

Photosensitizer-Free Synthesis of β -Keto Sulfones via Visible-Light-Induced Oxysulfonylation of Alkenes with Sulfonic Acids

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Table of Content

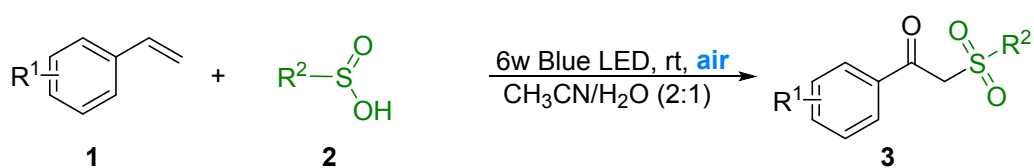
1. General information	S2
2. Experimental Section	S2
3. Characterization data of products	S3
4. References	S10
5. ¹H and ¹³C NMR spectra of products	S11

1. General information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification. All reagents were weighed and handled in air at room temperature. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference (^1H NMR: CDCl_3 7.26 ppm, ^{13}C NMR: CDCl_3 77.0 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. Mass spectra were performed on a spectrometer operating on ESI-TOF. There is about 2.0 cm distance between the reactor and LEDs.

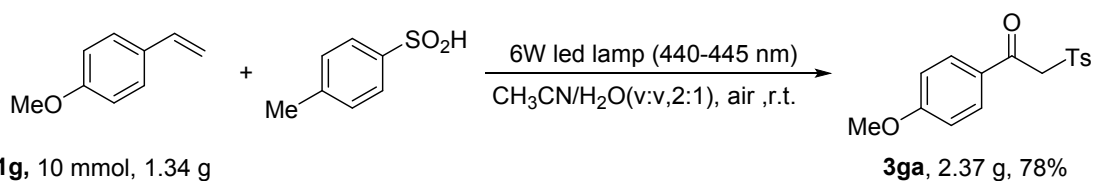
2. Experimental Section

General procedure for the preparation of β -Keto Sulfones



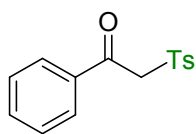
In a mixed solvent of CH_3CN and H_2O (1.8 mL, $V_{\text{CH}_3\text{CN}}:V_{\text{H}_2\text{O}} = 2:1$) was added alkenes **1** (0.3 mmol) and sulfonic Acids **2** (0.6 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 6W blue LED lamps (440 – 445 nm) for 12 – 24 h. the reaction was monitored by TLC. After completion of the reaction, the resulting mixture was extracted with EtOAc (5 mL \times 3) and the organic phase was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired products β -Keto Sulfones **3**.

Gram-scale synthesis of **3aa**

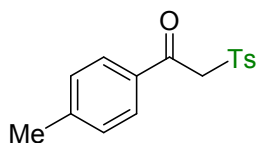


In a mixed solvent of CH_3CN and H_2O (60 mL, $V_{\text{CH}_3\text{CN}}:V_{\text{H}_2\text{O}} = 2:1$) was added 1-methoxy-4-vinylbenzene **1g** (1.34 g, 10 mmol) and 4-methylbenzenesulfonic acid (3.12 g, 20 mmol). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 6W blue LED lamps for 24h. After completion of the reaction, the resulting mixture was extracted with EtOAc (30 mL \times 3) and the organic phase was then removed under vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give 2.37 gram of **3ga**, yield 78%.

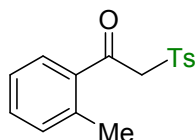
3. Characterization data of products



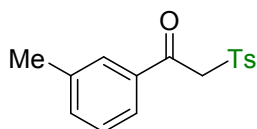
phenyl-2-tosylethan-1-one (3aa)¹: White solid; 66.6 mg (isolated yield 81%); ¹H NMR (400 MHz, CDCl₃) δ = 7.95 (d, *J* = 8.0 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 2 H), 7.62 (t, *J* = 8.0 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 2 H), 4.72 (s, 2 H), 2.44 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 188.1, 145.4, 135.7, 135.6, 134.3, 129.8, 129.3, 128.8, 128.6, 63.5, 21.7.



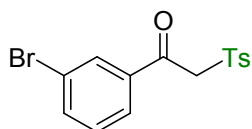
1-(p-tolyl)-2-tosylethan-1-one (3ba)²: White solid; 71.7 mg (isolated yield 83%); ¹H NMR (400 MHz, CDCl₃) δ = 7.78 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 7.26 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.8 Hz, 2 H), 4.62 (s, 2 H), 2.37 (s, 3 H), 2.35 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.6, 145.5, 135.7, 133.3, 129.8, 129.5, 129.5, 128.6, 123.8, 63.5, 21.8, 21.7.



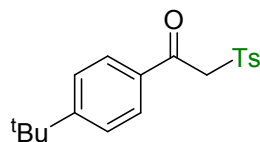
1-(o-tolyl)-2-tosylethan-1-one (3ca)³: White solid; 62.2 mg (isolated yield 72%); ¹H NMR (400 MHz, CDCl₃) δ = 7.76 – 7.72 (m, 3 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.30 – 7.24 (m, 2 H), 4.69 (s, 2 H), 2.44 (s, 3 H), 2.44 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 190.5, 145.2, 140.0, 135.9, 135.6, 132.7, 132.3, 130.4, 129.8, 128.5, 125.9, 65.5, 21.7, 21.5.



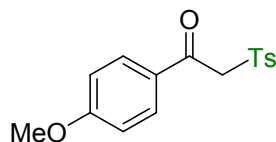
1-(m-tolyl)-2-tosylethan-1-one (3da)⁴: White solid; 65.6 mg (isolated yield 76%); ¹H NMR (400 MHz, CDCl₃) δ = 7.77 – 7.71 (m, 4 H), 7.42 (d, *J* = 7.6 Hz, 1 H), 7.38 – 7.32 (m, 3 H), 4.70 (s, 2 H), 2.44 (s, 3 H), 2.39 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 188.3, 145.3, 138.7, 135.7, 135.7, 135.1, 129.8, 129.7, 128.7, 128.6, 126.6, 63.5, 21.7, 21.3.



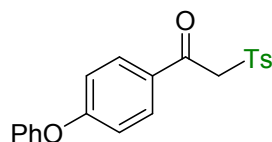
1-(3-bromophenyl)-2-tosylethan-1-one (3ea)³: White solid; 88.7 mg (isolated yield 84%); ¹H NMR (400 MHz, CDCl₃) δ = 8.00 – 7.98 (m, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.75 – 7.72 (m, 3 H), 7.39 – 7.33 (m, 3 H), 4.68 (s, 2 H), 2.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.0, 145.6, 137.3, 137.1, 135.4, 132.0, 130.4, 129.9, 128.5, 128.0, 123.1, 63.6, 21.7.



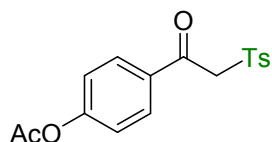
1-(4-(tert-butyl)phenyl)-2-tosylethan-1-one (3fa)⁵: White solid; 79.2 mg (isolated yield 80%); ¹H NMR (400 MHz, CDCl₃) δ = 7.88 (d, *J* = 8.4 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 4.69 (s, 2 H), 2.44 (s, 3 H), 1.33 (s, 9 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.6, 158.3, 145.2, 135.7, 133.2, 129.8, 129.3, 128.6, 125.8, 63.5, 35.2, 30.9, 21.7.



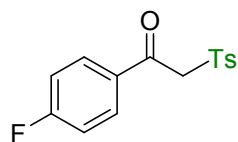
1-(4-methoxyphenyl)-2-tosylethan-1-one (3ga)¹: White solid; 73.9 mg (isolated yield 81%); ¹H NMR (400 MHz, CDCl₃) δ = 7.94 (d, *J* = 8.8 Hz, 2 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 4.66 (s, 2 H), 3.89 (s, 3 H), 2.44 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 186.3, 164.5, 145.3, 135.7, 131.9, 129.8, 128.8, 128.6, 114.0, 63.5, 55.6, 21.7.



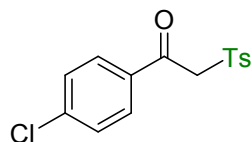
1-(4-phenoxyphenyl)-2-tosylethan-1-one (3ha): White solid; 80.1 mg (isolated yield 73%); ¹H NMR (400 MHz, CDCl₃) δ = 7.94 (d, *J* = 8.8 Hz, 2 H), 7.76 (d, *J* = 8.0 Hz, 2 H), 7.44 – 7.40 (m, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.25 – 7.22 (m, 1 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 4.67 (s, 2 H), 2.44 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 186.4, 163.2, 154.8, 145.3, 135.6, 131.9, 130.2, 130.1, 129.8, 128.5, 125.1, 120.5, 117.1, 63.5, 21.7; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₁H₁₉O₄S: 367.0999; found: 367.0993.



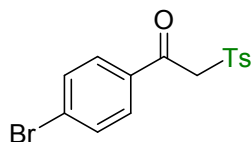
4-(2-tosylacetyl)phenyl acetate (3ia)⁶: White solid; 66.7 mg (isolated yield 67%); ¹H NMR (400 MHz, CDCl₃) δ = 7.98 (d, *J* = 8.8 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.8 Hz, 2 H), 4.69 (s, 2 H), 2.44 (s, 3 H), 2.33 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 186.9, 168.6, 155.2, 145.5, 135.5, 133.2, 131.0, 129.8, 128.5, 122.0, 63.6, 21.7, 21.1; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₇H₁₇O₅S: 333.0791; found: 333.0788.



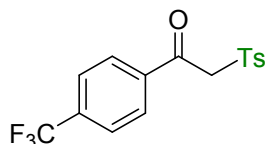
1-(4-fluorophenyl)-2-tosylethan-1-one (3ja)⁷: White solid; 70.9 mg (isolated yield 81%); ¹H NMR (400 MHz, CDCl₃) δ = 8.02 – 7.99 (m, 2 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.16 (t, *J* = 8.4 Hz, 2 H), 4.68 (s, 2 H), 2.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 186.5, 167.7, 145.5, 135.5, 132.3 (d, *J*_{C-F} = 9.5 Hz), 129.9, 128.5, 128.6, 116.1 (d, *J*_{C-F} = 20.5 Hz), 63.7, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ = -102.4.



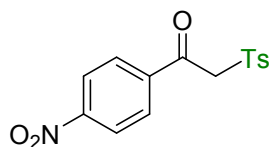
1-(4-chlorophenyl)-2-tosylethan-1-one (3ka)⁸: White solid; 79.5 mg (isolated yield 86%); ¹H NMR (400 MHz, CDCl₃) δ = 7.91 (dd, *J*₁ = 6.8 Hz, *J*₂ = 2.0 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.46 (dd, *J*₁ = 6.8 Hz, *J*₂ = 2.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.68 (s, 2 H), 2.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.0, 145.6, 141.1, 135.4, 134.0, 130.8, 129.9, 129.2, 128.5, 63.7, 21.7.



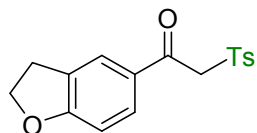
1-(4-bromophenyl)-2-tosylethan-1-one (3la)⁹: White solid; 88.7 mg (isolated yield 84%); ¹H NMR (400 MHz, CDCl₃) δ = 7.82 (d, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 7.6 Hz, 2 H), 4.67 (s, 2 H), 2.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.2, 145.6, 135.4, 134.4, 132.2, 130.8, 130.0, 129.9, 128.5, 63.7, 21.7.



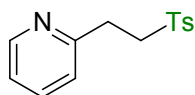
2-tosyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ma)³: White solid; 78.0 mg (isolated yield 76%); ¹H NMR (400 MHz, CDCl₃) δ = 8.07 (d, *J* = 8.4 Hz, 2 H), 7.75 – 7.73 (m, 4 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 4.74 (s, 2 H), 2.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.4, 145.7, 138.2, 135.4, 135.3 (q, *J*_{C-F} = 32.1 Hz), 129.9, 129.7, 128.5, 125.8 (q, *J*_{C-F} = 3.6 Hz), 123.3 (q, *J*_{C-F} = 271.3 Hz), 63.8, 21.7; ¹⁹F NMR (376 MHz, CDCl₃) δ = -63.3



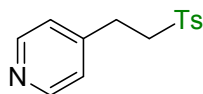
1-(4-nitrophenyl)-2-tosylethan-1-one (3na)¹: yellow solid; 61.2 mg (isolated yield 64%); ¹H NMR (400 MHz, CDCl₃) δ = 8.34 (d, *J* = 8.8 Hz, 2 H), 8.15 (d, *J* = 8.4 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.37 (d, *J* = 8.4 Hz, 2 H), 4.75 (s, 2 H), 2.47 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.0, 150.8, 145.9, 139.9, 135.2, 130.5, 130.0, 128.5, 124.0, 64.1, 21.8.



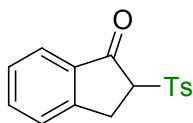
1-(2,3-dihydrobenzofuran-5-yl)-2-tosylethan-1-one (3oa): White solid; 69.2 mg (isolated yield 73%); ¹H NMR (400 MHz, CDCl₃) δ = 7.77 (d, *J* = 8.4 Hz, 2 H), 7.36–7.33 (m, 3 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 7.01 (d, *J* = 7.6 Hz, 1 H), 4.70 (s, 2 H), 4.59 (t, *J* = 8.8 Hz, 2 H), 3.45 (t, *J* = 8.8 Hz, 2 H), 2.45 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 188.6, 161.3, 145.3, 135.9, 132.6, 129.8, 129.5, 128.5, 128.4, 122.3, 114.9, 71.8, 64.1, 31.0, 21.7; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₇H₁₇O₄S: 317.0842; found: 317.0844.



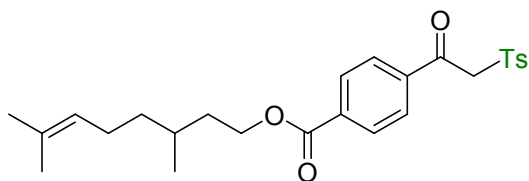
2-(2-tosylethyl)pyridine (3pa)⁷: White solid; 64.2 mg (isolated yield 82%); ¹H NMR (400 MHz, CDCl₃) δ = 8.42 (d, *J* = 4.4 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.59 – 7.55 (m, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.15 – 7.09 (m, 2 H), 3.60 – 3.56 (m, 2 H), 3.21 – 3.17 (m, 2 H), 2.42 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 157.1, 149.3, 144.6, 136.7, 136.0, 129.8, 128.1, 123.2, 121.8, 55.2, 30.8, 21.6.



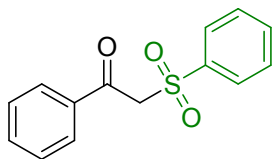
4-(2-tosylethyl)pyridine (3qa): White solid; 65.0 mg (isolated yield 83%); ¹H NMR (400 MHz, CDCl₃) δ = 8.43 (d, *J* = 5.2 Hz, 2 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.03 (d, *J* = 6.0 Hz, 1 H), 3.34– 3.30 (m, 2 H), 3.02 – 2.98 (m, 2 H), 2.41 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 149.8, 146.6, 145.0, 135.5, 129.9, 127.9, 123.5, 56.0, 28.0, 21.5; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₆NO₂S: 262.0896; found: 262.0901.



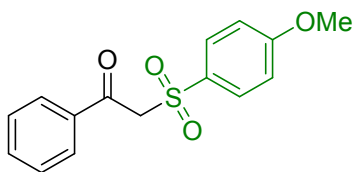
2-tosyl-2,3-dihydro-1H-inden-1-one (3sa)²: White solid; 60.9 mg (isolated yield 71%); ¹H NMR (400 MHz, CDCl₃) δ = 7.80 (d, *J* = 8.0 Hz, 2 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.40– 7.35 (m, 3 H), 4.26 (dd, *J*₁ = 8.4 Hz, *J*₂ = 3.2 Hz, 1 H), 3.81 (dd, *J*₁ = 18.0 Hz, *J*₂ = 3.2 Hz, 1 H), 3.53 (dd, *J*₁ = 18.0 Hz, *J*₂ = 8.4 Hz, 1 H), 2.44 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 194.6, 151.9, 145.3, 135.9, 135.7, 134.4, 129.7, 129.2, 128.1, 126.4, 124.8, 68.6, 28.1, 21.7.



3,7-dimethyloct-6-en-1-yl 4-(2-tosylacetyl)benzoate (3va): White solid; 88.9 mg (isolated yield 65%); ¹H NMR (400 MHz, CDCl₃) δ = 8.13 (d, *J* = 8.4 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 5.10 (t, *J* = 7.2 Hz, 1 H), 4.73 (s, 2 H), 4.43 – 4.36 (m, 2 H), 2.45 (s, 3 H), 2.05 – 1.95 (m, 2 H), 1.85 – 1.78 (m, 1 H), 1.68 – 1.56 (m, 9 H), 1.45 – 1.36 (m, 1 H), 0.98 (d, *J* = 6.4 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.8, 165.4, 145.6, 138.6, 135.5, 135.2, 131.5, 129.9, 129.9, 129.2, 128.6, 124.4, 64.2, 35.4, 29.5, 25.7, 21.7, 19.4, 17.7; HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₆H₃₃O₅S: 457.2043; found: 457.2045.

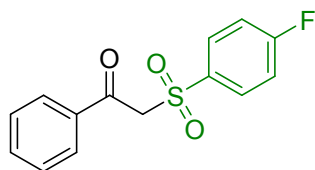


1-phenyl-2-(phenylsulfonyl)ethan-1-one (3ab)²: White solid; 57.7 mg (isolated yield 74%); ¹H NMR (400 MHz, CDCl₃) δ = 7.95 – 7.89 (m, 4 H), 7.67 – 7.61 (m, 2 H), 7.55 (t, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 8.0 Hz, 2 H), 4.74 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.9, 138.6, 135.7, 134.4, 134.3, 129.3, 129.2, 128.9, 128.6, 63.4.

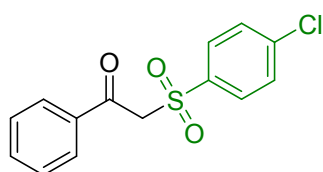


2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one (3ac)¹⁰: White solid; 70.5 mg (isolated yield 81%); ¹H

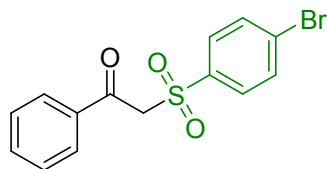
NMR (400 MHz, CDCl₃) δ = 7.96 – 7.93 (m, 2 H), 7.81 (d, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 2 H), 7.63 – 7.60 (m, 1 H), 7.48 (t, J = 8.0 Hz, 2 H), 6.99 – 6.97 (m, 2 H), 4.71 (s, 2 H), 3.87 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 188.3, 164.1, 135.7, 134.3, 130.8, 130.1, 129.3, 128.8, 114.3, 63.7, 55.7.



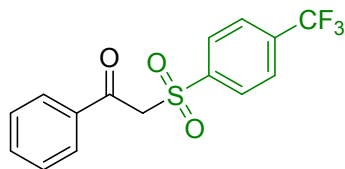
2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-one (3ad)¹⁰: White solid; 69.2 mg (isolated yield 83%); ¹H NMR (400 MHz, CDCl₃) δ = 7.95 – 7.90 (m, 4 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.94 (t, J = 8.0 Hz, 2 H), 7.24 – 7.20 (m, 2 H), 4.74 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 188.0, 166.1 (d, J_{C-F} = 255.9 Hz), 135.5, 134.6 (d, J_{C-F} = 2.9 Hz), 134.5, 131.6 (d, J_{C-F} = 9.5 Hz), 129.2, 128.9, 116.5 (d, J_{C-F} = 22.6 Hz), 63.4; ¹⁹F NMR (376 MHz, CDCl₃) δ = -102.3.



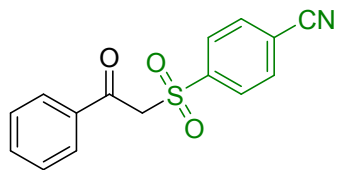
2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one (3ae)²: White solid; 75.8 mg (isolated yield 86%); ¹H NMR (400 MHz, CDCl₃) δ = 7.93 (d, J = 8.0 Hz, 2 H), 7.84 – 7.82 (m, 2 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.53 – 7.47 (m, 4 H), 4.75 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.9, 141.1, 137.0, 135.5, 134.6, 130.1, 129.5, 129.2, 128.9, 63.2.



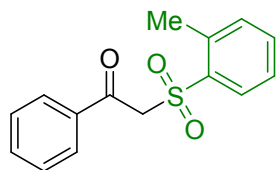
2-((4-bromophenyl)sulfonyl)-1-phenylethan-1-one (3af)¹¹: White solid; 82.1 mg (isolated yield 81%); ¹H NMR (400 MHz, CDCl₃) δ = 7.93 (d, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 2 H), 7.77 – 7.75 (m, 2 H), 7.70 – 7.62 (m, 3 H), 7.50 (t, J = 8.0 Hz, 2 H), 4.74 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.9, 137.5, 135.5, 134.6, 132.5, 130.2, 129.8, 129.2, 128.9, 63.2.



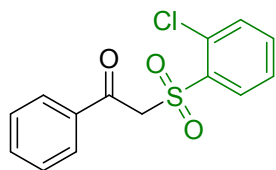
phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one (3ag)¹⁰: White solid; 74.8 mg (isolated yield 76%); ¹H NMR (400 MHz, CDCl₃) δ = 8.05 (d, J = 8.0 Hz, 2 H), 7.93 (d, J = 8.0 Hz, 2 H), 7.82 (d, J = 8.4 Hz, 2 H), 7.65 (t, J = 7.2 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 2 H), 4.79 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.7, 142.0, 135.8 (q, J_{C-F} = 32.8 Hz), 135.4, 134.7, 129.4, 129.2, 126.3 (q, J_{C-F} = 3.7 Hz), 123.0 (q, J_{C-F} = 272.0 Hz), 63.0; ¹⁹F NMR (376 MHz, CDCl₃) δ = -63.2.



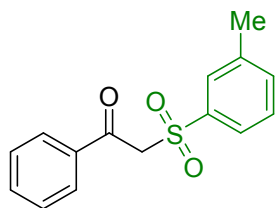
4-((2-oxo-2-phenylethyl)sulfonyl)benzonitrile (3ah)¹²: White solid; 61.6 mg (isolated yield 72%); ¹H NMR (400 MHz, CDCl₃) δ = 8.05 – 8.03 (m, 2 H), 7.93 – 7.91 (m, 2 H), 7.86 – 7.84 (m, 2 H), 7.68 – 7.64 (m, 1 H), 7.51 (t, J = 8.0 Hz, 2 H), 4.79 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.6, 142.5, 135.3, 134.8, 132.9, 129.5, 129.1, 129.0, 117.9, 117.0, 62.9.



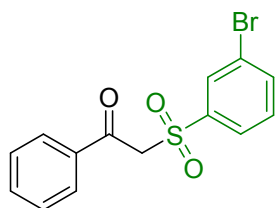
1-phenyl-2-(o-tolylsulfonyl)ethan-1-one (3ai)¹³: White solid; 52.6 mg (isolated yield 64%); ¹H NMR (400 MHz, CDCl₃) δ = 7.97 – 7.94 (m, 2 H), 7.89 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1 H), 7.64 – 7.60 (m, 1 H), 7.55 – 7.47 (m, 3 H), 7.36 – 7.31 (m, 2 H), 4.76 (s, 2 H), 2.73 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.9, 138.3, 136.8, 135.8, 134.4, 134.2, 132.8, 130.5, 129.4, 128.8, 126.6, 62.9, 20.5.



2-((2-chlorophenyl)sulfonyl)-1-phenylethan-1-one (3aj)¹⁰: White solid; 59.1 mg (isolated yield 67%); ¹H NMR (400 MHz, CDCl₃) δ = 8.06 – 8.04 (m, 1 H), 7.95 – 7.93 (m, 2 H), 7.64 – 7.58 (m, 3 H), 7.51 – 7.45 (m, 3 H), 5.06 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.8, 136.4, 135.7, 135.2, 134.5, 132.7, 132.0, 131.8, 129.1, 128.9, 127.5, 60.8.

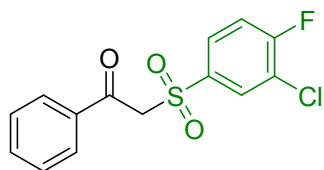


1-phenyl-2-(m-tolylsulfonyl)ethan-1-one (3ak)¹⁶: White solid; 67.4 mg (isolated yield 82%); ¹H NMR (400 MHz, CDCl₃) δ = 7.96 – 7.94 (m, 2 H), 7.88 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1 H), 7.64 – 7.60 (m, 1 H), 7.55 – 7.46 (m, 3 H), 7.35 – 7.31 (m, 2 H), 4.76 (s, 2 H), 2.73 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.9, 138.3, 136.8, 135.7, 134.3, 134.2, 132.8, 130.5, 129.4, 128.8, 126.6, 62.8, 20.5.

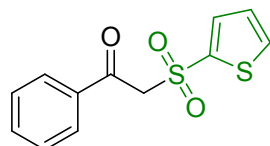


2-((3-bromophenyl)sulfonyl)-1-phenylethan-1-one (3al)¹⁴: White solid; 86.2 mg (isolated yield 85%); ¹H NMR

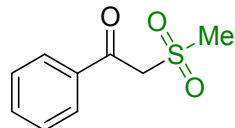
(400 MHz, CDCl₃) δ = 8.04 (s, 1 H), 7.93 (d, J = 7.6 Hz, 2 H), 7.84 (d, J = 8.0 Hz, 1 H), 7.78 (d, J = 8.4 Hz, 1 H), 7.64 (t, J = 7.2 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 2 H), 7.43 (t, J = 8.0 Hz, 1 H), 4.76 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.7, 140.4, 137.3, 135.5, 134.6, 131.4, 130.7, 129.2, 128.9, 127.3, 123.2, 63.2.



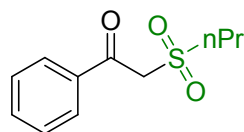
2-((3-chloro-4-fluorophenyl)sulfonyl)-1-phenylethan-1-one (3am): White solid; 83.3 mg (isolated yield 89%); ¹H NMR (400 MHz, CDCl₃) δ = 8.00 – 7.97 (m, 1 H), 7.93 (d, J = 7.6 Hz, 2 H), 7.84 – 7.79 (m, 1 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.50 (t, J = 8.0 Hz, 2 H), 7.31 (t, J = 8.8 Hz, 1 H), 4.76 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.8, 161.6 (d, J_{C-F} = 258.1 Hz), 135.5 (d, J_{C-F} = 3.6 Hz), 135.4, 134.7, 131.8 (d, J_{C-F} = 1.5 Hz), 129.5 (d, J_{C-F} = 8.8 Hz), 129.1, 129.0, 122.6 (d, J_{C-F} = 18.9 Hz), 117.5 (d, J_{C-F} = 22.6 Hz), 63.1; ¹⁹F NMR (376 MHz, CDCl₃) δ = -104.5; HRMS (ESI): m/z [M+H]⁺ calcd for C₁₄H₁₁ClFO₃S: 313.0096; found: 313.0092.



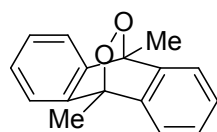
phenyl-2-(thiophen-2-ylsulfonyl)ethanone (3an)¹⁴: White solid; 50.3 mg (isolated yield 63%); ¹H NMR (400 MHz, CDCl₃) δ = 7.96 – 7.94 (m, 2 H), 7.74 (dd, J_1 = 5.2 Hz, J_2 = 1.6 Hz, 1 H), 7.70 (dd, J_1 = 4.0 Hz, J_2 = 1.6 Hz, 1 H), 7.65 – 7.61 (m, 1 H), 7.51 – 7.47 (m, 2 H), 7.14 – 7.12 (m, 1 H), 4.83 (s, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 187.8, 139.3, 135.6, 135.5, 135.0, 134.5, 129.2, 128.9, 127.9, 64.3.



2-(methylsulfonyl)-1-phenylethanone (3ao)⁷: White solid; 24.9 mg (isolated yield 42%); ¹H NMR (400 MHz, CDCl₃) δ = 8.00 – 7.98 (m, 2 H), 7.66 (t, J = 7.2 Hz, 1 H), 7.52 (t, J = 8.0 Hz, 2 H), 4.61 (s, 2 H), 3.15 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 189.2, 135.5, 134.7, 129.2, 129.0, 61.1, 41.8.



phenyl-2-(propylsulfonyl)ethanone (3ap)⁴: White solid; 30.5 mg (isolated yield 45%); ¹H NMR (400 MHz, CDCl₃) δ = 8.02 – 8.00 (m, 2 H), 7.65 (t, J = 7.2 Hz, 1 H), 7.53 (t, J = 7.6 Hz, 2 H), 4.56 (s, 2 H), 3.26 – 3.22 (m, 2 H), 1.97 – 1.91 (m, 2 H), 1.11 (t, J = 7.6 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 189.3, 135.7, 134.6, 129.3, 129.0, 59.5, 55.3, 15.8, 13.0.



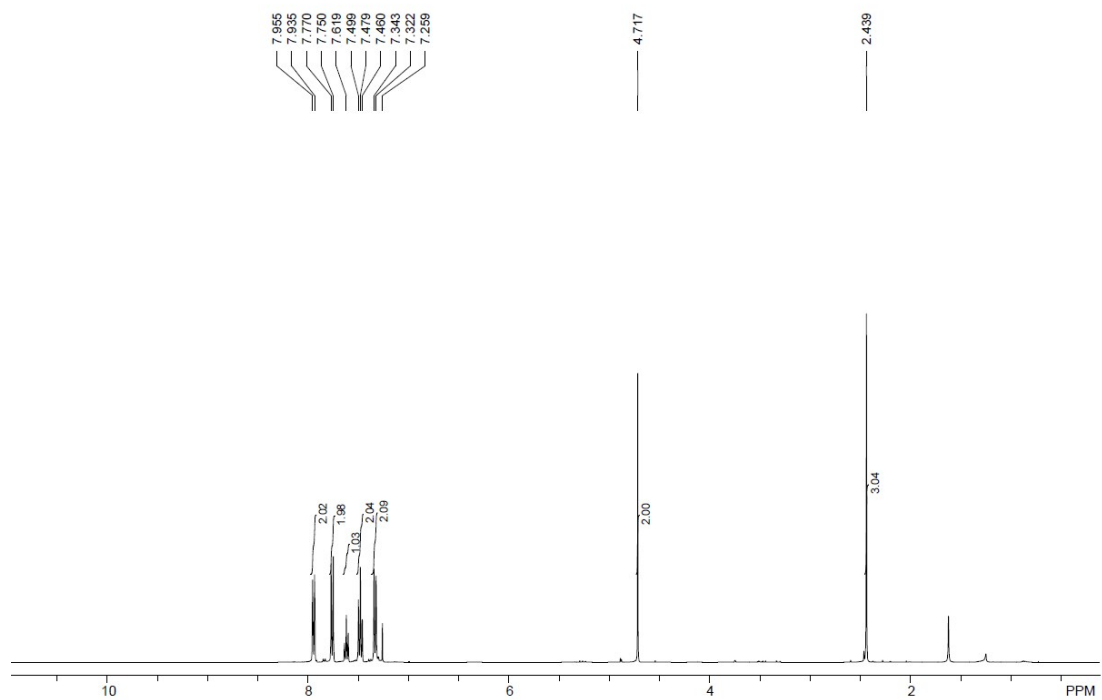
9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene (5b)¹⁵: White solid; 54.3 mg (isolated yield 76%); ¹H NMR (400 MHz, CDCl₃) δ = 7.41 – 7.38 (m, 3 H), 7.31 – 7.28 (m, 3 H), 2.16 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ = 140.7, 127.4, 120.7, 79.5, 13.7.

4. References

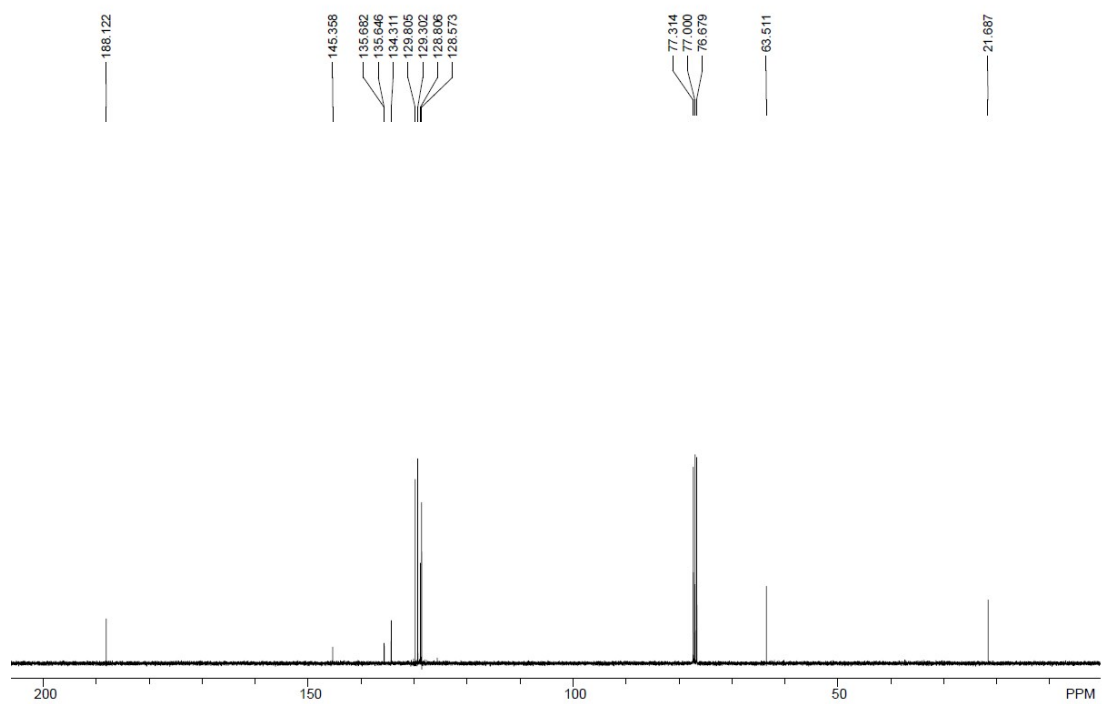
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5. ¹H and ¹³C NMR spectra of products

phenyl-2-tosylethan-1-one (3aa)

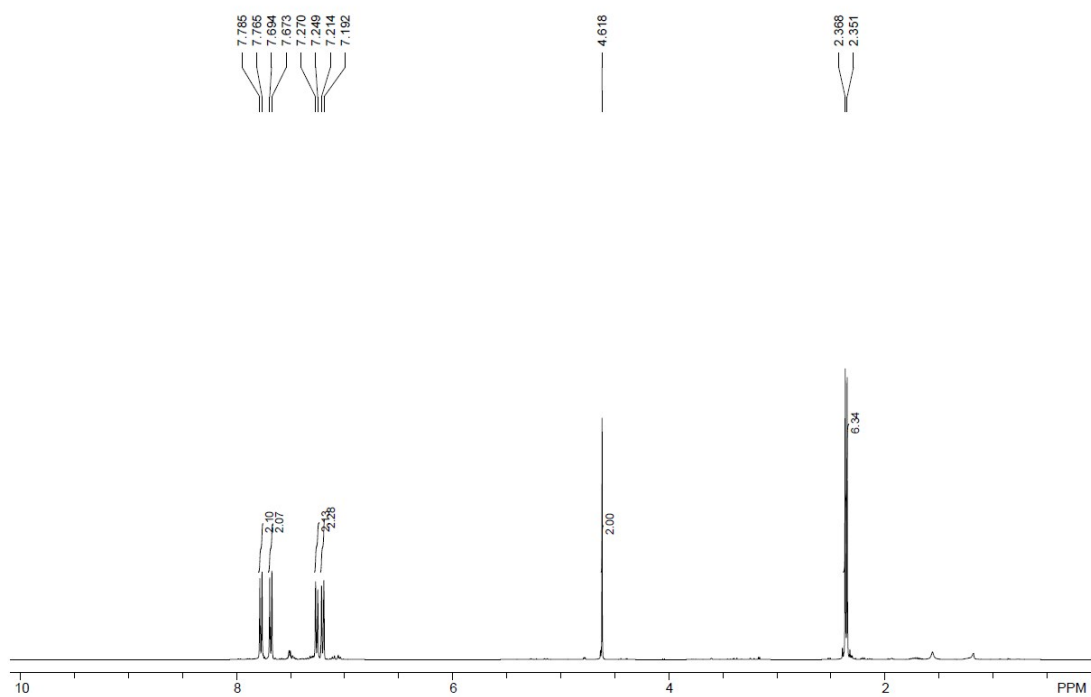


¹H spectra of 3aa

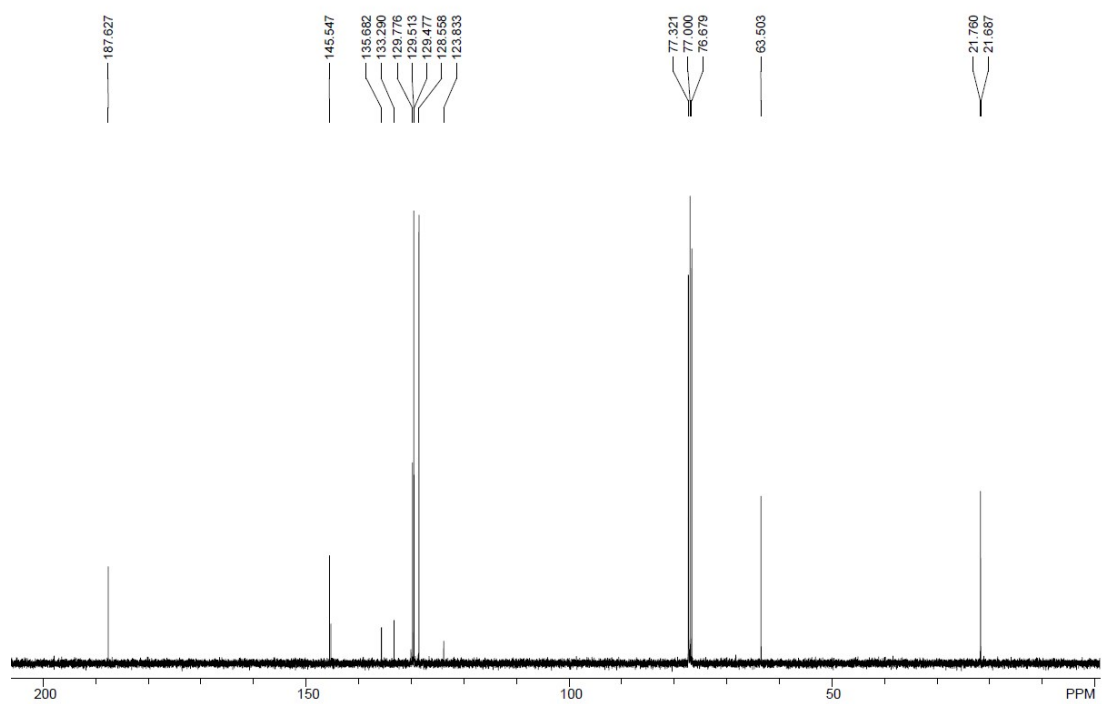


¹³C spectra of 3aa

1-(p-tolyl)-2-tosylethan-1-one (3ba)

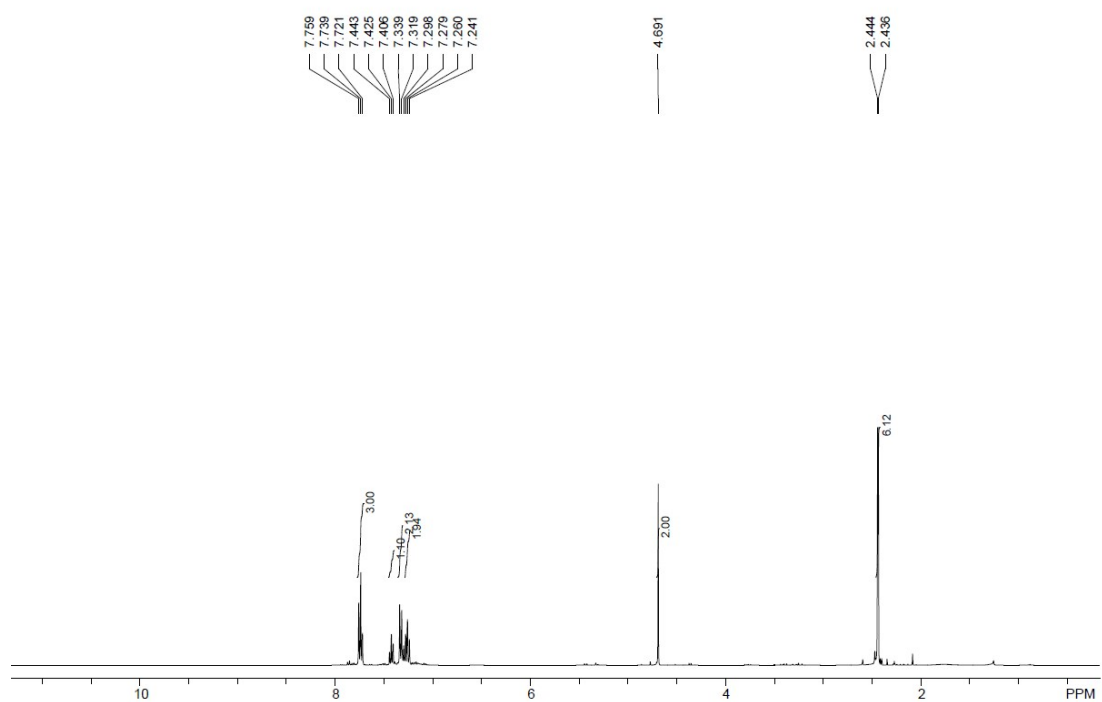


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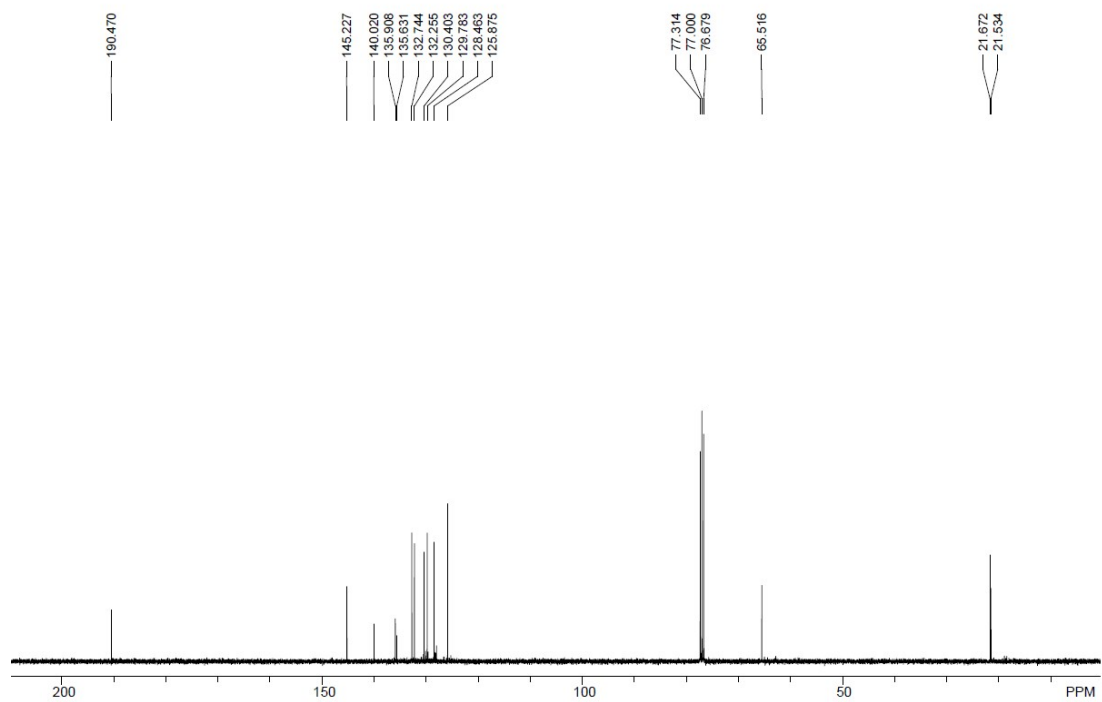


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1-(o-tolyl)-2-tosylethan-1-one (3ca)

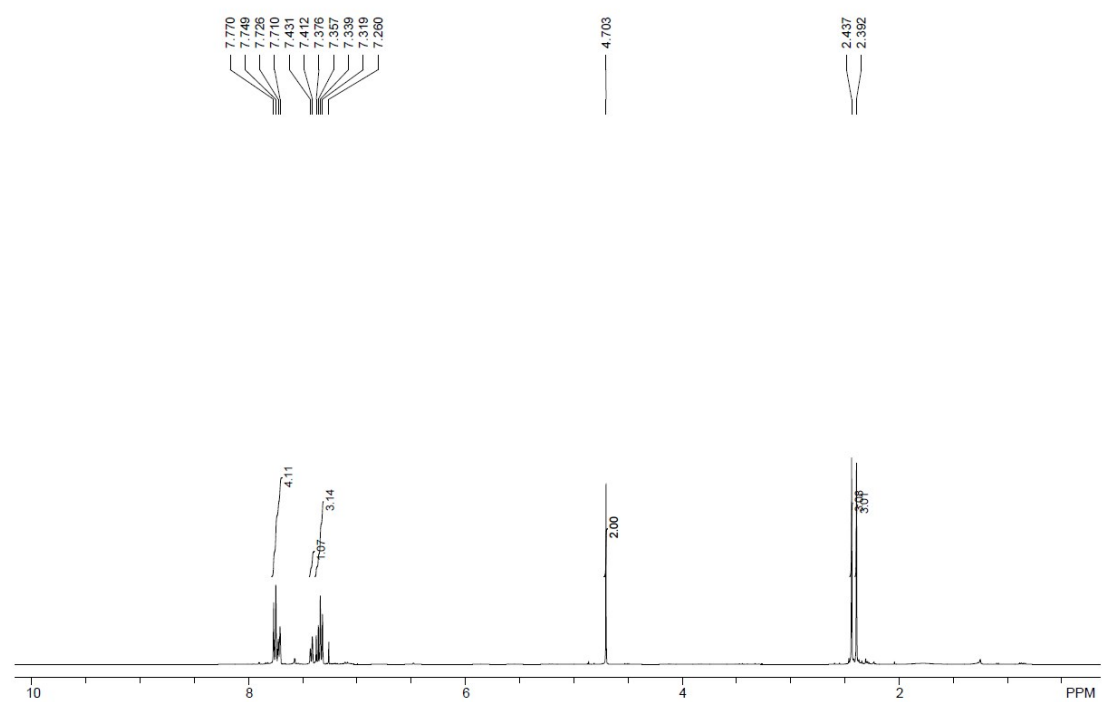


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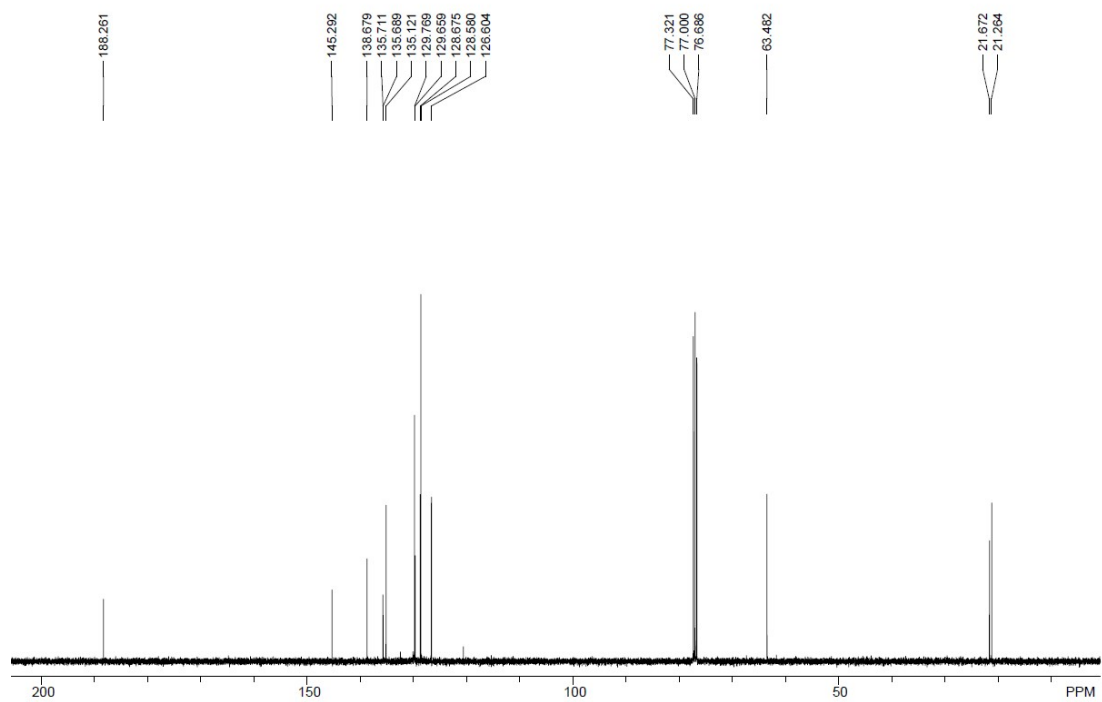


¹³C spectra of 3ca

1-(m-tolyl)-2-tosylethan-1-one (3da)

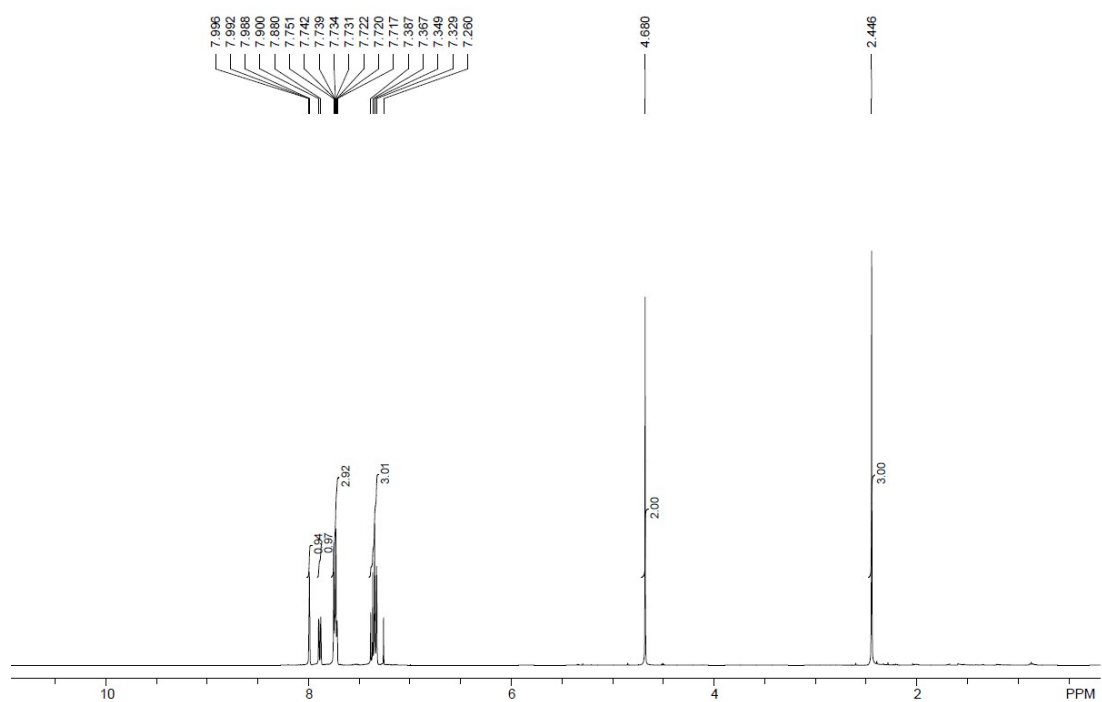


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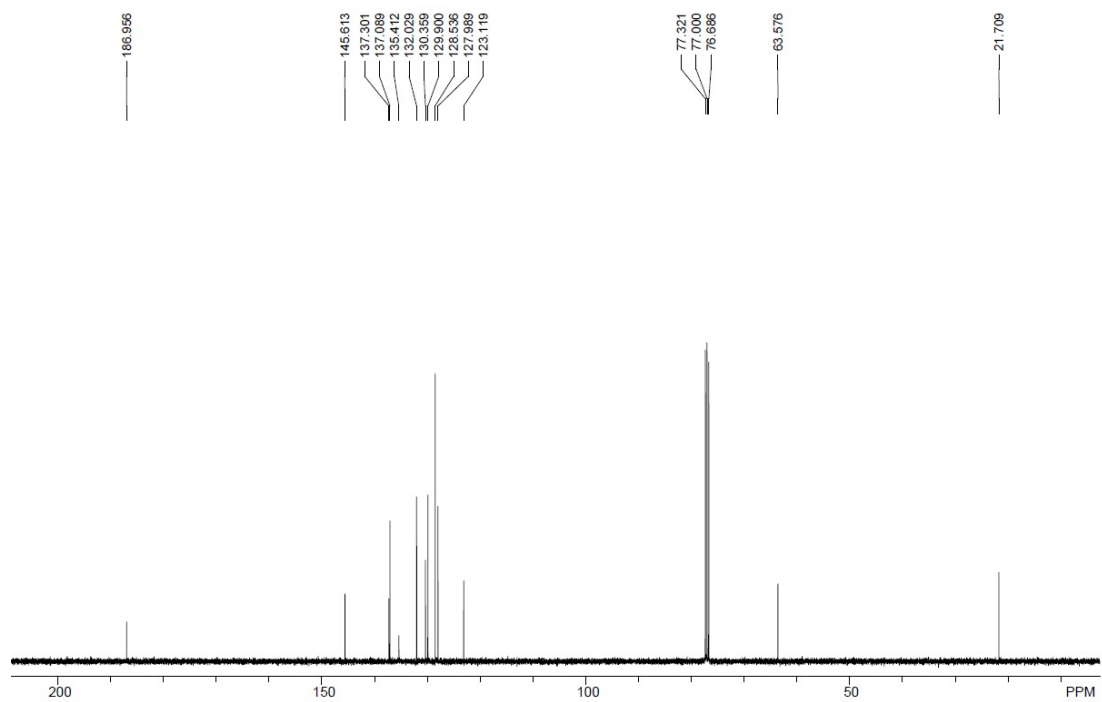


¹³C spectra of 3da

1-(3-bromophenyl)-2-tosylethan-1-one (3ea)

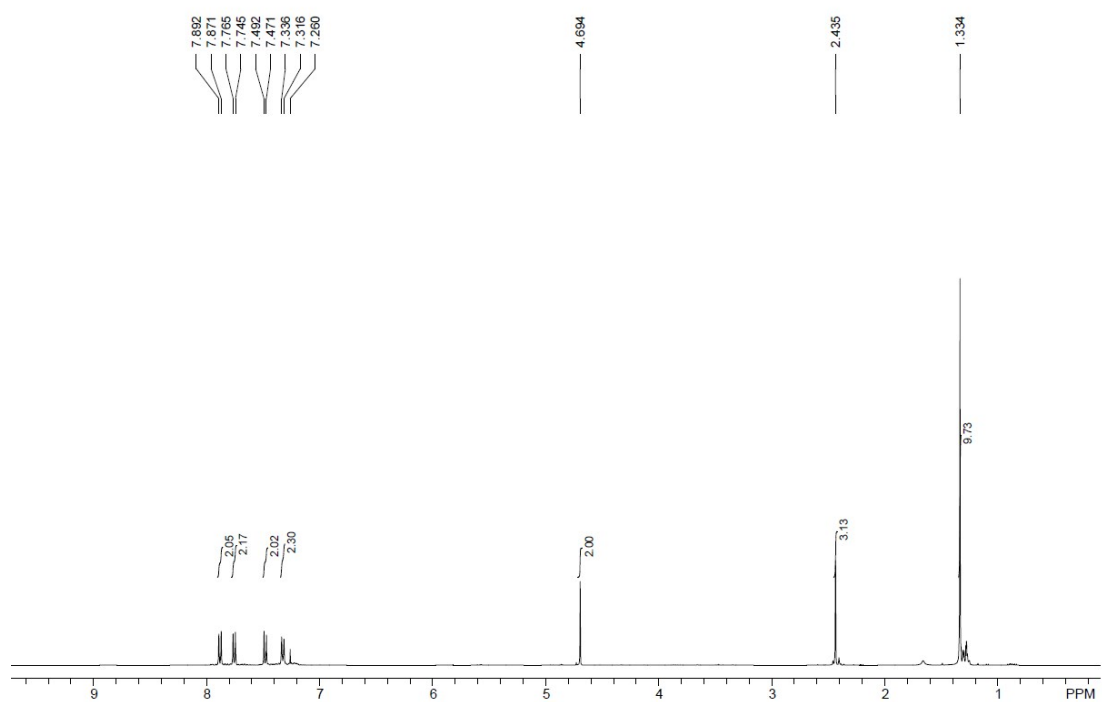


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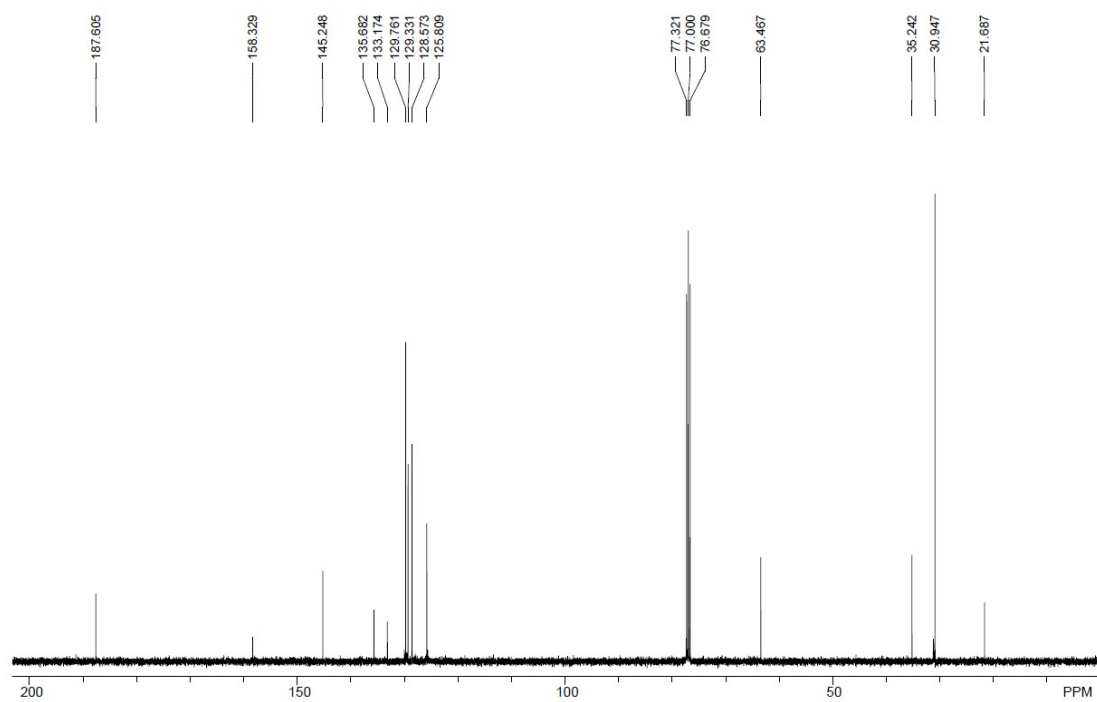


¹³C spectra of 3ea

1-(4-(tert-butyl)phenyl)-2-tosylethan-1-one (3fa)

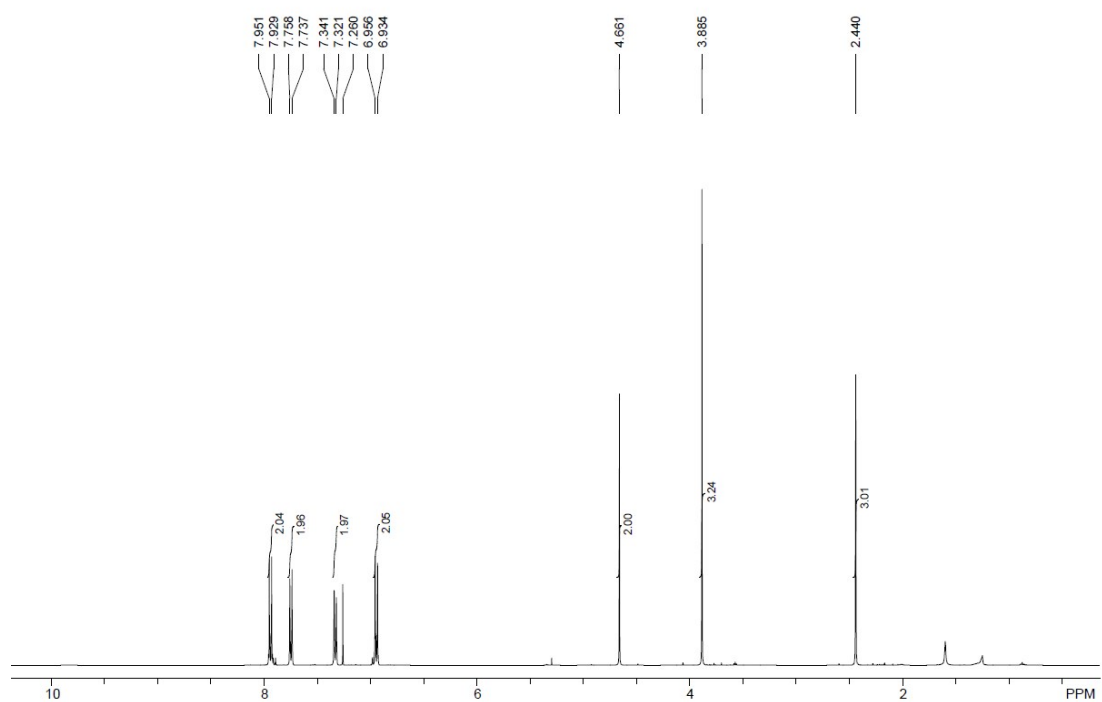


¹H spectra of 3fa

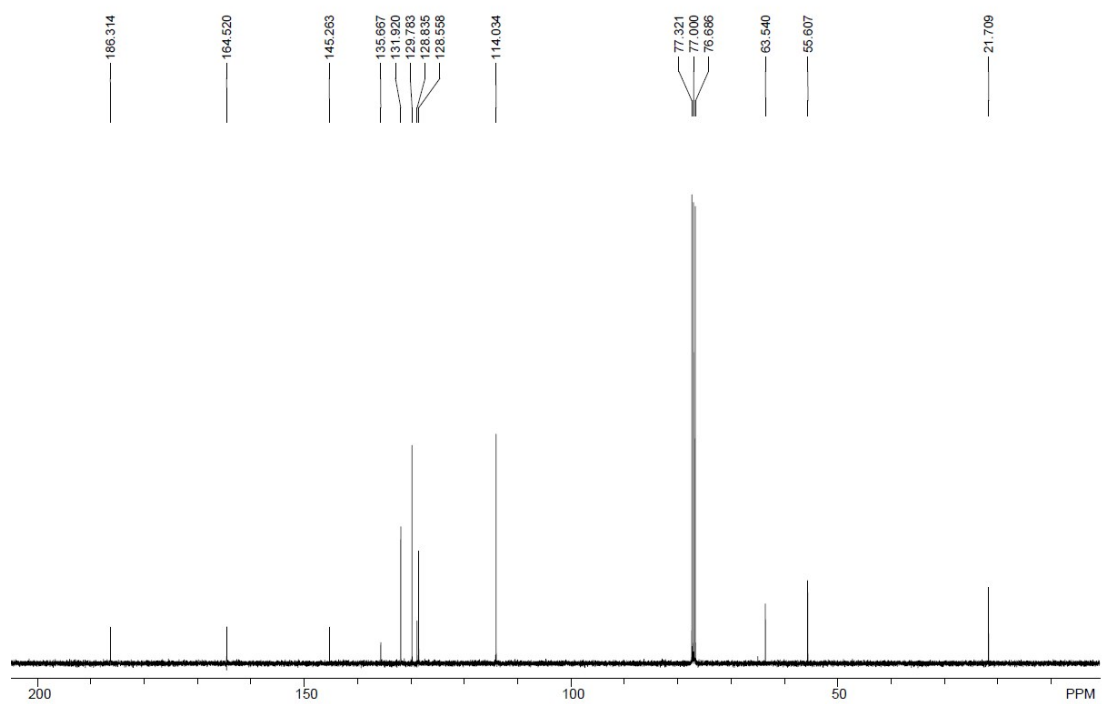


¹³C spectra of 3fa

1-(4-methoxyphenyl)-2-tosylethan-1-one (3ga)

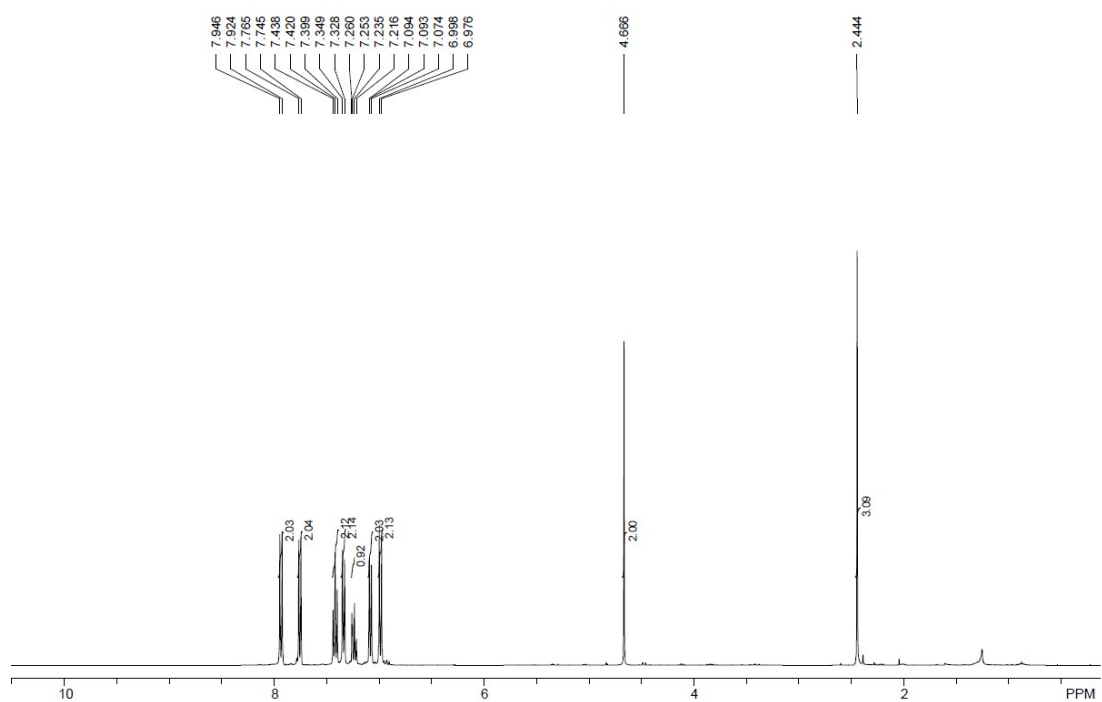


¹H spectra of 3ga

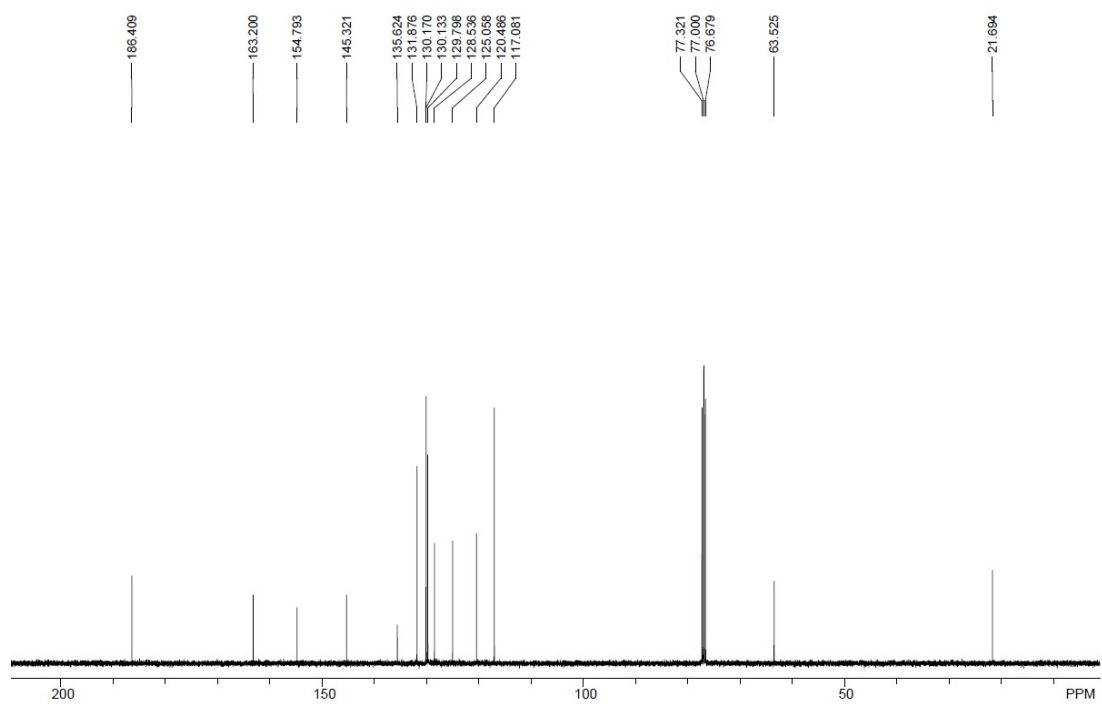


¹³C spectra of 3ga

1-(4-phenoxyphenyl)-2-tosylethan-1-one (3ha)

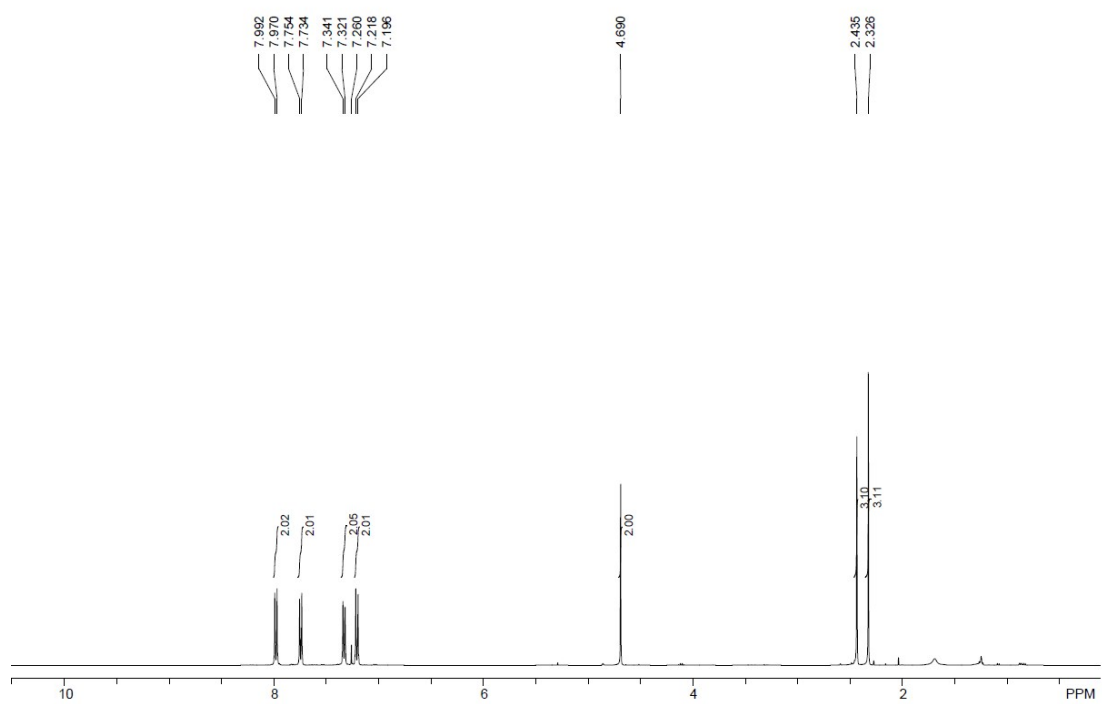


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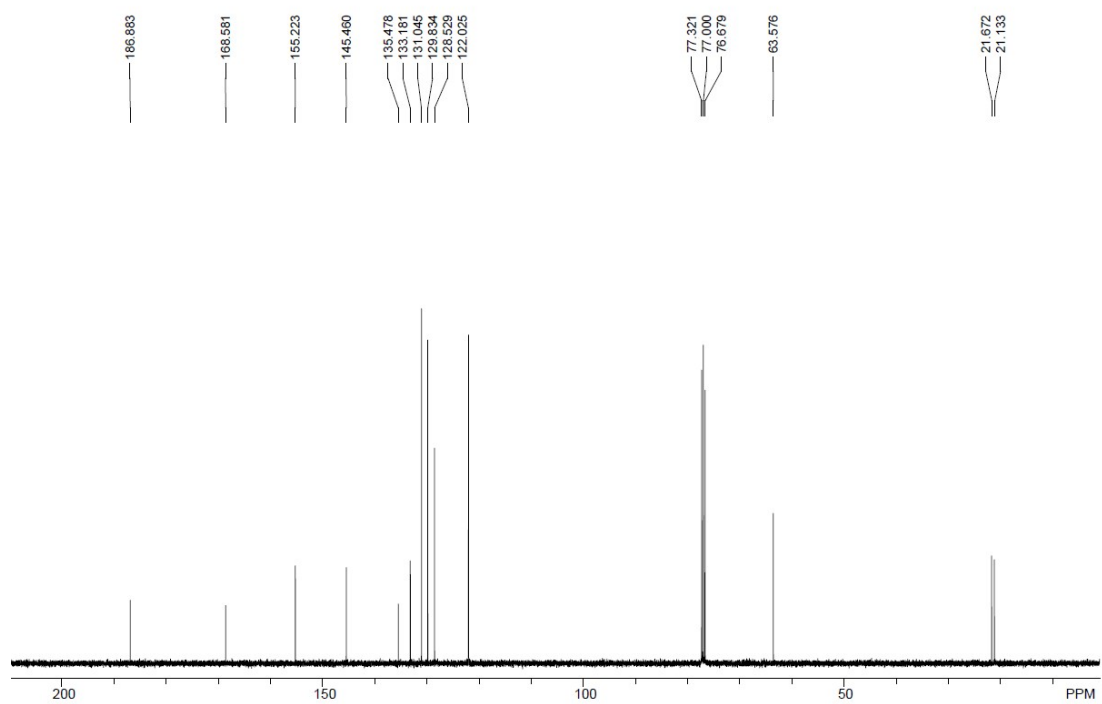


¹³C spectra of 3ha

4-(2-tosylacetyl)phenyl acetate (**3ia**)

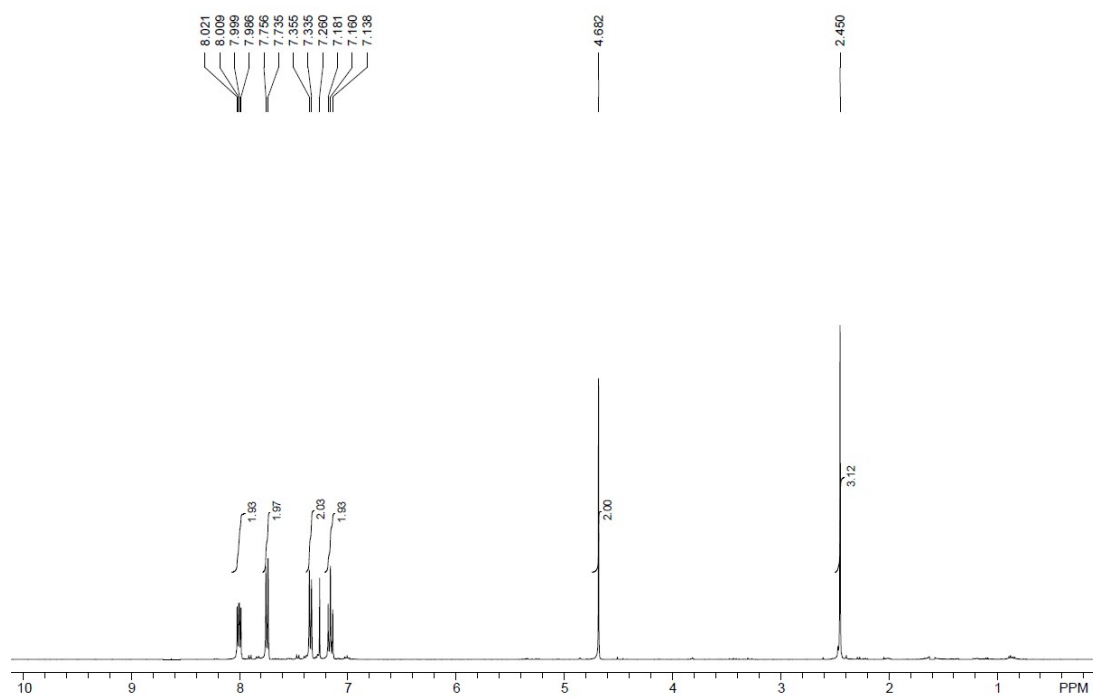


¹H spectra of **3ia**

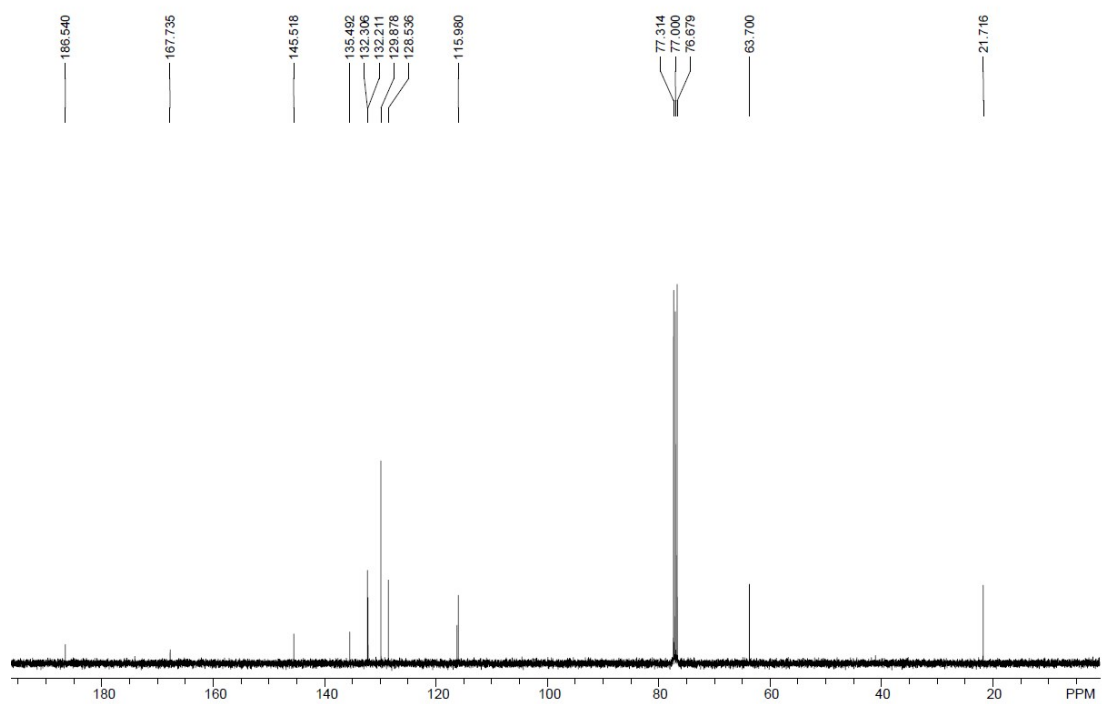


¹³C spectra of **3ia**

1-(4-fluorophenyl)-2-tosylethan-1-one (3ja)

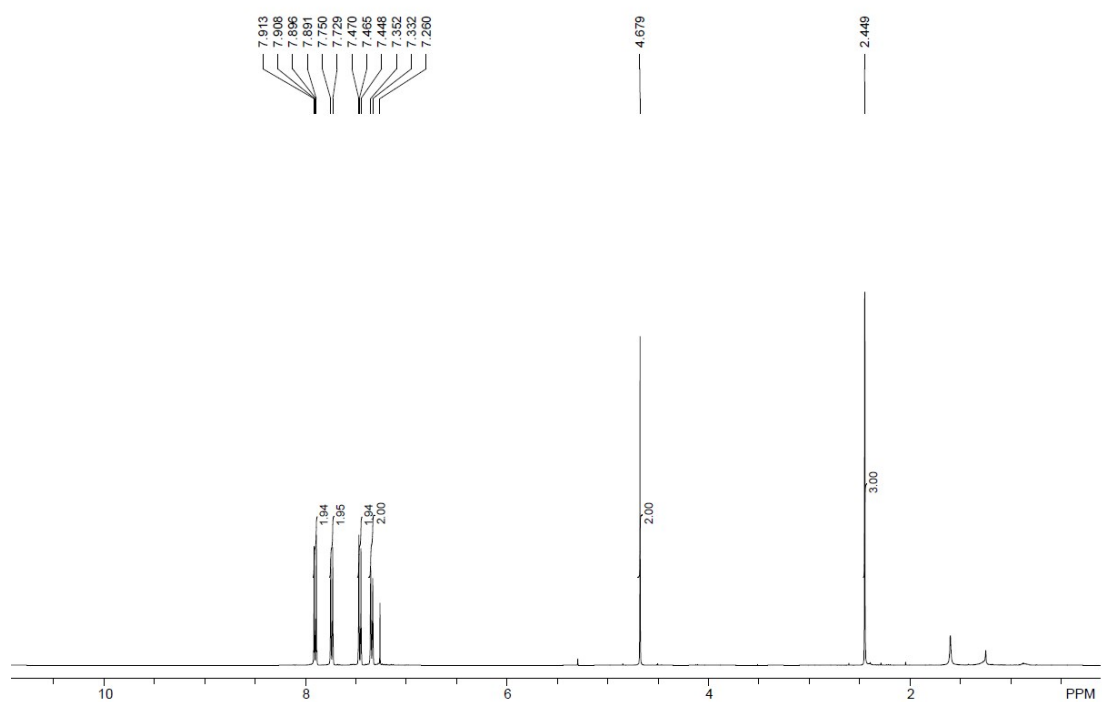


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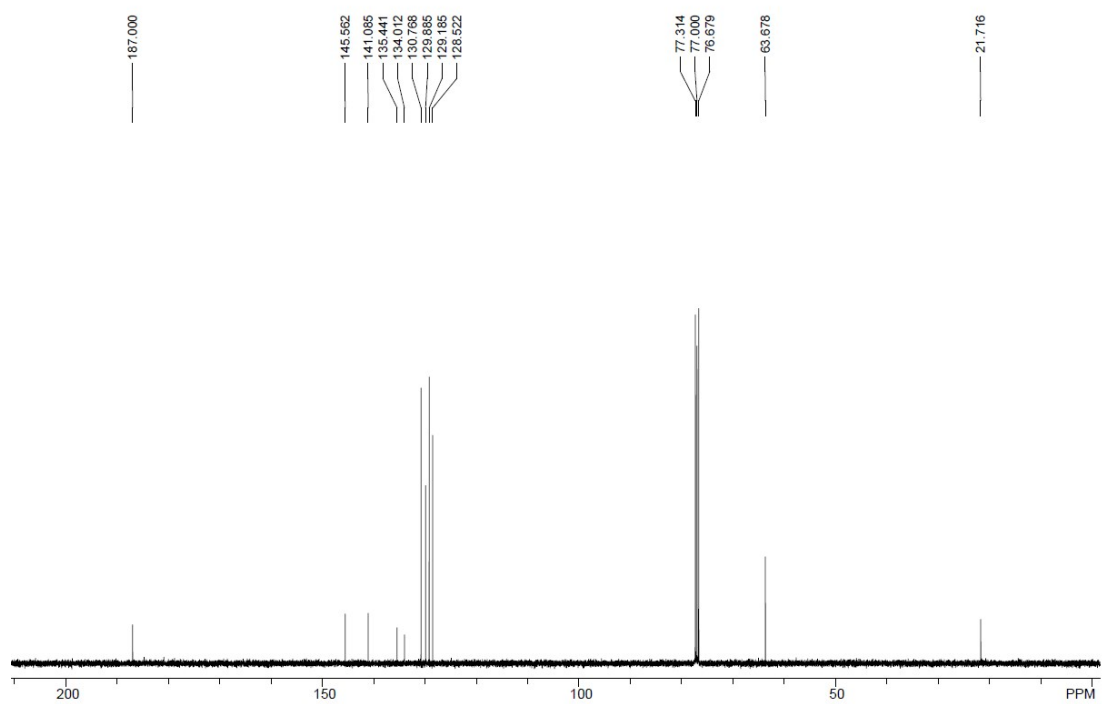


¹³C spectra of 3ja

1-(4-chlorophenyl)-2-tosylethan-1-one (3ka)

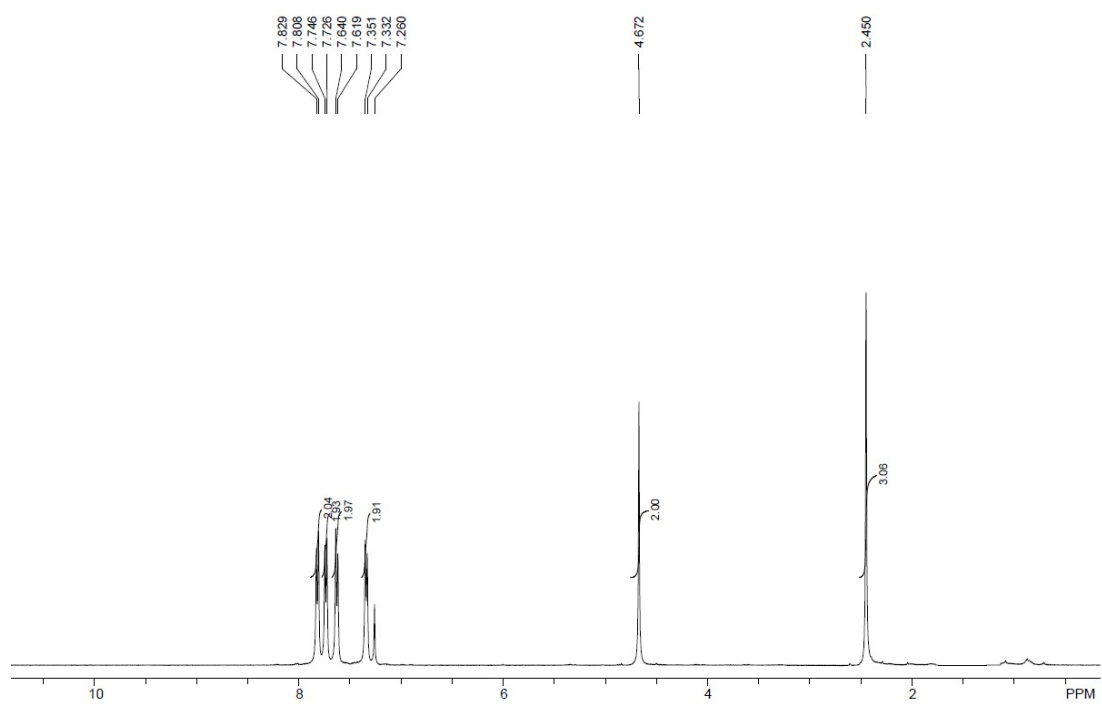


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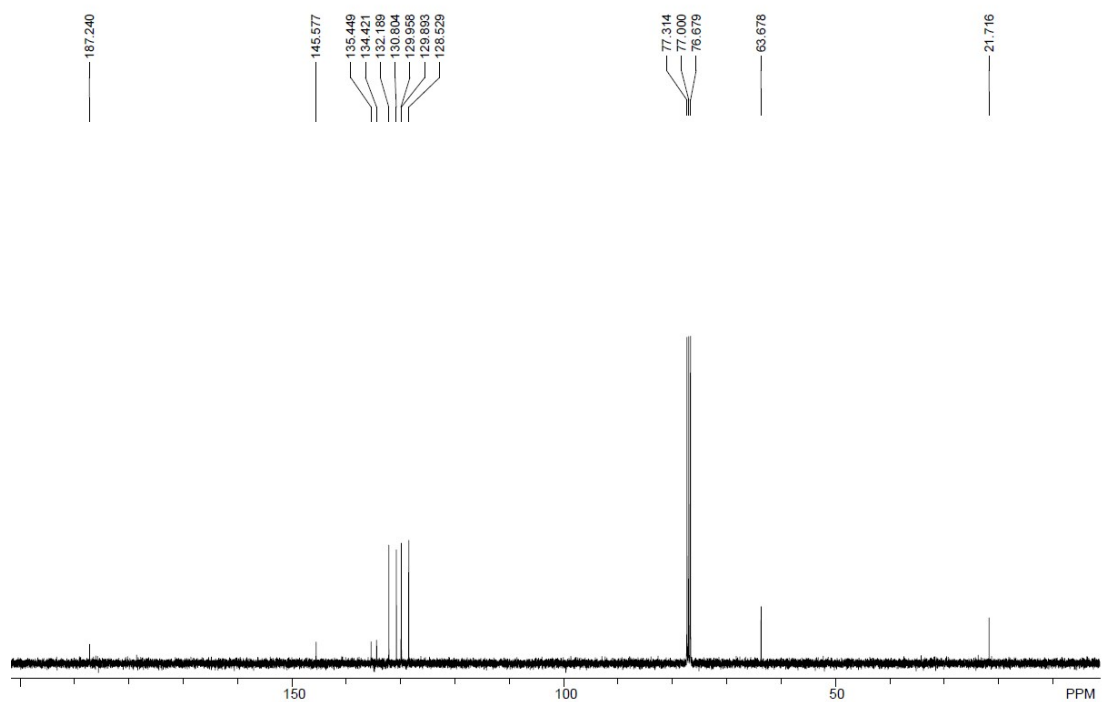


¹³C spectra of 3ka

1-(4-bromophenyl)-2-tosylethan-1-one (3la)

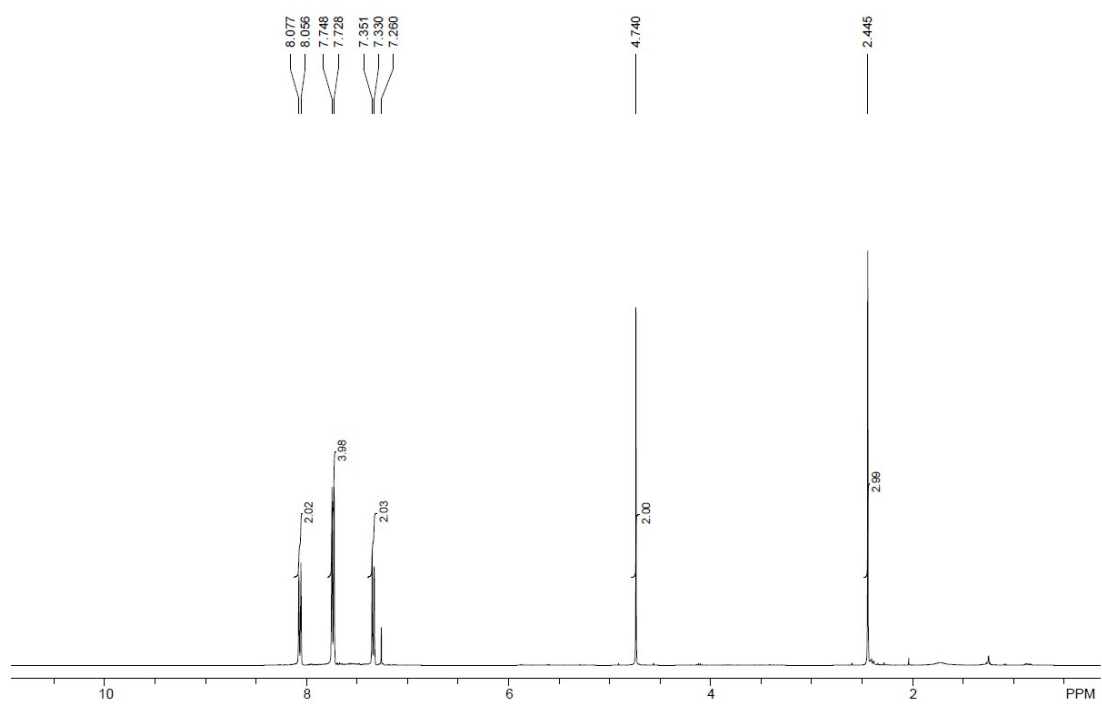


¹H spectra of 3la

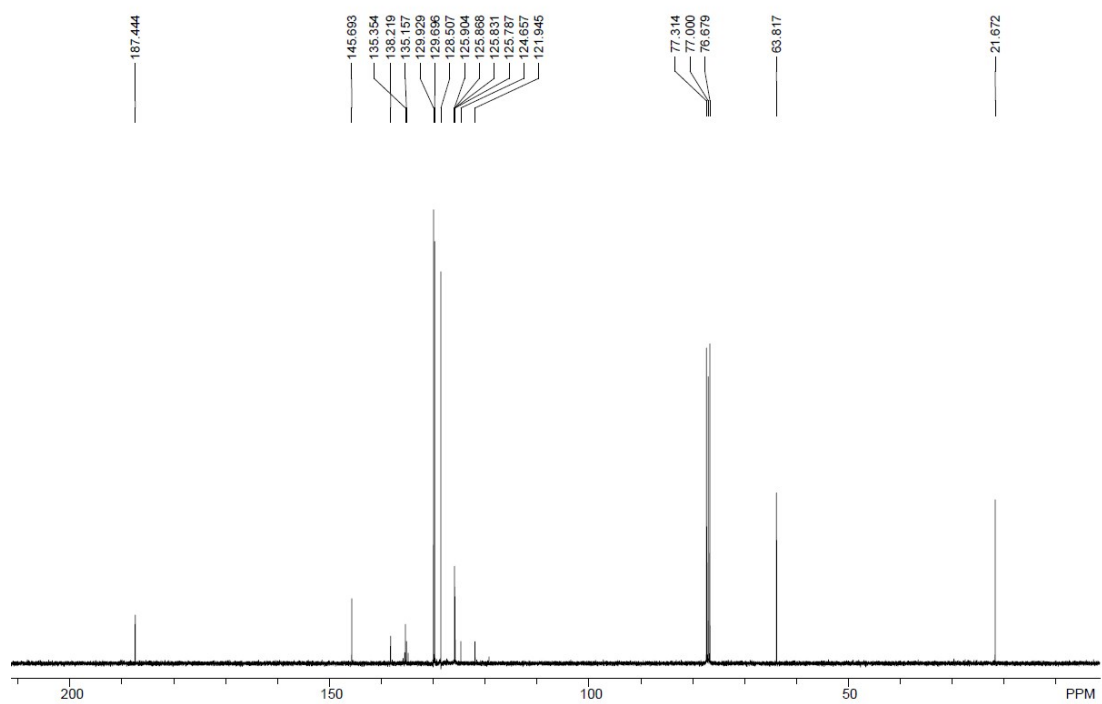


¹³C spectra of 3la

2-tosyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3ma)

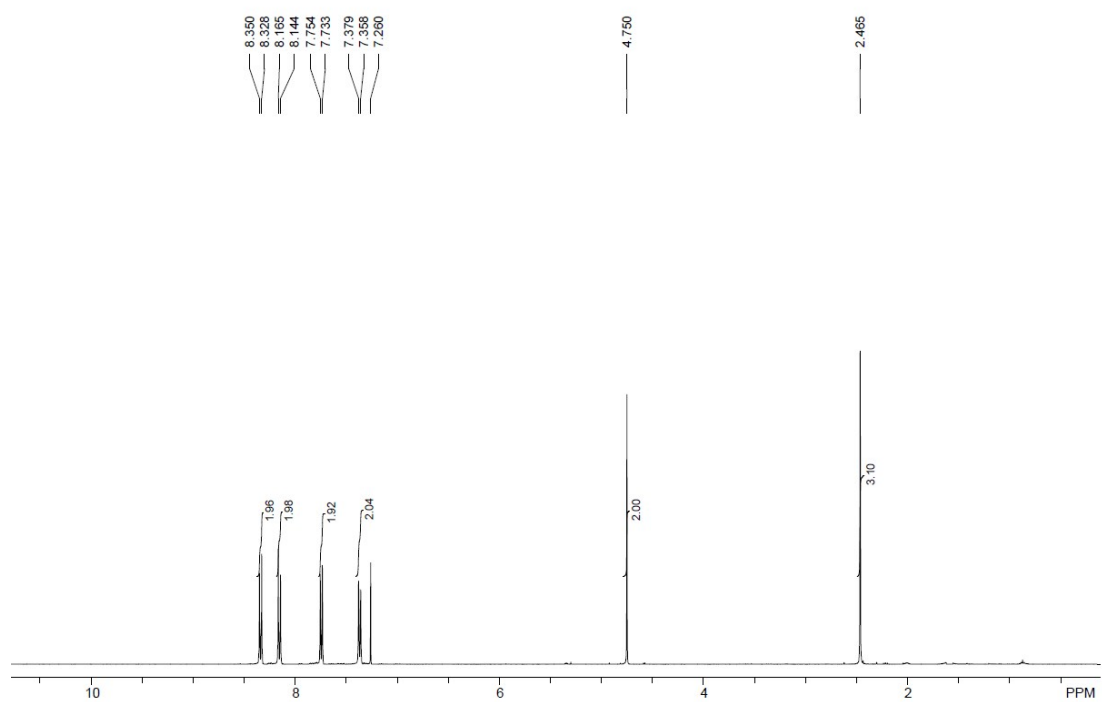


¹H spectra of 3ma

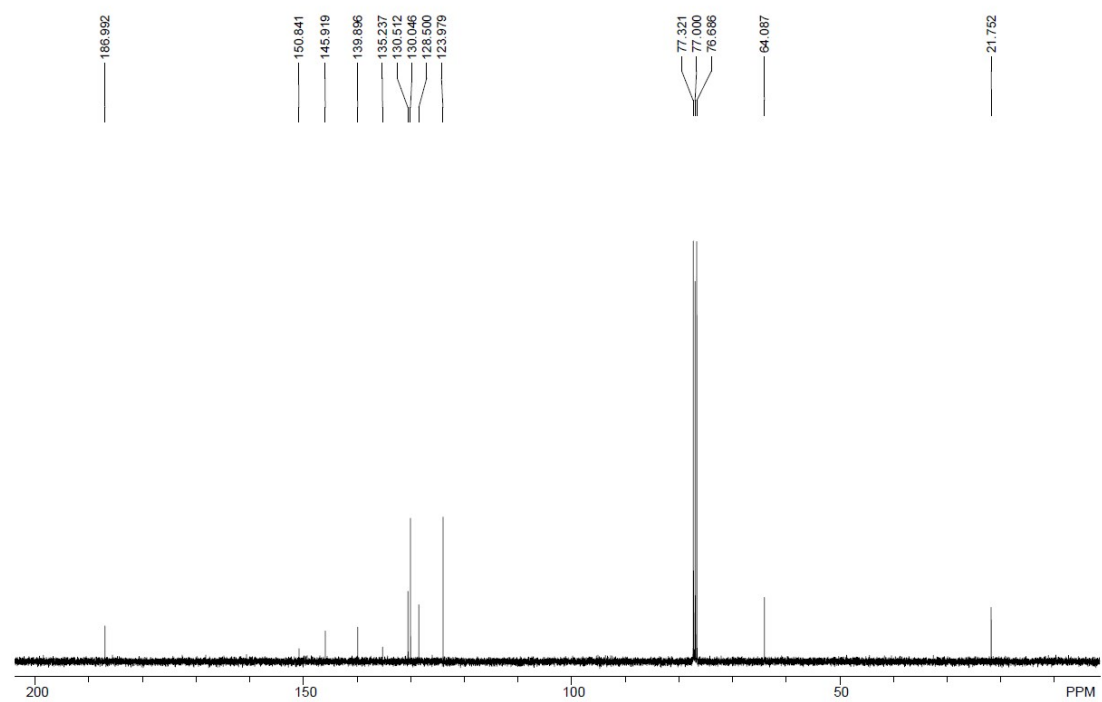


¹³C spectra of 3ma

1-(4-nitrophenyl)-2-tosylethan-1-one (3na)

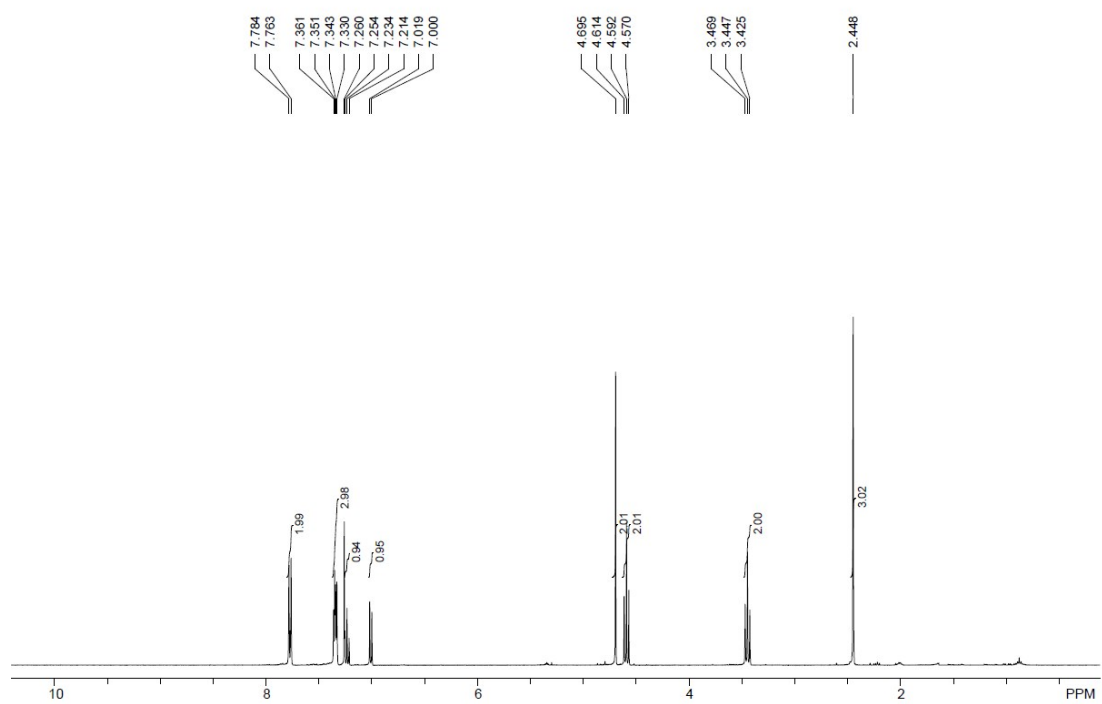


¹H spectra of 3na

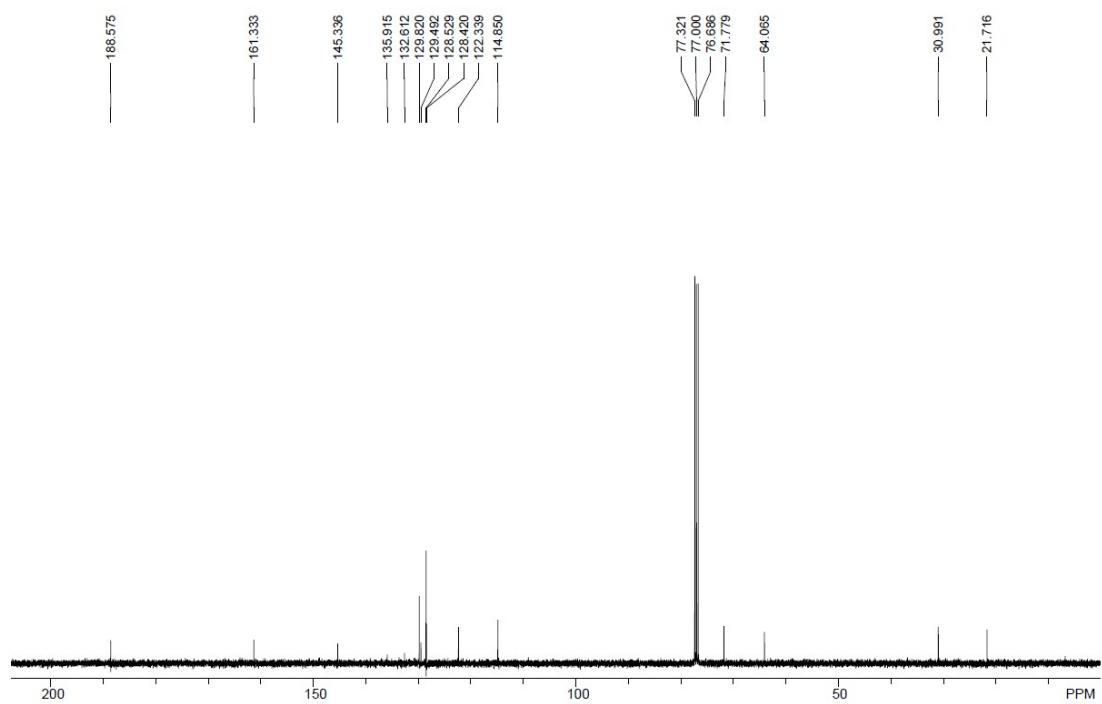


¹³C spectra of 3na

1-(2,3-dihydrobenzofuran-5-yl)-2-tosylethan-1-one (30a)

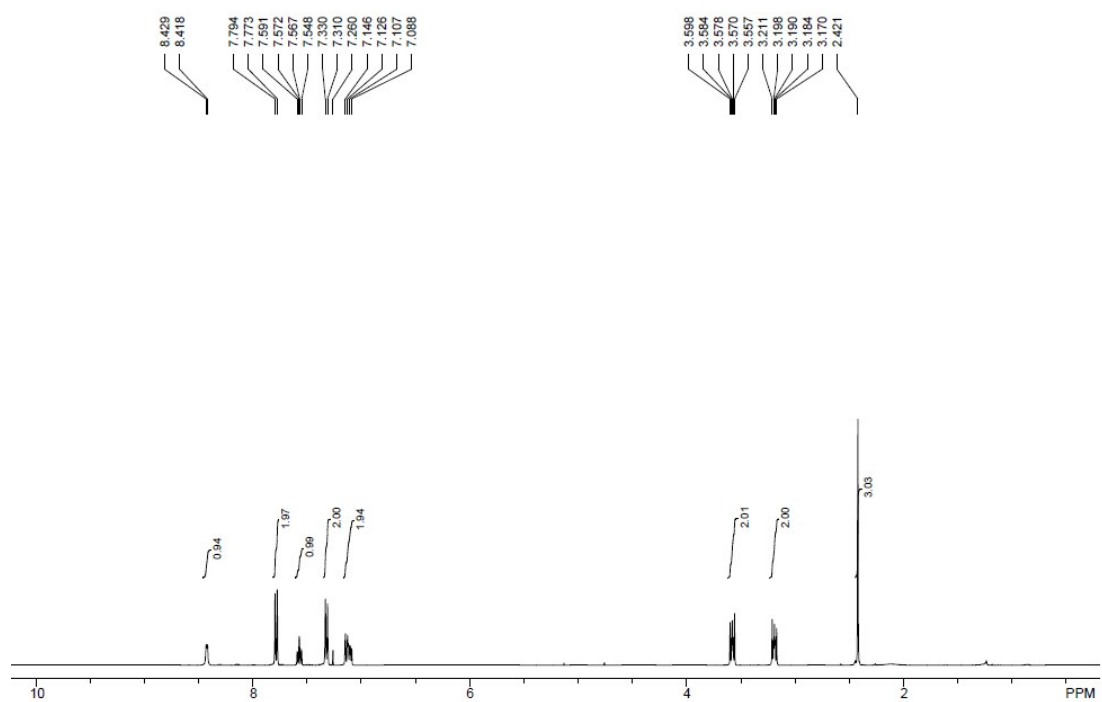


¹H spectra of 30a

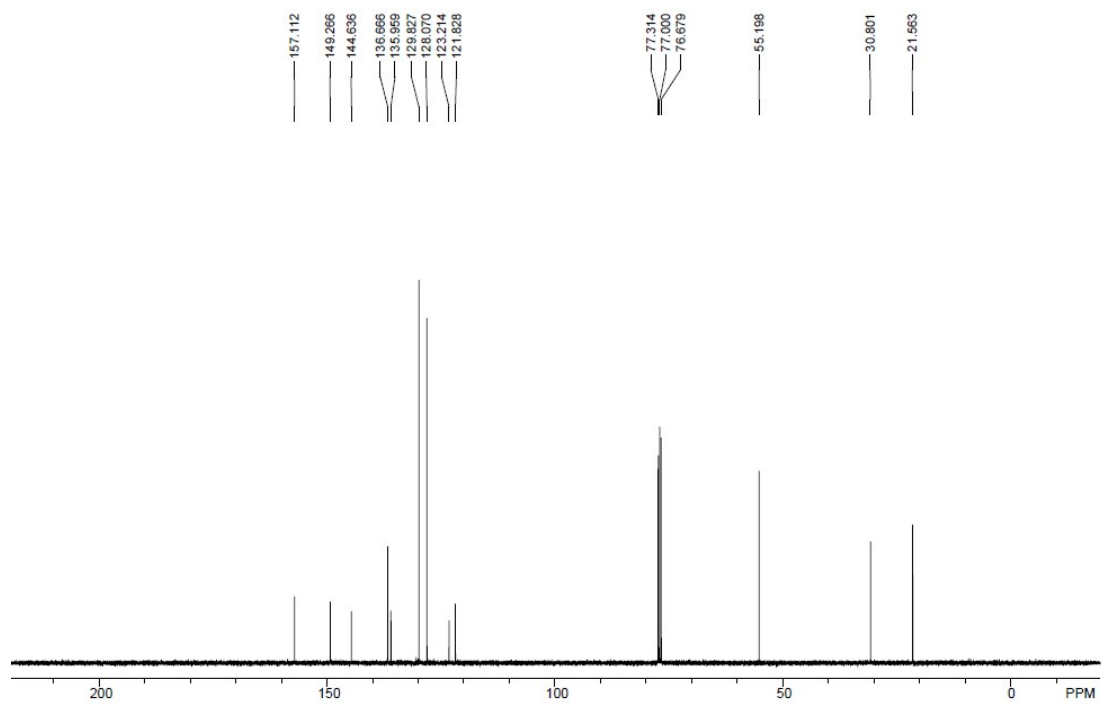


¹³C spectra of 30a

2-(2-tosylethyl)pyridine (3pa)

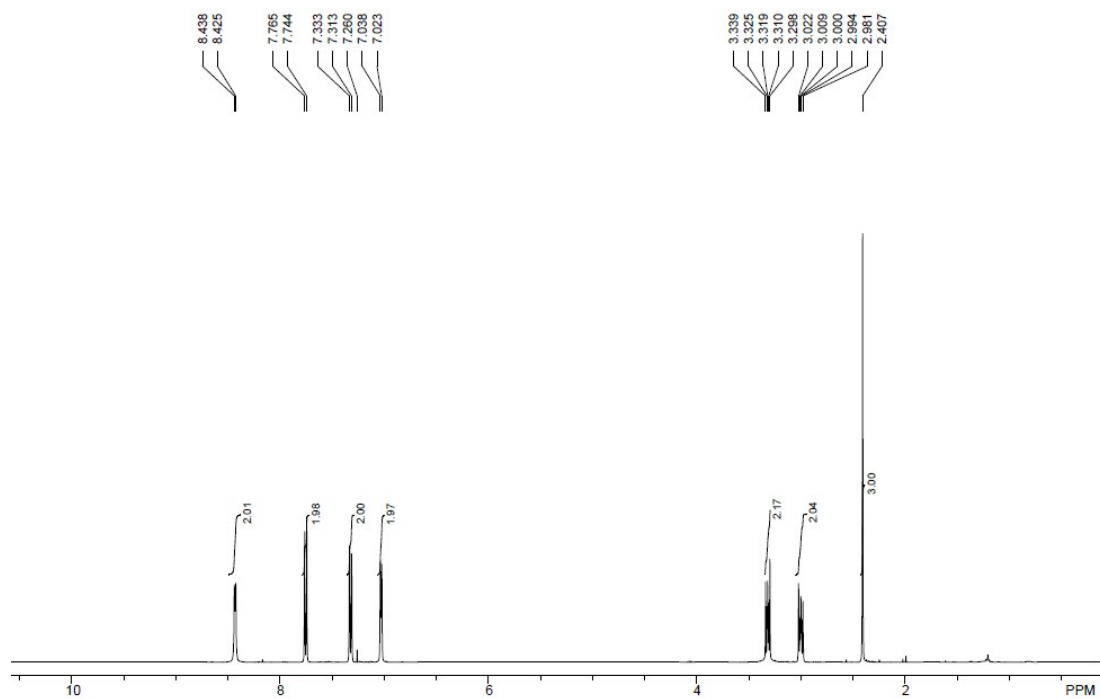


¹H spectra of 3pa

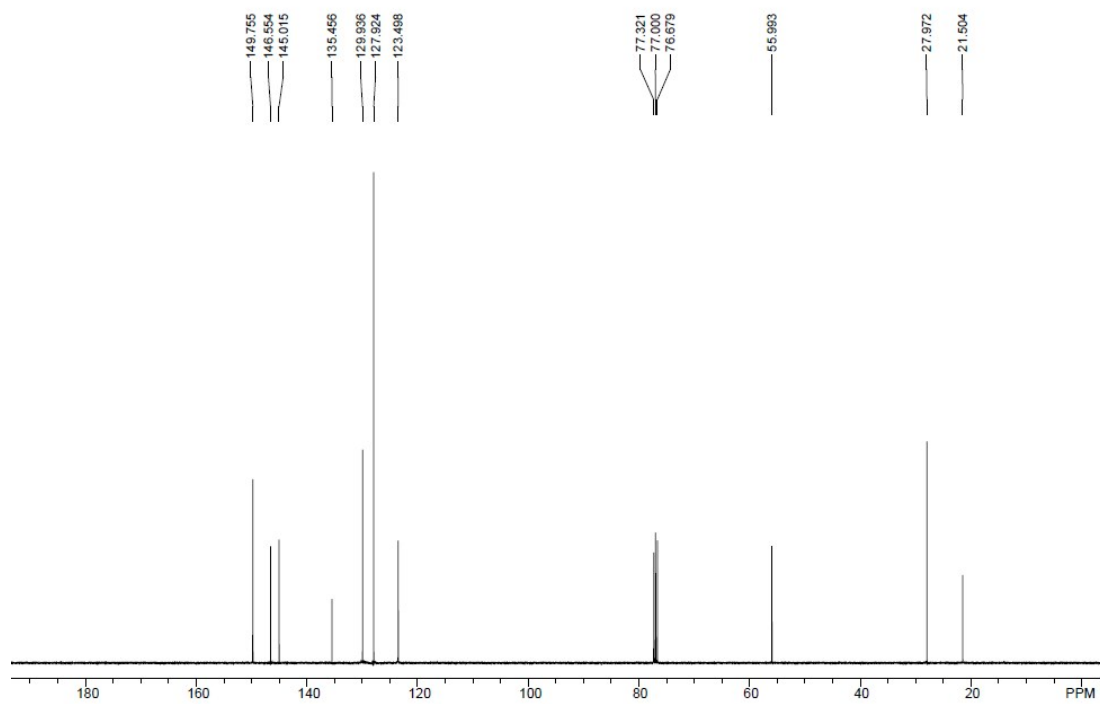


¹³C spectra of 3pa

4-(2-tosylethyl)pyridine (3qa)

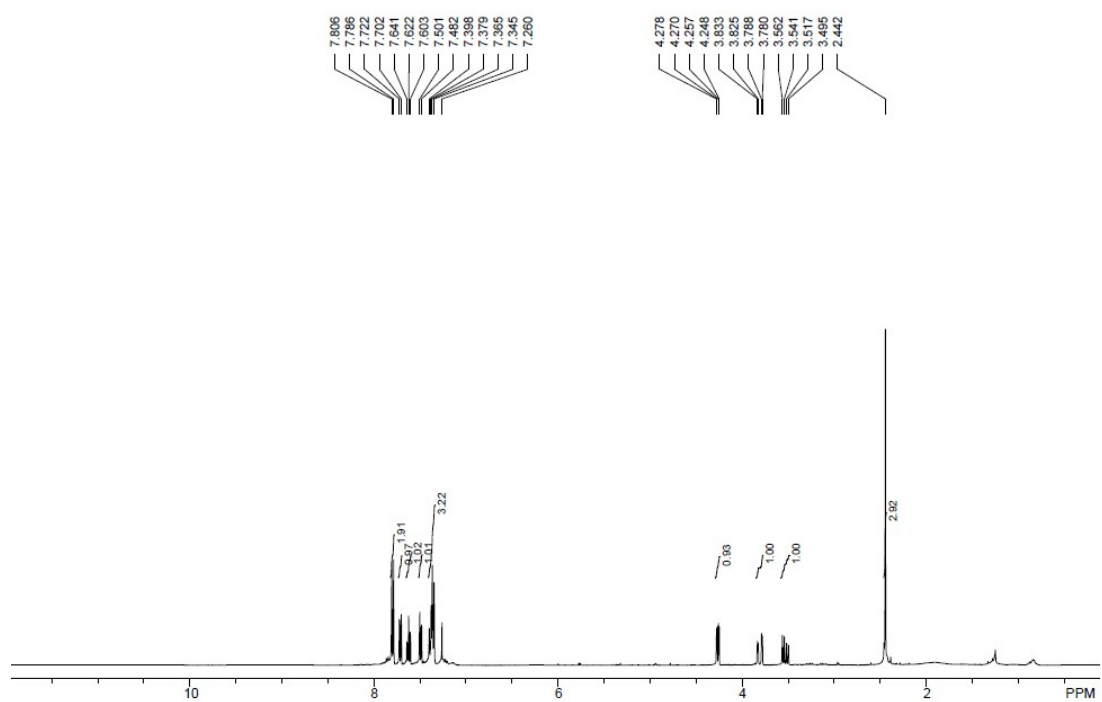


¹H spectra of 3qa

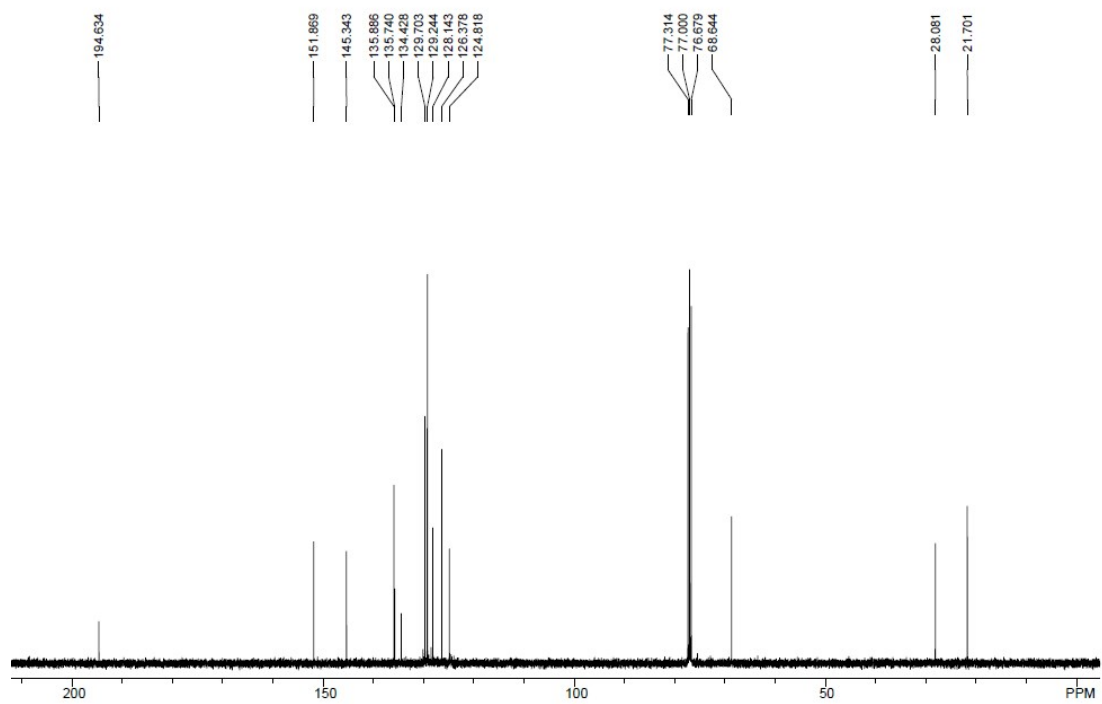


¹³C spectra of 3qa

2-tosyl-2,3-dihydro-1H-inden-1-one (3sa)

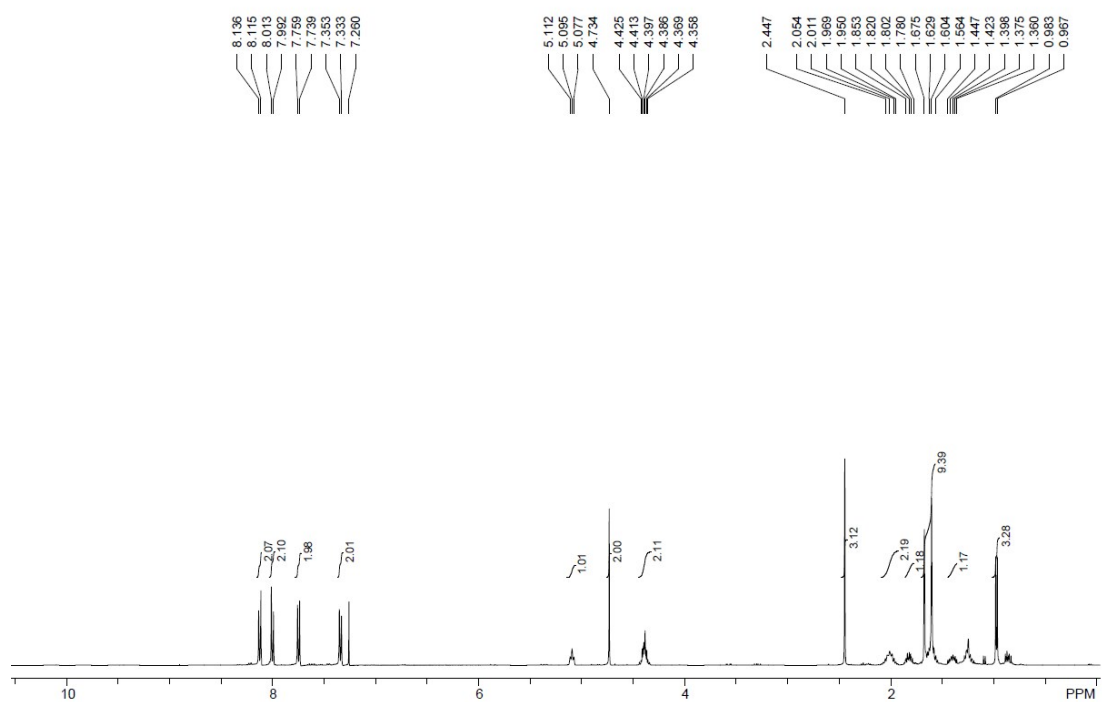


¹H spectra of 3sa

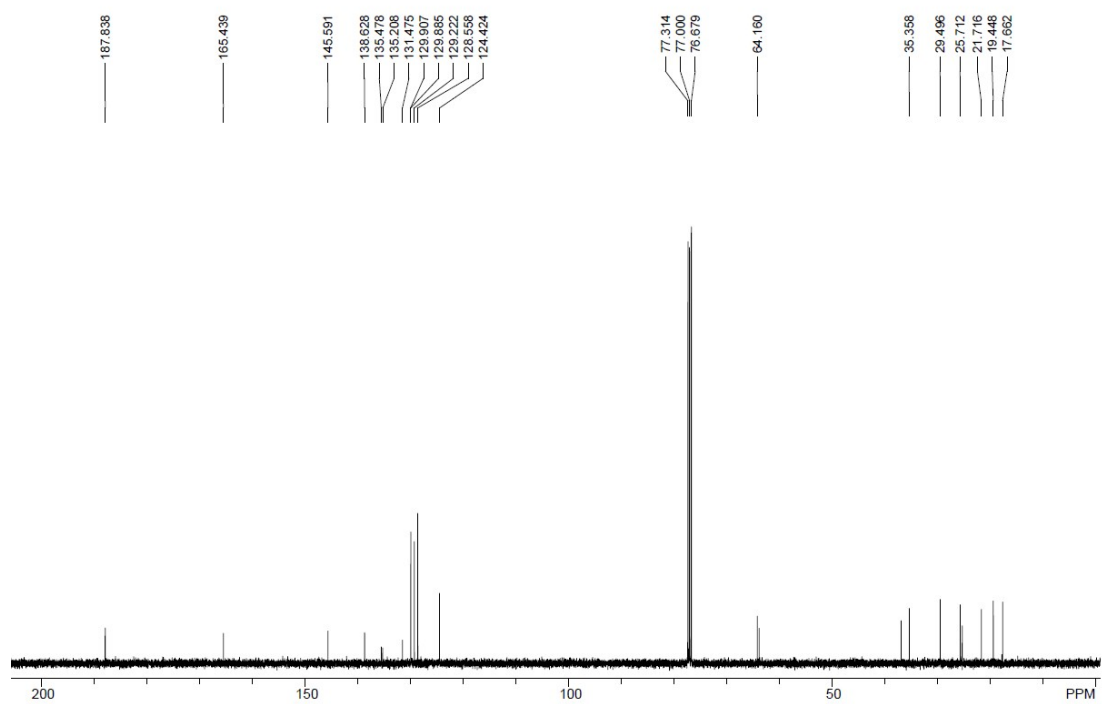


¹³C spectra of 3sa

3,7-dimethyloct-6-en-1-yl 4-(2-tosylacetyl)benzoate (3va)

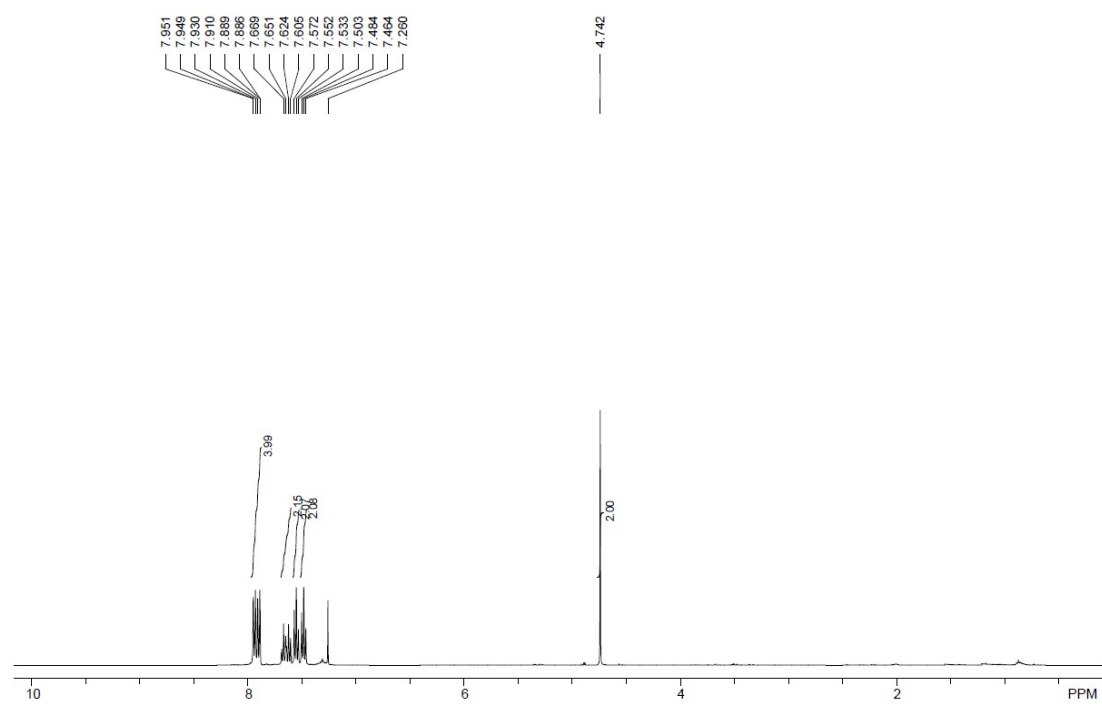


¹H spectra of 3va

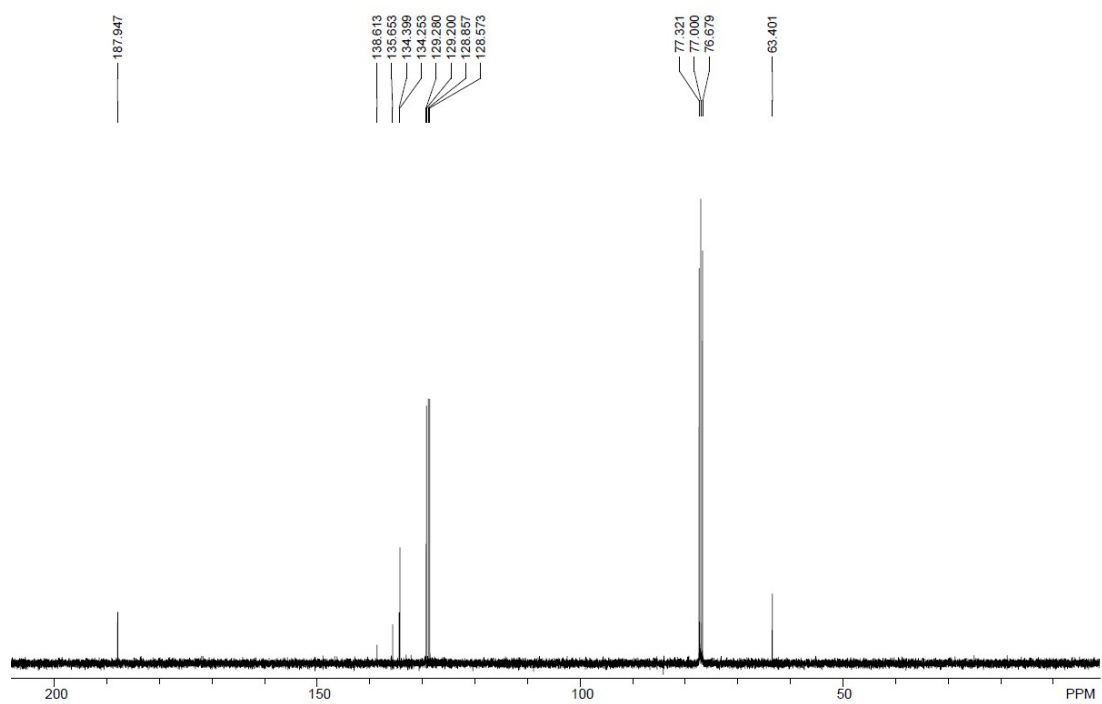


¹³C spectra of 3va

1-phenyl-2-(phenylsulfonyl)ethan-1-one (3ab)

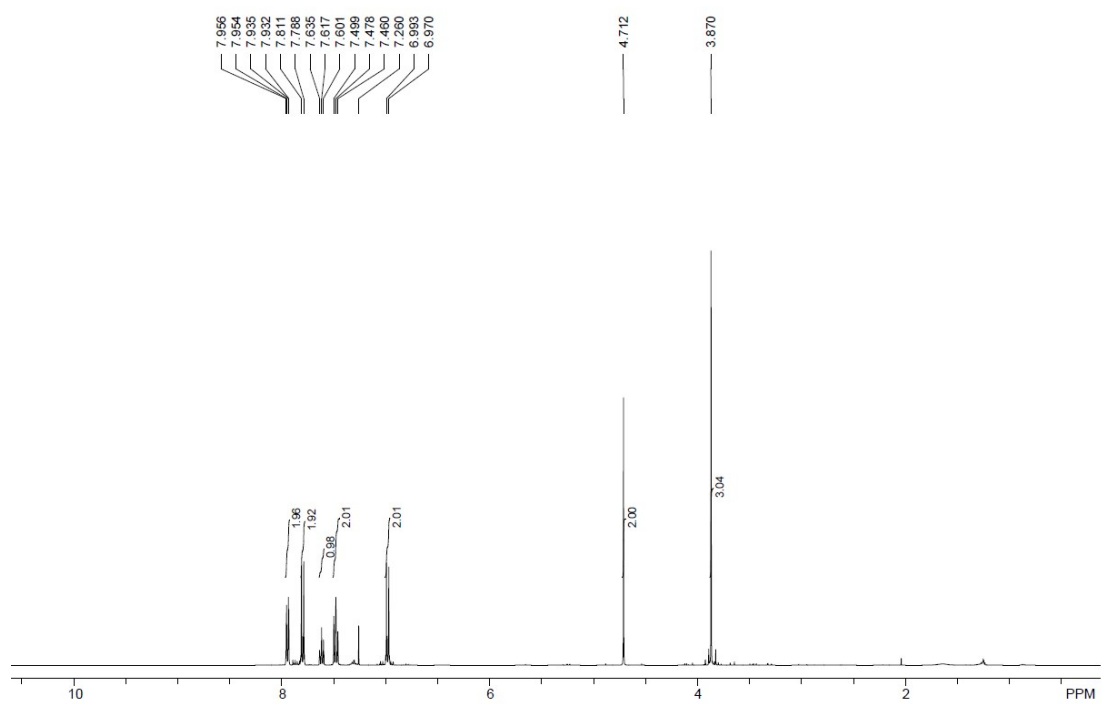


¹H spectra of 3ab

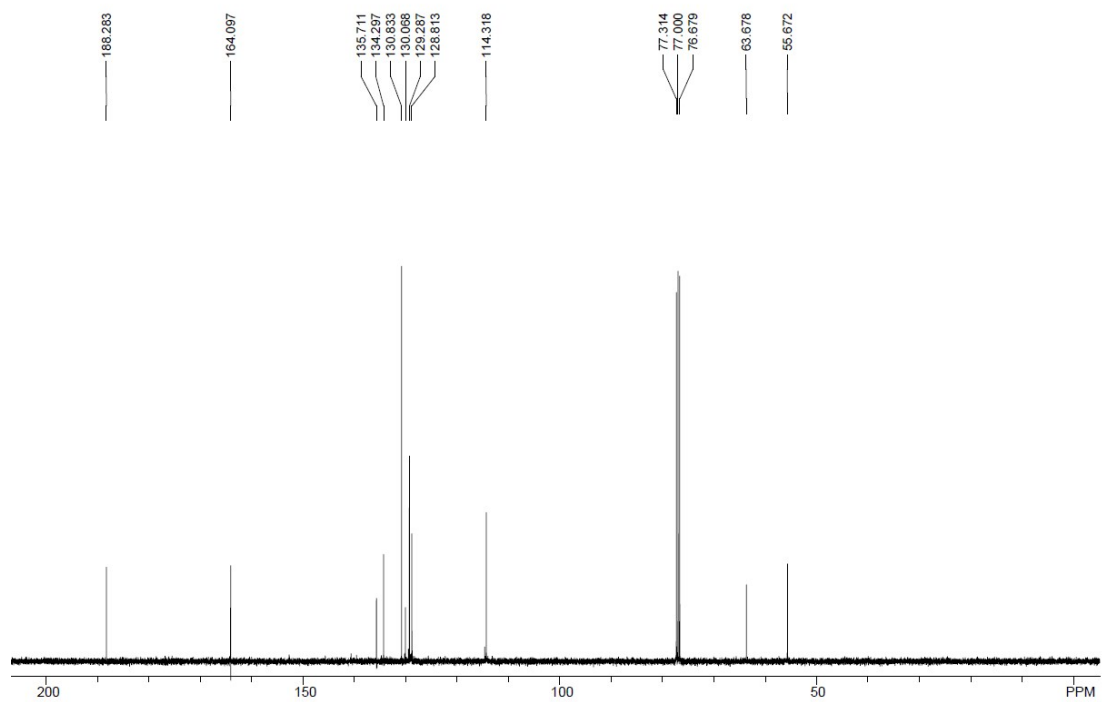


¹³C spectra of 3ab

2-((4-methoxyphenyl)sulfonyl)-1-phenylethan-1-one (3ac)

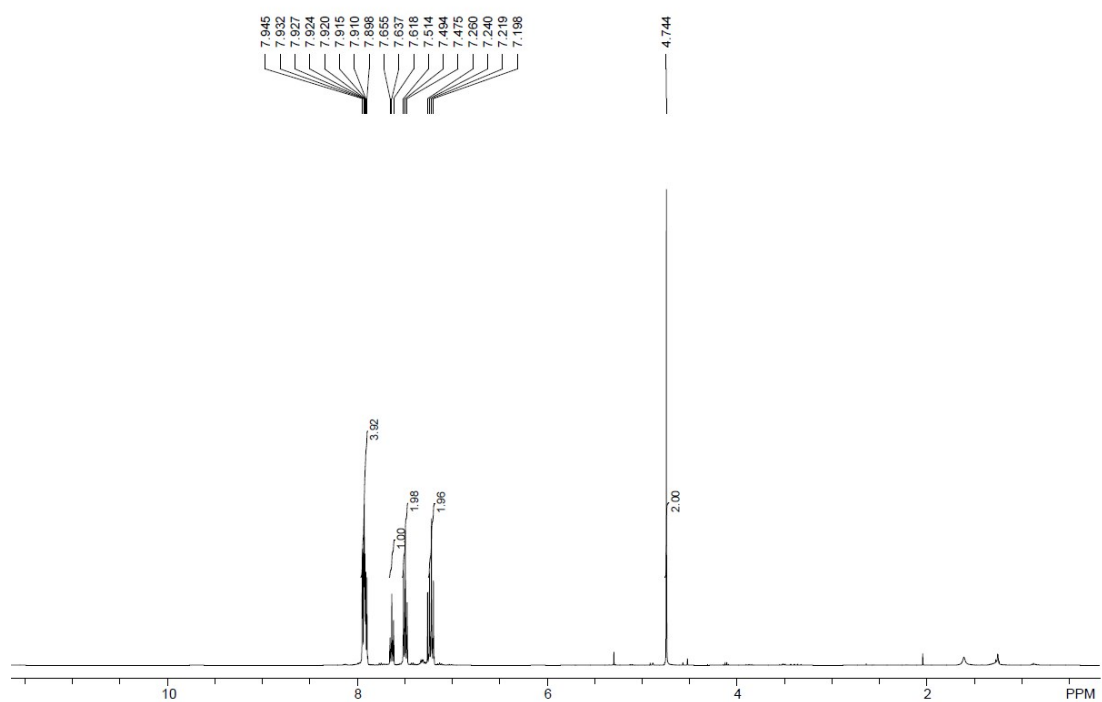


¹H spectra of 3ac

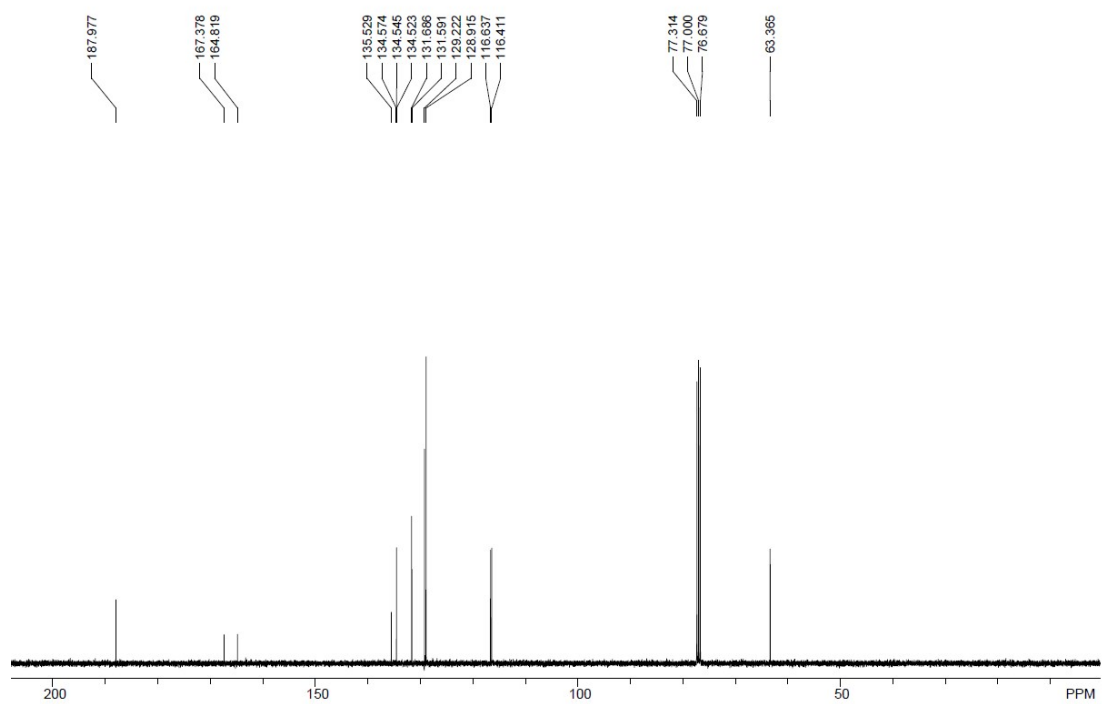


¹³C spectra of 3ac

2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-one (3ad)

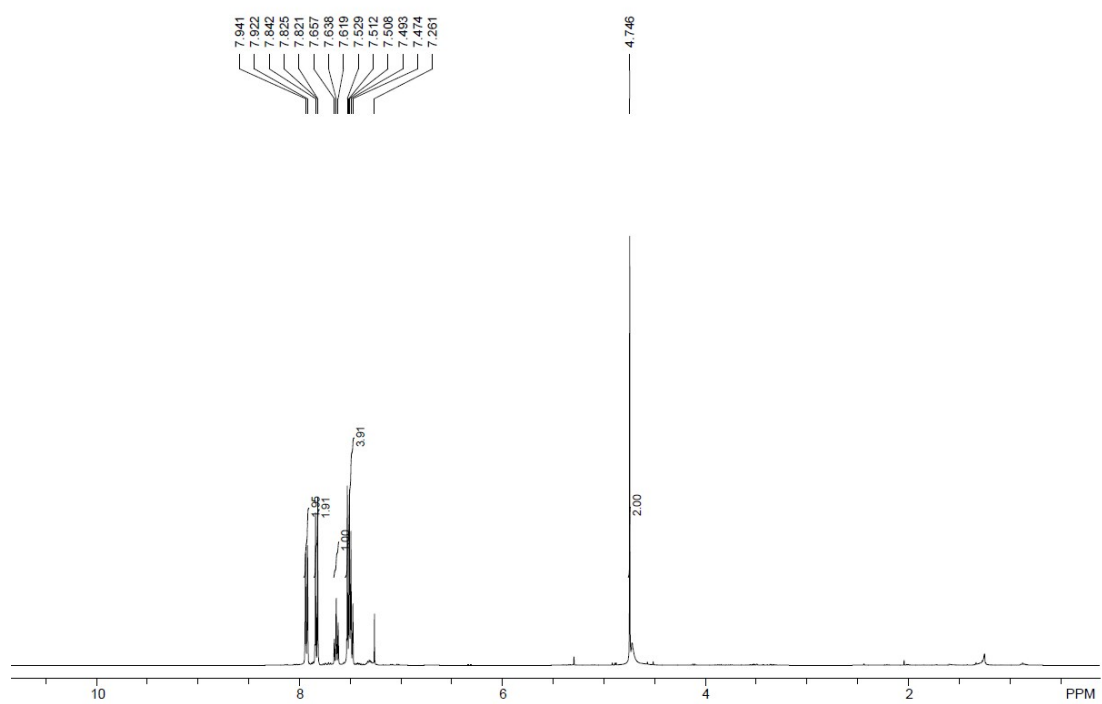


¹H spectra of 3ad

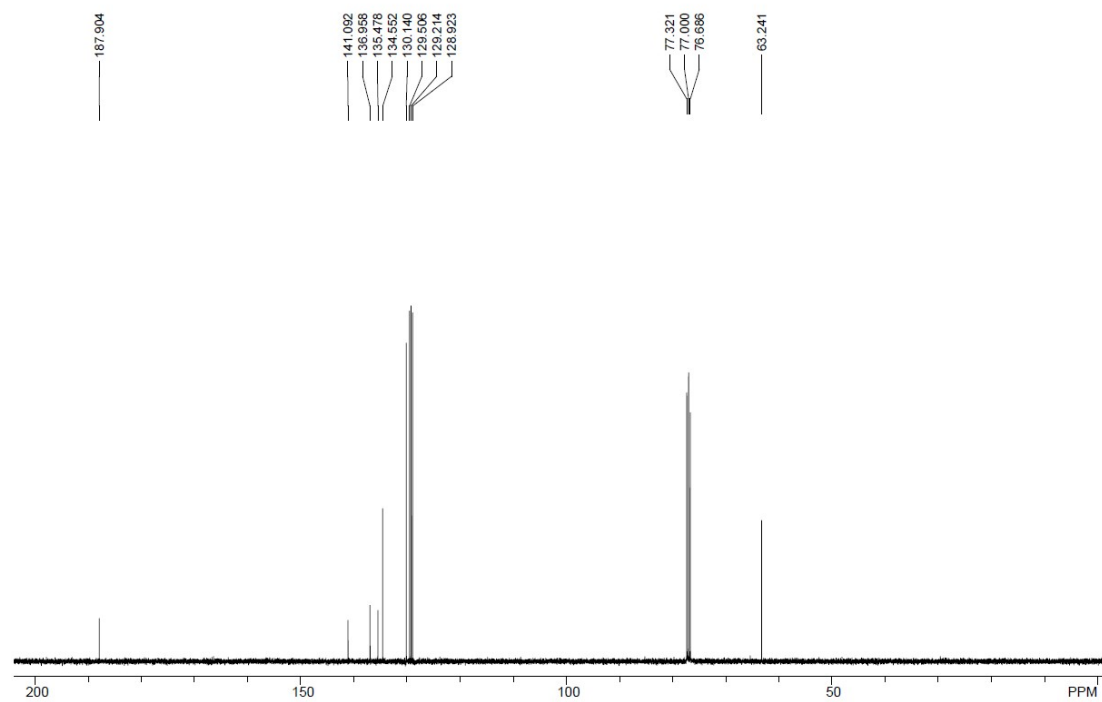


¹³C spectra of 3ad

2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one (3ae)

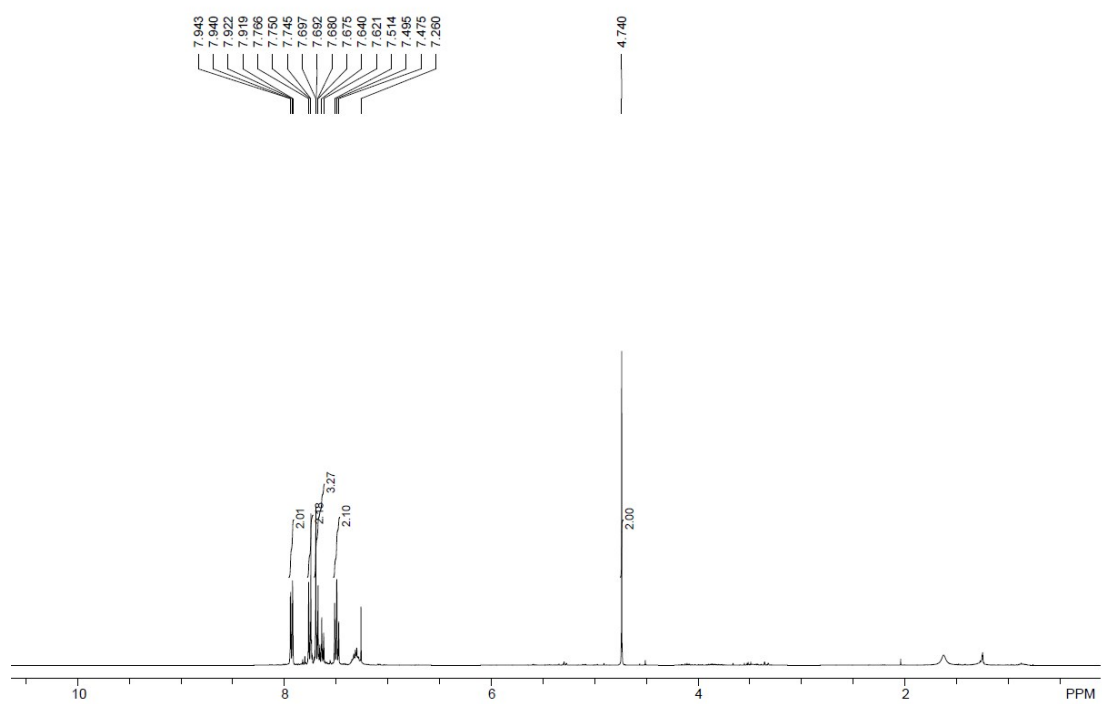


¹H spectra of 3ae

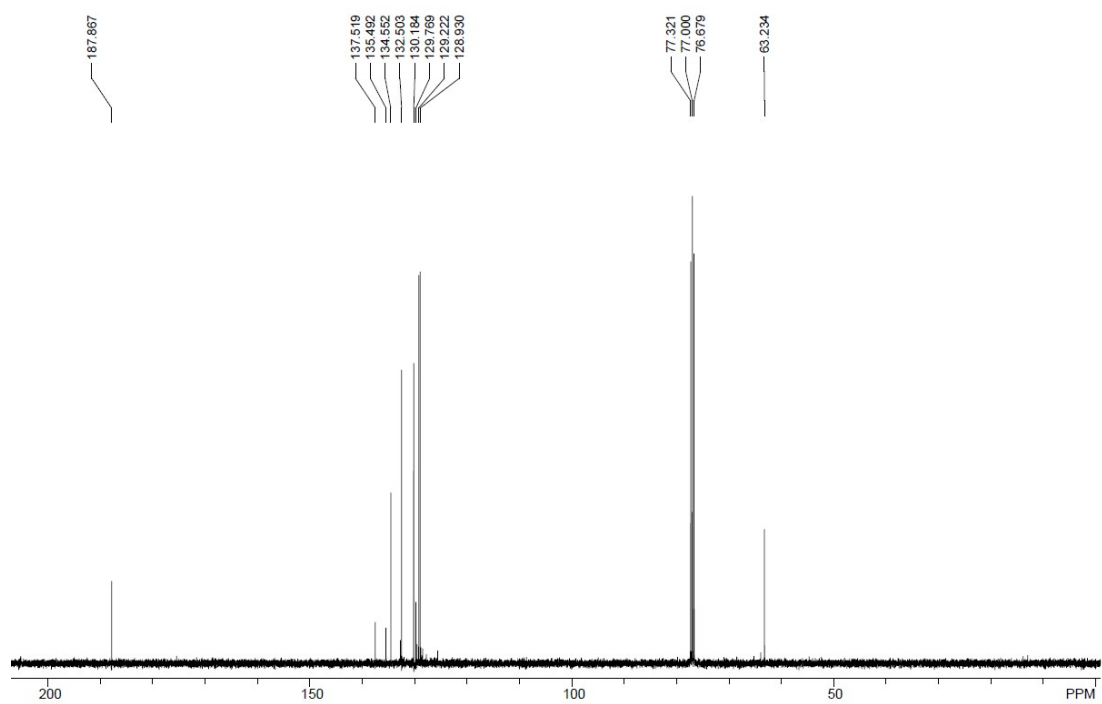


¹³C spectra of 3ae

2-((4-bromophenyl)sulfonyl)-1-phenylethan-1-one (3af)

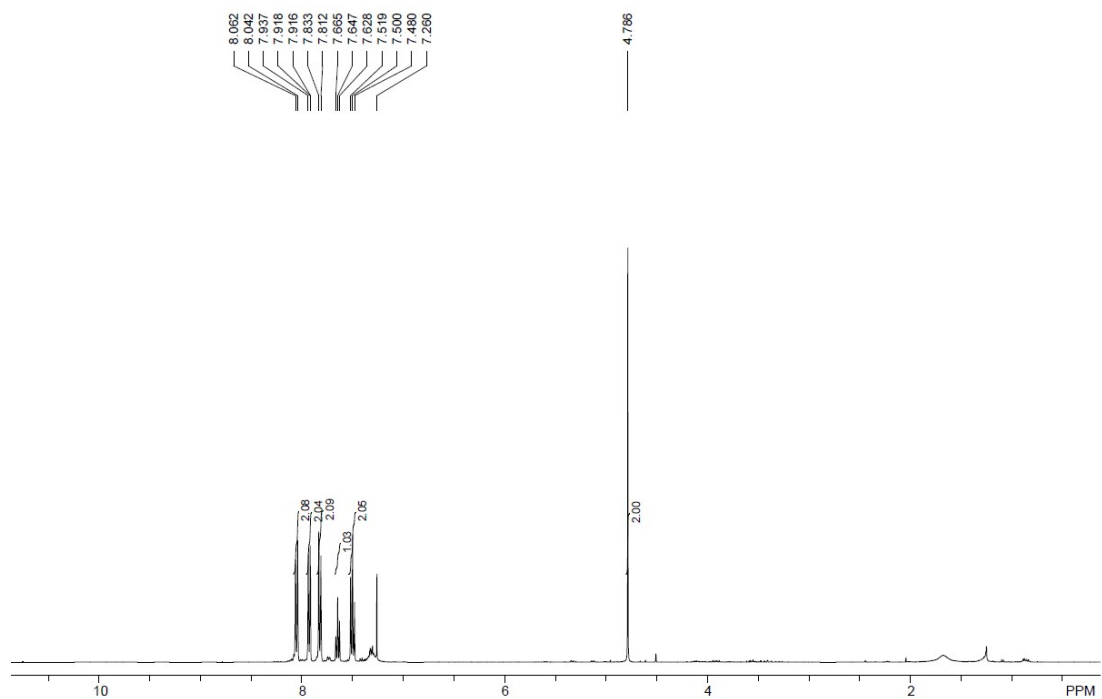


¹H spectra of 3af

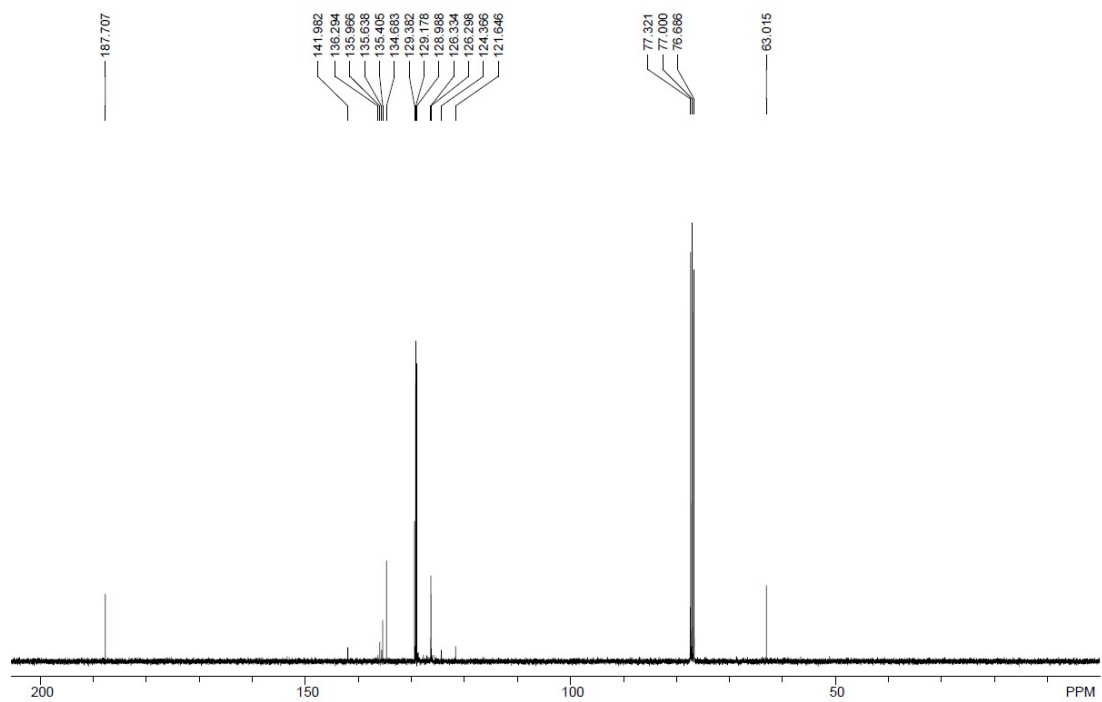


¹³C spectra of 3af

phenyl-2-((4-(trifluoromethyl)phenyl)sulfonyl)ethan-1-one (3ag)

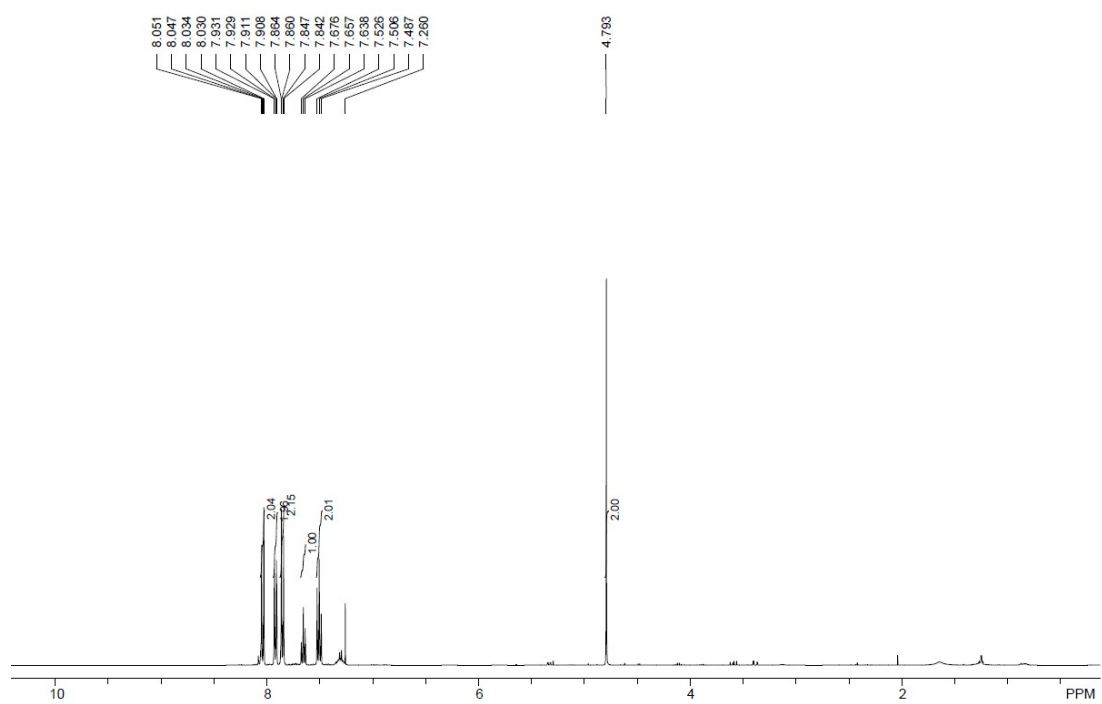


¹H spectra of 3ag

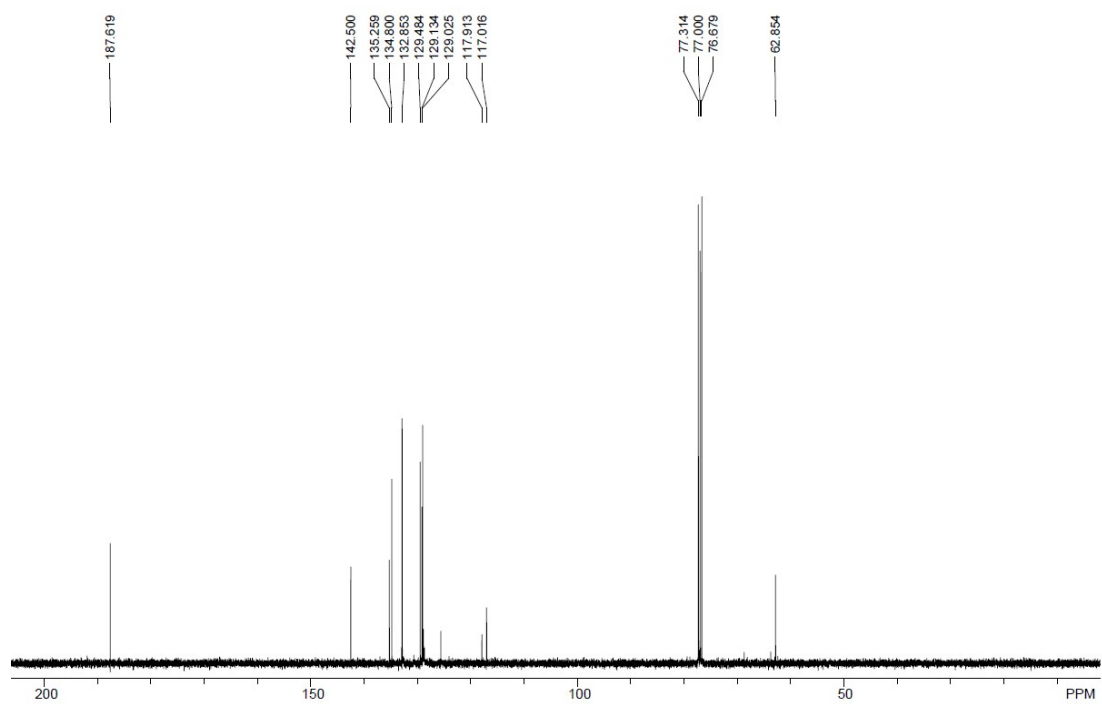


¹³C spectra of 3ag

4-((2-oxo-2-phenylethyl)sulfonyl)benzotrile (3ah)

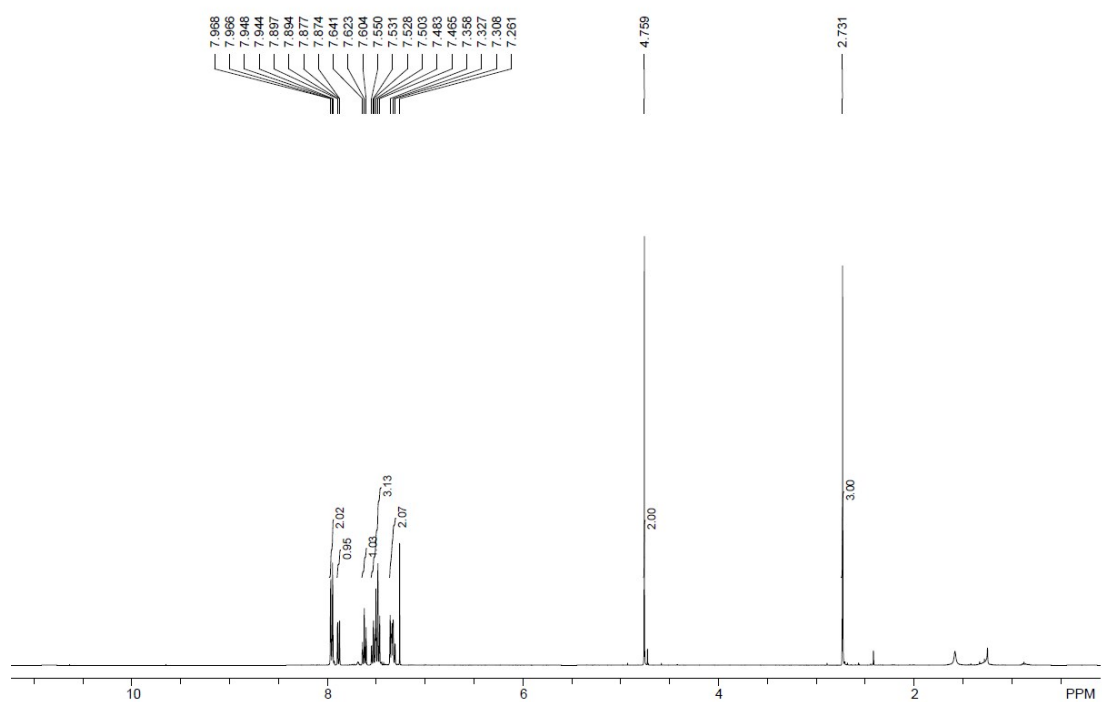


¹H spectra of 3ah

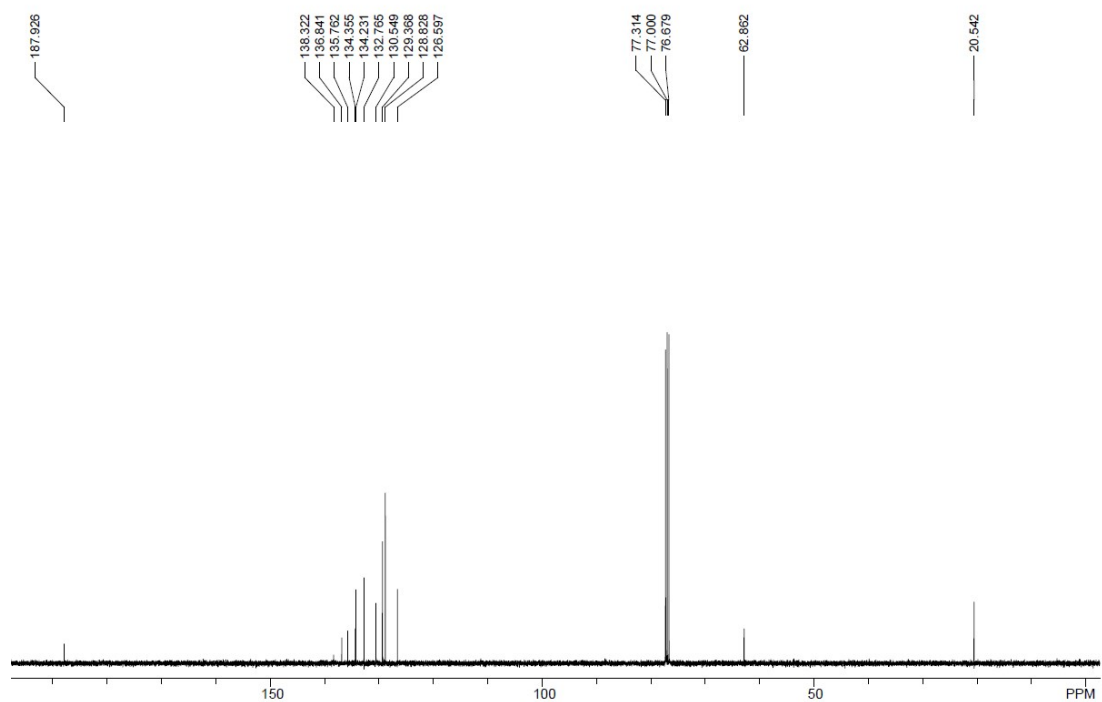


¹³C spectra of 3ah

1-phenyl-2-(o-tolylsulfonyl)ethan-1-one (3ai)

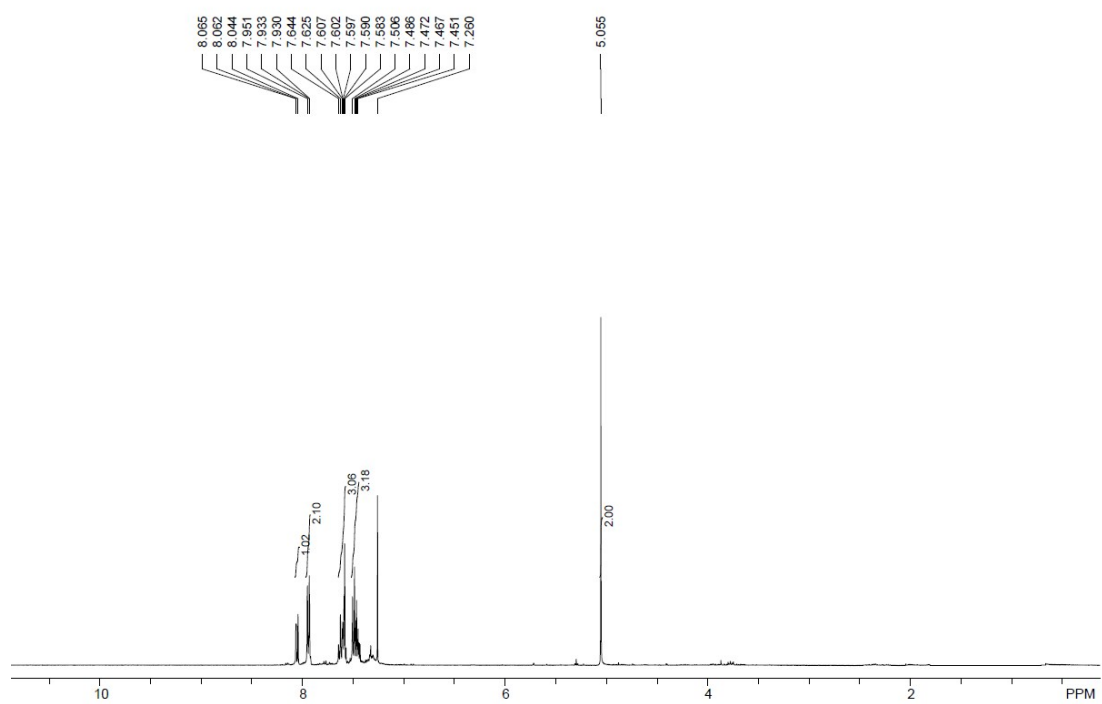


¹H spectra of 3ai

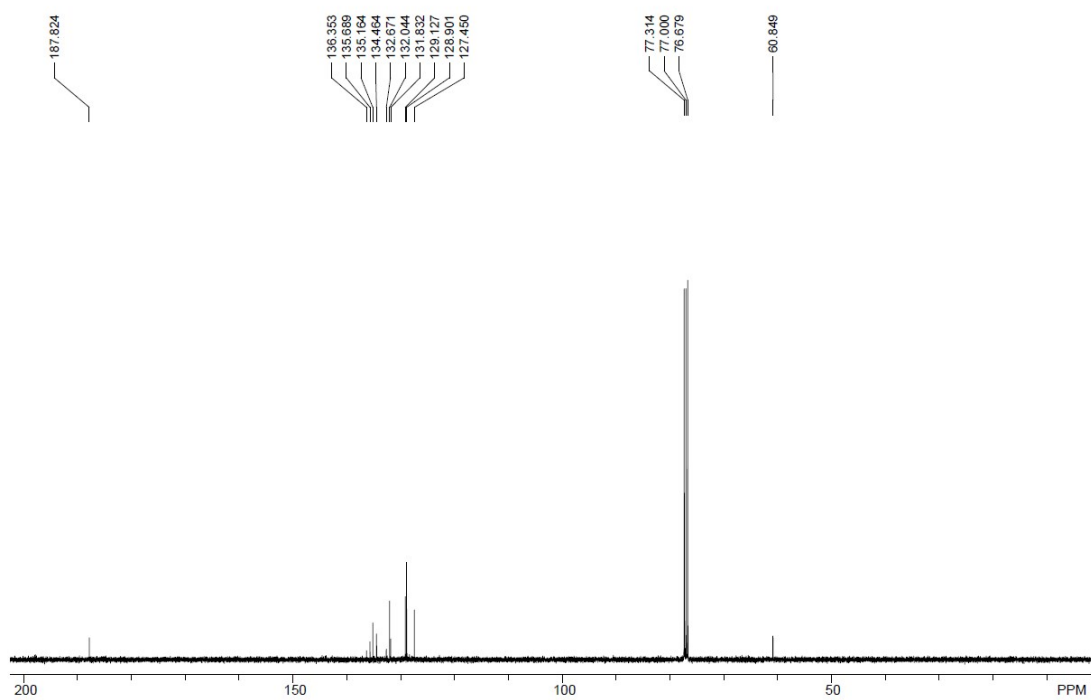


¹³C spectra of 3ai

2-((2-chlorophenyl)sulfonyl)-1-phenylethan-1-one (3aj)

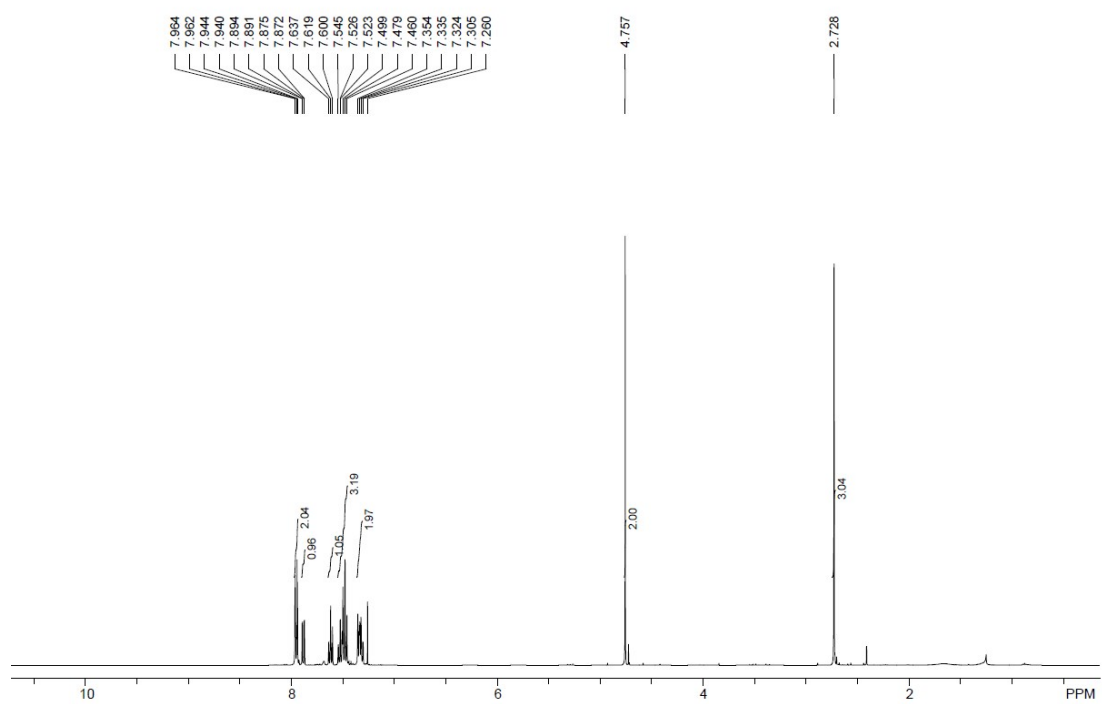


¹H spectra of 3aj

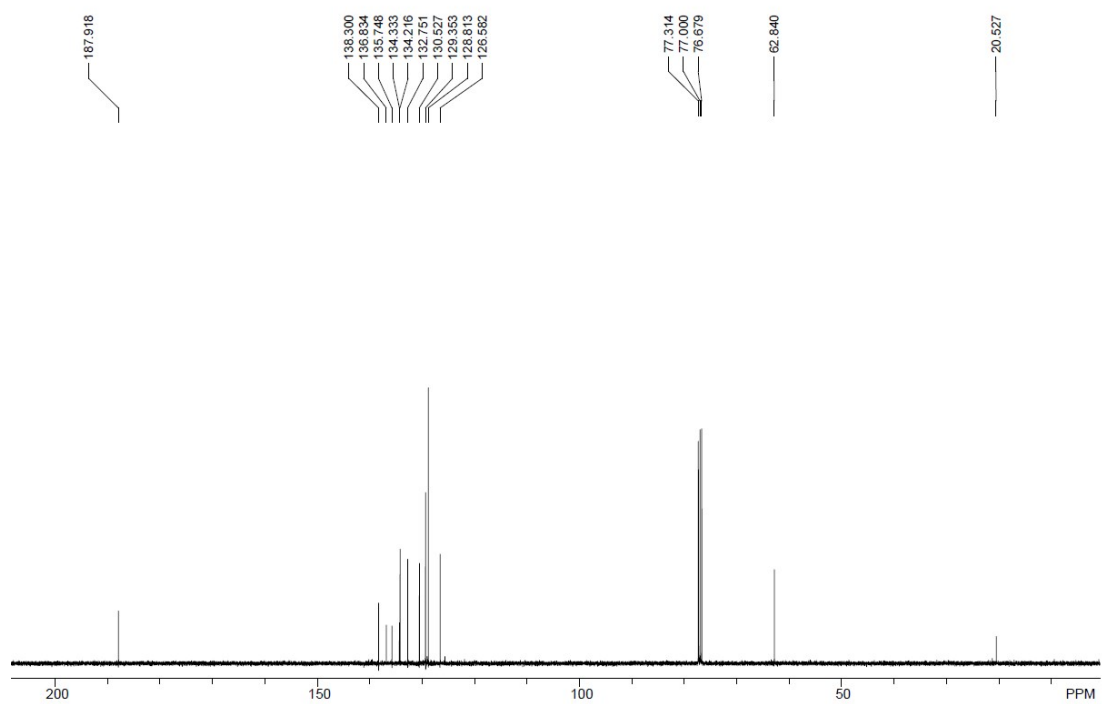


¹³C spectra of 3aj

1-phenyl-2-(m-tolylsulfonyl)ethan-1-one (**3ak**)

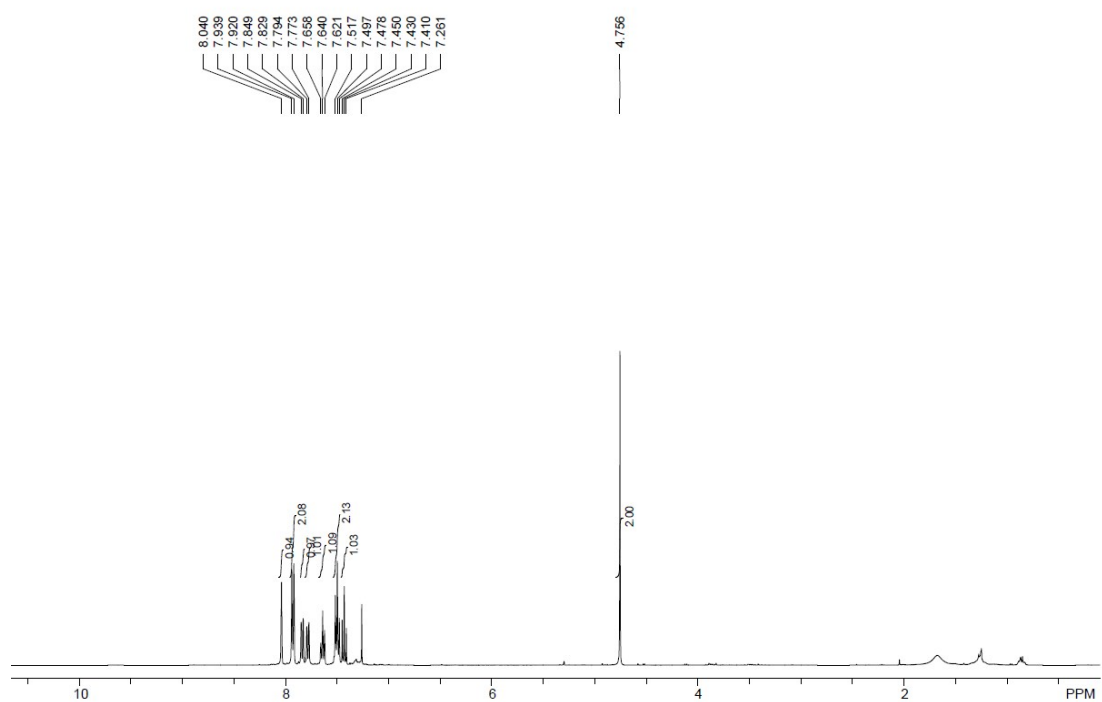


¹H spectra of **3ak**

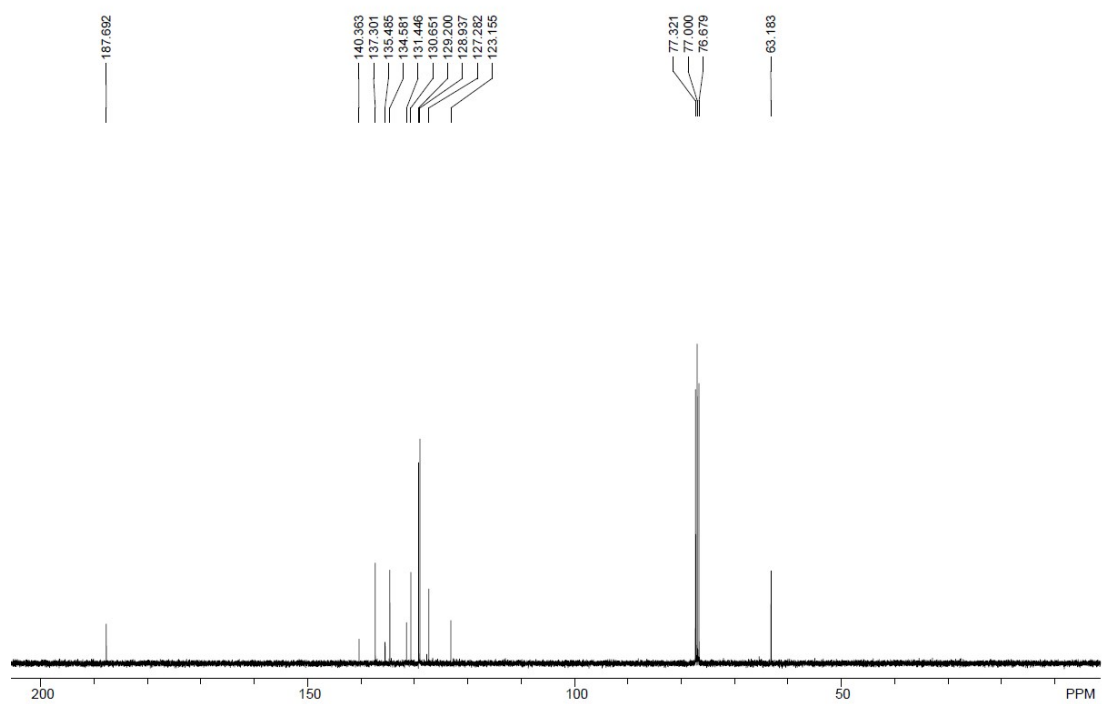


¹³C spectra of **3ak**

2-((3-bromophenyl)sulfonyl)-1-phenylethan-1-one (3al)

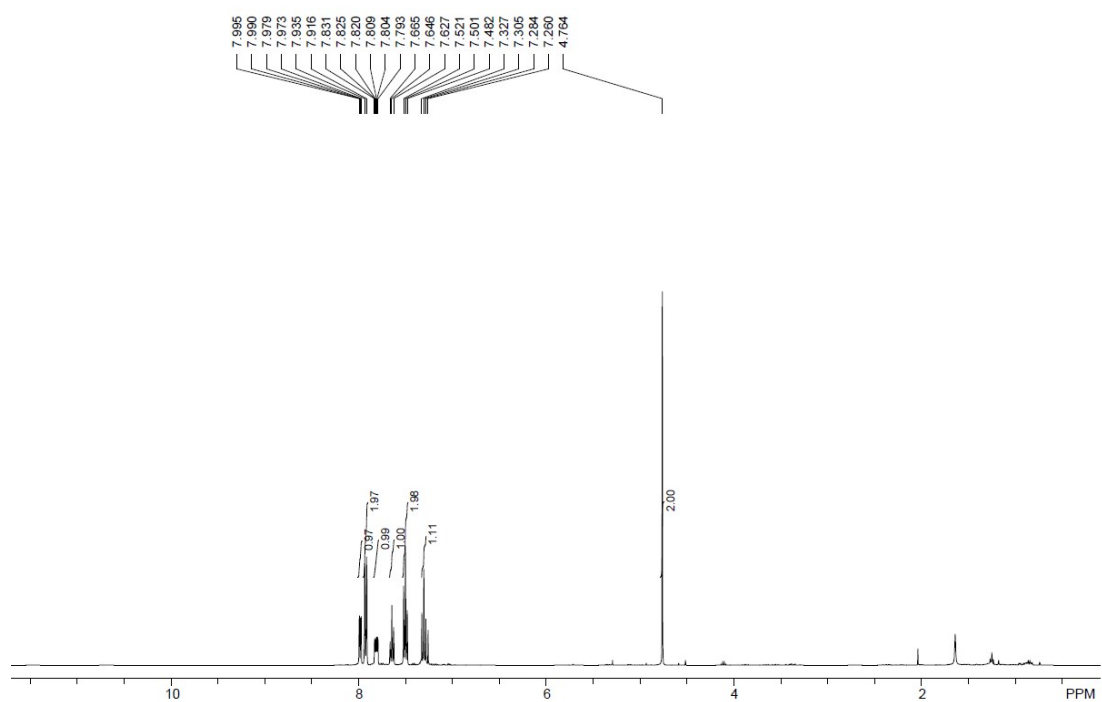


¹H spectra of 3al

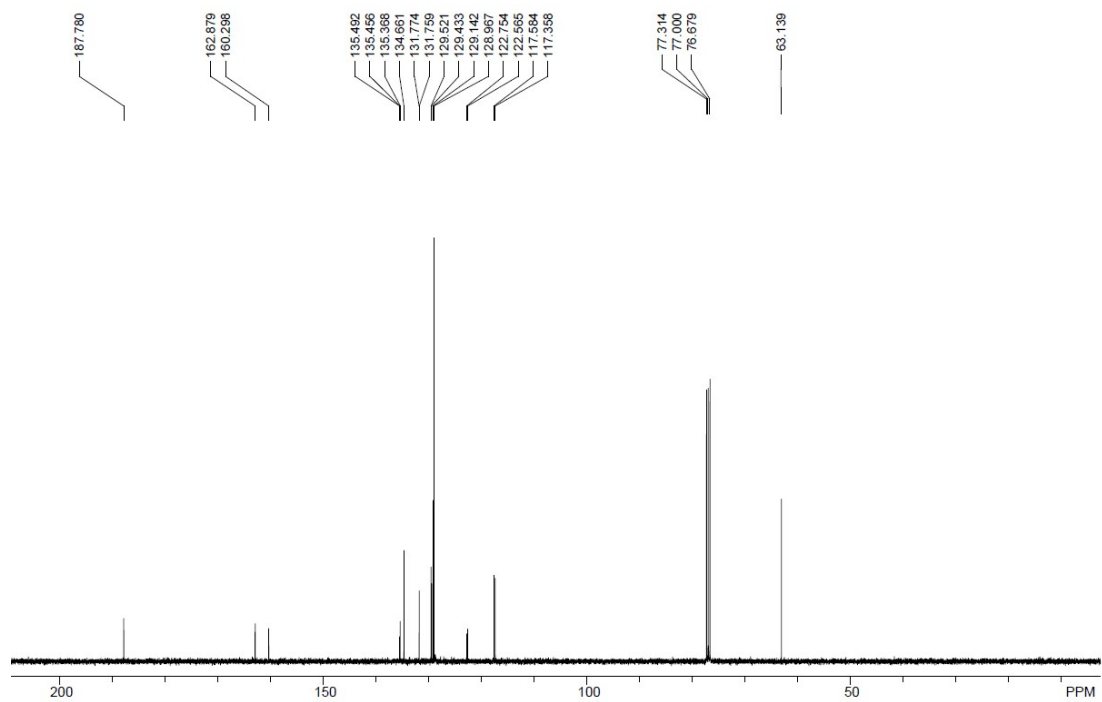


¹³C spectra of 3al

2-((3-chloro-4-fluorophenyl)sulfonyl)-1-phenylethan-1-one (3am)

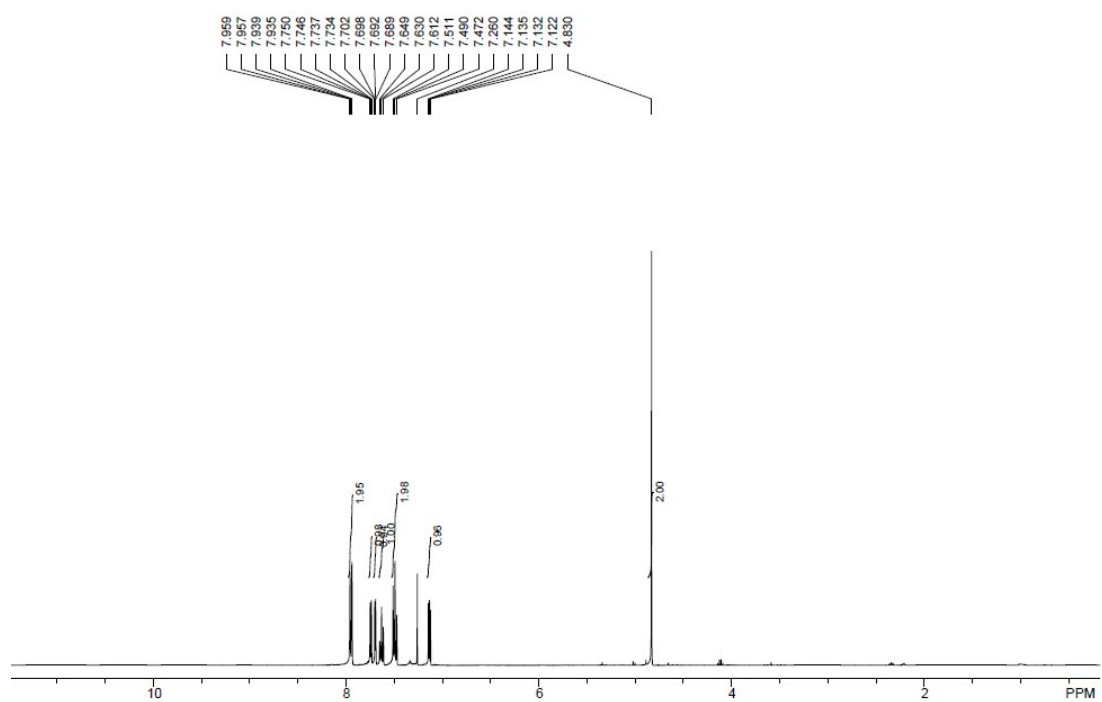


¹H spectra of 3am

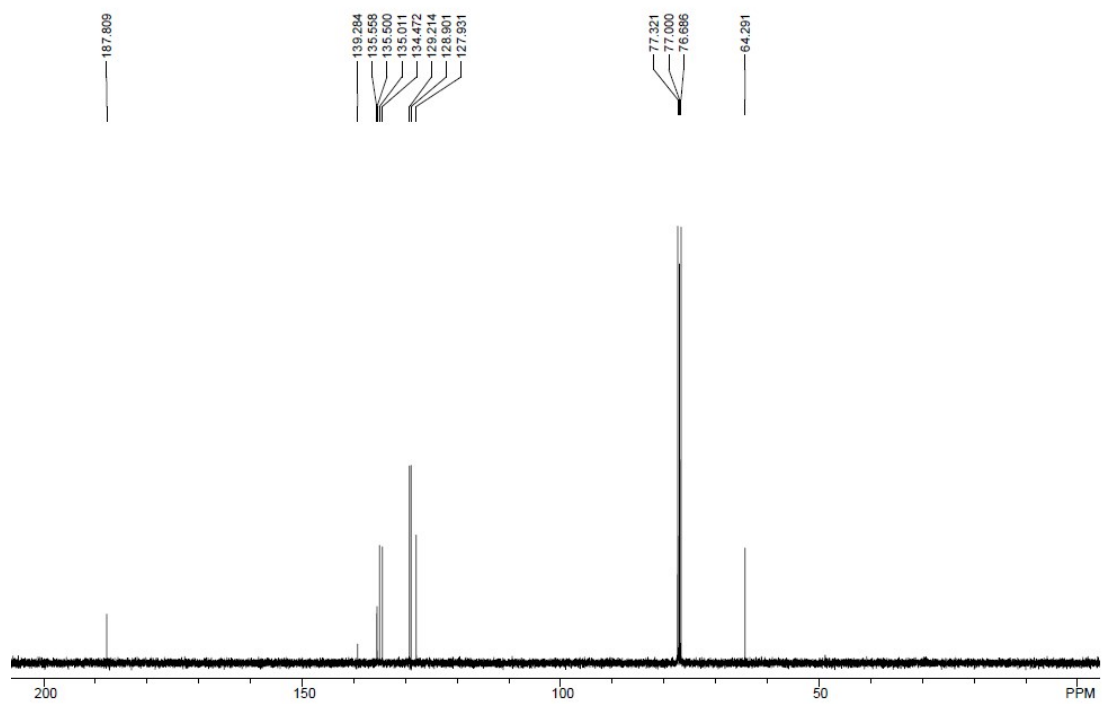


¹³C spectra of 3am

phenyl-2-(thiophen-2-ylsulfonyl)ethanone (3an)

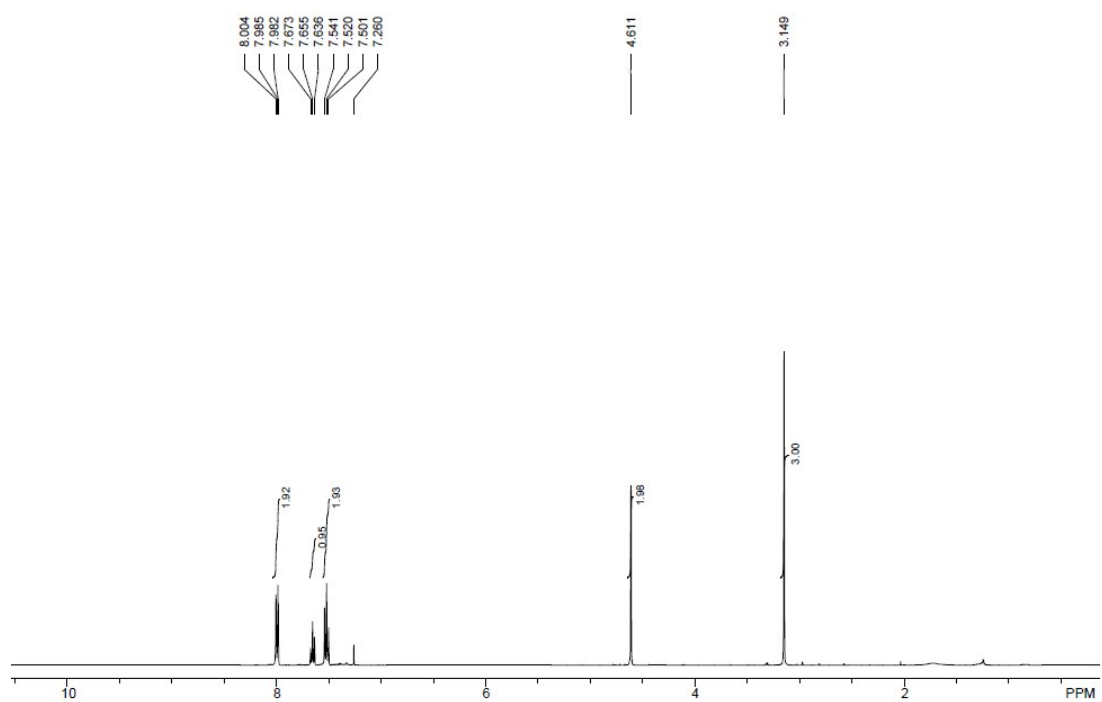


¹H spectra of 3an

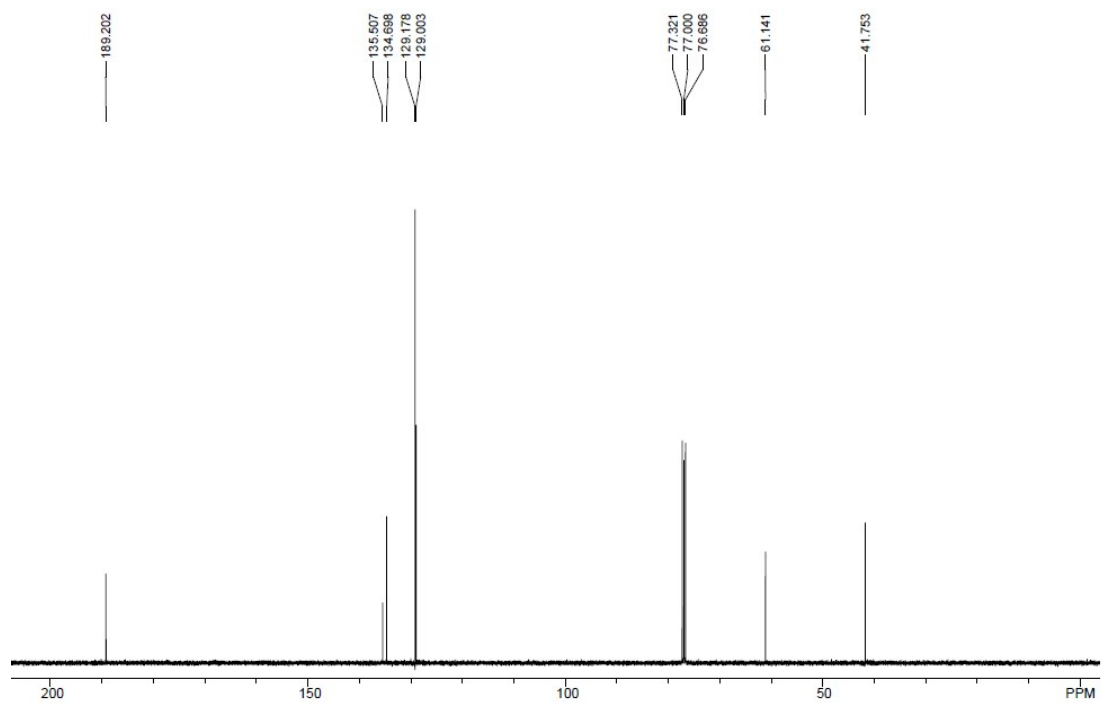


¹³C spectra of 3an

2-(methylsulfonyl)-1-phenylethanone (**3ao**)

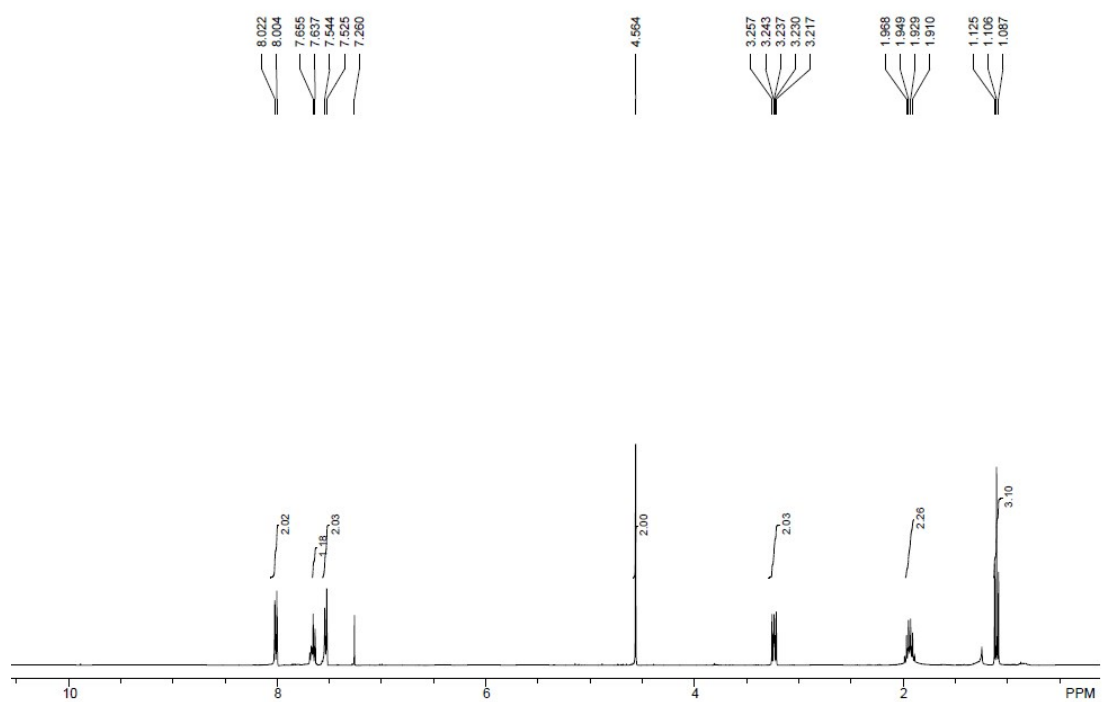


¹H spectra of **3ao**

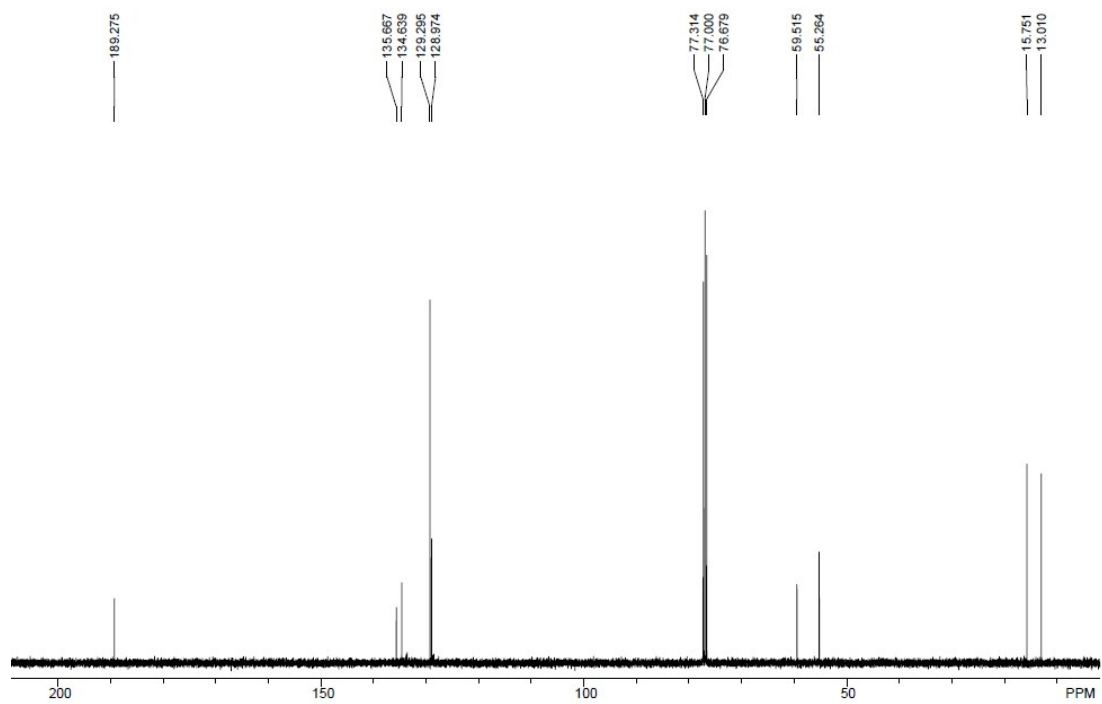


¹³C spectra of **3ao**

phenyl-2-(propylsulfonyl)ethanone (3ap)

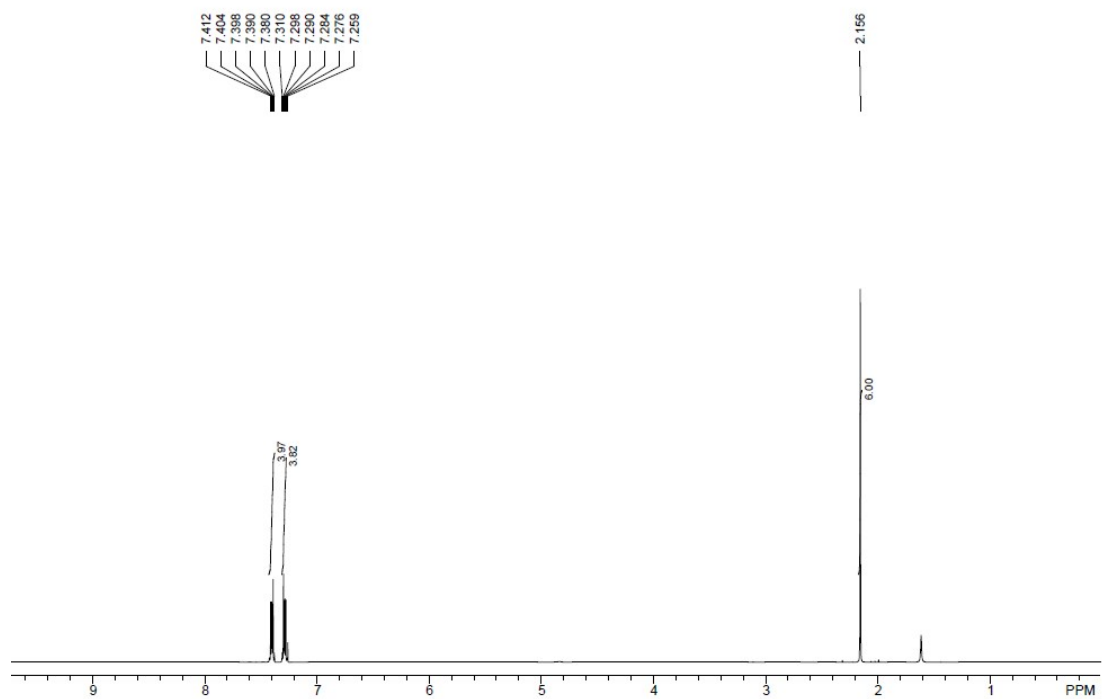


¹H spectra of 3ap

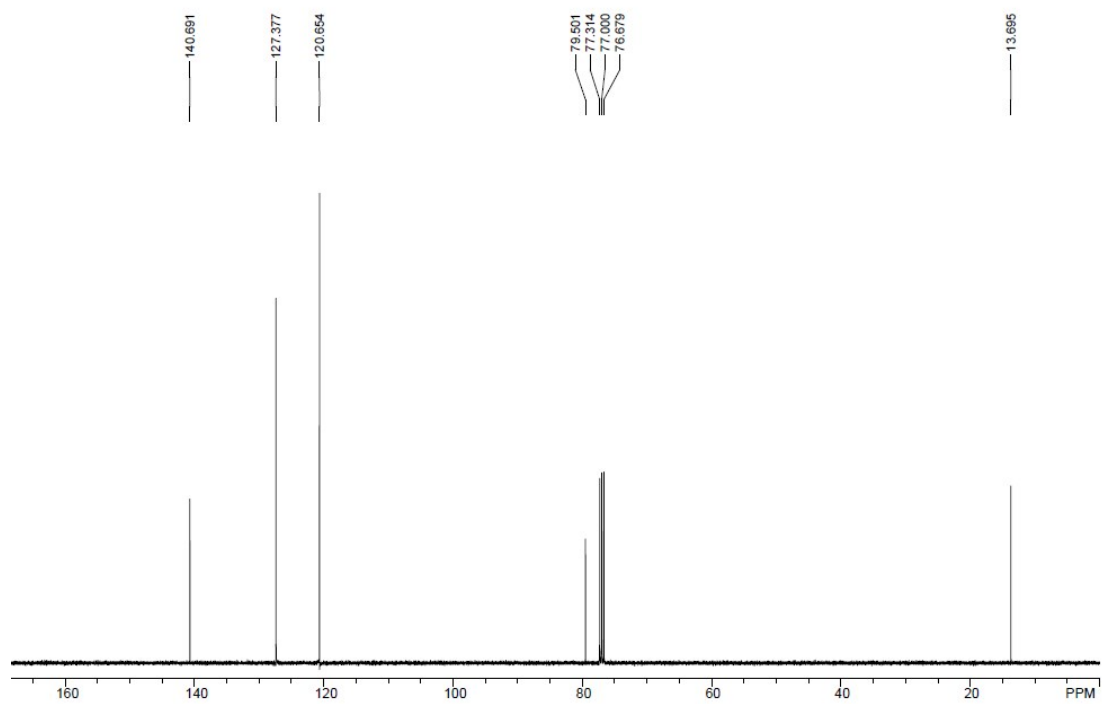


¹³C spectra of 3ap

9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene (5b)



¹H spectra of **5b**



¹³C spectra of **5b**