Supporting Information

Copper-Photocatalyzed Atom Transfer Radical Addition of Thiosulfonates to Alkenes

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1. General information

Unless otherwise noted, materials were either purchased from commercial suppliers and used as received or prepared via literature procedures. Solvents were deoxygenated and dried by thoroughly sparging with argon followed by passage through an activated column in a solvent purification system. All manipulations of air-sensitive materials were carried out in oven-dried glassware using standard Schlenk under N_2 atmosphere.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-400 Plus or Bruker (500MHz) AVANCE-NEO or Agilent Technologies DD2 (600 MHz) spectrometer in $CDCl_3$ or DMSO-d_6. Chemical shifts (δ) for NMR were quoted in parts per million (ppm) referenced to 0.0 pm for tetramethylsilane or 2.50 ppm for the solvent residual peak of DMSO-d_6. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on a Bruker 500 (125 MHz) or Agilent Technologies DD2 (150 MHz) spectrometer in $CDCl_3$ or DMSO-d_6, and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$ or 39.5 ppm of DMSO-d_6.

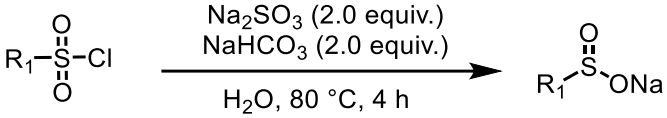
High-resolution mass spectra (HRMS) (ESI) were obtained with Bruker Daltonics APEXII 47 e FT-ICR, Agilent QTOF 700 or Agilent 1200 spectrometer. Accurate masses from high-resolution mass spectra were reported for the molecular ion $[M]^+$, $[M+H]^+$ or $[M+Na]^+$. Melting points were measured on an XT4A apparatus (uncorrected). Silicycle SiliaFlash® P60 silica gel (particle size 40–63 μm) was used for flash chromatography. Analytical thin layer chromatography was conducted with glass TLC plates (silica gel 60 F254), and spots were visualized under UV light or after treatment with standard TLC stains.

Unless otherwise noted, all photochemical reactions were carried out in dry Schlenk tube with magnetic stirring bar. The 40 W Bule LED lamps employed in this work were bought from Kessil Lighting 1689 Regatta Blvd, Richmond, CA 94804; wavelength (427 nm); The setup of photocatalytic reaction as illustrated in **Figure S1**. The distance from the light source to the irradiation vessel center is about 6.0 cm. The temperature is controlled by a fan. No filter was used in this reaction.

Figure S1. Photocatalytic Reaction Setup and Light Characteristics of 40 W Blue LED.

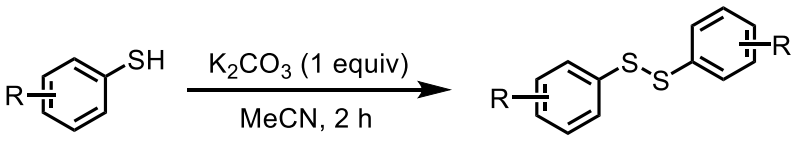
2. Experimental Procedures

2.1 General procedure for the preparation of sodium sulfonates.[1]



According to the reported literature[1]. In a clean 50 mL round-bottomed flask with a magnetic stirrer, anhydrous sodium sulfite (10 mmol, 2.0 equiv.), anhydrous sodium bicarbonate (10 mmol, 2.0 equiv.), and 5.0 mL of distilled H_2O (1.0 M). The corresponding sulfuryl chloride (5.0 mmol, 1.0 equiv.) was then added to the above mixture. The resulting mixture was stirred at 80 °C for 4 hours. After cooling to room temperature, the volatiles were removed on a rotary evaporator and the resulting solid was washed repeatedly with anhydrous ethanol. The combined ethanol washings were evaporated under reduced pressure to give the target sodium sulfite as an amorphous solid.

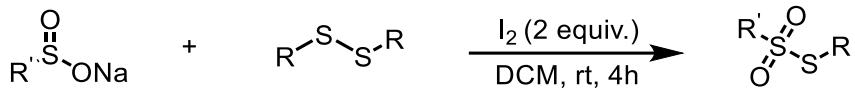
2.2 General procedure for the synthesis of disulfide.[2]



Thiophenol (10 mmol, 2.0 equiv.), potassium carbonate (10mmol, 2.0 equiv.) and 20.0 mL acetonitrile (0.5 M) were added to a clean 50 mL round-bottled flask. After the mixture was stirred at room temperature for 2 hours, the reaction mixture was extracted with ethyl acetate for 3 times. The composite organic layer was washed with water, dried with anhydrous sodium sulfate, concentrated

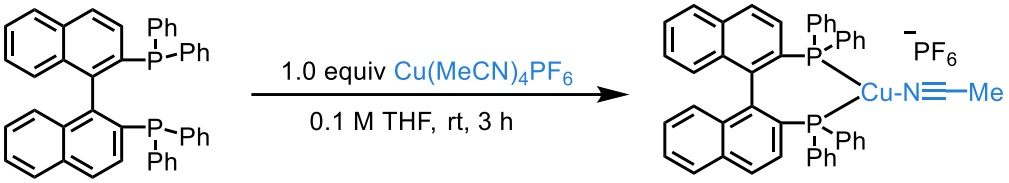
under reduced pressure. The pure target product was separated on silica gel by flash column chromatography using petroleum ether/ethyl acetate as eluent.

2.3 General procedure for the synthesis of thiosulfonates.[3]



In a dry 100 mL round-bottomed flask, disulfide (1 equiv.), sodium sulfonate (3.2 equiv.), I_2 (2 equiv.) and dichloromethane (0.25 M) were added. The resulting mixture was mixed at room temperature for 4-6 hours, after the disulfide was consumed, sodium thiosulfate aqueous solution was added to quench the mixture, and the mixture was washed with salt water. The organic phase was dried with anhydrous sodium sulfate, filtered, and distilled under vacuum, and the corresponding product was obtained by silica gel (petroleum ether/ethyl acetate =20/1) column chromatography.

2.3 General procedure for the synthesis of *rac*-BINAP-Cu(MeCN)PF$_6$.



rac-BINAP

89% yield

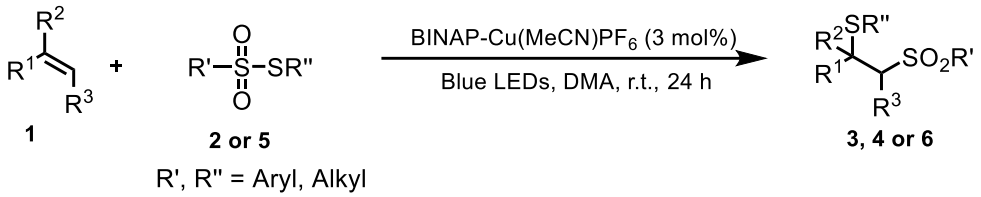
Prepared according to a reported reaction condition[4]: To an oven-dried 100 mL flask was added $Cu(MeCN)_4PF_6$ (745 mg, 2.00 mmol, 1.00 equiv), *rac*-BINAP (1.24 g, 2.00 mmol, 1.00 equiv), and 50 mL dry THF. The solution was allowed to stir at room temperature for 3 hours. Approximately 80 mL of dry hexanes was added to precipitate a white solid. There resulting solid was collected by vacuum filtration and dried under reduced pressure to give *rac*-BINAP-Cu(MeCN)PF_6 as a white solid in 89% yield (1.44 g).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (s, 4H), 7.64 (d, J = 8.7 Hz, 3H), 7.57 (s, 7H), 7.30 (t, J = 7.6 Hz, 2H), 7.18 (d, J = 6.3 Hz, 4H), 7.07 (d, J = 13.0 Hz, 4H), 6.68 (d, J = 7.6 Hz, 3H), 6.56 (q, J = 8.7, 7.6 Hz, 7H), 2.06 (s, 3H).

^{19}F NMR (376 MHz, DMSO-d_6) δ -72.26, -74.16.

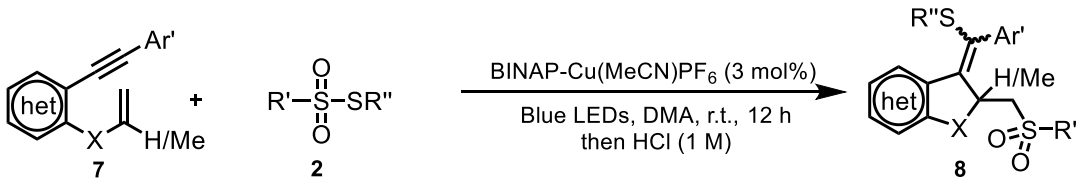
^{31}P NMR (162 MHz, DMSO-d_6) δ -0.59, -135.50, -139.90, -144.30, -148.69, -153.09.

2.4 Experimental procedures for copper(I) photocatalyzed 1,2-thiosulfonylation of olefins with thiosulfonates.



Corresponding olefins **1** (0.10 mmol), thiosulfonates **2** (0.20 mmol, 2.0 equiv.) and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with nitrogen (3 cycles). *N*,*N*-Dimethylacetamide (DMA) (2.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fans at rt for 24 h. After irradiation, the reaction mixture was quenched with NH_4Cl (aq) and subjected to three extractions using ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure, and the product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the pure target product **3**, **4 or 6**, and directly analyzed by ^{1}H NMR.

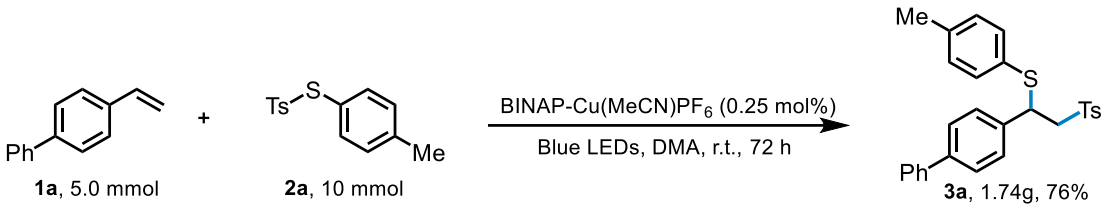
2.5 Experimental procedures for copper(I) photocatalyzed 1,7-thiosulfonylation of 1,6-alkynes with thiosulfonates.



Corresponding alkynes **7** (0.10 mmol), thiosulfonates **2** (0.20 mmol, 2.0 equiv.) and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with nitrogen (3 cycles). *N*,*N*-Dimethylacetamide (DMA) (2.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fans at rt for 12 h. After

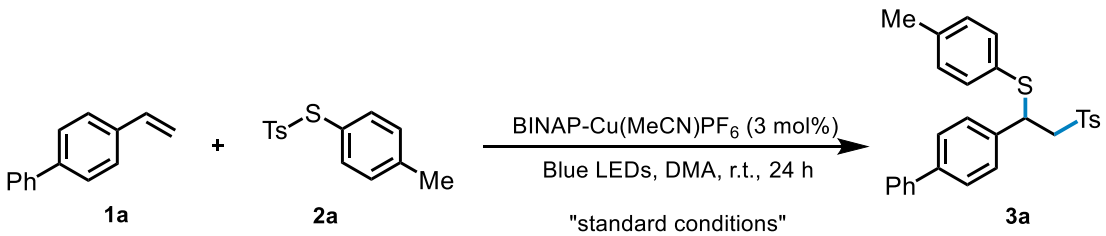
irradiation, the reaction mixture was quenched with hydrochloric acid (1.0 M) and subjected to three extractions using ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure, and the product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the pure target product **8**, and directly analyzed by ^{1}H NMR.

2.6 Procedure for the gram-scale synthesis of 3a.



Alkene **1a** (5.0 mmol, 0.90 g), thiosulfonate **2a** (10.0 mmol, 2.78 g) and Cu(BINAP)(MeCN)PF_6 (10.9 mg, 0.25 mol%) was sequentially added in a dry 100 mL Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with nitrogen (3 cycles). *N*, *N*-dimethylacetamide (DMA) (50 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427 nm) with fan at rt for 72 h. After irradiation, the reaction mixture was quenched with NH_4Cl (aq) and subjected to three extractions using ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure, and the product was isolated by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to provide the desired product **3a** in 76% yield.

3. Table S1. Optimization of reaction conditions.[a]



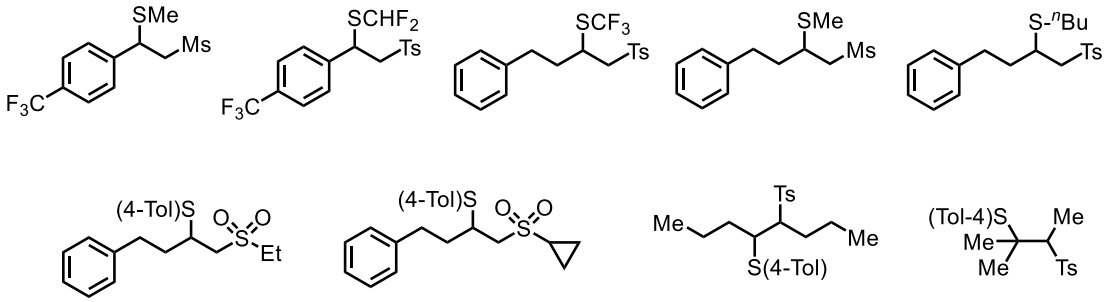
Entry	Change from the "standard conditions"	**3a** (%)[b]	Conversion of **1a** (%)[b]
1	none	82 (80)	100
2	without Cu(BINAP)(MeCN)PF_6	<1	0
3	without Blue light	0	0

4	without BINAP	8	12
5	without $Cu(MeCN)_4PF_6$	<1	<1
6	Under an atmosphere of air	<1	5
7	use of 2.0 mol% $Cu(BINAP)(MeCN)PF_6$	74	90
8	16 h	70	85
9	CuI, instead of $Cu(MeCN)_4PF_6$	17	35
10	CuCN, instead of $Cu(MeCN)_4PF_6$	22	35
11	$Cu(OTf)_2$, instead of $Cu(MeCN)_4PF_6$	32	67
12	$Cu(OAc)_2$, instead of $Cu(MeCN)_4PF_6$	44	78
13	**1a**:**2a** = 1:1	35	96
14	**1a**:**2a** = 1:1.5	54	100
15	**1a**:**2a** = 1:3	76	100
16	**1a**:**2a** = 2:1	30	65
17	Dmp and Xantphos, instead of BINAP	26	45
18	Xantphos, instead of BINAP	<1	5
19	DPEphos, instead of BINAP	<1	7
20	dppe, instead of BINAP	<1	6
21	dppp, instead of BINAP	<1	5
22	BINOL, instead of BINAP	<1	6
23	bpy, instead of BINAP	5	10
24	dmp, instead of BINAP	<1	6
25	1,10-phen, instead of BINAP	<1	8
26	DMF, instead of DMA	34	56
27	Acetonitrile, instead of DMA	<1	<1
28	Dichloromethane, instead of DMA	39	58
29	Chloroform, instead of DMA	33	70
30	THF, instead of DMA	51	82
31	Acetone, instead of DMA	10	31
32	1,4-dioxane, instead of DMA	36	75
33	DMSO, instead of DMA	24	64
34	DME, instead of DMA	18	38
35	Ethanol, instead of DMA	trace	<5
36	Ethyl acetate, instead of DMA	52	83
37	H_2O, instead of DMA	<1	<1

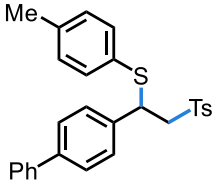
38	V_{H2O}/V_{DMA} (1:10), instead of DMA	<1	<5
39	white LED, instead of blue LED	15	30
40	green LED, instead of blue LED	<1	12
41	Violet LED, instead of blue LED	68	100
42	15 W blue LED	15	56
43	5 W blue LED	<5	<5
44	*fac*-Ir(ppy)$_3$, instead of Cu(BINAP)(MeCN)PF_6	21	100
45	4CzIPN, instead of Cu(BINAP)(MeCN)PF_6	9	20
46	Eosin Y, instead of Cu(BINAP)(MeCN)PF_6	22	46
47	Fluorescein, instead of Cu(BINAP)(MeCN)PF_6	34	76

[a] Reaction condition: **1** (0.1 mmol), **2** (0.20 mmol, 2.0 equiv.), Cu(BINAP)(MeCN)PF_6 (3.0 mol%) and degassed DMA (2.0 mL) at room temperature under irradiation with 40 W blue LED (427 nm) for 24 h. [b]NMR yield, determined using ^{1}H NMR analysis with CH_2Br_2 as an internal standard. The value in parentheses is isolated yield. BINAP, 2,2'-bis(dipenylphosphino)-1,1-binaphthalene; Xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; DMP, 2,9-Dimethyl-1,10-phenanthroline; DPEphos, (Oxydi-2,1-phenylene)bis(diphenylphosphine); Dppe, 1,2-Bis(diphenylphosphino)ethane; Dppp, 1,3-Bis(diphenylphosphino)propane; BINOL, 1,1'-Bi-2-naphthol; bpy, 2,2'-Bipyridine; 1,10-phen, 1,10-Phenanthroline.

4. Unsuccessful products.



5. Characterization data for all compounds.

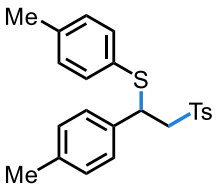


(1-([1,1'-biphenyl]-4-yl)-2-tosylethyl)(*p*-tolyl)sulfane (3a). The title compound was synthesized according to the General Procedure from 4-vinyl-1,1'-biphenyl (54.1 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3a** was obtained as a white solid (110.1 mg, 80% yield); mp: 121~122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.30 (m, 7H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 6.8 Hz, 4H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.61 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.85 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.66 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.34 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.2, 140.7, 140.4, 138.8, 136.4, 136.3, 133.9, 130.0, 129.4, 128.9, 128.8, 128.4, 127.9, 127.4, 127.0, 126.9, 60.6, 47.5, 21.5, 21.2.

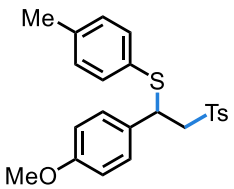
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{27}O_2S_2^+$: 459.1447; found: 459.1447.



***p*-Tolyl(1-(*p*-tolyl)-2-tosylethyl)sulfane (3b).**[5] The title compound was synthesized according to the General Procedure from 1-methyl-4-vinylbenzene (35.5 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1~10:1), product **3b** was obtained as a white solid (92.8 mg, 78% yield); mp: 118~119 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 4H), 6.93 (dd, *J* = 19.2, 8.4 Hz, 4H), 4.52 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.77 (dd, *J* = 15.0, 10.8 Hz, 1H), 3.59 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.1, 138.5, 137.6, 136.4, 134.4, 133.6, 129.9, 129.3, 129.2, 129.1, 127.9, 127.8, 60.6, 47.3, 21.5, 21.2, 21.1.

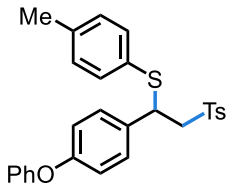


(1-(4-Methoxyphenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3c).[5] The title compound was synthesized according to the General Procedure from 1-methoxy-4-vinylbenzene (40.3 mg, 0.3 mmol), S-(*p*-tolyl) 4-

methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3c** was obtained as a white solid (90.4 mg, 73% yield); mp: 147~148 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.08 (dd, *J* = 14.4, 7.8 Hz, 4H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* =7.8 Hz, 2H), 4.54 (d, *J* = 10.8 Hz, 1H), 3.74 (br, 4H), 3.59 (d, *J* = 15.0 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 144.1, 138.5, 136.4, 133.6, 129.9, 129.4, 129.3, 129.2, 129.0, 127.9, 113.8, 60.7, 55.2, 47.0, 21.5, 21.1.

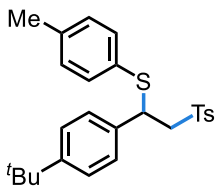


(1-(4-Phenoxyphenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3d). The title compound was synthesized according to the General Procedure from 1-phenoxy-4-vinylbenzene (58.9 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~5:1), product **3d** was obtained as a white solid (85.4 mg, 60% yield); mp: 123~124°C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.16 – 7.11 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 2H), 7.01 – 6.96 (m, 4H), 6.74 (dd, *J* = 6.6, 2.4 Hz, 2H), 4.57 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.78 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.62 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.9, 156.7, 144.3, 138.8, 136.5, 133.9, 132.1, 130.0, 129.8, 129.5, 129.3, 129.0, 128.0, 123.6, 119.1, 118.4, 60.6, 47.1, 21.6, 21.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{27}O_3S_2^+$: 475.1396; found: 475.1397.



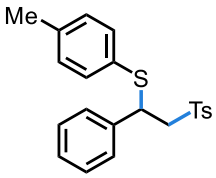
(1-(4-(*tert*-Butyl)phenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3e). The title compound was synthesized according to the General Procedure from 1-(*tert*-butyl)-4-vinylbenzene (48.1 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86

mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1~5:1), product **3e** was obtained as a white solid (94.7 mg, 72% yield); mp: 110~111 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.26 - 7.22 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 4.58 (dd, *J* = 10.8, 3.2 Hz, 1H), 3.87 - 3.81 (m, 1H), 3.61 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 150.8, 143.8, 138.6, 136.5, 134.0, 133.6, 130.0, 129.4, 129.3, 127.9, 127.5, 125.3, 60.5, 47.3, 34.4, 31.3, 21.5, 21.2.

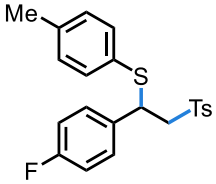
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{31}O_2S_2^+$: 439.1760; found: 439.1762.



(1-Phenyl-2-tosylethyl)(*p*-tolyl)sulfane (3f).[5] The title compound was synthesized according to the General Procedure from styrene (31.2 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3f** was obtained as a white solid (83.8 mg, 73% yield); mp: 108~109 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.04 (m, 11H), 4.55 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.80 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.63 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.2, 138.7, 137.6, 136.3, 133.8, 130.0, 129.4, 129.0, 128.4, 127.9, 127.7, 60.6, 47.6, 21.5, 21.2.

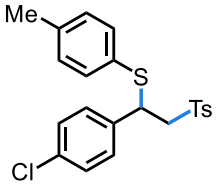


(1-(4-Fluorophenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3g).[5] The title compound was synthesized according to the General Procedure from 1-fluoro-4-vinylbenzene (36.6 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1~10:1), product **3g** was obtained as a white solid (94.9 mg, 79% yield); mp: 121~122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.06 (m, 6H), 7.02 – 6.98 (m, 2H), 6.82 – 6.76 (m, 2H), 4.55 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.74 (dd, *J* =14.8, 10.8 Hz, 1H), 3.62 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.1 (d, *J* = 245.55 Hz), 144.5, 138.9, 136.3, 133.9, 133.4 (d, *J* = 3.15 Hz), 130.0, 129.6 (d, *J* = 8.25 Hz), 129.5, 128.6, 127.9, 115.3 (d, *J* = 21.45 Hz), 60.6, 46.9, 21.5, 21.1.

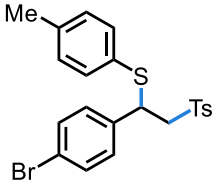
^{19}F NMR (376 MHz, $CDCl_3$): δ -113.96 – -114.03 (m).



(1-(4-Chlorophenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3h).[5] The title compound was synthesized according to the General Procedure from 1-chloro-4-vinylbenzene (41.6 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1), product **3h** was obtained as a white solid (102.6 mg, 82% yield); mp: 130~131 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.04 (m, 6H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.51 (dd, *J* =10.8, 4.0 Hz, 1H), 3.73 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.62 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 139.0, 136.2, 136.1, 134.0, 133.6, 130.0, 129.5, 129.3, 128.5, 128.4, 127.9, 60.5, 47.1, 21.5, 21.2.

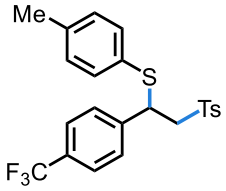


(1-(4-Bromophenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3i). The title compound was synthesized according to the General Procedure from 1-bromo-4-vinylbenzene (54.9 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1), product **3i** was obtained as a white solid (110.7 mg, 80% yield); mp: 119~120°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.15 (m, 4H), 7.09 (dd, *J* = 11.2, 8.0 Hz, 4H), 6.89 – 6.85 (m, 2H), 4.50 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.73 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.61 (dd, *J* =14.4, 3.6 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 139.0, 136.6, 136.1, 134.0, 131.4, 130.0, 129.6, 129.5, 128.4, 127.8, 121.7, 60.4, 47.1, 21.5, 21.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}BrO_2S_2^+$: 461.0239; found: 461.0238.

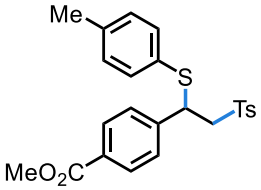


***p*-Tolyl(2-tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)sulfane (3j).**[5] The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1~10:1), product **3j** was obtained as a white solid (116.2 mg, 86% yield); mp: 140~141°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.19 –7.16 (m, 2H), 7.08 (dd, *J* = 8.4, 2.8 Hz, 4H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.58 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.80 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.67 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 141.6, 139.1, 136.0, 134.2, 130.1, 129.7 (q, *J* = 32.4 Hz), 129.5, 128.3, 128.0, 127.8, 125.2 (q, *J* = 3.75 Hz), 123.8 (q, *J* = 270.60 Hz), 60.2, 47.4, 21.3, 21.1.

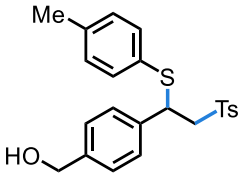
^{19}F NMR (376 MHz, CDCl3): δ -62.638.



Methyl-4-(1-(*p*-tolylthio)-2-tosylethyl)benzoate (3k).[5] The title compound was synthesized according to the General Procedure from methyl 4-vinylbenzoate (48.7 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1), product **3k** was obtained as a white solid (108.4 mg, 82% yield); mp: 127~128 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.01 (m, 6H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.56 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.76 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.63 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H).

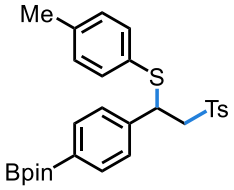
^{13}C NMR (150 MHz, $CDCl_3$): δ 168.8, 150.1, 144.5, 138.8, 136.1, 135.1, 133.9, 130.0, 129.6, 128.8, 128.7, 127.8, 121.4, 60.6, 47.1, 21.5, 21.2, 21.1.



(4-(1-(*p*-Tolylthio)-2-tosylethyl)phenyl)methanol (3l).[5] The title compound was synthesized according to the General Procedure from (4-vinylphenyl)methanol (40.2 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1~10:1), product **3l** was obtained as a white solid (82.9 mg, 67% yield); mp: 132~133 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 9.0 Hz, 4H), 7.05 (d, *J* = 8.4 Hz, 4H), 4.56 (s, 2H), 4.55 (d, *J* = 3.6 Hz, 1H), 4.53 (d, *J* = 3.6 Hz, 1H), 3.78 (dd, *J* = 14.7, 10.5 Hz, 1H), 3.60 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.3, 140.6, 138.6, 136.7, 136.0, 133.5, 129.9, 129.4, 128.9, 127.9, 127.8, 126.9, 64.5, 60.4, 47.2, 21.4, 21.1

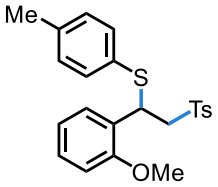


4,4,5,5-Tetramethyl-2-(4-(1-(*p*-tolylthio)-2-tosylethyl)phenyl)-1,3,2-dioxaborolane (3m). The title compound was synthesized according to the General Procedure from 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (69.0 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1~10:1), product **3m** was obtained as a white solid (76.3 mg, 50% yield); mp: 154~155 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.07 – 6.98 (m, 6H), 4.53 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.80 (dd, *J* = 14.8, 10.4 Hz, 1H), 3.62 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.33 (s, 3H), 2.33 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.2, 140.4, 138.7, 136.1, 134.8, 133.8, 130.0, 129.4, 128.8, 127.9, 127.2, 83.8, 60.3, 47.8, 24.9, 24.8, 21.5, 21.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{34}BO_4S_2^+$: 509.1986; found: 509.1985.

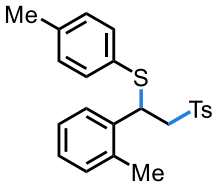


(1-(2-Methoxyphenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3n). The title compound was synthesized according to the General Procedure from 1-methoxy-2-vinylbenzene (40.3 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3n** was obtained as a white solid (89.1 mg, 72% yield); mp: 138~139°C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.10 (td, *J* = 7.8, 1.8 Hz, 1H), 7.06 – 7.05 (m, 4H), 6.93 (dd, *J* = 7.2, 1.8 Hz, 1H), 6.71 (t, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 4.87 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.06 (dd, *J* = 15.0, 10.8 Hz, 1H), 3.72 (s, 3H), 3.62 (dd, *J* = 15.0 3.6 Hz, 1H), 2.34 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.6, 144.0, 138.2, 136.0, 133.4, 129.9, 129.8, 129.1, 128.8, 127.9, 127.6, 125.6, 120.4, 110.7, 59.5, 55.3, 42.9, 21.5, 21.1.

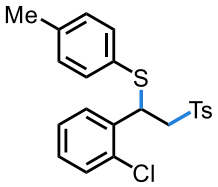
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{25}O_3S_2^+$: 413.4210; found: 413.4210.



***p*-Tolyl(1-(*o*-tolyl)-2-tosylethyl)sulfane (3o).**[5] The title compound was synthesized according to the General Procedure from 1-methyl-2-vinylbenzene (35.5 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3o** was obtained as a white solid (84.5 mg, 71% yield); mp: 109~110 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.05 – 7.00 (m, 4H), 6.84 – 6.80 (m, 2H), 4.81 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.88 (dd, *J* = 15.0, 10.8 Hz, 1H), 3.63 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.1, 138.8, 136.3, 136.2, 135.1, 133.9, 130.5, 130.0, 129.4, 129.1, 127.7, 127.4, 126.0, 60.1, 43.1, 21.5, 21.2, 19.4.

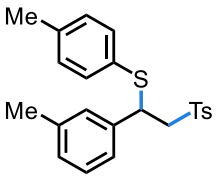


(1-(2-Chlorophenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3p). The title compound was synthesized according to the General Procedure from 1-chloro-2-vinylbenzene (41.6 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3p** was obtained as a white solid (97.6 mg, 78% yield); mp: 128~129 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.25 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.11 – 7.05 (m, 5H), 7.01 – 6.96 (m, 2H), 5.00 (d, *J* = 10.8 Hz, 1H), 3.92 – 3.87 (m, 1H), 3.64 (dd, *J* = 15.0, 3.6 Hz, 1H), 2.35 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.0, 138.9, 135.7, 135.0, 134.0, 133.8, 130.0, 129.8, 129.5, 128.7, 128.5, 128.0, 126.7, 60.6, 29.7, 21.5, 21.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}ClO_2S_2^+$: 439.1760; found: 439.1762.

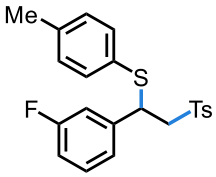


***p*-Tolyl(1-(*m*-tolyl)-2-tosylethyl)sulfane (3q).** The title compound was synthesized according to the General Procedure from 1-chloro-2-vinylbenzene (53.5 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3q** was obtained as a white solid (88.0 mg, 74% yield); mp: 135~136 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.8 Hz, 4H), 7.03 -7.00 (m, 1H), 6.93 – 6.87 (m, 2H), 6.75 (s, 1H), 4.52 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.80 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.60 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.1, 138.6, 138.0, 137.1, 136.3, 133.7, 130.0, 129.3, 129.2, 128.5, 128.4, 128.3, 127.9, 125.2, 60.5, 47.6, 21.5, 21.2, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{25}O_2S_2^+$: 397.1290; found: 397.1291.



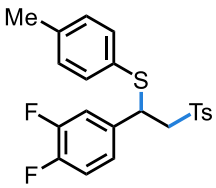
(1-(3-Fluorophenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3r). The title compound was synthesized according to the General Procedure from 1-fluoro-3-vinylbenzene (36.6 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3r** was obtained as a white solid (94.9 mg, 79% yield); mp: 151~152 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 - 7.06 (m, 5H), 6.86 – 6.80 (m, 2H), 6.69 – 6.66 (m, 1H), 4.52 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.74 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.62 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.5 (d, *J* = 245.40 Hz), 144.5, 140.2 (d, *J* = 7.05 Hz), 139.0, 136.1, 134.0, 130.0, 129.9 (d, *J* = 8.25 Hz), 129.5, 128.4, 127.9, 123.8 (d, *J* = 2.85 Hz), 114.8 (d, *J* = 20.55 Hz), 114.6 (d, *J* = 19.5 Hz), 60.4, 47.3, 21.5, 21.2.

^{19}F NMR (376 MHz, CDCl3): δ -62.638.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{22}FO_2S_2^+$: 401.1040; found: 401.1040.



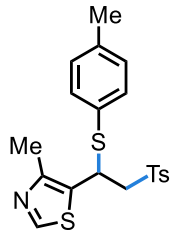
(1-(3,4-Difluorophenyl)-2-tosylethyl)(*p*-tolyl)sulfane (3s). The title compound was synthesized according to the General Procedure from 1,2-difluoro-4-vinylbenzene (42.0 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86

mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3s** was obtained as a white solid (80.4 mg, 64% yield); mp: 118~119 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.91 (q, *J* = 9.1 Hz, 1H), 6.82 – 6.77 (m, 1H), 6.79 – 6.74 (m, 1H), 4.49 (dd, *J* = 10.7, 3.7 Hz, 1H), 3.68 (dd, *J* = 14.7, 10.7 Hz, 1H), 3.61 (dd, *J* = 14.7, 3.7 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.8, 139.2, 136.2, 134.8, 134.1, 130.1, 129.5, 128.1, 127.8, 124.3, 124.3, 124.3, 124.2, 117.1, 117.0, 116.8, 116.7, 60.5, 46.8, 21.5, 21.2.

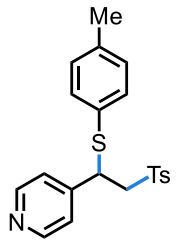
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{21}F_2O_2S_2^+$: 419.0946; found: 419.0946.



4-Methyl-5-(1-(*p*-tolylthio)-2-tosylethyl)thiazole (3t).[6] The title compound was synthesized according to the General Procedure from 4-methyl-5-vinylthiazole (37.5 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3t** was obtained as a white solid (96.9 mg, 80% yield); mp: 129~130 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.45 (d, *J* = 6.6 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 4H), 7.06 (d, *J* = 9.0 Hz, 2H), 4.89 (dd, *J* = 10.8, 4.2 Hz, 1H), 3.70 (dd, *J* = 15.0, 3.6 Hz, 1H), 3.63 (dd, *J* = 14.4, 10.2 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 151.2, 151.2, 144.7, 139.6, 136.2, 134.6, 130.7, 130.1, 129.6, 127.9, 127.7, 62.8, 40.8, 21.5, 21.2, 15.0.

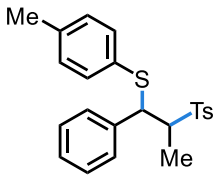


4-(1-(*p*-Tolylthio)-2-tosylethyl)pyridine (3u).[5] The title compound was synthesized according to the General Procedure from 4-vinylpyridine (31.5 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg,

3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3u** was obtained as a white solid (96.9 mg, 60% yield); mp: 120~121 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* = 5.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.13 (dd, *J* = 13.0, 8.0 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 6.0 Hz, 2H), 4.46 (dd, *J* = 10.5, 4.0 Hz, 1H), 3.76 (dd, *J* = 14.8, 10.3 Hz, 1H), 3.66 (dd, *J* = 14.5, 4.0 Hz, 1H), 2.37 (s, 3H), 2.31 (s, 3H).

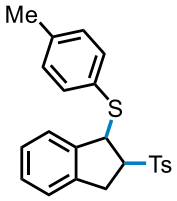
^{13}C NMR (125 MHz, $CDCl_3$): δ 149.7, 146.9, 144.9, 139.4, 135.9, 134.3, 130.0, 129.6, 127.8, 127.5, 122.7, 59.7, 46.7, 21.5, 21.1.



(1-Phenyl-2-tosylpropyl)(*p*-tolyl)sulfane (3v).[5] The title compound was synthesized according to the General Procedure from prop-1-en-1-ylbenzene (35.5 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3v** was obtained as a white solid (86.8 mg, 73% yield); mp: 108~109°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.26 - 7.22 (m, 4H), 7.19 - 7.14 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.82 (d, *J* = 4.8 Hz, 1H), 3.56 - 3.50 (m, 1H), 2.41 (s, 3H), 2.24 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H).

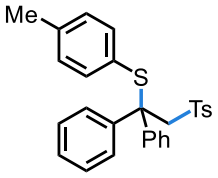
^{13}C NMR (150 MHz, $CDCl_3$): δ 144.4, 140.1, 137.4, 135.4, 132.5, 130.2, 129.6, 129.5, 129.0, 128.4, 128.3, 127.4, 66.1, 53.4, 21.6, 21.0, 10.8.



(2-Phenyl-1-tosylpropan-2-yl)(*p*-tolyl)sulfane (3w).[5] The title compound was synthesized according to the General Procedure from 1H-indene (34.8 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3w** was obtained as a white solid (88.8 mg, 75% yield); mp: 123~124 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 5.6 Hz, 1H), 7.21 - 7.16 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.97 (t, *J* = 2.0 Hz, 1H), 3.89 (d, *J* = 8.8 Hz, 1H), 3.43 (d, *J* = 17.6 Hz, 1H), 3.21 (dd, *J* = 17.6, 8.4 Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H).

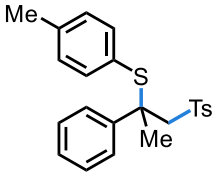
^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 140.2, 140.1, 138.2, 134.3, 133.4, 129.7, 129.6, 128.9, 128.6, 128.4, 127.3, 125.0, 124.3, 69.2, 53.1, 31.7, 21.5, 21.1.



(2-Phenyl-1-tosylpropan-2-yl)(*p*-tolyl)sulfane (3x).[5] The title compound was synthesized according to the General Procedure from ethene-1,1-diyldibenzene (54.1 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3x** was obtained as a white solid (92.2 mg, 67% yield); mp: 145~146 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (dd, *J* = 7.6, 2.0 Hz, 4H), 7.19 (d, *J* = 7.2 Hz, 6H), 7.13 - 7.11 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.78 - 6.76 (m, 2H), 4.30 (s, 2H), 2.34 (s, 3H), 2.28 (s, 3H).

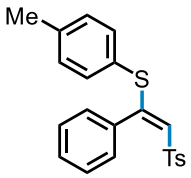
^{13}C NMR (150 MHz, $CDCl_3$): δ 143.4, 140.8, 139.8, 138.6, 137.1, 129.7, 129.3, 129.2, 127.4, 127.3, 127.2, 126.8, 66.6, 60.7, 21.4, 21.1.



(2-Phenyl-1-tosylpropan-2-yl)(*p*-tolyl)sulfane (3y).[5] The title compound was synthesized according to the General Procedure from prop-1-en-2-ylbenzene (35.5 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3y** was obtained as a white solid (86.8 mg, 73% yield); mp: 163~164 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 16.0, 7.6 Hz, 4H), 7.09 - 7.03 (m, 7H), 4.19 (d, *J* = 14.8 Hz, 1H), 3.64 (d, *J* = 14.8 Hz, 1H), 2.34 (s, 6H), 1.99 (s, 3H).

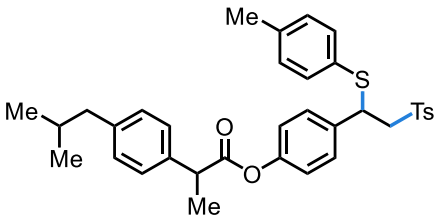
^{13}C NMR (150 MHz, $CDCl_3$): δ 143.8, 140.1, 140.0, 137.5, 137.4, 129.6, 129.4, 127.9, 127.6, 127.1, 127.0, 126.9, 66.9, 51.7, 24.6, 21.4, 21.2.



(*E*)-(1-Phenyl-2-tosylvinyl)(*p*-tolyl)sulfane (3z).[6] The title compound was synthesized according to the General Procedure from Phenylacetylene (30.6 mg, 0.3 mmol), *S*-phenyl 4-methylbenzenesulfonothioate (156.8 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3z** was obtained as a white solid (92.5 mg, 81% yield); mp: 116~117 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.30 - 7.20 (m, 8H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.90 (s, 1H), 2.39 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 160.2, 143.3, 141.0, 139.2, 135.3, 133.6, 130.9, 129.4, 129.1, 129.0, 127.8, 127.2, 125.3, 122.2, 21.5, 21.3.

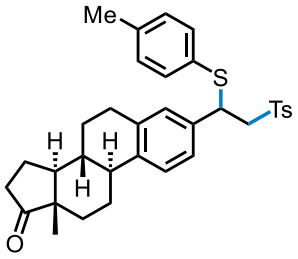


4-(1-(*p*-tolylthio)-2-tosylethyl)phenyl 2-(4-isobutylphenyl)propanoate (3aa). The title compound was synthesized according to the General Procedure from 4-vinylphenyl 2-(4-isobutylphenyl)propanoate (92.5 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **3aa** was obtained as a white solid (137.3 mg, 78% yield); mp: 121~122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.17 - 7.13 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.72 (dd, *J* = 8.4, 2.4 Hz, 2H), 4.54 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 1H), 3.74 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.61 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 2.25 (s, 3H), 1.90 – 1.83(m, 1H), 1.60 – 1.58 (m, 3H), 1.26 (br, 1H), 0.91 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 172.7, 150.3, 144.4, 140.8, 138.8, 137.1, 136.1, 134.9, 133.9, 123.0, 129.5, 129.5, 129.5, 128.7, 127.7, 127.1, 121.2, 121.2, 60.6, 47.1, 45.2, 31.5, 30.1, 22.6, 22.3, 21.3, 21.1, 18.4, 14.1.

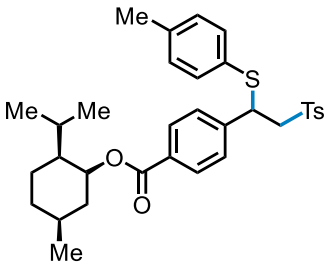
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{35}H_{39}O_4S_2^+$: 397.1290; found: 397.1291.



(8R,9S,13S,14S)-13-methyl-3-((R)-1-(p-tolylthio)-2-tosylethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3ab).[5] The title compound was synthesized according to the General Procedure from (8R,9S,13S,14S)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (84.12 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3ab** was obtained as a purple solid (117.3 mg, 70% yield, dr 1:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 2H), 7.26 – 7.19 (m, 2H), 7.09 – 7.00 (m, 5H), 6.91-6.86 (m, 1H), 6.70 – 6.65 (m, 1H), 4.53 – 4.47 (m, 1H), 3.83 – 3.77 (m, 1H), 3.59 – 3.53 (m, 1H), 2.74 – 2.67 (m, 1H), 2.62 – 2.44 (m, 3H), 2.33 – 2.30 (m, 6H), 2.17 – 2.08 (m, 2H), 2.04 – 1.91 (m, 4H), 1.60 – 1.57 (m, 1H), 1.50 – 1.42 (m, 4H), 0.92 – 0.87 (m, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 220.29(220.26), 143.56(143.51), 139.22(139.21), 138.30(138.28), 136.28(136.27), 136.19(136.17), 134.13(134.09), 133.23(133.20), 129.80, 129.20(129.19), 128.95(128.94), 128.07(127.88), 127.62(127.61), 125.31(125.24), 125.21(125.13), 60.25(60.19), 50.21(50.18), 47.64(47.63), 47.05(47.01), 44.07, 37.84(37.77), 35.57(31.31), 28.89(28.87), 26.17(26.13), 25.44(25.38), 21.43(21.37), 21.34(21.31), 20.95, 13.67(13.64).

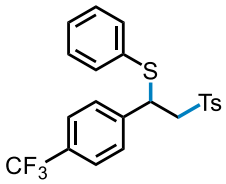


(1R,2S,5S)-2-Isopropyl-5-methylcyclohexyl 4-((R)-1-(*p*-tolylthio)-2-tosylethyl)benzoate (3ac). The title compound was synthesized according to the General Procedure from (1R,2S,5S)-2-isopropyl-5-methylcyclohexyl 4-vinylbenzoate (85.9 mg, 0.3 mmol), S-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1), product **3ac** was obtained as a white solid (120.3 mg, 71% yield); mp: 131~132 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.09-7.06 (m, 6H), 4.92 (td, *J* = 10.9, 4.4 Hz, 1H), 4.56 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.79 (dd, *J* = 14.4, 10.6 Hz, 1H), 3.65 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.33 (s, 6H), 2.11 (d, *J* = 12.8 Hz, 1H), 1.94 (td, *J* = 6.9, 2.7 Hz, 1H), 1.74 (d, *J* = 12.0 Hz, 2H), 1.60 - 1.52 (m, 3H), 1.15 - 1.05 (m, 2H), 0.94 (q, *J* = 3.6 Hz, 6H), 0.80 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.6, 144.6, 142.6, 139.1, 136.1, 134.0, 130.2, 130.1, 129.6, 129.5, 128.3, 127.9, 127.8, 74.9, 60.3, 47.5, 47.2, 41.0, 34.3, 31.4, 26.5, 23.6, 22.0, 21.5, 21.2, 20.8, 16.5.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{41}O_4S_2^+$: 565.2441; found: 565.2441.



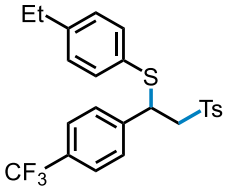
Phenyl(2-tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)sulfane (4a). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-phenyl 4-methylbenzenesulfonothioate (156.8 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4a** was obtained as a purple solid (113.9 mg, 87% yield); mp: 119 ~ 120 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.32-7.26 (m, 7H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 4.66 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.82 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.68 (dd, *J* = 14.8, 3.8 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7, 141.5, 136.0, 133.6, 131.8, 129.9 (q, *J* = 31.7 Hz), 129.5, 129.4, 128.8, 128.3, 127.8, 125.3 (q, *J* = 4.5 Hz), 123.8 (q, *J* = 274.8 Hz), 60.3, 47.1, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ - 62.68.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{20}F_3O_2S_2^+$: 437.0851; found: 437.0850.



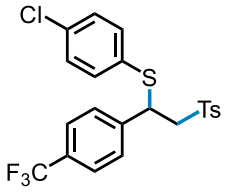
(4-Ethylphenyl)(2-tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)sulfane (4b). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-phenyl 4-ethylbenzenesulfonothioate (278.7 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4b** was obtained as a white solid (122.6 mg, 88% yield); mp: 146 ~147 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, *J* = 15.2, 8.0 Hz, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 4H), 7.04 (d, *J* = 7.6 Hz, 2H), 4.60 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.84-3.78 (m, 1H), 3.67 (dd, *J* = 11.2, 3.6 Hz, 1H), 2.63 (q, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 145.5, 144.6, 141.5, 136.0, 134.2, 129.6 (q, *J* = 33.5 Hz), 129.5, 129.0, 128.3, 128.3, 127.8, 125.2 (q, *J* = 3.3 Hz), 123.9 (q, *J* = 292.0 Hz), 60.3, 47.4, 28.5, 21.3, 15.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ - 62.68.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{24}F_3O_2S_2^+$: 465.1164; found: 465.1165.



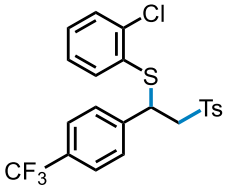
(4-Chlorophenyl)(2-tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)sulfane (4c). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(4-chlorophenyl) 4-methylbenzenesulfonothioate (179.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4c** was obtained as a white solid (124.3 mg, 88% yield); mp: 129 ~ 130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 19.2, 8.0 Hz, 4H), 7.21 (dd, *J* = 18.8, 8.8 Hz, 4H), 7.08 (q, *J* = 8.0 Hz, 4H), 4.62 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.81 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.66 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.8, 141.3, 135.9, 135.2, 135.0, 130.2, 130.0 (q, *J* = 32.9 Hz), 129.6, 129.5, 128.3, 127.8, 125.3 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.1 Hz), 60.2, 47.3, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ - 62.68.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{19}ClF_3O_2S_2^+$: 471.0462; found: 471.0463.



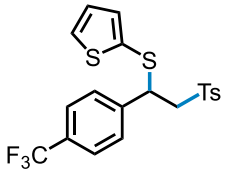
(2-Chlorophenyl)(2-tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)sulfane (4d). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(2-chlorophenyl) 4-methylbenzenesulfonothioate (179.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4d** was obtained as a white solid (114.4 mg, 81% yield); mp: 149~150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 - 7.31 (m, 6H), 7.26 - 7.15 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.82 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.89 (dd, *J* = 14.4, 11.0 Hz, 1H), 3.64 (dd, *J* = 14.8, 3.2 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7, 140.9, 137.6, 135.8, 134.7, 131.1, 130.4, 129.9, 129.8 (q, *J* = 30.1 Hz), 129.6, 128.3, 127.8, 127.5, 125.4 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 271.7 Hz), 60.1, 45.6, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.00.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{19}ClF_3O_2S_2^+$: 471.0462; found: 471.0463.



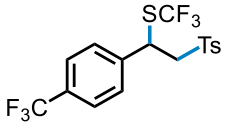
2-((2-Tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)thio)thiophene (4e). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(thiophen-2-yl) 4-methylbenzenesulfonothioate (162.2 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4e** was obtained as a purple solid (94.3 mg, 71% yield); mp: 149 ~ 150 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 4.4, 2.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 4H), 6.98 – 6.95 (m, 2H), 4.50 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.83 (dd, *J* = 14.8, 10.8 Hz, 1H), 3.75 (dd, *J* = 14.7, 4.0 Hz, 1H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7, 141.0, 137.1, 135.9, 132.1, 129.7 (q, *J* = 38.4 Hz), 129.5, 129.3, 128.3, 128.0, 127.8, 125.2 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 260.0 Hz), 59.9, 49.4, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.68.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{18}F_3O_2S_3^+$: 437.0851; found: 427.0850.



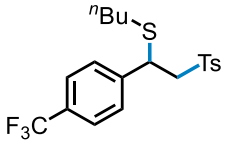
(2-Tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)(trifluoromethyl)sulfane (4f). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(trifluoromethyl) 4-methylbenzenesulfonothioate (153.8 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4f** was obtained as a white solid (70.7 mg, 55% yield); mp: 120 ~ 121 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 – 7.42 (m, 4H), 7.27 – 7.26 (m, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.91 (dd, *J* = 10.5, 3.9 Hz, 1H), 3.90 (dd, *J* = 14.7, 10.5 Hz, 1H), 3.80 (dd, *J* = 15.0, 4.2 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 145.1, 140.1, 135.8, 130.6 (q, *J* = 50.9 Hz), 129.5, 128.4 (q, *J* = 295.0 Hz), 128.4, 128.2, 125.9 (q, *J* = 3.9 Hz), 123.6 (q, *J* = 248.7 Hz), 60.8, 43.1, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -39.85, -62.88.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{15}F_6O_2S_2^+$: 429.0412; found: 429.0412.



Butyl(2-tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)sulfane (4g). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-butyl 4-methylbenzenesulfonothioate (146.6 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on

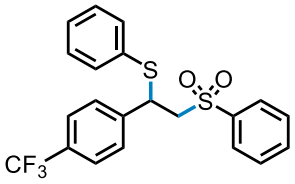
silica gel (petroleum ether/ethyl acetate = 10:1), product **4g** was obtained as a white solid (55.2 mg, 45% yield); mp: 113 ~ 114 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 – 7.41 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.35 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.75 (dd, *J* = 15.0, 10.5 Hz, 1H), 3.66 (dd, *J* = 14.5, 4.0 Hz, 1H), 2.34 (s, 3H), 2.33 – 2.29 (m, 1H), 1.50 – 1.43 (m, 2H), 1.35 – 1.25 (m, 3H), 0.84 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 143.0, 136.2, 129.7 (q, *J* = 32.5 Hz), 129.5, 128.2, 127.8, 125.3 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.6 Hz), 61.0, 43.0, 31.2, 30.9, 21.8, 21.3, 13.5.

^{19}F NMR (471 MHz, $CDCl_3$): δ -62.65.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{24}F_3O_2S_2^+$: 417.1164; found: 417.1165.



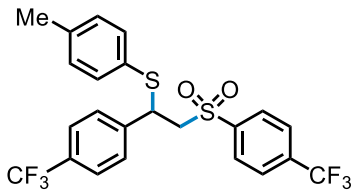
2-((2-Tosyl-1-(4-(trifluoromethyl)phenyl)ethyl)thio)thiophene (4h). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-phenyl benzenesulfonothioate (150.2 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4h** was obtained as a white solid (92.5 mg, 73% yield); mp: 125 ~ 126 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 - 7.50 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.32 - 7.25 (m, 7H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.68 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.83 (dd, *J* = 14.4, 10.8 Hz, 1H), 3.70 (dd, *J* = 15.0, 3.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 141.5, 139.1, 133.6, 133.5, 131.8, 130.0 (q, *J* = 32.0 Hz), 129.4, 129.0, 128.8, 128.3, 127.8, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 271.9 Hz), 60.3, 47.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ - 62.79.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{18}F_3O_2S_2^+$: 423.0695; found: 423.0695.



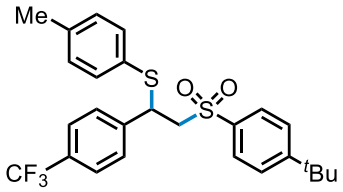
***p*-Tolyl(1-(4-(trifluoromethyl)phenyl)-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)sulfane (4i).** The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-(trifluoromethyl)benzenesulfonothioate (199.4 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4i** was obtained as a purple solid (109.0 mg, 72% yield); mp: 112 ~ 113 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 5.6 Hz, 4H), 4.59 (d, *J* = 8.0 Hz, 1H), 3.89 - 3.80 (m, 1H), 3.72 (d, *J* = 15.2 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 142.6, 141.2, 139.6, 135.2 (q, *J* = 33.0 Hz), 134.3, 130.2, 130.1 (q, *J* = 32.4 Hz), 128.4, 128.3, 127.8, 126.0 (q, *J* = 3.7 Hz), 125.4 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 129.0 Hz), 122.8 (q, *J* = 128.9 Hz), 60.3, 47.4, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.91, -63.54.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{18}F_6O_2S_2^+$: 505.0725; found: 505.0725.



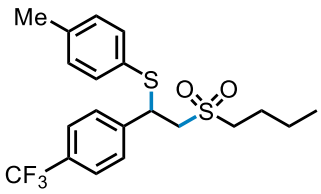
(2-((4-(*tert*-Butyl)phenyl)sulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(*p*-tolyl)sulfane (4j). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-(*tert*-butyl)benzenesulfonothioate (192.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4j** was obtained as a purple solid (115.0 mg, 78% yield); mp: 112~113 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 16.0, 8.0 Hz, 4H), 7.14 – 7.07 (m, 6H), 4.62 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.82 (t, *J* = 12.4 Hz, 1H), 3.69 (d, *J* = 13.2 Hz, 1H), 2.33 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.6, 141.7, 139.2, 136.1, 134.1, 130.1, 129.8 (q, *J* = 32.6 Hz), 128.3, 128.1, 127.6 125.9, 125.3 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 271.1 Hz), 60.2, 47.4, 35.1, 30.8, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.44.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{28}F_3O_2S_2^+$: 493.1477; found: 493.1476.



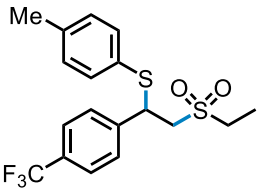
(2-(Butylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(*p*-tolyl)sulfane (4k). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(*p*-tolyl) butane-1-sulfonothioate (144.6 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4k** was obtained as a purple solid (103.7 mg, 83% yield); mp: 111~112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.27 - 7.22 (m, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.69 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.58 (dd, *J* = 14.6, 9.8 Hz, 1H), 3.46 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.58 - 2.43 (m, 2H), 2.33 (s, 3H), 1.67 - 1.52 (m, 2H), 1.27 - 1.18 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.0, 139.4, 134.1, 130.3 (q, *J* =31.9 Hz), 130.2, 128.4, 128.2, 125.8 (q, *J* =3.8 Hz), 123.7 (q, *J* = 270.8 Hz), 57.6, 54.1, 47.4, 23.7, 21.5, 21.2, 13.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.72.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{24}F_3O_2S_2^+$: 417.1164; found: 417.1166.



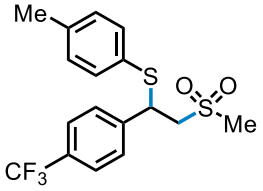
(2-(Ethylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(p-tolyl)sulfane (4l). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(*p*-tolyl) ethanesulfonothioate (129.8 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4l** was obtained as a purple solid (104.9 mg, 90% yield); mp: 114 ~ 115 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.70 (q, *J* = 4.5 Hz, 1H), 3.58 (dd, *J* = 14.8, 9.6 Hz, 1H), 3.48 (dd, *J* = 14.8, 4.6 Hz, 1H), 2.70 - 2.54 (m, 2H), 2.33 (s, 3H), 1.21 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 142.9, 139.3, 134.0, 130.4 (q, *J* = 33.6 Hz), 130.2, 128.3, 128.1, 125.8(q, *J* = 3.7 Hz), 123.8(q, *J* = 272.3 Hz), 56.8, 48.7, 47.2, 21.1, 6.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ - 62.64.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{20}F_3O_2S_2^+$: 389.0851; found:389.0852.



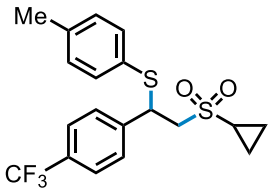
(2-(Methylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(*p*-tolyl)sulfane (4m). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-*p*-tolyl methanesulfonothioate (121.4 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate =10:1), product **4m** was obtained as a purple solid (92.1 mg, 82% yield); mp: 115~116 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.68 (dd, *J* = 9.6, 4.8 Hz, 1H), 3.62 (dd, *J* = 14.4, 9.6 Hz, 1H), 3.55 (dd, *J* = 15.0, 4.7 Hz, 1H), 2.53 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 142.8, 139.5, 134.2, 130.6 (q, *J* = 32.6 Hz), 130.2, 128.4, 128.0, 125.9 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 273.6 Hz), 59.8, 47.5, 42.5, 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.66.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{17}H_{18}F_3O_2S_2^+$: 375.0695; found:375.0695.



(2-(Cyclopropylsulfonyl)-1-(4-(trifluoromethyl)phenyl)ethyl)(*p*-tolyl)sulfane (4n). The title compound was synthesized according to the General Procedure from 1-(trifluoromethyl)-4-vinylbenzene (51.6 mg, 0.3 mmol), *S*-(p-tolyl) cyclopropanesulfonothioate (137.0 mg, 0.60 mmol, 2.0 equiv.), and

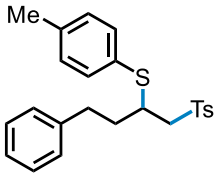
Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **4n** was obtained as a purple solid (90.1 mg, 75% yield); mp: 123~124 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 4.72 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.69 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.57 (dd, *J* = 14.8, 4.4 Hz, 1H), 2.34 (s, 3H), 1.89 - 1.85 (m, 1H), 1.09 (s, 2H), 0.78 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.3, 139.3, 134.2, 130.5 (q, *J* = 36.2 Hz), 130.2, 128.5, 128.4, 125.7 (q, *J* = 3.8 Hz) 123.9 (q, *J* = 295.5 Hz), 58.9, 47.4, 31.1, 21.1, 5.3, 5.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ - 62.62.

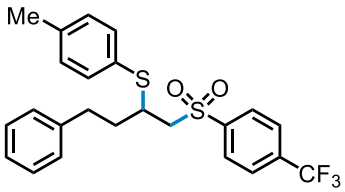
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{19}H_{20}F_3O_2S_2^+$: 461.0239; found:461.0239.



(4-Phenyl-1-tosylbutan-2-yl)(*p*-tolyl)sulfane (6a).[7] The title compound was synthesized according to the General Procedure from but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6a** was obtained as a colorless oil (87.5 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 16.2, 7.8 Hz, 4H), 7.27 - 7.23 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.96 (dd, *J* = 13.2, 8.0 Hz, 4H), 3.32 - 3.19 (m, 2H), 3.15 - 3.10 (m, 1H), 2.97 - 2.90 (m, 1H), 2.86 - 2.78 (m, 1H), 2.54 - 2.45 (m, 1H), 2.42 (s, 3H), 2.30 (s, 3H), 1.89 - 1.74 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.4, 140.8, 137.9, 135.5, 132.9, 129.8, 129.7, 128.8, 128.7, 128.4, 128.0, 126.1, 60.5, 42.1, 34.3, 32.4, 21.6, 21.1.



(4-Phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)butan-2-yl)(*p*-tolyl)sulfane (6b). The title compound was synthesized according to the General Procedure from but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-(trifluoromethyl)benzenesulfonothioate (199.4 mg, 0.60 mmol, 2.0 equiv.), and

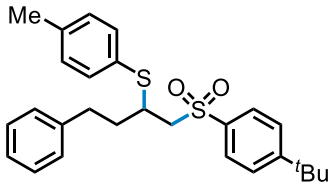
Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6b** was obtained as a white solid (101.7 mg, 73% yield); mp: 105~106 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.34 – 7.28 (m, 3H), 6.94 – 6.89 (m, 4H), 3.29 – 3.28 (m, 2H), 2.99 – 2.83 (m, 3H), 2.61 – 2.53 (m, 1H), 2.30 (s, 3H), 1.91 – 1.82 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 141.4, 140.6, 138.4, 135.0 (q, *J* = 33.4 Hz), 133.3, 13.0, 129.0, 128.6, 128.6, 128.5, 126.3, 126.0 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 274.5 Hz), 60.2, 42.3, 34.2, 32.4, 21.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -63.18.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{24}F_3O_2S_2^+$:505.0725; found:505.0726 .

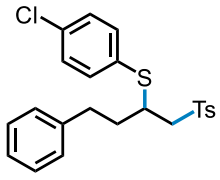


(1-((4-(*tert*-Butyl)phenyl)sulfonyl)-4-phenylbutan-2-yl)(*p*-tolyl)sulfane (6c). The title compound was synthesized according to the General Procedure from but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-(tert-butyl)benzenesulfonothioate (192.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6c** was obtained as a colorless oil (104.6 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, *J* = 18.8, 8.8 Hz, 4H), 7.33 – 7.30 (m, 2H), 7.23 (d, *J* = 6.8 Hz, 3H), 6.98 (s, 4H), 3.35 – 3.12 (m, 3H), 2.97 – 2.90 (m, 1H), 2.86 – 2.79 (m, 1H), 2.55 – 2.43 (m, 1H), 2.31 (s, 3H), 1.89 – 1.79 (m, 1H), 1.35 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.4, 140.9, 137.8, 132.7, 129.9, 129.0, 128.9, 128.8, 128.4 127.8, 126.1, 126.1, 60.4, 42.0, 35.2, 34.2, 32.4, 31.1, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{27}H_{33}O_2S_2^+$: 453.1916; found:453.1917.

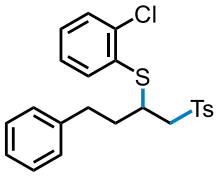


(4-Chlorophenyl)(4-phenyl-1-tosylbutan-2-yl)sulfane (6d). The title compound was synthesized according to the General Procedure from but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol), *S*-(4-chlorophenyl) 4-methylbenzenesulfonothioate (179.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6d** was obtained as a yellow solid (87.9 mg, 68% yield); mp: 87~88 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 - 7.23 (m, 7H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 - 7.05 (m, 2H), 6.97 - 6.92 (m, 2H), 3.30 - 3.19 (m, 2H), 3.16 - 3.09 (m, 1H), 2.97 - 2.91 (m, 1H), 2.86 - 2.78 (m, 1H), 2.59 - 2.51 (m, 1H), 2.43 (s, 3H), 1.91 - 1.82 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7, 140.5, 135.2, 133.8, 133.5, 131.4, 129.7, 129.2, 128.8, 128.5, 128.0, 126.2, 60.4, 42.3, 34.4, 32.4, 21.6.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{24}ClO_2S_2^+$: 431.0901; found:431.0901.

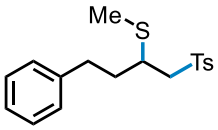


(2-Chlorophenyl)(4-phenyl-1-tosylbutan-2-yl)sulfane (6e). The title compound was synthesized according to the General Procedure from but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol), *S*-(2-chlorophenyl) 4-methylbenzenesulfonothioate (179.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6e** was obtained as a white solid (80.2 mg, 62% yield); mp: 83~84 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.34 - 7.17 (m, 8H), 7.13 (td, *J* = 7.6, 1.6 Hz, 1H), 7.00 (td, *J* = 7.6, 1.6 Hz, 1H), 6.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 3.44 (tt, *J* = 9.8, 2.8 Hz, 1H), 3.37 - 3.22 (m, 2H), 2.99 – 2.93 (m, 1H), 2.86 - 2.77 (m, 1H), 2.64 - 2.53 (m, 1H), 2.43 (s, 3H), 2.01 - 1.90 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7, 140.6, 135.7, 135.5, 132.6, 131.5, 130.1, 129.8, 128.7, 128.4, 128.1, 127.9, 127.3, 126.1, 60.2, 40.3, 34.6, 32.4, 21.6.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{24}ClO_2S_2^+$: 431.0901; found:431.0903.

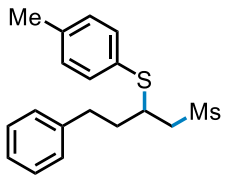


Methyl(4-phenyl-1-tosylbutan-2-yl)sulfane (6f). The title compound was synthesized according to the General Procedure from but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol), *S*-methyl 4-methylbenzenesulfonothioate (121.4 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6f** was obtained as a colorless oil (51.2 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 8.0, 2.6 Hz, 4H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.18 (d, *J* = 6.7 Hz, 2H), 3.42 – 3.28 (m, 2H), 2.89 – 2.81 (m, 2H), 2.75 – 2.68 (m, 1H), 2.44 (s, 3H), 2.32 – 2.23 (m, 1H), 1.95 (s, 3H), 1.88 – 1.79 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.8, 141.0, 129.9, 129.0, 128.6, 128.4, 128.0, 126.0, 61.4, 40.1, 34.8, 32.5, 21.6, 13.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{22}O_2S_2^+$: 334.1056; found: 334.1057.

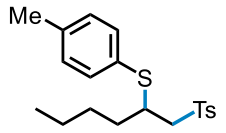


(1-(Methylsulfonyl)-4-phenylbutan-2-yl)(*p*-tolyl)sulfane (6g). The title compound was synthesized according to the General Procedure from but-3-en-1-ylbenzene (39.7 mg, 0.3 mmol), *S*-*p*-tolyl methanesulfonothioate (121.4 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6g** was obtained as a colorless oil (64.2 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 4H), 7.23 – 7.20 (m, 3H), 7.14 (d, J = 7.6 Hz, 2H), 3.52 – 3.46 (m, , 1H), 3.30 (dd, J = 14.4, 4.8 Hz, 1H), 3.18 – 3.12 (m, 1H), 3.01 – 2.93 (m, 1H), 2.88 – 2.83 (m, 1H), 2.80 (s, 3H), 2.39 – 2.20 (m, 1H), 2.34 (s, 3H), 1.98 – 1.89 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.7, 138.6, 133.6, 130.2, 128.6, 128.5, 128.4, 126.2, 59.3, 42.8, 42.0, 35.3, 32.5, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{23}O_2S_2^+$: 335.1134; found: 335.1134.

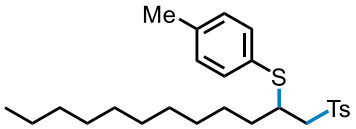


***p*-Tolyl(1-tosylhexan-2-yl)sulfane (6h).**[7] The title compound was synthesized according to the General Procedure from hex-1-ene (25.2 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate

(167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6h** was obtained as a colorless oil (70.7 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.38 - 3.31 (m, 2H), 3.23 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.07- 1.97 (m, 1H), 1.64 - 1.52 (m, 2H), 1.47 - 1.26 (m, 3H), 0.90 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 137.8, 136.4, 132.9, 129.9, 129.8, 129.2, 127.9, 60.6, 43.1, 32.9, 28.6, 22.3, 21.6, 21.1, 13.9.

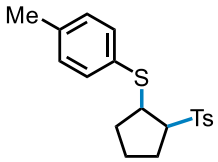


***p*-Tolyl(1-tosyldodecan-2-yl)sulfane (6i).** The title compound was synthesized according to the General Procedure from dodec-1-ene (50.5 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate =20:1), product **6i** was obtained as a colorless oil (96.5 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 3.35 – 3.31 (m, 2H), 3.23 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.44 (s, 3H), 2.32 (s, 3H), 2.05 – 1.97 (m, 1H), 1.58 – 1.53 (m, 2H), 1.45 – 1.42 (m, 1H), 1.27 (s, 14H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 137.8, 136.4, 132.3, 129.8, 129.7, 129.2, 127.9, 127.5, 60.5, 43.2, 33.2, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 26.4, 22.6, 21.6, 21.2, 14.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{39}O_2S_2^+$: 447.2386; found: 447.2386.

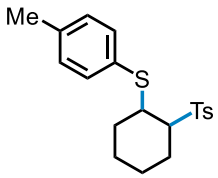


***p*-Tolyl-2-tosylcyclopentyl)sulfane (6j).**[8] The title compound was synthesized according to the General Procedure from cyclopentene (20.4 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification

by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6j** was obtained as a colorless oil (62.4 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 3.85 - 3.82 (m, 1H), 3.44 - 3.40 (m, 1H), 2.45 (s, 3H), 2.32 (s, 3H), 2.28 - 2.07 (m, 3H), 1.92 - 1.86 (m, 2H), 1.79 - 1.72 (m, 1H).

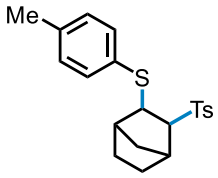
^{13}C NMR (150 MHz, $CDCl_3$): δ 144.4, 137.7, 135.2, 132.8, 130.1, 129.7, 129.6, 128.5, 69.6, 48.4, 33.3, 25.9, 24.5, 21.6, 21.1.



***p*-Tolyl(2-tosylcyclohexyl)sulfane (6k).**[8] The title compound was synthesized according to the General Procedure from cyclohexene (24.6 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6k** was obtained as a colorless oil (68.1 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 3H), 7.05 (dt, *J* = 8.0, 2.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.72 (q, *J* = 3.9 Hz, 1H), 3.07 – 3.04 (m, 1H), 2.46 (s, 3H), 2.41 – 2.39 (m, 1H), 2.32 (s, 3H), 2.19 – 2.10 (m, 1H), 2.08 – 2.03 (m, 1H), 1.97 – 1.88 (m, 1H), 1.80 – 1.75 (m, 1H), 1.65 – 1.52 (m, 3H).

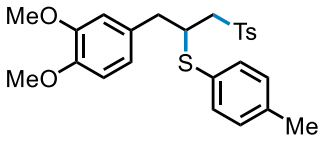
^{13}C NMR (150 MHz, $CDCl_3$): δ 144.3, 137.4, 135.3, 132.1, 130.2, 129.8, 129.6, 128.5, 62.7, 43.1, 27.6, 21.6, 21.5, 21.3, 21.1, 20.9.



***p*-Tolyl(3-tosylbicyclo[2.2.1]heptan-2-yl)sulfane (6l).**[8] The title compound was synthesized according to the General Procedure from bicyclo[2.2.1]hept-2-ene (28.3 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6l** was obtained as a colorless oil (64.8 mg, 58% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 3.72 – 3.69 (m, 1H), 2.82 (d, *J* = 4.5 Hz, 1H), 2.67 (dd, *J* = 6.5, 1.5 Hz, 1H), 2.44 (s, 3H), 2.34 – 2.32 (m, 1H), 2.31 (s, 3H), 2.13 – 2.07 (m, 1H), 2.00 – 1.97 (m, 1H), 1.69 – 1.62 (m, 1H), 1.45 – 1.38 (m, 2H), 1.24 – 1.19 (m, 1H).

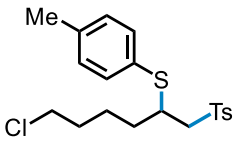
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 137.4, 135.6, 132.4, 131.0, 129.7, 129.6, 128.6, 72.3, 51.9, 41.3, 39.4, 36.6, 29.4, 22.2, 21.6, 21.0.



(1-(3,4-Dimethoxyphenyl)-3-tosylpropan-2-yl)(*p*-tolyl)sulfane (6m).[8] The title compound was synthesized according to the General Procedure from 4-allyl-1,2-dimethoxybenzene (53.5 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6m** was obtained as a colorless oil (93.2 mg, 68% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.81 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.61 – 3.56 (m, 1H), 3.33 (dd, *J* = 14.6, 9.0 Hz, 1H), 3.26 (td, *J* = 14.5, 4.2 Hz, 2H), 2.97 (dd, *J* = 14.3, 7.8 Hz, 1H), 2.43 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 148.7, 147.8, 144.6, 137.8, 136.2, 132.7, 129.8, 129.7, 129.2, 127.8, 121.8, 112.8, 110.9, 58.8, 55.8, 44.4, 38.9, 21.5, 21.0.

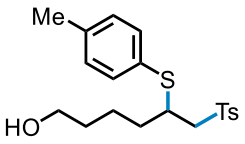


(6-Chloro-1-tosylhexan-2-yl)(*p*-tolyl)sulfane (6n). The title compound was synthesized according to the General Procedure from 6-chlorohex-1-ene (35.6 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6n** was obtained as a colorless oil (66.7 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.53 (t, *J* = 6.2 Hz, 2H), 3.34 (dd, *J* = 14.8, 2.8Hz, 2H), 3.22 (dd, *J* = 14.8, 10.4 Hz, 1H), 2.44 (s, 3H), 2.32 (s, 3H), 2.09 - 2.04 (m, 1H), 1.81 - 1.73 (m, 3H), 1.62 - 1.57 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.7, 138.0, 136.2, 133.0, 129.9, 129.8, 128.7, 127.8, 60.4. 44.6, 42.9, 32.2, 32.0, 23.8, 21.6, 21.0.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{26}ClO_2S_2^+$: 397.1057; found: 397.1057.

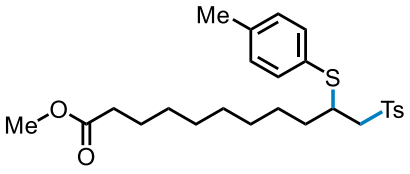


5-(*p*-Tolylthio)-6-tosylhexan-1-ol (6o). The title compound was synthesized according to the General Procedure from hex-5-en-1-ol (30.1 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6o** was obtained as a colorless oil (69.2 mg, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 5.4 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.64 – 3.62 (m, 2H), 3.38 – 3.31 (m, 2H), 3.25 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.43 (s, 3H), 2.31 (s, 3H), 2.22 – 2.13 (m, 1H), 2.08 – 2.03 (m, 1H), 1.71 – 1.52 (m, 5H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 137.8, 136.0, 132.8, 129.7, 129.6, 128.8, 127.7, 62.1, 60.2, 42.9, 32.6, 31.9, 22.4, 21.5, 20.9.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{20}H_{27}O_3S_2^+$: 379.1396; found: 379.1397.

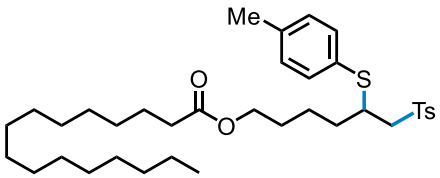


Methyl 10-(*p*-tolylthio)-11-tosylundecanoate (6p). The title compound was synthesized according to the General Procedure from methyl undec-10-enoate (59.5 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **6p** was obtained as a colorless oil (105.8 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.67 (s, 3H), 3.38 – 3.30 (m, 2H), 3.22 (dd, *J* = 14.4, 10.0 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 2.30 (d, *J* = 7.6 Hz, 2H), 2.06 – 1.98 (m, 1H), 1.65 – 1.52 (m, 4H), 1.43 (br, 1H), 1.29 (s, 8H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 174.3, 144.6, 137.8, 136.4, 132.9, 129.9, 129.8, 129.2, 127.9, 60.5, 51.4, 43.1, 34.1, 33.1, 29.2, 29.1, 29.0, 26.4, 24.9, 21.6, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{26}H_{37}O_4S_2^+$: 477.2128; found:477.2129.

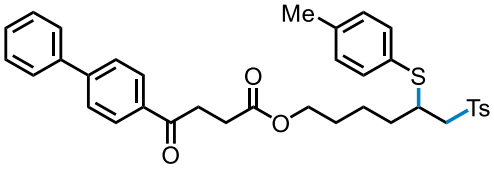


5-(*p*-Tolylthio)-6-tosylhexyl palmitate (6q). The title compound was synthesized according to the General Procedure from hex-5-en-1-yl palmitate (101.6 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6q** was obtained as a colorless oil (127.7 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.37 - 3.34 (m, 1H), 3.31 (d, *J* = 2.8 Hz, 1H), 3.21 (dd, *J* = 14.4, 10.0 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H), 2.30 (d, *J* = 7.6 Hz, 1H), 2.11 - 2.05 (m, 1H), 1.71 - 1.57 (m, 7H), 1.29 - 1.25 (m, 25H), 0.89 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 173.9, 144.7, 138.0, 136.4, 133.0, 129.9, 129.8, 128.9, 127.9, 63.9, 60.5, 43.0, 34.4, 32.8, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 28.2, 25.0, 23.0, 22.7, 21.6, 21.1, 14.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{36}H_{57}O_4S_2^+$: 617.3693; found:617.3694.



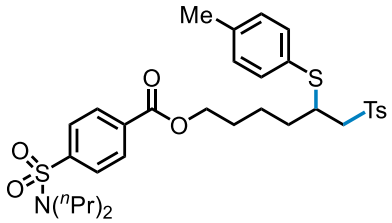
5-(*p*-Tolylthio)-6-tosylhexyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (6r). The title compound was synthesized according to the General Procedure from hex-5-en-1-yl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate (100.9 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol,

2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6r** was obtained as a colorless oil (103.3 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (t, *J* = 1.2 Hz, 1H), 8.05 (t, *J* = 1.2 Hz, 1H), 7.68 – 7.63 (m, 4H), 7.62 – 7.60 (m, 2H), 7.47 – 7.44 (m, 2H), 7.41 – 7.38 (m, 1H), 7.29 (dd, *J* = 5.6, 0.4 Hz, 2H), 7.12 – 7.10 (m, 2H), 7.02 (dd, *J* = 5.6, 0.4 Hz, 2H), 4.13 – 4.11 (m, 2H), 3.36 (t, *J* = 4.6 Hz, 3H), 3.32 (dd, *J* = 9.6 2.0 Hz, 1H), 3.22 (dd, *J* = 9.6, 6.8 Hz, 1H), 2.81 (t, *J* = 4.4 Hz, 2H), 2.44 (s, 3H), 2.32 (s, 3H), 2.10 – 2.05 (m, 1H), 1.71 – 1.66 (m, 2H), 1.63 – 1.61 (m, 2H), 1.56 – 1.53 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 197.7, 172.9, 145.8, 144.7, 139.8, 138.0, 136.4, 135.3, 133.0, 129.9, 129.8, 128.9, 128.6, 128.2, 127.9, 127.2, 64.4, 60.5, 43.0, 33.5, 32.8, 28.4, 28.2, 23.0, 21.6, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{36}H_{39}O_5S_2^+$: 615.2233; found:615.2234.

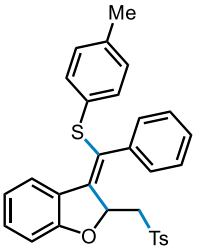


5-(*p*-Tolylthio)-6-tosylhexyl 4-(*N*,*N*-diethylsulfamoyl)benzoate (6s). The title compound was synthesized according to the General Procedure from hex-5-en-1-yl 4-(*N*,*N*-diethylsulfamoyl)benzoate (101.8 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (61.2 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1), product **6s** was obtained as a yellow oil (96.9 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.11 (dd, *J* = 6.4, 2.0 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 4.37 (t, *J* = 5.8 Hz, 2H), 3.45 – 3.39 (m, 1H), 3.35 (dd, *J* = 14.4, 2.8 Hz, 1H), 3.23 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.12 – 3.08 (m, 4H), 2.45 (s, 3H), 2.33 (s, 3H), 2.20 – 2.14 (m, 1H), 1.86 – 1.79 (m, 3H), 1.71 – 1.65 (m, 2H), 1.58 – 1.50 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.2, 144.8, 144.2, 138.1, 136.4, 133.7, 132.9, 130.2, 130.0, 129.9, 128.8, 127.9, 127.0, 65.3, 60.5, 49.9, 42.9, 32.8, 28.2, 23.1, 21.9, 21.6, 21.1, 11.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{45}NO_6S_3^+$: 646.2325; found: 646.2325.

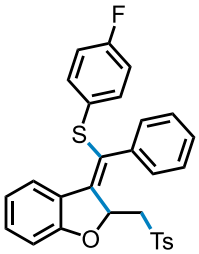


***(E)*-3-(Phenyl(*p*-tolylthio)methylene)-2-(tosylmethyl)-2,3-dihydrobenzofuran (8a).** The title compound was synthesized according to the General Procedure from 1-(phenylethynyl)-2-(vinyloxy)benzene (66.1 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1~3:1), product **8a** was obtained as a colorless oil (127.2 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.15 (m, 5H), 7.07 – 6.98 (m, 3H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.52 (t, *J* = 7.6 Hz, 1H), 6.24 (d, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 9.2 Hz, 1H), 4.04 (dt, *J* = 14.8, 1.4 Hz, 1H), 3.61 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.43 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.7, 144.3, 137.9, 137.6, 137.4, 136.8, 132.2, 130.9, 129.5, 129.4, 128.9, 128.8, 128.76, 128.75, 128.1, 128.0, 126.1, 124.6, 121.2, 110.8, 79.6, 58.9, 21.6, 21.0.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{27}O_3S_2^+$: 499.1396; found:499.1396.



(*E*)-3-(((4-Fluorophenyl)thio)(phenyl)methylene)-2-(tosylmethyl)-2,3-dihydrobenzofuran (8b). The title compound was synthesized according to the General Procedure from 1-(phenylethynyl)-2-(vinyloxy)benzene (66.1 mg, 0.3 mmol), *S*-(4-fluorophenyl) 4-methylbenzenesulfonothioate (169.4 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8b** was obtained as a colorless oil (126.7 mg, 84% yield).

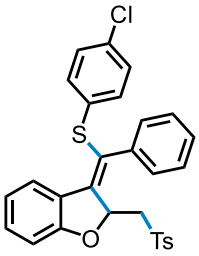
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 3H), 7.15 – 7.10 (m, 4H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.81 (t, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.52 (t, *J* = 7.4

Hz, 1H), 6.22 (d, *J* = 7.6 Hz, 1H), 6.06 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.00 (dd, *J* = 14.6, 2.2 Hz, 1H), 3.63 (dd, *J* = 14.8, 9.2 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.5, 162.4 (d, *J* = 249.2 Hz), 144.6, 137.3 (d, *J* = 157.0 Hz), 137.2, 134.6, 134.5, 130.5, 129.6, 129.4, 128.6, 128.5, 128.3, 127.7, 126.9 (d, *J* = 3.0 Hz), 123.7, 123.6, 120.9, 115.9 (d, *J* = 22.7 Hz), 111.0, 80.4, 59.9, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.04 – -113.13 (m).

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{24}FO_3S_2^+$: 503.1145; found:503.1146.

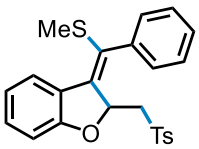


(*E*)-3-(((4-Chlorophenyl)thio)(phenyl)methylene)-2-(tosylmethyl)-2,3-dihydrobenzofuran (8c). The title compound was synthesized according to the General Procedure from 1-(phenylethynyl)-2-(vinyloxy)benzene (66.1 mg, 0.3 mmol), *S*-(4-chlorophenyl) 4-methylbenzenesulfonothioate (179.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8c** was obtained as a colorless oil (138.6 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.19 (m, 5H), 7.12 – 7.03 (m, 5H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.54 (t, *J* = 7.6 Hz, 1H), 6.30 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.03 (dd, *J* = 9.4, 1.8 Hz, 1H), 3.96 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.63 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.7, 144.6, 139.6, 137.1, 136.9, 133.6, 132.8, 130.8, 130.7, 129.6, 129.4, 128.9, 128.6, 128.5, 128.4, 126.5, 123.7, 123.6, 121.0, 111.1, 80.6, 60.0, 21.6.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{29}H_{24}ClO_3S_2^+$: 519.0850; found: 519.0850.



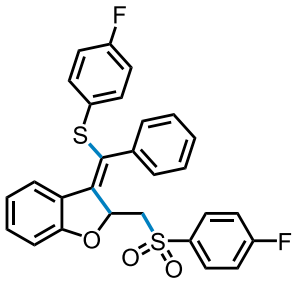
(*E*)-3-((Methylthio)(phenyl)methylene)-2-(tosylmethyl)-2,3-dihydrobenzofuran (8d). The title compound was synthesized according to the General Procedure from 1-(phenylethynyl)-2-

(vinyloxy)benzene (66.1 mg, 0.3 mmol), *S*-methyl 4-methylbenzenesulfonothioate (121.4 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8d** was obtained as a colorless oil (95.1 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.47 - 7.39 (m, 3H), 7.36 (d, *J* = 8.4 Hz, 3H), 7.27 (br, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 7.2 Hz, 1H), 6.49 (t, *J* = 7.6 Hz, 2H), 6.08 (d, *J* = 9.2 Hz, 1H), 5.95 (d, *J* = 9.6 Hz, 1H), 3.96 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.49 (dd, *J* = 14.6, 9.8 Hz, 1H), 2.47 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.0, 144.5, 137.3, 136.3, 134.3, 129.7, 129.6, 129.5, 129.4, 129.2, 129.1, 128.5, 124.1, 123.1, 120.8, 110.8, 80.1, 59.2, 21.7, 15.2.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{24}H_{23}O_3S_2^+$: 445.0903; found: 445.0903.



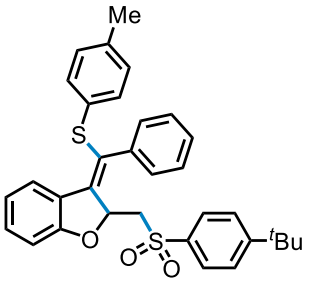
(*E*)-2-(((4-Fluorophenyl)sulfonyl)methyl)-3-(((4-fluorophenyl)thio)(phenyl)methylene)-2,3-dihydrobenzofuran (8e). The title compound was synthesized according to the General Procedure from 1-(phenylethynyl)-2-(vinyloxy)benzene (66.1 mg, 0.3 mmol), *S*-(4-fluorophenyl) 4-fluorobenzenesulfonothioate (161.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8e** was obtained as a white solid (130.7 mg, 86% yield); mp: 153~154 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 7.98 (m, 2H), 7.23 – 7.20 (m, 5H), 7.16 – 7.11 (m, 4H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 8.8 Hz, 2H), 6.55 - 6.51 (m, 2H), 6.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.07 (dd, *J* = 9.4, 1.8 Hz, 1H), 4.03 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.65 (dd, *J* = 14.8, 9.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.8 (d, *J* = 256.7 Hz), 162.5 (d, *J* = 249.2 Hz), 162.3, 137.0 (d, *J* = 99.7 Hz), 136.3 (d, *J* = 3.0 Hz), 134.7, 134.6, 131.4 (d, *J* = 10.6 Hz), 130.6, 129.4, 128.6, 128.4, 128.1, 126.7 (d, *J* = 4.53 Hz), 123.7, 123.6, 121.2, 116.2 (d, *J* = 36.2 Hz), 116.0 (d, *J* = 34.7 Hz), 110.8, 80.4, 59.9.

^{19}F NMR (376 MHz, CDCl3): δ -103.62 – -103.69 (m), -112.87– -112.94 (m).

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{21}F_2O_3S_2^+$: 475.0096; found:475.0098.

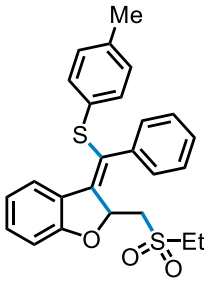


(*E*)-2-(((4-(*tert*-Butyl)phenyl)sulfonyl)methyl)-3-(phenyl(*p*-tolylthio)methylene)-2,3-dihydrobenzofuran (8f). The title compound was synthesized according to the General Procedure from 1-(phenylethynyl)-2-(vinyloxy)benzene (66.1 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-(*tert*-butyl)benzenesulfonothioate (192.3 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8f** was obtained as a colorless oil (146.0 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.22 - 7.17 (m, 5H), 7.04 – 6.98 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.57 (d, J = 8.0 Hz, 1H), 6.53 - 6.49 (m, 1H), 6.23 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.03 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.03 (dd, *J* = 14.6, 1.8 Hz, 1H), 3.62 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.22 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.6, 157.5, 138.1, 137.7, 137.3, 137.0, 132.1, 130.4, 129.5, 129.4, 128.5, 128.3, 128.2, 128.1, 128.0, 126.0, 123.9, 123.6, 120.8, 110.9, 80.5, 59.9, 35.2, 31.1, 21.0.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{33}O_3S_2^+$: 541.1866; found: 541.1867.

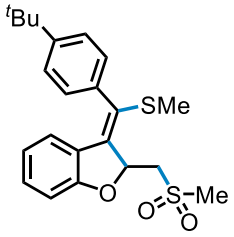


(*E*)-2-((Ethylsulfonyl)methyl)-3-(phenyl(*p*-tolylthio)methylene)-2,3-dihydrobenzofuran (8g). The title compound was synthesized according to the General Procedure from 1-(phenylethynyl)-2-(vinyloxy)benzene (66.1 mg, 0.3 mmol), *S*-(*p*-tolyl) ethanesulfonothioate (129.8 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8g** was obtained as a colorless oil (111.3 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.8 Hz, 5H), 7.11 (dd, *J* = 20.4, 8.4 Hz, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.59 (t, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 7.6 Hz, 1H), 6.14 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.88 (dt, *J* = 15.2, 1.6 Hz, 1H), 3.47 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.39 - 3.19 (m, 2H), 2.22 (s, 3H), 1.43 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.2, 137.9, 137.2, 137.0, 132.5, 130.5, 129.6, 129.5, 129.1, 128.5, 128.2, 128.0, 124.1, 123.9, 121.3, 110.8, 80.8, 55.5, 49.5, 21.0, 6.7.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{25}O_3S_2^+$: 437.1240; found:437.1239.

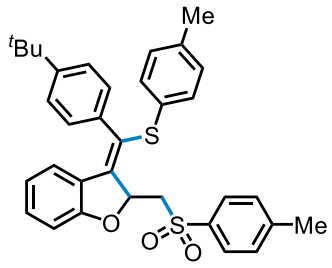


(*Z*)-3-((4-(tert-Butyl)phenyl)(methylthio)methylene)-2-((methylsulfonyl)methyl)-2,3-dihydrobenzofuran (8h). The title compound was synthesized according to the General Procedure from 1-((4-(*tert*-butyl)phenyl)ethynyl)-2-(vinyloxy)benzene (82.9 mg, 0.3 mmol), *S*-methyl methanesulfonothioate (75.7 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8h** was obtained as a colorless oil (102.7 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.28 – 7.25 (m, 3H), 7.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.03 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 1H), 5.76 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.06 (dd, *J* = 14.8, 10.4 Hz, 1H), 2.79 (s, 3H), 1.95 (s, 3H), 1.34 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 161.8, 152.1, 133.5, 132.4, 131.8, 130.1, 128.5, 126.5, 126.2, 125.0, 121.4, 110.3, 80.0, 58.1, 42.5, 34.8, 31.2, 15.4.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{27}O_3S_2^+$: 403.1396; found:403.1395.



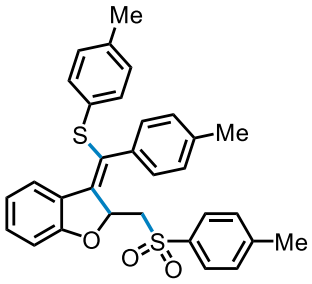
(*Z*)-3-((4-(*tert*-Butyl)phenyl)(p-tolylthio)methylene)-2-(tosylmethyl)-2,3-dihydrobenzofuran (8i). The title compound was synthesized according to the General Procedure from 1-((4-(*tert*-

butyl)phenyl)ethynyl)-2-(vinyloxy)benzene (82.9 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8i** was obtained as a white solid (141.5 mg, 85% yield); mp: 153-154 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.26-7.17 (m, 5H), 7.10-7.05 (m, 4H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.91 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.16 (dd, *J* = 14.8, 10.0 Hz, 1H), 3.02 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.43 (s, 3H), 2.20 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.7, 151.2, 144.3, 137.6, 137.1, 137.0, 136.5, 135.1, 131.8, 130.8, 129.4, 129.3, 129.2, 128.5, 128.2, 126.1, 125.6, 124.7, 121.1, 110.7, 79.7, 58.7, 34.6, 31.2, 21.6, 21.0.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{34}H_{35}O_3S_2^+$: 555.2022; found:555.2022.

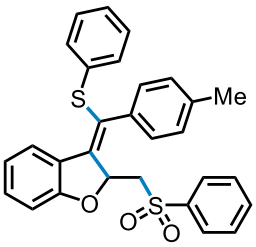


(*E*)-3-(*p*-tolyl(*p*-tolylthio)methylene)-2-(tosylmethyl)-2,3-dihydrobenzofuran (8j). The title compound was synthesized according to the General Procedure from 1-(*p*-tolylethynyl)-2-(vinyloxy)benzene (70.3 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8j** was obtained as a colorless oil (118.4 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.09 - 6.99 (m, 7H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.54 (t, *J* = 7.6 Hz, 1H), 6.33 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.00 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.03 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.60 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.43 (s, 3H), 2.29 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.6, 144.5, 138.5, 138.0, 137.3, 137.2, 134.3, 131.5, 130.4, 129.6, 129.5, 129.2, 129.1, 128.8, 128.5, 127.9, 124.0, 123.7, 120.8, 110.9, 80.6, 60.0, 21.6, 21.3, 21.0.

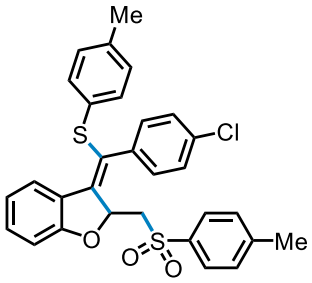
HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{31}H_{29}O_3S_2^+$: 513.1553; found:513.1534.



(*E*)-2-((Phenylsulfonyl)methyl)-3-((phenylthio)(*p*-tolyl)methylene)-2,3-dihydrobenzofuran (8k).[9] The title compound was synthesized according to the General Procedure from 1-(*p*-tolylethynyl)-2-(vinyloxy)benzene (70.3 mg, 0.3 mmol), *S*-(*p*-tolyl) benzenesulfonothioate (158.6 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8k** was obtained as a white solid (138.1 mg, 95% yield); mp: 152-153 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.13 (br, 7H), 7.03 (t, *J* = 6.0 Hz, 3H), 6.55 (t, *J* = 7.6 Hz, 2H), 6.38 (d, *J* = 9.6 Hz, 1H), 6.03 (dd, *J* = 9.6, 2.0 Hz, 1H), 4.04 (dd, *J* = 14.8, 2.0 Hz, 1H), 3.63 (dd, *J* = 14.8, 9.6 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.6, 140.2, 139.1, 138.2, 134.2, 133.5, 132.5, 131.2, 130.5, 129.3, 129.2, 128.9, 128.8, 128.4, 127.3, 127.2, 123.8, 123.7, 120.9, 110.9, 80.6, 59.9, 21.3.

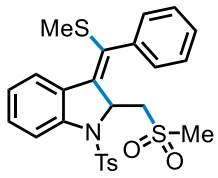


(*E*)-3-((4-Chlorophenyl)(*p*-tolylthio)methylene)-2-(tosylmethyl)-2,3-dihydrobenzofuran (8l). The title compound was synthesized according to the General Procedure from 1-((4-chlorophenyl)ethynyl)-2-(vinyloxy)benzene (76.4 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8l** was obtained as a white solid (132.7 mg, 83% yield); mp: 189-190 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.14 (br, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.57 (t, *J* = 7.8 Hz, 1H), 6.31 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.02 (dd, *J* = 9.3, 2.1 Hz, 1H), 4.00 (dd, *J* = 14.7, 2.1 Hz, 1H), 3.62 (dd, *J* = 14.7, 9.3 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.7, 144.6, 138.9, 137.9, 137.2, 135.8, 134.0, 132.0, 130.8, 130.7, 129.7, 129.6, 128.8, 128.5, 128.1, 126.5, 123.6, 123.5, 121.0, 111.2, 80.6, 59.9, 21.6, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{30}H_{26}ClO_3S_2^+$:498.1318; found:498.1320.

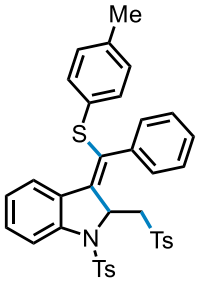


(*E*)-2-((Methylsulfonyl)methyl)-3-((methylthio)(phenyl)methylene)-1-tosylindoline (8m). The title compound was synthesized according to the General Procedure from 4-methyl-*N*-(2-(phenylethynyl)phenyl)-*N*-vinylbenzenesulfonamide (112.0 mg, 0.3 mmol), *S*-methyl methanesulfonothioate (75.7 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8l** was obtained as a yellow solid (109.3 mg, 70% yield); mp: 111-112 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.20 (m, 3H), 7.18 – 7.13 (m, 2H), 6.89 (s, 3H), 6.78 (td, *J* = 7.6, 1.2 Hz, 1H), 6.08 (d, *J* = 6.4 Hz, 1H), 5.64 (dd, *J* = 7.6, 2.8 Hz, 1H), 3.69 (dd, *J* = 15.4, 7.8 Hz, 1H), 3.57 (dd, *J* = 15.4, 1.8 Hz, 1H), 3.25 (s, 3H), 2.45 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.6, 143.7, 138.0, 136.1, 133.8, 133.0, 132.5, 131.3, 129.7, 129.4, 129.2, 128.3, 127.9, 126.1, 124.0, 119.9, 63.5, 58.8, 43.0, 21.6, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{26}NO_4S_2^+$: 500.1018; found: 500.1018.

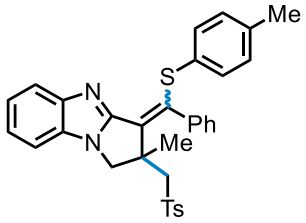


(*E*)-3-(Phenyl(*p*-tolylthio)methylene)-1-tosyl-2-(tosylmethyl)indoline (8n)[9]**.** The title compound was synthesized according to the General Procedure from 4-methyl-*N*-(2-(phenylethynyl)phenyl)-*N*-vinylbenzenesulfonamide (112.0 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8n** was obtained as a yellow solid (132.7 mg, 88% yield, *E*/*Z* > 20:1); mp: 90-91 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.24 (m, 4H), 7.16 (d, *J* = 8.0 Hz, 3H), 7.09 – 7.05 (m, 1H), 6.90 (s, 3H), 6.71 – 6.70 (m, 1H), 6.07 (d, *J* = 6.8 Hz, 1H), 5.47 (dd, *J* = 6.0, 3.2 Hz, 1H), 4.14 (dd, *J* = 15.2, 6.0 Hz, 1H), 3.99 (dd, *J* = 15.2, 3.2 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 144.2, 140.8, 137.8, 137.1, 136.6, 134.5, 133.5, 132.5, 131.2, 130.6, 129.6, 129.4, 129.3, 129.0, 128.2, 128.1, 127.8, 127.4, 127.2, 125.0, 123.8, 118.5, 63.2, 58.9, 21.6, 21.5, 21.1.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{25}H_{26}NO_4S_2^+$: 652.1644; found: 652.1644.



2-Methyl-3-(phenyl(*p*-tolylthio)methylene)-2-(tosylmethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (8o). The title compound was synthesized according to the General Procedure from 1-(2-methylallyl)-2-(phenylethynyl)-1H-benzo[d]imidazole (81.7 mg, 0.3 mmol), *S*-(*p*-tolyl) 4-methylbenzenesulfonothioate (167.0 mg, 0.60 mmol, 2.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (7.86 mg, 3.0 mol%). After purification by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1), product **8o** was obtained as a pink solid (140.4 mg, 85% yield, *E*/*Z* = 1.4:1); mp: 155-156 ºC.

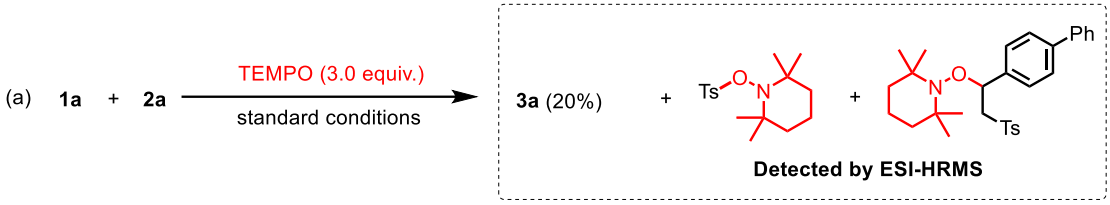
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 – 7.96 (m, 0.43H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 8.4 Hz 0.45H) 7.45 (d, *J* = 8.2 Hz, 1.13H), 7.36 – 7.34 (m, 0.81H), 7.31 – 7.26 (m, 4.42H), 7.23 (d, *J* = 8.0 Hz, 1.22H), 7.19 – 7.11 (m, 2.77H), 7.09 – 7.06 (m, 2.39H), 7.01 (d, *J* = 8.0 Hz, 1.24H), 7.01 (d, *J* = 6.2 Hz, 1.01H), 6.88 (d, *J* = 7.9 Hz, 1.16H), 5.00 (d, *J* = 10.8 Hz, 0.48H), 4.81 (d, *J* = 11.1 Hz, 0.67H), 4.44 (d, *J* = 14.4Hz, 0.46H) 4.14 – 4.07 (m, 1.60H), 3.26 – 3.16 (m, 1.22H), 2.42 (s, 1H), 2.41 (s, 1.6H), 2.19 (s, 1.2H), 2.17 (s, 1.63H), 2.02 (s, 1.22H), 1.39 (s, 1.70H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 155.1(149.2), 148.6, 144.9(144.6), 143.28, 139.77, 138.59, 137.9(137.7), 136.7(136.6), 134.9, 132.5, 131.8(131.7), 130.4(130.3), 130.0(129.8), 129.4(128.9), 128.1(128.0), 127.8(127.7), 127.5, 127.3, 126.8, 125.0, 122.9(122.6), 122.4(122.2), 120.9(120.8), 109.6(109.3), 63.5(61.5), 53.6(53.3), 50.4(50.3), 26.7(26.3), 21.6(21.5), 21.1(21.0).

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{33}H_{31}N_2O_2S_2^+$: 551.1821; found: 551.1821.

6. Mechanistic Studies.

6.1 Radical Inhibition Experiment.



Alkene **1a** (0.30 mmol), thiosulfonate **2a** (0.6 mmol, 2.0 equiv.), TEMPO (140.6 mg, 0.9 mmol, 3.0 equiv.), and Cu(BINAP)(MeCN)PF_6 (3.0 mol%) was sequentially added in a dry Schlenk tube equipped with a magnetic stirrer bar. The tube was capped with a rubber septum, and then it was evacuated and backfilled with nitrogen (3 cycles). *N*, *N*-dimethylacetamide (DMA) (6.0 mL) was added via syringe, and the resulting mixture was degassed via three freeze-pump-thaw cycles. Under efficient stirring, the reaction mixture was then irradiated by 40-watt blue-LED lamps (427nm) with fan at rt for 24 h. After irradiation, the reaction mixture was rapidly extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The mixture was analyzed by ^{1}H NMR and ESI-HRMS. The reaction was inhibited to varying degrees, with the target product obtained in yields of 20%. Trapping product (**Figure S2**) were detected by ESI-HRMS.

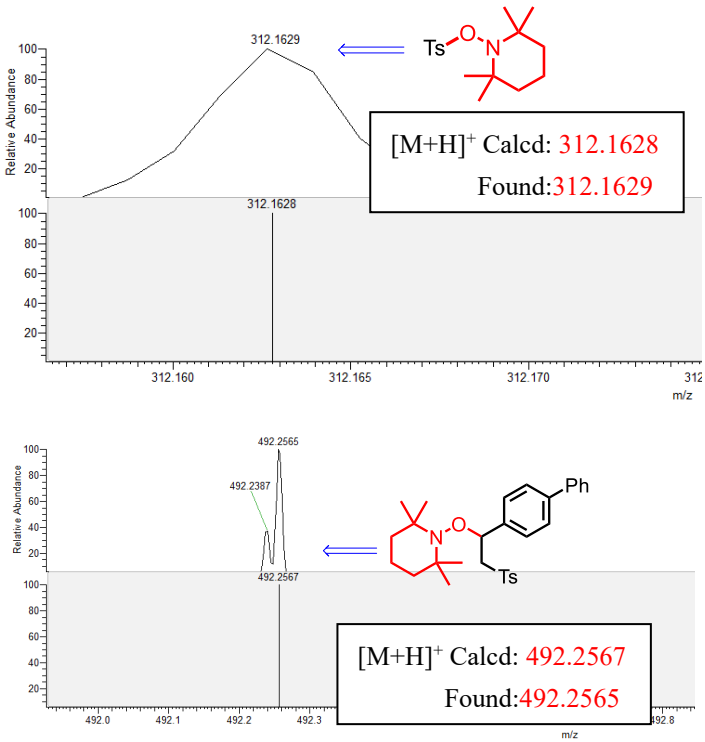
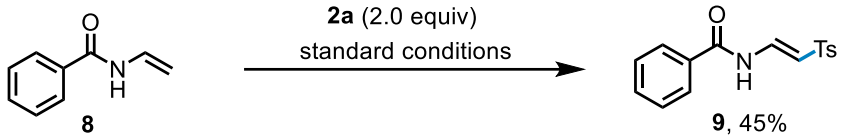


Figure S2

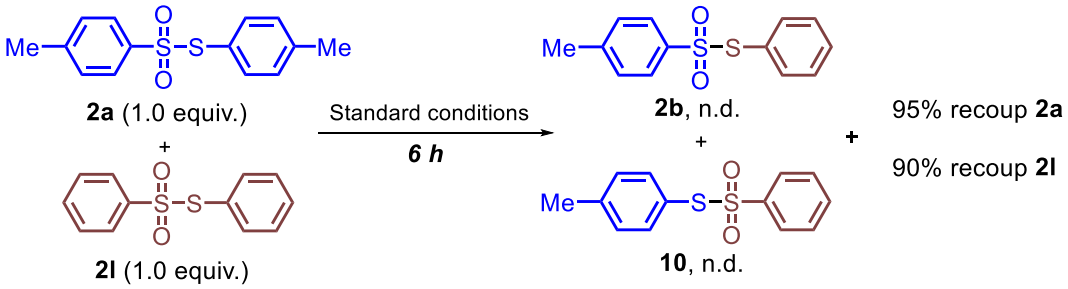
6.2 Radical capture experiment.



Acrylamide **8** (0.30 mmol), thiosulfonate **2a** (0.6 mmol, 2.0 equiv.) and Cu(BINAP)(MeCN)PF_6 (3.0 mol%) were successively added to a dry Schlenk tube equipped with a magnetic stirring rod. The tube is covered with a rubber diaphragm, then vacuumed and backfilled with nitrogen (3 cycles). *N,N*-dimethylacetamide (DMA) (6.0 mL) was added through a syringe and the resulting mixture was degassed through three freeze-pump-thawing cycles. Under high efficiency agitation, the reaction mixture was irradiated at room temperature for 24 h with a 40 W blue led lamp (427 nm) and a fan. After irradiation, the reaction mixture was rapidly extracted with ethyl acetate for 3 times. The bonded organic layer is washed with salt water, dried on anhydrous sodium sulfate, and concentrated under reduced pressure. The product was analyzed by ^{1}H NMR and **9** with a yield of 45% was obtained.[10] **(*E*)-*N*-(2-tosylvinyl)benzamide.** White solid (40.7 mg, 45% yield), m.p. 105–107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.02 (d, *J* = 10.8 Hz, 1H), 8.11 (dd, *J* = 13.7, 10.8 Hz, 1H), 7.85 (d, *J* = 5.6 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.30 – 7.24 (m, 2H), 6.46 (d, *J* = 13.7 Hz, 1H), 2.40 (s, 3H).

6.3 Radical capture experiment.

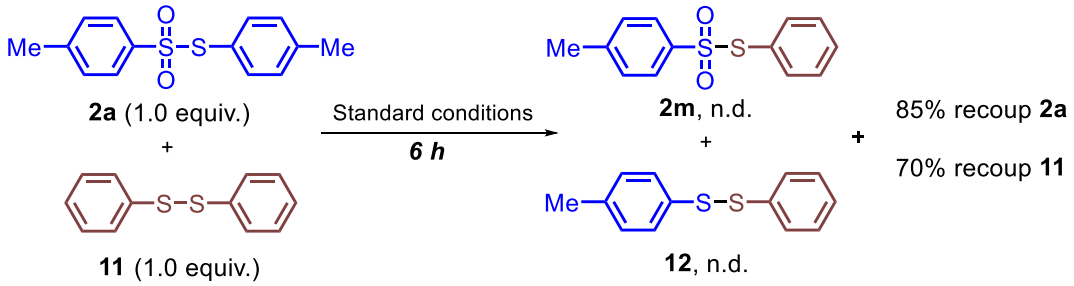
Scrambling experiment between thiosulfonates 2a and 2l.



Thiosulfonate **2a** (0.1 mmol), **2l** (0.1 mmol) and Cu(BINAP)(MeCN)PF_6 (3.0 mol%) were successively added to a dry Schlenk tube equipped with a magnetic stirring rod. The tube is covered with a rubber diaphragm, then vacuumed and backfilled with nitrogen (3 cycles). *N,N*-dimethylacetamide (DMA) (2.0 mL) was added through a syringe and degassed through three freezer pump-thawing cycles. Under the condition of high efficiency stirring, the reaction mixture was irradiated at room temperature for 24 h with a 40 W blue led lamp (427 nm) and a fan. After irradiation, the reaction mixture was

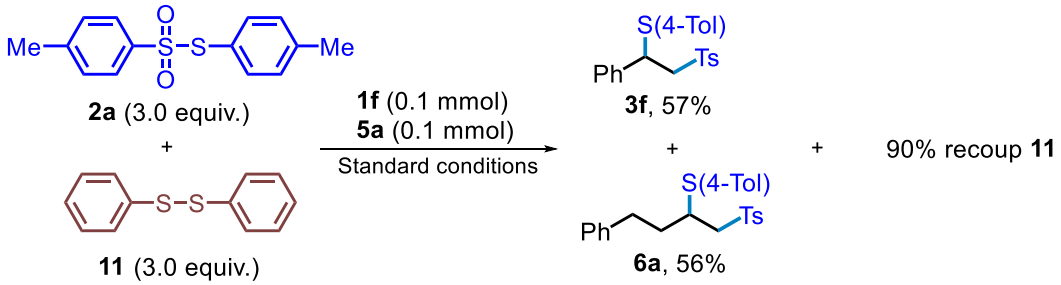
extracted with ethyl acetate for 3 times. The composite organic layer was washed with brine, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and directly analyzed by ^{1}H NMR. No cross products are detected.

Scrambling experiment between thiosulfonates 2a and disulfide 11.



Thiosulfonate **2a** (0.3 mmol, 1 equiv.), disulfide (0.3 mmol, 1 equiv.) and Cu(BINAP)(MeCN)PF_6 (3.0 mol%) were successively added to a dry Schlenk tube equipped with a magnetic stirring rod. The tube is covered with a rubber diaphragm, then vacuumed and backfilled with nitrogen (3 cycles). *N,N*-dimethylacetamide (DMA) (2.0 mL) was added through a syringe and degassed through three freezer pump-thawing cycles. Under the condition of high efficiency stirring, the reaction mixture was irradiated at room temperature for 24 h with a 40 W blue led lamp (427 nm) and a fan. After irradiation, the reaction mixture was extracted with ethyl acetate for 3 times. The composite organic layer was washed with brine, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and purified with petroleum ether/ethyl acetate as eluent was separated on silica gel by flash column chromatography, which was directly analyzed by ^{1}H NMR. No cross product is detected.

Scrambling experiment between thiosulfonates 2a, disulfide 11, alkene 1f and 5a.



Alkene **1f** (0.30 mmol), **5a** (0.30 mmol), thiosulfonate **2a** (0.9 mmol, 3 equiv.), disulfide **11** (0.9 mmol, 3 equiv.), and Cu(BINAP)(MeCN)PF_6 (3.0 mol%) were successively added to a dry Schlenk tube equipped with a magnetic stirring rod. The tube is covered with a rubber diaphragm, then vacuumed and backfilled with nitrogen (3 cycles). *N,N*-dimethylacetamide (DMA) (6.0 mL) was added through a

syringe and degassed through three freezer pump-thawing cycles. Under the condition of high efficiency stirring, the reaction mixture was irradiated at room temperature for 24 h with a 40 W blue led lamp (427 nm) and a fan. After irradiation, the reaction mixture was extracted with ethyl acetate for 3 times. The composite organic layer was washed with brine, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and purified with petroleum ether/ethyl acetate as eluent was separated on silica gel by flash column chromatography, which was directly analyzed by ^{1}H NMR. No cross products are detected.

6.4 UV-Vis absorption spectra.

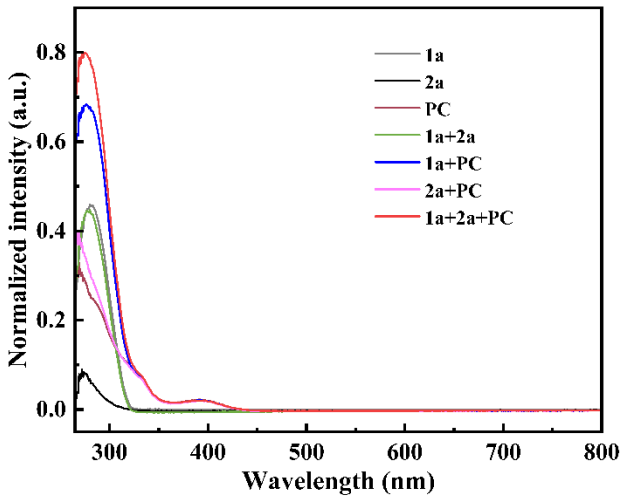


Figure S3. UV-Vis absorption spectra of **1a**, **2a**, **pc** and their combination.

The below reactants were added sequentially in graduated test tube and the added DMA solution was fixed to the graduated line to obtain a series of mixtures at a concentration of 1×10^{-4} M. The UV-visible absorption spectra were determined using a 1 cm cuvette in a UV-2800A spectrophotometer and the spectral data were recorded from 260~800 nm (**Figure S3)**.

The results show that only solutions of the complex Cu(MeCN)(BINAP)PF_6 and solutions containing the complex show significant absorption in the blue range in the visible region, whereas the other substrates and their mixtures show no absorption in the visible region.

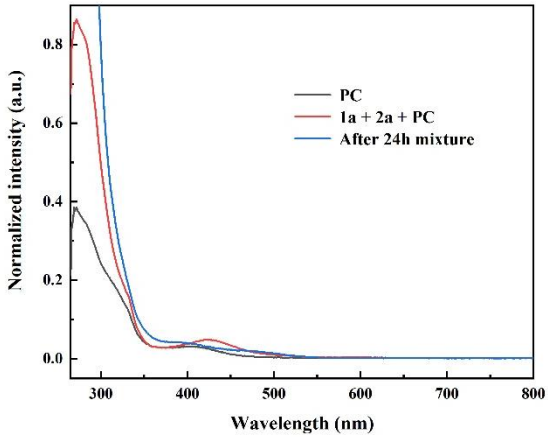


Figure S4. Determination of the resting state of Cu complex by UV-vis spectroscopy. After 24 h under standard reaction conditions, the *d-d* transition of Cu(II) between 500-800 nm was not distinctly observed when compared to the UV-Vis spectra of the pre-reaction system. Additionally, High-resolution mass spectrometry detected a signal at m/z = 849, it is predicted that the resting state of the Cu complex may BINAP-Cu^{I}(S-4-Tol)(MeCN) (**Figure S5**).

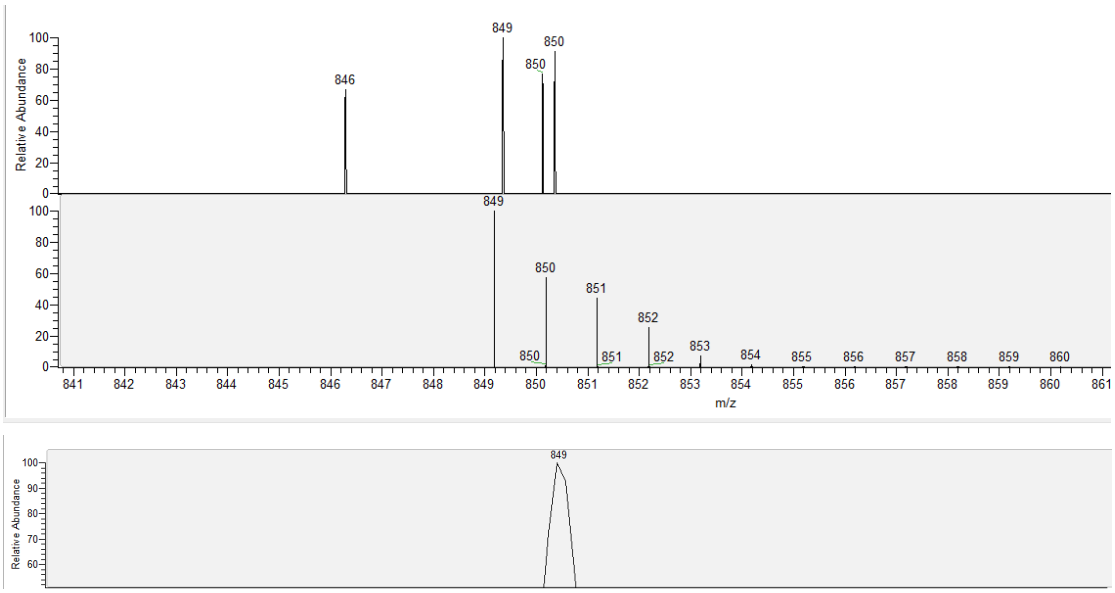


Figure S5

Note: **1a**: Alkene, **2a**: Thiosulfonate, **pc**: catalyst Cu(MeCN)(BINAP)PF_6.

6.6 Fluorescence Quenching Experiments.

Luminescence quenching experiments have been carried out in order to clarify the interaction between the excited state complex Cu(MeCN)(BINAP)PF_6 and substrates **1a** and **2a**.

Experimental methods: 0.3 mL of Cu(MeCN)(BINAP)PF_6 solution at a concentration of 10^{-4} mol/L

was taken in a cuvette, followed by the addition of a gradient volume of substrate **1a** or **2a** (10^{-4} mol/L), and then the volume of the solution was allowed to Constant volume to 3.0 mL to obtain samples to be tested at different concentration gradients. **Note**: No filters were used in any of the tests.

Fluorescence emission spectra were collected using HITACHI F-4500 for all experiments. All solutions were excited at λ = 290 nm, the slit width was set to 10 nm, and the sampling (scanning) interval was set to 10 nm. The emission spectra were recorded at wavelengths ranging from 560 to 600 nm, with the maximum emission peak at λ = 575 nm. (**Figure S6** and **Figure S7**).

The results show that the fluorescence intensity of the catalyst decreases with the increase of substrate concentration **2a**, and the Stern-Volmer constant is 1.011uM^{-1}, while the fluorescence of the catalyst is almost unaffected by the alkenes concentration (**1a**), with a Stern-Volmer constant of 0.080uM^{-1}. According to the Stern-Volmer constant, the fluorescence of the excited catalyst cannot be quenched by alkenes (**1a**), but can be quenched by thiosulfonates (**2a**).

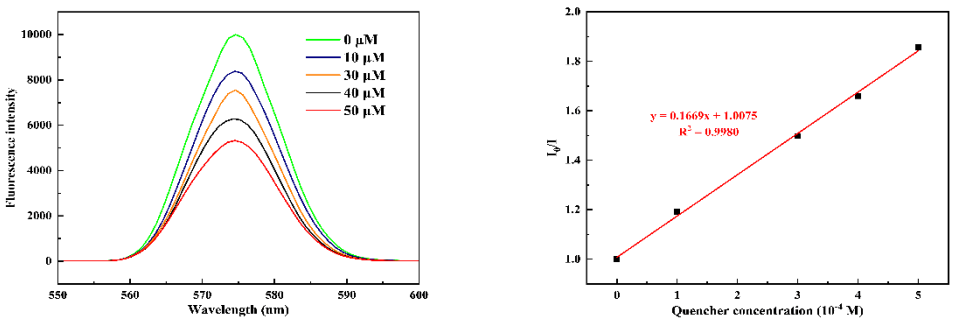


Figure S6. (a) complex Cu(MeCN)(BINAP)PF_6 emission quenching by **1a**; (b) Stern-Volmer plots.

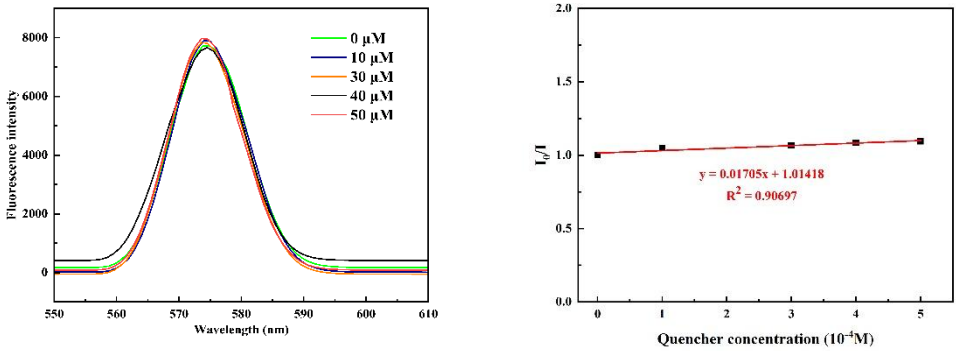


Figure S7. (a) complex Cu(MeCN)(BINAP)PF_6 emission quenching by **2a**; (b) Stern-Volmer plots.

6.7 Cyclic Voltammetry Experiments.

Cyclic voltammograms (CVs) were performed on a CHI760E electrochemistry workstation. Regular 3-electrode systems were used. Measurements were recorded in a DMA solution of Bu_4NPF_6 (0.1 M) at a scan rate of 100 mV/s under the protection of N_2 at room temperature using a glassy carbon disk (d = 0.5 cm) as a working electrode and a platinum wire as a counter electrode. An Ag/AgCl (3 M KCl) electrode was used as a reference electrode in all the experiments, and its potential (0.59 V vs. Fc^+/Fc) was calibrated with the ferrocenium/ferrocene (Fc^+/Fc) redox couple (**Figure S8**).

According to the emission spectrum of the catalyst, the triplet state energy corresponding to the maximum emission wavelength of 575 nm is 2.16 eV, and combined with the redox potential of its ground state, $E^01/2(Cu^{II}/Cu^{I})$ = -0.22 V (vs Ag/AgCl in DMA), the estimated redox potential of the catalyst in the excited state is $Eox(Cu^{II}/Cu^{I}*) = E^01/2(Cu^{II}/Cu^{I})—ET$ = -0.22—2.16 = -2.38 V (vs. Ag/AgCl in DMA).[10] The above estimates indicate that the catalyst in the excited state exhibits good reducing power and has the ability to reduce the thiosulfonate to sulfonyl radicals (**Figure S9~S11**)[11].

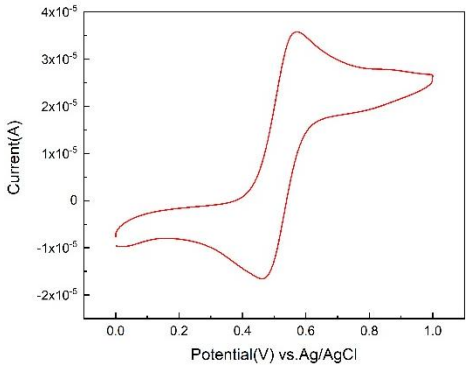


Figure S8. CV of ferrocenium [peak potential E_p (Fc+/Fc) = 0.59 V] in DMA.

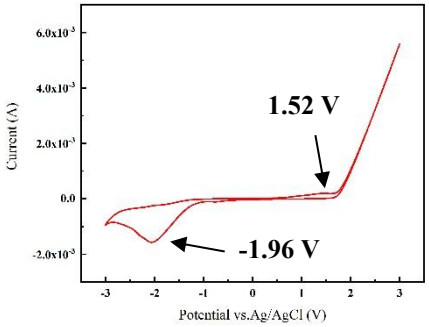


Figure S9. CV of [(BINAP)Cu(MeCN)][PF_6] $E^0_{1/2}(Cu^{II}/Cu^{I})$ = (1.52-1.96)/2 = -0.22 V (vs Ag/AgCl in DMA).

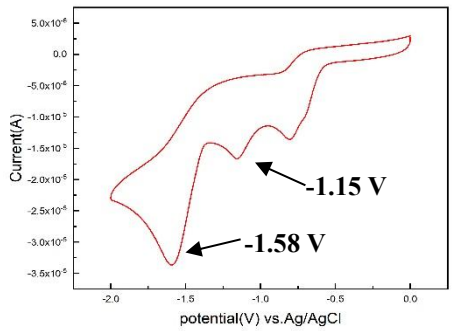


Figure S10. CV of thiosulfonate (**2a**) $E_p^{0/-1}$(**1a**) = -1.15 V (vs Ag/AgCl in DMA). E = -1.58 V (1,2-*di-p*-tolyldisulfane)

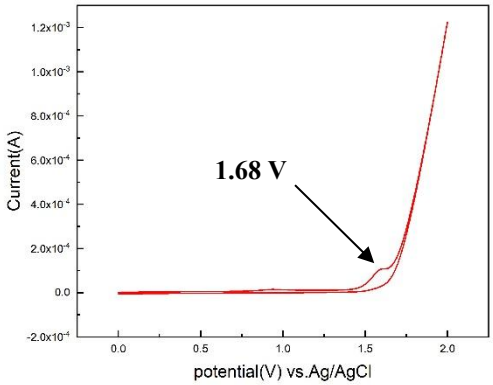


Figure S11. CV of sodium 4-vinylbiphenyl (**1a**) E_p^{ox} (**1a**) = 1.68 V (vs Ag/AgCl in DMA).

7. DFT computational study for 1,7-thiosulfonylation.

7.1 Computational details.

All the calculations were performed using the Gaussian 09 programs. All of the structures were fully optimized with the B3LYP method and 6-31+G(d) basis set. Grimmes's DFT-D3 dispersion correction was used to describe the van der waals interaction. The solvation energy corrections calculated at the M052x/6-31G(d) level with the SMD solvation model for DMA minus electronic energy in gas phase. The thermal correction to Gibbs free energy calculated by B3LYP/6-31+G(d) at 273.15K in gas phase. The B3LYP/6-31+G(d) calculated imaginary frequencies for the transition states in gas phase. The Single point energy calculated by B3LYP –D3/6-311++G(d,p) level of theory. Vibrational frequency calculations were performed to ensure that a transition state has only one imaginary frequency and a local minimum has no imaginary frequency. Transition states connecting relevant minima were further examined by running intrinsic reaction coordinate (IRC) calculations.

7.2 B3LYP absolute calculation energies (Hartree), energy corrections (Hartree), and imaginary frequency (cm-1)

Geometry	E(B3LYP-G3/ 6-311++G(d,p)[a]	G(corr-solv)[b]	G(corr-ther)[c]	IF[d]
1	-692.3043814	-0.0151539	0.183664	
2	-819.6923353	-0.0133161	0.088368	
1-a-ts	-1511.999392	-0.0325102	0.291449	-238.11
1-a-ts-P	-1512.002719	-0.0342351	0.293190	
1-b-ts	-1512.000310	-0.0288755	0.292272	-271.12
1-b-ts-P	-1512.009902	-0.0278676	0.294724	
1-c-ts	-1511.989758	-0.0319797	0.292376	-173.23
1-c-ts-P	-1511.990628	-0.0324088	0.292506	

[a]The single point energy calculated at the B3LYP-G3/6-311++G(d,p) level. [b]The solvation energy corrections calculated at the M052x/6-31G(d) level with the SMD solvation model for DMA minus electronic energy in the gas phase. [c]The thermal correction to Gibbs free energy calculated by B3LYP/6-31+G(d) at 273.15K in the gas phase. [d]The B3LYP/6-31+G(d) calculated imaginary frequencies for the transition states in the gas phase.

7.3 Free energy profiles for the reaction pathways

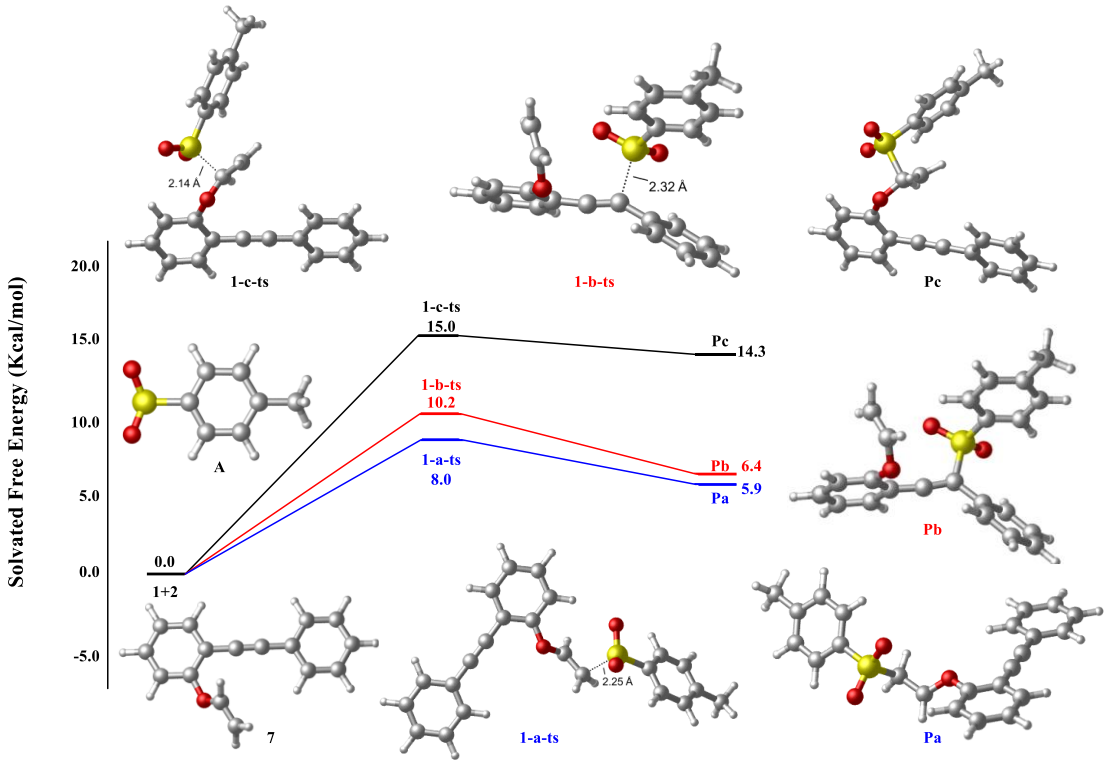


Figure S12. Computed free energy profiles for the three tentative reaction pathways at the B3LYP-

G3/6-311++G(d,p)//SMD(DMSO)-M052x/631G(d)//B3LYP/6-31+G(d) level. The relative free energies are given in kcal/mol. The preferred pathway is shown in blue.

Density functional theory (DFT) calculations were used to study the reaction mechanisms. The detailed information for the reaction mechanism is shown in Figure S10. Reactions of compound **7** with sulfonyl radical **A** resulted in the generation of products **Pa**, **Pb**, and **Pc** via the transition states **1-a-ts**, **1-b-ts,** and **1-c-ts** with an energy barrier of only 15.0/10.2/8.0 kcal/mol, respectively. From a thermodynamic perspective, the reaction pathway leading to product **Pa** through transition state **1-a-ts** is the most favorable, aligning with the experimental results.

7.4 Cartesian coordinates

B3LYP/6-31+G(d) geometries for all the optimized compounds and transition states

7

	x	y	z
C	3.94678200	0.26013300	-0.26483100
C	2.56076000	0.40136700	-0.20183400
C	1.72567200	-0.72282000	0.00001800
C	2.34497000	-1.98097400	0.17158900
C	3.72882300	-2.11854100	0.11912900
C	4.53325500	-0.99606400	-0.10719100
H	4.54820200	1.14757500	-0.43734800
H	1.71142300	-2.84852500	0.33069300
H	4.17895600	-3.09894500	0.24774400
H	5.61418500	-1.09589700	-0.15526900
C	0.30599400	-0.61616000	-0.00147000
C	-0.90965200	-0.55117300	-0.01248100
C	-2.33129700	-0.44025900	-0.03167500
C	-2.94311200	0.81484600	-0.23388100
C	-3.14656400	-1.57677500	0.14928400
C	-4.33253200	0.92376200	-0.25465000
H	-2.31705600	1.69124500	-0.37348800
C	-4.53527900	-1.45738300	0.12757800
H	-2.68007300	-2.54526500	0.30479000
C	-5.13348700	-0.20905600	-0.07414200
H	-4.79231000	1.89604100	-0.41254500
H	-5.15268300	-2.34097300	0.26787700
H	-6.21656000	-0.11977700	-0.09108800

O	2.04941200	1.66378300	-0.42484500
C	1.26412500	2.24577300	0.54377400
C	0.69250100	3.43486200	0.35179700
H	0.79988200	3.97631800	-0.58292800
H	0.10744900	3.88129500	1.14772900
H	1.17754100	1.67742000	1.46649300

A

	x	y	z
C	0.31748000	-1.21952200	-0.08058100
C	-0.36268200	0.00000800	-0.09055700
C	0.31736500	1.21950300	-0.08067300
C	1.71082000	1.20667300	-0.01984800
C	2.42847000	0.00012200	0.01275400
C	1.71083800	-1.20654500	-0.01972500
H	-0.23279000	-2.15473200	-0.09831800
H	2.24872600	2.15157700	0.00304700
H	2.24888400	-2.15138000	0.00333400
H	-0.23284100	2.15475800	-0.09841900
C	3.93558600	-0.00005100	0.10811600
H	4.25879000	-0.00581300	1.15789800
H	4.36809300	-0.88442800	-0.37154500
H	4.36772100	0.88965200	-0.36185900
S	-2.16962300	0.00001100	-0.23999500
O	-2.66627600	1.30295900	0.28943800
O	-2.66620800	-1.30307600	0.28917000

1-a-ts

	x	y	z
C	0.55608300	3.03170200	0.09674300
C	1.39081100	1.91496700	0.09664400
C	2.79667600	2.03426200	0.12983700
C	3.33876300	3.33564300	0.18025100
C	2.51363700	4.45784800	0.19777600
C	1.12362300	4.30669500	0.15384500
H	-0.51865700	2.89517500	0.00990200
H	4.41868300	3.44471100	0.20871400
H	2.95474400	5.44996100	0.23631300
H	0.47647300	5.17933600	0.14469100
C	3.63816800	0.88711500	0.12128400
C	4.37815200	-0.07957600	0.11752400

C	5.23304700	-1.22080200	0.10871800
C	4.69172900	-2.51853500	-0.00605600
C	6.63197200	-1.07299400	0.21347500
C	5.52911100	-3.63268900	-0.01478700
H	3.61549100	-2.63689100	-0.08998400
C	7.46172100	-2.19301400	0.20390000
H	7.05451500	-0.07628300	0.30123300
C	6.91528700	-3.47569100	0.09017000
H	5.09904900	-4.62693000	-0.10510200
H	8.53809600	-2.06474700	0.28493000
H	7.56519300	-4.34679900	0.08240600
O	0.86514100	0.63482900	0.00155000
C	-0.19549800	0.30922300	0.77600200
C	-1.05903200	-0.70340200	0.36480900
H	-0.70488600	-1.39839800	-0.39373400
H	-1.70699600	-1.12646600	1.12884300
C	-4.76638100	-1.55147000	-0.89389700
C	-4.24394800	-0.38426000	-0.33175700
C	-4.89899000	0.26479200	0.71830600
C	-6.09893700	-0.26150300	1.19738100
C	-6.64983400	-1.43251100	0.65203000
C	-5.96819600	-2.06220600	-0.40101500
H	-4.25396700	-2.03121100	-1.72223100
H	-6.62115800	0.25191800	2.00194300
H	-6.38710600	-2.96061500	-0.84896400
H	-4.48912400	1.18303800	1.12777200
C	-7.93455800	-2.00890300	1.19967100
H	-8.62047300	-1.21977700	1.52678700
H	-8.45081400	-2.62005800	0.45191300
H	-7.73748400	-2.65075000	2.06911200
S	-2.65221800	0.24351400	-0.91446100
O	-2.60644800	1.69633700	-0.59344400
O	-2.47282000	-0.22582400	-2.31343500
H	-0.38351400	0.94769400	1.63435500

Pa

	x	y	z
C	1.10049700	-3.51913700	-0.02964400
C	1.62090700	-2.22606400	-0.09395100
C	2.98954900	-1.97176800	0.15061900
C	3.81895800	-3.07183200	0.45117500

C	3.30803200	-4.36656600	0.50276700
C	1.94784800	-4.58904900	0.26465500
H	0.03630700	-3.67943700	-0.17160500
H	4.87247000	-2.88731800	0.63857500
H	3.96665200	-5.19856100	0.73535300
H	1.53738600	-5.59331800	0.32331900
C	3.51857900	-0.65250700	0.08896800
C	3.99853200	0.46537000	0.04065600
C	4.54890200	1.77939400	-0.01855800
C	3.73032700	2.88512900	-0.33133700
C	5.91947400	1.99795000	0.23425600
C	4.27067300	4.16864400	-0.38885900
H	2.67441000	2.72223200	-0.52602100
C	6.45132600	3.28507100	0.17481900
H	6.55504500	1.15107700	0.47617100
C	5.63121400	4.37467100	-0.13656900
H	3.62824500	5.01150200	-0.63104100
H	7.50921400	3.43858100	0.37222400
H	6.04918500	5.37692500	-0.18207500
O	0.82125600	-1.13055400	-0.34522400
C	-0.20106400	-1.22929400	-1.23571100
C	-1.32998800	-0.32435000	-1.05197500
H	-1.05006800	0.59102400	-0.52258100
H	-1.83561700	-0.09266000	-1.99387100
C	-3.94550800	1.07269600	1.14622900
C	-3.98048200	0.13952100	0.10633300
C	-4.97757500	0.18854200	-0.87131800
C	-5.94774900	1.18900000	-0.80100200
C	-5.93854500	2.13985400	0.23161900
C	-4.92416700	2.06531400	1.19962100
H	-3.17580100	1.00611600	1.90924900
H	-6.72908000	1.22630000	-1.55683700
H	-4.90351500	2.78938100	2.01109500
H	-5.00246800	-0.55833200	-1.65906400
C	-7.01400900	3.19711200	0.31976600
H	-7.85180300	2.85043600	0.93980700
H	-6.63388200	4.11955100	0.77181200
H	-7.41811800	3.44224800	-0.66814800
S	-2.69691400	-1.11720000	0.00473300
O	-3.22253200	-2.25227500	-0.78376900

O	-2.15288500	-1.33481600	1.35931900
H	-0.21902200	-2.08560700	-1.90005400

1-b-ts

	x	y	z
C	-4.71851500	-0.80525200	-0.77875900
C	-3.39431100	-0.38613700	-0.86265500
C	-2.89163700	0.62530300	-0.00319300
C	-3.78224200	1.19396200	0.94725200
C	-5.09849400	0.76503300	1.03385000
C	-5.57036100	-0.23496400	0.17042000
H	-5.07436600	-1.57426400	-1.45728800
H	-3.40459400	1.96584800	1.61024400
H	-5.76233500	1.20593300	1.77197200
H	-6.60385700	-0.56491800	0.22987000
C	-1.56849500	1.07435800	-0.09839500
C	-0.36027500	1.38292800	0.01981500
C	0.72765700	2.19735700	-0.50033100
C	1.40907500	3.11644400	0.31771700
C	1.09400100	2.07537700	-1.85432600
C	2.42797900	3.90592400	-0.21728800
H	1.14179200	3.19973400	1.36595300
C	2.11470400	2.86730900	-2.37979400
H	0.56918800	1.36204800	-2.48311400
C	2.78441200	3.78490600	-1.56397200
H	2.94439200	4.61785000	0.42143900
H	2.38680000	2.76755500	-3.42751000
H	3.57909900	4.40186500	-1.97559500
O	-2.55769200	-0.86893700	-1.85053600
C	-2.22572800	-2.20377600	-1.89289700
C	-2.40398900	-3.12154700	-0.94008700
H	-2.86031700	-2.90284700	0.01920600
H	-2.07296200	-4.13739400	-1.12710600
C	1.40798900	-2.14228700	0.34021800
C	1.77168800	-0.96651500	1.00113500
C	3.10124700	-0.54242600	1.04633900
C	4.08137700	-1.32808300	0.43857900
C	3.75179600	-2.52215500	-0.22098100
C	2.40337000	-2.91208200	-0.26173700
H	0.36804400	-2.45240000	0.30905700
H	5.11995900	-1.00699200	0.47962500

H	2.12747200	-3.83425700	-0.76894500
H	3.36095100	0.37605300	1.56250700
C	4.82460000	-3.38273000	-0.84648900
H	4.44619900	-3.92468500	-1.72013500
H	5.68542300	-2.78414500	-1.16328800
H	5.19181600	-4.13154200	-0.13148000
S	0.48204200	0.06692100	1.73497400
O	1.13925600	0.95618400	2.73352600
H	-1.75017400	-2.41862200	-2.84450000
O	-0.63409900	-0.82240200	2.14238300

Pb

	x	y	z
C	4.57984100	-0.89556300	0.85610300
C	3.24229000	-0.53109200	0.79930500
C	2.78167000	0.45565800	-0.12714200
C	3.75407200	1.04776100	-0.99565300
C	5.08359400	0.66753400	-0.93558000
C	5.50553400	-0.30403100	-0.01162100
H	4.89350800	-1.64108500	1.58047600
H	3.41990000	1.79579600	-1.70740300
H	5.80318300	1.12462900	-1.60911700
H	6.55121500	-0.59341100	0.03959400
C	1.46200900	0.85231000	-0.16209500
C	0.21321800	1.12861500	-0.39475000
C	-0.63046400	2.11111700	0.34026700
C	-1.39936600	3.08097700	-0.32501300
C	-0.62728700	2.08554400	1.74609400
C	-2.14615300	4.00587800	0.40838900
H	-1.40717600	3.10730900	-1.40918400
C	-1.37498200	3.01276400	2.47278600
H	-0.03695200	1.33204500	2.26015700
C	-2.13793000	3.97594800	1.80589700
H	-2.73203800	4.75593200	-0.11700300
H	-1.36346100	2.98019000	3.55935500
H	-2.72088000	4.69861600	2.37130100
O	2.32335100	-1.03053400	1.70502100
C	2.02458300	-2.37351600	1.72858400
C	2.34128700	-3.29970500	0.82083900
H	2.90762000	-3.08255900	-0.07817000
H	2.01530900	-4.32133200	0.98326200

C	-1.49242700	-2.06116900	-0.34575600
C	-1.84896100	-0.84907700	-0.94292000
C	-3.16446800	-0.38363700	-0.90216900
C	-4.13433500	-1.15063100	-0.25505300
C	-3.80895300	-2.37314900	0.35133300
C	-2.47593500	-2.81213400	0.29679500
H	-0.46604000	-2.41207200	-0.39207100
H	-5.16096700	-0.79263500	-0.22410200
H	-2.20427000	-3.75892200	0.75869400
H	-3.42243900	0.55516700	-1.38095600
C	-4.87202900	-3.21384000	1.01882100
H	-4.46478100	-3.77892200	1.86438900
H	-5.69871700	-2.59713900	1.38720000
H	-5.29489900	-3.94162100	0.31301400
S	-0.58423100	0.12942900	-1.76747500
O	-1.26571700	1.07329900	-2.67827600
H	1.44407300	-2.58928400	2.61991200
O	0.44694800	-0.78913300	-2.27980900

1-c-ts

	x	y	z
C	-0.53456400	-3.68652100	-0.58546600
C	-1.04790500	-2.39312300	-0.56024700
C	-2.27107700	-2.09821300	0.08247700
C	-2.94365100	-3.15660200	0.73061200
C	-2.42793900	-4.44959300	0.71704400
C	-1.22573500	-4.71715700	0.05390100
H	0.41064200	-3.85921100	-1.08927500
H	-3.88303200	-2.94256700	1.23156300
H	-2.96520500	-5.24867900	1.22032800
H	-0.81867200	-5.72435400	0.04121000
C	-2.83400800	-0.78996000	0.06304800
C	-3.33852100	0.31832800	0.04964200
C	-3.92663400	1.61763000	0.02289100
C	-3.40078500	2.62414800	-0.81416200
C	-5.04377900	1.91767800	0.83013700
C	-3.97857700	3.89239500	-0.83930300
H	-2.54364200	2.39599000	-1.44106500
C	-5.61494500	3.18886000	0.79835000
H	-5.45316200	1.14676800	1.47643900
C	-5.08597200	4.18049500	-0.03450000

H	-3.56485700	4.65821900	-1.49049600
H	-6.47582100	3.40641200	1.42533400
H	-5.53437400	5.17025700	-0.05721500
O	-0.36492700	-1.41078400	-1.27097300
C	0.22963700	-0.37208000	-0.58062300
C	0.53267900	0.75575400	-1.40238100
H	0.57947400	0.64070200	-2.47975100
H	0.85537800	1.68586200	-0.95049800
C	4.05908800	0.40722200	-0.90984000
C	3.26494000	0.13563400	0.20681200
C	3.36298300	0.90706700	1.36644600
C	4.27277900	1.96537800	1.40142300
C	5.08527500	2.26247900	0.29632000
C	4.96312300	1.46832400	-0.85550100
H	3.98044800	-0.21557700	-1.79545600
H	4.35689400	2.56475100	2.30523900
H	5.58874700	1.67887300	-1.72021600
H	2.75131100	0.66815400	2.23109600
C	6.09278200	3.38675800	0.35519600
H	5.79057100	4.15996300	1.06941400
H	7.07590300	3.01341500	0.67234100
H	6.22458500	3.85938100	-0.62423200
S	2.05929100	-1.20587400	0.13744700
O	1.80319400	-1.64069700	1.53384200
O	2.52864100	-2.17038300	-0.88599000
H	-0.19426800	-0.17887000	0.40739900

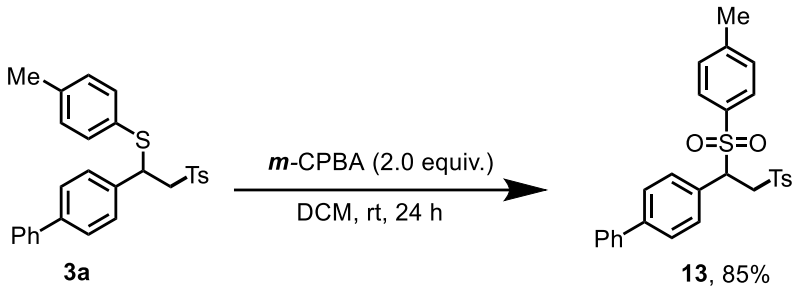
Pc

	x	y	z
C	0.39945900	3.96204000	-0.15450800
C	0.86803000	2.65745000	-0.29128700
C	1.95616400	2.18984600	0.48091600
C	2.52506200	3.07532200	1.42356600
C	2.05004000	4.37493100	1.56749000
C	0.98967600	4.82214000	0.77101200
H	-0.44011700	4.27700100	-0.76439800
H	3.35867000	2.72309400	2.02391000
H	2.50825500	5.03954100	2.29468100
H	0.61299700	5.83564400	0.87763400
C	2.50297000	0.88515500	0.31114800
C	3.00627500	-0.21644200	0.18202200

C	3.59698100	-1.50493600	0.01977200
C	3.29295900	-2.29610500	-1.10794700
C	4.49804400	-2.00786900	0.98156000
C	3.87467600	-3.55315100	-1.26426400
H	2.60445400	-1.90985900	-1.85383600
C	5.07512800	-3.26606400	0.81673300
H	4.73718200	-1.40295300	1.85137300
C	4.76640700	-4.04356100	-0.30441300
H	3.63372400	-4.15125400	-2.13942900
H	5.76856100	-3.64085600	1.56523700
H	5.21902300	-5.02362000	-0.43021800
O	0.29812600	1.87290400	-1.28428200
C	-0.34653300	0.67758300	-0.93623500
C	-0.20485100	-0.33520300	-1.97275700
H	-0.02929300	-0.02416000	-2.99609100
H	-0.45848500	-1.36712600	-1.76002800
C	-3.59510600	-1.26693100	-0.89528700
C	-2.99969400	-0.33066900	-0.04725100
C	-2.96120000	-0.53339100	1.33534100
C	-3.52132900	-1.69495100	1.86650800
C	-4.12576500	-2.65503300	1.03865000
C	-4.15311200	-2.42199300	-0.34495900
H	-3.63439000	-1.08037700	-1.96397800
H	-3.49582500	-1.85427200	2.94225100
H	-4.62333300	-3.15038600	-1.00175800
H	-2.51787200	0.21701200	1.98310600
C	-4.75968600	-3.89217500	1.63007600
H	-4.18329600	-4.26981000	2.48186800
H	-5.77345400	-3.67566000	1.99296100
H	-4.84039200	-4.69499400	0.88993600
S	-2.25178600	1.15274700	-0.74474900
O	-2.31954500	2.21931800	0.27768900
O	-2.81937500	1.36001800	-2.09168500
H	-0.09905500	0.33521800	0.07366100

8. Late-stage modification

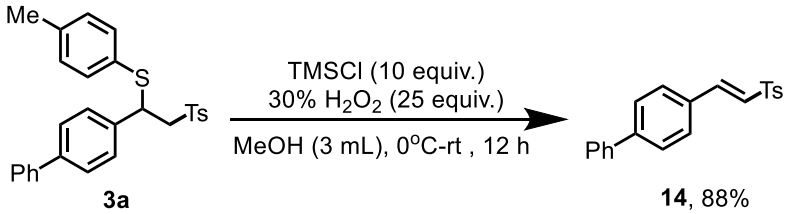
8.1 Experimental procedure for synthesis of 13.



According to the literature method[12], **3a** (170.0 mg, 0.37 mmol) was added to CH_2Cl_2 (4 mL) solution containing *m*-CPBA (0.75 mmol, 2 equiv.) and the resulting reaction mixture was stirred at room temperature for 24 h. Subsequently, the reaction was detected with a TLC plate until **3a** was completely consumed. The reaction mixture was concentrated under reduced pressure and extracted with dichloromethane (3×10 mL). The combined organic layer was washed with salt water, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 3:1) to afford the pure product 4-(1,2-ditosylethyl)-1,1'-biphenyl (**13**). White solid (154.3 mg, 85% yield), m.p.141–142 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 – 7.34 (m, 9H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.01 (dd, *J* = 29.6, 7.9 Hz, 4H), 4.62 (dd, *J* = 11.9, 2.5 Hz, 1H), 4.12 (dd, *J* = 14.6, 2.5 Hz, 1H), 3.99 (dd, *J* = 14.5, 11.9 Hz, 1H), 2.40 (s, 3H), 2.26 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 145.4, 144.7, 141.9, 140.0, 136.1, 133.0, 130.3, 129.6, 129.5, 129.2, 128.9, 128.1, 127.9, 127.8, 126.9, 126.8, 66.1, 54.1, 21.7, 21.5.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{28}H_{27}O_4S_2^+$: 491.1736; found: 491.1736.

8.2 Experimental procedure for synthesis of 14.

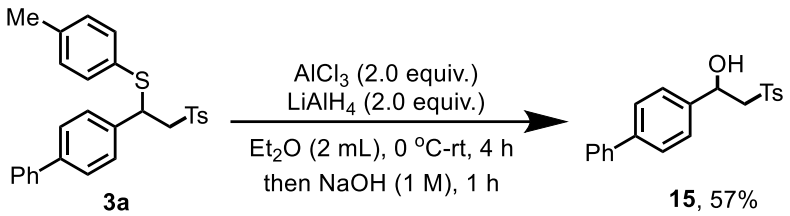


According to the literature method[13], **3a** (91.63 mg, 0.2 mmol) was added to MeOH (3 mL) solution containing TMSCl (2 mmol). Then the solution was cooled to 0 °C, Aqueous 30% H_2O_2 (25 equiv.) were added and the mixture was stirred at room temperature for 12 h. Subsequently, the reaction was detected

with a TLC plate until 3a was completely consumed. the reaction mixture was quenched by adding H_2O (10 mL), concentrated under reduced pressure and extracted with dichloromethane (3×10 mL). The combined organic layer was washed with salt water, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 7:1) to afford the pure product. **(*E*)-4-(2-tosylvinyl)-1,1'-biphenyl (14).** White solid (58.6 mg, 88% yield), m.p.100–101 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.63 – 7.58 (m, 4H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.40 – 7.34 (m, 3H), 6.88 (d, *J* = 15.2 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 144.4, 143.9, 141.5, 139.8, 137.8, 131.4, 123.0, 129.0, 128.9, 128.1, 127.7, 127.7, 127.4, 127.1, 21.6.

HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{19}O_2S^+$: 335.1153; found: 335.1152.

8.3 Experimental procedure for synthesis of 15.



$AlCl_3$ (2 mmol) was added into Et_2O (2 mL) solution containing **3a** (91.63 mg, 0.2 mmol). Then the solution was cooled to 0 ºC, $LiAlH_4$ (2 equiv.) was added, stirred at room temperature for 4 h, and the reaction was tested with TLC plate. The reaction mixture was quenched with NaOH (1 M), concentrated under reduced pressure, and extracted with ethyl acetate (3×10 mL). The organic layer was washed with salt water, dried with anhydrous sodium sulfate, concentrated under reduced pressure, and the crude product was purified on silica gel (petroleum ether: ethyl acetate = 5:1) by column chromatography to obtain the pure product **15** as colorless oil (40.2 mg, 57 % yield). 1-([1,1'-biphenyl]-4-yl)-2-tosylethan-1-ol (**15**)[14]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.52 (m, 4H), 7.45 – 7.40 (m, 3H), 7.37 (dd, *J* = 8.4, 1.9 Hz, 4H), 5.31 (d, *J* = 10.1 Hz, 1H), 3.76 (d, *J* = 2.0 Hz, 1H), 3.52 (dd, *J* = 14.3, 10.0 Hz, 1H), 3.37 (dd, *J* = 14.4, 1.9 Hz, 1H), 2.47 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 145.3, 141.3, 140.5, 139.6, 136.2, 130.1, 128.8, 128.0, 127.5, 127.1, 126.1, 68.3, 64.0, 21.7.

9. Crystallographic structure determination (8k CCDC 2401953)

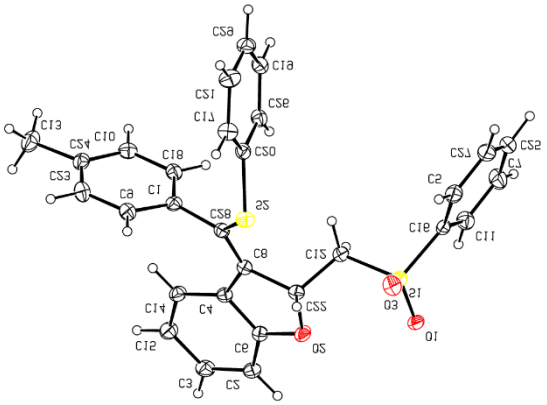


Table S2 Crystal data and structure refinement for 8k.

Identification code	8k
Empirical formula	$C_{29}H_{24}O_3S_2$
Formula weight	484.60
Temperature/K	149.98(10)
Crystal system	monoclinic
Space group	P21/n
a/Å	9.6399(2)
b/Å	18.0438(3)
c/Å	14.1965(2)
α /°	90
β /°	100.054(2)
γ /°	90
Volume/Å3	2431.42(7)
Z	4
ρ calcg/cm3	1.324
μ /mm 1	2.217
F(000)	1016.0
Crystal size/mm3	0.16 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8 to 133.188
Index ranges	-11 ≤ h ≤ 11, -21 ≤ k ≤ 16, -16 ≤ l ≤ 9
Reflections collected	14634
Independent reflections	4291 [Rint = 0.0363, Rsigma = 0.0346]
Data/restraints/parameters	4291/0/308

Goodness-of-fit on F2	1.036
Final R indexes [I>=2σ (I)]	R1 = 0.0453, wR2 = 0.1184
Final R indexes [all data]	R1 = 0.0531, wR2 = 0.1233
Largest diff. peak/hole / e Å-3	1.17/-0.38

Table S3 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 8k. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
S1	8031.4(6)	6421.8(3)	7365.6(4)	27.47(16)
S2	5625.2(6)	4459.3(3)	8305.7(4)	32.55(17)
O1	9111.5(16)	6510.2(9)	6791.7(12)	31.4(4)
O2	8357.8(18)	4947.8(9)	6110.7(13)	37.0(4)
O3	8442(2)	6219.6(10)	8351.7(13)	39.7(4)
S1	8031.4(6)	6421.8(3)	7365.6(4)	27.47(16)
S2	5625.2(6)	4459.3(3)	8305.7(4)	32.55(17)
O1	9111.5(16)	6510.2(9)	6791.7(12)	31.4(4)
O2	8357.8(18)	4947.8(9)	6110.7(13)	37.0(4)
O3	8442(2)	6219.6(10)	8351.7(13)	39.7(4)
C1	4220(2)	3648.9(12)	6736.6(16)	27.0(5)
C2	8521(3)	4198.2(14)	4725.3(18)	34.4(6)
C3	7962(3)	3597.8(14)	4177.7(19)	37.2(6)
C4	6649(2)	4056.8(12)	5673.3(17)	27.7(5)
C5	6464(3)	7463.0(15)	8082(2)	39.2(6)
C6	7853(2)	4403.1(12)	5467.1(18)	30.0(5)
C7	5913(3)	8252.7(15)	6378(2)	49.0(7)
C8	6344(2)	4380.7(12)	6561.0(17)	28.3(5)
C9	4206(3)	2948.2(13)	7138.3(18)	33.5(5)
C10	2178(3)	3309.9(14)	5576.5(17)	32.3(5)
C11	6760(3)	7631.1(14)	6442.4(19)	37.5(6)
C12	6793(2)	5746.4(12)	6806.6(18)	30.1(5)
C13	1184(3)	2008.4(16)	5501(2)	47.7(7)
C14	6102(3)	3454.9(13)	5105.2(17)	32.0(5)
C15	6769(3)	3232.0(14)	4365.7(19)	37.3(6)
C16	7015(2)	7238.9(12)	7294.1(17)	28.8(5)
C17	3541(3)	4500.2(14)	9374.1(18)	36.2(6)
C18	3187(3)	3832.9(13)	5966.4(17)	31.0(5)
C19	1686(3)	5305.9(13)	8058.4(19)	34.6(5)
C20	3907(2)	4692.1(12)	8505.7(17)	29.2(5)
C21	2254(3)	4727.5(16)	9593.3(19)	40.7(6)

C22	7454(2)	4978.4(12)	6830.5(18)	29.8(5)
C23	3229(3)	2430.1(14)	6731.4(19)	38.6(6)
C24	2213(3)	2595.9(13)	5947.8(18)	32.9(5)
C25	5336(3)	8473.8(15)	7156(3)	49.5(8)
C26	2978(3)	5094.4(12)	7841.2(17)	31.5(5)
C27	5619(3)	8089.3(16)	8004(2)	49.5(8)
C28	5375(2)	4177.0(12)	7091.7(17)	27.4(5)
C29	1335(3)	5133.1(14)	8937.9(19)	38.1(6)

Table S4 Anisotropic Displacement Parameters (Å2×10^3) for 8k. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	28.2(3)	26.8(3)	28.4(3)	-3.0(2)	7.5(2)	-1.2(2)
S2	29.9(3)	40.6(3)	27.3(3)	-2.2(2)	5.3(2)	1.9(2)
O1	25.2(8)	33.3(9)	37.3(10)	-5.0(7)	9.5(7)	-2.7(6)
O2	33.0(9)	36.1(9)	46.9(11)	-12.8(8)	20.9(8)	-9.4(7)
O3	46.2(10)	37.9(9)	33.8(10)	1.4(7)	4.0(8)	1.9(8)
C1	26.7(11)	32.1(12)	24.6(12)	-3.7(9)	10.8(10)	-0.6(9)
C2	31.6(13)	36.7(13)	38.7(14)	0.1(10)	16.6(11)	0.0(10)
C3	37.0(14)	43.6(14)	34.6(14)	-4.9(11)	16.3(11)	2.4(11)
C4	27.9(12)	28.1(11)	28.8(12)	-0.6(9)	10.2(10)	0.7(9)
C5	40.7(14)	38.9(14)	42.1(15)	-10.0(11)	18.6(12)	-7.3(11)
C6	27.9(12)	28.7(11)	34.5(13)	-2.5(9)	8.5(10)	-0.4(9)
C7	49.2(16)	33.2(14)	62.5(19)	6.2(13)	3.9(15)	3.6(12)
C8	26.6(12)	26.6(11)	32.5(13)	-2.6(9)	7.3(10)	0.6(9)
C9	36.5(13)	30.9(12)	33.2(13)	1.4(10)	6.2(11)	2.2(10)
C10	31.0(12)	40.1(13)	26.1(12)	-2.2(10)	6.1(10)	3.0(10)
C11	41.9(14)	36.1(13)	36.2(14)	-2.5(10)	11.5(12)	-0.4(11)
C12	27.0(12)	29.7(12)	34.1(13)	-2.2(10)	7.1(10)	-1.4(9)
C13	46.9(16)	49.1(16)	48.7(17)	-13.3(13)	12.9(14)	-17.1(13)
C14	27.4(12)	36.2(13)	34.0(14)	-4.7(10)	9.6(10)	-2.8(10)
C15	35.3(13)	41.3(14)	37.2(14)	-11.4(11)	11.5(11)	-4.0(11)
C16	25.2(11)	26.9(11)	35.7(13)	-6.6(9)	9.0(10)	-6.1(9)
C17	37.8(14)	44.5(14)	26.2(13)	1.6(10)	5.5(11)	3.1(11)
C18	36.8(13)	27.9(11)	31.1(13)	1.4(9)	13.6(11)	2.4(10)
C19	36.3(13)	29.4(12)	38.7(14)	1.3(10)	7.9(11)	3.2(10)
C20	32.2(12)	27.8(11)	28.3(12)	-5.5(9)	7.6(10)	-1.3(9)
C21	39.8(14)	57.3(16)	27.6(13)	-1.7(11)	13.3(11)	-0.9(12)
C22	27.4(12)	30.0(12)	33.4(13)	-2.9(9)	9.3(10)	0.5(9)
C23	49.4(15)	28.8(12)	37.7(14)	2.6(10)	7.7(12)	-0.9(11)

C24	33.2(12)	34.3(13)	34.0(14)	-5.3(10)	14.2(11)	-5.5(10)
C25	34.9(14)	30.6(13)	85(2)	-8.5(14)	16.6(15)	0.1(11)
C26	38.1(13)	27.9(11)	30.1(13)	0.1(9)	10.6(11)	0.8(10)
C27	42.1(15)	41.5(15)	72(2)	-20.3(15)	29.5(15)	-4.2(12)
C28	26.8(11)	26.6(11)	28.9(12)	0.4(9)	5.3(9)	2.5(9)
C29	32.5(13)	41.8(14)	42.3(15)	-7.1(11)	13.1(12)	2.2(11)

Table S5 Bond Lengths for 8k.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O1	1.4386(17)	C7	C11	1.381(4)
S1	O3	1.4339(18)	C7	C25	1.379(4)
S1	C12	1.791(2)	C8	C22	1.521(3)
S1	C16	1.763(2)	C8	C28	1.350(3)
S2	C20	1.779(2)	C9	C23	1.380(4)
S2	C28	1.773(2)	C10	C18	1.398(3)
O2	C6	1.372(3)	C10	C24	1.390(4)
O2	C22	1.455(3)	C11	C16	1.386(4)
C1	C9	1.388(3)	C12	C22	1.523(3)
C1	C18	1.385(3)	C13	C24	1.513(3)
C1	C28	1.485(3)	C14	C15	1.383(3)
C2	C3	1.387(4)	C17	C20	1.384(3)
C2	C6	1.378(3)	C17	C21	1.392(4)
C3	C15	1.392(4)	C19	C26	1.388(3)
C4	C6	1.393(3)	C19	C29	1.385(4)
C4	C8	1.465(3)	C20	C26	1.387(3)
C4	C14	1.400(3)	C21	C29	1.378(4)
C5	C16	1.380(3)	C23	C24	1.381(4)
C5	C27	1.386(4)	C25	C27	1.376(5)

Table S6 Bond Angles for 8k.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	S1	C12	108.47(10)	C22	C12	S1	111.42(16)
O1	S1	C16	108.93(10)	C15	C14	C4	119.0(2)
O3	S1	O1	118.51(11)	C14	C15	C3	121.1(2)
O3	S1	C12	107.97(11)	C5	C16	S1	119.2(2)
O3	S1	C16	108.96(11)	C5	C16	C11	121.5(2)
C16	S1	C12	102.88(11)	C11	C16	S1	119.33(18)
C28	S2	C20	104.50(11)	C20	C17	C21	120.1(2)
C6	O2	C22	107.97(17)	C1	C18	C10	120.4(2)
C9	C1	C28	120.4(2)	C29	C19	C26	120.6(2)
C18	C1	C9	119.0(2)	C17	C20	S2	118.18(19)

C18	C1	C28	120.5(2)	C17	C20	C26	120.1(2)
C6	C2	C3	116.7(2)	C26	C20	S2	121.59(18)
C2	C3	C15	121.1(2)	C29	C21	C17	119.9(2)
C6	C4	C8	107.5(2)	O2	C22	C8	106.13(18)
C6	C4	C14	118.1(2)	O2	C22	C12	108.57(19)
C14	C4	C8	133.9(2)	C8	C22	C12	111.48(19)
C16	C5	C27	118.6(3)	C9	C23	C24	121.8(2)
O2	C6	C2	122.8(2)	C10	C24	C13	121.3(2)
O2	C6	C4	113.2(2)	C23	C24	C10	118.2(2)
C2	C6	C4	123.9(2)	C23	C24	C13	120.4(2)
C25	C7	C11	119.9(3)	C27	C25	C7	120.6(3)
C4	C8	C22	105.14(19)	C20	C26	C19	119.4(2)
C28	C8	C4	129.4(2)	C25	C27	C5	120.3(3)
C28	C8	C22	125.3(2)	C1	C28	S2	118.77(16)
C23	C9	C1	120.0(2)	C8	C28	S2	118.32(18)
C24	C10	C18	120.4(2)	C8	C28	C1	122.4(2)
C7	C11	C16	119.1(2)	C21	C29	C19	119.9(2)

Table S7 Torsion Angles for 8k.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C12	C22	O2	-76.0(2)	C12	S1	C16	C5	98.7(2)
S1	C12	C22	C8	167.45(16)	C12	S1	C16	C11	-79.7(2)
S2	C20	C26	C19	-175.61(18)	C14	C4	C6	O2	-175.3(2)
O1	S1	C12	C22	67.10(19)	C14	C4	C6	C2	1.4(4)
O1	S1	C16	C5	-146.36(19)	C14	C4	C8	C22	174.1(3)
O1	S1	C16	C11	35.2(2)	C14	C4	C8	C28	-1.2(4)
O3	S1	C12	C22	-62.50(19)	C16	S1	C12	C22	-177.62(17)
O3	S1	C16	C5	-15.7(2)	C16	C5	C27	C25	0.4(4)
O3	S1	C16	C11	165.87(19)	C17	C20	C26	C19	0.4(4)
C1	C9	C23	C24	-2.6(4)	C17	C21	C29	C19	0.8(4)
C2	C3	C15	C14	0.0(4)	C18	C1	C9	C23	4.3(3)
C3	C2	C6	O2	174.7(2)	C18	C1	C28	S2	123.0(2)
C3	C2	C6	C4	-1.7(4)	C18	C1	C28	C8	-65.2(3)
C4	C8	C22	O2	-2.0(2)	C18	C10	C24	C13	-176.4(2)
C4	C8	C22	C12	116.0(2)	C18	C10	C24	C23	2.6(3)
C4	C8	C28	S2	159.2(2)	C20	S2	C28	C1	-47.0(2)
C4	C8	C28	C1	-12.6(4)	C20	S2	C28	C8	140.80(19)
C4	C14	C15	C3	-0.3(4)	C20	C17	C21	C29	1.1(4)
C6	O2	C22	C8	0.7(2)	C21	C17	C20	S2	174.5(2)
C6	O2	C22	C12	-119.2(2)	C21	C17	C20	C26	-1.7(4)
C6	C2	C3	C15	1.0(4)	C22	O2	C6	C2	-175.8(2)
C6	C4	C8	C22	2.5(2)	C22	O2	C6	C4	0.9(3)
C6	C4	C8	C28	-172.8(2)	C22	C8	C28	S2	-15.2(3)

C6	C4	C14	C15	-0.3(4)	C22	C8	C28	C1	173.0(2)
C7	C11	C16	S1	177.2(2)	C24	C10	C18	C1	-1.0(3)
C7	C11	C16	C5	-1.1(4)	C25	C7	C11	C16	0.0(4)
C7	C25	C27	C5	-1.5(4)	C26	C19	C29	C21	-2.1(4)
C8	C4	C6	O2	-2.3(3)	C27	C5	C16	S1	-177.40(19)
C8	C4	C6	C2	174.4(2)	C27	C5	C16	C11	1.0(4)
C8	C4	C14	C15	-171.1(3)	C28	S2	C20	C17	140.98(19)
C9	C1	C18	C10	-2.5(3)	C28	S2	C20	C26	-42.9(2)
C9	C1	C28	S2	-60.6(3)	C28	C1	C9	C23	-172.2(2)
C9	C1	C28	C8	111.2(3)	C28	C1	C18	C10	174.0(2)
C9	C23	C24	C10	-0.9(4)	C28	C8	C22	O2	173.5(2)
C9	C23	C24	C13	178.2(2)	C28	C8	C22	C12	-68.4(3)
C11	C7	C25	C27	1.4(4)	C29	C19	C26	C20	1.5(4)

Table S8 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 8k.

Atom	x	y	z	U(eq)
H2	9326.71	4455.71	4595.27	41
H3	8400.24	3433.35	3665.63	45
H5	6658.7	7193.57	8665.03	47
H7	5728.33	8527.7	5798.97	59
H9	4869.32	2825.19	7693.16	40
H10	1464.55	3443.34	5054.5	39
H11	7161.01	7474.53	5910.15	45
H12A	5973.8	5732.04	7140.67	36
H12B	6449.81	5892.18	6134.01	36
H13A	384.83	2245.5	5089.94	72
H13B	844.04	1728.1	6006.94	72
H13C	1656.32	1671.1	5118.07	72
H14	5285.31	3203.34	5225.81	38
H15	6406.13	2822.24	3979.43	45
H17	4168.68	4213.24	9821.02	43
H18	3162.93	4317.17	5701.61	37
H19	1037.08	5571.42	7599.88	42
H21	2010.36	4603.01	10193.81	49
H22	8015.87	4876.42	7478.74	36
H23	3256.21	1946.31	6997.93	46
H25	4737.11	8895.44	7104.98	59
H26	3223.7	5223.89	7242.85	38
H27	5234.67	8253.99	8540.05	59

H29	461.3	5294.07	9089.06	46
H2	9326.71	4455.71	4595.27	41
H3	8400.24	3433.35	3665.63	45
H5	6658.7	7193.57	8665.03	47
H7	5728.33	8527.7	5798.97	59
H9	4869.32	2825.19	7693.16	40
H10	1464.55	3443.34	5054.5	39
H11	7161.01	7474.53	5910.15	45
H12A	5973.8	5732.04	7140.67	36

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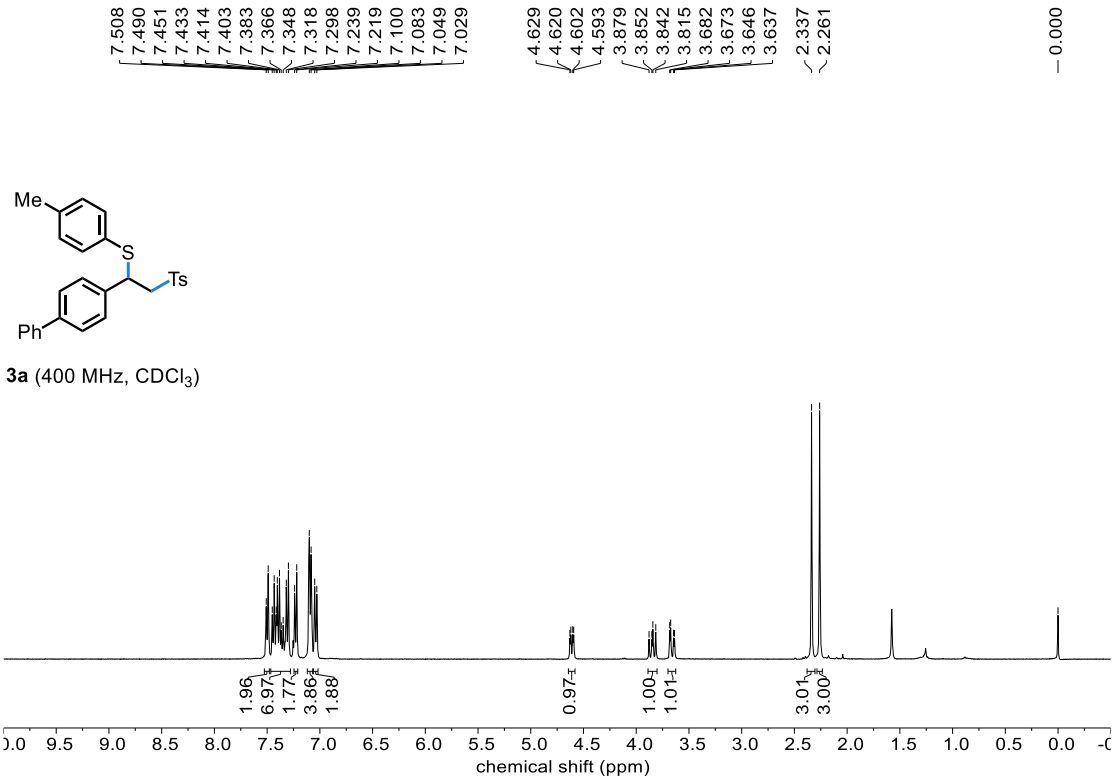
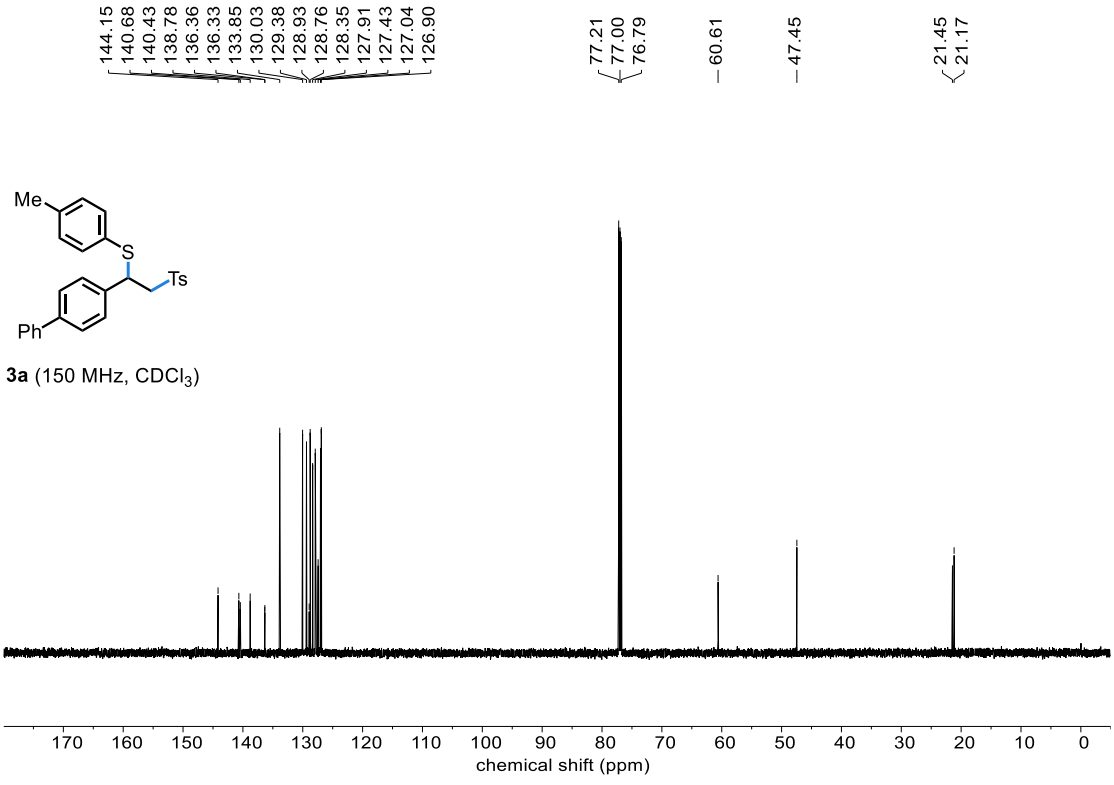
[14] Choudhuri, K.; Achar, T.; Mala, P. *Adv. Synth. Catal*., **2017**, 359, 3566−3576.

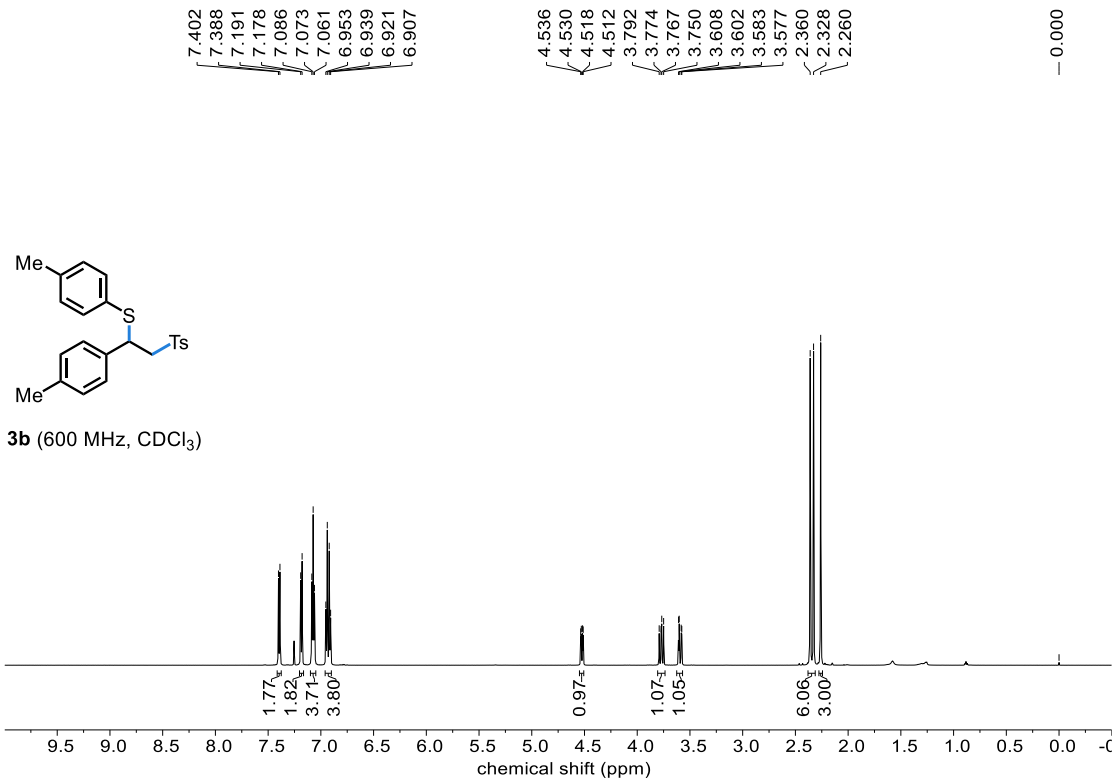
11. Cope of NMR Spectra

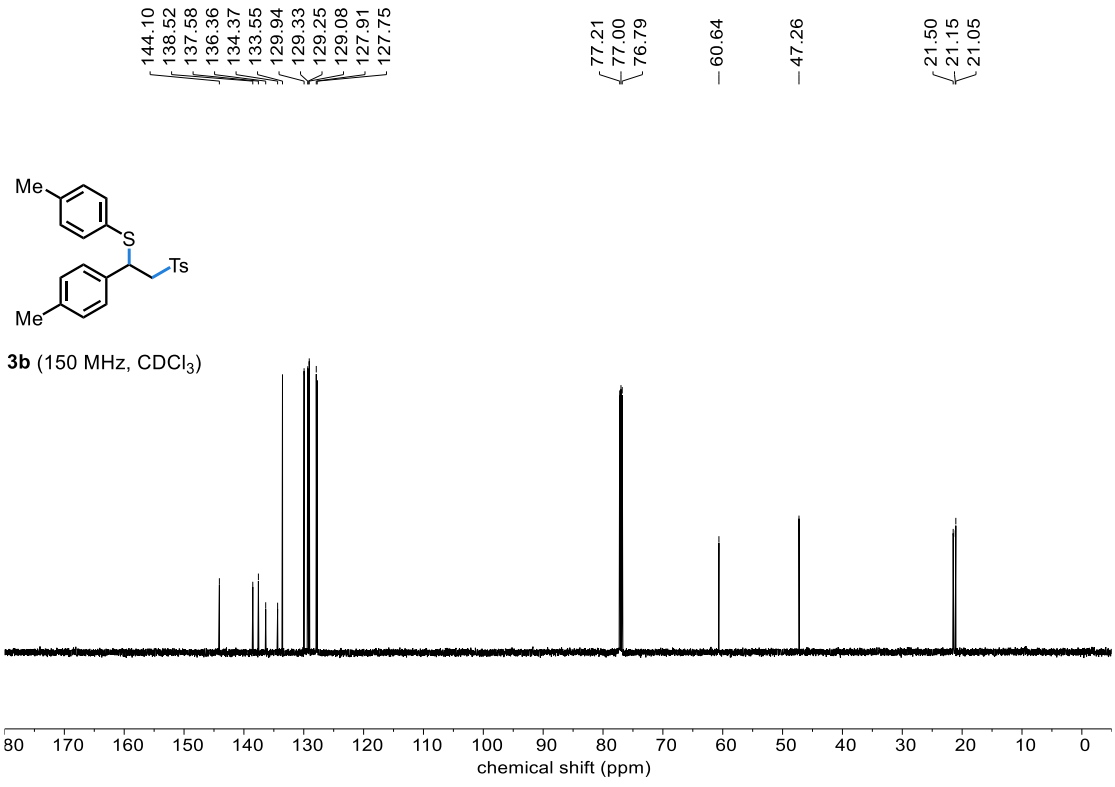


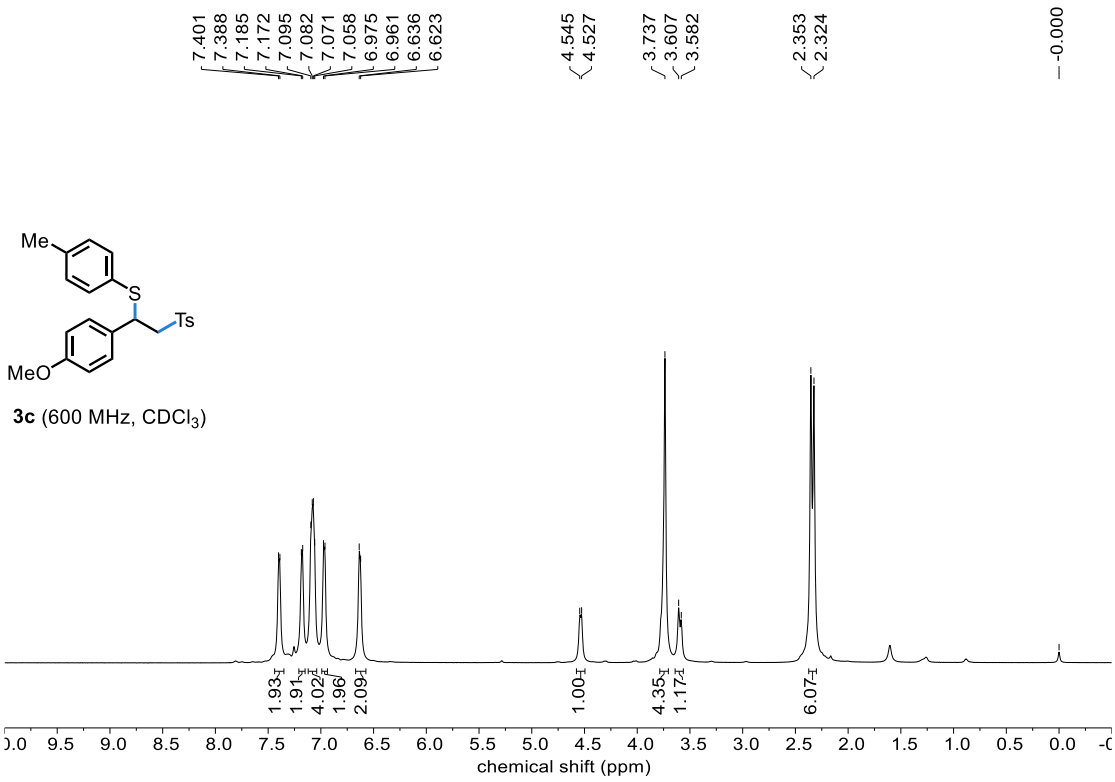
3a (400 MHz, $CDCl_3$)

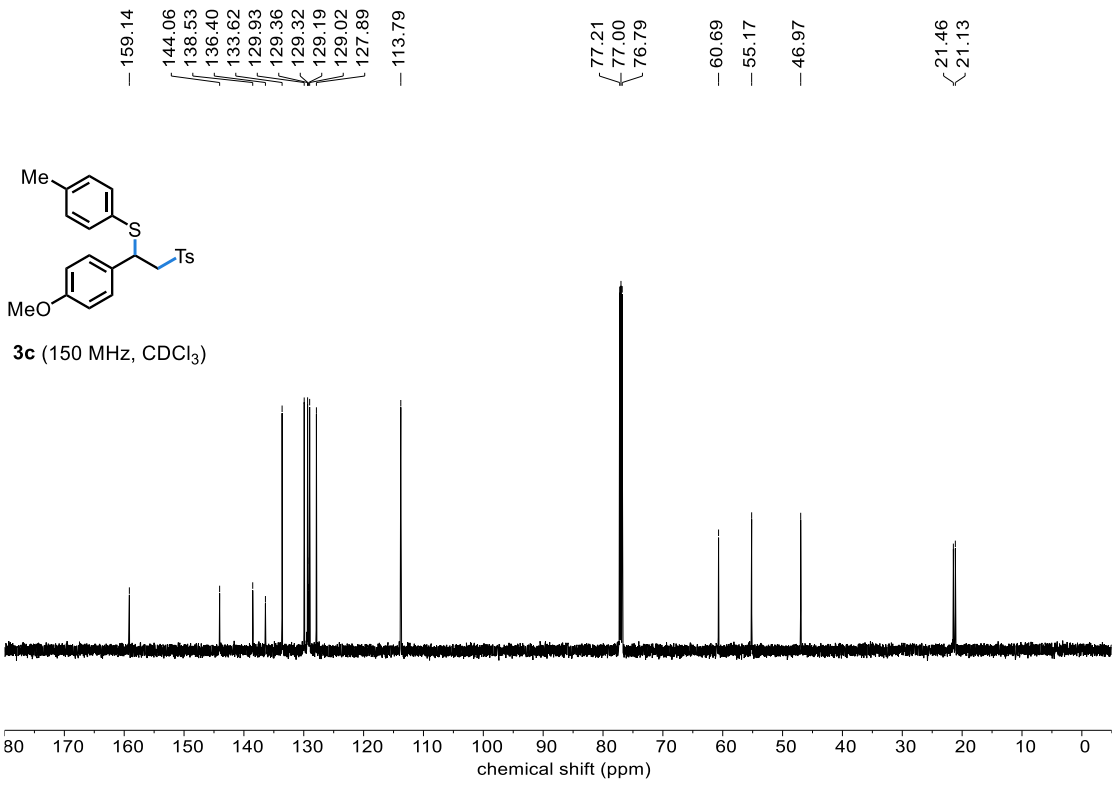


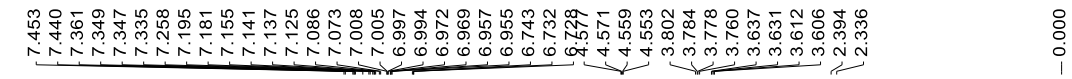
3a (150 MHz, $CDCl_3$)

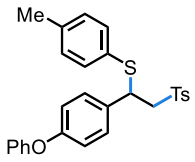

7.402
7.388
7.191
7.178
7.086
7.073
7.061
6.953
6.939
6.921
6.907
4.536
4.530
4.518
4.512
3.792
3.774
3.767
3.750
3.608
3.602
3.583
3.577
2.360
2.328
2.260
0.000
Me
S
Ts
Me
3b (600 MHz, CDCl3)
1.77
1.82
3.71
3.80
0.97
1.07
1.05
6.06
3.00
chemical shift (ppm)


144.10
138.52
137.58
136.36
134.37
133.55
129.94
129.33
129.25
129.08
127.91
127.75
77.21
77.00
76.79
60.64
47.26
21.50
21.15
21.05
Me
S
Ts
Me
3b (150 MHz, CDCl3)
chemical shift (ppm)

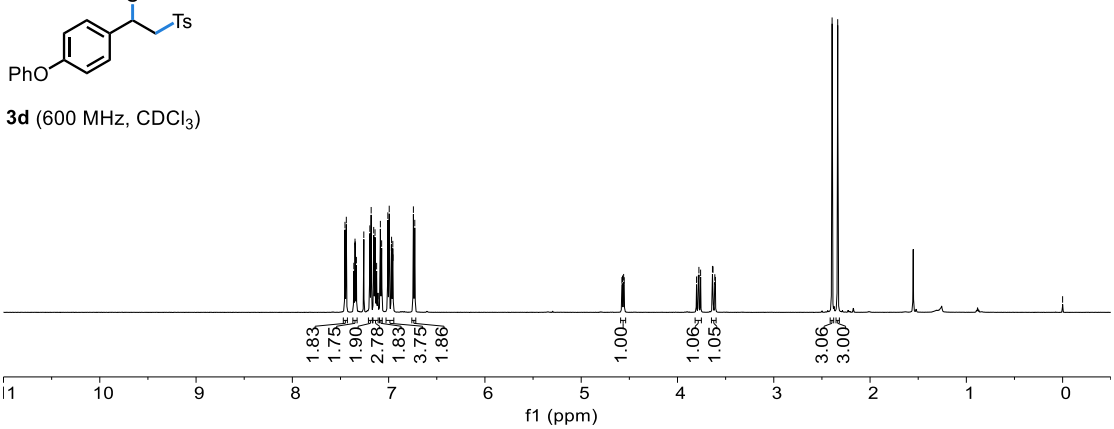

7.401
7.388
7.185
7.172
7.095
7.082
7.071
7.058
6.975
6.961
6.636
6.623
4.545
4.527
3.737
3.607
3.582
2.353
2.324
-0.000
Me
S
Ts
MeO
3c (600 MHz, CDCl3)
1.93
1.91
4.02
1.96
2.09
1.00
4.35
1.17
6.07
chemical shift (ppm)

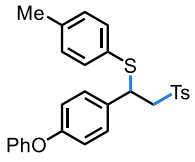

159.14
144.06
138.53
136.40
133.62
129.93
129.36
129.32
129.19
129.02
127.89
113.79
77.21
77.00
76.79
60.69
55.17
46.97
21.46
21.13
Me
S
Ts
MeO
3c (150 MHz, CDCl3)
chemical shift (ppm)



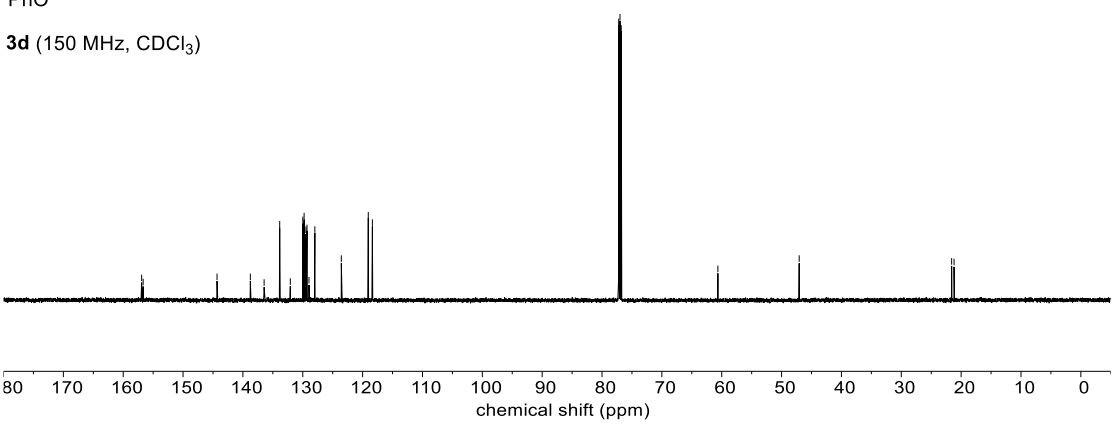


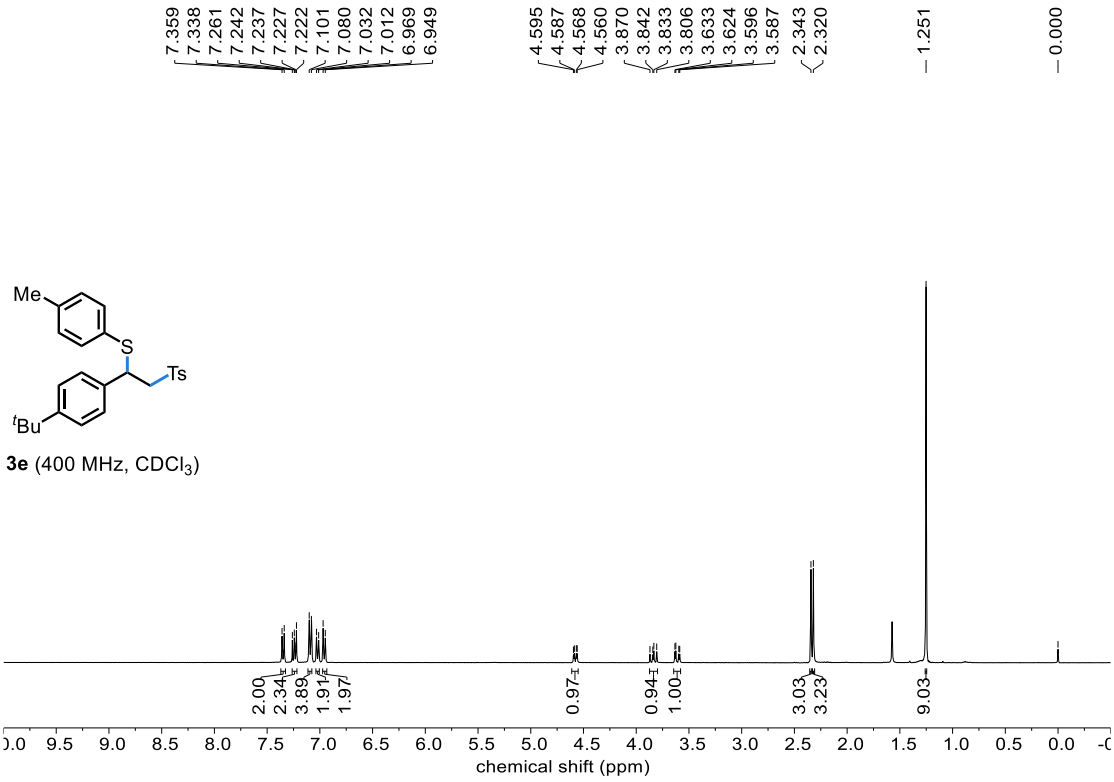
3d (600 MHz, $CDCl_3$)

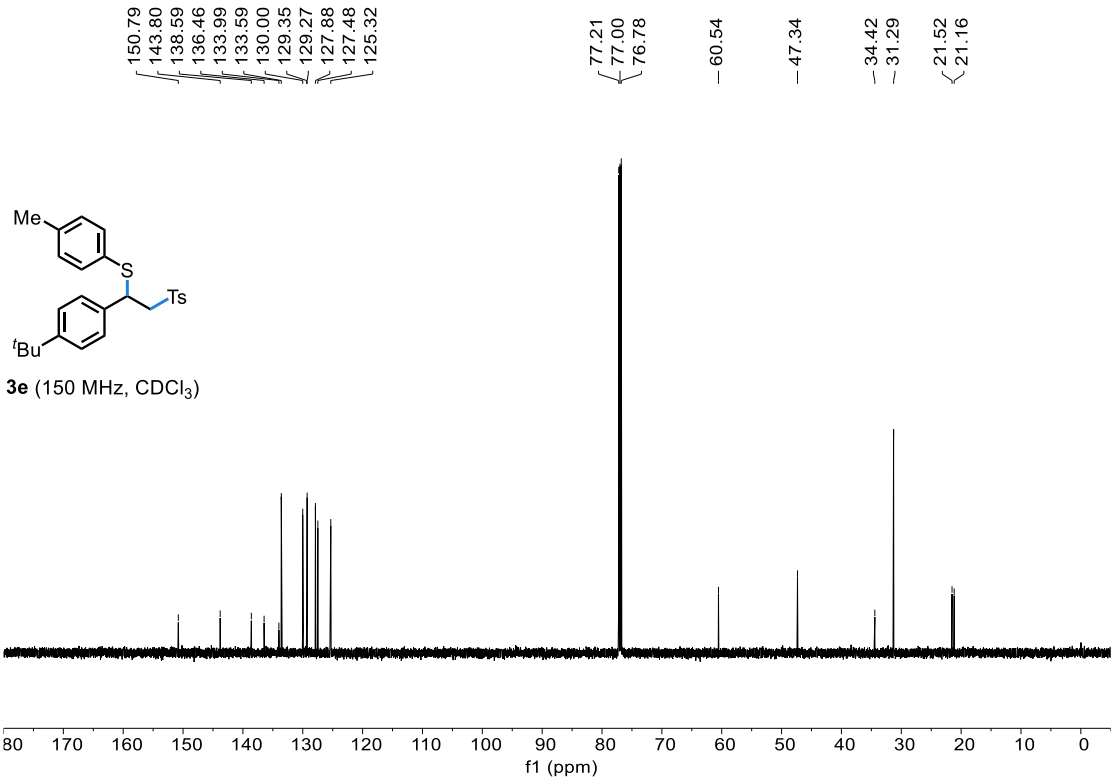


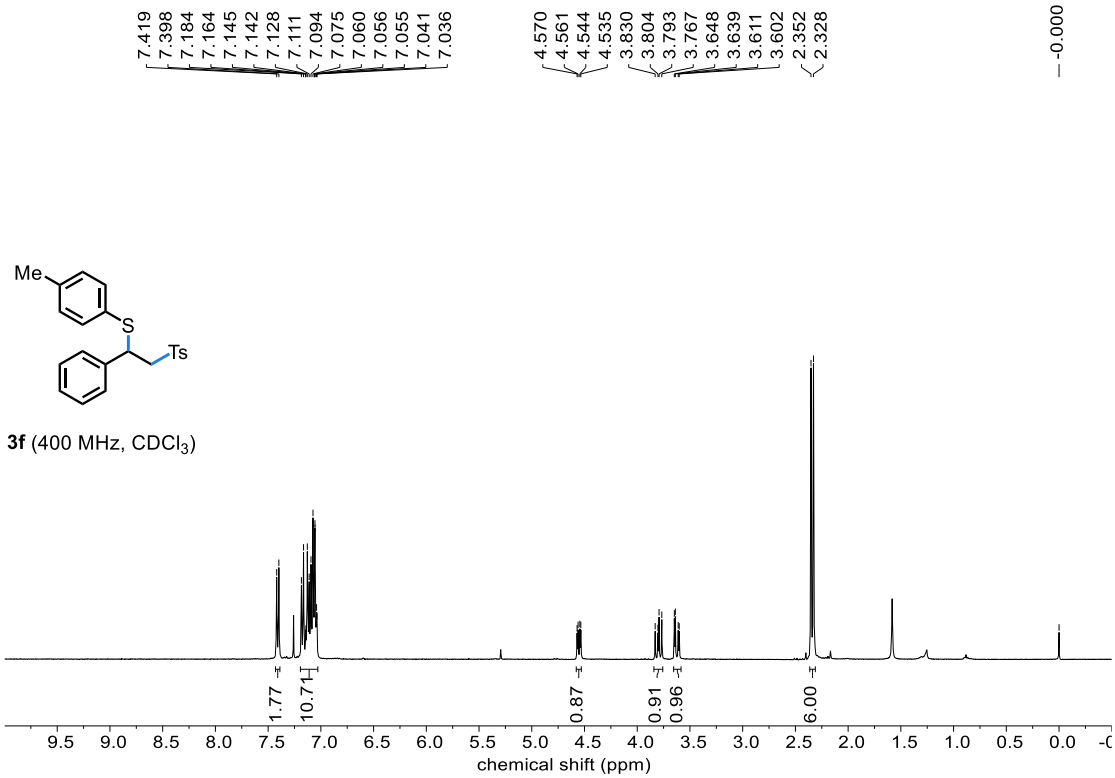


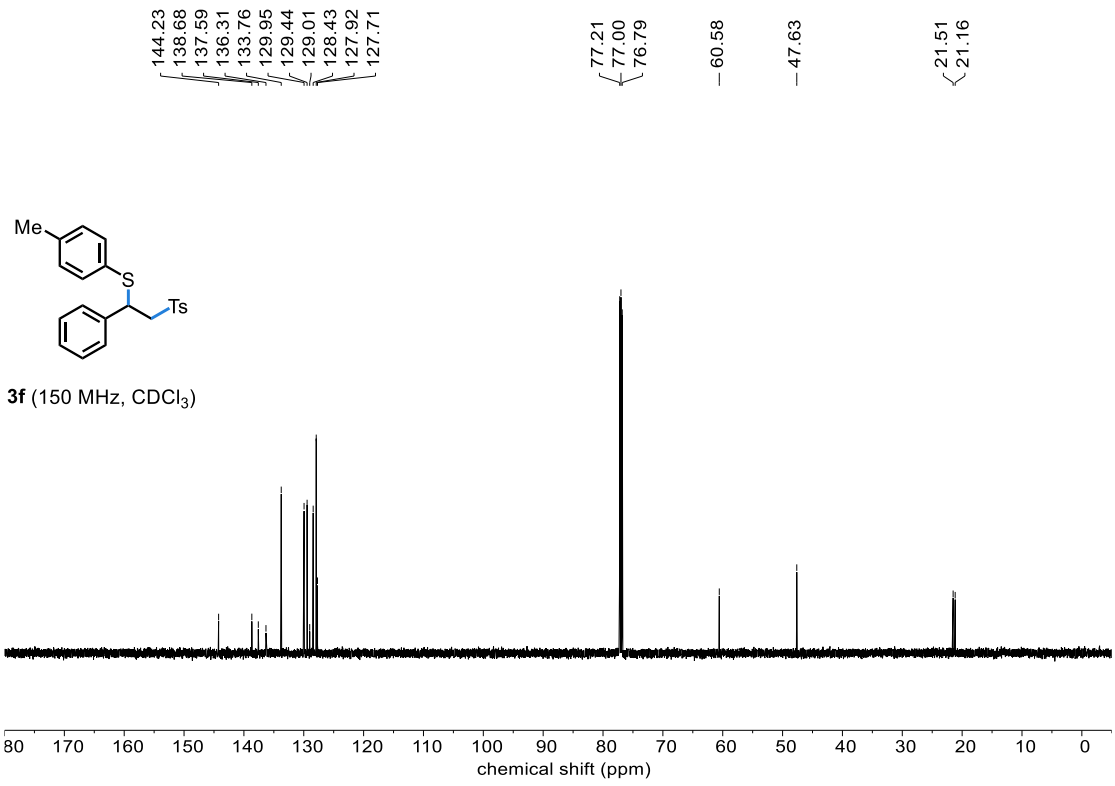
3d (150 MHz, $CDCl_3$)

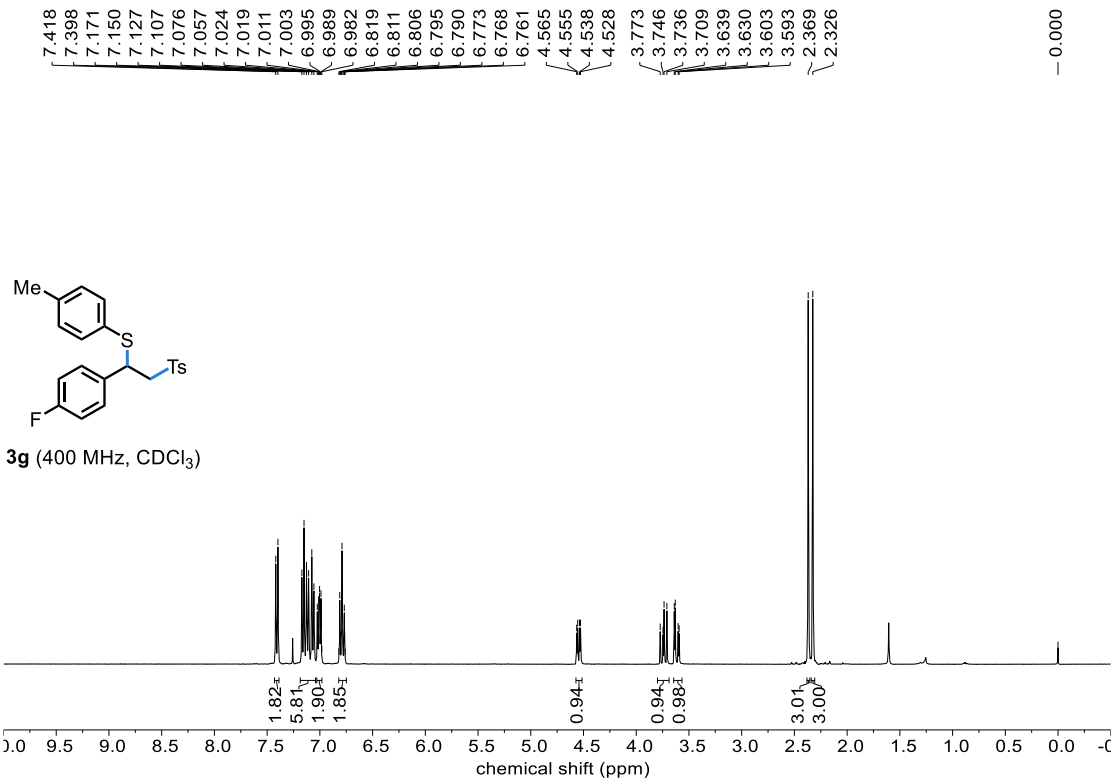


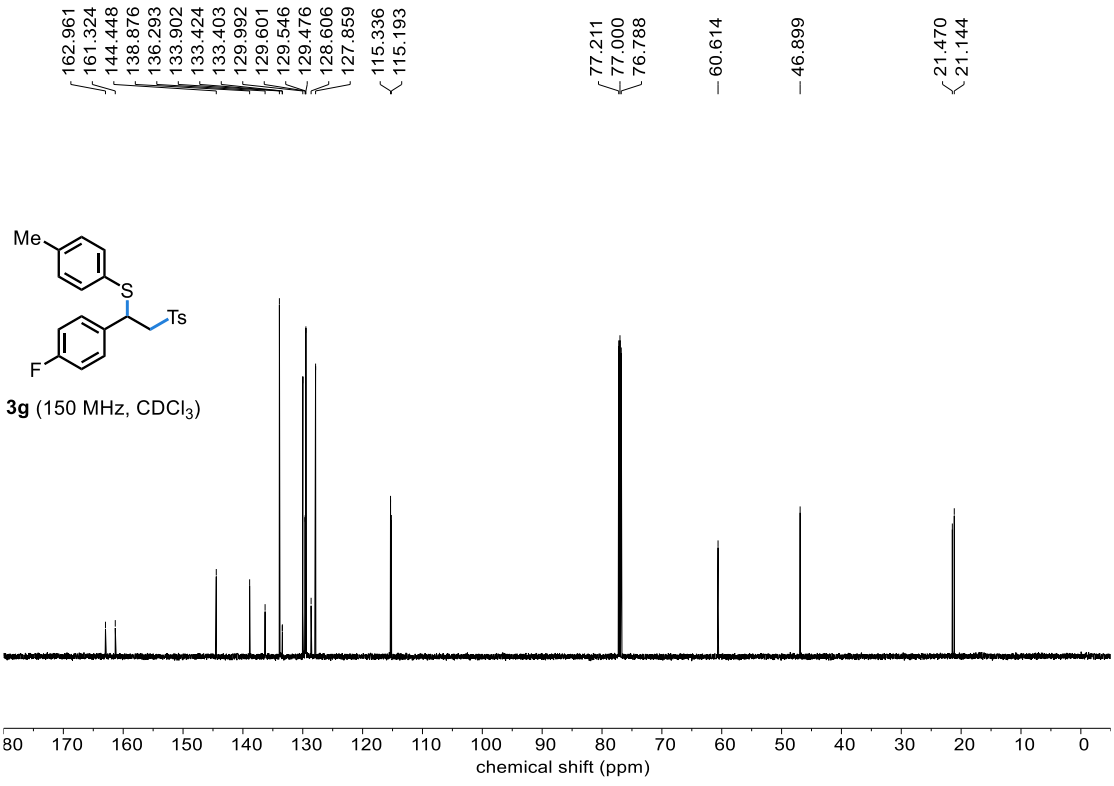

7.359
7.338
7.261
7.242
7.237
7.227
7.222
7.101
7.080
7.032
7.012
6.969
6.949
4.595
4.587
4.568
4.560
3.870
3.842
3.833
3.806
3.633
3.624
3.596
3.587
2.343
2.320
1.251
0.000
Me
S
Ts
tBu
3e (400 MHz, CDCl3)
2.00
2.34
3.89
1.91
1.97
0.97
0.94
1.00
3.03
3.23
9.03
chemical shift (ppm)

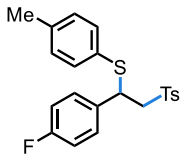

150.79
143.80
138.59
136.46
133.99
133.59
130.00
129.35
129.27
127.88
127.48
125.32
77.21
77.00
76.78
60.54
47.34
34.42
31.29
21.52
21.16
Me
S
Ts
tBu
3e (150 MHz, CDCl3)
f1 (ppm)


7.419
7.398
7.184
7.164
7.145
7.142
7.128
7.111
7.094
7.075
7.060
7.056
7.055
7.041
7.036
4.570
4.561
4.544
4.535
3.830
3.804
3.793
3.767
3.648
3.639
3.611
3.602
2.352
2.328
-0.000
Me
S
Ts
3f (400 MHz, CDCl3)
1.77
10.71
0.87
0.91
0.96
6.00
chemical shift (ppm)

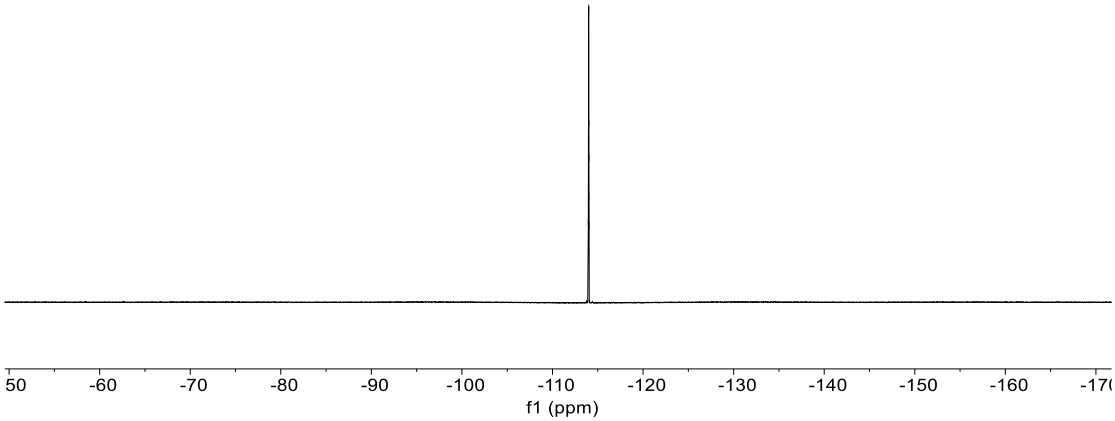

144.23
138.68
137.59
136.31
133.76
129.95
129.44
129.01
128.43
127.92
127.71
77.21
77.00
76.79
60.58
47.63
21.51
21.16
Me
S
Ts
3f (150 MHz, CDCl3)
chemical shift (ppm)

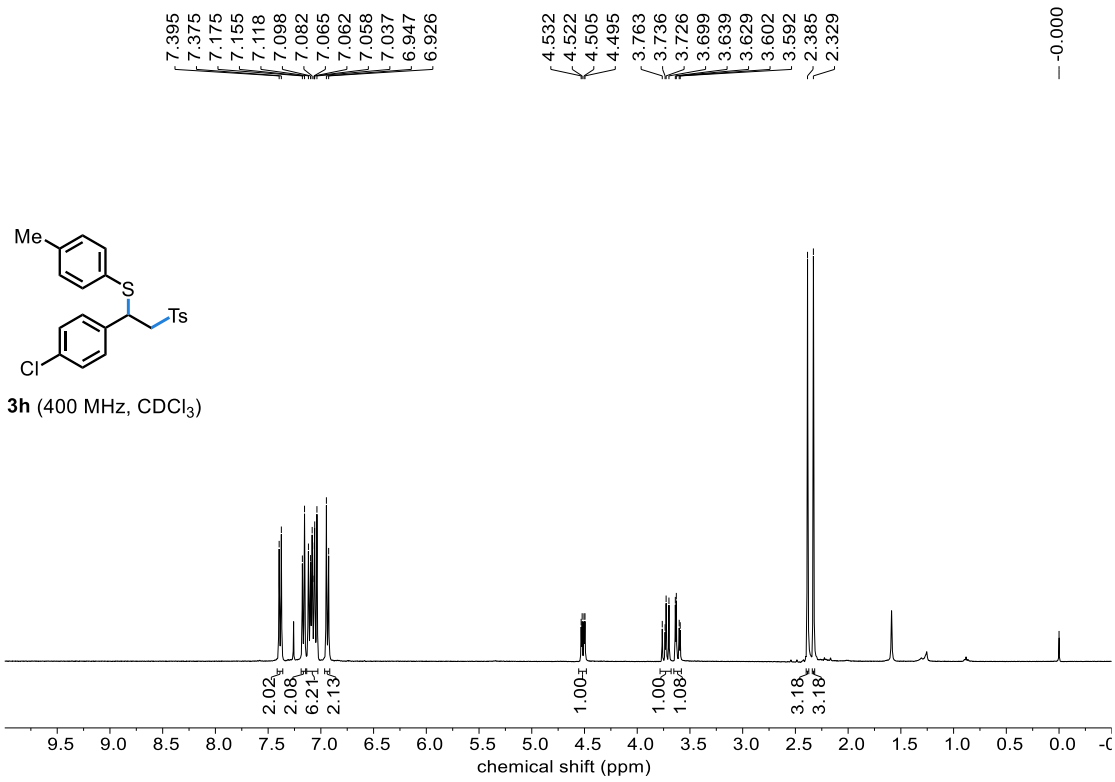

7.418
7.398
7.171
7.150
7.127
7.107
7.076
7.057
7.024
7.019
7.011
7.003
6.995
6.989
6.982
6.819
6.811
6.806
6.795
6.790
6.773
6.768
6.761
4.565
4.555
4.538
4.528
3.773
3.746
3.736
3.709
3.639
3.630
3.603
3.593
2.369
2.326
0.000
Me
S
Ts
F
3g (400 MHz, CDCl3)
1.82
5.81
1.90
1.85
0.94
0.94
0.98
3.01
3.00
chemical shift (ppm)

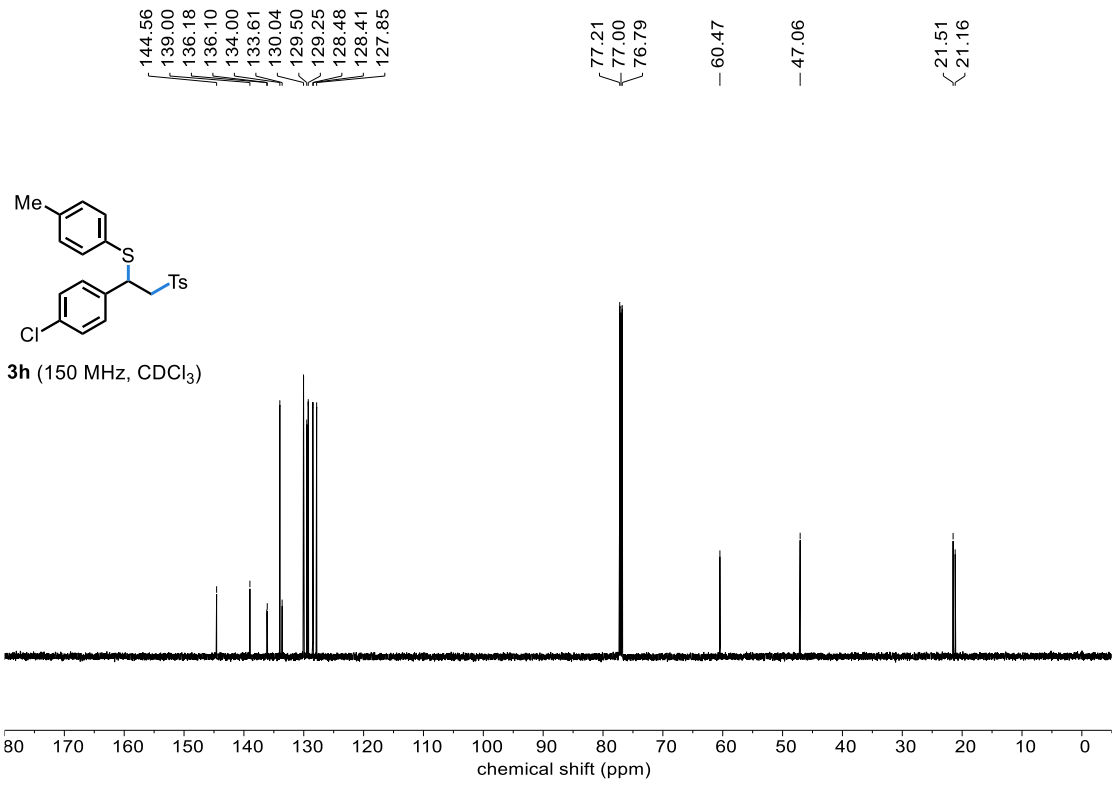

162.961
161.324
144.448
138.876
136.293
133.902
133.424
133.403
129.992
129.601
129.546
129.476
128.606
127.859
115.336
115.193
77.211
77.000
76.788
60.614
46.899
21.470
21.144
Me
S
Ts
F
3g (150 MHz, CDCl3)
chemical shift (ppm)

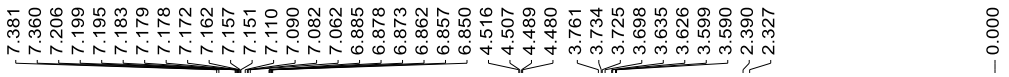


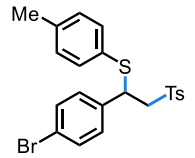
3g (376 MHz, $CDCl_3$)



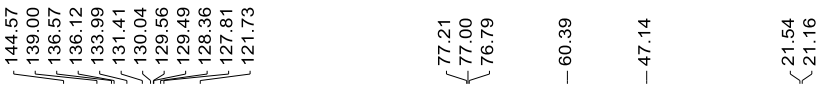

7.395
7.375
7.175
7.155
7.118
7.098
7.082
7.065
7.062
7.058
7.037
6.947
6.926
4.532
4.522
4.505
4.495
3.763
3.736
3.726
3.699
3.639
3.629
3.602
3.592
2.385
2.329
-0.000
Me
S
Ts
Cl
3h (400 MHz, CDCl3)
2.02
2.08
6.21
2.13
1.00
1.00
1.08
3.18
3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

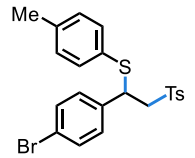

144.56
139.00
136.18
136.10
134.00
133.61
130.04
129.50
129.25
128.48
128.41
127.85
77.21
77.00
76.79
60.47
47.06
21.51
21.16
Me
S
Ts
Cl
3h (150 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)



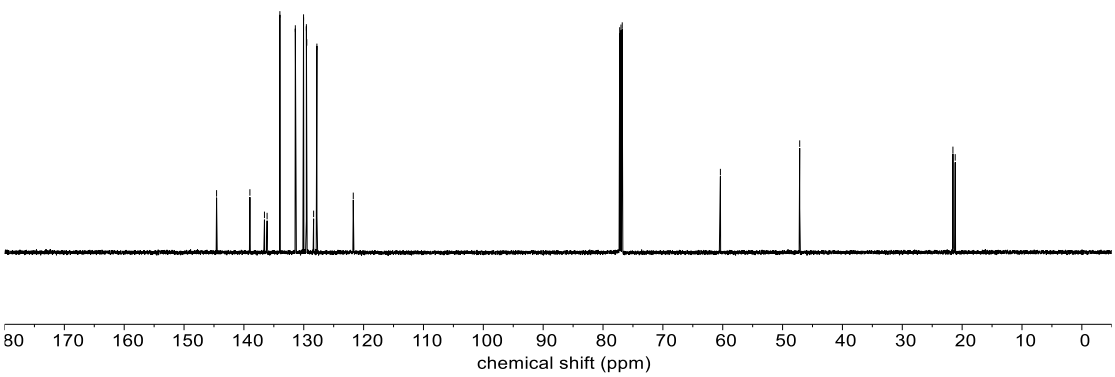


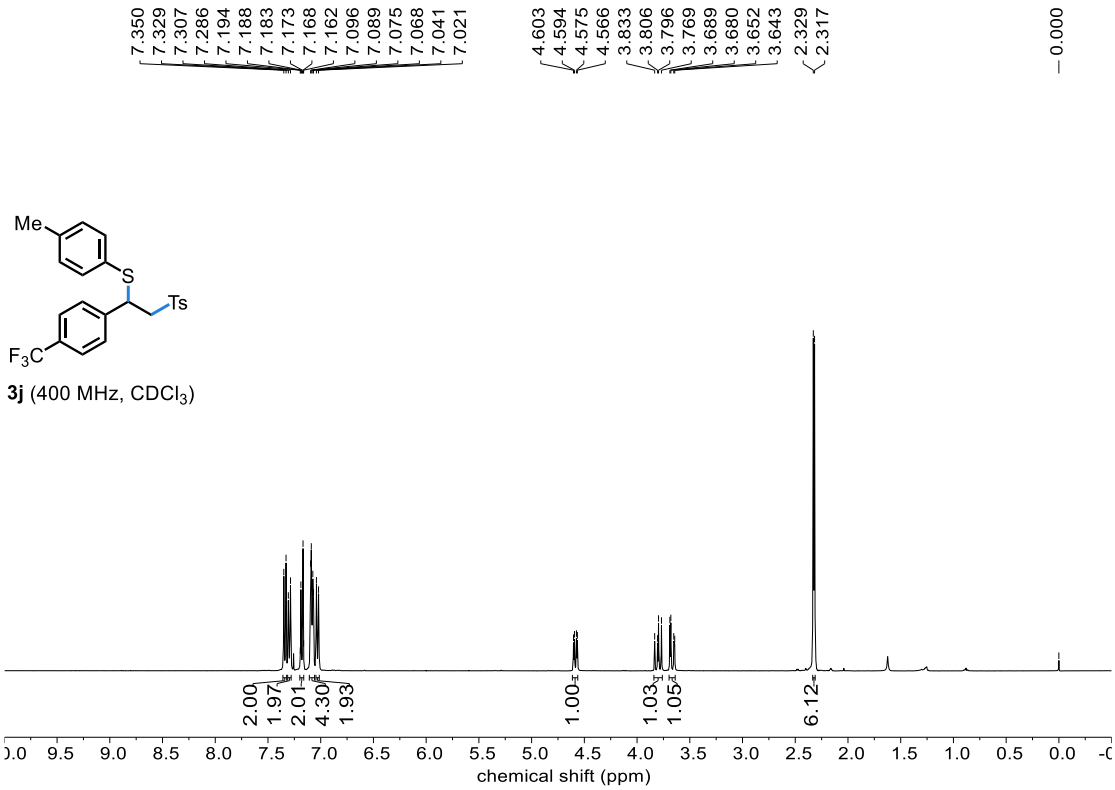
3i (400 MHz, $CDCl_3$)

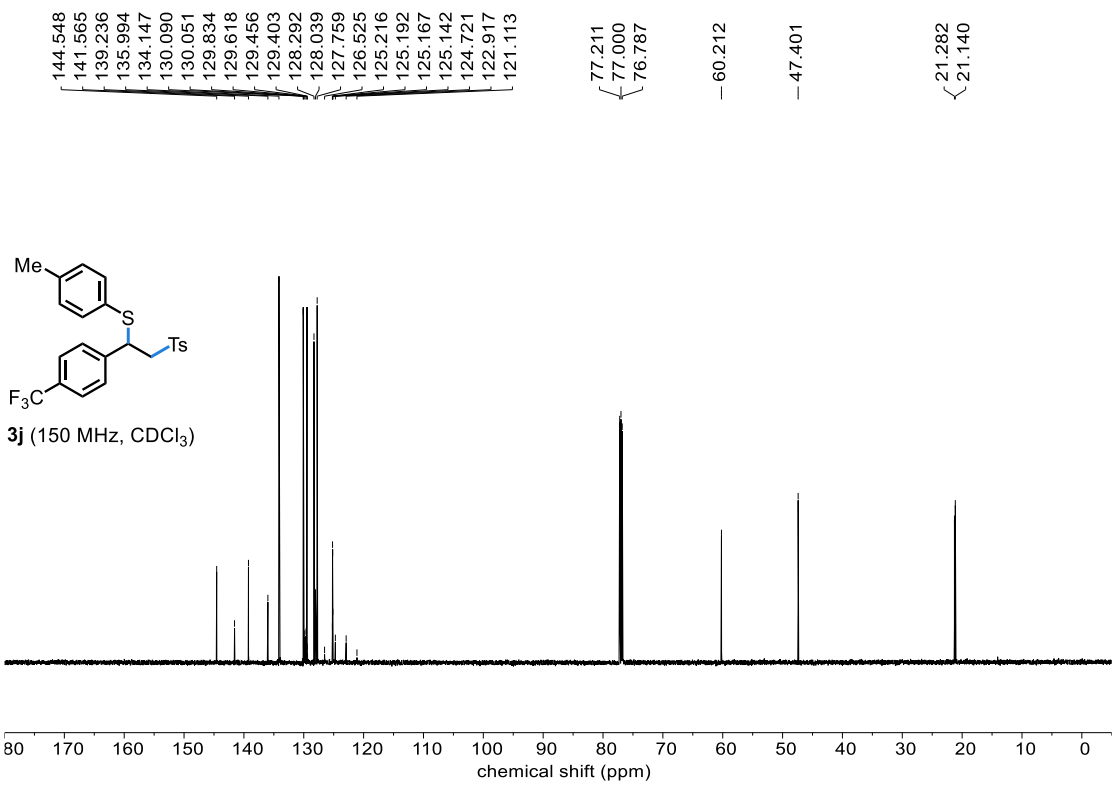


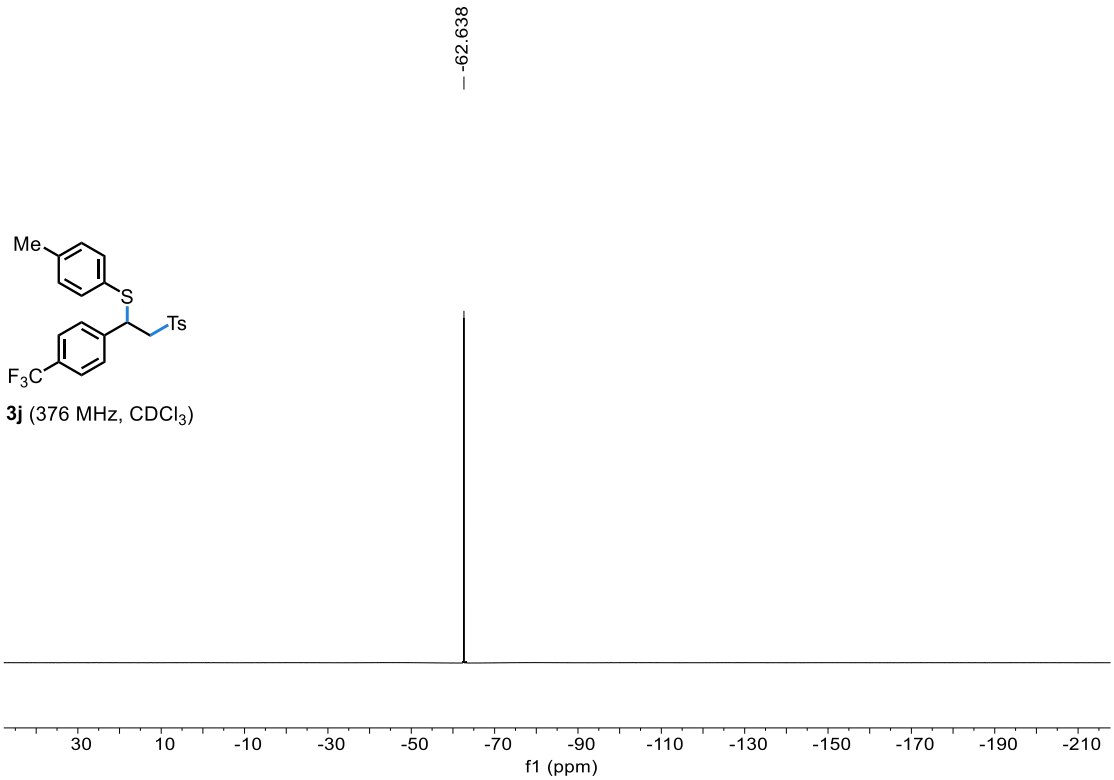


3i (150 MHz, $CDCl_3$)

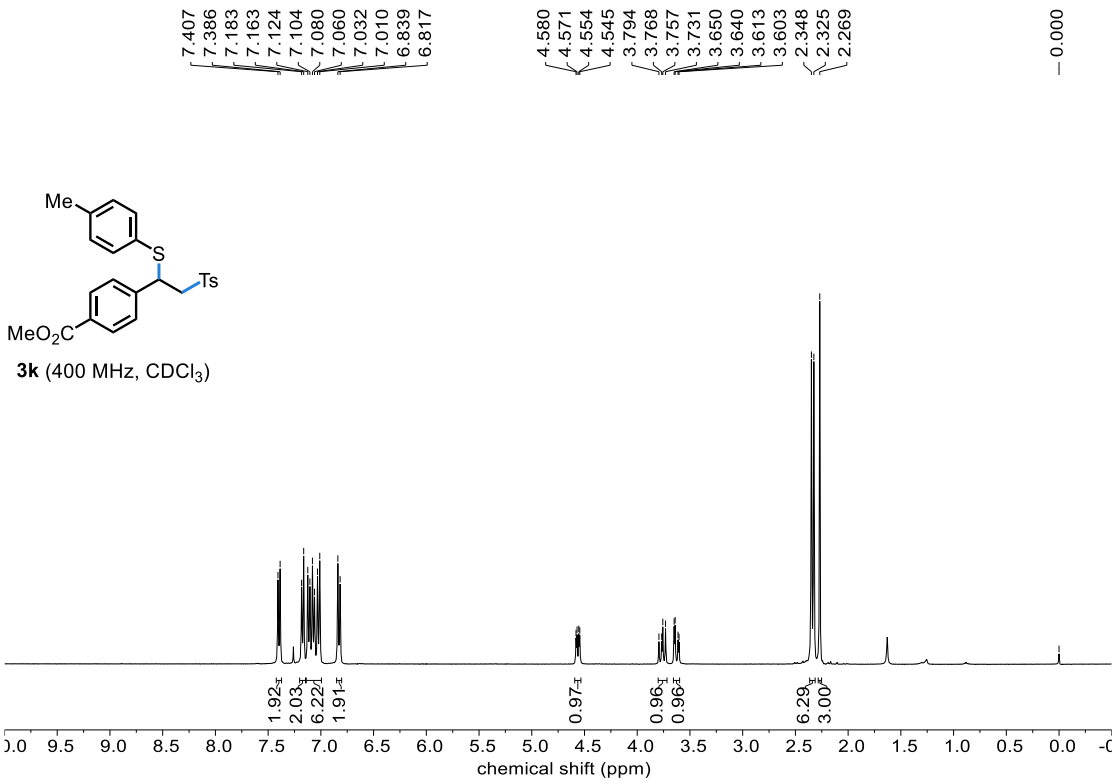


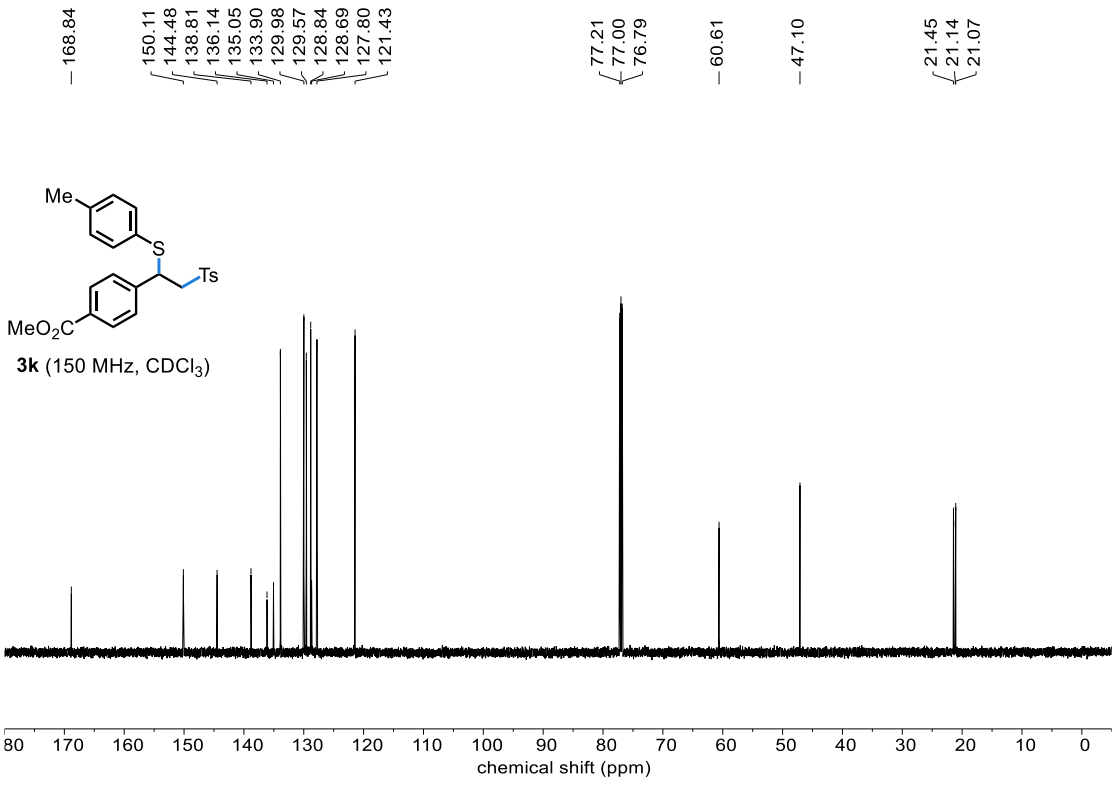

7.350
7.329
7.307
7.286
7.194
7.188
7.183
7.173
7.168
7.162
7.096
7.089
7.075
7.068
7.041
7.021
4.603
4.594
4.575
4.566
3.833
3.806
3.796
3.769
3.689
3.680
3.652
3.643
2.329
2.317
0.000
Me
S
Ts
F3C
3j (400 MHz, CDCl3)
2.00
1.97
2.01
4.30
1.93
1.00
1.03
1.05
6.12
chemical shift (ppm)

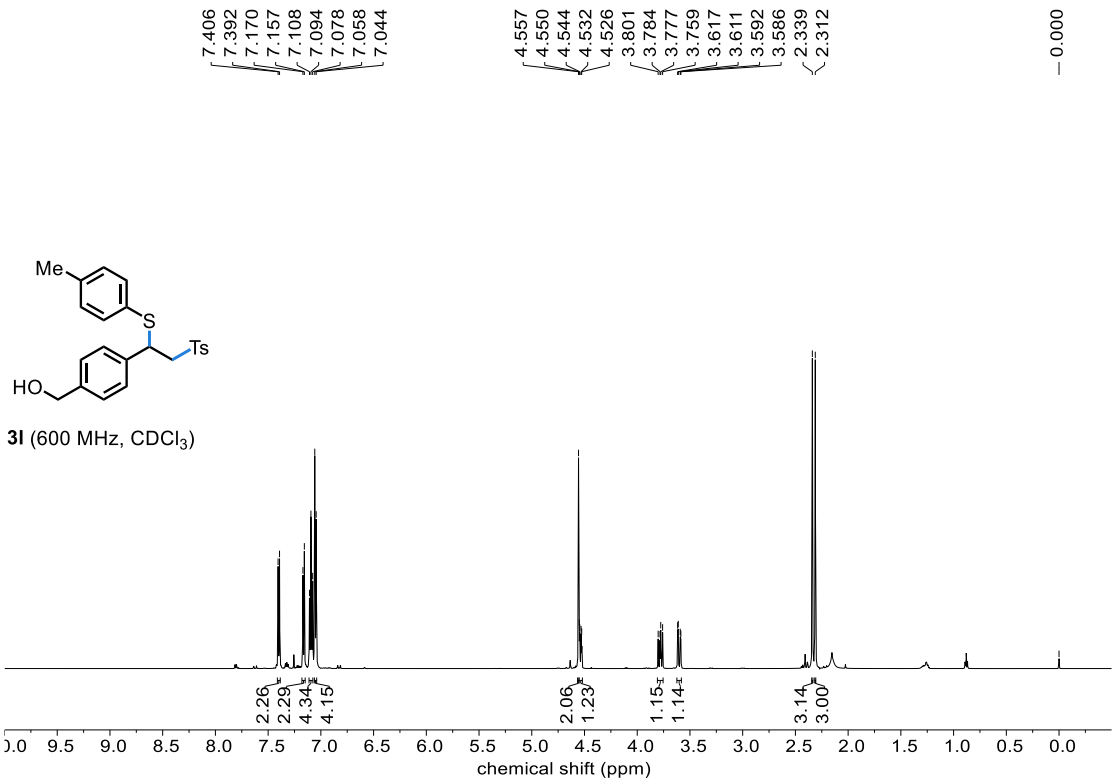

144.548
141.565
139.236
135.994
134.147
130.090
130.051
129.834
129.618
129.456
129.403
128.292
128.039
127.759
126.525
125.216
125.192
125.167
125.142
124.721
122.917
121.113
77.211
77.000
76.787
60.212
47.401
21.282
21.140
Me
S
Ts
F3C
3j (150 MHz, CDCl3)
chemical shift (ppm)

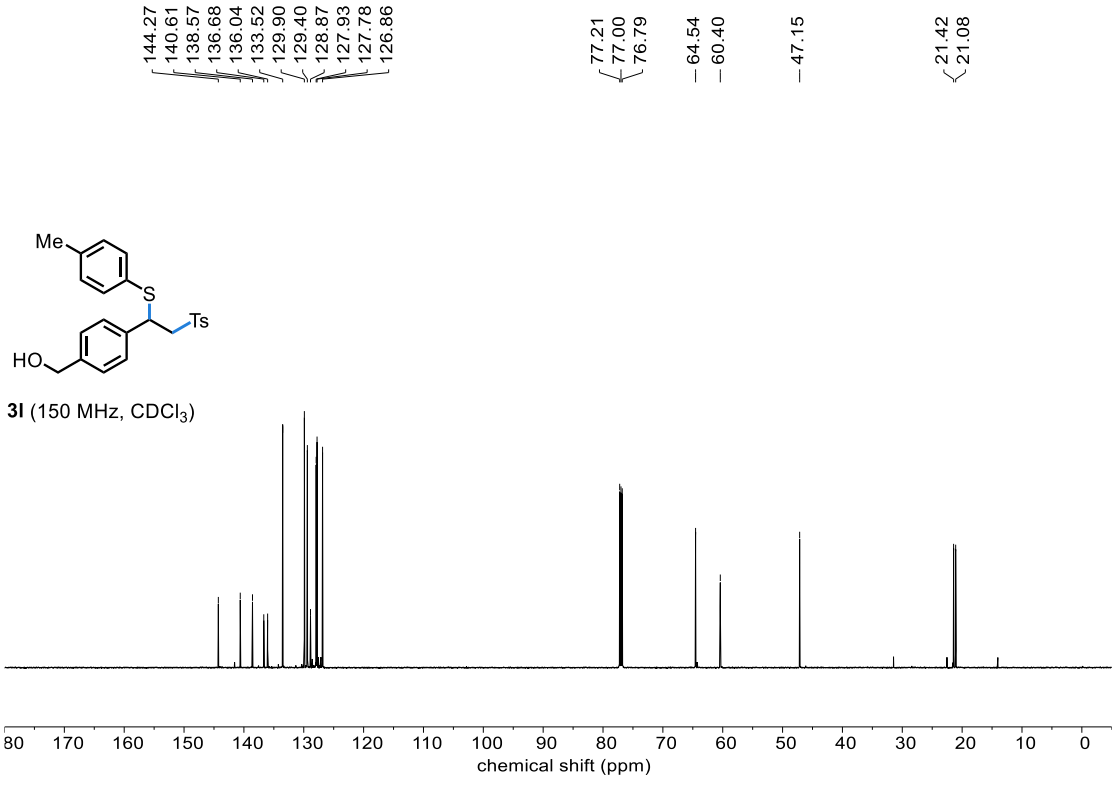


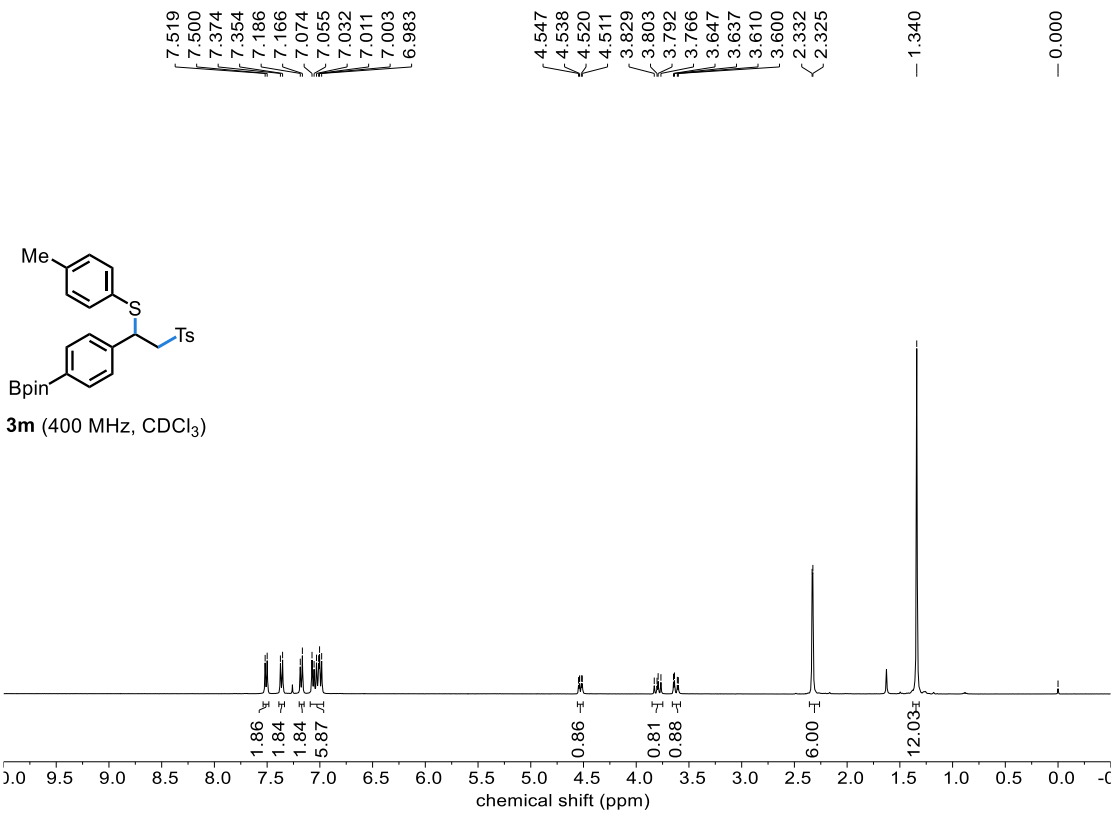
3j (376 MHz, $CDCl_3$)


7.407
7.386
7.183
7.163
7.124
7.104
7.080
7.060
7.032
7.010
6.839
6.817
4.580
4.571
4.554
4.545
3.794
3.768
3.757
3.731
3.650
3.640
3.613
3.603
2.348
2.325
2.269
0.000
Me
S
Ts
MeO2C
3k (400 MHz, CDCl3)
1.92
2.03
6.22
1.91
0.97
0.96
0.96
6.29
3.00
chemical shift (ppm)

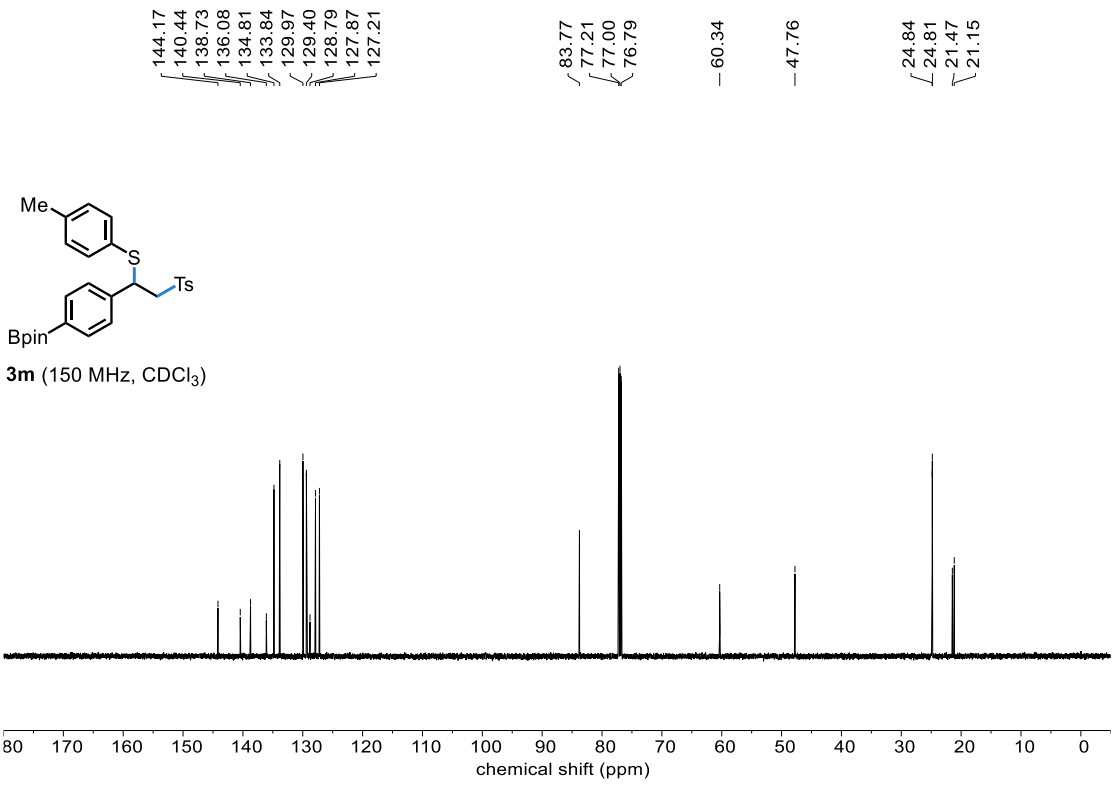

168.84
150.11
144.48
138.81
136.14
135.05
133.90
129.98
129.57
128.84
128.69
127.80
121.43
77.21
77.00
76.79
60.61
47.10
21.45
21.14
21.07
Me
S
Ts
MeO2C
3k (150 MHz, CDCl3)
chemical shift (ppm)


7.406
7.392
7.170
7.157
7.108
7.094
7.078
7.058
7.044
4.557
4.550
4.544
4.532
4.526
3.801
3.784
3.777
3.759
3.617
3.611
3.592
3.586
2.339
2.312
0.000
Me
S
Ts
HO
3l (600 MHz, CDCl3)
2.26
2.29
4.34
4.15
2.06
1.23
1.15
1.14
3.14
3.00
chemical shift (ppm)

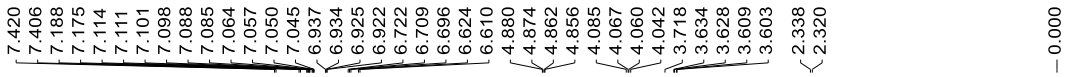

144.27
140.61
138.57
136.68
136.04
133.52
129.90
129.40
128.87
127.93
127.78
126.86
77.21
77.00
76.79
64.54
60.40
47.15
21.42
21.08
Me
S
Ts
HO
3l (150 MHz, CDCl3)
chemical shift (ppm)

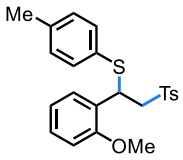


3m (400 MHz, $CDCl_3$)

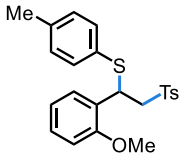


3m (150 MHz, $CDCl_3$)

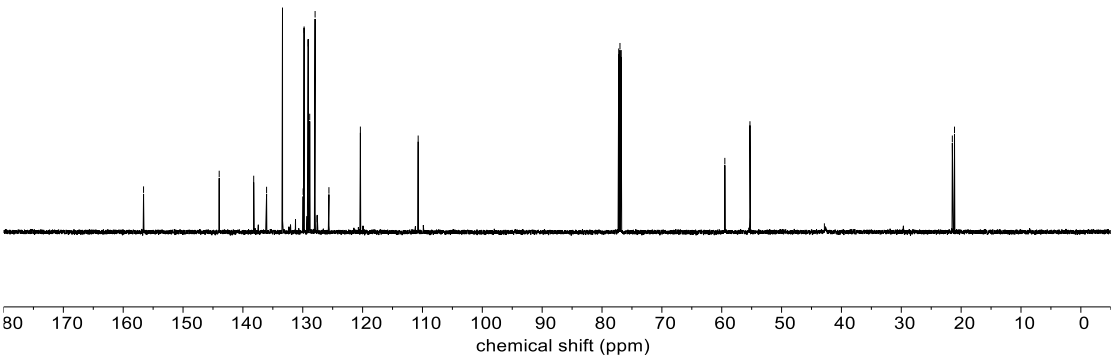


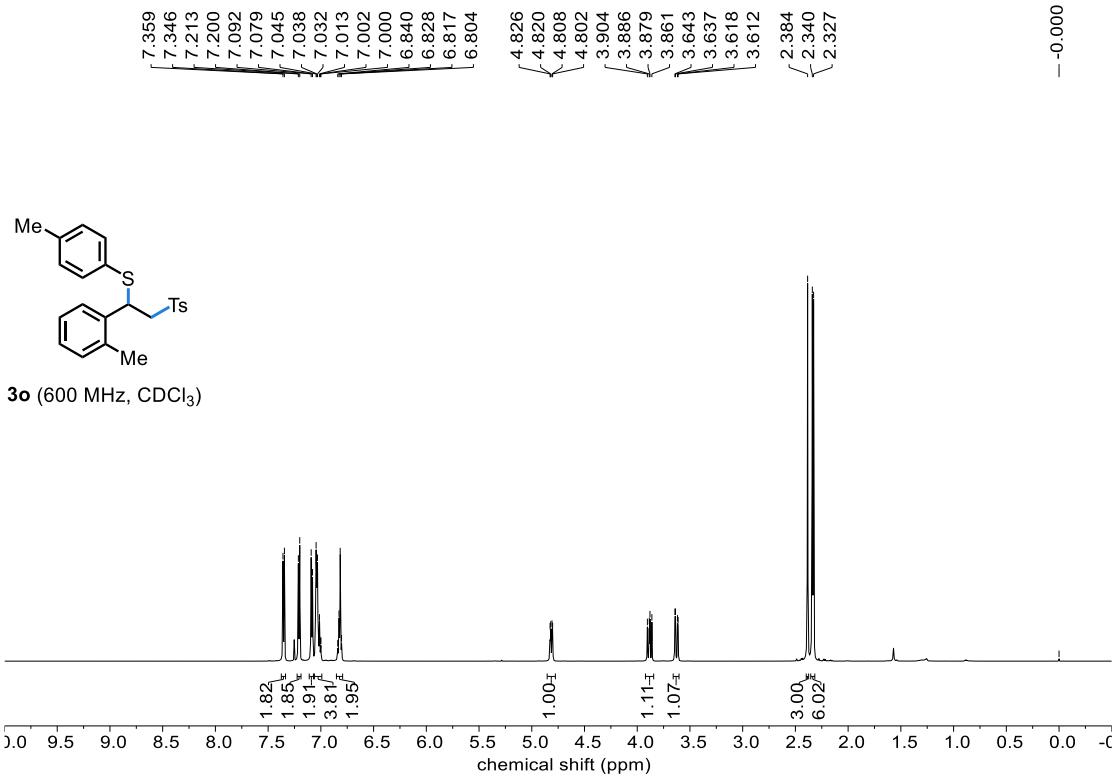


3n (600 MHz, $CDCl_3$)

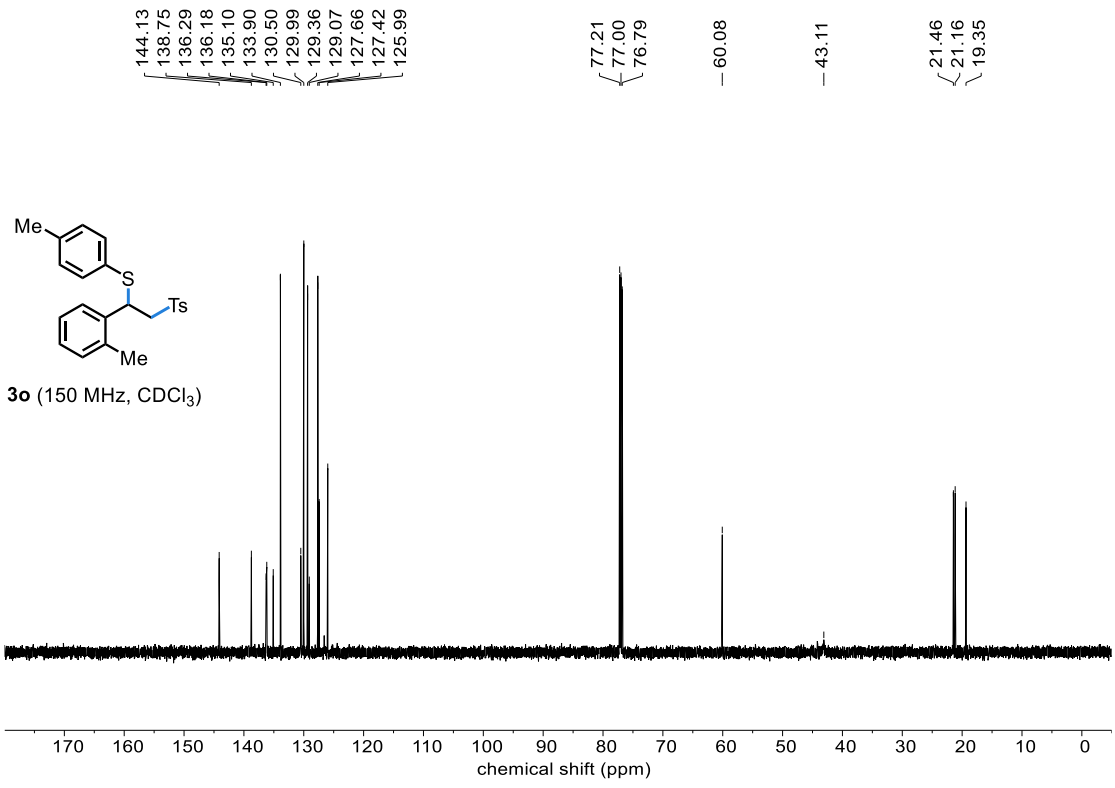


3n (150 MHz, $CDCl_3$)

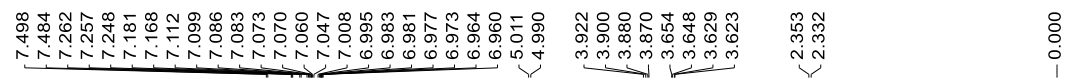


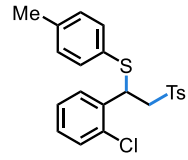


3o (600 MHz, $CDCl_3$)

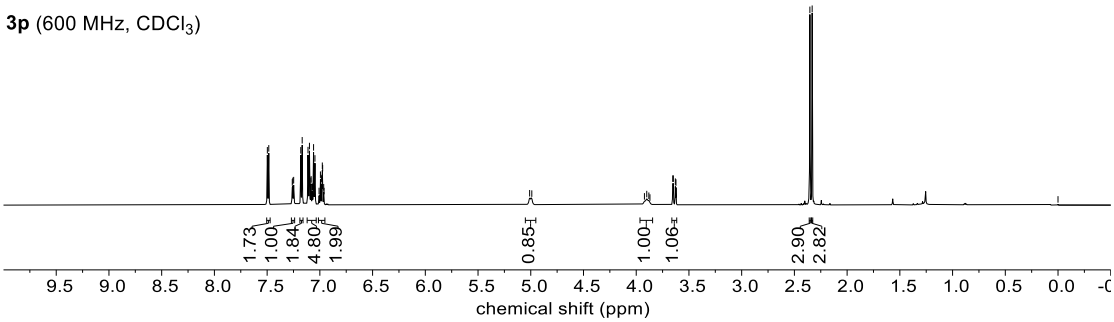


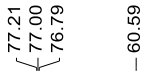
3o (150 MHz, $CDCl_3$)

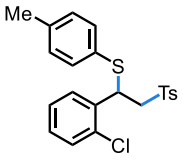




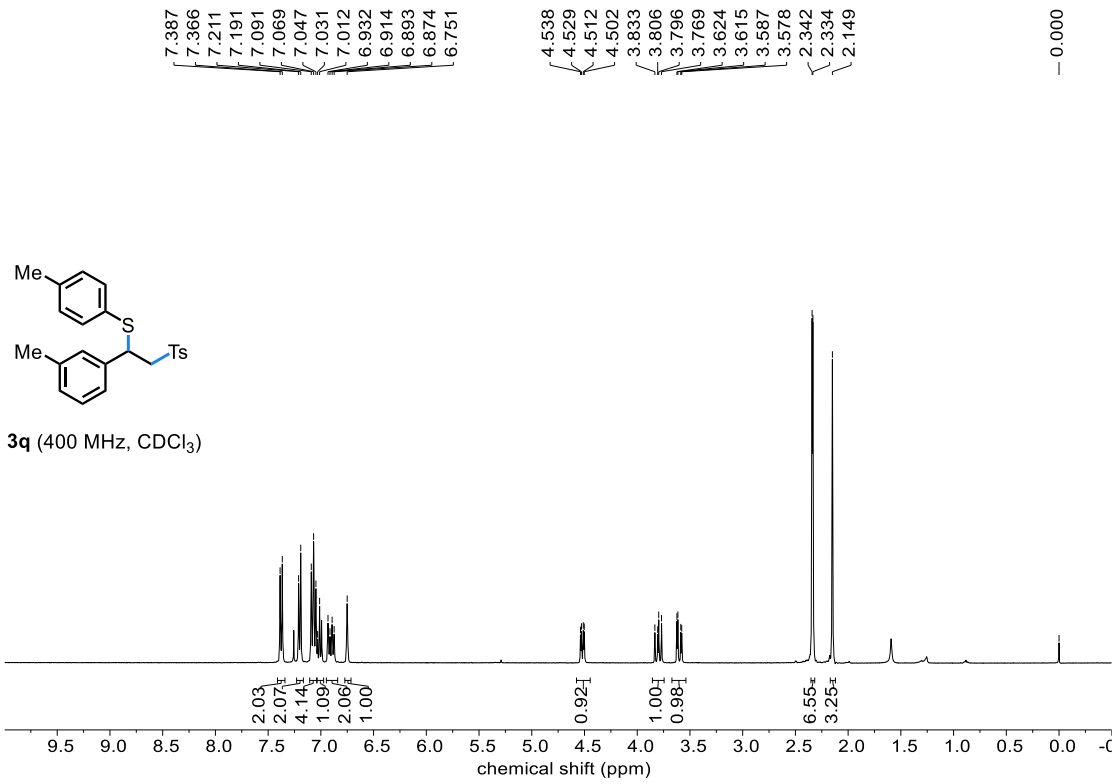
3p (600 MHz, $CDCl_3$)

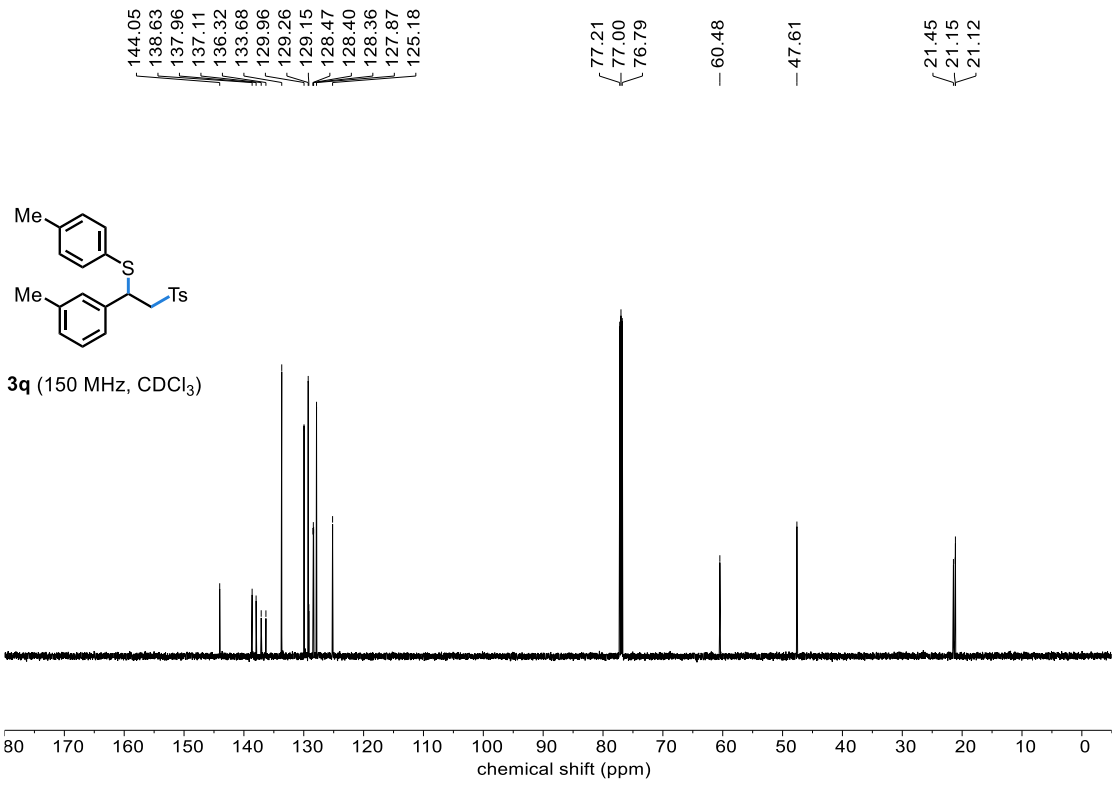


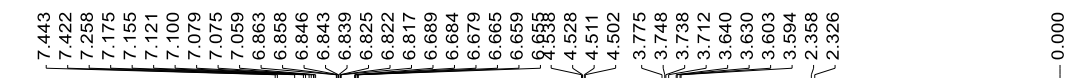


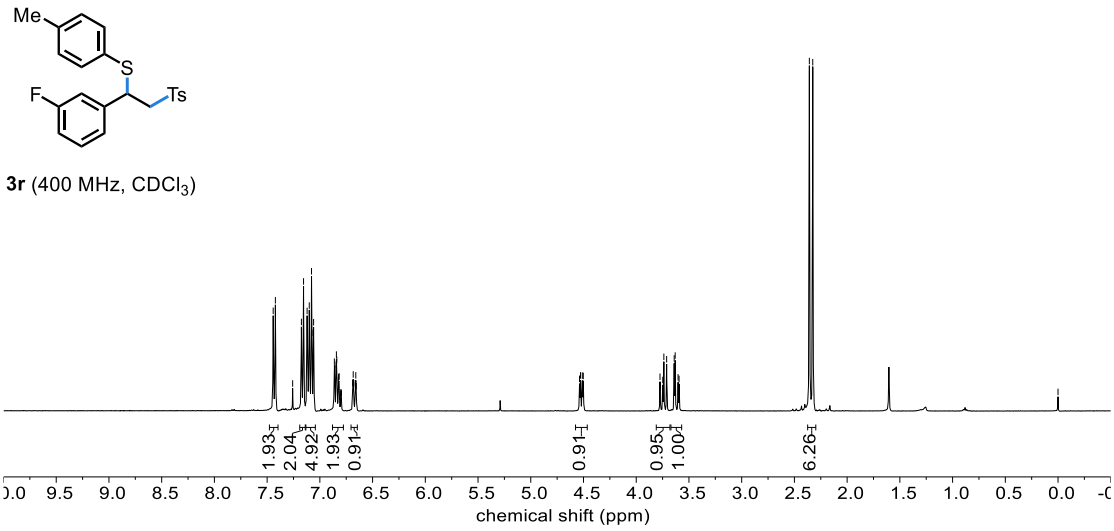


3p (150 MHz, $CDCl_3$)

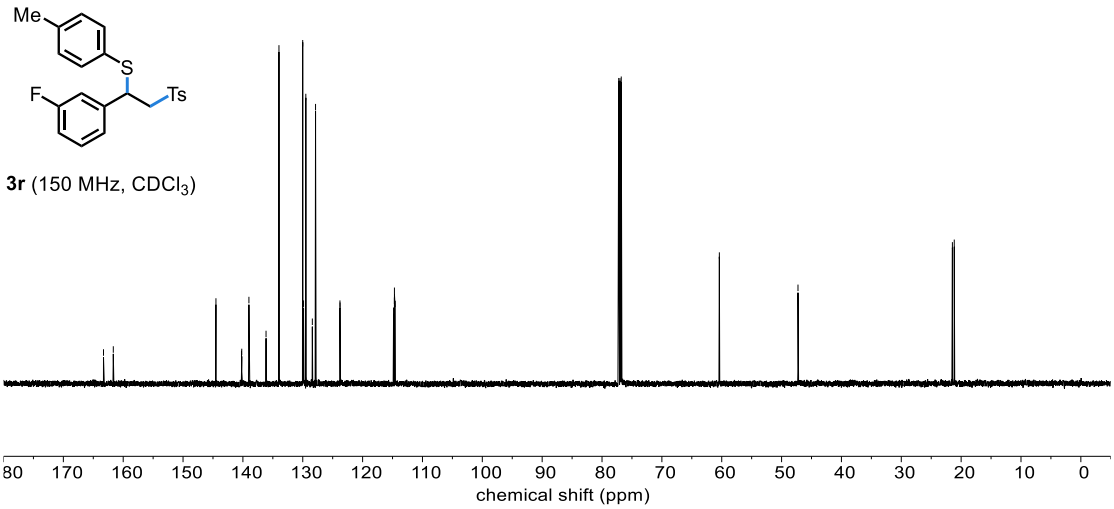

7.387
7.366
7.211
7.191
7.091
7.069
7.047
7.031
7.012
6.932
6.914
6.893
6.874
6.751
4.538
4.529
4.512
4.502
3.833
3.806
3.796
3.769
3.624
3.615
3.587
3.578
2.342
2.334
2.149
0.000
Me
S
Me
Ts
3q (400 MHz, CDCl3)
2.03
2.07
4.14
1.09
2.06
1.00
0.92
1.00
0.98
6.55
3.25
chemical shift (ppm)


144.05
138.63
137.96
137.11
136.32
133.68
129.96
129.26
129.15
128.47
128.40
128.36
127.87
125.18
77.21
77.00
76.79
60.48
47.61
21.45
21.15
21.12
Me
S
Me
Ts
3q (150 MHz, CDCl3)
chemical shift (ppm)

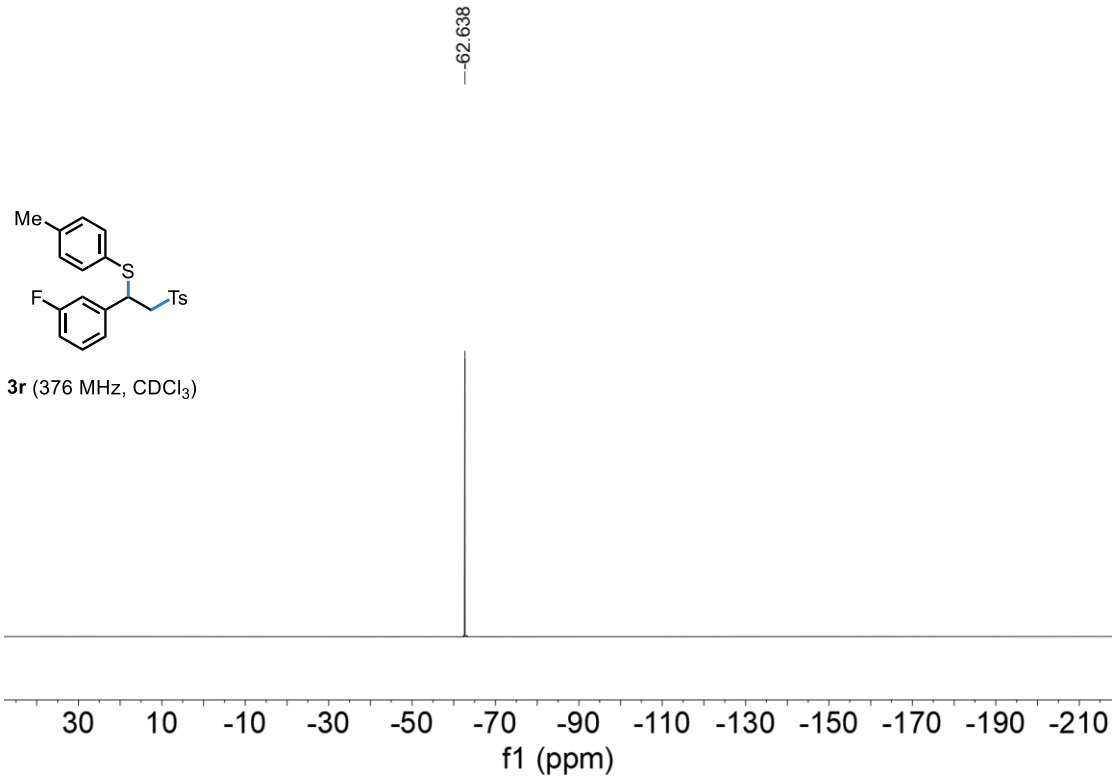




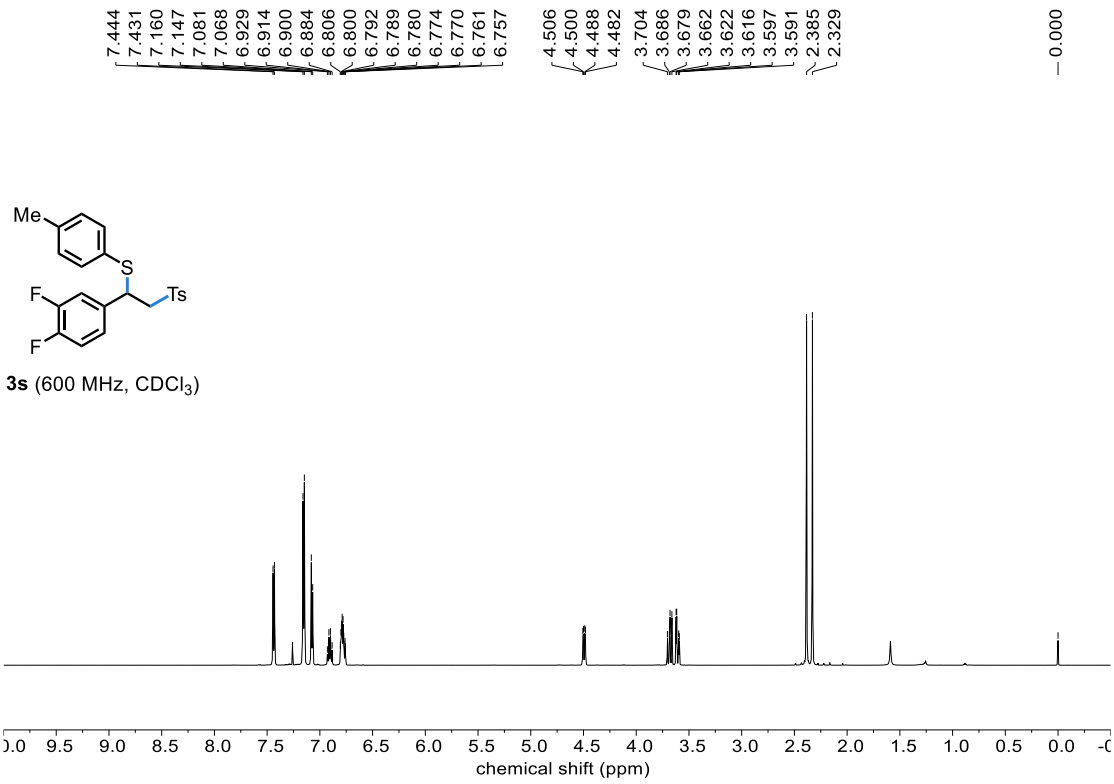
3r (400 MHz, $CDCl_3$)

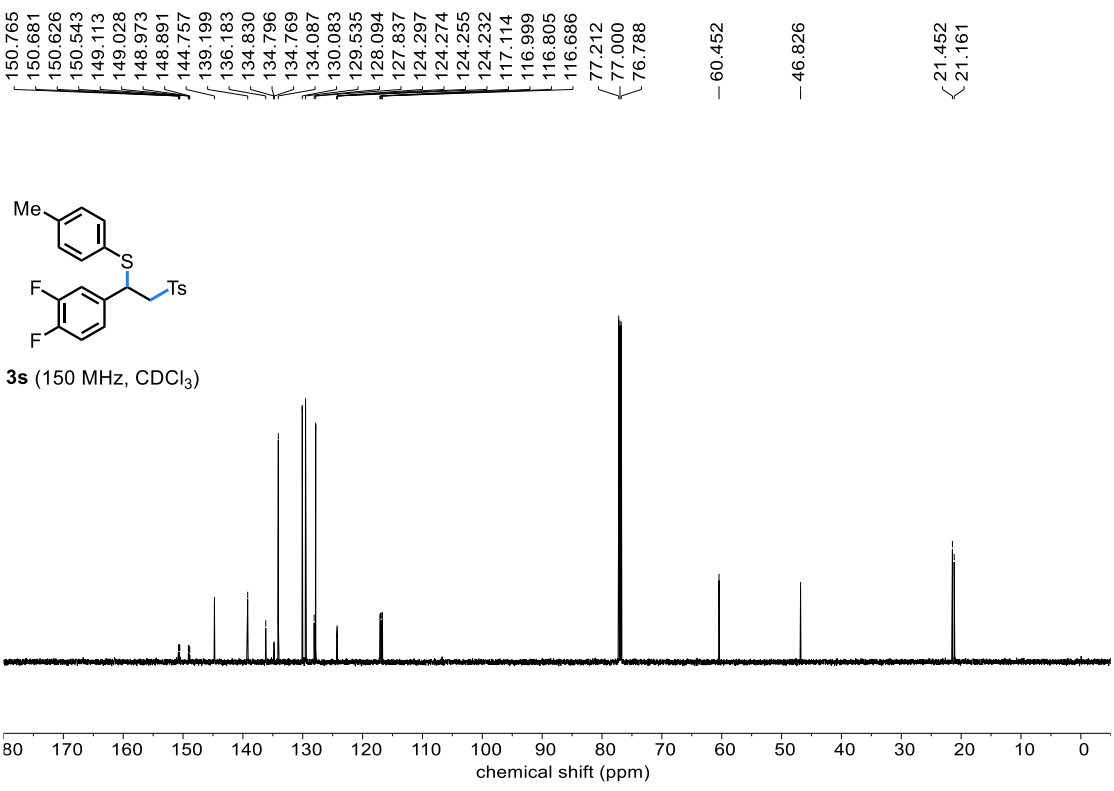


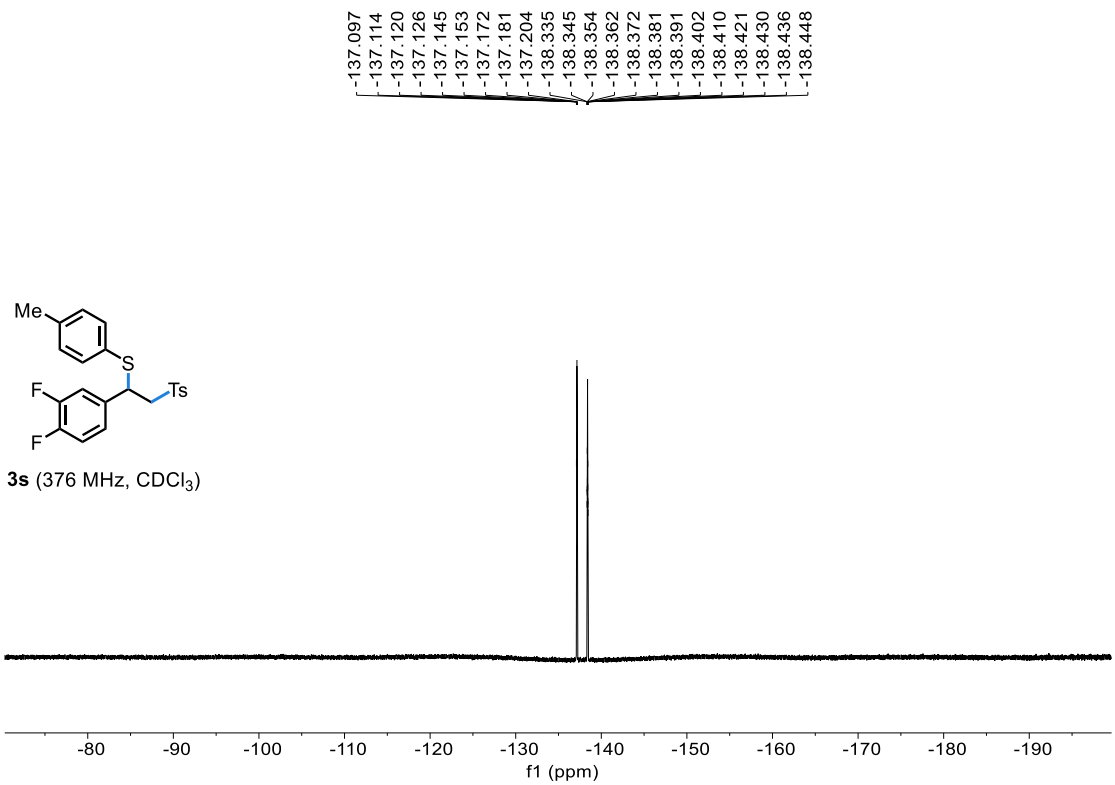
3r (150 MHz, $CDCl_3$)



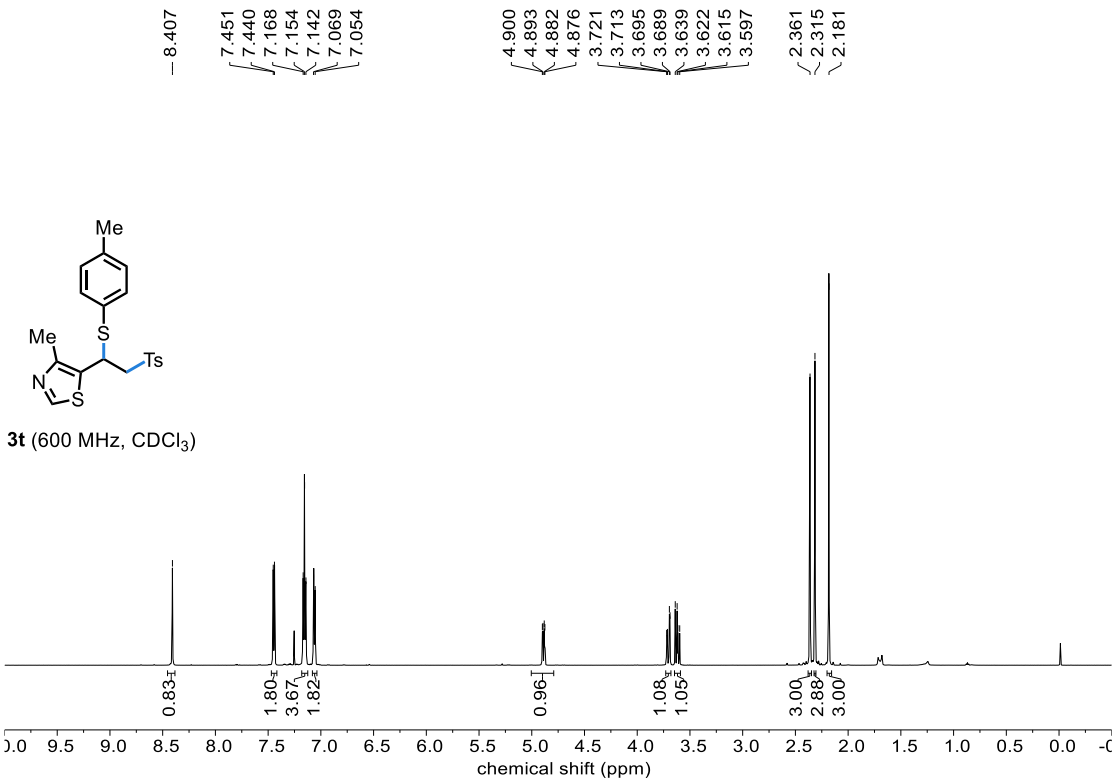
3r (376 MHz, $CDCl_3$)


7.444
7.431
7.160
7.147
7.081
7.068
6.929
6.914
6.900
6.884
6.806
6.800
6.792
6.789
6.780
6.774
6.770
6.761
6.757
4.506
4.500
4.488
4.482
3.704
3.686
3.679
3.662
3.622
3.616
3.597
3.591
2.385
2.329
0.000
Me
S
Ts
F
F
3s (600 MHz, CDCl3)
chemical shift (ppm)

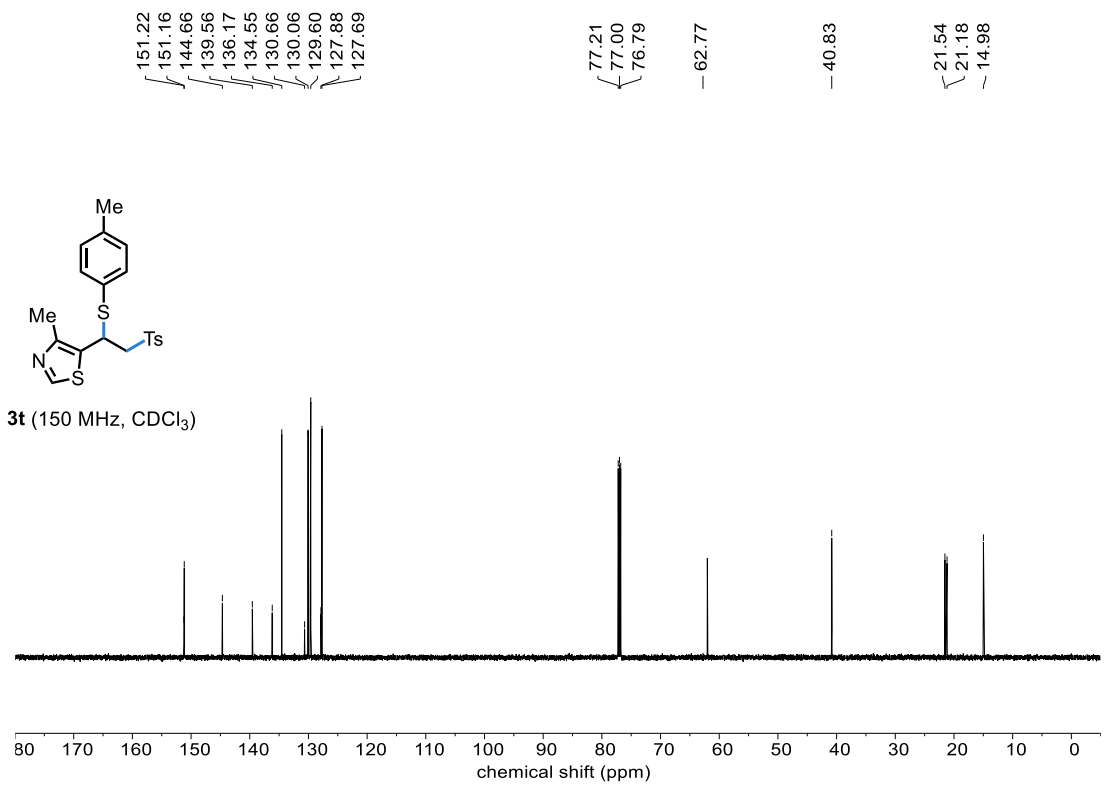

150.765
150.681
150.626
150.543
149.113
149.028
148.973
148.891
144.757
139.199
136.183
134.830
134.796
134.769
134.087
130.083
129.535
128.094
127.837
124.297
124.274
124.255
124.232
117.114
116.999
116.805
116.686
77.212
77.000
76.788
60.452
46.826
21.452
21.161
Me
S
Ts
F
F
3s (150 MHz, CDCl3)
chemical shift (ppm)



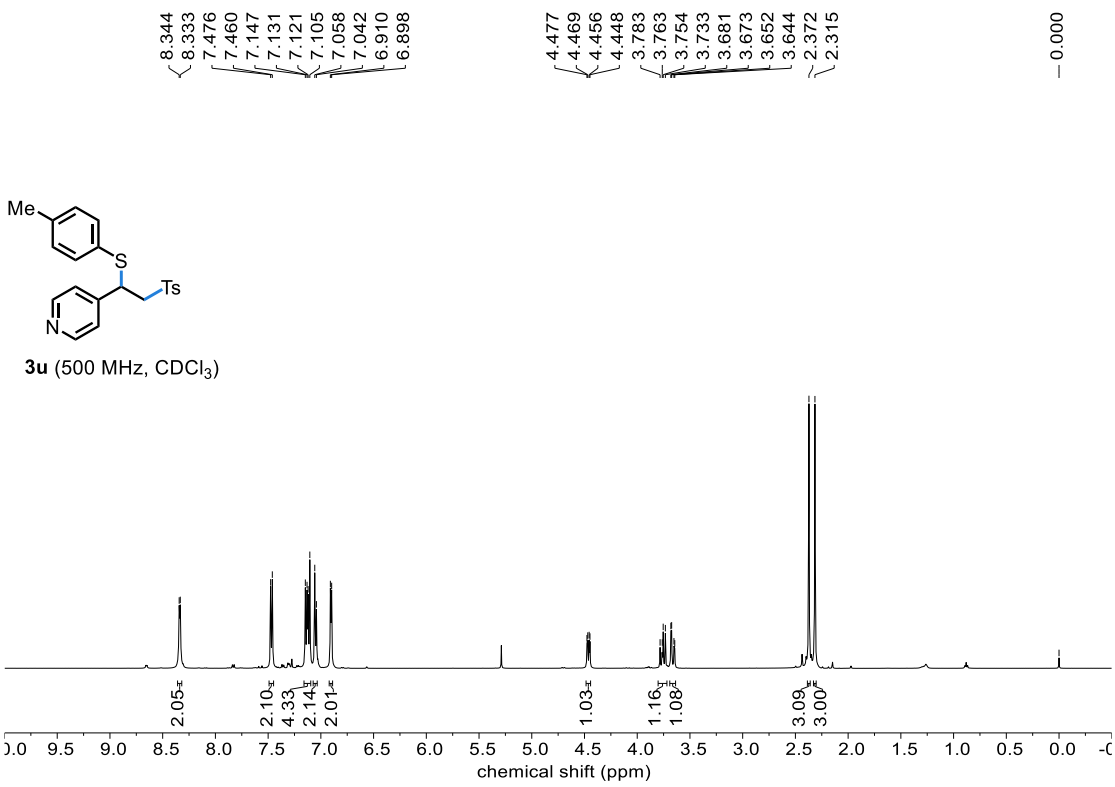
3s (376 MHz, $CDCl_3$)

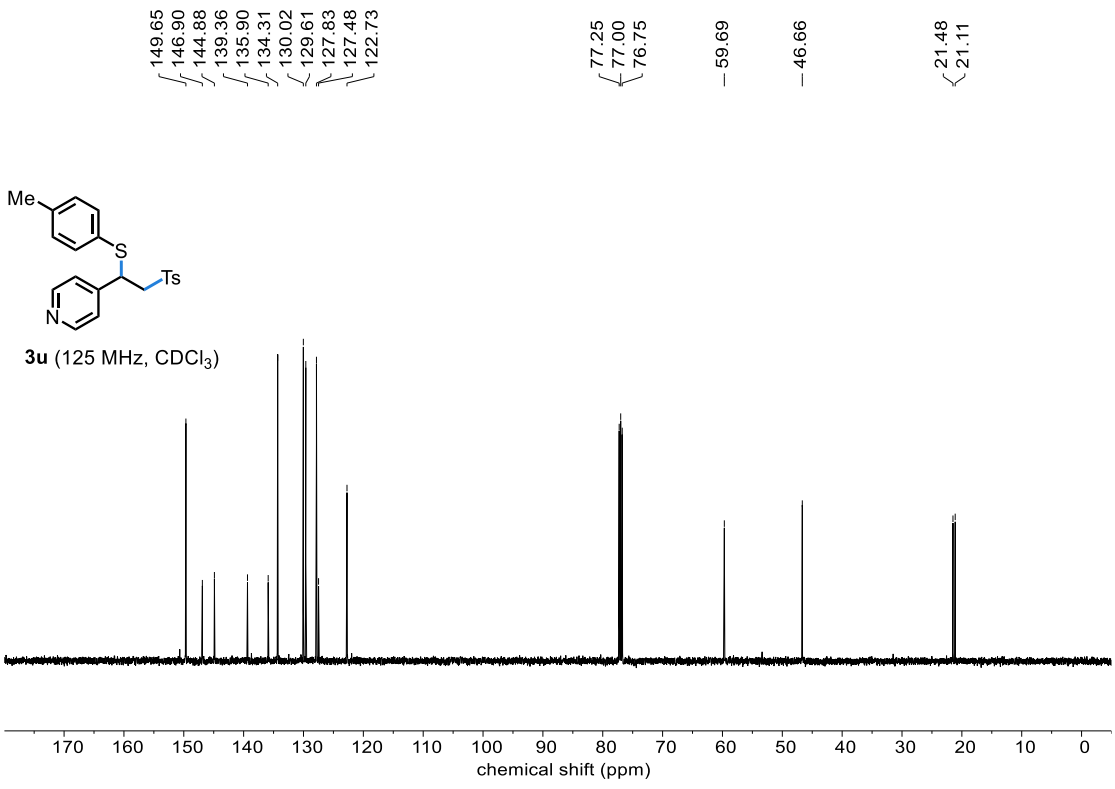


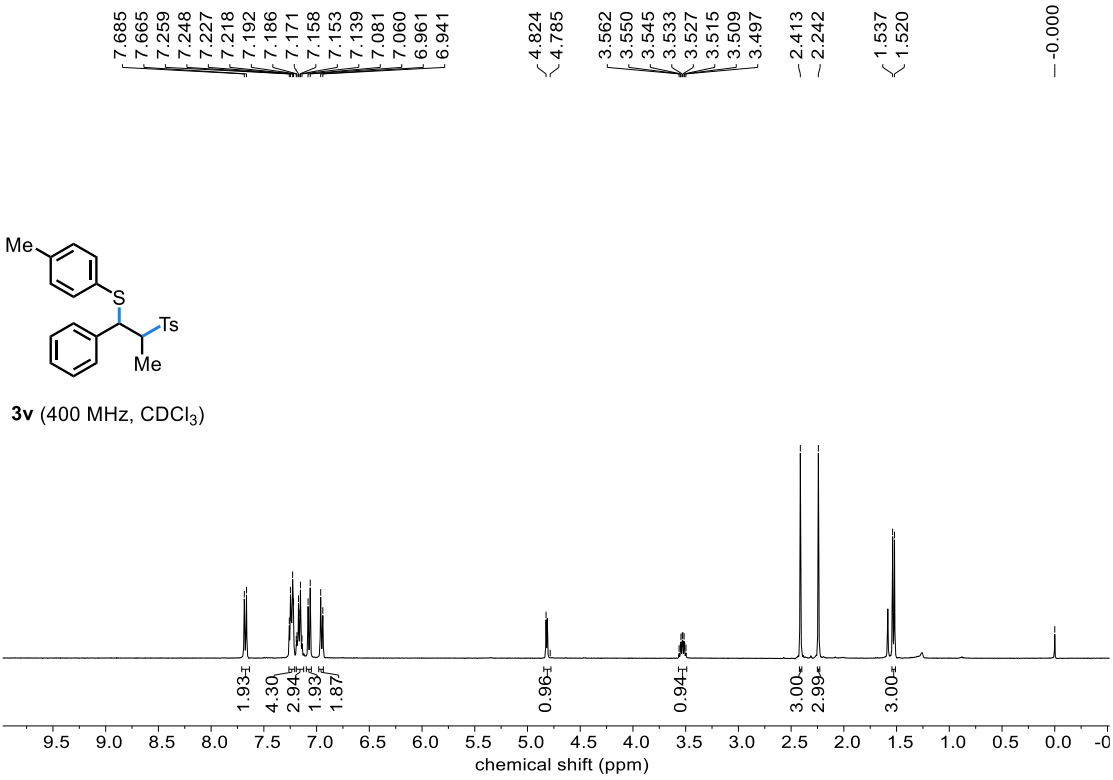
3t (600 MHz, $CDCl_3$)

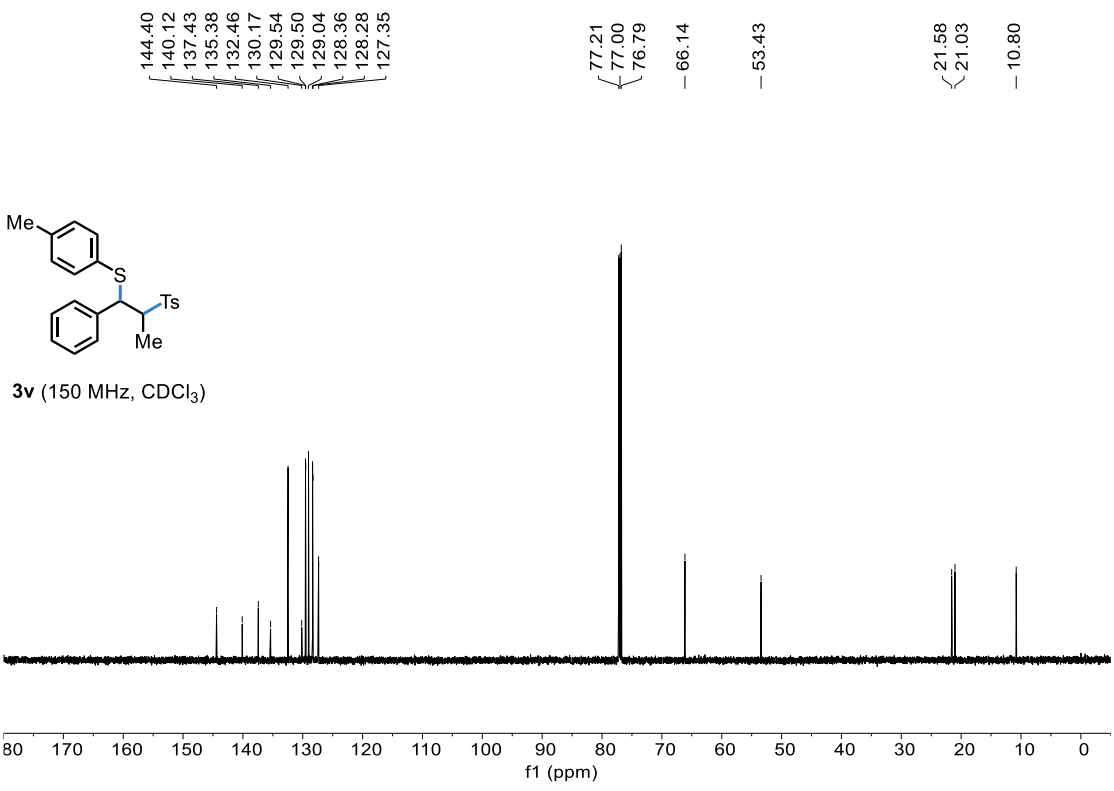


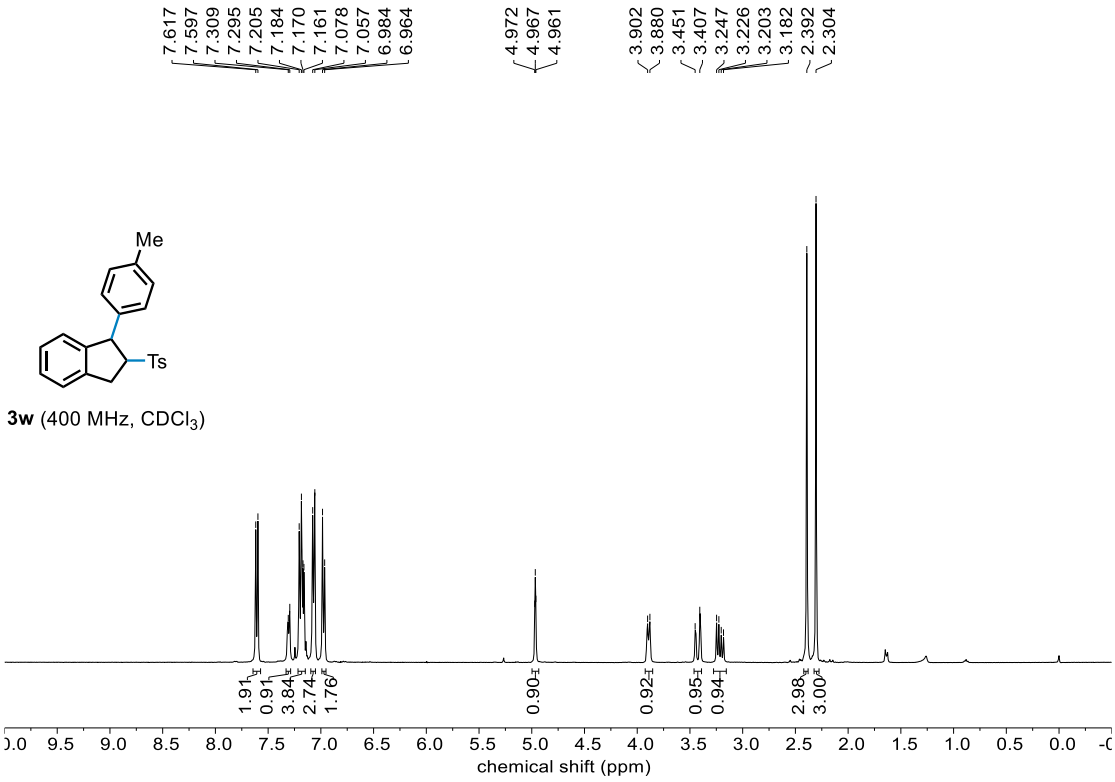
3t (150 MHz, $CDCl_3$)


8.344
8.333
7.476
7.460
7.147
7.131
7.121
7.105
7.058
7.042
6.910
6.898
4.477
4.469
4.456
4.448
3.783
3.763
3.754
3.733
3.681
3.673
3.652
3.644
2.372
2.315
0.000
Me
S
Ts
N
3u (500 MHz, CDCl3)
2.05
2.10
4.33
2.14
2.01
1.03
1.16
1.08
3.09
3.00
chemical shift (ppm)

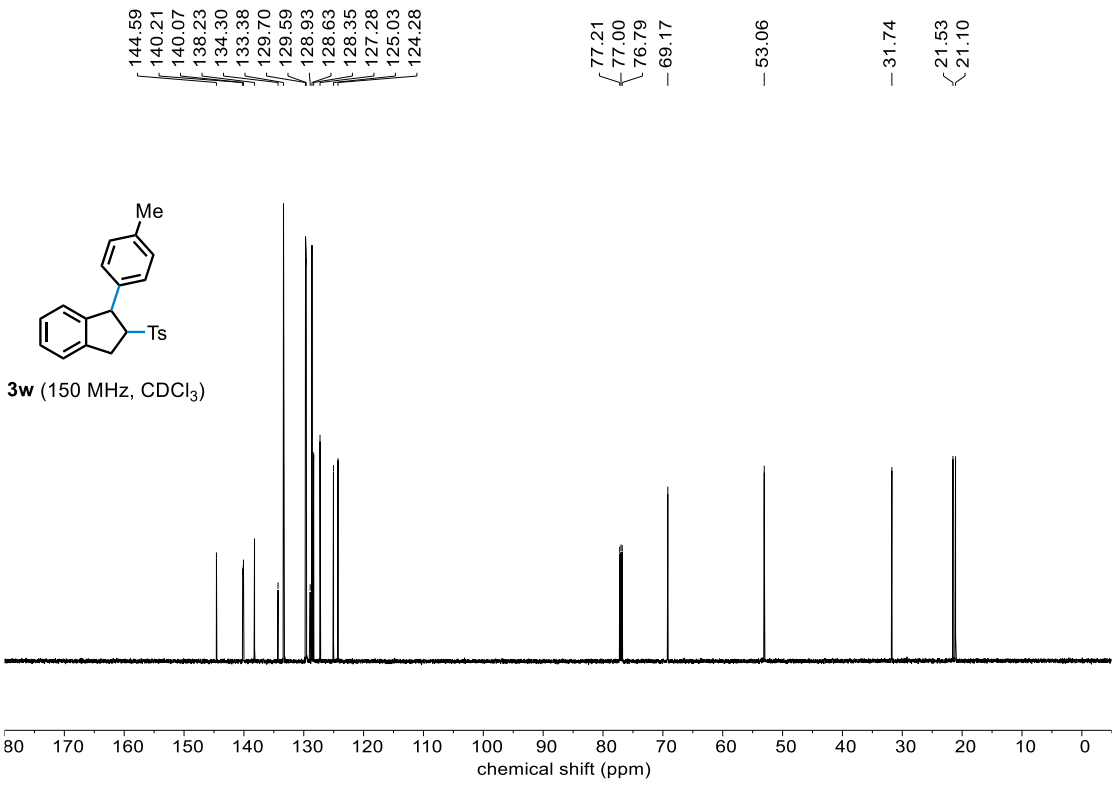

149.65
146.90
144.88
139.36
135.90
134.31
130.02
129.61
127.83
127.48
122.73
77.25
77.00
76.75
59.69
46.66
21.48
21.11
Me
S
Ts
N
3u (125 MHz, CDCl3)
chemical shift (ppm)


7.685
7.665
7.259
7.248
7.227
7.218
7.192
7.186
7.171
7.158
7.153
7.139
7.081
7.060
6.961
6.941
4.824
4.785
3.562
3.550
3.545
3.533
3.527
3.515
3.509
3.497
2.413
2.242
1.537
1.520
-0.000
Me
S
Ts
Me
3v (400 MHz, CDCl3)
1.93
4.30
2.94
1.93
1.87
0.96
0.94
3.00
2.99
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
chemical shift (ppm)

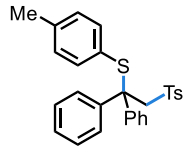

144.40
140.12
137.43
135.38
132.46
130.17
129.54
129.50
129.04
128.36
128.28
127.35
77.21
77.00
76.79
66.14
53.43
21.58
21.03
10.80
Me
S
Ts
Me
3v (150 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



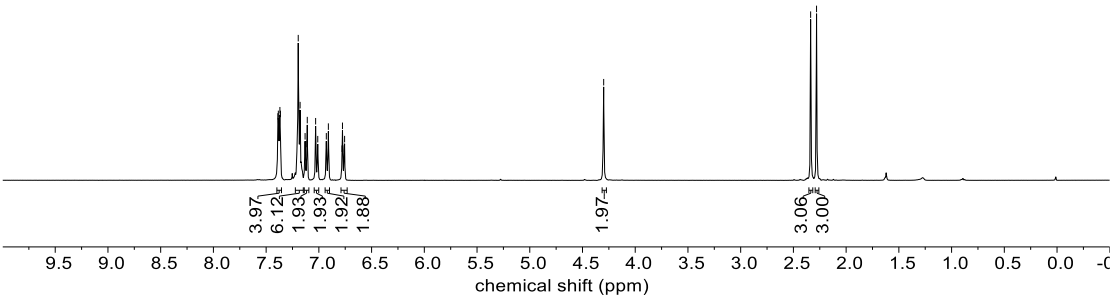
3w (400 MHz, $CDCl_3$)

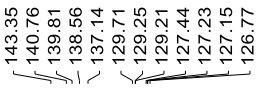


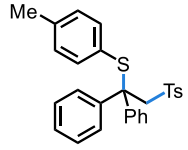
3w (150 MHz, $CDCl_3$)



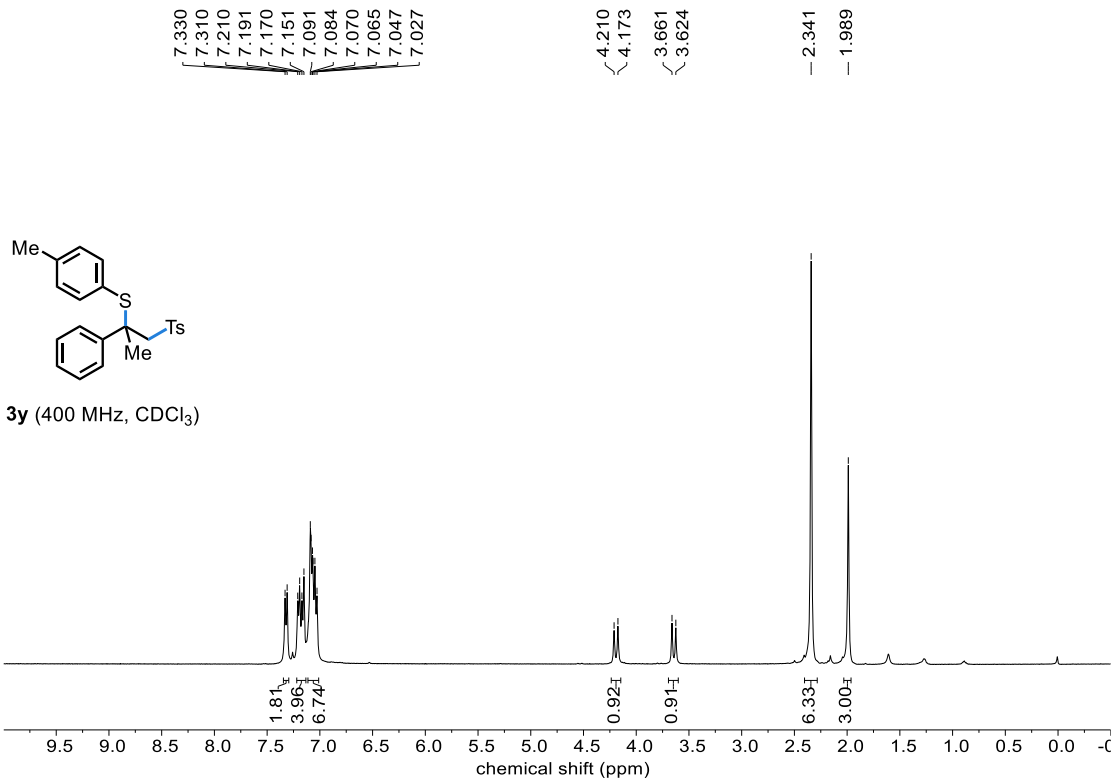
3x (400 MHz, $CDCl_3$)



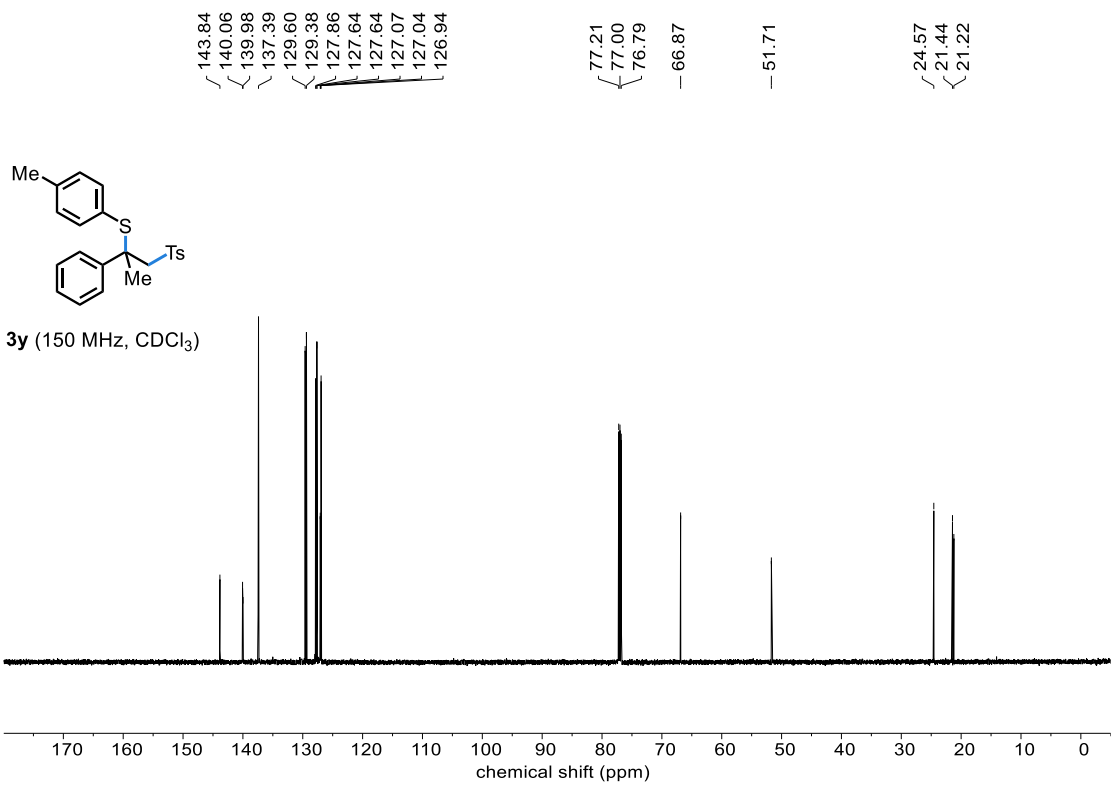




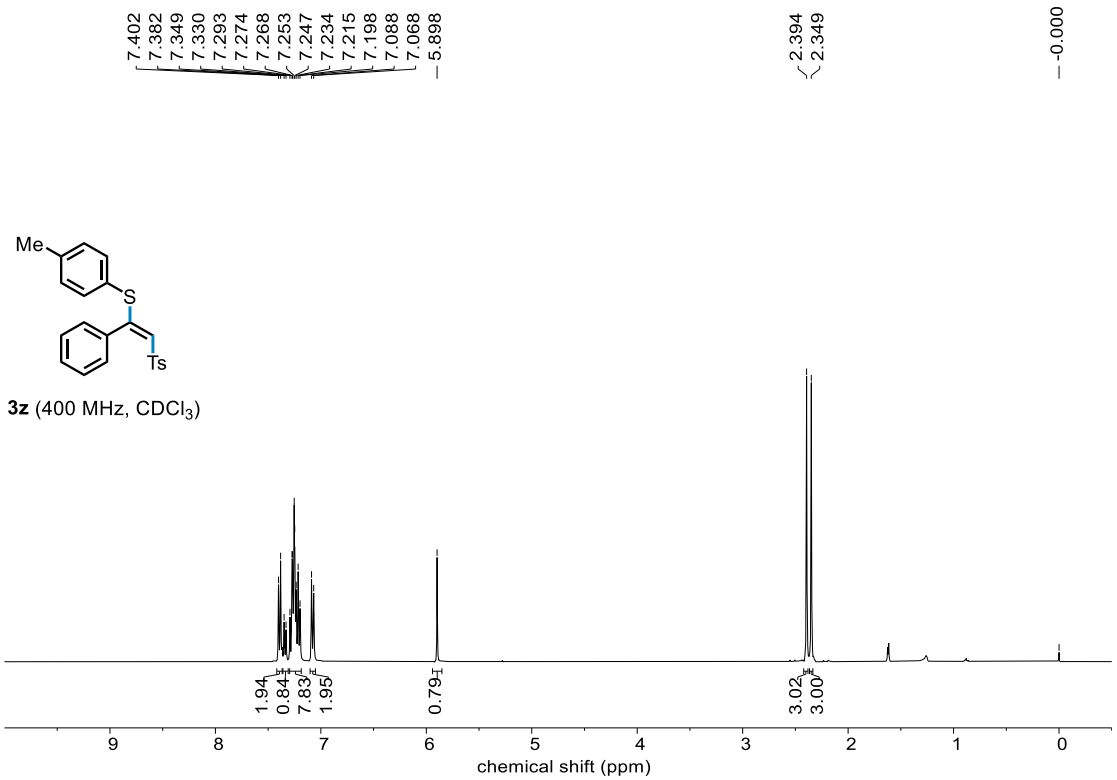
3x (150 MHz, $CDCl_3$)

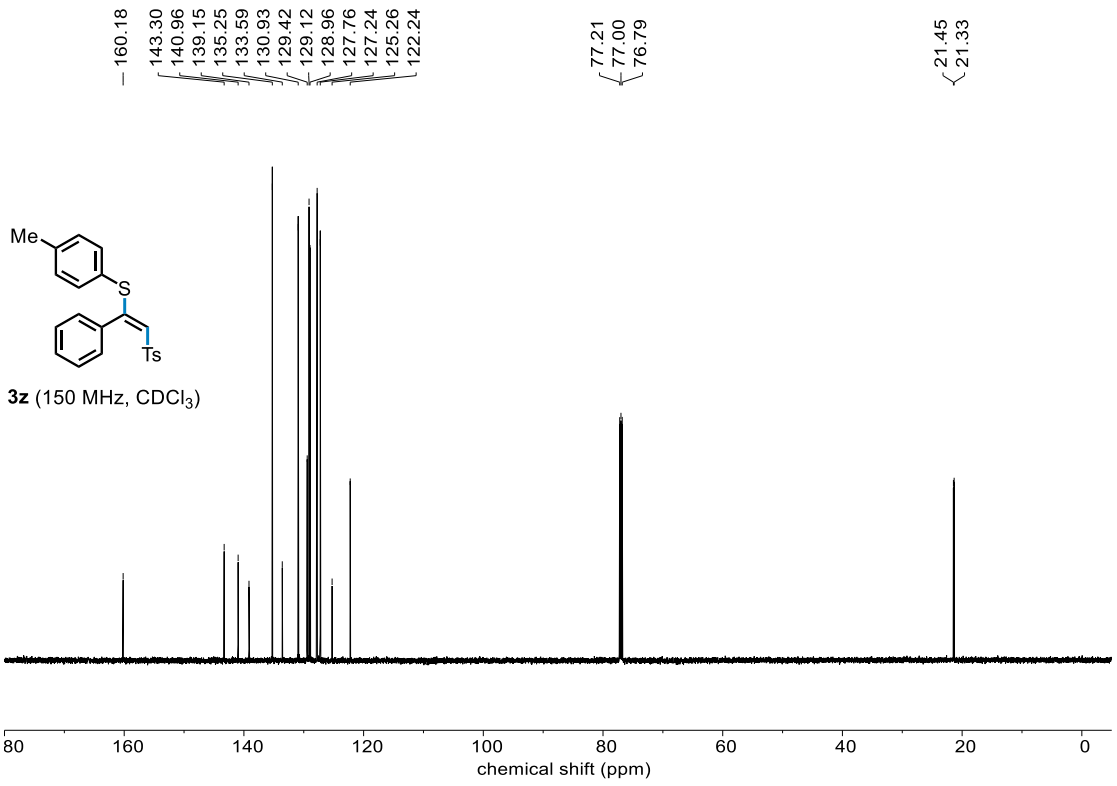


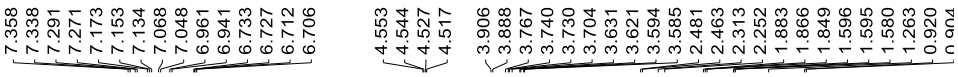
3y (400 MHz, $CDCl_3$)

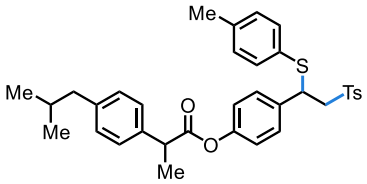


3y (150 MHz, $CDCl_3$)

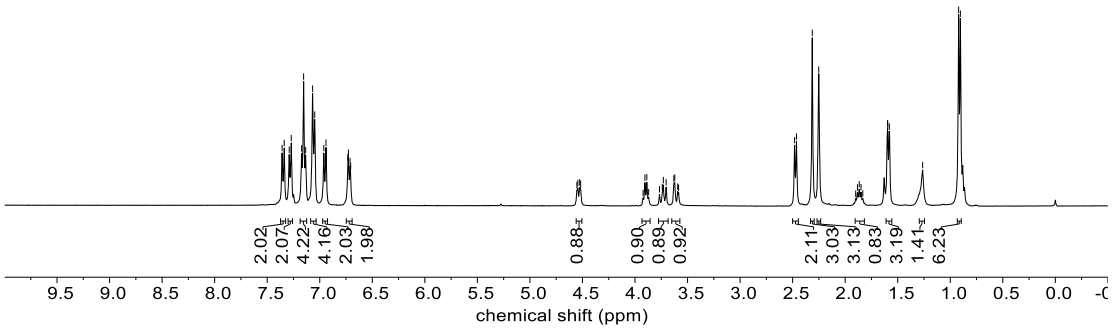

7.402
7.382
7.349
7.330
7.293
7.274
7.268
7.253
7.247
7.234
7.215
7.198
7.088
7.068
5.898
2.394
2.349
-0.000
Me
S
Ts
3z (400 MHz, CDCl3)
1.94
0.84
7.83
1.95
0.79
3.02
3.00
9
8
7
6
5
4
3
2
1
0
chemical shift (ppm)

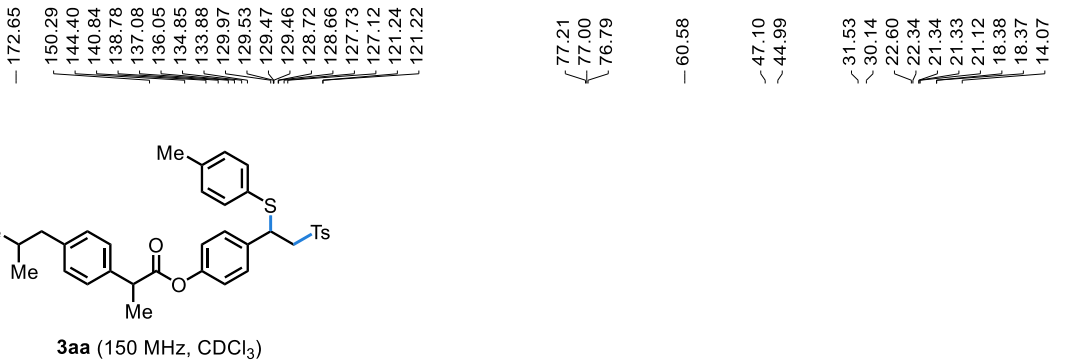

160.18
143.30
140.96
139.15
135.25
133.59
130.93
129.42
129.12
128.96
127.76
127.24
125.26
122.24
77.21
77.00
76.79
21.45
21.33
Me
S
Ts
3z (150 MHz, CDCl3)
80
160
140
120
100
80
60
40
20
0
chemical shift (ppm)



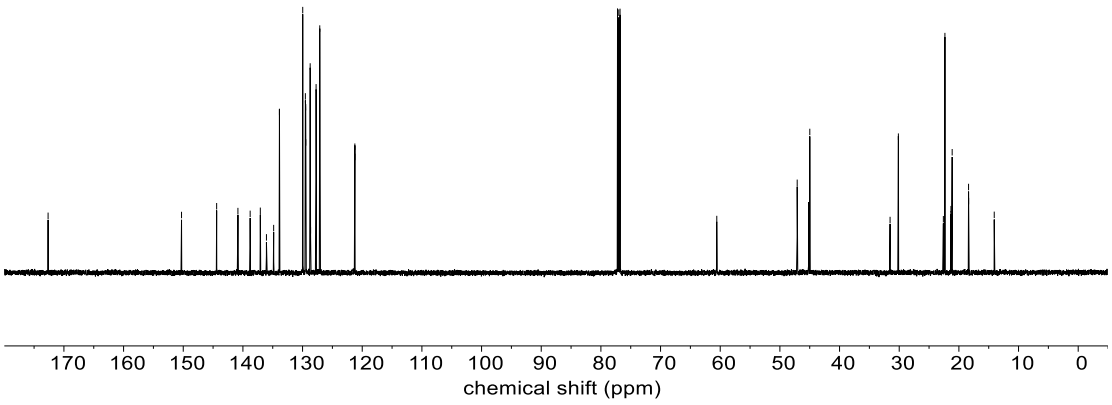


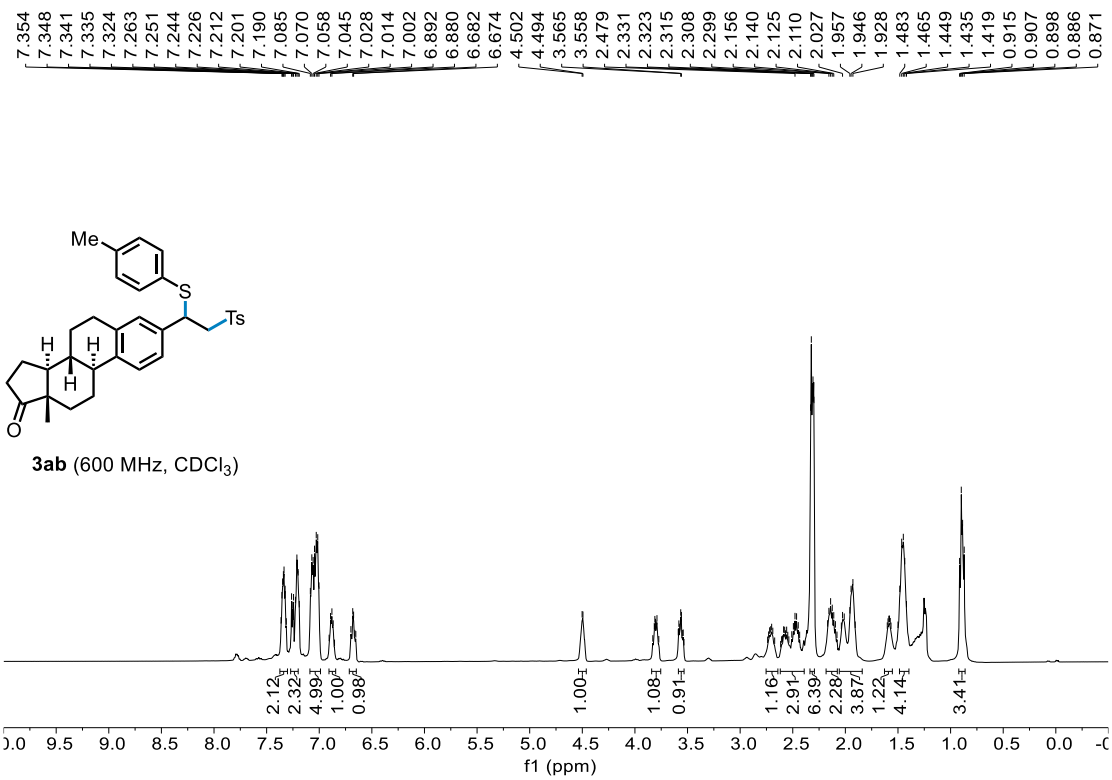
3aa (400 MHz, $CDCl_3$)

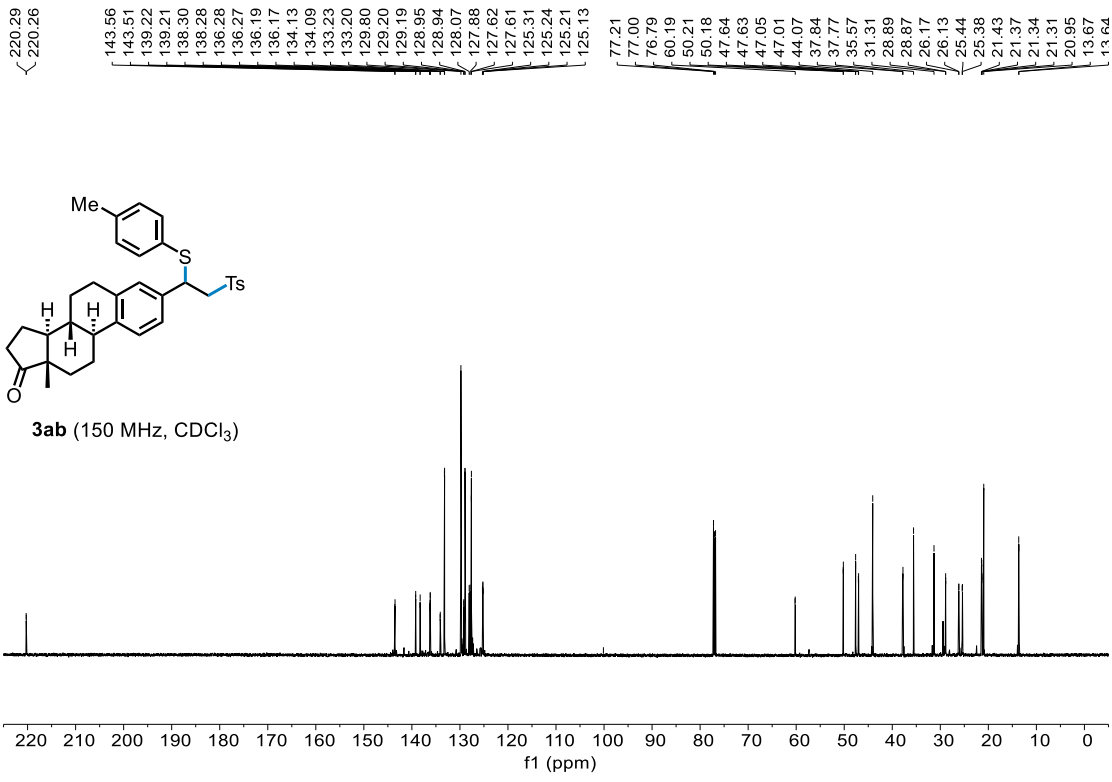


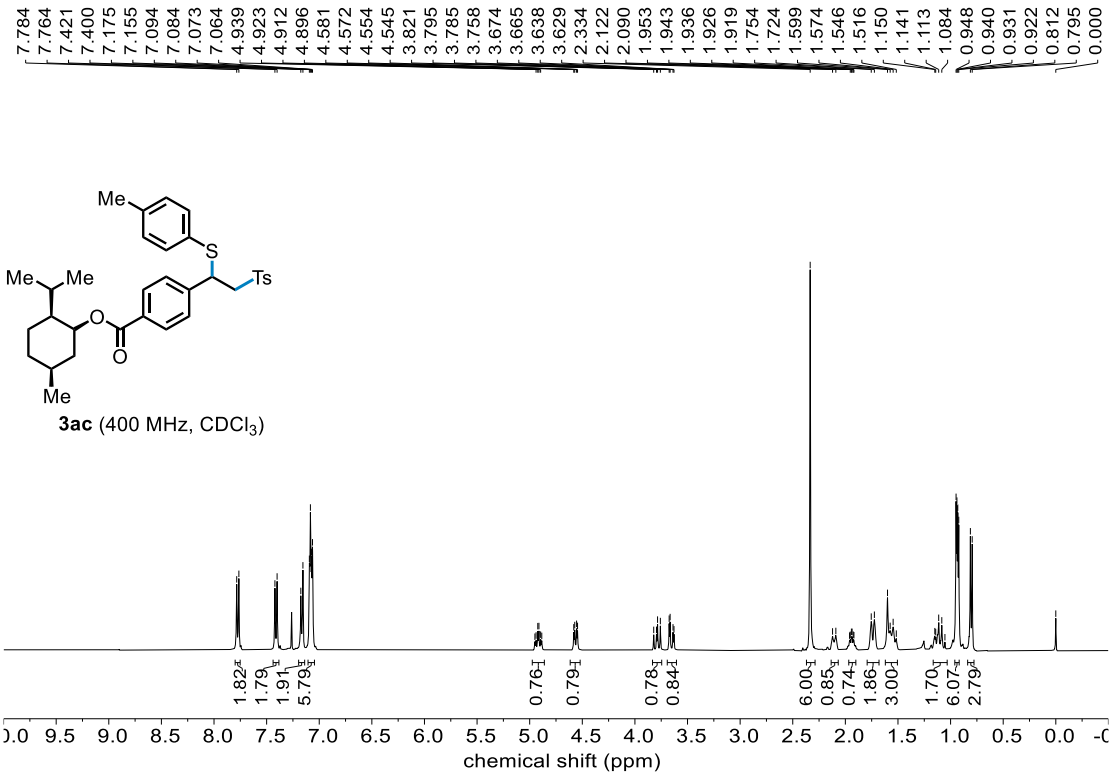


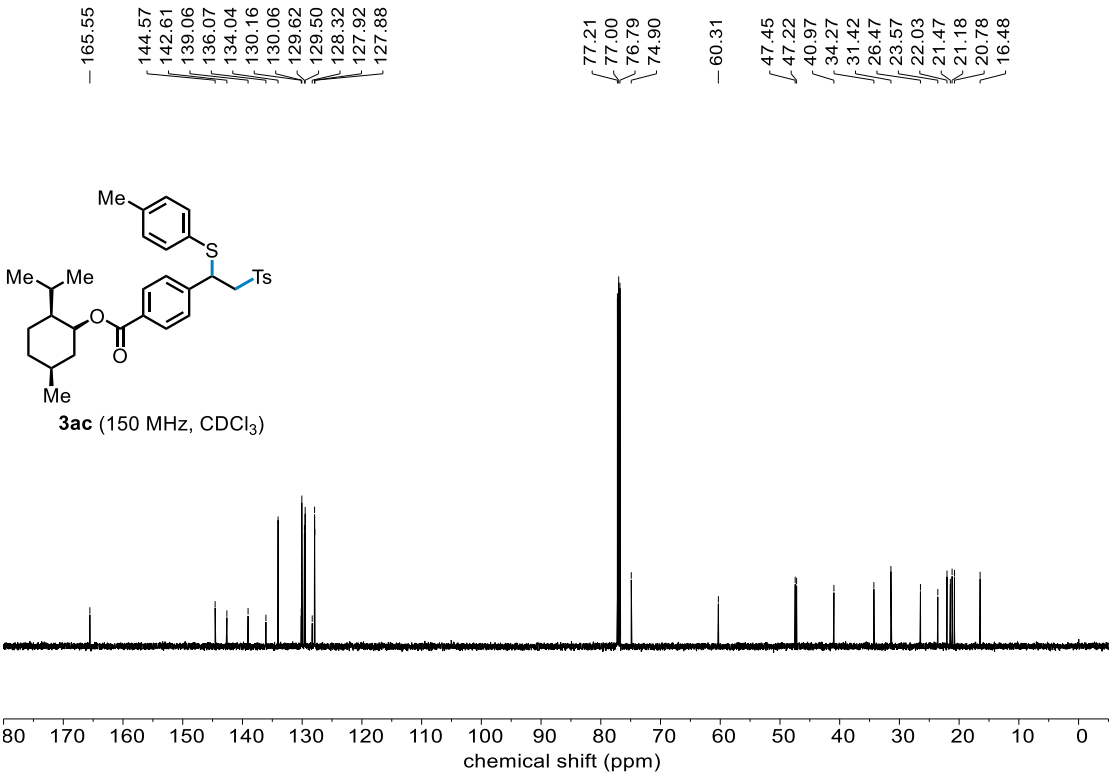
3aa (150 MHz, $CDCl_3$)

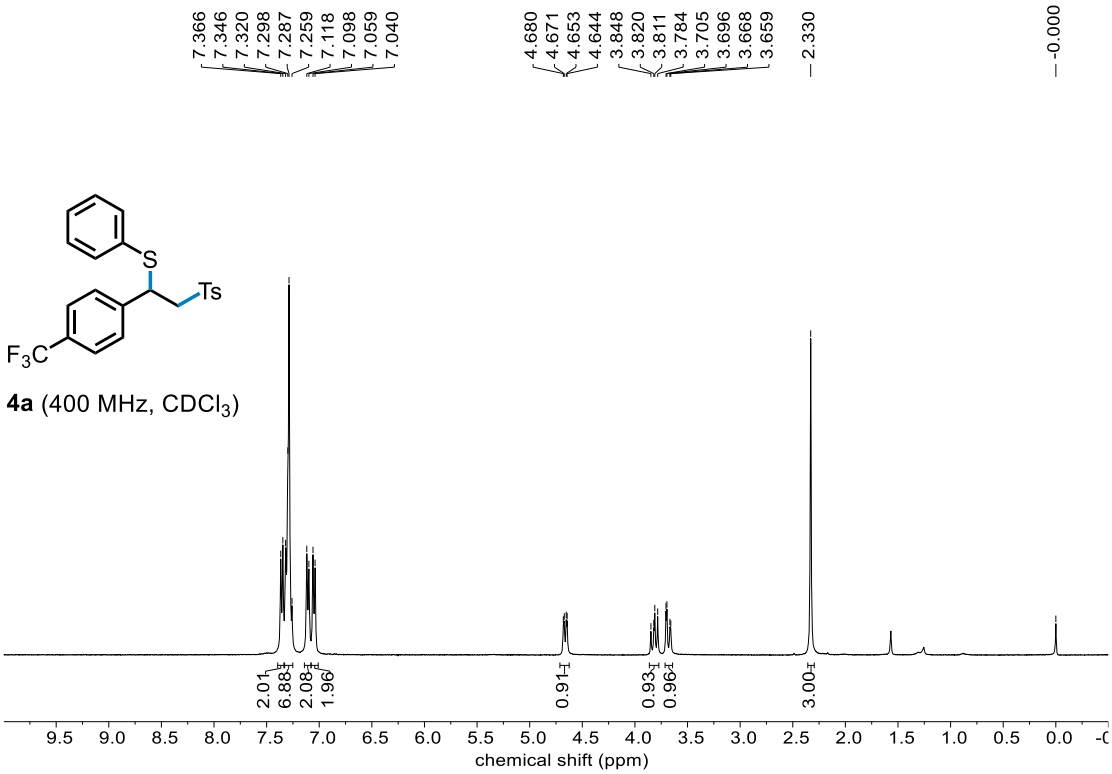


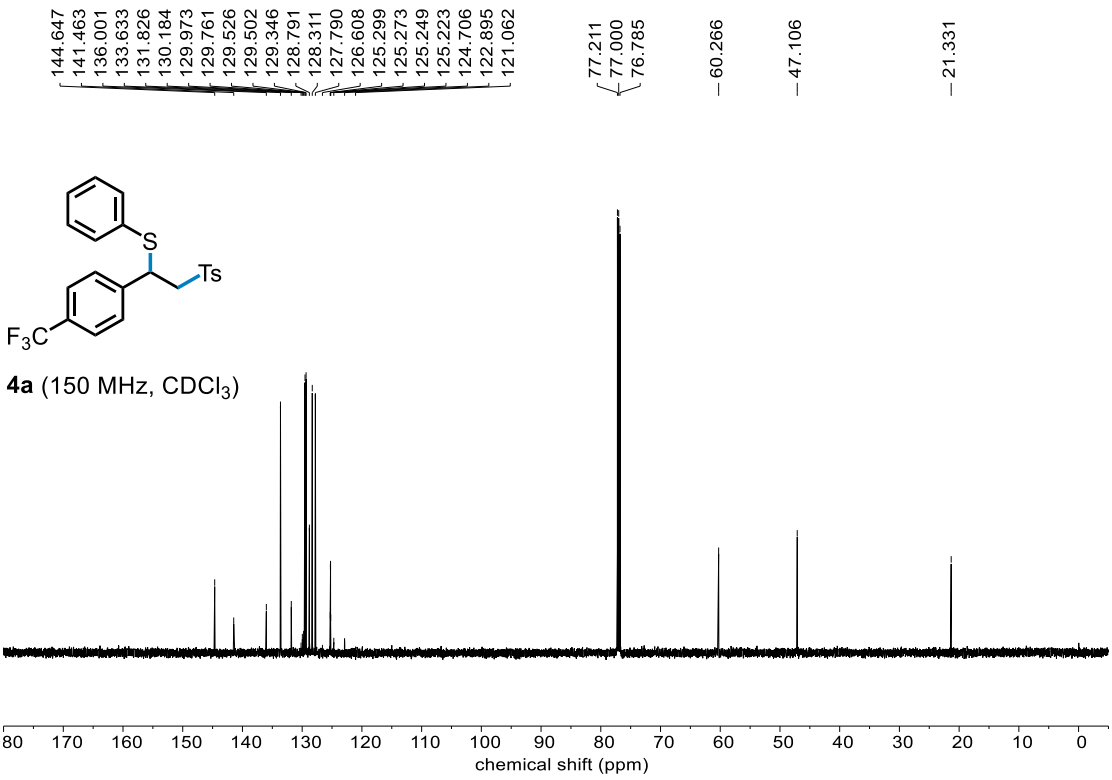

7.354
7.348
7.341
7.335
7.324
7.263
7.251
7.244
7.226
7.212
7.201
7.190
7.085
7.070
7.058
7.045
7.028
7.014
7.002
6.892
6.880
6.682
6.674
4.502
4.494
3.565
3.558
2.479
2.331
2.323
2.315
2.308
2.299
2.156
2.140
2.125
2.110
2.027
1.957
1.946
1.928
1.483
1.465
1.449
1.435
1.419
0.915
0.907
0.898
0.886
0.871
Me
S
Ts
H
H
H
O
3ab (600 MHz, CDCl3)
2.12
2.32
4.99
1.00
0.98
1.00
1.08
0.91
1.16
2.91
6.39
2.28
3.87
1.22
4.14
3.41
f1 (ppm)

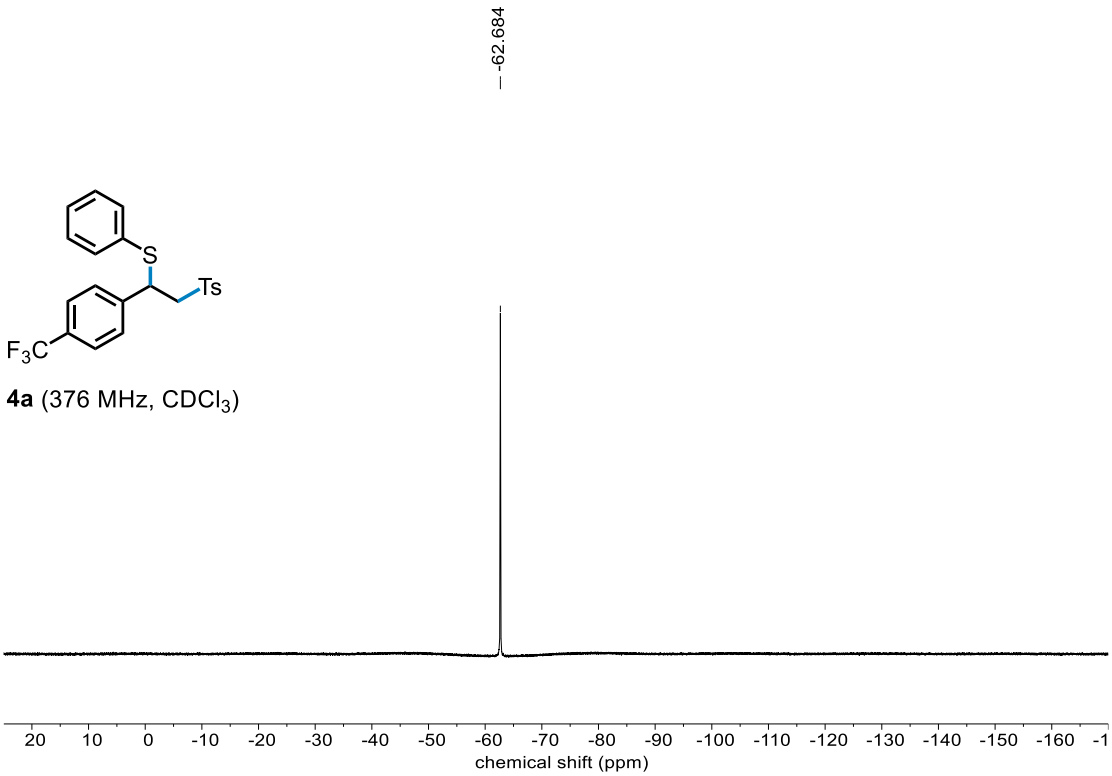

220.29
220.26
143.56
143.51
139.22
139.21
138.30
138.28
136.28
136.27
136.19
136.17
134.13
134.09
133.23
133.20
129.80
129.20
129.19
128.95
128.94
128.07
127.88
127.62
127.61
125.31
125.24
125.21
125.13
77.21
77.00
76.79
60.19
50.21
50.18
47.64
47.63
47.05
47.01
44.07
37.84
37.77
35.57
31.31
28.89
28.87
26.17
26.13
25.44
25.38
21.43
21.37
21.34
21.31
20.95
13.67
Me
S
Ts
H
H
H
O
3ab (150 MHz, CDCl3)
f1 (ppm)

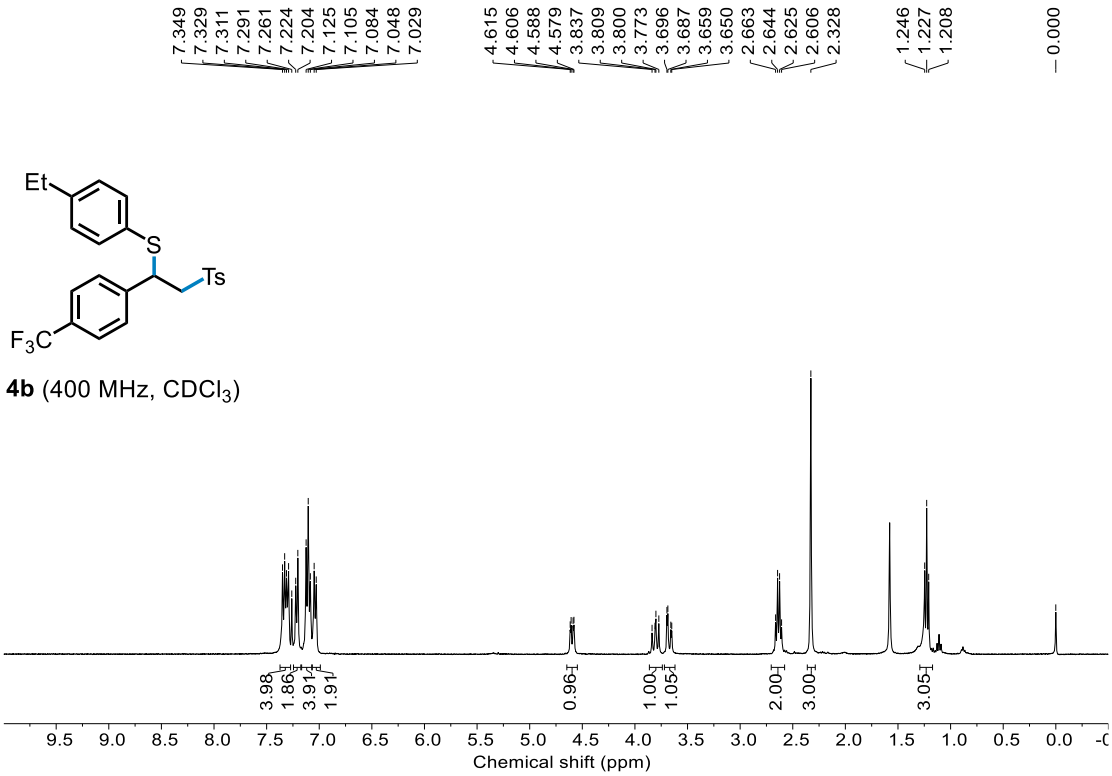

7.784
7.764
7.421
7.400
7.175
7.155
7.094
7.084
7.073
7.064
4.939
4.923
4.912
4.896
4.581
4.572
4.554
4.545
3.821
3.795
3.785
3.758
3.674
3.665
3.638
3.629
2.334
2.122
2.090
1.953
1.943
1.936
1.926
1.919
1.754
1.724
1.599
1.574
1.546
1.516
1.150
1.141
1.113
1.084
0.948
0.940
0.931
0.922
0.812
0.795
0.000
Me
S
Ts
Me
Me
O
O
Me
3ac (400 MHz, CDCl3)
1.82
1.79
1.91
5.79
0.76
0.79
0.78
0.84
6.00
0.85
0.74
1.86
3.00
1.70
6.07
2.79
chemical shift (ppm)

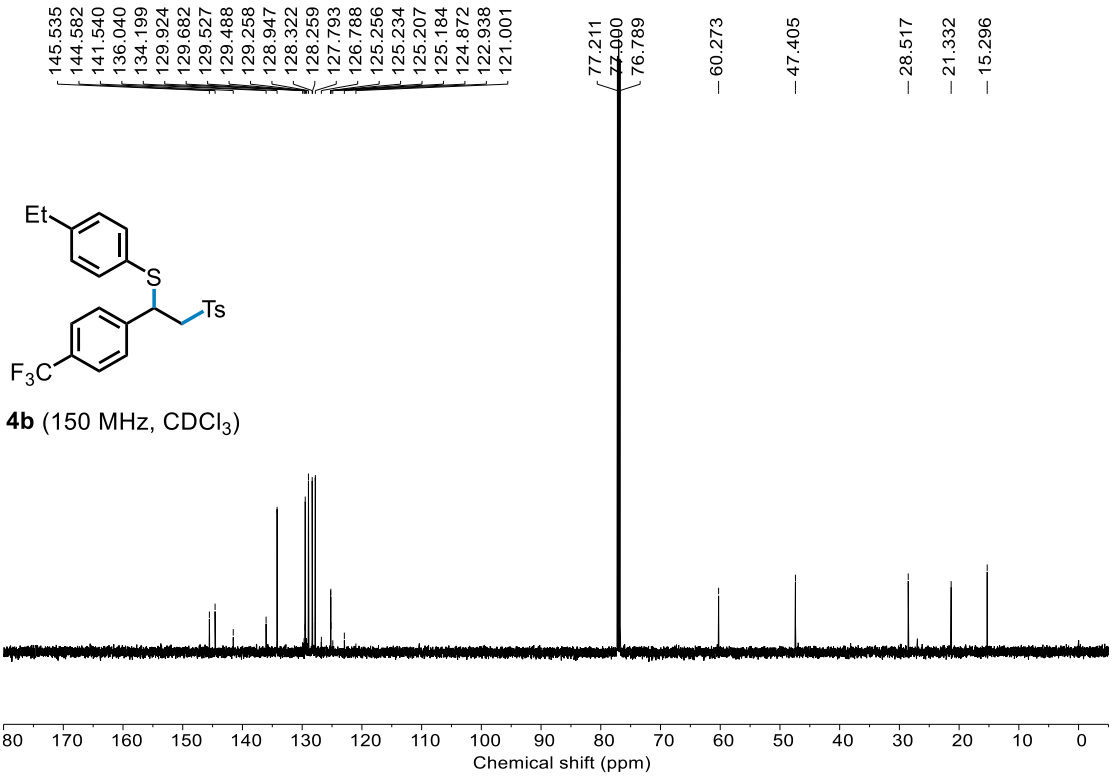

165.55
144.57
142.61
139.06
136.07
134.04
130.16
130.06
129.62
129.50
128.32
127.92
127.88
77.21
77.00
76.79
74.90
60.31
47.45
47.22
40.97
34.27
31.42
26.47
23.57
22.03
21.47
21.18
20.78
16.48
Me
S
Ts
Me
Me
O
O
Me
3ac (150 MHz, CDCl3)
chemical shift (ppm)

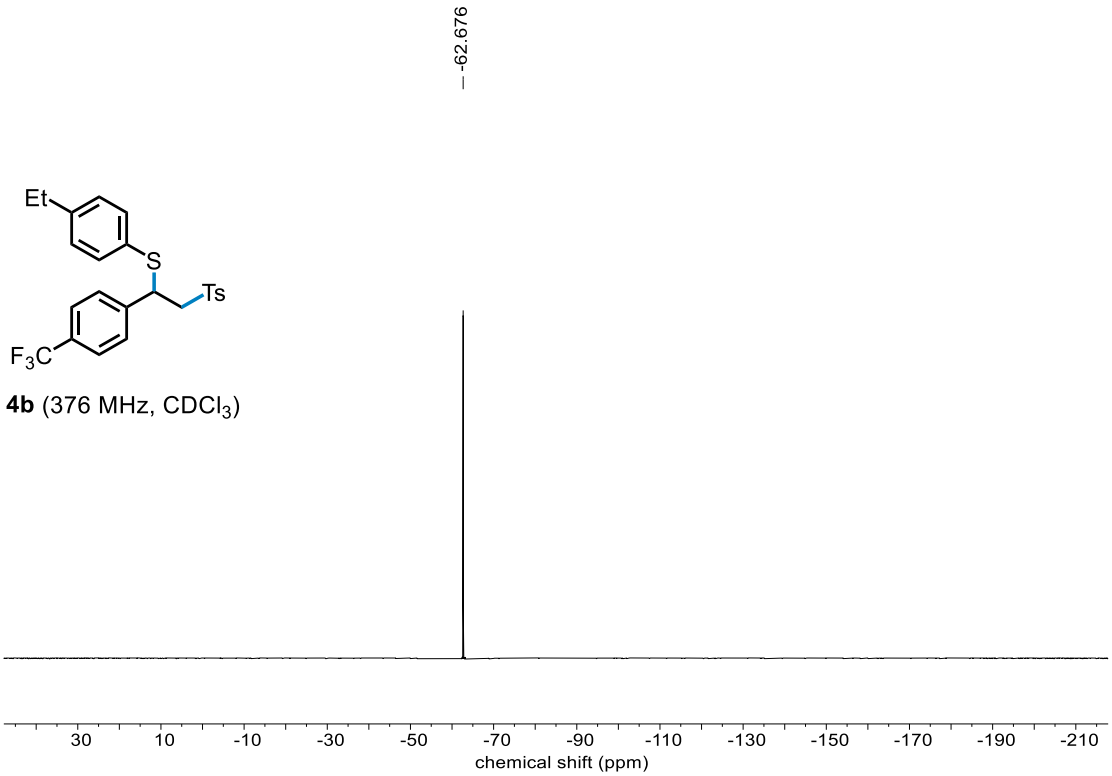

7.366
7.346
7.320
7.298
7.287
7.259
7.118
7.098
7.059
7.040
4.680
4.671
4.653
4.644
3.848
3.820
3.811
3.784
3.705
3.696
3.668
3.659
2.330
-0.000
S
Ts
F3C
4a (400 MHz, CDCl3)
2.01
6.88
2.08
1.96
0.91
0.93
0.96
3.00
chemical shift (ppm)


144.647
141.463
136.001
133.633
131.826
130.184
129.973
129.761
129.526
129.502
129.346
128.791
128.311
127.790
126.608
125.299
125.273
125.249
125.223
124.706
122.895
121.062
77.211
77.000
76.785
60.266
47.106
21.331
S
Ts
F3C
4a (150 MHz, CDCl3)
chemical shift (ppm)

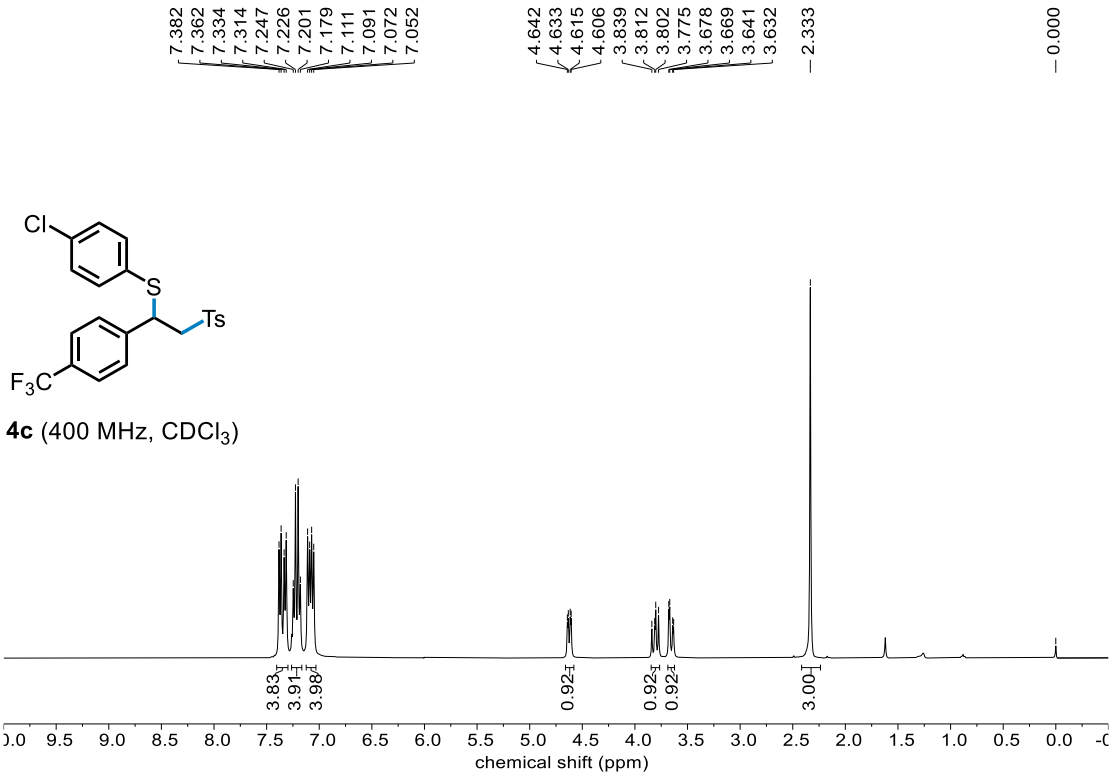

-62.684
S
Ts
F3C
4a (376 MHz, CDCl3)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -1
chemical shift (ppm)

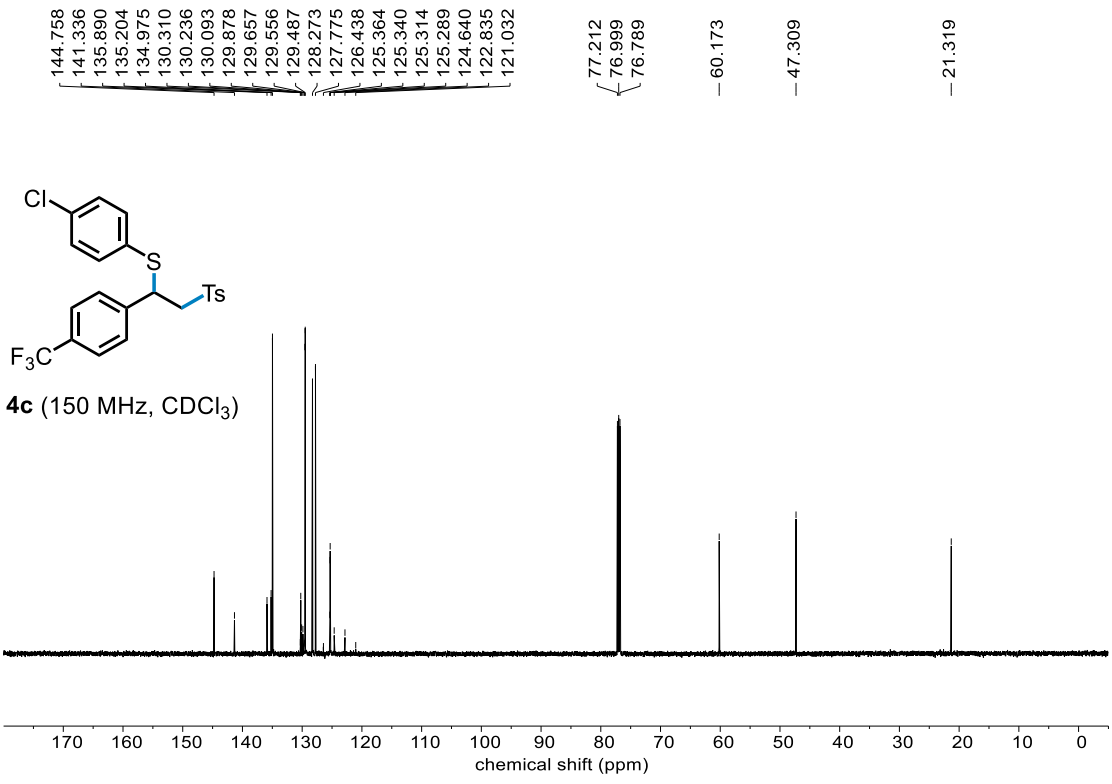

7.349
7.329
7.311
7.291
7.261
7.224
7.204
7.125
7.105
7.084
7.048
7.029
4.615
4.606
4.588
4.579
3.837
3.809
3.800
3.773
3.696
3.687
3.659
3.650
2.663
2.644
2.625
2.606
2.328
1.246
1.227
1.208
0.000
Et
S
Ts
F3C
4b (400 MHz, CDCl3)
3.98
1.86
3.91
1.91
0.96
1.00
1.05
2.00
3.00
3.05
Chemical shift (ppm)

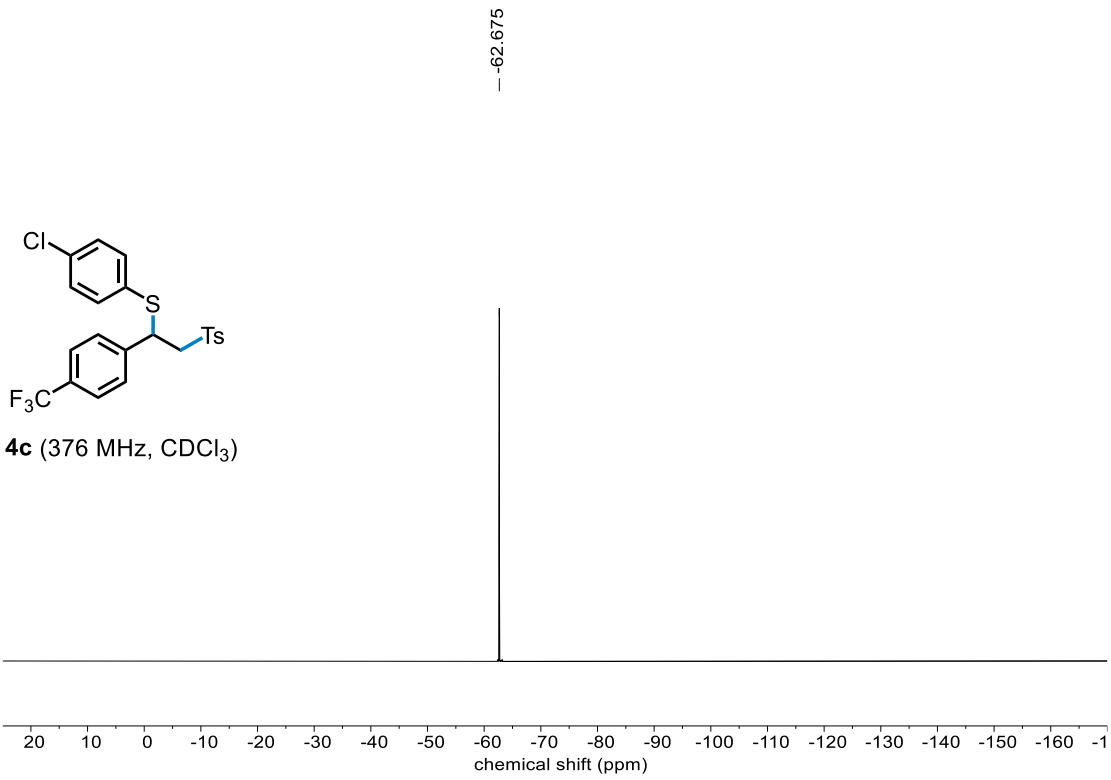

145.535
144.582
141.540
136.040
134.199
129.924
129.682
129.527
129.488
129.258
128.947
128.322
128.259
127.793
126.788
125.256
125.234
125.207
125.184
124.872
122.938
121.001
77.211
77.000
76.789
60.273
47.405
28.517
21.332
15.296
Et
S
Ts
F3C
4b (150 MHz, CDCl3)
Chemical shift (ppm)



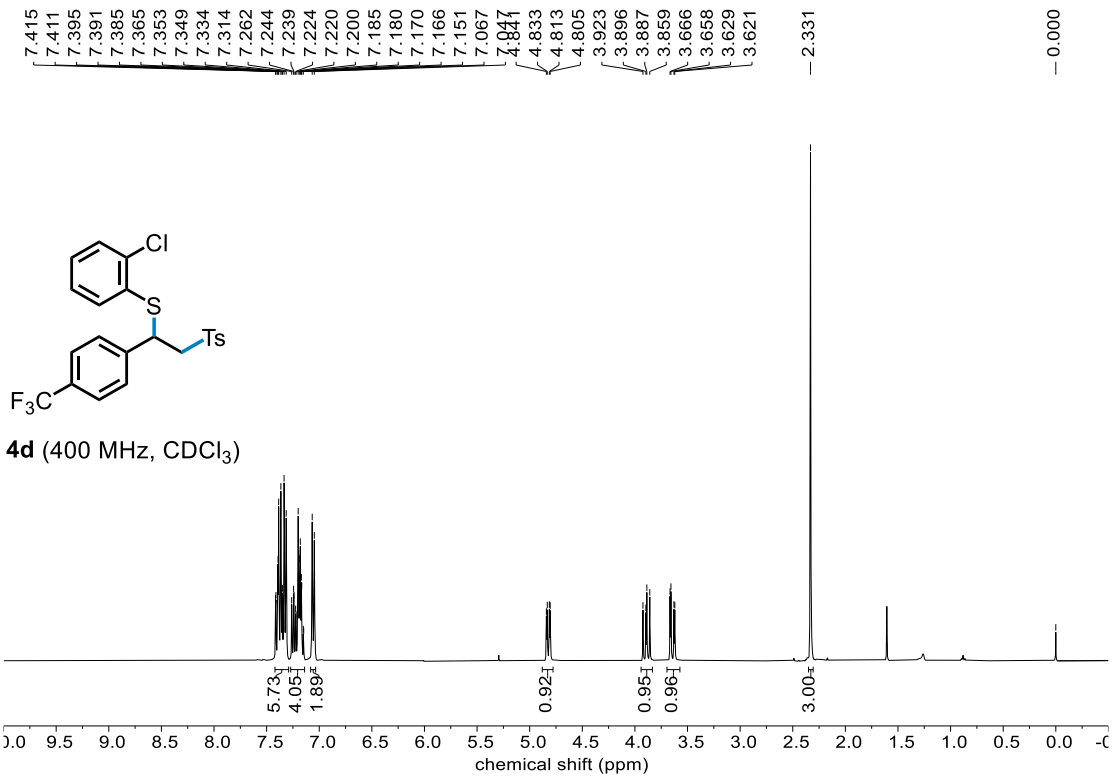
4b (376 MHz, $CDCl_3$)

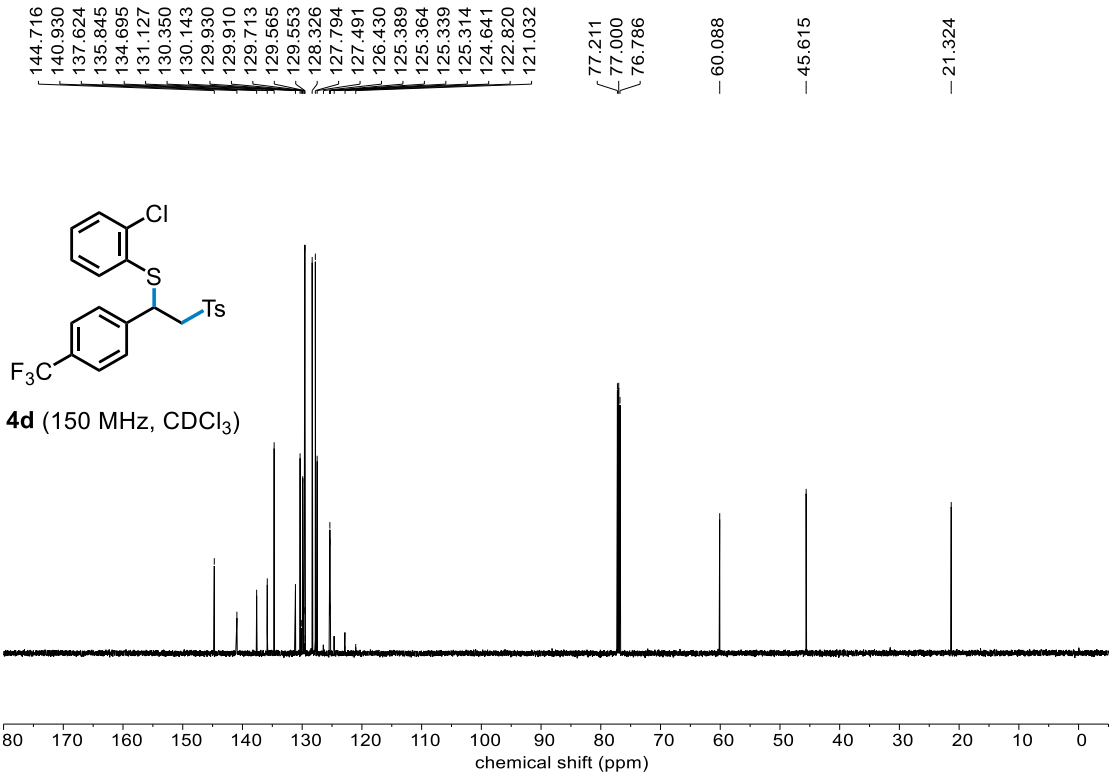

7.382
7.362
7.334
7.314
7.247
7.226
7.201
7.179
7.111
7.091
7.072
7.052
4.642
4.633
4.615
4.606
3.839
3.812
3.802
3.775
3.678
3.669
3.641
3.632
2.333
0.000
Cl
S
Ts
F3C
4c (400 MHz, CDCl3)
3.83
3.91
3.98
0.92
0.92
0.92
3.00
chemical shift (ppm)

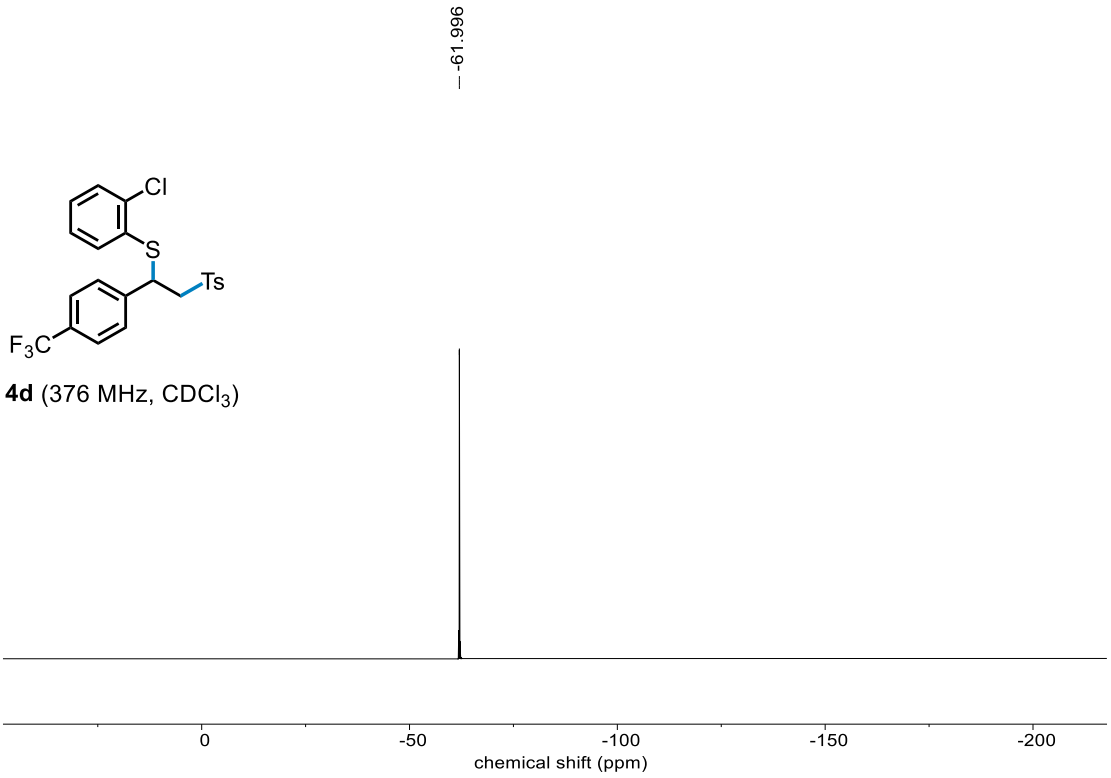

144.758
141.336
135.890
135.204
134.975
130.310
130.236
130.093
129.878
129.657
129.556
129.487
128.273
127.775
126.438
125.364
125.340
125.314
125.289
124.640
122.835
121.032
77.212
76.999
76.789
60.173
47.309
21.319
Cl
S
Ts
F3C
4c (150 MHz, CDCl3)
chemical shift (ppm)



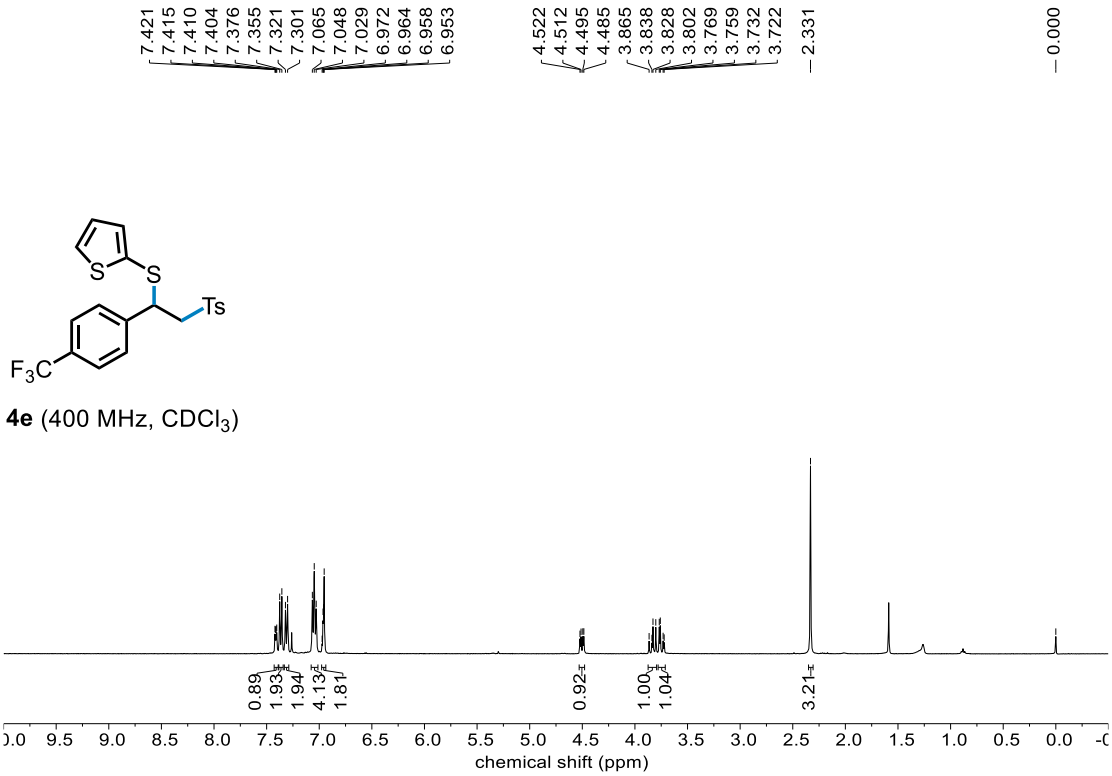
4c (376 MHz, $CDCl_3$)


7.415
7.411
7.395
7.391
7.385
7.365
7.353
7.349
7.334
7.314
7.262
7.244
7.239
7.224
7.220
7.200
7.185
7.180
7.170
7.166
7.151
7.067
7.047
7.041
4.833
4.813
4.805
3.923
3.896
3.887
3.859
3.666
3.658
3.629
3.621
2.331
0.000
Cl
S
Ts
F3C
4d (400 MHz, CDCl3)
5.73
4.05
1.89
0.92
0.95
0.96
3.00
chemical shift (ppm)

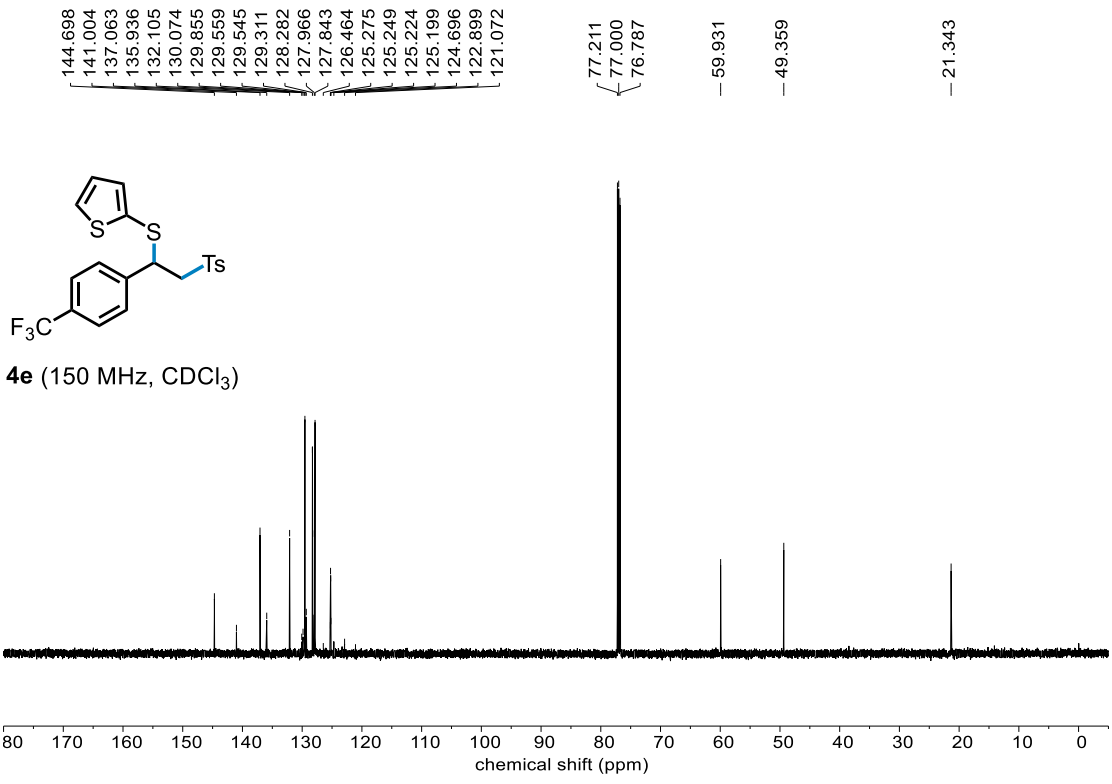

144.716
140.930
137.624
135.845
134.695
131.127
130.350
130.143
129.930
129.910
129.713
129.565
129.553
128.326
127.794
127.491
126.430
125.389
125.364
125.339
125.314
124.641
122.820
121.032
77.211
77.000
76.786
60.088
45.615
21.324
Cl
S
Ts
F3C
4d (150 MHz, CDCl3)
chemical shift (ppm)



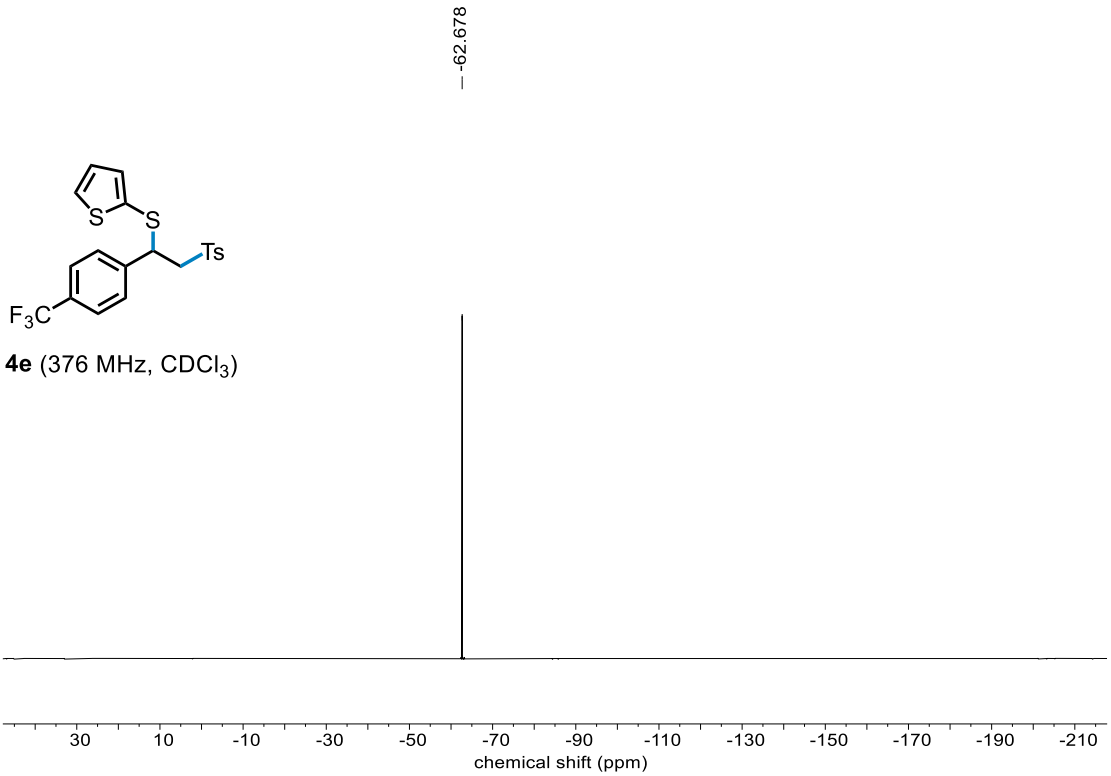
4d (376 MHz, $CDCl_3$)



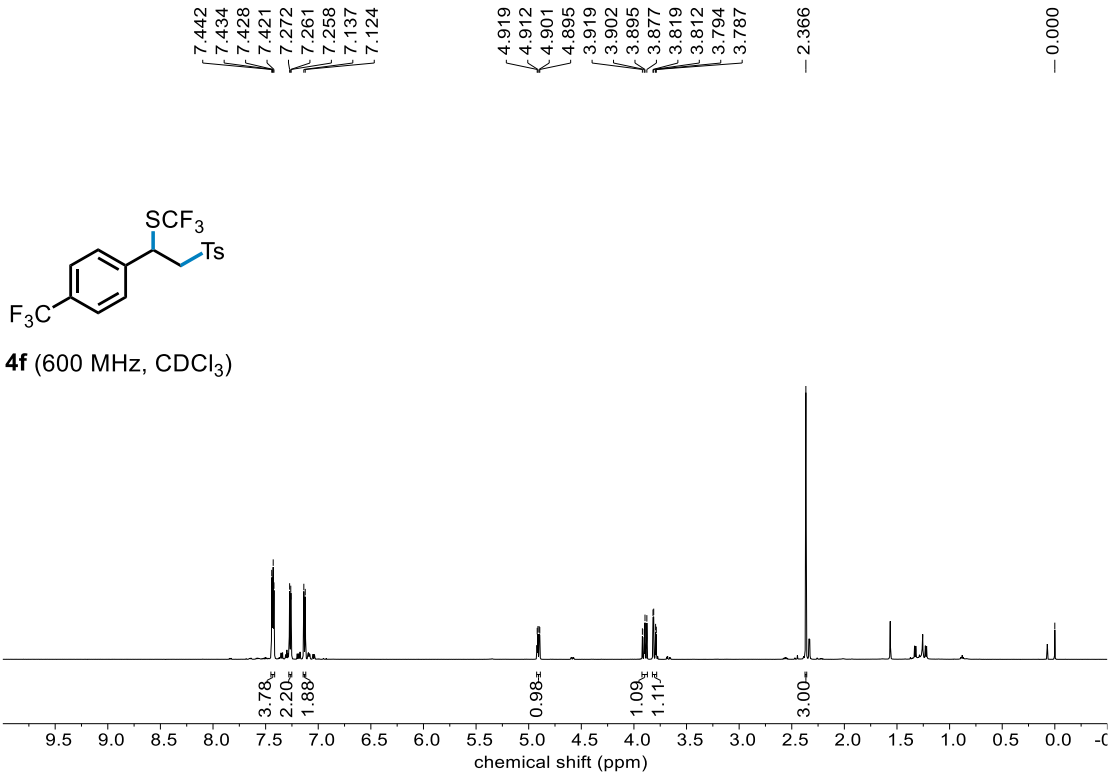
4e (400 MHz, $CDCl_3$)

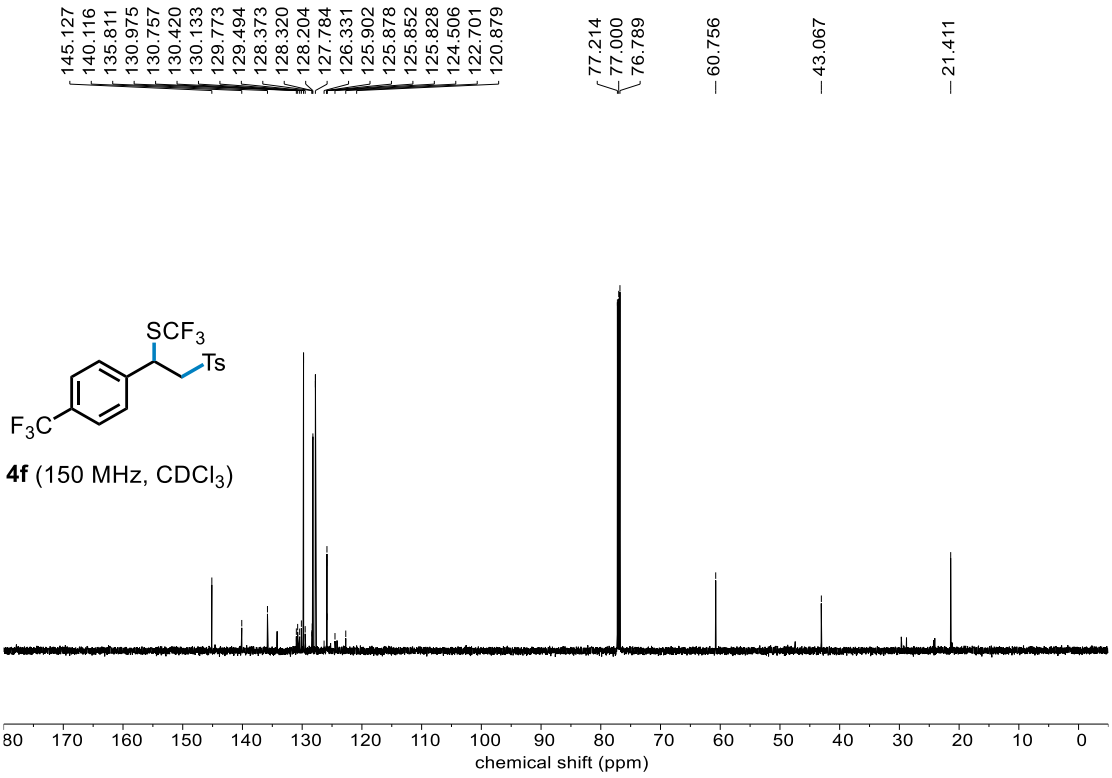


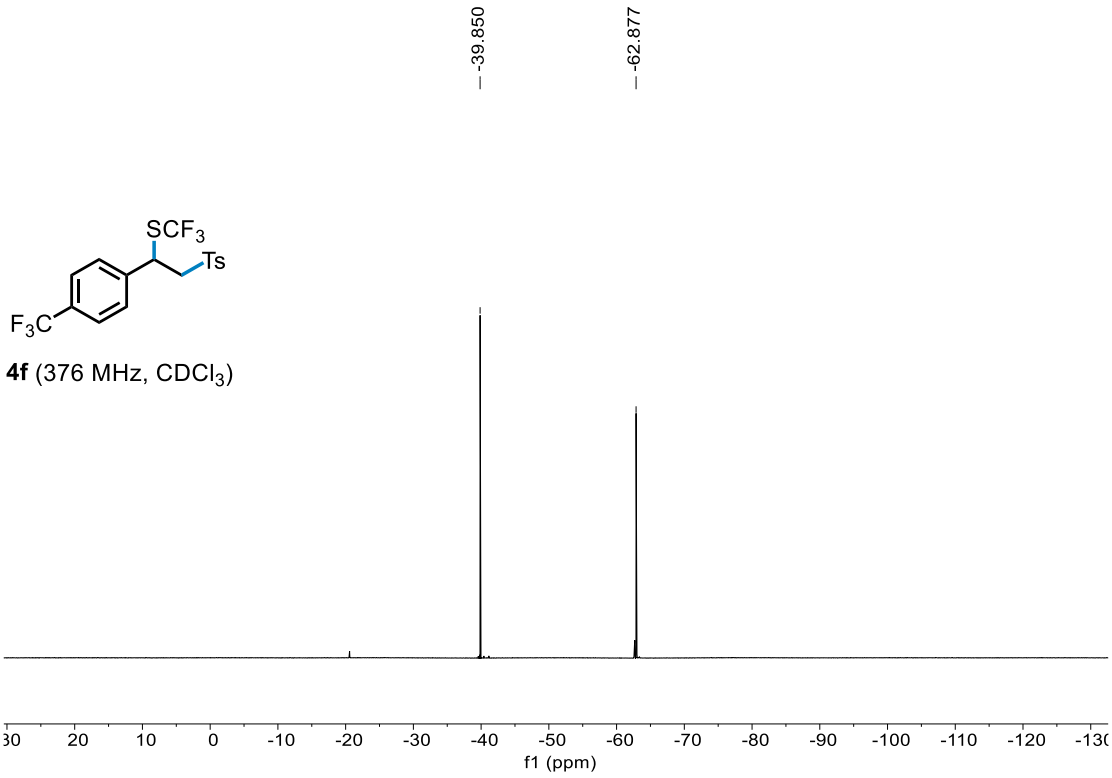
4e (150 MHz, $CDCl_3$)

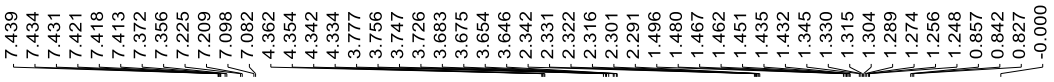


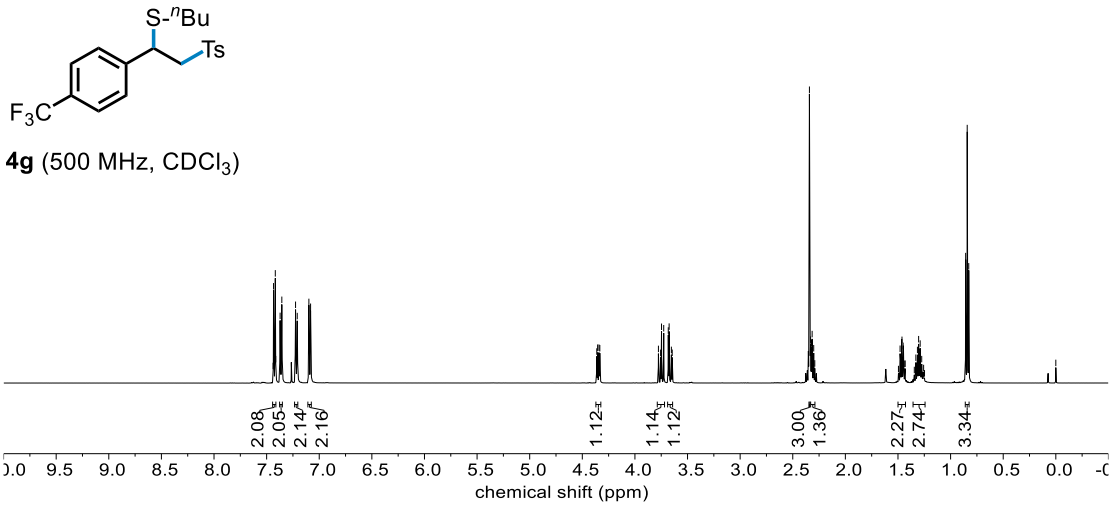
4e (376 MHz, $CDCl_3$)


7.442
7.434
7.428
7.421
7.272
7.261
7.258
7.137
7.124
4.919
4.912
4.901
4.895
3.919
3.902
3.895
3.877
3.819
3.812
3.794
3.787
2.366
0.000
SCF3
Ts
F3C
4f (600 MHz, CDCl3)
3.78
2.20
1.88
0.98
1.09
1.11
3.00
chemical shift (ppm)

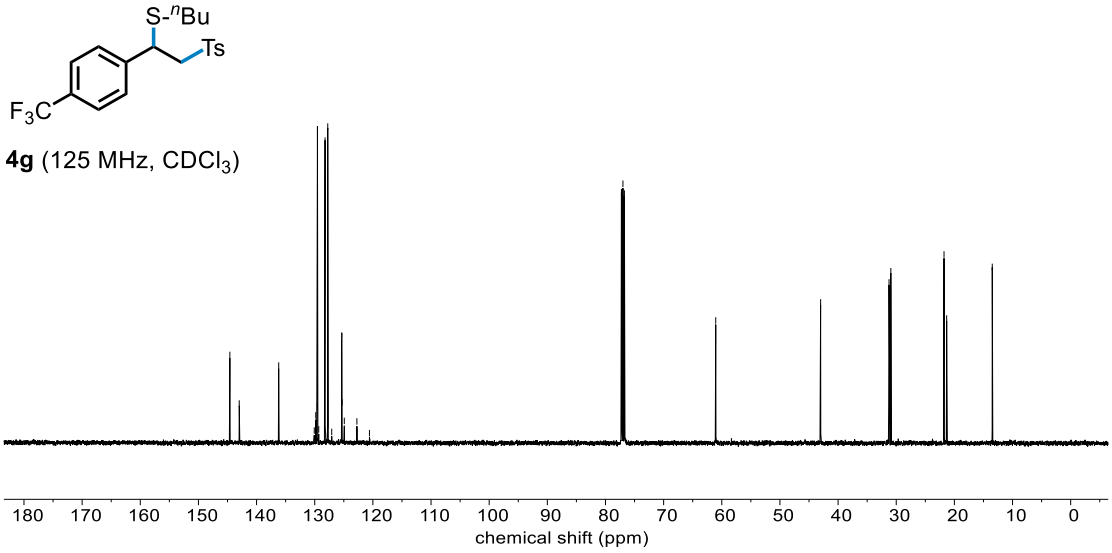

145.127
140.116
135.811
130.975
130.757
130.420
130.133
129.773
129.494
128.373
128.320
128.204
127.784
126.331
125.902
125.878
125.852
125.828
124.506
122.701
120.879
77.214
77.000
76.789
60.756
43.067
21.411
SCF3
Ts
F3C
4f (150 MHz, CDCl3)
chemical shift (ppm)

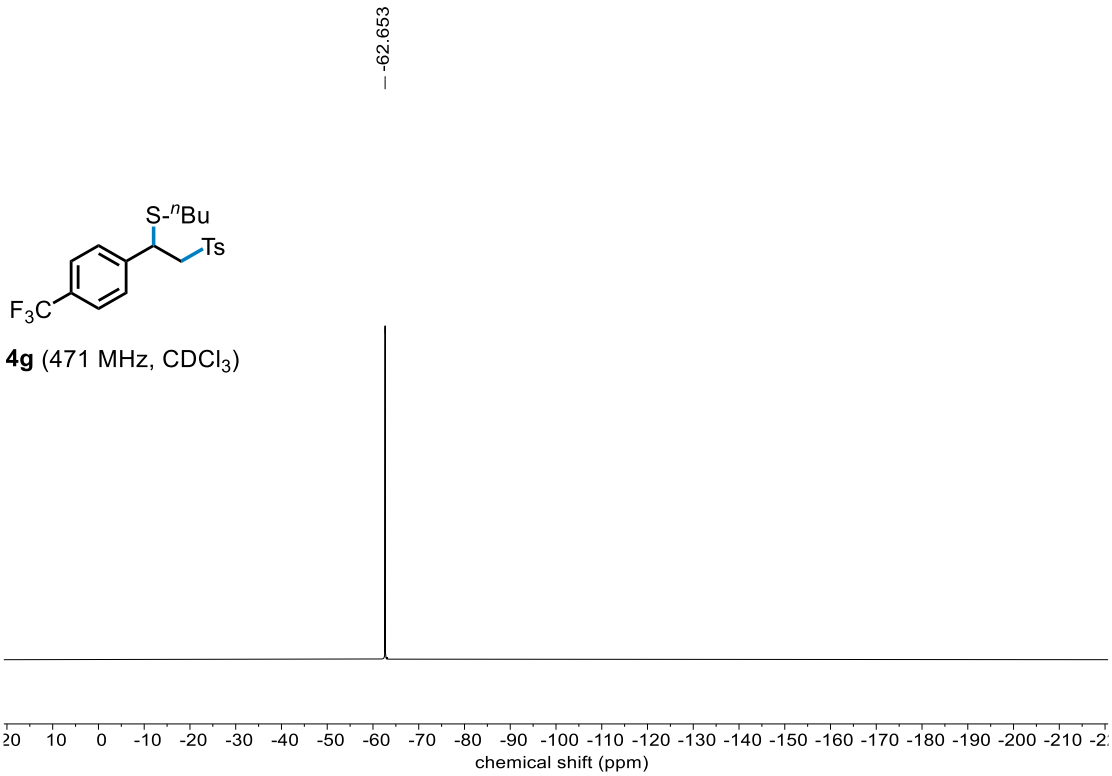

-39.850
-62.877
SCF3
Ts
F3C
4f (376 MHz, CDCl3)
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-13(
f1 (ppm)


7.439
7.434
7.431
7.421
7.418
7.413
7.372
7.356
7.225
7.209
7.098
7.082
4.362
4.354
4.342
4.334
3.777
3.756
3.747
3.726
3.683
3.675
3.654
3.646
2.342
2.331
2.322
2.316
2.301
2.291
1.496
1.480
1.467
1.462
1.451
1.435
1.432
1.345
1.330
1.315
1.304
1.289
1.274
1.256
1.248
0.857
0.842
0.827
-0.000

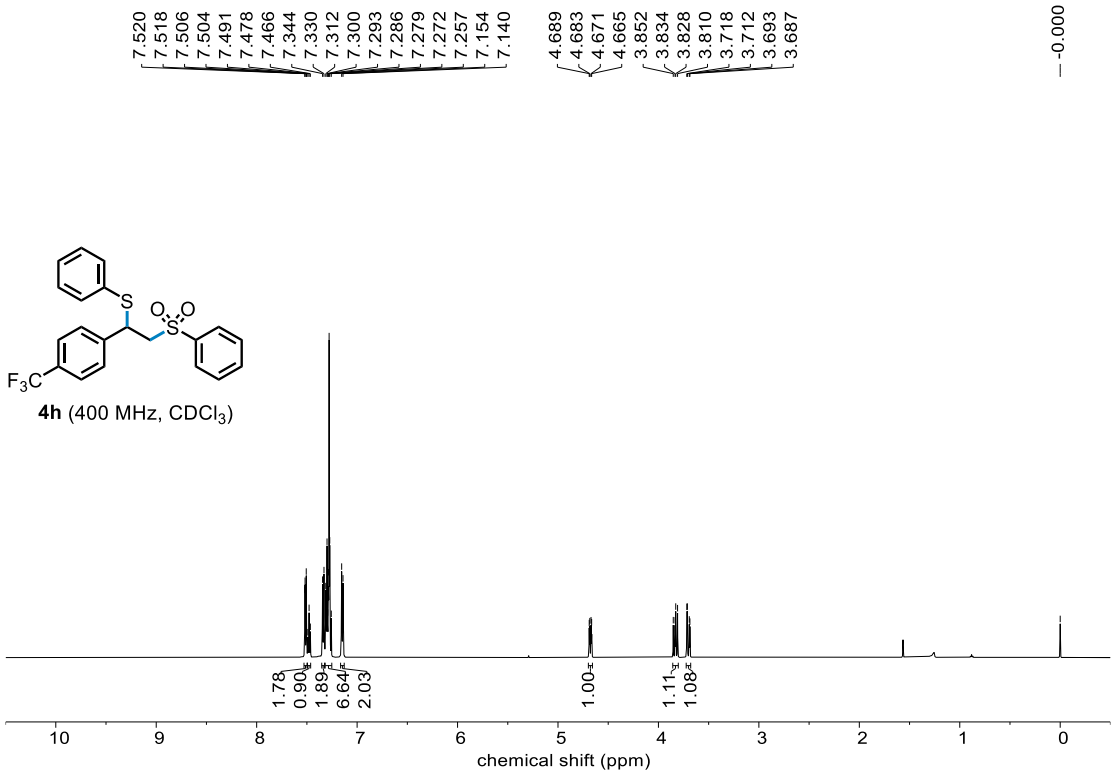

S-nBu
Ts
F3C
4g (500 MHz, CDCl3)
2.08
2.05
2.14
2.16
1.12
1.14
1.12
3.00
1.36
2.27
2.74
3.34
chemical shift (ppm)

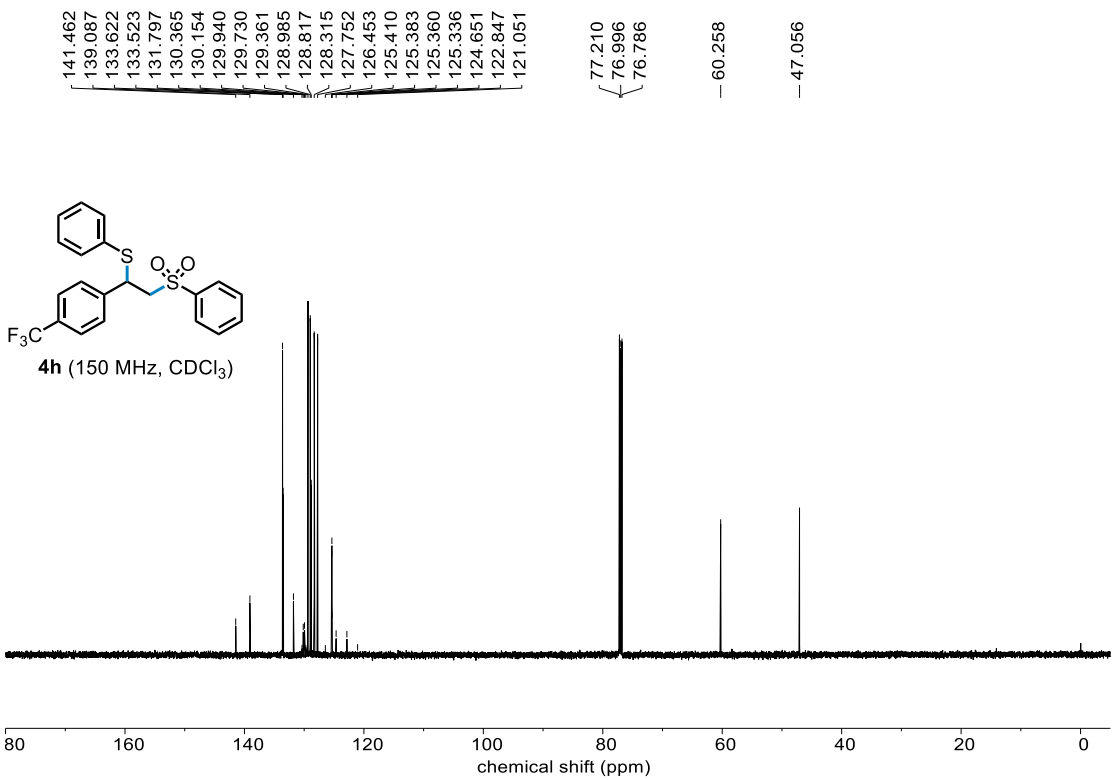

144.594
142.981
136.195
130.083
129.825
129.566
129.529
129.308
128.221
127.760
127.079
125.385
125.355
125.326
125.296
124.913
122.750
120.588
77.255
77.000
76.746
61.040
43.003
31.237
30.928
21.781
21.323
13.485

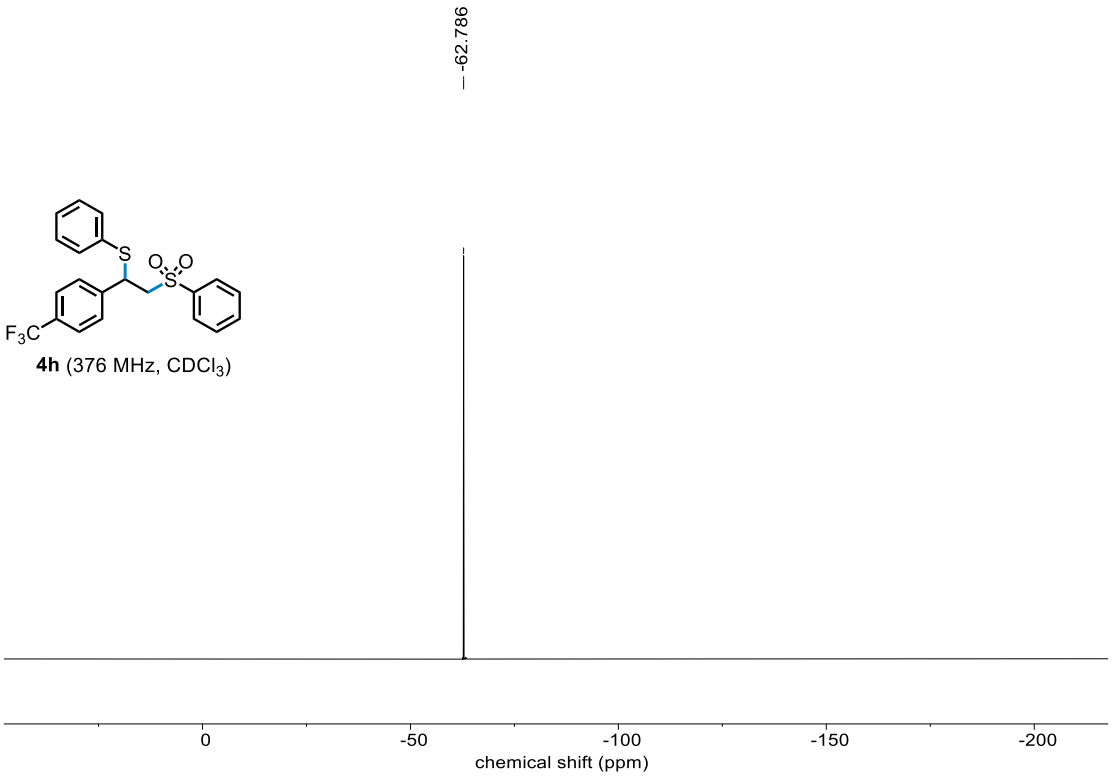

S-nBu
Ts
F3C
4g (125 MHz, CDCl3)
chemical shift (ppm)



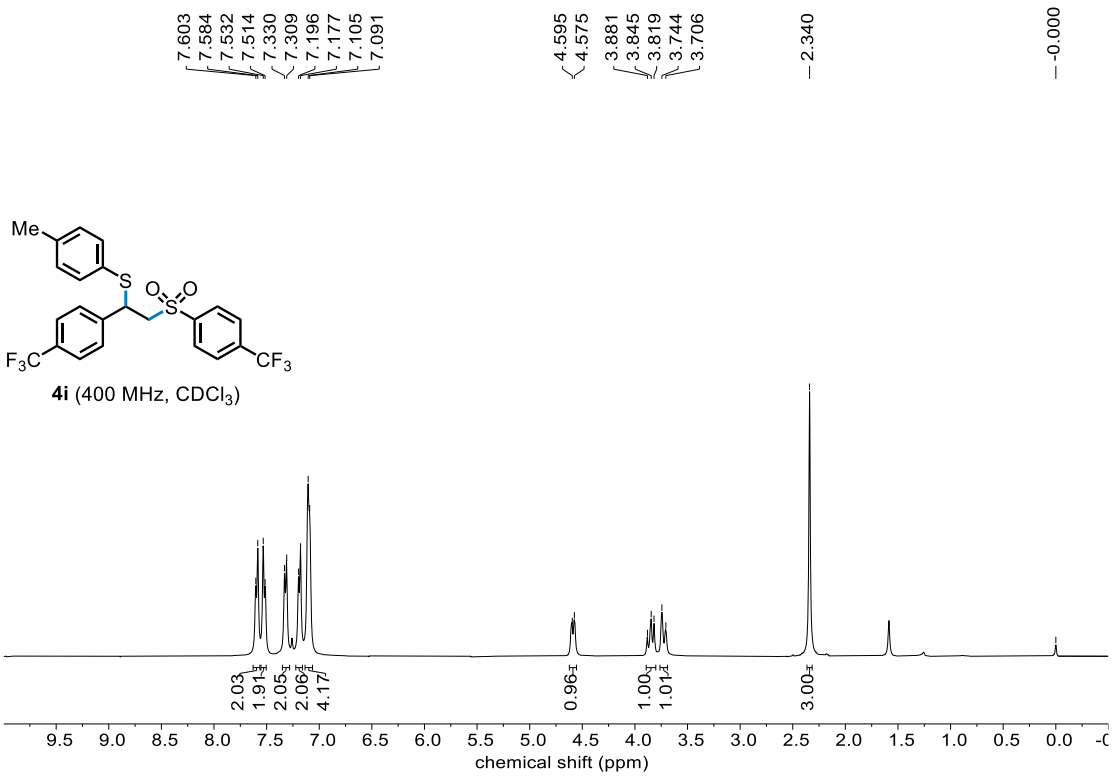
4g (471 MHz, $CDCl_3$)

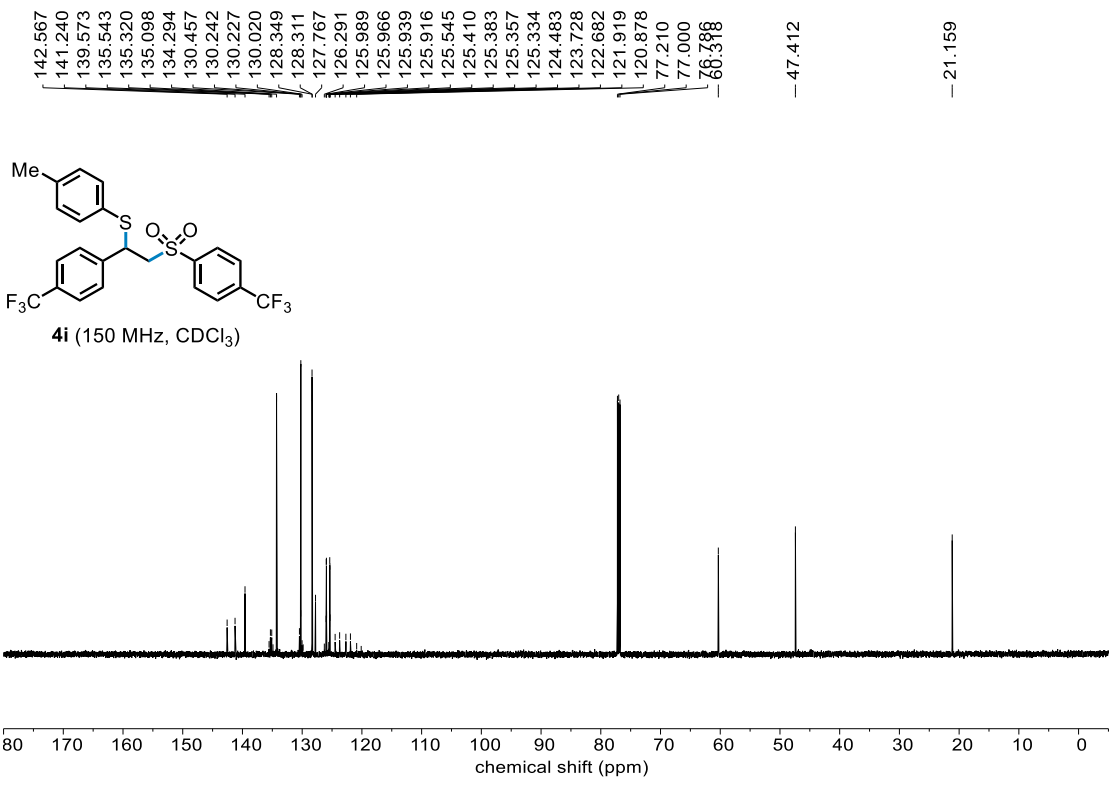

7.520
7.518
7.506
7.504
7.491
7.478
7.466
7.344
7.330
7.312
7.300
7.293
7.286
7.279
7.272
7.257
7.154
7.140
4.689
4.683
4.671
4.665
3.852
3.834
3.828
3.810
3.718
3.712
3.693
3.687
-0.000
F3C
4h (400 MHz, CDCl3)
1.78
0.90
1.89
6.64
2.03
1.00
1.11
1.08
chemical shift (ppm)

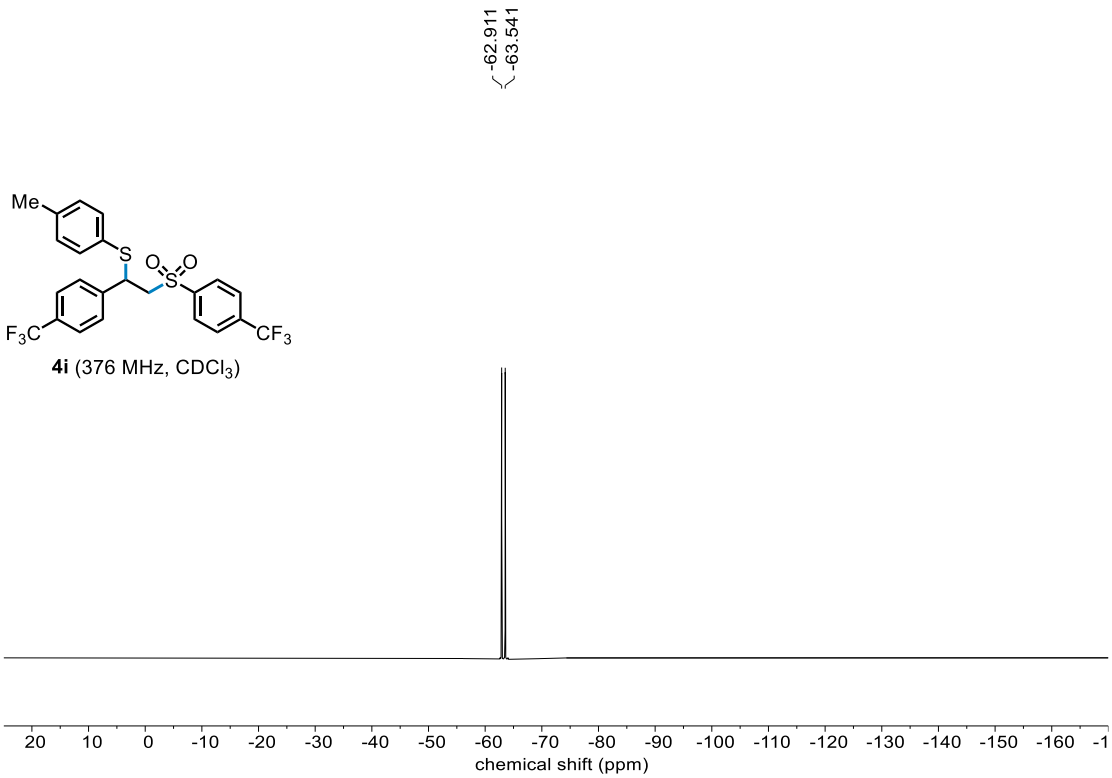

141.462
139.087
133.622
133.523
131.797
130.365
130.154
129.940
129.730
129.361
128.985
128.817
128.315
127.752
126.453
125.410
125.383
125.360
125.336
124.651
122.847
121.051
77.210
76.996
76.786
60.258
47.056
F3C
4h (150 MHz, CDCl3)
chemical shift (ppm)



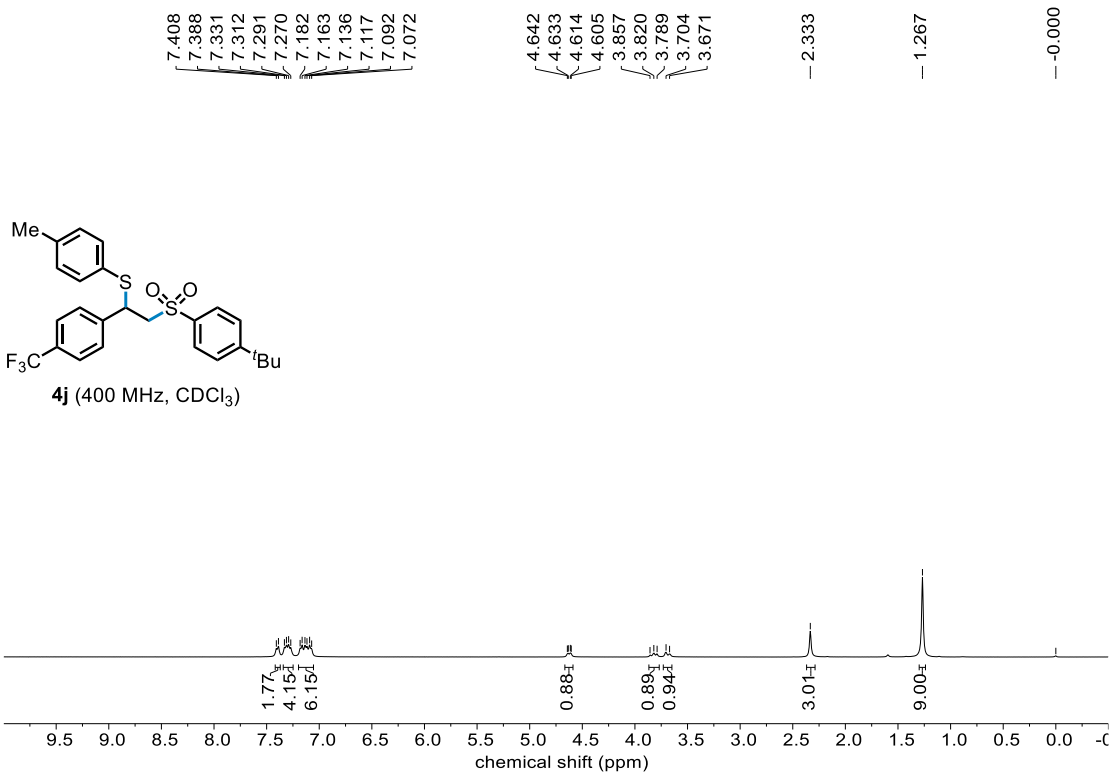
4h (376 MHz, $CDCl_3$)


7.603
7.584
7.532
7.514
7.330
7.309
7.196
7.177
7.105
7.091
4.595
4.575
3.881
3.845
3.819
3.744
3.706
2.340
-0.000
Me
S
O
O
S
F3C
CF3
4i (400 MHz, CDCl3)
2.03
1.91
2.05
2.06
4.17
0.96
1.00
1.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

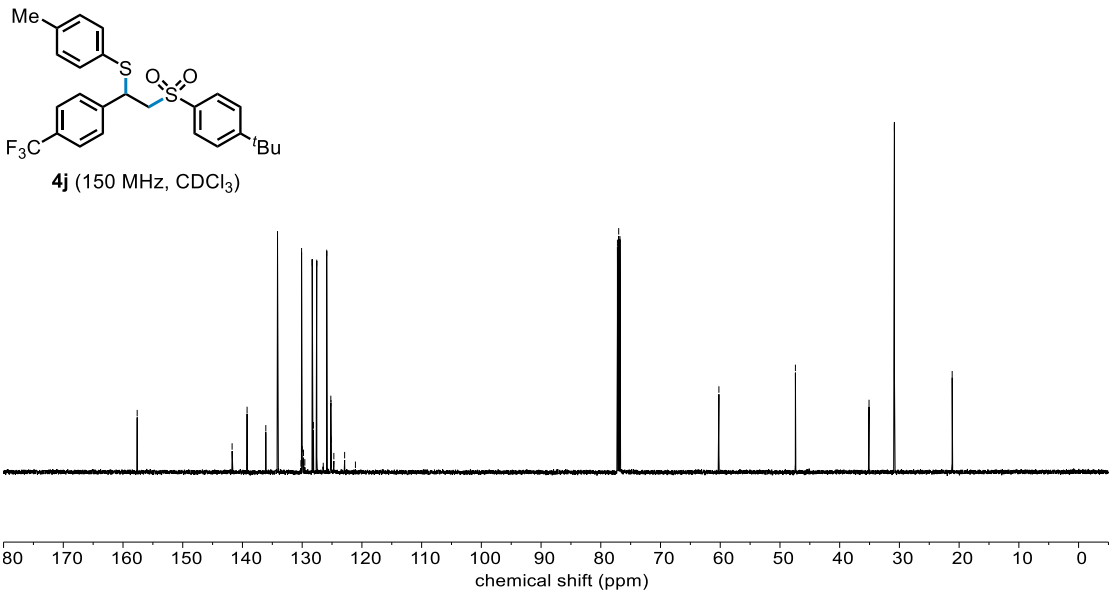

142.567
141.240
139.573
135.543
135.320
135.098
134.294
130.457
130.242
130.227
130.020
128.349
128.311
127.767
126.291
125.989
125.966
125.939
125.916
125.545
125.410
125.383
125.357
125.334
124.483
123.728
122.682
121.919
120.878
77.210
77.000
76.788
60.318
47.412
21.159
Me
S
O
O
S
F3C
CF3
4i (150 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)



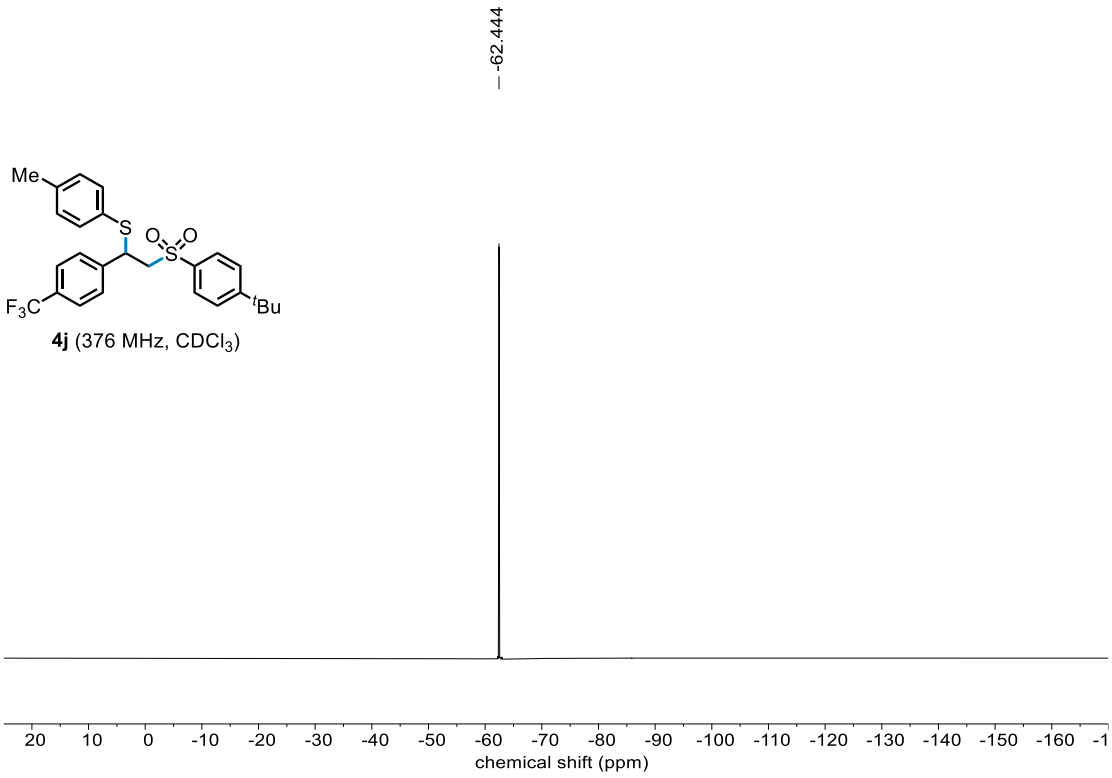
4i (376 MHz, $CDCl_3$)



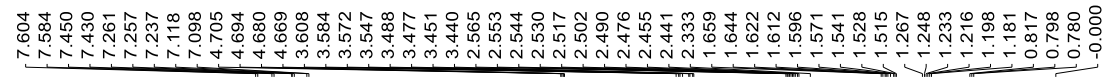
4j (400 MHz, $CDCl_3$)

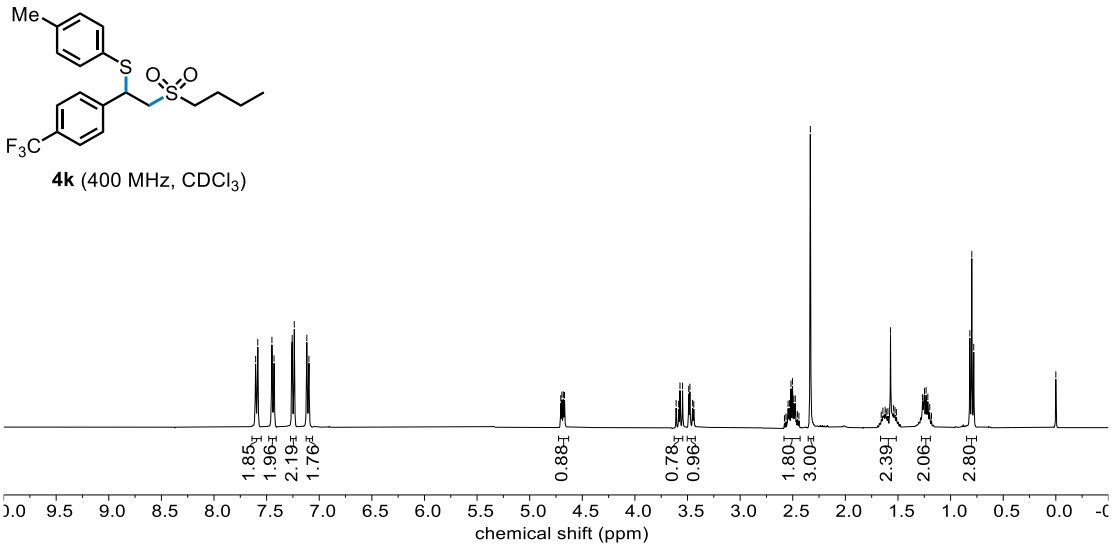


4j (150 MHz, $CDCl_3$)

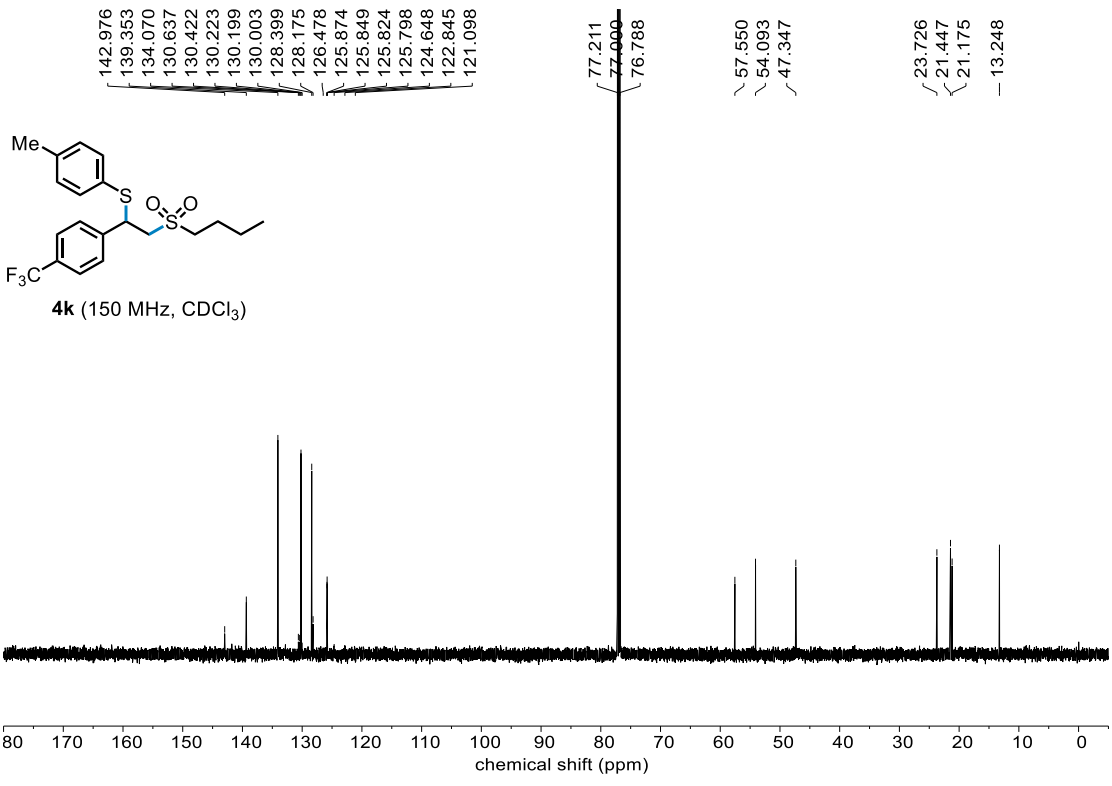


4j (376 MHz, $CDCl_3$)

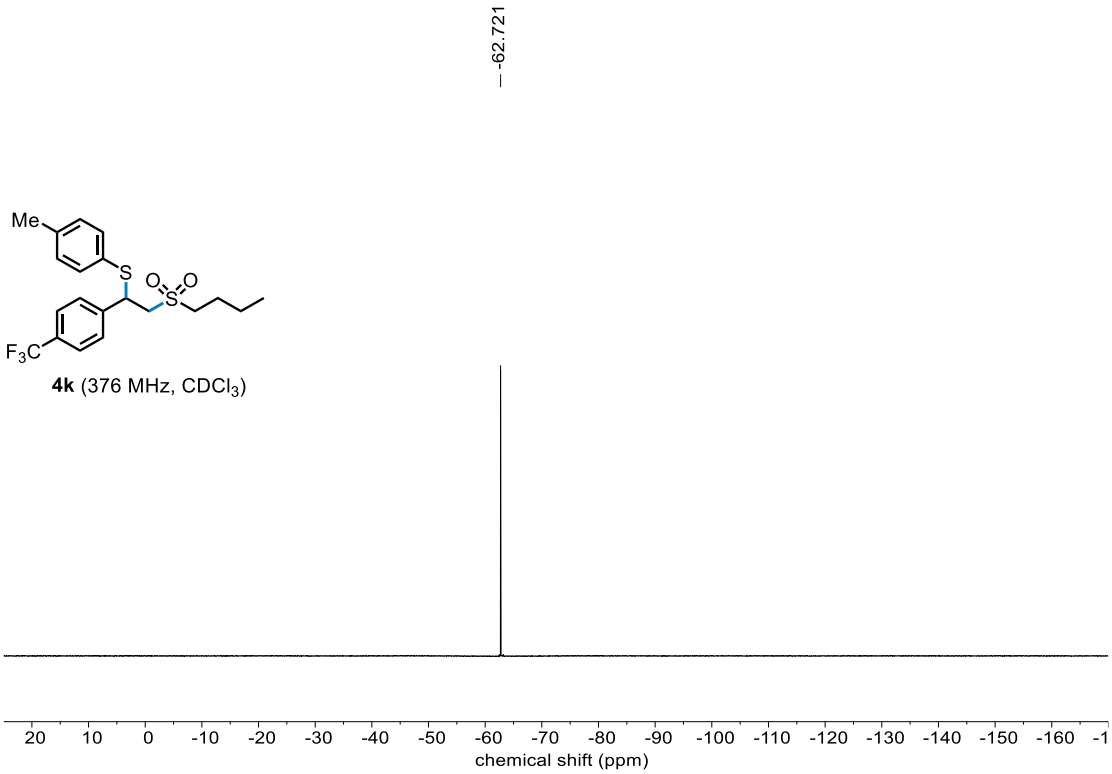




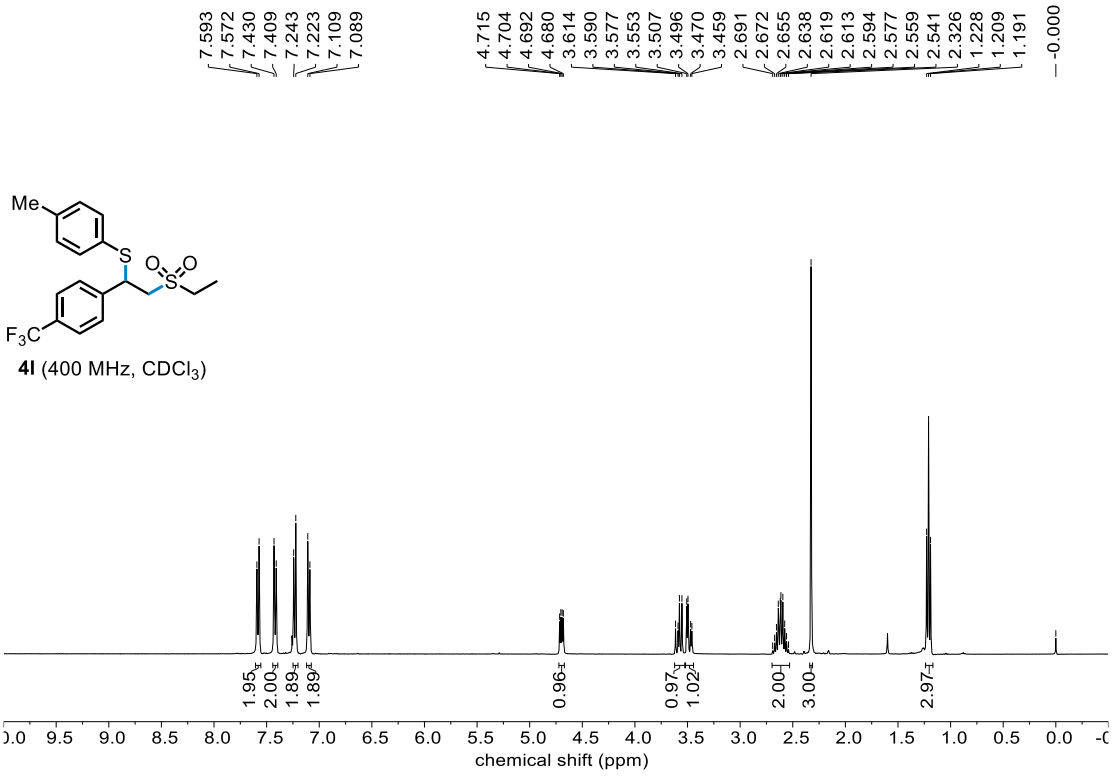
4k (400 MHz, $CDCl_3$)

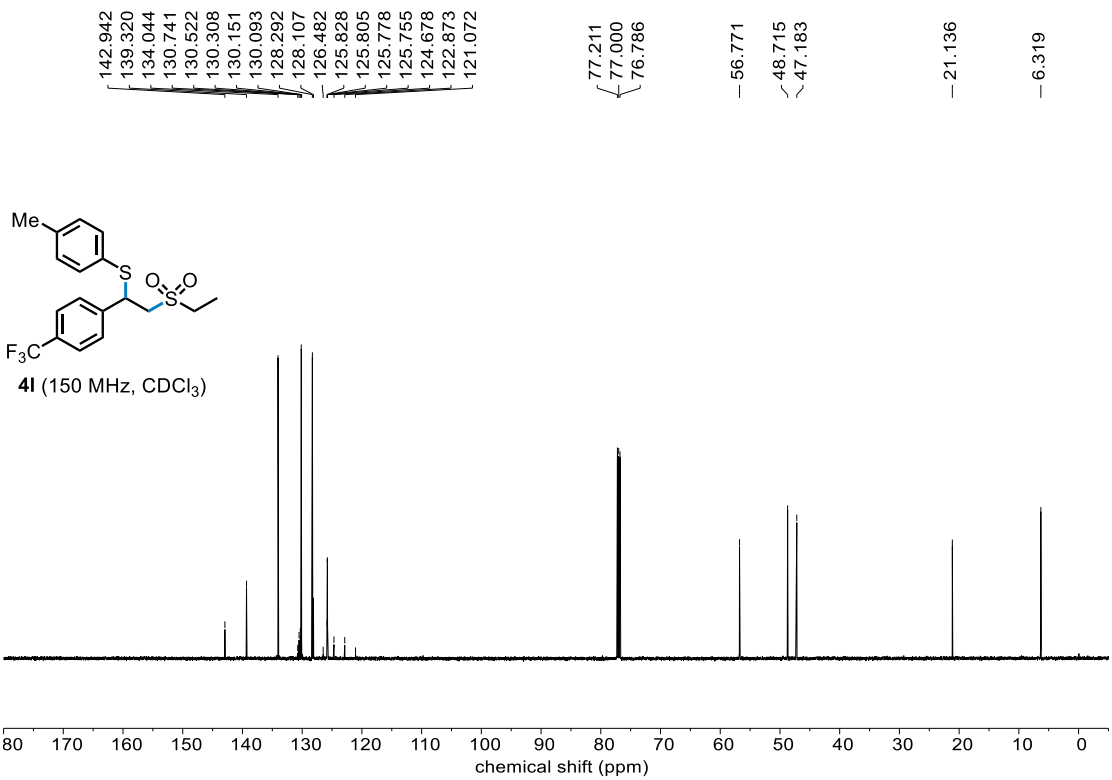


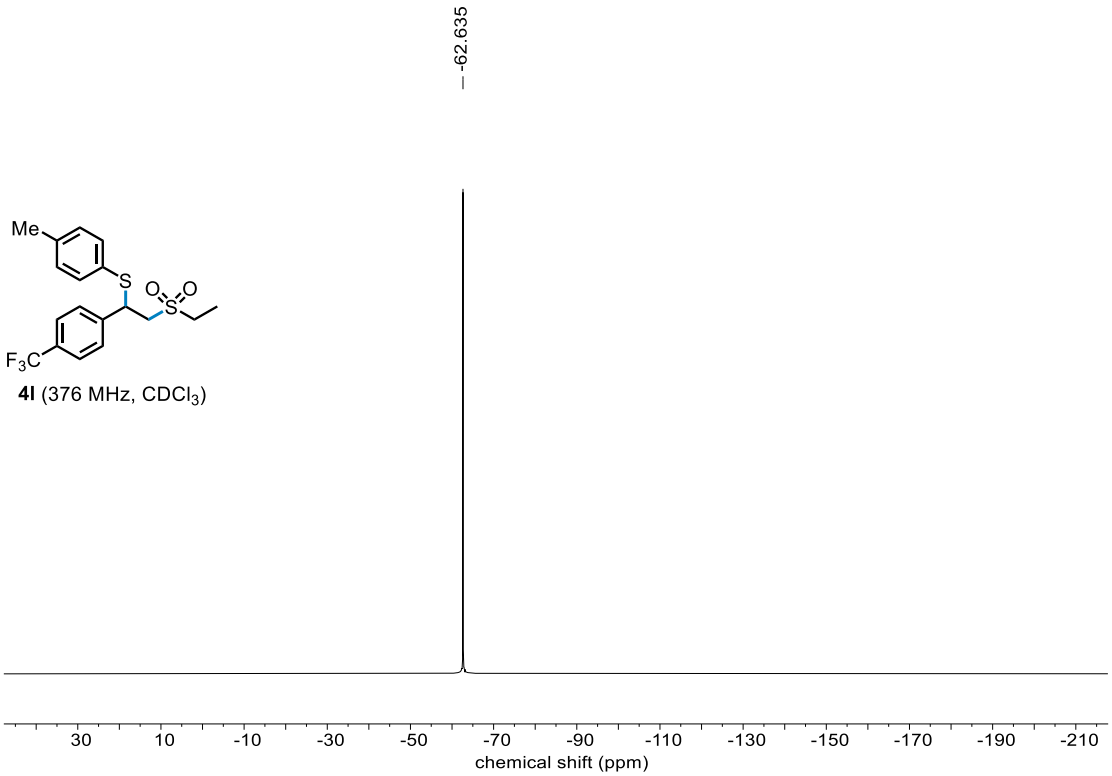
4k (150 MHz, $CDCl_3$)



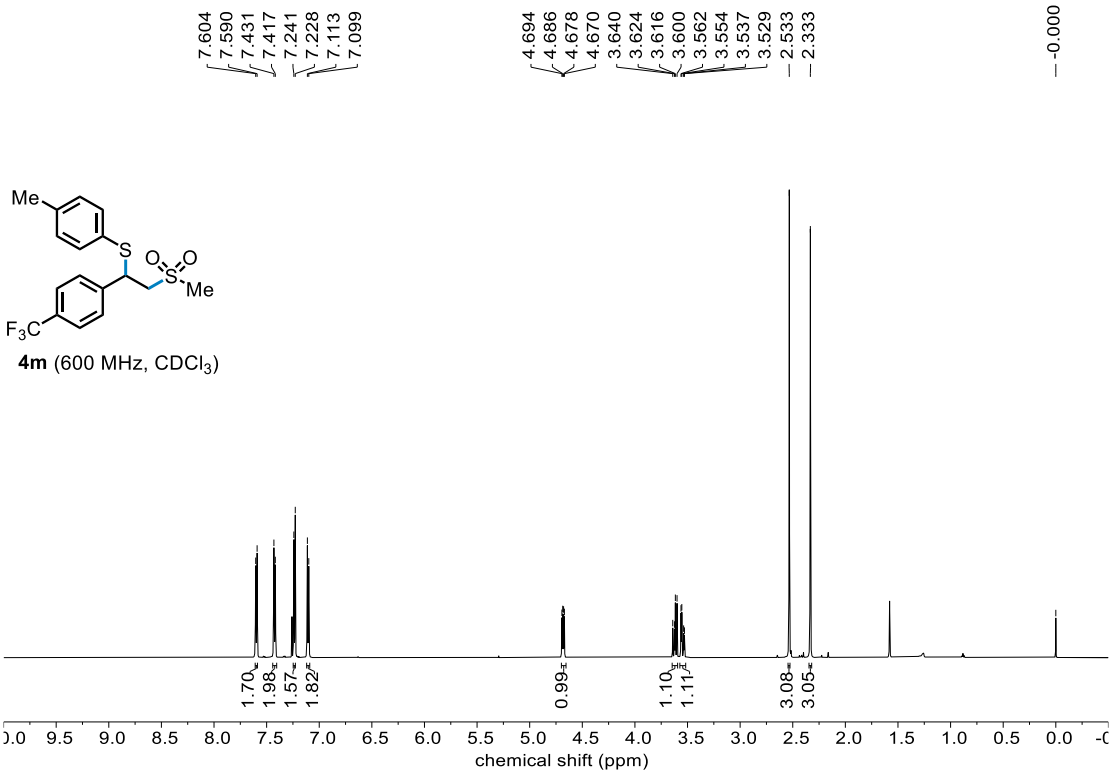
4k (376 MHz, $CDCl_3$)


7.593
7.572
7.430
7.409
7.243
7.223
7.109
7.089
4.715
4.704
4.692
4.680
3.614
3.590
3.577
3.553
3.507
3.496
3.470
3.459
2.691
2.672
2.655
2.638
2.619
2.613
2.594
2.577
2.559
2.541
2.326
1.228
1.209
1.191
-0.000
Me
S
O
O
S
F3C
4l (400 MHz, CDCl3)
1.95
2.00
1.89
1.89
0.96
0.97
1.02
2.00
3.00
2.97
chemical shift (ppm)

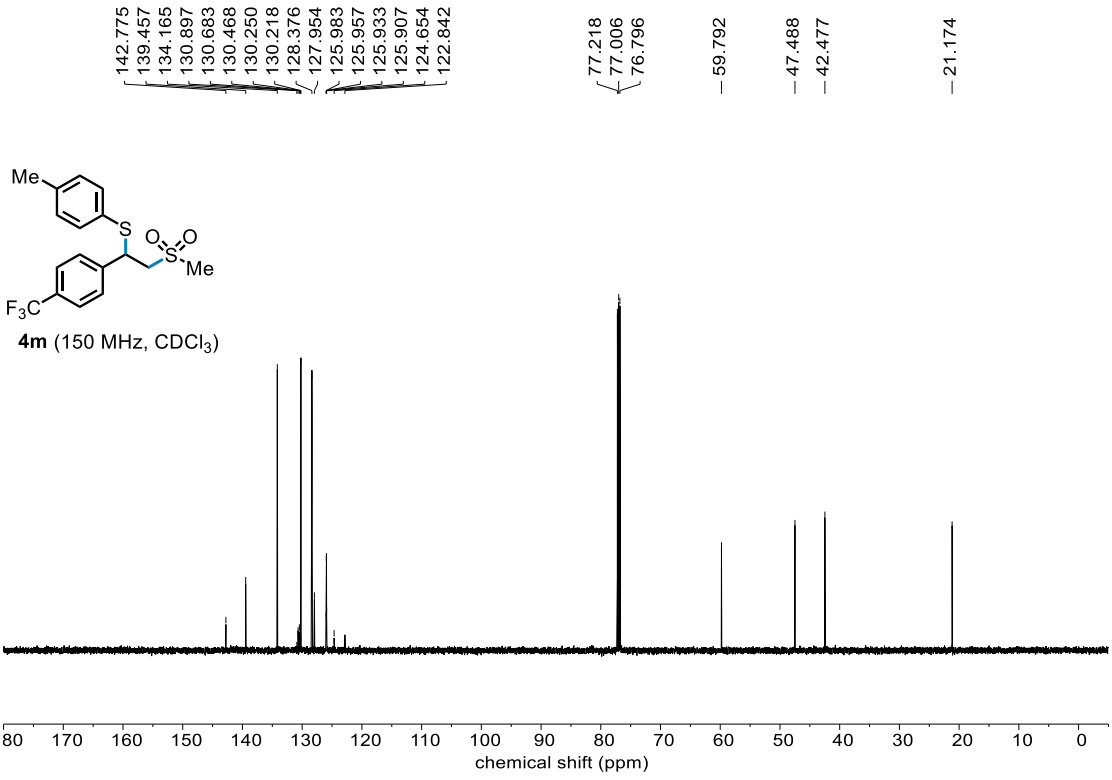

142.942
139.320
134.044
130.741
130.522
130.308
130.151
130.093
128.292
128.107
126.482
125.828
125.805
125.778
125.755
124.678
122.873
121.072
77.211
77.000
76.786
56.771
48.715
47.183
21.136
6.319
Me
S
O
O
S
F3C
4l (150 MHz, CDCl3)
chemical shift (ppm)



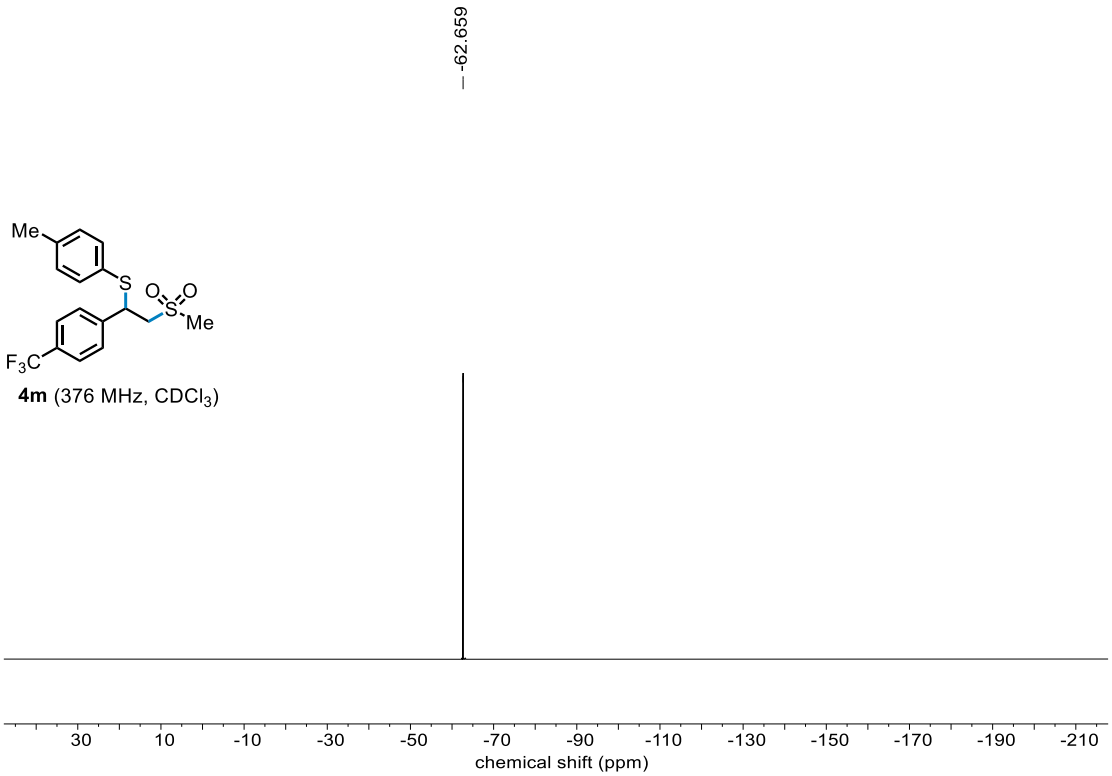
4l (376 MHz, $CDCl_3$)



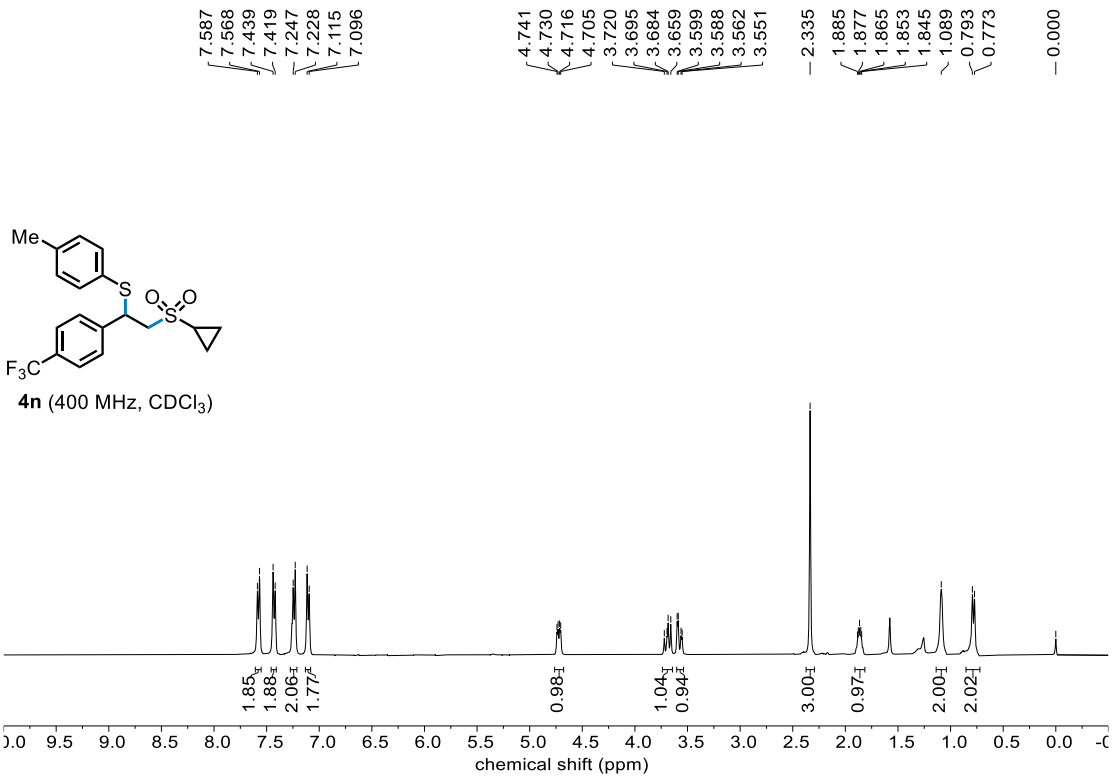
4m (600 MHz, $CDCl_3$)

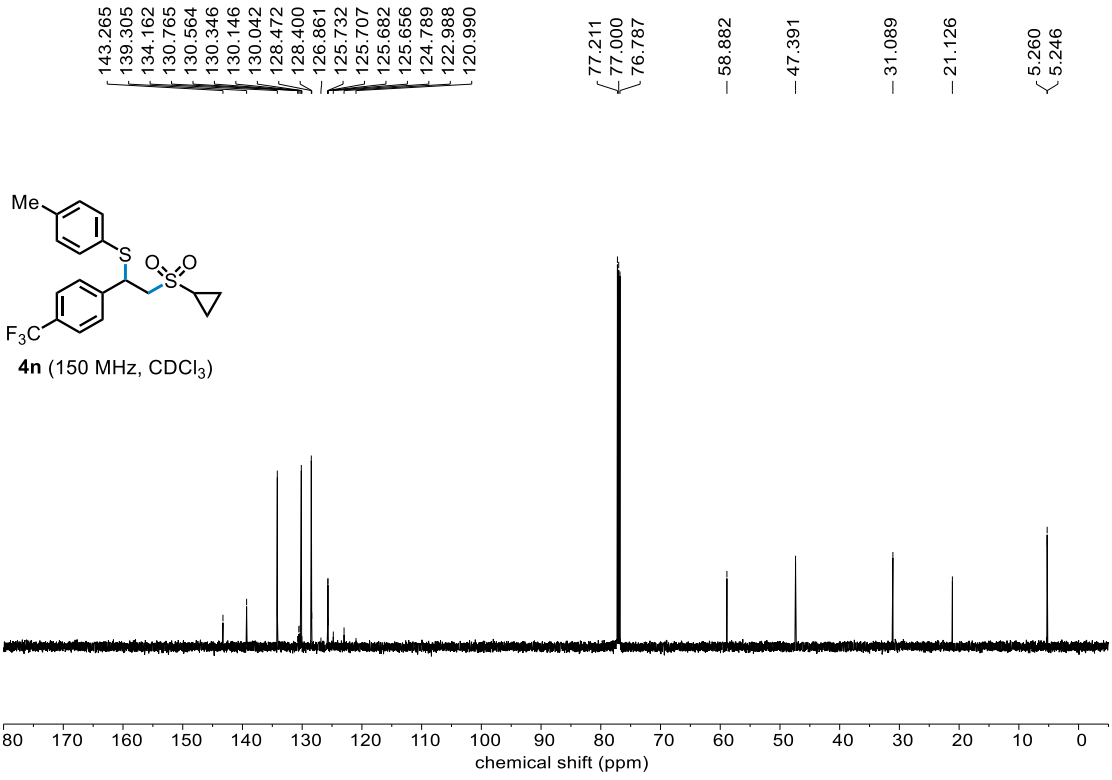


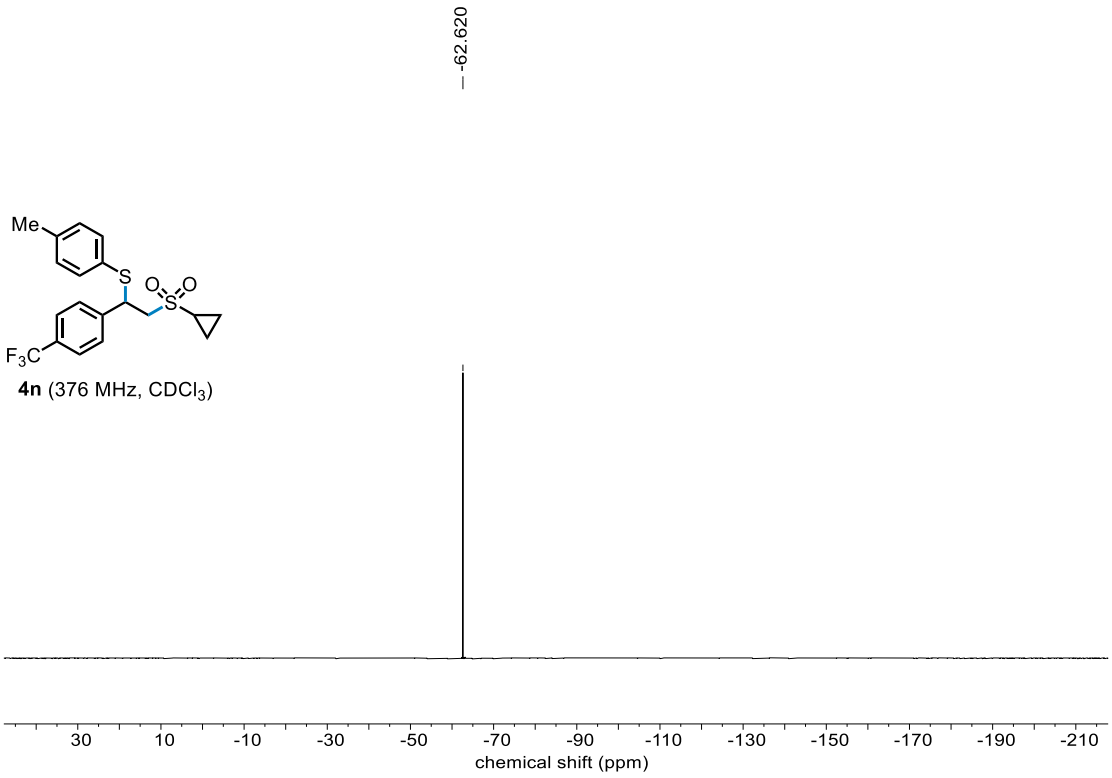
4m (150 MHz, $CDCl_3$)



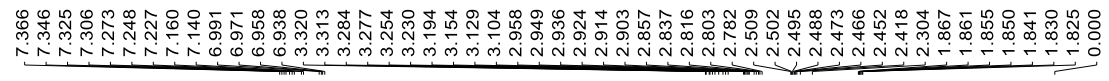
4m (376 MHz, $CDCl_3$)

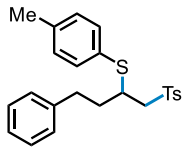

7.587
7.568
7.439
7.419
7.247
7.228
7.115
7.096
4.741
4.730
4.716
4.705
3.720
3.695
3.684
3.659
3.599
3.588
3.562
3.551
2.335
1.885
1.877
1.865
1.853
1.845
1.089
0.793
0.773
0.000
Me
S
O
O
S
F3C
4n (400 MHz, CDCl3)
1.85
1.88
2.06
1.77
0.98
1.04
0.94
3.00
0.97
2.00
2.02
chemical shift (ppm)


143.265
139.305
134.162
130.765
130.564
130.346
130.146
130.042
128.472
128.400
126.861
125.732
125.707
125.682
125.656
124.789
122.988
120.990
77.211
77.000
76.787
58.882
47.391
31.089
21.126
5.260
5.246
Me
S
O
O
S
F3C
4n (150 MHz, CDCl3)
chemical shift (ppm)

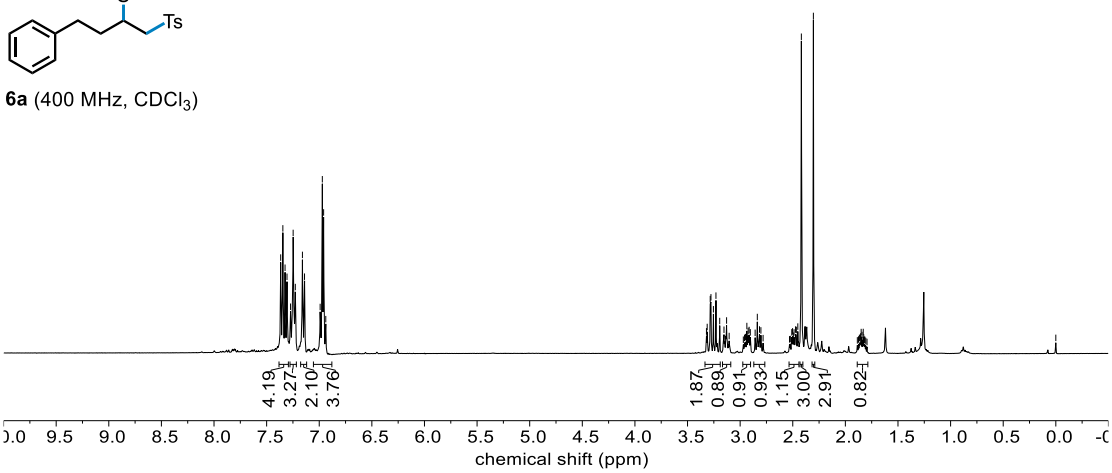


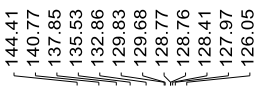
4n (376 MHz, $CDCl_3$)

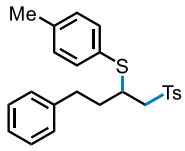




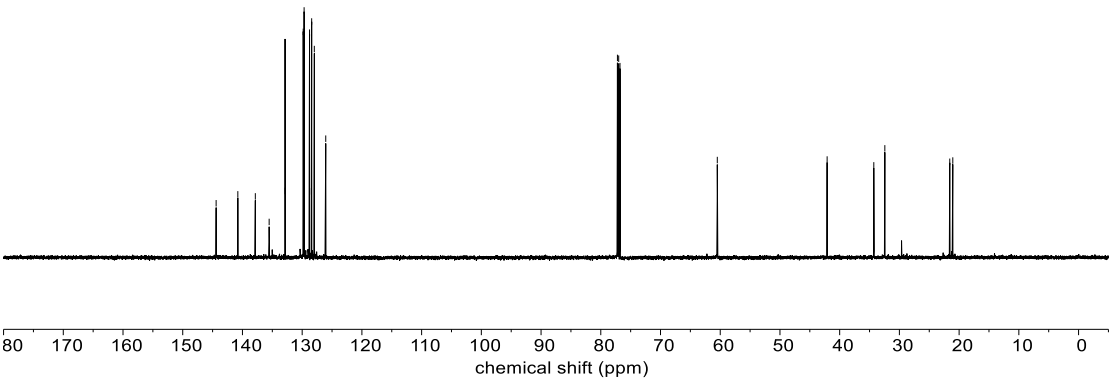
6a (400 MHz, $CDCl_3$)

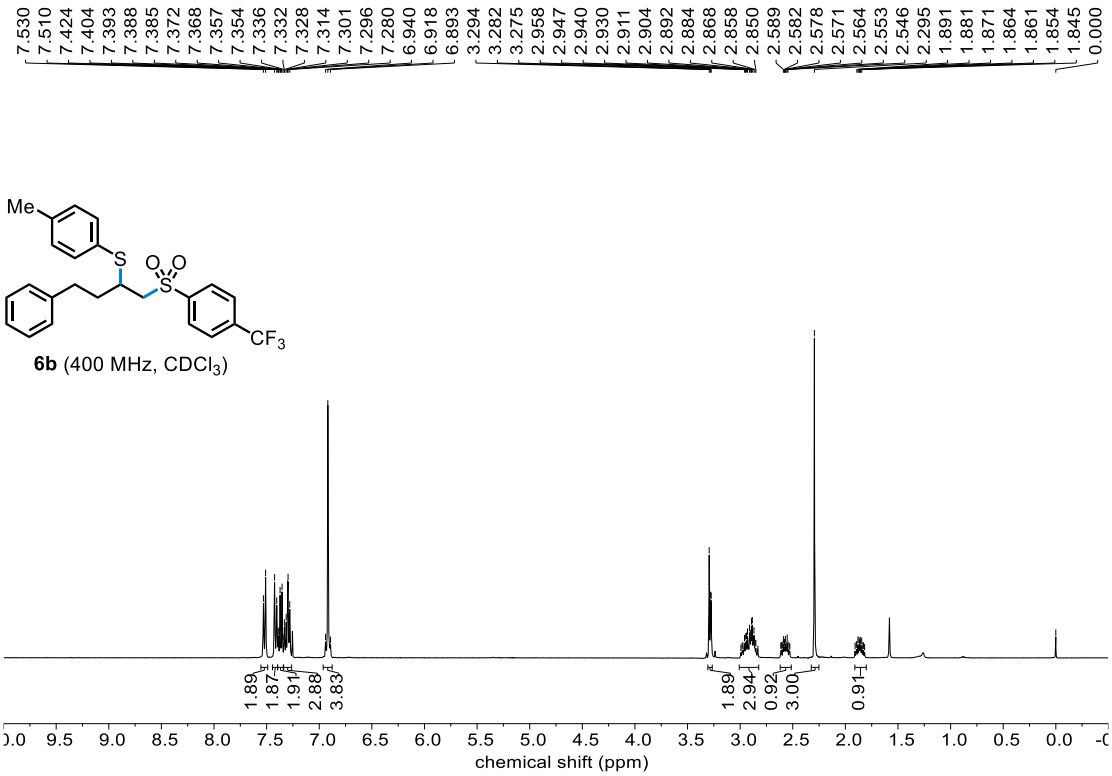


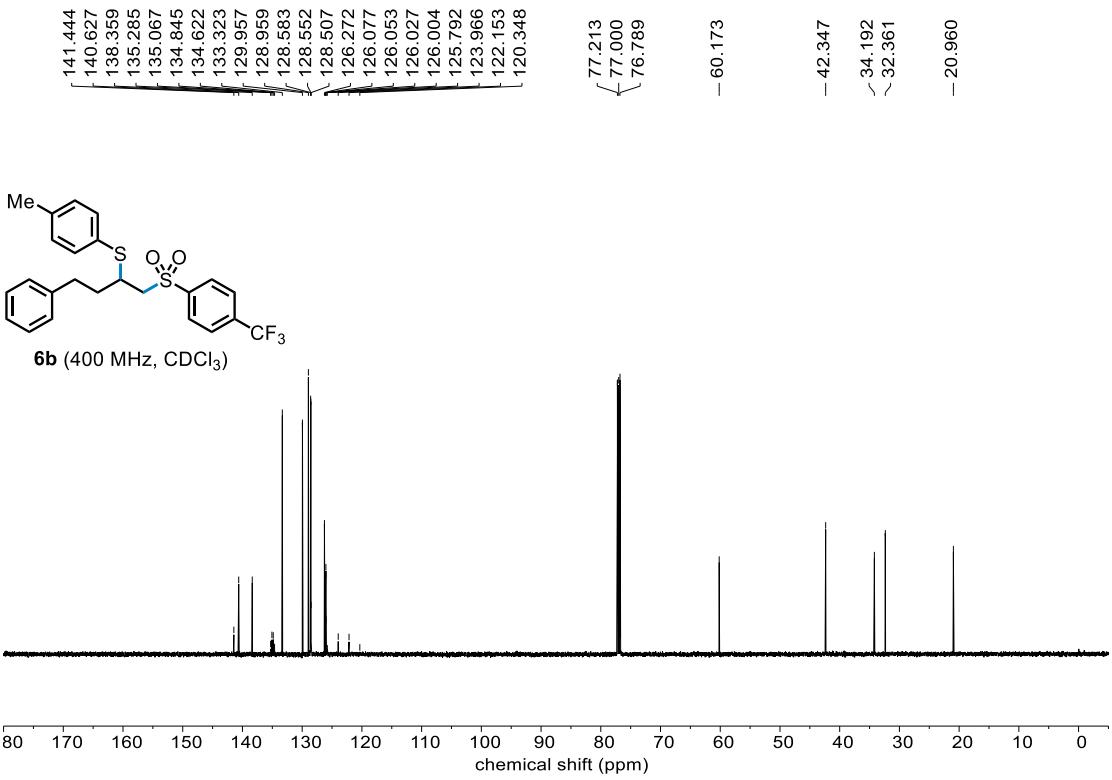


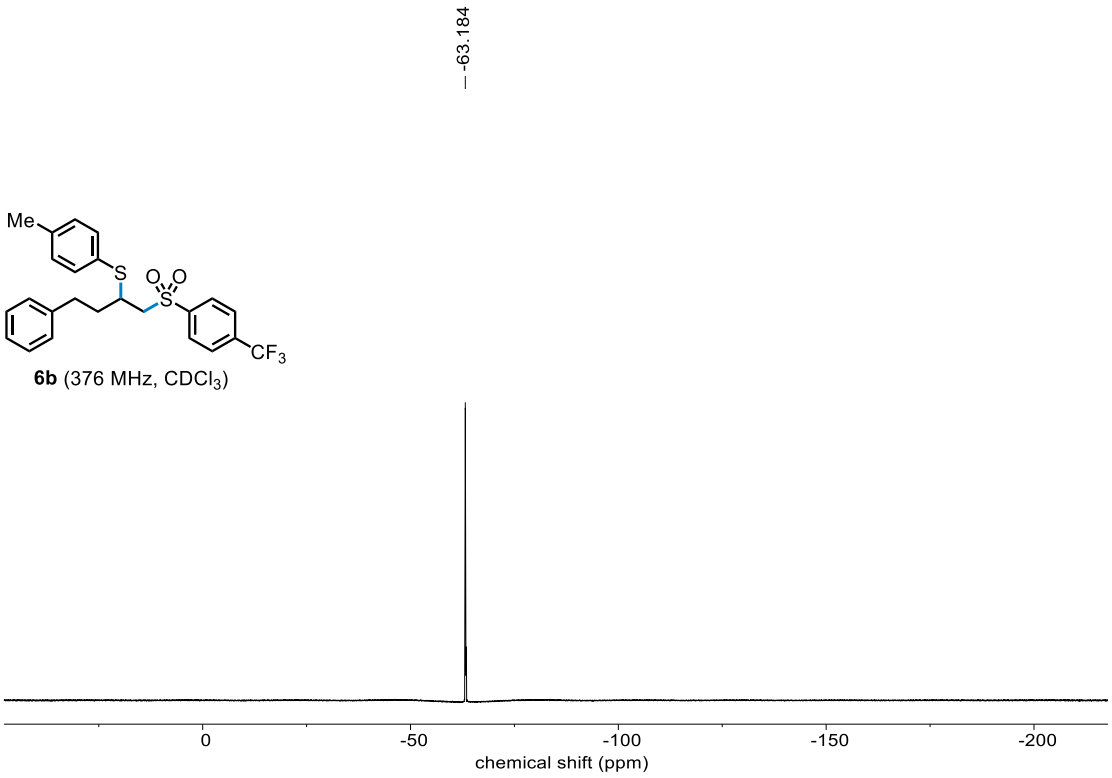


6a (150 MHz, $CDCl_3$)

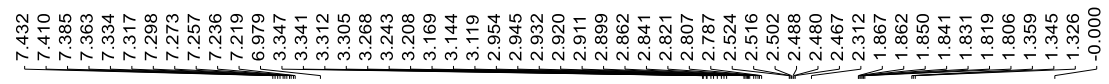


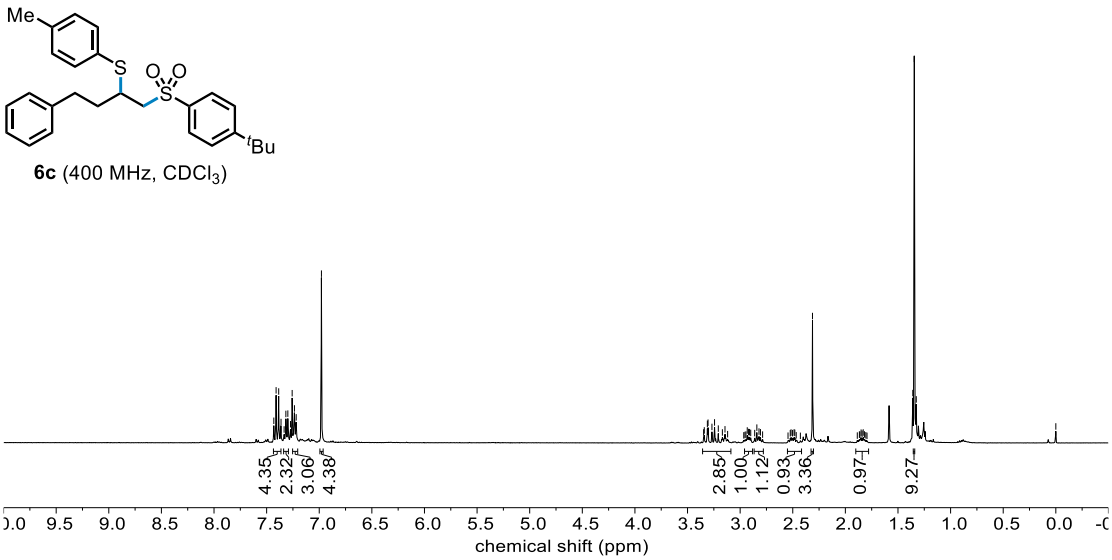

7.530
7.510
7.424
7.404
7.393
7.388
7.385
7.372
7.368
7.357
7.354
7.336
7.332
7.328
7.314
7.301
7.296
7.280
6.940
6.918
6.893
3.294
3.282
3.275
2.958
2.947
2.940
2.930
2.911
2.904
2.892
2.884
2.868
2.858
2.850
2.589
2.582
2.578
2.571
2.564
2.553
2.546
2.295
1.891
1.881
1.871
1.864
1.861
1.854
1.845
0.000
Me
S
O
O
S
CF3
6b (400 MHz, CDCl3)
1.89
1.87
1.91
2.88
3.83
1.89
2.94
0.92
3.00
0.91
chemical shift (ppm)


141.444
140.627
138.359
135.285
135.067
134.845
134.622
133.323
129.957
128.959
128.583
128.552
128.507
126.272
126.077
126.053
126.027
126.004
125.792
123.966
122.153
120.348
77.213
77.000
76.789
60.173
42.347
34.192
32.361
20.960
Me
S
O
O
S
CF3
6b (400 MHz, CDCl3)
chemical shift (ppm)



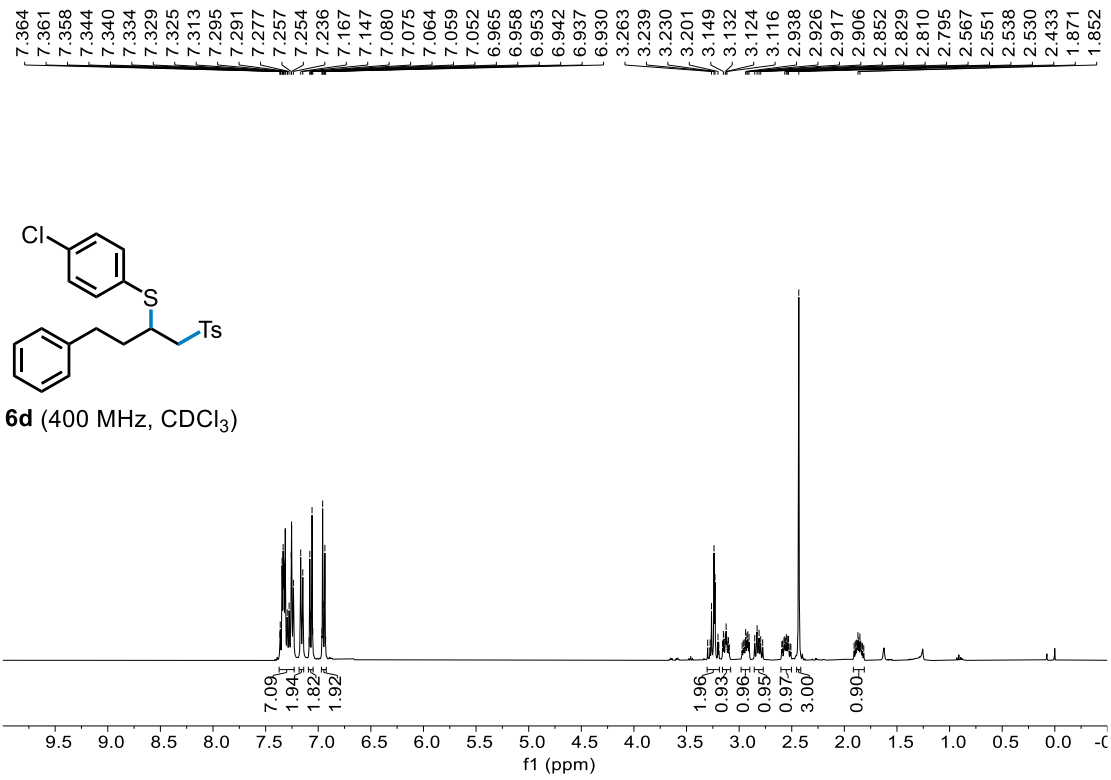
6b (376 MHz, $CDCl_3$)

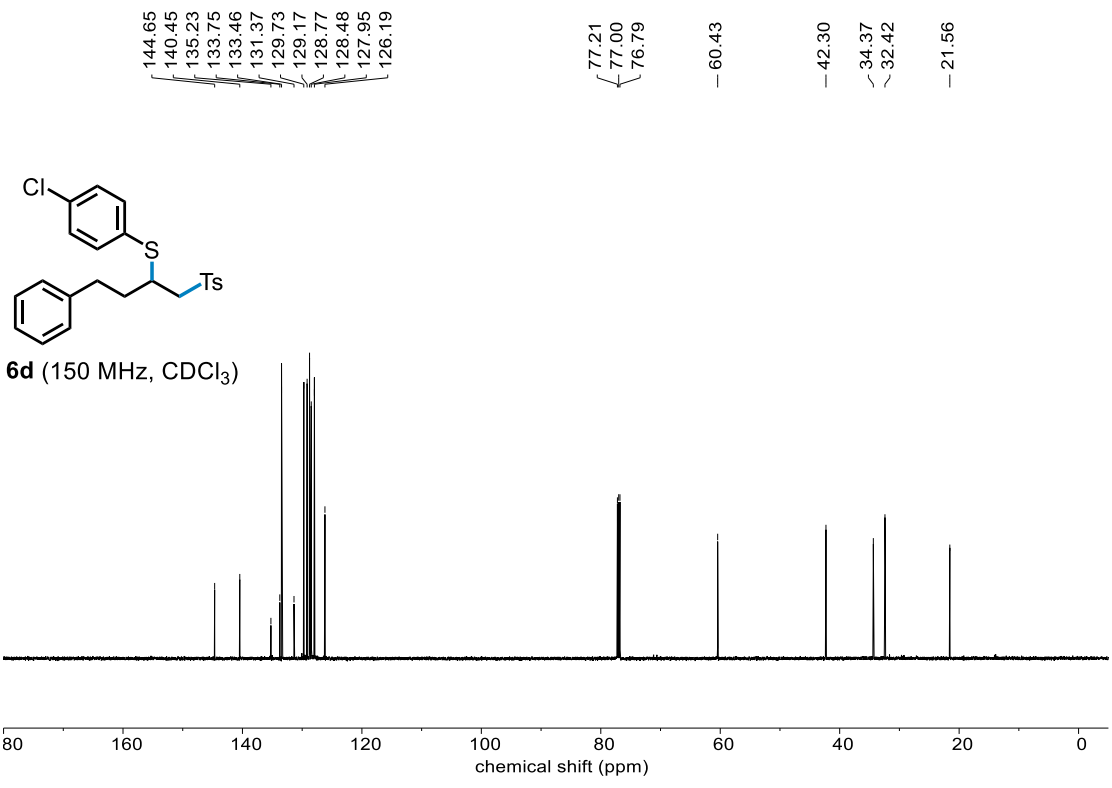


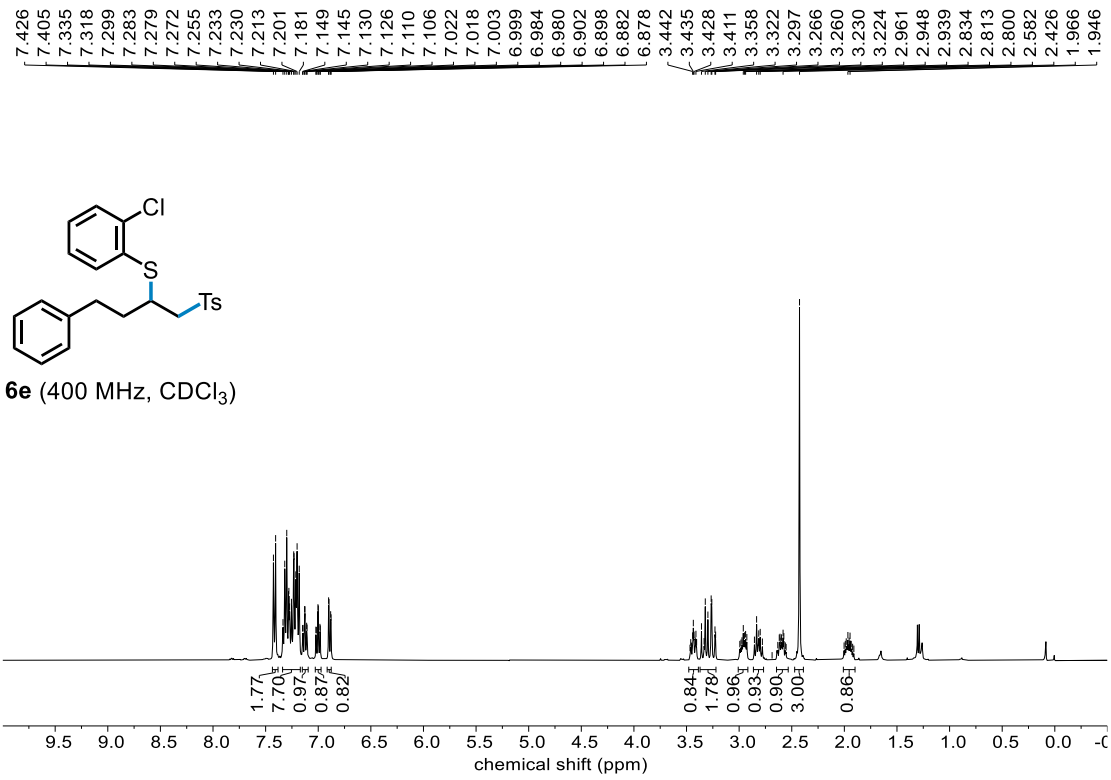


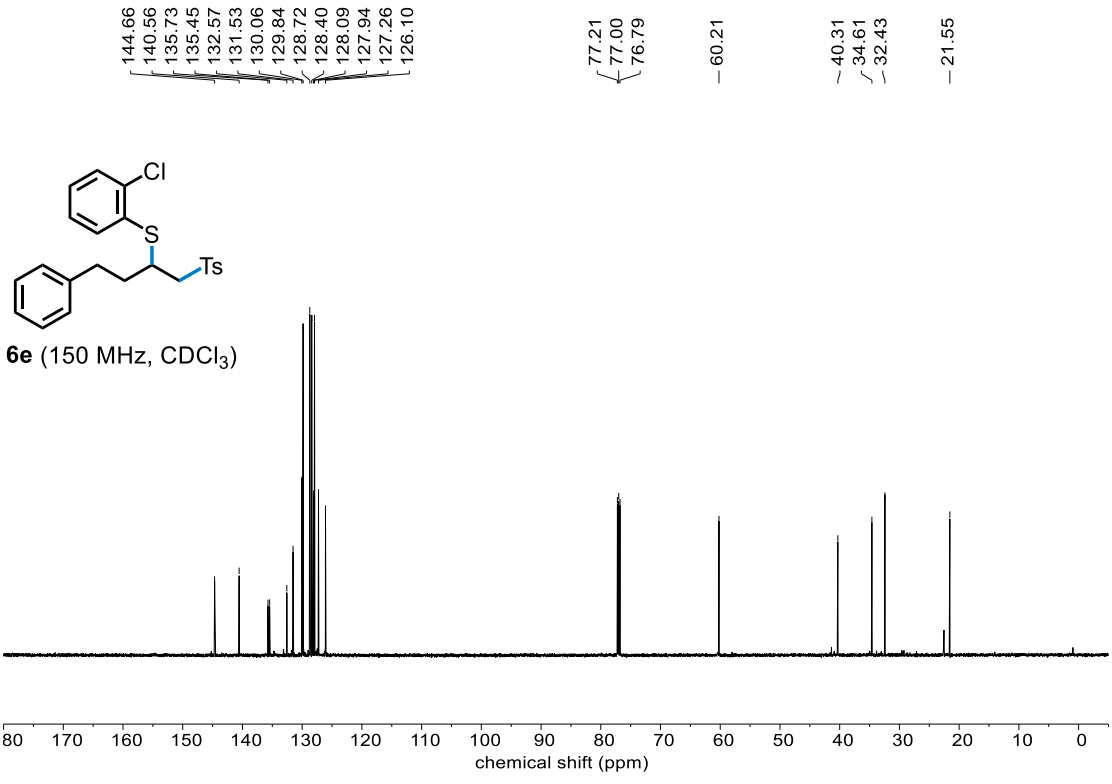
6c (400 MHz, $CDCl_3$)

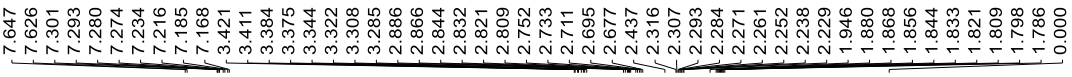
6c (150 MHz, $CDCl_3$)

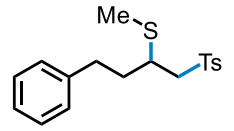

7.364
7.361
7.358
7.344
7.340
7.334
7.329
7.325
7.313
7.295
7.291
7.277
7.257
7.254
7.236
7.167
7.147
7.080
7.075
7.064
7.059
7.052
6.965
6.958
6.953
6.942
6.937
6.930
3.263
3.239
3.230
3.201
3.149
3.132
3.124
3.116
2.938
2.926
2.917
2.906
2.852
2.829
2.810
2.795
2.567
2.551
2.538
2.530
2.433
1.871
1.852
Cl
S
Ts
6d (400 MHz, CDCl3)
7.09
1.94
1.82
1.92
1.96
0.93
0.96
0.95
0.97
3.00
0.90
f1 (ppm)


144.65
140.45
135.23
133.75
133.46
131.37
129.73
129.17
128.77
128.48
127.95
126.19
77.21
77.00
76.79
60.43
42.30
34.37
32.42
21.56
Cl
S
Ts
6d (150 MHz, CDCl3)
chemical shift (ppm)

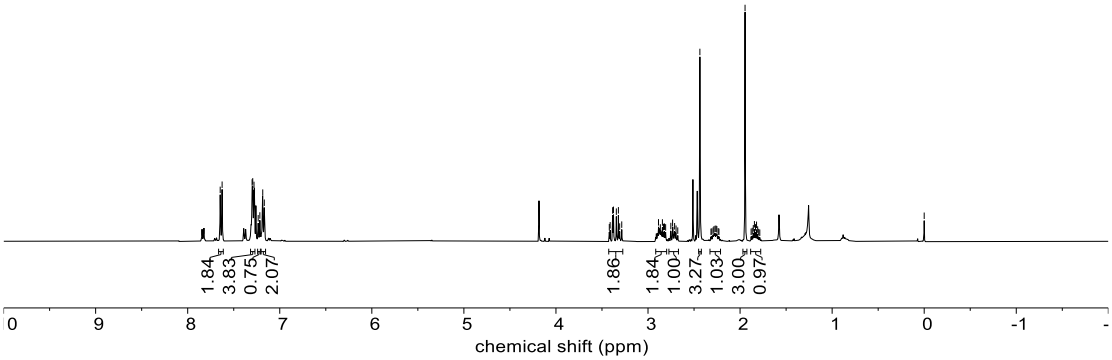

7.426
7.405
7.335
7.318
7.299
7.283
7.279
7.272
7.255
7.233
7.230
7.213
7.201
7.181
7.149
7.145
7.130
7.126
7.110
7.106
7.022
7.018
7.003
6.999
6.984
6.980
6.902
6.898
6.882
6.878
3.442
3.435
3.428
3.411
3.358
3.322
3.297
3.266
3.260
3.230
3.224
2.961
2.948
2.939
2.834
2.813
2.800
2.582
2.426
1.966
1.946
Cl
S
Ts
6e (400 MHz, CDCl3)
1.77
7.70
0.97
0.87
0.82
0.84
1.78
0.96
0.93
0.90
3.00
0.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

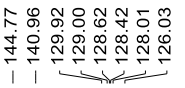

144.66
140.56
135.73
135.45
132.57
131.53
130.06
129.84
128.72
128.40
128.09
127.94
127.26
126.10
77.21
77.00
76.79
60.21
40.31
34.61
32.43
21.55
Cl
S
Ts
6e (150 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)

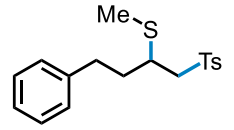




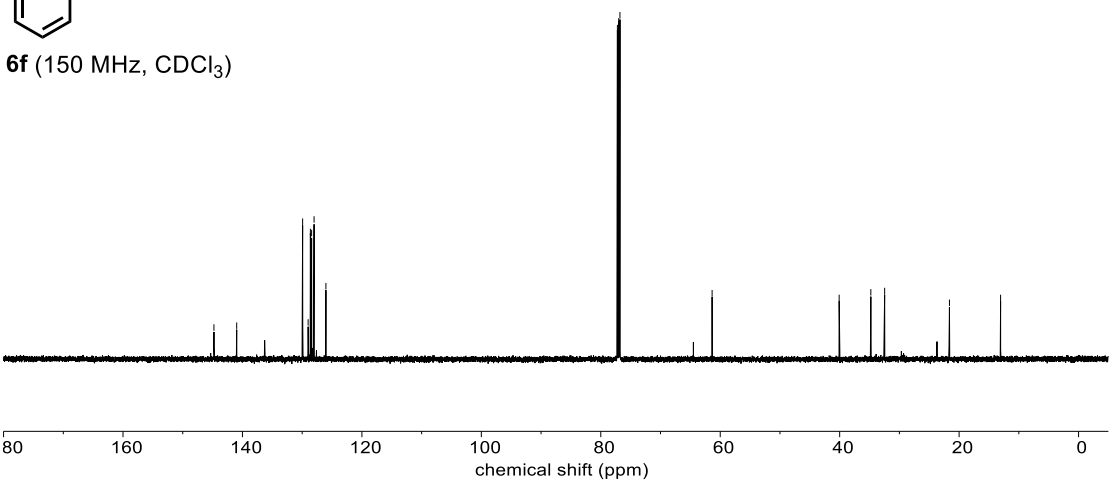
6f (400 MHz, $CDCl_3$)

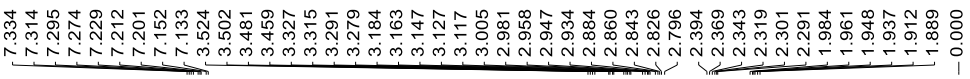


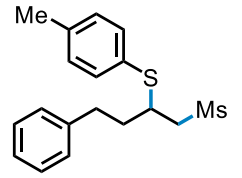




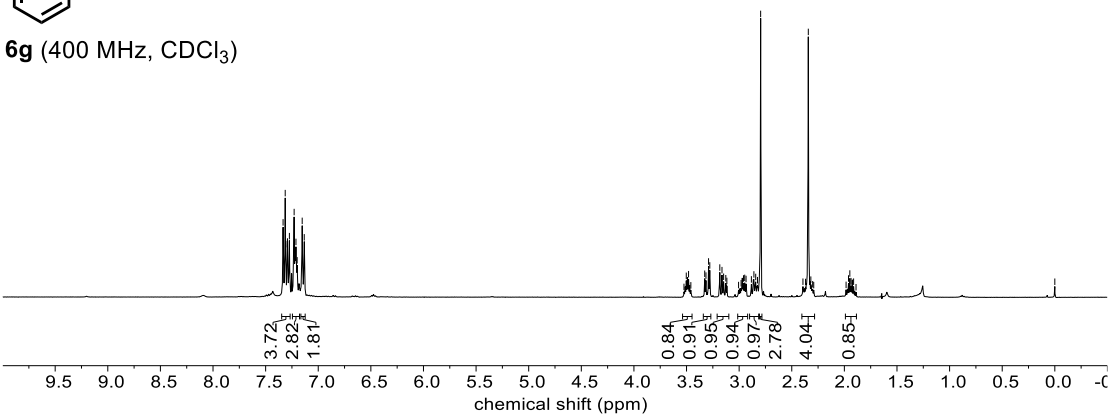
6f (150 MHz, $CDCl_3$)

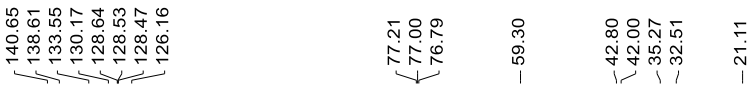


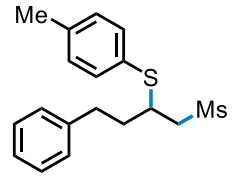




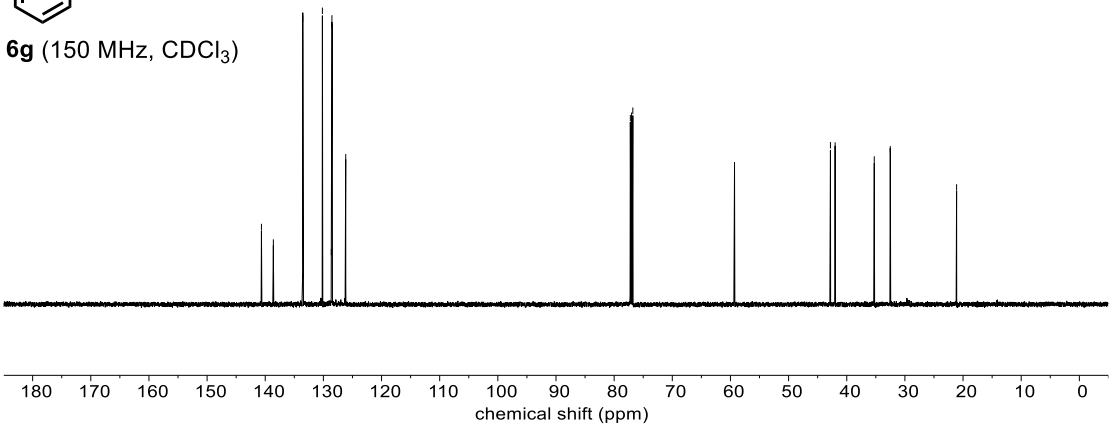
6g (400 MHz, $CDCl_3$)

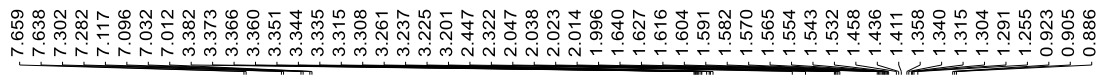


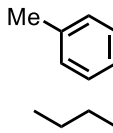




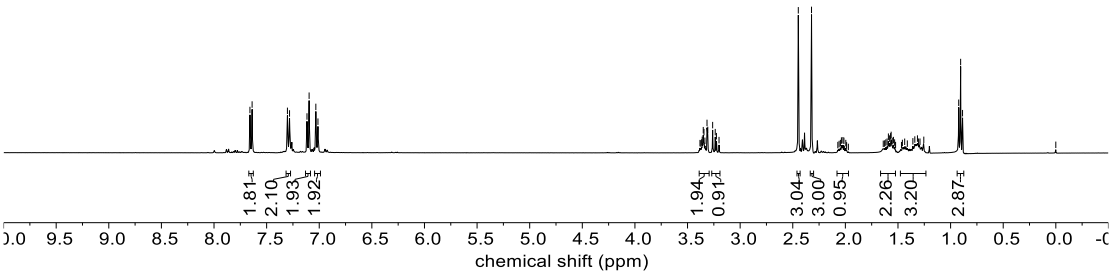
6g (150 MHz, $CDCl_3$)

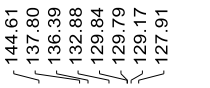


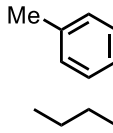




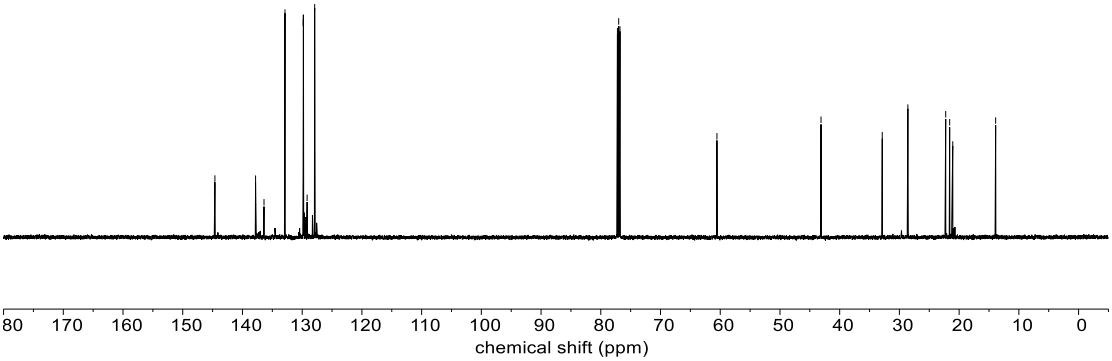
6h (400 MHz, $CDCl_3$)

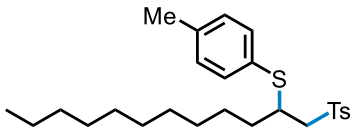




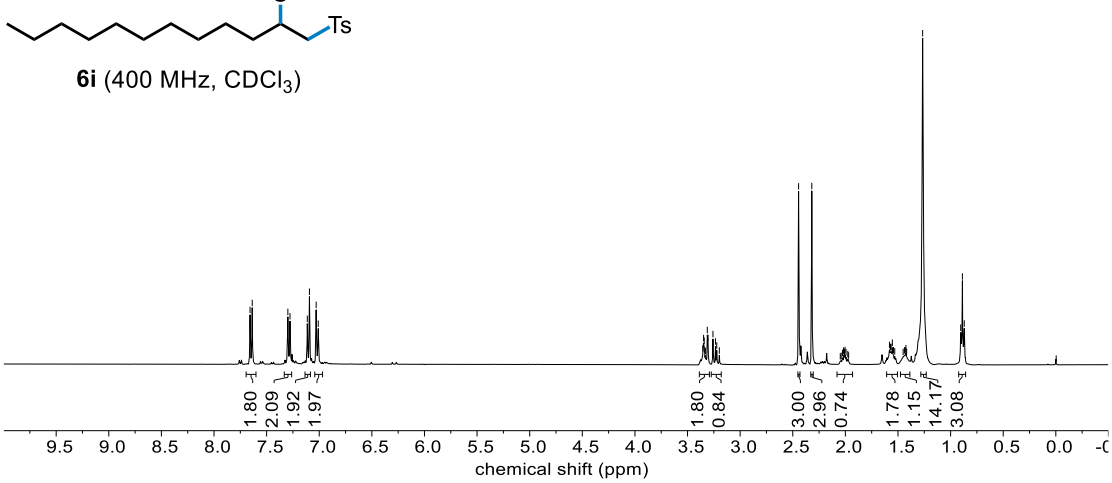


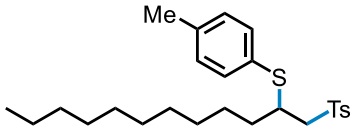
6h (150 MHz, $CDCl_3$)



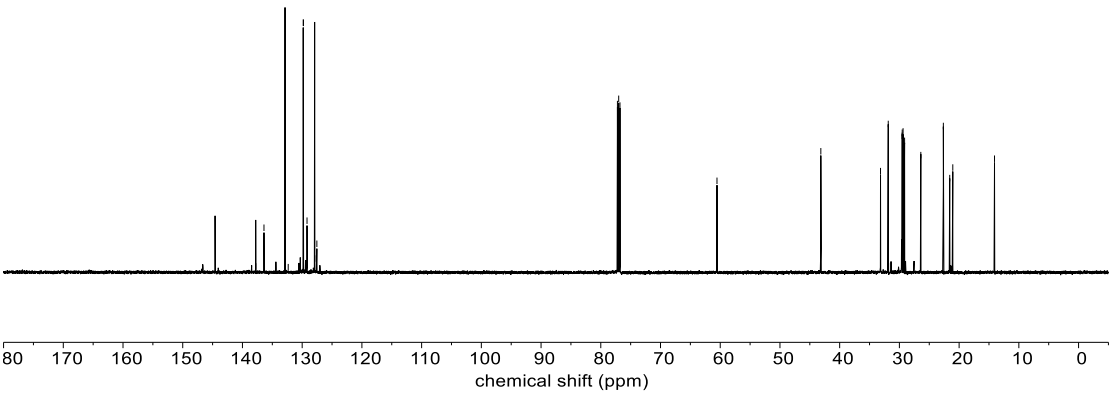


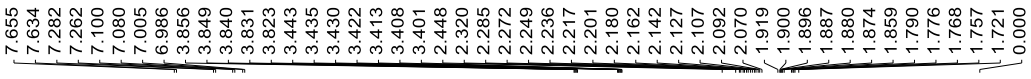
6i (400 MHz, $CDCl_3$)

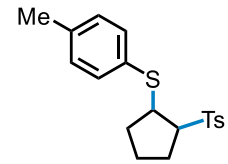




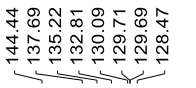
6i (150 MHz, $CDCl_3$)

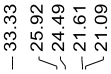


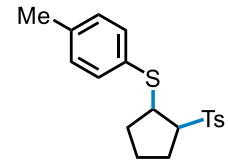




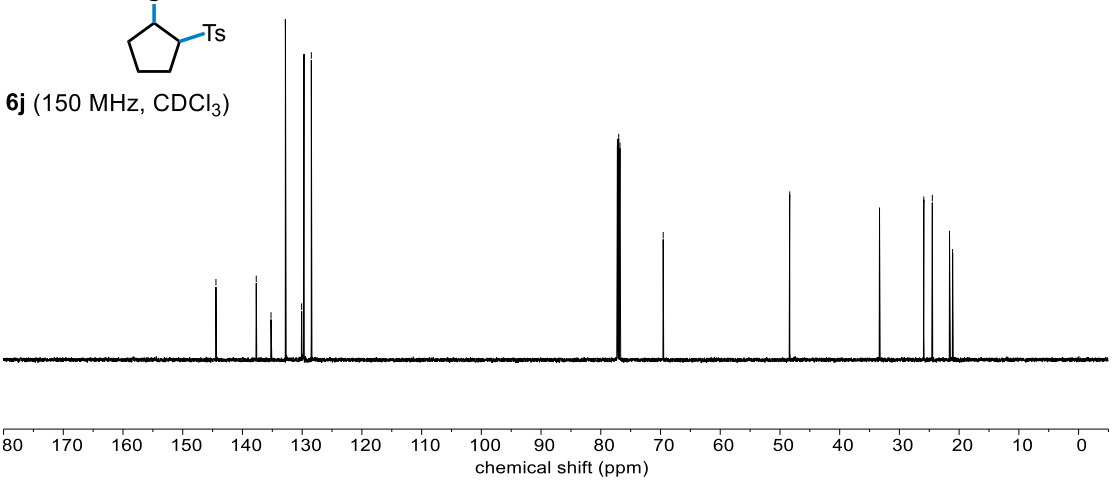
6j (400 MHz, $CDCl_3$)

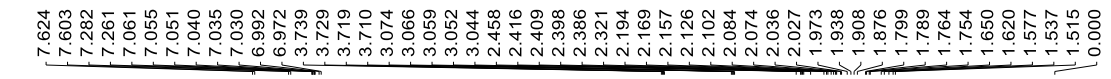


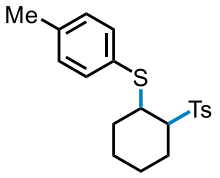




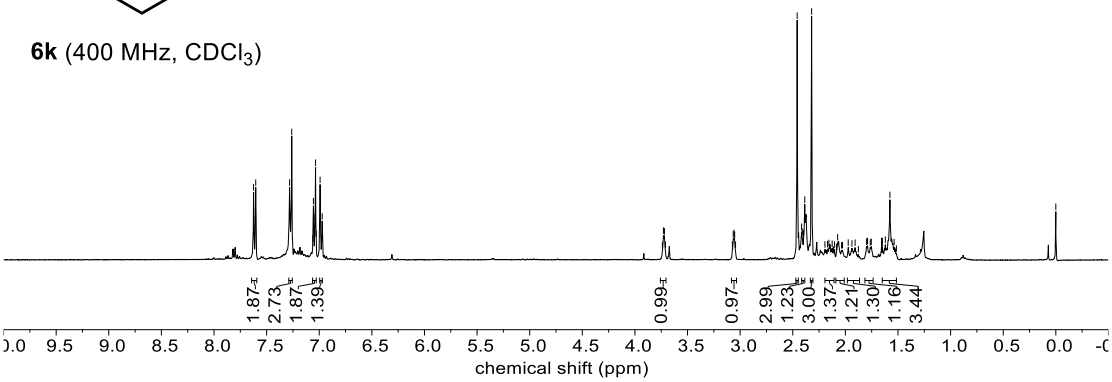
6j (150 MHz, $CDCl_3$)

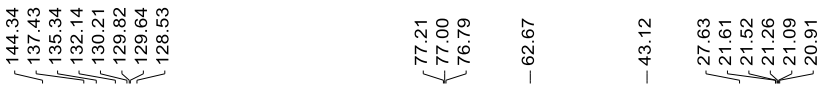


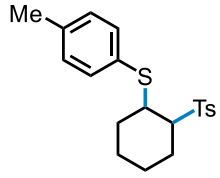




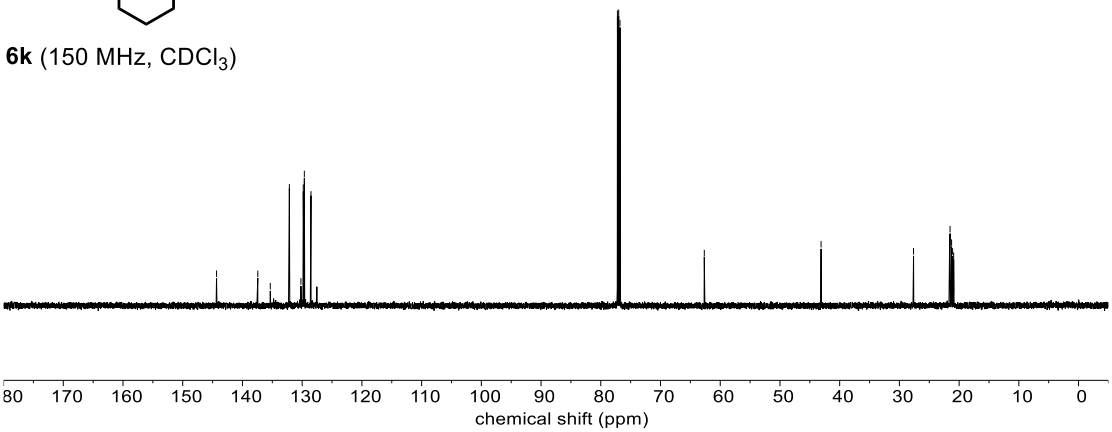
6k (400 MHz, $CDCl_3$)

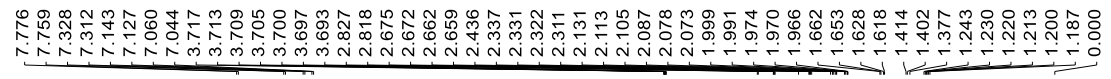


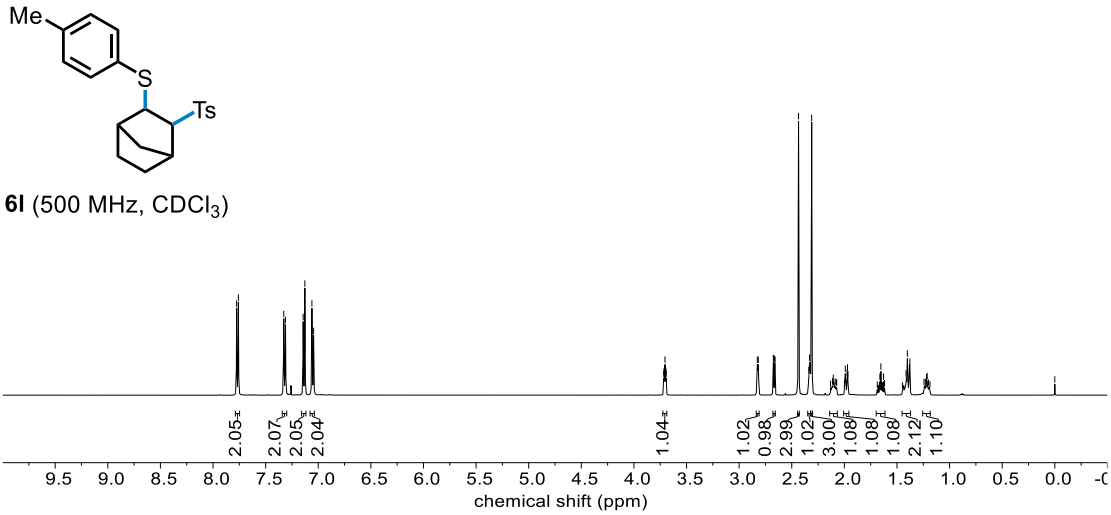


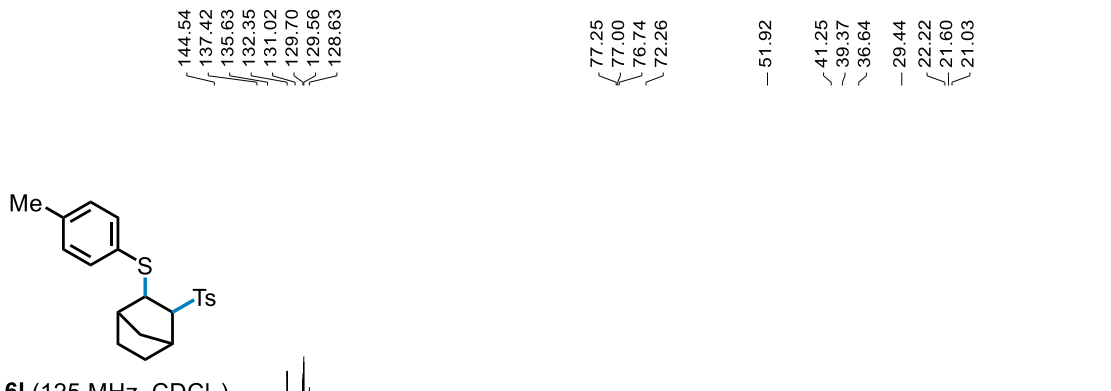


6k (150 MHz, $CDCl_3$)

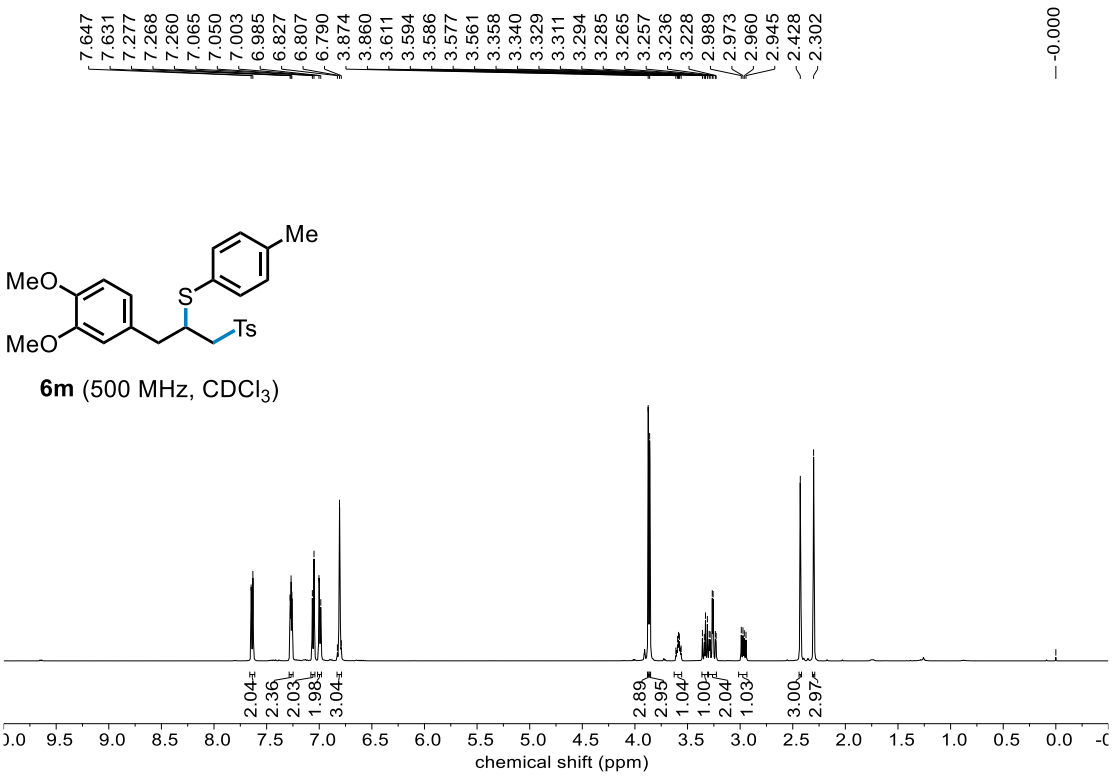


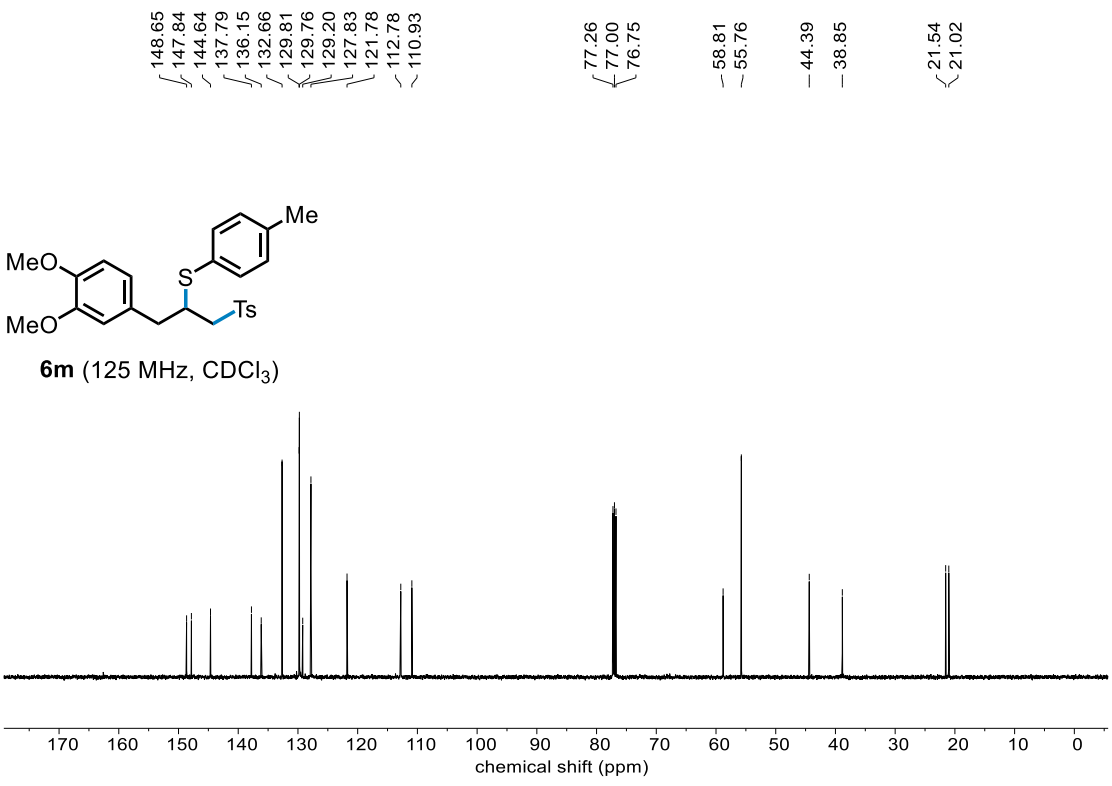

7.776
7.759
7.328
7.312
7.143
7.127
7.060
7.044
3.717
3.713
3.709
3.705
3.700
3.697
3.693
2.827
2.818
2.675
2.672
2.662
2.659
2.436
2.337
2.331
2.322
2.311
2.131
2.113
2.105
2.087
2.078
2.073
1.999
1.991
1.974
1.970
1.966
1.662
1.653
1.628
1.618
1.414
1.402
1.377
1.243
1.230
1.220
1.213
1.200
1.187
0.000

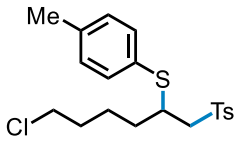

Me
S
Ts
6l (500 MHz, CDCl3)
2.05
2.07
2.05
2.04
1.04
1.02
0.98
2.99
1.02
3.00
1.08
1.08
1.08
2.12
1.10
chemical shift (ppm)


144.54
137.42
135.63
132.35
131.02
129.70
129.56
128.63
77.25
77.00
76.74
72.26
51.92
41.25
39.37
36.64
29.44
22.22
21.60
21.03

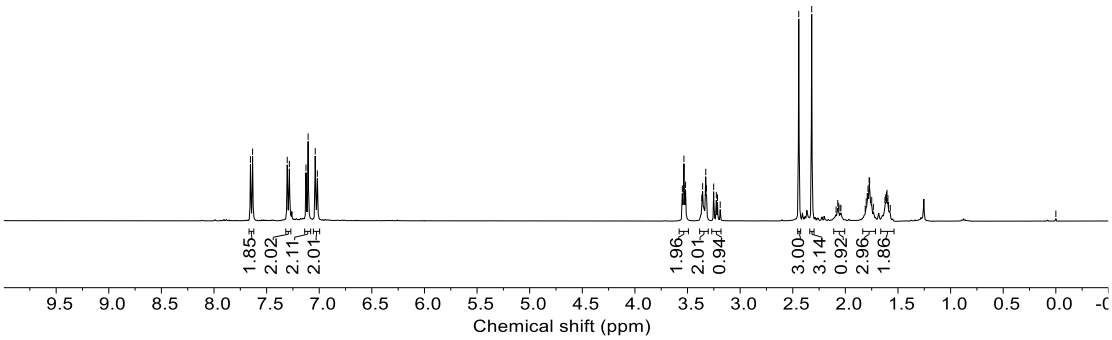
Me
S
Ts
6l (125 MHz, CDCl3)
chemical shift (ppm)

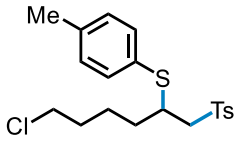

7.647
7.631
7.277
7.268
7.260
7.065
7.050
7.003
6.985
6.827
6.807
6.790
3.874
3.860
3.611
3.594
3.586
3.577
3.561
3.358
3.340
3.329
3.311
3.294
3.285
3.265
3.257
3.236
3.228
2.989
2.973
2.960
2.945
2.428
2.302
-0.000
MeO
MeO
S
Ts
Me
6m (500 MHz, CDCl3)
2.04
2.36
2.03
1.98
3.04
2.89
2.95
1.04
1.00
2.04
1.03
3.00
2.97
chemical shift (ppm)


148.65
147.84
144.64
137.79
136.15
132.66
129.81
129.76
129.20
127.83
121.78
112.78
110.93
77.26
77.00
76.75
58.81
55.76
44.39
38.85
21.54
21.02
MeO
MeO
S
Ts
Me
6m (125 MHz, CDCl3)
chemical shift (ppm)

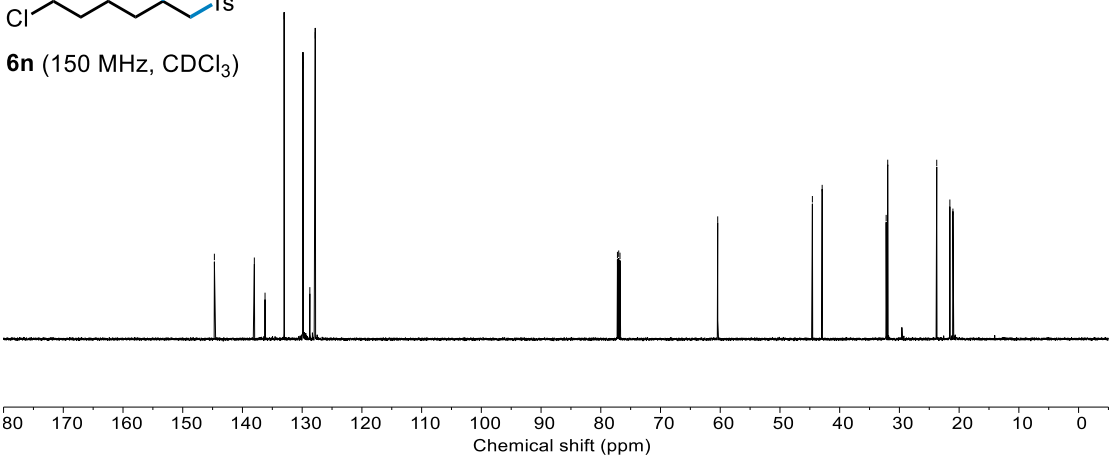


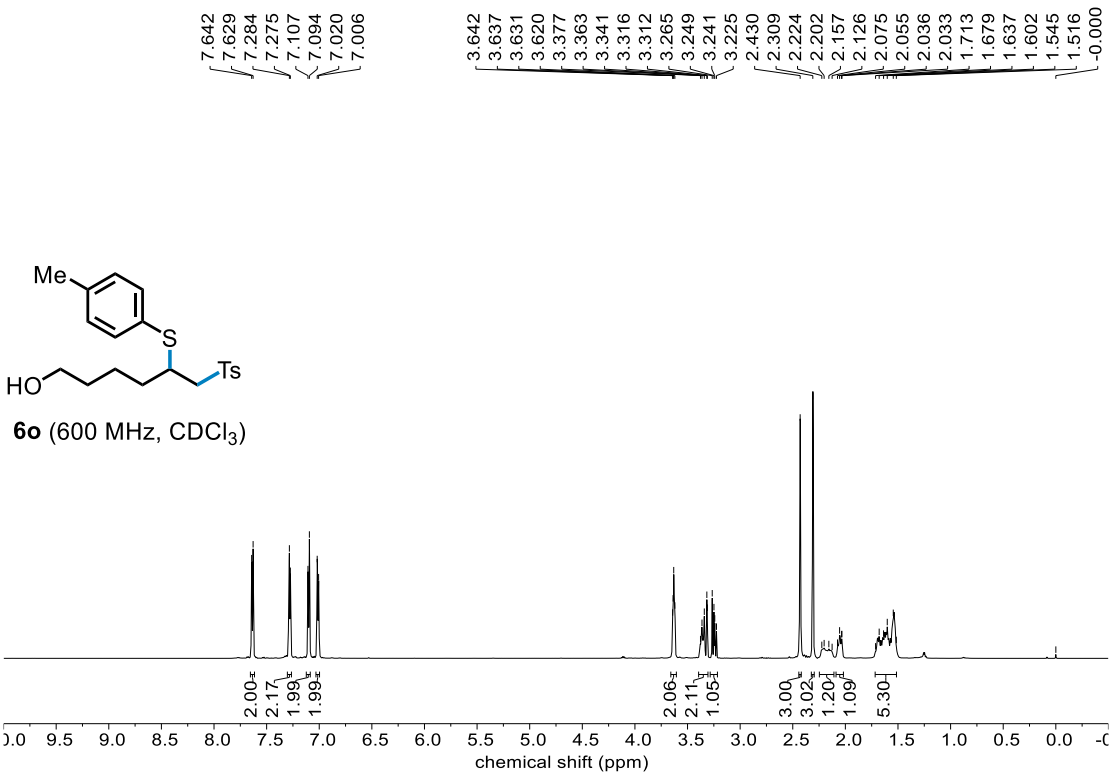
6n (400 MHz, $CDCl_3$)

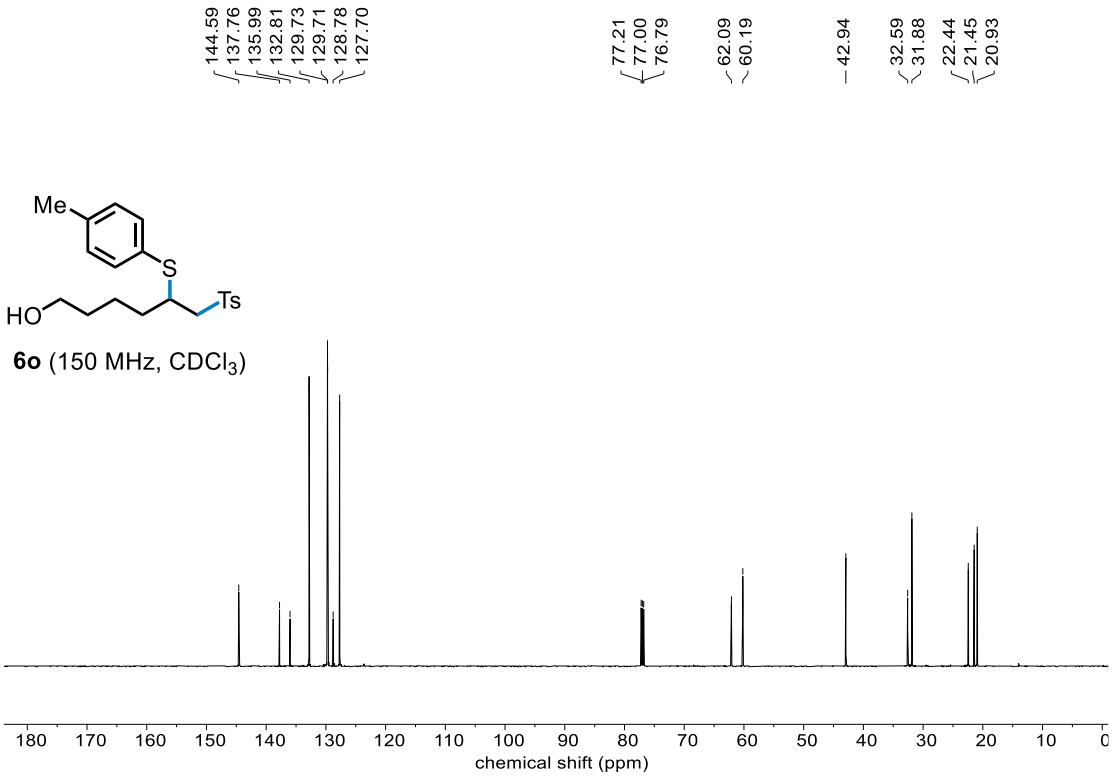


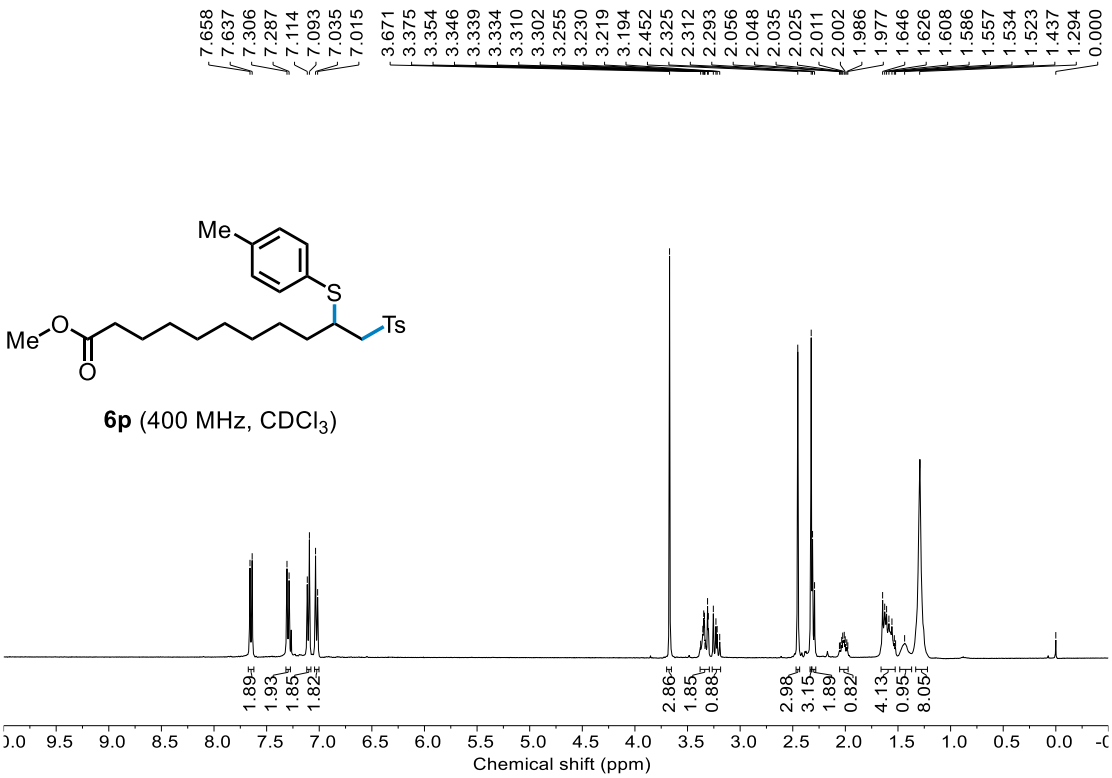


6n (150 MHz, $CDCl_3$)

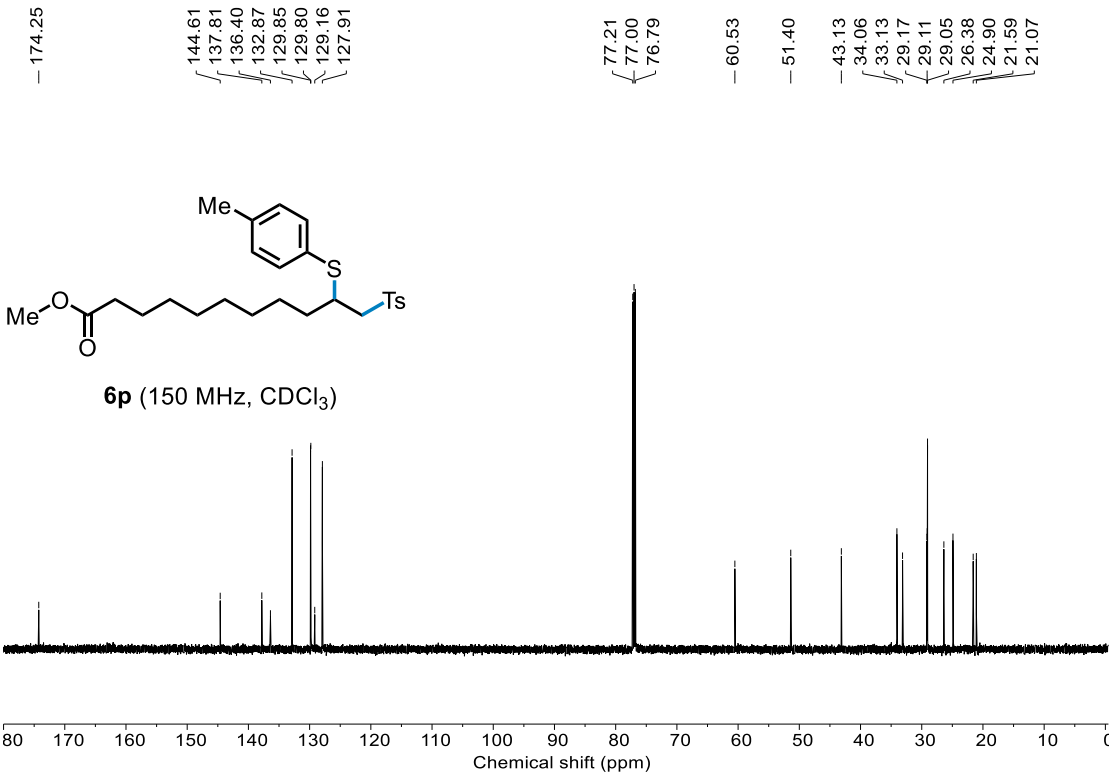



7.642
7.629
7.284
7.275
7.107
7.094
7.020
7.006
3.642
3.637
3.631
3.620
3.377
3.363
3.341
3.316
3.312
3.265
3.249
3.241
3.225
2.430
2.309
2.224
2.202
2.157
2.126
2.075
2.055
2.036
2.033
1.713
1.679
1.637
1.602
1.545
1.516
-0.000
Me
S
Ts
HO
6o (600 MHz, CDCl3)
2.00
2.17
1.99
1.99
2.06
2.11
1.05
3.00
3.02
1.20
1.09
5.30
chemical shift (ppm)

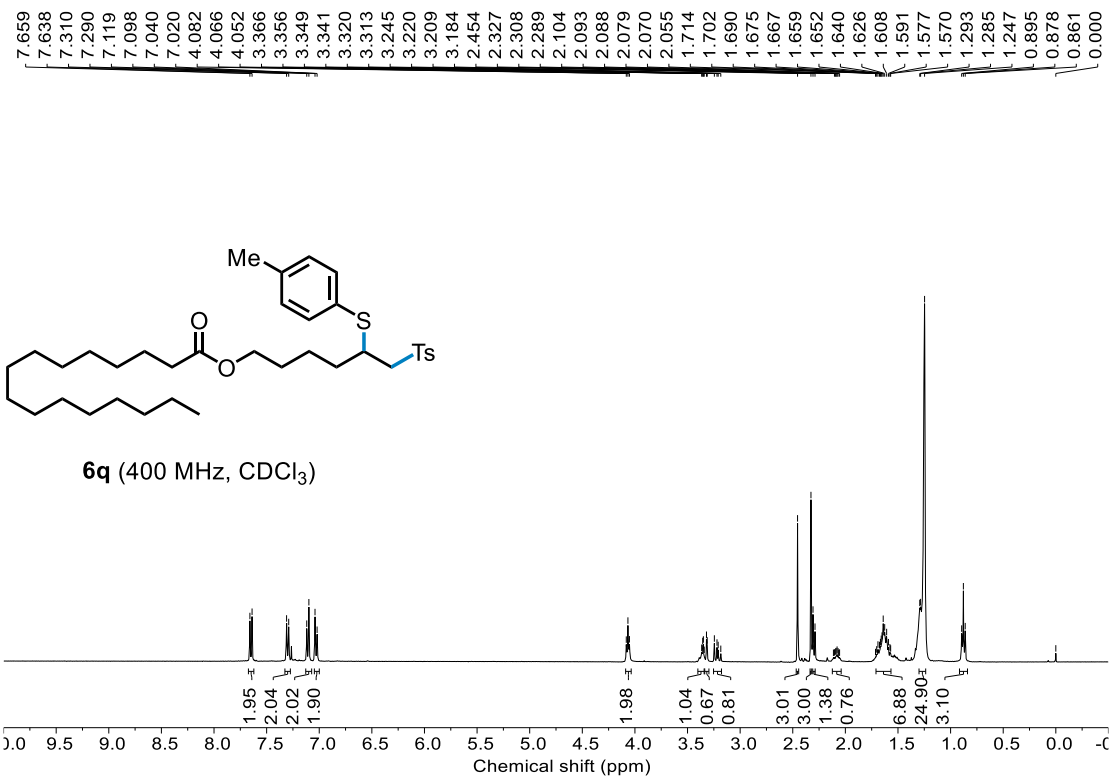

144.59
137.76
135.99
132.81
129.73
129.71
128.78
127.70
77.21
77.00
76.79
62.09
60.19
42.94
32.59
31.88
22.44
21.45
20.93
Me
S
Ts
HO
6o (150 MHz, CDCl3)
chemical shift (ppm)

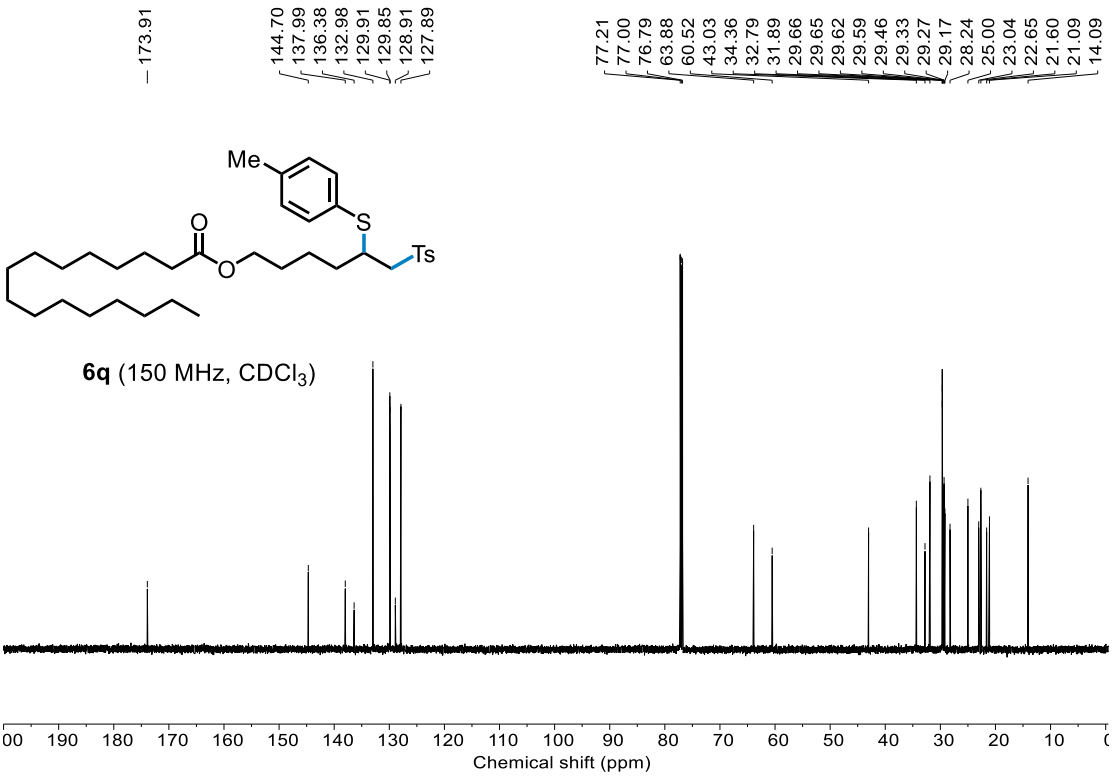


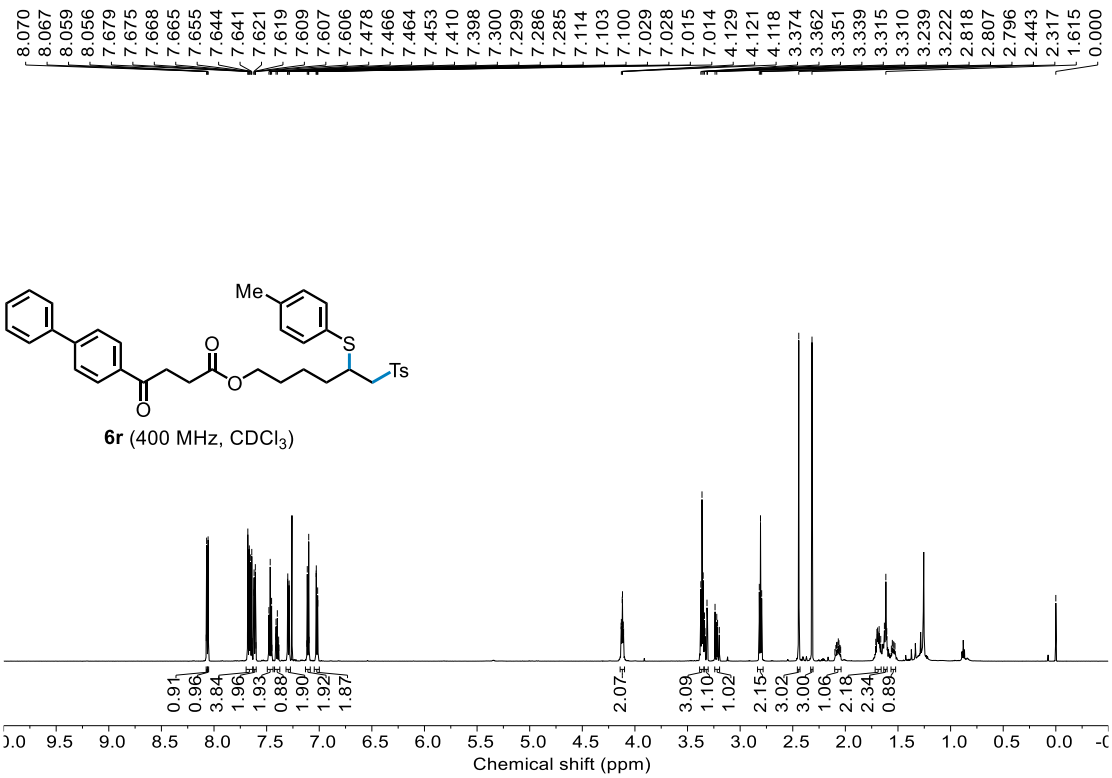
6p (400 MHz, $CDCl_3$)

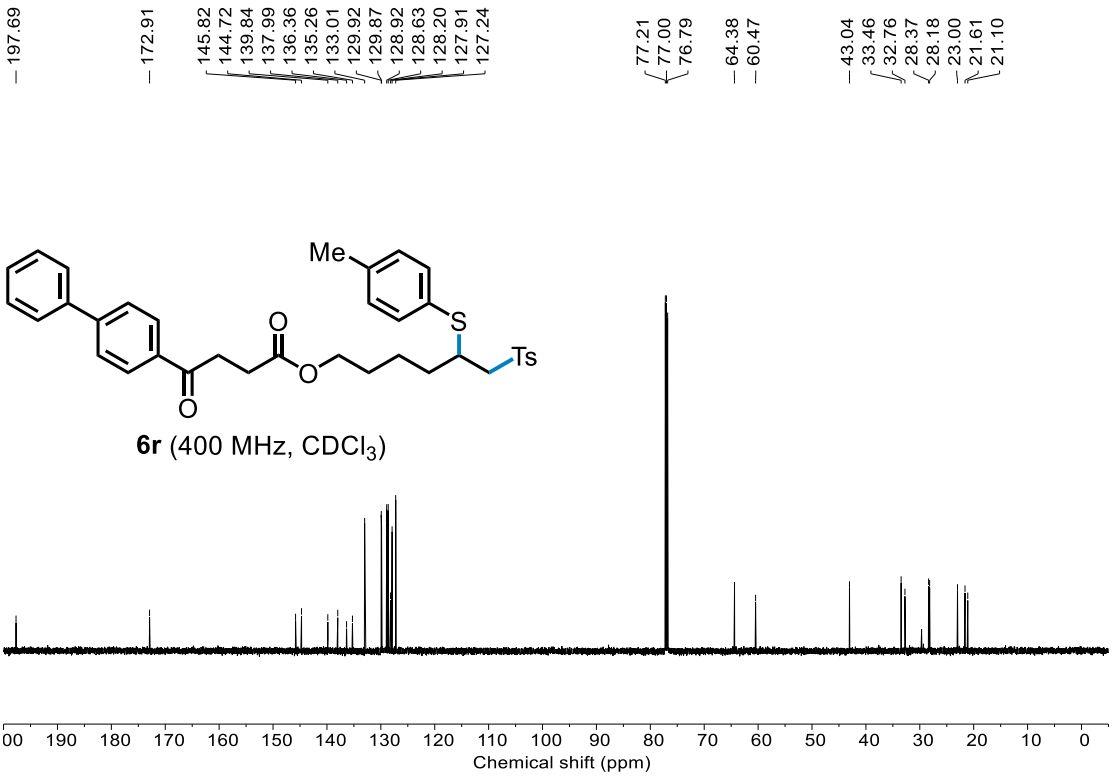


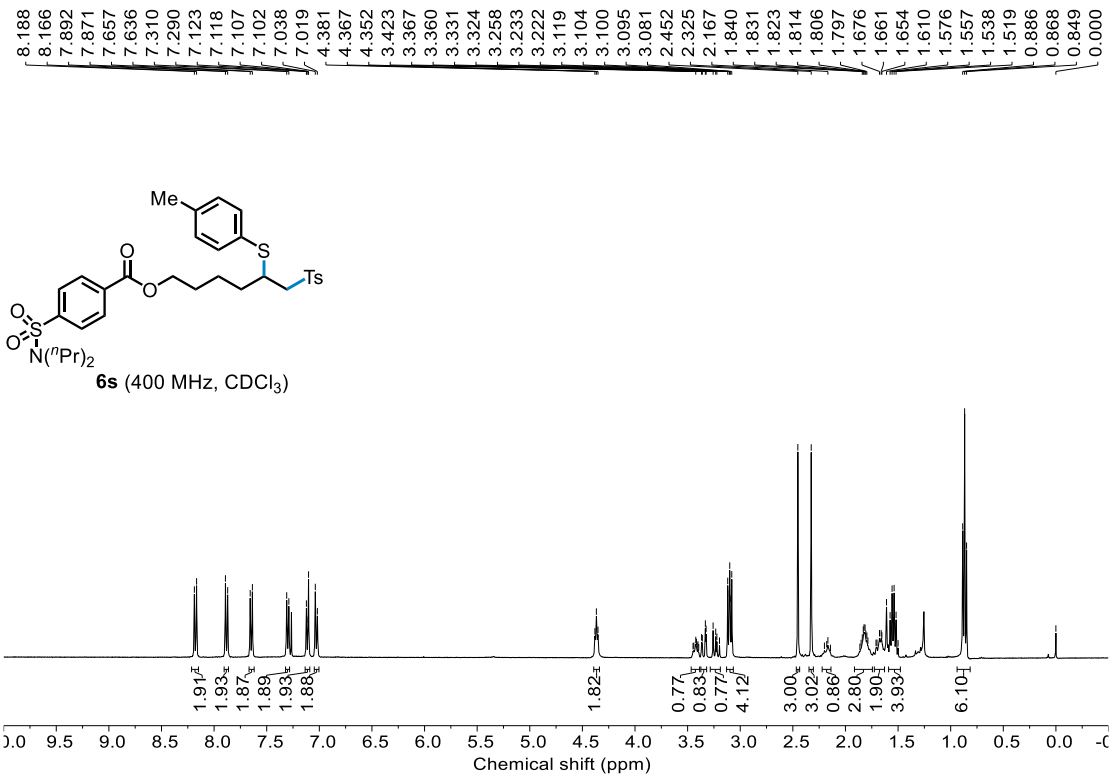
6p (150 MHz, $CDCl_3$)

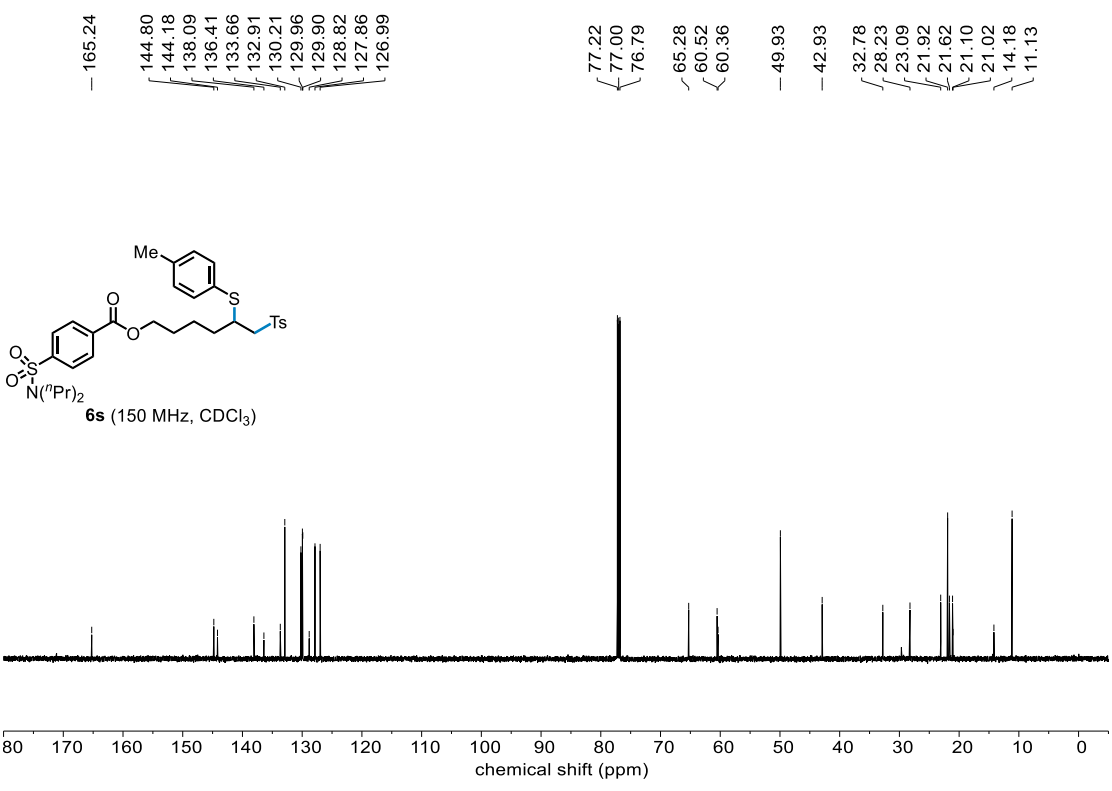

7.659
7.638
7.310
7.290
7.119
7.098
7.040
7.020
4.082
4.066
4.052
3.366
3.356
3.349
3.341
3.320
3.313
3.245
3.220
3.209
3.184
2.454
2.327
2.308
2.289
2.104
2.093
2.088
2.079
2.070
2.055
1.714
1.702
1.690
1.675
1.667
1.659
1.652
1.640
1.626
1.608
1.591
1.577
1.570
1.293
1.285
1.247
0.895
0.878
0.861
0.000
Me
S
Ts
O
O
6q (400 MHz, CDCl3)
1.95
2.04
2.02
1.90
1.98
1.04
0.67
0.81
3.01
3.00
1.38
0.76
6.88
24.90
3.10
Chemical shift (ppm)

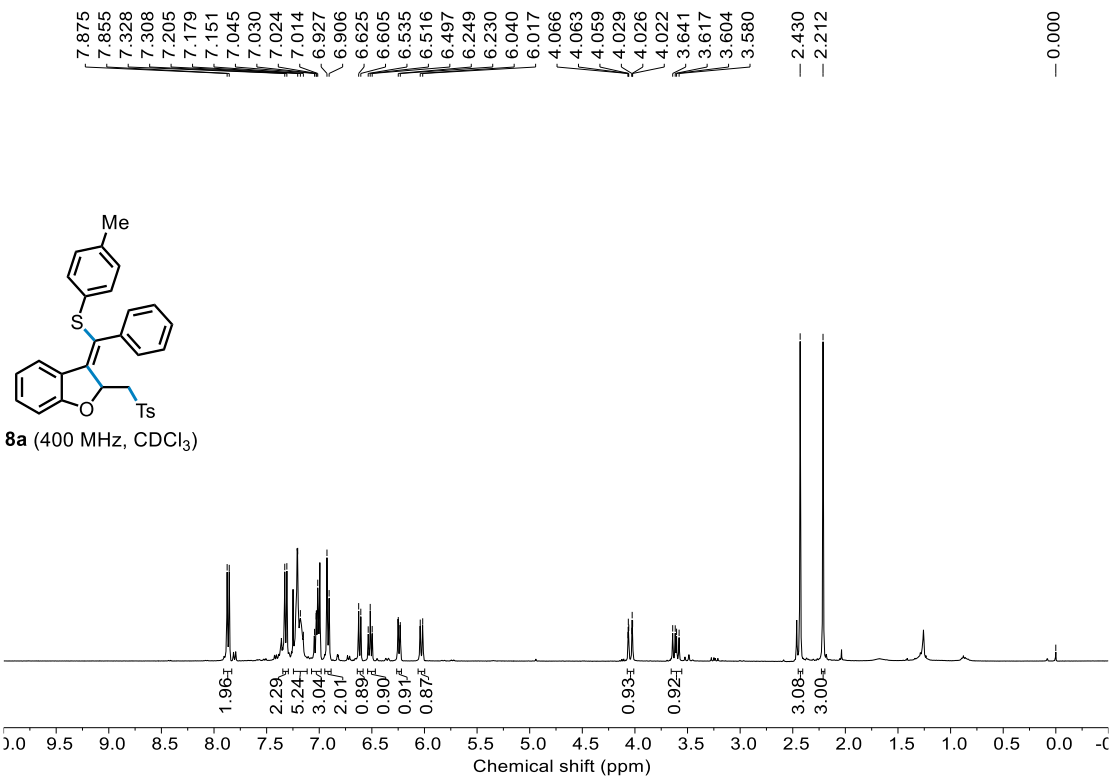

173.91
144.70
137.99
136.38
132.98
129.91
129.85
128.91
127.89
77.21
77.00
76.79
63.88
60.52
43.03
34.36
32.79
31.89
29.66
29.65
29.62
29.59
29.46
29.33
29.27
29.17
28.24
25.00
23.04
22.65
21.60
21.09
14.09
Me
S
Ts
O
O
6q (150 MHz, CDCl3)
Chemical shift (ppm)

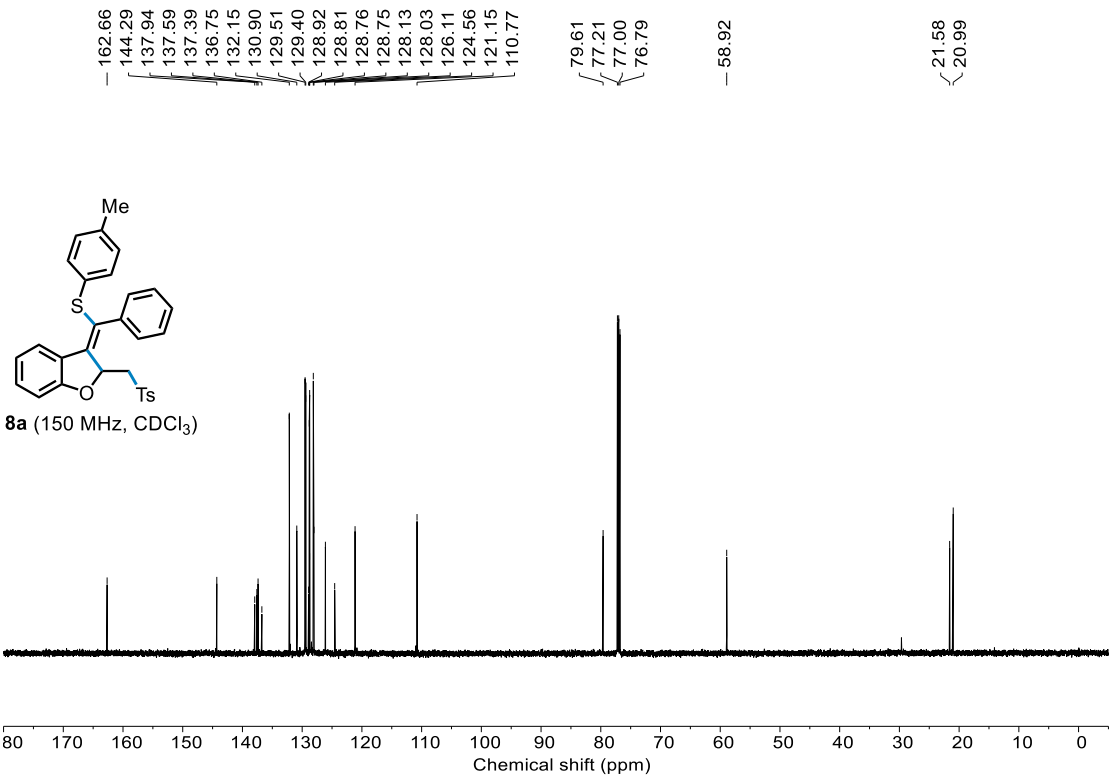

8.070
8.067
8.059
8.056
7.679
7.675
7.668
7.665
7.655
7.644
7.641
7.621
7.619
7.609
7.607
7.606
7.478
7.466
7.464
7.453
7.410
7.398
7.300
7.299
7.286
7.285
7.114
7.103
7.100
7.029
7.028
7.015
7.014
4.129
4.121
4.118
3.374
3.362
3.351
3.339
3.315
3.310
3.239
3.222
2.818
2.807
2.796
2.443
2.317
1.615
0.000
Me
S
Ts
O
O
O
6r (400 MHz, CDCl3)
0.91
0.96
3.84
1.96
1.93
0.88
1.90
1.92
1.87
2.07
3.09
1.10
1.02
2.15
3.02
3.00
1.06
2.18
2.34
0.89
Chemical shift (ppm)

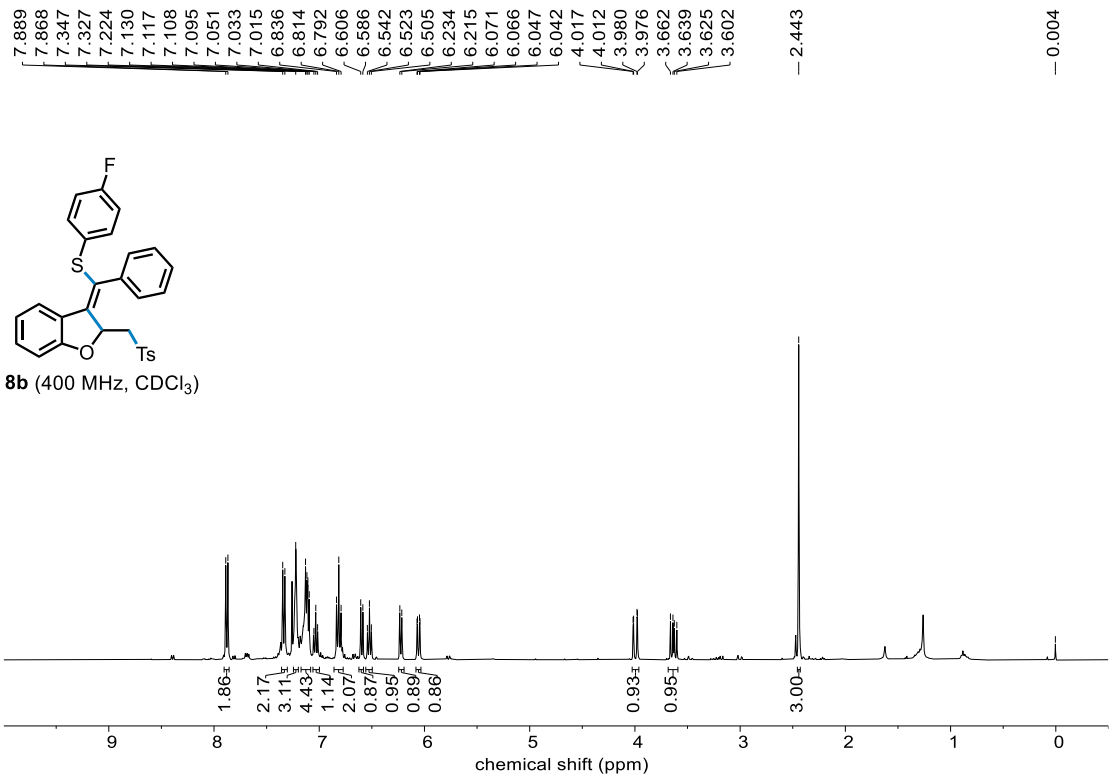

197.69
172.91
145.82
144.72
139.84
137.99
136.36
135.26
133.01
129.92
129.87
128.92
128.63
128.20
127.91
127.24
77.21
77.00
76.79
64.38
60.47
43.04
33.46
32.76
28.37
28.18
23.00
21.61
21.10
Me
S
Ts
O
O
O
6r (400 MHz, CDCl3)
Chemical shift (ppm)


8.188
8.166
7.892
7.871
7.657
7.636
7.310
7.290
7.123
7.118
7.107
7.102
7.038
7.019
4.381
4.367
4.352
3.423
3.367
3.360
3.331
3.324
3.258
3.233
3.222
3.119
3.104
3.100
3.095
3.081
2.452
2.325
2.167
1.840
1.831
1.823
1.814
1.806
1.797
1.676
1.661
1.654
1.610
1.576
1.557
1.538
1.519
0.886
0.868
0.849
0.000
Me
S
Ts
O
O
O
O
S
N(nPr)2
6s (400 MHz, CDCl3)
1.91
1.93
1.87
1.89
1.93
1.88
1.82
0.77
0.83
0.77
4.12
3.00
3.02
0.86
2.80
1.90
3.93
6.10
Chemical shift (ppm)

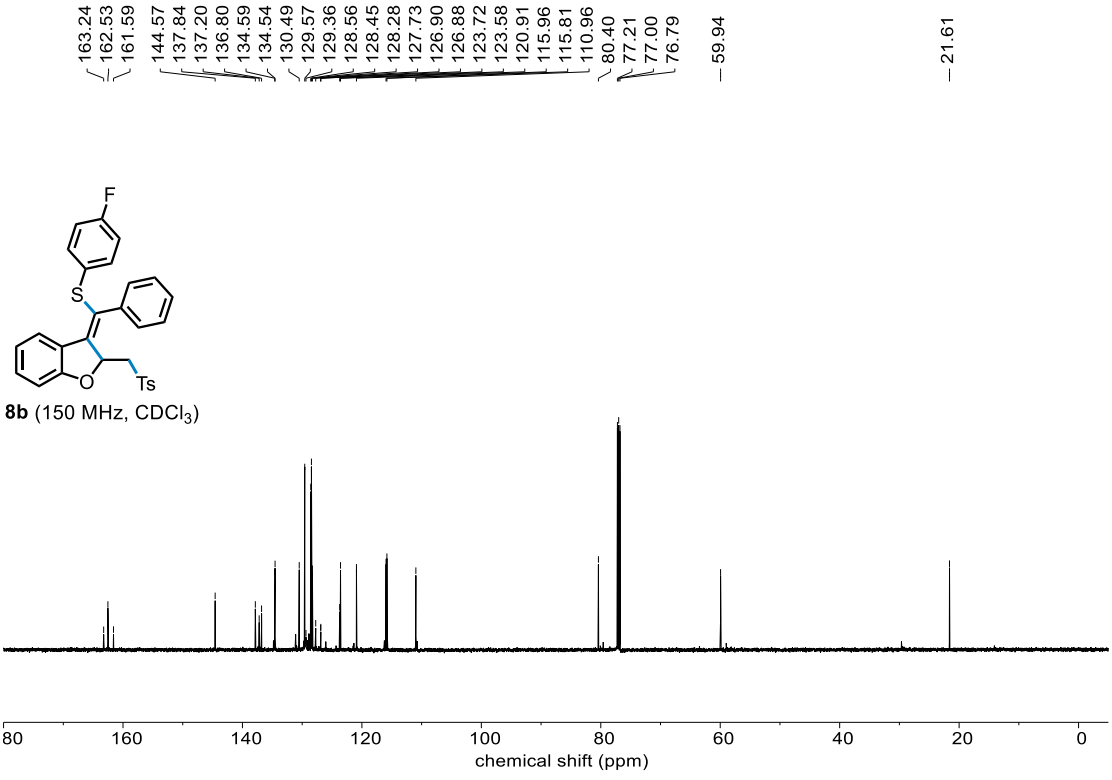

165.24
144.80
144.18
138.09
136.41
133.66
132.91
130.21
129.96
129.90
128.82
127.86
126.99
77.22
77.00
76.79
65.28
60.52
60.36
49.93
42.93
32.78
28.23
23.09
21.92
21.62
21.10
21.02
14.18
11.13
Me
S
Ts
O
O
O
O
S
N(nPr)2
6s (150 MHz, CDCl3)
chemical shift (ppm)


7.875
7.855
7.328
7.308
7.205
7.179
7.151
7.045
7.030
7.024
7.014
6.927
6.906
6.625
6.605
6.535
6.516
6.497
6.249
6.230
6.040
6.017
4.066
4.063
4.059
4.029
4.026
4.022
3.641
3.617
3.604
3.580
2.430
2.212
0.000
Me
S
O
Ts
8a (400 MHz, CDCl3)
1.96
2.29
5.24
3.04
2.01
0.89
0.90
0.91
0.87
0.93
0.92
3.08
3.00
Chemical shift (ppm)

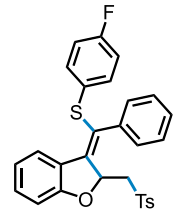

162.66
144.29
137.94
137.59
137.39
136.75
132.15
130.90
129.51
129.40
128.92
128.81
128.76
128.75
128.13
128.03
126.11
124.56
121.15
110.77
79.61
77.21
77.00
76.79
58.92
21.58
20.99
Me
S
O
Ts
8a (150 MHz, CDCl3)
Chemical shift (ppm)



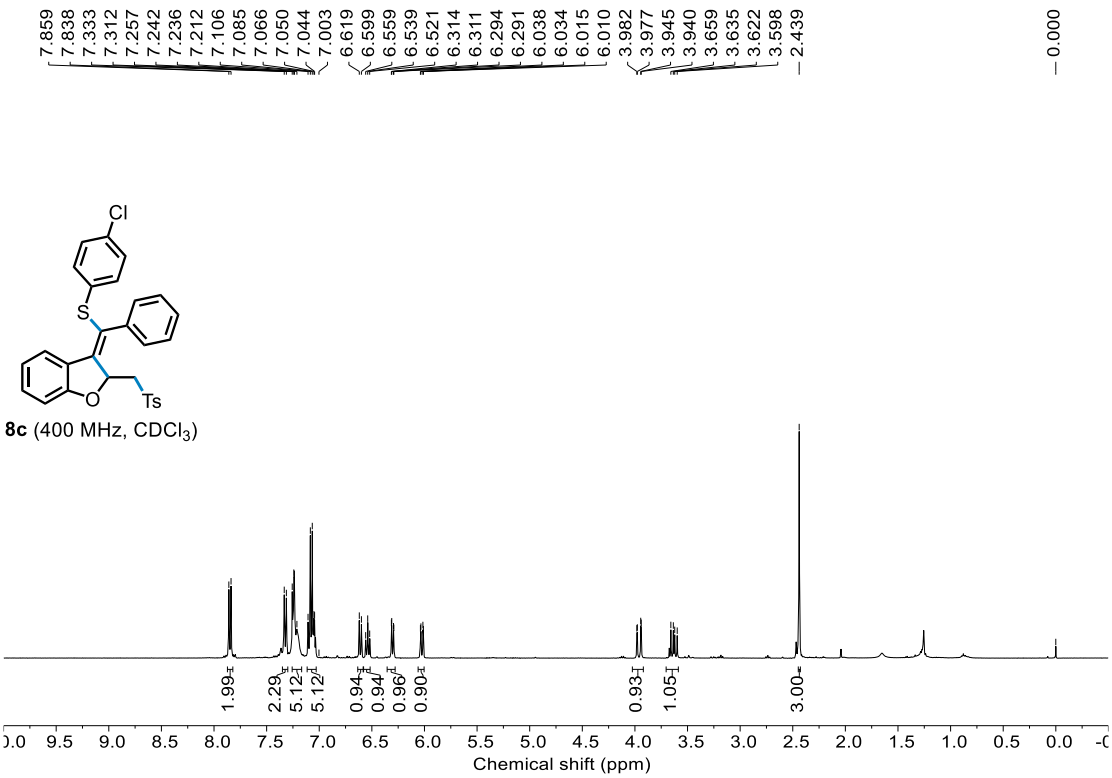
8b (400 MHz, $CDCl_3$)

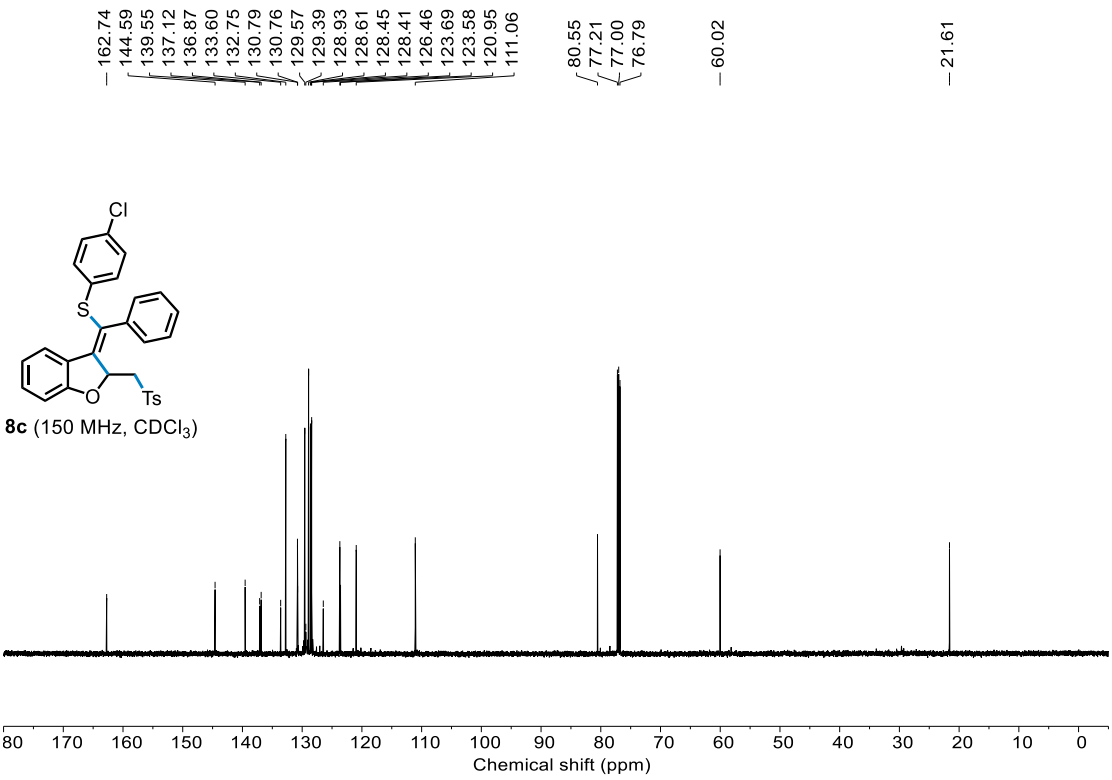


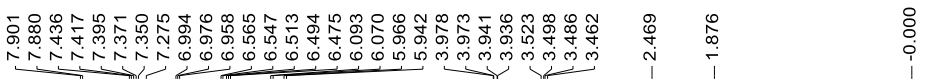
8b (150 MHz, $CDCl_3$)

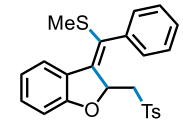


8b (376 MHz, $CDCl_3$)

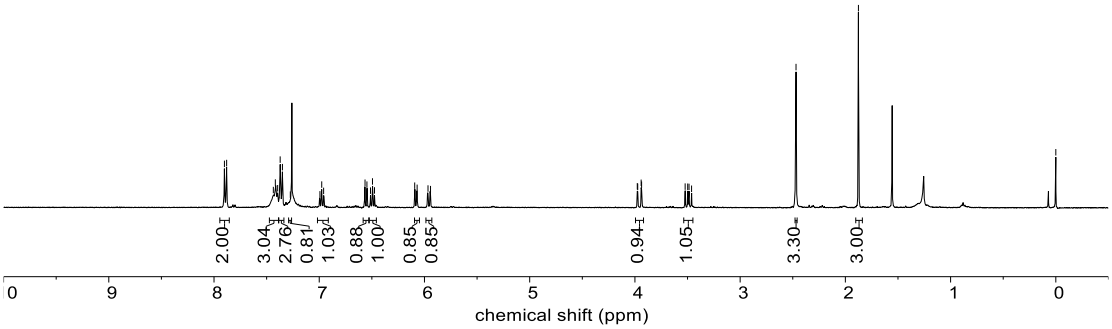

7.859
7.838
7.333
7.312
7.257
7.242
7.236
7.212
7.106
7.085
7.066
7.050
7.044
7.003
6.619
6.599
6.559
6.539
6.521
6.314
6.311
6.294
6.291
6.038
6.034
6.015
6.010
3.982
3.977
3.945
3.940
3.659
3.635
3.622
3.598
2.439
0.000
Cl
S
O
Ts
8c (400 MHz, CDCl3)
1.99
2.29
5.12
5.12
0.94
0.94
0.96
0.90
0.93
1.05
3.00
Chemical shift (ppm)

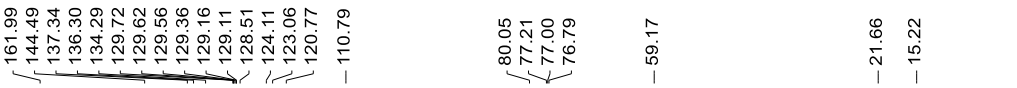

162.74
144.59
139.55
137.12
136.87
133.60
132.75
130.79
130.76
129.57
129.39
128.93
128.61
128.45
128.41
126.46
123.69
123.58
120.95
111.06
80.55
77.21
77.00
76.79
60.02
21.61
Cl
S
O
Ts
8c (150 MHz, CDCl3)
Chemical shift (ppm)

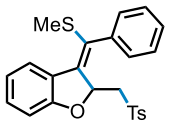




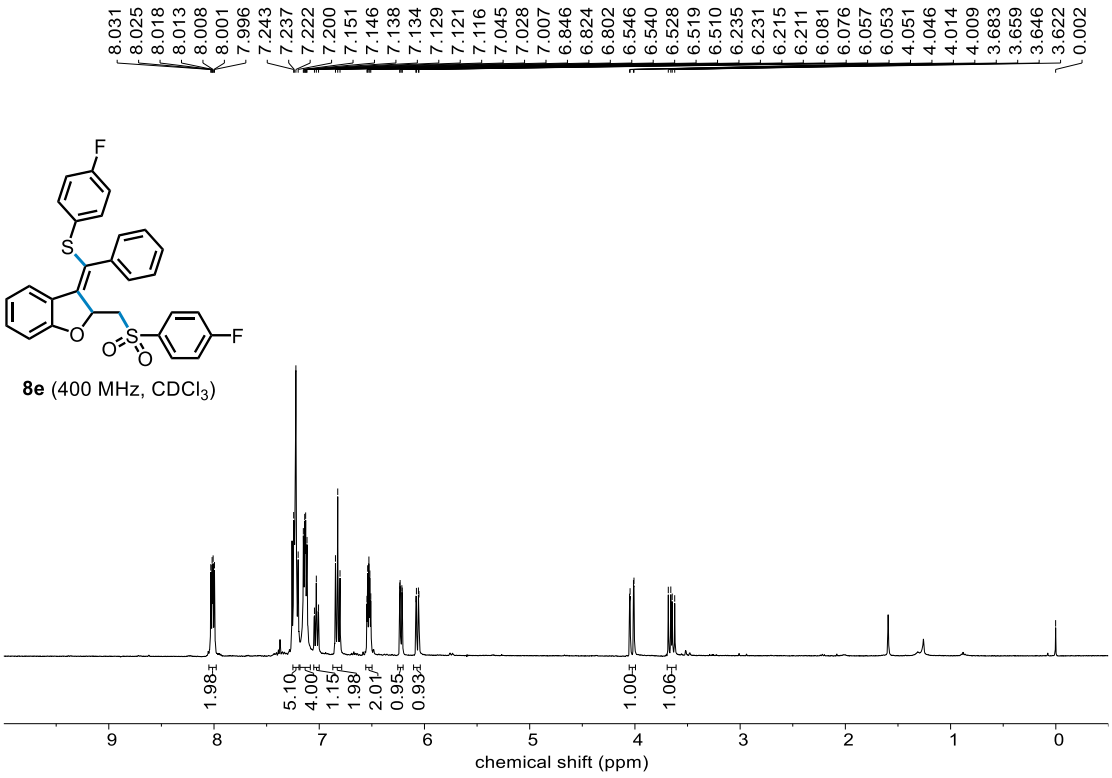
8d (400 MHz, $CDCl_3$)

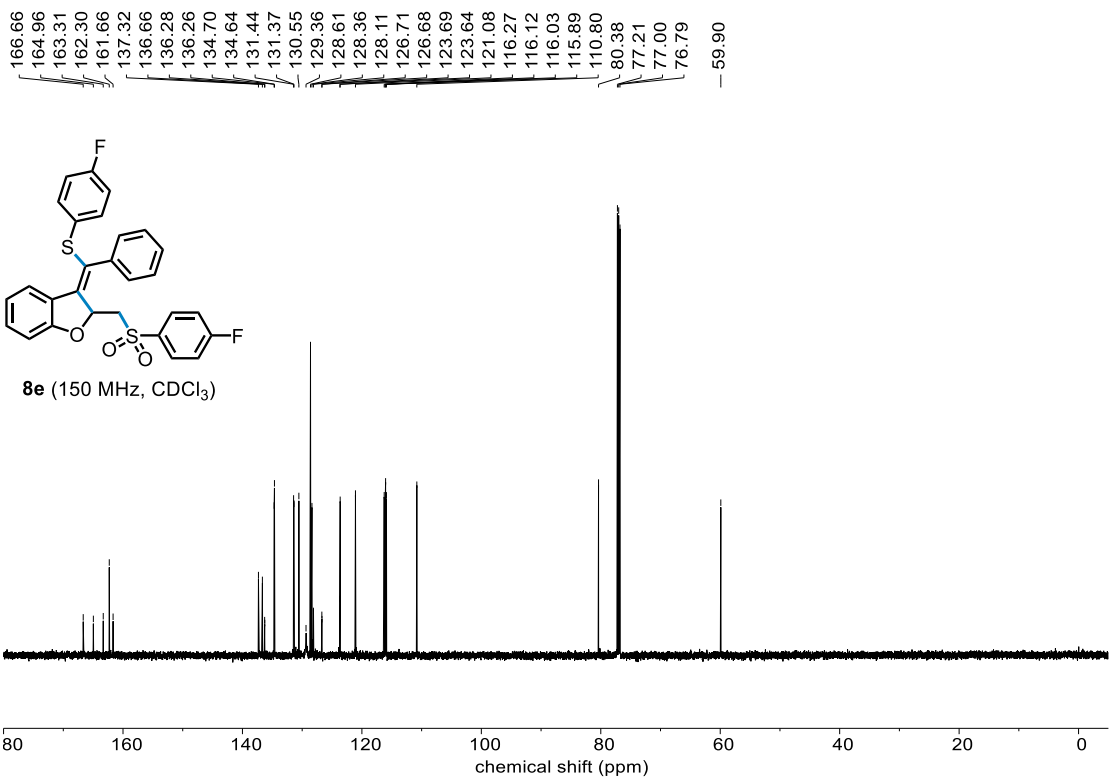


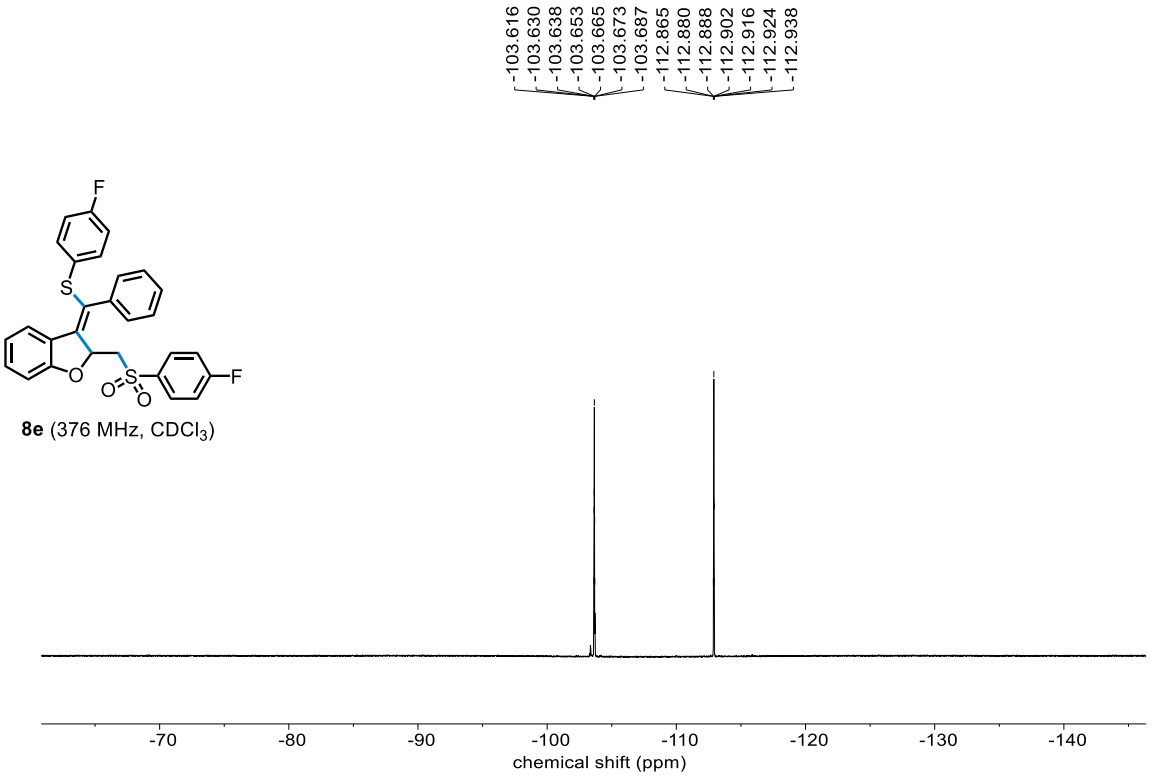




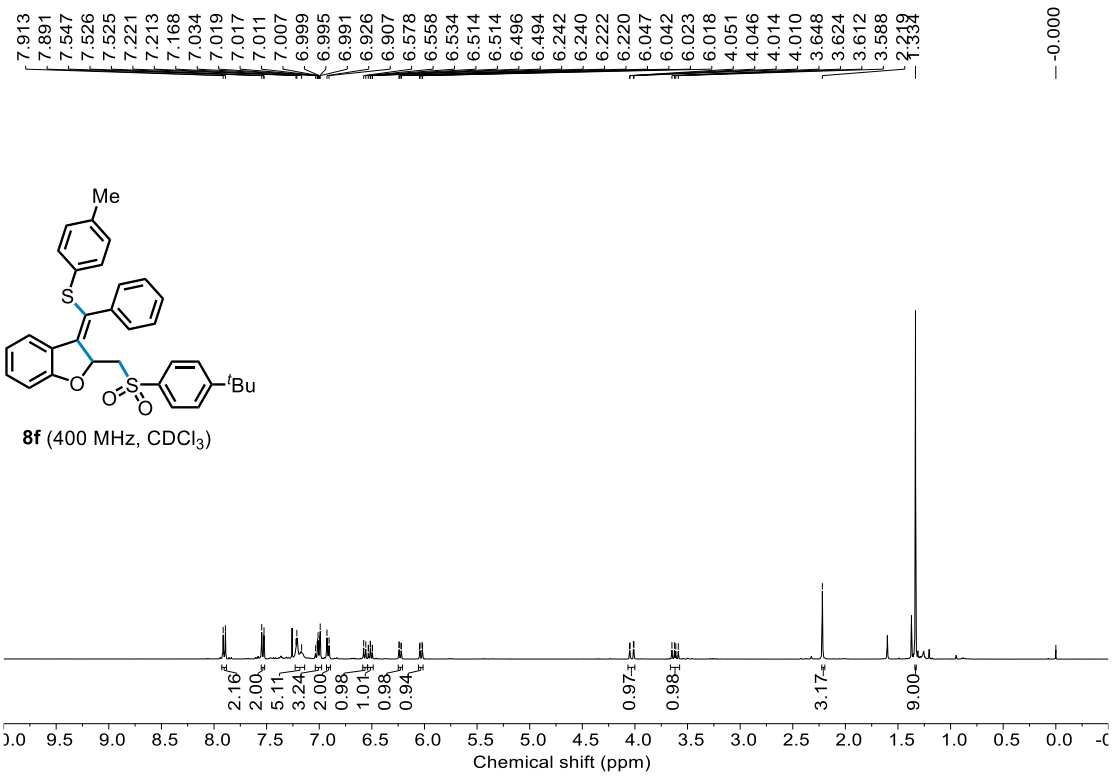
8d (150 MHz, $CDCl_3$)


8.031
8.025
8.018
8.013
8.008
8.001
7.996
7.243
7.237
7.222
7.200
7.151
7.146
7.138
7.134
7.129
7.121
7.116
7.045
7.028
7.007
6.846
6.824
6.802
6.546
6.540
6.528
6.519
6.510
6.235
6.231
6.215
6.211
6.081
6.076
6.057
6.053
4.051
4.046
4.014
4.009
3.683
3.659
3.646
3.622
0.002
F
S
O
S
O
O
F
8e (400 MHz, CDCl3)
1.98
5.10
4.00
1.15
1.98
2.01
0.95
0.93
1.00
1.06
9
8
7
6
5
4
3
2
1
0
chemical shift (ppm)

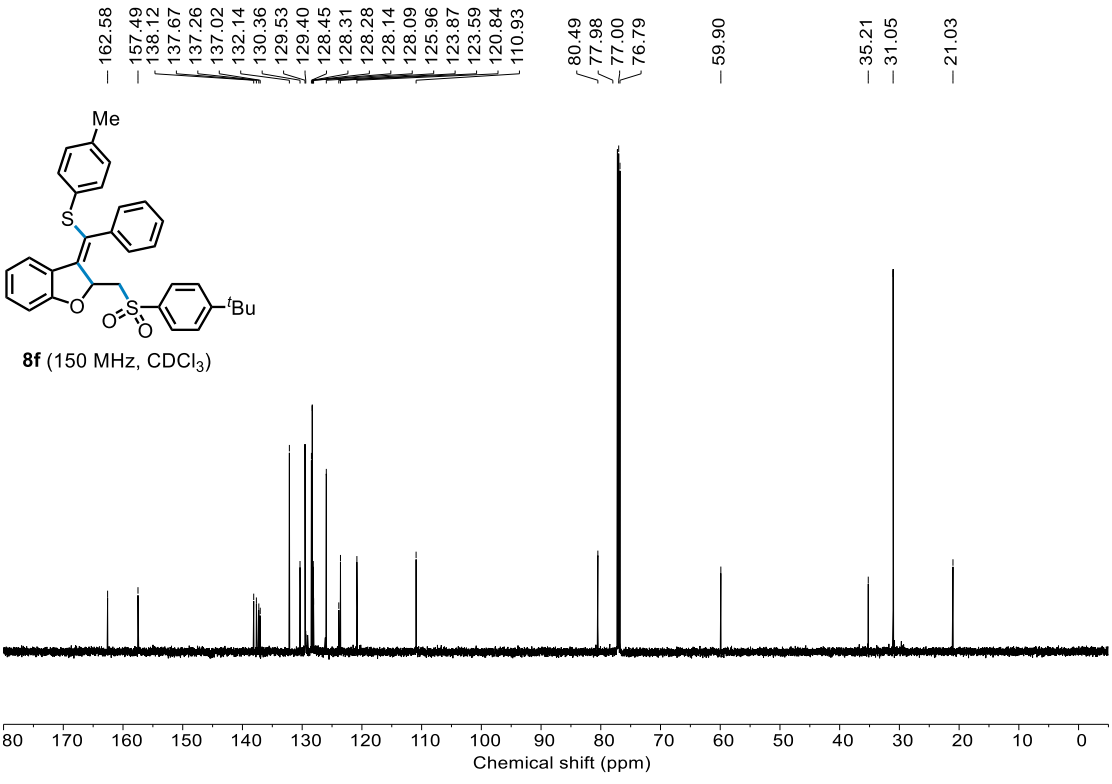

166.66
164.96
163.31
162.30
161.66
137.32
136.66
136.28
136.26
134.70
134.64
131.44
131.37
130.55
129.36
128.61
128.36
128.11
126.71
126.68
123.69
123.64
121.08
116.27
116.12
116.03
115.89
110.80
80.38
77.21
77.00
76.79
59.90
F
S
O
S
O
O
F
8e (150 MHz, CDCl3)
80
160
140
120
100
80
60
40
20
0
chemical shift (ppm)



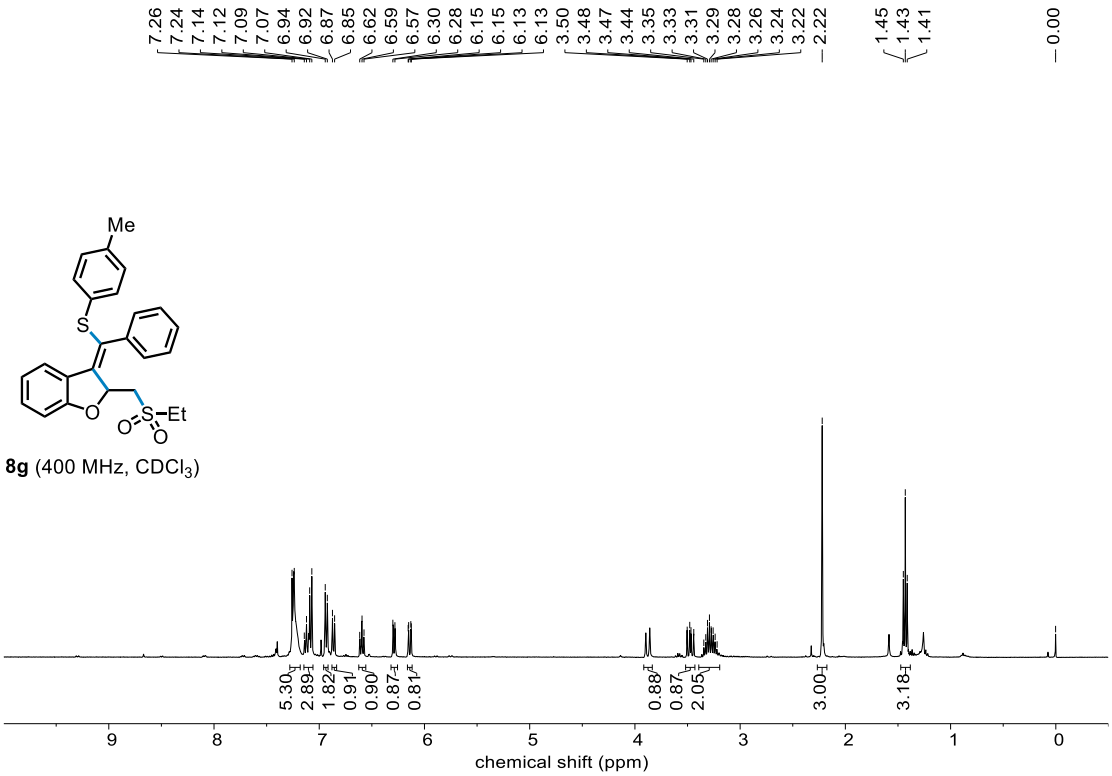
8e (376 MHz, $CDCl_3$)



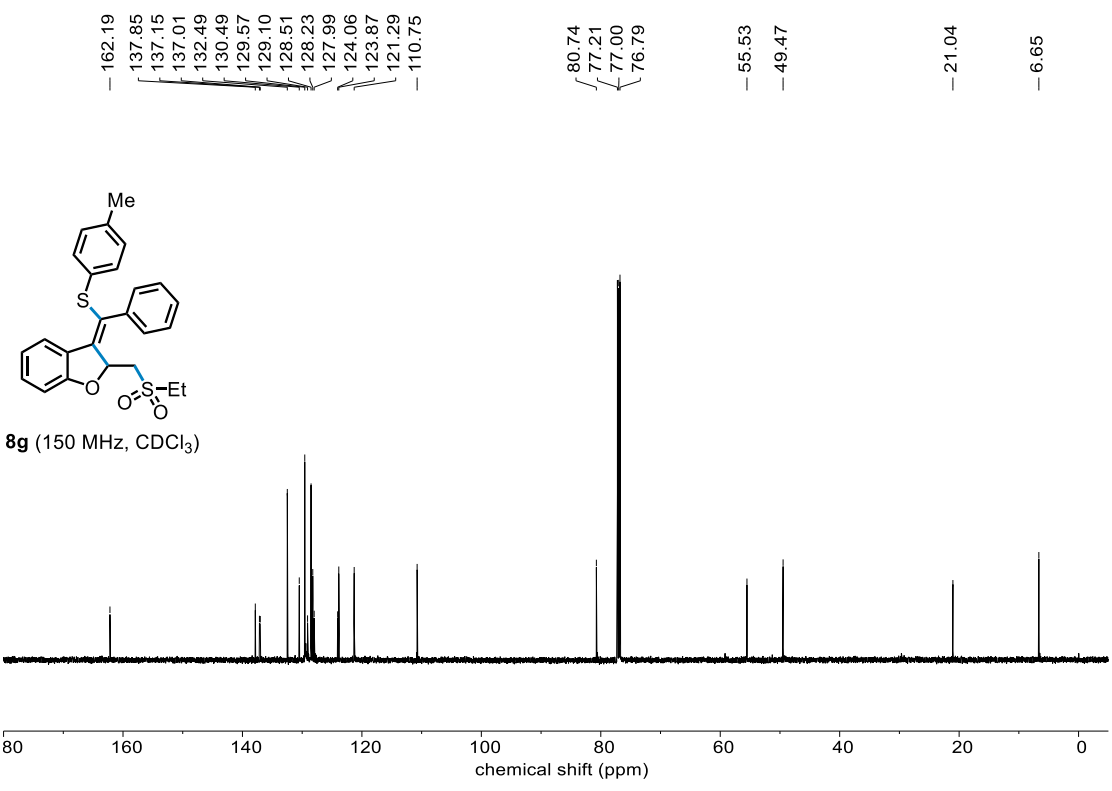
8f (400 MHz, $CDCl_3$)



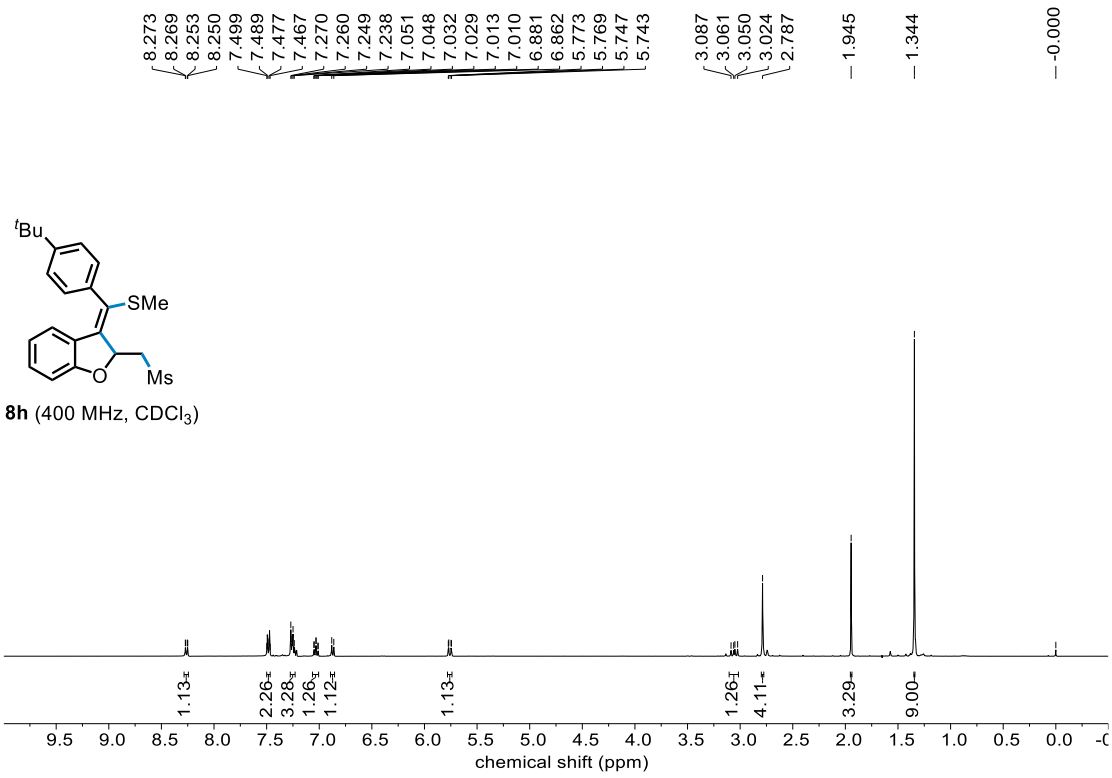
8f (150 MHz, $CDCl_3$)



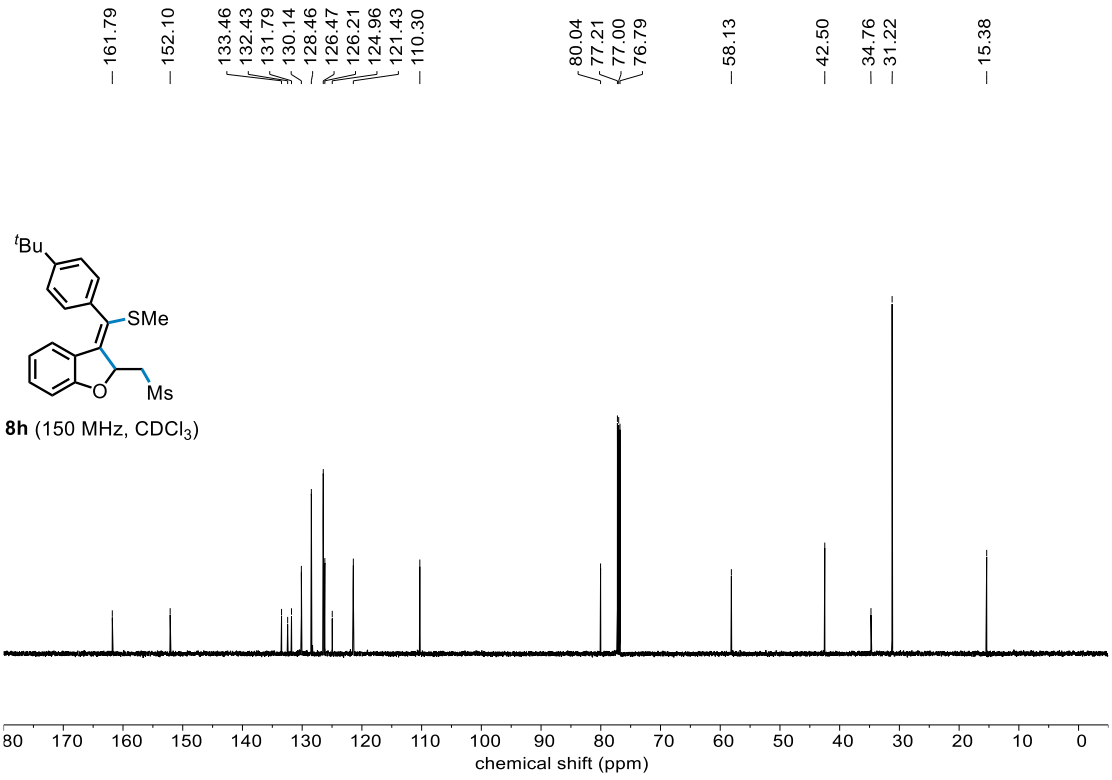
8g (400 MHz, $CDCl_3$)



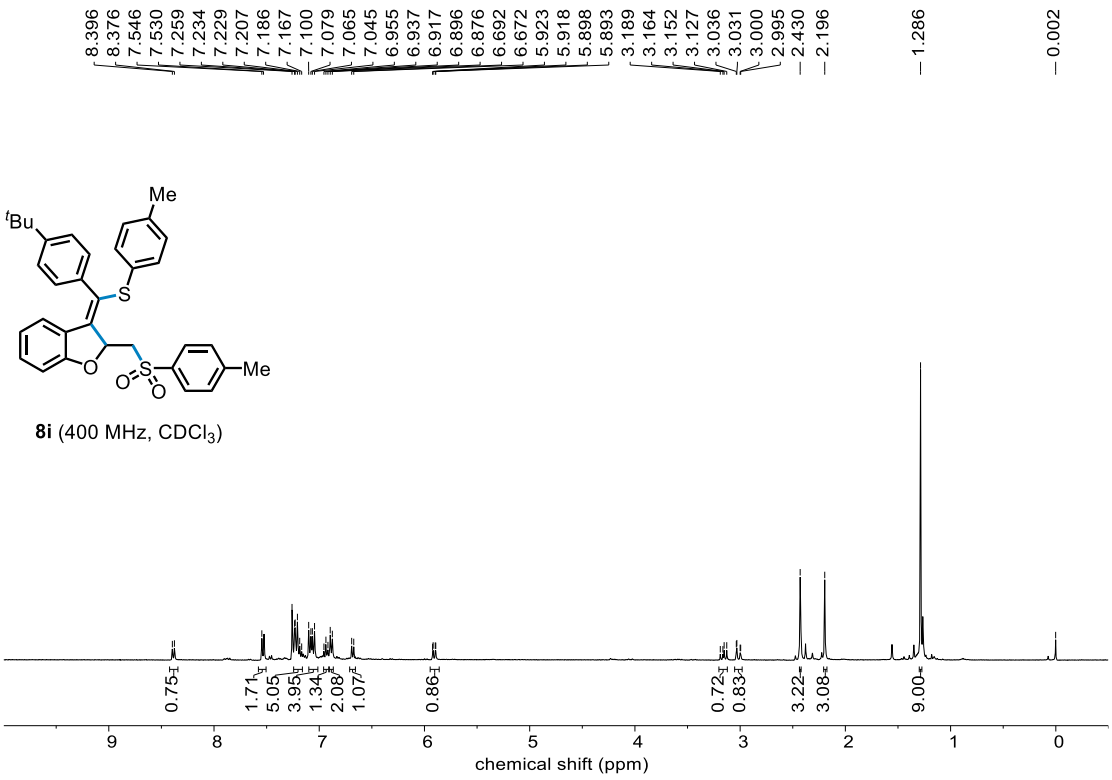
8g (150 MHz, $CDCl_3$)

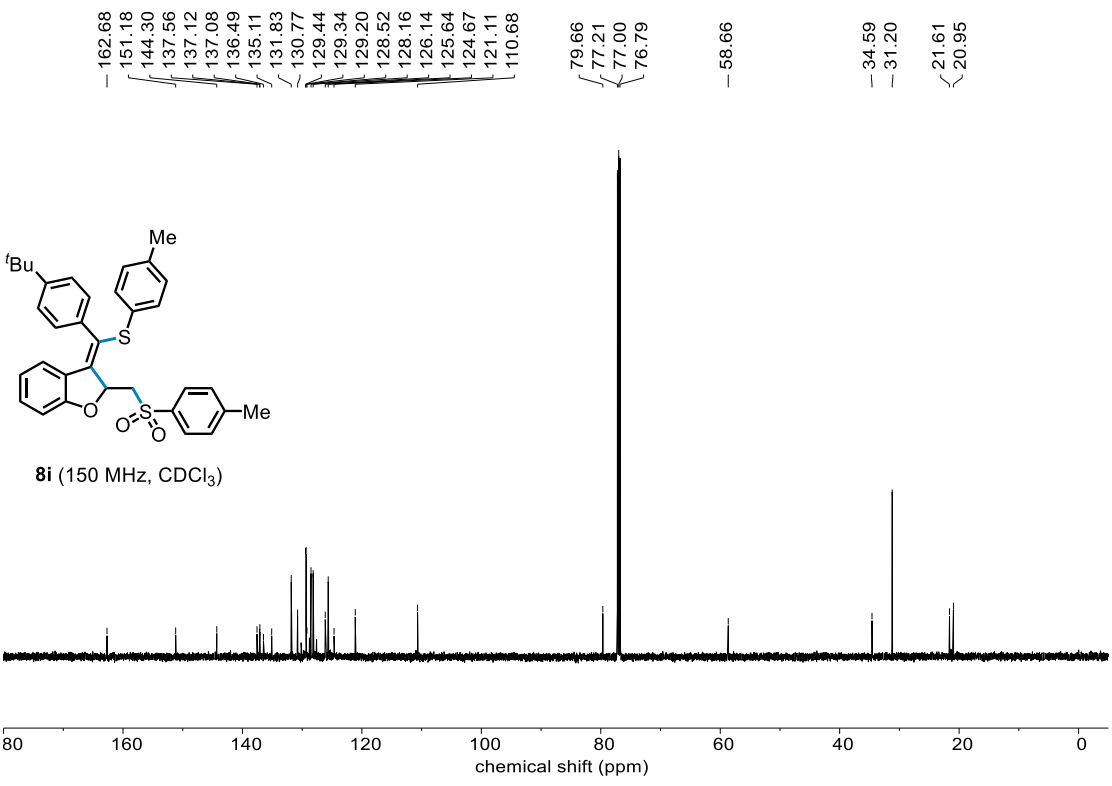


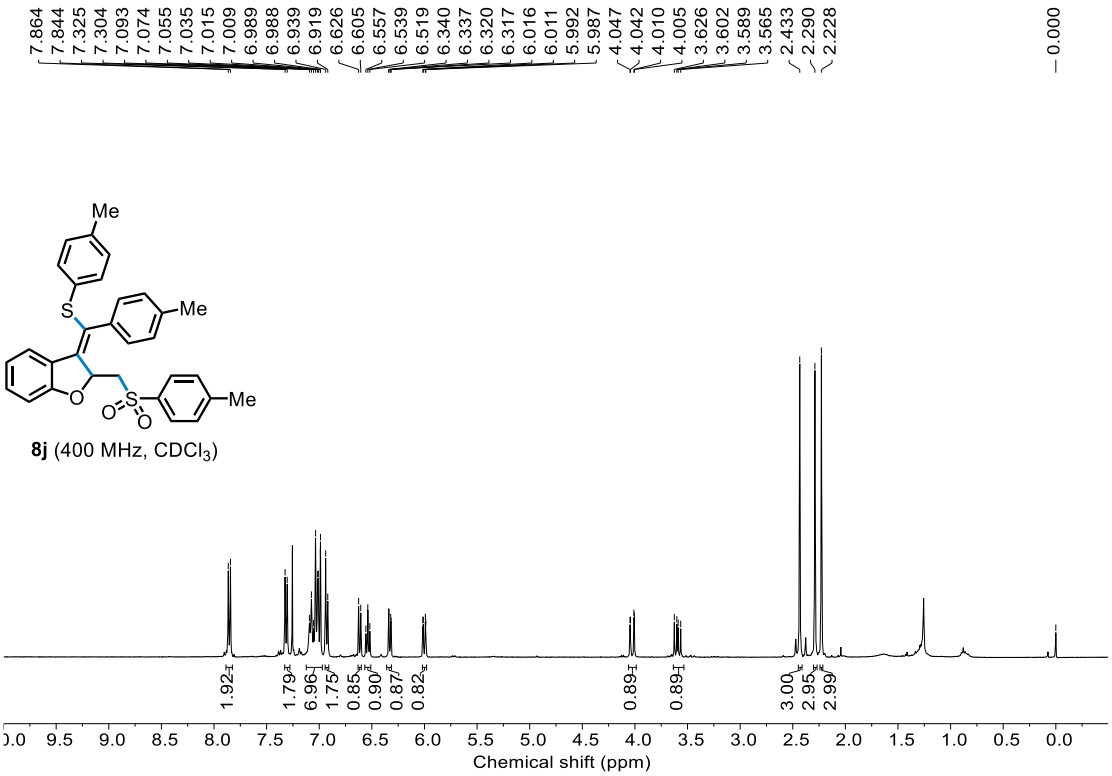
8h (400 MHz, $CDCl_3$)

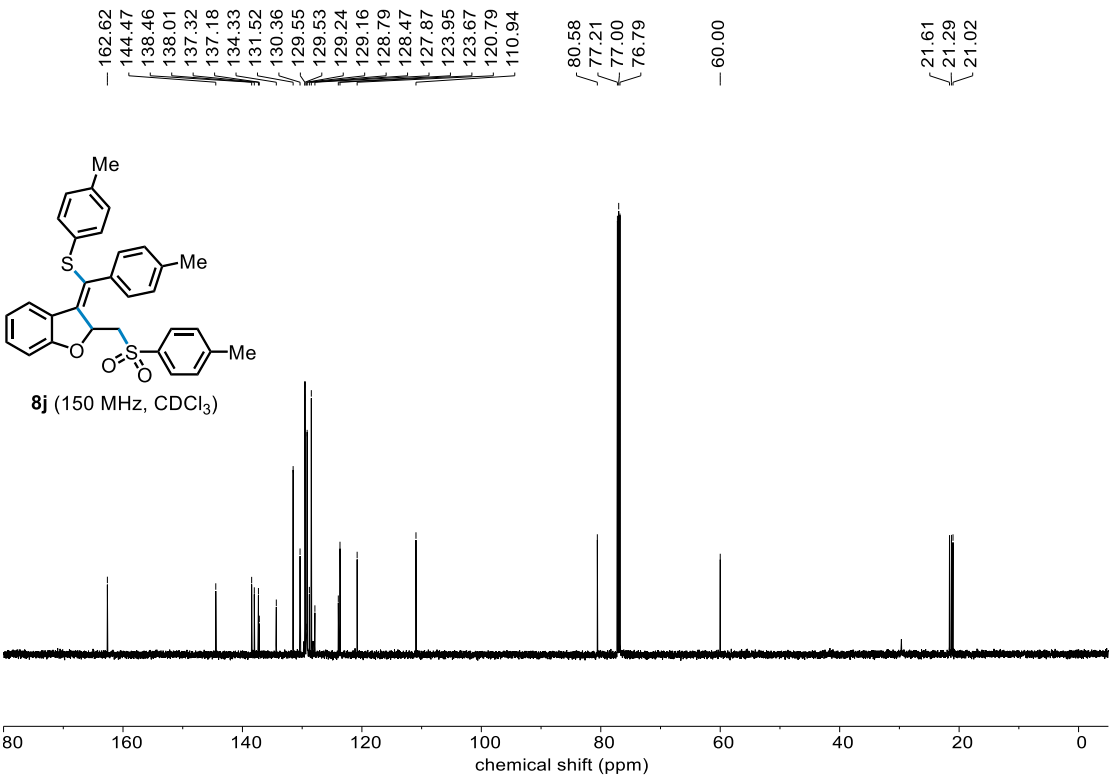


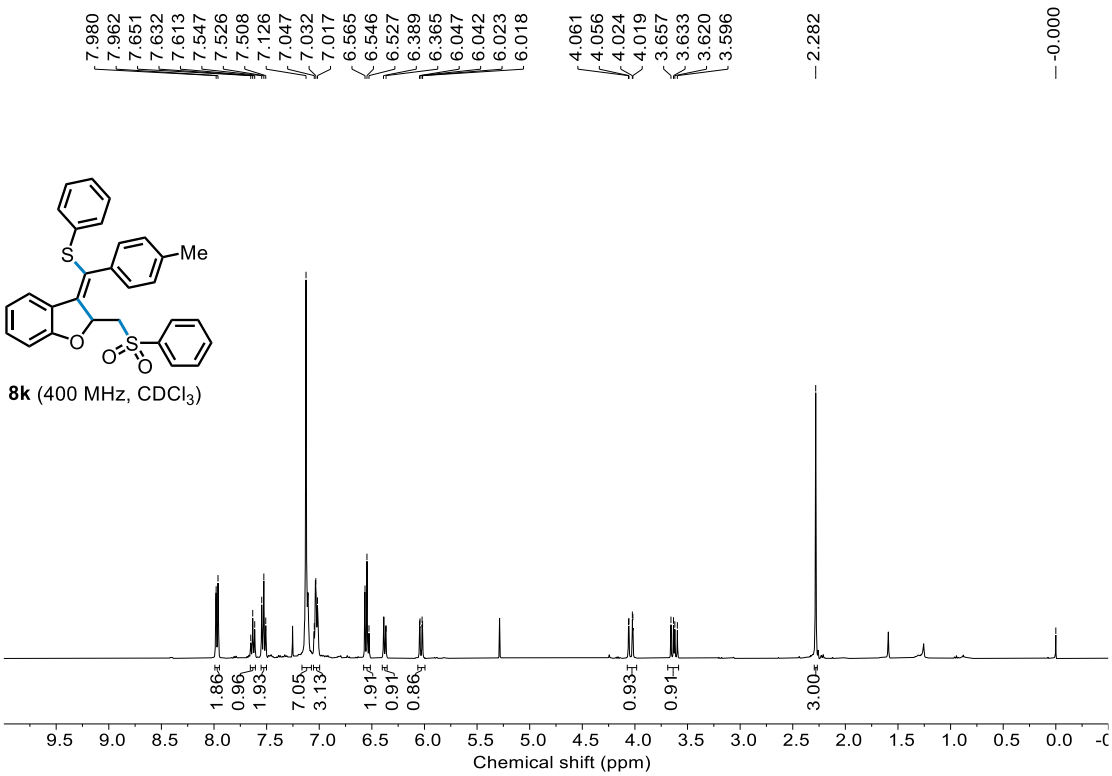
8h (150 MHz, $CDCl_3$)

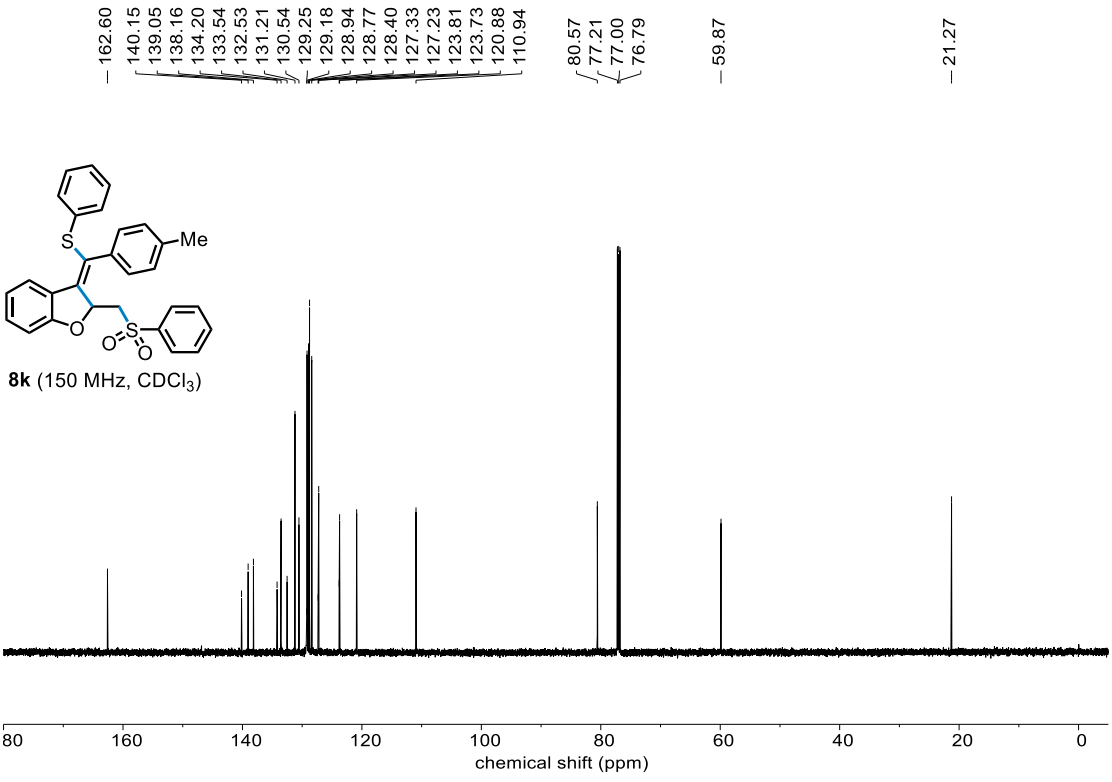

8.396
8.376
7.546
7.530
7.259
7.234
7.229
7.207
7.186
7.167
7.100
7.079
7.065
7.045
6.955
6.937
6.917
6.896
6.876
6.692
6.672
5.923
5.918
5.898
5.893
3.189
3.164
3.152
3.127
3.036
3.031
3.000
2.995
2.430
2.196
1.286
0.002
Me
tBu
S
O
S
O
O
Me
8i (400 MHz, CDCl3)
0.75
1.71
5.05
3.95
1.34
2.08
1.07
0.86
0.72
0.83
3.22
3.08
9.00
9
8
7
6
5
4
3
2
1
0
chemical shift (ppm)

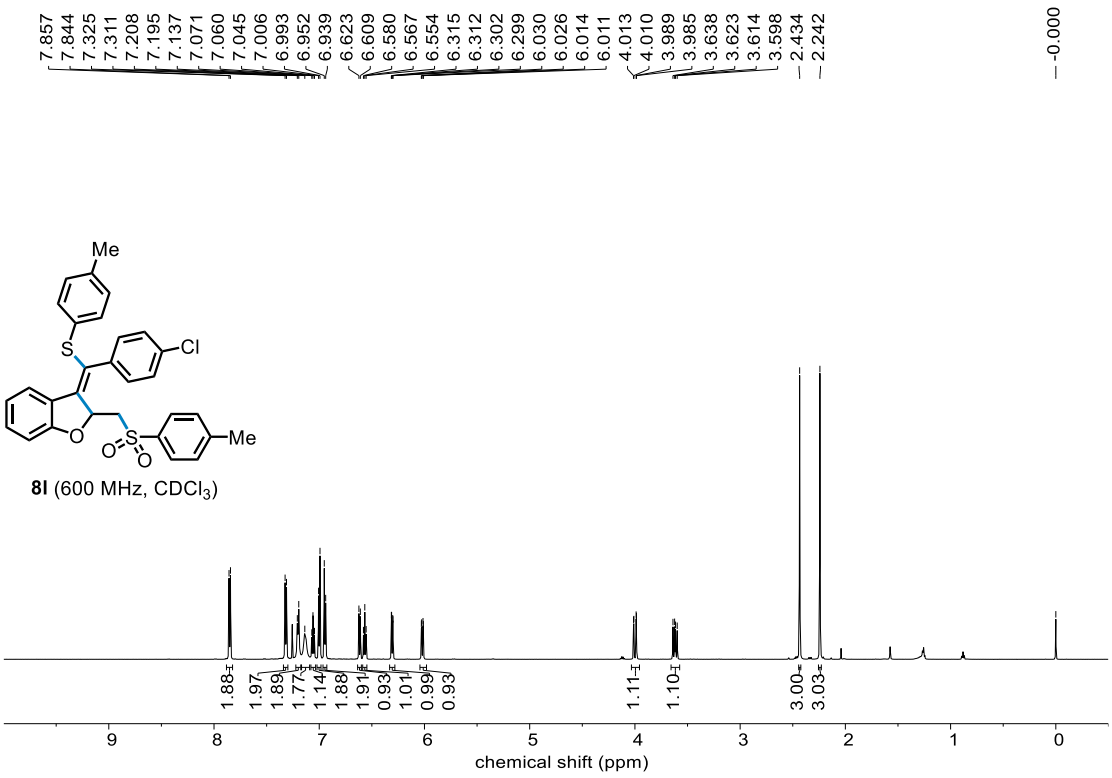

162.68
151.18
144.30
137.56
137.12
137.08
136.49
135.11
131.83
130.77
129.44
129.34
129.20
128.52
128.16
126.14
125.64
124.67
121.11
110.68
79.66
77.21
77.00
76.79
58.66
34.59
31.20
21.61
20.95
Me
tBu
S
O
S
O
O
Me
8i (150 MHz, CDCl3)
80
160
140
120
100
80
60
40
20
0
chemical shift (ppm)

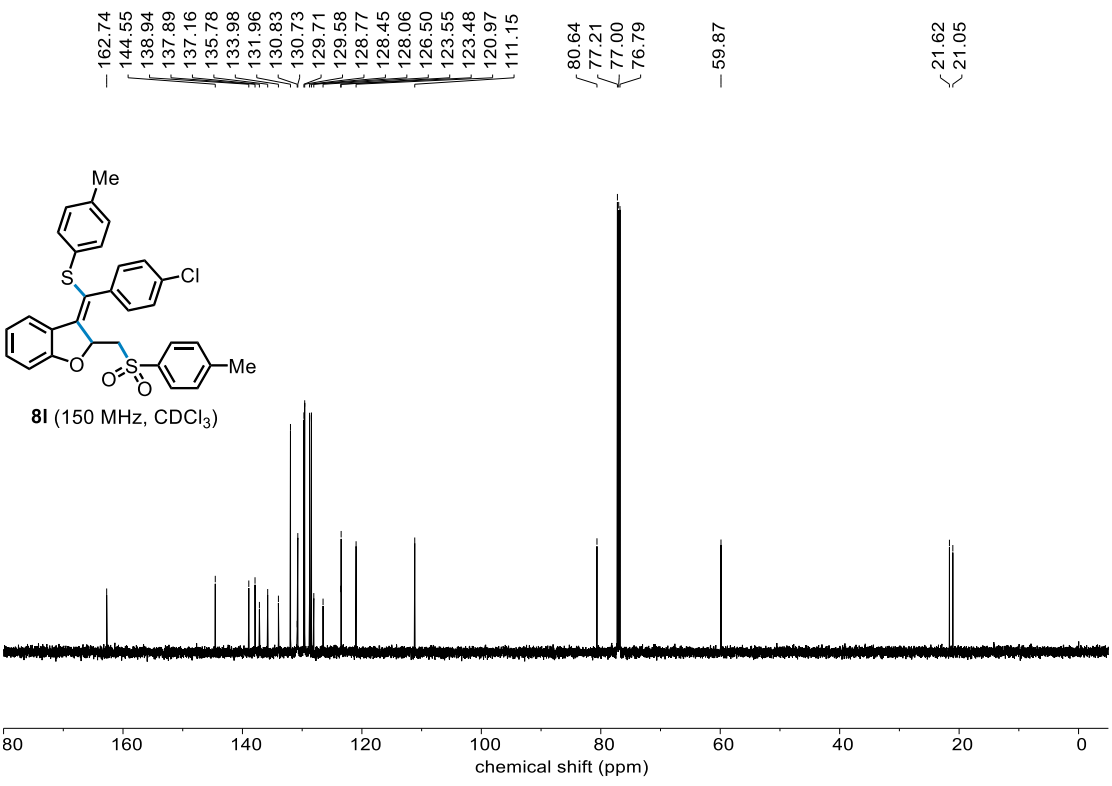

7.864
7.844
7.325
7.304
7.093
7.074
7.055
7.035
7.015
7.009
6.989
6.988
6.939
6.919
6.626
6.605
6.557
6.539
6.519
6.340
6.337
6.320
6.317
6.016
6.011
5.992
5.987
4.047
4.042
4.010
4.005
3.626
3.602
3.589
3.565
2.433
2.290
2.228
0.000
Me
Me
S
O
S
O
O
Me
8j (400 MHz, CDCl3)
1.92
1.79
6.96
1.75
0.85
0.90
0.87
0.82
0.89
0.89
3.00
2.95
2.99
Chemical shift (ppm)

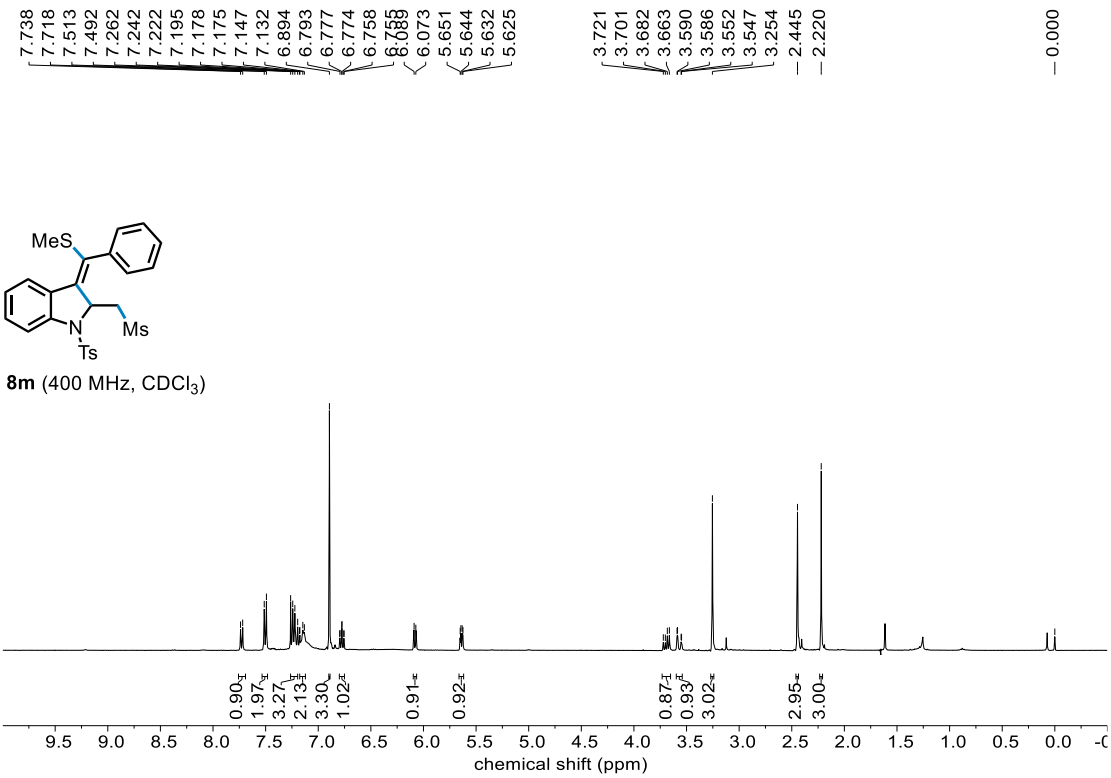

162.62
144.47
138.46
138.01
137.32
137.18
134.33
131.52
130.36
129.55
129.53
129.24
129.16
128.79
128.47
127.87
123.95
123.67
120.79
110.94
80.58
77.21
77.00
76.79
60.00
21.61
21.29
21.02
Me
Me
S
O
S
O
O
Me
8j (150 MHz, CDCl3)
chemical shift (ppm)

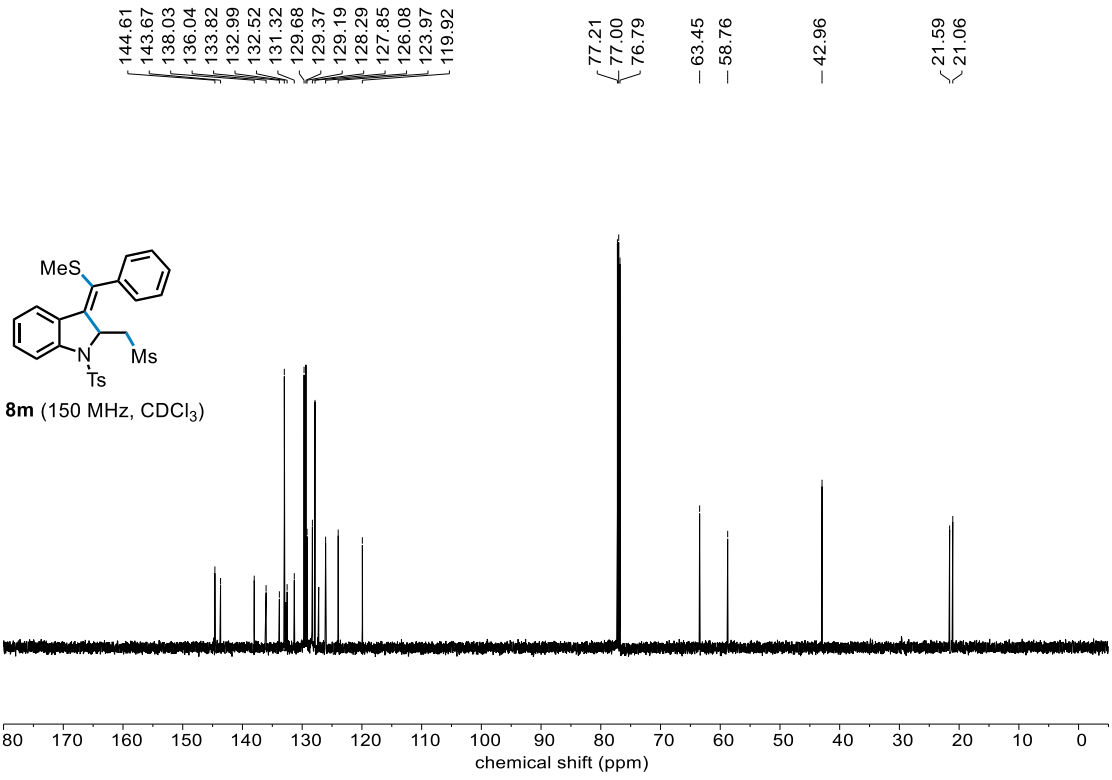

7.980
7.962
7.651
7.632
7.613
7.547
7.526
7.508
7.126
7.047
7.032
7.017
6.565
6.546
6.527
6.389
6.365
6.047
6.042
6.023
6.018
4.061
4.056
4.024
4.019
3.657
3.633
3.620
3.596
2.282
-0.000
Me
O
S
O
O
8k (400 MHz, CDCl3)
1.86
0.96
1.93
7.05
3.13
1.91
0.91
0.86
0.93
0.91
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift (ppm)

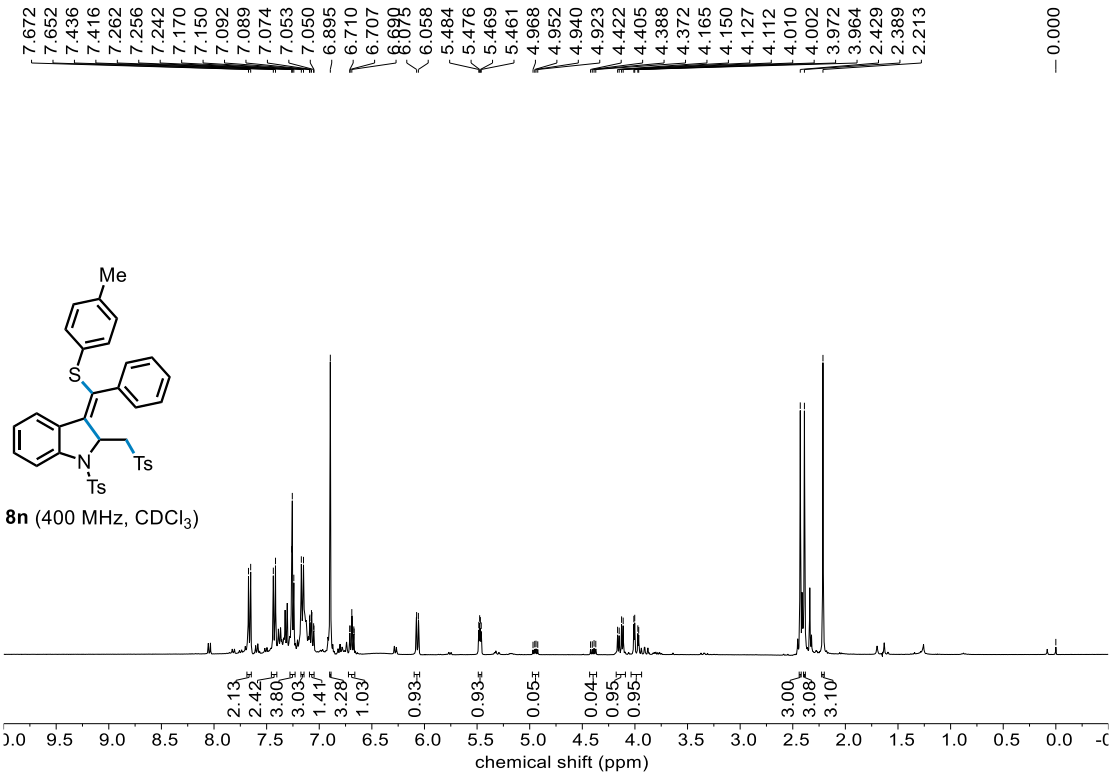

162.60
140.15
139.05
138.16
134.20
133.54
132.53
131.21
130.54
129.25
129.18
128.94
128.77
128.40
127.33
127.23
123.81
123.73
120.88
110.94
80.57
77.21
77.00
76.79
59.87
21.27
Me
O
S
O
O
8k (150 MHz, CDCl3)
80 160 140 120 100 80 60 40 20 0
chemical shift (ppm)

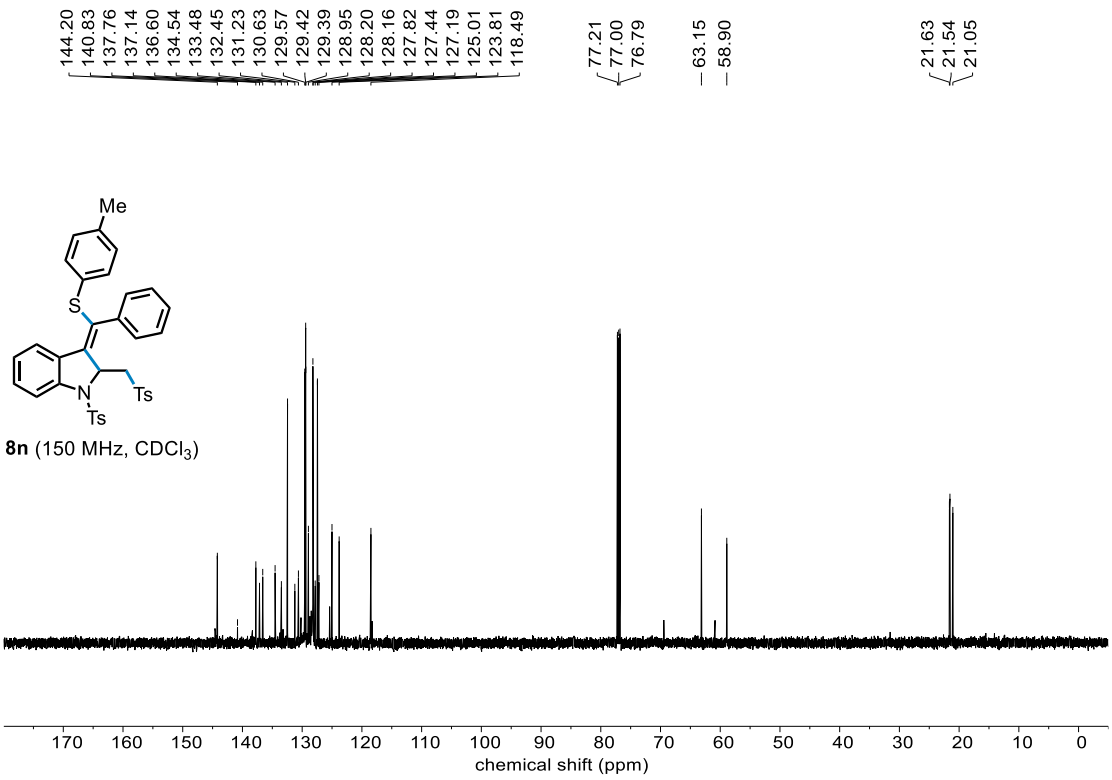

7.857
7.844
7.325
7.311
7.208
7.195
7.137
7.071
7.060
7.045
7.006
6.993
6.952
6.939
6.623
6.609
6.580
6.567
6.554
6.315
6.312
6.302
6.299
6.030
6.026
6.014
6.011
4.013
4.010
3.989
3.985
3.638
3.623
3.614
3.598
2.434
2.242
-0.000
Me
S
Cl
O
S
O
O
Me
8l (600 MHz, CDCl3)
1.88
1.97
1.89
1.77
1.14
1.88
1.91
0.93
1.01
0.99
0.93
1.11
1.10
3.00
3.03
9
8
7
6
5
4
3
2
1
0
chemical shift (ppm)

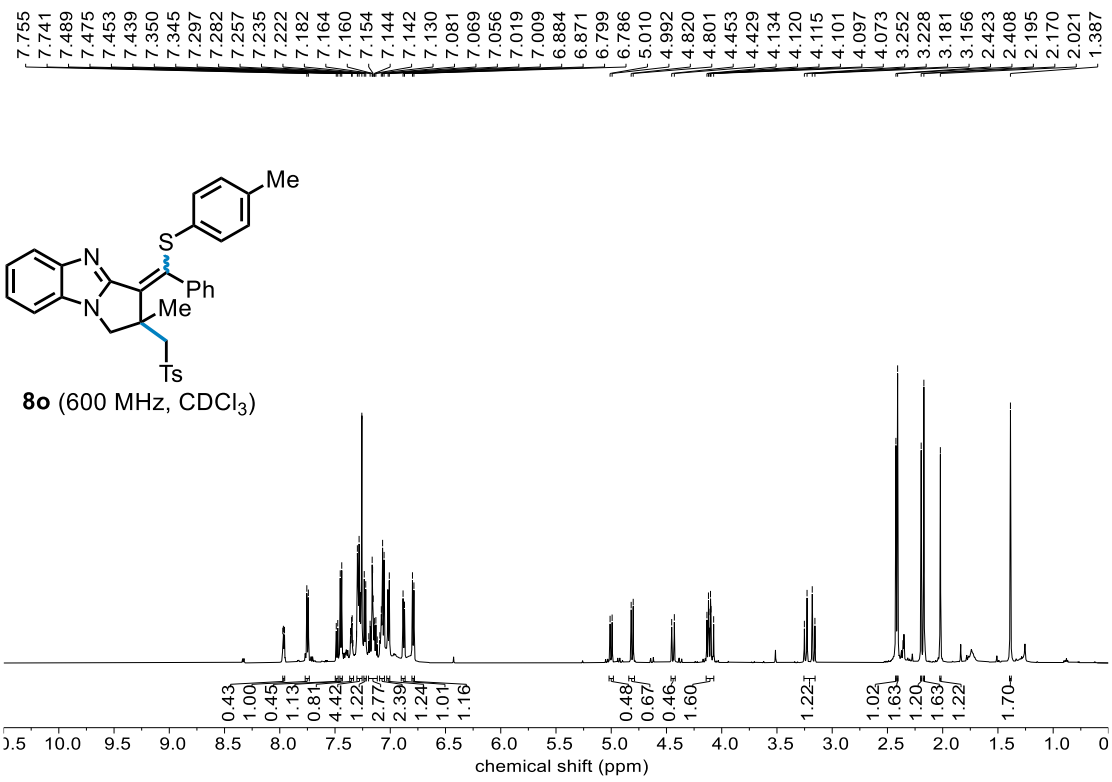

162.74
144.55
138.94
137.89
137.16
135.78
133.98
131.96
130.83
130.73
129.71
129.58
128.77
128.45
128.06
126.50
123.55
123.48
120.97
111.15
80.64
77.21
77.00
76.79
59.87
21.62
21.05
Me
S
Cl
O
S
O
O
Me
8l (150 MHz, CDCl3)
80
160
140
120
100
80
60
40
20
0
chemical shift (ppm)


7.738
7.718
7.513
7.492
7.262
7.242
7.222
7.195
7.178
7.175
7.147
7.132
6.894
6.793
6.777
6.774
6.758
6.073
5.651
5.644
5.632
5.625
3.721
3.701
3.682
3.663
3.590
3.586
3.552
3.547
3.254
2.445
2.220
0.000
MeS
Ms
N
Ts
8m (400 MHz, CDCl3)
0.90
1.97
3.27
2.13
3.30
1.02
0.91
0.92
0.87
0.93
3.02
2.95
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
chemical shift (ppm)

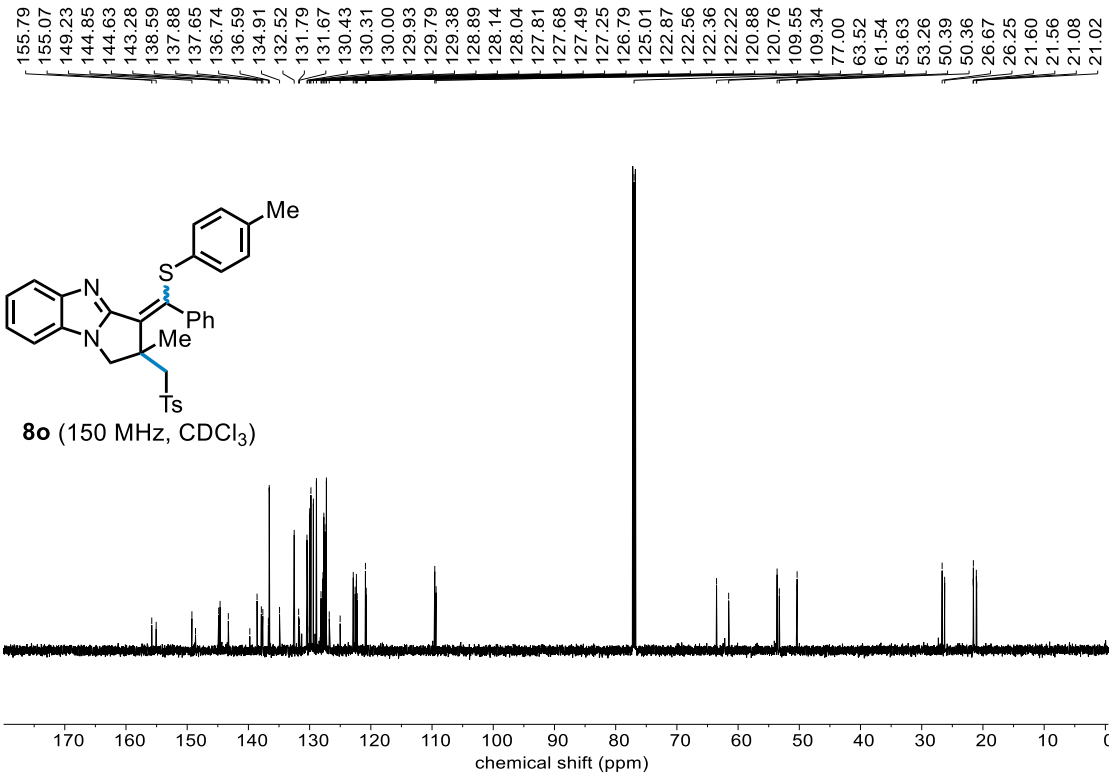

144.61
143.67
138.03
136.04
133.82
132.99
132.52
131.32
129.68
129.37
129.19
128.29
127.85
126.08
123.97
119.92
77.21
77.00
76.79
63.45
58.76
42.96
21.59
21.06
MeS
Ms
N
Ts
8m (150 MHz, CDCl3)
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
chemical shift (ppm)


7.672
7.652
7.436
7.416
7.262
7.256
7.242
7.170
7.150
7.092
7.089
7.074
7.053
7.050
6.895
6.710
6.707
6.690
6.675
6.058
5.484
5.476
5.469
5.461
4.968
4.952
4.940
4.923
4.422
4.405
4.388
4.372
4.165
4.150
4.127
4.112
4.010
4.002
3.972
3.964
2.429
2.389
2.213
0.000
Me
S
N
Ts
Ts
8n (400 MHz, CDCl3)
2.13
2.42
3.80
3.03
1.41
3.28
1.03
0.93
0.93
0.05
0.04
0.95
0.95
3.00
3.08
3.10
chemical shift (ppm)

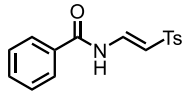

144.20
140.83
137.76
137.14
136.60
134.54
133.48
132.45
131.23
130.63
129.57
129.42
129.39
128.95
128.20
128.16
127.82
127.44
127.19
125.01
123.81
118.49
77.21
77.00
76.79
63.15
58.90
21.63
21.54
21.05
Me
S
N
Ts
Ts
8n (150 MHz, CDCl3)
chemical shift (ppm)



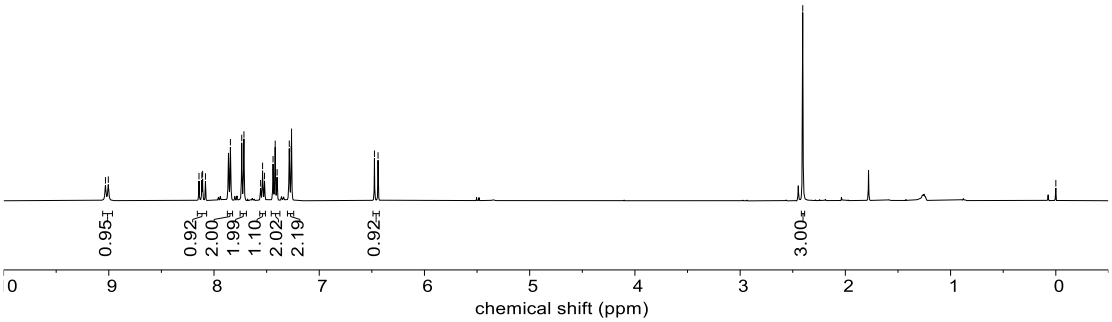
8o (600 MHz, $CDCl_3$)

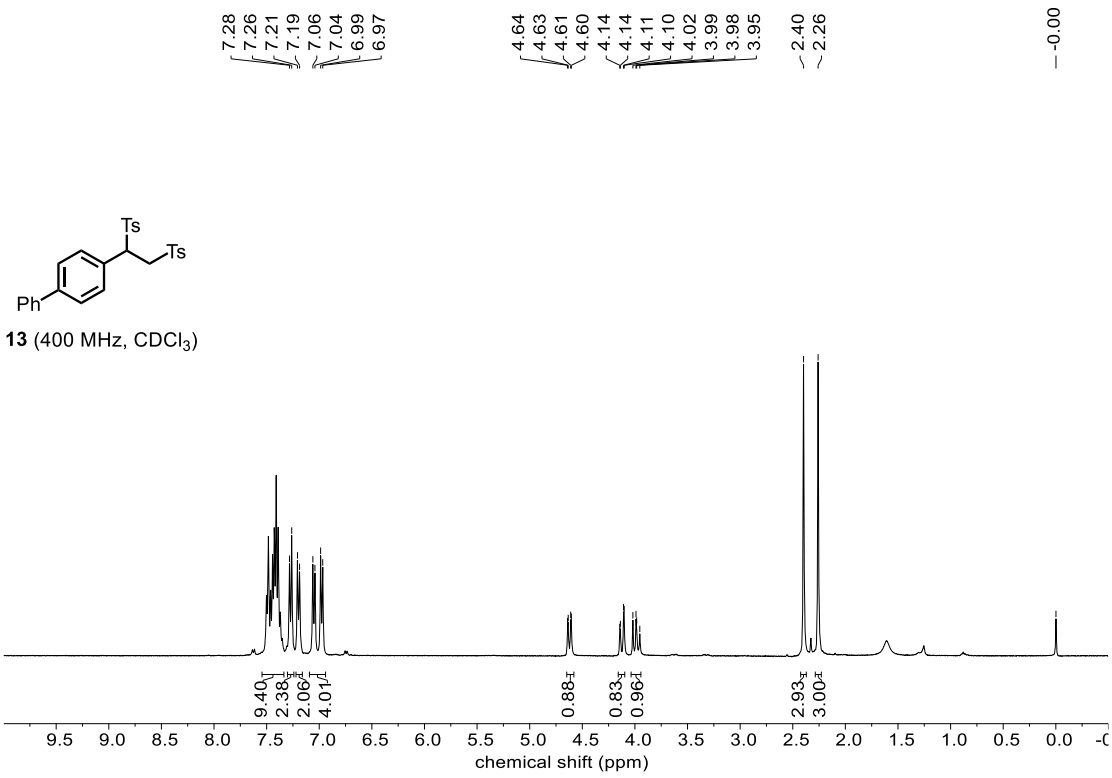


8o (150 MHz, $CDCl_3$)

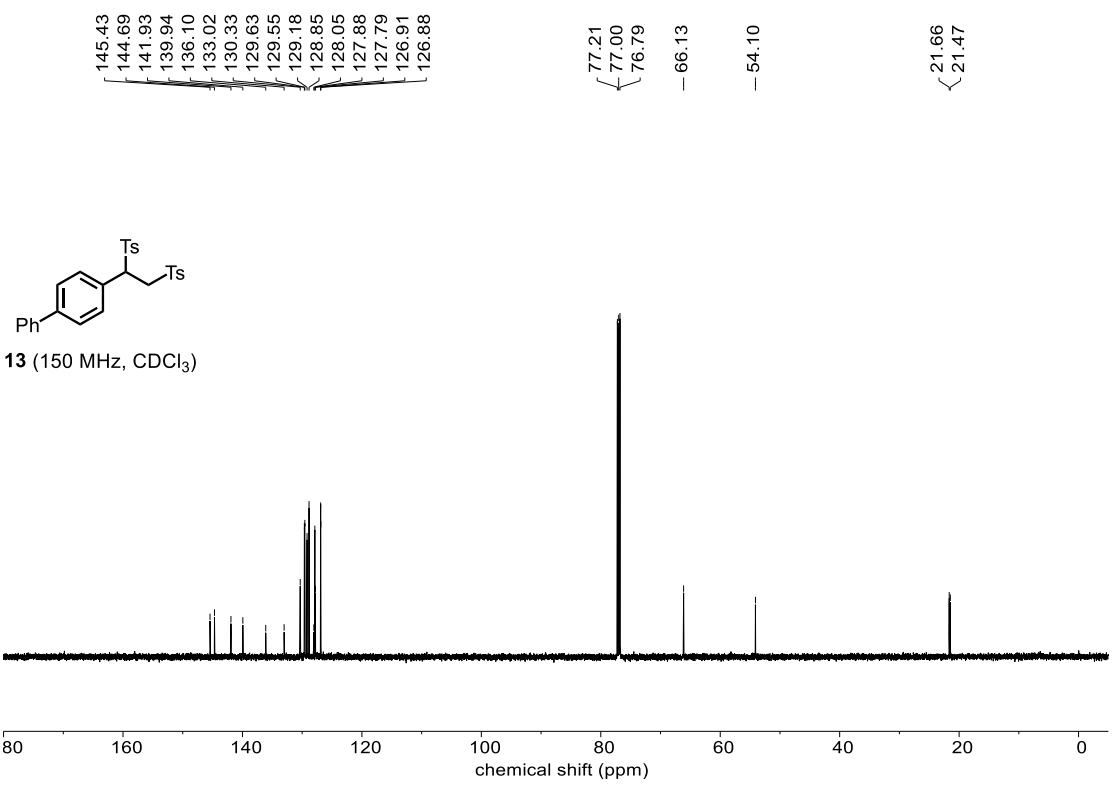


9 (400 MHz, $CDCl_3$)

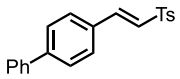




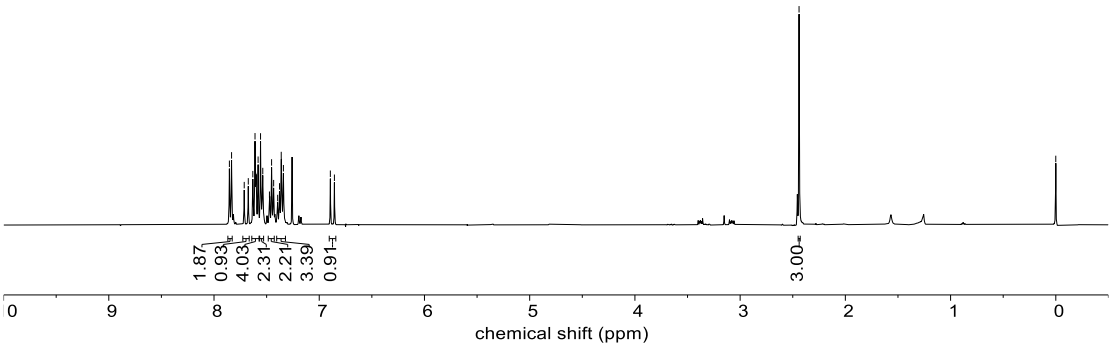
13 (400 MHz, $CDCl_3$)

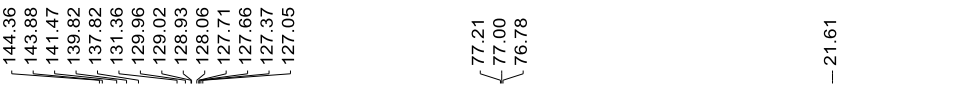


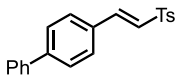
13 (150 MHz, $CDCl_3$)



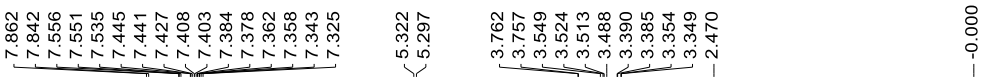
14 (400 MHz, $CDCl_3$)

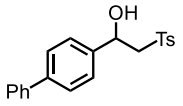




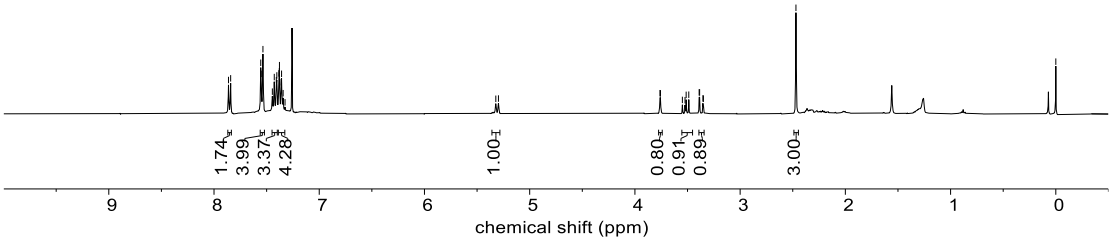


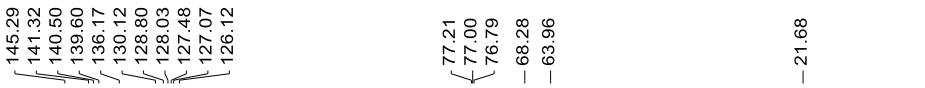
14 (150 MHz, $CDCl_3$)

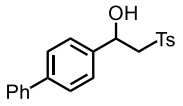




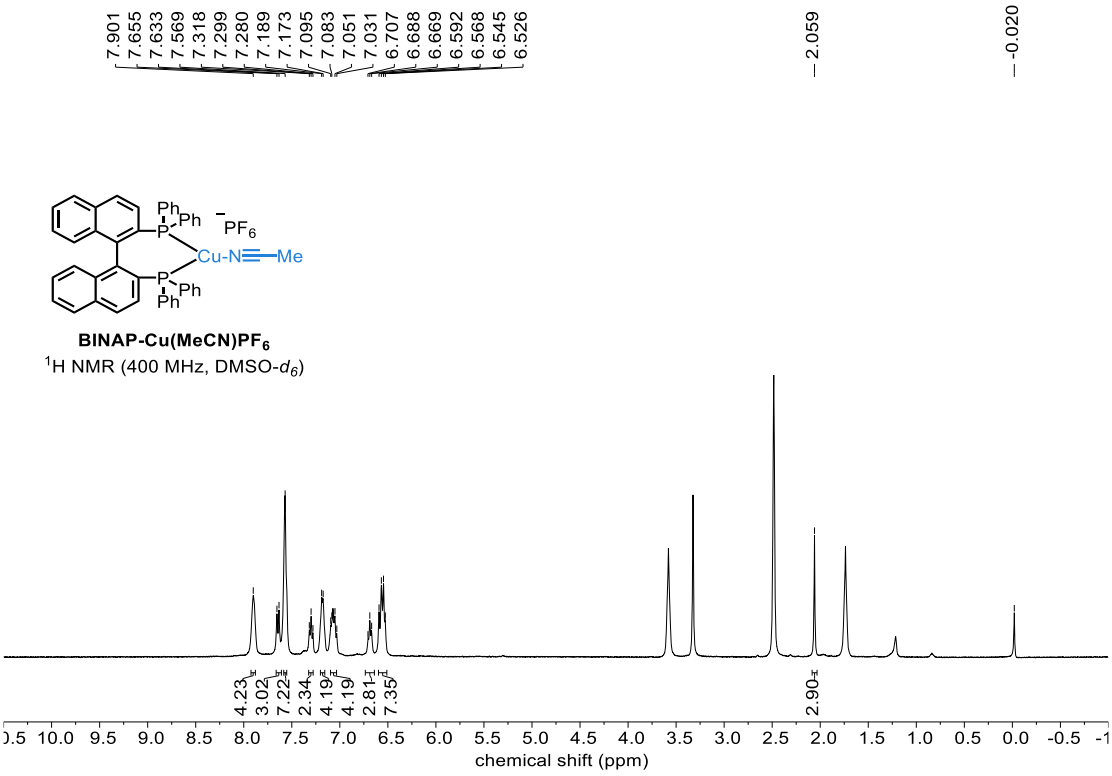
15 (400 MHz, $CDCl_3$)





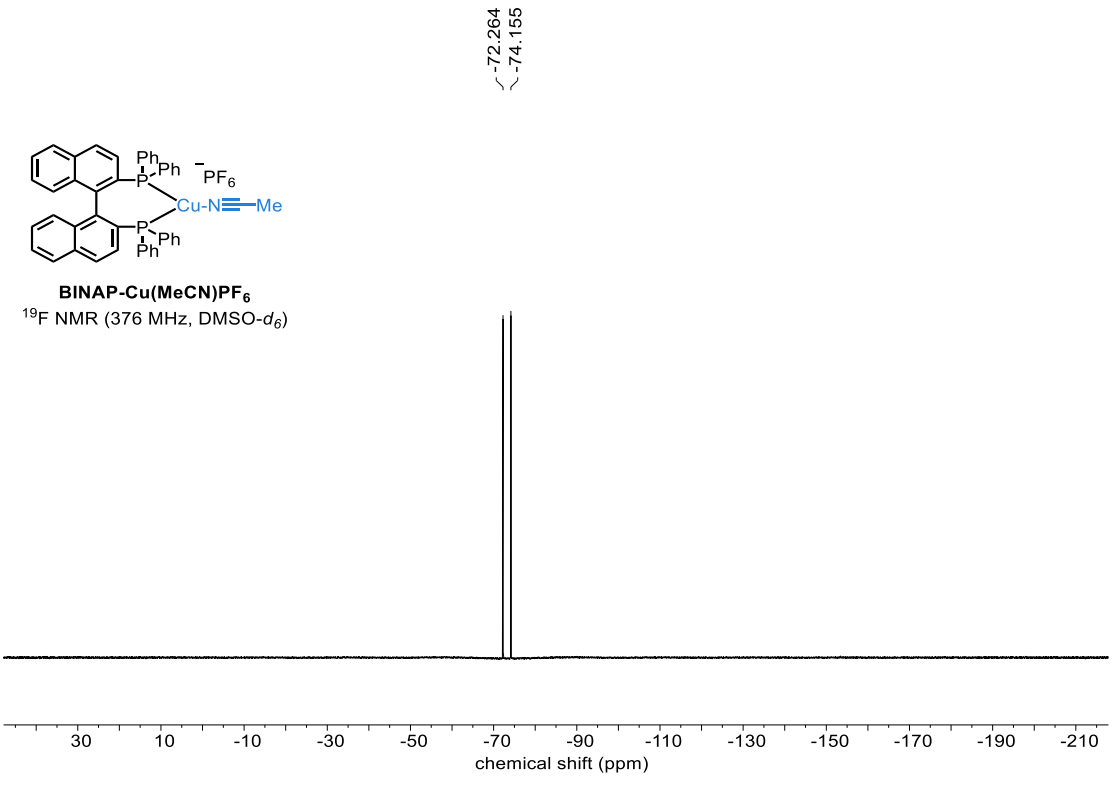


15 (150 MHz, $CDCl_3$)



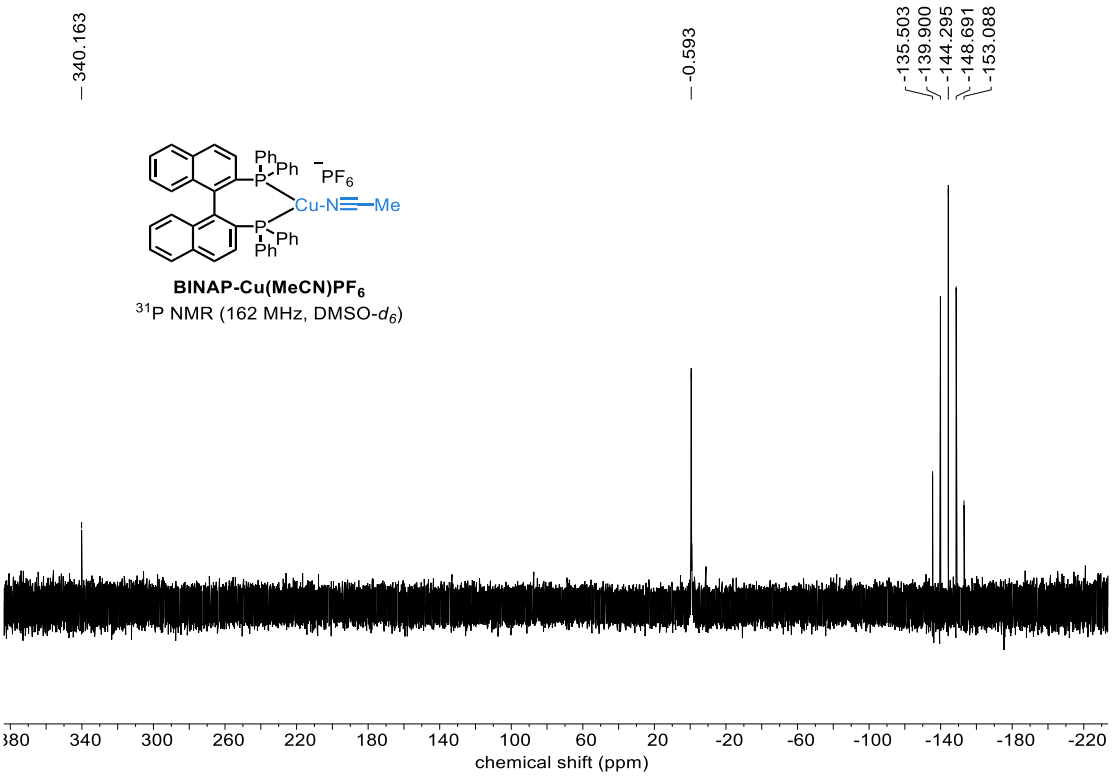
BINAP-Cu(MeCN)PF_6

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



BINAP-Cu(MeCN)PF_6

^{19}F NMR (376 MHz, DMSO-d_6)


340.163
-0.593
-135.503
-139.900
-144.295
-148.691
-153.088
Ph
Ph
P
PF6
Cu-N
Me
P
Ph
Ph
BINAP-Cu(MeCN)PF6
31P NMR (162 MHz, DMSO-d6)
380
340
300
260
220
180
140
100
60
20
-20
-60
-100
-140
-180
-220
chemical shift (ppm)