Supporting information for

Chemoselective One-pot Synthesis of β-keto Sulfones from Ketones

Vikas S Rawat, Perla L. M. Reddy and Bojja Sreedhar*.

Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology (Council of Scientific & Industrial Research), Hyderabad 500607, India

Tel.: +91-40-27193510; fax: +91-40-27160921.

E-mail: sreedharb@iict.res.in

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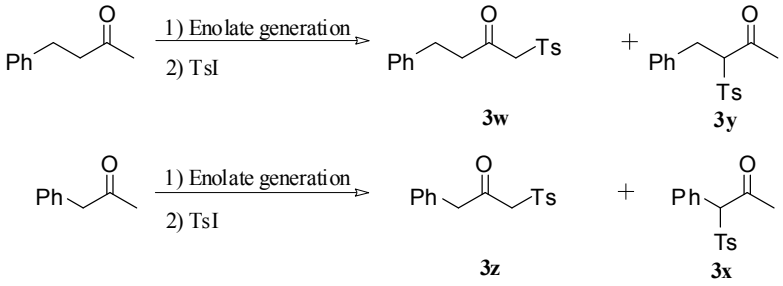
Introduction

The various procedures available for the preparation of β-keto sulfones are oxidation of β-keto sulfides, β-keto sulfoxides, and β-hydroxy sulfones,[1] alkylation of metallic arenesulfinates with lachrymatory and toxic α-haloketones or α-tosyloxy ketones,[2] acylation of α-sulfonyl carbanion with esters, nitriles and carboxylic acids via 1-acylimidazoles or *N*-acylbenzotriazoles,[3] acylation of gem-dilithiosulfones with esters[4a,b] and acid chlorides,[4c] ruthenium (II) complex catalyzed reaction of sulfonyl chlorides with silyl enol ethers,[5] $SnCl_2$-catalyzed reaction of diazo sulfones with aldehydes,[6] free-radical rearrangement of enol sulfonates,[7] Thorpe reaction of cyano sulfones,[8] Claisen condensations of esters with dimethyl sulfone,[9] AIBN-catalyzed reaction of polystyrene supported arene seleno sulfonates with alkyl and aryl acetylenes[10] and rhodium (I) complex catalyzed addition of arylboronic acids to alkyl- or arylsulfonylacetonitriles followed by acid hydrolysis.[11] More recent approaches include using alkyl- or aryl acetylenes in sulfonic acid catalyzed reaction with sulfonyl chlorides[12] and in nitroalkane catalyzed reaction with metallic arenesulfinates.[13]

Regioselectivity of the protocol

To investigate regioselectivity of the reaction, the tosyl iodide was made to react with performed enolate that was generated from the unsymmetrical alkyl ketones (benzyl acetone and 1-phenylpropan-2-one) by two methods - one by using LDA at -78 °C and the other TMSCl generated silyl enolate, at high temperature (60°C) and the results are compared with the present protocol (Table 1).

Table 1. Reaction of Various Generated Enolate of Ketones with Tosyl Iodide.



Entry	Base	Time(h)	Yield(%)(3w/3y)[d]	Yield(%)(3z/3x)[d]
1[a]	LDA	16	0/0	0/0
2[b]	DBU	6	0/0	0/0
3[c]	Et_3N	6	93/0	0/98

[a] Reaction condition: ketone (1 mmol), LDA (1.2 mmol in THF) at -78°C for 1 h then TsI (1.2 mmol in THF) then room temperature for 16 h. [b] ketone (1 mmol), TMSCl (1.2 mmol), DBU (1.2 mmol) in toluene at 60°C for 4 h and then TsI (1.2 mmol) at room temperature for 6 h. [c]ketone (1 mmol), TsI (1.2 mmol) and Et_3N (1.2 mmol) in 5 ml methanol at room temperature for 6 h. [d] Isolated yield.

Experimental Section

All glassware was dried prior to use. Ethyl acetate, hexane and acetone were distilled before use. Silica gel (100–200 mesh) was used for column chromatography and reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel coated glass plates $60F_{254}$ using UV light as visualizing agent and iodine or $KMnO_4$ solution followed by heating as developing agent. IR spectra were measured on a FT-IR spectrometer. ^{1}H NMR spectra were recorded at 300 MHz. The chemical shifts are expressed (ppm), referenced to TMS (0.00 ppm) peak. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet.^{13}C NMR spectra were recorded at 75 MHz. The chemical shifts are expressed (in ppm), reported from the central peak of deuterochloroform (77 ppm). The ^{13}C NMR spectra are proton decoupled. High-resolution mass spectra were obtained by using ESI-QTOF mass spectrometry.

General Procedure for the Synthesis of β-keto sulfone (3a-3x): At ambient temperature, 1 mmol of ketones in the presence of (121 mg, 1.2 mmol) Et_3N was stirred for 30 min in 5 mL of MeOH, then the mixture was treated with 1.2 mmol of sodium sulfinate salts (**4a** or **4b**), (254 mg, 1 mmol) of molecular iodine and stirred in dark (aluminium foil wrapped around vessel) at room temperature. After completion of the reaction (monitored by TLC) solvent was removed in vacuum, diluted with ethyl acetate (15 mL) and washed sequentially with sat. sodium thiosulfate soln, water then brine. The organic layer was dried over Na_2SO_4. Removal of the solvent in vacuum and purification of the residue by silica gel chromatography with *n*-hexane-acetone as eluent gave the desired products **3a-3x**.

Spectroscopic data for the compounds:

1-Phenyl-2-tosylethanone (3a):[14] White powder in (233 mg) 85% yield; MP 105-107 °C (Lit.[14] 106.1-108.0 °C). IR (KBr): 1150, 1317 (S=O), 1678 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 4.71 (s, 2H), 7.33 (d, 2H, *J* = 7.9 Hz), 7.48 (t, 2H, *J* = 6.9 and 7.9 Hz), 7.62 (t, 1H, *J* = 6.9 and 7.9 Hz), 7.76 (d, 2H, *J* = 7.9 Hz), 7.95 (d, 2H, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 63.5, 128.1, 128.5, 128.7, 129.2, 129.7, 129.9, 134.2, 135.7, 145.2, 188.0. ESI MS (*m/z*): 275 $(M+H)^+$, 297 $(M+Na)^+$. ESI-HRMS found: 275.0733 $(M+H)^+$ for $C_{15}H_{15}O_3S$ requires 275.0736.

1-Phenyl-2-(phenylsulfonyl)ethanone (3b):[18] White powder in (214 mg) 82% yield; MP 90-92 °C (Lit.[18] 93-95 °C). IR (KBr): 1155, 1313 (S=O), 1673 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.74 (s, 2H), 7.45-7.69 (m, 6H), 7.88-7.92 (m, 4H).^{13}C NMR (75 MHz, $CDCl_3$): δ 63.2, 127.2, 128.4, 128.7, 129.1, 129.1, 134.1, 134.2, 135.5, 138.6, 187.9. ESI MS (*m/z*): 261 $(M+H)^+$, 283 $(M+Na)^+$. ESI-HRMS found: 261.0581 $(M+H)^+$ for $C_{14}H_{13}O_3S$ requires 261.0579.

1-(Naphthalen-2-yl)-2-tosylethanone (3c):[15] White powder in (292 mg) 90% yield; MP 140-143 °C (Lit.[15] 149-150 °C). IR (KBr): 1153, 1309 (S=O), 1659 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 4.84 (s, 2H), 7.32 (d, 2H, *J* = 8.1 Hz), 7.55-7.67 (m, 2H), 7.78 (d, 2H, *J* = 8.3 Hz), 7.87-7.90 (m, 2H), 7.95-7.98 (m, 2H), 8.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 63.7, 123.8, 127.0, 127.7, 128.5, 128.7, 129.3, 129.8, 129.9, 132.1, 133.0, 135.6, 135.9, 145.3, 187.9. ESI MS (*m/z*): 325 $(M+H)^+$, 347 $(M+Na)^+$. ESI-HRMS found: 325.0903 $(M+H)^+$ for $C_{19}H_{17}O_3S$ requires, 325.0892.

1-(4-Methoxyphenyl)-2-tosylethanone (3d):[14] White powder in (253 mg) 83% yield; MP 124-126 °C (Lit.[14] 124.0-124.8 °C). IR (KBr): 1140, 1313 (S=O), 1675 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H), 3.88 (s, 3H), 4.65 (s, 2H), 6.94 (d, 2H, *J* = 8.9 Hz), 7.32 (d, 2H, *J* = 7.9 Hz), 7.74 (d, 2H, *J* = 8.9 Hz), 7.93 (d, 2H, *J* = 7.9 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 55.5, 63.4, 113.9, 128.4, 128.7, 129.7, 131.8, 135.6, 145.1, 164.4, 186.2. ESI MS (*m/z*): 305 $(M+H)^+$, 327 $(M+Na)^+$. ESI-HRMS found: 305.0851 $(M+H)^+$ for $C_{16}H_{17}O_4S$ requires 305.0842.

1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (3e):[11] White powder in (227 mg) 78 % yield; MP 115-117 °C (Lit.[11] 116-118 °C). IR (KBr): 1157, 1312 (S=O), 1664 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 4.68 (s, 2H), 6.94 (d, 2H, *J* = 8.9 Hz), 7.54 (t, 2H, *J* = 7.9 Hz), 7.65 (t, 1H, *J* = 7.9 Hz), 7.88 (d, 2H, *J* = 7.9 Hz), 7.93 (d, 2H, *J* = 8.9 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 63.4, 114.0, 128.5, 128.8, 129.1, 131.8, 134.1, 138.7, 164.5, 186.1. ESI MS (*m/z*): 291 $(M+H)^+$, 313 $(M+Na)^+$. ESI-HRMS found: 291.0688 $(M+H)^+$ for $C_{15}H_{15}O_4S$ requires 291.0685.

1-m-Tolyl-2-tosylethanone (3f):[13] White powder (242 mg) 84 % yield; MP 82-84 °C. IR (KBr): 1151, 1317 (S=O), 1672 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.43 (s, 3H), 4.69 (s, 2H), 7.31-7.36 (m, 3H), 7.41 (d, 1H, *J* = 7.9 Hz), 7.70-7.76 (m, 4H).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 21.6, 63.3, 126.0, 126.5, 128.4, 128.6, 129.2, 129.5, 129.6, 135.0, 135.6, 138.5, 145.1, 188.2. ESI MS (*m/z*): 289 $(M+H)^+$, 311 $(M+Na)^+$. ESI-HRMS found: 289.0895 $(M+H)^+$ for $C_{16}H_{17}O_3S$ requires 289.0892.

1-(2-Hydroxyphenyl)-2-tosylethanone (3g): White powder in (230 mg) 79% yield; MP 133-135 °C. IR (KBr): 1151, 1309 (S=O), 1645 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H), 4.70 (s, 2H), 6.91-7.00 (m, 2H), 7.35 (d, 2H, *J* = 8.3 Hz), 7.50-7.56 (m, 1H), 7.73-7.77 (m, 3H), 11.60 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 63.7, 118.5, 119.2, 119.4, 128.5, 129.9, 131.5, 135.5, 137.8, 145.5, 163.2, 193.3. ESI MS (*m/z*): 291 $(M+H)^+$, 313 $(M+Na)^+$. ESI-HRMS found: 291.0690 $(M+H)^+$, for $C_{15}H_{15}O_4S$ requires 291.0685.

1-(2-Hydroxyphenyl)-2-(phenylsulfonyl)ethanone (3h): White powder in (210 mg) 76% yield; MP 128-130 °C. IR (KBr): 1155, 1310 (S=O), 1627 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.73 (s, 2H), 6.91-7.00 (m, 2H), 7.50-7.59 (m, 3H), 7.66-7.74 (m, 2H), 7.88-7.91 (m, 2H), 11.58 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$): δ 63.5, 118.5, 119.1, 119.4, 128.4, 129.2, 131.4, 134.3, 137.8, 138.4, 163.1, 193.1. ESI MS (*m/z*): 277 $(M+H)^+$, 299 $(M+Na)^+$. ESI-HRMS found: 277.0531 $(M+H)^+$ for $C_{14}H_{13}O_4S$ requires 277.0529.

1-(2-Chlorophenyl)-2-tosylethanone (3i):[14] White powder in (293 mg) 95% yield; MP 95-97 °C (Lit.[14] 96.0–97.0°C). IR (KBr): 1142, 1311 (S=O), 1696 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H), 4.81 (s, 2H), 7.32-7.47 (m, 5H), 7.54-7.57 (m, 1H), 7.77 (d, 2H, *J* = 8.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 66.3, 127.1, 128.4, 129.7, 130.5, 130.5, 131.4, 133.0, 135.8, 137.2, 145.2, 190.1. ESI MS (*m/z*): 309 $(M+H)^+$, 331 $(M+Na)^+$. ESI-HRMS found: 309.0351 $(M+H)^+$ for $C_{15}H_{14}O_3ClS$ requires 309.0346.

1-(2-Chlorophenyl)-2-(phenylsulfonyl)ethanone (3j):[16] White powder in (274 mg) 93% yield; MP 88-90 °C. IR (KBr): 1156, 1321 (S=O), 1696 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.84 (s, 2H), 7.30-7.45 (m, 3H), 7.51-7.56 (m, 3H), 7.63-7.67 (m, 1H), 7.89 (d, 2H, *J* = 7.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 66.2, 127.1, 128.4, 129.1, 130.5, 130.6, 131.4, 133.1, 134.1, 137.1, 138.7, 190.1. ESI MS (*m/z*): 295 $(M+H)^+$, 317 $(M+Na)^+$. ESI-HRMS found: 295.0194 $(M+H)^+$ for $C_{14}H_{12}O_3ClS$ requires 295.0190.

1-(4-Bromophenyl)-2-tosylethanone (3k):[14] White powder in (336 mg) 95% yield; MP 142-144 °C (Lit.[14] 143.8-144.3 °C). IR (KBr): 1148, 1314 (S=O), 1678 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H), 4.67 (s, 2H), 7.34 (d, 2H, *J* = 7.5 Hz), 7.63 (d, 2H, *J* = 8.3 Hz), 7.74 (d, 2H, *J* = 8.3 Hz), 7.83 (d, 2H, *J* = 8.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 63.5, 128.4, 129.8, 130.7, 132.1, 134.3, 135.4, 145.5, 187.2. ESI MS (*m/z*): 355 $(M+2)^+$. ESI-HRMS found: 352.9849 $(M+H)^+$ for $C_{15}H_{14}O_3BrS$ requires 352.9841.

1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanone (3l):[14] White powder in (319 mg) 94% yield ; MP 134-136 °C (Lit.[14] 135.5–136.8 °C). IR (KBr): 1138, 1328 (S=O), 1689 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.70 (s, 2H), 7.53-7.71 (m, 5H), 7.82 (d, 2H, *J* = 8.3 Hz), 7.88 (d, 2H, *J* = 6.7 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 63.4, 128.4, 129.1, 129.8, 130.6, 132.1, 134.2, 138.5, 187.0. ESI MS (*m/z*): 339 $(M)^+$, 341 $(M+2)^+$. ESI-HRMS found: 338.9691 $(M)^+$ for $C_{14}H_{12}O_3BrS$ requires 338.9685.

1-(4-Iodophenyl)-2-tosylethanone (3m): White powder in (361 mg) 90% yield; MP 152-154 °C. IR (KBr): 1148, 1314 (S=O), 1679 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.45 (s, 3H), 4.66 (s, 2H), 7.34 (d, 2H, *J* = 8.1 Hz), 7.66 (d, 2H, *J* = 8.6 Hz), 7.74 (d, 2H, *J* = 8.3 Hz), 7.86 (d, 2H, *J* = 8.6 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 63.5, 102.9, 128.4, 129.8, 130.5, 134.9, 135.4, 138.1, 145.5, 187.5. ESI MS (*m/z*): 401 $(M+H)^+$, 423 $(M+Na)^+$. ESI-HRMS found: 400.9711 $(M+H)^+$ for $C_{15}H_{14}O_3IS$ requires 400.9702.

1-(4-iodophenyl)-2-(phenylsulfonyl)ethanone (3n):[17] White powder in (348 mg) 90% yield ; MP 134-135 °C. IR (KBr): 1137, 1300 (S=O), 1687 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.68 (s, 2H), 7.53-7.58 (m, 2H), 7.63-7.68 (m, 3H), 7.85-7.89 (m, 4H).^{13}C NMR (75 MHz, $CDCl_3$): δ 63.2, 103.0, 128.3, 129.1, 130.4, 134.2, 134.7, 138.0, 138.3, 187.3. ESI MS (*m/z*): 387 $(M+H)^+$, 409 $(M+Na)^+$. ESI-HRMS found: 386.9558 $(M+H)^+$ for $C_{14}H_{12}O_3IS$ requires 386.9546.

1-(4-Nitrophenyl)-2-(phenylsulfonyl)ethanone (3o):[18] Yellow powder in (296 mg) 97% yield; MP 137-138 °C (Lit.[18]138-139 °C). IR (KBr): 1156, 1313 (S=O), 1678 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.76 (s, 2H), 7.58 (t, 2H, *J* = 7.9 Hz), 7.71 (t, 1H, *J* = 6.9 Hz), 7.88 (d, 2H, *J* = 7.9 Hz), 8.15 (d, 2H, *J* = 8.9 Hz), 8.33 (d, 2 H, *J* = 8.9 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 63.9, 123.9, 128.4, 129.4, 130.4, 134.5, 138.3, 139.9, 150.8, 186.8. ESI MS (*m/z*): 328 $(M+Na)^+$. ESI-HRMS found: 328.0253 $(M+Na)^+$ for $C_{14}H_{11}O_5NNaS$ requires 328.0250.

5-Bromo-2-(phenylsulfonyl)-2,3-dihydro-1H-inden-1-one (3p): White powder in (302 mg) 86 % yield; MP 134-135 °C. IR (KBr): 1143, 1309 (S=O), 1714 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.48-3.57 (m, 1H), 3.82 (dd, 1H, *J* = 18.4, 3.2), 4.28 (dd, 1H, *J* = 8.5, 3.3), 7.51-7.61 (m, 4H), 7.67-7.72 (m, 2H), 7.90-7.93 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7, 68.6, 125.9, 129.1, 129.2, 129.7, 131.5, 131.9, 134.3, 134.5, 137.2, 153.2, 193.2. ESI MS (*m/z*): 351 $(M+H)^+$, 353 $(M+2)^+$. ESI-HRMS found: 350.9693 $(M+H)^+$ for $C_{15}H_{12}O_3BrS$ requires 350.9685.

1-(Pyridin-2-yl)-2-tosylethanone (3q):[2e] White powder in (201 mg) 73% yield; MP 78-80 °C. IR (KBr): 1155, 1317 (S=O), 1699 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 5.13 (s, 2H), 7.30 (d, 2H, *J* = 7.9 Hz), 7.46-7.48 (m, 1H), 7.79-7.87 (m, 3H), 8.01 (d, 1H, *J* = 6.9 Hz), 8.59 (d, 1H, *J* = 4.9 Hz) .^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 60.9, 122.4, 127.8, 128.4, 129.5, 136.5, 137.0, 144.8, 149.0, 151.8, 189.7. ESI MS (*m/z*): 276 $(M+H)^+$, 298 $(M+Na)^+$. ESI-HRMS found: 276.0689 $(M+H)^+$ for $C_{14}H_{14}O_3NS$ requires 276.0688.

2-(Phenylsulfonyl)-1-(thiophen-2-yl)ethanone (3r):[18] White powder in (208 mg) 78% yield; MP 87-89 °C (Lit.[18] 87-88 °C). IR (KBr): 1144, 1411 (S=O), 1648 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.63 (s, 2H), 7.15-7.18 (m, 1H), 7.53-7.58 (m, 2H), 7.64-7.69 (m, 1H), 7.74-7.81 (m, 2H), 7.88-7.91 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 64.4, 128.5, 128.6, 129.1, 134.2, 135.1, 136.3, 138.4, 143.0, 180.0. ESI MS (*m/z*): 267 $(M+H)^+$, 289 $(M+Na)^+$. ESI-HRMS found: 267.0146 $(M+H)^+$ for $C_{12}H_{11}O_3S_2$ requires 267.0144.

1-Tosylpropan-2-one (3S):[19] White crystals in (202 mg) 95% yield; MP 51-53 °C (Lit.[19] 52-53 °C). IR (KBr): 1152, 1320 (S=O), 1719 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H), 2.44 (s, 3H), 4.11 (s, 2H), 7.36 (d, 2H, *J* = 7.9 Hz), 7.75 (d, 2H, *J* = 8.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 31.4, 67.8, 128.1, 129.9, 135.5, 145.4, 196.0. ESI MS (*m/z*): 212 $(M+H)^+$, 235 $(M+Na)^+$. ESI-HRMS found: 213.0586 $(M+H)^+$ for $C_{10}H_{13}O_3S$ requires, 213.0579.

1-(Phenylsulfonyl)propan-2-one (3t):[20] White powder in (183 mg) 92% yield; MP 53-55 °C (Lit.[20] 56-57 °C). IR (KBr): 1152, 1316 (S=O), 1723 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.41 (s, 3H), 4.16 (s, 2H), 7.56-7.61 (m, 2H), 7.67-7.72 (m, 1H), 7.88-7.92 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.4, 67.6, 128.1, 129.3, 134.2, 138.5, 195.8. ESI MS (*m/z*): 198 $(M+H)^+$, 221 $(M+Na)^+$. ESI-HRMS found: 199.0431 $(M+H)^+$ for $C_9H_{11}O_3S$ requires, 199.0423.

2-Tosylcyclohexanone (3u):[21] Colorless liquid in (217 mg) 86% yield; IR (KBr): 1145, 1310 (S=O), 1715 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.70-1.88 (m, 2H), 1.97-2.06 (m, 1H), 2.17-2.28 (m, 2H), 2.38-2.57 (m, 5H), 2.75-2.85 (m, 1H), 3.81 (t, 1H, *J* = 5.2 Hz), 7.34 (d, 2H, *J* = 8.3 Hz), 7.76 (d, 2H, *J* = 8.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 21.8, 26.4, 27.4, 41.5, 72.7, 127.5, 127.9, 128.8, 129.1, 129.6, 129.9, 135.0, 140.8, 145.1, 202.4. ESI MS (*m/z*): 253 $(M+H)^+$, 275 $(M+Na)^+$. ESI-HRMS found: 253.0895 $(M+H)^+$ for $C_{13}H_{17}O_3S$ requires 253.0892.

2-(Phenylsulfonyl)cyclohexanone (3v):[20] White powder in (193 mg) 81% yield; MP 85-87 °C (Lit.[20] 86-87 °C). IR (KBr): 1148, 1311 (S=O), 1713 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.70-1.85 (m, 2H), 1.98-2.04 (m, 1H), 2.16-2.27 (m, 2H), 2.39-2.44 (m, 1H), 2.52-2.56 (m, 1H), 2.77-2.83 (m, 1H), 3.82-3.84 (m, 1H), 7.54 (t, 2H, *J* = 7.9 Hz), 7.65 (t, 1H, *J* = 7.9 Hz), 7.88 (d, 2H, *J* = 7.9 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 26.2, 27.3, 41.5, 72.3, 128.7, 128.8, 133.8, 137.9, 201.9. ESI MS (*m/z*): 239 $(M+H)^+$, 261 $(M+Na)^+$. ESI-HRMS found: 239.0733 $(M+H)^+$ for $C_{12}H_{15}O_3S$ requires 239.0736.

4-Phenyl-1-tosylbutan-2-one (3w):[22] colorless liquid in (281 mg) 93% yield; IR (KBr): 1147, 1329 (S=O), 1714 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.14 (s, 3H), 2.76 (t, 2H, *J* = 7.3, 7.9 Hz), 2.89 (t, 2H, *J* = 7.9, 7.3 Hz), 3.46 (s, 3H), 7.17-7.20 (m, 3H), 7.25-7.29 (m, 4H), 7.34 (d, 1H, *J* = 7.9 Hz), 7.59 (d, 1H, *J* = 8.2 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.4, 29.6, 30.0, 41.9, 45.1, 126.0, 127.0, 127.5, 128.2, 128.4, 129.3, 129.5, 130.1, 136.4, 208.1. ESI MS (*m/z*): 325 $(M+Na)^+$. ESI-HRMS found: 320.1310 $(M+NH_4)^+$ for $C_{17}H_{22}O_3NS$ requires 320.1314.

1-Phenyl-1-tosylpropan-2-one (3x):[23] white solid in (283 mg) 98% yield; MP 160-162 °C (Lit.[23] 161-162 °C). IR (KBr): 1145, 1320 (S=O), 1719 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 2.40 (s, 3H) 5.20 (s, 1H), 7.20 (d, 2H, *j* = 8.08 Hz), 7.25-7.30 (m, 4H) 7.35-7.38 (m, 1H), 7.44 (d, 2H, *j* = 8.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$): δ 21.6, 31.6, 80.2, 128.0, 128.6, 129.1, 129.5, 129.7, 130.3, 133.7, 145.1, 197.9. ESI MS (*m/z*): 289 $(M+Na)^+$. ESI-HRMS found: 289.0896 $(M+H)^+$ for $C_{16}H_{17}O_3S$ requires 289.0893.

References:

1 (*a*) B. M. Trost and D. P. Curran, *Tetrahedron Lett.* 1981, **22**, 1287; (*b*) G. K. Cooper and I. J. Dolby, *Tetrahedron Lett.* 1976, 17, 4675; (*c*) A. -L. Fan, S. Cao and Z. Zhang, *J. Heterocycl. Chem.* 1997, **34**, 1657; (*d*) T. Zweifel, M. Nielsen, J. Overgaard, C. B. Jacobsen and K. A. Jørgensen, *Eur. J. Org. Chem.* 2011, **2011**, 47.

2 (*a*) G. E. Vennstra and B. Zwaneburg, *Synthesis* 1975, 519; (*b*) J. Wildeman and A. M. V. Leusen, *Synthesis* 1979, 733; (*c*) Y. -Y. Xie and Z. -C. Chen, *Synth. Commun*. 2001, **31**, 3145; (*d*) N. Suryakiran, P. Prabhakar, K. Rajesh, V. Suresh and Y. Venkateswarlu, *J. Mol. Catal. A: Chem.* 2007, **270**, 201; (*e*) A. Kumar and M. K. Muthyala, *Tetrahedron Lett.* 2011, **52**, 5368; (*f*) D. Kumar, S. Sundaree, V. S. Rao and R. S. Varma, *Tetrahedron Lett.* 2006, **47**, 4197.

3 (*a*) W. E. Truce and R. H. Knospe, *J. Am. Chem. Soc.* 1955, **77**, 5063; (*b*) W. E. Truce, W. M. Bannister and R. H. Knospe, *J. Org. Chem.* 1962, **27**, 2821; (*c*) H. O. House and J. R. Larson, *J. Org. Chem.* 1968, **33**, 61; (*d*) M. W. Thomsen, B. M. Handwerker, S. A. Katz and R. B. Belser, *J. Org. Chem.* 1988, **53**, 906; (*e*) C. A. Ibarra, R. C. Rodriguez, M. C. Monreal, F. J. Navarro and J. M. Tesorero, *J. Org. Chem.* 1989, **54**, 5620; (*f*) A. R. Katritzky, A. A. A. -Fattah and M. Y. Wang, *J. Org. Chem.* 2003, **68**, 1443.

4 (*a*) E. M. Kaiser, L. E. Solter, R. A. Schwarz, R. D. Beard and C. R. Hauser, *J. Am. Chem. Soc.* 1971, **93**, 4237; (*b*) M. C. Mussatto, D. Savoia, C. Trombini and A. U. -Ronchi, *J. Org. Chem.* 1980, **45**, 4002.

5 (*a*) N. Kamigata, K. Udodaira and T. Shimizu, *J. Chem. Soc., Perkin Trans. 1* 1997, 783; (*b*) Y. Matano, N. Azuma and H. Suzuki, *J. Chem. Soc., Perkin Trans. 1* 1994, 1739.

6 C. R. Holmquist and E. J. Roskamp, *Tetrahedron Lett.* 1992, **33**, 1131.

7 N. Frydman and Y. Mazur, *J. Am. Chem. Soc.* 1970, **92**, 3203.

10 H. Qian and X. Huang, *Synthesis* 2006, 1934.

11 G. C. Tsui, Q. Glenadel, C. Lau and M. Lautens, *Org. Lett.* 2011, **13**, 208.

12 C. Xi, C. Lai, Y. Jiang and R. Hua, *Tetrahedron Lett.* 2005, **46**, 513.

13 B. Sreedhar and V. S. Rawat, *Synlett* 2012, **23**, 413.

14 N. Samakkanad, P. Katrun, T. Techajaroonjit, S. Hlekhlai, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram and C. Kuhakarn, *Synthesis* 2012, **44**, 1693.

15 K. Kim, S. R. Mani and H. J. Shine, *J. Org. Chem.* 1975, **40**, 3857.

16 X. Wan, Q. Meng, H. Zhang, Y. Sun, W. Fan and Z. Zhang, *Org. Lett.* 2007, **9**, 5613.

17 Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang and A. Lei, *J. Am. Chem. Soc.* 2013, **135**, 11481.

18 J. Yang, H. Li, M. Li, J. Peng and Y. Gu, *Adv. Synth. Catal.* 2012, **354**, 688.

19 R. E. Swenson, T. J. Sowin and H. Q. Zhang, *J. Org. Chem.* 2002, **67**, 9182.

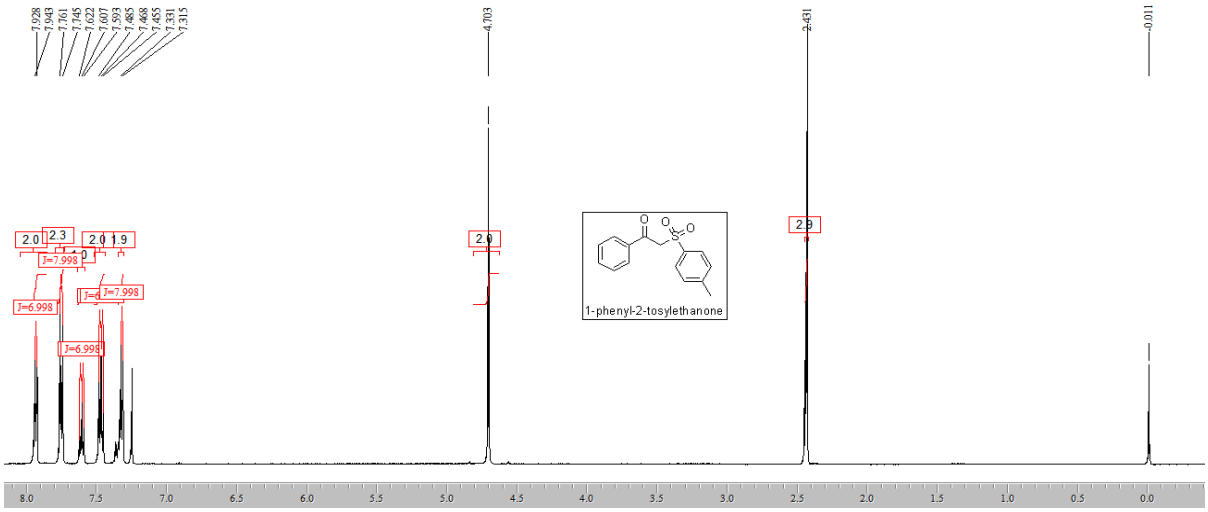
20. D. Enders, A. Grossmann, H. Huang and G. Raabe, *Eur. J. Org. Chem.* 2011, 4298.

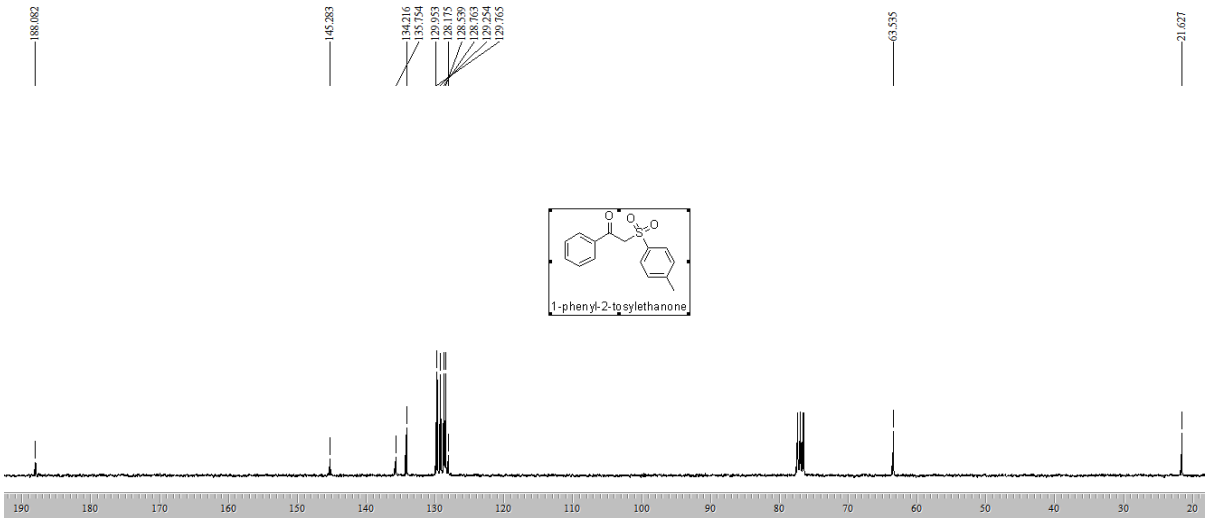
21. J. L. G. -Ruano and A. Rumbero, *Tetrahedron: Asymmetry* 1999, **10**, 4427.

22. N. Iwata, T. Morioka, T. Kobayashi, T. Asada, H. Kinoshita and K. Inomata, *Bull. Chem. Soc. Jpn.* 1992, **65**, 1379.

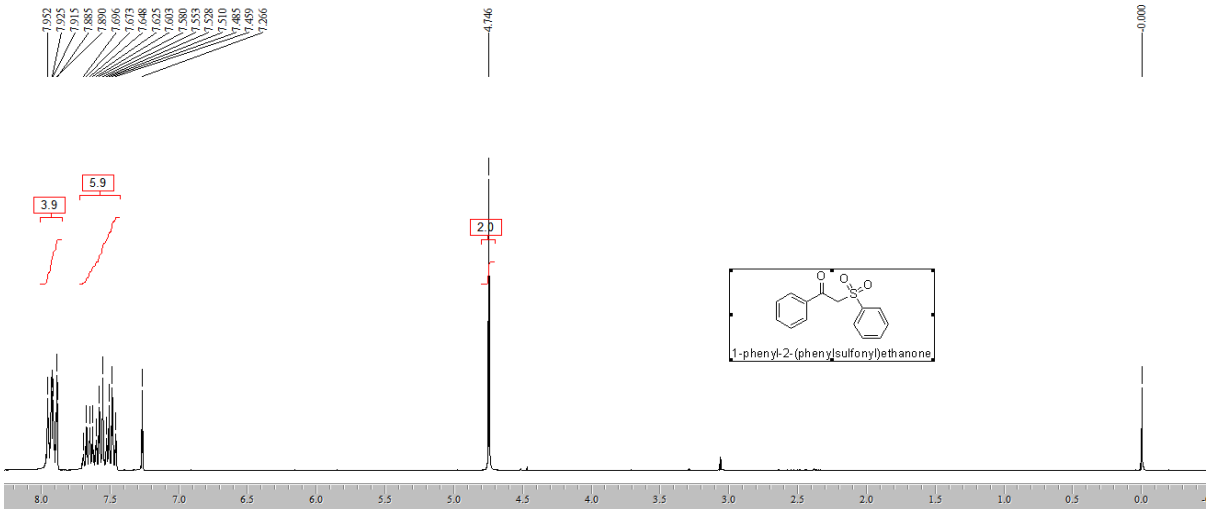
23. R. A. Henry and D. W. Moore, *J. Org. Chem.* 1967, **32**, 4145.

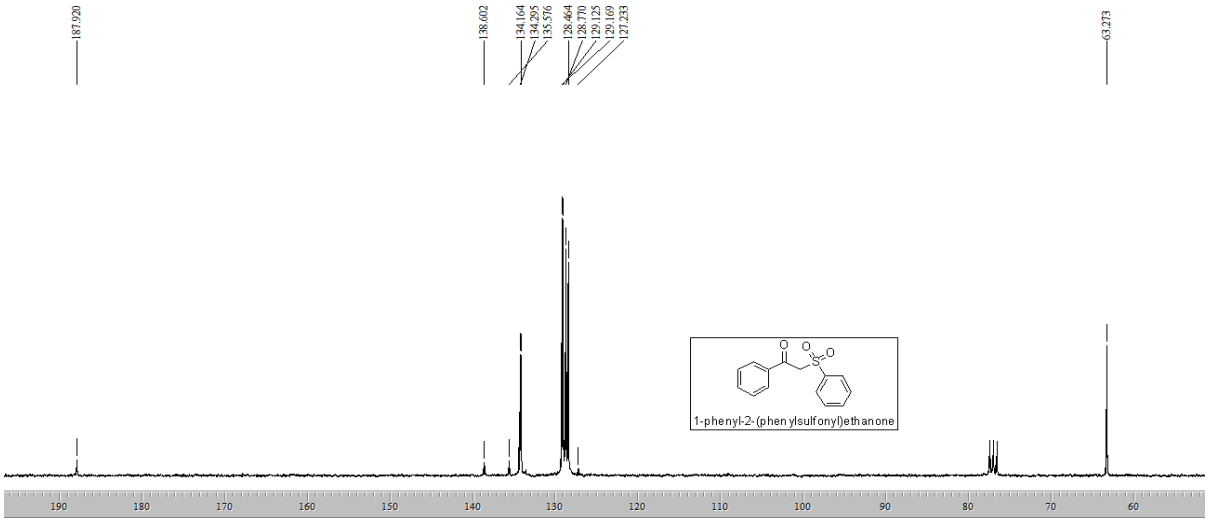
1. 1-Phenyl-2-tosylethanone (3a):



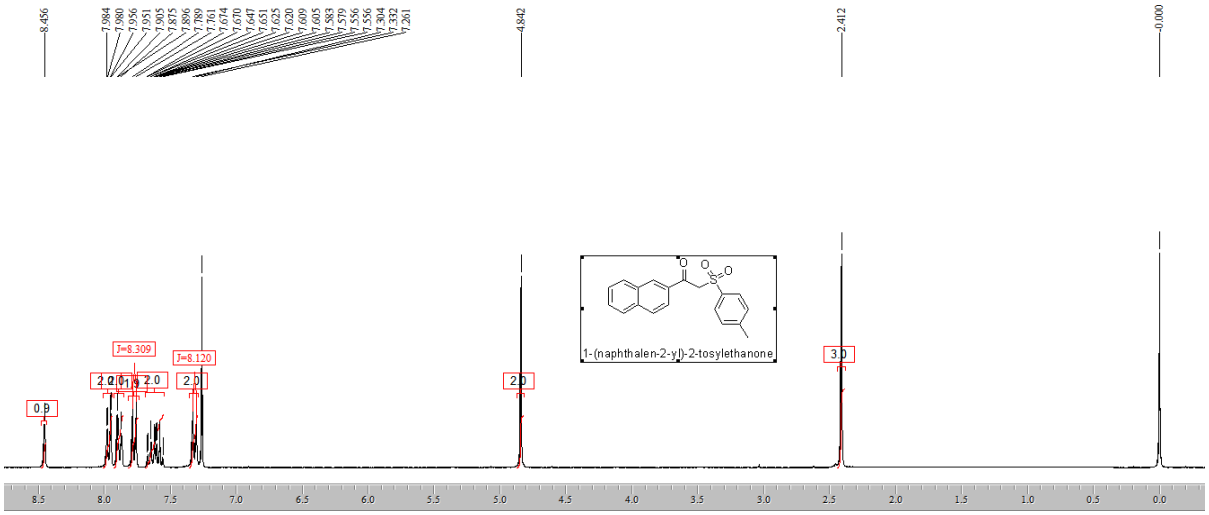


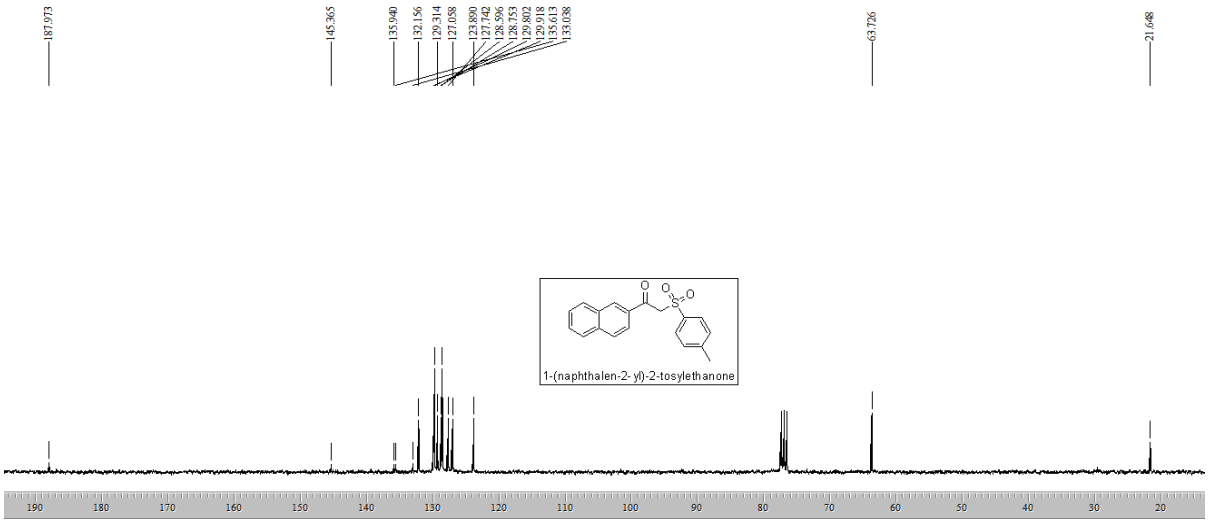
2. 1-Phenyl-2-(phenylsulfonyl)ethanone (3b):



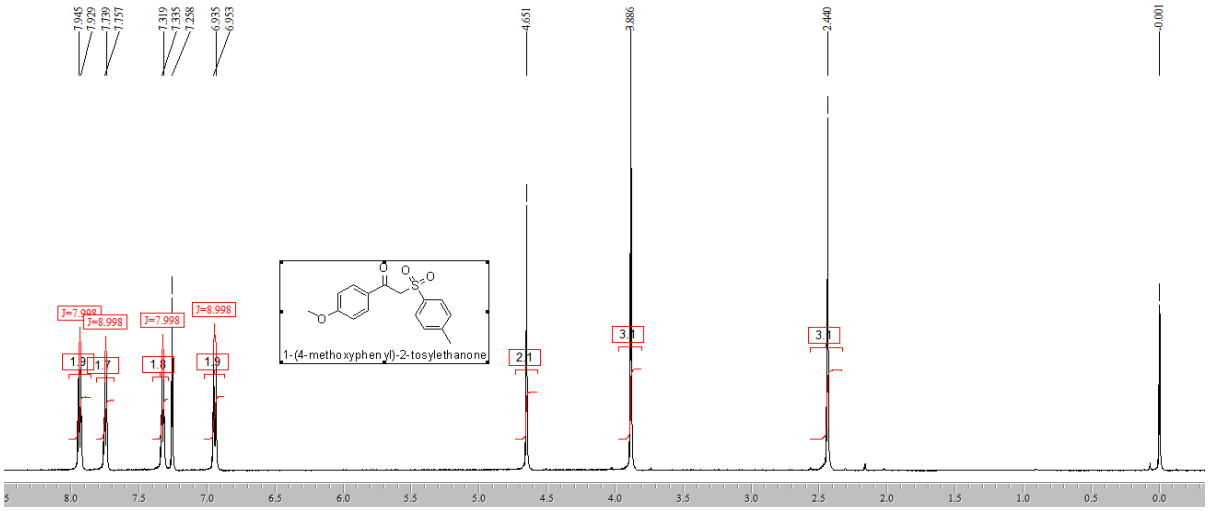


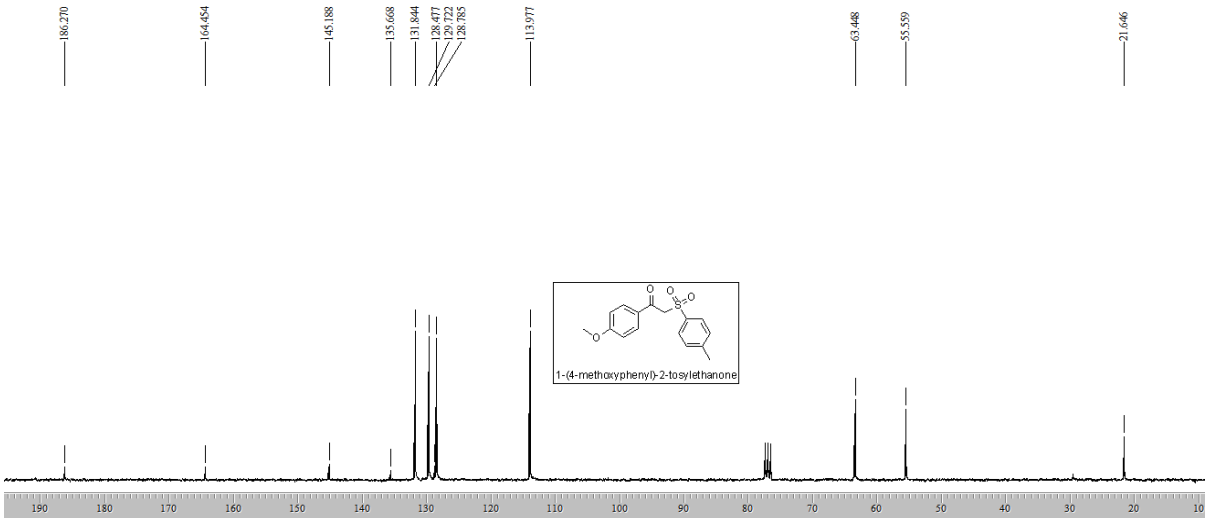
3. 1-(Naphthalen-2-yl)-2-tosylethanone (3c):



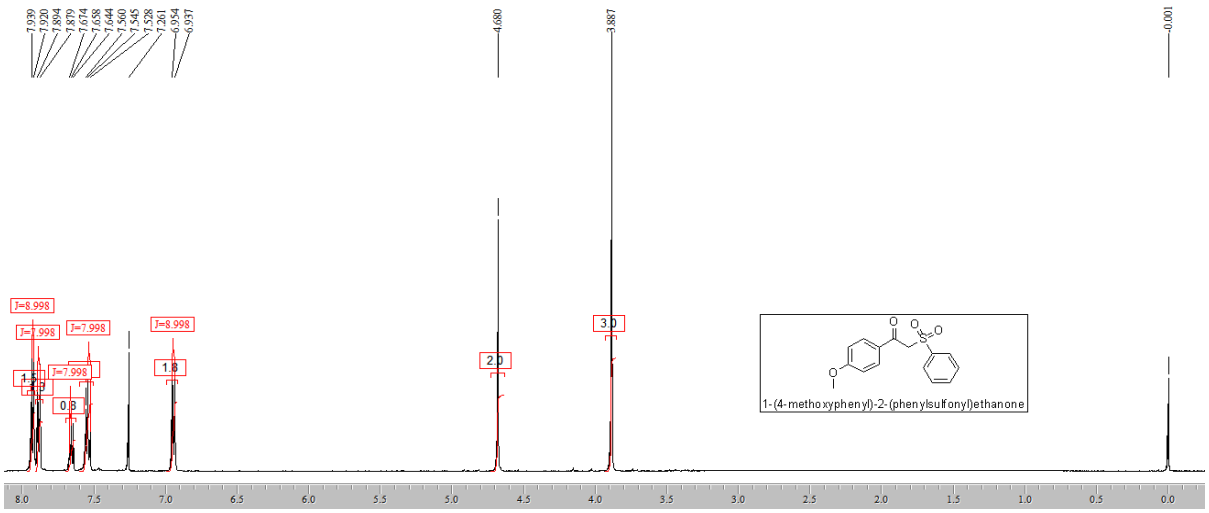


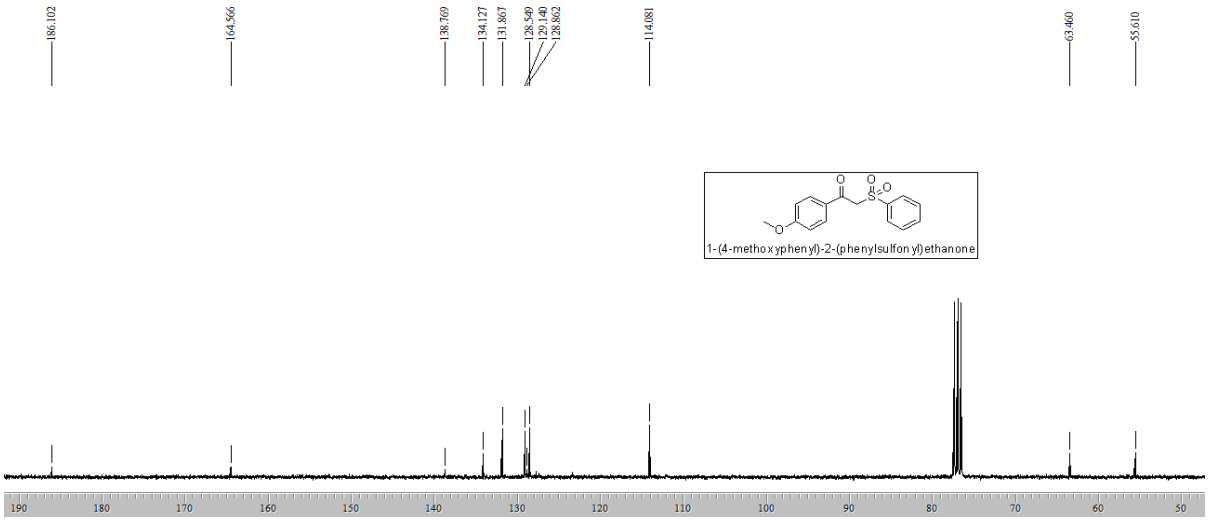
4. 1-(4-Methoxyphenyl)-2-tosylethanone (3d):



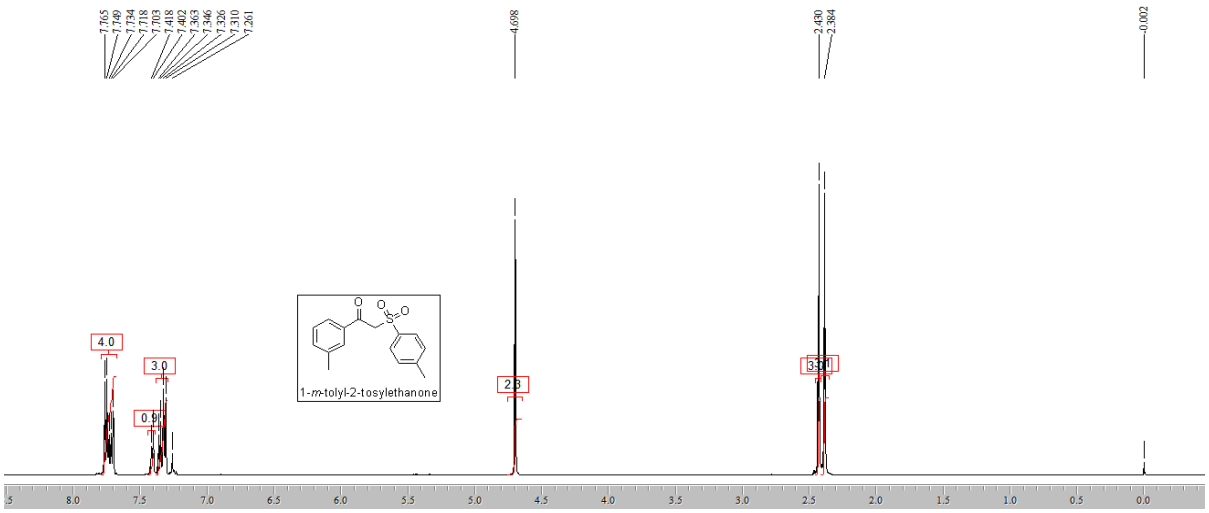


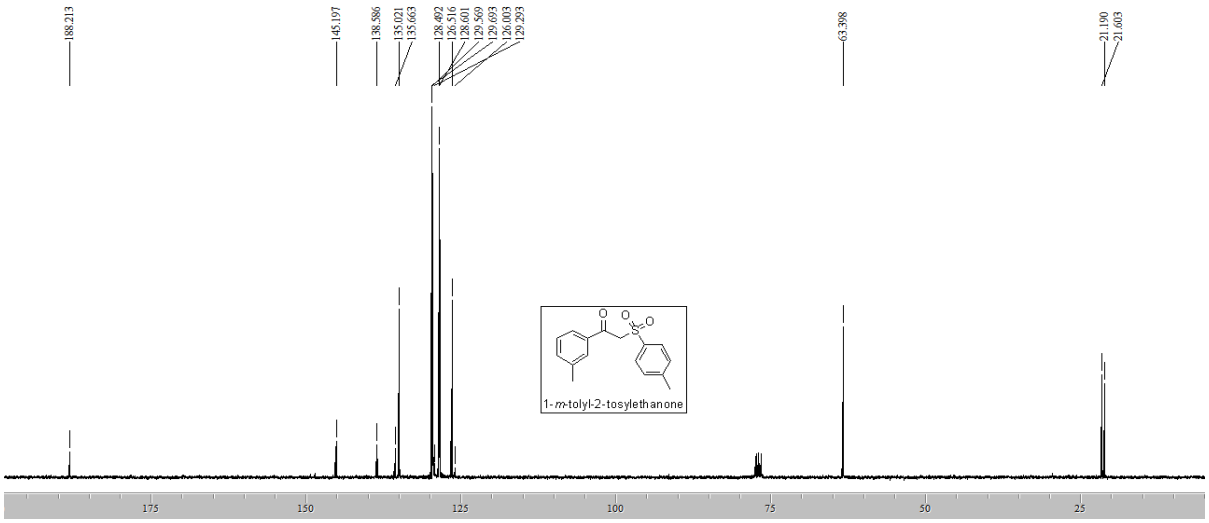
5. 1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (3e):



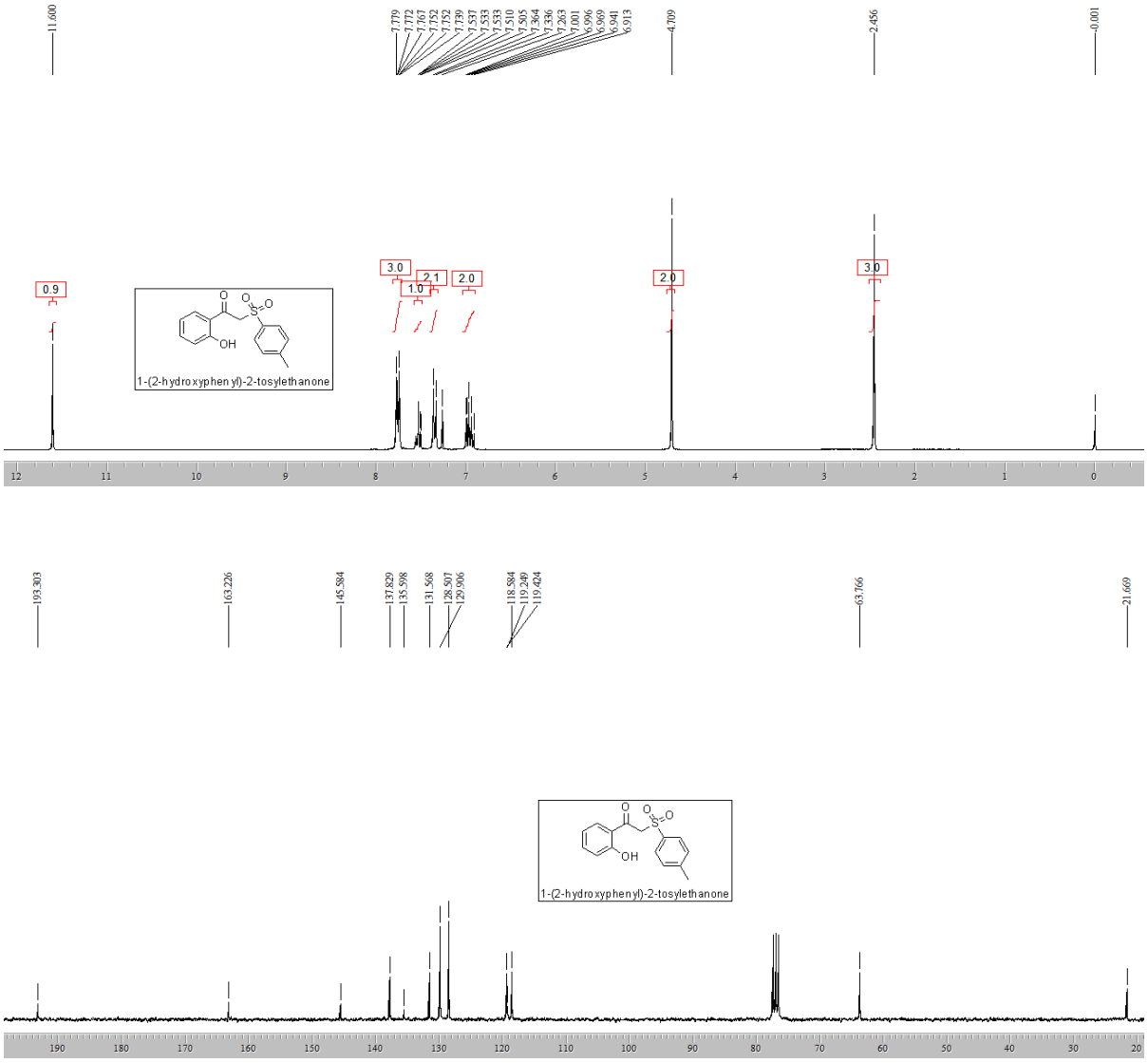


6. 1-m-Tolyl-2-tosylethanone (3f):

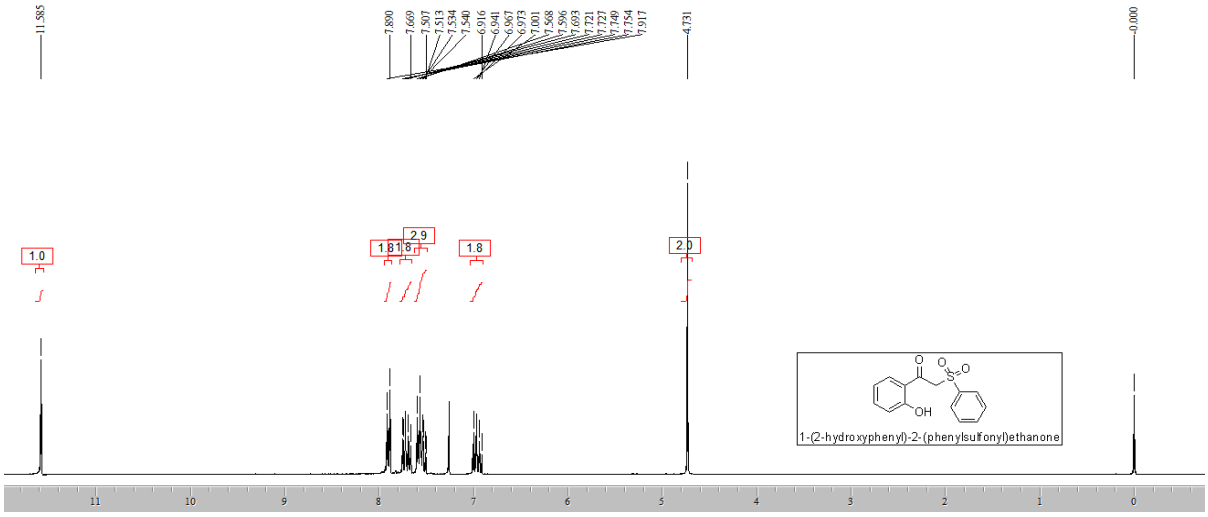


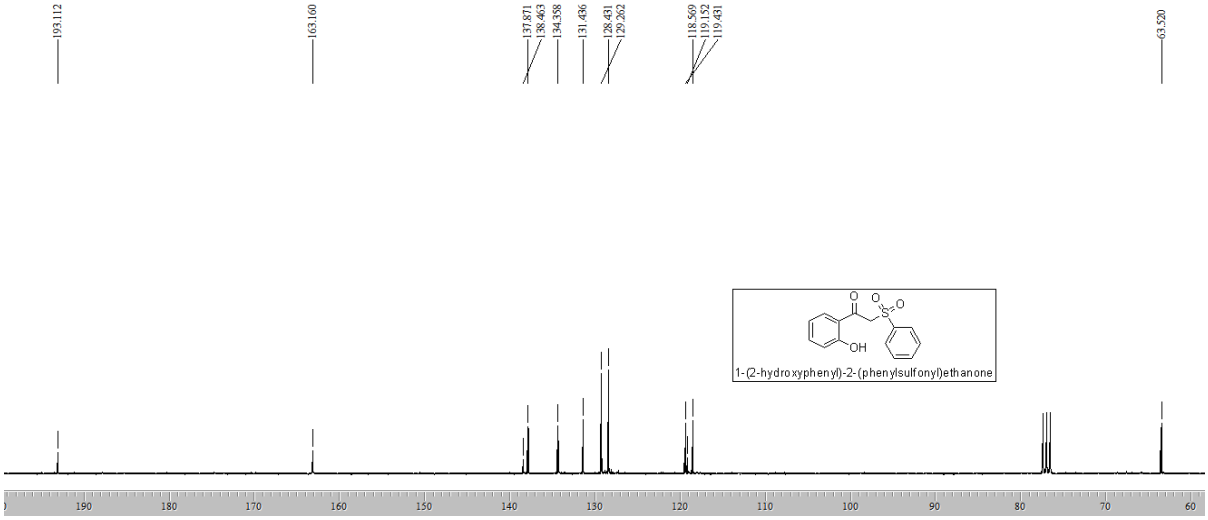


7. 1-(2-Hydroxyphenyl)-2-tosylethanone (3g):

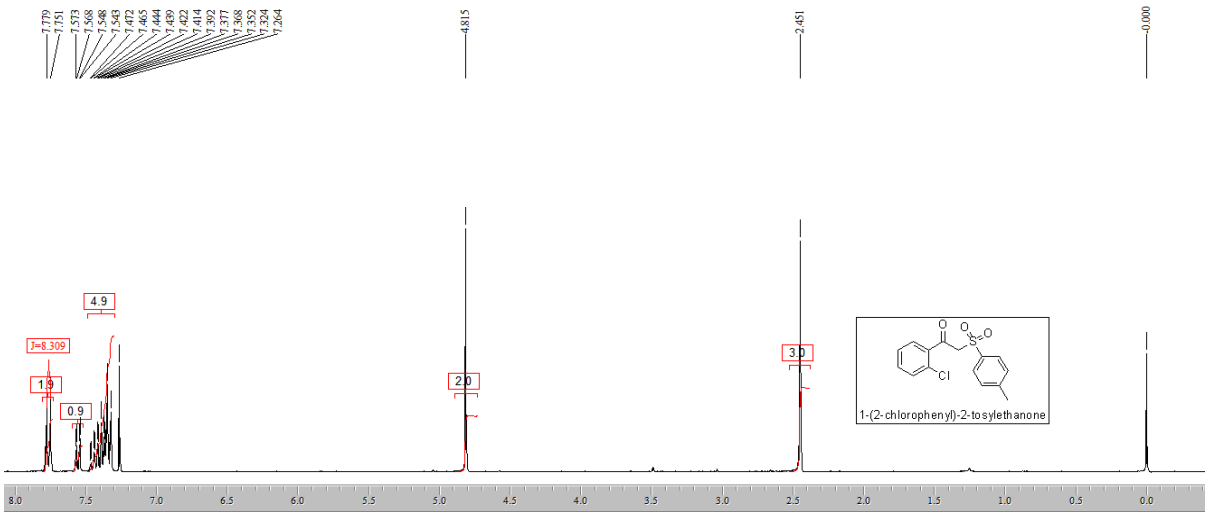


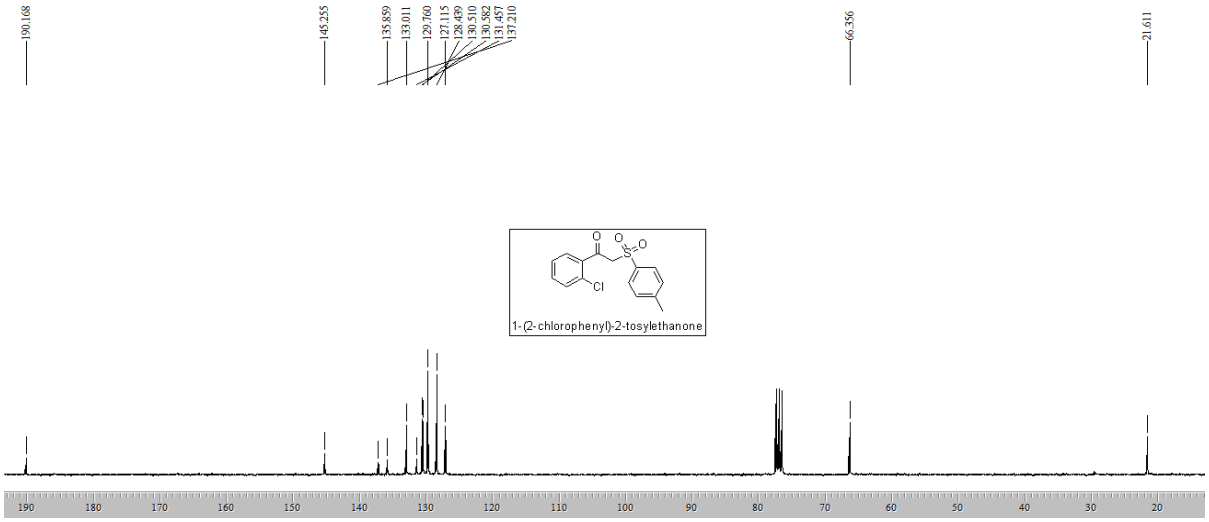
8. 1-(2-Hydroxyphenyl)-2-(phenylsulfonyl)ethanone (3h):



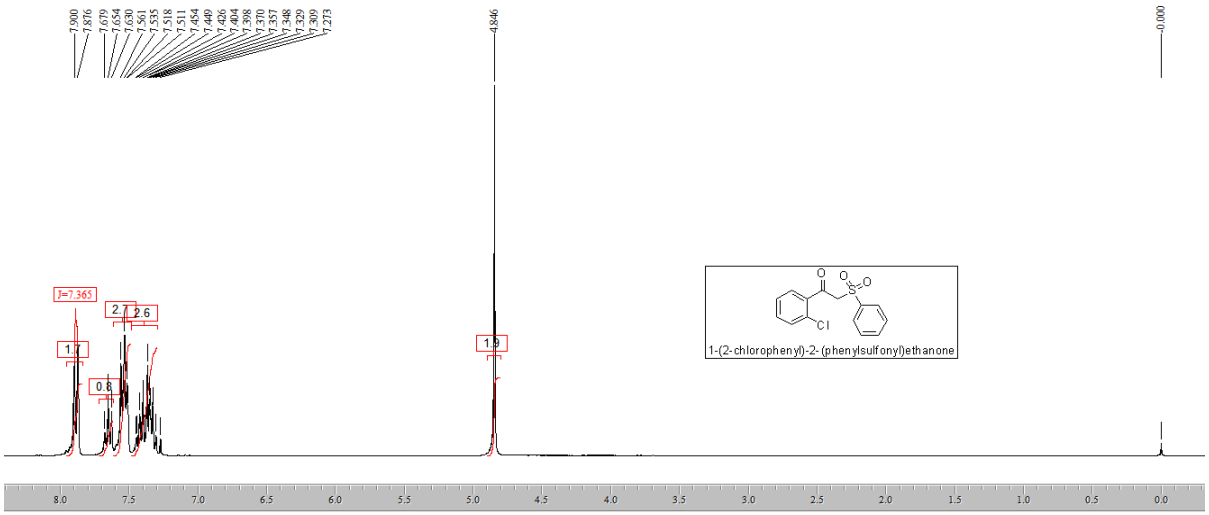


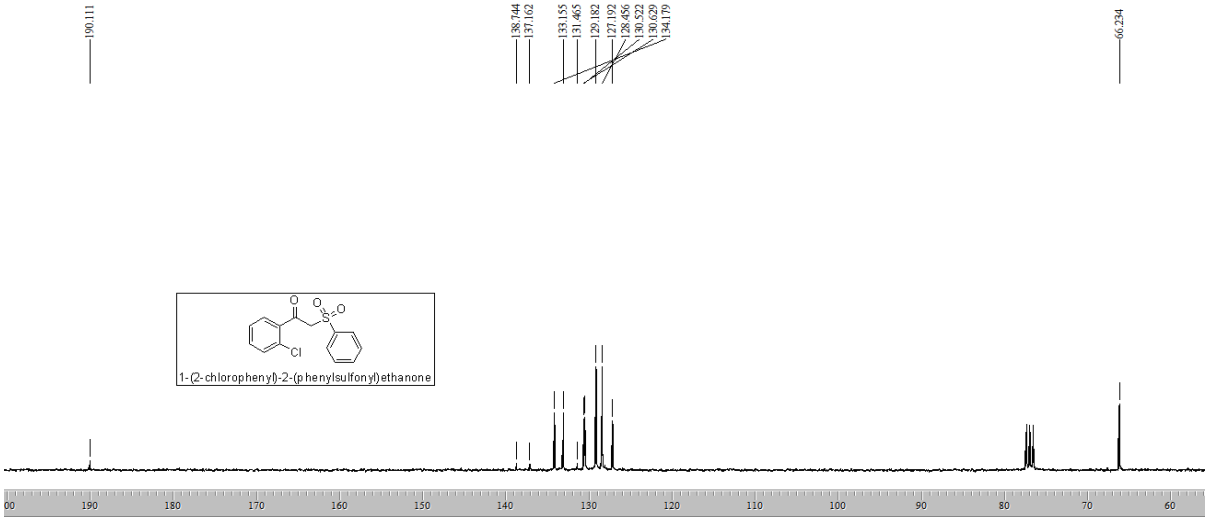
9. 1-(2-Chlorophenyl)-2-tosylethanone (3i):



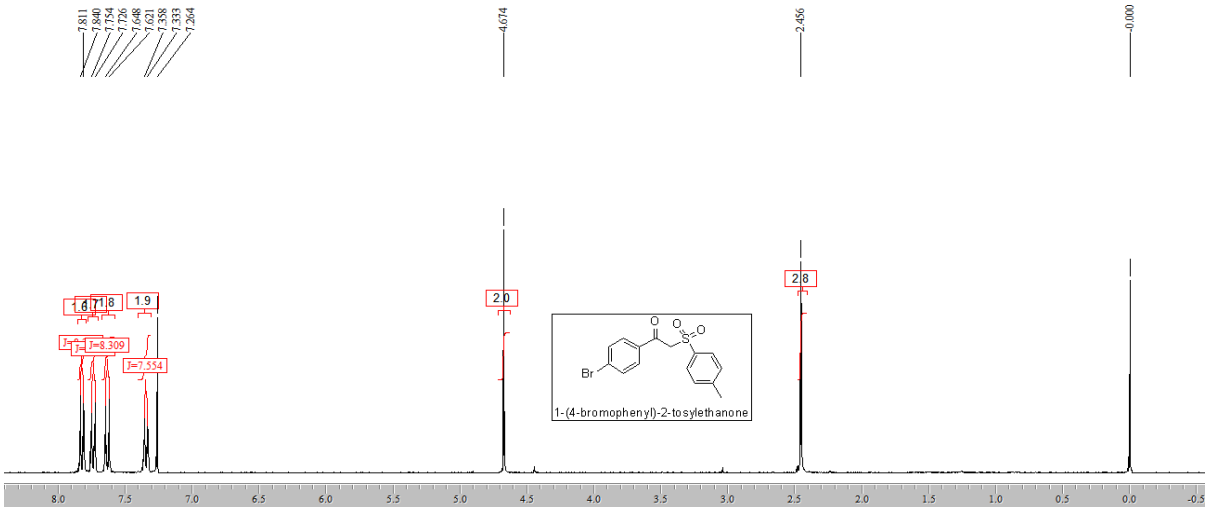


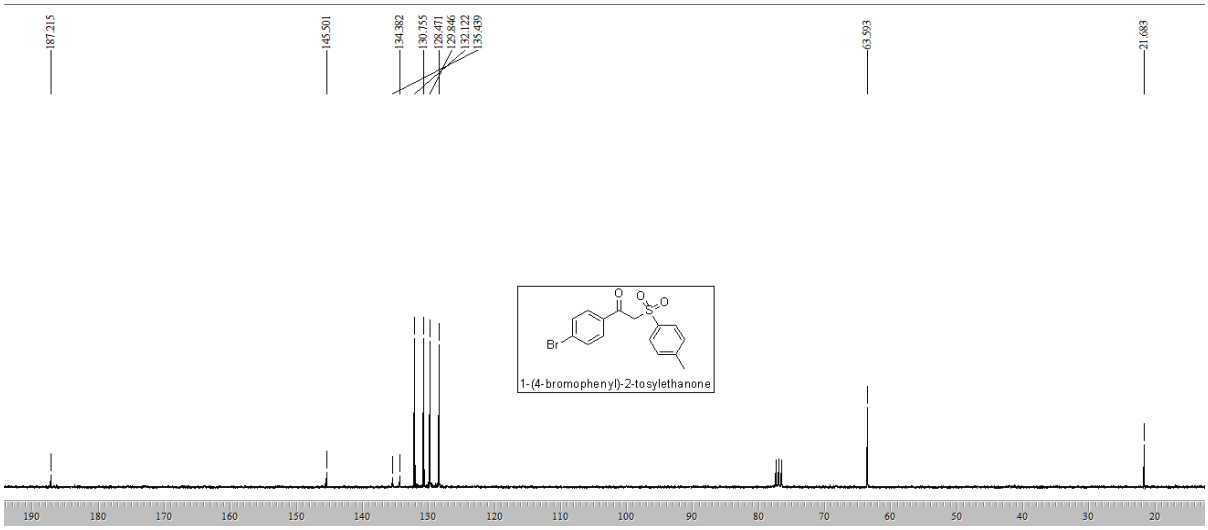
10. 1-(2-Chlorophenyl)-2-(phenylsulfonyl)ethanone (3j):



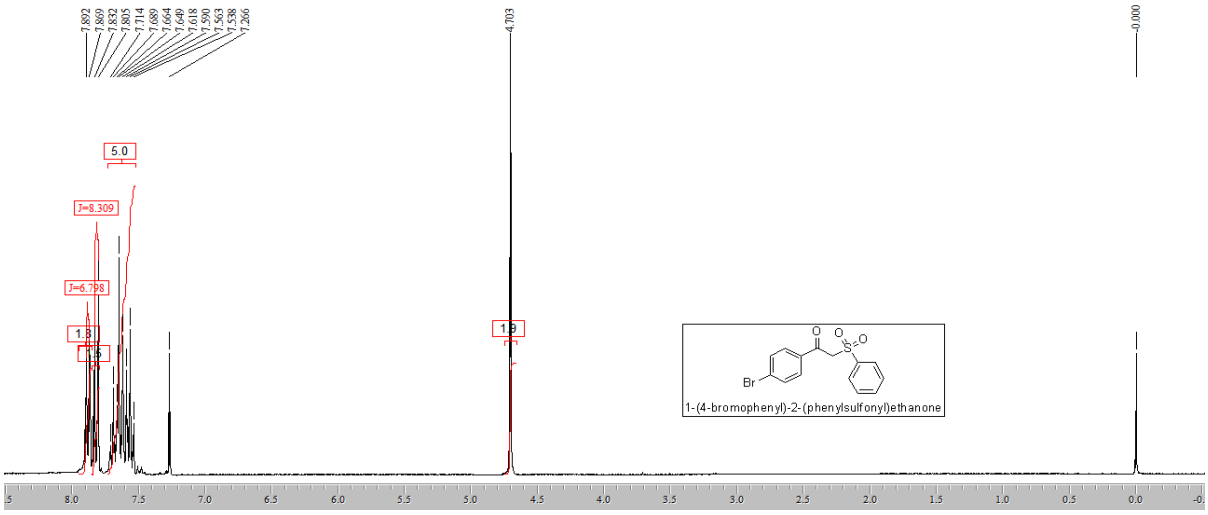


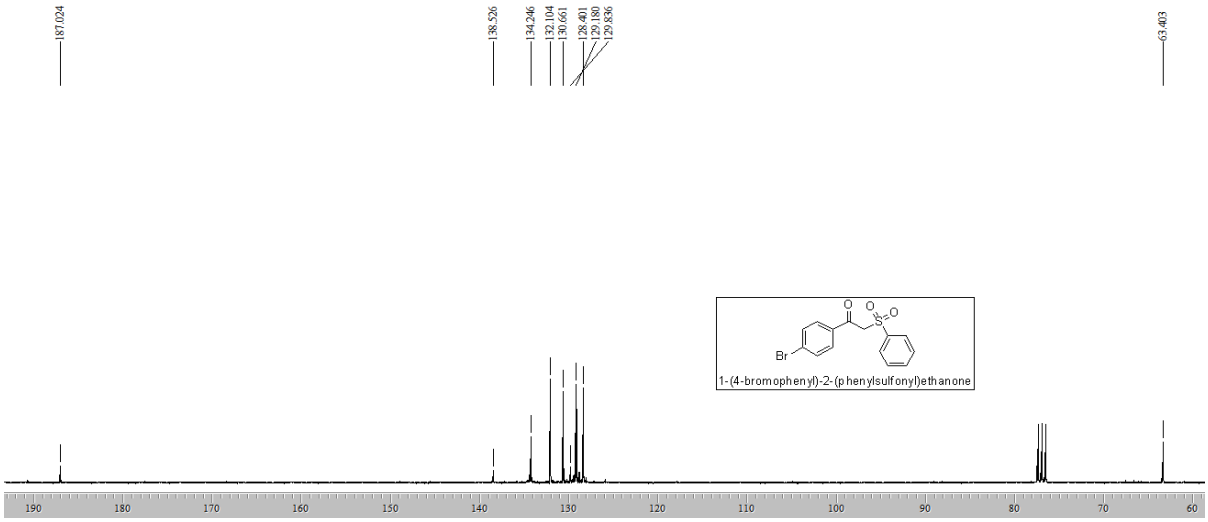
11. 1-(4-Bromophenyl)-2-tosylethanone (3k):



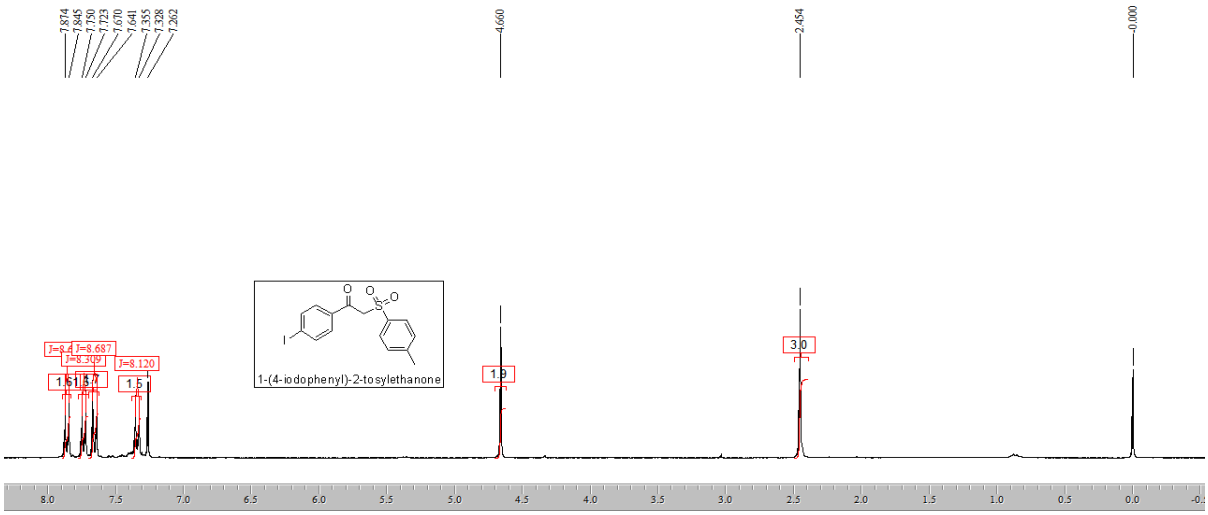


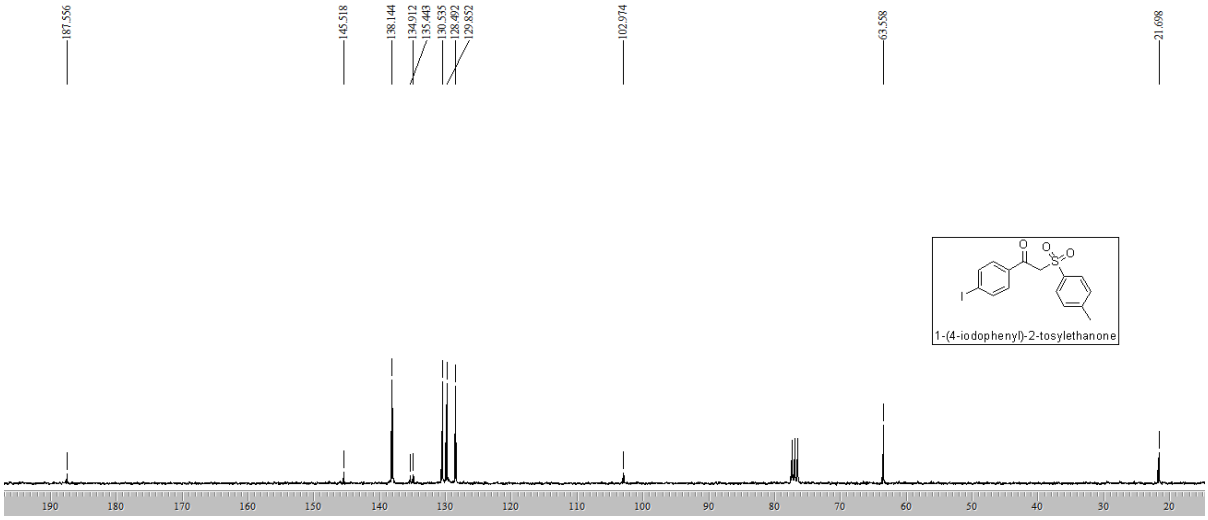
12. 1-(4-Bromophenyl)-2-(phenylsulfonyl)ethanone (3l):



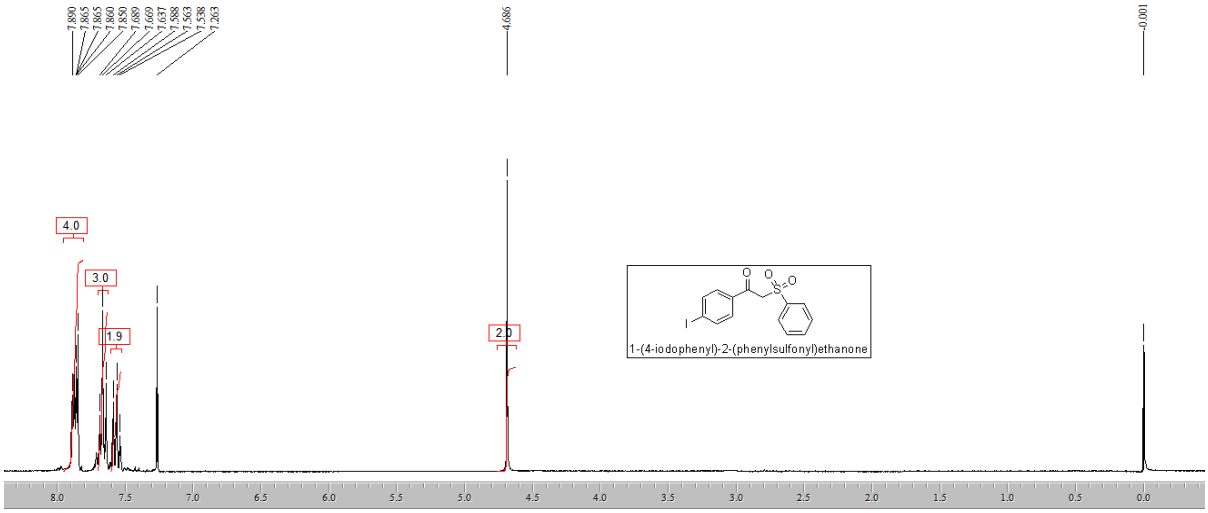


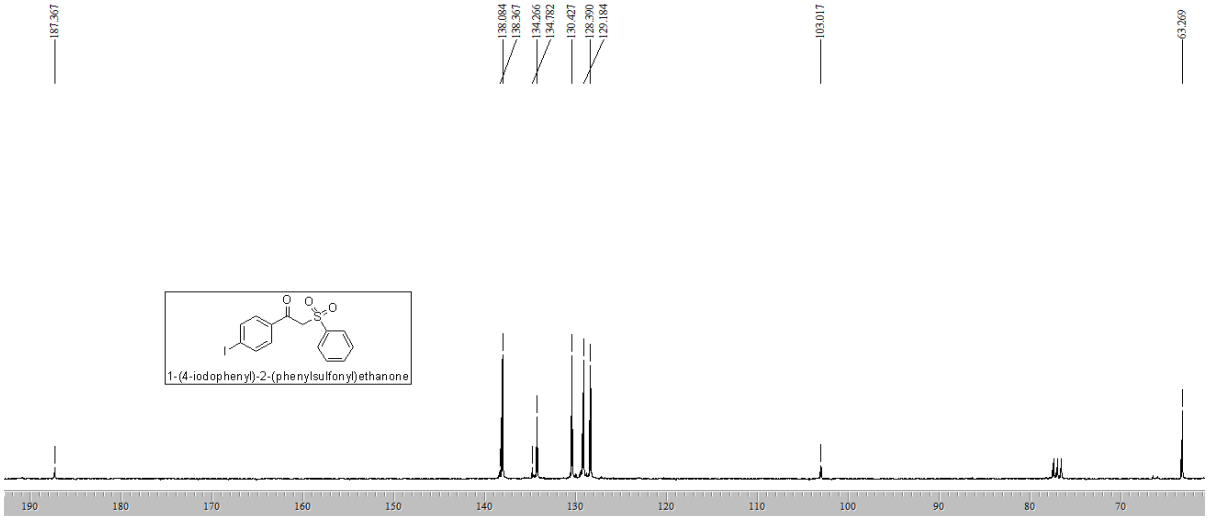
13. 1-(4-Iodophenyl)-2-tosylethanone (3m):



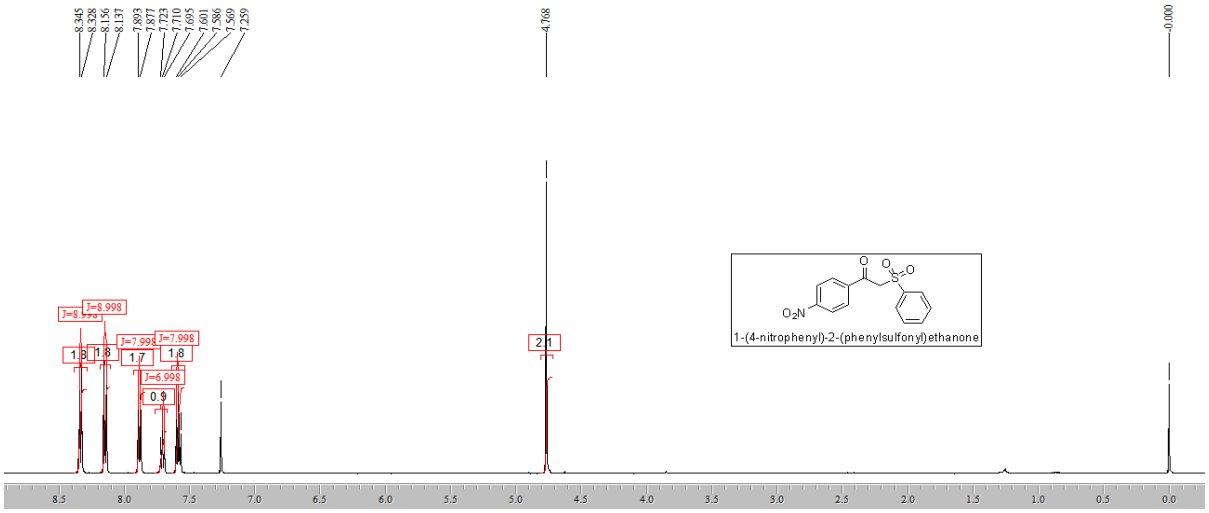


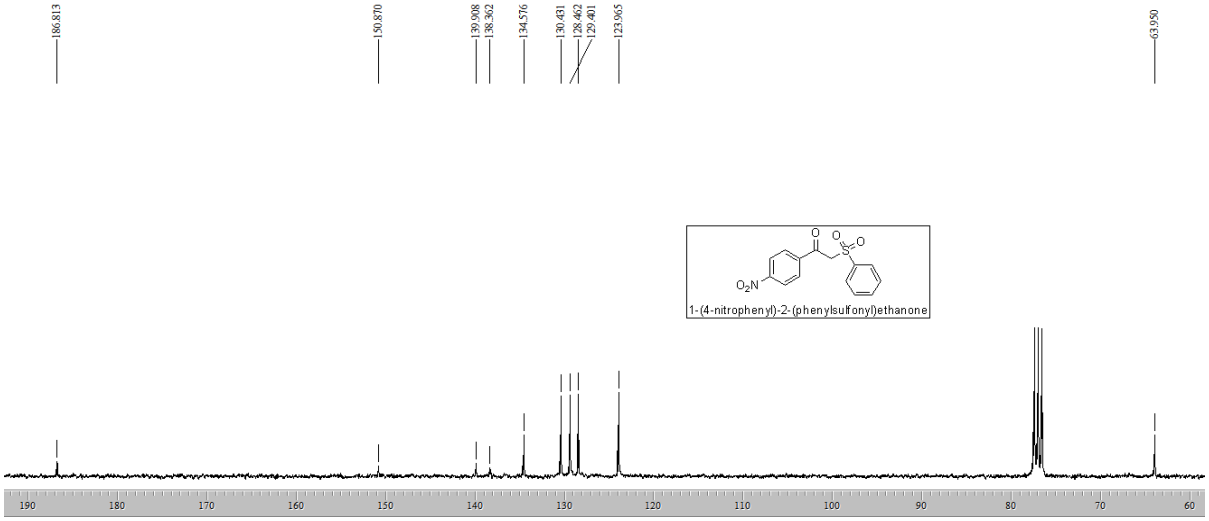
14. 1-(4-Iodophenyl)-2-(phenylsulfonyl)ethanone (3n):



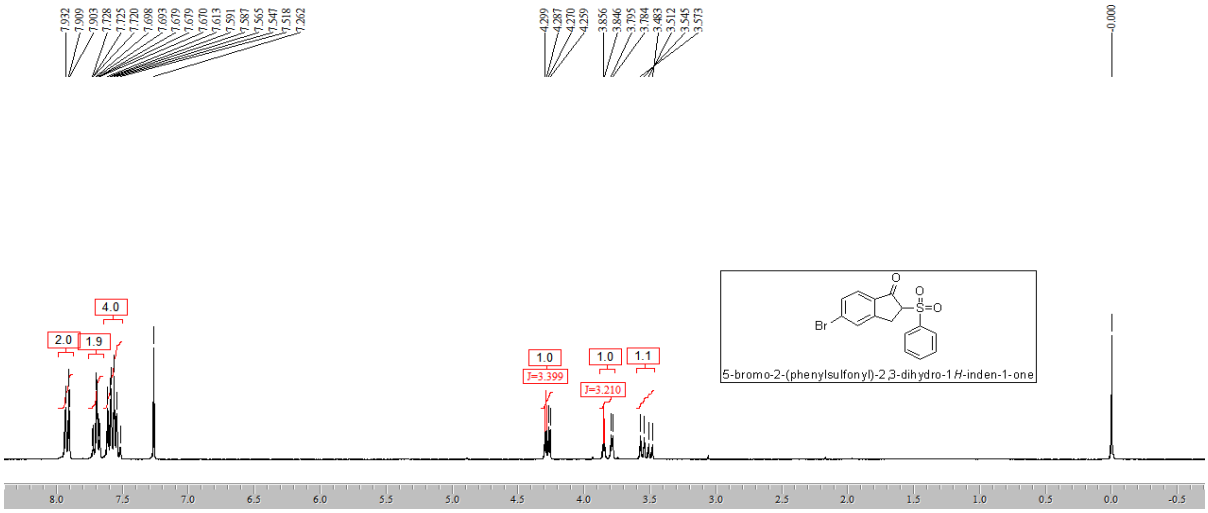


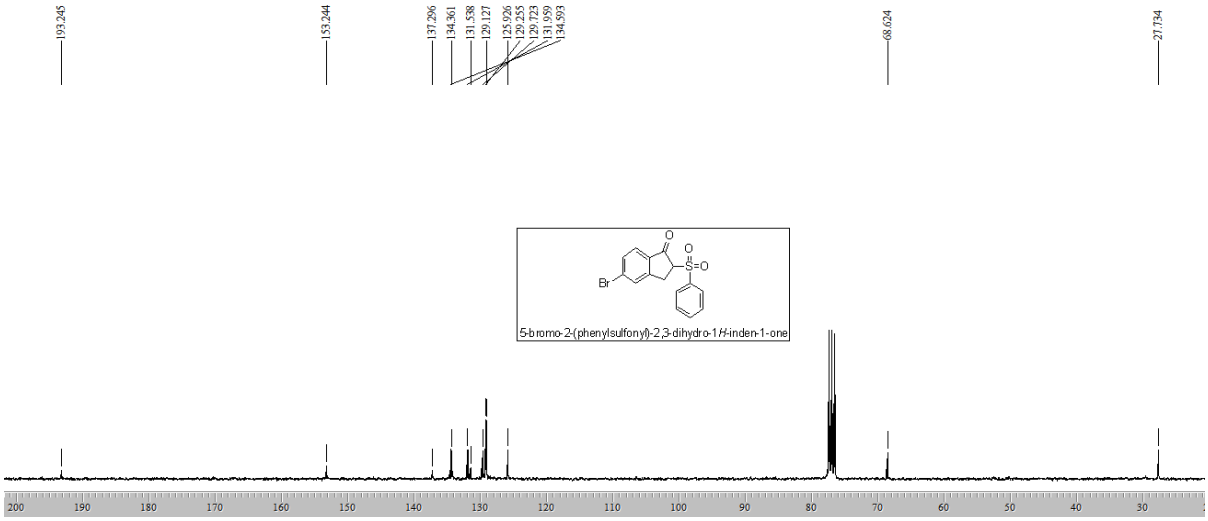
15. 1-(4-Nitrophenyl)-2-(phenylsulfonyl)ethanone (3o):



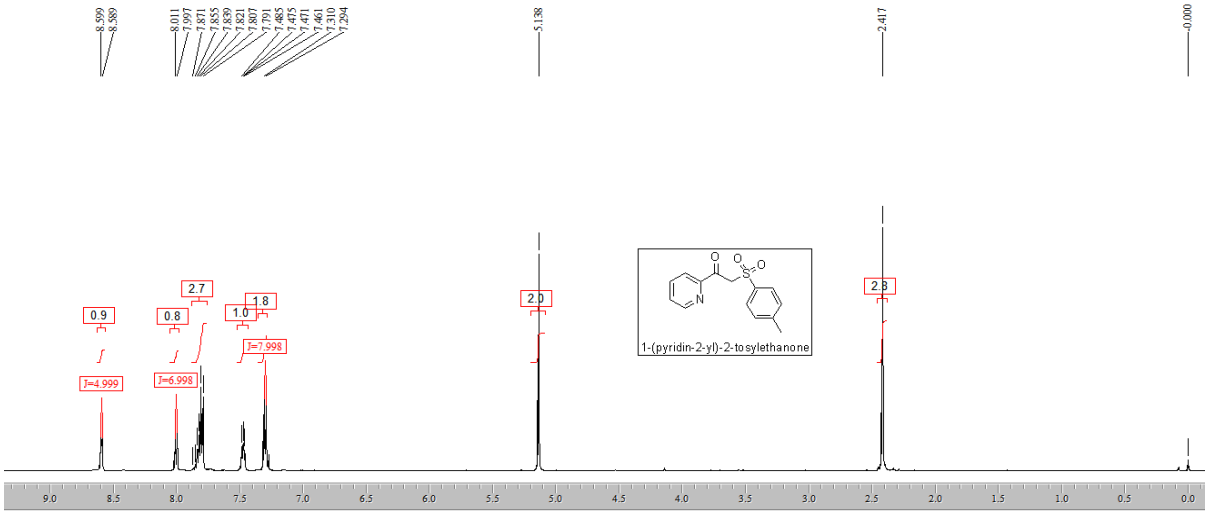


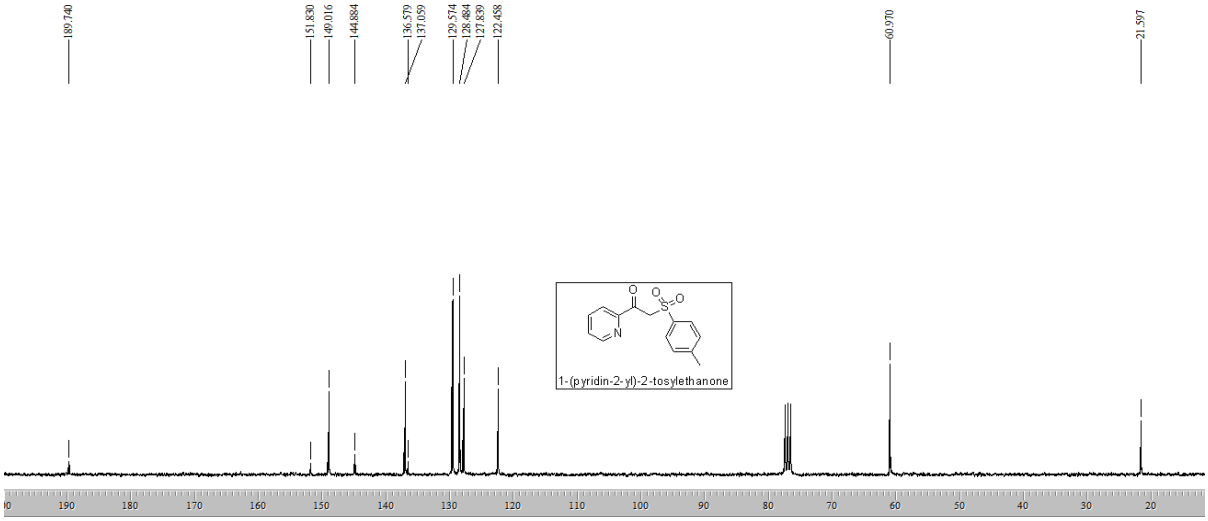
16. 5-Bromo-2-(phenylsulfonyl)-2,3-dihydro-1H-inden-1-one (3p):



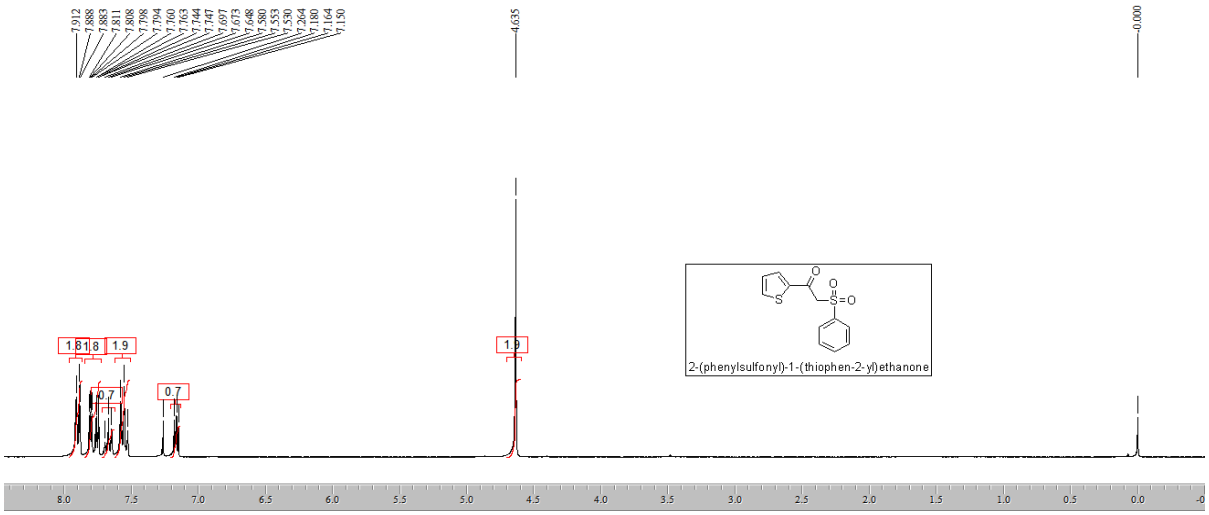


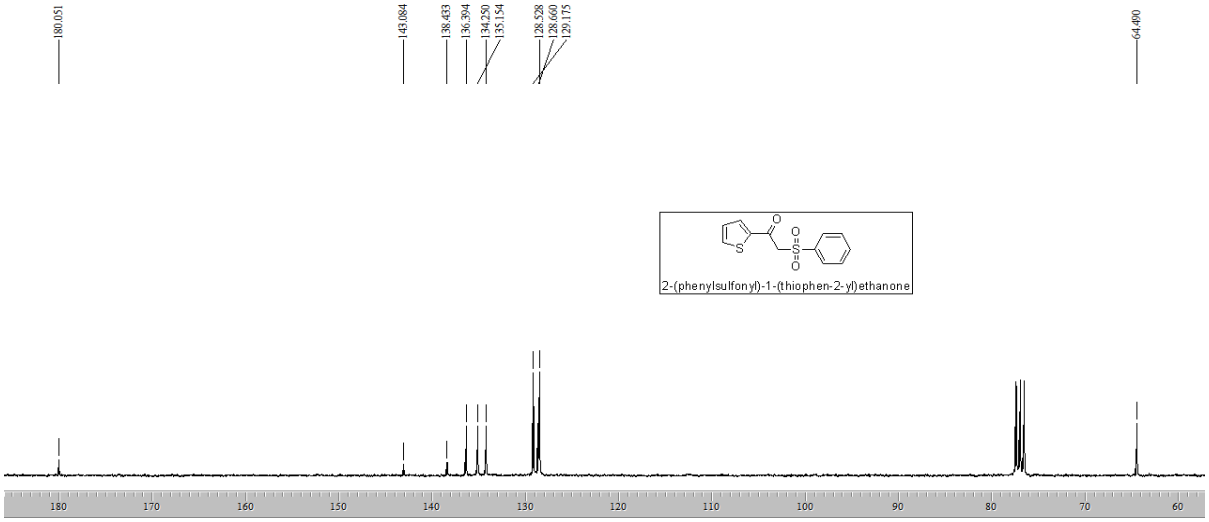
17. 1-(Pyridin-2-yl)-2-tosylethanone (3q):



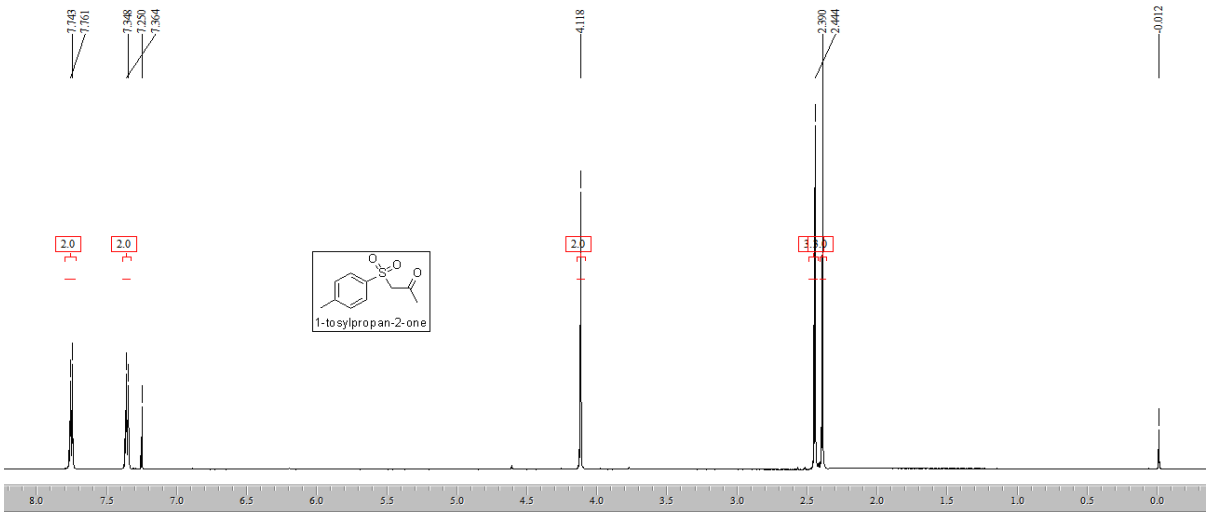


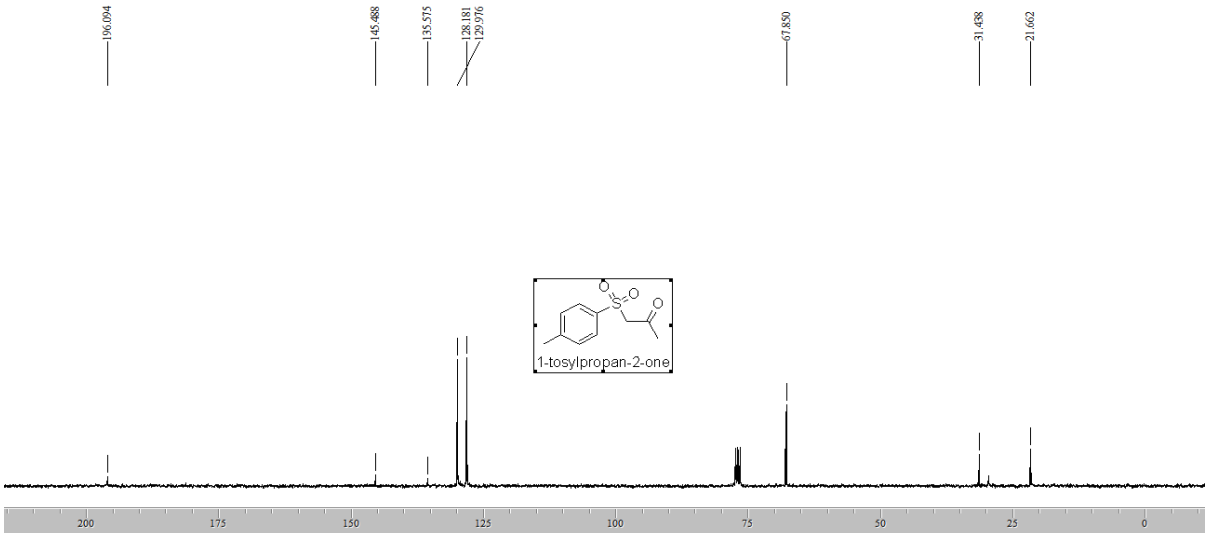
18. 2-(Phenylsulfonyl)-1-(thiophen-2-yl)ethanone (3r):



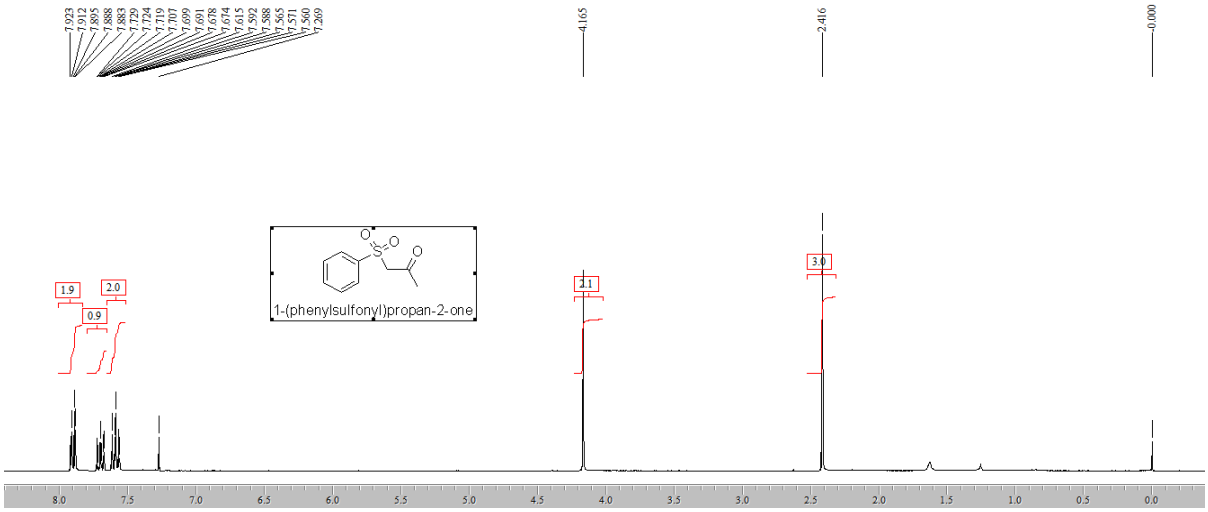


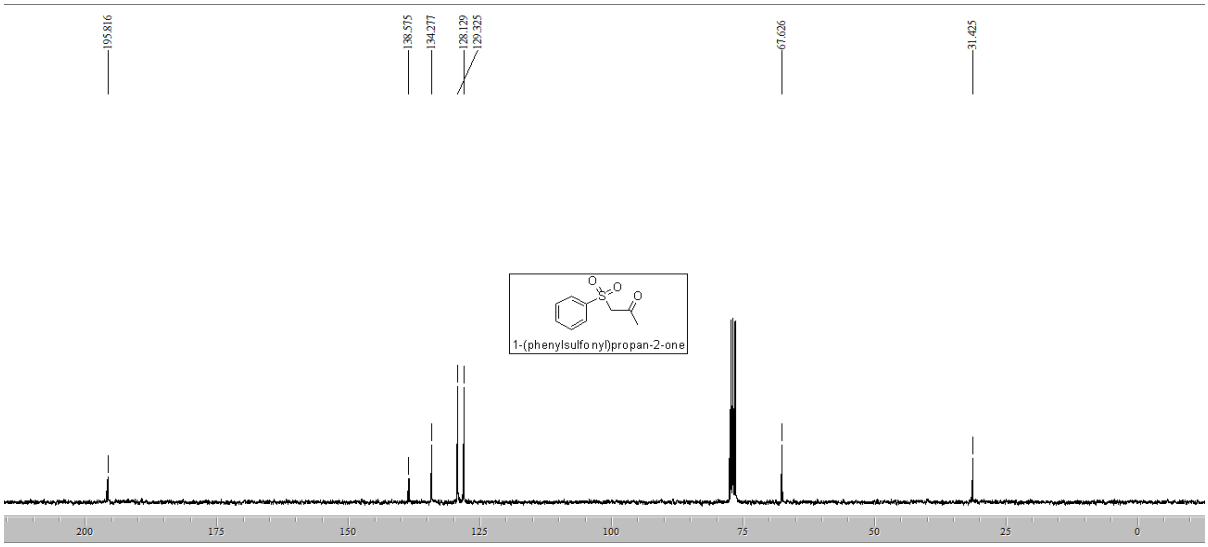
19. 1-Tosylpropan-2-one (3s):



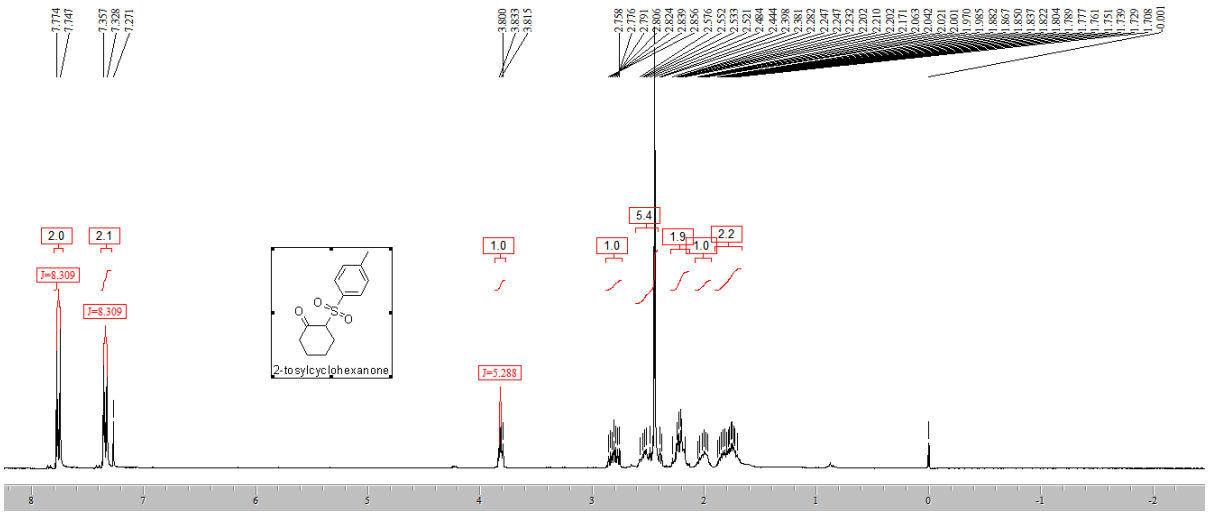


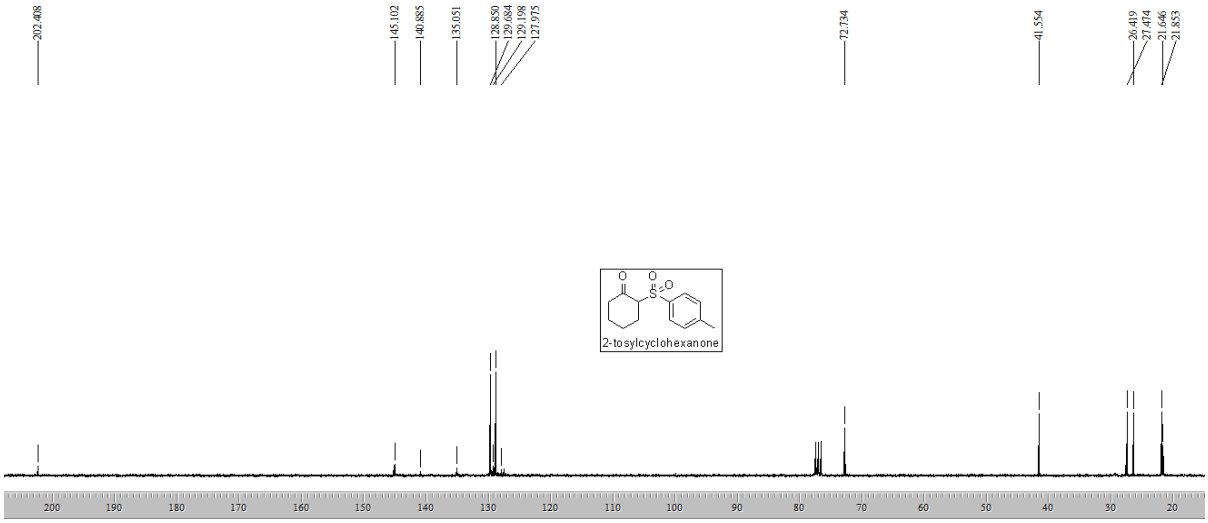
20. 1-(Phenylsulfonyl)propan-2-one (3t):



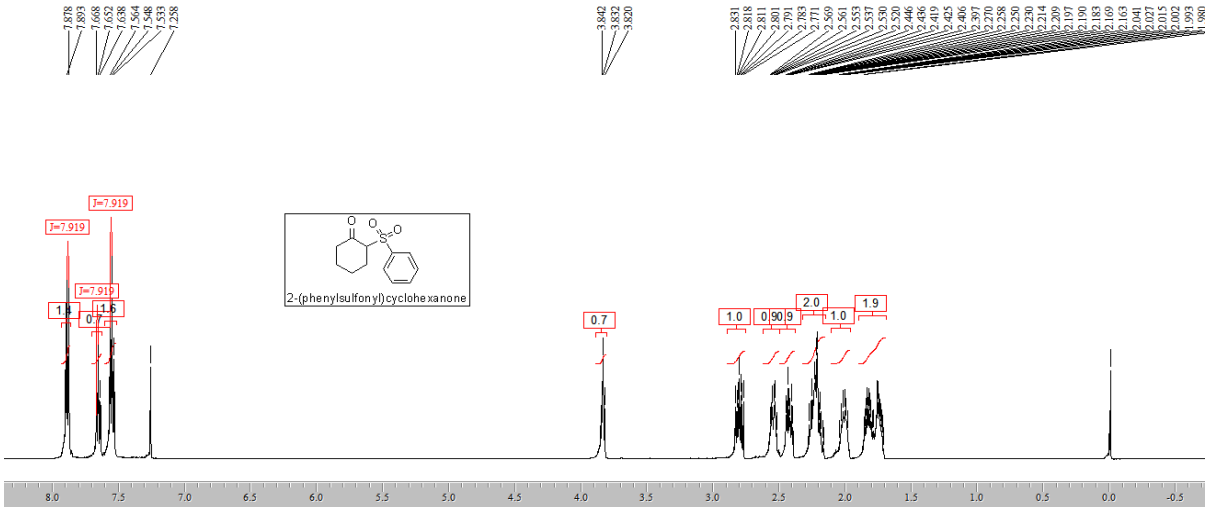


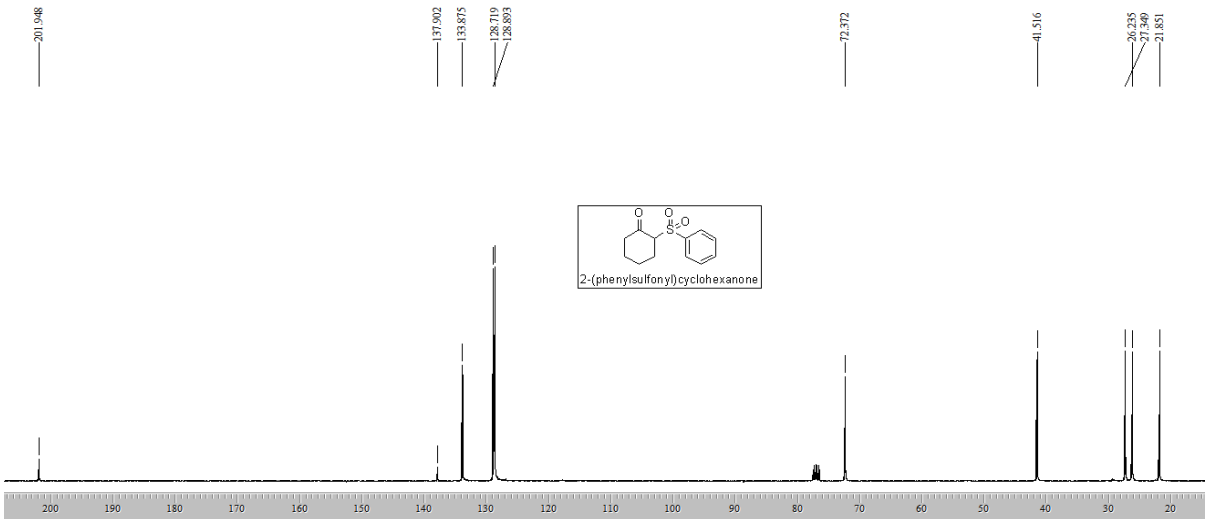
21. 2-Tosylcyclohexanone (3u):



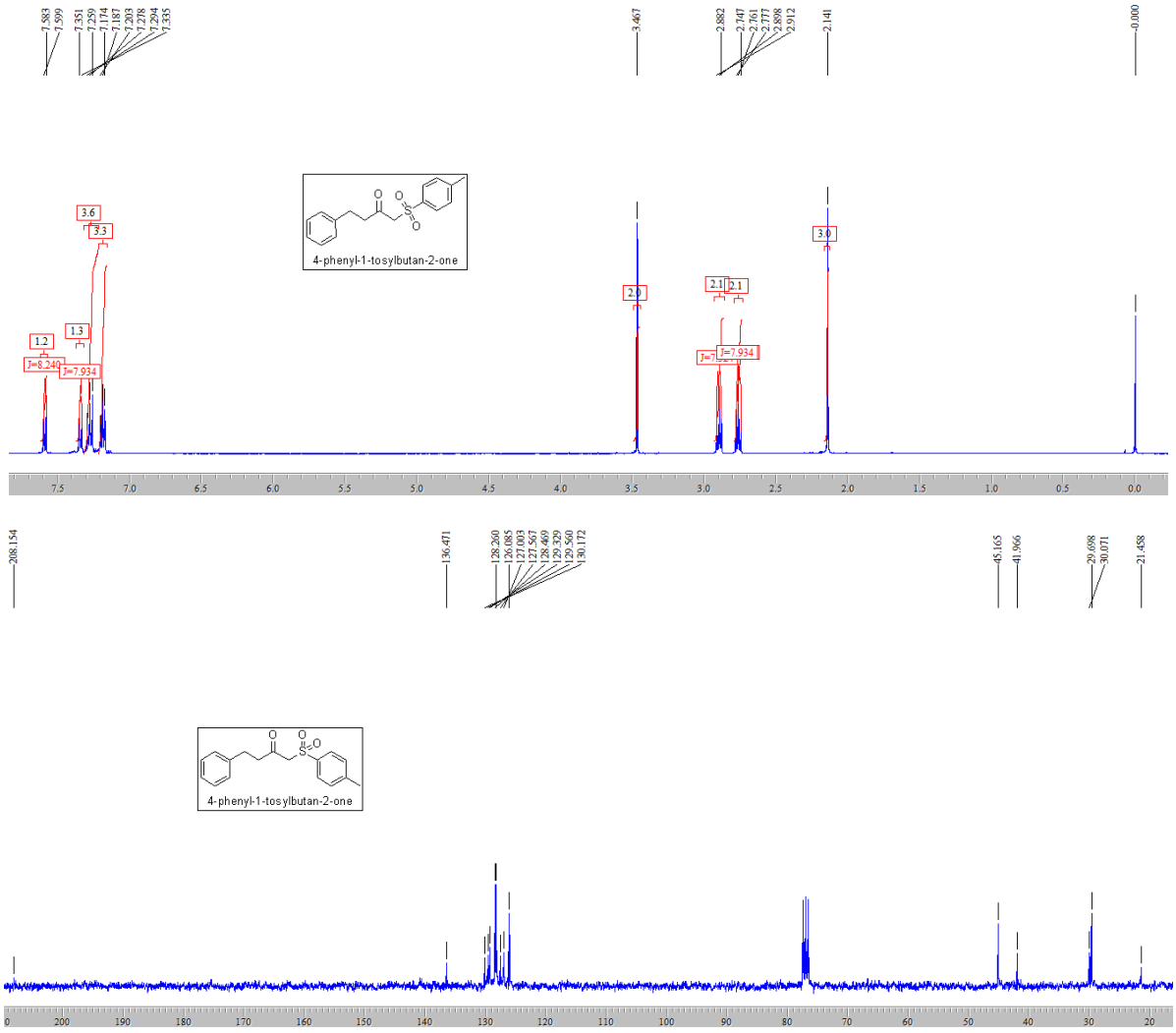


22. 2-(Phenylsulfonyl)cyclohexanone (3v):





23. 4-Phenyl-1-tosylbutan-2-one (3w):



24. 1-Phenyl-1-tosylpropan-2-one (3x):