Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Deaminative metal-free reaction of alkenylboronic acids, sodium metabisulfite and Katritzky salts

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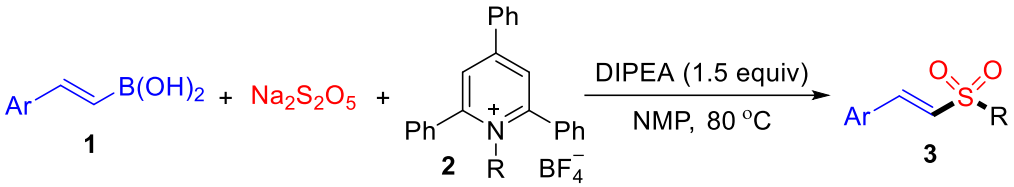
Table of Contents

1. General Information	S2
2. General procedures for the synthesis of (*E*)-alkylsulfonyl olefins	S3
3. Optimization of reaction conditions	S4
4. Mechanistic studies	S5-S6
5. References	S6
6. Characterization data for all products	S7-S15
7. ^{1}H, ^{19}F and ^{13}C NMR spectra of all products	S16-S43

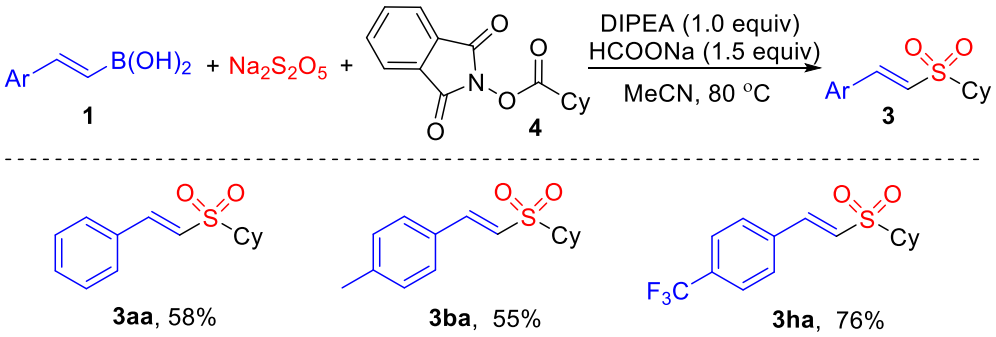
General information.

All reactions were carried out in oven dried Schlenk tubes under nitrogen atmosphere. Substitutional alkenylboronic acids and Katritzky salts were prepared according to the reported method.[1] Styrylboronic acid was purchased from bidepharm. Dry 1-Methyl-2-pyrrolidinone (NMP) and *N*,*N*-diisopropylethylamine (DIPEA) were purchased from Energy Chemical. ^{1}H, ^{19}F, ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance 400 MHz spectrometers. High resolution mass spectra (HRMS) were obtained using a commercial apparatus (ESI Source). Electrospray–ionisation HRMS data were acquired on a Q–Tof mass spectrometer (Waters SYNAPT G2-Si) LC-MS TOF. NMR spectra were taken using TMS (^{1}H, δ = 0), $CDCl_3$(^{1}H, δ = 7.26), $CDCl_3$(^{13}C, CPD δ = 77.0) as the internal standards, respectively. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

General procedures for the synthesis of (E)-vinyl sulfone derivatives



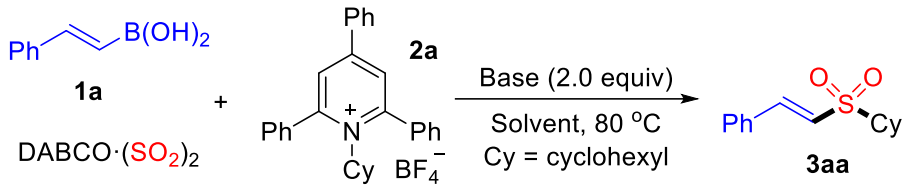
Alkenylboronic acid **1** (0.3 mmol, 1.0 equiv), sodium metabisulfite (0.45 mmol, 1.5 equiv), and Katritzky salt **2** (0.36 mmol, 1.2 equiv) were added sequentially into Schlenk tube under nitrogen. Then NMP (1.5 mL) and DIPEA (0.45 mmol, 1.5 equiv) were added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours as monitored by TLC. Upon completion, the mixture cooled to room temperature. Then, water (15 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phases were collected, washed with saturated brine solution and dried over anhydrous Na_2SO_4. Then, the filtrate was concentrated under vacuum and the residue was purified by flash column chromatography using *n*-hexane/ethyl acetate as eluent to afford pure product **3**.



Alkenylboronic acid **1** (0.3 mmol, 1.0 equiv), sodium metabisulfite (0.45 mmol, 1.5 equiv), *N*-hydroxyphthalimide ester **4** (0.36 mmol, 1.2 equiv) and sodium formate (0.45 mmol, 1.5 equiv) were added sequentially into Schlenk tube under nitrogen. Then MeCN (1.5 mL) and DIPEA (0.3 mmol, 1.0 equiv) were added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours as monitored by TLC. Upon completion, the mixture cooled to room temperature. Water (15 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phases were collected, washed with saturated brine solution and dried over anhydrous Na_2SO_4. The filtrate was concentrated under vacuum and the residue was purified by

flash column chromatography using *n*-hexane/ethyl acetate as eluent to afford pure product **3**.

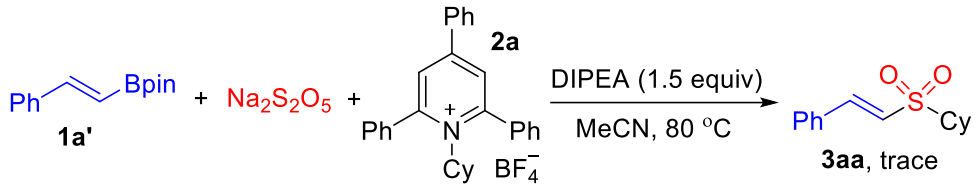
Table S1. Optimization of reaction conditions [a]



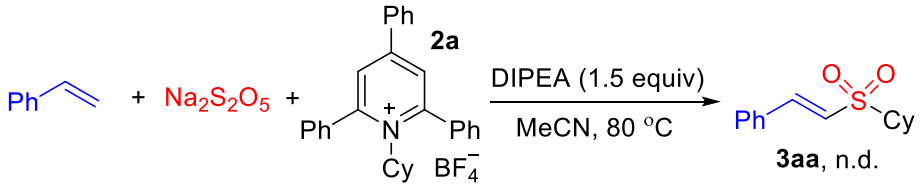
Entry	Base	Solvent	NMR Yield (%)
1	DBU	DMF	trace
2	DIPEA	DMF	32
3	Et_3N	DMF	20
4	DABCO	DMF	15
5	DMAP	DMF	23
6	TMEDA	DMF	9
7	Li_2CO_3	DMF	12
8	Na_2CO_3	DMF	24
9	K_2CO_3	DMF	17
10	Cs_2CO_3	DMF	9
11	Na_3PO_4	DMF	trace
12	Na_2HPO_4	DMF	trace
13	NaHCO3	DMF	4
14	NaOAc	DMF	11
15	DIPEA	DMA	27
16	DIPEA	NMP	38
17	DIPEA	DMSO	17
18	DIPEA	*t*-BuOH	9
19	DIPEA	Toluene	13
20	DIPEA	1,4-dioxane	24
21	DIPEA	EA	23
22	DIPEA	Actone	26
23	DIPEA	DCE	trace
24	DIPEA	MeCN	13

[a] Reaction condition: alkenylboronic acid **1a** (0.2 mmol, 1.0 equiv), DABCO·$(SO_2)_2$ (0.3 mmol, 1.5 equiv), 1-cyclohexyl-2,4,6-triphenyl-pyridin-1-ium tetrafluoroborate **2a** (0.3 mmol, 1.5 equiv), base (0.4 mmol, 2.0 equiv), solvent (1.0 mL), N_2, 80 °C, 12 h. [b] ^{1}H NMR yield using 1,3,5-trimethoxybenzene as internal standard.

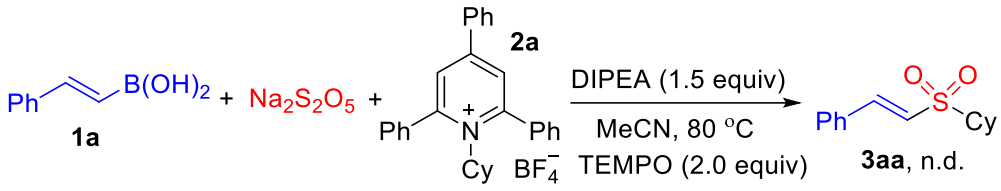
Mechanistic studies



4,4,5,5-Tetramethyl-2-styryl-1,3,2-dioxaborolane **1a'** (0.2 mmol, 1.0 equiv), sodium metabisulfite (0.3 mmol, 1.5 equiv), and Katritzky salt **2** (0.24 mmol, 1.2 equiv) were added sequentially into Schlenk tube under nitrogen. Then NMP (1.0 mL) and DIPEA (0.3 mmol, 1.5 equiv) were added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours as monitored by TLC. Upon completion, the mixture cooled to room temperature. Then, water (10 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phases were collected, washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. Then, the filtrate was concentrated and the crude was determined by NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.



Sodium metabisulfite (0.3 mmol, 1.5 equiv) and Katritzky salt **2** (0.24 mmol, 1.2 equiv) were added sequentially into Schlenk tube under nitrogen. Then styrene (0.2 mmol, 1.0 equiv), NMP (1.0 mL) and DIPEA (0.3 mmol, 1.5 equiv) were added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours as monitored by TLC. Upon completion, the mixture cooled to room temperature. Then, water (10 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phases were collected, washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. Then, the filtrate was concentrated and the crude was determined by NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

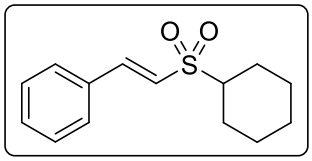


Styrylboronic acid **1a** (0.2 mmol, 1.0 equiv), sodium metabisulfite (0.3 mmol, 1.5 equiv), Katritzky salt **2** (0.24 mmol, 1.2 equiv) and 2,2,6,6-Tetramethylpiperidinooxy (TEMPO) (0.4 mmol, 2.0 equiv) were added sequentially into Schlenk tube under nitrogen. Then NMP (1.0 mL) and DIPEA (0.3 mmol, 1.5 equiv) were added rapidly by syringe. The resulting mixture was allowed to stir at 80 °C oil bath for 12 hours as monitored by TLC. Upon completion, the mixture cooled to room temperature. Then, water (10 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic phases were collected, washed with saturated NaCl solution and dried over anhydrous Na_2SO_4. Then, the filtrate was concentrated and the crude was determined by NMR analysis using 1,3,5-trimethoxybenzene as the internal standard.

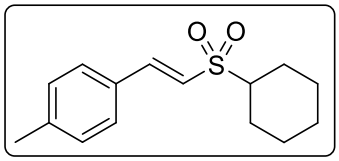
References

1. J. Hu, B. Cheng, X. Yang and T. P. Loh, *Adv. Synth. Catal*., 2019, **361**, 4902

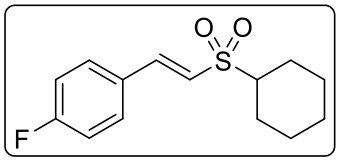
Characterization data for compounds



(*E*)-(2-(cyclohexylsulfonyl)vinyl)benzene (**3aa**): 54.3 mg, yield = 72%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 – 7.49 (m, 3H), 7.48 – 7.38 (m, 3H), 6.78 (d, *J* = 15.5 Hz, 1H), 2.88 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.28 – 2.16 (m, 2H), 1.91 (dt, *J* = 12.5, 3.2 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.50 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.39 – 1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.5, 132.4, 131.2, 129.1, 128.5, 122.7, 62.6, 25.4, 25.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{18}NaO_2S^+$ 273.0920, found 273.0932.

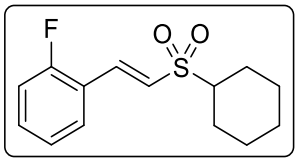


(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-methylbenzene (**3ba**): 58.0 mg, yield = 73%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.52 (d, *J* = 15.5 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 6.71 (d, *J* = 15.5 Hz, 1H), 2.86 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.39 (s, 3H), 2.28 – 2.16 (m, 2H), 1.96 – 1.85 (m, 2H), 1.78 – 1.66 (m, 1H), 1.58 - 1.42 (m, 2H), 1.39 – 1.11 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.5, 141.8, 129.8, 129.6, 128.5, 121.5, 62.6, 25.4, 25.1, 21.5. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{20}NaO_2S^+$ 287.1076, found 287.1083.

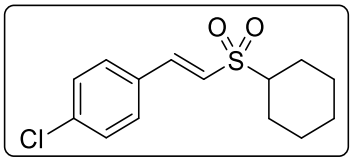


(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-fluorobenzene (**3ca**): 64.1 mg, yield = 80%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 – 7.46 (m, 3H), 7.12 (t, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 15.5 Hz, 1H), 2.87 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.28 – 2.16 (m, 2H), 2.00 – 1.87 (m, 2H), 1.80 – 1.64 (m, 1H), 1.50 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.39 – 1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 164.35 (d, *J* = 251.0 Hz), 144.2, 130.54 (d, *J* = 8.0 Hz), 128.66 (d, *J* = 3.0 Hz), 122.54 (d, *J* = 3.0 Hz), 116.32 (d, *J* = 22.0 Hz), 62.6, 25.4, 25.1. ^{19}F

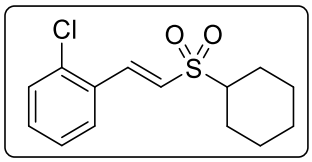
NMR (376 MHz, $CDCl_3$) δ ppm -107.62 – -107.82 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{17}FNaO_2S^+$ 291.0825, found 291.0834.



(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-2-fluorobenzene (**3da**): 48.2 mg, yield = 60%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 (d, *J* = 15.7 Hz, 1H), 7.50 (td, *J* = 7.6, 1.7 Hz, 1H), 7.46 – 7.38 (m, 1H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 7.18 – 7.10 (m, 1H), 6.94 (d, *J* = 15.7 Hz, 1H), 2.88 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.28 – 2.17 (m, 2H), 1.97 – 1.87 (m, 2H), 1.77 – 1.68 (m, 1H), 1.51 (qd, *J* = 12.4, 3.1 Hz, 2H), 1.39 – 1.12 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 161.51 (d, *J* = 254.0 Hz), 138.61 (d, *J* = 2.0 Hz), 132.72 (d, *J* = 9.0 Hz), 130.46 (d, *J* = 3.0 Hz), 125.96 (d, *J* = 9.0 Hz), 124.69 (d, *J* = 4.0 Hz), 120.61 (d, *J* = 11.0 Hz), 116.41 (d, *J* = 21.0 Hz), 62.5, 25.4, 25.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -112.28 – -112.45 (m). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{17}FNaO_2S^+$ 291.0825, found 291.0836.

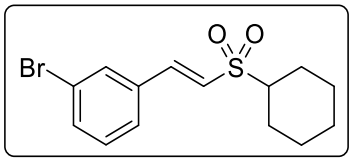


(*E*)-1-chloro-4-(2-(cyclohexylsulfonyl)vinyl)benzene (**3ea**): 52.4 mg, yield = 61%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51 (d, *J* = 15.6 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 15.5 Hz, 1H), 2.88 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.26 – 2.16 (m, 2H), 1.98 – 1.88 (m, 2H), 1.76 – 1.68 (m, 1H), 1.50 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.37 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.0, 137.3, 130.9, 129.7, 129.4, 123.5, 62.6, 25.4, 25.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{17}ClNaO_2S^+$ 307.0530, found 307.0545.

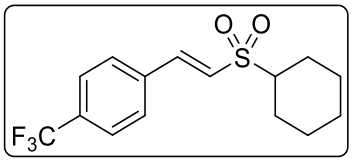


(*E*)-1-chloro-2-(2-(cyclohexylsulfonyl)vinyl)benzene (**3fa**): 48.2 mg, yield = 56%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.95 (d, *J* = 15.6 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.8

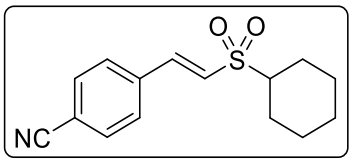
Hz, 1H), 7.46 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.37 (td, *J* = 7.6, 1.8 Hz, 1H), 7.32 (td, *J* = 7.5, 1.4 Hz, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 2.89 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.28 – 2.18 (m, 2H), 1.98 – 1.87 (m, 2H), 1.77 – 1.68 (m, 1H), 1.52 (qd, *J* = 12.5, 3.5 Hz, 2H), 1.38 – 1.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 141.7, 135.2, 131.9, 130.9, 130.4, 128.4, 127.2, 125.9, 62.6, 25.4, 25.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{17}ClNaO_2S^+$ 307.0530, found 307.0542.



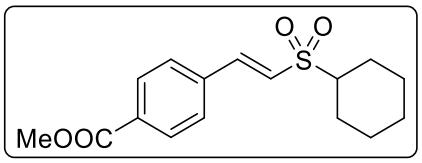
(*E*)-1-bromo-3-(2-(cyclohexylsulfonyl)vinyl)benzene (**3ga**): 46.7 mg, yield = 47%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (t, *J* = 1.8 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.49 (d, *J* = 15.5 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 6.79 (d, *J* = 15.5 Hz, 1H), 2.88 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.26 - 2.16 (m, 2H), 1.97 – 1.87 (m, 2H), 1.73 (m, 1H), 1.50 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.38 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.8, 134.4, 134.0, 131.0, 130.6, 127.2, 124.5, 123.2, 62.6, 25.4, 25.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{14}H_{17}Br^{79}NaO_2S^+$ 351.0025, found 351.0030, calcd for $C_{14}H_{17}Br^{81}NaO_2S^+$ 353.0004, found 353.0012.



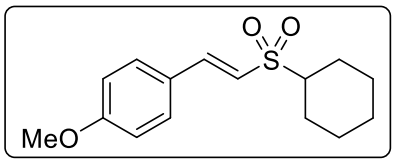
(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (**3ha**): 81.0 mg, yield = 85%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.79 – 7.52 (m, 5H), 6.89 (d, *J* = 15.5 Hz, 1H), 2.91 (t, *J* = 12.0 Hz, 1H), 2.33 – 2.13 (m, 2H), 2.01 – 1.86 (m, 2H), 1.81 – 1.69 (m, 1H), 1.51 (q, *J* = 11.5 Hz, 2H), 1.40 – 1.06 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.5, 135.7, 132.56 (q, *J* = 32.7 Hz), 128.7, 126.0 (q, *J* = 4.0 Hz), 125.7, 123.53 (q, *J* = 270.7 Hz), 62.5, 25.3, 25.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -63.01. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{15}H_{17}F_3NaO_2S^+$ 341.0794, found 341.0803.



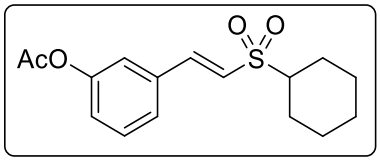
(*E*)-4-(2-(cyclohexylsulfonyl)vinyl)benzonitrile (**3ia**): 30.8 mg, yield = 37%, light yellow sliod. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.73 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 15.6 Hz, 1H), 6.90 (d, *J* = 15.5 Hz, 1H), 2.91 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.26 – 2.16 (m, 2H), 1.98 – 1.88 (m, 2H), 1.78 – 1.70 (m, 1H), 1.51 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 143.0, 136.6, 132.8, 128.9, 126.7, 118.0, 114.4, 62.5, 25.3, 25.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{15}H_{17}NNaO_2S^+$ 298.0872, found 298.0886.



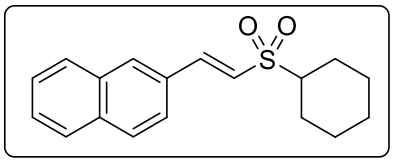
methyl (*E*)-4-(2-(cyclohexylsulfonyl)vinyl)benzoate (**3ja**): 37.9 mg, yield = 41%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09 (d, *J* = 8.0 Hz, 2H), 7.67 – 7.53 (m, 3H), 6.89 (d, *J* = 15.6 Hz, 1H), 3.94 (s, 3H), 2.90 (tt, *J* = 12.2, 3.5 Hz, 1H), 2.28 – 2.16 (m, 2H), 1.98 – 1.88 (m, 2H), 1.78 – 1.68 (m, 1H), 1.51 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.38 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.1, 144.0, 136.4, 132.2, 130.2, 128.3, 125.4, 62.5, 52.3, 25.3, 25.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{16}H_{20}NaO_4S^+$ 331.0975, found 331.0986.



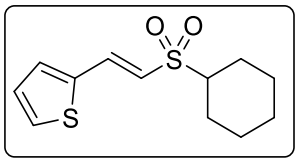
(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-methoxybenzene (**3ka**): 54.9 mg, yield = 65%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66 – 7.34 (m, 3H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 15.5 Hz, 1H), 3.85 (s, 3H), 2.85 (tt, *J* = 12.3, 3.5 Hz, 1H), 2.32 – 2.12 (m, 2H), 2.00 – 1.84 (m, 2H), 1.77 – 1.65 (m, 1H), 1.49 (q, *J* = 12.2 Hz, 2H), 1.38 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 162.0, 145.1, 130.2, 125.0, 119.8, 114.4, 62.6, 55.4, 25.4, 25.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{15}H_{20}NaO_3S^+$ 303.1025, found 303.1042.



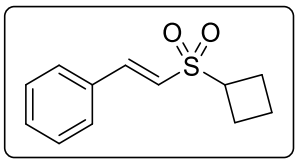
(*E*)-4-(2-(cyclohexylsulfonyl)vinyl)phenyl acetate (**3la**): 64.7 mg, yield = 70%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53 (d, *J* = 15.5 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 6.78 (d, *J* = 15.5 Hz, 1H), 2.87 (tt, *J* = 12.3, 3.4 Hz, 1H), 2.33 (s, 3H), 2.25 – 2.15 (m, 2H), 1.96 – 1.86 (m, 2H), 1.77 – 1.67 (m, 1H), 1.49 (q, *J* = 11.7, 11.2 Hz, 2H), 1.37 – 1.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.1, 151.0, 144.3, 133.8, 130.0, 126.1, 124.3, 124.0, 121.2, 62.5, 25.3, 25.0, 21.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{16}H_{20}Na_O4S^+$ 331.0975, found 331.0988.



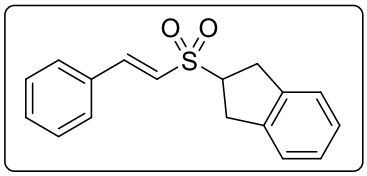
(*E*)-2-(2-(cyclohexylsulfonyl)vinyl)naphthalene (**3ma**): 68.3 mg, yield = 76%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.02 – 7.79 (m, 4H), 7.71 (d, *J* = 15.5 Hz, 1H), 7.65 – 7.46 (m, 3H), 6.88 (d, *J* = 15.5 Hz, 1H), 2.91 (t, *J* = 12.0 Hz, 1H), 2.34 – 2.17 (m, 2H), 2.02 – 1.84 (m, 2H), 1.78 – 1.67 (m, 1H), 1.53 (q, *J* = 11.7 Hz, 2H), 1.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.6, 134.5, 133.1, 130.8, 129.8, 128.9, 128.6, 127.8, 127.0, 123.3, 122.8, 62.6, 25.4, 25.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{18}H_{20}NaO_2S^+$ 323.1076, found 323.1086.



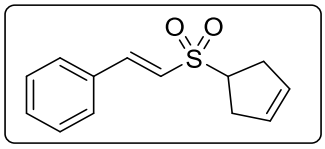
(*E*)-2-(2-(cyclohexylsulfonyl)vinyl)thiophene (**3na**): 32.3 mg, yield = 42%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66 (d, *J* = 15.2 Hz, 1H), 7.47 (d, *J* = 5.1 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.09 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.55 (d, *J* = 15.2 Hz, 1H), 2.86 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.28 – 2.15 (m, 2H), 1.92 (dt, *J* = 12.7, 3.1 Hz, 2H), 1.76 – 1.69 (m, 1H), 1.49 (qd, *J* = 12.5, 3.4 Hz, 2H), 1.36 – 1.13 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 138.0, 137.0, 132.4, 129.9, 128.4, 120.9, 62.8, 25.5, 25.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{12}H_{16}NaO_2S_2^+$ 279.0484, found 279.0494.



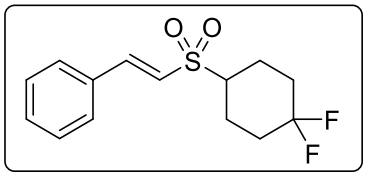
(*E*)-(2-(cyclobutylsulfonyl)vinyl)benzene (**3ab**): 24.2 mg, yield = 36%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.48 – 7.38 (m, 3H), 6.76 (d, *J* = 15.5 Hz, 1H), 3.79 (quint, *J* = 8.0 Hz, 1H), 2.65 – 2.51 (m, 2H), 2.38 – 2.26 (m, 2H), 2.11 – 2.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.1, 132.4, 131.3, 129.1, 128.5, 123.0, 55.7, 22.5, 17.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{12}H_{14}NaO_2S^+$ 245.0607, found 245.0619.



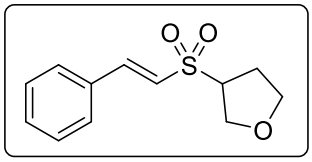
(*E*)-2-(styrylsulfonyl)-2,3-dihydro-1H-indene (**3ac**): 57.8 mg, yield = 68%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61 (d, *J* = 15.5 Hz, 1H), 7.48 – 7.34 (m, 5H), 7.24 – 7.13 (m, 4H), 6.67 (d, *J* = 15.5 Hz, 1H), 3.97 (quint, *J* = 7.1 Hz, 1H), 3.51 (dd, *J* = 16.9, 6.6 Hz, 2H), 3.38 (dd, *J* = 17.0, 8.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.5, 139.7, 132.3, 131.3, 129.0, 128.5, 127.2, 124.5, 122.7, 62.6, 33.8. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{17}H_{16}NaO_2S^+$ 307.0763, found 307.0772.



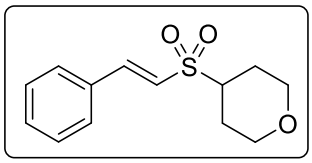
(*E*)-(2-(cyclopent-3-en-1-ylsulfonyl)vinyl)benzene (**3ad**): 30.5 mg, yield = 43%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.39 (m, 5H), 6.76 (d, *J* = 15.5 Hz, 1H), 5.70 (s, 2H), 3.88 – 3.72 (m, 1H), 3.01 – 2.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.2, 132.4, 131.3, 129.1, 128.51, 128.47, 122.6, 60.9, 34.0. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{13}H_{14}NaO_2S^+$ 257.0607, found 257.0621.



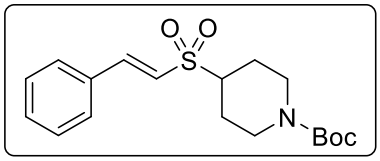
(*E*)-(2-((4,4-difluorocyclohexyl)sulfonyl)vinyl)benzene (**3ae**): 36.4 mg, yield = 42%, light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.70 – 7.39 (m, 6H), 6.77 (d, J = 15.5 Hz, 1H), 2.95 (t, J = 11.2 Hz, 1H), 2.40 – 2.20 (m, 4H), 2.02 – 1.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.6, 132.0, 131.6, 129.2, 128.6, 122.0, 59.9, 32.23 (t, J = 25.0 Hz), 22.3, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -94.22 (d, J = 240.3 Hz), -101.84 (dt, J = 240.4, 30.7 Hz). HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{14}H_{16}F_2NaO_2S^+$ 309.0731, found 309.0745.



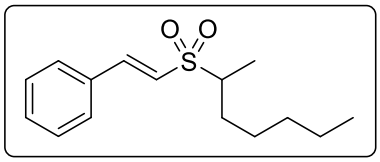
(*E*)-3-(styrylsulfonyl)tetrahydrofuran (**3af**): 56.0 mg, yield = 78%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.63 (d, J = 15.4 Hz, 1H), 7.57 – 7.38 (m, 5H), 6.80 (d, J = 15.5 Hz, 1H), 4.32 – 4.20 (m, 1H), 4.10 – 3.91 (m, 2H), 3.89 – 3.70 (m, 2H), 2.46 – 2.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.9, 132.1, 131.5, 129.2, 128.6, 122.8, 68.3, 67.6, 62.9, 27.5. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{12}H_{14}NaO_3S^+$ 261.0556, found 261.0566.



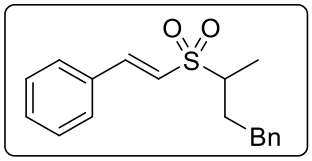
(*E*)-4-(styrylsulfonyl)tetrahydro-2*H*-pyran (**3ag**): 61.2 mg, yield = 81%, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59 (d, J = 15.5 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.49 – 7.40 (m, 3H), 6.78 (d, J = 15.5 Hz, 1H), 4.10 (dd, J = 11.3, 4.0 Hz, 2H), 3.39 (td, J = 11.9, 2.1 Hz, 2H), 3.13 (tt, J = 12.1, 3.9 Hz, 1H), 2.09 – 2.01 (m, 2H), 1.88 (qd, J = 12.5, 4.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 146.5, 132.0, 131.4, 129.1, 128.5, 121.9, 66.4, 59.5, 25.4. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{13}H_{16}NaO_3S^+$ 275.0712, found 275.0723.



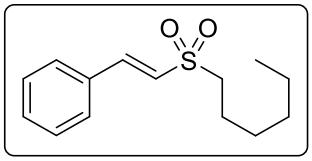
tert-butyl (*E*)-4-(styrylsulfonyl)piperidine-1-carboxylate (**3ah**): 86.2 mg, yield = 82%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.49 – 7.40 (m, 3H), 6.78 (d, *J* = 15.5 Hz, 1H), 4.28 (br, 2H), 3.03 (tq, *J* = 10.4, 3.4 Hz, 1H), 2.73 (t, *J* = 13.5 Hz, 2H), 2.19 – 2.08 (m, 2H), 1.70 (qd, *J* = 12.5, 4.6 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 154.2, 146.4, 132.0, 131.4, 129.1, 128.5, 122.0, 80.0, 60.6, 42.5, 28.2, 24.8. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{18}H_{25}NNaO_4S^+$ 374.1397, found 374.1410.



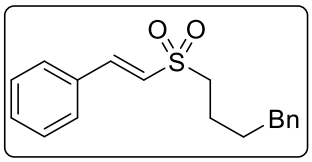
(*E*)-(2-(heptan-2-ylsulfonyl)vinyl)benzene (**3ai**): 61.9 mg, yield = 77%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* = 15.6 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.48 – 7.39 (m, 3H), 6.78 (d, *J* = 15.6 Hz, 1H), 3.03 – 2.90 (m, 1H), 2.11 – 1.99 (m, 1H), 1.56 – 1.44 (m, 2H), 1.42 – 1.24 (m, 8H), 0.93 – 0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.6, 132.4, 131.2, 129.1, 128.5, 122.7, 59.3, 31.4, 29.1, 26.3, 22.3, 13.9, 13.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{15}H_{22}NaO_2S^+$ 289.1233, found 289.1257.



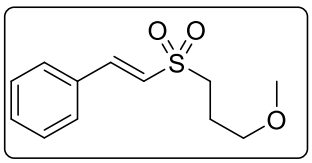
(*E*)-(2-((4-phenylbutan-2-yl)sulfonyl)vinyl)benzene (**3aj**): 46.1 mg, yield = 51%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.57 (d, *J* = 15.5 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.47 – 7.38 (m, 3H), 7.33 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 6.72 (dd, *J* = 15.7, 2.3 Hz, 1H), 3.03 – 2.84 (m, 2H), 2.73 – 2.61 (m, 1H), 2.50 – 2.36 (m, 1H), 1.91 – 1.75 (m, 1H), 1.43 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 145.8, 140.2, 132.3, 131.3, 129.1, 128.6, 128.5, 128.4, 126.4, 122.5, 58.3, 32.6, 30.8, 13.2. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{18}H_{20}NaO_2S^+$ 323.1076, found 323.1084.



(*E*)-(2-(hexylsulfonyl)vinyl)benzene (**3ak**): 23.7 mg, yield = 31%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.48 – 7.40 (m, 3H), 6.82 (d, *J* = 15.5 Hz, 1H), 3.10 – 3.02 (m, 2H), 1.89 – 1.77 (m, 2H), 1.43 (quint, *J* = 7.5 Hz, 2H), 1.36 – 1.27 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.7, 132.3, 131.3, 129.1, 128.5, 124.7, 55.2, 31.2, 28.0, 22.5, 22.3, 13.9. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{14}H_{20}NaO_2S^+$ 275.1076, found 275.1084.



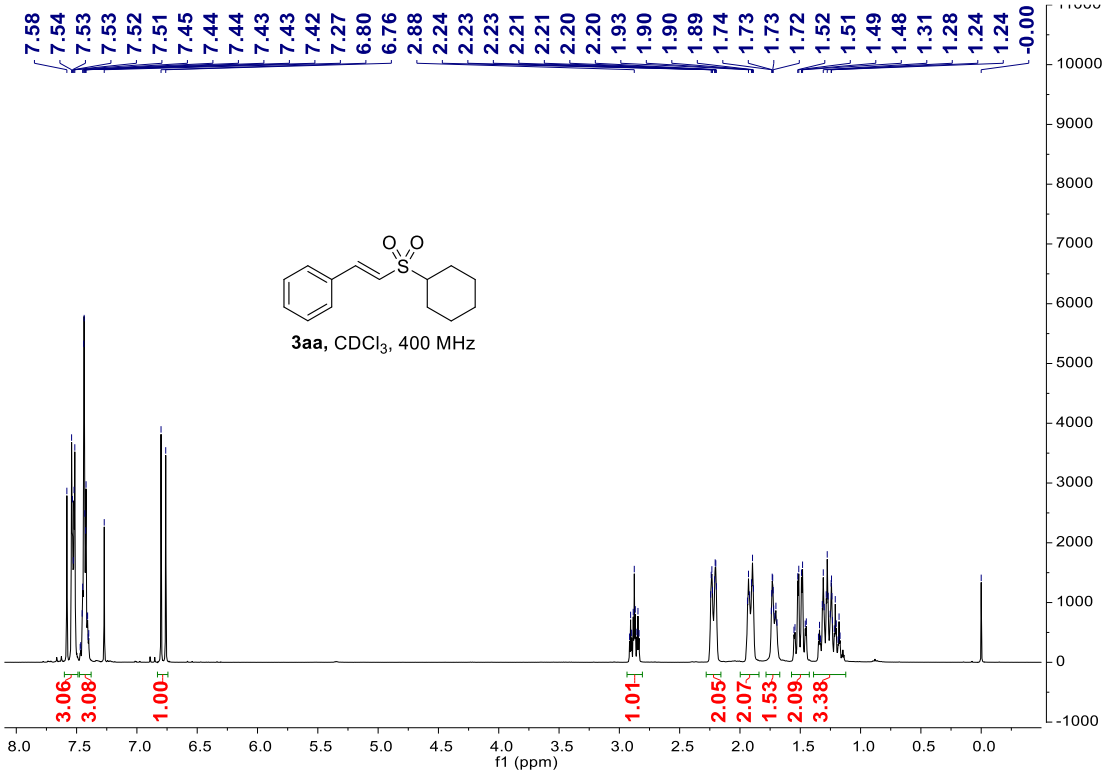
(*E*)-(2-((4-phenylbutyl)sulfonyl)vinyl)benzene (**3al**): 25.1 mg, yield = 28%, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.58 (d, *J* = 15.5 Hz, 1H), 7.53 – 7.39 (m, 5H), 7.29 – 7.22 (m, 2H), 7.21 – 7.10 (m, 3H), 6.79 (d, *J* = 15.5 Hz, 1H), 3.11 – 3.02 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.93 – 1.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.9, 141.2, 132.2, 131.4, 129.1, 128.6, 128.5, 128.3, 126.1, 124.7, 55.0, 35.3, 30.1, 22.2. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{18}H_20NaO_2S^+$ 323.1076, found 323.1087.

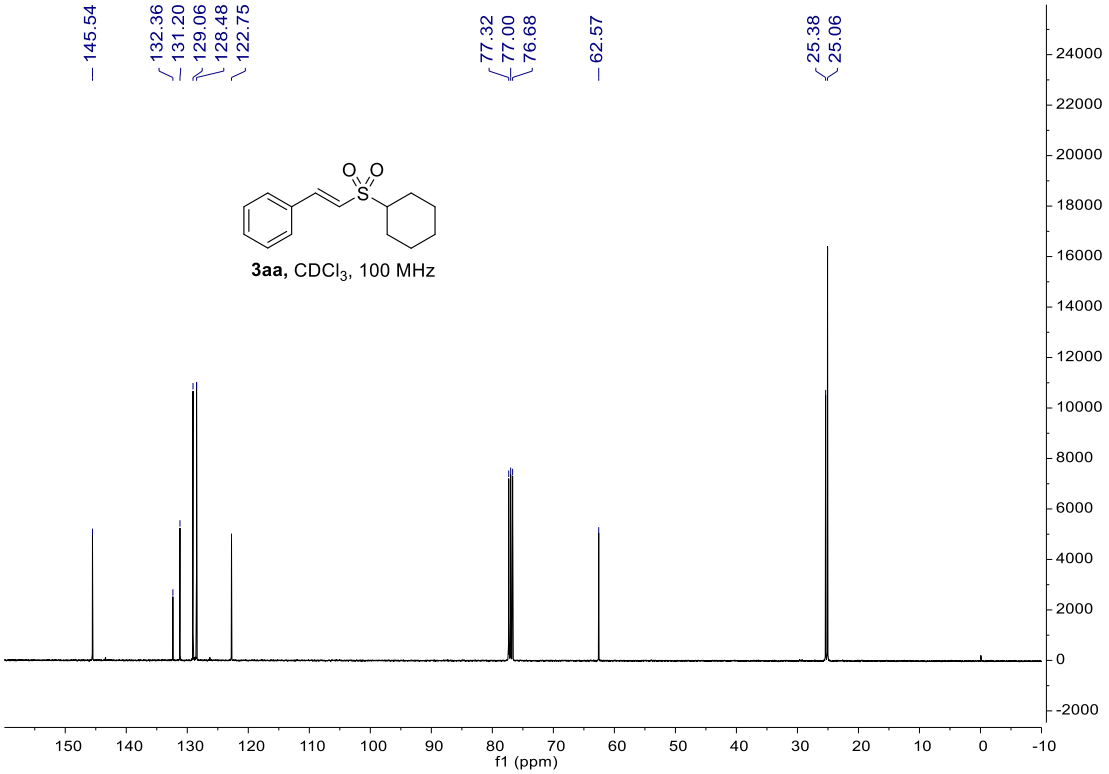


(*E*)-(2-((3-methoxypropyl)sulfonyl)vinyl)benzene (**3am**): 26.9 mg, yield = 37%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.48 – 7.39 (m, 3H), 6.83 (d, *J* = 15.5 Hz, 1H), 3.49 (t, *J* = 5.9 Hz, 2H), 3.33 (s, 3H), 3.22 – 3.14 (m, 2H), 2.16 – 2.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 144.9, 132.2, 131.4, 129.1, 128.5, 124.7, 70.1, 58.6, 52.3, 23.1. HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for : $C_{12}H_{16}NaO_3S^+$ 263.0712, found 263.0724.

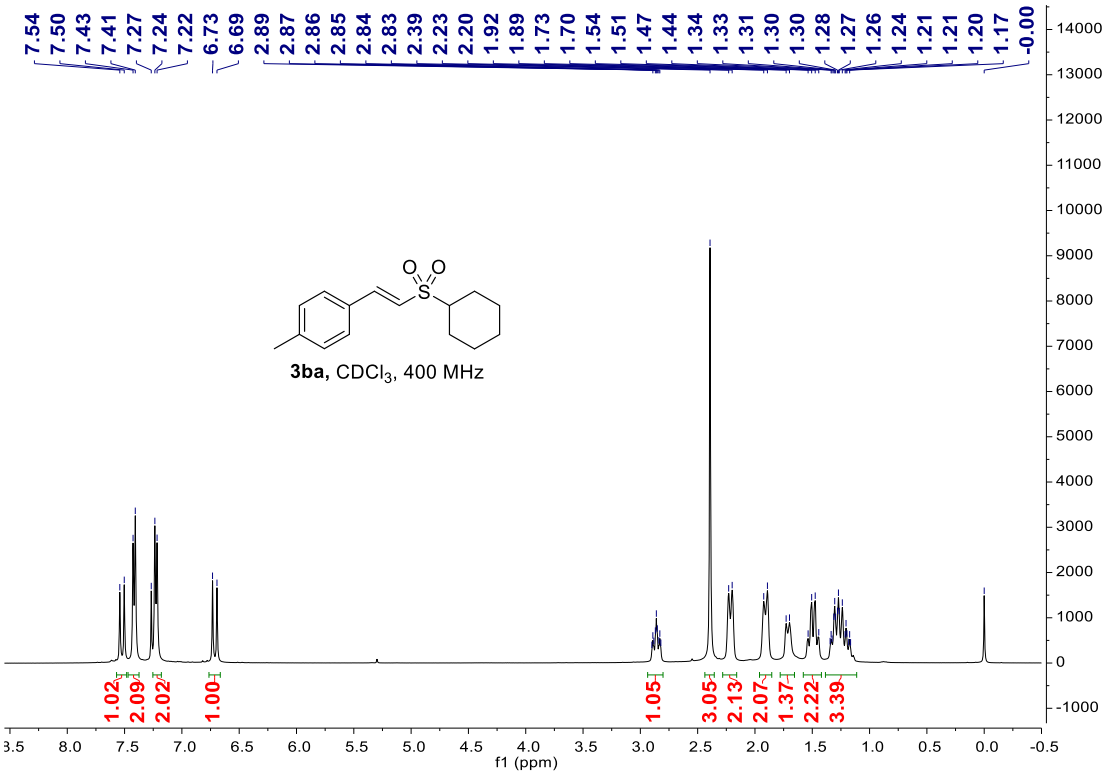
^{1}H, ^{19}F and ^{13}C NMR spectra of products

(*E*)-(2-(cyclohexylsulfonyl)vinyl)benzene (**3aa**)

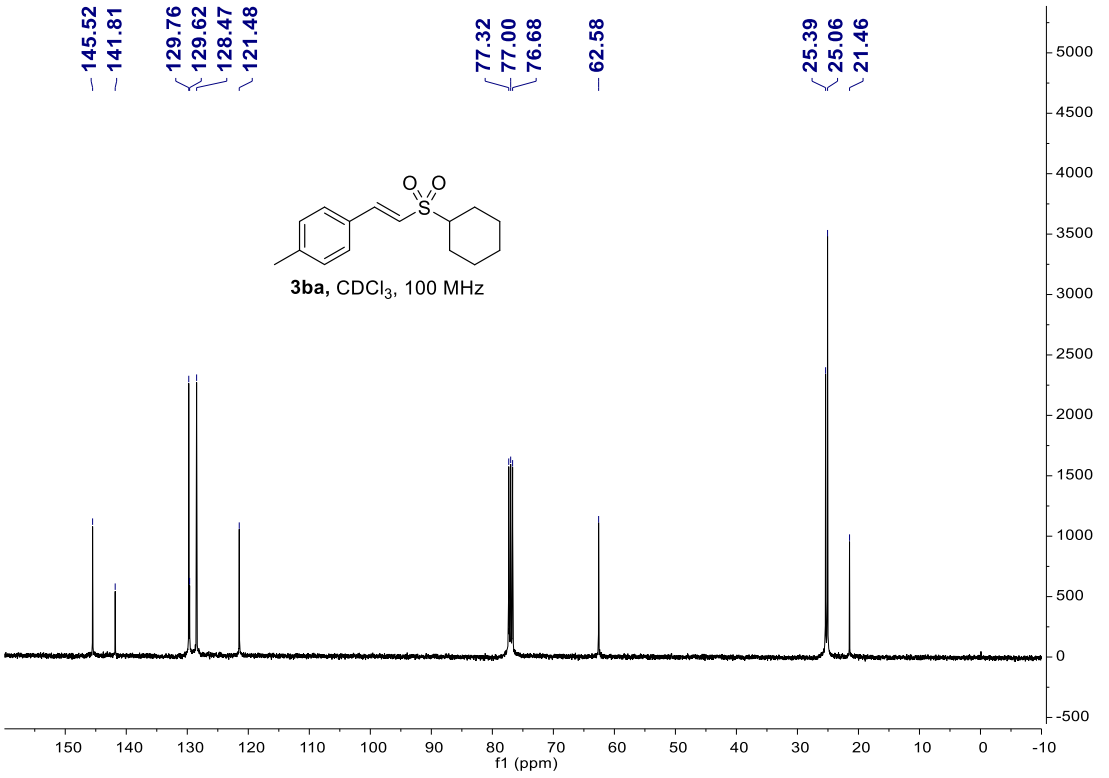




(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-methylbenzene (**3ba**)

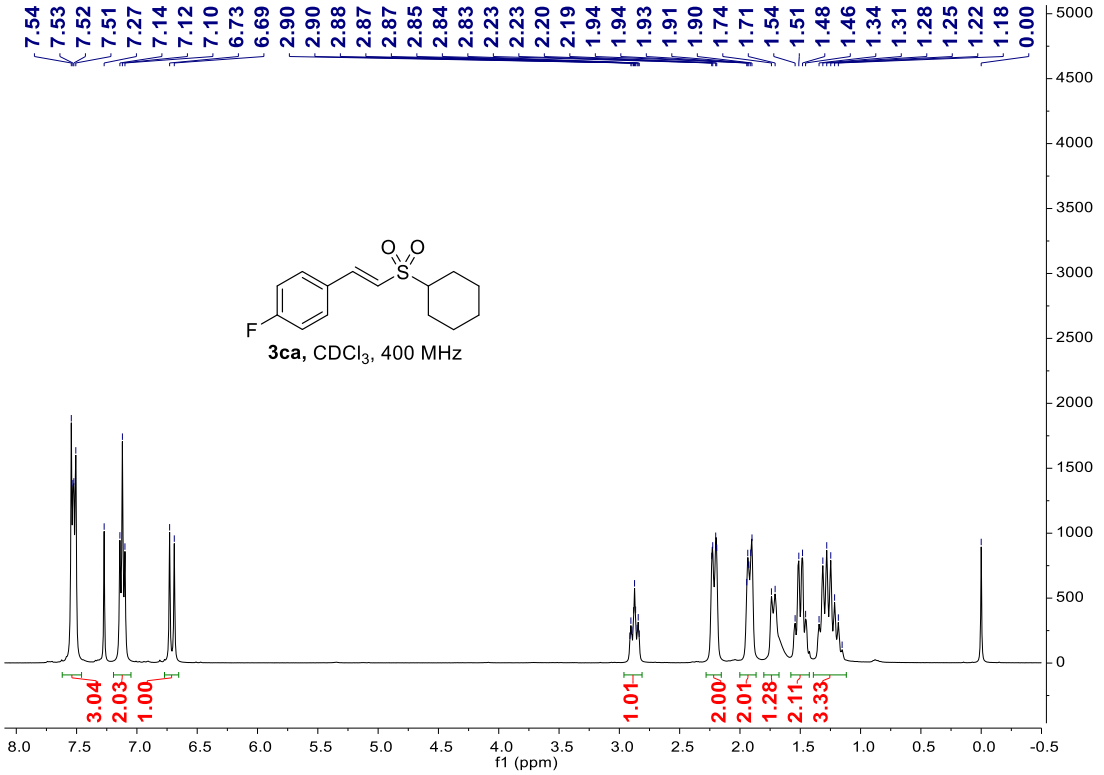


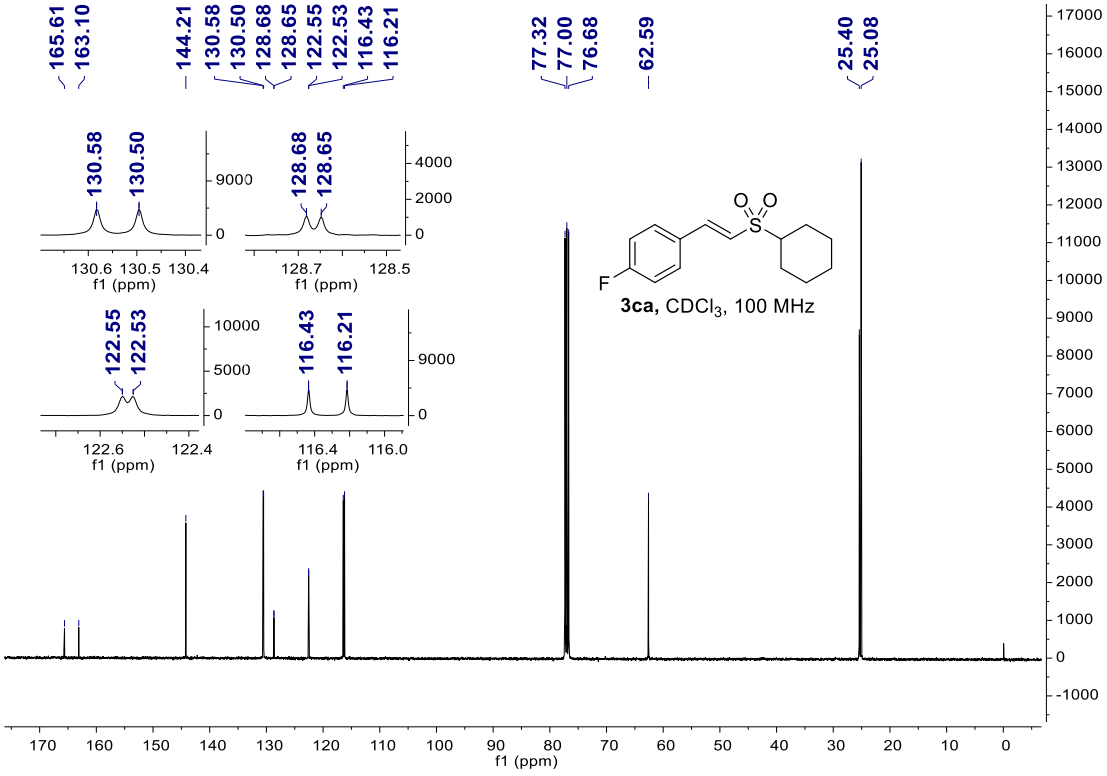
3ba, $CDCl_3$, 400 MHz

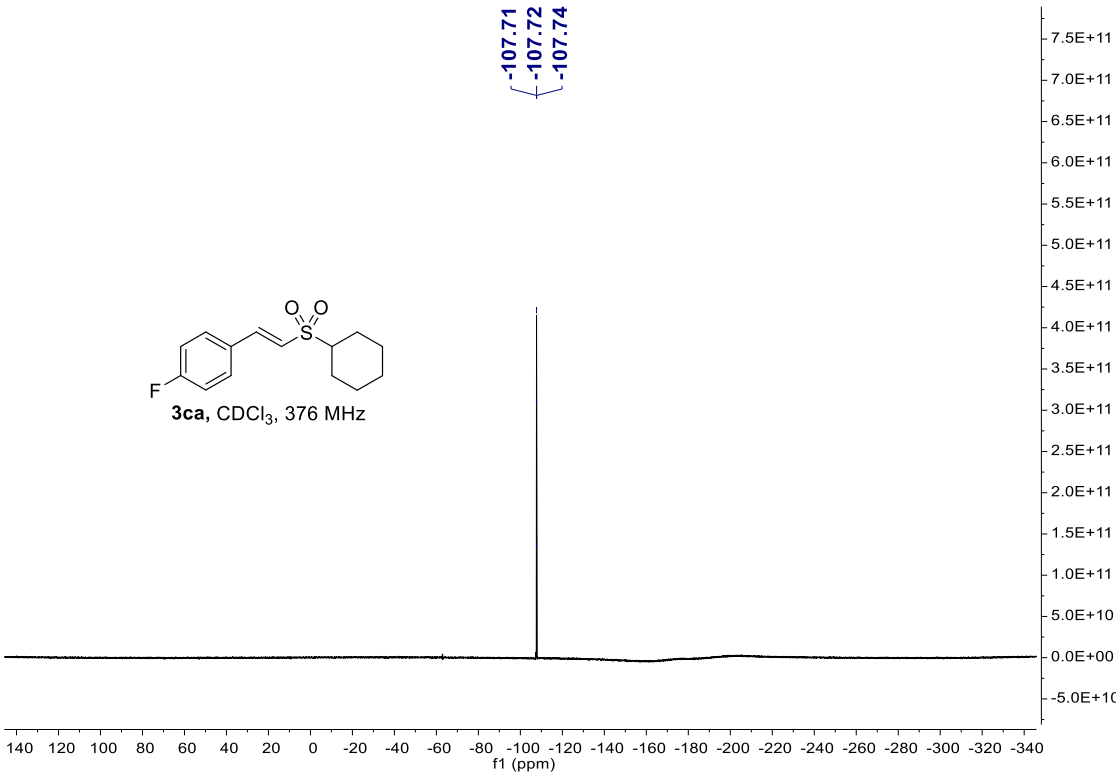


3ba, $CDCl_3$, 100 MHz

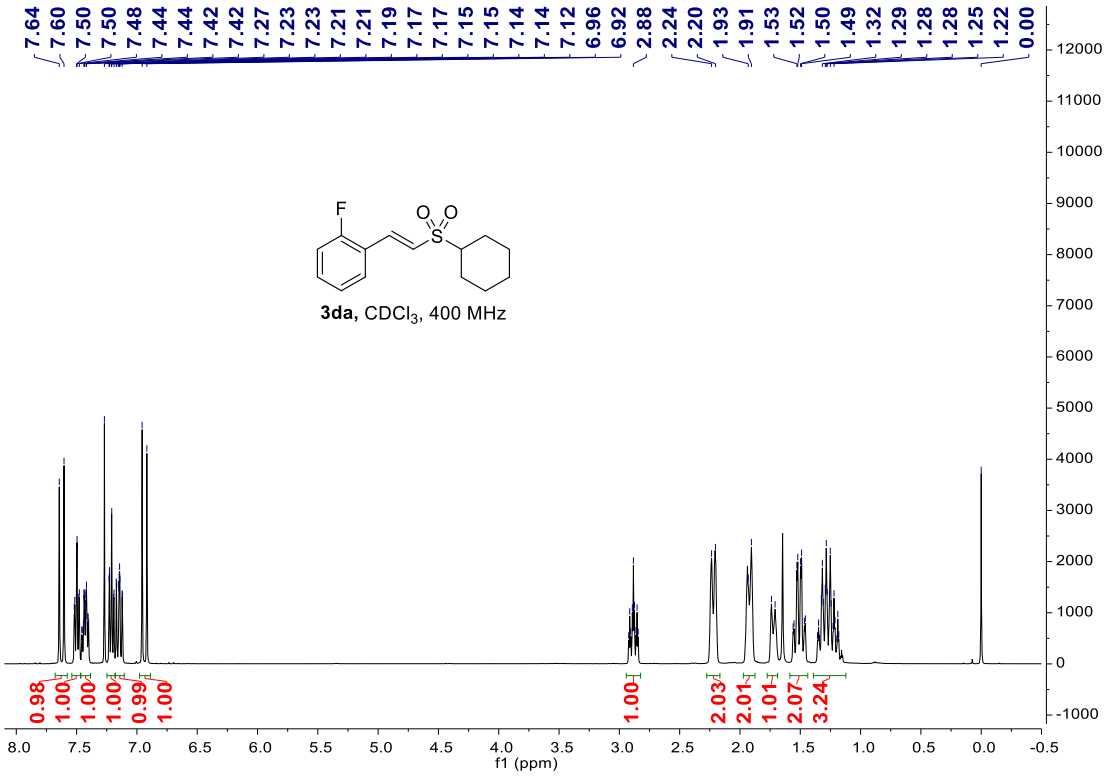
(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-fluorobenzene (**3ca**)

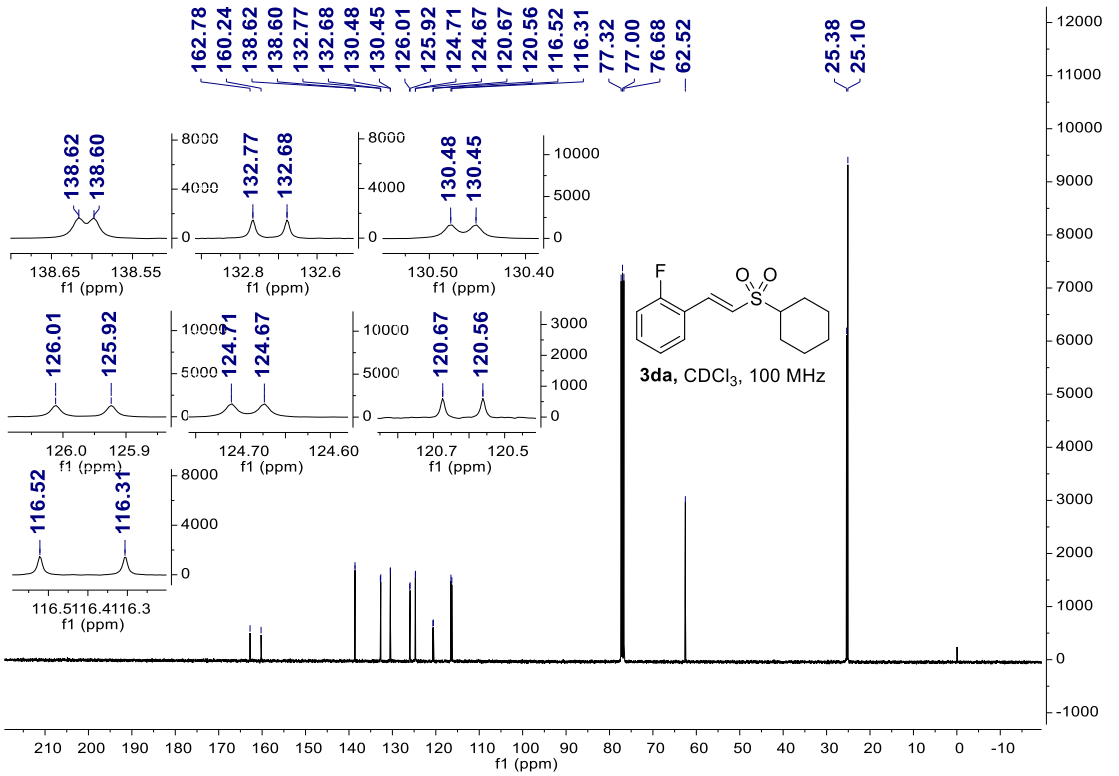


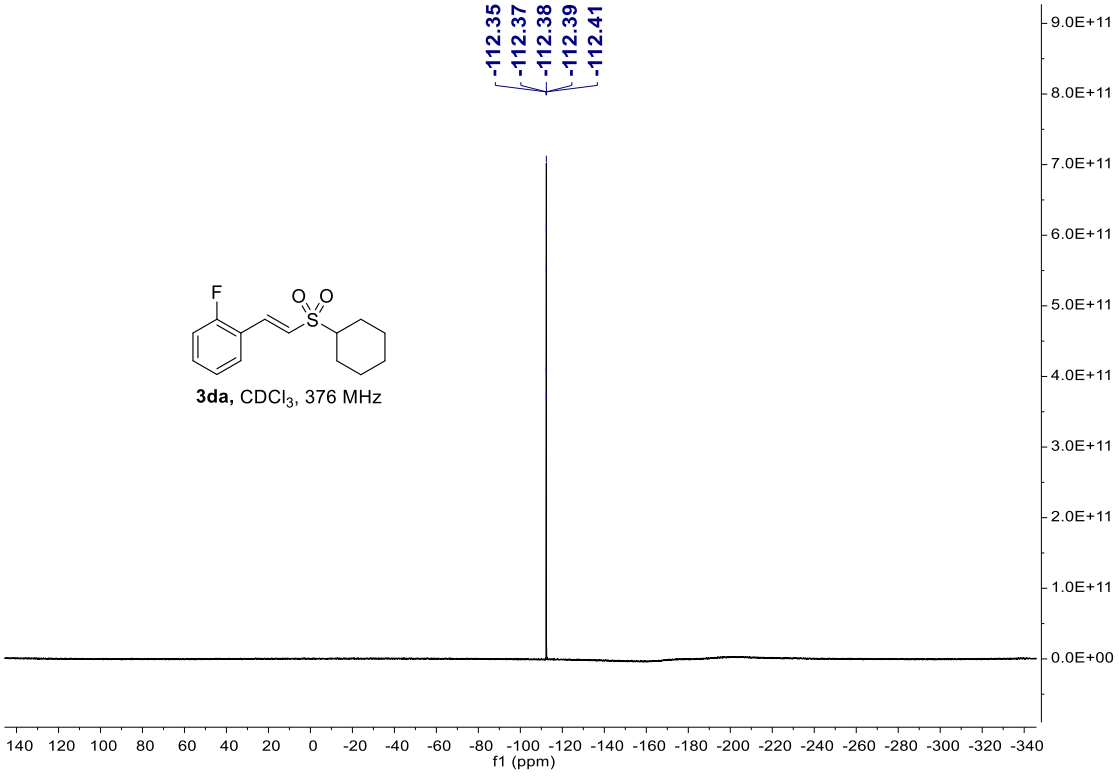




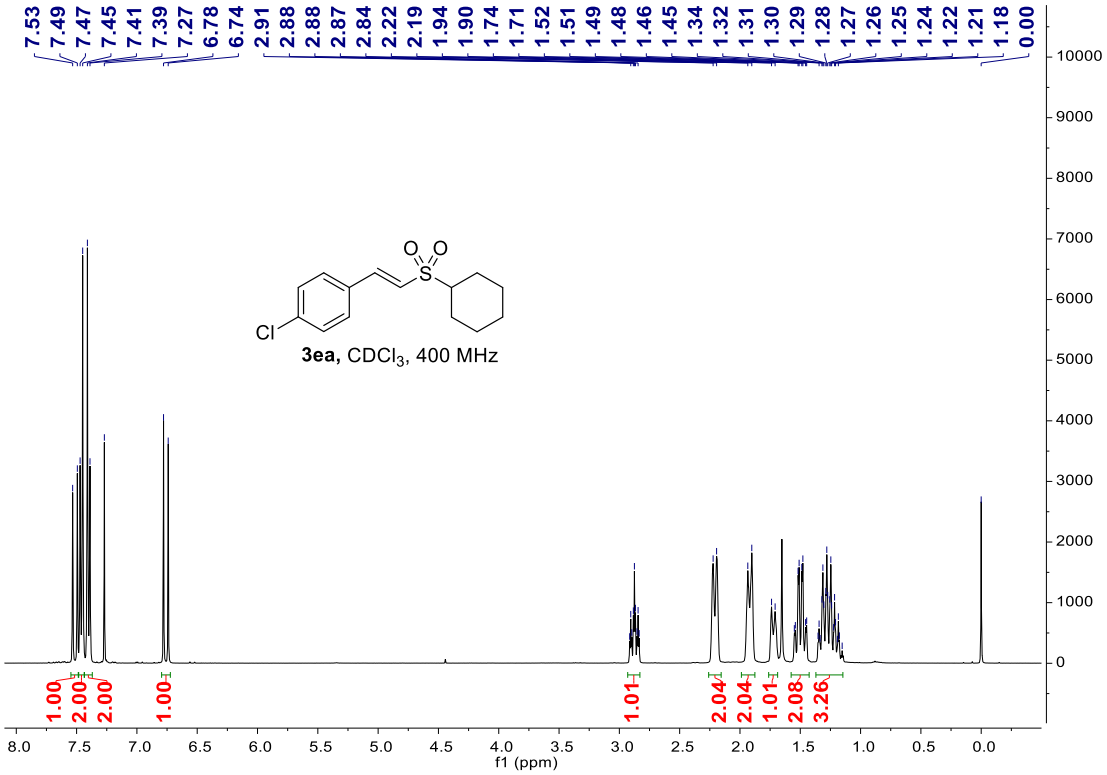
(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-2-fluorobenzene (**3da**)

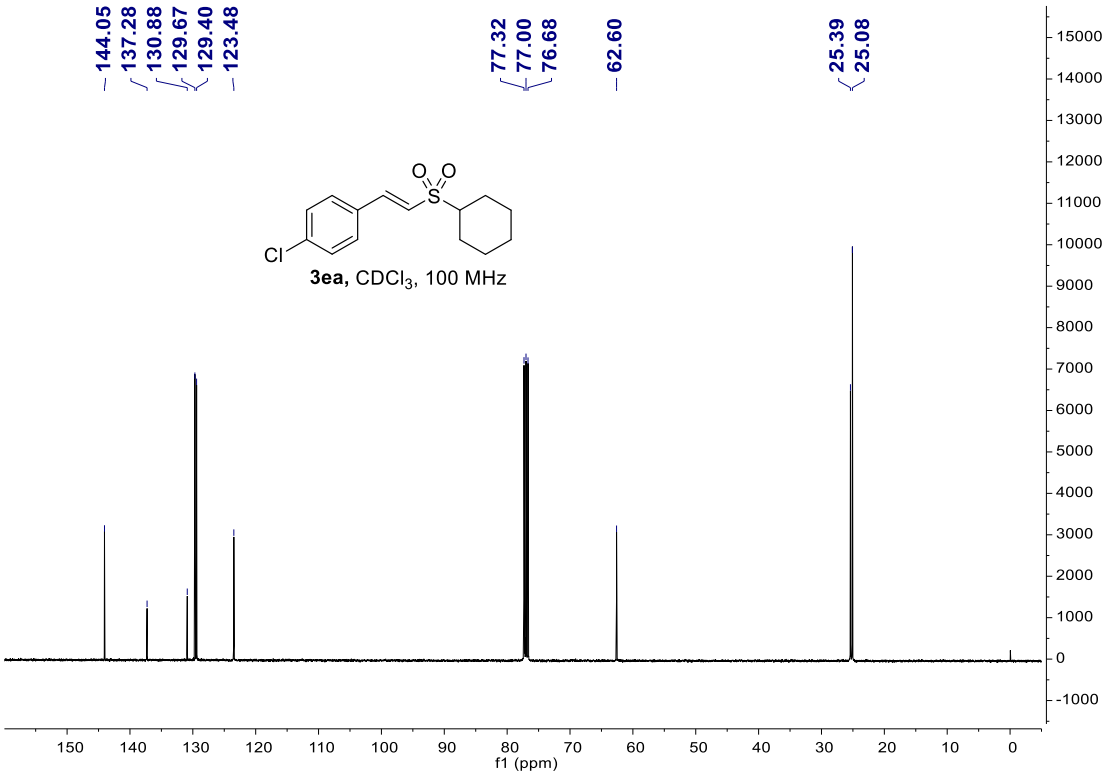



162.78
160.24
138.62
138.60
132.77
132.68
130.48
130.45
126.01
125.92
124.71
124.67
120.67
120.56
116.52
116.31
77.32
77.00
76.68
62.52
25.38
25.10
138.62
138.60
132.77
132.68
130.48
130.45
126.01
125.92
124.71
124.67
120.67
120.56
116.52
116.31
f1 (ppm)
F
O
O
S
3da, CDCl3, 100 MHz

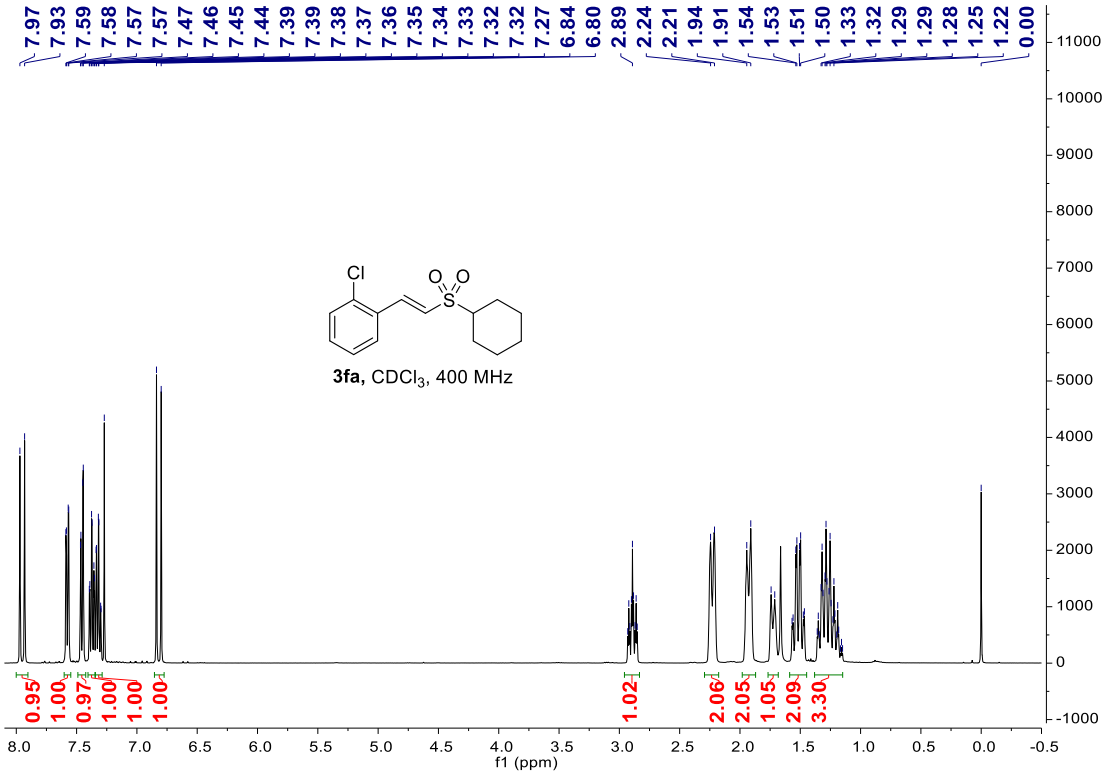

-112.35
-112.37
-112.38
-112.39
-112.41
f1 (ppm)
F
O
O
S
3da, CDCl3, 376 MHz

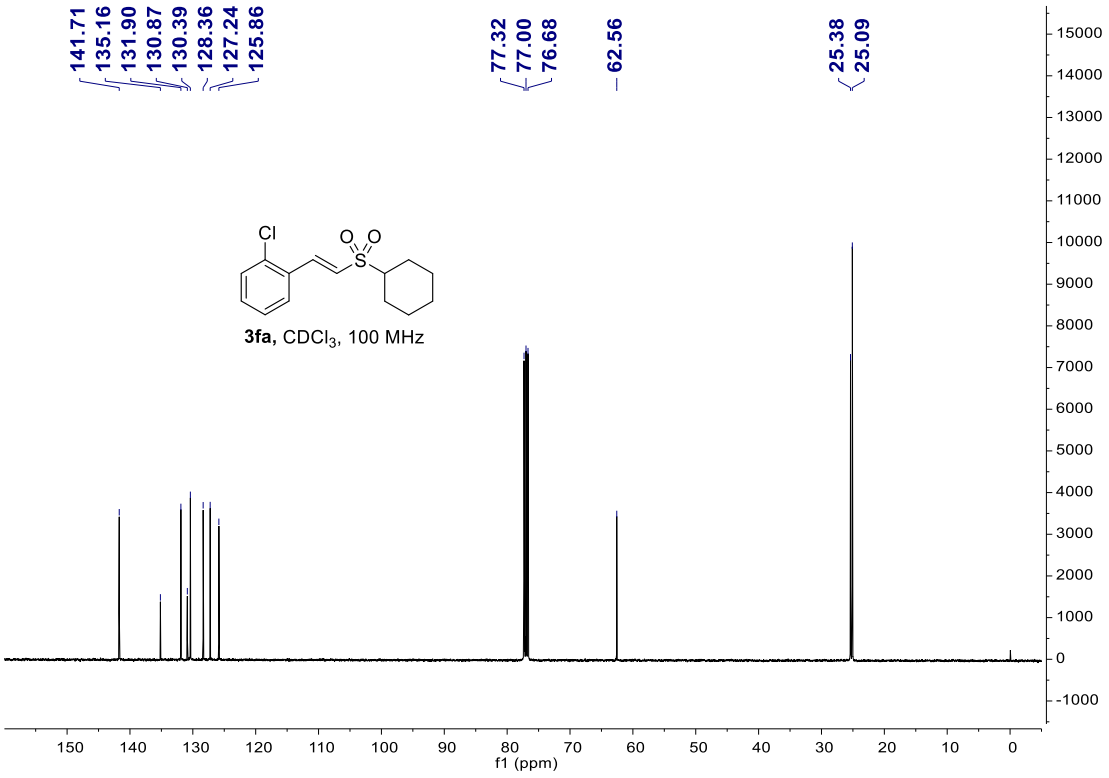
(*E*)-1-chloro-4-(2-(cyclohexylsulfonyl)vinyl)benzene (**3ea**)



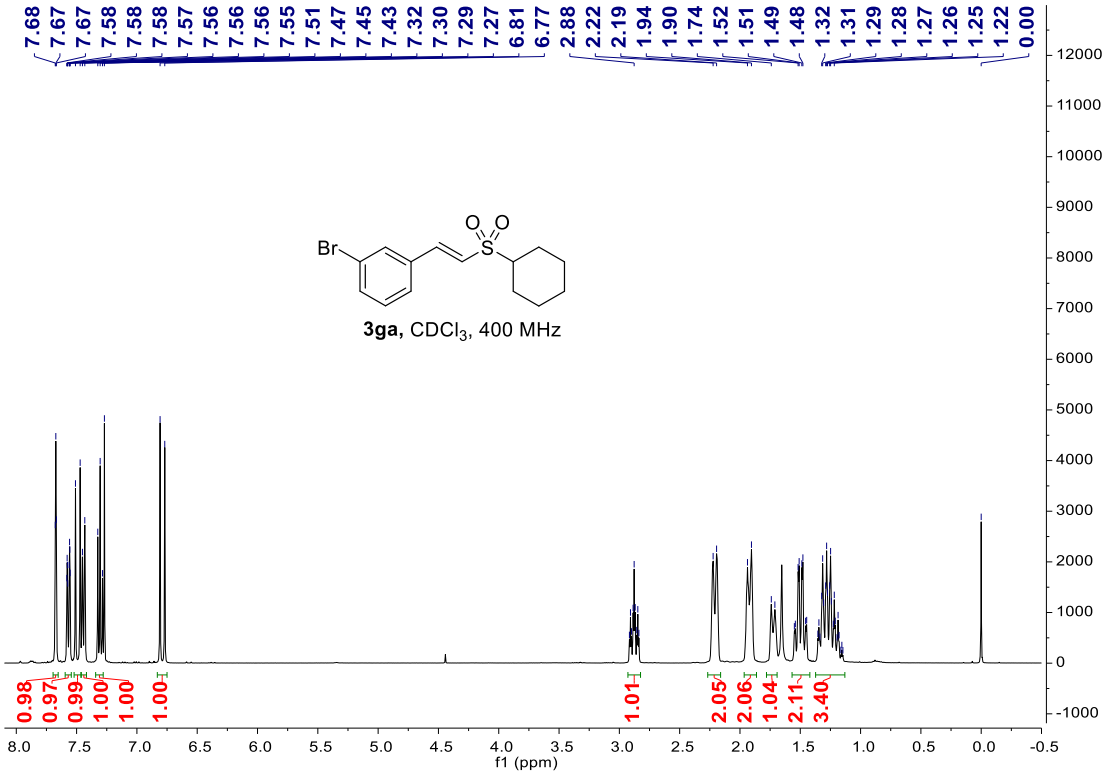


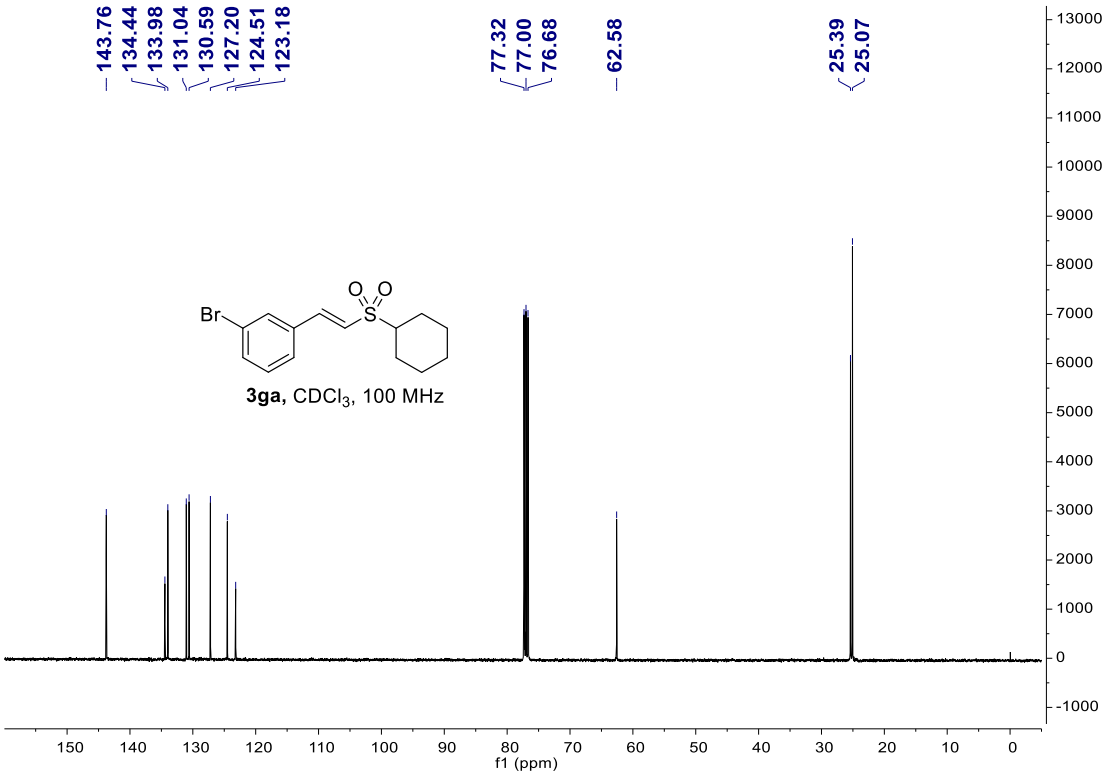
(*E*)-1-chloro-2-(2-(cyclohexylsulfonyl)vinyl)benzene (**3fa**)



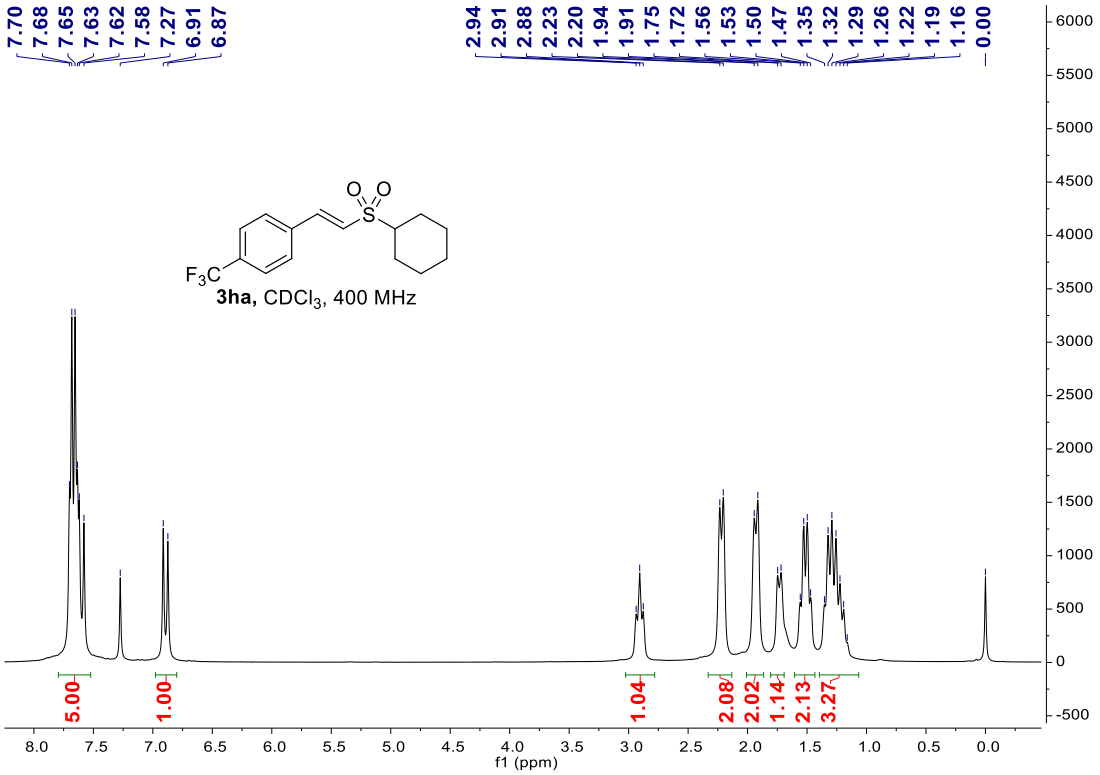


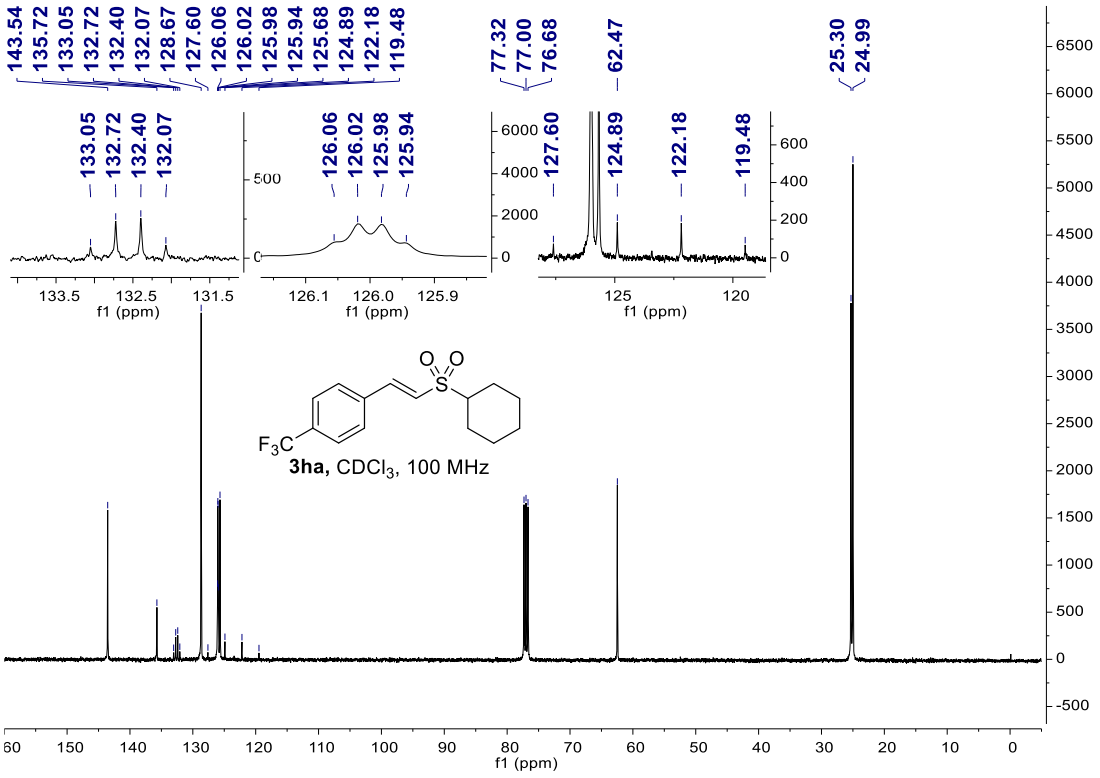
(*E*)-1-bromo-3-(2-(cyclohexylsulfonyl)vinyl)benzene (**3ga**)

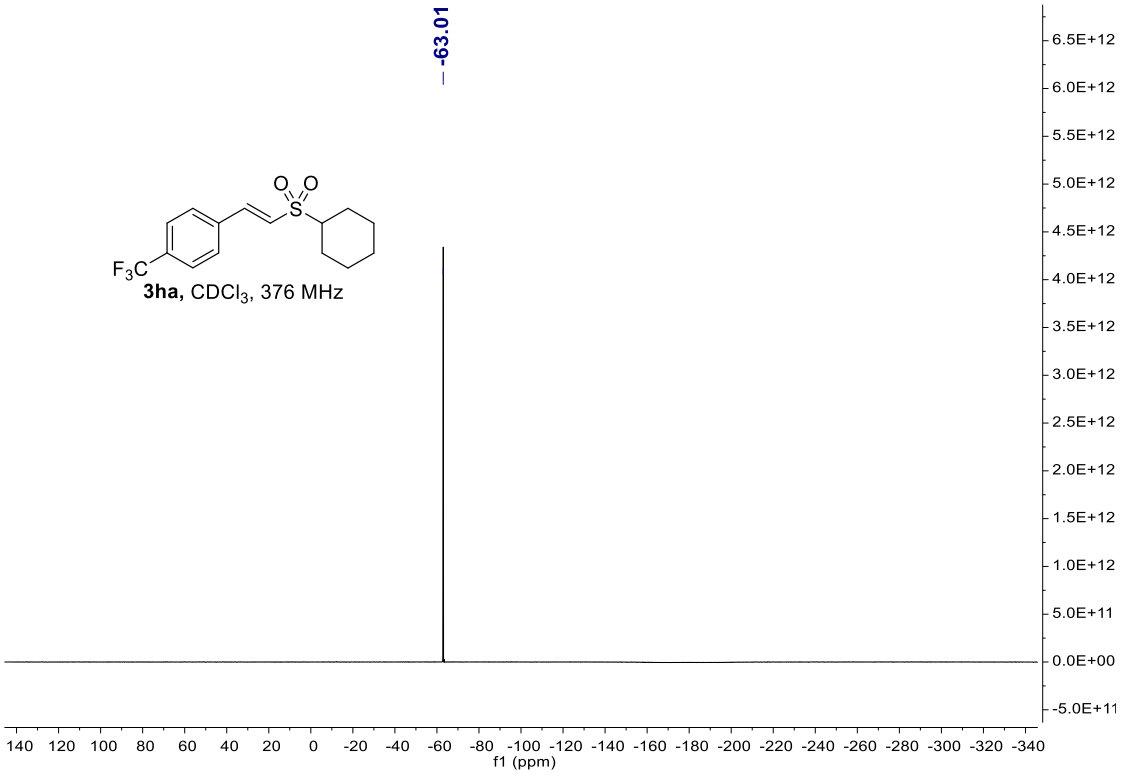




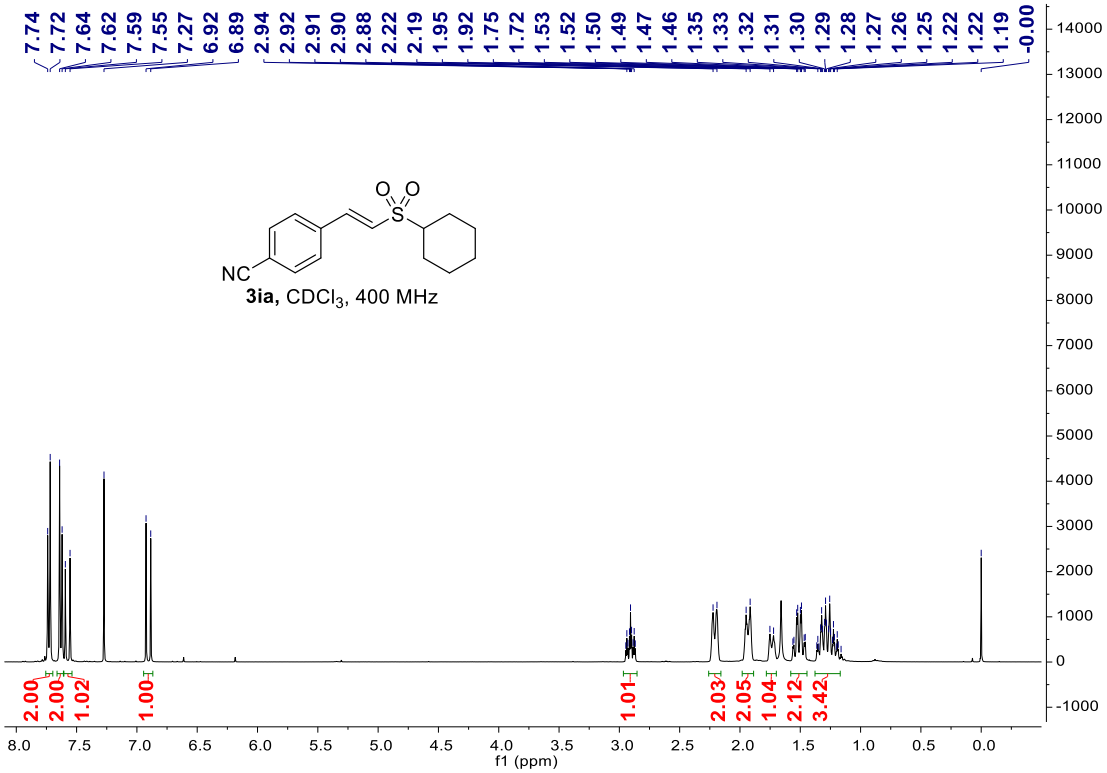
(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-(trifluoromethyl)benzene (**3ha**)

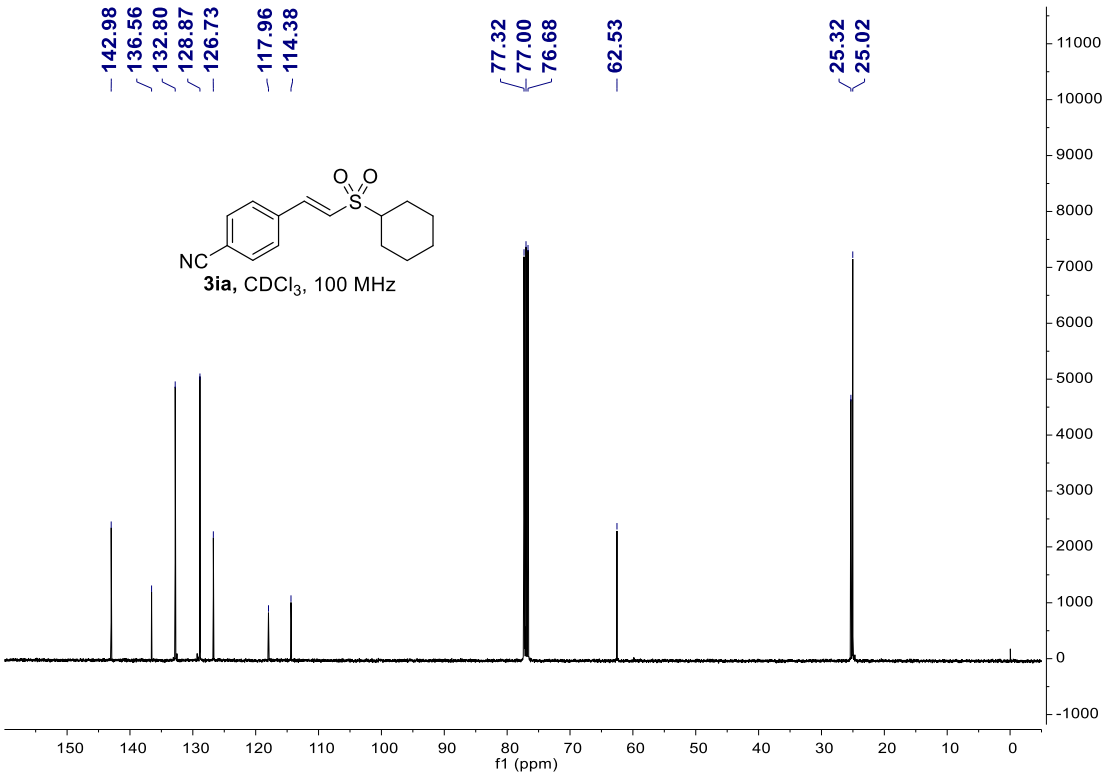




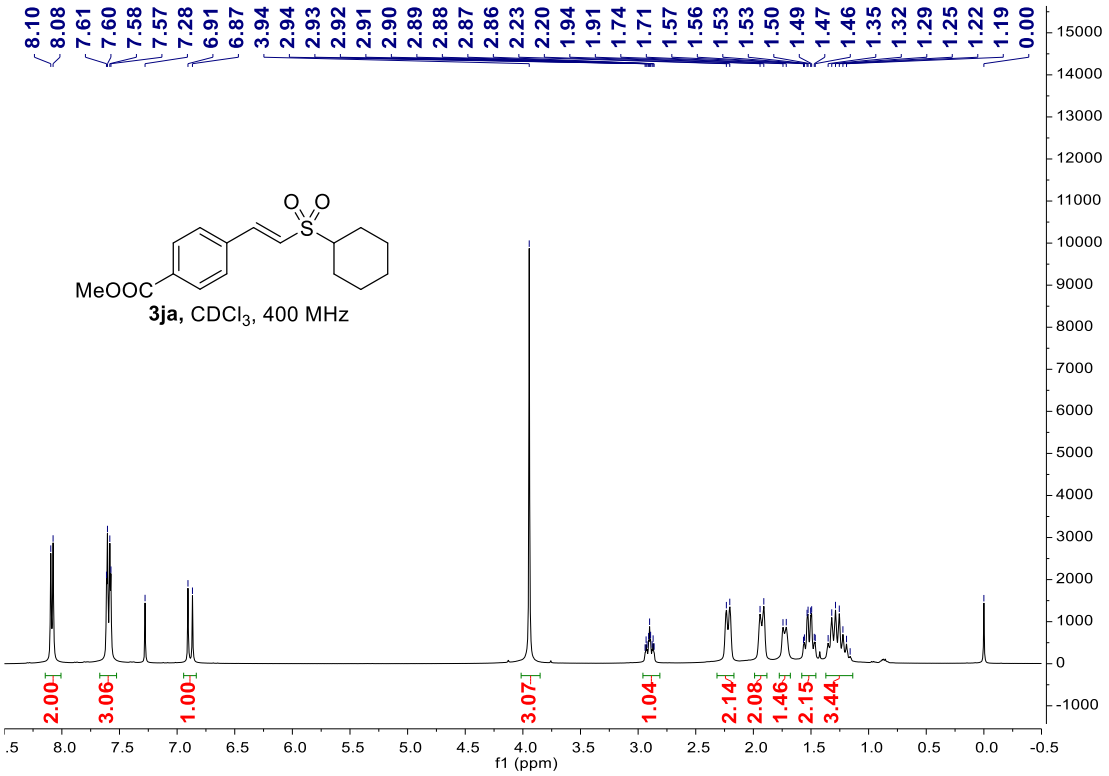


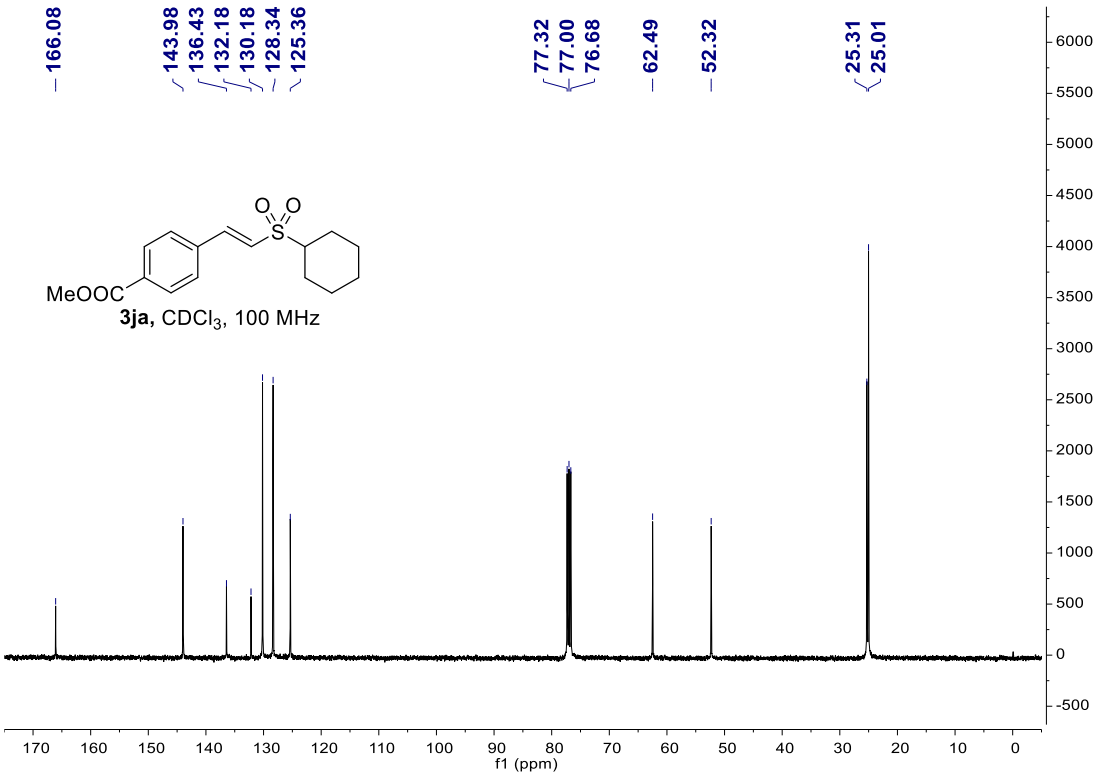
(*E*)-4-(2-(cyclohexylsulfonyl)vinyl)benzonitrile (**3ia**)



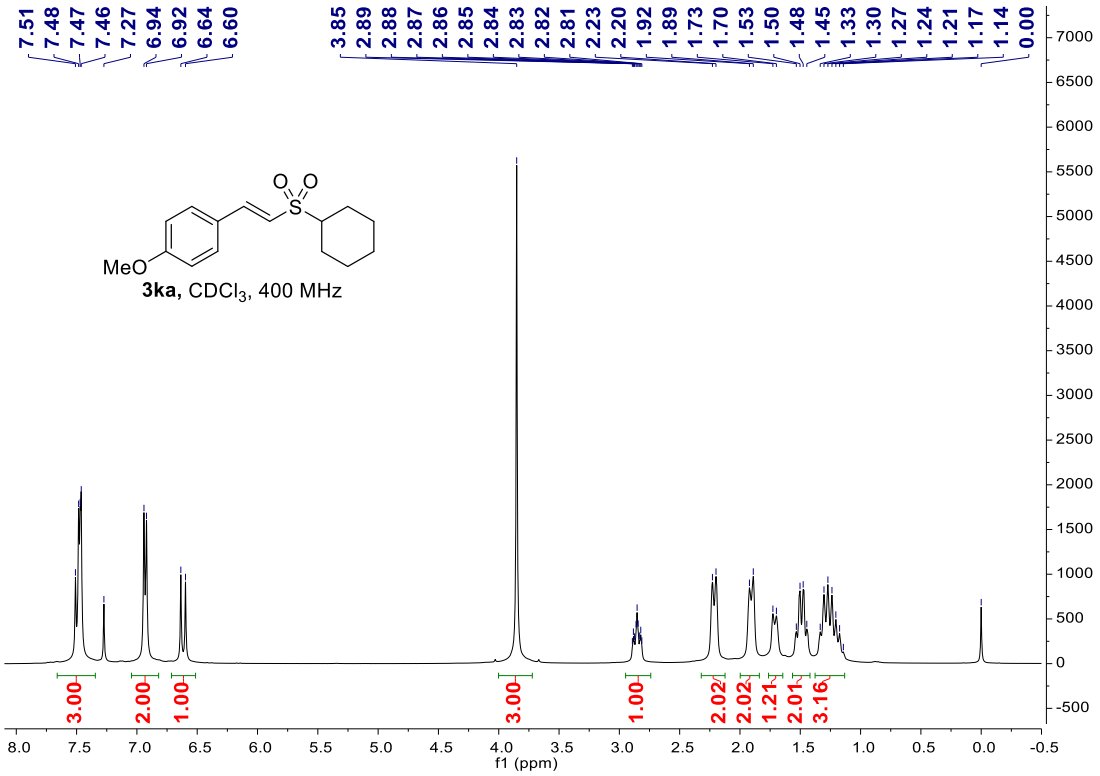


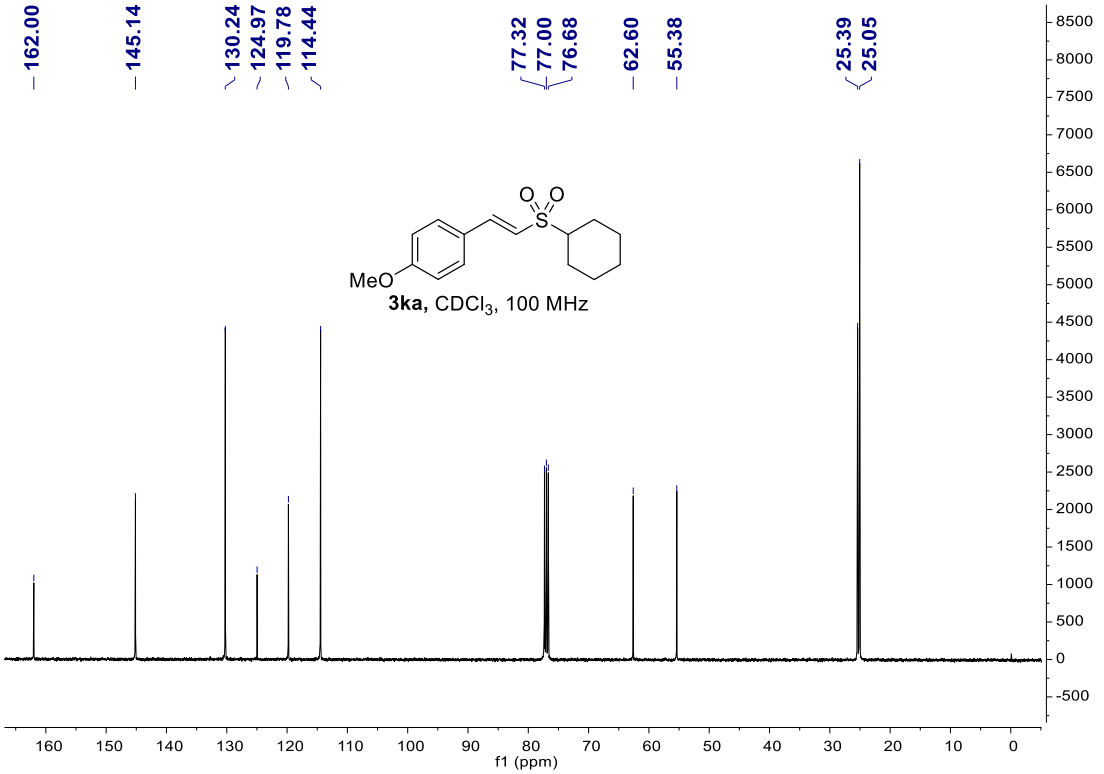
methyl (*E*)-4-(2-(cyclohexylsulfonyl)vinyl)benzoate (**3ja**)



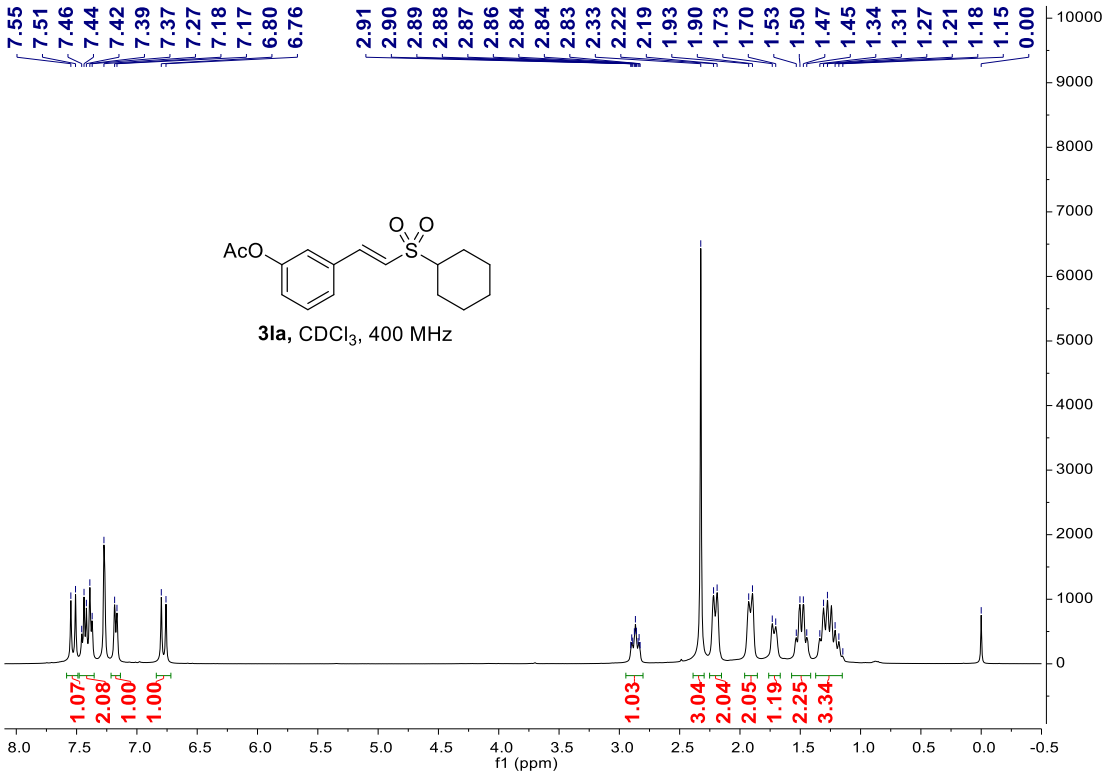


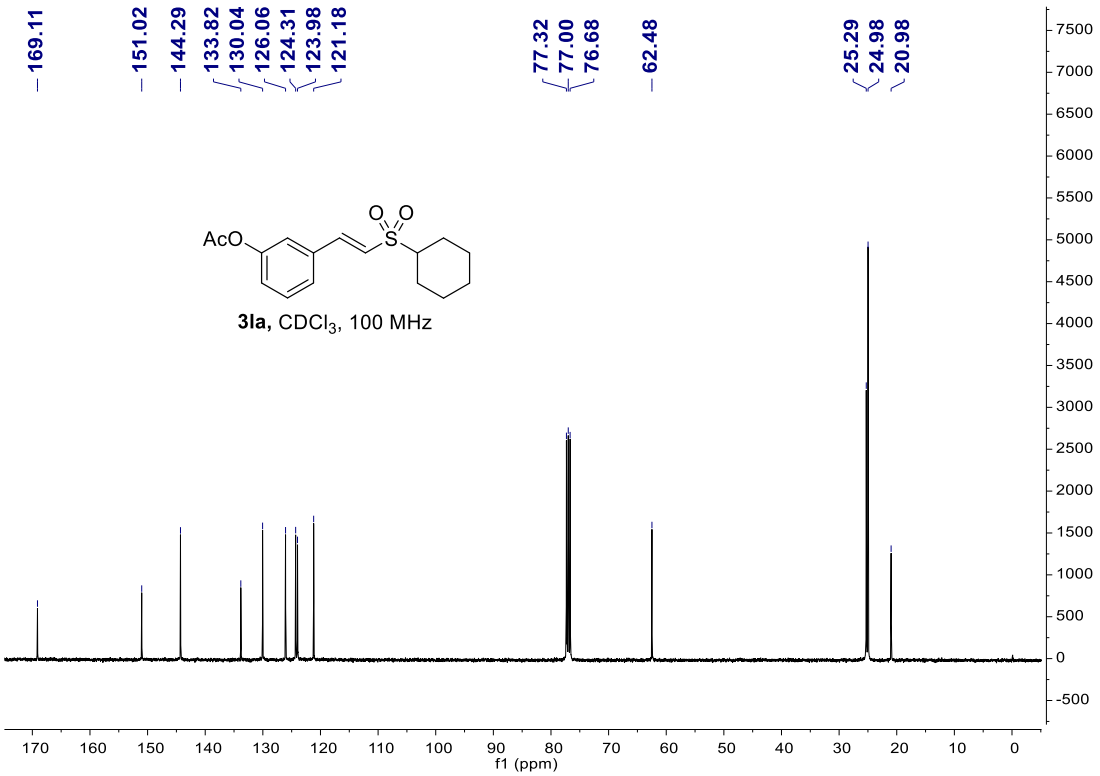
(*E*)-1-(2-(cyclohexylsulfonyl)vinyl)-4-methoxybenzene (**3ka**)



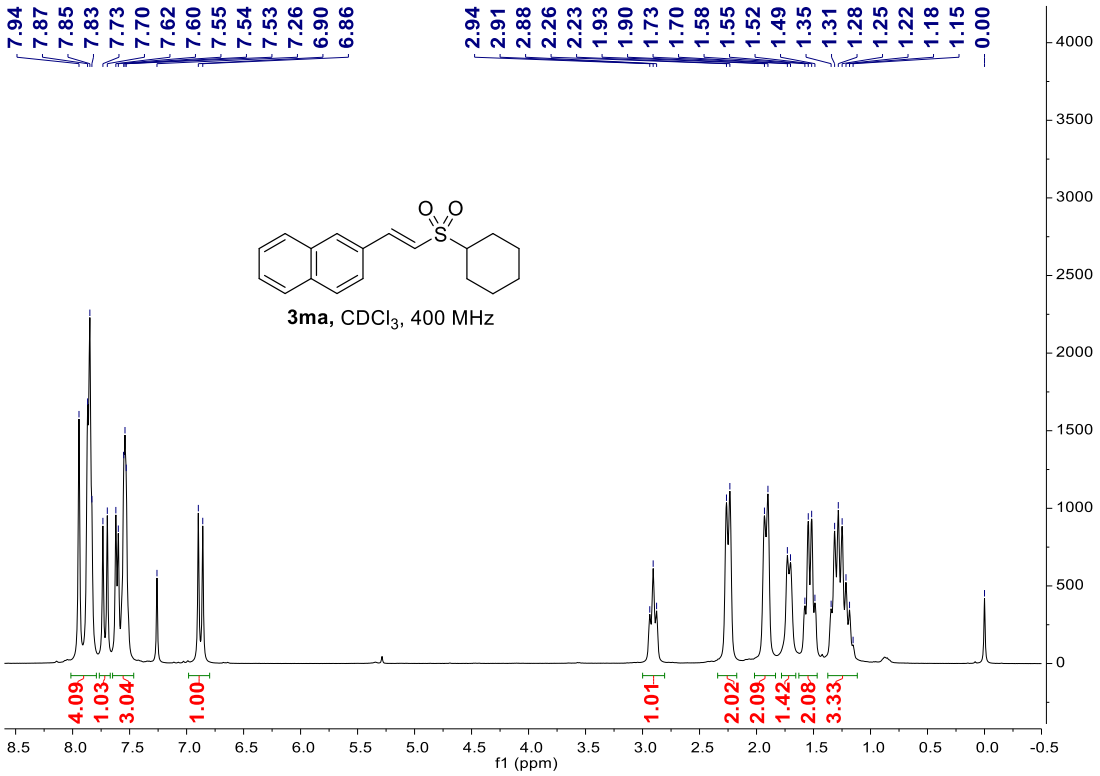


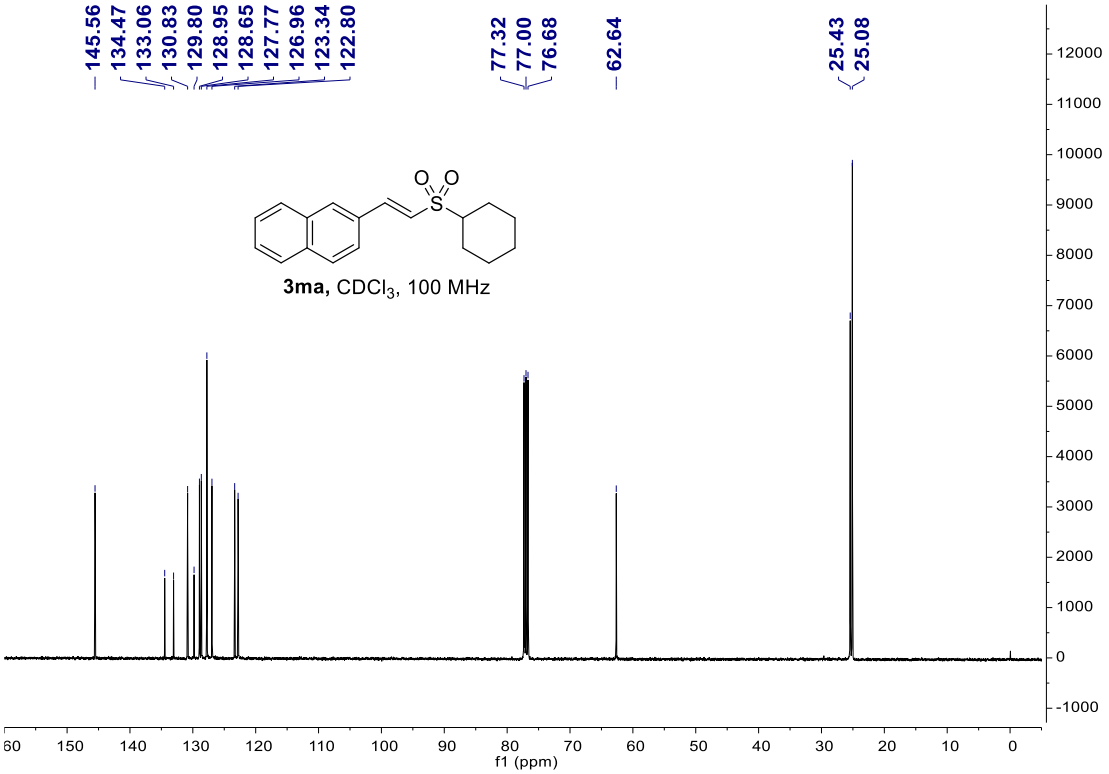
(*E*)-4-(2-(cyclohexylsulfonyl)vinyl)phenyl acetate (**3la**)



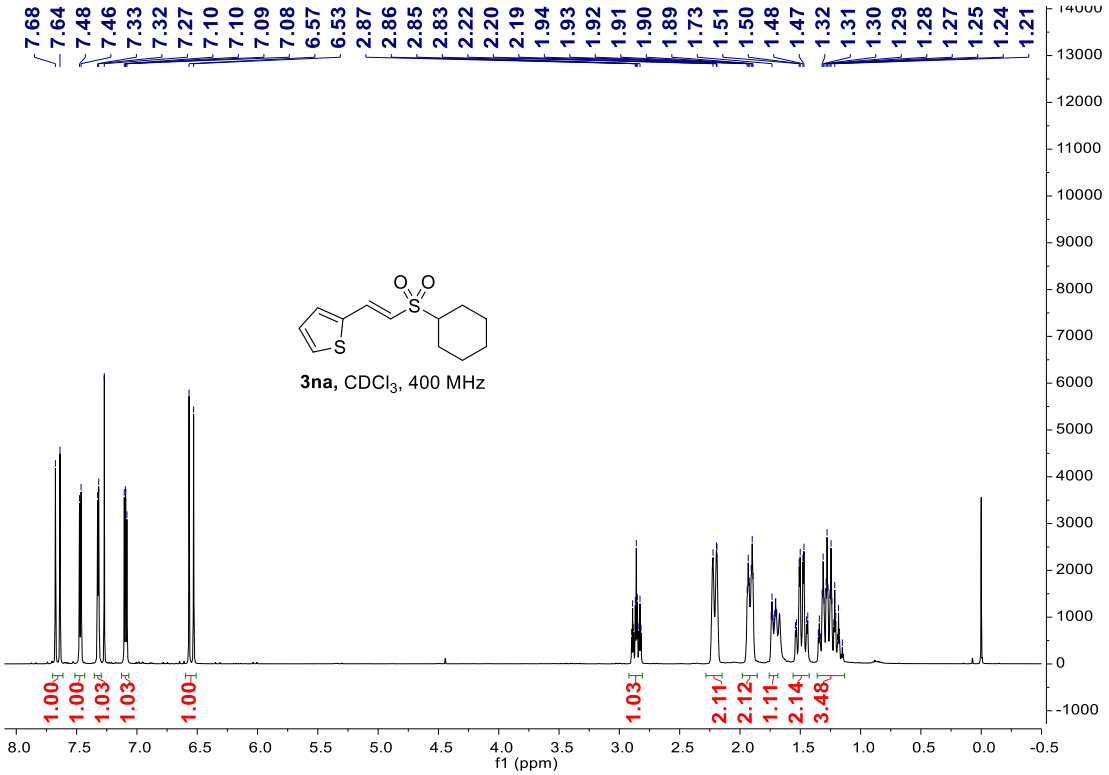


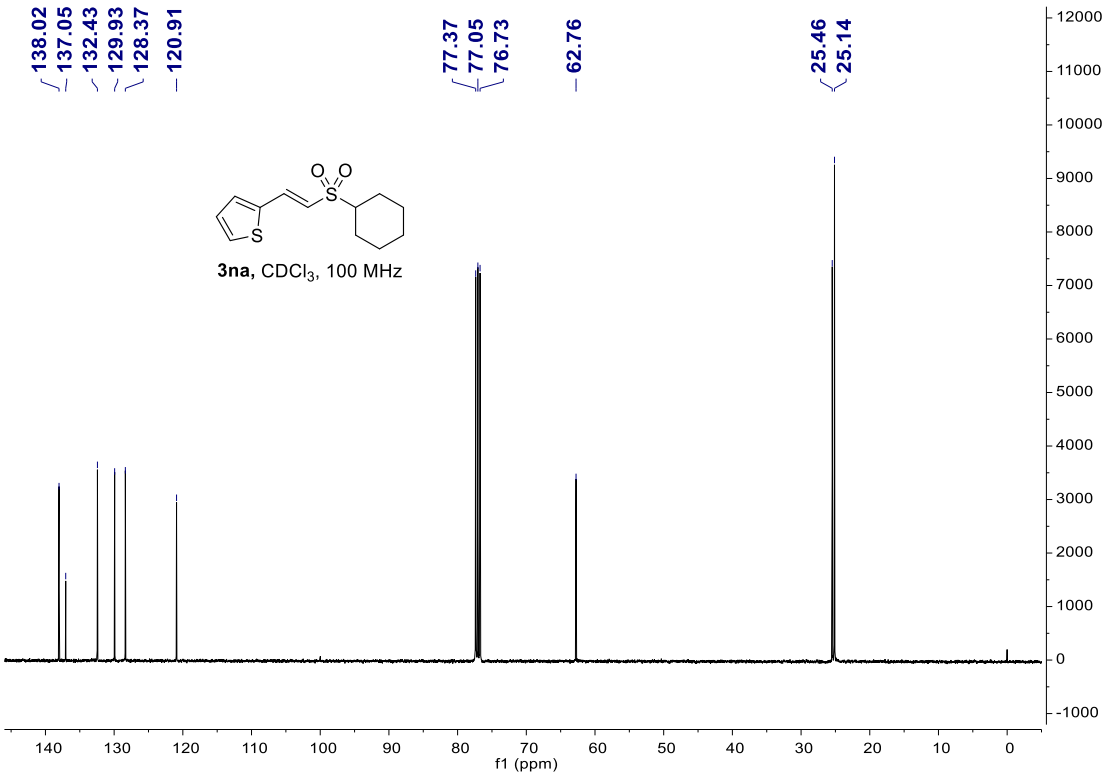
(*E*)-2-(2-(cyclohexylsulfonyl)vinyl)naphthalene (**3ma**)



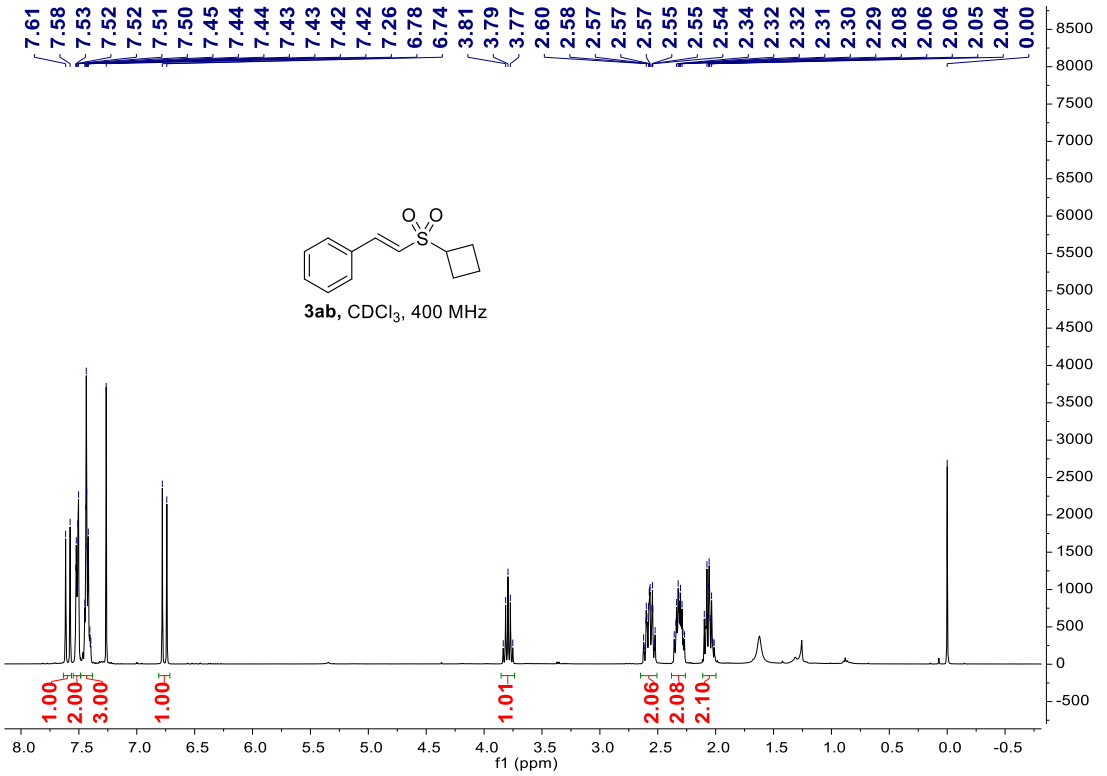


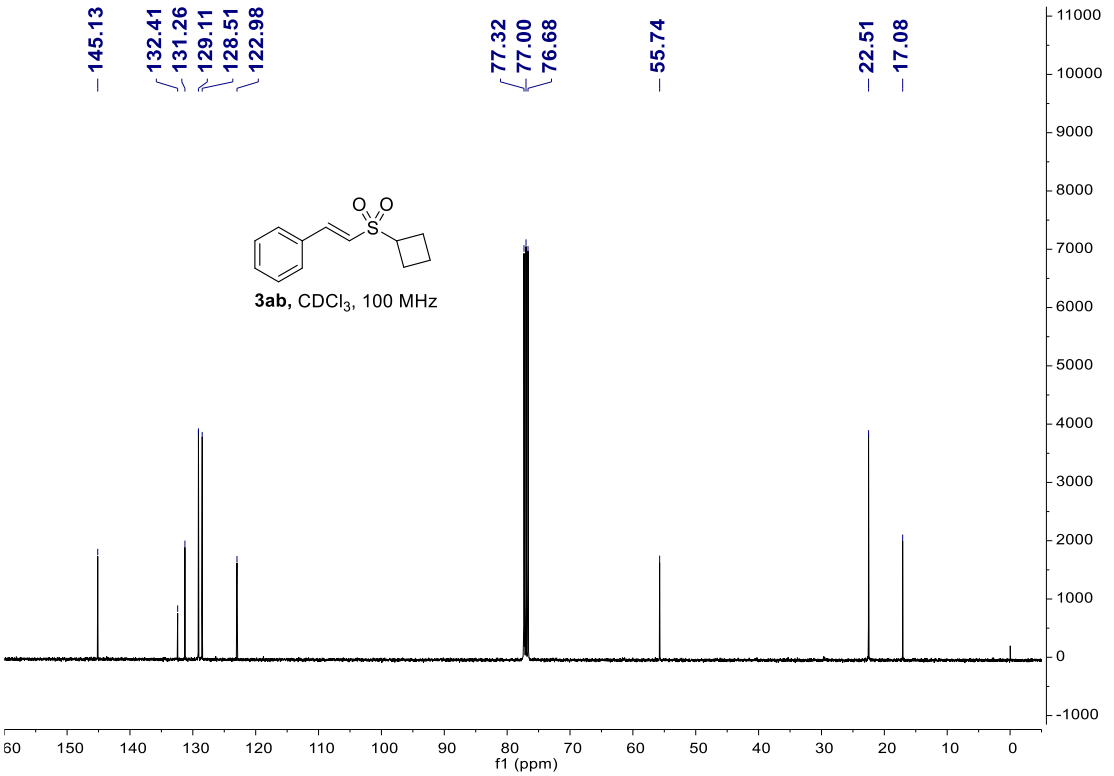
(*E*)-2-(2-(cyclohexylsulfonyl)vinyl)thiophene (**3na**)



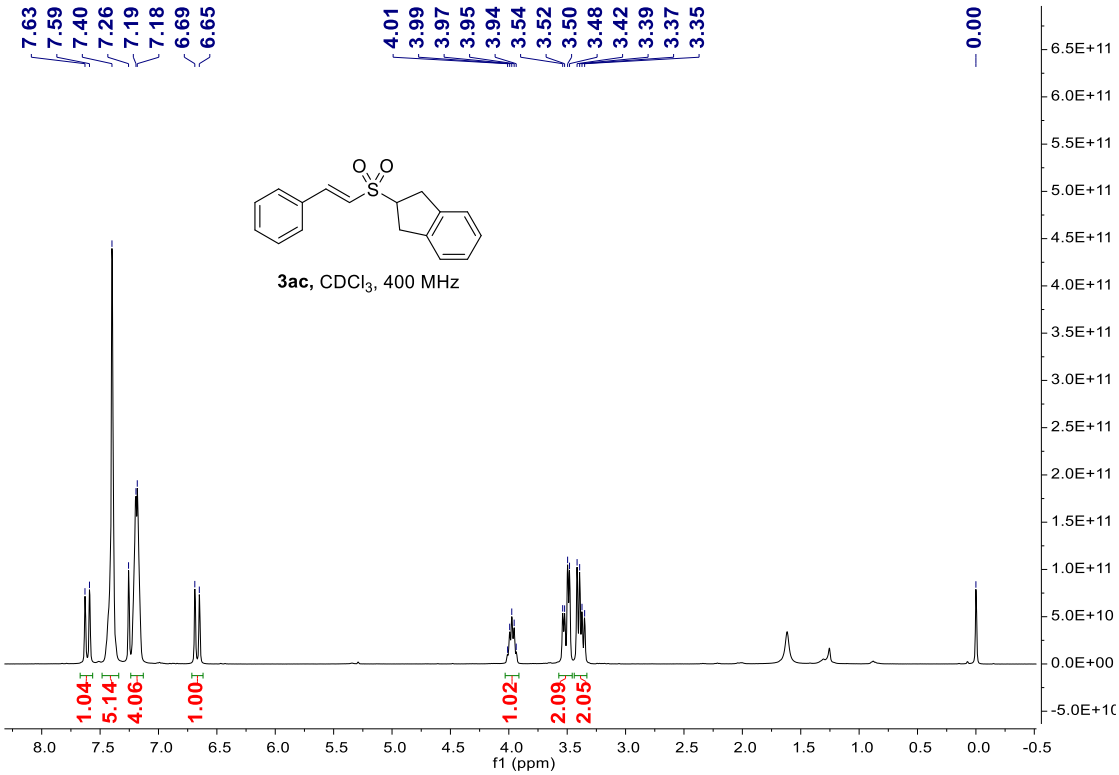


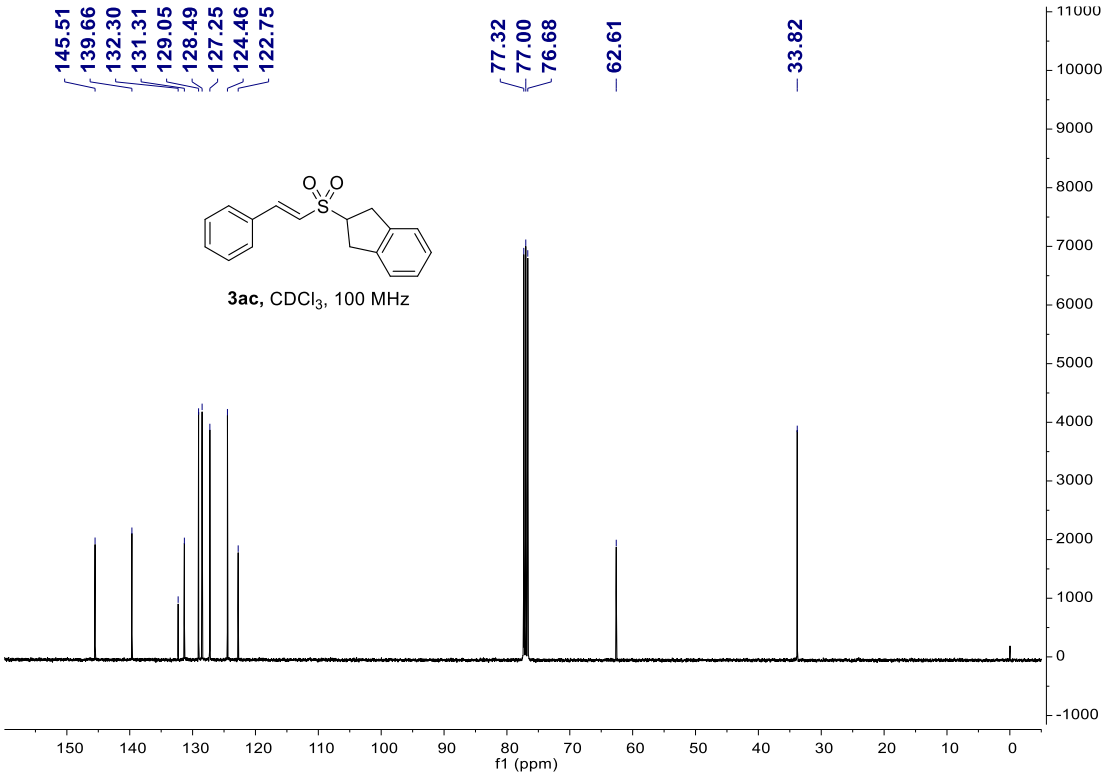
(*E*)-(2-(cyclobutylsulfonyl)vinyl)benzene (**3ab**)



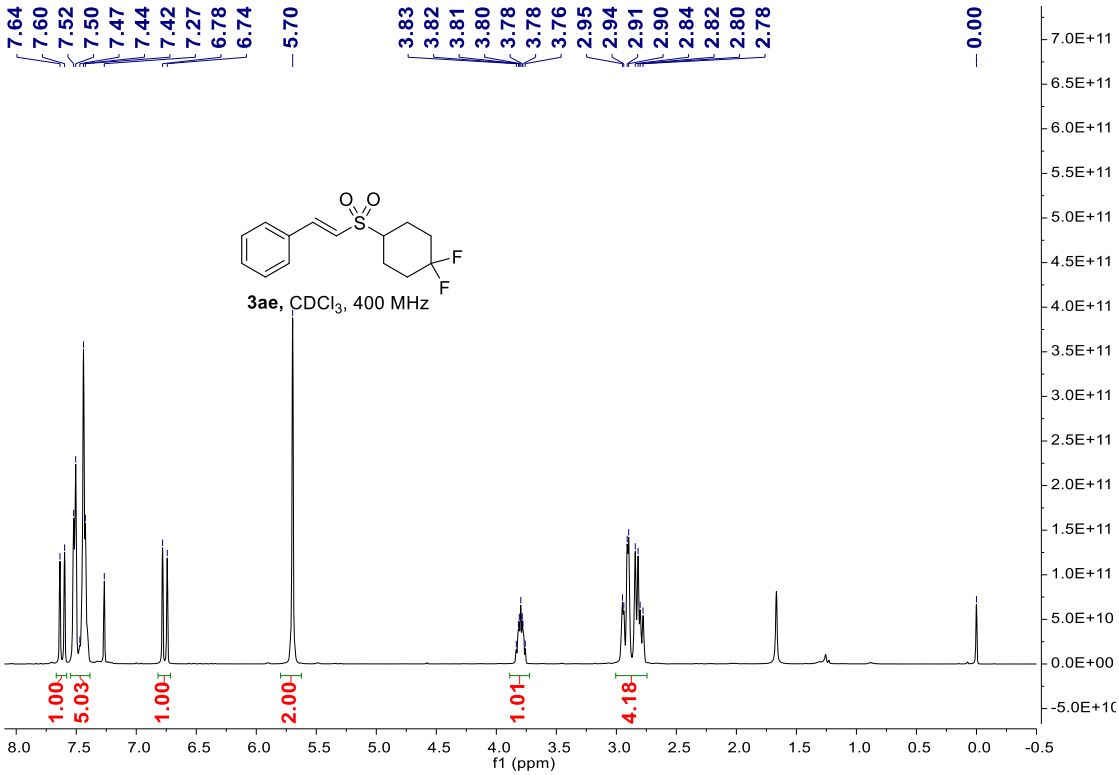


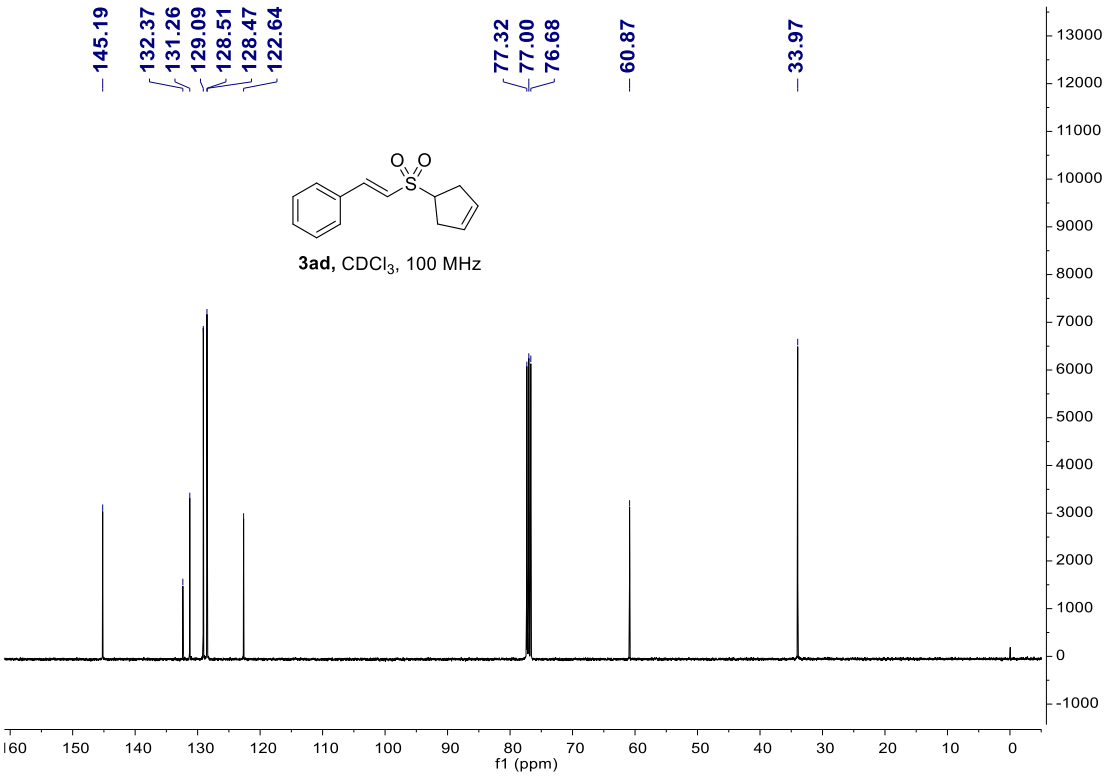
(*E*)-2-(styrylsulfonyl)-2,3-dihydro-1H-indene (**3ac**)



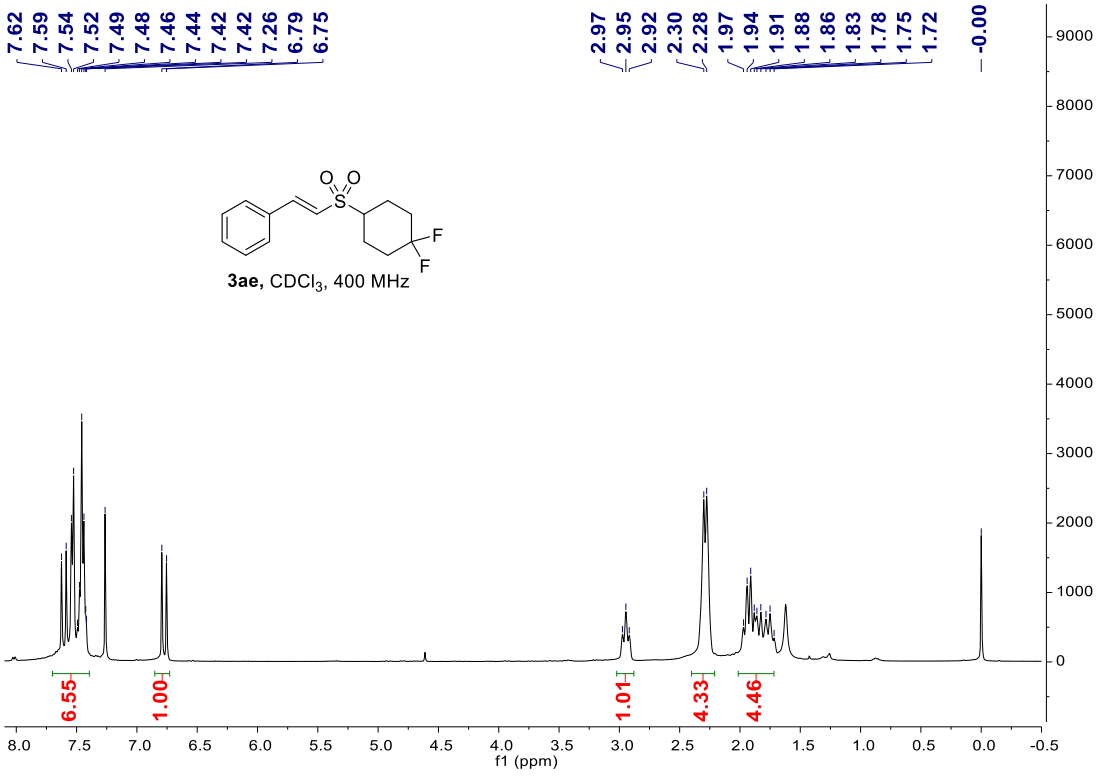


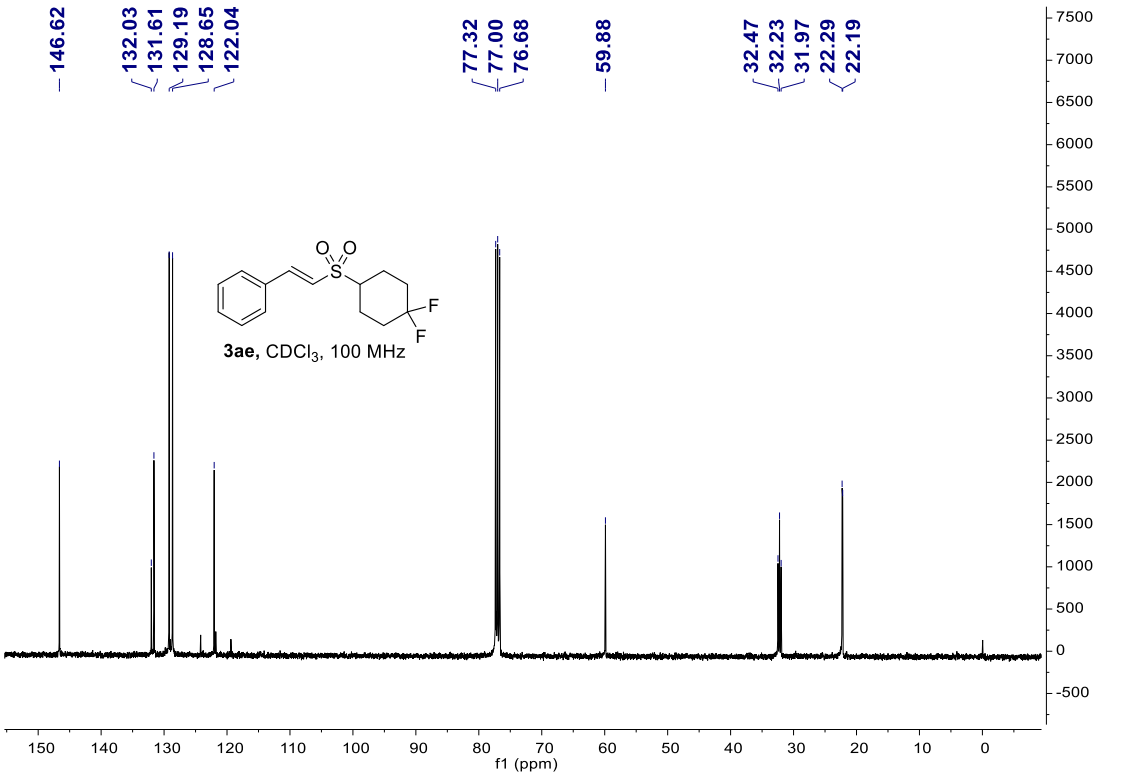
(*E*)-(2-(cyclopent-3-en-1-ylsulfonyl)vinyl)benzene (**3ad**)

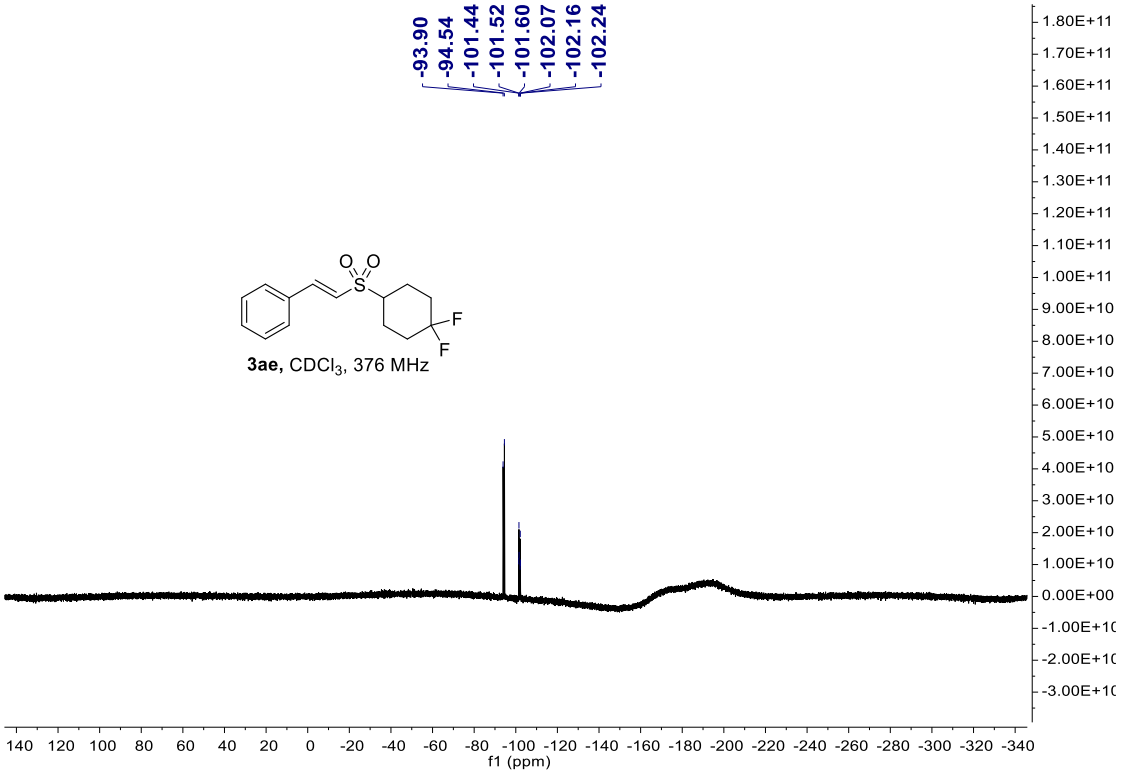




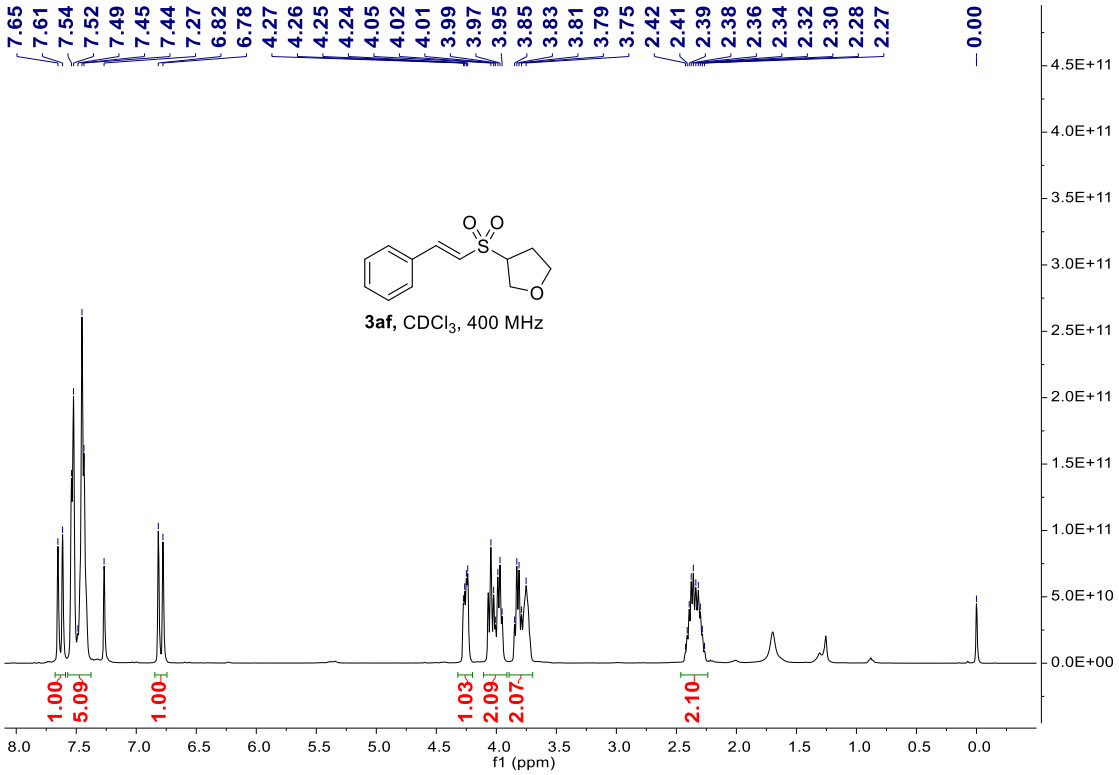
(*E*)-(2-((4,4-difluorocyclohexyl)sulfonyl)vinyl)benzene (**3ae**)

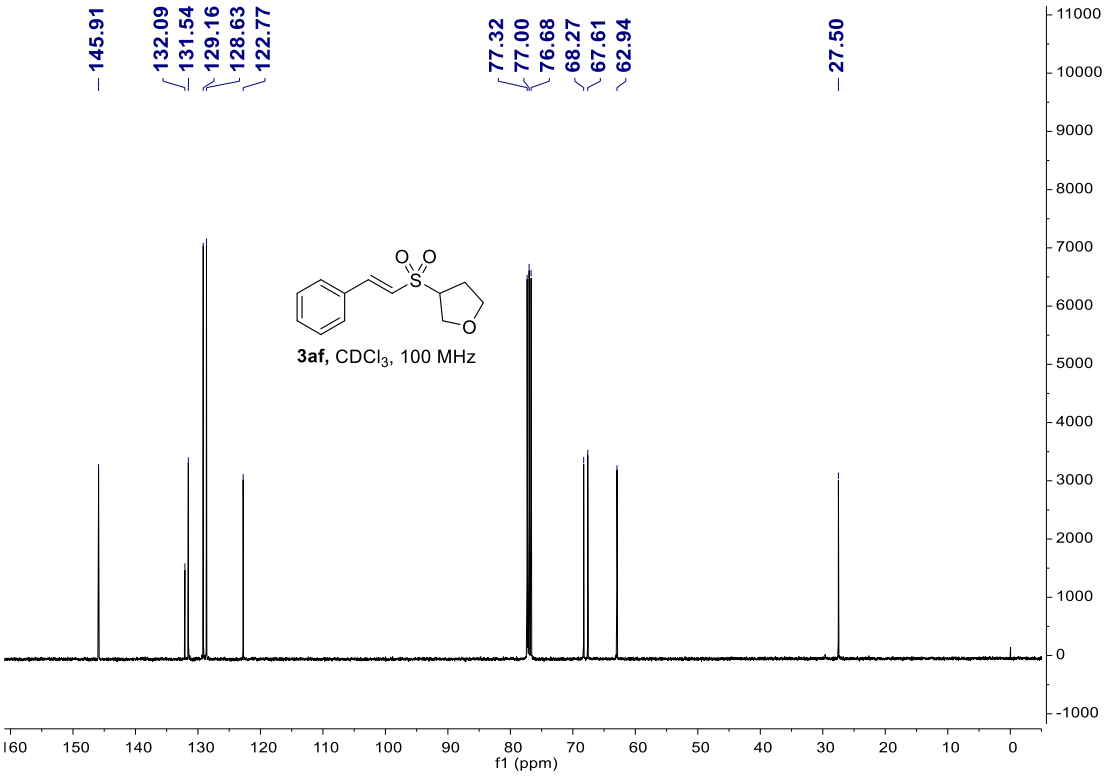



146.62
132.03
131.61
129.19
128.65
122.04
77.32
77.00
76.68
59.88
32.47
32.23
31.97
22.29
22.19
3ae, CDCl3, 100 MHz
f1 (ppm)

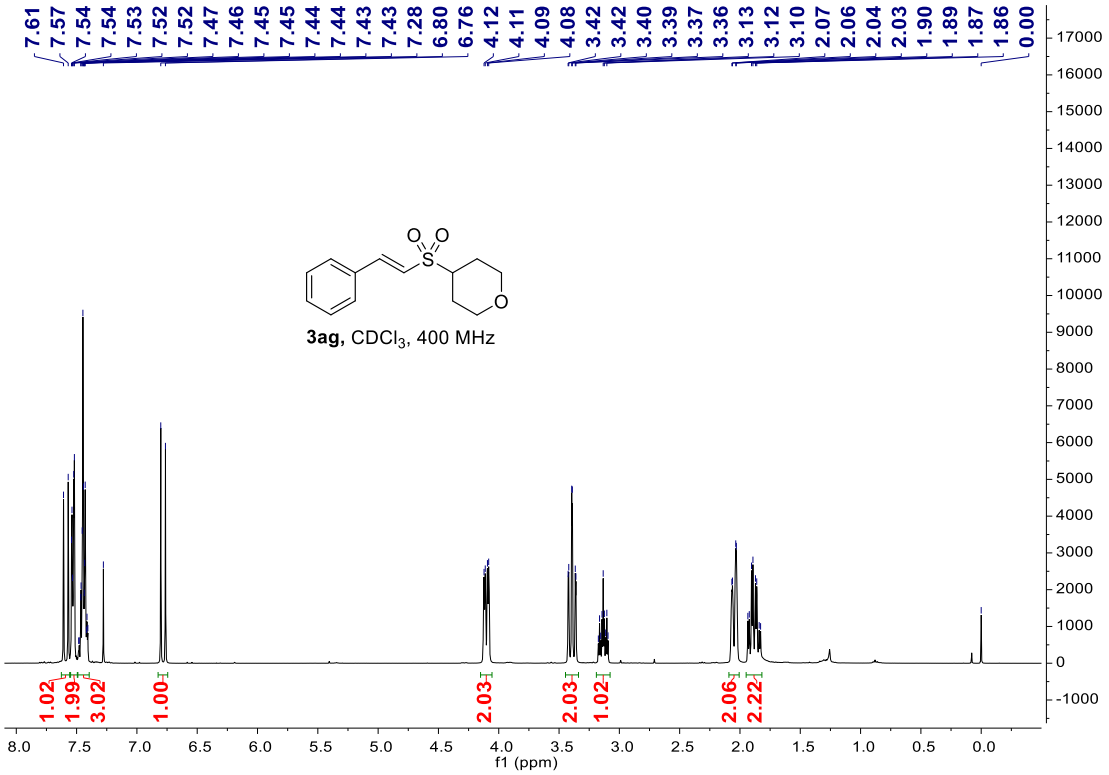

-93.90
-94.54
-101.44
-101.52
-101.60
-102.07
-102.16
-102.24
3ae, CDCl3, 376 MHz
f1 (ppm)

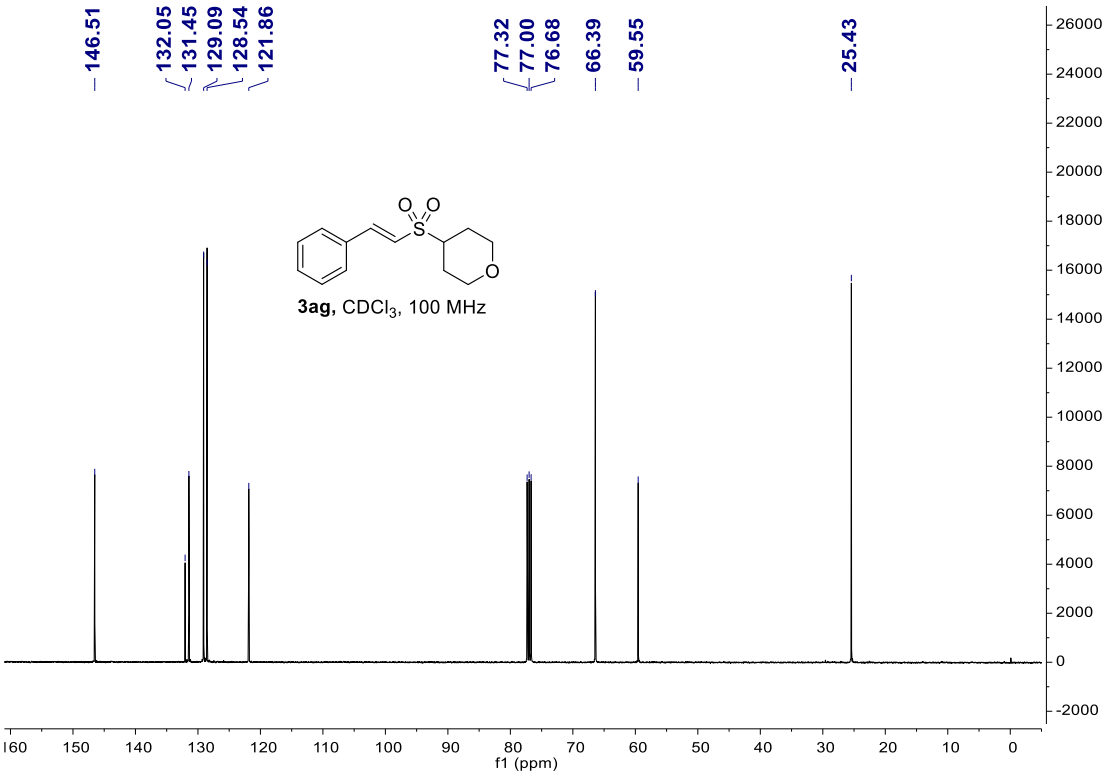
(*E*)-3-(styrylsulfonyl)tetrahydrofuran (**3af**)



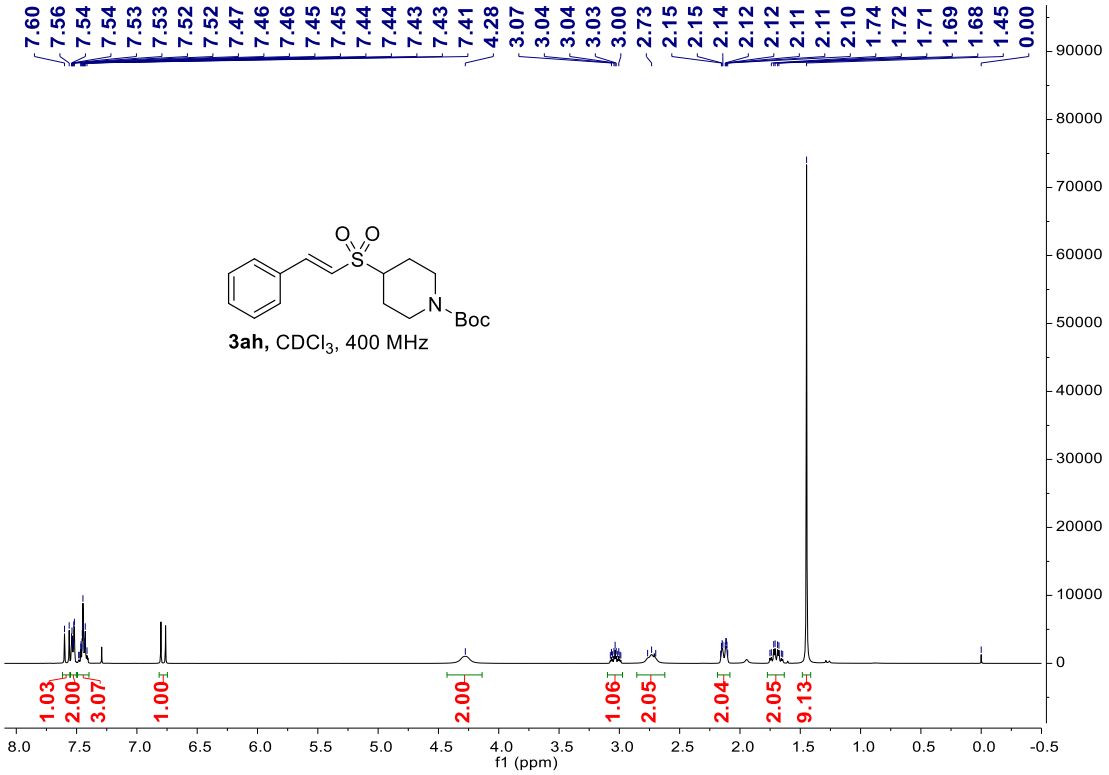


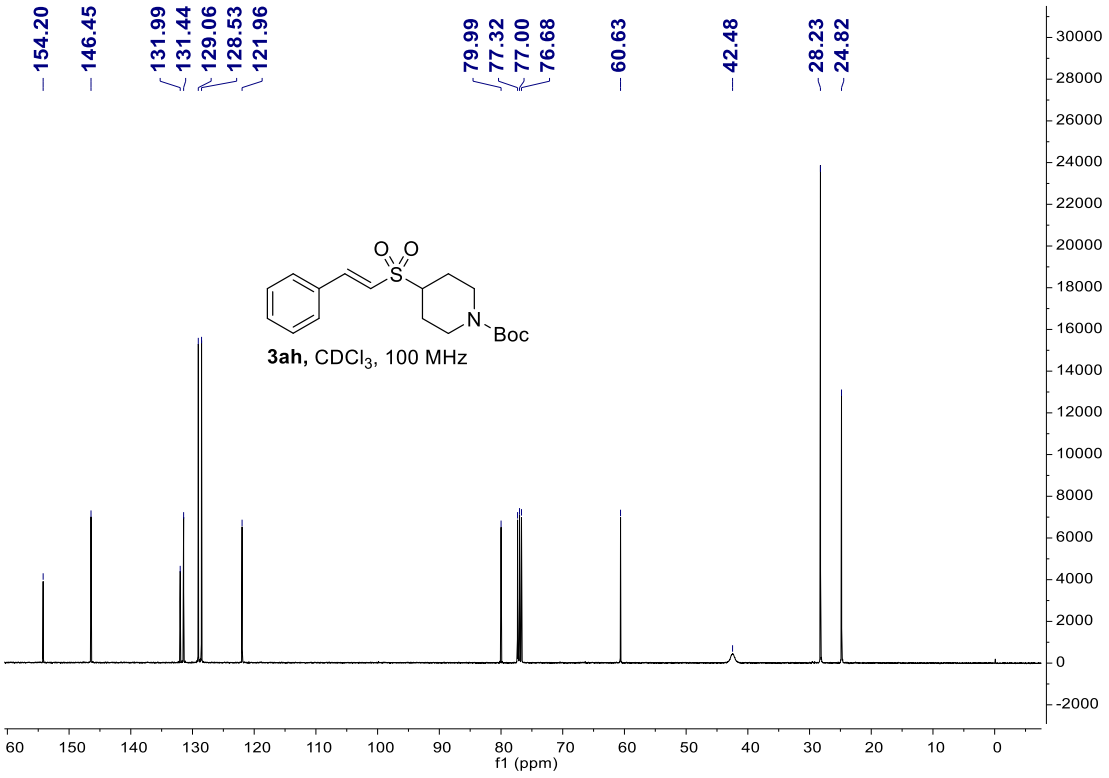
(*E*)-4-(styrylsulfonyl)tetrahydro-2*H*-pyran (**3ag**)



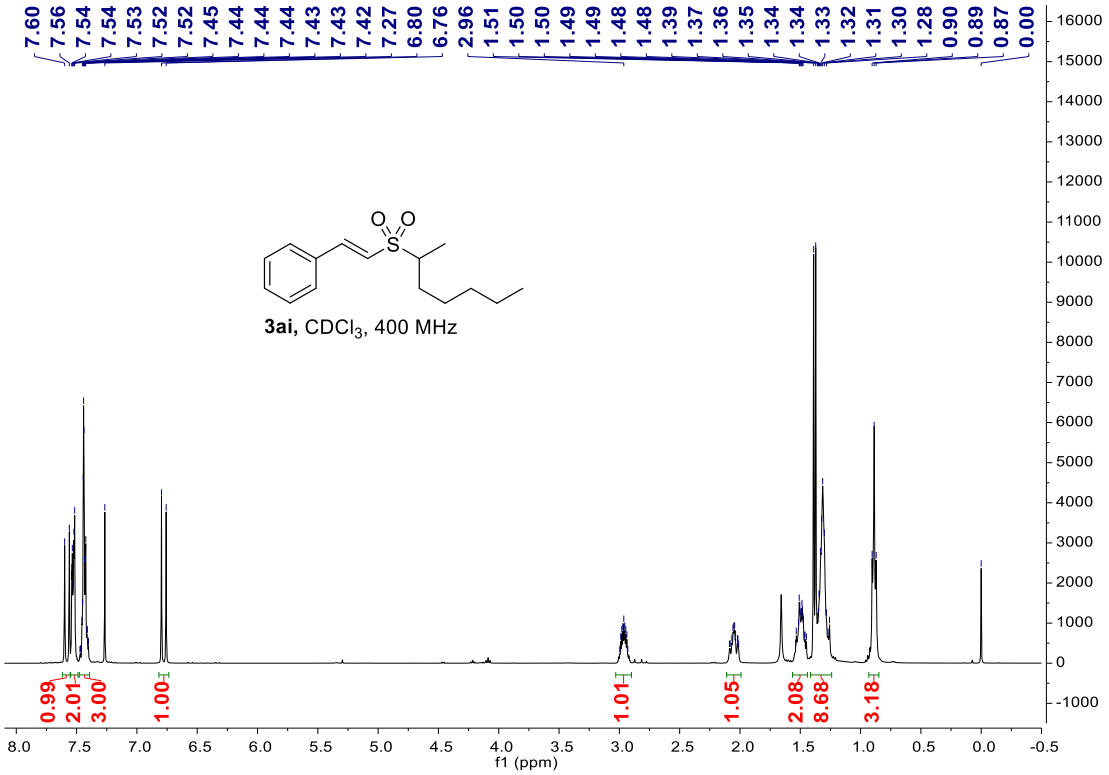


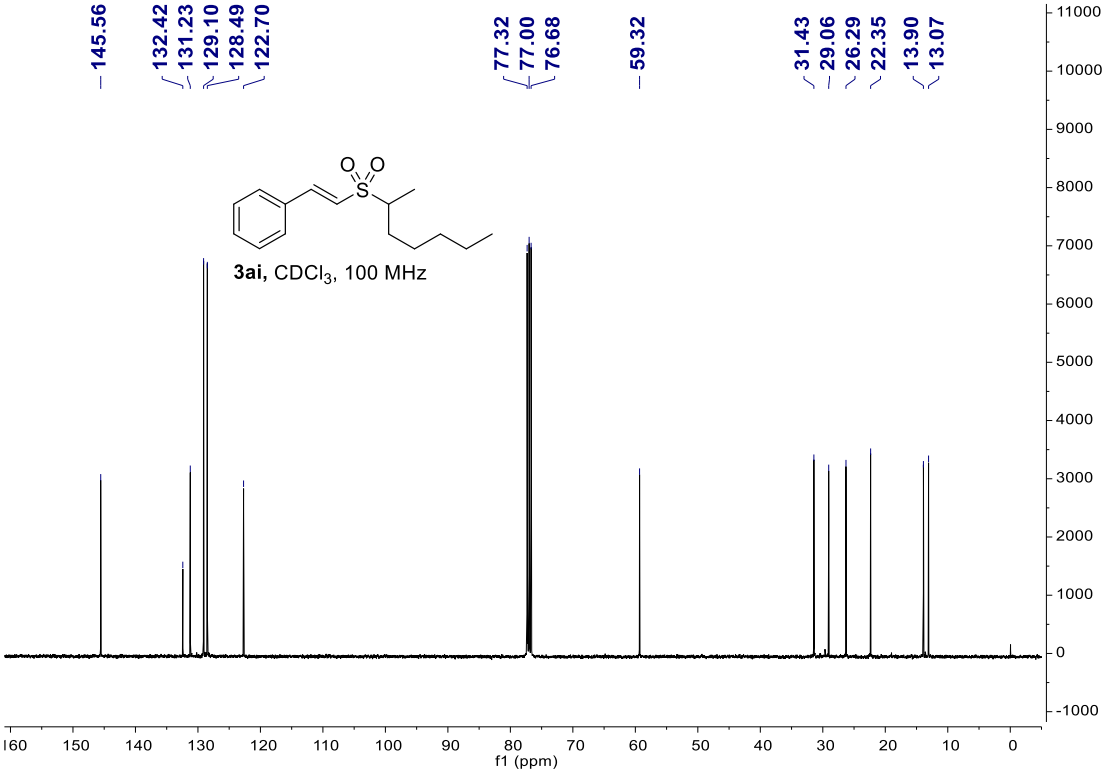
tert-butyl (*E*)-4-(styrylsulfonyl)piperidine-1-carboxylate (**3ah**)



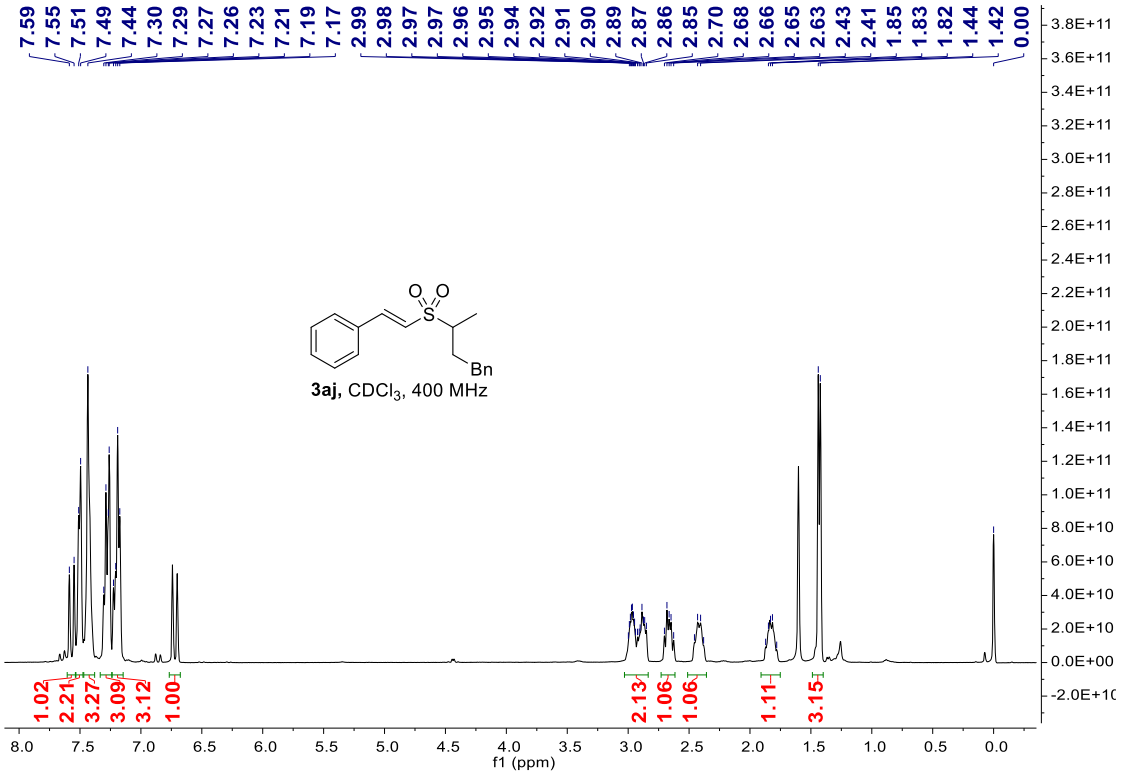


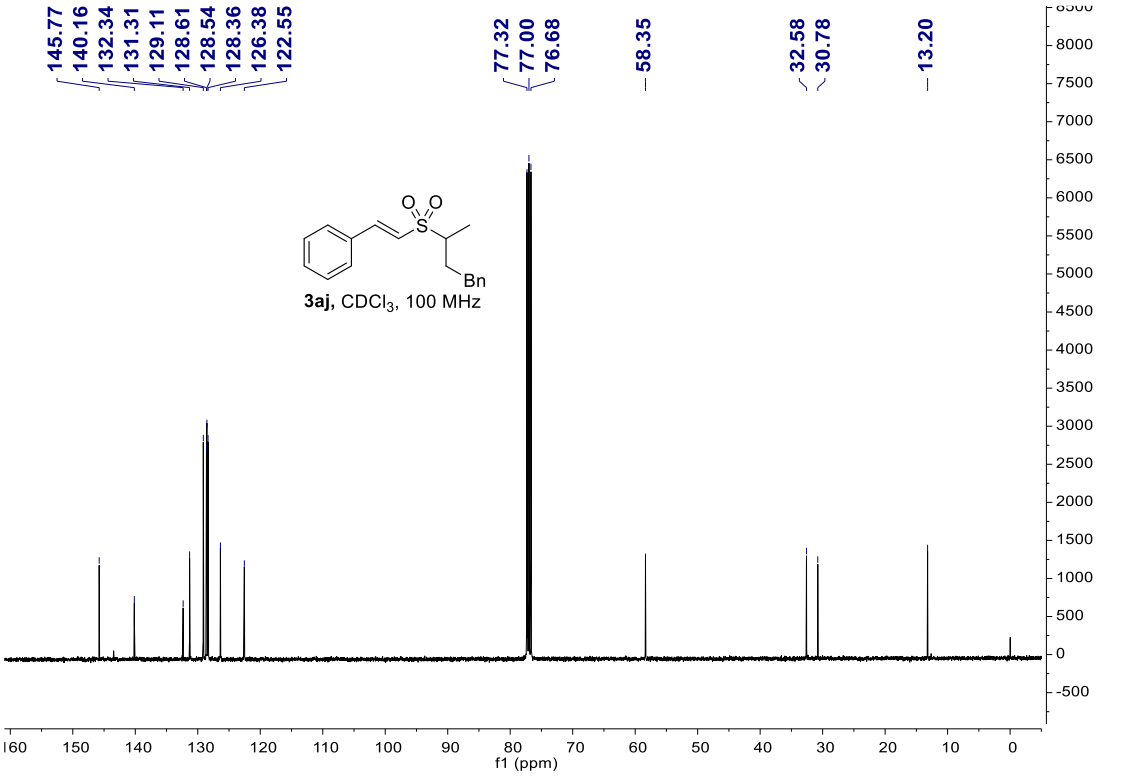
(*E*)-(2-(heptan-2-ylsulfonyl)vinyl)benzene (**3ai**)



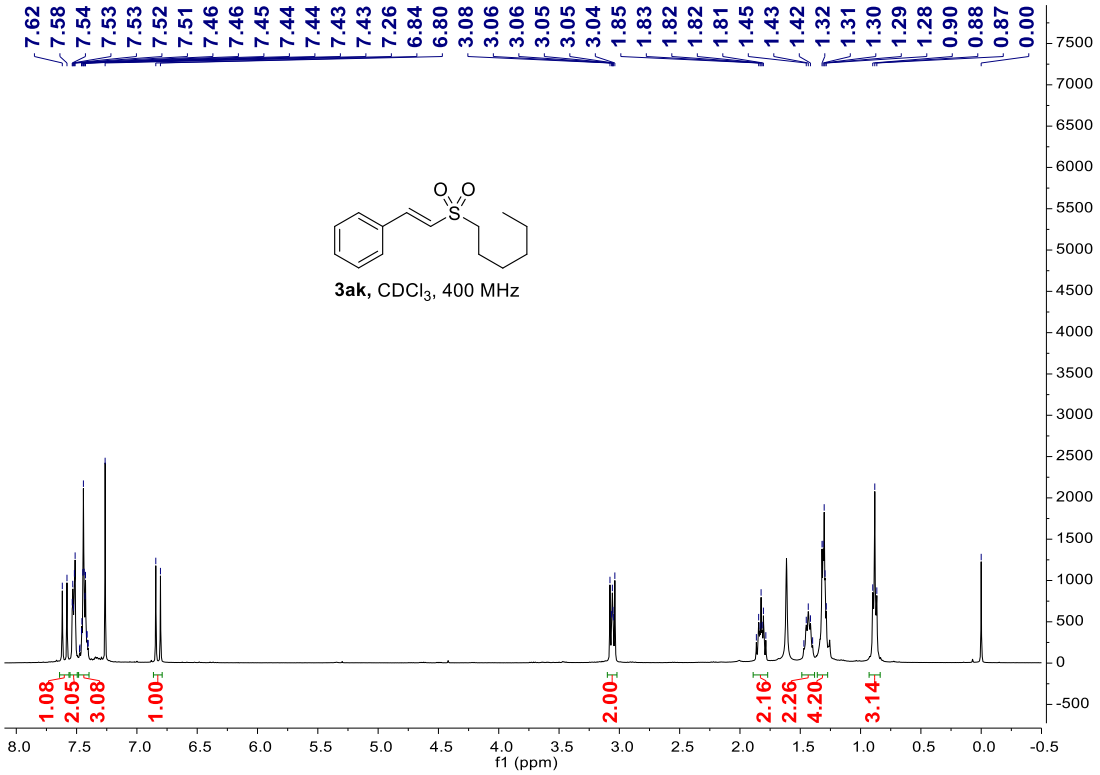


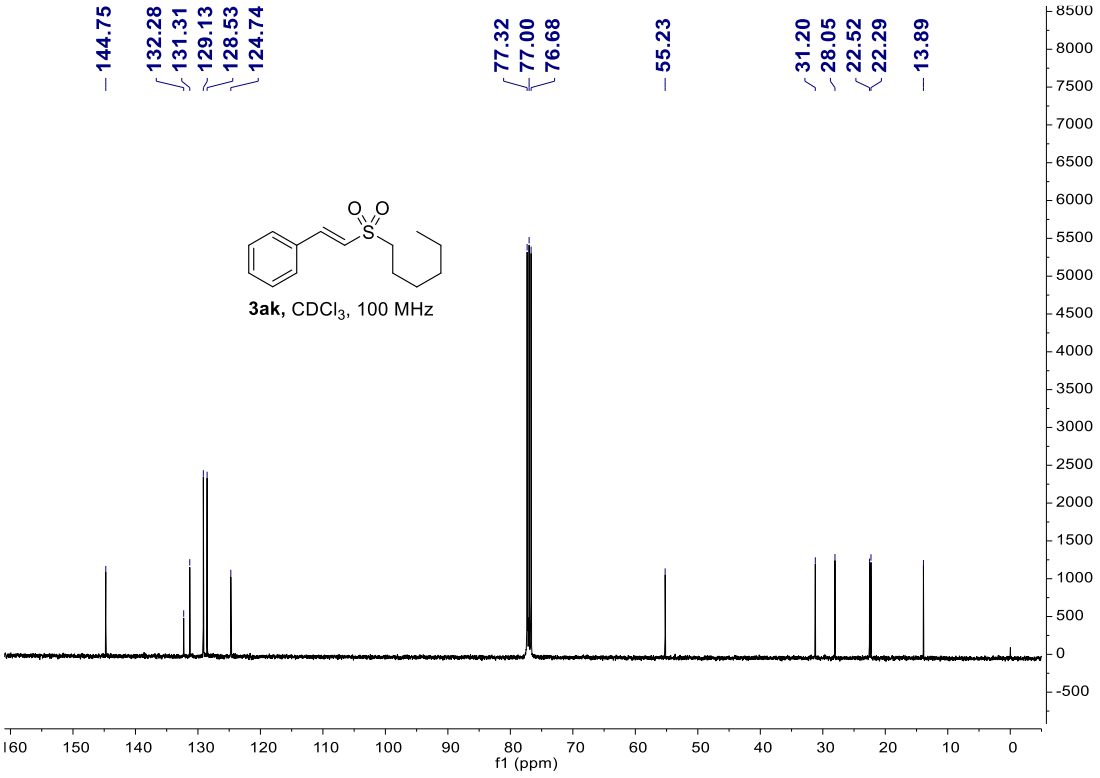
(*E*)-(2-((4-phenylbutan-2-yl)sulfonyl)vinyl)benzene (**3aj**)



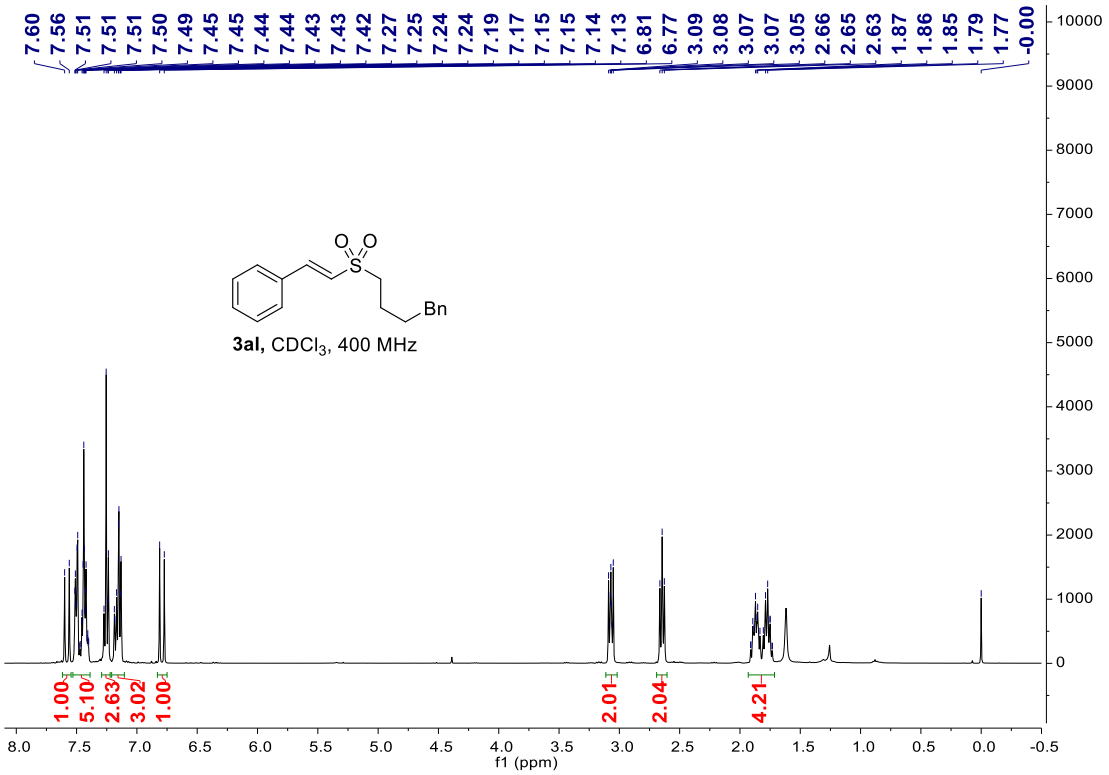


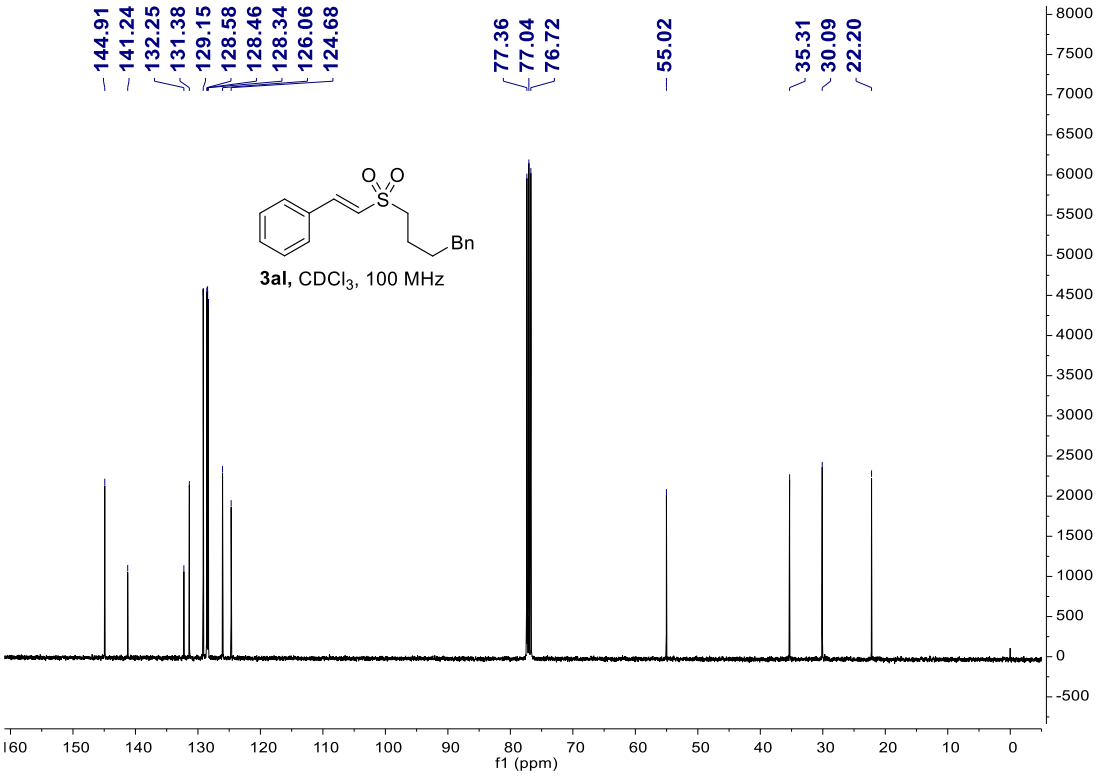
(*E*)-(2-(hexylsulfonyl)vinyl)benzene (**3ak**)



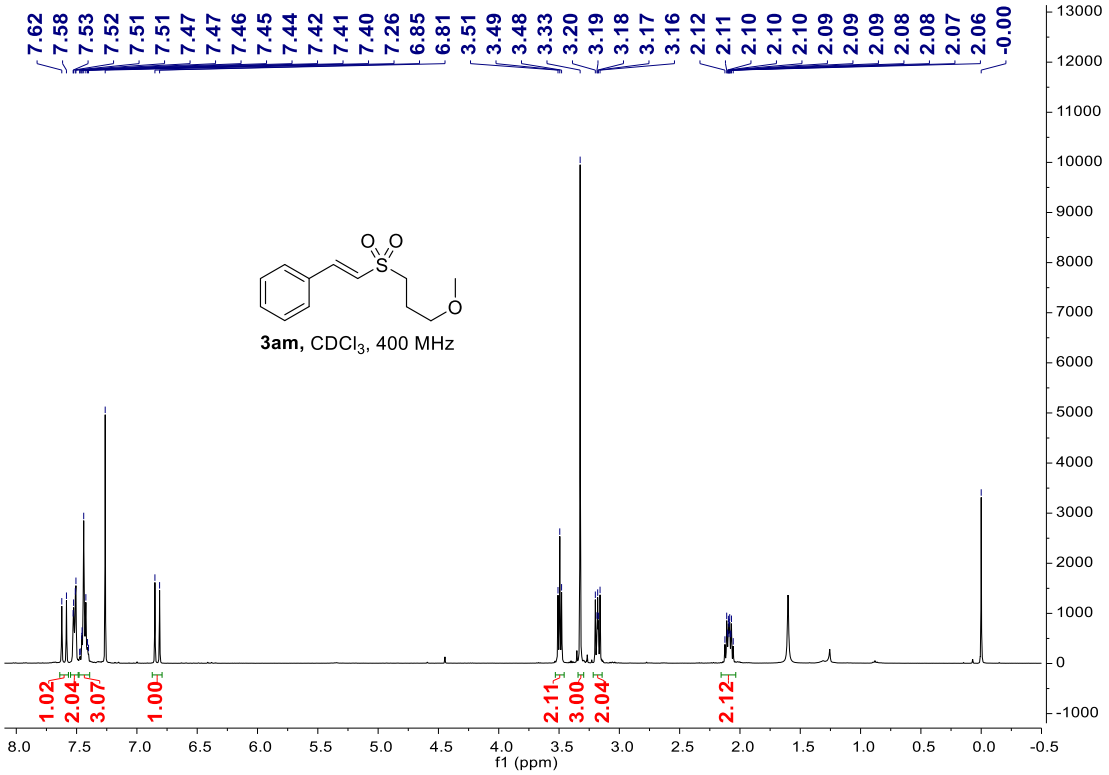


(*E*)-(2-((4-phenylbutyl)sulfonyl)vinyl)benzene (**3al**)

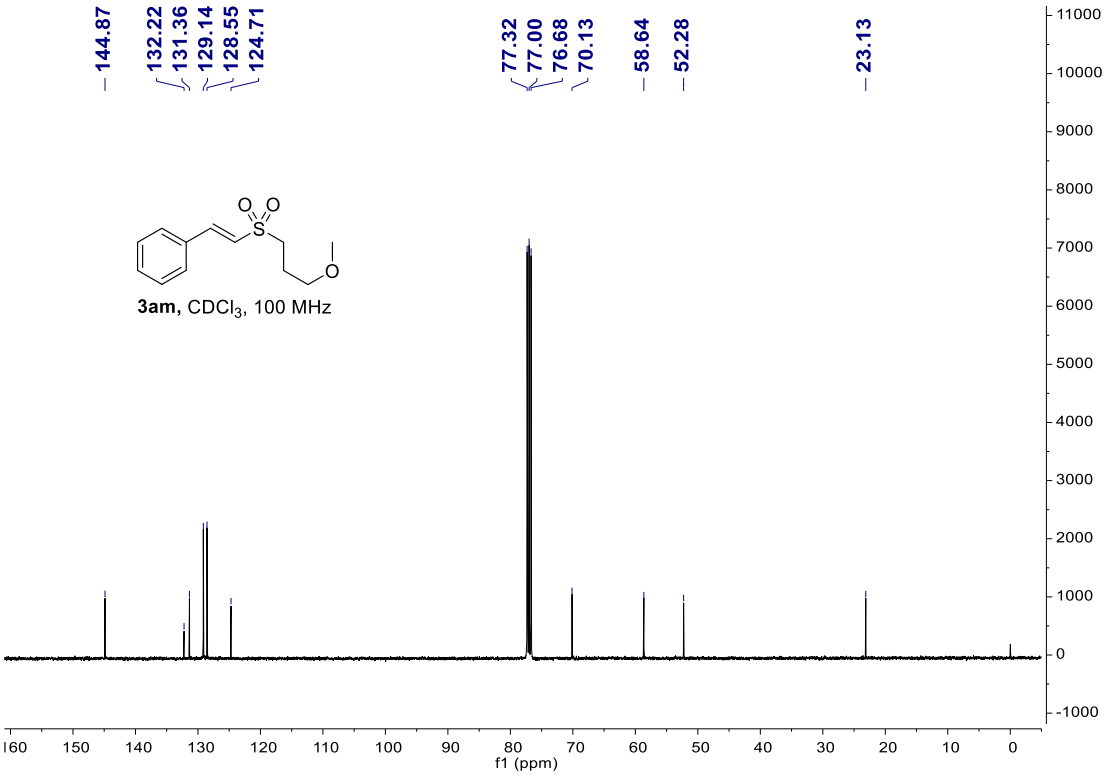




(*E*)-(2-((3-methoxypropyl)sulfonyl)vinyl)benzene (**3am**)



3am, $CDCl_3$, 400 MHz



3am, $CDCl_3$, 100 MHz