Electronic Supplementary Material (ESI) for Green Chemistry.

A sustainable oxidative esterification of thiols with alcohols by a cobalt nanocatalyst supported on doped carbon

Changjian Zhou,[a] Zhenda Tan,[a] Huanfeng Jiang[a] and Min Zhang*[a]

[a] State Key Laboratory of Pulp and Paper Engineering, and Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China
E-mail: minzhang@scut.edu.cn

Table of contents

1. General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR and infrared spectra (IR). Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400 and referenced to 7.27 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources (*J & K* Chemicals, TCI, Fluka, Acros, SCRC), used without further purification.

X-ray diffraction (XRD) was used for crystal structure identification as used by a Bruker D8 advanced X-ray diffractometer. Micromeritics ASAP 2020 was used to measure the specific surface area and pore structure (BET) by N_2 adsorption. Transmission electron microscopy (TEM) and Energy Dispersive X-ray spectroscopy (EDX) using a Tecnai-G20 to observe the morphology of samples. The atomic emission spectrometry (ICP) was used to analyse the metal content in the samples. The electronic states were measured by X-ray photoelectron spectroscopy (XPS) using an K-Alpha spectrometer with a monochromatized Al-Kα X-ray source (300W).

2. Procedure for the preparation of catalysts

The mixture of $Co(OAc)_2 \cdot 4H_2O$ (934 mg, 3.75 mmol) and 1,10-phenanthroline (2025 mg, 11.25 mmol) (Co : phenanthroline = 1 : 3 molar ratio) was added to ethanol (100 mL) and stirred at 100 °C for 1 hour. Silica was then introduced into the above solution by *in situ* hydrolysis of the added $Si(OC_2H_5)_4$ (TEOS) with aqueous ammonia. After that, the commercially available powder activated carbon (5000 mg) as the support was added to the solution and refluxed for 5 h at 100 °C, then the solvent of the suspension was removed and the remained solid was dried overnight at 60 °C under vacuum. Then, the sample was grounded to a fine powder and then pyrolyzed at 800 °C under a constant argon flow for 2 hours. After cooling down to room temperature, the catalyst material was finally afforded by treating the sample with HCl solution to remove non-supported cobalt particles, which is named as Co/N–SiO_2–AC (the Co content is 1.08 wt %, which is determined by ICP-OES measurements). Similarly, the materials prepared in absence of TEOS, 1,10-phenanthroline and metal source are donated as Co/N–AC, Co/SiO_2–AC and N–SiO_2/AC, respectively. And the catalysts prapared with different metal sources are denoted as Metal/N–SiO_2–AC, respectively.

3. Typical procedure for the synthesis of sulfinic ester 3aa

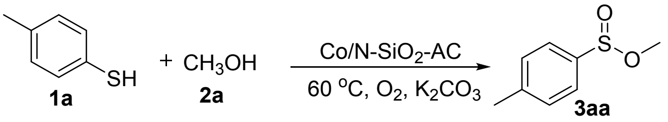
The mixture of 4-methylbenzenethiol (0.5 mmol), 1.5 mL methanol, K_2CO_3 (0.1 mmol) and forty milligrams of the catalyst (Co/N–SiO_2–AC, 1.46 mol % Co) was added into a 25 mL Schlenk tube, then stirred at 60 °C for 24 h under O_2 atmosphere. After that, the resulting mixture was filtered and washed with ethyl acetate, and then concentrated by removing the solvent under vacuum. Finally the residue was purified by preparative TLC on silica, eluting with petroleum ether (60 – 90 °C) : ethyl acetate (20 : 1, v/v) to give the sulfinic ester **3aa**.

4. Recycling reaction of catalyst for the synthesis of sulfinic ester 3aa

The used catalyst was collected by filtration and washed with pure methanol, then dried in the oven under vacuum. The catalyst was then used for the next catalytic reaction.

5. Screening of optimal conditions for the synthesis of sulfinic ester 3aa

Table S1 Screening of optimal conditions for the synthesis of methyl 4-methylbenzenesulfinate[a]



Entry	Catalyst	Additive	Yield (%)[b]
1	AC	K_2CO_3	0
2	N–AC	K_2CO_3	0
3	SiO_2–AC	K_2CO_3	0
4	Co/AC	K_2CO_3	0

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mL), catalyst (1.46 mol %, 0.43 mg Co, 0.0073 mmol, 40 mg), K_2CO_3 (20 mol %) were stirred at 60 °C for 24 h under O_2. [b] GC yield by using hexadecane as an internal standard.

6. BET measurement of the catalysts

Table S2 Pore structure of the catalysts

Samples	D (nm)	S_{BET} (m^2g^{-1})	V (cm^3g^{-1})
Co/N–SiO_2–AC	4.9	566.2	0.69
Co/N–AC	1.9	683.7	0.33
Co/N–SiO_2–AC (used)	3.8	425.2	0.41

7. Power x-ray diffraction

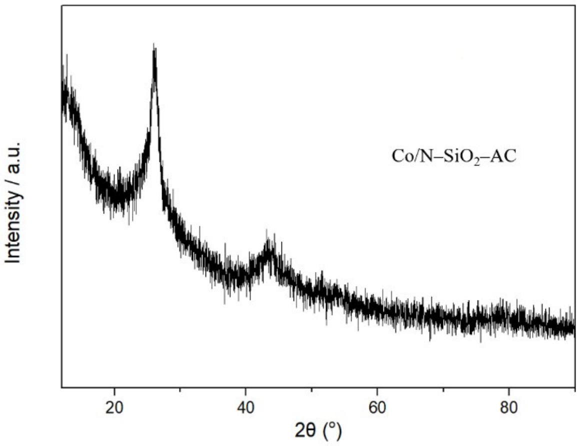


Fig. S1 XRD pattern of Co/N–SiO_2–AC.

8. EDX analysis of the catalyst

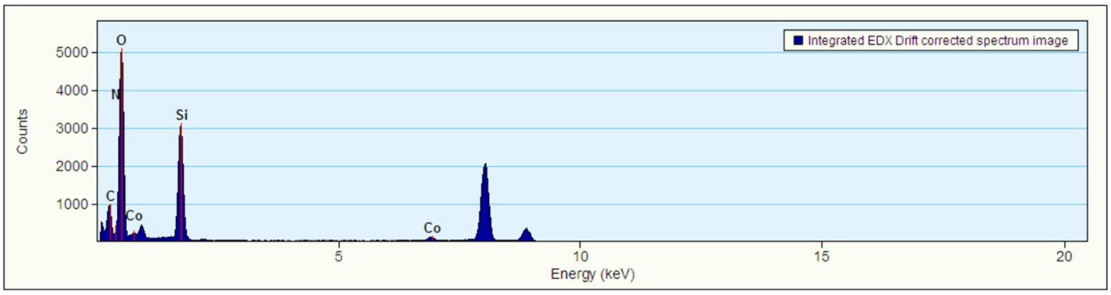


Fig. S2 EDX analysis of the Co/N–SiO_2–AC catalyst.

9. TEM measurement of the catalysts

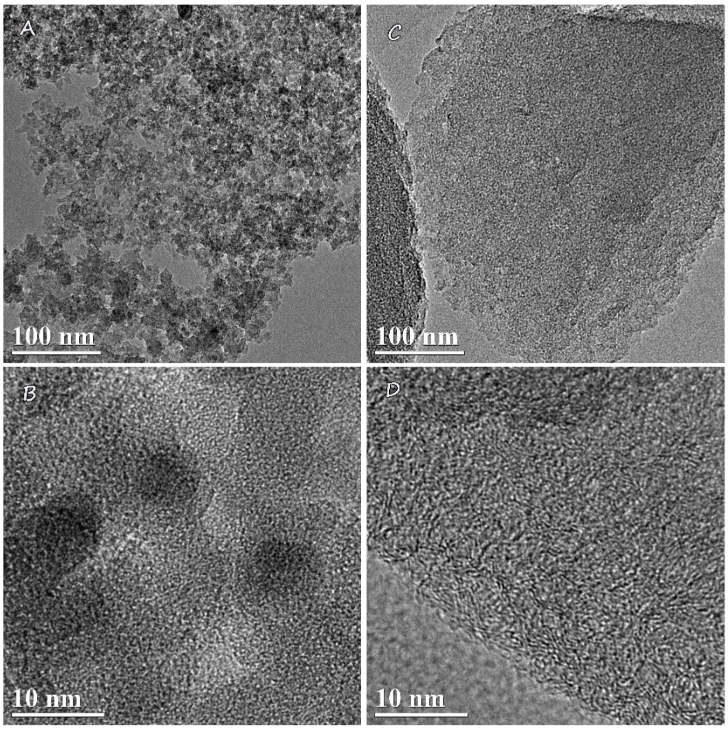


Fig. S3 TEM images of samples: (a, b) Co/N–SiO_2–AC, (c, d) Co/N–AC.

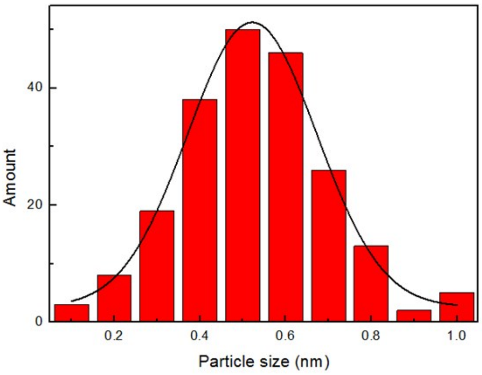


Fig. S4 Particle size distribution of Co/N–SiO_2–AC.

10. XPS spectra of N1s in the catalyst

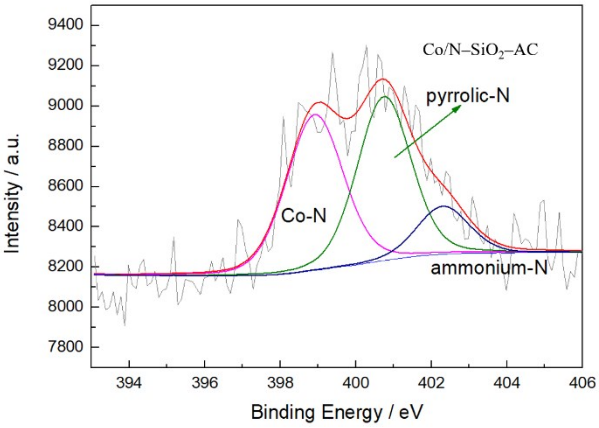


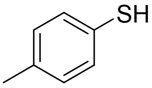
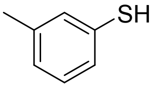
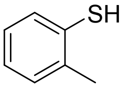
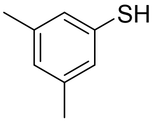
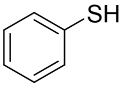
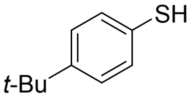
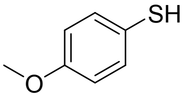
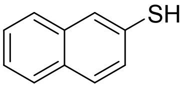
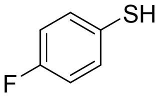
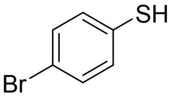
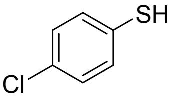
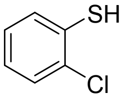
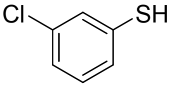
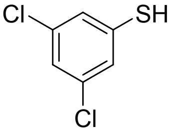
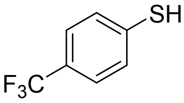
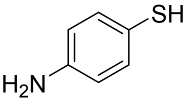
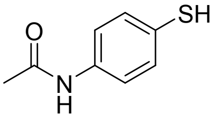
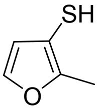
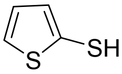
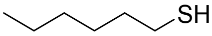
Fig. S5 XPS spectra of N1s in Co/N–SiO_2–AC.

Table S3 The binding energy and content of N in the catalyst

Sample	Binding Energy / eV (Area/%)		
	Co–N	Pyrrolic-N	Ammonia-N
Co/N–SiO_2–AC	398.9 (43.9)	400.7 (43.6)	402.2 (12.4)

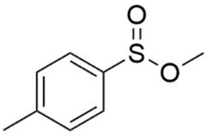
11. Substrates employed for synthesizing oxidative esterification

Table S4 Substrates employed for oxidative esterification

 **1a**	 **1b**	 **1c**	 **1d**
 **1e**	 **1f**	 **1g**	 **1h**
 **1i**	 **1j**	 **1k**	 **1l**
 **1m**	 **1n**	 **1o**	 **1p**
 **1q**	 **1r**	 **1s**	 **1t**

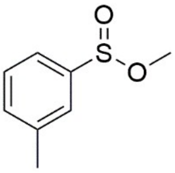
12.Analytic data of the obtained compounds

methyl 4-methylbenzenesulfinate (3aa)[1]



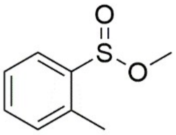
Colorless oil (77 mg, 91% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.37 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 142.86, 140.96, 129.75, 125.39, 49.38, 21.52. IR (KBr): 3058, 2362, 2335, 1738, 1516, 1455, 1327, 1141, 1077, 913, 810, 751 cm^{-1}.

methyl 3-methylbenzenesulfinate (3ba)



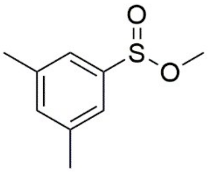
Colorless oil (72 mg, 85% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 3.46 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.85, 139.32, 133.08, 128.97, 125.69, 122.55, 49.73, 21.42. IR (KBr): 2941, 2832, 2362, 2335, 1693, 1598, 1455, 1217, 1131, 1087, 1026, 964, 853, 787, 689 cm^{-1}. HRMS: calcd for $C_8H_{11}O_2S$ [M+H]$^+$ 171.0474, found 171.0478.

methyl 2-methylbenzenesulfinate (3ca)[2]



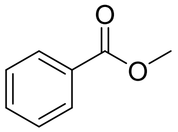
Colorless oil (64 mg, 75% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.90 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 – 7.46 (m, 2H), 7.24 (d, *J* = 7.2, 1H), 3.47 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 141.31, 136.71, 132.25,131.31, 126.35, 124.79, 49.94, 18.08. IR (KBr): 2943, 2837, 2362, 2335, 1645, 1460, 1384, 1324, 1275, 1129, 1023, 967, 913, 745, 680 cm^{-1}.

methyl 3,5-dimethylbenzenesulfinate (3da)[3]



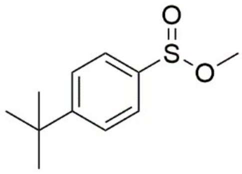
Colorless oil (74 mg, 80% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (s, 2H), 7.15 (s, 1H), 3.47 (s, 3H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.85, 139.13, 134.00, 122.89, 49.79, 21.33. IR (KBr): 3009, 2940, 2360, 2249, 1734, 1605, 1540, 1455, 1269, 1166, 1130, 965, 913, 853, 744, 690 cm^{-1}.

methyl benzenesulfinate (3ea)[4]



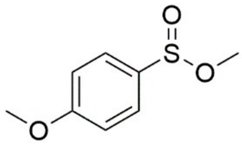
Colorless oil (68 mg, 87% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66 – 7.69 (m, 2H), 7.49 – 7.53 (m, 3H), 3.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.97, 132.24, 129.09, 125.40, 49.63. IR (KBr): 2940, 1444, 1327, 1129, 1081, 963, 754, 692 cm^{-1}.

methyl 4-(tert-butyl)benzenesulfinate (3fa)[3]



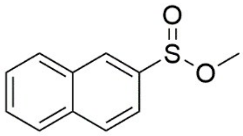
Colorless oil (90 mg, 85% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 3.48 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 156.00, 141.03, 126.18, 125.29, 49.76, 35.20, 31.28. IR (KBr): 2963, 2872, 2362, 1919, 1678, 1593, 1464, 1396, 1366, 1267, 1198, 1135, 1108, 965, 916, 834, 741 cm^{-1}.

methyl 4-methoxybenzenesulfinate (3ga)[3]



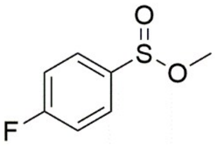
Colorless oil (73 mg, 88% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 162.80, 135.54, 127.24, 114.47, 55.60, 49.23. IR (KBr): 3062, 3010, 2943, 2841, 2362, 2045, 1900, 1737, 1588, 1493, 1461, 1300, 1257, 1164, 1080, 1024, 829, 803, 766, 713 cm^{-1}.

methyl naphthalene-2-sulfinate (3ha)[3]



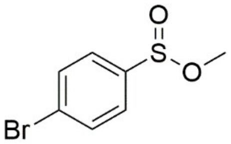
Colorless oil (85 mg, 83% yield), ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.27 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.68 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.58 – 7.64 (m, 2H), 3.50 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 141.16, 135.13, 132.69, 129.42, 129.15, 128.43, 128.13, 127.44, 126.67, 121.08, 49.73. IR (KBr): 3055, 2938, 2362, 2335, 1648, 1587, 1500, 1454, 1323, 1268, 1060, 1023, 962, 911, 859, 816, 747 cm^{-1}.

methyl 4-fluorobenzenesulfinate (3ia)[3]



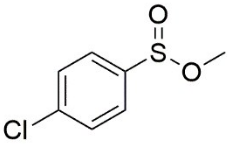
Colorless oil (71 mg, 82% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 – 7.74 (m, 2H), 7.22 – 7.26 (m, 2H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 165.16 (d, $J_{C\text{-}F}$ = 253.5 Hz), 139.95 (d, $J_{C\text{-}F}$ = 3.0 Hz), 127.98 (d, $J_{C\text{-}F}$ = 9.1 Hz), 116.46 (d, $J_{C\text{-}F}$ = 22.2 Hz). IR (KBr): 3068, 2362, 2335, 1707, 1585, 1488, 1399, 1367, 1232, 1083, 1032, 831, 757 cm^{-1}.

methyl 4-bromobenzenesulfinate (3ja)[3]



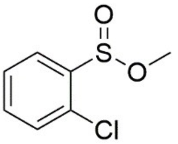
Colorless oil (88 mg, 75% yield), m.p: 143 – 145 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 143.11, 132.44, 127.17, 49.89. IR (KBr): 3088, 2361, 2334, 1739, 1706, 1515, 1390, 1268, 1189, 1068, 998, 821, 746 cm^{-1}.

methyl 4-chlorobenzenesulfinate (3ka)[3]



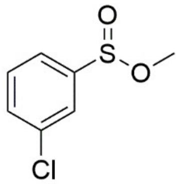
Colorless oil (79 mg, 83% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 142.55, 138.71, 129.47, 127.00, 49.84. IR (KBr): 3088, 2941, 2466, 2362, 1914, 1724, 1573, 1473, 1391, 1368, 1255, 1157, 1116, 1086, 1008, 824, 749, 700 cm^{-1}.

methyl 2-chlorobenzenesulfinate (3la)[3]



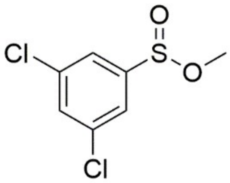
Colorless oil (64 mg, 67% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.93 – 7.95 (m, 1H), 7.48 – 7.51 (m, 2H), 7.43 – 7.45 (m, 1H), 3.59 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 141.24, 133.53, 132.87, 130.49, 127.28, 126.78, 51.42. IR (KBr): 2942, 2840, 2362, 2335, 1644, 1570, 1448, 1335, 1253, 1132, 1056, 1028, 967, 912, 745, 684 cm^{-1}.

methyl 3-chlorobenzenesulfinate (3ma)[3]



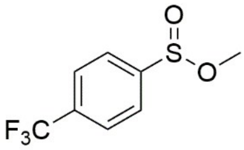
Colorless oil (76 mg, 80% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (s, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.47 – 7.55 (m, 2H), 3.51 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.03, 135.62, 132.46, 130.48, 125.66, 123.73, 50.03. IR (KBr): 3061, 2941, 2834, 2362, 2335, 1644, 1574, 1459, 1411, 1269, 1135, 1072, 1017, 962, 909, 788, 741 cm^{-1}.

methyl 3,5-dichlorobenzenesulfinate (3na)[5]



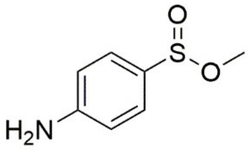
Colorless oil (67 mg, 60% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.57 (d, *J* = 2.0 Hz, 2H), 7.53 (t, *J* = 2.0 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 147.46, 136.37, 132.39, 124.14, 50.40. IR (KBr): 3070, 2942, 2357, 2337, 2254, 1733, 1566, 1455, 1417, 1100, 962, 909, 864, 798, 735, 689 cm^{-1}.

methyl 4-(trifluoromethyl)benzenesulfinate (3oa)[5]



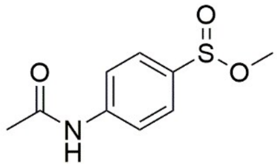
Colorless oil (78 mg, 70% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.84 (q, *J* = 8.4 Hz, 4H), 3.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 147.98, 134.23 (q, $J_{C\text{-}F}$ = 33.3 Hz), 127.60, 126.29 (q, $J_{C\text{-}F}$ = 2.0 Hz), 126.22, 124.89, 122.18. IR (KBr): 2946, 2839, 2362, 1644, 1456, 1400, 1324, 1170, 1134, 1059, 1016, 963, 841, 741 cm^{-1}.

methyl 4-aminobenzenesulfinate (3pa)



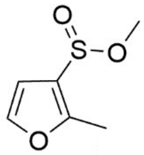
Colorless oil (64 mg, 75% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 3.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 150.54, 132.12, 127.16, 114.52, 49.09. IR (KBr): 2947, 2841, 2598, 2362, 2335, 1635, 1594, 1498, 1220, 1128, 1018, 913, 826, 742 cm^{-1}. HRMS: calcd for $C_7H_9NNaO_2S$ $[M+Na]^+$ 194.0246, found 194.0252.

methyl 4-acetamidobenzenesulfinate (3qa)



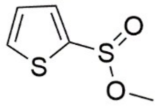
Colorless oil (86 mg, 81% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.93 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 3.44 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 169.68, 142.32, 138.06, 126.40, 119.87, 49.92, 24.53. IR (KBr): 3305, 3186, 2939, 2605, 2362, 2335, 1675, 1592, 1533, 1498, 1398, 1318, 1261, 1172, 1122, 1032, 1012, 963, 914, 830, 686 cm^{-1}. HRMS: calcd for $C_9H_{11}NNaO_3S$ [M+Na]$^+$ 236.0352, found 236.0356.

methyl 2-methylfuran-3-sulfinate (3ra)



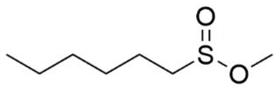
Colorless oil (56 mg, 70% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.32 (d, *J* = 2.0 Hz, 1H), 6.56 (d, *J* = 2.0 Hz, 1H), 3.62 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 154.71, 141.58, 124.59, 107.96, 50.07, 12.72. IR (KBr): 2927, 2852, 2362, 2335, 1648, 1578, 1514, 1125, 1056, 1024, 913, 743, 679 cm^{-1}. HRMS: calcd for $C_6H_8NaO_3S$ [M+Na]$^+$ 183.0086, found 183.0087.

methyl thiophene-2-sulfinate (3sa)



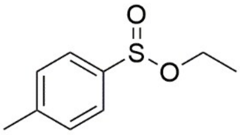
Colorless oil (73 mg, 90% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.66 (d, *J* = 4.8 Hz, 1H), 7.49 (d, *J* = 3.6 Hz, 1H), 7.17 (t, *J* = 4.4 Hz, 1H), 3.60 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 147.07, 131.73, 130.01, 127.85, 49.39. IR (KBr): 3099, 2924, 2362, 2335, 1645, 1501, 1458, 1399, 1333, 1141, 1095, 1037, 1010, 851, 721, 669 cm^{-1}. HRMS: calcd for $C_5H_6NaO_2S_2$ [M+Na]$^+$ 184.9701, found 184.9700.

methyl hexane-1-sulfinate (3ta)



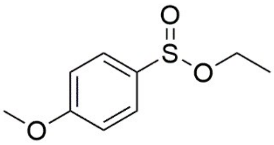
Colorless oil (37 mg, 45% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ3.76 (s, 3H), 2.64 – 2.80 (m, 2H), 1.65 – 1.72 (m, 2H), 1.38 – 1.45 (m, 2H), 1.28 – 1.33 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 57.11, 54.47, 31.51, 28.56, 22.49, 21.34, 14.07. IR (KBr): 1717, 1540, 1485, 1460, 1364, 1163, 1128, 1029, 913, 824, 744 cm^{-1}. HRMS: calcd for $C_7H_{16}NaO_2S$ [M+Na]$^+$ 187.0763, found 187.0765.

ethyl 4-methylbenzenesulfinate (3ab)[6]



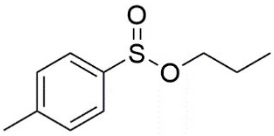
Colorless oil (82 mg, 89% yield); ^{1}H NMR (400 MHz, CDCl3): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.98 – 4.05 (m, 1H), 3.60 – 3.68 (m, 1H), 2.34 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.72, 141.99, 129.77, 125.29, 60.83, 21.58, 15.67. IR (KBr): 3038, 2923, 2362, 1916, 1707, 1594, 1490, 1450, 1326, 1234, 1139, 1077, 1034, 1006, 811, 757, 682 cm^{-1}.

ethyl 4-methoxybenzenesulfinate (3gb)



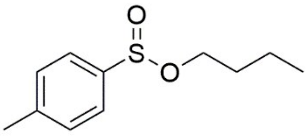
Colorless oil (80 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 4.03 – 4.09 (m, 1H), 3.83 (s, 3H), 3.66 – 3.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.60, 136.38, 126.98, 114.36, 60.54, 55.52, 15.55. IR (KBr): 2979, 1733, 1593, 1494, 1461, 1407, 1286, 1254, 1173, 1130, 881, 832, 798, 706 cm^{-1}. HRMS: calcd for $C_9H_{13}O_3S$ $[M+H]^+$ 201.0580, found 201.0582.

propyl 4-methylbenzenesulfinate (3ac)[6]



Colorless oil (84 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.95 – 4.01 (m, 1H), 3.54 – 3.60 (m, 1H), 2.42 (s, 3H), 1.60 – 1.69 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.59, 141.82, 129.66, 125.19, 66.06, 23.09, 21.48, 10.31. IR (KBr): 2967, 2882, 1733, 1595, 1458, 1385, 1329, 1195, 1133, 940, 806, 705 cm^{-1}.

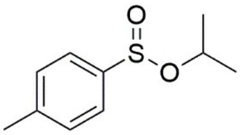
butyl 4-methylbenzenesulfinate (3ad)[6]



Colorless oil (88 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.00 – 4.06 (m, 1H), 3.59 – 3.65 (m, 1H), 2.43 (s, 3H), 1.57 – 1.66 (m, 2H), 1.31 – 1.40 (m, 2H), 0.88 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.72, 142.03, 129.80, 125.36, 64.51, 31.87, 21.64, 19.10, 13.72. IR

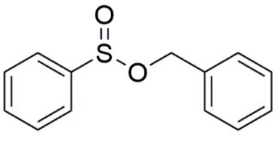
(KBr): 2961, 2835, 1733, 1612, 1551, 1498, 1442, 1364, 1132, 1009, 915, 857, 805, 741 cm^{-1}.

isopropyl 4-methylbenzenesulfinate (3ae)[5]



Colorless oil (74 mg, 75% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.49 – 4.55 (m, 1H), 2.34 (s, 3H), 1.30 (d, *J* = 6.4 Hz, 3H), 1.16 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 142.82, 142.55, 129.69, 125.12, 72.73, 24.05, 23.84, 21.57. IR (KBr): 3043, 2976, 2249, 1745, 1609, 1503, 1445, 1369, 1135, 1097,1016, 913, 842, 741 cm^{-1}.

benzyl benzenesulfinate (3ef)[7]



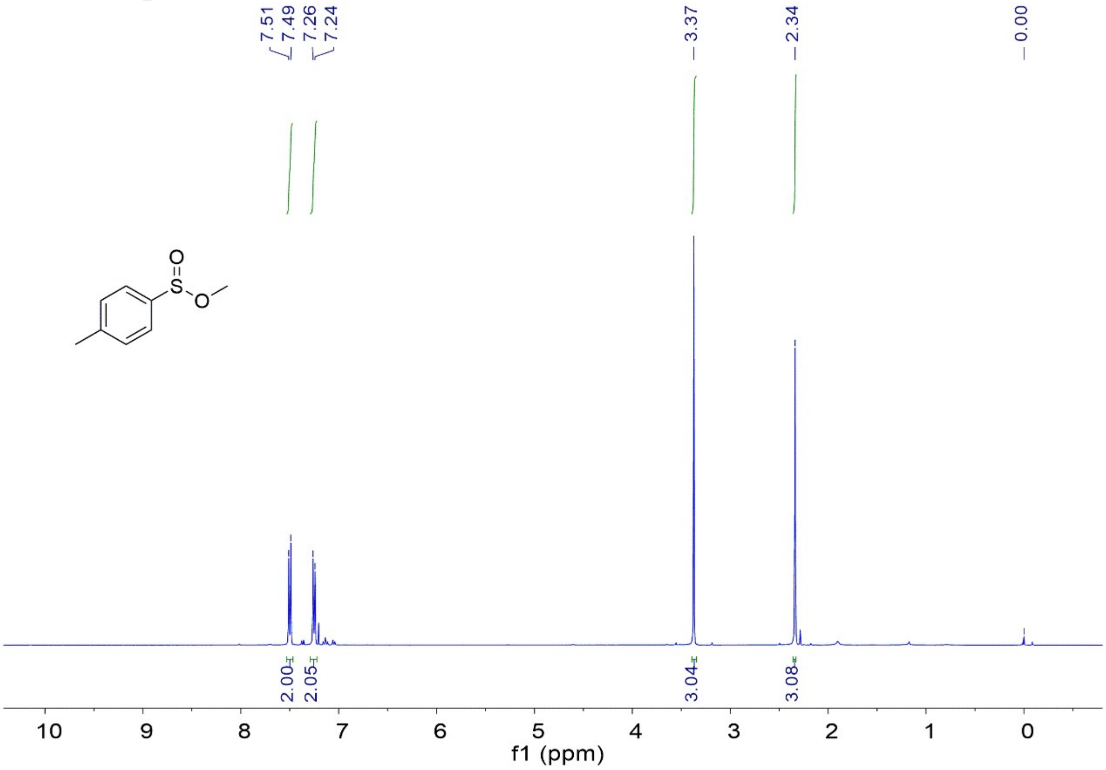
Colorless oil (17.4 mg, 15% yield); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 – 7.73 (m, 2H), 7.45 – 7.51 (m, 3H), 7.23 – 7.30 (m, 5H), 5.01 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (101 MHz, CDCl$_3$): δ 144.41, 135.29, 132.09, 128.96, 128.42, 128.34, 125.18, 65.73. IR (KBr): 3062, 2945, 1497, 1446, 1368, 1132, 1081, 905, 836, 753 cm^{-1}.

13.References

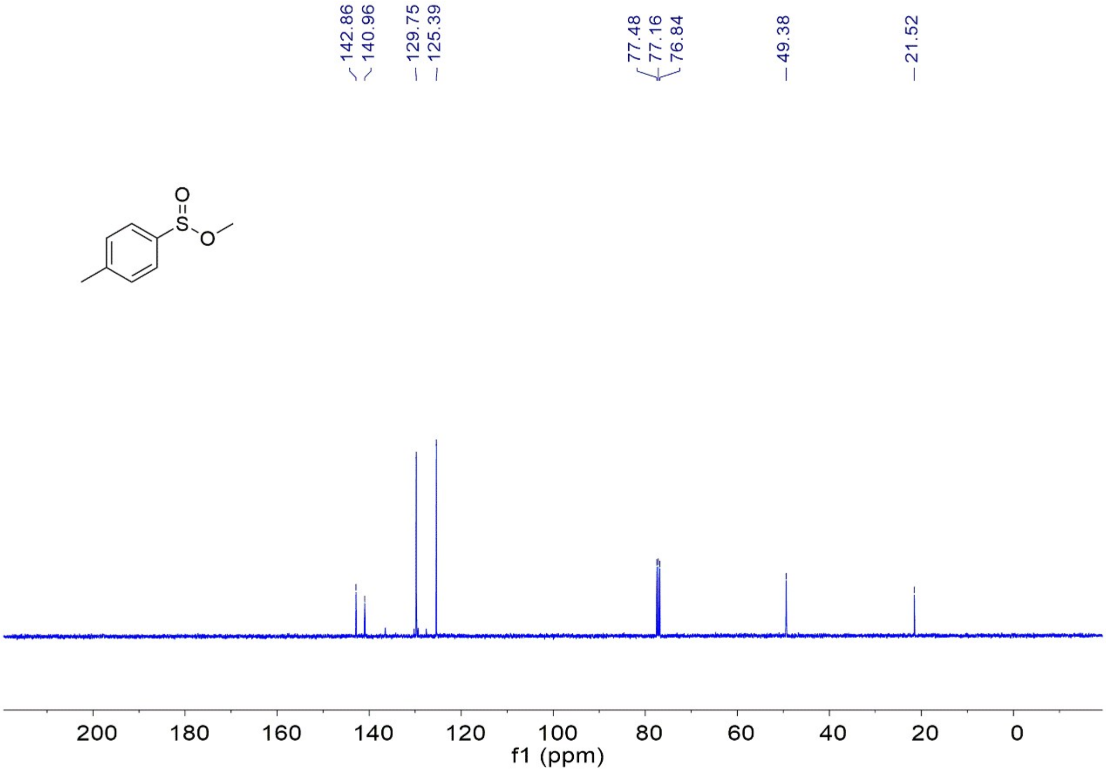
(1) J. L. García Ruano, J. Alemán, C. M. Belen and A. Parra, *Org. Lett.*, 2005, **7**, 179.
(2) R. Kowalczyk, A. J. F. Edmunds, R. G. Hall and C. Bolm, *Org. Lett.*, 2011, **13**, 768.
(3) B. N. Du, Z. Li, P. Qian, J. L. Han and Y. Pan, *Chem. Asian J.,* 2016, **11**, 478.
(4) M. F. Maldonado, F. Sehgelmeble, F. Bjarnemark, M. Svensson, J. Ahman and P. I. Arvidsson, *Tetrahedron*, 2012, **68**, 7456.
(5) J. A. Lujan-Montlongo, A. O. Estevez and F. F. Fleming, *Eur. J. Org. Chem.*, 2015, 1602.
(6) A. R. Hajipour, A. R. Falahati and A. E. Ruoho, *Tetrahedron Lett.*, 2006, **47**, 2717.
(7) P. K. Shyam, Y. K. Kim, C. Lee and H.Y. Jang, *Adv. Synth. Catal.*, 2016, **358**, 56.

14. ^{1}H-NMR and ^{13}C-NMR spectra of the obtained compounds

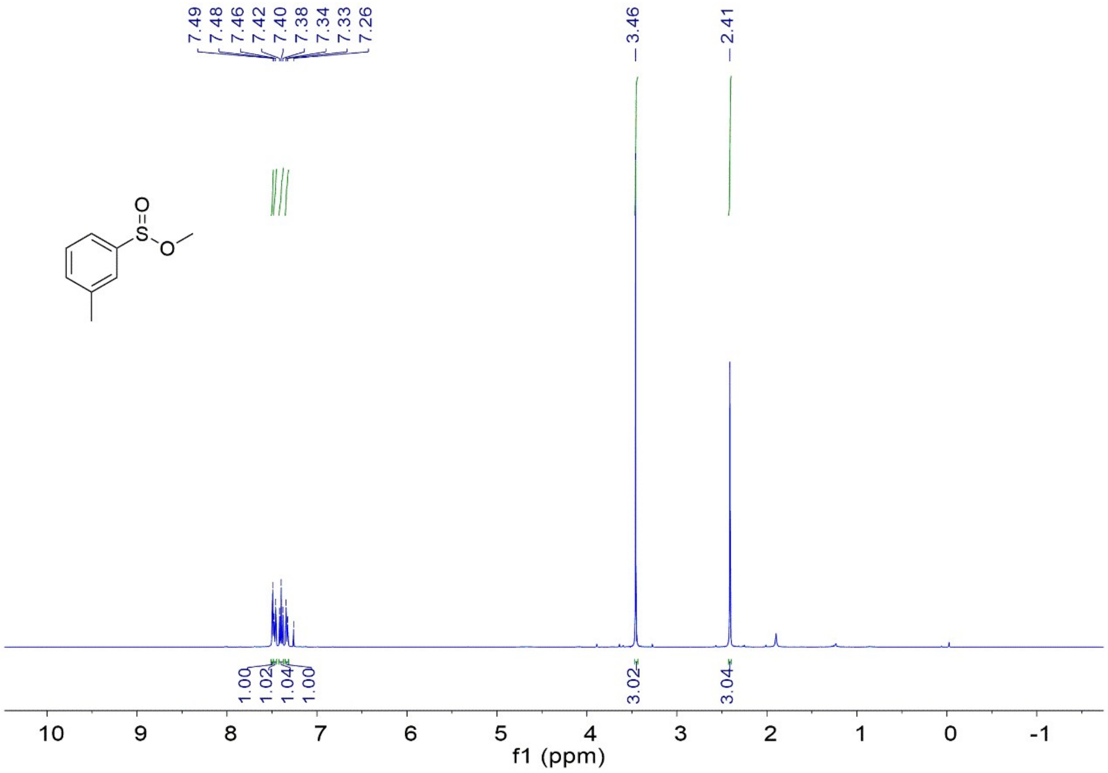
^{1}H-NMR spectrum of 3aa



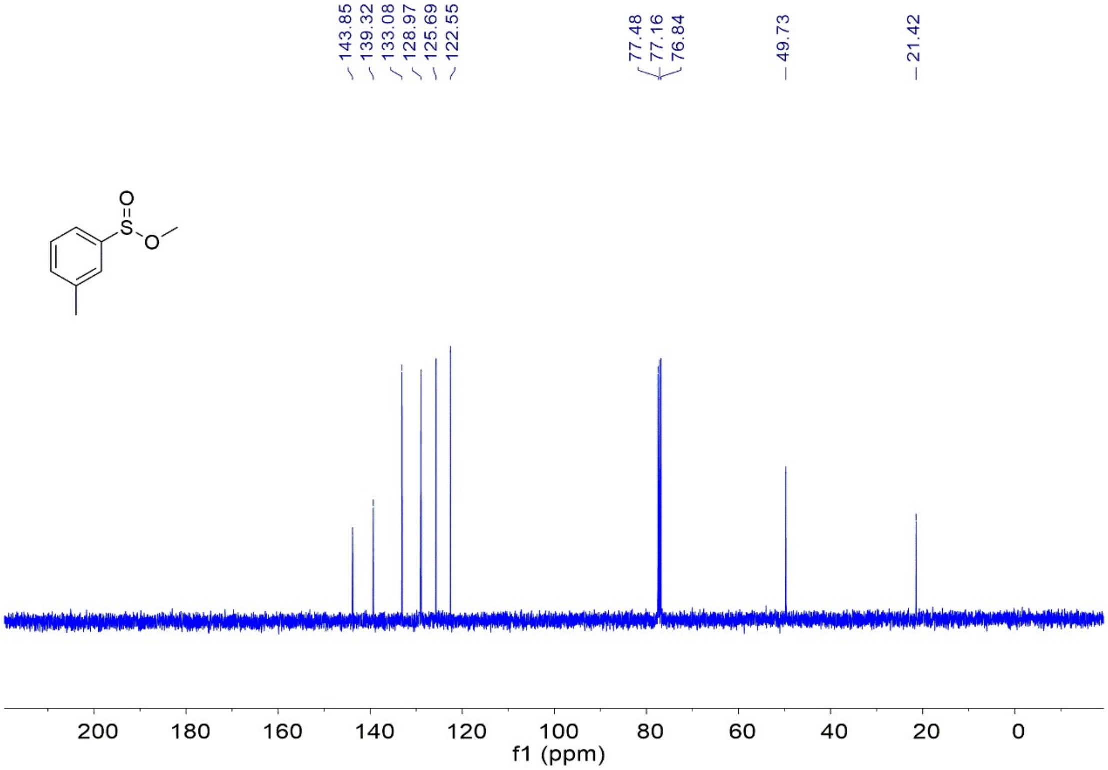
^{13}C-NMR spectrum of 3aa



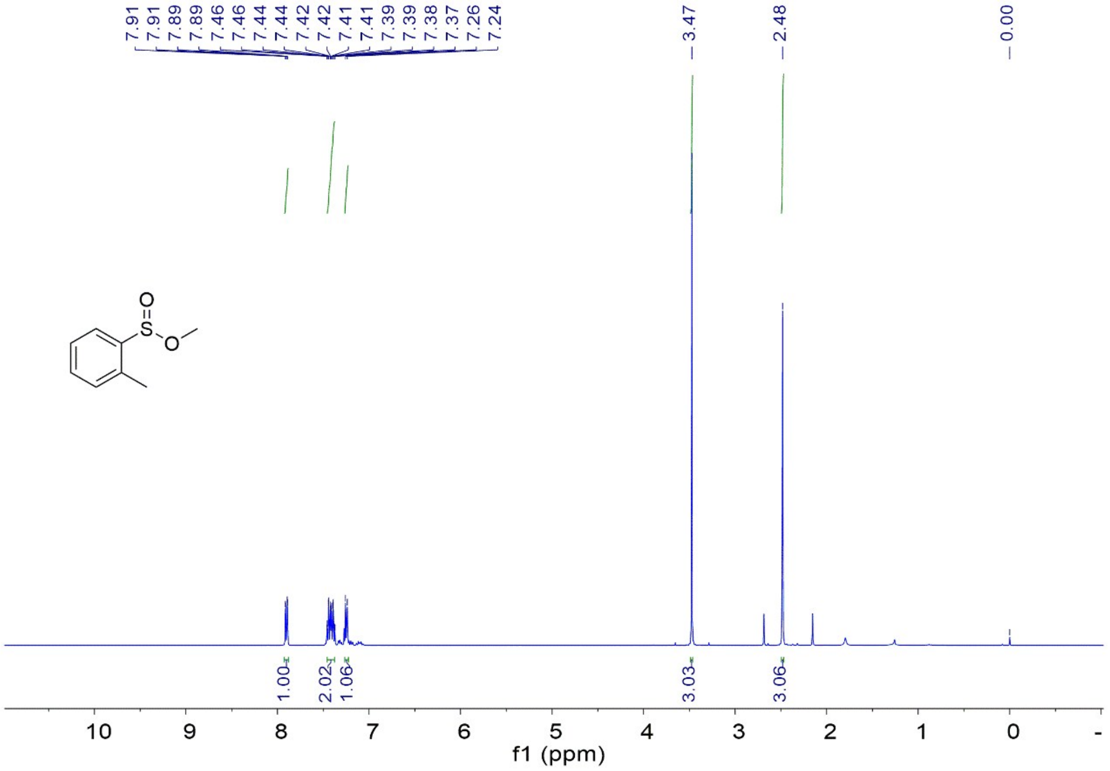
^{1}H-NMR spectrum of 3ba



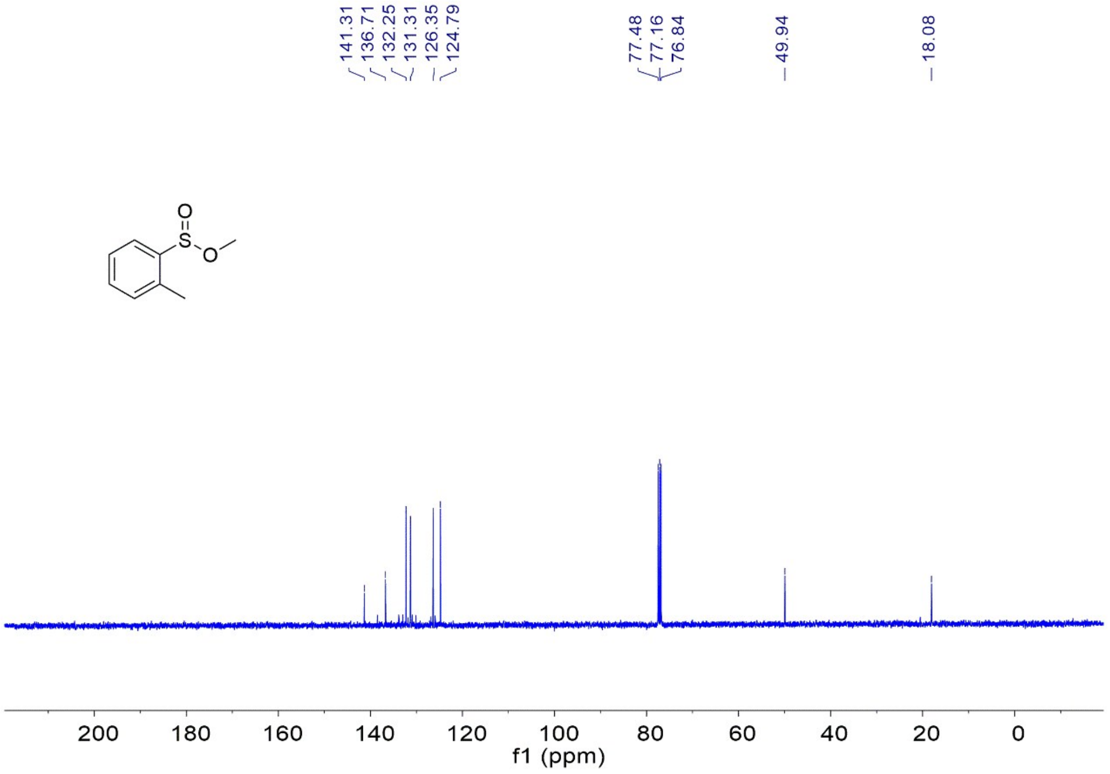
^{13}C-NMR spectrum of 3ba



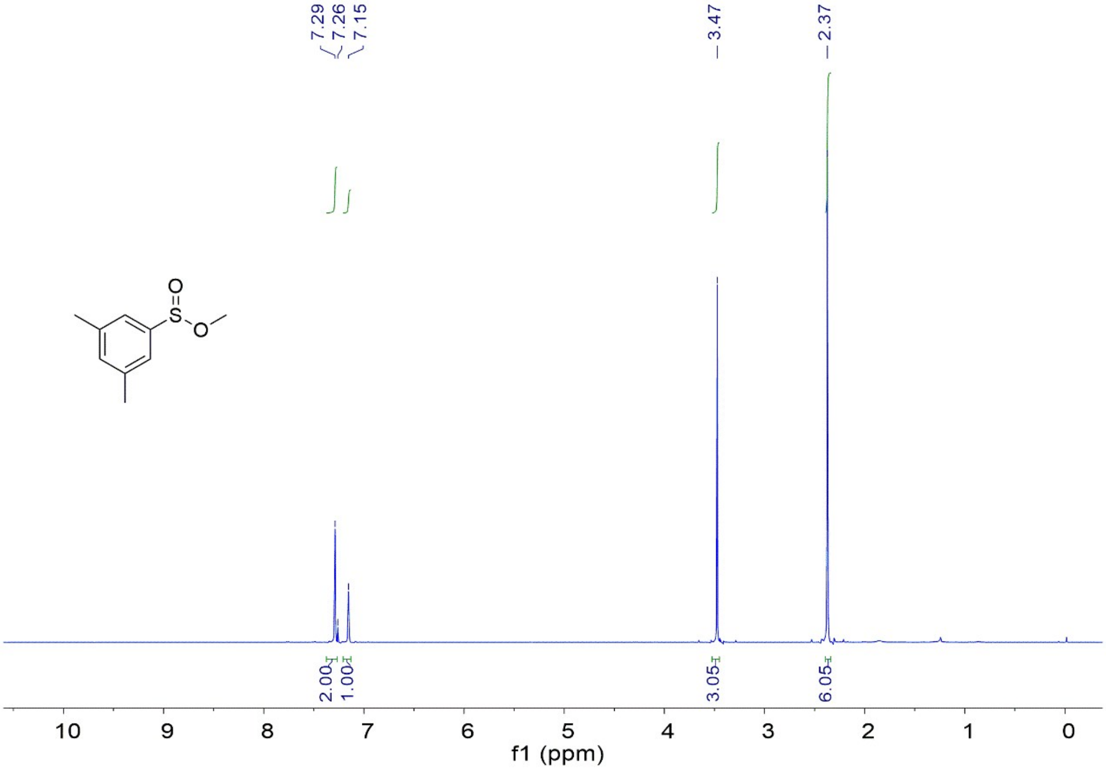
^{1}H-NMR spectrum of 3ca



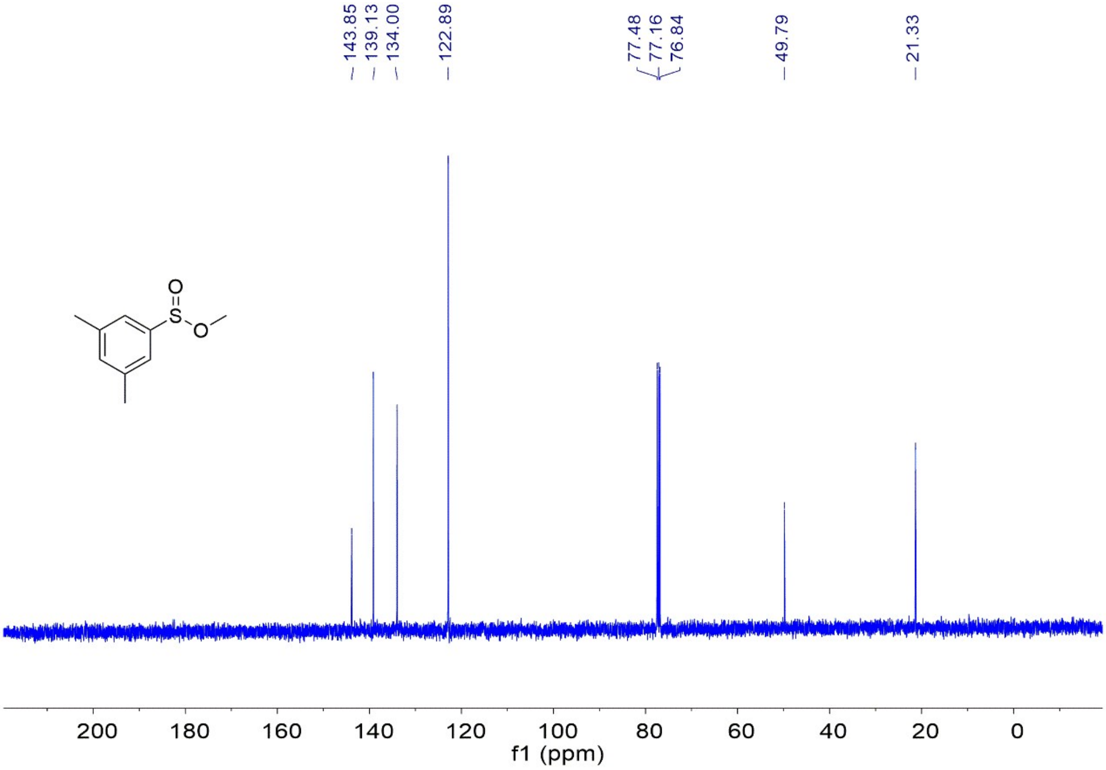
^{13}C-NMR spectrum of 3ca



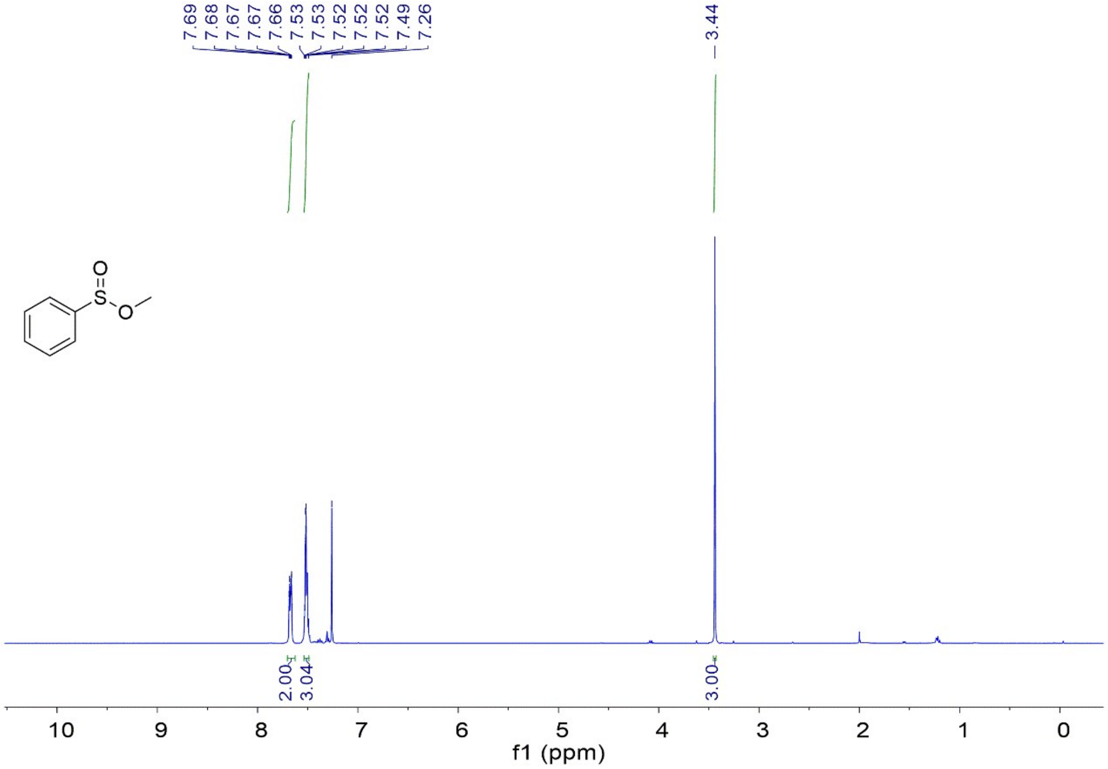
^{1}H-NMR spectrum of 3da



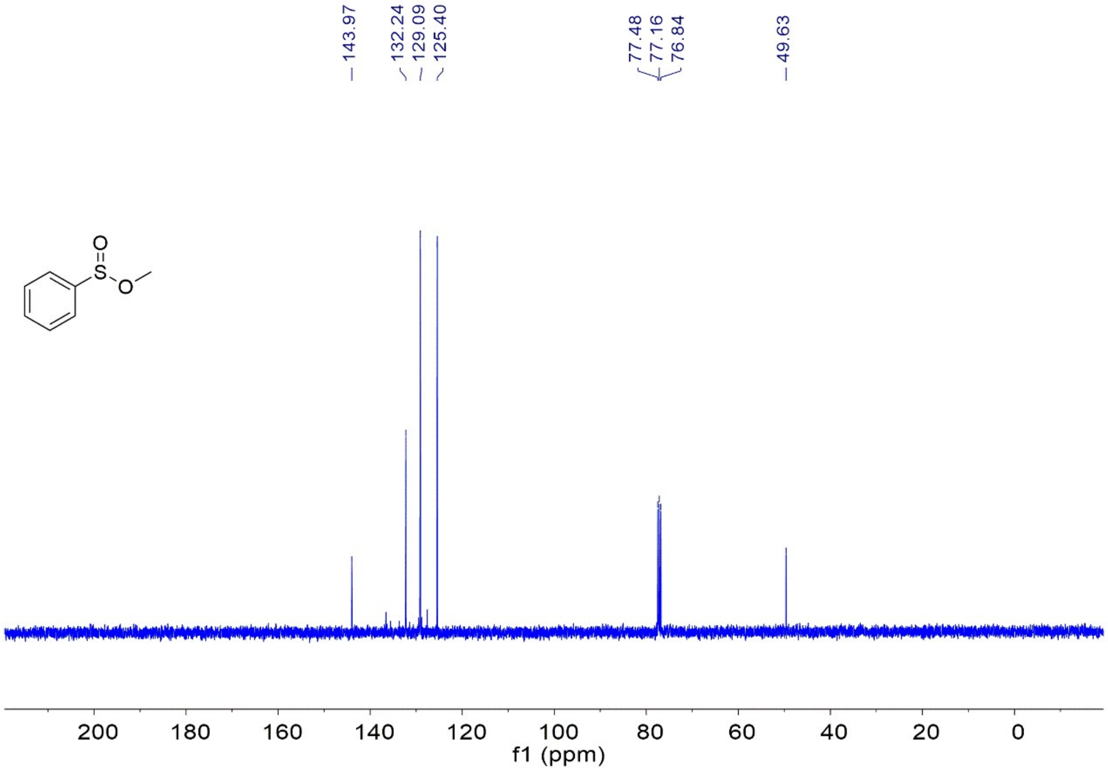
^{13}C-NMR spectrum of 3da



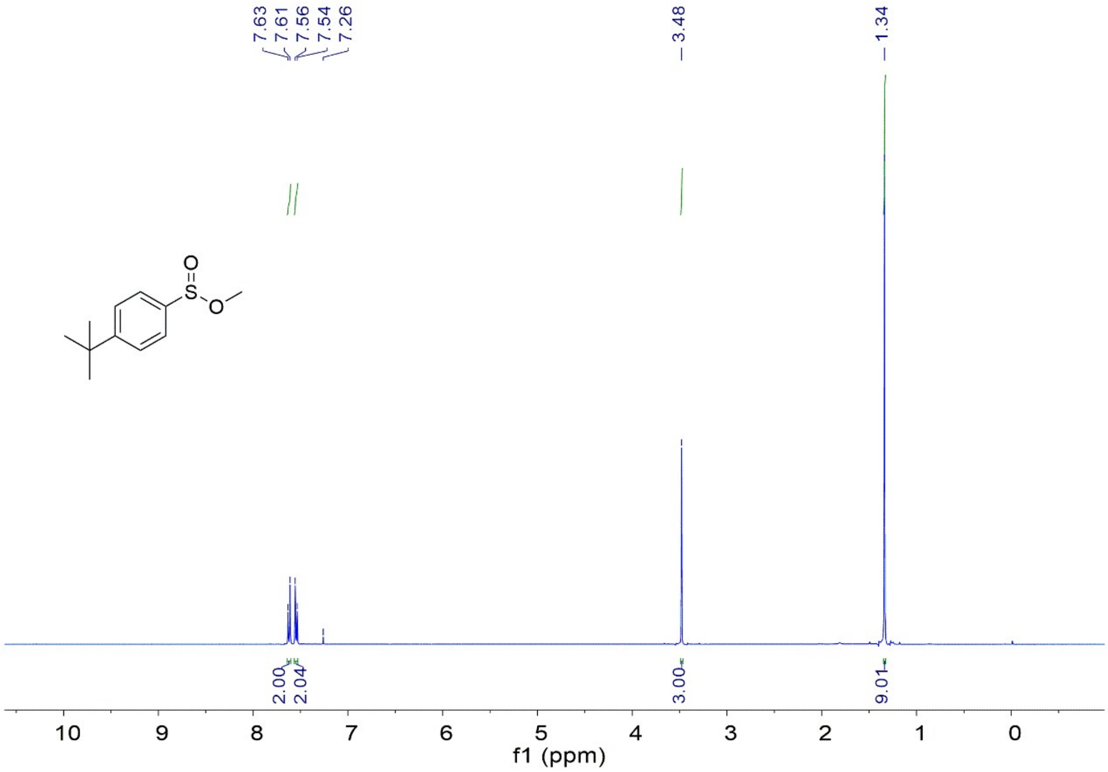
^{1}H-NMR spectrum of 3ea



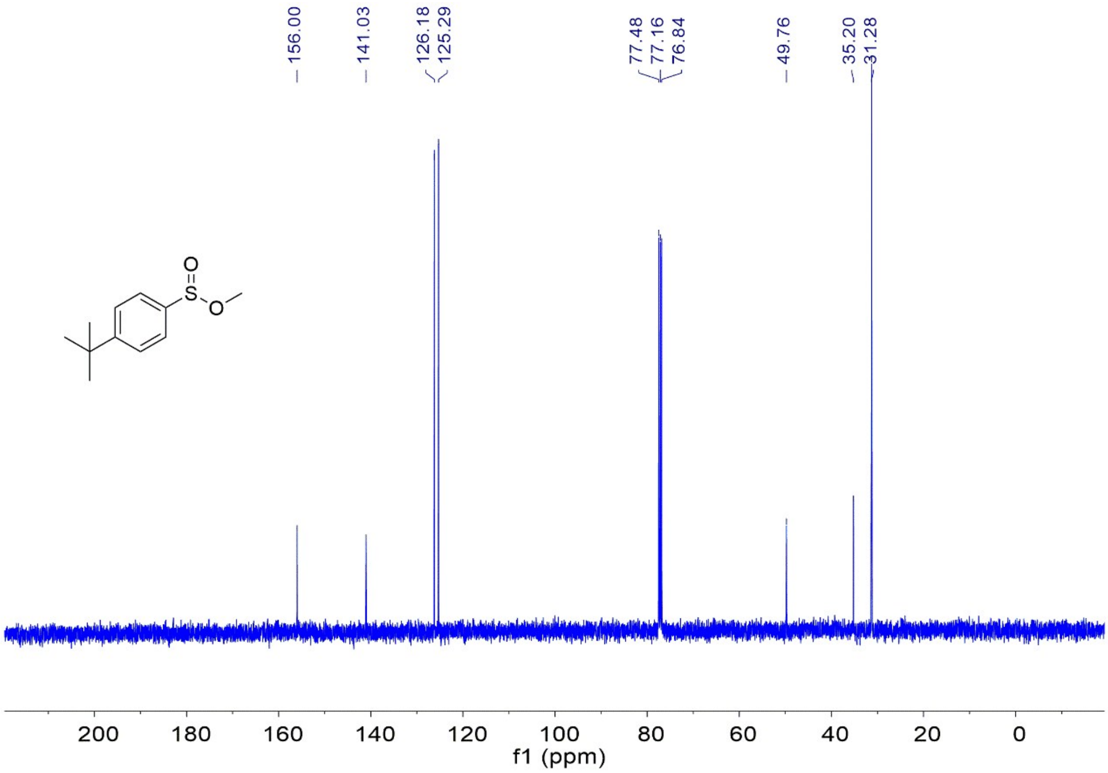
^{13}C-NMR spectrum of 3ea



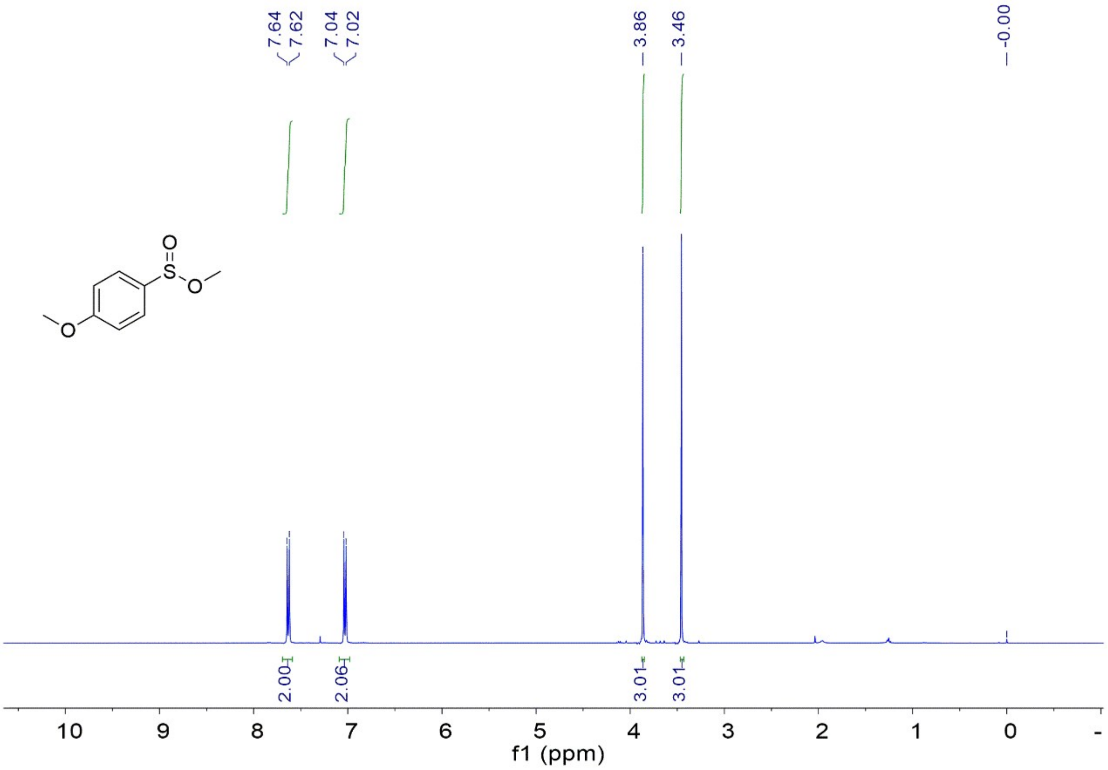
^{1}H-NMR spectrum of 3fa



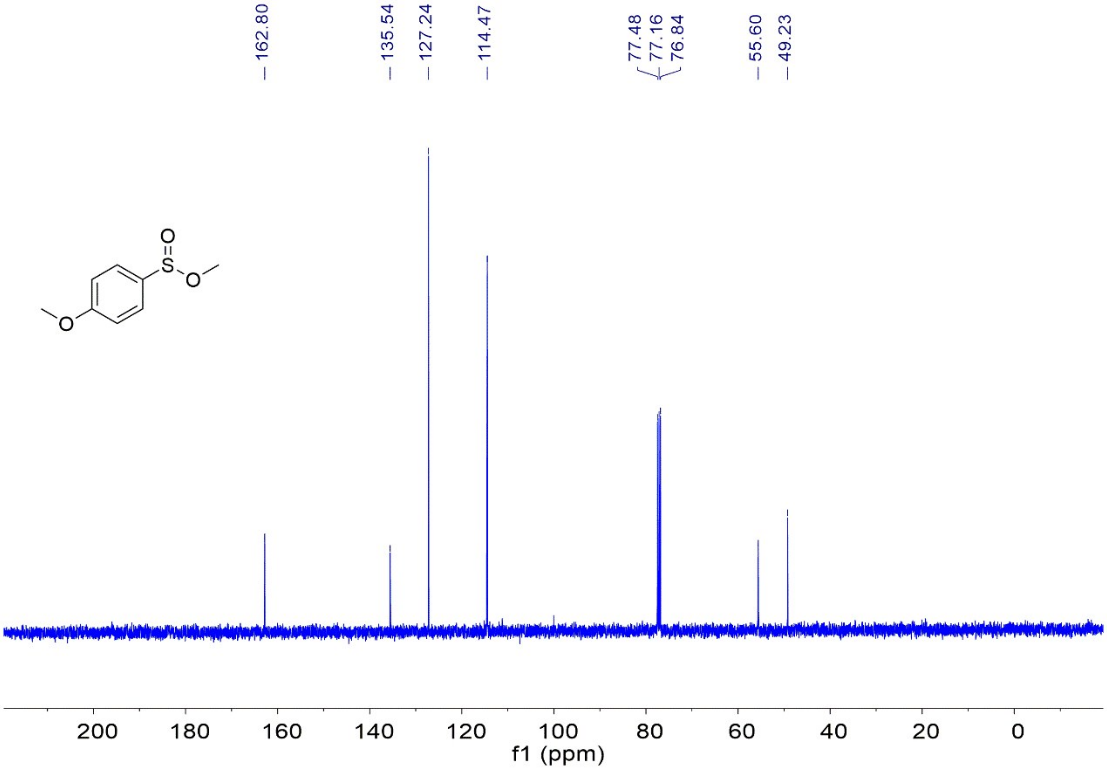
^{13}C-NMR spectrum of 3fa



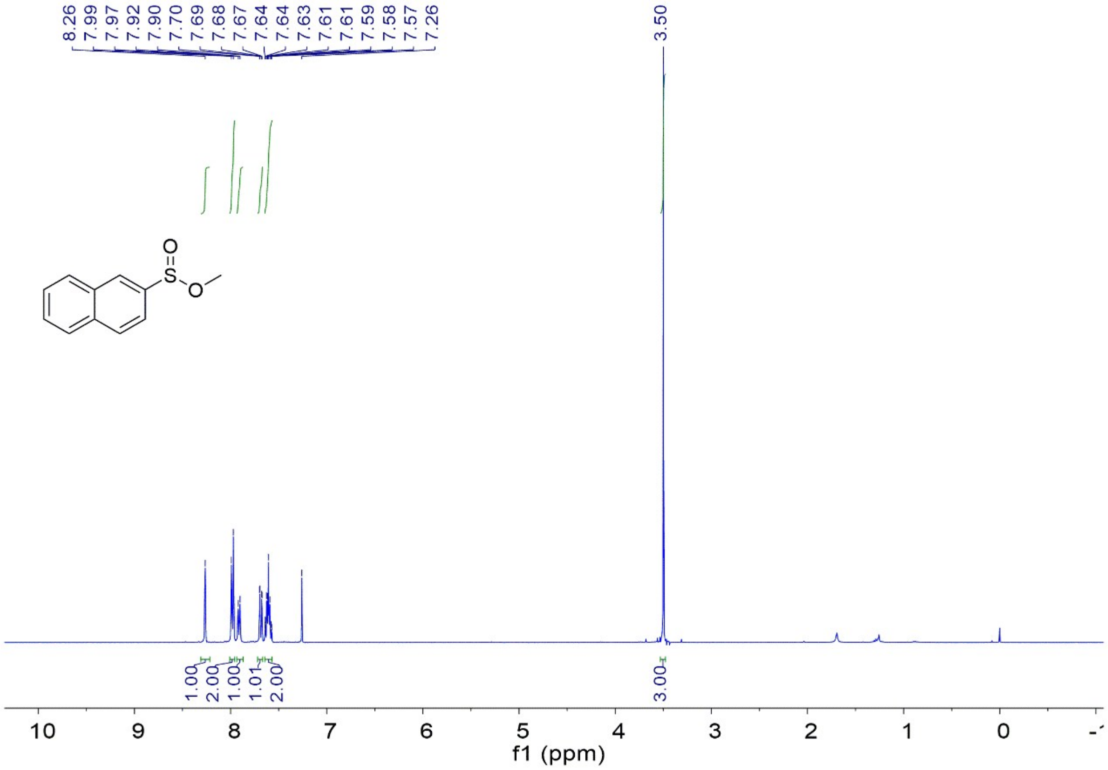
^{1}H-NMR spectrum of 3ga



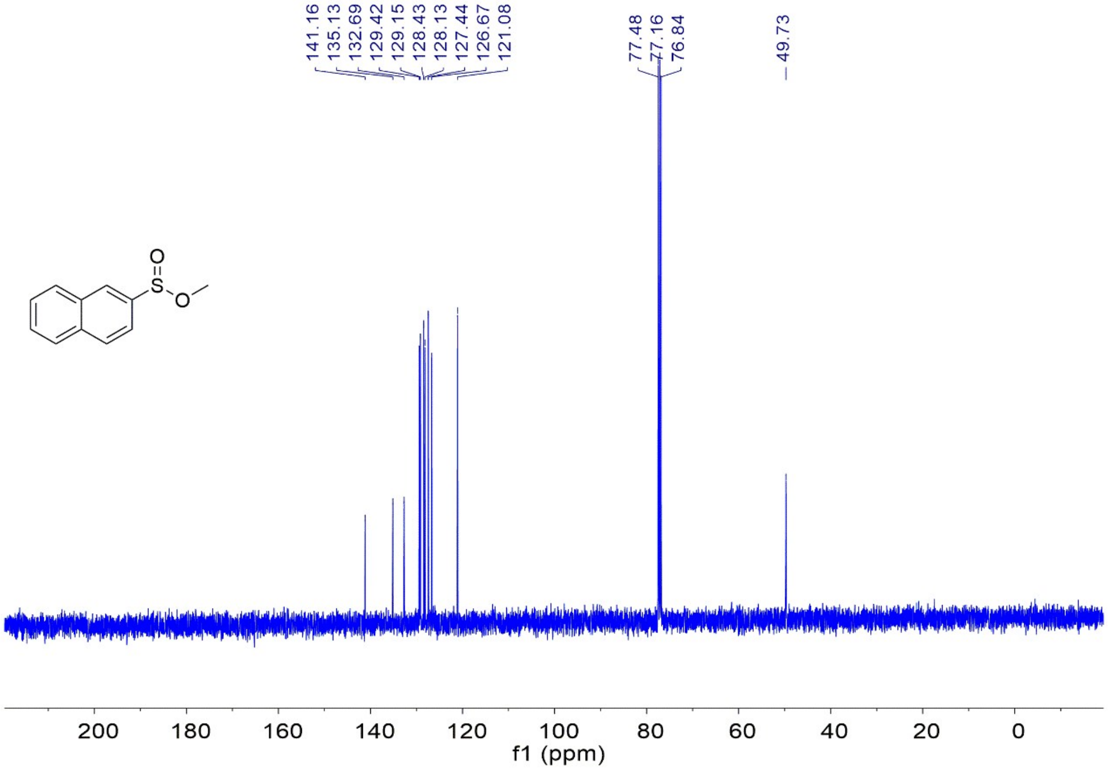
^{13}C-NMR spectrum of 3ga



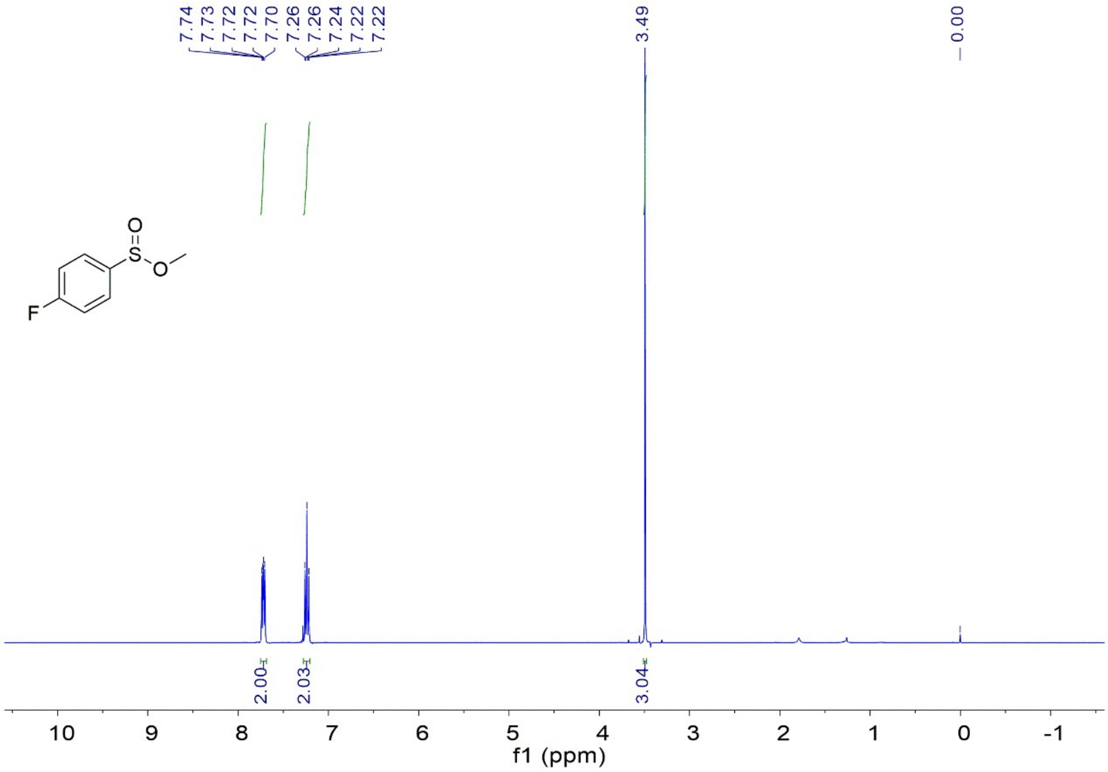
^{1}H-NMR spectrum of 3ha



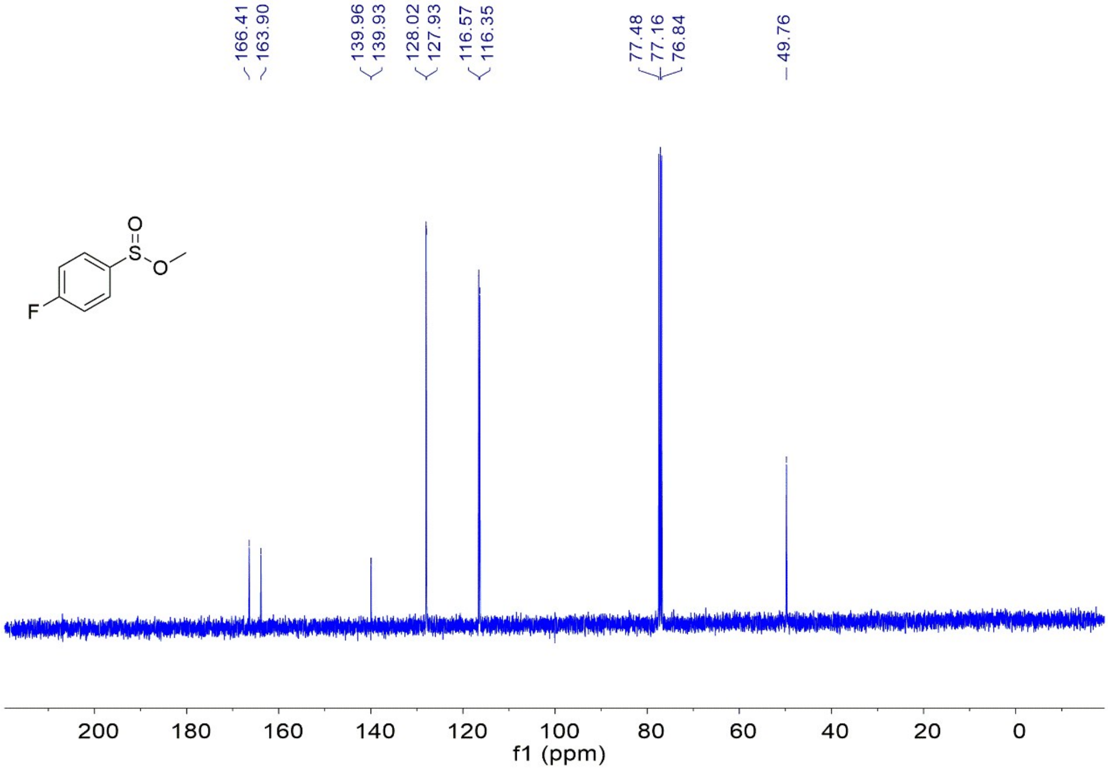
^{13}C-NMR spectrum of 3ha



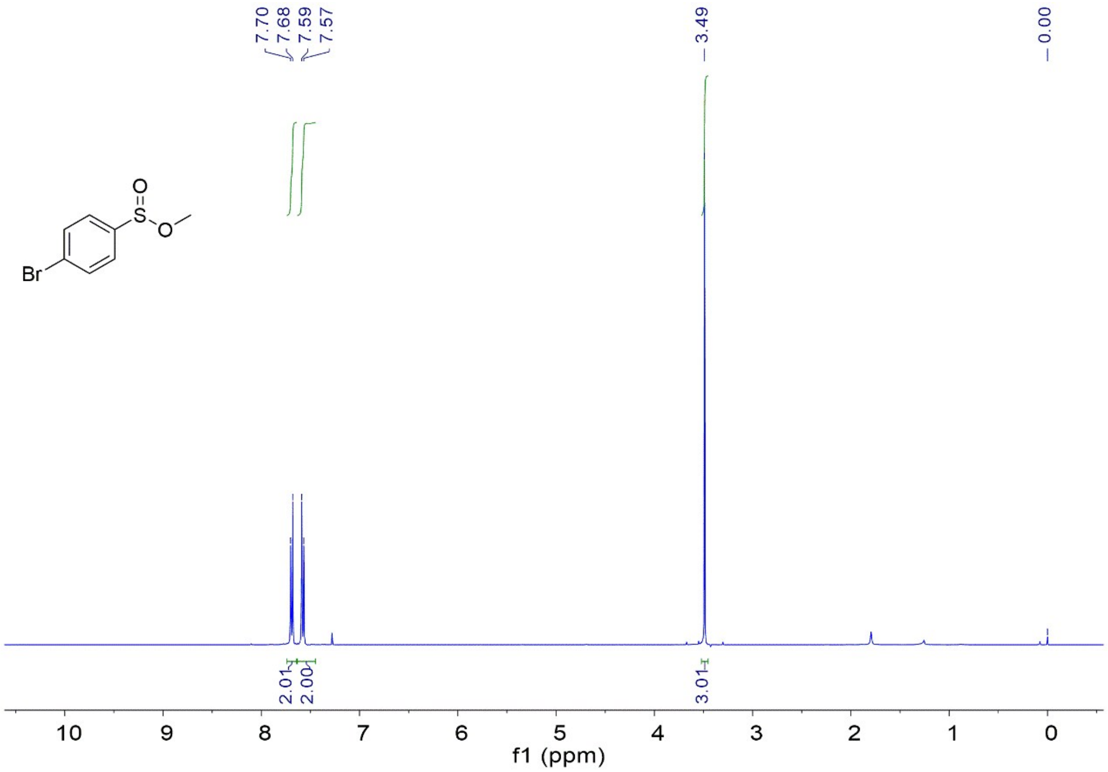
^{1}H-NMR spectrum of 3ia



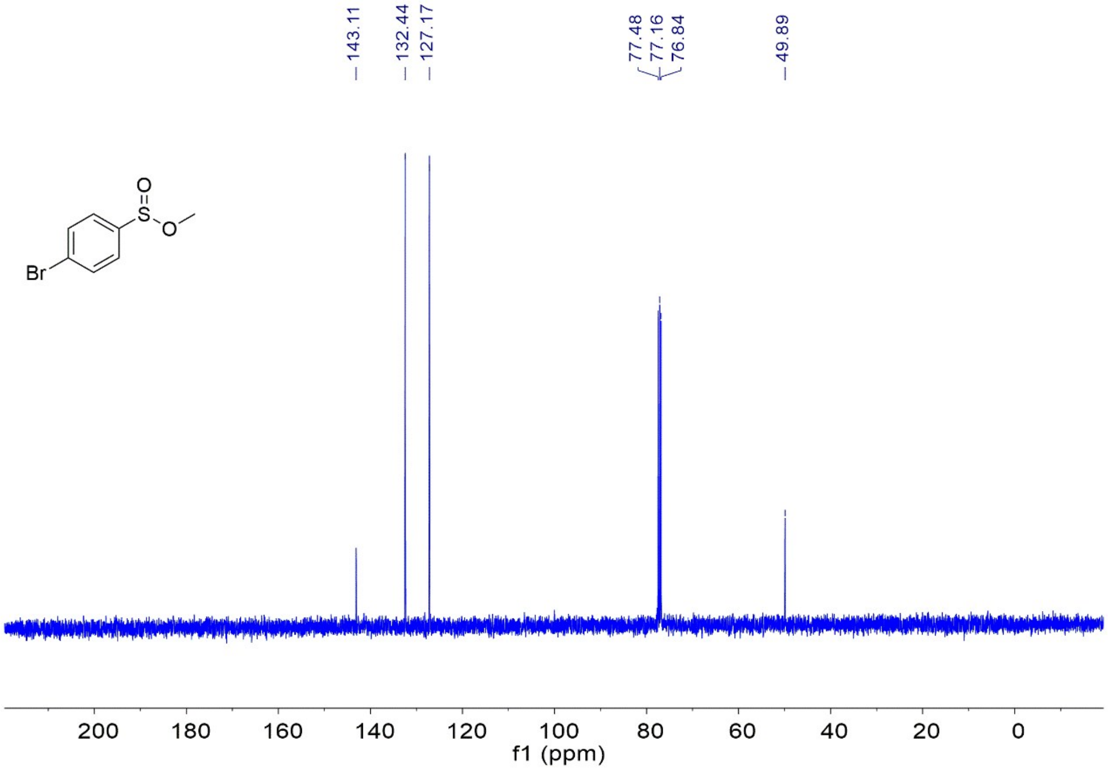
^{13}C-NMR spectrum of 3ia



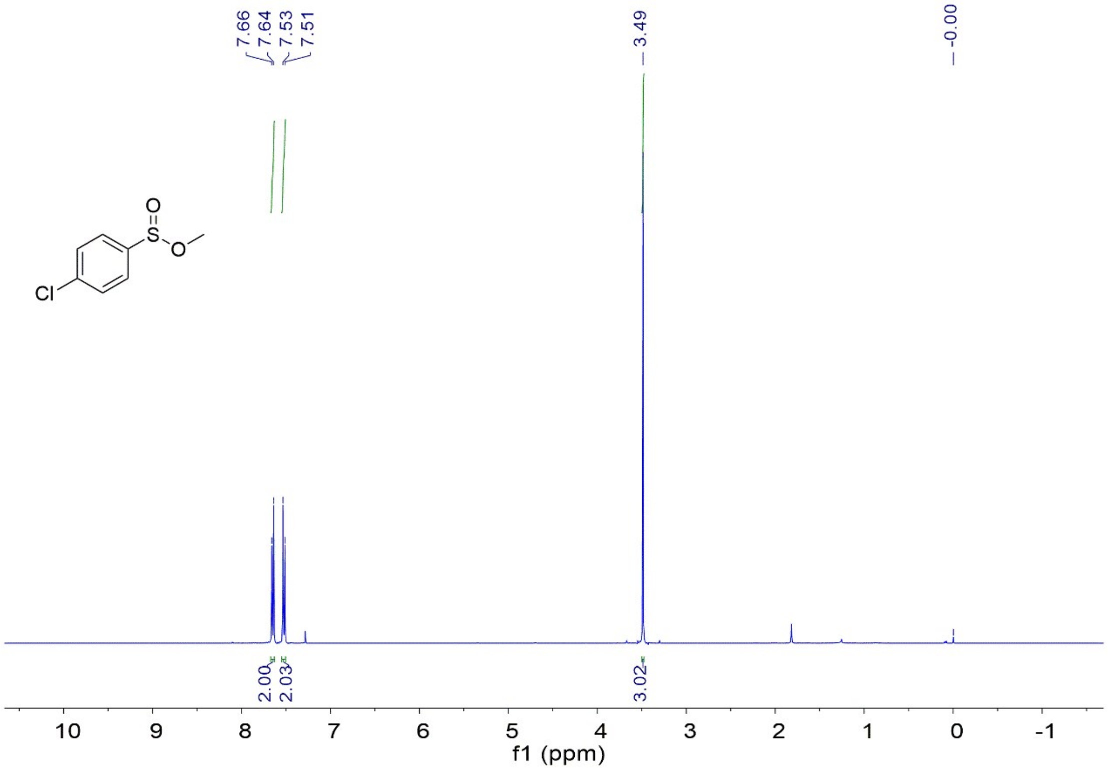
^{1}H-NMR spectrum of 3ja



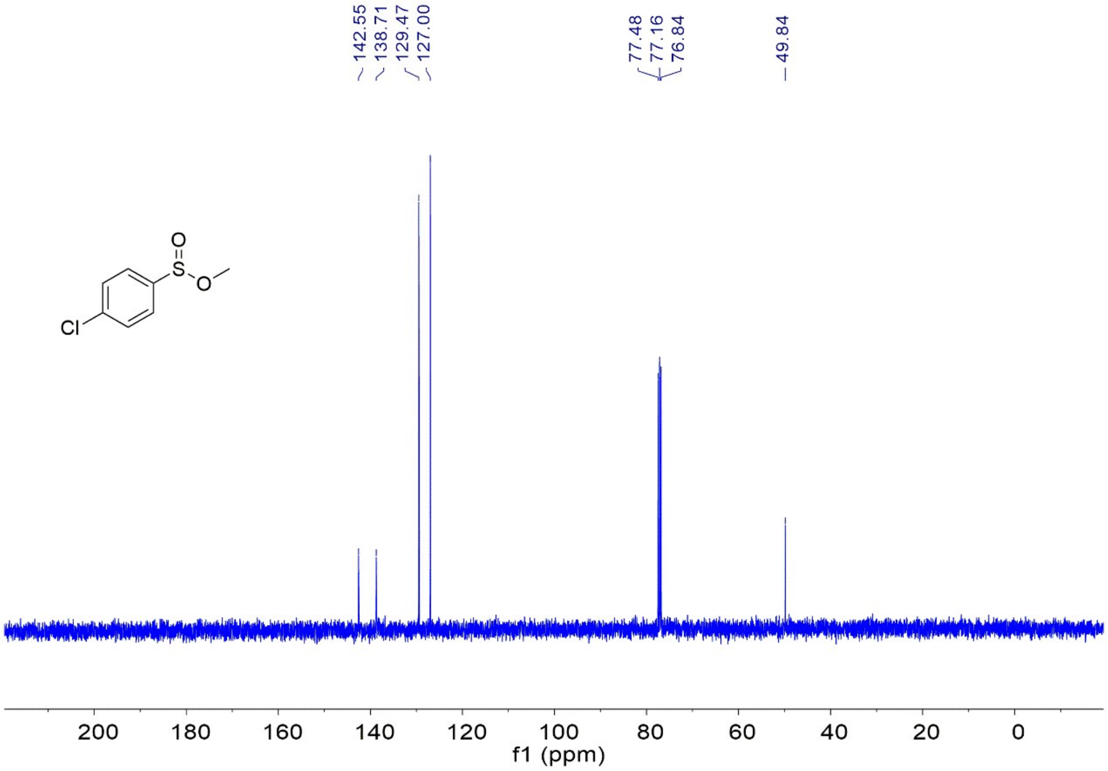
^{13}C-NMR spectrum of 3ja



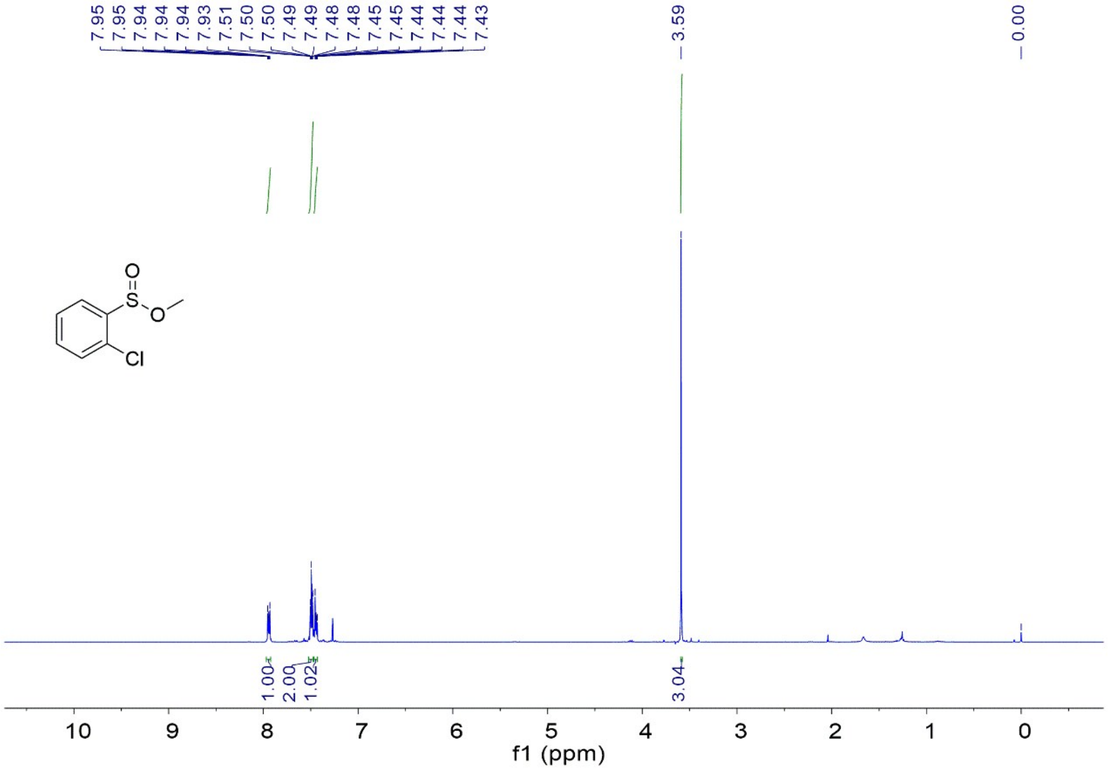
^{1}H-NMR spectrum of 3ka



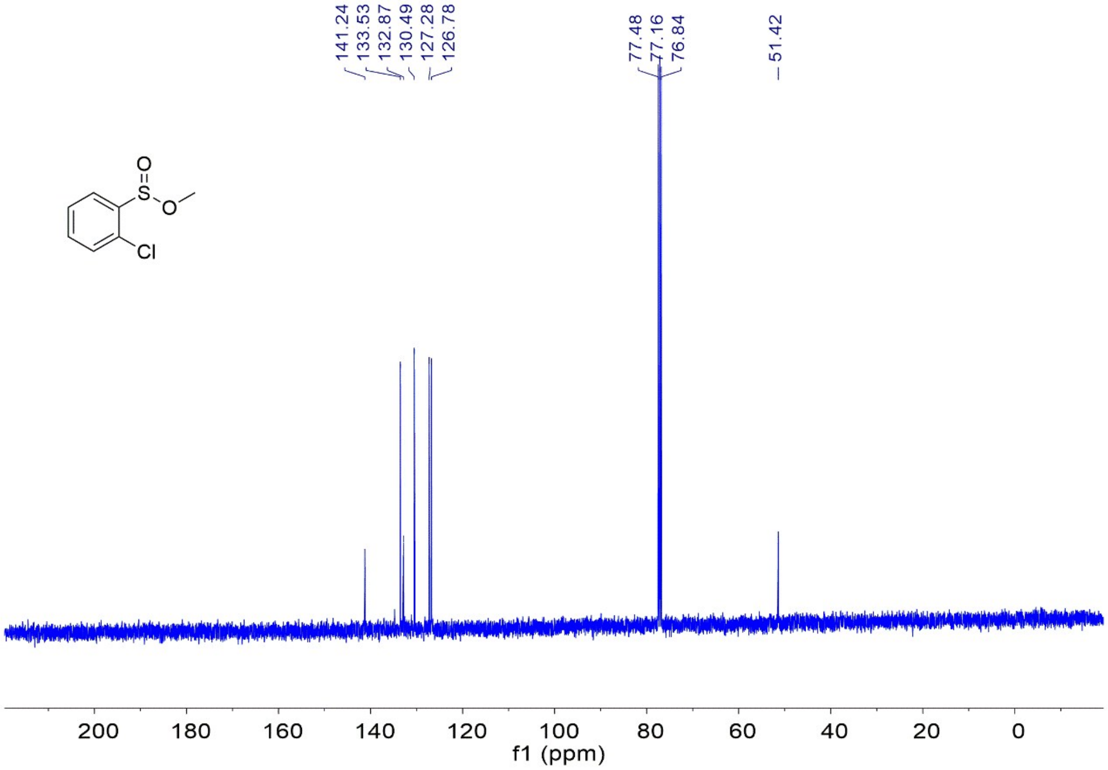
^{13}C-NMR spectrum of 3ka



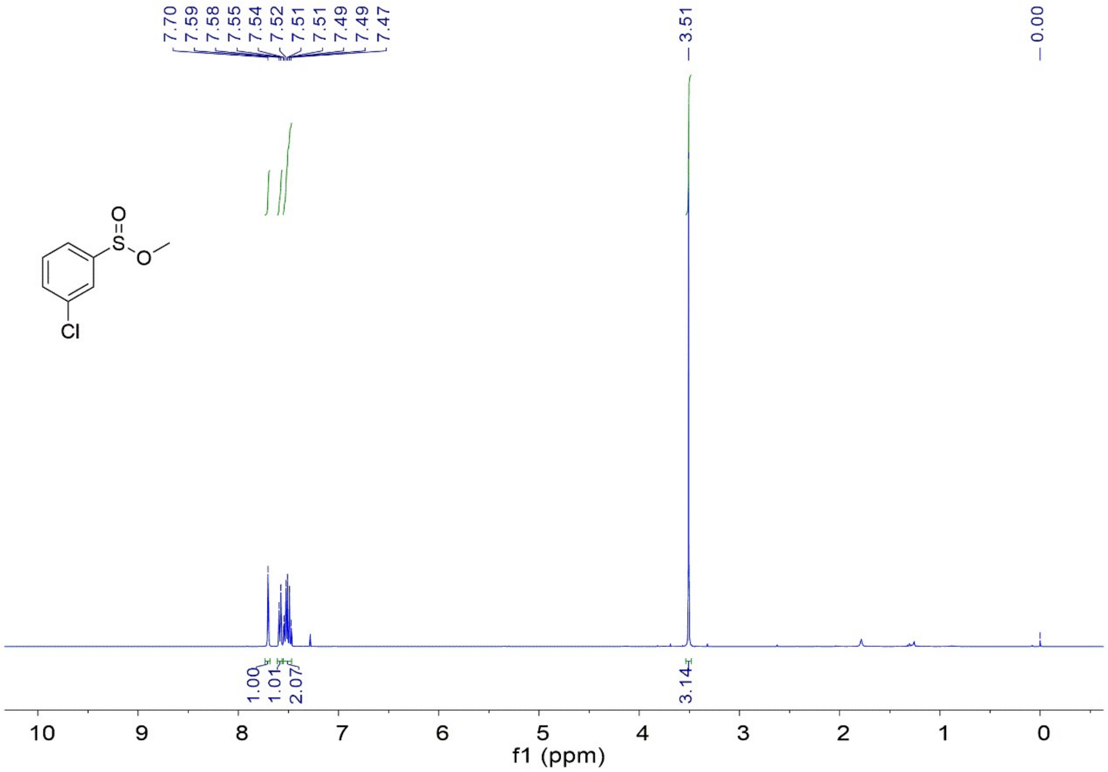
^{1}H-NMR spectrum of 3la



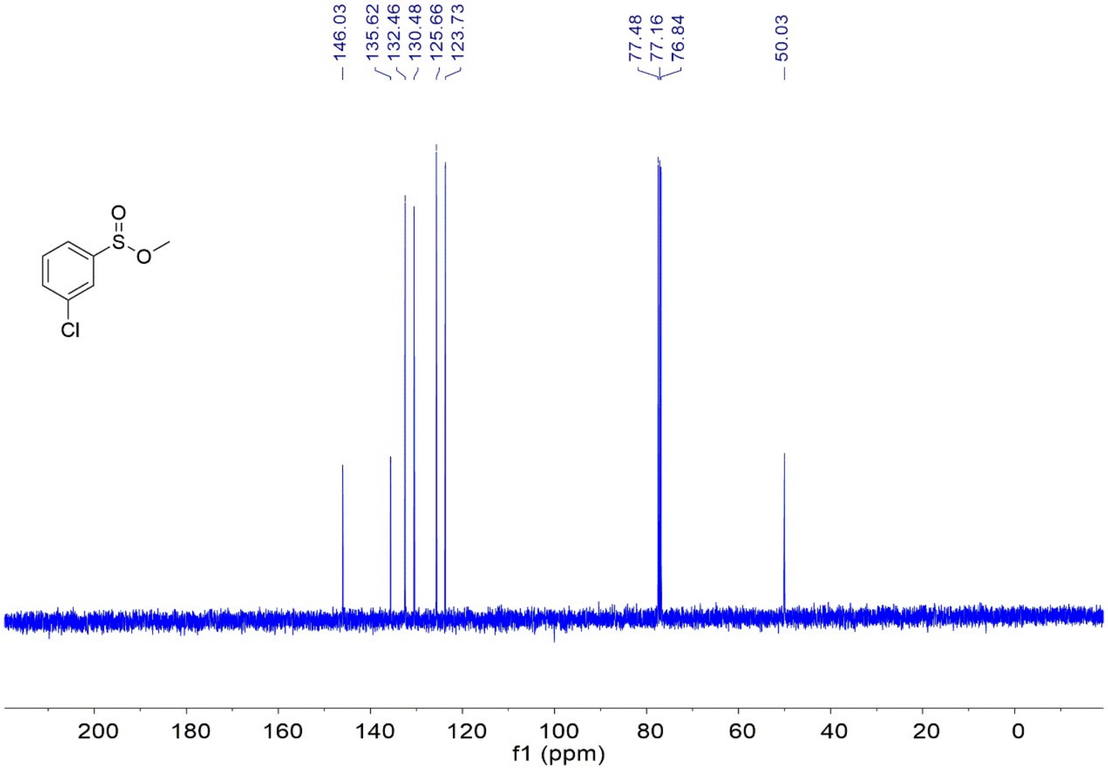
^{13}C-NMR spectrum of 3la



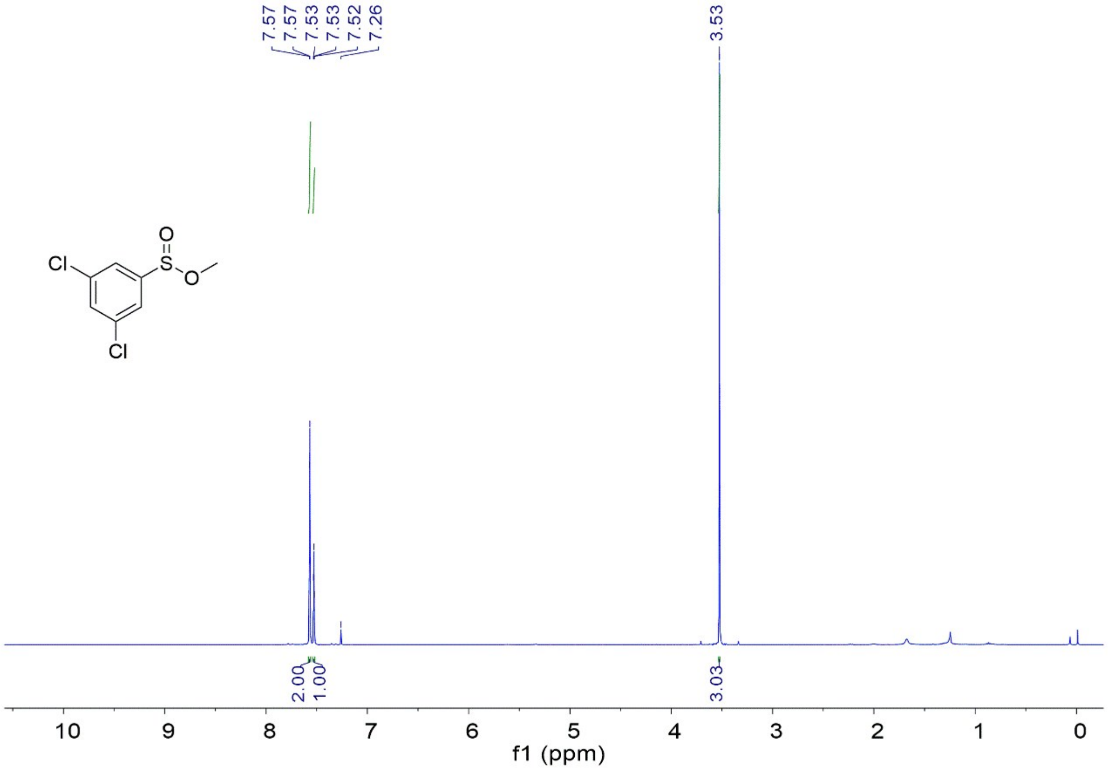
^{1}H-NMR spectrum of 3ma



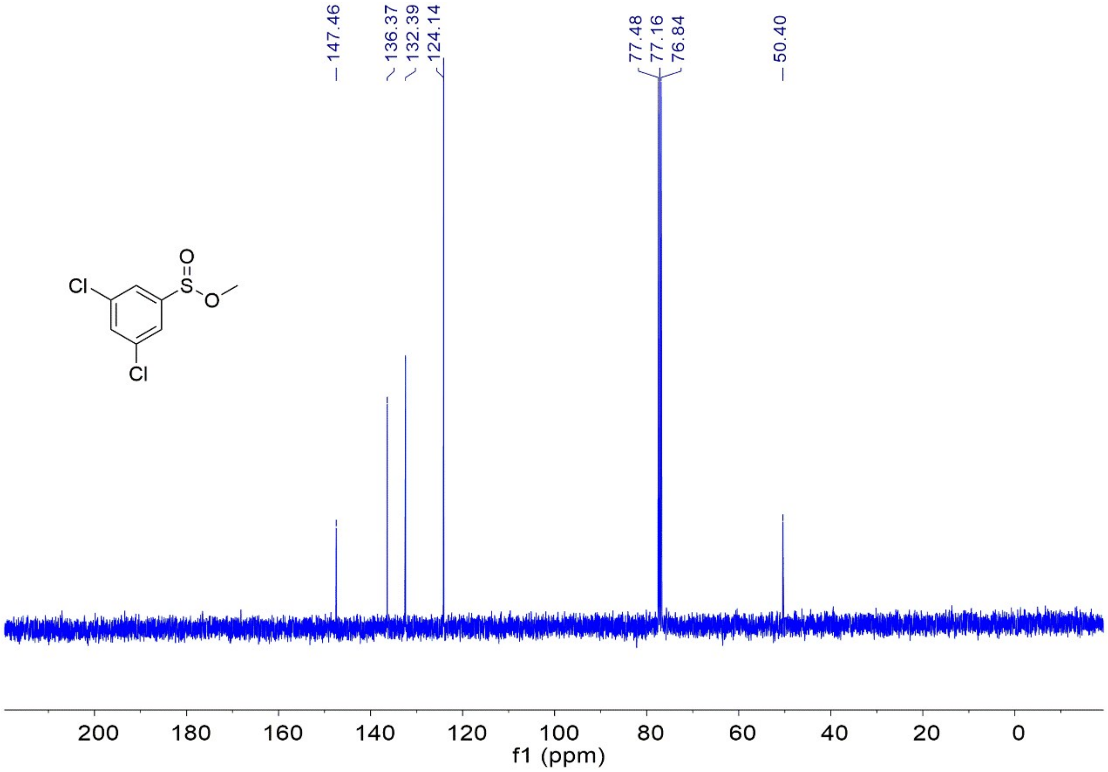
^{13}C-NMR spectrum of 3ma



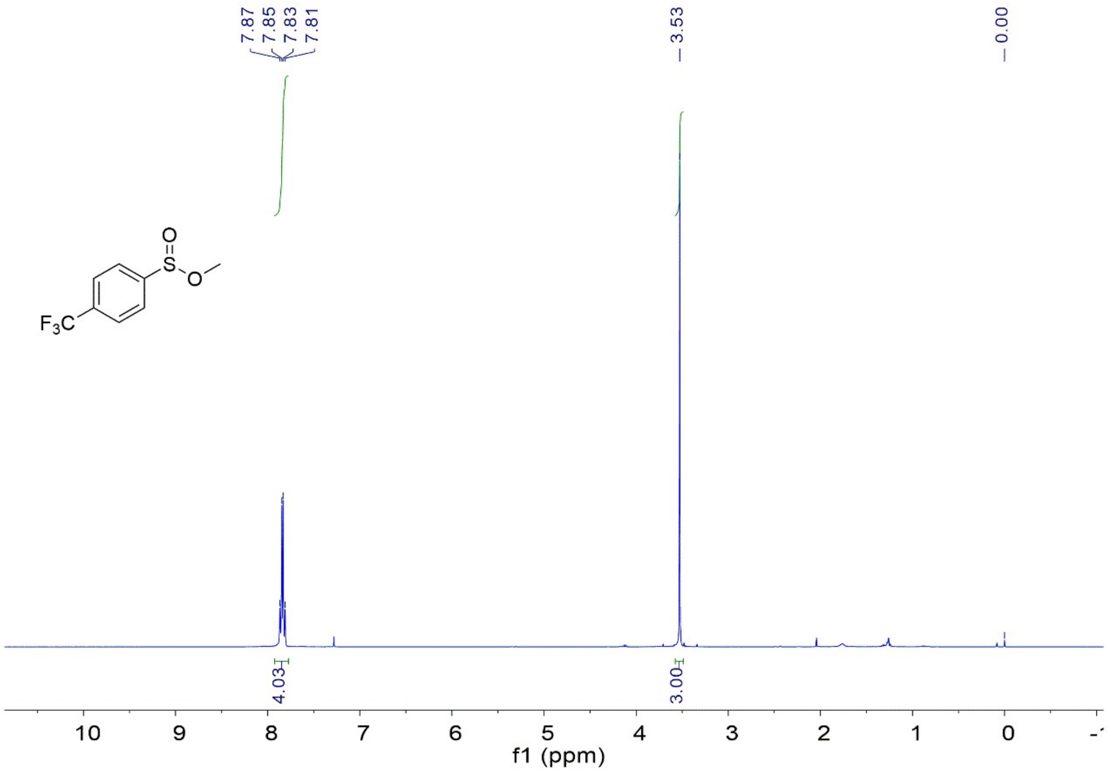
^{1}H-NMR spectrum of 3na



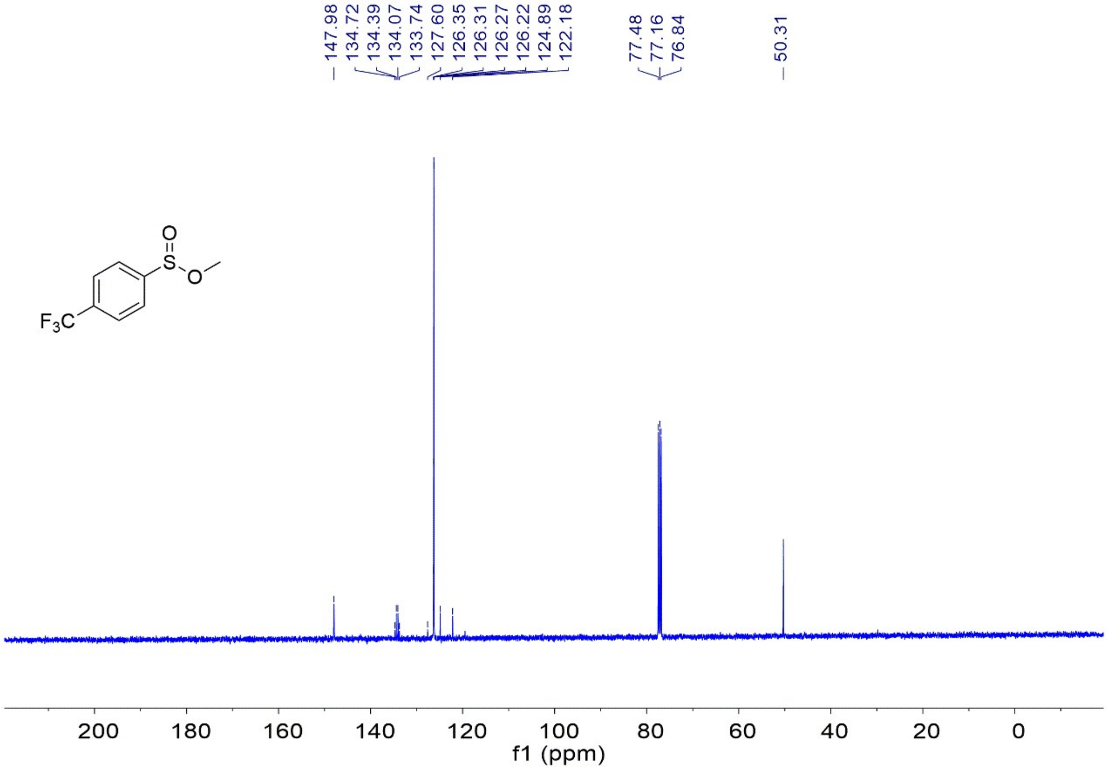
^{13}C-NMR spectrum of 3na



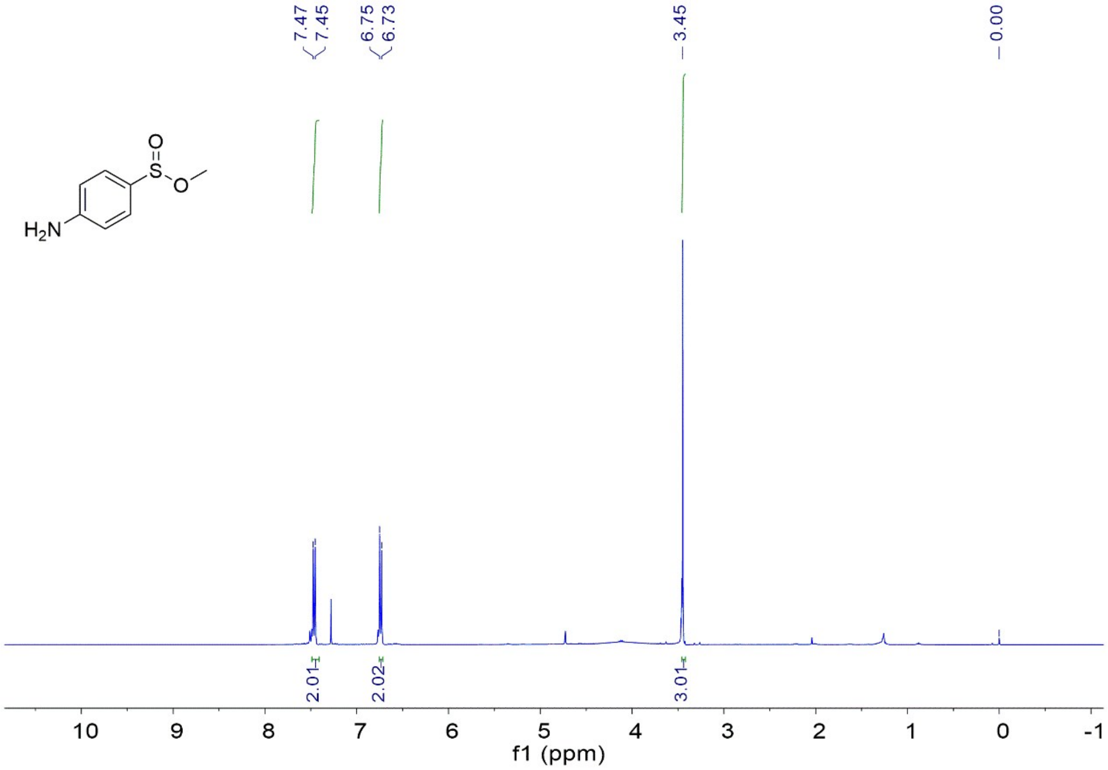
^{1}H-NMR spectrum of 3oa



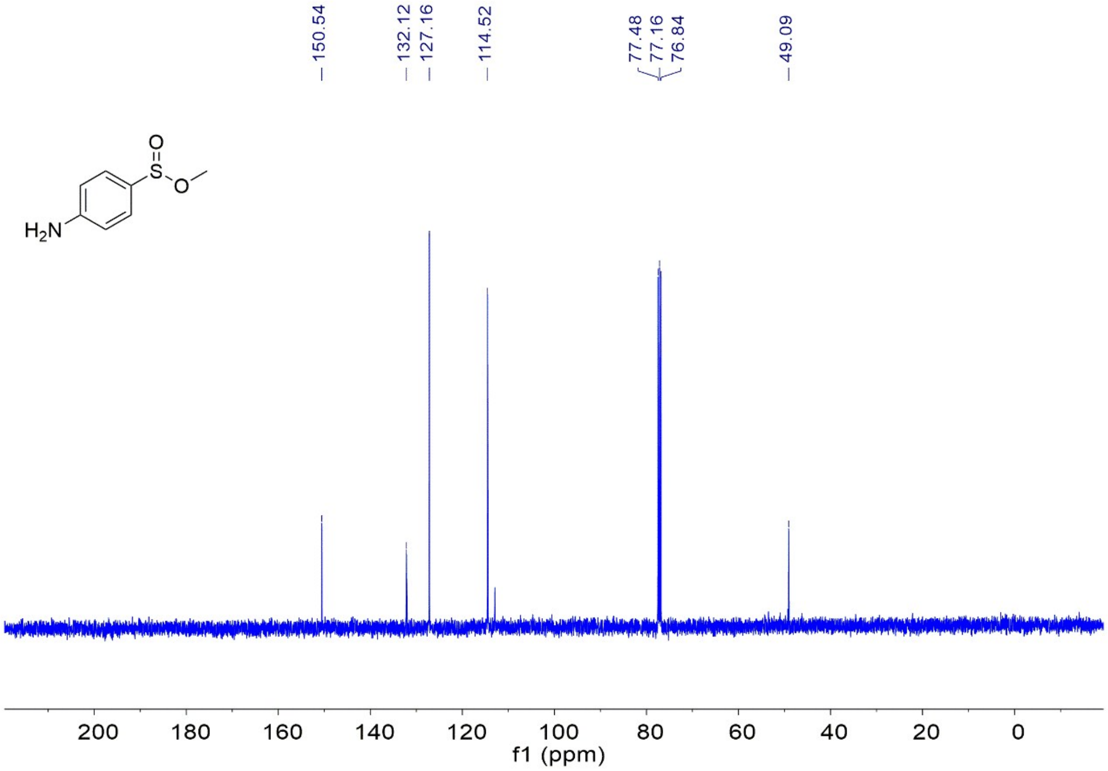
^{13}C-NMR spectrum of 3oa



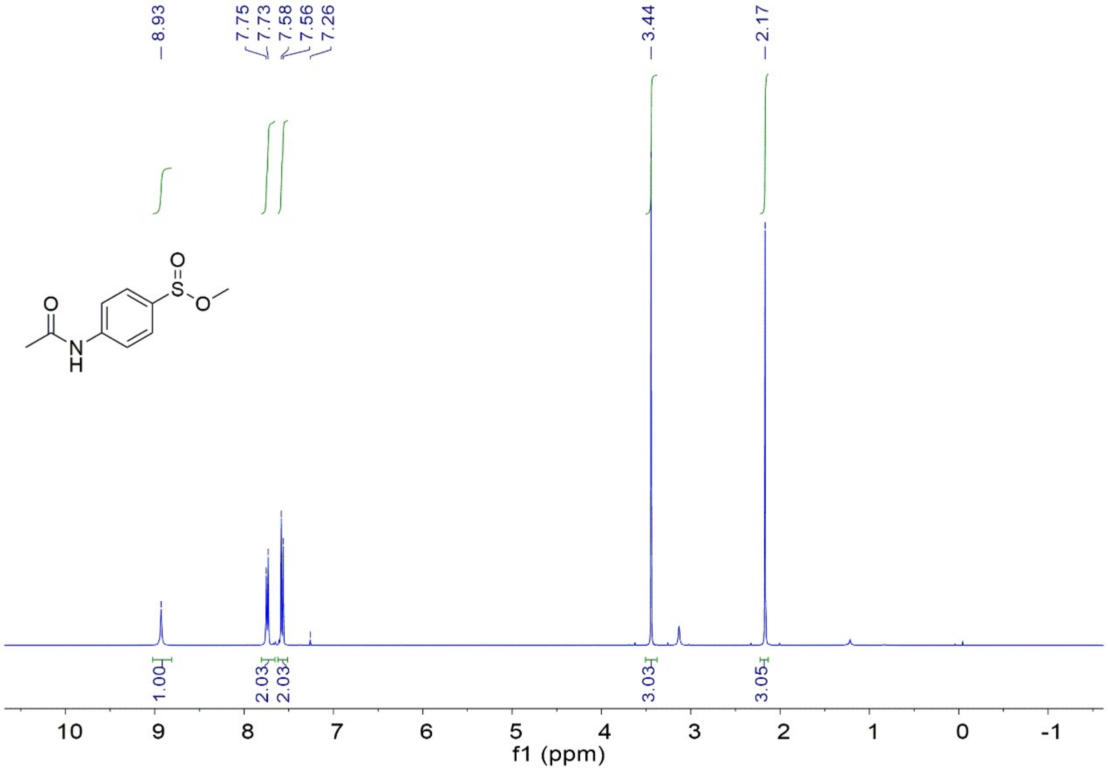
^{1}H-NMR spectrum of 3pa



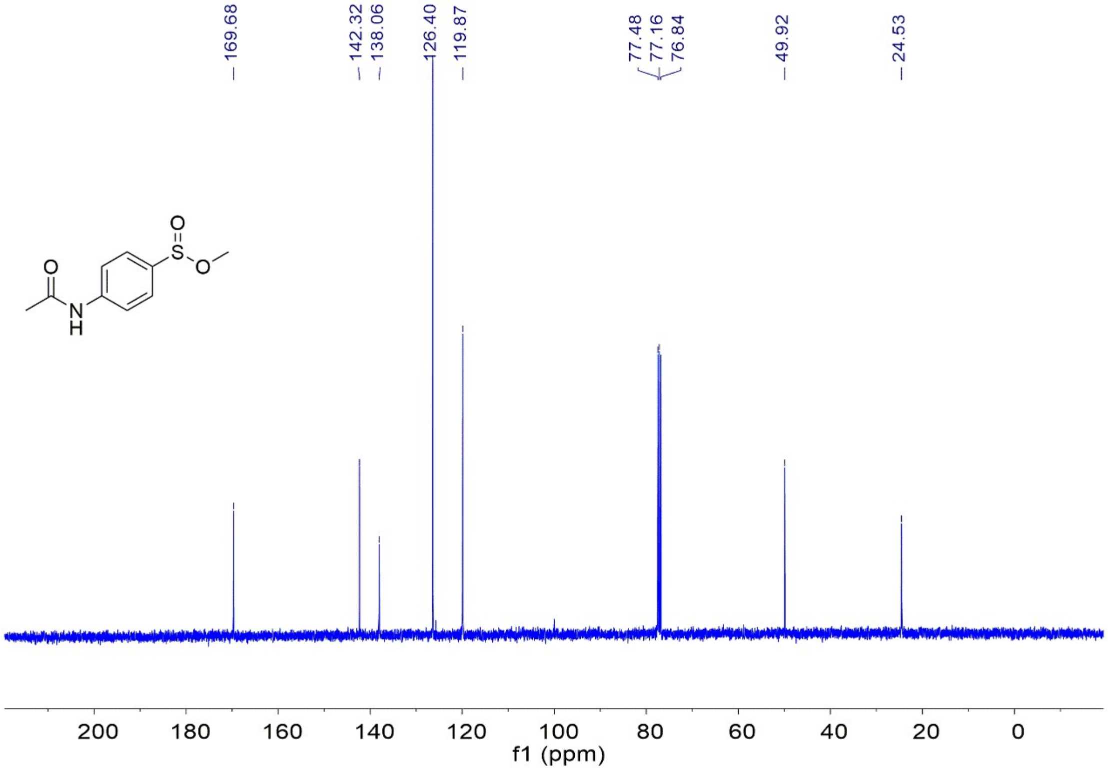
^{13}C-NMR spectrum of 3pa



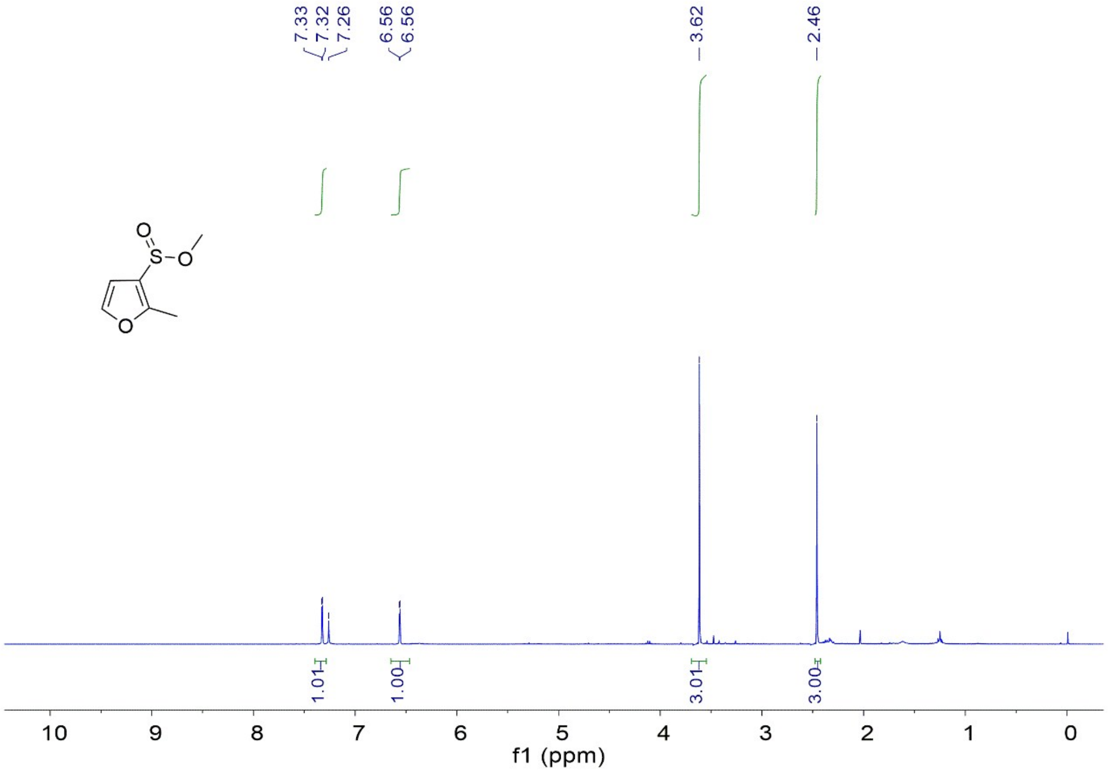
^{1}H-NMR spectrum of 3qa



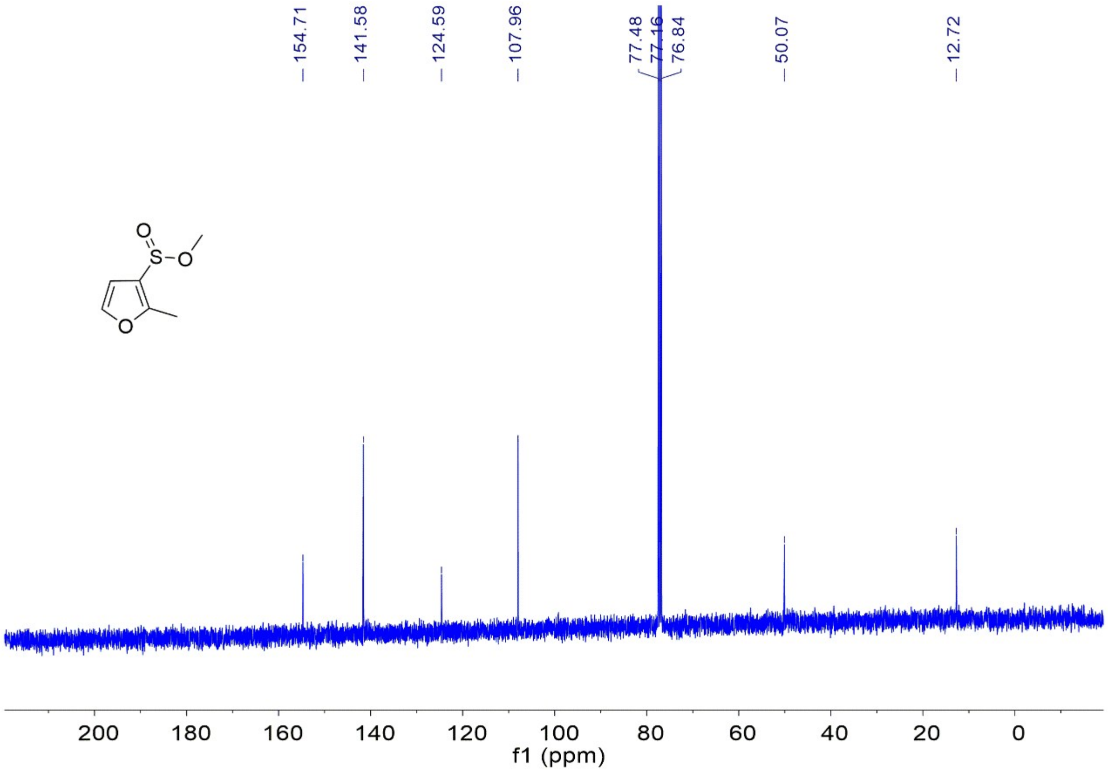
^{13}C-NMR spectrum of 3qa



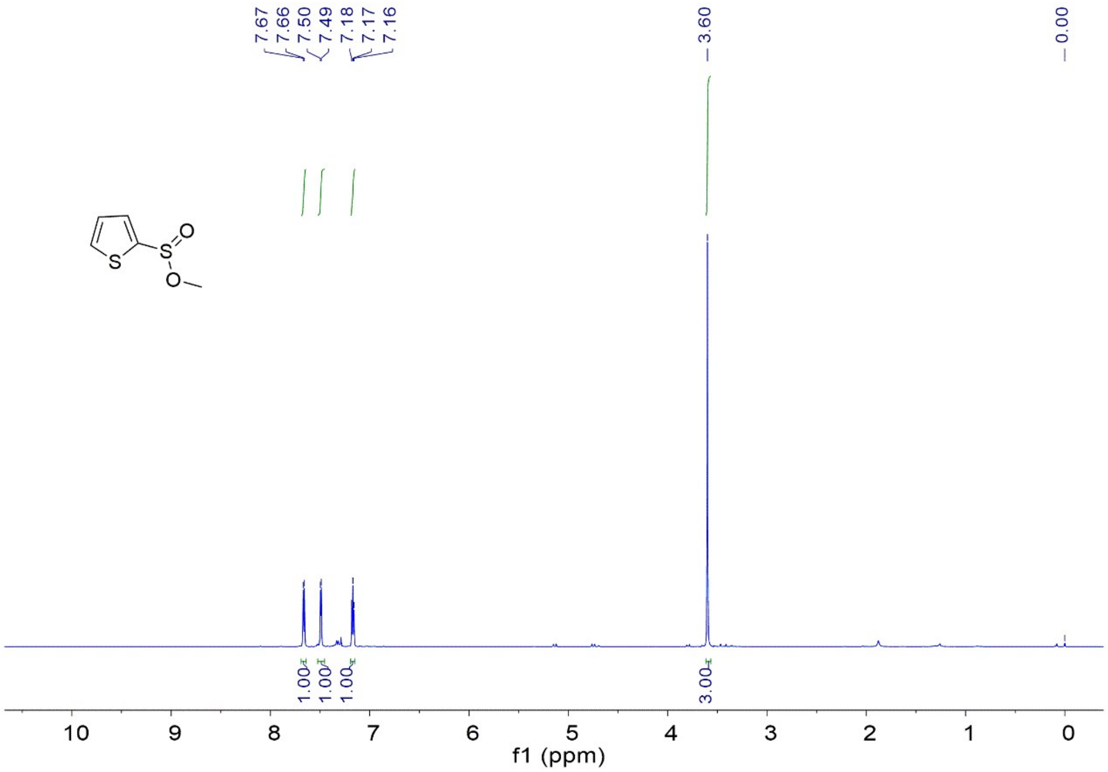
^{1}H-NMR spectrum of 3ra



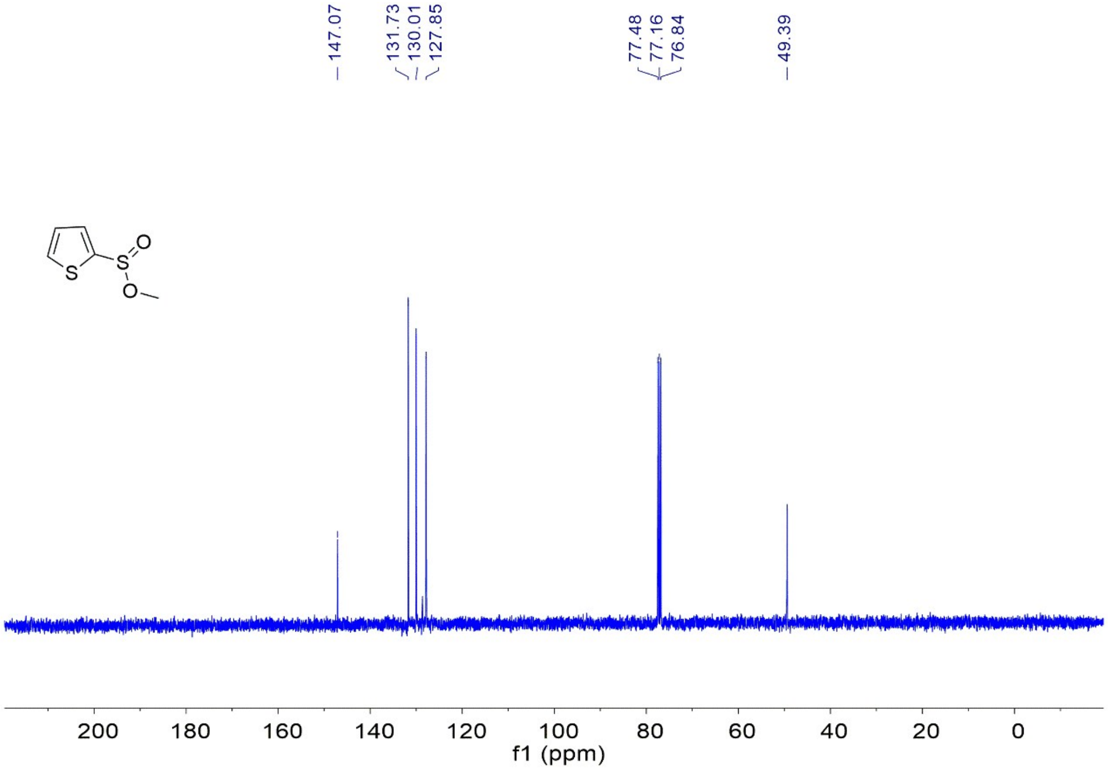
^{13}C- NMR spectrum of 3ra



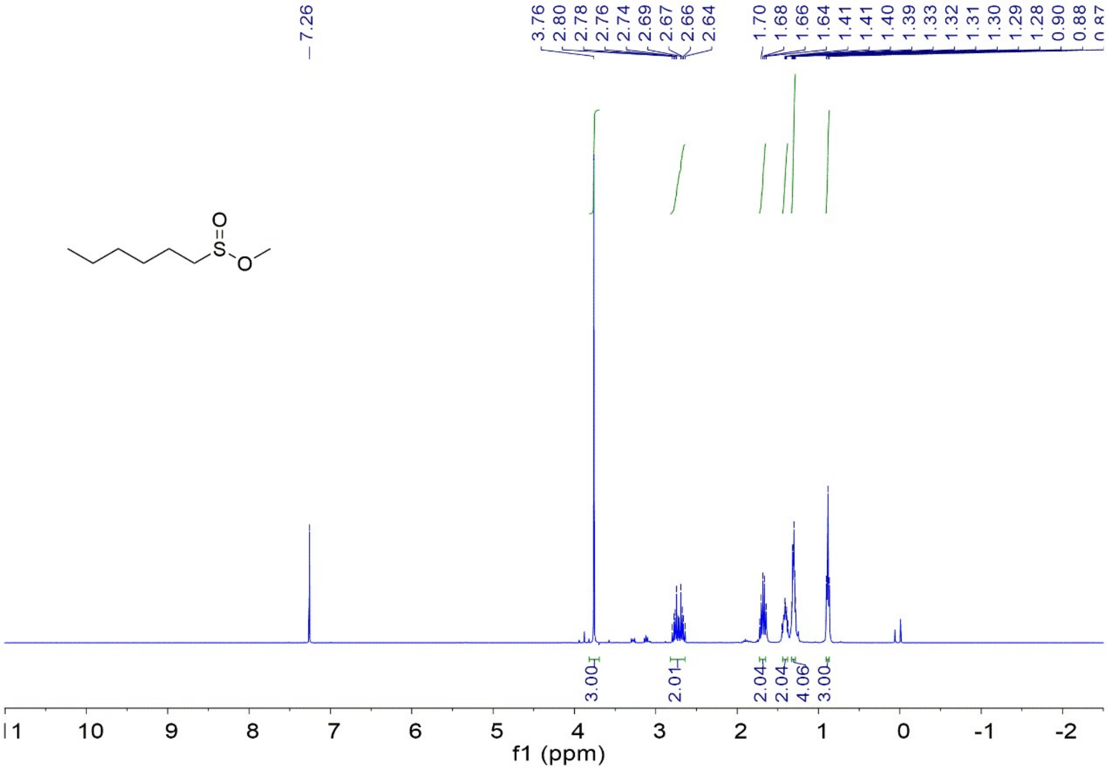
^{1}H-NMR spectrum of 3sa



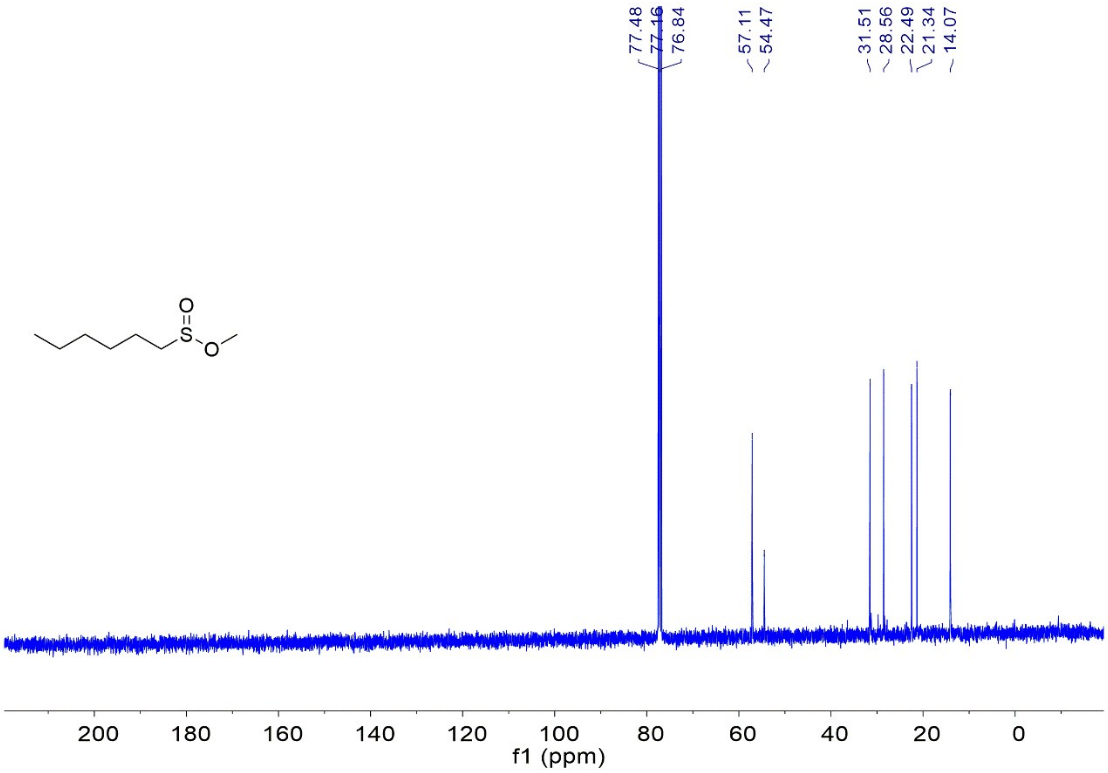
^{13}C-NMR spectrum of 3sa



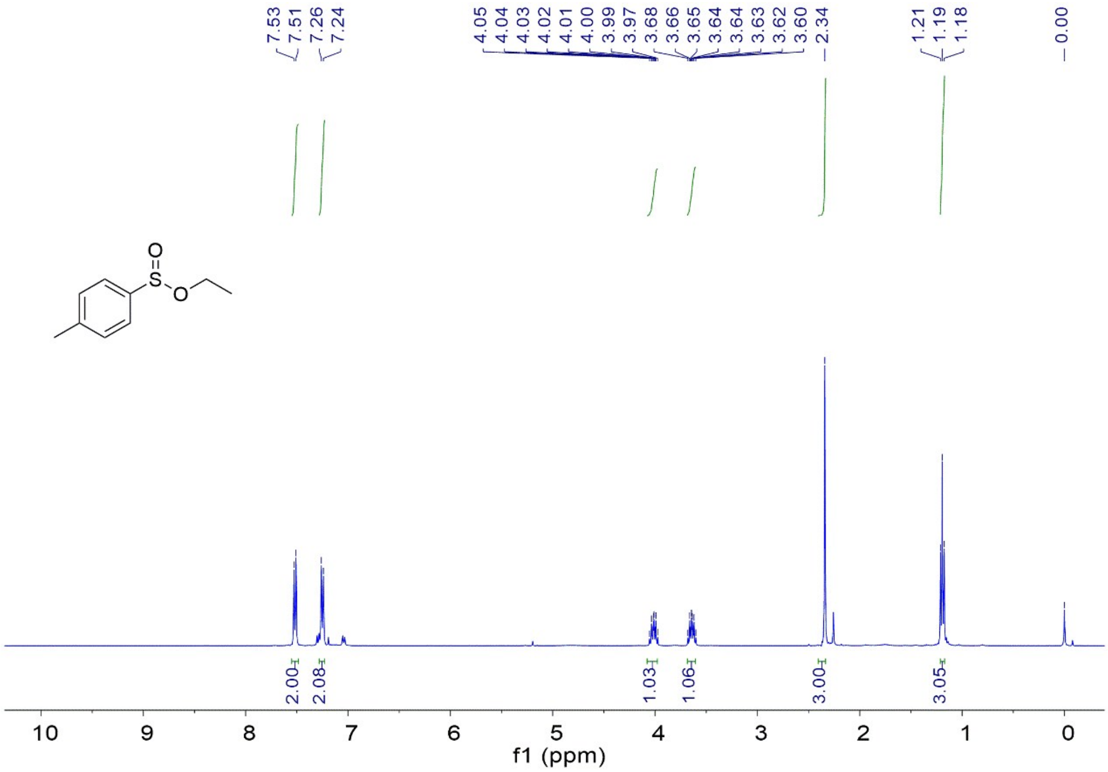
^{1}H-NMR spectrum of 3ta



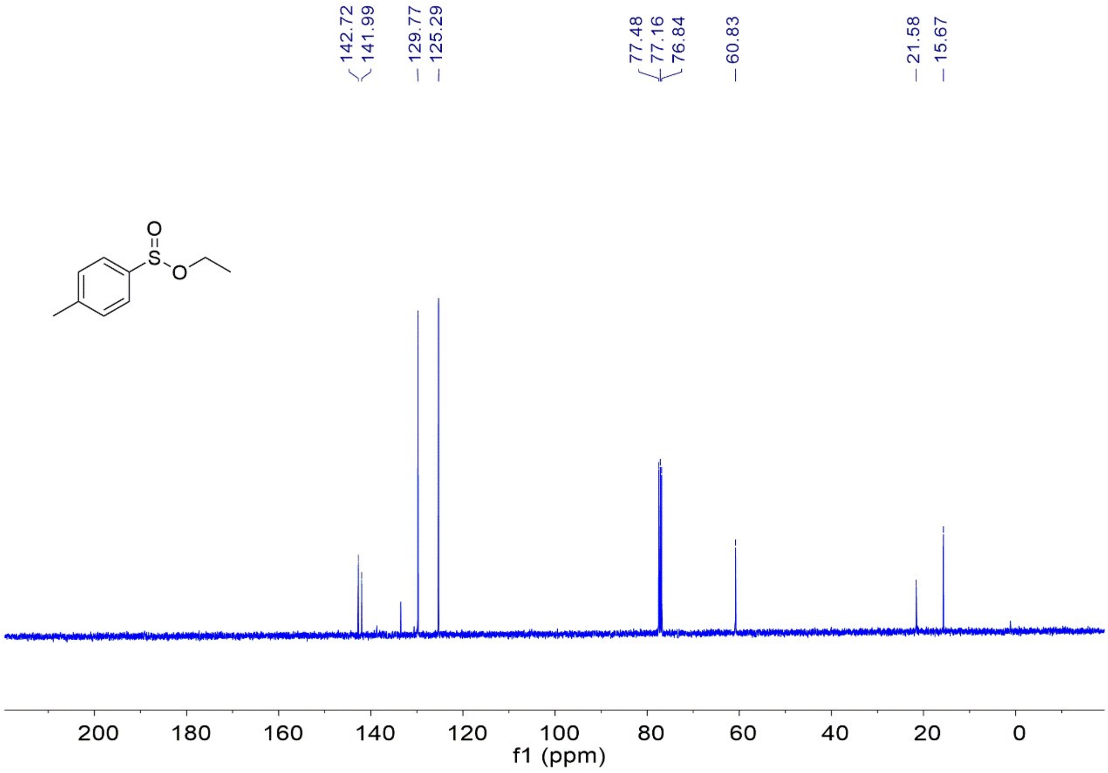
^{13}C-NMR spectrum of 3ta



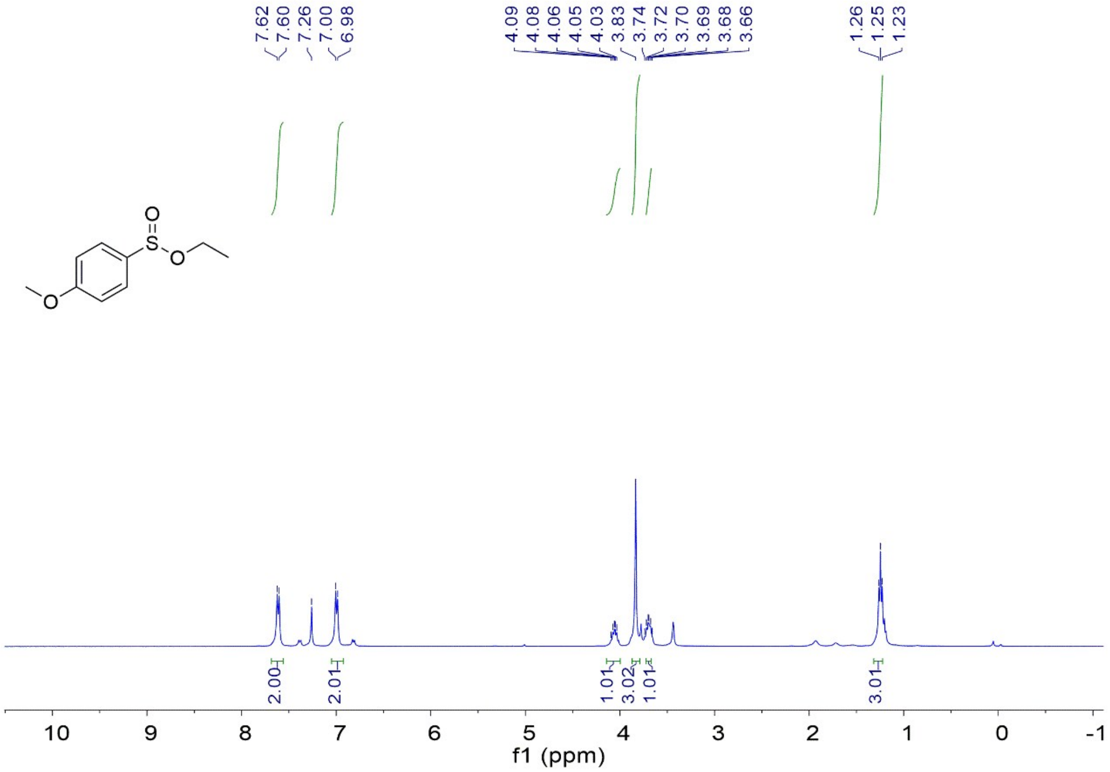
^{1}H-NMR spectrum of 3ab



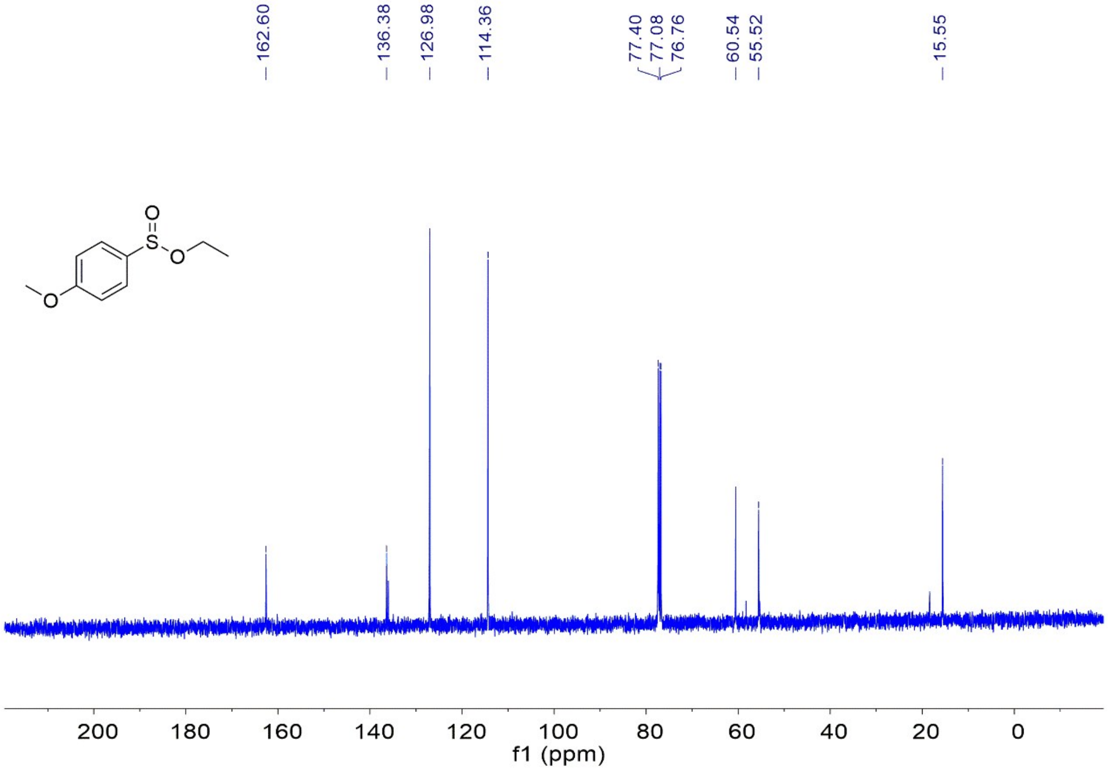
^{13}C-NMR spectrum of 3ab



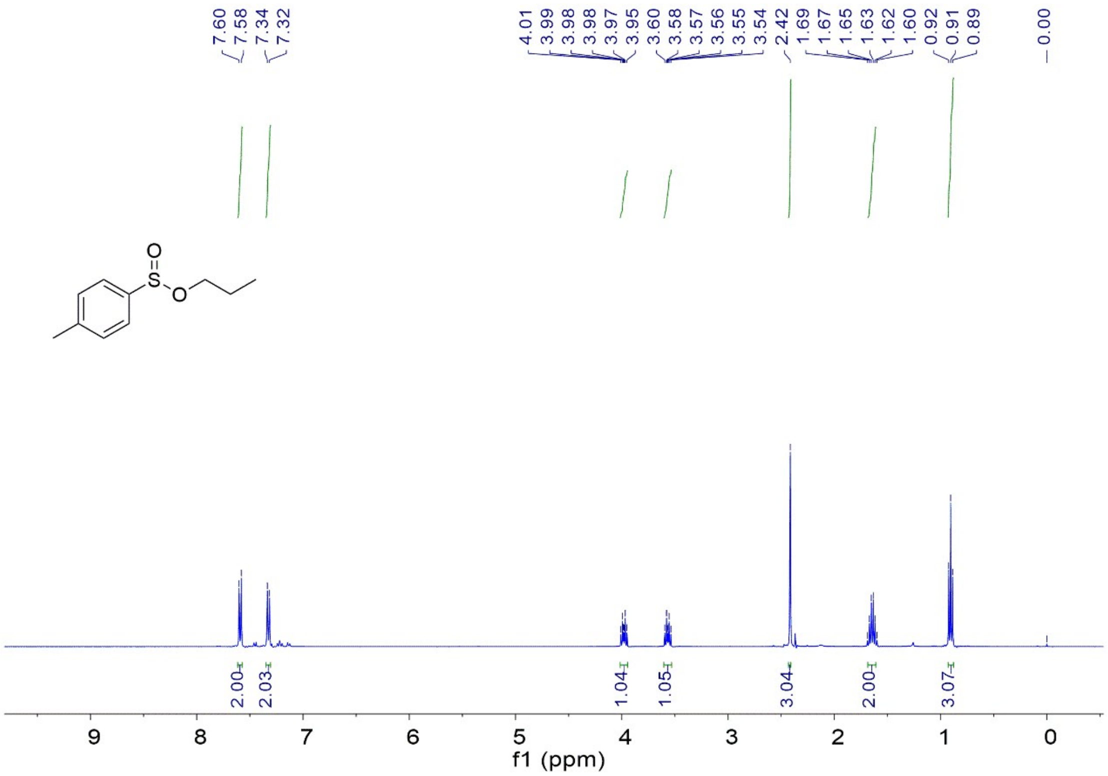
^{1}H-NMR spectrum of 3gb



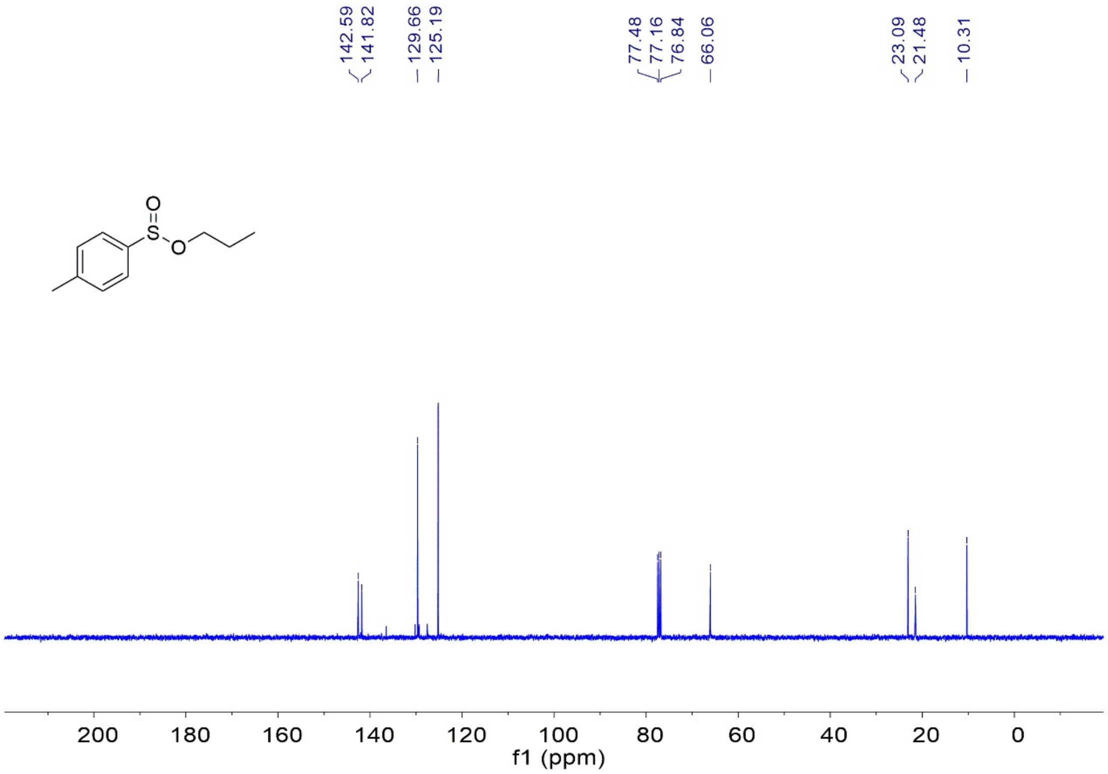
^{13}C-NMR spectrum of 3gb



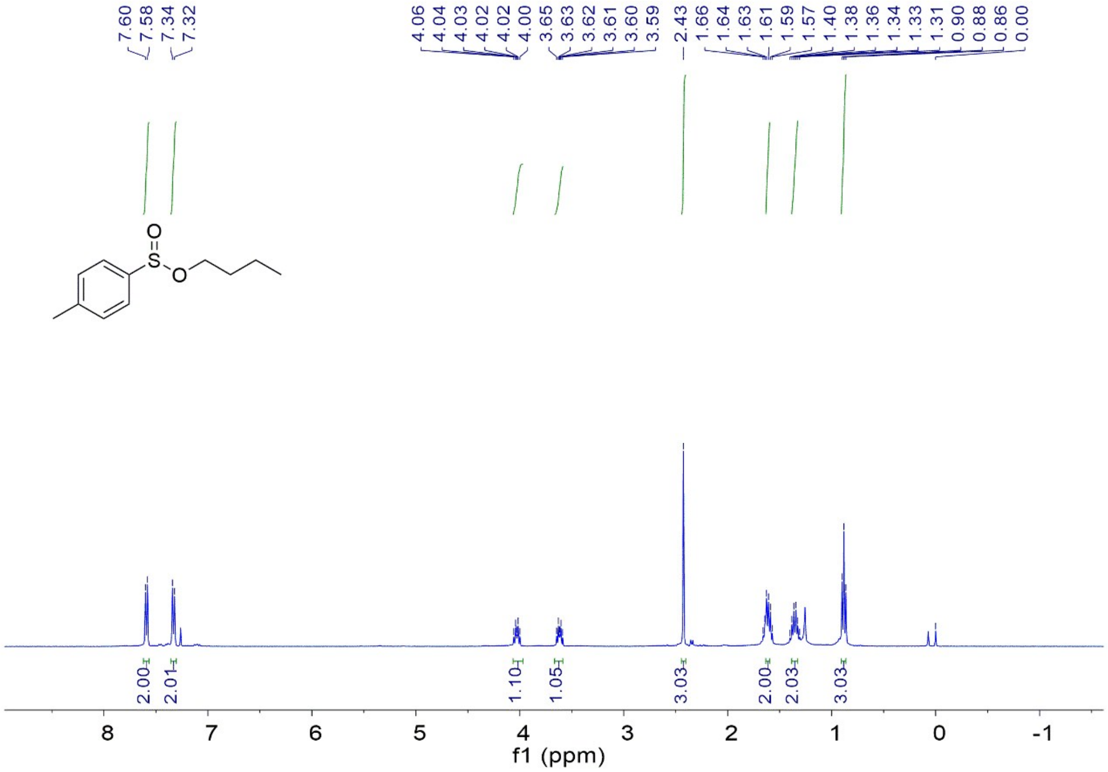
^{1}H-NMR spectrum of 3ac



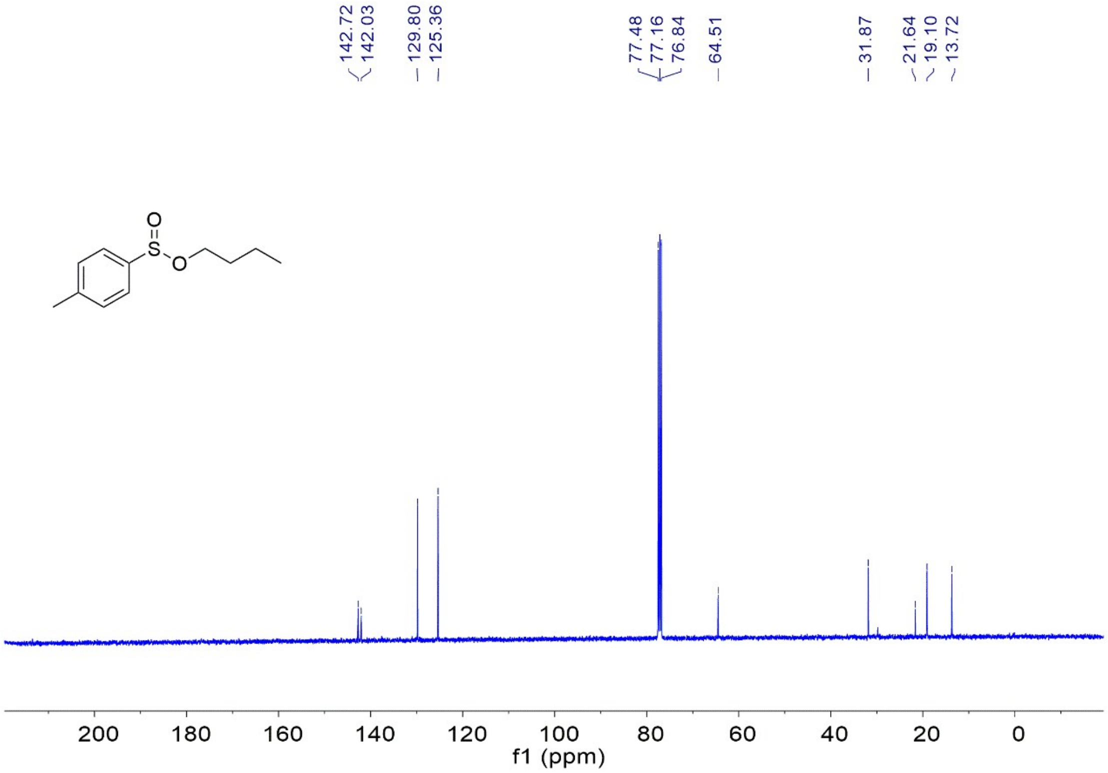
^{13}C-NMR spectrum of 3ac



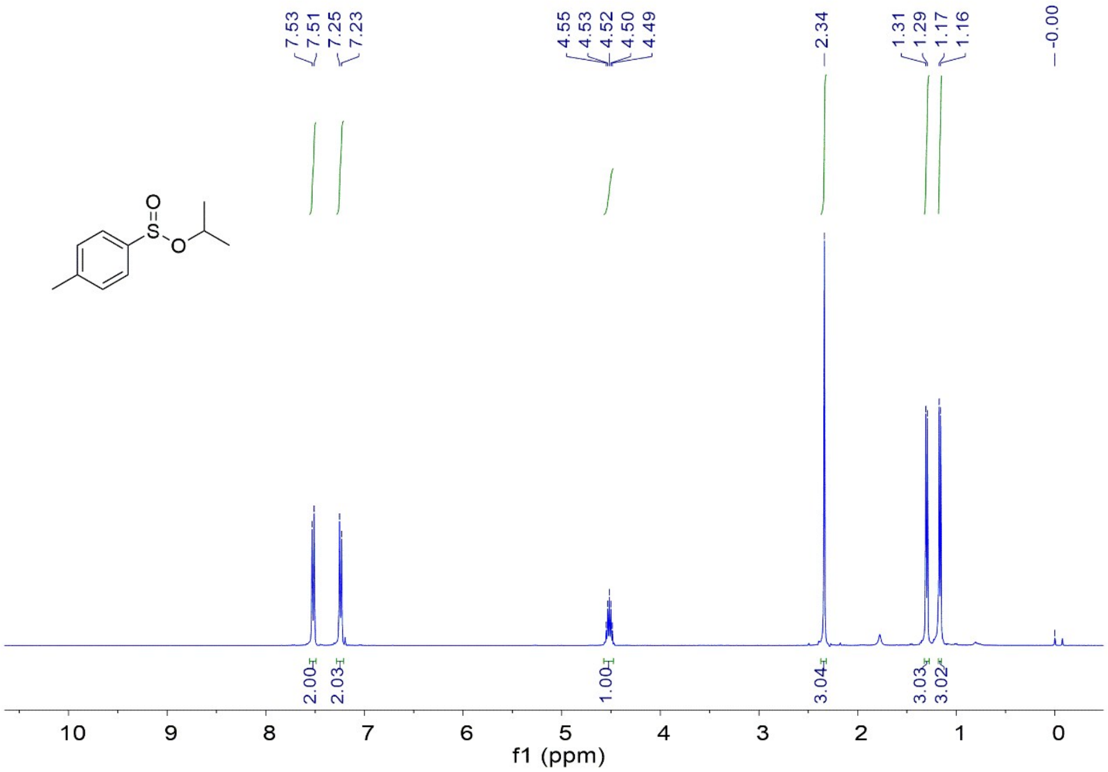
^{1}H-NMR spectrum of 3ad



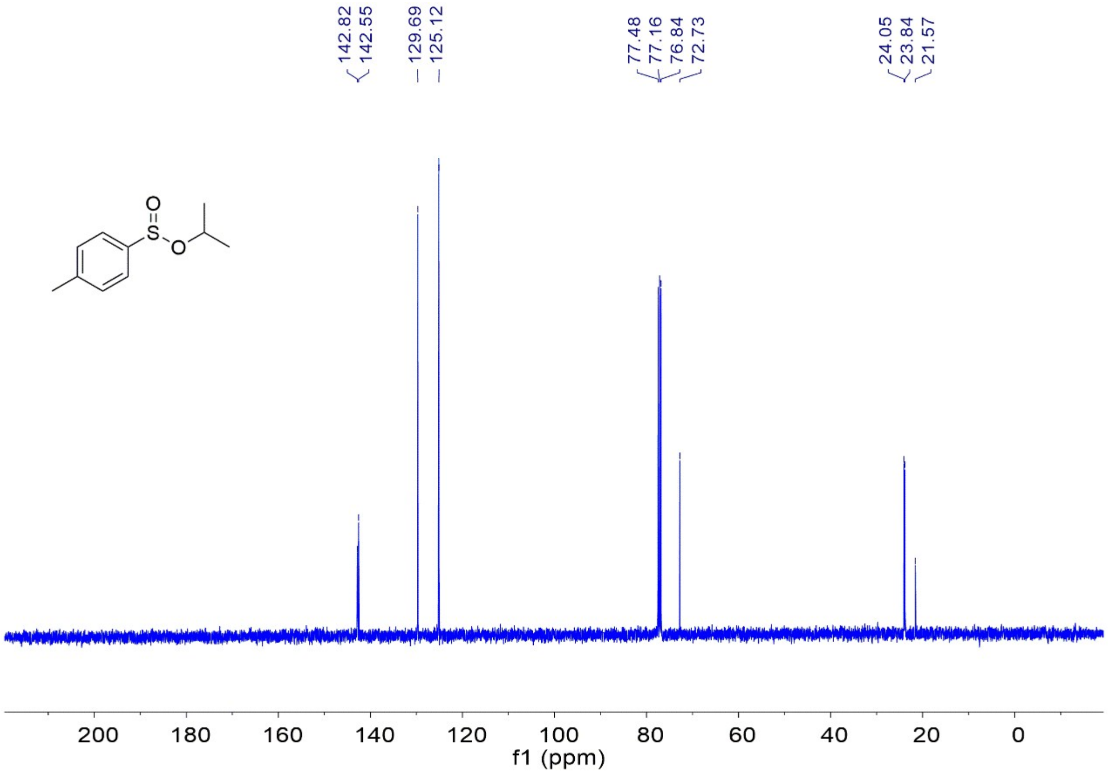
^{13}C-NMR spectrum of 3ad



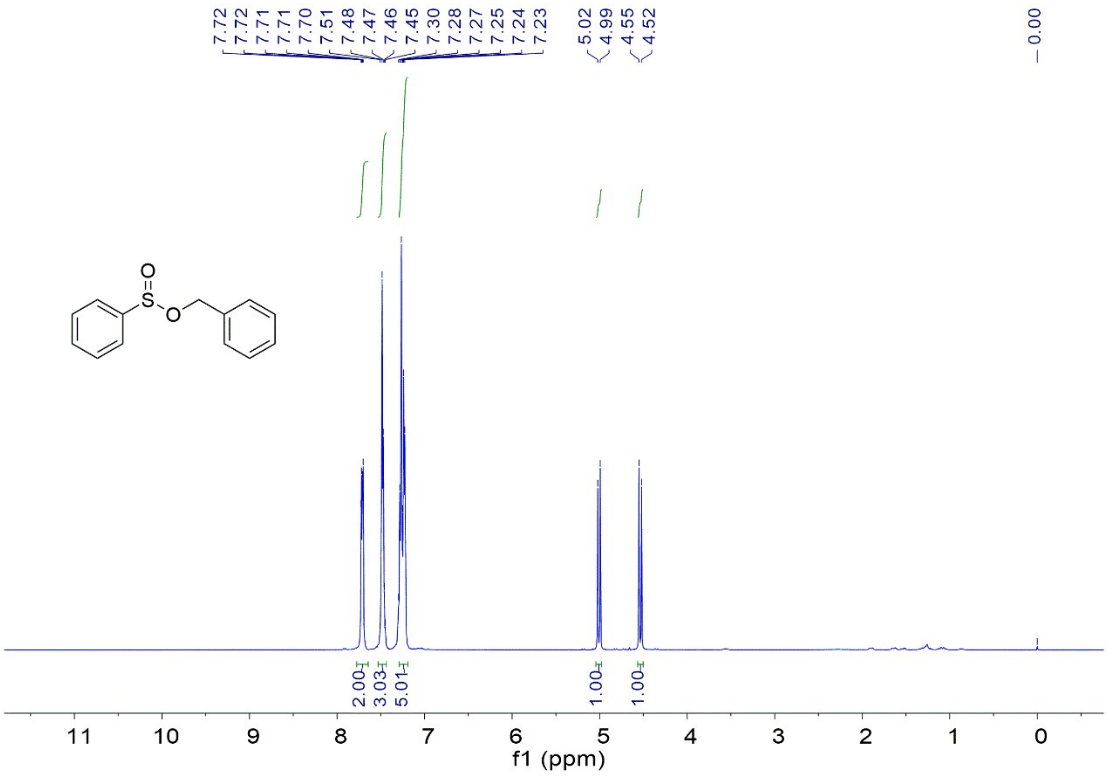
^{1}H-NMR spectrum of 3ae



^{13}C-NMR spectrum of 3ae



^{1}H-NMR spectrum of 3ef



^{13}C-NMR spectrum of 3ef