Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Catalyst-free sulfonylation of activated alkenes for highly efficient synthesis mono-substituted ethyl sulfones in water

*Yu Yang, Lin Tang, Sheng Zhang, Xuefeng Guo, Zhenggen Zha, Zhiyong Wang**

Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Soft Matter Chemistry & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei, 230026, P. R. China. Fax: (+86) 551-360-3185; E-mail: zwang3@ustc.edu.cn.

Contents:

General Remarks

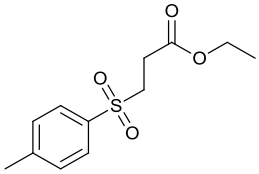
All substrates were purchased commercially without further purification. The yields were determined using arylsulfonyl hydrazides as an internal standard.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 FT spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. UV-Vis Spectrophotometry was carried out on Shimadzu UV-3000. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass).

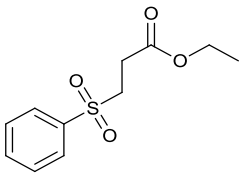
General procedures for the synthesis of Arylsulfonyl Hydrazides

Arylsulfonyl hydrazides **2b-2s** were prepared according to the literature procedure.[1] To a solution of an arylsulfonyl chloride (3.0 mmol) in tetrahyrdofuran (15 mL), was added hydrazine monohydrate (375 mg, 7.5 mmol) dropwise under nitrogen at 0 ℃. After vigorous stirring for 30 min at 0 ℃, the reaction mixture was added ethyl acetate (60 mL), and washed with saturated brine (3 x 10 mL). The organic layer was dried over sodium sulfate, filtered, concentrated and added to hexane (12 mL) over 5 min. The mixture was filtered, and the collected solid was dried in vacuum.

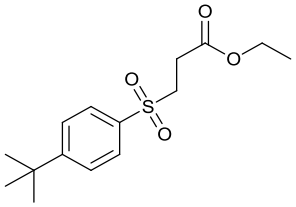
Characterization data of products



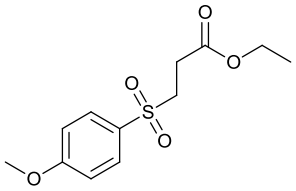
Propanoic acid, 3-[(4-methylphenyl)sulfonyl]-, ethyl ester (3aa). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 95% yield; mp = 42-43 ℃; The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 81% yield; mp = 115-117 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.46 (s, 3H), 2.73 (t, *J* = 7.8 Hz, 2H), 3.41 (t, *J* = 7.6 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 170.0, 145.0, 135.5, 130.0, 128.1, 61.3, 51.5, 27.9, 21.6, 14.0; IR (film, ν/cm^{-1}): 3389, 2932, 1731, 1075; HRMS $[M+H]^{+}$ calcd for $C_{12}H_{16}O_4S$: 257.0848, found 257.0833.



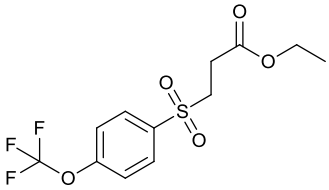
Propanoic acid, 3-(phenylsulfonyl)-, ethyl ester (3ab). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a colorless oil: 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.75 (t, *J* = 7.9 Hz, 2H), 3.44 (t, *J* = 7.6 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 7.51 - 7.61 (m, 2H), 7.66 - 7.70 (m, 1H), 7.91 - 7.94 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 170.0, 138.5, 134.0, 129.4, 128.2, 61.4, 51.5, 27.9, 14.1; IR (film, ν/cm^{-1}): 3390, 2933, 1732, 1044; HRMS $[M+H]^+$ calcd for $C_{11}H_{14}O_4S$: 243.0691, found 243.0693.



Propanoic acid, 3-[[4-(1,1-dimethylethyl)phenyl]sulfonyl]-, ethyl ester (3ac). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 94% yield; mp = 79-80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.1 Hz, 3H), 1.36 (s, 9H), 2.75 (t, *J* = 7.7 Hz, 2H), 3.42 (t, *J* = 7.8 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 170.1, 158.0, 135.5, 128.1, 126.4, 61.3, 51.6, 35.3, 31.1, 28.0, 14.0; IR (film, ν/cm^{-1}): 3275, 2929, 1727, 1045; HRMS $[M+H]^+$ calcd for $C_{15}H_{22}O_4S$: 299.1317, found 299.1314.

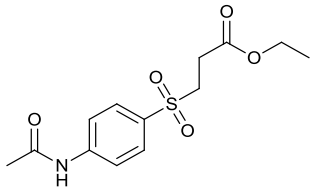


Propanoic acid, 3-[(4-methoxyphenyl)sulfonyl]-, ethyl ester (3ad). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a colorless oil: 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.73 (t, *J* = 7.7 Hz, 2H), 3.40 (t, *J* = 7.7 Hz, 2H), 3.89 (s, 3H), 4.09 (q, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 170.1, 164.0, 130.4, 130.0, 114.6, 61.3, 55.7, 51.8, 28.1, 14.1; IR (film, ν/cm^{-1}): 3389, 2932, 1731, 838; HRMS $[M+H]^+$ calcd for $C_{12}H_{16}O_5S$: 273.0797, found 273.0790.

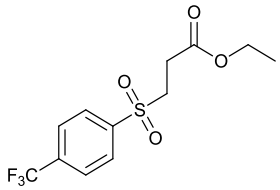


Propanoic acid, 3-[[4-(triflnoromethoxy)phenyl]sulfonyl]-, ethyl ester (3ae). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 91% yield; mp = 78-79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.76 (t, *J* = 7.4 Hz, 2H), 3.45 (t, *J* = 7.5 Hz, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 169.7, 153.2 (q, J_{CF} = 1.9 Hz), 136.8, 130.5, 121.1, 120.1 (q, J_{CF} = 258.2 Hz), 61.5, 51.6, 27.7, 14.0; IR (film, ν/cm^{-1}): 3444, 2928, 1734, 1321, 1149; HRMS $[M+H]^+$ calcd for $C_{12}H_{13}F_3O_4S$:

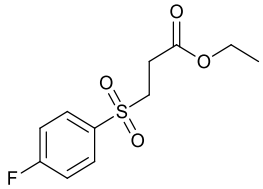
327.0514, found 327.0516.



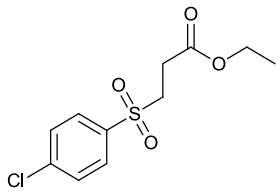
Propanoic acid, 3-[[4-(acetylamino)phenyl]sulfonyl]-, ethyl ester (3af). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow solid: 87% yield; mp = 135-136 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 2.23 (s, 3H), 2.73 (t, *J* = 7.7 Hz, 2H), 3.41 (t, *J* = 7.7 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 7.54 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 170.0, 268.6, 143.1, 133.0, 129.3, 119.4, 61.4, 51.7, 27.9, 24.8, 14.1; IR (film, ν/cm^{-1}): 3358, 2930, 1733, 1650,1317, 1043; HRMS $[M+H]^+$ calcd for $C_{13}H_{17}NO_5S$: 300.0906, found 300.0905.



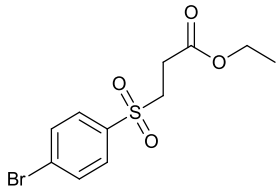
Propanoic acid, 3-[[(4-(trifluoromethyl)phenyl]sulfonyl]-, ethyl ester (3ag). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 97% yield; mp = 98-99 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.2 Hz, 3H), 2.77 (t, *J* = 7.6 Hz, 2H), 3.47 (t, *J* = 7.6 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 8.07 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 179.6, 142.1, 135.7 (q, J_{CF} = 33.2 Hz), 128.9, 126.5 (q, J_{CF} = 3.6 Hz), 123.0 (q, J_{CF} = 271.6 Hz), 61.5, 51.5, 27.6, 14.0; IR (film, ν/cm^{-1}): 3391, 2932, 1731, 1321, 1058; HRMS $[M+H]^+$ calcd for $C_{12}H_{13}F_3O_4S$: 311.0565, found 311.0559.



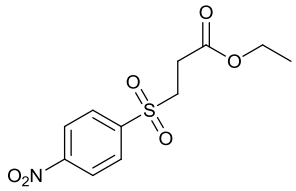
Propanoic acid, 3-[(4-fluorophenyl)sulfonyl]-, ethyl ester (3ah). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 91% yield; mp = 46-47 ℃; ^{1}H NMR (400 MHz, DMSO) δ 1.14 (t, *J* = 7.1 Hz, 3H), 2.62 (t, *J* = 7.2 Hz, 2H), 3.59 (t, *J* = 7.2 Hz, 2H), 3.98 (q, *J* = 7.1 Hz, 2H), 7.50 - 7.54 (m, 2H), 7.95 - 7.99 (m, 2H); ^{13}C NMR (100 MHz, DMSO) δ 170.0, 165.2 (d, J_{CF} = 251.4 Hz), 134.7 (d, J_{CF} = 28.6 Hz), 131.2 (d, J_{CF} = 10.0 Hz), 116.7 (d, J_{CF} = 22.8 Hz), 60.5, 50.6, 27.6, 13.9; IR (film, ν/cm^{-1}): 3445, 2928, 1735, 1318, 1053; HRMS $[M+H]^+$ calcd for $C_{11}H_{13}FO_4S$: 261.0596, found 261.0608.



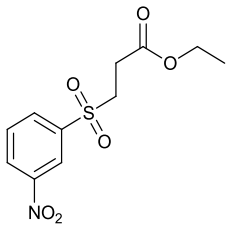
Propanoic acid, 3-[(4-chlorophenyl)sulfonyl]-, ethyl ester (3ai). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 93% yield; mp = 106-107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 3H), 2.75 (t, *J* = 7.7 Hz, 2H), 3.43 (t, *J* = 7.7 Hz, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 169.8, 140.9, 137.0, 129.7, 129.7, 61.5, 51.6, 27.8, 14.1; IR (film, ν/cm^{-1}): 3446, 2930, 1735, 1055; HRMS $[M+H]^+$ calcd for $C_{11}H_{13}ClO_4S$: 277.0301, found 277.0307.



Propanoic acid, 3-[(4-bromophenyl)sulfonyl]-, ethyl ester (3aj). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 90% yield; mp = 78-79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.74 (t, *J* = 7.6 Hz, 2H), 3.43 (t, *J* = 7.7 Hz, 2H), 4.10 (q, *J* = 7.3 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 169.8, 137.6, 132.8, 129.8, 129.5, 61.5, 51.6, 27.8, 14.1; IR (film, ν/cm^{-1}): 3440, 2932, 1732, 1046; HRMS $[M+H]^+$ calcd for $C_{11}H_{13}BrO_4S$: 320.9796, found 320.9790.

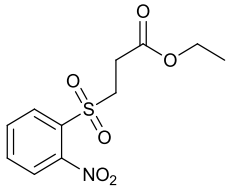


Propanoic acid, 3-[(4-nitrophenyl)sulfonyl]-, ethyl ester (3ak). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow solid: 91% yield; mp = 99-100 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 3H), 2.79 (t, *J* = 7.5 Hz, 2H), 3.50 (t, *J* = 7.5 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 2H), 8.43 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 169.6, 151.0, 144.3, 129.7, 124.6, 61.6, 51.5, 27.5, 14.0; IR (film, ν/cm^{-1}): 3362, 2925, 1724, 1530, 1349, 1045; HRMS $[M+H]^+$ calcd for $C_{11}H_{13}NO_6S$: 300.0542, found 300.0545.

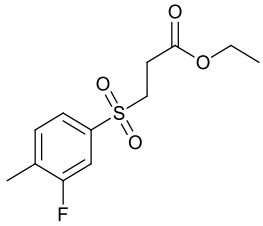


Propanoic acid, 3-[(3-nitrophenyl)sulfonyl]-, ethyl ester (3al). The title compound was prepared according to the general working procedure and purified by column chromatography to

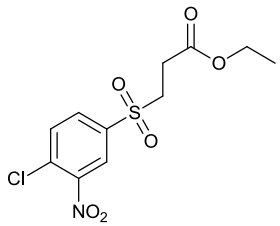
give the product as a light yellow solid: 98% yield; mp = 84-85 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 3H), 2.81 (t, *J* = 7.5 Hz, 2H), 3.52 (t, *J* = 7.5 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 7.81 - 7.85 (m, 1H), 8.25 – 8.28 (m, 1H), 8.53 – 8.55 (m, 1H), 8.77 – 8.78 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 169.6, 148.5, 140.9, 133.7, 130.9, 128.5, 123.6, 61.6, 51.5, 27.6, 14.0; IR (film, ν/cm^{-1}): 3358, 2928, 1727, 1534, 1322, 1044; HRMS $[M+H]^+$ calcd for $C_{11}H_{13}NO_6S$: 300.0542, found 300.0545.



Propanoic acid, 3-[(2-nitrophenyl)sulfonyl]-, ethyl ester (3am). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a light yellow oil: 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.87 (t, *J* = 7.6 Hz, 2H), 3.93 (t, *J* = 7.6 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 7.80 - 7.87 (m, 3H), 8.13 – 8.16 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 169.7, 149.3, 135.1, 132.7, 132.7, 132.2, 125.1, 61.5, 52.2, 27.7, 14.1; IR (film, ν/cm^{-1}): 3359, 2926, 1732, 1540, 1365, 1041; HRMS $[M+H]^+$ calcd for $C_{11}H_{13}NO_6S$: 300.0542, found 300.0545.

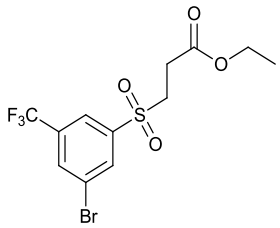


Propanoic acid, 3-[(3-fluoro-4-methylphenyl)sulfonyl]-, ethyl ester (3an). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 99% yield; mp = 59-60 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 2.38 (d, *J* = 2.0 Hz, 3H), 2.74 (t, *J* = 7.7 Hz, 2H), 3.42 (t, *J* = 7.5 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.61 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 169.8, 160.9 (d, J_{CF} = 249.5 Hz), 137.6 (d, J_{CF} = 6.5 Hz), 132.5 (d, J_{CF} = 5.0 Hz), 132.3 (d, J_{CF} = 17.3 Hz), 123.7 (d, J_{CF} = 3.8 Hz), 115.1 (d, J_{CF} = 25.2 Hz), 61.4, 51.5, 27.8, 14.9, 14.8, 14.0; IR (film, ν/cm^{-1}): 3359, 2929, 1731, 1312, 1044; HRMS $[M+H]^+$ calcd for $C_{12}H_{15}FO_4S$: 275.0753, found 275.0748.

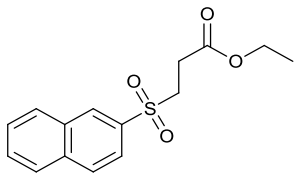


Propanoic acid, 3-[(4-chloro-3-nitrophenyl)sulfonyl]-, ethyl ester (3ao). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a yellow solid: 93% yield; mp = 106-107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 3H), 2.80 (t, *J* = 7.4 Hz, 2H), 3.50 (t, *J* = 7.4 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 7.80 (d, *J* = 8.4 Hz, 1H), 8.05 (dd, *J* = 8.4, 2.1 Hz, 1H), 8.40 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100

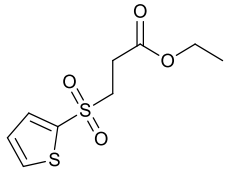
MHz, CDCl3) δ 169.5, 148.1, 138.9, 133.4, 132.2, 125.6, 61.7, 51.6, 27.6, 14.1; IR (film, ν/cm^{-1}): 3364, 2923, 1720, 1538, 1359, 1045; HRMS $[M+H]^+$ calcd for $C_{11}H_{12}ClNO_6S$: 322.0152, found 322.0151.



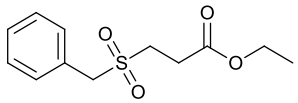
Propanoic acid, 3-[[(3-bromo-5-(trifluoromethyl)phenyl]sulfonyl]-, ethyl ester (3ap). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 99% yield; mp = 80-81 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H), 2.80 (t, *J* = 7.5 Hz, 2H), 3.49 (t, J = 7.5 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 8.06 (s, 1H), 8.11 (s, 1H), 8.25 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 169.5, 141.6, 134.5, 133.8 (q, J_{CF} = 3.6 Hz), 133.6 (q, J_{CF} = 34.1 Hz), 124.0, 123.9 (q, J_{CF} = 3.6 Hz), 122.1 (q, J_{CF} = 272.1 Hz), 61.6, 51.5, 27.5, 14.0; IR (film, ν/cm^{-1}): 3358, 2927, 1726, 1311, 1044; HRMS $[M+H]^+$ calcd for $C_{12}H_{12}BrF_3O_4S$: 388.9670, found 388.9672.



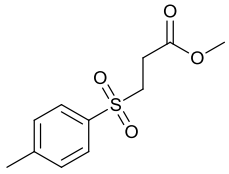
Propanoic acid, 3-(2-naphthalenylsulfonyl)-, ethyl ester (3aq). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 96% yield; mp = 51-52 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.1 Hz, 3H), 2.78 (t, *J* = 7.7 Hz, 2H), 3.51 (t, *J* = 7.7 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 7.65 - 7.72 (m, 2H), 7.88 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.02 (t, *J* = 8.6 Hz, 2H), 8.50 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 169.9, 135.4, 135.2, 132.1, 130.1, 130.0, 129.5, 129.4, 128.0, 127.8, 122.6, 61.3, 51.5, 27.9, 14.0; IR (film, ν/cm^{-1}): 3392, 2927, 1734, 1044; HRMS $[M+H]^+$ calcd for $C_{15}H_{16}O_4S$: 293.0848, found 293.0862.



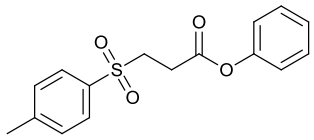
Propanoic acid, 3-(2-thienylsulfonyl)-, ethyl ester (3ar). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a colorless oil: 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 3H), 2.80 (t, *J* = 7.7 Hz, 2H), 3.54 (t, *J* = 7.7 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 7.18 (dd, *J* = 5.0, 3.8 Hz, 1H), 7.71 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.75 (dd, *J* = 5.0, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 169.8, 139.4, 134.6, 134.5, 128.1, 61.4, 52.9, 28.3, 14.1; IR (film, ν/cm^{-1}): 3360, 2923, 1738, 1022; HRMS $[M+H]^+$ calcd for $C_9H_{12}O_4S_2$: 249.0255, found 249.0261.



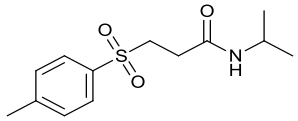
Propanoic acid, 3-[(phenylmethyl)sulfonyl]-, ethyl ester (3as). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 91% yield; mp = 111-112 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 2.79 (t, *J* = 7.5 Hz, 2H), 3.19 (t, *J* = 7.5 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.28 (s, 2H), 7.40 - 7.44 (m, 5H); ^{13}C NMR (100 MHz, CDCl3) δ 170.4, 130.6, 129.2, 129.1, 127.7, 61.4, 60.2, 46.7, 26.8, 14.1; IR (film, ν/cm^{-1}): 3363, 2933, 1727, 1048; HRMS $[M+H]^+$ calcd for $C_{12}H_{16}O_4S$: 257.0848, found 257.0845.



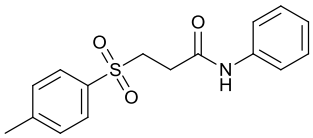
Propanoic acid, 3-[(4-methylphenyl)sulfonyl]-, methyl ester (3ba). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 99% yield; mp = 79-80 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 2.75 (t, *J* = 7.7 Hz, 2H), 3.41 (t, *J* = 7.7 Hz, 2H), 3.64 (s, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 170.4, 145.0, 135.5, 130.0, 128.1, 52.2, 51.5, 27.7, 21.6; IR (film, ν/cm^{-1}): 3362, 2924, 1723, 1043; HRMS $[M+H]^+$ calcd for $C_{11}H_{14}O_4S$: 243.0961, found 243.0962.



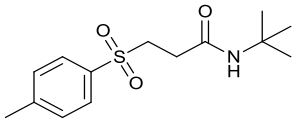
Propanoic acid, 3-[(4-methylphenyl)sulfonyl]-, phenyl ester (3da). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white crystal: 70% yield; mp = 83-84 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.00 (t, *J* = 7.7 Hz, 2H), 3.52 (t, *J* = 7.5 Hz, 2H), 7.01 - 7.04 (m, 2H), 7.21 - 7.25 (m, 1H), 7.34 - 7.40 (m, 4H), 7.82 - 7.85 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 168.7, 150.3, 145.2, 135.5, 130.4, 130.1, 129.4, 128.2, 126.1, 121.2, 51.5, 28.1, 21.6; IR (film, ν/cm^{-1}): 3276, 2921, 1746, 1025; HRMS $[M+H]^+$ calcd for $C_{16}H_{16}O_4S$: 305.0848, found 305.0845.



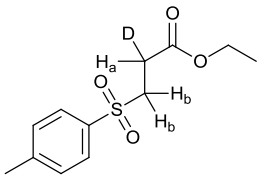
N-isopropyl-3-tosylpropanamide (3ea). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 99% yield; mp = 91-92 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, *J* = 6.6 Hz, 6H), 2.45 (s, 3H), 2.61 (t, *J* = 7.7 Hz, 2H), 3.44 (t, *J* = 7.7 Hz, 2H), 3.99 (m, 1H), 5.67 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 168.1, 145.1, 135.8, 130.0, 128.1, 52.2, 42.0, 29.2, 22.5, 21.7; IR (film, ν/cm^{-1}): 3335, 2929, 1649, 1543, 1314; HRMS $[M+H]^+$ calcd for $C_{13}H_{19}NO_3S$: 270.1164, found 270.1165.



N-phenyl-3-tosylpropanamide (3fa). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white solid: 99% yield; mp = 163-164 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 2.90 (t, *J* = 7.4 Hz, 2H), 3.54 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.89 (s, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 167.1, 145.3, 137.6, 135.6, 130.1, 129.0, 128.1, 124.5, 119.9, 52.0, 30.1, 21.6; IR (film, ν/cm^{-1}): 3338, 2925, 1689, 1545, 1308; HRMS $[M+H]^+$ calcd for $C_{16}H_{17}NO_3S$: 304.1007, found 304.1006.



N-(tert-butyl)-3-tosylpropanamide (3ga). The title compound was prepared according to the general working procedure and purified by column chromatography to give the product as a white oil: 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 9H), 2.45 (s, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 3.54 (t, *J* = 7.7 Hz, 2H), 5.92 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 167.8, 144.9, 135.7, 129.9, 127.9, 52.0, 51.4, 29.5, 28.5, 21.5; IR (film, ν/cm^{-1}): 3337, 2928, 1647, 1538, 1321; HRMS [M+H]+ calcd for $C_{14}H_{21}NO_3S$: 284.1320, found 284.1309.

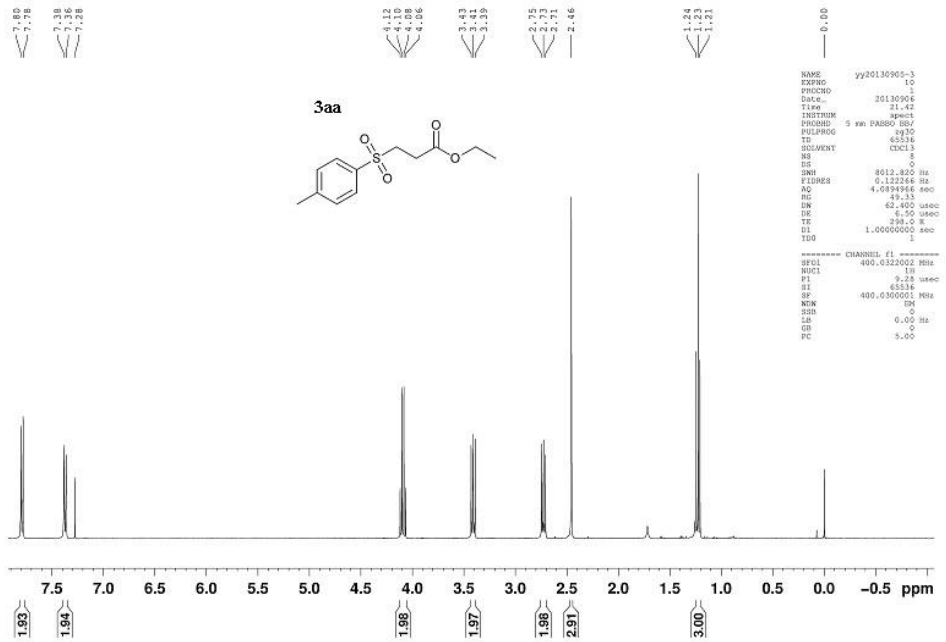


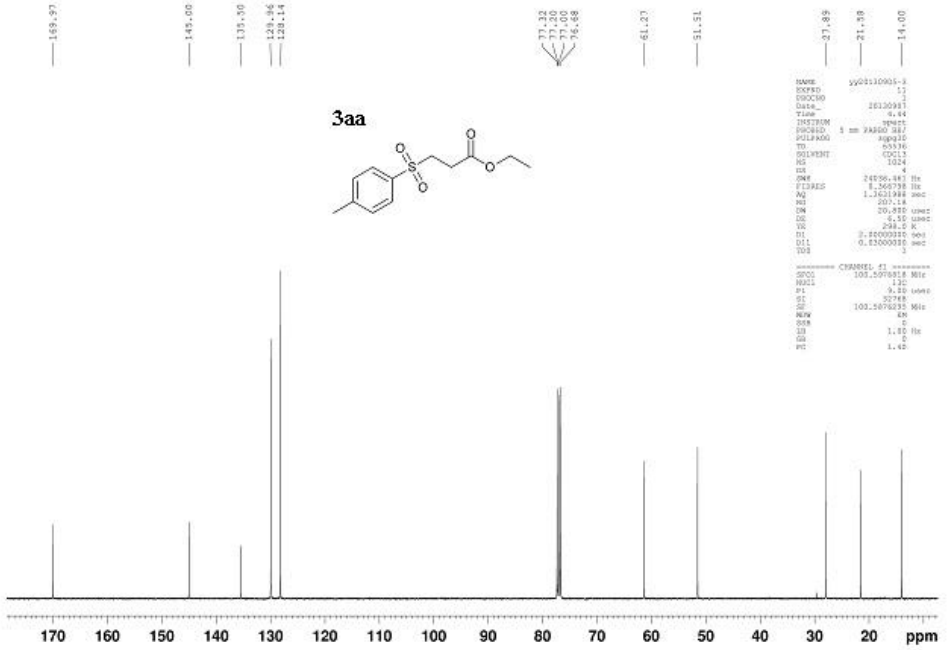
Deuterium generation propanoic acid, 3-[(4-methylphenyl)sulfonyl]-, ethyl ester (4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 2.46 (s, 3H), 2.68-2.74 (m, 1H), 3.40 (d, *J* = 7.7 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 7.36-7.38 (m, 2H), 7.77-7.80 (m, 2H).

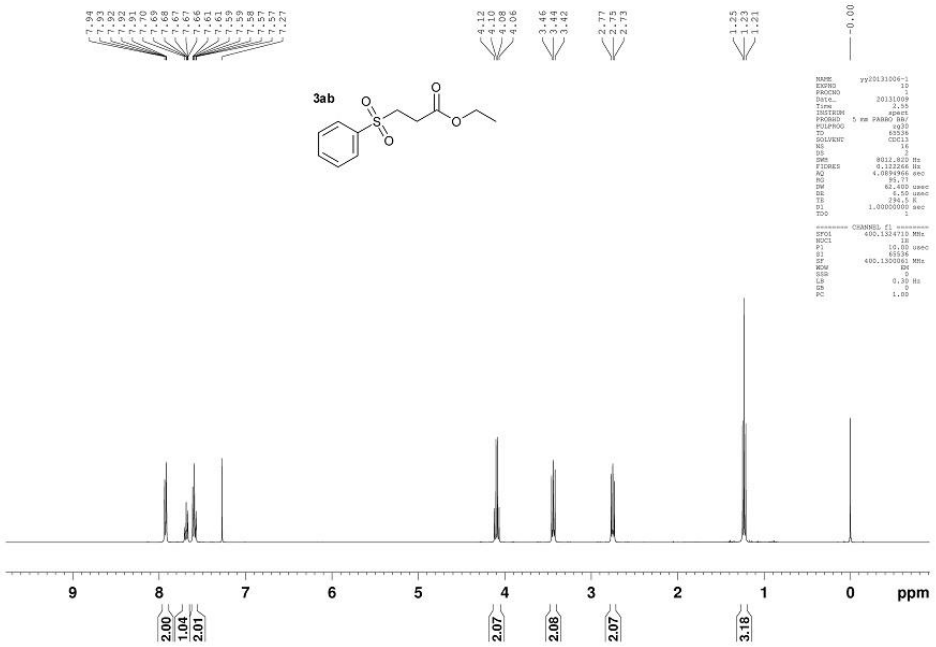
Reference

[1] F.-L. Yang, X.-T. Ma and S.-K. Tian, *Chem. Eur. J.*, 2012, **18**, 1582.

NMR Spectra of products



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7.61
7.59
7.59
7.58
7.57
7.57
7.27
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4.10
4.08
4.06
3.46
3.44
3.42
2.77
2.75
2.73
1.25
1.23
1.21
-0.00
9
8
7
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5
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2.01
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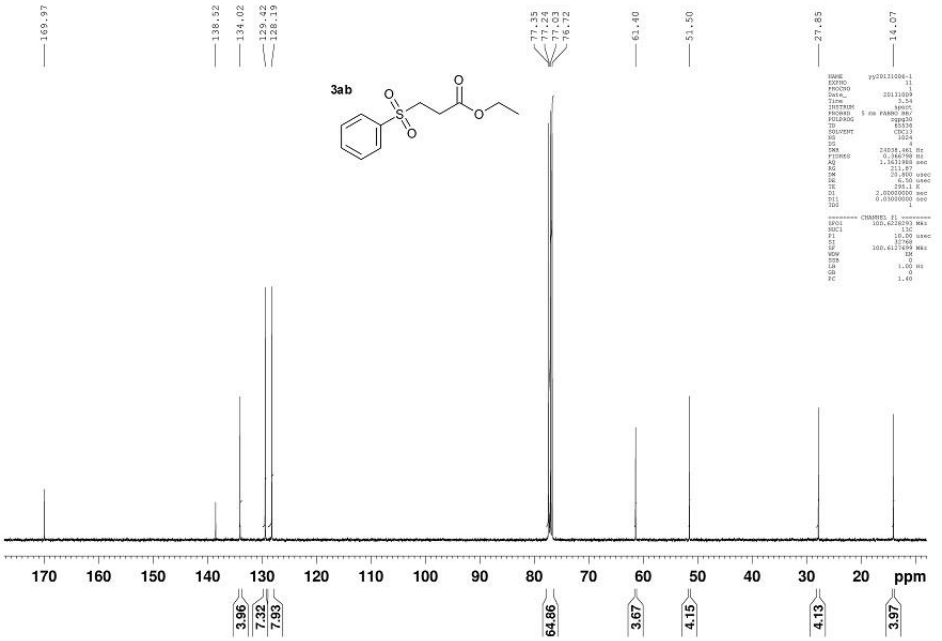
2.07
3.18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77.24
77.03
76.72
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51.50
27.85
14.07
170
160
150
140
130
120
110
100
90
80
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ppm
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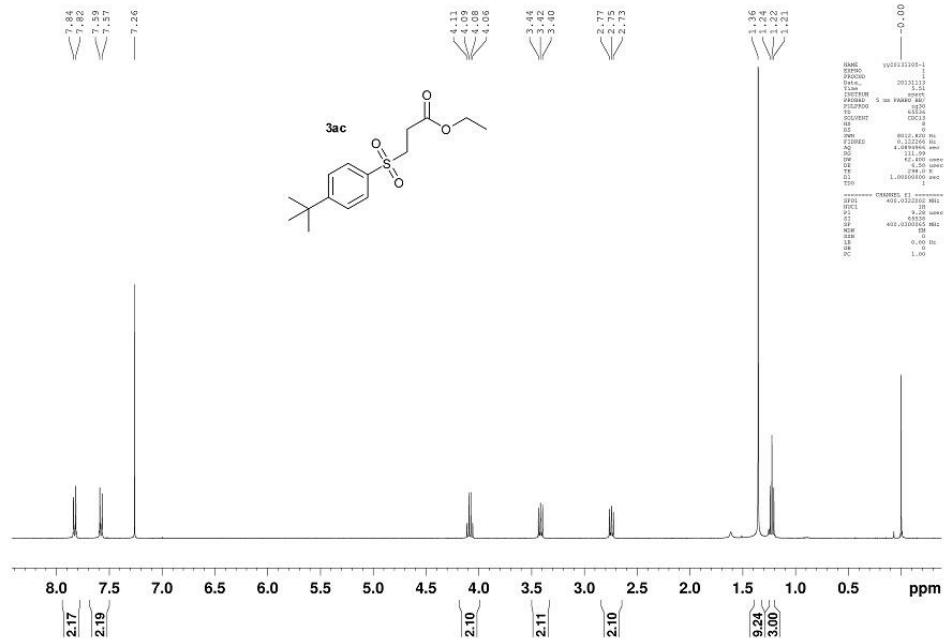
4.13
3.97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2.75
2.73
1.36
1.34
1.22
1.21
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3ac
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6.5
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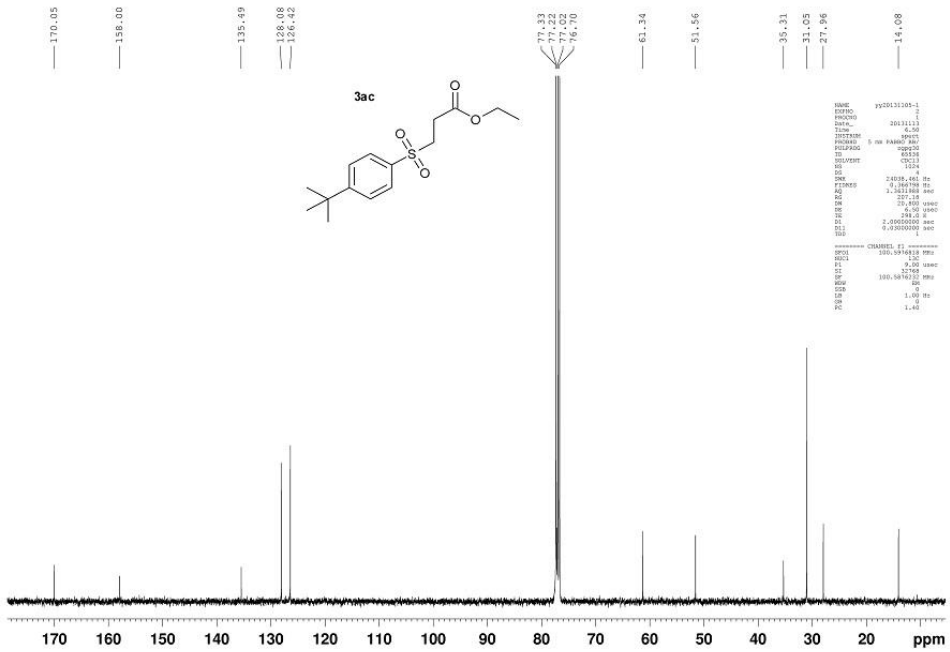
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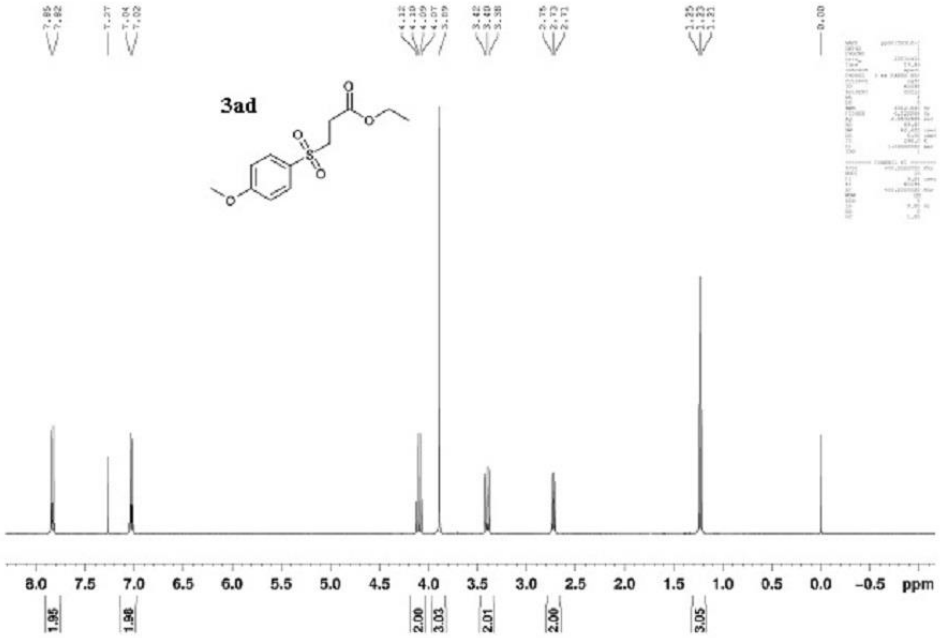
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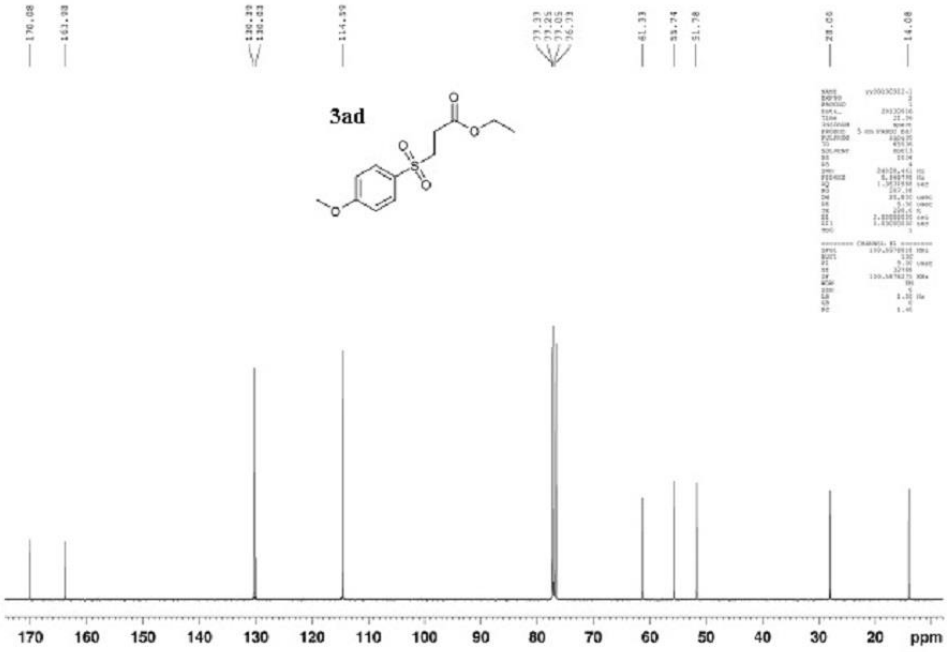
3.05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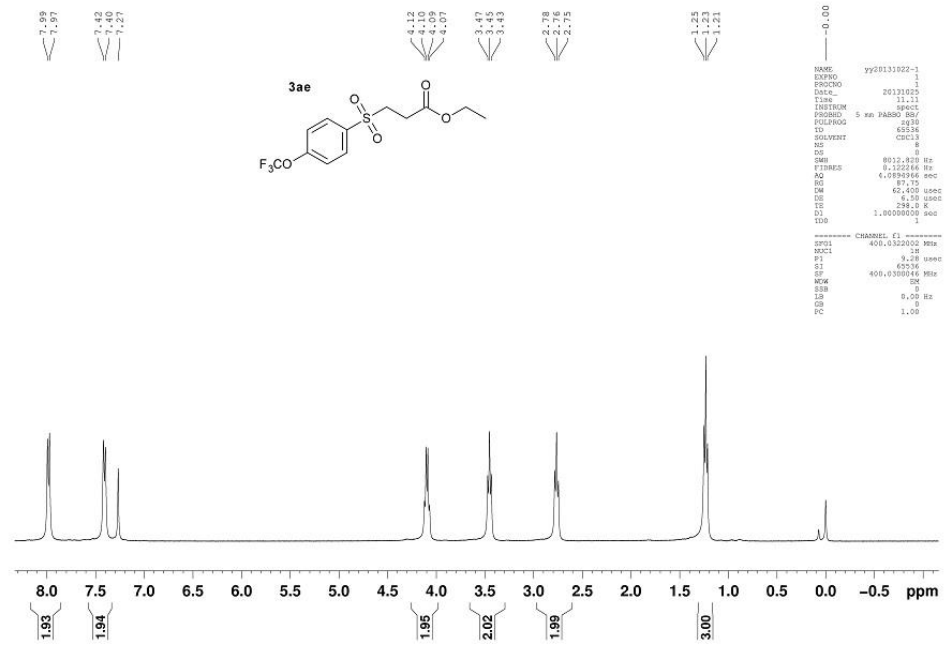
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2.5
2.0
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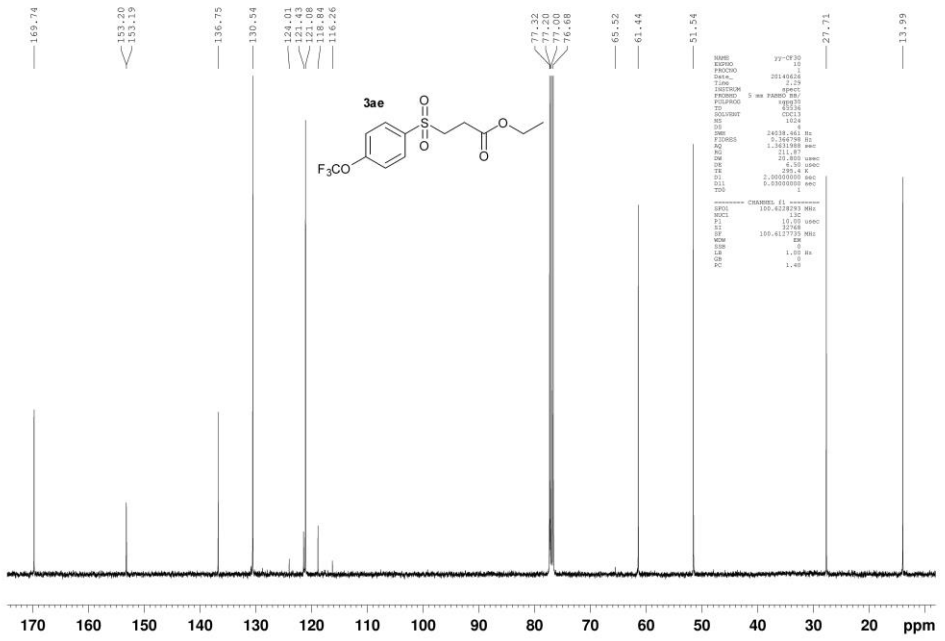
3.00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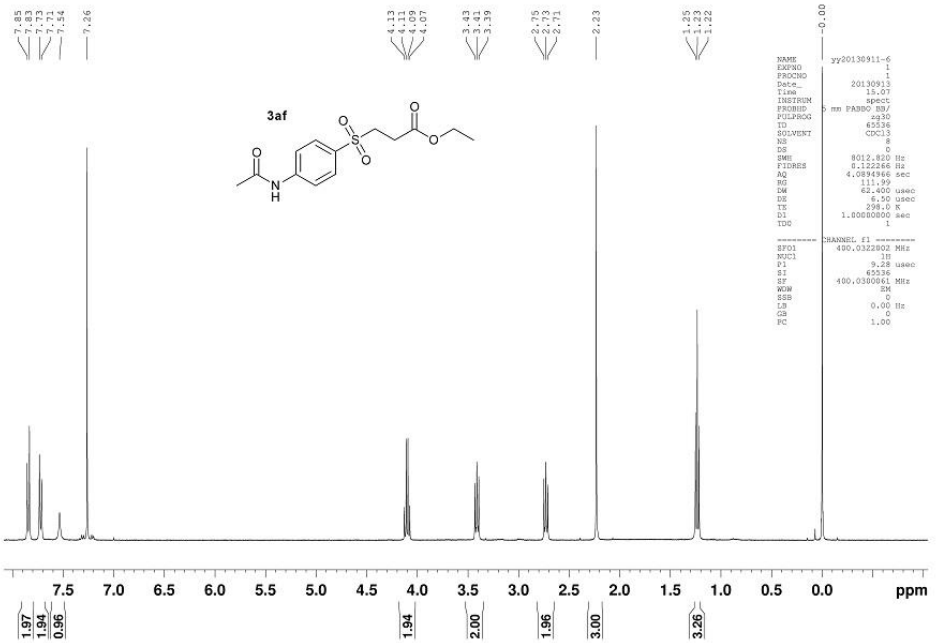
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6.0
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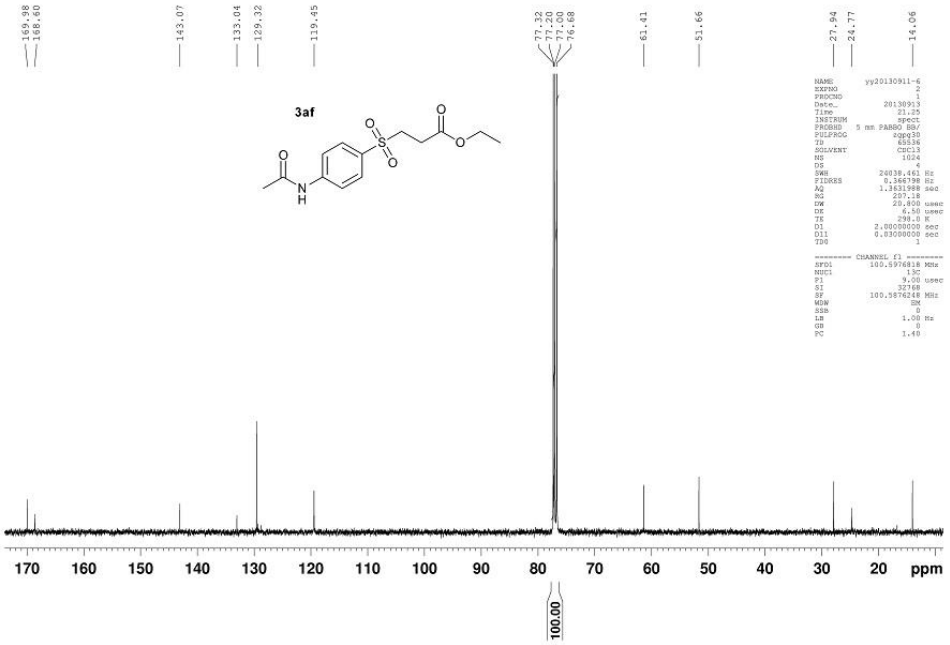
3.26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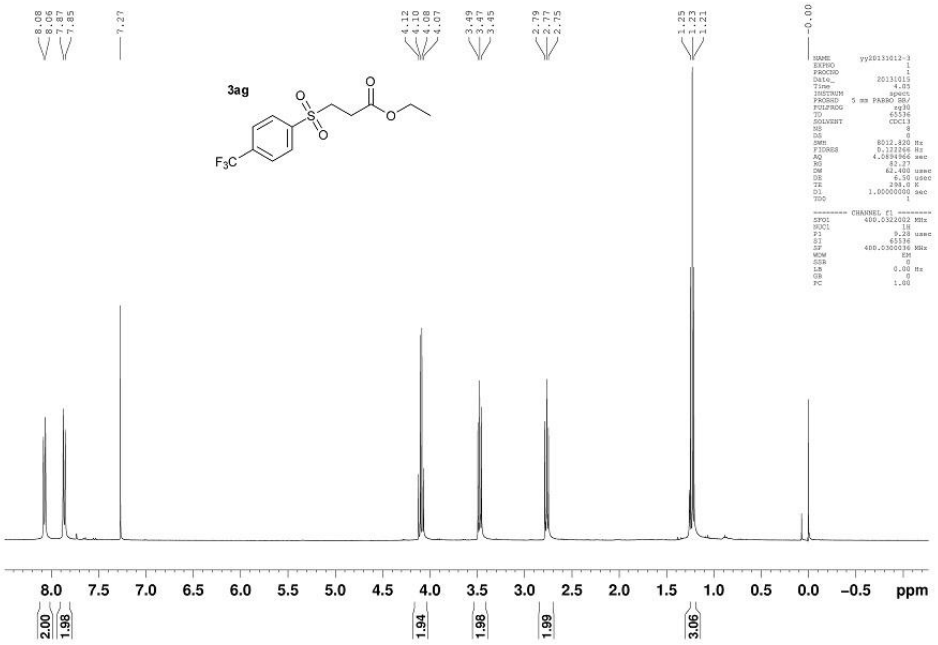
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2.75
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1.23
1.21
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3ag
F3C
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
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1.98
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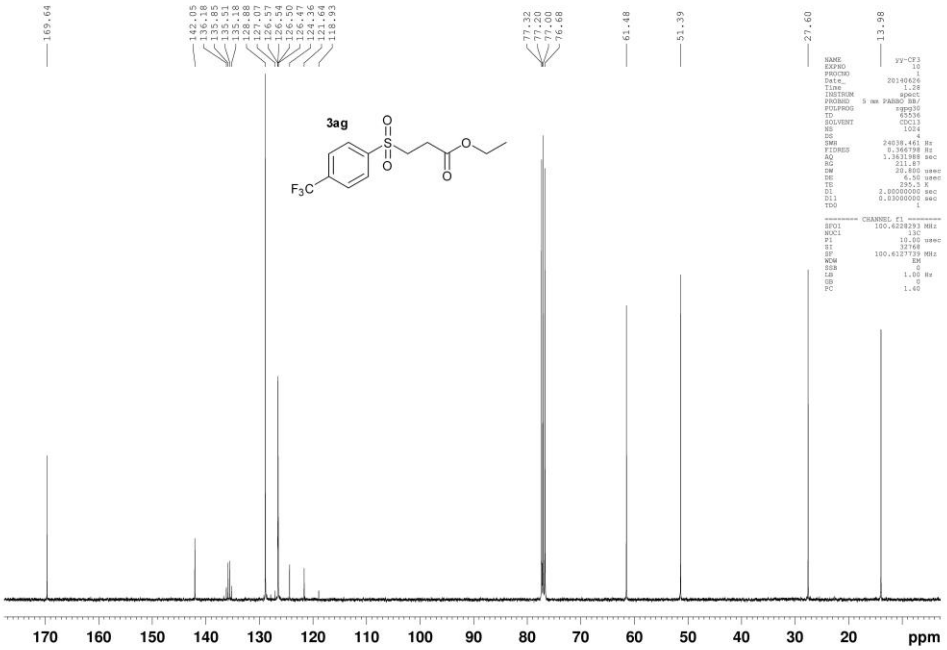
1.99
3.06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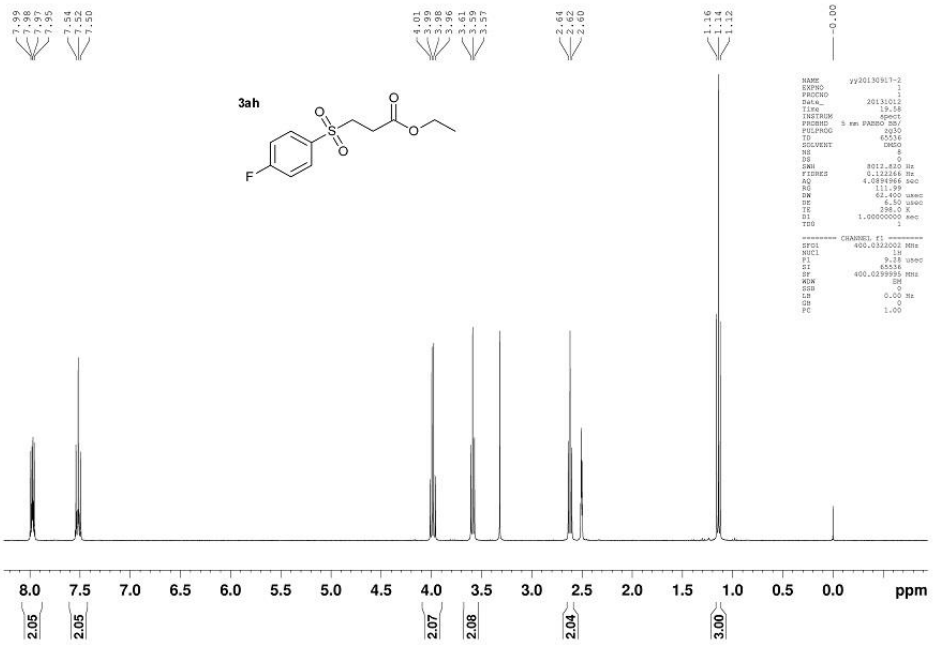
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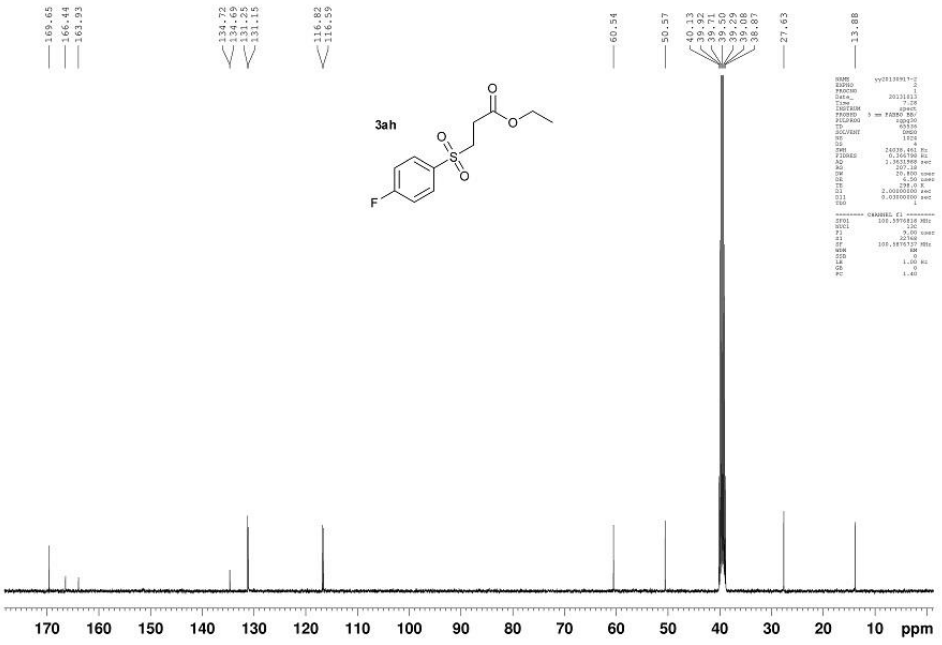
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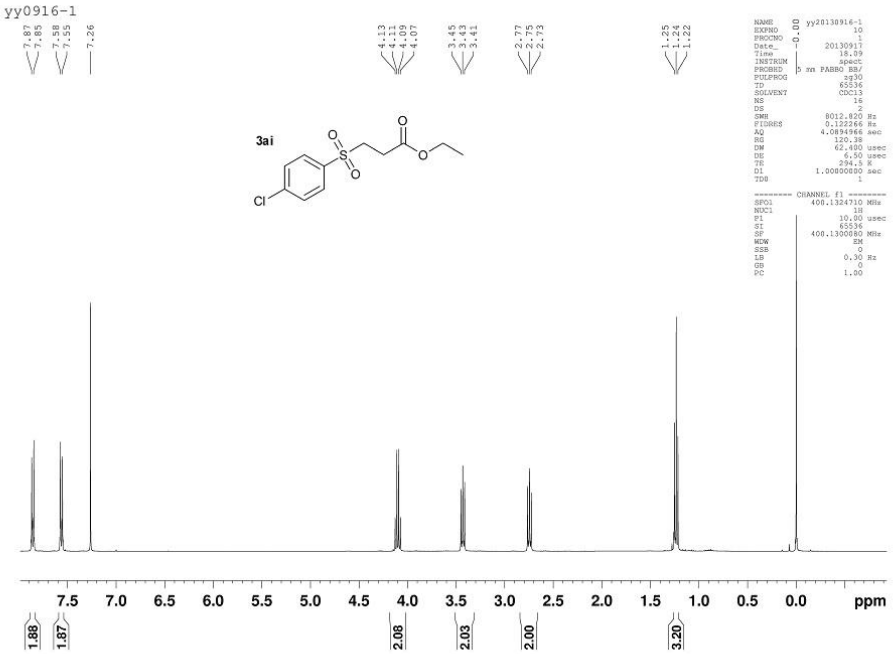
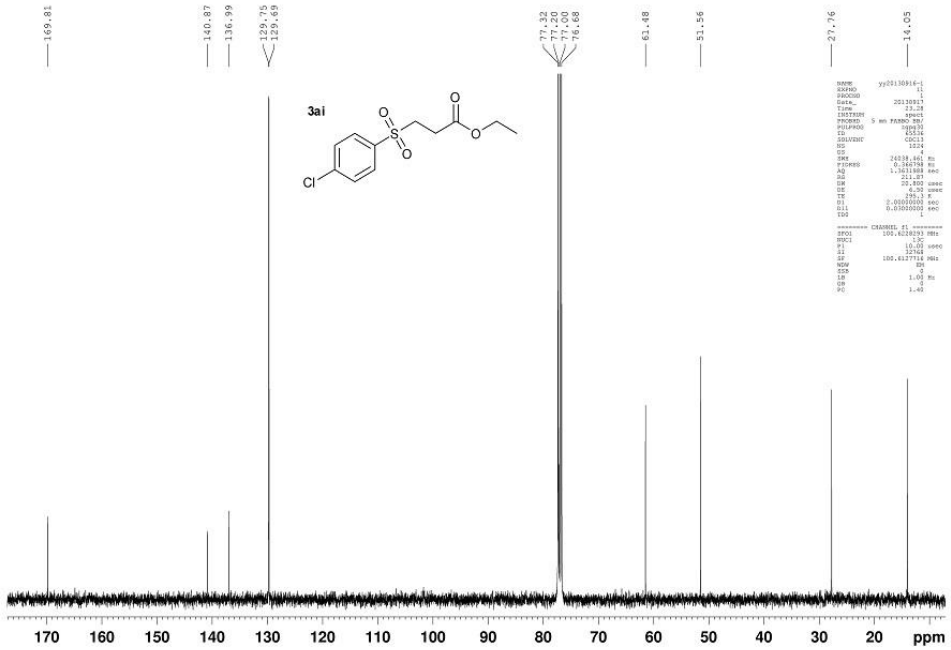
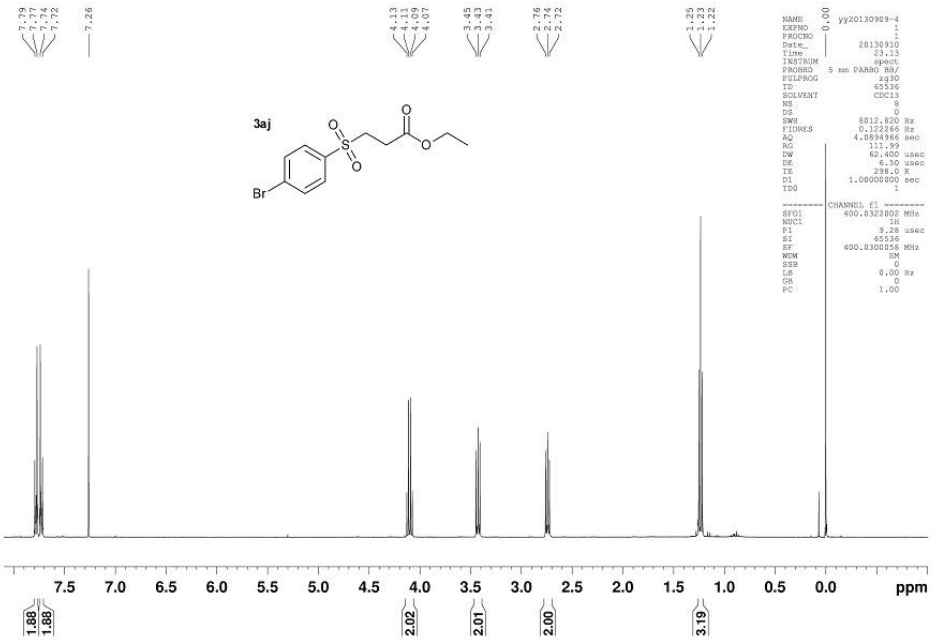
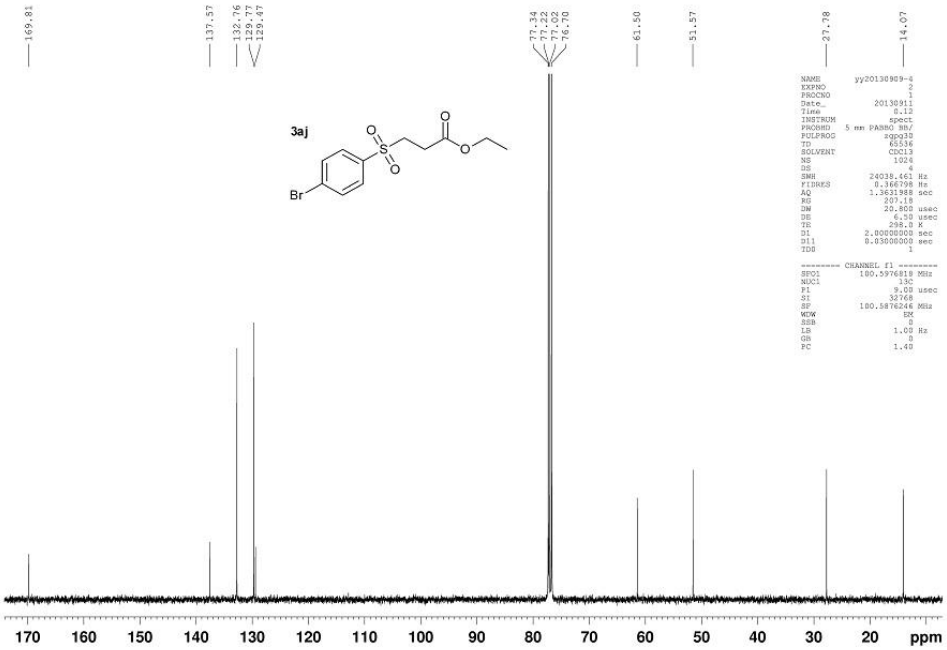
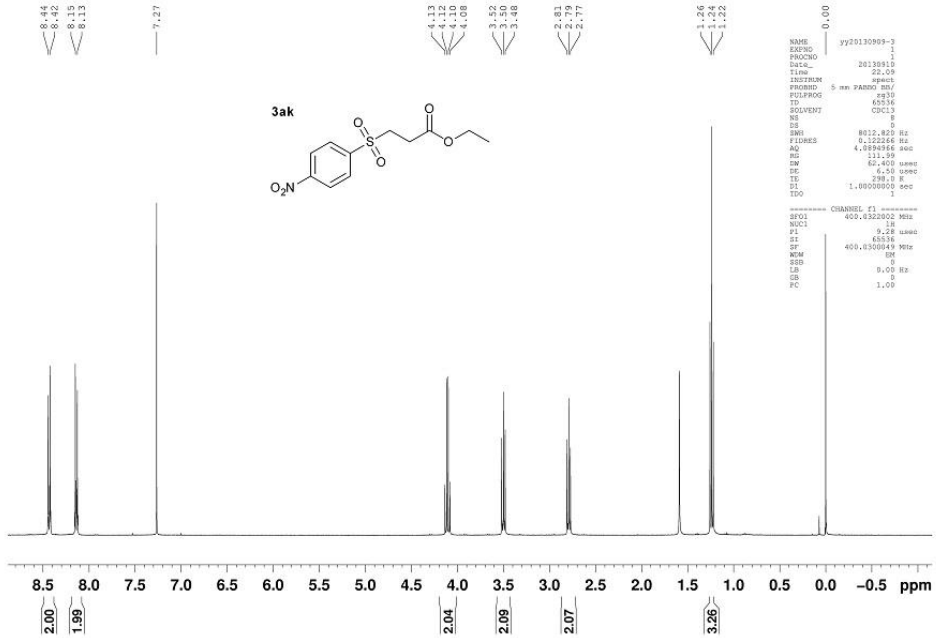
F
ppm

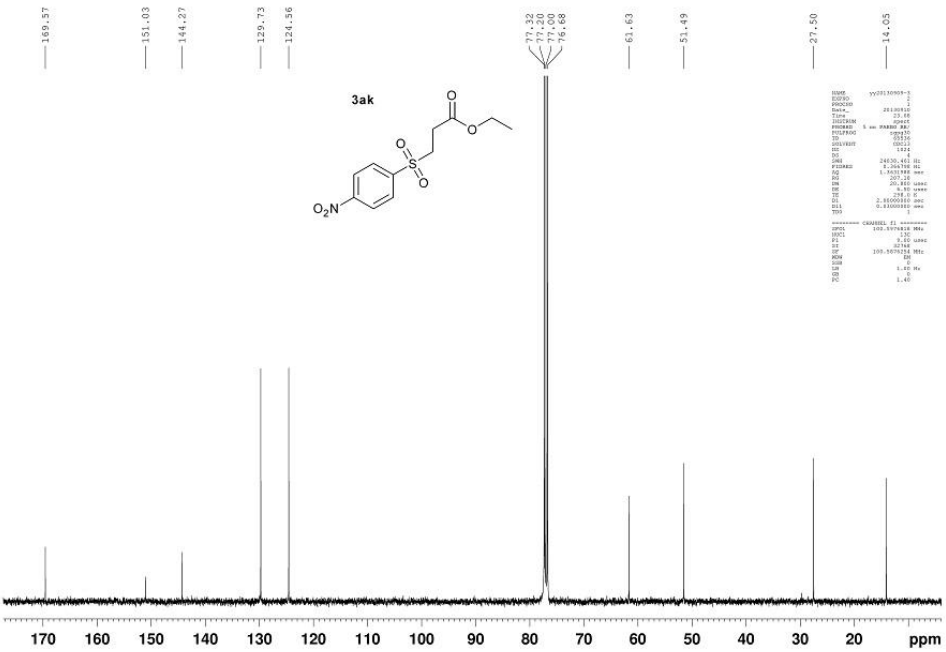

yy0916-1
7.87
7.85
7.58
7.55
7.26
4.13
4.11
4.09
4.07
3.45
3.43
3.41
2.77
2.75
2.73
1.25
1.24
1.22
3ai
Cl
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.88
1.87
2.08
2.03
2.00
3.20

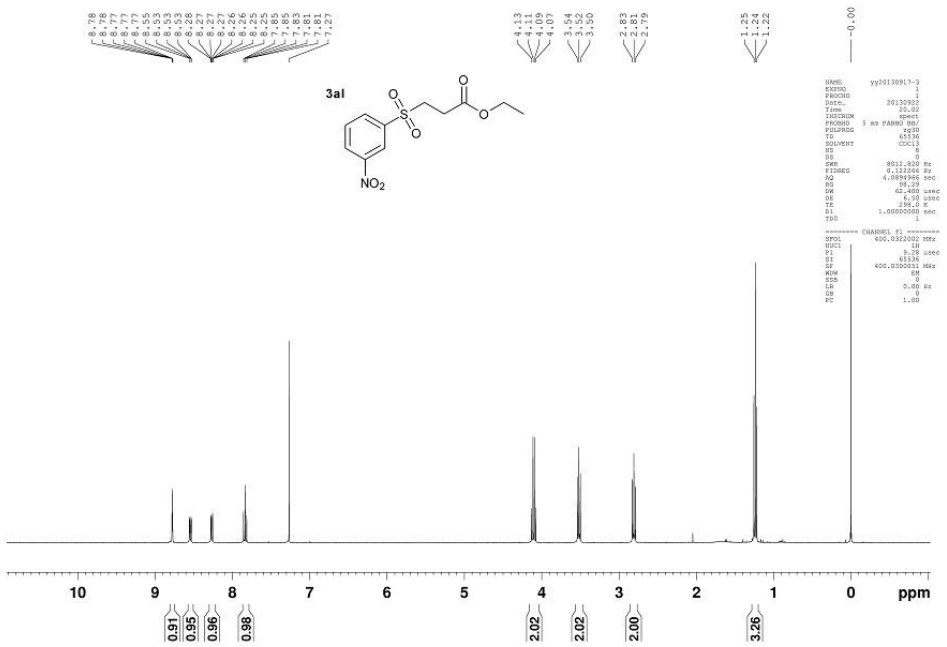

169.81
140.87
136.99
129.75
129.69
77.32
77.00
76.68
61.48
51.56
27.76
14.05
3ai
Cl
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

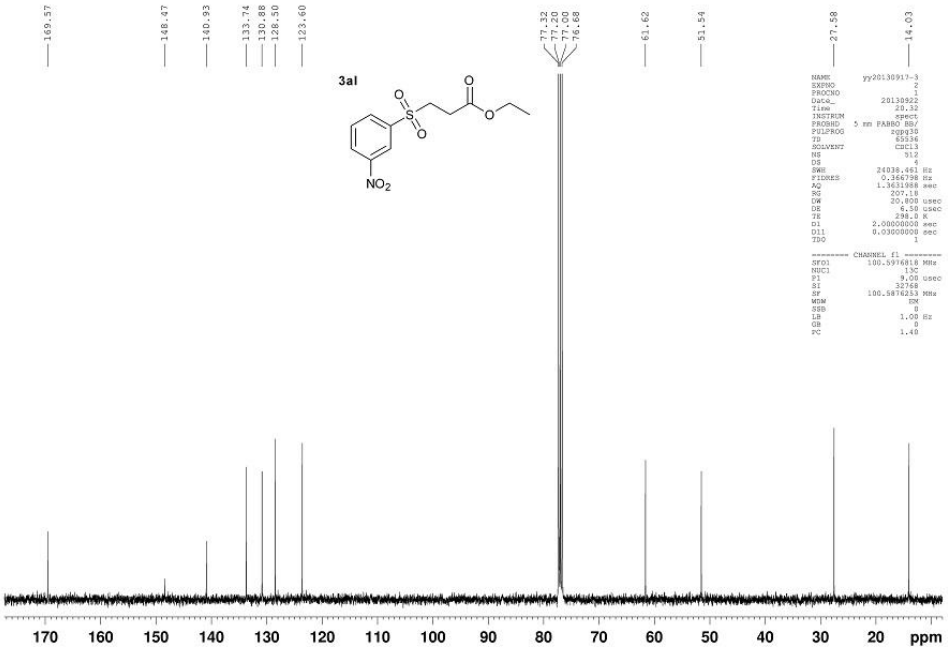

3aj
Br
ppm

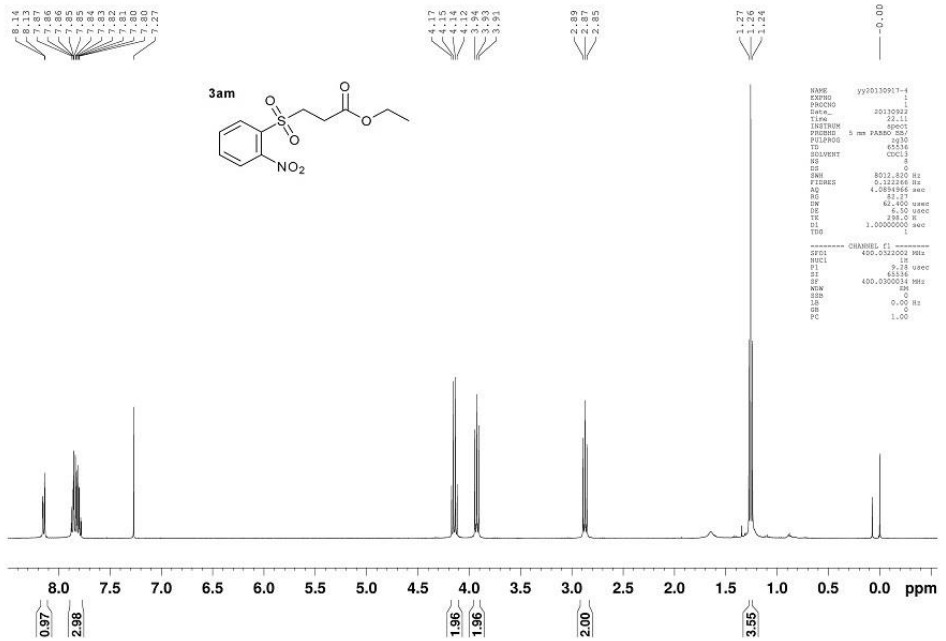

3aj
Br
ppm

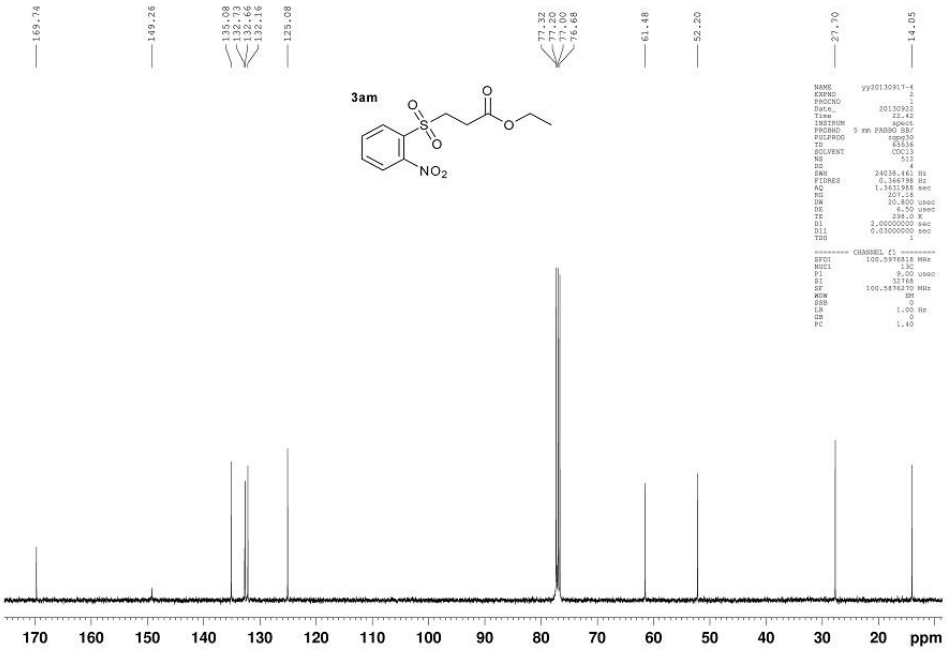

3ak
8.44
8.42
8.15
8.13
7.27
4.13
4.12
4.10
4.08
3.52
3.50
3.48
2.81
2.79
2.77
1.26
1.24
1.22
0.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
2.00
1.99
2.04
2.09
2.07
3.26

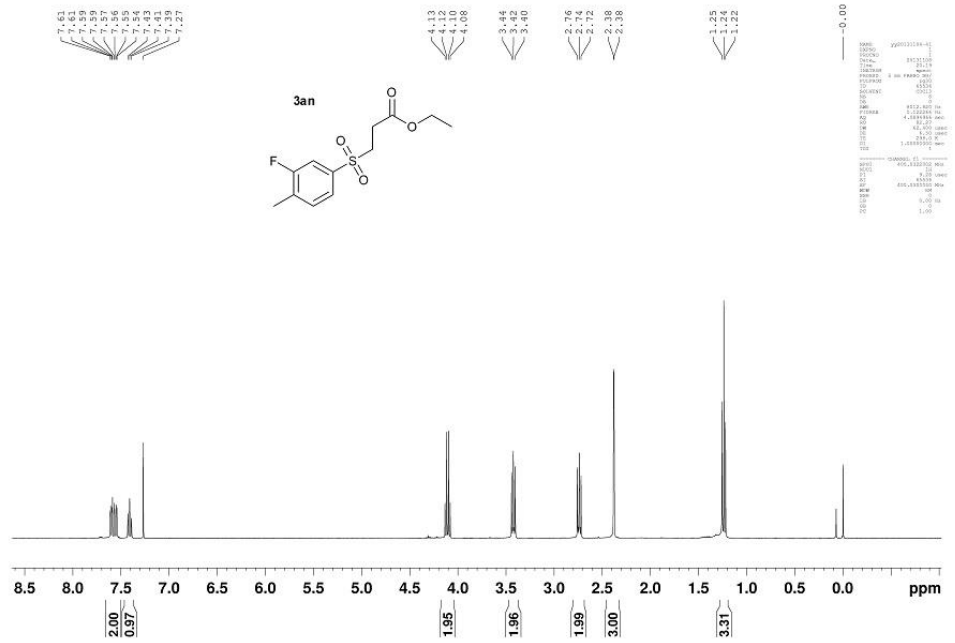

3ak
169.57
151.03
144.27
129.73
124.56
77.32
77.20
77.00
76.68
61.63
51.49
27.50
14.05
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

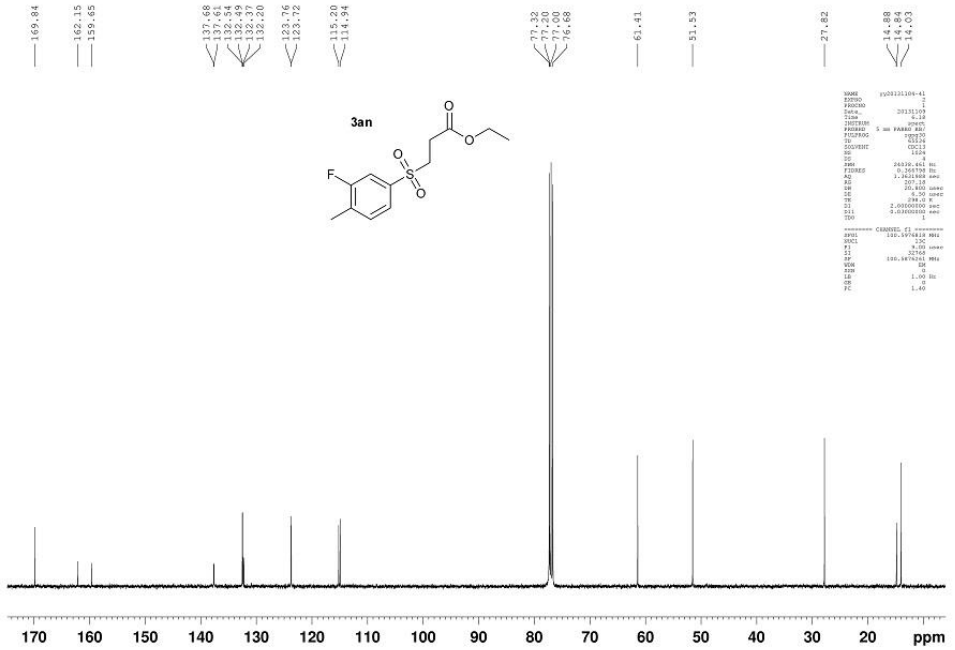

3al
NO2
ppm

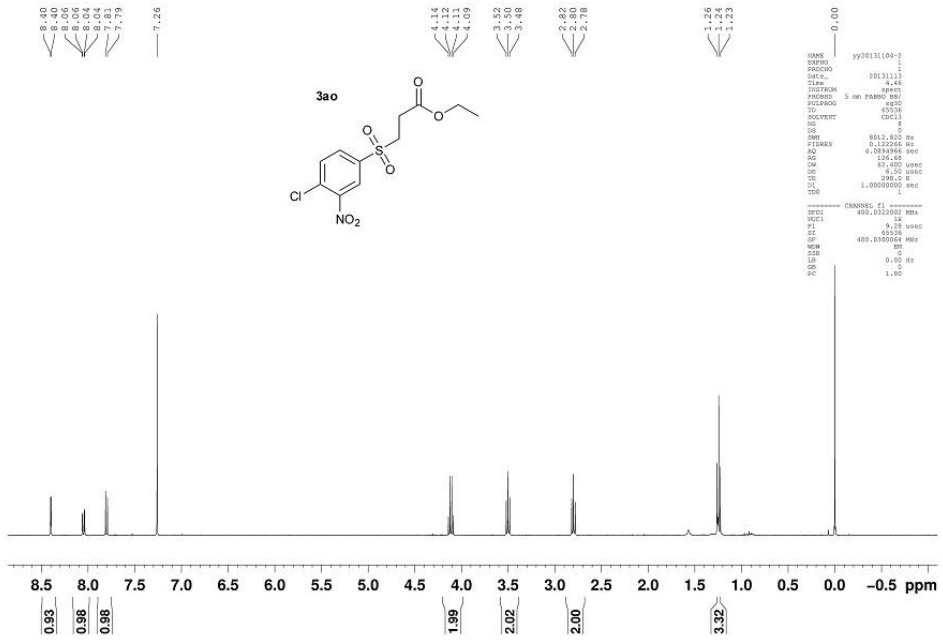

3al
NO2
ppm

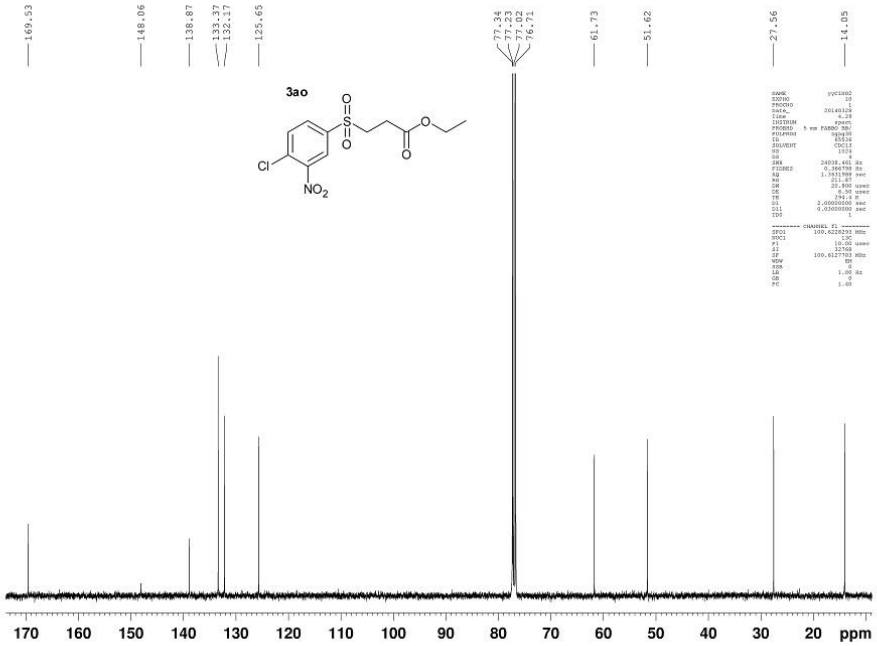

3am
8.14
8.13
7.87
7.86
7.86
7.85
7.85
7.84
7.83
7.82
7.81
7.80
7.80
7.27
4.17
4.15
4.14
4.12
3.94
3.93
3.91
2.89
2.87
2.85
1.27
1.26
1.24
0.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.97
2.98
1.96
1.96
2.00
3.55

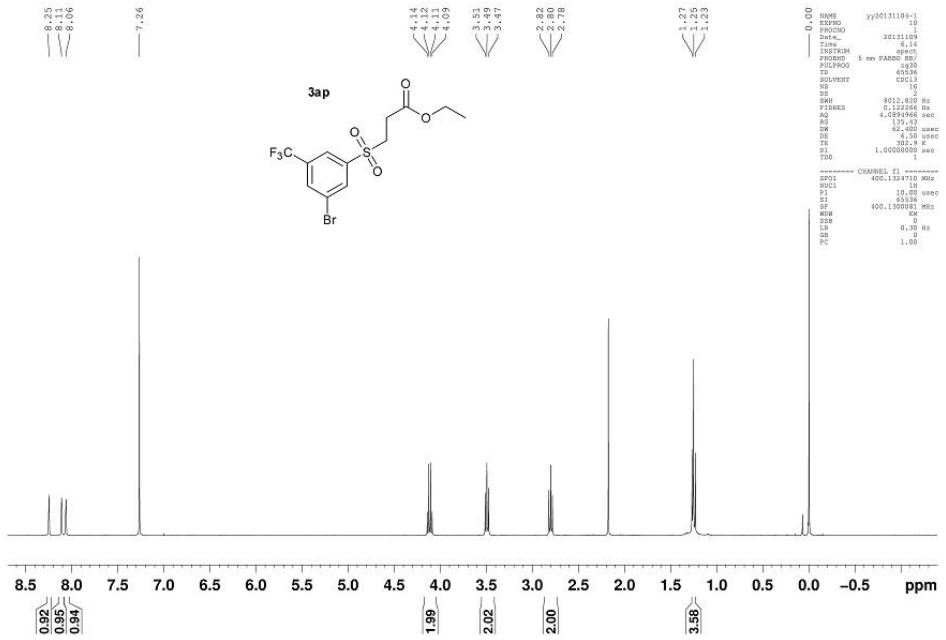

3am
169.74
149.26
135.08
132.73
132.66
132.16
125.08
77.32
77.20
77.00
76.68
61.48
52.20
27.70
14.05
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

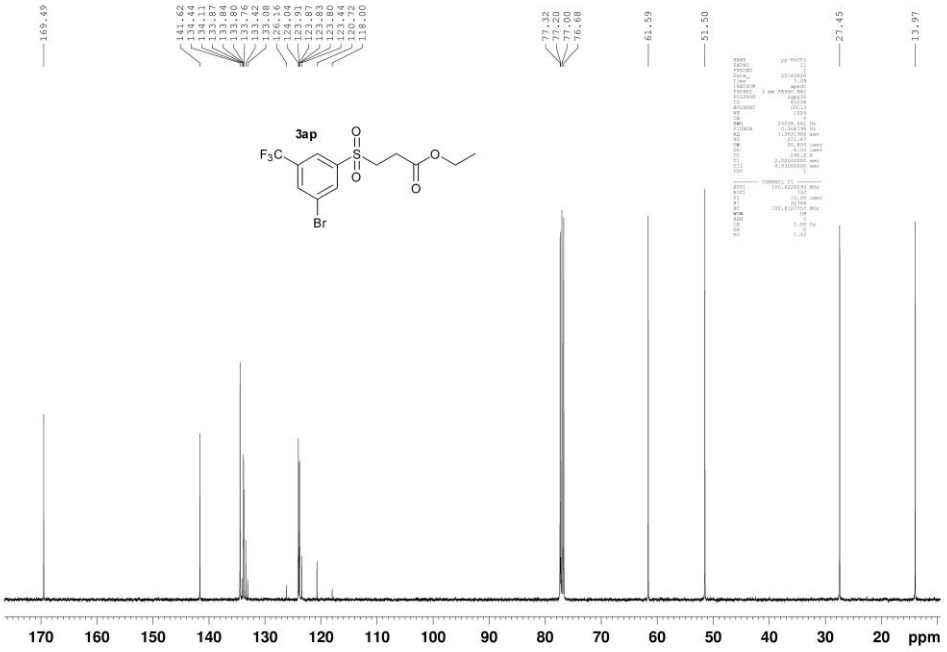

7.61
7.61
7.59
7.58
7.57
7.56
7.55
7.54
7.43
7.41
7.39
7.27
4.13
4.12
4.10
4.08
3.44
3.42
3.40
2.76
2.74
2.72
2.38
2.38
1.25
1.24
1.22
0.00
3an
F
O
O
S
O
O
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
0.97
1.95
1.96
1.99
3.00
3.31

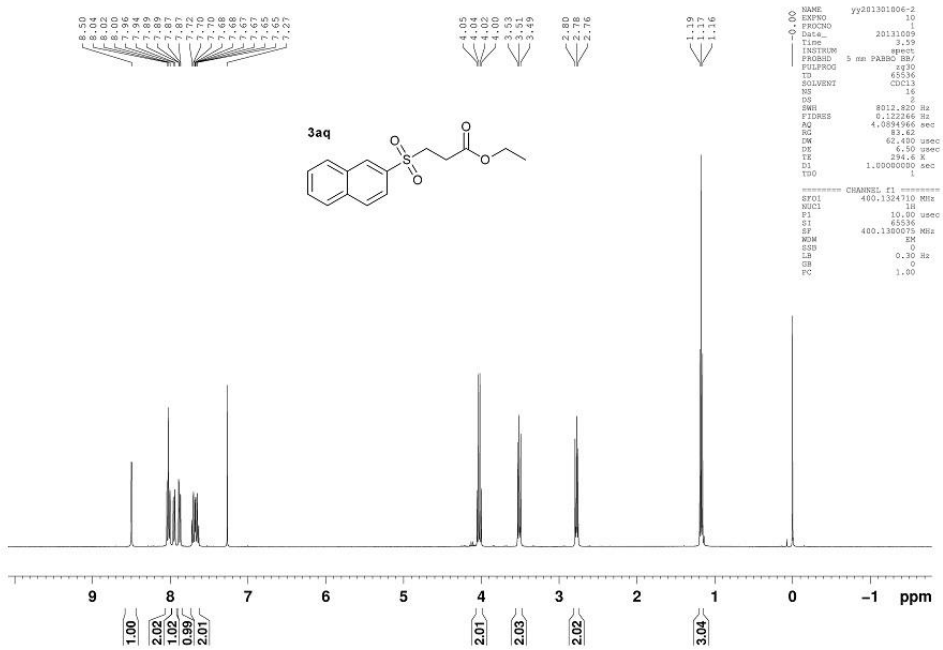

169.84
162.15
159.65
137.68
137.61
132.54
132.49
132.37
132.20
123.76
123.72
116.20
114.94
77.32
77.20
77.00
76.68
61.41
51.53
27.82
14.88
14.84
14.03
3an
F
O
O
S
O
O
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

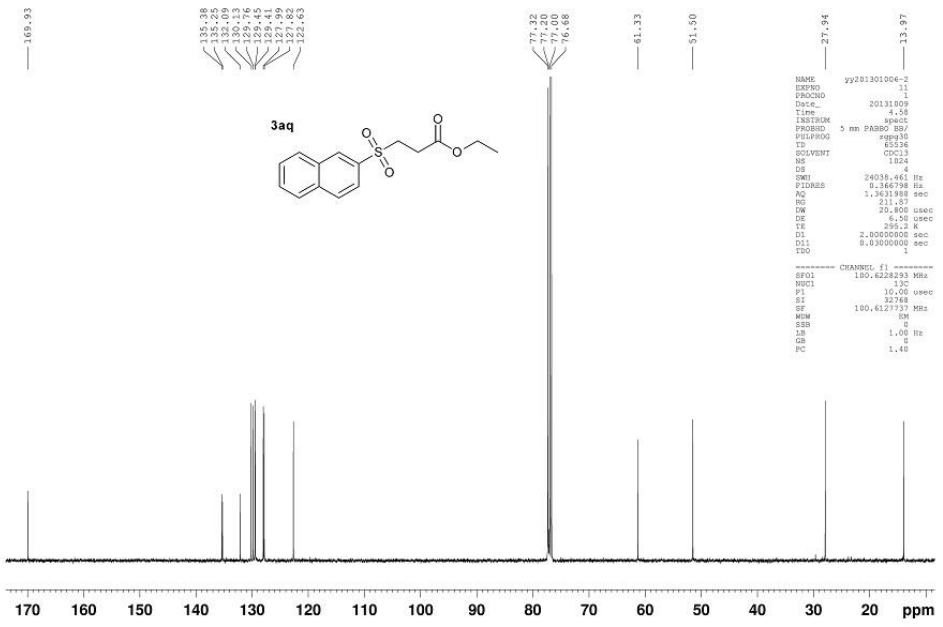

8.40
8.40
8.06
8.06
8.04
8.04
7.81
7.79
7.26
4.14
4.12
4.11
4.09
3.52
3.50
3.48
2.82
2.80
2.78
1.26
1.24
1.23
0.00
3ao
Cl
NO2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 ppm
0.93
0.98
0.98
1.99
2.02
2.00
3.32

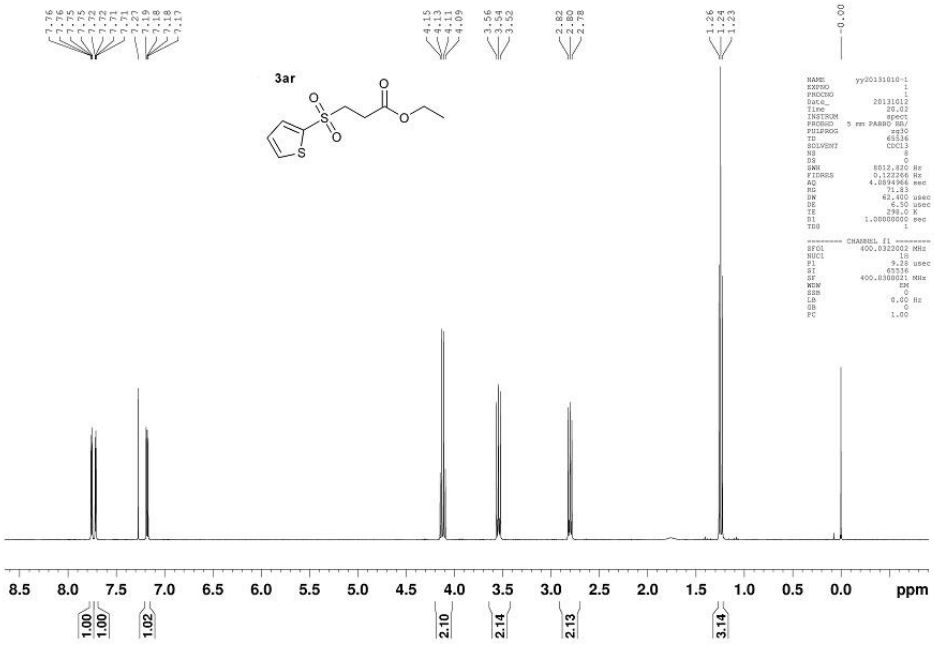

169.53
148.06
138.87
133.37
132.17
125.65
77.34
77.03
76.71
61.73
51.62
27.56
14.05
3ao
Cl
NO2
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

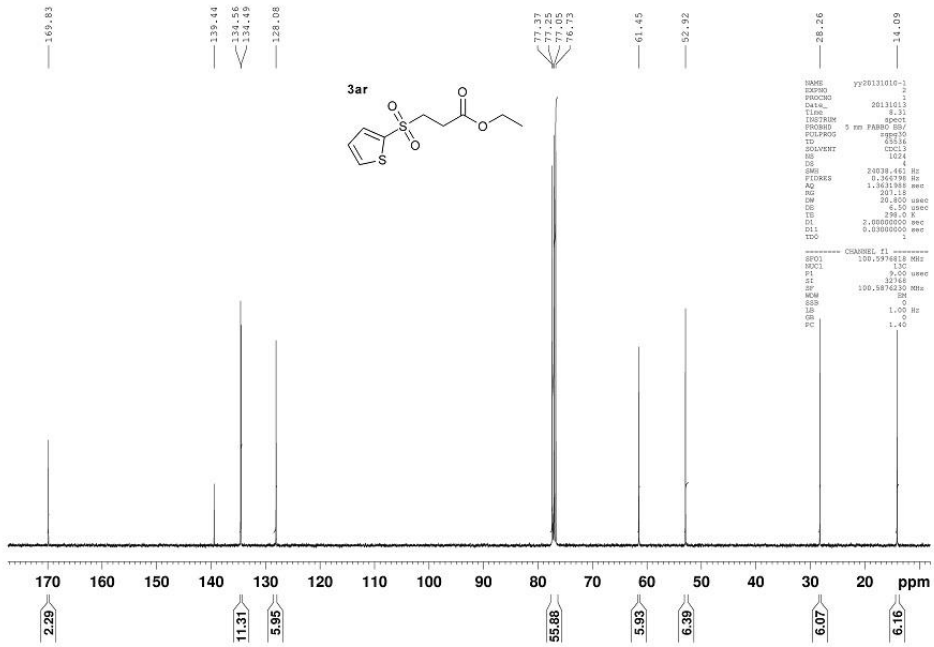

3ap
F3C
Br
O
O
O
O
ppm

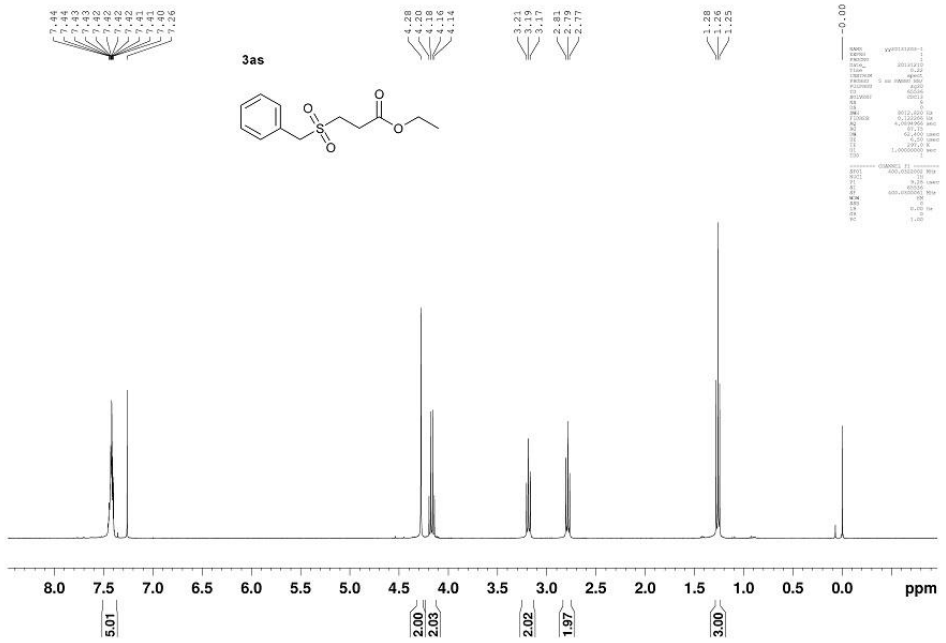

3ap
F3C
Br
O
O
O
O
ppm

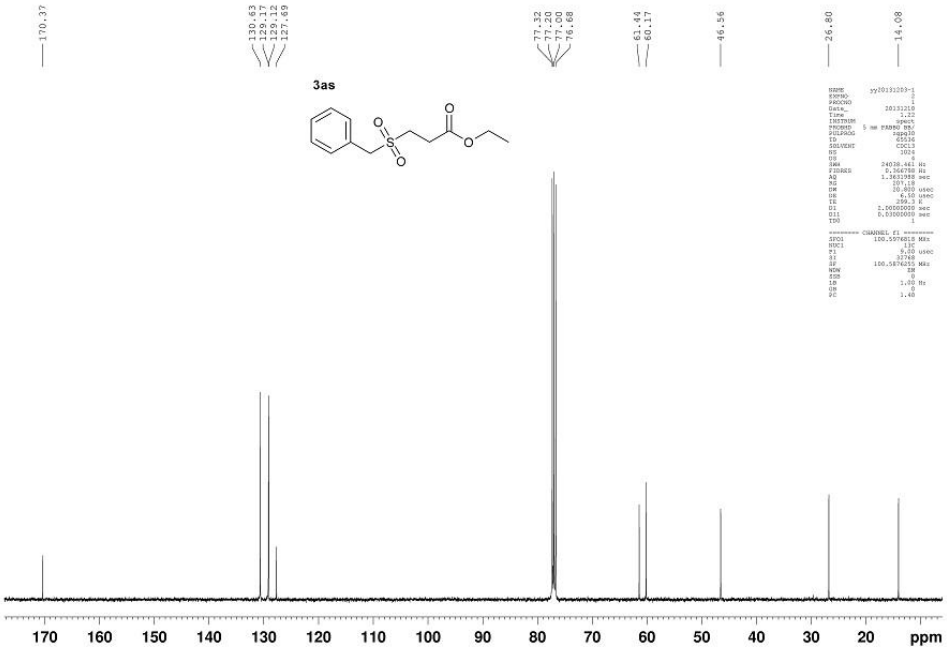

3aq
8.50
8.04
8.02
8.00
7.96
7.94
7.89
7.89
7.87
7.72
7.70
7.70
7.68
7.68
7.67
7.67
7.65
7.65
7.27
4.05
4.04
4.02
4.00
3.53
3.51
3.49
2.80
2.78
2.76
1.19
1.17
1.16
-0.00
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.00
2.02
1.02
0.99
2.01
2.01
2.03
2.02
3.04

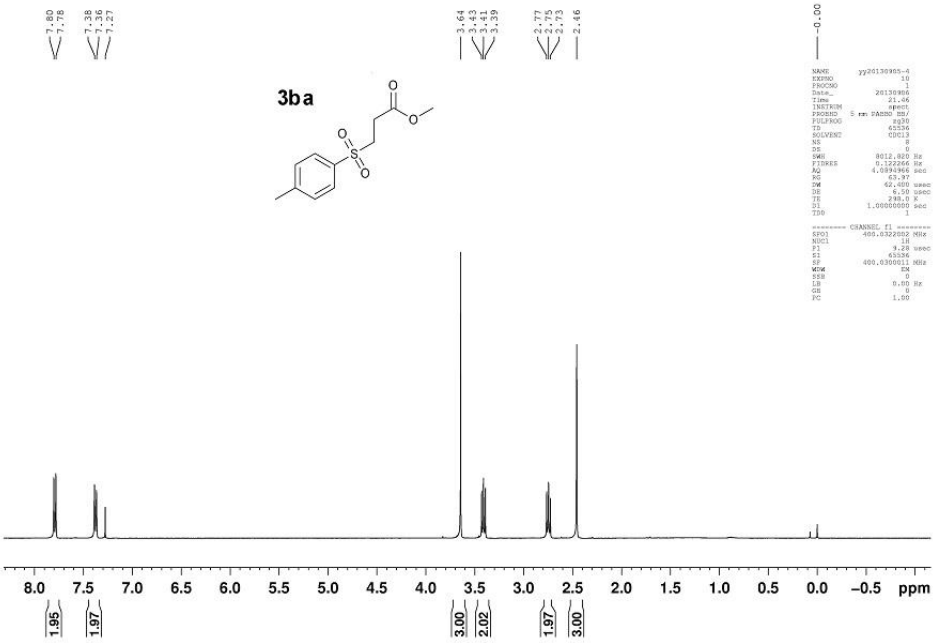

3aq
169.93
135.38
135.25
132.09
130.13
129.76
129.45
129.41
127.49
121.82
122.63
77.32
77.20
77.00
76.68
61.33
51.50
27.94
13.97
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

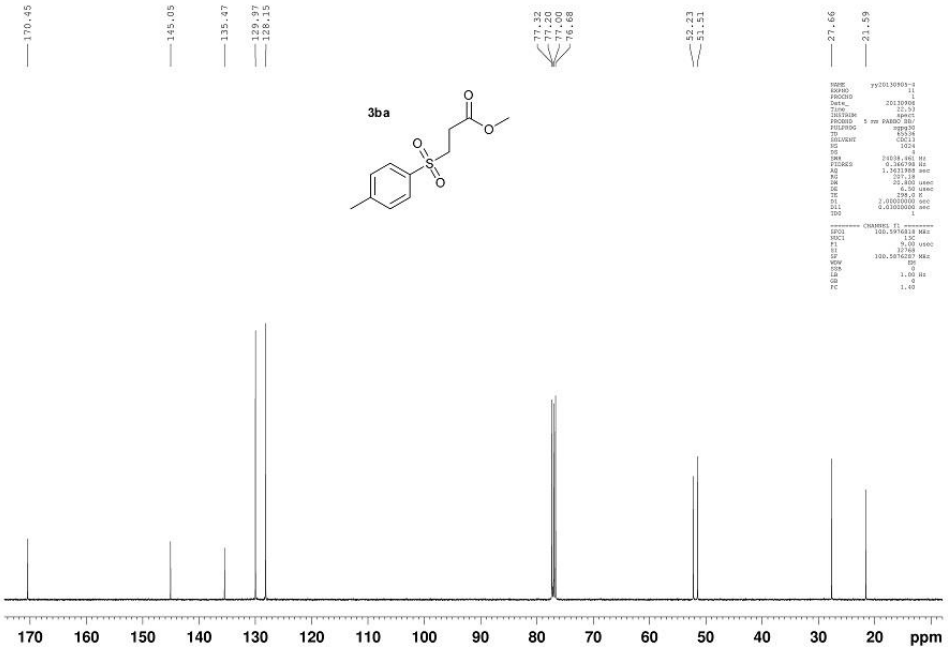

3ar
7.76
7.75
7.73
7.72
7.71
7.27
7.19
7.18
7.17
4.15
4.13
4.11
4.09
3.56
3.54
3.52
2.82
2.80
2.78
1.26
1.24
1.23
0.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.02
2.10
2.14
2.13
3.14

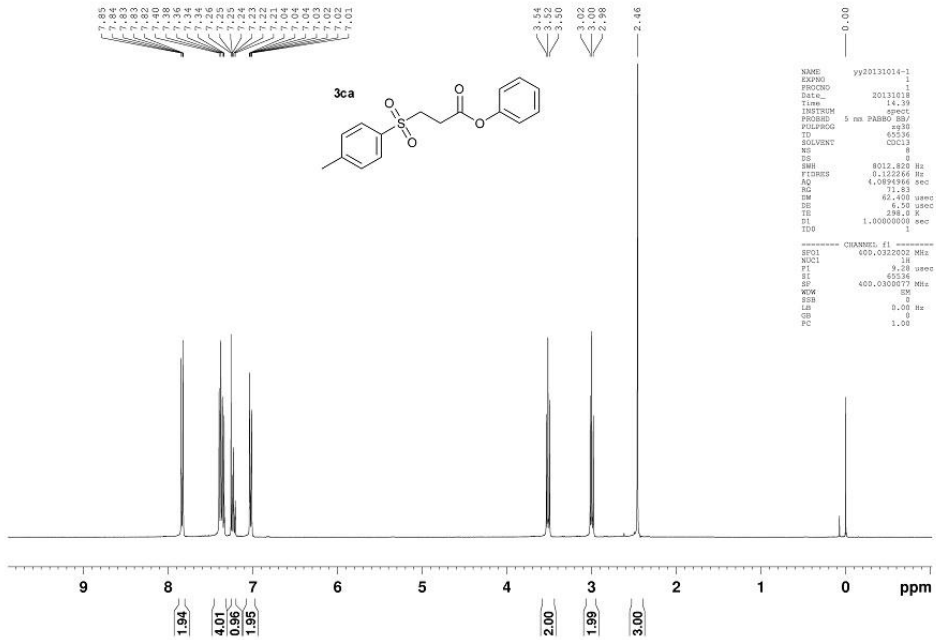

3ar
169.83
139.44
134.56
134.49
128.08
77.37
77.05
76.73
61.45
52.92
28.26
14.09
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
2.29
11.31
5.95
55.88
5.93
6.39
6.07
6.16

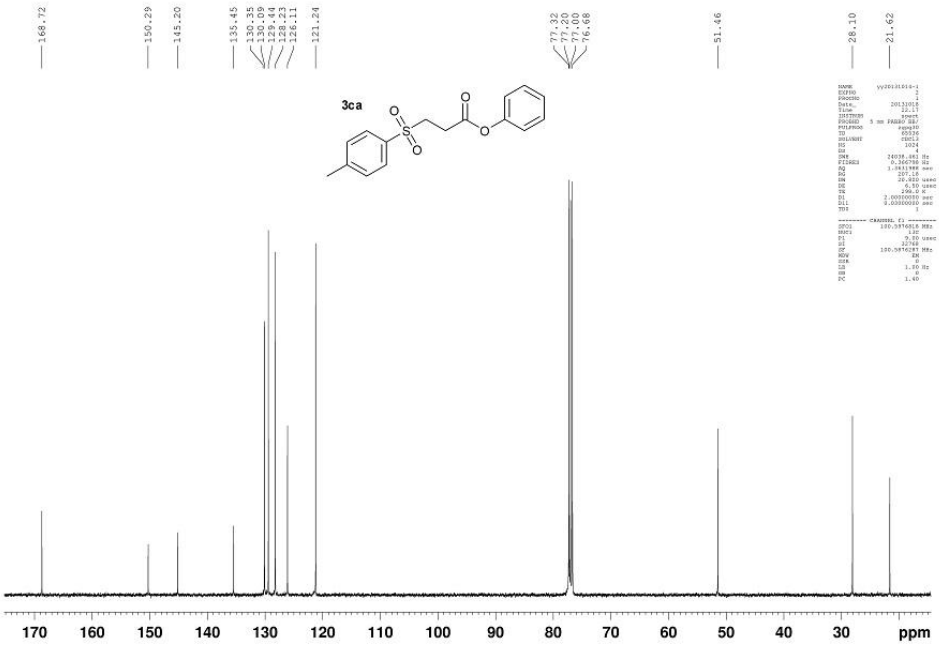

3as
7.44
7.44
7.43
7.43
7.42
7.42
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.26
4.28
4.20
4.18
4.16
4.14
3.21
3.19
3.17
2.81
2.79
2.77
1.28
1.26
1.25
0.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
5.01
2.00
2.03
2.02
1.97
3.00

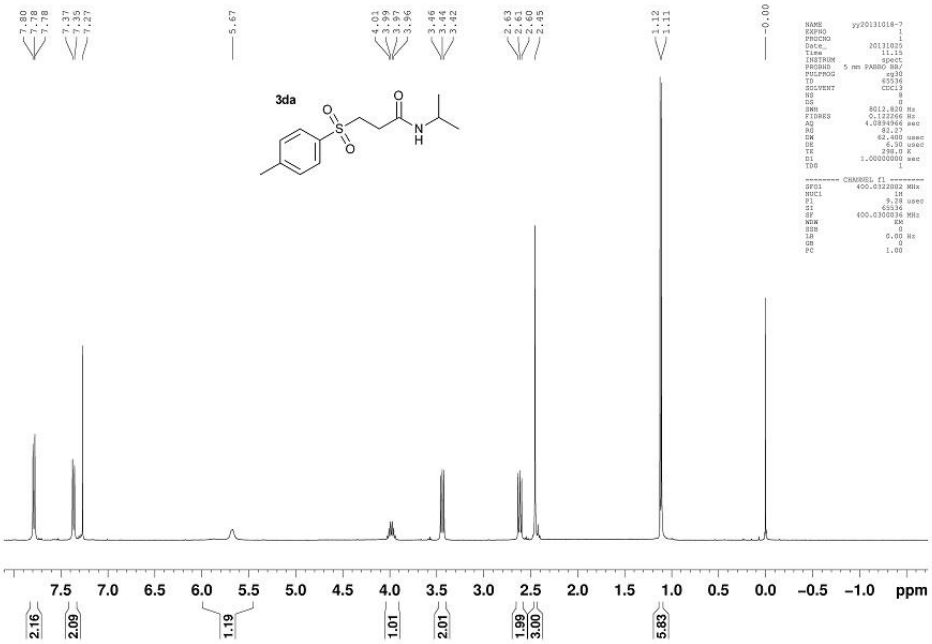

3as
170.37
130.63
129.17
129.12
127.69
77.32
77.20
77.00
76.68
61.44
60.17
46.56
26.80
14.08
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

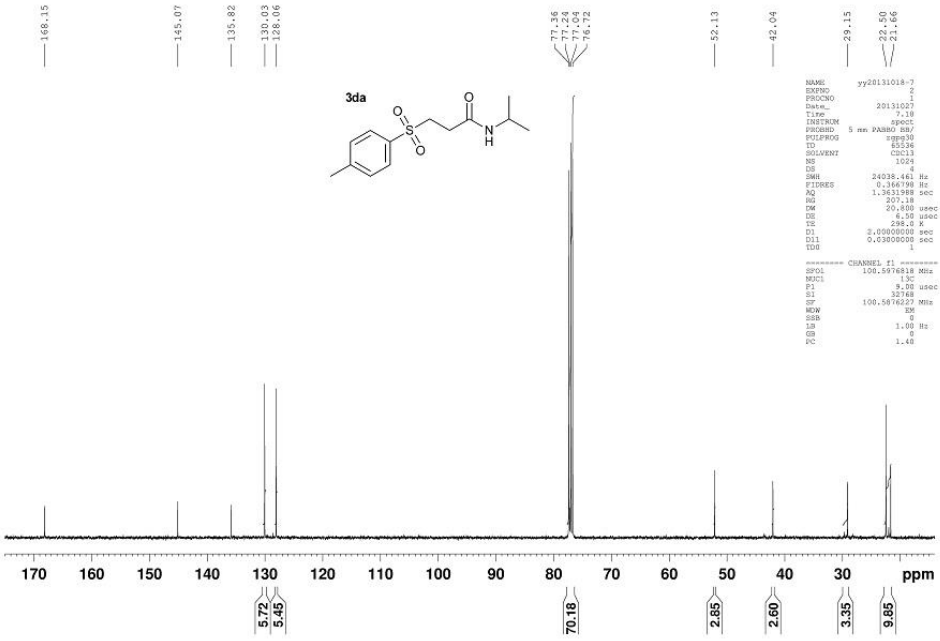

7.80
7.78
7.38
7.36
7.27
3.64
3.43
3.41
3.39
2.77
2.75
2.73
2.46
0.00
3ba
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
ppm
1.95
1.97
3.00
2.02
1.97
3.00

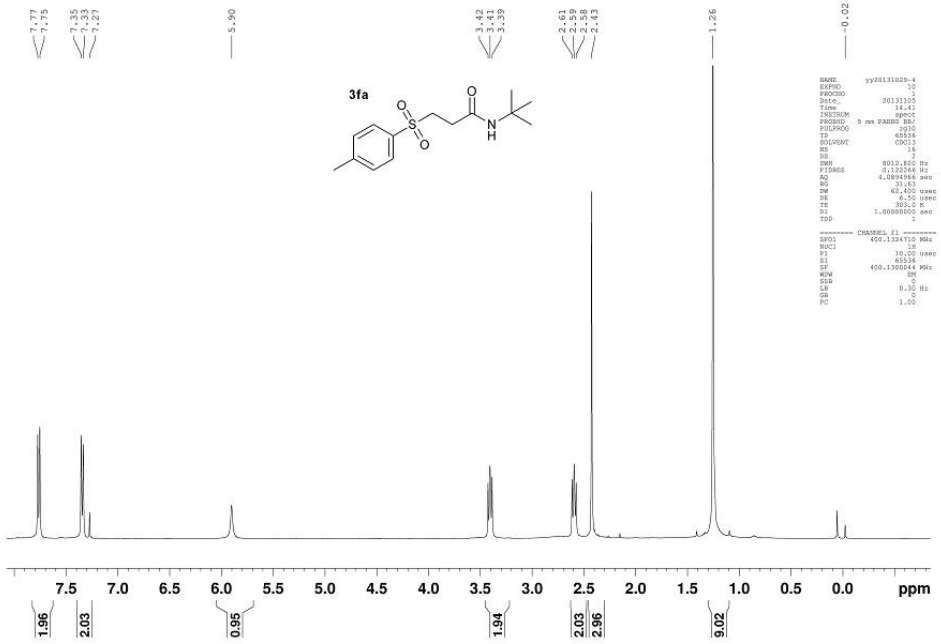

170.45
145.05
135.47
129.97
128.15
77.32
77.20
77.00
76.68
52.23
51.51
27.66
21.59
3ba
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

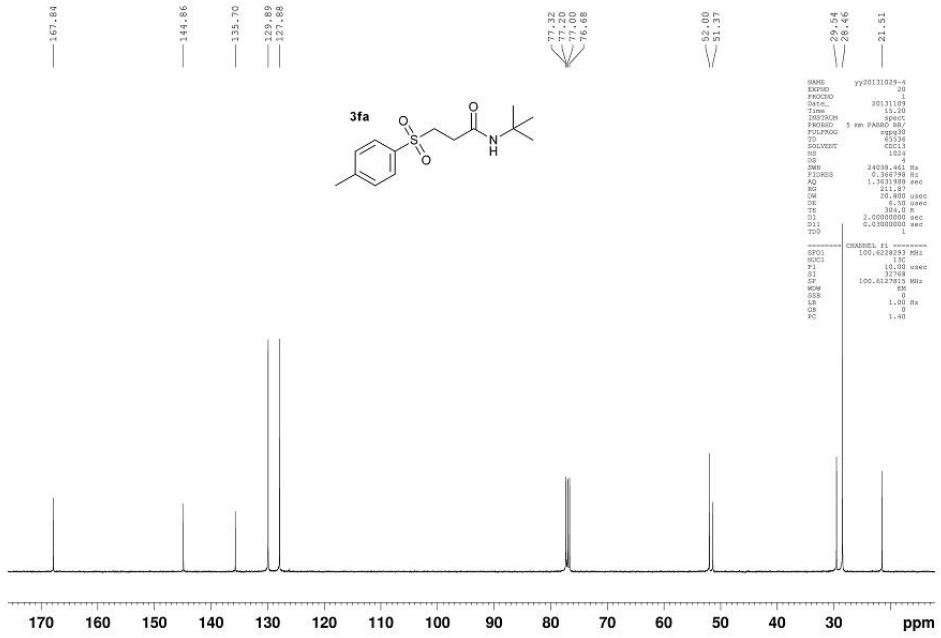

3ca
ppm

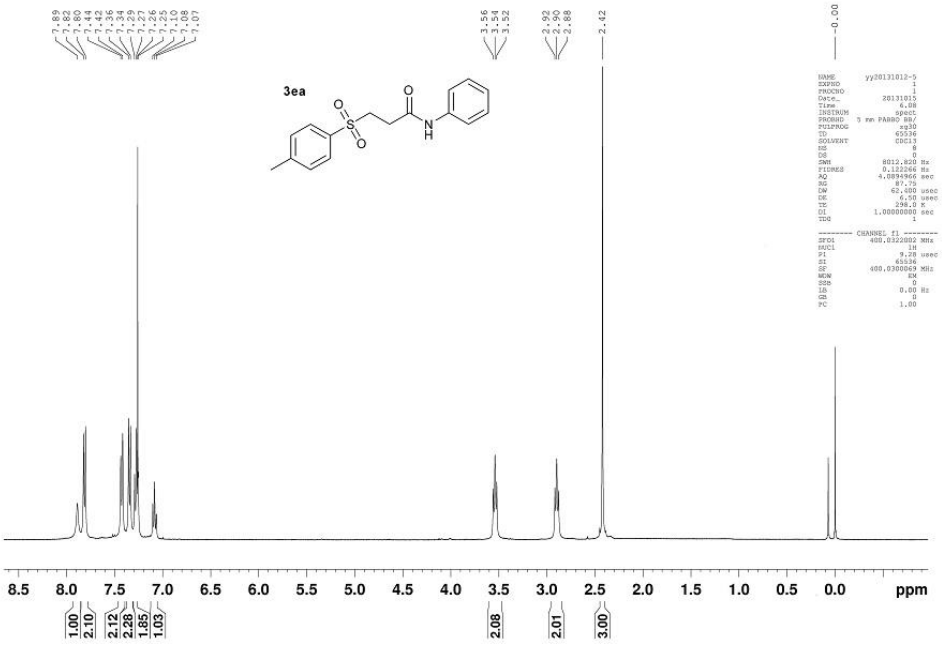

3ca
ppm

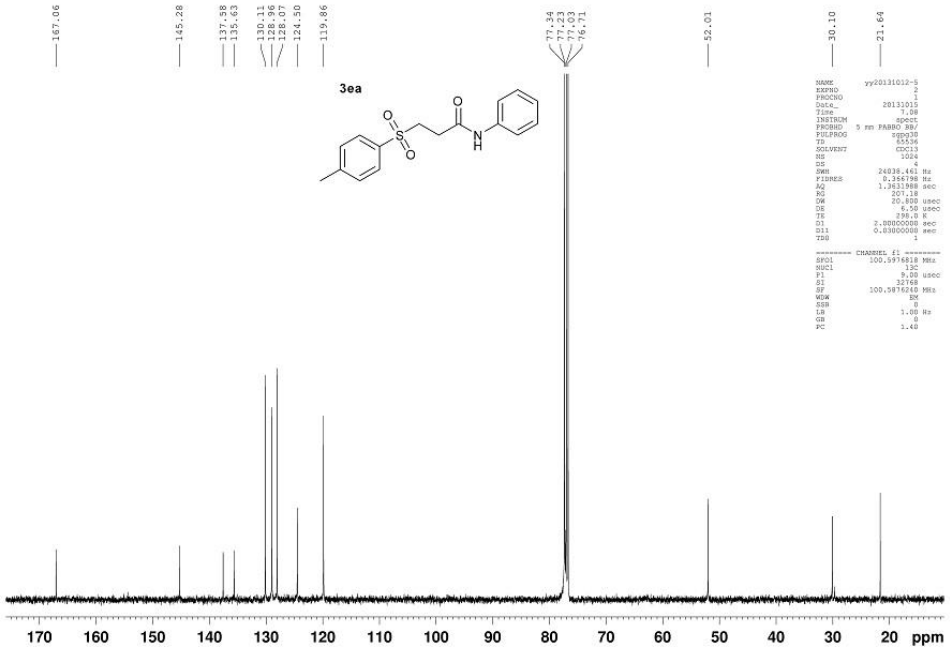

7.80
7.78
7.78
7.37
7.35
7.27
5.67
4.01
3.99
3.97
3.96
3.46
3.44
3.42
2.63
2.61
2.60
2.45
1.12
1.11
0.00
3da
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
ppm
2.16
2.09
1.19
1.01
2.01
1.99
3.00
5.83

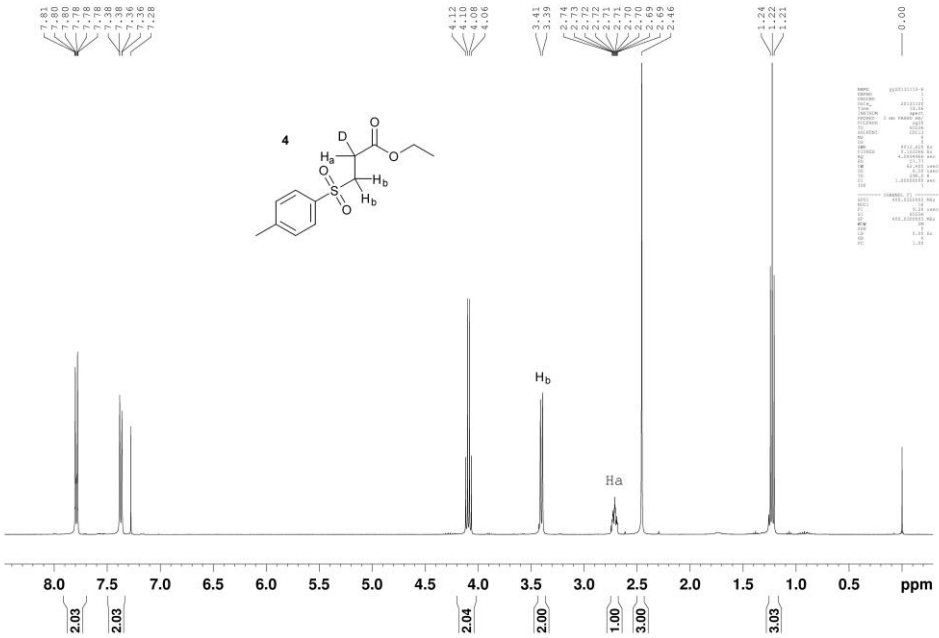

168.15
145.07
135.82
130.03
128.06
77.36
77.24
77.04
76.72
52.13
42.04
29.15
22.50
21.66
3da
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm
5.72
5.45
70.18
2.85
2.60
3.35
9.65


7.77
7.75
7.35
7.33
7.27
5.90
3.42
3.41
3.39
2.61
2.59
2.58
2.43
1.26
-0.02
3fa
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.96
2.03
0.95
1.94
2.03
2.96
9.02


167.84
144.86
135.70
129.89
127.88
77.32
77.20
77.00
76.68
52.00
51.37
29.54
28.46
21.51
3fa
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


3ea
7.89
7.82
7.80
7.44
7.42
7.36
7.34
7.29
7.27
7.26
7.25
7.10
7.08
7.07
3.56
3.54
3.52
2.92
2.90
2.88
2.42
-0.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
2.10
2.12
2.28
1.85
1.03
2.08
2.01
3.00


3ea
167.06
145.28
137.58
135.63
130.11
128.96
128.07
124.50
119.86
77.34
77.23
77.03
76.71
52.01
30.10
21.64
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


4
Hb
Ha
ppm