SUPPORTING INFORMATION

Copper-Catalyzed Intermolecular Difunctionalization of Styrenes with Thiosulfonates and Arylboronic Acids via a Radical Relay Pathway

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1. General Information

All reactions were carried out under dry argon. Anhydrous acetone was purchased from Changtai Chemical Technology and *N*,*N*-dimethylformamide (DMF) was purchased from J&K Chemicals. Solvents were directly used without further purification. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from J&K Chemicals, Adamas-beta, Macklin Reagent, Energy Chemicals, Aladdin, JiuDing Chemicals or Bide Pharmatech Ltd. The progress of the reactions was monitored by thin-layer chromatography using Whatman Partisil K6F 250 μm precoated 60 Å silica gel plates and visualized by short-wave ultraviolet light as well as by treatment with iodine. Flash chromatography was performed with silica gel (300–400 mesh). The NMR spectra were obtained using a Brüker 400 MHz Fourier-transform NMR spectrometer. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were taken with KBr plates with a Perkin-Elmer Spectrum Vertex 80 Series spectrometer. High resolution mass spectrometry (HRMS) data were obtained on a Bruker Apex IV RTMS using electrospray ionization (ESI) in positive mode. Melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Ultraviolet-Visible (UV) spectra were detected by Hitachi dual-beam UH5300. Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker ELEXSYS II E 500 EPR spectrometer.

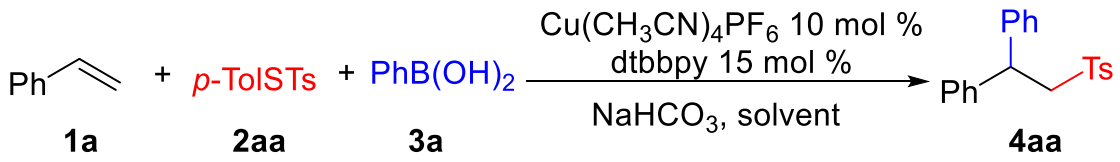
2. Preparation of Thiosulfonates: Thiosulfonates were prepared according to the literature procedures.[1]

3. Procedure and Characterization of Copper-Catalyzed Intermolecular Difunctionalization of Styrenes with Thiosulfonates and Aryboronic Acids via a Radical Relay Pathway

1) General Procedure for Catalysis: To an oven-dried microwave vial equipped with a stir bar was added *S*-methyl-4-methylbenzenesulfonothioate (**2a**) (40.4 mg, 0.20 mmol), phenylboronic acid (**3a**) (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbbpy) (4.0 mg, 15 mol %) under argon an atmosphere in a glove box. A mix solvent of acetone (0.6 mL) and DMF (0.1 mL) was added to the vial by syringe. The microwave vial was sealed with a cap and removed from the glove box. Then, styrene (**1a**) (11.6 μL, 0.10 mmol) and *tert*-butyl benzoperoxoate ($BzOO^tBu$) (57.1 μL, 0.30 mmol) were added by syringe under an argon atmosphere. The reaction mixture was heated to 40 ℃ in an oil bath and stirred for 12 h. Upon completion of the reaction, the sealed vial was cooled to room temperature, and opened to air. The reaction mixture was passed through a short pad of silica gel. The pad was then rinsed with EtOAc (10 mL). The resulting solution was subjected to reduced pressure to remove the volatile materials. The residue was purified by flash chromatography, as outlined below, to afford the pure product.

2) Optimization Reaction Condition

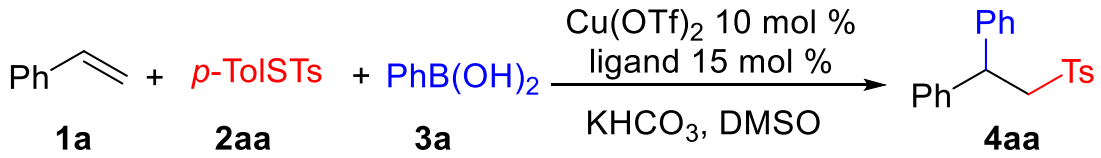
Table S1. Initial optimization of the solvent[a]



entry	solvent	assay yield[b] /%
1	DMA	15
2	DMF	29
3	DMSO	34
4	NMP	trace
5	MeOH	14
6	EtOH	7
7	MeCN	5
8	Toluene	N.P
9[c]	DMSO	40
10[d]	DMSO	44

[a]Reaction conditions: **2aa** (0.1 mmol), **1a** (1.5 equiv), **3a** (2.0 equiv., $NaHCO_3$ (2.0 equiv), $BzOO^tBu$ (2.0 equiv), $Cu(CH_3CN)_4PF_6$ (10 mol %), dtbbpy (15 mol %), solvent (1.0 mL), R.T. for 12 h. [b]Assay yield determined by ^1H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 (7.0 μL) as internal standard. [c]$Cu(OTf)_2$ instead of $Cu(CH_3CN)_4PF_6$.. [d]$Cu(OTf)_2$ instead of $Cu(CH_3CN)_4PF_6$, $KHCO_3$ instead of $NaHCO_3$, 40 °C.

Table S2. Optimization of the ligand[a]



entry	ligand	assay yield/%[b]
1	**L1**	44
2	**L2**	40
3	**L3**	34
4	**L4**	22
5	**L5**	N.P
6	**L6**	N.P
7	**L7**	N.P
8	**L8**	4
9	**L9**	4
10	**L10**	4
11	**L11**	N.P

[a]Reaction conditions: **1a** (0.1 mmol), **2aa** (1.5 equiv), **3a** (2.0 equiv), $KHCO_3$ (2.0 equiv), $BzOO^tBu$ (2.0 equiv), $Cu(OTf)_2$ (10 mol %), ligand (15 mol %), DMSO (1.0 mL), 40 °C for 12 h. [b]Assay yield determined by ^1H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 (7.0 μL) as internal standard.

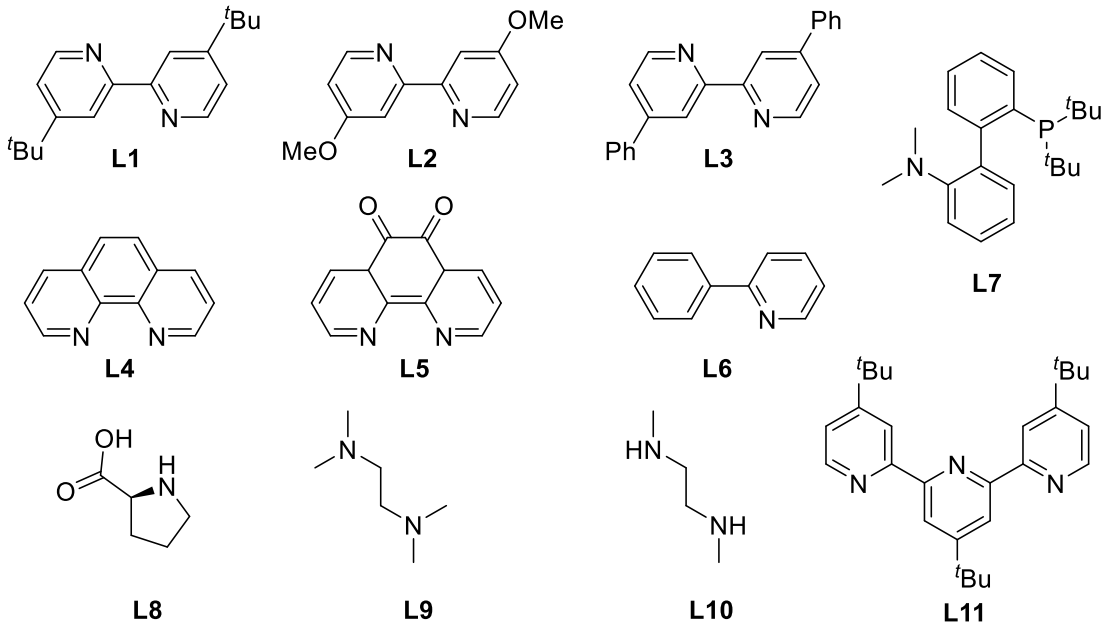
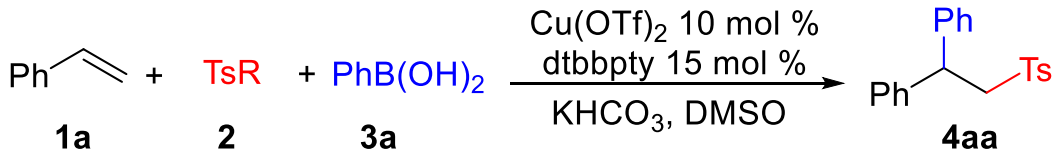


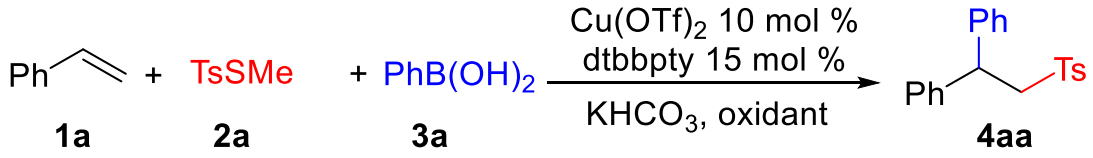
Table S3. Optimization of the leaving group[a]



entry	**2**	assay yield/%[b]
1	*p*-TolSTs	44
2	4-FPhTs	42
3	TsSMe	46
4[c]	TsCl	N.P
5	TsNa	N.P

[a]Reaction conditions: **1a** (0.1 mmol), **2** (1.5 equiv), **3a** (2.0 equiv), $KHCO_3$ (2.0 equiv), $BzOO^tBu$ (2.0 equiv), $Cu(OTf)_2$ (10 mol %), dtbbpy (15 mol %), DMSO (1.0 mL), 40 °C for 12 h. [b]Assay yield determined by ^1H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 (7.0 μL) as internal standard. [c]Ag_2CO_3 (2 equiv) was added.

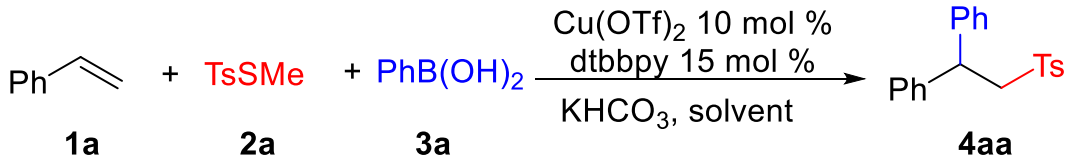
Table S4. Optimization of the oxidant[a]



entry	oxidant	assay yield/%[b]
1	BzOO^{t}Bu	46
2	TBHP (70% in H_2O)	38
3	TBHP (5.5 M in decane)	36
4	DTBP	N.P
5	$K_2S_2O_8$	9
6	$PhI(OAc)_2$	N.P
7	O_2	N.P

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), **3a** (2.0 equiv), $KHCO_3$ (2.0 equiv), oxidant (2.0 equiv), $Cu(OTf)_2$ (10 mol %), dtbbpy (15 mol %), DMSO (1.0 mL), 40 °C for 12 h. [b]Assay yield determined by ^{1}H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 (7.0 μL) as internal standard. DTBP: Di-*tert*-Butyl Peroxide.

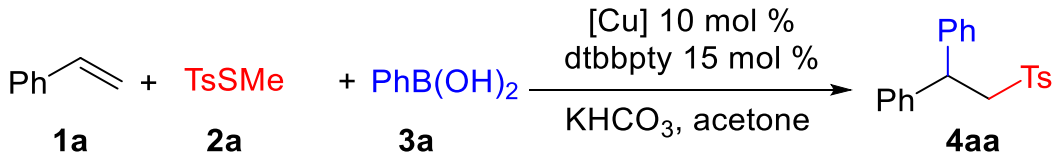
Table S5. Second optimization of the solvent[a]



entry	solvent	assay yield/%[b]
1	1,4-Dioxane	trace
2	IPA	20
3	acetone	40
4[c]	acetone	48

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (2.0 equiv), **3a** (2.0 equiv), Na_2CO_3 (2.0 equiv), BzOO^{t}Bu (2.0 equiv), $Cu(OTf)_2$ (10 mol %), dtbbpy (15 mol %), solvent (1.0 mL), 40 °C for 12 h. [b]Assay yield determined by ^{1}H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 (7.0 μL) as internal standard. [c]50 °C.

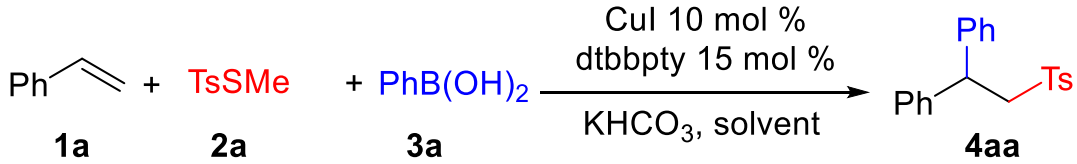
Table S6. Optimization of the copper catalyst[a]



entry	copper catalyst	assay yield/%[b]
1	$Cu(CH_3CN)_4PF_6$	40
2	$Cu(CH_3CN)_4BF_4$	44
3	$Cu(CF_3COO)_2{\cdot}H_2O$	44
4	Cu_2S	50
5	CuCl	44
6	$CuBr_2$	38
7	$CuCO_3(OH)_2$	50
8	$CuSO_4$	52
9	CuI	60
10	$Cu(acac)_2$	42
11	$CuCl_2$	42
12	$Cu(CN)_2$	42
13	CuO	trace
14	CuBr	trace

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (2.0 equiv), **3a** (2.0 equiv), base (2.0 equiv), BzOO^{t}Bu (2.0 equiv), copper catalyst (10 mol %), dtbbpy (15 mol %), acetone (1.0 mL) 50 ^{o}C for 12 h.

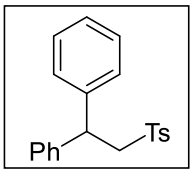
Table S7. Optimization of the mix solvent[a]



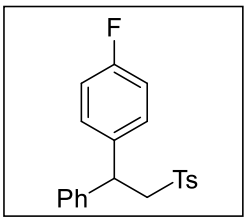
entry	solvent	assay yield/%[b]
1	acetone:DMSO = 7:3	42
2	acetone:DMF = 7:3	64
3	acetone:DMA = 7:3	30
4	acetone:MeOH = 7:3	48
5	acetone:EtOH = 7:3	44
6	acetone:MeCN = 7:3	46

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), **3a** (3.0 equiv), $KHCO_3$ (3.0 equiv), BzOO^{t}Bu (3.0 equiv), CuI (10 mol %), dtbbpy (15 mol %), solvent (1.0 mL), 50 ^{o}C for 12 h. [b]Assay yield determined by ^{1}H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 (7.0 μL) as internal standard.

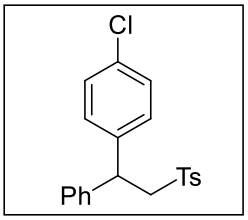
3) Characterization of Products



(2-Tosylethane-1,1-diyl)dibenzene (4aa): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), phenylboronic acid (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4aa** (27.0 mg, 80% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.22 – 7.16 (m, 4H), 7.16 – 7.09 (m, 8H), 4.60 (t, J = 7.1 Hz, 1H), 3.89 (d, J = 7.1 Hz, 2H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 141.5, 136.6, 129.5, 128.7, 128.0, 127.6, 126.9, 61.6, 46.2, 21.6 ppm. Other spectroscopic data were previously reported.[2]

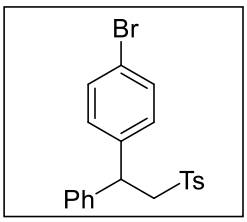


1-Fluoro-4-(1-phenyl-2-tosylethyl)benzene (4ab): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (4-fluorophenyl)boronic acid (35.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **4ab** (29.5 mg, 83% yield) as a colorless solid. R_f = 0.6 (EtOAc:hexanes = 1:6); m.p. = 172–176 ℃; m.p. = 167–169 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz, 2H), 7.24 – 7.05 (m, 9H), 6.91 – 6.83 (m, 2H), 4.61 (t, J = 7.1 Hz, 1H), 3.91 – 3.79 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7 (d, $J_{C\text{-}F}$ = 246.2 Hz), 144.4, 141.5, 137.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 136.6, 129.6, 129.2 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.8, 128.0, 127.4, 127.0, 115.5 (d, $J_{C\text{-}F}$ = 21.5 Hz), 61.6, 45.4, 31.0, 21.5 ppm; IR (thin film): 2922, 2349, 1508, 1290, 1219, 1164, 1135, 1086, 924, 840, 698, 633 cm^{-1}; HRMS calculated for $C_{21}H_{20}FO_2S$ 355.1163, found 355.1161 $[M+H]^+$.

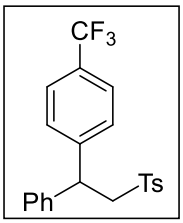


1-Chloro-4-(1-phenyl-2-tosylethyl)benzene (4ac): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (4-chlorophenyl)boronic acid (39.1 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4ac** (24.0 mg, 65% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 178–181 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.2 Hz, 2H), 7.23 – 7.02 (m, 11H), 4.59 (t, J = 7.1 Hz, 1H), 3.93 – 3.76 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.2, 139.7, 136.5, 132.8, 129.6, 129.1, 128.9, 128.8, 128.0, 127.4, 127.1, 61.4, 45.6, 21.6 ppm; IR

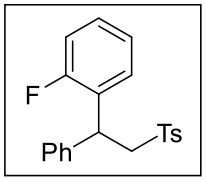
(thin film): 1480, 1293, 1164, 1136, 1086, 1014, 925, 809, 772, 747, 716, 697 cm^{-1}; HRMS calculated for $C_{21}H_{20}ClO_2S$ 371.0867, found 371.0862 $[M+H]^+$.



1-Bromo-4-(1-phenyl-2-tosylethyl)benzene (4ad): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (4-bromophenyl)boronic acid (35.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4ad** (23.2 mg, 56% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 176–179 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.3 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.24 – 7.12 (m, 5H), 7.12 – 7.07 (m, 2H), 6.98 (d, J = 8.5 Hz, 2H), 4.60 – 4.54 (m, 1H), 3.91 – 3.78 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 141.1, 140.2, 136.5, 131.7, 129.6, 129.5, 128.9, 128.0, 127.4, 127.1, 120.9, 61.3, 45.7, 21.6 ppm; IR (thin film): 1542, 1489, 1293, 1137, 925, 809, 745, 669, 658 cm^{-1}; HRMS calculated for $C_{21}H_{21}BrO_2S$ 415.0362, found 415.0362 $[M+H]^+$.

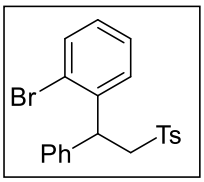


1-Methyl-4-((2-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl)sulfonyl)benzene (4ae): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (4-(trifluoromethyl)phenyl)boronic acid (47.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4ae** (24.2 mg, 60% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 140–146 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.25 – 7.05 (m, 9H), 4.68 (dd, J = 8.3, 5.9 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.90 – 3.79 (m, 1H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.6, 140.9, 136.4, 129.6, 129.2 (q, J_{C-F} = 32.7 Hz), 129.0, 128.2, 127.4, 127.3, 125.6 (q, J_{C-F} = 3.7 Hz), 124.0 (q, J_{C-F} = 272.1 Hz), 61.1, 46.2, 21.4 ppm; IR (thin film): 2361, 1653, 1419, 1327, 1162, 1128, 1087, 1060, 1019, 910, 812, 761, 700 cm^{-1}; HRMS calculated for $C_{22}H_{19}F_3O_2SNa$ 427.0950, found 427.0949 $[M+Na]^+$.

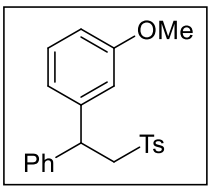


1-Fluoro-2-(1-phenyl-2-tosylethyl)benzene (4af): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (2-fluorophenyl)boronic acid (35.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4af** (21.3 mg, 60% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 104–106 ℃; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.06 (m, 9H), 7.03 – 6.94 (m, 1H), 6.91 – 6.81 (m, 1H), 4.80 (dd, *J* = 8.3, 6.1 Hz, 1H), 4.02 (dd, *J* = 14.6, 8.3 Hz, 1H), 3.85 (dd, *J* = 14.6, 6.1 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3 (d, J_{C-F} = 246.2 Hz), 144.3, 140.5, 136.3, 129.6, 129.3 (d, J_{C-F} = 4.2 Hz), 128.8, 128.3 (d, J_{C-F} = 13.4 Hz), 128.0, 127.6, 127.1, 124.3 (d, J_{C-F} = 3.4 Hz), 115.9 (d, J_{C-F} = 22.3 Hz), 60.0 (d, J_{C-F} = 2.7 Hz), 40.6, 21.6 ppm; IR (thin film): 2924, 1597, 1494, 1456, 1408, 1230, 1162, 1085, 1035, 914, 819, 740, 567, 462 cm^{-1}; HRMS calculated for $C_{21}H_{20}FO_2S$ 355.1163, found 355.1161 $[M+H]^+$.

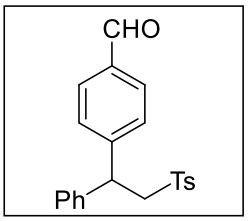


1-Bromo-2-(1-phenyl-2-tosylethyl)benzene (4ag): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (2-bromophenyl)boronic acid (50.2 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4ag** (23.5 mg, 57% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 106–108 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.13 (m, 7H), 7.14 – 7.08 (m, 2H), 7.03 – 6.96 (m, 1H), 5.09 (t, *J* = 7.1 Hz, 1H), 3.90 (dd, *J* = 14.7, 7.1 Hz, 1H), 3.81 (dd, *J* = 14.7, 7.1 Hz, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 140.1, 140.0, 136.2, 133.5, 129.6, 128.8, 128.7, 128.4, 128.2, 128.0, 127.6, 127.1, 124.6, 60.7, 44.7, 21.6 ppm; IR (thin film): 2358, 1597, 1467, 1438, 1138, 1085, 1020, 918, 813, 746, 698, 563, 514 cm^{-1}; HRMS calculated for $C_{21}H_{19}BrO_2SNa$ 437.0181, found 437.0176 $[M+Na]^+$.

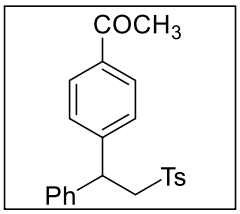


1-Methoxy-3-(1-phenyl-2-tosylethyl)benzene (4ah): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (3-methoxyphenyl)boronic acid (38.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:8) to give the product **4ah** (26.0 mg, 71% yield) as a colorless solid. R_f = 0.3 (EtOAc:hexanes = 1:6); m.p. = 74-76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.07 (m, 8H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.66 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.61 (d, *J* = 1.8 Hz, 1H), 4.56 (t, *J* = 7.1 Hz, 1H), 3.87 (d, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.2, 143.0, 141.4, 136.6, 129.7, 129.5, 128.7, 128.0, 127.6, 126.9, 120.0, 113.7, 111.9, 61.5, 55.1, 46.2, 21.6 ppm; IR (thin film): 2922, 1593, 1447, 1306, 1143, 1105, 997, 816, 757, 725, 702, 687, 652 cm^{-1}; HRMS calculated for $C_{22}H_{22}O_3SNa$ 389.1182, found 389.1177 $[M+Na]^+$.

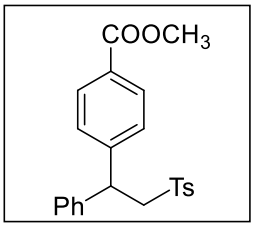
4-(1-Phenyl-2-tosylethyl)benzaldehyde (4ai): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (4-formylphenyl)boronic acid (37.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol),



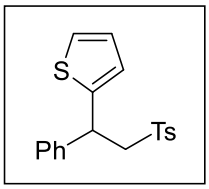
CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product **4ai** (19.0 mg, 52% yield) as a colorless solid. R_f = 0.2 (EtOAc:hexanes = 1:3); m.p. = 149–153 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.10 (m, 7H), 4.73 – 4.67 (m, 1H), 3.97 – 3.82 (m, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 148.2, 144.6, 140.6, 136.4, 135.2, 130.1, 129.7, 129.0, 128.4, 128.0, 127.5, 127.3, 61.0, 46.3, 21.6 ppm; IR (thin film): 2924, 1696, 1605, 1451, 1299, 1136, 1086, 912, 809, 762, 734, 700 cm^{-1}; HRMS calculated for $C_{22}H_{21}O_3S$ 365.1206, found 365.1203 $[M+H]^+$.



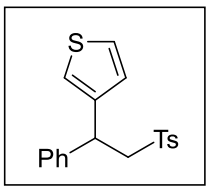
1-(4-(1-Phenyl-2-tosylethyl)phenyl)ethan-1-one (4aj): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (4-acetylphenyl)boronic acid (41.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1: 2) to give the product **4aj** (32.5 mg, 86% yield) as a colorless solid. R_f = 0.2 (EtOAc:hexanes = 1:3); m.p. = 125–129 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.07 (m, 9H), 4.68 (t, *J* = 7.1 Hz, 1H), 3.98 – 3.81 (m, 2H), 2.54 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 146.6, 144.6, 140.8, 136.5, 135.8, 129.6, 128.9, 128.8, 128.0, 127.9, 127.5, 127.2, 61.1, 46.1, 26.6, 21.6 ppm; IR (thin film): 1653, 1269, 1137, 1086, 912, 812, 756, 732, 702, 633 cm^{-1}; HRMS calculated for $C_{23}H_{23}O_3S$ 379.1362, found 379.1358 $[M+H]^+$.



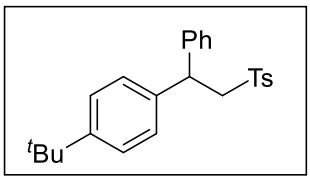
Methyl 4-(1-phenyl-2-tosylethyl)benzoate (4ak): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (45.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product **4ak** (34.5 mg, 88% yield) as a colorless solid. R_f = 0.2 (EtOAc:hexanes = 1:3); m.p. = 140–145 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.24 – 7.07 (m, 9H), 4.66 (t, *J* = 6.9 Hz, 1H), 3.97 – 3.81 (m, 5H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 146.4, 144.5, 140.9, 136.4, 130.0, 129.6, 128.9, 128.8, 128.0, 127.8, 127.5, 127.2, 61.2, 52.1, 46.2, 21.5 ppm; IR (thin film): 1718, 1430, 1275, 1191, 1135, 1084, 910, 765, 707 cm^{-1}; HRMS calculated for $C_{23}H_{23}O_4S$ 395.1312, found 395.1309 $[M+H]^+$.



2-(1-Phenyl-2-tosylethyl)thiophene (4al): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), thiophen-2-ylboronic acid (32.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4al** (11.0 mg, 32% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 125–127 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.12 (m, 7H), 7.10 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.86 – 6.79 (m, 1H), 6.77 (d, *J* = 3.5 Hz, 1H), 4.85 (t, *J* = 7.0 Hz, 1H), 3.95 – 3.83 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 144.3, 141.1, 136.6, 129.6, 128.8, 128.0, 127.6, 127.3, 126.8, 124.8, 124.6, 62.7, 42.0, 21.6 ppm; IR (thin film): 2919, 2360, 1597, 1408, 1287, 1169, 1135, 1083, 1017, 920, 873, 842, 807, 775, 759, 739, 723, 697, 628 cm^{-1}; HRMS calculated for $C_{19}H_{18}O_2S_2Na$ 365.0640, found 365.0637 $[M+Na]^+$.

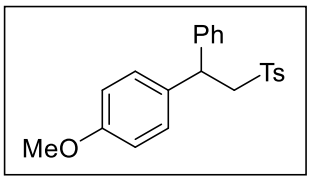


3-(1-Phenyl-2-tosylethyl)thiophene (4am): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), thiophen-3-ylboronic acid (32.0 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4am** (15.0 mg, 44% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 157–159 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.23 – 7.02 (m, 8H), 6.88 (s, 1H), 6.80 (d, *J* = 4.6 Hz, 1H), 4.68 (t, *J* = 6.8 Hz, 1H), 3.94 – 3.74 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 142.2, 141.2, 136.6, 129.6, 128.7, 127.9, 127.7, 127.0, 126.9, 126.2, 121.4, 62.0, 41.9, 21.6 ppm; IR (thin film): 2921, 1645, 1494, 1234, 1132, 1085, 921, 842, 798, 755, 698 cm^{-1}; HRMS calculated for $C_{19}H_{19}O_2S_2$ 343.0821, found 343.0820 $[M+H]^+$.

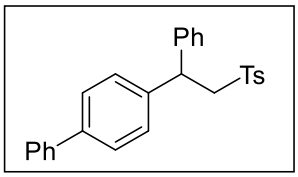


1-(*tert*-Butyl)-4-(1-phenyl-2-tosylethyl)benzene (5aa): The reaction was performed following the General Procedure with 1-(*tert*-butyl)-4-vinylbenzene (18.3 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **5aa** (27.2 mg, 70% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 172–176 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.06 (m, 9H), 7.02 (d, *J* = 8.3 Hz, 2H), 4.58 (t, *J* = 7.1 Hz, 1H), 3.97 – 3.81 (m, 2H), 2.35 (s, 3H), 1.24 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 144.0, 141.8, 138.3, 136.7, 129.4, 128.7, 128.0, 127.6,

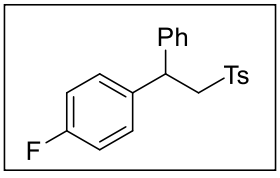
127.2, 126.8, 125.6, 61.7, 45.9, 34.3, 31.3, 21.6 ppm; IR (thin film): 2921, 2360, 1397, 1293, 1136, 1086, 809, 752, 699 cm^{-1}; HRMS calculated for $C_{25}H_{28}O_2SNa$ 415.1702, found 415.1701 $[M+Na]^+$.



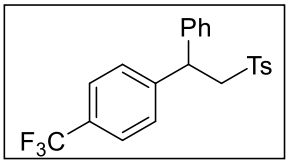
1-Methoxy-4-(1-phenyl-2-tosylethyl)benzene (5ab): The reaction was performed following the General Procedure with 1-methoxy-4-vinylbenzene (13.3 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:8) to give the product **5ab** (27.0 mg, 74% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.11 (m, 7H), 7.08 – 7.02 (m, 2H), 6.76 – 6.71 (m, 2H), 4.58 (t, *J* = 7.2 Hz, 1H), 3.88 (d, *J* = 7.2 Hz, 2H), 3.76 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 144.1, 141.9, 136.7, 133.5, 129.5, 128.7, 128.6, 128.0, 127.5, 126.8, 114.1, 61.8, 55.2, 45.4, 21.5 ppm. Other spectroscopic data were previously reported.[3]



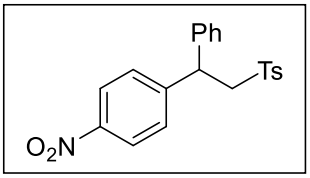
4-(1-Phenyl-2-tosylethyl)-1,1'-biphenyl (5ac): The reaction was performed following the General Procedure with 1-phenyl-4-vinylbenzene (18.1 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:8) to give the product **5ac** (36.0 mg, 87% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 175–179 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 4H), 7.45 – 7.35 (m, 4H), 7.36 – 7.29 (m, 1H), 7.24 – 7.13 (m, 7H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.65 (t, *J* = 7.1 Hz, 1H), 4.00 – 3.85 (m, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 141.5, 140.6, 140.3, 139.8, 136.6, 129.5, 128.8, 128.7, 128.1, 128.0, 127.6, 127.4, 127.3, 127.0, 61.6, 46.0, 21.5 ppm; IR (thin film): 2920, 2851, 2361, 1653, 1473, 1397, 1289, 1164, 1136, 1087, 908, 808, 728, 637 cm^{-1}; HRMS calculated for $C_{27}H_{24}O_2SNa$ 435.1389, found 435.1391 $[M+Na]^+$.



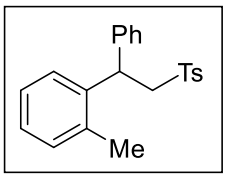
1-Fluoro-4-(1-phenyl-2-tosylethyl)benzene (4ab) (from 1-fluoro-4-vinylbenzene): The reaction was performed following the General Procedure with 1-fluoro-4-vinylbenzene (12.0 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4ab** (22.0 mg, 62% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6).



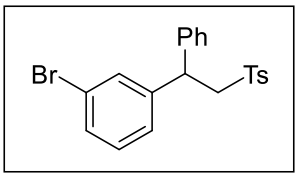
1-Methyl-4-((2-phenyl-2-(4-(trifluoromethyl)phenyl)ethyl) sulfonyl)benzene (4ae) (from 1-(trifluoromethyl)-4-vinyl benzene): The reaction was performed following the General Procedure with 1-(trifluoromethyl)-4-vinylbenzene (14.8 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **4ae** (26.3 mg, 65% yield) as a colorless solid. R_f = 0.6 (EtOAc:hexanes = 1:6).



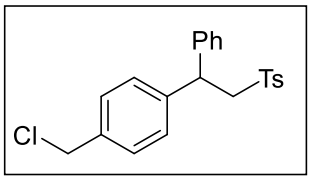
1-Methyl-4-((2-(4-nitrophenyl)-2-phenylethyl)sulfonyl)be nzene (5ad): The reaction was performed following the General Procedure with 1-nitro-4-vinylbenzene (12.8 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product **5ad** (25.0 mg, 66% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:3); m.p. = 96–100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.27 – 7.16 (m, 5H), 7.14 – 7.07 (m, 2H), 4.74 (dd, *J* = 8.3, 5.8 Hz, 1H), 3.94 (dd, *J* = 14.5, 8.5 Hz, 1H), 3.85 (dd, *J* = 14.5, 5.8 Hz, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 146.8, 144.9, 140.2, 136.4, 129.7, 129.2, 128.7, 128.0, 127.6, 127.4, 123.9, 60.9, 45.9, 21.6 ppm; IR (thin film): 2923, 2361, 1599, 1521, 1348, 1282, 1164, 1128, 925, 856, 810, 766, 746, 703, 655 cm^{-1}; HRMS calculated for $C_{21}H_{19}NO_4SNa$ 404.0927, found 404.0929 $[M+Na]^+$.



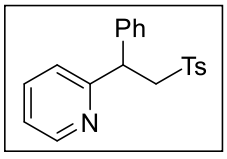
1-Methyl-2-(1-phenyl-2-tosylethyl)benzene (5ae): The reaction was performed following the General Procedure with 1-methyl-2-vinylbenzene (12.9 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **5ae** (23.5 mg, 67% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 123–126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.16 – 7.10 (m, 5H), 7.10 – 6.98 (m, 4H), 4.86 (t, *J* = 7.0 Hz, 1H), 3.91 – 3.79 (m, 2H), 2.36 (s, 3H), 2.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.0, 139.2, 136.7, 136.0, 130.9, 129.5, 128.6, 128.0, 127.9, 126.8, 126.7, 126.6, 126.1, 61.7, 41.6, 21.6, 19.8 ppm; IR (thin film): 2922, 1597, 1494, 1466, 1294, 1155, 1131, 1081, 909, 783, 748, 733, 700, 636 cm^{-1}; HRMS calculated for $C_{22}H_{22}O_2SNa$ 373.1233, found 373.1231 $[M+Na]^+$.



1-Bromo-3-(1-phenyl-2-tosylethyl)benzene (5af): The reaction was performed following the General Procedure with 1-bromo-3-vinylbenzene (15.8 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **5af** (32.5 mg, 79% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 155–158 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.02 (m, 11H), 4.59 – 4.54 (m, 1H), 3.93 – 3.77 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 143.4, 141.0, 136.3, 130.6, 130.3, 130.0, 129.6, 128.9, 127.9, 127.4, 127.2, 126.6, 122.7, 61.2, 46.0, 21.6 ppm; IR (thin film): 2361, 1559, 1541, 1473, 1397, 1299, 1164, 1135, 797, 773, 748, 704, 640 cm^{-1}; HRMS calculated for $C_{21}H_{19}BrO_2SNa$ 437.0181, found 437.0180 $[M+Na]^+$.

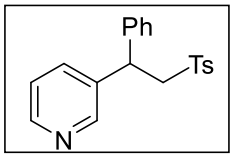


1-(Chloromethyl)-4-(1-phenyl-2-tosylethyl)benzene (5ag): The reaction was performed following the General Procedure with 1-(chloromethyl)-4-vinylbenzene (14.1 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:6) to give the product **5ag** (24.5 mg, 64% yield) as a colorless solid. R_f = 0.3 (EtOAc:hexanes = 1:6); m.p. = 133–136 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.06 (m, 11H), 4.62 (t, *J* = 7.1 Hz, 1H), 4.48 (s, 2H), 3.97 – 3.78 (m, 2H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 141.6, 141.4, 136.5, 136.1, 129.6, 129.0, 128.8, 128.1, 127.9, 127.5, 127.0, 61.4, 46.0, 45.8, 21.6 ppm; IR (thin film): 2977, 1597, 1494, 1314, 1296, 1163, 1136, 1087, 933, 906, 809, 763, 739, 700, 680, 638 cm^{-1}; HRMS calculated for $C_{22}H_{21}ClO_2SNa$ 407.0843, found 407.0841 $[M+Na]^+$.

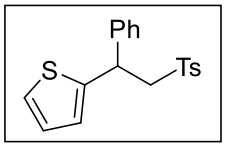


2-(1-Phenyl-2-tosylethyl)pyridine (5ah): The reaction was performed following the General Procedure with 2-vinylpyridine (10.8 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product **5ah** (21.3 mg, 63% yield) as a colorless solid. R_f = 0.2 (EtOAc:hexanes = 1:3); m.p. = 113–116 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.43 (m, 1H), 7.25 – 7.06 (m, 8H), 7.06 – 6.97 (m, 1H), 4.72 – 4.53 (m, 2H), 3.72 (dd, *J* = 14.2, 5.0 Hz, 1H), 2.36 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 149.1, 144.0, 141.3, 136.9, 136.6, 129.4, 128.8, 128.0, 127.8, 127.1, 123.7, 121.7, 60.4, 47.7, 21.5 ppm; IR

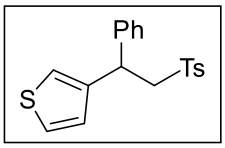
(thin film): 2867, 2361, 1588, 1419, 1286, 1131, 925, 797, 778, 744, 701, 636 cm^{-1}; HRMS calculated for $C_{20}H_{20}NO_2S$ 338.1209, found 338.1204 $[M+H]^+$.



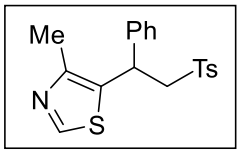
3-(1-Phenyl-2-tosylethyl)pyridine (5ai): The reaction was performed following the General Procedure with 3-vinylpyridine (10.7 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product **5ai** (17.5 mg, 52% yield) as a colorless solid. R_f = 0.2 (EtOAc:hexanes = 1:3); m.p. = 107–109 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 14.7 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.05 (m, 8H), 4.63 (t, *J* = 7.1 Hz, 1H), 3.95 – 3.81 (m, 2H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 148.1, 144.7, 140.6, 136.3, 135.1, 129.8, 129.0, 128.0, 127.4, 127.3, 123.6, 60.9, 43.9, 21.6 ppm; IR (thin film): 1304, 1136, 1084, 746, 697 cm^{-1}; HRMS calculated for $C_{20}H_{20}NO_2S$ 338.1209, found 338.1206 $[M+H]^+$.



2-(1-Phenyl-2-tosylethyl)thiophene (4al) (from 2-vinylthiophene): The reaction was performed following the General Procedure with 2-vinylthiophene (10.5 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4al** (17.0 mg, 50% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6).

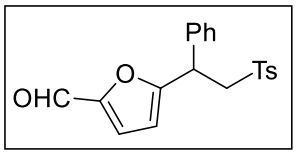


3-(1-Phenyl-2-tosylethyl)thiophene (4am) (from 3-vinylthiophene): The reaction was performed following the General Procedure with 3-vinylthiophene (11.0 mg, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **4am** (22.0 mg, 64% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6).

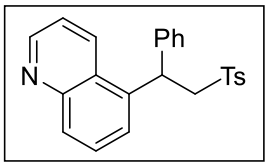


4-Methyl-5-(1-phenyl-2-tosylethyl)thiazole (5aj): The reaction was performed following the General Procedure with 4-methyl-5-vinylthiazole (11.5 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product **5aj** (21.4 mg, 60% yield) as a colorless solid. R_f = 0.3 (EtOAc:hexanes = 1:6); m.p. = 112–114 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 2H),

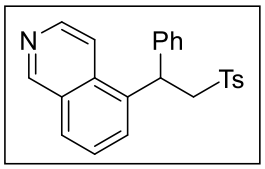
7.34 – 7.13 (m, 7H), 4.95 (dd, *J* = 7.8, 6.3 Hz, 1H), 3.92 – 3.75 (m, 2H), 2.48 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 149.3, 144.6, 140.5, 136.4, 133.0, 129.7, 129.1, 127.9, 127.5, 127.2, 62.9, 38.9, 21.6, 15.4 ppm; IR (thin film): 2361, 1559, 1397, 1290, 1153, 1082, 877, 802, 780, 749, 705 cm^{-1}; HRMS calculated for $C_{19}H_{20}NO_2S_2$ 358.0930, found 358.0935 $[M+H]^+$.



5-(1-Phenyl-2-tosylethyl)furan-2-carbaldehyde (5ak): The reaction was performed following the General Procedure with 5-vinylfuran-2-carbaldehyde (12.2 mg, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:4) to give the product **5ak** (10.6 mg, 30% yield) as a colorless solid. R_f = 0.3 (EtOAc:hexanes = 1:3); m.p. = 95–97 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.14 (m, 7H), 7.05 (d, *J* = 3.6 Hz, 1H), 6.29 (d, *J* = 3.6 Hz, 1H), 4.75 (dd, *J* = 9.0, 5.4 Hz, 1H), 4.12 (dd, *J* = 14.5, 9.0 Hz, 1H), 3.66 (dd, *J* = 14.5, 5.4 Hz, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 159.8, 152.4, 144.7, 138.1, 136.2, 129.8, 129.2, 128.0, 127.6, 122.5, 110.4, 59.6, 40.7, 21.6 ppm; IR (thin film): 2980, 1679, 1511, 1297, 1135, 1084, 1024, 805, 751, 703 cm^{-1}; HRMS calculated for $C_{20}H_{19}O_4S$ 355.0999, found 355.0996 $[M+H]^+$.

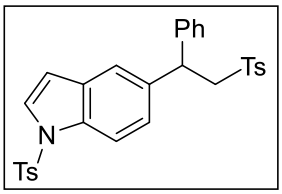


5-(1-Phenyl-2-tosylethyl)quinolone (5al): The reaction was performed following the General Procedure with 5-vinylquinoline (15.5 mg, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product **5al** (24.0 mg, 62% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:1); m.p. = 170–172 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 2.5 Hz, 1H), 8.50 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.35 (m, 4H), 7.33 – 7.09 (m, 6H), 7.03 (d, *J* = 7.8 Hz, 2H), 5.45 (t, *J* = 6.7 Hz, 1H), 3.99 (d, *J* = 6.7 Hz, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 148.8, 144.5, 140.6, 137.3, 136.3, 131.6, 129.5, 129.1, 128.9, 128.7, 127.9, 127.8, 127.2, 126.2, 125.5, 121.4, 61.5, 40.9, 21.5 ppm; IR (thin film): 2924, 1593, 1493, 1453, 1315, 1261, 1144, 984, 805, 775, 708, 661, 622 cm^{-1}; HRMS calculated for $C_{24}H_{22}NO_2S$ 388.1366, found 388.1365 $[M+H]^+$.

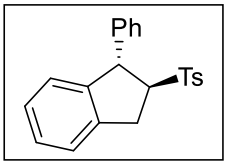


5-(1-Phenyl-2-tosylethyl)isoquinoline (5am): The reaction was performed following the General Procedure with 5-vinylisoquinoline (15.5 mg, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash

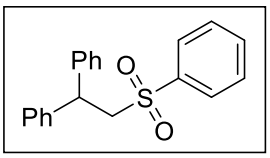
chromatography on silica gel (eluted with EtOAc:hexanes = 1:1) to give the product **5am** (21.0 mg, 54% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:1); m.p. = 164–167 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.54 (d, *J* = 5.5 Hz, 1H), 7.86 (d, *J* = 5.5 Hz, 1H), 7.83 – 7.73 (m, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.25 – 7.11 (m, 5H), 7.05 (d, *J* = 7.8 Hz, 2H), 5.39 (t, *J* = 6.5 Hz, 1H), 3.98 (d, *J* = 6.5 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 144.5, 143.8, 140.3, 136.4, 136.2, 133.8, 130.2, 129.5, 129.2, 128.9, 128.0, 127.9, 127.3, 127.2, 126.6, 116.1, 61.1, 41.0, 21.5 ppm; IR (thin film): 1496, 1316, 1146, 1087, 985, 776, 708, 661, 621 cm^{-1}; HRMS calculated for $C_{24}H_{22}NO_2S$ 388.1366, found 388.1364 $[M+H]^+$.



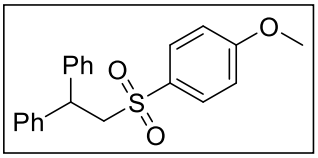
5-(1-Phenyl-2-tosylethyl)-1-tosyl-1*H*-indole (5an): The reaction was performed following the General Procedure with 1-tosyl-5-vinyl-1*H*-indole (29.7 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product **5an** (34.0 mg, 64% yield) as a colorless solid. R_f = 0.2 (EtOAc:hexanes = 1:3); m.p. = 182–185 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 3H), 7.50 (d, *J* = 3.7 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.09 (m, 8H), 7.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.47 – 6.44 (m, 1H), 4.66 (t, *J* = 7.2 Hz, 1H), 3.98 – 3.82 (m, 2H), 2.33 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.2, 141.8, 136.5, 136.2, 135.3, 133.5, 130.9, 130.0, 129.3, 128.8, 127.9, 127.5, 126.9, 126.6, 124.6, 120.2, 113.7, 108.7, 61.8, 46.2, 21.6, 21.4 ppm; IR (thin film): 2360, 2341, 1457, 1367, 1290, 1172, 1126, 996, 807, 761, 727, 702, 670 cm^{-1}; HRMS calculated for $C_{30}H_{28}NO_4S_2$ 530.1454, found 530.1450 $[M+H]^+$.



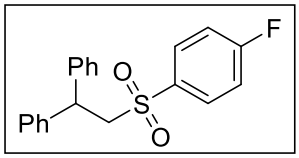
(1*S*,2*S*)-1-Phenyl-2-tosyl-2,3-dihydro-1*H*-indene (5ao): The reaction was performed following the General Procedure with 1*H*-indene (18.3 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:15) to give the product **5ao** (14.6 mg, 42% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 124–128 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.08 (m, 8H), 6.94 – 6.88 (m, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 4.84 (d, *J* = 6.6 Hz, 1H), 4.07 – 3.98 (m, 1H), 3.64 – 3.53 (m, 1H), 3.44 – 3.31 (m, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 143.8, 142.7, 139.4, 135.3, 129.7, 128.7, 128.6, 128.1, 127.6, 127.5, 126.9, 125.2, 124.2, 71.6, 52.4, 33.1, 21.6 ppm; IR (thin film): 2920, 2361, 1596, 1454, 1419, 1287, 1144, 815, 782, 755, 699, 670, 631 cm^{-1}; HRMS calculated for $C_{22}H_{21}O_2S$ 349.1257, found 349.1255 $[M+H]^+$.



(2-(Phenylsulfonyl)ethane-1,1-diyl)dibenzene (6aa): The reaction was performed following the General Procedure with **1a** (18.3 μL, 0.10 mmol), *S*-methyl-benzenesulfonothioate (37.6 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **6aa** (22.5 mg, 70% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.51 – 7.44 (m, 1H), 7.37 – 7.29 (m, 2H), 7.23 – 7.09 (m, 10H), 4.63 (t, *J* = 7.1 Hz, 1H), 3.92 (d, *J* = 7.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 139.6, 133.3, 128.9, 128.8, 128.0, 127.6, 127.0, 61.5, 46.2 ppm. IR (thin film): 2927, 2362, 1736, 1494, 1448, 1306, 1295, 1135, 779, 684, 630 cm^{-1}; HRMS calculated for $C_{20}H_{18}O_2S$ 323.1100, found 323.1098 $[M+H]^+$. Other spectroscopic data were previously reported.[4]

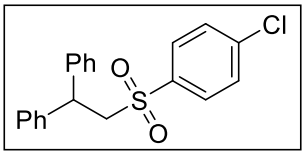


(2-((4-Methoxyphenyl)sulfonyl)ethane-1,1-diyl)dibenzene (6ab): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl 4-methoxybenzenesulfonothioate (43.6 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:8) to give the product **6ab** (26.8 mg, 76% yield) as a colorless solid. R_f = 0.3 (EtOAc:hexanes = 1:6); m.p. = 124–126 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.9 Hz, 2H), 7.24 – 7.05 (m, 10H), 6.77 (d, *J* = 8.9 Hz, 2H), 4.60 (t, *J* = 7.1 Hz, 1H), 3.88 (d, *J* = 7.1 Hz, 2H), 3.82 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 141.5, 131.1, 130.2, 128.7, 127.6, 126.9, 114.1, 61.7, 55.6, 46.3 ppm; IR (thin film): 1594, 1497, 1296, 1254, 1161, 1136, 1084, 1015, 934, 904, 804, 743, 701 cm^{-1}; HRMS calculated for $C_{21}H_{21}O_3S$ 353.1206, found 353.1205 $[M+H]^+$.

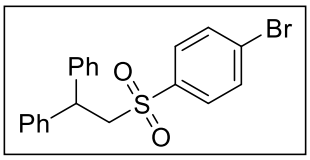


(2-((4-Fluorophenyl)sulfonyl)ethane-1,1-diyl)dibenzene (6ac): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl 4-fluorobenzenesulfonothioate (41.2 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:8) to give the product **6ac** (24.8 mg, 73% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 150–153 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.56 (m, 2H), 7.23 – 7.04 (m, 10H), 7.03 – 6.89 (m, 2H), 4.62 (t, *J* = 7.2 Hz, 1H), 3.92 (d, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4 (d, $J_{C\text{-}F}$ = 256.3 Hz), 141.1, 135.6 (d, $J_{C\text{-}F}$ = 3.1 Hz), 130.8 (d, $J_{C\text{-}F}$ = 9.7 Hz), 128.8, 127.6, 127.1, 116.1 (d, $J_{C\text{-}F}$ = 22.7 Hz), 61.7, 46.4 ppm; IR (thin film): 1591, 1492, 1311, 1289, 1237, 1153,

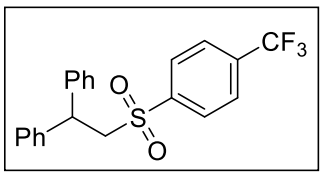
1085, 834, 770, 704, 636 cm^{-1}; HRMS calculated for $C_{20}H_{18}FO_2S$ 341.1006, found 341.1003 $[M+H]^+$.



(2-((4-Chlorophenyl)sulfonyl)ethane-1,1-diyl)dibenzene (6ad): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl 4-chlorobenzenesulfonothioate (44.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **6ad** (21.6 mg, 70% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 160–163 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 2H), 7.27 – 7.23 (m, 2H), 7.22 – 7.08 (m, 10H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.92 (d, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.0, 138.0, 129.5, 129.1, 128.8, 127.6, 127.1, 61.6, 46.3 ppm; IR (thin film): 2973, 1582, 1493, 1454, 1399, 1308, 1277, 1161, 1138, 1088, 923, 905, 818, 780, 747, 704 cm^{-1}; HRMS calculated for $C_{20}H_{17}ClO_2SNa$ 379.0530, found 379.0531 $[M+Na]^+$.

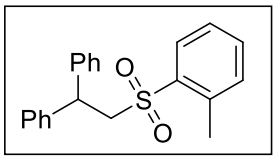


(2-((4-Bromophenyl)sulfonyl)ethane-1,1-diyl)dibenzene (6ae): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl 4-bromobenzenesulfonothioate (53.2 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **6ae** (20.5 mg, 51% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 160–162 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 4H), 7.23 – 7.06 (m, 10H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.91 (d, *J* = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 138.5, 132.1, 129.5, 128.8, 128.6, 127.6, 127.1, 61.6, 46.3 ppm; IR (thin film): 1574, 1493, 1308, 1163, 1138, 1085, 906, 816, 777, 747, 704 cm^{-1}; HRMS calculated for $C_{20}H_{17}BrO_2SNa$ 423.0025, found 423.0021 $[M+Na]^+$.

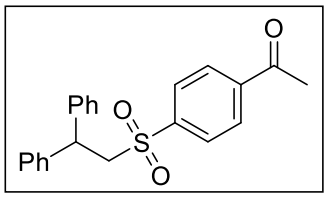


(2-((4-(Trifluoromethyl)phenyl)sulfonyl)ethane-1,1-diyl)dibenzene (6af): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl 4-(trifluoromethyl)benzenesulfonothioate (51.2 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and $BzOO^tBu$ (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:10) to give the product **6af** (28.6 mg, 73% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 133–136 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.03 (m, 10H), 4.63 (t, *J* = 7.3 Hz, 1H), 3.96 (d, *J* = 7.3 Hz, 2H) ppm; ^{13}C NMR (100

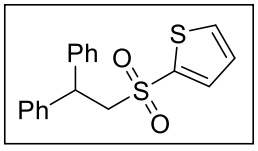
MHz, $CDCl_3$) δ 143.0, 140.8, 134.7 (q, J_{C-F} = 33.2 Hz), 128.8, 128.6, 127.6, 127.2, 125.9 (q, J_{C-F} = 3.7 Hz), 123.1 (q, J_{C-F} = 273.1 Hz), 61.5, 46.4 ppm; IR (thin film): 1404, 1322, 1164, 1126, 1088, 1061, 905, 835, 791, 764, 744, 702 cm^{-1}; HRMS calculated for $C_{21}H_{17}F_3O_2SNa$ 413.0794, found 413.0792 $[M+Na]^+$.



(2-(*o*-Tolylsulfonyl)ethane-1,1-diyl)dibenzene (6ag): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl 2-methylbenzene sulfonothioate 40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:12) to give the product **6ag** (25.3 mg, 75% yield) as a colorless solid. R_f = 0.5 (EtOAc:hexanes = 1:6); m.p. = 130–133 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H), 7.41 – 7.30 (m, 1H), 7.22 – 7.06 (m, 12H), 4.60 (t, *J* = 7.0 Hz, 1H), 3.94 (d, *J* = 7.0 Hz, 2H), 2.60 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 137.6, 137.5, 133.4, 132.4, 130.3, 128.7, 127.5, 127.0, 126.4, 60.6, 46.1, 20.4 ppm; IR (thin film): 1494, 1455, 1304, 1159, 1125, 1081, 1057, 920, 904, 771, 745, 702 cm^{-1}; HRMS calculated for $C_{21}H_{21}O_2S$ 337.1257, found 337.1253 $[M+H]^+$.

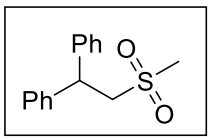


1-(4-((2,2-Diphenylethyl)sulfonyl)phenyl)ethan-1-one (6ah): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl 4-acetylbenzenesulfonothioate (46.0 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1: 3) to give the product **6ah** (21.8 mg, 60% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:3); m.p. = 139–141 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.08 (m, 10H), 4.64 (t, *J* = 7.2 Hz, 1H), 3.95 (d, *J* = 7.2 Hz, 2H), 2.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 143.3, 141.0, 140.3, 128.8, 128.5, 128.4, 127.6, 127.1, 61.5, 46.3, 26.9 ppm; IR (thin film): 1683, 1295, 1259, 1135, 1086, 784, 746, 702, 617 cm^{-1}; HRMS calculated for $C_{22}H_{20}O_3SNa$ 387.1025, found 387.1023 $[M+Na]^+$.

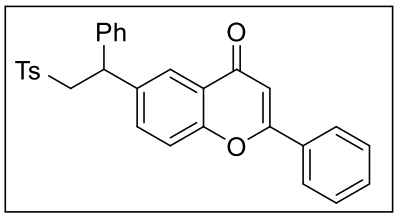


2-((2,2-Diphenylethyl)sulfonyl)thiophene (6ai): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl thiophene-2-sulfonothioate (38.8 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:8) to give the product **6ai** (20.3 mg, 62% yield) as a colorless solid. R_f = 0.4 (EtOAc:hexanes = 1:6); m.p. = 152–154 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.32 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.25 –

7.12 (m, 10H), 6.89 (dd, *J* = 5.0, 3.8 Hz, 1H), 4.67 (t, *J* = 7.1 Hz, 1H), 4.02 (d, *J* = 7.1 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 140.6, 134.4, 133.9, 128.8, 127.7, 127.6, 127.0, 62.8, 46.4 ppm; IR (thin film): 1598, 1494, 1452, 1403, 1307, 1230, 1132, 1091, 1022, 905, 791, 768, 739, 724, 703, 629 cm^{-1}; HRMS calculated for $C_{18}H_{16}O_2S_2Na$ 351.0484, found 351.0482 $[M+Na]^+$.

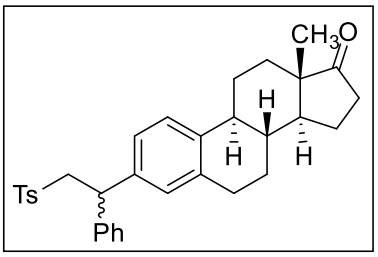


(2-(Methylsulfonyl)ethane-1,1-diyl)dibenzene (6aj): The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), *S*-methyl-methanesulfonothioate (25.2 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product **6aj** (13.0 mg, 50% yield) as a colorless solid. R_f = 0.3 (EtOAc:hexanes = 1:2); m.p. = 101–105 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 8H), 7.28 – 7.22 (m, 2H), 4.67 (t, *J* = 7.3 Hz, 1H), 3.78 (d, *J* = 7.3 Hz, 2H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 129.2, 127.7, 127.5, 60.9, 46.3, 42.0 ppm; IR (thin film): 3648, 2160, 1473, 1419, 1397, 650 cm^{-1}; HRMS calculated for $C_{15}H_{16}O_2SNa$ 283.0763, found 283.0762 $[M+Na]^+$.

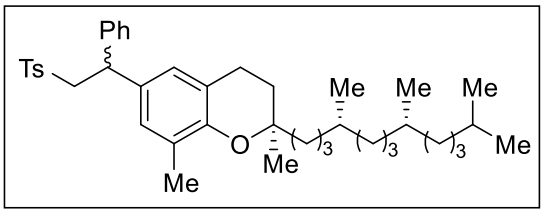


3-Phenyl-6-(1-phenyl-2-tosylethyl)-4*H*-chromen-4-one (5ap): The reaction was performed following the General Procedure with 3-phenyl-6-vinyl-4*H*-chromen-4-one (24.8 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^tBu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product **5ap** (19.4 mg, 40% yield) as a colorless solid. R_f = 0.2 (EtOAc:hexanes = 1:3); m.p. = 192–194 ℃; ^{1}H NMR (400 MHz, CDCl3) δ 7.93 – 7.86 (m, 3H), 7.59 – 7.49 (m, 6H), 7.44 (d, *J* = 8.6 Hz, 1H), 7.26 – 7.09 (m, 7H), 6.79 (s, 1H), 4.73 (dd, *J* = 8.3, 6.1 Hz, 1H), 4.04 (dd, *J* = 14.5, 8.5 Hz, 1H), 3.89 (dd, *J* = 14.5, 6.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 163.5, 155.1, 144.4, 141.1, 138.6, 136.5, 134.1, 131.8, 131.6, 129.6, 129.1, 129.0, 128.0, 127.5, 127.3, 126.3, 123.8, 123.6, 118.6, 107.4, 61.2, 45.8, 21.5 ppm; IR (thin film): 1650, 1452, 1397, 1287, 1134, 1085, 900, 868, 811, 772, 704, 685 cm^{-1}; HRMS calculated for $C_{30}H_{25}O_4S$ 481.1468, found 481.1467 $[M+H]^+$.

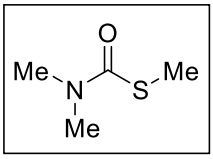
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(1-phenyl-2-tosylethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (5aq): The reaction was performed following the General Procedure with (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (28.0 mg, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %)



and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:3) to give the product **5aq** (26.6 mg, 52% yield, dr = 1:1) as a colorless solid. R_f = 0.3 (EtOAc:hexanes = 1:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.3, 2.3 Hz, 2H), 7.22 – 7.04 (m, 8H), 6.94 – 6.89 (m, 1H), 6.81 (s, 1H), 4.56 – 4.50 (m, 1H), 3.88 (d, *J* = 7.2 Hz, 2H), 2.86 – 2.64 (m, 2H), 2.49 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.40 – 2.30 (m, 4H), 2.24 – 2.16 (m, 1H), 2.12 (dd, *J* = 18.8, 9.0 Hz, 1H), 2.06 – 1.92 (m, 3H), 1.66 – 1.55 (m, 1H), 1.53 – 1.42 (m, 4H), 1.38 – 1.29 (m, 1H), 0.89 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.8, 144.0, 141.6, 138.9, 138.8, 138.4, 136.8, 136.7, 129.4, 128.7, 128.2, 128.1, 128.0, 127.6, 126.8, 125.7, 125.6, 125.0, 124.9, 61.6, 50.5, 48.0, 45.9, 44.3, 38.1, 38.0, 35.9, 31.6, 29.4, 26.5, 25.7, 21.7, 21.6, 13.9 ppm; IR (thin film): 2925, 2360, 1735, 1598, 1495, 1453, 1298, 1085, 1007, 813, 756, 699, 642 cm^{-1}; HRMS calculated for $C_{33}H_{37}O_3S$ 513.2458, found 513.2457 $[M+H]^+$.



(2*R*)-2,8-Dimethyl-6-(1-phenyl-2-tosylethyl)-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chromane (5ar): The reaction was performed following the General Procedure with (*R*)-2,8-dimethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)-6-vinylchromane (41.2 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:15) to give the product **5ar** (27.0 mg, 42% yield, dr = 1:1) as a colorless oil. R_f = 0.6 (EtOAc:hexanes = 1:6); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.04 (m, 7H), 6.60 – 6.58 (m, 2H), 4.45 (t, *J* = 7.2 Hz, 1H), 3.92 – 3.78 (m, 2H), 2.69 – 2.48 (m, 2H), 2.35 (s, 3H), 1.98 (d, *J* = 4.1 Hz, 3H), 1.78 – 1.62 (m, 2H), 1.57 – 1.47 (m, 3H), 1.38 – 1.33 (m, 3H), 1.29 – 1.22 (m, 6H), 1.20 (d, *J* = 6.1 Hz, 4H), 1.16 – 1.10 (m, 3H), 1.08 – 1.03 (m, 3H), 0.91 – 0.80 (m, 14H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 143.8, 142.3, 136.8, 131.2, 131.1, 129.2, 128.6, 128.0, 127.5, 127.4, 127.3, 126.6, 126.3, 126.1, 126.0, 120.3, 120.2, 75.9, 75.8, 62.0, 61.9, 45.7, 40.5, 40.4, 39.4, 37.5, 37.3, 32.8, 32.7, 31.0, 28.0, 24.8, 24.5, 24.2, 24.1, 22.8, 22.7, 22.3, 21.6, 21.0, 20.9, 19.8, 19.7, 16.1 ppm; IR (thin film): 2924, 2361, 1599, 1455, 1377, 1299, 1228, 1149, 1134, 1086, 872, 812, 754, 699, 653 cm^{-1}; HRMS calculated for $C_{42}H_{60}O_3SNa$ 667.4155, found 667.4153 $[M+Na]^+$.

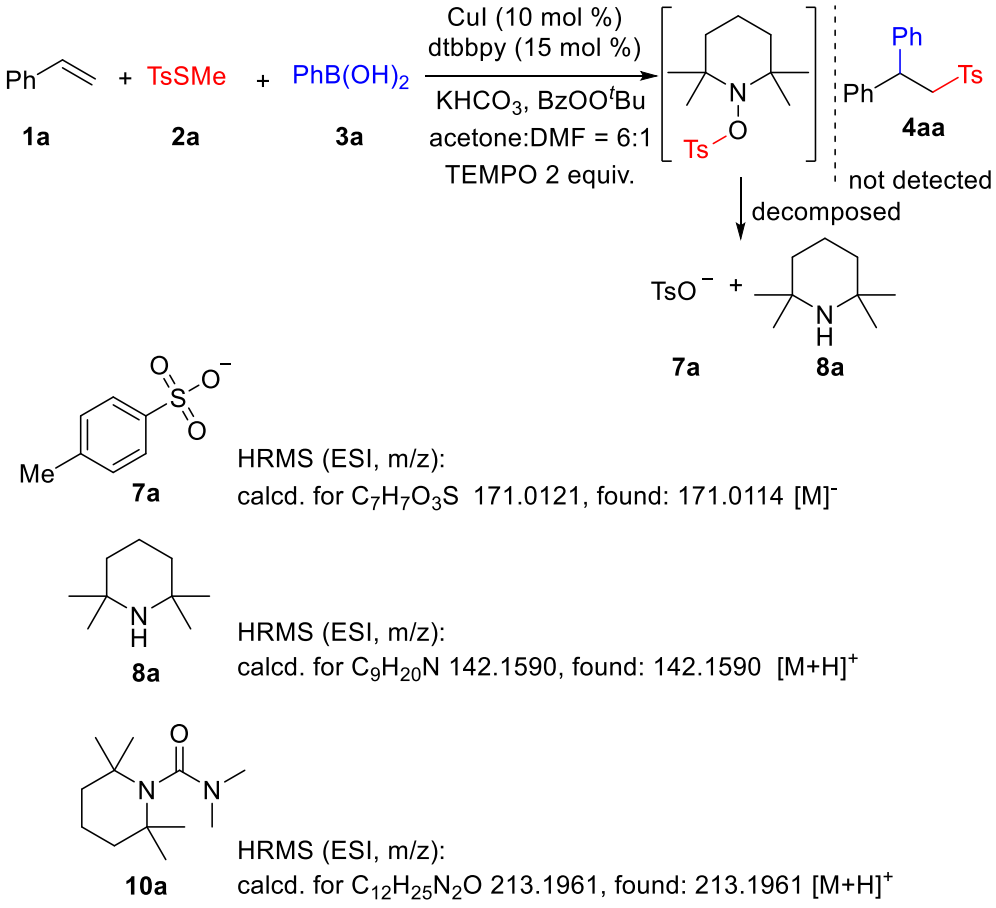


***S*-Methyl dimethylcarbamothioate (11a)**: The reaction was performed following the General Procedure with **1a** (11.6 μL, 0.10 mmol), **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy

(4.0 mg, 15 mol %) and BzOO^{t}Bu (57.1 μL, 0.30 mmol). **11a** was obtained in 72% assay yield (determined by ^{1}H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 as internal standard). The crude product was purified by flash chromatography on silica gel (eluted with EtOAc:hexanes = 1:2) to give the product **11a** (14.2 mg, 60% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (s, 6H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 36.6, 13.1 ppm. Other spectroscopic data were previously reported.[5]

5. Mechanism Study

1) Typical procedure for radical trapping with TEMPO

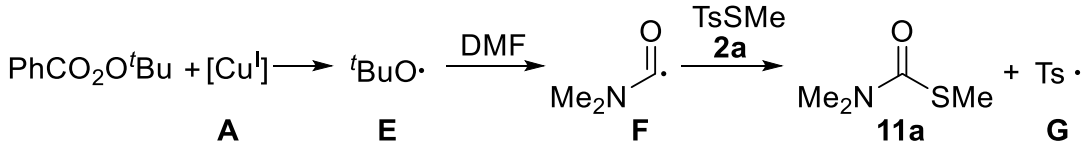


Scheme S1: Radical trapping with TEMPO

To an oven-dried microwave vial equipped with a stir bar was added *S*-methyl 4-methylbenzenesulfonothioate (**2a**) (40.4 mg, 0.20 mmol), phenylboronic acid **(3a)** (30.5 mg, 0.25 mmol), TEMPO (32.2 mg, 0.2 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) under an argon atmosphere in a glove box. A mix solvent of acetone (0.6 mL) and DMF (0.1 mL) was added to the vial by syringe. The microwave vial was sealed with a cap and removed from the glove box. Then, styrene (**1a**) (11.6 μL, 0.10 mmol) and BzOO^{t}Bu (57.1 μL, 0.30 mmol) were added by syringe under an argon atmosphere. The reaction mixture was heated to 40 ℃ in an oil bath and stirred for 12 h. Upon completion of the reaction, the sealed vial was cooled to room temperature, and opened to air. No product **4aa**

was detected by ^{1}H NMR.

2) Investigation of methyl thiosulfonate in the standard reaction



Scheme S2: Complementary mechanism

To an oven-dried microwave vial equipped with a stir bar was added **2a** (40.4 mg, 0.20 mmol), **3a** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) under an argon atmosphere in a glove box. A mix solvent of acetone (0.6 mL) and DMF (0.1 mL) was added to the vial by syringe. The microwave vial was sealed with a cap and removed from the glove box. Then, **1a** (11.6 μL, 0.10 mmol) and BzOO^{t}Bu (57.1 μL, 0.30 mmol) were added by syringe under argon atmosphere. The reaction mixture was heated to 40 ℃ in an oil bath and stirred for 12 h. The resulting solution was subjected to reduced pressure to remove the volatile materials. **11a** was obtained in 72% assay yield (determined by ^{1}H NMR analysis of the crude reaction mixtures using 0.1 mmol CH_2Br_2 as internal standard). The relevant literature supports this reaction process.[6] Radical **F** can be trapped by TEMPO in radical trapping experiments.

3) UV/Vis-Absorption Spectra of the Reaction Components

Preparation of the samples for UV-Vis spectra measurement. *(All the samples were used freshly for UV-Vis spectra measurement.)*

Copper complexes: To an oven-dried microwave vial equipped with a stir bar was added CuI (1.9 mg) and dtbbpy (4.0 mg) under an argon atmosphere in a glove box. A mix solvent (1 mL, acetone:DMF = 6:1) was added to the vial by syringe. After stirring for 10 minutes, the solution (120 μL) was diluted with mix solvent (3.5 mL, acetone:DMF = 6:1). The diluted solution was immediately transferred into a cuvette by syringe, and it was capped and removed from the glove box. Measurement of solution in the colorimetric vessel by UV was conducted.

Copper complexes and BzOO^{t}Bu: To an oven-dried microwave vial equipped with a stir bar was added CuI (1.9 mg) and dtbbpy (4.0 mg) under an argon atmosphere in a glove box. A mix solvent of acetone (1.2 mL) and DMF (0.2 mL) was added to the vial by syringe. After stirring for 10 minutes, BzOO^{t}Bu (57.1 μL) was added to the solution under argon atmosphere. The solution was immediately transferred into a cuvette by syringe, and it was capped and removed from the glove box. Measurement of the resulting solution by UV was conducted.

Reaction solution: To an oven-dried microwave vial equipped with a stir bar was added *S*-methyl 4-methylbenzenesulfonothioate (**2a**) (40.4 mg, 0.20 mmol), phenylboronic acid (**3a**) (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg), dtbbpy (4.0 mg, 15 mol %) under an argon atmosphere in a glove box. A mix solvent of acetone (0.6 mL) and DMF (0.1 mL) was added to the vial by syringe.

The microwave vial was sealed and removed from the glove box. Then, styrene (**1a**) (11.6 μL, 0.10 mmol) and BzOO^{t}Bu (57.1 μL, 0.30 mmol) were added by syringe under an argon atmosphere. The reaction mixture was heated to 40 ℃ in an oil bath and stirred for 6 h. The reaction solution was transferred into a cuvette by syringe under an argon atmosphere, and then a mix solvent of acetone (0.6 mL) and DMF (0.1 mL) was added under argon. Measurement of the solution in colorimetric vessel by UV was conducted.

4) EPR Studies with DMPO

Typical procedure for EPR studies: To an oven-dried microwave vial equipped with a stir bar was added *S*-methyl-4-methylbenzenesulfonothioate **(2a)** (40.4 mg, 0.20 mmol), phenylboronic acid **(3a)** (30.5 mg, 0.25 mmol), $KHCO_3$ (25.0 mg, 0.25 mmol), CuI (1.9 mg, 10 mol %), dtbbpy (4.0 mg, 15 mol %) under an argon atmosphere in a glove box. A mix solvent of acetone (0.6 mL) and DMF (0.1 mL) was added to the vial by syringe. The microwave vial was sealed and removed from the glove box. Then, styrene (**1a**) (11.6 μL, 0.10 mmol) and BzOO^{t}Bu (57.1 μL, 0.30 mmol) were added by syringe under an argon atmosphere. The reaction was stirred at 40 ℃ for 1 h. Then, DMPO (5,5-dimethyl-1-pyrroline *N*-oxide, 22.6 mg, 0.20 mmol) was added by syringe under an argon atmosphere. After stirring for an additional 10 minutes, the reaction mixture was immediately analyzed by electron paramagnetic resonance (EPR). The EPR spectrum was recorded at room temperature. We hypothesized that sulfonyl radicals were generated in the reaction by DMPO capturing. We did data fitting and HRMS analysis, which further confirmed our hypothesis. EPR spectrometer operated at 9.843461 GHz. Typical spectrometer parameters were: scan range: 200 G; center field set: 3502.60 G; scan time: 20.48 s; modulation amplitude: 1.0 G; modulation frequency: 100.00 kHz. The fitting data are A_N = 13.60 G, A_H = 9.31 G. The existence of **9a** was further established by HRMS. HRMS calculated for $C_{13}H_{18}NO_3S$ 268.1007, found 268.1004 $[M]^{+\cdot}$

5) EPR Studies of Cu(II)

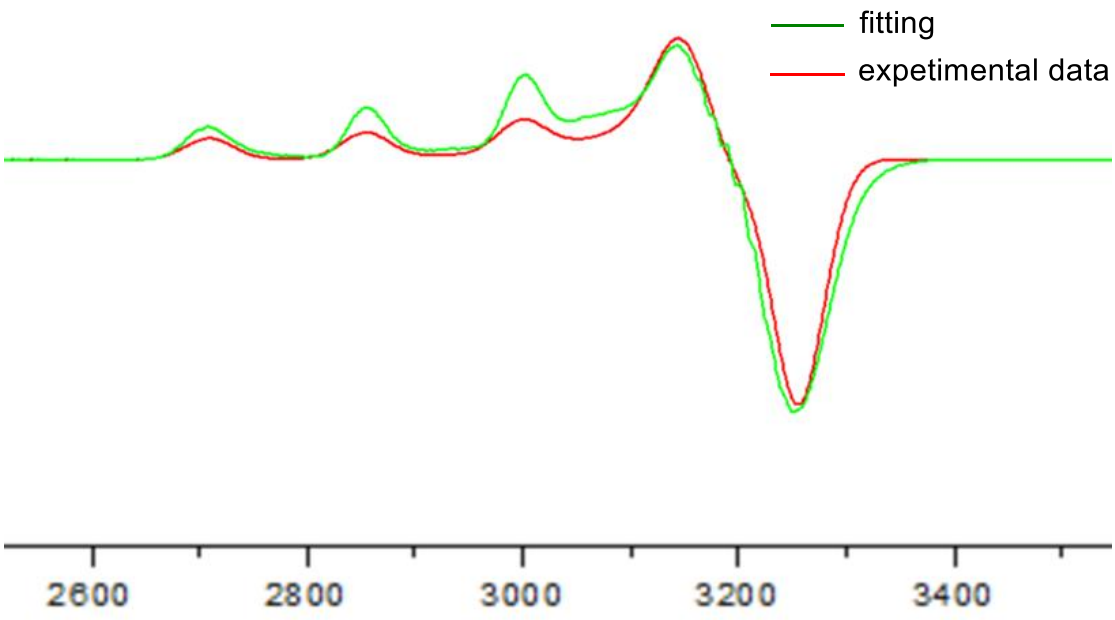


Figure S1. EPR spectra of Cu(II) (the fitting data and experimental data)

Typical procedure for EPR studies: To an oven-dried microwave vial equipped with a stir bar was added CuI (1.9 mg) and dtbbpy (4.0 mg) under argon atmosphere in a glove box. A mix solvent of acetone (1.2 mL) and DMF (0.2 mL) was added to the vial by syringe. After stirring for 10 minutes, BzOO^{t}Bu (57.1 μL) was added to the solution under argon atmosphere. The mixture was analyzed by electron paramagnetic resonance (EPR) immediately. EPR spectrum was recorded at -173 ℃. We did data fitting and further confirmed the Cu(II). EPR spectrometer operated at 9.300692 GHz. Typical spectrometer parameters are shown as follows, scan range: 200 G; center field set: 2900 G; scan time: 140 s; modulation amplitude: 1.0 G; modulation frequency: 100.00 kHz.

6. References

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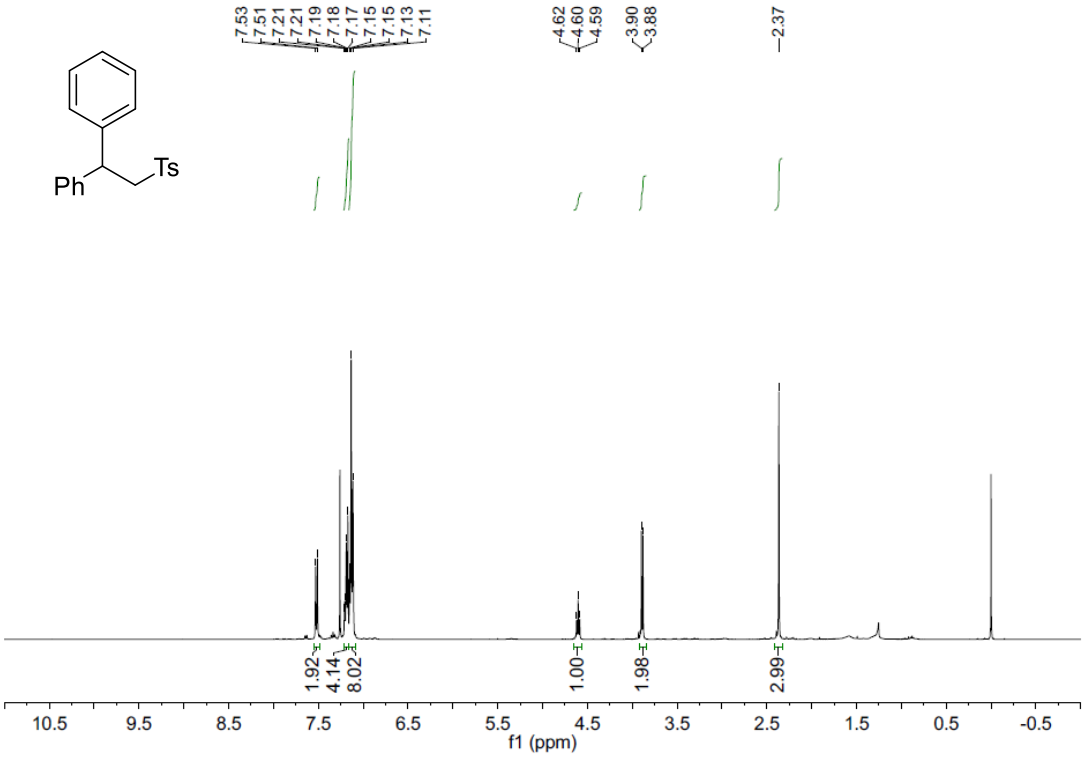
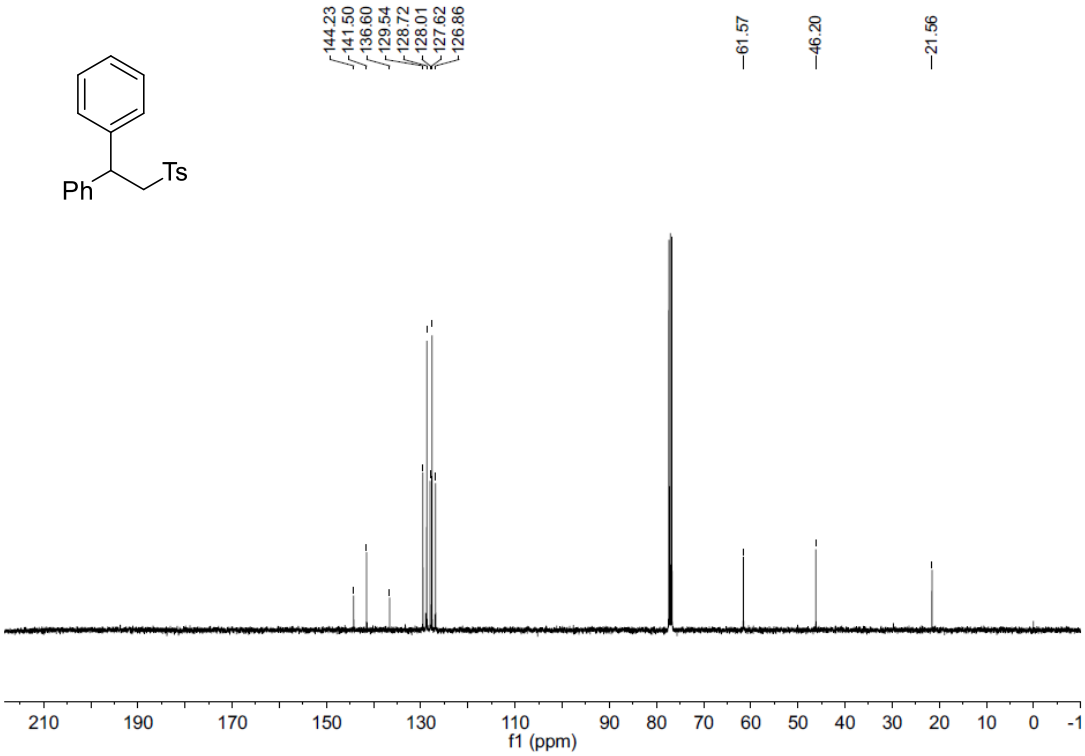
(6) Xiang, J.-n.; Yuan, Y.-q.; Guo, S.-r. $Cu(OAc)_2$-Catalyzed Thiolation of Acyl C-H Bonds with Thiols Using TBHP as An Oxidant. *Synlett* **2013**, *24*, 443-448.

7. NMR Spectra

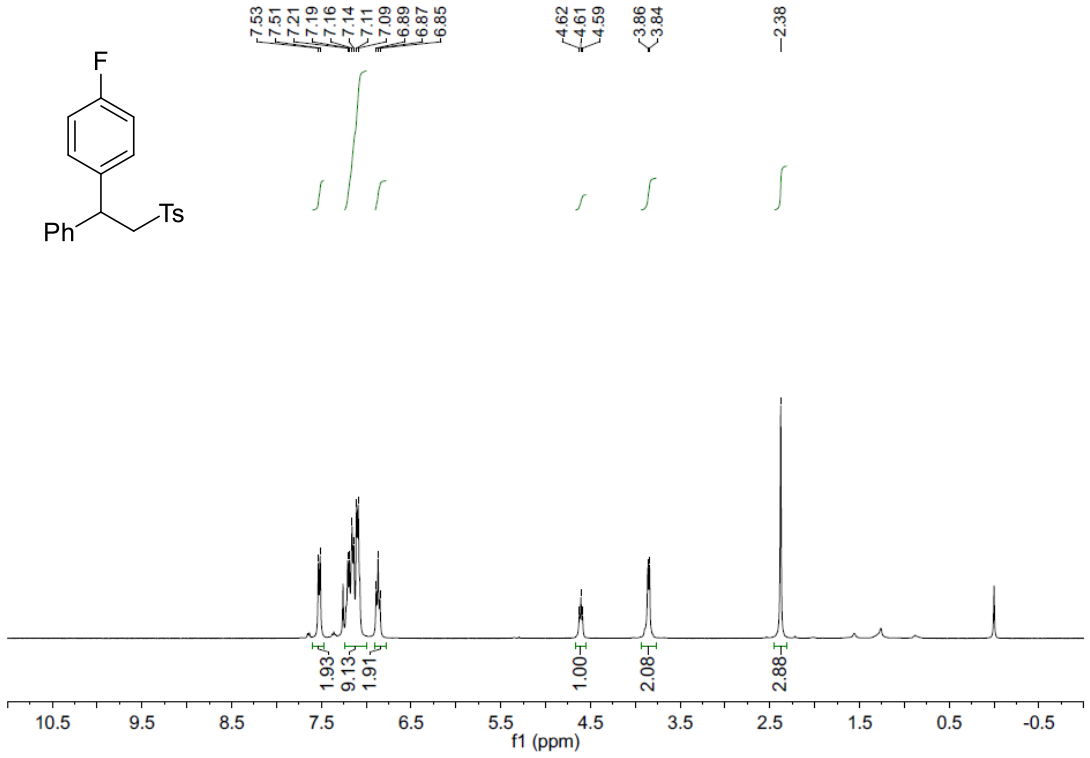
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-Tosylethane-1,1-diyl)dibenzene (4aa)



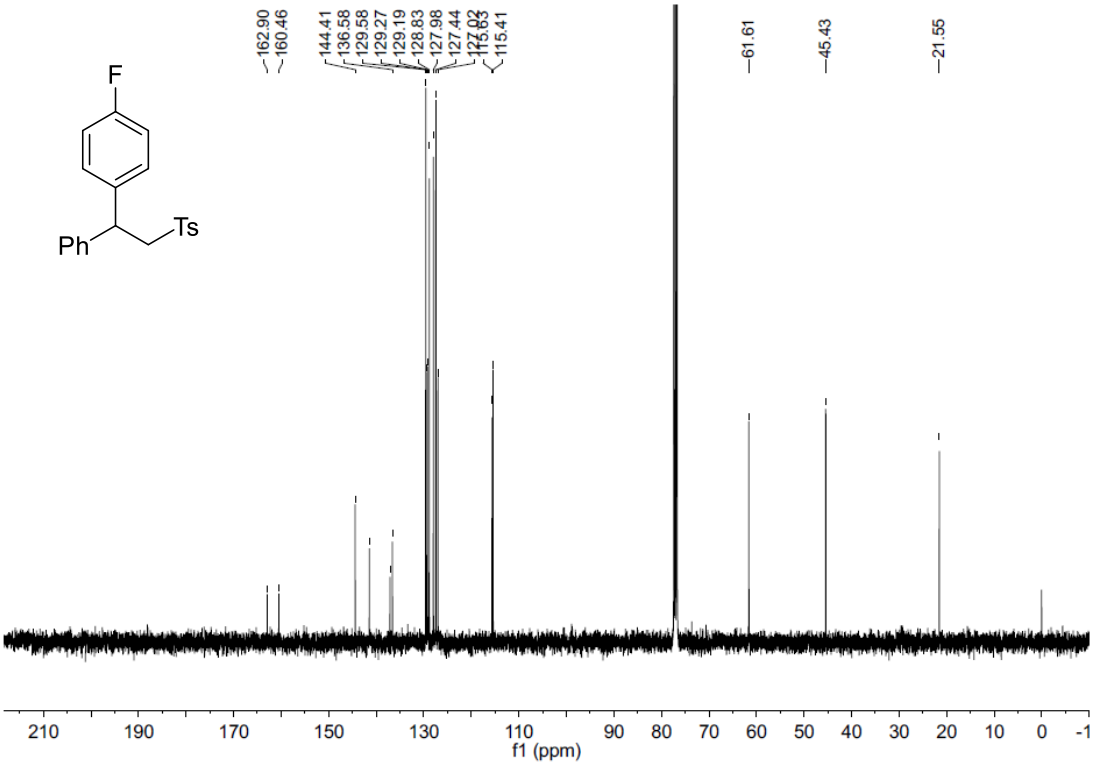
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-Tosylethane-1,1-diyl)dibenzene (4aa)



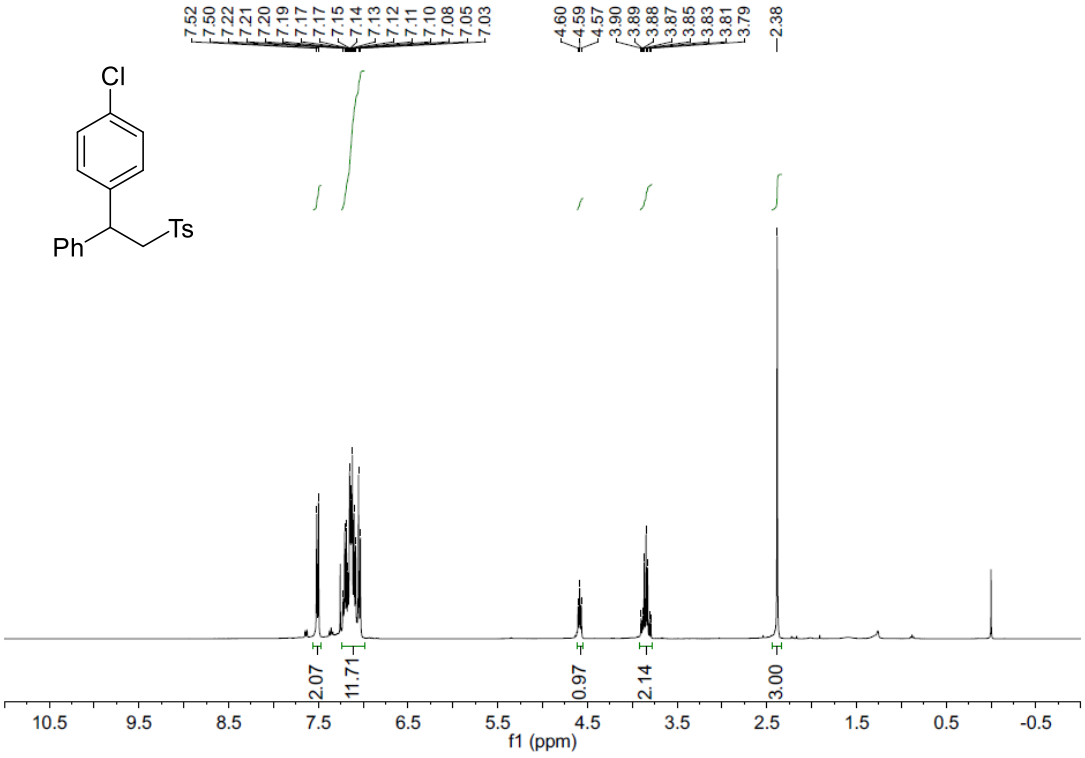
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Fluoro-4-(1-phenyl-2-tosylethyl)benzene (4ab)



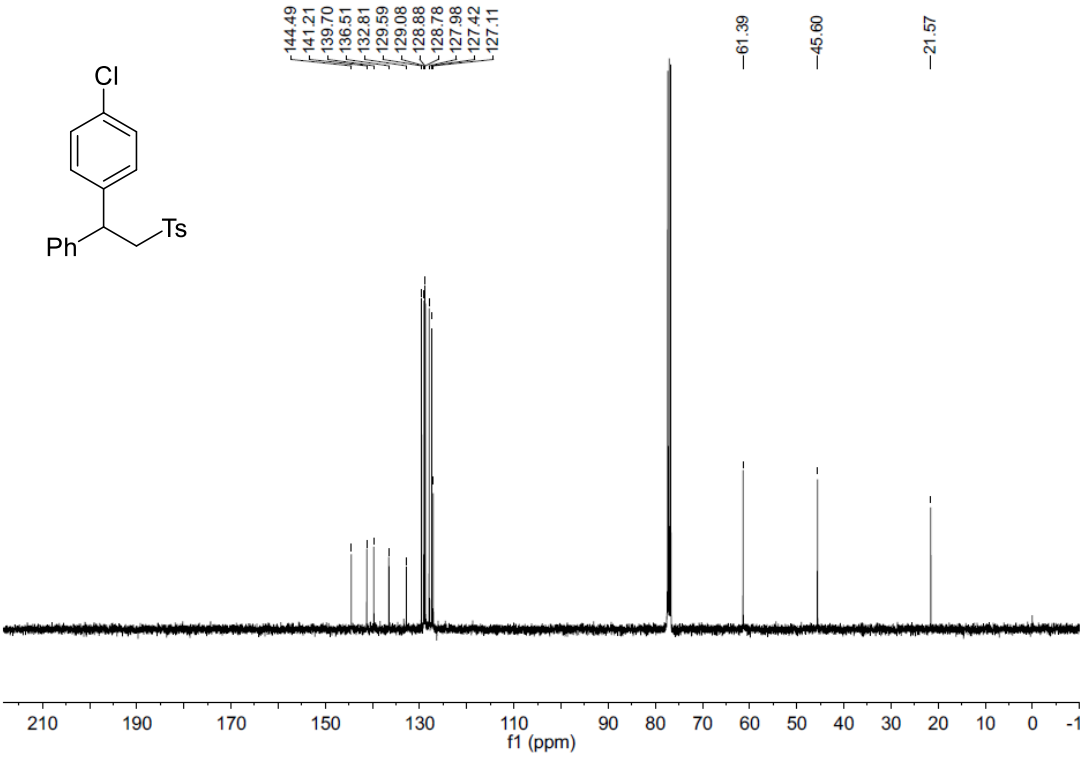
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Fluoro-4-(1-phenyl-2-tosylethyl)benzene (4ab)



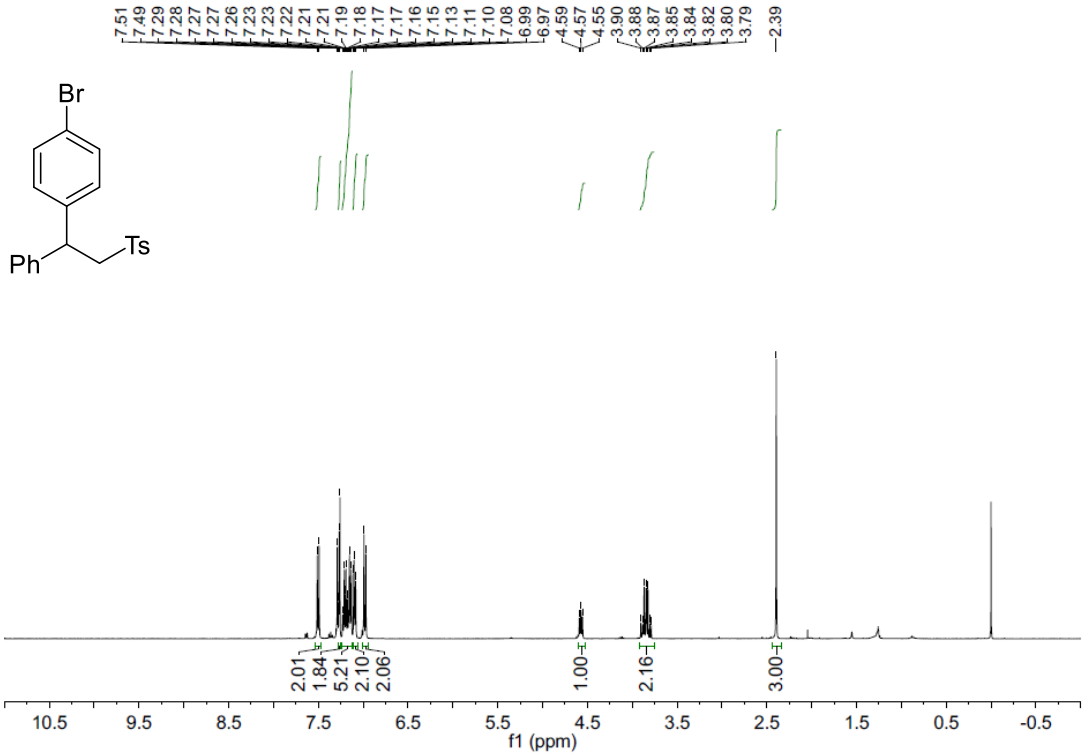
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Chloro-4-(1-phenyl-2-tosylethyl)benzene (4ac)



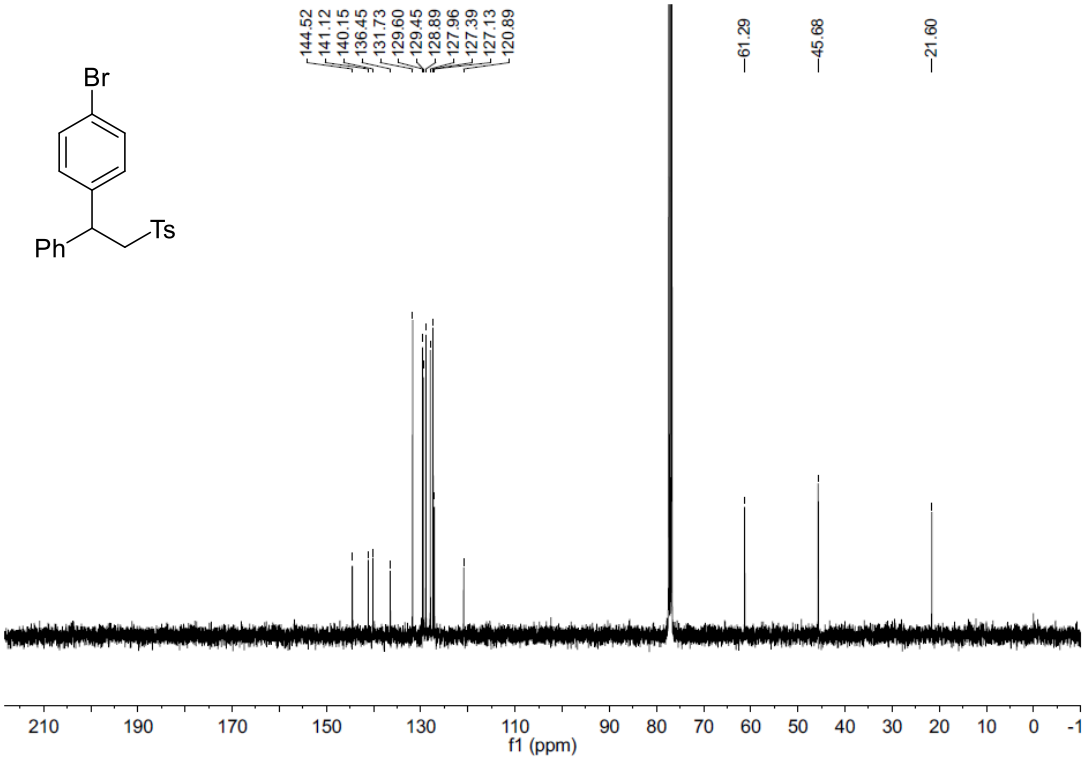
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Chloro-4-(1-phenyl-2-tosylethyl)benzene (4ac)



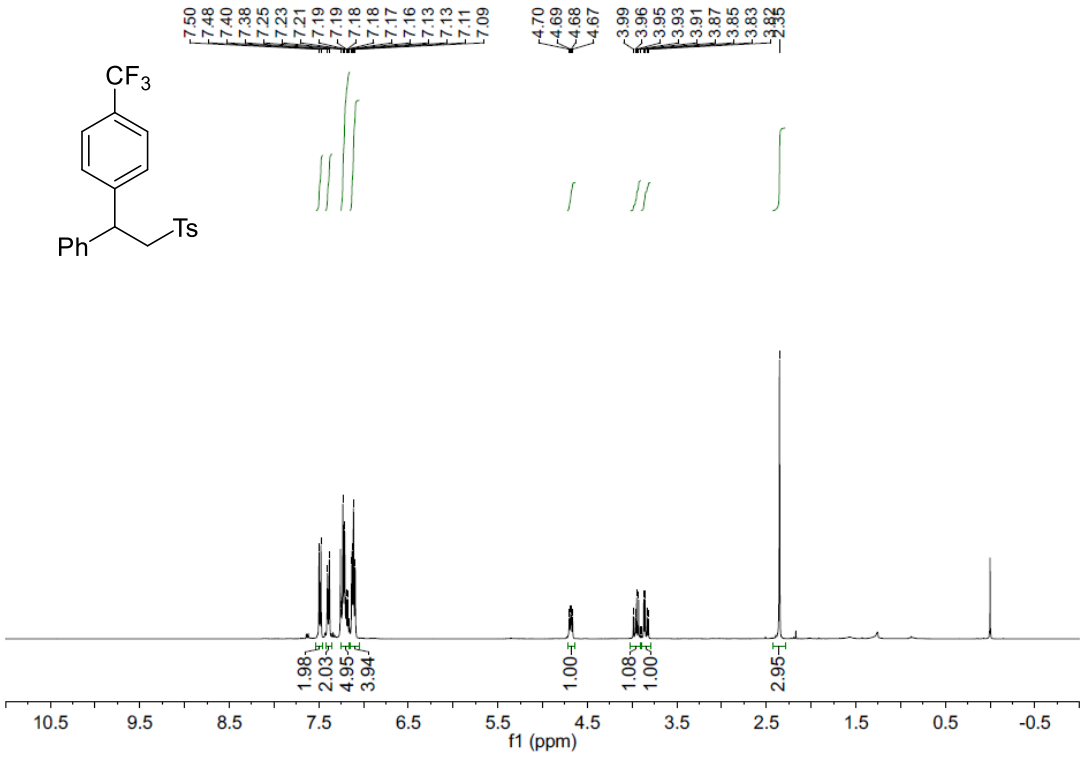
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Bromo-4-(1-phenyl-2-tosylethyl)benzene (4ad)



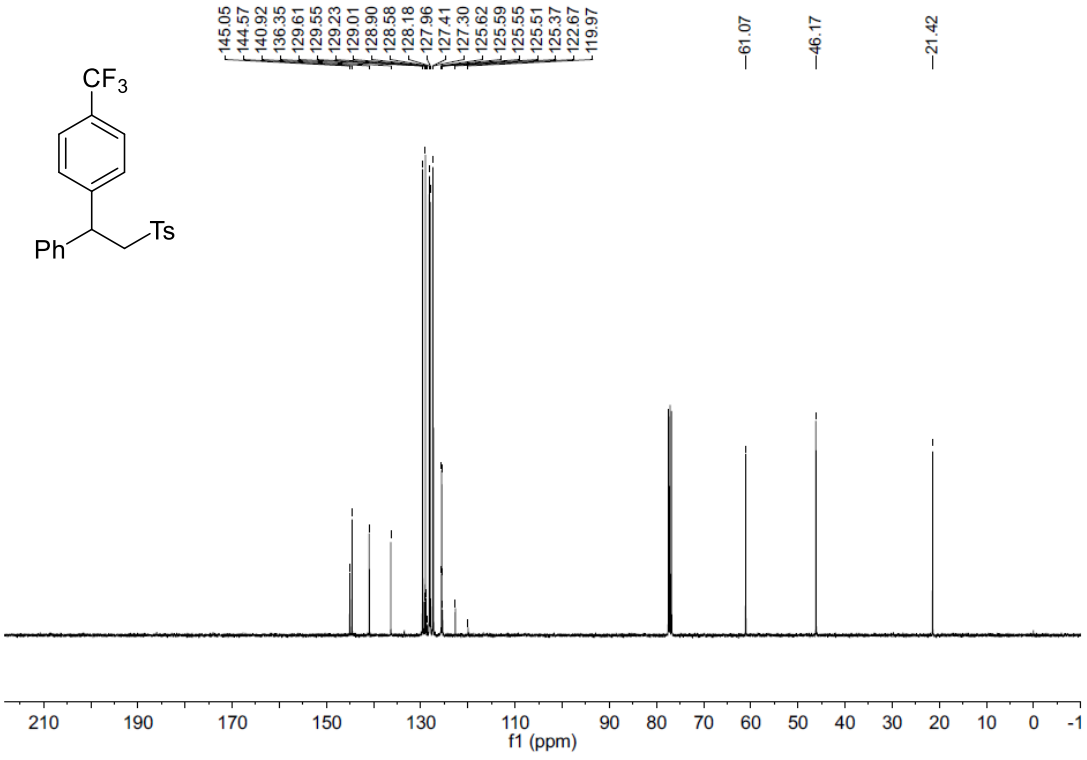
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Bromo-4-(1-phenyl-2-tosylethyl)benzene (4ad)



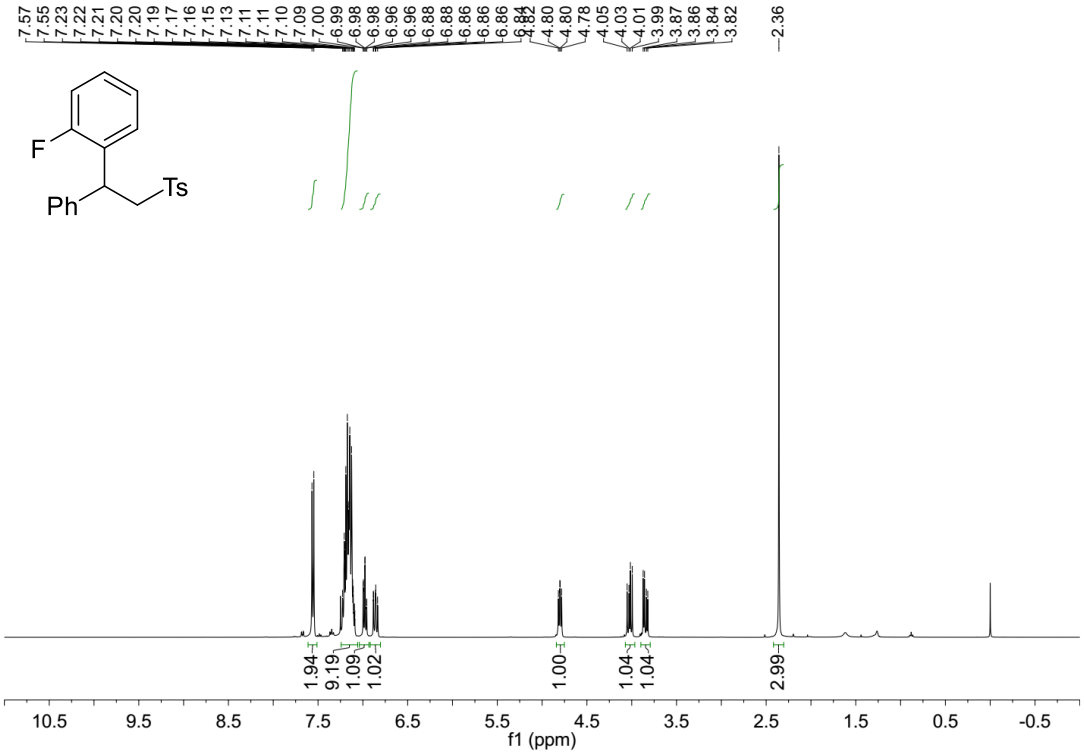
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Methyl-4-((2-phenyl-2-(4-(trifluoromethyl) phenyl)ethyl)sulfonyl)benzene (4ae)



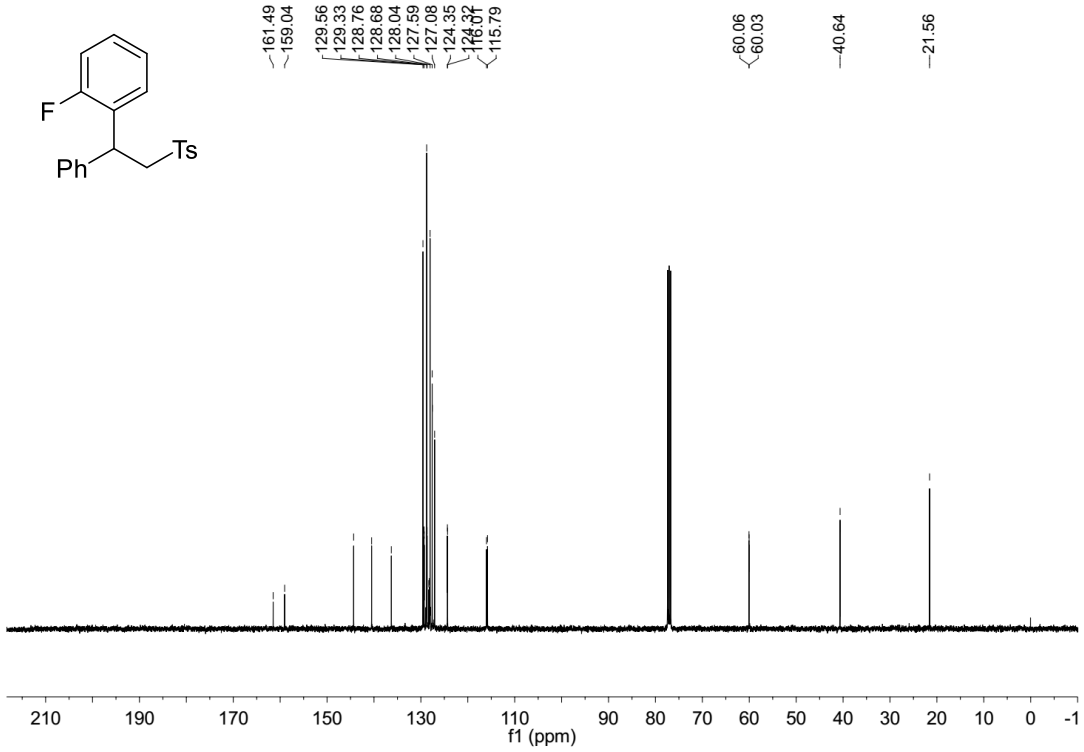
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Methyl-4-((2-phenyl-2-(4-(trifluoromethyl) phenyl)ethyl)sulfonyl)benzene (4ae)



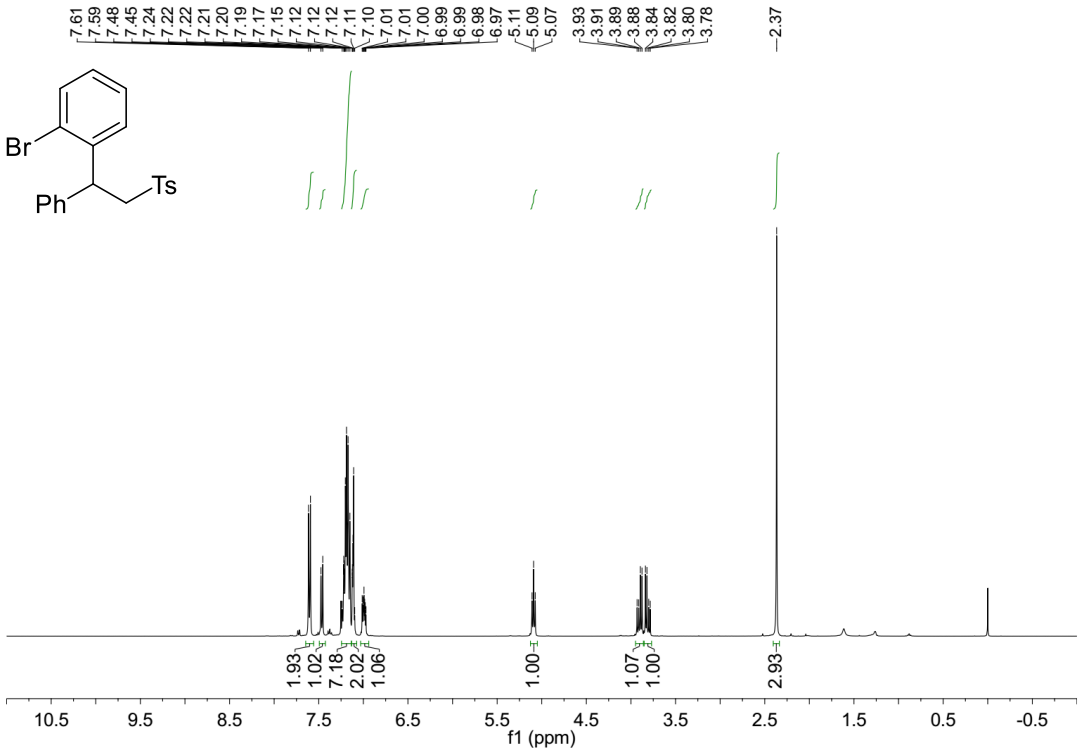
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Fluoro-2-(1-phenyl-2-tosylethyl)benzene (4af)



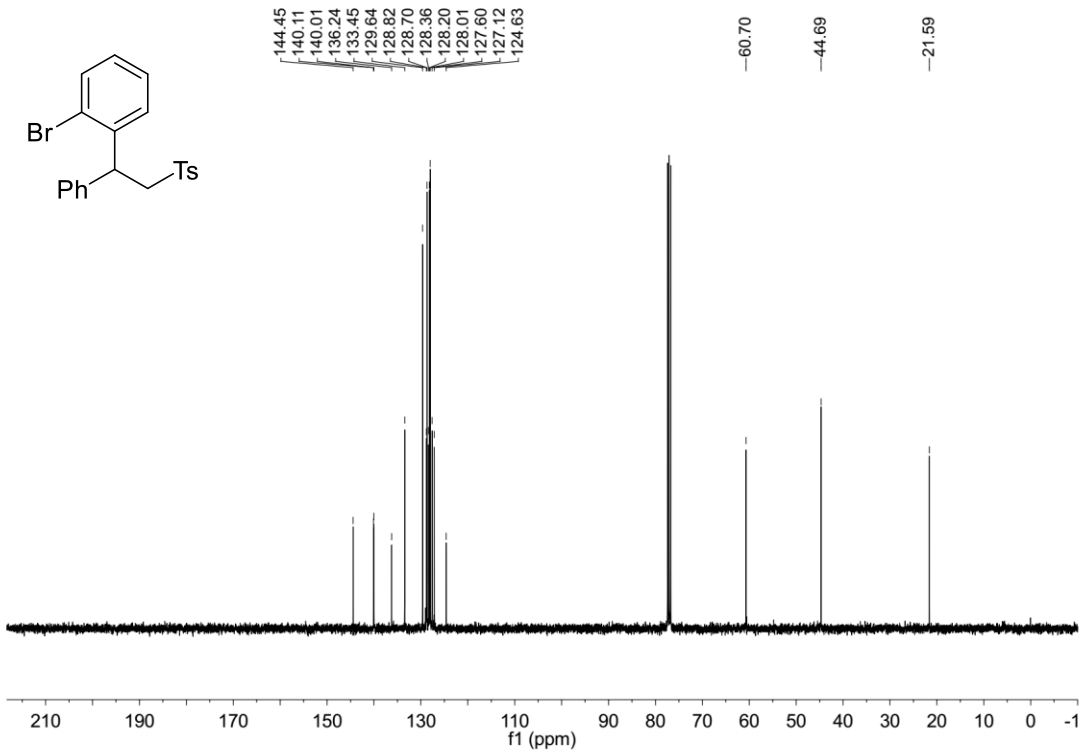
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Fluoro-2-(1-phenyl-2-tosylethyl)benzene (4af)



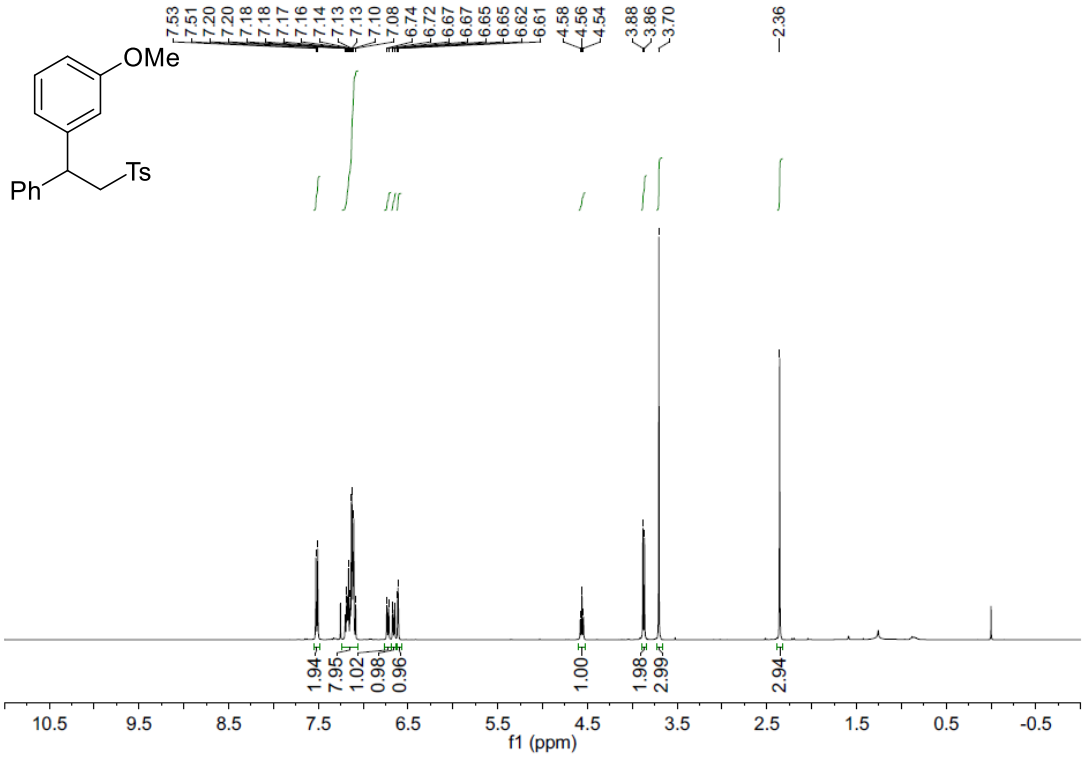
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Bromo-2-(1-phenyl-2-tosylethyl)benzene (4ag)



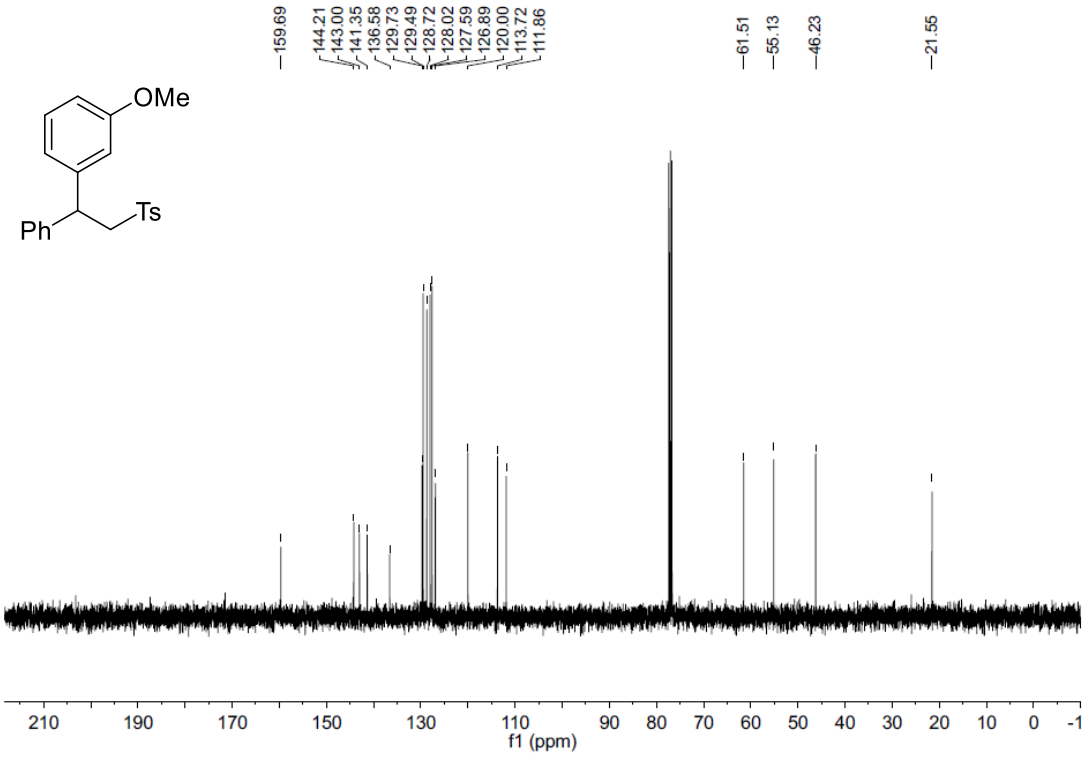
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Bromo-2-(1-phenyl-2-tosylethyl)benzene (4ag)



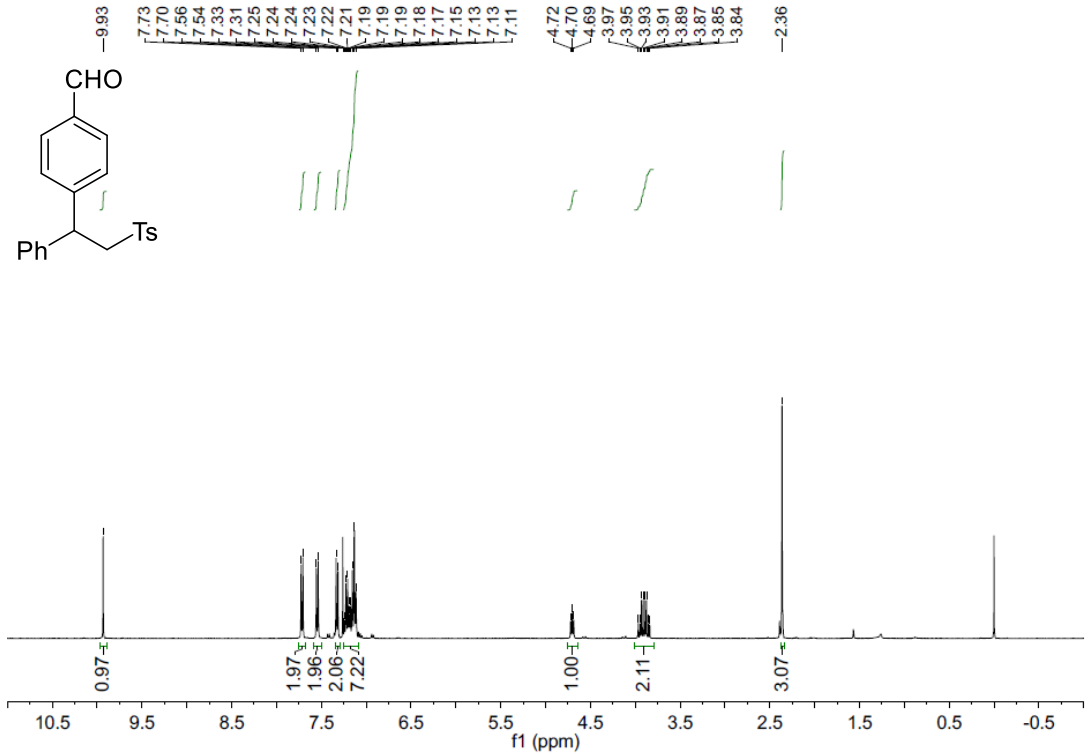
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Methoxy-3-(1-phenyl-2-tosylethyl)benzene (4ah)



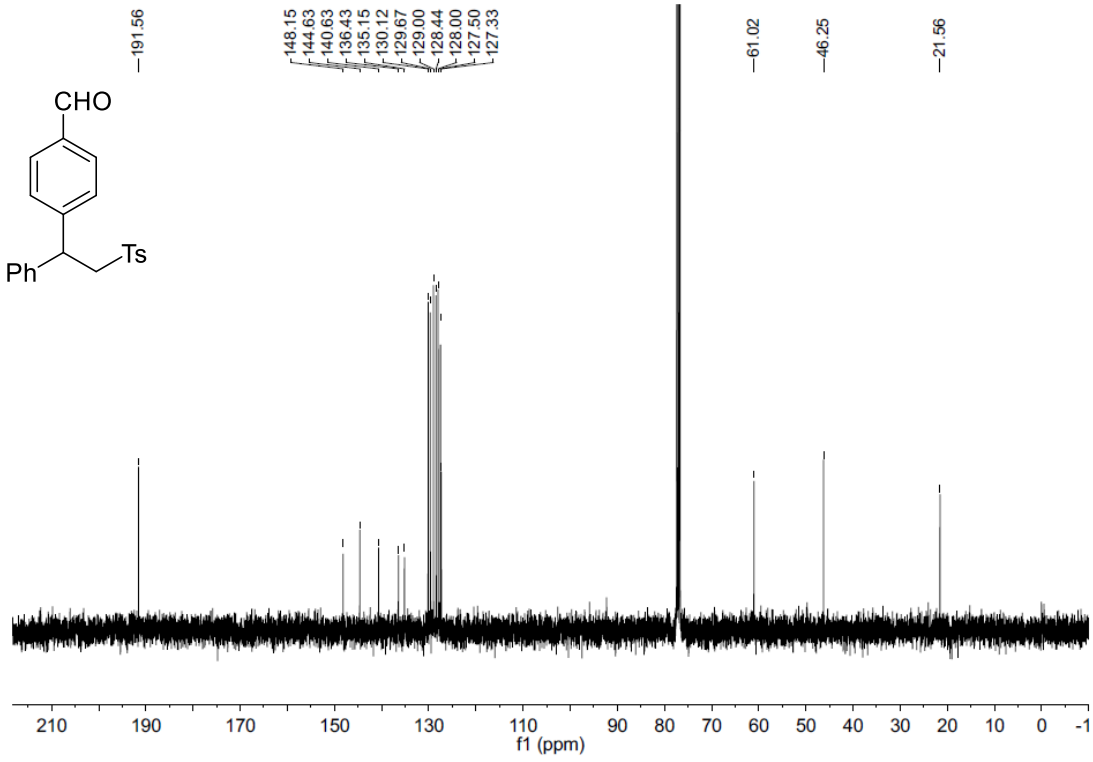
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Methoxy-3-(1-phenyl-2-tosylethyl)benzene (4ah)



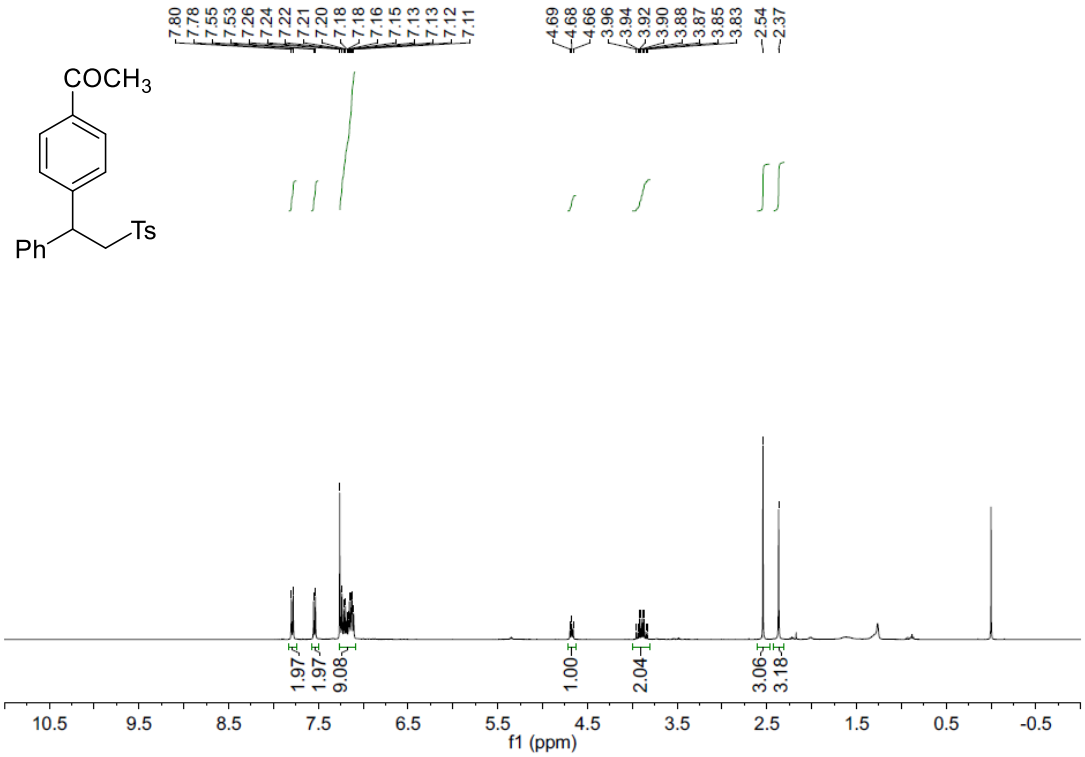
^{1}H NMR ($CDCl_3$, 400 MHz) of 4-(1-Phenyl-2-tosylethyl)benzaldehyde (4ai)



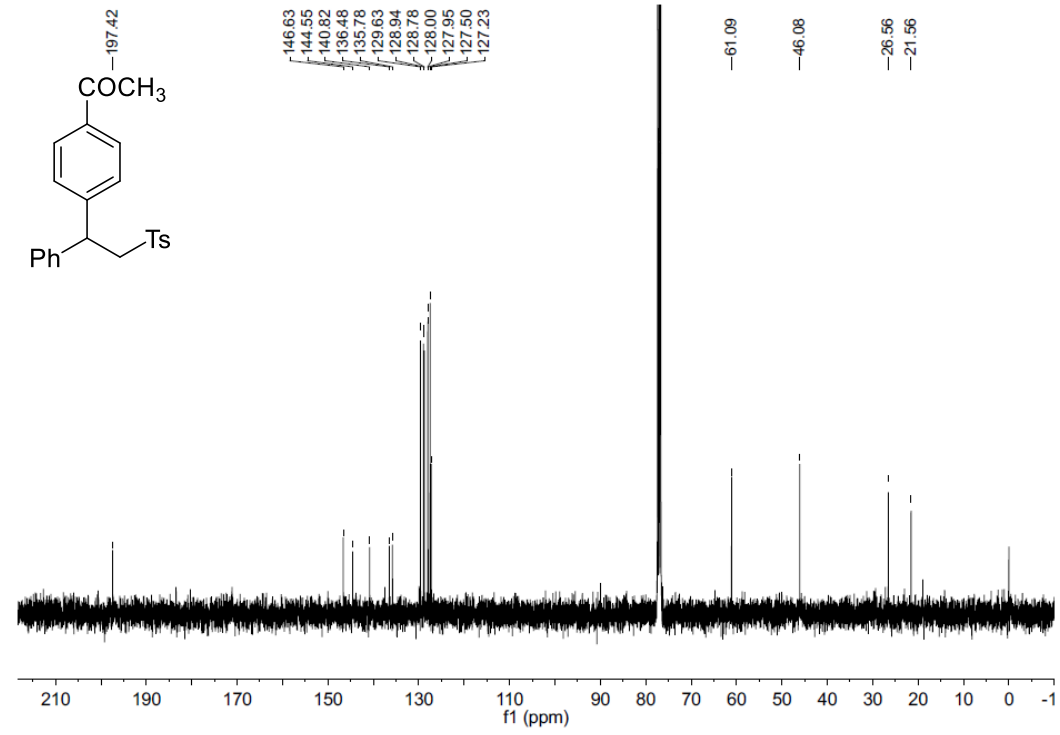
^{13}C NMR ($CDCl_3$, 100 MHz) of 4-(1-Phenyl-2-tosylethyl)benzaldehyde (4ai)



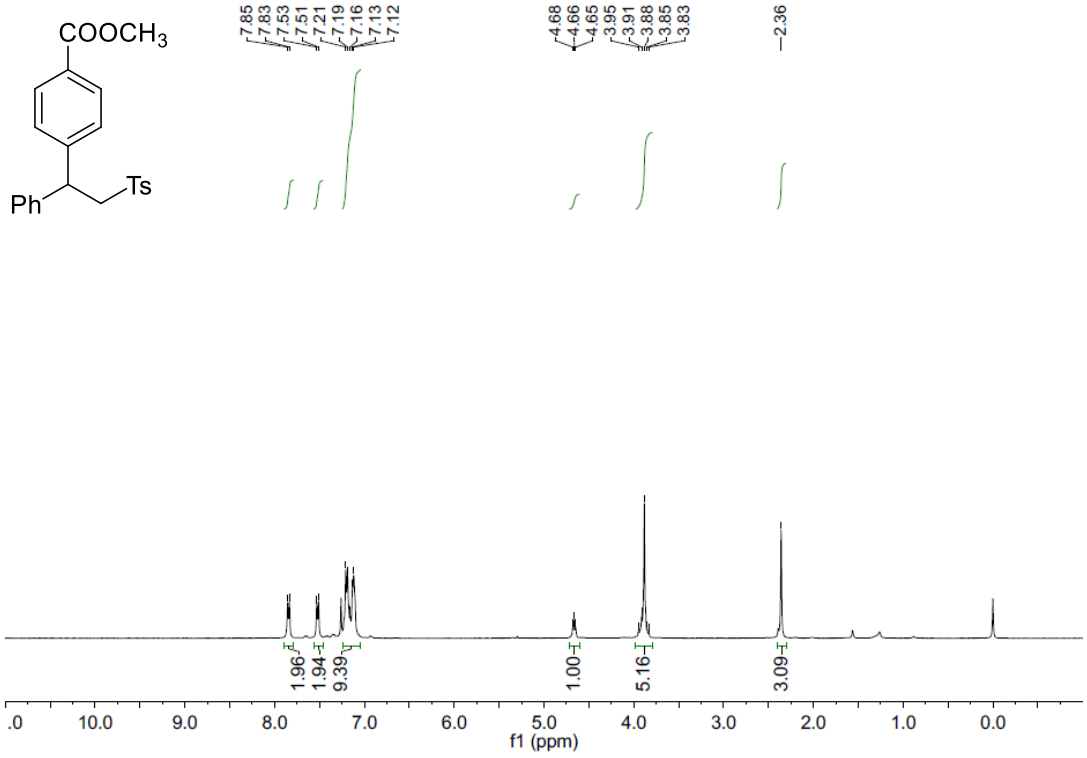
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-(4-(1-Phenyl-2-tosylethyl)phenyl)ethan-1-one (4aj)



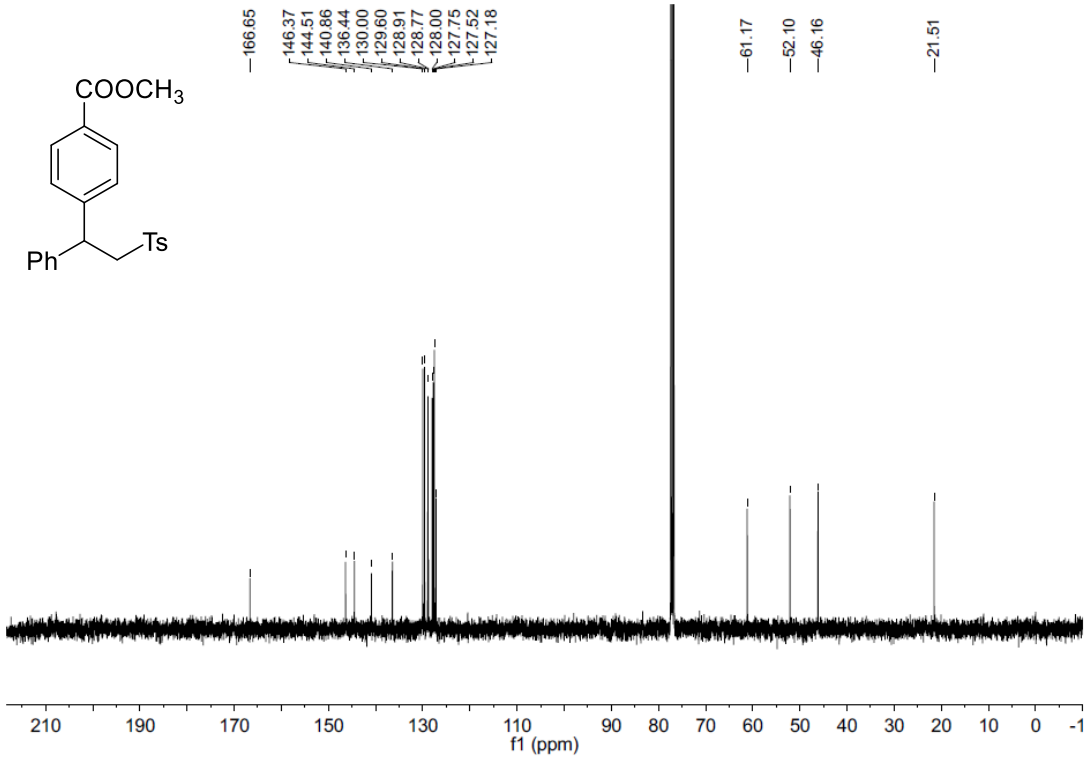
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-(4-(1-Phenyl-2-tosylethyl)phenyl)ethan-1-one (4aj)



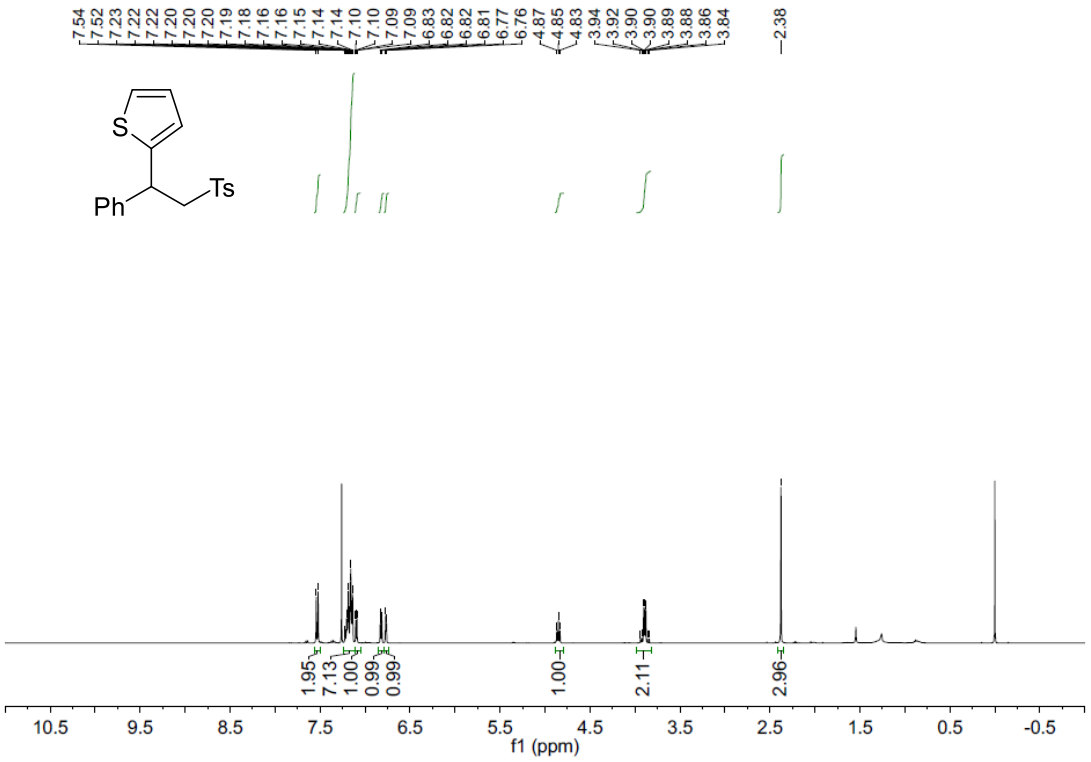
^{1}H NMR ($CDCl_3$, 400 MHz) of Methyl 4-(1-phenyl-2-tosylethyl)benzoate (4ak)



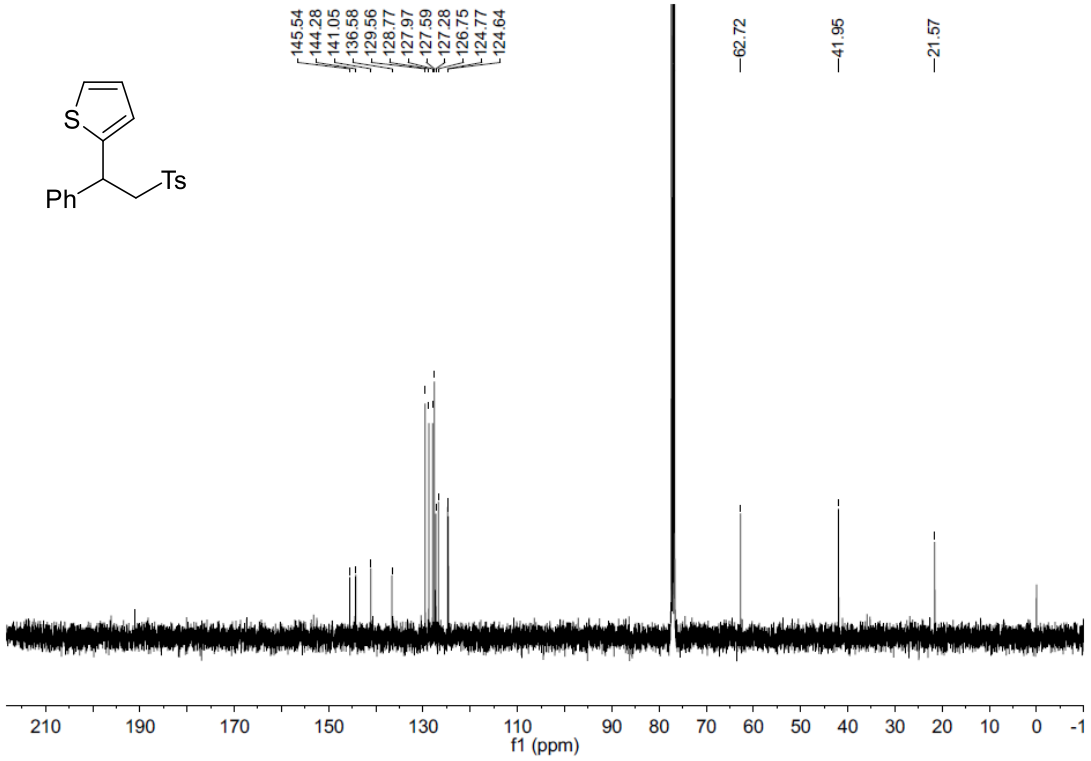
^{13}C NMR ($CDCl_3$, 100 MHz) of Methyl 4-(1-phenyl-2-tosylethyl)benzoate (4ak)



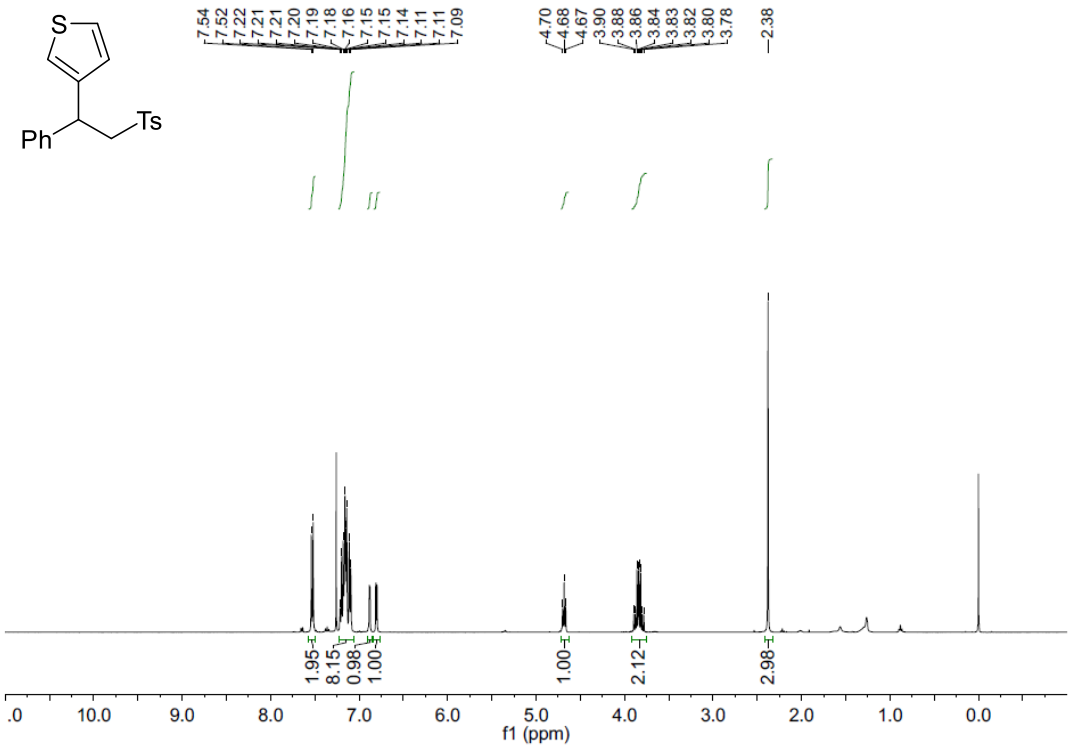
^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(1-Phenyl-2-tosylethyl)thiophene (4al)



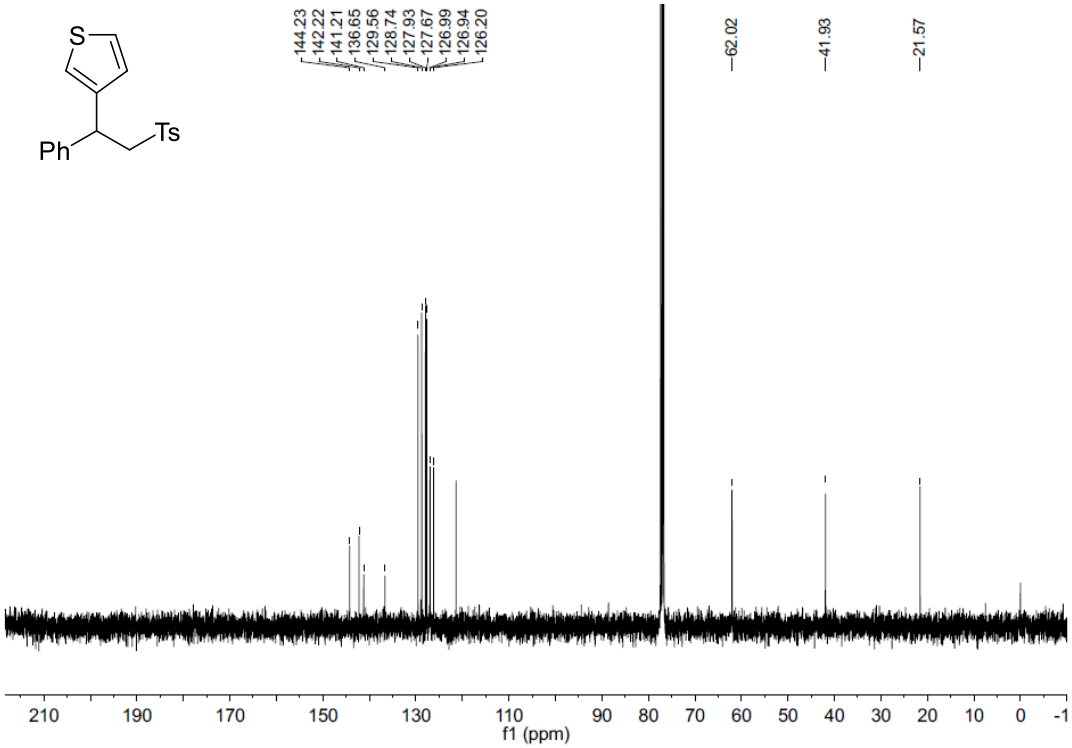
^{13}C NMR ($CDCl_3$, 100 MHz) of 2-(1-Phenyl-2-tosylethyl)thiophene (4al)



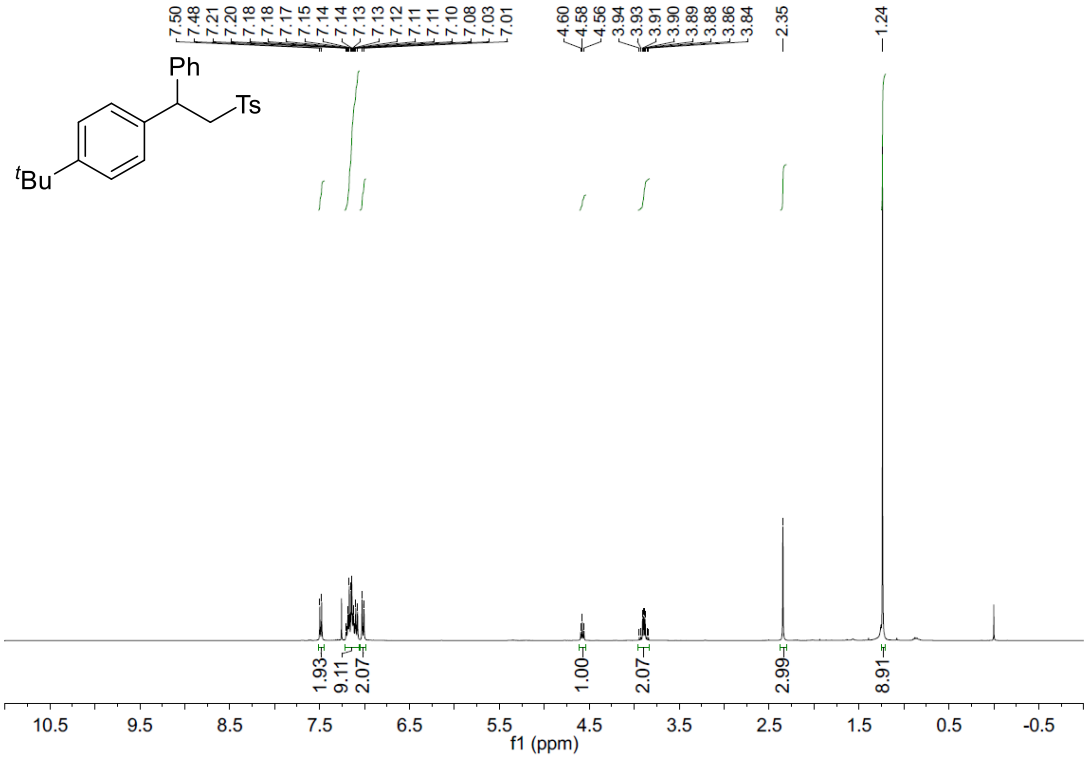
^{1}H NMR ($CDCl_3$, 400 MHz) of 3-(1-Phenyl-2-tosylethyl)thiophene (4am)



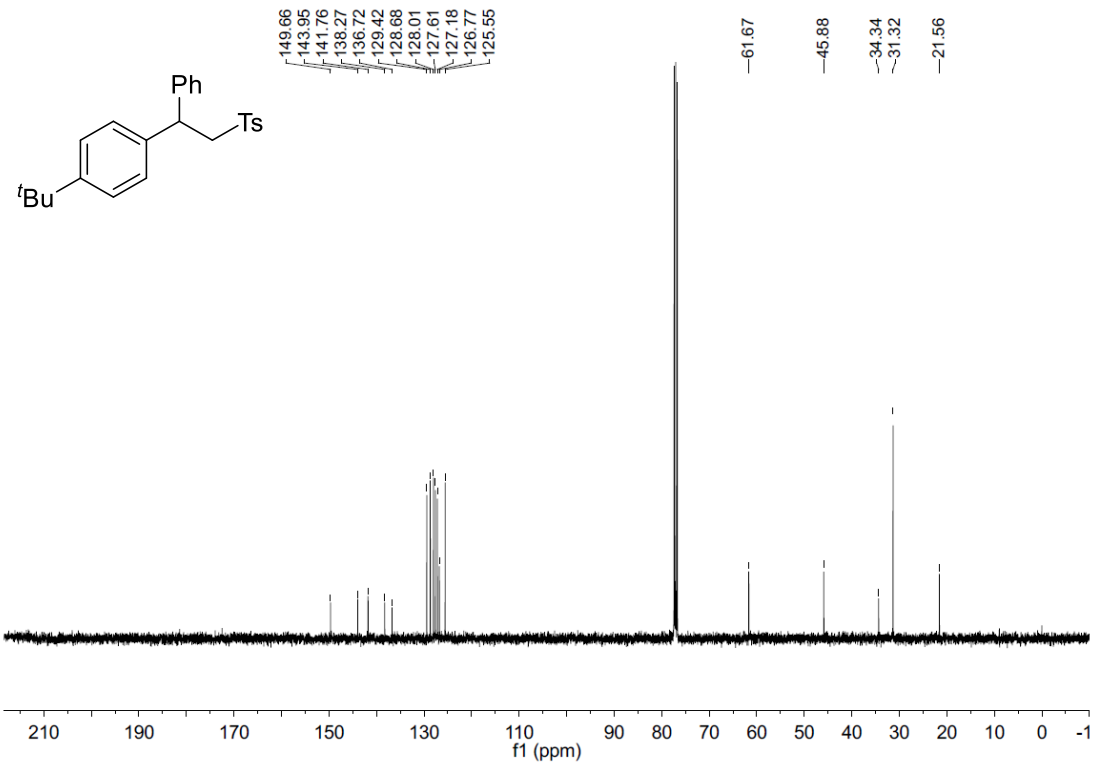
^{13}C NMR ($CDCl_3$, 100 MHz) of 3-(1-Phenyl-2-tosylethyl)thiophene (4am)



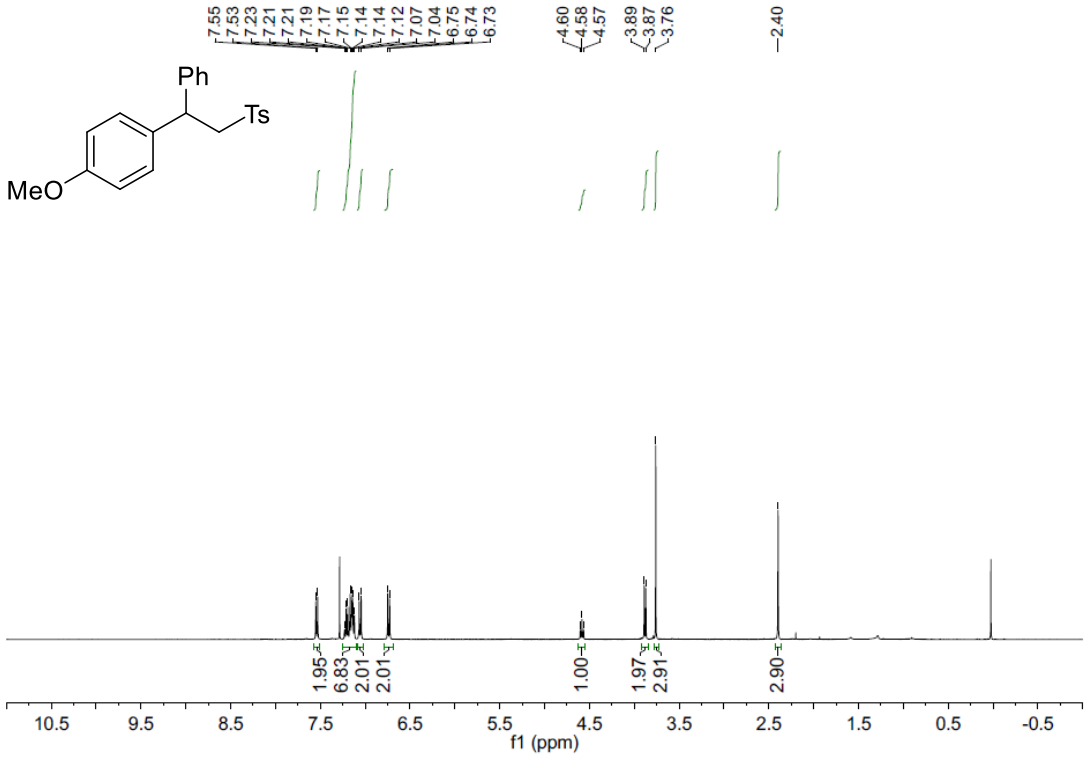
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-(*tert*-Butyl)-4-(1-phenyl-2-tosylethyl)benzene (5aa)



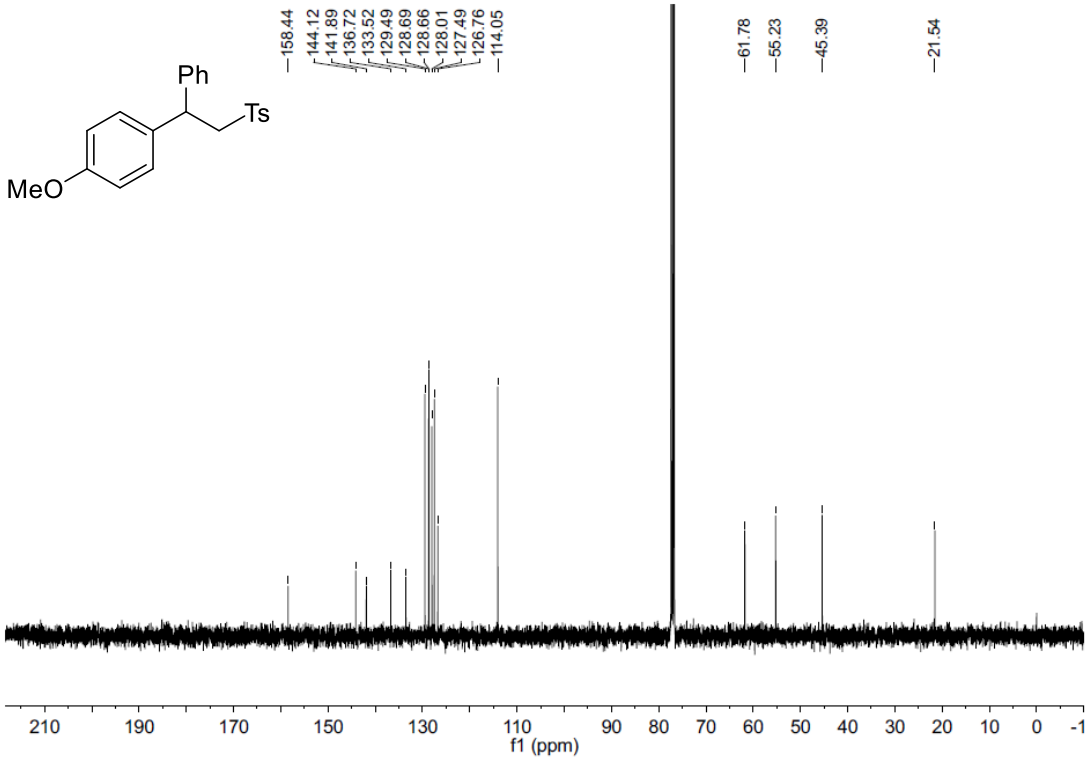
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-(*tert*-Butyl)-4-(1-phenyl-2-tosylethyl)benzene (5aa)



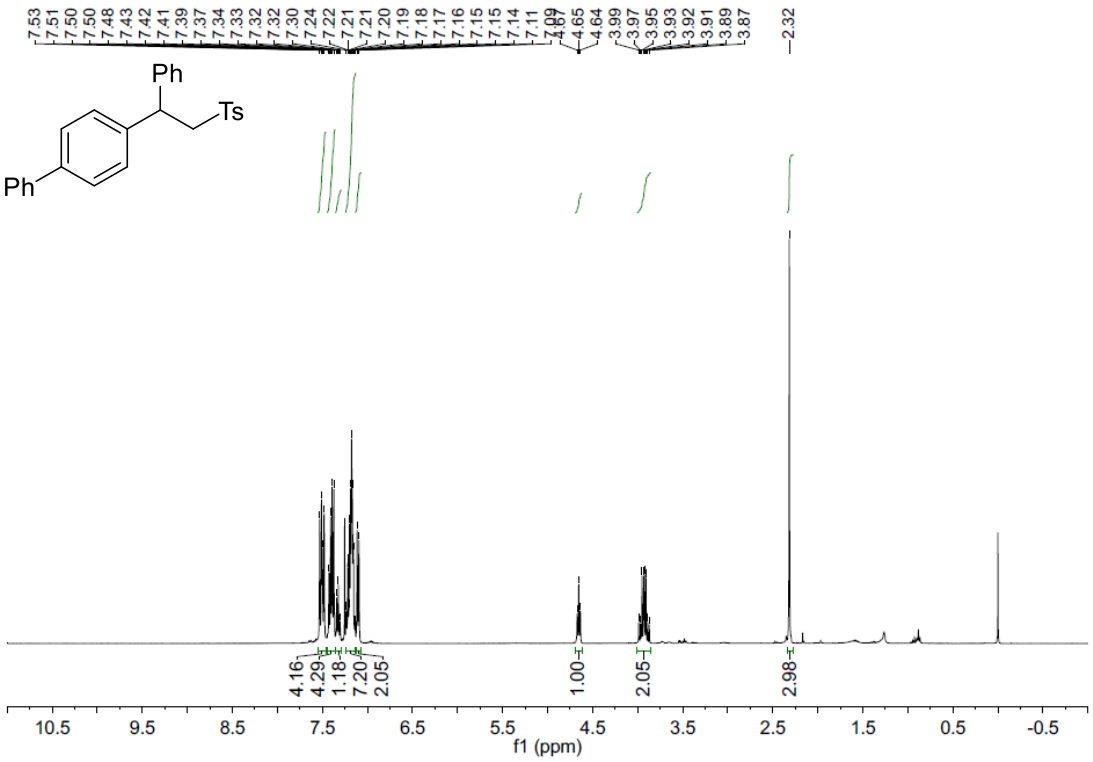
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Methoxy-4-(1-phenyl-2-tosylethyl)benzene (5ab)



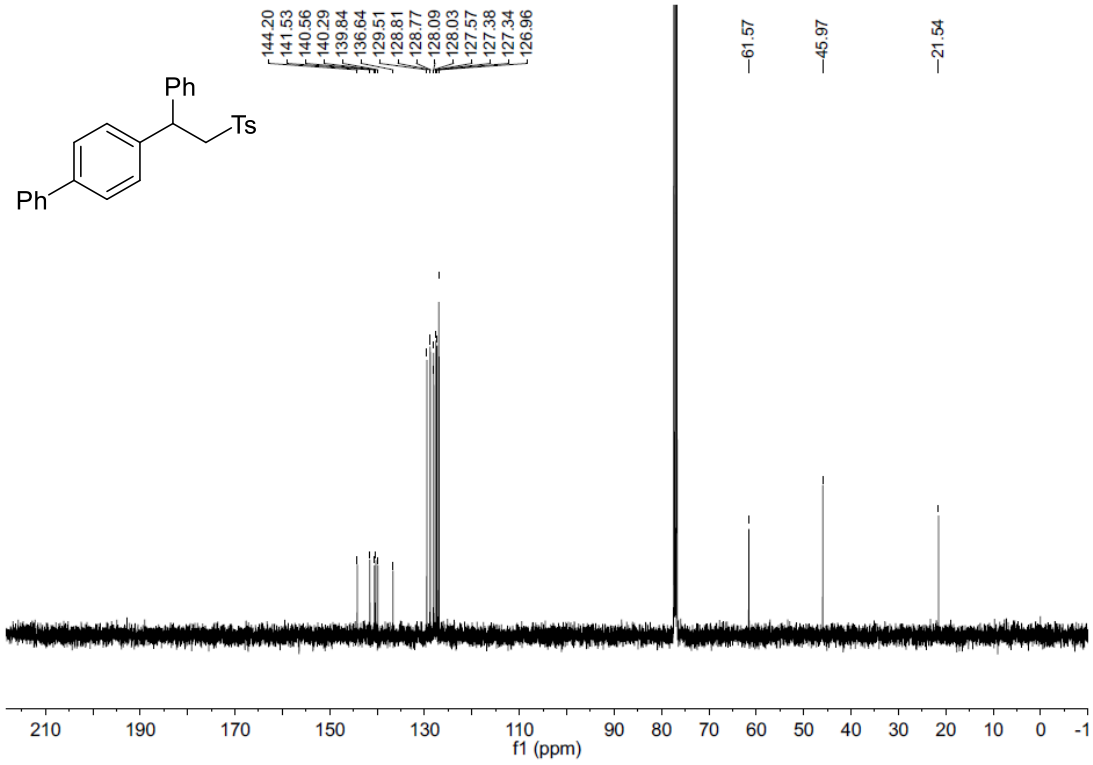
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Methoxy-4-(1-phenyl-2-tosylethyl)benzene (5ab)



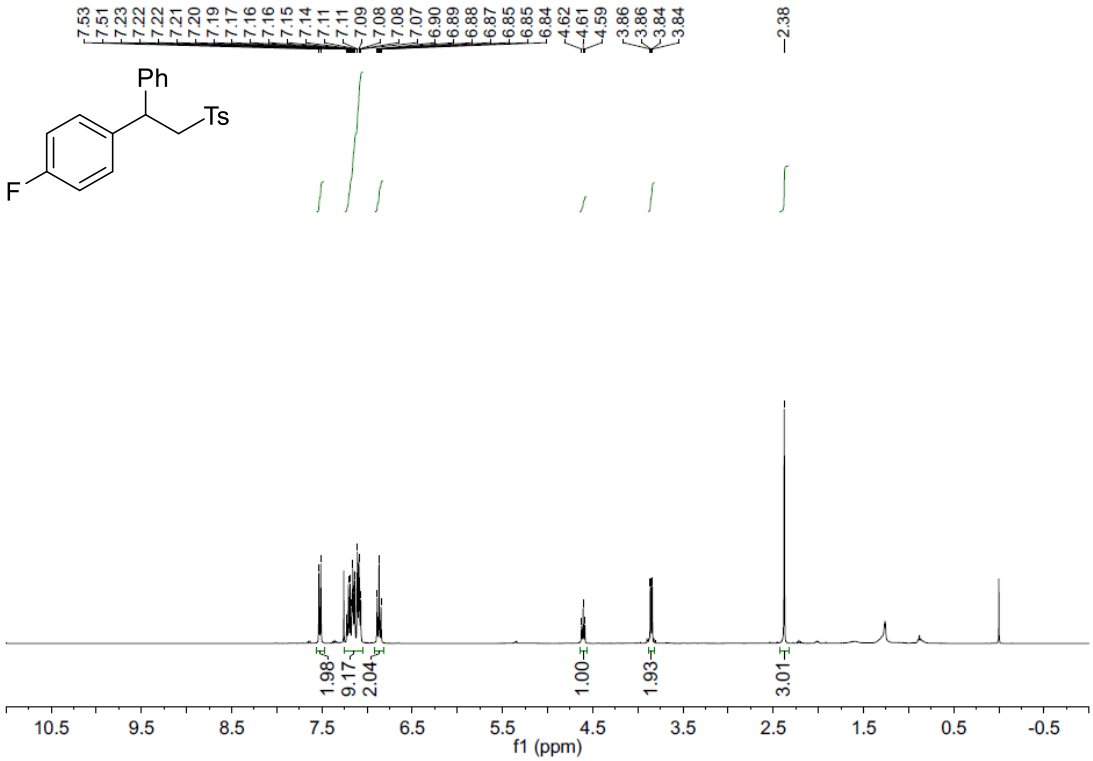
^{1}H NMR ($CDCl_3$, 400 MHz) of 4-(1-Phenyl-2-tosylethyl)-1,1'-biphenyl (5ac)



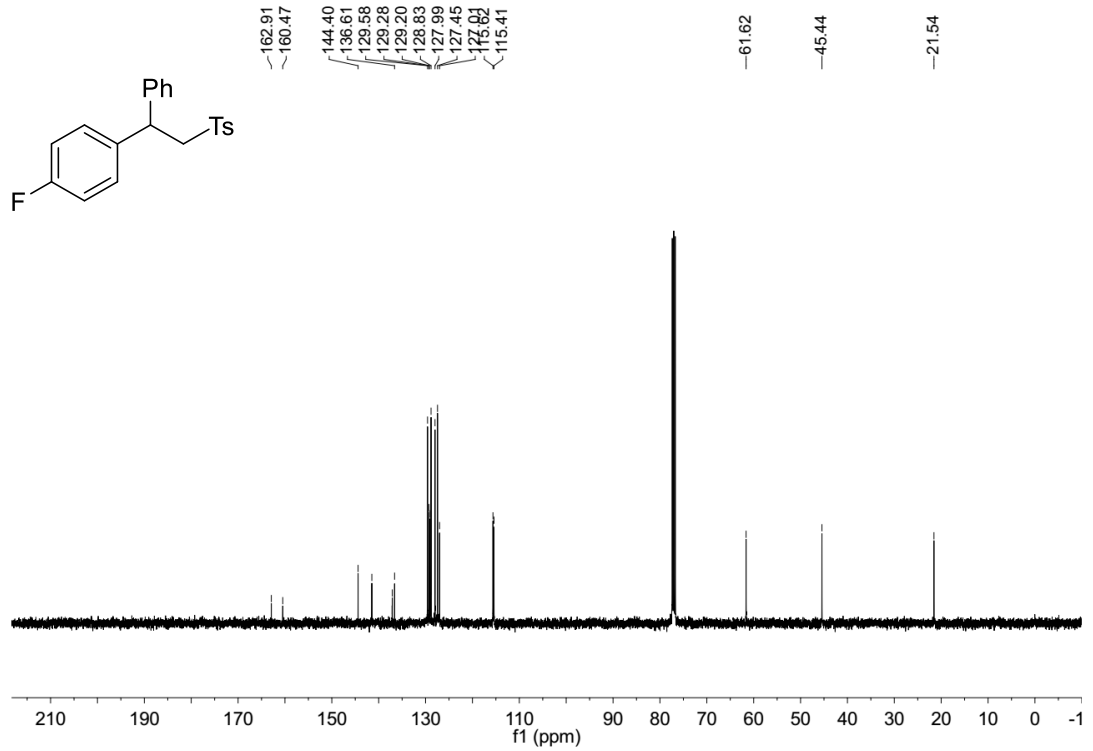
^{13}C NMR ($CDCl_3$, 100 MHz) of 4-(1-Phenyl-2-tosylethyl)-1,1'-biphenyl (5ac)



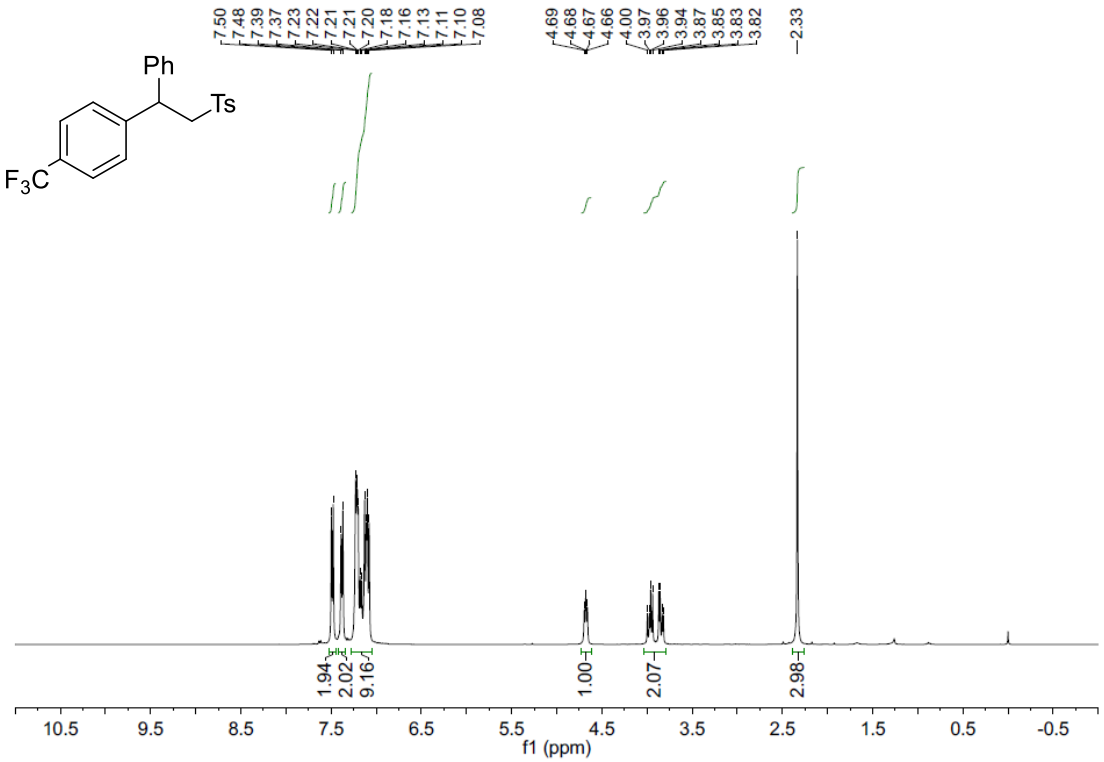
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Fluoro-4-(1-phenyl-2-tosylethyl)benzene (4ab) (from 1-fluoro-4-vinylbenzene)



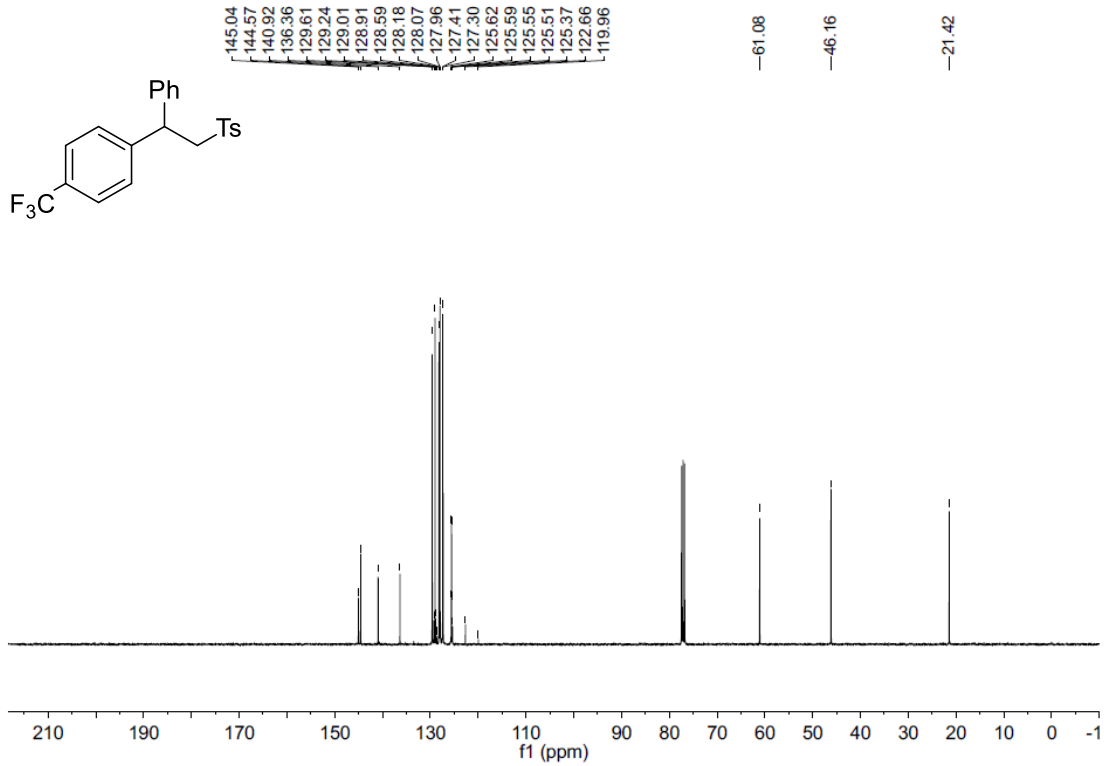
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Fluoro-4-(1-phenyl-2-tosylethyl)benzene (4ab) (from 1-fluoro-4-vinylbenzene)



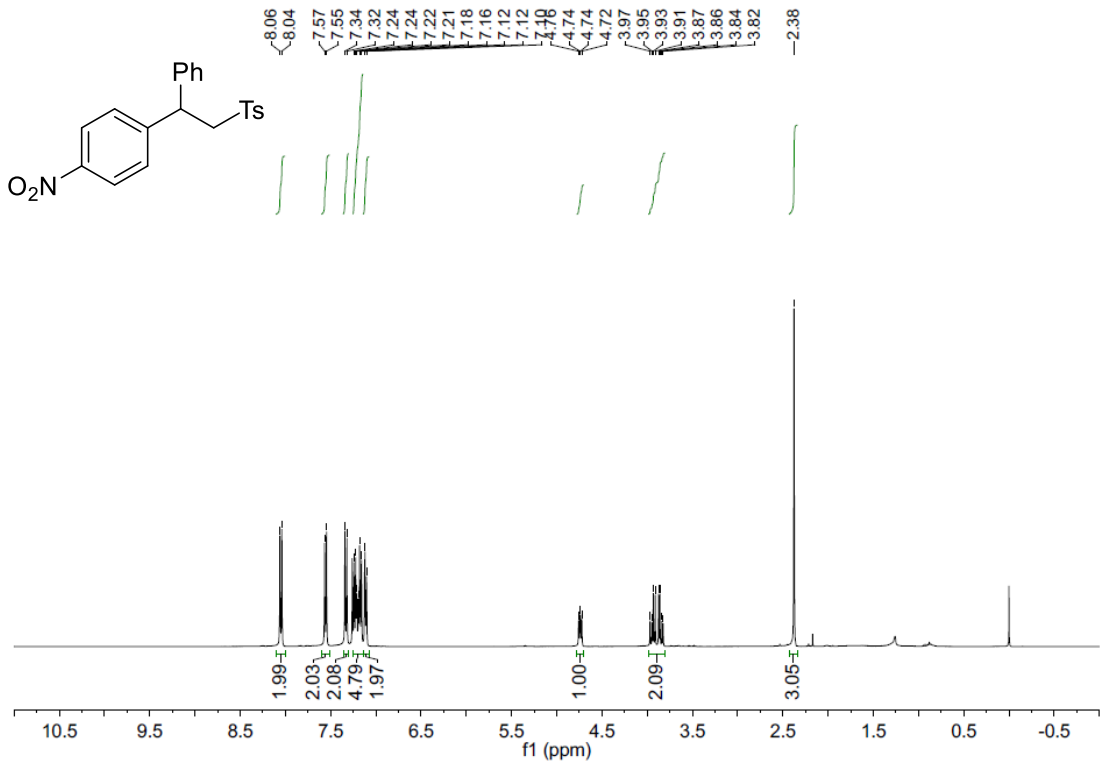
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Methyl-4-((2-phenyl-2-(4-(trifluoromethyl) phenyl)ethyl)sulfonyl)benzene (4ae) (from 1-(trifluoromethyl)-4-vinylbenzene)



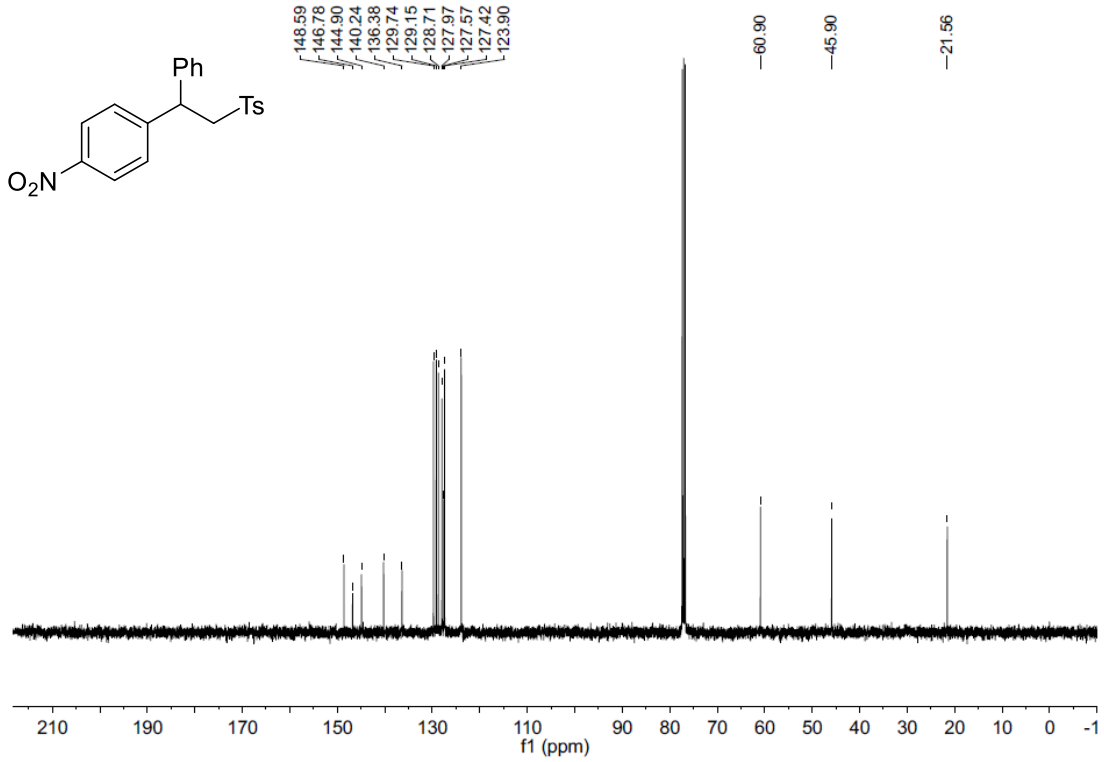
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Methyl-4-((2-phenyl-2-(4-(trifluoromethyl) phenyl)ethyl)sulfonyl)benzene (4ae) (from 1-(trifluoromethyl)-4-vinylbenzene)



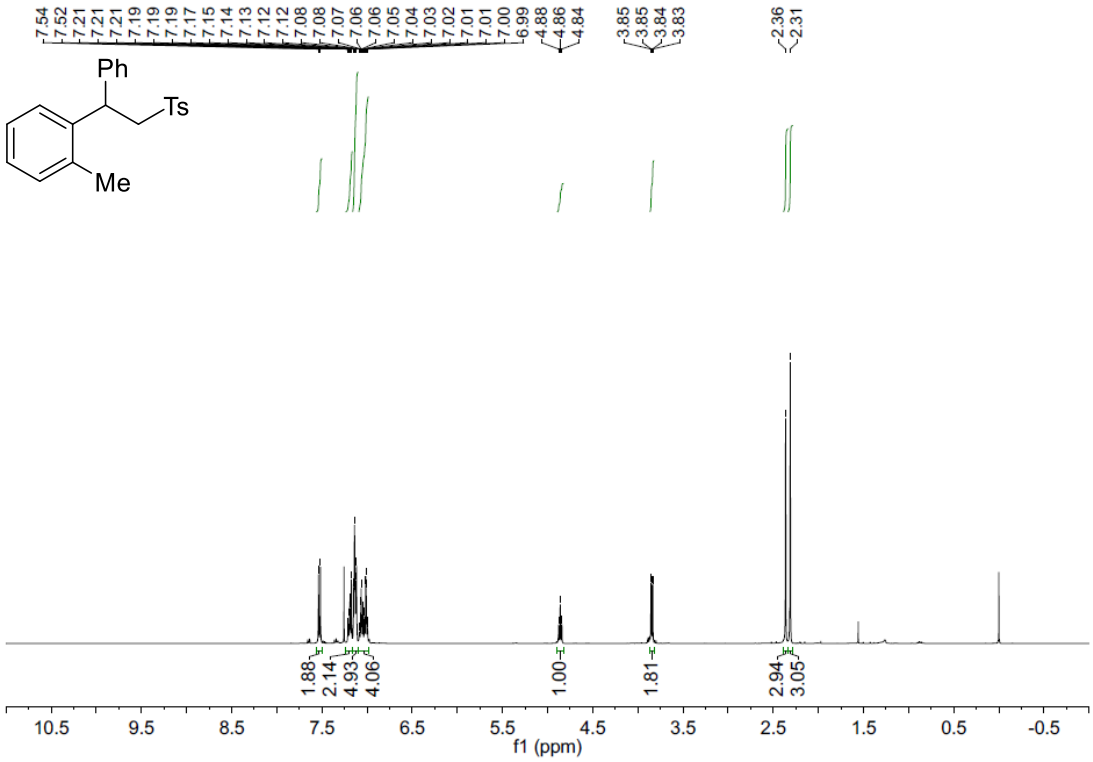
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Methyl-4-((2-(4-nitrophenyl)-2-phenylethyl) sulfonyl)benzene (5ad)



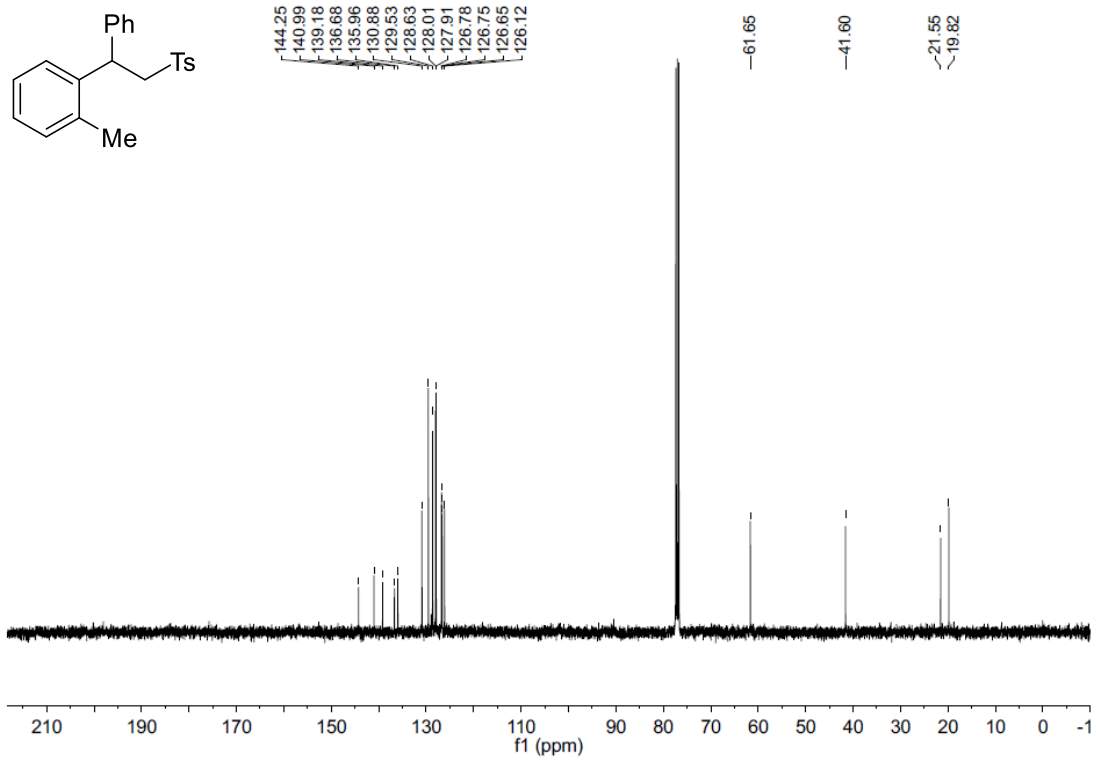
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Methyl-4-((2-(4-nitrophenyl)-2-phenylethyl) sulfonyl)benzene (5ad)



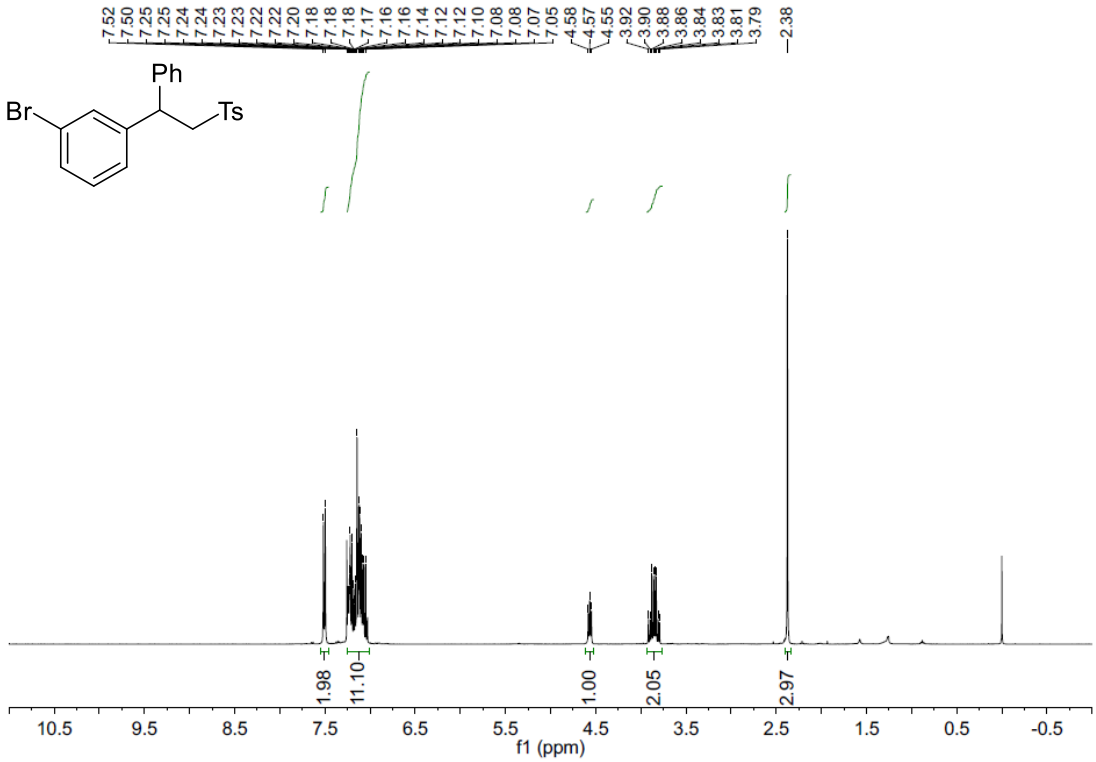
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Methyl-2-(1-phenyl-2-tosylethyl)benzene (5ae)



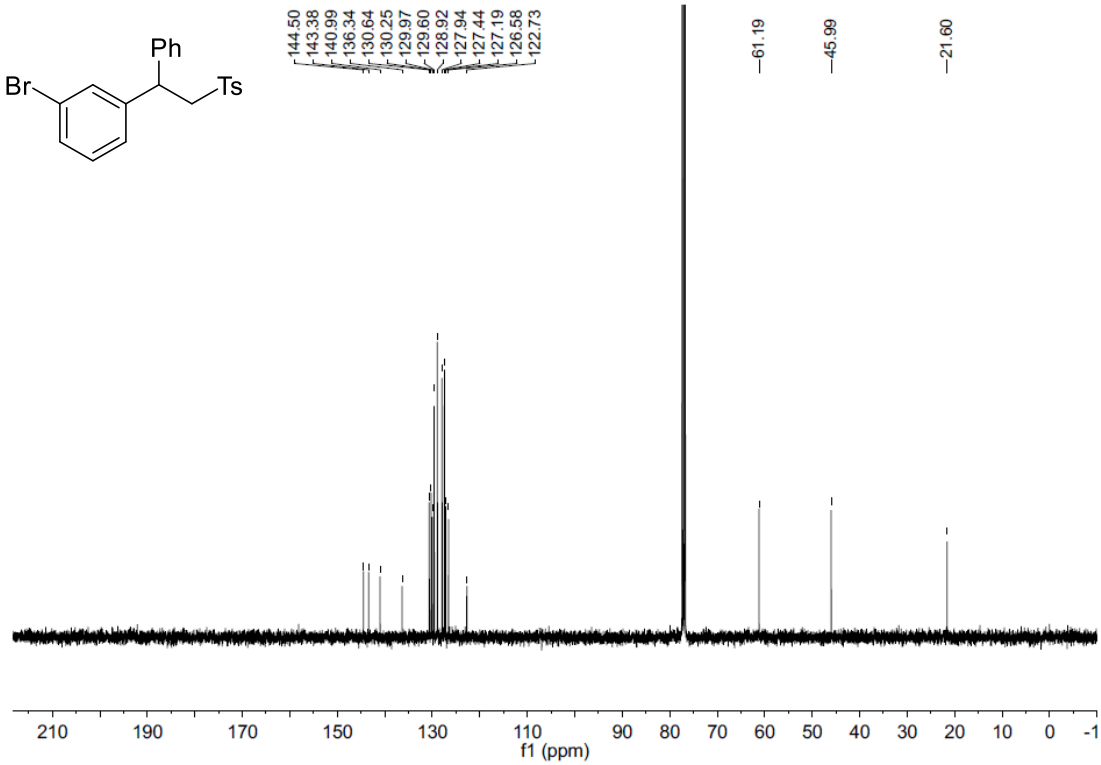
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Methyl-2-(1-phenyl-2-tosylethyl)benzene (5ae)



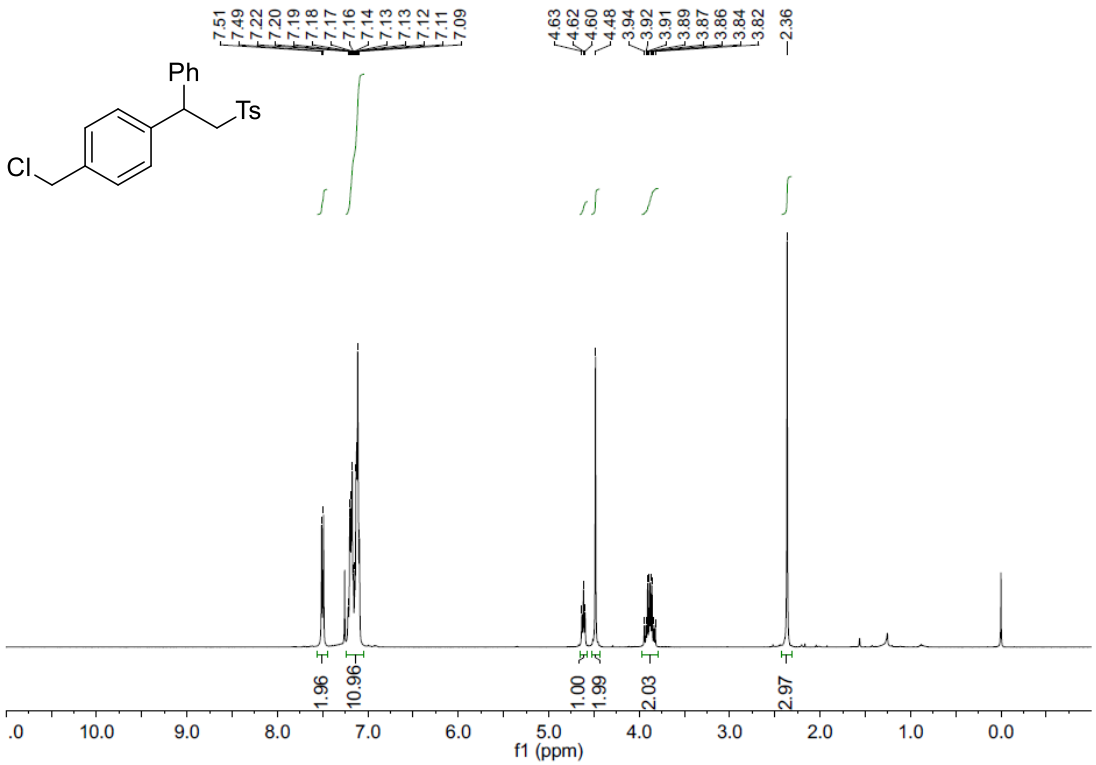
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-Bromo-3-(1-phenyl-2-tosylethyl)benzene (5af)



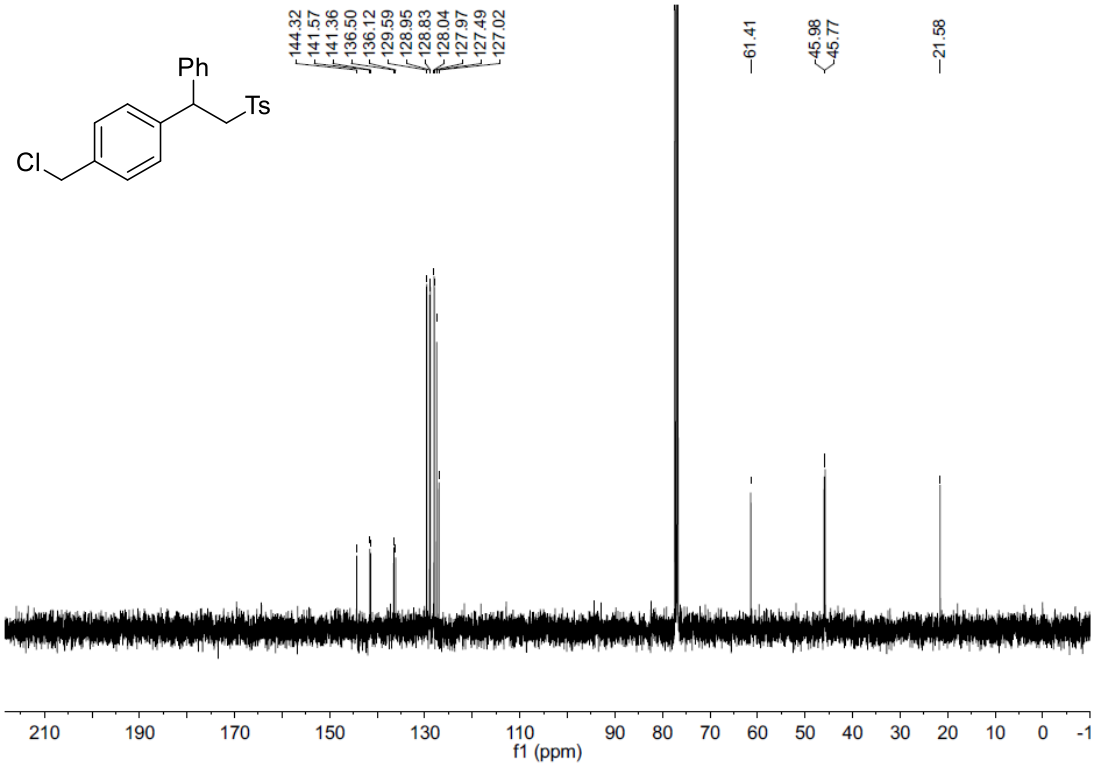
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-Bromo-3-(1-phenyl-2-tosylethyl)benzene (5af)



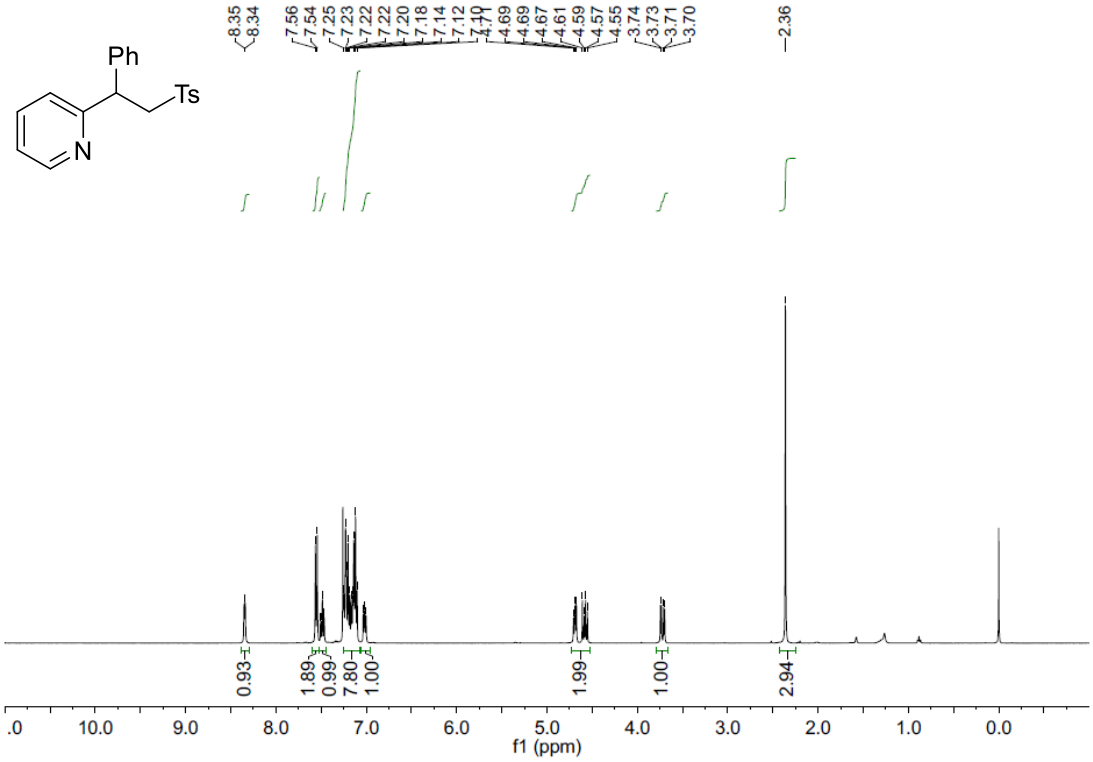
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-(Chloromethyl)-4-(1-phenyl-2-tosylethyl) benzene (5ag)



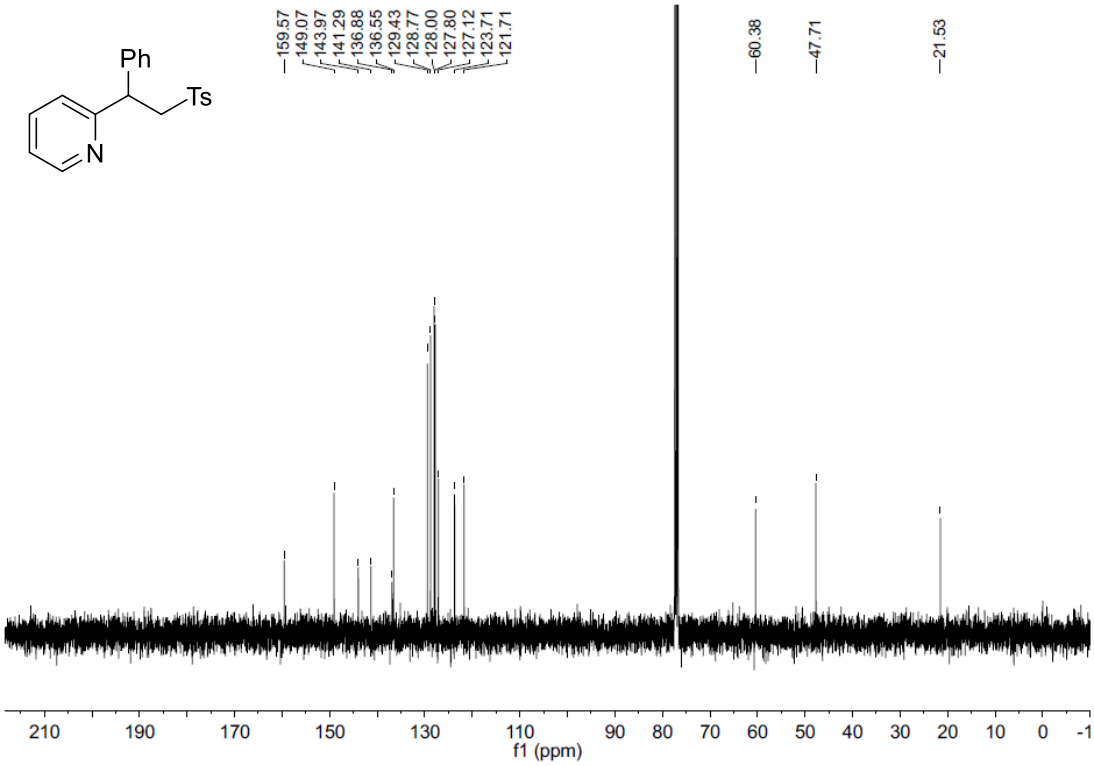
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-(Chloromethyl)-4-(1-phenyl-2-tosylethyl) benzene (5ag)



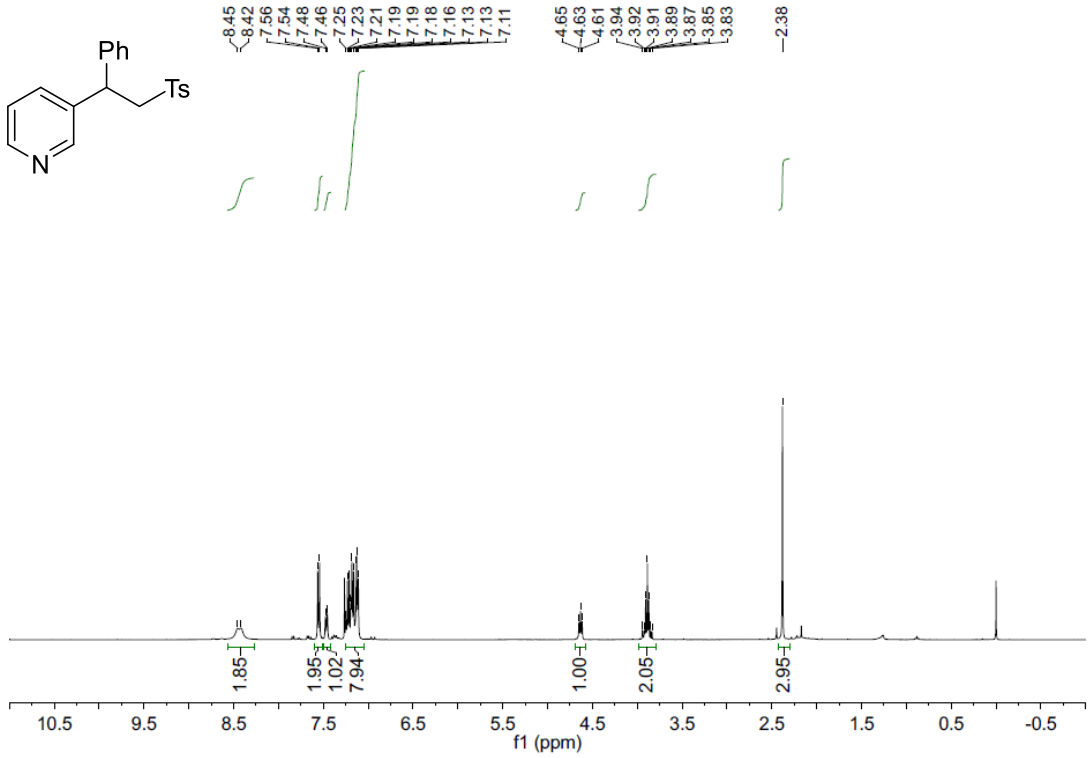
^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(1-Phenyl-2-tosylethyl)pyridine (5ah)



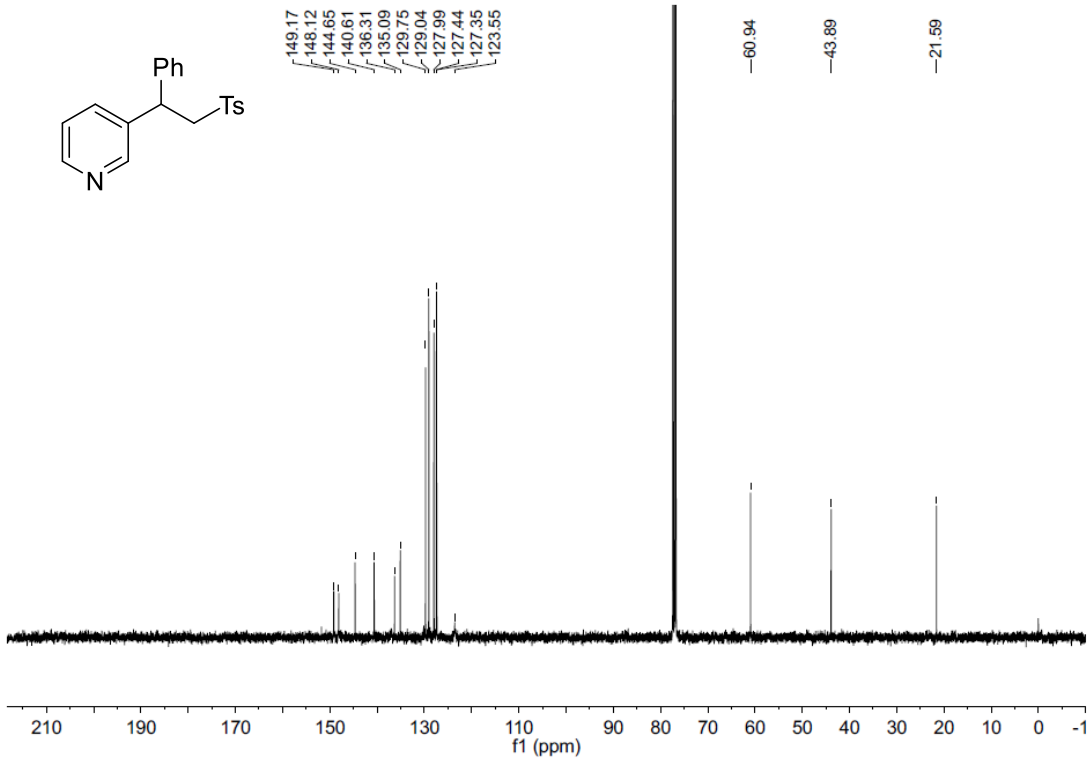
^{13}C NMR ($CDCl_3$, 100 MHz) of 2-(1-Phenyl-2-tosylethyl)pyridine (5ah)



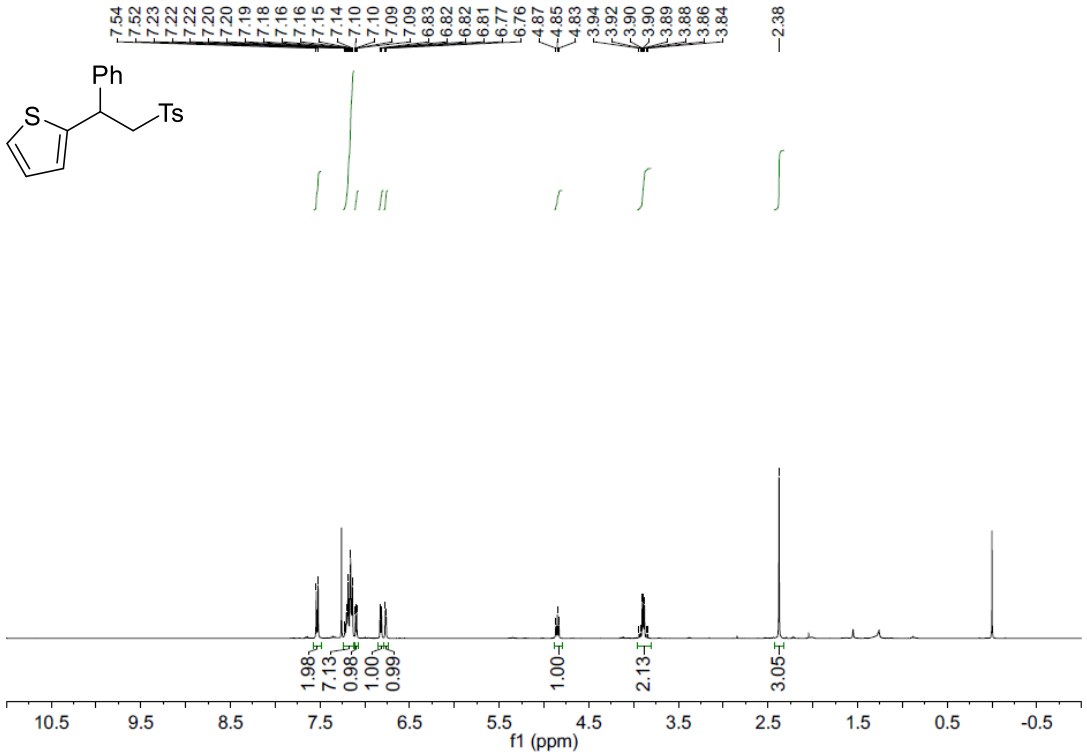
^{1}H NMR ($CDCl_3$, 400 MHz) of 3-(1-Phenyl-2-tosylethyl)pyridine (5ai)



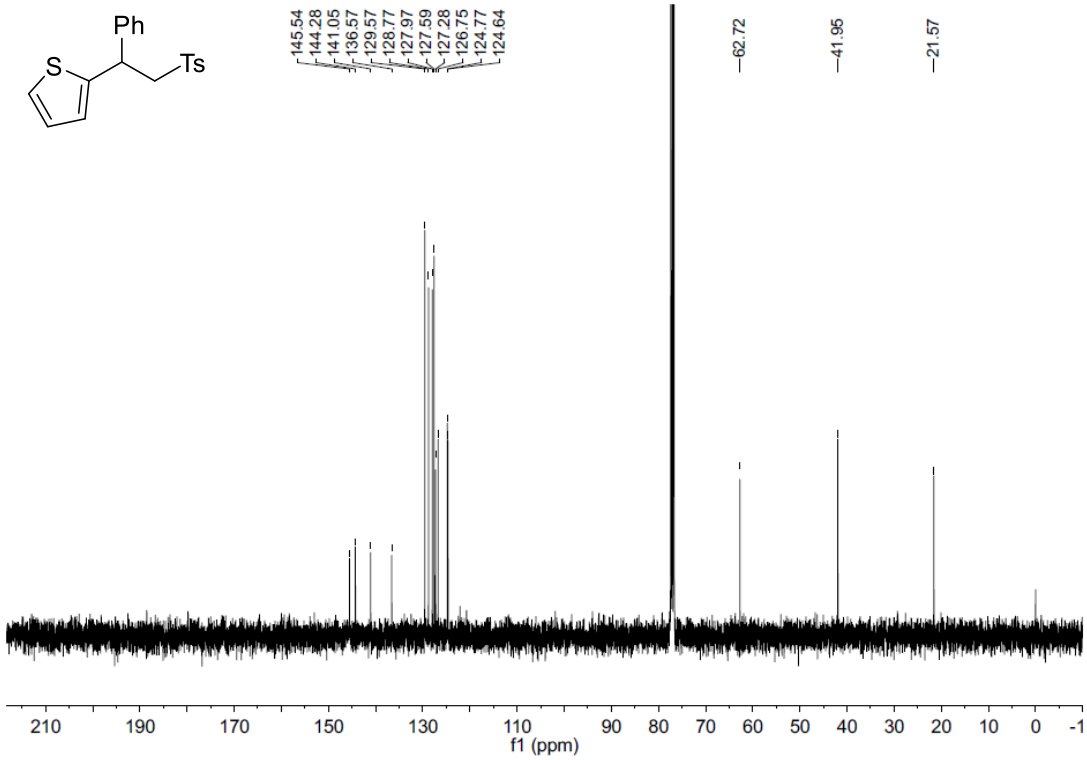
^{13}C NMR ($CDCl_3$, 100 MHz) of 3-(1-Phenyl-2-tosylethyl)pyridine (5ai)



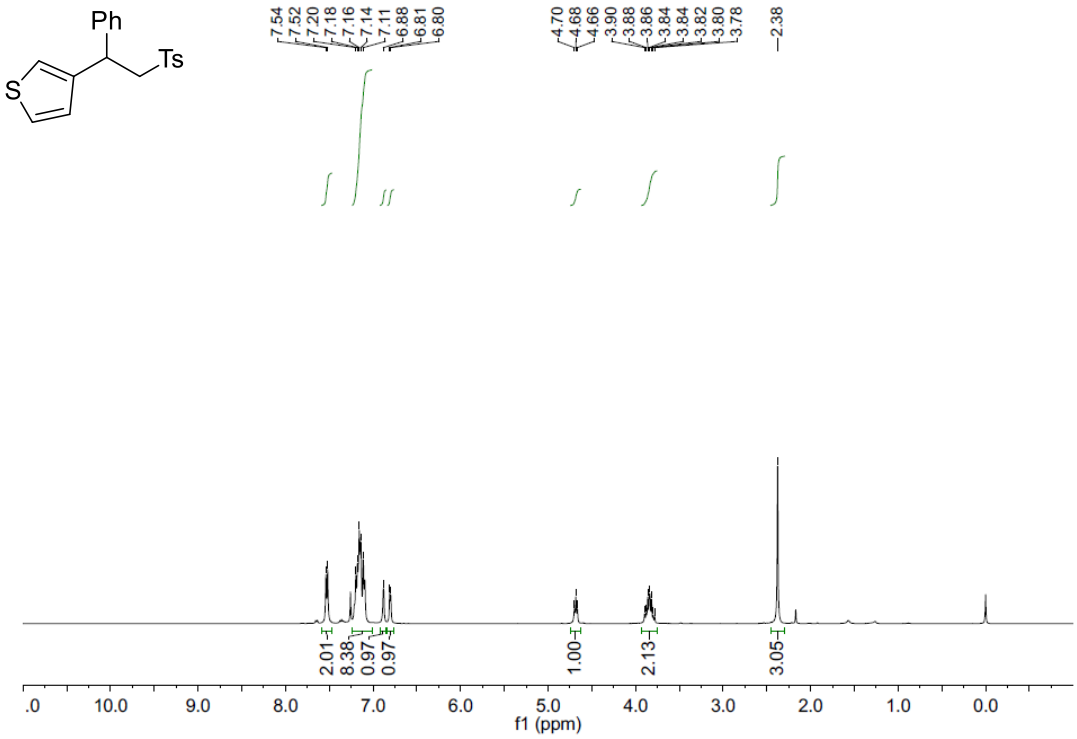
^{1}H NMR ($CDCl_3$, 400 MHz) of 2-(1-Phenyl-2-tosylethyl)thiophene (4al) (from 2-vinylthiophene)



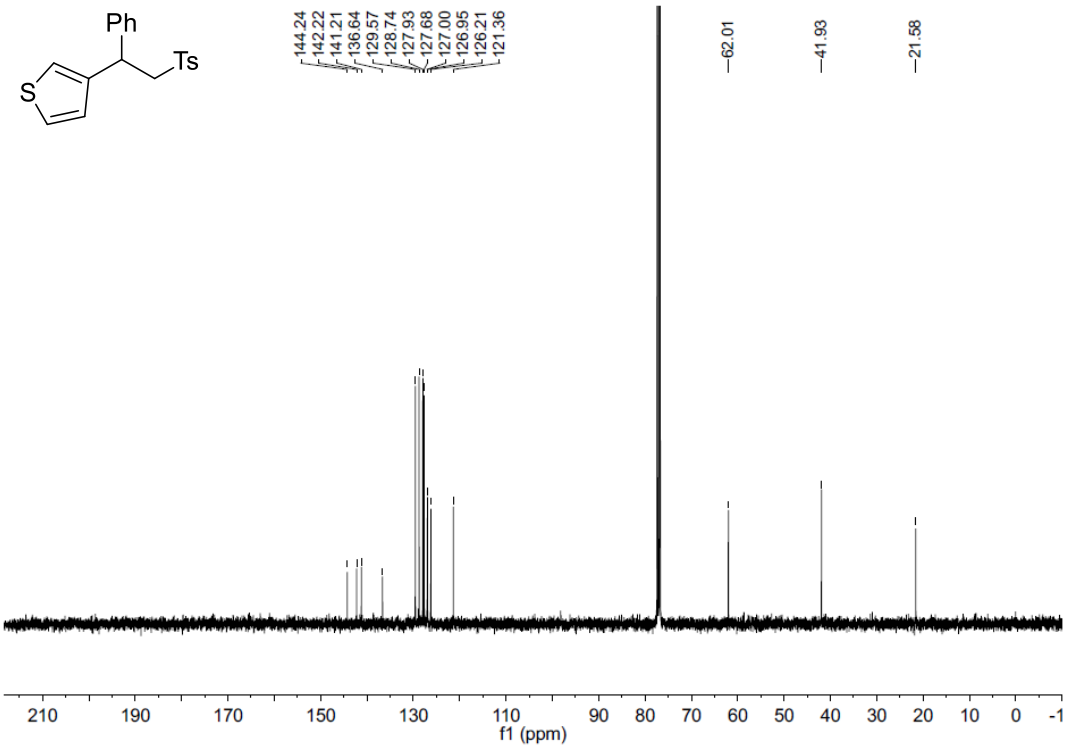
^{13}C NMR ($CDCl_3$, 100 MHz) of 2-(1-Phenyl-2-tosylethyl)thiophene (4al) (from 2-vinylthiophene)



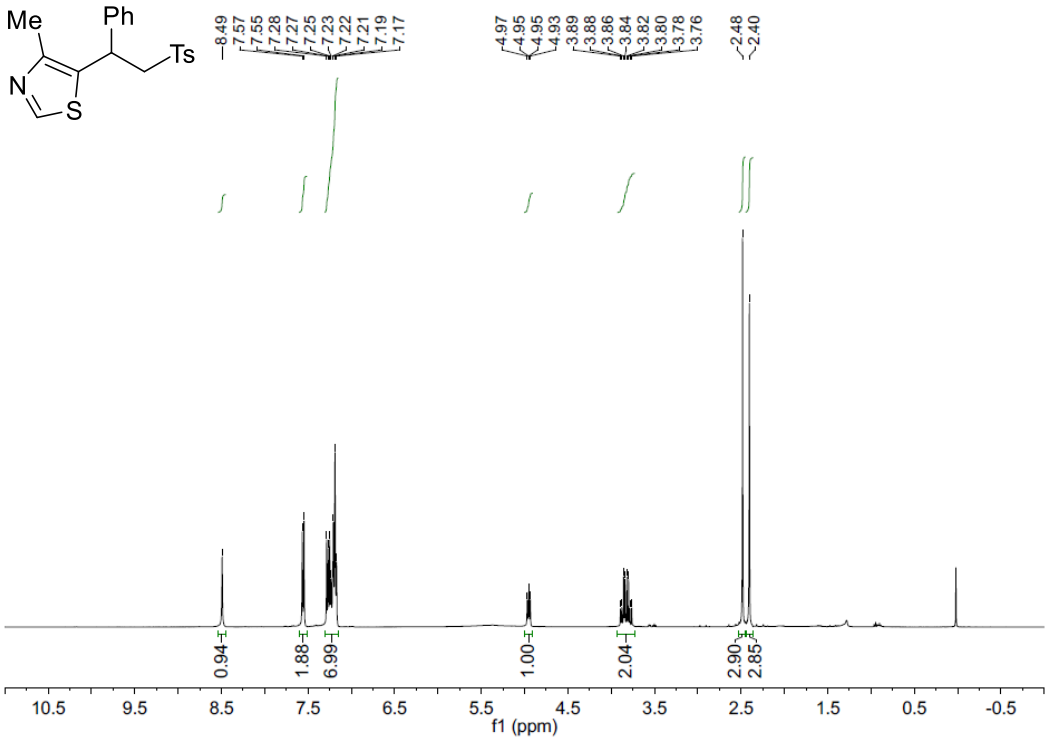
^{1}H NMR ($CDCl_3$, 400 MHz) of 3-(1-Phenyl-2-tosylethyl)thiophene (4am) (from 3-vinylthiophene)



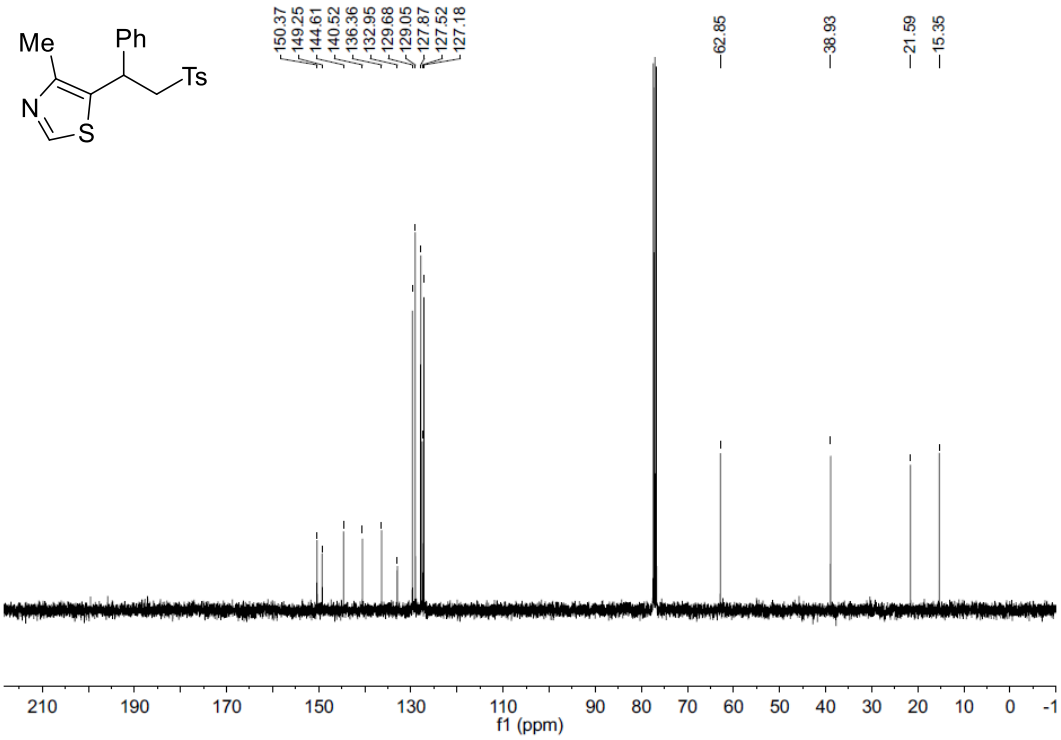
^{13}C NMR ($CDCl_3$, 100 MHz) of 3-(1-Phenyl-2-tosylethyl)thiophene (4am) (from 3-vinylthiophene)



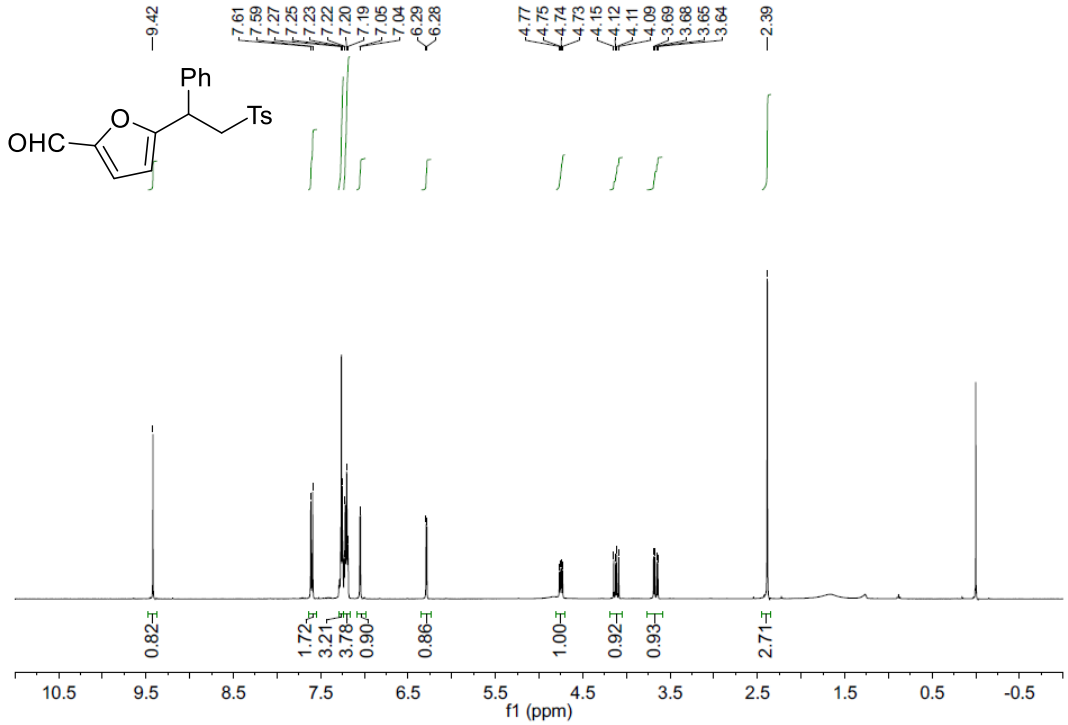
^{1}H NMR ($CDCl_3$, 400 MHz) of 4-Methyl-5-(1-phenyl-2-tosylethyl)thiazole (5aj)



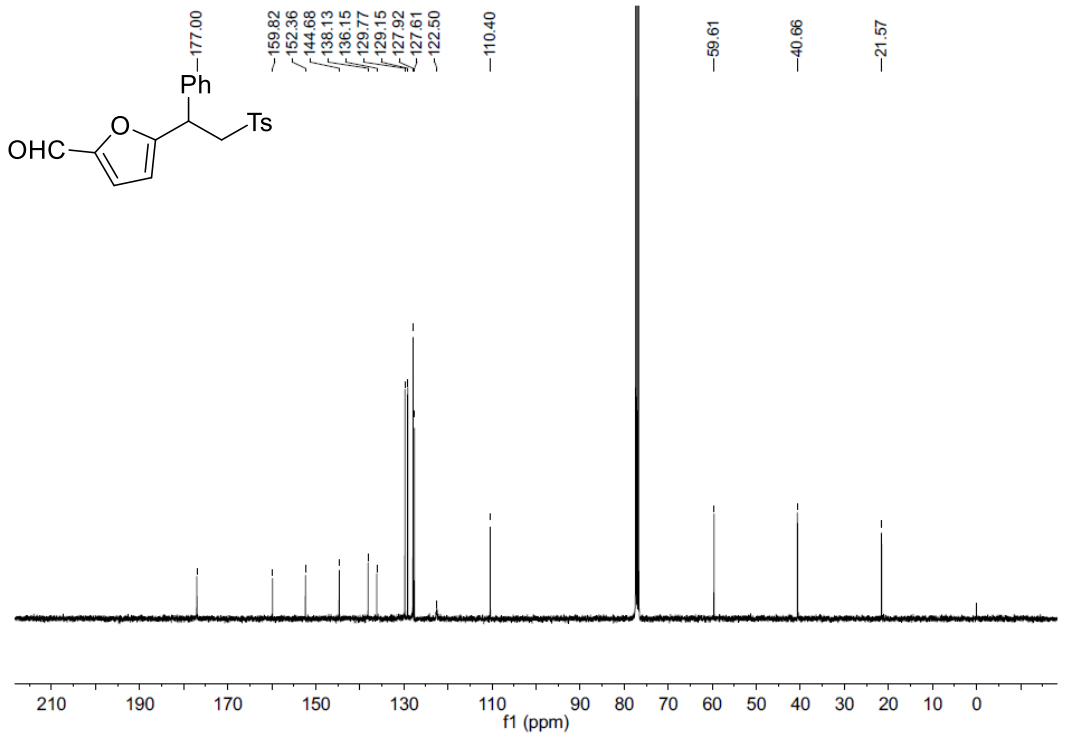
^{13}C NMR ($CDCl_3$, 100 MHz) of 4-Methyl-5-(1-phenyl-2-tosylethyl)thiazole (5aj)



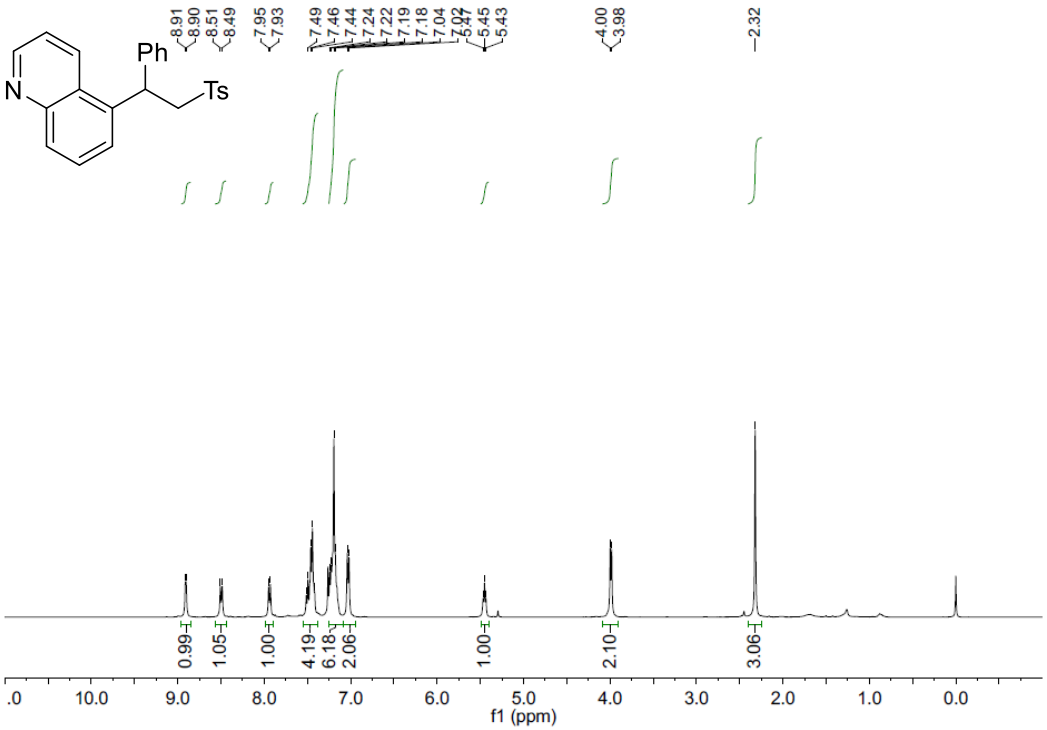
^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(1-Phenyl-2-tosylethyl)furan-2-carbaldehyde (5ak)



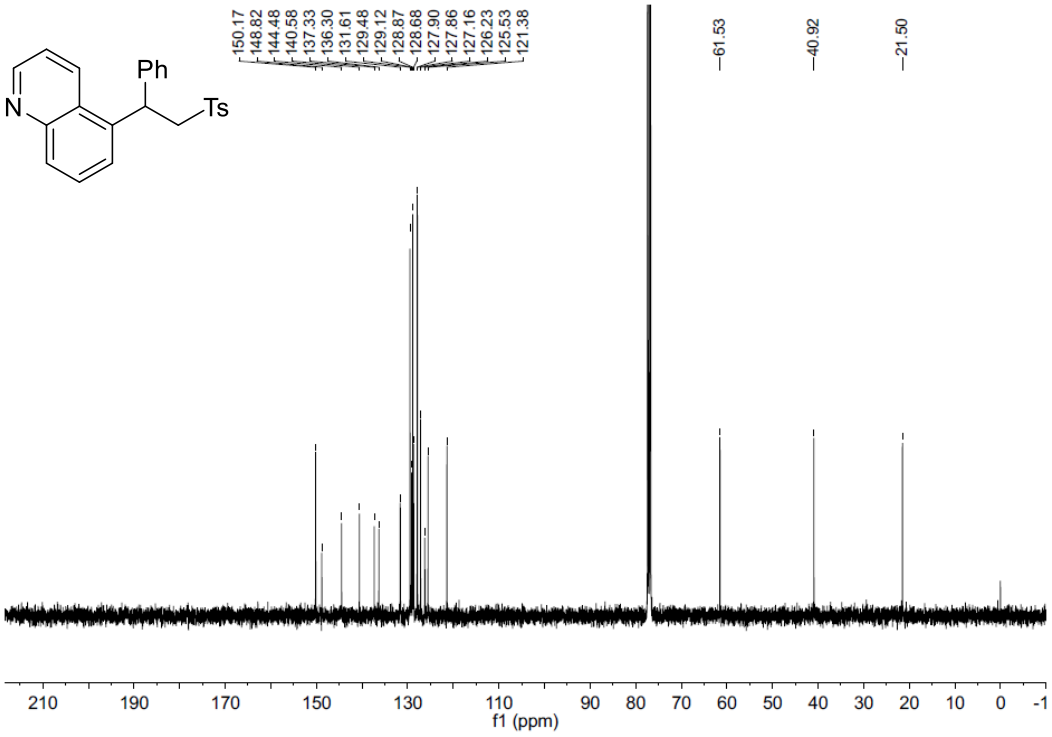
^{13}C NMR ($CDCl_3$, 100 MHz) of 5-(1-Phenyl-2-tosylethyl)furan-2-carbaldehyde (5ak)



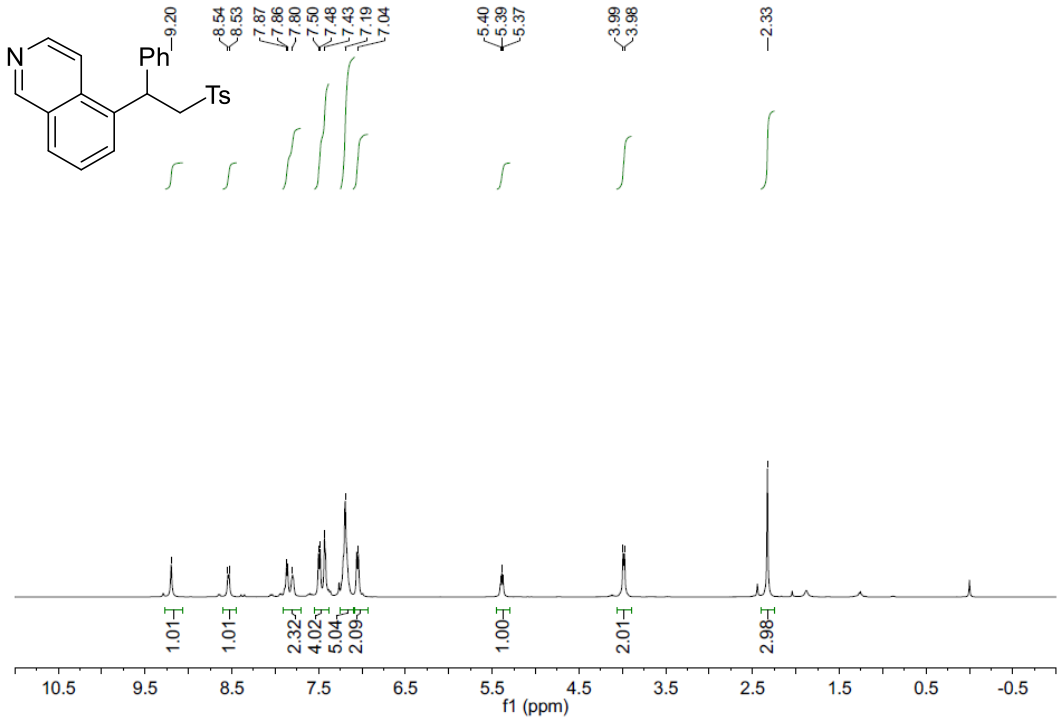
^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(1-Phenyl-2-tosylethyl)quinolone (5al)



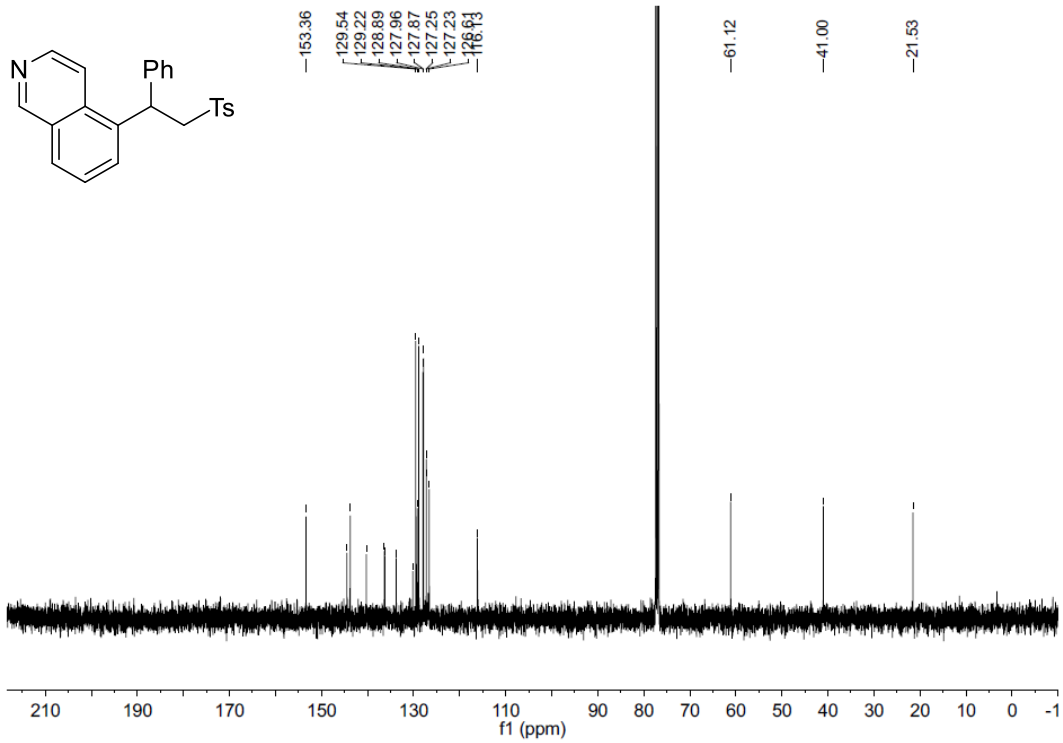
^{13}C NMR ($CDCl_3$, 100 MHz) of 5-(1-Phenyl-2-tosylethyl)quinolone (5al)



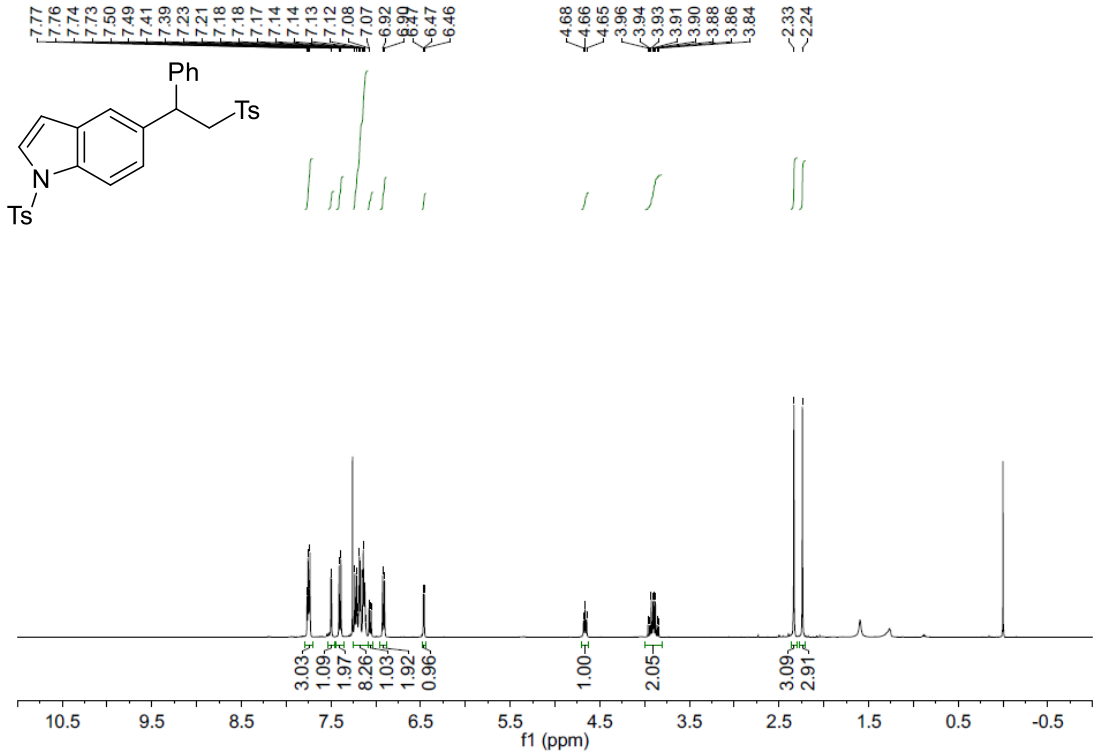
^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(1-Phenyl-2-tosylethyl)isoquinoline (5am)



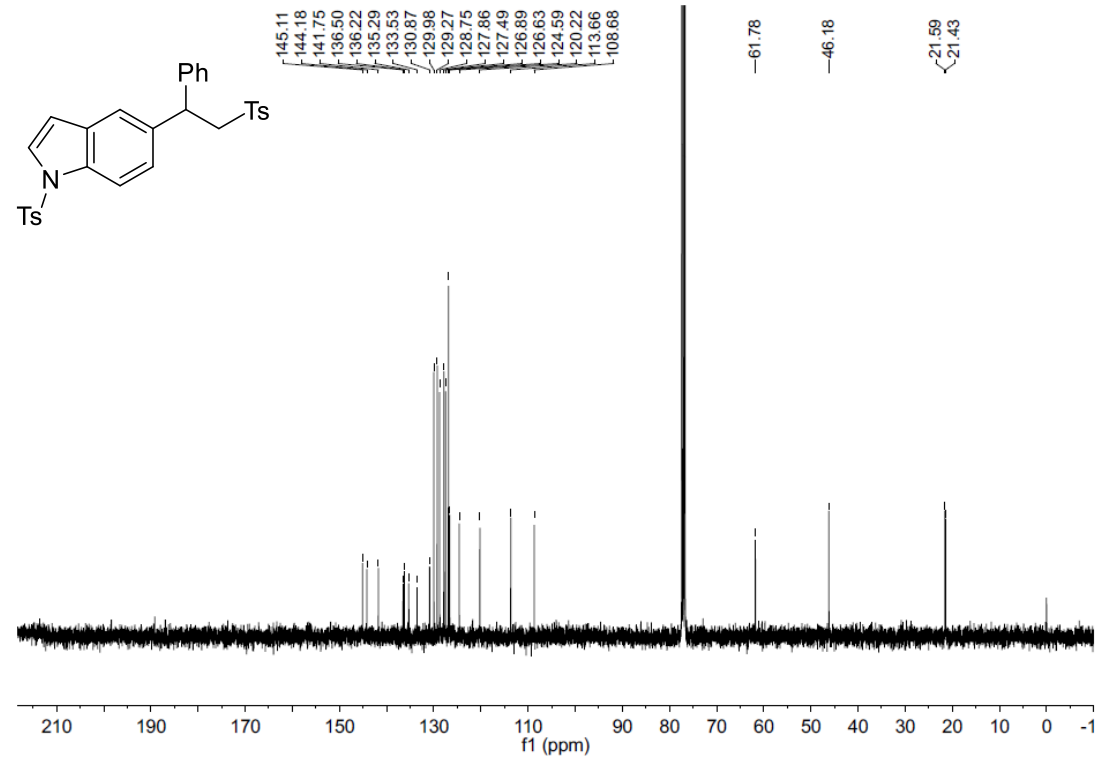
^{13}C NMR ($CDCl_3$, 100 MHz) of 5-(1-phenyl-2-tosylethyl)isoquinoline (5am)



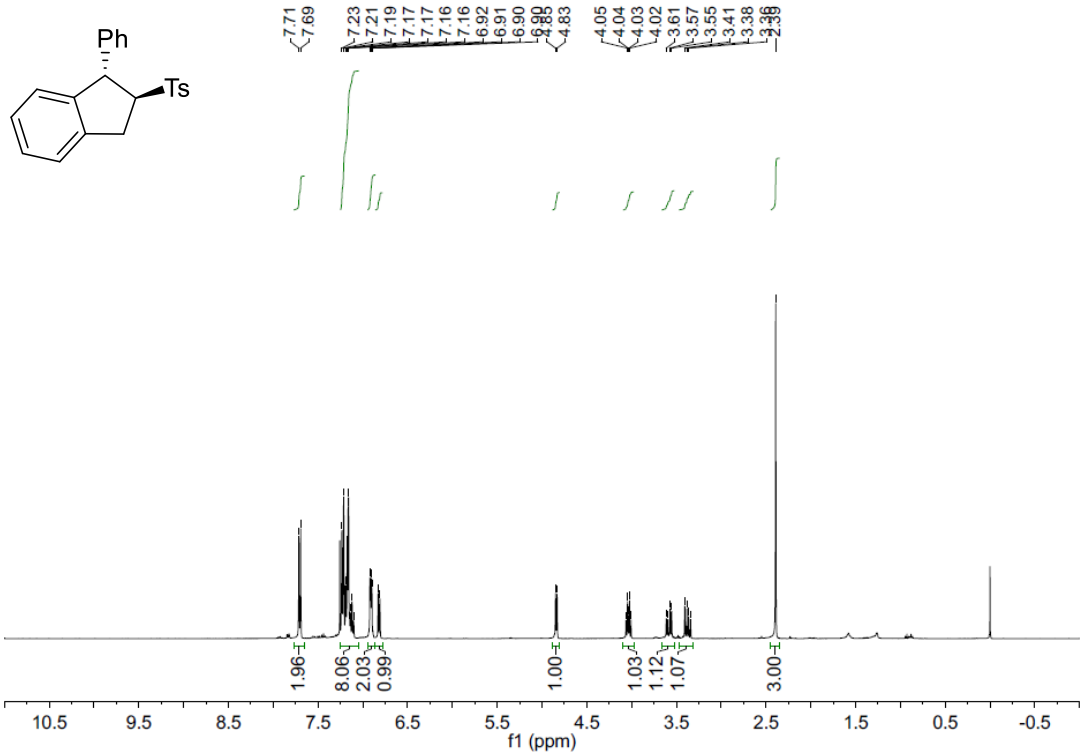
^{1}H NMR ($CDCl_3$, 400 MHz) of 5-(1-Phenyl-2-tosylethyl)-1-tosyl-1*H*-indole (5an)



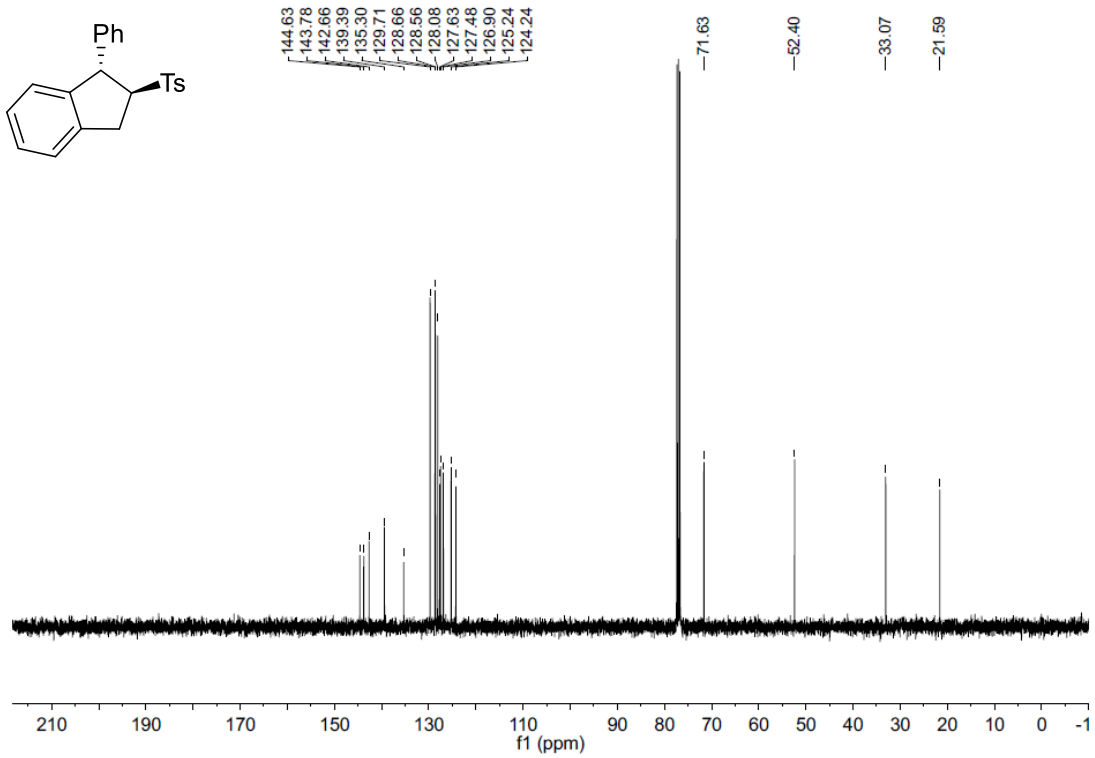
^{13}C NMR ($CDCl_3$, 100 MHz) of 5-(1-Phenyl-2-tosylethyl)-1-tosyl-1*H*-indole (5an)



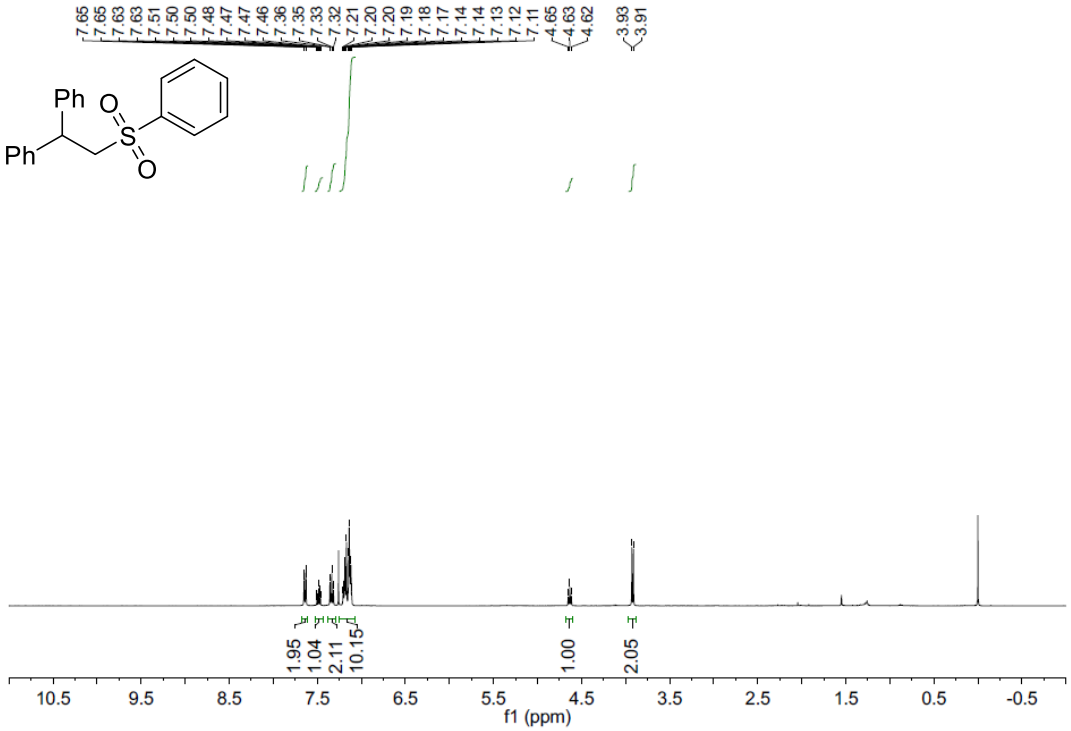
^{1}H NMR ($CDCl_3$, 400 MHz) of (1*S*,2*S*)-1-Phenyl-2-tosyl-2,3-dihydro-1*H*- indene (5ao)



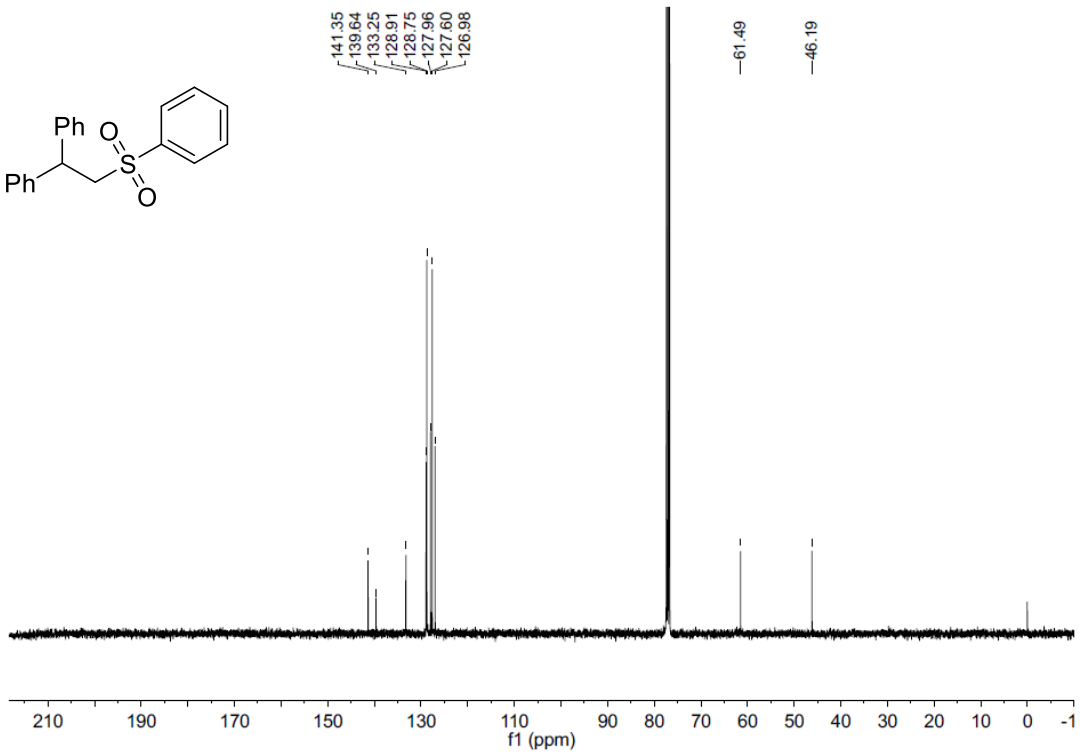
^{13}C NMR ($CDCl_3$, 100 MHz) of (1*S*,2*S*)-1-Phenyl-2-tosyl-2,3-dihydro-1*H* –indene (5ao)



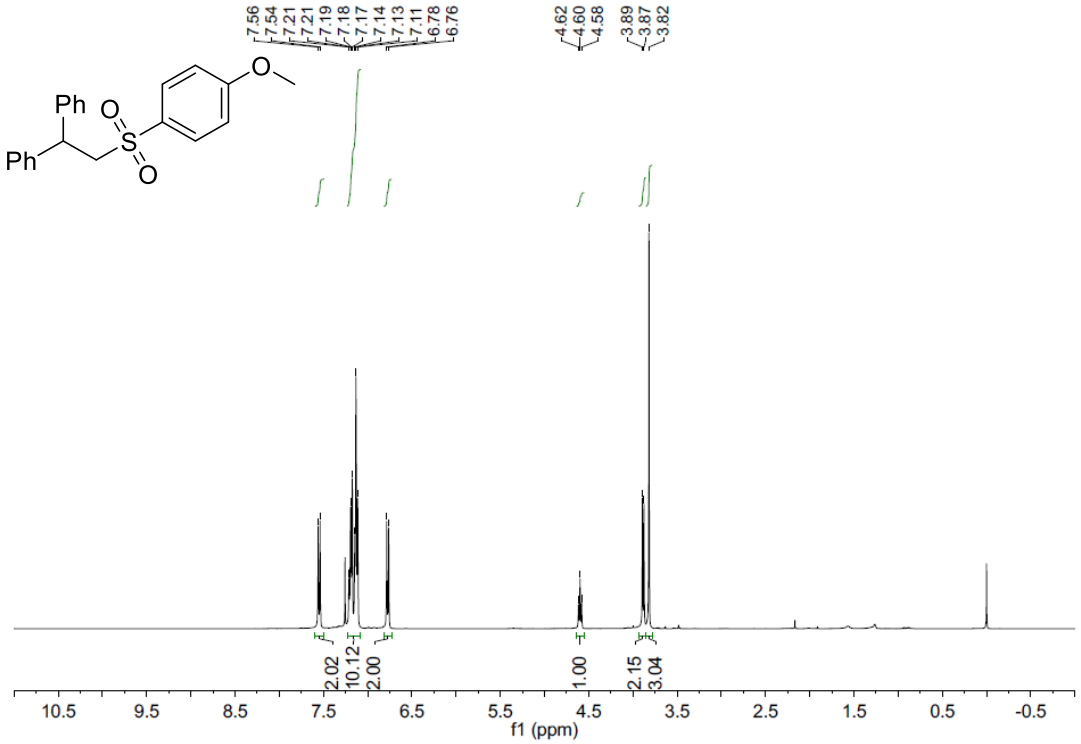
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-(Phenylsulfonyl)ethane-1,1-diyl)dibenzene (6aa)



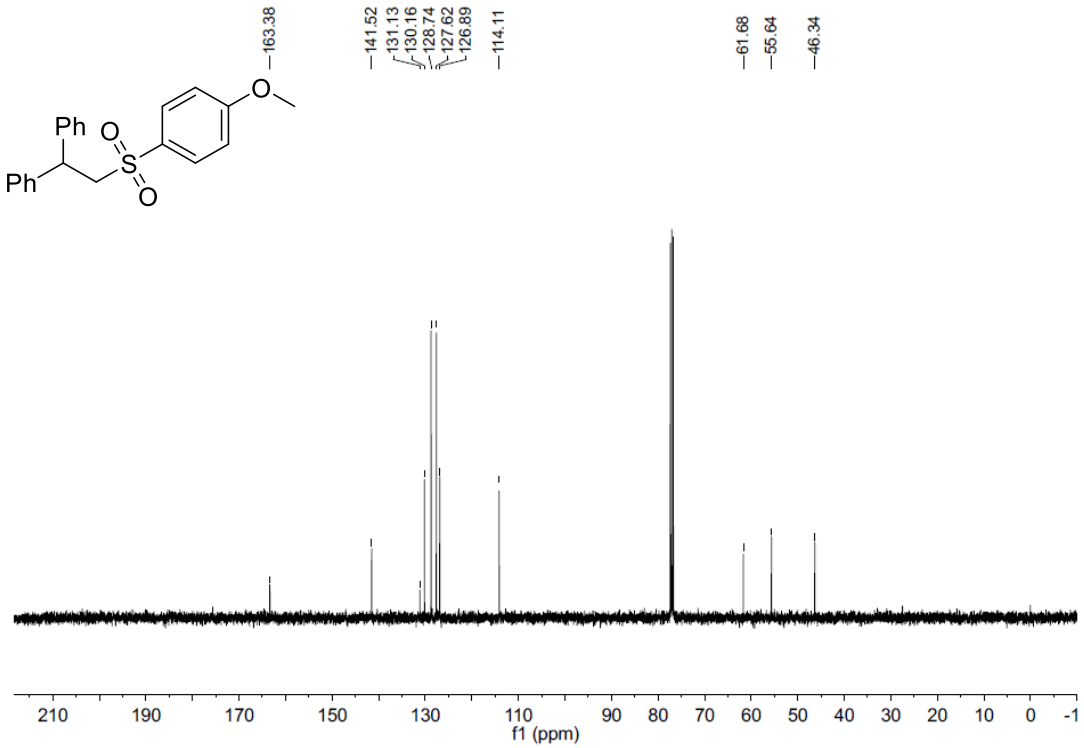
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-(Phenylsulfonyl)ethane-1,1-diyl)dibenzene (6aa)



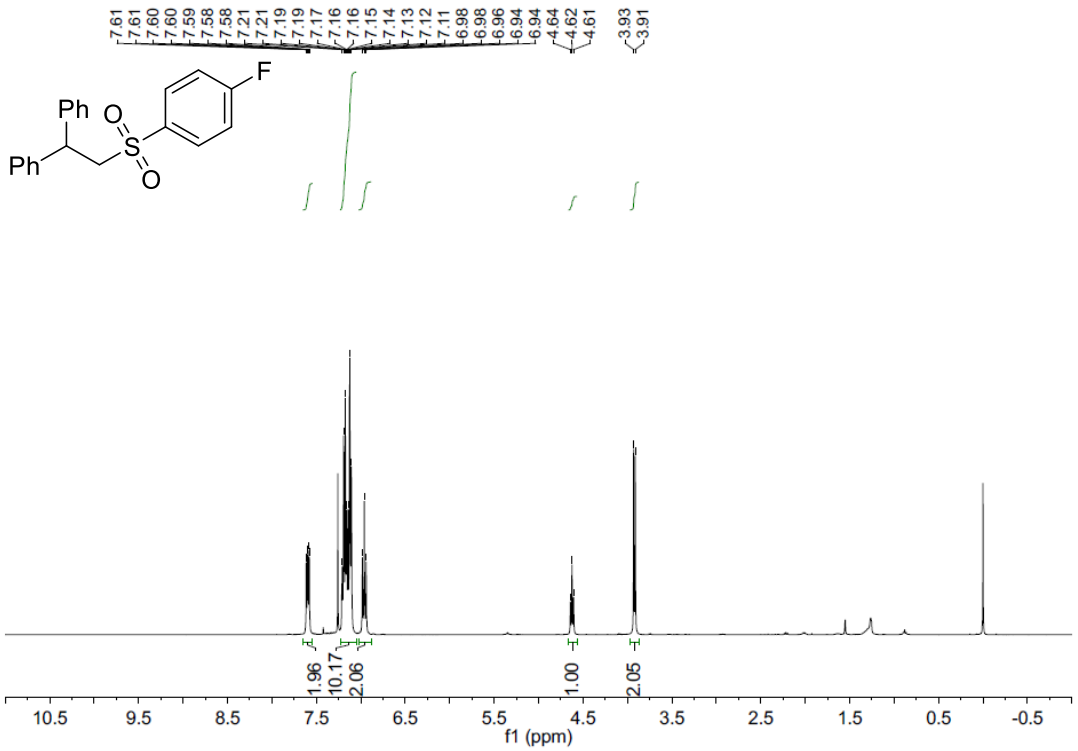
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-((4-Methoxyphenyl)sulfonyl)ethane-1,1-diyl) dibenzene (6ab)



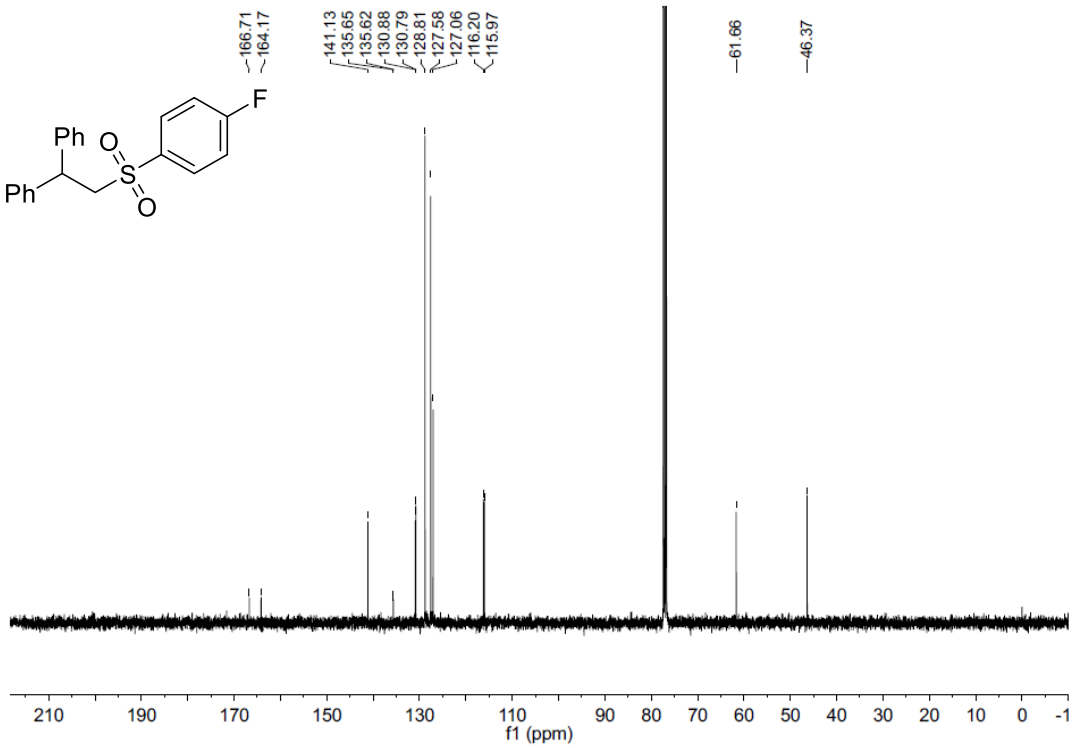
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-((4-Methoxyphenyl)sulfonyl)ethane-1,1-diyl) dibenzene (6ab)



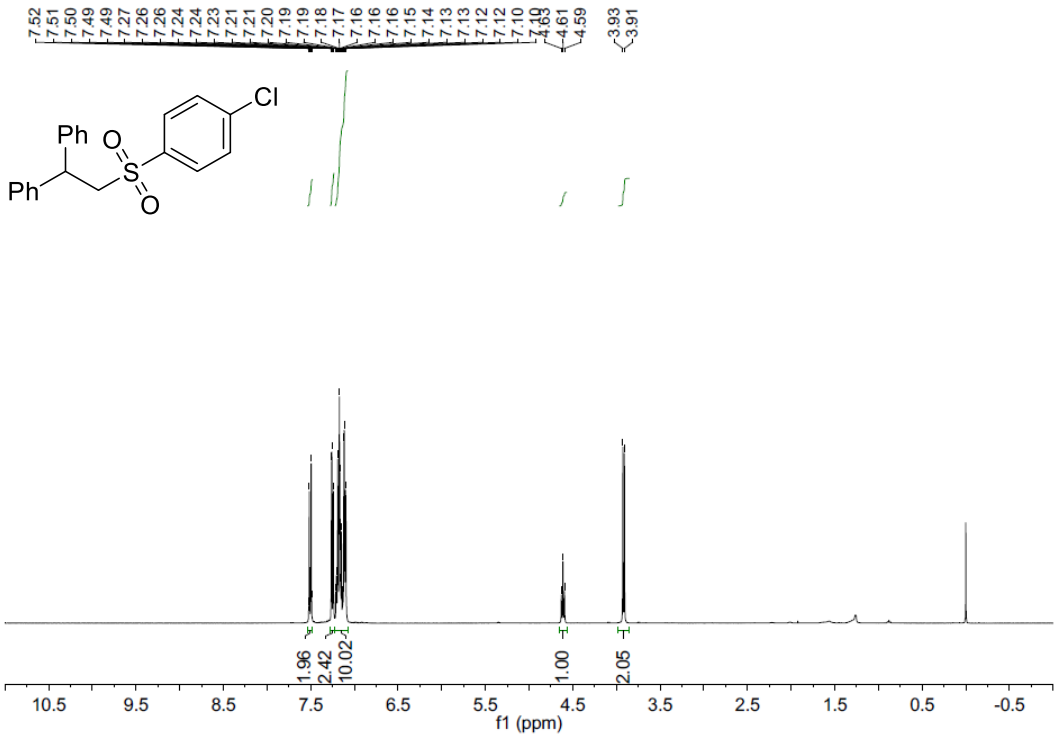
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-((4-Fluorophenyl)sulfonyl)ethane-1,1-diyl) dibenzene (6ac)



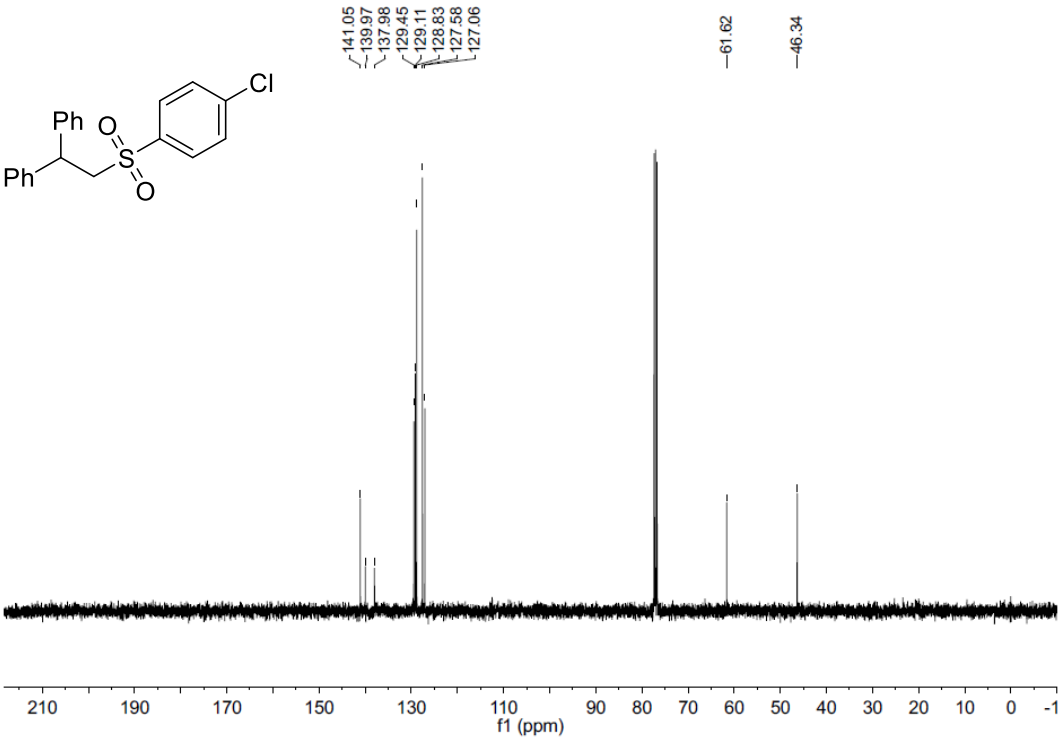
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-((4-Fluorophenyl)sulfonyl)ethane-1,1-diyl)dibenzene (6ac)



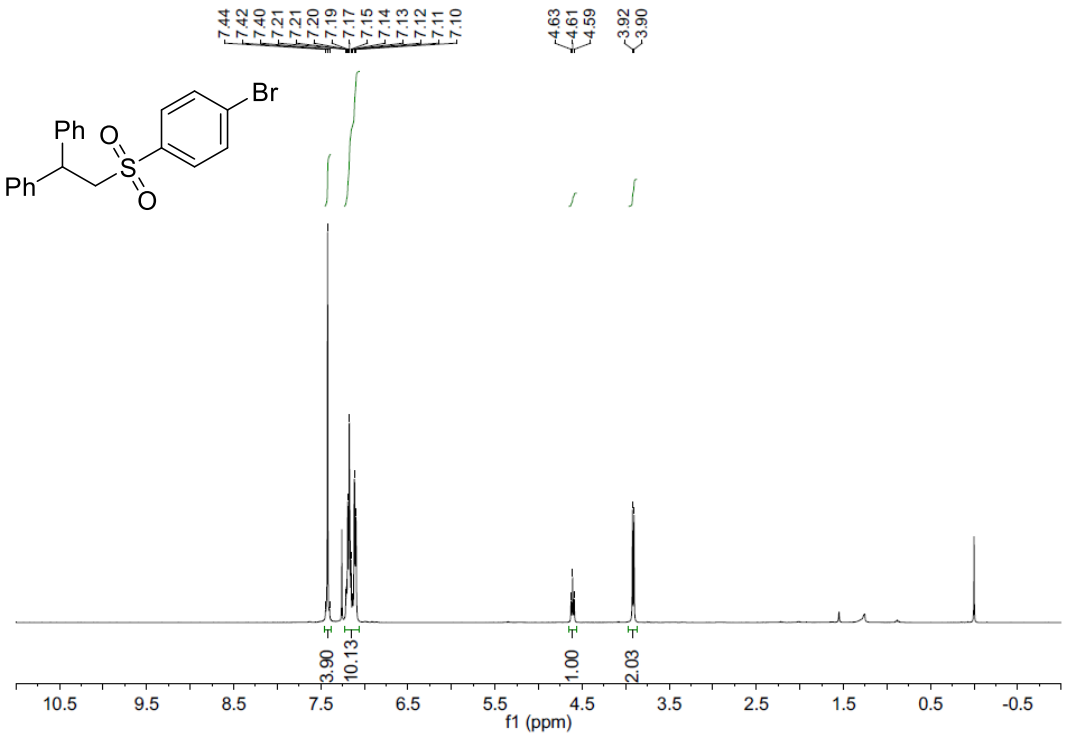
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-((4-Chlorophenyl)sulfonyl)ethane-1,1-diyl) dibenzene (6ad)



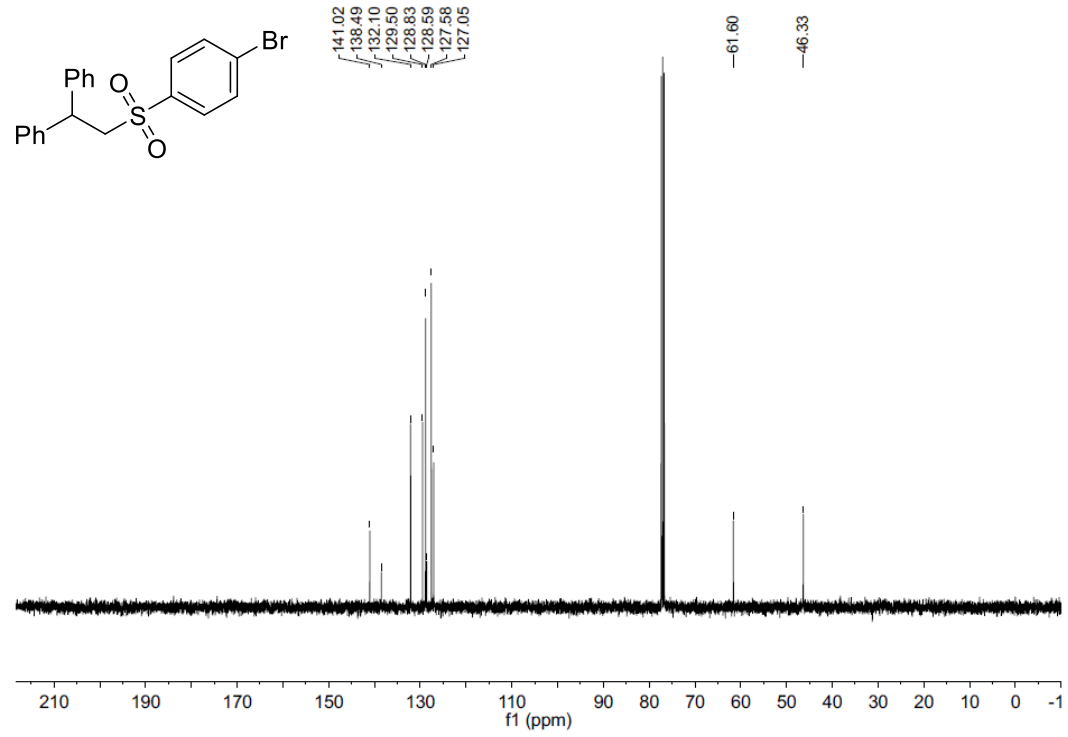
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-((4-Chlorophenyl)sulfonyl)ethane-1,1-diyl) dibenzene (6ad)



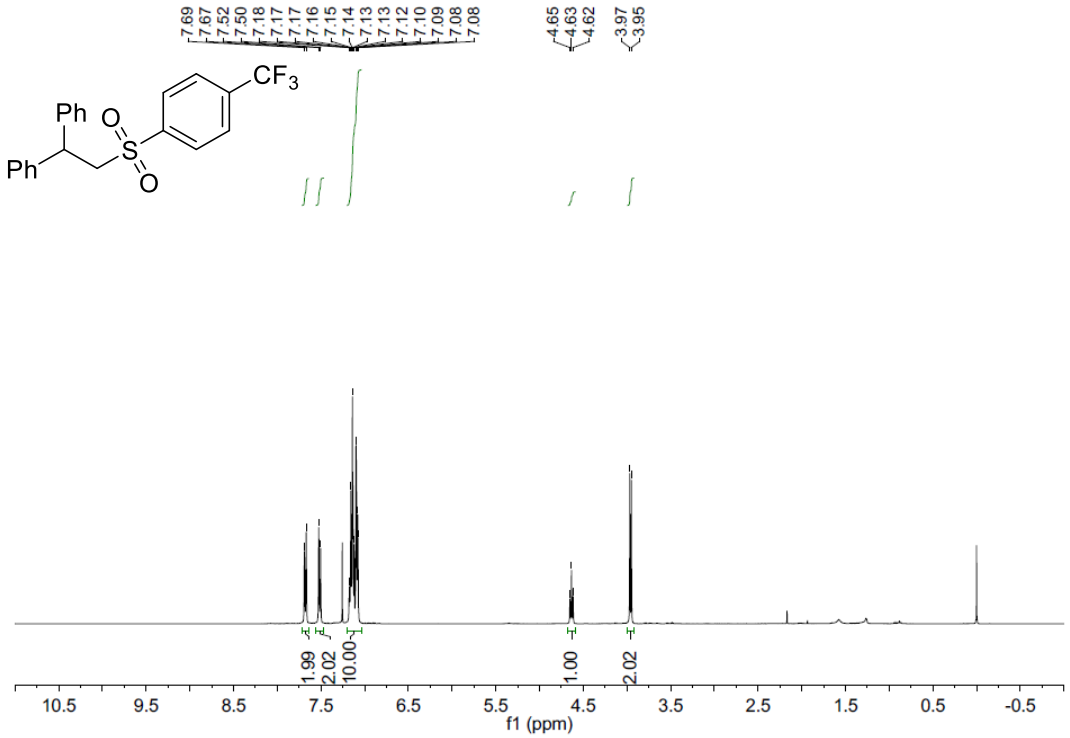
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-((4-Bromophenyl)sulfonyl)ethane-1,1-diyl) dibenzene (6ae)



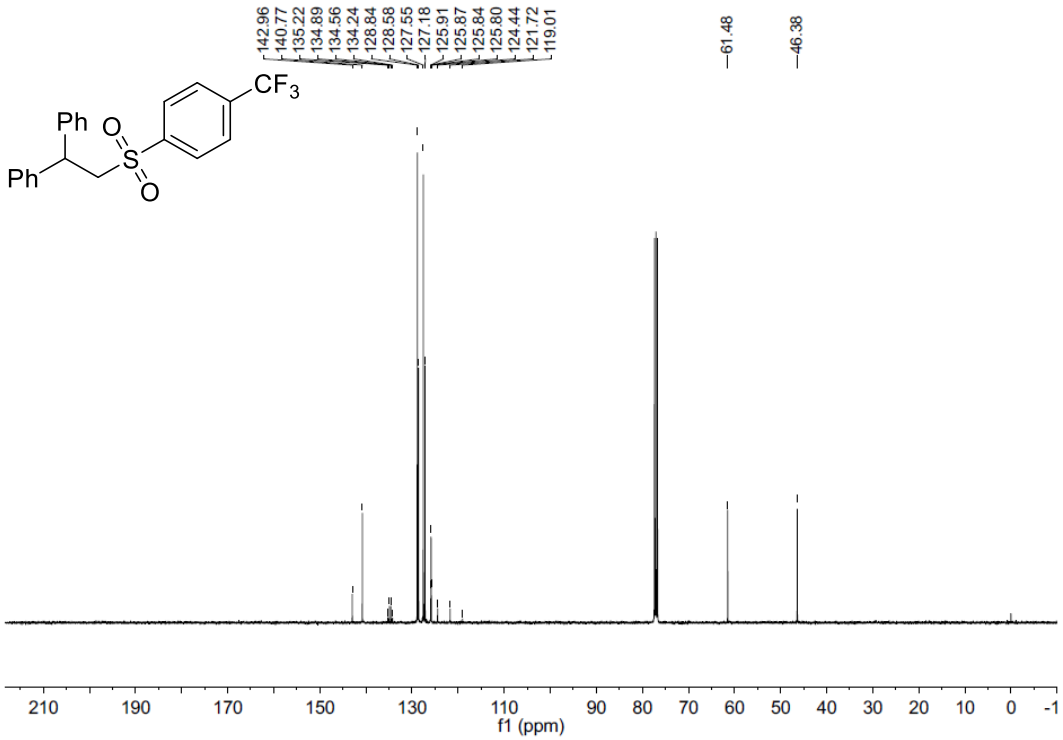
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-((4-Bromophenyl)sulfonyl)ethane-1,1-diyl) dibenzene (6ae)



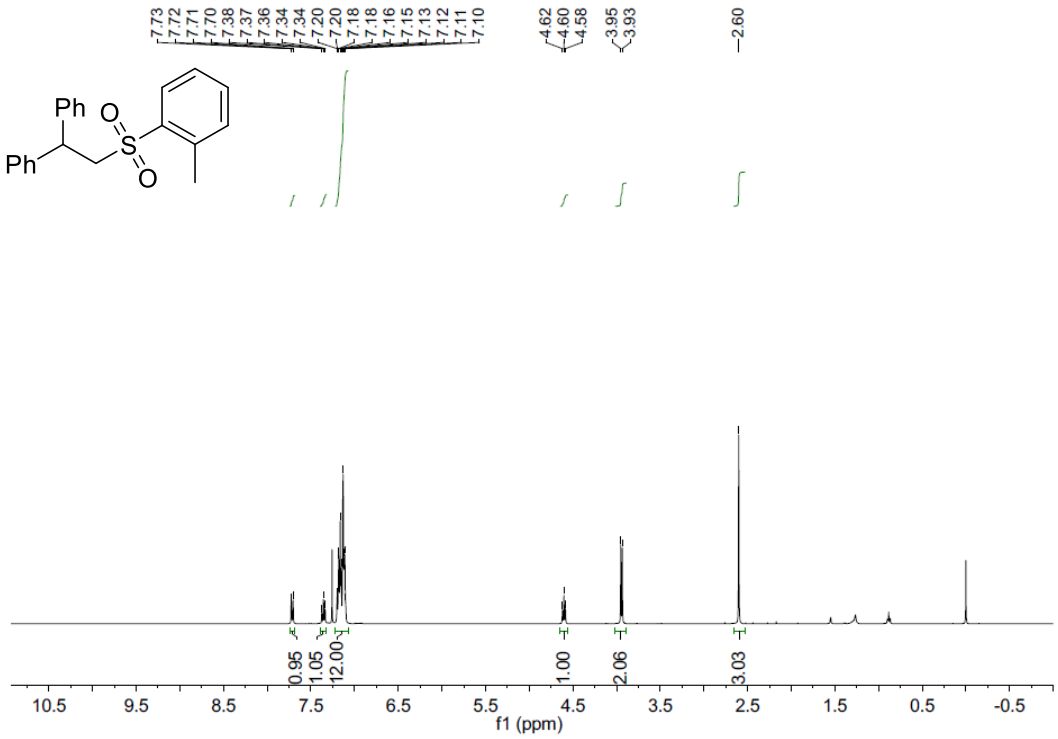
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-((4-(Trifluoromethyl)phenyl)sulfonyl)ethane-1,1-diyl)dibenzene (6af)



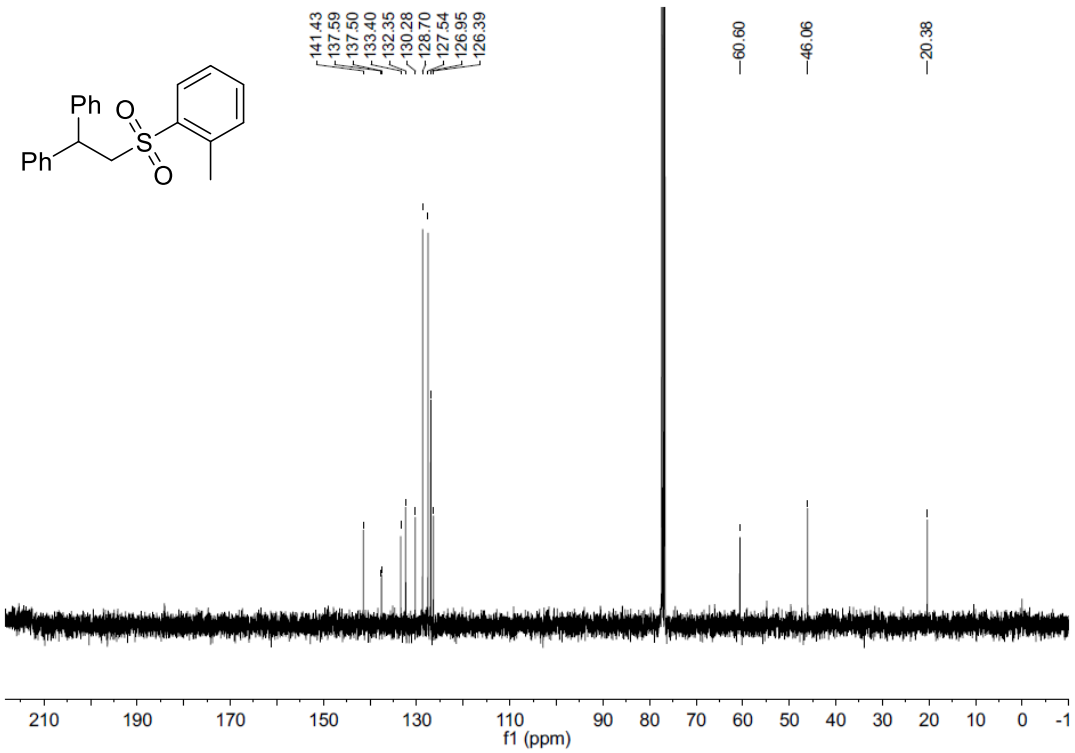
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-((4-(Trifluoromethyl)phenyl)sulfonyl) ethane-1,1-diyl)dibenzene (6af)



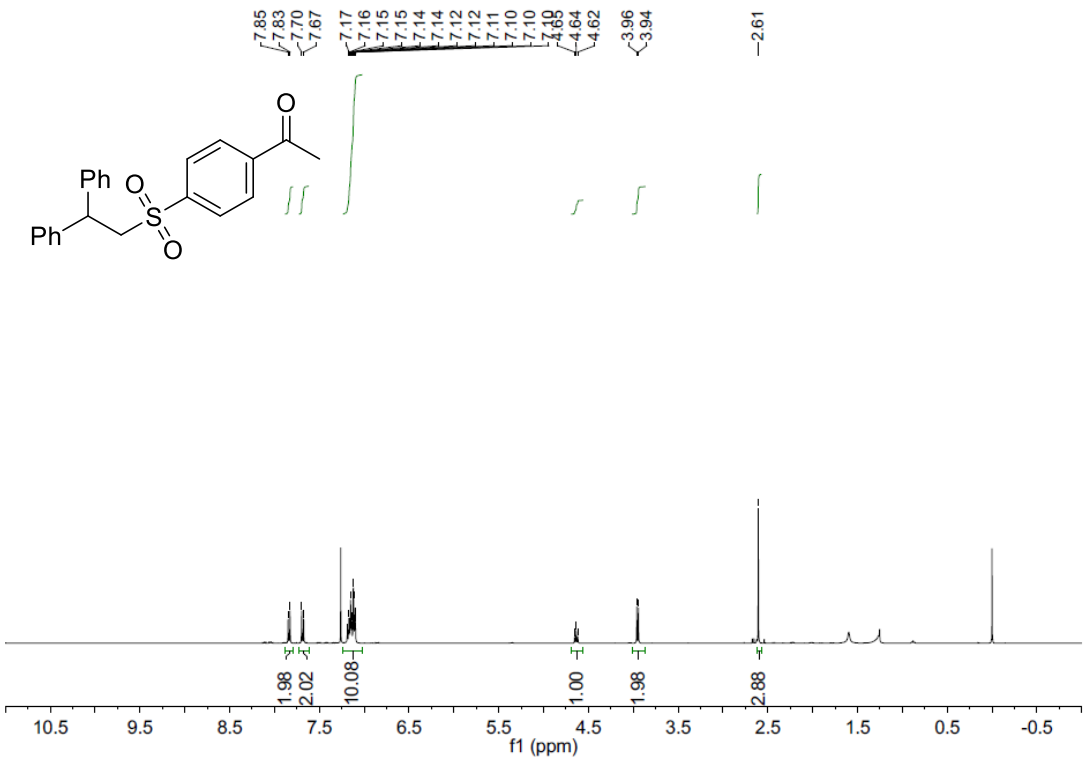
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-(*o*-Tolylsulfonyl)ethane-1,1-diyl)dibenzene (6ag)



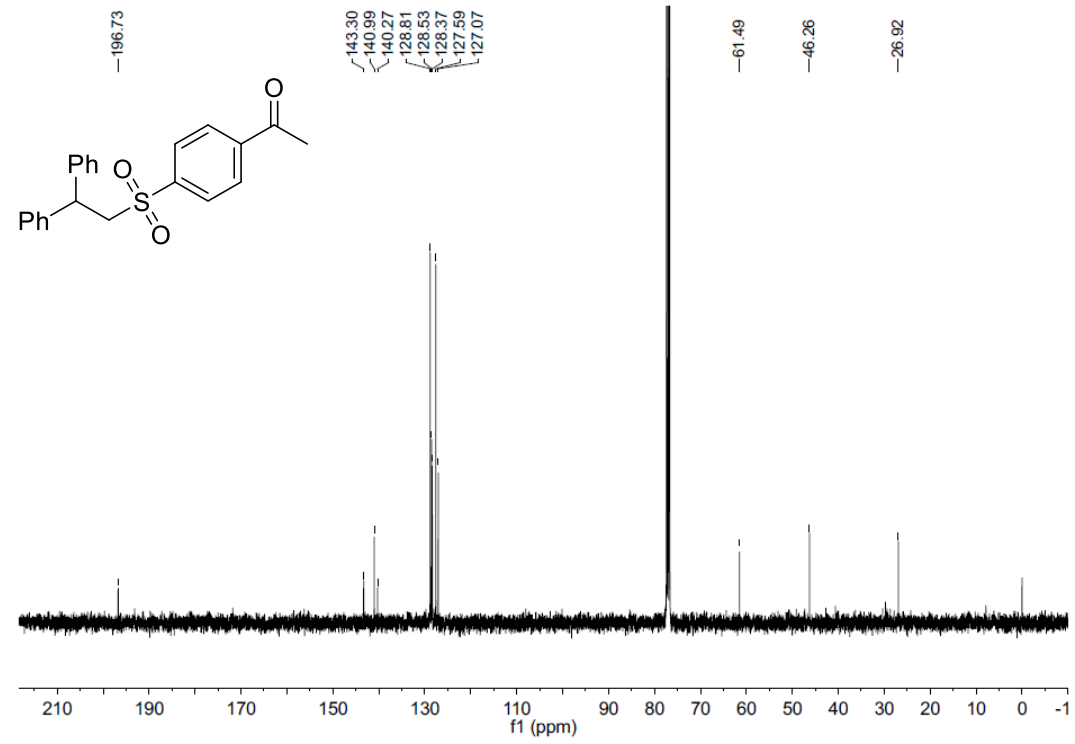
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-(*o*-Tolylsulfonyl)ethane-1,1-diyl)dibenzene (6ag)



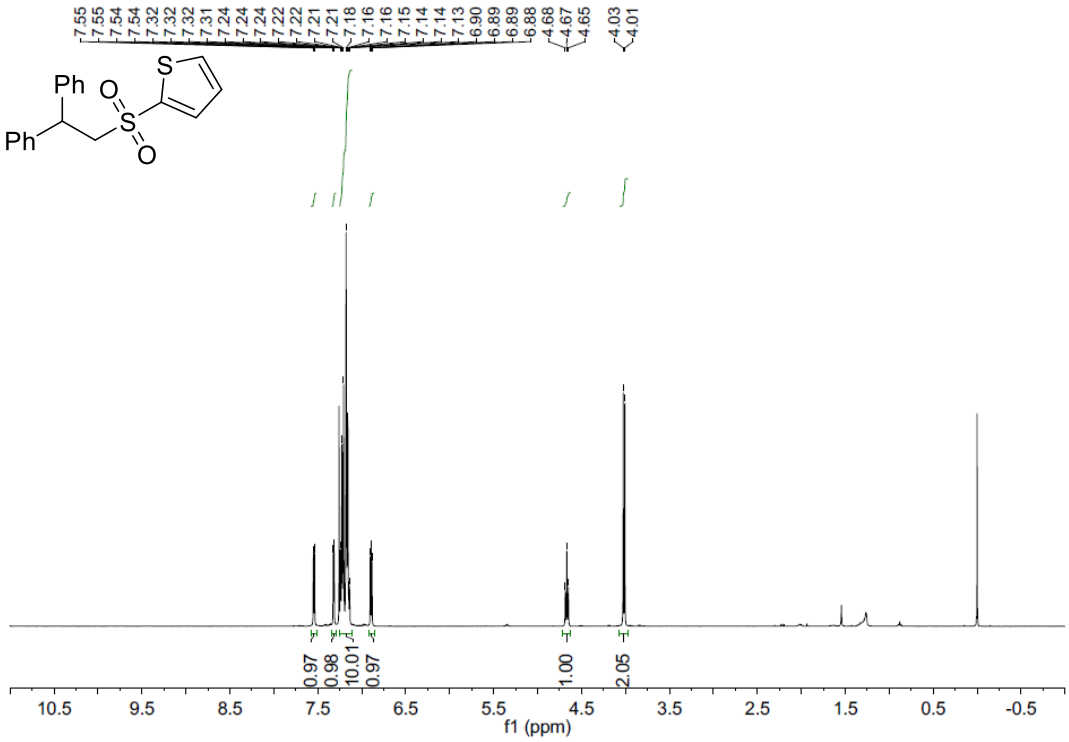
^{1}H NMR ($CDCl_3$, 400 MHz) of 1-(4-((2,2-Diphenylethyl)sulfonyl)phenyl) ethan-1-one (6ah)



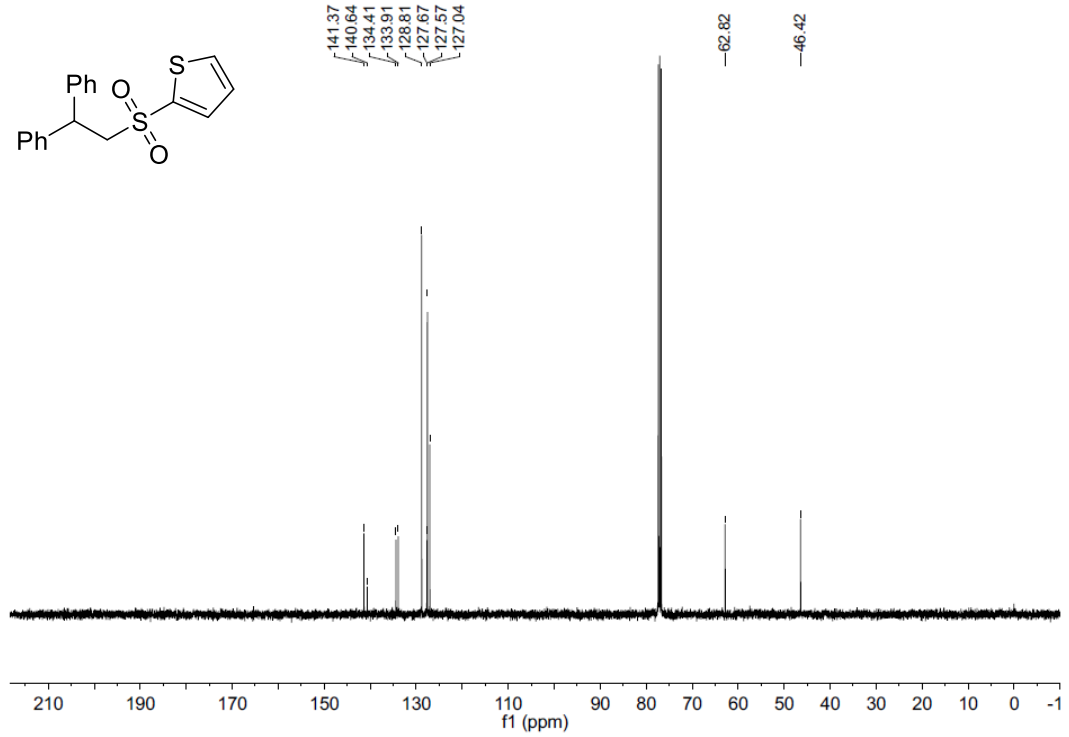
^{13}C NMR ($CDCl_3$, 100 MHz) of 1-(4-((2,2-Diphenylethyl)sulfonyl)phenyl) ethan-1-one (6ah)



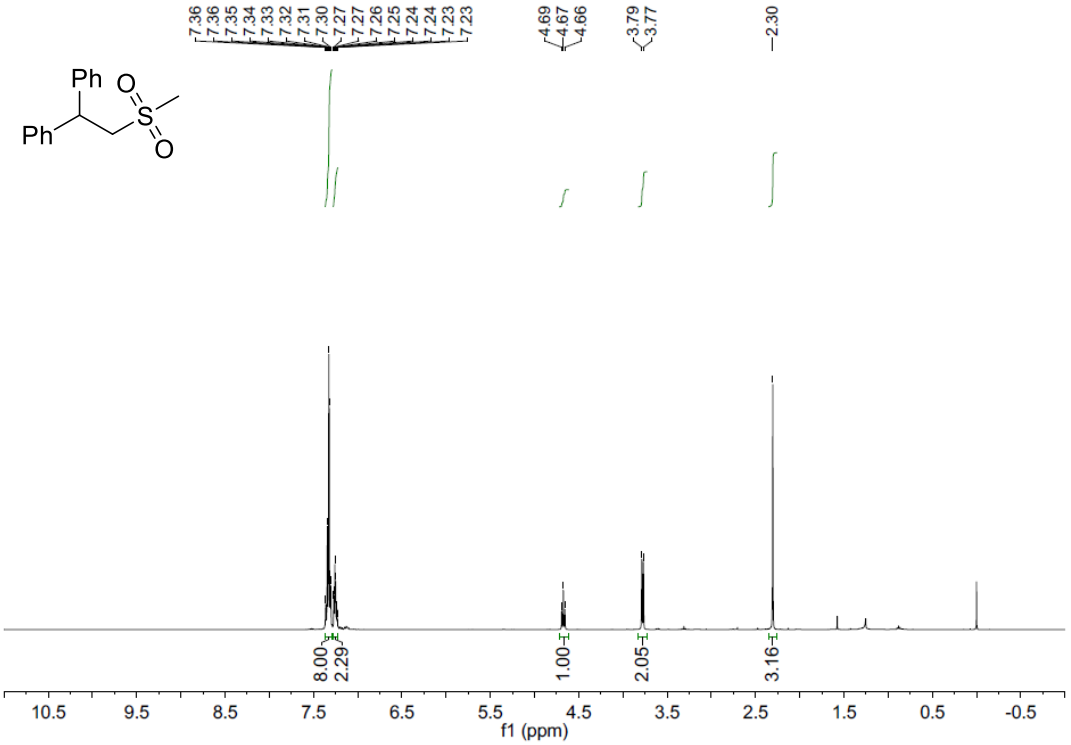
^{1}H NMR ($CDCl_3$, 400 MHz) of 2-((2,2-Diphenylethyl)sulfonyl)thiophene (6ai)



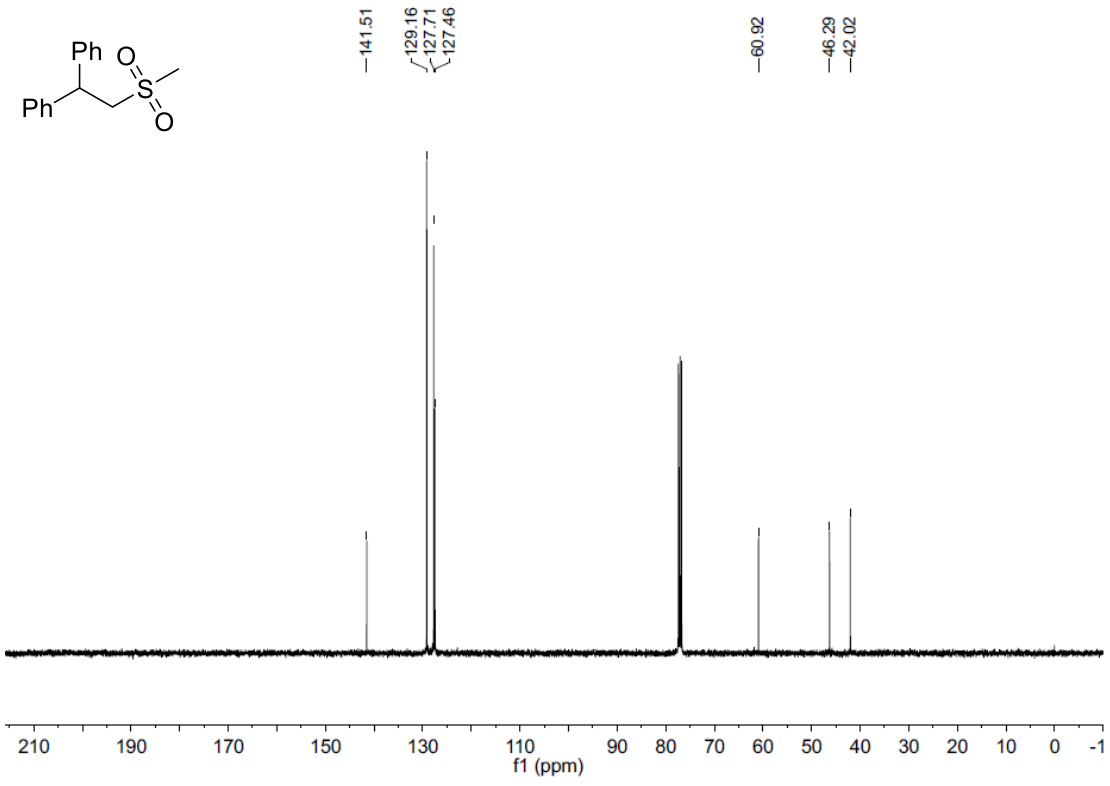
^{13}C NMR ($CDCl_3$, 100 MHz) of 2-((2,2-Diphenylethyl)sulfonyl)thiophene (6ai)



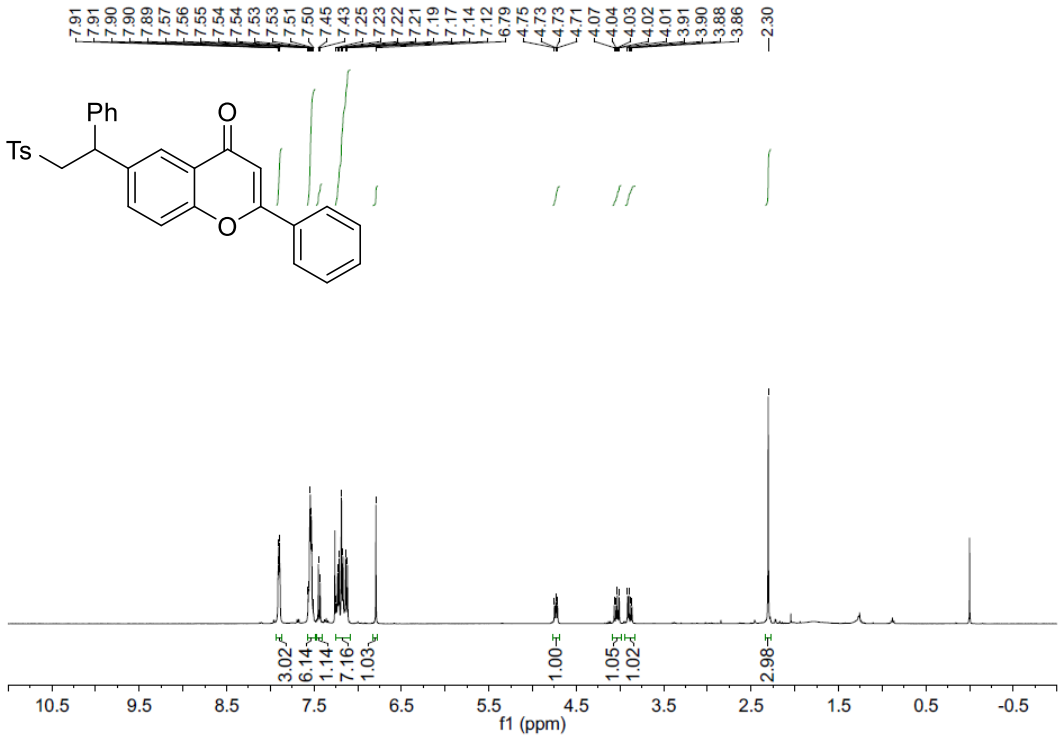
^{1}H NMR ($CDCl_3$, 400 MHz) of (2-(Methylsulfonyl)ethane-1,1-diyl)dibenzene (6aj)



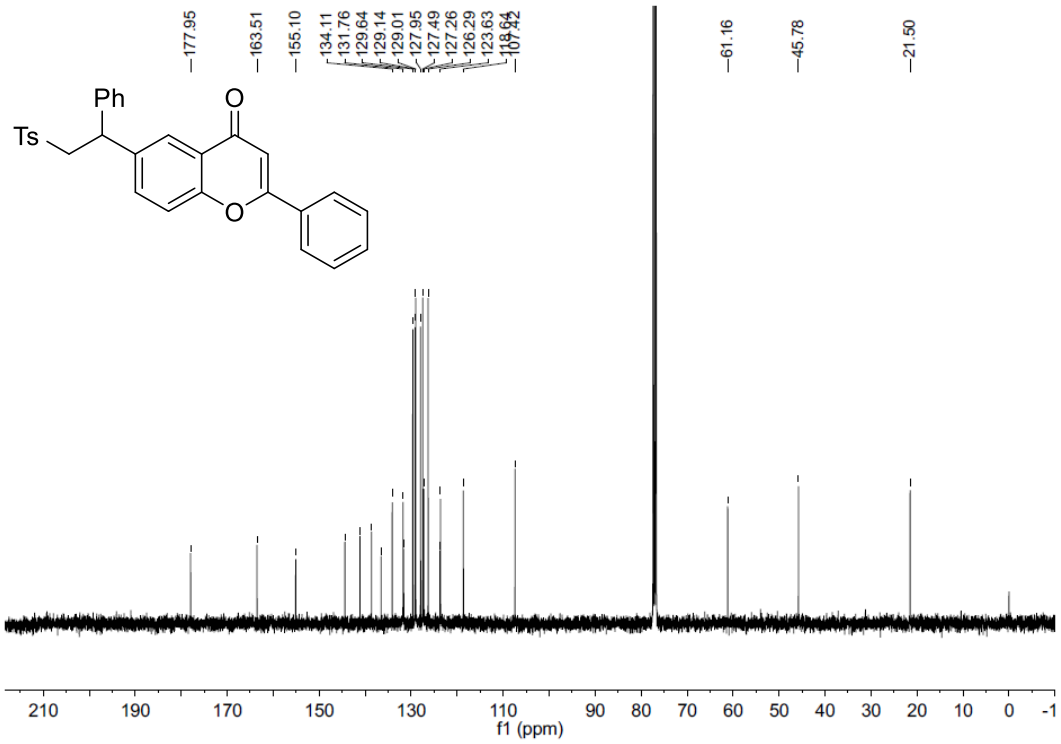
^{13}C NMR ($CDCl_3$, 100 MHz) of (2-(Methylsulfonyl)ethane-1,1-diyl)dibenzene (6aj)



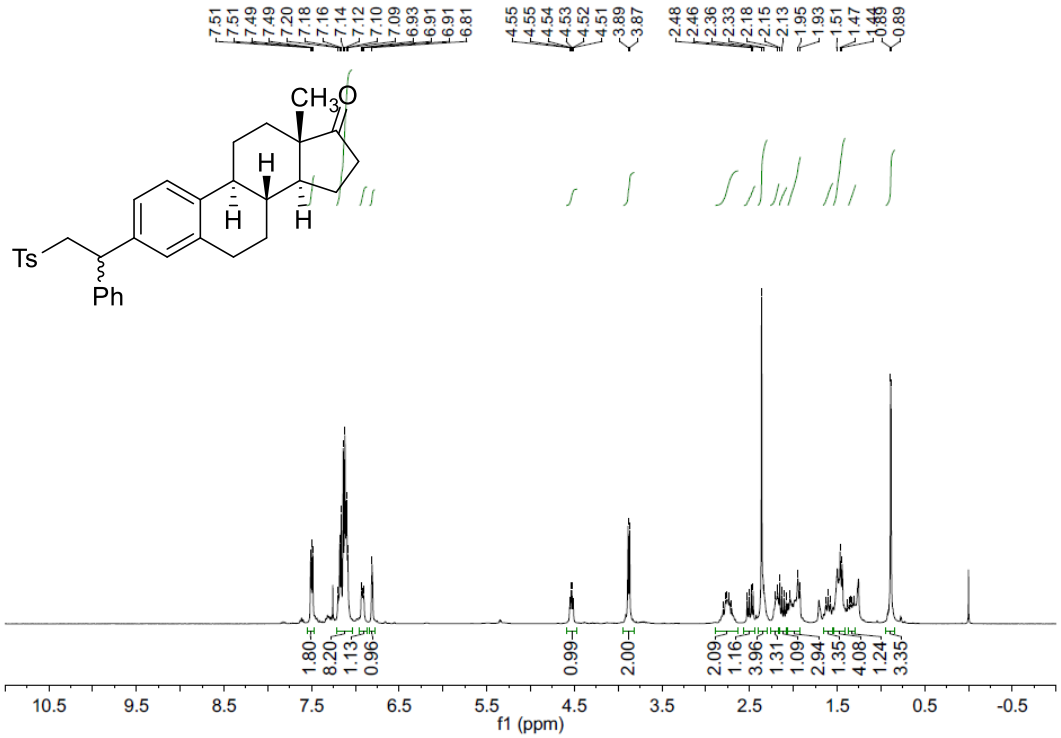
^{1}H NMR ($CDCl_3$, 400 MHz) of 3-Phenyl-6-(1-phenyl-2-tosylethyl)-4*H*-chromen-4-one (5ap)



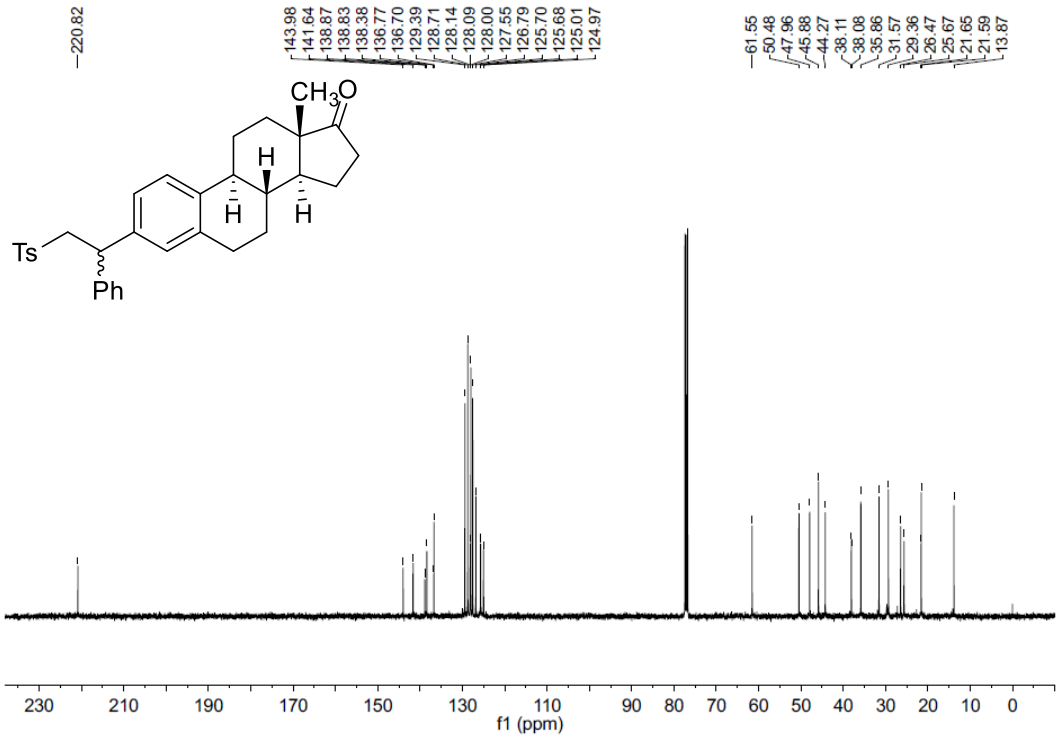
^{13}C NMR ($CDCl_3$, 100 MHz) of 3-Phenyl-6-(1-phenyl-2-tosylethyl)-4*H*-chromen-4-one (5ap)



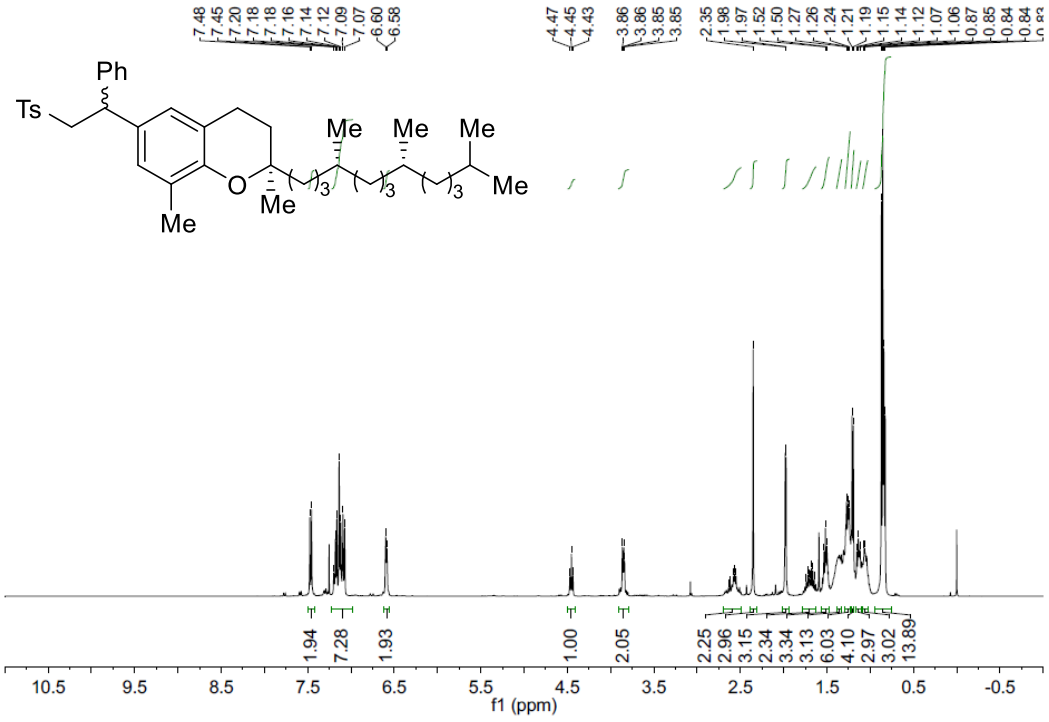
^{1}H NMR ($CDCl_3$, 400 MHz) of (8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(1-phenyl-2-tosylethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (5aq)



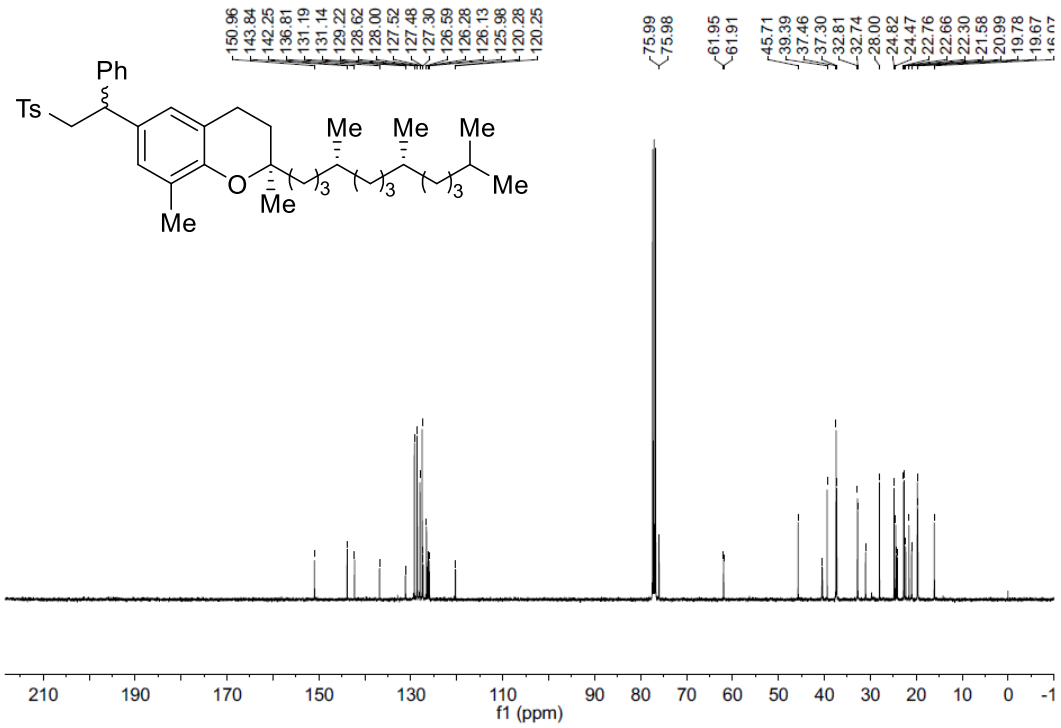
^{13}C NMR ($CDCl_3$, 100 MHz) of (8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(1-phenyl-2-tosylethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (5aq)



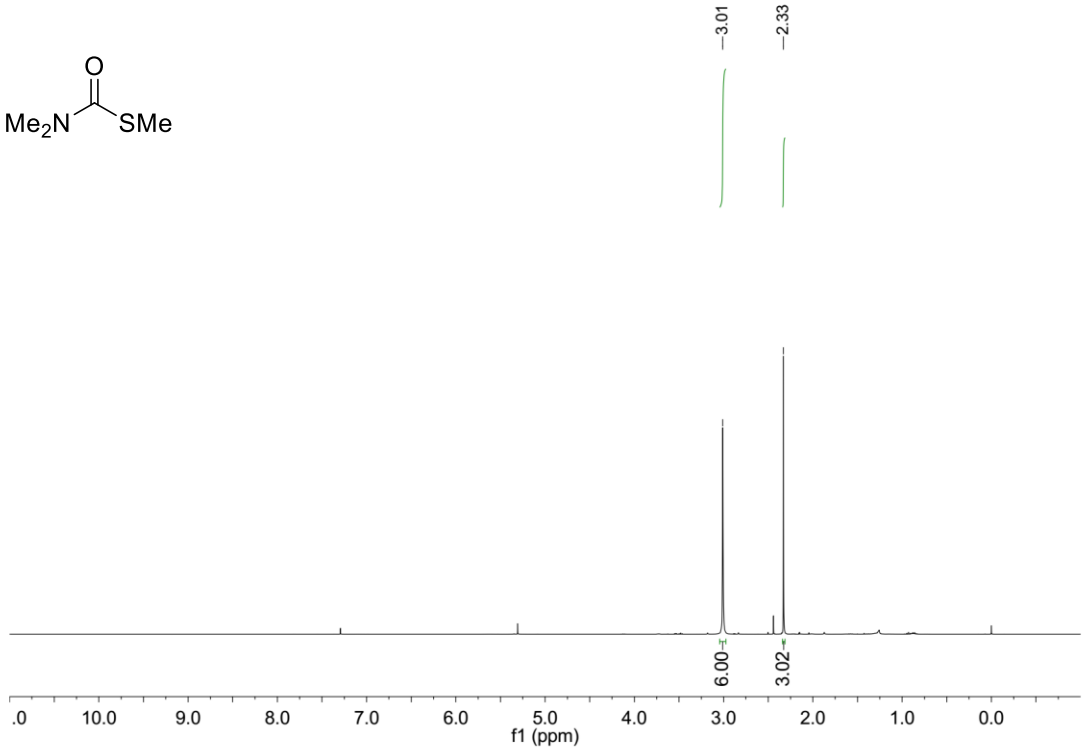
^{1}H NMR ($CDCl_3$, 400 MHz) of (2*R*)-2,8-Dimethyl-6-(1-phenyl-2-tosylethyl)-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chromane (5ar)



^{13}C NMR ($CDCl_3$, 100 MHz) of (2*R*)-2,8-Dimethyl-6-(1-phenyl-2-tosylethyl)-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chromane (5ar)



^{1}H NMR ($CDCl_3$, 400 MHz) of *S*-methyl dimethylcarbamothioate (11a)



^{13}C NMR ($CDCl_3$, 100 MHz) of *S*-methyl dimethylcarbamothioate (11a)