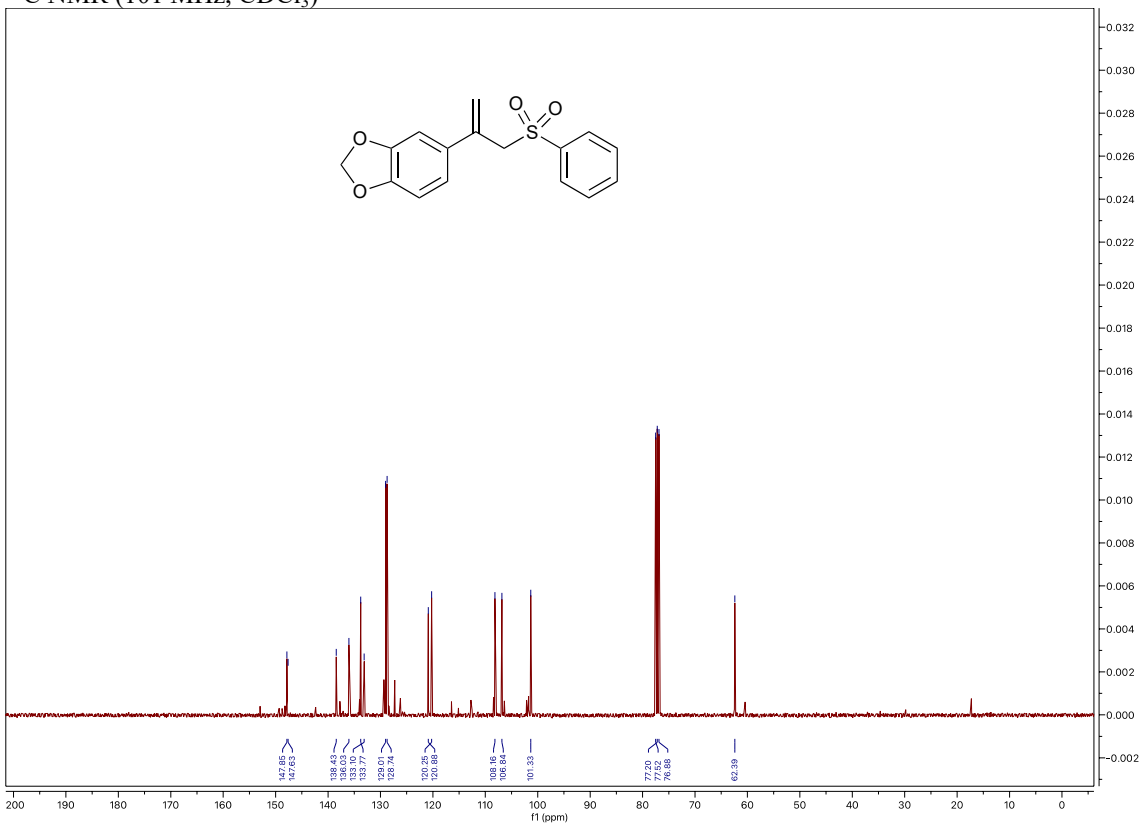
^{13}C NMR (101 MHz, $CDCl_3$)



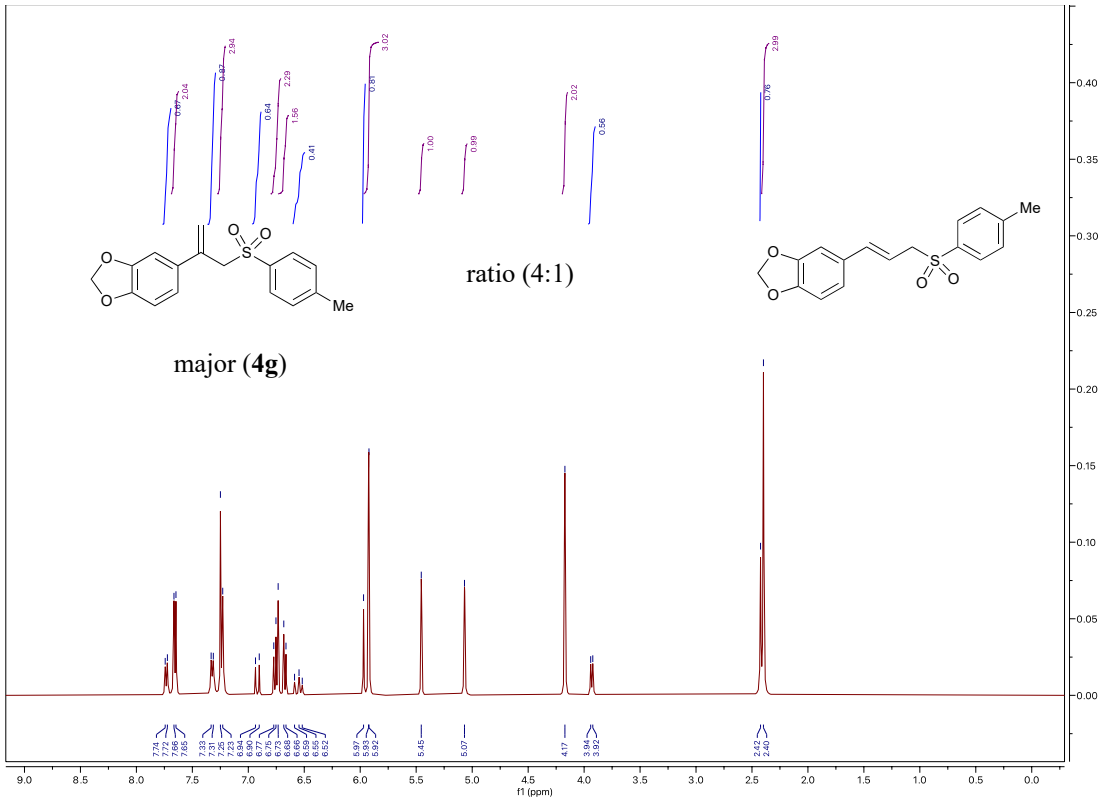
^{1}H NMR (400 MHz, $CDCl_3$)



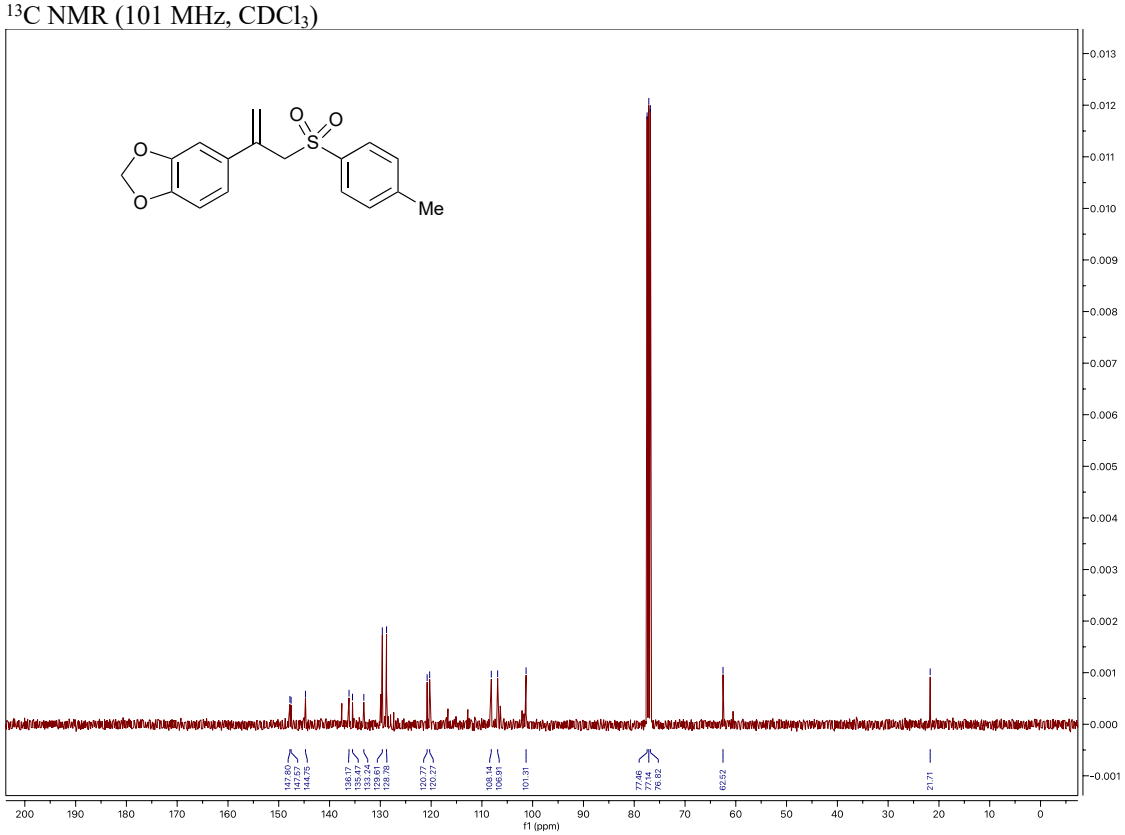
^{13}C NMR (101 MHz, $CDCl_3$)



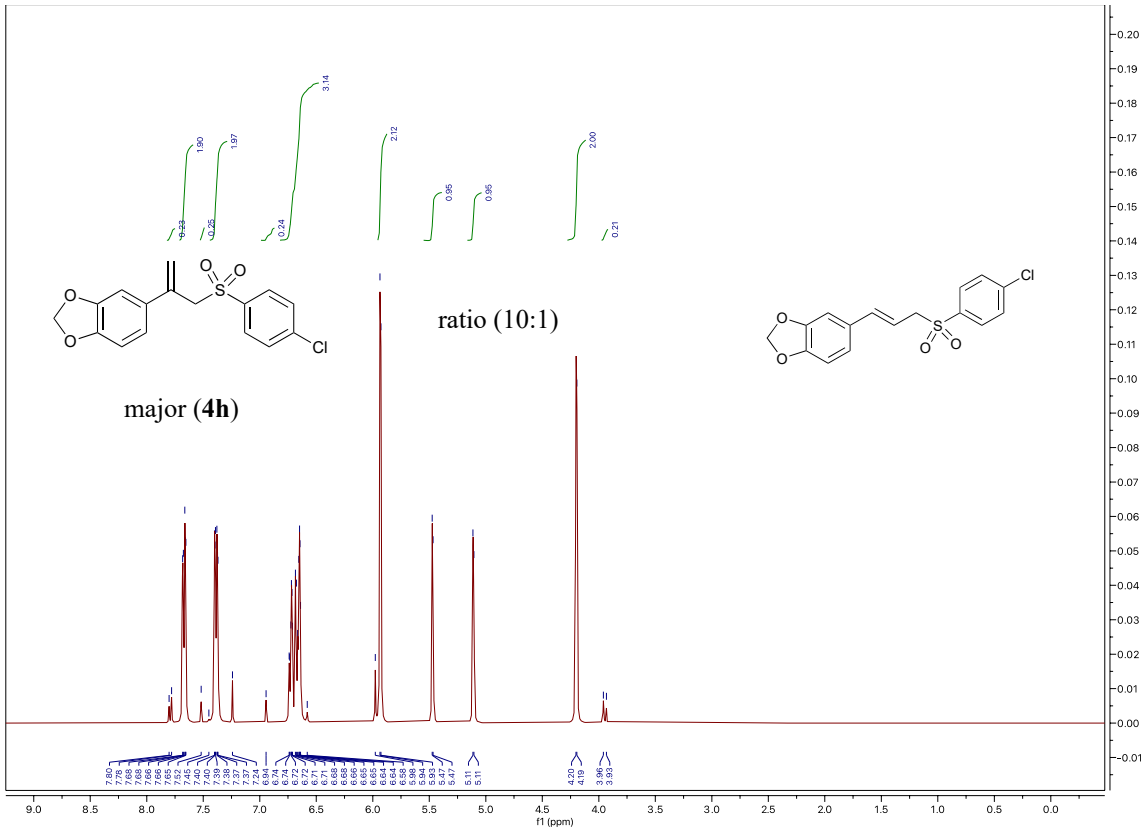
^{1}H NMR (400 MHz, $CDCl_3$)



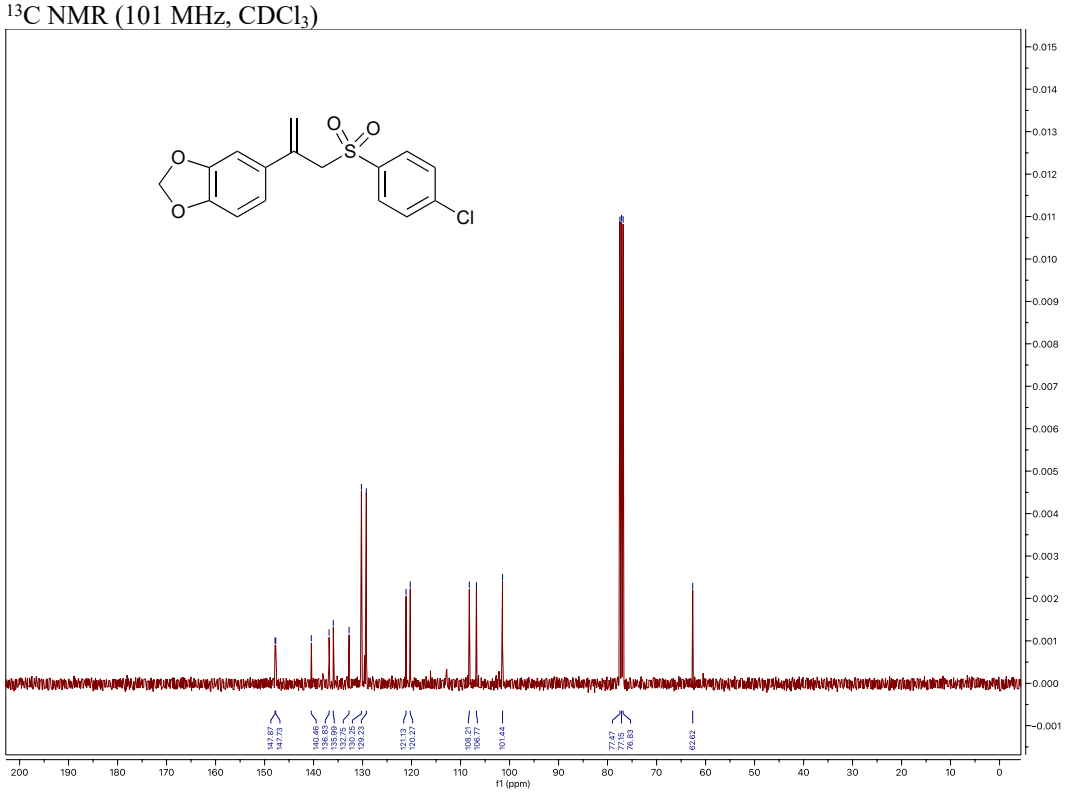
^{13}C NMR (101 MHz, $CDCl_3$)



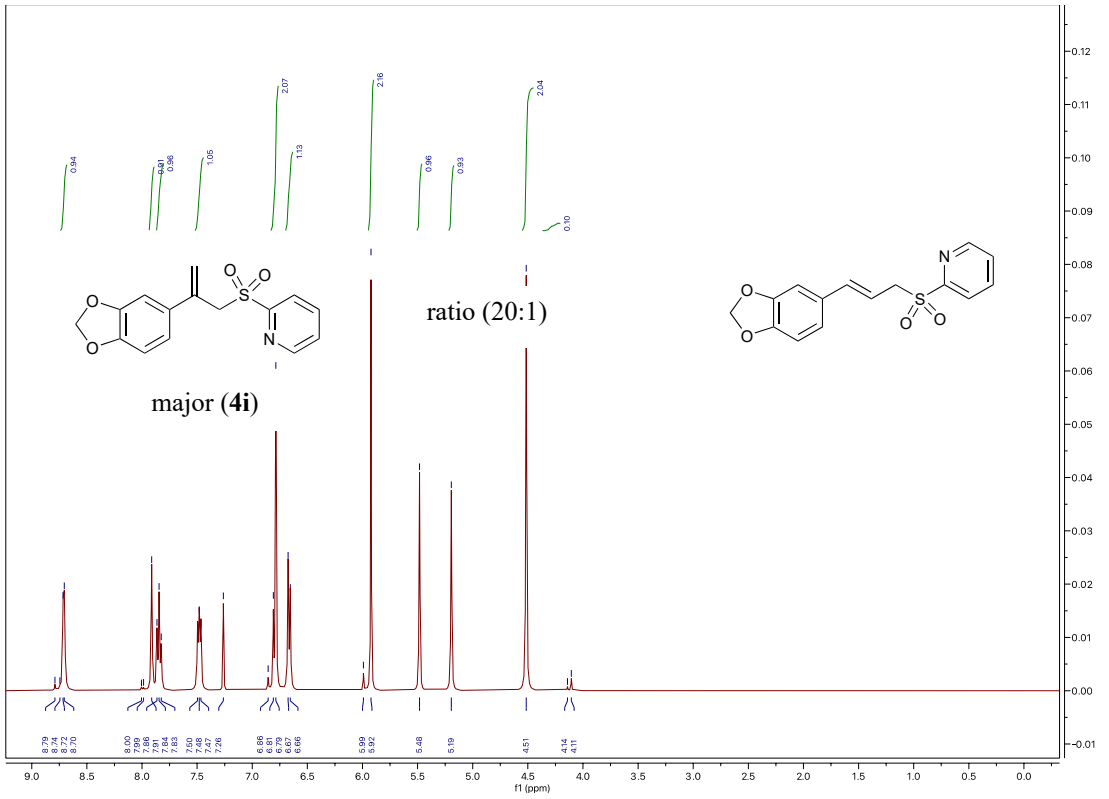
^{1}H NMR (400 MHz, $CDCl_3$)



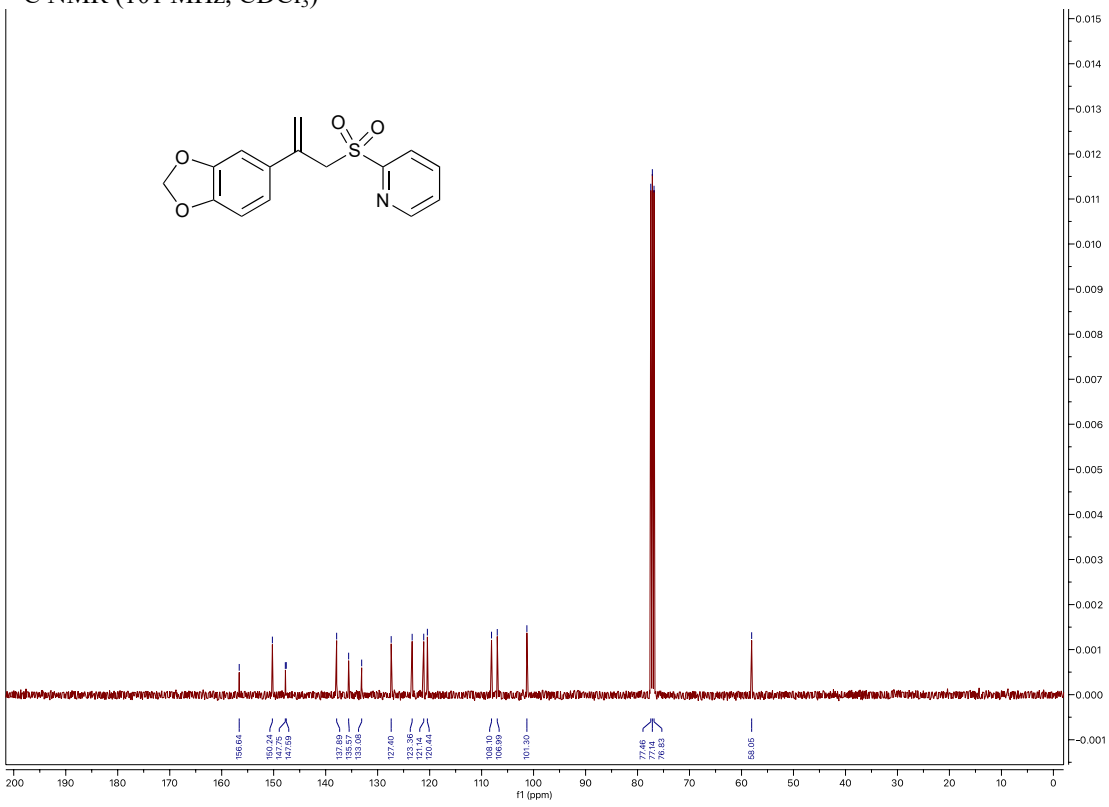
^{13}C NMR (101 MHz, $CDCl_3$)



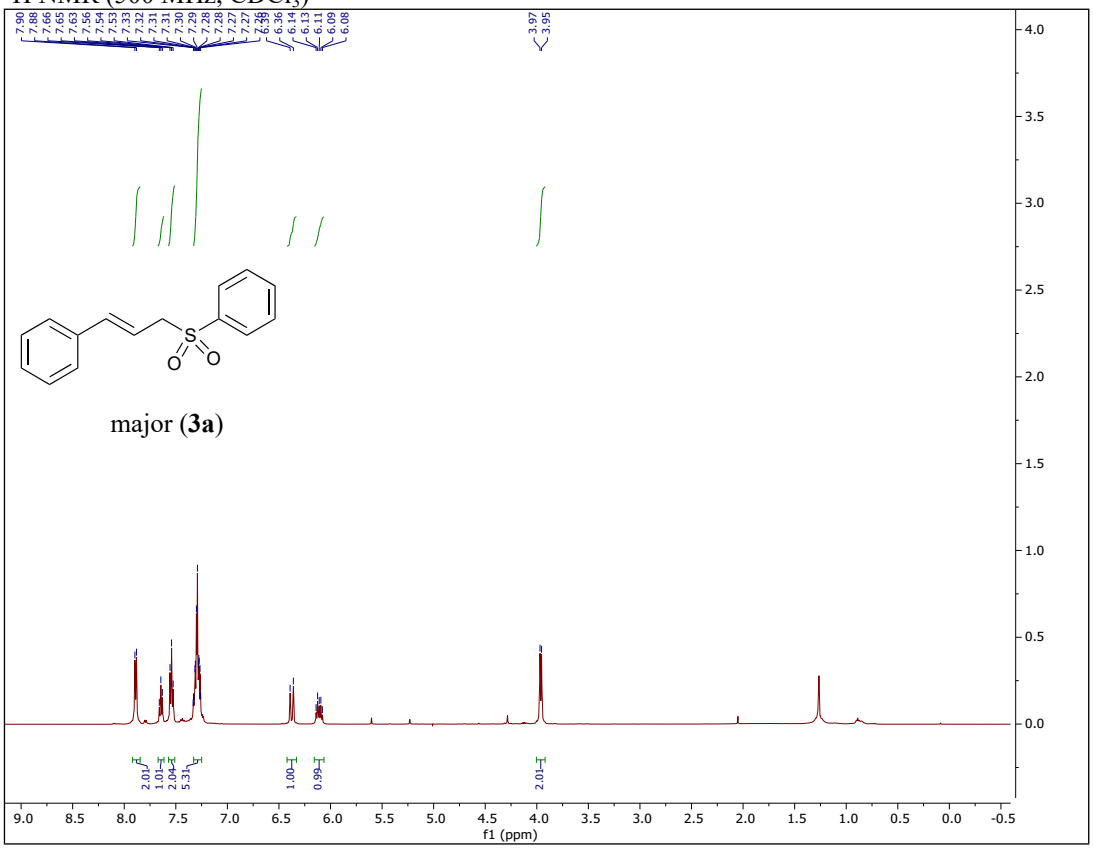
^{1}H NMR (400 MHz, $CDCl_3$)



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

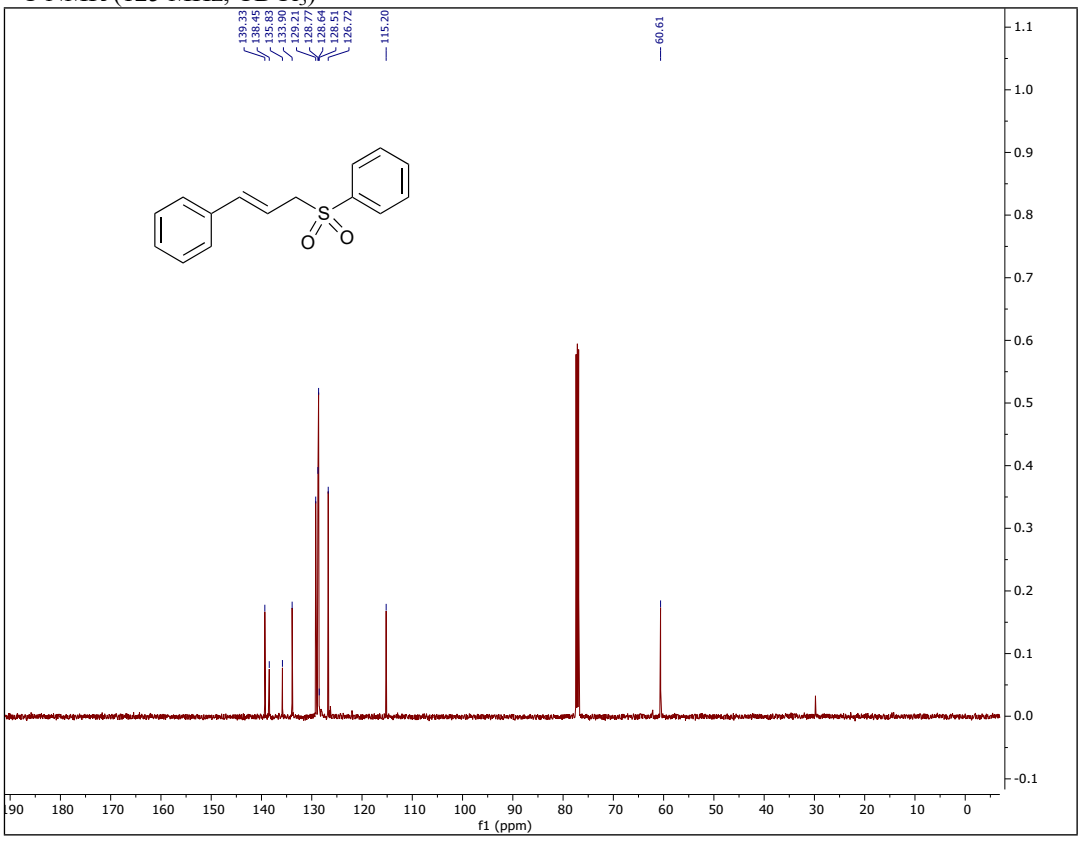


^{1}H NMR (500 MHz, $CDCl_3$)

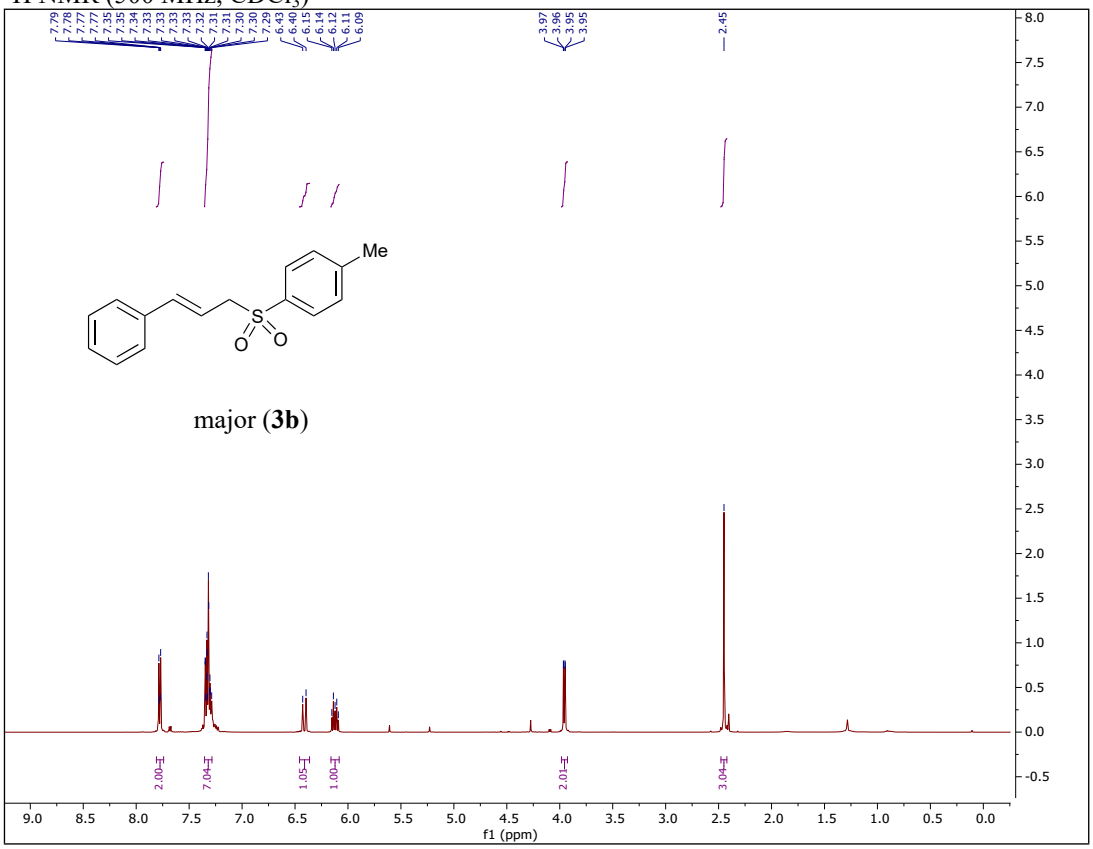


major (**3a**)

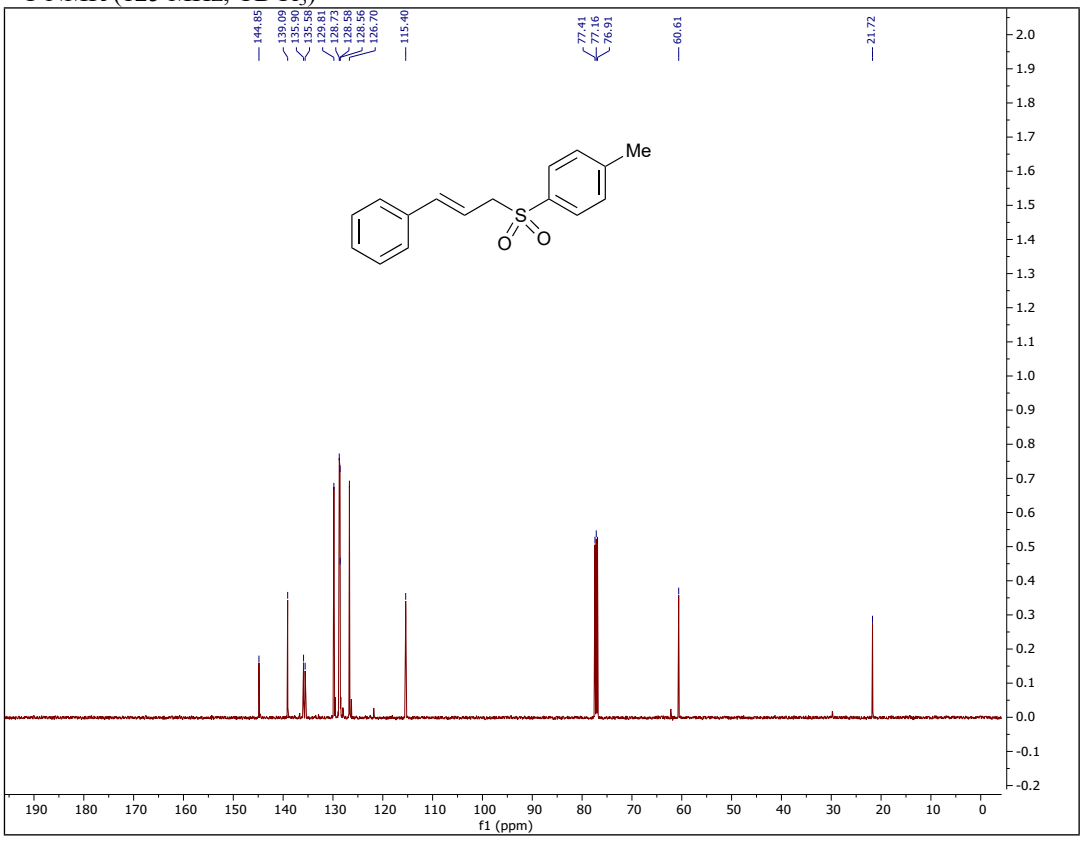
^{13}C NMR (125 MHz, $CDCl_3$)



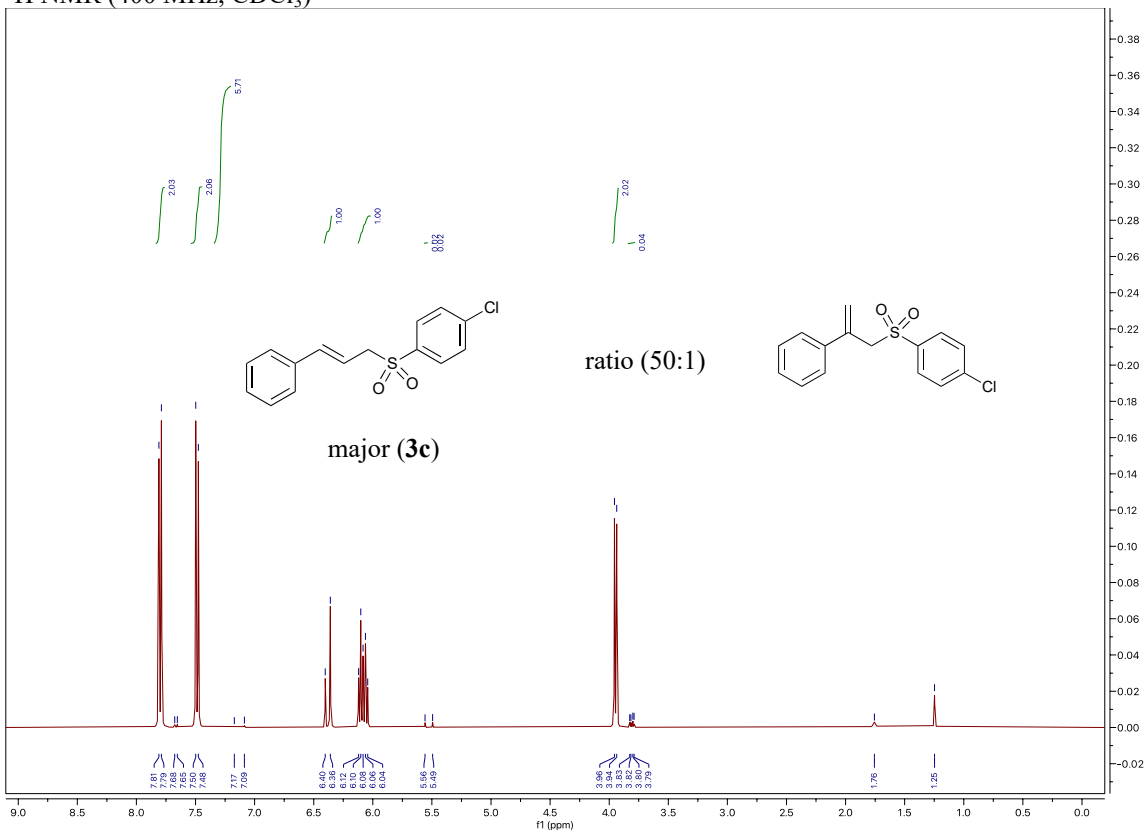
^{1}H NMR (500 MHz, $CDCl_3$)



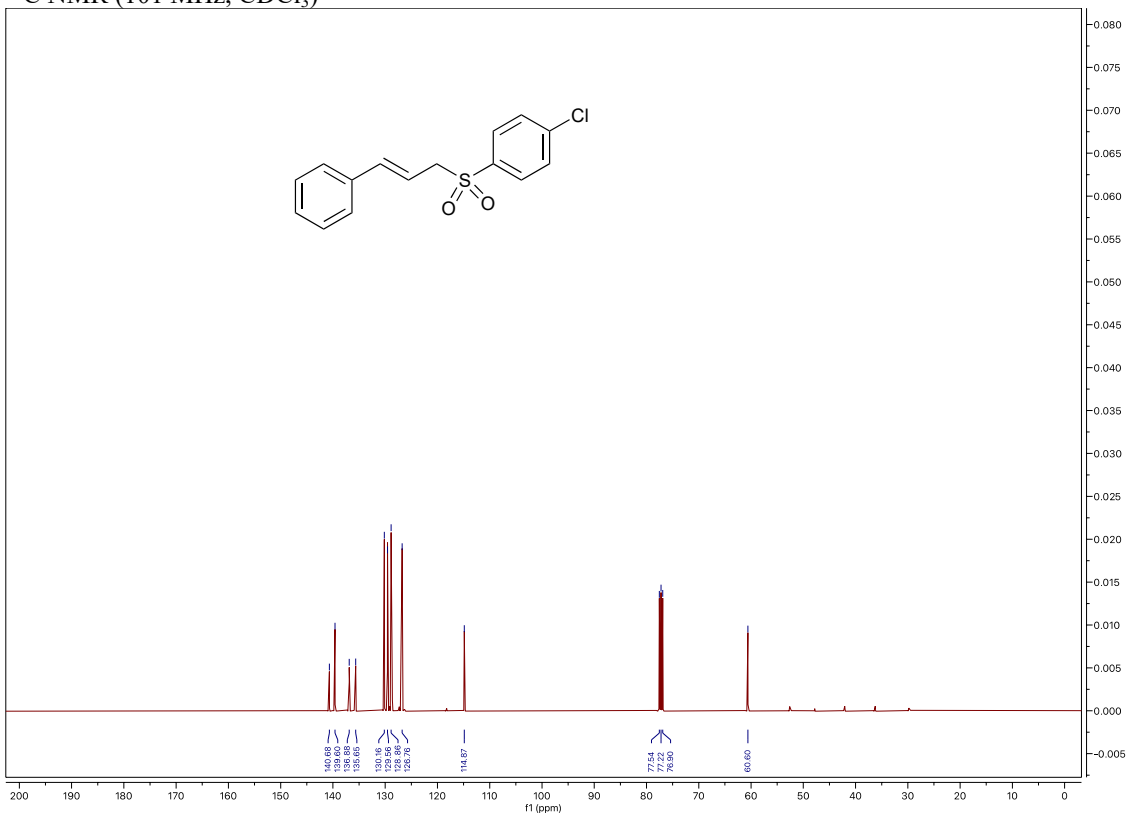
^{13}C NMR (125 MHz, $CDCl_3$)



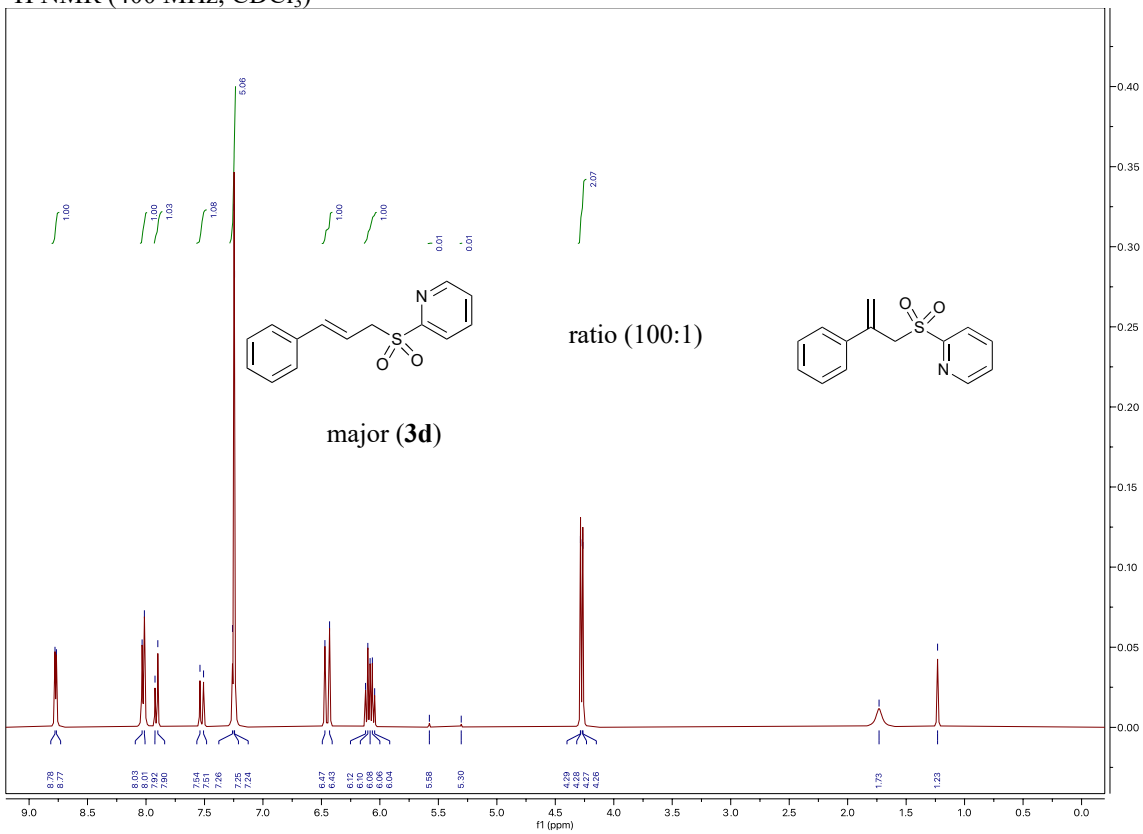
^{1}H NMR (400 MHz, $CDCl_3$)



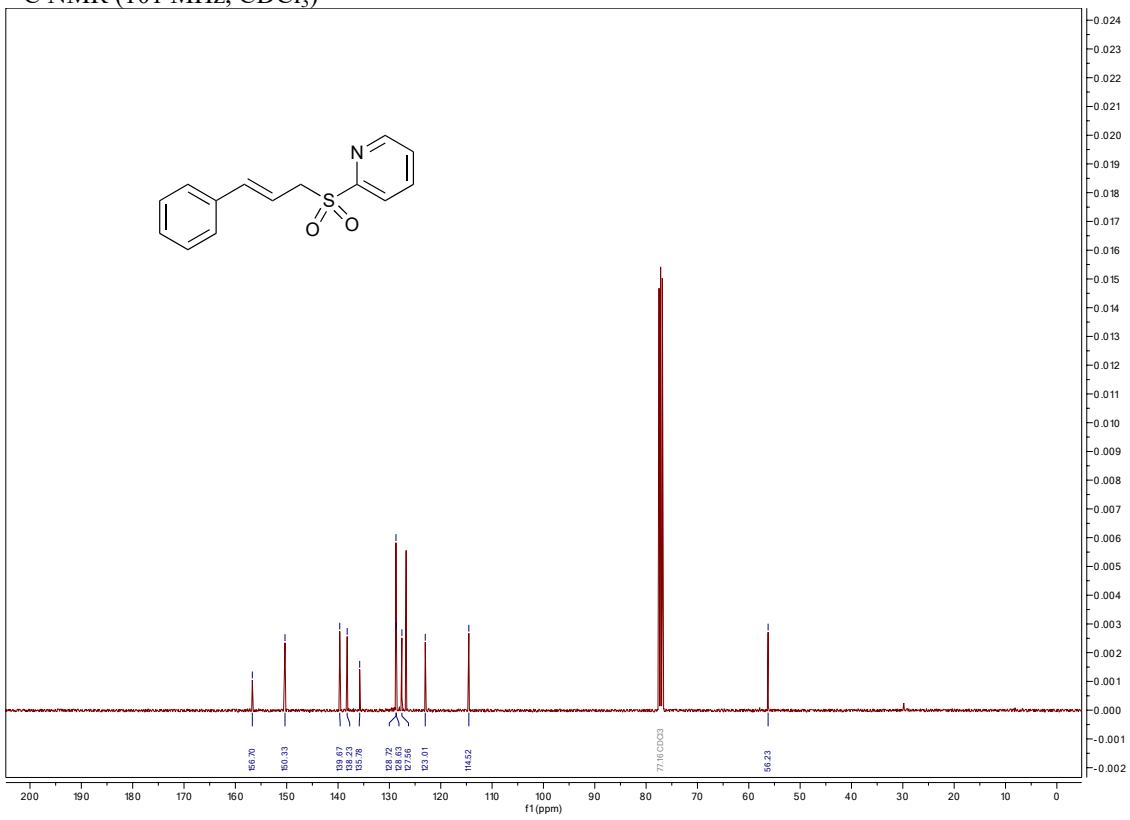
^{13}C NMR (101 MHz, $CDCl_3$)



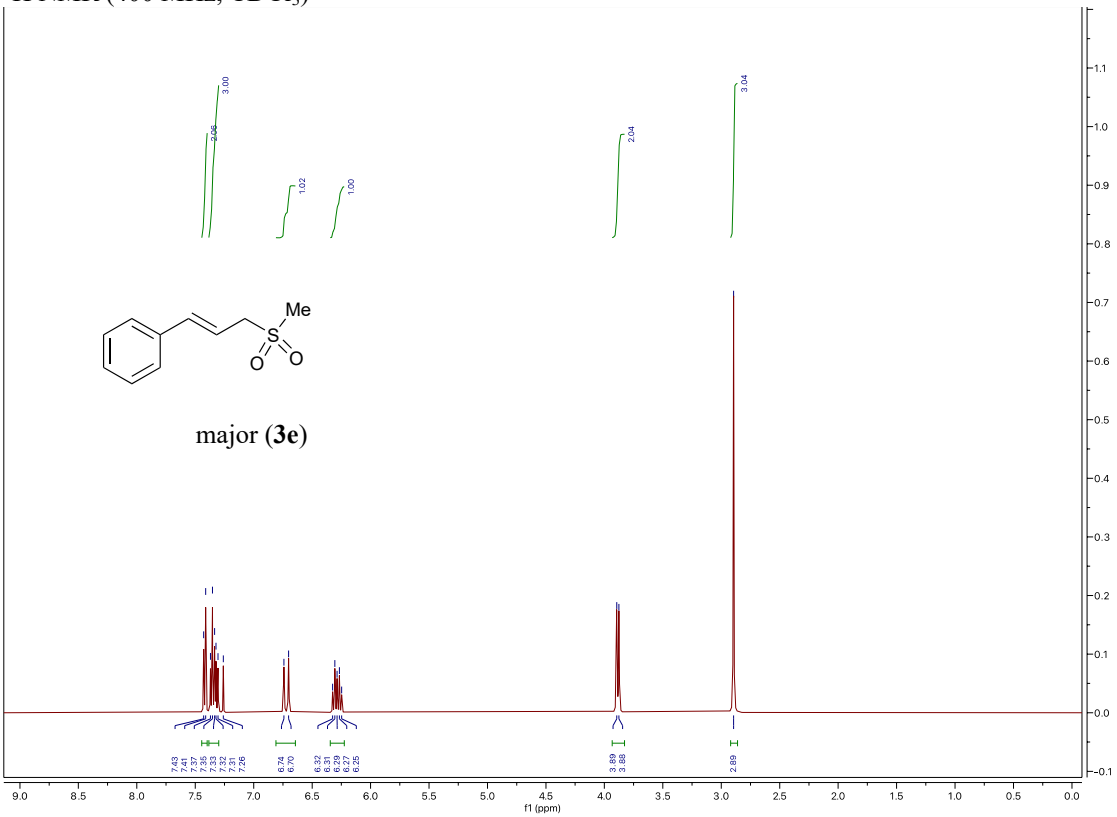
^{1}H NMR (400 MHz, $CDCl_3$)



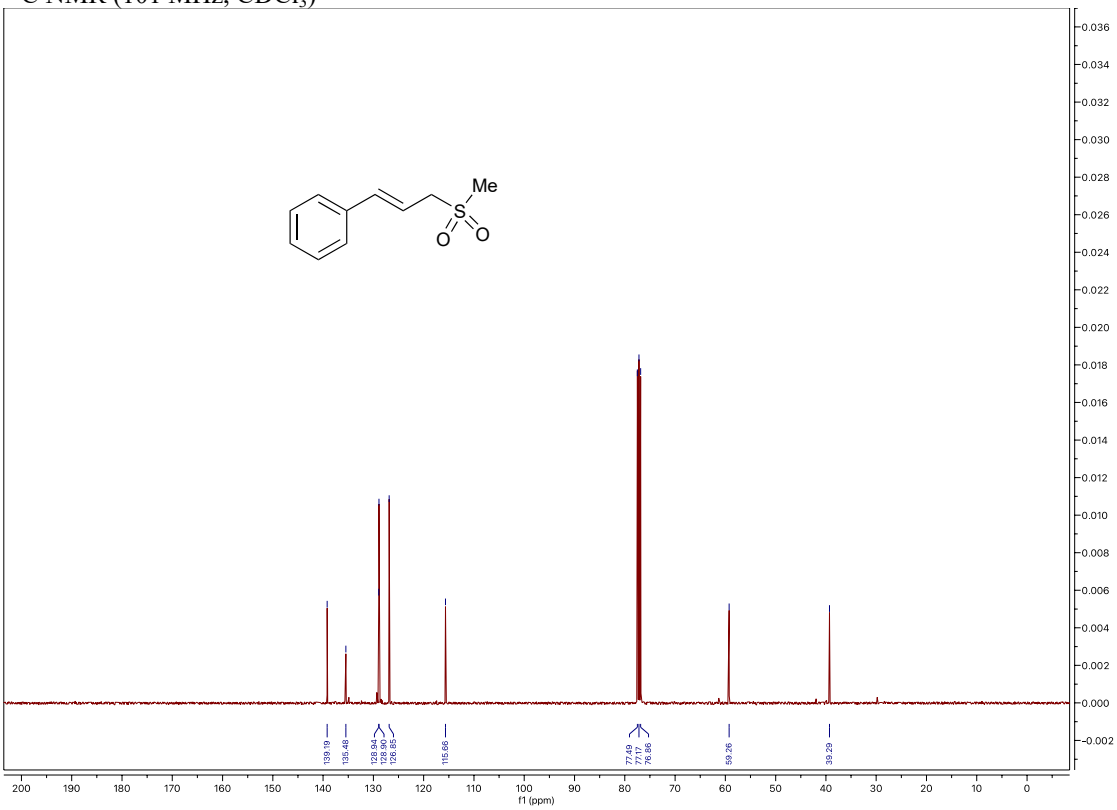
^{13}C NMR (101 MHz, $CDCl_3$)



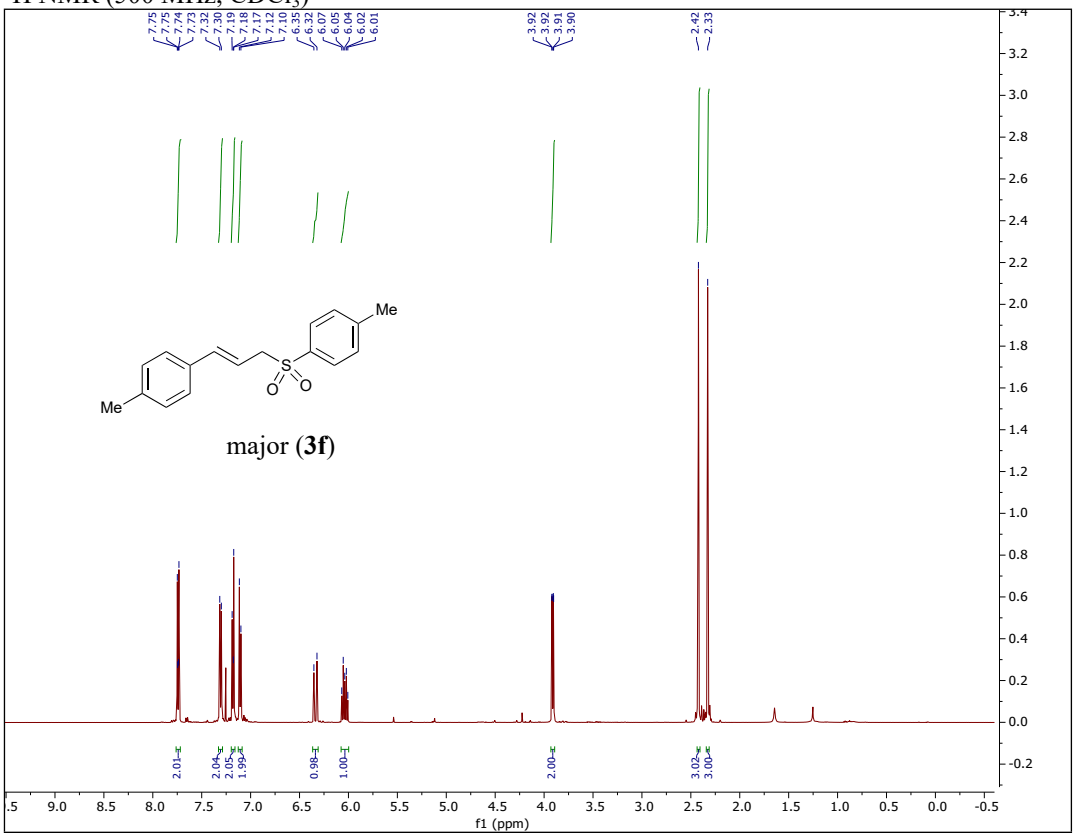
^{1}H NMR (400 MHz, $CDCl_3$)



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

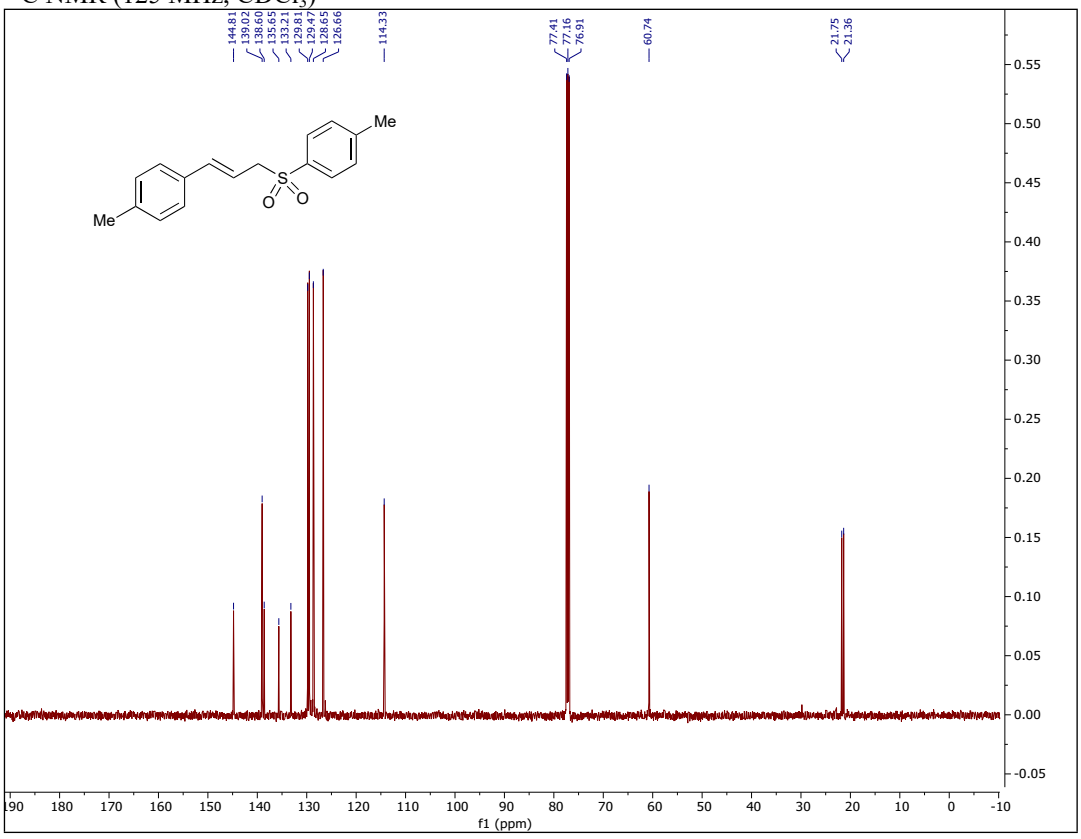


^{1}H NMR (500 MHz, $CDCl_3$)

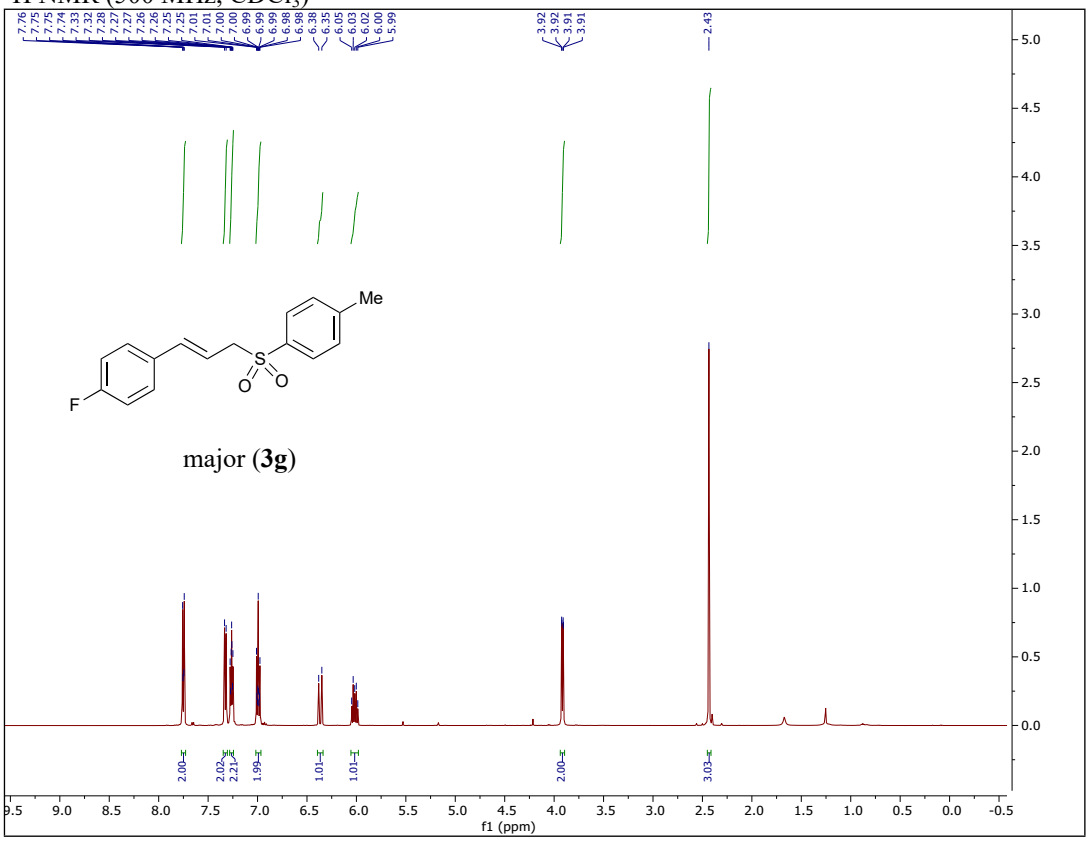


major (**3f**)

^{13}C NMR (125 MHz, $CDCl_3$)

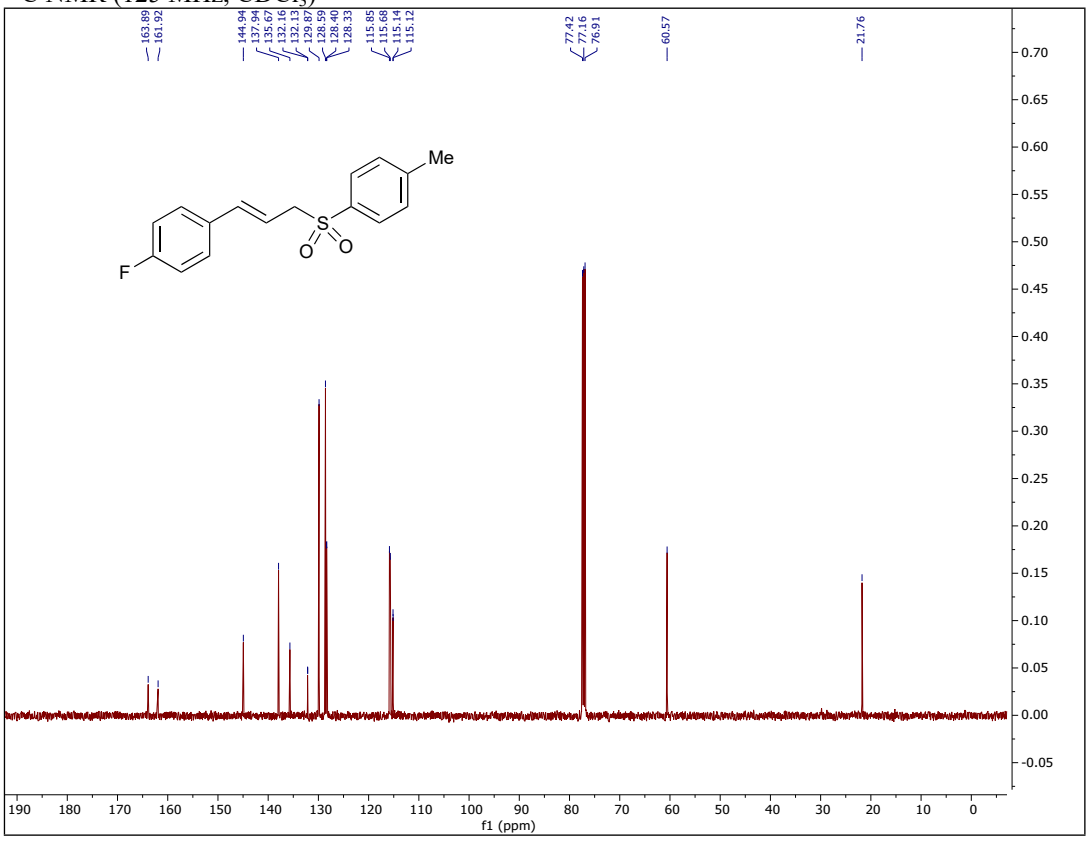


^{1}H NMR (500 MHz, $CDCl_3$)

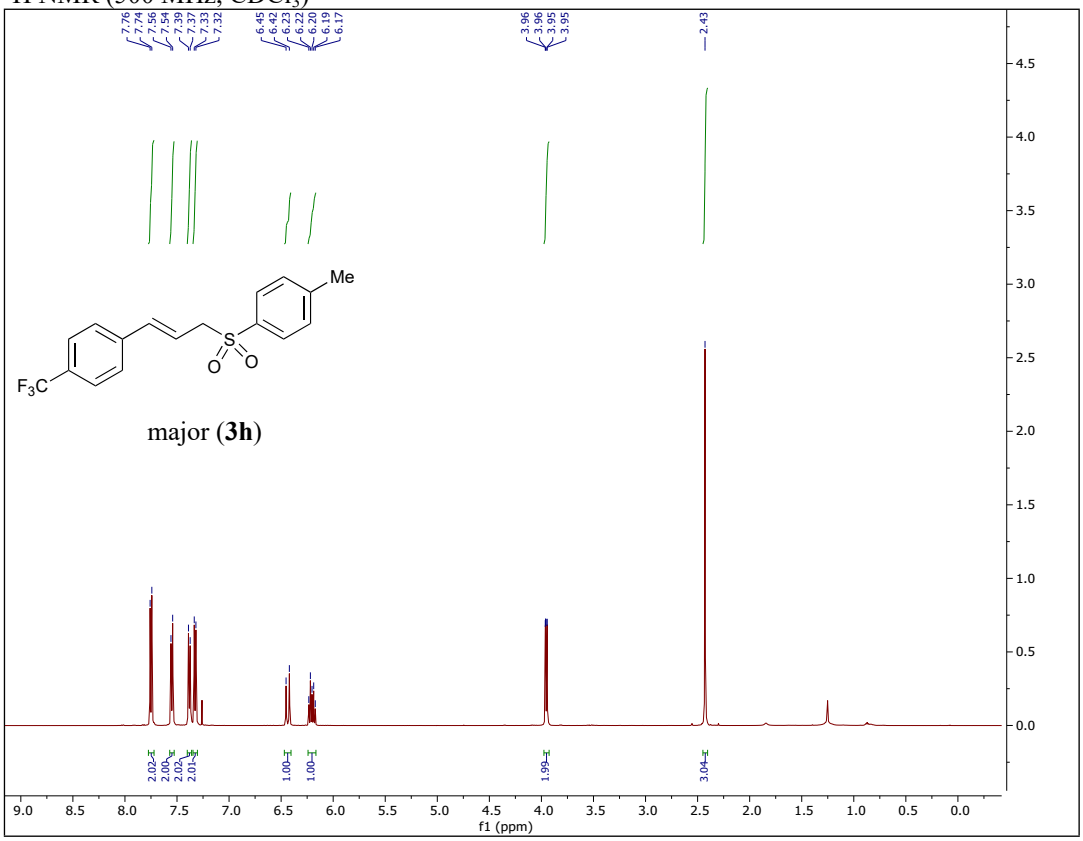


major (**3g**)

^{13}C NMR (125 MHz, $CDCl_3$)

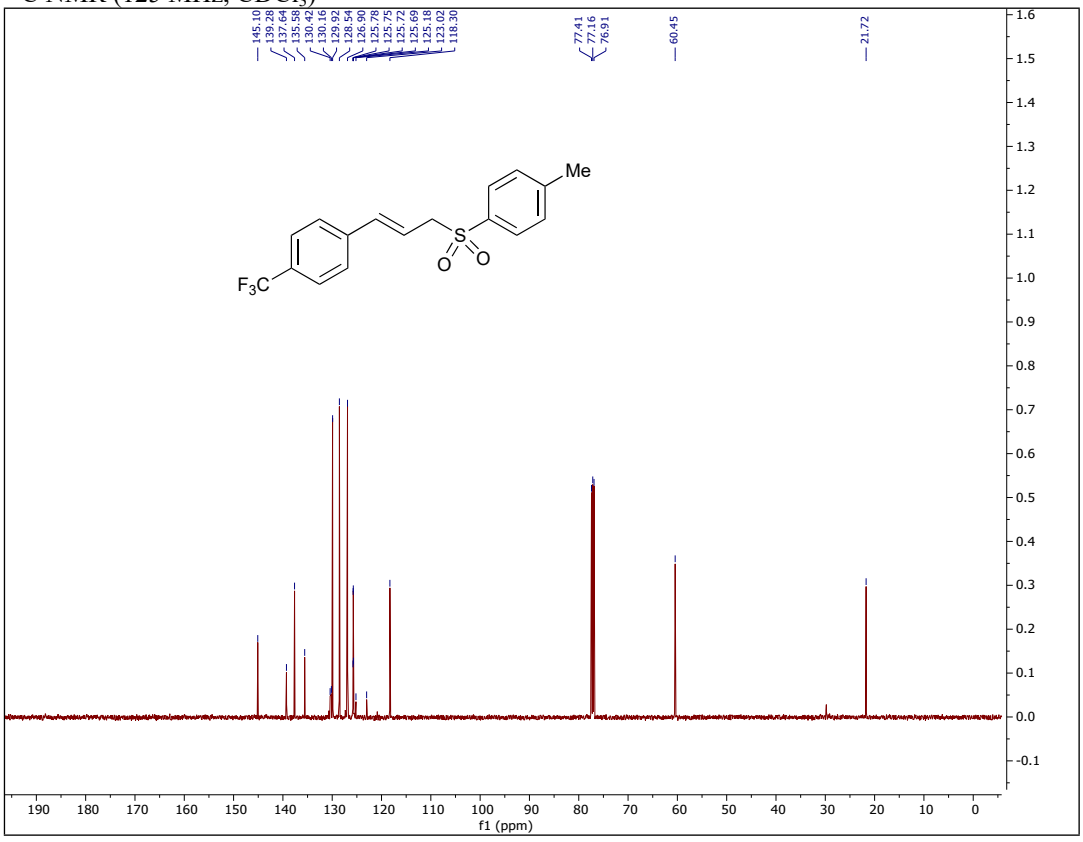


^{1}H NMR (500 MHz, $CDCl_3$)

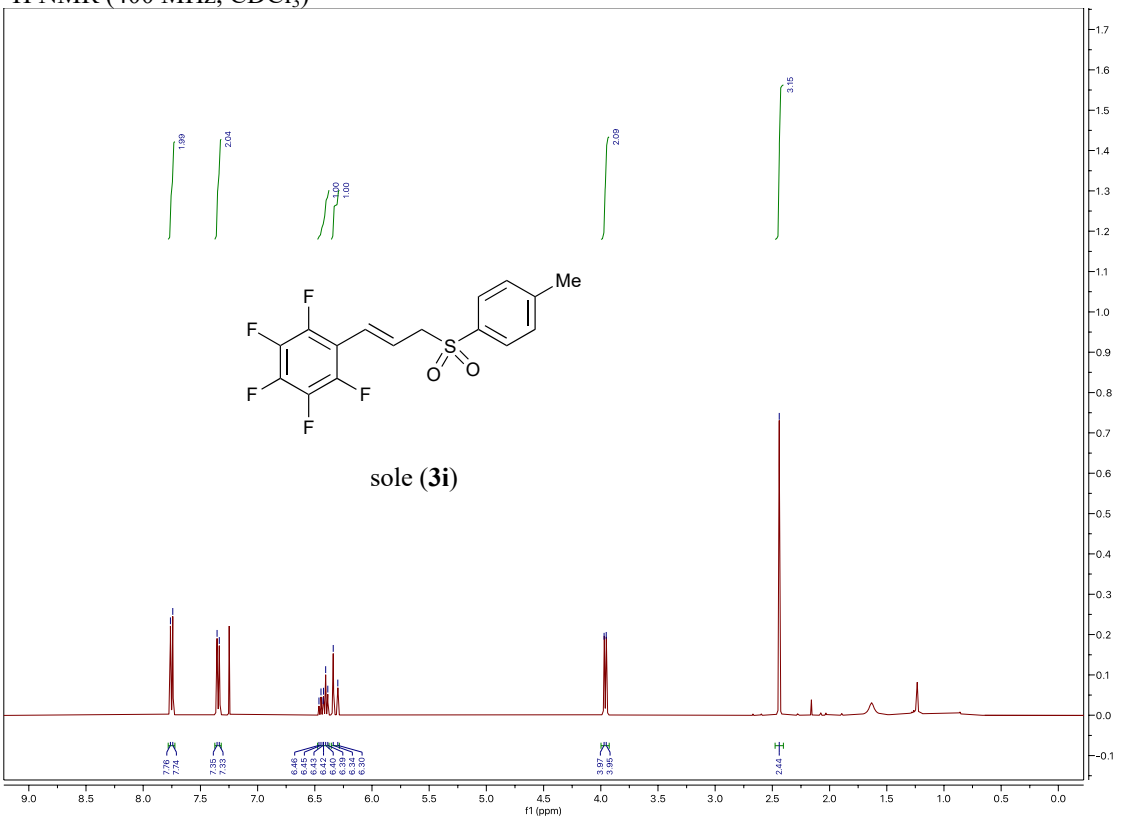


major (**3h**)

^{13}C NMR (125 MHz, $CDCl_3$)

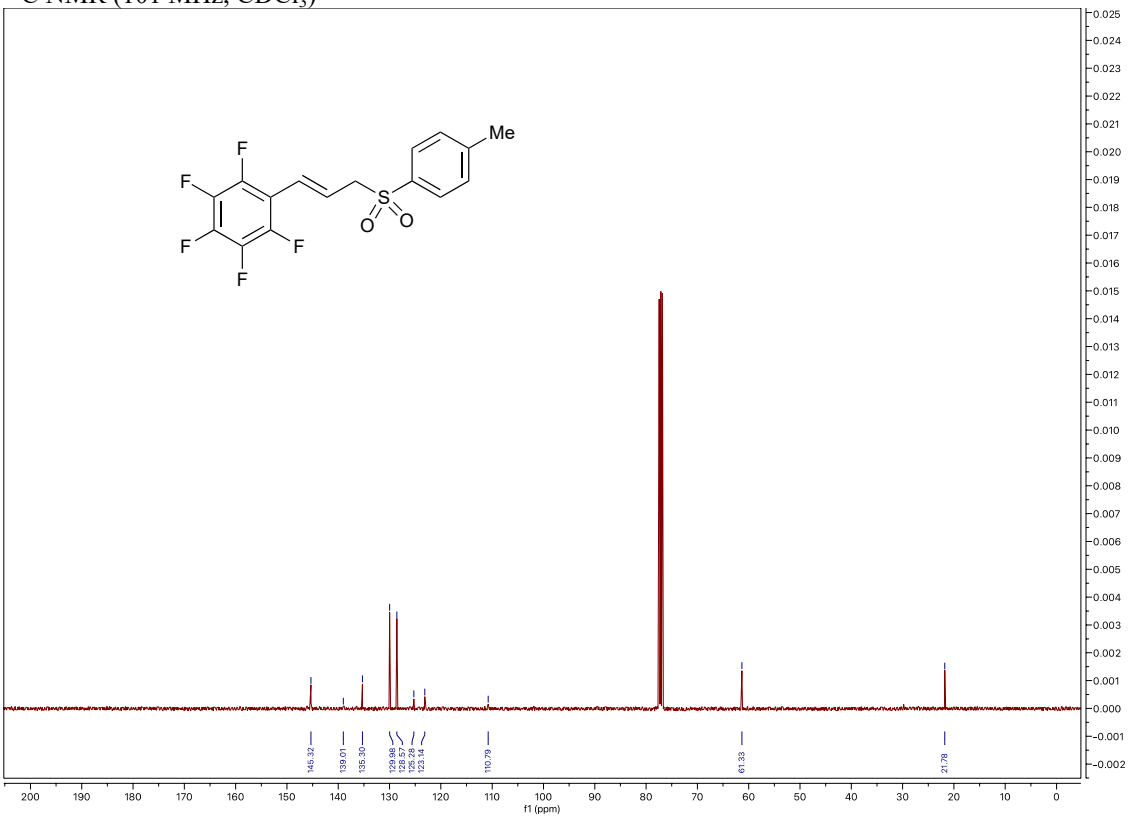


^{1}H NMR (400 MHz, $CDCl_3$)

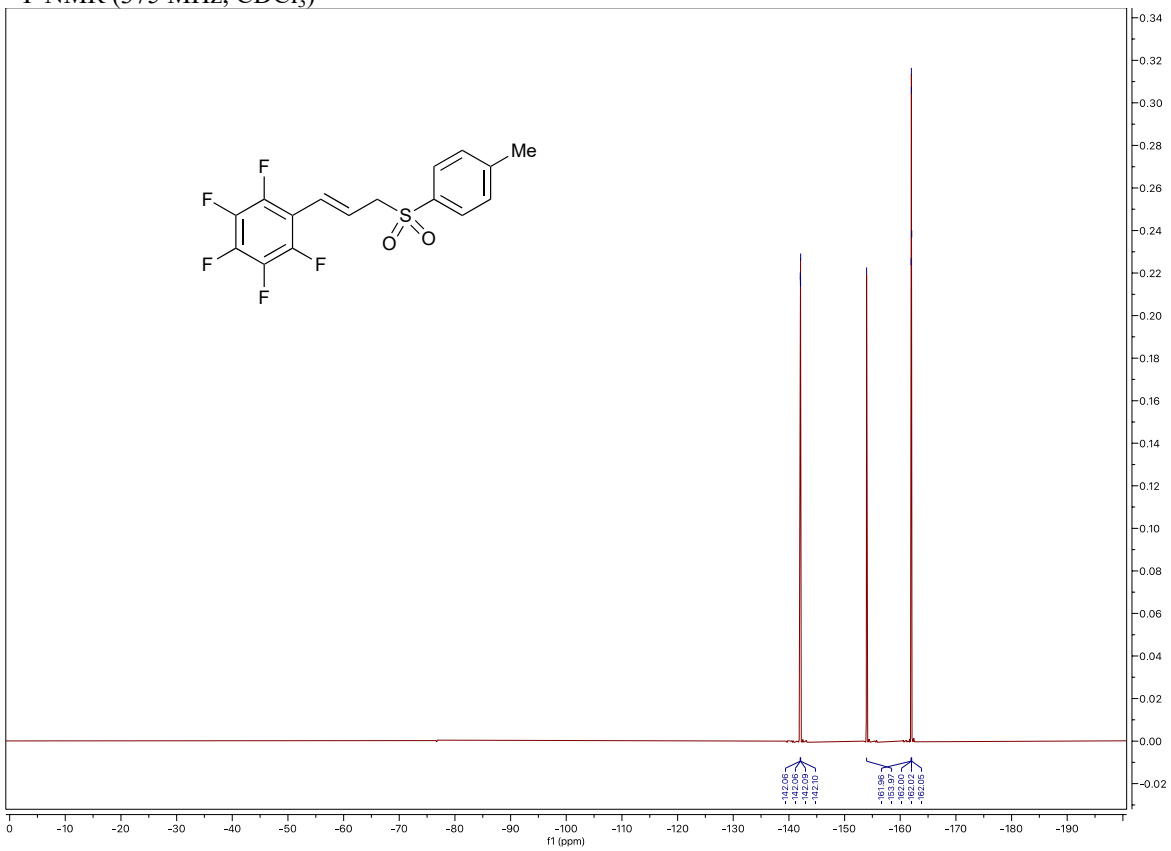


sole (**3i**)

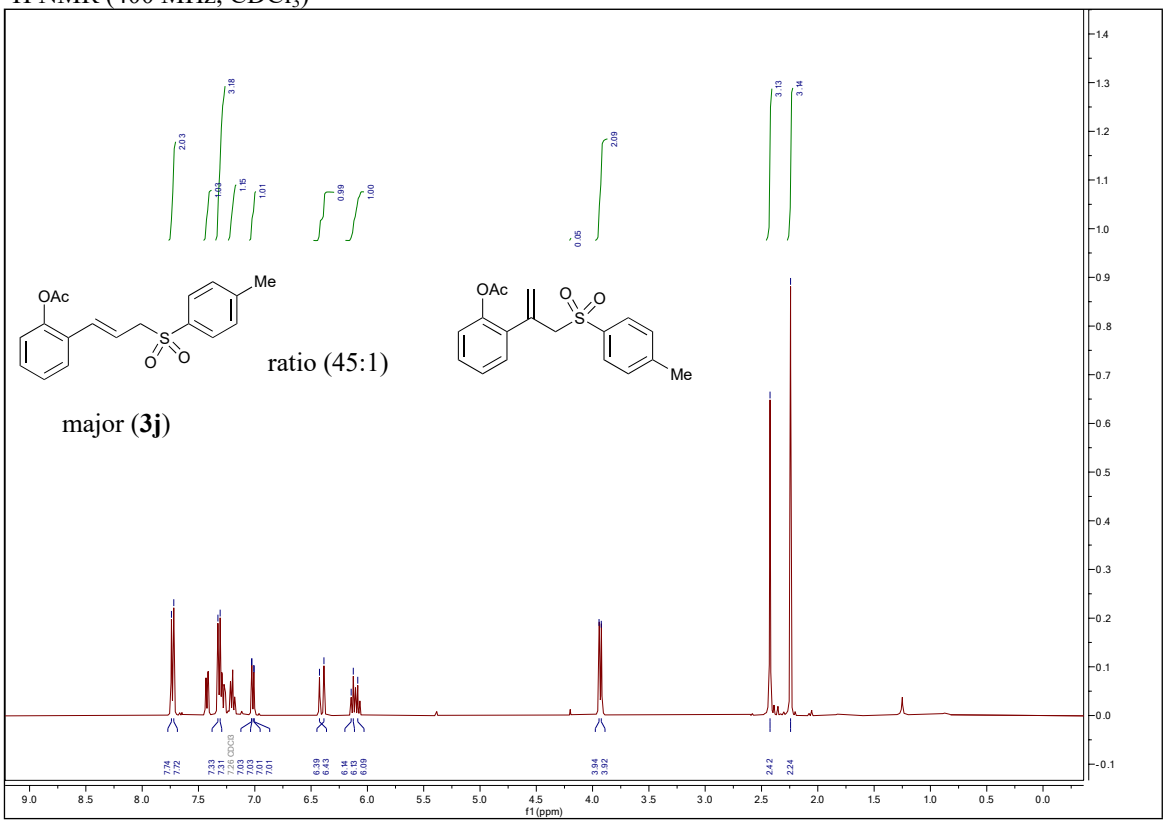
^{13}C NMR (101 MHz, $CDCl_3$)



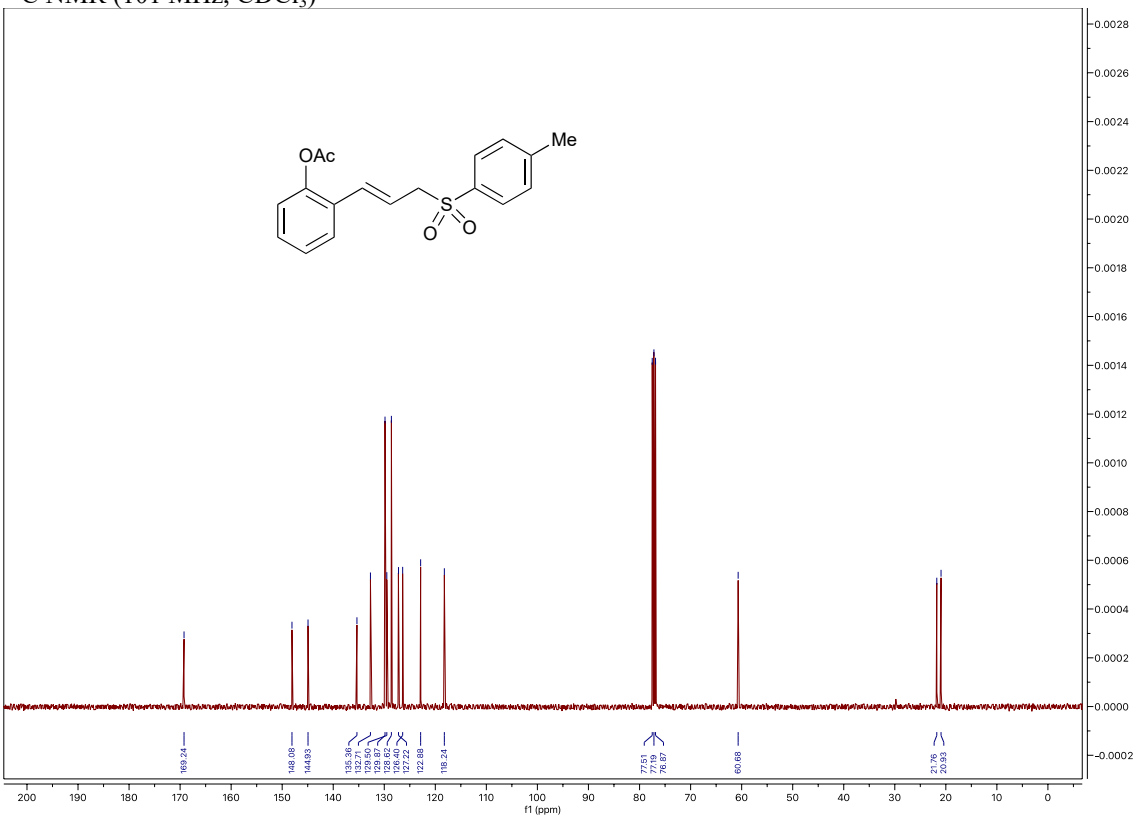
^{19}F NMR (375 MHz, $CDCl_3$)



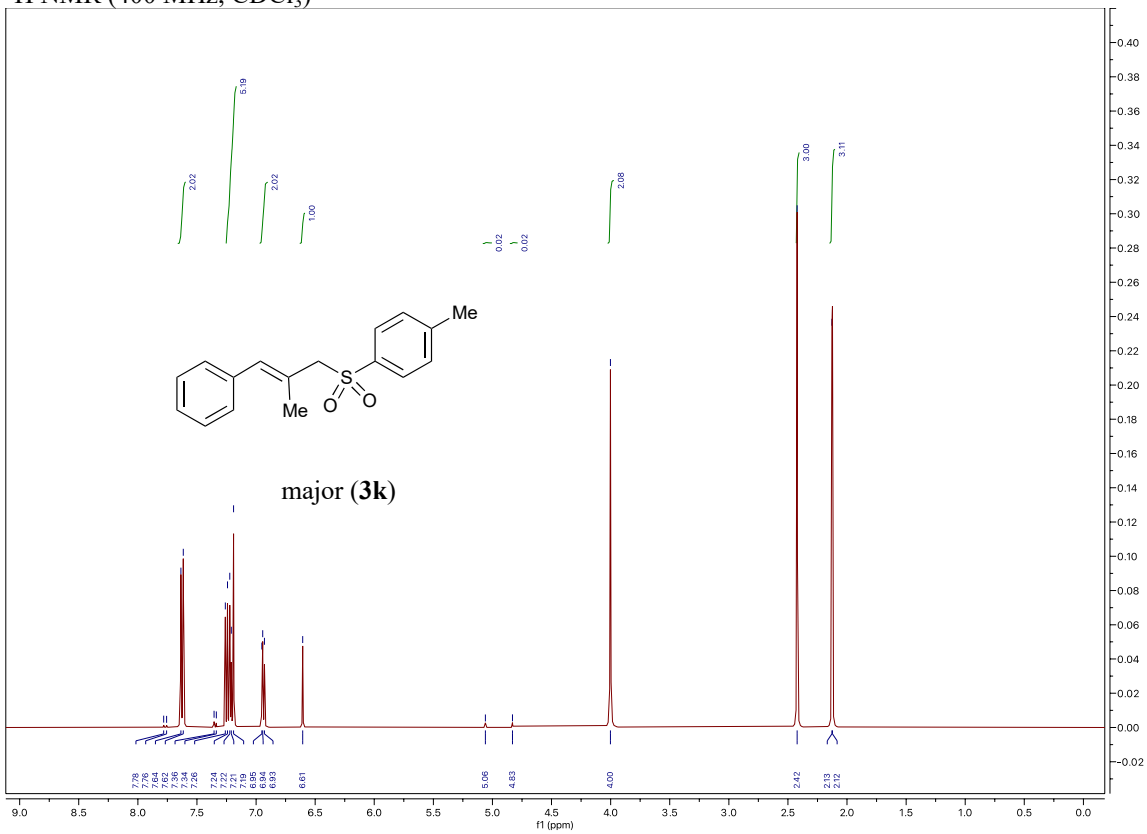
^{1}H NMR (400 MHz, $CDCl_3$)



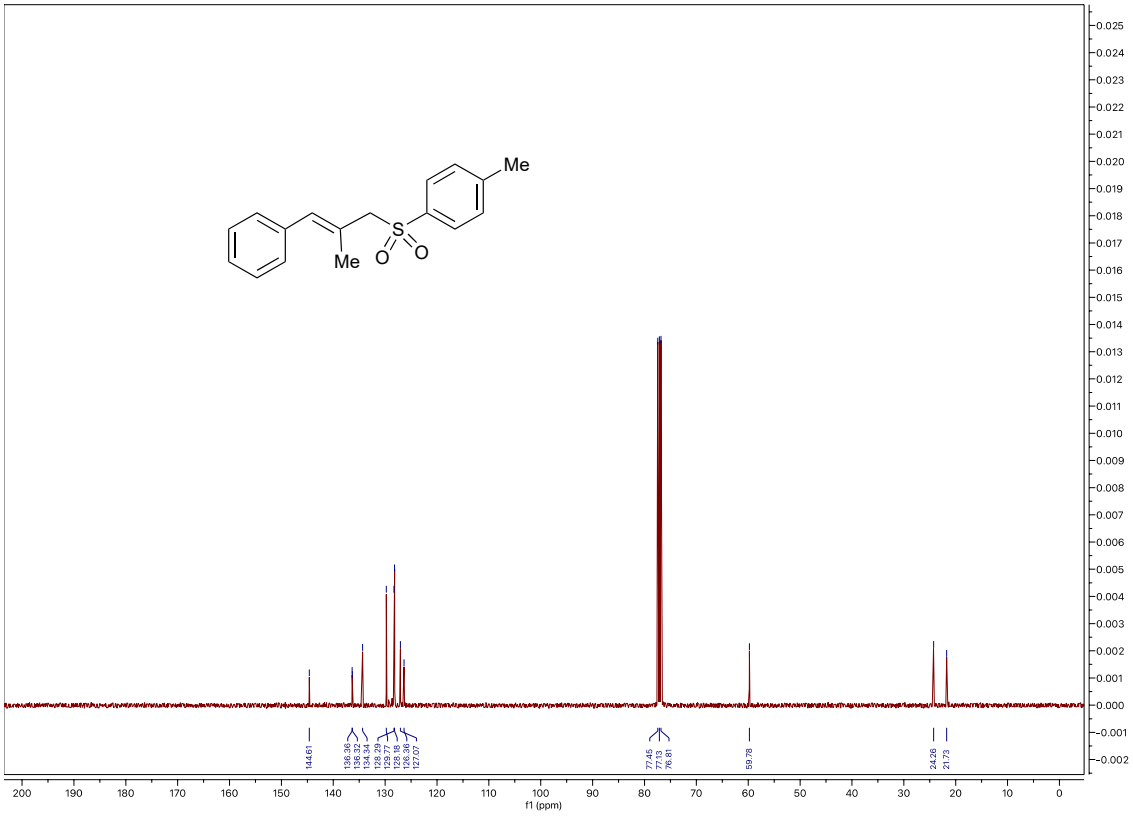
^{13}C NMR (101 MHz, $CDCl_3$)



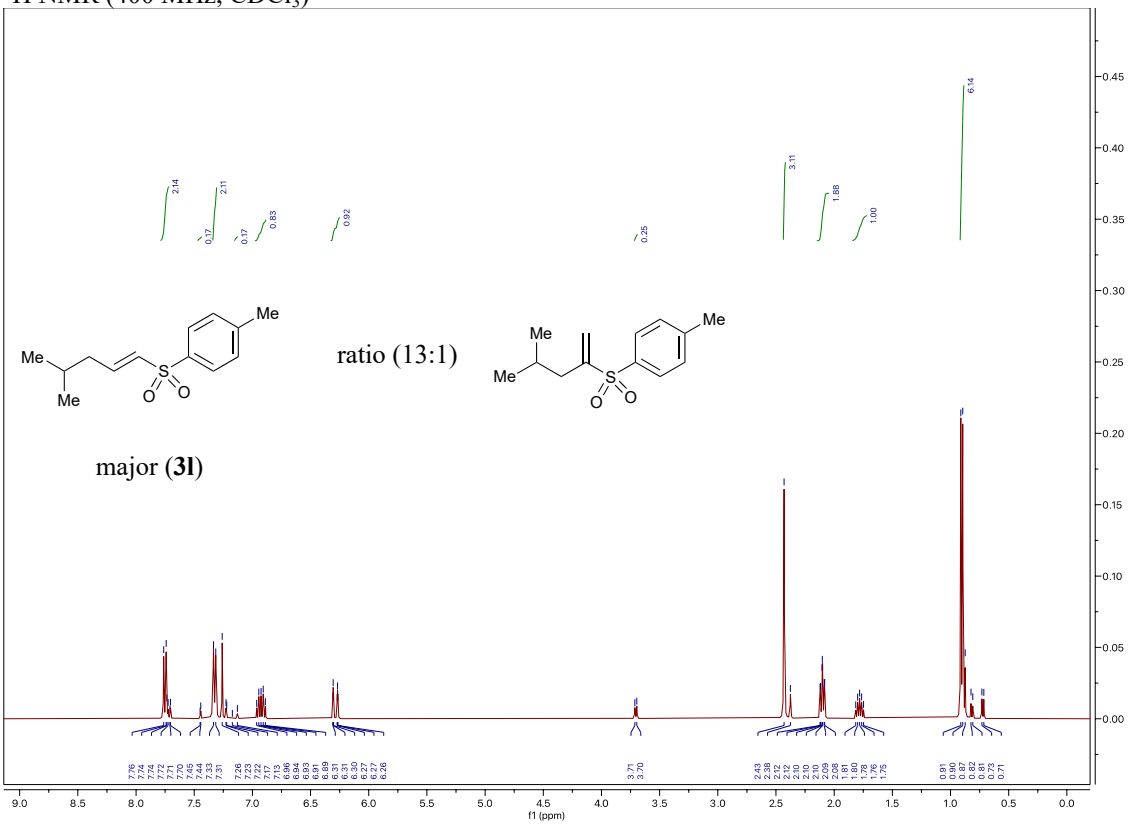
^{1}H NMR (400 MHz, $CDCl_3$)



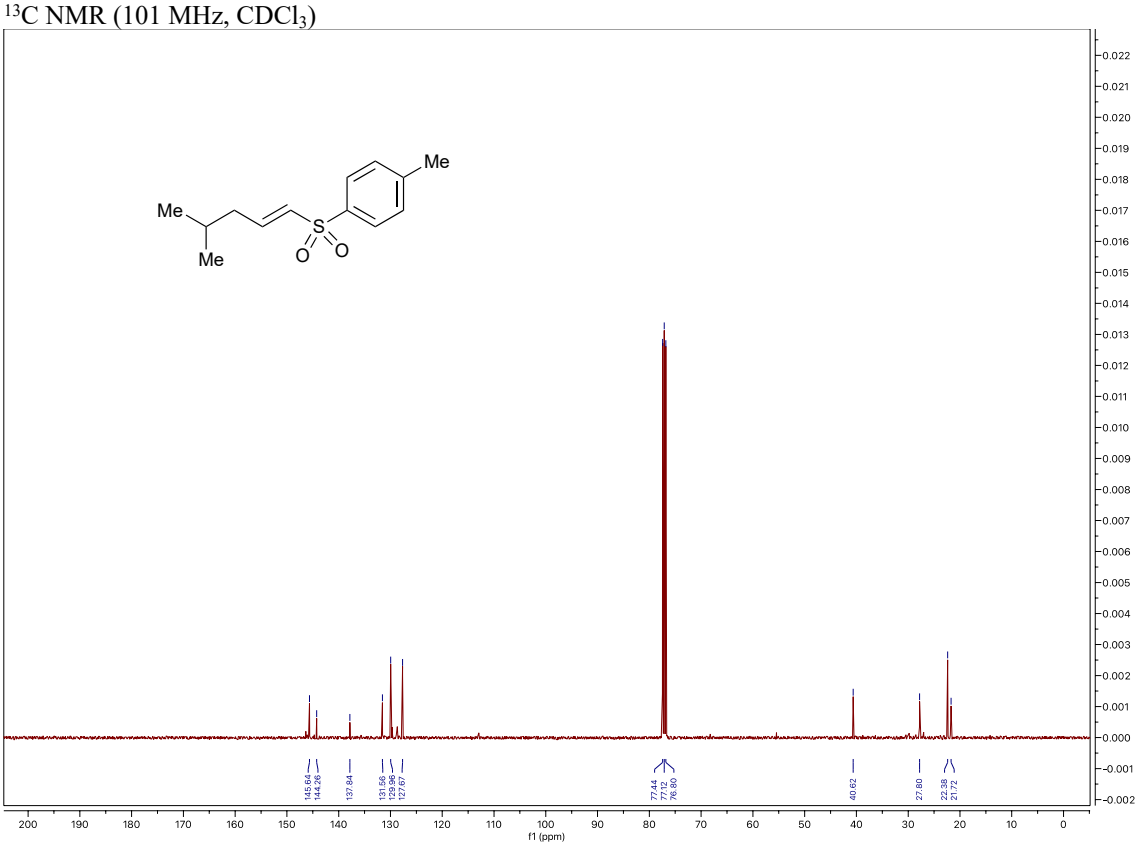
^{13}C NMR (101 MHz, $CDCl_3$)



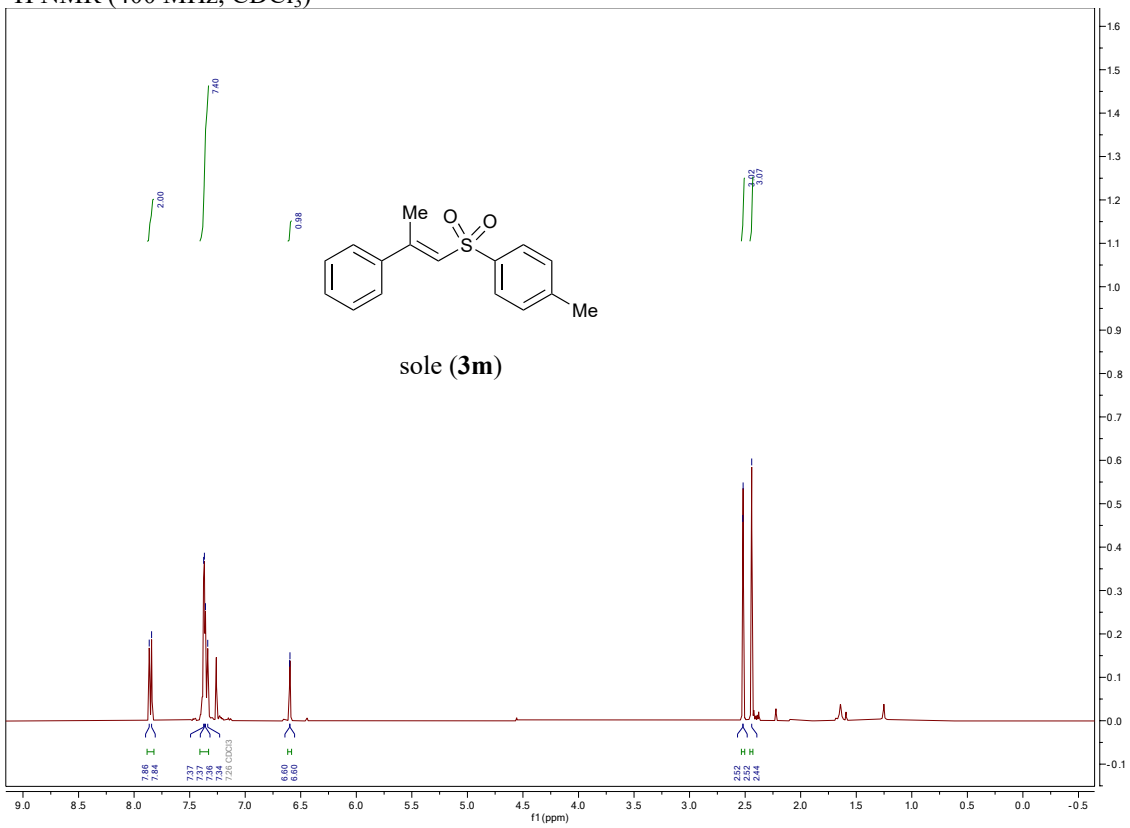
^{1}H NMR (400 MHz, $CDCl_3$)



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

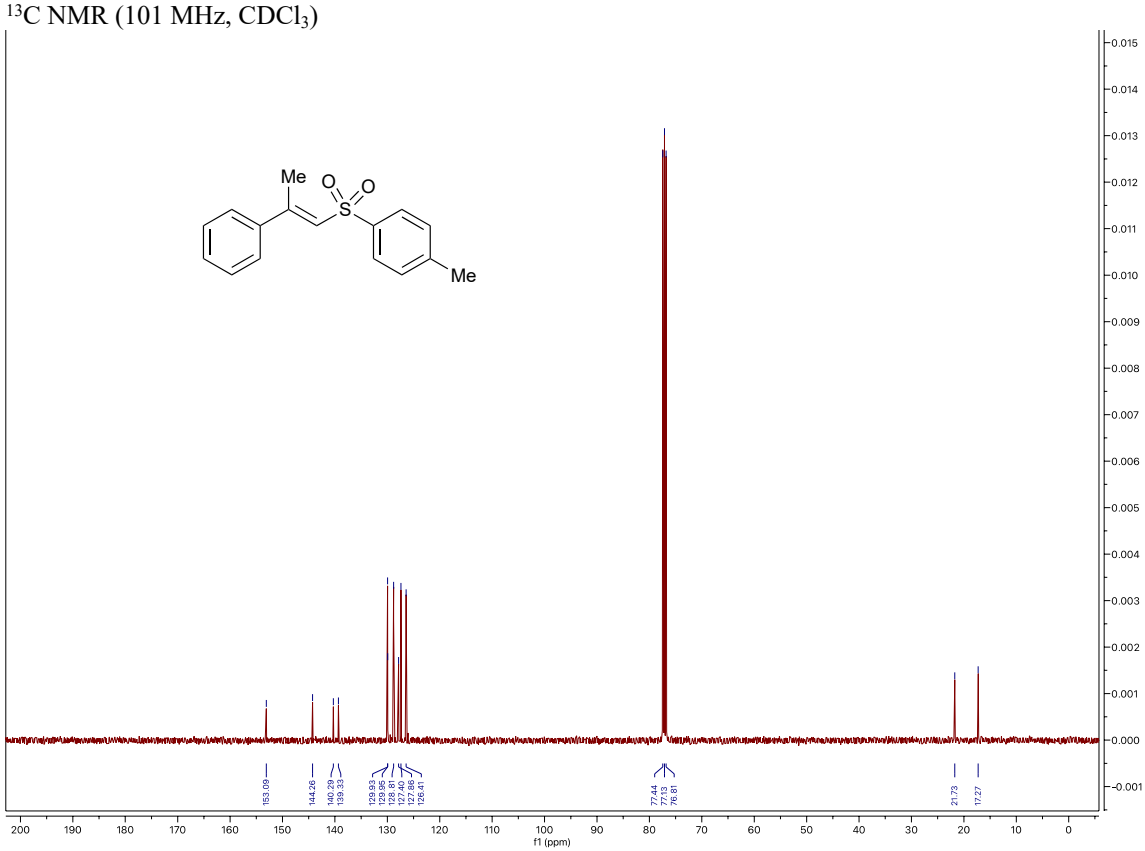


^{1}H NMR (400 MHz, $CDCl_3$)

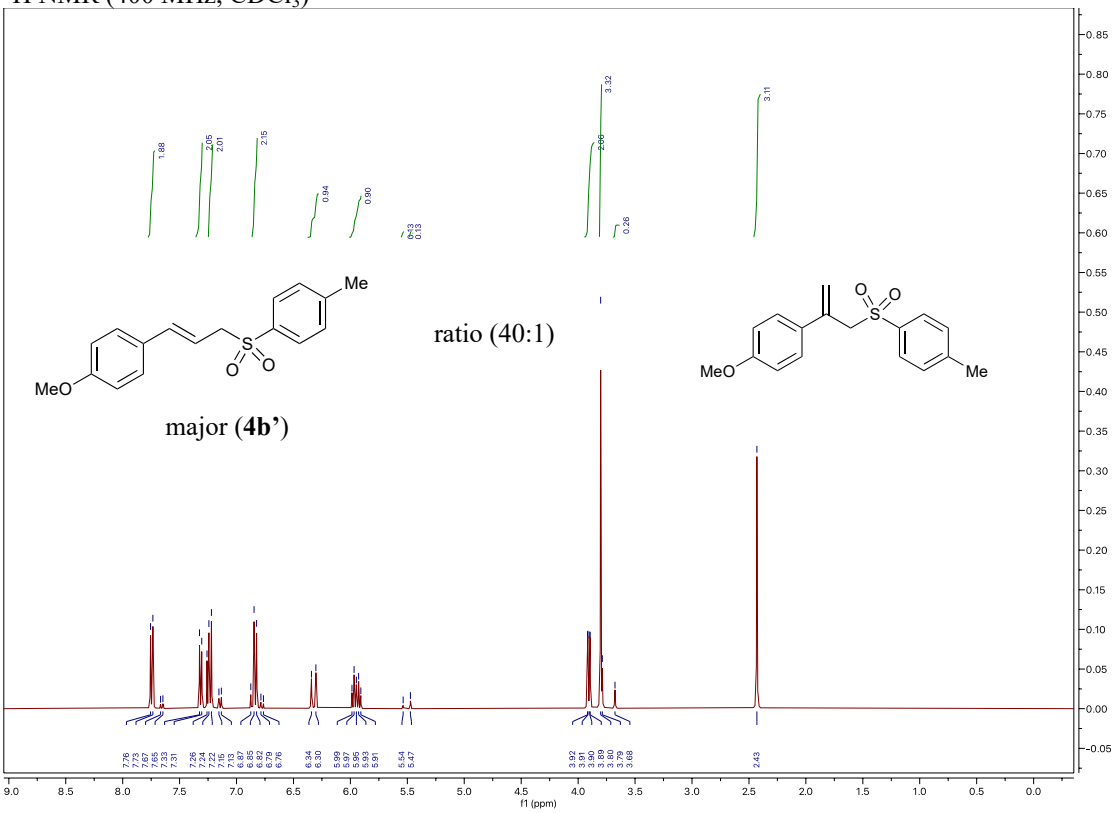


sole (**3m**)

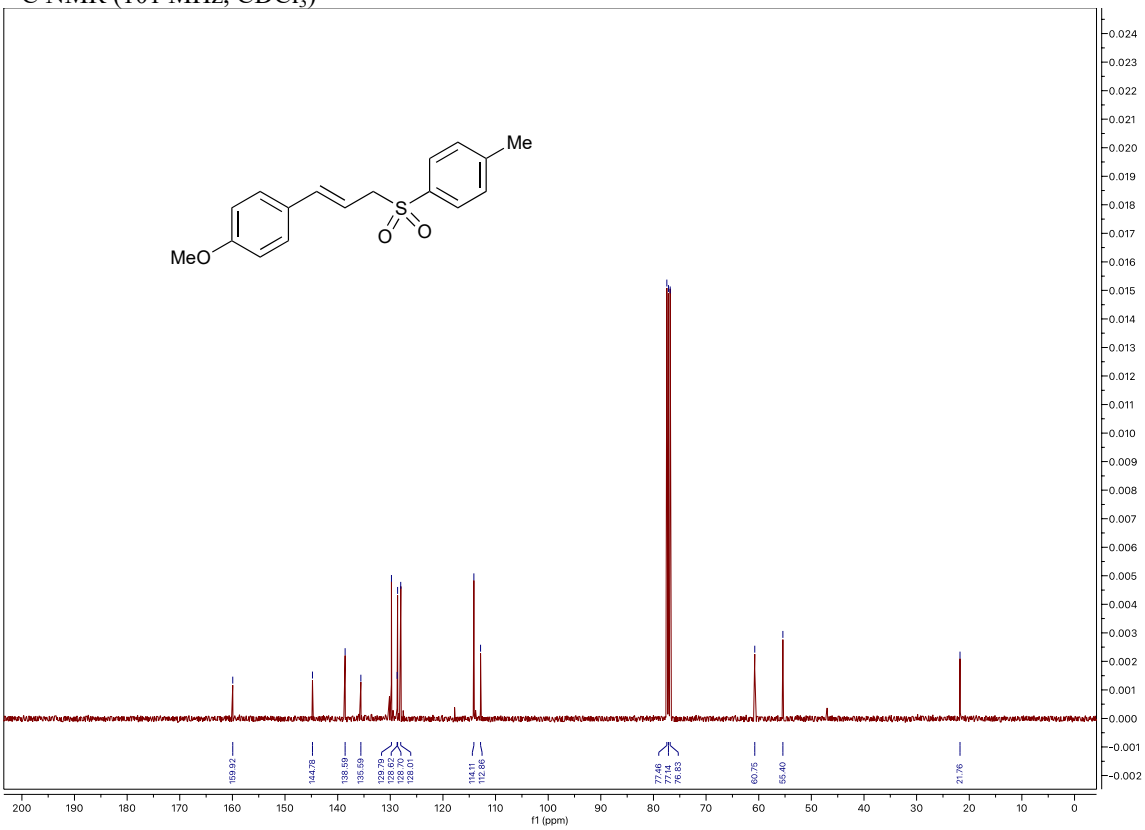
^{13}C NMR (101 MHz, $CDCl_3$)



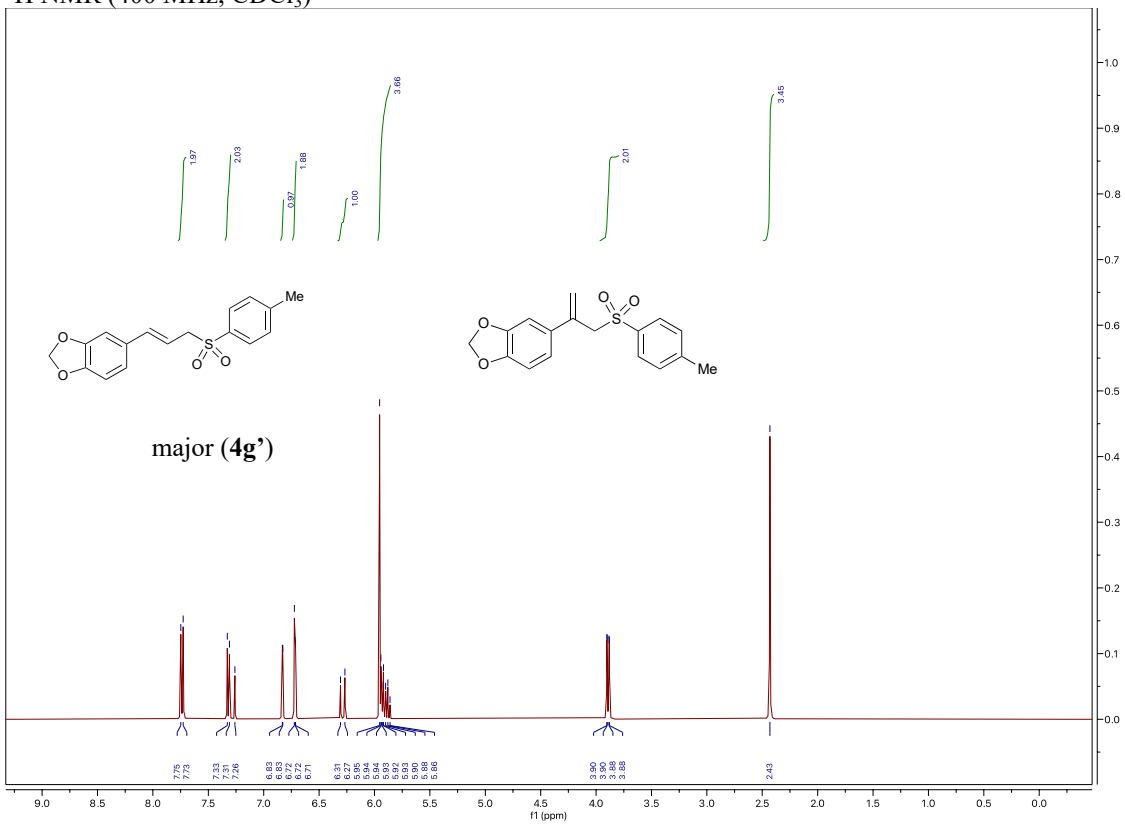
^{1}H NMR (400 MHz, $CDCl_3$)



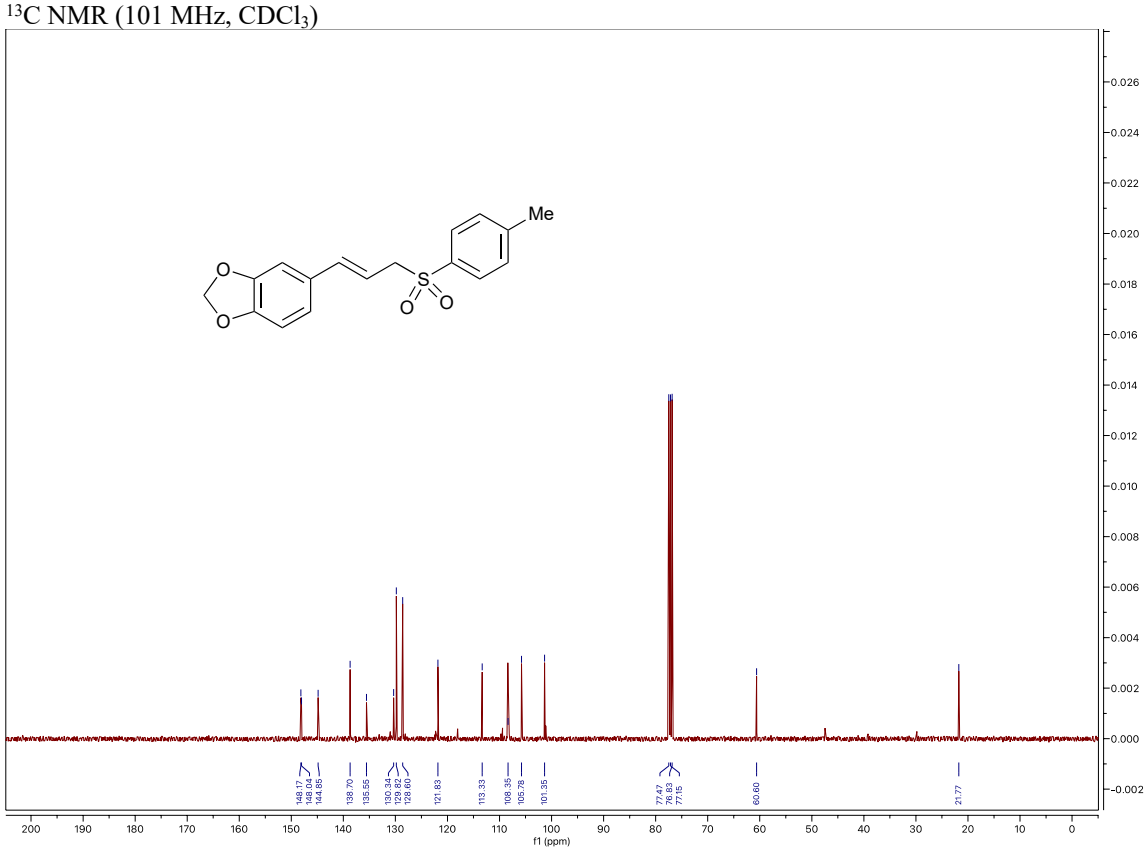
^{13}C NMR (101 MHz, $CDCl_3$)



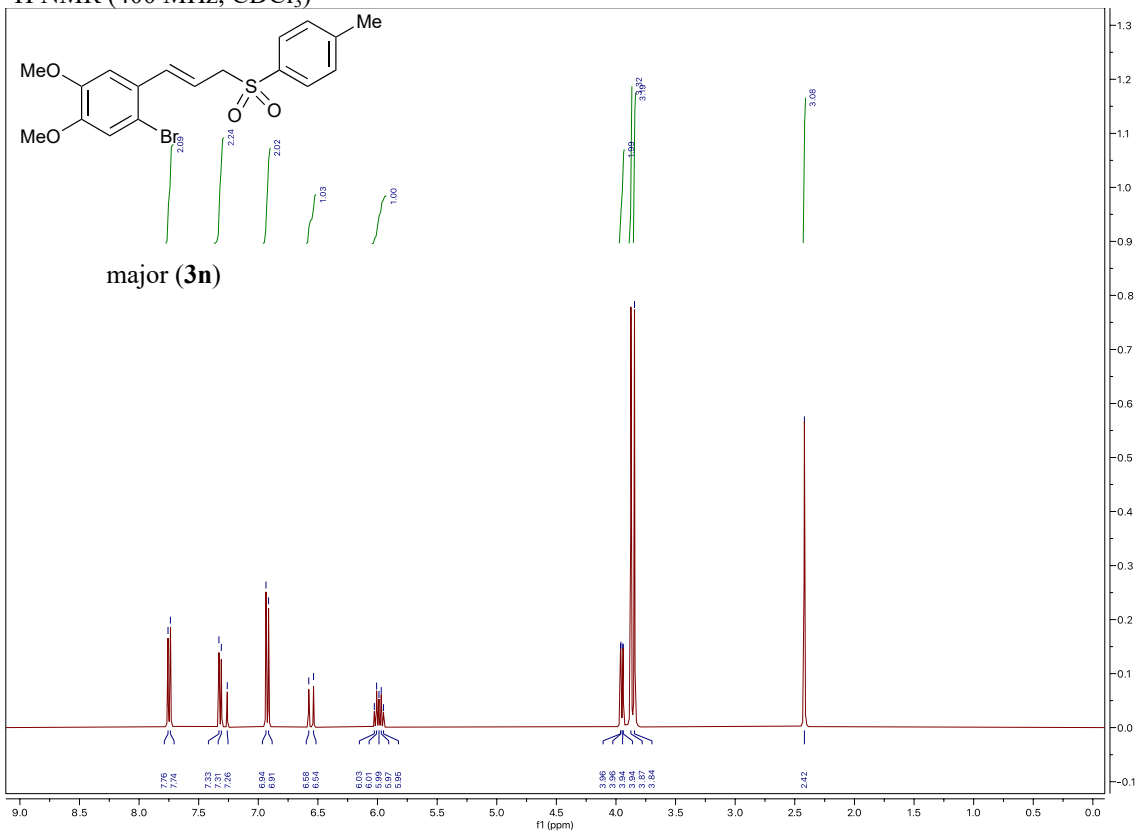
^{1}H NMR (400 MHz, $CDCl_3$)



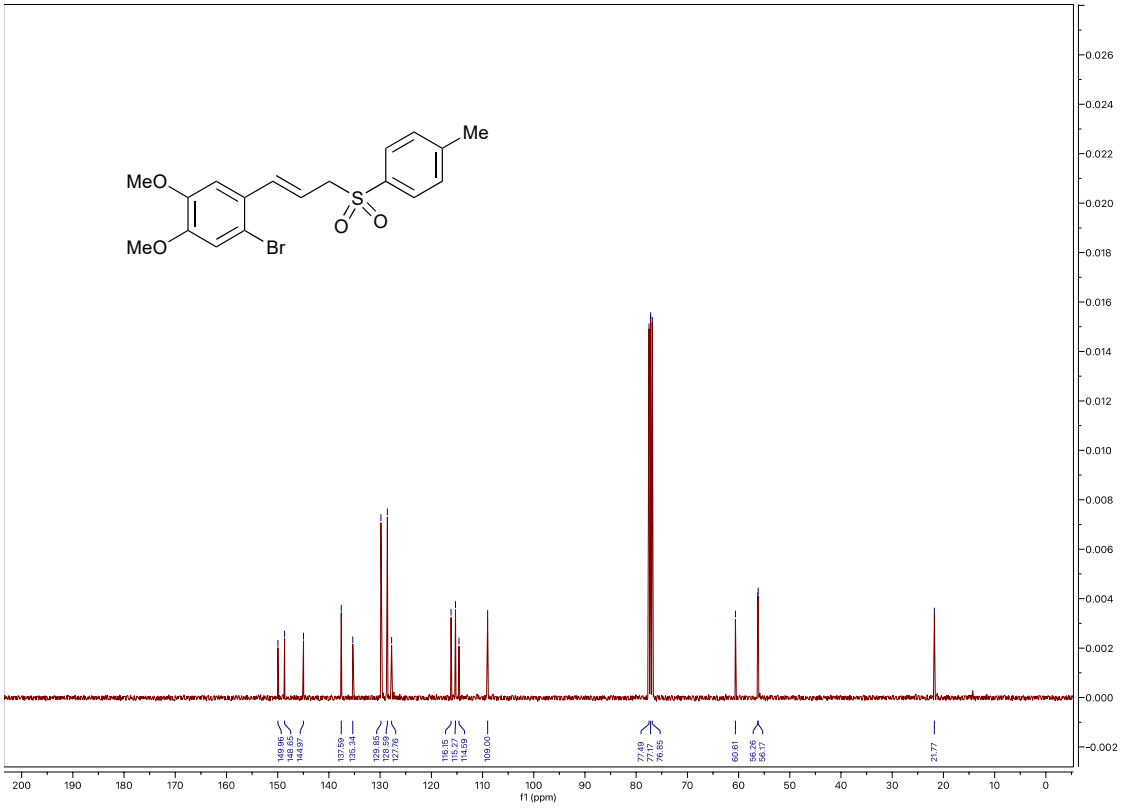
^{13}C NMR (101 MHz, $CDCl_3$)



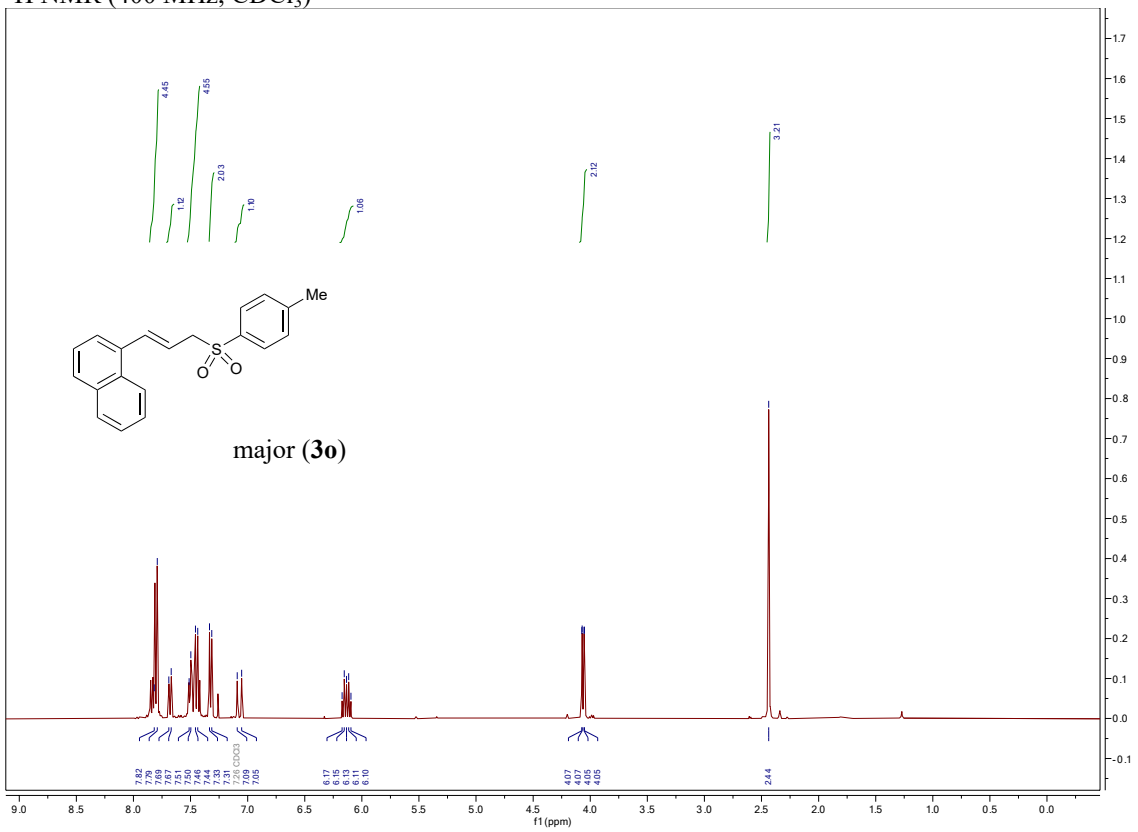
^{1}H NMR (400 MHz, $CDCl_3$)



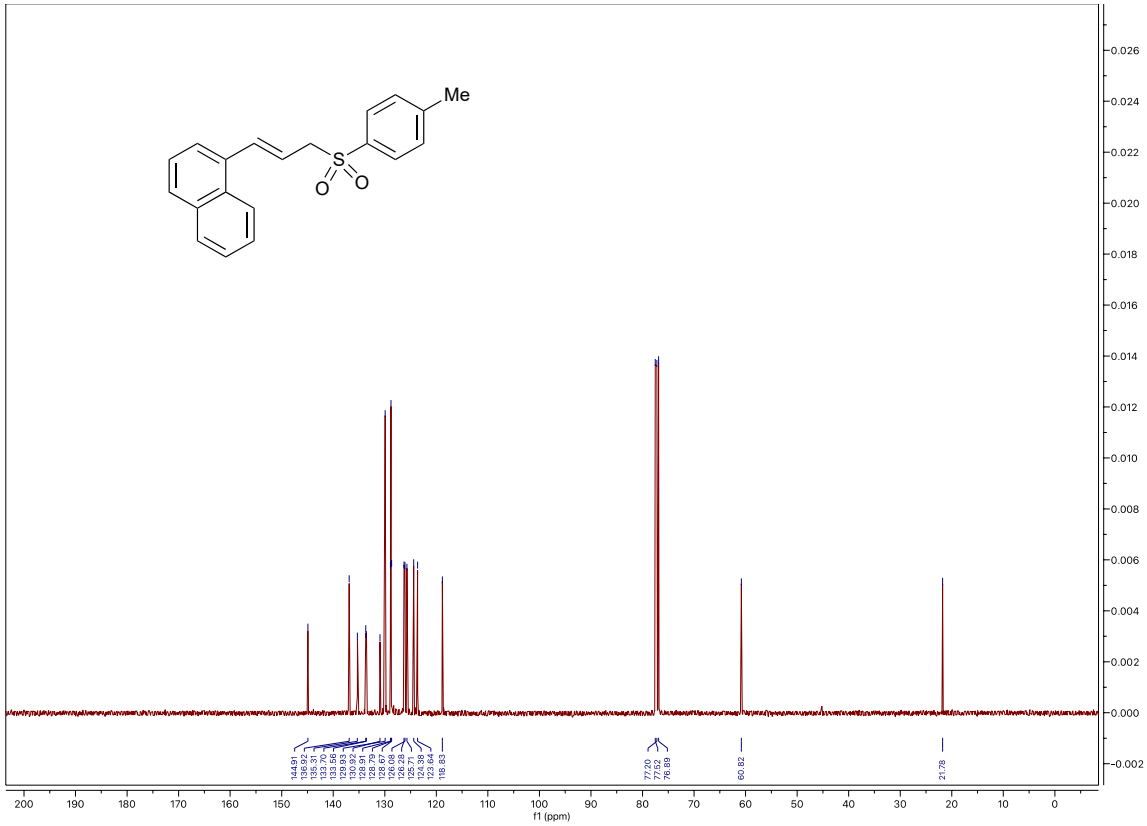
^{13}C NMR (101 MHz, $CDCl_3$)



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



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



X-Ray Acquisition Data of Compounds 3b & 4c

Experimental

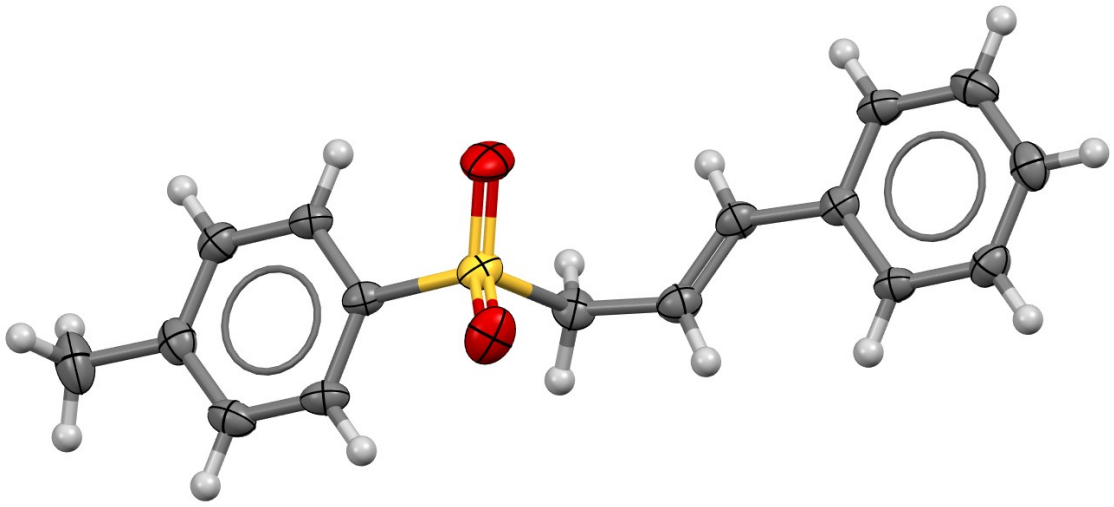
Single crystals of both samples were coated with a trace of Fomblin oil and were transferred to the goniometer head of a Bruker Quest diffractometer. Data collection of both crystals used Mo Kα wavelength (λ = 0.71073 Å) on an instrument with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator and a PhotonII area detector. The instrument is equipped with an Oxford Cryosystems low temperature device and examination and data collection were performed at 150 K. Data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3 and SADABS. The space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs and refined by full matrix least squares against F2 with all reflections using Shelxl2018 and the graphical interfaces Shelxle. H atoms were positioned geometrically and constrained to ride on their parent atoms. C-H bond distances were constrained to 0.95 Å for aromatic and alkene C-H moieties, and to 0.99 and 0.98 Å for aliphatic CH_2 and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate, but not to tip, to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH_3 and 1.2 for C-H and CH_2 units, respectively.

Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. Tables S1 and S2 contains the relevant crystallographic data for both compounds. **CCDC 2259946** (compound **3b**) and **2259947** (compound **4c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

TABLE S1: Crystallographic information for **3b**:

3b _0m	
Crystal data	
Chemical formula	$C_{16}H_{16}O_2S$
M_r	272.35
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	150
a, b, c (Å)	10.3670 (4), 5.5115 (2), 12.1835 (5)
β (°)	95.746 (2)
V (Å^3)	692.64 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.23
Crystal size (mm)	0.55 × 0.21 × 0.13
Data collection	
Diffractometer	Bruker AXS D8 Quest
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.695, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22252, 5306, 4738
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.772
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.105, 1.04
No. of reflections	5306
No. of parameters	173
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.42, −0.36
Absolute structure	Flack x determined using 1973 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	0.032 (18)

Asymmetric unit for **3b** shown with 50% probability ellipsoids.



Packing Diagram for **3b** viewed down the b axis.

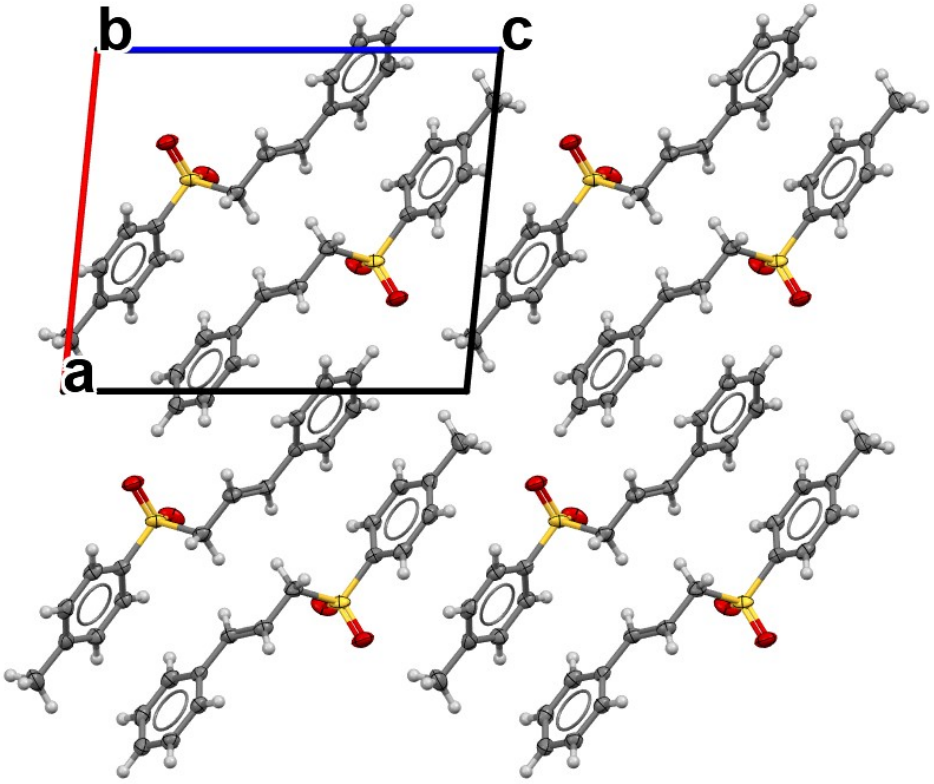
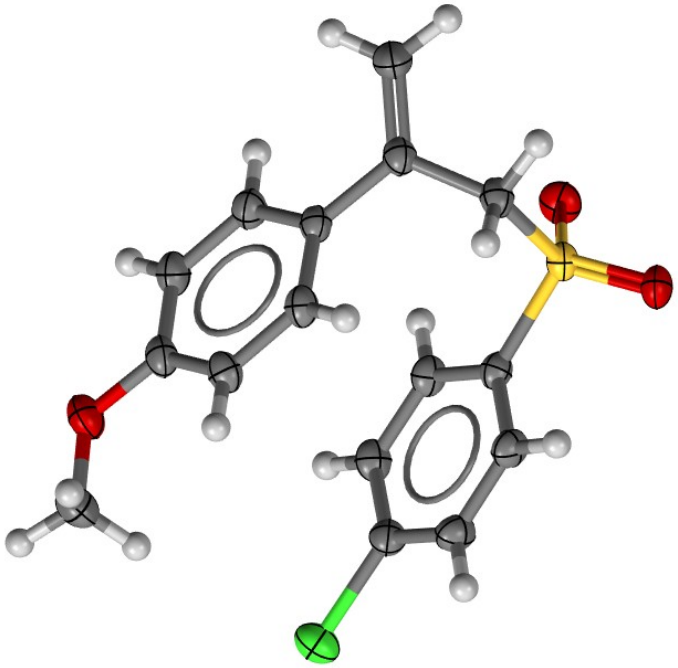


TABLE S2: Crystallographic information for **4c**:

	4c _2_0m
Crystal data	
Chemical formula	$C_{16}H_{15}ClO_3S$
M_r	322.79
Crystal system, space group	Triclinic, *P*1
Temperature (K)	150
a, *b*, *c* (Å)	7.5988 (4), 7.6069 (4), 13.6966 (7)
α, β, γ (°)	91.485 (3), 95.543 (3), 108.404 (3)
V (Å^3)	746.37 (7)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.40
Crystal size (mm)	0.32 × 0.27 × 0.13
Data collection	
Diffractometer	Bruker AXS D8 Quest
Absorption correction	Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T_{min}, T_{max}	0.683, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32913, 5696, 4696
R_{int}	0.037
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.771
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.053, 0.154, 1.04
No. of reflections	5696
No. of parameters	191
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.23, −0.54

Asymmetric unit for **4c** shown with 50% probability ellipsoids.



Packing diagram for **4c** viewed down the b axis.