Efficient Synthesis of γ-Keto Sulfones by NHC-Catalyzed Intermolecular Stetter Reaction

Anup Bhunia, Santhivardhana Reddy Yetra, Sachin Suresh Bhojgude, and Akkattu T. Biju*

Organic Chemistry Division, CSIR-National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune - 411008, India
at.biju@ncl.res.in

Supporting Information

1. General Information

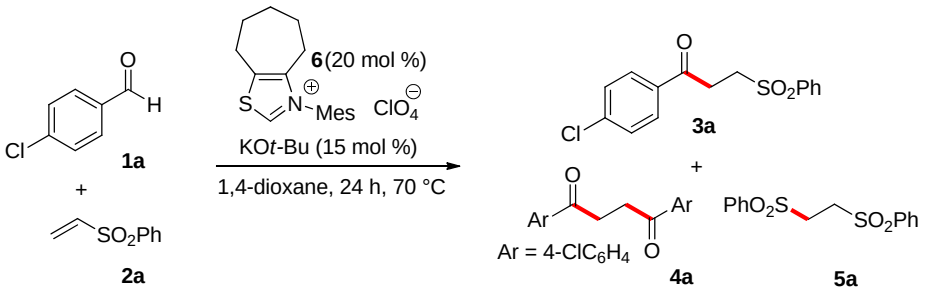
Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel. Dry 1,4-dioxane was purchased from commercial sources and stored under argon over 4 Å molecular sieves. The aldehydes were purchased from Aldrich or Acros and were purified either by distillation or washing with $NaHCO_3$ after dissolving in ether or dichloromethane, prior to use. The phenyl vinyl sulfone, methyl vinyl sulfone and divinyl sulfone were purchased from Sigma Aldrich and used as received, without any further purification. KO*t*-Bu was dried by heating at 110 °C for 12 h and left to cool under argon. The thiazolium salt **6** was synthesized following the literature procedure.[1]

Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254}. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 400, AV 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm, DMSO-d6 δH = 2.52 ppm). Infrared spectra were recorded on a Perkin-Elmer 1615 FT Infrared Spectrophotometer Model 60B. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump.

[1] (a) Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. *Eur. J. Org. Chem.* **2011**, 5475. (b) Lebeuf, R.; Hirano, K.; Glorius, F. *Org. Lett.* **2008**, *10*, 4243.

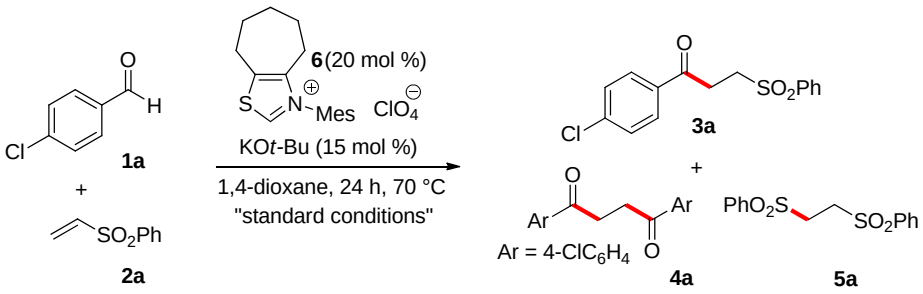
2. General Procedure for the Optimization of Reaction Conditions



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added dry KO*t*-Bu (4.2 mg, 0.037 mmol) and the thiazolium **6** (18.5 mg, 0.05 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in 1,4-dioxane under argon atmosphere (1.0 mL). The resultant reaction mixture was kept stirring at 30 °C (rt) for 45 min. To the stirring solution 4-chlorobenzaldehyde **1a** (35.1 mg, 0.25 mmol) and the phenyl vinyl sulfone **2a** (42.0 mg, 0.25 mmol) were successively added. Then the reaction mixture is placed in a preheated oil bath at 70° C for the indicated time. The reaction mixture was cooled and the mixture was diluted with CH_2Cl_2 (2.0 mL) and filtered through a short pad of silica gel and eluted with CH_2Cl_2 (10.0 mL). The solvent was evaporated to obtain the crude product whose yield was determined by ^{1}H NMR analysis using CH_2Br_2 (18.0 μL, 0.25 mmol) as the internal standard.

3. Optimization Studies

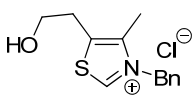
Our optimization study commenced with treatment of 4-chloroobenzaldehyde **1a** with phenyl vinyl sulfone **2a**. We started off by using the carbene generated from thiazolium salt **6**. Treatment of **1a** with **2a** in the presence of the carbene generated from **6** by deprotonation using KO*t*-Bu resulted in the formation of γ-keto sulfone **3a** in 56% yield along with the undesired side products **4a** and **5a** derived from the base-induced elimination of the sulfonyl group of **3a** was observed in low yields. (based on ^{1}H NMR, entry 1). Remarkably, in contrast to this NHC, other common NHCs derived from **7-10** are far less effective (entries 2-5). Other Bases such as K_2CO_3, Na_2CO_3, Et_3N and DBU furnished the desired product **3a** in reduced yields (entries 6-9), and solvents other than 1,4-dioxane resulted in inferior reactivity and/or selectivity (entries 10-12). The reaction is sluggish at 60 °C (entry 13), and the yield of **3a** was reduced considerably when the amount of **6** and KO*t*-Bu was reduced (entry 14). Addition of special additive e.g; 18-crown-6 or Moleculae sieves has no special effect on selectivity. Finally, increasing the amount of **1a** to 1.4 equiv and reducing the reaction time to 22 h, improved the reactivity, with **3a** obtained in 81% yield (entry 15). Under the optimized conditions, the symmetric 1,4-diketone **4a** was isolated in 8% yield and no disulfone **5a** was formed.



entry	variation of the standard conditions[a]	yield of **3a** (%)[b]	yield of **4a** (%)[b]	yield of **5a** (%)[b]
1	None	56	10	<1
2	**7** instead of **6**	9	3	<1
3	**8** instead of **6**	<1	50	44
4	**9** instead of **6**	<1	23	23
5	**10** instead of **6**	<1	20	2

6	K_2CO_3 instead of KO*t*-Bu	47	12	<1
7	Na_2CO_3 instead of KO*t*-Bu	<1	<1	<1
8	Et_3N instead of KO*t*-Bu	37	8	<1
9	DBU instead of KO*t*-Bu	<1	43	30
10	THF instead of 1,4-dioxane	34	19	18
11	Toluene instead of 1,4-dioxane	48	7	7
12	Ethanol instead of 1,4-dioxane	<1	29	17
13	Reaction run at 60 °C	35	3	<1
14	15 mol % of **6**, 10 mol % KOt-Bu	34	8	<1
15	**1.4 equiv of 1a, reaction time: 22 h**	**80(81)**	**8(8)**	**<1**
16	20 mol% KO*t*-Bu instead of 15 mol% KO*t*-Bu	36	17	<1
17	25 mol% KO*t*-Bu instead of 15 mol% KO*t*-Bu	17	34	11
18	2 ml of 1,4-dioxane instead of 1 ml 1,4-dioxane	33	7	0
19	1.2 equiv of **1a** & 20 mol% KO*t*-Bu	45	10	<1
20	1.4 equiv of **1a** & 20 mol% KO*t*-Bu	63	21	<1
21	20 mol% of KO*t*-Bu & 20 mol% 18-crown-6	40	10	<1
22	15 mol% KF & 30 mol% [18]-crown-6 instead of KO*t*-Bu	43	10	<1
23	1.4 equiv of **1a**, 15 mol% KO*t*-Bu & 15 mol% [18]-crown-6	18	15	<1
24	1.4 equiv of **1a,** 15 mol% KO*t*-Bu & 100 mg 4 Å MS	22	11	<1
25	1.4 equiv of **1a**, reaction time: 16 h	60	7	<1
26	1.4 equiv of **1a**, reaction time: 20 h	69	8	<1
27	1.4 equiv of **1a**, reaction time: 24 h	70	17	<1

[a] Standard conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), NHC·HX (20 mol %), KO*t*-Bu (15 mol %), 1,4-dioxane (1.0 mL), 70 °C and 24 h. [b] The yields were determined by ^{1}H-NMR analysis (DMSO-d6) of crude products using CH_2Br_2 as the internal standard. Isolated yield in 1.0 mmol scale in parentheses.



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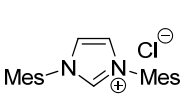

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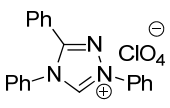

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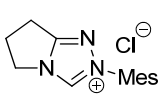

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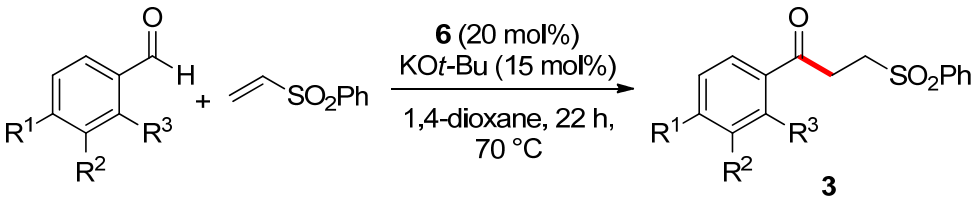
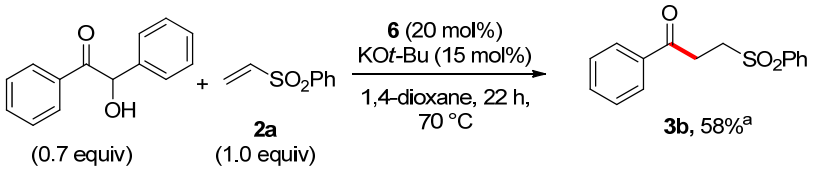
4. General Procedure for the NHC-Catalyzed Intermolecular Stetter Reaction



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was taken dry KO*t*-Bu (16.8 mg, 0.15 mmol) and the thiazolium salt **6** (74.4 mg, 0.20 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added 1,4-dioxane (4.00 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 30 °C (rt) for 45 min. To this mixture was added the aldehyde **1** (1.4 mmol) (*solid* aldehydes were weighed in air and transferred to the schlenk tube by closing the argon flow and *liquid* aldehydes were transferred via syringe with argon flow) and the vinyl sulfone **2** (1.0 mmol) were successively added. Then the reaction mixture was placed in preheated oil bath at 70° C. When TLC control showed the completion of the reaction (typically after 22 h), the mixture was diluted with CH_2Cl_2 (5.0 mL) and filtered through a short pad of silica gel and eluted with CH_2Cl_2. The solvent was evaporated and the crude residue purified by flash column chromatography on silica gel to afford the corresponding γ-keto sulfones **3** in moderate to good yields.

5. Mechanistic Experiments

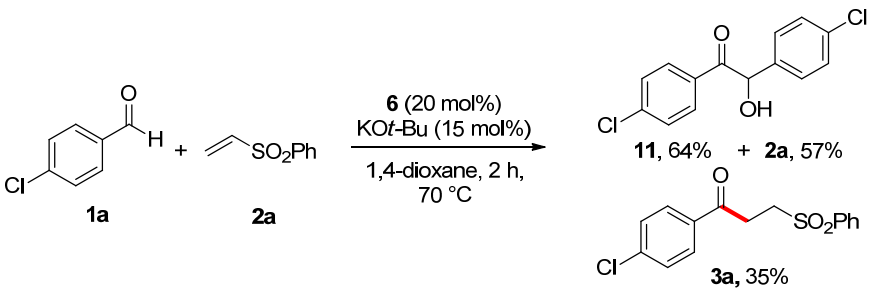
Reaction Employing Benzoin as Substrate



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added dry KO*t*-Bu (16.8 mg, 0.15 mmol) and the thiazolium salt **6** (74.4mg, 0.20 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in 1,4-dioxane under argon atmosphere (4.0 mL). The resultant reaction mixture was kept stirring at 30 °C (rt) for 45 min. To this mixture was added the benzoin (149 mg, 0.7 mmol) and the phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) was successively added. Then the reaction mixture is placed in a preheated oil bath at 70° C. After 22 h, the reaction mixture cooled and the mixture was diluted with CH_2Cl_2 (5 mL) and filtered through a short pad of silica gel and eluted with CH_2Cl_2. The solvent was evaporated and the crude residue purified by flash column chromatography on silica gel to afford the corresponding γ-keto sulfone **3b** in 58% yield.

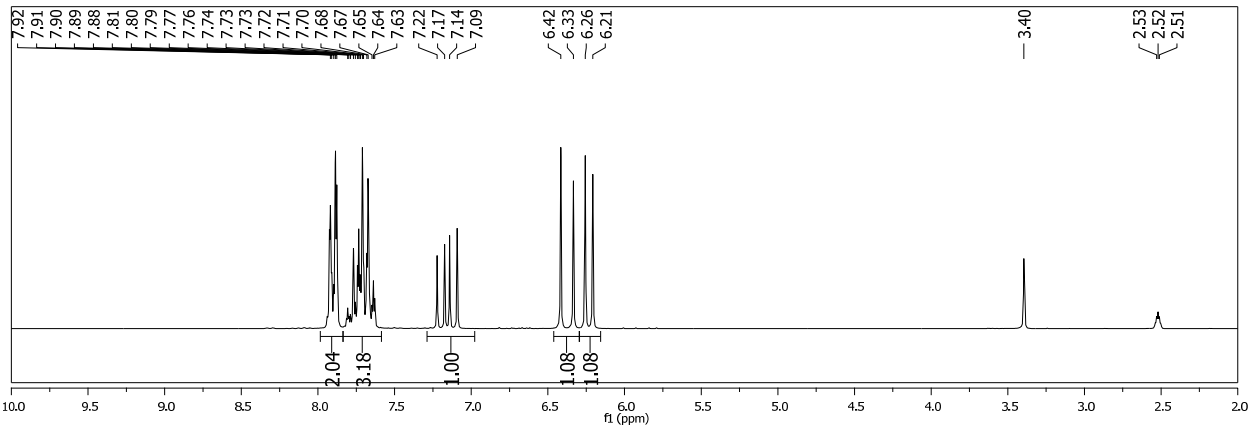
This experiment reveals the reversibility of the formation of Breslow intermediate under the present reaction conditions.

Experiment to Confirm the Formation of Benzoin Under the Optimized Conditions

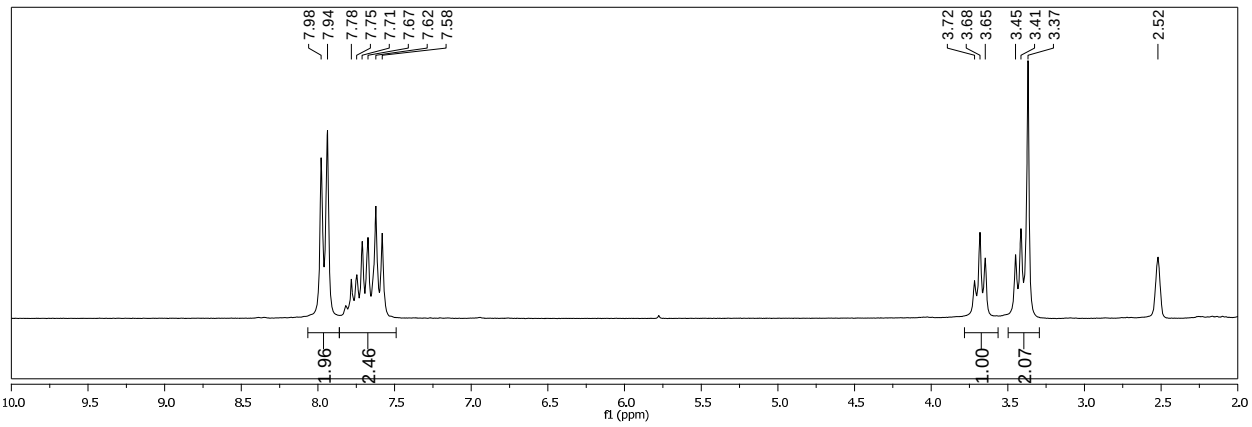


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added dry KO*t*-Bu (4.2 mg, 0.037 mmol) and the thiazolium **6** (18.5 mg, 0.05 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. After that the mixture was dissolved in 1,4-dioxane under argon atmosphere (1.0 mL). The resultant reaction mixture was kept stirring at 30 °C (rt) for 45 min. To this stirring solution 4-chlorobenzaldehyde **1a** (49.1 mg, 0.35 mmol) and the phenyl vinyl sulfone **2a** (42.0 mg, 0.25 mmol) were successively added. Then the reaction mixture is placed in preheated oil bath at 70° C. After 2 hour heating the reaction is quenched and the mixture was diluted with CH_2Cl_2 (2.0 mL) and filtered through a short pad of silica gel and eluted with CH_2Cl_2 (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ^{1}H NMR using CH_2Br_2 (18.0 μL, 0.25 mmol) as the internal standard. ^{1}H NMR study shows that the crude mixture contains 64% 4-chlorobenzoin, 35% product and 57% unreacted **2a**.

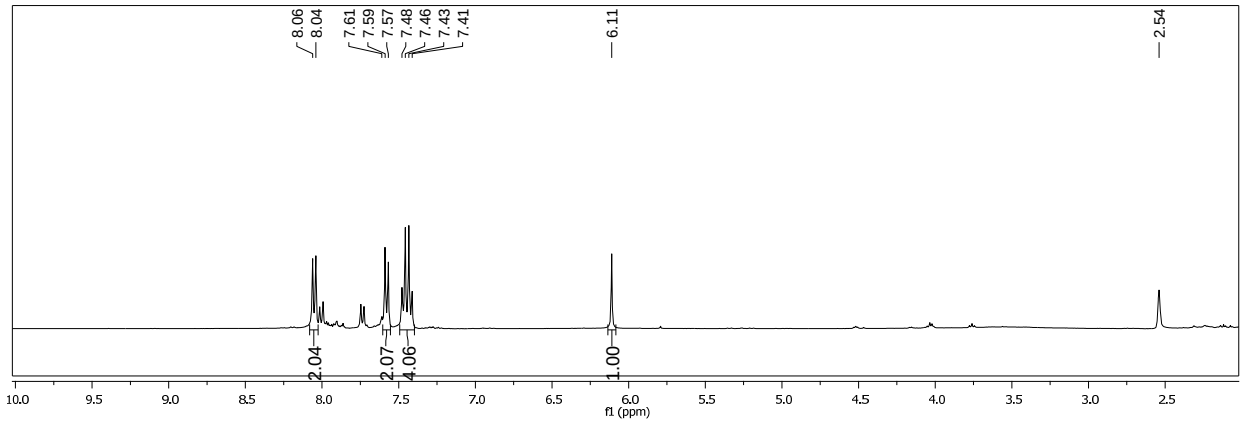
^{1}H-NMR Spectrum of Phenyl Vinyl Sulfone (DMSO-d6)



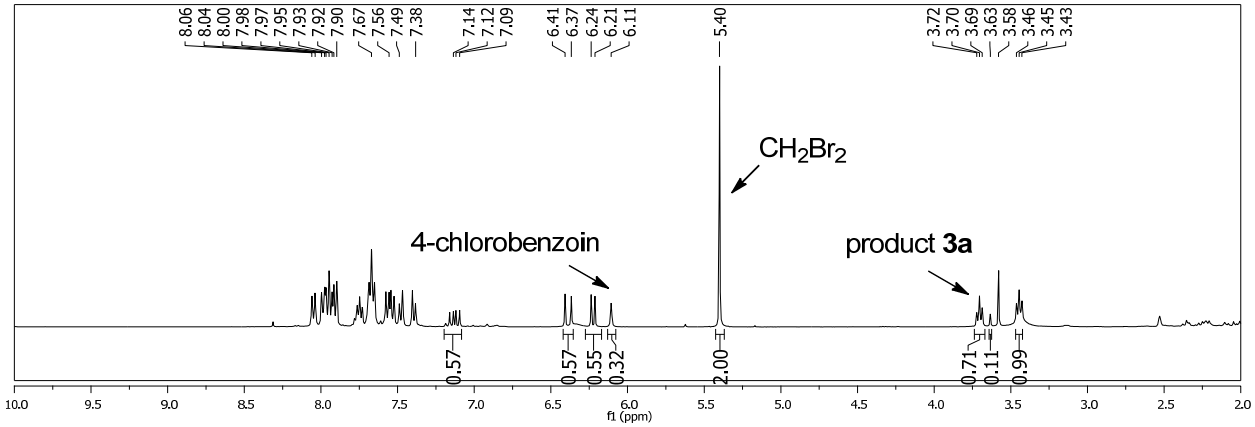
^{1}H-NMR Spectrum of 3a (DMSO-d6)



^{1}H-NMR Spectrum of 4-Chlorobenzoin (DMSO-d6)



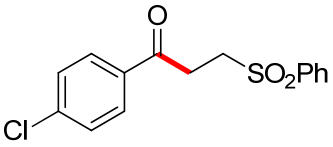
^{1}H-NMR of Crude Reaction Mixture after 2 h (DMSO-d6)



This experiment confirms the formation of benzoin under the reaction conditions, which sheds light on the reversibility of the formation of Breslow intermediate under the present reaction conditions.

6. Synthesis and Characterization of γ-Keto Sulfones

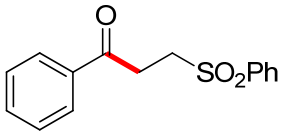
1-(4-Chlorophenyl)-3-(phenylsulfonyl)propan-1-one (3a)[2]



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and 4-chlorobenzaldehyde **1a** (0.197 g, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(4-chlorophenyl)-3-(phenylsulfonyl)propan-1-one **3a** as a white solid (0.247 g, 81%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.72; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.94 (d, *J* = 7.4 Hz, 2H, H$_{ar}$), 7.82 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 7.67 (t, *J* = 7.4 Hz, 1H, H$_{ar}$), 7.57 (t, *J* = 8.4, 2H, H$_{ar}$), 7.43 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 3.57-3.52 (m, 2H, CH$_2$), 3.48-3.44 (m, 2H, CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 194.37, 140.43, 139.12, 134.22, 134.11, 129.58, 129.25, 128.08, 51.00, 31.43. **HRMS**: calculated [M+Na]$^+$ for $C_{15}H_{13}ClNaO_3S$: 331.0166, found: 331.0203. **FTIR (cm^{-1}):** 3019, 2977, 1690, 1591, 1477, 1422, 1319, 1216, 1152, 1046, 1086, 928, 909, 849, 669.

1-Phenyl-3-(phenylsulfonyl)propan-1-one (3b)[3]



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and benzaldehyde **1b** (0.148 g, 142 μL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-phenyl-3-(phenylsulfonyl)propan-1-one **3b** as a white solid (0.206 g, 75%).

***R*$_f$** (Pet. ether /EtOAc = 60/40): 0.56; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.95 (dd, J_1 = 7.9 Hz, J_2 = 16.0 Hz, 4H, H$_{ar}$), 7.67 (m, 1H, H$_{ar}$), 7.58 (m, 3H, H$_{ar}$), 7.47 (m, 2H, H$_{ar}$), 3.57-3.54 (m, 2H, CH$_2$), 3.50-3.46 (m, 2H, CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 195.49, 139.09, 133.87, 129.51, 128.87, 128.12, 128.06, 51.06, 31.46. **HRMS**: calculated [M+Na]$^+$ for $C_{15}H_{14}NaO_3S$: 297.0561, found: 297.0591. **FTIR (cm^{-1})**: 3020, 1686, 1448, 1319, 1216, 1151, 1087, 771, 687, 668.

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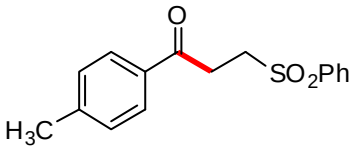
[2] Xiang, J.; Ipek, M.; Suri, V.; Tam, M.; Xing, Y.; Huang, N.; Zhang, Y.; Tobin, J.; Mansour, T. S.; McKew, J. *Bioorg. Med. Chem.* **2007**, *15*, 4396.

[3] Lee, J. Y.; Lim, K.-C.; Meng, X.; Kim, S. *Synlett.* **2010**, 1647.

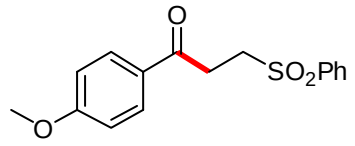
3-(Phenylsulfonyl)-1-(*p*-tolyl)propan-1-one (3c)[4]



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g. 1.0 mmol) and 3-methylbenzaldehyde **1c** (0.168 g, 166 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4 mL) at 70 °C for 22 h followed by flash column chromatography afforded 3-(phenylsulfonyl)-1-(*p*-tolyl)propan-1-one **3c** as a white solid (0.208 g, 72%).

***R*$_f$** (Pet. Ether/EtOAc = 60/40): 0.62; **^{1}H NMR (400 MHz, CDCl$_3$)** δ : 7.96 (d, *J* = 7.7 Hz, 2H, H$_{ar}$), 7.82 (d, *J* = 7.7 Hz, 2H, H$_{ar}$), 7.67 (t, *J* = 8.4Hz ,1H, H$_{ar}$),7.60-7.56 (m, 2H, H$_{ar}$), 7.26(d, *J* = 7.8 Hz, 2H, H$_{ar}$), 3.58-3.54 (m, 2H, CH$_2$), 3.49-3.45 (m, 2H, CH$_2$), 2.41 (s, 3H, CH$_3$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 195.04, 144.78, 139.06, 133.97, 133.35, 129.50, 129.46, 128.20, 128.02, 51.08, 31.27, 21.74. **HRMS**: calculated [M+Na]$^+$ for $C_{16}H_{16}O_3SNa$: 311.0712, found: 311.0743. **FTIR (cm^{-1})**: 3417, 3020, 1682, 1608, 1448, 1417, 1353, 1318, 1215, 1151, 1182, 1087, 929, 756, 687, 668.

1-(4-Methoxyphenyl)-3-(phenylsulfonyl)propan-1-one (3d)[4]

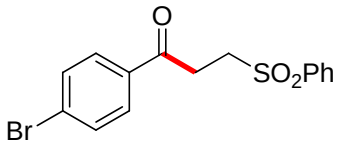


Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and 4-methoxybenzaldehyde **1d** (0.190 g, 170 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 30 h followed by flash column chromatography afforded 1-(4-methoxyphenyl)-3-(phenylsulfonyl)propan-1-one **3d** as a white solid (0.255 g, 84%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.46; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.94 (d, *J* = 8.2 Hz, 2H, H$_{ar}$), 7.89 (d, *J* = 8.2 Hz, 2H, H$_{ar}$), 7.66 (t, *J* = 7.4 Hz, 1H, H$_{ar}$), 7.57 (t, *J* = 7.4 Hz, 2H, H$_{ar}$), 6.92 (d, *J* = 8.2 Hz, 2H, H$_{ar}$), 3.36 (s, 3H, CH$_3$), 3.56-3.51 (m, 2H, CH$_2$), 3.46-3.41 (m, 2H, CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 193.96, 164.10, 139.17, 134.03, 130.50, 129.52, 128.96, 128.09, 114.04, 55.65, 51.25, 31.03. **HRMS:** calculated [M+Na]$^+$ for $C_{16}H_{16}NaO_4$: 327.0662, found: 327.0697. **FTIR (cm^{-1}):** 3019, 2360, 1676, 1600, 1512, 1420, 1308, 1255, 1218, 1172, 1150, 1087, 1025, 977, 771.

[4] Hansen, O. R.; Hammer, R. *Acta Chem. Scand.* **1953**, *7*, 1331.

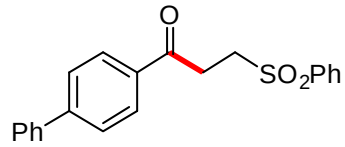
1-(4-Bromophenyl)-3-(phenylsulfonyl)propan-1-one (3e)[2]



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and 4-bromobenzaldehyde **1e** (0.259 g, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(4-bromophenyl)-3-(phenylsulfonyl)propan-1-one **3e** as a white solid (0.220 g, 62%).

***R**f* (Pet. ether /EtOAc = 60/40): 0.60; **^{1}H NMR (400 MHz, $CDCl_3$)**, δ: 7.94 (d, *J* = 8 Hz, 2H, H_{ar}), 7.78 (d, *J* = 8.2 Hz, 2H, H_{ar}), 7.69-7.56 (m, 5H, H_{ar}), 3.56-3.53 (m, 2H, CH_2), 3.48-3.44 (m, 2H, CH_2). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 194.59, 139.12, 134.62, 134.13, 132.27, 129.59, 129.22, 128.09, 51.00, 31.42. **HRMS**: calculated $[M+Na]^+$ for $C_{15}H_{13}NaBrO_3S$: 374.9666, found: 374.9707. **FTIR (cm^{-1}):** 3065, 2974, 1687, 1630, 1579, 1529, 1486, 1399, 1360, 1289, 1266, 1216, 1172, 1129, 1089, 1009, 956, 914, 865, 821, 753, 715, 681.

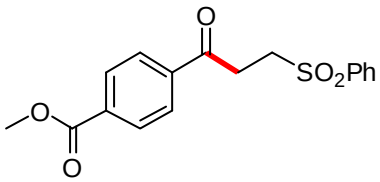
1-([1,1'-Biphenyl]-4-yl)-3-(phenylsulfonyl)propan-1-one (3f)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and [1,1'-biphenyl]-4-carbaldehyde **1f** (0.255 g, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-([1,1'-biphenyl]-4-yl)-3-(phenylsulfonyl)propan-1-one **3f** as a white solid (0.260 g, 75%).

***R**f* (Pet. ether /EtOAc = 60/40): 0.63; **^{1}H NMR (400 MHz, $CDCl_3$),)** δ: 8.02-7.97 (m, 4H, H_{ar}), 7.72-7.58 (m, 7H, H_{ar}), 7.51-7.41 (m, 3H, H_{ar}), 3.60-3.57 (m, 2H, CH_2), 3.55-3.53 (m, 2H, CH_2). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 196.03, 146.52, 139.59, 139.09, 134.47, 133.99, 129.47, 129.03, 128.70, 128.46, 128.03, 127.43, 127.29, 51.09, 31.39. **HRMS:** calculated $[M+Na]^+$ for $C_{21}H_{18}NaO_3S$: 373.0874, found: 373.0911. **FTIR (cm^{-1})**: 3020, 2400, 1681, 1604, 1216, 1045, 770, 669.

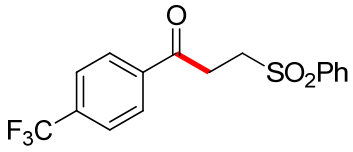
Methyl 4-(3-(phenylsulfonyl)propanoyl)benzoate (3g)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and methyl 4-formylbenzoate

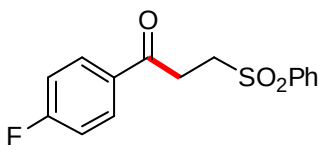
1g (0.250 g, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded methyl 4-(3-(phenylsulfonyl)propanoyl)benzoate **3g** as a white solid (0.305 g, 92%).
R_f (Pet. ether/EtOAc = 60/40): 0.46; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.12 (d, *J* = 7.3 Hz, 2H, H_{ar}), 7.96 (t, *J* = 7.7 Hz, 4H, H_{ar}), 7.67 (t, *J* = 7.7 Hz, 1H, H_{ar}), 7.58 (t, *J* = 7.7 Hz, 2H, H_{ar}), 3.94 (s, 3H, CH_3), 3.59-3.50 (m, 4H, $2CH_2$). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 195.14, 166.11, 139.10, 139.01, 134.63, 134.15, 130.11, 129.60, 128.12, 52.67, 50.97, 31.85. **HRMS:** calculated $[M+Na]^+$ for $C_{17}H_{16}NaO_5S$: 355.0611, found: 355.0648. **FTIR (cm^{-1}):** 3418, 3019, 2400, 1724, 1694, 1437, 1285, 1216, 1152, 1111, 1046, 768, 669.

3-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (3h)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and 4-(trifluoromethyl) benzaldehyde **1h** (0.243 g, 191 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.2 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 3-(phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one **3h** as a white solid (0.275 g, 80%).
R_f (Pet. ether /EtOAc = 60/40): 0.70; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.03 (d, *J* = 8 Hz, 2H, H_{ar}), 7.95 (d, *J* = 8Hz, 2H, H_{ar}), 7.75-7.67 (m, 3H, H_{ar}), 7.61-7.57 (m, 2H, H_{ar}), 3.57-3.53 (m, 4H, $2CH_2$). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 194.73, 138.77(d, $J_{(C-F)}$ = 56.3 Hz), 134.22, 129.64, 128.58, 128.11, 126.04(d, $J_{(C-F)}$ = 3.8 Hz), 125.99, 50.99, 31.79. **HRMS**: calculated $[M+Na]^+$ for $C_{16}H_{13}F_3NaO_3S$: 365.0435, found: 365.0474. **FTIR (cm^{-1}):** 3020, 2400, 1681, 1604, 1216, 1045, 770, 669.

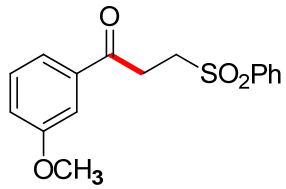
1-(4-Fluorophenyl)-3-(phenylsulfonyl)propan-1-one (3i)[2]



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and 4-fluorobenzaldehyde **1i** (0.174 g, 152 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(4-fluorophenyl)-3-(phenylsulfonyl)propan-1-one **3i** as a white solid (0.182 g, 62%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.64; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.95-7.92 (m, 4H, H$_{ar}$), 7.65 (t, *J* = 8.2 Hz, 1H, H$_{ar}$), 7.56 (t, *J* = 7.5 Hz, 2H, H$_{ar}$), 7.11 (t, *J* = 9.3 Hz, 2H, H$_{ar}$), 3.56-3.52 (m, 2H, CH$_2$), 3.46-3.43 (m, 2H, CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 193.92, 166.13 (d, $J_{C\text{-}F}$ = 258.15 Hz), 139.09, 134.05, 132.34 (d, $J_{C\text{-}F}$ = 2.8 Hz), 130.85 (d, $J_{C\text{-}F}$ = 9.9 Hz), 129.52, 128.04, 116.03 (d, $J_{C\text{-}F}$ = 22.1 Hz), 51.00, 31.34. **HRMS:** calculated [M+Na]$^+$ for $C_{15}H_{13}FNaO_3S$: 315.0462, found: 315.0497. **FTIR (cm^{-1})**: 3021, 2401, 1683, 1601, 1509, 1448, 1416, 1309, 1217, 1152, 1088, 979, 929, 842, 668.

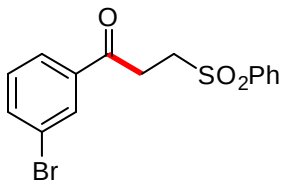
1-(3-Methoxyphenyl)-3-(phenylsulfonyl)propan-1-one (3j)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g. 1.0 mmol) and 3-methoxybenzaldehyde **1j** (0.191 g, 170 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(3-methoxyphenyl)-3-(phenylsulfonyl)propan-1-one **3j** as a white solid (0.186 g, 61%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.56; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.96-7.94 (m, 2H, H$_{ar}$), 7.69-7.65 (m, 1H, H$_{ar}$), 7.60-7.56 (m, 2H, H$_{ar}$),7.51-7.49 (m, 1H, H$_{ar}$),7.42-7.41 (m, 1H, H$_{ar}$),7.37 (t, *J* = 8.1 Hz, 1H, H$_{ar}$), 3.84 (s, 3H, CH$_3$), 3.57-3.53 (m, 2H, CH$_2$), 3.50-3.46 (m, 2H, CH$_2$). **^{13}C NMR (100MHz, CDCl$_3$)** δ: 195.41, 160.03, 139.14, 137.22, 134.09, 129.94, 129.57, 128.12, 120.80, 120.40, 112.37, 55.61, 51.15, 31.61. **HRMS:** calculated [M+Na]$^+$ for $C_{16}H_{16}O_4SNa$: 327.0662, found: 327.0695. **FTIR (cm^{-1})**: 3413, 3019, 2400, 1686, 1599, 1430, 1318, 1267, 1215, 1151, 1087, 1041, 928, 757, 669.

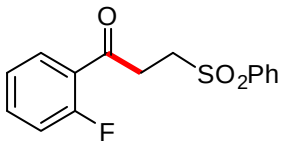
1-(3-Bromophenyl)-3-(phenylsulfonyl)propan-1-one (3k)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.084 g, 0.5 mmol) and 3-bromobenzaldehyde **1k** (0.130 g, 82 µL, 0.7 mmol) with thiazolium salt **6** (37.2 mg, 0.10 mmol) and KO*t*-Bu (8.4 mg, 0.075 mmol) in 1,4-dioxane (2.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(3-bromophenyl)-3-(phenylsulfonyl) propan-1-one **3k** as a white solid (0.150 g, 85%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.62; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 8.02 (s, 1H, H$_{ar}$) 7.94 (d, *J* = 7.8 Hz, 2H, H$_{ar}$), 7.83 (d, *J* = 8.2 Hz, 1H, H$_{ar}$), 7.69-7.65 (m, 2H, H$_{ar}$), 7.57 (t, *J* = 7.8 Hz, 2H, H$_{ar}$), 7.34 (t, *J* = 7.8 Hz, 1H, H$_{ar}$), 3.56-3.52 (m, 2H, CH$_2$), 3.47-3.43 (m, 2H, CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 194.27, 138.99, 137.51, 136.71, 134.13, 131.15, 130.49, 129.57, 128.06, 126.70, 123.73, 50.89, 31.53. **HRMS:** calculated [M+Na]$^+$ for $C_{15}H_{13}BrNaO_3S$: 374.9661, found: 374.9708. **FTIR (cm^{-1}):** 3054, 2305, 2254, 1694, 1568, 1448, 1421, 1318, 1264, 1217, 1152, 1087, 911, 669, 651.

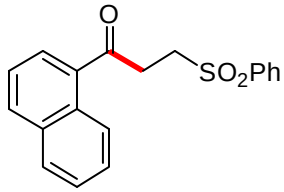
1-(2-Fluorophenyl)-3-(phenylsulfonyl)propan-1-one (3l)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and 2-fluorobenzaldehyde **1l** (0.174 g, 149 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(2-fluorophenyl)-3-(phenylsulfonyl)propan-1-one **3l** as a white solid (0.128 g, 44%, yield based on recovered **2**a is 68%)

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.59; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.95-7.93 (m, 2H, H$_{ar}$), 7.85-7.78 (m, 1H, H$_{ar}$), 7.68-7.65 (m, 1H, H$_{ar}$), 7.59-7.51 (m, 3H, H$_{ar}$), 7.24-7.20 (m, 1H, H$_{ar}$), 7.16-7.11 (m, 1H, H$_{ar}$), 3.58-3.53 (m, 2H, CH$_2$), 3.49-3.43 (m, 2H, CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 193.68 (d, $J_{(C-F)}$ = 4.3 Hz), 162.24 (d, $J_{(C-F)}$ = 255.0 Hz), 139.05, 135.53(d, $J_{(C-F)}$ = 9.1 Hz), 134.03, 130.73(d, $J_{(C-F)}$ = 2.6 Hz), 129.51, 128.20, 124.75 (d, $J_{(C-F)}$ = 3.9 Hz), 124.45 (d, $J_{(C-F)}$ = 12.2 Hz), 116.90 (d, $J_{(C-F)}$ = 24.2 Hz), 50.96 (d, $J_{(C-F)}$ = 2.4 Hz), 36.49 (d, $J_{(C-F)}$ = 9.7 Hz). **HRMS**: calculated [M+Na]$^+$ for $C_{15}H_{13}FNaO_3S$: 315.0462, found: 315.0498. **FTIR (cm^{-1}):** 3448, 3020, 2928, 2400, 1685, 1610, 1481, 1453, 1319, 1278, 1217, 1151, 1087, 1025, 980, 770, 687, 669.

1-(Naphthalen-1-yl)-3-(phenylsulfonyl)propan-1-one (3m)

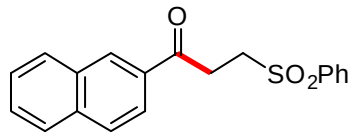


Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and 1-naphthaldehyde **1m** (0.218 g, 190 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by

flash column chromatography afforded 1-(naphthalen-1-yl)-3-(phenylsulfonyl) propan-1-one **3m** as a white solid (0.123 g, 38%, yield based on recovered **2a** is 75%)

R_f (Pet-ether/EtOAc = 60/40): 0.64; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 8.55 (d, *J* = 8.4 Hz, 1H, H_{ar}), 8.00 (d, *J* = 8.4 Hz, 1H, H_{ar}), 7.96 (d, *J* = 7.2 Hz, 2H, H_{ar}), 7.90 (d, *J* = 7.2 Hz, 1H, H_{ar}), 7.86 (d, *J* = 8.4 Hz, 1H, H_{ar}), 7.64 (t, *J* = 7.2 Hz, 1H, Har), 7.57-7.64 (m, 5H, H_{ar}) 3.67-3.64 (m, 2H, CH_2), 3.59-3.55 (m, 2H, CH_2). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 198.77, 139.10, 134.04, 134.00, 133.74, 130.09, 129.50, 128.57, 128.46, 128.36, 128.06, 126.70, 125.65, 124.39, 51.29, 34.33. **HRMS:** calculated $[M+Na]^+$ for $C_{19}H_{16}NaO_3S$: 347.0712, found: 347.0754. **FTIR (cm^{-1})**: 3019, 2400, 1683, 1509, 1422, 1309, 1217, 1151, 1086, 1046, 928, 669.

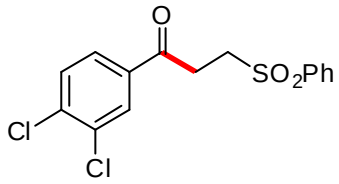
1-(Naphthalen-2-yl)-3-(phenylsulfonyl)propan-1-one (3n)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.84 g, 0.5 mmol) and 2-naphthaldehyde **1n** (0.109 g, 0.7 mmol) with thiazolium salt **6** (37.2 mg, 0.10 mmol) and KO*t*-Bu (8.4 mg, 0.075 mmol) in 1,4-dioxane (2.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(Naphthalen-2-yl)-3-(phenylsulfonyl)propan-1-one **3n** as a white solid (0.145 g, 89%).

R_f (Pet. ether/EtOAc = 60/40): 0.64; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 8.45 (s, 1H, H_{ar}), 7.99-7.94 (m, 4H, H_{ar}), 7.89-7.86 (m, 2H, H_{ar}), 7.67 (t, *J* = 7.2 Hz, 1H, H_{ar}), 7.63-7.55 (m, 4H, H_{ar}), 3.65-3.63 (m, 4H, $2CH_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 195.42, 139.16, 135.89, 134.06, 133.17, 132.46, 130.15, 129.54, 128.99, 128.79, 128.09, 127.89, 127.13, 123.52, 51.23, 31.43. **HRMS:** calculated $[M+Na]^+$ for $C_{19}H_{16}NaO_3S$: 347.0712, found: 347.0751. **FTIR (cm^{-1}):** 3060, 2302, 1678, 1446, 1310, 1266, 1146, 1087, 911.

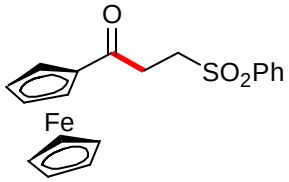
1-(3,4-dichlorophenyl)-3-(phenylsulfonyl)propan-1-one (3o)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g. 1.0 mmol) and 3,4-dichlorobenzaldehyde **1o** (0.245 g, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(3,4-dichlorophenyl)-3-(phenylsulfonyl)propan-1-one **3o** as a white solid (0.241 g, 70%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.64; **^{1}H NMR (400 MHz, CDCl3) δ**: 7.99(d, *J*=1.7Hz, 1H, H_{ar}), 7.95 (d, *J*=7.4 Hz, 2H, H_{ar}), 7.76-7.74 (m, 1H, H_{ar}), 7.69 (t, *J*=7.4 Hz, 1H, H_{ar}), 7.61-7.55 (m, 3H, H_{ar}), 3.56-3.53(m, 2H, CH_2), 3.48-3.44 (m, 2H, CH_2) . **^{13}C NMR (100 MHz, CDCl3):** □ 193.51, 139.04, 138.64, 135.38, 134.22, 133.76, 131.09, 130.18, 129.64, 128.10, 127.19, 50.90, 31.51. **HRMS**: calculated $[M+Na]^+$ for $C_{15}H_{12}Cl_2O_3SNa$: 364.9776, found: 364.9771. **FTIR (cm^{-1})**: 3412, 2923, 1697, 1446, 1389, 1309, 1279, 1143, 1086, 1027, 783, 750, 693.

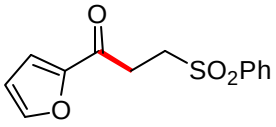
1-(2-Ferrocenyl)-3-(phenylsulfonyl)propan-1-one (3p)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and ferreocene carboxaldehyde **1p** (0.300 g, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(2-ferrocenyl)-3-(phenylsulfonyl) propan-1-one **3p** as a red solid (0.211 g, 55%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.53; **^{1}H NMR (400 MHz, CDCl$_3$) δ**: 7.97 (d, *J* = 7.1 Hz, 2H, H_{ar}), 7.08-7.59 (m, 3H, H_{ar}), 4.87 (bs, 2H, H_{ar}), 4.54 (bs, 2H, H_{ar}), 3.55-3.48 (m, 2H, CH_2), 3.27-3.20 (m, 2H, CH_2). **^{13}C NMR (100 MHz, CDCl$_3$) δ**: 199.60, 139.23, 134.04, 129.54, 128.08, 73.16, 69.64, 50.87, 31.99. **HRMS:** calculated $[M+Na]^+$ for $C_{19}H_{18}FeNaO_3S$: 405.0218, found: 405.0267. **FTIR (cm^{-1})**: 3413, 3020, 2400, 1669, 1455, 1380, 1308, 1215, 1151, 1086, 1029, 756, 668.

1-(Furan-2-yl)-3-(phenylsulfonyl)propan-1-one (3q)

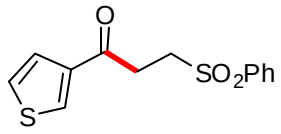


Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1.0 mmol) and furan-2-carbaldehyde **1q** (0.134 g, 116 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(furan-2-yl)-3-(phenylsulfonyl)propan-1-one **3q** as a white solid (0.259g, 98%).

***R*$_f$** (Pet ether/EtOAc = 60/40): 0.47; **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 7.93 (d, *J* = 7.5 Hz, 2H, H_{ar}), 7.66 (t, *J* = 7.5 Hz, 1H, H_{ar}), 7.59-7.55 (m, 3H, H_{ar}), 7.21 (d, *J* = 3.6 Hz, 1H, H_{ar}), 6.55-6.54 (m, 1H, H_{ar}), 3.54-3.51 (m, 2H, CH_2), 3.35-3.32 (m, 2H, CH_2). **^{13}C NMR (125 MHz, CDCl$_3$)** δ:

184.48, 151.86, 147.05, 139.02, 134.08, 129.52, 128.17, 117.96, 112.70, 50.60, 31.30. **HRMS:** calculated $[M+Na]^+$ for $C_{13}H_{12}NaO_4S$: 287.0349, found: 287.0380. **FTIR (cm^{-1})**: 3019, 2977. 3444, 3020, 2400, 1634, 1319, 1217, 1025, 928, 771, 669.

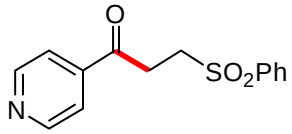
3-(Phenylsulfonyl)-1-(thiophen-3-yl)propan-1-one (3r)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1 mmol) and thiophene-3-carbaldehyde **1r** (0.157 g, 123 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 18 h followed by flash column chromatography afforded 3-(phenylsulfonyl)-1-(thiophen-2-yl)propan-1-one **3r** as a white solid (0.193 g, 69%).

R_f (Pet. ether/EtOAc = 60/40): 0.60; **^{1}H NMR (500 MHz, $CDCl_3$),** δ: 8.08 (dd, J_1 = 1.2 Hz, J_2 = 2.8 Hz, 1H, H_{ar}), 7.95-7.93 (m, 2H, H_{ar}), 7.67 (t, J = 7.4 Hz, 1H, H_{ar}), 7.58 (t, J = 8.0 Hz, 2H, H_{ar}), 7.50 (dd, J_1 = 1.2 Hz, J_2 = 5.0 Hz, 1H, H_{ar}), 7.34-7.32 (m, 1H, H_{ar}), 3.55-3.52 (m, 2H, CH_2), 3.42-3.39 (m, 2H, CH_2). **^{13}C NMR (125 MHz, $CDCl_3$)** δ: 189.71, 141.15, 139.21, 134.09, 132.82, 129.56, 128.13, 126.98, 126.80, 50.97, 32.46. **HRMS:** calculated $[M+Na]^+$ for $C_{13}H_{12}NaO_3S2$: 303.0120, found: 303.0153. **FTIR (cm^{-1})**: 3446, 3019, 2977, 2400, 1680, 1512, 1417, 1309, 1265, 1216, 1151, 1087, 1046, 928, 849, 771, 669, 626.

3-(Phenylsulfonyl)-1-(pyridin-4-yl) propan-1-one (3s)

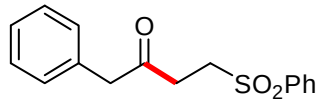


Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1 mmol) and pyridine 4-carbaxaldehyde **1s** (0.150 g, 132 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 15 h followed by flash column chromatography afforded 3-(phenylsulfonyl)-1-(pyridin-4-yl)propan-1-one **3s** as a white solid (0.171 g, 62%).

R_f (Pet. ether/EtOAc = 60/40): 0.35; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 8.84 (d, J = 5.7 Hz, 2H, H_{ar}), 7.95 (d, J = 8.0 Hz, 2H, H_{ar}), 7.75 (d, J = 5.7 Hz, 2H, H_{ar}), 7.71-7.67 (m, 1H, H_{ar}), 7.59 (t, J = 8.0 Hz, 2H, H_{ar}), 3.59-3.55 (m, 2H, CH_2), 3.53-3.49 (m, 2H, CH_2). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 195.11, 150.67, 142.18, 139.00, 134.29, 129.69, 128.12, 121.32, 50.71, 31.91.

HRMS: calculated $[M+Na]^+$ for $C_{14}H_{13}NNaO_3S$: 298.0508, found: 298.0545. **FTIR (cm^{-1}):** 3445, 3054, 1634, 1421, 1265, 896, 739.

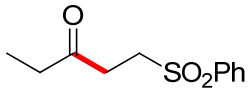
1-Phenyl-4-(phenylsulfonyl)butan-2-one (3t)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g. 1 mmol) and phenyl acetaldehyde **1t** (0.168 g, 163 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-phenyl-4-(phenylsulfonyl)butan-2-one **3t** as a white solid (0.173 g, 60%).

R_f (Pet. ether/EtOAc = 60/40): 0.43; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.86 (d, *J*=7.6Hz, 2H, H_{ar}), 7.65 (t, *J*=7.4Hz, 1H, H_{ar}), 7.54 (t, *J*=7.6 Hz, 2H, H_{ar}), 7.34-7.27 (m, 2H, H_{ar}), 7.16 (d, *J*=7.2 Hz, 1H, H_{ar}), 3.70 (s, 2H, CH_2), 3.38-3.55 (m, 2H, CH_2), 2.96-2.93 (m, 2H, CH_2). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 203.61, 138.77, 133.87, 133.21, 129.34, 128.79, 127.85, 127.27, 50.42, 49.77, 34.27 **HRMS:** calculated $[M+Na]^+$ for $C_{16}H_{16}O_3SNa$: 311.0712, found: 311.0745. **FTIR (cm^{-1}):** 3022, 2931, 1721, 1603, 1586, 1480, 1496, 1447, 1413, 1353, 1309, 1216, 1150, 1086, 1031, 1000, 928, 755, 699, 668.

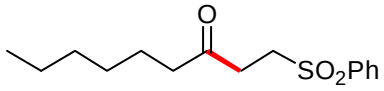
1-(Phenylsulfonyl)pentan-3-one (3u)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.84 g, 0.5 mmol) and propionaldehyde **1u** (0.146 g, 183 µL, 2.5 mmol) with thiazolium salt **6** (37.2 mg, 0.10 mmol) and KO*t*-Bu (8.4 mg, 0.075 mmol) in 1,4-dioxane (2.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(phenylsulfonyl)pentan-3-one **3u** as a white solid (0.054 g, 48%).

R_f (Pet. ether/EtOAc = 60/40): 0.50; **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.91 (d, *J* = 7.68 Hz, 2H, H_{ar}), 7.67-7.65 (m, 1H, H_{ar}), 7.6-7.56 (m, 2H, H_{ar}), 3.39 (t, *J* = 7.25 Hz, 2H, CH_2), 2.90 (t, *J* = 7.42 Hz, 2H, CH_2), 2.45 (q, *J* = 7.4 Hz, 2H, CH2), 1.03 (t, *J* = 7.67 Hz, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$) δ**: 206.75, 134.06, 129.53, 128.09, 50.7, 36.17, 34.65, 29.80. **HRMS:** calculated $[M+Na]^+$ for $C_{11}H_{14}NaO_3S$: 249.0561, found: 249.0584. **FTIR (cm^{-1}):** 3020, 1720, 1639, 1521, 1475, 1423, 1308, 1216, 1153, 1086, 1045, 908, 850, 741, 669, 626.

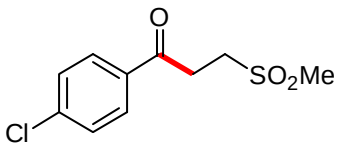
1-(Phenylsulfonyl)nonan-3-one (3v)



Following the general procedure, treatment of phenyl vinyl sulfone **2a** (0.168 g, 1 mmol) and heptanal **1v** (0.160 g, 195 µL, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(phenylsulfonyl)nonan-3-one **3v** as a white solid (0.225 g, 79%).

R_f (Pet. ether/EtOAc = 60/40): 0.72; **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 7.90 (d, *J* = 7.6 Hz, 2H, H_{ar}), 7.66 (t, *J* = 7.6 Hz, 1H, H_{ar}), 7.57 (t, *J* = 7.6 Hz, 2H, H_{ar}), 3.36 (t, *J* = 7.8 Hz, 2H, CH_2), 2.89 (t, *J* = 7.8 Hz, 2H, CH_2), 2.41 (t, *J* = 7.5 Hz, 2H, CH_2), 1.54-1.51 (m, 2H, CH_2), 1.29-1.24 (m, 6H, $3CH_2$), 0.86 (t, *J* = 6.9 Hz, 3H, CH_3). **^{13}C NMR (125 MHz, CDCl$_3$)** δ: 206.42, 139.18, 134.04, 129.53, 128.10, 50.70, 43.01, 34.99, 31.61, 28.87, 23.77, 22.56, 14.11. **HRMS:** calculated $[M+Na]^+$ for $C_{15}H_{22}NaO_3S$: 305.1182, found: 305.1215. **FTIR (cm^{-1}):** 3445, 3020, 2254, 1716, 1644, 1448, 1380, 1265, 1216, 1151, 1087, 911, 741, 669, 650.

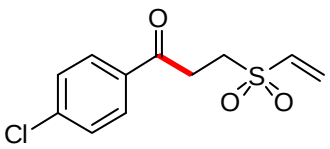
1-(4-Chlorophenyl)-3-(methylsulfonyl)propan-1-one (3w)



Following the general procedure, treatment of methyl vinyl sulfone **2b** (0.106 g, 88 µL, 1.0 mmol) and 4-chloro benzaldehyde **1a** (0.197 g, 1.4 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(4-chlorophenyl)-3-(methylsulfonyl)propan-1-one **3w** as a white solid (0.232 g, 94%).

R_f (Pet. ether/EtOAc = 60/40): 0.031; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.93 (d, *J* = 8.5 Hz, 2H, H_{ar}), 7.47 (d, *J* = 8.5 Hz, 2H, H_{ar}), 3.57-3.50 (m, 4H, $2CH_2$), 3.00 (s, 3H, CH_3). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 194.64, 140.70, 134.15, 129.69, 129.38, 49.37, 41.90, 31.23. **HRMS:** calculated $[M+Na]^+$ for $C_{10}H_{11}ClNaO_3S$: 269.0010, found: 269.0042. **FTIR (cm^{-1}):** 3414, 3020, 2400, 1690, 1420, 1314, 1216, 1123, 1093, 1045, 929, 770, 669.

1-(4-Chlorophenyl)-3-(vinylsulfonyl)propan-1-one (3x)

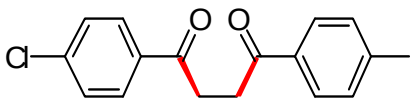


Following the general procedure, treatment of (vinylsulfonyl) ethene **2c** (0.120 g, 116 µL, 1 mmol) and 4-chlorobenzaldehyde **1a** (0.141

g, 1.0 mmol) with thiazolium salt **6** (74.4 mg, 0.20 mmol) and KO*t*-Bu (16.8 mg, 0.15 mmol) in 1,4-dioxane (4.0 mL) at 70 °C for 22 h followed by flash column chromatography afforded 1-(4-chlorophenyl)-3-(vinylsulfonyl)propan-1-one **3x** as a white solid (0.137 g, 53%).

***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.53; **^{1}H NMR (400 MHz, CDCl$_3$)** δ: 7.90 (d, *J* = 8.8 Hz, 2H, H$_{ar}$), 7.46 (d, *J* = 8.8 Hz, 2H, H$_{ar}$), 6.70 (dd, J_1 = 10.14 Hz, J_2 = 16.8 Hz, 1H, H$_{ar}$), 6.46 (d, *J* = 16.8 Hz, 1H, H$_{ar}$), 6.18 (d, *J* = 9.8 Hz, 1H, H$_{ar}$), 3.51-3.44 (m, 4H, 2CH$_2$). **^{13}C NMR (100 MHz, CDCl$_3$)** δ: 194.43, 140.59, 136.37, 134.20, 130.91, 129.64, 129.34, 48.84, 31.23. **HRMS:** calculated $[M+Na]^+$ for $C_{11}H_{11}ClNaO_3S$: 281.0010, found: 281.0047. **FTIR (cm^{-1}):** 3020, 2935, 2400, 1688, 1591, 1401, 1317, 1215, 1124, 1138, 1094, 1014, 979, 953, 835.770,668.

1-(4-Chlorophenyl)-4-(*p*-tolyl)butane-1,4-dione (12)[5]



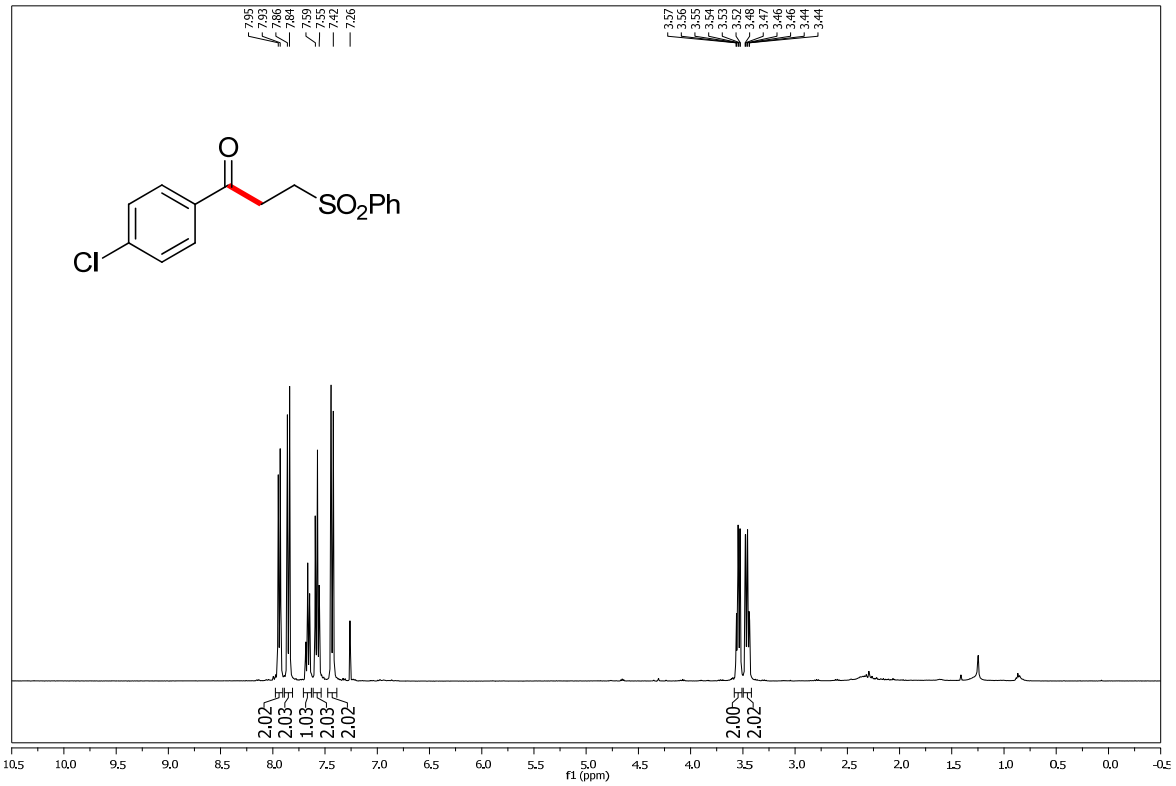
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was taken 1-(4-chlorophenyl)-3-(phenylsulfonyl) propan-1-one **3a** (0.077 g, 0.25 mmol) and 4-methyl benzaldehyde **1c** (0.030 g, 30 µL, 0.25 mmol) and thiazolium salt **6** (18.6 mg, 0.05 mmol). To this mixture was added 1,4-dioxane (1.0 mL) followed by DBU (45.6 mg, 45 µL, 0.30 mmol). The resulting mixture was stirred in a pre-heated oil bath at 70 °C for 22 h. After the reaction was complete, the reaction mixture was cooled to room temperature, and the crude mixture was purified by flash column chromatography on silica gel to afford 1-(4-chlorophenyl)-4-(*p*-tolyl)butane-1,4-dione **12** as a white solid (63 mg, 88%).

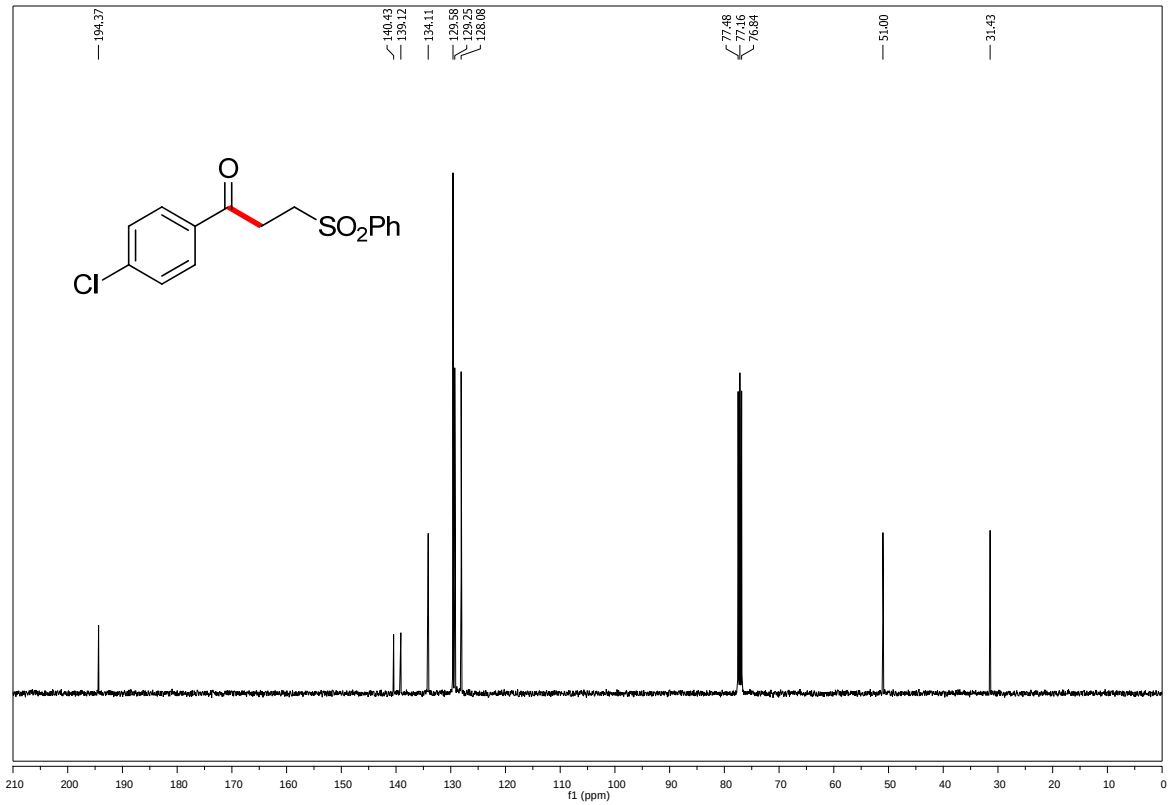
***R*$_f$** (Pet. ether/EtOAc = 60/40): 0.84; **^{1}H NMR (500 MHz, CDCl$_3$)** δ: 7.98 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 7.93 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 7.45 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 7.27 (d, *J* = 8.4 Hz, 2H, H$_{ar}$), 3.46-3.43 (m, 2H, CH$_2$), 3.41-3.39 (m, 2H, CH$_2$), 2.42 (s, 3H, CH$_3$). **^{13}C NMR (125 MHz, CDCl$_3$)** δ: 193.27, 197.77, 144.18, 139.70, 135.32, 134.36, 129.70, 129.44, 129.06, 128.38, 32.69, 32.59, 21.08. **HRMS:** calculated $[M+Na]^+$ for $C_{17}H_{15}ClNaO_2$: 309.0653, found: 309.0692. **FTIR (cm^{-1}):** 3053, 2685, 2305, 2254, 1681, 1606, 1422, 1265, 1216, 1180, 1094, 991, 742, 669, 650.

[5] (a) Shen, Z.-L.; Goh, K. K. K.; Cheong, H.-L.; Wong, C. H. A.; Lai, Y.-C.; Yang, Y.-S.; Loh, T.-P. *J. Am. Chem. Soc.* **2010**, *132*, 15852. (b) V. V. Zhdankin, M. Mullikin, R. Tykwinski, B. Berglund, R. Caple, N. S. Zefirov, A. S. Kozmin, *J. Org. Chem.* **1989**, *54*, 2605. (c) Stetter, H.; Lorenz, G. *Chem. Ber.* **1985**, *118*. 1115

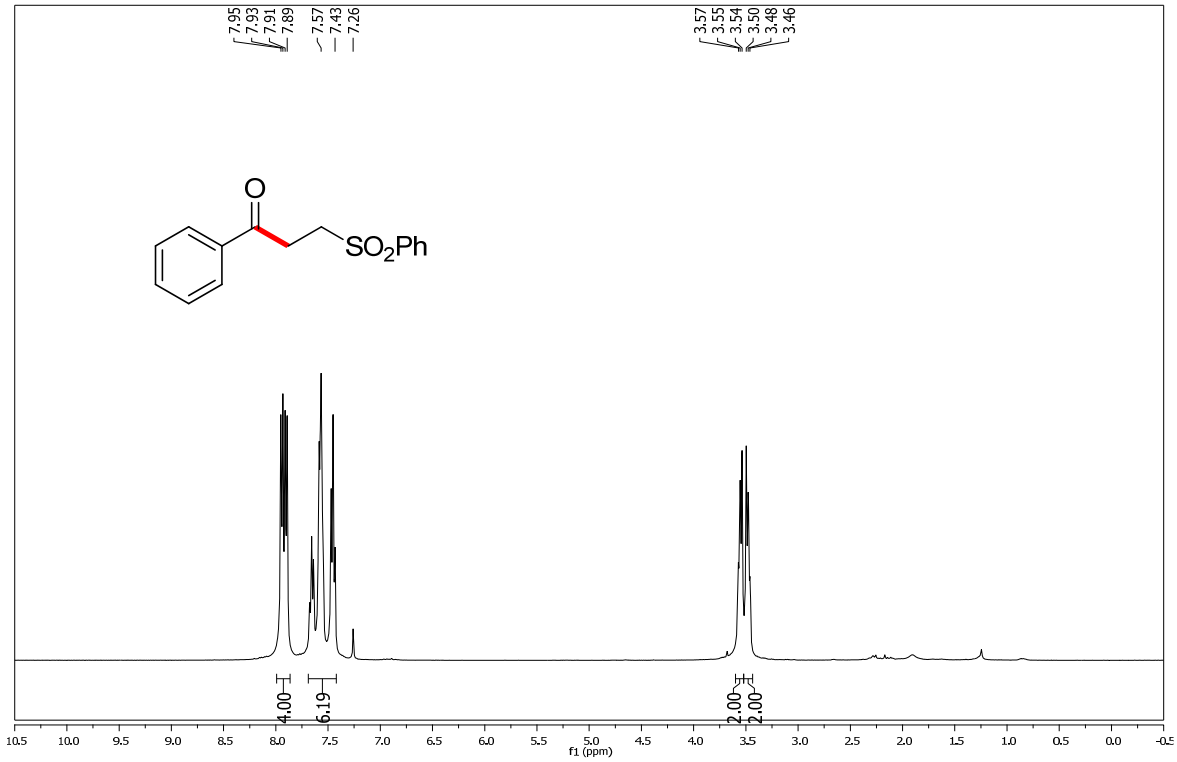
7. ^{1}H and ^{13}C NMR Spectra of γ-Keto Sulfones

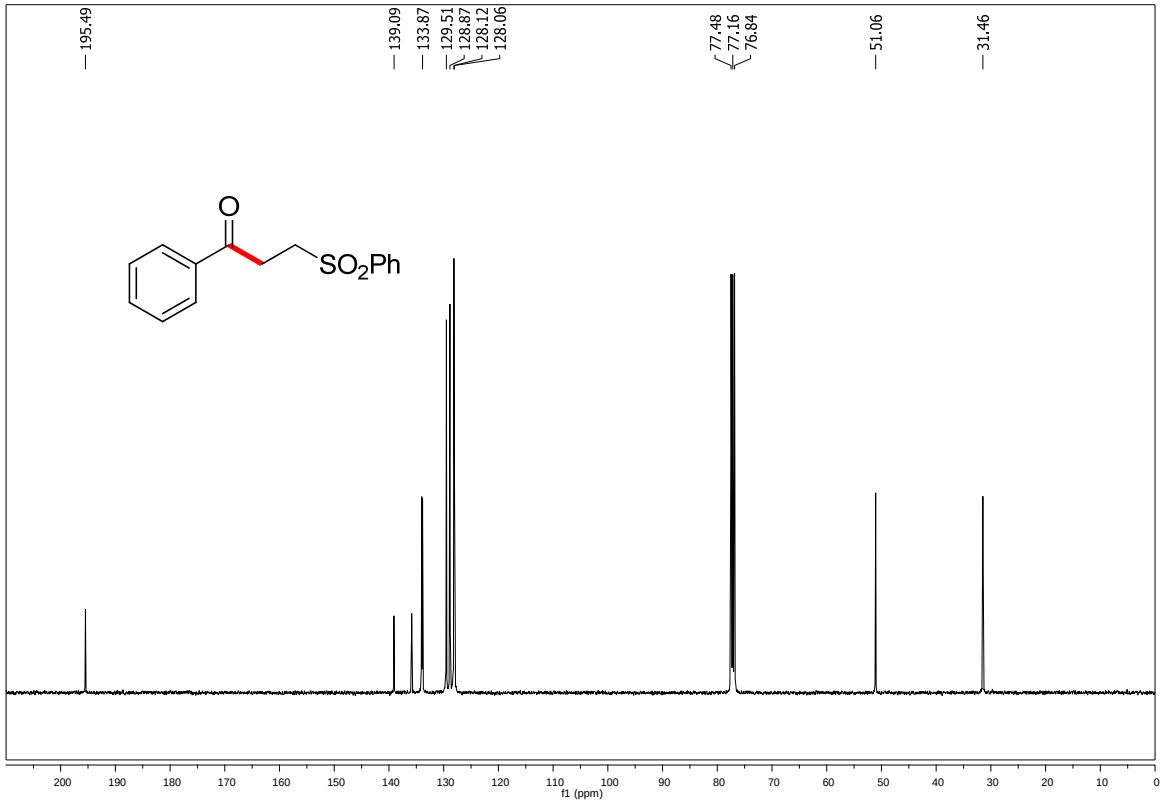
1-(4-Chlorophenyl)-3-(phenylsulfonyl)propan-1-one (3a)



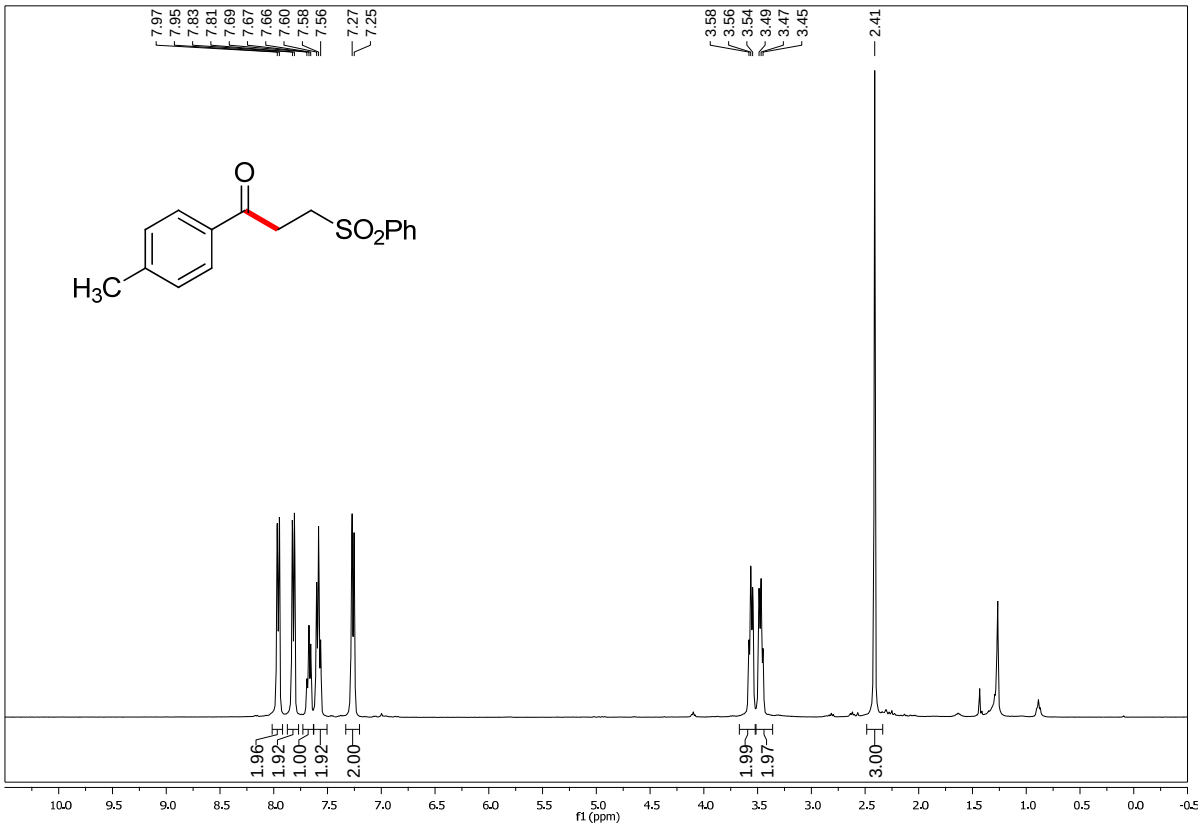


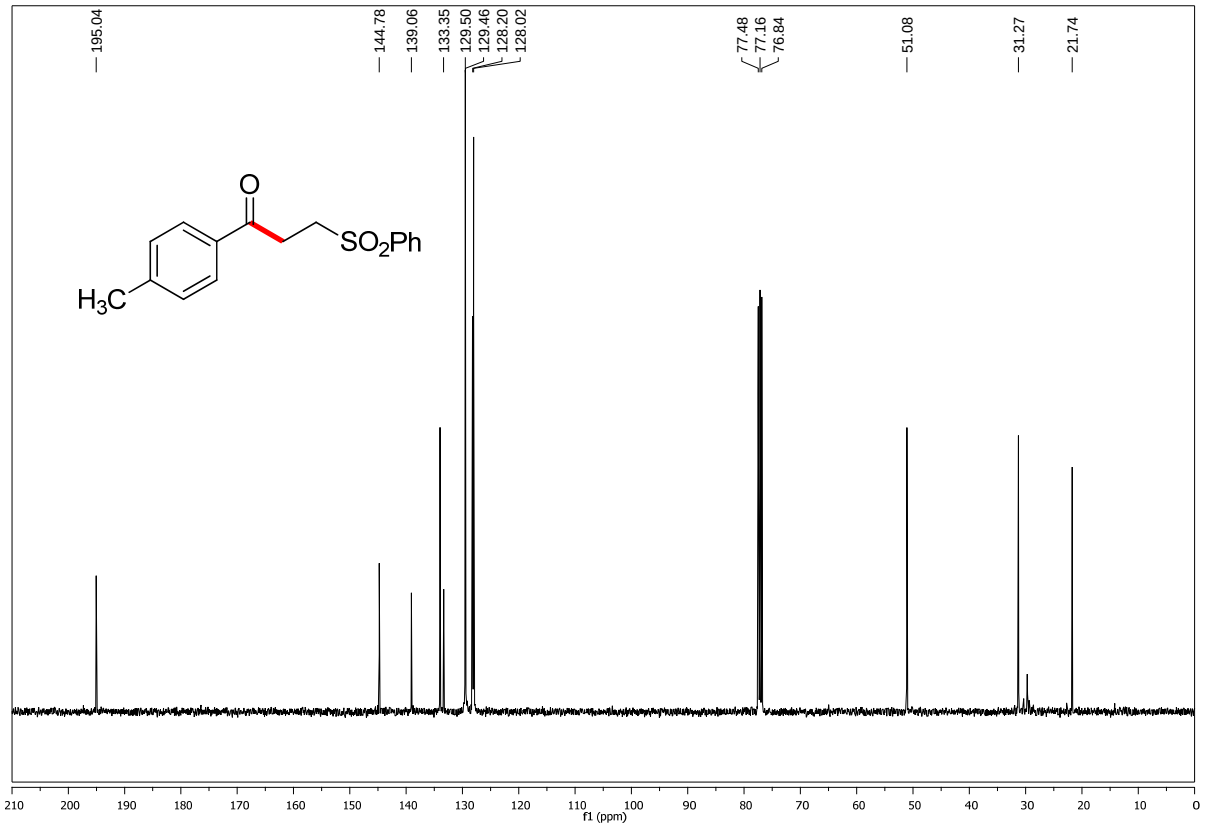
1-Phenyl-3-(phenylsulfonyl)propan-1-one (3b)



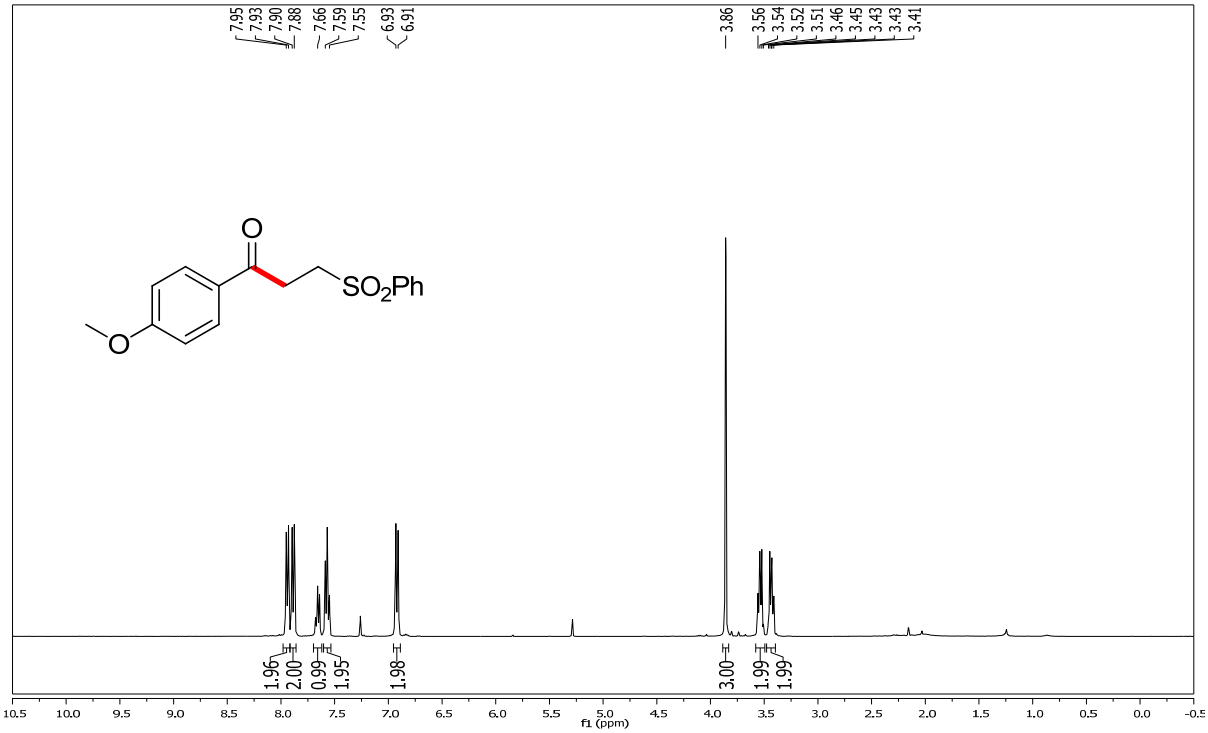


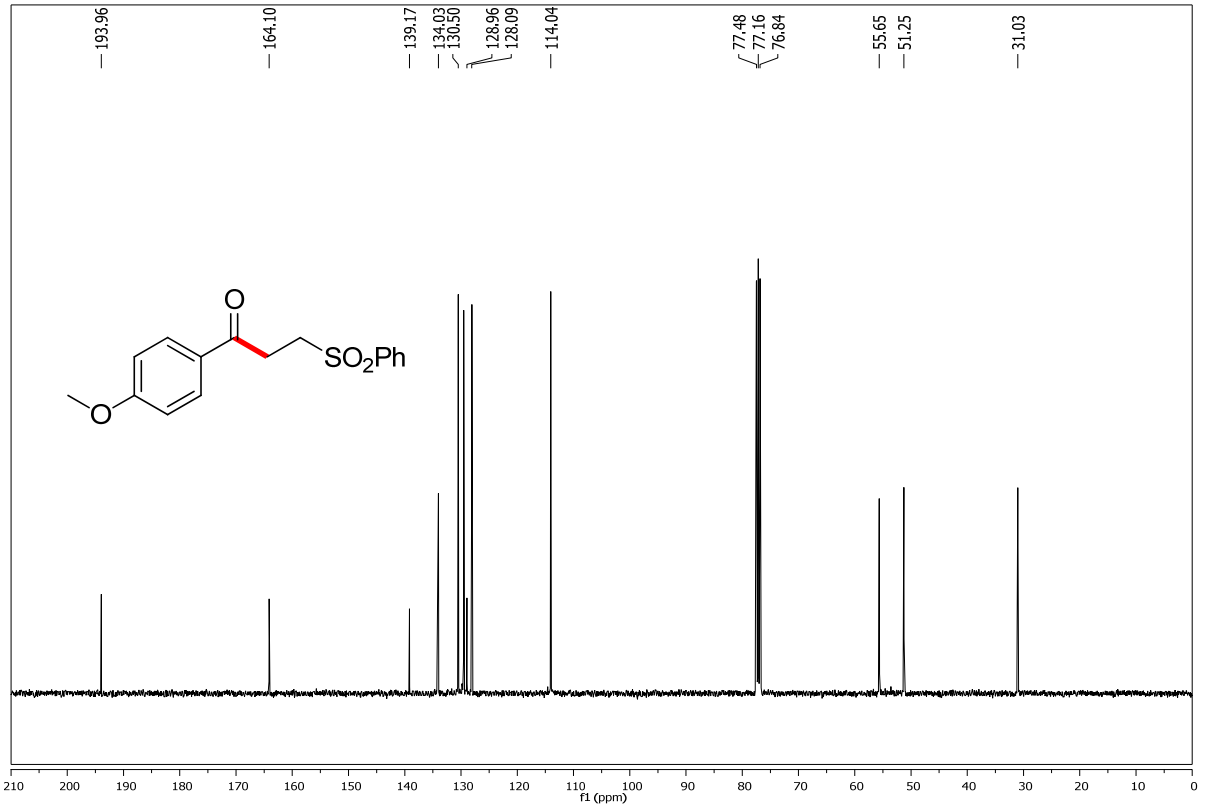
3-(Phenylsulfonyl)-1-(*p*-tolyl)propan-1-one (3c)



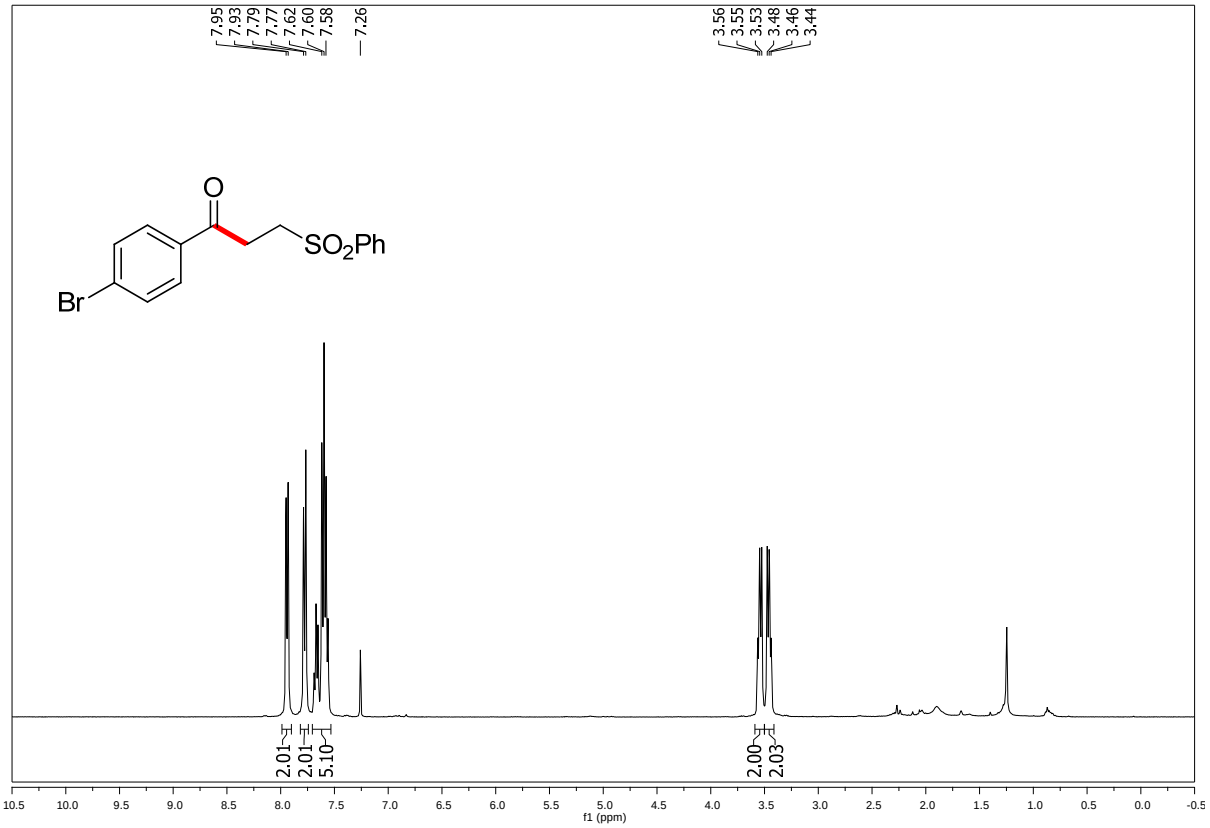


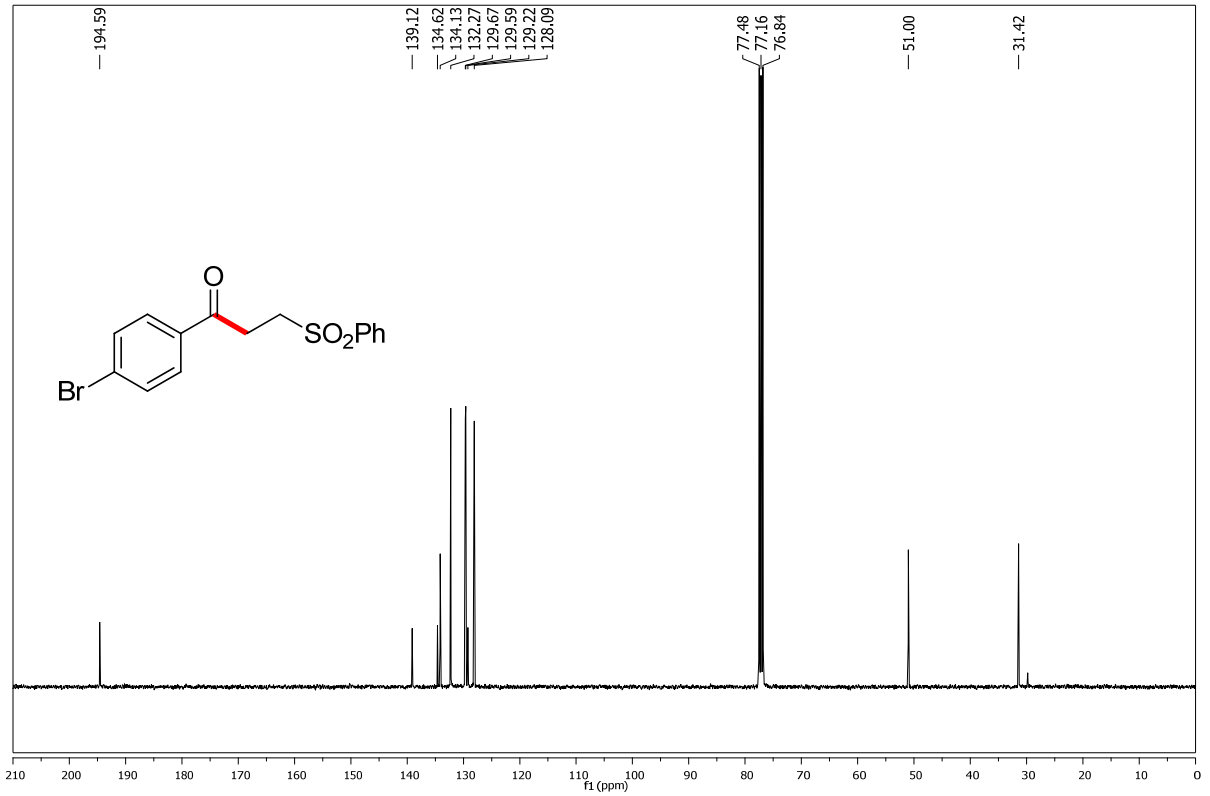
1-(4-Methoxyphenyl)-3-(phenylsulfonyl)propan-1-one (3d)



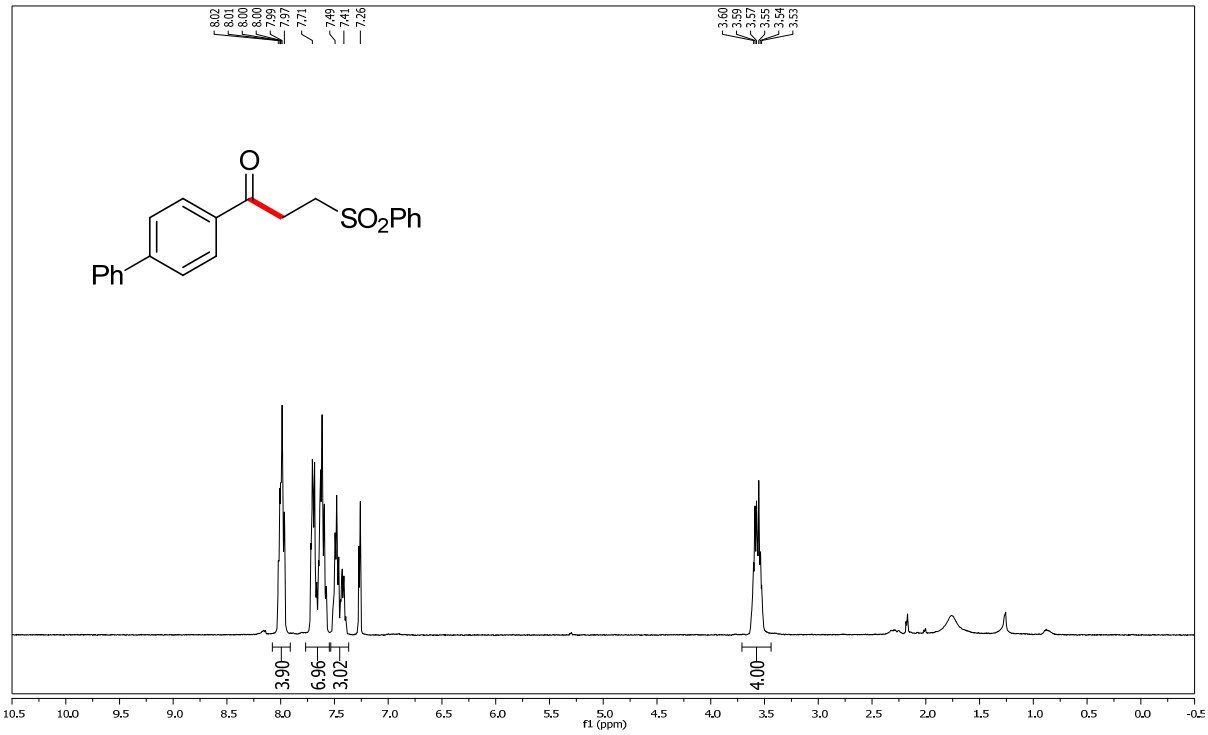


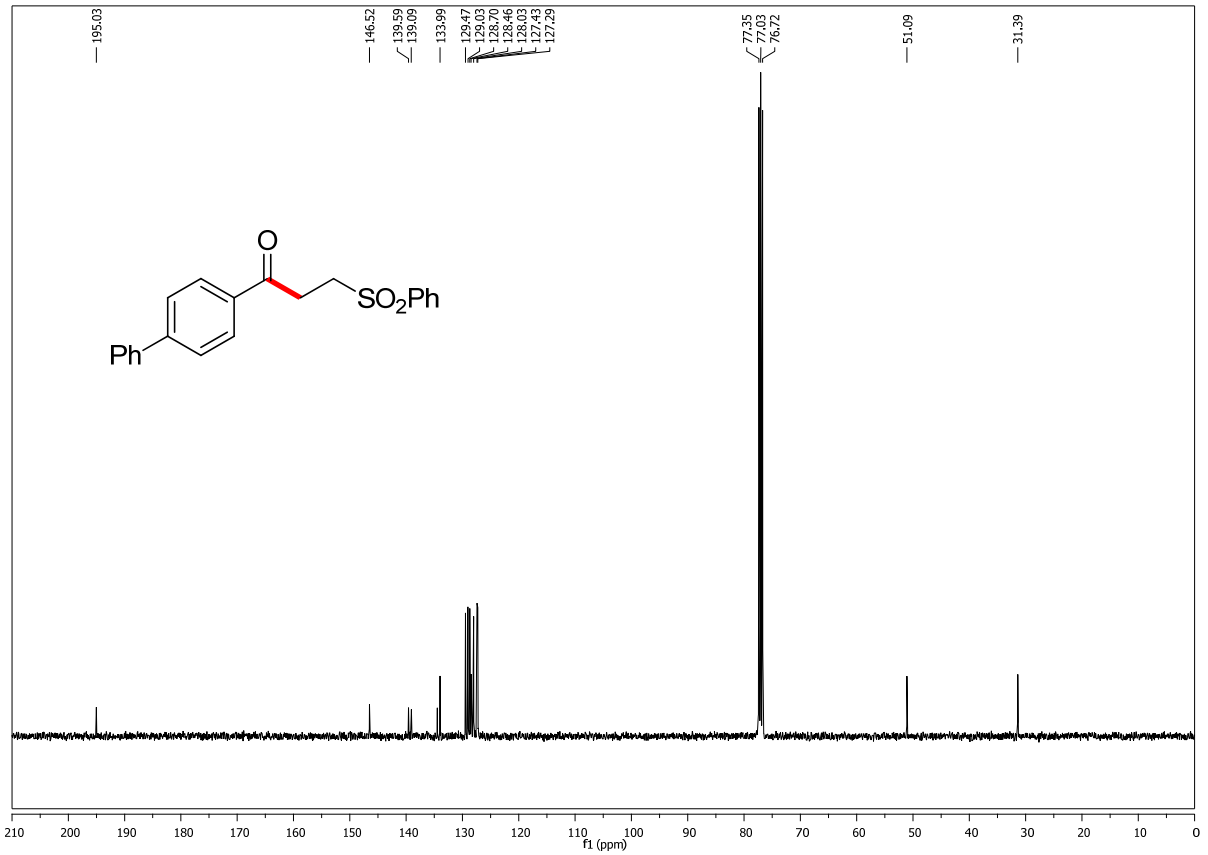
1-(4-Bromophenyl)-3-(phenylsulfonyl)propan-1-one (3e)



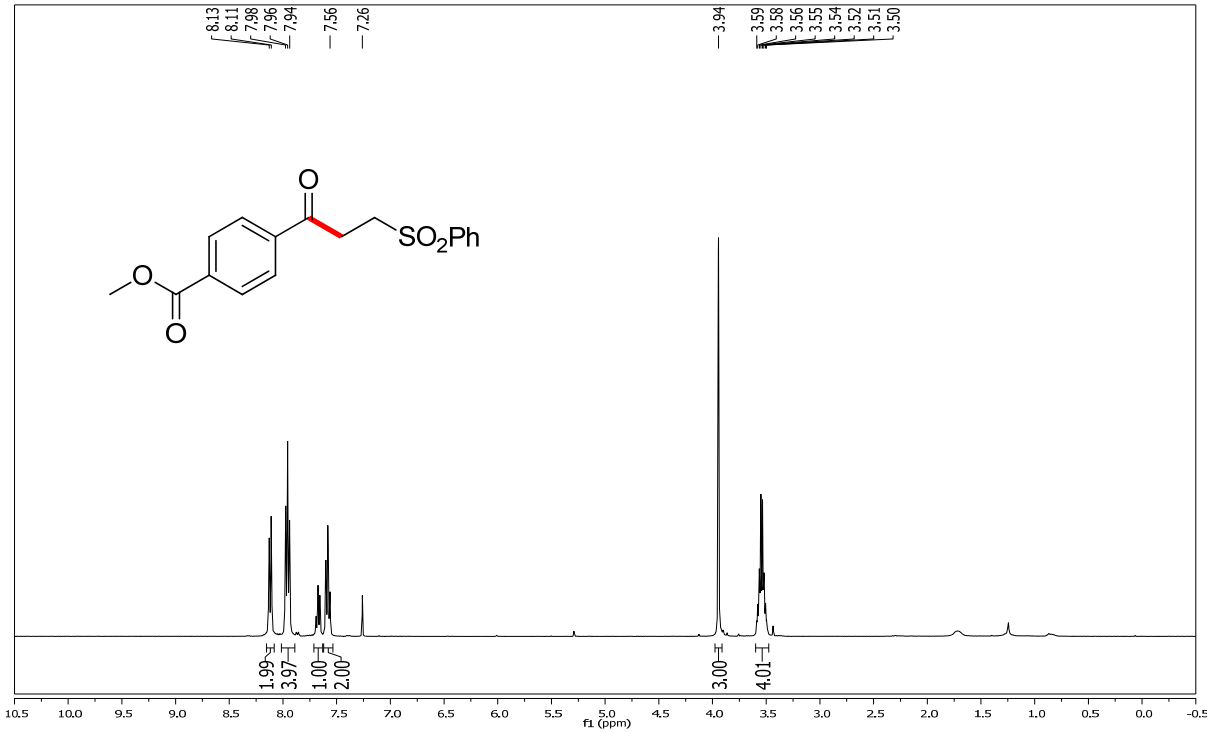


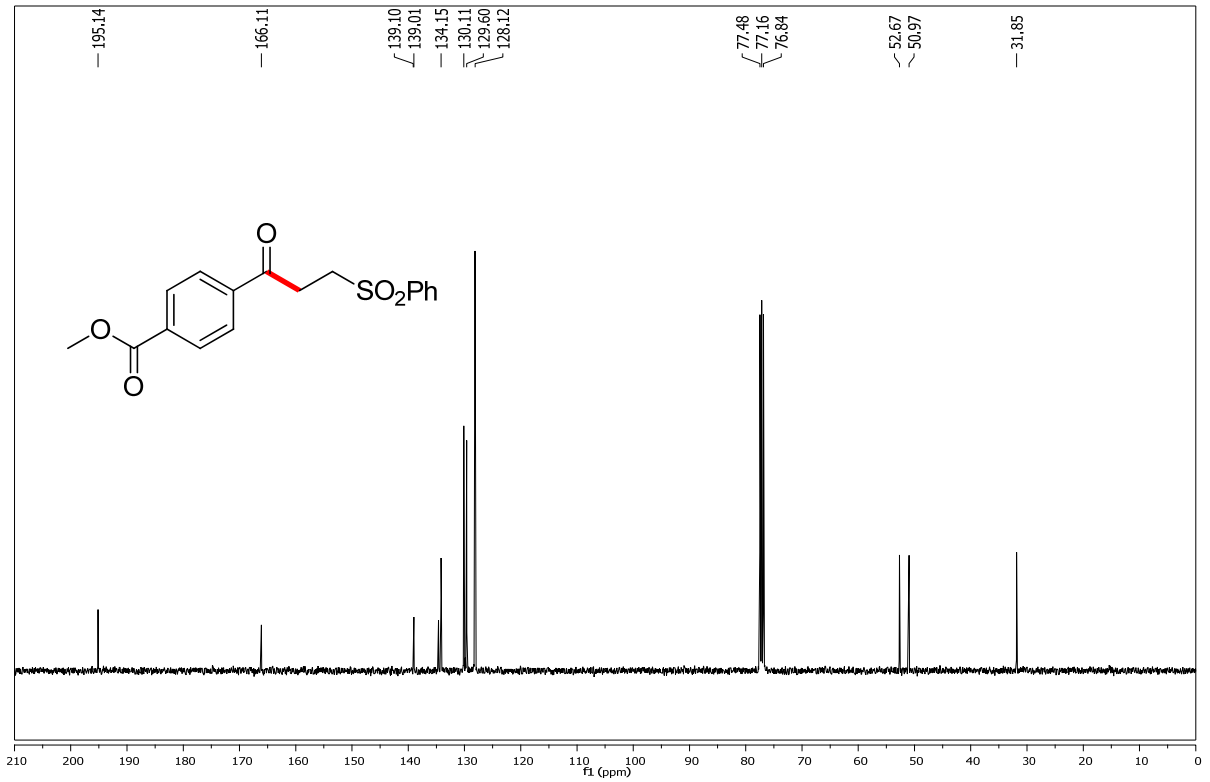
1-([1,1'-Biphenyl]-4-yl)-3-(phenylsulfonyl)propan-1-one (3f)



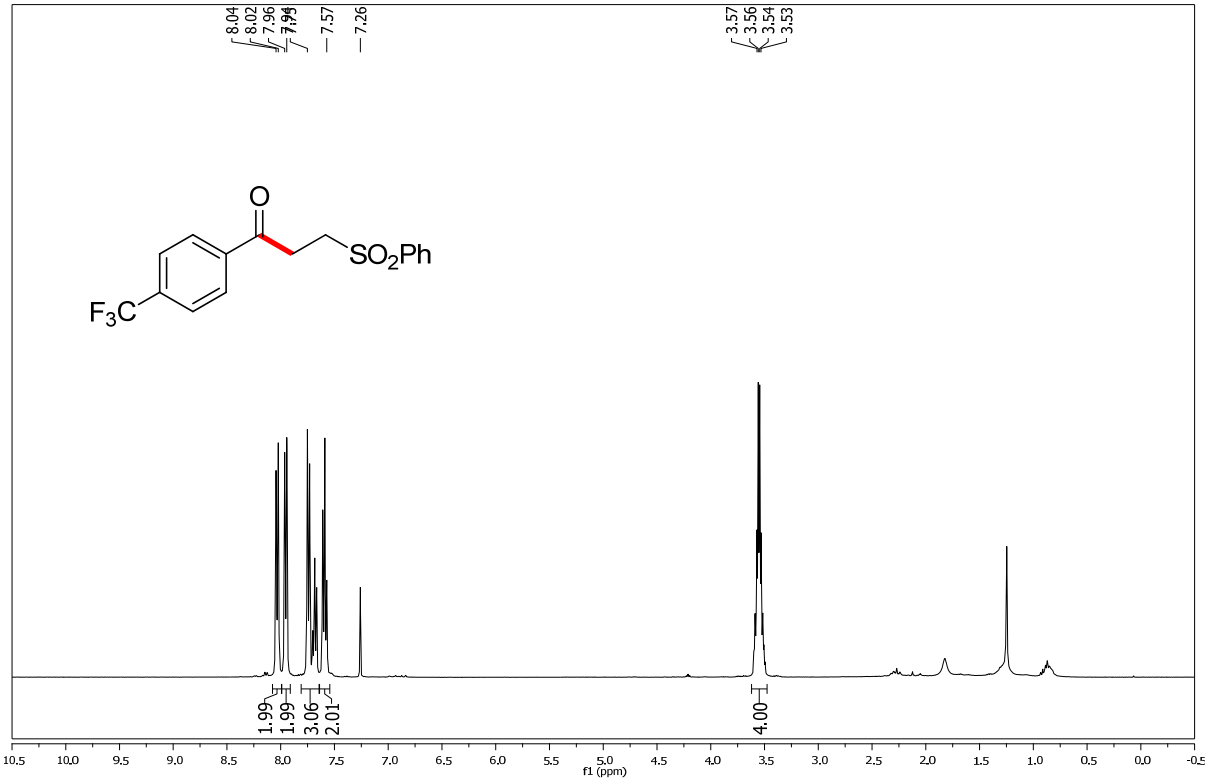


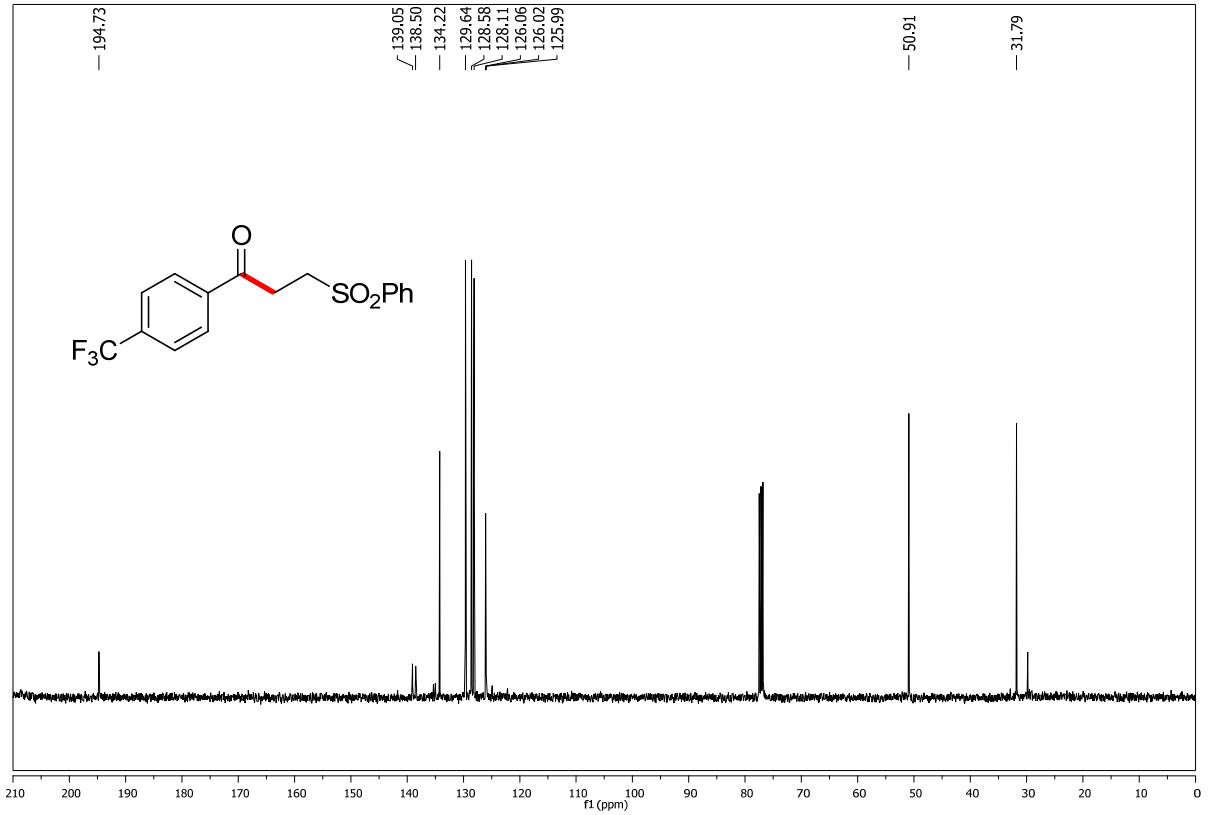
Methyl 4-(3-(phenylsulfonyl)propanoyl)benzoate (3g)



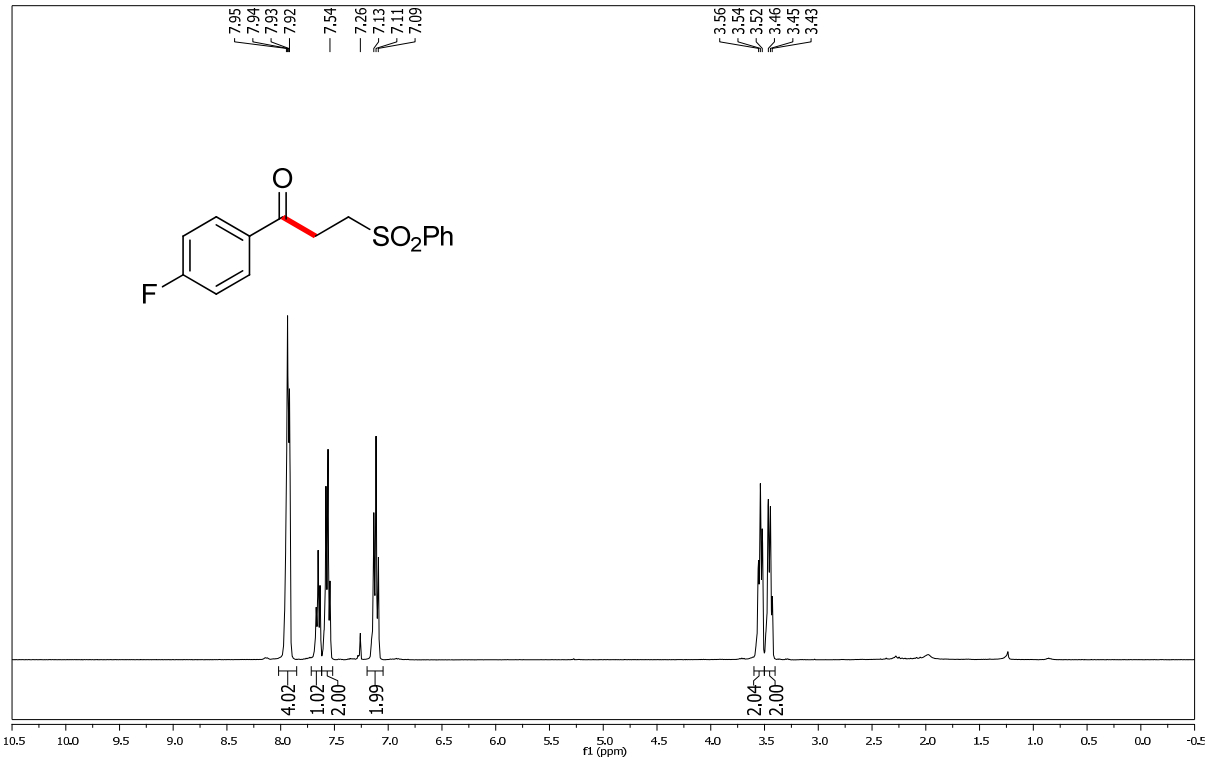


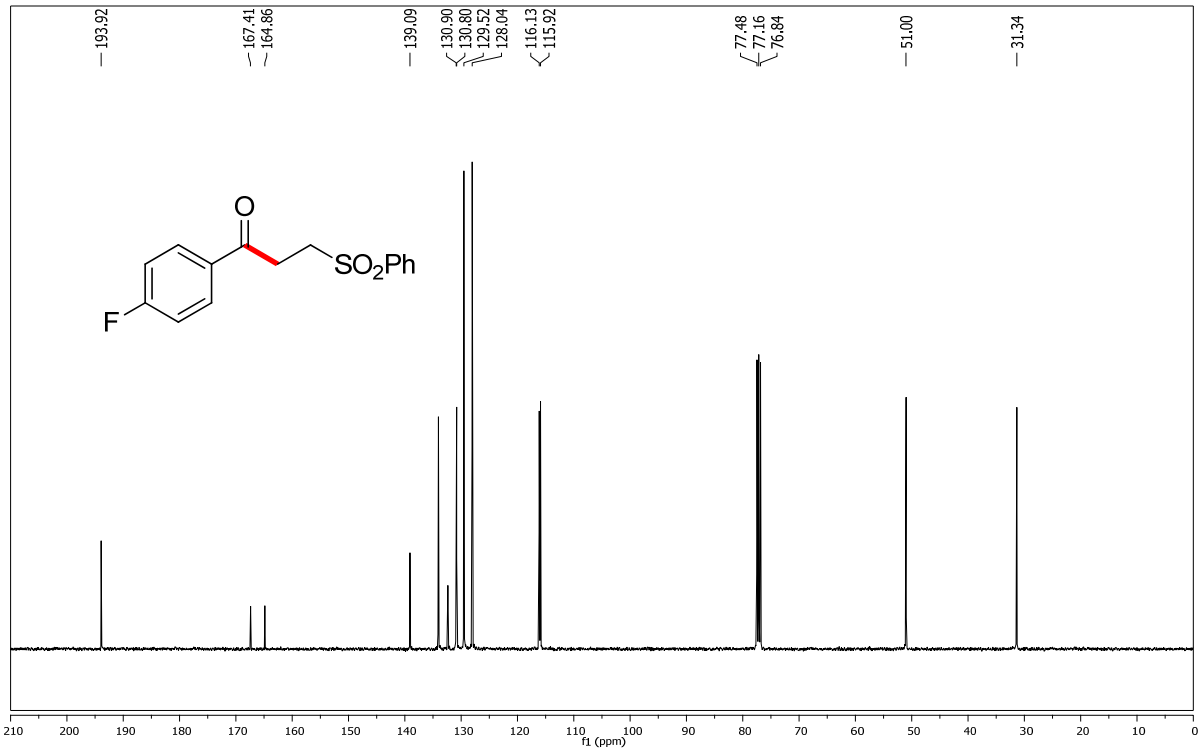
3-(Phenylsulfonyl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (3h)



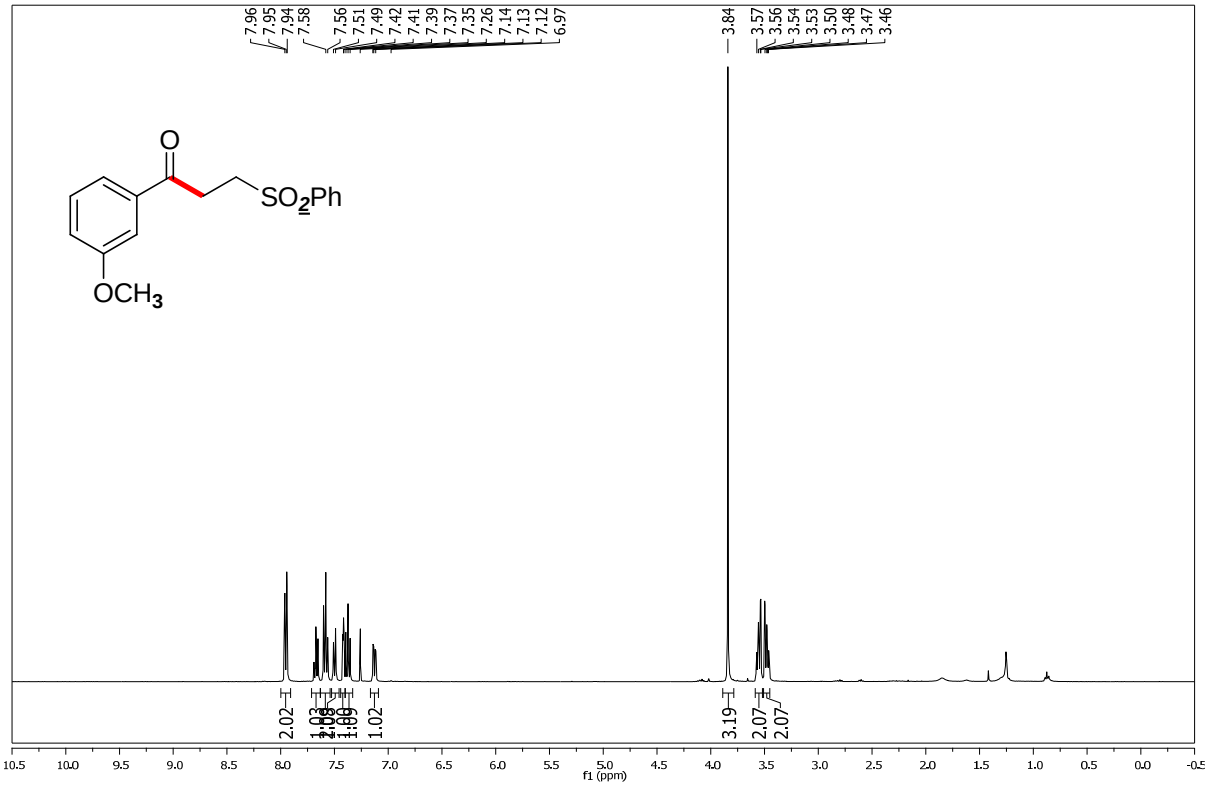


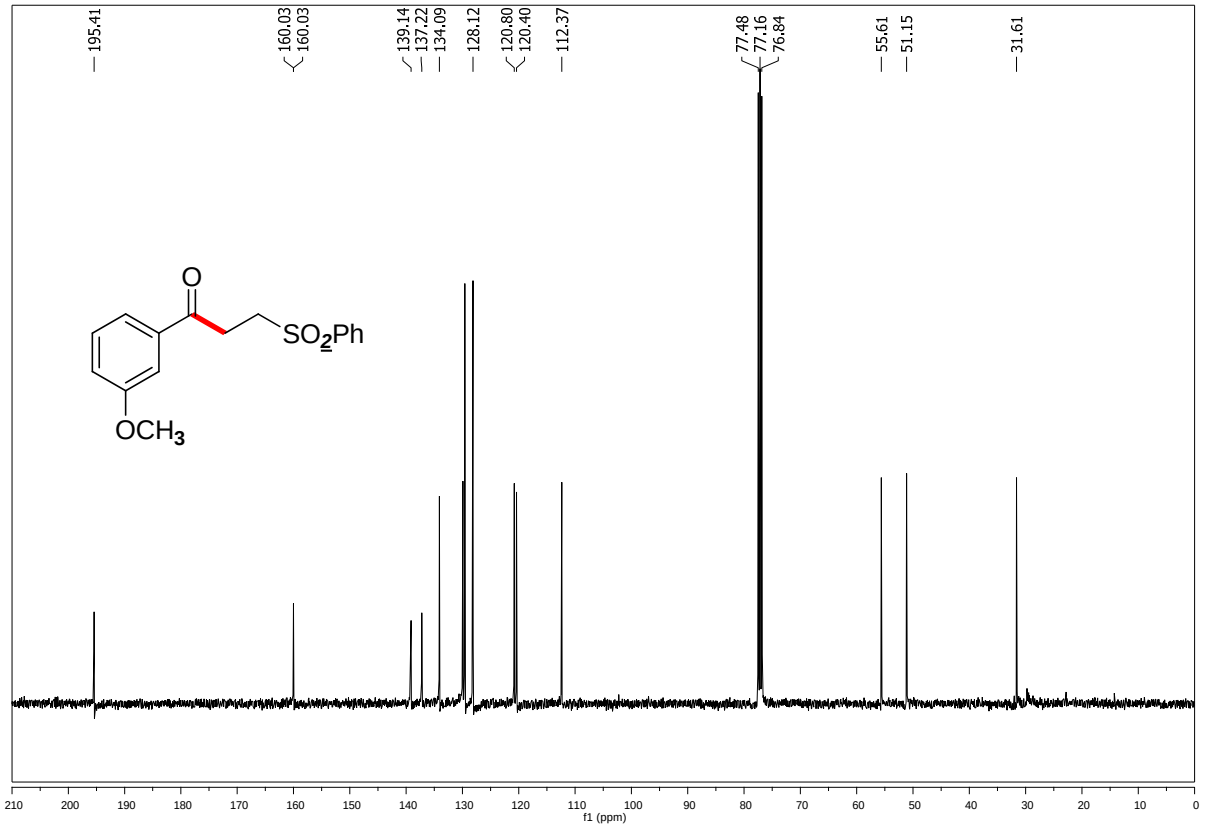
1-(4-Fluorophenyl)-3-(phenylsulfonyl)propan-1-one (3i)



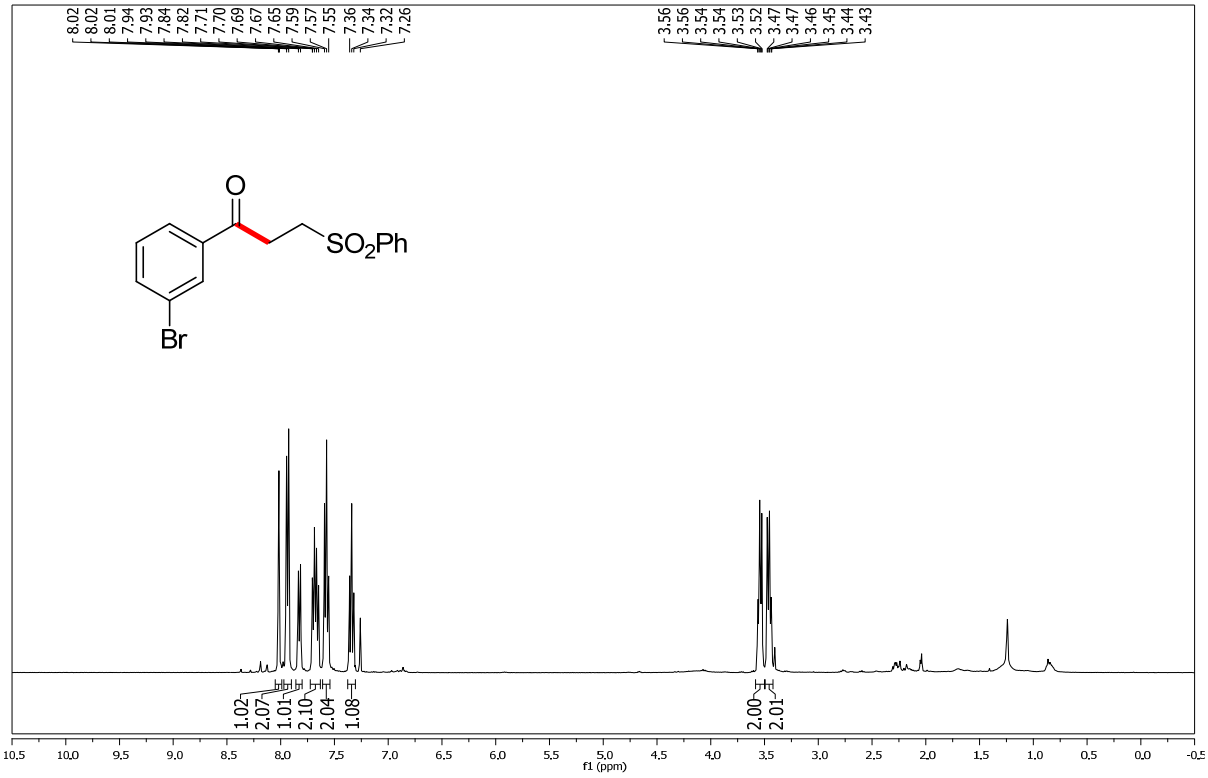


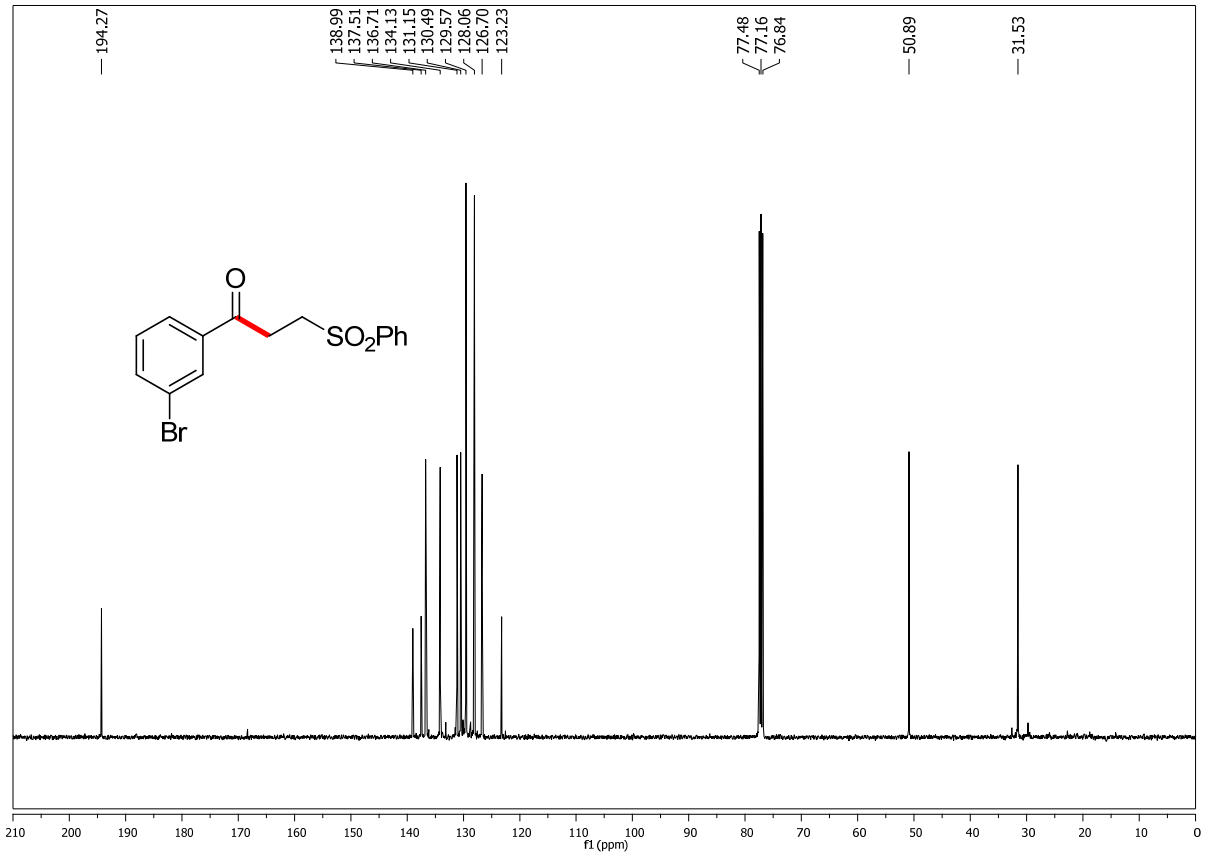
1-(3-Methoxyphenyl)-3-(phenylsulfonyl)propan-1-one (3j)



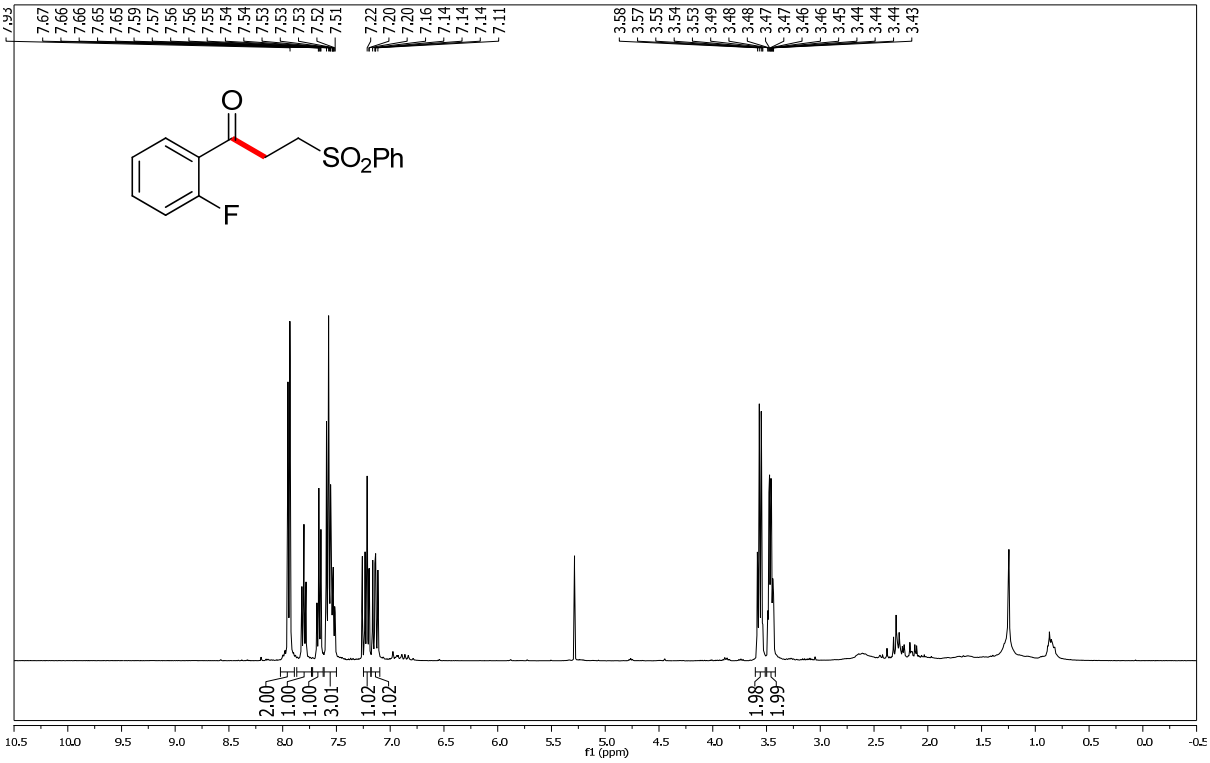


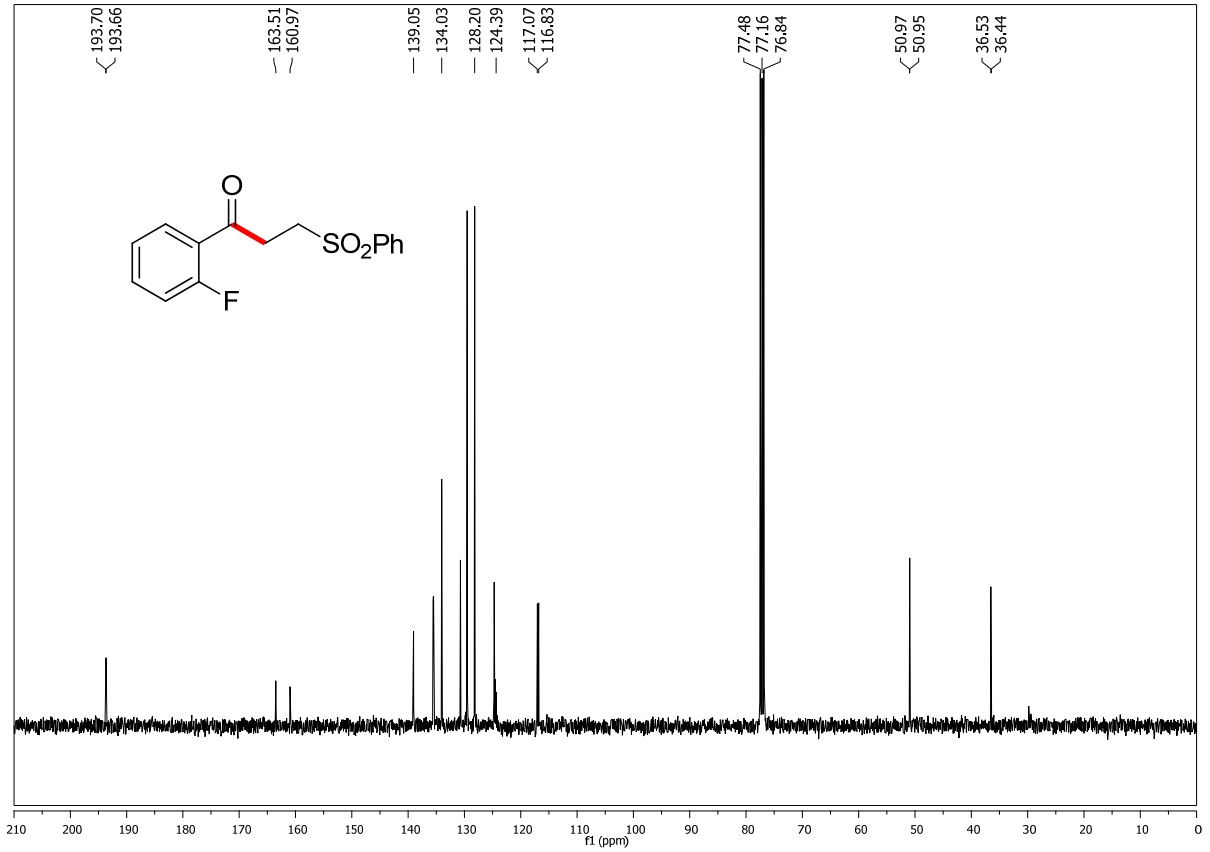
1-(3-Bromophenyl)-3-(phenylsulfonyl)propan-1-one (3k)



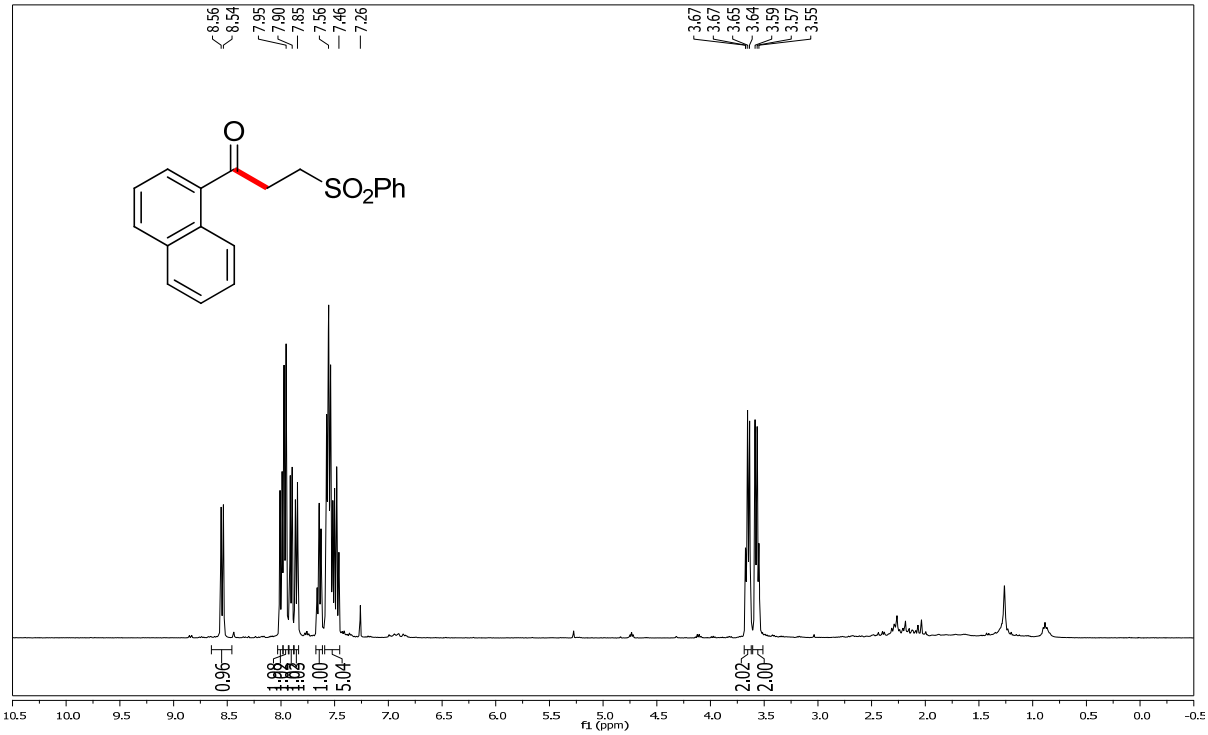


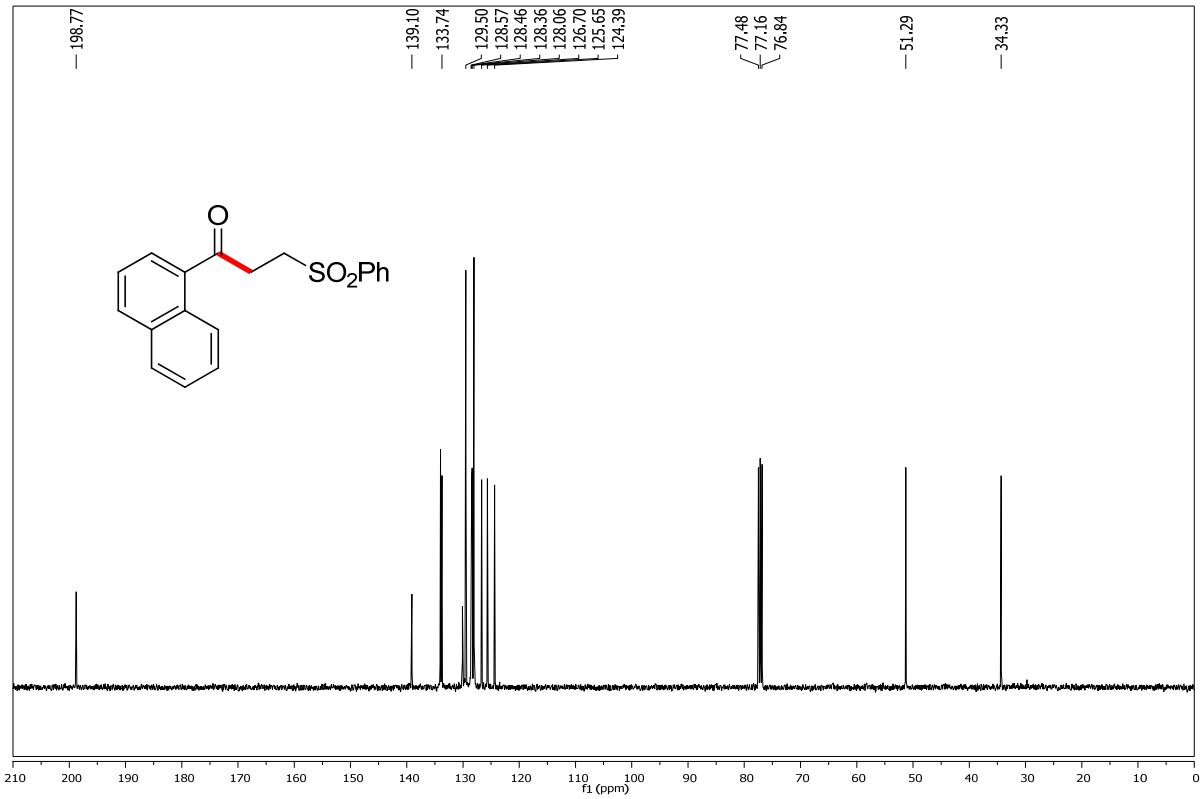
1-(2-Fluorophenyl)-3-(phenylsulfonyl)propan-1-one (3l)



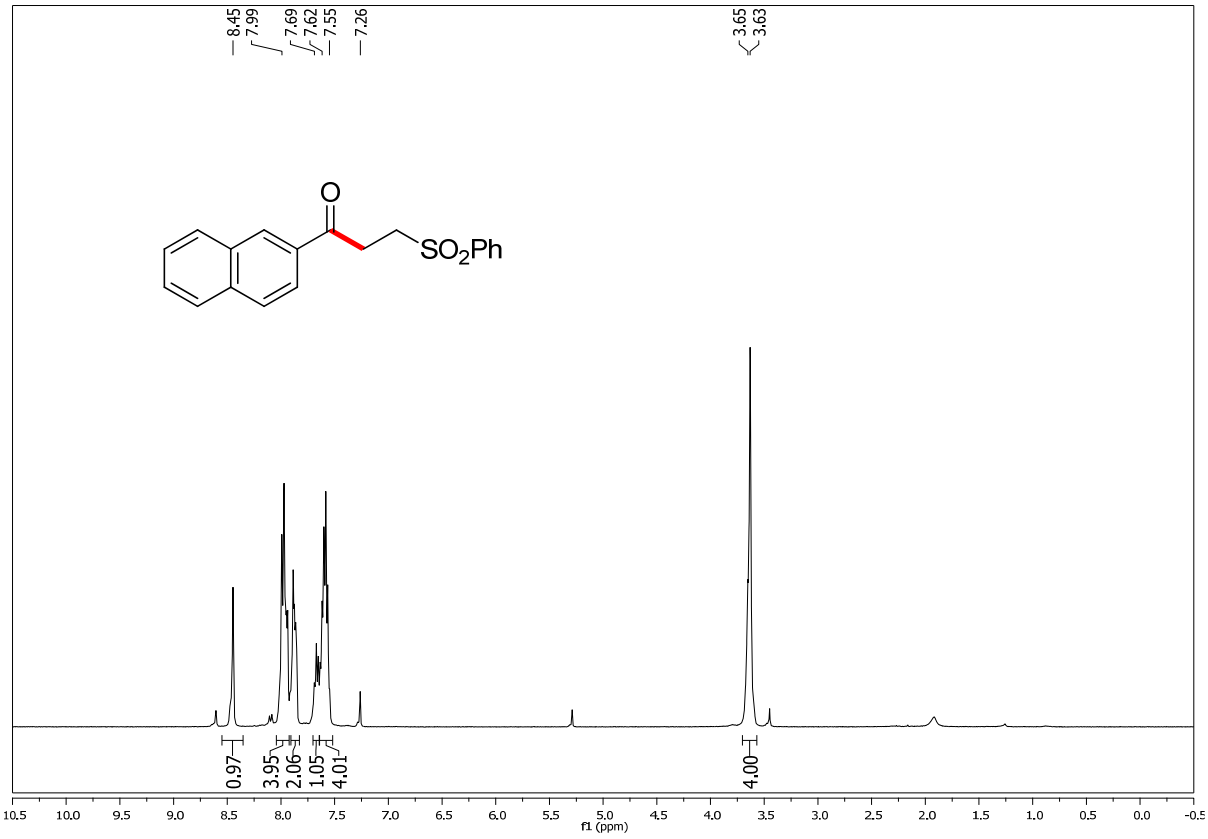


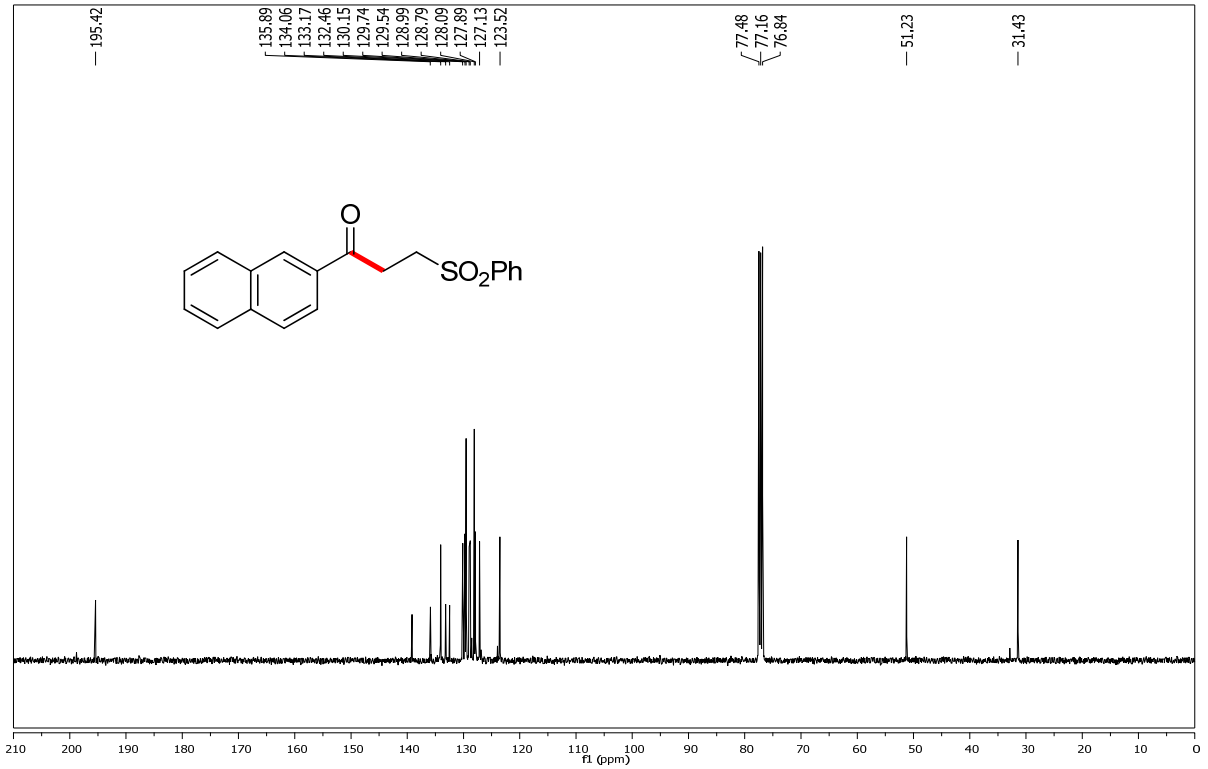
1-(Naphthalen-1-yl)-3-(phenylsulfonyl)propan-1-one (3m)



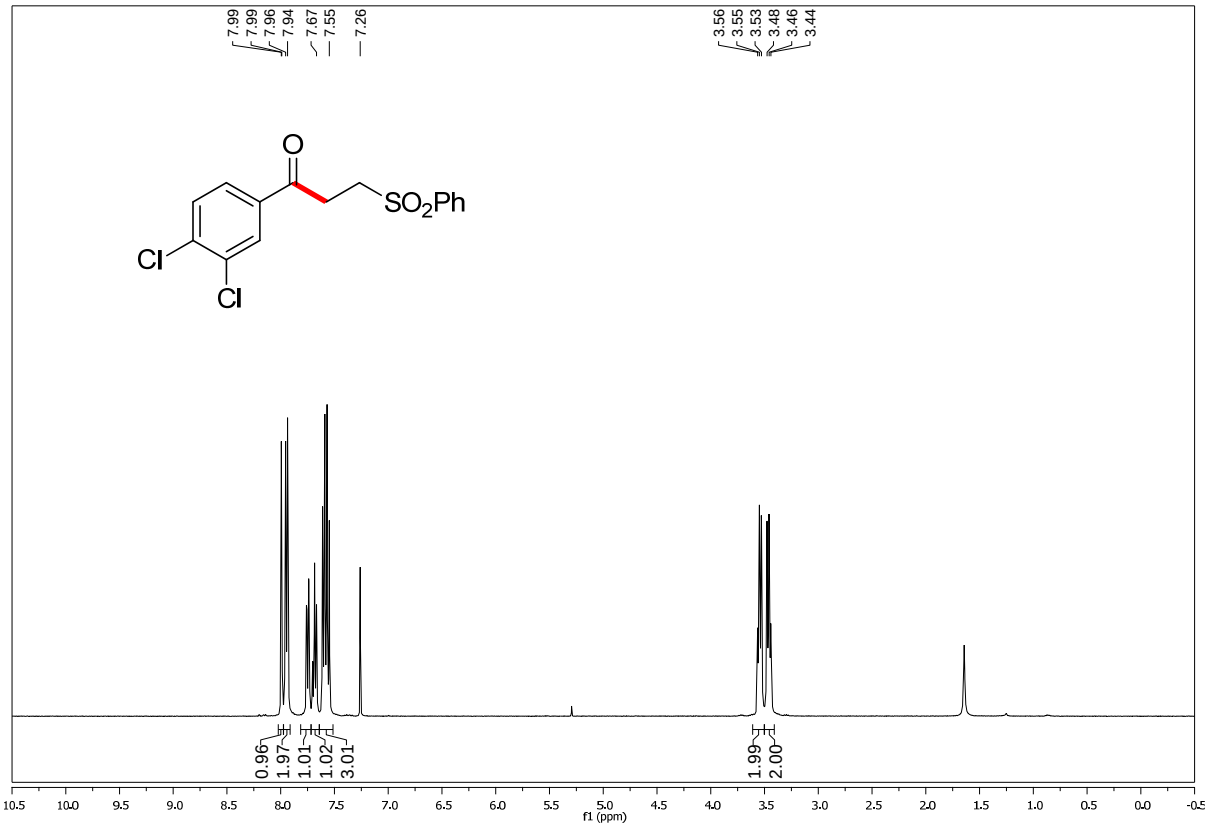


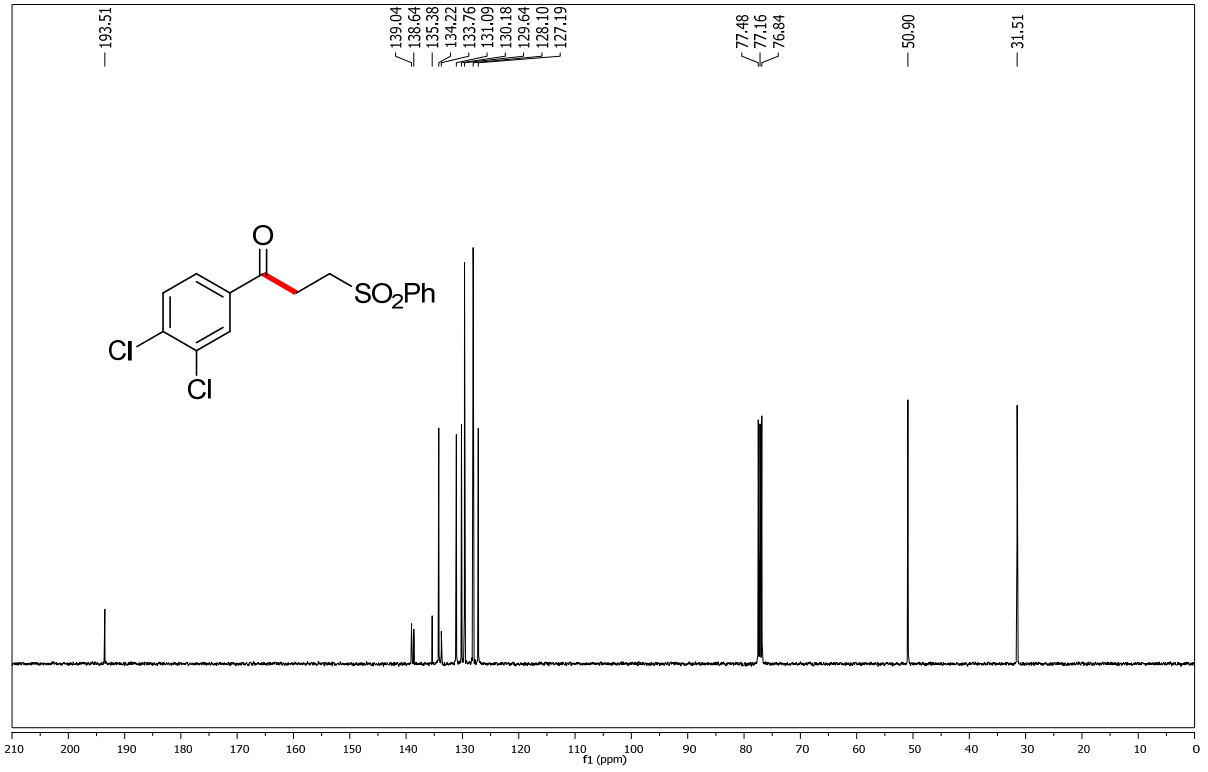
1-(Naphthalen-2-yl)-3-(phenylsulfonyl)propan-1-one (3n)



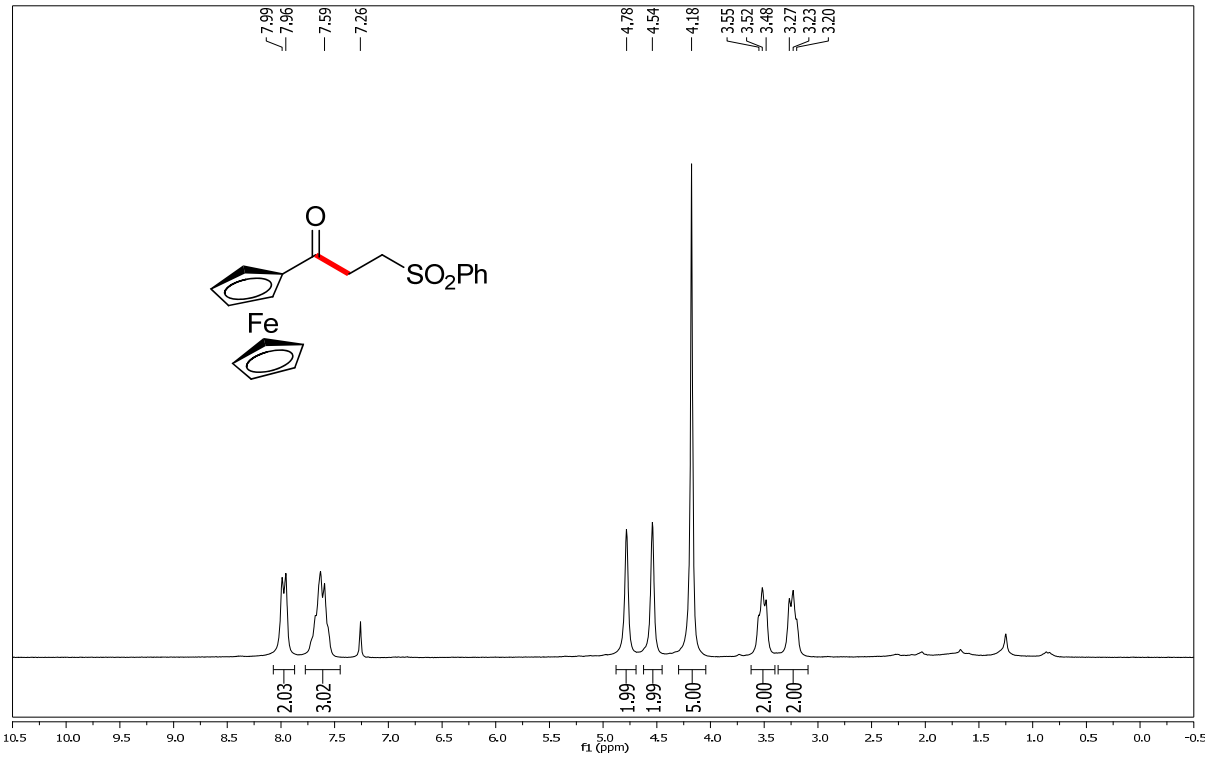


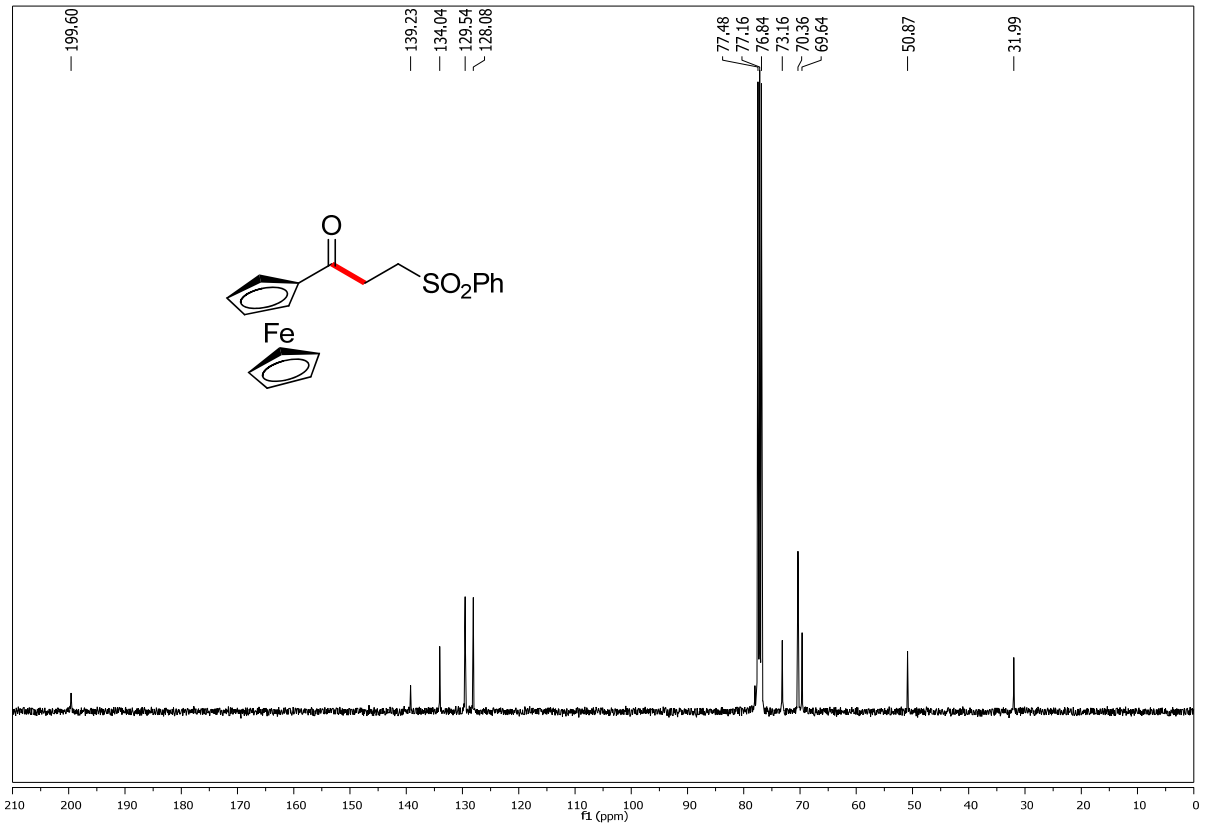
1-(3,4-Dichlorophenyl)-3-(phenylsulfonyl)propan-1-one (3o)



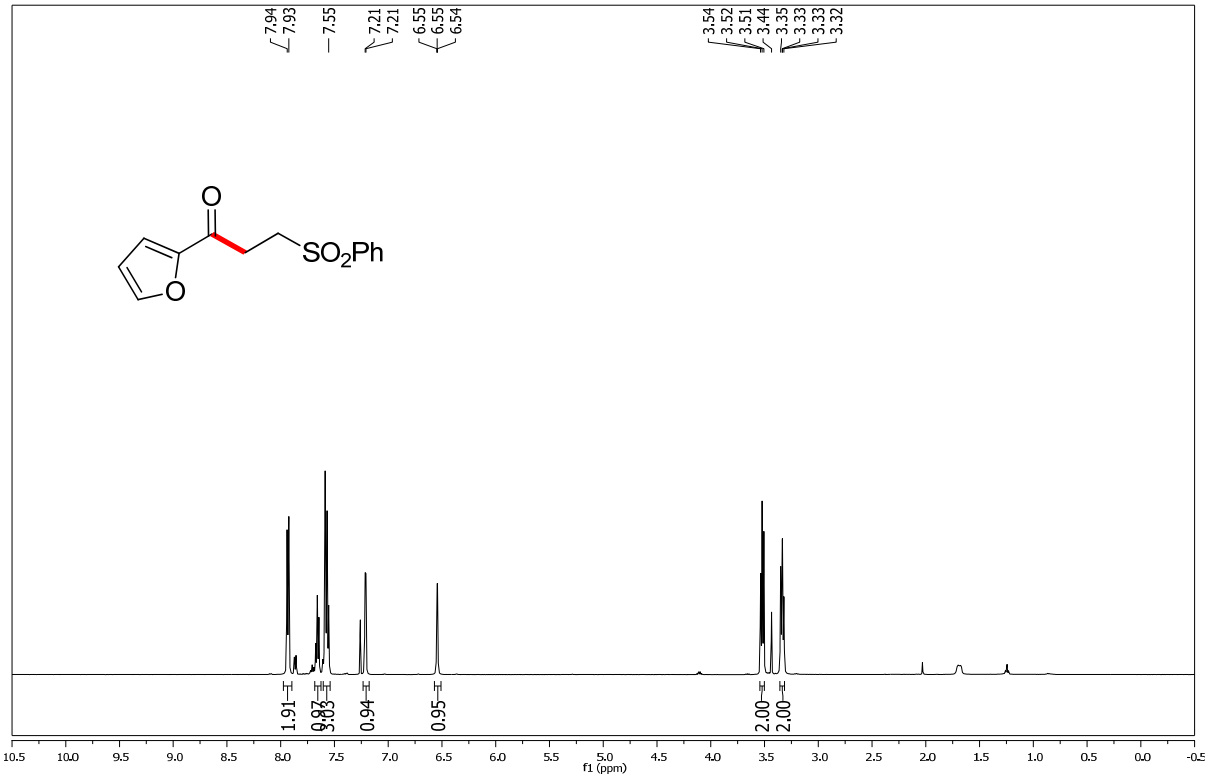


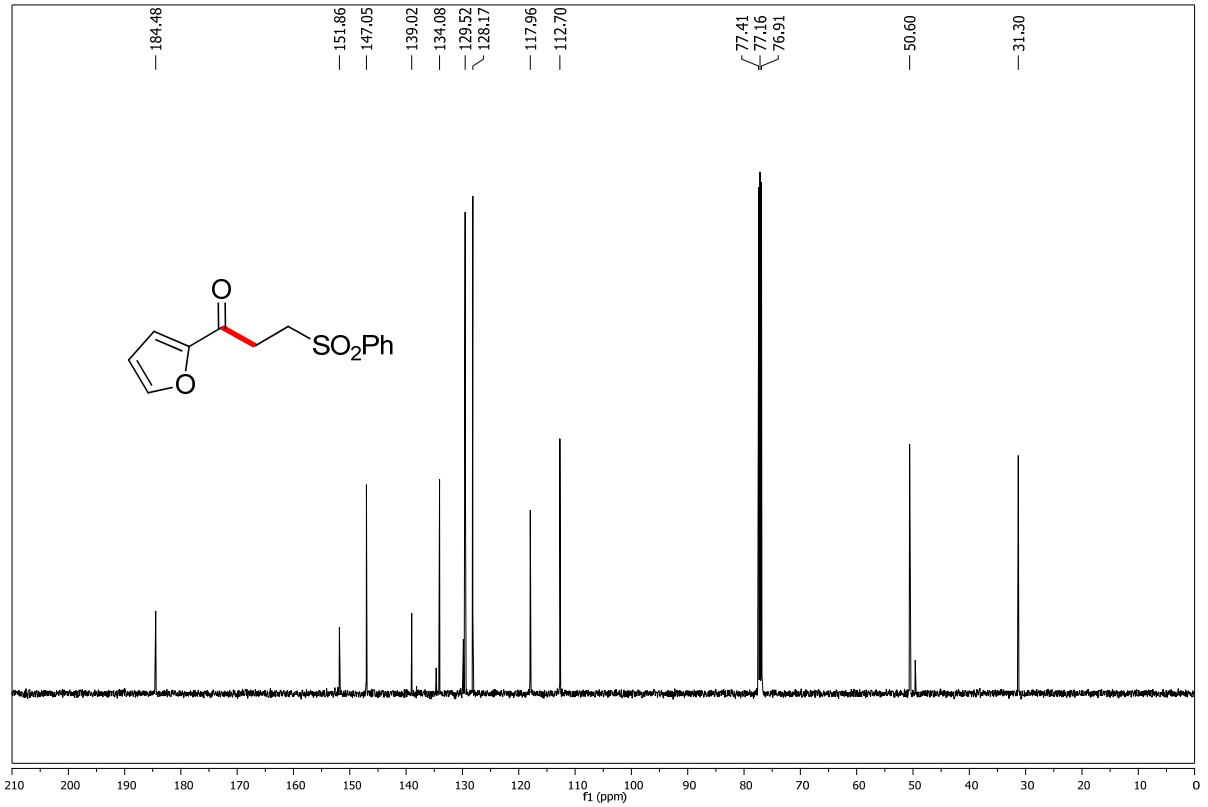
1-(2-Ferrocenyl)-3-(phenylsulfonyl)propan-1-one (3p)



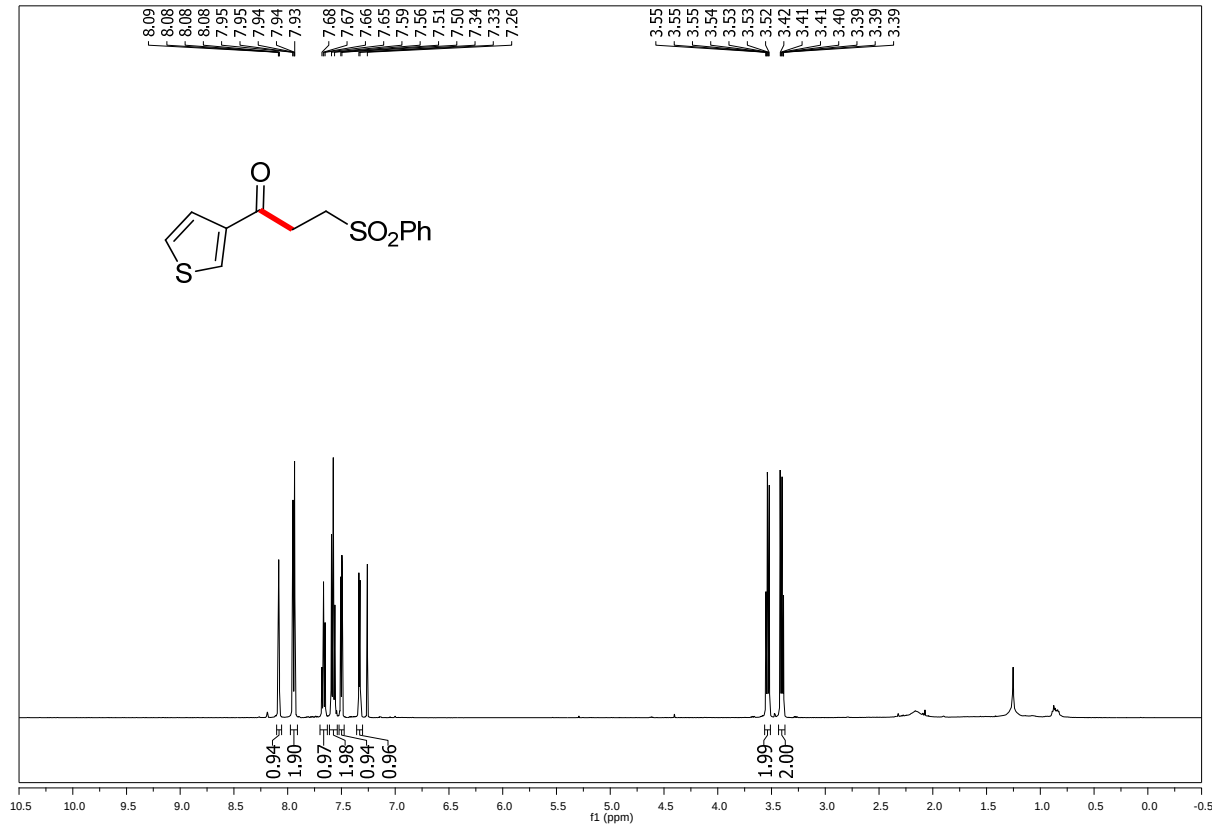


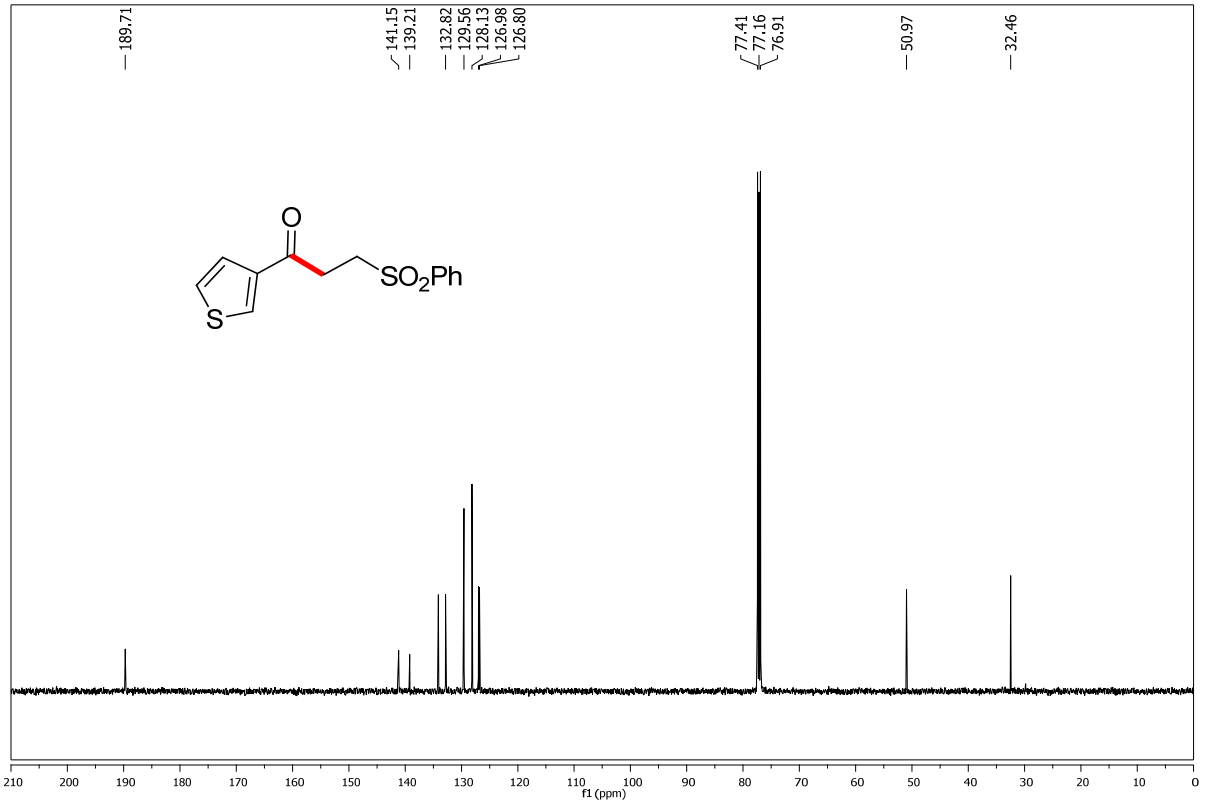
1-(Furan-2-yl)-3-(phenylsulfonyl)propan-1-one (3q)



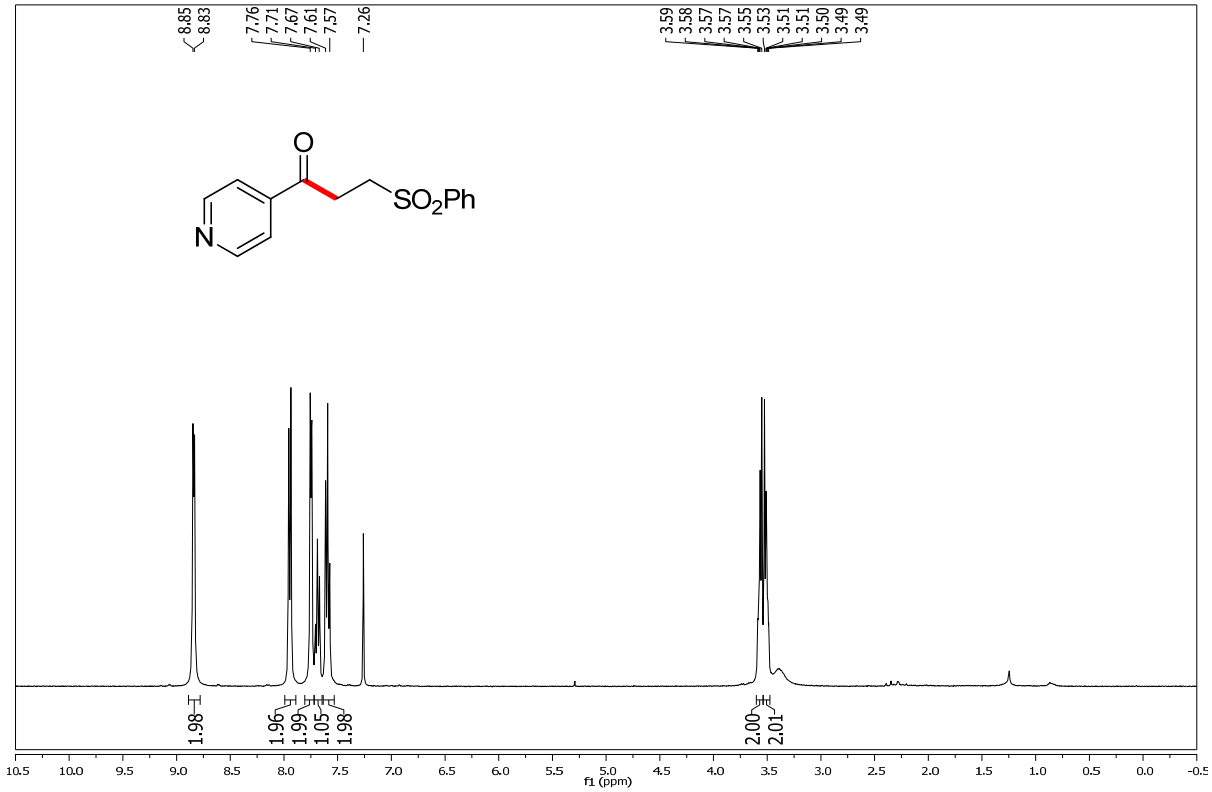


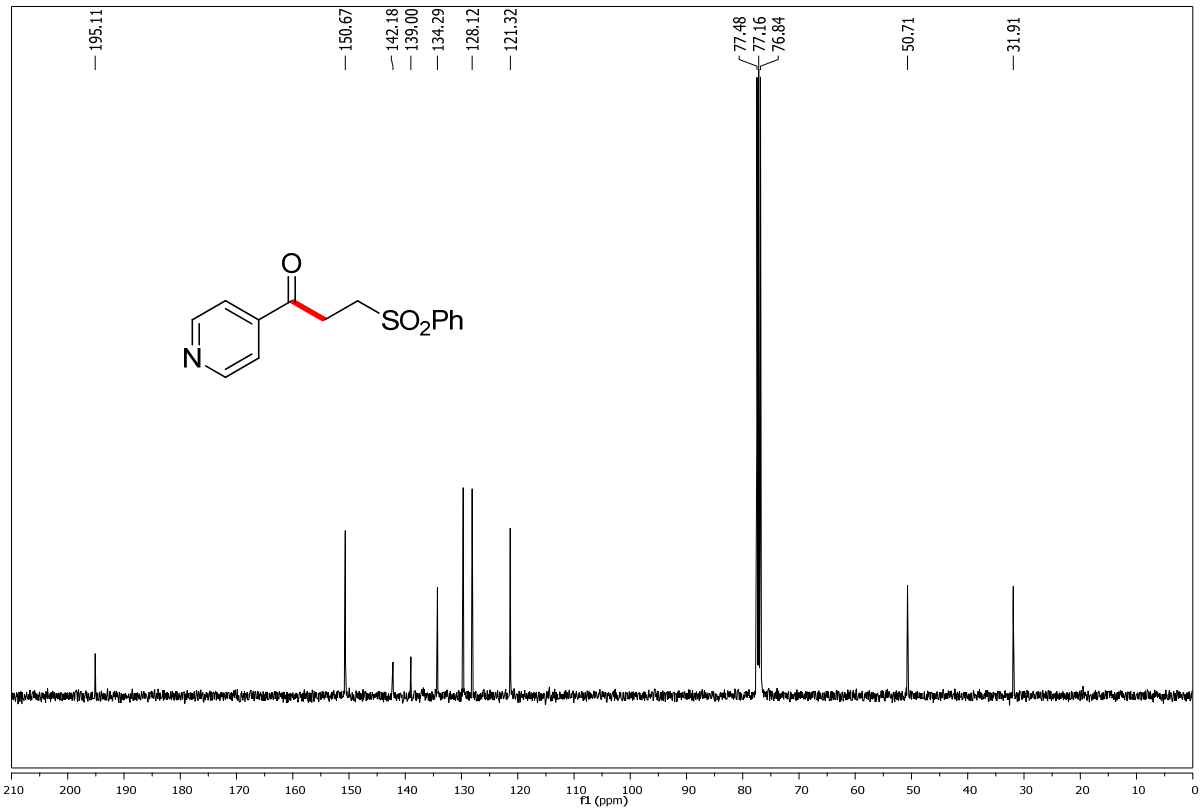
3-(Phenylsulfonyl)-1-(thiophen-3-yl)propan-1-one (3r)



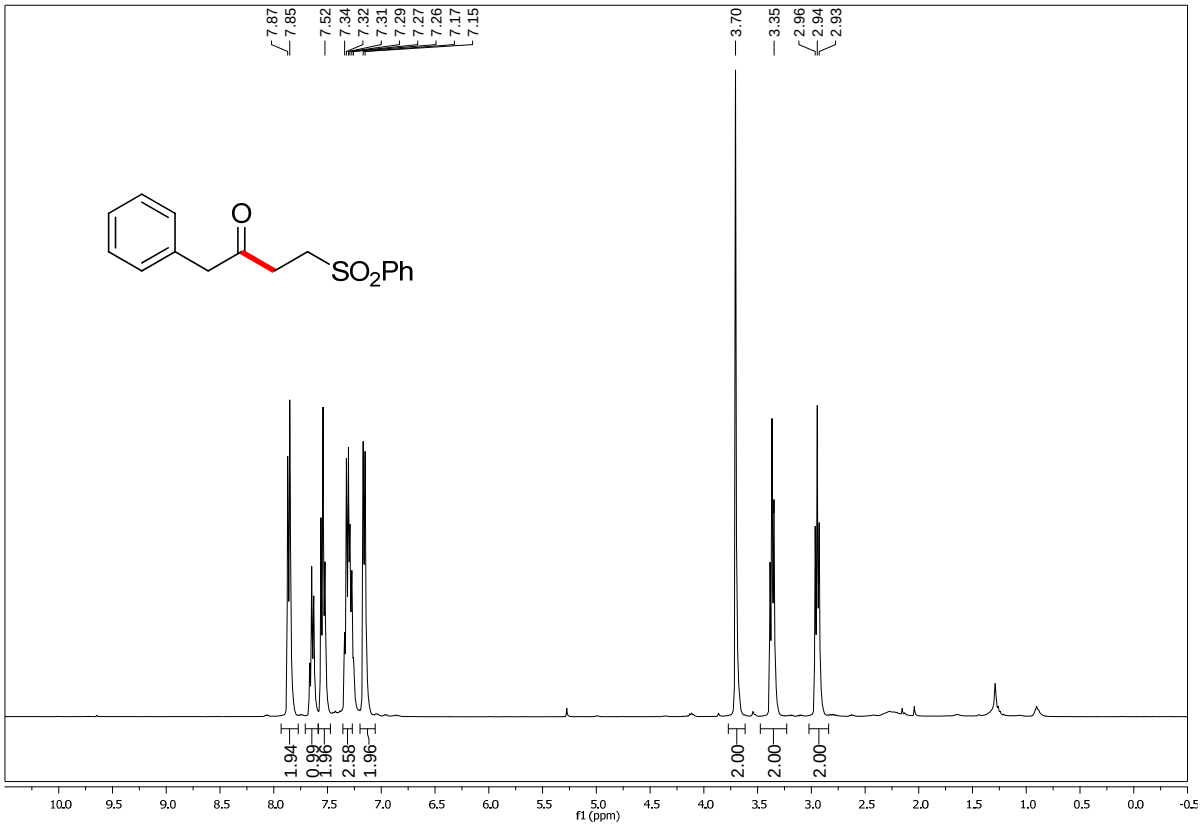


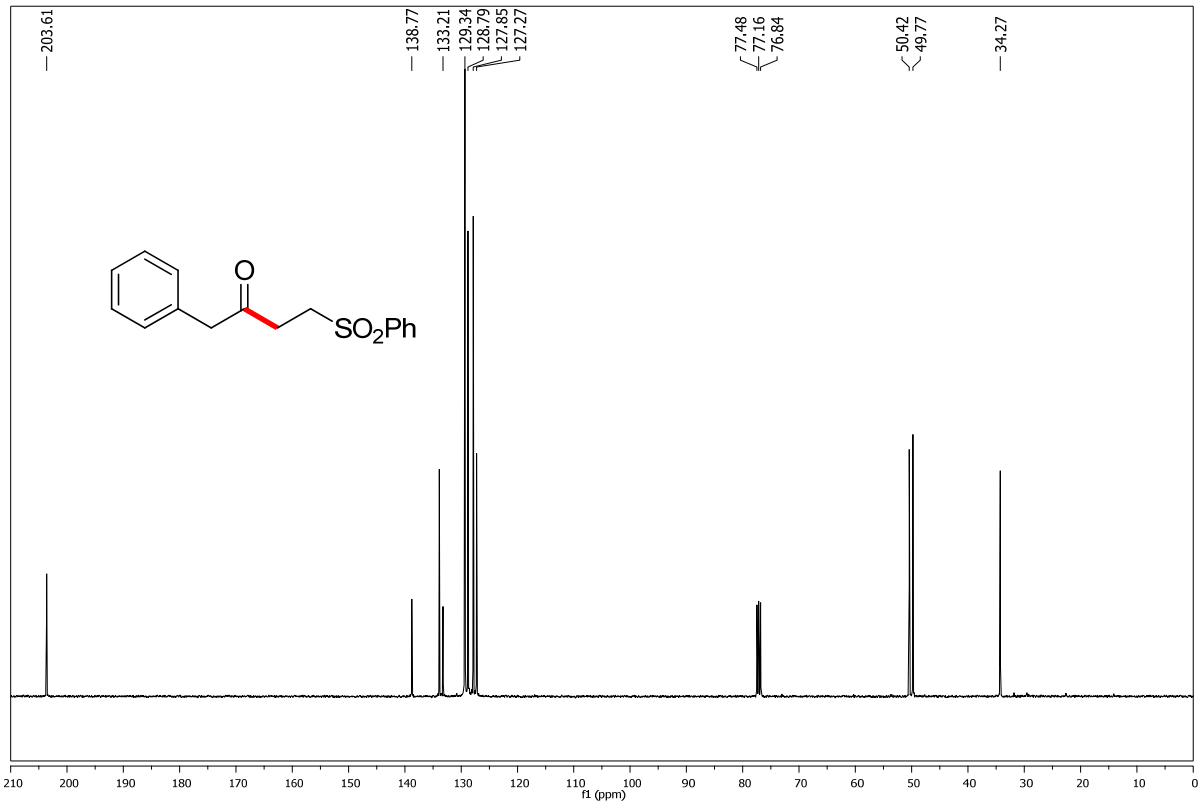
3-(Phenylsulfonyl)-1-(pyridin-4-yl) propan-1-one (3s)



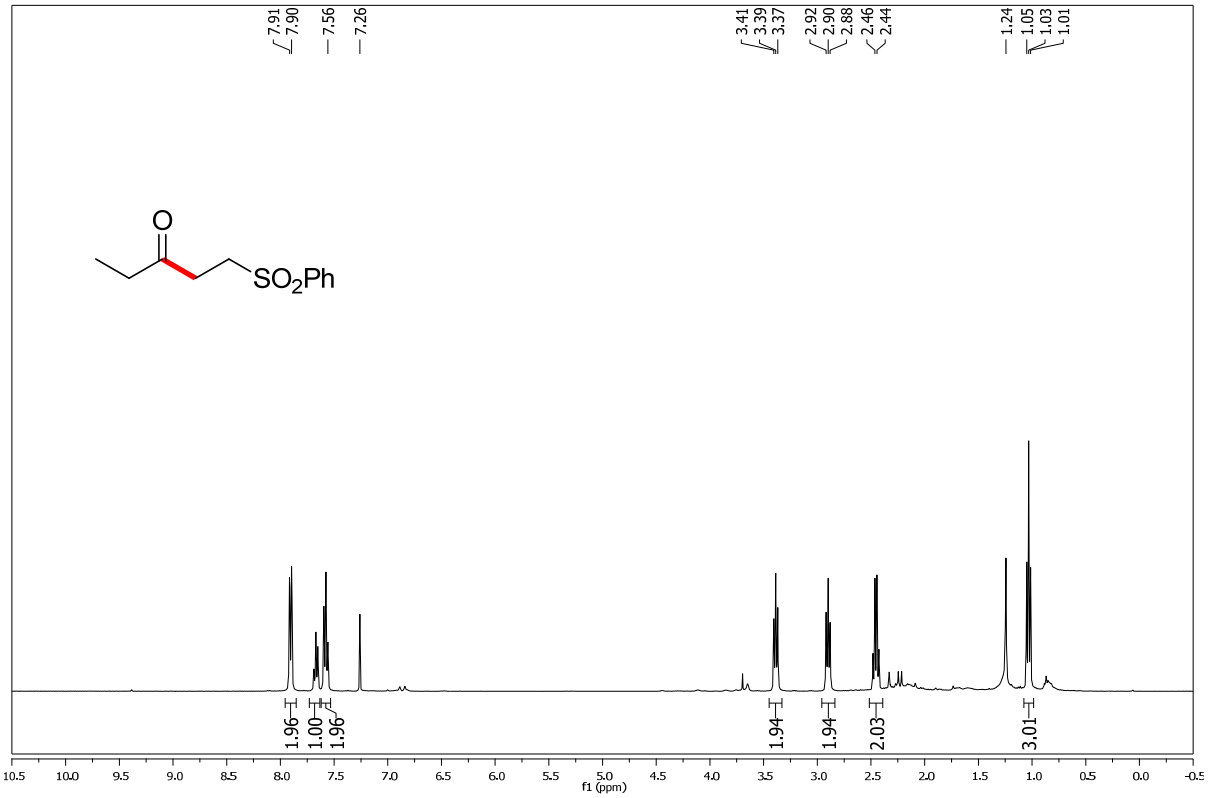


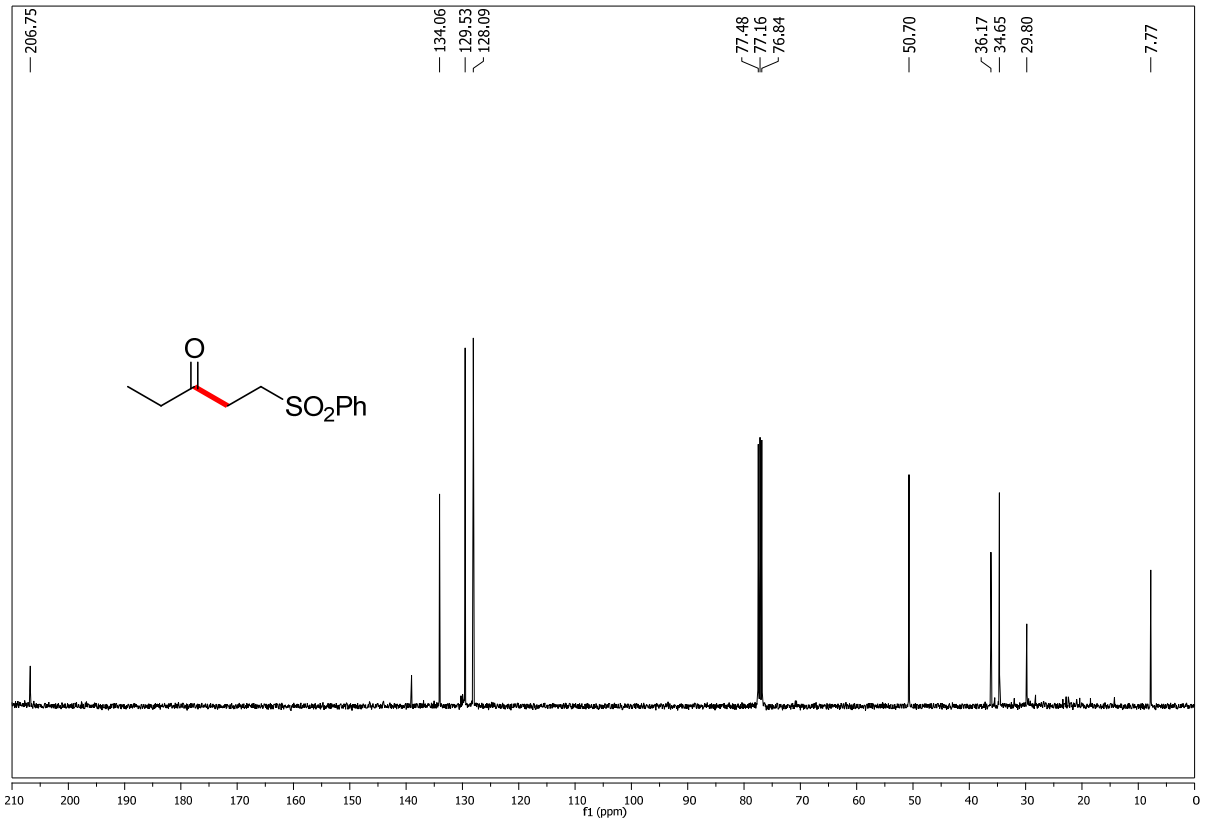
1-Phenyl-4-(phenylsulfonyl)butan-2-one (3t)



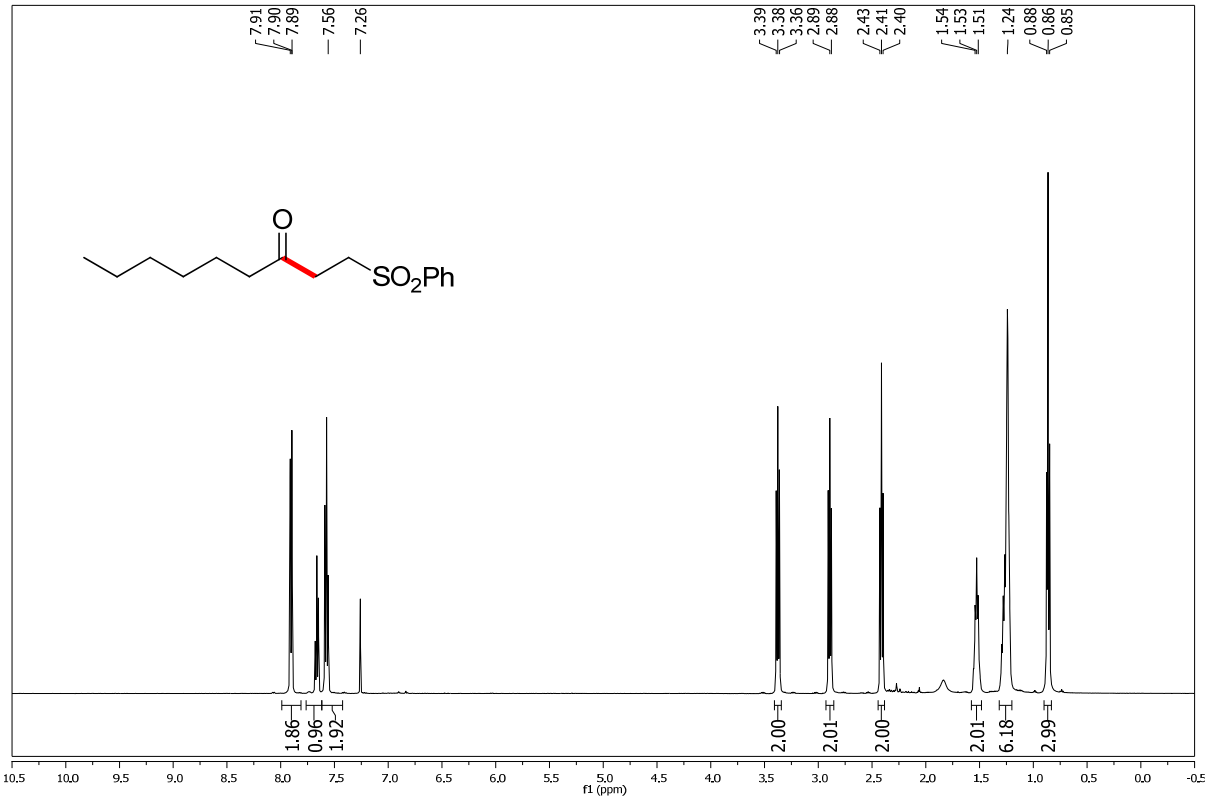


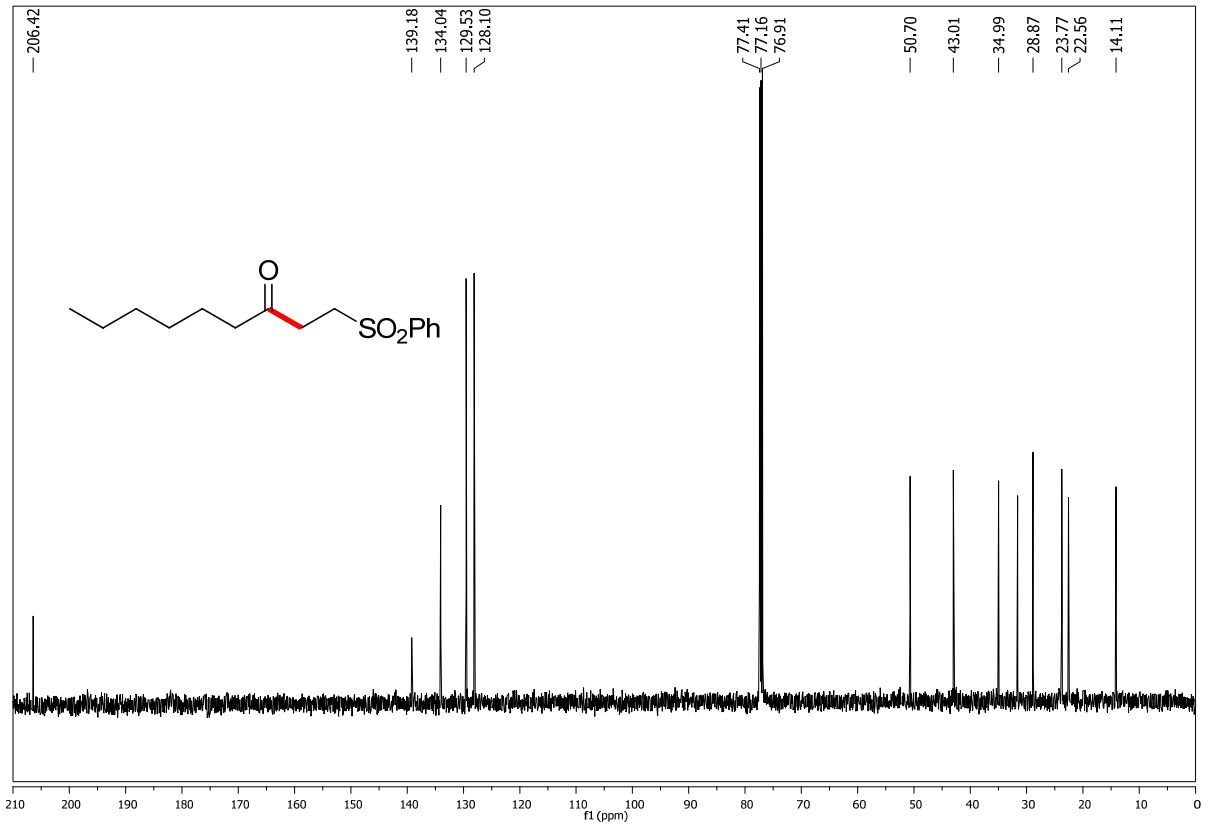
1-(Phenylsulfonyl)pentan-3-one (3u)



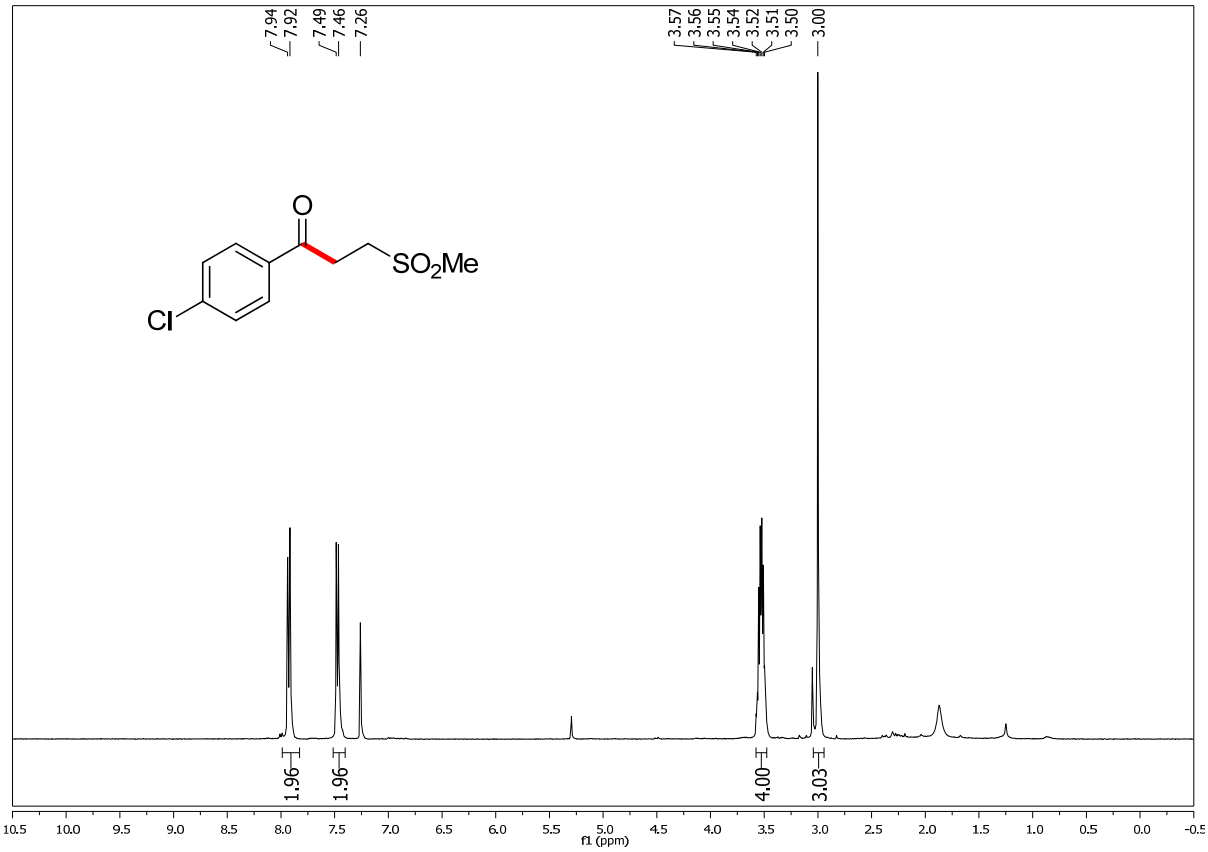


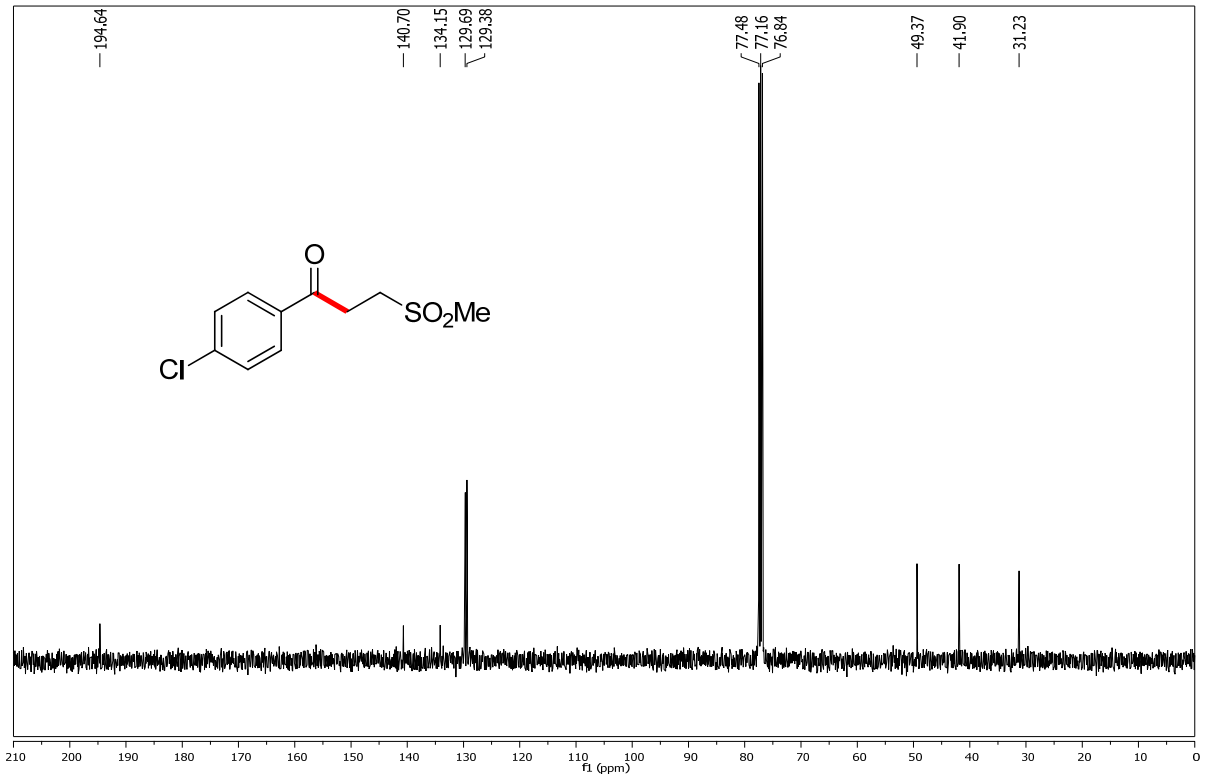
1-(Phenylsulfonyl)nonan-3-one (3v)



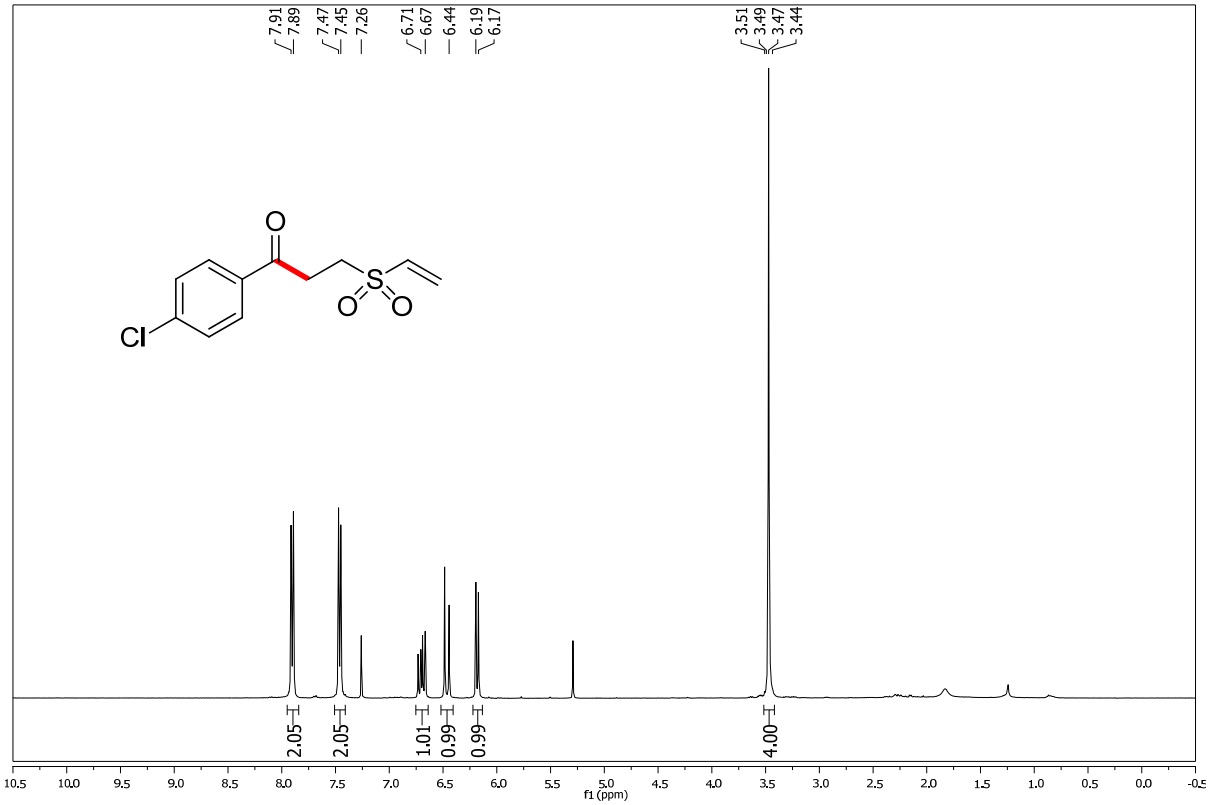


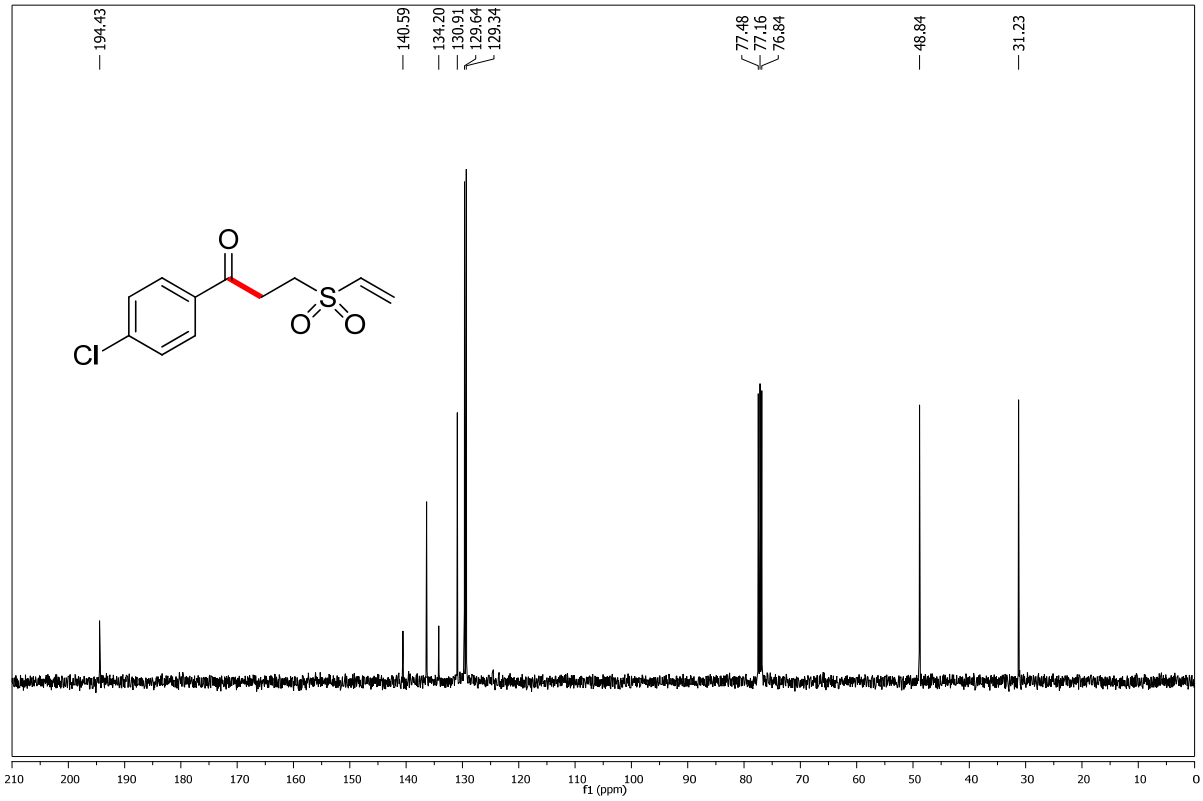
1-(4-Chlorophenyl)-3-(methylsulfonyl)propan-1-one (3w)





1-(4-Chlorophenyl)-3-(vinylsulfonyl)propan-1-one (3x)





1-(4-Chlorophenyl)-4-(*p*-tolyl)butane-1,4-dione (12)