Supporting Information

For

H_2O_2-Mediated Metal-free Protocol towards Unsymmetrical Thiosulfonates from Sulfonyl Hydrazides and Disulfides in PEG-400

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General information

All product mixtures were analyzed by thin layer chromatography glass-backed silica TLC plates with a fluorescent indicator from Branch of Qingdao Haiyang Chemical CO. LTD. UV-active compounds were detected with a UV lamp (λ□= 254 nm). For flash column chromatography, silica gel (200 - 300 mesh) was used as stationary phase and a mixture of petroleum and ethyl acetate was used as eluent. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 in deuterated chloroform at 25 °C with residue solvent peaks as internal standards (δ = 7.26 ppm for ^{1}H-NMR and δ = 77.16 ppm for ^{13}C-NMR). Chemical shifts δ are reported in ppm, and spin-spin coupling constants (*J*) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were recorded on a ThermoFinnigan MAT95XP microspectrometer and High resolution mass spectra (HRMS) were recorded on Agilent Technologies Accurate Mass Q-TOF 6530 microspectrometer. Melting points were recorded on a national standard melting point apparatus (Model: Taike XT-4) and were uncorrected.
All solvents were dried according to known methods.[S1] All the chemicals were purchased commercially and were used without further purification.

General procedure towards thiosulfonates 3

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with sulfonyl hydrazide **1** (1.0 mmol, 2 equiv), and disulfide **2** (0.5 mmol) in PEG-400 (1.5 mL), then H_2O_2 (30% in H_2O, 950 mg, 4.2 mmol) were added dropwise and the reaction mixture was allowed to stir at 100 ^{o}C for 2 h. After the completion of the reaction (monitored by TLC), the solution was washed with H_2O and saturated sodium chloride, then extracted with dichloromethane (15 mL × 3) and dried over anhydrous sodium sulfate. The organic phase was combined and then concentrated. The crude product was purified by column chromatography using silica gel (200 - 300 mesh) as stationary phase and petroleum ether/ethyl acetate (40/1) used as eluent to give the desired product in noted yields.
Compounds **EXCEPT 3ca, 3ma, 3na, 3oa, 3pa, 3an, 3ao, 3ap** were known compounds and the data obtained herein were in accordance with the previous reports.[S2 – S5]

References:

[S1] D. D. Perrin, W. L. F. Armarego, In Purification of Laboratory Chemicals, 3rd ed.; Pergamon Press: New York, 1988.

[S2] G. Liang, J. Chen, J. Chen, W. Li, J. Chen and H. Wu, Tetrahedron Lett., 2012, 53, 6768.

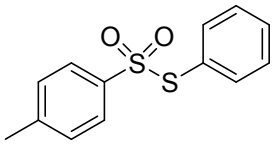
[S3] Nobukazu Taniguchi, Eur. J. Org. Chem., 2014, 26, 5691-5694.

[S4] Nobukazu Taniguchi, J. Org. Chem., 2015, 80, 1764-1770.

[S5] G.-Y. Zhang, S.-S. Lv, A. Shoberu and J.-P. Zou, J. Org. Chem., 2017, 82, 9801-9807.

Data

p-Tolyl sulfonothioic phenyl ester (**3aa**)



Follow the general procedure, **3aa** was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 78% yield (103.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (t, *J* = 7.1 Hz, 3H), 7.39 – 7.31 (m, 4H), 7.20 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H) (ppm).

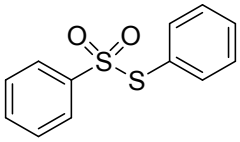
^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.7, 140.3, 136.6, 131.3, 129.4, 129.4, 128.1, 127.6, 21.7 (ppm).

IR (in KBr): ν = 1590, 1428, 1313, 1127 (cm^{-1}).

MS (EI) m/z (%) = 77.0 (4), 91.0 (37), 109.0 (27), 155.0 (68), 264.0 (100, M^+).

HRMS (ESI) (m/z)[$C_{13}H_{12}S_2O_2 + H^+$]: Calcd. 265.0351, Found. 265.0345.

Phenyl sulfonothioic phenyl ester **(3ba)**



Follow the general procedure, **3ba** was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 79% yield (99.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.53 (m, 3H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.28 (m, 4H) (ppm).

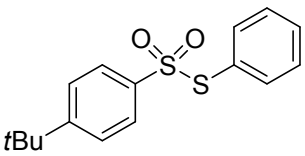
^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.9, 136.6, 133.7, 131.5, 129.5, 128.8, 127.8, 127.6 (ppm).

IR (in KBr): ν =3080, 1315, 1130,780 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (24), 109.0 (47), 141.0 (84), 250.0 (100, M^+).

HRMS (ESI) (m/z)[$C_{12}H_{10}S_2O_2 + H^+$]: Calcd. 251.0195, Found. 251.0198.

p-tert-Butylphenyl sulfonothioic phenyl ester (**3ca**)



Follow the general procedure, **3ca** was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 81% yield (124.2 mg).

m.p.: 42 - 44 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (t, *J* = 9.3 Hz, 3H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 6.3 Hz, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 1.33 (s, 9H) (ppm).

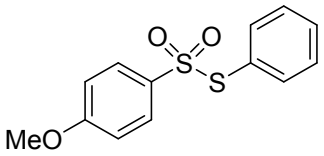
^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.7, 140.2, 136.6, 131.3, 129.4, 128.1, 127.5, 125.7, 35.3, 31.1 (ppm).

IR (in KBr): ν = 2960, 1594,1457,1324,1148 (cm^{-1}).

MS (ESI) m/z (%) = 109.0 (25), 133.1 (48), 197.0 (100), 306.0 (95, M^+).

HRMS (ESI) (m/z) [$C_{16}H_{18}S_2O_2 + H^+$]: Calcd. 307.0821, Found. 307.0829.

p-Methoxyphenyl sulfonothioic phenyl ester (**3da**)



Follow the general procedure, **3da** was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 72% yield (101.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (t, *J* = 10.0 Hz, 3H), 7.35 (q, *J* = 7.4 Hz, 4H), 6.86 (d, *J* = 7.8 Hz, 2H), 3.86 (s, 3H) (ppm).

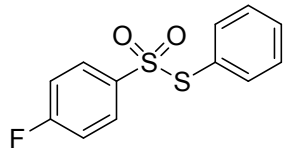
^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.6, 136.7, 134.9, 131.3, 129.9, 129.4, 128.2, 113.8, 55.7 (ppm).

IR (in KBr): ν = 1596, 1494, 1327, 1148, 720(cm^{-1}).

MS (ESI) m/z (%) = 77.0 (8), 107.0 (42), 109.0 (61), 171.0 (100), 280.0 (92, M^+).

HRMS (ESI) (m/z)[$C_{13}H_{12}S_2O_2$ + H^+]: Calcd. 281.0301, Found. 281.0306.

p-Fluorophenyl sulfonothioic phenyl ester (**3ea**)



Follow the general procedure, **3ea** was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 64% yield (86.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 – 7.54 (m, 2H), 7.49 (s, 1H), 7.37 (d, *J* = 3.5 Hz, 4H), 7.09 (t, *J* = 8.3 Hz, 2H) (ppm).

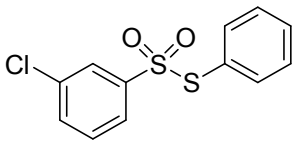
^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.5 (d, *J* = 256.8 Hz), 139.0 ($J_{C\text{-}F}$ = 3.2 Hz), 136.6, 131.6, 130.5 ($J_{C\text{-}F}$ = 9.7 Hz), 129.6, 127.7, 116.1 ($J_{C\text{-}F}$ = 22.8 Hz) (ppm).

IR (in KBr): ν = 1712, 1587, 1430, 1127 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (7), 95.0 (26), 109.0 (56), 158.0 (85), 268.0 (100, M^+).

HRMS (ESI) (m/z)[$C_{12}H_9FO_2S_2$+ H^+]: Calcd. 269.0101, Found. 269.0110.

m-Chlorophenyl sulfonothioic phenyl ester (**3ga**)



Follow the general procedure, **3ga** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (100.4 mg).

m.p.: 65 - 67 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.44 (m, 2H), 7.42 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.26 (m, 5H) (ppm).

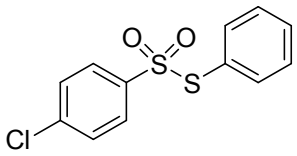
^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.2, 136.6, 135.1, 133.7, 131.8, 130.1, 129.6, 127.6, 127.4, 125.6 (ppm).

IR (in KBr): ν = 1599, 1484, 1343, 1126 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (9), 109.0 (26), 111.0 (56), 174.0 (100), 264.0 (68, M^+).

HRMS (ESI) (m/z)[$C_{12}H_9ClO_2S_2$+ H^+]: Calcd.284.9805, Found.284.9814.

p-Chlorophenyl sulfonothioic phenyl ester (**3ha**)



Follow the general procedure, **3ha** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 73% yield (103.2 mg).

m.p.: 80 – 82 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 7.5 Hz, 3H), 7.42 – 7.34 (m, 6H) (ppm).

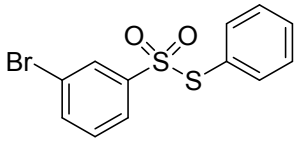
^{13}C NMR (100 MHz, $CDCl_3$) δ = 141.4, 140.3, 136.6, 131.7, 129.6, 129.1, 129.0, 127.6 (ppm).

IR (in KBr): ν = 1584, 1450, 1340, 1128 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (7), 109.0 (24), 111.0 (57), 174.0 (100), 264.0 (75, M^+).

HRMS (ESI) (m/z) [$C_{12}H_9ClO_2S_2 + H^+$]: Calcd. 284.9805, Found. 284.9801.

m-Bromophenyl sulfonothioic phenyl ester (**3ja**)



Follow the general procedure, **3ja** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 70% yield (114.6 mg).

m.p.: 57 – 59 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.9 Hz, 1H), 7.62 (s, 1H), 7.51 (dd, *J* = 14.3, 5.9 Hz, 2H), 7.38 (d, *J* = 4.2 Hz, 4H), 7.30 (t, *J* = 8.0 Hz, 1H) (ppm).

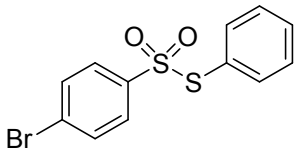
^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.3, 136.6, 136.6, 131.8, 130.5, 130.3, 129.7, 127.5, 125.9, 122.7 (ppm).

IR (in KBr): ν = 1594, 1450, 1334, 1126 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (6), 109.0 (28), 154.0 (43), 218.0 (67), 328.0 (100, M^+).

HRMS (ESI) (m/z) [$C_{12}H_9BrO_2S_2 + H^+$]: Calcd. 328.9300, Found. 328.9308.

p-Bromophenyl sulfonothioic phenyl ester (**3ka**)



Follow the general procedure, **3ka** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (116.4 mg).

m.p.: 76 – 77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 5.4 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.31 (m, 4H) (ppm).

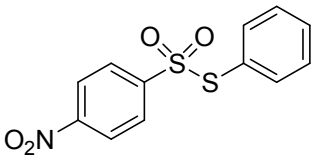
^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.0, 136.6, 132.1, 131.6, 129.6, 129.0, 128.9, 127.6 (ppm).

IR (in KBr): ν = 1595, 1442, 1310, 1138 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (4), 109.0 (32), 154.0 (21), 218.0 (72), 328.0 (100, M^+).

HRMS (ESI) (m/z)[$C_{12}H_9BrO_2S_2 + H^+$]: Calcd. 328.9300, Found. 328.9296.

p-Nitrophenyl sulfonothioic phenyl ester (**3la**)



Follow the general procedure, **3la** was obtained as yellow liquid with petroleum ether/ethyl acetate (40/1) used as eluent in 68% yield (100.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 3.0 Hz, 1H), 7.40 (t, *J* = 6.3 Hz, 4H).ppm.

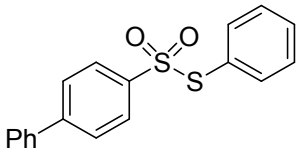
^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.4, 147.9, 136.5, 132.1, 129.9, 128.8, 126.9, 124.1.(ppm).

IR (in KBr): ν = 1590, 1456, 1320, 1132 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (5), 109.0 (54), 122.0 (43), 185.0 (100), 295.0 (86, M^+).

HRMS (ESI) (m/z)[$C_{12}H_9NO_2S_2 + H^+$]: Calcd. 296.0046, Found. 296.0054.

4-Biphenyl sulfonothioic phenyl ester (**3ma**)



Follow the general procedure, **3ma** was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 77% yield (125.6 mg).

m.p.: 102 – 103 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (dd, *J* = 16.6, 9.1 Hz, 6H), 7.40 (t, *J* = 7.3 Hz, 3H), 7.38 – 7.31 (m, 3H), 7.27 (t, *J* = 7.4 Hz, 2H) (ppm).

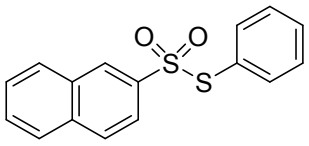
^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.5, 141.6, 138.9, 137.0, 136.7, 131.5, 129.5, 129.1, 128.8, 128.1, 127.4, 127.3 (ppm).

IR (in KBr): ν = 1589, 1445, 1321, 1143 (cm^{-1}).

MS (ESI) m/z (%) = 77.0 (12), 109.0 (25), 153.0 (56), 217.0 (100), 327.0 (76, M^+).

HRMS (ESI) (m/z)[$C_{18}H_{14}S_2O_2 + H^+$]: Calcd. 327.0508, Found. 327.0512.

2-Napthyl sulfonothioic phenyl ester (**3na**)



Follow the general procedure, **3na** was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 68% yield (102.3 mg).

m.p.: 51 – 53 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (s, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.26 (m, 2H).ppm.

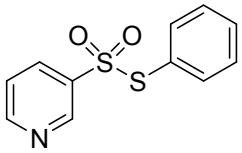
^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.6, 136.7, 136.6, 135.1, 131.6, 131.4, 129.5, 129.4, 129.3, 129.3, 128.1, 128.0, 127.7, 122.4 (ppm).

IR (in KBr): ν = 1590, 1452, 1311, 1145, 761(cm^{-1}).

MS (ESI) m/z (%) = 77.0 (8), 109.0 (28), 127.0 (35), 191.0 (72), 300.0 (100, M^+).

HRMS (ESI) (m/z)[$C_{16}H_{12}S_2O_2$ + H^+]: Calcd. 301.0351, Found. 301.0353.

3-Pyridinyl sulfonothioic phenyl ester (**3oa**)



Follow the general procedure, **3oa** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 72% yield (90.2 mg).

m.p.: 87 – 88 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (t, *J* = 8.4 Hz, 3H), 7.47 (d, *J* = 6.6 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.31 (m, 3H) (ppm).

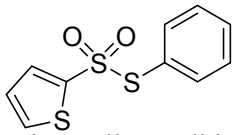
^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.0, 136.6, 133.7, 131.5, 129.5, 128.8, 127.8, 127.6 (ppm).

IR (in KBr): ν = 1593, 1467, 1331, 1145 , 731(cm^{-1}).

MS (ESI) m/z (%) = 77.0 (6), 78.0 (35), 109.0 (42), 141.0 (100), 251.0 (87, M^+).

HRMS (ESI) (m/z)[$C_{11}H_9NO_2S_2$ + H^+]: Calcd. 252.0147, Found. 252.0154.

2-Thiophenyl sulfonothioic phenyl ester (**3pa**)



Follow the general procedure, **3pa** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 64% yield (82.3 mg).

m.p.: 72 – 73 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 4.8 Hz, 1H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.27 (s, 1H), 6.99 (s, 1H) (ppm).

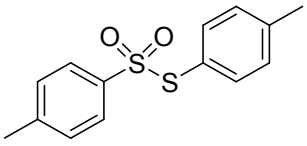
^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.6, 134.0, 133.8, 131.6, 129.6, 128.1, 127.0 (ppm).

IR (in KBr): ν = 1578, 1483, 1315, 1130, 745(cm^{-1}).

MS (ESI) m/z (%) = 82.0 (24), 91.0 (6), 123.0 (47), 146.0 (76), 255.0 (100, M^+).

HRMS (ESI) (m/z)[$C_{10}H_8O_2S_3$+ H^+]: Calcd.256.9759, Found. 256.9753.

4-Tolyl sulfonothioic 4-tolyl ester (**3ab**)



Follow the general procedure, **3ab** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 80% yield (111.5 mg).

m.p.: 76 – 77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 8.9 Hz, 4H), 7.14 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H) (ppm).

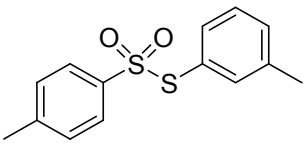
^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.6, 142.1, 140.5, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5 (ppm).

IR (in KBr): ν = 1594, 1490, 1328, 1143 (cm^{-1}).

MS (ESI) m/z (%) = 91.0 (35), 123.0 (52), 155.0 (78), 278.0 (100, M^+).

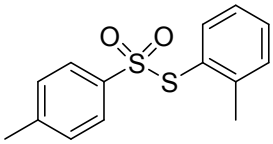
HRMS (ESI) (m/z)[$C_{14}H_{14}O_2S_2 + H^+$]: Calcd. 279.0508, Found. 279.0502.

4-Tolyl sulfonothioic 3-tolyl ester (**3ac**)



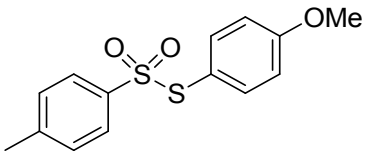
Follow the general procedure, **3ac** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 78% yield (108.6 mg).
m.p.: 76 – 77 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 7.3 Hz, 2H), 7.22 (d, *J* = 10.3 Hz, 4H), 7.14 (d, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.6, 142.1, 140.5, 136.5, 130.2, 129.4, 127.6, 124.6, 21.7, 21.5 (ppm).
IR (in KBr): ν = 1598, 1494, 1326, 1140 (cm^{-1}).
MS (ESI) m/z (%) = 91.0 (100), 123.0 (73), 155.0 (68), 278.0 (46, M^+).
HRMS (ESI) (m/z)[$C_{14}H_{14}O_2S_2 + H^+$]: Calcd. 279.0508, Found. 279.0514.

4-Tolyl sulfonothioic 2-tolyl ester **(3ad)**



Follow the general procedure, **3ad** was obtained as white solid with petroleum ether/ethyl acetate (40/1) used aseluent in 65% yield (90.4 mg).
m.p.: 101 – 102°C.
1H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 7.7 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 2.42 (s, 3H), 2.15 (s, 3H) (ppm).
13C NMR (100 MHz, $CDCl_3$) δ = 144.8, 144.2, 140.7, 138.3, 131.9, 131.0, 123.0, 127.5, 127.3, 126.9, 21.7, 20.7 (ppm).
IR (in KBr): ν = 1590, 1492, 1341, 1138 (cm^{-1}).
MS (ESI) m/z (%) = 91.0 (76), 123.0 (31), 155.0 (27), 278.0 (100, M^+).
HRMS (ESI) (m/z)[$C_{12}H_{10}S_2O_2 + H^+$]: Calcd. 279.0508, Found. 279.0516.

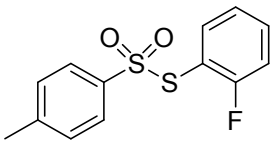
4-Tolyl sulfonothioic 4-methoxyphenyl ester (**3ae**)



Follow the general procedure, **3ae** was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 75% yield (110.4 mg).
m.p.: 127 – 128 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 7.6 Hz, 2H), 3.83 (s, 3H), 2.42 (s, 3H).ppm.
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 144.6, 140.3, 138.4, 129.4, 127.6, 118.7, 115.0, 55.5, 21.7.(ppm).

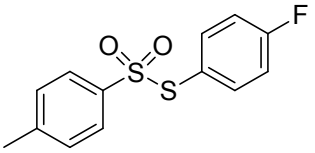
IR (in KBr): ν = 1590, 1493, 1325, 1141 cm^{-1}.
MS (ESI) m/z (%) = 91.0 (56), 107.0 (25), 139.0 (43), 155.0 (100), 294.0 (78, M^+).
HRMS (ESI) (m/z)[$C_{14}H_{14}O_2S_2 + H^+$]: Calcd. 295.0457, Found. 295.0450.

4-Tolyl sulfonothioic 2-fluorophenyl ester (**3af**)



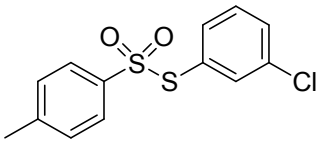
Follow the general procedure, **3af** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 64% yield (90.1 mg).
m.p.: 65 – 67 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (t, *J* = 7.7 Hz, 4H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 8.6 Hz, 1H), 2.43 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9 (J_{C-F} = 253.7 Hz), 145.1, 140.7, 139.1, 134.2 (J_{C-F} = 8.3 Hz), 129.5, 127.5, 125.0 (J_{C-F} = 3.9 Hz), 116.4 (J_{C-F} = 22.7 Hz), 115.3 (J_{C-F} = 17.8 Hz), 21.7 (ppm).
IR (in KBr): ν = 1725, 1587, 1493, 1329, 1141 (cm^{-1}).
MS (ESI) m/z (%) = 91.0 (100), 95.0 (48), 127.0 (25), 155.0 (67), 282.0 (24, M^+).
HRMS (ESI) (m/z)[$C_{13}H_{11}FO_2S_2 + H^+$]: Calcd. 283.0257, Found. 283.0249.

4-Tolyl sulfonothioic 4-fluorophenyl ester (**3ag**)



Follow the general procedure, **3ag** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 60% yield (85.5 mg).
m.p.: 92 – 93 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 8.0 Hz, 2H), 2.43 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.8 (J_{C-F} = 253.7 Hz), 145.0, 140.1, 138.9 (J_{C-F} = 9.1 Hz), 129.5, 127.6, 123.6 (J_{C-F} = 3.6 Hz), 116.8(J_{C-F} = 22.2 Hz), 21.7 (ppm).
IR (in KBr): ν = 1730, 1584, 1498, 1326, 1140 cm^{-1}.
MS (ESI) m/z (%) = 91.0 (100), 95.0 (39), 127.0 (34), 155.0 (52), 282.0 (23, M^+).
HRMS (ESI) (m/z)[$C_{14}H_{11}FO_2S_2 + H^+$]: Calcd. 283.0257, Found. 283.0264.

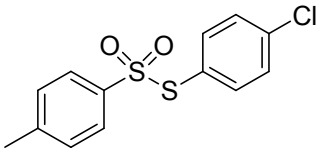
4-Tolyl sulfonothioic 3-chlorophenyl ester (**3ai**)



Follow the general procedure, **3ai** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (105.5 mg).
m.p.: 77 – 79 °C.

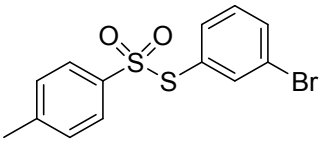
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 8.1 Hz, 3H), 7.30 (d, *J* = 5.8 Hz, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 140.0, 136.1, 134.9, 134.7, 131.5, 130.4, 129.7, 129.5, 127.7, 21.7 (ppm).
IR (in KBr): ν = 1572, 1429, 1330, 1142 cm^{-1}.
MS (ESI) m/z (%) = 91.0 (100), 111.0 (37), 142.0 (56), 155.0 (38), 297.0 (65, M^+).
HRMS (ESI) (m/z)[$C_{13}H_{11}ClO_2S_2 + H^+$]: Calcd. 298.9962, Found. 298.9957.

4-Tolyl sulfonothioic 4-chlorophenyl ester (**3aj**)



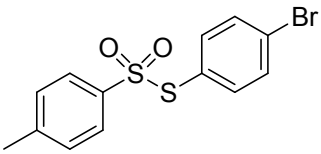
Follow the general procedure, **3aj** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used aseluent in 68 % yield (101.4 mg).
m.p.: 86 – 87 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.26 – 7.22 (m, 2H), 2.43 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.0, 140.2, 138.2, 137.7, 129.7, 129.5, 127.6, 126.6, 21.7 (ppm).
IR (in KBr): ν = 1576, 1427, 1338, 1145 (cm^{-1}).
MS (ESI) m/z (%) = 91.0 (100), 111.0 (45), 142.0 (32), 155.0 (67), 297.0 (87, M^+).
HRMS (ESI) (m/z)[$C_{13}H_{11}ClO_2S_2 + H^+$]: Calcd. 298.9962, Found. 298.9969.

4-Tolyl sulfonothioic 3-bromophenyl ester (**3ak**)



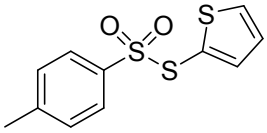
Follow the general procedure, **3ak** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 71% yield (121.6 mg).
m.p.: 73 – 74 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.23 (d, *J* = 9.2 Hz, 3H), 2.44 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.2, 139.9, 138.9, 135.1, 134.3, 130.7, 129.9, 129.5, 127.7, 122.7, 21.7 (ppm).
IR (in KBr): ν = 1528, 1421, 1338, 1149(cm^{-1}).
MS (ESI) m/z (%) = 91.0 (84), 154.0 (24), 155.0 (38), 186.0 (68), 341.0 (100, M^+).
HRMS (ESI) (m/z)[$C_{13}H_{11}BrO_2S_2 + H^+$]: Calcd. 342.9457, Found. 342.9459.

4-Tolyl sulfonothioic 4-bromophenyl ester (**3al**)



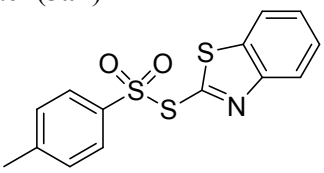
Follow the general procedure, **3al** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 70% yield (119.3 mg).
m.p.: 102 – 103 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.45 (m, 4H), 7.23 (t, *J* = 6.9 Hz, 4H), 2.43 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.1, 140.2, 137.9, 132.7, 129.6, 127.6, 127.2, 126.6, 21.7 (ppm).
IR (in KBr): ν = 1524, 1420, 1336, 1149 (cm^{-1}).
MS (ESI) m/z (%) = 91.0 (73), 154.0 (36), 155.0 (45), 186.0 (81), 341.0 (100, M^+).
HRMS (ESI) (m/z)[$C_{13}H_{11}BrO_2S_2$+ H^+]: Calcd. 342.9457, Found. 342.9463.

4-Tolyl sulfonothioic 2-thiophenyl ester (**3am**)



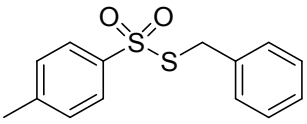
Follow the general procedure, **3am** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 62% yield (83.2 mg).
m.p.: 51 – 52 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 5.1 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 7.15 (s, 1H), 7.07 (s, 1H), 2.44 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.1, 139.5, 139.4, 135.1, 129.6, 128.4, 127.9, 21.7 (ppm).
IR (in KBr): ν = 1545, 1421, 1332, 1179,727 (cm^{-1}).
MS (ESI) m/z (%) = 82.0 (56), 91.0 (100), 114.0 (47), 155.0 (28), 269.0 (61, M^+).
HRMS (ESI) (m/z)[$C_{11}H_{10}O_2S_3$ + H^+]: Calcd. 270.9916, Found. 270.9907.

4-Tolyl sulfonothioic 2-benzothiazolyl ester (**3an**)



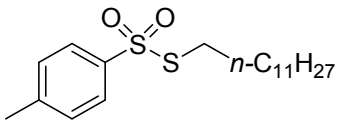
Follow the general procedure, **3an** was obtained as yellow solid with petroleum ether/ethyl acetate (40/1) used as eluent in 58% yield (93.2 mg).
m.p.: 62 – 63 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.58 (d, J = 7.3 Hz, 1H), 7.54 (d, *J* = 9.2 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.7, 151.9, 144.9, 136.0, 134.4, 129.2, 128.0, 126.7, 126.4, 124.5, 121.2, 20.7 (ppm).
IR (in KBr): ν = 1556, 1428, 1334, 1140 cm^{-1}.
MS (ESI) m/z (%) = 91.0 (56), 134.0 (81), 155.0 (45), 165.0 (100), 320.0 (23, M^+).
HRMS (ESI) (m/z)[$C_{14}H_{11}NO_2S_3$ + H^+]: Calcd. 322.0025, Found. 322.0028.

4-Tolyl sulfonothioic benzyl ester (**3ao**)



Follow the general procedure, **3ao** was obtained as white solid with petroleum ether/ethyl acetate (40/1) used as eluent in 77% yield (97.2 mg).
m.p.: 62 – 63 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 3H), 7.18 (s, 2H), 4.24 (s, 2H), 2.43 (s, 3H) (ppm).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.7, 142.0, 133.7, 129.8, 129.2, 128.8, 128.0, 127.0, 40.3, 21.7 (ppm).
IR (in KBr): ν = 3120, 1423, 1348, 1127 cm^{-1}.
MS (ESI) m/z (%) =91.0 (68), 123.0 (41), 155.0 (100), 264.0 (46, M^+)
HRMS (ESI) (m/z)[$C_{14}H_{14}O_2S_2$+ H^+]: Calcd. 279.0508, Found. 279.0517.

4-Tolyl sulfonothioic decane ester **(3ap)**



Follow the general procedure, **3ba** was obtained as colorless liquid with petroleum ether/ethyl acetate (40/1) used aseluent in 48% yield (122.4 mg).
1H NMR (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 1.23 (d, *J* = 18.1 Hz, 20H), 0.88 (t, *J* = 5.9 Hz,3H) (ppm).
13C NMR (100 MHz, $CDCl_3$) δ = 144.6, 142.2, 129.8, 127.0, 36.1, 31.9, 29.6, 29.5, 29.4, 28.9, 28.6, 28.5, 22.7, 21.7, 14.2 (ppm).
IR (in KBr): ν = 3080, 1415, 1130,780 (cm^{-1}).
MS (ESI) m/z (%) = 91.0 (24), 155.0 (56), 201.0 (37) ,356 (100, M^+).
HRMS (ESI) (m/z)[$C_{12}H_{10}S_2O_2$ + H^+]: Calcd. 357.1916, Found. 357.1909.

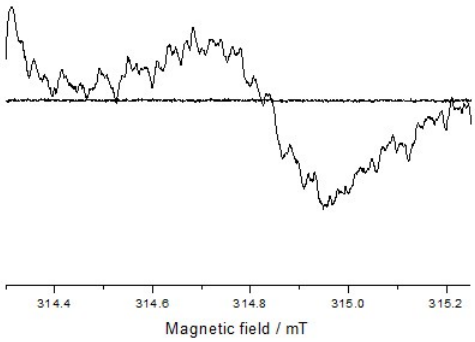
EPR sample preparation and spectra

***p*-Tolyl sulfonyl hydrazide in PEG-400:**

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with *p*-tolyl sulfonyl hydrazide(110.4 mg) and PEG-400 (1.0 mL) and the mixture was allowed to stir at 100 °C for 1 h in air. Then the mixture was introduced in an EPR tube, and the spectrum was measured at room temperature but no signal was observed.

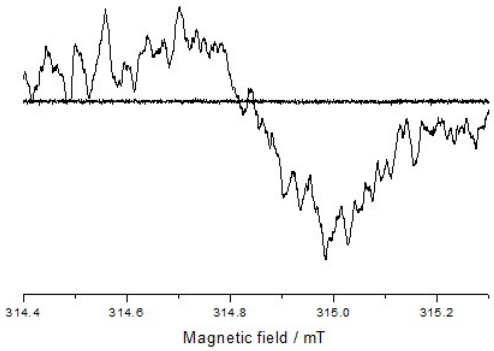
Dphenyl disulfide:

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with diphenyl disulfide(65.4 mg) and PEG-400 (1.0 mL). the mixture was allowed to stir at 100 °C for 1 h in air, then was introduced in an EPR tube, and the spectrum was measured at room temperature. A broad spectrum centered at g_e value = 2.0072 with additional weak narrow signals stemming from the solution was observed.



***p*-Tolyl sulfonyl hydrazide + H_2O_2 (30% in water):**

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with *p*-tolyl sulfonyl hydrazide (110.4 mg), H_2O_2 (476.1 mg, 30% in water) in PEG-400 (1.0 mL). the mixture was allowed to stir at 100 ^oC for 1 h in air, then was introduced in an EPR tube, and the spectrum was measured at room temperature. A broad spectrum centered at g_e value = 2.0086 with additional weak narrow signals stemming from the solution was observed.

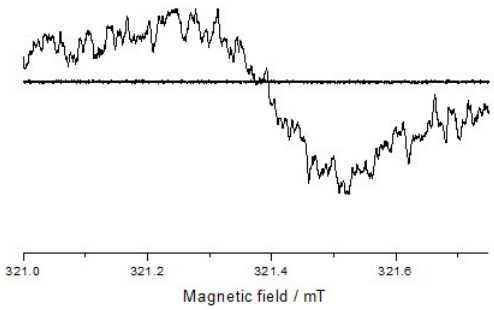


Diphenyl disulfide + 30%H_2O_2:

A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with diphenyl disulfide (65.4 mg), 30% H_2O_2 (476.1 mg) in PEG-400 (1.0 mL) and the mixture was allowed to stir at 100 ^oC for 1 h. Then the mixture was introduced in an EPR tube, and the spectrum was measured at room temperature. No signal was observed.

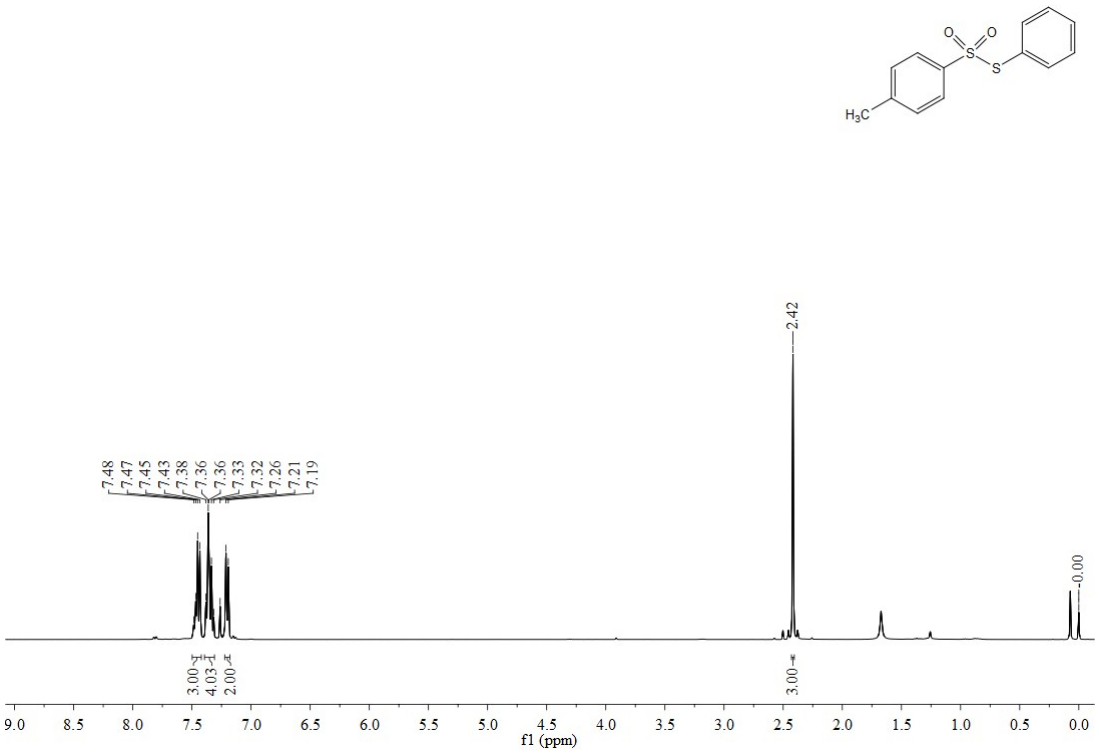
Reaction mixtures:

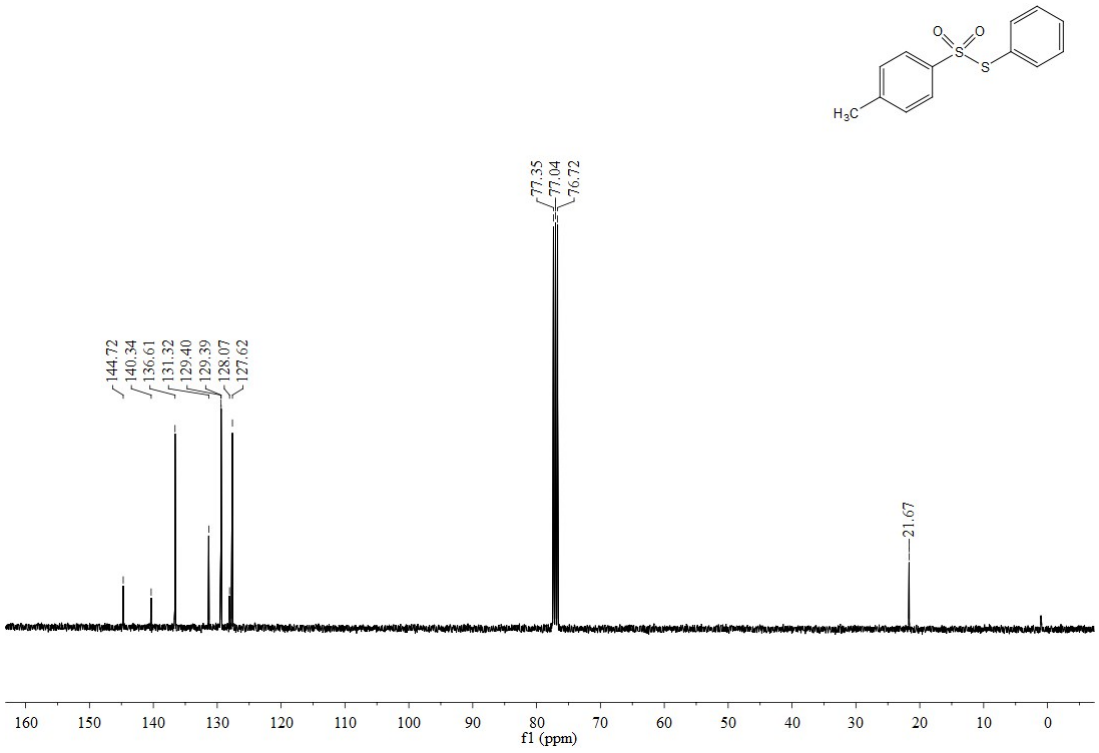
A Schlenk tube (25 mL) equipped with a magnetic bar was loaded with *p*-tolyl sulfonyl hydrazide (110.4 mg), diphenyl disulfide (65.4 mg) and H_2O_2(476.1 mg, 30% in water) in PEG-400 (1.0 mL). The mixture was allowed to stir at 100 ^oC for 1 h in air, then was introduced in an EPR tube, and the spectrum was measured at room temperature. A broad spectrum centered at g-Value = 2.007 with additional weak narrow signals stemming from the solution was observed.


321.0
321.2
321.4
321.6
Magnetic field / mT

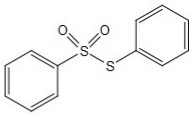
Spectra:

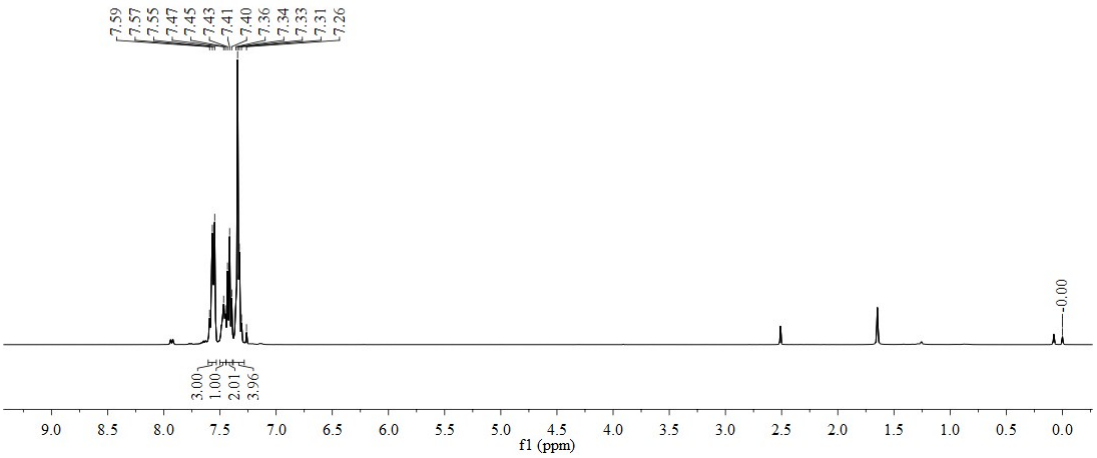
^{1}H, ^{13}C and spectra of 3aa

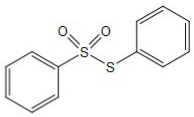


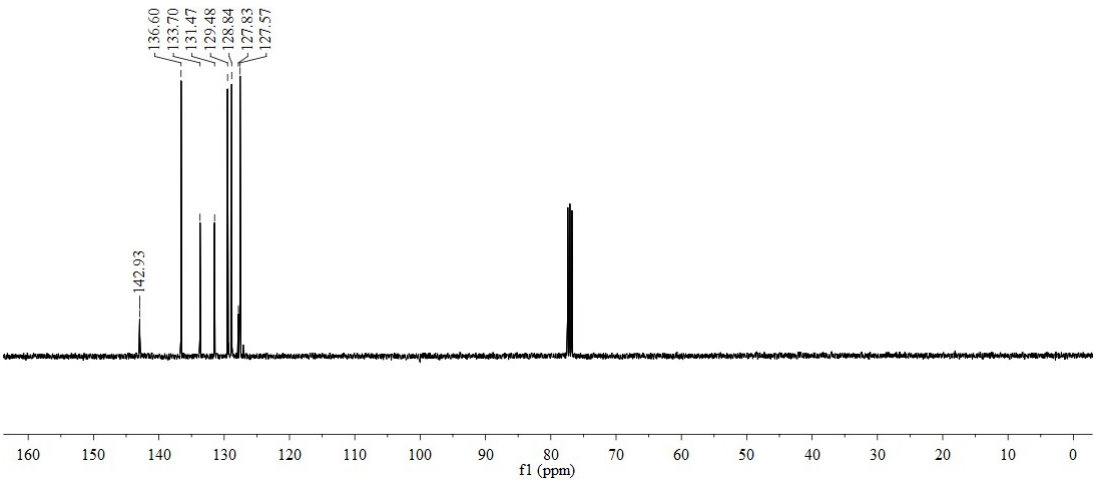


^{1}H, ^{13}C and spectra of 3ba

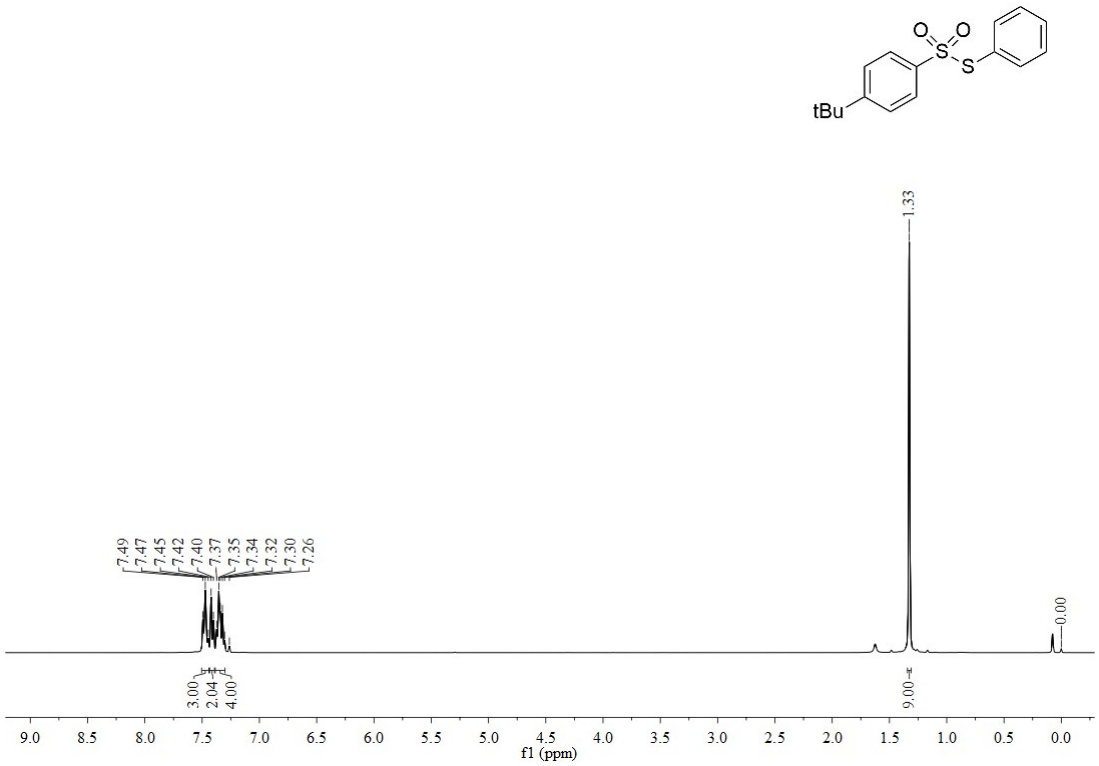


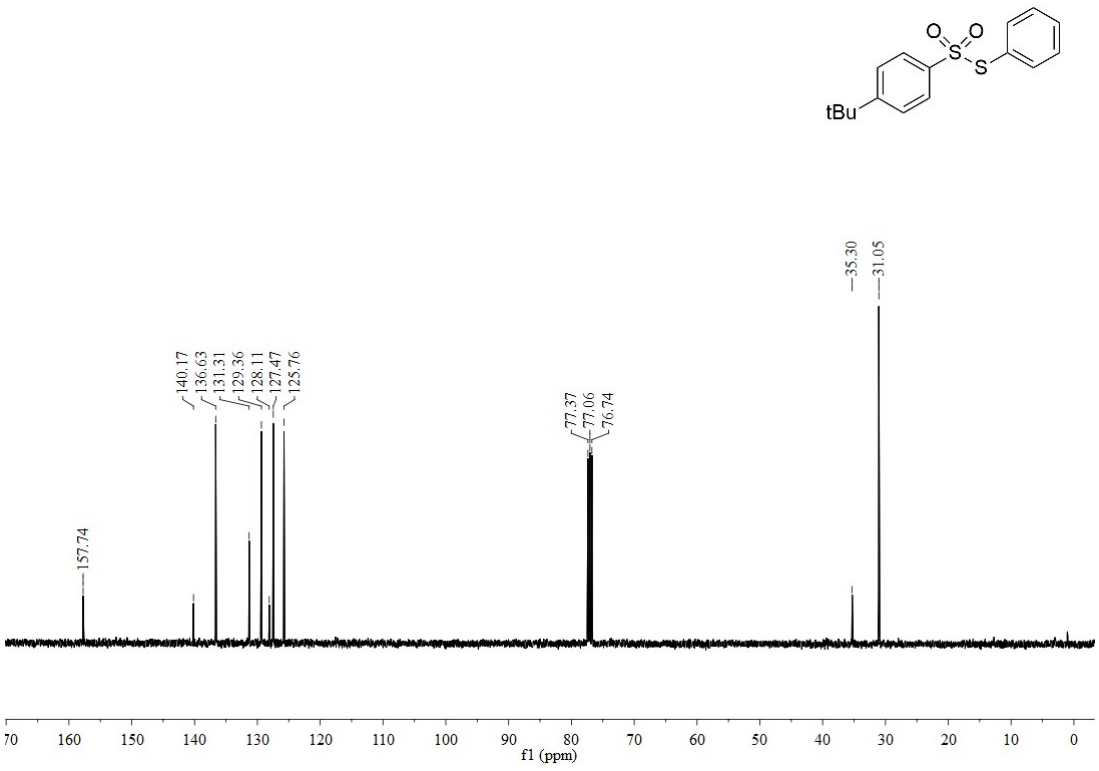




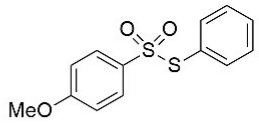


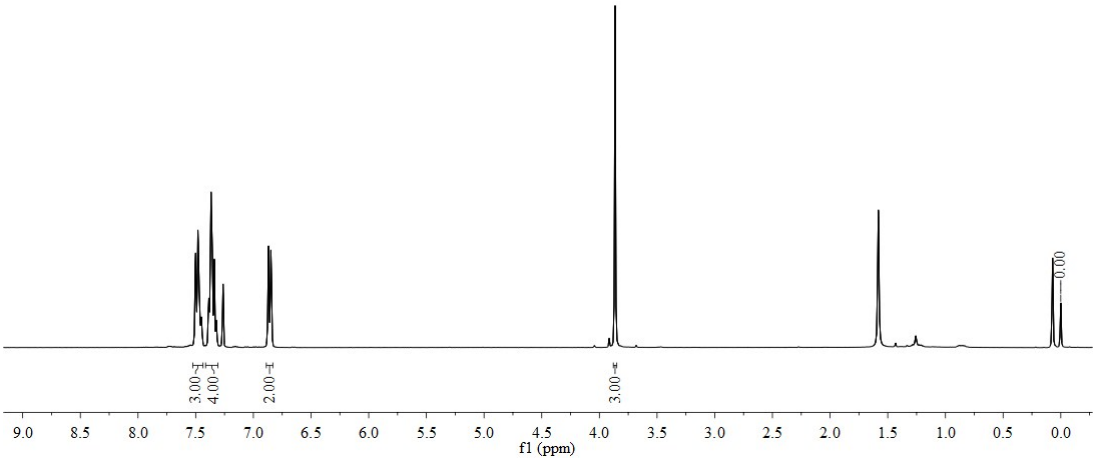
^{1}H, ^{13}C and spectra of 3ca

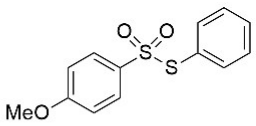


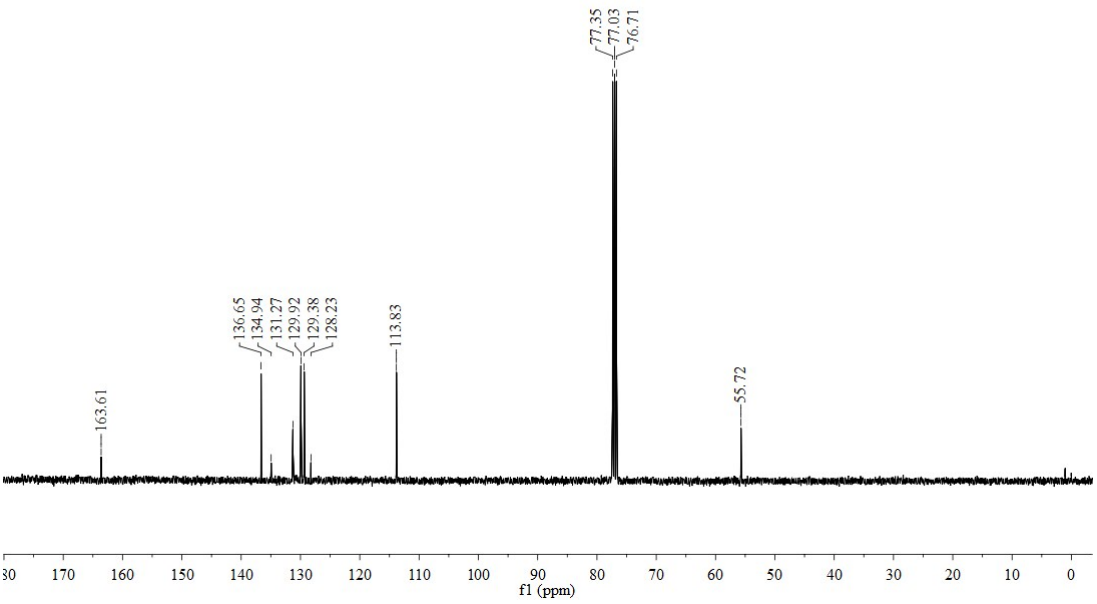


^{1}H, ^{13}C and spectra of 3da

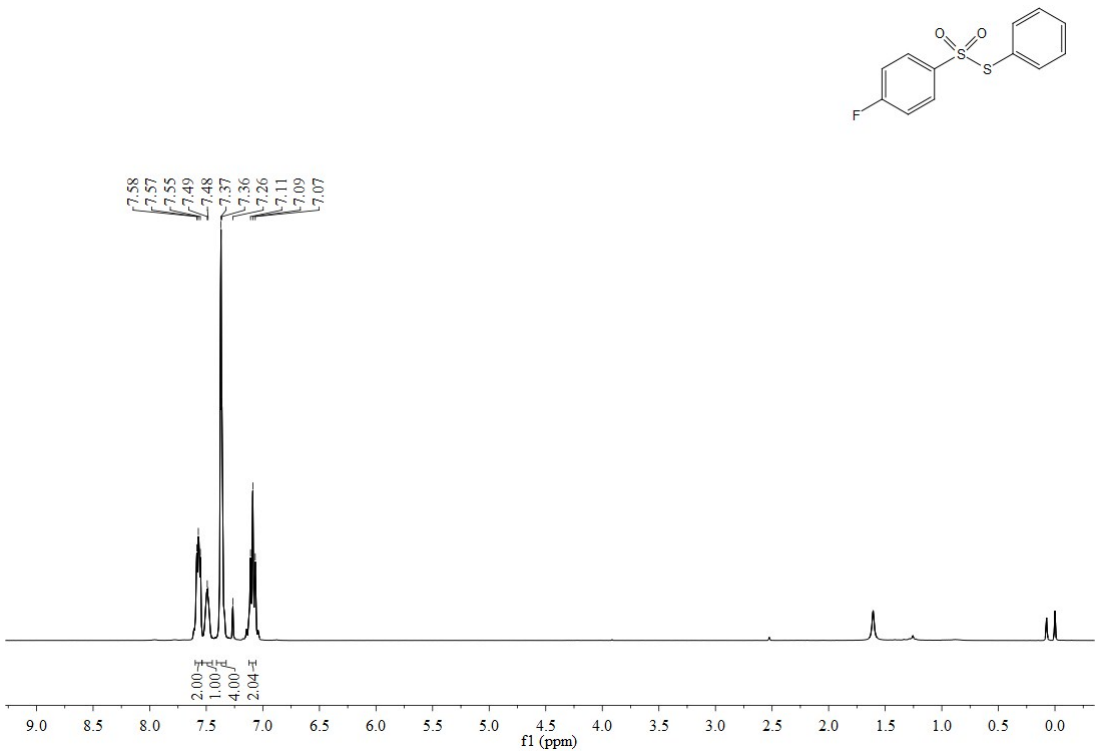


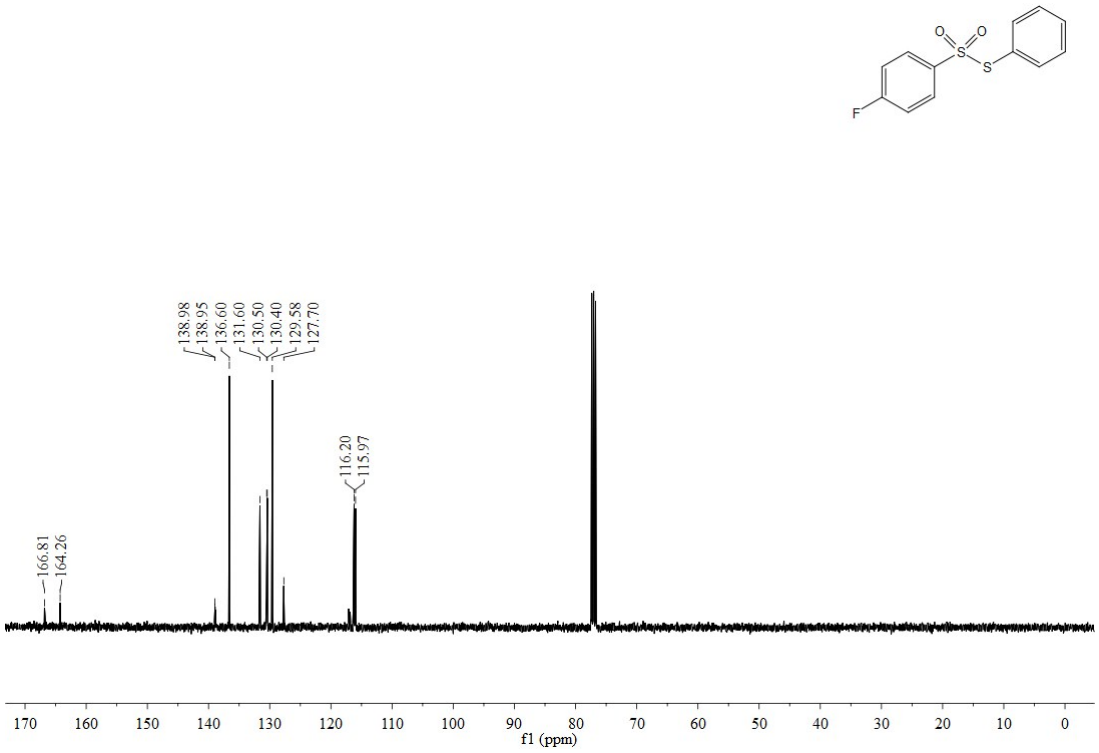




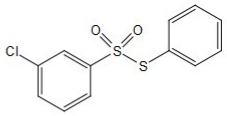


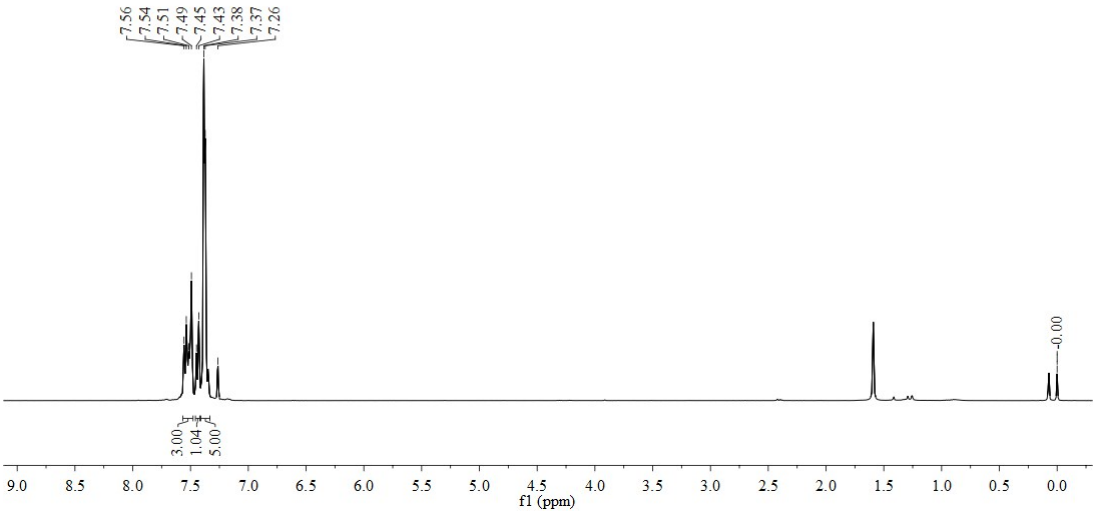
^{1}H, ^{13}C and spectra of 3ea

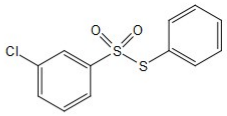


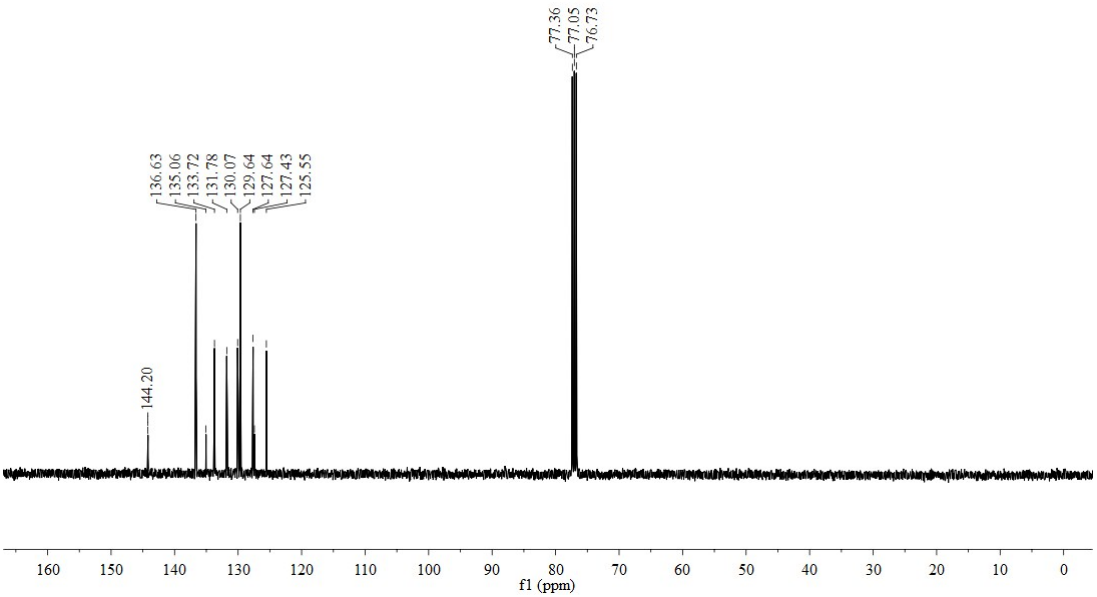


^{1}H, ^{13}C and spectra of 3ga

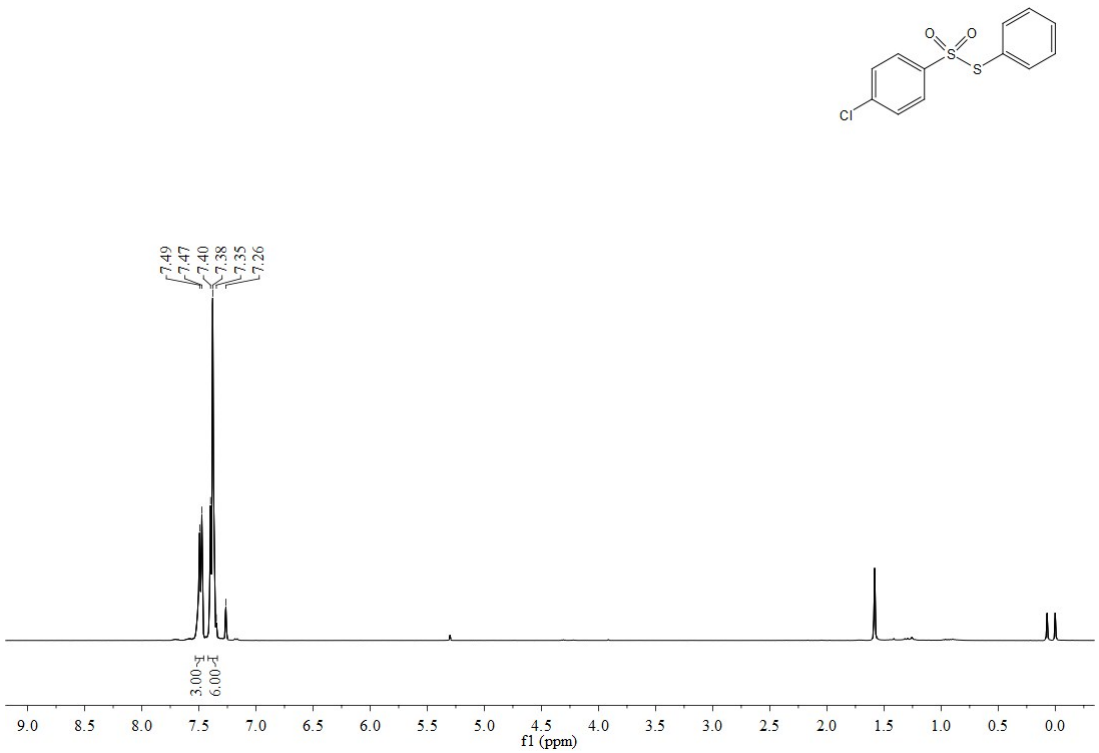


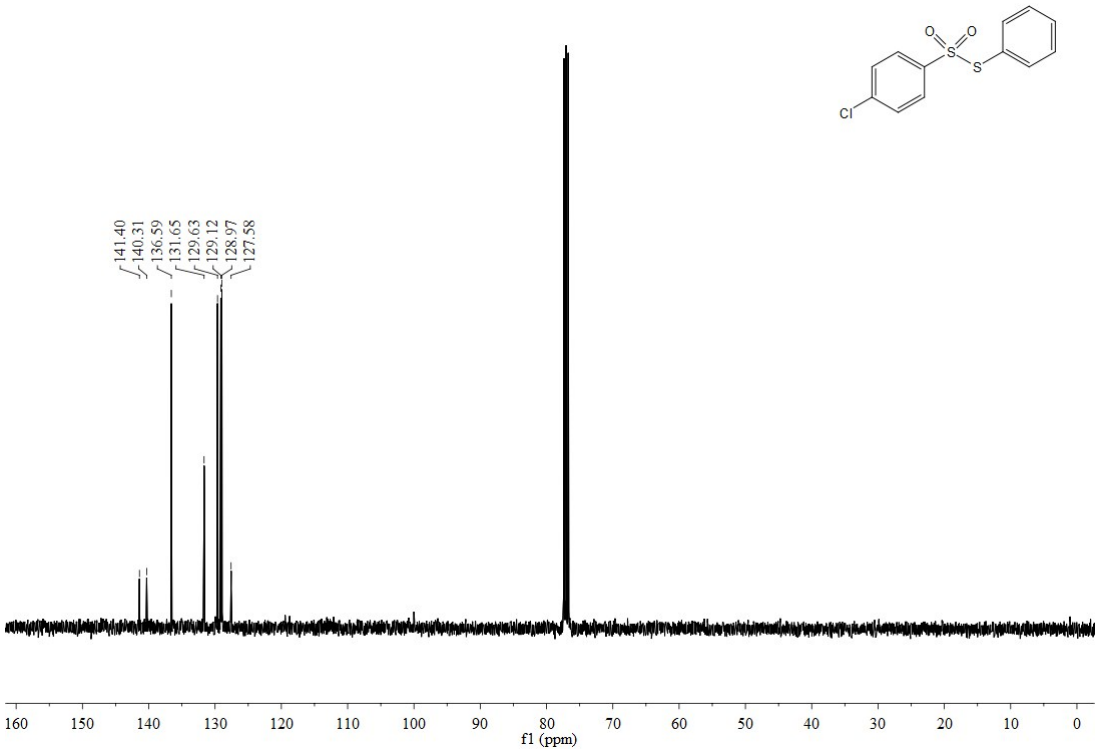




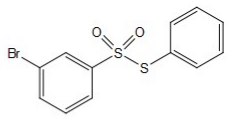


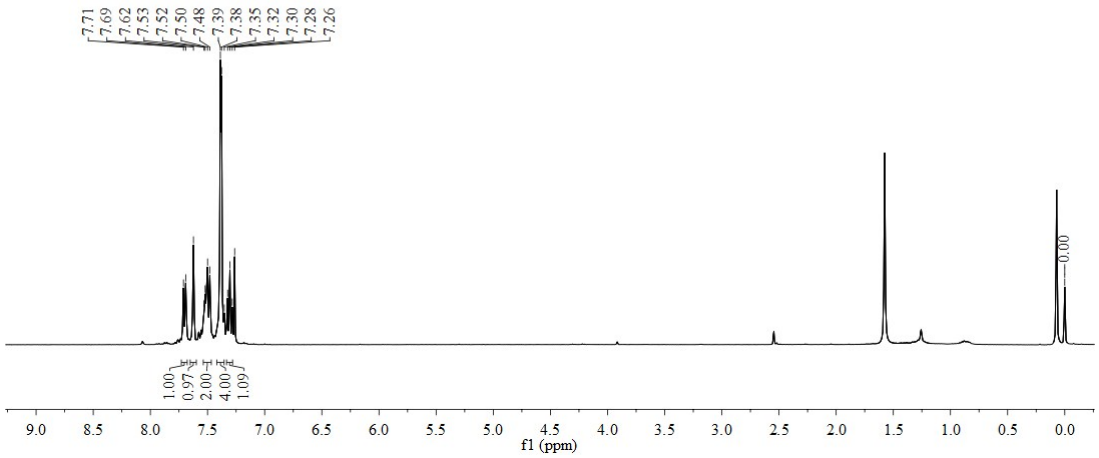
^{1}H, ^{13}C and spectra of 3ha

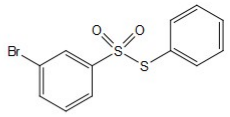




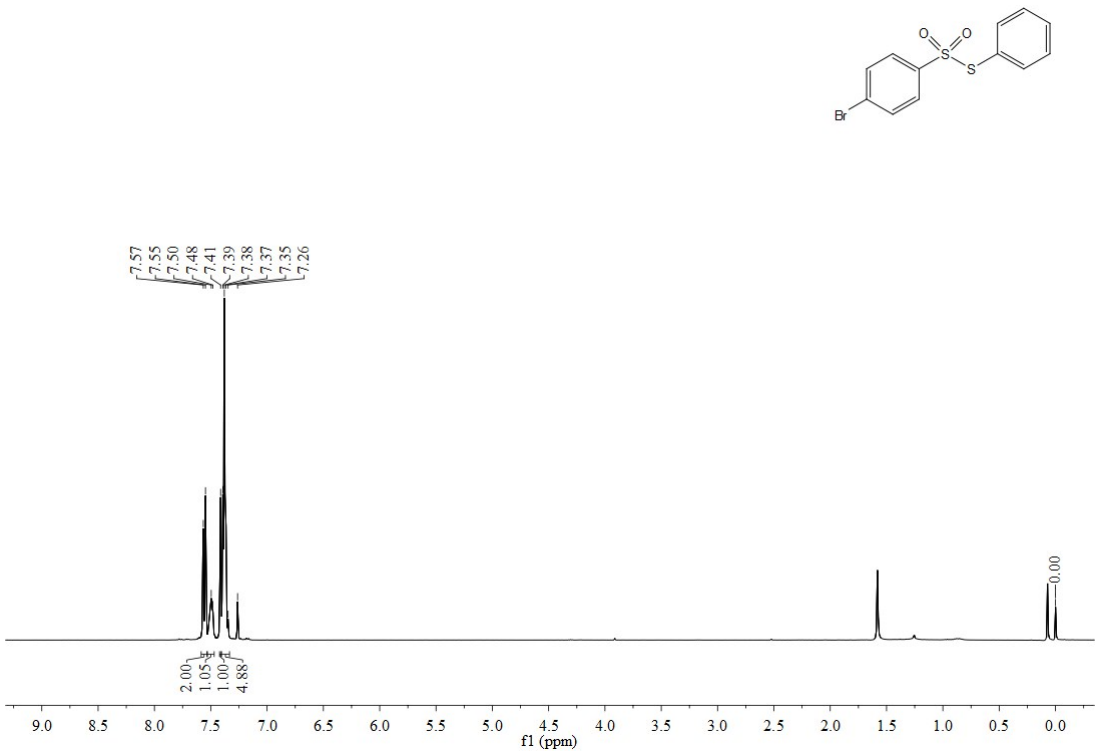
^{1}H, ^{13}C and spectra of 3ja

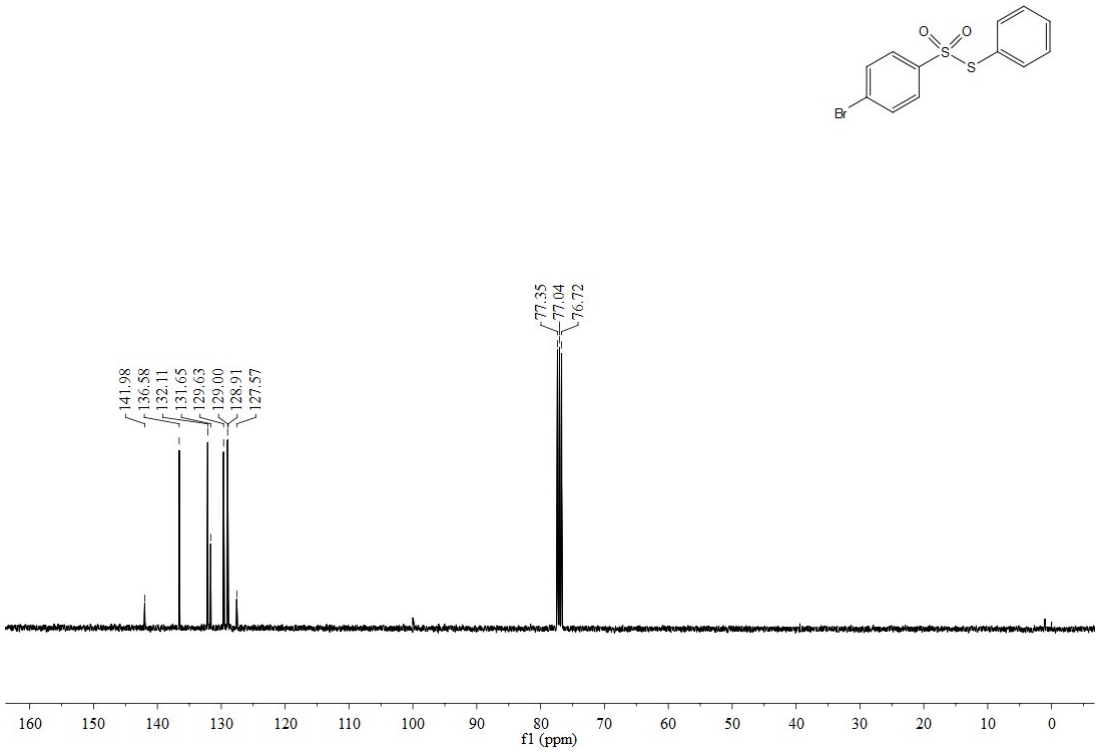




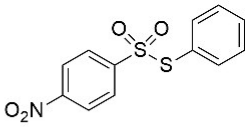


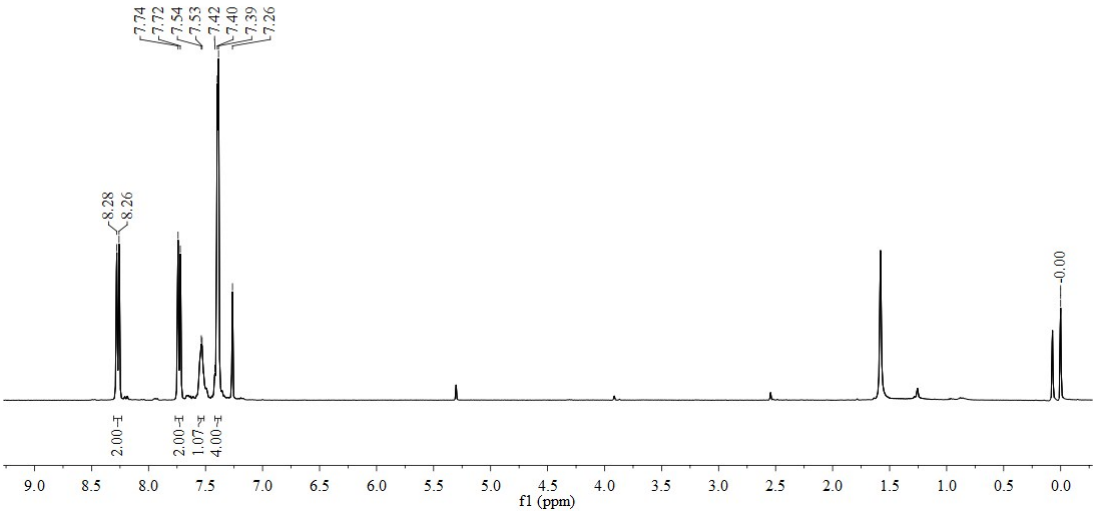
^{1}H, ^{13}C and spectra of 3ka

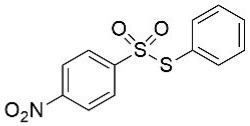


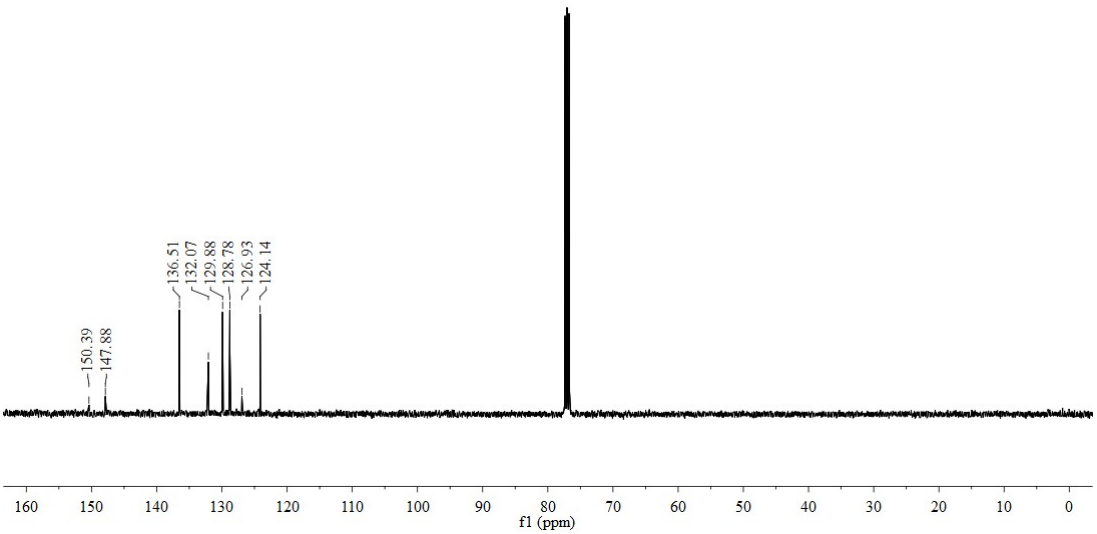


^{1}H, ^{13}C and spectra of 3la

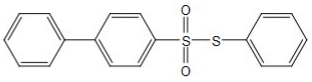


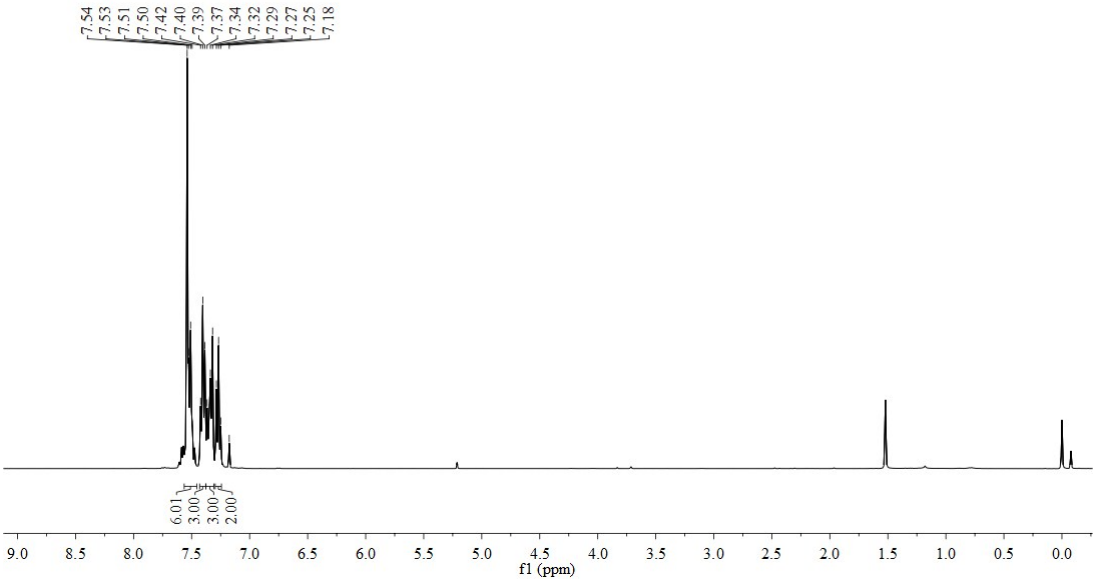


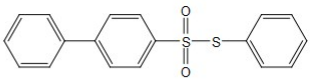


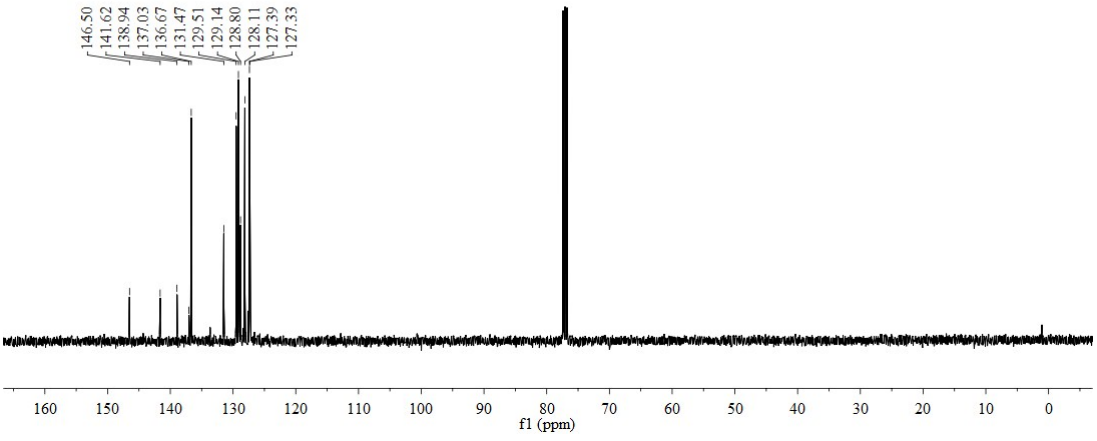


^{1}H, ^{13}C and spectra of 3ma

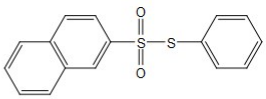


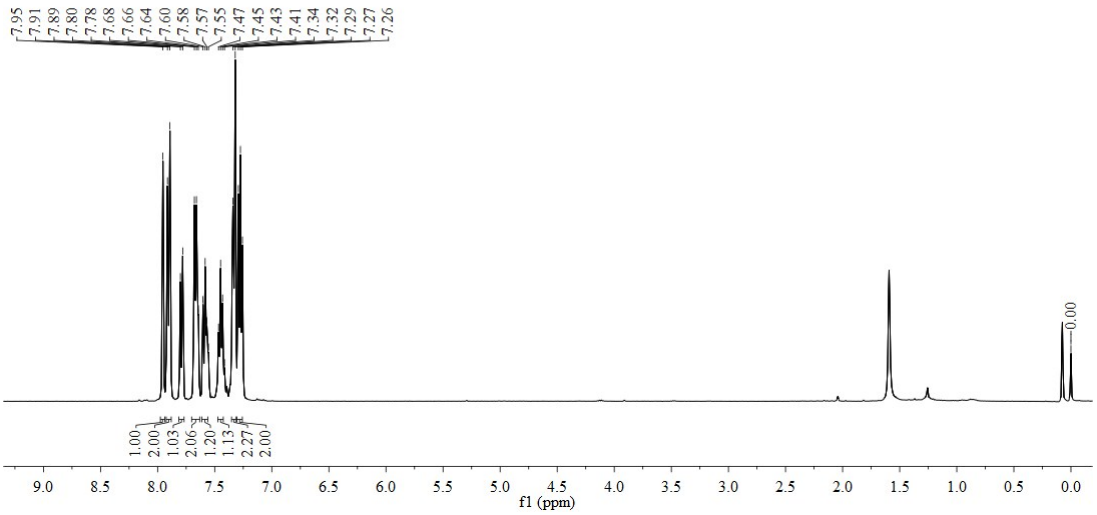


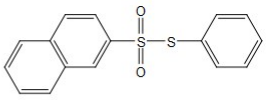


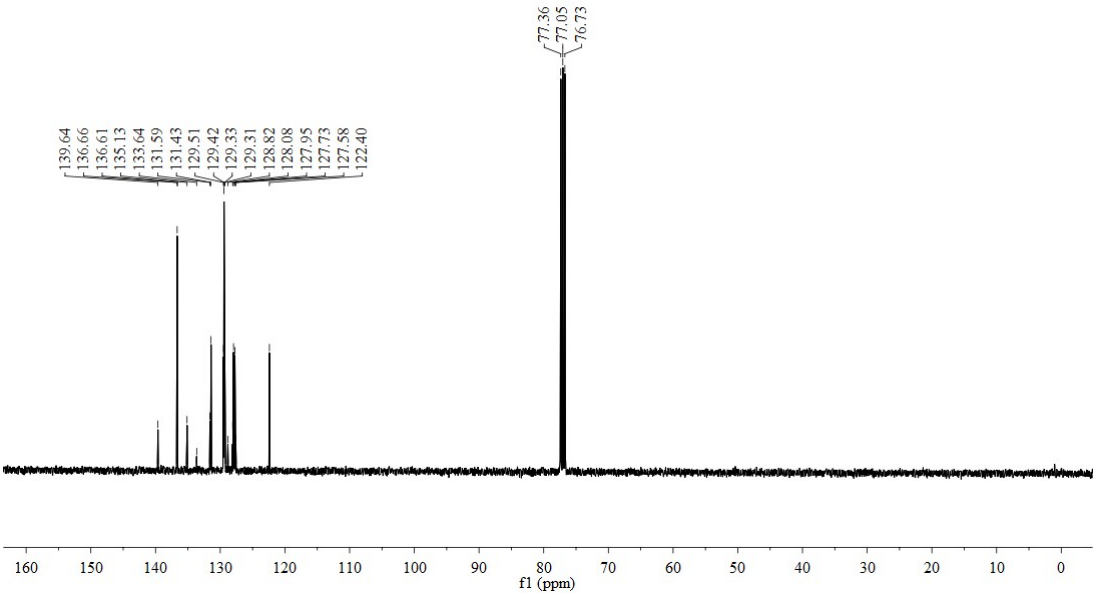


^{1}H, ^{13}C and spectra of 3na

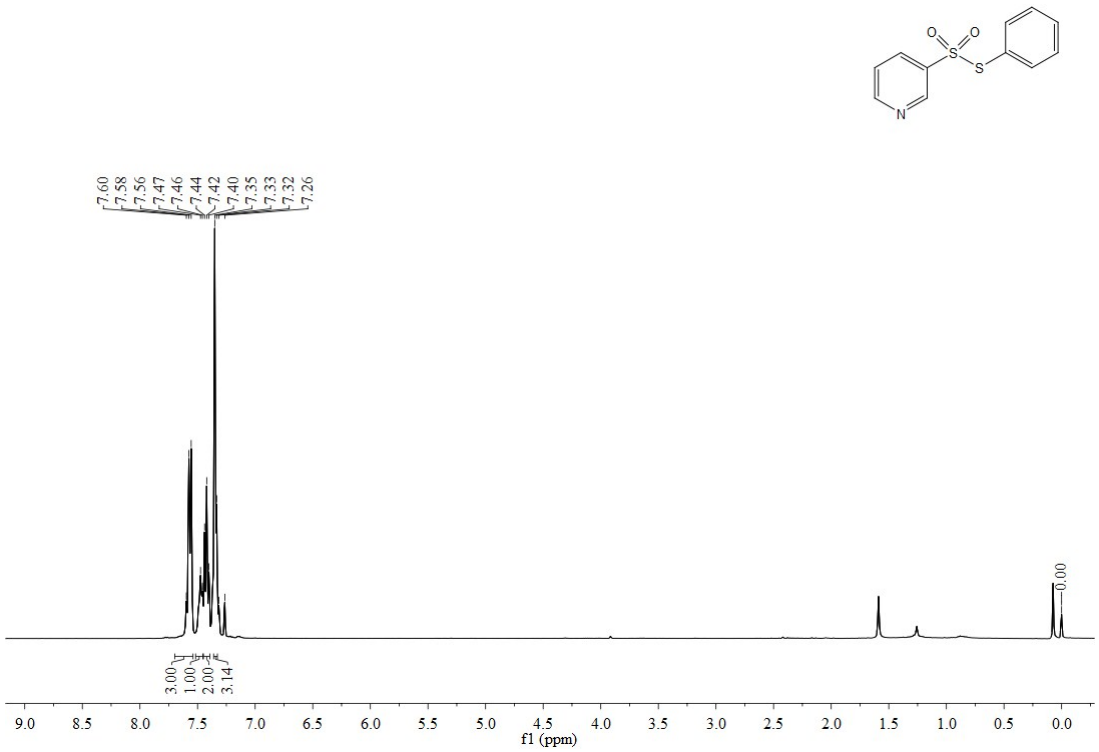


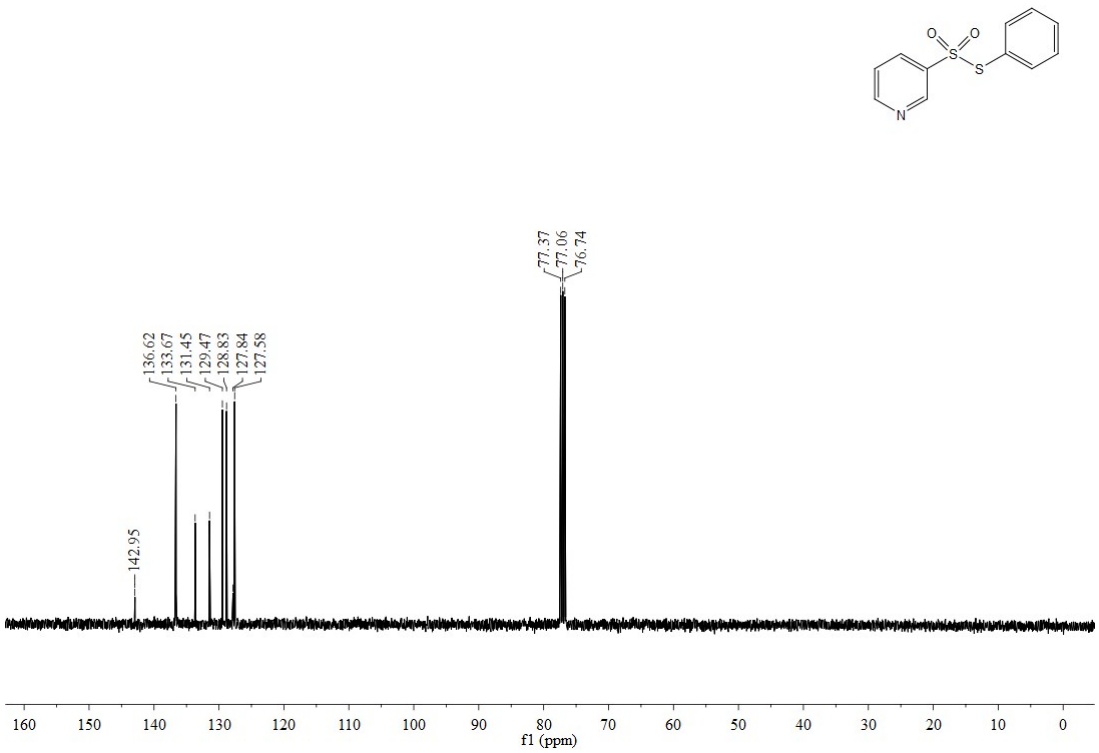




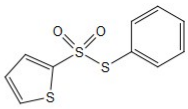


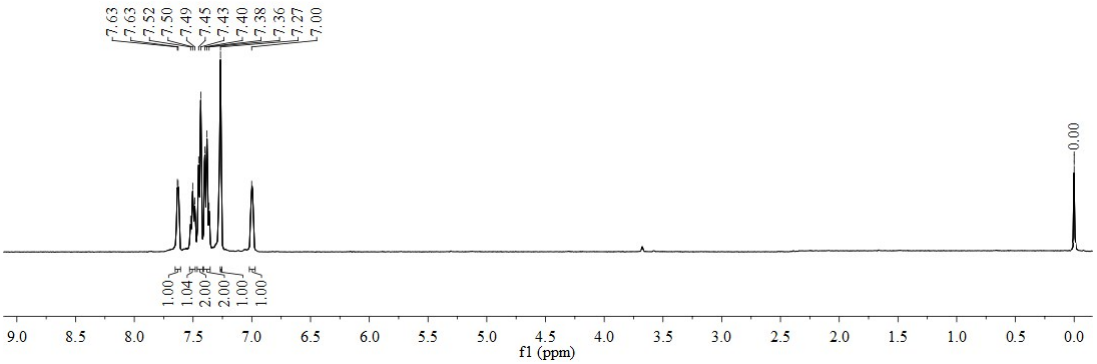
^{1}H, ^{13}C and spectra of 3oa

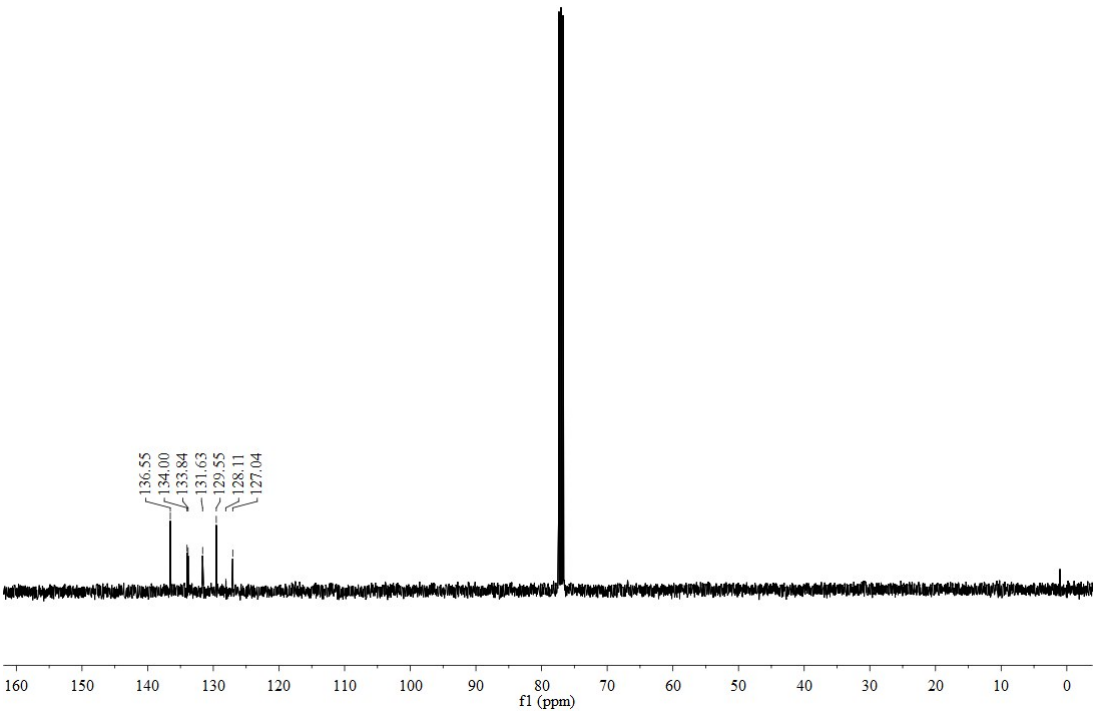




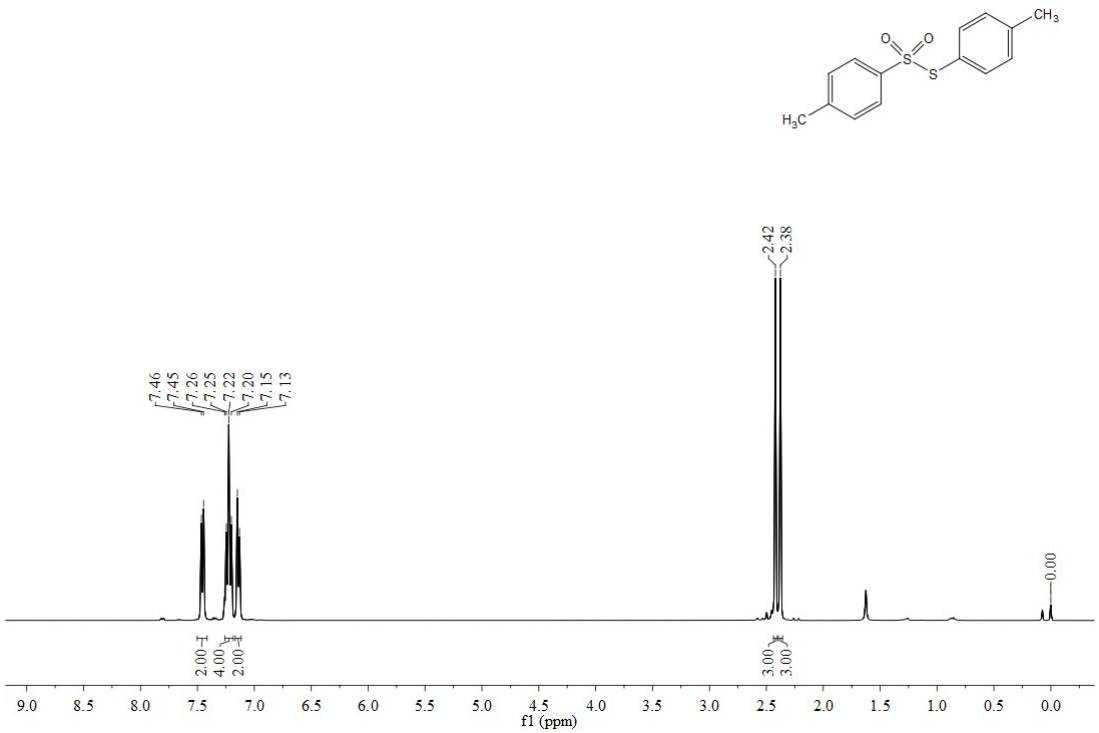
^{1}H, ^{13}C and spectra of 3pa

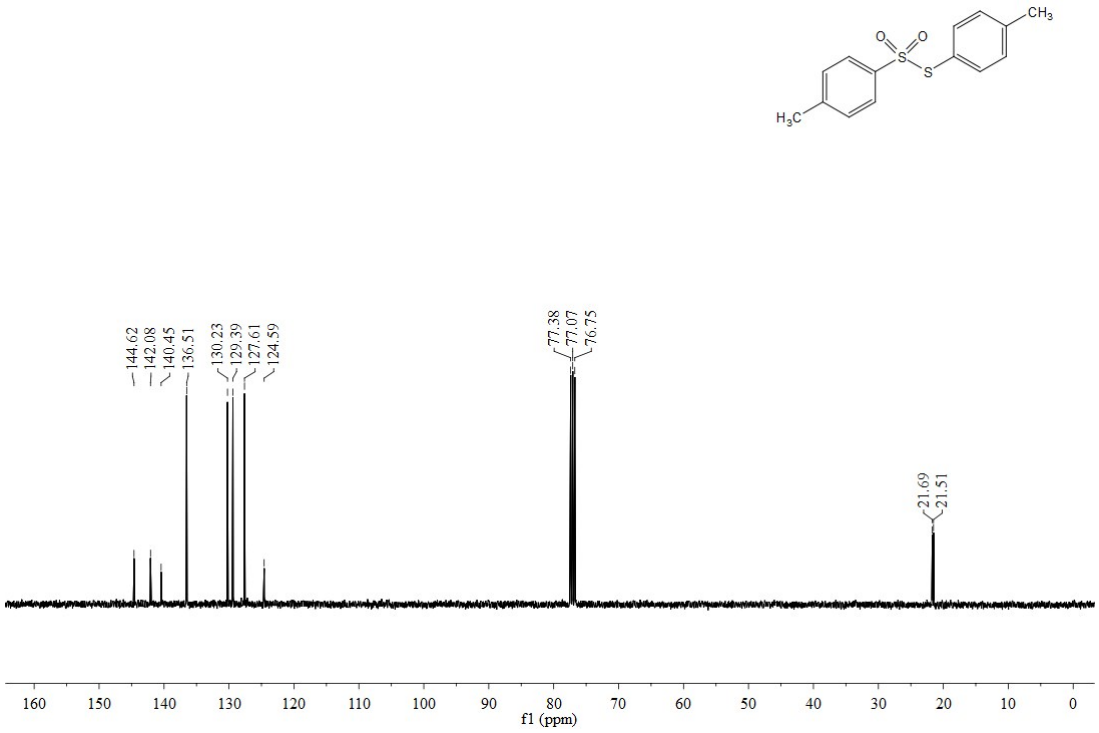




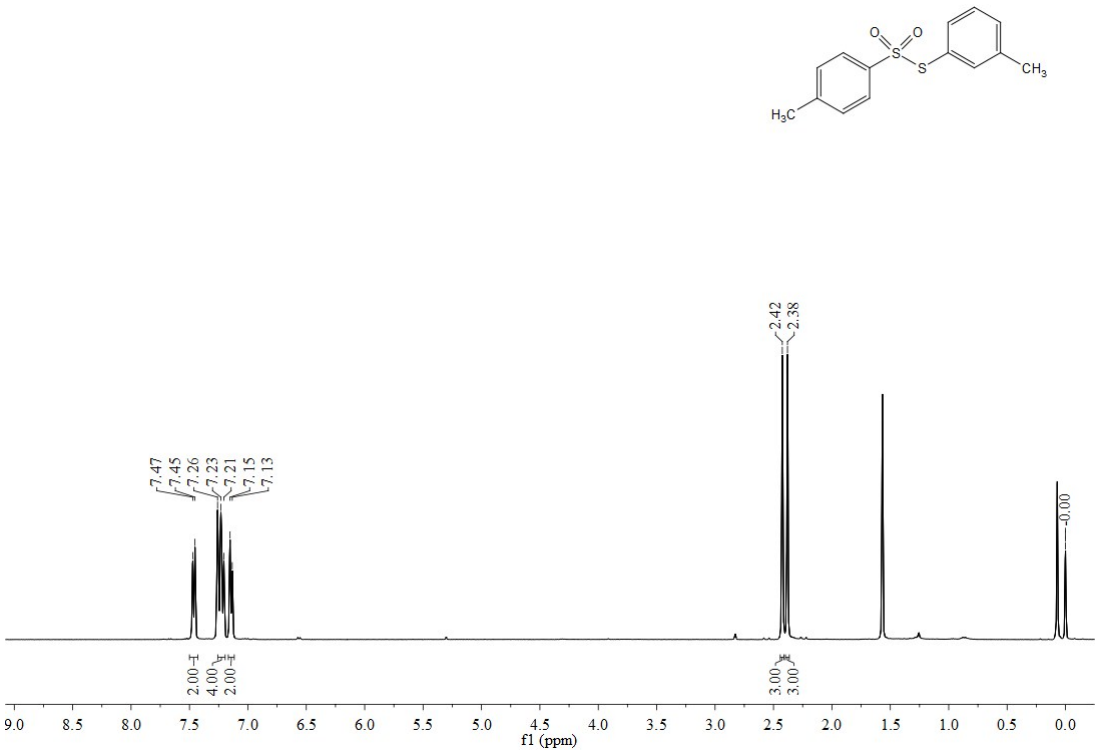


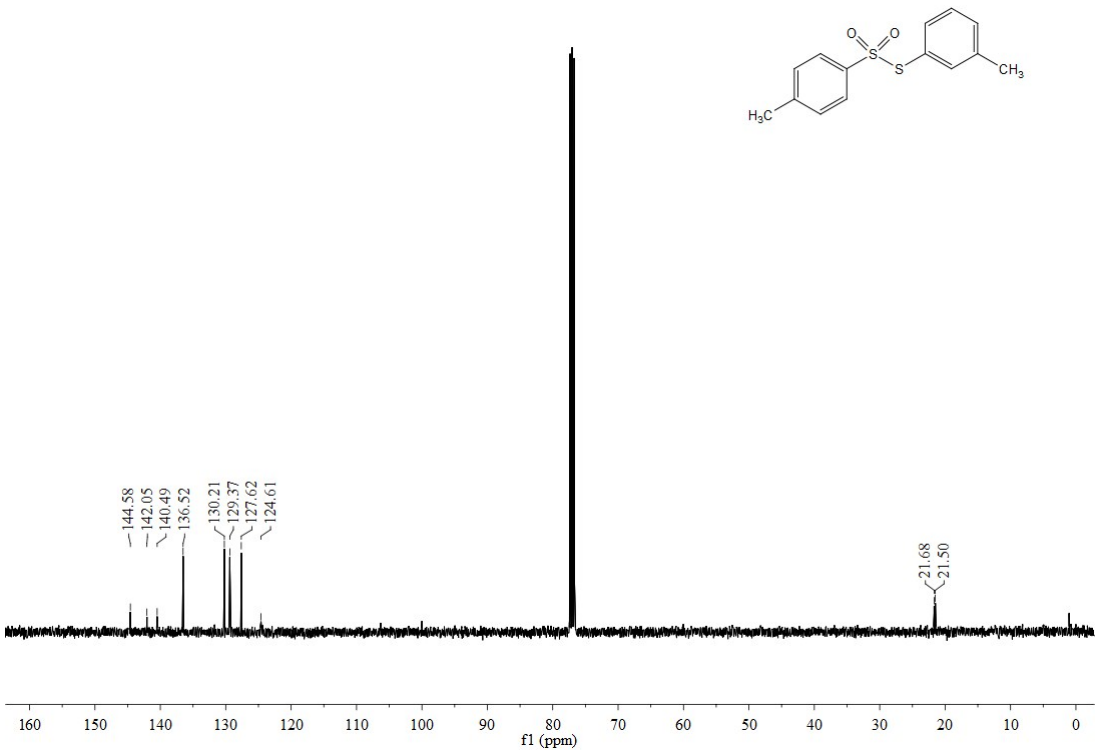
^{1}H, ^{13}C and spectra of 3ab



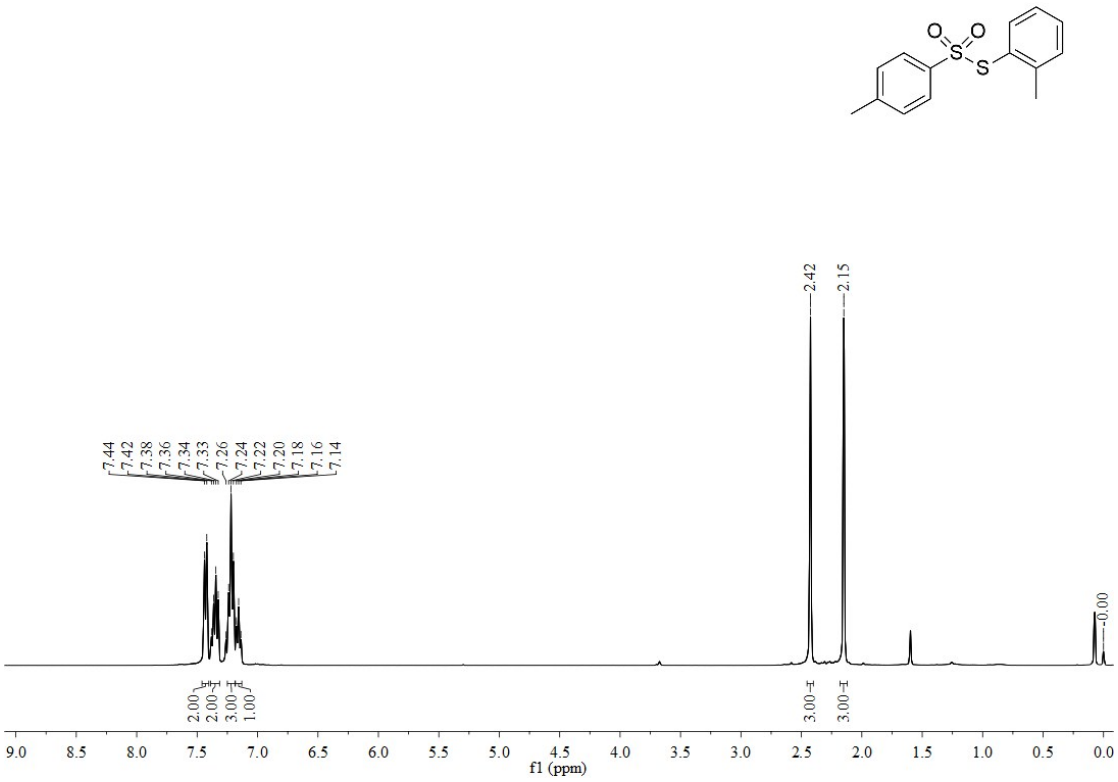


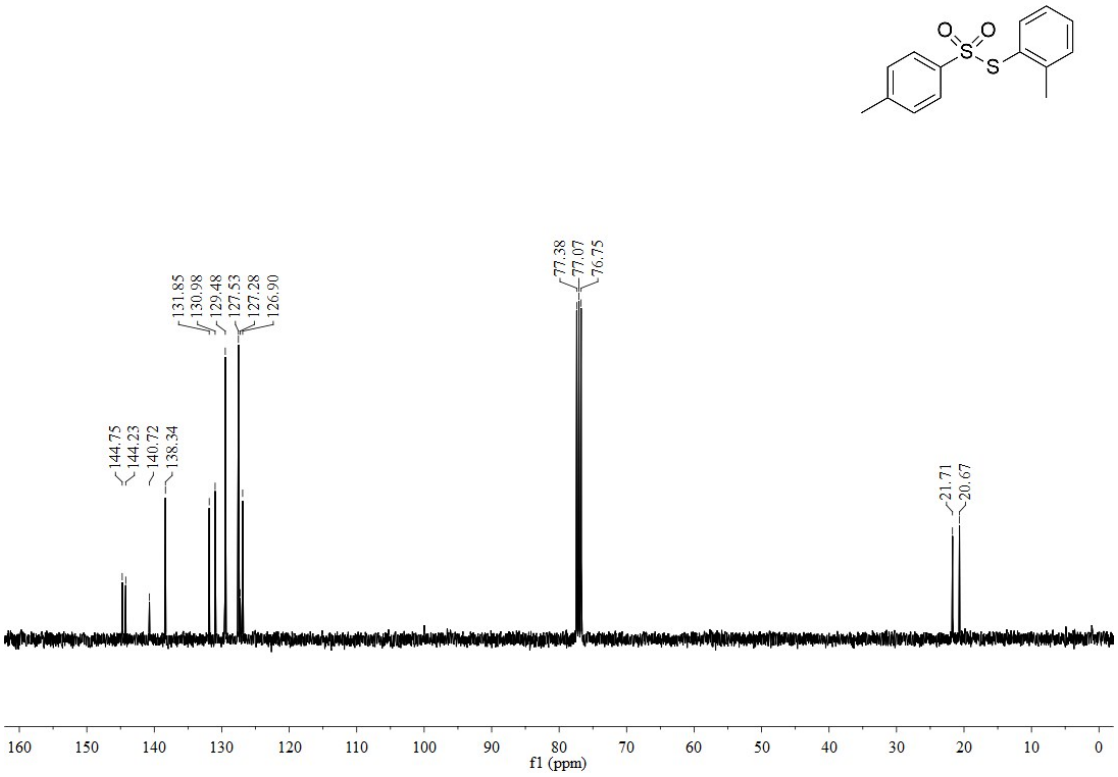
^{1}H, ^{13}C and spectra of 3ac



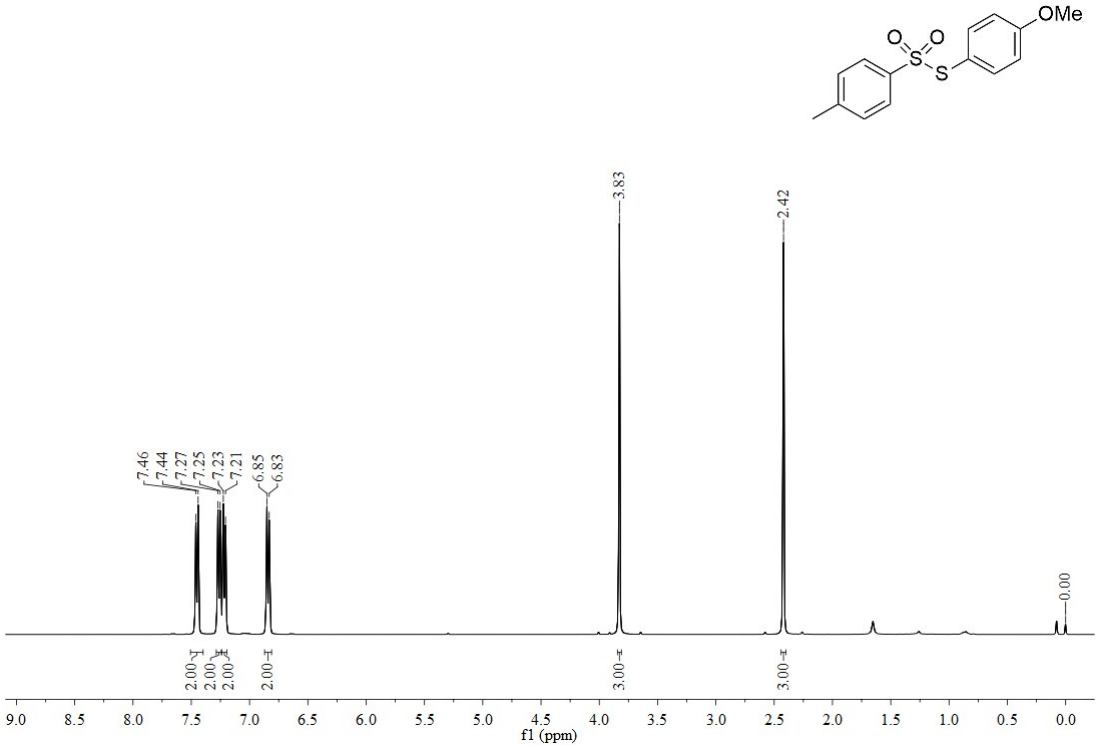


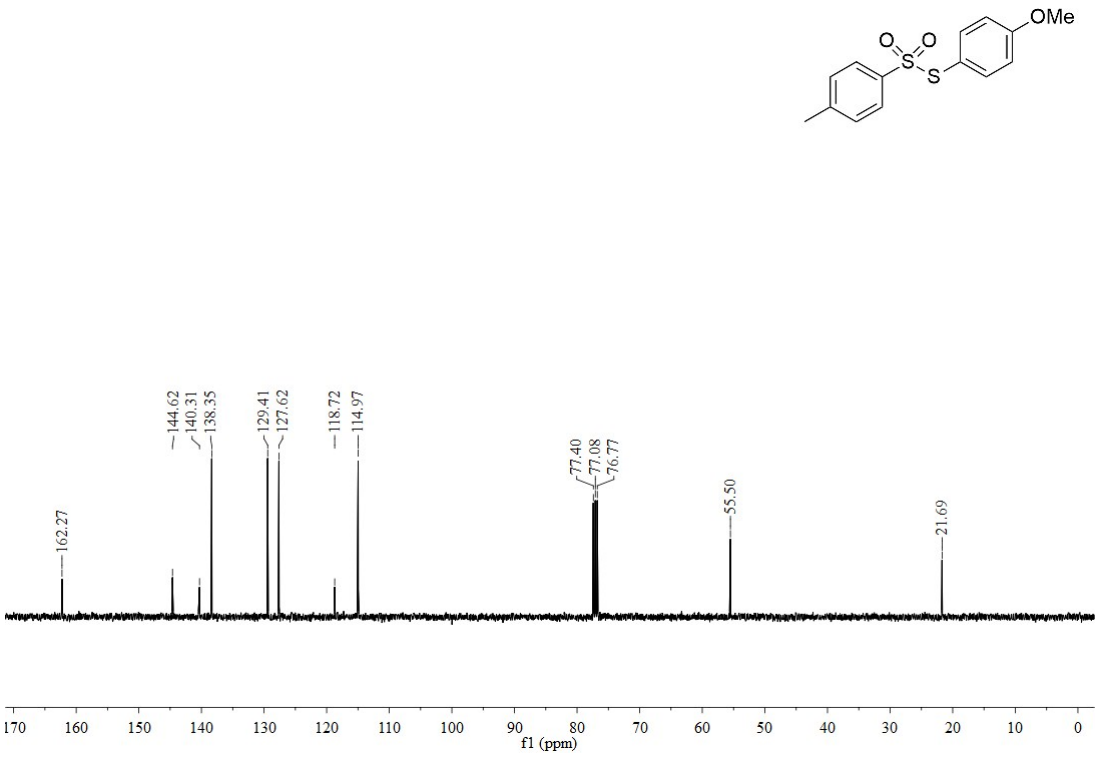
^{1}H, ^{13}C and spectra of 3ad



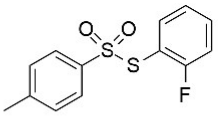


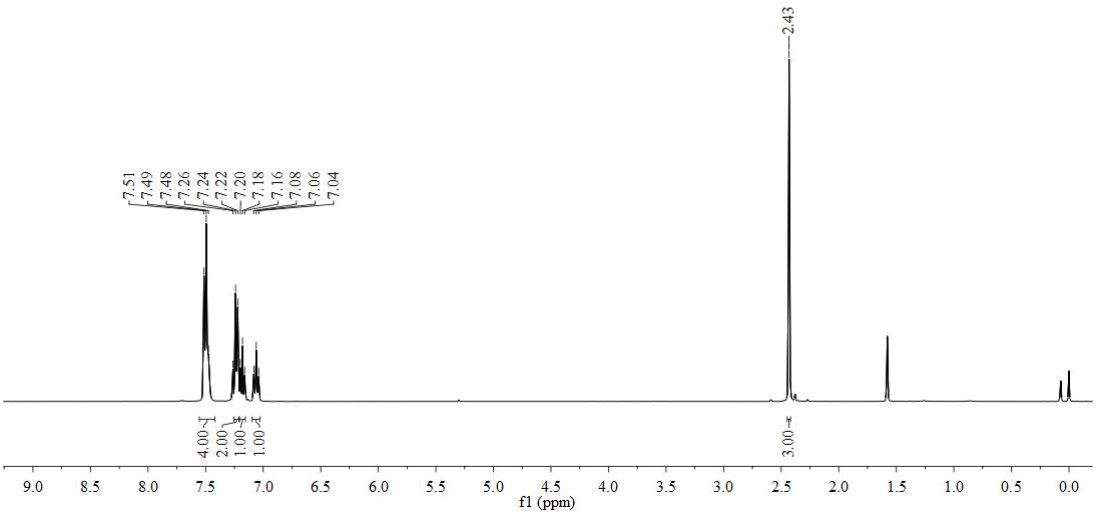
^{1}H, ^{13}C and spectra of 3ae

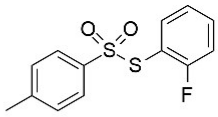


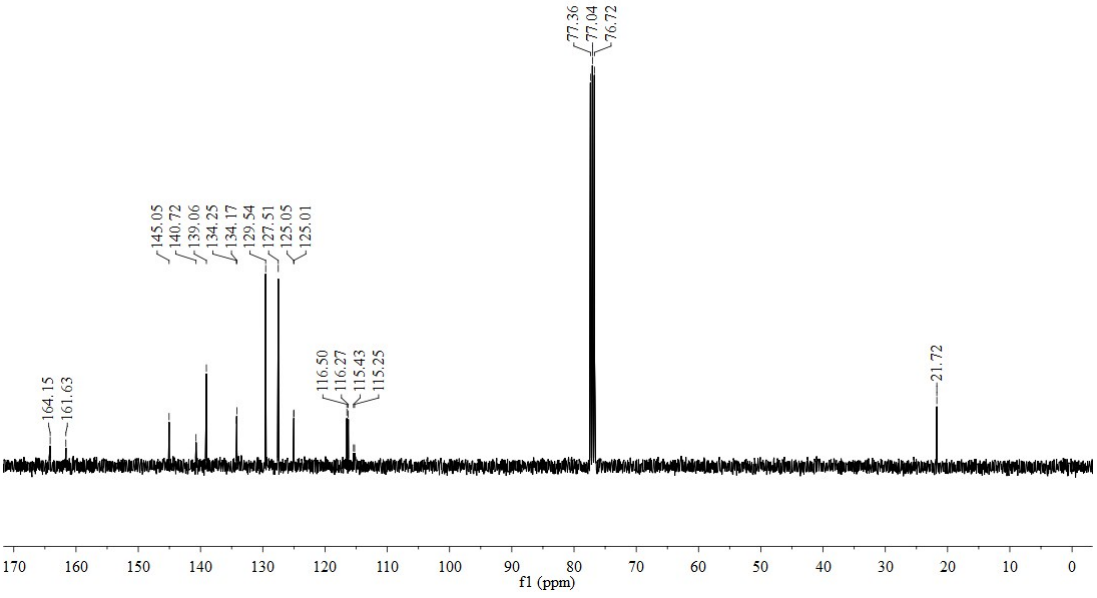


^{1}H, ^{13}C and spectra of 3af

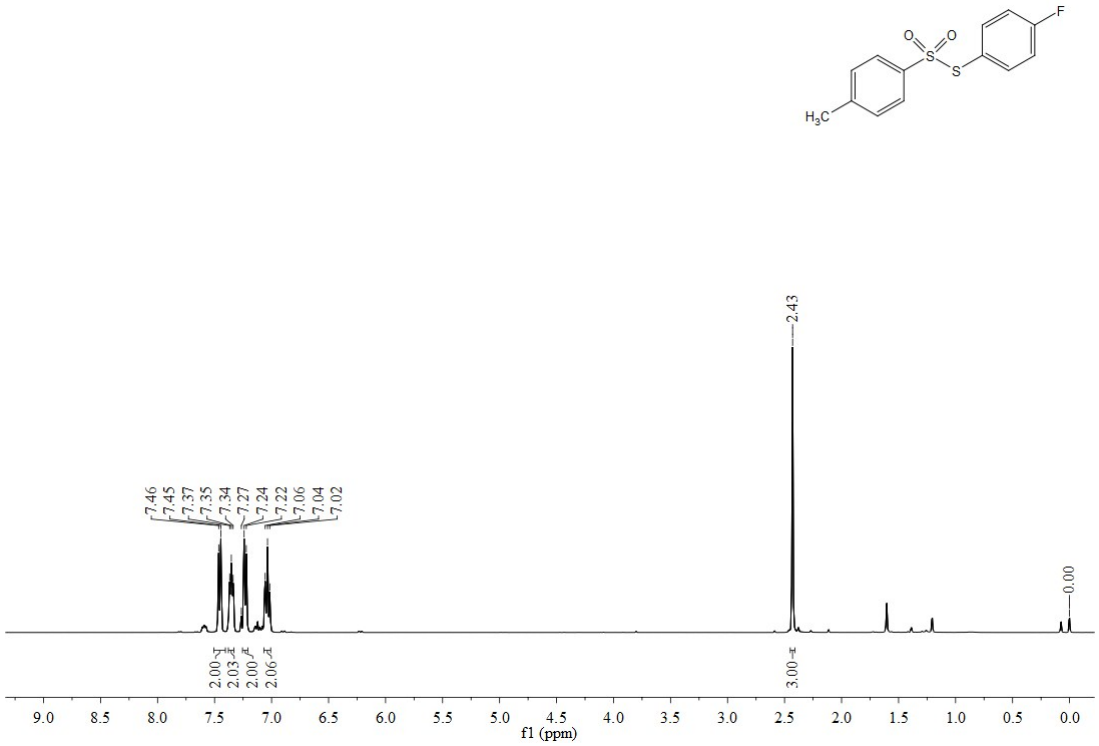


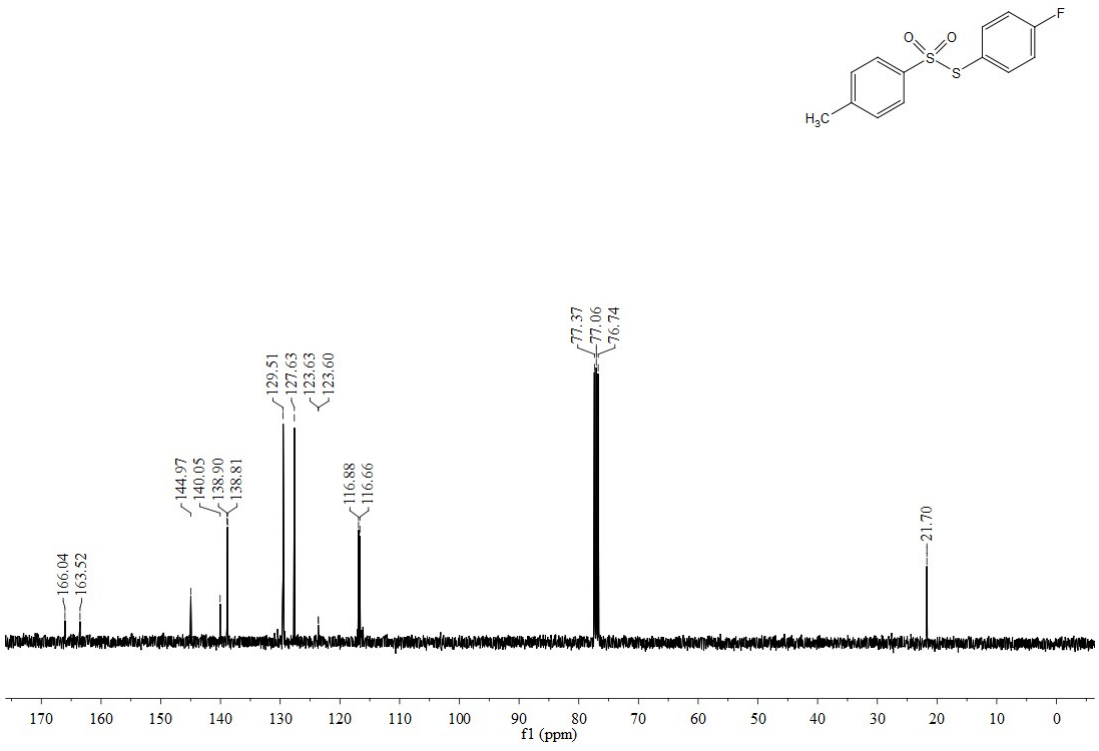




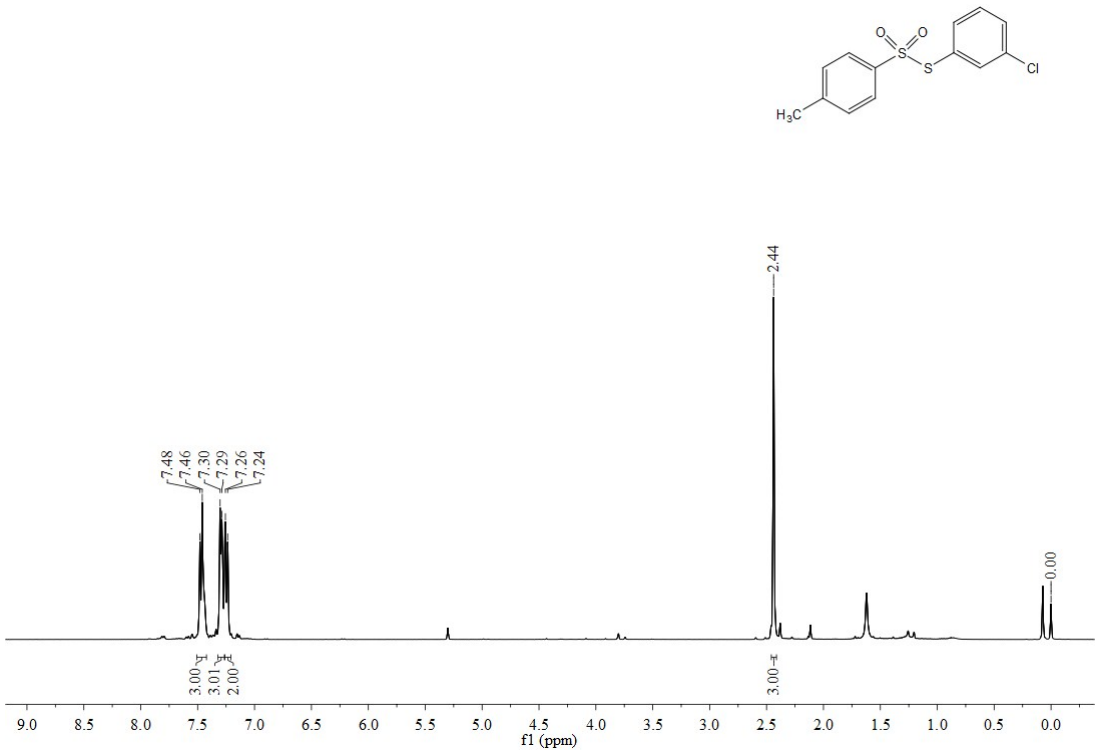


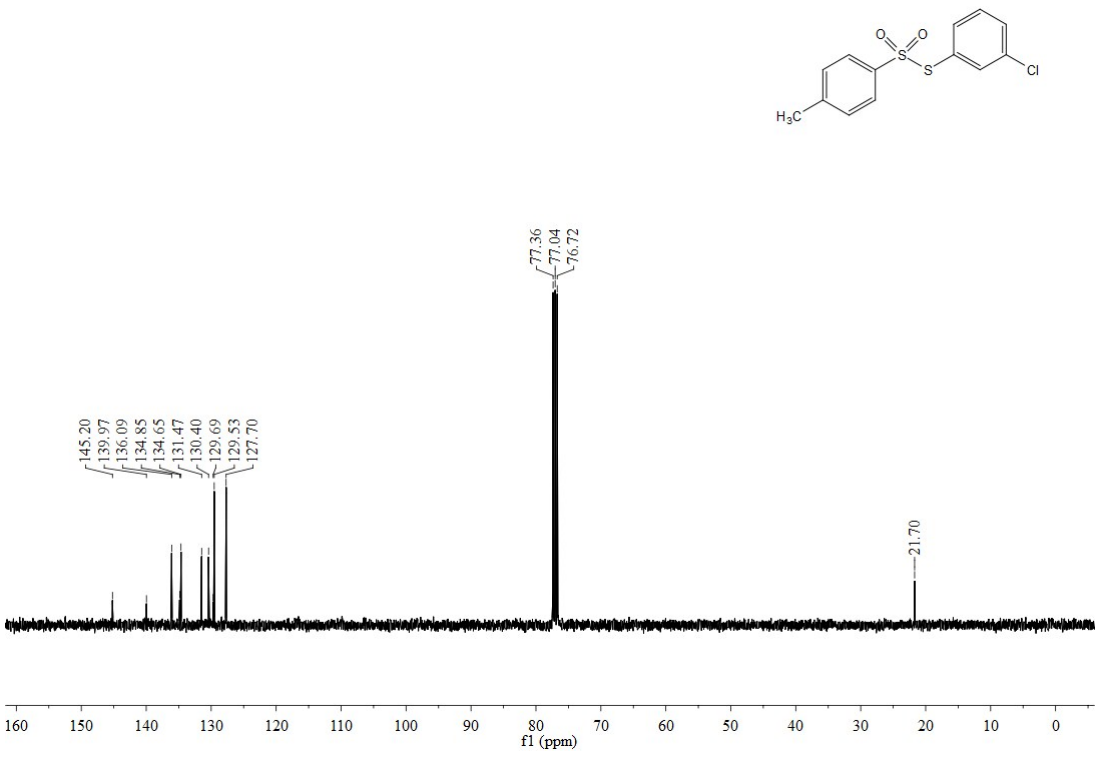
^{1}H, ^{13}C and spectra of 3ag



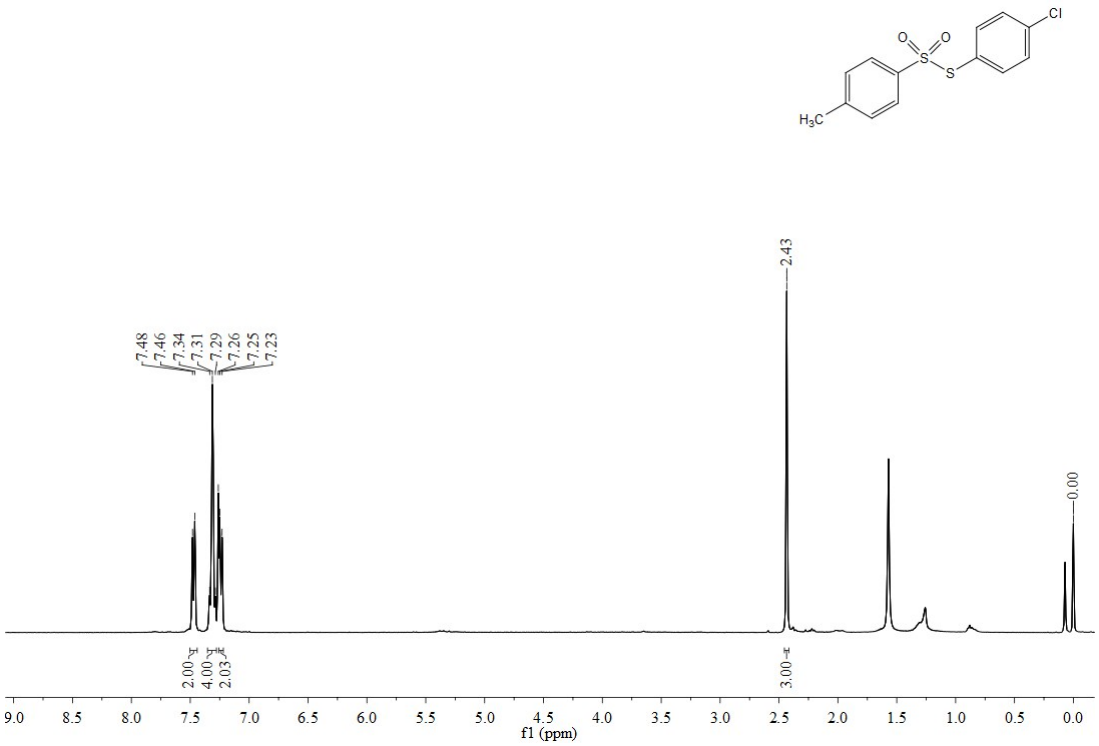


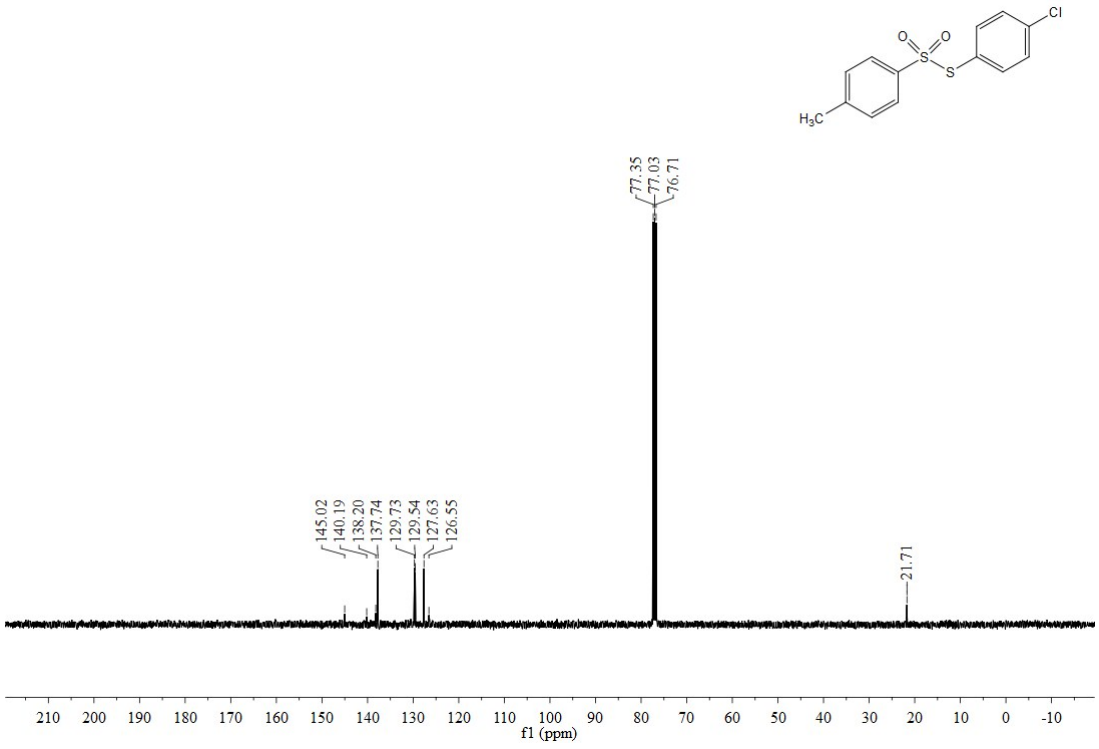
^{1}H, ^{13}C and spectra of 3ai



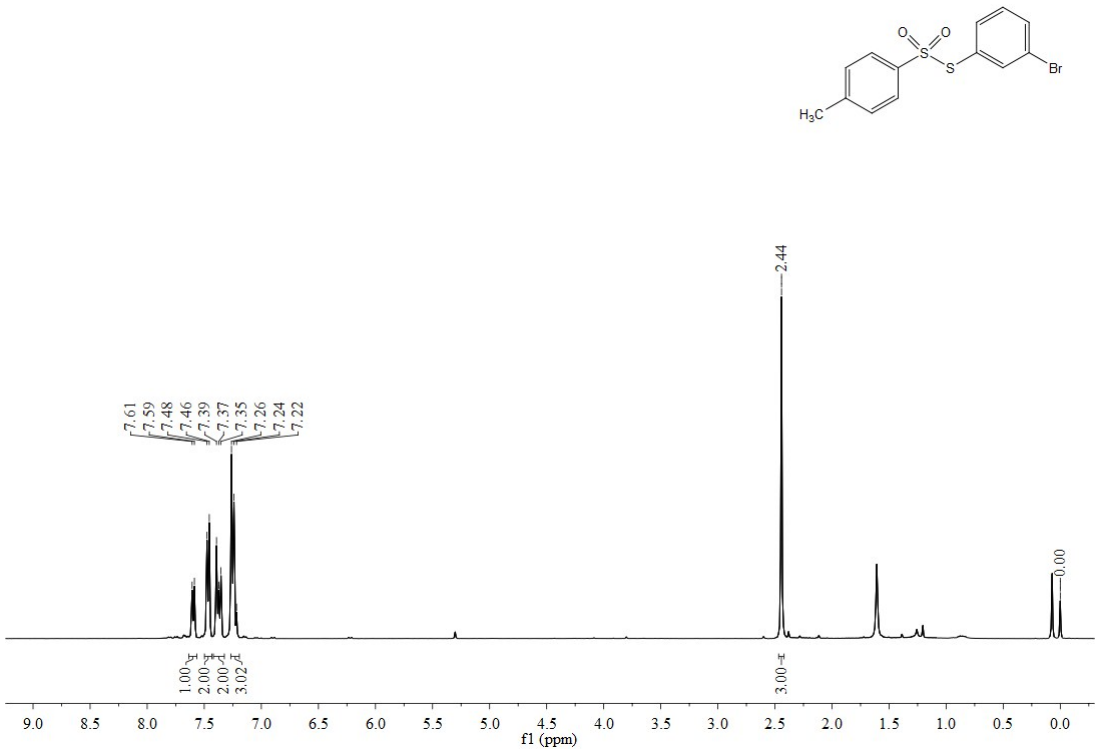


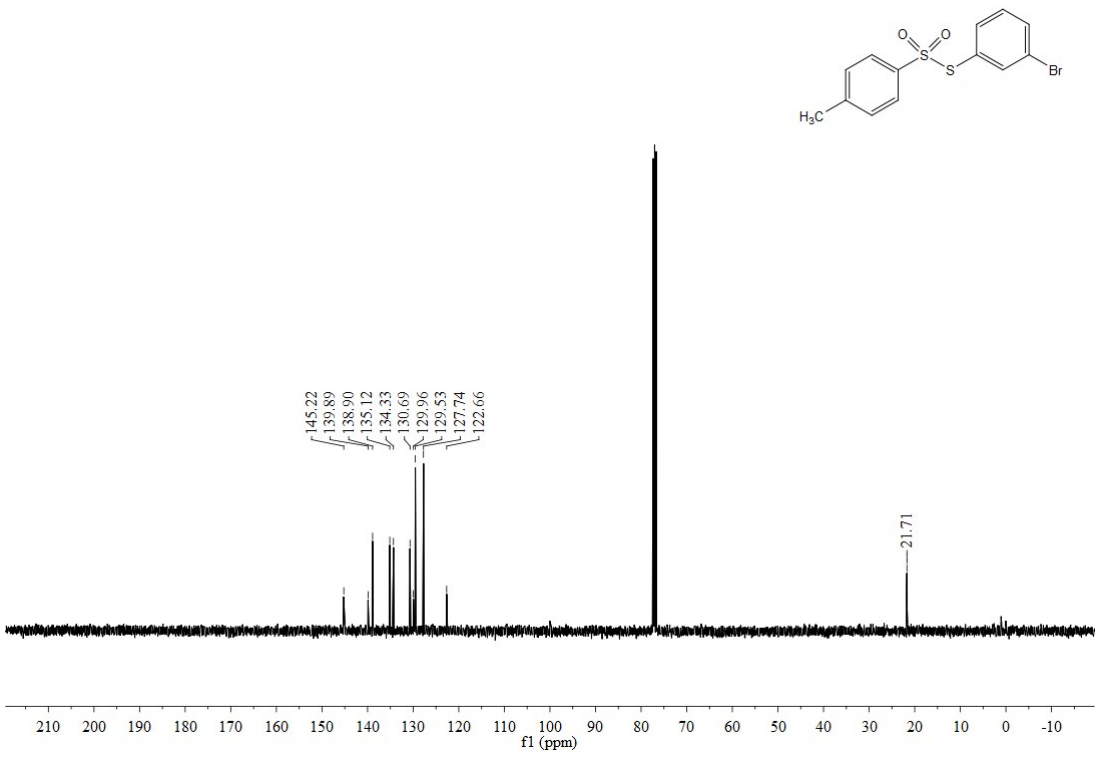
^{1}H, ^{13}C and spectra of 3aj



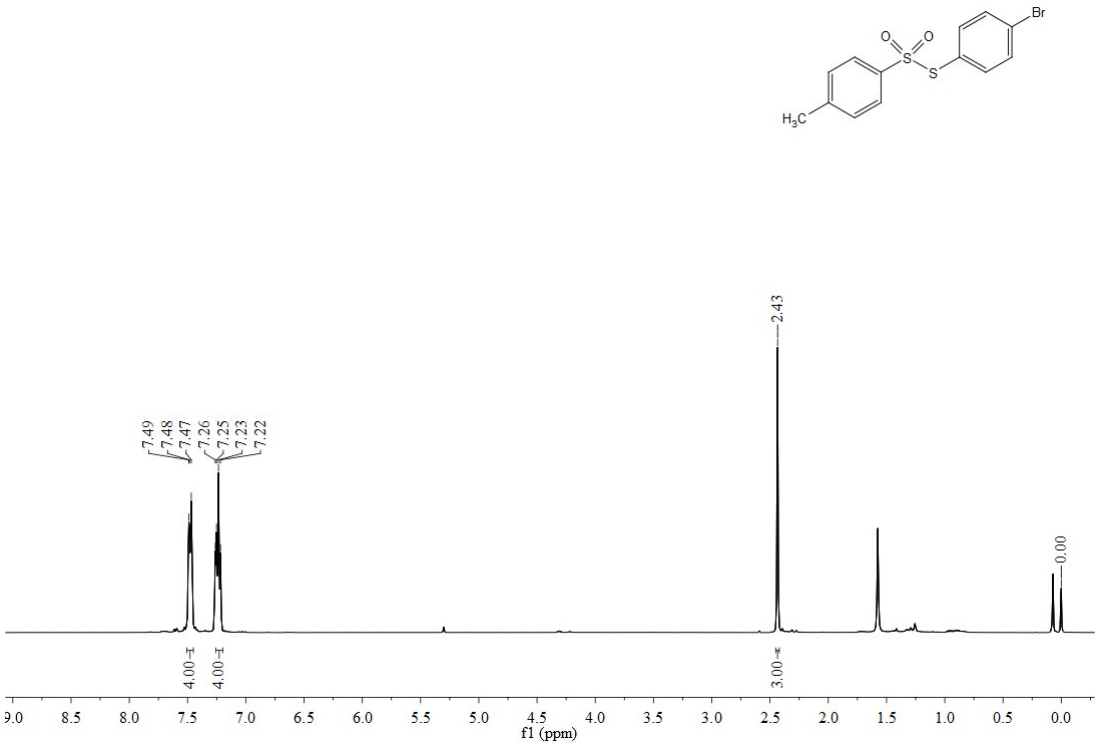


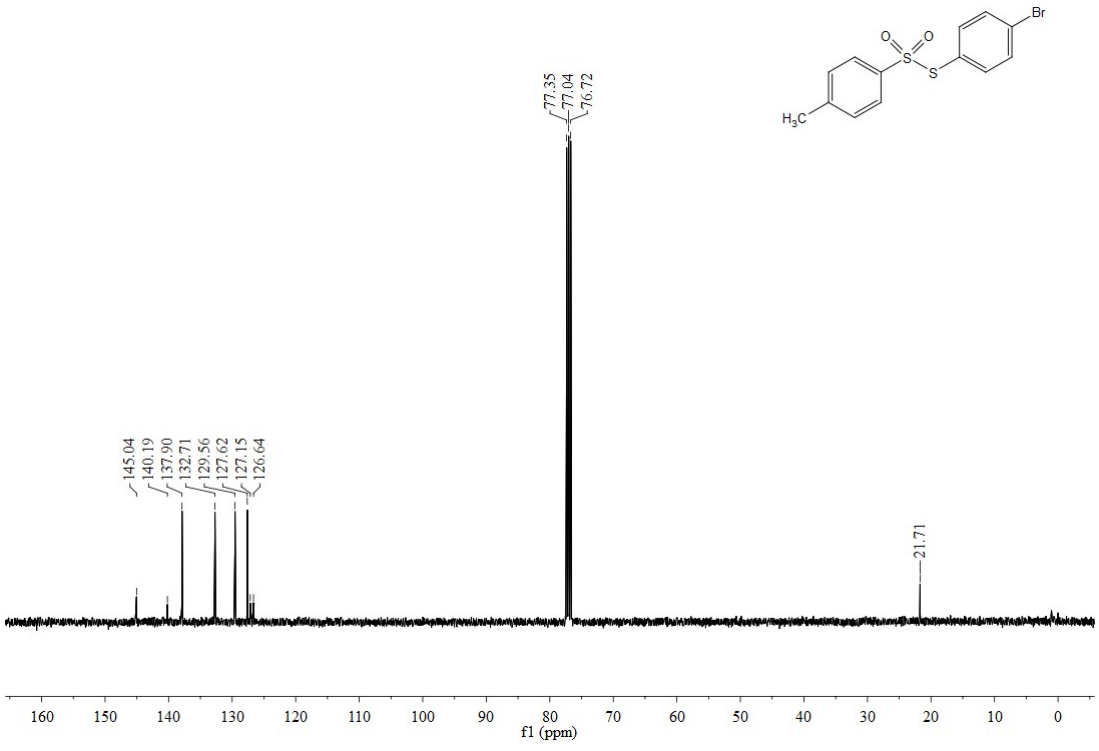
^{1}H, ^{13}C and spectra of 3ak



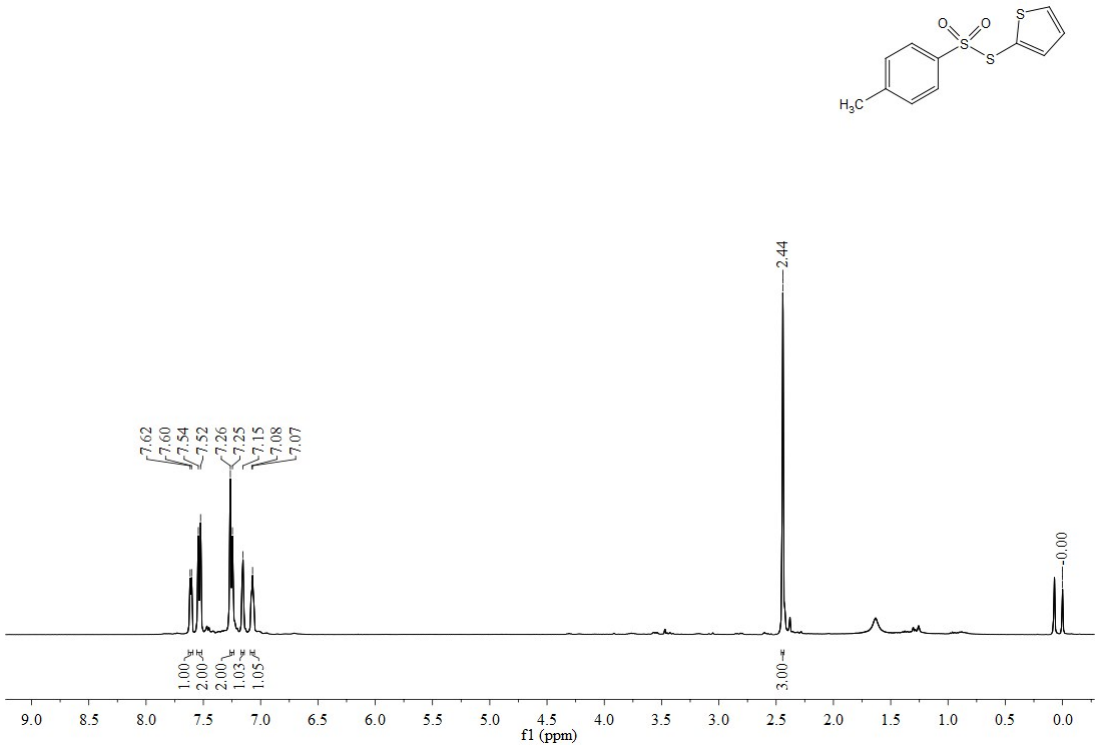


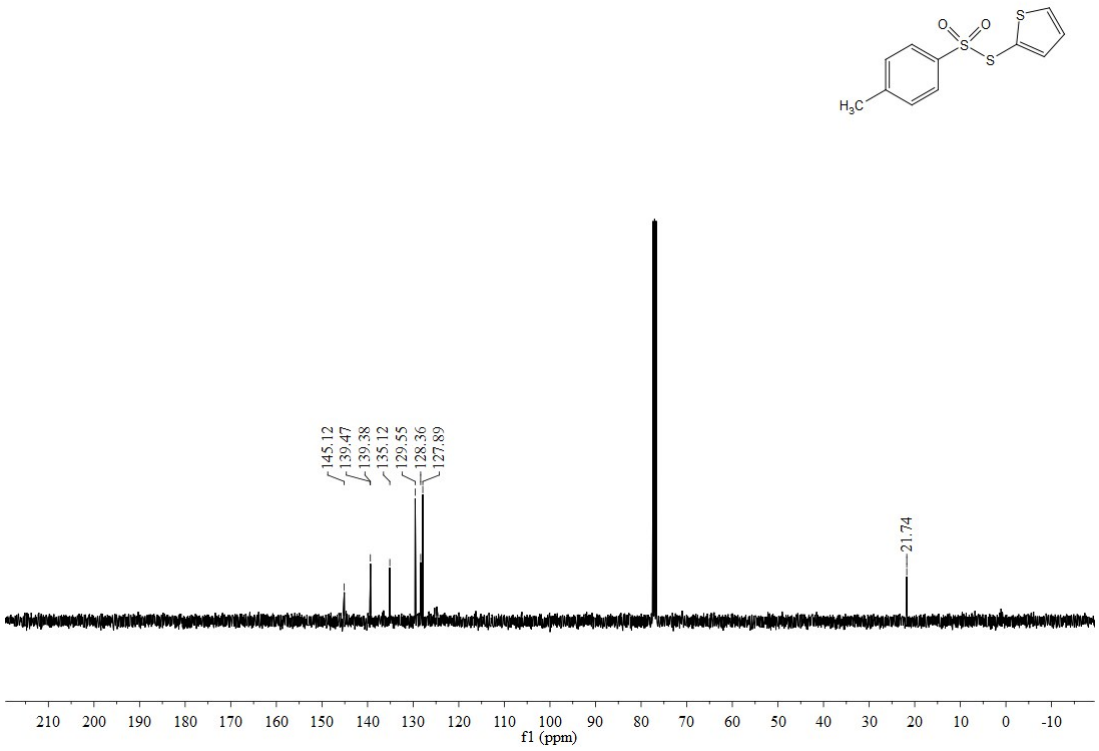
^{1}H, ^{13}C and spectra of 3al



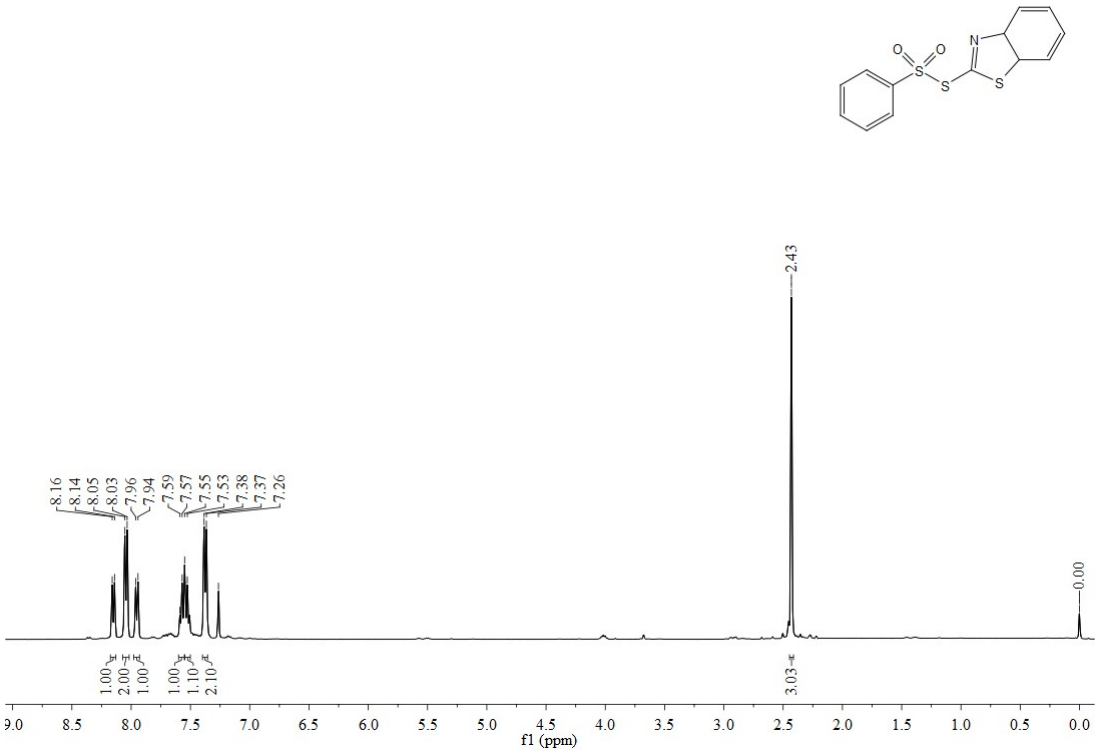


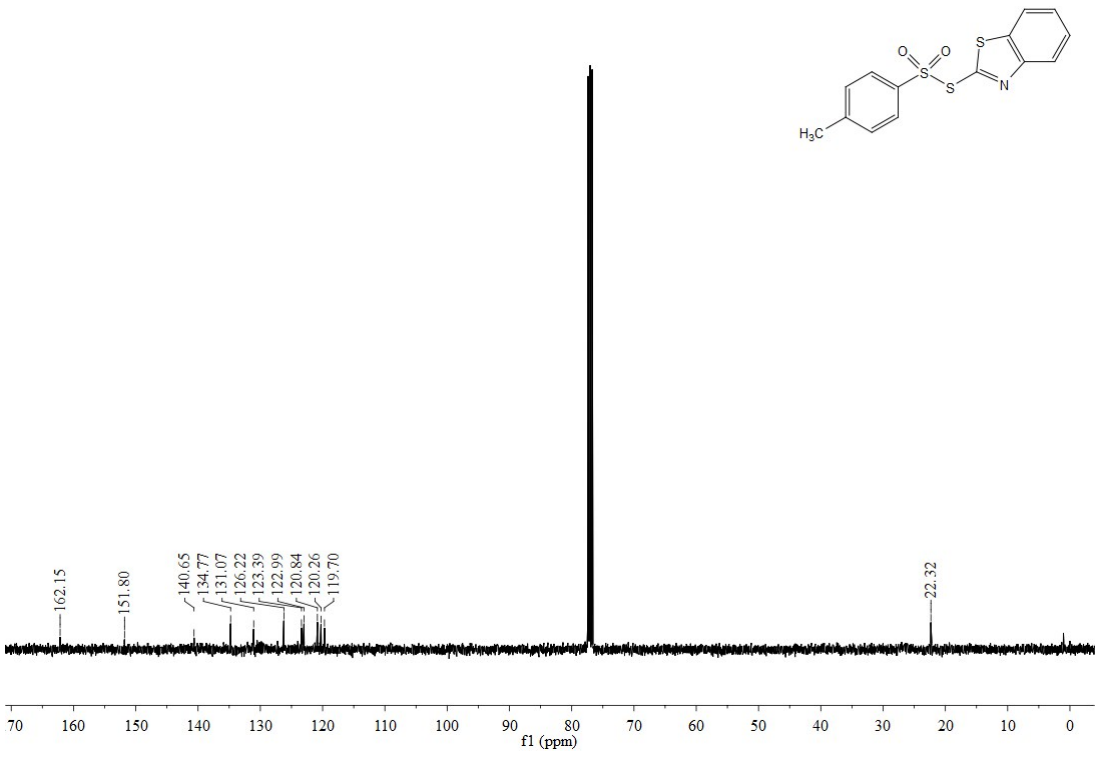
^{1}H, ^{13}C and spectra of 3am



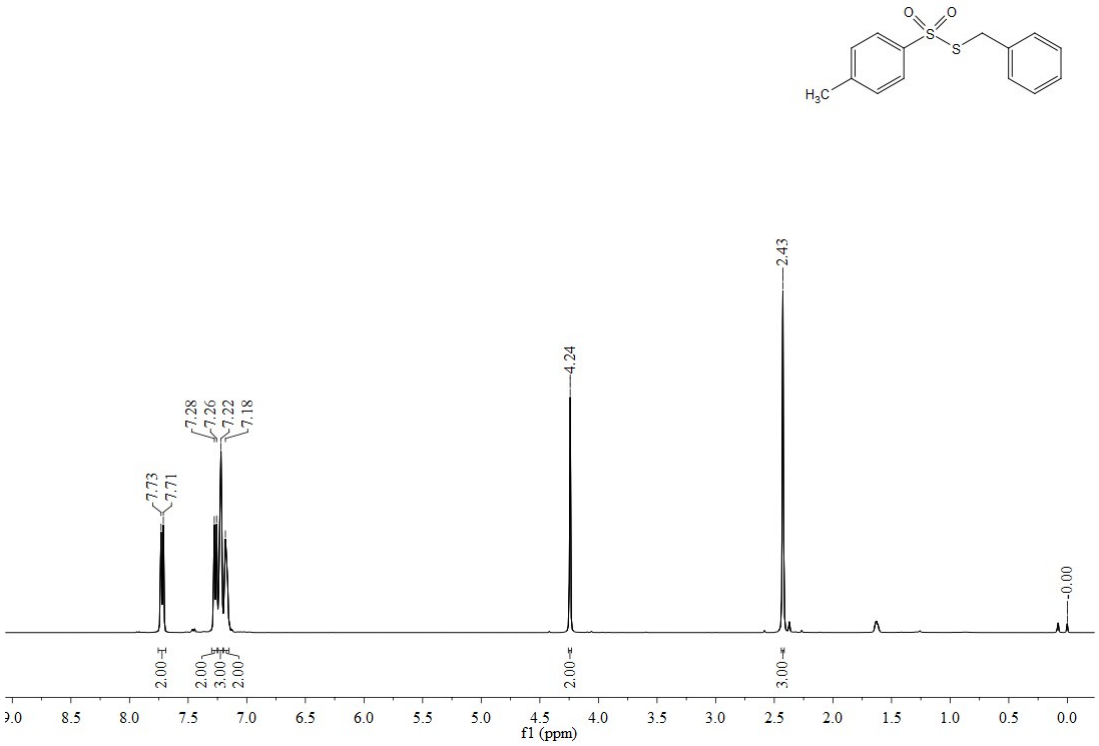


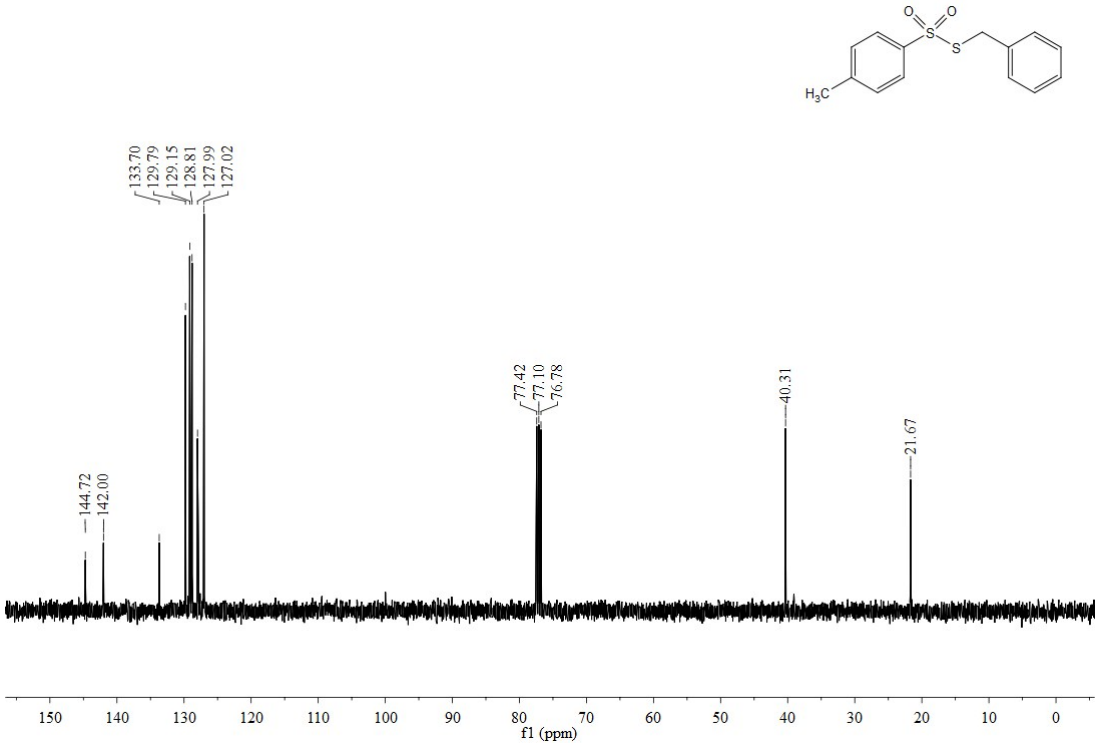
^{1}H, ^{13}C and spectra of 3an





^{1}H, ^{13}C and spectra of 3ao





^{1}H, ^{13}C and spectra of 3ap