Supporting Information for:

Construction of Multi-Functionalized Carbon Chain Launched by Ni-Catalyzed Carbosulfonylation of Butadiene

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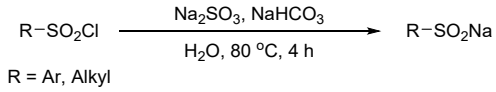
1 General experimental details

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. Unless otherwise stated, all reactions were conducted under inert atmosphere using standard Schlenk techniques or in a nitrogen-filled glove-box. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz or 700 MHz instrument with tetramethylsilane (TMS) as internal standard. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI) or Agilent 6540 Accurate-MS spectrometer (Q-TOF). Sulfinates and halide substrates were purchased commercially or synthesized according to the literature.[1]

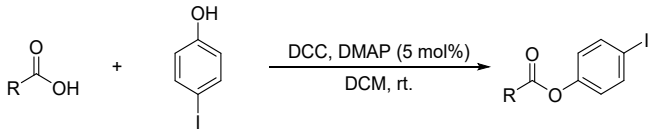
2 General procedures for the preparation of substrates

General procedures for the synthesis of sodium sulfinates[2]

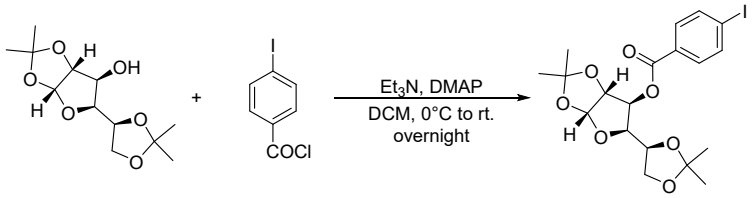


Known sodium sulfinates were synthesized according to literature procedures. A solution of sodium sulfite (1.26 g, 10.0 mmol) and sodium bicarbonate (0.84 g, 10.0 mmol) in H_2O (5 mL) was treated with sulphonyl chloride (5.0 mmol) and stirred at 80 ℃ for 4 h. Water was removed by rotary evaporator. Then the remaining solid was dissolved and recrystallized by ethanol to get a white solid.

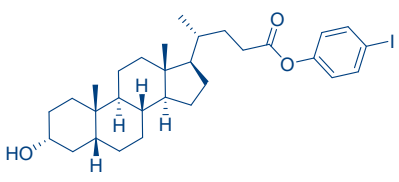
General procedures for the synthesis of derivatives of aryl iodide[3]



The corresponding carboxylic acid (1.2 eq.), 4-iodophenol (1.0 eq.) and 4-dimethylaminopyridine (5 mol%) were mixed in a flask with a stirring bar. DCM (20 mL) was added. Then a solution of DCC (1.2 eq.) in DCM (5 mL) was added slowly at 0 °C. The reaction mixture was stirred at room temperature for 4 h. Then the white precipitate was filtered off, and the solution was concentrated under a vacuum and then purified by column chromatography on silica gel.

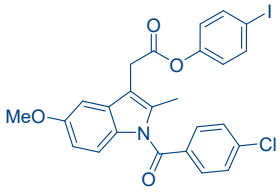


To a solution of diacetone-D-glucose (1.34 g, 5 mmol), triethylamine (1.4 mL, 10 mmol) and 4-dimethylaminopyridine (60 mg, 0.5 mmol) in DCM (15 mL) was added the solution of 4-iodobenzoyl chloride (1.62 g, 6 mmol) in DCM (10 mL) dropwise at 0 ºC. After being stirred for 30 min, the mixture was allowed to stir at room temperature overnight. The reaction was quenched with saturated NH_4Cl solution (20 mL) and extracted with DCM (20 mL × 3). The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (EA:PE = 1:5) to afford the desired compound.

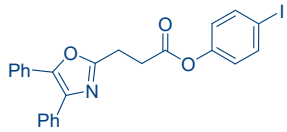


4-Iodophenyl (*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a] phenanthren-17-yl)pentanoate: White solid, 2.48 g, 86% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 – 7.61 (m, 2H), 6.91 – 6.75 (m, 2H), 3.67 – 3.53 (m, 1H), 2.66 – 2.52 (m,

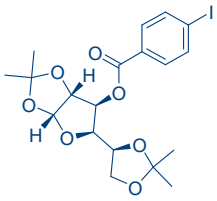
1H), 2.52 – 2.40 (m, 1H), 1.86 – 1.03 (m, 26H), 0.96 (d, *J* = 6.1 Hz, 3H), 0.92 (s, 3H), 0.65 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 172.37, 150.60, 138.42, 123.81, 89.74, 71.70, 56.51, 55.93, 42.78, 42.09, 40.43, 40.19, 36.39, 35.84, 35.40, 35.36, 34.58, 31.33, 30.89, 30.50, 28.28, 27.23, 26.46, 24.24, 23.44, 20.85, 18.36, 12.12; **HRMS** calculated for $C_{30}H_{47}INO_3$ $[M+NH_4]^+$ 596.2595, found 596.2604.



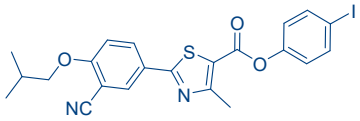
4-Iodophenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol -3-yl) acetate: Yellow solid, 564 mg, 84% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 – 7.61 (m, 4H), 7.52 – 7.45 (m, 2H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.69 (dd, *J* = 9.0 Hz, 2.5, 1H), 3.89 (s, 2H), 3.83 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 168.96, 168.31, 156.13, 150.51, 139.43, 138.48, 136.31, 133.75, 131.22, 130.83, 130.41, 129.19, 123.60, 115.06, 111.79, 111.70, 101.18, 90.00, 55.76, 30.54, 13.45; **HRMS** calculated for $C_{25}H_{20}ClINO_4$ $[M+H]^+$ 560.0120, found 560.0121.



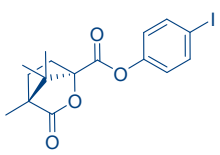
4-Iodophenyl 3-(4,5-diphenyloxazol-2-yl)propanoate: Yellow liquid, 2.20 g, 89% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.70 – 7.59 (m, 4H), 7.60 – 7.52 (m, 2H), 7.42 – 7.25 (m, 6H), 6.91 – 6.81 (m, 2H), 3.27 (t, *J* = 7.0 Hz, 2H), 3.13 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 170.36, 161.35, 150.51, 145.65, 138.50, 135.20, 132.41, 128.93, 128.73, 128.64, 128.62, 128.19, 127.90, 126.58, 123.80, 90.04, 31.25, 23.52; **HRMS** calculated for $C_{24}H_{19}INO_3$ $[M+H]^+$ 496.0404, found 496.0402.



(3a*R*,5*R*,6*S*,6a*R*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl tetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-iodobenzoate: White solid, 1.30 g, 53% yield. **^{1}H NMR** (700 MHz, Chloroform-*d*) δ = 7.82 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 5.95 (d, *J* = 3.7 Hz, 1H), 5.57 – 5.44 (m, 1H), 4.62 (d, *J* = 3.7 Hz, 1H), 4.41 – 4.26 (m, 2H), 4.12 (dd, *J* = 8.7, 5.2 Hz, 1H), 4.07 (dd, *J* = 8.7, 4.3 Hz, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H); **^{13}C NMR** (176 MHz, Chloroform-*d*) δ = 164.74, 137.93, 137.78, 131.05, 129.00, 112.40, 109.45, 105.13, 101.42, 83.33, 79.94, 72.53, 67.35, 26.87, 26.75, 26.23, 25.23; **HRMS** calculated for $C_{19}H_{23}INaO_7$ $[M+Na]^+$ 513.0381, found 513.0358.



4-Iodophenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methyl thiazole-5-carboxylate: White solid, 2.10 g, 81% yield. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.22 (d, *J* = 2.3 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.04 (d, *J* = 8.9 Hz, 1H), 7.02 – 6.97 (m, 2H), 3.92 (d, *J* = 6.5 Hz, 2H), 2.82 (s, 3H), 2.27 – 2.16 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 168.39, 163.41, 162.74, 160.03, 150.08, 138.61, 132.70, 132.27, 125.75, 123.79, 120.18, 115.33, 112.69, 103.11, 90.32, 75.76, 28.17, 19.08, 17.77; **HRMS** calculated for $C_{22}H_{20}IN_2O_3S$ $[M+H]^+$ 519.0234, found 519.0192.



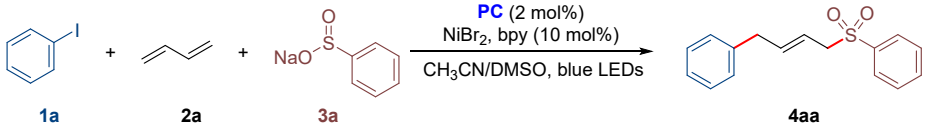
4-Iodophenyl (1*R*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate: White solid, 1.70 g, 85% yield. **^{1}H NMR** (400 MHz, Chloroform-

d) δ = 7.75 – 7.66 (m, 2H), 6.95 – 6.85 (m, 2H), 2.55 (ddd, *J* = 13.7, 10.8, 4.2 Hz, 1H), 2.19 (ddd, *J* = 13.7, 9.3, 4.5 Hz, 1H), 2.00 (ddd, *J* = 13.4, 10.8, 4.6 Hz, 1H), 1.77 (ddd, *J* = 13.4, 9.3, 4.2 Hz, 1H), 1.17 (s, 3H), 1.14 (s, 3H), 1.09 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 177.70, 165.87, 149.80, 138.68, 123.47, 90.72, 90.56, 54.91, 54.79, 30.79, 28.94, 16.90, 16.86, 9.75; **HRMS** calculated for $C_{16}H_{18}IO_4$ $[M+H]^+$ 401.0244, found 401.0223.

3 Experiments section

3.1 Optimization of reaction conditions

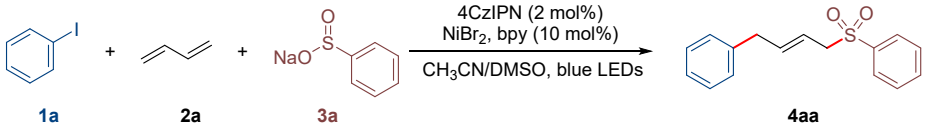
Table S1 PC screening



Entry	PC	Yield (%)	*E/Z*
1	$Ru(bpy)_3(PF_6)_2$	60	9/1
2	$Ru(bpy)_3Cl_2•6H_2O$	51	8/1
3	$Ru(Phen)_3(PF_6)_2$	59	6/1
4	$Ir(ppy)_3$	60	10/1
5	$[Ir(ppy)_2(dtbbpy)]PF_6$	55	11/1
6	$[Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	50	11/1
7	4CzIPN	67	12/1

Standard conditions: **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.40 mmol), PC (2 mol%), $NiBr_2$ (10 mol%), bpy (10 mol%), CH_3CN (1.8 mL), DMSO (0.2 mL), blue LEDs, 18 h, under N_2. Yields were determined by GC-FID analysis of the crude reaction mixture using mesitylene as internal standard.

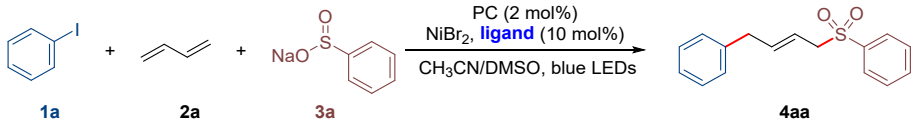
Table S2 Screening equivalence

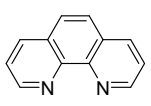


Entry	**1a**/**2a**/**3a** (mmol)	Yield (%)	*E/Z*
1	0.2/0.2/0.2	59	10/1
2	0.2/0.2/0.4	67	12/1
3	0.2/0.4/0.2	51	12/1
4	0.4/0.2/0.2	47	10/1
5	0.2/0.6/0.4	88	13/1

Standard conditions: **1a**/**2a**/**3a**, 4CzIPN (2 mol%), $NiBr_2$ (10 mol%), bpy (10 mol%), CH_3CN (1.8 mL), DMSO (0.2 mL), blue LEDs, 18 h, under N_2. Yields were determined by GC-FID analysis of the crude reaction mixture using mesitylene as internal standard.

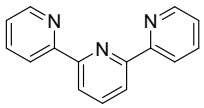
Table S3 Ligands screening





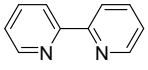
L1

69%[a], *E/Z* = 13/1



L2

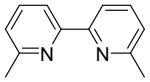
N.D.[a]



L3

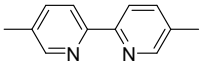
88%[a], *E/Z* = 13/1

91%[b], *E/Z* = 14/1



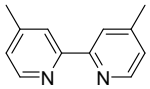
L4

35%[b], *E/Z* = 11/1



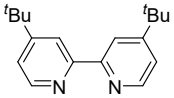
L5

90%[b], *E/Z* = 8/1



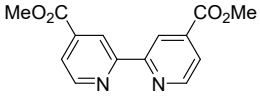
L6

90%[b], *E/Z* = 10/1



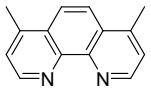
L7

89%[b], *E/Z* = 10/1



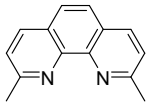
L8

66%[b], *E/Z* = 16/1



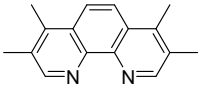
L9

15%[a], *E/Z* = 6/1



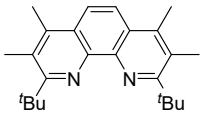
L10

9%[a], *E/Z* = 5/1



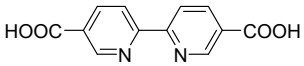
L11

34%[a], *E/Z* = 7/1



L12

N.D.[a]

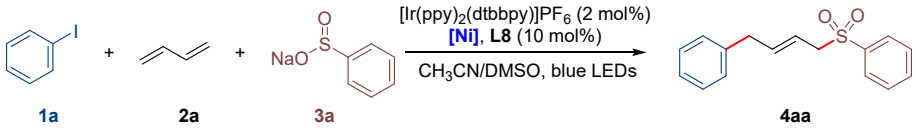


L13

34%[b], *E/Z* = 9/1

Standard conditions: **1a** (0.20 mmol), **2a** (0.60 mmol), **3a** (0.40 mmol), PC (2 mol%), $NiBr_2$ (10 mol%), ligand (10 mol%), CH_3CN (1.8 mL), DMSO (0.2 mL), blue LEDs, 18 h, under N_2. Yields were determined by GC-FID analysis of the crude reaction mixture using mesitylene as internal standard. [a]PC = 4CzIPN. [b]PC = $[Ir(ppy)_2(dtbbpy)]PF_6$.

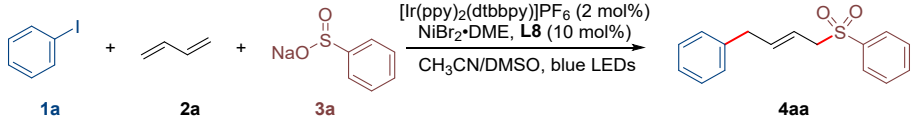
Table S4 Ni screening



Entry	[Ni]	Yield (%)	*E/Z*
1	$NiBr_2$	62	15/1
2	$NiCl_2$	33	9/1
3	$NiBr_2(PPh_3)_2$	65	20/1
4	$NiBr_2$•DME	83(84)[a]	20/1
5	$NiCl_2$•DME	68	12/1
6	$NiCl_2$•dppp	24	7/1
7	$Ni(OAc)_2$•$4H_2O$	15	5/1

Standard conditions: **1a** (0.20 mmol), **2a** (0.60 mmol), **3a** (0.40 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), [Ni] (10 mol%), **L8** (10 mol%), CH_3CN (1.8 mL), DMSO (0.2 mL), blue LEDs, 18 h, under N_2. Yields were determined by GC-FID analysis of the crude reaction mixture using mesitylene as internal standard. [a]CH_3CN (1.0 mL), 24 h, isolated yield.

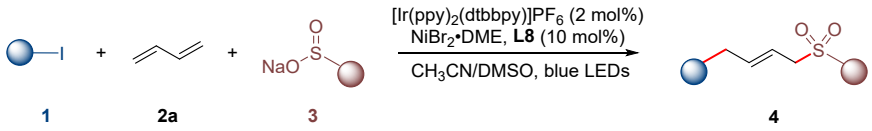
Table S5 Control experiments



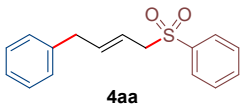
Entry	Deviation from standard condition	Yield (%)	*E/Z*
1	None	84	20/1
2	No $[Ir(ppy)_2(dtbbpy)]PF_6$	N.D.	-
3	No $NiBr_2$•DME	N.D.	-
4	No **L8**	trace	-
5	No light	N.D.	-

Standard conditions: **1a** (0.20 mmol), **2a** (0.60 mmol), **3a** (0.40 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), $NiBr_2$•DME (10 mol%), **L8** (10 mol%), CH_3CN (1.0 mL), DMSO (0.2 mL), blue LEDs, 24 h, under N_2. Yields were determined by GC-FID analysis of the crude reaction mixture using mesitylene as internal standard.

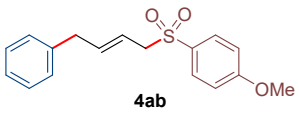
3.2 General procedures for three-component carbosulfonylation of butadiene



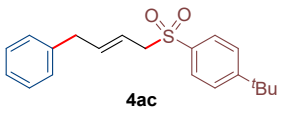
To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added **1** (0.20 mmol, 1.0 equiv.), **2a** (0.60 mmol, 2 M in THF, 3.0 equiv.), **3** (0.40 mmol, 2.0 equiv.), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), $NiBr_2$•DME (10 mol%), **L8** (10 mol%), CH_3CN (1.0 mL), DMSO (0.2 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 24 h. After the reaction was completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product **4**.


4aa

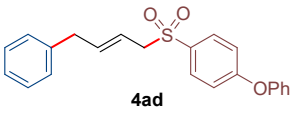
(*E*)-((4-Phenylbut-2-en-1-yl)sulfonyl)benzene (4aa): White solid, m.p. 147-148 °C. 46.0 mg, 84% yield, *E*/*Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.82 – 7.68 (m, 2H), 7.57 – 7.49 (m, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.05 (m, 3H), 7.04 – 6.89 (m, 2H), 5.58 (dt, *J* = 15.1, 6.8 Hz, 1H), 5.40 (dtt, *J* = 15.1, 7.4, 1.5 Hz, 1H), 3.70 (d, *J* = 7.3 Hz, 2H), 3.24 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 139.95, 138.87, 138.22, 133.61, 129.02, 128.51, 128.49, 126.35, 117.53, 59.98, 38.88; **HRMS** calculated for $C_{16}H_{17}O_2S$ $[M+H]^+$ 273.0944, found 273.0948.


4ab

(*E*)-1-Methoxy-4-((4-phenylbut-2-en-1-yl)sulfonyl) benzene (4ab): White solid, m.p. 105-106 °C. 48.5 mg, 80% yield, *E*/*Z* > 20/1, R_f = 0.20 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.77 – 7.68 (m, 2H), 7.32 – 7.18 (m, 3H), 7.09 – 6.99 (m, 2H), 6.96 – 6.85 (m, 2H), 5.65 (dtt, *J* = 15.3, 6.7, 1.1 Hz, 1H), 5.49 (dtt, *J* = 15.1, 7.4, 1.4 Hz, 1H), 3.85 (s, 3H), 3.75 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.33 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 163.65, 139.65, 138.99, 130.66, 129.75, 128.52, 128.48, 126.32, 117.91, 114.16, 60.24, 55.65, 38.91; **HRMS** calculated for $C_{17}H_{19}O_3S$ $[M+H]^+$ 303.1049, found 303.1054.

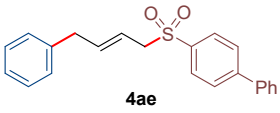

4ac

(*E*)-1-(Tert-butyl)-4-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4ac): White solid, m.p. 98-99 °C. 63.9 mg, 97% yield, *E*/*Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.73 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.34 – 7.23 (m, 2H), 7.22 – 7.14 (m, 1H), 7.11 – 7.01 (m, 2H), 5.68 (dtt, *J* = 15.2, 6.7, 1.1 Hz, 1H), 5.49 (dtt, *J* = 15.1, 7.3, 1.5 Hz, 1H), 3.75 (dd, *J* = 7.4, 1.1 Hz, 2H), 3.34 (d, *J* = 6.8 Hz, 2H), 1.32 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 157.51, 139.77, 138.98, 135.30, 128.55, 128.51, 128.36, 126.33, 125.97, 117.63, 59.97, 38.97, 35.24, 31.09; **HRMS** calculated for $C_{20}H_{25}O_2S$ $[M+H]^+$ 329.1570, found 329.1572.


4ad

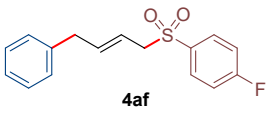
(*E*)-1-Phenoxy-4-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4ad): White solid, m.p. 93-94 °C. 29.6 mg, 41% yield, *E*/*Z* = 17/1, R_f = 0.25

(petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.78 – 7.68 (m, 2H), 7.47 – 7.35 (m, 2H), 7.31 – 7.21 (m, 3H), 7.21 – 7.15 (m, 1H), 7.10 – 7.01 (m, 4H), 7.00 – 6.92 (m, 2H), 5.69 (dtt, *J* = 15.2, 6.7, 1.2 Hz, 1H), 5.49 (dtt, *J* = 15.2, 7.4, 1.5 Hz, 1H), 3.76 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.34 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 162.43, 154.90, 139.88, 138.91, 131.63, 130.79, 130.24, 128.53, 128.51, 126.39, 125.15, 120.44, 117.73, 117.35, 60.16, 38.93; **HRMS** calculated for $C_{22}H_{21}O_3S$ $[M+H]^+$ 365.1206, found 365.1208.



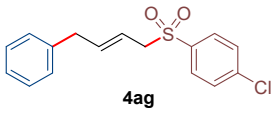
4ae

(*E*)-4-((4-Phenylbut-2-en-1-yl)sulfonyl)-1,1'-biphenyl (4ae): White solid, m.p. 69-70 °C. 53.4 mg, 77% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.86 (d, *J* = 8.4 Hz, 2H), 7.71 – 7.63 (m, 2H), 7.61 – 7.53 (m, 2H), 7.53 – 7.38 (m, 3H), 7.26 – 7.11 (m, 3H), 7.06 – 6.98 (m, 2H), 5.75 – 5.64 (m, 1H), 5.52 (dtt, *J* = 15.1, 7.4, 1.5 Hz, 1H), 3.81 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.34 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 146.52, 140.03, 139.11, 138.92, 136.71, 129.11, 129.06, 128.70, 128.53, 128.51, 127.59, 127.41, 126.36, 117.60, 60.09, 38.94; **HRMS** calculated for $C_{22}H_{21}O_2S$ $[M+H]^+$ 349.1257, found 349.1257.



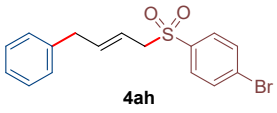
4af

(*E*)-1-Fluoro-4-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4af): White solid, m.p. 85-86 °C. 51.3 mg, 88% yield, *E/Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.86 – 7.73 (m, 2H), 7.32 – 7.16 (m, 3H), 7.16 – 7.07 (m, 2H), 7.06 – 6.97 (m, 2H), 5.65 (dtt, *J* = 15.2, 6.8, 1.1 Hz, 1H), 5.47 (dtt, *J* = 15.1, 7.4, 1.5 Hz, 1H), 3.77 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.32 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 165.75 (d, *J* = 256.1 Hz), 140.28, 138.81, 134.09 (d, *J* = 3.1 Hz), 131.39 (d, *J* = 9.6 Hz), 128.56, 128.46, 126.45, 117.42, 116.28 (d, *J* = 22.5 Hz), 60.08, 38.90; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -103.58; **HRMS** calculated for $C_{16}H_{16}FO_2S$ $[M+H]^+$ 291.0850, found 291.0850.



4ag

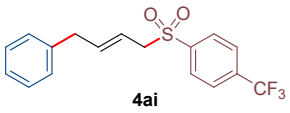
(*E*)-1-Chloro-4-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4ag): White solid, m.p. 99-100 °C. 46.4 mg, 76% yield, *E/Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.77 – 7.67 (m, 2H), 7.46 – 7.37 (m, 2H), 7.34 – 7.16 (m, 3H), 7.04 – 6.97 (m, 2H), 5.65 (dtt, *J* = 15.1, 6.8, 1.1 Hz, 1H), 5.47 (dtt, *J* = 15.1, 7.4, 1.4 Hz, 1H), 3.77 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.32 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 140.39, 140.37, 138.77, 136.47, 130.02, 129.32, 128.58, 128.44, 126.47, 117.31, 60.00, 38.89; **HRMS** calculated for $C_{16}H_{16}ClO_2S$ $[M+H]^+$ 307.0554, found 307.0557.



4ah

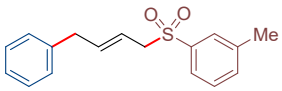
(*E*)-1-Bromo-4-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4ah): White solid, m.p. 107-108 °C. 42.7 mg, 61% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.33 – 7.25 (m, 2H), 7.25 – 7.18 (m, 1H), 7.01 (d, *J* = 7.3 Hz, 2H), 5.65 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.48 (dt, *J* = 15.1, 7.4 Hz, 1H), 3.77 (d, *J* = 7.3 Hz, 2H), 3.33 (d, *J* = 6.8 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 140.42, 138.76, 136.98, 132.31,

130.08, 128.97, 128.60, 128.43, 126.48, 117.27, 59.98, 38.89; **HRMS** calculated for $C_{16}H_{15}BrNaO_2S$ $[M+Na]^+$ 372.9868, found 372.9885.



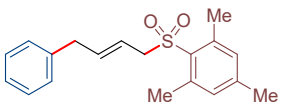
4ai

(*E*)-1-((4-Phenylbut-2-en-1-yl)sulfonyl)-4-(trifluoromethyl) benzene (4ai): White solid, m.p. 94-95 °C. 51.8 mg, 76% yield, *E/Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.91 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.16 (m, 3H), 7.07 – 6.96 (m, 2H), 5.71 – 5.59 (m, 1H), 5.54 – 5.42 (m, 1H), 3.84 – 3.74 (m, 2H), 3.32 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (176 MHz, Chloroform-*d*) δ = 141.44, 140.78, 138.68, 135.29 (q, *J* = 33.2 Hz), 129.22, 128.60, 128.40, 126.51, 126.08 (q, *J* = 3.6 Hz), 123.10 (q, *J* = 273.1 Hz), 116.92, 59.83, 38.93; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -63.15; **HRMS** calculated for $C_{17}H_{16}F_3O_2S$ $[M+H]^+$ 341.0818, found 341.0820.



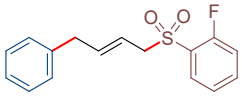
4aj

(*E*)-1-Methyl-3-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4aj): Colorless liquid, 39.5 mg, 69% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.69 – 7.58 (m, 2H), 7.47 – 7.33 (m, 2H), 7.32 – 7.14 (m, 3H), 7.09 – 6.98 (m, 2H), 5.69 (dtt, *J* = 15.1, 6.7, 1.2 Hz, 1H), 5.48 (dtt, *J* = 15.0, 7.4, 1.5 Hz, 1H), 3.77 (dd, *J* = 7.4, 1.1 Hz, 2H), 3.34 (d, *J* = 6.7 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 139.76, 139.32, 138.88, 138.19, 134.40, 128.90, 128.69, 128.50, 128.46, 126.34, 125.64, 117.62, 59.98, 38.85, 21.32; **HRMS** calculated for $C_{17}H_{19}O_2S$ $[M+H]^+$ 287.1100, found 287.1100.



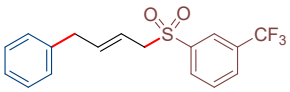
4ak

(*E*)-1,3,5-Trimethyl-2-((4-phenylbut-2-en-1-yl)sulfonyl) benzene (4ak): Colorless liquid, 46.6 mg, 74% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.29 – 7.13 (m, 3H), 7.02 – 6.94 (m, 2H), 6.91 (s, 2H), 5.67 (dtt, *J* = 15.3, 6.6, 1.1 Hz, 1H), 5.49 (dtt, *J* = 15.1, 7.5, 1.5 Hz, 1H), 3.78 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.31 (d, *J* = 6.7 Hz, 2H), 2.61 (s, 6H), 2.29 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 143.16, 140.20, 139.64, 138.84, 132.15, 132.13, 128.48, 128.44, 126.29, 117.50, 59.88, 38.89, 23.08, 21.04; **HRMS** calculated for $C_{19}H_{23}O_2S$ $[M+H]^+$ 315.1413, found 315.1416.



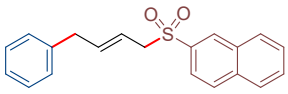
4al

(*E*)-1-Fluoro-2-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4al): Colorless liquid, 53.3 mg, 92% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ = 7.90 – 7.81 (m, 1H), 7.66 – 7.55 (m, 1H), 7.29 (td, *J* = 7.6, 1.1 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.18 – 7.14 (m, 2H), 6.90 (dd, *J* = 7.0, 1.9 Hz, 2H), 5.82 – 5.73 (m, 1H), 5.54 – 5.45 (m, 1H), 4.00 (d, *J* = 7.6 Hz, 2H), 3.28 (d, *J* = 7.0 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 160.68, 158.14, 140.24, 138.75, 136.14, 136.05, 130.98, 128.47, 128.36, 126.30, 126.22, 126.07, 124.72, 124.68, 117.13, 117.06, 116.85, 59.29, 59.26, 38.83; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -108.81; **HRMS** calculated for $C_{16}H_{16}FO_2S$ $[M+H]^+$ 291.0850, found 291.0851.



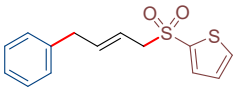
4am

(*E*)-1-((4-Phenylbut-2-en-1-yl)sulfonyl)-3-(trifluoromethyl) benzene (4am): Colorless liquid, 44.7 mg, 66% yield, *E/Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.12 (s, 1H), 7.98 (dt, *J* =7.9, 1.3 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.31 – 7.14 (m, 3H), 7.01 (dd, *J* = 7.0, 1.8 Hz, 2H), 5.74 – 5.62 (m, 1H), 5.45 (dtt, *J* = 15.1, 7.4, 1.6 Hz, 1H), 3.85 – 3.75 (d, *J* = 7.4 Hz, 2H), 3.32 (d, *J* = 6.6 Hz, 2H); **^{13}C NMR** (176 MHz, Chloroform-*d*) δ = 140.86, 139.36, 138.56, 131.91, 131.77 (q, *J* = 33.7 Hz), 130.33 (q, *J* = 3.7 Hz), 129.84, 128.59, 128.45, 126.47, 125.62 (q, *J* = 3.9 Hz), 123.13 (q, *J* = 273.0 Hz), 116.89, 59.93, 38.84; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -62.75; **HRMS** calculated for $C_{17}H_{16}F_3O_2S$ $[M+H]^+$ 341.0818, found 341.0821.



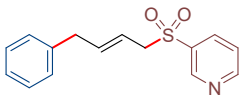
4an

(*E*)-2-((4-Phenylbut-2-en-1-yl)sulfonyl)naphthalene (4an): White solid, 32.8 mg, m.p. 95-96 °C. 51% yield, *E/Z* = 17/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.42 (d, *J* = 1.8 Hz, 1H), 7.99 – 7.90 (m, 3H), 7.79 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.72 – 7.59 (m, 2H), 7.15 – 7.05 (m, 3H), 6.93 – 6.86 (m, 2H), 5.73 – 5.59 (m, 1H), 5.51 (dtt, *J* = 15.3, 7.4, 1.4 Hz, 1H), 3.87 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.29 (d, *J* = 6.7 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 139.86, 138.74, 135.30, 135.19, 132.09, 130.33, 129.48, 129.32, 129.26, 128.41, 128.36, 128.01, 127.68, 126.28, 123.12, 117.69, 60.07, 38.80; **HRMS** calculated for $C_{20}H_{19}O_2S$ $[M+H]^+$ 323.1100, found 323.1102.



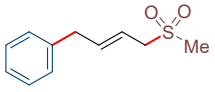
4ao

(*E*)-2-((4-Phenylbut-2-en-1-yl)sulfonyl)thiophene (4ao): Yellow liquid, 52.9 mg, 95% yield, *E/Z* = 20/1, R_f = 0.35 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.65 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.57 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 7.10 – 7.03 (m, 3H), 5.75 (dtt, *J* = 15.0, 6.7, 1.2 Hz, 1H), 5.53 (dtt, *J* = 15.1, 7.4, 1.5 Hz, 1H), 3.86 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.36 (d, *J* = 6.8 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 140.36, 139.02, 138.86, 134.58, 134.04, 128.56, 128.55, 127.72, 126.40, 117.48, 61.21, 38.93; **HRMS** calculated for $C_{14}H_{15}O_2S_2$ $[M+H]^+$ 279.0508, found 279.0509.



4ap

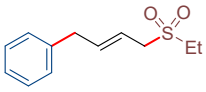
(*E*)-3-((4-Phenylbut-2-en-1-yl)sulfonyl)pyridine (4ap): Yellow liquid, 23.0 mg, 42% yield, *E/Z* = 10/1, R_f = 0.35 (petroleum ether/ethyl acetate 1/1). **^{1}H NMR** (700 MHz, Chloroform-*d*) δ = 9.05 (d, *J* = 2.2 Hz, 1H), 8.82 (dd, *J* = 4.9, 1.6 Hz, 1H), 8.05 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.30 – 7.25 (m, 2H), 7.23 – 7.19 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 5.69 (dt, *J* = 14.2, 6.8 Hz, 1H), 5.52 – 5.45 (m, 1H), 3.82 (d, *J* = 7.5 Hz, 2H), 3.34 (d, *J* = 6.8 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 154.16, 149.43, 141.06, 138.57, 136.45, 134.53, 128.63, 128.48, 126.50, 123.51, 116.83, 60.31, 38.91; **HRMS** calculated for $C_{15}H_{16}NO_2S$ $[M+H]^+$ 274.0896, found 274.0901.



4aq

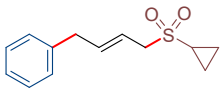
(*E*)-(4-(Methylsulfonyl)but-2-en-1-yl)benzene (4aq): Colorless liquid, 31.4 mg, 43% yield, *E/Z* = 17/1, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.34 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.20 –

7.14 (m, 2H), 6.08 – 5.96 (m, 1H), 5.76 – 5.61 (m, 1H), 3.69 (d, *J* = 7.4 Hz, 2H), 3.46 (d, *J* = 6.8 Hz, 2H), 2.82 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 140.07, 138.77, 128.70, 128.52, 126.55, 117.91, 58.62, 39.08, 39.03; **HRMS** calculated for $C_{11}H_{14}NaO_2S$ $[M+Na]^+$ 233.0607, found 233.0608.



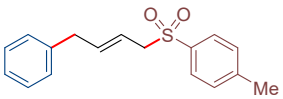
4ar

(*E*)-(4-(Ethylsulfonyl)but-2-en-1-yl)benzene (4ar): Colorless liquid, 33.6 mg, 75% yield, *E*/*Z* > 20/1, R_f = 0.30 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.35 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.19 – 7.13 (m, 2H), 6.00 (dtt, *J* = 15.1, 6.9, 1.3 Hz, 1H), 5.63 (dtt, *J* = 15.1, 7.4, 1.6 Hz, 1H), 3.67 (d, *J* = 7.4 Hz, 2H), 3.45 (d, *J* = 6.8 Hz, 2H), 2.95 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 139.69, 138.85, 128.67, 128.51, 126.51, 117.71, 55.96, 45.62, 39.02, 6.49; **HRMS** calculated for $C_{12}H_{17}O_2S$ $[M+H]^+$ 225.0944, found 225.0942.



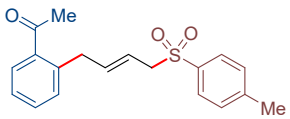
4as

(*E*)-(4-(Cyclopropylsulfonyl)but-2-en-1-yl)benzene (4as): Colorless liquid, 37.5 mg, 79% yield, *E*/*Z* = 18/1, R_f = 0.35 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.34 – 7.27 (m, 2H), 7.25 – 7.13 (m, 3H), 6.08 – 5.96 (m, 1H), 5.65 (dtt, *J* = 15.1, 7.5, 1.6 Hz, 1H), 3.72 (dd, *J* = 7.4, 1.1 Hz, 2H), 3.46 (d, *J* = 6.8 Hz, 2H), 2.34 (tt, *J* = 8.0, 4.8 Hz, 1H), 1.20 (dt, *J* = 4.8, 1.5 Hz, 2H), 1.00 – 0.92 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 139.56, 138.96, 128.64, 128.55, 126.46, 117.65, 57.71, 39.04, 28.42, 4.66; **HRMS** calculated for $C_{13}H_{17}O_2S$ $[M+H]^+$ 237.0944, found 237.0943.



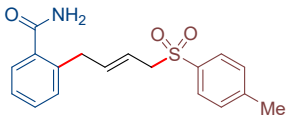
4ba

(*E*)-1-Methyl-4-((4-phenylbut-2-en-1-yl)sulfonyl)benzene (4ba): White solid, m.p. 67-68 °C. 52.4 mg, 91% yield, *E*/*Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.69 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.23 (m, 4H), 7.23 – 7.15 (m, 1H), 7.07 – 6.98 (m, 2H), 5.73 – 5.59 (m, 1H), 5.53 – 5.43 (m, 1H), 3.75 (dd, *J* = 7.3, 1.1 Hz, 2H), 3.32 (d, *J* = 6.7 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.54, 139.75, 138.95, 135.26, 129.63, 128.51, 128.46, 126.31, 117.72, 60.06, 38.89, 21.65; **HRMS** calculated for $C_{17}H_{19}O_2S$ $[M+H]^+$ 287.1100, found 287.1099.



4bb

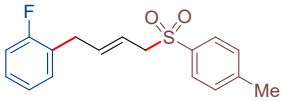
(*E*)-1-(2-(4-Tosylbut-2-en-1-yl)phenyl)ethan-1-one (4bb): Yellow liquid, 64.9 mg, 99% yield, *E*/*Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 3/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.69 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.32 (td, *J* = 7.6, 1.4 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.13 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.69 (dtt, *J* = 15.3, 6.7, 1.1 Hz, 1H), 5.42 (dtt, *J* = 15.1, 7.4, 1.5 Hz, 1H), 3.73 (dd, *J* = 7.5, 1.1 Hz, 2H), 3.59 (dd, *J* = 6.7, 1.4 Hz, 2H), 2.55 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 201.49, 144.43, 139.91, 139.14, 137.22, 135.17, 131.82, 131.32, 129.54, 128.49, 126.45, 117.46, 60.05, 37.00, 29.58, 21.64; **HRMS** calculated for $C_{19}H_{21}O_3S$ $[M+H]^+$ 329.1206, found 329.1214.



4bc

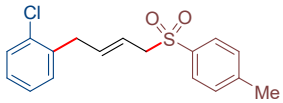
(*E*)-2-(4-Tosylbut-2-en-1-yl)benzamide (4bc): Yellow solid, m.p. 124-125 °C. 52.8 mg, 80% yield, *E*/*Z* > 20/1, R_f = 0.20 (petroleum ether/ethyl acetate 3/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 8.3 Hz,

2H), 7.44 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.34 (td, *J* = 7.6, 1.5 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.09 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.26 (s, 1H), 6.07 (s, 1H), 5.82 – 5.71 (m, 1H), 5.39 (dtt, *J* = 15.2, 7.5, 1.6 Hz, 1H), 3.72 (dd, *J* = 7.4, 1.1 Hz, 2H), 3.56 (dd, *J* = 6.5, 1.5 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 171.97, 144.64, 140.07, 137.12, 135.30, 135.28, 130.50, 130.40, 129.70, 128.35, 127.36, 126.56, 117.64, 59.96, 36.27, 21.66; **HRMS** calculated for $C_{18}H_{20}NO_3S$ $[M+H]^+$ 330.1158, found 330.1167.



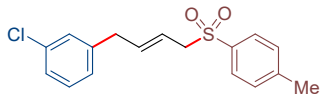
4bd

(*E*)-1-Fluoro-2-(4-tosylbut-2-en-1-yl)benzene (4bd): White solid, m.p. 93-94 °C. 60.0 mg, 99% yield, *E*/*Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.63 – 7.55 (m, 2H), 7.20 – 7.08 (m, 3H), 7.00 – 6.86 (m, 3H), 5.53 (dt, *J* = 15.3, 6.6 Hz, 1H), 5.44 – 5.33 (m, 1H), 3.66 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.26 (d, *J* = 6.5 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 160.79 (d, *J* = 245.5 Hz), 144.55, 138.16, 135.01, 130.58 (d, *J* = 4.6 Hz), 129.58, 128.52, 128.18 (d, *J* = 8.0 Hz), 125.87 (d, *J* = 15.9 Hz), 124.10 (d, *J* = 3.7 Hz), 118.16, 115.26 (d, *J* = 21.8 Hz), 59.97, 31.97 (d, *J* = 3.1 Hz), 21.66; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -118.34; **HRMS** calculated for $C_{17}H_{18}FO_2S$ $[M+H]^+$ 305.1006, found 305.1007.



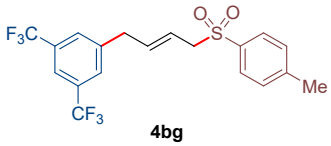
4be

(*E*)-1-Chloro-2-(4-tosylbut-2-en-1-yl)benzene (4be): Colorless liquid, 29.0 mg, 45% yield, *E*/*Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.72 – 7.63 (m, 2H), 7.39 – 7.29 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.13 (m, 2H), 7.09 – 7.01 (m, 1H), 5.62 (dt, *J* = 15.4, 6.6 Hz, 1H), 5.52 – 5.41 (m, 1H), 3.75 (d, *J* = 7.7 Hz, 2H), 3.43 (d, *J* = 6.3 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.53, 137.89, 136.69, 135.01, 133.89, 130.41, 129.57, 129.47, 128.53, 127.88, 126.91, 118.37, 59.99, 36.43, 21.66; **HRMS** calculated for $C_{17}H_{18}ClO_2S$ $[M+H]^+$ 321.0711, found 321.0712.



4bf

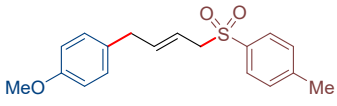
(*E*)-1-Chloro-3-(4-tosylbut-2-en-1-yl)benzene (4bf): Colorless liquid, 57.4 mg, 89% yield, *E*/*Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 3/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.73 – 7.63 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.15 (m, 2H), 7.01 (s, 1H), 6.95 – 6.88 (m, 1H), 5.61 (dt, *J* = 15.2, 6.6 Hz, 1H), 5.53 – 5.42 (m, 1H), 3.76 (d, *J* = 7.5 Hz, 2H), 3.29 (d, *J* = 6.6 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.71, 140.97, 138.75, 135.10, 134.22, 129.74, 129.68, 128.59, 128.46, 126.76, 126.55, 118.46, 59.93, 38.49, 21.67; **HRMS** calculated for $C_{17}H_{18}ClO_2S$ $[M+H]^+$ 321.0711, found 321.0708.



4bg

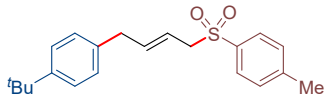
(*E*)-1-(4-Tosylbut-2-en-1-yl)-3,5-bis (trifluoromethyl)benzene (4bg): Yellow liquid, 62.2 mg, 74% yield, *E*/*Z* = 19/1, R_f = 0.25 (petroleum ether/ethyl acetate 3/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.74 (s, 1H), 7.72 – 7.66 (m, 2H), 7.54 (s, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.69 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.54 (dtt, *J* = 15.3, 7.4, 1.5 Hz, 1H), 3.80 (d, *J* = 7.3 Hz, 2H), 3.49 (d, *J* = 6.6 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (176 MHz, Chloroform-*d*) δ = 144.88, 141.47, 137.26, 135.30, 131.79 (q, *J* = 33.2 Hz), 129.67, 128.68 (d, *J* = 3.8 Hz), 128.31, 123.26 (q, *J* = 272.6 Hz),

120.51 (p, *J* = 3.9 Hz), 119.74, 59.72, 38.42, 21.52; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -62.83; **HRMS** calculated for $C_{19}H_{17}F_6O_2S$ $[M+H]^+$ 423.0848, found 423.0850.



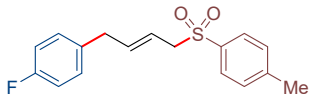
4bh

(*E*)-1-Methoxy-4-(4-tosylbut-2-en-1-yl)benzene (4bh): White solid, m.p. 105-106 °C. 49.9 mg, 79% yield, *E/Z* = 15/1, R_f = 0.20 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.62 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.75 – 6.69 (m, 2H), 5.55 (dt, *J* = 14.2, 6.7 Hz, 1H), 5.42 – 5.32 (m, 1H), 3.71 (s, 3H), 3.67 (d, *J* = 7.6 Hz, 2H), 3.18 (d, *J* = 6.7 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 158.10, 144.55, 140.25, 135.25, 130.96, 129.64, 129.46, 128.50, 117.30, 113.85, 60.06, 55.29, 38.00, 21.67; **HRMS** calculated for $C_{18}H_{21}O_3S$ $[M+H]^+$ 317.1206, found 317.1206.



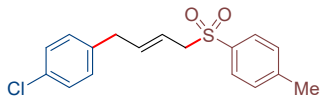
4bi

(*E*)-1-(Tert-butyl)-4-(4-tosylbut-2-en-1-yl)benzene (4bi): White solid, m.p. 70-71 °C. 59.0 mg, 86% yield, *E/Z* = 15/1, R_f = 0.35 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.75 – 7.64 (m, 2H), 7.32 – 7.24 (m, 4H), 7.02 – 6.92 (m, 2H), 5.64 (dt, *J* = 15.1, 6.8 Hz, 1H), 5.48 (dtt, *J* = 15.1, 7.4, 1.5 Hz, 1H), 3.75 (d, *J* = 7.3 Hz, 2H), 3.30 (d, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.31 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 149.17, 144.52, 139.96, 135.89, 135.25, 129.65, 128.57, 128.21, 125.36, 117.53, 60.10, 38.39, 34.42, 31.43, 21.70; **HRMS** calculated for $C_{21}H_{27}O_2S$ $[M+H]^+$ 343.1726, found 343.1727.



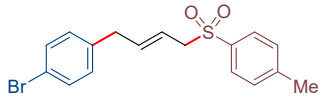
4bj

(*E*)-1-Fluoro-4-(4-tosylbut-2-en-1-yl)benzene (4bj): White solid, m.p. 83-84 °C. 44.5 mg, 73% yield, *E/Z* = 19/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.72 – 7.67 (m, 2H), 7.31 – 7.25 (m, 2H), 7.00 – 6.88 (m, 4H), 5.68 – 5.59 (m, 1H), 5.46 (dtt, *J* = 15.1, 7.5, 1.5 Hz, 1H), 3.76 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.30 (d, *J* = 6.7 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 161.48 (d, *J* = 244.2 Hz), 144.64, 139.59, 135.26, 134.57 (d, *J* = 3.3 Hz), 129.92 (d, *J* = 7.9 Hz), 129.65, 128.45, 117.85, 115.21 (d, *J* = 21.2 Hz), 59.97, 38.02, 21.66; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -116.89; **HRMS** calculated for $C_{17}H_{18}FO_2S$ $[M+H]^+$ 305.1006, found 305.1005.



4bk

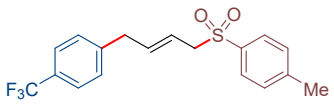
(*E*)-1-Chloro-4-(4-tosylbut-2-en-1-yl)benzene (4bk): White solid, m.p. 99-100 °C. 61.3 mg, 96% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 – 7.65 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.19 (m, 2H), 6.98 – 6.91 (m, 2H), 5.66 – 5.56 (m, 1H), 5.52 – 5.41 (m, 1H), 3.76 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.29 (d, *J* = 6.7 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.67, 139.20, 137.41, 135.18, 132.07, 129.87, 129.65, 128.55, 128.43, 118.12, 59.94, 38.17, 21.67; **HRMS** calculated for $C_{17}H_{18}ClO_2S$ $[M+H]^+$ 321.0711, found 321.0712.



4bl

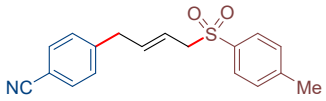
(*E*)-1-Bromo-4-(4-tosylbut-2-en-1-yl)benzene (4bl): White solid, m.p. 99-100 °C. 61.6 mg, 84% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum

ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 – 7.63 (m, 2H), 7.40 – 7.33 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.93 – 6.86 (m, 2H), 5.66 – 5.55 (m, 1H), 5.51 – 5.41 (m, 1H), 3.75 (dd, *J* = 7.3, 1.1 Hz, 2H), 3.27 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.68, 139.09, 137.93, 135.16, 131.51, 130.27, 129.66, 128.43, 120.12, 118.18, 59.93, 38.24, 21.69; **HRMS** calculated for $C_{17}H_{18}BrO_2S$ $[M+H]^+$ 365.0205, found 365.0207.



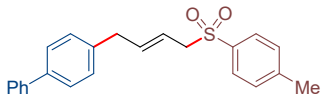
4bm

(*E*)-1-Methyl-4-((4-(4-(trifluoromethyl)phenyl)but-2-en-1-yl) sulfonyl)benzene (4bm): White solid, m.p. 138-139 °C. 63.6 mg, 90% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 – 7.65 (m, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.69 – 5.59 (m, 1H), 5.55 – 5.45 (m, 1H), 3.77 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.39 (d, *J* = 6.7 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (176 MHz, Chloroform-*d*) δ = 144.69, 143.08, 138.55, 135.24, 129.64, 128.85, 128.69 (q, *J* = 32.4 Hz), 128.41, 125.35 (q, *J* = 3.7 Hz), 124.23 (q, *J* = 271.8 Hz), 118.65, 59.90, 38.59, 21.53; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ = -62.34; **HRMS** calculated for $C_{18}H_{18}F_3O_2S$ $[M+H]^+$ 355.0974, found 355.0978.



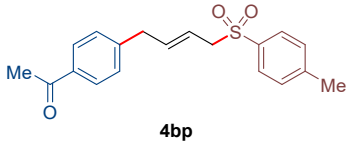
4bn

(*E*)-4-(4-Tosylbut-2-en-1-yl)benzonitrile (4bn) : Yellow solid, m.p. 116-117 °C. 47.8 mg, 77% yield, *E/Z* > 20/1, R_f = 0.55 (petroleum ether/ethyl acetate 5/1); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 5.73 – 5.62 (m, 1H), 5.52 (dtt, *J* = 15.2, 7.4, 1.4 Hz, 1H), 3.82 – 3.74 (m, 2H), 3.41 (d, *J* = 6.7 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.79, 144.56, 137.87, 135.34, 132.28, 129.73, 129.32, 128.37, 119.12, 118.87, 110.27, 59.84, 38.82, 21.69; **HRMS** calculated for $C_{18}H_{18}NO_2S$ $[M+H]^+$ 312.1053, found 312.1054.



4bo

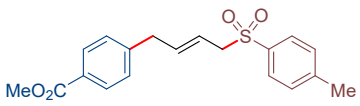
(*E*)-4-(4-Tosylbut-2-en-1-yl)-1,1'-biphenyl (4bo): White solid, m.p. 96-97 °C. 67.0 mg, 92% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.54 (m, 2H), 7.52 – 7.46 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.30 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.06 (m, 2H), 5.72 – 5.62 (m, 1H), 5.56 – 5.45 (m, 1H), 3.76 (d, *J* = 7.3 Hz, 2H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.60, 140.86, 139.66, 139.32, 138.06, 135.28, 129.67, 128.98, 128.84, 128.53, 127.25, 127.21, 126.99, 117.86, 60.07, 38.55, 21.69; **HRMS** calculated for $C_{23}H_{23}O_2S$ $[M+H]^+$ 363.1413, found 363.1417.



4bp

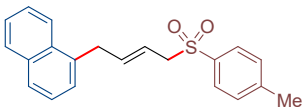
(*E*)-1-(4-(4-Tosylbut-2-en-1-yl)phenyl)ethan-1-one (4bp): White solid, m.p. 116-117 °C. 56.7 mg, 86% yield, *E/Z* > 20/1, R_f = 0.15 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.67 (dt, *J* = 15.1, 6.7 Hz, 1H), 5.56 – 5.45 (m, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 3.39 (d, *J* = 6.7 Hz, 2H), 2.59 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 197.76, 144.70, 144.60, 138.56, 135.40, 135.23, 129.69, 128.73, 128.60, 128.41,

118.55, 59.92, 38.75, 26.62, 21.66; **HRMS** calculated for $C_{19}H_{24}NO_3S$ $[M+NH_4]^+$ 346.1471, found 346.1481.



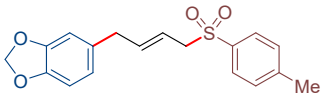
4bq

Methyl (*E*)-4-(4-tosylbut-2-en-1-yl)benzoate (4bq) : White solid, m.p. 107-108 °C. 77.5 mg, 99% yield, *E/Z* = 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.99 – 7.89 (m, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.64 (dt, *J* = 15.1, 6.8 Hz, 1H), 5.55 – 5.43 (m, 1H), 3.91 (s, 3H), 3.78 (d, *J* = 7.4 Hz, 2H), 3.38 (d, *J* = 6.7 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 166.92, 144.67, 144.34, 138.63, 135.16, 129.77, 129.68, 128.52, 128.41, 128.28, 118.55, 59.93, 52.10, 38.78, 21.63; **HRMS** calculated for $C_{19}H_{21}O_4S$ $[M+H]^+$ 345.1155, found 345.1164.



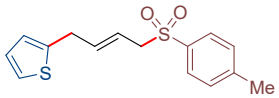
4br

(*E*)-1-(4-Tosylbut-2-en-1-yl)naphthalene (4br): Colorless liquid, 36.2 mg, 54% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.92 – 7.84 (m, 2H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.52 – 7.48 (m, 2H), 7.41 – 7.33 (m, 1H), 7.16 (d, *J* = 6.9 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.78 (dtt, *J* = 15.4, 6.4, 1.2 Hz, 1H), 5.46 (dtt, *J* = 15.2, 7.4, 1.6 Hz, 1H), 3.77 (d, *J* = 6.5 Hz, 2H), 3.72 (dd, *J* = 7.4, 1.1 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.40, 139.43, 135.09, 134.94, 133.83, 131.69, 129.45, 128.78, 128.46, 127.23, 126.38, 126.06, 125.70, 125.56, 123.77, 118.04, 60.04, 35.97, 21.58; **HRMS** calculated for $C_{21}H_{21}O_2S$ $[M+H]^+$ 337.1257, found 337.1252.



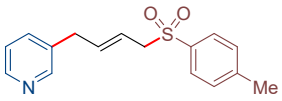
4bs

(*E*)-5-(4-Tosylbut-2-en-1-yl)benzo[d][1,3]dioxole (4bs): Yellow liquid, 58.8 mg, 89% yield, *E/Z* = 13/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.74 – 7.65 (m, 2H), 7.33 – 7.27 (m, 2H), 6.74 – 6.67 (m, 1H), 6.52 – 6.44 (m, 2H), 5.92 (s, 2H), 5.60 (dtt, *J* = 15.4, 6.6, 1.0 Hz, 1H), 5.50 – 5.39 (m, 1H), 3.76 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.23 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 147.65, 146.00, 144.64, 139.85, 135.18, 132.68, 129.67, 128.50, 121.31, 117.64, 108.98, 108.18, 100.90, 60.03, 38.54, 21.66; **HRMS** calculated for $C_{18}H_{19}O_4S$ $[M+H]^+$ 331.0999, found 331.0997.



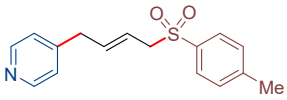
4bt

(*E*)-2-(4-Tosylbut-2-en-1-yl)thiophene (4bt): Yellow liquid, 31.7 mg, 54% yield, *E/Z* = 10/1, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.75 – 7.68 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.70 – 6.65 (m, 1H), 5.69 (dtt, *J* = 15.4, 6.5, 1.1 Hz, 1H), 5.53 (dtt, *J* = 15.1, 7.4, 1.4 Hz, 1H), 3.77 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.52 (d, *J* = 6.6 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.65, 141.47, 138.73, 135.25, 129.70, 128.51, 126.93, 124.95, 123.91, 118.13, 59.89, 32.87, 21.68; **HRMS** calculated for $C_{15}H_{17}O_2S_2$ $[M+H]^+$ 293.0664, found 293.0648.



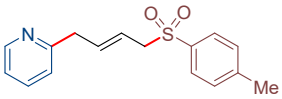
4bu

(*E*)-3-(4-Tosylbut-2-en-1-yl)pyridine (4bu): Yellow liquid, 36.1 mg, 63% yield, *E*/*Z* = 18/1, R_f = 0.25 (petroleum ether/ethyl acetate 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.46 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.33 (d, *J* = 2.6 Hz, 1H), 7.72 – 7.66 (m, 2H), 7.36 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.20 (ddd, *J* = 7.8, 4.8, 0.9 Hz, 1H), 5.71 – 5.60 (m, 1H), 5.51 (dtt, *J* = 15.3, 7.4, 1.4 Hz, 1H), 3.77 (dd, *J* = 7.3, 1.0 Hz, 2H), 3.34 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 149.88, 147.86, 144.76, 138.45, 135.99, 135.19, 134.33, 129.69, 128.39, 123.37, 118.70, 59.87, 35.96, 21.66; **HRMS** calculated for $C_{16}H_{17}NNaO_2S$ $[M+Na]^+$ 310.0872, found 310.0873.



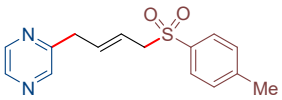
4bv

(*E*)-4-(4-Tosylbut-2-en-1-yl)pyridine (4bv): Yellow liquid, 57.1 mg, 99% yield, *E*/*Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.48 (d, *J* = 5.0 Hz, 2H), 7.75 – 7.64 (m, 2H), 7.27 (s, 2H), 7.03 – 6.92 (m, 2H), 5.72 – 5.48 (m, 2H), 3.79 (d, *J* = 7.1 Hz, 2H), 3.34 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 149.78, 147.91, 144.78, 137.37, 135.19, 129.71, 128.37, 123.80, 119.36, 59.84, 38.01, 21.65; **HRMS** calculated for $C_{16}H_{18}NO_2S$ $[M+H]^+$ 288.1053, found 288.1074.



4bw

(*E*)-2-(4-Tosylbut-2-en-1-yl)pyridine (4bw): Yellow liquid, 14.3 mg, 25% yield, *E*/*Z* = 15/1, R_f = 0.25 (petroleum ether/ethyl acetate 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.50 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.60 (td, *J* = 7.7, 1.9 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.13 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 7.05 (dt, *J* = 7.8, 1.1 Hz, 1H), 5.82 – 5.71 (m, 1H), 5.58 (dtt, *J* = 15.2, 7.4, 1.5 Hz, 1H), 3.78 (dd, *J* = 7.4, 1.0 Hz, 2H), 3.53 (dd, *J* = 7.0, 1.3 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 159.03, 149.39, 144.56, 138.12, 136.59, 135.25, 129.61, 128.49, 122.82, 121.48, 118.57, 60.06, 41.52, 21.66; **HRMS** calculated for $C_{16}H_{17}NNaO_2S$ $[M+Na]^+$ 310.0872, found 310.0877.



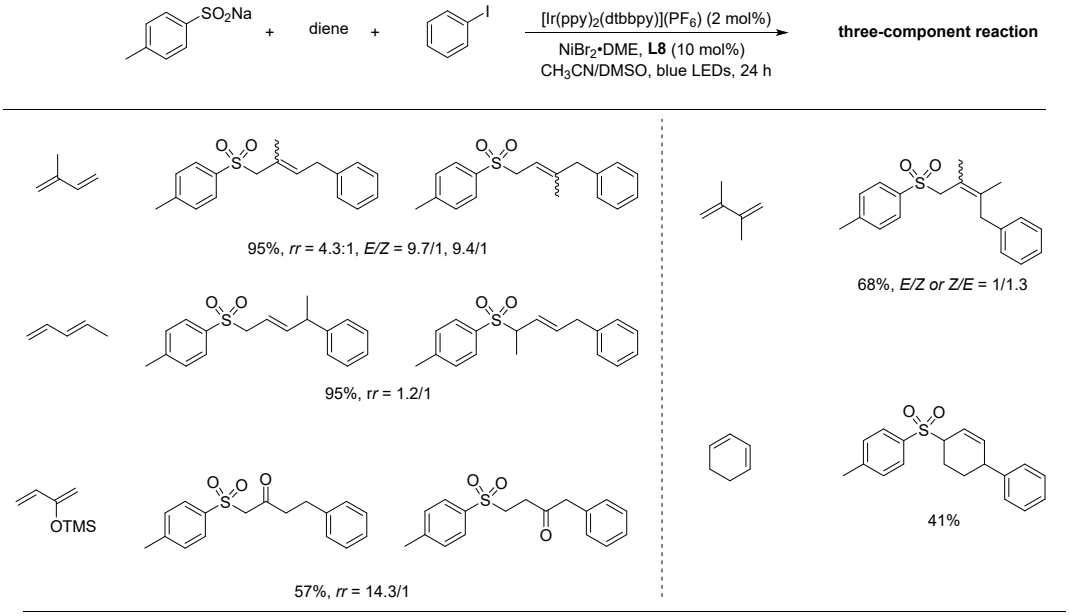
4bx

(*E*)-2-(4-Tosylbut-2-en-1-yl)pyrazine (4bx): Yellow solid, m.p. 82-83 °C. 19.4 mg, 34% yield, *E*/*Z* = 14/1, R_f = 0.25 (petroleum ether/ethyl acetate 1/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.49 – 8.45 (m, 1H), 8.45 – 8.42 (m, 1H), 8.35 (d, *J* = 1.5 Hz, 1H), 7.73 – 7.67 (m, 2H), 7.31 – 7.24 (m, 2H), 5.81 – 5.70 (m, 1H), 5.68 – 5.57 (m, 1H), 3.79 (d, *J* = 7.1 Hz, 2H), 3.56 (d, *J* = 6.7 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 154.74, 144.75, 144.46, 144.14, 142.63, 136.56, 135.14, 129.66, 128.45, 119.67, 59.93, 38.71, 21.67; **HRMS** calculated for $C_{15}H_{17}N_2O_2S$ $[M+H]^+$ 289.1005, found 289.1010.

3.3 Substrates scope for dienes

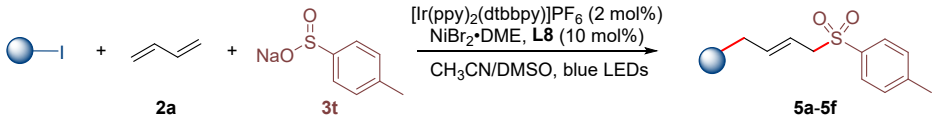
Significant progress of sulfonylarylation have been achieved on carbosulfonylation of conventional alkene and alkynes by Rueping, Lu, Nevado and Chu.[4] Only one example of conjugated diene, 2,3-dimethyl-1,3-butadiene could undergo the cross-coupling reaction.[4i] Subtrates scope for conjugated dienes was showed in table S6 by using our method.

Table S6 Substrates scope for dienes

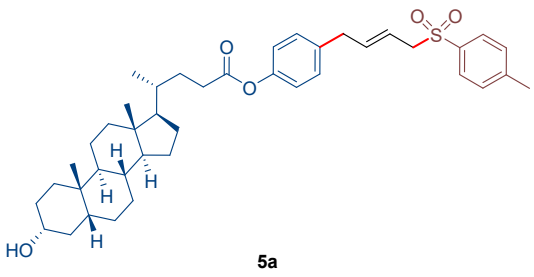


4 Late-stage functionalization and synthetic transformations

4.1 Late-stage functionalization

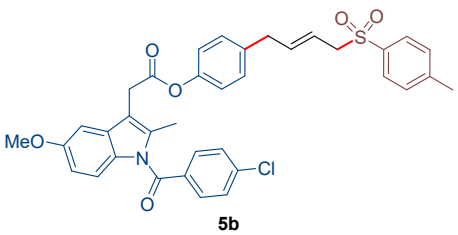


To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added derivatives of aryl iodide (0.20 mmol, 1.0 equiv.), **2a** (0.60 mmol, 2 M in THF, 3.0 equiv.), **3t** (0.40 mmol, 2.0 equiv.), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), $NiBr_2$•DME (10 mol%), **L8** (10 mol%), CH_3CN (1.0 mL), DMSO (0.2 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 24 h. After the reaction was completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product **5a-5f**.



5a

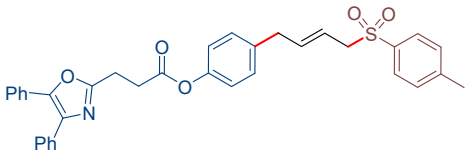
((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-Hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta [a]phenanthren-17-yl)pentanoate (5a): White solid, m.p. 68-69 °C. 115.7 mg, 79% yield, *E/Z* = 15/1, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.68 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.98 – 6.93 (m, 2H), 5.62 (dt, *J* = 15.1, 6.7 Hz, 1H), 5.55 – 5.44 (m, 1H), 3.76 (d, *J* = 7.2 Hz, 2H), 3.62 (tt, *J* = 11.0, 4.6 Hz, 1H), 3.32 (d, *J* = 6.7 Hz, 2H), 2.60 (ddd, *J* = 14.9, 9.7, 4.9 Hz, 1H), 2.52 – 2.38 (m, 4H), 2.03 – 0.81 (m, 32H), 0.67 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 172.85, 149.23, 144.66, 139.46, 136.35, 135.14, 129.67, 129.39, 128.47, 121.54, 117.91, 71.82, 59.98, 56.51, 55.97, 42.78, 42.08, 40.42, 40.19, 38.27, 36.42, 35.85, 35.40, 35.36, 34.58, 31.38, 30.99, 30.52, 28.27, 27.20, 26.43, 24.23, 23.40, 21.62, 20.84, 18.34, 12.09; **HRMS** calculated for $C_{41}H_{57}O_5S$ $[M+H]^+$ 661.3921, found 661.3898.



5b

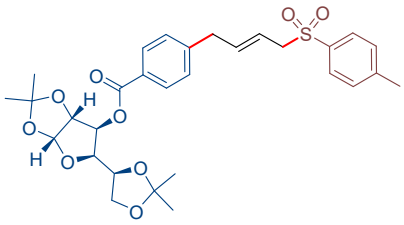
(*E*)-4-(4-Tosylbut-2-en-1-yl)phenyl 2-(1-(4-chloro benzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5b): Yellow liquid, 85.4 mg, 67% yield, *E/Z* = 11/1, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.70 – 7.62 (m, 4H), 7.50 – 7.42 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 2.6 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.96 – 6.88 (m, 3H), 6.72 – 6.66 (m, 1H), 5.65 – 5.55 (m, 1H), 5.46 (dt, *J* = 15.2, 7.5 Hz, 1H), 3.90 (s, 2H), 3.82 (s, 3H), 3.74 (d, *J* = 7.3 Hz, 2H), 3.29 (d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 169.38, 168.30, 156.14, 149.18, 144.64, 139.34, 136.67, 136.20, 135.23, 133.84, 131.20, 130.88, 130.53, 129.67, 129.42, 129.16, 128.43,

121.36, 118.00, 115.03, 112.06, 111.77, 101.33, 59.95, 55.75, 38.21, 30.57, 21.55, 13.46; **HRMS** calculated for $C_{36}H_{33}ClNO_6S$ $[M+H]^+$ 642.1712, found 642.1750.



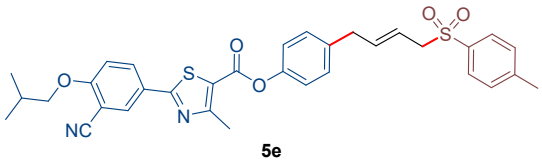
5c

(*E*)-4-(4-Tosylbut-2-en-1-yl)phenyl 3-(4,5-diphenyloxazol-2-yl)propanoate (5c): Colorless liquid, 107.1 mg, 95% yield, *E/Z* = 14/1, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.71 – 7.62 (m, 4H), 7.61 – 7.54 (m, 2H), 7.41 – 7.29 (m, 6H), 7.28 – 7.22 (m, 2H), 7.04 – 6.95 (m, 4H), 5.67 – 5.56 (m, 1H), 5.48 (dtt, *J* = 15.2, 7.3, 1.3 Hz, 1H), 3.80 – 3.71 (m, 2H), 3.36 – 3.26 (m, 4H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.73, 161.48, 149.10, 145.59, 144.68, 139.40, 136.60, 135.15, 132.38, 129.66, 129.43, 128.91, 128.68, 128.59, 128.56, 128.45, 128.14, 127.89, 126.53, 121.48, 117.97, 59.98, 38.26, 31.26, 23.54, 21.58; **HRMS** calculated for $C_{35}H_{32}NO_5S$ $[M+H]^+$ 578.1996, found 578.1993.



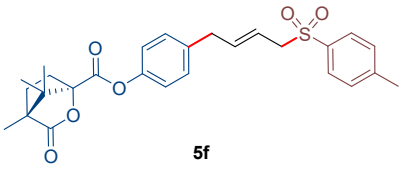
5d

(3a*R*,5*R*,6*S*,6a*R*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 4-((*E*)-4-tosylbut-2-en-1-yl)benzoate (5d): Colorless liquid, 114.1 mg, 99% yield, *E/Z* > 20/1, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.92 (d, *J* = 7.9 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 5.96 (d, *J* = 3.7 Hz, 1H), 5.66 (dt, *J* = 14.1, 6.7 Hz, 1H), 5.56 – 5.44 (m, 2H), 4.63 (d, *J* = 3.7 Hz, 1H), 4.42 – 4.29 (m, 2H), 4.16 – 4.05 (m, 2H), 3.78 (d, *J* = 7.4 Hz, 2H), 3.40 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H), 1.56 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 165.00, 145.03, 144.66, 138.45, 135.28, 129.93, 129.69, 128.72, 128.41, 127.67, 118.67, 112.35, 109.38, 105.12, 83.38, 79.92, 76.56, 72.57, 67.23, 59.91, 38.77, 26.88, 26.75, 26.22, 25.25, 21.64; **HRMS** calculated for $C_{30}H_{36}NaO_9S$ $[M+Na]^+$ 595.1972, found 595.1961.



5e

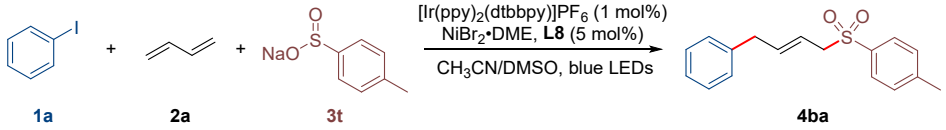
(*E*)-4-(4-Tosylbut-2-en-1-yl)phenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (5e): White solid, m.p. 96-97 °C. 101.3 mg, 84% yield, *E/Z* = 15/1, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 8.22 (d, *J* = 2.3 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 4H), 7.04 (d, *J* = 9.0 Hz, 1H), 5.66 (dt, *J* = 14.1, 6.7 Hz, 1H), 5.51 (dt, *J* = 15.1, 7.4 Hz, 1H), 3.92 (d, *J* = 6.5 Hz, 2H), 3.77 (d, *J* = 7.4 Hz, 2H), 3.36 (d, *J* = 6.7 Hz, 2H), 2.83 (s, 3H), 2.44 (s, 3H), 2.29 – 2.14 (m, 1H), 1.10 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 168.16, 162.99, 162.68, 160.49, 148.70, 144.70, 139.35, 136.98, 135.22, 132.71, 132.19, 129.69, 129.56, 128.46, 125.80, 121.59, 120.58, 118.05, 115.37, 112.73, 103.03, 75.74, 59.97, 38.29, 28.16, 21.64, 19.07, 17.72; **HRMS** calculated for $C_{33}H_{33}N_2O_5S_2$ $[M+H]^+$ 601.1825, found 601.1833.



5f

4-((*E*)-4-Tosylbut-2-en-1-yl)phenyl (1*R*,4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1 carboxylate (5f): White solid, m.p. 127-128 °C. 63.3 mg, 66% yield, *E*/*Z* = 17/1, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.02 – 6.89 (m, 4H), 5.56 (dt, *J* = 15.1, 6.7 Hz, 1H), 5.41 (dtt, *J* = 15.2, 7.4, 1.5 Hz, 1H), 3.69 (d, *J* = 7.3 Hz, 2H), 3.26 (d, *J* = 6.7 Hz, 2H), 2.49 (ddd, *J* = 13.4, 10.8, 4.3 Hz, 1H), 2.34 (s, 3H), 2.12 (ddd, *J* = 13.6, 9.3, 4.5 Hz, 1H), 1.93 (ddd, *J* = 13.1, 10.6, 4.4 Hz, 1H), 1.69 (ddd, *J* = 13.4, 9.4, 4.2 Hz, 1H), 1.09 (s, 3H), 1.07 (s, 3H), 1.02 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 177.87, 166.17, 148.41, 144.68, 139.22, 137.21, 135.20, 129.68, 129.61, 128.43, 121.26, 118.11, 90.85, 59.93, 54.90, 54.70, 38.21, 30.76, 28.97, 21.62, 16.89, 9.75; **HRMS** calculated for $C_{27}H_{31}O_6S$ $[M+H]^+$ 483.1836, found 483.1841.

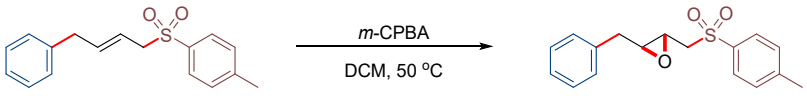
4.2 Large-scale reaction



1a 2a 3t 4ba

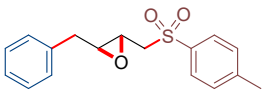
To an oven-dried 100 mL vial was added derivatives of **1a** (0.56 mL, 5.0 mmol, 1.0 equiv.), **2a** (3.0 mL, 6.0 mmol, 2 M in THF, 1.2 equiv.), **3t** (0.98 g, 5.5 mmol, 1.1 equiv.), $[Ir(ppy)_2(dtbbpy)]PF_6$ (45.7 mg, 1 mol%), $NiBr_2$•DME (77.2 mg, 5 mol%), **L8** (68.1 mg, 5 mol%), CH_3CN (20 mL), DMSO (4 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 48 h. After the reaction was completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product **4ba** with 82% yield (1.17 g, *E*/*Z* > 20/1).

4.3 Synthetic transformations



4ba **6a**, 93% yield

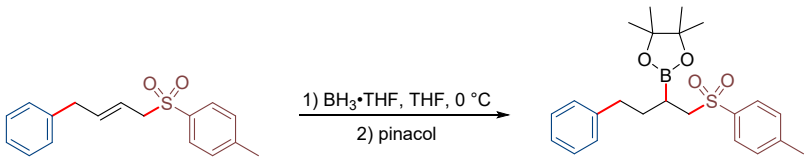
To an oven-dried 4 mL vial was added substrate **4ba** (57.3 mg, 0.20 mmol, 1.0 equiv.), *m*-CPBA (51.8 mg, 0.30 mmmol) and DCM (1.0 mL). The resulting mixture was stirred at 50 °C for 24 h. Then the reaction was quenched by adding a solution of $Na_2S_2O_3$ in water and the mixture was extracted by DCM for three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography to afford the corresponding product **6a** in 93% yield.



6a

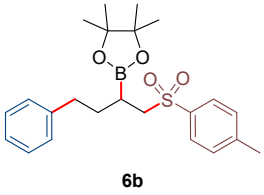
2-Benzyl-3-(tosylmethyl)oxirane (6a): Colorless liquid, 56.1 mg, 93% yield, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.27

(m, 2H), 7.26 – 7.23 (m, 1H), 7.19 – 7.13 (m, 2H), 3.34 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.22 (dd, *J* = 14.5, 5.3 Hz, 1H), 3.10 (ddd, *J* = 6.7, 5.2, 1.6 Hz, 1H), 2.87 – 2.82 (m, 1H), 2.82 – 2.77 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 145.14, 136.23, 136.19, 130.01, 129.04, 128.63, 128.16, 126.92, 59.03, 57.82, 51.31, 37.74, 21.74; **HRMS** calculated for $C_{17}H_{19}O_3S$ $[M+H]^+$ 303.1049, found 303.1052.



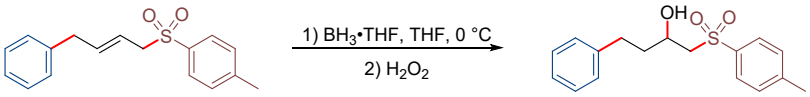
4ba **6b**, 53% yield

To an oven-dried 4 mL vial was added substrate **4ba** (57.3 mg, 0.20 mmol), BH_3•THF (0.60 mL, 0.60 mmol, 1 M in THF) and THF (2.0 mL) at 0 °C. The reaction mixture was stirred for 4 h at room temperature and the reaction was added pinacol (70.9 mg, 0.60 mmol) at 0 °C. The reaction mixture was stirred for 4 h at room temperature. Then the reaction was treated with DCM. The separated organic phase was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography to afford the corresponding product **6b** in 53% yield.



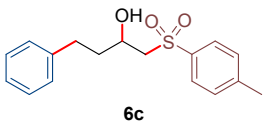
6b

4,4,5,5-Tetramethyl-2-(4-phenyl-1-tosylbutan-2-yl)-1,3,2-dioxaborolane (6b): Colorless liquid, 43.9 mg, 53 % yield, R_f = 0.25 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.76 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.17 – 7.12 (m, 1H), 7.10 – 7.05 (m, 2H), 3.36 (dd, *J* = 14.0, 9.3 Hz, 1H), 3.10 (dd, *J* = 14.0, 5.1 Hz, 1H), 2.63 – 2.49 (m, 2H), 2.44 (s, 3H), 1.87 – 1.67 (m, 2H), 1.54 – 1.44 (m, 1H), 1.29 (s, 12H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.35, 141.70, 136.63, 129.81, 128.35, 128.17, 125.87, 83.89, 57.85, 34.66, 32.28, 24.92, 24.88, 21.64; **HRMS** calculated for $C_{23}H_{32}BO_4S$ $[M+H]^+$ 415.2109, found 415.2120.



4ba **6c**, 50% yield

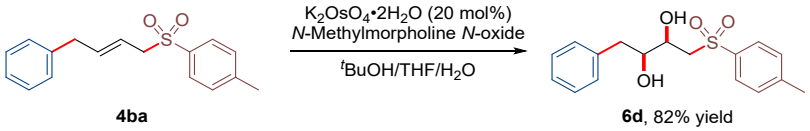
To an oven-dried 4 mL vial was added substrate **4ba** (57.3 mg, 0.20 mmol), BH_3•THF (0.60 mL, 0.60 mmol, 1 M in THF) and THF (2.0 mL) at 0 °C. The reaction mixture was stirred for 4 h at room temperature and the reaction was added H_2O_2 (2.0 mL) at 0 °C. The reaction mixture was stirred for 4 h at room temperature. Then the reaction was treated with DCM. The separated organic phase was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography to afford the corresponding product **6c** in 50% yield.



6c

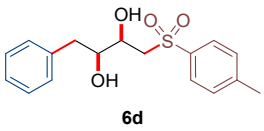
4-Phenyl-1-tosylbutan-2-ol (6c): Colorless liquid, 30.3 mg, 50% yield, R_f = 0.25 (petroleum ether/ethyl acetate 10/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.78 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 –

7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 7.13 – 7.08 (m, 2H), 4.19 – 4.09 (m, 1H), 3.47 (s, 1H), 3.23 (dd, J = 14.2, 9.2 Hz, 1H), 3.14 (dd, J = 14.2, 2.0 Hz, 1H), 2.75 (ddd, J = 14.9, 9.6, 5.7 Hz, 1H), 2.65 (ddd, J = 13.7, 9.3, 6.6 Hz, 1H), 1.86 (dddd, J = 13.8, 9.4, 8.2, 5.7 Hz, 1H), 1.78 – 1.68 (m, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 145.20, 141.04, 136.18, 130.12, 128.48, 128.39, 127.95, 126.03, 65.32, 62.33, 38.05, 31.31, 21.69; **HRMS** calculated for $C_{17}H_{21}O_3S$ $[M+H]^+$ 305.1206, found 305.1208.



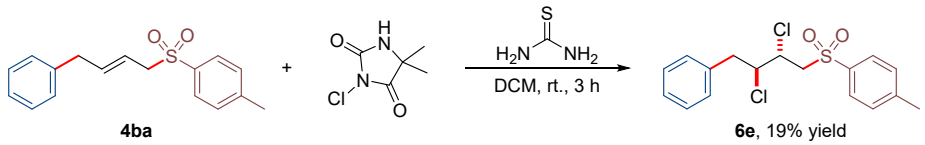
4ba **6d**, 82% yield

To an oven-dried 4 mL vial was added substrate **4ba** (57.3 mg, 0.20 mmol), K_2OsO_4•$2H_2O$ (12.5 mg, 20 mol%), *N*-Methylmorpholine *N*-oxide (70.3 mg, 0.60 mmol), ^{t}BuOH (0.5 mL), THF (0.5 mL) and H_2O (0.5 mL). The reaction mixture was stirred for 12 h at room temperature. Then the reaction was quenched with Na_2SO_3 (252 mg, 2.0 mmol, 10 equiv.) and stirred for 1 h, added H_2O (0.5 mL) and diluted with EtOAc (5 mL). The aqueous layer was extracted with EtOAc (3 x 3 mL), and combined organic layers were washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography to afford the corresponding product **6d** in 82% yield.



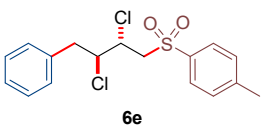
6d

1-Phenyl-4-tosylbutane-2,3-diol (6d): White solid, m.p. 115-116 °C. 52.4 mg, 82% yield, R_f = 0.25 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.77 – 7.73 (m, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.25 – 7.21 (m, 1H), 7.20 – 7.15 (m, 2H), 4.14 – 4.05 (m, 1H), 3.71 (d, J = 6.7 Hz, 1H), 3.49 (d, J = 3.6 Hz, 1H), 3.42 (dd, J = 14.4, 9.3 Hz, 1H), 3.23 (dd, J = 14.4, 2.5 Hz, 1H), 2.90 (dd, J = 13.7, 5.7 Hz, 1H), 2.81 (dd, J = 13.7, 8.1 Hz, 1H), 2.45 (s, 3H), 2.25 (d, J = 6.6 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 145.17, 137.46, 136.19, 130.07, 129.34, 128.67, 127.93, 126.66, 74.44, 67.28, 59.81, 39.71, 21.68; **HRMS** calculated for $C_{17}H_{21}O_4S$ $[M+H]^+$ 321.1155, found 321.1148.



4ba **6e**, 19% yield

To an oven-dried 4 mL vial was added substrate **4ba** (57.3 mg, 0.20 mmol), thiourea (6.0 mg, 40 mol%), 1,3-dichloro-5,5-dimethylhydantoin (59.1 mg, 0.30 mmol) and DCM (2.0 mL). The reaction mixture was stirred for 3 h at room temperature. After the reaction was completed, the target product was purified by column chromatography to afford the corresponding product **6e** in 19% yield.



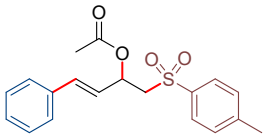
6e

1-((2,3-Dichloro-4-phenylbutyl)sulfonyl)-4-methylbenzene (6e): Colorless liquid, 13.6 mg, 19% yield, R_f = 0.40 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.60 – 7.55 (m, 2H), 7.39 – 7.31 (m, 3H), 7.30 – 7.21 (m, 4H), 4.66 (td, J = 7.5, 1.9 Hz, 1H), 4.30

(ddd, J = 7.7, 4.9, 1.8 Hz, 1H), 3.82 (dd, J = 14.8, 7.7 Hz, 1H), 3.48 (dd, J = 14.8, 4.9 Hz, 1H), 3.18 (d, J = 7.6 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 145.38, 136.08, 135.60, 130.12, 129.26, 128.94, 128.06, 127.45, 63.83, 60.74, 55.56, 41.74, 21.70; **HRMS** calculated for $C_{17}H_{19}Cl_2O_2S$ $[M+H]^+$ 357.0477, found 357.0459.

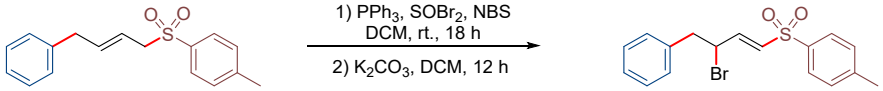
4ba **6f**, 34% yield

To an oven-dried 4 mL vial was added substrate **4ba** (57.3 mg, 0.20 mmol), $[Cp^*IrCl_2]_2$ (8.0 mg, 5 mol%), $AgBF_4$ (7.8 mg, 20 mol%), AgOAc (66.7 mg, 0.40 mmol) and DCE (1.5 mL). The reaction mixture was stirred for 17 h at room temperature. After the reaction was completed, the target product was purified by column chromatography to afford the corresponding product **6f** in 34% yield.



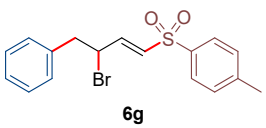
6f

(*E*)-4-Phenyl-1-tosylbut-3-en-2-yl acetate (6f): Colorless liquid, 23.4 mg, 34% yield, R_f = 0.30 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.84 – 7.75 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.32 – 7.23 (m, 5H), 6.60 (dd, J = 15.8, 1.0 Hz, 1H), 6.01 (dd, J = 15.8, 7.4 Hz, 1H), 5.85 – 5.77 (m, 1H), 3.63 (dd, J = 14.7, 8.3 Hz, 1H), 3.42 (dd, J = 14.8, 3.9 Hz, 1H), 2.43 (s, 3H), 1.86 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 169.37, 144.96, 136.59, 135.38, 134.42, 129.93, 128.63, 128.54, 128.30, 126.77, 124.14, 68.91, 59.65, 21.63, 20.84; **HRMS** calculated for $C_{19}H_{20}NaO_4S$ $[M+Na]^+$ 367.0975, found 367.0946.



4ba **6g**, 86% yield

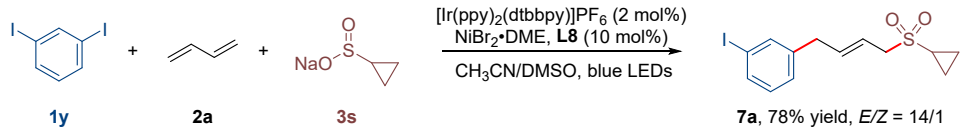
To an oven-dried 4 mL vial was added substrate **4ba** (57.3 mg, 0.20 mmol), PPh_3 (2.1 mg, 4 mol%), $SOBr_2$ (25.0 mg, 0.12 mmol), NBS (53.4 mg, 0.30 mmol), DCM (0.5 mL). The reaction mixture was stirred for 18 h at room temperature in nitrogen atmosphere. Then, K_2CO_3 (55.3 mg, 0.40 mmol) and DCM (1.0 mL) were added to the reaction mixture in air atmosphere. After the reaction was completed, the target product was purified by column chromatography to afford the corresponding product **6g** in 86% yield.



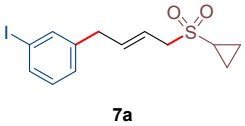
6g

(*E*)-1-((3-Bromo-4-phenylbut-1-en-1-yl)sulfonyl)-4-methylbenzene (6g): White solid, m.p. 105-106 °C. 63.0 mg, 86% yield, R_f = 0.30 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.66 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.29 – 7.24 (m, 3H), 7.15 – 7.10 (m, 2H), 6.98 (dd, J = 14.9, 8.8 Hz, 1H), 6.32 (d, J = 14.8 Hz, 1H), 4.64 (q, J = 7.7 Hz, 1H), 3.29 (dd, J = 14.1, 7.0 Hz, 1H), 3.22 (dd, J = 14.1, 7.7 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 144.75, 142.95, 136.72, 136.41, 132.25, 130.01, 129.24, 128.71, 127.80, 127.41, 48.73, 44.31, 21.70; **HRMS** calculated for $C_{17}H_{18}BrO_2S$ $[M+H]^+$ 365.0205, found 365.0194.

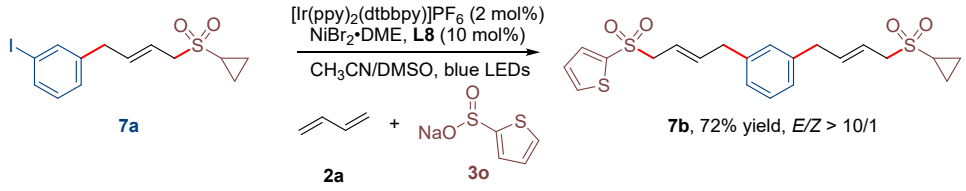
4.4 Iterative reaction



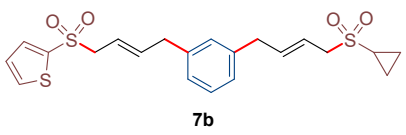
To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added **1y** (165.0 mg, 0.50 mmol), **2a** (0.4 mL, 0.80 mmol, 2 M in THF), **3s** (76.9 mg, 0.60 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (9.1 mg, 2 mol%), $NiBr_2$•DME (15.4 mg, 10 mol%), **L8** (13.6 mg, 10 mol%), CH_3CN (2.5 mL), DMSO (0.5 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 24 h. After the reaction was completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product **7a** in 78% yield.


7a

(*E*)-1-(4-(Cyclopropylsulfonyl)but-2-en-1-yl)-3-iodobenzene (7a) : Colorless liquid, 141.6 mg, 78% yield, *E/Z* = 14/1, R_f = 0.30 (petroleum ether/ethyl acetate 5/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.59 – 7.49 (m, 2H), 7.17 – 7.13 (m, 1H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.03 – 5.90 (m, 1H), 5.72 – 5.60 (m, 1H), 3.74 (dd, *J* = 7.4, 1.1 Hz, 2H), 3.40 (d, *J* = 6.9 Hz, 2H), 2.36 (tt, *J* = 8.0, 4.8 Hz, 1H), 1.27 – 1.19 (m, 2H), 1.04 – 0.97 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 141.41, 138.55, 137.50, 135.52, 130.40, 127.89, 118.41, 94.61, 57.62, 38.41, 28.54, 4.73; **HRMS** calculated for $C_{13}H_{16}IO_2S$ $[M+H]^+$ 362.9910, found 362.9912.

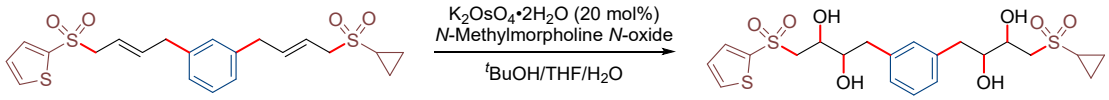


To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added **7a** (141.6 mg, 0.39 mmol), **2a** (0.3 mL, 0.60 mmol, 2 M in THF), **3o** (85.1 mg, 0.50 mmol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (7.1 mg, 2 mol%), $NiBr_2$•DME (12.0 mg, 10 mol%), **L8** (10.6 mg, 10 mol%), CH_3CN (2.0 mL), DMSO (0.4 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 24 h. After the reaction was completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product **7b** in 72% yield.


7b

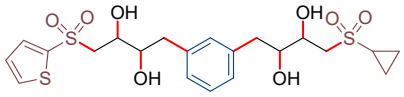
2-(((*E*)-4-(3-((*E*)-4-(Cyclopropylsulfonyl)but-2-en-1-yl)phenyl)but-2-en-1-yl)sulfonyl)thiophene (7b): Colorless liquid, 122.5 mg, 72% yield, *E/Z* > 10/1 R_f = 0.20 (petroleum ether/ethyl acetate 2/1). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.69 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.59 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 7.10 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.03 (dt, *J* = 7.5, 1.4 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.07 – 5.97 (m, 1H), 5.82 – 5.73

(m, 1H), 5.63 (dtt, *J* = 15.1, 7.4, 1.5 Hz, 1H), 5.52 (dtt, *J* = 15.1, 7.5, 1.5 Hz, 1H), 3.87 (d, *J* = 7.5 Hz, 2H), 3.74 (d, *J* = 7.5 Hz, 2H), 3.43 (d, *J* = 6.9 Hz, 2H), 3.35 (d, *J* = 6.8 Hz, 2H), 2.36 (tt, *J* = 8.0, 4.9 Hz, 1H), 1.23 – 1.15 (m, 2H), 1.00 – 0.95 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 140.29, 139.47, 139.29, 139.23, 139.12, 134.50, 134.16, 128.83, 128.80, 127.78, 126.68, 126.61, 117.61, 117.44, 61.16, 57.62, 38.91, 38.81, 28.53, 4.67; **HRMS** calculated for $C_{21}H_{25}O_4S_3$ $[M+H]^+$ 437.0909, found 437.0912.



7b **7c**, 61% yield, *dr* = 1/1

To an oven-dried 4 mL vial was added substrate **7b** (60.1 mg, 0.14 mmol), K_2OsO_4•$2H_2O$ (8.7 mg, 20 mol%), *N*-Methylmorpholine *N*-oxide (49.2 mg, 0.60 mmol), ^{t}BuOH (0.5 mL), THF (0.5 mL) and H_2O (0.5 mL). The reaction mixture was stirred for 19 h at room temperature. Then the reaction was quenched with Na_2SO_3 and stirred for 1 h, added H_2O and diluted with EtOAc. The aqueous layer was extracted with EtOAc, and combined organic layers were washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography to afford the corresponding product **7c** in 61% yield.



7c

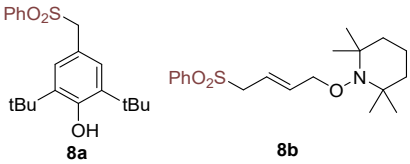
1-(Cyclopropylsulfonyl)-4-(3-(2,3-dihydroxy-4-(thiophen-2-ylsulfonyl)butyl)phenyl)butane-2,3-diol (7c): Colorless liquid, 43.3 mg, 61% yield, *dr* = 1/1, R_f = 0.20 (DCM/MeOH 10/1). **^{1}H NMR** (400 MHz, DMSO-d_6) δ = 8.07 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.71 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.24 (dd, *J* = 4.9, 3.7 Hz, 1H), 7.19 – 7.12 (m, 1H), 7.09 – 7.04 (m, 2H), 7.01 (dt, *J* = 7.5, 1.4 Hz, 1H), 5.35 (d, *J* = 6.3 Hz, 1H), 5.20 (d, *J* = 6.2 Hz, 1H), 4.86 (dd, *J* = 16.9, 6.6 Hz, 2H), 4.06 – 3.88 (m, 2H), 3.68 – 3.60 (m, 1H), 3.56 (dd, *J* = 14.5, 3.1 Hz, 2H), 3.32 – 3.18 (m, 2H), 2.86 – 2.70 (m, 3H), 2.58 – 2.40 (m, 3H), 1.07 – 0.85 (m, 4H); **^{13}C NMR** (101 MHz, DMSO-d_6) δ = 141.65, 139.89, 139.74, 135.30, 134.56, 130.74, 130.71, 128.67, 128.18, 127.27, 127.23, 74.56, 74.54, 74.38, 74.36, 68.47, 68.36, 60.75, 57.16, 38.43, 31.01, 5.16, 4.39; **HRMS** calculated for $C_{21}H_{29}O_8S_3$ $[M+H]^+$ 505.1019, found 505.1022.

5 Mechanistic investigations

5.1 Radical inhibition experiments

In order to identify the radical process was involved in the reaction, radical inhibition experiments were conducted. Reactions were inhibited to varying degrees when added using BHT or TEMPO as additive under standard condition. The BHT-sulfinate adduct **8a** and TEMPO-alkyl adduct **8b** were detected by **HRMS** analysis, which implies possible radical intermediates.

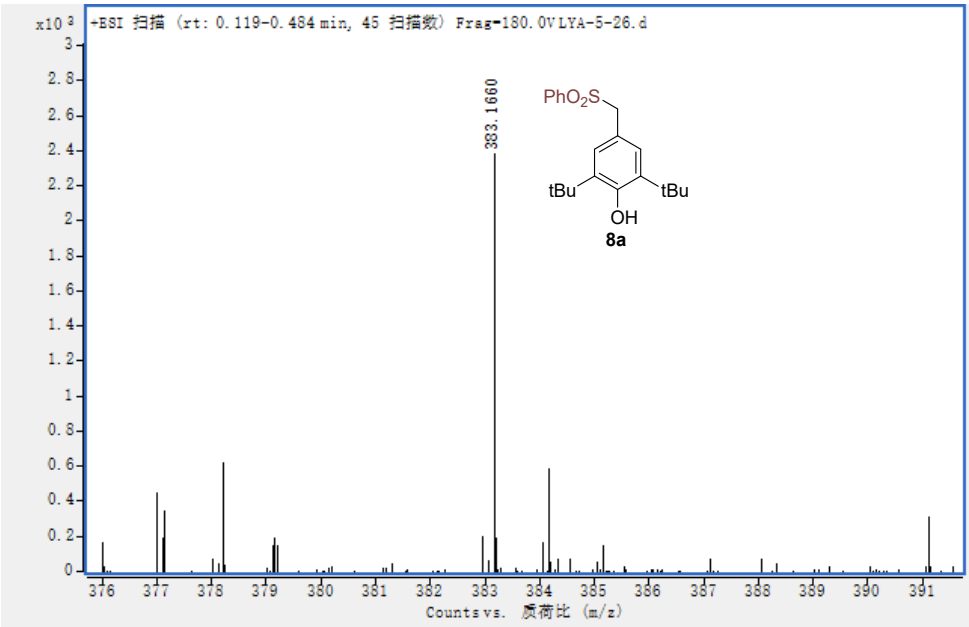
Entry	Additives	Yield of **4aa**
1	None	84%
2	BHT (1.0 eq.)	73%
3	TMEPO (1.0 eq.)	6%
4	TMEPO (2.0 eq.)	N.D.



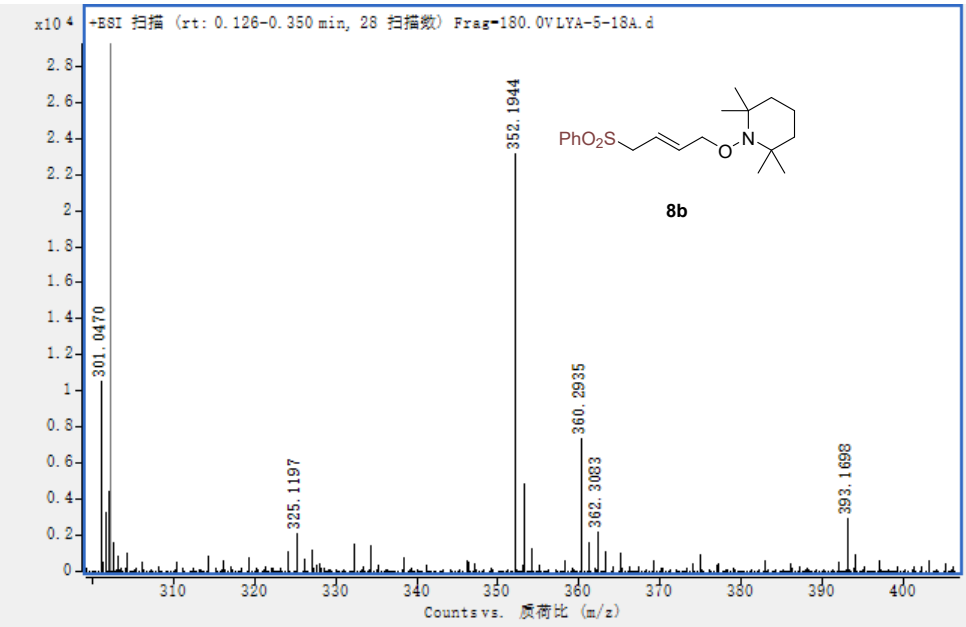
[M+Na] = 383.1651
found 383.1660

[M+H] = 352.1941
found 352.1944

detected by **HRMS**



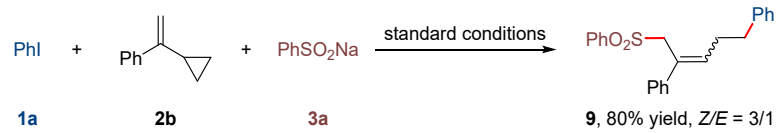
Supplementary Figure S1. HRMS (m/z) (ESI) spectra of BHT-sulfinate adduct 8a

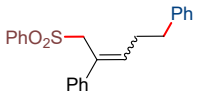


Supplementary Figure S2. HRMS (m/z) (ESI) spectra of TEMPO-alkyl adduct 8b

5.2 Radical clock experiment

Following the **General procedure 3.2** radical clock experiments with (1-cyclopropylvinyl) benzene was carried out,[5] which showed the formation of radical rearranged products **9** with 80% yield, *Z*/*E* = 3/1.





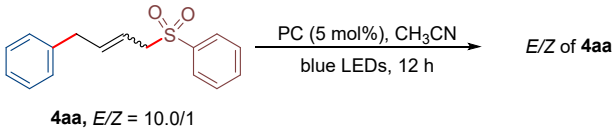
9

(5-(Phenylsulfonyl)pent-3-ene-1,4-diyl)dibenzene (9): Colorless liquid, 58.1 mg (***E***+***Z***), 80% total yield, *Z*/*E* = 3/1, R_f = 0.40 (petroleum ether/ethyl acetate 5/1). *Z*-isomer: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.74 – 7.67 (m, 2H), 7.52 – 7.46 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.10 (m, 8H), 6.00 (t, *J* = 7.4 Hz, 1H), 4.23 (s, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.5 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 141.12, 140.78, 139.01, 137.48, 133.51, 128.86, 128.54, 128.53, 128.45, 128.43, 128.30, 127.23, 126.40, 126.11, 57.63, 35.18, 31.23; *E*-isomer: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.77 – 7.71 (m, 2H), 7.58 – 7.52 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.14 (m, 6H), 7.05 (dd, *J* = 7.0, 1.7 Hz, 2H), 6.97 – 6.87 (m, 2H), 5.71 (t, *J* = 7.4 Hz, 1H), 4.11 (s, 2H), 2.58 (dd, *J* = 8.7, 6.7 Hz, 2H), 2.32 (q, *J* = 7.6 Hz, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 141.10, 138.90, 138.13, 137.63, 133.41, 128.87, 128.80, 128.44, 128.43, 128.40, 128.35, 128.14, 127.27, 125.97, 64.96, 35.49, 31.18; **HRMS** calculated for $C_{23}H_{23}O_2S$ $[M+H]^+$ 363.1413, found 363.1415.

5.3 *E/Z* isomerization

To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added **4aa** (0.10 mmol), PC (2 mol%), CH_3CN (0.5 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 12 h. The *E/Z* ratios of TM were analyzed by GC-FID analysis. The product **4aa** was irradiated under different photosensitizers with no significant isomerization. These results ruled out the involvement of photocatalytic *E-Z* isomerization of **4aa**.

Table S7 *E/Z* isomerization

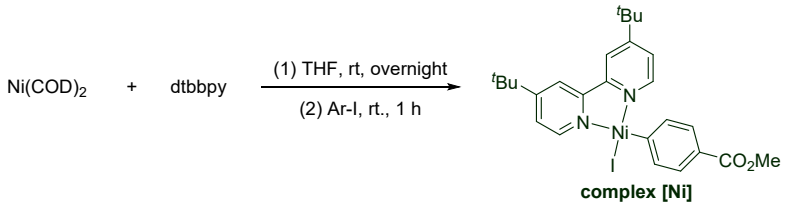


Entry	PC	*E/Z* of **4aa**
1	None	10.0/1
2	$Ir(ppy)_3$	10.3/1
3	$[Ir(ppy)_2(dtbbpy)]PF_6$	9.7/1
4	$Ru(bpy)_3(PF_6)_2$	10.0/1

Standard conditions: **4aa** (0.10 mmol), PC (2 mol%), CH_3CN (0.5 mL), blue LEDs, 12 h, under N_2. The ratios of *E/Z* were determined by GC-FID analysis.

5.4 Control experiments with Ar-Ni(II)-I

Synthesis of Ar-Ni(II)-I complex

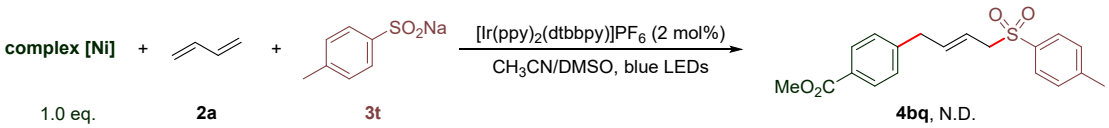


In a glove box, a suspension of $Ni(COD)_2$ (330 mg, 1.2 mmol, 1 equiv.) in 8 mL of dry THF was stirred for 1 minute in an oven-dried 20 mL screw-cap vial, at which point a solution of dtbbpy (322 mg, 1.2 mmol, 1 equiv.) in 5 mL of dry THF was added dropwise. The resulting mixture was allowed to stir overnight at ambient temperature. Methyl 4-iodobenzoate (315 mg, 1.2 mmol, 1 equiv.) was added via syringe. The resultant mixture was allowed to stir for another 1 h. The solvent was removed under vacuum, and the residue was filtrated with a fritted funnel. The solid was washed with ether (3×3mL), pentane (3×3mL) and dried in vacuum. Complex [Ni] was obtained as orange-red solid in 76% yield (230 mg), which was stored in the glove box at -20 °C. The data are consistent with literature.[6]

^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ = 9.44 (d, *J* = 5.8 Hz, 1H), 7.77 (d, *J* = 9.9 Hz, 2H),

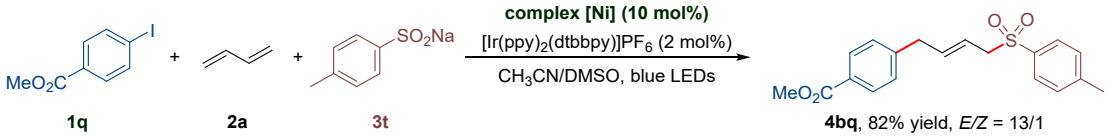
7.70 (d, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 5.7 Hz, 1H), 7.09 (d, *J* = 6.1 Hz, 1H), 6.79 (d, *J* = 6.1 Hz, 1H), 3.84 (s, 3H), 1.32 (s, 9H), 1.26 (s, 9H).

Stoichiometric reaction with Ar-Ni(II)-I complex



To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added Ar-Ni(II)-I complex (0.10 mmol, 1.0 eq.), **2a** (0.30 mmol, 3.0 eq.), **3t** (0.20 mmol, 2.0 eq.), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), CH_3CN (0.5 mL), DMSO (0.1 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 24 h. No product **4bq** was detected by GC-FID analysis. This result revealed that Ni(II)–aryl species may not be involved in the catalytic cycle.

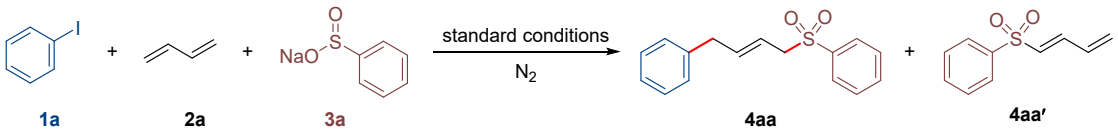
Catalytic amount reaction with Ar-Ni(II)-I complex



To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added **1q** (0.20 mmol, 1.0 eq.), **2a** (0.60 mmol, 3.0 eq.), **3t** (0.40 mmol, 2.0 eq.), Ar-Ni(II)-I complex (10 mol%), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), CH_3CN (1.0 mL), DMSO (0.2 mL) in the nitrogen glove box. The reaction mixture was stirred under irradiation with blue LEDs box at room temperature for 24 h. After the reaction was completed, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether and ethyl acetate to afford the corresponding product **4bq** in 82% yield.

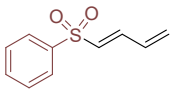
5.5 Studies of side product

Table S8 Control experiment of side product



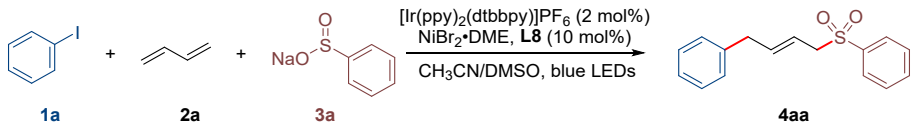
Entry	Variation	**4aa** (%)	**4aa′** (%)
1	None	84	N.D.
2	w/o butadiene	-	N.D.
3	w/o PhI	-	N.D.
4	air	47	trace
5	O_2	14	5

Standard conditions: **1a** (0.20 mmol), **2a** (0.60 mmol), **3a** (0.40 mol), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), $NiBr_2$•DME (10 mol%), **L8** (10 mol%), CH_3CN (1.0 mL), DMSO (0.2 mL), blue LEDs, 24 h, under N_2. Yields were determined by GC-FID analysis of the crude reaction mixture using mesitylene as internal standard.

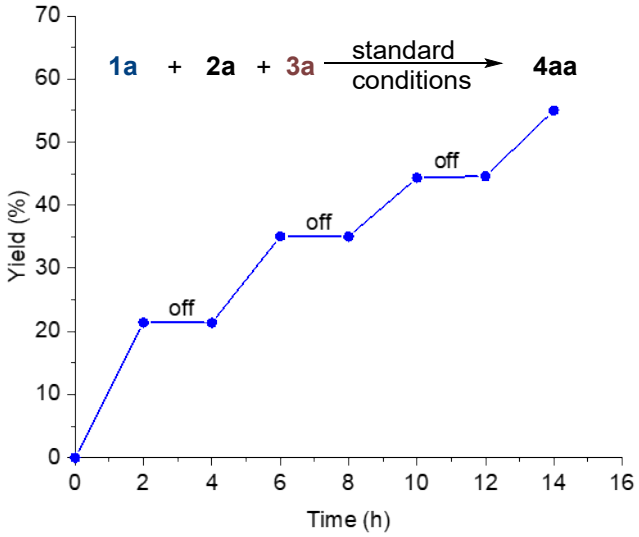

4aa′

(*E*)-(Buta-1,3-dien-1-ylsulfonyl)benzene (4aa′): Colorless liquid, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ = 7.92 – 7.88 (m, 2H), 7.67 – 7.58 (m, 1H), 7.58 – 7.51 (m, 2H), 7.32 – 7.22 (m, 1H), 6.49 – 6.31 (m, 2H), 5.74 (dd, *J* = 16.9, 1.0 Hz, 1H), 5.62 (dd, *J* = 10.0, 1.1 Hz, 1H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ = 142.22, 140.54, 133.40, 132.45, 130.76, 129.31, 128.31, 127.64.

5.6 Light on or off experiments



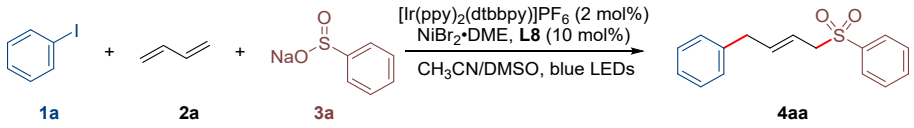
To an oven-dried 4 mL vial with a PTFE-coated stirring bar was added **1a** (0.20 mmol, 1.0 equiv.), **2a** (0.60 mmol, 2 M in THF, 3.0 equiv.), **3a** (0.40 mmol, 2.0 equiv.), $[Ir(ppy)_2(dtbbpy)]PF_6$ (2 mol%), $NiBr_2$•DME (10 mol%), **L8** (10 mol%), CH_3CN (1.0 mL), DMSO (0.2 mL) in the nitrogen glove box. The vial was capped with a septum and wrapped with parafilm. The reaction was sequentially stirred under blue LEDs and under the dark atmosphere. Every two hours an aliquot of 20 μL was removed via syringe and analyzed by GC-FID. After a total of 16 h the determined yields were plotted against the reaction time.

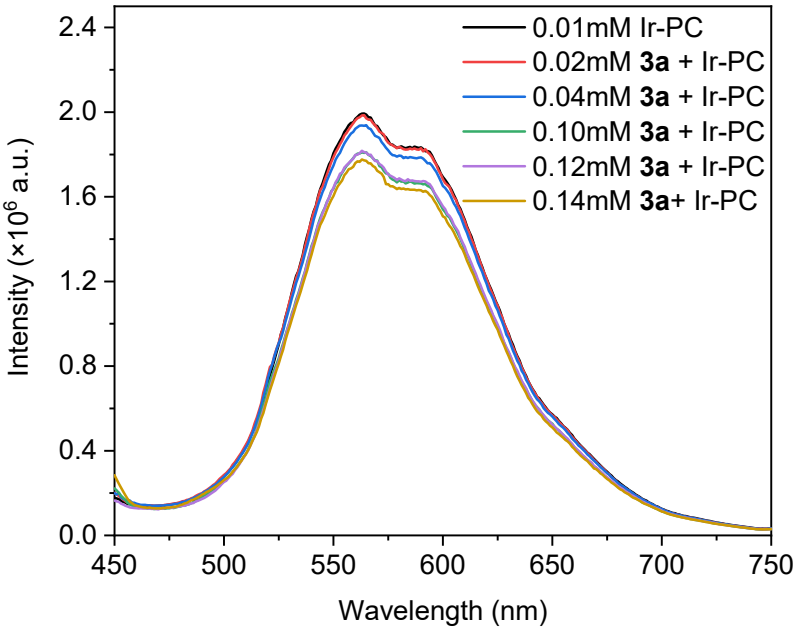


Supplementary Figure S3. Effect of blue LEDs irradiation

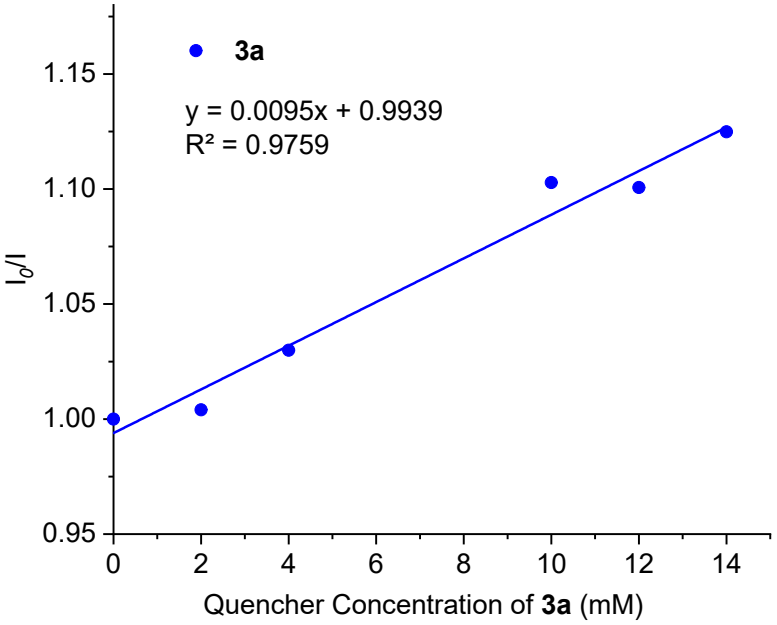
5.7 Stern-Volmer fluorescence quenching studies

Stern-Volmer experiments were carried out using stock solutions of photocatalyst $[Ir(ppy)_2(dtbbpy)]PF_6$ (0.01 mM), **1a**, **2a**, **3a** and $NiBr_2$•DME in anhydrous DMSO. The emission intensity at 555 nm was collected with excited wavelength of 365 nm in TFE using a PTI QM-400 Spectrofluorophotometer. After degassing the sample with a stream of argon for 10 minutes, the emission intensity of the sample was collected and plots were constructed according to the Stern-Volmer equation $I0/I = 1 + Kqt0[Q]$.

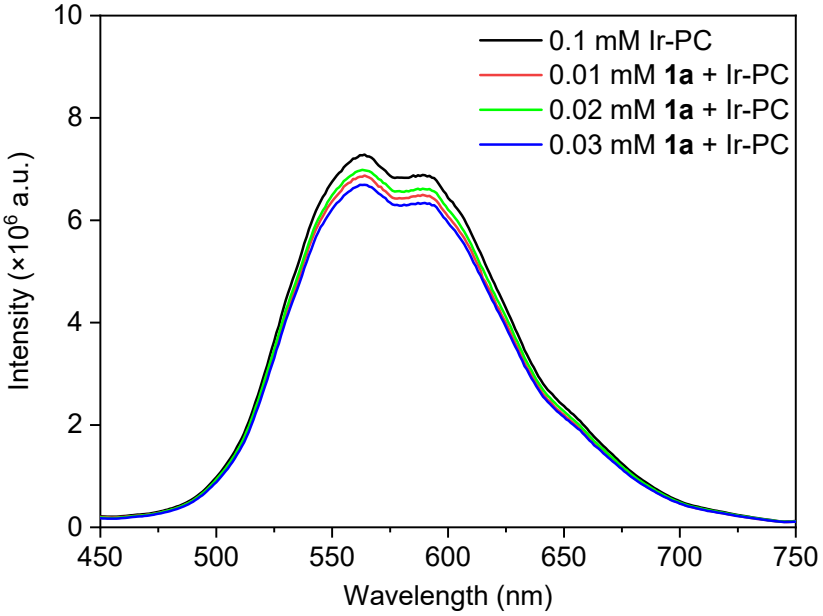




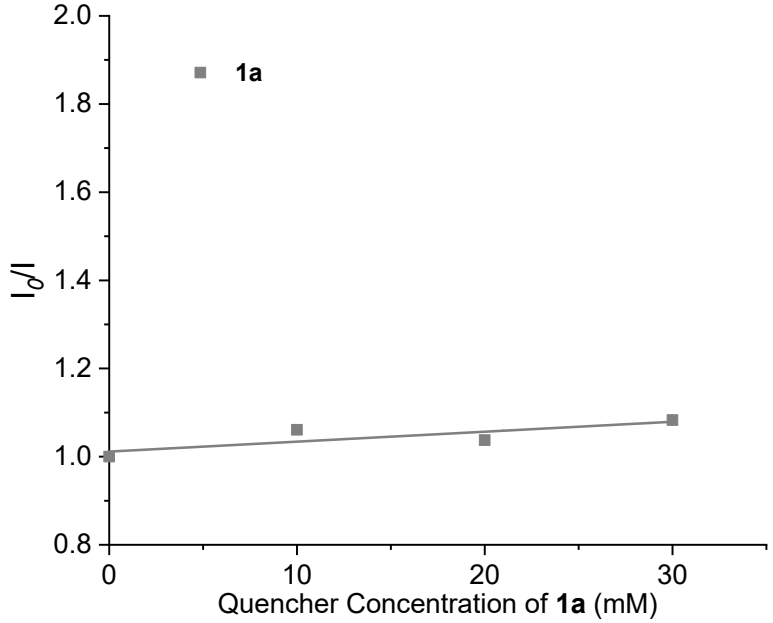
Supplementary Figure S4. $[Ir(ppy)_2(dtbbpy)]PF_6$ emission quenching with 3a



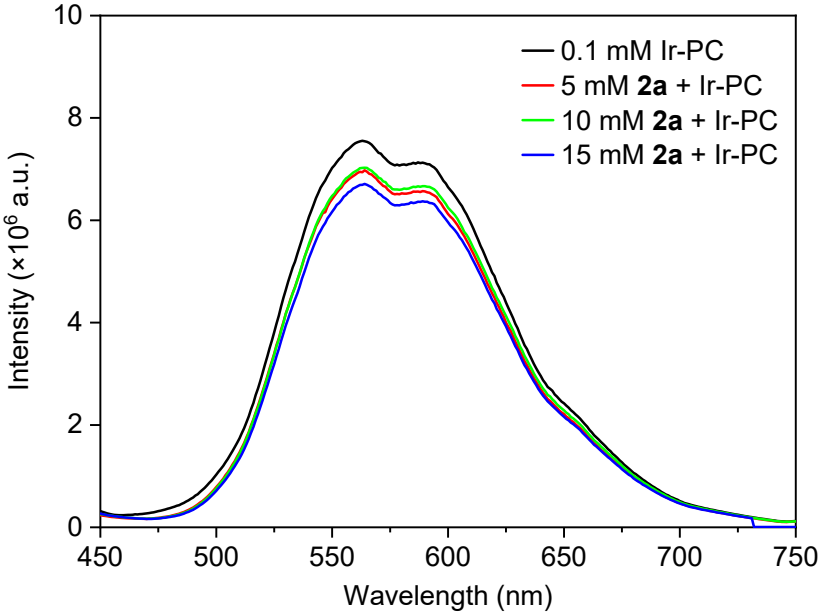
Supplementary Figure S5. Stern-Volmer quenching studies with PC and 3a



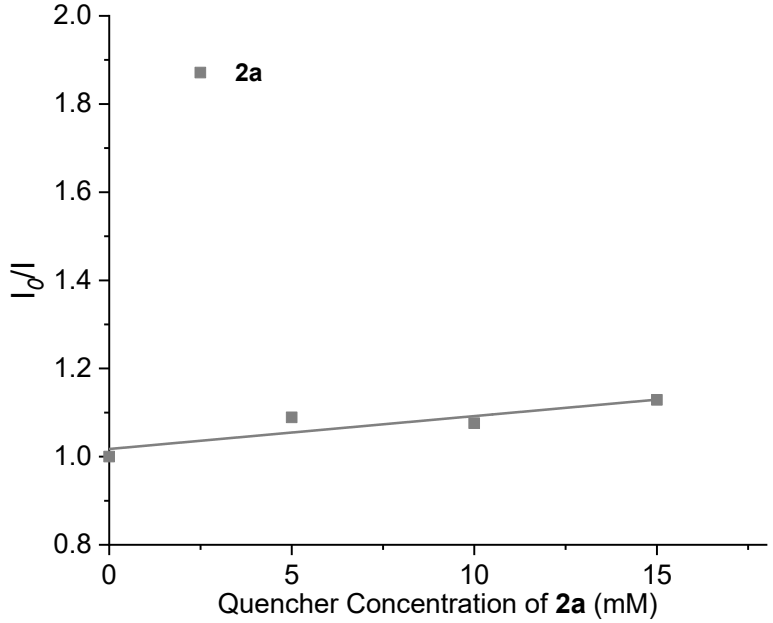
Supplementary Figure S6. $[Ir(ppy)_2(dtbbpy)]PF_6$ emission quenching with 1a



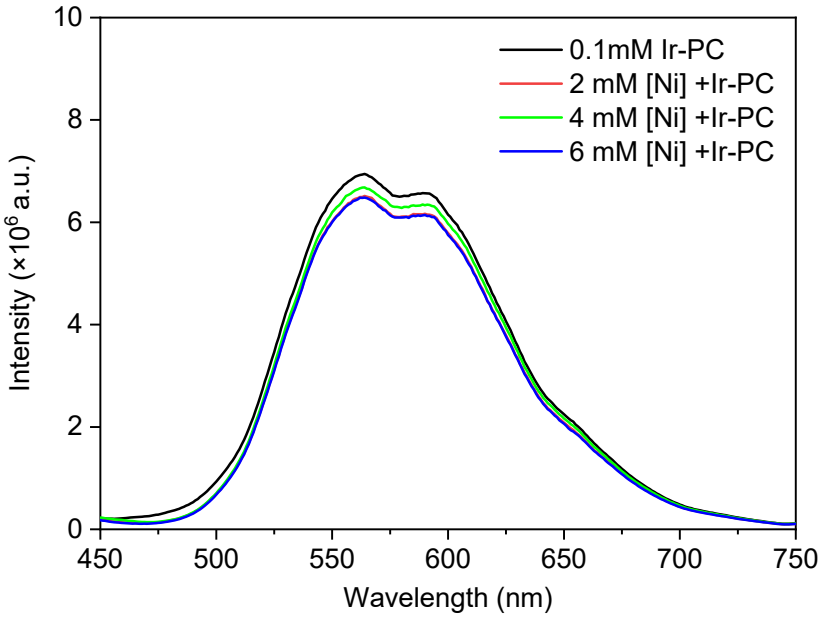
Supplementary Figure S7. Stern-Volmer quenching studies with PC and 1a



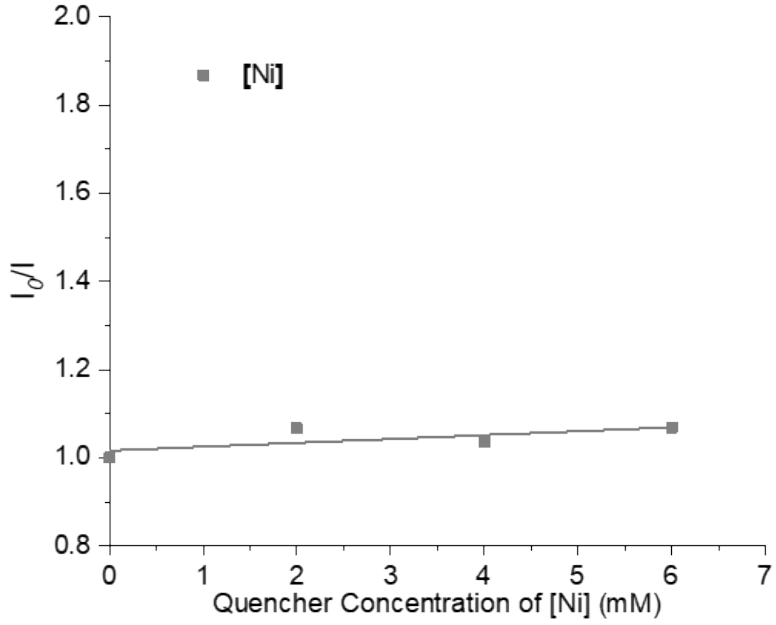
Supplementary Figure S8. $[Ir(ppy)_2(dtbbpy)]PF_6$ emission quenching with 2a



Supplementary Figure S9. Stern-Volmer quenching studies with PC and 2a

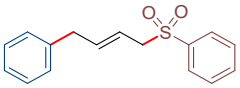


Supplementary Figure S10. $[Ir(ppy)_2(dtbbpy)]PF_6$ emission quenching with $NiBr_2$•DME

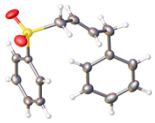


Supplementary Figure S11. Stern-Volmer quenching studies with PC and $NiBr_2$•DME

6 X-ray crystal structures



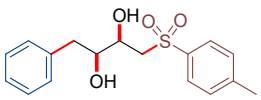
4aa



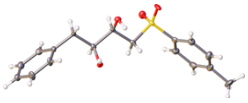
CCDC: 2335639

Table S9 Crystal data and structure refinement for 4aa

Identification code	**4aa**
Empirical formula	$C_{16}H_{16}O_2S$
Formula weight	272.35
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.78749(19)
b/Å	15.2412(2)
c/Å	10.1184(2)
α/°	90
β/°	108.564(2)
γ/°	90
Volume/Å^3	1430.86(5)
Z	4
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	1.964
F(000)	576.0
Crystal size/mm^3	0.19 × 0.16 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.898 to 152.962
Index ranges	-11 ≤ h ≤ 11, -19 ≤ k ≤ 15, -12 ≤ l ≤ 12
Reflections collected	14904
Independent reflections	2936 [R_{int} = 0.0349, R_{sigma} = 0.0250]
Data/restraints/parameters	2936/0/172
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0565, wR_2 = 0.1563
Final R indexes [all data]	R_1 = 0.0626, wR_2 = 0.1645
Largest diff. peak/hole / e Å^{-3}	0.35/-0.51



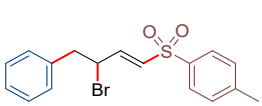
6d



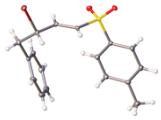
CCDC: 2369901

Table S10 Crystal data and structure refinement for 6d

Identification code	**6d**
Empirical formula	$C_{17}H_{20}O_4S$
Formula weight	320.39
Temperature/K	99.8(7)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.5500(4)
b/Å	5.11540(10)
c/Å	27.0569(7)
α/°	90
β/°	98.321(3)
γ/°	90
Volume/Å^3	1581.77(8)
Z	4
ρ_{calc}g/cm^3	1.345
μ/mm^{-1}	1.954
F(000)	680.0
Crystal size/mm^3	0.19 × 0.16 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.96 to 133.16
Index ranges	-13 ≤ h ≤ 13, -3 ≤ k ≤ 6, -28
Reflections collected	5523
Independent reflections	2666 [R_{int} = 0.0322, R_{sigma} =
Data/restraints/parameters	2666/0/202
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.1269, wR_2 = 0.3400
Final R indexes [all data]	R_1 = 0.1303, wR_2 = 0.3416
Largest diff. peak/hole / e Å^{-3}	2.35/-0.56



6g



CCDC: 2369903

Table S11 Crystal data and structure refinement for 6g

Identification code	**6g**
Empirical formula	$C_{17}H_{17}O_2SBr$
Formula weight	365.27
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	10.1138(3)
b/Å	17.7266(5)
c/Å	8.8048(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1578.55(8)
Z	4
ρ_{calc}g/cm^3	1.537
μ/mm^{-1}	2.737
F(000)	744.0
Crystal size/mm^3	0.19 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.596 to 61.968
Index ranges	-14 ≤ h ≤ 14, -24 ≤ k ≤ 24, -12 ≤ l ≤
Reflections collected	32705
Independent reflections	4406 [R_{int} = 0.0827, R_{sigma} = 0.0599]
Data/restraints/parameters	4406/1/191
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0350, wR_2 = 0.0583
Final R indexes [all data]	R_1 = 0.0503, wR_2 = 0.0612
Largest diff. peak/hole / e Å^{-3}	0.39/-0.39
Flack parameter	-0.006(6)

7 References

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8 Copies of NMR spectra

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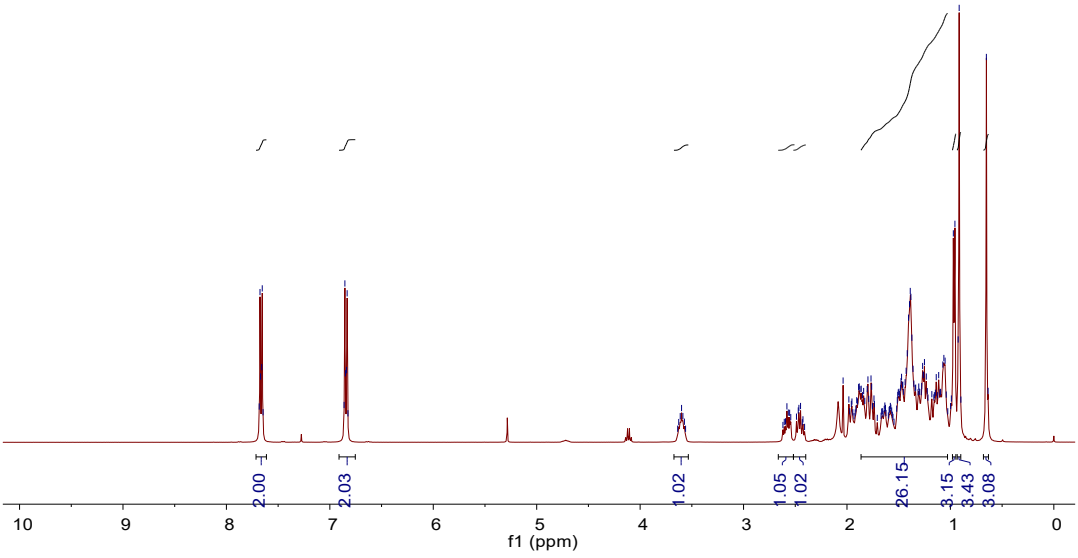

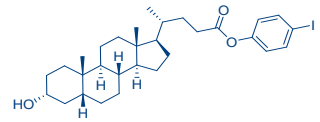

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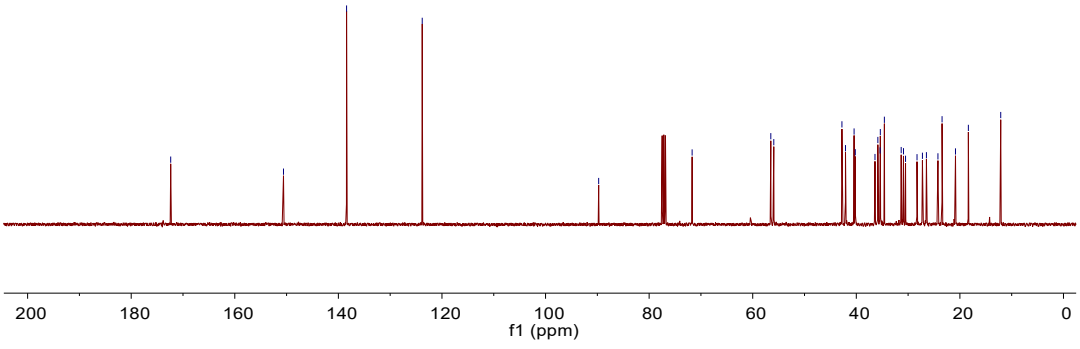

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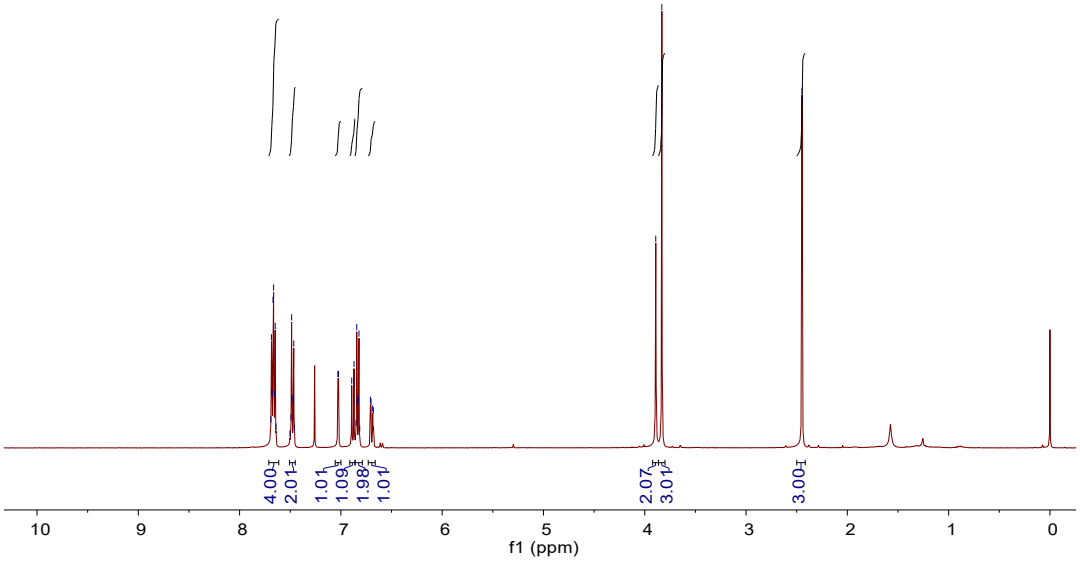

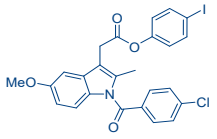

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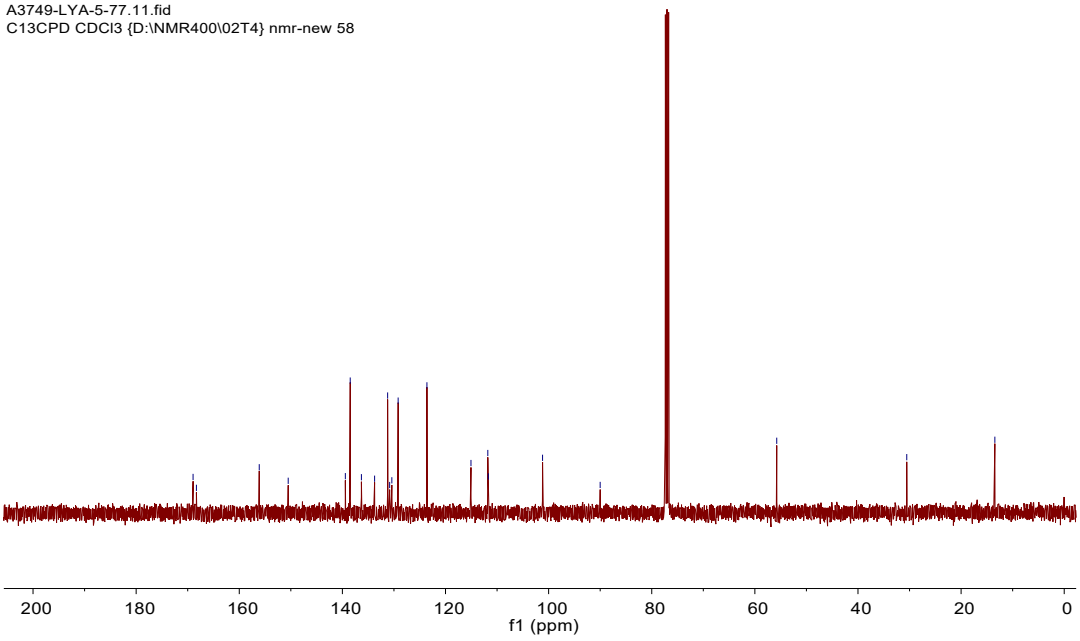

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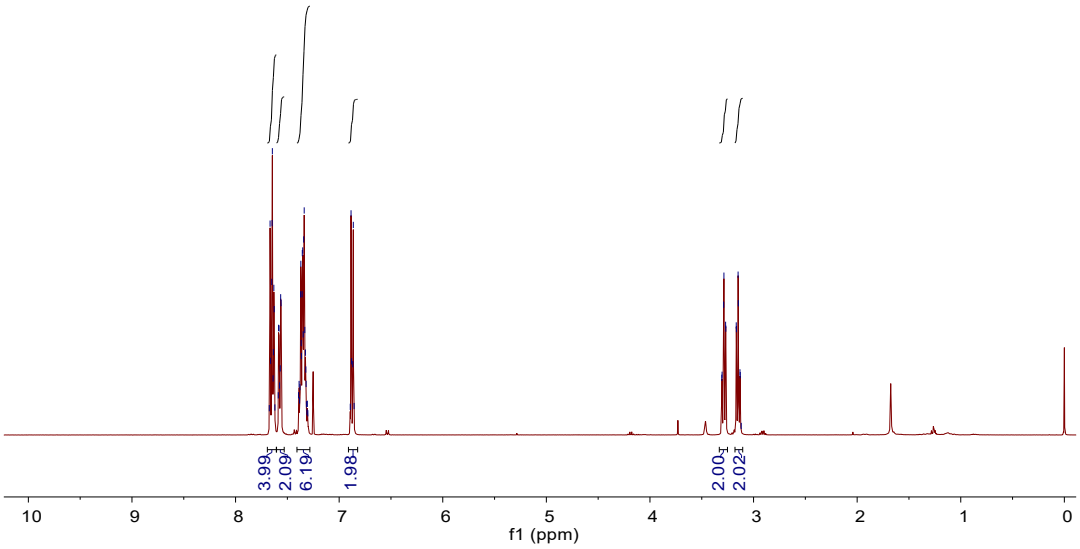

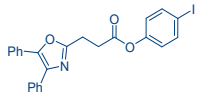

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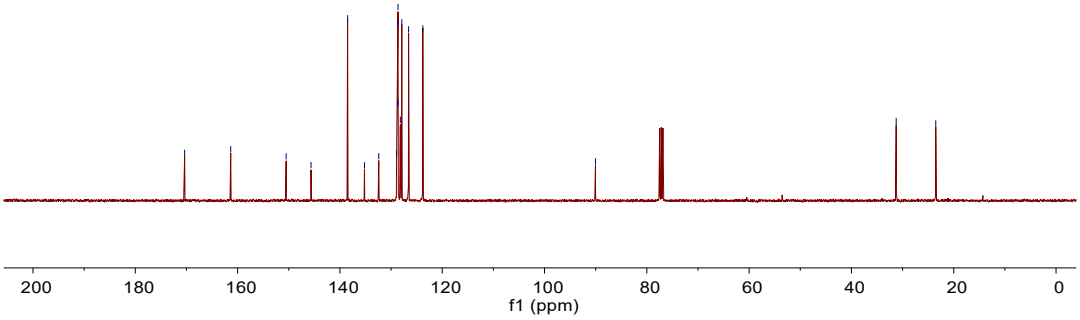

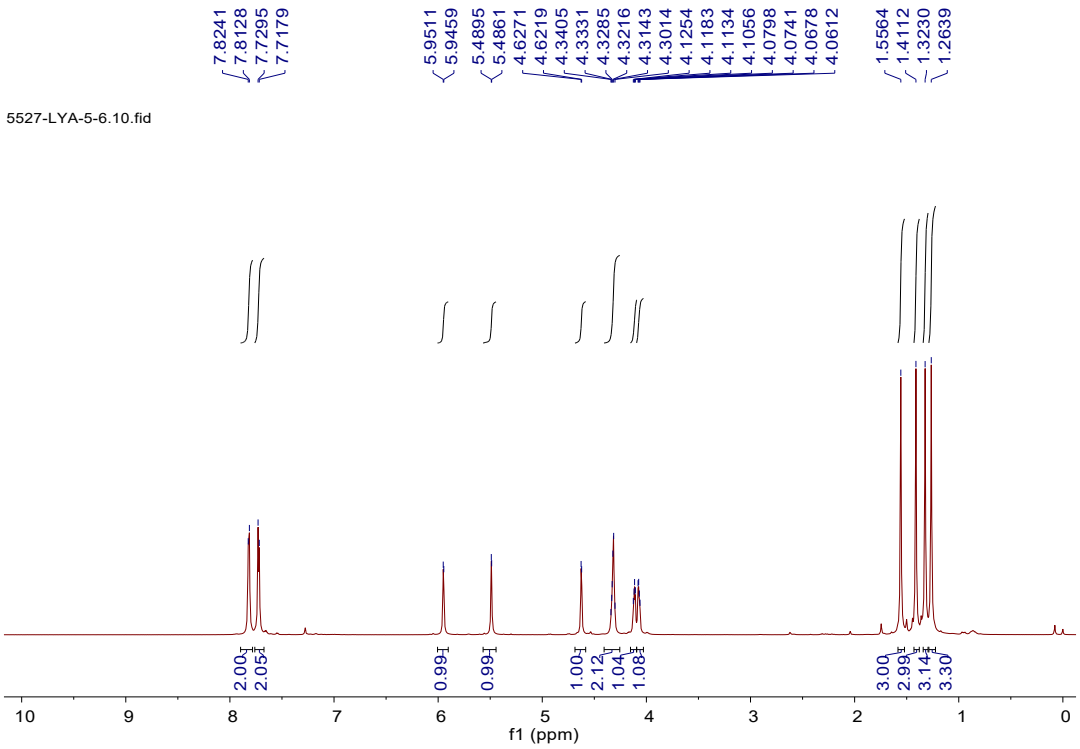
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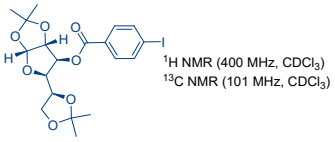
3.30
f1 (ppm)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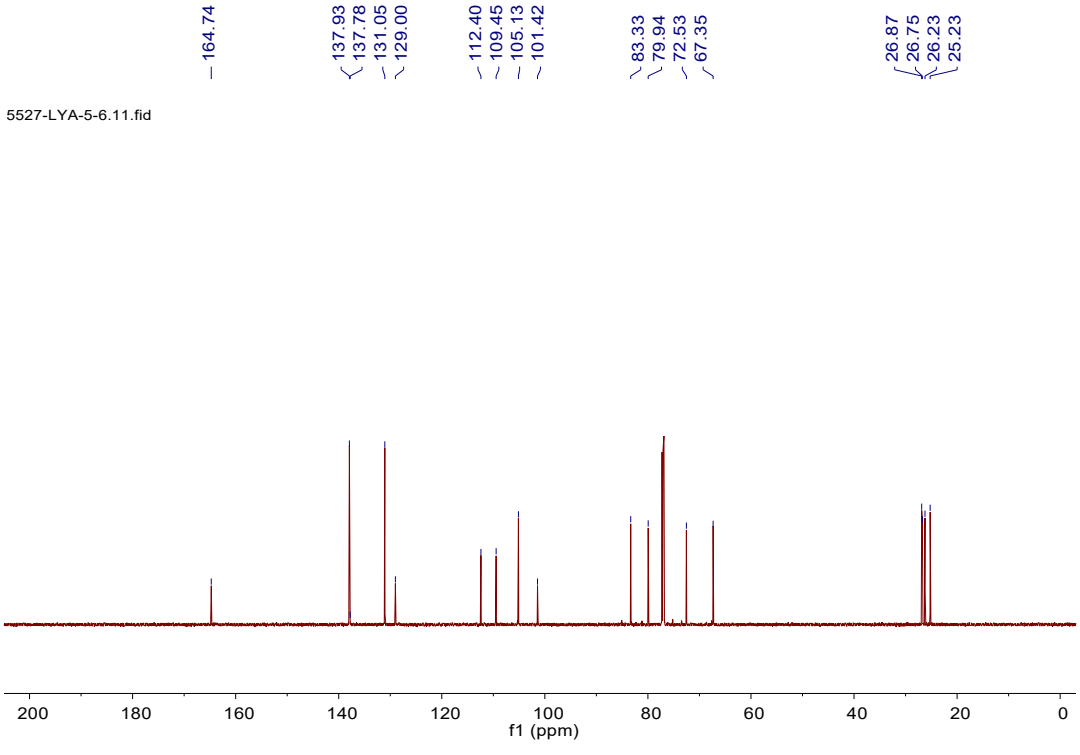
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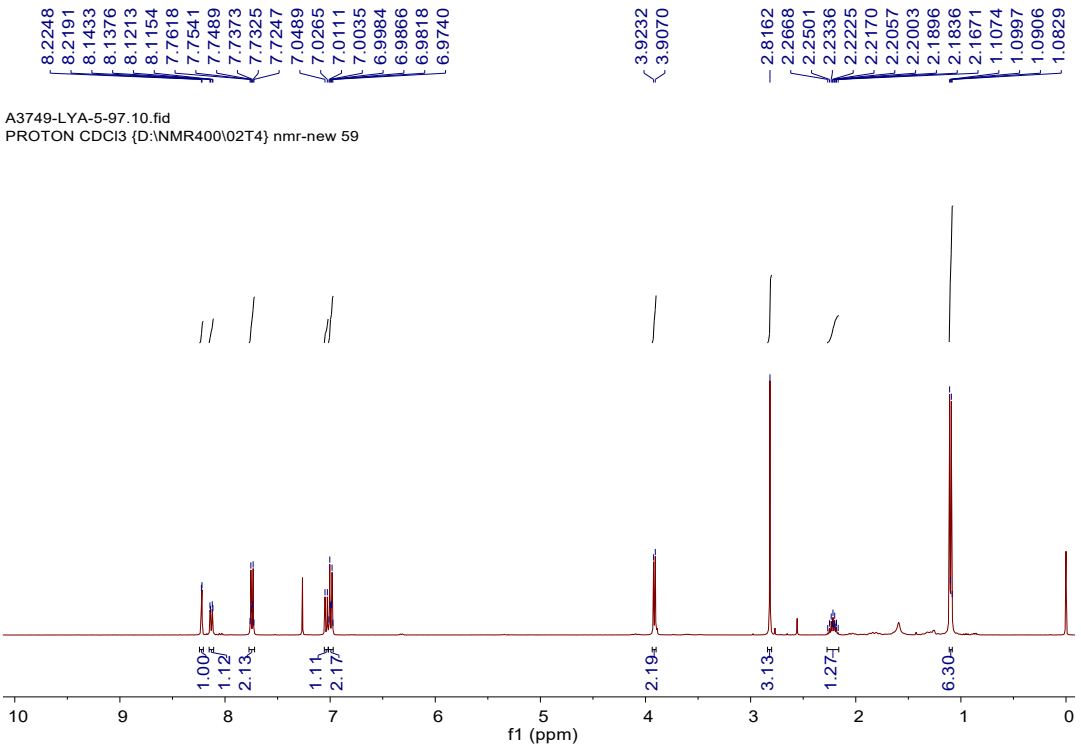
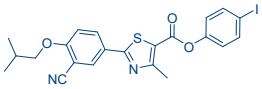
67.35
26.87
26.75
26.23
25.23
5527-LYA-5-6.11.fid
f1 (ppm)





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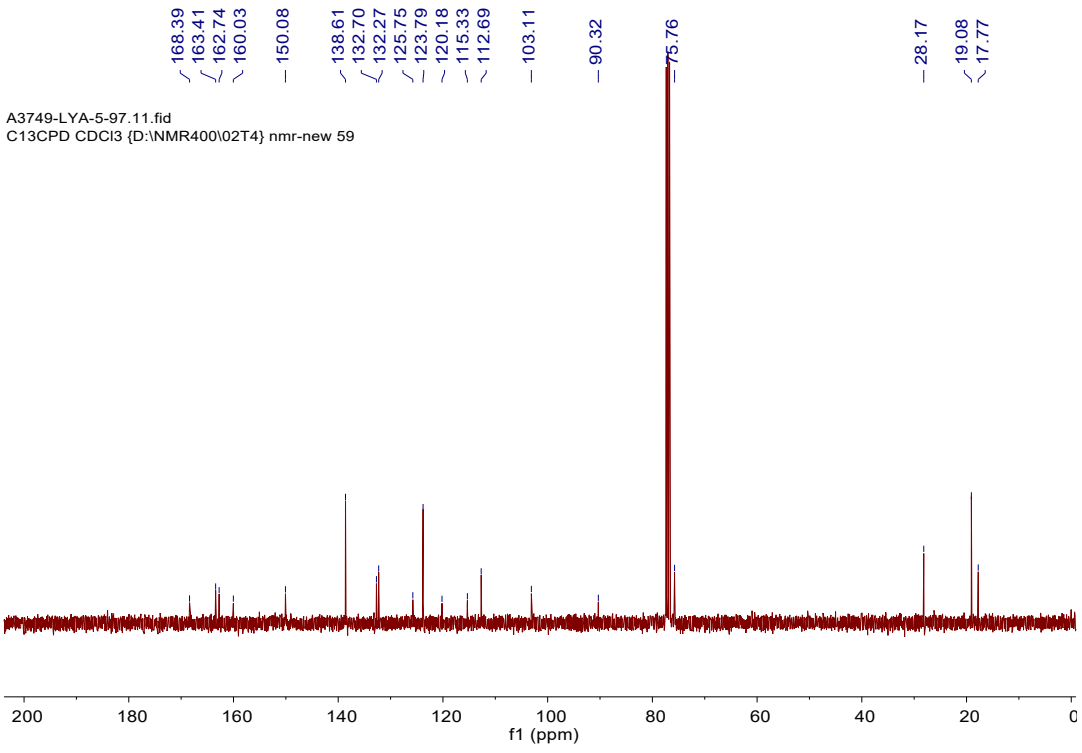

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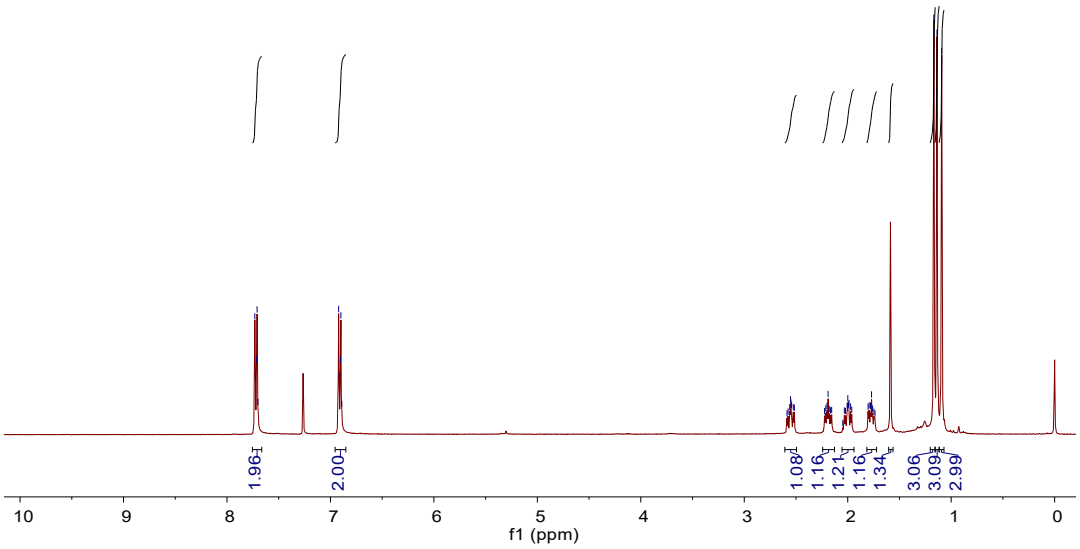
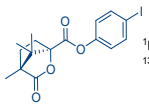
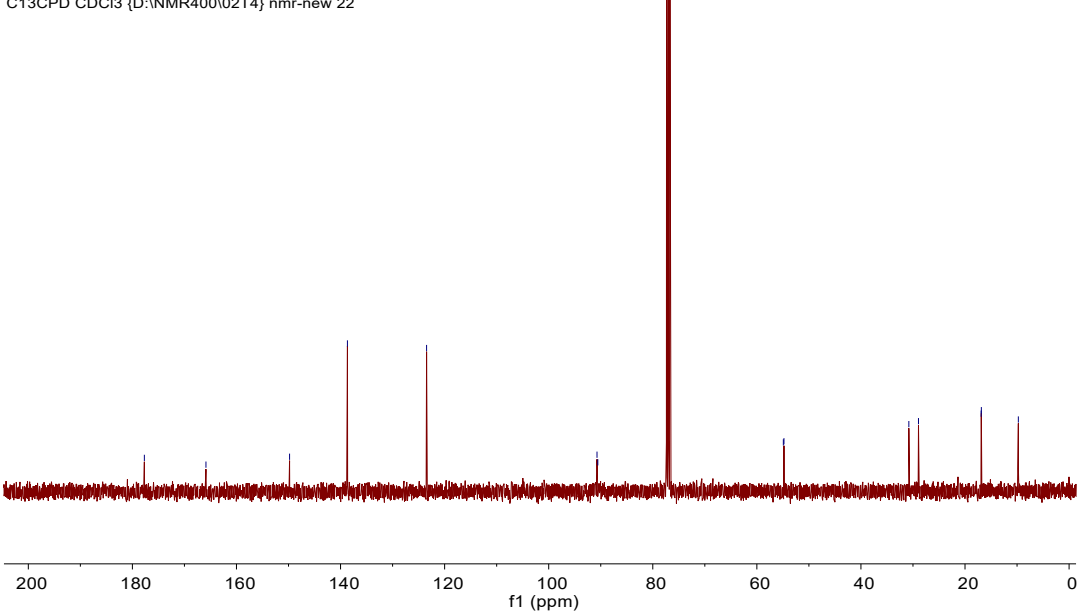


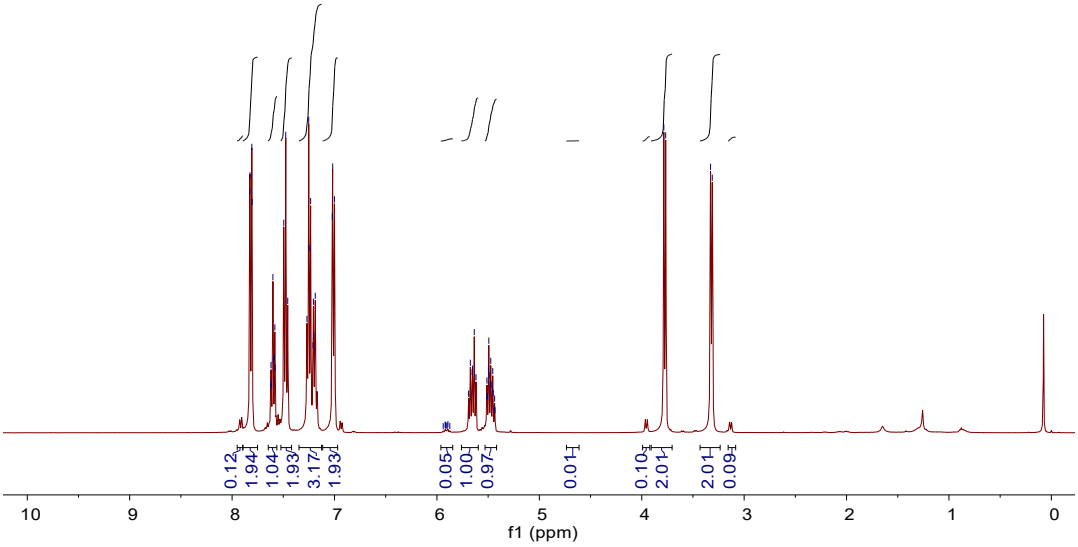


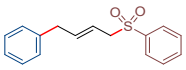
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A3749-LYA-6-7B.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 22



9840-LYA-4-33C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 25

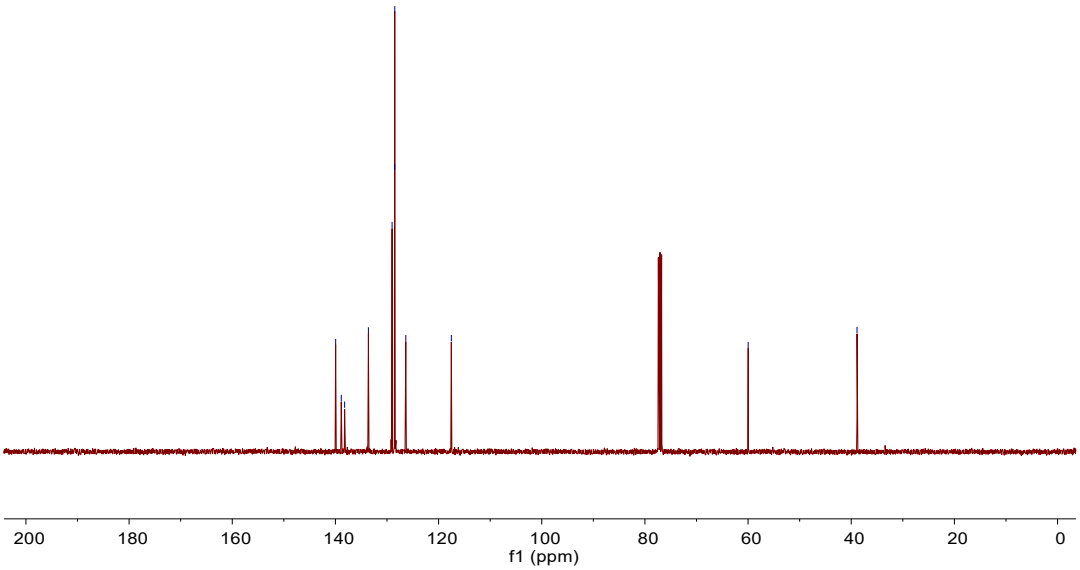




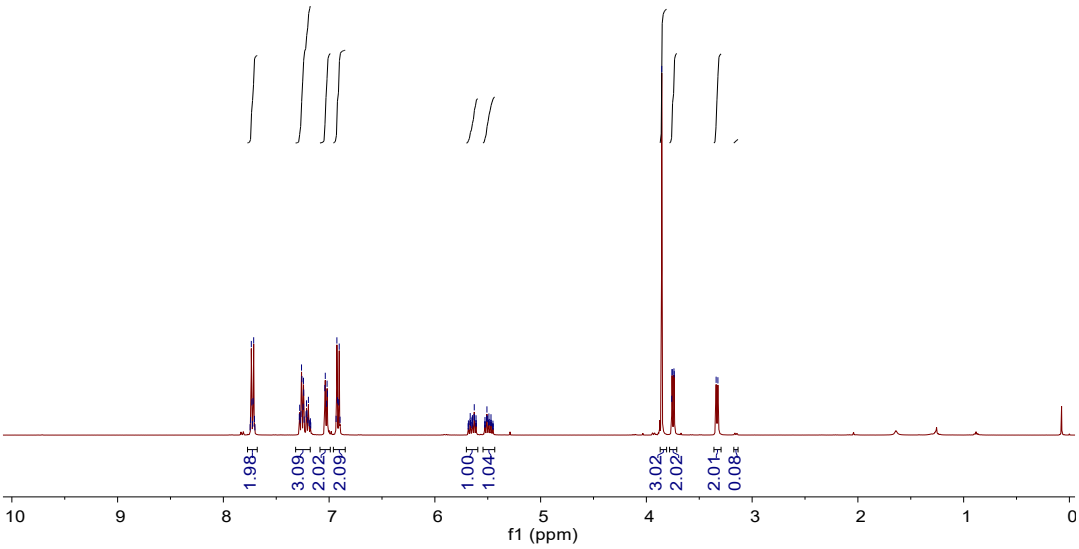
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

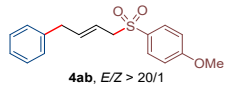
4aa, *E*/*Z* = 20/1

9754-LYA-4-17E.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 21



A0251-LYA-4-50A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 48

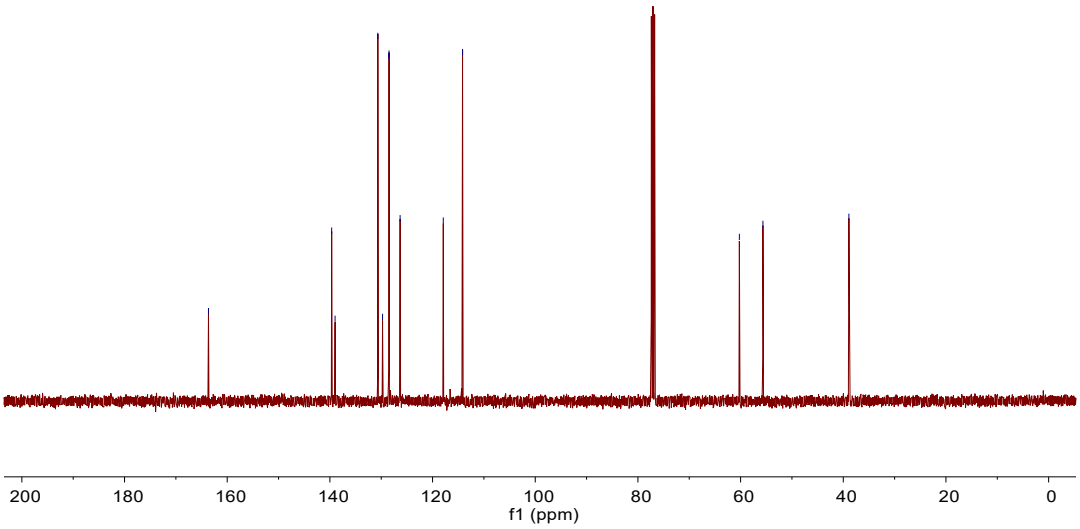




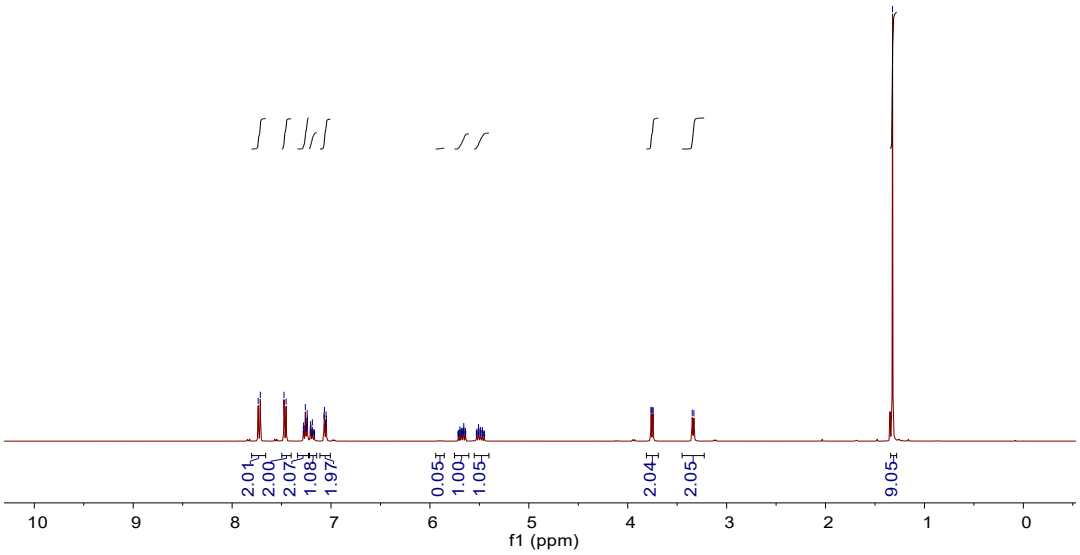
4ab, *E*/*Z* > 20/1

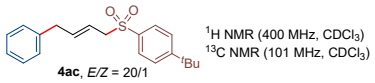
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A0251-LYA-4-50A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 48



9840-LYA-4-42B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 53

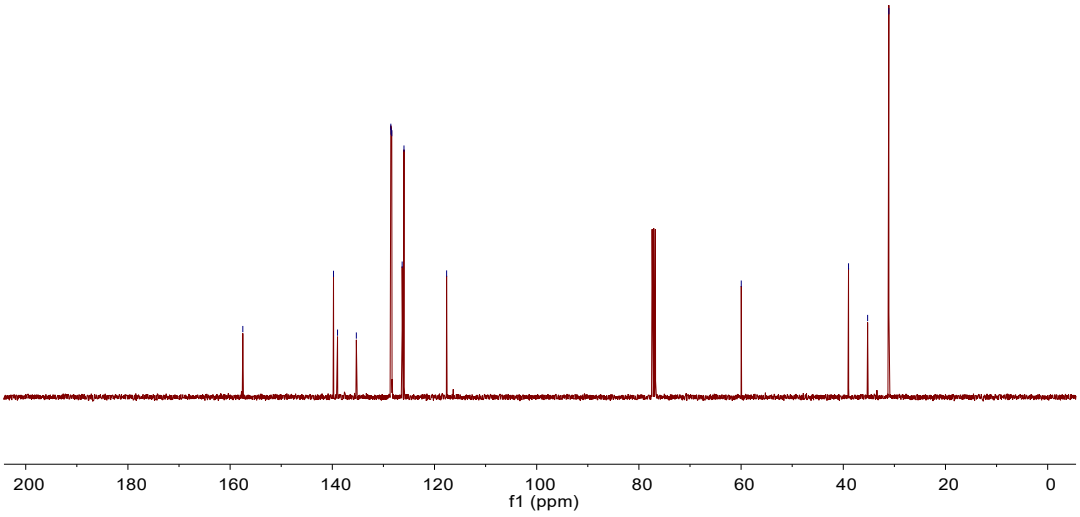




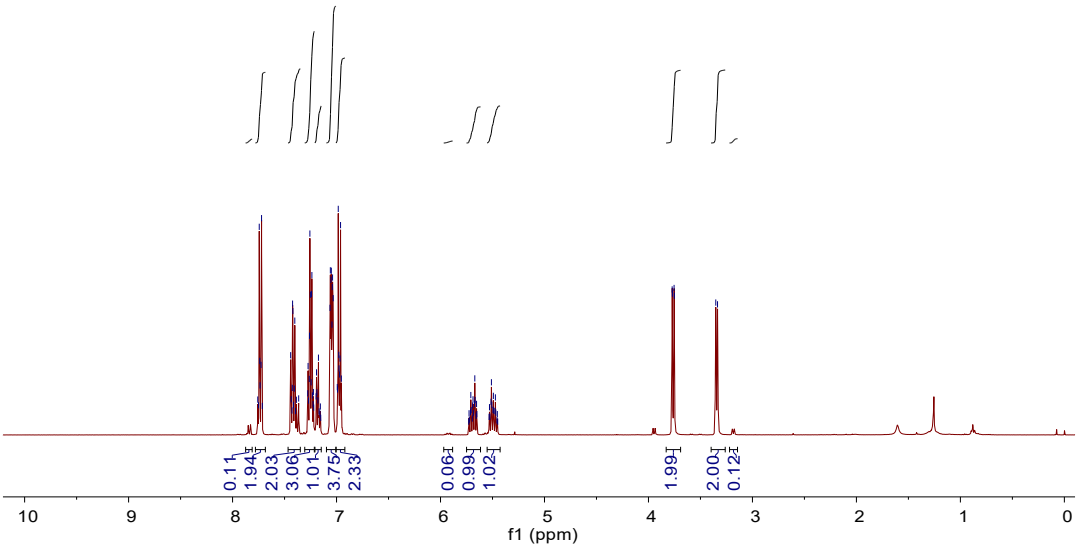
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

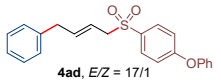
4ac, *E*/*Z* = 20/1

9545-LYA-4-20A-TM.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 1



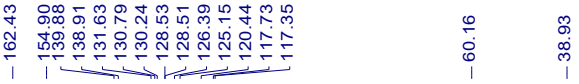
9910-LYA-4-43B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 3



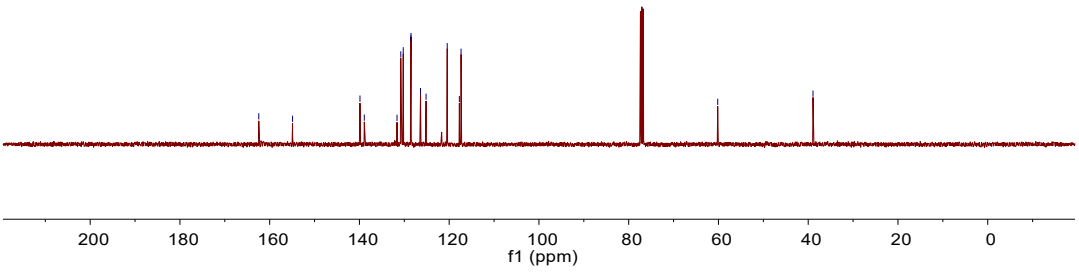


4ad, *E/Z* = 17/1

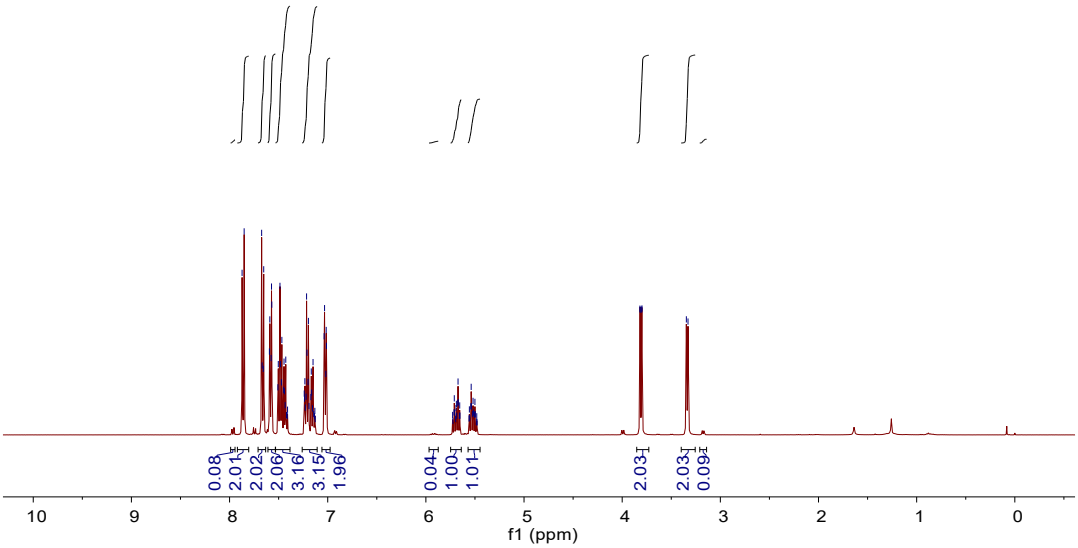
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

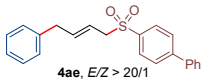


9910-LYA-4-43B.20.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 58



9910-LYA-4-43A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 57

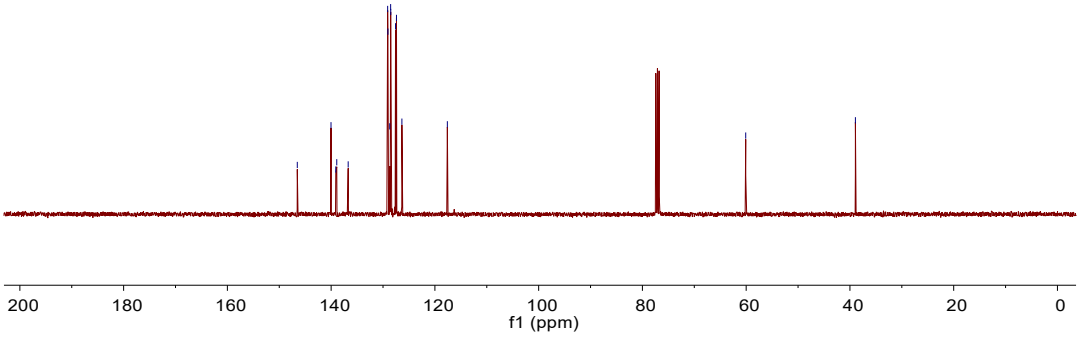




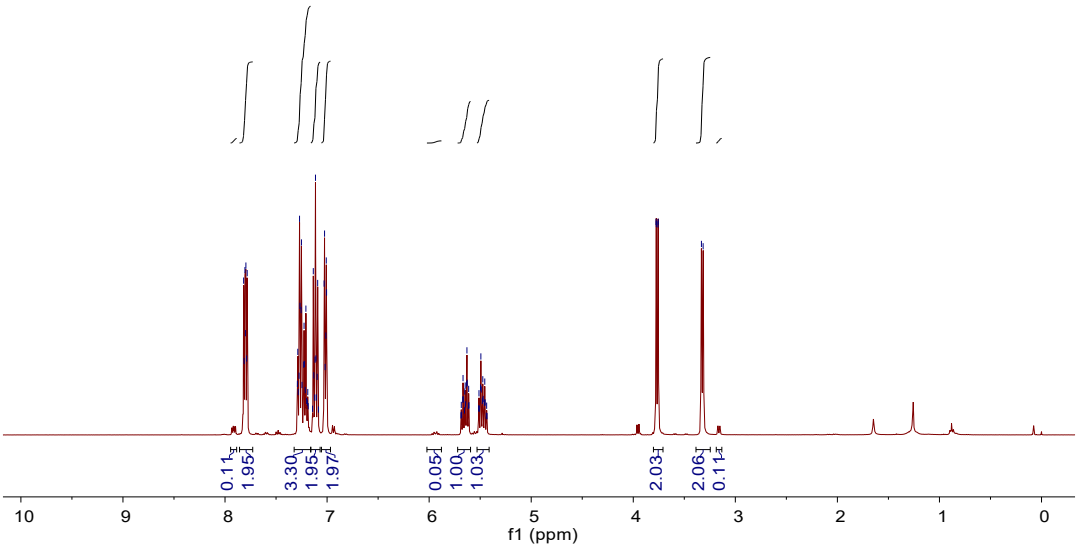
4ae, *E*/*Z* > 20/1

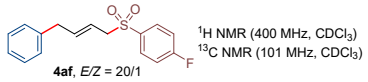
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

9910-LYA-4-43A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 57



9910-LYA-4-46A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 20

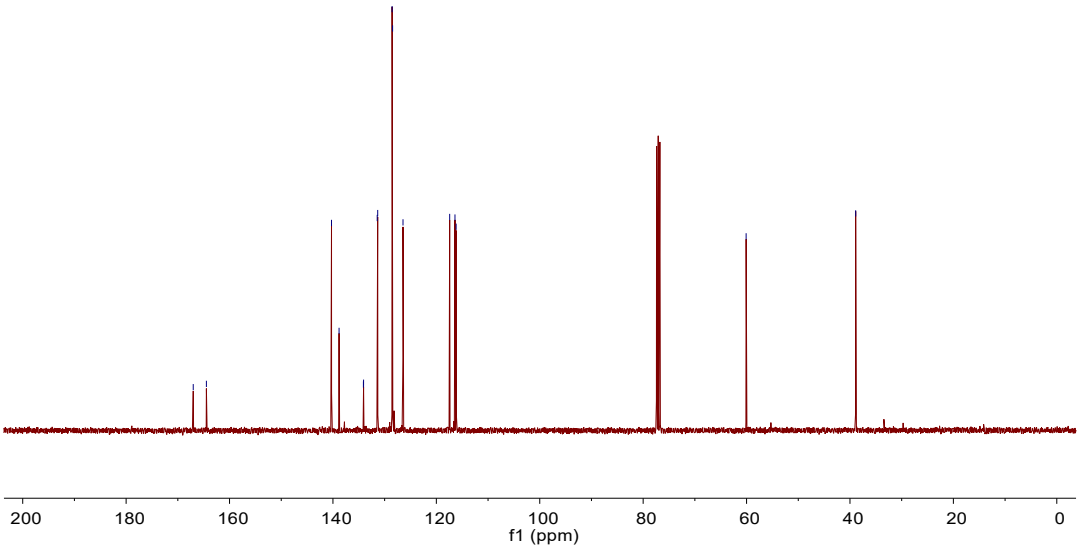


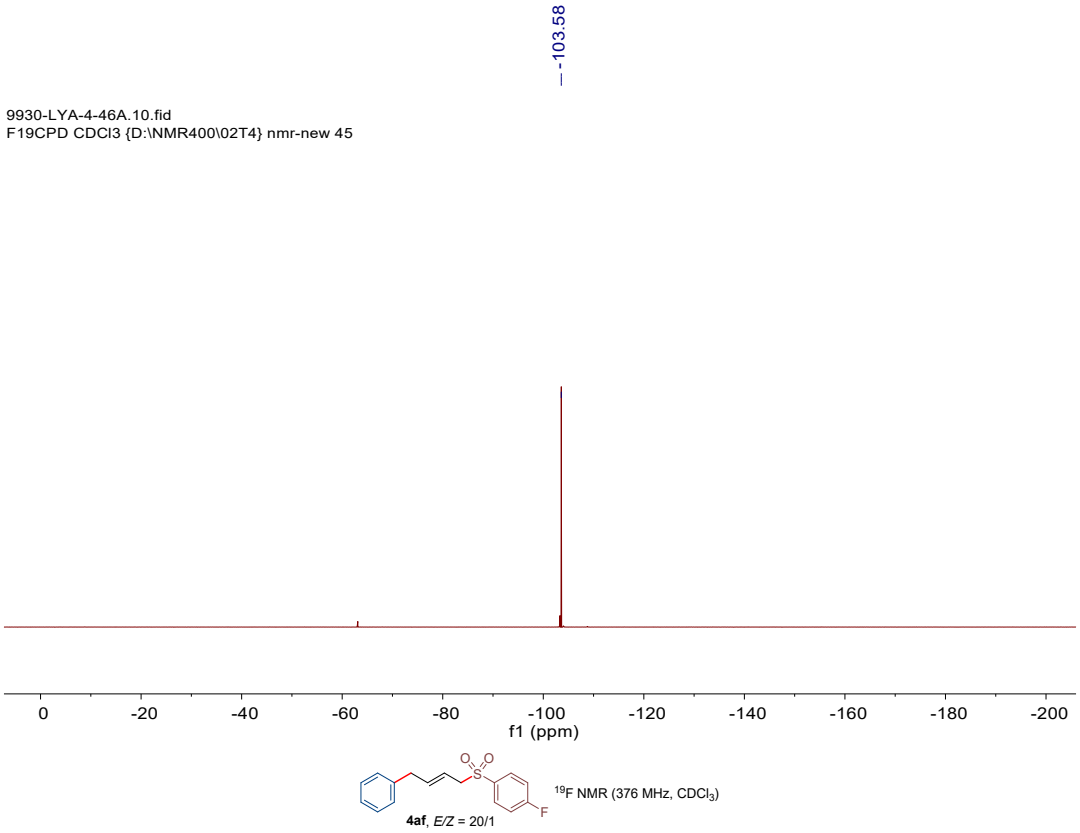


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

4af, *E*/*Z* = 20/1

9910-LYA-4-46A.21.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 60

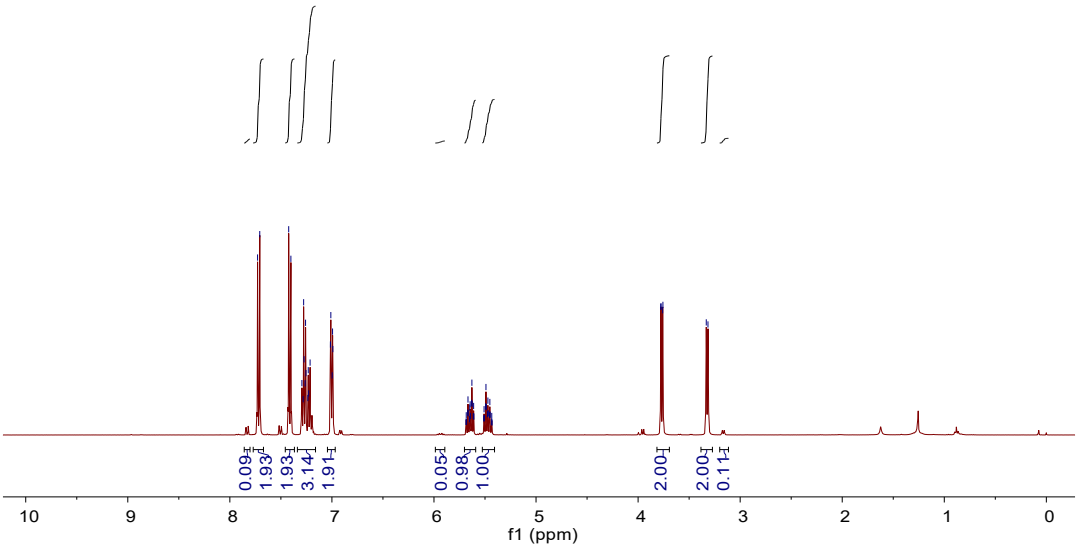


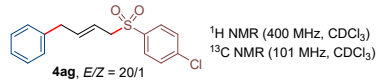


^{19}F NMR (376 MHz, $CDCl_3$)

4af, *E*/*Z* = 20/1

9910-LYA-4-46B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 4

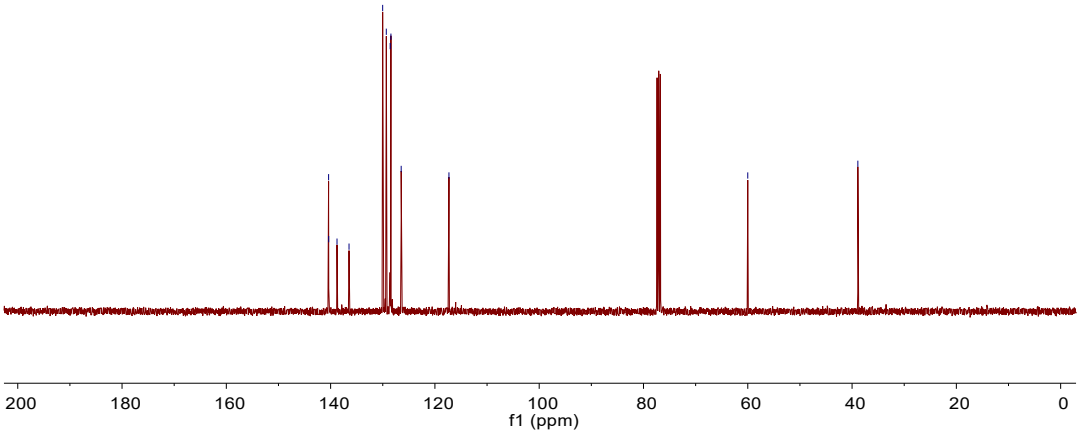


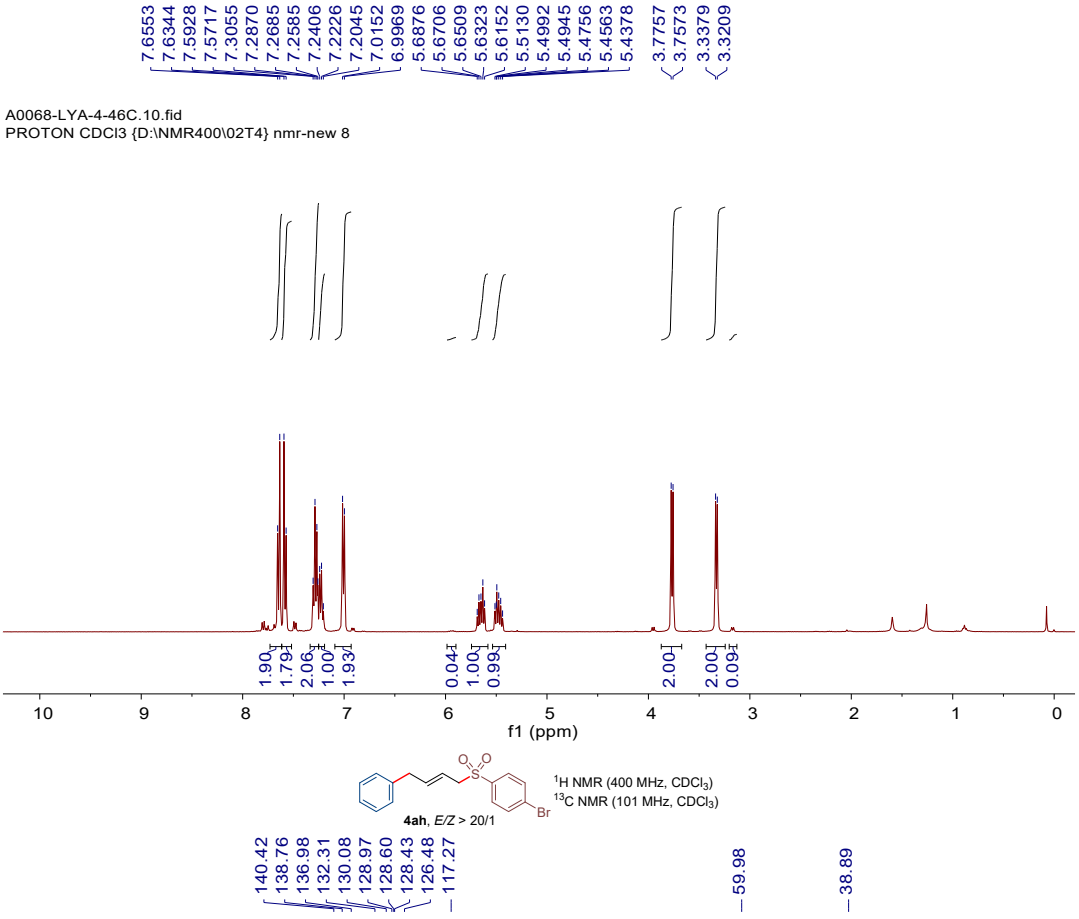


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

4ag, *E*/*Z* = 20/1

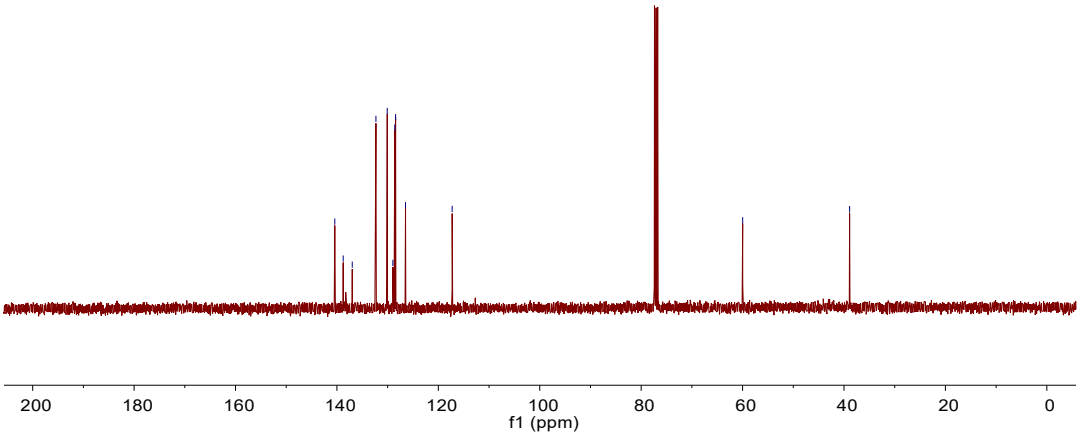
9910-LYA-4-46B.20.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 59





A0068-LYA-4-46C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 8

A0087-LYA-4-46C.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 53



9545-LYA-4-20D.10.fid
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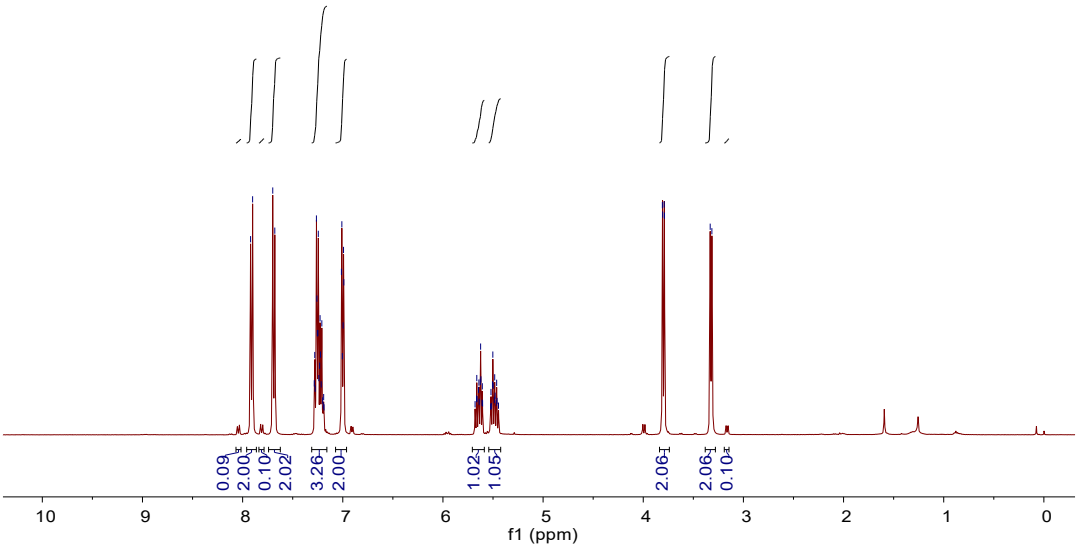
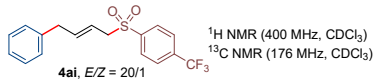
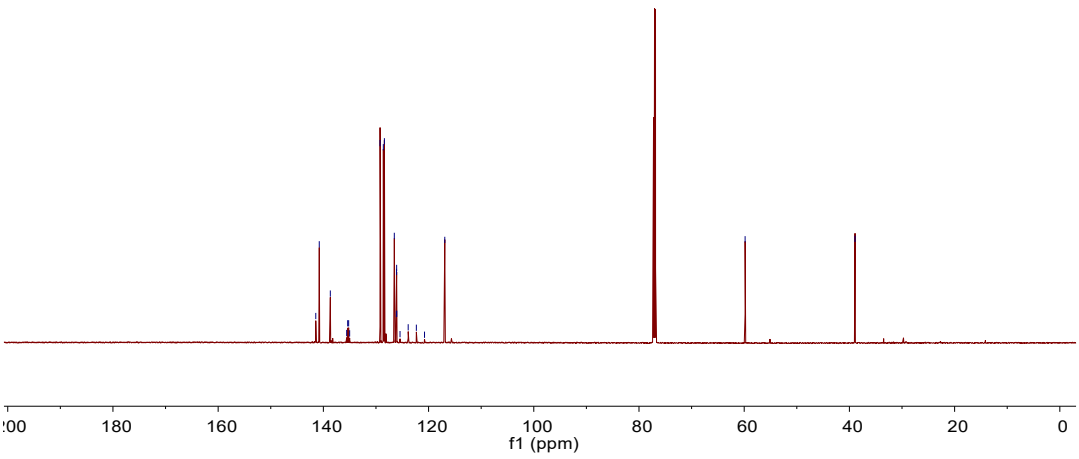


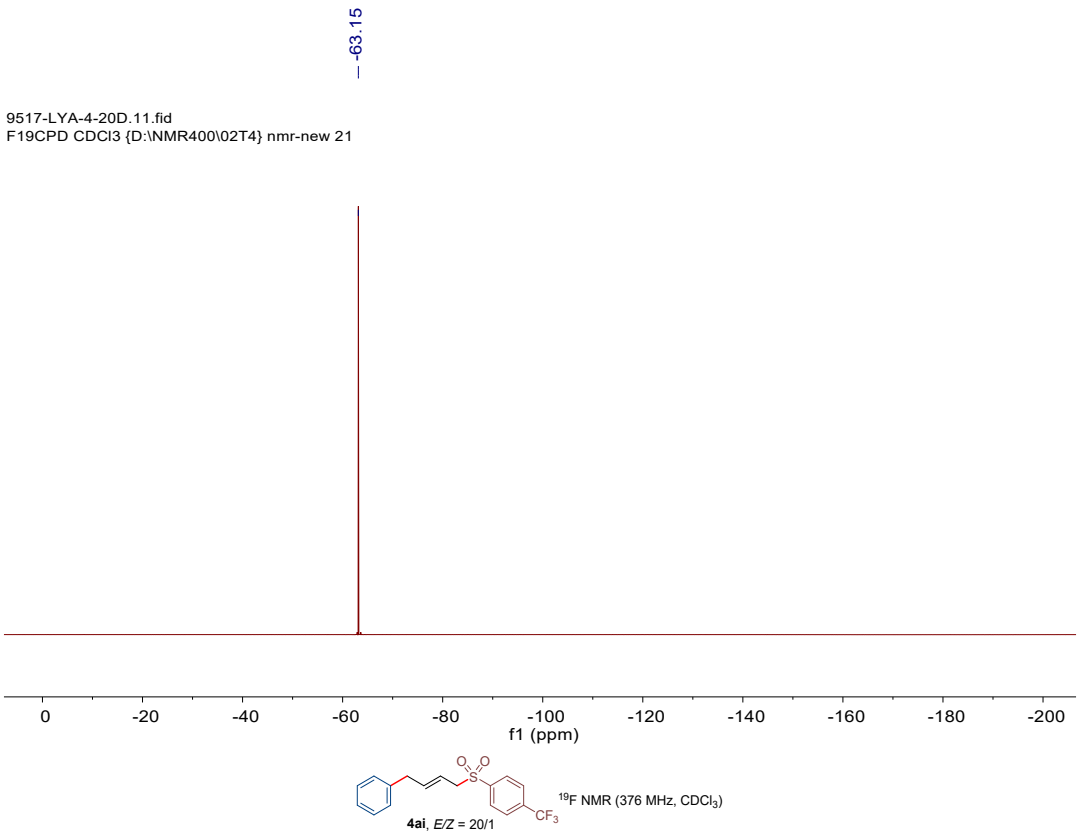


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (176 MHz, $CDCl_3$)

4ai, *E*/*Z* = 20/1

5262-LYA-4-20D.10.fid

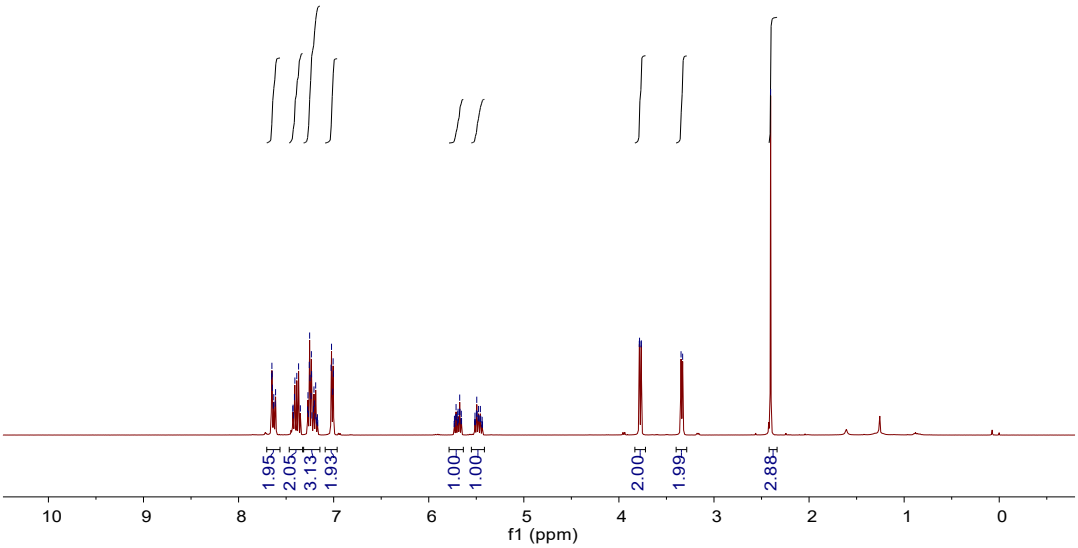


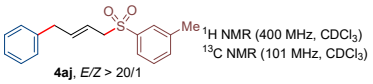


^{19}F NMR (376 MHz, $CDCl_3$)

4ai, *E*/*Z* = 20/1

A0110-LYA-4-50B2.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 28

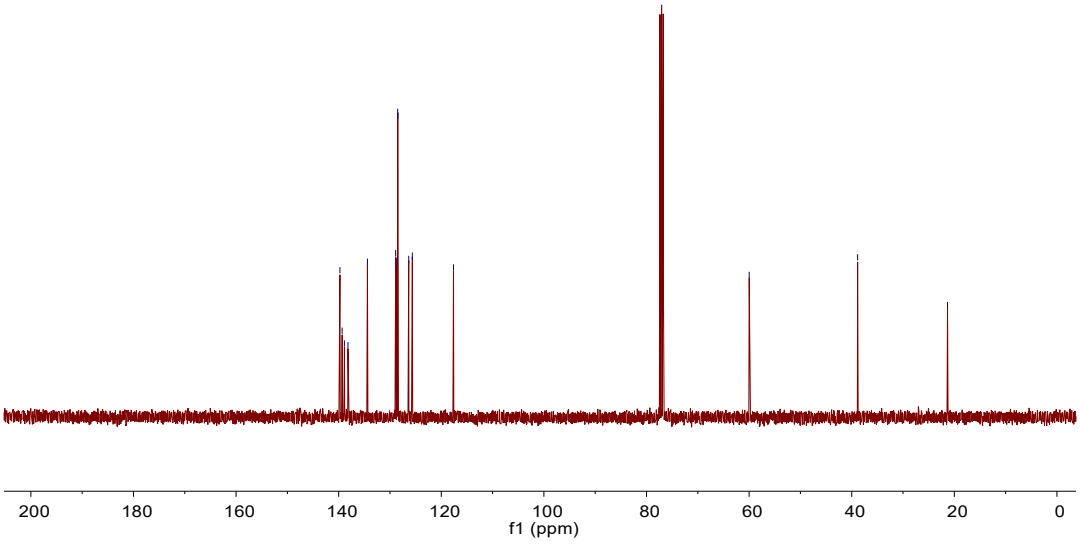


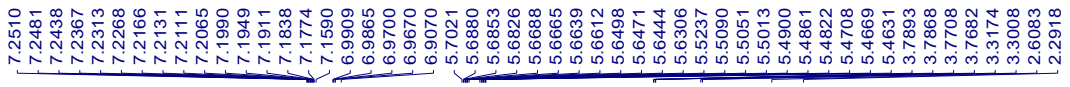


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

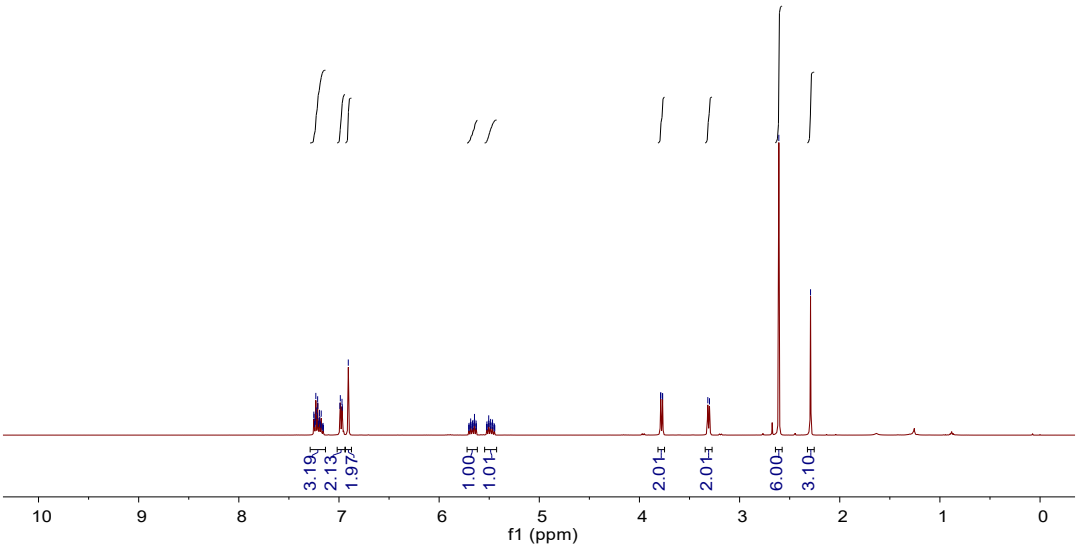
4aj, *E*/*Z* > 20/1

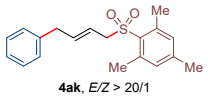
A0110-LYA-4-50B2.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 28





A0161-LYA-4-50C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 5

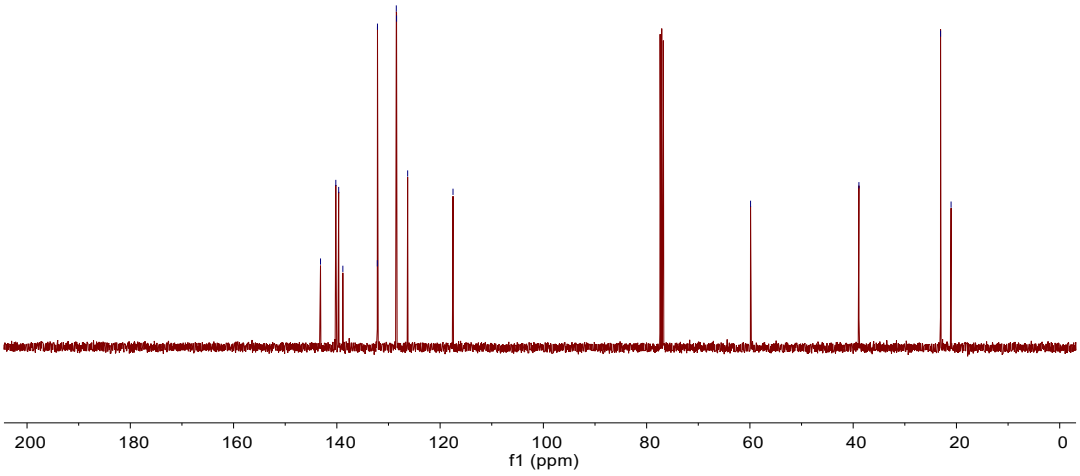




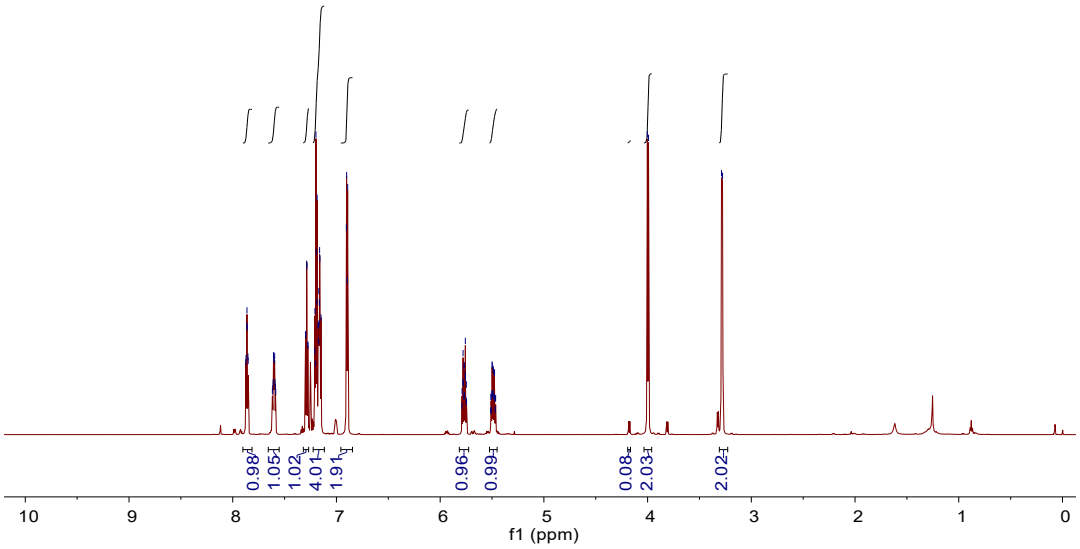
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

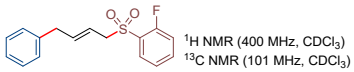
4ak, *E*/*Z* > 20/1

A0161-LYA-4-50C.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 5



5262-LYA-4-49A.10.fid

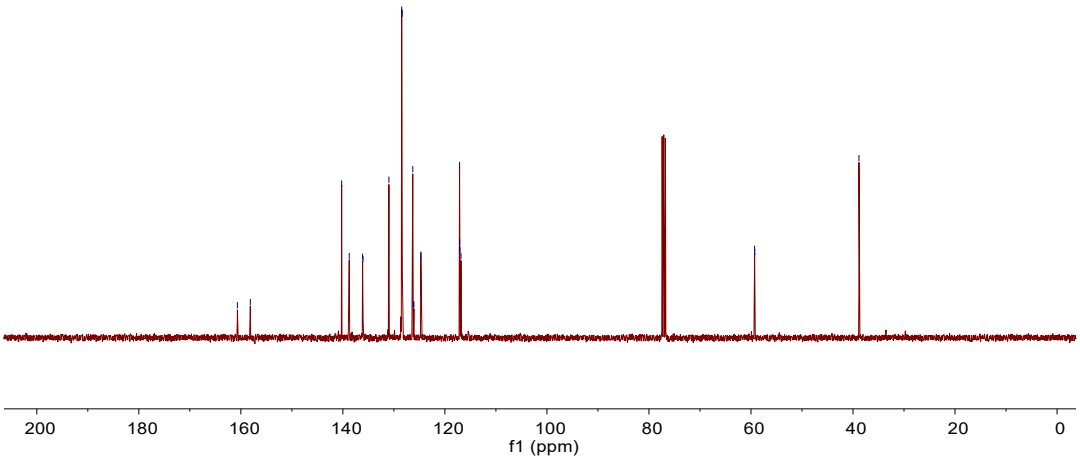


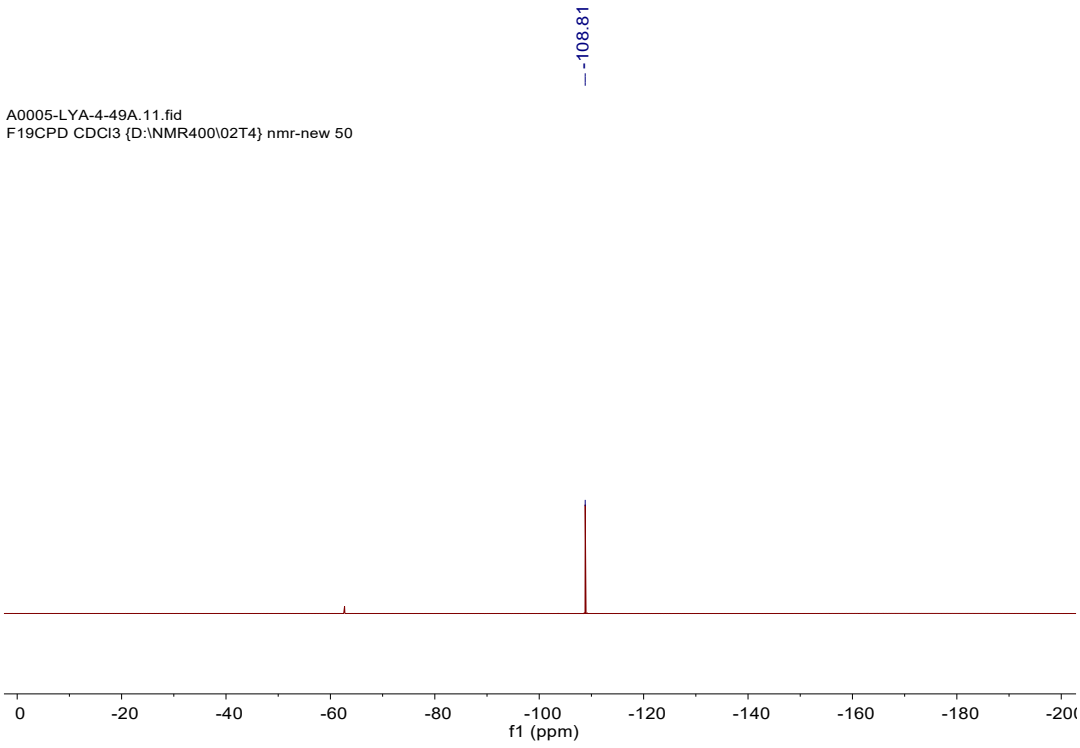


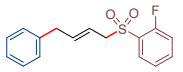
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

4al, *E*/*Z* > 20/1

A0005-LYA-4-49A.12.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 50



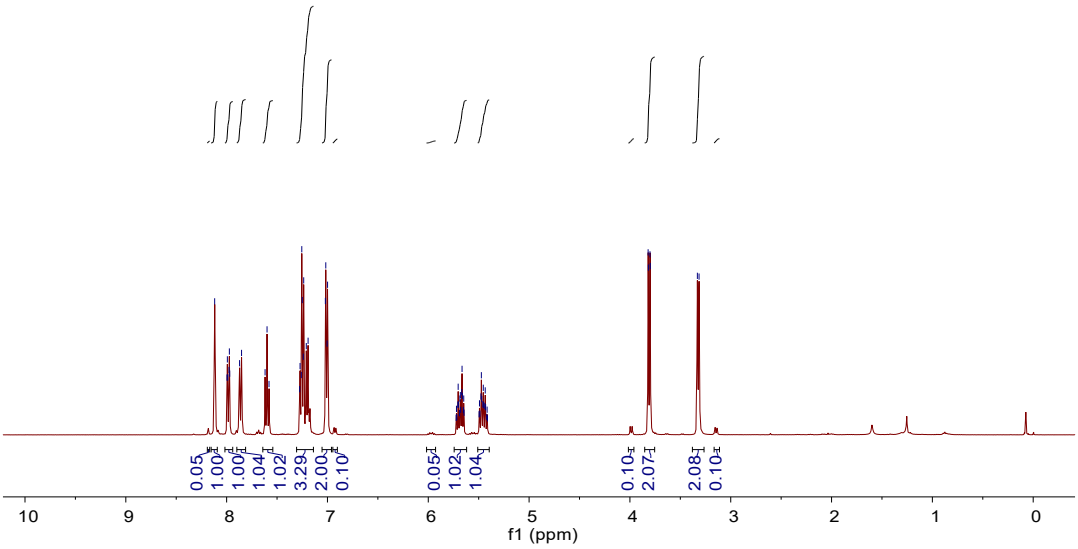


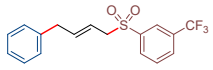


^{19}F NMR (376 MHz, $CDCl_3$)

4al, *E*/*Z* > 20/1

A0005-LYA-4-49B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 51

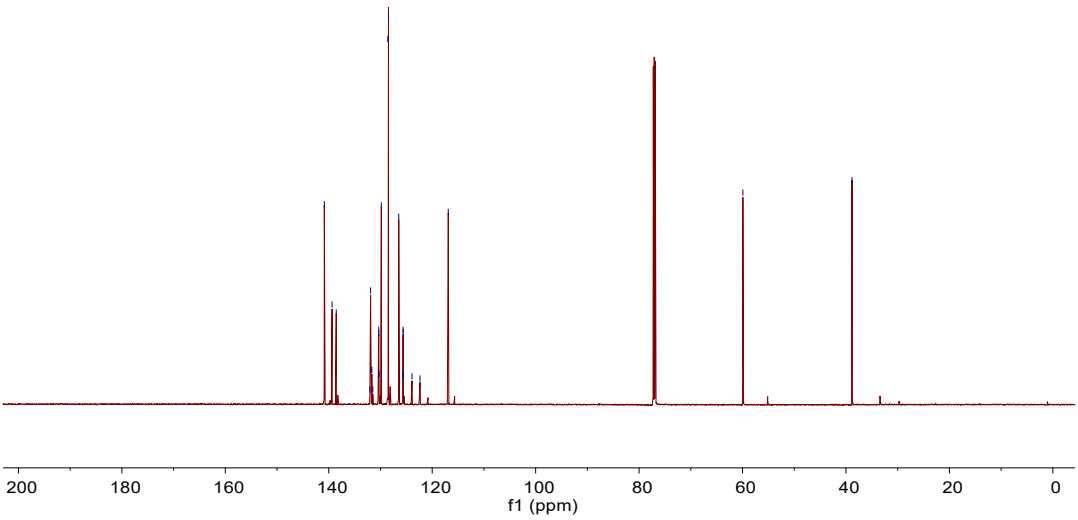


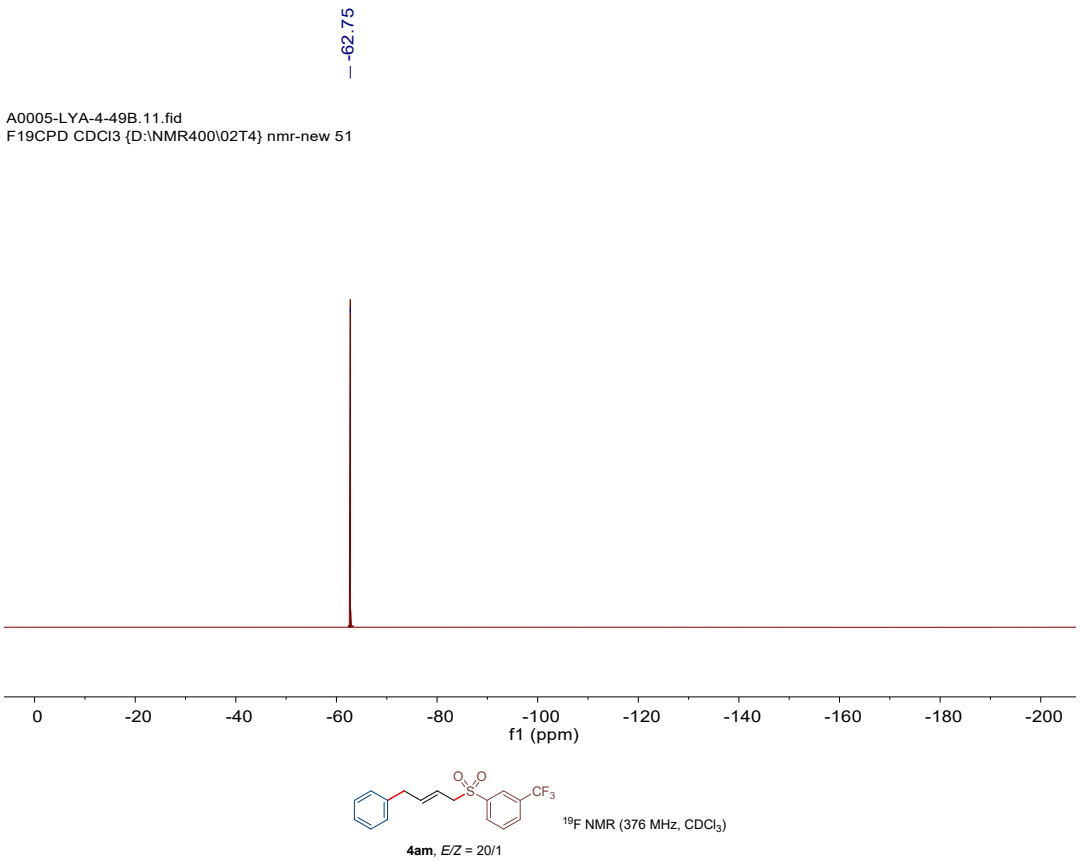


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (176 MHz, $CDCl_3$)

4am, *E*/*Z* = 20/1

5262-LYA-4-49B.10.fid

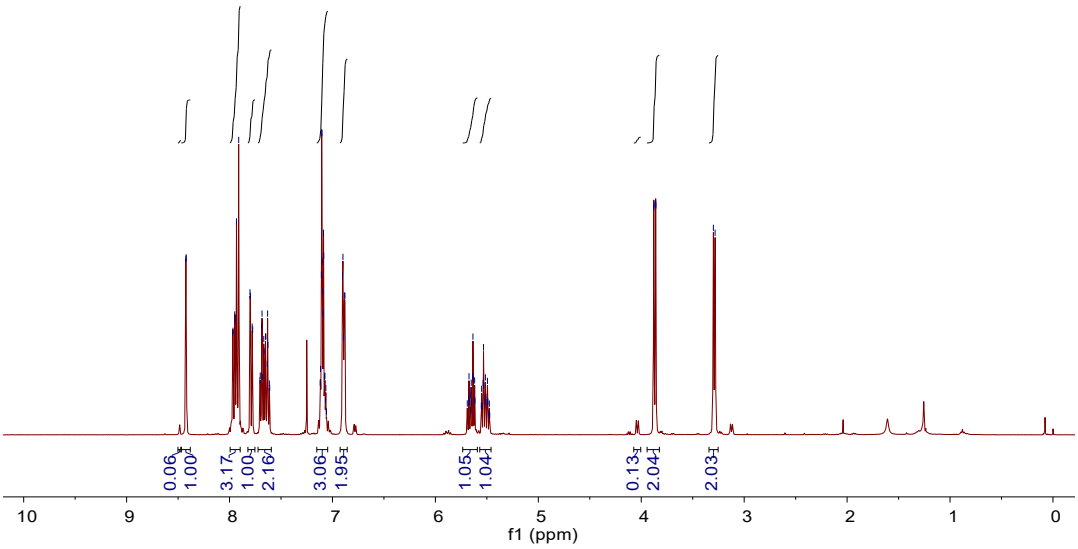


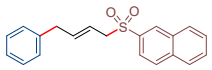


^{19}F NMR (376 MHz, $CDCl_3$)

4am, *E*/*Z* = 20/1

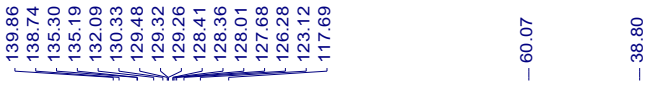
9910-LYA-4-42C-TM.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 19



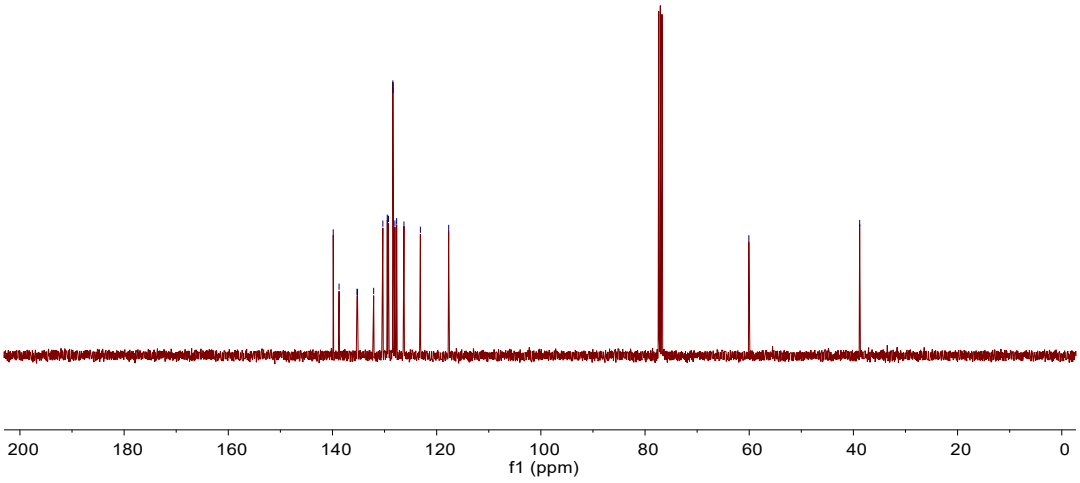


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

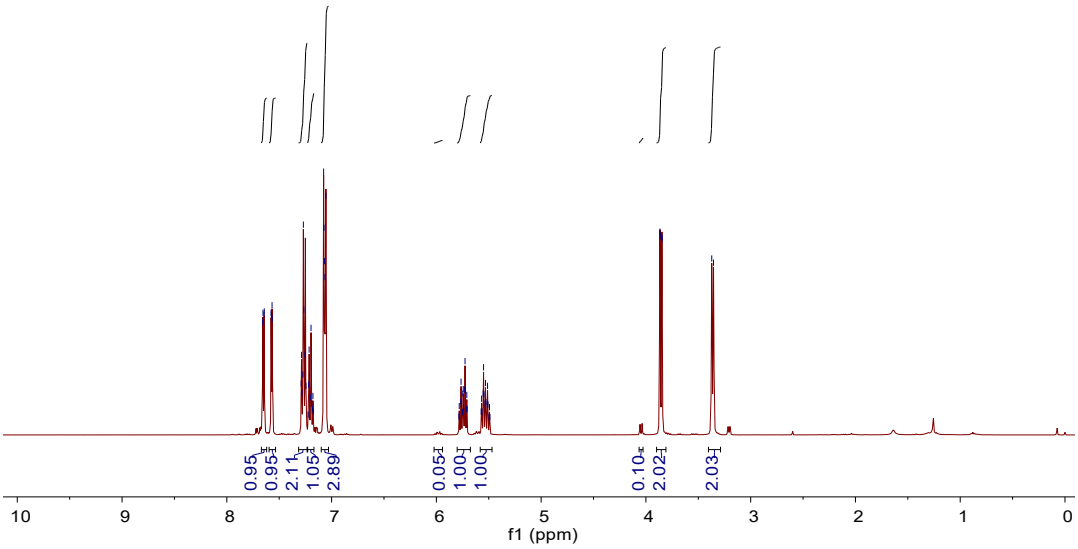
4an, *E*/*Z* = 17/1

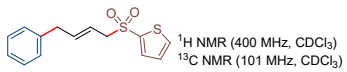


9910-LYA-4-42C-TM.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 19



A0005-LYA-4-48A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 49

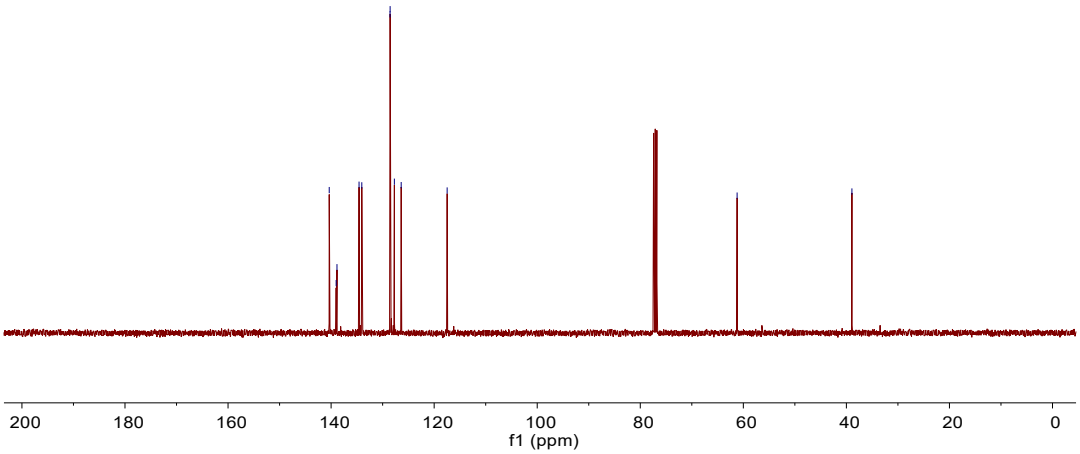




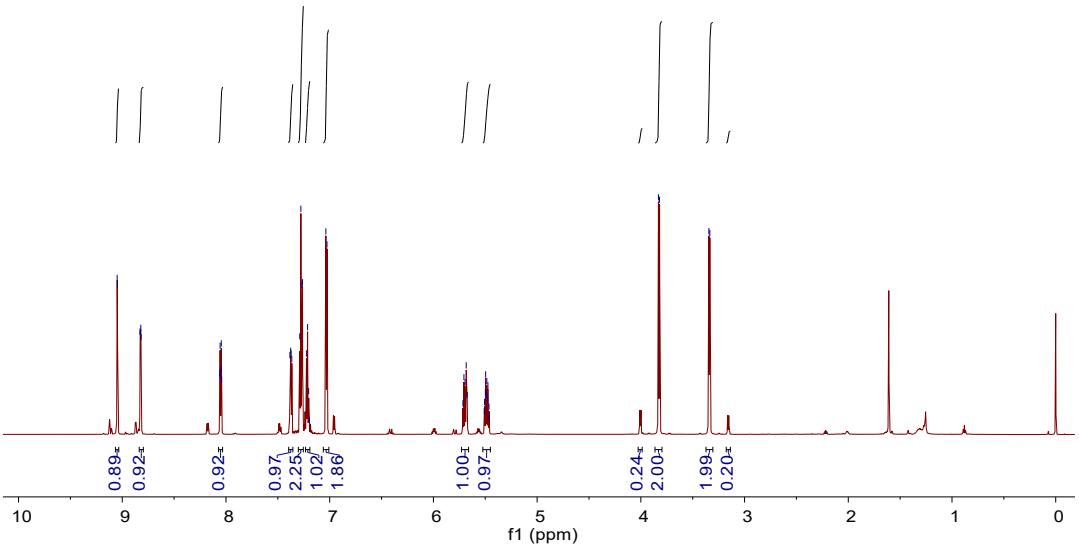
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

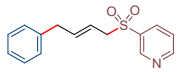
4ao, *E*/*Z* = 20/1

A0005-LYA-4-48A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 49



5549-LYA-5-11.10.fid

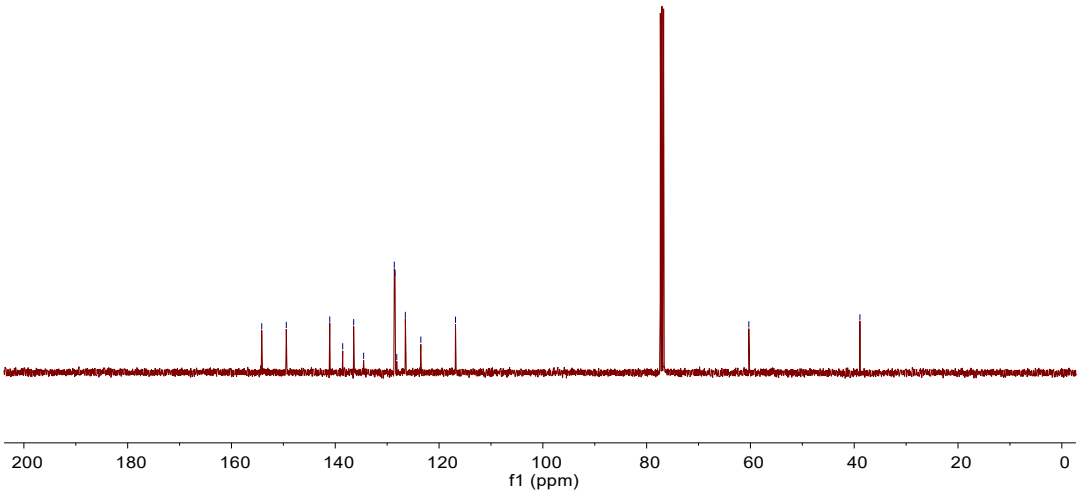




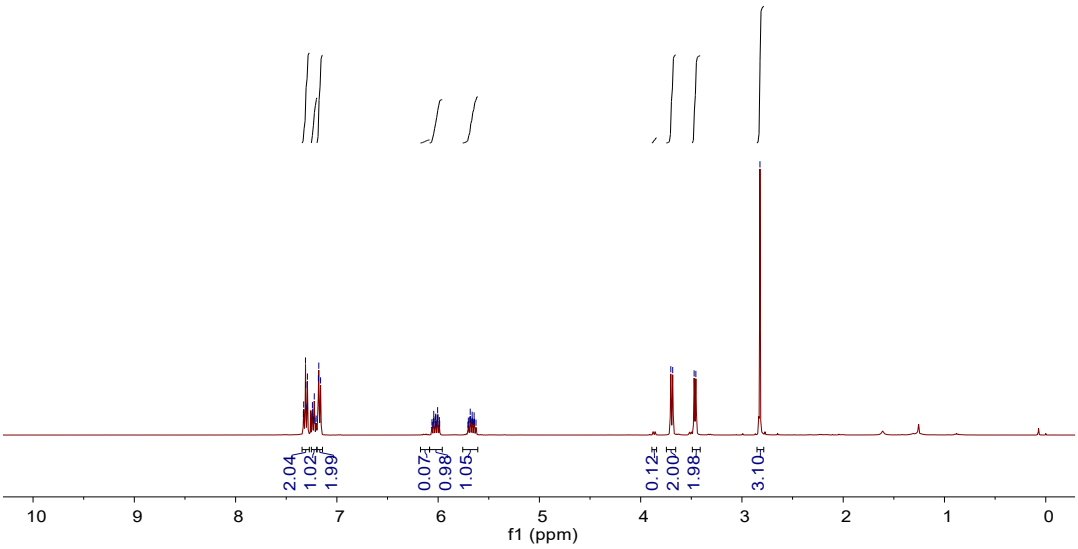
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

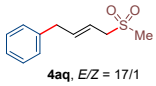
4ap, *E*/*Z* = 10/1

A1443-LYA-4-23C.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 2



A0005-LYA-4-44A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 39

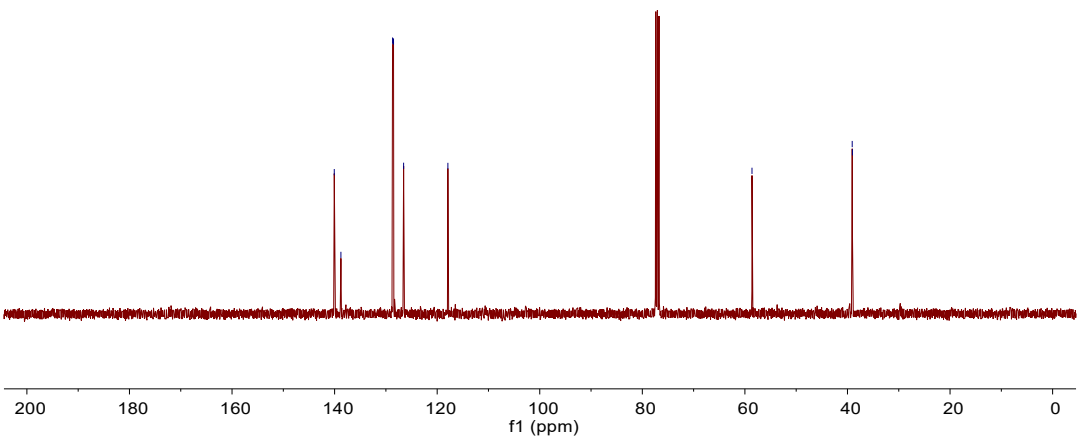




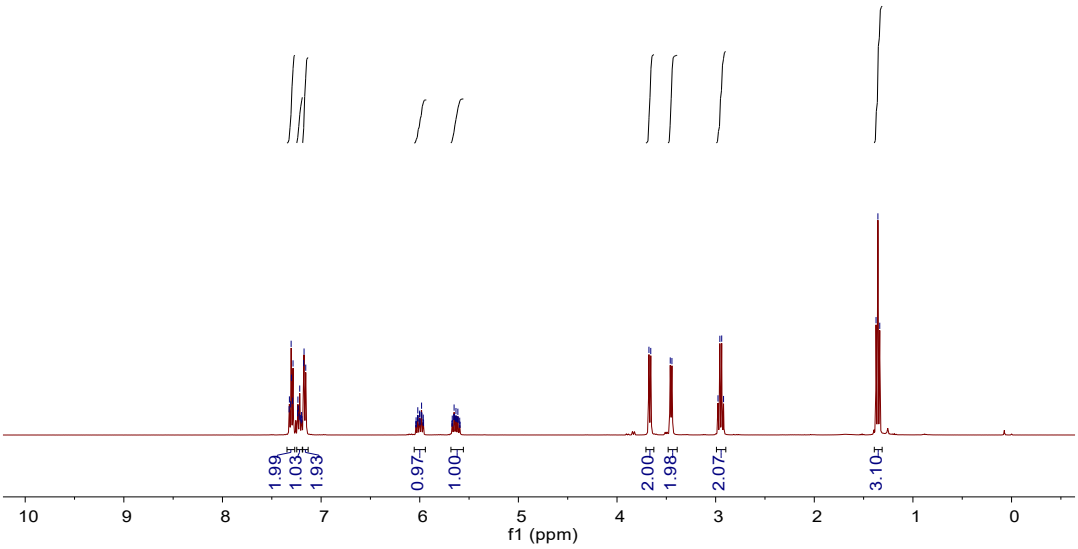
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

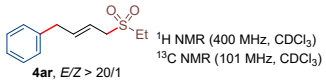
4aq, *E*/*Z* = 17/1

9937-LYA-4-44A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 30



A0005-LYA-4-44C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 45

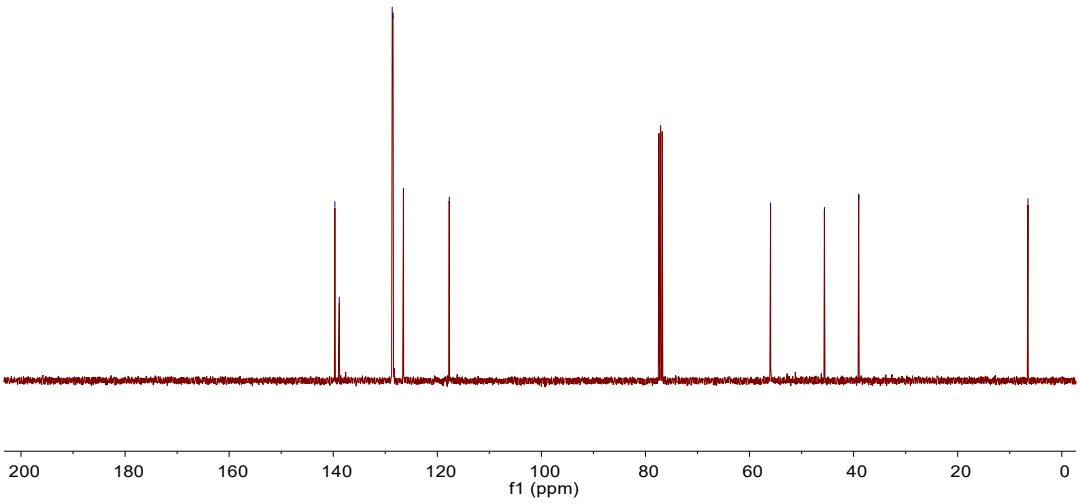




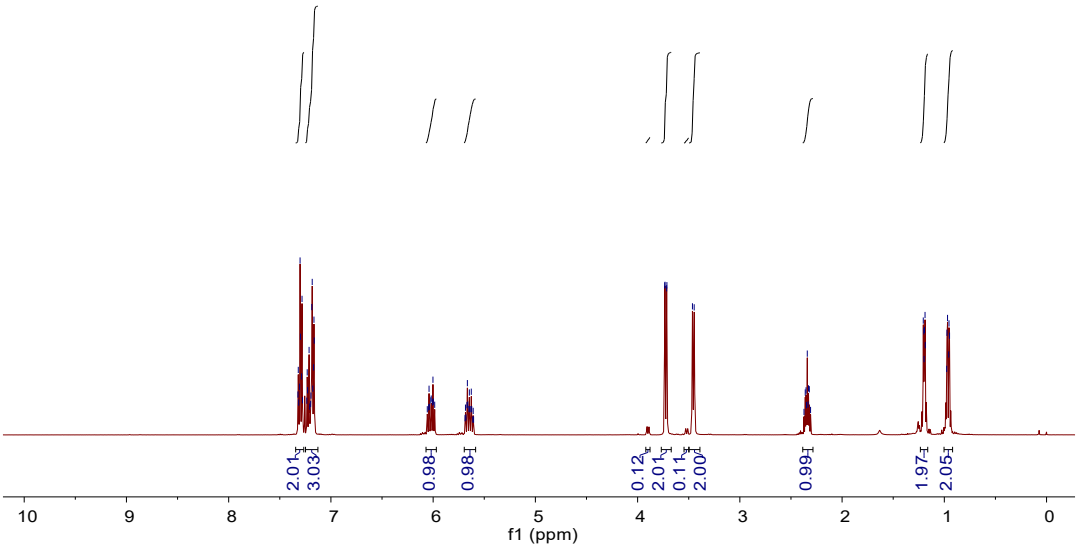
4ar, *E*/*Z* > 20/1

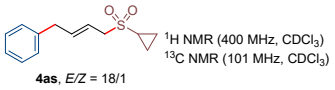
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

9960-LYA-4-44C.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 54



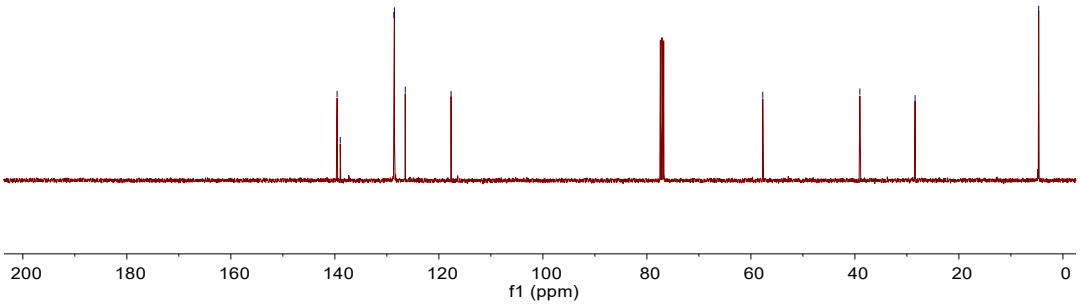
9960-LYA-4-44D.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 55



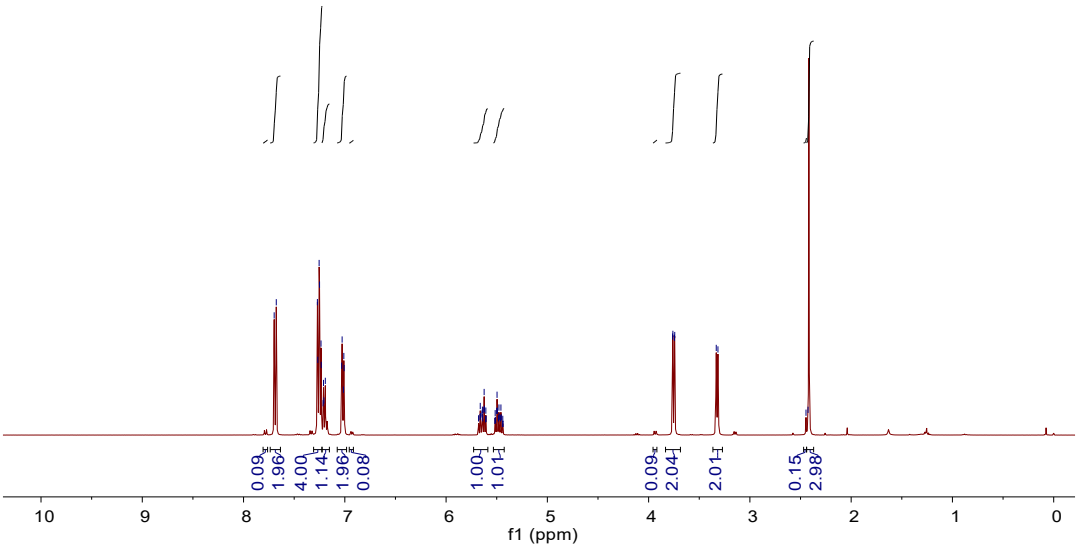


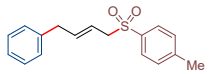
4as, *E*/*Z* = 18/1

9960-LYA-4-44D.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 55



9578-LYA-4-18A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 6

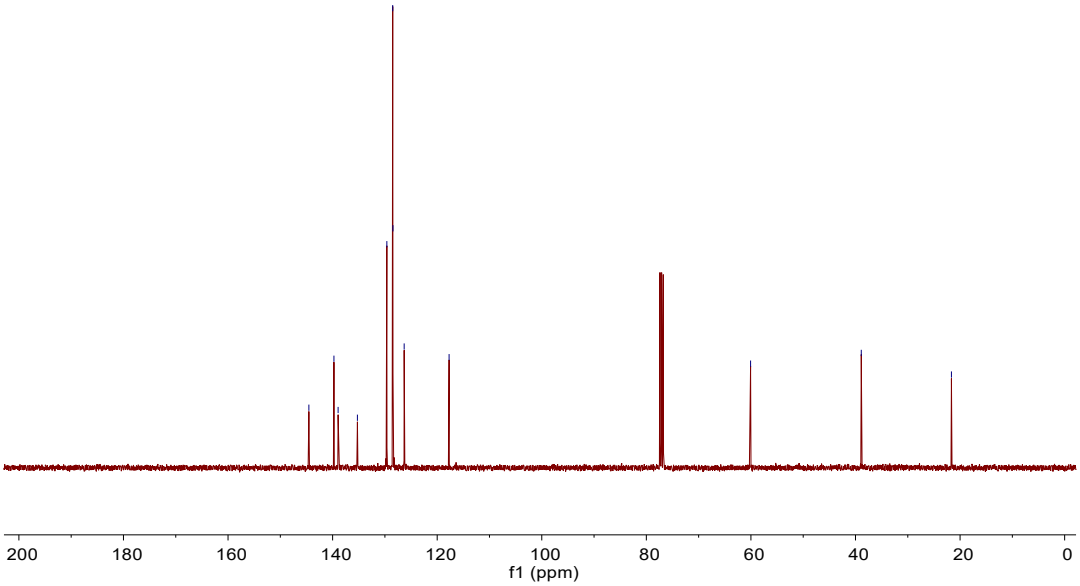




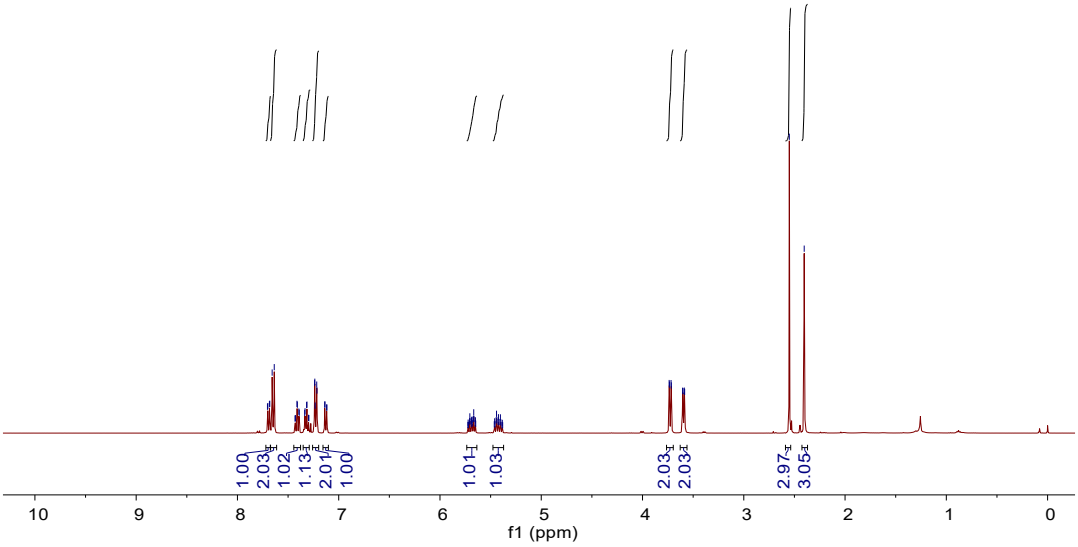
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

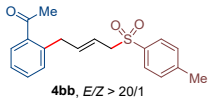
4ba, *E*/*Z* = 20/1

9578-LYA-4-18A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 6



A0887-LYA-4-74B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 51

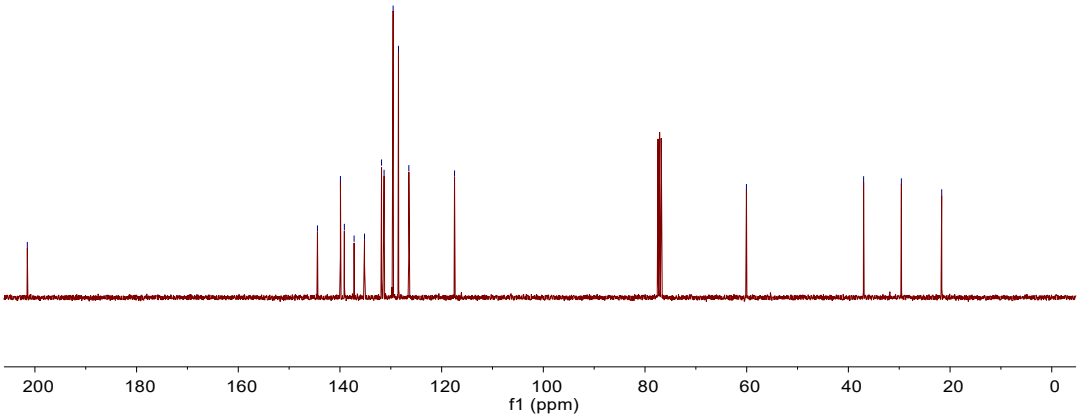




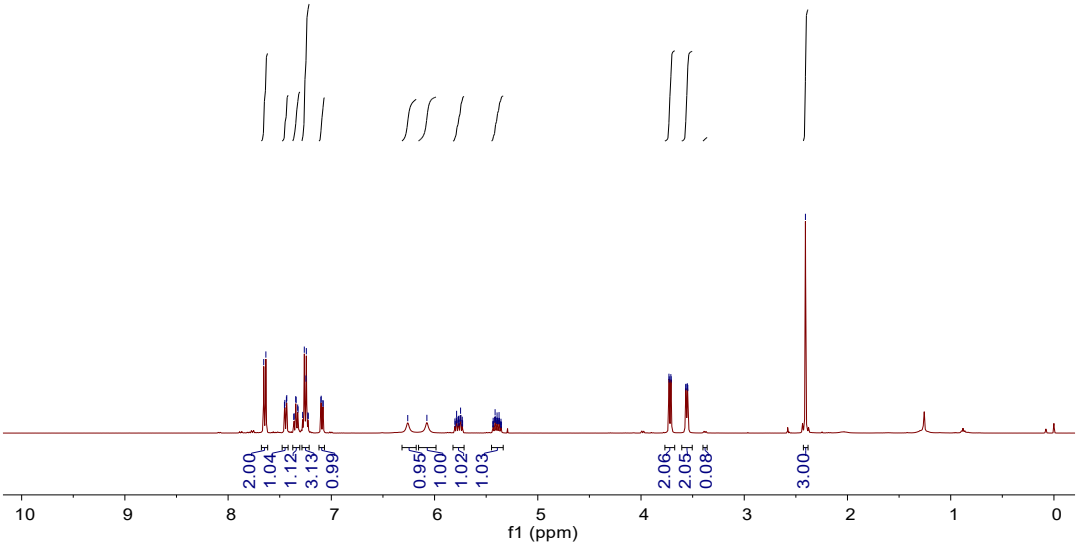
4bb, *E*/*Z* > 20/1

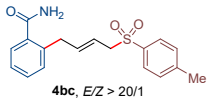
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A0600-LYA-4-74B.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 43



A0761-LYA-4-74C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 11

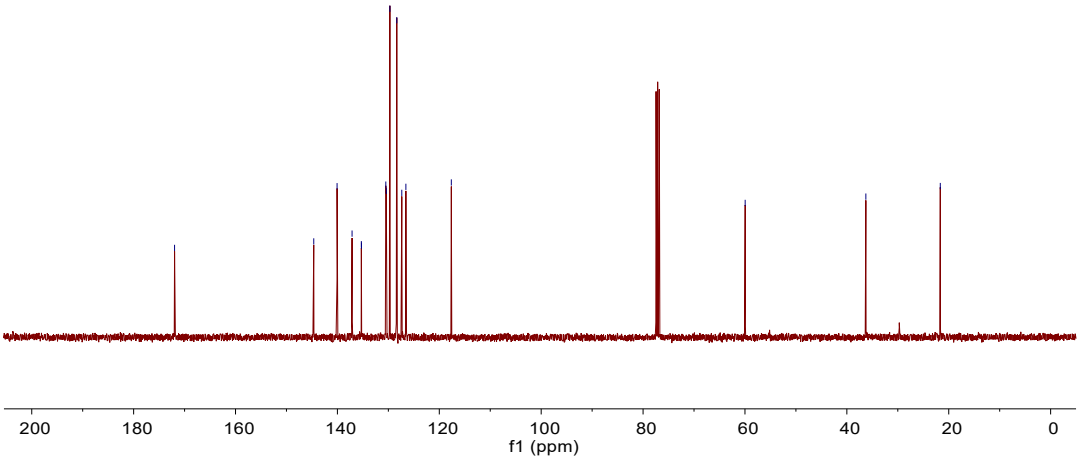




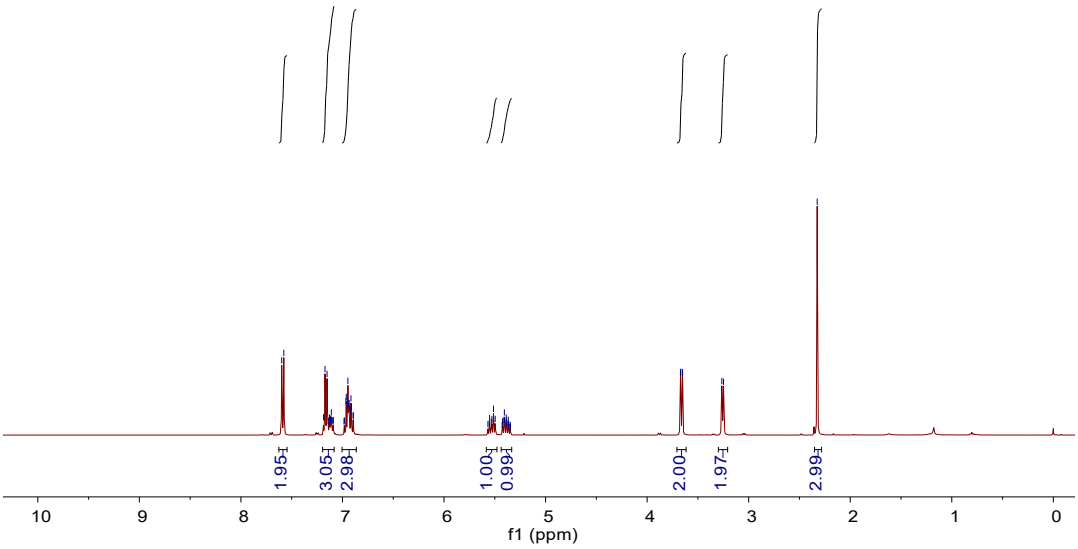
4bc, *E*/*Z* > 20/1

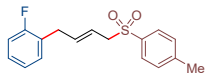
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A0887-LYA-4-74C.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 60



A0446-LYA-4-66B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 54

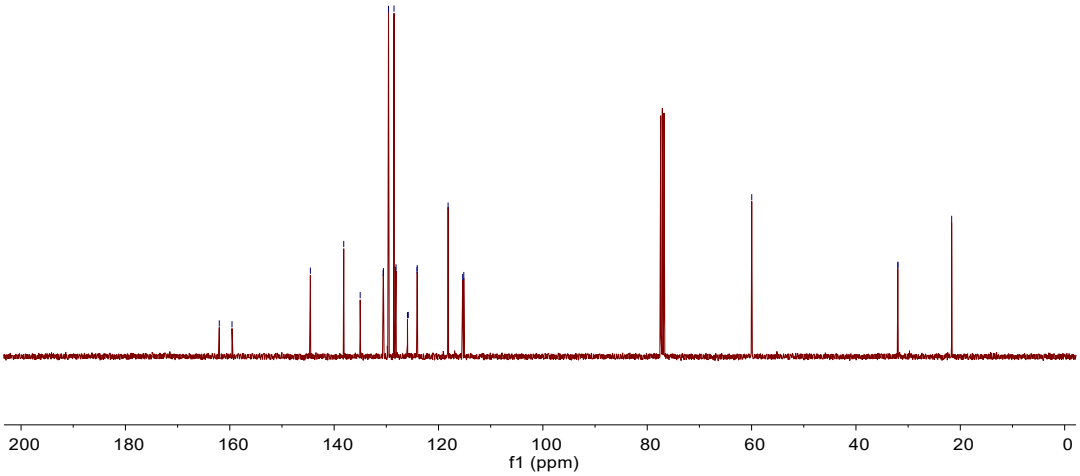


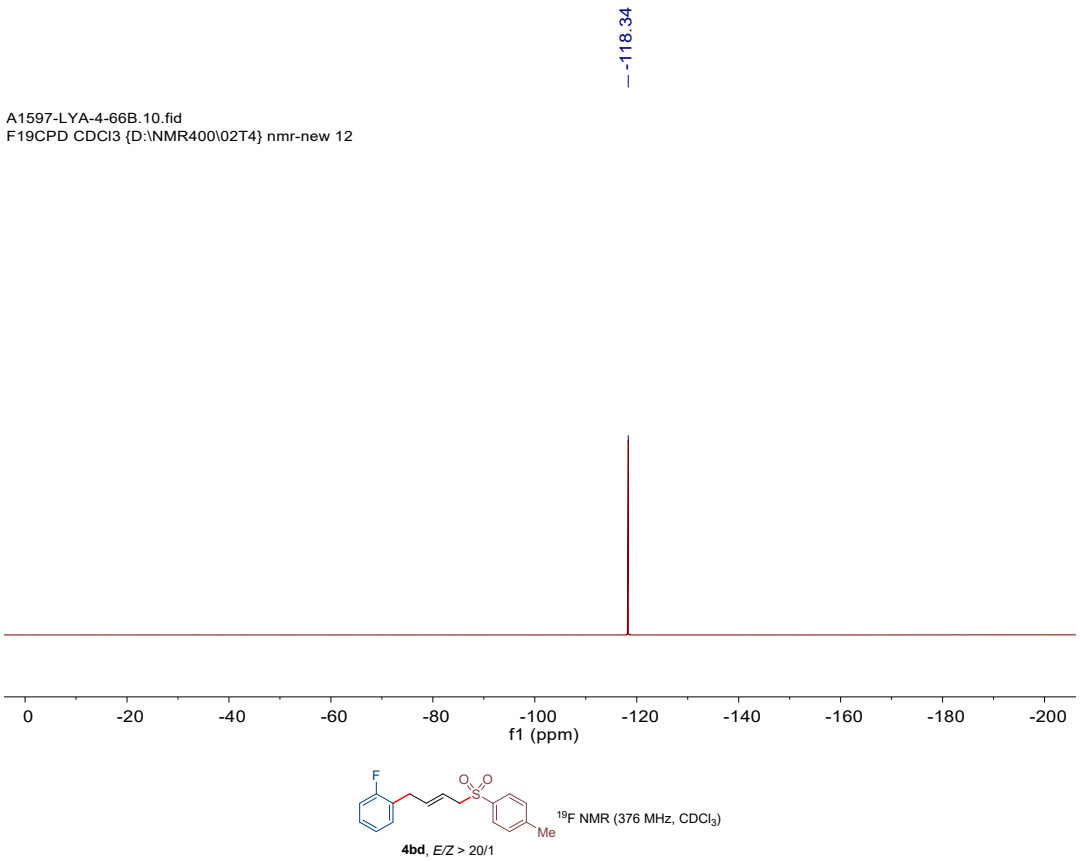


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

4bd, *E*/*Z* > 20/1

A0503-LYA-4-66B.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 9

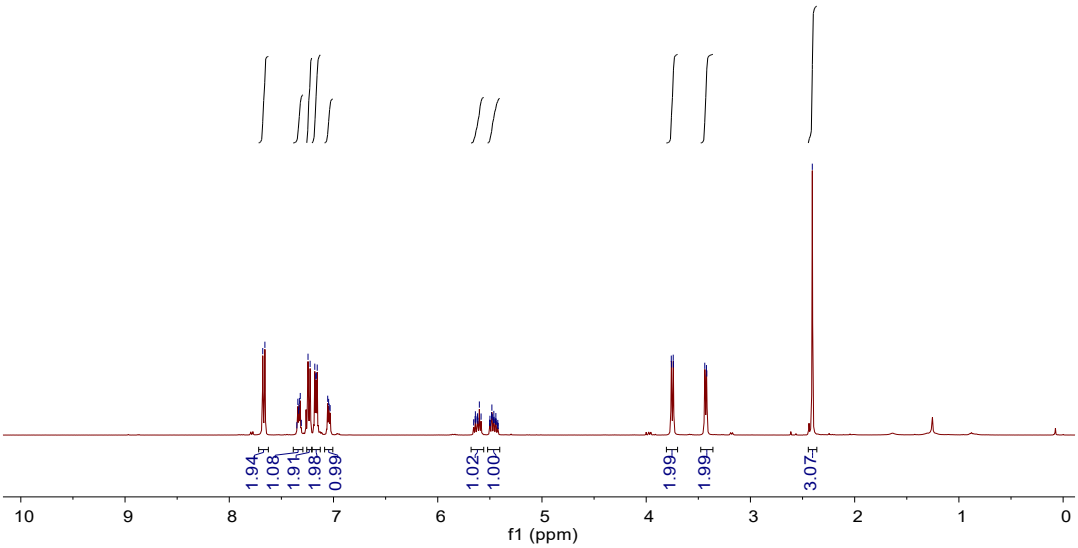


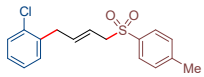


^{19}F NMR (376 MHz, $CDCl_3$)

4bd, *E*/*Z* > 20/1

A0446-LYA-4-66C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 53

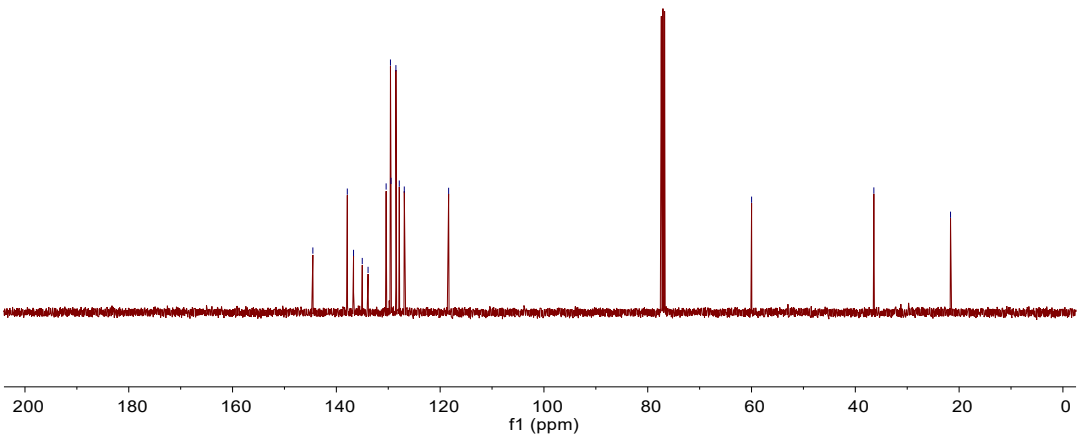




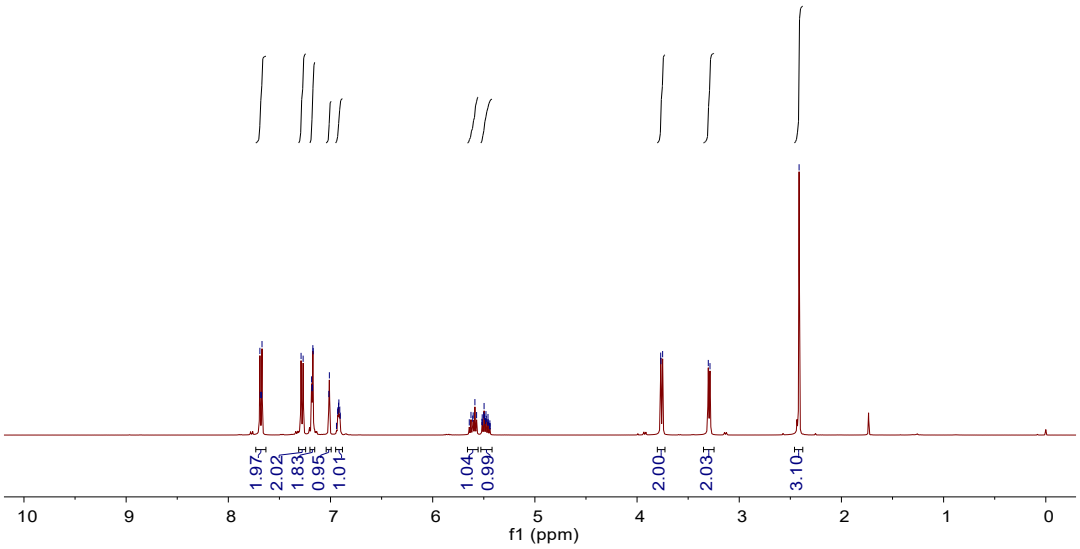
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

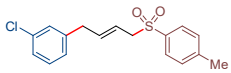
4be, *E*/*Z* > 20/1

A0503-LYA-4-66C.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 10



A2578-LYA-5-81A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 11

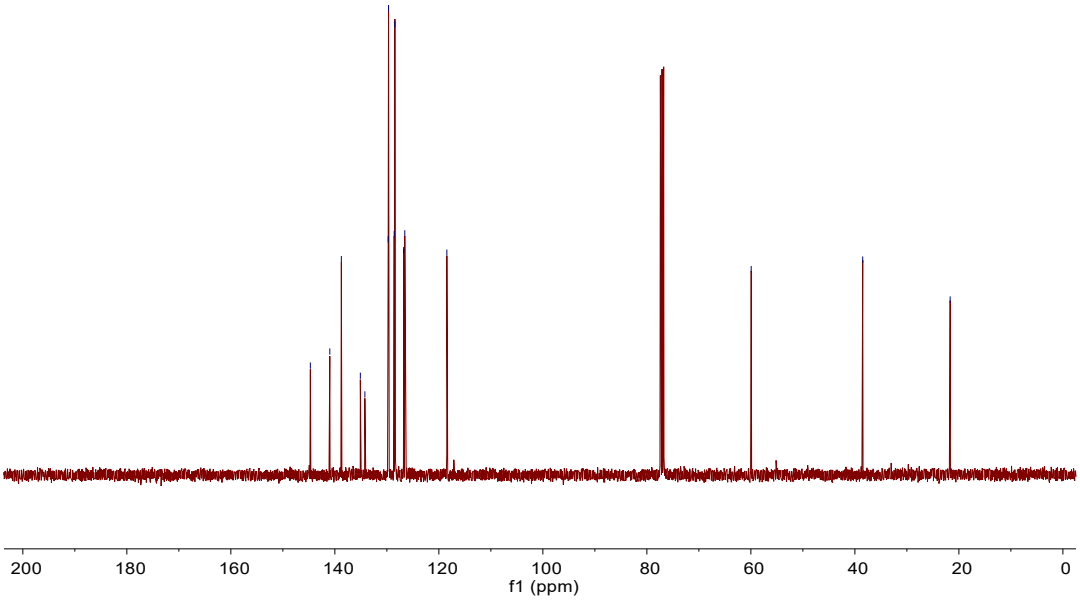




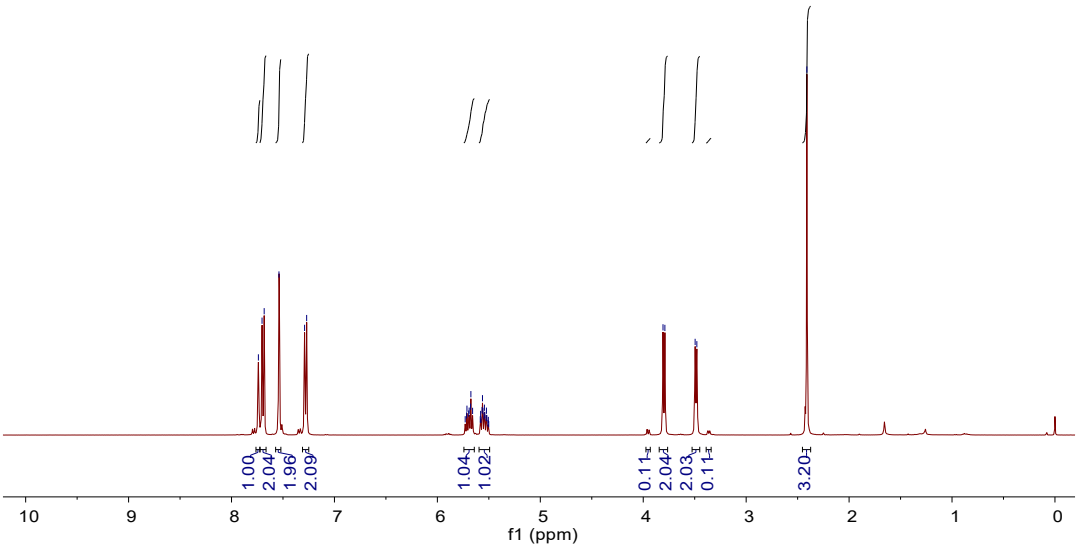
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

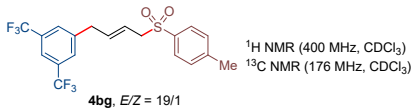
4bf, *E*/*Z* > 20/1

A0351-LYA-4-56B2.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 2



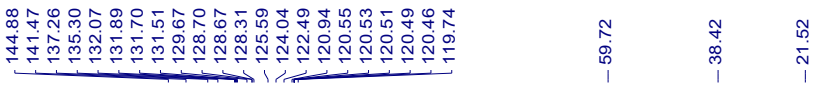
A1126-LYA-4-82D.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 3



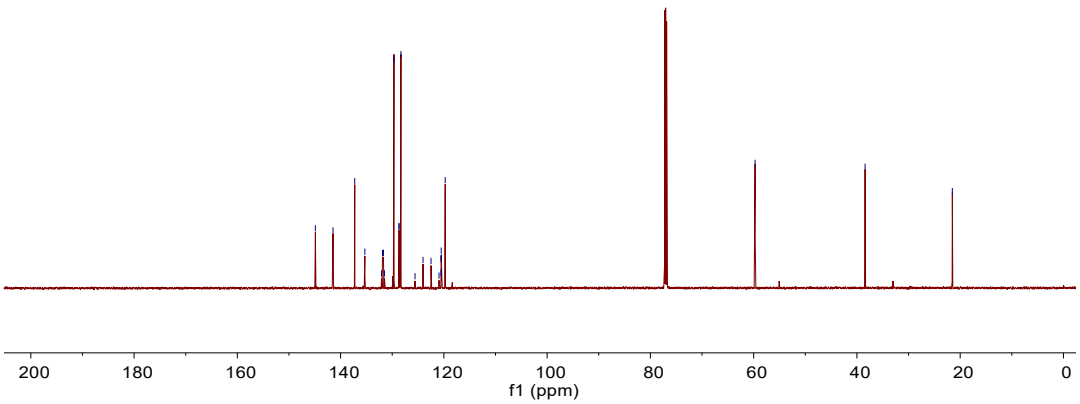


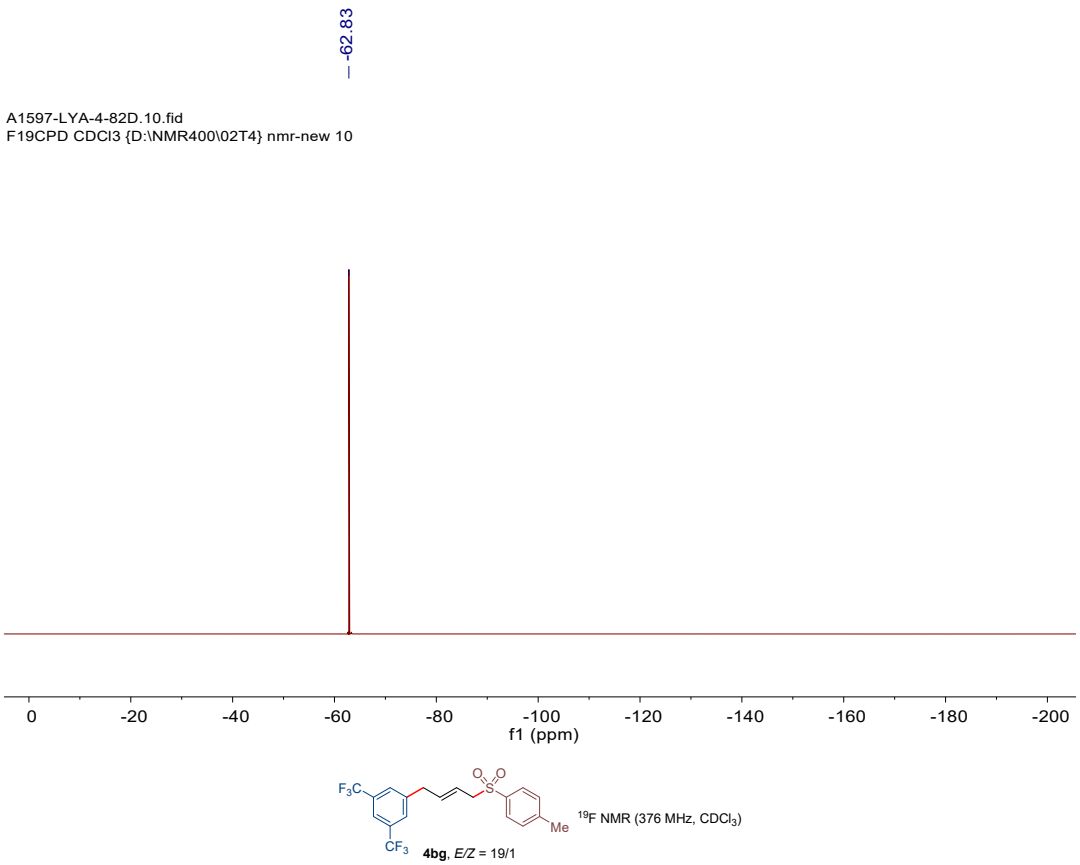
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (176 MHz, $CDCl_3$)

4bg, *E*/*Z* = 19/1



5493-LYA-4-82D.10.fid

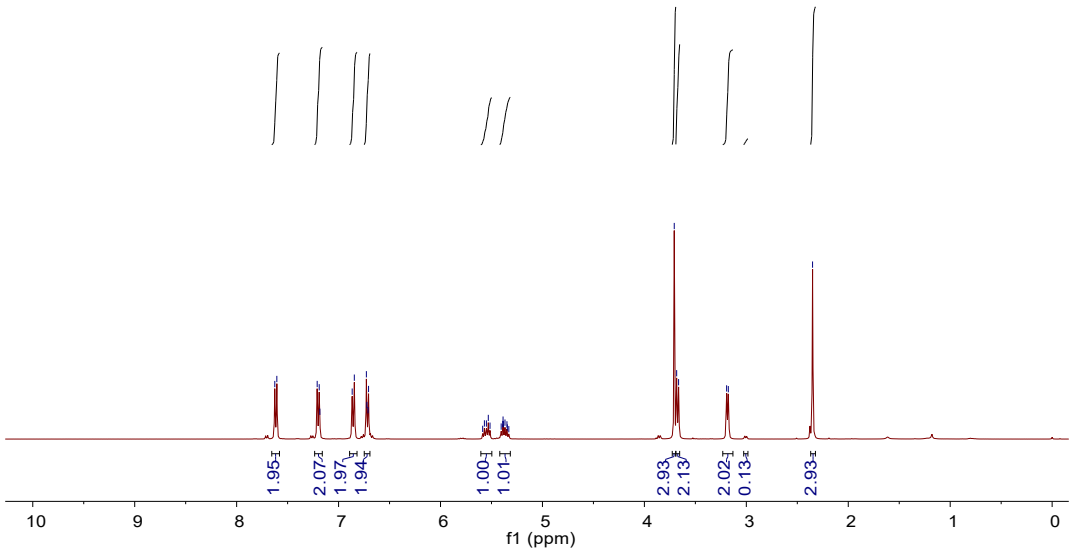


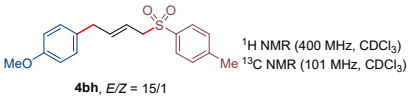


^{19}F NMR (376 MHz, $CDCl_3$)

4bg, *E*/*Z* = 19/1

A0517-LYA-4-61B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 51

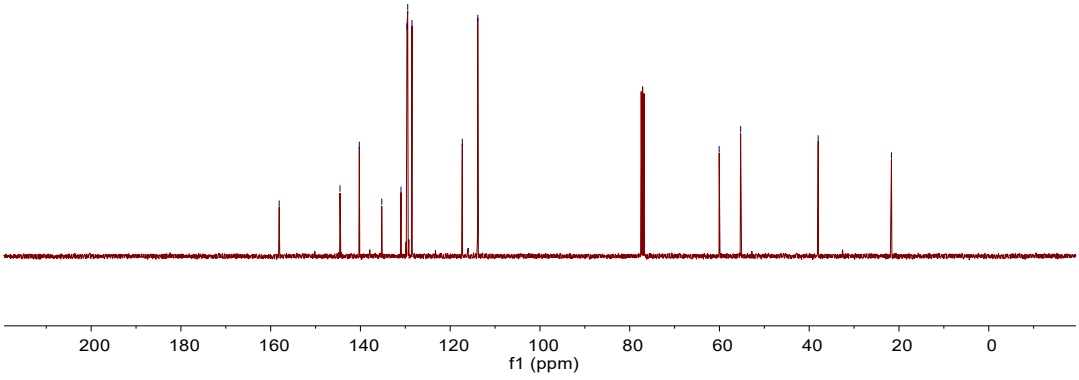




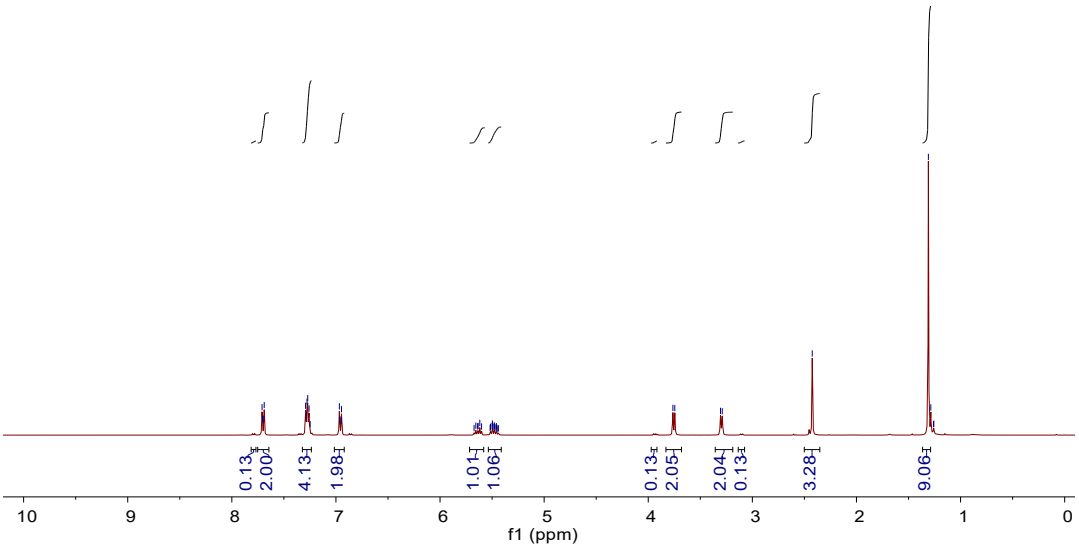
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

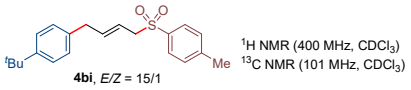
4bh, *E*/*Z* = 15/1

A0438-LYA-4-61B.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 10



A0437-LYA-4-61C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 12

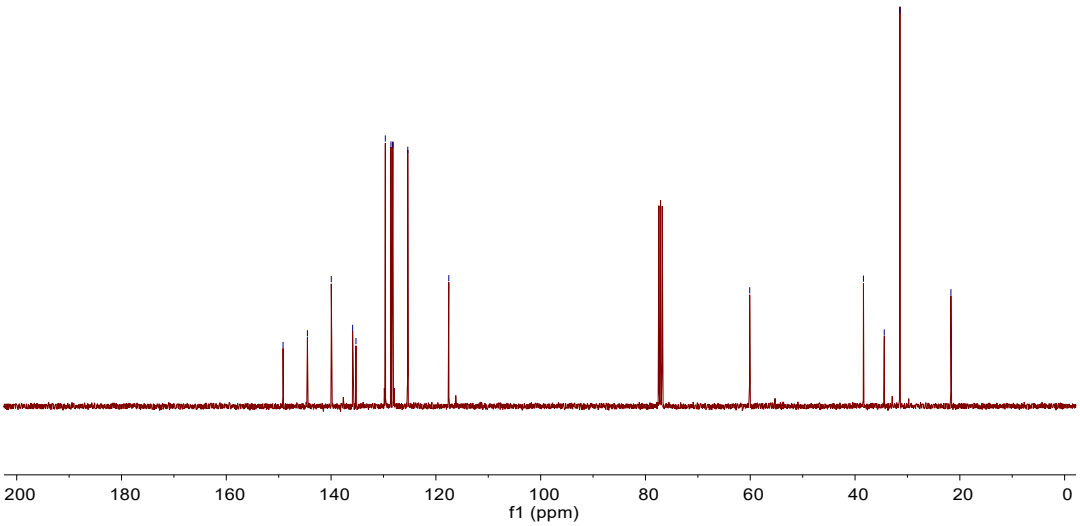




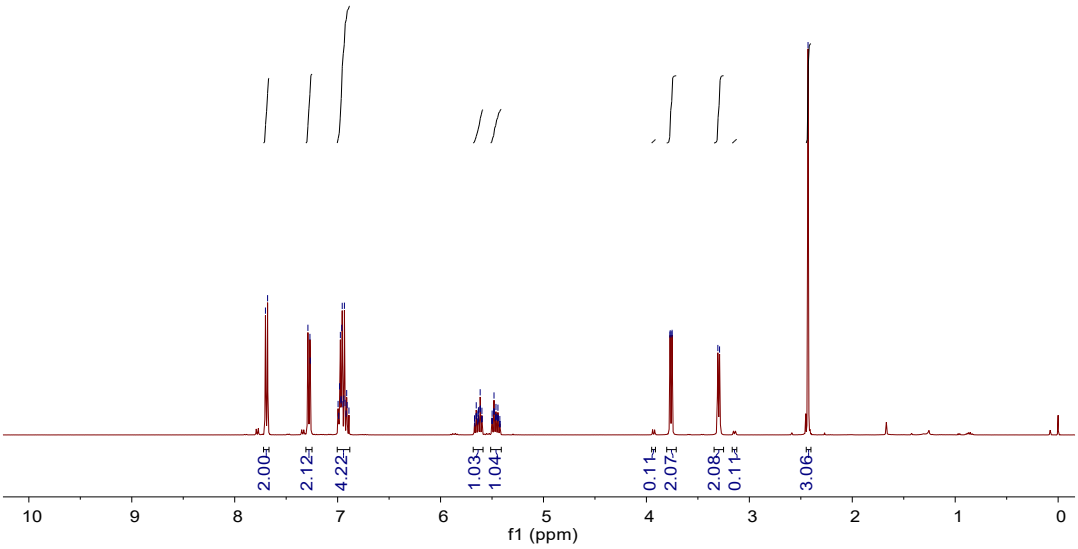
4bi, *E*/*Z* = 15/1

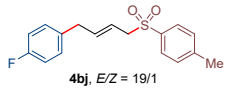
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A0437-LYA-4-61C.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 12



A0909-LYA-4-81A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 43

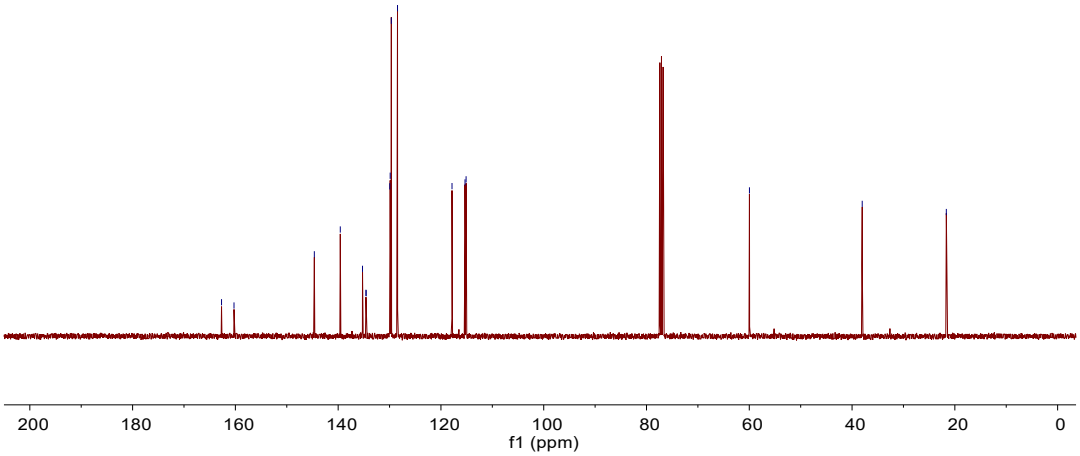


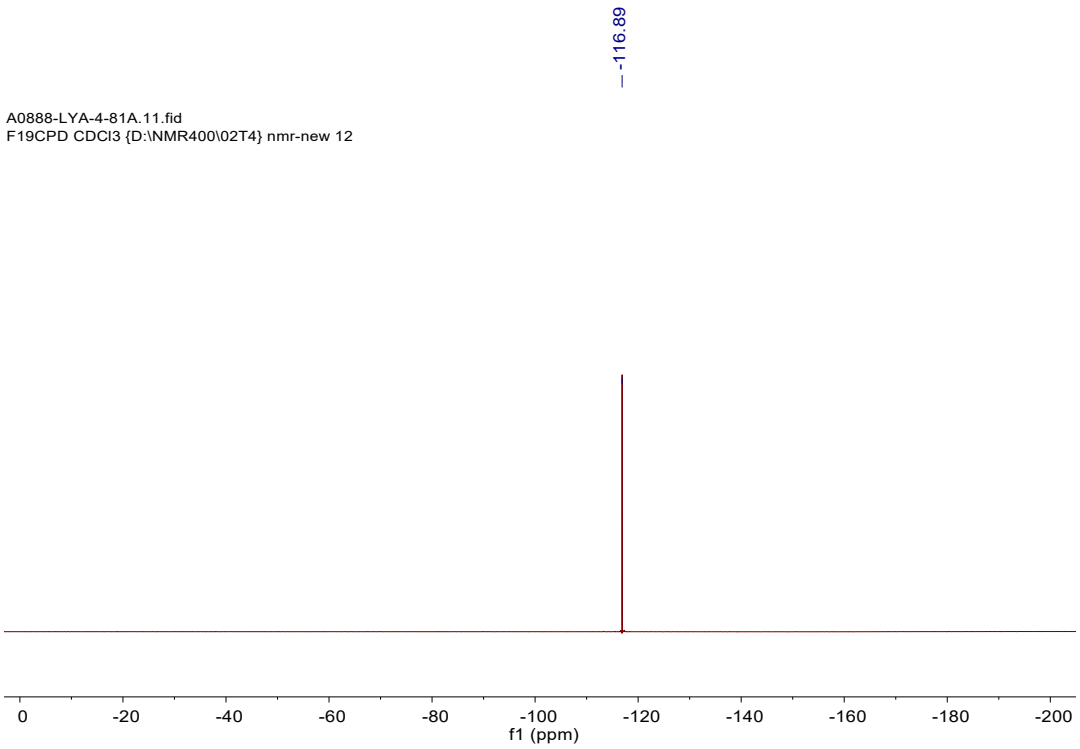


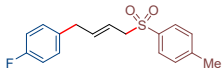
4bj, *E*/*Z* = 19/1

^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A0888-LYA-4-81A.12.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 12

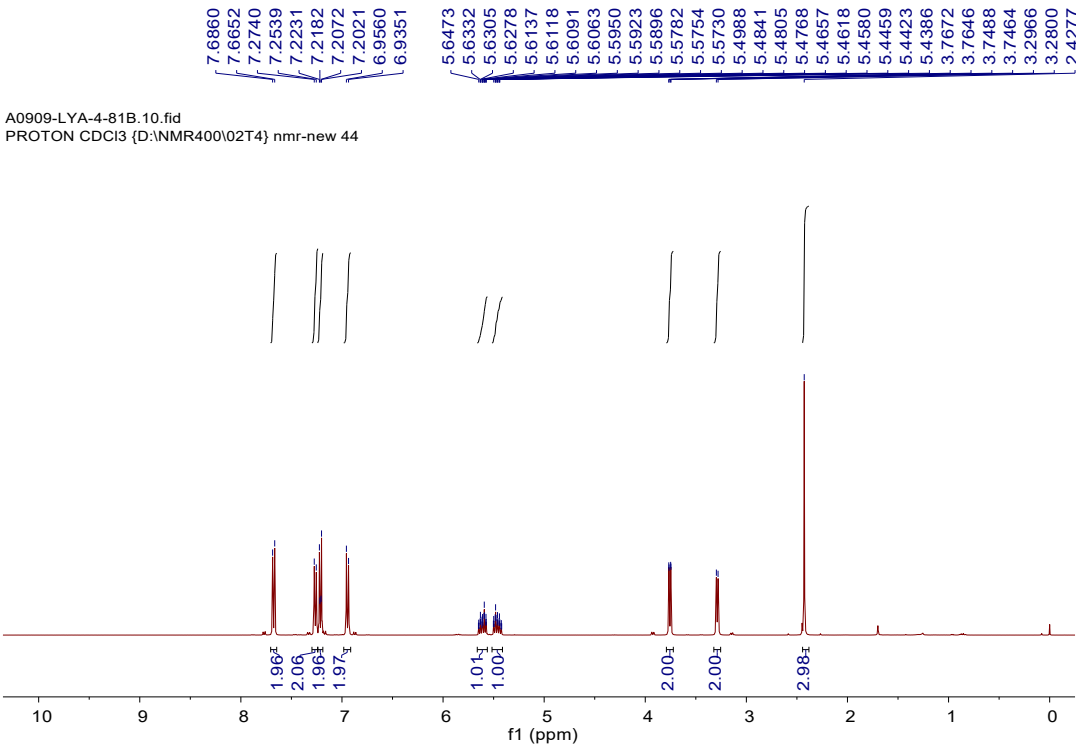




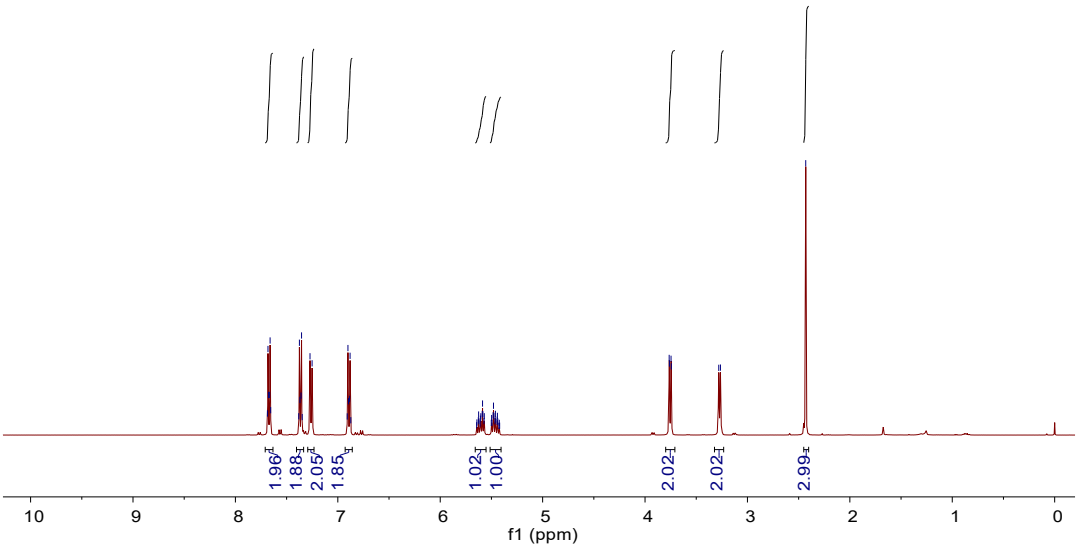


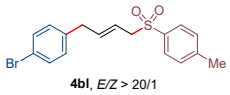
^{19}F NMR (376 MHz, $CDCl_3$)

4bj, *E*/*Z* = 19/1


7.6860
7.6652
7.2740
7.2539
7.2231
7.2182
7.2072
7.2021
6.9560
6.9351
5.6473
5.6332
5.6305
5.6278
5.6137
5.6118
5.6091
5.6063
5.5950
5.5923
5.5896
5.5782
5.5754
5.5730
5.4988
5.4841
5.4805
5.4768
5.4657
5.4618
5.4580
5.4459
5.4423
5.4386
3.7672
3.7646
3.7488
3.7464
3.2966
3.2800
2.4277
A0909-LYA-4-81B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 44
1.96
2.06
1.96
1.97
1.01
1.00
2.00
2.00
2.98
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)
Cl
Me
4bk, E/Z > 20/1
1H NMR (400 MHz, CDCl3)
13C NMR (101 MHz, CDCl3)
144.67
139.20
137.41
135.18
132.07
129.87
129.65
128.55
128.43
118.12
59.94
38.17
21.67
A0888-LYA-4-81B.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 13
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

A0988-LYA-4-81C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 25



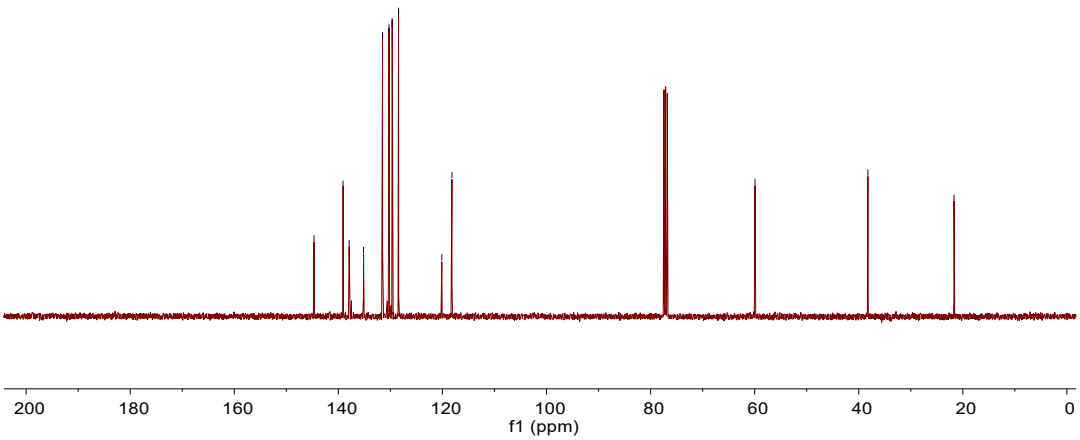


4bl, *E*/*Z* > 20/1

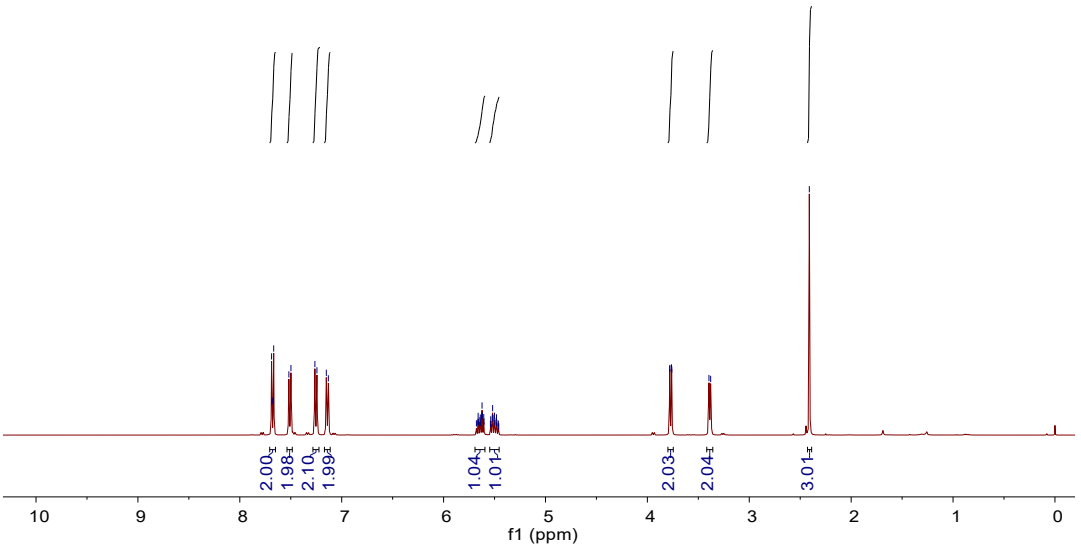
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

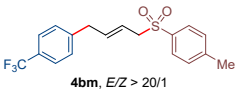
144.68
139.09
137.93
135.16
131.51
130.27
129.66
128.43
120.12
118.18
59.93
38.24
21.69

A0888-LYA-4-81C.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 14



A0988-LYA-4-81D.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 24

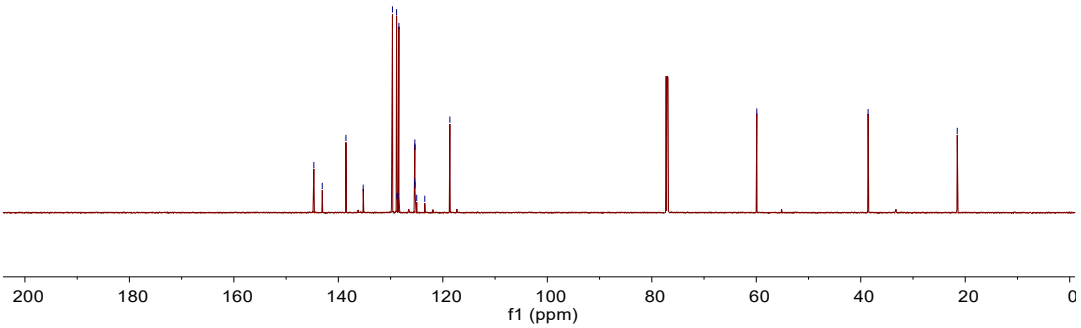


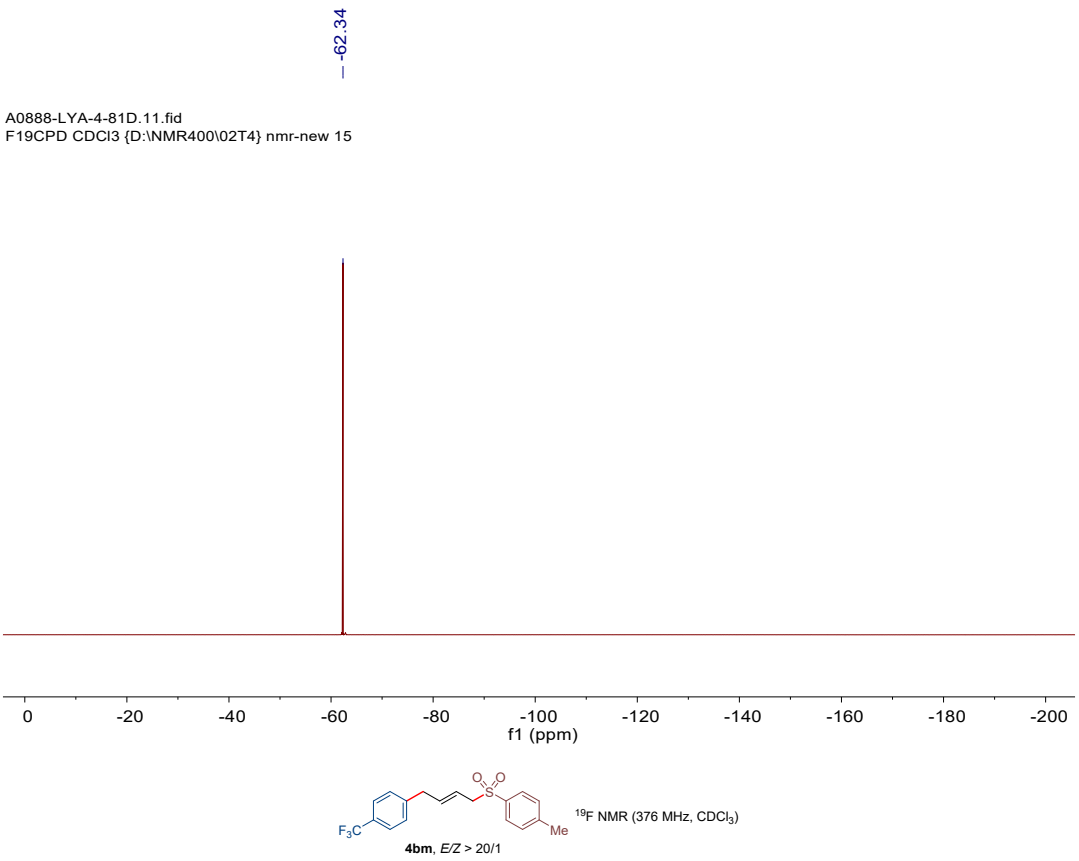


4bm, *E*/*Z* > 20/1

^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (176 MHz, $CDCl_3$)

5493-LYA-4-81D.10.fid

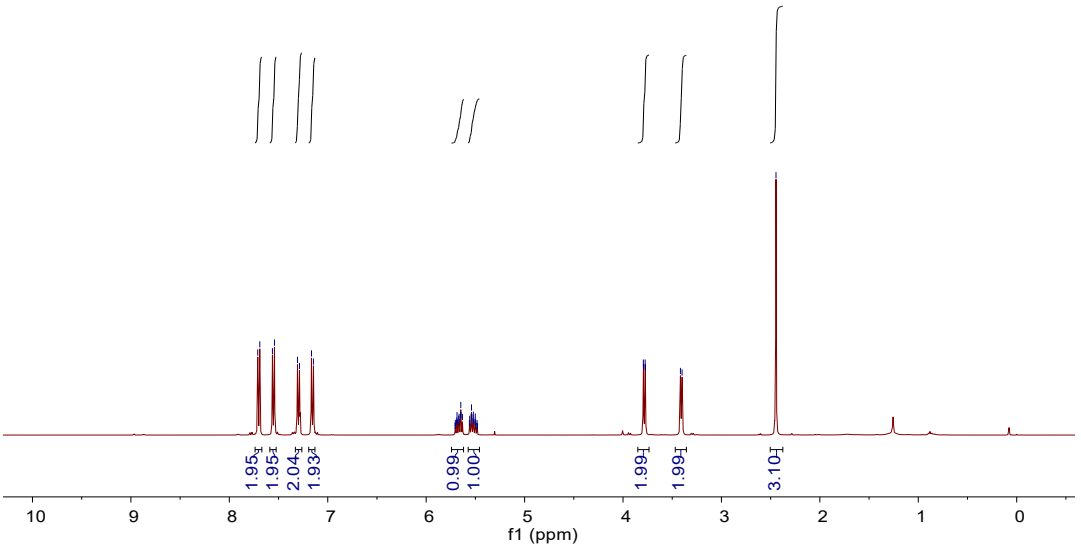


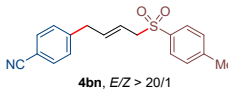


^{19}F NMR (376 MHz, $CDCl_3$)

4bm, *E*/*Z* > 20/1

A0391-LYA-4-57A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 18

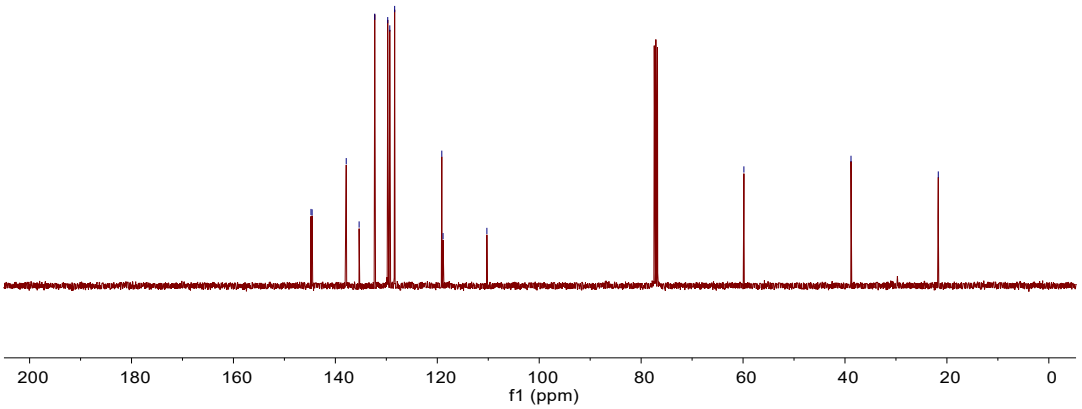




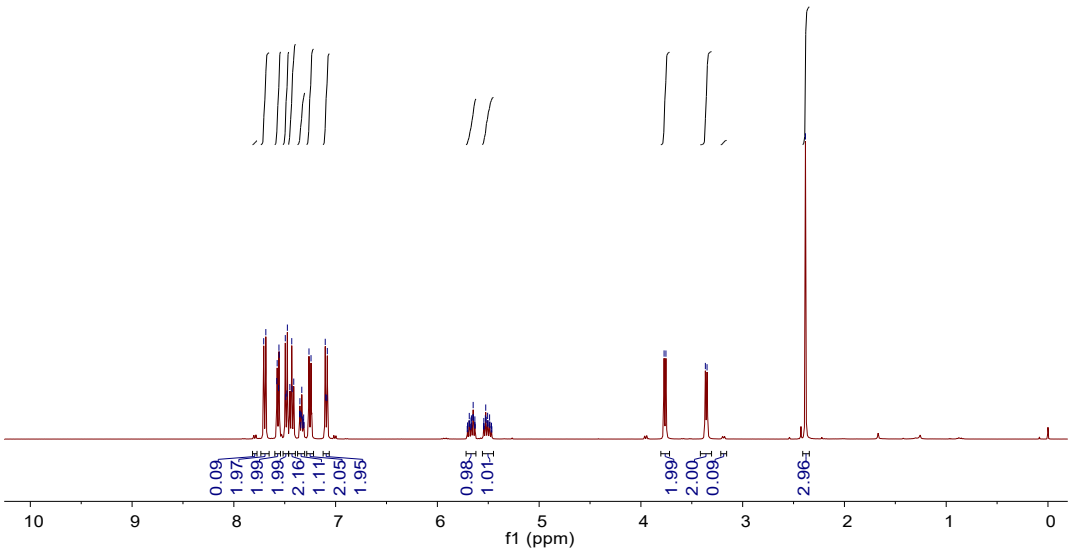
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

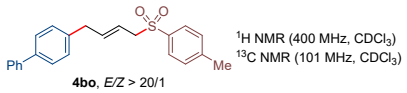
4bn, *E*/*Z* > 20/1

A0391-LYA-4-57A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 18



A0954-LYA-4-82A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 26

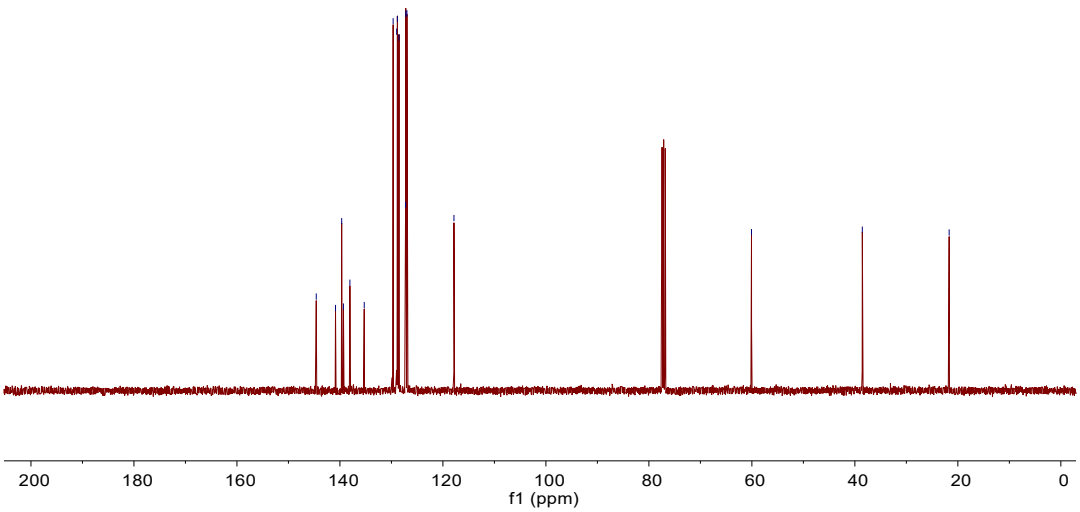




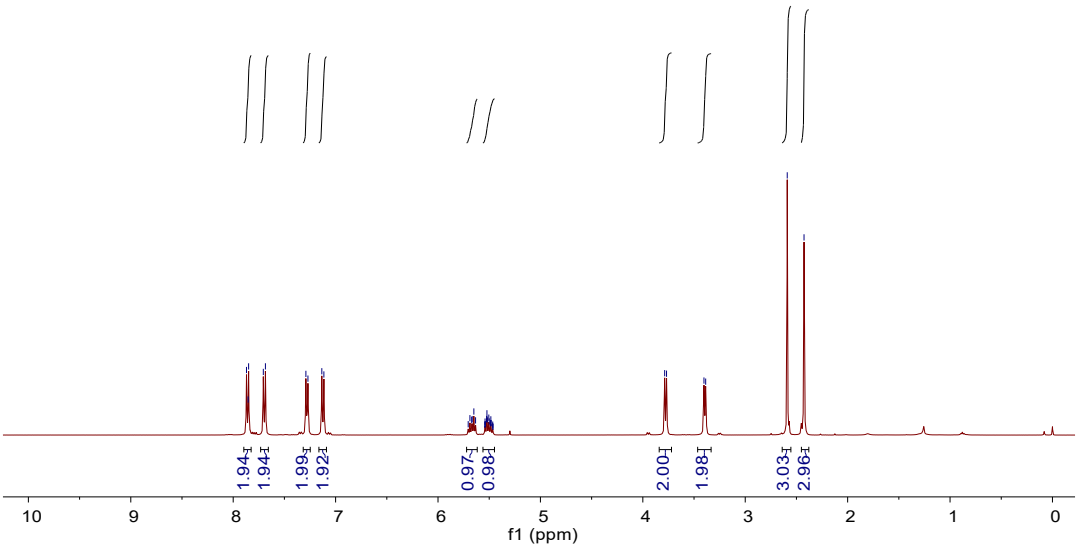
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

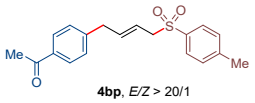
4bo, *E*/*Z* > 20/1

A1597-LYA-4-82A.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 11



A0600-LYA-4-61A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 18

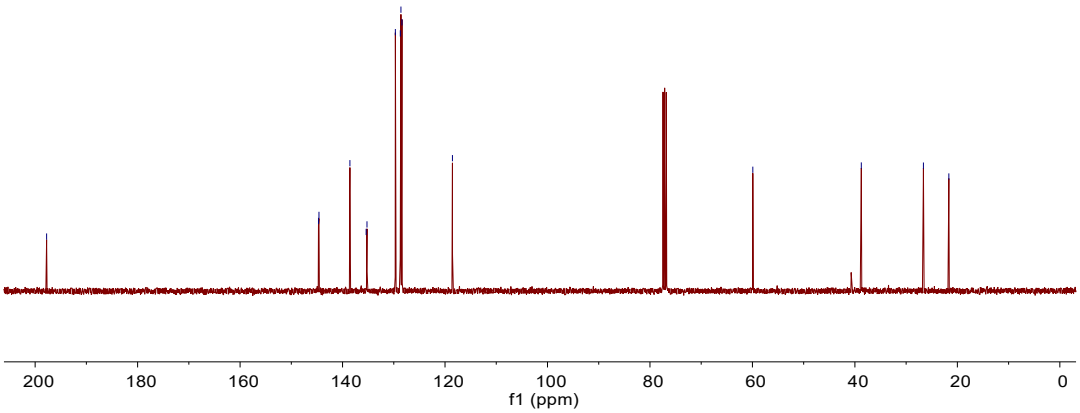




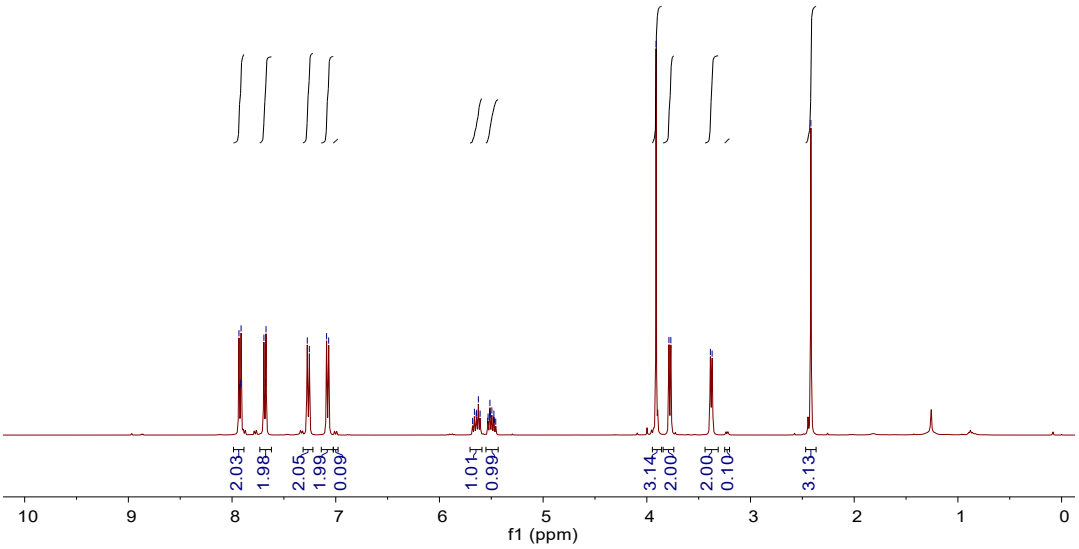
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

4bp, *E/Z* > 20/1

A0438-LYA-4-61A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 9



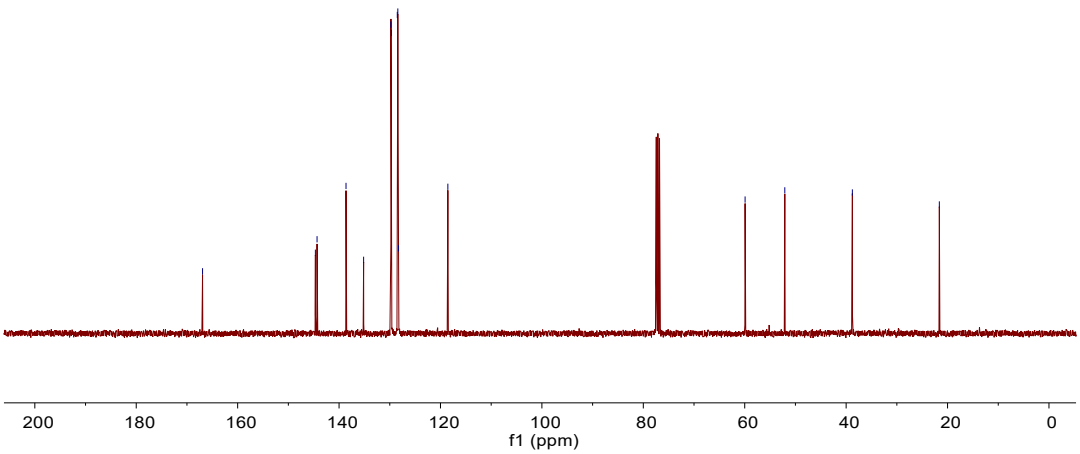
A0437-LYA-4-56C2.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 11



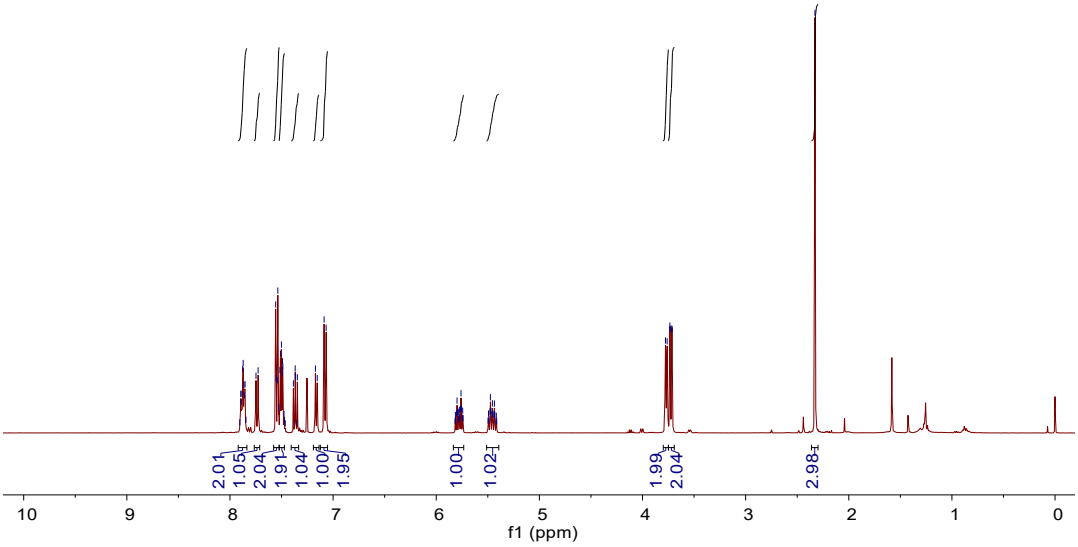
4bq, *E*/*Z* = 20/1

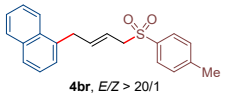
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A0306-LYA-4-56C2.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 53



A2597-LYA-5-81B2.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 52

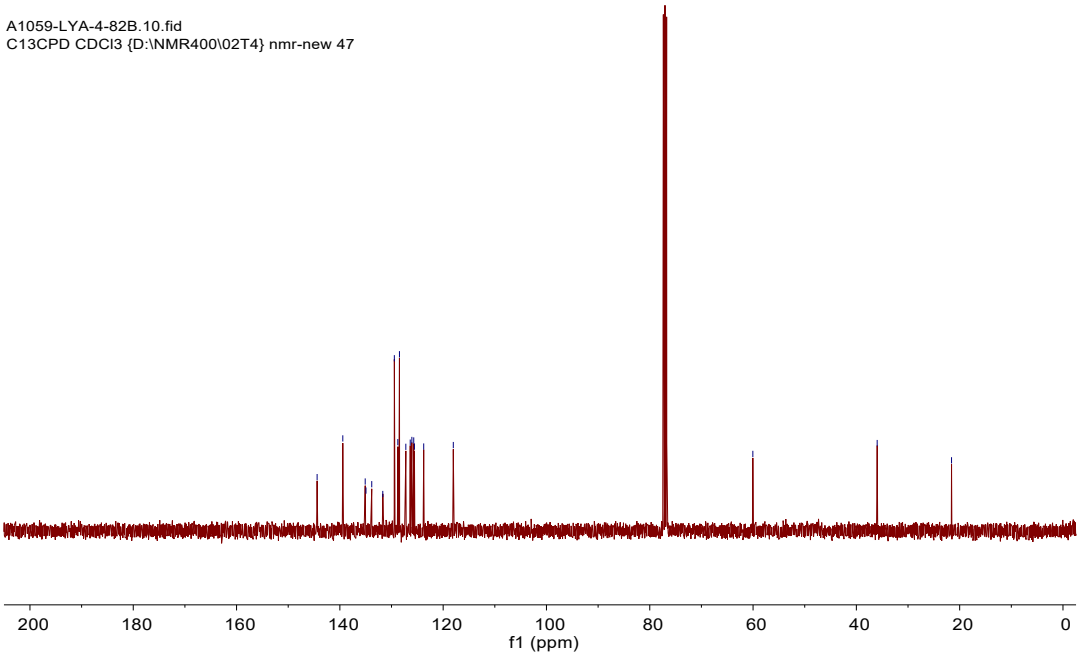




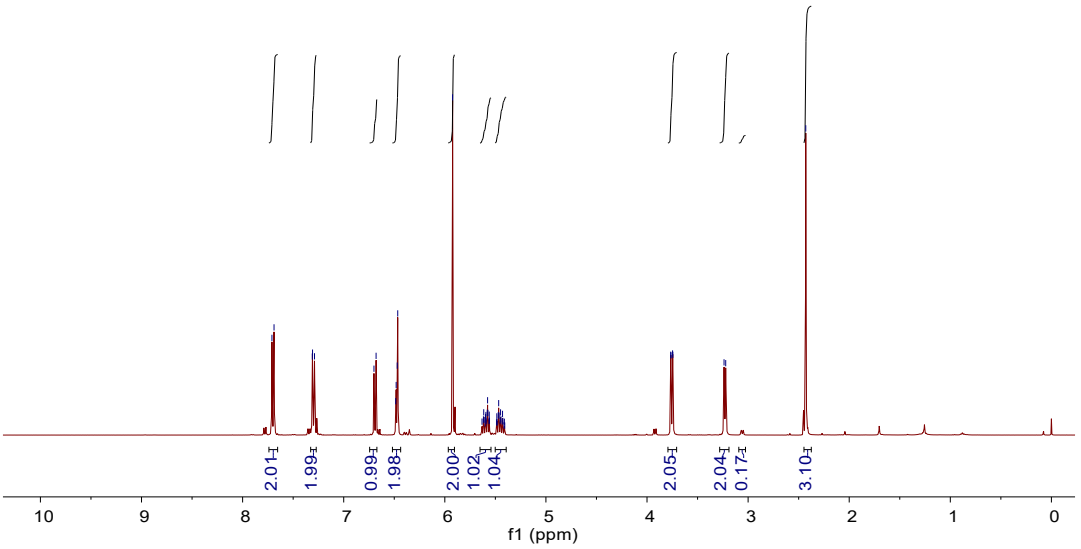
4br, *E*/*Z* > 20/1

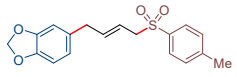
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A1059-LYA-4-82B.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 47



A0600-LYA-4-57C2.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 17



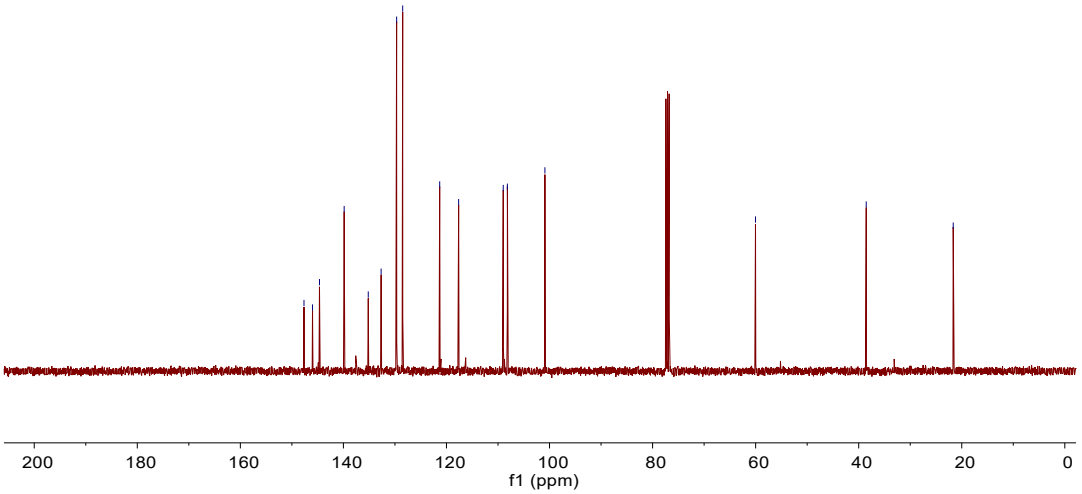


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

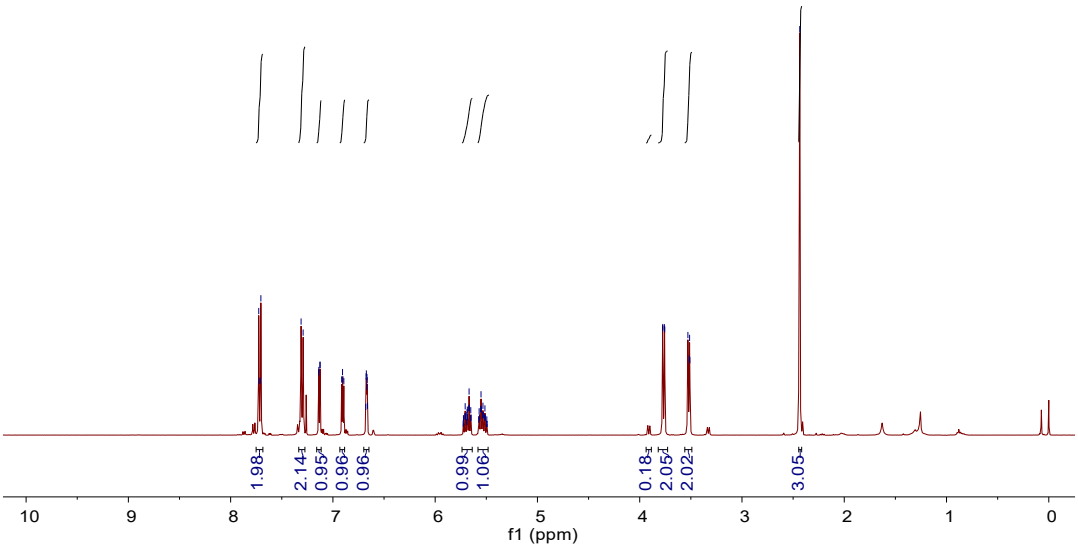
4bs, *E*/*Z* = 13/1

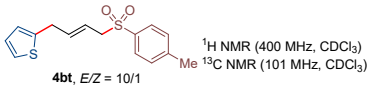
147.65
146.00
144.64
139.85
135.18
132.68
129.67
128.50
121.31
117.64
108.98
108.18
100.90
60.03
38.54
21.66

A0600-LYA-4-57C2.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 17



A1064-LYA-4-82C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 45



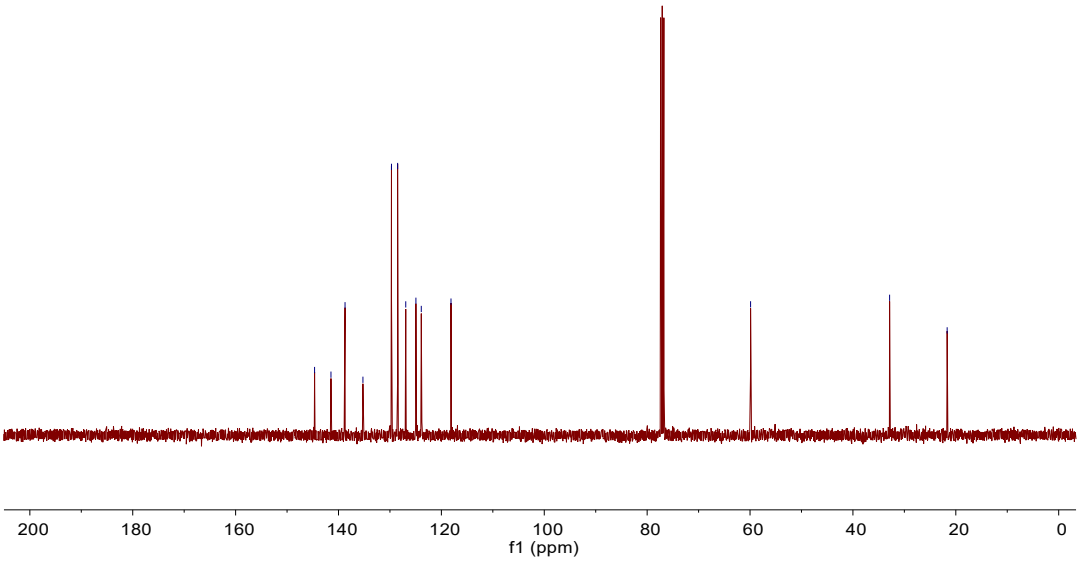


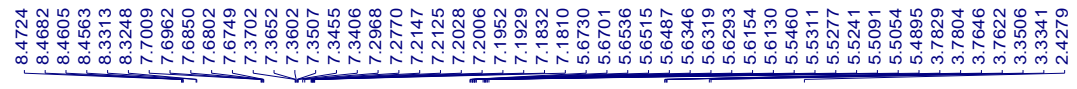
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

4bt, *E*/*Z* = 10/1

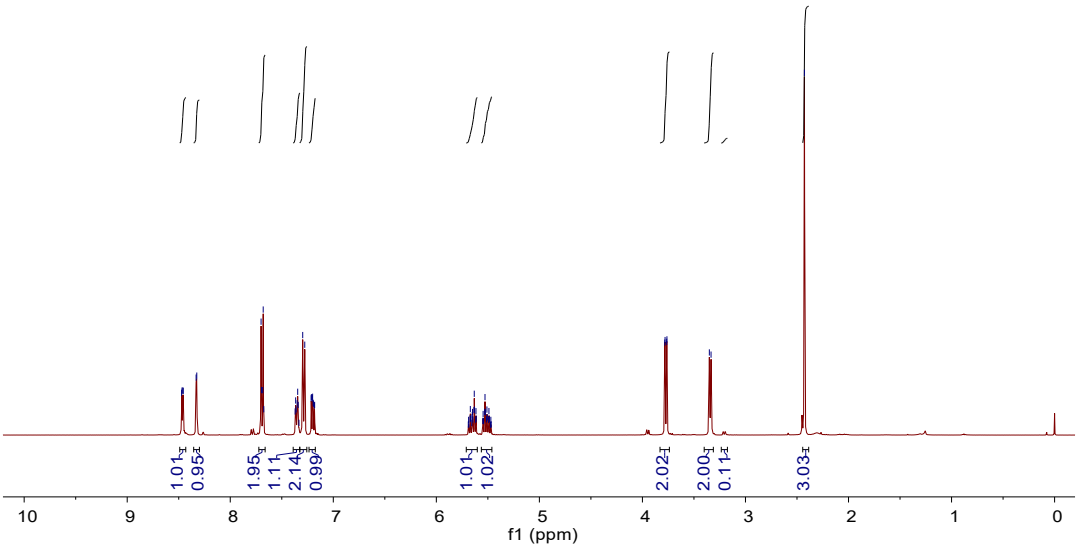
144.65
141.47
138.73
135.25
129.70
128.51
126.93
124.95
123.91
118.13
59.89
32.87
21.68

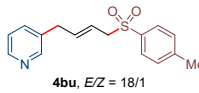
A1126-LYA-4-82C.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 1





A1059-LYA-4-89B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 46

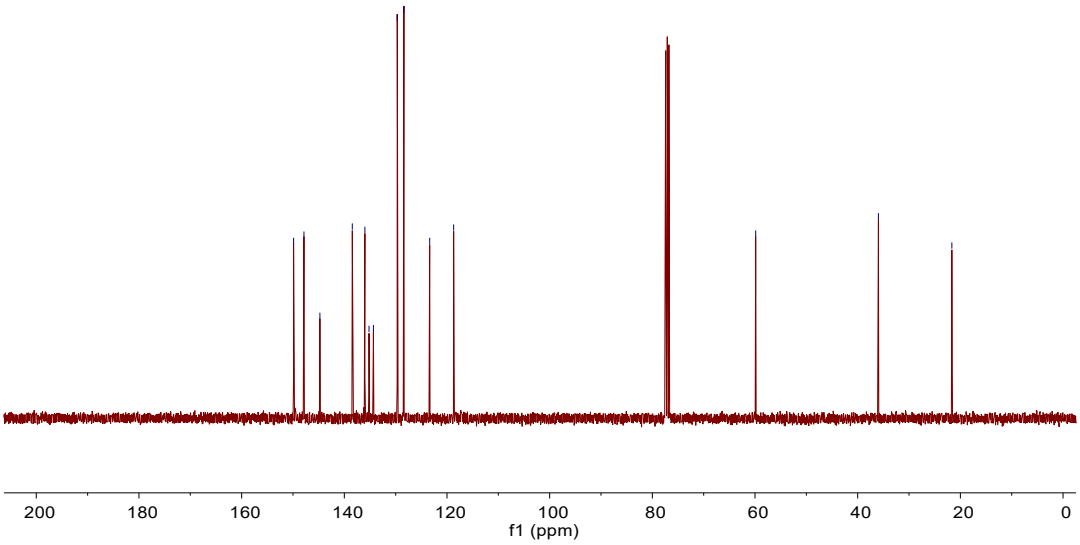




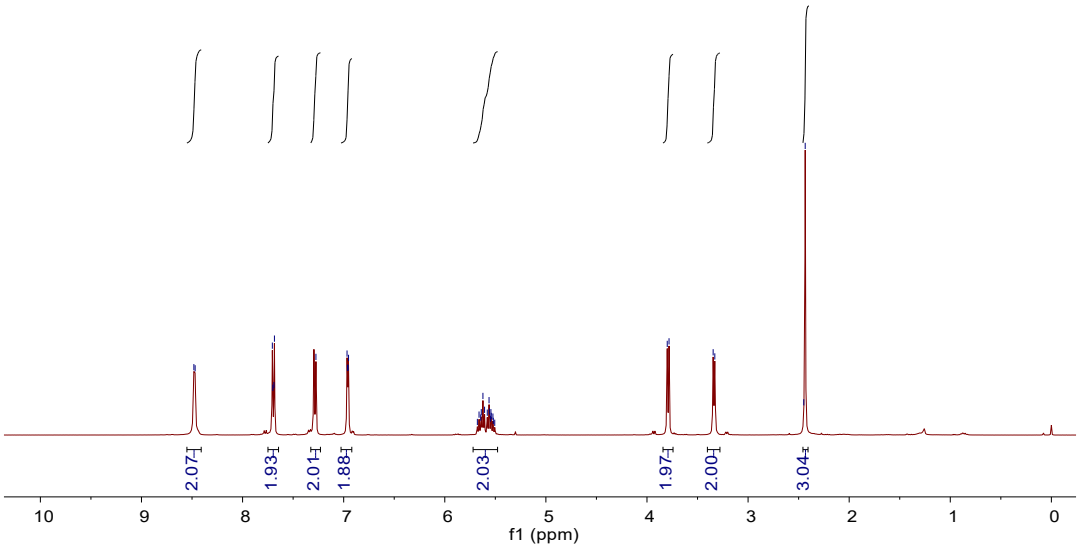
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

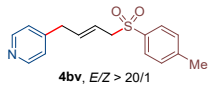
4bu, *E*/*Z* = 18/1

A1059-LYA-4-89B.20.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 46



A1059-LYA-4-89C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 43



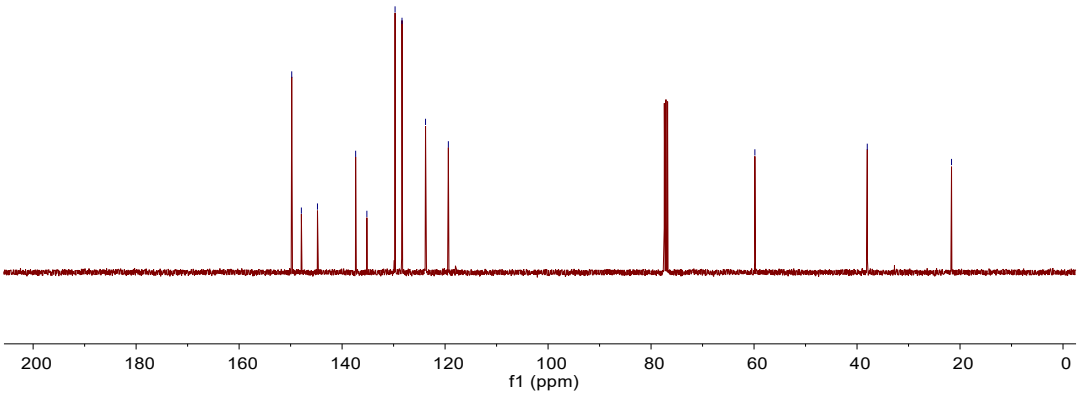


4bv, *E*/*Z* > 20/1

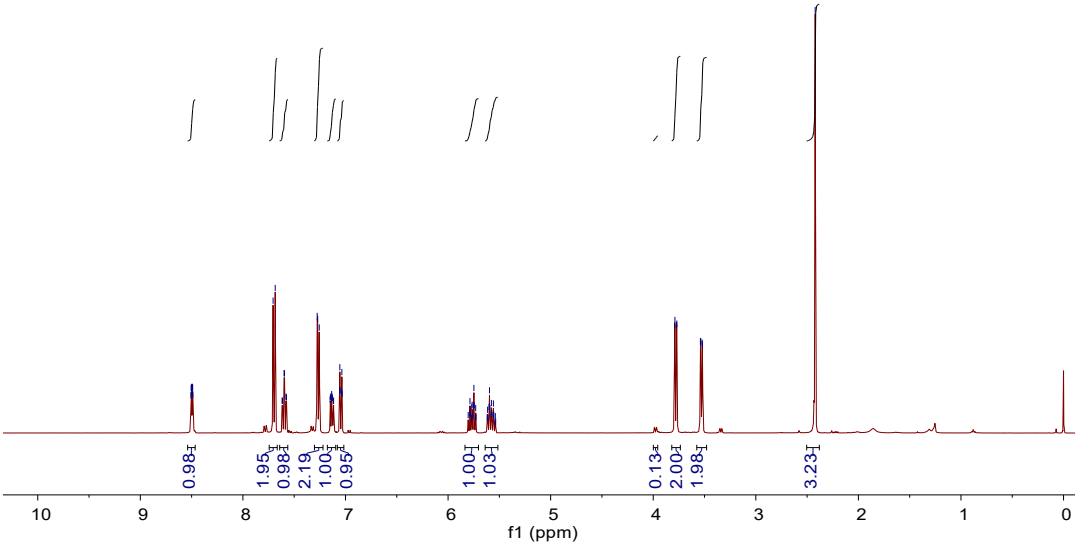
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

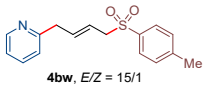
149.78
147.91
144.78
137.37
135.19
129.71
128.37
123.80
119.36
59.84
38.01
21.65

A1126-LYA-4-89C.10.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 2



A1059-LYA-4-89A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 42



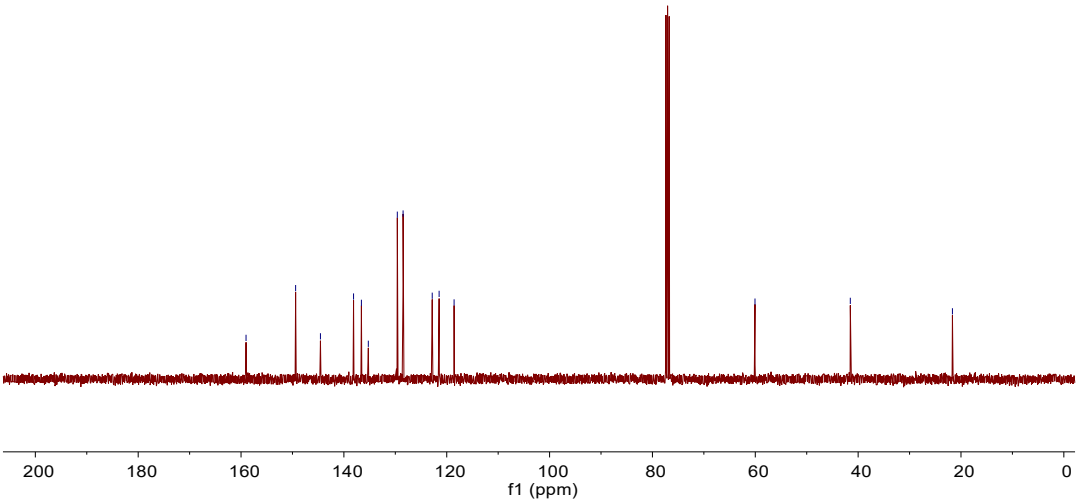


4bw, *E*/*Z* = 15/1

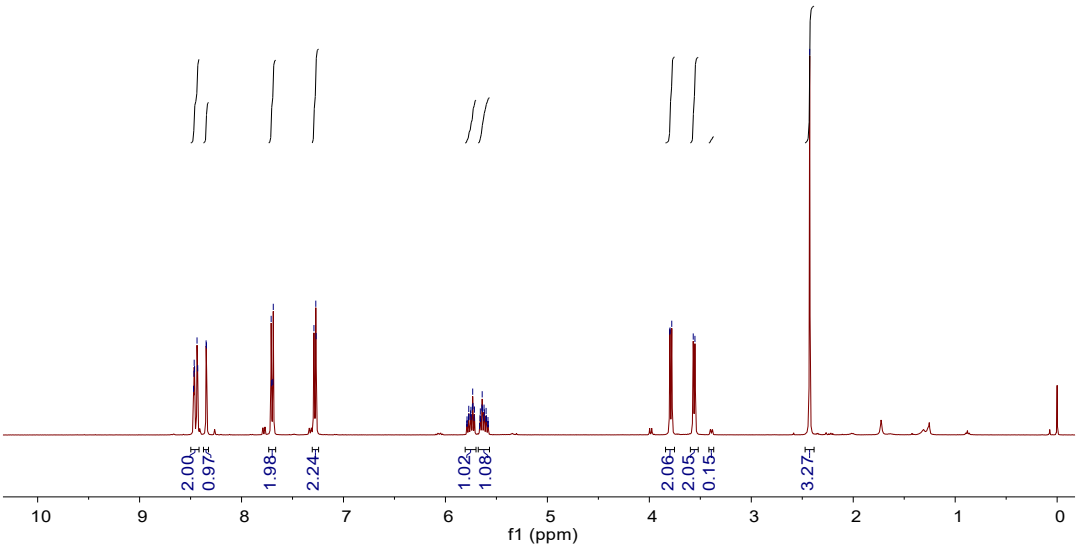
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

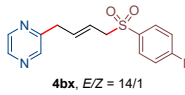
159.03
149.39
144.56
138.12
136.59
135.25
129.61
128.49
122.82
121.48
118.57
60.06
41.52
21.66

A1059-LYA-4-89A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 42



A1398-LYA-4-101B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 44

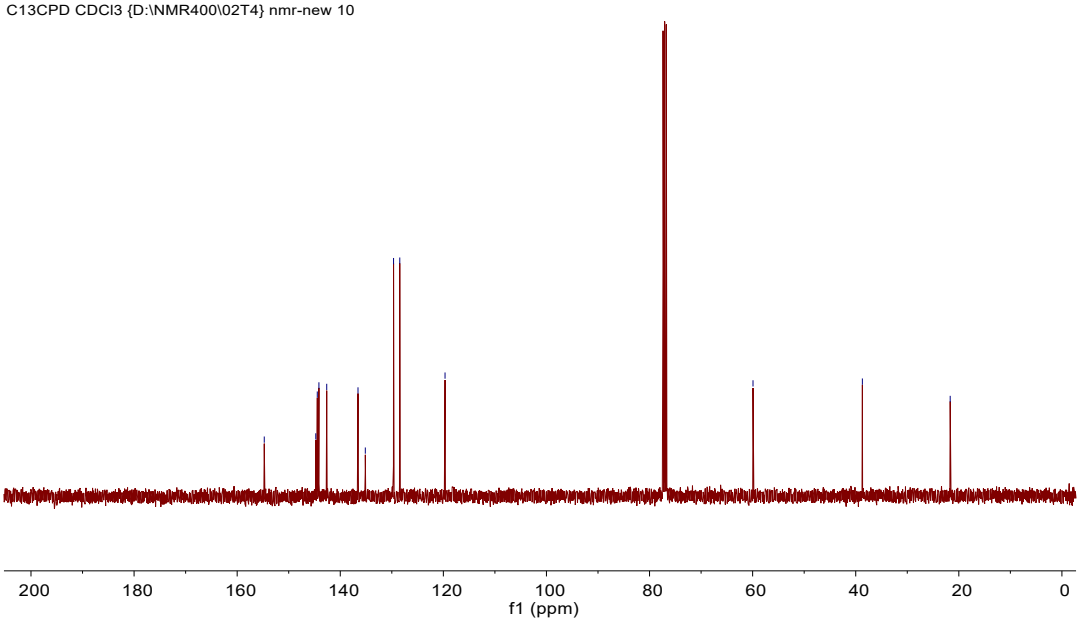




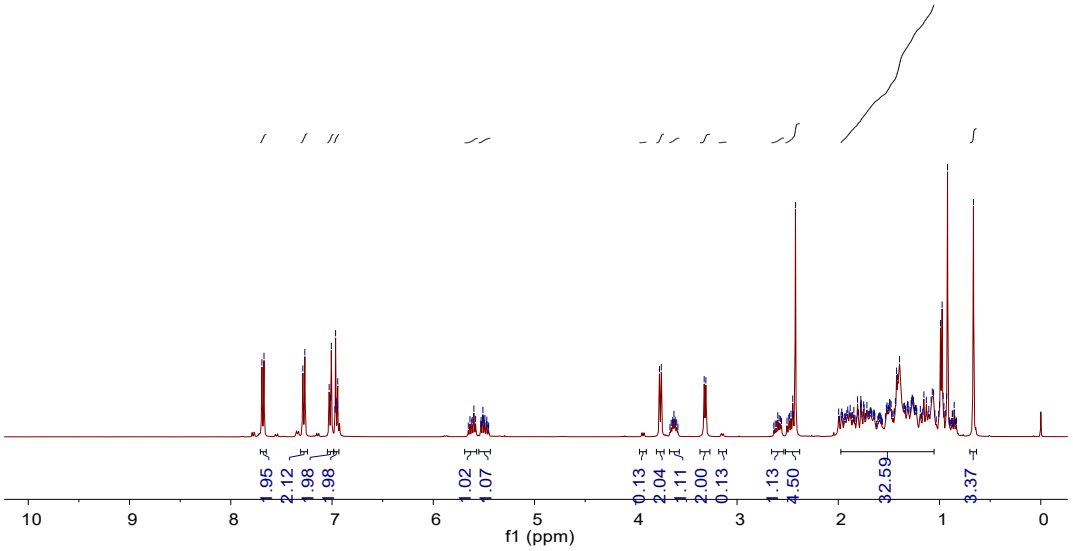
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

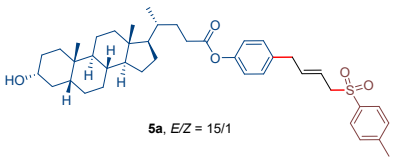
4bx, *E*/*Z* = 14/1

A1262-LYA-4-101B.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 10



A3306-LYA-6-15B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 16

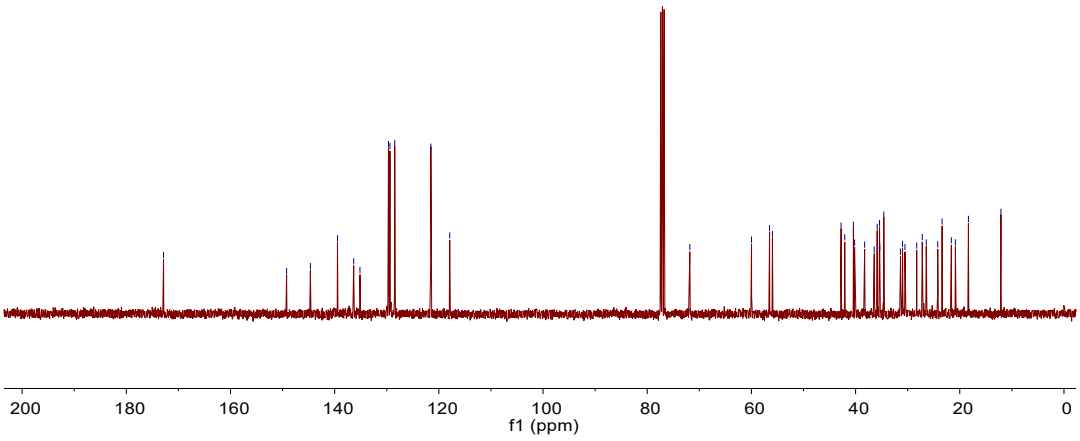




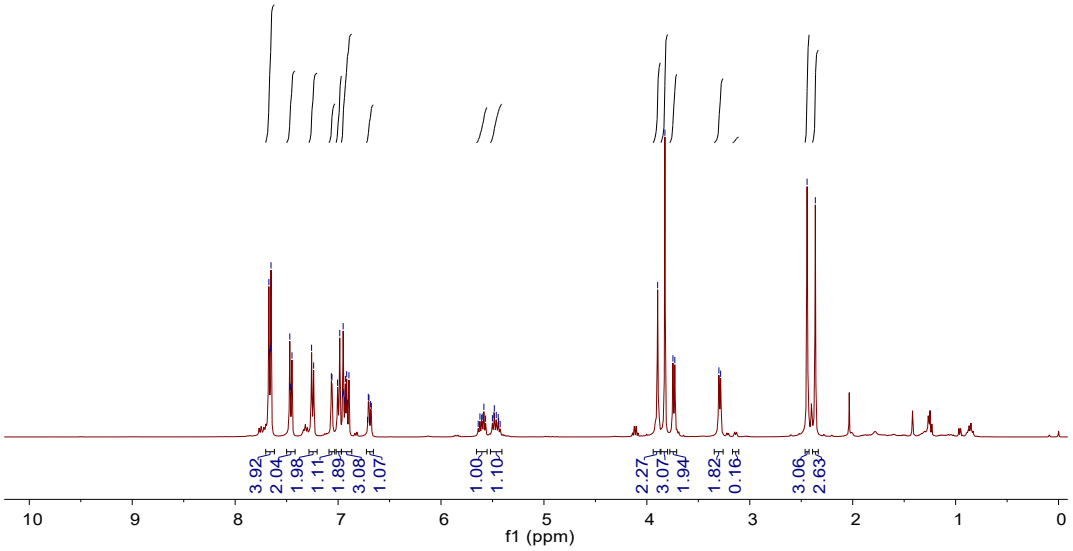
5a, *E*/*Z* = 15/1

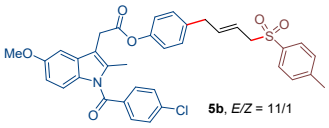
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A3306-LYA-6-15B.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 16



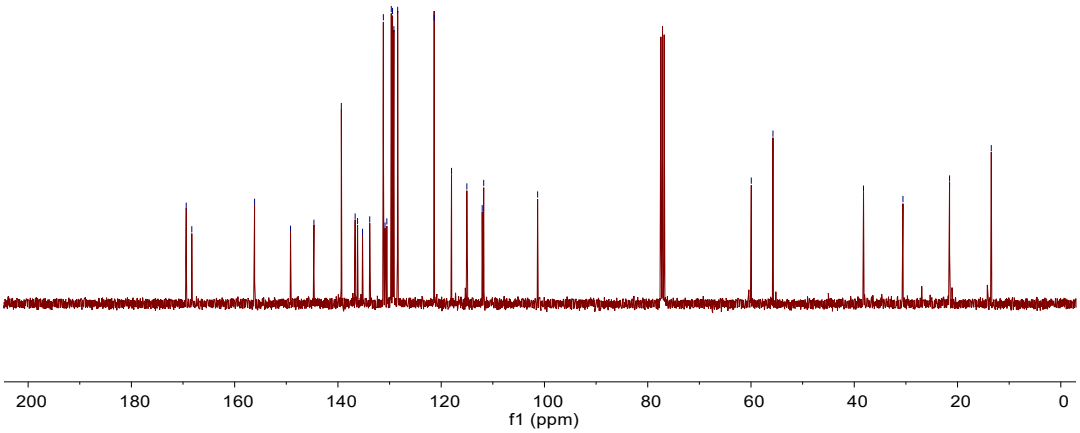
A2921-LYA-5-91.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 48



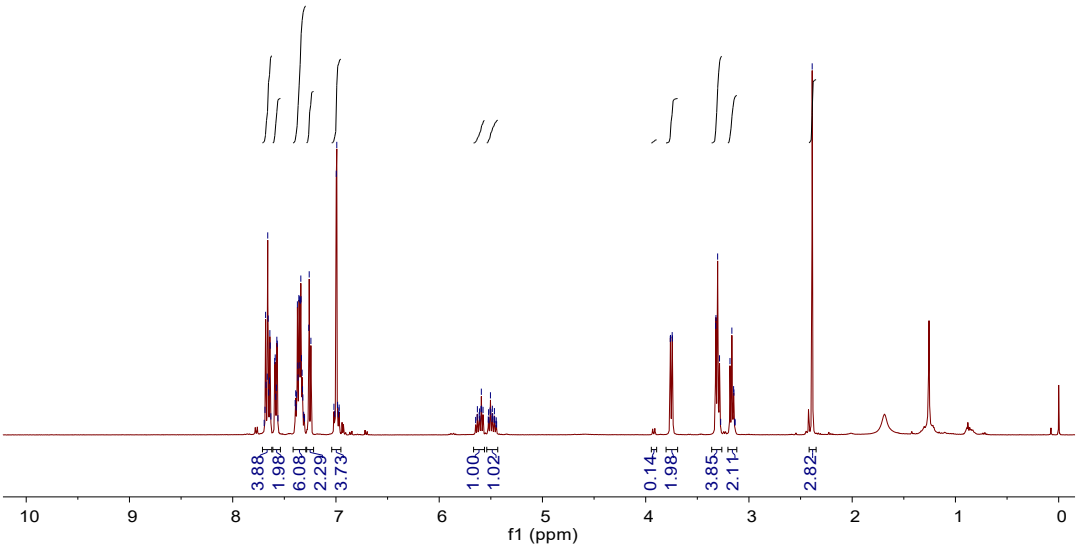


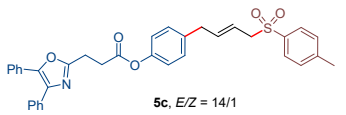
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A2921-LYA-5-91.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 48



A5003-LYA-7C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 19

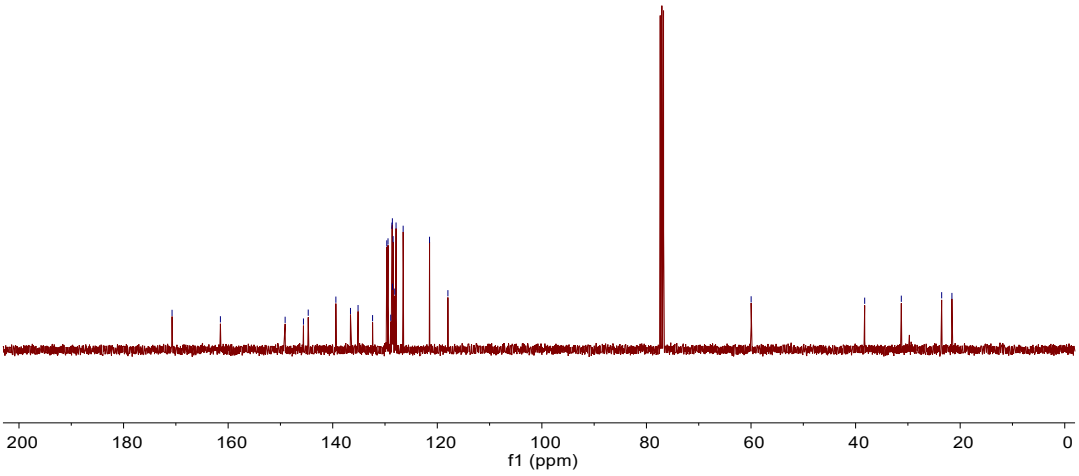


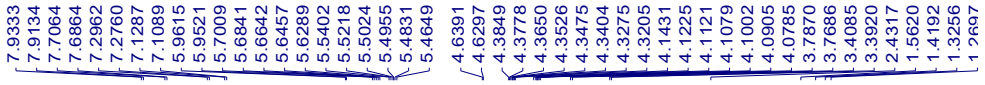


5c, *E*/*Z* = 14/1

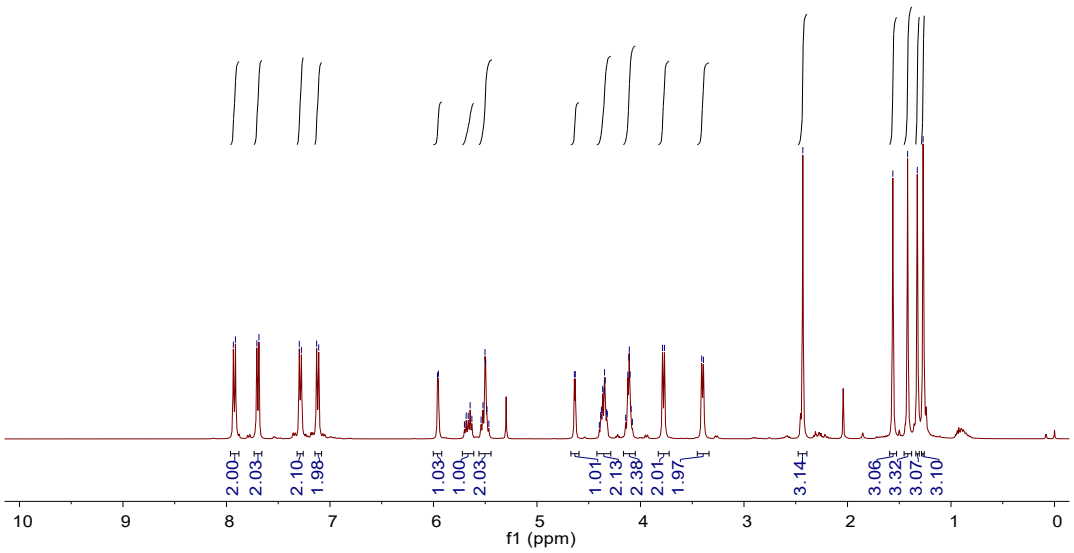
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

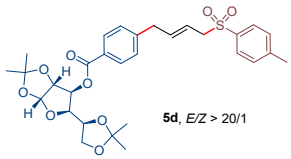
A5003-LYA-7C.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 19





A1453-LYA-5-9.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 11

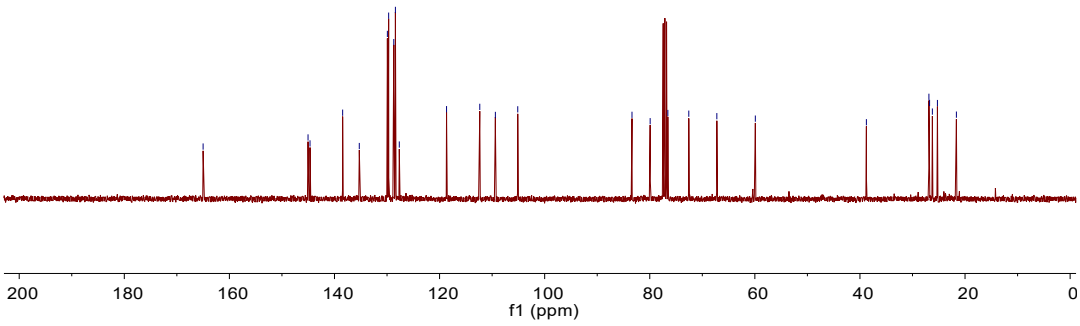




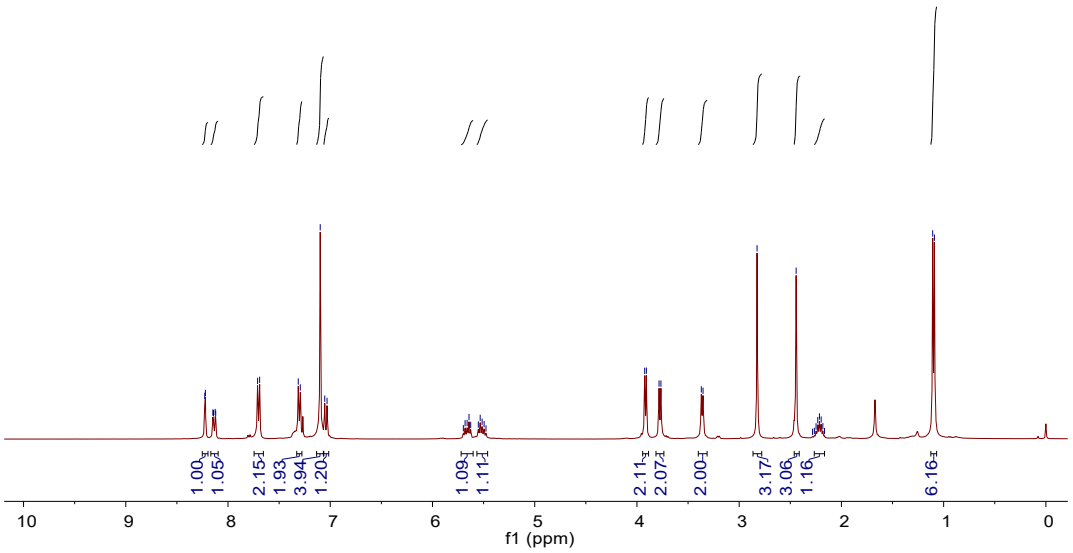
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

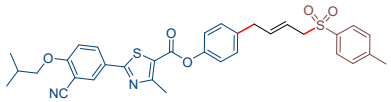
5d, *E*/*Z* > 20/1

A1453-LYA-5-9.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 11



A3206-LYA-6-4.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 36

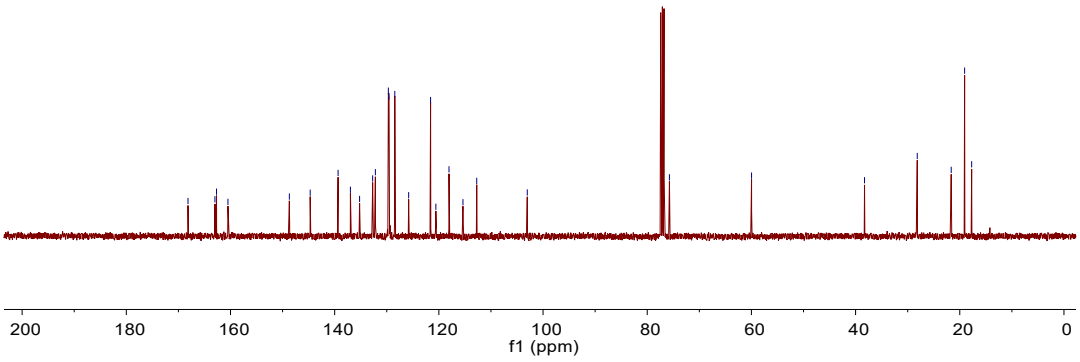


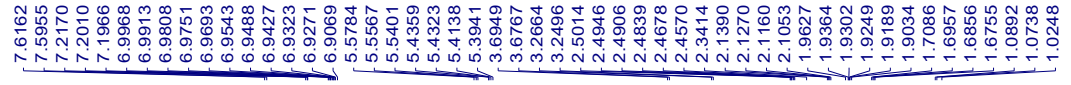


^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

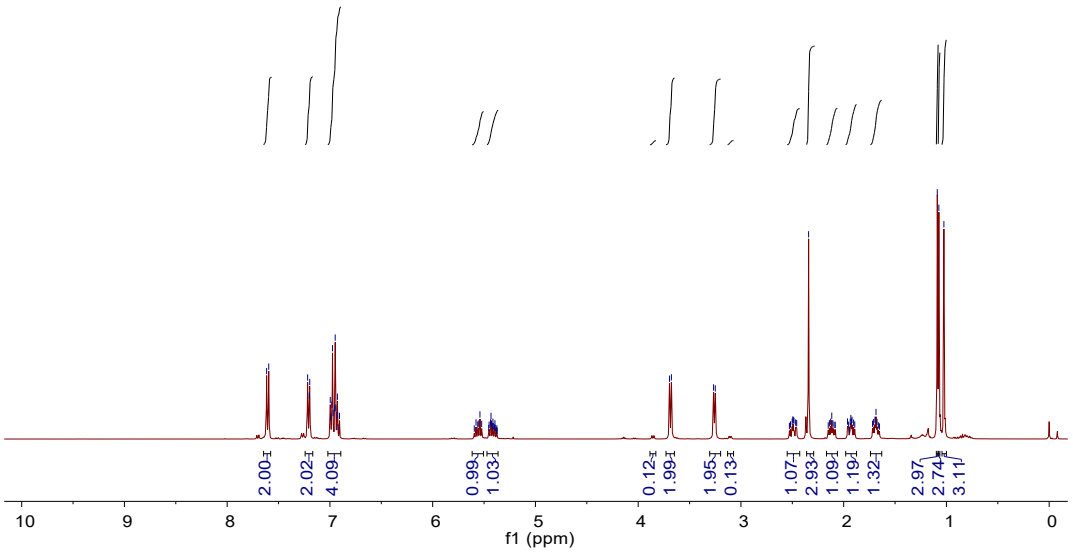
5e, *E*/*Z* = 15/1

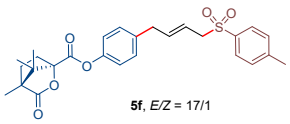
A3204-LYA-6-4.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 25





A3306-LYA-6-21.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 17



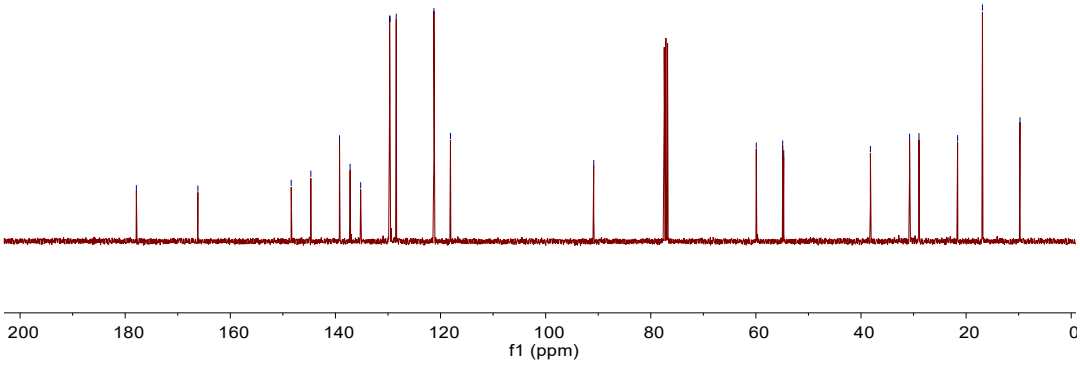


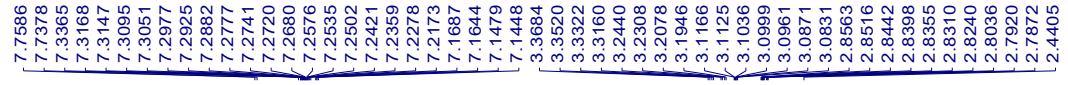
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

5f, *E*/*Z* = 17/1

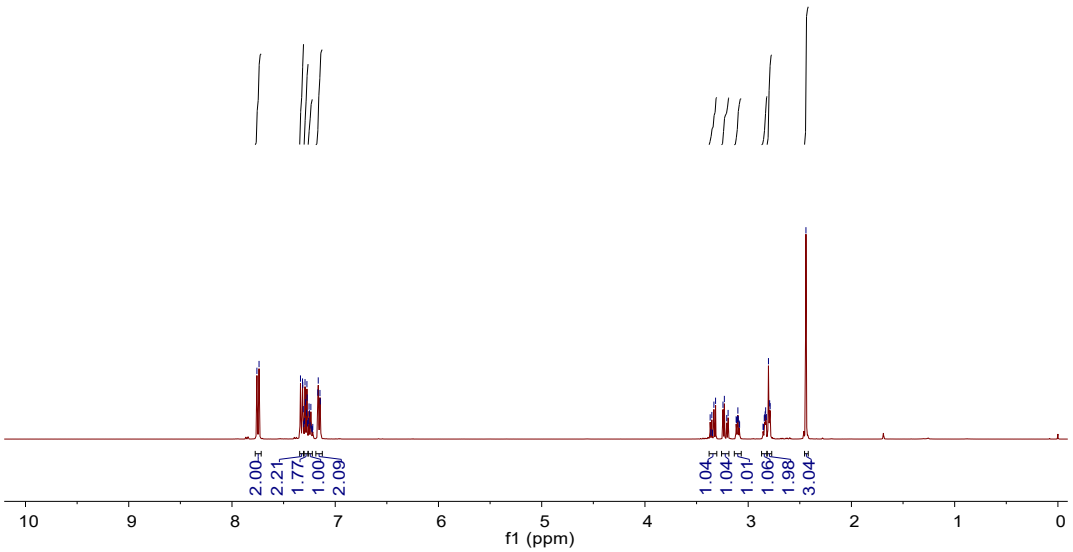
177.87
166.17
148.41
144.68
139.22
137.21
135.20
129.68
129.61
128.43
121.26
118.11
90.85
59.93
54.90
54.70
38.21
30.76
28.97
21.62
16.89
9.75

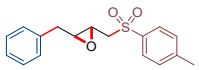
A3306-LYA-6-21.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 17





A1586-LYA-5-29.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 32



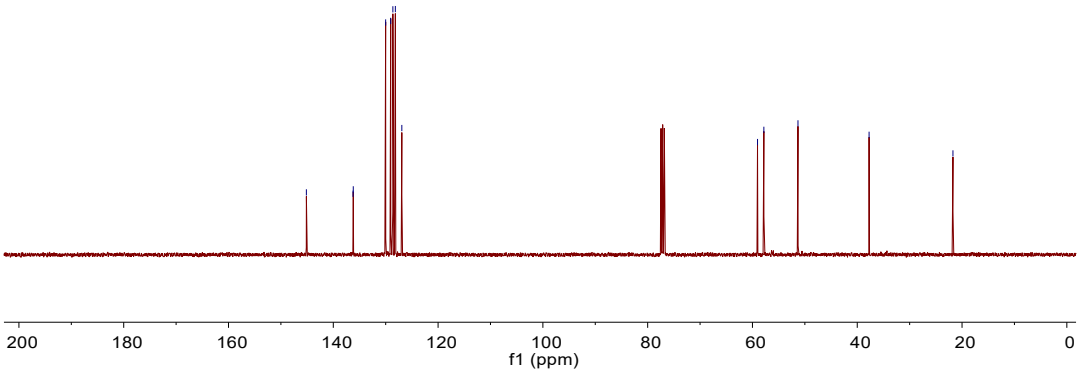


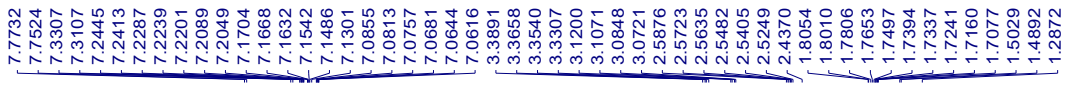
6a

^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

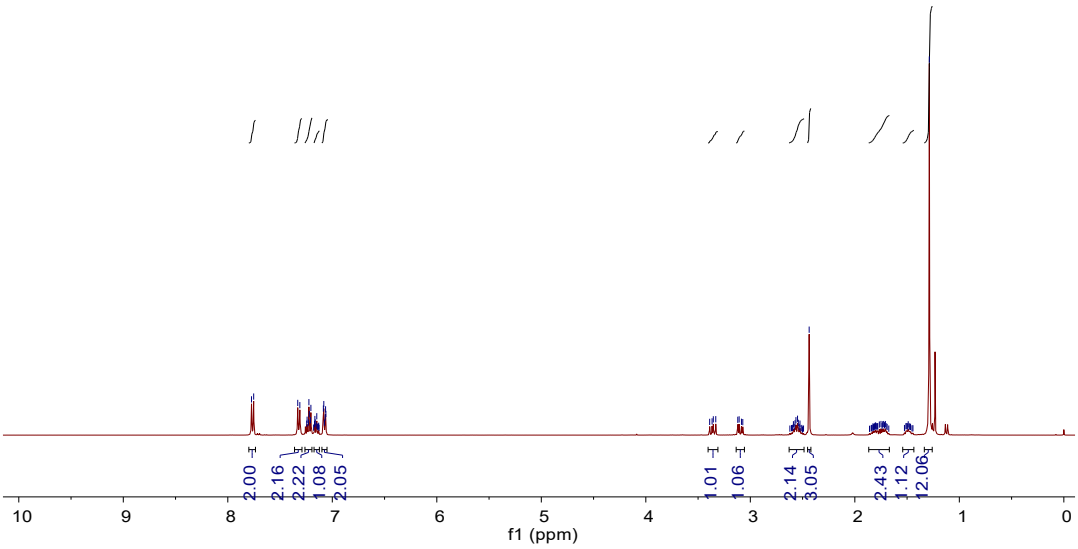
145.14
136.23
136.19
130.01
129.04
128.63
128.16
126.92
59.03
57.82
51.31
37.74
21.74

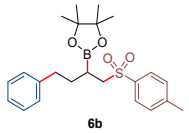
A1586-LYA-5-29.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 32





A1586-LYA-5-31.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 31

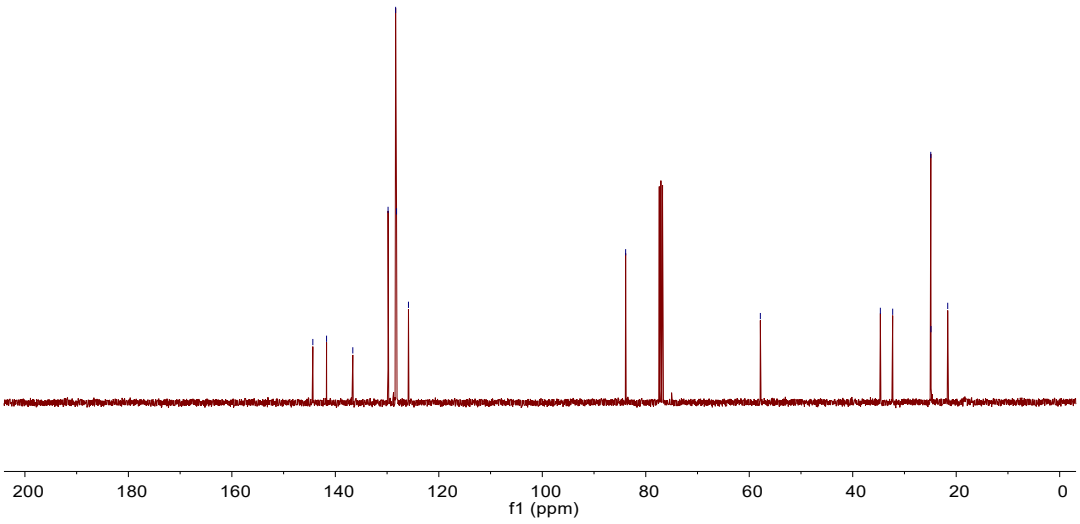




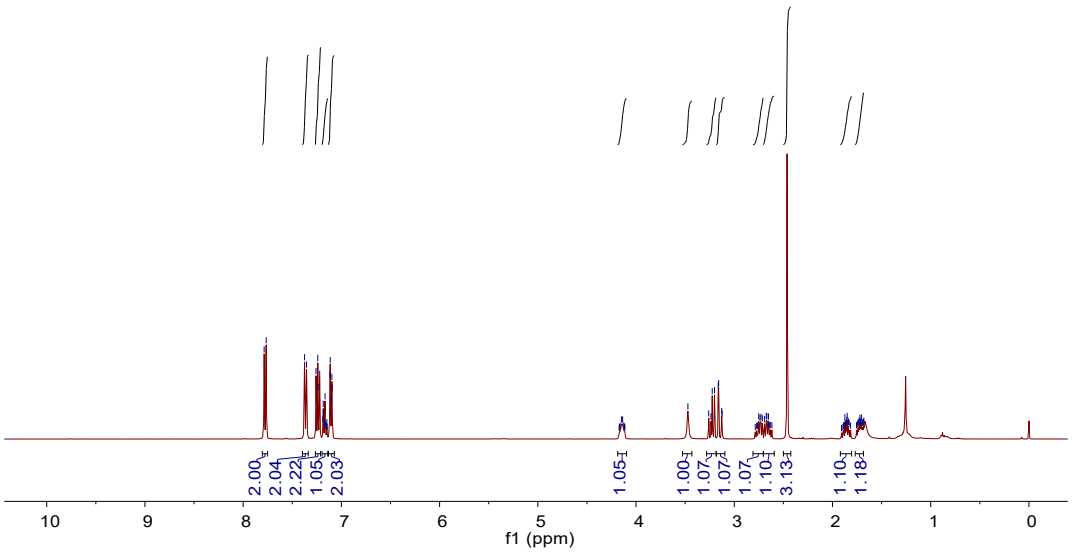
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

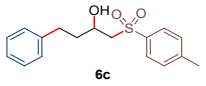
144.35
141.70
136.63
129.81
128.35
128.17
125.87
83.89
57.85
34.66
32.28
24.92
24.88
21.64

A1586-LYA-5-31.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 31



A4853-LYA-5-37.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 21



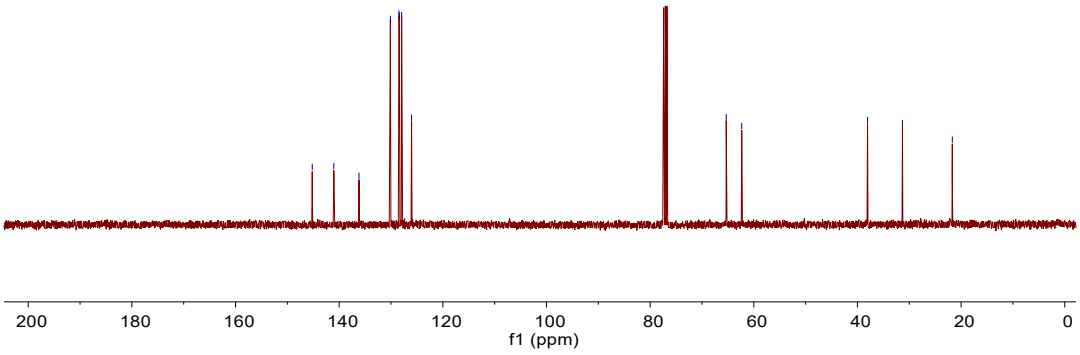


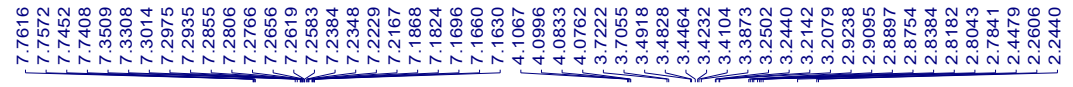
6c

^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

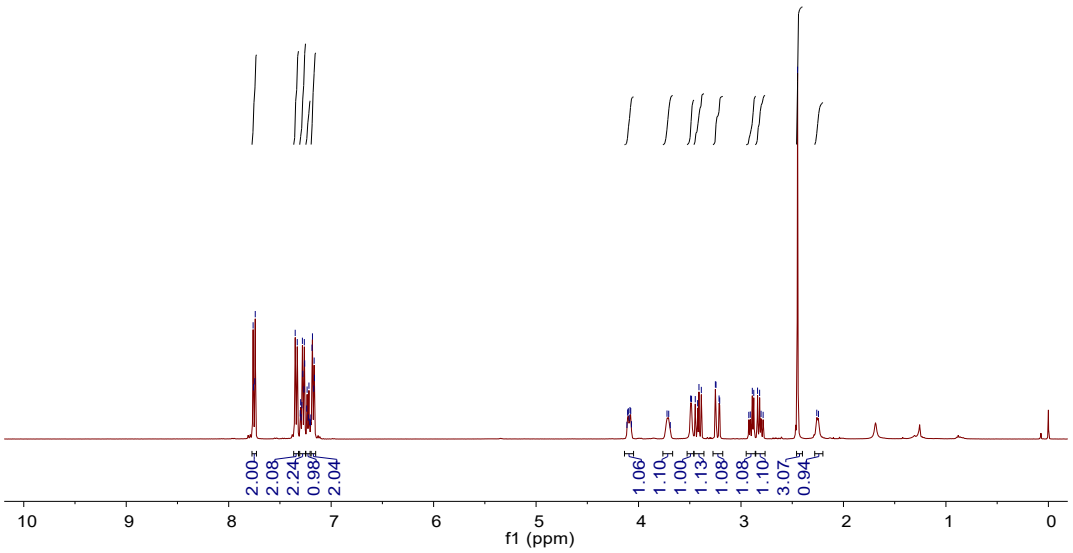
145.20
141.04
136.18
130.12
128.48
128.39
127.95
126.03
65.32
62.33
38.05
31.31
21.69

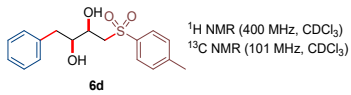
A1682-LYA-5-37-2.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 46





A2921-LYA-5-96C.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 47



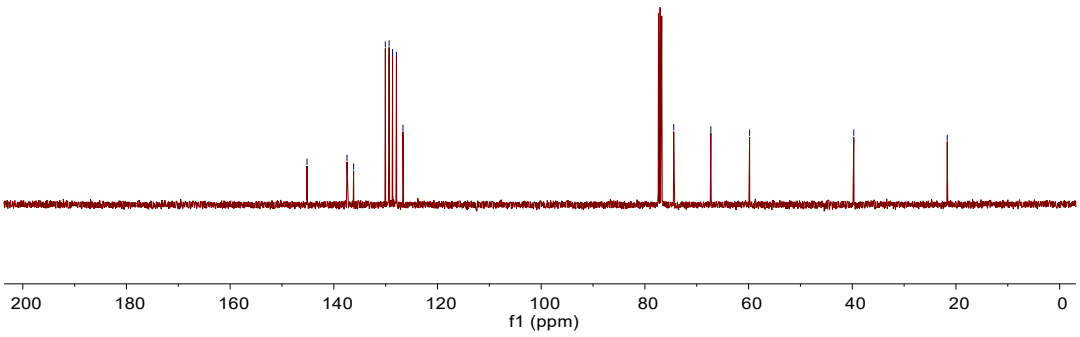


6d

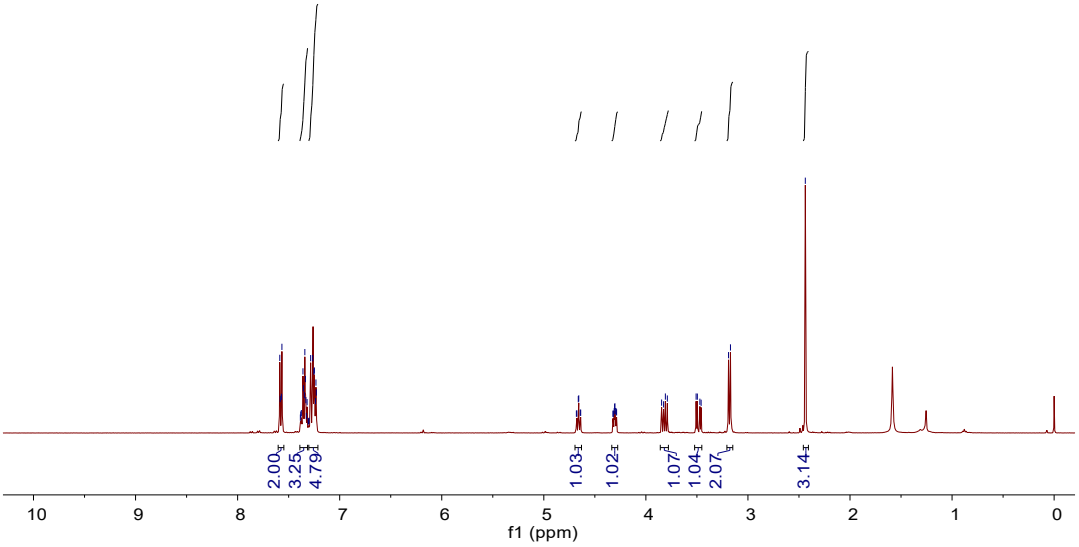
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

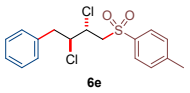
145.17
137.46
136.19
130.07
129.34
128.67
127.93
126.66
74.44
67.28
59.81
39.71
21.68

A1682-LYA-5-39.21.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 47



A4853-LYA-6-11A-1.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 22

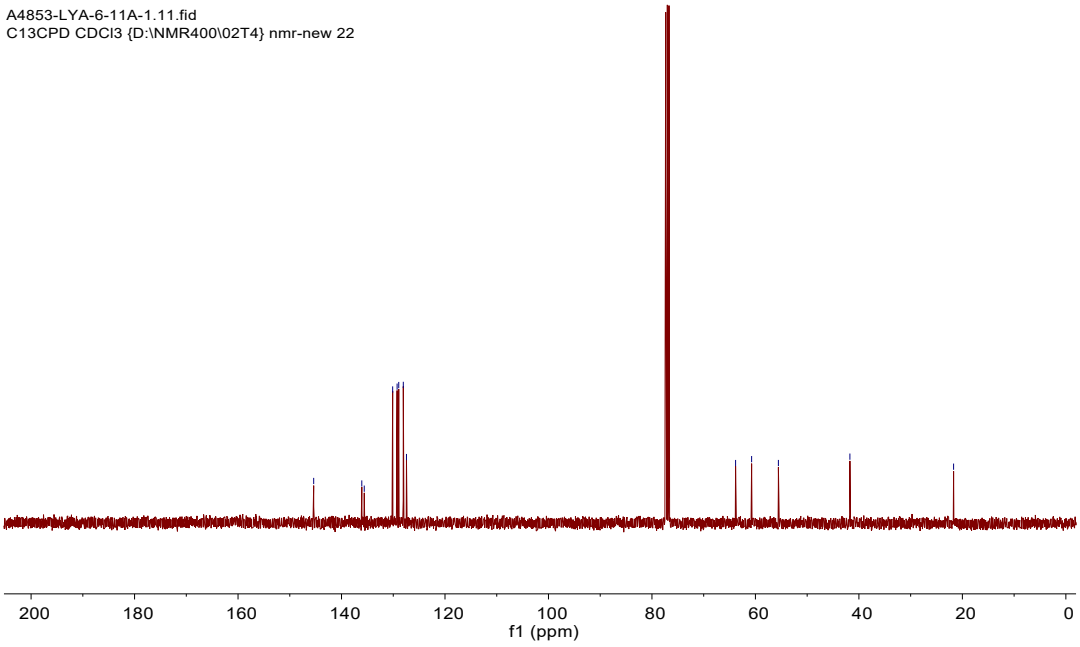




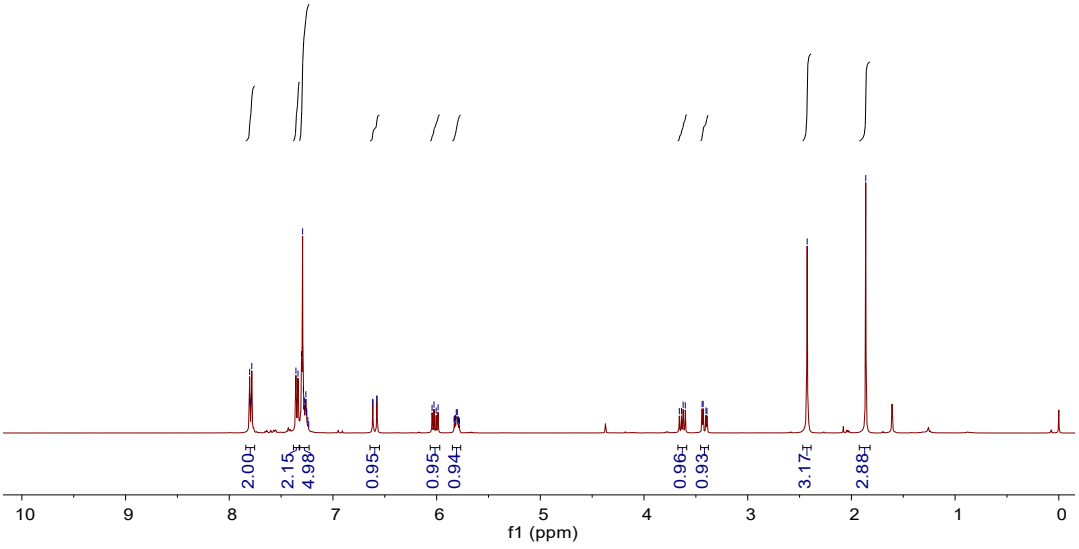
6e

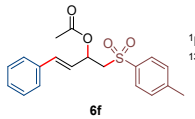
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A4853-LYA-6-11A-1.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 22



A1983-LYA-5-49A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 12

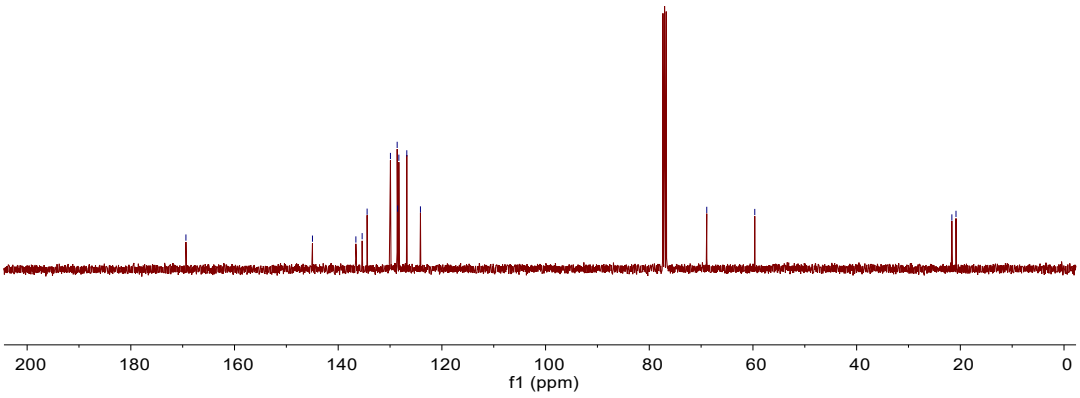




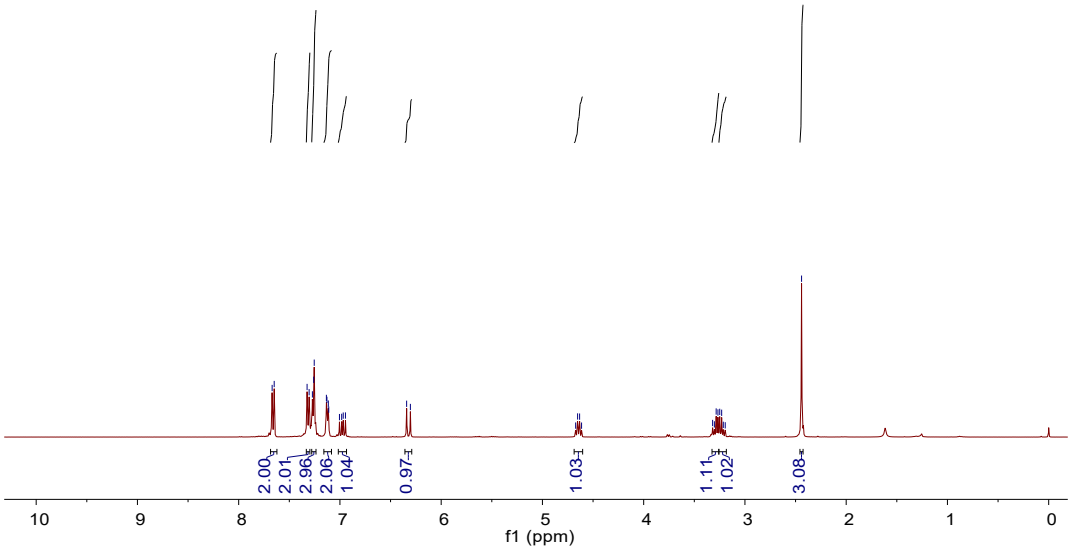
6f

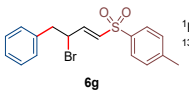
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

A1983-LYA-5-49A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 12



A3472-LYA-6-20B1.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 14

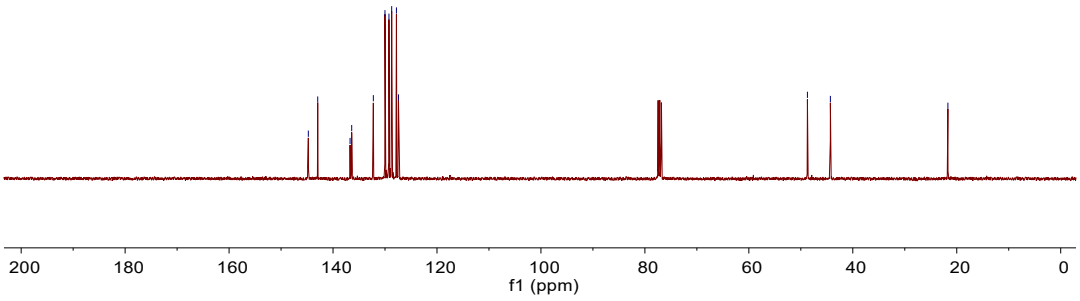




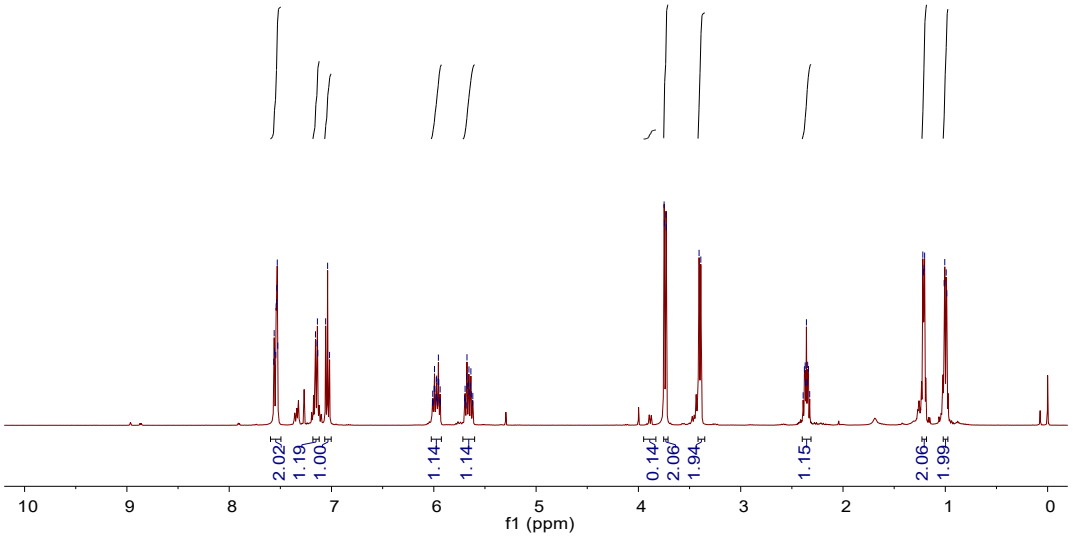
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

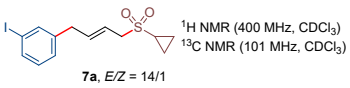
6g

A3083-LYA-5-98.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 10



A2268-LYA-5-64.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 19

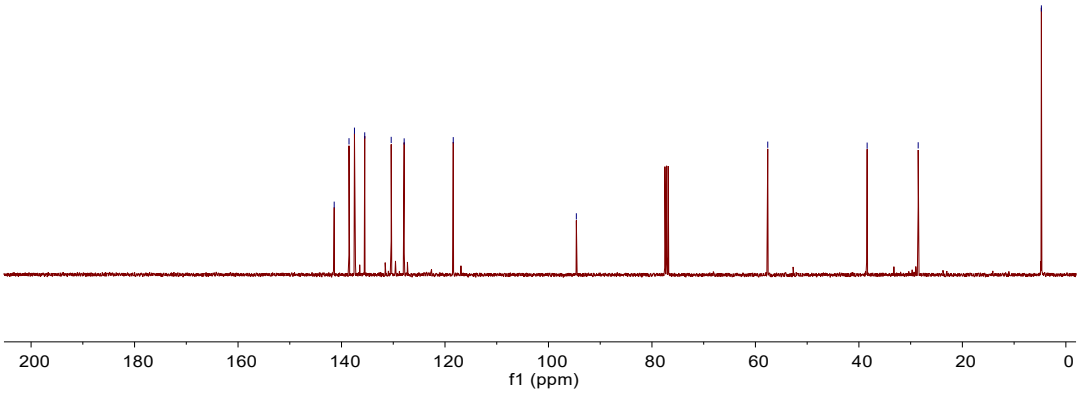




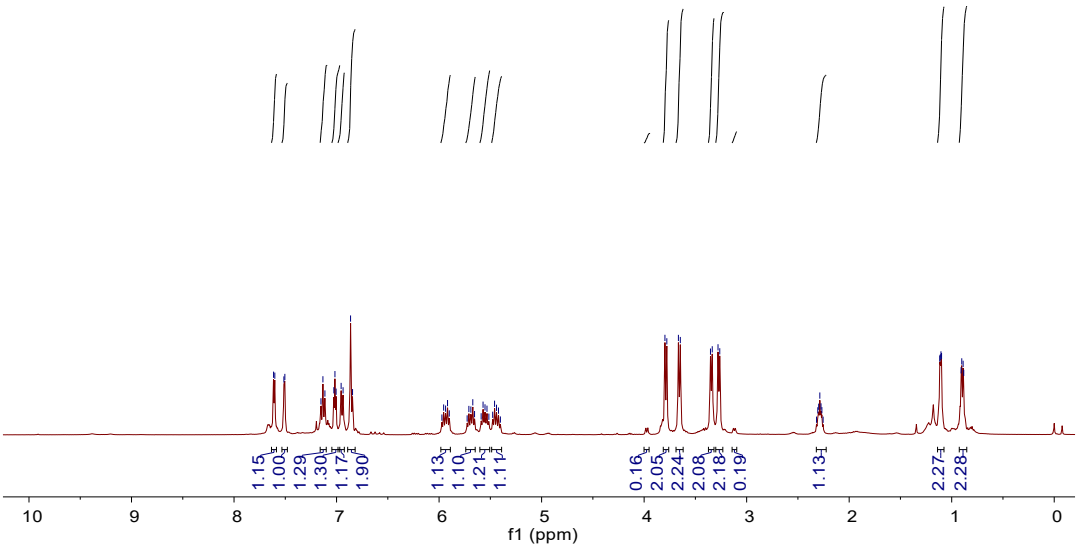
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

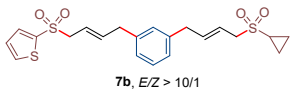
7a, *E*/*Z* = 14/1

A4939-LYA-6-78.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 5



A2578-LYA-5-75TM.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 14

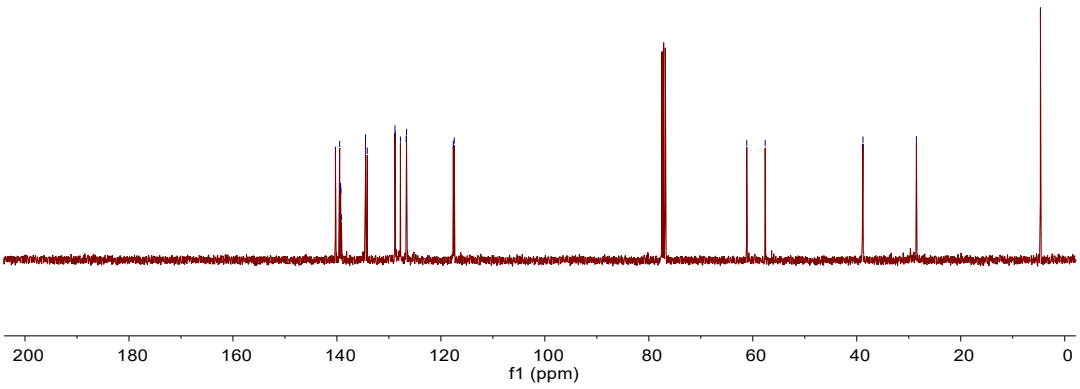


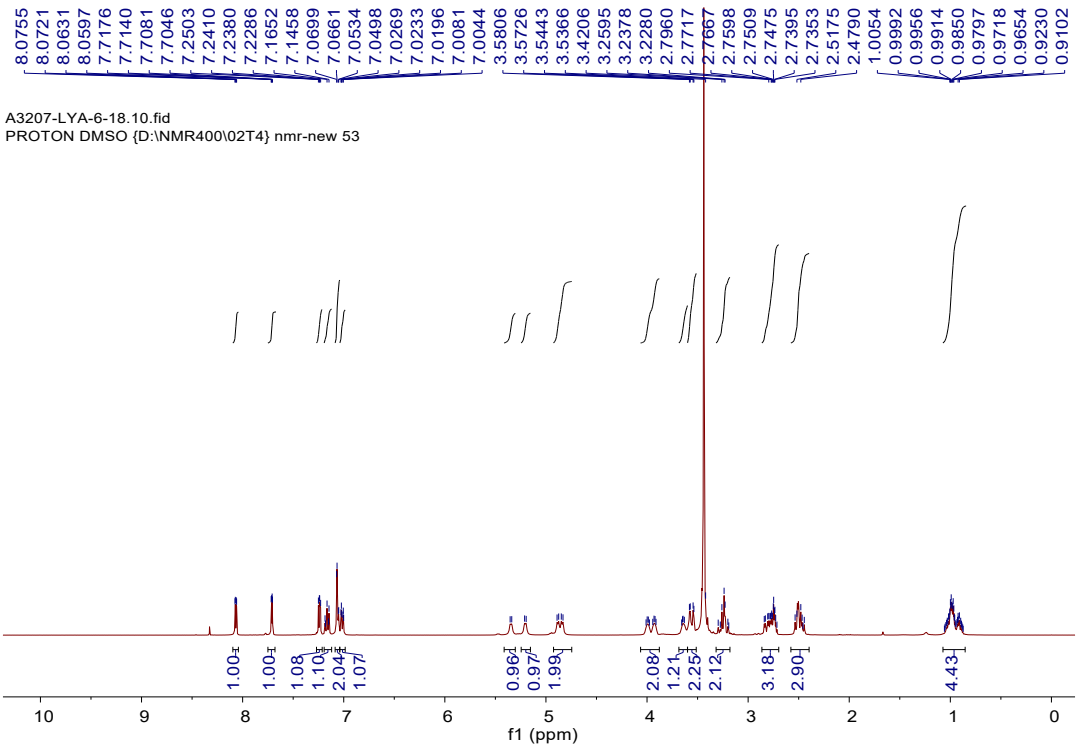


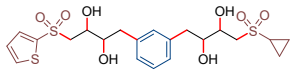
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

7b, *E*/*Z* > 10/1

A2578-LYA-5-75TM.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 14

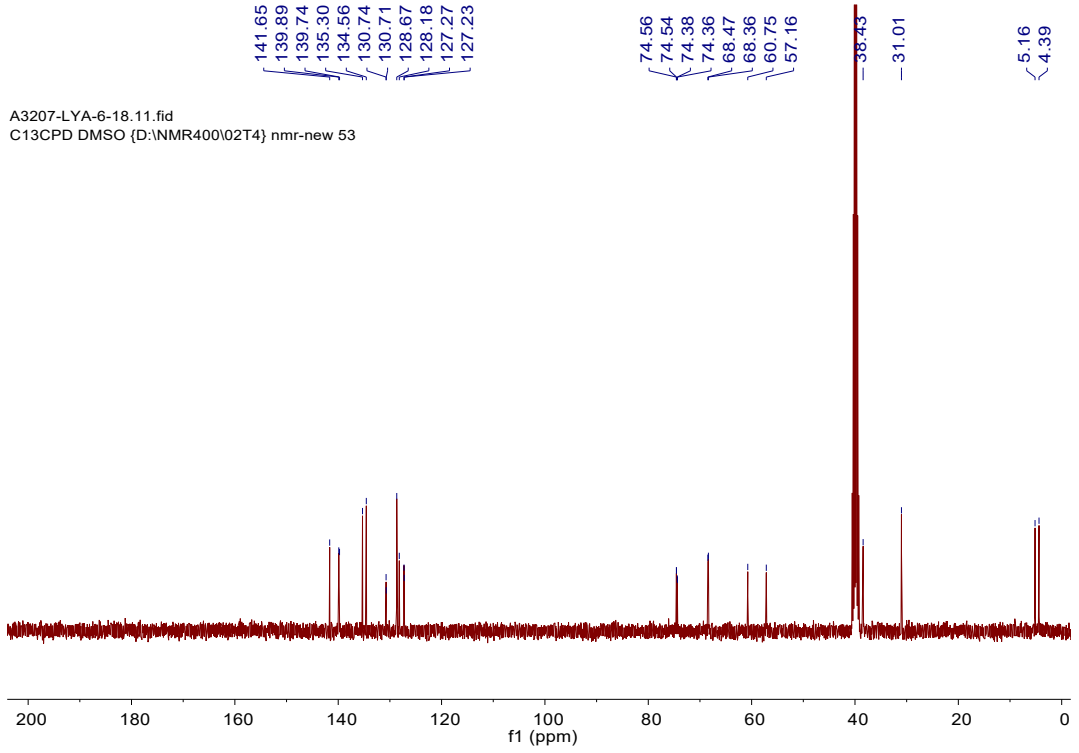




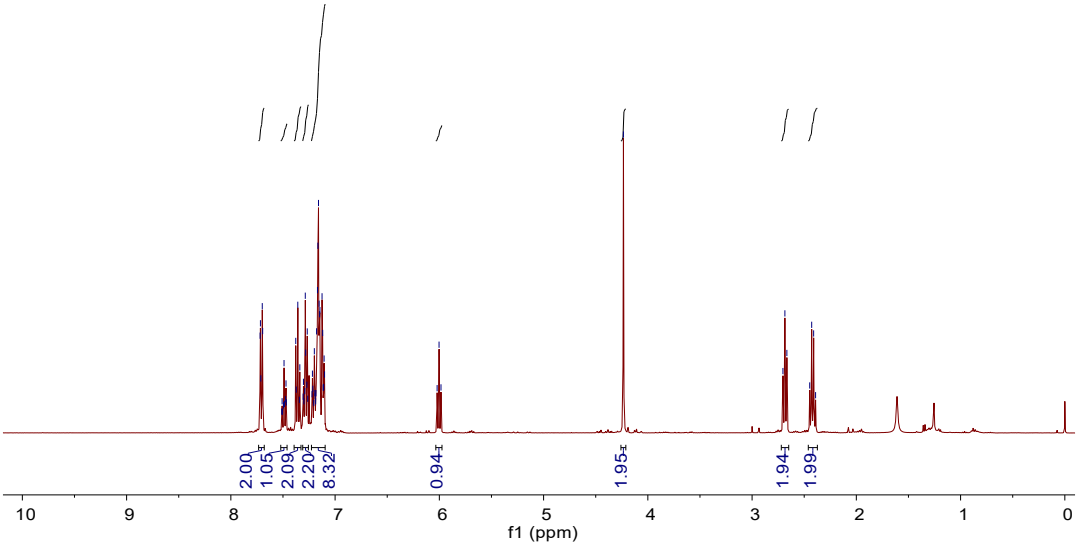


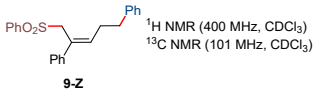
7c, *dr* = 1/1

^{1}H NMR (400 MHz, DMSO-d_6)
^{13}C NMR (101 MHz, DMSO-d_6)



A4558-LYA-5-28A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 25



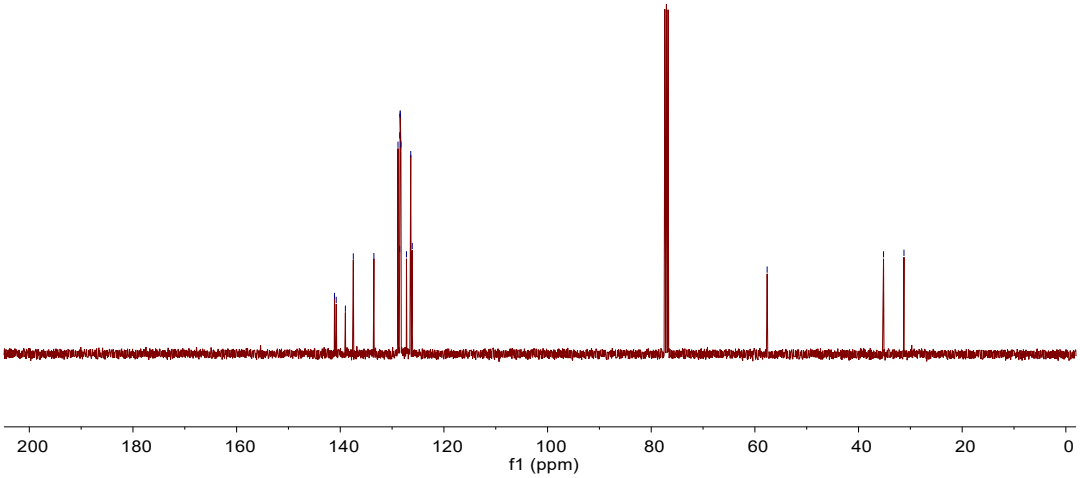


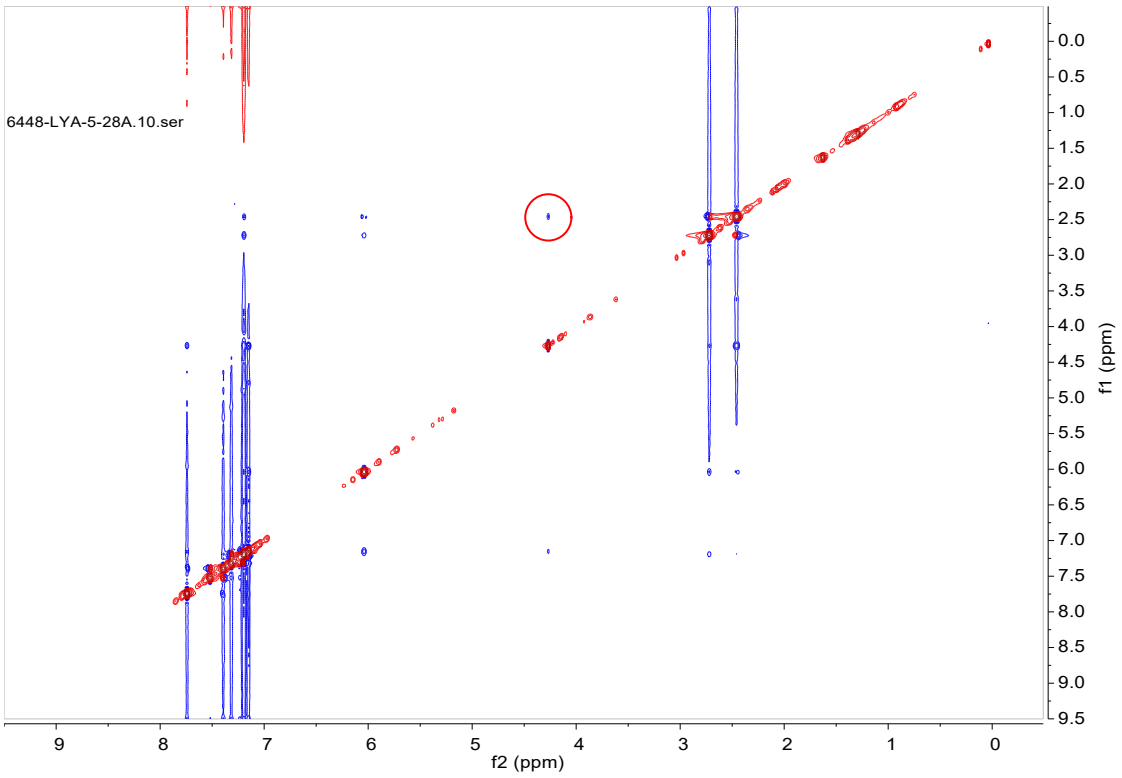
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

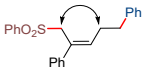
9-Z

141.12
140.78
139.01
137.48
133.51
128.86
128.54
128.53
128.45
128.43
128.30
127.23
126.40
126.11
57.63
35.18
31.23

A4558-LYA-5-28A.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 25



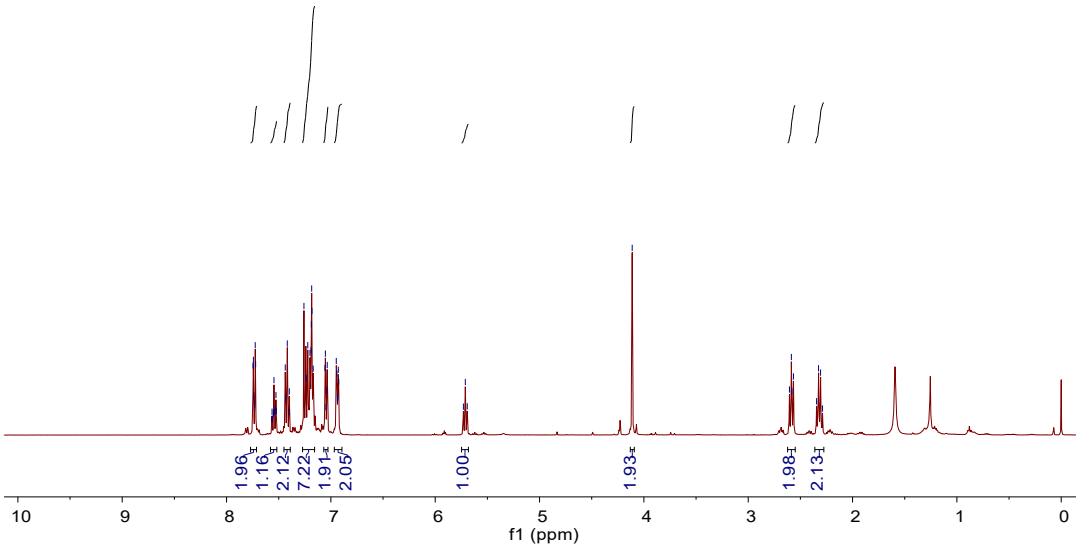


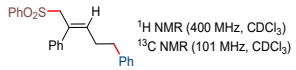


9-Z

2D NOE (700MHz, $CDCl_3$)

A4558-LYA-5-28B.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 26

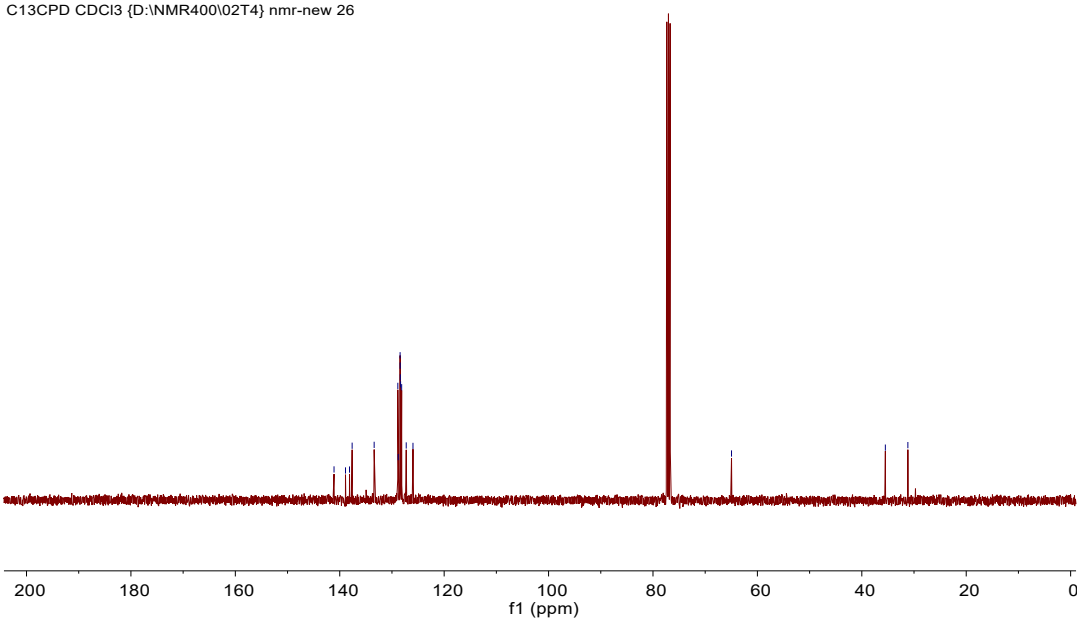


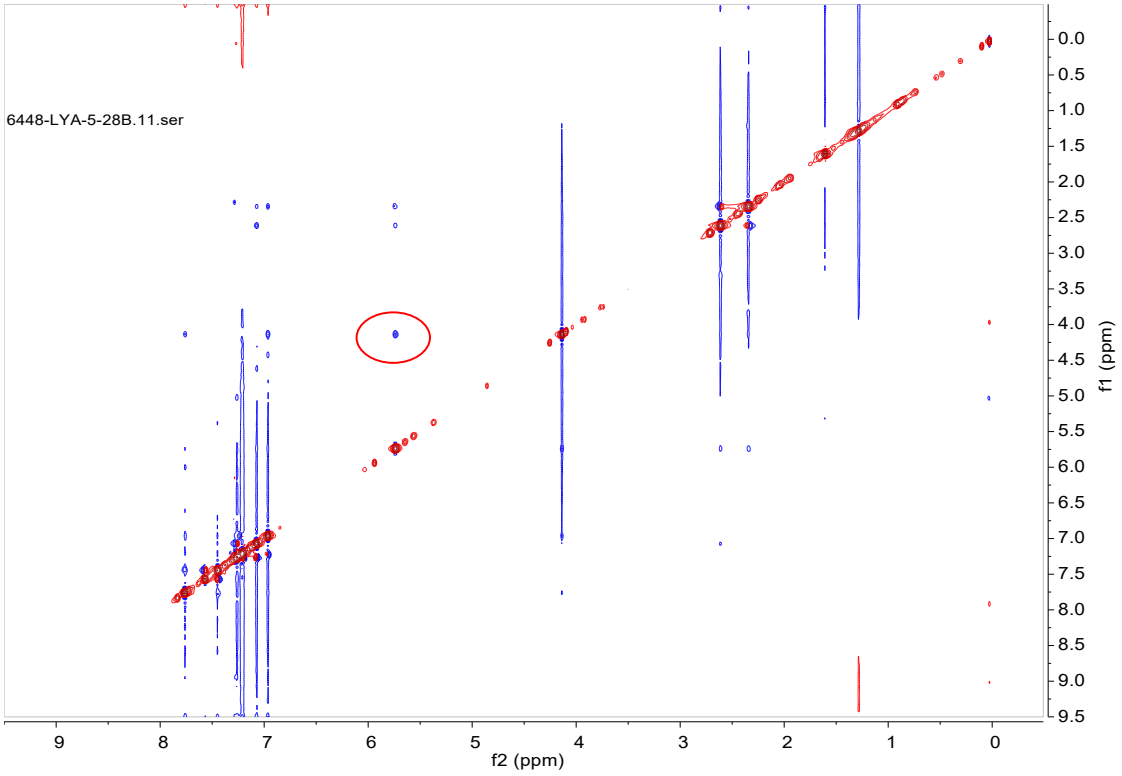


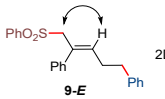
^{1}H NMR (400 MHz, $CDCl_3$)
^{13}C NMR (101 MHz, $CDCl_3$)

9-*E*

A4558-LYA-5-28B.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 26

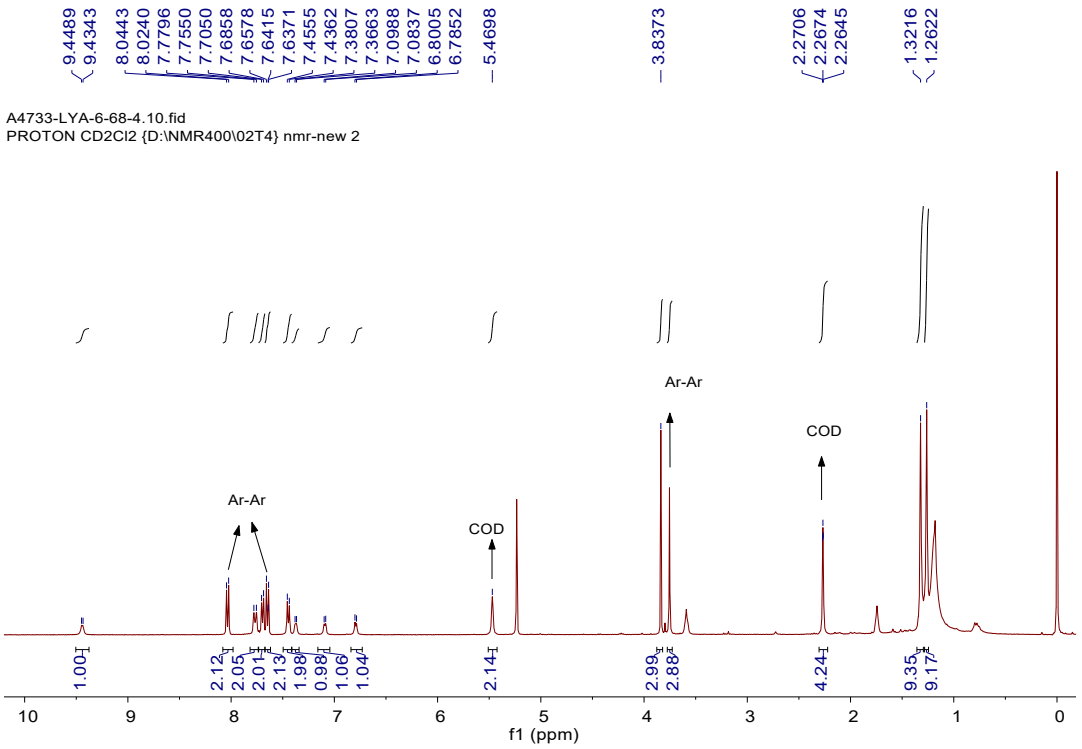


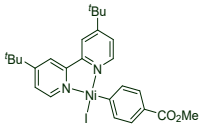




9-*E*

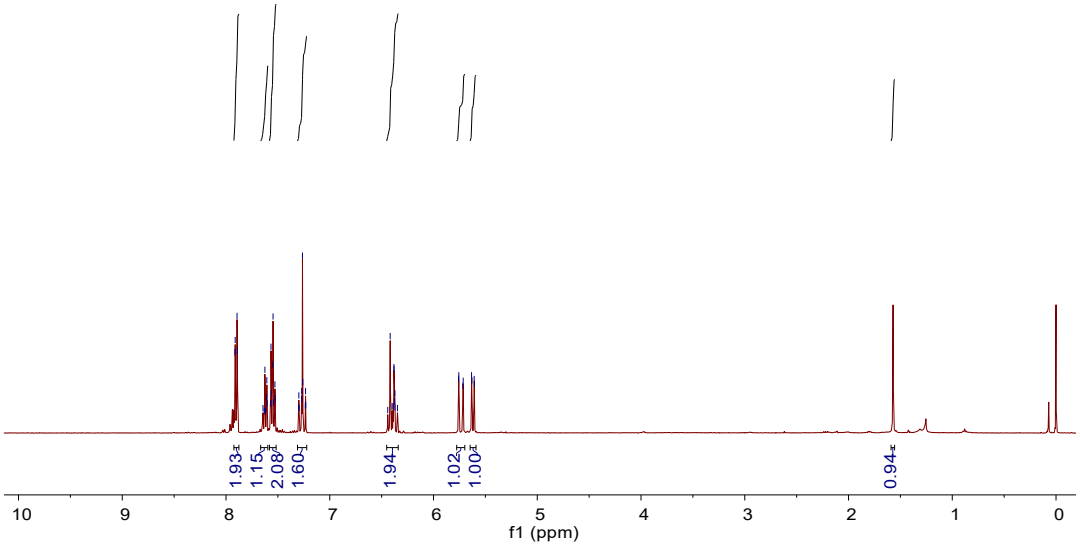
2D NOE (700MHz, $CDCl_3$)

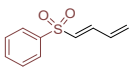

9.4489
9.4343
8.0443
8.0240
7.7796
7.7550
7.7050
7.6858
7.6578
7.6415
7.6371
7.4555
7.4362
7.3807
7.3663
7.0988
7.0837
6.8005
6.7852
5.4698
3.8373
2.2706
2.2674
2.2645
1.3216
1.2622
A4733-LYA-6-68-4.10.fid
PROTON CD2Cl2 {D:\NMR400\02T4} nmr-new 2
Ar-Ar
COD
Ar-Ar
COD
1.00
2.12
2.05
2.01
2.13
1.98
0.98
1.06
1.04
2.14
2.99
2.88
4.24
9.35
9.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


tBu
tBu
N
N
Ni
I
CO2Me

complex [Ni]

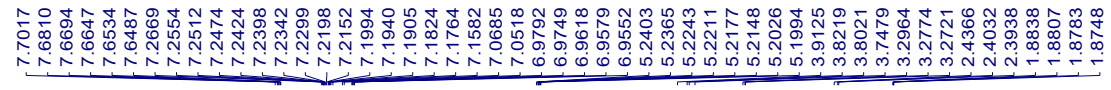
A1565-LYA-5-27C3.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 52



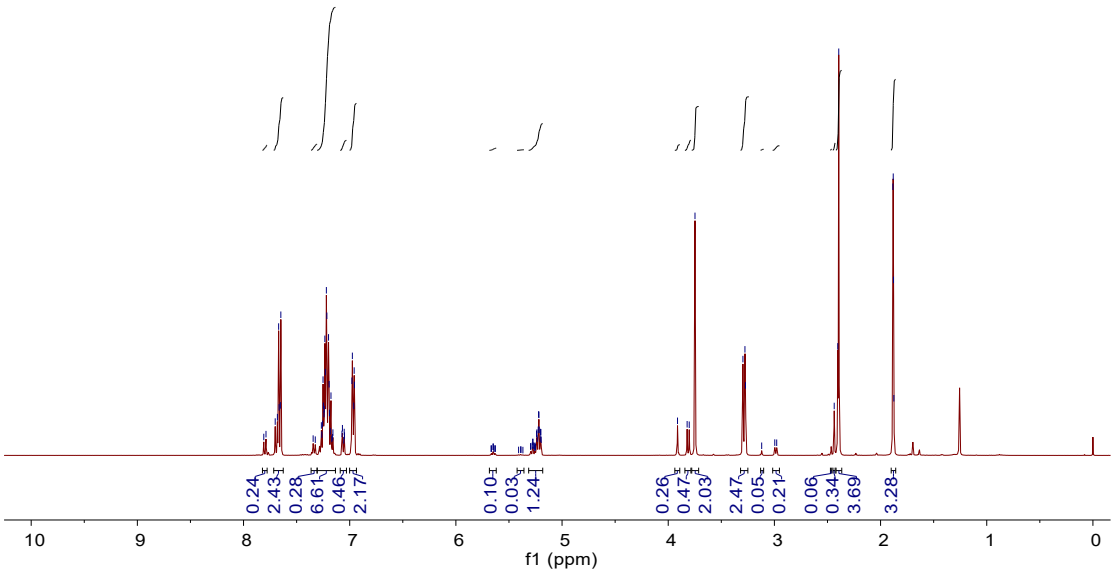


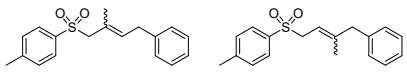
4aa′

A1565-LYA-5-27C3.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 52

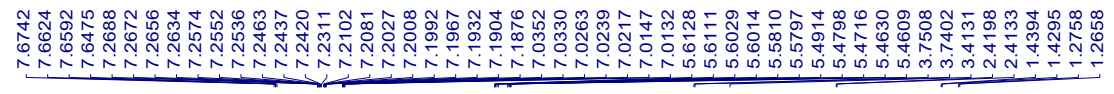


A1175-LYA-4-96A.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 29

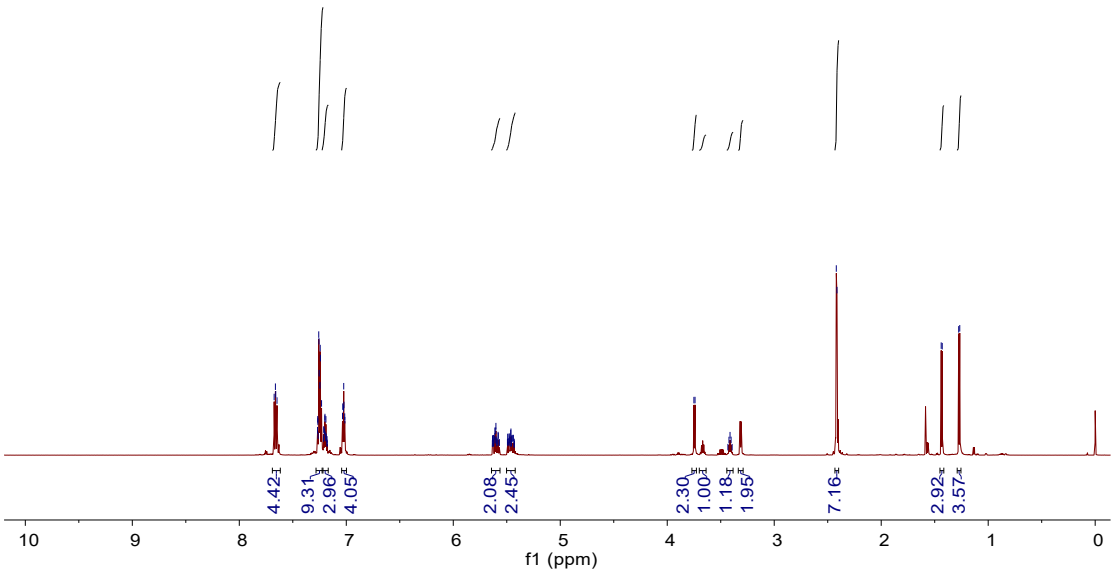


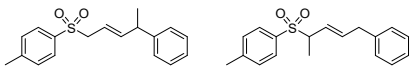


rr = 4.3:1, *E*/*Z* = 9.7/1, 9.4/1

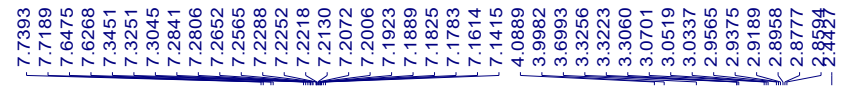


5527-LYA-5-5A.10.fid

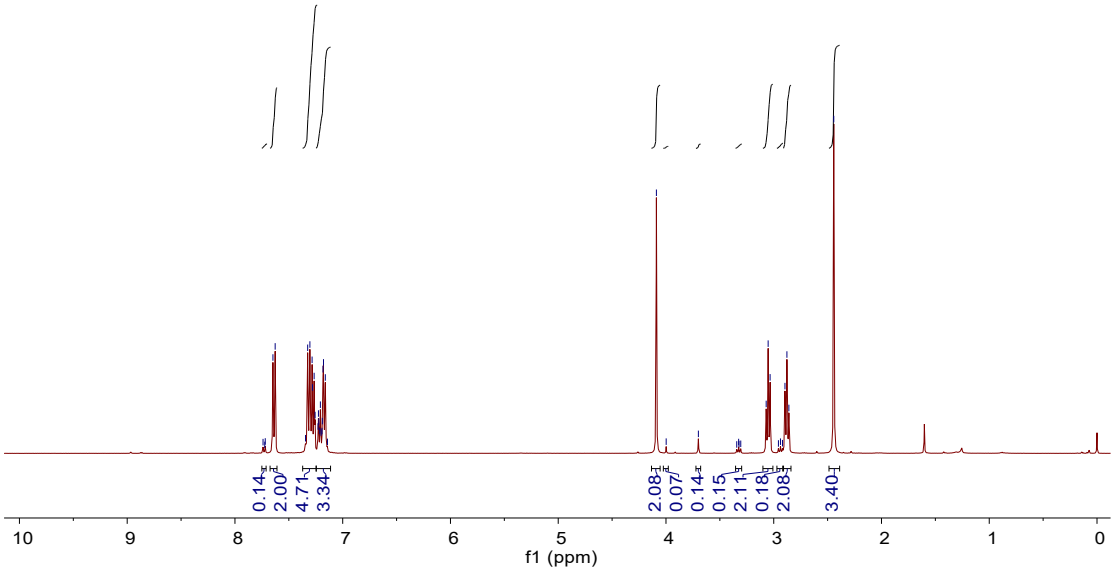


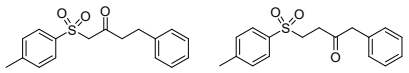


rr = 1.2/1

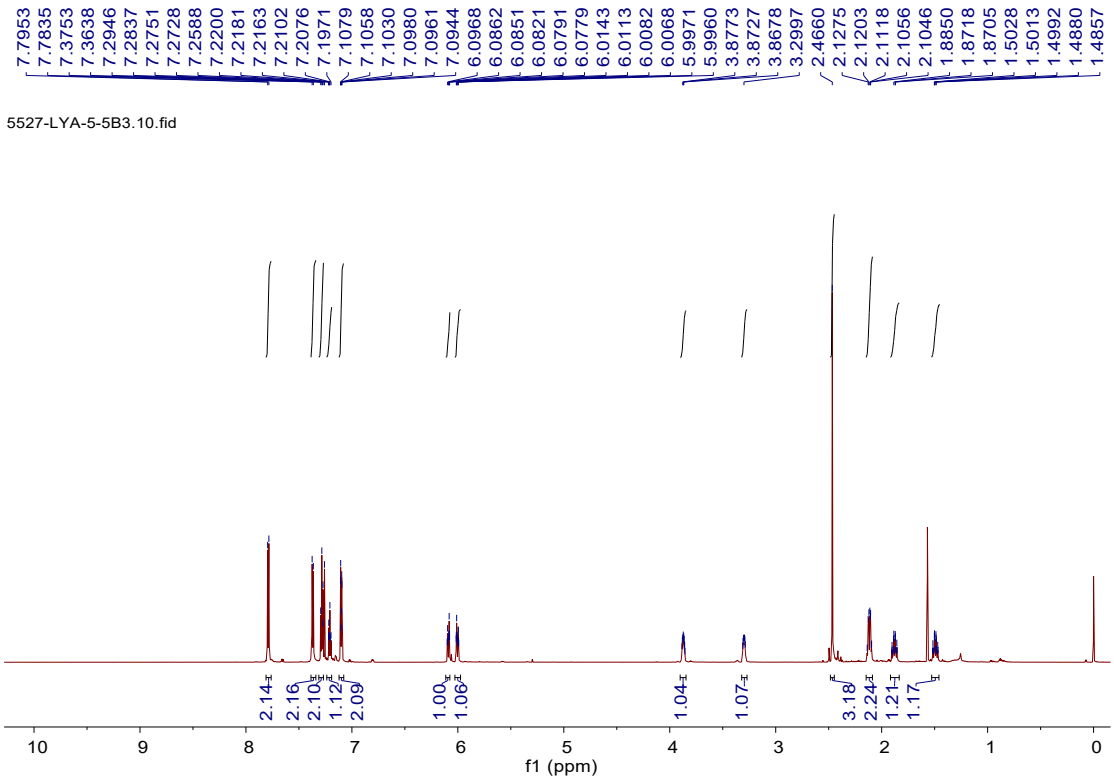


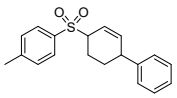
A1398-LYA-5-5C2.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 53

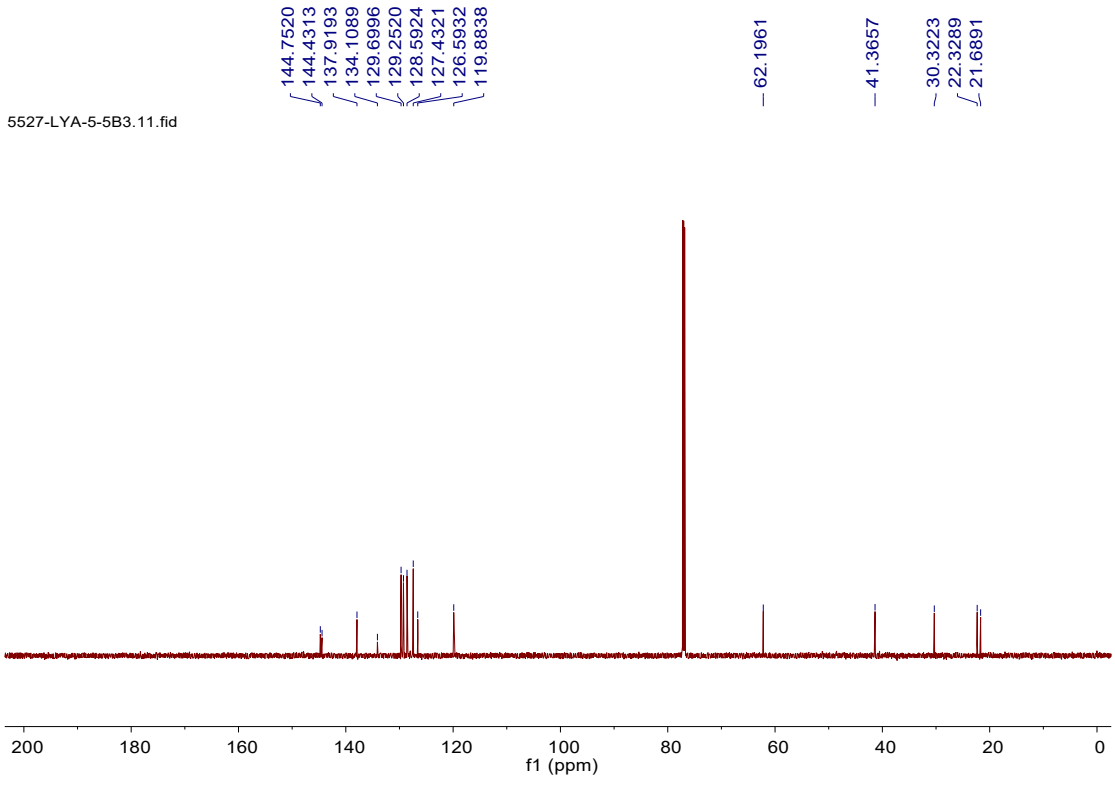


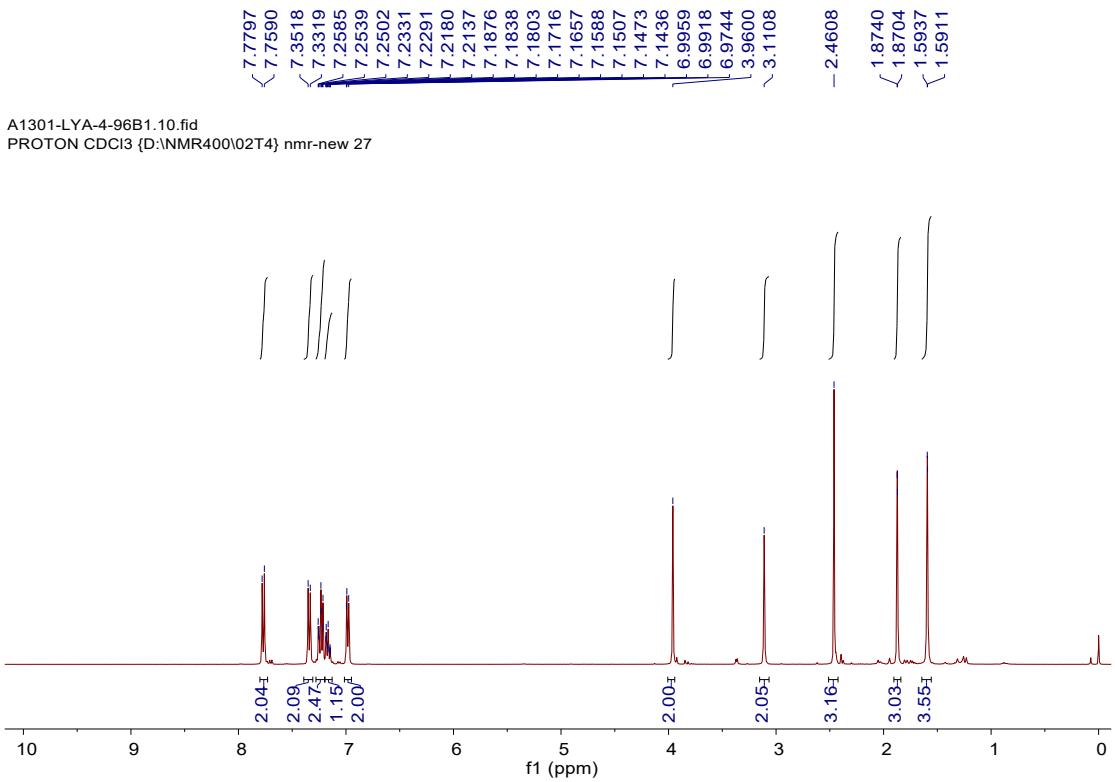


rr = 14/1

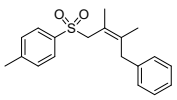

7.7953
7.7835
7.3753
7.3638
7.2946
7.2837
7.2751
7.2728
7.2588
7.2200
7.2181
7.2163
7.2102
7.2076
7.1971
7.1079
7.1058
7.1030
7.0980
7.0961
7.0944
6.0968
6.0862
6.0851
6.0821
6.0791
6.0779
6.0143
6.0113
6.0082
6.0068
5.9971
5.9960
3.8773
3.8727
3.8678
3.2997
2.4660
2.1275
2.1203
2.1118
2.1056
2.1046
1.8850
1.8718
1.8705
1.5028
1.5013
1.4992
1.4880
1.4857
5527-LYA-5-5B3.10.fid
2.14
2.16
2.10
1.12
2.09
1.00
1.06
1.04
1.07
3.18
2.24
1.21
1.17
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

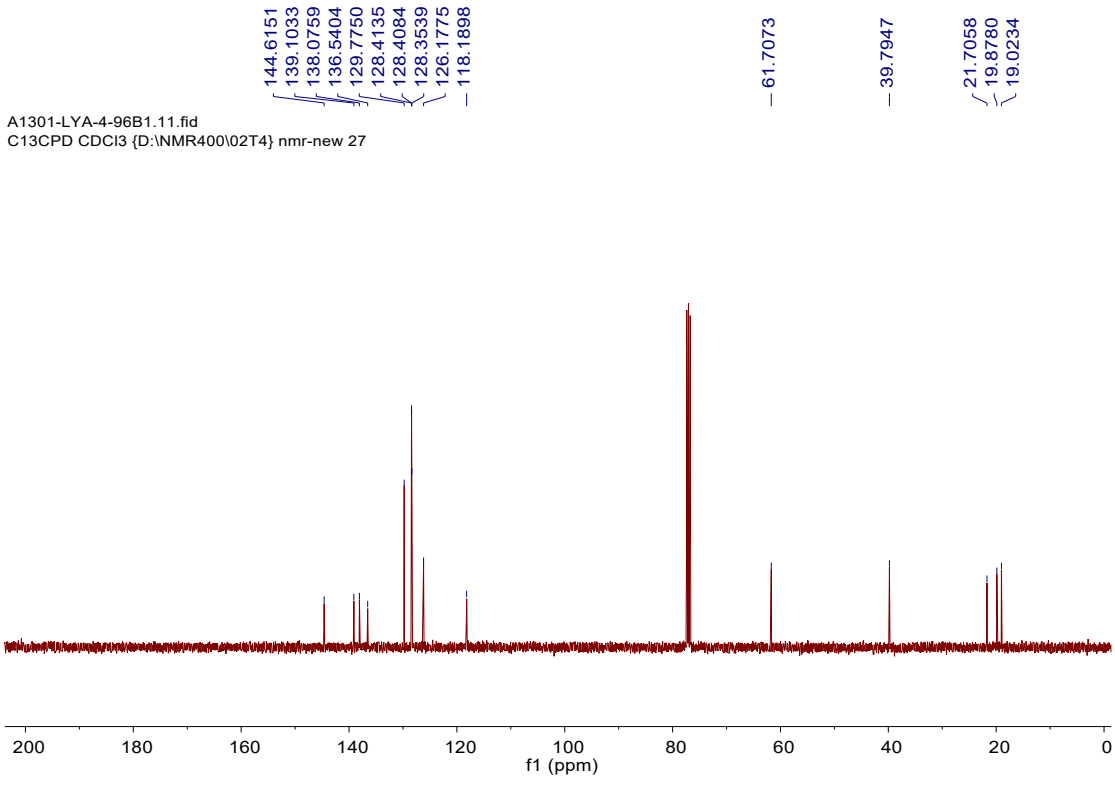



144.7520
144.4313
137.9193
134.1089
129.6996
129.2520
128.5924
127.4321
126.5932
119.8838
62.1961
41.3657
30.3223
22.3289
21.6891
5527-LYA-5-5B3.11.fid
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

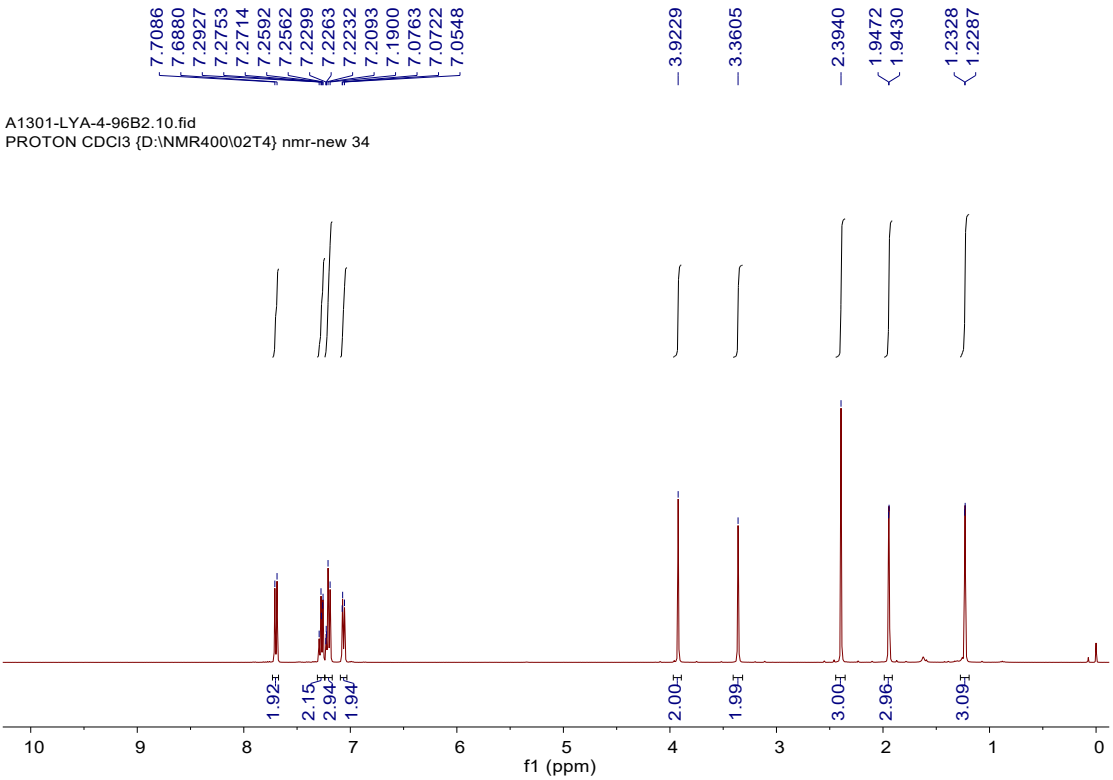


A1301-LYA-4-96B1.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 27

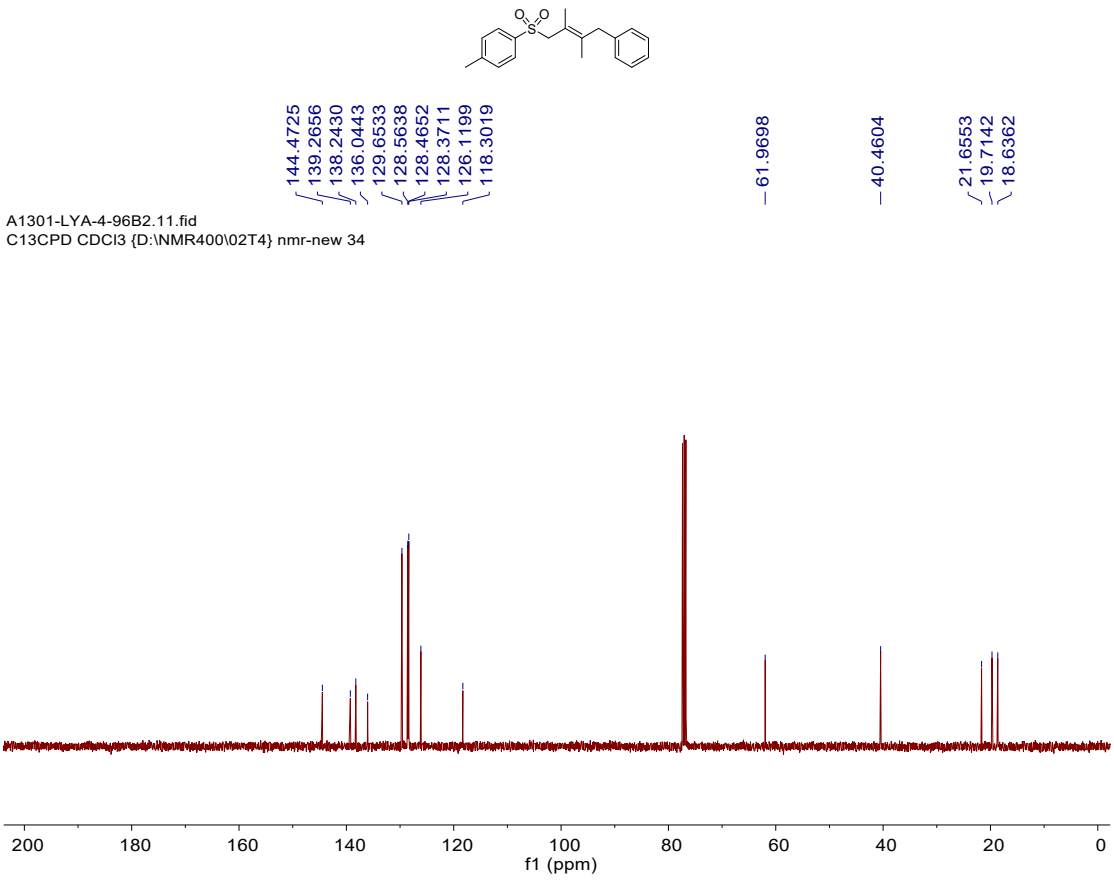




A1301-LYA-4-96B1.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 27



A1301-LYA-4-96B2.10.fid
PROTON CDCl3 {D:\NMR400\02T4} nmr-new 34



A1301-LYA-4-96B2.11.fid
C13CPD CDCl3 {D:\NMR400\02T4} nmr-new 34