KASHYAP, S.

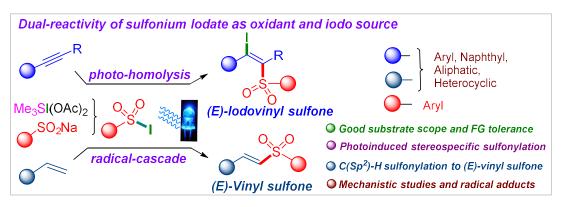
Supporting Information The Royal Society of Chemistry (RSC)

Photo-induced Stereo- and Regiospecific Sulfonylation of C=C Multiple Bond Exploiting the Dual-reactivity of Sulfonium Iodate(I) Species

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Abstract: Vinyl sulfones are privileged motifs for assembling prevalent biologically active molecules and represent "gateway functional groups" in medicinal chemistry and drug discovery. Augmented on our focus research toward bisfunctionalization of C-C multiple bonds, herein, we present a photo-induced (*E*)-stereospecific direct iodosulfonylation of alkynes and $C(sp^2)$ -H sulfonylation of alkenes by employing sulfonium iodate species. The scope and limitation of the atom-economical protocol were well illustrated with a broad range of structurally diverse substrates tolerating various sensitive moieties to access (*E*)-vinyl sulfones in highly regioselective transformation. The mechanistic investigations involving radical/spin trapping control experiments and isolation of unprecedented BHT-Tosyl adduct evidenced the photochemical radical-sulfonylation with tosyl iodide generated *in situ* and discovering the intrinsic dual-reactivity of Me₃SI(OAc)₂ as oxidant as well as the source of iodine.

Supporting Material

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A. General Experimental Information.

General Synthesis Information:

Reactions were run in screw capped glass vials (4 mL) stirred with Teflon®-coated magnetic stir bars. Moisture and air-sensitive reactions were performed in flame-dried round bottom flasks, fitted with rubber septa or glass gas adapters, under a positive pressure of nitrogen. Moisture and air-sensitive liquids or solutions were transferred via nitrogen-flushed syringe. Experiments were monitored by thin layer chromatography (TLC). Melting points were obtained in open capillary tubes using a micro melting point apparatus and were uncorrected.

Materials:

Unless otherwise noted, materials were obtained from commercial suppliers and used without purification. Removal of solvent under reduced pressure refers to distillation with a Büchi rotary evaporator attached to a vacuum pump (~3 mmHg). Products obtained as solids or high boiling oils were dried under vacuum (~1 mmHg).

Chromatography:

Analytical TLC was performed using Whatman 250-micron aluminium backed UV F254 precoated silica gel flexible plates. Subsequent to elution, ultraviolet illumination at 254 nm allowed for visualization of UV active materials. Staining with p-anisaldehyde, basic potassium permanganate solution, or Molisch's reagents allowed for further visualization.

Physical Data:

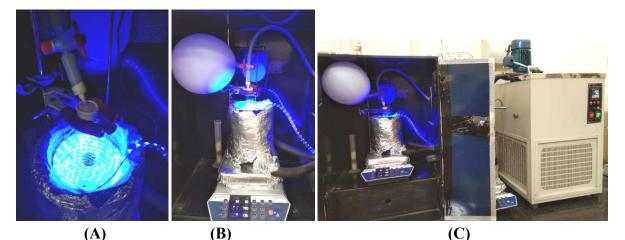
Proton and Carbon nuclear magnetic resonance spectra (¹H, ¹³C NMR) were recorded on Avance 300, 400 or 500 MHz and ECS 4000 MHz (JEOL) NMR spectrometers. The proton resonances are annotated as: chemical shift (δ) relative to tetramethylsilane (δ 0.0) using the residual solvent signal as an internal standard or tetramethylsilane itself: chloroform-d (δ 7.26, singlet), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (*J*, Hz), and number of protons for a given resonance is indicated by nH. The chemical shifts of ¹³C NMR are reported in ppm relative to the central line of the triplet at 77.00 ppm for CDCl₃. IR spectra were recorded on a PerkinElmer FT-IR spectrometer and wave numbers of maximum absorption peaks are presented in cm⁻¹. Mass analyses (ESI-MS) and HRMS were performed on Xevo G2-S QTTOF (Waters, USA) Spectrometer. Shimadzu UV-1800 Spectrophotometer for UV studies. A blue LED apparatus (7 W ribbon $\lambda_{max} \sim 460$ nm) equipped with a magnetic stirrer and chiller was used as the light source.

Abbreviations used:

pTsNa: p-toluenesulfinate, PhSO₂Na: sodium benzenesulfinate, 4-ClPhSO₂Na: sodium 4chloro benzenesulfinate, PhSO₂NHNH₂: sulfonyl hydrazide, CF₃SO₂Na: Langlois reagent, PhSO₂I: *p*-tolylsulfonyl iodide, *t*-Bu: *tert*-butyl, MeCN: acetonitrile, DCE: dichloroethane, DCM: dichloromethane, MeOH: methanol, EtOH: ethanol, AcOH: acetic acid, THF: tetrahydrofuran, EtOAc: ethylacetate, DMF: N, N-dimethylformaide. TLC: thin layer chromatography, CFL: compact fluorescent lamp, PIDA: phenyliodnium diacetate, BAIB: bis(acetoxy)iodobenzene, emitting diodes, TEMPO: LEDs: light 2,2,6,6-2,6-di-tert-butyl-4-methylphenol, tetramethylpiperidin-1-yl)oxyl, BHT: RT: room temperature.

General Procedure for Sulfonylation:

An oven-dried, 10 mL glass tube was equipped with a magnetic stir bar, a rubber septum, and a threaded Teflon cap. A nitrogen-filled balloon was fitted through the septum to sustain a nitrogen atmosphere. To this vessel was added a solution of alkene/alkyne (1.0 equiv.) in solvent (3 mL) via syringe followed by the sequential addition Me₃SI(OAc)₂ (1.2-2.5 equiv.) and sulfonyl source (1.5-2.5 equiv.) at room temperature (25 °C). The reaction mixture was then purged with nitrogen (gas) for another 5 minutes with the aid of an exit needle on the septum. A stirring rate was established at 900 rpm. The reaction tube was irradiated with visible light, a common 7 W Blue LED ribbon (λ_{max} ~460 nm) under stirring. The distance between the light source and the reaction flask was maintained approximately 3-4 cm, resulted in the temperature increasing up to 35 °C. The tube was then submerged in an insulated bath to maintain temperature. For safety reasons, the reaction was carried out behind an anti-blast shield. The reaction was stirred until the complete consumption of starting material, typically for 6-12 h (adjudged by TLC). The reaction mixture was diluted with DCM (10 mL), guenched with saturated NaHCO₃ (5 mL) and saturated aqueous sodium thiosulfate (2 mL) and extracted with DCM (3×30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na2SO4, concentrated in vacuo and purified by silica gel column chromatography (using gradient eluent of hexanes/EtOAc) to obtain the desired iodovinyl sulfone 4-33 or vinyl sulfone 34-43.



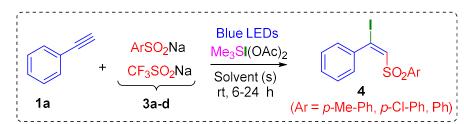
Light and Equipment Setup for the Photochemical Reaction:

Figure S1. Reaction conditions for visible light mediated sulfonylation; (A) Blue LED irradiation setup, (B) Reaction vessel and insulated bath with circulation pipes (inlet, outlet), N_2 ballon and vaccum tubing. (C) The complete reaction setup with reaction vessel, insulated bath, chiller and the circulation tubings.

B. Optimizations Studies.

 Table S1. Preliminary Studies and Optimization of (E)-Stereospecific Sulfonylation using

 Sulfonium Iodate Reagent.^a



S. No	Reagent (equiv)	3a-d (equiv)	Solvent	Yield % ^b
1.	Me ₃ SI(OAc) ₂ (1.2)	pTsNa (1.5) (3a)	MeCN	4a ; 37
2.	$Me_3SI(OAc)_2$ (1.2)	pTsNa (1.5) (3a)	DCE	4a ; 68
3.	$Me_3SI(OAc)_2(1.2)$	pTsNa (1.5) (3a)	THF	4a ; 69
4.	$Me_3SI(OAc)_2(1.2)$	pTsNa (1.5) (3a)	1,4-Dioxane	4a ; 65
5.	$Me_3SI(OAc)_2$ (1.2)	pTsNa (1.5) (3a)	AcOH	4a ; 71
6.	$Me_3SI(OAc)_2$ (1.2)	pTsNa (1.5) (3a)	DMF	4a ; 49
7.	$Me_3SI(OAc)_2$ (1.2)	pTsNa (1.5) (3a)	Toluene	4a ; 38
8.	$Me_3SI(OAc)_2 (1.2)$	pTsNa (1.5) (3a)	H ₂ O	4a ; 50
9.	$Me_3SI(OAc)_2 (1.2)$	pTsNa (1.5) (3a)	MeCN: H ₂ O; 2:1	4a ; 54
10.	Me ₃ SI(OAc) ₂ (1.2)	pTsNa (1.5) (3a)	MeCN: AcOH; 2:1	4a; 86
11.°	$Me_3SI(OAc)_2 (1.2)$	pTsNa (1.5) (3a)	MeCN: AcOH; 2:1	4a; 28
12. ^d	$Me_3SI(OAc)_2 (1.2)$	pTsNa (1.5) (3a)	MeCN: AcOH; 2:1	4a; 41
13. ^e	$Me_3SI(OAc)_2 (1.2)$	pTsNa (1.5) (3a)	MeCN: AcOH; 2:1	4a; 53
14.	$Me_3SI(OAc)_2 (1.2)$	4-Cl PhSO ₂ Na (1.5) (3b)	MeCN: AcOH; 2:1	4b ; 76
15.	$Me_3SI(OAc)_2 (1.2)$	PhSO ₂ Na (1.5) (3c)	MeCN: AcOH; 2:1	4c ; 60
16.	$Me_3SI(OAc)_2 (1.2)$	CF ₃ SO ₂ Na (1.5) (3d)	MeCN: AcOH; 2:1	4d ; NR

^a Reaction conditions: Phenyl acetylene **1a** (1.0 mmol, 1.0 equiv), $Me_3SI(OAc)_2$ (1.2 equiv), $ArSO_2Na$; **3a-3c** or CF_3SO_2Na ; **3d** (1.5 equiv), solvent (2 mL), stirred at 25 to 35 °C for 12 h, irradiated with Blue LEDs (7W), unless otherwise noted. ^b The isolated and unoptimized yields after chromatography. ^c The reaction was performed in dark condition. ^d The reaction was performed in light. ^e The reaction was performed in green LEDs.

Table S2. Screening of *(E)*-Stereospecific Vinyl-Sulfonylation using Sulfonium Iodate Reagent.^{*a*}

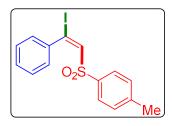


S. No	Reagent (equiv)	3a (equiv)	Solvent	Yield % ^b
1.	$Me_3SI(OAc)_2$ (1.5)	pTsNa (1.5)	MeCN	28
2.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	MeCN	57
3.	$Me_3SI(OAc)_2$ (1.2)	pTsNa (2.5)	MeCN	36
4.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	H_2O	20
5.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	AcOH	12
6.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	1,4-Dioxane	12
7.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	Toluene	18
8.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	MeOH	22
9.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	1,4-Dioxane	8
10.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	DCM	70
11.	Me ₃ SI(OAc) ₂ (1.5)	pTsNa (2.5)	MeCN	91
12. °	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	MeCN	33
13.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	CH ₃ CN: H ₂ O; 2:1	46
14.	$Me_{3}SI(OAc)_{2}$ (1.5)	pTsNa (2.5)	CH ₃ CN: AcOH; 1:2	27
15.	$Me_3SI(OAc)_2$ (1.5)	pTsNa (2.5)	CH ₃ CN: AcOH; 1:1	33
16.	$Me_3SI(OAc)_2$ (1.5)	pTsNa (2.5)	CH ₃ CN: AcOH; 2:1	32

^a Reaction conditions: 2a (1.0 mmol, 1.0 equiv), $Me_3SI(OAc)_2$ (1.5 equiv), $ArSO_2Na$ (2.5 equiv), solvent (2 mL), stirred at 25°C for 12 h, irradiated with a Blue LEDs (7W), unless otherwise noted. ^b The isolated and unoptimized yields after chromatography. ^c The reaction was performed in dark condition.

C. Chemical Synthesis and Spectroscopic Characterization Data.

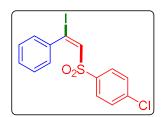
Representative Procedure for Iodovinyl sulfonylation:



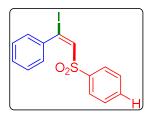
(*E*)-1-((2-iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (4a): A preformed solution of ethynylbenzene **1a** (102 mg, 1.0 mmol, 1.0 equiv) in CH₃CN:AcOH (2:1; 3 mL) was treated with 4-Methylphenyl sulfinic acid sodium salt (267 mg, 1.5 mmol, 1.5 equiv.) followed by Me₃SI(OAc)₂ (386 mg, 1.2 mmol, 1.2 equiv.) at room temperature (25 °C). The resulting mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED strips). Following the usual workup and purification by silica gel column chromatography using hexanes as eluent, the desired compound **4a** was obtained as pale-yellow oil (330 mg, 0.86 mmol, 86%). Rf (4% EtOAc/Hexane) 0.5; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (s, 1H), 7.31-7.25 (m, 3H), 7.24 (d, *J* = 1.5 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.52, 141.21, 139.60, 137.25, 129.72, 129.62, 127.86, 127.81, 127.64, 114.13, 21.58; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[1-10]

Procedure for Gram-scale synthesis of iodovinyl sulfone:

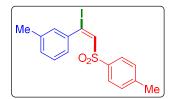
A preformed solution of ethynylbenzene **1a** (1 g, 9.804 mmol) in CH₃CN: AcOH (2:1; 10 mL) was treated with 4-Methylphenyl sulfinic acid sodium salt (2.6 g, 14.706 mmol, 1.5 equiv.) followed by $Me_3SI(OAc)_2$ (3.8 g, 11.765 mmol, 1.2 equiv.) at room temperature (25 °C). The resulting mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED). Following the usual workup and purification by silica gel column chromatography using hexanes as eluent, the desired compound **4a** was obtained as pale-yellow oil (3.0 g, 7.843 mmol, 80%). The overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[1-10]



(*E*)-1-chloro-4-((2-iodo-2-phenylvinyl)sulfonyl)benzene (4b): Following general iodovinyl sulfonylation procedure using ethynylbenzene 1a (90 mg, 100 µL, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (234 mg, 0.579 mmol, 76%). ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.44 (m, 2H), 7.39 (s, 1H), 7.34-7.27 (m, 5H), 7.20 (d, J = 1.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 140.94, 140.20, 139.44, 138.60, 129.94, 129.26, 129.22, 128.01, 127.60, 115.23; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[1, 4,7]

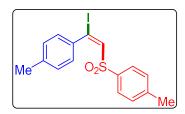


(*E*)-1-iodo-2-(phenylsulfonyl)vinyl)benzene (4c): Following general iodovinyl sulfonylation procedure using ethynylbenzene 1a (90 mg, 100 μ L, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (169 mg, 0.457 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.39 (s, 1H), 7.36-7.28 (m, 6H), 7.19 (dd, *J* = 8.2, 1.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 140.96, 140.20, 139.45, 138.62, 129.95, 129.27, 129.23, 128.01, 127.61, 115.22; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[1, 3-7]

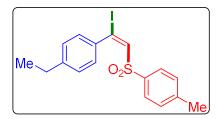


(E)-1-(1-iodo-2-tosylvinyl)-3-methylbenzene (5): Following general iodovinyl sulfonylation procedure using 1-ethynyl-3-methylbenzene **1b** (90 mg, 100 μ L, 0.775 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white

solid (194 mg, 0.488 mmol, 63%). ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.4 Hz, 2H), 7.35 (s, 1H), 7.20-7.15 (m, 3H), 7.10 (d, J = 7.9 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.92 (s, 1H), 2.40 (s, 3H), 2.28 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.41, 141.18, 139.52, 137.62, 137.34, 130.50, 129.51, 127.95, 127.88, 127.79, 124.74, 114.48, 21.56, 21.22; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[5]

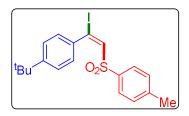


(*E*)-1-((1-iodo-2-(p-tolyl)vinyl)sulfonyl)-4-methylbenzene (6): Following general iodovinyl sulfonylation procedure using 1-ethynyl-4-methylbenzene 1c (92 mg, 100 μ L, 0.789 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (192 mg, 0.481 mmol, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.30 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.50, 140.57, 140.16, 137.39, 136.82, 129.61, 128.53, 127.83, 127.77, 114.73, 21.60, 21.43; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature. ^[2,5,7,10,15]

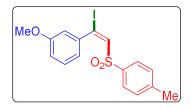


(*E*)-1-ethyl-4-(1-iodo-2-tosylvinyl)benzene (7): Following general iodovinyl sulfonylation procedure using 1-ethynyl-4-ethylbenzene 1d (93 mg, 100 μ L, 0.715 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (186 mg, 0.450 mmol, 63%). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.17 (dd, *J* = 8.2, 2.0 Hz, 4H), 7.10 (d, *J* = 8.3 Hz, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.40, 144.39, 140.85, 137.35, 136.95, 129.54, 127.91, 127.87, 127.34, 114.75, 28.71, 21.59, 15.28; the overall

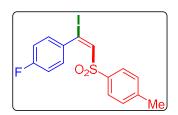
spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[2-4]



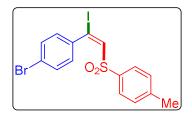
(*E*)-1-(*tert-butyl*)-4-(1-iodo-2-tosylvinyl)benzene (8): Following general iodovinyl sulfonylation procedure using 1-(tert-butyl)-4-ethynylbenzene 1e (88 mg, 100 µL, 0.557 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow semi-solid (159 mg, 0.362 mmol, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.37 (s, 1H), 7.25 (d, *J* = 9.9 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 4H), 2.37 (s, 3H), 1.32 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 153.21, 144.24, 141.21, 137.20, 136.56, 129.41, 127.87, 127.70, 124.77, 114.71, 34.78, 31.16, 31.07, 21.55; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature. ^[3]



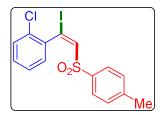
(*E*)-1-(1-iodo-2-tosylvinyl)-3-methoxybenzene (9): Following general iodovinyl sulfonylation procedure using 1-ethynyl-3-methoxybenzene 1f (104 mg, 100 µL, 0.787 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (209 mg, 0.504 mmol, 64%). Mp: 89-91 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.44 (m, 2H), 7.35 (s, 1H), 7.23-7.16 (m, 3H), 6.87-6.80 (m, 2H), 6.65 (dd, *J* = 2.6, 1.6 Hz, 1H), 3.76 (s, 3H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.65, 144.46, 141.46, 140.59, 137.11, 129.52, 128.96, 127.87, 119.97, 115.85, 113.55, 112.46, 55.16, 21.53; HRMS (ESI) *m*/*z* [M + NH₄]⁺ calculated for [C₁₆H₁₉NIO₃S]⁺: 432.0125; found: 432.0112.



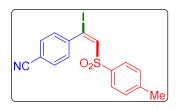
(*E*)-1-fluoro-4-(1-iodo-2-tosylvinyl)benzene (10): Following general iodovinyl sulfonylation procedure using 4-fluoro-2-ethynylbenzene **1g** (105 mg, 0.873 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (340 mg, 0.847 mmol, 97%). ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.35 (s, 1H), 7.26 (dd, *J* = 9.2, 4.8 Hz, 3H), 7.22 (s, 1H), 6.98 (t, *J* = 8.6 Hz, 2H), 2.41 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 163.17 (d, ¹*J*_{CF} = 251.4 Hz), 144.78, 141.61, 137.19, 135.67, 135.65 (d, ⁴*J*_{CF} = 3.6 Hz), 130.02, 129.98 (d, ³*J*_{CF} = 8.8 Hz), 127.78, 115.06 (d, ²*J*_{CF} = 22.1 Hz), 114.95, 112.54, 21.60; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[1,3]



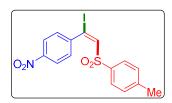
(*E*)-1-bromo-4-(1-iodo-2-tosylvinyl)benzene (11): Following general iodovinyl sulfonylation procedure using 4-bromo-2-ethynylbenzene **1h** (100 mg, 0.552 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (158 mg, 0.342 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.34 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.90, 141.73, 138.54, 137.09, 131.15, 129.79, 129.24, 127.87, 124.19, 111.93, 21.65; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[2,3,6]



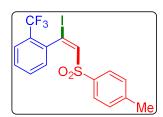
(*E*)-1-chloro-2-(1-iodo-2-tosy)vinyl)benzene (12): Following general iodovinyl sulfonylation procedure using 2-chloro-1-ethynylbenzene 1i (112 mg, 100 μ L, 0.817 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow solid (229 mg, 0.547 mmol, 67%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.36 (s, 1H), 7.29-7.27 (m, 3H), 7.25-7.21 (m, 3H), 2.40 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.44, 161.93, 141.50, 140.10, 135.55, 133.63, 130.07, 129.07, 127.73, 115.28, 115.20, 115.06, 114.98, 113.13; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[1]



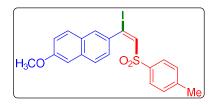
(*E*)-4-(1-iodo-2-tosylvinyl)benzonitrile (13): Following general iodovinyl sulfonylation procedure using 4-ethynyl benzonitrile 1j (100 mg, 0.787 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow semi solid (248 mg, 0.606 mmol, 77%). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.60 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.38-7.34 (m, 3H), 7.27 (d, *J* = 9.6 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.26, 144.08, 142.22, 136.80, 131.69, 129.99, 128.20, 127.80, 117.97, 113.28, 109.76, 21.65; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[2]



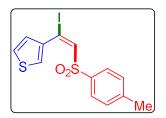
(*E*)-1-((1-iodo-2-(4-nitrophenyl)vinyl)sulfonyl)-4-methylbenzene (14): Following general iodovinyl sulfonylation procedure using 1-ethynyl-4-nitrobenzene 1k (100 mg, 0.680 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (277 mg, 0.646 mmol, 95%). ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.31 (s, 1H), 7.21 (d, J = 7.8 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.01, 145.94, 145.39, 142.38, 136.75, 130.05, 128.48, 127.83, 123.20, 109.11, 21.66; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature. ^[4]



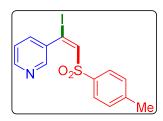
(*E*)-1-(1-iodo-2-tosylvinyl)-2-(trifluoromethyl)sulfonyl)benzene (15): Following general iodovinyl sulfonylation procedure using 1-ethynyl-2-(trifluoromethyl)benzene 11 (150 mg, 100 μ L, 0.829 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (273 mg, 0.605 mmol, 73%). Mp: 154-156 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 3H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.28 (s, 3H), 7.26 (s, 1H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.39 (d, ¹*J*_{CF} = 251.9 Hz), 140.85, 137.15 (d, ²*J*_{CF} = 50.5 Hz), 129.54, 127.89 (d, ⁴*J*_{CF} = 4.8 Hz), 127.34, 114.75, 25.15 (d, ³*J*_{CF} = 8.9 Hz), 15.28; HRMS (ESI) *m*/*z* [M + NH₄]⁺ calculated for [C₁₆H₁₆NF₃IO₂S]⁺: 469.9893; found: 469.9879.



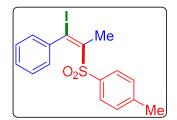
(*E*)-2-(1-iodo-2-tosylvinyl)-6-methoxynaphthalene (16): Following general iodo vinyl sulfonylation procedure using 2-ethynyl-6-methoxynaphthalene 1m (100 mg, 0.549 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow solid (209 mg, 0.450 mmol, 82%). Mp: 126-128 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 9.2 Hz, 2H), 7.43 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.24-7.16 (m, 2H), 7.10 (d, *J* = 2.5 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H), 2.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.90, 144.42, 141.25, 137.32, 134.96, 134.50, 130.07, 129.44, 127.86, 127.43, 127.32, 126.48, 125.61, 119.65, 114.92, 105.75, 55.39, 21.52; HRMS (ESI) m/z [M + NH₄]⁺ calculated for [C₂₀H₂₁NIO₃S]⁺: 482.0281; found: 482.0267.



(*E*)-3-(1-iodo-2-tosylvinyl)thiophene (17): Following general iodovinyl sulfonylation procedure using 3-ethynylthiophene **1n** (100 mg, 0.926 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow semi solid (224 mg, 0.574 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.51 (m, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.28 (s, 1H), 7.13 (d, *J* = 8.3 Hz, 3H), 6.90 (dd, *J* = 5.1, 1.3 Hz, 1H), 2.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.50, 141.31, 138.68, 137.09, 129.54, 128.34, 127.60, 127.51, 125.26, 107.45, 21.56; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[1-3,7]

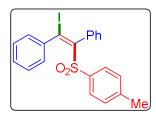


(*E*)-3-(1-iodo-2-tosylvinyl)pyridine (18): Following general iodovinyl sulfonylation procedure using 3-ethynyl pyridine 10 (100 mg, 0.971 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (224 mg, 0.583 mmol, 60%). Mp: 150-152 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.56 (dd, J = 4.9, 1.6 Hz, 1H), 8.45 (dd, J = 2.4, 0.9 Hz, 1H), 7.64-7.60 (m, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.44 (s, 1H), 7.30-7.25 (m, 3H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.37, 147.49, 145.13, 142.72, 136.97, 136.03, 135.21, 129.99, 127.80, 122.62, 108.99, 21.65; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[3]

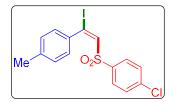


(*E*)-1-((1-iodo-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (19): Following general iodovinyl sulfonylation procedure using prop-1-yn-1-ylbenzene 1p (93 mg, 0.704 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (174 mg, 0.436 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.4 Hz, 2H), 7.24-7.21 (m, 3H), 7.16 (d, J = 8.5 Hz, 2H), 7.12-7.09 (m, 2H), 2.51 (s, 3H), 2.39 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.13, 143.89, 142.94, 137.22, 129.50, 129.42,

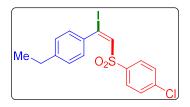
128.59, 127.67, 127.56, 115.73, 27.05, 21.60; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[2,3]



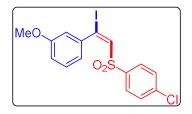
(*E*)-(*1-iodo-2-tosylethene-1,2-diyl*)*dibenzene* (20): Following general iodovinyl sulfonylation procedure using 1,2-diphenylethyne **1q** (100 mg, 0.561 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (170 mg, 0.370 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.24 (m, 8H), 7.20-7.16 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 2.29 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 149.00, 144.23, 142.46, 139.30, 136.67, 130.23, 129.16, 128.96, 128.48, 128.29, 127.81, 127.31, 118.05, 21.59; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[2]



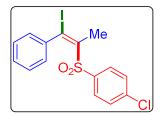
(*E*)-1-chloro-4-((2-iodo-2-(p-tolyl)vinyl)sulfonyl)benzene (21): Following general iodovinyl sulfonylation procedure using 1-ethynyl-4-methylbenzene 1c (92 mg, 100 µL, 0.789 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (257 mg, 0.615 mmol, 78%). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 10.1 Hz, 3H), 7.14-7.07 (m, 4H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 140.46, 140.27, 140.15, 138.66, 136.62, 129.27, 129.17, 128.62, 127.70, 115.83, 21.43; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[5-7]



(*E*)-1-chloro-4-((2-(4-ethylphenyl)-2-iodovinyl)sulfonyl)benzene (22): Following general iodovinyl sulfonylation procedure using 1-ethynyl-4-ethylbenzene 1d (93 mg, 100 μ L, 0.715 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (232 mg, 0.536 mmol, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.36 (s, 1H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.13-7.07 (m, 4H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.68, 140.51, 140.02, 138.55, 136.71, 129.28, 129.03, 127.78, 127.42, 115.74, 28.68, 15.36; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[4]

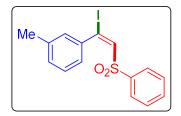


(*E*)-1-(2-((4-chlorophenyl)sulfonyl)-1-iodovinyl)-3-methoxybenzene (23): Following iodovinyl sulfonylation procedure using 1-ethynyl-3-methoxybenzene **1f** (104 mg, 100 μ L, 0.787 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow semi solid (225 mg, 0.519 mmol, 66%). Mp: 73-75 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.7 Hz, 2H), 7.38 (s, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.19 (dd, *J* = 8.4, 7.6 Hz, 1H), 6.85 (dd, *J* = 8.4, 3.6 Hz, 1H), 6.78 (dd, *J* = 7.6, 2.6 Hz, 1H), 6.60 (dd, *J* = 2.6, 1.7 Hz, 1H), 3.77 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.72, 141.28, 140.57, 140.18, 133.39, 129.05, 128.91, 127.85, 120.04, 116.02, 114.16, 112.59, 55.27; HRMS (ESI) *m/z* [M + NH₄]⁺ calculated for [C₁₅H₁₆NCIIO₃S]⁺: 451.9579; found: 451.9566.

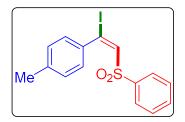


(E)-1-chloro-4-((1-iodo-1-phenylprop-1-en-2-yl)sulfonyl)benzene (24): Following general iodovinyl sulfonylation procedure using prop-1-yn-1-ylbenzene 1p (93 mg, 0.704 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow solid (188 mg, 0.451 mmol, 64%). Mp: 121-123 °C; ¹H NMR (400

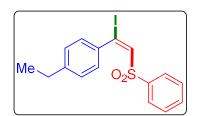
MHz, CDCl₃) δ 7.37 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 7.24-7.20 (m, 3H), 7.06 (dd, J = 7.6, 2.0 Hz, 2H), 2.55 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 143.99, 142.58, 139.75, 138.81, 129.05, 129.03, 128.83, 127.76, 127.70, 116.15, 26.82; HRMS (ESI) m/z [M + H]⁺ calculated for [C₁₅H₁₃ClIO₂S]⁺: 418.9364; found: 418.9365.



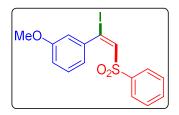
(*E*)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-3-methylbenzene (25): Following general iodovinyl sulfonylation procedure using 1-ethynyl-3- methylbenzene **1b** (90 mg, 100 µL, 0.775 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (187 mg, 0.488 mmol, 63%). ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.51 (m, 3H), 7.40-7.34 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.90 (s, 1H), 2.26 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 140.92, 140.14, 139.36, 137.60, 133.27, 130.55, 128.80, 127.86, 127.79, 127.75, 124.66, 115.05, 21.20; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[5-7]



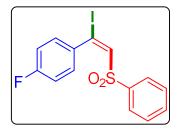
(*E*)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-4-methylbenzene (26): Following general iodovinyl sulfonylation procedure using 1-ethynyl-4-methylbenzene 1c (92 mg, 100 μ L, 0.789 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow solid (182 mg, 0.473 mmol, 60%).¹H NMR (400 MHz, CDCl₃) δ 7.62-7.58 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.42-7.37 (m, 2H), 7.33 (s, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 2.35 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 140.50, 140.42, 140.20, 136.68, 133.40, 128.97, 128.64, 128.46, 127.72, 115.32, 21.37; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[5-7]



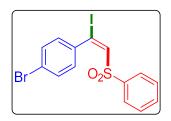
(*E*)-1-ethyl-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (27): Following general iodovinyl sulfonylation procedure using 1-ethynyl-4-ethylbenzene 1d (93 mg, 100 µL, 0.715 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (211 mg, 0.529 mmol, 74%). ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 7.7 Hz, 2H), 7.51 (d, J = 7.4 Hz, 1H), 7.39-7.33 (m, 3H), 7.15 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 2.63 (q, J = 7.6 Hz, 2H), 1.24 (t, J = 7.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.37, 140.53, 140.11, 136.75, 133.30, 128.80, 127.69, 127.31, 115.34, 28.60, 15.24; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[4]



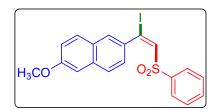
(*E*)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-3-methoxybenzene (28): Following general iodovinyl sulfonylation procedure using 1-ethynyl-3-methoxybenzene 1f (104 mg, 100 μ L, 0.787 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as a white solid (208 mg, 0.519 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.52 (m, 3H), 7.41-7.36 (m, 3H), 7.20 -7.15 (m, 1H), 6.86-6.79 (m, 2H), 6.67-6.65 (m, 1H), 3.76 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.84, 141.24, 140.47, 140.16, 138.56, 129.35, 129.14, 119.94, 115.95, 114.54, 112.60, 55.28; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[5]



(E)-1-fluoro-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (29): Following general iodovinyl sulfonylation procedure using 4-fluoro-2-ethynylbenzene **1g** (105 mg, 0.873 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (203 mg, 0.524 mmol, 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.48 (m, 3H), 7.36 (dd, J = 8.2, 7.4 Hz, 2H), 7.31 (s, 1H), 7.20-7.15 (m, 2H), 6.90 (t, J = 8.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 163.18 (d, ¹ $J_{CF} = 251.6$ Hz), 141.50, 140.10, 134.59 (d, ² $J_{CF} = 193.2$ Hz), 130.07, 129.07, 127.73, 115.13 (dd, ³ $J_{CF} = 21.9$, 7.4 Hz), 114.98, 113.13; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[5-7]

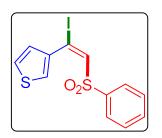


(*E*)-1-bromo-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (30): Following general iodovinyl sulfonylation procedure using 4-bromo-2-ethynylbenzene 1h (100 mg, 0.552 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (161 mg, 0.359 mmol, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.0 Hz, 2H), 7.43 (dd, J = 16.4, 6.9 Hz, 5H), 7.36 (d, J = 1.4 Hz, 1H), 7.13-7.08 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.13, 140.51, 138.38, 138.29, 131.22, 129.42, 129.23, 129.13, 124.40, 113.20; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature. ^[6,7]

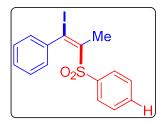


(*E*)-2-(1-iodo-2-phenylsulfonyl)vinyl)-6-methoxynaphthalene (31): Following general iodovinyl sulfonylation procedure using 2-ethynyl-6-methoxynaphthalene 1m (100 mg, 0.549 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow solid (149 mg, 0.329 mmol, 60%). Mp: 108-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.63 (m, 2H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.52-7.42 (m, 4H), 7.26-7.22 (m, 2H), 7.18 (ddd, *J* = 8.9, 3.6, 2.2 Hz, 2H), 7.09 (d, *J* = 2.5 Hz, 1H), 3.93 (s, 3H); ¹³C NMR

(101 MHz, CDCl₃) δ 158.93, 141.08, 141.01, 140.92, 140.85, 140.21, 134.95, 134.35, 133.30, 130.11, 128.81, 128.72, 127.76, 127.37, 127.32, 126.55, 125.56, 125.45, 119.77, 119.66, 115.64, 105.78, 105.64, 55.36; HRMS (ESI) m/z [M + NH₄]⁺ calculated for [C₁₉H₁₉NIO₃S]⁺: 468.0125; found: 468.0112.

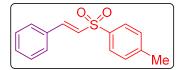


(*E*)-3-(1-iodo-2-(phenylsulfonyl)vinyl)thiophene (32): Following general iodovinyl sulfonylation procedure using 3-ethynylthiophene **1n** (100 mg, 0.926 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow semi solid (230 mg, 0.611 mmol, 66%). ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.57 (m, 3H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43-7.36 (m, 3H), 7.19 (dd, *J* = 5.1, 3.1 Hz, 1H), 6.92 (dd, *J* = 5.1, 1.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 141.12, 139.98, 138.63, 133.43, 128.89, 128.24, 127.53, 125.39, 107.96; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature. ^[1-3]



(*E*)-1-((1-iodo-1-phenylprop-1-en-2-yl)sulfonyl)benzene (33): Following general iodo vinyl sulfonylation procedure using prop-1-yn-1-ylbenzene 1p (93 mg, 0.704 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow solid (173 mg, 0.451 mmol, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.46 (m, 3H), 7.36 (d, *J* = 7.3 Hz, 2H), 7.22-7.18 (m, 3H), 7.09-7.06 (m, 2H), 2.53 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 143.85, 142.69, 140.20, 133.05, 128.74, 127.56, 116.03, 26.89; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[7]

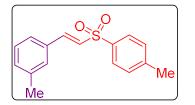
Representative Procedure for Vinyl sulfonylation:



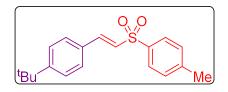
(*E*)-1-methyl-4-(styrylsulfonyl)benzene (34): A preformed solution of styrene 2a (104 mg, 1.0 mmol, 1.0 equiv) in CH₃CN (3 mL) was treated with 4-Methylphenyl sulfinic acid sodium salt (445 mg, 2.5 mmol, 2.5 equiv.) followed by Me₃SI (306 mg, 1.5 mmol, 1.5 equiv) and PhI(OAc)₂ (483 mg, 1.5 mmol, 1.5 equiv) generating Me₃SI(OAc)₂ *in-situ* at room temperature (25 °C). The resulting mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED strips). Following the usual workup and purification by silica gel column chromatography using hexanes as eluent, the desired compound **34** was obtained as white solid (235 mg, 0.91 mmol, 91%). Rf (4% EtOAc/Hexane) 0.5; ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 15.4 Hz, 1H), 7.46 (d, *J* = 5.7 Hz, 2H), 7.40-7.31 (m, 5H), 6.87 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.37, 141.90, 137.67, 132.40, 131.07, 129.94, 129.03, 128.49, 127.67, 127.55, 21.57; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[10-17]

Procedure for Gram-scale synthesis of vinyl sulfone:

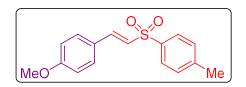
A preformed solution of styrene **2a** (1.1 g, 10.576 mmol) in CH₃CN (10 mL) was treated with 4-Methylphenyl sulfinic acid sodium salt (4.7 g, 26.44 mmol, 2.5 equiv.) followed by Me₃SI (3.2 g, 15.865 mmol, 1.5 equiv) and PhI(OAc)₂ (5.1 g, 15.865 mmol, 1.5 equiv) generating Me₃SI(OAc)₂ *in-situ* at room temperature (25 °C). The resulting mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED). Following the usual workup and purification by silica gel column chromatography using hexanes as eluent, the desired compound **34** was obtained as white solid (3.4 g, 8.989 mmol, 85%). The overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[10-17]



(*E*)-1-methyl-3-(2-tosylvinyl)benzene (35): Following general vinyl sulfonylation procedure using 1-methyl-3-vinylbenzene **2b** (90 mg, 0.762 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as dark yellow solid (126 mg, 0.465 mmol, 61%). ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 5.3 Hz, 3H), 7.21 (d, *J* = 2.9 Hz, 1H), 6.84 (dd, *J* = 15.4, 2.5 Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.26, 142.03, 138.70, 137.69, 132.26, 131.86, 129.86, 129.00, 128.85, 127.58, 127.22, 125.68, 21.52, 21.16; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[11,13,16]

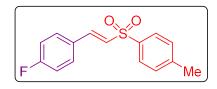


(*E*)-1-(*tert-butyl*)-4-(2-tosylvinyl)sulfonyl)benzene (36): Following general vinyl sulfonylation procedure using 1-(tert-butyl)-4-vinylbenzene 2c (90 mg, 0.562 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (109 mg, 0.348 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 15.4 Hz, 1H), 7.31 (d, J = 2.2 Hz, 4H), 7.22 (d, J = 7.9 Hz, 2H), 6.74 (d, J = 15.4 Hz, 1H), 2.32 (s, 3H), 1.20 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 154.68, 144.12, 141.77, 137.79, 129.80, 129.51, 128.29, 127.48, 126.44, 125.91, 34.81, 30.94, 21.47; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[11,13,14]

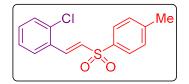


(*E*)-1-methoxy-4-(2-tosylvinyl)sulfonyl)benzene (37): Following general vinyl sulfonylation procedure using 1-methoxy-4-vinylbenzene 2d (100 mg, 0.746 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale yellow semi solid (146 mg, 0.507 mmol, 68%).¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.62 (s, 1H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 7.4 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 15.3 Hz, 1H), 3.83 (s, 3H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 161.93, 144.09, 141.69, 138.14, 130.26, 129.85, 127.51, 125.01, 124.76, 114.44, 55.38, 21.54; the

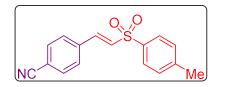
overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[10,16,17]



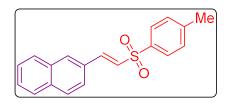
(E)-1-fluoro-4-(2-tosylvinyl)sulfonyl)benzene (38): Following general vinyl sulfonylation procedure using 1-fluoro-4-vinylbenzene **2e** (100 mg, 0.819 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (140 mg, 0.508 mmol, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.47 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 164.21 (d, ¹*J*_{CF} = 252.8 Hz), 144.43, 140.54, 137.53, 130.53, 130.49 (d, ⁴*J*_{CF} = 8.7 Hz), 127.45 (d, ²*J*_{CF} = 36.6 Hz), 116.22 (d, ³*J*_{CF} = 22.1 Hz), 21.56; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[11-14,16]



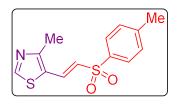
(*E*)-1-chloro-2-(2-tosylvinyl)sulfonyl)benzene (39): Following general vinyl sulfonylation procedure using 1-chloro-2-vinylbenzene 2f (110 mg, 0.797 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (152 mg, 0.518 mmol, 65%). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 15.6 Hz, 1H), 7.77 (t, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.27 (q, *J* = 6.9 Hz, 3H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 15.2 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.57, 137.82, 137.28, 135.23, 131.78, 130.74, 130.34, 130.00, 128.17, 127.85, 127.16, 21.60; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[10,13,14]



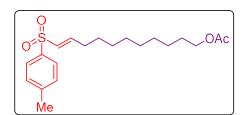
(*E*)-4-(tosylvinyl)sulfonyl)benzonitrile (40): Following general vinyl sulfonylation procedure using 1-cyano-4-vinylbenzene **2g** (110 mg, 0.853 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (198 mg, 0.699 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ 7.78-7.73 (m, 2H), 7.57 (d, *J* = 17.6 Hz, 3H), 7.53-7.48 (m, 2H), 7.32-7.27 (m, 2H), 6.91 (dd, *J* = 15.5, 2.0 Hz, 1H), 2.37 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.94, 139.18, 136.78, 136.65, 132.68, 131.27, 130.09, 128.82, 127.83, 117.99, 114.09, 21.58; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[11,12,14,17]



(*E*)-2-(2-tosylvinyl)naphthalene (41): Following general vinyl sulfonylation procedure using 2-vinylnaphthalene **2h** (100 mg, 0.649 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as white solid (128 mg, 0.415 mmol, 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.24 (m, 7H), 7.20-7.16 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 2.29 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 149.00, 144.23, 142.46, 139.30, 136.67, 130.23, 129.16, 128.96, 128.48, 128.29, 127.81, 127.31, 118.05, 21.59; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[12-14,16,17]

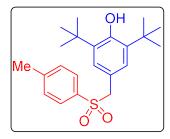


(*E*)-4-methyl-5-(2-tosylvinyl)thiazole (42): Following general vinyl sulfonylation procedure using 4-methyl-5-vinylthiazole 2i (109 mg, 0.872 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as yellow solid (199 mg, 0.715 mmol, 82%). Mp: 122-124 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 1H), 7.85-7.77 (m, 3H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.59 (d, *J* = 15.0 Hz, 1H), 2.59 (s, 3H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 157.19, 153.72, 144.53, 137.28, 131.02, 129.95, 128.37, 127.61, 126.01, 21.51, 15.62; HRMS (ESI) *m*/*z* [M + H]⁺ calculated for [C₁₃H₁₄NO₂S₂]⁺: 280.0460; found: 280.0461.

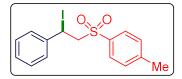


(*E*)-11-tosylundec-10-en-1-yl acetate (43): Following general vinyl sulfonylation procedure using undec-10-en-1-yl acetate **2j** (100 mg, 0.505 mmol) and purified by silica gel column chromatography, eluting with hexanes afforded the title compound as pale-yellow liquid (140 mg, 0.384 mmol, 76%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.37-7.30 (m, 2H), 7.01-6.89 (m, 1H), 6.30 (dd, *J* = 15.1, 1.6 Hz, 1H), 4.04 (td, *J* = 6.8, 2.2 Hz, 2H), 2.43 (d, *J* = 2.4 Hz, 3H), 2.26-2.17 (m, 2H), 2.04 (d, *J* = 2.4 Hz, 3H), 1.60 (dd, *J* = 10.4, 4.2 Hz, 2H), 1.50-1.39 (m, 2H), 1.26 (s, 10H); ¹³C NMR (101 MHz, CDCl₃) δ 171.15, 146.54, 144.05, 137.64, 130.44, 129.75, 127.47, 64.47, 31.31, 29.17, 29.04, 29.02, 28.86, 28.43, 27.43, 25.73, 21.48, 20.92; HRMS (ESI) *m/z* [M + H]⁺ calculated for [C₂₀H₃₁O₄S]⁺: 367.1938; found: 367.1938.

D. Mechanistic Studies and spectroscopic data.

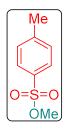


2,6-di-tert-butyl-4-(tosylmethyl)phenol (44): A preformed solution of PhI(OAc)₂ (646 mg, 2.006 mmol, 2.2 equiv.), Me₃SI (409 mg, 2.006 mmol, 2.2 equiv.), p-TsNa (487 mg, 2.735 mmol, 3.0 equiv.) and BHT (802 mg, 3.647 mmol, 4.0 equiv.) dissolved in 5 mL of MeCN: AcOH in 2:1 ratio, was treated with phenyl acetylene (1a) (93 mg, 100 µL, 0.912 mmol, 1.0 equiv.) at room temperature. The mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED strips). The distance between the light source and the reaction flask was approximately 3-4 cm, resulted in the temperature increasing up to 35 °C. For safety reasons, the reaction was carried out behind an antiblast shield. The reaction was stirred until the completion of starting material, typically for 15 h (adjudged by TLC). The reaction mixture was diluted with DCM (10 mL), guenched with saturated NaHCO₃ (5 mL) and saturated aqueous sodium thiosulfate (2 mL) and extracted with DCM (3×30 mL). The combined organic layers were washed with brine solution, dried over anhydrous Na₂SO₄, concentrated in vacuo and purified by silica gel column chromatography using hexanes as eluent to afford the compound 44 as white solid (246 mg, 0.657 mmol, 72%). Rf (10% EtOAc) 0.5; Mp: 133-135 °C; IR (Film): 3565, 2958, 1745, 1431, 1292, 1229, 1138, 887, 790, 755, 636, 518 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.3 Hz, 2H), 7.29-7.15 (m, 2H), 6.73 (s, 2H), 5.27 (d, J = 21.2 Hz, 1H), 4.19 (s, 2H), 2.41 (s, 3H), 1.32 (s, 18H); ¹³C NMR (101 MHz, CDCl₃) δ 154.15, 144.29, 135.90, 134.81, 129.25, 128.85, 127.62, 118.86, 63.19, 34.06, 29.98, 21.50; HRMS (ESI) m/z [M + NH₄]⁺ calculated for [C₂₂H₃₄NO₃S]⁺: 392.2254; found: 392.2256.



(*R*)-1-((2-iodo-2-phenylethyl)sulfonyl0-4-methylbenzene (45): A preformed solution of styrene 2a (91 mg, 100 µL, 0.871 mmol, 1.0 equiv) in CH₃CN:AcOH (2:1; 3 mL) was treated

with 4-Methylphenyl sulfinic acid sodium salt (233 mg, 1.306 mmol, 1.5 equiv.) followed by Me₃SI (215 mg, 1.045 mmol, 1.2 equiv) and PhI(OAc)₂ (337 mg, 1.045 mmol, 1.2 equiv) generating Me₃SI(OAc)₂ *in-situ* at room temperature (25 °C). The resulting mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED strips). Following the usual workup and purification by silica gel column chromatography using hexanes as eluent, the desired compound **45** was obtained as white solid (222 mg, 0.575 mmol, 66%). Rf (4% EtOAc/Hexane) 0.5; ¹H NMR (400 MHz, CDCl₃) δ 7.85-7.77 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32-7.21 (m, 5H), 5.27-5.21 (m, 1H), 3.47 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.30 (dd, *J* = 14.3, 1.8 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.07, 140.66, 136.00, 129.92, 128.56, 128.10, 127.86, 125.53, 68.30, 63.78, 21.51; the overall spectroscopic data are in complete agreement with assigned structures and consistent with literature.^[18,19]



Methyl-4-methylbenzene sulfonate (46): A preformed solution of styrene **2a** (91 mg, 100 μ L, 0.871 mmol) in MeOH (3 mL) was treated with 4-Methylphenyl sulfinic acid sodium salt (388 mg, 2.178 mmol, 2.5 equiv.) followed by Me₃SI (266 mg, 1.3067 mmol, 1.5 equiv) and PhI(OAc)₂ (421 mg, 1.3067 mmol, 1.5 equiv) generating Me₃SI(OAc)₂ *in-situ* at room temperature (25 °C). The resulting mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED strips). Following the usual workup and purification by silica gel column chromatography using hexanes as eluent, the desired compound **46** was obtained as white solid (110 mg, 0.592 mmol, 68%). Rf (4% EtOAc/Hexane) 0.5; ¹H NMR (400 MHz, CDCl₃) 7.69 (d, *J* = 8.3 Hz, 2H), 7.30-7.24 (m, 2H), 3.63 (s, 3H), 2.35 (s, 3H).



Ethyl-4-methylbenzene sulfonate (47): A preformed solution of styrene **2a** (91 mg, 100 μ L, 0.871 mmol) in EtOH (3 mL) was treated with 4-Methylphenyl sulfinic acid sodium salt (388 mg, 2.178 mmol, 2.5 equiv.) followed by Me₃SI (266 mg, 1.3067 mmol, 1.5 equiv) and PhI(OAc)₂ (421 mg, 1.3067 mmol, 1.5 equiv) generating Me₃SI(OAc)₂ *in-situ* at room temperature (25 °C). The resulting mixture was stirred under nitrogen atmosphere and irradiated with visible light (7 W Blue LED strips). Following the usual workup and purification by silica gel column chromatography using hexanes as eluent, the desired compound **47** was obtained as white solid (157 mg, 0.784 mmol, 90%). Rf (4% EtOAc/Hexane) 0.5; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H).

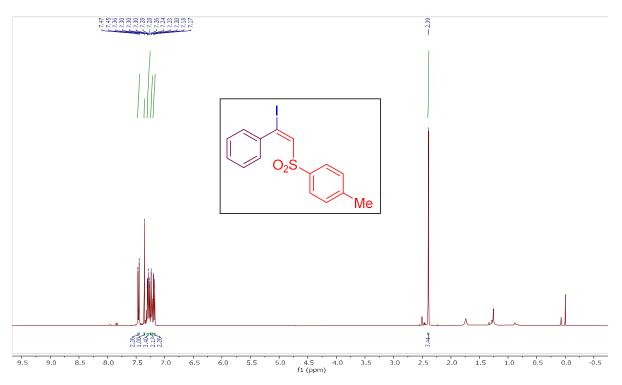
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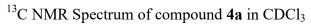
mediated reaction of aryl Sulfinates with alkenes, alkynes, and α , β -unsaturated carbonyl compounds: synthesis of vinyl sulfones and β -iodovinyl sulfones.

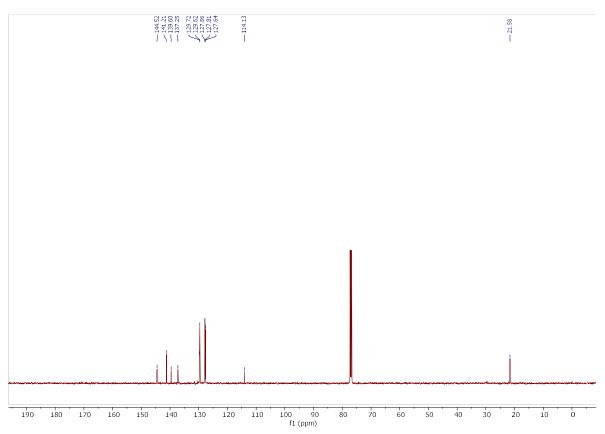
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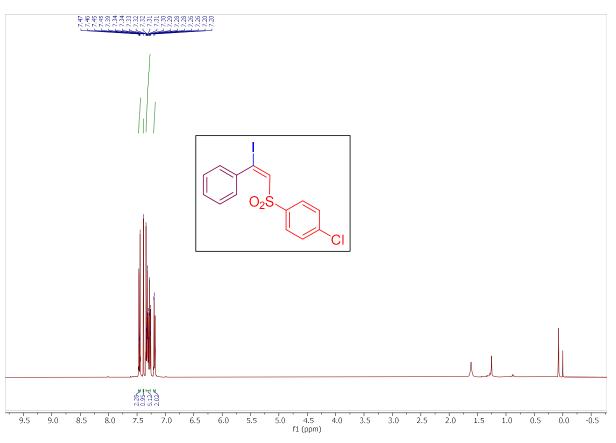
F. ¹H and ¹³C NMR Spectra.



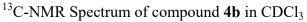
¹H NMR Spectrum of compound **4a** in CDCl₃

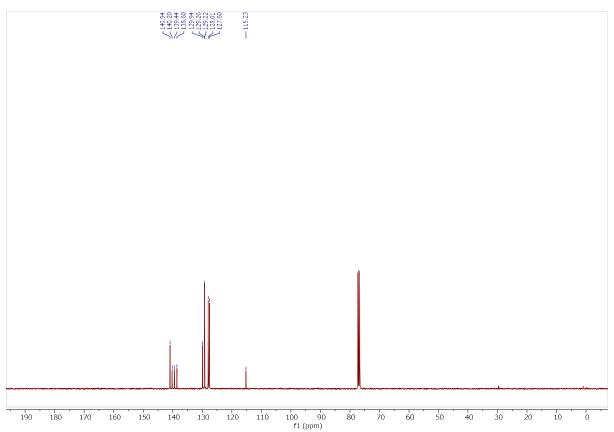


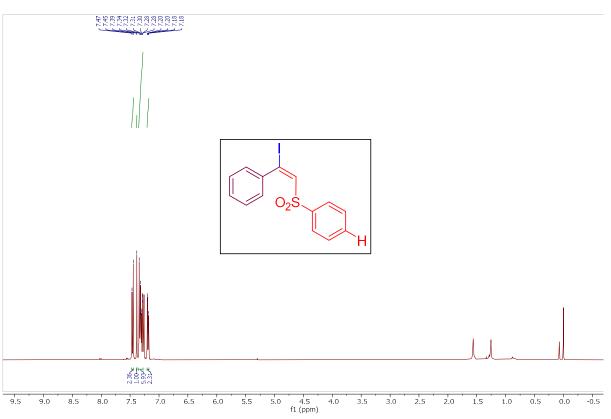




$^1\text{H-NMR}$ Spectrum of compound 4b in CDCl_3

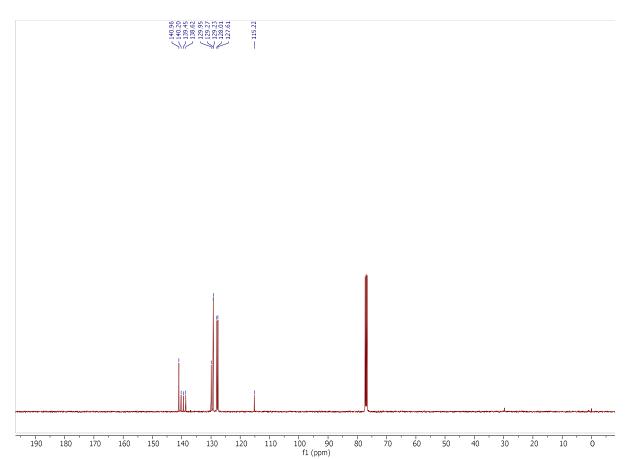


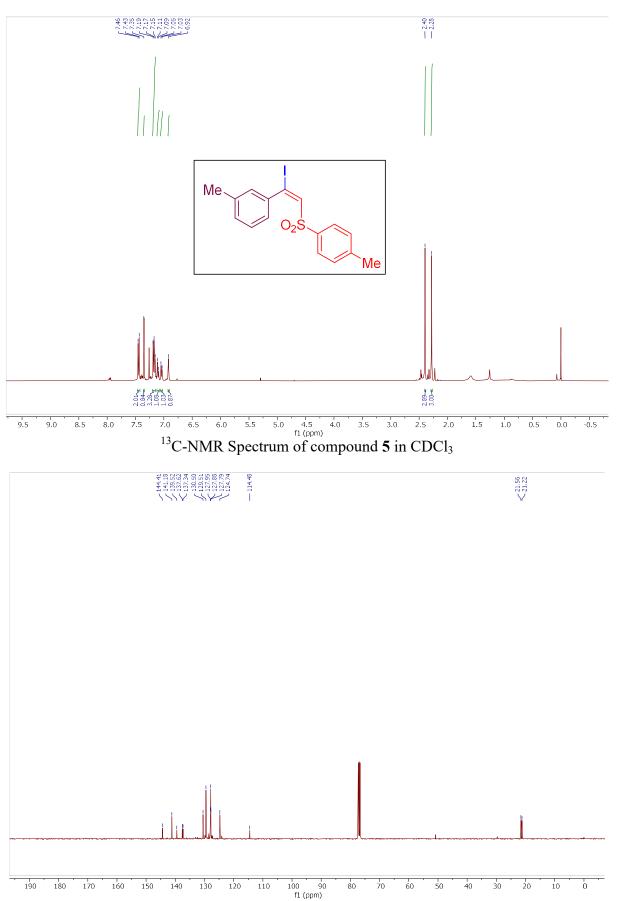




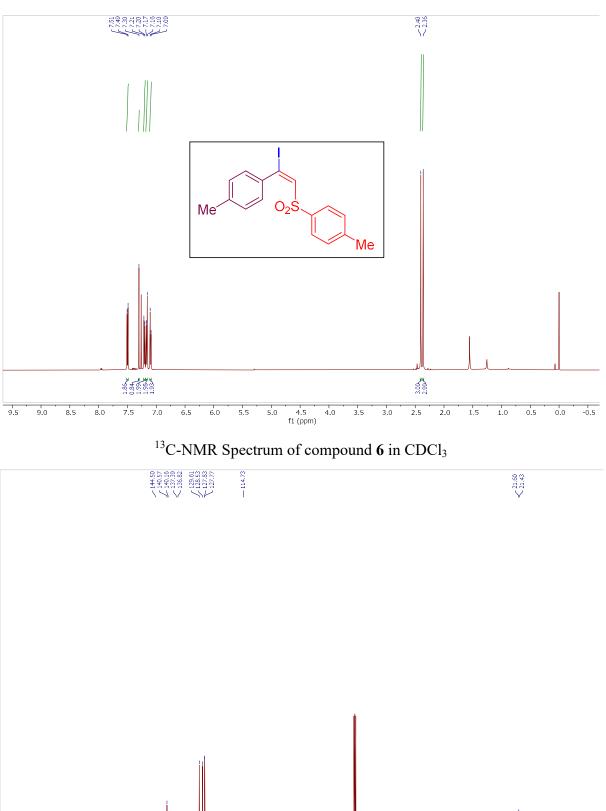
^1H NMR Spectrum of compound 4c in CDCl_3

 ^{13}C NMR Spectrum of compound 4c in CDCl₃

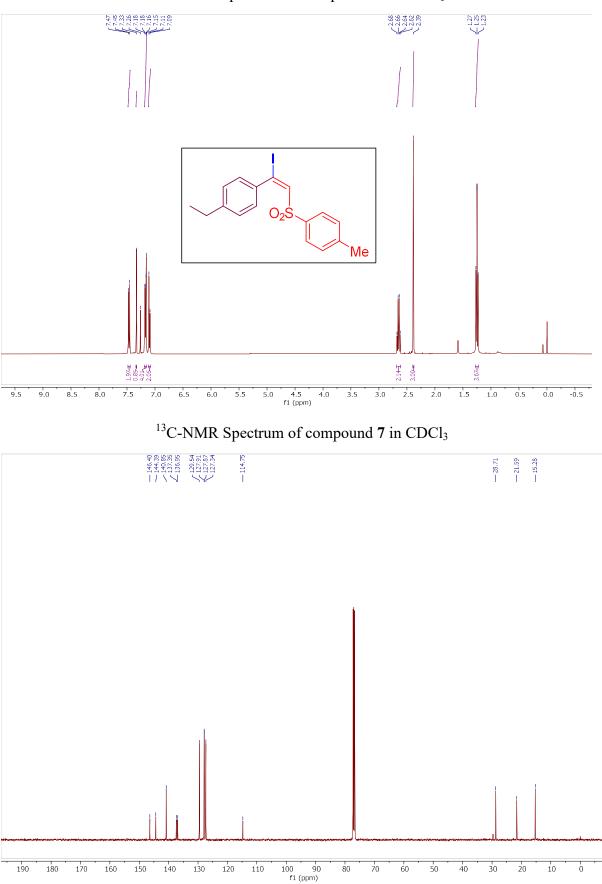




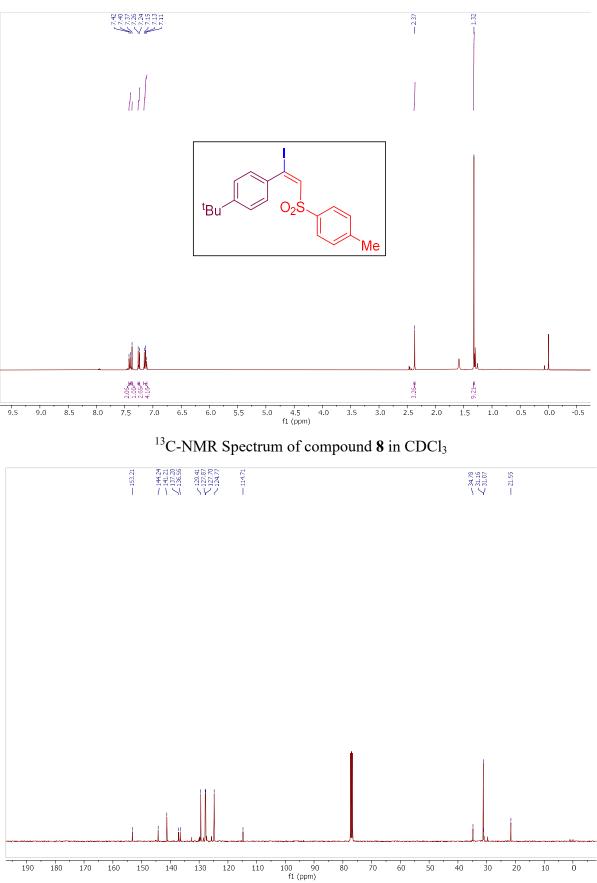
¹H-NMR Spectrum of compound **5** in CDCl₃



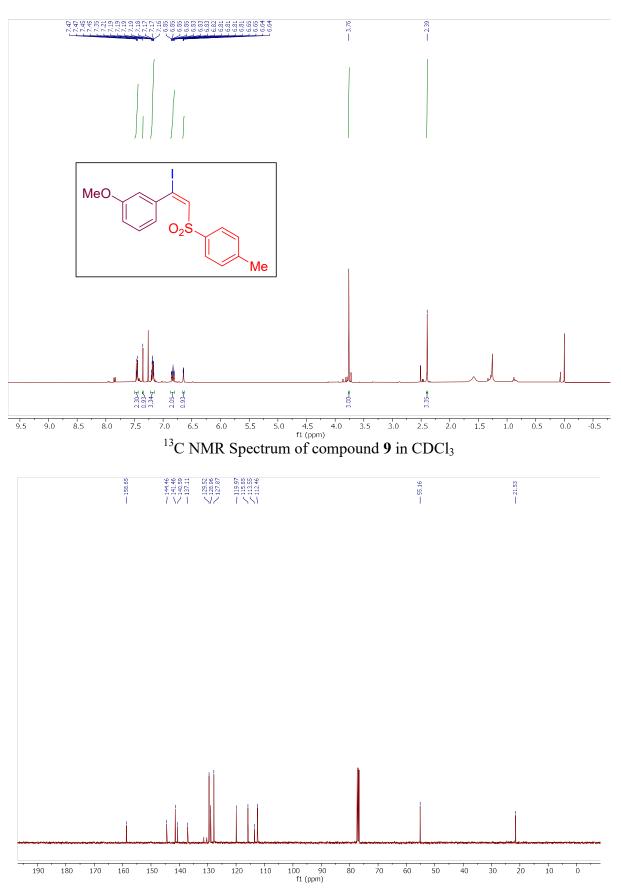
¹H-NMR Spectrum of compound **6** in CDCl₃



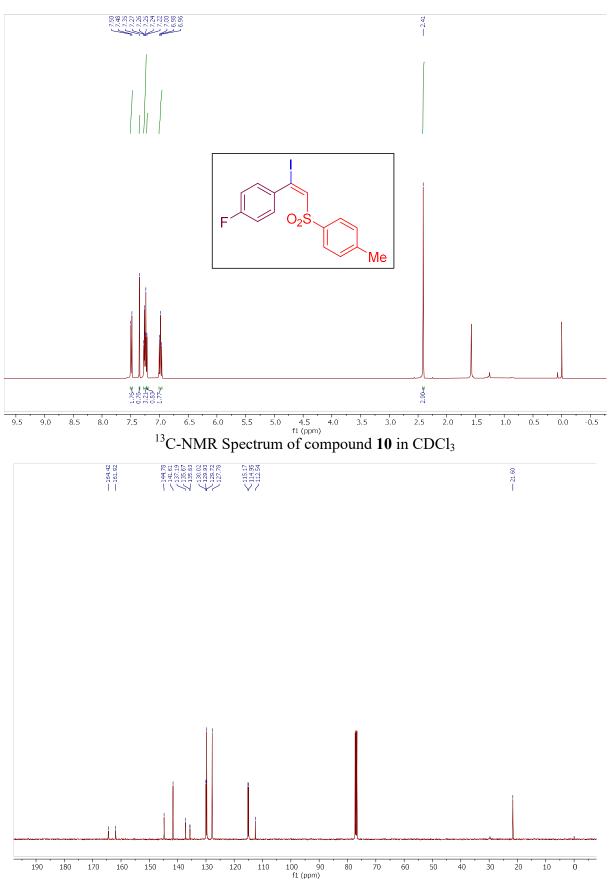
1 H-NMR Spectrum of compound 7 in CDCl₃



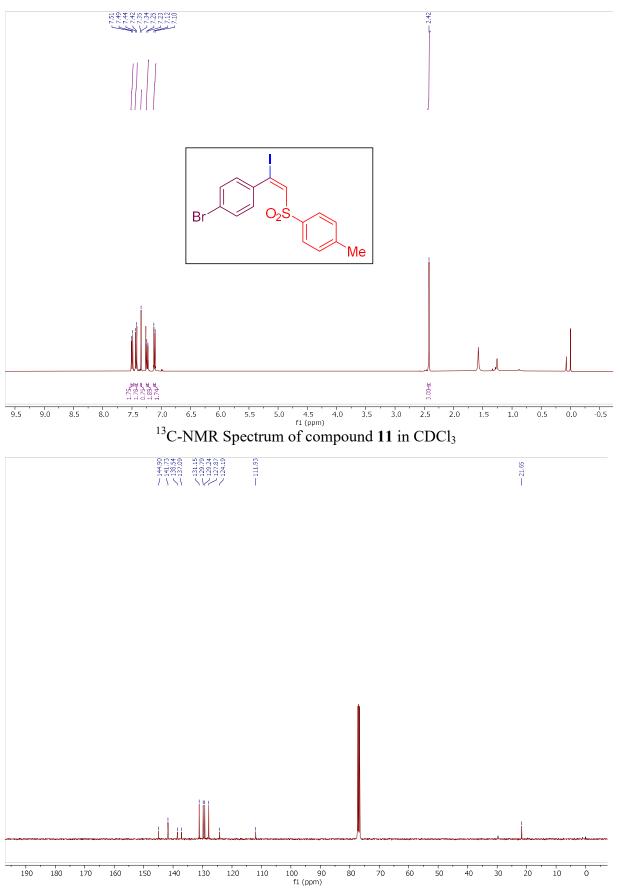
1 H-NMR Spectrum of compound **8** in CDCl₃



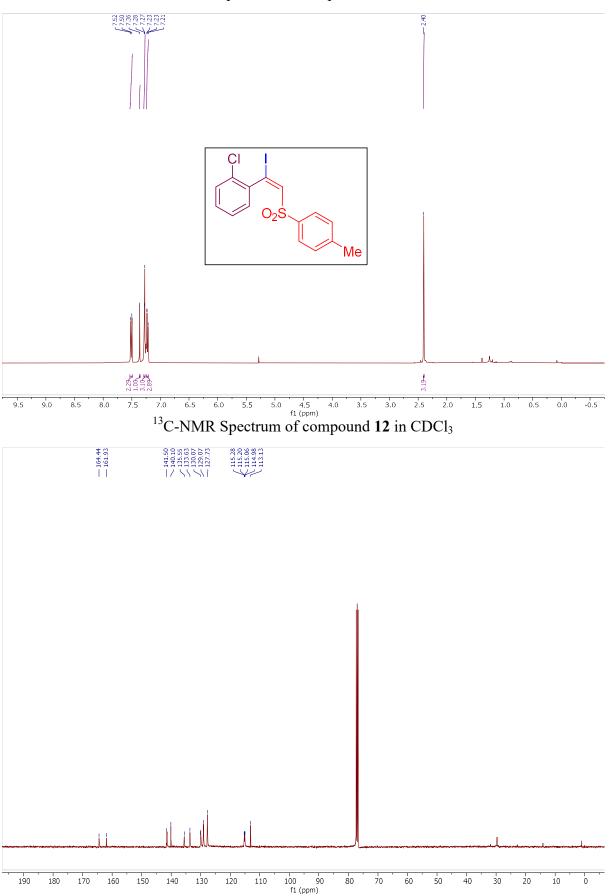
1 H NMR Spectrum of compound 9 in CDCl₃



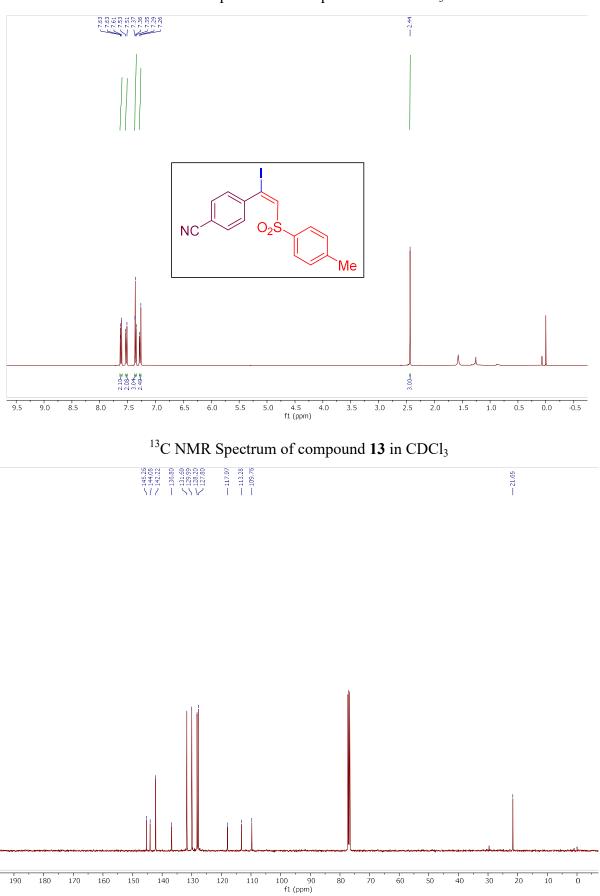
¹H-NMR Spectrum of compound **10** in CDCl₃



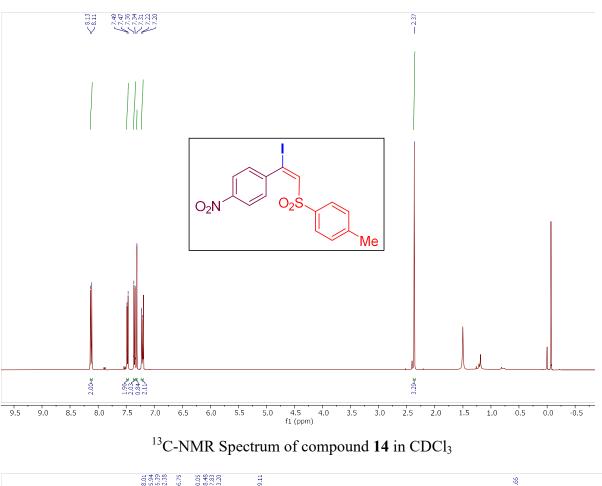
¹H-NMR Spectrum of compound **11** in CDCl₃

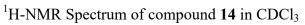


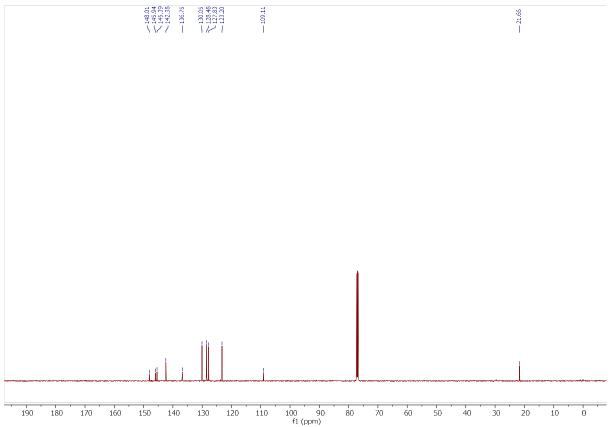
¹H-NMR Spectrum of compound **12** in CDCl₃

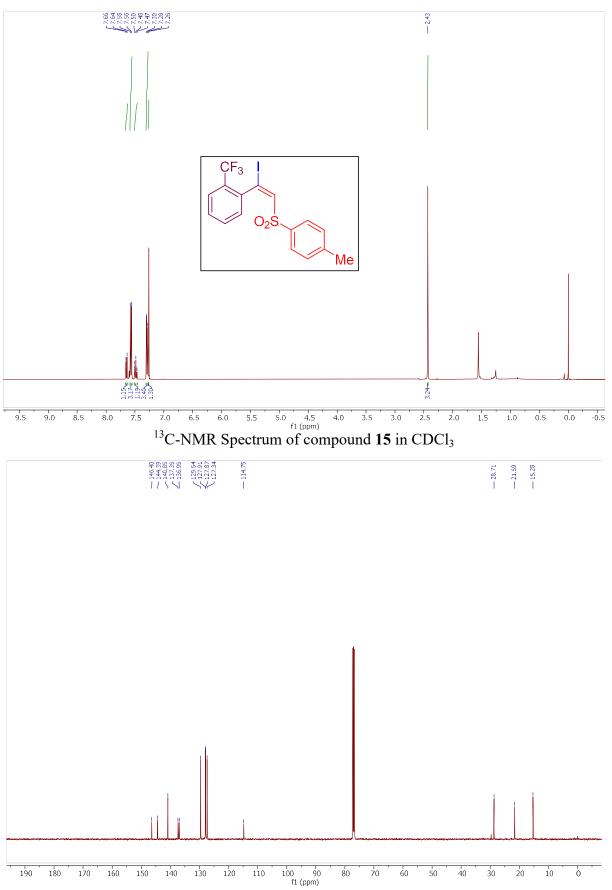


¹H NMR Spectrum of compound **13** in CDCl₃

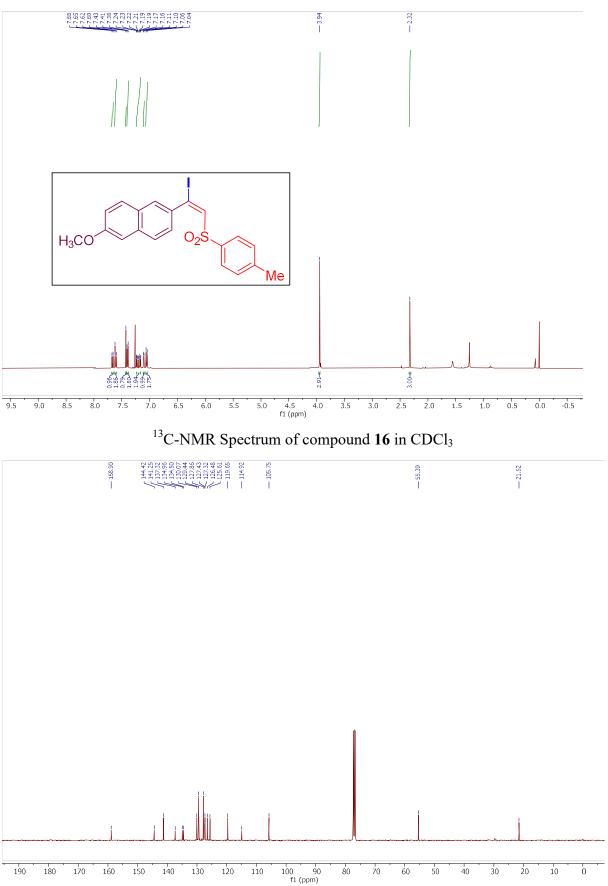




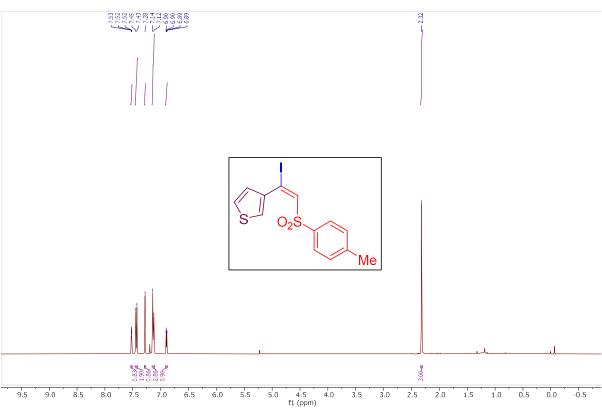




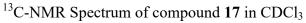
¹H-NMR Spectrum of compound **15** in CDCl₃

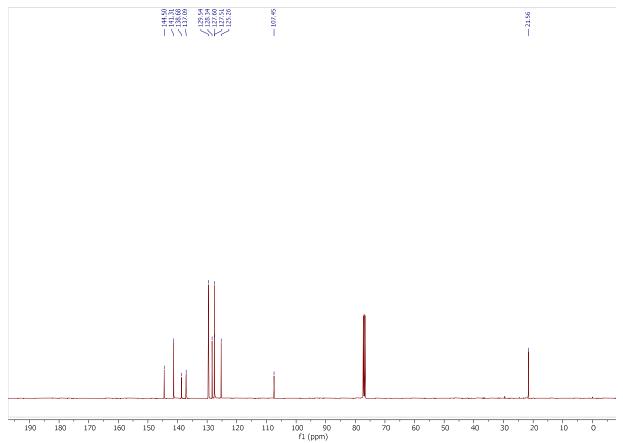


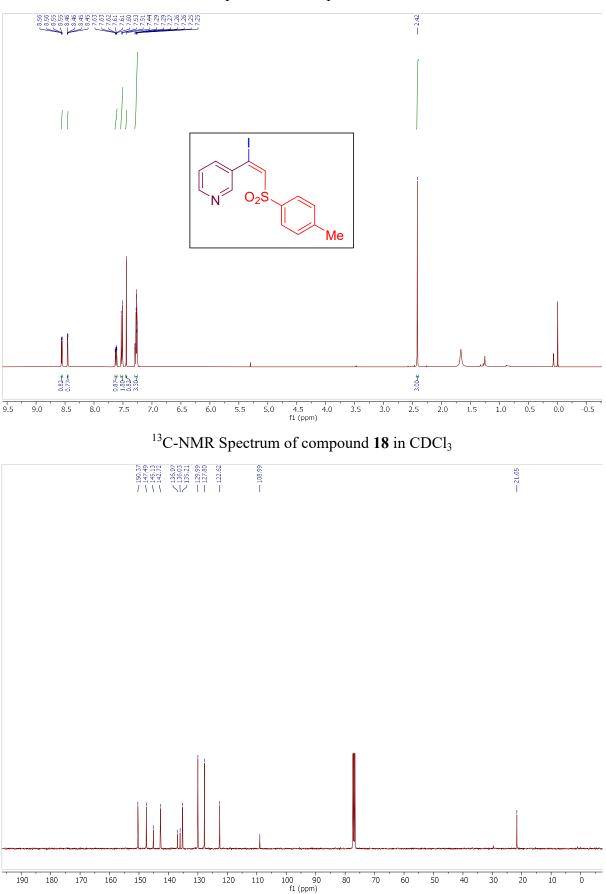
1 H-NMR Spectrum of compound 16 in CDCl₃



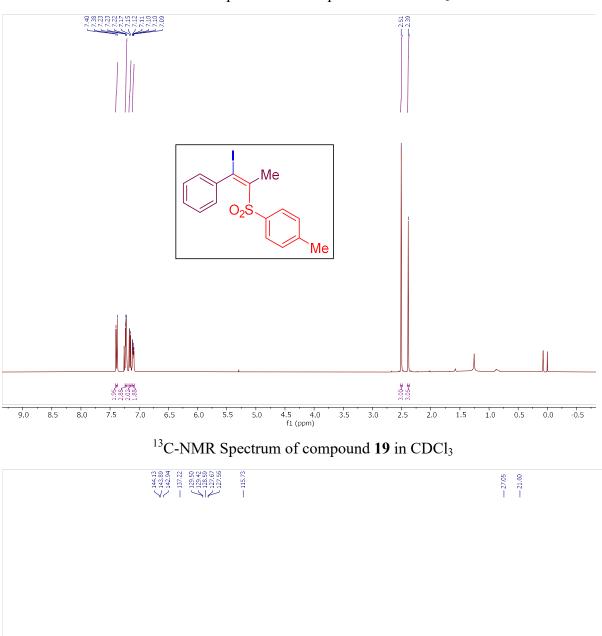
¹H-NMR Spectrum of compound **17** in CDCl₃



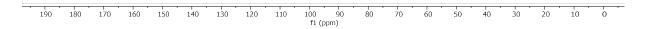


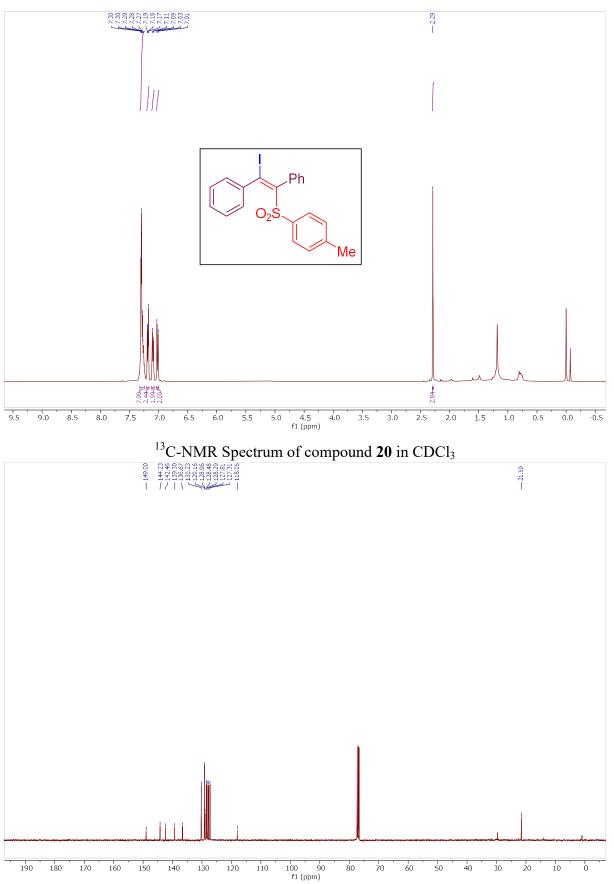


¹H-NMR Spectrum of compound **18** in CDCl₃

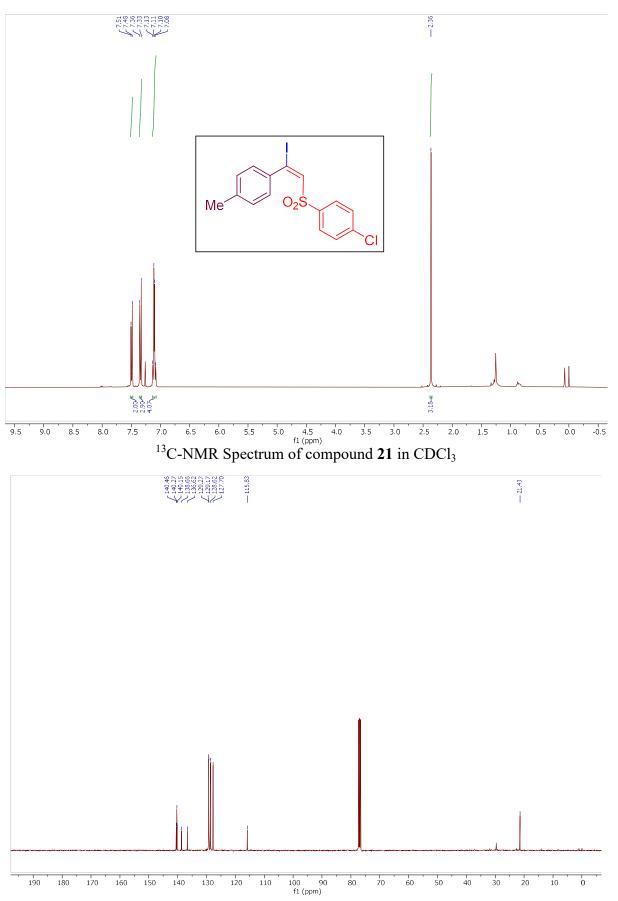


¹H-NMR Spectrum of compound **19** in CDCl₃

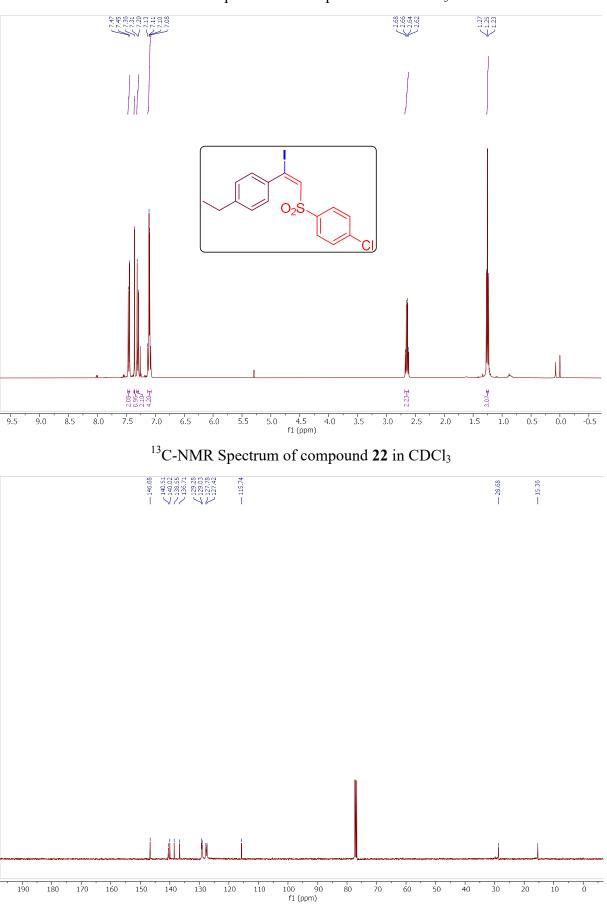




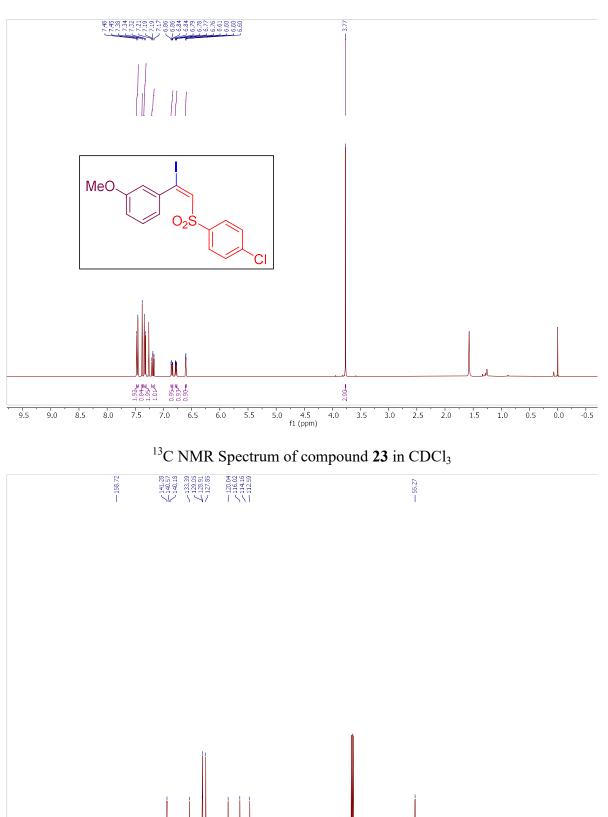
¹H-NMR Spectrum of compound **20** in CDCl₃



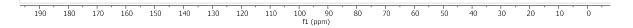
¹H-NMR Spectrum of compound **21** in CDCl₃

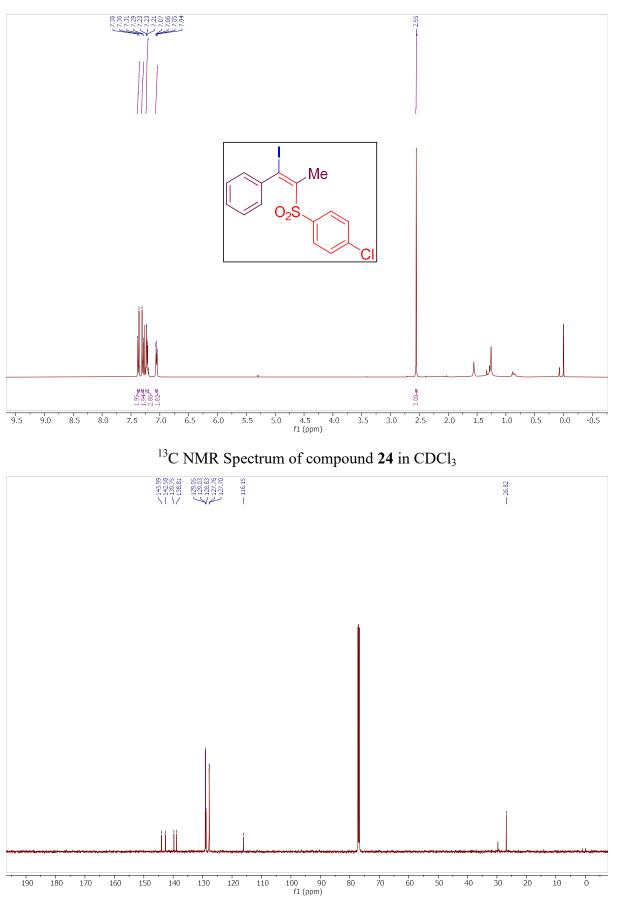


1 H-NMR Spectrum of compound **22** in CDCl₃

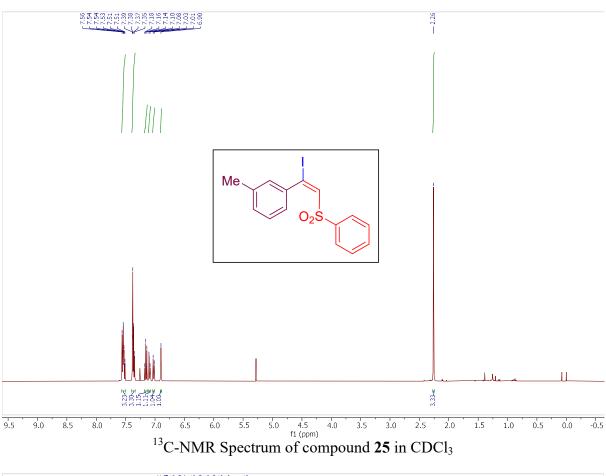


1 H NMR Spectrum of compound **23** in CDCl₃

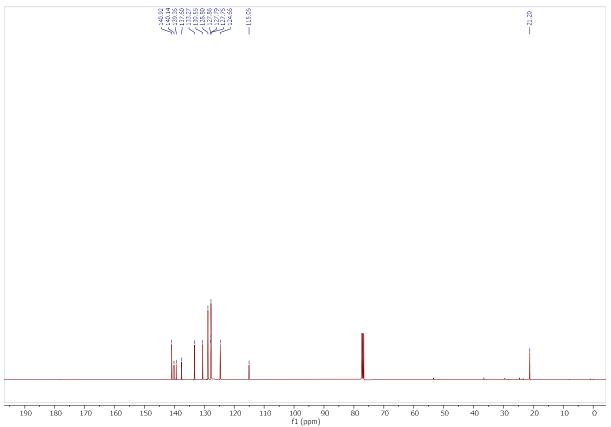


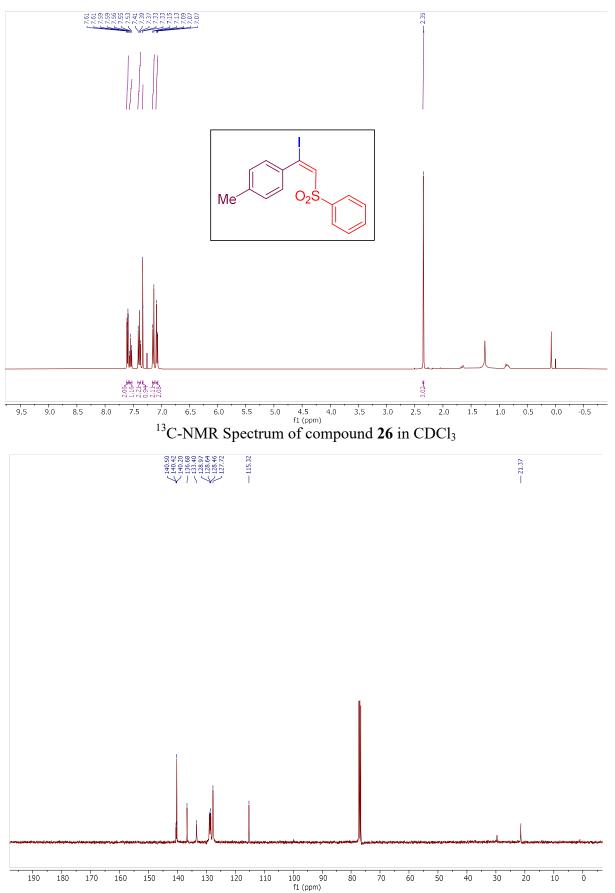


¹H NMR Spectrum of compound **24** in CDCl₃

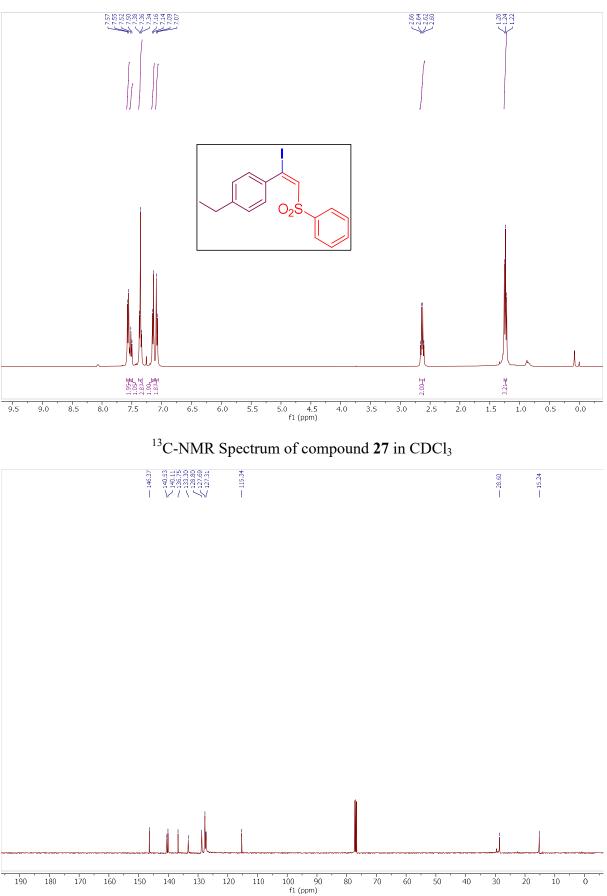


¹H-NMR Spectrum of compound **25** in CDCl₃

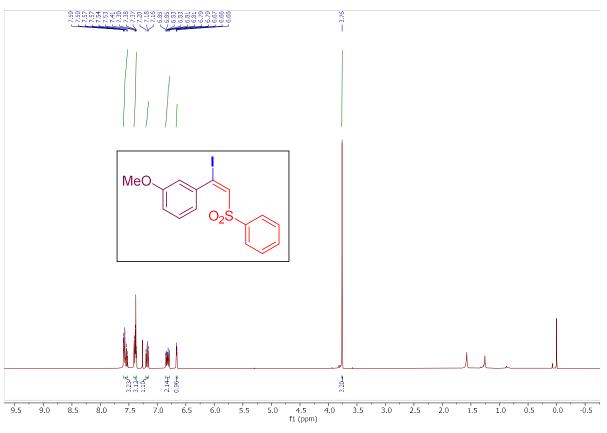




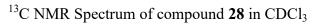
¹H-NMR Spectrum of compound **26** in CDCl₃

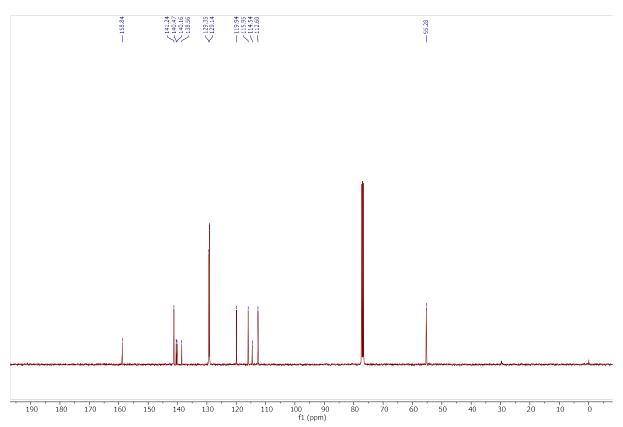


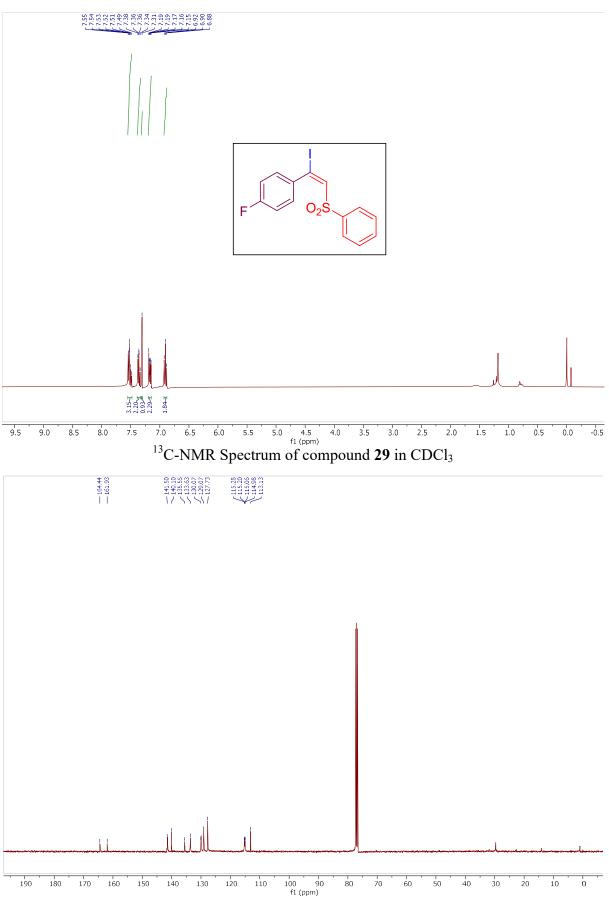
¹H-NMR Spectrum of compound **27** in CDCl₃



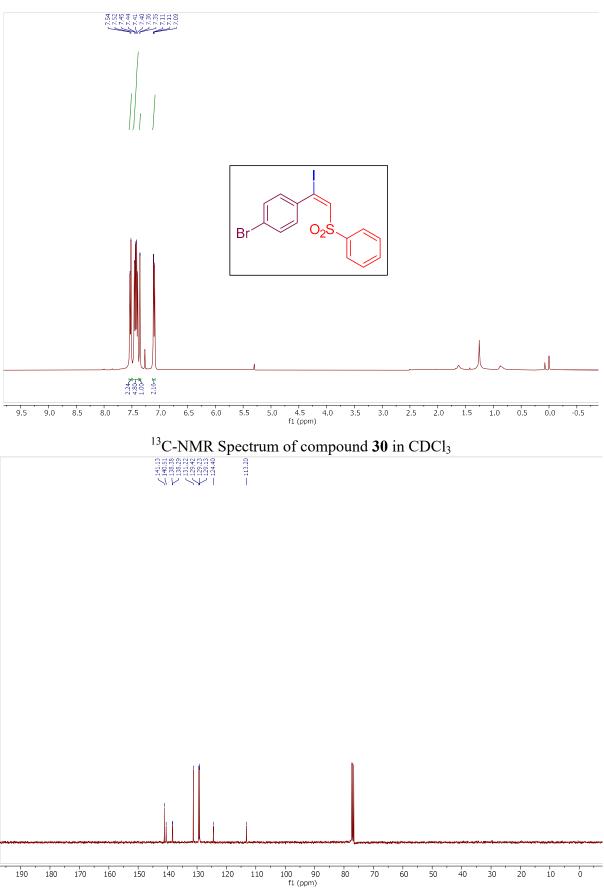
¹H NMR Spectrum of compound **28** in CDCl₃



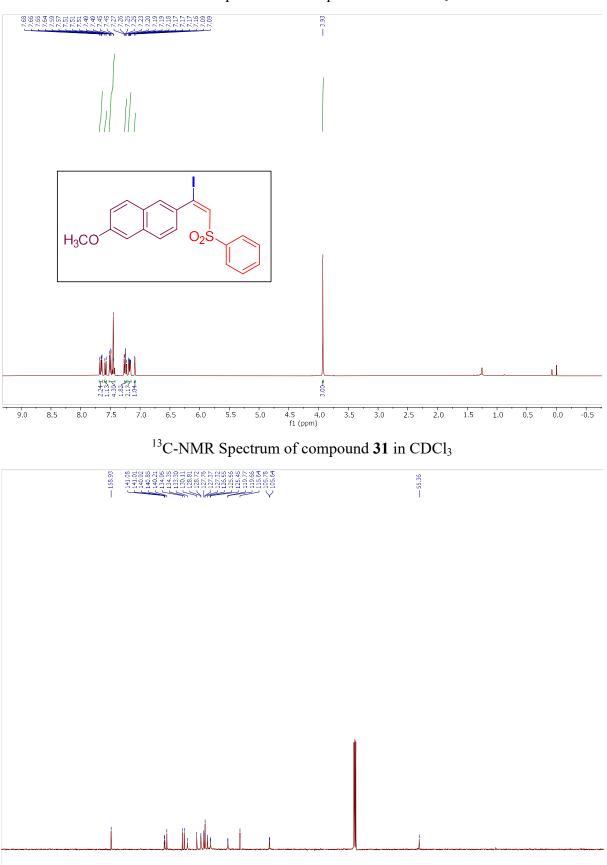




¹H-NMR Spectrum of compound **29** in CDCl₃

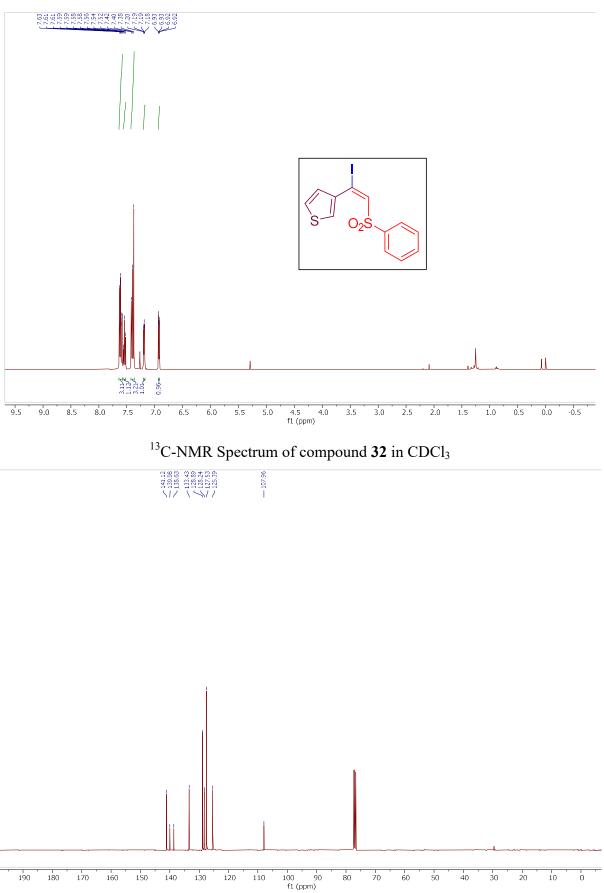


¹H-NMR Spectrum of compound **30** in CDCl₃

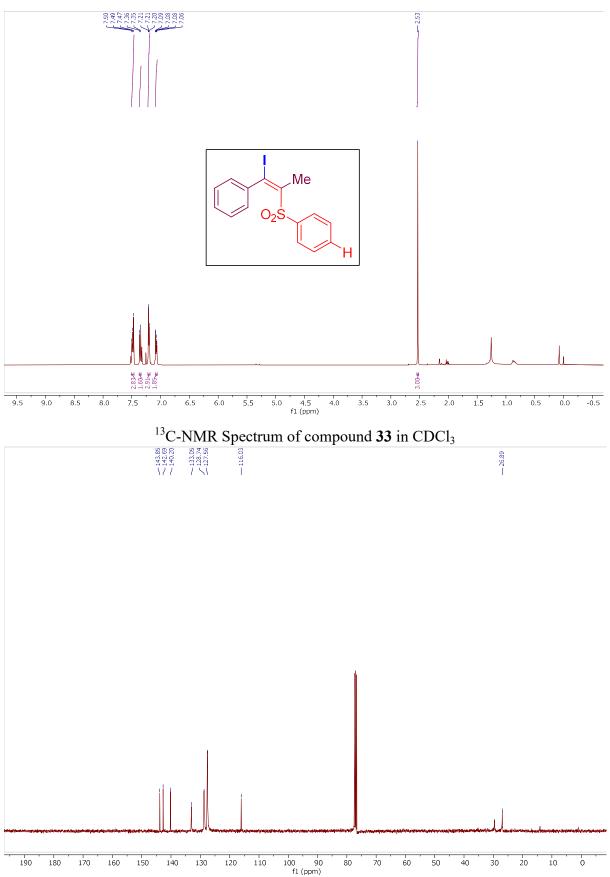


1 H-NMR Spectrum of compound **31** in CDCl₃

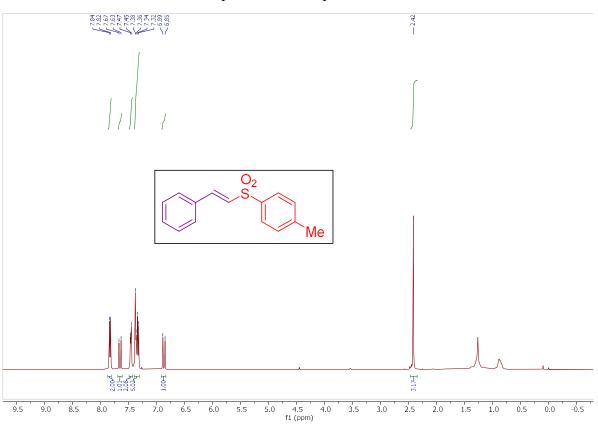
100 90 f1 (ppm)



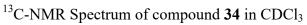
¹H-NMR Spectrum of compound **32** in CDCl₃

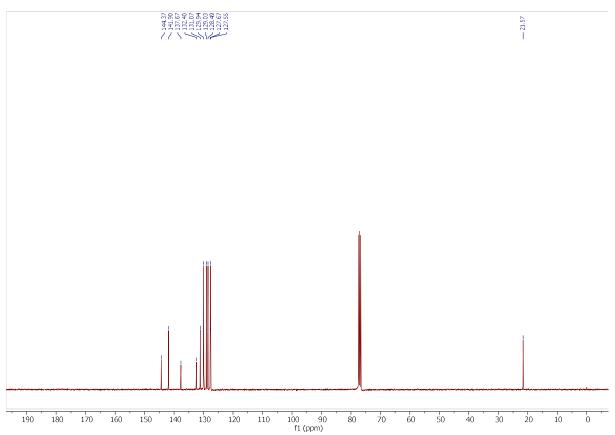


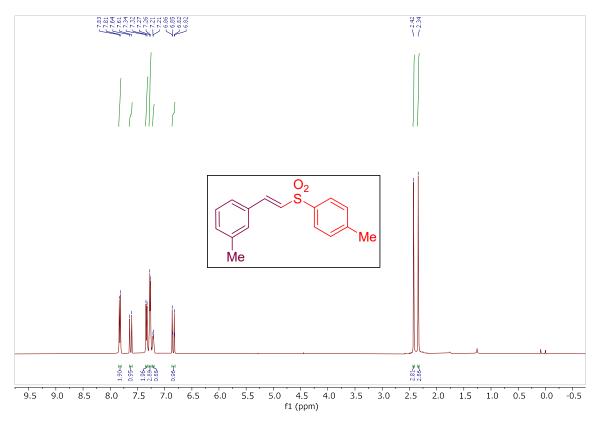
1 H-NMR Spectrum of compound **33** in CDCl₃



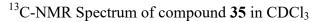
1 H-NMR Spectrum of compound **34** in CDCl₃

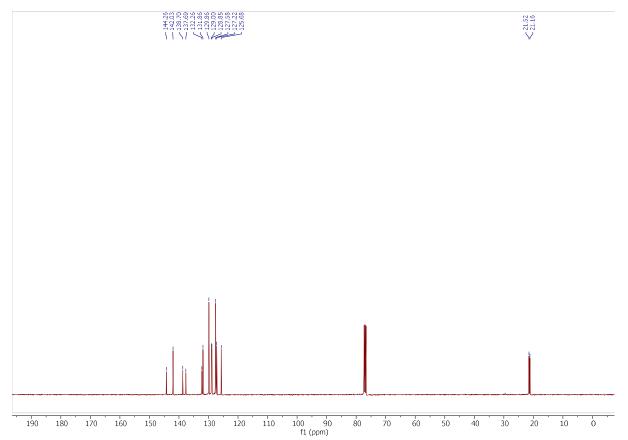


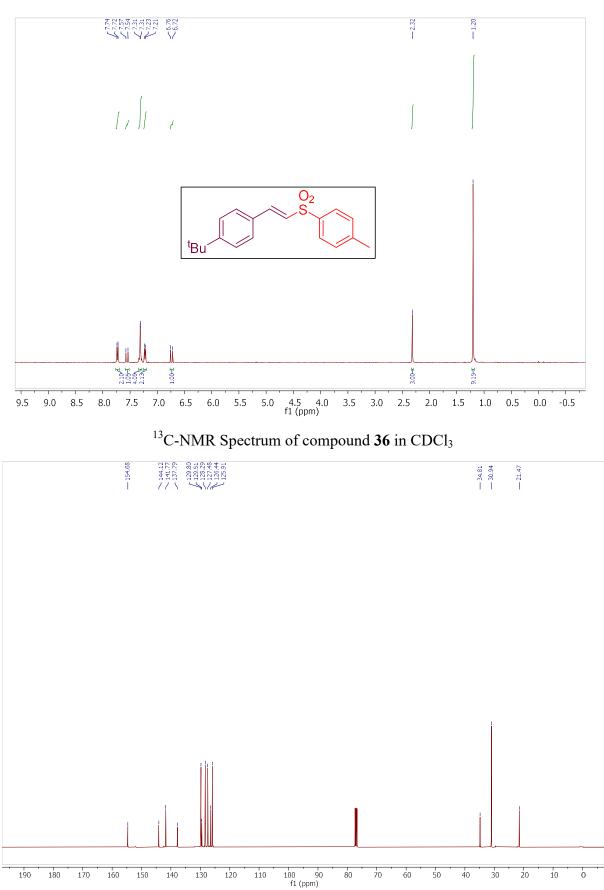




¹H-NMR Spectrum of compound **35** in CDCl₃



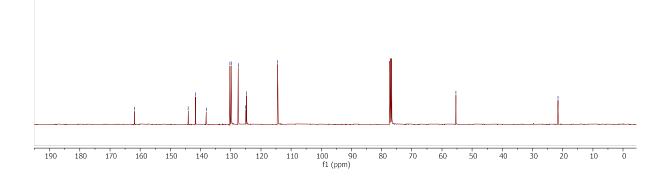


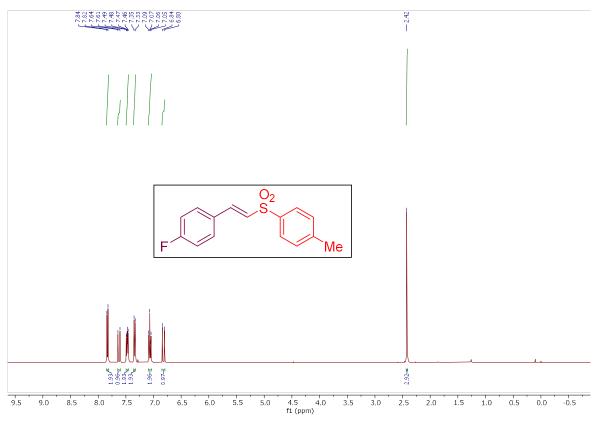


¹H-NMR Spectrum of compound **36** in CDCl₃

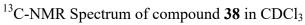
Z 7.83 7.62 7.62 7.64 7.64 7.64 7.62 7.34 7.73 7.33 -2.43O₂ Me MeO 3.27H 3.33H 1.82 A 1.00H 2.5 4.0 7.5 7.0 4.5 f1 (ppm) 9.0 6.5 6.0 3.5 3.0 2.0 1.5 1.0 8.5 8.0 5.5 5.0 0.5 0.0 ¹³C-NMR Spectrum of compound **37** in CDCl₃ - 161.93 \sim 144.09 \sim 141.69 \sim 138.14 \sim 138.14 \sim 130.26 \sim 1229.85 \sim 127.51 \sim 125.01 \sim 124.76 — 114.44

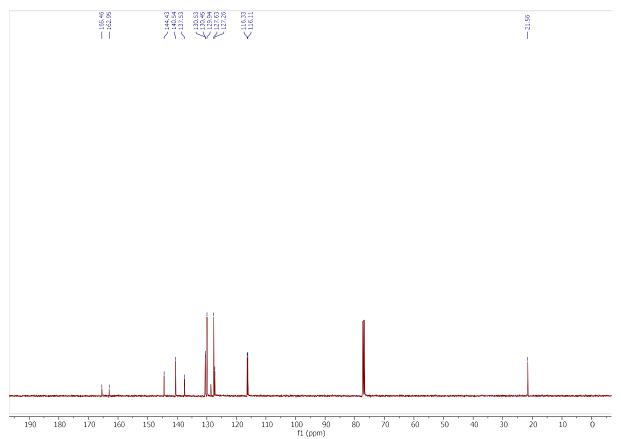
¹H-NMR Spectrum of compound **37** in CDCl₃

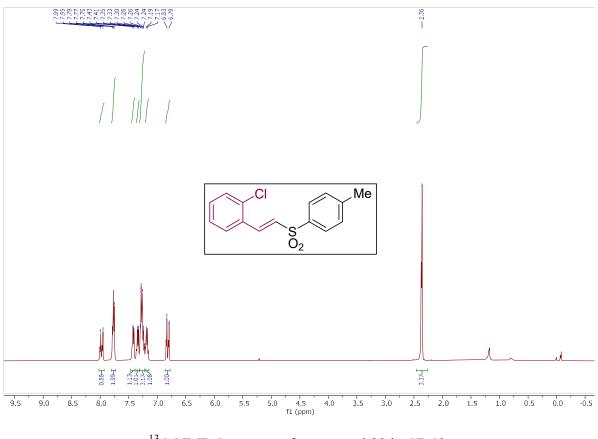




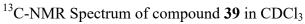
¹H-NMR Spectrum of compound **38** in CDCl₃

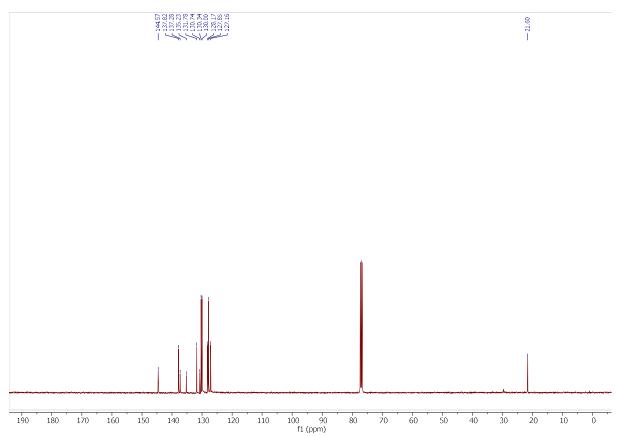


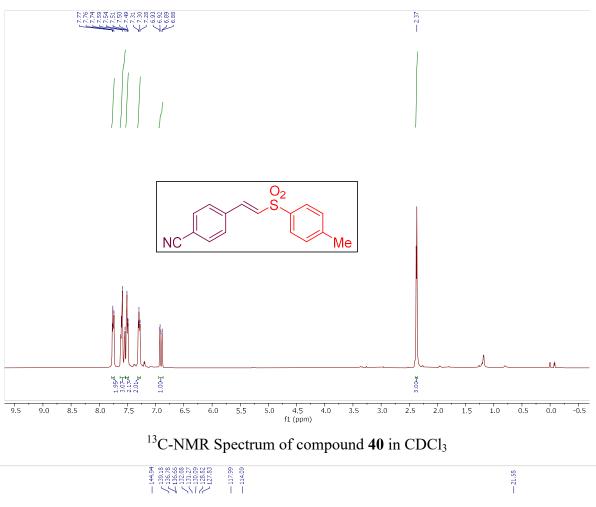




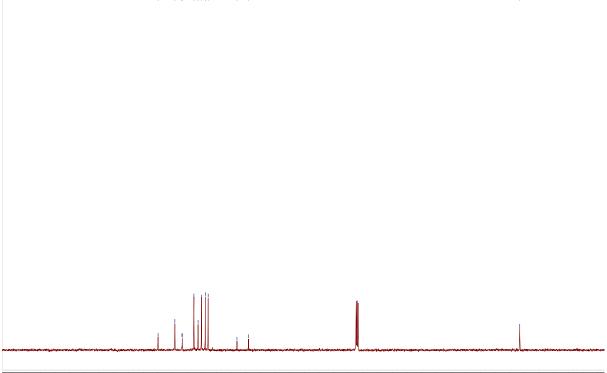
1 H-NMR Spectrum of compound **39** in CDCl₃



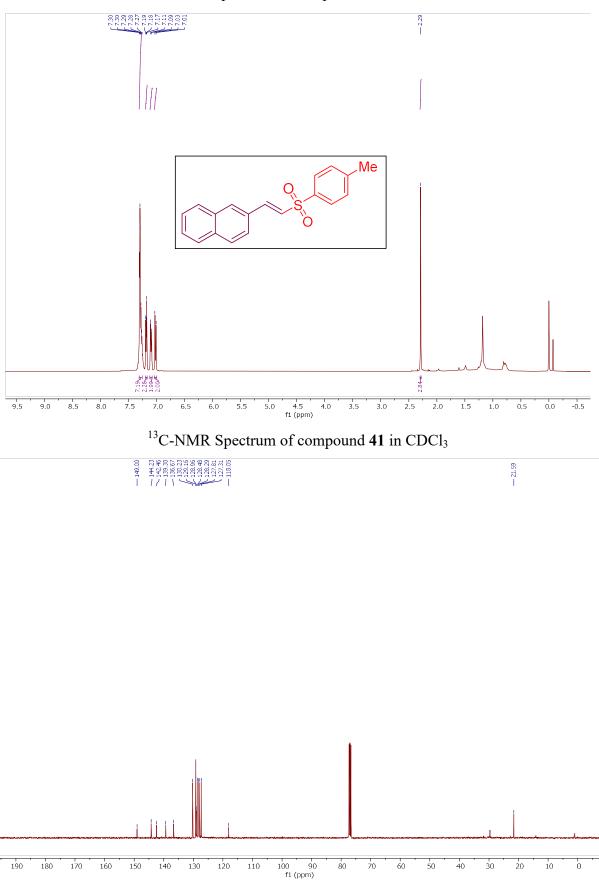




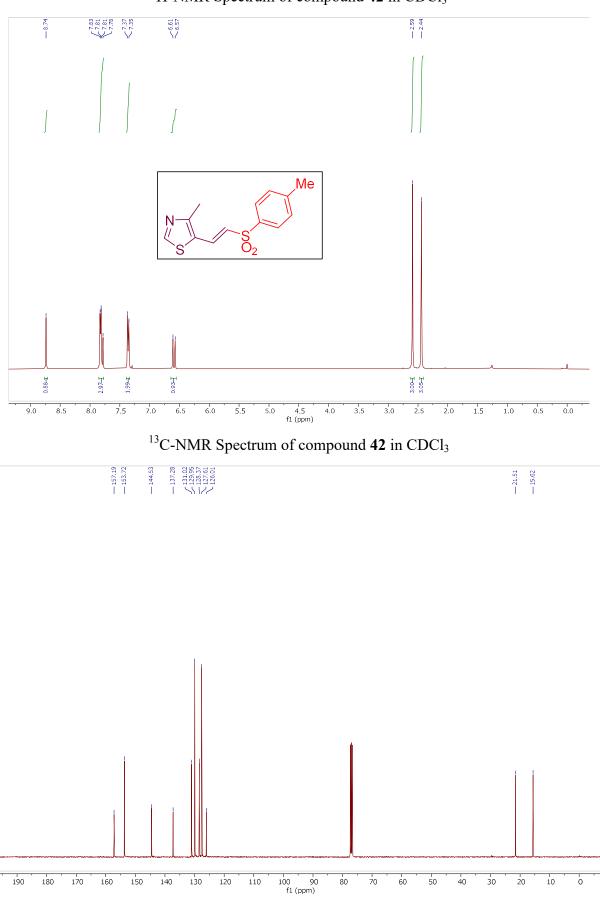
¹H-NMR Spectrum of compound **40** in CDCl₃

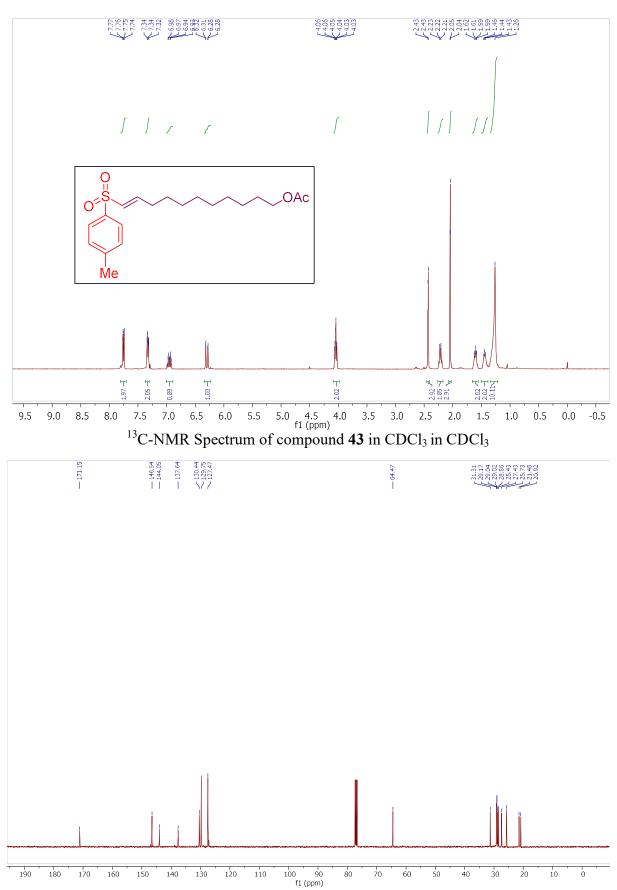


100 90 f1 (ppm)

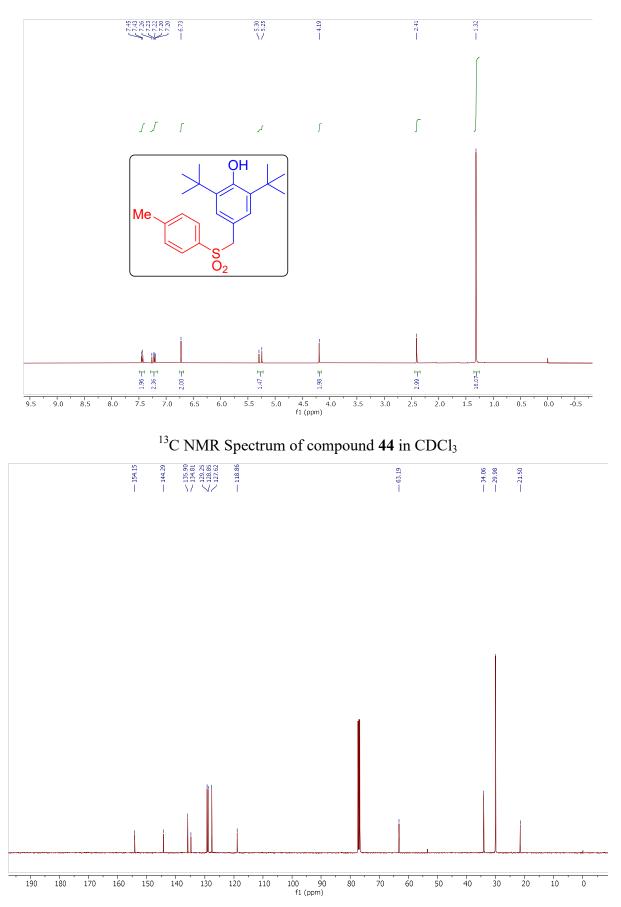


 1 H-NMR Spectrum of compound **41** in CDCl₃

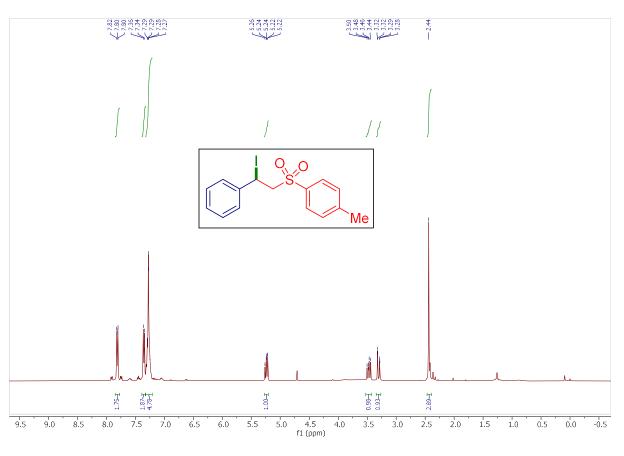


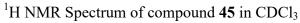


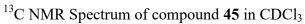
¹H-NMR Spectrum of compound **43** in CDCl₃

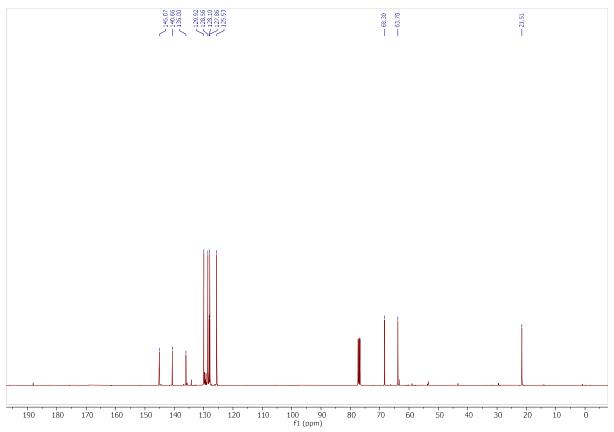


¹H NMR Spectrum of compound 44 in CDCl₃

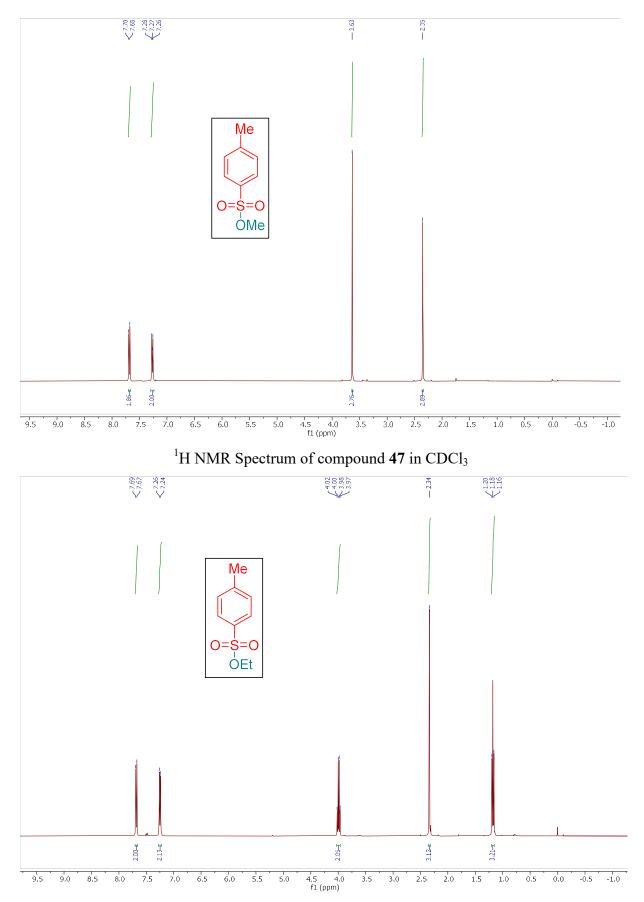


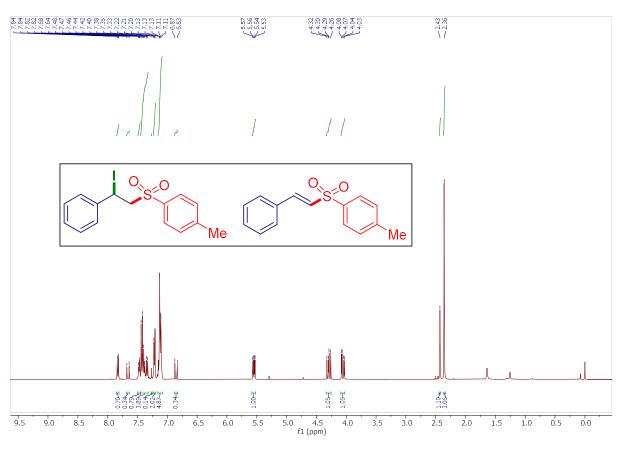






¹H NMR Spectrum of compound **46** in CDCl₃





^1H NMR Spectrum of mixture 45 and 34 in CDCl_3

 ^{13}C NMR Spectrum of mixture **45** and **34** in CDCl_3

